Reaction of (α,β-Epoxyalkyl)silanes with α-Sulfonyl Anions and α-Sulfonyl Anions in the Presence of a Lewis Acid. A Method for the Synthesis of (*Z*)-*sec*-Allylic Alcohols and β,γ-Unsaturated Alkyl Phenyl Sulfones

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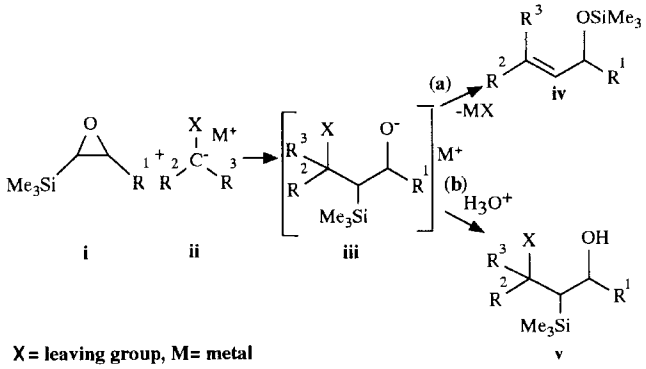
The reaction of 2-alkyl-3-(trimethylsilyl)oxiranes (**1a** or **1b**) with anions generated from alkyl phenyl sulfones (**2a–f**) followed by hydrolysis affords *sec*-allyl alcohols **3–7**. An analogous reaction in the presence of $BF_3 \cdot Et_2O$ affords adducts **8–11**. Treatment of **8–11** with NaOH under phase-transfer conditions affords stereospecifically the corresponding allylic alcohols **4a–5c**. Reaction of oxirane **1a** with anions derived from sterically hindered sulfones **2e** or **2f** in the presence of $BF_3 \cdot Et_2O$ was investigated. Reaction of compounds **8**, **9** with phosphorus tribromide in pyridine affords β,γ-unsaturated sulfones **19**.

We have recently developed a method[1] of allyl alcohol synthesis which involves the reaction of a (trimethylsilyl)-oxirane (Scheme 1, **i**) with some carbanions bearing in the α-position a leaving group (**ii**, X = leaving group). The reaction is initiated by the attack of the anion **ii** at the oxirane **i** in the α-position to the silicon atom to form the intermediate **iii**. The fate of the latter depends on the nature of the cation (M^+): in the species with Li^+ there occurs a spontaneous migration of the silyl group from C to O with elimination of the leaving group to afford *O*-(trimethylsilyl)allyl alcohol (**iv**, path a). On the other hand, an intermediate with the cation strongly bound to the oxygen atom is stable and provides adduct **v** after protonation (path b)[2]. Some aspects of the synthesis of prim allylic alcohols by this method with the use of lithioalkyl phenyl sulfones (**ii**, X = $PhSO_2$, M = Li) and α,α-dilithioalkyl phenyl sulfones (**ii**, X = $PhSO_2$, R^3 = M = Li) have been described[3]. Its practical application to the synthesis of optically active allylic alcohols has been reported by this[4] and other[5] laboratories. Now we present an account of our studies of the direct (by the path a) synthesis of *sec*-allylic alcohols (corresponding to **iv**) as well as of the preparation of adducts **v** (X = SO_2Ph) and their transformation into allylic alcohols and β,γ-unsaturated sulfones.

Scheme 1



Results and Discussion

Synthesis of *sec*-Allylic Alcohols by the Reaction of (α,β-Epoxyalkyl)silanes with α-Sulfonyl Anions

cis- or *trans*-2-Hexyl-3-(trimethylsilyl)oxirane (Scheme 2, **1a** and **1b**, respectively) was allowed to react with the anions generated from alkyl phenyl sulfones **2a–f** and butyllithium in THF/hexane. The respective allylic *O*-(trimethylsilyl) alcohol was obtained, and the crude product was treated with TosOH in acetone to give the free alcohols **3–7**. The latter were briefly chromatographed on a silica gel column to remove the unreacted sulfone and other minor contaminations (*E* and *Z* isomers of the product were not separated). The results are presented in Table 1. As can be seen the sterically unhindered sulfones (**2a**, **2b**, **2c**) were converted into the respective allylic alcohols in good yields. The isomer with *Z* configuration of the double bond prevails[6] in all cases when geometric isomers can be formed with the exception of the reaction of epoxide **1a** with isobutyl phenyl sulfone (**2d**) (entry 8). The isomer *E*:*Z* ratio was lowest when the reaction was carried out at −20°C (method A, reaction time 24 h). At this temperature the product yield was, however, poor. When the reaction was carried out at room temperature (method C) the product yield was high but the selectivity markedly decreased. An acceptable compromise between reaction selectivity and product yield was achieved by starting the reaction at −20°C and then continuing it at room temperature (method B). Sulfones with β-branched (**2d**) and *sec*-alkyl groups (**2e** and **2f**) were chosen to examine the steric hindrance

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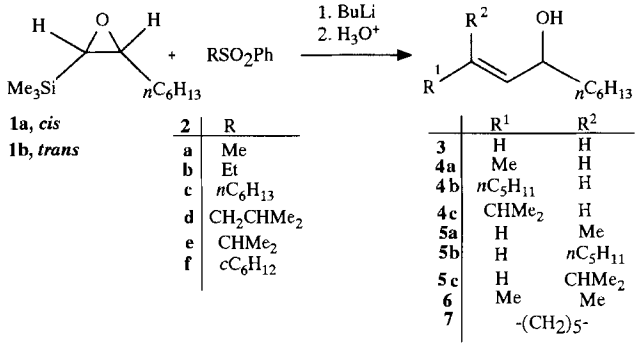
effect on the reaction course. The yields of the products and the reaction stereoselectivity were low (entries 8, 9 and 10). *trans*-Substituted oxirane **1b** gave in the reaction with anions generated from primary alkyl sulfones **2b** and **2c** a lower yield of the product than its *cis* isomer with the same stereochemical outcome (entries 11 and 12).

Scheme 2



1a, *cis*
1b, *trans*

2	R
a	Me
b	Et
c	nC_6H_{13}
d	CH_2CHMe_2
e	$CHMe_2$
f	cC_6H_{12}

	R^1	R^2
3	H	H
4a	Me	H
4b	nC_5H_{11}	H
4c	$CHMe_2$	H
5a	H	Me
5b	H	nC_5H_{11}
5c	H	$CHMe_2$
6	Me	Me
7	-$(CH_2)_5$-	

Table 1. Reaction of (trimethylsilyl)oxiranes **1a** and **1b** with sulfones according to Scheme 2

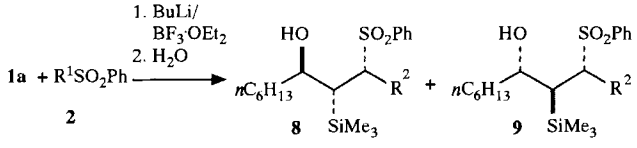
No	Oxirane	Sulfone	Method	Product	Yield (%)	*E*:*Z* ratio
1	**1a**	**2a**	C	**3**	70	–
2	**1a**	**2b**	A	**4a, 5a**	55	1:11
3	**1a**	**2b**	B	**4a, 5a**	75	1:9
4	**1a**	**2b**	C	**4a, 5a**	80	1:4
5	**1a**	**2c**	A	**4b, 5b**	53	1:16
6	**1a**	**2c**	B	**4b, 5b**	78	1:11
7	**1a**	**2c**	C	**4b, 5b**	80	1:6
8	**1a**	**2d**	B	**4c, 5c**	14	4:1
9	**1a**	**2e**	C	**6**	47	–
10	**1a**	**2f**	C	**8**	3	–
11	**1b**	**2b**	B	**4a, 5a**	27	1:9
12	**1b**	**2c**	B	**4b, 5b**	22	1:11

The results presented in Table 1 indicate furthermore that the method may be conveniently applied to the stereocontrolled synthesis of unbranched alkenes. Lithium derivatives of sulfones with branched bulky alkyl groups react reluctantly with α,β-epoxysilanes. Some time ago we have encountered a similar difficulty in effecting the reaction of sterically hindered sulfones, when we dealt with "all-carbon" oxiranes. We have succeeded in promoting the reaction by using α-sulfonyl anions in combination with a Lewis acid, preferentially with $BF_3 \cdot OEt_2$[7]. Considering the Lewis acid-catalyzed reaction of α,β-epoxysilanes with α-sulfonyl anions, we reasoned that the initial adduct (Scheme 1, **iii**, X = SO_2Ph, M = BF_3Li), if formed, would be stable since the oxido group would be complexed by the Lewis acid and lithium ion. The protonated adduct (**v**, X = SO_2Ph) could be, however, easily transformed into the corresponding allyl alcohol by elimination of the silyl and sulfur substituents[8]. Moreover, adduct **v**, if available, would be useful as an intermediate in the synthesis of β,γ-unsaturated sulfones. These considerations prompted us to examine the reaction of α-sulfonyl anions with α,β-epoxysilanes in the presence of $BF_3 \cdot Et_2O$. It should be noted that BF_3-assisted reactions of α,β-epoxysilanes with alkenyl cuprates have been reported[9].

