# A Novel Stereoselective Reaction Cascade Leading from α-Silylated Allylic Alcohols to Aldol-Type Products

by **Jürg Fässler**[1]), **Valentin Enev**[2]), and **Stefan Bienz***

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

The treatment of α-silylated allylic alcohols with epoxidizing reagents afforded in a highly stereocontrolled fashion α-silylated aldols. The transformation is proposed to proceed either by a reaction cascade involving stereospecific epoxidation of the allylic-alcohol moiety followed by an acid-supported pinacol-type rearrangement, or by a sequence consisting of a π-face-selective electrophilic attack at the allylic silane moiety with hyperconjugative stabilization of the evolving carbocation, followed by rearrangement of the thus obtained pentacoordinated silanium ion (see *Scheme 3*). Depending on the reaction conditions, the π-face selectivity of the oxidation step is controlled by the stereogenic C-atom or the more remote Si-center of chirality.

**Introduction.** – We have shown by our preceding investigations that chiral silyl groups can act as powerful stereochemical directors in diastereoselective transformations (for a minireview containing also preliminary results of this investigation, see [1]). For instance, treatment of acylsilanes **1** with organometallic reagents gave rise to the corresponding α-silylated alcohols **2** in high chemical and stereochemical yields (*Scheme 1*) [2][3]. With this reaction, we have prepared some α-silylated allylic alcohols (compounds of type **3**) that combine the structural and possibly also the chemical features of allylic alcohols, allylic silanes, and α-silylated alcohols. So far, the 'allylic-alcohol' feature of such compounds has been used for highly stereoselective *Ireland* ester enolate [4] and for oxy-*Cope*-type rearrangements [5].

Since allylic alcohols are also appreciated as excellent substrates for stereoselective epoxidation reactions [6], and α-silylated alcohols are known to readily undergo the *Brook* rearrangement [7], we planned the combined use of these two features of compounds **3** for a novel stereoselective reaction cascade: π-face-selective epoxidation was expected to afford oxiranes **4** that, upon base treatment, should lead to compounds of type **5** by *Brook* rearrangement and concomitant eliminative opening of the epoxides. Compounds **5** are silyl enol ethers of aldols, and their precursors, acylsilanes **6** and vinyl halides **7**, could be regarded in a retro-synthetic way as acyl-cation and β-hydroxy-anion equivalents, respectively.

**Results and Discussion.** – 1. *Synthesis of α-Silylated Allylic Alcohols.* For the investigation of the aforementioned oxidation reaction, a number of α-silylated allylic alcohols were prepared (*Scheme 2*), *i.e.*, alcohols **16a**–**g** substituted by the 'achiral' (*t*-Bu)$Me_2$Si group, and alcohols **17a**–**i** substituted by the 'chiral' ($BnOCH_2$)(*t*-Bu)MeSi

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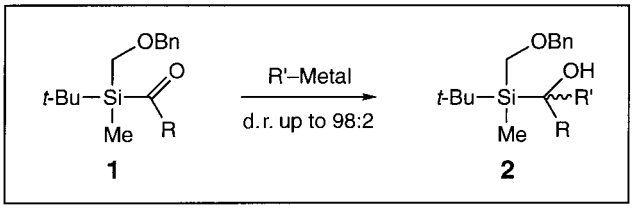
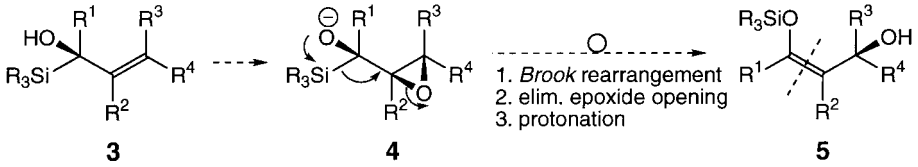
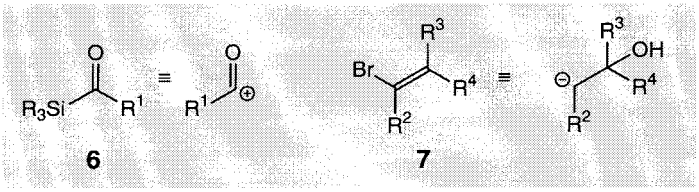
[1]) Part of the Ph.D. thesis of *J. F.*, University of Zurich.

[2]) Postdoctoral fellow on leave from the Bulgarian Academy of Science, Sofia.

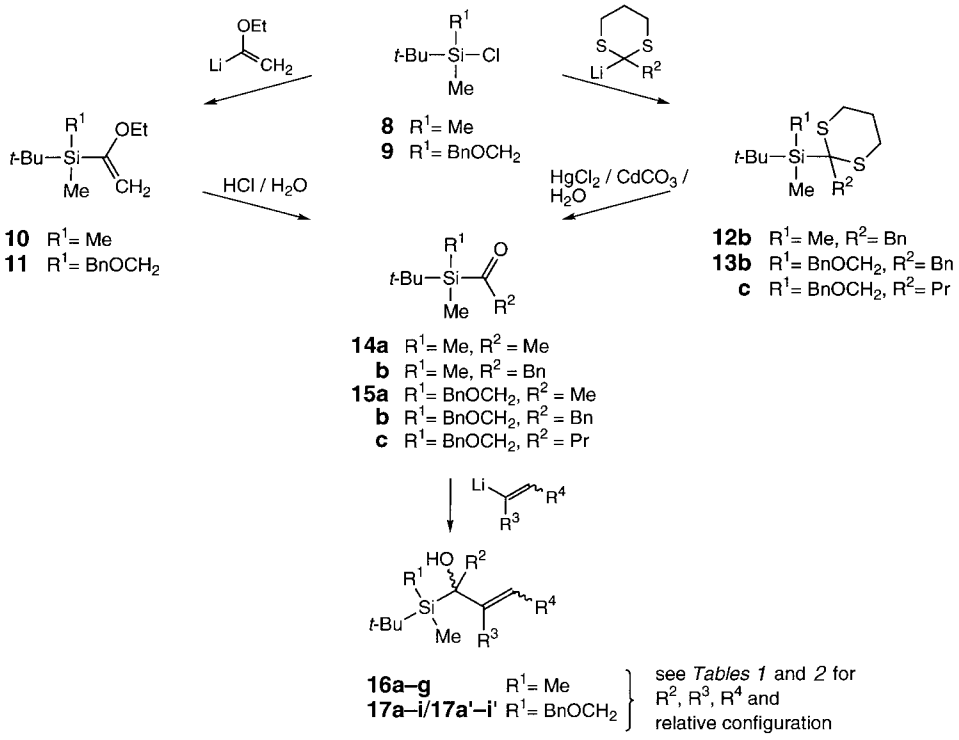
*Scheme 1*




*Scheme 2*



group. We have already described the synthesis of the alcohols **17a** and **17b** [4], and the remaining $\alpha$-silylated allylic alcohols were prepared accordingly. The chlorosilanes **8** and **9** were treated with acyl-anion equivalents to afford the vinyl ethers **10** and **11** or the dithioacetals **12b** and **13b**,**c**, respectively. These intermediary products were hydrolyzed to the corresponding acylsilanes **14a**,**b** and **15a** – **c** by exposure to $HCl/H_2O$ or to $HgCl_2/CdCO_3/H_2O$, respectively. Treatment of the acylsilanes with different vinyl organometallic reagents, finally, afforded the desired compounds of type **16** and **17**.

As already noted earlier, the stereochemical course of the addition reaction to the chiral (alkoxymethyl)-substituted acylsilanes of type **15** depends on the reaction conditions and the nature of the organometallic reagent [3][4]. Again, best results were obtained when the transformations were performed in $Et_2O$ with organometallic reagents that were freshly prepared from the corresponding vinyl bromides by sequential treatment with excess of elemental Li (2% Na) and 0.5 equiv. of $MgBr_2$ [4]. Under these conditions, the diastereoselectivities were high for all investigated transformations (diastereoisomer ratio (d.r.) up to 98:2). Since the stereochemical course of the subsequent reactions can be studied more efficiently with mixtures of diastereoisomers (particularly differently composed mixtures of diastereoisomers) rather than with diastereoisomerically pure compounds, the reactions of the $\alpha$-silylated allylic alcohols of type **17** were performed under various, including non-ideal, conditions. Thus, the d.r. values of the starting alcohols of type **17** given in *Table 2* (see below) do not reflect the highest ratios that can be reached by an optimal handling of the reaction.

The enantiomerically enriched $\alpha$-[(*t*-Bu)$Me_2$Si]-substituted allylic alcohols (–)-**16a** and (–)-**16b** were obtained by reaction of **14a** with (*E*)- and (*Z*)-prop-1-enylmagnesium bromide in the presence of (+)-(*R*)-1,1′-bi-2-naphthol [8]. The addition products were obtained with fair $\pi$-face selectivities (e.r. *ca.* 85:15), but the reaction was not further optimized for better selectivities, since the stereochemical outcome was sufficient for the purpose of determining the degree of stereoselectivity of the subsequent transformation (see below). The absolute configurations of the major products, (–)-**16a** and (–)-**16b**, could not be determined. In analogy to [8], they were tentatively assigned to be (*S*).

2. *Oxidation of α-Silylated Allylic Alcohols.* The oxidation of $\alpha$-silylated allylic alcohols proceeded slightly differently than anticipated. Treatment of the alcohols of type **16** and **17** with epoxidizing reagents like 3-chloroperbenzoic acid (MCPBA), *t*-BuOOH/[Ti(i-PrO)$_4$], *t*-BuOOH/[VO(acac)$_2$] (Hacac = acetylacetone = pentane-2,4-dione), or dimethyldioxirane (DMD) led to $\alpha$-silylated $\beta$-hydroxy ketones of type **18** and **19**[3]) (*Scheme 3*), respectively, rather than to the expected compounds of type **5**. The results of a number of relevant experiments are summarized in *Tables 1* and *2*.

The transformation of the alcohols of type **16** and **17** into the $\alpha$-silylated aldols of type **18** and **19**, however, can still be rationalized with cascades consisting of two subsequent reactions (*Scheme 3*). We can still suggest that an epoxidation reaction represents the first step of the conversion. This reaction, however, would be followed by

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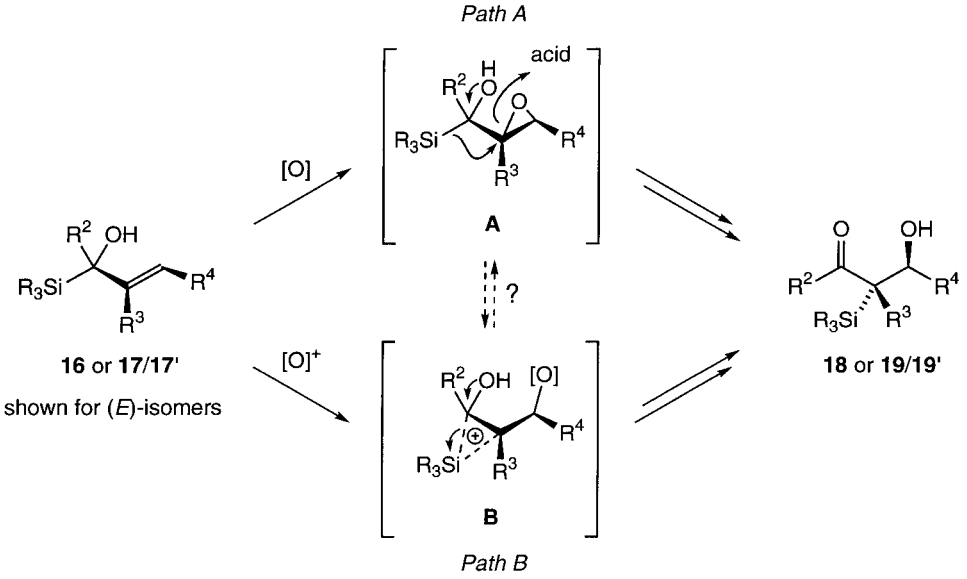
[3]) Compounds of this type have already been prepared by aldol-type reactions with $\alpha$-silylated ketones [9] or esters [10] as the starting materials. The stereoselectivities, however, were rather low, with the exception of the reactions of $\gamma$-lactone enolates.

*Scheme 3* [a])



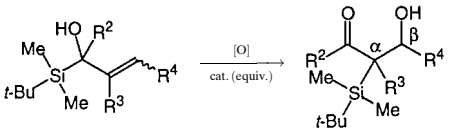

[a]) See *Tables 1* and *2* for $R^2$, $R^3$, $R^4$, and configuration.

a pinacol-type rather than a *Brook* rearrangement. Thus, oxidation of the starting alkene **16** or **17** could lead, in a first step, to a reactive oxirane **A** that would, under the *Lewis*-acidic conditions, rapidly undergo a [1,2] shift of the silyl group to the adjacent C-atom with concomitant *anti*-opening of the epoxide moiety (*Path A* in *Scheme 3*)[4]). Alternatively, the silyl group, being located perpendicularly to the plane of the C=C bond, might assist the reaction with the electrophilic oxidizing reagent due to its $\beta$-effect. An intermediary silanium ion **B** could be formed by an *anti*-attack of the electrophile and a concomitant 'bridging' stabilization of the evolving carbocation. Such transient species would be expected to rearrange to form the final products (*Path B* in *Scheme 3*).

Cationic [1,2] shifts of silyl groups are not without literature precedence (see [12] and refs. cit. therein for some fundamental and more recent investigations), and both mechanisms proposed in *Scheme 3* are reasonable in many respects. However, it was not possible to distinguish *Paths A* and *B* and to establish the exact course of the transformation. Notably, we were unable to capture or even to detect any oxirane intermediates so far. For instance, no intermediary oxiranes were observed on monitoring the transformations by $^1$H-NMR, not even when the oxidation was carried out at $-40°$ under pH-neutral conditions with DMD. This result seems to support *Path B*, but, in fact, the finding does not completely exclude the possibility of highly reactive epoxide intermediates (*Path A*). As a consequence of the $\beta$-effect of the

4) Such a reaction was tentatively proposed by *Scheller et al.* as a side reaction on the way to $\alpha,\beta$-epoxyacylsilanes [11].

Table 1. *Oxidation of α-Silylated Allylic Alcohols* **16**




| *Entry* | Starting material | | | | | Conditions | | | Product | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | No. | $R^2$ | $R^3$ | $R^4$ | Double bond | [O] | catalyst | Equiv. | No. | C-Skeleton ($\alpha,\beta$) | Yield [%] |
| *1* | **16a** | Me | H | Me | (*E*) | *t*-BuOOH | [Ti(i-PrO)$_4$] | 1.0 | **18a** | *anti* | 70 |
| *2* | **16a** | Me | H | Me | (*E*) | *t*-BuOOH | [VO(acac)$_2$] | 0.02 | **18a** | *anti* | 69 |
| *3* | **16a** | Me | H | Me | (*E*) | MCPBA | – | – | **18a** | *anti* | 69 |
| *4* | **16a** | Me | H | Me | (*E*) | DMD[a]) | – | – | **18a** | *anti* | 65 |
| *5* | (−)-**16a**[b]) | Me | H | Me | (*E*) | *t*-BuOOH | [Ti(i-PrO)$_4$] | 1.0 | (−)-**18a**[c]) | *anti* | 68 |
| *6* | **16b** | Me | H | Me | (*Z*) | *t*-BuOOH | [Ti(i-PrO)$_4$] | 1.0 | **18b** | *syn* | 55 |
| *7* | **16b** | Me | H | Me | (*Z*) | *t*-BuOOH | [VO(acac)$_2$] | 0.02 | **18b** | *syn* | 60 |
| *8* | **16b** | Me | H | Me | (*Z*) | MCPBA | – | – | **18b** | *syn* | 70 |
| *9* | **16b** | Me | H | Me | (*Z*) | DMD | – | – | **18b** | *syn* | 41 |
| *10* | (−)-**16b**[b]) | Me | H | Me | (*Z*) | *t*-BuOOH | [Ti(i-PrO)$_4$] | 1.0 | (−)-**18b**[c]) | *syn* | 59 |
| *11* | **16c** | Me | Me | Me | (*E*) | MCPBA | – | – | **18c** | *anti* | 53 |
| *12* | **16d** | Me | Me | Me | (*Z*) | MCPBA | – | – | **18d** | *syn* | 80[d]) |
| *13* | **16e** | Bn | H | Me | (*E*) | MCPBA | – | – | **18e** | *anti* | 96 |
| *14* | **16f** | Bn | H | Me | (*Z*) | MCPBA | – | – | **18f** | *syn* | 80 |
| *15* | **16g** | Bn | $-(CH_2)_4-$ | | (*E*) | MCPBA | – | – | **18g** | *anti* | 86 |
| *16* | **16g** | Bn | $-(CH_2)_4-$ | | (*E*) | DMD | – | – | **18g** | *anti* | 72[e]) |

[a]) DMD = Dimethyldioxirane. [b]) e.r. = 85 : 15. [c]) e.r. = 80 : 20. [d]) Yield of crude product; the product decomposed upon purification (elimination of $R_3SiOH$, see below). [e]) An additional oxidation product (compound **26**, see below) was formed in 14% yield.

silicon group, it is additionally conceivable and even likely that the rearrangement of species of type **A** – if they are effectively formed – would proceed *via* intermediates of type **B**.

Consistent with both mechanisms is the stereochemical course of the transformation. With respect to the stereogenic centers of the C-framework, it was found that the (*E*)-configured starting materials of type **16** and **17** provided exclusively the corresponding *anti*-configured products of type **18** and **19**, respectively, whereas the (*Z*)-configured starting compounds led to the *syn*-configured α-silylated aldols only. The relative configurations of the stereogenic centers on the C-frameworks were unambiguously determined for some examples by single-crystal X-ray diffraction analysis (see *Exper. Part*). Evidently, both reaction *Paths A* and *B* would lead to the same stereochemical result.

The explanation of the stereoselectivities related to the π-face differentiation of the alkenes in the oxidation step is less trivial. At a first glance, the results of our investigations reveal that these π-face selectivities are usually high. However, a closer examination shows that the stereochemical course of the reactions – with respect to the stereogenic C- and Si-atoms of the starting α-silylated allylic alcohols – is not uniform for all transformations. In most cases, the stereoselectivity is controlled by the stereogenic C-atom of the starting compounds. The (*CR**)-configured alcohols **17a**–**i**

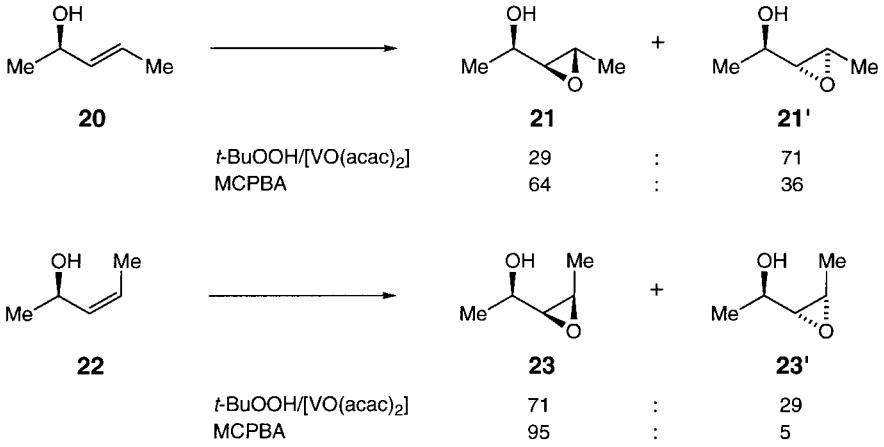
usually afforded the products **19a**–**i** with ($\alpha R^*$)-configuration (configuration at the newly formed stereogenic C-atom in $\alpha$-position to the C=O group). This was deduced, *e.g.*, from the single-crystal X-ray structure of a derivative of **19b**, uncovering all relative configurations of **19b**, the knowledge of the relative configurations of the stereogenic centers of the corresponding starting material **17b** [13], and the assumption of retention of configuration at the Si-center throughout the reaction.

