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The Geometry of the Carbanionic Moiety Influences the Non-Induced Diastereoselectivity of the [2,3]-Wittig Rearrangement of Lithiated Diallyl Ethers

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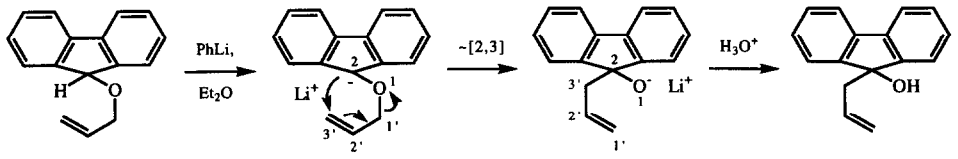
Key Words: Allyl alcohol, preparation of / Allyl anion / Diastereoselectivity, non-induced / Homoallyl alcohol, preparation of / O,S-acetal / O,S-acetal, vinylogous / Rearrrangement, [2,3] / Stereoselectivity / Wittig rearrangement

Abstract: Lithiated diallyl ethers with *cis*- or *trans*-configuration of the anionic moiety were generated from the diallyl ethers **10**, from the vinylogous O,S-acetals **13**, and from the O,S-acetals **14** by treatment with *n*BuLi (in the case of **10**) or with lithium naphthalenide (in the case of **13** and **14**). [2,3]-Wittig rearrangements ensued whose *syn,anti*-selectivity was studied.

Wittig rearrangements are base-induced isomerizations of α-metalated ethers giving alcoholates [1]. The first report about such a reaction is a 1942 paper by Wittig and Löhmann [2]. It describes the [1,2]-Wittig rearrangement of dibenzyl ether with PhLi leading to 1,2-diphenylethanol. The first [2,3]-Wittig rearrangement was discovered by the same research group seven years later [3]. It was - again PhLi-mediated - the conversion of allyl fluorenyl ether **1** into the carbinol **4**. Interestingly, it lasted several years until Wittig's pupil Schöllkopf set out together with Fellenberger to *prove* that the fluorenide intermediate **2** of this reaction gives the lithium alkoxide **3** of carbinol **4** through a [2,3] and not through a [1,2] sigmatropic shift [4].

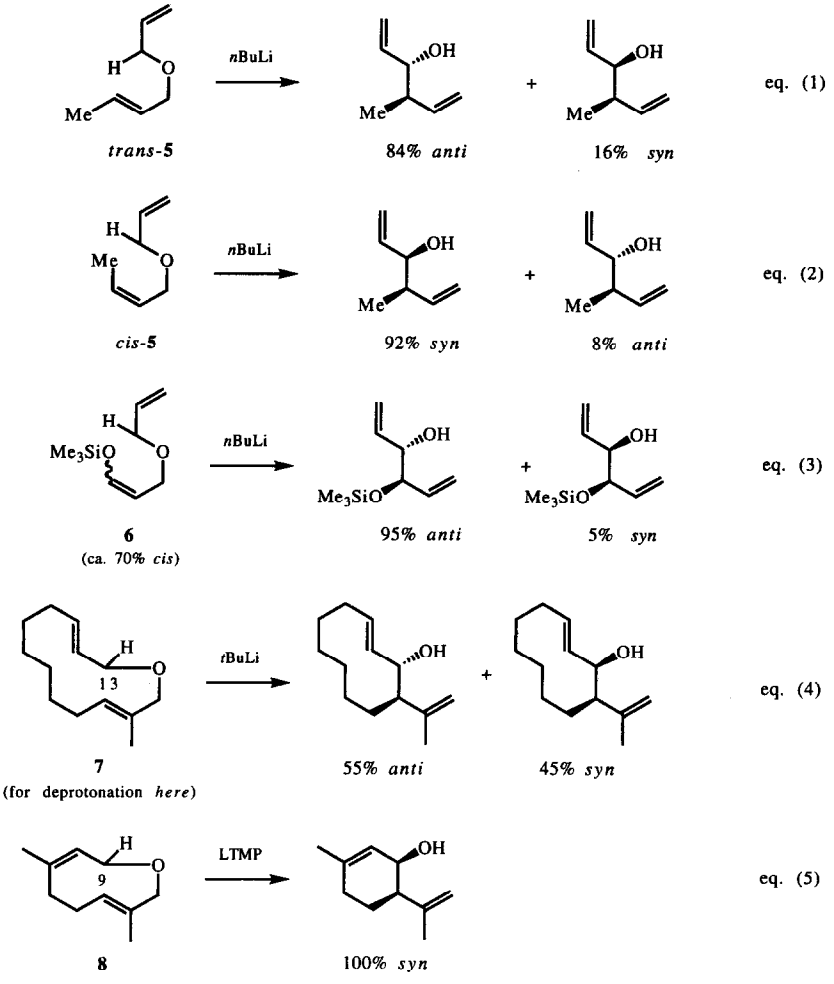


Scheme 1. **1** **2** **3** **4**

By now, the [2,3] mode of the Wittig rearrangement has become a worthwhile tool in synthesis [1]. The most frequently used entry into this rearrangement is deprotonation of an acceptor substituted allyl ether with one of the BuLi isomers or with a lithium amide. [2,3]-Wittig rearrangements where the carbanionic moiety is O-CH_2-Li are usually performed by the Wittig-Still procedure [5], i.e., Sn/Li exchange in an α-

tributylstannylated or α-trimethylstannylated allyl ether. [2,3]-Wittig rearrangements of allyl ethers with an O-C(Alk)H-Li moiety are initiated through the reductive cleavage of O,S-acetals derived from allyl alcohols as demonstrated by Broka *et al.* [6] and ourselves [7]; this approach was based upon the reductive lithiation methodology [8] pioneered by Cohen [9] and Screttas [10].

[2,3]-Wittig rearrangements of lithiated allyl ethers with the substructure $R^1R^2C{=}C\text{-}C\text{-}O\text{-}C(R^3)(R^4)\text{-}Li$ - provided that R^1 is unequal to R^2 and R^3 unequal to R^4 - can exhibit a "non-induced diastereoselectivity" since two vicinal stereocenters are created. Of the two diastereomeric (racemic) rearrangement products which may be obtained, one is frequently obtained in excess over the other [1]. Such non-induced diastereoselectivities of Wittig rearrangements are also referred to as *syn,anti* selectivities (cf. stereoformulae of Scheme 2 for illustration). Yet, *why* a given metalated ether rearranges with a certain non-induced diastereoselectivity is not explicable in a straightforward manner [1].

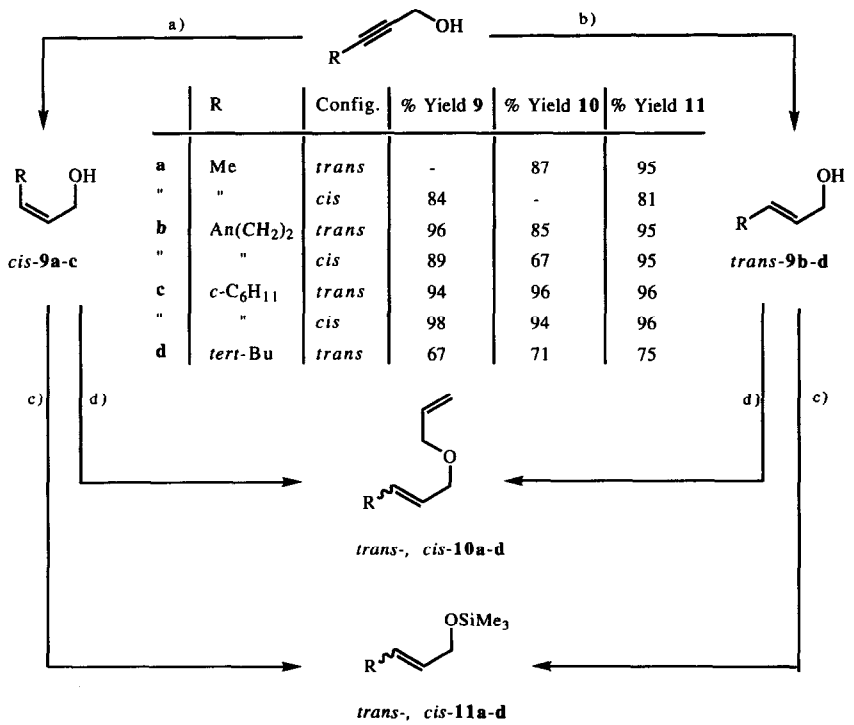


Scheme 2. Non-induced diastereoselectivity of [2,3]-Wittig rearrangements of diallyl ethers

The present report elucidates a hitherto unrecognized factor which influences the *syn,anti*-selectivity in the particular case of the [2,3]-Wittig rearrangement of lithiated diallyl ethers. It complements the previously identified factors (Scheme 2) which are firstly the double bond configuration of the nonlithiated allyl moiety [*cf.* eq. (2) [11] vs. eq. (1) [11]]; secondly, the substituent at C-3 of the nonlithiated allyl moiety [*cf.* eq. (3) [12] vs. eq. (2)]; and thirdly, the ring size of the starting material if cyclic diallyl ethers are ringcontracted through the rearrangement [*cf.* eq. (5) [13] vs. eq. (4) [14]].

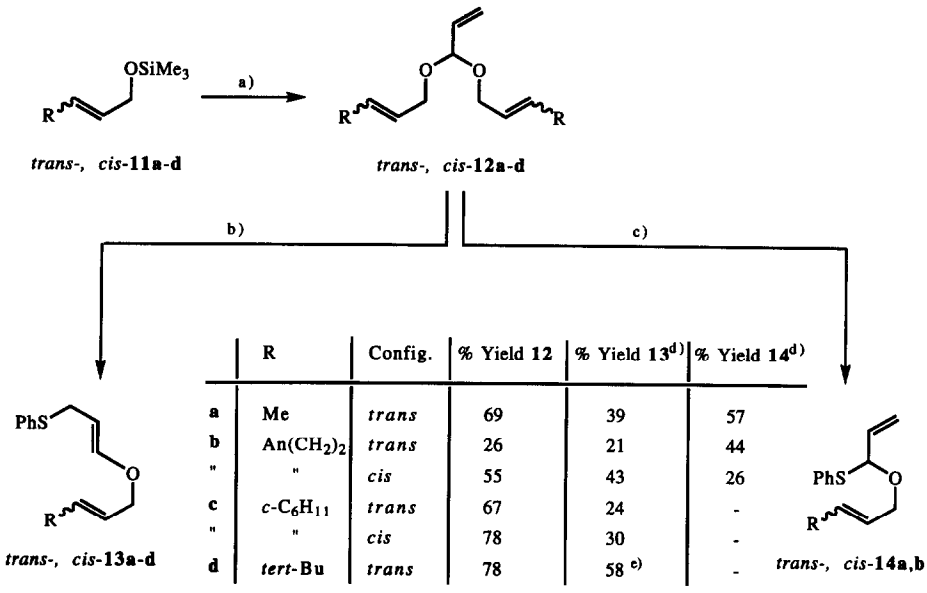
Starting Materials

A prerequisite for our study was the synthesis of three types of rearrangement precursors: diallyl ethers **10**, vinylogous O,S-acetals **13**, and O,S-acetals **14**. Incorporated into them were the *trans*- and *cis*-configurated alcohols **9** which were obtained from the corresponding propargyl alcohols (Scheme 3). The semihydrogenations of the latters over Lindlar catalyst were *cis*-selective. However, the *tert*-butylated alcohol did not take up hydrogen. Therefore, we could not include derivatives of allyl alcohol *cis*-**9d** in our study. The complementary *trans*-reduction of the propargyl alcohols was realized with $LiAlH_4$ and the Fiesers' workup [15]. The obtained allyl alcohols and the commercially available *trans*-crotyl alcohol (95% *trans*) were allylated with NaH / allyl bromide providing the diallyl ethers **10** as our first rearrangement precursors in 67-96% yield (Scheme 3).



	R	Config.	% Yield **9**	% Yield **10**	% Yield **11**
a	Me	*trans*	-	87	95
"	"	*cis*	84	-	81
b	An$(CH_2)_2$	*trans*	96	85	95
"	"	*cis*	89	67	95
c	*c*-C_6H_{11}	*trans*	94	96	96
"	"	*cis*	98	94	96
d	*tert*-Bu	*trans*	67	71	75

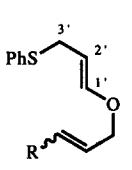
Scheme 3. a) H_2 (5 bar), Lindlar Pd, CH_2Cl_2, room temp., 2 d.- b) $LiAlH_4$ (3 eq.), THF, room temp., 18 h.- c) Me_3SiCl (1.5 eq.), imidazole (2.0 eq.), CH_2Cl_2, room temp., 16 h.- d) NaH (2 eq.), allyl bromide (2 eq.), THF, room temp., 14 h.



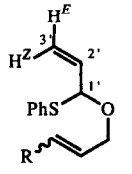
	R	Config.	% Yield 12	% Yield 13[d]	% Yield 14[d]
a	Me	*trans*	69	39	57
b	$An(CH_2)_2$	*trans*	26	21	44
"	"	*cis*	55	43	26
c	*c*-C_6H_{11}	*trans*	67	24	-
"	"	*cis*	78	30	-
d	*tert*-Bu	*trans*	78	58 [e]	-

Scheme 4. a) Acrolein (0.45 mol per mol of 11), $Me_3SiO\text{-}SO_2\text{-}CF_3$ (5 mol-%), CH_2Cl_2, -78°C, 5 h.- b) $Bu_2Sn(SPh)_2$ and BF_3 etherate (0.50 and 1.0 mol per mol of 12, respectively), toluene, -78°C, 1 h.- c) Et_3Al (3.0 eq.), PhSH (1.5 eq.), toluene, 0°C, 2 h.- d) Yields of pure fractions of 13 and 14, respectively; the rest (sometimes: bulk) of these materials was not liberated from impurities.- e) Enol ether moiety: 87:13 trans:cis.