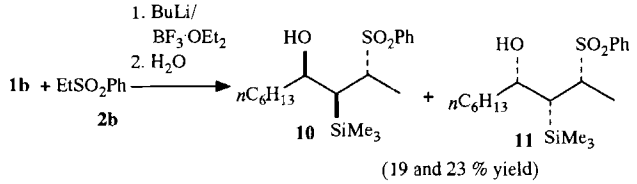
Synthesis of Allylic Alcohols and β,γ-Unsaturated Sulfones by BF_3-Assisted Reaction of α,β-(Epoxyalkyl)silanes with α-Sulfonyl Anions

Lithio sulfone, generated from sulfones **2b–d** (1-mol equiv.) and butyllithium (1-mol equiv.) in THF/hexane, was treated at −20°C with α,β-epoxysilane **1a** or **1b** (0.7-mol equiv.) and then with $BF_3 \cdot Et_2O$ (0.7-mol equiv.) (Scheme 3). The expected adduct was obtained. The results are presented in the scheme. Sterically unhindered sulfones **2b** and **2c** were converted into the corresponding adducts as mixtures of epimers that were easy to separate by CC. The epimers differ in configuration on the carbon bearing the phenylsulfonyl group. The epimers with the relative *l* and *u* configuration on this and the vicinal center ($CHSiMe_3$) are formed in comparable amounts. A high yield of the reaction involving β-branched sulfone **2d** (74% vs. 14% in the uncatalyzed reaction) is noteworthy.

Scheme 3



Sulfone		Product (Yield %)		
R^1	No	R^2	No	
Et	**2b**	Me	**8a** (43)	**9a** (31)
nC_6H_{13}	**2c**	nC_5H_{11}	**8b** (35)	**9b** (35)
CH_2CHMe_2	**2d**	$CHMe_2$	**8c**, **9c** (2:3 ratio) (74)	

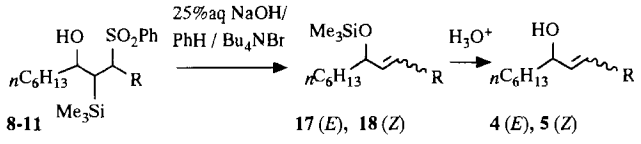


(19 and 23 % yield)

The reaction of lithiated sulfone **2b** with *trans*-oxirane **1b** in the presence of $BF_3 \cdot OEt_2$ (Scheme 3) afforded the corresponding adducts **10** and **11** in 19 and 23% yields, respectively. We expected that adducts **8a**, **9a** and congeners upon treatment with butyllithium would provide stereospecifically the respective (*E*)- or (*Z*)-*O*-(trimethylsilyl)allyl alcohols in a process analogous to that depicted in Scheme 1, path a. In practice, however, diastereomerically pure adducts were converted into mixtures of the corresponding (*E*)- and (*Z*)-allylic alcohols (as *O*-trimethylsilyl derivatives). For example, the reaction of adduct **9a** with butyllithium at room temperature, followed by hydrolysis of the *O*-trimethylsilyl group, afforded a mixture of (*E*)- and (*Z*)-allylic alcohols **4a** and **5a** in a 1:2 ratio (72% yield). These results imply that the migration of the trimethylsilyl group from C to O and abstraction of the proton from the α-position to the phenylsulfonyl group occur at comparable

rates when butyllithium is used as a base. Under phase-transfer conditions, however, in the system of 25% aq NaOH/benzene/tetrabutylammonium bromide the adducts were converted into corresponding *O*-(trimethylsilyl)allylic alcohols virtually stereospecifically and in excellent yields (Scheme 4). An inseparable mixture of compounds **8c** and **9c** was transformed into a mixture of (*E*)- and (*Z*)-*O*-trimethylsilyl alcohols **17c** and **18c** (88% yield, in a 3:2 ratio as determined by ^{1}H NMR). The *O*-trimethylsilyl derivatives of allylic alcohols, obtained in this reaction, were hydrolyzed to the free alcohols whose yields are given in Scheme 4. It should be noted that a mixture of alcohols **4c** and **5c** was separated by chromatography to give the pure isomers (53% yield of *E* and 36% yield of *Z* isomer).

Scheme 4



R	Starting material		Trimethylsilyl ether			Alcohol		
	Conf.[a]	No	conf.	No	Yield,(%)	Conf.	No	Yield,(%)
Me	*l*	**8a**	(*Z*)	**18a**	90	(*Z*)	**5a**	83
Me	*u*	**9a**	(*E*)	**17a**	85	(*E*)	**4a**	85
nC_5H_{11}	*l*	**8b**	(*Z*)	**18b**	92	(*Z*)	**5b**	92
nC_5H_{11}	*u*	**9b**	(*E*)	**17b**	90	(*E*)	**4b**	93
$CHMe_2$	*l*	**8c**	(*Z*)	**18c**	88	(*Z*)	**5c**	36 [b]
$CHMe_2$	*u*	**9c**	(*E*)	**17c**		(*E*)	**4c**	53 [b]
Me	*u*	**10**	(*E*)	**17a**	93			
Me	*l*	**11**	(*Z*)	**18a**	85			

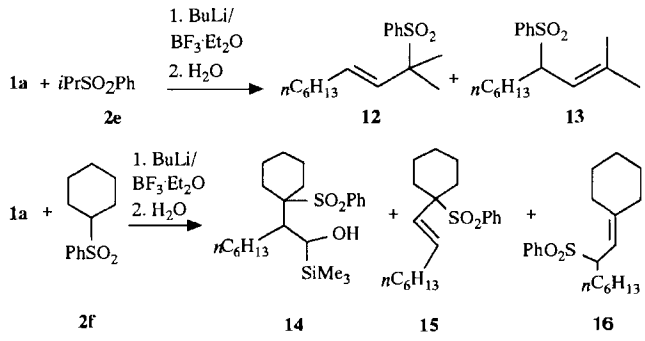
[a] Relative configuration in the $C(SiMe)_3$-$C(SO_2Ph)$ system.
[b] Separated by CC.

It should also be noted that stereochemical assignments of adducts **8**–**11** were made on the basis of their respective products of $PhSO_2^-$ and Me_3Si^+ group elimination under basic conditions on the assumption that epimers with the relative *l* configuration provide (*Z*)-*O*-(trimethylsilyl)allyl alcohols and epimers with *u* configuration lead to *E* isomers[8].

In view of the favorable effect of $BF_3 \cdot OEt_2$ on the reaction of epoxysilanes with sterically hindered α-sulfonyl anions, it was of interest to evaluate the limit of applicability of this catalyst. To this end, the reactions of isopropyl phenyl sulfone (**2e**) and cyclohexyl phenyl sulfone (**2f**) with oxirane **1a** were examined. Oxirane **1a** was treated with the lithium derivative of sulfone **2e** and $BF_3 \cdot EtO_2$, and the crude reaction product was chromatographed on a silica gel column. An inseparable mixture of **12** and **13** (40% yield, ratio of 2:7 as determined by ^{1}H NMR) was obtained (Scheme 5). Apparently, the product of initial α-attack undergoes a Peterson elimination to give compound **12**. Formation of compound **13** reflects the 1,3 shift of the phenylsulfonyl group in **12**[11].

An analogous reaction of cyclohexyl phenyl sulfone (**2f**) with oxirane **1a** followed by chromatography afforded "β-adduct" **14** in 28% yield and an inseparable mixture of unsaturated sulfones **15** and **16** in 13% yield (ratio of 1:2 determined by ^{1}H NMR) (Scheme 5). This result suggests that

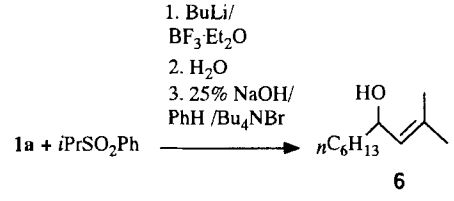
Scheme 5



a very sterically hindered nucleophile tends to attack an (α,β-epoxyalkyl)silane unselectively at the α- and β-position[10].