The determination of the $\pi$-face selectivities with respect to the stereogenic C-atom of the starting compounds is not trivial for racemic materials: this center of chirality is lost in the course of the transformations and cannot be directly related to the configurations of the newly formed stereogenic centers of the corresponding products. Compounds of type **17**, however, bear the 'chiral' ($BnOCH_2$)(*t*-Bu)MeSi group, which can be used as a stereochemical marker. With the configuration at the Si-atom taken as a constant, the relative configurations of this center with respect to the stereogenic centers of the starting materials and the products reveal indirectly the configurations of the 'destroyed' stereogenic unit of the starting compounds relative to those of the newly formed chirality units of the products.

As a referee pointed out correctly, the determination of the $\pi$-face selectivity relies on the assumption of 'retention of configuration at silicon' in the involved [1,2] silicon shift. It was criticized correctly that migration of the silicon group with inversion of configuration at silicon, together with oxidation of the double bond with opposite $\pi$-face selectivity with respect to the center of chirality at ($CR^*$), would result in the same relative configurations in the products. To our knowledge, the stereochemical course of nucleophilic [1,2] silicon shifts with respect to a stereogenic Si-center has not been investigated yet, and we cannot found our assumption on literature precedence. We assume, however, that inversion of configuration at the Si-center is rather unlikely. Retention of configuration is in agreement with the observed retention of configuration at the C-atom in related nucleophilic [1,2] shifts of alkyl groups (for a review, see, *e.g.*, [14]) and with the common understanding of the $\beta$-effect of silicon groups (see [15]). Hyperconjugative or 'bridging' stabilization of the intermediary $\beta$-carbocation (which is either actually existing or only partially developing in the course of opening of the epoxide) with subsequent move of the silicon group to the adjacent C-center would not allow inversion of configuration at the Si-center. Additionally, related electrophilic [1,2] silicon shifts, as far as investigated, proceed with retention of configuration at the Si-center, too (*e.g.*, [16] and refs. cited therein). The latter reactions are described to proceed through three-membered intermediary ring structures with the pentacoordinate Si-atom, which are similar to the proposed intermediary structures **B**. The three-membered cationic silanium species **B** would involve the same molecular orbitals as the corresponding anionic siliconates, only with different electronic occupations, and should lead to the same stereochemical results upon fragmentation.

The stereochemical course of the transformations is largely independent of the oxidizing reagents for all investigated compounds. Same directions and comparable degrees of stereoselectivity were observed with *t*-BuOOH/[$Ti(i\text{-}PrO)_4$] (cat.), *t*-BuOOH/[$VO(acac)_2$] (cat.), as well as with MCPBA, or DMD as the oxidizing systems. This is, at first sight, not in accordance with the literature. *Rossiter et al.* found that the $\pi$-face selectivity of epoxidations of the (*E*)-configured allylic alcohol **20** with *t*-BuOOH/[$VO(acac)_2$] (forming preferentially **21′**) is reversed as compared to the selectivity of the corresponding reaction performed with MCPBA (forming preferentially **21**, *Scheme 4*) [17]. However, it is readily recognized from the data of this same investigation and of others [18] that the stereoselectivities of allylic-alcohol epoxidations are rather low, and that the $\pi$-face selectivities in dependence of the oxidizing reagents already alter upon small structural variation of the starting materials. For instance, the oxidation of the (*Z*)-configured allylic alcohol **22** afforded preferentially epoxide **23** for both reagents, MCPBA as well as *t*-BuOOH/[$VO(acac)_2$]. Thus, small contributions to the stabilization (or destabilization) of a specific transition state may dominate in the reaction and direct the stereoselectivity of the overall process.

*Scheme 4*




The origin of the $\pi$-face selectivity of reactions with $\alpha$-stereogenic olefins in a more general sense is under controversy. For instance, *Cieplak et al.* postulate a stereoelectronic effect to be responsible for the preference of one $\pi$-face over the other. This effect would consist of a more efficient stabilizing interaction of one of the occupied allylic $\sigma$ orbitals with the $\sigma^*_{\ddagger}$ orbital of the incipient bond. *Cieplak et al.* support their model with striking experimental evidence obtained on rigid systems, and they claim to disprove the models of other investigators. For a detailed discussion and reference to several models, see [19]. *Houk* and co-workers, on the basis of profound *ab initio* and MM2 calculations on acyclic systems [20], favor a model of staggered transition structures, including steric and electronic effects. For acyclic systems, this model is consistent with the *Cieplak* model with respect to the prediction of the $\pi$-face-selectivity[5]), but it differs in the explanation of the origin of the selectivity. The results of our oxidation reactions do not add any argument for or against one of the models in discussion; it is consistent with both.

Indisputably, the gross conformation of the transition state structures for the oxidation reactions of $\alpha$-silylated allylic alcohols should be **C1** and **C2** (*Fig. 1*). These structures should be determined by the stereoelectronic effect of the silicon group (by the $\beta$-effect [15]). In agreement with *Cieplak*, the rather strongly donating silicon group should be arranged *anti*-periplanar to the incipient bond to ensure best stabilizing overlap with the developing empty $\sigma^*_{\ddagger}$ orbital, and the same arrangement is proposed by *Houk* and co-workers. If the donating silicon group is located *anti*-periplanar to the developing bond to the electrophile, minimized steric strain and maximized electron donation from the high-lying $\sigma$(C–Si) orbital to the transition state LUMO would be achieved. To distinguish between the two structures **C1** and **C2** – structure **C1** has to be favored to explain the stereoselectivity of the reaction – additional arguments have to be brought into play. *Houk* and co-workers state that preference of 'inside' or 'outside'

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[5]) Several models, upraised to explain the stereochemical course of addition reactions to $\alpha$-stereogenic alkenes and related compounds, should naturally be consistent over a broad spectrum of reactions and substrates: all models have finally to explain the same experimental results.

positions of the electron-withdrawing group (in our case the OH group) depends upon the specific dihedral angle as well as the interactions between the attacking electrophile and the groups in the 'inside' or 'outside' positions. The angle of attack of the electrophile and thus the dihedral angles as shown in **C1** and **C2** result tentatively from the electronic structures of the compounds. These possess the highest HOMO value at the terminal C-atoms of the allylsilane moieties (calculated with MacSpartanPlus under AM1 with a simplified molecule and a constrained dihedral angle C(1)–C(2)–C(3)–Si 90°), and the attack of the electrophiles would be expected to occur close to these positions. In the argumentation of *Houk* and co-workers, structure **C1** with the OH group in 'inside' position would then be preferred due to minimized electron withdrawal by the $\sigma^*$(C–OH) orbital from the already electron-deficient transition state, and in the logic of *Cieplak*, the same arrangement should be favored due to lesser repulsive interactions between the filled incipient $\sigma_+$ orbital and the filled $\sigma$(C–OH) and $\sigma$(C–$R^2$) orbitals in **C1**. For **C1**, the less donating $\sigma$(C–OH) orbital is more 'in line' with the $\sigma_+$ orbital than the $\sigma$(C–$R^2$) orbital and consequently should lead to lesser repulsive interaction. This arrangement is opposite for **C2**. The expectation that the electrophile would be connected to the OH group – either *via* transition-metal coordinations or by H-bonding – would additionally favor the arguments for the preferred 'inside' position of the OH group. To complete the argumentation, calculation of the conformational strains of ground-state structures related to **C1** and **C2** (MM2/Chem3D for **16a**) led to the suggestion that already the ground-state precursor of **C1** should be preferred by *ca.* 3 kJ/mol over the corresponding structure related to **C2**.

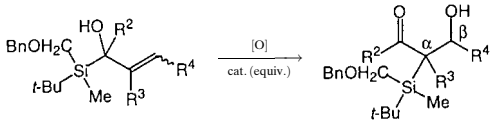

Fig. 1. *Comparison of the expected transition-state conformations of compound* **16a**/*[$O^+$] with the allylic Si–C bond close to* anti-*periplanar to the incipient σ-bond*

In the case of our $\alpha$-silylated allylic alcohols, the $\beta$-effect of the silyl group – a rather strong effect (see, *e.g.*, [16]) – is considered to determine the structure of the transition state, overcoming the 'dihedral preferences' of the various oxidizing reagents described in [17]. To efficiently stabilize the evolving carbocation (or partial carbocation in the case of epoxide formation) in $\beta$-position to the silyl group, the Si–C bond has to be aligned perpendicularly to the plane of the olefin (or parallel to the $\pi$ system). The two possible ground-state conformations **C1** and **C2** are shown in *Fig. 1*, and a preferred transition state related to **C1** would account for the observed stereoselectivity. In fact, such a transition state would be expected to be favored. It is readily recognized, by scrutinizing the structures, that an attack *anti* to the silyl group would be hindered for **C2** because of repulsive steric interactions of the reagent with the $R^2$ group; this is not the case for **C1**.

Exceptions with respect to the 'normal' stereochemical behavior of compounds of type **17** in the oxidation reactions were found when the transformations were performed with *t*-BuOOH and with higher than catalytic amounts of [Ti(i-PrO)$_4$] as the

*Lewis* acid: the more *Lewis* acid was used for the transformations, the less selective, with respect to the stereogenic C-atom of the starting compounds (or the more selective with respect to the Si-center of chirality), the reactions became. For instance, the treatment of a 1:1 mixture of **17e** and **17e′** with *t*-BuOOH and in presence of 0.1, 0.75, and 1.5 equiv. of [Ti(i-PrO)$_4$] afforded increasing amounts of the (*SiR**,*αR**)-configured product **19e** relative to the (*SiR**,*αS**)-configured stereoisomer **19e′** (62:38, 85:15, and 96:4, resp. *Table 2*, *Entries 34–36*). Similar results were obtained with **17a**/**17a′** and **17h**/**17h′** as the starting compounds (*Entries 17–19*, *23–25*, and *41–44*).

Table 2. *Oxidation of α-Silylated Allylic Alcohols* **17**

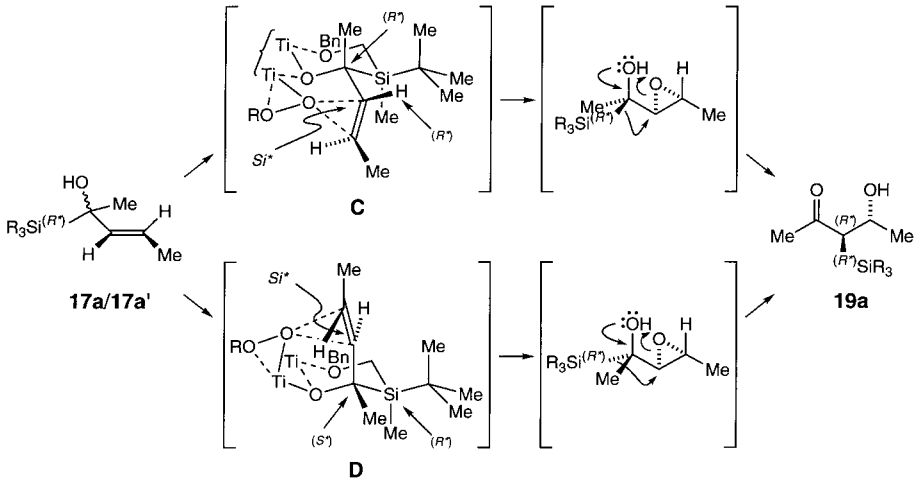



| *Entry* | Starting material | | | | | | Conditions | | | Product | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No.[a]) | $R^2$ | $R^3$ | $R^4$ | Double bond | d.r. (*l*/*u*) | [O] | catalyst | Equiv. | No.[a]) | C-Skeleton (*α*,*β*) | d.r. (Si,*α*: *l*/*u*) | Yield [%] |
| *17* | **17a** | Me | H | Me | (*E*) | 84:16 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 0.1 | **19a** | *anti* | 82:18 | 48 |
| *18* | **17a** | Me | H | Me | (*E*) | 84:16 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 0.5 | **19a** | *anti* | 85:15 | 60 |
| *19* | **17a** | Me | H | Me | (*E*) | 78:22 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 1.0 | **19a** | *anti* | 92:8 | 68 |
| *20* | **17a** | Me | H | Me | (*E*) | 87:13 | *t*-BuOOH | [VO(acac)$_2$] | 0.02 | **19a** | *anti* | 86:14 | 77 |
| *21* | **17a** | Me | H | Me | (*E*) | 78:22 | *t*-BuOOH | [VO(acac)$_2$] | 1.0 | **19a** | *anti* | 76:24 | 34 |
| *22* | **17a** | Me | H | Me | (*E*) | 93:7 | MCPBA | – | – | **19a** | *anti* | 91:9 | 93 |
| *23* | **17a′** | Me | H | Me | (*E*) | 16:84 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 0.1 | **19a′** | *anti* | 22:78 | 34 |
| *24* | **17a′** | Me | H | Me | (*E*) | 16:84 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 1.0 | **19a′** | *anti* | 23:77 | 83 |
| *25* | **17a′** | Me | H | Me | (*E*) | 19:81 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 3.0 | **19a** | *anti* | 100:0 | 11 |
| *26* | **17a′** | Me | H | Me | (*E*) | 13:87 | *t*-BuOOH | [VO(acac)$_2$] | 0.05 | **19a′** | *anti* | 13:87 | 87 |
| *27* | **17a′** | Me | H | Me | (*E*) | 16:84 | MCPBA | – | – | **19a′** | *anti* | 23:77 | 91 |
| *28* | **17b** | Me | H | Me | (*Z*) | 89:11 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 0.1–1.0 | **19b** | – | – | 0[b]) |
| *29* | **17b** | Me | H | Me | (*Z*) | 89:11 | *t*-BuOOH | [VO(acac)$_2$] | 0.02 | **19b** | – | – | 0[b]) |
| *30* | **17b** | Me | H | Me | (*Z*) | 85:15 | MCPBA | – | – | **19b** | *syn* | 82:18 | 80[c]) |
| *31* | **17b** | Me | H | Me | (*Z*) | 89:11 | DMD[d]) | – | – | **19b** | *syn* | 87:13 | 90[c]) |
| *32* | **17c** | Me | Me | Me | (*E*) | 87:13 | MCPBA | – | – | **19c** | *anti* | 84:16 | 67 |
| *33* | **17d** | Me | Me | Me | (*Z*) | 83:17 | MCPBA | – | – | **19d** | *syn* | 78:22 | 78 |
| *34* | **17e** | Bn | H | Me | (*E*) | 50:50 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 0.1 | **19e** | *anti* | 62:38 | 15 |
| *35* | **17e** | Bn | H | Me | (*E*) | 50:50 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 0.75 | **19e** | *anti* | 85:15 | 26 |
| *36* | **17e** | Bn | H | Me | (*E*) | 50:50 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 1.5 | **19e** | *anti* | 96:4 | 33 |
| *37* | **17e** | Bn | H | Me | (*E*) | 95:5 | MCPBA | – | – | **19e** | *anti* | 94:6 | 77 |
| *38* | **17e** | Bn | H | Me | (*E*) | 50:50 | MCPBA | – | – | **19e** | *anti* | 50:50 | 85 |
| *39* | **17f** | Bn | H | Me | (*Z*) | 56:44 | MCPBA | – | – | **19f** | – | – | 0[c]) |
| *40* | **17g** | Me | $-(CH_2)_4-$ | | (*E*) | 88:12 | MCPBA | – | – | **19g** | *anti* | 86:14 | 77 |
| *41* | **17h′** | Pr | H | Me | (*E*) | 32:68 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 0.1 | **19h′** | *anti* | 34:66 | 61 |
| *42* | **17h′** | Pr | H | Me | (*E*) | 37:63 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 0.75 | **19h′** | *anti* | 44:56 | 59 |
| *43* | **17h** | Pr | H | Me | (*E*) | 95:5 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 1.0 | **19h** | *anti* | 96:4 | 64 |
| *44* | **17h′** | Pr | H | Me | (*E*) | 37:63 | *t*-BuOOH | [Ti(i-PrO)$_4$] | 1.5 | **19h** | *anti* | 57:43 | 52 |
| *45* | **17h** | Pr | H | Me | (*E*) | 97:3 | MCPBA | – | – | **19h** | *anti* | 97:3 | 75 |
| *46* | **17i** | Pr | H | Me | (*Z*) | 73:27 | MCPBA | – | – | **19i** | *syn* | 77:23 | 80[c]) |

[a]) Number of the major diastereoisomer (racemate). [b]) Formation of BnOCH$_2$(*t*-Bu)MeSiOH (**25b**; 70–80%) and volatile and/or polymeric material. [c]) Yield of crude product; the product decomposed upon purification (elimination of $R_3SiOH$, see below). [d]) DMD = Dimethyldioxirane. [e]) Formation of BnOCH$_2$(*t*-Bu)MeSiOH (**25b**; 71%) and elimination product **24c** (75%), see below.

This behavior is tentatively explained by the increasing importance of intermediary bimetallic chelate structures of type **C** (for the (*SiR**,*R**)-configured starting materials **17**; shown for **17a**) and **D** (for the (*SiR**,*S**)-configured starting materials **17′**; shown for **17a′**) (*Scheme 5*). In both chelate structures, independent of the relative configurations of the stereogenic units, the C=C bonds should preferentially present their *Si**-faces to the oxidizing species. Epoxidations would thus lead to two distinguishable epimeric oxiranes that would finally form the same (*SiR**,*αR**)-configured product **19a** upon rearrangement because the differentiating stereogenic centers are lost in the final step of the transformations.

*Scheme 5*




It might be argued that chelate complexes would be preferred at low *Lewis*-acid concentrations, and, therefore, that increased stereoselectivities should be expected in the presence of catalytic rather than higher amounts of [Ti(i-PrO)$_4$]. Models show, however, that monometallic chelate complexes, which would have to be expected in presence of low amounts of *Lewis* acid, would not be prone to deliver oxygen to the double bond. The oxidizing moiety would be 'drawn away' from the double bond by complexation of the metal to both O-atoms of the starting material. Only bimetallic complexes, which are expected to be formed in presence of more *Lewis* acid, would be able to place a peroxide unit in suitable position for oxidation. Oxidation at low levels of metal catalyst are thus postulated to occur from monodentate non-chelate complexes, and oxidation at higher levels of the [Ti(i-PrO)$_4$] could be explained by intermediary bimetallic complexes of type **C** and **D**.

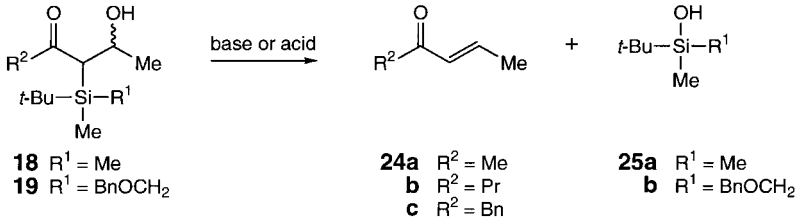
It is rather interesting to note that, out of two stereogenic centers in a molecule both apt to get strongly involved in the structure of a transition state, the more remote chirality center may dominate and control the overall stereochemical course of a reaction. This is only possible when the isolated directing effect of the more proximate chirality unit is not too strong. This seems to be the case in the oxidation reactions of $\alpha$-silylated allylic alcohols. For instance, the oxidations of the enantiomerically enriched compounds (−)-**16a** and (−)-**16b** (e.r. *ca.* 85:15) with *t*-BuOOH in presence of [Ti(i-PrO)$_4$] gave the optically active silylated aldols (−)-**18a** and (−)-**18b**[6]), respectively, in an e.r. of *ca.* 80:20. Thus, the stereoselectivities are not complete, and stereo-

[6]) The absolute configurations of (−)-**18a** and (−)-**18b** have not been determined, since we have not been able to prepare suitable crystalline derivatives thereof.

differentiations related to the stereogenic C-atoms are calculated to be *ca.* 90%. This corresponds to a $\Delta\Delta G^{\neq}$ of *ca.* 5.6 kJ/mol for the two diastereoisomeric transition states, an energy difference that is low enough to be overcome by other effects.

