CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200800455

Anionic Cross-Coupling Reaction of α-Metallated Alkenyl Sulfoximines and Alkenyl Sulfoximines with Cuprates Featuring a 1,2-Metal-Ate Rearrangement of Sulfoximine-Substituted Higher Order Alkenyl Cuprates and an α-Metallation of Alkenyl Sulfoximines by Cuprates

Hans-Joachim Gais,* C. Venkateshwar Rao, and Ralf Loo[a]

Abstract: (*E*)- and (*Z*)-configured α-lithioalkenyl sulfoximines, which are available through lithiation of the corresponding alkenyl sulfoximines, undergo a anionic cross-coupling reaction (ACCR) with organocuprates with formation of the corresponding alkenyl cuprates and sulfinamide. The alkenyl cuprates can be trapped by electrophiles. The ACCR presumably proceeds via the formation of a higher-order sulfoximine-substituted alkenyl cuprate, which undergoes a 1,2-metal-ate rearrangement whereby the sulfoximine group acts as the nucleofuge. The parent (*E*)- and (*Z*)-configured alkenyl sulfoximines suffer upon treatment with an organocuprate a deprotonation at the α-position with formation of the corresponding α-cuprioalkenyl sulfoximines. These derivatives also enter into a similar ACCR with organocuprates. The ACCR of sulfoximines substituted homoallylic alcohols allows a stereoselective access to enantio- and diastereopure substituted homoallylic alcohols.

Keywords: asymmetric catalysis · cross-coupling · cuprates · lithium · metalation

Introduction

Some time ago we had observed that α-lithioalkenyl sulfoximines of type (*E*)-**2**, which were prepared by lithiation–isomerization of the alkenyl sulfoximines (*Z*)-**1**, readily engage at 0 °C in a Ni^0-catalyzed anionic cross-coupling reaction (ACCR) with PhLi. The ACCR finally afforded (*Z*)-configured phenyl-substituted alkenylsilanes of type **6** together with sulfinamide **4a** (Scheme 1).[1–3] This noteworthy Ni^0-catalyzed ACCR of α-lithioalkenyl sulfoximines with PhLi is not restricted to lithioalkenyl sulfoximines of type (*E*)-**2** and PhLi but can be extended to other α-lithio- and α-magnesioalkenyl sulfoximines as well by using lithium- and magnesiumorganyls.[4,5]

It is assumed that the ACCR proceeds via the formation of a nickel-ate-complex of type (*Z*)-**3** which undergoes a migratory insertion/reductive elimination to afford the alkenyllithium derivative (*Z*)-**5**,[2,5] having perhaps the (*Z*)-configuration (see below) and **4a**. The conversion of the putative nickel-ate complex (*Z*)-**3** to the (*Z*)-configured alkenyllithium derivative (*Z*)-**5** would be an example of a 1,2-metal-ate rearrangement (1,2-MR) of an alkenyl-ate complex involving the sulfoximine group as nucleofuge. Previously, ACCR's involving 1,2-MR's of alkenyl-ate complexes had been demonstrated for B, Al, Zr, Zn and Cu as metal and halogen-, alkoxy-, phenylsulfanyl-, carbamoyloxy- and amino-substituents as nucleofuge[6–14] (Scheme 2). All of these ACCR's are stoichiometric in the metal except the one based on Cu for which also a catalytic version has been described.[11b]

The α-phenyl-substituted alkenyllithium derivative (*Z*)-**5** could not be isolated because of the establishment of an equilibrium with (*E*)-**5** followed by a 1,5-O,C-Si migration (MG) of the latter with formation of the alkenylsilane **6**. In the Ni^0-catalyzed ACCR's the sulfoximine group showed an exceptional ability to function as a nucleofuge. Because of a formal analogy between the nickel-ate complex (*Z*)-**3** and the higher order (HO) cuprates (*E*)-**7** and (*Z*)-**7** (Scheme 3), we became interested to see 1) whether HO cuprates of this type can be generated from (*Z*)-**2** and (*E*)-**2**, respectively, and organocuprates and 2) if they would undergo a stereoselective copper-based 1,2-MR[6,11–14] to give the corresponding lower order (LO) cuprates (*Z*)-**8** and (*E*)-**8**, respectively.

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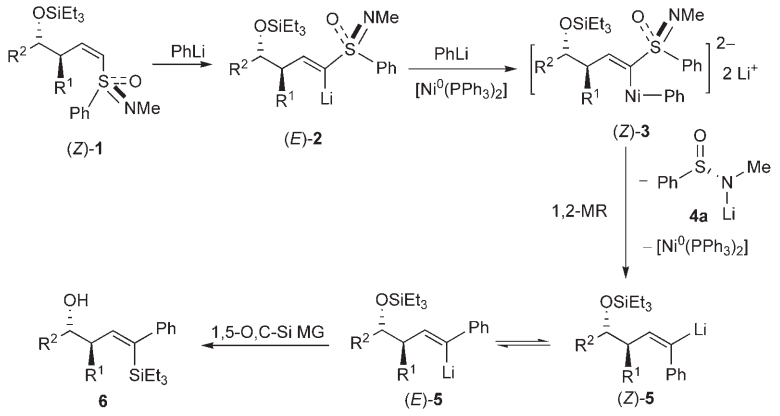
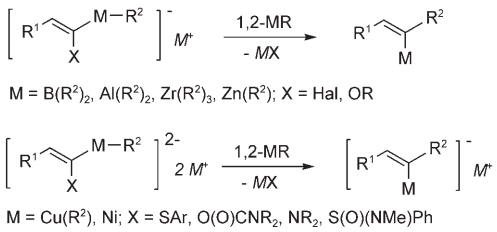


Scheme 1. Ni^0-catalyzed ACCR of α-lithioalkenyl sulfoximines (*E*)-**2** with PhLi (a possible coordination of the Ni atom of (*Z*)-**3** by PPh_3 is not shown).



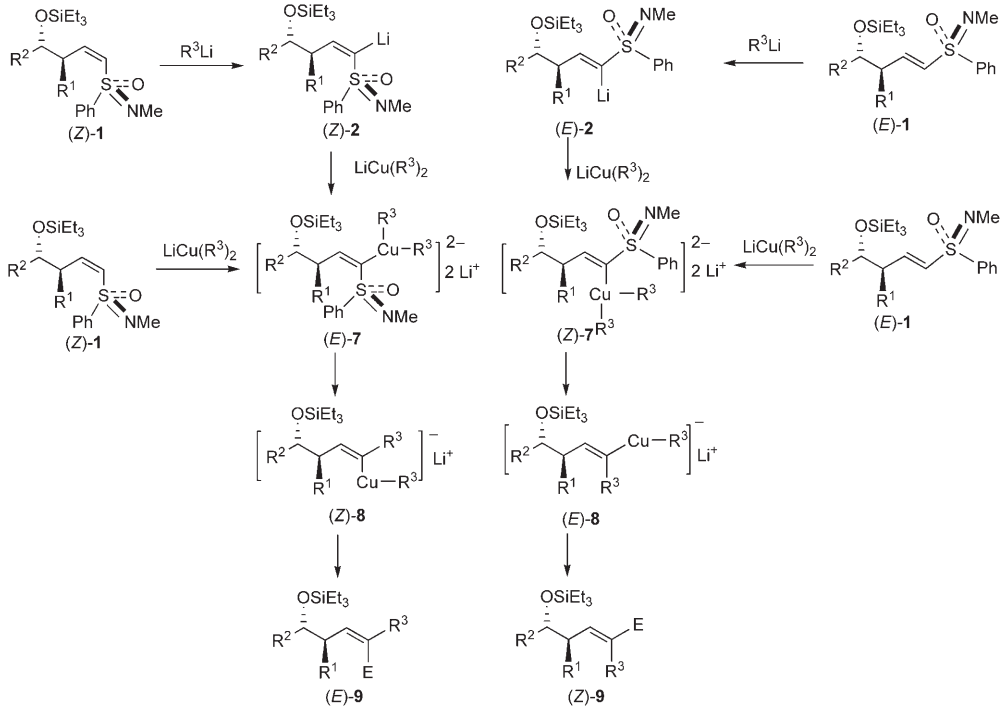
Scheme 2. 1,2-Metal-ate rearrangement of alkenyl metal derivatives.

Trapping of the latter with electrophiles should afford the homoallyl alcohols (*E*)-**9** and (*Z*)-**9**, respectively.

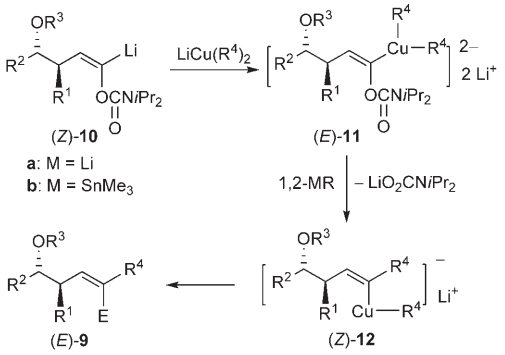
Alkenylcuprates of type (*Z*)-**8** and (*E*)-**8** should be less prone to a *Z*/*E* isomerization than the corresponding alkenyllithium derivatives. Therefore, a stochiometric ACCR of (*Z*)-**2** and (*E*)-**2** with organocuprates could give access to highly substituted homoallyl alcohols of type (*E*)-**9** and (*Z*)-**9**, which are not readily available otherwise.[15,16] This route to (*E*)-**9** and (*Z*)-**9** should benefit from 1) the facile synthesis of copper reagents including those carrying functional groups;[17] 2) the high reactivity of alkenyl cuprates of type (*Z*)-**8** and (*E*)-**8**; and 3) the ready availability of the alkenyl sulfoximines (*Z*)-**1** and (*E*)-**1**[18–21] as well as their α-lithio derivatives (*Z*)-**2** and (*E*)-**2**, respectively.[1,2,19,22–24]

Support for the feasibility of a synthesis of sulfoximine-substituted HO alkenyl cuprates of type (*E*)-**7** and (*Z*)-**7** and their 1,2-MR came from studies of the carbamoyloxy-substituted HO alkenyl cuprates (*E*)-**11** (Scheme 4). It had been shown that cuprates (*E*)-**11**, which were prepared from the lithiated or stannylated alkenyl carbamates (*Z*)-**10** and $LiCu(R^3)_2$, readily undergo a 1,2-MR with formation of the alkenyl cuprates (*Z*)-**12**, the trapping of which with electrophiles afforded (*E*)-**9**.[6,12]

This route which can, however, only provide an access to the (*E*)-configured homoallyl alcohols (*E*)-**9** is hampered by the limited stability of the α-lithioalkenyl carbamates (*Z*)-**10**, which suffer an elimination with formation of the corresponding alkynes even at low temperatures.[6,12] In contrast,



Scheme 3. Synthesis and 1,2-MR of sulfoximine-substituted HO alkenyl cuprates.



Scheme 4. Synthesis and 1,2-MR of carbamoyloxy-substituted HO alkenyl cuprates.

the lithioalkenyl sulfoximines (*Z*)-**2** and (*E*)-**2** are stable towards elimination up to room temperature. They are readily available through lithiation of the corresponding alkenyl sulfoximines (*Z*)-**1** and (*E*)-**1**, respectively (cf. Scheme 3),[1,2,19,22–24] which in turn can be obtained in enantio- and diastereopure via the reaction of the corresponding enantiopure bis(allylsulfoximine)titanium complexes with aldehydes (see below).[18–21]

In this paper we describe the ACCR of α-lithioalkenyl sulfoximines of type (*Z*)-**2** and (*E*)-**2** with organocuprates, which stereoselectively gives alkenyl cuprates of type (*Z*)-**8** and (*E*)-**8**, respectively, via a copper-based 1,2-MR (cf. Scheme 3). This ACCR has been applied to the stereoselective synthesis of enantio- and diastereopure homoallyl alcohols of type (*E*)-**9** and (*Z*)-**9**. We report furthermore about the surprising observation that the alkenyl sulfoximines (*Z*)-**1** and (*E*)-**1** are deprotonated upon treatment with organocuprates at the α-position with formation of α-cuprioalkenyl sulfoximines, which readily undergo a similar ACCR with organocuprates as (*Z*)-**2** and (*E*)-**2**.

Results and Discussion

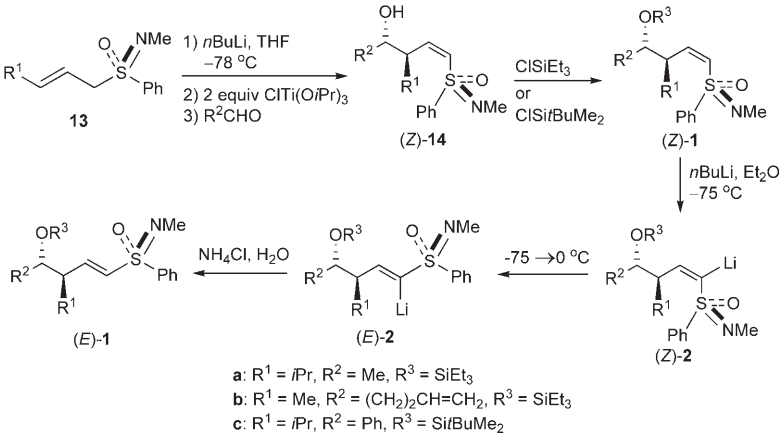
Asymmetric synthesis of alkenyl sulfoximines: The enantio- and diastereopure sulfoximine-substituted homoallyl alcohols (*Z*)-**14a** and (*Z*)-**14c** were obtained, as previously described,[18] from the enantiopure allyl sulfoximines **13a** and **13c**, respectively, through their successive treatment with BuLi, 2 equiv of $ClTi(OiPr)_3$ and the corresponding aldehydes in 76 and 81% yield (Scheme 5). Silylation of alcohols (*Z*)-**14a** and (*Z*)-**14c** afforded the silyl ethers (*Z*)-**1a** and (*Z*)-**1c** in 97 and 95% yield, respectively.

The new, unsaturated alkenyl sulfoximine (*Z*)-**1b** was obtained by a similar two step route from **13b** and pent-4-enal via (*Z*)-**14b** with ≥98% diastereoselectivity and 94% yield, respectively. Treatment of the alkenyl sulfoximines (*Z*)-**1a–c** with BuLi at −70°C gave the corresponding (*Z*)-configured alkenyllithium derivatives (*Z*)-**2a–c**, which suffered a complete isomerization to the corresponding (*E*)-isomers (*E*)-**2a–c** upon warming the solution to −10°C. Protonation of (*E*)-**2a–c** with NH_4Cl furnished the corresponding (*E*)-configured isomers (*E*)-**1a–c** in almost quantitative yield.

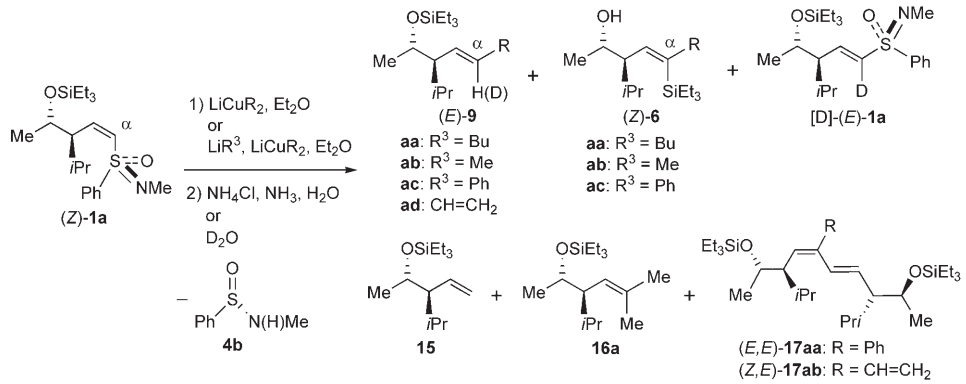
ACCR's of alkenyl sulfoximines and α-lithioalkenyl sulfoximines

(*Z*)-Configured alkenyl sulfoximine and organocuprate: First the reactivity of the alkenyl sulfoximine (*Z*)-**1a** towards $LiCuBu_2$, $LiCuMe_2$, $LiCuPh_2$ and $LiCu(CH{=}CH_2)_2$ in Et_2O was studied by applying an excess of the cuprate (Scheme 6, Table 1).

The cuprates were prepared from CuI and the corresponding lithiumorganyl by using a slight excess of CuI in order to eventually avoid the presence of the free lithiumorganyl. No reaction was observed between (*Z*)-**1a** and $LiCuBu_2$ at −40°C (Table 1, entry 1). Quenching of the reaction mixture with D_2O led to the quantitative recovery of the sulfoximine (*Z*)-**1a** containing, however, no D atom at the α-position. Surprisingly, warming up the reaction mixture of (*Z*)-**1a** and $LiCuBu_2$ to 0°C and quenching the mixture with D_2O furnished the (*E*)-configured alkene [D]-(*E*)-**9aa** carrying a D atom (≥98%) at the α-position with an *E*/*Z* selectivity of ≥44:1 in 47% yield (entry 2). The starting material (*Z*)-**1a** containing no D atom was recovered in 26% yield. Then the reaction of (*Z*)-**1a** with $LiCuBu_2$ was run first at low temperatures and then at 0°C. This led to a higher conversion of sulfoximine (*Z*)-**1a** and alkene (*Z*)-**6aa** was isolated in 78% yield with an *E*/*Z* selectivity of ≥44:1 (entry 3). The starting sulfoximine (*Z*)-**1a** was recovered in 13% yield. In a final experiment the reaction mixture obtained from a treatment of (*Z*)-**1a** with an excess of



Scheme 5. Asymmetric synthesis of sulfoximine-substituted homoallylic alcohols and α-lithioalkenyl sulfoximines.



Scheme 6. ACCR of (*Z*)-configured alkenyl sulfoximines with cuprates and cuprates admixed the corresponding lithiumorganyls.

Table 1. ACCR of the alkenyl sulfoximine (*Z*)-**1a** with $LiCuR_2$.

Entry	$LiCuR_2$ (equiv)	Conditions	Derivative	(*E*)-**9a** [%]	*E*/*Z*	(*Z*)-**6a** [%]	(*Z*)-**1a** [%]
1	$LiCuBu_2$[a] (5)	−40 °C, 1 h	**a**	0	–	0	97
2	$LiCuBu_2$[a] (7)	−40→0 °C, 4 h	**a**	47[b] (≥98 % D)	≥44:1	0	26
3	$LiCuBu_2$[a] (7)	−15→0 °C, 3 h	**a**	78	≥44:1	0	13
4	$LiCuBu_2$[a] (3)	−40 °C→RT, 18 h	**a**	52[b]	≥44:1	23	0
5	$LiCuMe_2$ (3)	−40 °C→RT, 18 h	**b**	75[c] (≥98 % D)	30:1	0	0[d,e]
6	$LiCuPh_2$ (4)	−40 °C→RT, 18 h	**c**	85[f]	35:1	0	0
7	$LiCu(CH{=}CH_2)_2$ (2)	−15 °C→RT, 4 h	**d**	66[g]	22:1	0	0

[a] *n*-Butyl cuprate was used. [b] According to GC/MS alkene **15** was formed in low yield. [c] According to GC/MS alkene **16a** was formed in low yield. [d] (*E*)-**1a** was isolated in low yield. [e] Work-up with D_2O gave [D]-(*E*)-**1a** (≥98 % D) in low yield. [f] According to GC/MS diene (*E*,*E*)-**17aa** was formed in low yield. [g] According to GC/MS diene (*E*,*E*)-**17ab** was formed in low yield.