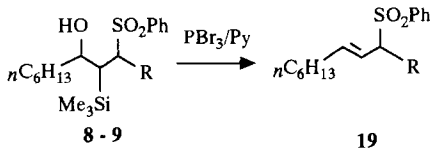
Interestingly, when the crude product of the reaction of sulfone **2e** with oxirane **1a** (without chromatography) was treated with a base under two-phase conditions alcohol **6** (Scheme 6) was obtained in 50% yield, and no unsaturated sulfones were detected. This experiment indicates that the Peterson elimination and allylic rearrangement of the sulfone occur in the course of chromatography of the crude reaction products.

Scheme 6



Having in hand the adducts of general structure **v** (Scheme 1), we directed our attention to the preparation of allylic sulfones which are useful but not readily available intermediates in synthesis[12]. Our initial experiments were aimed at the hydroxyl group esterification with *p*-TosCl. We expected a facile fragmentation of the sulfonates with formation of the respective unsaturated sulfones and TosOSiMe$_3$. The reaction of adducts with *p*-TosCl proved, however, to be sluggish. Moreover, a complex mixture of products was formed, partly owing to silylation of alcohols by TosOSiMe$_3$ which was in fact generated in the reaction. Ul-

Scheme 7



R	Adduct No.	Product No.	Yield, (%)
Me	**8a**	**19a**	83
Me	**9a**	**19a**	85
nC_5H_{11}	**8b**	**19b**	89
nC_5H_{11}	**9b**	**19b**	85
$CHMe_2$	**8c** , **9c**	**19c**	90

timately, we found that treatment of the adduct with PBr_3 in pyridine at room temperature affords the required β,γ-unsaturated sulfones in very good yields. The results are presented in Scheme 7.

It should be noted that products with *E* configuration of the double bond were always obtained, and therefore a mixture of diastereomeric adducts may be used to generate isomerically pure unsaturated sulfones.

Experimental

^1H and ^{13}C NMR: Bruker AM 500 (500 and 125 MHz) or Varian GEM 200 (200 and 50 MHz), as indicated (for $CDCl_3$ solutions with $SiMe_4$ as an internal standard). – MS: AMD 604 (70 eV ionization potential). – All reactions involving organometallic reagents were carried out under Ar. Ratios of diastereomeric mixtures were derived from suitable ^1H-NMR integrals. Organic solutions were dried with Na_2SO_4. – Column chromatography (CC): silica gel, Merck, 60, 230–400 mesh (SiO_2).

Reactions of Epoxysilanes **1a** *and* **1b** *with Phenyl Alkyl Sulfonyl Anions in the Presence of* $BF_3 \cdot Et_2O$ *According to Schemes 3 and 5. – General Procedure:* To a solution of phenyl alkyl sulfone **2b–f** (3.75 mmol) in dry THF (20 ml) stirred at −20°C BuLi in hexane (1.6 M, 2.3 ml, 3.75 mmol) was added dropwise. The mixture was stirred for 10 min whereupon epoxysilane **1a** or **1b** (500 mg, 2.5 mmol) and $BF_3 \cdot Et_2O$ (550 mg, 3.75 mmol) were consecutively added. Stirring was continued for 3 h, and then the mixture was diluted with water (50 ml) and extracted with CH_2Cl_2 (2 × 30 ml). The combined organic extracts were dried, the solvent was removed and the residue chromatographed on SiO_2.

(2R,3R*,4R*)-2-(Phenylsulfonyl)-3-(trimethylsilyl)decan-4-ol* (**8a**) (395 mg, 43%) and *(2R*,3S*,4S*)-2-(phenylsulfonyl)-3-(trimethylsilyl)decan-4-ol* (**9a**) (285 mg, 31%) were obtained from **1a** and sulfone **2b** (635 mg) (elution with hexane/AcOEt, 95:5). – **8a**: ^1H NMR (500 MHz): δ = 0.18 [s, 9H, $Si(CH_3)_3$], 0.87 (t, *J* = 6.9 Hz, 3H, 10-H), 1.20–1.39 (m, 10H, aliphatic H), 1.39 (d, *J* = 7.2 Hz, 3H, 1-H), 1.59 (dd, *J* = 4.2, 1.7 Hz, 1H, 3-H), 3.54 (qd, *J* = 7.2, 1.7 Hz, 1H, 2-H), 4.02 (m, 1H, 4-H), 7.53 (m, 2H, *m*-ArH), 7.62 (tt, *J* = 7.4, 1.3 Hz, 1H, *p*-ArH), 7.87 (m, 2H, *o*-ArH). – ^{13}C NMR (125 MHz): δ = 0.22, 13.99, 16.38, 22.50, 25.98, 29.11, 31.72, 32.61, 37.34, 59.34, 71.79, 128.64, 129.01, 133.34, 138.60. – MS, *m/z* (%): 256 (10), 215 (80), 199 (34), 166 (87), 143 (35), 135 (82), 125 (42), 115 (57), 97 (55), 83 (100), 73 (75) $[Si(CH_3)_3]$. – $C_{19}H_{34}O_3SSi$ (370.6): calcd. C 61.57, H 9.25; found C 61.43, H 9.14. – **9a**: ^1H NMR (500 MHz): δ = 0.09 [s, 9H, $Si(CH_3)_3$], 0.89 (t, *J* = 6.9 Hz, 3H, 10-H), 1.24–1.36 (m, 6H, aliphatic H), 1.39 (d, *J* = 7.3 Hz, 3H, 1-H), 1.46–1.60 (m, 4H, aliphatic H), 1.83 (dd, *J* = 8.4, 1.1 Hz, 1H, 3-H), 3.42 (qd, *J* = 7.3, 1.1 Hz, 1H, 2-H), 3.85 (m, 1H, 4-H), 7.58 (m, 2H, *m*-ArH), 7.66 (tt, *J* = 7.4, 1.3 Hz, 1H, *p*-ArH), 7.90 (m, 2H, *o*-ArH). – ^{13}C NMR (125 MHz): δ = −0.39, 12.11, 14.06, 22.60, 26.02, 29.25, 31.89, 33.78, 38.27, 61.56, 69.14, 128.72, 129.21, 133.63, 138.18. – MS, *m/z* (%): 256 (10), 215 (80), 199 (35), 166 (90), 143 (35), 135 (80), 125 (41), 113 (67), 97 (56), 83 (100), 73 (75) $[Si(CH_3)_3]$. – $C_{19}H_{34}O_3SSi$ (370.6): calcd. C 61.57, H 9.25; found C 61.84, H 9.07.

(7R,8R*,9R*)-9-(Phenylsulfonyl)-8-(trimethylsilyl)tetradecan-7-ol* (**8b**) (370 mg, 35%) and *(7S*,8S*,9R*)-9-(phenylsulfonyl)-8-(trimethylsilyl)tetradecan-7-ol* (**9b**) (371 mg, 35%) were obtained from **1a** and sulfone **2c** (850 mg) (elution with hexane/AcOEt, 97:3). – **8b**: ^1H NMR (500 MHz): 0.21 [s, 9H, $Si(CH_3)_3$], 0.74 (t, *J* = 7.0 Hz, 3H, CH_3), 0.89 (t, *J* = 6.9 Hz, 3H, CH_3), 0.91–1.21 (m, 6H, aliphatic H), 1.21–1.35 (m, 9H, aliphatic H), 1.48–1.70 (m, 3H, aliphatic H), 2.12 (m, 1H, aliphatic H), 3.31 (dd, *J* = 7.4, 4.4 Hz, 1H, 9-H), 4.24 (m, 1H, 7-H), 7.56 (m, 2H, *m*-ArH), 7.64 (tt, *J* = 7.4, 1.3 Hz, 1H, *p*-ArH), 7.89 (m, 2H, *o*-ArH). – ^{13}C NMR (125 MHz): δ = 0.07, 13.81, 14.04, 22.09, 22.60, 25.95, 27.48, 29.26, 30.74, 30.92, 31.89, 34.54, 37.61, 65.56, 71.44, 128.56, 129.16, 133.52, 139.22. – MS, *m/z* (%): 256 (55), 215 (100), 199 (57), 166 (85), 143 (15), 135 (83), 125 (33), 115 (90), 97 (70), 83 (30), 73 (80) $[Si(CH_3)_3]$. – $C_{23}H_{42}O_3SSi$ (426.7): calcd. C 64.73, H 9.92; found C 64.87, H 10.10. – **9b**: ^1H NMR (500 MHz): 0.12 [s, 9H, $Si(CH_3)_3$], 0.78 (t, *J* = 7.0 Hz, 3H, CH_3), 0.89 (t, *J* = 6.8 Hz, 3H, CH_3), 1.05–1.65 (m, 18H, aliphatic H), 1.72–1.82 (m, 1H, aliphatic H), 3.39 (t, *J* = 5.7 Hz, 1H, 9-H), 3.85 (m, 1H, 7-H), 7.57 (m, 2H, *m*-ArH), 7.65 (tt, *J* = 7.4, 1.2 Hz, 1H, *p*-ArH), 7.89 (m, 2H, *o*-ArH). – ^{13}C NMR (125 MHz): δ = −0.08, 13.80, 14.06, 22.12, 22.60, 26.09, 27.72, 28.32, 29.27, 31.48, 31.88, 34.29, 38.66, 66.38, 69.61, 128.61, 129.19, 133.58, 139.07. – MS, *m/z* (%): 256 (10), 215 (100), 199 (27), 166 (50), 135 (46), 125 (20), 115 (20), 97 (43), 83 (46), 73 (43) $[Si(CH_3)_3]$. – $C_{23}H_{42}O_3SSi$ (426.7): calcd. C 64.73, H 9.92; found C 64.89, H 10.22.