Various products of the type **18** and **19** strongly differ in their stabilities. Generally, the compounds **18** with the 'achiral' (*t*-Bu)$Me_2$Si group are more stable than the corresponding analogs of type **19** with the 'chiral' ($BnOCH_2$)(*t*-Bu)MeSi group, and the *α,β-anti* products arising from (*E*)-configured starting materials are much more stable than the *α,β-syn* analogs formed from the (*Z*)-configured isomers. Especially the differences in stability of the *α,β-syn* and *α,β-anti* products is striking: some of the *syn*-products (particularly those of type **19**) could be isolated as crude products only, others could not be captured at all. The decomposition of the silylated aldols **18** and **19** proceeded by a defined path, though, namely by elimination of the corresponding silanol units **25a** or **25b** under formation of aldol-condensation products of type **24** (*Scheme 6*). The elimination product formed from the benzyl ketones **18e**,**f** and **19e**,**f**, *i.e.*, the *α,β*-unsaturated ketone **24c**, was isolated (this compound was obtained in 75% yield after chromatography of the mixture arising from oxidation of **17f**); the more volatile compounds **24a**,**b** formed from starting ketones with $R^2 = Me$ or Pr were lost during workup and purification.

*Scheme 6*




**18** $R^1$ = Me
**19** $R^1$ = $BnOCH_2$

**24a** $R^2$ = Me
**b** $R^2$ = Pr
**c** $R^2$ = Bn

**25a** $R^1$ = Me
**b** $R^1$ = $BnOCH_2$

With the knowledge of the decomposition path of the compounds **18** and **19**, it is easily understood that the *syn*-configured aldols, particularly those with $R^3 = H$, loose more readily the silanol unit than the *anti*-configured analogs: the *syn*-configured substrates reach readily the ideal arrangement for the *Peterson* elimination (conformation **C3**, *Fig. 2*) [21]. The respective conformation for *anti*-configured molecules (**C4**) is more strained and thus less attractive. The increased stability of the (*t*-Bu)$Me_2$Si-substituted compounds as compared to the ($BnOCH_2$)(*t*-Bu)MeSi-substituted analogs is not clear. It is possible – and equally hypothetical – that the O-atom of the $BnOCH_2$ group acts intramolecularly as a weak base and accelerates the *Peterson* reaction. A similar effect was considered responsible for the increased reactivity of ($BnOCH_2$)(*t*-Bu)MeSi-substituted oxy-*Cope*-rearrangement precursors as compared to the respective (*t*-Bu)$Me_2$Si analogs [5].

With one exception, no additional new compounds apart from the silylated aldols of type **18** or **19**, and their elimination products, were found in the mixtures that were obtained by oxidation of the *α*-silylated allylic alcohols of type **16** and **17**: the reaction of **16g** with DMD afforded the 'overoxidized' product **26** along with the expected aldol **18g** (*Scheme 7*). The mechanism for the formation of **26** is not clear. We assume, however, that an allylic oxidation of the precursor **16g** is occurring prior to the 'normal' oxidative reaction cascade. This might be possible because the 'normal' oxidation of the

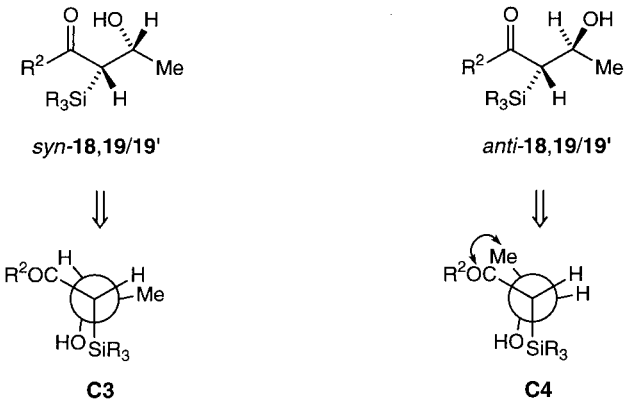
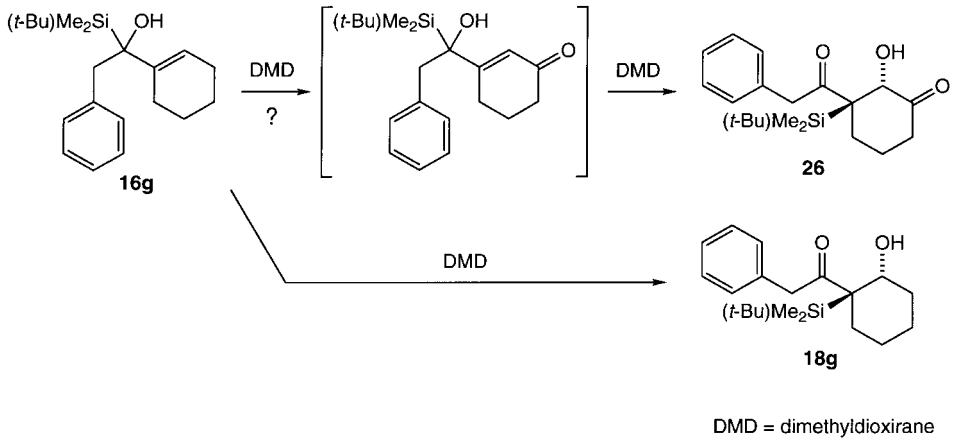



Fig. 2. *Comparison of the* syn-*periplanar conformations of* syn- *and* anti-*configured* α*-silylated aldols as required for the base-induced* Peterson *olefination*

alkene moiety of **16g** is retarded as compared to the respective reaction of the other investigated α-silylated allylic alcohols. That this is the case is illustrated by the reaction times that are necessary for complete consumption of the starting materials: the oxidation of **16g** with DMD and MCPBA needed 4.5 and 12 h, respectively; the corresponding reaction times needed for complete conversion of the other substrates were usually 40–90 min (DMD) or 1–2 h (MCPBA).

*Scheme 7*




We thank Prof. Dr. *M. Hesse* and Mr. *A. Guggisberg* for regular and helpful discussions, the members of our analytical laboratories, particularly Dr. *A. Linden* for the single-crystal X-ray analyses, for their excellent services, and the *Swiss National Science Foundation* for their generous financial support.

## Experimental Part

*General*. Unless otherwise stated: manipulations involving air- and $H_2O$-sensitive reagents were carried out under Ar in oven-dried glass equipment. For reactions, $Et_2O$ and THF were freshly distilled from Na with

benzophenone ketyl as indicator; benzene (anal. grade) was stored over Na. All org. solvents were distilled prior to use. Anh. $MgBr_2$ was prepared from 1,2-dibromoethane and Mg. All other starting materials were purchased from commercial sources and used as received. Solns. for workup procedures were prepared in deionized $H_2O$. Workup implies: dilution with sat. aq. $NH_4Cl$ soln., extraction with $Et_2O$, washing with brine until pH 7, and drying ($MgSO_4$) of the extracts prior to evaporation of the solvents *in vacuo*. Flash chromatography (FC): *Merck* silica gel 60 (40–63 μm). M.p.: *Mettler FP5*/*FP52*. IR Spectra: neat liquid films between NaCl plates; *Perkin-Elmer 297* or *781*; in $cm^{-1}$. $^1$H-NMR Spectra: in $CDCl_3$; *Bruker AC-300* (300 MHz), *ARX-300* (300 MHz), or *AMX-600* (600 MHz); $\delta$ in ppm rel. to $CHCl_3$ ($\delta$ 7.26), $J$ in Hz. $^{13}$C-NMR Spectra: in $CDCl_3$; *Bruker ARX-300* (75.5 MHz); $\delta$ in ppm rel. to $CDCl_3$ ($\delta$ 77.0); multiplicities from DEPT-135 and DEPT-90 experiments. Some spectra are not corrected (uncorr.) to chemical shifts rel. to the solvent due to overlapping signals. NMR Spectra of the compounds of type **17**/**17′** and **19**/**19′** were extracted from the corresponding spectra of mixtures; the d.r. were determined with the crude products. Chemical-ionization MS (CI-MS): *Finnigan MAT 90*, with $NH_3$ as the reactant gas; in $m/z$ (rel. %).

**1. Synthesis of the Starting α-Silylated Allylic Alcohols.** – 1.1. *Synthesis of Acylsilane Precursors.* 1.1.1. *(*tert*-Butyl)(1-ethoxyethenyl)dimethylsilane* (**10**). To a soln. of ethyl vinyl ether (4.7 ml, 49 mmol) in THF (30 ml) at −80°, *t*-BuLi (24 ml of a 1.56M soln. in pentane, 37 mmol) was added. The turbid mixture was allowed to warm to 0° over a period of 2 h (→ dark violet soln.). After recooling to −80°, a soln. of (*tert*-butyl)(chloro)dimethylsilane ((*t*-Bu)$Me_2$SiCl; 4.03 g, 32.9 mmol) in THF (10 ml) was added, the temp. was raised to 4° over a period of 2.5 h, and the dark blue mixture was kept at this temp. for 18 h. Workup led to volatile **10** (5.01 g, 26.9 mmol, 82%) as a slightly yellow liquid. This product was used for the next step without further purification. $^1$H-NMR: 4.62, 4.25 (2*d*, $J$ = 1.6, $CH_2$=); 3.69 (*q*, $J$ = 7.0, MeC$H_2$); 1.27 (*t*, $J$ = 7.0, *Me*$CH_2$); 0.91 (*s*, *t*-Bu); 0.07 (*s*, MeSi).

1.1.2. *[(Benzyloxy)methyl](*tert*-butyl)(1-ethoxyethenyl)methylsilane* (**11**) was described in [2].

1.1.3. *2-Benzyl-2-[(*tert*-butyl)dimethylsilyl]-1,3-dithiane* (**12b**). To a soln. of 2-benzyl-1,3-dithiane [22] (9.21 g, 43.8 mmol) in THF (100 ml) at −25°, BuLi (23 ml of a 2M soln. in pentane, 46 mmol) was added. After 5 h at −20°, the mixture was cooled to −70° and a soln. of (*t*-Bu)$Me_2$SiCl (6.35 g, 42.1 mmol) in THF (10 ml) was added. It was kept at −70° for 0.5 h, allowed to warm to 23° within 2.5 h (deeply red soln.), and stirred for another 15 h. Workup and FC (hexane → hexane/$Et_2O$ 16:1) afforded **12b** (13.30 g, 41.0 mmol, 97%). Yellowish oil. IR: 3080*w*, 3055*w*, 3020*m*, 2950*s*, 2920*s*, 2890*s*, 2850*s*, 2820*m*, 1945*w*, 1800*w*, 1600*w*, 1490*m*, 1470*s*, 1460*s*, 1450*s*, 1420*m*, 1390*m*, 1360*m*, 1270*m*, 1255*s*, 1245*s*, 1200*w*, 1165*w*, 1110*w*, 1075*m*, 1030*w*, 1005*m*, 925*s*, 910*m*, 895*m*, 845*s*, 830*s*, 820*s*, 810*s*, 770*s*, 735*s*, 700*s*, 660*s*. $^1$H-NMR: 7.66–7.60 (*m*, 2 arom. H); 7.35–7.24 (*m*, 3 arom. H); 3.43 (*s*, PhC$H_2$); 2.22–2.17, 1.76–1.57 (2*m*, $CH_2CH_2CH_2$); 1.10 (*s*, *t*-Bu); 0.21 (*s*, $Me_2$Si). $^{13}$C-NMR: 139.1 (*s*, arom. C); 131.4, 127.9 (2*d*, 2 × 2 arom. C); 126.7 (*d*, arom. C); 48.4 (*t*, Ph*C*$H_2$); 38.6 (*s*, SCS); 28.8 (*q*, *Me*$_3$C); 25.2 (*t*, 2 $SCH_2$); 23.3 (*t*, $SCH_2CH_2$); 20.1 (*s*, $Me_3C$); −6.5 (*q*, $Me_2$Si). CI-MS: 325 (100, $[M+H]^+$), 267(18), 233(56), 209(33), 177(28), 73(44). Anal. calc. for $C_{17}H_{28}S_2Si$ (324.614): C 62.90, H 8.69, S 19.75; found: C 62.76, H 8.00, S 19.92.

1.1.4. *2-Benzyl-2-{[(benzyloxy)methyl](*tert*-butyl)methylsilyl}-1,3-dithiane* (**13b**). According to *1.1.3*, the reaction of 2-benzyl-1,3-dithiane [22] (865 mg, 4.11 mmol) with BuLi (2.1 ml of a 2M soln. in pentane, 4.2 mmol) in THF (10 ml) and with [(benzyloxy)methyl](*tert*-butyl)(chloro)methylsilane [2] (991.7 mg, 3.86 mmol in THF (2 ml)) afforded, after FC (hexane/$Et_2O$ 60:1), **13b** (1258 mg, 2.92 mmol, 76%). Slightly yellow oil. IR: 3080*w*, 3055*m*, 3025*m*, 2950*s*, 2925*s*, 2890*s*, 2850*s*, 1940*w*, 1870*w*, 1800*w*, 1600*w*, 1490*m*, 1460*s*, 1450*s*, 1420*m*, 1390*m*, 1375*m*, 1360*m*, 1275*m*, 1250*m*, 1205*m*, 1165*w*, 1155*w*, 1105*m*, 1090*s*, 1070*s*, 1025*m*, 1005*m*, 980*w*, 925*m*, 910*m*, 845*m*, 825*s*, 785*s*, 770*s*, 735*s*, 700*s*. $^1$H-NMR (uncorr.): 7.50–7.47 (*m*, 2 arom. H); 7.22–7.14 (*m*, 8 arom. H); 4.38 (*s*, PhC$H_2$O); 3.41 (*s*, PhC$H_2$C); 3.40, 3.34 (*AB*, $J$ = 13.3, $SiCH_2$); 2.05–2.01 (*m*, 2 $SCH_2$); 1.59–1.39 (*m*, $SCH_2CH_2$); 1.04 (*s*, *t*-Bu); 0.16 (*s*, MeSi). $^{13}$C-NMR: 139.0 (*s*, 2 arom. C); 131.4, 128.1, 127.9, 127.5 (4*d*, 4 × 2 arom. C); 127.2, 126.7 (2*d*, 2 arom. C); 77.1 (*t*, Ph*C*$H_2$O); 60.4 (*t*, $SiCH_2$); 48.9 (*t*, Ph$CH_2$C); 38.1 (*s*, SCS); 29.1 (*q*, *Me*$_3$C); 25.3 (*t*, 2 $SCH_2$); 23.1 (*t*, $SCH_2CH_2$); 20.4 (*s*, $Me_3C$); −8.8 (*q*, MeSi). CI-MS: 448 (1, $[M+NH_4]^+$), 431 (43, $[M+H]^+$), 339(26), 325(100, $[M+H-PhCHO]^+$ [23]), 238(86), 209(73), 108(28), 91(45).

1.1.5. *2-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-2-propyl-1,3-dithiane* (**13c**). According to *1.1.3*, the reaction of 2-propyl-1,3-dithiane [22] (560 mg, 3.45 mmol) with BuLi (1.81 ml of a 2M soln. in pentane, 3.62 mmol) in THF (10 ml) and with [(benzyloxy)methyl](*tert*-butyl)(chloro)methylsilane [2] (800 mg, 3.12 mmol in THF (1 ml)) afforded, after FC (hexane/$Et_2O$ 50:1), **13c** (1084 mg, 2.83 mmol, 91%). Slightly yellow oil. IR: 3080*w*, 3055*w*, 3020*m*, 2950*s*, 2925*s*, 2900*s*, 2850*s*, 2730*w*, 2700*w*, 1945*w*, 1865*w*, 1800*w*, 1580*w*, 1490*w*, 1460*s*, 1420*m*, 1385*m*, 1375*m*, 1360*m*, 1295*w*, 1265*m*, 1250*s*, 1235*m*, 1200*w*, 1165*w*, 1090*s*, 1070*s*, 1025*m*, 1010*m*, 980*w*, 930*w*, 915*m*, 900*w*, 865*w*, 825*s*, 790*s*, 770*m*, 735*s*, 695*s*, 680*m*. $^1$H-NMR: 7.36–7.22 (*m*, 5 arom. H);

4.50, 4.49 (*AB*, $J = 12.3$, PhC$H_2$); 3.55, 3.52 (*AB*, $J = 13.2$, SiC$H_2$); 3.10–3.00 (symm. *m*, 2 H); 2.44–2.26 (*m*, 4 H); 2.06–1.81 (*m*, 2 H); 1.64–1.45 (*m*, 2 H); 1.10 (*s*, *t*-Bu); 0.94 (*t*, $J = 7.3$, *Me*C$H_2$); 0.28 (*s*, MeSi). $^{13}$C-NMR: 139.1 (*s*, arom. C); 128.1, 127.4 (2*d*, 2 × 2 arom. C); 127.1 (*d*, arom. C); 77.0 (*t*, PhC$H_2$); 60.4 (*t*, SiC$H_2$); 40.9 (*s*, SCS); 40.3 (*t*, MeC$H_2$C$H_2$); 28.5 (*q*, *Me*$_3$C); 24.9 (*t*, MeC$H_2$); 23.6, 23.5 (2*t*, 2 SC$H_2$); 21.2 (*t*, SC$H_2$C$H_2$); 20.0 (*s*, Me$_3$*C*); 14.3 (*q*, *Me*C$H_2$); −8.2 (*q*, MeSi). CI-MS: 383 (8, $[M+H]^+$), 277 (100, $[M+H-PhCHO]^+$ [23]), 161 (21). Anal. calc. for $C_{20}H_{34}OS_2Si$ (382.694): C 62.77, H 8.96, S 16.76; found: C 62.76, H 9.01, S 16.51.

1.2. *Synthesis of Acylsilanes.* 1.2.1. *Acetyl(*tert*-butyl)dimethylsilane* (**14a**). Crude **10** (5.01 g, 26.9 mmol, see *1.1.1*) in acetone (20 ml) was treated at 23° with aq. HCl soln. (10%, 5 ml) for 45 min, then NaOAc · 3 $H_2O$ (10.9 g, 80 mmol) and $H_2O$ (50 ml) were added, and the mixture was extracted with $Et_2O$. The combined org. layers were washed with sat. aq. NaCl soln., dried ($MgSO_4$), and carefully evaporated *in vacuo*. The residue was filtered through a plug of $SiO_2$ (pentane/$Et_2O$ 10 : 1) and yielded, after distillation (bulb-to-bulb, *ca.* 20 mbar, *ca.* 120°), **14a** (2.97 g, 18.8 mmol, 57% from chlorosilane). Slightly yellow oil. IR: 3260*w*, 2950*s*, 2925*s*, 2880*s*, 2850*s*, 2735*w*, 2710*w*, 1640*s*, 1465*s*, 1410*s*, 1365*s*, 1340*s*, 1260*s*, 1250*s*, 1135*s*, 1005*m*, 955*w*, 940*m*, 915*w*, 835*s*, 820*s*, 805*s*, 775*s*, 735*m*, 675*s*. $^1$H-NMR: 2.26 (*s*, *Me*CO); 0.92 (*s*, *t*-Bu); 0.17 (*s*, $Me_2$Si). $^{13}$C-NMR: 246.8 (*s*, CO); 37.5 (*q*, *Me*CO); 26.4 (*q*, *Me*$_3$C); 16.4 (*s*, Me$_3$*C*); −7.1 (*q*, $Me_2$Si).