Table 1. ^{1}H-NMR data of vinylogous (13) and simple O,S-acetals (14) in $CDCl_3$ or in C_6D_6 (cis-13c, 14b)



13



14

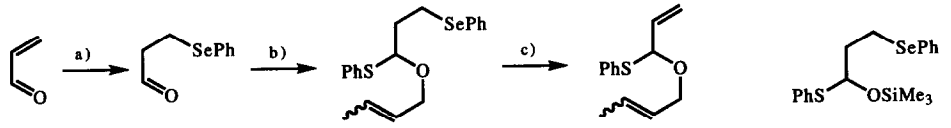
	R	Config.	$\delta_{1'\text{-H}}$	$\delta_{2'\text{-H}}$	$J_{1',2'}$	$\delta_{3'\text{-H}}$	$\delta_{3'\text{-H}^E}$	$\delta_{3'\text{-H}^Z}$	$\delta_{2'\text{-H}}$	$\delta_{1'\text{-H}}$	$J_{1',2'}$
a	Me	*trans*	6.31	4.89	12.5	3.49	5.08	5.23	5.88	5.25	5.4
"	"	*cis*	6.33	4.89	12.6	3.50	5.09	5.23	5.89	5.25	5.3
b	$An(CH_2)_2$	*trans*	6.30	4.88	12.6	3.49	4.91	5.28	5.91	5.12	4.8
"	"	*cis*	6.24	4.82	12.6	3.46	4.90	5.25	5.88	5.08	4.9
c	*c*-C_6H_{11}	*trans*	6.32	4.88	12.5	3.49					
"	"	*cis*	6.20	4.86	12.5	3.25					
d	*tert*-Bu	*trans*	6.35	4.91	12.5	3.51					

Trimethylsilylation of the same allyl alcohols **9a-d** with Me_3SiCl / imidazole furnished the TMS ethers *trans*- and *cis*-**11a-d** (75-96%; Scheme 3). The TMS ethers were then converted into acrolein acetals by the Noyori procedure [16, 17], i.e., treatment with (trimethylsilyl)triflate and acrolein (Scheme 4). Five acetals **12** were isolated in 55-78% and acetal *trans*-**12** in 26% yield. Next, we had to transform these acetals into the *vinylogous* O,S-acetals **13** on the one hand and into the *simple* O,S-acetals **14** on the other hand. While we could not reach complete chemoselectivity in this regard, we found conditions with sufficient bias towards either desired direction. Following closely related experiments by Otera *et al.* [17], the reaction of O,O-acetals

12 with $Bu_2Sn(SPh)_2$ led mainly to the *vinylogous* O,S-acetals **13**. Repeated passages through flash chromatography columns charged with silica gel [18] provided them isomerically pure in yields between 21 and 58%; their enol ether moiety contains a *trans* C=C bond as judged from $^3J_{olefinic}$ = 12.5-12.6 Hz in the ^{1}H-NMR spectra (Table 1). As expected [17] we did not obtain isolable amounts of the *cis* enol ether counterparts.

Our best conditions for the conversion of O,O-acetals **12** into the *simple* O,S-acetals **14** represent a modification of Masaki's method for the conversion of O,O-ketals into O,S-ketals [19]. Instead of using a reagent Et_2AlSPh resulting from equimolar amounts of Et_3Al and PhSH, we let **12** react with twice as much Et_3Al (3.0 eq.) as PhSH (1.5 eq.). Since again repeated passages over flash silica gel were required to separate the O,S-acetals **14** from isomers and other contaminants, we were only able to obtain the less nonpolar compounds *trans*- and *cis*-**14a** as well as *cis*-**14b** in pure form (NMR data: Table 1). The preparation of *trans*- and *cis*-**14c** as well as of *trans*-**14d**, although not less successful as evidenced by the ^{1}H-NMR spectra of the crude reaction mixtures, had therefore to be abandoned.

Because of the labor behind the described tranformations, we explored two alternative routes to the crotyl ether based O,S-acetals *trans*- and *cis*-**14a** and the corresponding vinylogous O,S-acetals *trans*- and *cis*-**13a**. One started from γ-(phenylseleno)propionaldehyde (**15**) which was readily available by the Michael addition of PhSeH to acrolein [20] (Scheme 5). This aldehyde was subjected to our one-pot synthesis of O,S-acetals which is a reaction between a silyl ether (*trans*- or *cis*-**11a**), $PhSSiMe_3$, and (trimethylsilyl)triflate in CH_2Cl_2 at dry ice temperature [21]. The Se-containing O,S-acetals *trans*- and *cis*-**16a** resulted in fairly low yields of 47 and 33%, only. The problem was a side reaction in which about half of the starting aldehyde **15** did not incorporate the TMS ethers but formed the O-silylated O,S-acetal **17** through an Evans-type reaction [22] with $PhSSiMe_3$ and (trimethylsilyl)triflate, alone. Fortunately, the PhSe group in the O,S-acetals **16a** could be oxidized selectively [23] by MCPBA at -78°C. A iPr_2NH-mediated ß-elimination of PhSeOH from the putative selenium oxide intermediate in refluxing CH_2Cl_2 [24] led to the O,S-acetals *trans*- and *cis*-**14a** in 73 and 81% yield, respectively. Gratifyingly, they resulted without the need of separation from isomers.

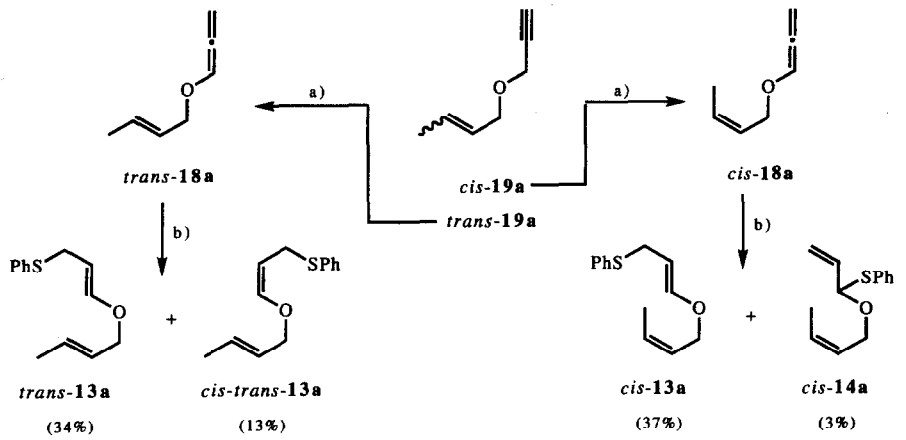


15 *trans-, cis*-**16a** *trans-, cis*-**14a** **17**

Scheme 5. a) PhSeH, EtOH, 0 - -20°C, overnight.- b) trans-11a (0.9 eq.) or cis-11a (0.9 eq.), $Me_3SiO\text{-}SO_2\text{-}CF_3$ (0.45 eq.), CH_2Cl_2, -78°C, 1 h; pyridine; 47% trans-16a / 34% 17 and 33% cis-16a / 48% 17, respectively.- c) MCPBA (1.0 eq.), CH_2Cl_2, -78°C, 1 h; iPr_2NH (2 eq.), transfer into boiling CH_2Cl_2, 30 min; 73% trans-14a and 81% cis-14a, respectively.

The alternative route to the crotyl alcohol based vinylogous O,S-acetals *trans*-,*cis*-**13a** started from the known [11] crotyl propargyl ethers *trans*- and *cis*-**19a** (Scheme 6). A *tert*-BuOK mediated isomerization [25] converted them into the allenyl ethers *trans*- and *cis*-**18a**, respectively. Only after considerable experimentation were we able to add PhSH to these compounds [26] and to retrieve products through flash chromatography on silica. The allenyl ether with the *trans*-configurated crotyl group delivered two vinylogous O,S-acetals: 34% *trans*-**23a** with a *trans*-enol ether moiety and 13% *cis-trans*-**13a** with a *cis*-enol ether moiety. From PhSH and the allenyl ether with the *cis* crotyl group we obtained a single vinylogous

O,S-acetal *cis*-**13a** with a *trans*-enol ether moiety in 37% yield. Furthermore, we isolated 3% of the simple O,S-acetal *cis*-**14a**.



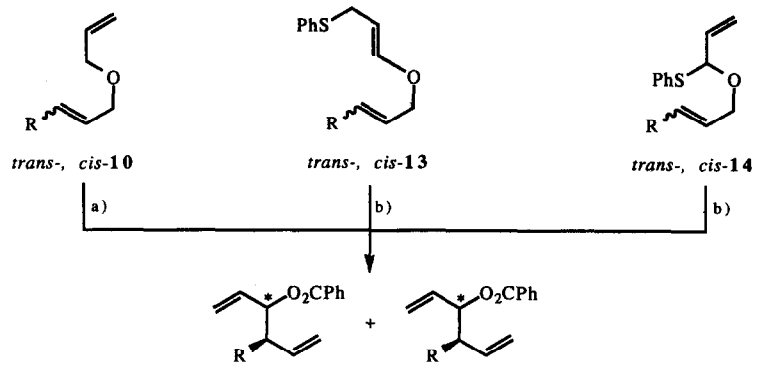
Scheme 6. a) tert-BuOK (0.13 eq.), THF, room temp., 1 h, 50°C, 5 h; 57% trans-18a and 78% cis-18a.- b) PhSH (1.0 eq.), HBF_4 (cat.), CH_2Cl_2, -40°C → -10°C, 2 h; aq. NaOH (2 M).

REARRANGEMENTS

With the precursors **10** (diallyl ethers), **13** (vinylogous O,S-acetals), and **14** (simple O,S-acetals) in our hands, their respective [2,3]-Wittig rearrangements were performed as summarized in Scheme 7. The allyl ethers **10** were lithiated in THF with *n*-BuLi (1.2 eq.) essentially under Nakai's conditions [11], i.e., starting at -78°C and raising the temperature to ambient during several hours. The O,S-acetals **14** and their vinylogues **13** were dissolved in THF and added to THF solutions of LiNaphth (3 eq.) at -78°C; after 1 h, the starting materials were completely consumed. In order to determine the diastereoselectivity of these reactions, the rearranged alcoholates were esterified with PhCOCl. The resulting benzoates **20a-d** were analyzed by capillary GLC of the crude reaction mixtures and revealed the isomer ratios listed in Scheme 7. Subsequently, flash chromatography provided either the pure benzoates (**20a**, **b**) or benzoates (**20c**, **d**) which could not be separated entirely from PhSC(=O)Ph or $Bu_2C(OH)Ph$. These contaminants are the benzoylation products of excess reagent in the *n*-BuLi induced and of the stoichometric byproduct PhS^-Li^+ of the LiNaphth induced rearrangements, respectively.

The vinylogous O,S-acetal *cis-trans*-**13a** was rearranged/benzoylated under similar conditions and gave 83% of the benzoates **20a** as a 19:81 *syn,anti*-mixture (Scheme 8).

Last but not least, two vinylogous O,S-acetals (*trans*-**13a**, *cis*-**13a**) were submitted to [2,3]-Wittig rearrangements via allyl *potassium* intermediates upon cleavage of the C-S bond of the starting materials with potassium naphthalenide (*cf.* [19b]); here, the benzoylated rearrangement products **20a** were isolated in 77 and 54% yield, respectively (Scheme 9).



20a-d (isomer 1) **20a-d** (isomer 2)

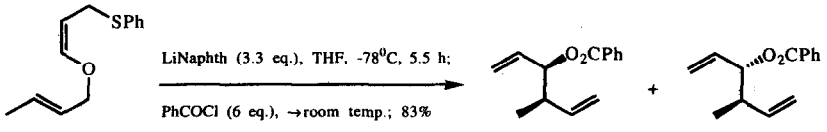
Yields and isomer ratios[d] of **20** starting from *trans*-configurated compounds

	R	Config.	from **10**	from **13** [e]	from **14**
a	Me	*trans*	93% (22:78)	83% (81:19)	71% (34:66)
b	$An(CH_2)_2$	*trans*	75%[f] (23:77)	81%[f] (77:23)	82%[f] (28:72)
c	$c\text{-}C_6H_{11}$	*trans*	88% (9:91)	79%[f] (44:56)	
d	*tert*-Bu	*trans*	98% (9:91)	94%[f] (15:85)	

Yields and isomer ratios[d] of **20** starting from *cis*-configurated compounds

	R	Config.	from **10**	from **13**	from **14**
a	Me	*cis*	88% (92: 8)[5]	74% (92: 8)	50% (85:15)
b	$An(CH_2)_2$	*cis*	66%[f] (93: 7)	78%[f] (92: 8)	73%[f] (91: 9)
c	$c\text{-}C_6H_{11}$	*cis*	90% (89:11)	69% (91: 9)	

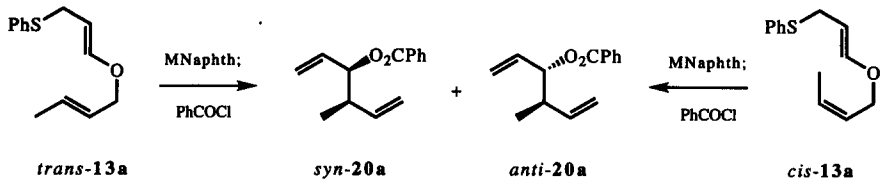
Scheme 7. a) n-BuLi (1.2 eq.), THF, -78°C → room temp., 5 h; → -78°C, PhCOCl (1.2 eq.), → room temp., 16 h.- b) LiNaphth (3.0 eq.), THF, -78°C, 1-4 h; PhCOCl (1.2 eq.), -78°C → room temp., 16 h.- d) (Isomer 1):(isomer 2); isomer 1 eluted from the GLC column after isomer 2.- e) Enol ether moiety of trans-13d: 87:13 trans:cis.- f) Contained $Bu_2C(OH)Ph$ (starting from 10), PhSC(=O)Ph (starting from 13/14), and naphthalene (starting from trans-13c); yield estimated from the ^1H-NMR spectrum.



cis-trans-**13a** *syn*-**20a** *anti*-**20a**

19 : 81

Scheme 8.