(3R,4R*,5R*)-2-Methyl-3-(phenylsulfonyl)-4-(trimethylsilyl)-undecan-5-ol* (**8c**) and *(3R*,4S*,5S*)-2-methyl-3-(phenylsulfonyl)-4-(trimethylsilyl)undecan-5-ol* (**9c**) (736 mg, 74%) were obtained from epoxide **1a** and sulfone **2d** (745 mg) as an inseparable mixture of a ratio of 2:3 (elution with hexane/AcOEt, 95:5). – ^1H NMR (500 MHz) (diagnostic signals): δ = 0.19 [s, 2/5 × 9H, $Si(CH_3)_3$], 0.21 [s, 3/5 × 9H, $Si(CH_3)_3$], 3.57 (m, 1H, 3-H), 4.03 (m, 3/5 × 1H, 5-H), 4.32 (m, 2/5 × 1H, 5-H), 7.56 (m, 2H, *m*-ArH), 7.62 (m, 1H, *p*-ArH), 7.89 (m, 2/5 × 2H, *o*-ArH), 7.93 (m, 3/5 × 2H, *o*-ArH). – MS, *m/z* (%): 256 (13), 215 (53), 199 (35), 166 (87), 135 (100), 125 (32), 115 (50), 97 (55), 73 (67) $[Si(CH_3)_3]$. – $C_{21}H_{38}O_3SSi$ (398.7): calcd. C 63.26, H 9.61; found C 63.07, H 9.60.

(2R,3S*,4R*)-2-(Phenylsulfonyl)-3-(trimethylsilyl)decan-4-ol* (**10**) (177 mg, 19%) and *(2R*,3R*,4S*)-2-(phenylsulfonyl)-3-(trimethylsilyl)decan-4-ol* (**11**) (212 mg, 23%) were obtained from epoxide **1b** and sulfone **2b** (635 mg) (elution with hexane AcOEt, 95:5). – **10**: ^1H NMR (500 MHz): 0.19 [s, 9H, $Si(CH_3)_3$], 0.88 (t, *J* = 7.1 Hz, 3H, 10-H), 1.22–1.32 (m, 7H, aliphatic H), 1.32 (d, *J* = 7.3 Hz, 3H, 1-H), 1.36–1.58 (m, 3H, aliphatic H), 1.95 (t, *J* = 3.4 Hz, 1H, 3-H), 3.62 (qd, *J* = 7.3, 3.2 Hz, 1H, 2-H), 4.11 (dt, *J* = 9.0, 3.4 Hz, 1H, 4-H), 7.56 (m, 2H, *m*-ArH), 7.65 (tt, *J* = 7.4, 1.3 Hz, 1H, *p*-ArH), 7.91 (m, 2H, *o*-ArH). – ^{13}C NMR (125 MHz): δ = 0.99, 14.04, 16.19, 22.59, 26.70, 29.24, 31.82, 35.21, 35.60, 58.48, 71.22, 128.85, 129.09, 133.55, 138.05. – MS, *m/z* (%): 256 (13), 215 (35), 199 (44), 166 (46), 143 (38), 135 (60), 125 (20), 115 (26), 97 (62), 83 (100), 73 (70) $[Si(CH_3)_3]$. – $C_{19}H_{34}O_3SSi$ (370.6): calcd. C 61.57, H 9.25; found C 61.30, H 9.30. – **11**: ^1H NMR (500 MHz): δ = 0.05 [s, 9H, $Si(CH_3)_3$], 0.90 (t, *J* = 6.8 Hz, 3H, 10-H), 1.25–1.37 (m, 2H, aliphatic H), 1.48 (d, *J* = 7.1 Hz, 3H, 1-H), 1.50–1.62 (m, 3H, aliphatic H), 3.18 (qd, *J* = 7.1, 1.0 Hz, 1H, 2-H), 4.27 (dd, *J* = 8.6, 5.4 Hz, 1H, 4-H), 7.56 (m, 2H, *m*-ArH), 7.64 (tt, *J* = 7.4, 1.3 Hz, *p*-ArH), 7.85 (m, 2H, *o*-ArH). – ^{13}C NMR (125 MHz): δ = 0.15, 11.26, 14.06, 22.58, 26.50, 29.14, 31.81, 33.28, 39.26, 60.23, 70.88, 128.73, 129.09, 133.40, 138.32. – MS, *m/z* (%): 256 (1), 215 (11), 199 (15), 166 (18), 143 (46), 135 (22), 125 (15), 97 (50), 83 (100), 73 (36) $[Si(CH_3)_3]$. – $C_{19}H_{34}O_3SSi$ (370.6): calcd. C 61.57, H 9.25; found C 61.34, H 9.52.

2-Methyl-2-(phenylsulfonyl)dec-3-ene (**12**) and *2-methyl-4-(phenylsulfonyl)dec-2-ene* (**13**) (295 mg, 40%) were obtained from epoxide **1a** and sulfone **2e** (690 mg) as an inseparable mixture a ratio of 7:2 (elution with hexane/AcOEt, 97:3). – ^1H NMR (200

MHz): δ = 0.84 (t, *J* = 6.7 Hz, 7/9 × 3H, 10-H), 0.86 (t, *J* = 6.7 Hz, 2/9 × 3H, 10-H), 1.16 (d, *J* = 1.4 Hz, 7/9 × 3H, vinylic CH_3), 1.41 (s, 2/9 × 6H, 2 CH_3), 1.65 (d, *J* = 1.3 Hz, 7/9 × 3H, vinylic CH_3), 3.68 (td, *J* = 10.8, 3.2 Hz, 7/9 × 1H, 4-H), 4.91 (dm, *J* = 10.4 Hz, 7/9 × 1H, 3-H), 5.40 (dt, *J* = 15.7, 6.3 Hz, 2/9 × 1H, 4-H), 5.58 (dt, *J* = 15.7, 1.1 Hz, 2/9 × 1H, 3-H), 7.42–7.65 (m, 3H, ArH), 7.80 (m, 2H, ArH). – ^{13}C NMR (50 MHz): δ = 13.95, 14.03, 17.94, 21.20, 22.47, 25.75, 26.50, 27.33, 28.82, 31.49, 31.60, 32.61, 64.96, 117.48, 120.26, 128.19, 128.29, 128.61, 129.09, 130.59, 133.21, 133.33, 135.46, 138.10, 141.86. – MS, *m/z* (%): 153 (49), 125 (4), 111 (10), 97 (59), 69 (100). – $C_{17}H_{26}O_2S$ (294.4): calcd. C 69.34, H 8.90; found C 69.29, H 8.79.