1.2.2. *(*tert*-Butyl)dimethyl(phenylacetyl)silane* (**14b**). To a suspension of $HgCl_2$ (19.07 g, 70.2 mmol) and $CdCO_3$ (6.06 g, 35.1 mmol) in toluene/acetone/$H_2O$ (115/36/22 ml) at 23°, a soln. of **12b** (4.56 g, 14.0 mmol) in acetone (14 ml) was added. The mixture was refluxed for 1 h, filtered through a plug of $SiO_2$ (acetone/$Et_2O$ 1 : 1), and the solvent was evaporated *in vacuo*. FC (hexane/$Et_2O$ 50 : 1) afforded **14b** (2.11 g, 9.0 mmol, 64%). Yellow oil. IR: 3080*w*, 3055*m*, 3025*m*, 2950*s*, 2925*s*, 2880*s*, 2850*s*, 1940*w*, 1870*w*, 1800*w*, 1645*s*, 1630*s*, 1600*m*, 1580*m*, 1490*m*, 1460*s*, 1405*m*, 1390*m*, 1360*m*, 1290*m*, 1250*s*, 1175*m*, 1080*w*, 1030*m*, 1005*m*, 995*m*, 935*m*, 835*s*, 820*s*, 800*s*, 775*s*, 700*s*, 675*s*. $^1$H-NMR: 7.31–7.17 (*m*, 3 arom. H); 7.09–7.06 (*m*, 2 arom. H); 3.85 (*s*, PhC$H_2$); 0.89 (*s*, *t*-Bu); 0.13 (*s*, $Me_2$Si). $^{13}$C-NMR: 243.3 (*s*, CO); 133.1 (*s*, arom. C); 129.8, 128.5 (2*d*, 2 × 2 arom. C); 126.7 (*d*, arom. C); 56.6 (*t*, PhC$H_2$); 26.4 (*q*, *Me*$_3$C); 16.7 (*s*, Me$_3$*C*); −6.6 (*q*, $Me_2$Si). CI-MS: 252 (100, $[M+NH_4]^+$), 235 (27, $[M+H]^+$), 132 (24). Anal. calc. for $C_{14}H_{22}OSi$ (234.413): C 71.73, H 9.46; found: C 71.48, H 9.18.

1.2.3. *Acetyl[(Benzyloxy)methyl](*tert*-butyl)methylsilane* (**15a**) was described in [2].

1.2.4. *[(Benzyloxy)methyl](*tert*-butyl)methylsilane* (**15b**). According to *1.2.2*, the reaction of **13b** (1.25 g, 2.90 mmol) with $HgCl_2$ (3.96 g, 14.6 mmol) and $CdCO_3$ (1.26 g, 7.3 mmol) in toluene/acetone/$H_2O$ (24/10.5/3 ml) afforded, after FC (hexane/$Et_2O$ 30 : 1), **15b** (741.3 mg, 2.18 mmol, 75%). Slightly yellow oil. IR: 3080*w*, 3055*w*, 3025*m*, 2950*s*, 2925*s*, 2880*s*, 2850*s*, 2805*w*, 1945*w*, 1870*w*, 1800*w*, 1645*s*, 1630*s*, 1600*w*, 1580*w*, 1490*m*, 1460*m*, 1450*s*, 1430*w*, 1375*m*, 1360*m*, 1290*w*, 1250*m*, 1200*w*, 1175*w*, 1080*s*, 1070*s*, 1025*m*, 1005*w*, 995*w*, 935*w*, 905*w*, 825*s*, 775*s*, 735*s*, 695*s*. $^1$H-NMR: 7.39–7.13 (*m*, 8 arom. H); 7.07–7.05 (*m*, 2 arom. H); 4.48 (*s*, PhC$H_2$O); 3.93 (*s*, PhC$H_2$C); 3.40, 3.34 (*AB*, $J = 13.1$, SiC$H_2$); 0.94 (*s*, *t*-Bu); 0.19 (*s*, MeSi). $^{13}$C-NMR: 241.8 (*s*, CO); 138.3, 133.0 (2*s*, 2 arom. C); 129.9, 128.4, 128.3, 127.7 (4*d*, 4 × 2 arom. C); 127.6, 126.6 (2*d*, 2 arom. C); 77.3 (*t*, PhC$H_2$O); 59.5 (*t*, SiC$H_2$); 57.2 (*t*, PhC$H_2$C); 26.8 (*q*, *Me*$_3$C); 16.9 (*s*, Me$_3$*C*); −9.4 (*q*, MeSi). CI-MS: 358 (24, $[M+NH_4]^+$), 341 (57, $[M+H]^+$), 238 (100). Anal. calc. for $C_{21}H_{28}O_2Si$ (340.537): C 74.07, H 8.29; found: C 73.14, H 8.16.

1.2.5. *[(Benzyloxy)methyl](*tert*-butyl)methyl(1-oxobutyl)silane* (**15c**). According to *1.2.2*, the reaction of **13c** (1.65 g, 4.30 mmol) with $HgCl_2$ (7.98 g, 29.4 mmol) and $CdCO_3$ (2.54 g, 14.7 mmol) in toluene/acetone/$H_2O$ (35/15.5/4.5 ml) afforded, after FC (hexane/$Et_2O$ 30 : 1), **15c** (918 mg, 3.14 mmol, 73%). Slightly yellow oil. IR: 3080*w*, 3055*m*, 3025*m*, 2950*s*, 2925*s*, 2850*s*, 2805*m*, 2730*w*, 2710*w*, 1945*w*, 1865*w*, 1805*w*, 1635*s*, 1600*w*, 1585*w*, 1490*m*, 1460*s*, 1430*m*, 1385*m*, 1375*s*, 1360*s*, 1310*w*, 1300*w*, 1250*s*, 1200*m*, 1105*s*, 1090*s*, 1070*s*, 1025*m*, 1005*m*, 935*m*, 925*m*, 900*m*, 825*s*, 800*s*, 775*s*, 735*s*, 695*s*. $^1$H-NMR (uncorr.): 7.35–7.22 (*m*, 5 arom. H); 4.46 (*s*, PhC$H_2$); 3.41, 3.36 (*AB*, $J = 13.0$, SiC$H_2$); 2.60 (*t*, $J = 7.2$, MeC$H_2$C$H_2$); 1.57–1.45 (*sext.*-like *m*, MeC$H_2$); 0.94 (*s*, *t*-Bu); 0.84 (*t*, $J = 7.4$, *Me*C$H_2$); 0.20 (*s*, MeSi). $^{13}$C-NMR: 246.2 (*s*, CO); 138.4 (*s*, arom. C); 128.2, 127.6 (2*d*, 2 × 2 arom. C); 127.5 (*d*, arom. C); 77.3 (*t*, PhC$H_2$); 59.4 (*t*, SiC$H_2$); 53.0 (*t*, MeC$H_2$C$H_2$); 26.8 (*q*, *Me*$_3$C); 16.8 (*s*, Me$_3$*C*); 15.2 (*t*, MeC$H_2$); 13.8 (*q*, *Me*C$H_2$); −9.7 (*q*, MeSi). CI-MS: 293 ($[M+H]^+$).

1.3. *Addition of Vinyl Organometallic Reagents to the Acylsilanes.* 1.3.1. rac-*(*E*)- and* rac-*(Z)-2-[(*tert*-Butyl)dimethylsilyl]pent-3-en-2-ol* (**16a** and **16b**, resp.). A suspension of Li (with 2% Na, suspension (15%) in hexane, *Fluka*, *ca.* 80 mmol) in $Et_2O$ (17.5 ml) at 23° was treated with 1,2-dibromoethane (30 mg, activation of Li(Na)). The mixture was cooled to −10°, and a mixture of (*E*)- and (*Z*)-1-bromopropene (1.61 ml, 19.0 mmol, *Fluka*) was added dropwise. The suspension was kept at −10 to −5° for 1.5 h, excess Li was filtered off (glass filter), and the slightly red-violet filtrate was cooled to −80°. To this soln. of (*E*/*Z*)-prop-1-enyllithium, a soln. of **14a** (1.21 g, 7.64 mmol) in $Et_2O$ (2 ml) was added dropwise, the mixture was stirred for 1.5 h and then quenched at −80° with sat. aq. $NH_4Cl$ soln. Workup and FC (pentane/$Et_2O$ 25 : 1) afforded **16a** (387.1 mg, 1.93 mmol,

25%, second eluting isomer) and **16b** (1014.5 mg, 5.06 mmol, 66%, first eluting isomer) as slightly yellow oils. Total yield of **16a** and **16b**: 91%.

*Data of* **16a**: IR: 3460*m* (br.), 3015*m*, 2950*s*, 2925*s*, 2880*s*, 2850*s*, 2730*w*, 2705*w*, 1460*s*, 1410*m*, 1390*m*, 1375*m*, 1360*s*, 1305*m*, 1245*s*, 1160*m*, 1070*m*, 1030*m*, 1005*m*, 975*s*, 935*m*, 910*m*, 855*s*, 835*s*, 820*s*, 810*s*, 790*s*, 765*s*, 675*m*. $^1$H-NMR: 5.66, 5.41 (*AB* of $ABX_3$, $J_{AB}=15.4$, $J_{AX}=1.5$, $J_{BX}=6.4$, CH=CH); 1.71 (*dd*, $J=6.4$, 1.5, *Me*CH); 1.30 (*s*, *Me*C(OH)); 0.94 (*s*, *t*-Bu); 0.00, −0.01 (2*s*, $Me_2Si$). $^{13}$C-NMR: 138.6 (*d*, MeCH=CH); 119.6 (*d*, MeCH); 69.6 (*s*, SiC(OH)); 27.7 (*q*, $Me_3C$); 26.7 (*q*, *Me*C(OH)); 18.0 (*s*, $Me_3C$); 17.8 (*q*, *Me*CH); −7.7, −7.9 (2*q*, $Me_2Si$). CI-MS: 201 (17, $[M+H]^+$), 200 (100, $[M+NH_4-H_2O]^+$), 183 (66, $[M+H-H_2O]^+$), 176(39), 132(52).

*Data of* **16b**: IR: 3460*m* (br.), 3000*m*, 2950*s*, 2925*s*, 2890*s*, 2855*s*, 2710*w*, 1675*m*, 1640*m*, 1465*s*, 1405*m*, 1390*m*, 1375*m*, 1365*s*, 1255*s*, 1205*m*, 1150*m*, 1105*m*, 1070*m*, 1015*m*, 1005*m*, 950*m*, 940*m*, 895*m*, 835*s*, 820*s*, 805*s*, 770*s*, 735*s*, 700*s*, 670*s*. $^1$H-NMR: 5.39–5.26 (*m*, CH=CH); 1.87 (*d*, $J=5.6$, *Me*CH); 1.40 (*s*, *Me*C(OH)); 0.97 (*s*, *t*-Bu); 0.04, 0.035 (2*s*, $Me_2Si$). $^{13}$C-NMR: 136.4 (*d*, MeCH=*C*H); 121.6 (*d*, MeCH); 72.2 (*s*, SiC(OH)); 28.2 (*q*, *Me*C(OH)); 27.8 (*q*, $Me_3C$); 18.1 (*s*, $Me_3C$); 14.4 (*q*, *Me*CH); −7.48, −7.53 (2*q*, $Me_2Si$). CI-MS: 200 (100, $[M+NH_4-H_2O]^+$), 183 (69, $[M+H-H_2O)^+$), 176(27), 132(48).

1.3.2. *(−)-(*E*)- and (+)-(*Z*)-2-[(*tert*-Butyl)dimethylsilyl]pent-3-en-2-ol* ((−)-**16a** and (−)-**16b**, resp.). BuLi (2.5 ml, *ca.* 1.6M in hexane, *ca.* 4 mmol) was added dropwise at −80° to a soln. of (+)-(*R*)-1,1′-bi-2-naphthol (501.3 mg, 1.75 mmol) in THF (5 ml). After 5 min, (*E*/*Z*)-prop-1-enylmagnesium bromide (4 ml, 0.5M soln. in THF, 2 mmol) was added, and the mixture was stirred for 15 min. After cooling to −90°, **14a** (230.4 mg, 1.46 mmol) in THF (2.5 ml) was added over a period of 15 min, and the mixture was kept at −90° for 30 min. Workup and FC (pentane/$Et_2O$ 25 : 1) afforded (−)-**16a** (78.7 mg, 0.39 mmol, 27%, second eluting isomer) and (−)-**16b** (142 mg, 0.71 mmol, 49%, first eluting isomer) as slightly yellow oils. Total yield of (−)-**16a** and (−)-**16b**: 76%. Data of (−)-**16a** and (−)-**16b** are identical with those of the racemic material (see *1.3.1*) except for the chiroptical properties. $[\alpha]_D^{25}$ ((−)-**16a**; e.r. *ca.* 85 : 15): −22.0 ($c=1.0$, $CHCl_3$); $[\alpha]_D^{25}$ ((−)-**16b**; e.r. *ca.* 85 : 15): −2.3 ($c=3.0$, $CHCl_3$). The e.r. values were determined by $^1$H-NMR with the chiral shift reagent [Eu(hfbc)$_3$](hfbc = 3-(heptafluorobutanoyl)-(+)-camphor).

1.3.3. rac-*(*E*)- and* rac-*(*Z*)-2-[(*tert*-Butyl)dimethylsilyl]-3-methylpent-3-en-2-ol* (**16c** and **16d**, resp.). According to *1.3.1*, the reaction of (*E*/*Z*)-1-methylprop-1-enyllithium (prepared from a mixture of (*E*/*Z*)-2-bromobut-2-ene (0.78 ml, 7.6 mmol) and Li (2% Na, *ca.* 35 mmol)) in $Et_2O$ (5 ml); with **14a** (400 mg, 2.5 mmol in $Et_2O$ (2 ml)) at −60° for 1.5 h afforded, after FC (hexane/$Et_2O$ 50 : 1), **16c** (134.2 mg, 0.63 mmol, 25%, second eluting isomer) and **16d** (278.2 mg, 1.30 mmol, 51%, first eluting isomer) as colorless oils. Total yield of **16c** and **16d**: 76%.

*Data of* **16c**: IR: 3470*m* (br.), 3040*w*, 2950*s*, 2925*s*, 2885*s*, 2850*s*, 2730*w*, 2700*w*, 1640*m*, 1460*s*, 1410*m*, 1385*m*, 1375*m*, 1360*s*, 1335*m*, 1245*s*, 1135*m*, 1085*m*, 1065*m*, 1010*m*, 1005*m*, 935*m*, 885*m*, 835*s*, 805*s*, 765*s*, 675*s*. $^1$H-NMR: 5.45 (*qq*, $J=7.0$, 1.5, MeC*H*); 1.62–1.60 (*m*, *Me*CH, *Me*C=); 1.35 (*s*, *Me*C(OH)); 0.91 (*s*, *t*-Bu); 0.06, 0.03 (2*s*, $Me_2Si$). $^{13}$C-NMR: 142.7 (*s*, Me*C*=); 114.7 (*d*, Me*C*H); 72.8 (*s*, SiC(OH)); 27.3 (*q*, $Me_3C$); 26.7 (*q*, *Me*C(OH)); 26.4 (*q*, *Me*C=); 18.4 (*s*, $Me_3C$); 14.6 (*q*, *Me*CH); −5.9, −6.6 (2*q*, $Me_2Si$). CI-MS: 215 (16, $[M+H]^+$), 214 (63, $[M+NH_4-H_2O]^+$), 199(22), 197 (100, $[M+H-H_2O]^+$), 157(30), 144(33), 133(75), 116(27).

*Data of* **16d**: IR: 3560*m*, 3470*m* (br.), 2950*s*, 2925*s*, 2885*s*, 2850*s*, 2705*w*, 1635*w*, 1460*s*, 1410*m*, 1385*m*, 1375*s*, 1365*s*, 1275*m*, 1245*s*, 1200*m*, 1095*m*, 1065*m*, 1050*m*, 1030*m*, 1015*m*, 1005*m*, 935*m*, 885*s*, 830*s*, 805*s*, 765*s*, 670*s*. $^1$H-NMR: 5.20 (*qq*, $J=7.4$, 1.3, MeC*H*); 1.86 (*dq*, $J=7.4$, 1.4, *Me*CH); 1.65–1.63 (symm. *m*, *Me*C=); 1.44 (*s*, *Me*C(OH)); 1.14 (*s*, OH); 1.00 (*s*, *t*-Bu); 0.06, 0.05 (2*s*, $Me_2Si$). $^{13}$C-NMR: 140.8 (*s*, Me*C*=); 119.7 (*d*, Me*C*H); 74.9 (*s*, SiC(OH)); 27.8 (*q*, *Me*C(OH)); 27.7 (*q*, $Me_3C$); 24.1 (*q*, *Me*C=); 18.6 (*s*, $Me_3C$); 15.7 (*q*, *Me*CH); −5.85, −5.89 (2*q*, $Me_2Si$). CI-MS: 215 (21, $[M+H]^+$), 214 (59, $[M+NH_4-H_2O]^+$), 199(30), 197 (100, $[M+H-H_2O]^+$), 157(22), 144(26).

1.3.4. rac-*(*E*)- and* rac-*(*Z*)-2-[(*tert*-Butyl)dimethylsilyl]-1-phenylpent-3-en-2-ol* (**16e** and **16f**, resp.). According to *1.3.1*, the reaction of (*E*/*Z*)-prop-1-enyllithium (prepared from (*E*/*Z*)-1-bromoprop-1-ene (1.31 ml, 15.3 mmol) and Li (2% Na, *ca.* 70 mmol)) in $Et_2O$ (30 ml) with **14b** (1.20 g, 5.12 mmol in $Et_2O$ (2 ml)) at −80° for 1.5 h afforded, after FC (hexane/toluene 5 : 1), **16e** (456.2 mg, 1.65 mmol, 32%, second eluting isomer) and **16f** (616.4 mg, 2.23 mmol, 44%, first eluting isomer) as colorless oils. Total yield of **16e** and **16f**: 76%.

*Data of* **16e**: IR: 3525*m*, 3075*w*, 3050*w*, 3020*m*, 2950*s*, 2920*s*, 2780*s*, 2750*s*, 1600*w*, 1490*m*, 1465*m*, 1460*m*, 1450*m*, 1435*m*, 1410*w*, 1390*m*, 1375*w*, 1360*m*, 1315*m*, 1245*s*, 1220*m*, 1110*m*, 1090*w*, 1055*w*, 1030*w*, 1010*w*, 970*s*, 930*m*, 905*w*, 870*w*, 835*s*, 820*s*, 810*s*, 790*m*, 765*s*, 750*m*, 720*m*, 700*s*, 665*s*. $^1$H-NMR (uncorr.): 7.24–7.09 (*m*, 3 arom. H); 7.02–6.99 (*m*, 2 arom. H); 5.55, 5.00 (*AB* of $ABX_3$, $J_{AB}=15.4$, $J_{AX}=1.5$, $J_{BX}=6.5$, CH=CH); 2.91, 2.77 (*AB*, $J=13.1$, PhC$H_2$); 1.55 (*dd*, $J=6.5$, 1.5, *Me*CH); 0.91 (*s*, *t*-Bu); 0.00 (*s*, $Me_2Si$). $^{13}$C-NMR: 136.5

(*d*, MeCH=*C*H); 135.6 (*s*, arom. C); 130.8, 127.8 (2*d*, 2 × 2 arom. C); 126.3 (*d*, arom. C); 121.0 (*d*, Me*C*H); 71.5 (*s*, SiC(OH)); 44.0 (*t*, Ph*C*H$_2$); 27.8 (*q*, *Me*$_3$C); 18.2 (*s*, Me$_3$*C*); 17.6 (*q*, *Me*CH); −7.4, −7.7 (2*q*, Me$_2$Si). CI-MS: 294 (5, $[M+NH_4]^+$), 276 (25, $[M+NH_4-H_2O]^+$), 259 (93, $[M+H-H_2O]^+$), 219(100), 143(16), 132(57), 115(15), 90(44), 73(53).