$LiCuBu_2$ at −40 °C was stirred for a longer time at room temperature. Notably, besides 52 % of alkene (*E*)-**9aa** the (*Z*)-configured alkenyl silane (*Z*)-**6aa** was obtained in 23 % yield, both as single stereoisomers (entry 4). Thus, in all experiments the ACCR of the (*Z*)-configured alkenyl sulfoximine (*Z*)-**1a** proceeded with high *E*/*Z* selectivity under inversion of the configuration of the double bond and afforded the (*E*)-configured alkene (*E*)-**9aa**. In entries 2 and 4 the unsubstituted alkene **15** was obtained as a side product in low yield. Next the ACCR of (*Z*)-**1a** with $LiCuMe_2$ was studied. Here the (*E*)-configured alkene (*E*)-**9ab** was obtained in 75 % yield with high stereoselectivity (entry 5). In this case the formation of the corresponding silane (*Z*)-**6ab** and alkene **15** was not observed. The only side product was the dimethylated alkene **16a** which was obtained in low yield. Interestingly, however, a work-up of the reaction mixture with D_2O not only furnished the deuterated alkene [D]-(*E*)-**9ab** (≥98 % D) but also allowed the isolation of a small amount of the alkenyl sulfoximine [D]-(*E*)-**1a** being fully deuterated at the α-position. Under similar reaction conditions the ACCR of (*Z*)-**1a** with $LiCuPh_2$ also proceeded with high stereoselectivity and gave the (*E*)-configured alkene (*E*)-**9ac** in 85 % yield (entry 6). In this case the (*E*,*E*)-configured diene (*E*,*E*)-**17aa** was formed as a single stereoisomer in low yield. Having obtained favorable results in the ACCR of (*Z*)-**1a** with $LiCuBu_2$, $LiCuMe_2$ and $LiCuPh_2$, the reactivity of the alkenyl sulfoximine towards $LiCu(CH{=}CH_2)_2$ was studied. Treatment of (*Z*)-**1a** with an excess of $LiCu(CH{=}CH_2)_2$ afforded diene (*E*)-**9ad** in 62 % yield with an *E*/*Z* selectivity of 22:1. In this case the (*E*,*E*)-configured diene (*E*,*E*)-**17ab** was formed as a single stereoisomer in low yield. In all reactions listed in Table 1 sulfinamide **4b** of ≥98 % *ee* was formed in high yield.

(*Z*)-Configured alkenyl sulfoximine, lithiumorganyl and organocuprate: The isolation of the fully deuterated alkene [D]-(*E*)-**9aa** and the alkenyl silane (*Z*)-**6aa** from the reaction of (*Z*)-**1a** with an excess of $LiCuBu_2$ and [D]-(*E*)-**9ab** from the reaction of (*Z*)-**1a** with an excess of $LiCuMe_2$ gave a strong indication for the operation of an ACCR involving a HO cuprate of type (*E*)-**7** and its conversion to a LO cuprate of type (*Z*)-**8** (cf. Scheme 3) through a stereoselective 1,2-MR. Thus, in the first step a metalation of the alkenyl sulfoximine (*Z*)-**1a** at the α-position by the organocuprate must have occurred, in which a α-cuprio analogue of the α-lithioalkenyl sulfoximine (*E*)-**2a** was formed. In order to further substantiate this surprising notion and to gain information about this reaction, experiments were undertaken in which a mixture of an excess of $LiCu(R^3)_2$ and 0.3 to 0.8 equiv of R^3Li was used. It was speculated that the application of $LiCu(R^3)_2$ in combination with R^3Li would first lead to the formation of the α-lithioalkenyl sulfoximine (*E*)-**2a** which may then react with the cuprate. However, there was also the possibility of an alteration of the course of the reaction because of the establishment of an equilibrium between $LiCu(R^3)_2$, R^3Li and $Li_2Cu(R^3)_3$ (see below).[25]

Treatment of the (*Z*)-configured alkenyl sulfoximine (*Z*)-**1a** with 2 equiv of $LiCuBu_2$ and 0.7 equiv of BuLi in Et_2O first at −15 °C and then at room temperature for 18 h gave the (*E*)-configured alkene (*E*)-**9aa** with an *E*/*Z* selectivity of only 1.7:1 in 51 % yield (Table 2, entry 1, cf. Scheme 6) together with the (*Z*)-configured alkenyl silane (*Z*)-**6aa** (21 %) as a single isomer. The reaction of (*Z*)-**1a** with 5 equiv of $LiCuMe_2$ and 0.8 equiv of LiMe under similar conditions proceeded also with a low stereoselectivity and

Table 2. ACCR of the alkenyl sulfoximine (*Z*)-**1a** with $LiCuR_2$ and LiR.

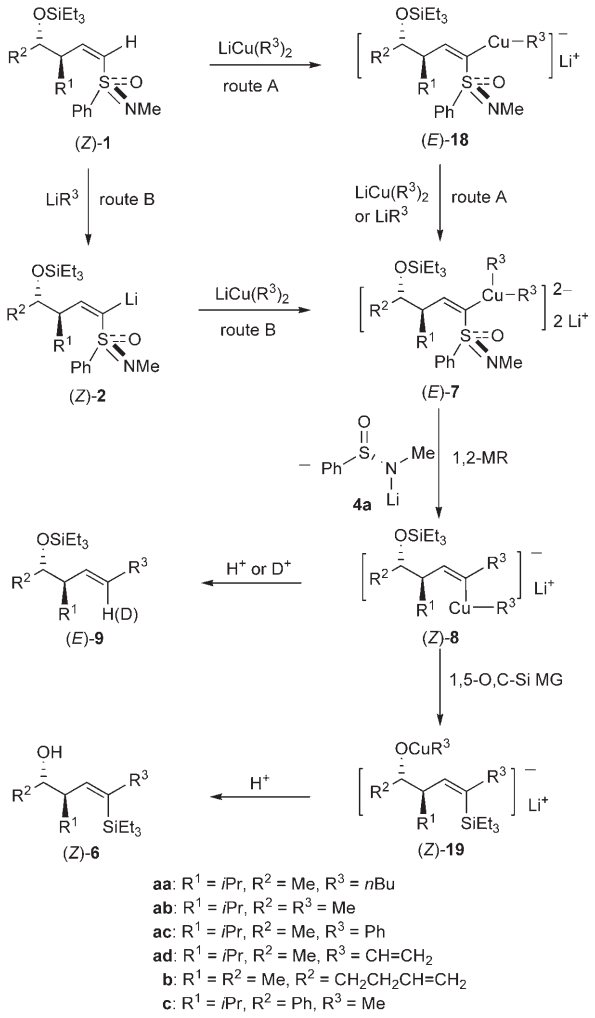
Entry	$LiCuR_2$/RLi (equiv)	Conditions	Derivative	(*E*)-**9a** [%]	*E*/*Z*	(*Z*)-**6a** [%]	(*E*)-**1a** [%]
1	$LiCuBu_2$/BuLi[a](2/0.7)	−15 °C→RT, 18 h	**a**	51	1.7:1	21	0
2	$LiCuMe_2$/MeLi (5/0.8)	−15 °C→RT, 3 h	**b**	50[b]	3:1	0	5
3	$LiCuPh_2$/PhLi (3/0.3)	−15 °C→RT, 3 h	**c**	11[c]	4.8:1	74	0

[a] *n*-BuLi and *n*-butyl cuprate were used. [b] According to GC/MS alkene **16a** was formed in low yield. [c] According to GC/MS diene (*E*,*E*)-**17aa** was formed in low yield.

afforded a mixture of alkenes (*E*)-**9ab** and (*Z*)-**9ab** in a ratio of 3:1 in 50% yield (entry 2). Here, alkene **16a** was isolated as a minor product. The ACCR of (*Z*)-**1a** with 3 equiv of $LiCuPh_2$ and 0.3 equiv of LiPh under the same conditions gave the (*Z*)-configured alkenyl silane **6ac** in 74% yield as a single stereoisomer and only 11% of a mixture of alkenes (*E*)-**9ac** and (*Z*)-**9ac** in a ratio of 4.8:1 (entry 3). In addition diene (*E*,*E*)-**17aa** was obtained as a single stereoisomer, as in the previous experiment with $LiCuPh_2$, in minor amounts.

Because of the results obtained with the cuprates and the mixtures of cuprates and the corresponding lithiumorganyls, the ACCR of (*Z*)-**1a** with the organocuprates may be rationalized as follows (Scheme 7, route A). The cuprate causes deprotonation/cupration of the alkenyl sulfoximine (*Z*)-**1** at the α-position to give the sulfoximine-substituted alkenyl cuprate (*E*)-**18** (see below). Then the (*E*)-configured LO cuprate (*E*)-**18** reacts with $LiCu(R^3)_2$ to afford the (*E*)-configured higher order organocuprate (*E*)-**7**. Subsequently, this cuprate undergoes a stereoselective 1,2-MR with inversion of configuration and elimination of sulfinamide **4a** to yield the (*Z*)-configured LO cuprate (*Z*)-**8**. Protonation and silyl migration of (*Z*)-**8** furnishes after work-up the (*E*)-configured alkene (*E*)-**9** and the (*Z*)-configured vinyl silane (*Z*)-**6**, respectively.

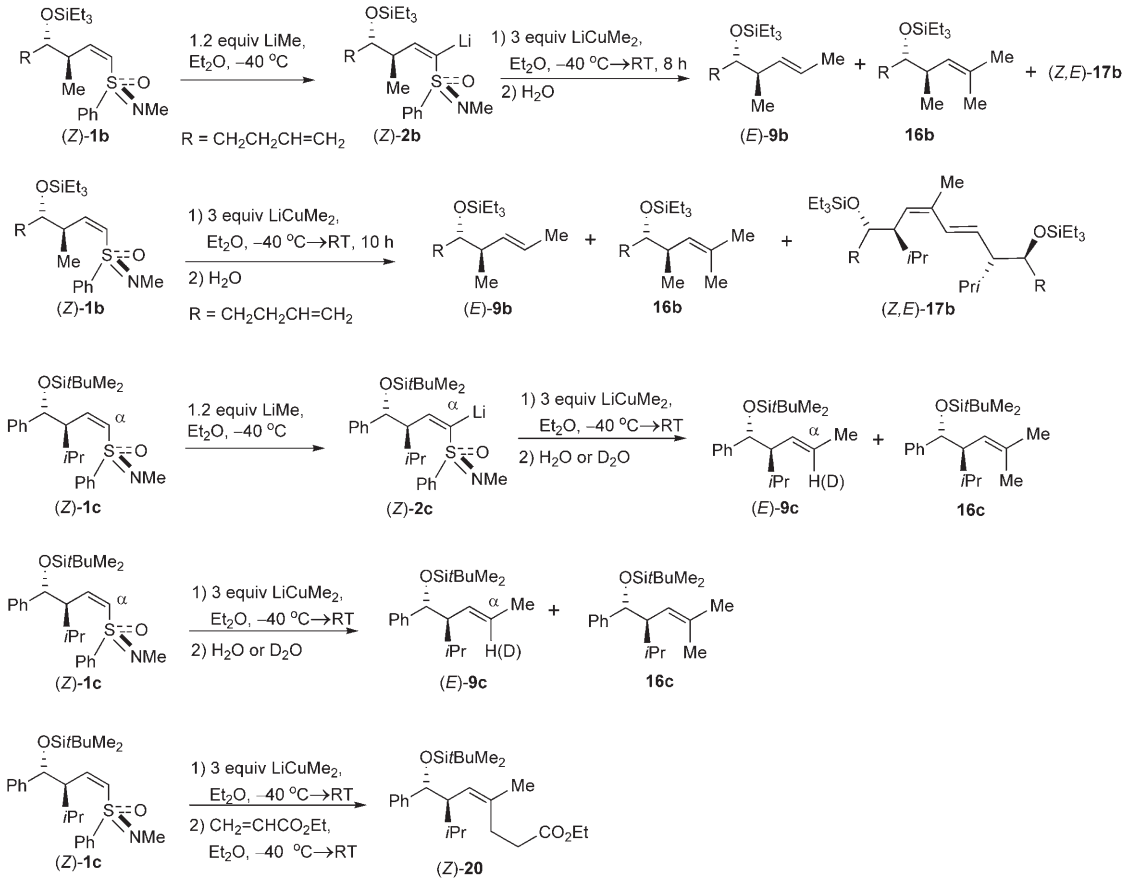
In contrast, the ACCR of the alkenyl sulfoximine (*Z*)-**1** with $LiCu(R^3)_2$ and LiR^3 may proceed at least in part as follows (route B). Reaction of (*Z*)-**1** with LiR^3 first gives the (*Z*)-configured α-lithioalkenyl sulfoximine (*Z*)-**2** which subsequently combines with $LiCu(R^3)_2$ to form the HO cuprate (*E*)-**7**. Proof for the formation of the substituted (R^3) cuprate (*Z*)-**8** as the final product in both routes A and B comes from 1) the deuteration of (*Z*)-**8aa** and (*Z*)-**8ab** which gave alkenes [D]-(*E*)-**9aa** and [D]-(*E*)-**9ab**, respectively, and 2) the stereoselective 1,5-O,C-Si migration (retro-Brook rearrangement) of (*Z*)-**8aa** and (*Z*)-**8ac**,[1,11j,26] which furnished via the corresponding copper alcoholates (*Z*)-**19aa** and (*Z*)-**19ac** the alkenyl silanes (*Z*)-**6aa** and (*Z*)-**6aa**, respectively. A major difference between the ACCR of (*Z*)-**1** with $LiCu(R^3)_2$ and $LiCu(R^3)_2$/LiR^3 is the lower *E*/*Z* selectivity in the later case. This may be ascribed to the operation of two effects. First, in route B the isomerization of the α-lithioalkenyl sulfoximine (*Z*)-**2** to its (*E*)-configured isomer (*E*)-**2** may have effectively competed with the reaction of the former with the cuprate because of the relatively high reaction temperature. Thus, both the (*E*)- and (*Z*)-configured HO cuprates (*E*)-**7** and (*Z*)-**7** could have been formed. Second, a consecutive 1,5-O,C-Si MR, which became significant because of higher temperature and longer reaction time, took place. Because of steric reasons, the Si MR led to a selective depletion of the (*Z*)-configured alkenyl cuprate (*Z*)-**8** and thus to a diminished *E*/*Z* ratio of alkene (*E*)-**9**.



Scheme 7. Mechanistic rationalization of the ACCR of alkenyl sulfoximines and α-lithioalkenyl sulfoximines with cuprates.

(Z)-Configured α-lithioalkenyl sulfoximines and organocuprates: In order to seek a further confirmation for the proposed formation of the higher order cuprates (*E*)-**7** from the alkenyllithium derivatives (*Z*)-**2** and $LiCu(R^3)_2$ in the reaction of (*Z*)-**1** with $LiCu(R^3)_2$/LiR^3 (cf. Scheme 7), the α-lithioalkenyl sulfoximine (*Z*)-**2b** for example was first generated upon treatment of (*Z*)-**1b** with 1.1 equiv of LiR^3 and then in a second step treated with $LiCu(R^3)_2$ (Scheme 8).

Thus, sulfoximine (*Z*)-**1b** was treated with LiMe, which afforded the (*Z*)-configured lithioalkenyl sulfoximine (*Z*)-**2b** in practically quantitative yield as shown by deuteration.



Scheme 8. ACCR of (*Z*)-configured alkenyl sulfoximines and α-lithioalkenyl sulfoximines with $LiCuMe_2$.

The reaction of (*Z*)-**2b** with $LiCuMe_2$ (3 equiv) at −40 °C to room temperature gave the (*E*)-configured alkene (*E*)-**9b** with an *E*/*Z* selectivity of ≥40:1 and the dimethylated alkene **16b** in a ratio of 7:3 (Table 3, entry 4). No ACCR was observed between (*Z*)-**2b** with $LiCuMe_2$ at −40 °C (entry 1). Instead, the isomeric alkenyl sulfoximines (*E*)-**1b** was isolated in almost quantitative yield. At 0 °C the slow formation of (*E*)-**9b** with an *E*/*Z* selectivity of ≥40:1 and **16b** (entry 2) occurred. The reaction at room temperature furnished diene (*Z*,*E*)-**17b** as a side product (entries 3–5). These results give strong support to the mechanistic picture outlined in Scheme 7 in general and for the intermediacy of the HO cuprates (*E*)-**7** in particular.

In order to have a more complete picture the reactivity of the parent alkenyl sulfoximine (*Z*)-**1b** was also studied and the investigations were extended to the alkenyl sulfoximine (*Z*)-**1c**. The reaction of the alkenyl sulfoximine (*Z*)-**1b** with 3 equiv of $LiCuMe_2$ at −40 °C to room temperature afforded a mixture of the (*E*)-configured alkene (*E*)-**9b** with an *E*/*Z* selectivity of ≥40:1 and the dimethylated alkene **16b** in a ratio of 9:1 (Table 4, entry 4). When the same reaction was run at −40 °C to room temperature for a longer time a mixture of alkene (*E*)-**9b**, alkene **16b** and diene (*Z*,*E*)-**17b** was isolated in a ratio of 8:1:1 (entry 5). No ACCR was observed between (*Z*)-**1b** and $LiCuMe_2$ (3 equiv) at −40 °C (entry 1). Instead, the (*E*)-configured alkenyl sulfoximine (*E*)-**1b** was isolated in high yield. The conversion of (*Z*)-**1b** and the formation of (*E*)-**9b**, **16b** and (*Z*,*E*)-**17b** in the reaction of (*Z*)-**1b** with $LiCuMe_2$ showed similar time and temperature dependencies (entries 1–5) as that of (*Z*)-**2b** with $LiCuMe_2$. Thus the ACCR of the α-lithioalkenyl sulfoximine (*Z*)-**2b** and the parent alkenyl sulfoximine (*Z*)-**1b** with an excess of $LiCuMe_2$ gave almost the same results.

Table 3. ACCR of the α-lithioalkenyl sulfoximine (*Z*)-**2b** with $LiCuMe_2$.

Entry	equiv	Conditions	(*E*)-**9b** [%]	*E*/*Z*	(*E*)-**9b**:**16b**	**16b** [%]	(*E*)-**1b** [%]
1	3	−40 °C, 1 h	0		–		100
2	3	−40→0 °C, 4 h	10	≥40:1	7:3	4	62
3	3	−40 °C→RT, 4 h	35[a]	≥40:1	7:3	12	–
4	3	−40 °C→RT, 8 h	41[a]	≥40:1	7:3	18	–
5	3	−40 °C→RT, 12 h	41[a]	≥40:1	7:3	18	–

[a] According to GC/MS (*Z*,*E*)-**17b** was formed in low yield.

Because of the results obtained in the ACCR of the α-lithioalkenyl sulfoximine (*Z*)-**2b** with the cuprate, the analogous reaction of (*Z*)-**2c** was also studied. Treatment of the alkenyl sulfoximine (*Z*)-**1c** with MeLi quantitatively afforded

Table 4. ACCR of the alkenyl sulfoximine (*Z*)-**1b** with $LiCuMe_2$.

Entry	equiv	Conditions	(*E*)-**9b** [%]	*E*/*Z*	(*E*)-**9b**:**16b**	**16b** [%]	(*E*)-**1b** [%]
1	3	−40 °C, 1 h	0		–		100
2	3	−40→0 °C, 4 h	10	≥40:1	9:1	1	50
3	3	−40 °C→RT, 4 h	37	≥40:1	9:1	4	10
4	3	−40 °C→RT, 8 h	70[a]	≥40:1	9:1	10	
5	3	−40 °C→RT, 10 h	64[a]	≥40:1	8:1	8	

[a] According to GC/MS (*Z*,*E*)-**17b** was formed in low yield.

the lithioalkenyl sulfoximine (*Z*)-**2c** as shown by deuteration. The ACCR of (*Z*)-**2c** with $LiCuMe_2$ (3 equiv) gave a mixture of the (*E*)-configured alkene (*E*)-**9c** with an *E*/*Z* selectivity of ≥40:1 and the dimethylated alkene **16c** in a ratio of 7:3 (Table 5, entry 4). In a similar ACCR of (*Z*)-**2c** with $LiCuMe_2$ the mixture was quenched with D_2O after the indicated reaction time, which led to the isolation of alkene (*E*)-**9c** with an *E*/*Z* selectivity of ≥40:1 being fully deuterated at the α-position. No reaction was observed between (*Z*)-**1c** and $LiCuMe_2$ (3 equiv) at −40 °C (entry 1). Instead, the (*E*)-configured alkenyl sulfoximine (*E*)-**1c** was isolated in high yield. The conversion of (*Z*)-**2c** and the formation of (*E*)-**9c** and **16c** in the reaction of (*Z*)-**2c** with $LiCuMe_2$ showed similar time and temperature dependencies (entries 1–5) as that of (*Z*)-**2b** with $LiCuMe_2$. These results give further proof for the formation of LO alkenyl cuprates of type (*E*)-**8** (cf. Scheme 7) in the ACCR of the α-lithioalkenyl sulfoximines (*E*)-**2** with cuprates.