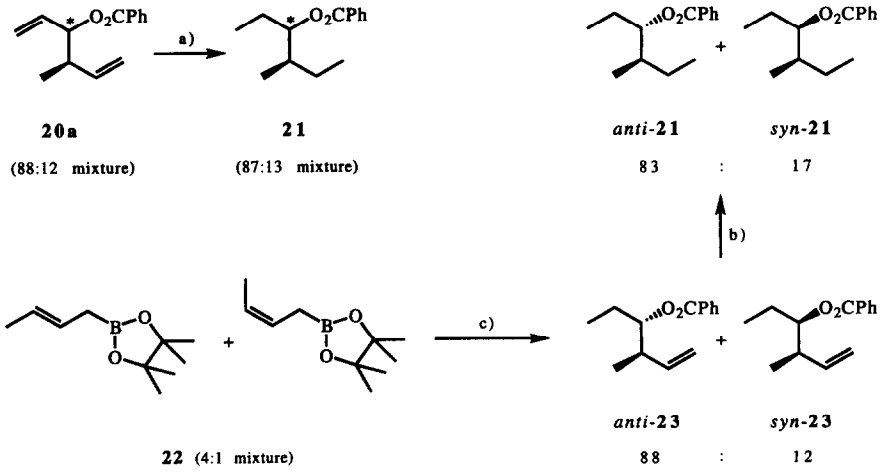


trans-**13a** *syn*-**20a** *anti*-**20a** *cis*-**13a**

from *trans*-**13a**:			from *cis*-**13a**:	
% Yield	*syn:anti*	M	% Yield	*syn:anti*
83	81:19	Li	74	92: 8
77	95: 5	K	54	92: 8

Scheme 9. Counterion effect on the non-induced diastereoselectivity

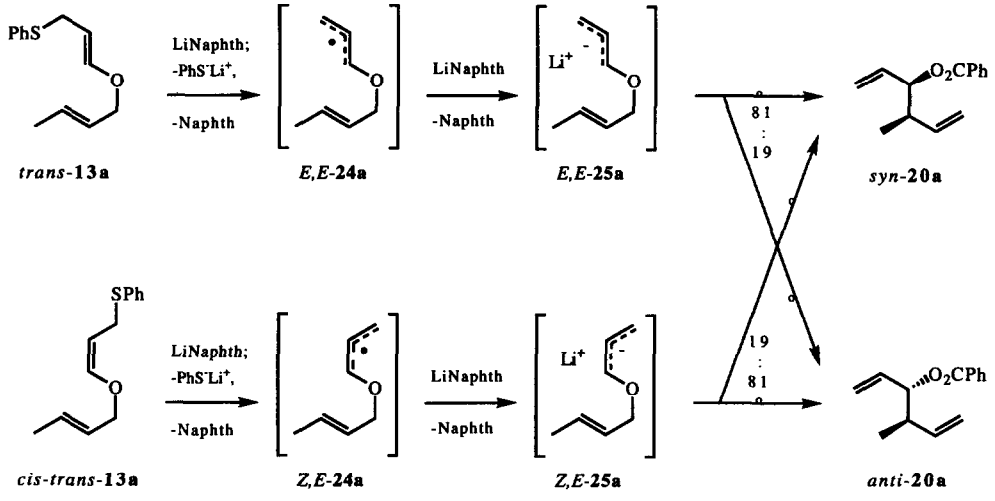
Unfortunately, the stereostructure of the obtained benzoates **20** could not be deduced from their ^{1}H- or ^{13}C-NMR data. The configuration of **20c** (R = *c*-C_6H_{11}) and **20d** (R = *tert*-Bu) remains therefore unknown. The structure of benzoate **20a** (R = Me) was established unambiguously through the chemical correlation depicted in Scheme 10. Hydrogenation as a 88:12 mixture of isomer 1 (≡ slower isomer by capillary GLC) and 2 (≡faster isomer by capillary GLC) provided the saturated benzoates **21** as a 87:13 mixture of diastereomers. An independent synthesis provided the same benzoates **21** with a reversed diastereomer ratio (17:83) through the hydrogenation of benzoates **23**. These were prepared from propionaldehyde and Hoffmann's crotylboronate **22** (4:1 *trans*:*cis* mixture) as a configurationally predictable 88:12 *anti*,*syn*-mixture [27]. Comparing (GLC, ^{1}H-NMR spectroscopy) the benzoates **21** derived from the configurationally assigned precursors **23** with the benzoates originating from the rearrangement products **20a**, the latters' stereochemical identity turned out to be *syn* = isomer 1, *anti* = isomer 2. Presumably, isomer 1 of rearrangement product **20b** should also be *syn* and isomer 2 of **20b** *anti* because of the similarity between isomer 1 (2) of **20b** with *syn*-**20a** (*anti*-**20a**) with respect to relative migratory aptitude on the GLC column and to ^{13}C-NMR shifts and to the stereoselectivities of the formation reactions (Scheme 7).



*Scheme 10. a) 10% Pd/C, H_2 (1 bar), AcOEt, room temp., 2 h; 88%.- b) Same as a), 1 h; 94%.- c) **22** (1.24 eq), propionaldehyde, pentane, -78°C → room temp., overnight; aq. workup; KH, THF, 0 → -78°C; PhCOCl, → room temp.; 63%.*

Discussion

The non-induced diastereoselectivities of the [2,3]-Wittig rearrangements of Scheme 7 can be analyzed going through the included tables - one for the *trans*- and one for *cis*-configurated starting materials - vertically or horizontally. "Vertical comparisons" concern the generation of a series of benzoates from a common type of precursor. The structural variation takes place only in that part of the molecule which becomes the *non-lithiated moiety* of the lithioether. However, we do not know the stereostructure of the rearrangement products **20c** and **d**. Therefore, meaningful "vertical comparisons" are not yet possible. What is possible, though, are "horizontal comparisons". They concern the generation of pairs of diastereomers of given benzoates from allyl ethers *trans*-,*cis*-**20**, from vinylogous O,S-acetals *trans*-,*cis*-**23**, and from simple O,S-acetals *trans*-,*cis*-**24**. These precursors differ from one another only in the moiety which becomes the *allyl lithium part* of the lithioether. As Schemes 7 and 8 reveal, there is a substantial effect of the precursor structure upon the non-induced diastereoselectivity of Wittig rearrangements starting from *trans*-olefins and essentially no such effect starting from *cis*-olefins.

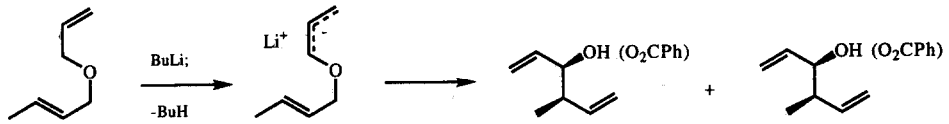


*Scheme 11. Formation of rearrangement products syn,anti-**20a** from precursors with trans-configurated crotyl moiety*

The nature of the precursor effect upon the stereoselectivity of the rearrangements in the *trans*-series emerges from Scheme 11. Shown are the *syn*,*anti*-selectivities of the LiNaphth induced rearrangements of the vinylogous O,S-acetals *trans*- vs. *cis-trans*-**13a**. They are exactly reversed: *syn*:*anti* 81:19 was observed starting from *trans*-**13a**, *syn*:*anti* 19:81 starting from *cis-trans*-**13a**. The substrates *trans*- and *cis-trans*-**13a** differ from one another only in that the former is a *trans*- and the latter a *cis*-configurated enol ether. This difference must translate into a structural difference between the lithioether obtained with LiNaphth from *trans*-**13a** and the lithioether obtained from *cis-trans*-**13a**: If there were an identical lithioether intermediate, the rearrangements *trans*-**13a** → **20a** and *cis-trans*-**13a** → **20a** would display the *same* *syn*,*anti*-selectivity which is not the case. Therefore, the C=C bond configurations of the enol ether moieties are retained until the rearrangement begins. This excludes isomerizations *E*,*E*-**24a** ⇄ *Z*,*E*-**24a** between the allyl radicals which are generated - along with PhS⁻Li⁺ - when the first equivalent of LiNaphth cleaves the C-S bond. There is

neither an interconversion *E,E*-**25a** ⇄ *Z,E*-**25a** of the lithiated allyl ethers which are obtained from these radicals through electron transfer from the second equivalent of the reductant.

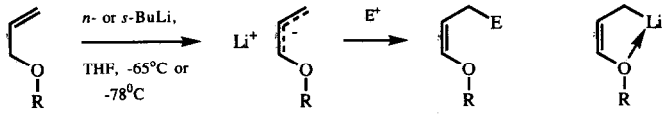
In the rearrangements of Scheme 11 there need not be 100% of retention of configuration since the diastereoselectivities were not 100:0 but 81:19. 81% retention and 19% inversion of configuration would still be in line with this ratio *if* both lithioethers - *E,E*-**25a** and *Z,E*-**25a** - rearranged with *complete* stereocontrol. More plausible, however, is the assumption that there is no crossover at all between the *E,E*- and the *Z,E*-series of allyl radical (**24a**) and lithioether (**25a**) intermediates of these Wittig rearrangements: It is conceivable that the vinylogous O,S-acetal *trans*-**13a** reacts exclusively via lithioether *E,E*-**25a** with the *exo*-oxygenated allyl anion moiety and *cis*-**13a** exclusively via lithioether *Z,E*-**25a** with the *endo*-oxygenated allyl anion moiety. In this view, lithioether *E,E*-**25a** would rearrange with 81:19 *syn*- and lithioether *Z,E*-**25a** with 81:19 *anti*-selectivity. That the configuration of the carbanionic moiety of lithiated diallyl ethers influences the diastereoselectivity of the [2,3]-Wittig rearrangement is here documented for the first time.



trans-**10a** *Z,E*-**25a** *syn*-**26a** (*syn*-**20a**) *anti*-**26a** (*anti*-**20a**)

Scheme 12.

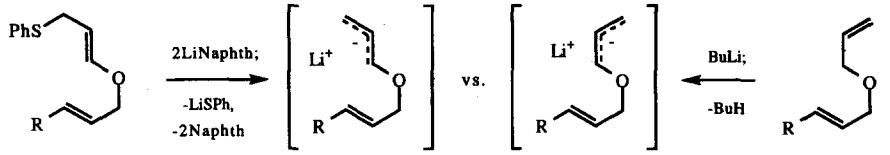
Our interpretation agrees perfectly with the 79:21 *syn,anti*-selectivity reported by Nakai *et al.* for the BuLi-induced Wittig rearrangement of allyl ether *trans*-**10a** giving **26a** [11] (Scheme 12); we reproduced this ratio - benzoylation as **20a** (93%) included - almost exactly (78:22). This is because Nakai's rearrangement should proceed selectively via the same lithioether *Z,E*-**25a** with *endo*-oxygenated allyl anion moiety which we had created purposely by the method of Scheme 11. In fact any allyl ether **27** seems to give lithioethers **28** with *endo*-oxygenated allyl anion moiety as shown by Evans' [28] and Still's [29] groups through selective trapping with electrophiles as *cis*-enol ethers **29** (Scheme 13). In order to account for the high stereoselectivity of this metalation reaction, Still visualized the *endo*-oxygenated allyl lithium **28** as chelated structure **28a** [29].



Scheme 13. **27** **28** **29** **28a**

Table 2 surveys substituent effects upon the non-induced diastereoselectivity in pairs of [2,3]-Wittig rearrangements which proceed - according to the previously said - via isomeric allyl anions. The LiNaphth induced Wittig rearrangements of the vinylogous O,S-acetals *trans*-**13** should occur essentially if not completely via lithioethers *E,E*-**25** with *exo*-oxygenated allyl anion moiety. The BuLi induced rearrangements of diallyl ethers *trans*-**10** should lead to product exclusively via lithioethers *Z,E*-**25** with *endo*-oxygenated allyl anion moiety. Table 2 shows that the difference of the diastereoselectivities resulting via allyl anions *E,E*- vs. *Z,E*-**25** is greatest when the substituent R is smallest (**a**, R = Me: 81:19 vs. 22:78). It decreases with increasing size of R and vanishes almost when R = *tert*-Bu (**d**: 15:85 vs. 9:91).

Table 2. R effects and non-induced diastereoselectivity ("ds") of [2,3]-Wittig rearrangements of lithioethers with exo- vs. endo-oxygenated allyl anion moieties (R-CH=CH-CH_2 moiety always trans configurated). Isomer ratios are syn:anti for a and b, (isomer 1) : (isomer 2) for c and d

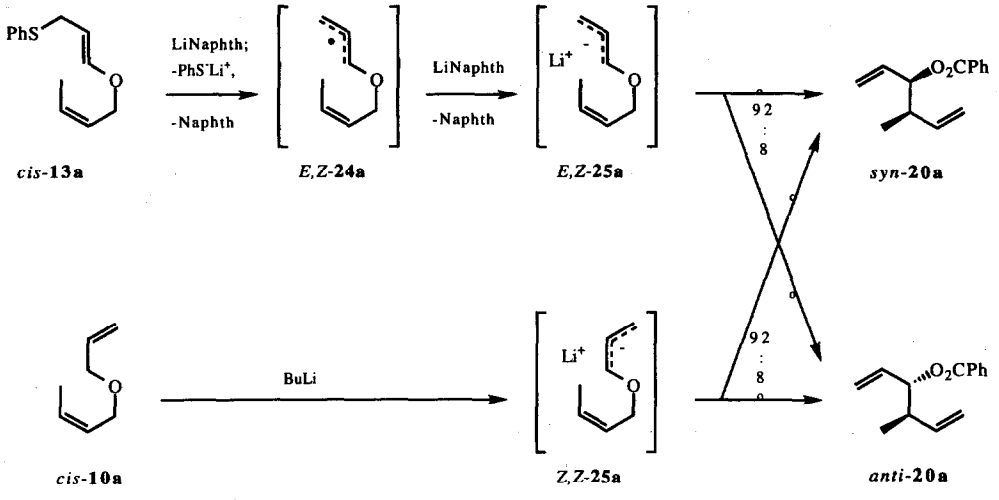


trans-**13a-d** *E,E*-**25a-d** *Z,E*-**25a-d** *trans*-**10a-d**

	R	ds (yield) via *E,E*-**25**	ds (yield) via *Z,E*-**25**
a	Me	81:19 (83%)	22:78 (93%)
b	$(CH)_2An$	77:23 (81%[b])	23:77 (75%[b])
c	*c*-C_6H_{11}	44:56 (79%[b])	9:91 (88%)
d	*tert*-Bu	15:85 (94%[b])	9:91 (98%)

a) Enol ether moiety of trans-13d: 87:13 trans:cis.- b) Contained $Bu_2C(OH)Ph$ (starting from 10), PhSC(=O)Ph (starting from 13/14), and naphthalene (starting from trans-13c); yield estimated from ^{1}H-NMR spectrum.