*Data of* **16f**: IR: 3535*m*, 3080*w*, 3060*w*, 3020*m*, 2950*s*, 2925*s*, 2880*s*, 2850*s*, 1600*w*, 1490*m*, 1465*m*, 1460*m*, 1450*m*, 1400*m*, 1390*m*, 1360*m*, 1305*m*, 1245*s*, 1215*w*, 1105*m*, 1080*w*, 1030*m*, 1005*m*, 930*m*, 905*w*, 865*m*, 835*s*, 820*s*, 805*s*, 785*m*, 770*s*, 745*m*, 700*s*, 665*s*. $^1$H-NMR (uncorr.): 7.20–7.05 (*m*, 5 arom. H); 5.28, 5.20 (*AB* of *ABX*$_3$, $J_{AB}$ = 12.2, $J_{AX}$ = 1.3, $J_{BX}$ = 6.9, CH=CH); 2.85, 2.77 (*AB*, *J* = 13.1, PhC*H*$_2$); 1.46 (*dd*, *J* = 6.9, 1.3, *Me*CH); 0.92 (*s*, *t*-Bu); 0.01, 0.00 (2*s*, Me$_2$Si). $^{13}$C-NMR: 136.2 (*s*, arom. C); 134.1 (*d*, MeCH=*C*H); 130.6, 128.0 (2*d*, 2 × 2 arom. C); 126.5 (*d*, arom. C); 123.6 (*d*, Me*C*H); 74.7 (*s*, SiC(OH)); 44.7 (*t*, Ph*C*H$_2$); 28.0 (*q*, *Me*$_3$C); 18.4 (*s*, Me$_3$*C*); 13.9 (*q*, *Me*CH); −7.29, −7.32 (2*q*, Me$_2$Si). CI-MS: 294 (20, $[M+NH_4]^+$), 276 (23, $[M+NH_4-H_2O]^+$), 259 (99, $[M+H-H_2O]^+$), 219(17), 132(100).

1.3.5. rac-*1-[(*tert-*Butyl)dimethylsilyl]-1-(cyclohex-1-en-1-yl)-2-phenylethanol* (**16g**). According to *1.3.1*, the reaction of cyclohex-1-en-1-yllithium (prepared from 1-bromocyclohex-1-ene [24] (597 mg, 3.71 mmol) by treatment with *t*-BuLi (4.77 ml of a 1.56M soln. in pentane, 7.4 mmol) at −80° for 75 min) in pentane/Et$_2$O 1:2 (15 ml) with **14b** (436 mg, 1.86 mmol in Et$_2$O (2.5 ml)) at −80° to −50° (warm-up from −80 to −50° for 40 min, at −50° for 1.5 h) and in presence of LiClO$_4$ (610 mg, 5.73 mmol) afforded, after FC (hexane/Et$_2$O 100:1), **16g** (292 mg, 0.92 mmol, 50%) as a colorless oil, along with recovered **14b** (147 mg, 0.63 mmol, 34%). IR: 3520*m*, 3080*w*, 3060*m*, 3025*m*, 2925*s*, 2885*s*, 2850*s*, 2730*w*, 2700*w*, 1940*w*, 1800*w*, 1645*w*, 1600*w*, 1580*w*, 1490*m*, 1470*m*, 1460*s*, 1450*s*, 1410*m*, 1390*m*, 1360*m*, 1345*m*, 1305*m*, 1250*s*, 1215*m*, 1175*w*, 1155*w*, 1135*m*, 1120*w*, 1085*m*, 1075*m*, 1030*m*, 1015*m*, 1005*m*, 985*w*, 930*s*, 915*m*, 905*m*, 860*m*, 825*s*, 810*s*, 770*s*, 725*s*, 700*s*, 685*m*, 665*s*. $^1$H-NMR (uncorr.): 7.11–7.00 (*m*, 3 arom. H); 6.93–6.90 (*m*, 2 arom. H); 5.14–5.12 (*m*, CH=); 2.97, 2.74 (*AB*, *J* = 13.4, PhC*H*$_2$); 2.09–2.02 (*m*, 1 H); 1.89–1.73 (*m*, 3 H); 1.54–1.29 (*m*, 4 H); 0.81 (*s*, *t*-Bu); 0.00, −0.06 (2*s*, Me$_2$Si). $^{13}$C-NMR: 140.7 (*s*, *C*=CH); 135.4 (*s*, arom. C); 130.6, 127.9 (2*d*, 2 × 2 arom. C); 126.4 (*d*, arom. C); 119.6 (*d*, CH=); 73.4 (*s*, SiC(OH)); 41.4 (*t*, Ph*C*H$_2$); 27.5 (*q*, *Me*$_3$C); 27.4, 25.3, 23.0, 22.4 (4*t*); 18.8 (*s*, Me$_3$*C*); −5.6, −6.2 (2*q*, Me$_2$Si). CI-MS: 334 (21, $[M+NH_4]^+$), 316 (25, $[M+NH_4-H_2O]^+$), 299 (100, $[M+H-H_2O]^+$), 259(12), 183(12), 132(14).

1.3.6. *(*R*,R*,E)-, (*R*,S*,E)-, and (*R*,R*,Z)-2-{[(Benzyloxy)methyl](*tert-*butyl)methylsilyl}pent-3-en-2-ol* (**17a** and **17a′**, resp.) were described in [4].

1.3.7. *(*R*,R*,E)-, (*R*,S*,E)-, and (*R*,S*,Z)-2-{[(Benzyloxy)methyl](*tert-*butyl)methylsilyl}-3-methylpent-3-en-2-ol* (**17c**, **17c′**, **17d** and **17d′**, resp.). According to *1.3.1*, the reaction of (*E*/*Z*)-1-methylprop-1-enyllithium (prepared from (*E*/*Z*)-2-bromobut-2-ene (0.21 ml, 2.1 mmol) and Li (2% Na, *ca.* 20 mmol)) in Et$_2$O (4 ml) with **15b** (109.3 mg, 0.41 mmol) at −90 to −40° (1 h at −90°, warm-up to −40° for 1 h) and in presence of MgBr$_2$ (1.0 ml of a *ca.* 1M soln. in benzene/Et$_2$O 1:1, *ca.* 1.0 mmol) afforded, after FC (hexane/Et$_2$O 25:1), **17c**/**17c′** (38.4 mg, 0.12 mmol, 29%, second eluting isomers, d.r. 92:8) and **17d**/**17d′** (46.4 mg, 0.15 mmol, 35%, first eluting isomers, d.r. 88:12) as colorless oils. Total yield of **17c**/**17c′** and **17d**/**17d′**: 64%.

*Data of* **17c**/**17c′**: $^1$H-NMR (**17c**): 7.37–7.24 (*m*, 5 arom. H); 5.44–5.37 (*q*-like *m*, MeC*H*); 4.48 (*s*, PhC*H*$_2$); 3.40, 3.31 (*AB*, *J* = 12.6, SiCH$_2$); 3.09 (br. *s*, OH); 1.64–1.62 (*m*, *Me*CH); 1.60 (*s*, MeC=); 1.46 (*s*, *Me*C(OH)); 0.97 (*s*, *t*-Bu); 0.09 (*s*, MeSi). $^1$H-NMR (**17c′**): 7.37–7.24 (*m*, 5 arom. H); 5.63–5.56 (*q*-like *m*, MeC*H*); 4.51 (*s*, PhC*H*$_2$); 3.40, 3.28 (*AB*, *J* = 11.9, SiCH$_2$); 2.27 (br. *s*, OH); 1.64–1.62 (*m*, *Me*CH); 1.60 (*s*, MeC=); 1.38 (*s*, *Me*C(OH)); 0.95 (*s*, *t*-Bu); 0.05 (*s*, MeSi).

*Data of* **17d**/**17d′**: $^1$H-NMR (**17d**): 7.37–7.24 (*m*, 5 arom. H); 5.26 (*qq*, *J* = 7.3, 1.3, MeC*H*); 4.53, 4.44 (*AB*, *J* = 11.7, PhC*H*$_2$); 3.44, 3.37 (*AB*, *J* = 12.7, SiCH$_2$); 3.23 (br. *s*, OH); 1.82 (*dq*, *J* = 7.4, 1.4, *Me*CH); 1.68 (*t*-like *m*, *J* = 1.4, MeC=); 1.54 (*s*, *Me*C(OH)); 1.03 (*s*, *t*-Bu); 0.09 (*s*, MeSi). $^1$H-NMR (**17d′**): 7.37–7.24 (*m*, 5 arom. H); 5.20–5.09 (*q*-like *m*, MeC*H*); 4.50 (*s*, PhC*H*$_2$); 3.45, 3.30 (*AB*, *J* = 11.9, SiCH$_2$); 2.27 (br. *s*, OH); 1.91 (*dq*, *J* = 7.4, 1.3, *Me*CH); 1.64 (*t*-like *m*, *J* = 1.3, MeC=); 1.48 (*s*, *Me*C(OH)); 1.04 (*s*, *t*-Bu); −0.04 (*s*, MeSi). CI-MS: 321 (38, $[M+H]^+$); 303 (86, $[M+H-H_2O]^+$), 256(25), 238(70), 185(95), 173(100).

1.3.8. *(*R*,R*,E)-, (*R*,S*,E)-, (*R*,R*,Z)-, and (*R*,S*,Z)-2-{[(Benzyloxy)methyl](*tert-*butyl)methylsilyl}-1-phenylpent-3-en-2-ol* (**17e**, **17e′**, **17f**, and **17f′**, resp.). According to *1.3.1*, the reaction of (*E*/*Z*) prop-1-enyllithium (prepared from (*E*/*Z*)-1-bromoprop-1-ene (0.11 ml, 1.3 mmol) and Li (2% Na, *ca.* 6 mmol)) in Et$_2$O (3 ml) with **15b** (148 mg, 0.44 mmol) at −90 to −70° (40 min at −90°, 1 h at −80°, 1 h at −70°) and in presence of MgBr$_2$ (0.65 ml of a *ca.* 1M soln. in benzene/Et$_2$O 1:1, *ca.* 0.65 mmol) afforded, after FC (hexane/Et$_2$O 50:1), **17e**/**17e′** (77.9 mg, 0.20 mmol, 47%, second eluting isomers, d.r. 95:5) and **17f**/**17f′** (56.5 mg, 0.15 mmol, 34%, first eluting isomers, d.r. 88:12) as colorless oils. Total yield of **17e**/**17e′** and **17f**/**17f′**: 80%.

*Data of* **17e**/**17e′**: IR: 3515*m*, 3460*w* (br.), 3080*w*, 3055*m*, 3020*m*, 2950*s*, 2925*s*, 2880*s*, 2850*s*, 2810*m*, 1950*w*, 1875*w*, 1800*w*, 1710*w*, 1655*w*, 1600*w*, 1580*w*, 1490*m*, 1460*m*, 1450*m*, 1430*m*, 1385*m*, 1375*m*, 1360*m*, 1320*w*, 1245*m*,

1220*w*, 1200*w*, 1155*w*, 1105*m*, 1090*s*, 1065*s*, 1025*m*, 1005*m*, 970*s*, 930*m*, 900*m*, 870*w*, 825*s*, 805*m*, 780*m*, 760*m*, 745*s*, 730*s*, 695*s*, 680*m*. $^1$H-NMR (**17e**; uncorr.): 7.29–6.99 (*m*, 10 arom. H); 5.51, 5.09 (*AB* of *ABX*$_3$, $J_{AB}$ = 15.3, $J_{AX}$ = 6.5, $J_{BX}$ = 1.5, CH=CH); 4.40 (*s*, PhC$H_2$O); 3.34, 3.30/3.02, 2.85 (2*AB*, *J* = 12.7, 13.5, PhC$H_2$C, SiC$H_2$); 2.20 (*s*, OH); 1.52 (*dd*, *J* = 6.5, 1.5, *Me*CH); 0.96 (*s*, *t*-Bu); 0.00 (*s*, MeSi). $^1$H-NMR (**17e′**; uncorr.): 7.29–6.99 (*m*, 10 arom. H); 5.51, 5.12 (*AB* of *ABX*$_3$, $J_{AB}$ = 15.3, $J_{AX}$ = 6.5, $J_{BX}$ = 1.5, CH=CH); 4.35 (*s*, PhC$H_2$O); 3.37, 3.15/2.97, 2.78 (2*AB*, *J* = 12.7, 13.5, PhC$H_2$C, SiC$H_2$); 2.63 (*s*, OH); 1.53 (*dd*, *J* = 6.5, 1.5, *Me*CH); 0.92 (*s*, *t*-Bu); 0.03 (*s*, MeSi). $^{13}$C-NMR (**17e**): 138.3, 136.4 (2*s*, 2 arom. C); 135.4 (*d*, MeCH=*C*H); 130.7, 128.3, 127.7 (3*d*, 3 × 2 arom. C); 127.5 (*d*, 3 arom. C); 126.0 (*d*, arom. C); 121.5 (*d*, Me*C*H); 77.5 (*t*, Ph*C*H$_2$O); 72.0 (*s*, SiC(OH)); 60.8 (*t*, SiCH$_2$); 44.2 (*t*, PhCH$_2$C); 28.1 (*q*, *Me*$_3$C); 18.2 (*s*, Me$_3$*C*); 17.7 (*q*, *Me*CH); −10.1 (*q*, MeSi). $^{13}$C-NMR (**17e′**): 138.2, 136.6 (2*s*, 2 arom. C); 135.6 (*d*, MeCH=*C*H); 130.8, 128.3, 127.8 (3*d*, 3 × 2 arom. C); 127.5 (*d*, 3 arom. C); 126.0 (*d*, arom. C); 121.2 (*d*, Me*C*H); 77.5 (*t*, Ph*C*H$_2$O); 72.3 (*s*, SiC(OH)); 60.8 (*t*, SiCH$_2$); 44.4 (*t*, PhCH$_2$C); 28.0 (*q*, *Me*$_3$C); 18.2 (*s*, Me$_3$*C*); 17.7 (*q*, *Me*CH); −9.7 (*q*, MeSi). CI-MS: 400 (2, $[M+NH_4]^+$), 383 (9, $[M+H]^+$), 365 (5, $[M+H-H_2O]^+$), 238 (100).

*Data of* **17f**/**17f′**: IR: 3530*m*, 3470*m* (br.), 3080*m*, 3060*m*, 3025*m*, 3000*m*, 2925*s*, 2880*s*, 2850*s*, 2810*m*, 2735*w*, 2710*w*, 1945*w*, 1870*w*, 1850*w*, 1640*w*, 1600*w*, 1580*w*, 1490*m*, 1460*m*, 1450*s*, 1430*m*, 1405*m*, 1375*m*, 1360*m*, 1310*m*, 1250*s*, 1210*m*, 1175*w*, 1155*w*, 1105*m*, 1085*s*, 1065*s*, 1025*m*, 1010*m*, 930*m*, 905*m*, 865*m*, 825*s*, 805*s*, 785*s*, 770*s*, 740*s*, 695*s*. $^1$H-NMR (**17f**; uncorr.): 7.22–7.02 (*m*, 10 arom. H); 5.20–5.07 (*m*, CH=CH); 4.36, 4.32 (*AB*, *J* = 11.8, PhC$H_2$O); 3.34, 3.29/2.95, 2.80 (2*AB*, *J* = 12.6, 13.4, PhC$H_2$C, SiC$H_2$); 2.4 (br. *s*, OH); 1.44 (*d*, *J* = 5.4, *Me*CH); 0.91 (*s*, *t*-Bu); 0.00 (*s*, MeSi). $^1$H-NMR (**17f′**; uncorr.): 7.22–7.02 (*m*, 10 arom. H); 5.20–5.07 (*m*, CH=CH); 4.34, 4.32 (*AB*, *J* = 12.0, PhC$H_2$O); 3.35, 3.18/2.90, 2.74 (2*AB*, *J* = 12.8, 13.4, PhC$H_2$C, SiC$H_2$); 2.4 (br. *s*, OH); 1.40 (*d*, *J* = 5.7, *Me*CH); 0.91 (*s*, *t*-Bu); −0.02 (*s*, MeSi). $^{13}$C-NMR (**17f**): 138.2, 137.2 (2*s*, 2 arom. C); 132.9 (*d*, MeCH=*C*H); 130.6 (*d*, 2 arom. C); 128.3 (*d*, 3 arom. C); 127.8, 127.6 (2*d*, 2 × 2 arom. C); 126.1 (*d*, arom. C); 123.8 (*d*, Me*C*H); 77.6 (*t*, Ph*C*H$_2$O); 75.4 (*s*, SiC(OH)); 61.1 (*t*, SiCH$_2$); 44.9 (*t*, PhCH$_2$C); 28.2 (*q*, *Me*$_3$C); 18.3 (*s*, Me$_3$*C*); 14.0 (*q*, *Me*CH); −9.7 (*q*, MeSi). $^{13}$C-NMR (**17f′**): 138.2, 137.1 (2*s*, 2 arom. C); 133.1 (*d*, MeCH=*C*H); 130.7 (*d*, 2 arom. C); 128.3 (*d*, 3 arom. C); 127.8, 127.6 (2*d*, 2 × 2 arom. C); 126.1 (*d*, arom. C); 123.4 (*d*, Me*C*H); 77.6 (*t*, Ph*C*H$_2$O); 75.4 (*s*, SiC(OH)); 61.0 (*t*, SiCH$_2$); 44.7 (*t*, PhCH$_2$C); 28.1 (*q*, *Me*$_3$C); 18.5 (*s*, Me$_3$*C*); 14.0 (*q*, *Me*CH); −9.4 (*q*, MeSi). CI-MS: 383 (1, $[M+H]^+$), 365 (1, $[M+H-H_2O]^+$), 238 (100).

1.3.9. *(*R*,R*)- and (*R*,S*)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-(cyclohex-1-en-1-yl)ethanol* (**17g** and **17g′**, resp.). According to *1.3.1*, the reaction of cyclohex-1-en-1-yllithium (prepared at −80° from 1-bromocyclohex-1-ene [24] (273 mg, 1.70 mmol) and *t*-BuLi (2.19 ml of a 1.56M soln. in pentane, 3.4 mmol)) in pentane/Et$_2$O (2.2/7.2 ml) with **15a** (226.0 mg, 0.86 mmol in Et$_2$O (2.5 ml)) at −90 to −45° (60 min at −90°, warm-up −90 to −45° for 1 h) and in presence of MgBr$_2$ (2.2 ml of a *ca.* 1M soln. in benzene/Et$_2$O 1:1, *ca.* 2.2 mmol) afforded, after FC (hexane/CH$_2$Cl$_2$ 1:1 followed by hexane/AcOEt 20:1), **17g**/**17g′** (263.7 mg, 0.76 mmol, 89%, d.r. 88:12). Slightly yellow oil. IR: 3460*m* (br.), 3085*w*, 3060*m*, 3030*m*, 2930*s*, 2890*s*, 2850*s*, 2730*w*, 2710*w*, 1950*w*, 1870*w*, 1800*w*, 1725*w*, 1640*w*, 1495*w*, 1460*m*, 1450*m*, 1405*w*, 1380*m*, 1365*m*, 1300*w*, 1270*m*, 1250*m*, 1205*m*, 1175*w*, 1155*m*, 1140*m*, 1090*s*, 1070*s*, 1030*m*, 1015*m*, 1005*m*, 980*w*, 950*w*, 920*m*, 890*m*, 860*m*, 825*s*, 780*m*, 765*m*, 735*s*, 700*s*, 675*m*. $^1$H-NMR (**17g**; uncorr.): 7.30–7.17 (*m*, 5 arom. H); 5.49–5.46 (*m*, CH=); 4.40 (*s*, PhC$H_2$); 3.32, 3.25 (*AB*, *J* = 12.5, SiC$H_2$); 3.07 (*s*, OH); 1.99–1.91 (*m*, 4 H); 1.62–1.34 (*m*, 4 H); 1.37 (*s*, *Me*C(OH)); 0.91 (*s*, *t*-Bu); 0.00 (*s*, MeSi). $^1$H-NMR (**17g′**; uncorr.): 7.30–7.17 (*m*, 5 arom. H); 5.66–5.62 (*m*, CH=); 4.43 (*s*, PhC$H_2$); 3.40, 3.28 (*AB*, *J* = 12.6, SiC$H_2$); 3.07 (*s*, OH); 1.99–1.91 (*m*, 4 H); 1.62–1.34 (*m*, 4 H); 1.29 (*s*, *Me*C(OH)); 0.90 (*s*, *t*-Bu); −0.04 (*s*, MeSi). $^{13}$C-NMR (**17g**): 143.2 (*s*, *C*=CH); 138.0 (*s*, arom. C); 128.3, 127.8 (2*d*, 2 × 2 arom. C); 127.6 (*d*, arom. C); 119.1 (*d*, CH=); 77.6 (*t*, Ph*C*H$_2$); 72.1 (*s*, SiC(OH)); 61.6 (*t*, SiCH$_2$); 27.9 (*q*, *Me*$_3$C); 26.2 (*t*); 25.5 (*q*, *Me*C(OH)); 25.4, 23.1, 22.4, (3*t*); 18.3 (*s*, Me$_3$*C*); −8.9 (*q*, MeSi). $^{13}$C-NMR (**17g′**): 142.3 (*s*, *C*=CH); 137.8 (*s*, arom. C); 128.3, 127.8 (2*d*, 2 × 2 arom. C); 127.6 (*d*, arom. C); 118.3 (*d*, CH=); 77.6 (*t*, Ph*C*H$_2$); 72.0 (*s*, SiC(OH)); 61.7 (*t*, SiCH$_2$); 27.5 (*q*, *Me*$_3$C); 26.5 (*q*, *Me*C(OH)); 26.2; 25.3, 23.1, 22.4, (4*t*); 18.3 (*s*, Me$_3$*C*); −7.8 (*q*, MeSi). CI-MS: 346 (21, $[M+NH_4-H_2O]^+$), 329 (93, $[M+H-H_2O]^+$), 238 (48), 216 (17), 199 (100), 148 (14).