Compound **14** (297 mg, 28%) and an inseparable mixture of **15** and **16** (109 mg, 13%) were obtained in a ratio of 1:2 from the reaction of epoxide **1a** with sulfone **2f** (780 mg) (elution with hexane/AcOEt, 97:3). – **14**: ^{1}H NMR (500 MHz): δ = 0.15 [s, 9H, $Si(CH_3)_3$], 0.81–0.92 (m, 2H, aliphatic H), 0.87 (t, *J* = 6.9 Hz, 3H, CH_3), 1.12–1.65 (m, 15H, aliphatic H), 2.02 (m, 1H, aliphatic H), 2.27 (m, 1H, aliphatic H), 2.44 (m, 1H, aliphatic H), 2.95 (br. d, *J* = 12.2 Hz, 1H, aliphatic H), 3.86 (d, *J* = 10.7 Hz, 1H, 1-H), 7.56 (m, 2H, *m*-ArH), 7.65 (tt, *J* = 7.4, 1.3 Hz, 1H, *p*-ArH), 7.87 (m, 2H, *o*-ArH). – ^{13}C NMR (125 MHz): δ = –1.95, 14.01, 21.77, 22.25, 22.59, 25.04, 28.99, 29.94, 31.04, 31.35, 31.72, 31.77, 42.45, 68.17, 72.27, 128.62, 130.69, 133.46, 137.09. – MS, *m/z* (%): 215 (0.8), 197 (0.9), 193 (1.1), 143 (6), 111 (100), 81 (10), 69 (70). – $C_{23}H_{40}O_3SSi$ (424.7): calcd. C 65.04, H 9.49; found C 65.06, H 9.29. – **15** and **16** (ratio of 1:2): ^{1}H NMR (500 MHz) (diagnostic signals): δ = 0.86 (t, *J* = 6.9 Hz, 2/3 × 3H, CH_3), 0.88 (t, *J* = 6.9 Hz, 1/3 × 3H, CH_3), 3.77 (td, *J* = 10.8, 3.2 Hz, 2/3 × 1H, C*H*SO_2Ph), 4.88 (d, *J* = 10.5 Hz, vinylic H), 5.16 (d, *J* = 16.0 Hz, 1/3 × 1H, vinylic H), 5.44 (dt, *J* = 16.0, 6.9 Hz, 1/3 × 1H, vinylic H), 7.45–7.52 (m, 2H, *m*-ArH), 7.57–7.62 (m, 1H, *p*-ArH), 7.76 (m, 1/3 × 2H, *o*-ArH), 7.83 (m, 2/3 × 2H, *o*-ArH). – ^{13}C NMR (125 MHz): δ = 13.98, 14.01, 21.56, 22.49, 22.54, 25.23, 26.25, 26.46, 26.95, 26.99, 28.03, 28.62, 28.73, 28.83, 29.09, 31.52, 31.57, 32.94, 37.14, 63.80, 68.12, 114.17, 125.25, 128.05, 128.60, 129.17, 130.87, 133.19, 135.41, 138.28, 139.17, 149.05. – MS, *m/z* (%): 193 (93) [M^+ – $PhSO_2$], 151 (3), 137 (10), 123 (16), 109 (100), 95 (41), 81 (35), 67 (50). – $C_{20}H_{30}O_2S$ (334.5): calcd. C 71.81, H 9.04; found C 71.61, H 8.87.

Preparation of O-Trimethylsilyl Allylic Alcohols **17**, **18** *from Adducts* **8**–**11** *According to Scheme 4. – General Procedure:* A mixture of 25% aq NaOH (10 ml), benzene (10 ml), **8a**–**11** (0.50 mmol), and Bu_4NBr (0.1 eq) was vigorously stirred for 1 h (until the starting material was consumed, TLC). The mixture was extracted with Et_2O (2 × 30 ml). The combined organic extracts were washed with water and dried. The solvent was removed and the residue chromatographed on SiO_2 (hexane/Et_2O, 97:3).

Compound **9a** (185 mg) was converted into *(E)-4-(trimethylsilyloxy)dec-2-ene* (**17a**) (97 mg, 85%). – ^{1}H NMR: δ = 0.07 [s, 9H, $Si(CH_3)_3$], 0.86 (t, *J* = 6.9 Hz, 3H, 10-H), 1.15–1.27 (m, 8H, aliphatic H), 1.36–1.49 (m, 2H, aliphatic H), 1.65 (ddd, *J* = 6.4, 1.5, 0.7 Hz, 3H, 1-H), 3.96 (q, *J* = 6.8 Hz, 1H, 4-H), 5.39 (ddq, *J* = 15.3, 6.8, 1.5 Hz, 1H, 3-H), 5.51 (dqd, *J* = 15.3, 6.4, 0.9 Hz, 1H, 2-H). – ^{13}C NMR: δ = 0.35, 14.08, 17.57, 22.63, 25.57, 29.23, 31.87, 38.24, 73.71, 125.03, 134.82. – MS, *m/z* (%): 228 (1) [M^+], 143 (100), 75 (32), 73 (70) [$Si(CH_3)_3$]. – $C_{13}H_{28}OSi$: calcd. 228.1909; found 228.1909 (MS).

Compound **8a** (185 mg) gave *(Z)-4-(trimethylsilyloxy)dec-2-ene* (**18a**) (103 mg, 90%). – ^{1}H NMR: δ = 0.08 [s, 9H, $(Si(CH_3)_3]$, 0.86 (t, *J* = 6.9 Hz, 3H, 10-H), 1.23–1.41 (m, 9H, aliphatic H), 1.45–1.53 (m, 1H, aliphatic H), 1.62 (dd, *J* = 6.7, 1.6 Hz, 3H, 1-H), 4.38 (q, *J* = 8.5 Hz, 1H, 4-H), 5.33 (ddq, *J* = 11.0, 8.5, 1.6 Hz, 1H, 3-H), 5.41 (dqd, *J* = 11.0, 6.9, 1.0 Hz, 1H, 2-H). – ^{13}C NMR: δ = 0.28, 13.26, 14.09, 22.63, 25.35, 29.24, 31.89, 38.20, 68.17, 123.29, 134.81. – MS, *m/z* (%): 228 (1) [M^+], 143 (100), 75 (15), 73 (25) [$Si(CH_3)_3$]. – $C_{13}H_{28}OSi$: calcd. 228.1909; found 228.1911 (MS).

Compound **9b** (213 mg) was converted into *(E)-8-(trimethylsilyloxy)tetradec-6-ene* (**17b**) (128 mg, 90%). – ^{1}H NMR (200 MHz): δ = 0.07 [s, 9H, $Si(CH_3)_3$], 0.85 (t, *J* = 6.5 Hz, 6H, 1-H and 14-H), 1.05–1.60 (m, 16H, aliphatic H), 1.97 (br. q, *J* = 6.7 Hz, 2H, 5-H), 3.96 (q, *J* = 6.4, 1H, 8-H), 5.34 (dd, *J* = 15.4, 6.4 Hz, 1H, 7-H), 5.48 (dt, *J* = 15.4, 6.2 Hz, 1H, 6-H). – ^{13}C NMR: δ = 0.36, 14.01, 14.05, 22.50, 22.62, 25.61, 28.94, 29.23, 31.38, 31.90, 32.09, 38.35, 73.85, 130.56, 133.56. – MS, *m/z* (%): 284 (1) [M^+], 199 (100), 129 (36), 75 (22), 73 (42) [$Si(CH_3)_3$]. – $C_{17}H_{36}OSi$: calcd. 284.2535; found 284.2536 (MS).

Compound **8b** (213 mg) was converted into *(Z)-8-(trimethylsilyloxy)tetradec-6-ene* (**18b**) (131 mg, 92%). – ^{1}H NMR (200 MHz): δ = 0.86 (t, *J* = 6.8 Hz, 3H, CH_3), 0.87 (t, *J* = 6.7, 3H, CH_3), 1.02–1.52 (m, 16H, aliphatic H), 2.01 (m, 2H, 5-H), 4.35 (m, 1H, 8-H), 5.22–5.39 (m, 2H, 6-H and 7-H). – ^{13}C NMR: δ = 0.34, 14.01, 14.08, 22.54, 22.63, 25.43, 27.78, 29.25, 29.36, 31.62, 31.90, 38.41, 68.59, 129.47, 133.75. – MS, *m/z* (%): 284 (1) [M^+], 199 (100), 129 (60), 75 (35), 73 (70) [$Si(CH_3)_3$]. – $C_{17}H_{36}OSi$: calcd. 284.2535; found 284.2533 (MS).