The bottom half of Scheme 7 reveals that when one starts from *cis*-olefins *exo*- vs. *endo*-oxygenation of the allyl anion moiety does not influence the *syn,anti*-selectivity of the [2,3]-Wittig rearrangement. Scheme 14 illustrates this finding for the specific case of Wittig rearrangements of allyl anions with a *cis*-crotyl ether moiety; here, the configurations of the products are known.



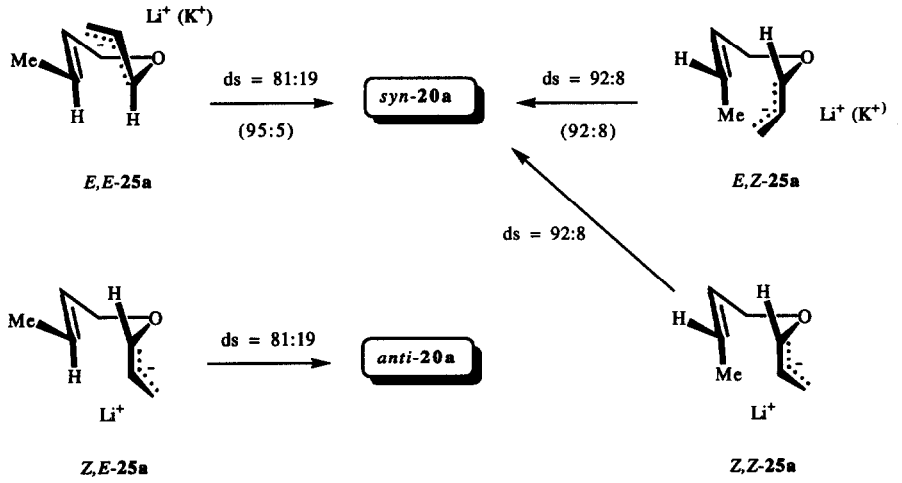
cis-**13a** *E,Z*-**24a** *E,Z*-**25a** *syn*-**20a**

cis-**10a** *Z,Z*-**25a** *anti*-**20a**

Scheme 14. Formation of rearrangement products syn,anti-20a from precursors with cis-configurated crotyl moiety

The last lesson to be learned from Scheme 7 comes from an inspection of the diastereoselectivities of the Wittig rearrangements of the four O,S-acetals *trans*-,*cis*-**14a,b**. They are similar to those observed in the

corresponding diallyl ether (**10**) rearrangements. This means that compounds **14** furnish essentially *endo*-substituted allyl anions upon treatment with LiNaphth.



Scheme 15. Transition structures rationalizing the simple diastereoselectivity of C-C bond formation through [2,3]-Wittig rearrangements of metalated diallyl ethers

The essence of our study with regard to a refined understanding of the transition state of the [2,3]-Wittig rearrangement [30] and to a future comprehension of its non-induced diastereoselectivity is summarized in Scheme 15: Allyl anions with an *exo*- (*E,E*-**25a**) vs. *endo*-disposed (*Z,E*-**25a**) *trans*-crotyloxy substituent exhibit *opposite* facial selectivities during C-C bond formation, allyl anions with an *exo*- (*E,Z*-**25a**) vs. *endo*-disposed (*Z,Z*-**25a**) *cis*-crotyloxy substituent exhibit the *same*. It is noteworthy that *E,E*-**25a** and *E,Z*-**25a** showed unchanged and even increased diastereoselectivities, respectively, when they were rearranged in the presence of potassium instead of lithium as the counterion.

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Experimental

All reactions were performed in oven-dried (100°C) glassware under dry nitrogen. During reductions with LiNaphth, stirring bars with glass coating were used. THF was freshly distilled from K/Na. The molarity of THF solutions of LiNaphth 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 [18] 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 (combustion analyses: Table 3). Isomer ratios of diastereomeric mixtures were derived from capillary GLC and suitable ^1H- and ^{13}C-NMR integrals. - ^1H NMR (tetramethylsilane or $CHCl_3$ internal standard in $CDCl_3$): Bruker AC 200, AC 250, AC 300, AMX 300, WH 400, Varian VXL 200, 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; IR (film): Perkin Elmer FT-IR 1600.

*trans-5-(4-Methoxyphenyl)-1-(2-propenyloxy)-2-pentene (trans-**10b**; representative procedure for the preparation of diallyl ethers **10**):* At 0°C *trans*-**9b** (74.6 mg, 0.388 mmol) in THF (1 ml) was added under vigorous stirring to a suspension of NaH (20 mg, 0.78 mmol, 2.0 equiv.) in THF (1 ml). The mixture was allowed to warm to room temp. and stirred for 1 h. At 0°C allyl bromide (66 µl, 94 mg, 0.78 mmol, 2.0 equiv.) was added. The mixture was allowed to warm to room temp.. After 14 h the reaction was quenched with satd. aqueous NH_4Cl solution (1.0 ml) and extracted with tBuOMe (3 x 5 ml). Flash chromatography [petroleum ether/tBuOMe (50:1)] yielded *trans*-**10b** (76.5, 85%).- ^{1}H NMR (300 MHz): δ = 2.34 (br. dt, $J_{4,3} \approx J_{4,5} \approx 7$, 4-$H_2$), 2.65 (t with extra peak indicating transition to higher order spectrum, $J_{5,4} \approx 7.8$, 5-H_2), 3.77 (s, OCH_3), 3.92 (dd, $J_{1,2} = 6.1$, $J_{allyl} = 1.2$, 1-H_2), superimposed by 3.93 (dt, $J_{1',2'} = 5.7$, $J_{allyl} = 1.5$, 1'-H_2), 5.17 (dm_c, $J_{cis} = 10.3$, 3'-H^E), 5.26 (ddt, $J_{trans} = 17.2$, $J_{gem} \approx J_{allyl} \approx 1.7$, 3'-$H^Z$), AB signal ($\delta_A = 5.59$, $\delta_B = 5.73$, $J_{AB} = 15.3$, in addition split by $J_{A,vic} = 6.1$, $J_{A,allyl} \approx 1.2$, $J_{B,vic} \approx 6.5$, J_{allyl} not completely resolved, 2-H, 3-H), 5.91 (ddt, $J_{trans} = 17.2$, $J_{cis} = 10.4$, $J_{2',1'} = 5.7$, 2'-H), AA'BB' signal centered at 6.82 and 6.99 (C_6H_4).- IR: ν = 2930 cm^{-1}, 2850, 1610, 1510, 1245, 1175, 1105, 1035.

*trans-1-Cyclohexyl-3-(2-propenyloxy)-1-propene (trans-**10c**):* ^{1}H NMR (200 MHz): δ = 0.94-1.39 and 1.50-1.80 [2m, 2 x 5H, $(CH_2)_5$], 1.97 (m_c, 1"-H), 3.93 (d, $J_{1,2} = 5.8$, J_{allyl} not resolved, 3-H_2), in part superimposed by 3.96 (dt, $J_{1',2'} = 5.8$, $J_{allyl} \approx 1.4$, 1'-H_2), 5.17 (ddt, $J_{cis} = 10.2$, $J_{gem} \approx J_{allyl} \approx 1.5$, 3'-$H^E$), 5.27 (ddt, $J_{trans} = 17.3$, $J_{gem} \approx J_{allyl} \approx 1.7$, 3'-$H^Z$), 5.51 ($dm_c$, $J_{trans} = 15.5$, 2-H), 5.65 (dd, $J_{trans} = 15.5$, $J_{1,1''} = 6.2$, J_{allyl} = not resolved, 1-H), 5.93 (ddt, $J_{trans} = 17.4$, $J_{cis} = 10.3$, $J_{2',3'} = 5.6$, 2'-H).- IR: ν = 2925 cm^{-1}, 2850, 1450, 1350, 1095, 970, 920.

*trans-4,4-Dimethyl-1-(2-propenyloxy)-2-pentene (trans-**10d**):* ^{1}H NMR (200 MHz): δ = 1.02 [s, $C(CH_3)_3$], 3.95 (m_c, 1-H_2, 1'-H_2), 5.18 (dm_c, $J_{cis} \approx 10$, 3'-H^E), 5.27 (ddt, $J_{trans} = 17.4$, $J_{gem} \approx J_{allyl} \approx 1.2$, 3'-$H^Z$), AB signal ($\delta_A = 5.48$, $\delta_B = 5.72$, $J_{AB} = 15.6$, in additon split by $J_{A,1} = 6.1$, $^4J_{B,1} = 1.1$, A: 2-H, B: 3-H), 5.93 (ddt, $J_{trans} = 17.2$, $J_{cis} = 10.4$, $J_{2',1'} = 5.7$, 2'-H).- IR: ν = 2960 cm^{-1}, 2865, 1460, 1365, 1105, 1085, 975, 920.

*cis-5-(4-Methoxyphenyl)-1-(2-propenyloxy)-2-pentene (cis-**10b**):* ^{1}H NMR (300 MHz): δ = 2.35 (m_c, 4-H_2), 2.62 (t, $J_{5,4} = 7.7$, 5-H_2), 3.77 (s, OCH_3), 3.90 (dt, $J_{1',2'} = 5.7$, $J_{allyl} = 1.4$, 1'-H), 3.95 (d, $J_{1,2} = 5.1$, J_{allyl} not resolved, 1-H_2), 5.16 (ddt, $J_{cis} = 10.4$, $J_{gem} \approx J_{allyl} \approx 1.5$, 3'-$H^E$), 5.25 (ddt, $J_{trans} = 17.3$, $J_{gem} \approx J_{allyl} \approx 1.7$, 3'-$H^Z$), 5.58 ($m_c$, 2-H, 3-H), 5.90 (ddt, $J_{trans} = 17.2$, $J_{cis} = 10.4$, $J_{2',1'} = 5.7$, 2'-H), AA'BB' signal centered at 6.82 and 7.09 (C_6H_4).- IR: ν = 3010 cm^{-1}, 2930, 2835, 1610, 1510, 1465, 1300, 1245, 1175, 1095, 1035, 925, 825.

*cis-3-Cyclohexyl-1-(2-propenyloxy)-2-propene (cis-**10c**):* ^{1}H NMR (200 MHz): δ = 0.95-1.40 and 1.51-1.80 [2 m, 2 x 5H, $(CH_2)_5$], 2.25 (m_c, 1"-H), 3.98 (dt, $J_{1',2'} = 5.6$, $J_{allyl} \approx 1.4$, 1'-H_2), 4.05 (d with extra peaks indicating transition to higher order spectrum, $J_{1,2} = 5.1$, J_{allyl} incompletely resolved, 1-H_2), 5.19 (dm_c, $J_{cis} \approx 10$, 3-H^E), in part superimposed by 5.28 (ddt, $J_{trans} = 17.3$, $J_{gem} \approx J_{allyl} \approx 1.7$, 3-$H^Z$), 5.42 ($m_c$, 2-H and 3-H), 5.93 (ddt, $J_{trans} = 17.2$, $J_{cis} = 10.4$, $J_{2',1'} = 5.5$, 2'-H).- IR: ν = 2925 cm^{-1}, 2850, 1450, 1085, 920.

*trans-1-(Trimethylsilyloxy)-2-butene (trans-**11a**; representative procedure for the preparation of silyl ethers **11**):* Trimethylchlorosilane (44.9 ml, 38.5 g, 354 mmol, 1.5 eq.) was added dropwise to *trans*-**9a** (20.0 ml, 17.0 g, 236 mmol) and imidazole (32.10 g, 471.5 mmol, 2.0 eq.) in CH_2Cl_2 (150 ml). The mixture was stirred at room temp. overnight, the solvent removed and the residue distilled (15 cm Vigreux column) to give 29.92 g

Table 3. Combustion analyses

Compound	Molecular formula	Molecular mass	%C Calcd.(Found)	%H Calcd. (Found)
trans-**9b**	$C_{12}H_{16}O_2$	192.3	74.97 (74.74)	8.39 (8.53)
trans-**9c**	$C_9H_{16}O$	140.2	77.09 (76.78)	11.50 (11.73)
trans-**9d**	$C_{17}H_{14}O$	114.2	73.63 (73.56)	12.36 (12.38)
cis-**9b**	$C_{12}H_{16}O_2$	192.3	74.97 (75.18)	8.39 (8.70)
cis-**9c**	$C_9H_{16}O$	140.2	77.09 (76.87)	11.50 (11.51)
trans-**10b**	$C_{15}H_{20}O_2$	232.3	77.55 (77.48)	8.68 (8.66)
trans-**10c**	$C_{12}H_{20}O$	180.3	79.94 (79.85)	11.18 (11.09)
trans-**10d**	$C_{10}H_8O$	154.3	77.87 (77.83)	11.67 (11.76)
cis-**10b**	$C_{15}H_{20}O_2$	232.3	77.55 (77.70)	8.68 (8.76)
trans-**11b**	$C_{15}H_{24}O_2Si$	264.4	68.13 (68.12)	9.15 (9.02)
trans-**11d**	$C_{10}H_{22}OSi$	186.4	64.45 (64.70)	11.90 (11.94)
cis-**11b**	$C_{15}H_{24}O_2Si$	264.4	68.13 (67.94)	9.15 (9.40)
trans-**12a**	$C_{11}H_{18}O_2$	182.3	72.49 (72.55)	9.95 (9.96)
trans-**12b**	$C_{27}H_{34}O_4$	422.6	76.75 (76.81)	8.11 (8.08)
trans-**12c**	$C_{21}H_{34}O_2$	318.5	79.19 (79.33)	10.76 (10.80)
trans-**12d**	$C_{17}H_{30}O_2$	266.4	76.64 (76.63)	11.35 (11.46)1
cis-**12b**	$C_{27}H_{34}O_4$	422.6	76.75 (76.65)	8.11 (8.05)
cis-**12c**	$C_{21}H_{34}O_2$	318.5	79.19 (79.17)	10.76 (10.77)
trans-**13a**	$C_{13}H_{16}OS$	220.3	70.87 (70.68)	7.32 (7.26)1
cis-trans-**13a**	$C_{13}H_{16}OS$	220.3	70.87 (70.83)	7.32 (7.17)
trans-**13c**	$C_{18}H_{24}OS$	288.5	74.95 (75.08)	8.39 (8.69)
trans-**13d**	$C_{16}H_{22}OS$	262.4	73.23 (72.92)	8.45 (8.56)
cis-**13a**	$C_{13}H_{16}OS$	220.3	70.87 (70.82)	7.32 (7.11)
cis-**13c**	$C_{18}H_{24}OS$	288.5	74.95 (74.80)	8.39 (8.43)
trans-**14a**	$C_{13}H_{16}OS$	220.3	70.87 (70.95)	7.32 (7.38)
cis-**14a**	$C_{13}H_{16}OS$	220.3	70.87 (70.79)	7.32 (7.19)
trans-**16b**	$C_{19}H_{22}OSSe$	377.4	60.47 (60.52)	5.88 (5.96)
cis-**16b**	$C_{19}H_{22}OSSe$	377.4	60.47 (60.35)	5.88 (5.76)
20a	$C_{14}H_{16}O_2$	216.3	77.75 (77.86)	7.46 (7.48)
20c	$C_{19}H_{24}O_2$	284.4	80.24 (80.07)	8.51 (8.52)
20d	$C_{17}H_{22}O_2$	258.4	79.03 (79.29)	8.58 (8.73)
23	$C_{14}H_{18}O_2$	218.3	77.03 (77.31)	8.31 (8.19)