1.3.10. *(*R*,R*,E)-, (*R*,S*,E)-, (*R*,R*,Z)-, and (*R*,S*,Z*)-4-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}hept-2-en-4-ol* (**17h**, **17h′**, **17i**, and **17i′**, resp.). According to *1.3.1*, the reaction of (*E*/*Z*)-prop-1-en-1-yllithium (prepared from (*E*/*Z*)-1-bromoprop-1-ene (0.18 ml, 2.11 mmol) and Li (2% Na, *ca.* 20 mmol)) in Et$_2$O (5 ml) with **15c** (208.3 mg, 0.71 mmol, in Et$_2$O (1 ml)) at −90 to −40° (45 min at −90°, warm-up −90 to −40° for 1 h) and in presence of MgBr$_2$ (1.1 ml of a *ca.* 1M soln. in benzene/Et$_2$O 1:1, *ca.* 1.1 mmol) afforded, after FC (hexane/Et$_2$O 25:1), **17h**/**17h′** (108.1 mg, 0.32 mmol, 45%, second eluting isomers, d.r. 97:3) and **17i**/**17i′** (109.3 mg, 0.33 mmol, 46%, first eluting isomers, d.r. 81:19) as colorless oils. Total yield of **17h**/**17h′** and **17i**/**17i′**: 91%.

*Data of* **17h**/**17h′**: IR: 3480*m* (br.), 3080*w*, 3060*w*, 3025*m*, 2955*s*, 2925*s*, 2850*s*, 2810*m*, 2720*w*, 1950*w*, 1870*w*, 1800*w*, 1700*w*, 1600*w*, 1490*m*, 1460*m*, 1450*m*, 1430*m*, 1405*m*, 1385*m*, 1375*m*, 1360*m*, 1300*m*, 1255*s*, 1200*m*, 1150*m*, 1085*s*, 1065*s*, 1025*s*, 1015*s*, 970*s*, 920*m*, 900*m*, 870*m*, 820*s*, 800*s*, 765*m*, 735*s*, 695*s*, 680*m*. $^1$H-NMR (**17h**; $C_6D_6$; uncorr.): 7.25–7.21 (*m*, 3 arom. H); 7.16–7.13 (*m*, 1 arom. H); 7.09–7.05 (*m*, 1 arom. H); 5.64, 5.52 (*AB* of *ABX*$_3$, $J_{AB}$ = 15.3, $J_{AX}$ = 6.4, $J_{BX}$ = 1.5, CH=CH); 4.23, 4.22 (*AB*, *J* = 11.8, PhC*H*$_2$); 3.33, 3.27 (*AB*, *J* = 12.5, SiCH$_2$); 2.70 (*s*, OH); 1.93–1.88 (*m*, 1 H); 1.69 (*dd*, *J* = 6.4, 1.5, *Me*CH); 1.68–1.61 (*m*, 2 H); 1.48–1.37 (*m*, 1 H); 1.06 (*s*, *t*-Bu); 0.96 (*t*, *J* = 7.3, *Me*CH$_2$); 0.10 (*s*, MeSi). $^1$H-NMR (**17h′**; $C_6D_6$; uncorr.): 7.25–7.21 (*m*, 3 arom. H); 7.16–7.13 (*m*, 1 arom. H); 7.09–7.05 (*m*, 1 arom. H); 5.65, 5.52 (*AB* of *ABX*$_3$, $J_{AB}$ = 15.3, $J_{AX}$ = 6.4, $J_{BX}$ = 1.5, CH=CH); 4.22, 4.20 (*AB*, *J* = 11.8, PhC*H*$_2$); 3.36, 3.23 (*AB*, *J* = 12.5, SiCH$_2$); 2.91 (*s*, OH); 1.85–1.80 (*m*, 1 H); 1.69 (*dd*, *J* = 6.4, 1.5, *Me*CH); 1.60–1.53 (*m*, 2 H); 1.48–1.37 (*m*, 1 H); 1.07 (*s*, *t*-Bu); 0.96 (*t*, *J* = 7.3, *Me*CH$_2$); 0.06 (*s*, MeSi). $^{13}$C-NMR (**17h**): 137.9 (*s*, arom. C); 135.4 (*d*, MeCH=*C*H); 128.4, 127.8 (2*d*, 2 × 2 arom. C); 127.7 (*d*, arom. C); 121.1 (*d*, Me*C*H); 77.6 (*t*, Ph*C*H$_2$); 72.8 (*s*, SiC(OH)); 61.1 (*t*, SiCH$_2$); 40.8 (*t*, MeCH$_2$*C*H$_2$); 28.1 (*q*, *Me*$_3$C); 18.0 (*s*, Me$_3$*C*); 17.9 (*q*, *Me*CH); 15.7 (*t*, Me*C*H$_2$); 14.7 (*q*, *Me*CH$_2$); −10.1 (*q*, MeSi). $^{13}$C-NMR (**17h′**): 137.9 (*s*, arom. C); 135.8 (*d*, MeCH=*C*H); 128.4, 127.8 (2*d*, 2 × 2 arom. C); 127.7 (*d*, arom. C); 120.6 (*d*, Me*C*H); 77.6 (*t*, Ph*C*H$_2$); 72.7 (*s*, SiC(OH)); 61.0 (*t*, SiCH$_2$); 40.4 (*t*, MeCH$_2$*C*H$_2$); 28.0 (*q*, *Me*$_3$C); 18.0 (*s*, Me$_3$*C*); 17.9 (*q*, *Me*CH); 15.2 (*t*, Me*C*H$_2$); 14.7 (*q*, *Me*CH$_2$); −9.8 (*q*, MeSi). Interpretation supported by $^1$H/$^{13}$C-HSQC. CI-MS: 334 (2, $[M + NH_4 - H_2O]^+$), 317 (1, $[M + H - H_2O]^+$), 238 (100).

*Data of* **17i**/**17i′**: IR: 3480*s*, 3080*w*, 3060*w*, 3025*m*, 3000*m*, 2950*s*, 2925*s*, 2900*s*, 2850*s*, 2810*m*, 2730*w*, 2710*w*, 1950*w*, 1870*w*, 1800*w*, 1645*w*, 1585*w*, 1490*m*, 1460*s*, 1450*s*, 1430*m*, 1400*m*, 1390*m*, 1375*s*, 1360*s*, 1300*m*, 1275*w*, 1245*s*, 1205*m*, 1150*m*, 1085*s*, 1065*s*, 1025*m*, 995*s*, 940*m*, 900*m*, 870*w*, 850*m*, 825*s*, 800*s*, 785*s*, 765*s*, 745*s*, 715*s*, 695*s*, 680*m*. $^1$H-NMR (**17i**; uncorr.): 7.27–7.15 (*m*, 5 arom. H); 5.30, 5.06 (*AB* of *ABX*$_3$, $J_{AB}$ = 12.1, $J_{AX}$ = 7.2, $J_{BX}$ = 1.6, CH=CH); 4.44, 4.34 (*AB*, *J* = 11.8, PhC*H*$_2$); 3.39, 3.28 (*AB*, *J* = 12.5, SiCH$_2$); 3.13 (br. *s*, OH); 1.78 (*dd*, *J* = 7.2, 1.6, *Me*CH); 1.68–1.39, 1.36–1.21 (2*m*, CH$_2$CH$_2$); 0.88 (*s*, *t*-Bu); 0.81 (*t*, *J* = 7.2, *Me*CH$_2$); 0.00 (*s*, MeSi). $^1$H-NMR (**17i′**; uncorr.): 7.27–7.15 (*m*, 5 arom. H); 5.26, 5.13 (*AB* of *ABX*$_3$, $J_{AB}$ = 12.1, $J_{AX}$ = 7.2, $J_{BX}$ = 1.6, CH=CH); 4.44, 4.34 (*AB*, *J* = 11.8, PhC*H*$_2$); 3.39, 3.26 (*AB*, *J* = 12.5, SiCH$_2$); 3.13 (br. *s*, OH); 1.76 (*dd*, *J* = 7.2, 1.6, *Me*CH); 1.68–1.39, 1.36–1.21 (2*m*, CH$_2$CH$_2$); 0.91 (*s*, *t*-Bu); 0.80 (*t*, *J* = 7.2, *Me*CH$_2$); −0.05 (*s*, MeSi). $^{13}$C-NMR (**17i**): 137.9 (*s*, arom. C); 133.3 (*d*, MeCH=*C*H); 128.4, 127.8 (2*d*, 2 × 2 arom. C); 127.7 (*d*, arom. C); 123.1 (*d*, Me*C*H); 77.7 (*t*, Ph*C*H$_2$); 76.1 (*s*, SiC(OH)); 61.5 (*t*, SiCH$_2$); 41.9 (*t*, MeCH$_2$*C*H$_2$); 28.2 (*q*, *Me*$_3$C); 18.0 (*s*, Me$_3$*C*); 16.0 (*t*, Me*C*H$_2$); 14.7, 14.3 (2*q*, *Me*CH, *Me*CH$_2$); −9.7 (*q*, MeSi). $^{13}$C-NMR (**17i′**): 137.9 (*s*, arom. C); 133.6 (*d*, MeCH=*C*H); 128.4, 127.8 (2*d*, 2 × 2 arom. C); 127.7 (*d*, arom. C); 122.1 (*d*, Me*C*H); 77.7 (*t*, Ph*C*H$_2$); 75.8 (*s*, SiC(OH)); 61.4 (*t*, SiCH$_2$); 41.3 (*t*, MeCH$_2$*C*H$_2$); 28.1 (*q*, *Me*$_3$C); 18.2 (*s*, Me$_3$*C*); 15.4 (*t*, Me*C*H$_2$); 14.7, 14.3 (2*q*, *Me*CH, *Me*CH$_2$); −9.5 (*q*, MeSi). CI-MS: 334 (1, $[M + NH_4 - H_2O]^+$), 317 (1, $[M + H - H_2O]^+$), 238 (100).

**2. Reactions Summarized in *Tables 1* and *2*. –** 2.1. *General Procedures and Results. Procedure A with MCPBA*. To a soln. of α-silylated allylic alcohol in $CH_2Cl_2$ (0.1–0.15M) at 0°, an aq. soln. of $NaHCO_3$ (0.5M, 1.5 equiv.) and MCPBA (70%) were added. The mixture was stirred for 20 min to 12 h, sat. aq. $NaHCO_3$ soln. was added, and the mixture was extracted with $Et_2O$. Workup and FC afforded the products according to *Tables 1* and *2* and as described below.

*Procedure B with* t-*BuOOH/[Ti(i-PrO)*$_4$*]*. To a soln. of α-silylated allylic alcohol in benzene (0.08–0.12M) at 23° [Ti(i-PrO)$_4$] and, after 15–20 min, dropwise a soln. of *t*-BuOOH in toluene (3M) was added. The mixture was stirred for 15 min to 21 h before sat. aq. $NH_4Cl$ soln. was added. Workup and FC afforded the products according to *Tables 1* and *2* and as described below.

*Procedure C with* t-*BuOOH/[VO(acac)*$_2$*]* [25]. To a soln. of α-silylated allylic alcohol in benzene (0.1–0.15M) at 23°, [VO(acac)$_2$](vanadyl acetylacetonate) was added. To the resulting green mixture, a soln. of *t*-BuOOH in toluene (3M) was added dropwise, and the color turned red. The mixture was stirred for 25 min to 4 h, and sat. aq. $NH_4Cl$ soln. was added. Workup and FC afforded the products according to *Tables 1* and *2* and as described below.

*Procedure D with Dimethyldioxirane* (DMD). To neat α-silylated allylic alcohol at 0°, a soln. of DMD in acetone [26] (*ca*. 0.08M) was added. The mixture was stirred for 40 min to 4.5 h, concentrated *in vacuo*, dissolved in acetone/$Et_2O$ 1:1, and filtered over a plug of $MgSO_4$. FC afforded the products according to *Tables 1* and *2* and as described below.

*Entry 1*. According to *Procedure B*, the reaction of **16a** (77.0 mg, 0.38 mmol) with *t*-BuOOH (0.57 mmol) in presence of [Ti(i-PrO)$_4$] (0.38 mmol, 1.0 equiv.) for 20 min afforded, after FC (hexane/$Et_2O$ 2:1), **18a** (58.0 mg, 0.27 mmol, 70%).

*Entry 2*. According to *Procedure C*, the reaction of **16a** (70.8 mg, 0.35 mmol) with *t*-BuOOH (0.54 mmol) in presence of [VO(acac)$_2$] (2.0 mg, 0.0075 mmol) for 4 h afforded, after FC (hexane/$Et_2O$ 2:1), **18a** (53.0 mg, 0.25 mmol, 69%).

*Entry 3*. According to *Procedure A*, the reaction of **16a** (76.0 mg, 0.38 mmol) with MCPBA (122 mg, 0.49 mmol) for 1 h afforded, after FC (hexane/$Et_2O$ 2:1), **18a** (56.9 mg, 0.26 mmol, 69%).

*Entry 4*. According to *Procedure D*, the reaction of **16a** (63.0 mg, 0.31 mmol) with DMD (*ca*. 0.6 mmol) for 1.5 h afforded, after FC (hexane/$Et_2O$ 2:1), **18a** (44.3 mg, 0.21 mmol, 65%).

*Entry 5*. According to *Procedure B*, the reaction of (−)-**16a** (48.0 mg, 0.24 mmol, e.r. *ca*. 85:15) with *t*-BuOOH (0.36 mmol) in presence of [Ti(i-PrO)$_4$] (0.24 mmol, 1.0 equiv.) for 20 min afforded, after FC (hexane/$Et_2O$ 2:1), (−)-**18a** (35.2 mg, 0.16 mmol, 68%, e.r. *ca*. 80:20, $[\alpha]_D^{25}$: − 102.6 ($c = 0.5$, $CHCl_3$)).

*Entry 6*. According to *Procedure B*, the reaction of **16b** (89.8 mg, 0.45 mmol) with *t*-BuOOH (0.67 mmol) in presence of [Ti(i-PrO)$_4$] (0.45 mmol, 1.0 equiv.) for 20 min afforded, after FC (hexane/$Et_2O$ 2:1), **18b** (53.3 mg, 0.25 mmol, 55%).

*Entry 7*. According to *Procedure C*, the reaction of **16b** (81.2 mg, 0.41 mmol) with *t*-BuOOH (0.60 mmol) in presence of [$VO(acac)_2$] (2.1 mg, 0.008 mmol) for 4 h afforded, after FC (hexane/$Et_2O$ 2:1), **18b** (52.6 mg, 0.24 mmol, 60%).

*Entry 8*. According to *Procedure A*, the reaction of **16b** (88.0 mg, 0.44 mmol) with MCPBA (142 mg, 0.57 mmol) for 40 min afforded, after FC (hexane/$Et_2O$ 2:1), **18b** (66.4 mg, 0.31 mmol, 70%).

*Entry 9*. According to *Procedure D*, the reaction of **16b** (61.5 mg, 0.31 mmol) with DMD (*ca*. 0.6 mmol) for 40 min afforded, after FC (hexane/$Et_2O$ 2:1), **18b** (27.4 mg, 0.13 mmol, 41%).

*Entry 10*. According to *Procedure B*, the reaction of (−)-**16b** (38.0 mg, 0.19 mmol, e.r. *ca*. 85:15) with *t*-BuOOH (0.28 mmol) in presence of [Ti(i-PrO)$_4$] (0.19 mmol, 1.0 equiv.) for 20 min afforded, after FC (hexane/$Et_2O$ 2:1), (−)-**18b** (24.2 mg, 0.11 mmol, 59%, e.r. *ca*. 80:20, $[\alpha]_D^{25} = -29.7$ ($c = 1$, $CHCl_3$)).

*Entry 11*. According to *Procedure A*, the reaction of **16c** (98.6 mg, 0.46 mmol) with MCPBA (150 mg, 0.61 mmol) for 1 h afforded, after FC (hexane/$Et_2O$ 2:1), **18c** (56.2 mg, 0.24 mmol, 53%).

*Entry 12*. According to *Procedure A*, the reaction of **16d** (102.0 mg, 0.48 mmol) with MCPBA (152 mg, 0.62 mmol) for 1 h afforded **18d** (crude product, 87.7 mg, 0.38 mmol, 80%).

*Entry 13*. According to *Procedure A*, the reaction of **16e** (312.9 mg, 1.13 mmol) with MCPBA (362 mg, 1.47 mmol) for 2 h afforded, after FC (hexane/AcOEt 10:1), **18e** (317.0 mg, 1.08 mmol, 96%).

*Entry 14*. According to *Procedure A*, the reaction of **16f** (230.9 mg, 0.84 mmol) with MCPBA (253 mg, 1.03 mmol) for 1 h afforded, after FC (hexane/AcOEt 10:1 → 8:1), **18f** (196.5 mg, 0.67 mmol, 80%).

*Entry 15*. According to *Procedure A*, the reaction of **16g** (197.5 mg, 0.62 mmol) with MCPBA (230 mg, 0.94 mmol) at 23° for 12 h afforded, after FC (hexane/$Et_2O$ 10:1), **18g** (179.1 mg, 0.54 mmol, 86%).

*Entry 16*. According to *Procedure D*, the reaction of **16g** (56.3 mg, 0.18 mmol) with DMD (*ca*. 0.35 mmol) for 4.5 h afforded, after FC (hexane/$Et_2O$ 10:1 → 5:1 → 3:1) **18g** (first eluting, 42.3 mg, 0.13 mmol, 72%) and **26** (second eluting, 8.4 mg, 0.024 mmol, 14%).

*Entry 17*. According to *Procedure B*, the reaction of **17a**/**17a**′ (64.7 mg, 0.21 mmol, d.r. 84:16, treated with molecular sieves (4 Å, powdered, 35 mg) for 30 min [27]) with *t*-BuOOH (0.33 mmol) in presence of [Ti(i-PrO)$_4$] (0.12 ml of a 0.17M soln. in benzene, 0.02 mmol, 0.1 equiv.) for 2 h afforded, after FC (hexane/$Et_2O$ 3:1), **19a**/**19a**′ (32.8 mg, 0.10 mmol, 48%, d.r. 82:18).

*Entry 18*. According to *Procedure B*, the reaction of **17a**/**17a**′ (60.5 mg, 0.20 mmol, d.r. 84:16, treated with molecular sieves (4 Å, powdered, 30 mg) for 30 min [27]) with *t*-BuOOH (0.30 mmol) in presence of [Ti(i-PrO)$_4$] (0.32 ml of a 0.34M soln. in benzene, 0.11 mmol, 0.5 equiv.) for 30 min afforded, after FC (hexane/$Et_2O$ 3:1), **19a**/**19a**′ (38.3 mg, 0.12 mmol, 60%, d.r. 85:15).

*Entry 19*. According to *Procedure B*, the reaction of **17a**/**17a**′ (56.3 mg, 0.18 mmol, d.r. 78:22) with *t*-BuOOH (0.28 mmol) in presence of [Ti(i-PrO)$_4$] (0.18 mmol, 1.0 equiv.) for 15 min afforded, after FC (hexane/$Et_2O$ 3:1), **19a**/**19a**′ (40.0 mg, 0.12 mmol, 68%, d.r. 92:8).