In a final set of experiments the (*Z*)-configured alkenyl sulfoximine (*Z*)-**1c** was subjected to reaction with 3 equiv of $LiCuMe_2$, at various temperatures and different reaction times (Table 6, entries 1–5). A mixture of alkenes (*E*)-**9c** with an *E*/*Z* selectivity of ≥40:1 and **16c** was obtained at room temperature in a ratio of 9:1 (entry 4). In a similar ACCR of (*Z*)-**1c** with $LiCuMe_2$ the reaction mixture was quenched with D_2O. This led to the isolation of alkene (*E*)-**9cb** with an *E*/*Z* selectivity of ≥40:1 being fully deuterated at the α-position. No reaction was observed between (*Z*)-**1c** and $LiCuMe_2$ (3 equiv) at −40 °C (entry 1). Instead, the (*E*)-configured alkenyl sulfoximine (*E*)-**1c** was isolated in high yield. A further confirmation of the formation of the LO cuprate (*E*)-**8cb** in this ACCR was provided by its conjugate addition to ethyl acrylate. Thus, the alkenyl sulfoximine (*Z*)-**1c** was first treated at −40 °C with 3 equiv of $LiCuMe_2$ and the mixture was warmed to room temperature. Then ethyl acrylate was added at −40 °C and the mixture was warmed to room temperature. This led to the isolation of the ester (*Z*)-**20** having a (*Z*)-configured trisubstituted double bond in 50% yield.

(*E*)-Configured alkenyl sulfoximine and organocuprate: Surprisingly, the (*E*)-configured alkenyl sulfoximines (*E*)-**1a–c** showed only a low reactivity in the ACCR with $LiCuR_2$. Practically no ACCR was observed between (*E*)-**1a** and $LiCuBu_2$ in Et_2O at 0 °C. Similarly, the treatment of the alkenyl sulfoximine (*E*)-**1c** with 3 equiv of $LiCuMe_2$ at −40 °C to room temperature led to the recovery of (*E*)-**1c** in high yield (Scheme 9) (Table 7, entries 1–3). In the experiment with (*E*)-**1c** at room temperature the α-methylated alkenyl sulfoximine (*E*)-**22** was obtained in 10% yield (entry 3). Surprisingly, however, a D_2O quench of the mixture led to the isolation of the starting alkenyl sulfoximine [D]-(*E*)-**1c** being deuterated at the α-position (90%). Finally, the application of both 10 equiv of $LiCuMe_2$ and room temperature saw a complete conversion of the alkenyl sulfoximine (*E*)-**1c** and gave in a highly stereoselective ACCR a mixture of the alkenes (*Z*)-**9c** with a *Z*/*E* selectivity of ≥40:1 and **16c** in a ratio of 9:1 (entries 4 and 5).

These results give direct proof for a metalation of the (*E*)-configured alkenyl sulfoximine (*E*)-**1a–c** by $LiCu(R^3)_2$ at the α-position with formation of (*Z*)-**18** (cf. Scheme 7). Because of the similarity in the reactivity of (*E*)-**1** and (*Z*)-**1** in the ACCR with $LiCu(R^3)_2$, it can safely be assumed that the (*E*)-configured alkenyl sulfoximines (*E*)-**1** are also first metalated by the cuprate at the α-position.

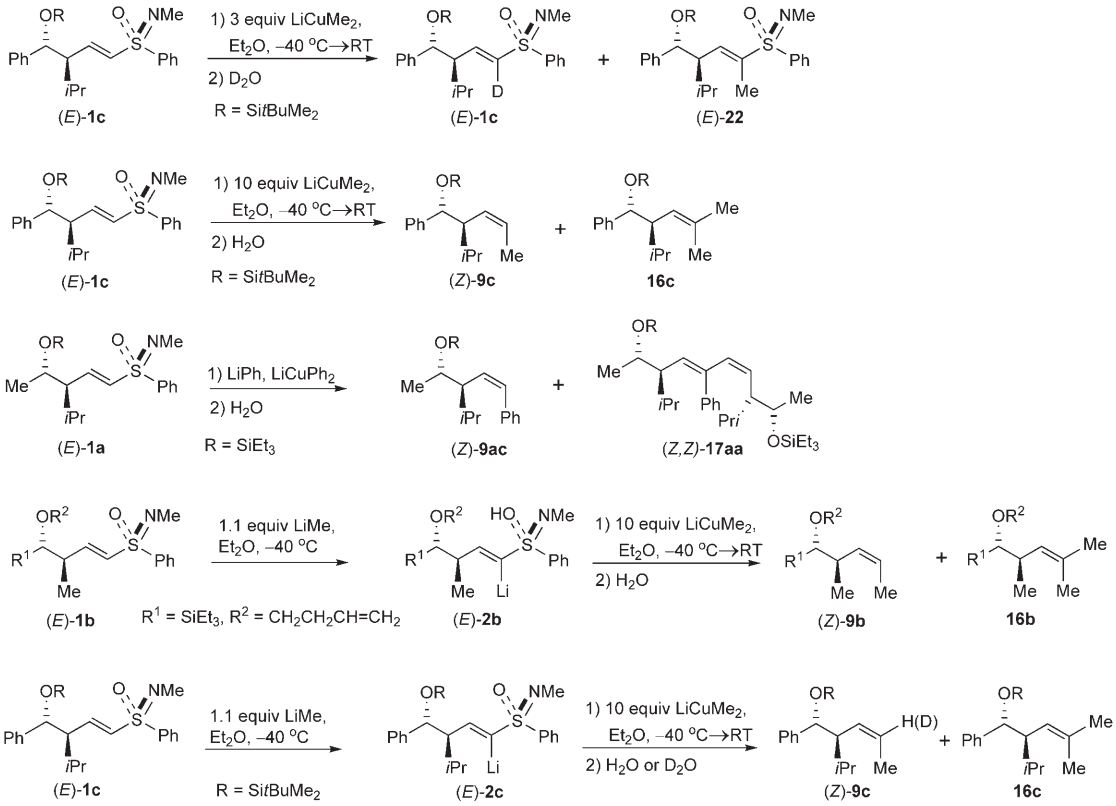
(*E*)-Configured α-lithioalkenyl sulfoximines and organocuprates: Having observed a surprisingly low reactivity of the (*E*)-configured alkenyl sulfoximines (*E*)-**1** in the ACCR with cuprates and obtained evidence for their α-metalation by the cuprates, it was of interest to study the ACCR of the corresponding (*E*)-configured α-lithioalkenyl sulfoximines (*E*)-**2** with organocuprates. Treatment of (*E*)-**1a** with an excess of $LiCuPh_2$ and PhLi at room temperature stereoselectively afforded the (*Z*)-configured alkene (*Z*)-**9ac** with

Table 5. ACCR of the α-lithioalkenyl sulfoximine (*Z*)-**2c** with $LiCuMe_2$.

Entry	equiv	Conditions	(*E*)-**9c** [%]	*E*/*Z*	(*E*)-**9c**:**16c**	**16c** [%]	(*E*)-**1c** [%]
1	3	−40 °C, 1 h	0	–	–	–	100
2	3	−40→0 °C, 4 h	7	≥40:1	7:3	1	70
3	3	−40 °C→RT, 4 h	39	≥40:1	7:3	8	12
4	3	−40 °C→RT, 8 h	50	≥40:1	7:3	19	–
5	3	−40 °C→RT, 10 h	43	≥40:1	7:3	14	–

Table 6. ACCR of the alkenyl sulfoximine (*Z*)-**1c** with $LiCuMe_2$.

Entry	equiv	Conditions	(*E*)-**9c** [%]	*E*/*Z*	(*E*)-**9c**:**16c**	**16c** [%]	(*E*)-**1c** [%]
1	3	−40 °C, 1 h	0		–		100
2	3	−40 °C→0 °C, 4 h	8	≥40:1	9:1	1	75
3	3	−40 °C→RT, 4 h	41	≥40:1	9:1	4	10
4	3	−40 °C→RT, 8 h	71 (98% D)	≥40:1	9:1	9	–
5	3	−40 °C→RT, 10 h	62	≥40:1	9:1	6	–



Scheme 9. ACCR of (*E*)-configured alkenyl sulfoximines and α-lithioalkenyl sulfoximines with $LiCuMe_2$.

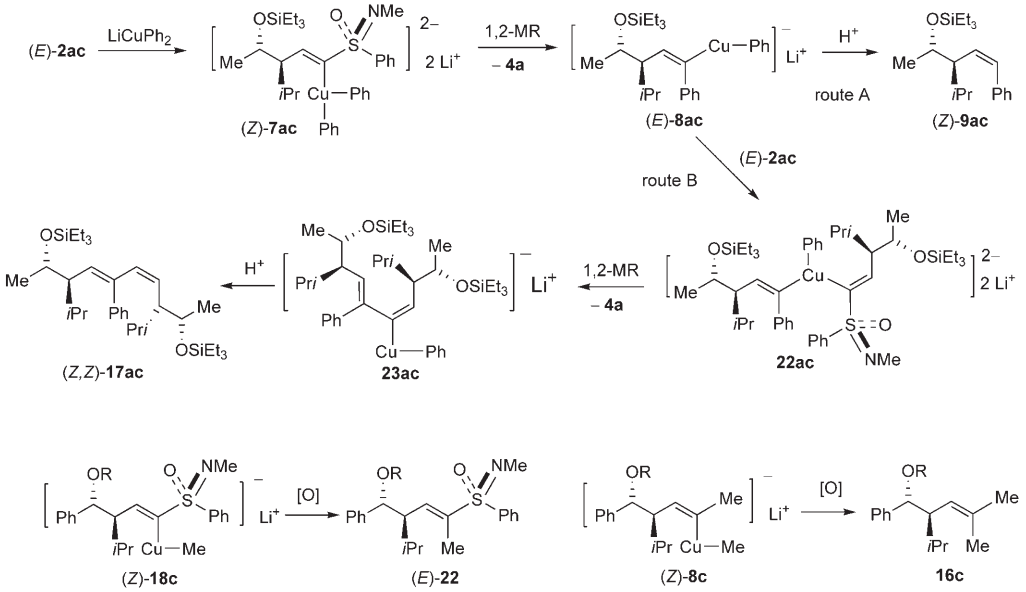
Table 7. ACCR of the alkenyl sulfoximine (*E*)-**1c** with $LiCuMe_2$.

Entry	equiv	Conditions	(*Z*)-**9c** [%]	*Z*/*E*	(*Z*)-**9c**:**16c**	**16c** [%]	(*E*)-**1c** [%]
1	3	−40 °C, 1 h	0		–		100
2	3	−40→0 °C, 4 h	0	–	–		100
3	3	−40 °C→RT, 4 h	2[a]	≥40:1	9:1	–	80 (90 % D)
4	10	−40 °C→RT, 12 h	59	≥40:1	9:1	5	12
5	10	−40 °C→RT, 20 h	72	≥40:1	9:1	7	–

[a] According to ^{1}H NMR **22** was formed in 10 % yield.

a *Z*/*E* selectivity of 15:1 in 60 % yield and diene (*Z*,*Z*)-**17aa** as a single stereoisomer in 30 % yield (cf. Scheme 9). The formation of diene (*Z*,*Z*)-**17aa**, the extend of which increased with increasing concentration of (*E*)-**2a**, is remarkable. These results suggest the operation of two consecutive stereoselective 1,2-MR's of the sulfoximine-substituted HO cuprates (*Z*)-**7ac** and **23** (Scheme 10, routes A and B). Lithiation of (*E*)-**1a** with PhLi affords the (*E*)-configured α-lithioalkenyl sulfoximine (*E*)-**2a** which reacts with $LiCuPh_2$ with formation of the (*Z*)-configured HO phenyl-substituted cuprate (*Z*)-**7ac**, the stereoselective 1,2-MR of which gives the (*E*)-configured LO cuprate (*E*)-**8ac**. The lower order cuprate (*E*)-**8ac** remains as such (route A) or, in a competing slow reaction, combines with the (*E*)-configured α-lithioalkenyl sulfoximine (*E*)-**2a** to yield the (*E*,*Z*)-configured HO cuprate **23** (route B) which in turn suffers a stereoselective 1,2-MR and gives the (*E*,*Z*)-configured LO cuprate **24**. Protonation of (*E*)-**8ac** and **24** yield alkene (*Z*)-**9ac** and diene (*Z*,*Z*)-**17aa**, respectively. Dienes (*E*,*E*)-**17aa** and (*Z*,*E*)-**17ab** (cf. Scheme 6) could be derived from the isomer (*Z*)-**2a** by a similar pathway.

These results indicate that (*E*)-configured α-lithioalkenyl sulfoximines are also capable to undergo a stereoselective ACCR with organocuprates. In order to further substantiate this notion the reactivity of the (*E*)-configured α-lithioalkenyl sulfoximines (*E*)-**2b** and (*E*)-**2c** was studied. The alkenyllithium derivative (*E*)-**2c** was obtained in almost quantitative yield through lithiation of (*E*)-**1c** with MeLi as shown by deuteration. Almost no reaction was observed between (*E*)-**2c** and 3 equiv of $LiCuMe_2$ at −40 °C, 0 °C and room temperature (Table 8, entries 1–3). The starting alkenyl sulfoximine (*E*)-**1c** was recovered in high yield. Only the treatment of (*E*)-**2c** with 10 equiv of $LiCuMe_2$ at room temperature for a prolonged period of time furnished a mixture of the (*Z*)-configured alkene (*Z*)-**9c** with a *Z*/*E* selectivity of ≥40:1 and alkene **16c** in a ratio of 7:3 (entries 4 and 5). A similar ACCR was observed in the case of (*E*)-**2b**. Lithiation of the alkenyl sulfoximine (*E*)-**1b** with MeLi afforded the (*E*)-configured lithiated alkenyl sulfoximine (*E*)-**2b**. Treatment of (*E*)-**2c** with 10 equiv of $LiCuMe_2$ at room temperature followed by the addition of D_2O gave a mixture of alkene (*Z*)-**9b**, being



Scheme 10. Mechanistic rationalization of the formation of side products in the ACCR of α-lithioalkenyl sulfoximines with cuprates.

Table 8. ACCR of the α-lithioalkenyl sulfoximine (*E*)-**2c** with $LiCuMe_2$.

Entry	equiv	Conditions	(*Z*)-**9c** [%]	*Z*/*E*	(*Z*)-**9c**:**16c**	**16c** [%]	(*E*)-**1c** [%]
1	3	−40 °C, 1 h	0	–			100
2	3	−40 °C→0 °C, 4 h	0	–			100
3	3	−40 °C→RT, 4 h	2[a]	≥40:1	–	–	80
4	10	−40 °C→RT, 12 h	42	≥40:1	7:3	11	10
5	10	−40 °C→RT, 20 h	52	≥40:1	7:3	23	–

[a] According to ^{1}H NMR (*E*)-**22** was formed in low yield.

fully deuterated at the α-position with an *E*/*Z* selectivity of ≥40:1 and alkene **16b** in a ratio of 7:3.

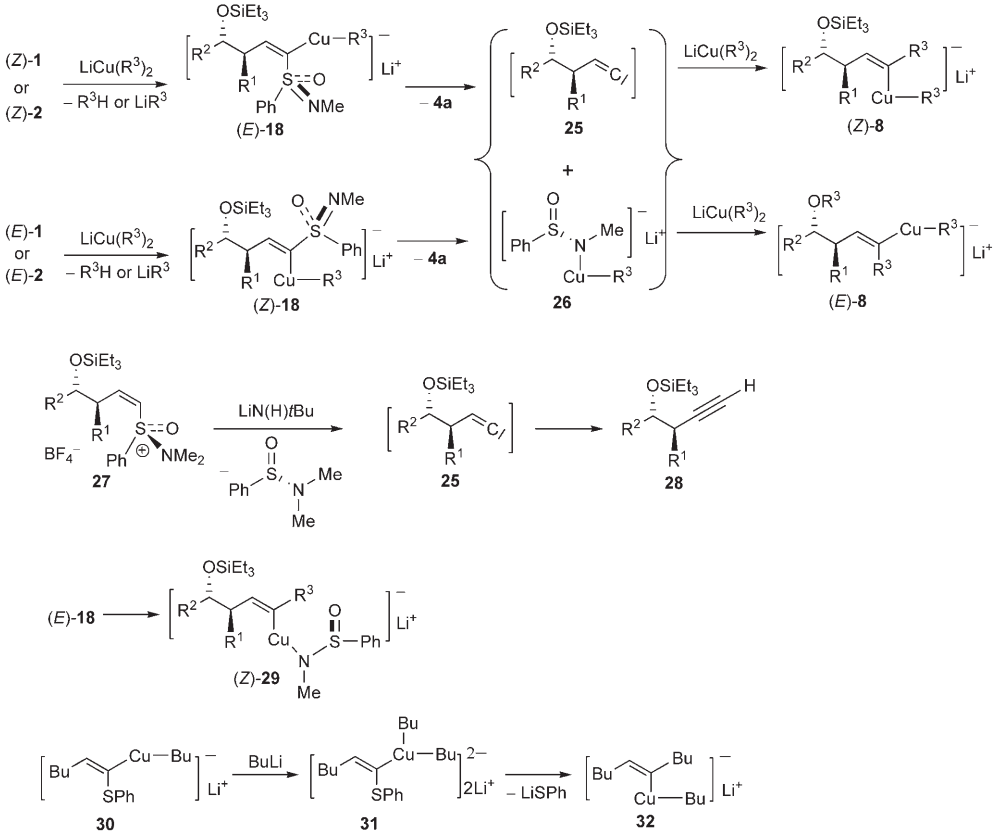
The ACCR of the alkenyl sulfoximines (*Z*)-**1a**, (*Z*)-**1b**, (*Z*)-**1c** and (*E*)-**1c** as well as that of the α-lithioalkenyl sulfoximines (*Z*)-**2b**, (*Z*)-**2c** and (*E*)-**2b** with $LiCuMe_2$ gave considerable amounts of the dimethylated alkenes **16a–c**, respectively, besides the corresponding monomethylated alkenes. In addition the reaction of the alkenyl sulfoximine (*E*)-**1c** with $LiCuMe_2$ gave a small amount of the α-methylated alkenyl sulfoximine (*E*)-**22** (cf. Schemes 8 and 9). Formation of these methylated alkenes can perhaps be explained by an oxidation of the intermediate cuprates (*Z*)-**8**, (*E*)-**8** and (*Z*)-**18**, respectively,[27,28] as exemplified for (*Z*)-**18c** and (*Z*)-**8c** in Scheme 10. Either sulfinamide **4a**[29] or the starting sulfoximine could act as an oxidant.[30]