(88%, bp. 125-127°C).- ^{1}H NMR (300 MHz): δ = 0.13 [s, $OSi(CH_3)_3$], 1.69 (dm_c, $J_{4,3}$ = 6.1, 4-H_3), 4.06 (dm_c, $J_{1,2}$ = 5.5, 1-H_2), AB signal (δ_A = 5.58, δ_B = 5.67, J_{AB} = 15.2, in additon split by $J_{A,1}$ = 5.6, $J_{A,4}$ =1.2, $J_{B,4}$ = 6.2, A: 2-H, B: 3-H).- IR: ν = 3385 cm^{-1}, ca. 3000, 2860, 1450, 1375, 1250, 1135, 1095, 1050, 965, 870, 840, 755.

trans-5-(4-Methoxyphenyl)-1-(trimethylsilyloxy)-2-pentene (trans-11b).- ^{1}H NMR (250 MHz): δ = 0.12 [s, $Si(CH_3)_3$], 2.31 (m_c, 4-H_2), 2.64 (m_c, 5-H_2), 3.78 (s, OCH_3), 4.07 (dd, $J_{1,2}$ = 5.3, $J_{1,3}$ = 0.8, 1-H_2), AB signal (δ_A = 5.59, δ_B = 5.68, J_{AB} = 15.4, in addition split by $J_{A,vic}$ = 5.1, $J_{B,vic}$ = 5.8, 2-H, 3-H), AA'BB' signal centered at 6.82 and 7.08 (C_6H_4).- IR: ν = 3000 cm^{-1}, 2955, 2850, 1610, 1515, 1465, 1300, 1250, 1175, 1120, 1040, 970, 875, 840, 750.

trans-1-Cyclohexyl-3-(trimethylsilyloxy)-1-propene (trans-11c): ^{1}H NMR (250 MHz): δ = 0.12 [s, $Si(CH_3)_3$], 0.83-1.38 and 1.55-1.80 [2m, 2 x 5H, $(CH_2)_5$], 1.96 (m_c, 1'-H), 4.08 (m_c, 3-H_2), AB signal with transition to higher order spectrum (δ_A = 5.49, δ_B = 5.58, J_{AB} = 15.6, in addition split by $J_{A,3}$ = 5.2, $J_{B,1'}$ = 5.8, A: 2-H, B: 1-H).- IR: ν = 2925 cm^{-1}, 2850, 1670, 1450, 1380, 1250, 1115, 1095, 1060, 970, 870, 840, 750.

4,4-Dimethyl-1-(trimethylsiloxy)-2-pentene (trans-11d): ^{1}H NMR (200 MHz): δ = 0.13 [s, $Si(CH_3)_3$], 1.01 [s, $C(CH_3)_3$], 4.10 (dd, $J_{1,2}$ = 5.5, J_{allyl} = 1.1, 1-H_2), AB signal (δ_A = 5.45, δ_B = 5.64, J_{AB} = 15.6, in additon split by $J_{A,1}$ = 5.6, $^4J_{B,1}$ = 1.1, A: 2-H, B: 3-H).- IR: ν = 2960 cm^{-1}, 2865, 1250, 1110, 1070, 975, 870, 840.

cis-1-(Trimethylsilyloxy)-2-butene (cis-11a): ^{1}H NMR (300 MHz): δ = 0.14 [s, $OSi(CH_3)_3$], 1.65 (dm_c, $J_{4,3}$ = 5.2, 4-H_3), 4.20 (dm_c, $J_{1,2}$ = 4.8, 1-H_2), 5.46-5.59 (m, 2-H, 3-H).

cis-5-(4-Methoxyphenyl)-1-(trimethylsilyloxy)-2-pentene (cis-11b): ^{1}H NMR (250 MHz): δ = 0.11 [s, $Si(CH_3)_3$], 2.33 (m_c, 4-H_2), 2.61 (m_c, 5-H_2), 3.79 (s, OCH_3), 4.09 (br. d, $J_{1,2}$ = 4.6, $J_{1,3}$ not resolved, 1-H_2), 5.31-5.50 (m, 2-H, 3-H), AA'BB' signal centered at 6.83 and 7.10 (C_6H_4).- IR: ν = 3010 cm^{-1}, 2955, 2855, 1610, 1510, 1460, 1300, 1250, 1175, 1085, 875, 840.

cis-1-Cyclohexyl-3-(trimetylsilyloxy)-1-propene (cis-11c): ^{1}H NMR (250 MHz): δ = 0.13 [s, $Si(CH_3)_3$], 0.86-1.45 and 1.68-1.79 [2m, 2 x 5H, $(CH_2)_5$], 2.24 (m_c, 1'-H), 4.20 (dd, $J_{3,2}$ = 6.4, $J_{3,1}$ = 1.2, 3-H_2), AB signal [δ_A = 5.30, δ_B = 5.41, J_{AB} = 10.7, in addition split by $J_{A,1'} \approx$ 9.3, $J_{A,3}$ incompletely resolved (ca. 1.0), $J_{B,3} \approx$ 5.9, A: 1-H, B: 2-H].- IR: ν = 3010 cm^{-1}, 2925, 2850, 1590, 1450, 1250, 1085, 875, 840, 750, 705.

3,3-Bis-(trans-2-butenyloxy)-1-propene (trans-12a): ^{1}H NMR (300 MHz): δ = 1.71 (dd, $J_{4',3'}$ = 6.2, $J_{4',2'}$ = 1.2, 2 x 4'-H_3), AB signal (δ_A = 3.95, δ_B = 4.03, J_{AB} = 11.7, in addition split by $J_{A,2'}$ = 6.3, $J_{A,3'} \approx$ 1.0, $J_{B,2'}$ = 6.0, $J_{B,3'} \approx$ 1.1, 2 x 1'-H_2), 4.96 (dt, $J_{3,2}$ = 4.9, $J_{3,1}$ = 1.0, 3-H), 5.30 (dt, J_{cis} = 10.6, $J_{allyl} = J_{gem}$ = 1.3, 1-H^E), 5.40 (dt, J_{trans} = 17.4, $J_{allyl} = J_{gem}$ = 1.3, 1-H^Z), AB signal (δ_A = 5.59, δ_B = 5.73, J_{AB} = 15.3, in addition split by $J_{A,1'}$ = 6.1, $J_{A,4'}$ = 1.4, $J_{B,4'}$ = 6.3, $J_{B,1'}$ = 1.4, H_A = 2 x 2'-H, H_B = 2 x 3'-H), superimposes in part 5.85 (ddd, J_{trans} = 17.5, J_{cis} = 10.6, $J_{2,3}$ = 4.9, 2-H).- IR: ν = 3020 cm^{-1}, 2940, 2860, 1450, 1410, 1375, 1340, 1145, 1085, 1020, 965, 935.

3,3-Bis-[trans-5-(4-methoxyphenyl)-2-pentenyloxy]-1-propene (trans-12b; representative procedure for the preparation of O,O-acetals 12) (method: ref. [16, 17]): At -78°C TMSOTf (1.0 M in toluene, 0.1 ml, 0.1 mmol, 5 mol %) was added to a stirred toluene solution (1.0 ml) of acrolein (0.13 ml, 0.11 g, 1.9 mmol, 0.45 equiv.) and TMS ether **11b** (1.13 g 4.27 mmol). The mixture was stirred at -78°C for an additional 3 h and quenched by addition of dry pyridine (0.5 ml) at the same temp.. Extraction with satd. aq. $NaHCO_3$ (10 ml) and ether (3 x 15 ml), drying over Na_2CO_3 and Na_2SO_4, evaporation, and flash chromatography over deactivated silica gel

[pretreated with 25 % aq. NH_3 (3.5 weight %); petroleum ether/tBuOMe (200:1 → 10:1)] yielded **12b** (289 mg, 26%).- ^{1}H NMR (400 MHz): δ = 2.34 (dt, $J_{4',3'} = J_{4',5'}$ = 7.1, 2 x 4'-H_2), 2.64 (t with extra peak indicating transition to higher order spectrum, $J_{5',4'}$ = 7.8, 2 x 5'-H_2), 3.78 (s, 2 x OCH_3), 2 identical AB signals (δ_A = 3.94, δ_B = 4.03, J_{AB} = 11.9, in addition split by $J_{A,2'}$ = 6.5, $J_{A,3'}$ = 1.0, $J_{B,2'}$ = 6.0, $J_{B,3'}$ = 1.1, 2 x 1'-H_2), 4.92 (dt, $J_{3,2}$ = 5.0, $J_{3,1}$ = 1.1, 3-H), 5.29 (ddd, J_{cis} = 10.6, $J_{gem} = J_{allyl}$ = 1.3, 1-H^E), 5.38 (ddd, J_{trans} = 17.4, $J_{gem} = J_{allyl}$ = 1.4, 1-H^Z), AB signal (δ_A = 5.59, δ_B = 5.74, J_{AB} = 15.4, in addition split by $J_{A,1'}$* = 6.2, $J_{A,4'}$* = 1.4, $J_{B,4'}$* = 6.5, br. B part, i.e., $J_{B,1'}$* not resolved, A,B = 2 x 2'-H, 2 x 3'-H), 5.83 (ddd, J_{trans} = 17.3, J_{cis} = 10.6, $J_{2,3}$ = 4.9, 2-H), 2 AA'BB' signals centered at 6.82 und 7.08 (2 x C_6H_4); * the starred *J* values are all at once interchangeable.- IR: ν = 2995 cm^{-1}, 2930, 2855, 1610, 1515, 1465, 1300, 1245, 1175, 1105, 1035, 970, 825.

3,3-Bis-(trans-3-cyclohexyl-2-propenyloxy)-1-propene (trans-12c): ^{1}H NMR (250 MHz): δ = 0.85-1.40 und 1.56-1.83 [2m, 2 x 10H, 2 x $(CH_2)_5$], 1.98 (m_c, 2 x 1"-H), 2 identical AB signals (δ_A = 3.97, δ_B = 4.04, J_{AB} = 11.9, in addition split by $J_{A,2'}$ = 6.3, $J_{B,2'}$ = 5.8, 2 x 1'-H_2), 4.96 (dt, $J_{3,2}$ = 4.9, $J_{3,1} \approx$ 1, 3-H), 5.29 (ddd, J_{cis} = 10.4, $J_{gem} = J_{allyl}$ = 1.4, 1-H^E), AB signal (δ_A = 5.39, δ_B = 5.85, J_{AB} = 17.2, in addition split by $J_{A,gem} = J_{A,allyl}$ = 1.4, J_{cis} = 10.7, $J_{B,3}$ = 4.9, A: 1-H^Z, B: 2-H), 2 identical AB signals (δ_A = 5.51, δ_B = 5.65, J_{AB} = 15.6, in addition split by $J_{A,1'}$ = 6.0, $J_{A,1"}$ = 1.2, $J_{B,1"}$ = 6.1, br. B part, i.e., $J_{B,1'}$ not resolved, A: 2 x 2'-H, B: 2 x 3'-H).- IR: ν = 2920 cm^{-1}, 2850, 1720, 1450, 1410, 1340, 1135, 1095, 1025, 970, 935.

3,3-Bis-(trans-4,4-dimethyl-2-pentenyloxy)-1-propene (trans-12d, slightly contaminated): ^{1}H NMR (200 MHz): δ = 1.01 [s, 2 x $C(CH_3)_3$], AB signal (δ_A = 3.97, δ_B = 4.06, J_{AB} = 11.8, in additon split by $J_{A,2'}$ = 6.4, $^4J_{A,3'}$ = 1.1, $J_{B,2'}$ = 6.0, $^4J_{B,3'}$ = 1.1, 2 x 1'-H_2), 4.95 (dt, $J_{3,2}$ = 4.9, $^4J_{3,1} \approx$ 1, 3-H), 5.29 (ddd, J_{cis} = 10.5, $J_{gem} \approx J_{allyl} \approx$ 1.4, 1-H^E), 5.39 (ddd, J_{trans} = 17.5, $J_{gem} \approx J_{allyl} \approx$ 1.4, 1-H^Z), AB signal (δ_A = 5.47, δ_B = 5.71, J_{AB} = 15.7, in additon split by $J_{A,1'}$ = 6.1, $^4J_{B,1'}$ = 1.1, A: 2 x 2'-H, B: 2 x 3'-H), 5.86 (ddd, J_{trans} = 17.6, J_{cis} = 10.4, $J_{2,3}$ = 5.0, 2-H).- IR: ν = 2960 cm^{-1}, 2905, 2865, 1475, 1460, 1360, 1140, 1100, 1035, 975, 935.