*Entry 20*. According to *Procedure C*, the reaction of **17a**/**17a**′ (106.5 mg, 0.35 mmol, d.r. 87:13) with *t*-BuOOH (0.42 mmol) in presence of [$VO(acac)_2$] (2.1 mg, 0.0075 mmol) for 3 h afforded, after FC (hexane/$Et_2O$ 3:1), **19a**/**19a**′ (85.7 mg, 0.27 mmol, 77%, d.r. 86:14).

*Entry 21*. According to *Procedure C*, the reaction of **17a**/**17a**′ (55.7 mg, 0.18 mmol, d.r. 78:22) with *t*-BuOOH (0.27 mmol) in presence of [$VO(acac)_2$] (48 mg, 0.18 mmol) for 25 min afforded, after FC (hexane/$Et_2O$ 3:1), **19a**/**19a**′ (20.1 mg, 0.06 mmol, 34%, d.r. 76:24).

*Entry 22*. According to *Procedure A*, the reaction of **17a**/**17a**′ (58.7 mg, 0.19 mmol, d.r. 93:7) with MCPBA (58.5 mg, 0.24 mmol) for 50 min afforded, after FC (hexane/$Et_2O$ 3:1), **19a**/**19a**′ (57.3 mg, 0.18 mmol, 93%, d.r. 91:9).

*Entry 23*. According to *Procedure B*, the reaction of **17a**′/**17a** (52.7 mg, 0.17 mmol, d.r. 84:16, treated with molecular sieves (4 Å, powdered, 35 mg) for 30 min [27]) with *t*-BuOOH (0.26 mmol) in presence of [Ti(i-PrO)$_4$] (0.1 ml of a 0.17M soln. in benzene, 0.017 mmol, 0.1 equiv.) for 2.5 h afforded, after FC (hexane/$Et_2O$ 3:1), **19a**′/**19a** (19.0 mg, 0.059 mmol, 34%, d.r. 78:22).

*Entry 24*. According to *Procedure B*, the reaction of **17a′**/**17a** (73.3 mg, 0.24 mmol, d.r. 84:16) with *t*-BuOOH (0.36 mmol) in presence of [Ti(i-PrO)$_4$] (0.24 mmol, 1.0 equiv.) for 15 min afforded, after FC (hexane/Et$_2$O 3:1), **19a′**/**19a** (64.1 mg, 0.20 mmol, 83%, d.r. 77:23).

*Entry 25*. According to *Procedure B*, the reaction of **17a′**/**17a** (69.0 mg, 0.23 mmol, d.r. 81:19) with *t*-BuOOH (0.33 mmol) in presence of [Ti(i-PrO)$_4$] (0.68 mmol, 3.0 equiv.) for 15 min afforded, after FC (hexane/Et$_2$O 3:1), **19a**/**19a′** (7.8 mg, 0.024 mmol, 11%, d.r. 100:0).

*Entry 26*. According to *Procedure C*, the reaction of **17a′**/**17a** (70.0 mg, 0.23 mmol, d.r. 87:13) with *t*-BuOOH (0.33 mmol) in presence of [VO(acac)$_2$] (3.0 mg, 0.011 mmol) for 2 h afforded, after FC (hexane/Et$_2$O 3:1), **19a′**/**19a** (64.1 mg, 0.20 mmol, 87%, d.r. 87:13).

*Entry 27*. According to *Procedure A*, the reaction of **17a′**/**17a** (54.2 mg, 0.18 mmol, d.r. 84:16) with MCPBA (55 mg, 0.22 mmol) for 50 min afforded, after FC (hexane/Et$_2$O 3:1), **19a′**/**19a** (51.7 mg, 0.16 mmol, 91%, d.r. 77:23).

*Entry 28*. According to *Procedure B*, the reaction of **17b**/**17b′** (d.r. 89:11) with *t*-BuOOH (1.1–1.3 equiv.) in presence of [Ti(i-PrO)$_4$] (0.1–1.0 equiv.) afforded no **19b**/**19b′**. Silanol **25b** (70–80%) was isolated after FC (hexane/Et$_2$O 2:1), and polymeric material was detected by TLC.

*Entry 29*. According to *Procedure C*, the reaction of **17b**/**17b′** (71.8 mg, 0.23 mmol, d.r. 89:11) with *t*-BuOOH (0.26 mmol) in presence of [VO(acac)$_2$] (1.3 mg, 0.0049 mmol) for 8 h afforded no **19b**/**19b′**. Silanol **25b** (40.7 mg, 0.17 mmol, 74%) was isolated after FC (hexane/Et$_2$O 2:1), and polymeric material was detected by TLC.

*Entry 30*. According to *Procedure A*, the reaction of **17b**/**17b′** (58.4 mg, 0.19 mmol, d.r. 85:15) with MCPBA (61 mg, 0.25 mmol) for 20 min afforded crude **19b**/**19b′** (49.2 mg, 0.15 mmol, 80%, d.r. 82:18).

*Entry 31*. According to *Procedure D*, the reaction of **17b**/**17b′** (86.0 mg, 0.28 mmol, d.r. 89:11) with DMD (*ca*. 0.4 mmol) for 40 min afforded crude **19b**/**19b′** (81.4 mg, 0.25 mmol, 90%, d.r. 87:13).

*Entry 32*. According to *Procedure A*, the reaction of **17c**/**17c′** (53.7 mg, 0.17 mmol, d.r. 87:13) with MCPBA (54 mg, 0.22 mmol) for 1 h afforded, after FC (hexane/Et$_2$O 5:1), **19c**/**19c′** (37.8 mg, 0.11 mmol, 67%, d.r. 84:16).

*Entry 33*. According to *Procedure A*, the reaction of **17d**/**17d′** (56.2 mg, 0.18 mmol, d.r. 83:17) with MCPBA (55 mg, 0.22 mmol) for 45 min afforded crude **19d**/**19d′** (46.0 mg, 0.14 mmol, 78%, d.r. 78:22).

*Entry 34*. According to *Procedure B*, the reaction of **17e**/**17e′** (59.5 mg, 0.16 mmol, d.r. 50:50, treated with molecular sieves (4 Å, powdered, 35 mg) for 30 min [27]) with *t*-BuOOH (0.23 mmol) in presence of [Ti(i-PrO)$_4$] (0.09 ml of a 0.17M soln. in benzene, 0.015 mmol, 0.1 equiv.) for 21 h afforded, after FC (hexane/Et$_2$O 25:1 → 10:1 → 5:1), **19e**/**19e′** (9.5 mg, 0.024 mmol, 15%, d.r. 62:38).

*Entry 35*. According to *Procedure B*, the reaction of **17e**/**17e′** (66.9 mg, 0.18 mmol, d.r. 50:50) with *t*-BuOOH (0.27 mmol) in presence of [Ti(i-PrO)$_4$] (0.13 mmol, 0.75 equiv.) for 2 h afforded, after FC (hexane/Et$_2$O 10:1 → 7:1 → 5:1), **19e**/**19e′** (18.1 mg, 0.05 mmol, 26%, d.r. 85:15).

*Entry 36*. According to *Procedure B*, the reaction of **17e**/**17e′** (67.4 mg, 0.18 mmol, d.r. 50:50) with *t*-BuOOH (0.27 mmol) in presence of [Ti(i-PrO)$_4$] (0.27 mmol, 1.5 equiv.) for 20 min afforded, after FC (hexane/Et$_2$O 10:1 → 7:1 → 5:1), **19e**/**19e′** (23.2 mg, 0.06 mmol, 33%, d.r. 96:4).

*Entry 37*. According to *Procedure A*, the reaction of **17e**/**17e′** (70.3 mg, 0.18 mmol, d.r. 95:5) with MCPBA (49.8 mg, 0.20 mmol) for 4.5 h afforded, after FC (hexane/AcOEt 10:1), **19e**/**19e′** (56.1 mg, 0.14 mmol, 77%, d.r. 94:6).

*Entry 38*. According to *Procedure A*, the reaction of **17e**/**17e′** (40.8 mg, 0.11 mmol, d.r. 50:50) with MCPBA (32 mg, 0.13 mmol) for 4.5 h afforded, after FC (hexane/AcOEt 10:1), **19e**/**19e′** (36.1 mg, 0.09 mmol, 85%, d.r. 50:50).

*Entry 39*. According to *Procedure A*, the reaction of **17f**/**17f′** (72.1 mg, 0.19 mmol, d.r. 56:44) with MCPBA (55.8 mg, 0.23 mmol) for 3 h afforded, after FC (hexane/Et$_2$O 10:1 → 2:1), no **19f**/**19f′** but **24c** (22.6 mg, 0.14 mmol, 75%) and **25b** (32.0 mg, 0.13 mmol, 71%).

*Entry 40*. According to *Procedure A*, the reaction of **17g**/**17g′** (176.0 mg, 0.51 mmol, d.r. 88:12) with MCPBA (163 mg, 0.66 mmol) for 3 h afforded, after FC (hexane/Et$_2$O 7:1), **19g**/**19g′** (142.1 mg, 0.39 mmol, 77%, d.r. 86:14).

*Entry 41*. According to *Procedure B*, the reaction of **17h′**/**17h** (57.5 mg, 0.17 mmol, d.r. 68:32, treated with molecular sieves (4 Å, powdered, 35 mg) for 30 min [27]) with *t*-BuOOH (0.26 mmol) in presence of [Ti(i-PrO)$_4$] (0.1 ml of a 0.17M soln. in benzene, 0.017 mmol, 0.1 equiv.) for 4 h afforded, after FC (hexane/AcOEt 8:1), **19h′**/**19h** (36.9 mg, 0.11 mmol, 61%, d.r. 66:34).

*Entry 42*. According to *Procedure B*, the reaction of **17h′**/**17h** (56.7 mg, 0.17 mmol, d.r. 63:37) with *t*-BuOOH (0.27 mmol) in presence of [Ti(i-PrO)$_4$] (0.13 mmol, 0.75 equiv.) for 55 min afforded, after FC (hexane/AcOEt 8:1), **19h′**/**19h** (34.9 mg, 0.10 mmol, 59%, d.r. 56:44).

*Entry 43*. According to *Procedure B*, the reaction of **17h**/**17h′** (73.5 mg, 0.22 mmol, d.r. 95:5) with *t*-BuOOH (0.33 mmol) in presence of [Ti(i-PrO)$_4$] (0.22 mmol, 1.0 equiv.) for 80 min afforded, after FC (hexane/AcOEt 8:1), **19h**/**19h′** (49.4 mg, 0.14 mmol, 64%, d.r. 96:4).

*Entry 44*. According to *Procedure B*, the reaction of **17h′**/**17h** (53.0 mg, 0.16 mmol, d.r. 63:37) with *t*-BuOOH (0.24 mmol) in presence of [Ti(i-PrO)$_4$] (0.24 mmol, 1.5 equiv.) for 1 h afforded, after FC (hexane/AcOEt 8:1), **19h**/**19h′** (28.9 mg, 0.08 mmol, 52%, d.r. 57:43).

*Entry 45*. According to *Procedure A*, the reaction of **17h**/**17h′** (106.9 mg, 0.32 mmol, d.r. 97:3) with MCPBA (86.7 mg, 0.35 mmol) for 4 h afforded, after FC (hexane/AcOEt 8:1), **19h**/**19h′** (84.1 mg, 0.24 mmol, 75%, d.r. 97:3).

*Entry 46*. According to *Procedure A*, the reaction of **17i**/**17i′** (60.4 mg, 0.18 mmol, d.r. 73:27) with MCPBA (65 mg, 0.26 mmol) for 1.5 h afforded crude **19i**/**19i′** (50.6 mg, 0.14 mmol, 80%, d.r. 77:23).

2.2. *(*R*,R*)-3-[(*tert-*Butyl)dimethylsilyl]-4-hydroxypentan-2-one* (**18a**). Colorless, wax-like solid. M.p. 24.3–26.8° (from oil). IR: 3460*m* (br.), 2955*s*, 2930*s*, 2900*s*, 2885*s*, 2855*s*, 1670*s*, 1465*s*, 1415*s*, 1395*m*, 1355*s*, 1255*s*, 1220*m*, 1170*s*, 1110*s*, 1070*m*, 1030*m*, 1015*s*, 965*m*, 935*m*, 870*m*, 835*s*, 805*s*, 770*s*, 750*m*, 715*m*, 685*m*. $^1$H-NMR: 4.05 (*qd*, *J* = 6.4, 3.5, MeC*H*); 3.57 (br. *s*, OH); 2.69 (*d*, *J* = 3.5, SiCH); 2.16 (*s*, MeC(O)); 1.25 (*d*, *J* = 6.4, *Me*CH); 0.94 (*s*, *t*-Bu); 0.18, 0.04 (2*s*, Me$_2$Si). $^{13}$C-NMR: 214.5 (*s*, CO); 68.1 (*d*, Me*C*H); 52.2 (*d*, SiCH); 34.0 (*q*, *Me*C(O)); 26.9 (*q*, *Me*$_3$C); 24.6 (*q*, *Me*CH); 17.8 (*s*, Me$_3$*C*); −5.3, −5.7 (2*q*, Me$_2$Si). CI-MS: 217 (34, [*M* + H]$^+$), 199 (100, [*M* + H − H$_2$O]$^+$).

2.3. *(*R*,S*)-3-[(*tert-*Butyl)dimethylsilyl]-4-hydroxypentan-2-one* (**18b**). Colorless oil. IR: 3440*s* (br.), 2955*s*, 2925*s*, 2895*s*, 2880*s*, 2855*s*, 1675*s*, 1465*s*, 1415*m*, 1390*m*, 1355*s*, 1320*m*, 1260*s*, 1170*s*, 1135*s*, 1105*s*, 1055*m*, 1005*m*, 960*m*, 935*m*, 865*m*, 835*s*, 820*s*, 805*s*, 770*s*, 735*m*, 715*m*, 685*m*, 670*m*. $^1$H-NMR: 4.32–4.24 (*quint.*-like *m*, MeC*H*); 2.69 (*d*, *J* = 7.1, SiCH); 2.11 (*s*, MeC(O)); 1.23 (*d*, *J* = 6.2, *Me*CH); 0.95 (*s*, *t*-Bu); 0.21, 0.00 (2*s*, Me$_2$Si). $^{13}$C-NMR: 211.5 (*s*, CO); 68.0 (*d*, Me*C*H); 53.9 (*d*, SiCH); 33.0 (*q*, *Me*C(O)); 27.0 (*q*, *Me*$_3$C); 24.2 (*q*, *Me*CH); 17.6 (*s*, Me$_3$*C*); −4.7, −4.9 (2*q*, Me$_2$Si). CI-MS: 234 (16, [*M* + NH$_4$]$^+$), 217 (23, [*M* + H]$^+$), 199 (100, [*M* + H − H$_2$O]$^+$), 159 (35), 102 (17).

2.4. *(*R*,R*)-3-[(*tert-*Butyl)dimethylsilyl]-4-hydroxy-3-methylpentan-2-one* (**18c**). Colorless crystalline solid. M.p. 61.4–64.9° (from oil). IR (KBr): 3490*s*, 2980*s*, 2960*s*, 2935*s*, 2905*m*, 2890*m*, 2860*m*, 1670*s*, 1475*m*, 1470*m*, 1445*m*, 1425*m*, 1385*m*, 1375*m*, 1350*m*, 1290*m*, 1260*m*, 1255*m*, 1220*m*, 1145*m*, 1110*m*, 1075*m*, 1060*m*, 1005*m*, 945*w*, 895*m*, 845*m*, 830*m*, 820*m*, 805*s*, 765*m*. $^1$H-NMR: 3.94 (*q*, *J* = 6.4, MeC*H*); 3.65 (br. *s*, OH); 2.15 (*s*, MeC(O)); 1.30 (*s*, MeCSi); 1.17 (*d*, *J* = 6.4, *Me*CH); 0.96 (*s*, *t*-Bu); 0.12, 0.10 (2*s*, Me$_2$Si). $^{13}$C-NMR: 216.2 (*s*, CO); 72.5 (*d*, Me*C*H); 54.0 (*s*, Me*C*Si); 30.7 (*q*, *Me*C(O)); 28.1 (*q*, *Me*$_3$C); 19.44 (*s*, Me$_3$*C*); 19.38, 16.7 (2*q*, *Me*CH, *Me*CSi); −4.8, −5.2 (2*q*, Me$_2$Si). CI-MS: 213 [*M* + H − H$_2$O]$^+$.

2.5. *(*R*,S*)-3-[(*tert-*Butyl)dimethylsilyl]-4-hydroxy-3-methylpentan-2-one* (**18d**). Colorless crystals. M.p. 68.3–68.5° (hexane). IR: 3440*m* (br.), 2955*s*, 2930*s*, 2880*s*, 2855*s*, 1660*s*, 1465*s*, 1420*s*, 1360*s*, 1280*s*, 1250*s*, 1220*s*, 1145*m*, 1115*s*, 1070*s*, 1015*m*, 1005*m*, 940*m*, 905*m*, 830*s*, 820*s*, 805*s*, 780*s*, 765*s*, 750*m*, 745*m*, 700*m*, 670*s*. $^1$H-NMR: 4.63 (*q*, *J* = 6.2, MeC*H*); 2.14 (*s*, MeC(O)); 1.27 (*s*, MeCSi); 1.06 (*d*, *J* = 6.2, *Me*CH); 0.90 (*s*, *t*-Bu); 0.22, 0.14 (2*s*, Me$_2$Si). $^{13}$C-NMR: 212.0 (*s*, CO); 70.5 (*d*, Me*C*H); 54.0 (*s*, Me*C*Si); 30.0 (*q*, *Me*C(O)); 27.8 (*q*, *Me*$_3$C); 19.5 (*s*, Me$_3$*C*); 19.1, 11.9 (2*q*, *Me*CH, *Me*CSi); −4.9, −6.1 (2*q*, Me$_2$Si). CI-MS: 248 (4, [*M* + NH$_4$]$^+$), 231 (4, [*M* + H]$^+$), 213 (100, [*M* + H − H$_2$O]$^+$), 173 (21), 132 (10). For the single-crystal X-ray analysis of **18d**, see *Chapt. 4*.

2.6. *(*R*,R*)-3-[(*tert-*Butyl)dimethylsilyl]-4-hydroxy-1-phenylpentan-2-one* (**18e**). Colorless oil. IR: 3470*m* (br.), 3080*w*, 3055*w*, 3020*m*, 2950*s*, 2920*s*, 2890*s*, 2875*s*, 2850*s*, 2705*w*, 1940*w*, 1870*w*, 1800*w*, 1665*s*, 1600*w*, 1585*w*, 1495*m*, 1460*s*, 1450*s*, 1405*s*, 1360*m*, 1340*s*, 1250*s*, 1195*m*, 1185*m*, 1125*s*, 1100*s*, 1055*s*, 1020*s*, 1005*m*, 935*m*, 910*m*, 870*s*, 835*s*, 825*s*, 805*s*, 770*s*, 730*s*, 700*s*, 660*s*. $^1$H-NMR (uncorr.): 7.25–7.07 (*m*, 5 arom. H); 3.90 (*qd*, *J* = 6.3, 2.8, MeC*H*); 3.59, 3.56 (*AB*, *J* = 14.9, PhC*H*$_2$); 2.67 (*d*, *J* = 2.8, SiCH); 0.88 (*s*, *t*-Bu); 0.87 (*d*, *J* = 6.3, *Me*CH); 0.12, 0.00 (2*s*, Me$_2$Si). $^{13}$C-NMR: 213.2 (*s*, CO); 133.1 (*s*, arom. C); 129.6, 128.6 (2*d*, 2 × 2 arom. C); 127.2 (*d*, arom. C); 68.2 (*d*, Me*C*H); 53.1 (*t*, Ph*C*H$_2$); 50.3 (*d*, SiCH); 27.0 (*q*, *Me*$_3$C); 24.5 (*q*, *Me*CH); 17.8 (*s*, Me$_3$*C*); −4.9, −5.6 (2*q*, Me$_2$Si). CI-MS: 293 (7, [*M* + H]$^+$), 275 (100, [*M* + H − H$_2$O]$^+$). The relative configurations of the stereogenic centers in **18e** were secured by a single-crystal X-ray analysis of a derivative [28].