Mechanistic considerations: The experimental data obtained from the ACCR's of the alkenyl sulfoximines (*Z*)-**1**, (*E*)-**1** and their α-lithio derivatives (*Z*)-**2** and (*E*)-**2** with organocuprates in combination with the results of the intermolecular trapping experiments with D_2O and ethyl acrylate and the intramolecular trapping with the silyl group are consistent with 1) the stereoselective formation of HO cuprates of type (*Z*)-**7** and (*E*)-**7**; 2) their stereoselective 1,2-MR; and 3) the direct deprotonation/cupration of the alkenyl sulfoximines (*E*)-**1** and (*Z*)-**1** by cuprates with formation of the sulfoximine-substituted alkenyl cuprates (*Z*)-**18** and (*E*)-**18**. Scheme 7 (see above) shows the mechanistic picture for the ACCR of the (*Z*)-configured substrates (*Z*)-**1** and (*Z*)-**2**. A similar mechanistic picture is proposed for the stereoselective ACCR of the (*E*)-configured isomers (*E*)-**1** and (*E*)-**2** (not shown). It should be emphasized, however, that a definite structural proof for the sulfoximine-substituted higher order alkenyl cuprates (*E*)-**7** and (*Z*)-**7** as depicted in Schemes 2, 7 and 10 featuring a dianionic tricoordinate Cu atom, is lacking. Although HO cuprates with a trivalent dianionic Cu atom have frequently been proposed as key intermediates for example in the ACCR's of α-lithioenol ethers,[6,11] α-lithioalkenyl carbamates[6,12] and α-lithioalkenyl sulfides,[14] a direct proof for their existence is not available. The existence of HO cuprates with three negatively charged organic moieties bound directly to a Cu^I atom has been demonstrated for the phenyl derivatives $[Li_5(CuPh_2)_3(CuPh_3)(SMe_2)_4]$ and $[Li_3(CuPh_2)(CuPh_3)(SMe_2)_4]$ in the crystal and in solution.[25,31,32] However, the structural evidence that had been obtained for the existence of trialkyl-substituted HO cuprates in solution is ambiguous.[25,33–35] Ab initio calculations of a complex between the LO cuprate $LiCuMe_2$ and LiMe for example led to an energy minimum structure containing a six-membered ring composed of a dimethylcopper unit coupled to a dilithium–methyl bridge.[36] The alternative structure of a HO cuprate with the three methyl groups bound to the Cu atom was found to be much higher in energy. This brings about the question of a possible alternative mechanism for the ACCR's of alkenyl sulfoximines and

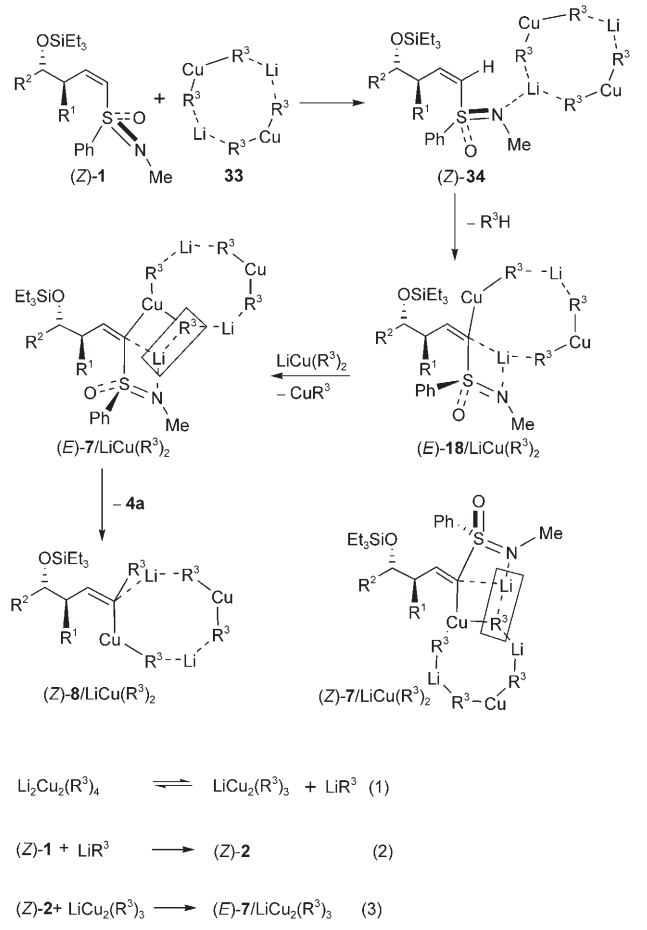
lithiated alkenyl sulfoximines with cuprates, which does not involve higher order cuprates of type **7** undergoing a stereoselective 1,2-MR. For example, it could be proposed that the reaction of the alkenyl sulfoximine (*Z*,*E*)-**1** and the lithiated alkenyl sulfoximine (*Z*,*E*)-**2** with organocuprates only leads to the formation of a LO cuprate of type (*Z*,*E*)-**18** (Scheme 11). Then these cuprates could suffer an α-elimination with formation of the alkylidene carbene **25** and heterocuprate **26**. Carbene **25** could subsequently react with $LiCuR_2$ to give the lower order cuprate (*Z*,*E*)-**8**. However, there are two observations speaking against such a mechanism. First, we had previously generated alkylidene carbenes **25** through an α-elimination of aminosulfoxonium salts **27**[37] and observed that they suffer a fast 1,2-H-atom shift even at low temperatures with formation of the alkynes **28**. Second, it would be rather difficult to rationalize how carbene **25** generated from (*E*)-**18** should stereoselectively give the (*Z*)-configured cuprate (*Z*)-**8** while the same carbene derived from (*Z*)-**18** should stereoselectively afford the (*E*)-configured isomer (*E*)-**8**. Therefore, an α-elimination of (*Z*,*E*)-**18** is not a liable pathway. Alternatively, it could be argued that the LO cuprate (*E*)-**18** rather than being converted to the HO cuprate (*E*)-**7** undergoes a stereoselective 1,2-MR with formation of the alkenyl heterocuprates (*Z*)-**29**, the reaction of which with electrophiles could also lead to the alkenes that have been isolated. A similar reaction would serve to convert (*Z*)-**18** into (*E*)-**29** (not shown I Scheme 11). However, it is unlikely that LO cuprate (*Z*,*E*)-**18** undergoes a 1,2-MR. It has been demonstrated, for example, that the phenylsulfanyl-substituted LO cuprate **30** is not capable of undergoing a 1,2-MR.[14] In contrast, the HO cuprate **31**, which was obtained through treatment of **30** with *n*BuLi, underwent a 1,2-MR with formation of the LO cuprate **32**.

An interesting and surprising feature of the ACCR of (*Z*)-**1** and (*E*)-**1** with $LiCu(R^3)_2$ is the ready deprotonation the alkenyl sulfoximines by the cuprate at the α-position. We are not aware of any report describing the deprotonation of a functionalized alkene at the α-position upon action of an organocuprate with formation of the corresponding alkenyl cuprate. Alkenyl cuprates carrying a carbanion-stabilizing functional group at the α-position as for example a sulfoximine,[38] sulfinyl[39,40] or sulfonyl group[39] have so far been obtained through a carbocupration of the corresponding functionalized alkynes.[35]

Why do alkenyl sulfoximines of type **1** engage in such a reaction with cuprates. Sulfoximines are capable to react with Lewis and Brønsted acids at the N atom of the sulfoximine group. Thus, the dimeric cuprate **33** may coordinate via the Li atom to the sulfoximine group of the alkenyl sulfoximine (*Z*)-**1**[30] (Scheme 12) with formation of complex (*Z*)-**34**. This complex could then undergo an intramolecular deprotonation/cupration at the α-position to afford (*E*)-**18**/$LiCu(R^3)_2$ which can be regarded as a complex between (*E*)-**18** (cf. Scheme 7) and $LiCu(R^3)_2$. Then $LiCu(R^3)_2$ reacts



Scheme 11. Alternative mechanistic rationalization for the ACCR of alkenyl sulfoximines and α-lithioalkenyl sulfoximines with cuprates.



$Li_2Cu_2(R^3)_4 \rightleftharpoons LiCu_2(R^3)_3 + LiR^3$ (1)

(*Z*)-**1** + LiR^3 → (*Z*)-**2** (2)

(*Z*)-**2** + $LiCu_2(R^3)_3$ → (*E*)-**7**/$LiCu_2(R^3)_3$ (3)

Scheme 12. α-Deprotonation of alkenyl sulfoximines by cuprates (a possible coordination of the Li atoms of the various species by solvent molecules is not shown).

with complex (*E*)-**18**/$LiCu(R^3)_2$ under transfers of LiR^3 with formation of the HO cuprate (*E*)-**7**/$LiCu(R^3)_2$. A similar mechanistic Scheme could be proposed for the reaction of the (*E*)-configured isomers (*E*)-**1** (not shown). Alternatively, the deprotonation of the alkenyl sulfoximine (*Z*)-**1** could be caused by LiR^3 being perhaps in equilibrium with the dimeric cuprate [Scheme 12, Eq. (1)][25,35,41] with formation of (*Z*)-**2** [Eq. (2)]. The subsequent reaction of (*Z*)-**2** with $LiCu_2(R^3)_3$ would also lead to the alkenyl cuprate (*E*)-**7**/$LiCu(R^3)_2$ [Eq. (3)]. However, the distinction between the two mechanisms may be superfluous.

The facile deprotonation/cupration of the alkenyl sulfoximines (*Z*)-**1** and (*E*)-**1** upon reaction with cuprates via a prior complexation of the cuprate by the sulfoximine group explains the surprising failure of the alkenyl sulfoximines to undergo a conjugate addition with cuprates. The LO sulfoximine-substituted alkenyl cuprates (*E*)-**18** and (*Z*)-**18** are as metalated species not expected to undergo a conjugate addition easily. Cuprate (*E*)-**7**/$LiCu(R^3)_2$ is characterized by a tricoordinate Cu atom, the organic residues of which are each coordinated to a Li atom and a dicoordinate Cu atom. Such structural motifs had been found in the crystal structures of $[Li_5(CuPh_2)_3(CuPh_3)(SMe_2)_4]$ and $[Li_3(CuPh_2)(CuPh_3)(SMe_2)_4]$.[25,31,32] The reaction sequence is concluded with the stereoselective 1,2-MR of (*E*)-**7**/$LiCu(R^3)_2$ to give the lower order cuprate (*Z*)-**8** which forms a complex with $LiCu(R^3)_2$. A similar sequence of events would serve to convert the (*E*)-configured alkenyl sulfoximine (*E*)-**1** via (*E*)-**29**, (*Z*)-**18**/$LiCu(R^3)_2$ and (*Z*)-**7**/$LiCu(R^3)_2$ to (*E*)-**8**/$LiCu(R^3)_2$ (not shown in Scheme 12). The (*Z*)-configured alkenyl sulfoximines (*Z*)-**1** show a significantly higher reactivity in the ACCR with cuprates than their (*E*)-configured isomers (*E*)-**1**. This could be ascribed to a different rate of cupration of (*Z*)-**1** and (*E*)-**1** with formation of the lower order cuprates (*E*)-**18** and (*Z*)-**18**, respectively. However, the same difference in reactivity was found for the lithiated alkenyl sulfoximines (*Z*)-**2** and (*E*)-**2**. Thus the different behavior may be due to differences in the formation of (*E*)-**7** and (*Z*)-**7** either via route A from (*E*)-**18** and (*Z*)-**18**, respectively, or route B (cf. Scheme 7) from (*Z*)-**2** and (*E*)-**2**, respectively. Finally, complex (*E*)-**7**/$LiCu(R^3)_2$ could also undergo the 1,2-MR faster than complex (*Z*)-**7**/$LiCu(R^3)_2$ because of an intramolecular complexation of the Li or Cu atom by the silyloxy group in the latter case (cf. Scheme 12).

Conclusion

(*Z*)- and (*E*)-Configured α-lithioalkenyl sulfoximines of type **2** readily undergo a highly stereoselective anionic cross-coupling reaction with organocuprates. This reaction, which proceeds under inversion of configuration of the double bond, allows a stereoselective synthesis of (*E*)- and (*Z*)-configured substituted homoallyl alcohols in good yields. The key step of the cross-coupling reaction is a stereoselective 1,2-metal-ate rearrangement of the corresponding α-sulfoximine-substituted HO alkenyl cuprates. An intra- or intermolecular trapping of the thereby formed alkenyl cuprates with electrophiles gives a stereoselective access to disubstituted homoallyl alcohols. Although there is experimental evidence speaking for the involvement of HO alkenyl cuprates in the 1,2-metal-ate rearrangement, direct structural proof for their formation has thus fare not been obtained. Not only α-lithioalkenyl sulfoximines but also the parent alkenyl sulfoximines can participate in a highly stereoselective ACCR with organocuprates. This type of ACCR commences with an unprecedented metalation of the alkenyl sulfoximine by the cuprate at the α-position with formation of a α-sulfoximine-substituted alkenyl cuprate, which could be trapped with electrophiles. Apparently the reaction of the α-cuprioalkenyl sulfoximine and that of the corresponding α-lithioalkenyl sulfoximine with LO cuprates leads to the formation of the same sulfoximine-substituted HO alkenyl cuprate, which subsequently suffers the 1,2-metalate rearrangement. The rapid formation of sulfoximine-substituted LO alkenyl cuprates from the corresponding alkenyl sulfoximines upon reaction with a cuprate offers an explanation for their, at a first glance, surprising failure to undergo a conjugate addition with the latter.

Experimental Section

General: All reactions were carried under an argon atmosphere in dry solvents with syringe and Schlenk techniques in oven-dried glassware. The alkenyl sulfoximines (*Z*)-**1a** and (*Z*)-**1c** were prepared according to the literature.[18–22] THF and Et_2O were distilled under argon from lead/sodium in the presence of benzophenone. CH_2Cl_2 and DMF were distilled from CaH_2. CuI was purified according to the literature.[42] Bulk solvents for column chromatography and extractions were distilled prior to use. Reagents were obtained from commercial sources and used directly without further purification unless otherwise specified. *n*BuLi, MeLi and PhLi were obtained from commercial sources and standardized by titration with diphenylacetic acid. Vinyllithium was prepared according to the literature[43] and standardized by titration with diphenylacetic acid. TLC was performed on E. Merck pre-coated plates (silica gel 60 F254, layer thickness 0.2 mm) and chromatography was performed with E. Merck silica gel (0.040–0.063 mm) in the flash mode with a positive nitrogen pressure. HPLC was carried out with a Dynamax SD-1 pump by using Varian 320 UV/VIS and Knauer RI detectors by using a chromasil Si-100 column. Melting points were determined with a Büchi 535 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Varian mercury 300 and Varian Inova 400 instruments. Chemical shifts are reported relative to TMS (0.00 ppm) as internal standard. The following abbreviations are used to designate the multiplicity of the peaks in ^{1}H NMR spectra: s= singlet, d= doublet, t= triplet, q= quartet, sex= sextet, sep= septet, o= octet, m= multiplet, br= broad and combination thereof. Peaks in the ^{13}C NMR spectra were denoted as "u" for carbons with zero or two protons attached or as "d" for carbons with one or three attached protons, as determined from the APT pulse sequence. Assignments in the ^{1}H NMR spectra were made by GMQCOSY, GNOE and HETCOR experiments and those in the ^{13}C NMR spectra were made by DEPT experiments. IR spectra were recorded on a Perkin–Elmer PE 1759 FT instrument, and the abbreviations used to designate the intensity of the peaks are vs= very strong, s= strong, m= medium, and w= weak. High resolution mass spectra were recorded either on a Varian MAT 95 Spectrometer or on a Micromass LCT Spectrometer (ESI, TOF). Optical rotations were measured on a Perkin–Elmer 241 polarimeter at approximately 22 °C. Specific rotation is in grad × mL per dm × g, and *c* is in g/100 mL. GC: Chrompack CP-9000, H_2; column DB 5 (Carlo Erba) 50 m × 0.32 mm, 0.25 μm; temperature program: S 1: 100 °C, 5 min, 20 K min^{-1}, 250 °C, 5 min, 30 K min^{-1}, 300 °C, 15 min. S 2: 50 °C, 5 min, 30 K min^{-1}, 150 °C, 2 min, 20 K min^{-1}, 250 °C, 2 min, 10 K min^{-1}, 300 °C, 15 min.

Triethyl (−)-(*E*,2*S*,3*R*)-3-isopropyl-5-[(*S*)-*N*-methyl-phenylsulfonimidoyl)]-pent-4-en-2-yloxy)silane [(*E*)-1a]: MeLi (0.50 mL of 1.60 M solution in Et_2O, 0.80 mmol) was added at −78 °C to a solution of sulfoximine (*Z*)-**1a** (212 mg, 0.54 mmol) in Et_2O (20 mL). After the mixture was stirred at −35 °C for 2 h, saturated aqueous NH_4Cl (10 mL) was added. The mixture was extracted several times with Et_2O and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (EtOAc/hexane 4:1) gave the alkenyl sulfoximine (*E*)-**1a** (210 mg, 99 %) as a colorless oil. R_f= 0.55 (EtOAc/hexane 80:20); $[\alpha]_D$= −81.9 (*c*= 1.25 in CH_2Cl_2); GC: t_R= 12.83 min (S2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.47 (br q, *J* = 7.9 Hz, 6H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.1 Hz, 3H), 1.73 (m, 1H), 1.86 (o, *J* = 6.7 Hz, 1H), 2.77 (s, 3H), 4.00 (qd, *J* = 6.1, 3.9 Hz, 1H), 6.28 (d, *J* = 15.1 Hz, 1H), 6.76 (dd, *J* = 15.1, 10.4 Hz, 1H), 7.46–7.58 (m, 3H), 7.90 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.1 (u), 6.9 (d), 20.2 (d), 20.3 (d), 22.9 (d), 28.2 (d), 29.6 (d), 57.3 (d), 68.0 (d), 128.5 (d), 129.2 (d), 132.2 (d), 132.4 (d), 140.1 (u), 147.6 ppm (d); GC-MS (EI, 70 eV): *m*/*z* (%): 396 [M^+] (100), 394 (17), 380 (16), 367 (14), 366 (29), 352 (35), 340 (19), 322 (11), 270 (17), 258 (39), 240 (30), 225 (18), 197 (15), 191 (12), 156 (18), 131 (37), 125 (32), 116 (13), 115 (55), 111 (13), 109 (23), 107 (22), 103 (56), 93 (16), 87 (38), 81 (23), 79 (17), 77 (20), 75 (36), 69 (11), 67 (17), 59 (45), 55 (16), 51 (21); IR (capillary): $\tilde{\nu}$= 3387 (w, br), 3063 (vs), 2958 (s), 2935 (s), 2910 (s), 2875 (vs), 2801 (m), 2732 (w), 1963 (w), 1815 (w), 1628 (w), 1583 (s), 1458 (s), 1446 (s), 1417 (s), 1386 (m), 1375 (m), 1356 (m), 1324 (m), 1276 (m), 1248 (vs), 1190 (m), 1153 (vs), 1130 (s), 1070 (s), 1010 (s), 990 (s), 966 (s), 940 (m), 897 (m), 872 (s), 852 (m), 813 cm^{-1} (m); elemental analysis calcd (%) for $C_{21}H_{37}NO_2SSi$ (395.68): C 63.75, H 9.42, N 3.54, found: C 63.83, H 9.35, N 3.51.

(*Z*,3*R*,4*S*)-3-Methyl-1-[(*S*)-*N*-methyl-(*S*)-phenylsulfonimidoyl]-oct-1,7-dien-4-ol [(*Z*)-14b]: *n*BuLi (2.22 mL of 1.60 M solution in hexane, 3.6 mmol) was added at −78 °C to a solution of the allyl sulfoximine (*E*)-**13b** (700 mg, 3.3 mmol) in THF (10 mL). After the mixture was stirred for 10 min at −78 °C, $ClTi(OiPr)_3$ (4.2 mL of 1 M solution in THF, 6.9 mmol) was added. The mixture was stirred for 10 min at −78 °C, allowed to warm to room temperature and stirred for 45 min at this temperature. Then it was cooled to −78 °C and 4-pentenal (300 mg, 3.6 mmol) was added. The mixture was stirred for 2 h at −78 °C and then slowly allowed to warm to room temperature over a period of 3 h. Then it was poured into saturated aqueous $(NH_4)_2CO_3$ and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (hexane/EtOAc 60:40) gave the hydroxy sulfoximine (*Z*)-**14b** (650 mg, 66 %) as colorless crystals. M.p. 72 °C; $[\alpha]_D$= −111.1 (*c*= 1.4 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.4 Hz, 3H), 1.43–1.57 (m, 1H), 1.67–1.80 (m, 1H), 2.14–2.39 (m, 2H), 2.66 (s, 3H), 3.41 (ddd, *J* = 10.5, 7.9, 2.97 Hz, 1H), 3.52–3.65 (m, 1H), 3.80 (br s, 1H, OH), 4.96–5.12 (m, 2H), 5.80–5.94 (m, 1H), 6.15 (t, *J* = 10.9 Hz, 1H), 6.43 (d, *J* = 10.9 Hz, 1H), 7.50–7.64 (m, 3H, Ph), 7.89–7.94 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.5 (d), 29.2 (d), 29.5 (u), 34.6 (u), 38.4 (d), 74.3 (d), 114.7 (u), 128.8 (d), 129.3 (d), 131.7 (d), 132.8 (d), 138.7 (d), 139.7 (u), 147.9 ppm (d); IR (KBr): $\tilde{\nu}$= 3229 (w), 2971 (m), 2928 (m), 2799 (m), 1618 (w), 1446 (w), 1249 (w), 1215 (w), 1153 (w), 1108 (w), 1001 (m), 961 (s), 910 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 294 (6) [M^++1], 276 (8), 238 (20.0), 195 (35), 125 (100), 109 (18), 107 (31), 77 (25), 55 (39); HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{16}H_{23}NO_2S$: 293.1449 [M^+]; found: 293.1450.