3,3-Bis-[cis-5-(4-methoxyphenyl)-2-pentenyloxy]-1-propene (cis-12b): ^{1}H NMR (500 MHz): δ = 2.35 (dt with extra peak indicating transition to higher order spectrum, $J_{4',3'} \approx J_{4',5'} \approx$ 7.3, 2 x 4'-H_2), 2.61 (t, $J_{5',4'}$ = 7.8, 2 x 5'-H_2), 3.78 (s, 2 x OCH_3), AB signal (δ_A = 4.97, δ_B = 5.04, J_{AB} = 11.6, in additon split by $J_{A,2'}$ = 6.1, $J_{B,2'}$ = 5.9, in A and B part J_{allyl} incompletely resolved, 2 x 1'-H_2), 4.88 (dt, $J_{3,2}$ = 4.9, J_{allyl} = 1.1, 3-H), 5.29 (ddd, J_{cis} = 10.6, $J_{gem} \approx J_{allyl} \approx$ 1.4, 1-H^E), 5.38 (ddd, J_{trans} = 17.4, $J_{gem} \approx J_{allyl} \approx$ 1.4, 1-H^Z), 5.58 (m_c, 2'-H, 3'-H), 5.81 (ddd, J_{trans} = 17.4, J_{cis} = 10.6, $J_{2,3}$ = 4.9, 2-H), 2 identical AA'BB' signals centered at 6.82 und 7.08 (2 x C_6H_4).- IR: ν = 2930 cm^{-1}, 1510, 1615, 1455, 1245, 1035.

3,3-Bis-(cis-3-cyclohexyl-2-propenyloxy)-1-propene (cis-12c): ^{1}H NMR (500 MHz): δ = 1.02 - 1.32 and 1.53 - 1.74 [2m, 2 x 10H, 2 x $(CH_2)_5$], 2.27 (m_c, 2 x 1"-H), AB signal (δ_A = 4.10, δ_B = 4.15, J_{AB} = 12.1, in additon split by $J_{A,2'}$ = 5.6, $^4J_{A,3'}$ incompletely resolved, $J_{B,2'}$ = 5.1, $^4J_{B,3'}$ incompletely resolved, 2 x 1'-H_2), 4.98 (dt, $J_{3,2}$ = 4.9, J_{allyl} = 1.3, 3-H), 5.32 (ddd, J_{cis} = 10.7, $J_{gem} \approx J_{allyl} \approx$ 1.3, 1-H^E), 5.39 - 5.48 (m, 2 x 2'-H, 2 x 3'-H, 1-H^Z), 5.87 (ddd, J_{trans} = 17.4, J_{cis} = 10.5, $J_{2,3}$ = 4.8, 2-H).- IR: ν = 3010 cm^{-1}, 2925, 2850, 1655, 1450, 1135, 1080, 1025, 935, 890.

trans-1-[trans-3-(Phenylthio)-1-propenyloxy]-2-butene (trans-13a) and trans-1-[cis-3-(phenylthio)-1-propenyloxy]-2-butene (cis-trans-13a; representative procedure for the obtention of 13a from allenyl ethers 18a): Thiophenol (1.02 ml, 1.10 g, 10.0 mmol, 1 equiv.) and HBF_4 (2 drops of a 50% solution in ether) were added to *trans*-**18a** (1.443 g of a 76.3% solution in THF, 10.0 mmol) in CH_2Cl_2 (10 ml) at -40°C. The mixture was stirred for 2 h at -20 to -10°C, then quenched by rapid addition of 2 N NaOH (10 ml) and allowed to warm

to room temp. After extractive workup (2 N NaOH/ether), the organic layer was dried ($MgSO_4/Na_2CO_3$) and the solvent evaporated under reduced pressure. Flash chromatography (PE/E 200/1 to 100/1) gave *trans*-**13a** (750.1 mg, 34%), *cis-trans*-**13a** (275.6 mg, 13%), and *trans*-1-[1,3-bis(phenylthio)propyl]-2-butene (183.9 mg, 6%).- *trans*-**13a**, ^{1}H NMR: δ = 1.71 (dm_c, $J_{4,3}$ = 6.3, 4-H_3), 3.49 (dd, $J_{3',2'}$ = 7.7, $J_{3',1'}$ = 1.0, 3'-H_2), 4.10 (br. d, $J_{1,2}$ = 6.2, 1-H_2), 4.89 (dt, $J_{2',1'}$ = 12.5, $J_{2',3'}$ = 7.7, 2'-H), AB signal (δ_A = 5.56, δ_B = 5.73, $J_{A,B}$ = 15.3, in addition split by $J_{A,1}$ = 6.2, $J_{A,4}$ = 1.5, $J_{B,4}$ = 6.4, $J_{B,1}$ = 1.1, A: 2-H, B: 3-H), 6.31 (br. d, $J_{1',2'}$ = 12.5, 1'-H), 7.15-7.23 and 7.23-7.37 (2m, Ar-H).- *cis-trans*-**13a**, ^{1}H NMR (300 MHz): δ = 1.73 (dm_c, $J_{4,3}$ = 6.3, 4-H_3), 3.66 (dd, $J_{3,2'}$ = 7.7, $J_{3',1'}$ = 1.2, 3'-H_2), 4.18 (dm_c, $J_{1,2}$ = 6.2, 1-H_2), 4.50 (td, $J_{2',3'}$ = 7.7, $J_{2',1'}$ = 6.1, 2'-H), AB signal (δ_A = 5.55, δ_B = 5.73, $J_{A,B}$ = 15.3, in addition split by $J_{A,1}$ = 6.2, $J_{A,4}$ = 1.5, $J_{B,4}$ = 6.4, $J_{B,1}$ = 1.1, A: 2-H, B: 3-H), 6.06 (dt, $J_{1',2'}$ = 6.2, $J_{1',3'}$ = 1.1, 1'-H), 7.10-7.18 and 7.20-7.38 (2m, Ar-H).

trans-5-(4-Methoxyphenyl)-1-[trans-3-(phenylthio)-1-propenyloxy]-2-pentene (trans-13b; representative procedure for the preparation of vinylogous O,S-acetals 13b,c,d; method: ref. [17]): At -78°C BF_3OEt_2 (1.0 M toluene solution, 0.66 ml, 0.66 mmol, 1.0 equiv.) was slowly added to a solution of O,O-acetal **13b** (280 mg, 0.663 mmol) and $Bu_2Sn(SPh)_2$ (150 mg, 0.33 mmol, 0.5 equiv.) in toluene (2 ml). After stirring for 30 min at this temperature the reaction was quenched with dry pyridine (0.5 ml). The mixture was poured into aq. 1.0 M NaOH solution (5 ml) and extracted with tBuOMe (3 x 5 ml). The combined extracts were dried (Na_2CO_3/Na_2SO_4) and evaporated. Flash chromatography over deactivated silica gel [pretreated over 25 % aq. NH_3 (3.5 weight %); petroleum ether/tBuOMe (200:1 → 50:1)] yielded *trans*-**13b** (48.5 mg, 21%).- ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.33 (m_c, 4-H_2), 2.64 (t, $J_{5,4}$ = 7.8, 5-H_2), 3.49 (dd, $J_{3',2'}$ = 7.8, J_{allyl} = 0.9, 3'-H_2), 3.79 (s, OCH_3), 4.11 (br. d, $J_{1,2}$ = 6.0, 1-H_2), 4.88 (dt, $J_{2',1'}$ = 12.5, $J_{2',3'}$ = 7.7, 2'-H), AB signal (δ_A = 5.56, δ_B = 5.74, J_{AB} = 15.3, in additon split by $J_{A,vic}$ = 6.2, $^4J_{A,allyl}$ = 1.4, $J_{B,vic}$ = 6.6, $^4J_{B,allyl}$ incompletely resolved, 2-H, 3-H), 6.30 (d, $J_{1',2'}$ = 12.6, 1'-H), AA'BB' signal centered at 6.83 and 7.09 (C_6H_4), 7.16-7.36 (m, SC_6H_5).

trans-1-(trans-3-Cyclohexyl-2-propenyloxy)-3-(phenylthio)-1-propene (trans-13c): ^{1}H NMR (250 MHz): δ = 0.96-1.36 and 1.59-1.77 [2 m, 2 x 5H, $(CH_2)_5$], 1.96 (m_c, 1"-H), 3.49 (dd, $J_{3,2}$ = 7.8, $J_{3,1}$ = 1.1, 3-H_2), 4.11 (d, $J_{1',2'}$ = 5.8, 1'-H_2), 4.88 (dt, $J_{2,1}$ = 12.5, $J_{2,3}$ = 7.8, 2-H), AB signal (δ_A = 5.48, δ_B = 5.66, J_{AB} = 15.6, in addition split by $J_{A,1'}$ = 6.0, $J_{A,1"}$ = 1.2, $J_{B,1"}$ = 6.4, $J_{B,1'}$ not resolved, A: 2'-H, B: 3'-H), 6.32 (br. d, $J_{1,2}$ = 12.5, 1-H), 7.14-7.37 (m, SC_6H_5).- IR: ν = 2920 cm^{-1}, 2850, 1660, 1645, 1585, 1480, 1450, 1195, 1150, 1090, 1025, 970, 930, 740, 690.

trans-4,4-Dimethyl-1-[trans-3-(phenylthio)-2-propenyloxy]-2-pentene (trans-13d): ^{1}H NMR (200 MHz): δ = 1.03 [s, $C(CH_3)_3$], 3.51 (dd, $J_{3',2'}$ = 7.5, J_{allyl} = 1.0, 3'-H_2), 4.14 (dd, $J_{1,2}$ = 6.1, J_{allyl} ≈ 0.8, 1-H_2), 4.91 (dt, $J_{2',1'}$ = 12.5, $J_{2',3'}$ = 7.7, 2'-H), AB signal (δ_A = 5.47, δ_B = 5.75, J_{AB} = 15.9, in additon split by $J_{A,1}$ = 6.1, $^4J_{B,1}$ ≈ 1.0, A: 2-H, B: 3-H), 6.35 (d, $J_{1',2'}$ = 12.4, J_{allyl} not resolved, 1'-H), 7.15-7.40 (m, C_6H_5).- IR: ν = 3060 cm^{-1}, 2960, 2865, 1645, 1585, 1480, 1365, 1200, 1145, 1025, 975, 740, 690.

cis-1-[trans-3-(Phenylthio)-1-propenyloxy]-2-butene (cis-13a): ^{1}H NMR (300 MHz): δ = 1.65 (dm_c, $J_{4,3}$ = 6.9, 4-H_3), 3.50 (dd, $J_{3',2'}$ = 7.7, $J_{3',1'}$ = 1.0, 3'-H_2), 4.24 (br. d, $J_{1,2}$ = 6.5, 1-H_2), 4.89 (dt, $J_{2',1'}$ = 12.5, $J_{2',3'}$ = 7.7, 2'-H), AB signal (δ_A = 5.53, δ_B = 5.69, $J_{A,B}$ = 11.0, in addition split by $J_{A,1}$ = 6.4, $J_{A,4}$ = 1.7, $J_{B,4}$ = 6.9, $J_{B,1}$ = 1.4, A: 2-H, B: 3-H), 6.33 (br. d, $J_{1',2'}$ = 12.6, 1'-H), 7.15-7.23 and 7.23-7.38 (2m, Ar-H).

cis-5-(4-Methoxyphenyl)-1-[trans-3-(phenylthio)-1-propenyloxy]-2-pentene (cis-13b): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (dt, $J_{4,3}$ ≈ $J_{4,5}$ ≈ 7.5, 4-H_2), 2.62 (t, $J_{5,4}$ ≈ 7.6, 5-H_2), 3.46 (dd, $J_{3',2'}$ = 7.7, J_{allyl} = 1.0, 3'-H_2), 3.77 (s, OCH_3), 4.09 (br. d, $J_{1,2}$ = 6.2, 1-H_2), 4.82 (dt, $J_{2',1'}$ = 12.4, $J_{2',3'}$ = 7.7, 2'-H), AB signal (δ_A =

5.50, δ_B = 5.61, J_{AB} = 11.1, in additon split by $J_{A,vic}$ = 6.2, $^4J_{A,allyl}$ = 1.3, $J_{B,vic}$ = 7.3, $^4J_{B,allyl}$ = 1.3, 2-H, 3-H), 6.24 (d, $J_{1',2'}$ = 12.7, J_{allyl} not resolved, 1'-H), AA'BB' signal centered at 6.82 and 7.08 (C_6H_4), 7.14-7.36 (m, SC_6H_5).

*trans-1-(cis-3-Cyclohexyl-2-propenyloxy)-3-(phenylthio)-1-propene (cis-**13c**):* ^{1}H NMR (300 MHz, C_6D_5H internal standard in C_6D_6): δ = 0.83-1.24 and 1.46-1.66 [2 m, 2 x 5H, $(CH_2)_5$], 2.08 (m_c, 1"-H), 3.25 (dd, $J_{3,2}$ = 7.7, J_{allyl} = 1.1, 3-H_2), 4.05 (dd, $J_{1',2'}$ = 6.2, J_{allyl} = 1.3, 1'-H_2), 4.86 (dt, $J_{2,1}$ = 12.6, $J_{2,3}$ = 7.7, 2-H), AB signal (δ_A = 5.29, δ_B = 5.44, J_{AB} = 11.0, in additon split by $J_{A,1"}$ = 9.7, $^4J_{A,1'}$ = 1.4, $J_{B,1'}$ = 6.3, $^4J_{B,1"}$ = 0.8, A: 3'-H, B: 2'-H), 6.20 (d, $J_{1,2}$ = 12.4, 1-H), 6.90-7.08 and 7.27-7.33 (2 m 2H and 3H, SC_6H_5).