A mixture of compounds **8c** and **9c** (200 mg, ratio of 2:3) was converted into a mixture of *(E)-2-methyl-5-(trimethylsilyloxy)-undec-3-ene* (**17c**) and *(Z)-2-methyl-5-(trimethylsilyloxy)undec-3-ene* (**18c**) (125 mg, ratio of 3:2, 88%). – ^{1}H NMR (200 MHz): δ = 0.06 [s, 3/5 × 9H, $Si(CH_3)_3$], 0.07 [s, 2/5 × 9H, $Si(CH_3)_3$], 0.85 (t, *J* = 6.7 Hz, 3H, 11-H), 0.94 (d, *J* = 7.0 Hz, 6H, CH_3 and 1-H), 1.05–1.51 (m, 10H, aliphatic H), 2.23 (oct, *J* = 6.8 Hz, 3/5 × 1H, 2-H), 2.55 (oct, *J* = 6.6 Hz, 2/5 × 1H, 2-H), 3.95 (q, *J* = 6.1 Hz, 3/5 × 1H, 5-H), 4.36 (m, 2/5 × 1H, 5-H), 5.04–5.51 (m, 2H, 3- and 4-H). – ^{13}C NMR: δ = 0.33, 0.41, 14.09, 22.25, 22.39, 22.63, 22.89, 23.34, 25.52, 25.63, 27.13, 29.23, 30.85, 31.90, 38.37, 38.86, 68.73, 73.98, 130.59, 131.37, 136.54, 137.81. – MS, *m/z* (%): 241 (3) [M^+ – CH_3], 171 (100), 81 (61), 75 (25), 73 (56) [$Si(CH_3)_3$]. – $C_{14}H_{29}OSi$: calcd. 241.1988; found 241.1987 (MS) [M^+ – CH_3].

Compound **10** (185 mg) was converted into **17a** (106 mg, 93%).

Compound **11** (185 mg) was converted into **18a** (97 mg, 85%).

Preparation of Allylic Alcohols **4**, **5** *by Hydrolysis of their O-Trimethylsilyl Derivatives* **17**, **18**. *According to Scheme 4. – General Procedure:* A solution of a silyl ether (**17a**–**18a**) (0.4 mmol) in wet acetone (10 ml) containing *p*-TosOH (2 mg) was set aside for 0.5 h whereupon it was diluted with water (30 ml) and extracted with CH_2Cl_2 (2 × 30 ml). The combined organic extracts were washed with satd. $NaHCO_3$ (30 ml), dried, and the solvent was removed. The residue was chromatographed on SiO_2 (hexane/Et_2O, 95:5).

Compound **17a** (92 mg) was converted into *(E)-dec-2-en-4-ol* (**4a**) (54 mg, 85%). – ^{1}H NMR (500 MHz): δ = 0.88 (t, *J* = 7.1 Hz, 3H, 10-H), 1.23–1.39 (m, 8H, aliphatic H), 1.43–1.58 (m, 2H, aliphatic H), 1.69 (ddd, *J* = 6.4, 1.5, 0.6 Hz, 3H, 1-H), 4.02 (q, *J* = 6.4 Hz, 1H, 4-H), 5.48 (ddq, *J* = 15.3, 7.1, 1.5 Hz, 1H, 3-H), 5.64 (dqd, *J* = 15.3, 6.4, 1.0 Hz, 1H, 2-H). – ^{13}C NMR: δ = 13.98, 17.56, 22.54, 25.39, 29.19, 31.77, 37.29, 73.06, 126.50, 134.45. – MS, *m/z* (%): 156 (0.3) [M^+], 141 (0.4) [M^+ – CH_3], 138 (0.5) [M^+ – H_2O], 71 (100). – $C_{10}H_{20}O$: calcd. 156.1514; found 156.1514 (MS).

Compound **18a** was converted into *(Z)-dec-2-en-4-ol* (**5a**) (52 mg, 83%). – ^{1}H NMR (500 MHz): δ = 0.87 (t, *J* = 7.1 Hz, 3H,

10-H), 1.23–1.47 (m, 9H, aliphatic H), 1.54–1.63 (m, 1H, aliphatic H), 1.68 (dd, J = 6.9, 1.8 Hz, 3H, 1-H), 4.46 (m, 1H, 4-H), 5.39 (ddq, J = 10.9, 8.8, 1.8 Hz, 1H, 3-H), 5.56 (dqd, J = 10.9, 6.9, 1.1 Hz, 1H, 2-H). – ^{13}C NMR: δ = 13.22, 14.00, 22.55, 25.24, 29.23, 31.79, 37.44, 67.36, 126.07, 133.69. – MS, *m/z* (%): 156 (0.5) [M^+], 141 (0.7) [$M^+ - CH_3$], 138 (1) [$M^+ - H_2O$], 71 (100). – $C_{10}H_{20}O$: calcd. 156.1514; found 156.1514 (MS).

Compound **17b** (114 mg) was converted into *(E)-tetradec-8-en-7-ol* (**4b**) (79 mg, 93%). – ^{1}H NMR (500 MHz): δ = 0.88 (t, J = 7.0 Hz, 3H, CH_3), 0.89 (t, J = 6.9 Hz, 3H, CH_3), 1.22–1.42 (m, 13H, aliphatic H), 1.42–1.59 (m, 3H, aliphatic H), 2.02 (q, J = 7.1 Hz, 2H, 10-H), 4.03 (q, J = 6.7 Hz, 1H, 7-H), 5.45 (ddt, J = 15.4, 7.1, 1.4 Hz, 8-H), 5.63 (dtd, J = 15.4, 6.7, 0.8 Hz, 9-H). – ^{13}C NMR (125 MHz): δ = 14.00, 14.03, 22.49, 22.58, 25.43, 28.87, 29.21, 31.35, 31.81, 32.14, 37.36, 73.21, 132.15, 133.06. – MS, *m/z* (%): 212 (1) [M^+], 194 (3) [$M^+ - H_2O$], 141 (15), 127 (60), 109 (66), 67 (70), 57 (100). – $C_{14}H_{28}O$: calcd. 212.2140; found 212.2142 (MS).

Compound **18b** (114 mg) was converted into *(Z)-tetradec-8-en-7-ol* (**5b**) (78 mg, 92%). – ^{1}H NMR (500 MHz): δ = 0.88 (t, J = 7.1 Hz, 3H, CH_3), 0.89 (t, J = 6.9 Hz, 3H, CH_3), 1.23–1.46 (m, 15H, aliphatic H), 1.55–1.63 (m, 1H, aliphatic H), 2.08 (m, 2H, 10-H), 4.42 (m, 1H, 7-H), 5.36 (ddt, J = 11.0, 8.8, 1.5 Hz, 8-H), 5.48 (dtd, J = 11.0, 7.5, 0.9 Hz, 9-H). – ^{13}C NMR (125 MHz): δ = 13.98, 14.04, 22.49, 22.58, 25.34, 27.66, 29.25, 29.38, 31.47, 31.84, 37.54, 67.73, 132.33, 132.64. – MS, *m/z* (%): 212 (0.5) [M^+], 194 (1) [$M^+ - H_2O$], 141 (15), 127 (60), 109 (100), 67 (63), 57 (78). – $C_{14}H_{28}O$: calcd. 212.2140; found 212.2143 (MS).

A mixture of **18c** and **17c** (ratio of 2:3, 103 mg) was converted into *(E)-2-methylundec-3-en-5-ol* (**4c**) (39 mg, 53%) and *(Z)-2-methylundec-3-en-5-ol* (**5c**) (26 mg, 36%). – **4c**: ^{1}H NMR (500 MHz): δ = 0.88 (t, J = 7.1 Hz, 3H, 11-H), 0.98 (d, J = 6.8 Hz, 3H, CH_3), 0.99 (d, J = 6.8 Hz, 3H, CH_3), 1.21–1.39 (m, 7H, aliphatic H), 1.43–1.61 (m, 3H, aliphatic H), 2.28 (oct. d, J = 6.5, 1.2 Hz, 1H, 2-H), 4.02 (q, J = 6.7 Hz, 1H, 5-H), 5.40 (ddd, J = 15.5, 7.1, 1.3 Hz, 1H, 4-H), 5.60 (ddd, J = 15.5, 6.5, 0.9 Hz, 1H, 3-H). – ^{13}C NMR (125 MHz): δ = 14.03, 22.28, 22.32, 22.57, 25.43, 29.20, 30.64, 31.79, 37.39, 73.21, 130.11, 138.96. – MS, *m/z* (%): 169 (2) [$M^+ - CH_3$], 166 (2) [$M^+ - H_2O$], 141 (35), 99 (90), 81 (100), 57 (42). – $C_{11}H_{21}O$: calcd. 169.1592; found 169.1592 (MS) [$M^+ - CH_3$].