Triethyl (*Z*,3*R*,4*S*)-3-methyl-1-[(*S*)-*N*-methyl-(*S*)-phenylsulfonimidoyl]-octa-1,7-dien-4-yloxy)silane [(*Z*)-1b]: to a solution of alcohol (*Z*)-**14b** (150 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) imidazole (103 mg, 1.5 mmol) and $ClSiEt_3$ (92 mg, 0.6 mmol) were successively added. After the mixture was stirred for 10 h at room temperature, half-saturated aqueous $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (hexane/EtOAc 80:20) afforded the silyl ether (*Z*)-**1b** (198 mg, 97 %) as a colorless liquid. $[\alpha]_D$= −81.3 (*c*= 1.1 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.49–0.55 (m, 6H), 0.56 (d, *J* = 6.86 Hz, 3H), 0.86 (t, *J* = 7.69 Hz, 9H), 1.38–1.46 (m, 1H), 2.01–2.13 (m, 1H), 2.60 (s, 3H, NMe), 3.39–3.49 (m, 1H), 3.55 (ddd, *J* = 9.3, 6.6 Hz, 1H), 4.86–4.90 (m, 1H), 4.97 (dq, *J* = 3.6 Hz, 1H), 5.67–5.78 (m, 1H), 6.21 (t, *J* = 11.0 Hz, 1H), 6.31 (d, *J* = 11.0 Hz, 1H), 7.42–7.52 (m, 3H, Ph), 7.81–7.86 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.3 (u), 7.1 (d), 16.0 (d), 29.3 (d), 29.8 (u), 35.0 (u), 36.1 (d), 74.8 (d), 114.5 (u), 128.7 (d), 129.1 (d), 131.1 (d), 132.3 (d), 138.4 (d), 140.6 (u), 147.5 ppm (d); IR (neat): $\tilde{\nu}$= 3065 (m), 2951 (w), 2879 (w), 1637 (s), 1451 (m), 1245 (s), 1149 (w), 1011 (w), 911 (m), 865 (m), 741 (w), 694 (m), 538 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 407 (2), 378 (76), 352 (87), 270 (25), 195 (85), 115 (100), 87 (75); HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{22}H_{37}NO_2SSi$: 407.2314 [M^+]; found: 407.2311.

Triethyl (*E*,3*R*,4*S*)-3-methyl-1-[(*S*)-*N*-methyl-(*S*)-phenylsulfonimidoyl]octa-1,7-dien-4-yloxy)silane [(*E*)-1b]: *n*BuLi (0.2 mL of 1.6 M solution in hexane, 0.26 mmol) was added at −78 °C to a solution of the vinyl sulfoximine (*Z*)-**1b** (100 mg, 0.24 mmol) in THF (5 mL). After the mixture was stirred at −30 °C for 1 h, it was quenched with saturated NH_4Cl and extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (hexane/EtOAc 80:20) gave (*E*)-**1b** (82 mg, 82 %) as an oily liquid. $[\alpha]_D$= +11.7 (*c*= 2.0 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.49–0.56 (m, 6H), 0.90 (t, *J* = 7.9 Hz, 9H), 1.05 (d, *J* = 6.9 Hz, 3H), 1.27–1.36 (m, 1H), 1.39–1.50 (m, 1H), 1.90–1.96 (m, 2H), 2.43–2.52 (m, 1H), 2.73 (s, 3H, NMe), 3.64 (q, *J* = 11.0 Hz, 1H), 4.86–4.94 (m, 2H), 5.62–5.73 (m, 1H), 6.29 (d, *J* = 15.1 Hz, 1H), 6.81–6.88 (dd, *J* = 15.1, 7.4 Hz, 1H), 7.48–7.58 (m, 3H, Ph), 7.85 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.2 (u), 7.0 (d), 14.8 (d), 29.4 (u), 29.5 (d), 33.5 (u), 41.5 (d), 74.4 (d),

114.6 (u), 128.5 (d), 129.1 (d), 130.2 (d), 132.3 (d), 138.0 (d), 139.5 (u), 148.7 ppm (d); IR (neat): $\tilde{\nu}$ = 3065 (m), 2951 (w), 2879 (w), 1637 (s), 1451 (m), 1245 (s), 1149 (w), 1011 (w), 911 (m), 865 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 407 (5) [M^+], 378 (47), 352 (50), 195 (44), 115 (100), 87 (65); HRMS (EI, 70 eV): *m/z*: calcd for $C_{22}H_{37}NO_2SSi$: 407.2314 [M^+]; found: 407.2315.

(*Z*,1*R*,2*R*)-*tert*-Butyl{2-isopropyl-1-phenyl-4-[(*S*)-*N*-methyl-(*S*)-phenylsulfonimidoyl]-but-3-enyloxy}dimethylsilane [(*Z*)-1c]: Imidazole (200 mg, 4 mmol) and $ClSiMe_2tBu$ (3 mmol) were added portionwise at 0 °C to a solution of the hydroxy sulfoximine (*Z*)-**14c** (150 mg, 0.4 mmol) in CH_2Cl_2 (5 mL). After the mixture was stirred for 10 h at room temperature, half-saturated aqueous $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (hexane/EtOAc 80:20) afforded silyl ether (*Z*)-**1c** (180 mg, 95%) as a colorless liquid. $[\alpha]_D$ = −80.7 (*c* = 1.3 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.0 (s, 3H), 0.28 (s, 3H), 0.89 (d, *J* = 7.9 Hz, 3H), 1.13 (s, 9H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.91–2.01 (seq, *J* = 13.7 Hz, 1H), 2.54 (s, 3H, NMe), 3.79–3.86 (m, 1H), 5.17 (d, *J* = 3.6 Hz, 1H), 6.35 (d, *J* = 11.3 Hz, 1H), 6.53 (t, *J* = 11.5 Hz, 1H), 7.42–7.55 (m, 5H, Ph), 7.98–8.02 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.8 (d), −4.1 (d), 18.3 (u), 20.3 (d), 21.5 (d), 26.0 (d), 28.5 (d), 29.0 (d), 50.9 (d), 75.1 (d), 126.6 (d), 127.0 (d), 127.8 (d), 128.5 (d), 128.8 (d), 131.2 (d), 132.2 (d), 140.5 (u), 143.4 (u), 145.7 ppm (d); IR (neat): $\tilde{\nu}$ = 2956 (w), 2859 (w), 2802 (s), 1467 (m), 1365 (m), 1253 (w), 1150 (w), 1086 (w), 963 (s), 921 (m), 863 (w), 839 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 457 (11), 400 (42), 303 (16), 302 (59), 221 (90), 170 (42), 75 (53), 73 (100); HRMS (EI): *m/z*: calcd for $C_{26}H_{39}NO_2SSi$: 457.2470 [M^+]; found 457.2470.

(*E*,1*R*,2*R*)-*tert*-Butyl{2-isopropyl-1-phenyl-4-[(*S*)-*N*-methyl-(*S*)-phenylsulfonimidoyl]-but-3-enyloxy}dimethylsilane [(*E*)-1c]: *n*BuLi (2.5 mL of 1.6 M solution in hexane, 4 mmol) was added at −40 °C to a solution of sulfoximine (*Z*)-**1c** (150 mg, 0.32 mmol) in Et_2O (5 mL). After the mixture was stirred for 10 min, it was allowed to warm to room temperature. Then half-saturated aqueous NH_4Cl was added and the mixture was extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (hexane/EtOAc 80:20) afforded sulfoximine (*E*)-**1c** (140 mg, 93%) as a colorless liquid. $[\alpha]_D$ = +54.7 (*c* = 3.4 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.30 (s, 3H), 0.00 (s, 3H), 1.13 (s, 9H), 0.94 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.85 (seq, *J* = 13.8 Hz, 1H), 2.05 (sep, *J* = 10.9 Hz, 1H), 2.77 (s, 3H, NMe), 4.88 (d, *J* = 4.2 Hz, 1H), 5.95 (d, *J* = 15.1 Hz, 1H), 6.88 (dd, *J* = 15.3, 10.4 Hz, 1H), 6.95–6.99 (m, 2H, Ph), 7.02–7.15 (m, 3H, Ph), 7.55–7.68 (m, 3H, Ph), 7.85–7.89 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.8 (d), −4.1 (d), 18.3 (u), 20.3 (d), 21.5 (d), 26.0 (d), 28.5 (d), 29.0 (d), 50.9 (d), 75.1 (d), 126.6 (d), 127.0 (d), 127.8 (d), 128.5 (d), 128.8 (d), 131.2 (d), 132.2 (d), 140.5 (u), 143.4 (u), 145.7 ppm (d); IR (neat): $\tilde{\nu}$ = 3028 (s), 2956 (s), 2879 (s), 2802 (s), 1447 (m), 1388 (m), 1247 (s), 1150 (s), 1076 (s), 1044 (s), 874 (s), 807 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 457 (11), 400 (42), 303 (16), 302 (59), 221 (100), 115 (42), 75 (23), 73 ppm (13); HMRS (EI): *m/z*: calcd for $C_{26}H_{39}SSiNO_2$: 457.2470 [M^+]; found 457.2470.

Reactions of (*Z*)-1a und (*E*)-1a with $LiCuBu_2$ and $LiCuBu_2$/LiBu

a) A suspension of CuI (195 mg, 1.03 mmol) in Et_2O (10 mL) at −40 °C was treated with *n*BuLi (1.22 mL of 1.60 M solution in hexane, 1.95 mmol). After the mixture was stirred for 1 h, it was treated with a solution of the alkenyl sulfoximine (*Z*)-**1a** (76 mg, 0.19 mmol) in Et_2O (1 mL). Then the mixture was stirred for 1 h at −40 °C and D_2O (0.1 mL) was added. Purification by chromatography (EtOAc/hexane 80:20) gave (*Z*)-**1a** (190 mg, 97%) containing no D atom (≤ 3%) at the α-position.

b) A suspension of CuI (268 mg, 1.41 mmol) in Et_2O (10 mL) at −40 °C was treated with *n*BuLi (1.60 mL of 1.60 M solution hexane, 2.56 mmol). After the mixture was stirred for 30 min, it was treated with a solution of the alkenyl sulfoximine (*Z*)-**1a** (73 mg, 0.18 mmol) in Et_2O (2 mL). Then the mixture was warmed within 3 h to 0 °C, stirred for 1 h at this temperature and treated with saturated aqueous NH_4Cl/NH_3 (10 mL). Purification by chromatography (EtOAc/hexane 80:20) gave a mixture (28 mg) of (*E*)-**9aa** (47% chemical yield) and **15** (4% chemical yield) (R_f = 0.78) in a ratio of 93:7 and sulfoximine (*Z*)-**1a** (19 mg, 26%) as colorless oils.

c) A suspension of CuI (244 mg, 1.28 mmol) in Et_2O (10 mL) at −40 °C was treated with *n*BuLi (1.52 mL of 1.60 M solution in hexane, 2.43 mmol). After the mixture was stirred for 30 min, it was warmed to −15 °C and a solution of the alkenyl sulfoximine (*Z*)-**1a** (135 mg, 0.34 mmol) in Et_2O (2 mL) was added. The mixture was warmed within 1.5 h to 0 °C and stirring was continued for 1.5 h at this temperature. Then saturated aqueous NH_4Cl/NH_3 (10 mL) was added. Extraction with Et_2O gave a mixture of (*E*)-**9aa**, (*E*)-**1a** and **4b** (143 mg) in a ratio of 6:1:6 and **4b**. Chromatography (EtOAc/hexane 80:20) gave (*E*)-**9aa** (79 mg, 78%) containing only traces of (*Z*)-**9aa** (≤ 2%). Quenching of the above mixture with D_2O instead of saturated aqueous NH_4Cl/NH_3 gave [D]-(*Z*)-**9aa** with a D content at the α-position of ≥ 98% according to NMR spectroscopy.

d) A suspension of CuI (244 mg, 1.28 mmol) in Et_2O (10 mL) at −40 °C was treated with *n*BuLi (1.52 mL of 1.60 M solution in hexane, 2.44 mmol). After the mixture was stirred for 1 h, it was treated with a solution of the alkenyl sulfoximine (*Z*)-**1a** (202 mg, 0.51 mmol) in Et_2O (2 mL). The mixture was warmed within 18 h to room temperature. Then saturated aqueous NH_4Cl/NH_3 (10 mL) was added. Extraction with Et_2O gave a mixture of (*E*)-**9aa**, **15a**, **4b** and (*Z*)-**6aa**. Separation by chromatography first with hexane and then with EtOAc/hexane 50:50 gave a mixture (83 mg) of (*E*)-**9aa** (52% chemical yield) and **15a** (3% chemical yield) (R_f = 0.23) in a ratio of 94:6 and then (*Z*)-**6aa** (35 mg, 23%) (R_f = 0.67) as colorless oils.

e) A suspension of CuI (186 mg, 0.98 mmol) in Et_2O (10 mL) at −40 °C was treated with *n*BuLi (1.42 mL of 1.60 M solution in hexane, 2.28 mmol). After the mixture was stirred for 30 min, it was warmed to −15 °C and a solution of the alkenyl sulfoximine (*Z*)-**1a** (202 mg, 0.51 mmol) in Et_2O (2 mL) was added. The mixture was warmed within 18 h to room temperature and saturated aqueous NH_4Cl/NH_3 (10 mL) was added. Extraction with Et_2O gave a mixture of (*E*)-**9aa**, (*Z*)-**9aa** and (*Z*)-**6aa** in a ratio of 44:25:31 and **4b**. Chromatography first with pentane and then with EtOAc gave a mixture of (*E*)-**9aa** and (*Z*)-**9aa** (53 mg, 51%) (R_f = 0.23) in a ratio of 1.7:1 as a colorless oil and then (*Z*)-**6aa** (23 mg, 21%) as a yellow oil.

f) A suspension of CuI (228 mg, 1.20 mmol) in Et_2O (10 mL) at −40 °C was treated with *n*BuLi (1.7 mL of 1.60 M solution in hexane, 2.76 mmol). After the mixture was stirred for 1 h, it was warmed to −15 °C and treated with a solution of (*E*)-**1a** (138 mg, 0.35 mmol) in Et_2O (2 mL). The mixture was warmed within 3.5 h to 0 °C and treated with saturated aqueous NH_4Cl/NH_3 (10 mL). Purification by chromatography (EtOAc/hexane 80:20) gave (*E*)-**1a** (135 mg, 98%).

Triethyl (−)-(*E*,2*S*,3*R*)-3-isopropylnon-4-en-2-yloxy)silane [(*E*)-9aa]: $[\alpha]_D$ = −38.3 (*c* = 0.48 in Et_2O); GC: t_R = 8.22 (S1) and 10.07 min (S2); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.62 (br q, *J* = 7.9 Hz, 6H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 6.7 Hz, 3H), 1.03 (t, *J* = 7.9 Hz, 9H), 1.14 (d, *J* = 6.4 Hz, 3H), 1.33 (m, 4H), 1.48 (ddd, *J* = 9.6, 7.7, 3.2 Hz, 1H), 1.87 (m, 1H), 2.05 (br q, *J* = 6.7 Hz, 2H), 4.03 (qd, *J* = 6.2, 3.2 Hz, 1H), 5.36 (dt, *J* = 15.4, 6.6 Hz, 1H), 5.51 ppm (ddt, *J* = 15.4, 9.7, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ = 5.7 (u), 7.3 (d), 14.1 (d), 21.2 (d), 21.8 (d), 23.3 (d), 22.6 (u), 28.7 (d), 32.3 (u), 32.9 (u), 58.4 (d), 69.1 (d), 129.6 (d), 133.2 ppm (d); GC-MS (EI, 70 eV): *m/z* (%): 299 [M^+] (2), 270 (23), 269 (100), 160 (11), 159 (85), 131 (Et_3SiO, 69), 115 (Et_3Si, 40), 111 (15), 103 (16), 97 (20), 75 (10), 69 (13); IR (CH_2Cl_2): $\tilde{\nu}$ = 2957 (vs), 2927 (vs), 2876 (vs), 2732 (w), 1734 (w), 1459 (m), 1416 (m), 1371 (m), 1323 (w), 1260 (m), 1239 (m), 1163 (m), 1130 (m), 1071 (s), 1007 (s), 977 (m), 943 (m), 892 (w), 805 cm^{-1} (w); elemental analysis calcd (%) for $C_{18}H_{38}OSi$ (298.58): C 72.41, H 12.83; found: C 72.08, H 12.64; HMRS (EI, 70 eV): *m/z*: calcd for $C_{18}H_{38}OSi$: 269.2300 [$M^+ - C_2H_5$]; found 269.2300.

Triethyl (−)-(*Z*,2*S*,3*R*)-3-isopropylnon-4-en-2-yloxy)silane [(*Z*)-9aa]: GC: t_R = 8.42 min (S1); GC-MS (EI, 70 eV): *m/z* (%): 270 [$M^+ - C_2H_5$] (19), 269 (100), 160 (7), 159 (48), 131 (20), 115 (11), 111 (11), 103 (6), 97 (11), 69 (6), 55 (4).

Triethyl (2*S*,3*R*)-3-isopropylpent-4-en-2-yloxy)silane (15): GC: t_R = 7.89 min (S2); ^{1}H NMR (300 MHz, $CDCl_3$, in part): δ = 4.85 (dd, *J* = 17.4, 2.4 Hz, 1H), 5.01 (dd, *J* = 10.2, 2.4 Hz, 1H), 5.61 ppm (dt, *J* = 17.4, 10.2 Hz, 1H); GC-MS (EI, 70 eV): *m/z* (%): 243 [M^+] (1), 241 (2),

214 (16), 213 (100), 160 (5), 159 (30), 131 (8), 115 (5), 111 (5), 103 (3), 69 (8), 59 (2), 55 (2).

(*Z*,2*S*,3*R*)-3-Isopropyl-5-(triethylsilyl)-non-4-en-2-ol [(*Z*)-6aa]: GC: t_R= 11.60 min (S2); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.75 (br q, J = 7.9 Hz, 6H), 0.87 (d, J = 6.9 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H), 1.01 (t, J = 8.0 Hz, 9H), 1.17 (d, J = 6.2 Hz, 3H), 1.25–1.47 (m, 6H), 1.79 (m, 1H), 1.99–2.12 (m, 2H), 3.72 (q, J = 6.0 Hz, 1H), 6.04 ppm (br d, J = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ = 4.9 (u), 8.0 (d), 14.2 (d), 19.1 (d), 21.5 (d), 2.0 (d), 23.3 (u), 2.90 (d), 4.0, 38.0 (u), 54.2 (d), 67.7 (d), 142.0 (d), 142.9 ppm (u); GC-MS (EI, 70 eV): *m*/*z* (%): 297 [M^+−2] (3), 269 (11), 203 (33), 191 (17), 165 (69), 161 (28), 159 (7), 149 (9), 145 (14), 138 (22), 123 (9), 117 (17), 115 (75), 114 (10), 111 (41), 109 (16), 104 (10), 103 (90), 97 (49), 95 (20), 89 (100), 85 (12), 83 (17), 81 (13), 69 (28), 61 (17), 59 (10).