*trans-1-[1-(Phenylthio)-2-propenyloxy]-2-butene (trans-**14a**; representative procedure for the obtention of **14a** from phenylseleno ethers **16a**):* MCPBA (109.1 mg of a 85% mixture with 3-chlorobenzoic acid; 0.5374 mmol, 1.0 equiv.) in CH_2Cl_2 (2-3 ml), precooled to -78°C, was added via a dry-ice cooled cannula to *trans*-**16a** (202.6 mg, 0.5368 mmol) in CH_2Cl_2 (1 ml) at -78°C. After 1 h, iPr_2NH (0.150 ml, 108 mg, 1.07 mmol, 2.0 equiv.) was added. The resulting mixture was transferred via a dry-ice cooled cannula into refluxing CH_2Cl_2 (10 ml). After heating for 30 min, quenching with satd. aq. $NaHCO_3$ solution (10 ml), and extractive workup ($NaHCO_3$/ether), the organic layer was dried ($MgSO_4$) and evaporated. Flash chromatography (PE/E 200/1) gave *trans*-**14a** (86.7 mg, 73%) and recovered *trans*-**16a** (12.8 mg, 6%).- ^{1}H NMR (300 MHz): δ = 1.71 (dm_c, $J_{4,3}$ = 6.3, 4-H_3), AB signal (δ_A = 4.07, δ_B = 4.32, $J_{A,B}$ = 11.7, in addition split by $J_{A,2}$ = 6.8, $^4J_{A,3} \approx {}^5J_{A,4} \approx$ 1.0, $J_{B,2}$ = 5.7, $^4J_{B,3} \approx {}^5J_{B,4} \approx$ 1.2, 1-H_2), 5.08 (dm_c, $J_{3'(E),2'}$ = 10.5, 3'-H^E), 5.23 (dm_c, $J_{3(Z),2}$ = 17.0, 3-H^Z), superimposes 5.25 (dm_c, $J_{1',2'}$ = 5.1, 1'-H), AB signal (δ_A = 5.57, δ_B = 5.73, $J_{A,B}$ = 15.3, in addition split by $J_{A,1\text{-}H(A)}$ = 6.8, $J_{A,1\text{-}H(B)}$ = 5.5, $^4J_{A,4}$ = 1.4, $J_{B,4}$ = 6.3, $^4J_{B,1\text{-}H(A)} \approx {}^4J_{B,1\text{-}H(B)} \approx$ 1.0, A: 2-H, B: 3-H), 5.88 (ddd, $J_{2',3'(Z)}$ = 16.9, $J_{2',3'(E)}$ = 10.5, $J_{2',1'}$ = 5.6, 2'-H), 7.21-7.34 and 7.42-7.52 (2m, Ar-H).

*trans-5-(4-Methoxyphenyl)-1-[1-(phenylthio)-2-propenyloxy]-2-pentene (trans-**14b**; representative procedure for the preparation of O,S-acetals **14b**;* method: ref. [23, 24]): At 0°C PhSH (0.53 ml, 0.53 mmol, 1.5 equiv.) was added dropwise under vigorous stirring to a solution of Et_3Al (1.2 M in toluene, 0.89 ml, 1.1 mmol, 3.0 equiv.). The mixture was allowed to warm to room temp. and stirred for 1 h. At 0°C, O,O-acetal **12b** (150 mg, 0.355 mmol) was added. After 2 h the reaction was quenched with satd. aq. Na_2CO_3 solution (5.0 ml) and extracted with tBuOMe (3 x 6 ml). Flash chromatography over deactivated silica gel [pretreated with 25 % aq. NH_3 (3.5 weight %); petroleum ether/tBuOMe (200:1 → 50:1)] yielded **14b** (53 mg, 44%).- ^{1}H NMR (300 MHz, C_6D_5H internal standard in C_6D_6): δ = 2.17 (m_c, 4-H_2), 2.48 (t, $J_{5,4}$ = 7.4, 5-H), 3.34 (s, OCH_3), br. AB signal (δ_A = 3.99, δ_B = 4.31, J_{AB} = 12.2, in additon split by $J_{A,2}$ = 6.2, $J_{B,2}$ = 5.3, 1-H_2), 4.91 (dt, J_{cis} = 10.5, $J_{gem} \approx J_{allyl} \approx$ 1.4, 3'-H^E), 5.12 (dm_c, $J_{1',2'}$ = 4.7, 1'-H), 5.28 (ddd, J_{trans} = 17.1, $J_{gem} \approx J_{allyl} \approx$ 1.5, 3'-H^Z), AB signal (δ_A = 5.46, δ_B = 5.62, J_{AB} = 15.5, in additon split by $J_{A,vic}$ = 5.9, J_{allyl} incompletely resolved, $J_{B,vic}$ = 6.5, J_{allyl} not resolved, 2-H, 3-H), 5.91 (ddd, J_{trans} = 17.1, J_{cis} = 10.5, $J_{2',1'}$ = 4.9, 2'-H), AA'BB' signal centered at 6.80 and 6.94, (C_6H_4), ca 6.80-7.09 (m, *m*-, *p*-SC_6H_5), 7.55 (m_c, *o*-SC_6H_5).

*1-cis-1-[1-(Phenylthio)-2-propenyloxy]-2-butene (cis-**14a**):* ^{1}H NMR (300 MHz): δ = 1.69 (d, $J_{4,3}$ = 6.9, 4-H_3), AB signal (δ_A = 4.25, δ_B = 4.42, $J_{A,B}$ = 12.0, in addition split by $J_{A,2}$ = 7.1, $J_{B,2}$ = 6.2, 1-H_2), 5.09 (dm_c, $J_{3'(E),2'}$ = 10.5, 3'-H^E), 5.23 (dm_c, $J_{3'(Z),2'} \approx$ 17.4, Z-3-H^Z), superimposes 5.25 (d, $J_{1',2'} \approx$ 5.3, 1'-H), 5.51-5.62 and 5.65-5.77 (2m, 2-H, 3-H), 5.89 (ddd, $J_{2',3(Z)'}$ = 17.2, $J_{2',3'(E)}$ = 10.5, $J_{2',1'}$ = 5.3, 2'-H), 7.23-7.35 and 7.42-7.52 (2m, Ar-H).

cis-5-(4-Methoxyphenyl)-1-[1-(phenylthio)-2-propenyloxy]-2-pentene (cis-14b): ^{1}H NMR (300 MHz, C_6D_5H internal standard in C_6D_6): δ = 2.28 (td, $J_{4,5} \approx J_{4,3} \approx 7$, 4-$H_2$), 2.48 (t, $J_{5,4}$ = 7.5, 5-H), 3.34 (s, OCH_3), AB signal (δ_A = 4.09, δ_B = 4.34, J_{AB} = 12.2, in additon split by $J_{A,2}$ = 6.8, $J_{B,2}$ = 5.6, 1-H_2), 4.90 (ddd, J_{cis} = 10.6, $J_{gem} \approx J_{allyl} \approx 1.5$, 3'-$H^E$), 5.08 (dt, $J_{1',2'}$ = 4.9, J_{allyl} = 1.5, 1'-H), 5.25 (ddd, J_{trans} = 17.1, $J_{gem} \approx J_{allyl} \approx 1.5$, 3'-$H^Z$), 5.45-5.68 (m, 2-H, 3-H), 5.88 (ddd, J_{trans} = 17.2, J_{cis} = 10.6, $J_{2',1'}$ = 4.9, 2'-H), AA'BB' signal centered at 6.83 and ca. 7.1 (C_6H_4), BB' part superimposed by 6.92-7.08 (m, *m*-,*p*-SC_6H_5), 7.54 (m_c, *o*-SC_6H_5).

3-(Phenylseleno)propanal (15) (method: ref. [20]): Acrolein (1.41 ml, 1.20 g, 21.4 mmol) was added to selenophenol (3.32 ml, 5.03 g, 32.0 mmol, 1.5 equiv.) in ethanol (60 ml) at 0°C. The solution was stirred for 3 h at 0°C and stood in a freezer (-20°C) overnight. The solvent was removed and the residue taken up in ether. The ether solution was washed with distilled water and brine and dried ($MgSO_4$) and the solvent removed. Flash chromatography (PE/E 15/1 to 10/1) gave 2.7884 g (61%).- ^{1}H NMR (300 MHz): δ = 2.87 (t, $J_{2,3}$ = 7.1, 2-H_2), 3.11 (t, $J_{3,2}$ = 7.2, 3-H_2), 7.20-7.33 and 7.47-7.56 (2m, Ar-H), 9.74 (s, CHO).

trans-1-[3-(Phenylseleno)-1-(phenylthio)propoxy]-2-butene [trans-16a; representative procedure for the one-pot synthesis of O,S-acetals 16a along with 3-(phenylseleno)-1-(phenylthio)-1-(trimethylsilyloxy)propane (17); method: ref. [21]]: *trans*-**11a** (0.180 ml, 145 mg, 1.00 mmol, 1.0 equiv.) followed by $PhSSiMe_3$ (0.190 ml, 182 mg, 1.00 mmol, 1.0 equiv.) were added to TMSOTf (0.5 M in CH_2Cl_2; 1.00 ml, 0.500 mmol, 50 mol%) at -78°C. 15 (0.670 ml of a 25.3% solution in CH_2Cl_2, 896 mg, 1.06 mmol, 1.1 equiv.) was added dropwise and the solution stirred for 1 h at -78°C. The reaction mixture was quenched by the addition of pyridine (0.2 ml) and allowed to warm to room temp.. After extractive workup ($NaHCO_3$/ether), the combined organic layers were dried ($MgSO_4$) and the solvent removed. Flash chromatography (PE/E 200/1) gave *trans*-**16a** (176.6 mg, 47%) and **17** (133.9 mg, 34%). Increasing the amount of catalyst to 200 mol%, with a reaction time of 30 min, gave *trans*-**16a** (34%) and **17** (43%).- *trans*-**16a**, ^{1}H NMR (300 MHz): δ = 1.71 (dm_c, $J_{4,3}$ = 6.3, 4-H_3), 2.01-2.23 (m, 2'-H_2), 3.00 (t, $J_{3',2'}$ = 7.2, 3'-H_2), AB signal (δ_A = 3.93, δ_B = 4.32, $J_{A,B}$ = 11.6, in addition split by $J_{A,2}$ = 6.9, $J_{B,2}$ = 5.8, 1-H_2), 4.87 (dd, $J_{1',2'\text{-H(A)}}$ = 7.2, $J_{1',2'\text{-H(B)}}$ = 5.9, 1'-H), AB signal (δ_A = 5.54, δ_B = 5.69, $J_{A,B} \approx$ 15, in addition split by $J_{A,1\text{-H(A)}} \approx 7$, $J_{A,1\text{-H(B)}} \approx$ 5.6, $^4J_{A,4}$ = 1.5, $J_{B,4}$ = 6.3, A: 2-H, B: 3-H), 7.16-7.34 and 7.37-7.49 (2m, Ar-H).- 17, ^{1}H NMR (300 MHz): δ = 0.05 [s, $OSi(CH_3)_3$], 2.12 (td, $J_{2,3} \approx J_{2,1} \approx 7$, 2-$H_2$), 2.99 ($m_c$, 3-$H_2$), 5.21 (t, $J_{1,2}$ = 6.2, 1-H), 7.16-7.34 and 7.39-7.51 (2m, Ar-H).

cis-1-[3-(Phenylseleno)-1-(phenylthio)propoxy]-2-butene (cis-16a): ^{1}H NMR (300 MHz): δ = 1.67 (dm_c, $J_{4,3}$ = 6.7, 4-H_3), 2.01-2.22 (m, 2'-H_2), 2.92-3.08 (m, 3'-H_2), AB signal (δ_A = 4.14, δ_B = 4.42, $J_{A,B}$ = 11.9, in addition split by $J_{A,2}$ = 7.3, $J_{B,2}$ = 6.1, 1-H_2), 4.87 (dd, $J_{1',2'\text{-H(A)}}$ = 7.3, $J_{1',2'\text{-H(B)}}$ = 5.8, 1'-H), AB signal (δ_A = 5.53, δ_B = 5.70, $J_{A,B}$ = 10.9, in addition split by $J_{A,1\text{-H(A)}}$ = 7.4, $J_{A,1\text{-H(B)}}$ = 5.9, $^4J_{A,4}$ = 1.8, $J_{B,4}$ = 6.9, $J_{B,1\text{-H(B)}}$ = 1.4, A: 2-H, B: 3-H), 7.18-7.33 and 7.39-7.49 (2m, Ar-H).

trans-1-(1,2-Propadienyloxy)-2-butene (trans-18a; representative procedure for the preparation of allenyl ethers; method: ref. [25]): *tert*-BuOK (1.376 g, 12.26 mmol, 0.13 equiv.) was added to *trans*-**19a** [11] (10.20 g, 92.60 mmol) in THF (40 ml). The reaction mixture was stirred for 1 h at room temp., 5 h at 50°C and then overnight again at room temp. Most of the solvent was evaporated and the residue purified by vacuum transfer (0.2-0.4 Torr) to give a mixture (7.658 g) of *trans*-**18a** (5.842 g by ^{1}H NMR, 57%) and THF.- ^{1}H NMR (300 MHz): δ = 1.73 (dm_c, $J_{4,3}$ = 6.2, 4-H_3), 4.01 (br. d, $J_{1,2}$ = 6.2, 1-H_2), 5.44 (d, $^4J_{3',1'}$ = 5.9, 3'-H_2), AB signal (δ_A = 5.64, δ_B = 5.77, $J_{A,B}$ = 15.2, in addition split by $J_{A,1}$ = 6.2, $J_{B,4}$ = 6.3, A: 2-H, B: 3-H), 6.73 (t, $^4J_{1',3'}$ = 5.9, 1'-H).

cis-1-(1,2-Propadienyloxy)-2-butene (cis-18a): ^{1}H NMR (300 MHz): δ = 1.67 (dm_c, $J_{4,3}$ = 6.5, 4-H_3), 4.15 (br. d, $J_{1,2}$ = 6.1, 1-H_2), 5.45 (d, $^4J_{3',1'}$ = 6.2, 3'-H_2), 5.55-5.77 (m, 2-H, 3-H), 6.75 (t, $^4J_{1',3'}$ = 6.0, 1'-H).

General procedure for the reductive cleavage of simple and vinylogous O,S-acetals: A solution of **13** (1.0 equiv.) or **14** (1.0 equiv.) in THF (1-2 ml) was added to a stirred (glass-covered stirrer bar) solution of alkali metal naphthalenide (3.0 eq., 0.29-0.36 M in THF) at -78°C. Stirring was continued for 1-4 h. Benzoyl chloride (5.5 equiv.) was added rapidly to the vigorously stirred solution and the cooling bath removed. The mixture was stirred for 3 -12 h at room temp. and then quenched with satd. $NaHCO_3$ solution (ca. 5 ml). After extractive workup ($NaHCO_3$/ether), the organic layer was dried ($MgSO_4$) and evaporated. Products were analyzed by GLC (CP Sil 5 CB, 25 m, 0.25 mm, Chrompack; isomer 1 elutes after isomer 2) and purified by flash chromatography without separation of isomers.