5c: ^{1}H NMR (500 MHz): δ = 0.88 (t, J = 7.1 Hz, 3H, 11-H), 0.95 (d, J = 6.7 Hz, 3H, CH_3), 1.00 (d, J = 6.6 Hz, 3H, CH_3), 1.23–1.45 (m, 9H, aliphatic H), 1.51–1.64 (m, 1H, aliphatic H), 2.64 (m, 1H, 2-H), 4.43 (m, 1H, 5-H), 5.23 (ddd, J = 10.9, 8.8, 0.7 Hz, 1H, 4-H), 5.30 (td, J = 10.9, 0.7 Hz, 1H, 3-H). – ^{13}C NMR (125 MHz): δ = 14.05, 22.58, 23.24, 23.35, 25.40, 27.06, 29.25, 31.81, 37.70, 67.96, 130.21, 139.61. – MS, *m/z* (%): 169 (2) [M^+], 166 (3) [$M^+ - H_2O$], 141 (30), 99 (80), 81 (100), 67 (23), 57 (41). – $C_{11}H_{21}O$: calcd. 169.1592; found 169.1592 (MS) [$M^+ - H_2O$].

Preparation of a Mixture of Alcohols **4a** *and* **5a** *by the Reaction of Adduct* **8a** *with BuLi:* To a stirred solution of **8a** (110 mg, 0.3 mmol) in THF (5 ml) BuLi in hexane (1.6 M, 0.3 mmol) was added at room temp. Stirring was continued for 2 h, whereupon the mixture was diluted with water (20 ml) and extracted with CH_2Cl_2 (2 × 20 ml). The combined organic extracts were dried, the solvent was removed and the residue dissolved in wet acetone (10 ml) containing *p*-TosOH (2 mg). The solution was kept for 20 min, then diluted with water (20 ml) and subsequently extracted with CH_2Cl_2 (2 × 20 ml). The combined organic extracts were washed with a satd. $NaHCO_3$ (20 ml), dried, and the solvent was removed. The residue was chromatographed on SiO_2 (hexane/Et_2O, 95:5). An inseparable mixture of **4a** and **5a** in a ratio of 1:2 (33 mg, 72%) was obtained.

Preparation of Allylic Alcohols **3–7** *by the Reaction of Lithiated Sulfones* **2a–f** *with Epoxysilanes* **1a** *and* **1b** *According to Scheme 2. – General Procedure:* To a solution of alkyl phenyl sulfone **2a–f** (2.65 mmol) in dry THF (20 ml), stirred at −20°C, BuLi in hexane (1.6 M, 1.4 ml, 2.24 mmol) was added dropwise. The mixture was stirred for 10 min, and then **1a** or **1b** (300 mg, 1.5 mmol) was added.

Method A: Stirring at −20°C was continued for 24 h, whereupon the mixture was allowed to warm to room temp.

Method B: Stirring at −20°C was continued for 4 h, whereupon the mixture was allowed to warm to room temp. (during ca. 4 h) and was then ketp for 16 h.

Method C: Stirring was continued at room temp. for 24 h.

The mixture was diluted with water (50 ml) and extracted with CH_2Cl_2 (2 × 30 ml). The combined organic extracts were dried, and the solvent was removed to give the crude trimethylsilyl ether. This product was dissolved in wet acetone (20 ml) containing *p*-TosOH (3 mg). The solution was set aside for 20 min (until the starting material was consumed, TLC), subsequently diluted with water (50 ml) and extracted with CH_2Cl_2 (2 × 30 ml). The combined organic extracts were washed with a satd. $NaHCO_3$, dried, and the solvent was removed. The residue was chromatographed on SiO_2 (hexane/Et_2O, 97:3) to give the corresponding allylic alcohols.

Reaction of **1a** with **2a** (413 mg) led to *non-1-en-3-ol* (**3**) (150 mg, 70%, method C). – ^{1}H NMR (500 MHz): δ = 0.88 (t, J = 7.1 Hz, 3H, CH_3), 1.20–1.60 (m, 10H, aliphatic H), 4.10 (q, J = 6.2 Hz, 1H, 3-H), 5.10 (dt, J = 10.4, 1.4 Hz, 1H, 1-H), 5.22 (dt, J = 17.2, 1.4 Hz, 1H, 1-H), 5.87 (ddd, J = 17.2, 10.4, 6.2 Hz, 1H, 2-H). – ^{13}C NMR (50 MHz): δ = 14.05, 22.57, 25.27, 29.19, 31.76, 37.01, 73.25, 114.49, 141.31. – MS, *m/z* (%): 124 (1) [$M^+ - H_2O$], 113 (5), 72 (20), 57 (100) [C_3H_5O]. – C_9H_{16}: calcd. 124.1252; found 124.1246 (MS) [$M^+ - H_2O$].

Reaction of **1a** with sulfone **2b** (450 mg) led to a mixture of **4a** and **5a** (129 mg, 55%, ratio 1:11, method A; 176 mg, 75%, ratio 1:9, method B; 187 mg, 80%, ratio 1:4, method C).

Reaction of **1a** with sulfone **2c** (600 mg) afforded a mixture of **5b** and **4b** (167 mg, 53%, ratio 16:1, method A; 248 mg, 78%, ratio 11:1, method B; 254 mg, 80%, ratio 6:1, method C).

Reaction of **1a** with sulfone **2d** (525 mg) led to a mixture of **4c** and **5c** (39 mg, 14%, ratio 4:1, method B).

Reaction of **1** with sulfone **2e** (490 mg) yielded *2-methylundec-2-en-4-ol* (**6**) (120 mg, 47%, method C). – ^{1}H NMR (500 MHz): δ = 0.88 (t, J = 6.9, 3H, 11-H), 1.25–1.60 (m, 10H, aliphatic H), 1.69 (d, J = 1.3 Hz, 3H, vinylic CH_3), 1.73 (d, J = 1.3 Hz, 3H, vinylic CH_3), 4.33 (dt, J = 8.7, 6.5 Hz, 1H, 4-H), 5.16 (hept. d, J = 1.3, 8.7 Hz, 1H, 3-H). – ^{13}C NMR (50 MHz): δ = 14.06, 18.21, 22.60, 25.43, 25.76, 29.29, 31.84, 37.77, 68.76, 128.33, 134.98. – MS, *m/z* (%): 170 (2) [M^+], 155 (15) [$M^+ - CH_3$], 113 (15), 85 (100) [C_5H_9O]. – $C_{11}H_{22}O$: calcd. 170.1671; found 170.1667 (MS).

Reaction of **1a** with sulfone **2f** (594 mg) led to **7** (9.5 mg, 3%, method C). – ^{1}H NMR (500 MHz): δ = 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.20–1.60 (m, 16H, aliphatic H), 2.00–2.20 (m, 4H, aliphatic H), 4.38 (dt, J = 8.8, 6.5 Hz, 1H, 7-H), 5.09 (dt, J = 8.8, 1.1 Hz, 1H, 8-H). – MS, *m/z* (%): 210 (2) [M^+], 192 (4) [$M^+ - H_2O$], 125 (100) [$C_8H_{13}O$], 79 (32), 67 (20). – $C_{14}H_{24}$: calcd. 192.1878; found 192.1886 (MS) [$M^+ - H_2O$].

Preparation of Alcohol **6** *by the Reaction of Sulfone* **2e** *with Oxirane* **1a** *in the Presence of* $BF_3 \cdot Et_2O$ *(Scheme 6):* To a solution of **2e** (690 mg, 3.75 mmol) in dry THF (20 ml), stirred at −20°C, BuLi in hexane (1.6 M, 2.3 ml, 3.75 mmol) was added dropwise. The mixture was stirred for 10 min, whereupon **1a** (500 mg, 2.5 mmol) and $BF_3 \cdot Et_2O$ (550 mg, 3.75 mmol) were consecutively added. Stirring was continued for 3 h, then the mixture was diluted with water (50 ml) and extracted with CH_2Cl_2 (2 × 30 ml). The combined organic extracts were dried, and the solvent was removed. The residue was dissolved in benzene (25 ml), and 25% aq NaOH (25 ml) and Bu_4NBr (0.1 eq) were added to the obtained solution. The mixture was vigorously stirred for 1 h, then diluted with water (50 ml) and extracted with Et_2O (2 × 30 ml). The combined organic extracts were washed with water, dried, and the solvent was removed. The residue was dissolved in wet acetone (30 ml) containing *p*-TsOH (3 mg), and the obtained solution was set aside for 0.5 h. It was subsequently diluted with water (60 ml) and extracted with CH_2Cl_2 (2 × 30 ml). The combined organic extracts were washed with a satd. $NaHCO_3$ (30 ml), and the solvent was removed. The residue was chromatographed on SiO_2 (hexane/Et_2O, 95:5) to yield alcohol **6** (213 mg, 50%).