Reactions of (*Z*)-1a and (*E*)-1a with $LiCuMe_2$ and $LiCuMe_2$/LiMe

a) A suspension of CuI (259 mg, 1.36 mmol) in Et_2O (10 mL) at −40 °C was treated with MeLi (1.62 mL of 1.60 M solution in Et_2O, 2.59 mmol). After the mixture was stirred for 1 h, a solution of (*Z*)-**1a** (202 mg, 0.51 mmol) in Et_2O (2 mL) was added. The mixture was warmed within 18 h to room temperature and saturated aqueous NH_4Cl/NH_3 (10 mL) was added. Purification by chromatography (EtOAc/hexane 50:50) gave a mixture (105 mg) of (*E*)-**9ab** (75% chemical yield), (*Z*)-**9ab** (2% chemical yield) and **16ab** (2% chemical yield) (R_f= 0.75) in a ratio of 30:1:1 as a colorless oil.

b) A suspension of CuI (325 mg, 1.71 mmol) in Et_2O (10 mL) at −40 °C was treated with MeLi (2.00 mL of 1.60 M solution in Et_2O, 3.20 mmol). After the mixture was stirred for 1 h, a solution of (*Z*)-**1a** (145 mg, 0.37 mmol) in Et_2O (2 mL) was added. The mixture was warmed within 18 h to room temperature and treated with D_2O (0.1 mL). Work-up gave a mixture (144 mg) of [D]-(*E*)-**9ab** (D content at the α-position ≥98%), **4b** and [D]-(*E*)-**1a** (D content at the α-position ≥98%) in a ratio of 15:17:1. Purification by chromatography (EtOAc/hexane 80:20) (R_f= 0.77) gave a mixture (73 mg) of [D]-(*E*)-**9ab** (71% chemical yield) [D]-(*E*)-**9ab** (3% chemical yield) and **16a** (2% chemical yield).

c) A suspension of CuI (252 mg, 1.32 mmol) in Et_2O (10 mL) at −40 °C was treated with MeLi (1.90 mL of 1.60 M solution in Et_2O, 3.04 mmol). After the mixture was stirred for 1 h, it was warmed to −15 °C and a solution of (*Z*)-**1a** (151 mg, 0.38 mmol) in Et_2O (2 mL) was added. The mixture was warmed within 1.5 h to 0 °C and stirring was continued for 1.5 h at this temperature. Then saturated aqueous NH_4Cl/NH_3 (10 mL) was added. Extraction with Et_2O gave a mixture of (*E*)-**9ab** and (*Z*)-**9ab** in a ratio of 2.3:1 and sulfoximine (*E*)-**1a** (5%). Purification by chromatography (hexane/EtOAc 80:20) gave a mixture (50 mg) of (*E*)-**9ab** (38% chemical yield), (*Z*)-**9ab** (12% chemical yield) and **16a** (1%) (R_f= 0.73).

Triethyl (−)-(*E*,2*S*,3*R*)-3-isopropylhex-4-en-2-yloxy)silane [(*E*)-9ab]: $[\alpha]_D$= −33.0 (*c*= 0.55 in *n*-hexane); GC: t_R= 5.50 (S1) and 8.21 min (S2); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.61 (br q, J = 7.9 Hz, 6H), 0.93 (d, J = 6.7 Hz, 3H), 0.99 (d, J = 7.0 Hz, 3H), 1.03 (t, J = 8.0 Hz, 9H), 1.13 (d, J = 6.2 Hz, 3H), 1.49 (ddd, J = 9.7, 7.7, 3.4 Hz, 1H), 1.65 (dd, J = 6.2, 1.6 Hz, 3H), 1.84 (m, 1H), 3.99 (qd, J = 6.2, 3.4 Hz, 1H), 5.34 (dq, J = 15.2, 6.2 Hz, 1H), 5.51 ppm (ddq, J = 15.2, 9.5, 1.6 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6): δ = 5.7 (u), 7.3 (d), 18.2 (d), 20.9 (d), 21.8 (d), 23.0 (d), 28.7 (d), 58.3 (d), 69.1 (d), 127.4 (d), 130.8 ppm (d); GC-MS (EI, 70 eV): *m*/*z* (%): 256 [M^+] (1), 255 (2), 228 (16), 227 (100), 159 (36), 131 (17), 115 (12), 103 (6), 69 (21); IR (capillary): $\tilde{\nu}$= 2956 (vs), 2930 (vs), 2876 (vs), 2731 (w), 1727 (w), 1667 (w), 1602 (w), 1458 (s), 1416 (m), 1376 (m), 1320 (w), 1239 (m), 1164 (m), 1149 (m), 1129 (m), 1073 (s), 1016 (s), 975 (m), 945 (m), 918 (w), 891 (w), 876 (w), 842 cm^{-1} (w); elemental analysis calcd (%) for $C_{15}H_{32}OSi$ (256.50): C 70.24, H 12.57; found: C 70.05, H 12.79; HMRS (EI, 70 eV): *m*/*z*: calcd for $C_{15}H_{32}OSi$: 227.1831 [$M^+-C_2H_5$], found: 227.1830.

Triethyl (−)-(*Z*,2*S*,3*R*)-3-isopropylhex-4-en-2-yloxy)silane [(*Z*)-9ab]: GC: t_R= 8.42 min (S2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.57 (br q, J = 7.9 Hz, 6H), 0.81 (d, J = 6.7 Hz, 3H), 0.95 (m, 12H), 1.08 (d, J = 6.4 Hz, 3H), 1.58 (dd, J = 6.7, 2.0 Hz, 3H), 1.72 (m, 1H), 1.94 (ddd, J = 10.4, 7.7, 3.7 Hz, 1H), 4.00 (qd, J = 6.0, 3.7 Hz, 1H), 5.30 (m, 1H), 5.61 ppm (dq, J = 11.4, 6.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.29 (u), 6.96 (d), 13.43 (d), 20.18 (d), 21.45 (d), 22.46 (d), 28.72 (d), 50.90 (d), 68.88 (d), 125.06 (d), 130.25 ppm (d).

Triethyl (1*S*,2*R*)-3-isopropyl-5-methylhex-4-en-2-yloxy)silane (16a): GC: t_R= 8.58 min (S2); GC-MS (EI, 70 eV): *m*/*z* (%): 269 [M^+−2] (1), 243 (4), 242 (17), 241 (100), 240 (3), 185 (2), 160 (3), 159 (30), 131 (19), 115 (13), 103 (7), 83 (22), 81 (8), 69 (14).

Reactions of (*Z*)-1a and (*E*)-1a with $LiCuPh_2$ and $LiCuPh_2$/LiPh

a) A suspension of CuI (148 mg, 0.78 mmol) in Et_2O (15 mL) at −40 °C was treated with PhLi (0.80 mL of 1.80 M solution in cyclohexane/Et_2O, 1.44 mmol). After the mixture was stirred for 1 h, a solution of (*Z*)-**1a** (74 mg, 0.19 mmol) in Et_2O (2 mL) was added and the mixture was warmed within 18 h to room temperature. Then saturated aqueous NH_4Cl/NH_3 (10 mL) was added. Purification by chromatography (hexane/EtOAc 80:20) gave a mixture of **4b**, (*E*)-**9ac** (85% chemical yield), (*Z*)-**9ac** (2% chemical yield) and (*E*,*E*)-**17aa** (2% chemical yield).

b) A suspension of CuI (559 mg, 2.94 mmol) in Et_2O (15 mL) at −40 °C was treated with PhLi (3.80 mL of 1.80 M solution in cyclohexane/Et_2O, 6.83 mmol). After the mixture was stirred for 30 min, it was warmed to −15 °C and a solution of (*Z*)-**1a** (400 mg, 1.01 mmol) in Et_2O (5 mL) was added. The mixture was warmed within 1.5 h to 0 °C and stirring was continued for 3.5 h at this temperature. Then saturated aqueous NH_4Cl/NH_3 (10 mL) was added. Purification by chromatography (cyclohexane/EtOAc 91:9) gave (*Z*)-**6ac** (239 mg, 74%) (R_f= 0.31) as a colorless oil. In addition a mixture of (*E*)-**9ac**, (*Z*)-**9ac** and (*E*,*E*)-**17aa** (150 mg) was obtained.

c) A suspension of CuI (144 mg, 0.76 mmol) in Et_2O (10 mL) at −40 °C was treated with PhLi (1.10 mL of 1.80 M solution in cyclohexane/Et_2O, 1.98 mmol). After the mixture was stirred for 1 h, it was warmed to −15 °C and a solution of (*E*)-**1a** (188 mg, 0.48 mmol) in Et_2O (2 mL) was added. The mixture was warmed within 1.5 h to 0 °C and stirring was continued for 2 h at this temperature. Then saturated aqueous NH_4Cl/NH_3 (10 mL) was added. Purification by chromatography afforded a mixture of **4b**, (*Z*)-**9ac** (60% chemical yield), (*E*)-**9ac** (4% chemical yield) and (*Z*,*Z*)-**17aa** (30% chemical yield). Further purification by chromatography (hexane/EtOAc 80:20) gave a mixture (64 mg) of (*Z*)-**9ac** (22% chemical yield) and (*Z*,*Z*)-**17aa** (11% chemical yield) (R_f = 0.81) in a ratio of 2:1. In addition a mixture (56 mg) of (*E*)-**9ac**, (*Z*)-**9ac** and (*Z*,*Z*)-**17aa** containing biphenyl was obtained. A separation could only be achieved after desilylation of the mixture of (*E*)-**9ac**, (*Z*)-**9ac** und (*Z*,*Z*)-**17aa** at the stage of the corresponding alcohols (see Scheme 13).

Triethyl (−)-(*Z*,2*S*,3*R*)-3-(isopropyl)-5-phenyl-5-(triethylsilyl)pent-4-en-2-ol [(*Z*)-6ac]: $[\alpha]_D$= −43.8 (*c*= 0.79 in Et_2O); GC: t_R= 10.88 min (S1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.66 (br q, J = 7.9 Hz, 6H), 0.92 (t, J = 7.9 Hz, 9H), 0.92 (d, J = 6.9 Hz, 3H), 1.03 (d, J = 6.8 Hz, 3H), 1.26 (d, J = 6.3 Hz, 3H), 1.62 (br s, 1H), 1.90 (o, J = 6.7 Hz, 1H), 2.16 (dt, J = 11.4, 6.0 Hz, 1H), 3.84 (q, J = 6.2 Hz, 1H), 6.05 (d, J = 11.4 Hz, 1H), 7.05 (m, 2H), 7.17 (tt, J = 7.4, 1.3 Hz, 1H), 7.25 ppm (br t, J = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 4.3 (u), 7.6 (d), 18.9 (d), 21.1 (d), 21.8 (d), 28.8 (d), 54.0 (d), 68.0 (d), 125.5 (d), 127.6 (d), 127.8 (d), 146.3 (d), 146.5, 147.9 ppm (u); MS (EI, 70 eV): *m*/*z* (%): 290 [M^+−Et] (5), 289 (7), 274 (19), 271 (12), 246 (10), 245 (34), 243 (13), 215 (14), 201 (11), 173 (12), 163 (14), 159 (13), 158 (22), 145 (13), 135 (16), 131 (12), 116 (12), 115 (Et_3Si, 100), 107 (11), 105 (12), 103 (87), 87 (61), 75 (40); IR (capillary): $\tilde{\nu}$= 3399 (m, br), 3075 (w), 3055 (w), 3014 (w), 2956 (vs), 2934 (s), 2910 (s), 2874 (vs), 2731 (w), 1939 (w), 1866 (w), 1799 (w), 1744 (w), 1596 (m), 1489 (m), 1461 (s), 1441 (s), 1419 (s), 1385 (m), 1367 (m), 1351 (w), 1319 (w), 1238 (m), 1207 (w), 1156 (m), 1138 (w), 1106 (w), 1072 (w), 1043 (m), 1031 (w), 1002 (s), 971 (w), 912 (m), 878 (w), 838 (w), 813 cm^{-1} (m); elemental analysis calcd (%) for $C_{20}H_{34}OSi$ (318.57): C 75.40, H 10.76; found: C 75.19, H 11.02.

Triethyl (*E*,2*S*,3*R*)-3-isopropyl-5-phenylpent-4-en-2-yloxy)silane [(*E*)-9ac]: GC: t_R = 10.53 min (S1); ^{1}H NMR (300 MHz, $CDCl_3$, in part): δ = 0.86 (d, J = 6.7 Hz, 3H), 1.13 (d, J = 6.2 Hz, 3H), 1.70 (ddd, J = 9.5, 7.4, 3.7 Hz, 1H), 1.86 (m, 1H), 4.07 (qd, J = 6.2, 3.7 Hz, 1H), 6.16 (dd, J = 15.9, 9.4 Hz, 1H), 6.30 ppm (d, J = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.3 (u), 7.0 (d), 20.5 (d), 21.6 (d), 22.9 (d), 28.6 (d), 58.4 (d), 68.8 ppm (d); GC-MS (EI, 70 eV): *m*/*z* (%): 294 (2), 293 (7), 292 (32),

221 (10), 205 (17), 189 (10), 179 (11), 161 (28), 133 (36), 131 (19), 129 (10), 118 (14), 116 (22), 104 (6), 90 (26).

(7*E*,9*E*,5*S*,6*R*,11*S*,12*S*)-3,3,14,14-Tetraethyl-5,11-diisopropyl-5,12-dimethly-8-phenyl-4,13-dioxa-3,14-disilahexadeca-7,9-diene [(*E*,*E*)-17aa]: GC: t_R = 16.50 min (S1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50 (br q, J = 7.9 Hz, 6H), 0.57 (br q, J = 7.9 Hz, 6H), 0.75 (d, J = 6.7 Hz, 3H), 0.88 (d, J = 6.7 Hz, 3H), 0.88 (t, J = 7.9 Hz, 9H), 0.91 (m, 3H), 0.94 (t, J = 7.9 Hz, 9H), 0.99 (d, J = 6.7 Hz, 3H), 1.10 (d, J = 6.1 Hz, 3H), 1.13 (d, J = 6.1 Hz, 3H), 1.61 (ddd, J = 9.6, 7.4, 3.7 Hz, 1H), 1.70 (o, J = 6.7 Hz, 1H), 1.84 (o, J = 6.7 Hz, 1H), 2.21 (ddd, J = 10.8, 8.0, 3.4 Hz, 1H), 3.97 (qd, J = 6.1, 3.7 Hz, 1H), 4.09 (qd, J = 6.1, 3.4 Hz, 1H), 5.40 (dd, J = 15.8, 9.6 Hz, 1H), 5.42 (d, J = 10.8 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 7.20–7.34 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.27 (u), 5.31 (u), 6.9 (d), 7.0 (d), 20.5 (d), 20.7 (d), 21.5 (d), 21.6 (d), 22.7 (d), 22.9 (d), 28.5, 29.1 (d), 51.9 (d), 58.8 (d), 68.9 (d), 69.1 (d), 127.7 (d), 128.9 (d), 126.4 (d), 129.7 (d), 130.8 (d), 133.9 (d), 141.3 (d), 143.6 ppm (u); GC-MS (EI, 70 eV): m/z (%): 427 [$M^+-C_2H_6$] (1), 373 (1), 271 (1), 270 (2), 221 (6), 205 (19), 163 (8), 162 (14), 161 (100), 159 (11), 133 (29), 131 (9).

Triethyl (*Z*,2*S*,3*R*)-3-isopropyl-5-phenylpent-4-en-2-yloxy)silane [(*Z*)-9ac]: GC: t_R = 10.36 min (S1); ^{1}H NMR (500 MHz, $CDCl_3$, in part): δ = 0.58 (m, 6H), 0.87 (d, J = 6.7 Hz, 3H), 0.96 (m, 9H), 1.0 (m, 3H), 1.10 (d, J = 6.1 Hz, 3H), 1.78 (o, J = 6.7 Hz, 1H), 2.31 (ddd, J = 11.1, 7.3, 4.0 Hz, 1H), 4.00 (qd, J = 6.1, 4.0 Hz, 1H), 5.35 (t, J = 11.6 Hz, 1H), 6.63 (d, J = 12.0 Hz, 1H), 7.14–7.32 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.3 (u), 7.1 (d), 20.1 (d), 21.2 (d), 22.7 (d), 28.8 (d), 51.1 (d), 68.9 (d), 128.0 (d), 128.8 ppm (d); GC-MS (EI, 70 eV): m/z (%): 293 (2), 292 (10), 221 (6), 205 (10), 189 (4), 179 (8), 161 (16), 132 (21), 131 (7), 129 (5), 118 (6), 116 (13), 104 (3), 90 (36).

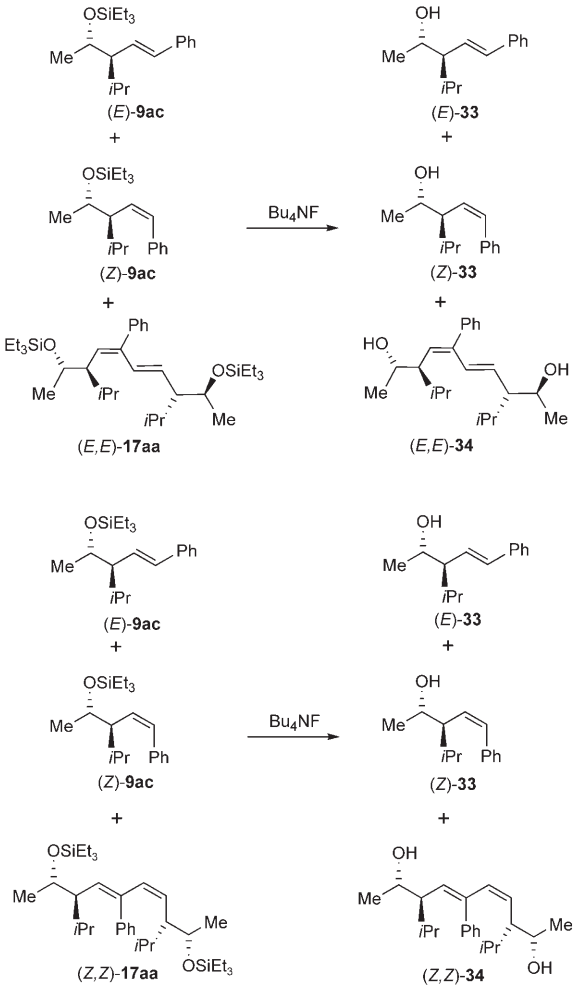
(7*Z*,9*Z*,5*S*,6*R*,11*S*,12*S*)-3,3,14,14-Tetraethyl-6,11-diisopropylmethyl-5,12-dimethy-8-phenyl-4,13-dioxa-3,14-disilahexadeca-7,9-diene [(*Z*,*Z*)-17aa]: ^{1}H NMR (300 MHz, $CDCl_3$, in part): δ = 0.58 (m, 12H), 0.78 (d, J = 6.4 Hz, 3H), 0.80 (d, J = 6.4 Hz, 3H), 0.86 (d, J = 6.0 Hz, 3H), 0.96 (m, 18H), 1.0 (m, 3H), 1.02 (d, J = 6.1 Hz, 3H), 1.03 (d, J = 6.1 Hz, 3H), 1.57–1.79 (m, 4H), 3.35 (m, 2H), 5.35 (t, J = 11.6 Hz, 1H), 5.70 (d, J = 10.1 Hz, 1H), 6.26 (d, J = 12.1 Hz, 1H), 7.14–7.32 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9 (d), 21.2 (d), 21.5 (d), 22.9 (d), 23.3 (d), 28.9 (d), 29.0 (d), 50.3 (d), 51.9 (d), 68.4 (d), 69.1 ppm (d).

Desilylation of the mixture of (*E*)-9ac, (*Z*)-9ac and (*E*,*E*)-17aa (Scheme 13)

a) A solution of a mixture of (*E*)-**9ac**, (*Z*)-**9ac** und (*E*,*E*)-**17aa** (150 mg) in THF (10 mL) at 0°C was treated with Bu_4NF (78 mg, 0.30 mmol). After the mixture was stirred for 60 h at room temperature, the solvent was removed in vacuo. Purification by chromatography (hexane/EtOAc 80:20) gave a mixture of alcohols (*E*)-**33** and (*Z*)-**33** (22 mg, 11% based on (*Z*)-**1a**) in a ratio of 4.8:1 and diol (*E*,*E*)-**34** (6 mg, 4% based on (*Z*)-**1a**) (R_f = 0.16).