*(2-Methyl-1-vinyl-3-butenyl)benzoate (anti,syn-20a): anti-***20a** (isomer 2), ^{1}H NMR (300 MHz): δ = 1.10 (d, $J_{2\text{-Me},2}$ = 6.8, 2-CH_3), 2.60 (m_c, 2-H), ca. 5.08 (dm_c, $J_{cis} \approx 10$, 4-H^E), superimposes 5.12 (dm_c, $J_{trans} \approx 17$, 4-H^Z), 5.26 (ddd, J_{cis} = 10.6, $J_{allyl} \approx J_{gem} \approx 1.3$, 2'-$H^E$), 5.33 (ddd, J_{trans} = 17.3, $J_{allyl} \approx J_{gem} \approx 1.4$, 2'-$H^Z$), 5.43 (dd, $J_{1,1'} \approx J_{1,2} \approx 6.1$, 1-H), 5.84 (ddd, J_{trans} = 17.2, J_{cis} = 10.3, $J_{3,2}$ = 7.7, 3-H)*, superimposes 5.87 (ddd, J_{trans} = 17.3, J_{cis} = 10.6, $J_{1',1}$ = 6.6, 1'-H)*, 7.39-7.65 and 8.00-8.10 (2m, Ar-H); *assignment and *J* indices perhaps interchangeable.- *syn-***20a** (isomer 1), ^{1}H NMR (300 MHz): δ = 1.12 (d, $J_{2\text{-Me},2}$ = 6.9, 2-CH_3), 2.63 (m_c, 2-H), 5.09 (ddd, J_{cis} = 10.5, $J_{allyl} \approx J_{gem} \approx 1.1$, 4-$H^E$), superimposes 5.11 (ddd, J_{trans} = 17.3, $J_{allyl} \approx J_{gem} \approx 1.4$, 4-$H^Z$), 5.25 (ddd, J_{cis} = 10.6, $J_{allyl} \approx J_{gem} \approx 1.3$, 2'-$H^E$), 5.31 (ddd, J_{trans} = 17.3, $J_{allyl} \approx J_{gem} \approx 1.4$, 2'-$H^Z$), 5.43 ($ddm_c$, $J_{1,1'} \approx J_{1,2} \approx 6.0$, 1-H), 5.86 (ddd, J_{trans} = 17.1, J_{cis} = 10.6, $J_{3,2}$ = 6.6, 3-H)*, superimposes 5.88 (ddd, J_{trans} = 17.3, J_{cis} = 10.6, $J_{1',1}$ = 5.6, 1'-H)*, 7.37-7.61 and 8.00-8.11 (2m, Ar-H); *assignment and *J* indices interchangeable.

{2-[2-(4-Methoxyphenyl)ethyl]-1-vinyl-3-butenyl}benzoate (20b): **20b** (isomer 1), ^{1}H NMR (500 MHz): δ = 1.64 (dddd, J_{gem} = 13.6, $J_a = J_b$ = 10.0, J_c = 4.9, 1"-H^1), 1.88 (dddd, J_{gem} = 13.6, J_a = 10.5, J_b = 6.9, J_c = 3.4, 1"-H^2), 2.44-2.53 (m, 2-H, 2"-H^2), 2.68 (ddd, J_{gem} = 14.3, J_a = 9.6, J_c = 4.6, 2"-H^1), 3.79 (s, OCH_3), 5.15 and 5.29 (2ddd, J_{trans} = 17.0, J_a = 1.8, J_b = 0.8; J_{trans} = 17.3, $J_{gem} \approx J_{allyl} \approx 1.4$; 4-$H^Z$, 2'-$H^Z$), 5.22 and - in part superimposing - 5.24 (dd and ddd, J_{cis} = 10.4, J_a = 1.8; J_{cis} = 10.4, $J_{gem} \approx J_{allyl} \approx 1.4$; 4-$H^E$, 2'-$H^E$), 5.49 (ddt, $J_{1,2} \approx J_{1,1'} \approx 6.0$, $J_{allyl} \approx 1.2$, 1-H), 5.72 (ddd, J_{trans} = 17.2, J_{cis} = 10.3, $J_{3,2}$ = 9.2, 3-H), 5.87 (ddd, J_{trans} = 17.2, J_{cis} = 10.6, $J_{1',1}$ = 6.4, 1'-H), AA'BB' signal centered at 6.82 and 7.09 (C_6H_4), 7.41-7.47, 7.53-7.58, and 8.01-8.07 (3m, Ar-H).- **20b** (isomer 2), ^{1}H NMR (500 MHz): δ = 1.64 (m_c, 1"-H^1), 1.87 (m_c, 1"-H^2), 2.41 (m_c, 2-H), AB signal (δ_A = 2.50, δ_B = 2.66, J_{AB} = 13.8, in addition split by $J_{A,1''\text{-H(1)}}$ = 9.6, $J_{A,1''\text{-H(2)}}$ = 7.1, $J_{B,1''\text{-H(2)}}$ = 9.9, $J_{B,1''\text{-H(1)}}$ = 5.1, A: 2"-H^1, B: 2"-H^2), 3.78 (s, OCH_3), 5.15 and 5.31 (dm_c and ddd, J_{trans} = 17.2; J_{trans} = 17.2, $J_{gem} \approx J_{allyl} \approx 1.3$; 4-$H^Z$, 2'-$H^Z$), 5.21 and - in part superimposing - 5.24 (dd and ddd, J_{cis} = 10.2, J_a = 1.9; J_{cis} = 10.5, $J_{gem} \approx J_{allyl} \approx 1.2$; 4-$H^E$, 2'-$H^E$), 5.51 (dd, $J_{1,1'}$ = 6.7, $J_{1,2}$ = 5.5, J_{allyl} incompletely resolved, 1-H), 5.76 (ddd, J_{trans} = 17.2, J_{cis} = 10.3, $J_{3,2}$ = 9.2, 3-H), 5.85 (ddd, J_{trans} = 17.3, J_{cis} = 10.6, $J_{1',1}$ = 6.7, 1'-H), AA'BB' signal centered at 6.81 and 7.08 (C_6H_4), 7.42-7.47, 7.54-7.59, and 8.02-8.06 (3m, Ar-H).

(2-Cyclohexyl-1-vinyl-3-butenyl)benzoate (20c): **20c** (isomer 1), ^{1}H NMR (500 MHz): δ = 0.8-1.8 (m, cyclohexyl), 2.31 (ddd, $J_{2,3}$ = 10.1, $J_{2,1} \approx J_{2,1''} \approx 6.8$, 2-H), 5.04 and 5.31 (2ddd, J_{trans} = 17.0, J_a = 2.1, J_b = 0.7; J_{trans} = 17.1, $J_{gem} \approx J_{allyl} \approx 1.4$; 4-$H^Z$, 2'-$H^Z$), 5.16 and 5.23 (dd and ddd, J_{cis} = 10.3, J_a = 2.2; J_{cis} = 10.5, $J_{gem} \approx J_{allyl} \approx 1.4$; 4-$H^E$, 2'-$H^E$), 5.63 (ddd, J_{trans} = 17.0, $J_{cis} = J_{3,2}$ = 10.1, 3-H), superimposes 5.66 (ddt, $J_{1,2} = J_{1,1'}$ = 6.8, J_{allyl} = 1.2, 1-H), 5.89 (ddd, J_{trans} = 17.1, J_{cis} = 10.6, $J_{1',1}$ = 6.6, 1'-H), 7.41-7.58 and 8.04-8.08 (2m, Ar-H).- **20c** (isomer 2), ^{1}H NMR (500 MHz): δ = 0.87-1.80 (m, cyclohexyl), 2.11 (ddd, $J_{2,3}$ = 9.8, $J_{2,1''}$ =

6.6, $J_{2,1}$ = 5.3, 2-H), 5.04 and 5.30 (2ddd, J_{trans} = 17.1, J_a = 2.1, J_b = 0.6; J_{trans} = 17.2, $J_{gem} \approx J_{allyl} \approx$ 1.3; 4-H^Z, 2'-H^Z), 5.16 and 5.22 (dd and ddd, J_{cis} = 10.3, J_a = 2.2; J_{cis} = 10.4, $J_{gem} \approx J_{allyl} \approx$ 1.2; 4-H^E, 2'-H^E), 5.69 (ddt, $J_{1,1'}$ = 6.7, $J_{1,2}$ = 5.3, $J_{1,2'}$ = 1.0, 1-H), 5.78 (ddd, J_{trans} = 17.1, $J_{cis} = J_{3,2}$ = 10.0, 3-H), 5.85 (ddd, J_{trans} = 17.1, J_{cis} = 10.4, $J_{1',1}$ = 6.8, 1'-H), 7.42-7.46, 7.54-7.58, and 8.04-8.09 (3m, Ar-H).

(2-tert-Butyl-1-vinyl-3-butenyl)benzoate (20d): **20d** (isomer 2), ^{1}H NMR (500 MHz): δ = 0.96 [s, $C(CH_3)_3$], 1.98 (dd, $J_{2,3}$ = 10.2, J_a = 1.6, 2-H), 5.06 and 5.20 (dd and ddd, J_{trans} = 17.1, J_a = 2.0, J_{trans} = 17.0, $J_{gem} \approx J_{allyl} \approx$ 1.2; 4-H^Z, 2'-H^Z), 5.14 and 5.27 (ddd and dd, J_{cis} = 10.3, $J_{gem} \approx J_{allyl} \approx$ 1.2; J_{cis} = 10.3, J_a = 2.2; 4-H^E, 2'-H^E), 5.82 (ddd, J_{trans} = 16.9, J_{cis} = 10.4, $J_{1',1}$ = 6.3, 1'-H), 5.88 (dm_c, $J_{1,1'}$ = 6.2, 1-H), 6.05 (ddd, J_{trans} = 17.1, $J_{cis} = J_{3,2}$ = 10.2, 3-H), 7.42-7.47, 7.54-7.58 and, 8.03-8.06 (3m, Ar-H).

(1-Ethyl-2-methylbutyl)benzoate (anti,syn-21): A mixture of **23** (142.4 mg, 0.6523 mmol, 12:88 *syn:anti*) and 10% Pd/C (10.2 mg, 7%w/w) in a small amount of ethyl acetate was hydrogenated at atmospheric pressure. The reaction mixture was filtered through silica gel and the solvent evaporated to give 134.5 mg (94%, 17:83 *syn:anti*). **20a** was hydrogenated analogously.- *anti*-**21**, ^{1}H NMR (300 MHz): δ = 0.927 and 0.933 (2t, superimposing each other $J_{4,3} \approx J_{2',1'} \approx$ 7.4, 4-H_3 and 2'-H_3), superimposes 0.94 (d, $J_{2\text{-}Me,2}$ = 6.9, 2-CH_3), 1.13-1.84 (m, 1'-H_2, 2-H and 3-H_2), 5.01 (dt, $J_{1,2} = J_{1,1'}$ = 6.1, 1-H), 7.40 -7.59 and 7.97-8.15 (2m, Ar-H).- *syn*-**21**, ^{1}H NMR (300 MHz): δ = 0.925 and 0.932 (2t, $J_{4,3}$ and $J_{2',1'}$ = 7.4 and 7.5, 4-H_3, 2'-H_3), 0.99 (d, $J_{2\text{-}Me,2}$ = 6.8, 2-CH_3), 1.13-1.30 and 1.41-1.82 (2m, 1'-H_2, 2-H, 3-H_2), 5.07 (dt, $J_{1,2}$ = 7.8, $J_{1,1'}$ = 4.7, 1-H), 7.39-7.60 and 7.99-8.09 (2m, Ar-H).

(1-Ethyl-2-methyl-3-butenyl)benzoate (anti,syn-23) (method: ref. [27]): Propanal (0.290 ml, 235 mg, 4.04 mmol, 1.00 equiv.) was added to 2-(2-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4:1 *E:Z*; 910.1 mg, 4.999 mmol, 1.24 equiv.) in petroleum ether (10 ml) at -78°C. The mixture was allowed to warm to room temp. overnight, poured into satd. $NaHCO_3$ solution (20 ml) and extracted with ether (3 x 20 ml). The organic layer was dried ($MgSO_4$) and most of the solvent removed by careful distillation. The residue was diluted with THF (4 ml). KH (181 mg, 4.52 mmol, 1.12 equiv.) was added at 0°C. The mixture was stirred for 1 h at room temp. and then cooled to -78°C. Benzoyl chloride (0.610 ml, 738 mg, 5.25 mmol, 1.30 equiv.) was added rapidly and the mixture again allowed to warm to room temp.. The reaction mixture was poured into satd. $NaHCO_3$ solution (20 ml) and extracted with ether (3 x 20 ml). The organic layer was dried ($MgSO_4$) and evaporated. Flash chromatography (PE/E 200/1 to 100/1) gave 557.1 mg (63%, 88:12 *anti:syn*).- *anti*-**23**, ^{1}H NMR (300 MHz): δ = 0.93 (t, $J_{2',1'}$ = 7.4, 2'-H_3), 1.07 (d, $J_{2\text{-}Me,2}$ = 6.9, 2-CH_3), 1.61-1.79 (m, 1'-H_2), 2.55 (m_c, 2-H), 4.99-5.14 (m, 1-H, 4-H_2), 5.85 (ddd, J_{trans} = 17.2, J_{cis} = 10.3, $J_{3,2}$ = 8.0, 5-H), 7.40-7.60 and 8.00-8.09 (2m, Ar-H).- *syn*-**23**, ^{1}H NMR (300 MHz): δ = 0.93 (t, $J_{2',1'}$ = 7.4, 2'-H_3), 1.09 (d, $J_{2\text{-}Me,2}$ = 6.7, 2-CH_3), 1.58-1.81 (m, 1'-H_2), 2.56 (m_c, 2-H), 4.98-5.13 (m, 1-H, 4-H_2), 5.81 (ddd, J_{trans} = 17.3, J_{cis} = 10.4, $J_{3,2}$ = 7.5, 3-H), 7.39-7.65 and 7.99-8.09 (2m, Ar-H).

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