Preparation of Allylic Sulfones **19a–c** *According to Scheme 7. – General Procedure:* A solution of **8a–9c** (0.15 mmol) in dry pyridine (3 ml) was treated with PBr_3 (400 mg, 1.5 mmol). After 1.5 h the mixture was diluted with water (20 ml) and extracted with CH_2Cl_2 (2 × 20 ml). The combined organic extracts were washed with 10% HCl (20 ml) and satd. $NaHCO_3$ solution (20 ml), dried, and the solvent was removed. The residue was chromatographed on SiO_2 (hexane/AcOEt, 97:3).

Compound **8a** (56 mg) was converted into *(E)-2-(phenylsulfonyl)dec-3-ene* (**19a**) (35 mg, 83%). – ^{1}H NMR (500 MHz): δ = 0.88 (t, *J* = 7.1 Hz, 3H, 10-H), 1.14–1.32 (m, 10H, aliphatic H), 1.43 (d, *J* = 7.0 Hz, 3H, 1-H), 1.96 (br. q, *J* = 6.7 Hz, 2H, 5-H), 3.65 (quint, *J* = 7.2 Hz, 1H, 2-H), 5.37 (ddt, *J* = 15.5, 7.9, 1.2 Hz, 1H, 3-H), 5.40 (dt, *J* = 15.5, 6.6 Hz, 1H, 4-H), 7.52 (br. t, *J* = 7.5 Hz, 2H, *m*-ArH), 7.62 (tt, *J* = 7.5, 1.2 Hz, 1H, *p*-ArH), 7.83 (m, 2H, *o*-ArH). – ^{13}C NMR (125 MHz): δ = 13.42, 14.03, 22.52, 28.66, 28.67, 31.59, 32.44, 63.76, 128.67, 129.27, 133.41, 137.20, 138.86. – MS, *m/z* (%): 139 (37) [M^+ – $PhSO_2$], 97 (60), 83 (100), 77 (15), 69 (37). – $C_{16}H_{24}O_2S$ (280.4): calcd. C 68.53, H 8.63; found C 68.43, H 8.50.

Compound **9a** (56 mg) was converted nto **19a** (36 mg, 85%), which was identical in all respects with the material described above.

Compound **8b** (64 mg) was converted into *(E)-6-(phenylsulfonyl)tetradec-7-ene* (**19b**) (45 mg, 89%). – ^{1}H NMR (500 MHz): δ = 0.86 (t, *J* = 6.9 Hz, 3H, CH_3), 0.87 (t, *J* = 7.0 Hz, 3H, CH_3), 1.12–1.42 (m, 14H, aliphatic H), 1.58–1.67 (m, 1H, aliphatic H), 1.95 (q, *J* = 7.0 Hz, 2H, 9-H), 2.09 (m, 1H, aliphatic H), 3.43 (ddd, *J* = 11.0, 9.4, 3.3 Hz, 1H, 6-H), 5.18 (ddt, *J* = 15.4, 9.4, 1.3 Hz, 1H, 7-H), 5.37 (dt, *J* = 15.4, 6.7 Hz, 1H, 8-H), 7.51 (br. t, *J* = 7.5 Hz, 2H, *m*-ArH), 7.60 (tt, *J* = 7.5, 1.2 Hz, 1H, *p*-ArH), 7.81 (m, 2H, *o*-ArH). – ^{13}C NMR (125 MHz): δ = 13.87, 14.01, 22.31, 22.52, 26.22, 26.79, 28.62, 28.65, 31.22, 31.56, 32.45, 69.33, 121.95, 128.62, 129.14, 133.27, 137.84, 140.50. – MS, *m/z* (%): 195 (25) [M^+ – $PhSO_2$], 139 (10), 125 (22), 111 (45), 97 (60), 83 (72), 69 (100). – $C_{20}H_{32}O_2S$ (336.5): calcd. C 71.38, H 9.59; found C 71.30, H 9.77.

Compound **9b** (64 mg) was converted into **19b** (45 mg, 85%), which was identical in all respects with the above described material.

A mixture of **8c** and **9c** (60 mg, ratio of 2:3) was converted into *(E)-2-methyl-3-(phenylsulfonyl)undec-4-ene* (**19c**) (42 mg, 90%). – ^{1}H NMR (500 MHz): δ = 0.87 (t, *J* = 7.0 Hz, 3H, 11-H), 0.98 (d, *J* = 6.9 Hz, 3H, CH_3), 1.12 (d, *J* = 6.8 Hz, 3H, CH_3), 1.13–1.31 (m, 7H, aliphatic H), 1.89–1.98 (m, 2H, aliphatic H), 2.67 (sept, d, *J* = 6.8, 3.5 Hz, 1H, 2-H), 3.28 (ddd, *J* = 10.2, 3.5, 0.3 Hz, 1H, 3-H), 5.21 (dt, *J* = 15.3, 6.8 Hz, 1H, 5-H, 5.44 (ddt, *J* = 15.3, 10.2, 1.4 Hz, 1H, 4-H), 7.50 (br. t, *J* = 7.8 Hz, 2H, *m*-ArH), 7.59 (tt, *J* = 7.4, 1.3 Hz, 1H, *p*-ArH), 7.81 (m, 2H, *o*-ArH). – ^{13}C NMR (125 MHz): δ = 14.03, 18.06, 21.93, 22.53, 26.70, 28.62, 28.72, 31.57, 32.54, 74.58, 118.74, 128.60, 128.82, 133.14, 138.89, 141.48. – MS, *m/z* (%): 167 (30) [M^+ – $PhSO_2$], 125 (10), 111 (92), 97 (66), 83 (45), 69 (100). – $C_{18}H_{28}O_2S$ (308.5): calcd. C 70.08, H 9.15; found C 70.18, H 9.00.

[1] M. Masnyk, J. Wicha, *Tetrahedron Lett.* **1988**, *29*, 2497–2500.
[2] For reviews on organosilicon chemistry, see: [2a] W. P. Weber, *Silicon Reagents For Organic Synthesis*, Springer, Berlin, **1983**. – [2b] E. V. Colvin, *Silicon in Organic Synthesis*, Batterworths, London, **1981**.
[3] P. Jankowski, S. Marczak, M. Masnyk, J. Wicha, *J. Organomet. Chem.* **1991**, *403*, 49–61.
[4] [4a] B. Achmatowicz, P. Raubo, J. Wicha, *J. Org. Chem.* **1992**, *57*, 6593–6598. – [4b] P. Raubo, J. Wicha, *Synth. Commun.* **1993**, *23*, 1273–1288.
[5] Y. Kobayashi, T. Ito, I. Yamakawa, H. Urabe, F. Sato, *Synlett* **1991**, 813–815.
[6] For a discussion on the reaction stereochemistry, see ref.[3]
[7] [7a] S. Marczak, J. Wicha, *Synth. Commun.* **1990**, *20*, 1511–1520. – [7b] B. Achmatowicz, E. Baranowska, A. R. Daniewski, J. Pankowski, J. Wicha, *Tetrahedron Lett.* **1985**, *26*, 5597–5600. – [7c] For leading references on the use of Lewis acids in combination with organometallic reagents, see: Y. Yamamoto, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 947–1038.
[8] For leading references, see: P. Kocienski, *Phosphorus Sulfur* **1985**, *24*, 97–127.
[9] A. Alexakis, D. Jachiet, *Tetrahedron Lett.* **1988**, *29*, 217–220.
[10] P. Janowski, J. Wicha, *J. Chem. Soc., Chem. Commun.* **1992**, 802–803.
[11] [11a] P. Lin, G. H. Whitham, *J. Chem. Soc., Chem. Commun.* **1983**, 1102–1103. – [11b] P. Kocienski, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 945–948.
[12] K. Inomata, S-i. Sasaoka, T. Kobayashi, Y. Tanaka, S. Igarashi, T. Ohtani, H. Kinoshita, H. Kotake, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1767–1779.

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