(*E*,2*S*,3*R*)-3-Isopropyl-5-phenylpent-4-en-2-ol [(*E*)-33]: GC: t_R = 8.16 min (S1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, J = 6.7 Hz, 3H), 0.96 (d, J = 6.7 Hz, 3H), 1.22 (d, J = 6.1 Hz, 3H), 1.58 (br s, 1H), 1.85 (m, 1H), 1.90 (m, 1H), 3.93 (q, J = 6.1 Hz, 1H), 6.13 (dd, J = 15.8, 9.7 Hz, 1H), 6.44 (d, J = 15.8 Hz, 1H), 7.22 (m, 1H), 7.31 (m, 2H), 7.39 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.86 (d), 21.5 (d), 21.9 (d), 28.7 (d), 58.0 (d), 68.0 (d), 126.3 (d), 128.6 (d), 127.4 (d), 128.1 (s), 134.4 (d), 137.4 (u); GC-MS (EI, 70 eV): m/z (%): 160 (6), 145 (2), 131 (2), 128 (3), 117 (18), 104 (10), 89 (37), 77 (1), 61 ppm (10).

(*Z*,2*S*,3*R*)-3-Isopropyl-5-phenylpent-4-en-2-ol [(*Z*)-33]: GC: t_R = 7.66 min (S1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H), 1.17 (d, J = 6.1 Hz, 3H), 1.49 (br s, 1H), 1.83 (o, J = 6.8 Hz, 1H), 2.45 (dt, J = 11.4, 6.0 Hz, 1H), 3.90 (q, J = 6.1 Hz, 1H), 5.61 (t, J = 11.7 Hz, 1H), 6.78 (d, J = 11.9 Hz, 1H), 7.22–7.31 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.6 (d), 21.4 (d), 21.5 (d), 29.0 (d), 50.7 (d), 68.4 (d), 128.2 (d), 128.7, (d), 126.7 (d), 130.5 (d), 133.7 (d), 137.7 ppm (u); GC-MS (EI, 70 eV): m/z (%): 161 [$M^+-C_3H_7$] (1), 160 (4), 131 (2), 129 (2), 128 (2), 117 (15), 104 (9), 89 (45), 77 (1), 61 (12), 45 (11), 43 (100), 42 (12), 32 (9).



Scheme 13. Desilylation of silyl ethers (*E*)-**9ac**, (*Z*)-**9ac**, (*E*,*E*)-**17aa** and (*Z*,*Z*)-**17aa**.

(4*E*,6*E*,2*S*,3*R*,8*SR*,9*S*)-3,8-Diisopropyl-5-phenyldeca-4,6-diene-2,9-diol [(*E*,*E*)-34]: ^{1}H NMR (500 MHz, C_6D_6): δ = 0.75 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 6.6 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.6 Hz, 3H), 1.03 (d, J = 6.2 Hz, 3H), 1.12 (d, J = 6.2 Hz, 3H), 1.62 (dddd, J = 9.7, 6.6, 5.2, 1.2 Hz, 1H), 1.68 (o, J = 6.6 Hz, 1H), 1.85 (o, J = 6.8 Hz, 1H), 2.31 (ddd, J = 10.9, 7.0, 4.8 Hz, 1H), 3.63 (q, J = 5.8 Hz, 1H), 3.81 (qu, J = 5.9 Hz, 1H), 5.52 (d, J = 11.0 Hz, 1H), 5.65 (ddd, J = 15.6, 9.7, 1.2 Hz, 1H), 6.59 (d, J = 15.6 Hz, 1H), 7.11 (tt, J = 7.3, 1.3 Hz, 1H), 7.19 (t, J = 7.5 Hz, 2H), 7.41 ppm (dd, J = 8.0, 1.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8 (d), 19.0 (d), 21.4 (d), 21.5 (d), 21.7 (d), 22.0 (d), 28.5 (d), 29.5 (d), 51.6 (d), 58.4 (d), 67.8 (d), 68.6 (d), 128.1 (d), 128.8 (d), 127.2 (d), 129.5 (d), 131.8 (d), 132.9 (d), 142.7 (u), 143.6 ppm (u).

Desilylation of the mixture of (*E*)-9ac, (*Z*)-9ac and (*Z*,*Z*)-17aa: A solution of a mixture (*E*)-**9ac**, (*Z*)-**9ac** and (*Z*,*Z*)-**17aa** (120 mg) in THF (10 mL) at 0°C was treated with Bu_4NF (50 mg, 0.19 mmol). After the mixture was stirred for 18 h at room temperature, the solvent was removed in vacuo. Purification by chromatography (hexane/EtOAc 80:20) gave a mixture of alcohols (*E*)-**33** and (*Z*)-**33** (24 mg, 25% based on (*Z*)-**1a**) (R_f = 0.31) in a ratio of 3:16 and diol (*Z*,*E*)-**34** (16 mg, 20% based on (*Z*)-**1a**) (R_f = 0.17).

(4*Z*,6*Z*,2*S*,3*R*,8*S*,9*S*)-3,8-Diisopropyl-5-phenyl-deca-4,6-diene-2,9-diol [(*Z*,*E*)-34]: GC: t_R = 11.79 min (S1); ^{1}H NMR (500 MHz, C_6D_6): δ = 0.78 (d, J = 6.9 Hz, 3H), 0.79 (d, J = 6.7 Hz, 3H), 0.84 (d, J = 6.7 Hz, 3H), 0.88 (d, J = 6.7 Hz, 3H), 1.04 (d, J = 6.2 Hz, 3H), 1.10 (d, J = 6.2 Hz, 3H), 1.33 (br s, 1H), 1.40 (br s, 1H), 1.63–1.90 (m, 4H), 3.66 (br q, J = 6.1 Hz, 1H), 3.85 (br q, J = 6.1 Hz, 1H), 5.32 (t, J = 11.8 Hz, 1H),

5.75 (d, J = 10.7 Hz, 1H), 6.46 (d, J = 11.8 Hz, 1H), 7.18 (m, 2H), 7.27–7.35 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.5 (d), 19.3 (d), 21.4 (d), 21.6 (d), 21.7 (d), 21.7 (d), 28.8 (d), 29.2 (d), 50.0 (d), 51.5 (d), 68.4 (d), 68.5 (d), 128.1 (d), 129.8 (d), 126.8 (d), 128.8 (d), 131.4 (d), 136.5 (d), 140.4 (u), 142.7 ppm (u).

Reaction of (*Z*)-1a and (*E*)-1a with LiCu(CH=CH$_2$)$_2$: A suspension of CuI (282 mg, 1.48 mmol) in Et_2O (80 mL) at −40 °C was treated with vinyllithium (approximately 70 mg, 2 mmol) in Et_2O (10 mL). After the mixture was stirred for 1 h, it was warmed to −15 °C and a solution of (*Z*)-**1a** (156 mg, 0.39 mmol) in Et_2O (2 mL) was added. The mixture was warmed within 1.5 h to 0 °C and stirring was continued at this temperature for 2.5 h. Then saturated aqueous NH_4Cl/NH_3 was added. Purification by chromatography (hexane/EtOAc 80:20) (R_f = 0.69) gave a mixture (75 mg) of (*E*)-**9ad** (66% chemical yield), (*Z*)-**9ad** (3% chemical yield) and (*Z*,*E*)-**17ab** (1% chemical yield) in a ratio of 94:4:2 as a colorless oil.

Triethyl (−)-(*E*,2*S*,3*R*)-3-isopropylhept-4,6-dien-2-yloxy)silane [(*E*)-9ad]: $[\alpha]_D$ = −75.8 (c = 1.04 in Et_2O); GC: t_R = 7.23 min (S1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.57 (br q, J = 7.9 Hz, 6H), 0.80 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.95 (t, J = 7.9 Hz, 9H), 1.09 (d, J = 6.2 Hz, 3H), 1.57 (ddd, J = 10.0, 7.2, 4.0 Hz, 1H), 1.77 (o, J = 6.8 Hz, 1H), 3.99 (qd, J = 6.2, 4.0 Hz, 1H), 4.95 (dd, J = 10.0, 1.7 Hz, 1H), 5.07 (dd, J = 16.8, 1.7 Hz, 1H), 5.61 (dd, J = 15.2, 10.0 Hz, 1H), 5.98 (dd, J = 15.2, 10.2 Hz, 1H), 6.35 ppm (dt, J = 16.8, 10.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.2 (u), 6.9 (d), 20.2 (d), 21.6 (d), 22.8 (d), 28.4 (d), 57.9 (d), 68.7 (d), 114.3 (u), 133.4 (d), 134.6 (d), 137.5 ppm (d); GC-MS (EI, 70 eV): m/z (%): 268 [M^+] (1), 267 (5), 253 (2), 241 (4), 240 (16), 239 [$M^+-C_2H_5$] (97), 219 (12), 204 (12), 203 (78), 195 (10), 159 (100), 157 (15), 155 (9), 137 (24), 131 (Et_3SiO, 12), 115 (Et_3Si, 3), 103 (5), 95 (8), 81 (14); IR (capillary): $\tilde{\nu}$ = 3086 (w), 3037 (w), 2957 (vs), 2911 (s), 2877 (vs), 2733 (w), 1796 (w), 1651 (w), 1603 (w), 1460 (m), 1415 (m), 1383 (m), 1372 (m), 1357 (m), 1323 (w), 1264 (w), 1239 (m), 1159 (s), 1129 (s), 1109 (s), 1070 (s), 1005 (vs), 958 (s), 939 (m), 895 (s), 852 (w), 820 cm^{-1} (w). (*Z*)-**9ad**: GC: t_R = 7.47 min (S1); ^{1}H NMR (400 MHz, $CDCl_3$, in part): δ = 0.81 (d, J = 6.9 Hz, 3H), 4.04 (qd, J = 6.1, 3.5 Hz, 1H), 5.05 (br d, J = 10.0 Hz, 1H), 5.17 (dd, J = 17.0, 1.7 Hz, 1H), 5.44 (t, J = 11.0 Hz, 1H), 6.19 (t, J = 11.0 Hz, 1H), 6.35 ppm (dt, J = 17.0, 10.5 Hz, 1H).

(7*Z*,9*E*,5*S*,6*R*,11*S*,12*S*)-3,3,14,14-Tetraethyl-6,11-diisopropyl-5,12-dimethyl-8-vinyl-4,13-dioxa-3,14-disilahexadeca-7,9-diene [(*Z*,*E*)-17ab]: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.57 (m, 12H), 0.82 (d, J = 6.9 Hz, 3H), 0.84 (d, J = 6.9 Hz, 3H), 0.94 (m, 24H), 1.06 (d, J = 6.1 Hz, 3H), 1.11 (d, J = 6.1 Hz, 3H), 1.57 (ddd, J = 9.7, 7.8, 3.1 Hz, 1H), 1.78 (m, 2H), 2.15 (ddd, J = 10.7, 8.0, 3.6 Hz, 1H), 4.04 (qd, J = 6.1, 3.1 Hz, 1H), 4.04 (qd, J = 6.1, 3.6 Hz, 1H), 4.98 (dd, J = 10.7, 1.7 Hz, 1H), 5.27 (dd, J = 17.2, 1.7 Hz, 1H), 5.52 (br d, J = 10.7 Hz, 1H), 5.62 (dd, J = 16.2, 9.9 Hz, 1H), 5.97 (br d, J = 16.2 Hz, 1H), 6.46 ppm (dd, J = 17.2, 10.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.27 (u), 5.28 (u), 7.0 (d), 20.5 (d), 20.9 (d), 21.4 (d), 21.6 (d), 22.8 (d), 23.0 (d), 28.5, 29.0 (d), 51.9 (d), 58.9 (d), 68.8 (d), 68.9 (d), 112.9 (u), 128.0 (d), 131.5 (d), 133.0 (d), 139.7 (d), 144.3 ppm (u).

Reaction of (*Z*)-2b with LiCuMe$_2$

a) A suspension of CuI (140 mg, 0.73 mmol) in Et_2O (5 mL) at −40 °C was treated with MeLi (0.6 mL of 5% solution in Et_2O, 1.34 mmol). After the yellow mixture was stirred for 1 h, the lithioalkenyl sulfoximine (*Z*)-**2b**, which was prepared from the alkenyl sulfoximine (*Z*)-**1b** (100 mg, 0.25 mmol) and MeLi (0.12 mL of 5% solution in Et_2O, 0.27 mmol), in Et_2O (2 mL) was added. The mixture was stirred for 1 h at −40 °C and then allowed to warm room temperature and stirred for 8 h. The mixture was quenched with aqueous NH_4Cl and extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (hexane) gave a mixture of alkene (*E*)-**9b** and dimethyl alkene **16b** (39 mg) in a ratio of 7:3 as a colorless liquid. GC-MS analysis showed the formation of (*E*)-**9b** and **16b** together with 5% of diene (*Z*,*E*)-**17b**. Separation by HPLC (pentane) gave (*E*)-**9b** (27 mg, 41%) and **16b** (12 mg, 18%) as colorless liquids.

b) A suspension of CuI (140 mg, 0.73 mmol) in Et_2O (5 mL) at −40 °C was treated with MeLi (0.6 mL of 5% solution in Et_2O, 1.34 mmol). After the yellow mixture was stirred for 1 h, a solution of the alkenyl sulfoximine (*Z*)-**1b** (100 mg, 0.24 mmol) in Et_2O (2 mL) was added. The mixture was stirred for 1 h at −40 °C and then allowed to warm room temperature and stirred for 10 h. The mixture was quenched with aqueous NH_4Cl and extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. GC-MS analysis showed the formation of (*E*)-**9b**, **16b** and 5% of (*Z*,*E*)-**17b**. Purification by chromatography (hexane) yielded alkene (*E*)-**9b** along with the dimethyl alkene **16b** (49 mg) in a ratio of 9:1 as a colorless liquid. Separation by HPLC (pentane) gave (*E*)-**9b** (42 mg, 64%) and **16b** (5 mg, 8%) as colorless liquids.

Triethyl [(5*S*,6*R*,*E*)-6-methylnona-1,7-dien-5-yloxy]silane [(*E*)-9b]: $[\alpha]_D$ = +15.0 (c = 0.7 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50–0.57 (m, 6H), 0.87 (d, J = 6.9 Hz, 3H), 0.89 (t, J = 7.7 Hz, 9H), 1.35–1.32 (m, 2H), 1.59 (d, J = 5.8 Hz, 3H), 1.88–1.98 (m, 1H), 2.01–2.11 (m, 1H), 2.13–2.22 (m, 1H), 3.45 (m, 1H), 4.84–4.96 (m, 2H), 5.36–5.51 (m, 2H), 5.77–5.88 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.0, (u), 7.1 (d), 15.4 (d), 18.2 (d), 30.2 (u), 32.6 (u), 42.4 (d), 75.7 (d), 114.0 (u), 124.7 (d), 133.5 (d), 139.0 ppm (d); IR (neat): $\tilde{\nu}$ = 3075 (m), 2955 (w), 2880 (w), 1640 (m), 1454 (s), 1238 (s), 1080 (w), 1012 (w), 970 (s), 825 cm^{-1} (s); MS (EI, 70 eV): m/z (%): 199 (100), 143 (6), 115 (38), 87 (22); HRMS (EI, 70 eV): m/z: calcd for $C_{11}H_{23}OSi$: 199.1518 [$M^+-C_5H_9$]; found: 199.1519.

[(5*S*,6*R*)-6,8-Dimethylnona-1,7-dien-5-yloxy]triethylsilane (16b): GC: t_R = 9.58 min; $[\alpha]_D$ = +5.2 (c = 0.6 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.52–0.57 (m, 6H), 0.85 (d, J = 6.9 Hz, 3H), 0.89 (m, 9H), 1.35–1.42 (m, 2H), 1.54 (d, J = 1.5 Hz, 3H), 1.62 (d, J = 1.2 Hz, 3H), 1.86–1.99 (m, 1H), 1.99–2.14 (m, 1H), 2.34–2.46 (m, 1H), 3.46 (dq, J = 9.9, 3.71, 1H), 4.84–4.94 (m, 2H), 4.96 (m, 1H), 5.68–5.82 ppm (m, 1H); IR (neat): $\tilde{\nu}$ = 2927 (w), 2875 (s), 1637 (s), 1458 (m), 1216 (s), 1156 (m), 1011 (m), 912 (m), 759 cm^{-1} (w); GC-MS (EI, 70 eV): m/z (%):253 [M^+ −29] (6), 200 (17), 199 (100), 143 (12), 115 (95), 103 (28), 87 (44), 67 (28); HRMS (EI, 70 eV): m/z: calcd for $C_{15}H_{29}OSi$: 253.1987 [$M^+-C_2H_5$]; found: 253.1989.

(5*S*,6*R*,7*Z*,9*E*,11*R*,12*S*)-5,12-Di(but-3-enyl)-3,3,14,14-tetraethyl-6,11-diiso-propyl-8-methyl-4,13-dioxa-disilahexadeca-7,9-diene [(*Z*,*E*)-17b]: GC: t_R = 20.51 min; H NMR (400 MHz, $CDCl_3$): δ = 0.50–0.58 (m, 12H), 0.90 (t, J = 7.7 Hz, 18H), 0.96 (d, J = 6.9 Hz, 3H), 1.01 (d, J = 6.6 Hz, 3H), 1.35–1.44 (m, 4H), 1.66 (d, J = 1.1 Hz, 3H), 1.88–2.02 (m, 2H), 2.02–2.12 (m, 2H), 2.34–2.38 (m, 1H), 2.64–2.71 (m, 1H), 3.47–3.57 (m, 2H), 4.84–4.97 (m, 4H), 5.07 (d, J = 9.7 Hz, 1H), 5.50 (m, 1H), 5.68–5.79 (m, 2H), 6.32 ppm (d, J = 15.65 Hz, 1H); GC-MS (EI, 70 eV): m/z (%): 520 [M^+], 333 (1), 199 (100), 115 (36), 87 (25), 67 (11).

Reaction of (*Z*)-2c with LiCuMe$_2$: A suspension of CuI (249 mg, 1.3 mmol) in Et_2O (10 mL) at −40 °C was treated with MeLi (1.05 mL, 2.4 mmol). After the yellow mixture was stirred for 1 h, the lithioalkenyl sulfoximine (*Z*)-**2c**, which was prepared from (*Z*)-**1c** (200 mg, 0.43 mmol) and MeLi (0.22 mL of 5% solution in Et_2O, 0.43 mmol), in Et_2O (2 mL) was transferred through a cannula to the mixture. The mixture was stirred for 1 h at −40 °C and allowed to warm room temperature and stirred for 8 h. Then the mixture was quenched with D_2O and extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. A ^{1}H NMR spectrum showed the formation of [D]-(*E*)-**9c** and **16c** in a ratio of 7:3). Purification by chromatography (hexane/EtOAc 98:2) gave [D]-(*E*)-**9c** (71 mg, 50%) and **16c** (28 mg, 19%) as colorless liquids.

***tert*-Butyl (1*R*,2*R*,*E*)-2-isopropyl-1-phenylpent-3-enyloxy)dimethylsilane ([D]-(*E*)-9c)**: $[\alpha]_D$ = +60.4 (c = 0.7 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.27 (s, 3H), 0.0 (s, 3H), 0.78 (d, J = 6.9 Hz, 3H), 0.84 (s, 9H), 0.85 (d, J = 7.2 Hz, 3H), 1.43–1.52 (m, 1H), 1.64 (d, J = 1.1 Hz, 3H), 1.87 (dt, J = 11.5, 5.8 Hz, 1H), 4.63 (d, J = 6.0 Hz, 1H), 5.30 (d, J = 9.9 Hz, 1H), 7.17–7.29 ppm (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.8 (d), −4.2 (d), 18.1 (d), 18.3 (u), 18.8 (d), 22.0 (d), 25.9 (d), 27.8 (d), 58.7 (d), 76.4 (d), 126.6 (d), 126.9 (d), 127.4 (d), 129.0 (d), 144.7 ppm (u); IR (KBr): $\tilde{\nu}$ = 3029 (w), 2956 (s), 2888 (s), 2859 (s), 1464 (s), 1364 (m), 1253 (s), 1200 (w), 1126 (m), 1089 (s), 1067 (s), 976 (m), 870 cm^{-1}

(s); MS (EI, 70 eV): *m/z* (%): 263 (3), 262 (15), 222 (19), 221 (100), 165 (5), 115 (3), 75 (10), 73 (38); HRMS (EI, 70 eV): *m/z*: calcd for $C_{16}H_{24}OSiD$: 262.1737 [$M^+-C_4H_9$]; found: 262.1738.

***tert*-Butyl [(1*R*,2*R*)-2-isopropyl-4-methyl-1-phenylpent-3-enyloxy]dimethylsilane (16c)**: $[\alpha]_D = +27.5$ ($c = 0.6$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.28$ (s, 3H), 0.0 (s, 3H), 0.79 (d, $J = 6.9$ Hz, 3H), 0.85 (s, 9H), 0.89 (d, $J = 6.7$ Hz, 3H), 1.25 (d, $J = 1.5$ Hz, 3H), 1.48–1.57 (m, 1H), 1.69 (d, $J = 1.5$ Hz, 3H), 2.17 (dt, $J = 11.6$, 5.7 Hz, 1H), 4.66 (d, $J = 5.7$ Hz, 1H), 5.08 (dp, $J = 10.4$, 2.8 Hz, 1H), 7.17–7.27 ppm (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -5.0$ (d), −4.4 (d), 17.9 (d), 18.9 (d), 21.7 (d), 25.7 (d), 26.0 (d), 28.5 (d), 53.4 (d), 76.4 (d), 123.2 (d), 126.5 (d), 126.4 (d), 127.4 (d), 133.2 (d), 145.0 ppm (u); IR (neat): $\tilde{\nu} = 3065$ (m), 2951 (w), 2879 (w), 1637 (s), 1451 (m), 1245 (s), 1149 (w), 1011 (w), 911 (m), 865 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 333 [M^+] (1), 318 (1), 375 (10), 221 (38), 201 (100), 73 (1); HRMS (EI, 70 eV): *m/z*: calcd for $C_{20}H_{33}OSi$: 317.2300 [M^+-CH_3]; found: 317.2299.

Reaction of (*Z*)-1c with $LiCuMe_2$

a) A suspension of CuI (249 mg, 1.3 mmol) in Et_2O (10 mL) at −40 °C was treated with MeLi (1.05 mL, 2.4 mmol). After the yellow mixture was stirred for 1 h, the alkenyl sulfoximine (*Z*)-**1c** (200 mg, 0.43 mmol) in Et_2O (2 mL) was added. The mixture was stirred for 1 h at −40 °C and allowed to room temperature and stirred for 8 h. Then the reaction mixture was quenched with saturated NH_4Cl and extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (EtOAc/hexane 2:98) afforded alkene (*E*)-**9c** (98 mg, 71%) and dimethyl alkene **16c** (13 mg, 9%) as colorless liquids in a ratio of 9:1. When the reaction mixture was quenched with D_2O and extracted with Et_2O, dried ($MgSO_4$) concentrated in vacuo. Purification by column chromatography (hexane/EtOAc 98:2) afforded a mixture of [D]-(*E*)-**9c** (98% D) and **16c** in a ratio of 9:1 in similar yields.

***tert*-Butyl (1*R*,2*R*,*E*)-2-isopropyl-1-phenylpent-3-enyloxy)dimethylsilane [(*E*)-9c]**: $[\alpha]_D = +61.9$ ($c = 2.1$ in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.27$ (s, 3H), 0.0 (s, 3H), 0.78 (d, $J = 6.9$ Hz, 3H), 0.84 (s, 9H), 0.85 (d, $J = 7.2$ Hz, 3H), 1.43–1.52 (m, 1H), 1.66 (dd, $J = 6.3$, 1.7 Hz, 3H), 1.87 (dt, $J = 11.5$, 5.8 Hz, 1H), 5.17 (dq, $J = 15.1$, 6.2 Hz, 1H), 5.34 (ddq, $J = 15.3$, 9.7, 1.5 Hz, 1H), 7.17–7.29 ppm (m, 5H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.8$ (d), −4.2 (d), 18.2 (d), 18.3 (u), 18.8 (d), 22.0 (d), 25.9 (d), 27.8 (d), 58.7 (d), 76.4 (d), 126.6 (d), 126.9 (d), 127.4 (d), 127.7 (d), 129.1 (d), 144.7 ppm (u); IR (neat): $\tilde{\nu} = 3026$ (s), 2956 (w), 2887 (w), 2859 (w), 1463 (s), 1253 (w), 1198 (m), 1089 (w), 972 (s), 873 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%): 261 (22) [M^+], 221 (100), 185 (1), 115 (5), 73 (33); HRMS (EI, 70 eV): *m/z*: calcd for $C_{16}H_{25}OSi$; 261.1674 [$M^+-C_4H_9$]; found: 261.1676.

b) A suspension of CuI (124 mg, 0.65 mmol) in Et_2O (5 mL) at −40 °C was treated with MeLi (0.527 mL, 1.22 mmol). After the yellow mixture was stirred for 1 h, a solution of the alkenyl sulfoximine (*Z*)-**1c** (100 mg, 0.21 mmol) in Et_2O (5 mL) was added and the mixture was allowed to stir for 1 h. Then the mixture was allowed to warm to room temperature and stirred until TLC indicated a complete consumption of the starting material. The mixture was quenched with ethyl acrylate (2 mmol). Then the mixture was allowed to stir for 1 h, and treated with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (hexane/EtOAc 95:5) gave ester (*Z*)-**20** (40 mg, 50%) as a colorless liquid.

(*R*,*Z*)-Ethyl 6-(*R*)-(*tert*-butyldimethylsilyloxy)(phenyl)methyl)-4,7-dimethyl-oct-4-enoate [(*Z*)-20]: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.25$ (s, 3H), 0.01 (s, 3H), 0.79 (d, $J = 6.7$ Hz, 3H), 0.88 (s, 9H), 0.96 (d, $J = 6.6$ Hz, 3H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.35–1.45 (m, 2H), 1.69 (s, 3H), 2.12 (t, $J = 7.7$ Hz, 1H), 4.10 (q, $J = 7.9$ Hz, 2H), 4.80 (d, $J = 4.5$ Hz, 1H), 5.25 (d, $J = 10.6$ Hz, 1H), 7.17–7.29 ppm (m, 5H, Ph); IR (neat): $\tilde{\nu} = 3060$ (m), 2957 (w), 2860 (w), 1734 (w), 1601 (s), 1463 (w), 1254 (w), 1183 (w), 1090 (w), 916 (m), 837 (w), 735 cm^{-1} (m); GC-MS (EI, 70 eV): *m/z* (%): 361 [M^+-57] (5), 221 (100), 165 (2), 115 (3), 73 (26).

Reaction of (*E*)-1c with $LiCuMe_2$

a) A suspension of CuI (249 mg, 1.3 mmol) in Et_2O (10 mL) at −40 °C was treated with MeLi (1.05 mL, 2.5 mmol). After the yellow mixture was stirred for 1 h, the alkenyl sulfoximine (*E*)-**1c** (200 mg, 0.43 mmol) in Et_2O (2 mL) was added. The mixture was allowed to warm to room temperature and stirred for 4 h. Then the mixture was quenched with D_2O and extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (hexane/EtOAc 80:20) afforded the α-methylalkenyl sulfoximine (*E*)-**22** (2 mg, 10%) and sulfoximine [D]-(*E*)-**1c** (164 mg, 80%) (90% D) as colorless liquids.

***tert*-Butyl-{(*E*,1*R*,2*R*)-2-isopropyl-1-phenyl-4-[(*S*)-*N*-methyl-phenylsulfonimidoyl]pent-3-enyloxy}dimethylsilane [(*E*)-22]**: $[\alpha]_D = +58.5$ ($c = 0.8$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.31$ (s, 3H), −0.04 (s, 3H), 0.85 (d, $J = 6.9$ Hz, 3H), 0.88 (s, 9H), 1.05 (d, $J = 6.6$ Hz, 3H), 1.16 (d, $J = 1.4$ Hz, 3H), 1.90 (sex, $J = 13.2$ Hz, 1H), 2.02 (sep, $J = 11.0$ Hz, 1H), 2.73 (s, 3H, NMe), 4.92 (d, $J = 3.0$ Hz, 1H), 5.95 (d, $J = 15.1$ Hz, 1H), 6.86 (m, 1H), 6.85–6.95 (m, 4H), 6.96–7.02 (m, 1H, Ph), 7.48–7.53 (m, 2H, Ph), 7.55–7.60 (m, 1H, Ph), 7.81–7.89 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.8$ (d), −4.1 (d), 18.3 (u), 20.3 (d), 21.5 (d), 26.0 (d), 28.5 (d), 29.0 (d), 50.9 (d), 75.1 (d), 126.6 (d), 127.0 (d), 127.8 (d), 128.5 (d), 128.8 (d), 131.2 (d), 132.2 (d), 140.5 (u), 143.4 (u), 145.7 ppm (d); IR (neat): $\tilde{\nu} = 2956$ (w), 2860 (w), 2801 (s), 1467 (s), 1366 (s), 1250 (s), 1143 (w), 1091 (w), 921 (m), 866 (w), 837 cm^{-1}(w); MS (EI, 70 eV): *m/z* (%): 471 (3) [M^+], 456 (1), 428 (4), 414 (26), 365 (10), 250 (7), 221 (100), 115 (4), 75 (9); HRMS (EI, 70 eV): calcd for $C_{27}H_{41}NO_2SSi$: 471.2627 [M^+]; found: 471.2626.

[D]-(*E*)-1c: $[\alpha]_D = +62.4$ ($c = 4.5$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.30$ (s, 3H), −0.0 (s, 3H), 0.85 (s, 9H), 0.94 (d, $J = 6.9$ Hz, 3H), 1.05 (d, $J = 6.7$ Hz, 3H), 1.85 (sex, $J = 13.2$ Hz, 1H), 2.02–2.09 (m, 1H), 2.77 (s, 3H, NMe), 4.88 (d, $J = 4.0$ Hz, 1H), 6.86 (d, $J = 10.4$ Hz, 1H), 6.95–6.99 (m, 2H), 7.02–7.15 (m, 3H, Ph), 7.54–7.67 (m, 3H, Ph), 7.85–7.89 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -4.8$ (d), −4.1 (d), 18.3 (u), 20.3 (d), 21.5 (d), 26.0 (d), 28.5 (d), 29.0 (d), 50.9 (d), 75.1 (d), 126.6 (d), 127.0 (d), 127.8 (d), 128.5 (d), 128.8 (d), 131.2 (d), 132.2 (d), 140.5 (u), 143.4 (u), 145.7 ppm (d); IR (neat): $\tilde{\nu} = 3021$ (m), 2956 (w), 2860 (s), 2802 (m), 1466 (s), 1388 (s), 1250 (w), 1153 (w), 1086 (w), 984 (m), 855 (w), 754 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%): 459 (2) [$M^+ + 1$], 458 (5), 415 (11), 401 (31), 222 (19), 221 (100), 115 (5), 73 (47); HRMS (EI, 70 eV): *m/z*: calcd for $C_{26}H_{38}DNO_2SSi$: 458.2533 [M^+]; found: 458.2534.

b) A suspension of CuI (830 mg, 4.3 mmol) in Et_2O (20 mL) at −40 °C was treated with MeLi (3.7 mL, 8.4 mmol). After the yellow mixture was stirred for 1 h, the alkenyl sulfoximine (*E*)-**1c** (200 mg, 0.43 mmol) in Et_2O (2 mL) was added. The mixture was stirred for 1 h at −40 °C and allowed to warm to room temperature and stirred for 20 h. Then the mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (hexane/EtOAc 98:2) gave (*Z*)-**9c** (100 mg, 72%) and **16c** (8 mg, 6%) as colorless liquids in a ratio of 9:1.

***tert*-Butyl (1*R*,2*R*,*Z*)-2-isopropyl-1-phenylpent-3-enyloxy)dimethylsilane [(*Z*)-9c]**: $[\alpha]_D = +25.6$ ($c = 3.3$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.29$ (s, 3H), 0.0 (s, 3H), 0.80 (d, $J = 6.9$ Hz, 3H), 0.85 (s, 9H), 0.93 (d, $J = 6.7$ Hz, 3H), 1.20 (dd, $J = 6.7$, 1.7 Hz, 3H), 1.58 (sex, $J = 13.4$ Hz, 1H), 2.25 (sep, $J = 10.6$ Hz, 1H), 4.73 (d, $J = 5.0$ Hz, 1H), 5.35 (m, 1H), 5.52 (dq, $J = 10.7$, 6.7 Hz, 1H), 7.16–7.25 ppm (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -5.0$ (d), −4.3 (d), 12.87 (d), 18.1 (u), 19.2 (d), 21.7 (d), 25.8 (d), 28.4 (d), 52.3 (d), 76.0 (d), 125.9 (d), 126.5 (d), 126.7 (d), 127.4 (d), 128.9 (d), 144.1 ppm (u); IR (neat): $\tilde{\nu} = 3063$ (s), 3016 (w), 2956 (w), 2859 (w), 1467 (s), 1253 (w), 1125 (s), 1089 (w), 977 (s), 836 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%): 262 (4) [M^+], 261 (21), 222 (19), 221 (100), 115 (4), 73 (37); HRMS (EI, 70 eV): *m/z*: calcd for $C_{16}H_{25}OSi$: 261.1674 [$M^+-C_4H_9$]; found: 261.1674.

Reaction of (*E*)-2b with $LiCuMe_2$: A suspension of CuI (463 mg, 2.4 mmol) in Et_2O (10 mL) at −40 °C was treated with MeLi (2.09 mL of 5% solution in Et_2O, 4.7 mmol). After the yellow mixture was stirred for 1 h, the α-lithioalkenyl sulfoximine (*E*)-**2b** (prepared from 100 mg, 0.24 mmol, of sulfoximine (*E*)-**1b** and MeLi, 0.12 mL, 0.24 mmol) in Et_2O (2 mL) was added. The mixture was stirred for 1 h at −40 °C and allowed to warm to room temperature and stirred for 12 h. Then the mix-

ture was quenched with aqueous NH_4Cl and extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by chromatography (hexane) gave a mixture (40 mg) of (*Z*)-**9b** and **16b** in a ratio of 7:3 as a colorless liquid. HPLC (pentane) gave (*E*)-**9b** (27 mg, 41%) and **16b** (12 mg, 18%) as colorless liquids.

Triethyl [(5*S*,6*R*,*Z*)-6-methylnona-1,7-dien-5-yloxy]silane [(*Z*)-9b]: $[\alpha]_D = -27.0$ ($c = 0.5$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.60$–0.67 (m, 6H), 0.97 (d, $J = 6.9$ Hz, 3H), 0.99 (t, $J = 7.7$ Hz, 9H), 1.45–1.54 (m, 2H), 1.64 (dd, $J = 6.7$, 1.5 Hz, 3H), 1.96–2.08 (m, 1H), 2.08–2.22 (m, 1H), 2.57–2.69 (m, 1H), 3.59 (m, 1H), 4.92–5.06 (m, 2H), 5.28–5.38 (m, 1H), 5.42–5.54 (m, 1H), 5.76–5.90 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 5.2$, (u), 7.0 (d), 13.1 (d), 16.0 (d), 30.2 (u), 33.1 (u), 36.6 (d), 75.3 (d), 114.2 (u), 123.7 (d), 132.9 (d), 138.9 ppm (d); IR (neat): $\tilde{\nu} =$ 3078 (w), 3013 (m), 2955 (s), 2878 (s), 1641 (m), 1456 (m), 1238 (m), 1067 (s), 1009 (s), 909 (m), 850 cm^{-1} (m); MS (CI, isobutane): *m*/*z* (%):269 [M^+] (15), 253 (3), 239 (14), 199 (43), 179 (3), 165 (6), 151 (23), 137 (100); HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{14}H_{27}OSi$: 239.1831 [$M^+ - C_2H_5$]; found: 239.1832.

[(5*S*,6*R*)-6,8-Dimethylnona-1,7-dien-5-yloxy]triethylsilane (16b): GC: $t_R = 9.58$ min; $[\alpha]_D = +5.2$ ($c = 0.6$ in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.52$–0.57 (m, 6H), 0.85 (d, $J = 6.9$ Hz, 3H), 0.89 (m, 9H), 1.35–1.42 (m, 2H), 1.54 (d, $J = 1.5$ Hz, 3H), 1.62 (d, $J = 1.2$ Hz, 3H), 1.86–1.99 (m, 1H), 1.99–2.14 (m, 1H), 2.34–2.46 (m, 1H), 3.46 (dq, $J =$ 9.9, 3.71, 1H), 4.84–4.94 (m, 2H), 4.96 (m, 1H), 5.68–5.82 ppm (m, 1H); IR (neat): $\tilde{\nu} =$ 2927 (w), 2875 (s), 1637 (s), 1458 (m), 1216 (s), 1156 (m), 1011 (m), 912 (m), 759 cm^{-1} (w); GC-MS (EI, 70 eV): *m*/*z* (%): 253 [$M^+ - 29$] (6), 200 (17), 199 (100), 143 (12), 115 (95), 103 (28), 87 (44), 67 (28); HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{16}H_{32}OSi$: 239.183119 [$M^+ - C_2H_5$]; found: 239.183266.

Reaction of (*E*)-2c with LiCuMe$_2$: A suspension of CuI (826 mg, 4.3 mmol) in Et_2O (20 mL) at −40 °C was treated with MeLi (3.7 mL, 8.4 mmol). After the yellow mixture was stirred for 1 h, the α-lithioalkenyl sulfoximine (*E*)-**2c** (prepared from 215 mg, 0.47 mmol, of (*E*)-**1c** and MeLi, 0.22 mL, 0.47 mmol) in Et_2O (2 mL) was transferred through a canula. The mixture was stirred for 1 h at −40 °C and allowed to warm to room temperature and stirred for 20 h. Then the mixture was quenched with D_2O and extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. ^{1}H NMR spectroscopy showed the formation of [D]-(*Z*)-**9c** and **16c** in a ratio of 7:3. Purification by chromatography (hexane/EtOAc 98:2) gave [D]-(*Z*)-**9c** (72 mg, 52%) and **16c** (33 mg, 23%).

***tert*-Butyl (1*R*,2*R*,*Z*)-2-isopropyl-1-phenylpent-3-enyloxy)dimethylsilane ([D]-(*Z*)-9c)**: $[\alpha]_D = +24.6$ ($c = 0.7$ in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.26$ (s, 3H), 0.02 (s, 3H), 0.82 (d, $J = 6.9$ Hz, 3H), 0.87 (s, 9H), 0.94 (d, $J = 6.9$ Hz, 3H), 1.21 (d, $J = 1.7$ Hz, 3H), 1.61 (sex, $J =$ 13.5 Hz, 1H), 2.24–2.31 (m, 1H), 4.76 (d, $J = 5.0$ Hz, 1H), 5.37 (m, 1H), 7.24–7.27 ppm (m, 5H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -5.0$ (d), −4.3 (d), 12.8 (d), 18.1 (u), 19.4 (d), 21.8 (d), 25.9 (d), 28.5 (d), 52.3 (d), 76.0 (d), 126.5 (d), 126.6 (d), 127.4 (d), 128.8 (d), 144.1 ppm (u); IR (neat): $\tilde{\nu} =$ 3063 (m), 2956 (w), 2888 (w), 1464 (w), 1253 (w), 1126 (s), 1089 (w), 976 (s), 835 cm^{-1} (w); MS (EI, 70 eV): *m*/*z* (%): 263 (3), 262 (15), 222 (19), 221 (100), 165 (6), 115 (4), 73 (43); HRMS (EI, 70 eV): *m*/*z*: calcd for $C_{20}H_{33}DOSi$: 262.1737 [$M^+ - C_4H_9$]; found: 262.1740.

Acknowledgement

Financial support of this work by the Deutsche Forschungsgemeinschaft (SFB 380 and GK 440) is gratefully acknowledged. We thank Dr. Jan Runsink for NMR spectroscopic investigations.

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Received: March 12, 2008
Published online: June 9, 2008