2.7. *(*R*,S*)-3-[(*tert-*Butyl)dimethylsilyl]-4-hydroxy-1-phenylpentan-2-one* (**18f**). Colorless crystals. M.p. 95.4–97.3° (hexane). IR (KBr): 3360*s* (br.), 3330*s*, 3060*w*, 3030*w*, 2950*s*, 2925*s*, 2885*s*, 2850*s*, 1675*s*, 1660*s*, 1600*m*, 1585*w*, 1495*m*, 1465*s*, 1440*m*, 1425*m*, 1360*s*, 1350*s*, 1330*s*, 1280*s*, 1270*s*, 1260*s*, 1245*s*, 1200*m*, 1185*m*, 1130*s*, 1115*s*, 1090*s*, 1080*s*, 1060*s*, 1040*s*, 1005*m*, 955*s*, 935*m*, 920*w*, 885*m*, 860*m*, 850*s*, 830*s*, 820*s*, 805*s*, 765*s*, 735*s*, 700*s*. $^1$H-NMR (uncorr.): 7.30–7.13 (*m*, 5 arom. H); 4.16 (*sext.*-like *m*, MeC*H*); 3.60 (*s*, PhC*H*$_2$); 2.76 (*d*, *J* = 7.2, SiCH); 1.86 (br. *s*, OH); 0.97 (*d*, *J* = 6.2, *Me*CH); 0.94 (*s*, *t*-Bu); 0.18, 0.00 (2*s*, Me$_2$Si). $^{13}$C-NMR: 210.0 (*s*, CO); 133.6 (*s*, arom. C); 129.6, 128.6 (2*d*, 2 × 2 arom. C); 127.0 (*d*, arom. C); 68.2 (*d*, Me*C*H); 52.7 (*t*, Ph*C*H$_2$); 52.0 (*d*, SiCH); 27.2 (*q*, *Me*$_3$C); 24.0 (*q*, *Me*CH); 17.7 (*s*, Me$_3$*C*); −4.2, −5.1 (2*q*, Me$_2$Si). CI-MS (isobutane): 293 (2, [*M* + H]$^+$), 275 (11, [*M* + H − H$_2$O]$^+$), 161 (100, [*M* + H − (*t*-Bu)Me$_2$SiOH]$^+$). Anal. calc. for C$_{17}$H$_{28}$O$_2$Si (292.493): C 69.81, H 9.65; found: C 69.67, H 9.71. For the single-crystal X-ray analysis of **18f**, see *Chapt. 4*.

2.8. *1-{(*R*,R*)-1-[(*tert-*Butyl)dimethylsilyl]-2-hydroxycyclohexyl}-2-phenylethanone* (**18g**). Colorless crystals. M.p. 79.2–80.1° (EtOH). IR (KBr): 3505*m*, 3445*s*, 3060*w*, 3030*w*, 2930*s*, 2895*s*, 2855*s*, 1655*s*, 1605*w*,

1500*s*, 1470*s*, 1450*s*, 1420*s*, 1410*s*, 1365*m*, 1340*s*, 1310*s*, 1250*s*, 1215*m*, 1205*m*, 1170*w*, 1150*s*, 1135*m*, 1130*m*, 1085*s*, 1065*s*, 1060*s*, 1035*s*, 1015*w*, 1005*w*, 980*m*, 950*w*, 940*w*, 925*m*, 905*w*, 870*m*, 855*s*, 830*s*, 820*s*, 780*m*, 765*s*, 725*s*, 695*s*. $^1$H-NMR (uncorr.): 7.21–7.08 (*m*, 3 arom. H); 7.02–7.00 (*m*, 2 arom. H); 4.56 (*d*, *J* = 11.4, OH); 3.78, 3.56 (*AB*, *J* = 17.1, PhC$H_2$); 3.45 (br. *td*, *J* = 11.4, 3.7, C*H*(OH)); 2.41–2.36 (*m*, 1 H); 1.71–1.02 (*m*, 7 H); 0.89 (*s*, *t*-Bu); 0.08, 0.00 (2*s*, $Me_2$Si). $^{13}$C-NMR: 215.3 (*s*, CO); 133.9 (*s*, arom. C); 129.9, 128.3 (2*d*, 2 × 2 arom. C); 126.8 (*d*, arom. C); 75.0 (*d*, CH(OH)); 57.1 (*s*, SiC*C*(O)); 47.5 (*t*, PhC$H_2$); 33.1, 31.5 (2*t*); 28.5 (*q*, $Me_3$C); 25.4, 24.4 (2*t*); 19.8 (*s*, $Me_3C$); −4.7, −5.3 (2*q*, $Me_2$Si). CI-MS: 333 (19, $[M+H]^+$), 315 (100, $[M+H-H_2O]^+$), 218 (33, $[M+NH_4-(t\text{-Bu})Me_2SiOH]^+$), 201 (41, $[M+H-(t\text{-Bu})Me_2SiOH]^+$). Anal. calc. for $C_{20}H_{32}O_2Si$ (332.557): C 72.23, H 9.70; found: C 72.13, H 9.62. For the single-crystal X-ray analysis of **18g**, see *Chapt. 4*.

2.9. *(*SiR*,3R*,4R*)- and (*SiR*,3S*,4S*)-3-[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-4-hydroxypentan-2-one* (**19a** and **19a′**, resp.). Colorless oil. IR: 3450*m* (br.), 3085*w*, 3060*w*, 3030*m*, 2960*s*, 2930*s*, 2880*s*, 2850*s*, 2810*m*, 2740*w*, 2710*w*, 1950*w*, 1870*w*, 1805*w*, 1670*s*, 1585*w*, 1495*w*, 1465*s*, 1450*s*, 1430*m*, 1410*s*, 1390*m*, 1355*s*, 1330*m*, 1250*s*, 1215*m*, 1165*s*, 1105*s*, 1070*s*, 1030*s*, 1015*s*, 970*m*, 930*m*, 905*m*, 870*m*, 825*s*, 800*s*, 780*m*, 765*m*, 735*s*, 695*s*, 680*m*, 655*m*. $^1$H-NMR (**19a**; uncorr.): 7.22–7.10 (*m*, 5 arom. H); 4.30, 4.27 (*AB*, *J* = 11.9, PhC$H_2$), 3.97 (*qd*, *J* = 6.4, 2.8, MeC*H*, OH underneath); 3.19, 2.99 (*AB*, *J* = 13.1, SiC$H_2$); 2.71 (*d*, *J* = 2.8, SiCH); 2.04 (*s*, MeC(O)); 1.11 (*d*, *J* = 6.4, *Me*CH); 0.86 (*s*, *t*-Bu); 0.00 (*s*, MeSi). $^1$H-NMR (**19a′**; uncorr.): 7.28–7.16 (*m*, 5 arom. H); 4.41, 4.37 (*AB*, *J* = 12.1, PhC$H_2$); 4.08–3.97 (*m*, MeC*H*(OH)); 3.32, 3.30 (*AB*, *J* = 13.0, SiC$H_2$); 2.71 (*d*, *J* = 2.5, SiCH); 2.11 (*s*, MeC(O)); 1.16 (*d*, *J* = 6.1, *Me*CH); 0.88 (*s*, *t*-Bu); 0.00 (*s*, MeSi). $^{13}$C-NMR (**19a**): 214.3 (*s*, CO); 138.0 (*s*, arom. C); 128.2, 127.8 (2*d*, 2 × 2 arom. C); 127.6 (*d*, arom. C); 77.4 (*t*, PhC$H_2$); 67.7 (*d*, MeCH); 60.8 (*t*, SiC$H_2$); 50.7 (*d*, SiCH); 33.6 (*q*, *Me*C(O)); 27.3 (*q*, $Me_3$C); 24.3 (*q*, *Me*CH); 17.8 (*s*, $Me_3C$); −8.6 (*q*, MeSi). $^{13}$C-NMR (**19a′**): 213.6 (*s*, CO); 138.1 (*s*, arom. C); 128.3, 127.8 (2*d*, 2 × 2 arom. C); 127.6 (*d*, arom. C); 77.4 (*t*, PhC$H_2$); 67.5 (*d*, MeCH); 60.5 (*t*, SiC$H_2$); 51.8 (*d*, SiCH); 33.5 (*q*, *Me*C(O)); 27.3 (*q*, $Me_3$C); 24.1 (*q*, *Me*CH); 17.9 (*s*, $Me_3C$); −8.0 (*q*, MeSi). CI-MS: 340 (7, $[M+NH_4]^+$), 323 (75, $[M+H]^+$), 305 (100, $[M+H-H_2O]^+$), 279 (10), 256 (13), 238 (28).

2.10. *(*SiR*,3R*,4S*)- and (*SiR*,3S*,4R*)-3-[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-4-hydroxypentan-2-one* (**19b** and **19b′**, resp.) Colorless oil. IR: 3420*m* (br.), 3080*w*, 3060*w*, 3025*m*, 2950*s*, 2025*s*, 2880*s*, 2850*s*, 2810*m*, 1675*s*, 1490*w*, 1460*m*, 1450*m*, 1425*m*, 1375*m*, 1355*m*, 1250*s*, 1215*m*, 1170*m*, 1130*m*, 1090*s*, 1070*s*, 1025*m*, 1010*m*, 960*w*, 935*w*, 900*w*, 860*w*, 825*s*, 805*m*, 770*m*, 740*s*, 695*s*. $^1$H-NMR (**19b**; uncorr.): 7.21–7.09 (*m*, 5 arom. H); 4.31, 4.27 (*AB*, *J* = 11.8, PhC$H_2$); 4.23–4.14 (*m*, MeC*H*); 3.24, 3.02 (*AB*, *J* = 12.7, SiC$H_2$); 2.60 (*d*, *J* = 8.5, SiCH); 1.99 (*s*, MeC(O)); 1.04 (*d*, *J* = 6.0, *Me*CH); 0.82 (*s*, *t*-Bu); 0.00 (*s*, MeSi). $^1$H-NMR (**19b′**; uncorr.): 7.21–7.09 (*m*, 5 arom. H); 4.42, 4.31 (*AB*, *J* = 11.8, PhC$H_2$); 4.23–4.14 (*m*, MeC*H*); 3.25, 3.02 (*AB*, *J* = 13.1, SiC$H_2$); 2.66 (*d*, *J* = 9.8, SiCH); 1.92 (*s*, MeC(O)); 1.03 (*d*, *J* = 5.9, *Me*CH); 0.81 (*s*, *t*-Bu); −0.03 (*s*, MeSi). $^{13}$C-NMR (**19b**; $C_6D_6$, uncorr.): 209.7 (*s*, CO); 139.0 (*s*, arom. C); 128.9, 128.2 (2*d*, 2 × 2 arom. C); 128.1 (*d*, arom. C); 78.0 (*t*, PhC$H_2$); 68.7 (*d*, MeCH); 62.5 (*t*, SiC$H_2$); 54.4 (*d*, SiCH); 33.6 (*q*, *Me*C(O)); 28.2 (*q*, $Me_3$C); 24.9 (*q*, *Me*CH); 18.5 (*s*, $Me_3C$); −7.1 (*q*, MeSi). $^{13}$C-NMR (**19b′**,$C_6D_6$, uncorr.): 208.7 (*s*, CO); 138.1 (*s*, arom. C); 128.9, 128.2 (2*d*, 2 × 2 arom. C); 128.1 (*d*, arom. C); 78.0 (*t*, PhC$H_2$); 68.4 (*d*, MeCH); 61.4 (*t*, SiC$H_2$); 55.5 (*d*, SiCH); 33.2 (*q*, *Me*C(O)); 27.9 (*q*, $Me_3$C); 24.8 (*q*, *Me*CH); 18.4 (*s*, $Me_3C$); −7.6 (*q*, MeSi). CI-MS: 340 (3, $[M+NH_4]^+$), 323 (2, $[M+H]^+$), 256 (100), 108 (22).

For the preparation of the (4-bromophenyl)carbamate derivative of **19b**, and its single-crystal X-ray analysis, see *Chapt. 3* and *4*.

2.11. *(*SiR*,3R*,4R*)- and (*SiR*,3S*,4S*)-3-[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-4-hydroxy-3-methylpentan-2-one* (**19c** and **19c′**, resp.). Colorless oil. $^1$H-NMR (**19c**): 7.35–7.28 (*m*, 5 arom. H); 4.48, 4.44 (*AB*, *J* = 11.9, PhC$H_2$); 3.96 (*q*, *J* = 6.3, MeC*H*); 3.43, 3.26 (*AB*, *J* = 13.0, SiC$H_2$); 2.16 (*s*, MeC(O)); 1.38 (*s*, SiCMe); 1.16 (*d*, *J* = 6.3, *Me*CH); 1.01 (*s*, *t*-Bu); 0.14 (*s*, MeSi). $^1$H-NMR (**19c′**): 7.35–7.28 (*m*, 5 arom. H); 4.46 (*s*, PhC$H_2$); 3.88 (*q*, *J* = 6.4, MeC*H*); 3.47, 3.34 (*AB*, *J* = 13.1, SiC$H_2$); 2.21 (*s*, MeC(O)); 1.32 (*s*, SiCMe); 1.17 (*d*, *J* = 6.3, *Me*CH); 1.01 (*s*, *t*-Bu); 0.13 (*s*, MeSi). $^{13}$C-NMR (**19c**): 216.8 (*s*, CO); 138.1 (*s*, arom. C); 128.3, 127.7 (2*d*, 2 × 2 arom. C); 127.6 (*d*, arom. C); 77.4 (*t*, PhC$H_2$); 72.6 (*d*, MeCH); 61.3 (*t*, SiC$H_2$); 53.7 (*s*, Si*C*Me); 30.8 (*q*, *Me*C(O)); 28.6 (*q*, $Me_3$C); 19.6 (*s*, $Me_3C$); 18.9, 17.3 (2*q*, *Me*CH, SiC*Me*); −7.1 (*q*, MeSi). $^{13}$C-NMR (**19c′**): 216.7 (*s*, CO); 138.1 (*s*, arom. C); 128.3, 127.7 (2*d*, 2 × 2 arom. C); 127.6 (*d*, arom. C); 77.4 (*t*, PhC$H_2$); 72.5 (*d*, MeCH); 61.2 (*t*, SiC$H_2$); 53.9 (*s*, Si*C*Me); 30.8 (*q*, *Me*C(O)); 28.5 (*q*, $Me_3$C); 19.6 (*s*, $Me_3C$); 18.8, 17.4 (2*q*, *Me*CH, SiC*Me*); −7.9 (*q*, MeSi).

2.12. *(*SiR*,3R*,4S*)- and (*SiR*,3S*,4R*)-3-[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-4-hydroxy-3-methylpentan-2-one* (**19d** and **19d′**, resp.). Colorless oil. $^1$H-NMR (**19d**): 7.46–7.31 (*m*, 5 arom. H); 4.65 (*q*, *J* = 6.3, MeC*H*); 4.59, 4.56 (*AB*, *J* = 11.7, PhC$H_2$); 3.64, 3.36 (*AB*, *J* = 13.0, SiC$H_2$); 2.14 (*s*, MeC(O)); 1.30 (*s*, SiCMe); 0.99 (*d*, *J* = 6.3, *Me*CH); 0.88 (*s*, *t*-Bu); 0.19 (*s*, MeSi). $^{13}$C-NMR (**19d**; $C_6D_6$, signals in aromatic region not given): 209.6 (*s*, CO); 77.9 (*t*, PhC$H_2$); 68.6 (*d*, MeCH); 62.5 (*t*, SiC$H_2$); 54.4 (*s*, Si*C*Me); 33.5 (*q*, *Me*C(O)); 28.2

(*q*, *Me*$_3$C); 27.8, 24.8 (2*q*, *Me*CH, SiC*Me*); 18.4 (*s*, Me$_3$*C*); −7.2 (*q*, MeSi). $^1$H- and $^{13}$C-NMR data of **19d′** (minor component of the mixture) cannot be given due to rapid decomposition of the sample **19d**/**19d′**.

2.13. *(*SiR*,3R*,4R*)- and (*SiR*,3S*,4S*)-3-[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-4-hydroxy-1-phenylpentan-2-one* (**19e** and **19e′**). Colorless oil. IR: 3470*m* (br.), 3080*m*, 3060*m*, 3025*m*, 2960*s*, 2925*s*, 2880*s*, 2850*s*, 2810*m*, 2735*w*, 2710*w*, 1950*w*, 1870*w*, 1800*w*, 1665*s*, 1600*m*, 1580*w*, 1490*m*, 1460*s*, 1450*s*, 1430*m*, 1405*s*, 1390*m*, 1375*m*, 1360*m*, 1340*s*, 1250*s*, 1200*m*, 1185*m*, 1155*m*, 1130*s*, 1100*s*, 1070*s*, 1025*s*, 980*m*, 935*m*, 905*m*, 870*m*, 825*s*, 805*s*, 780*m*, 740*s*, 710*s*, 700*s*, 665*m*. $^1$H-NMR (**19e**; uncorr.): 7.22–6.97 (*m*, 10 arom. H); 4.35, 4.32 (*AB*, *J* = 11.8, PhC*H*$_2$O); 3.87 (*qd*, *J* = 6.3, 2.1, MeC*H*); 3.61, 3.58 (*AB*, *J* = 14.6, PhC*H*$_2$C); 3.23, 3.04 (*AB*, *J* = 13.2, SiCH$_2$); 2.86 (*d*, *J* = 2.1, SiCH); 0.90 (*s*, *t*-Bu); 0.78 (*d*, *J* = 6.3, *Me*CH); 0.01 (*s*, MeSi). $^1$H-NMR (**19e′**; uncorr.): 7.22–6.97 (*m*, 10 arom. H); 4.37, 4.35 (*AB*, *J* = 11.8, PhC*H*$_2$O); 3.95–3.85 (*m*, MeC*H*); 3.61, 3.58 (*AB*, *J* = 14.6, PhC*H*$_2$C); 3.32, 3.29 (*AB*, *J* = 13.1, SiCH$_2$); 2.79 (*d*, *J* = 2.2, SiCH); 0.87 (*s*, *t*-Bu); 0.85 (*d*, *J* = 6.2, *Me*CH); 0.00 (*s*, MeSi). $^{13}$C-NMR (**19e**): 213.2 (*s*, CO); 138.0, 133.6 (2*s*, 2 arom. C); 129.7, 128.6, 128.3, 127.9 (4*d*, 4 × 2 arom. C); 127.7, 127.0 (2*d*, 2 arom. C); 77.5 (*t*, PhCH$_2$O); 67.9 (*d*, MeCH); 61.2 (*t*, SiCH$_2$); 52.6 (*t*, PhCH$_2$C); 48.5 (*d*, SiCH); 27.5 (*q*, *Me*$_3$C); 24.2 (*q*, *Me*CH); 17.9 (*s*, Me$_3$*C*); −8.5 (*q*, MeSi). $^{13}$C-NMR (**19e′**): 212.6 (*s*, CO); 138.3, 133.4 (2*s*, 2 arom. C); 129.7, 128.6, 128.3, 127.8 (4*d*, 4 × 2 arom. C); 127.6, 127.1 (2*d*, 2 arom. C); 77.5 (*t*, PhCH$_2$O); 67.7 (*d*, MeCH); 60.8 (*t*, SiCH$_2$); 52.8 (*t*, PhCH$_2$C); 49.9 (*d*, SiCH); 27.5 (*q*, *Me*$_3$C); 24.0 (*q*, *Me*CH); 18.1 (*s*, Me$_3$*C*); −7.7 (*q*, MeSi). CI-MS: 416 (51, [*M* + NH$_4$]$^+$), 399 (16, [*M* + H]$^+$), 381 (3, [*M* + H − H$_2$O]$^+$), 256 (100), 178 (47).

2.14. *1-((*SiR*,1R*,2R*)- and (*SiR*,1S*,2S*)-1-[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-2-hydroxycyclohexyl)ethanone* (**19g** and **19g′**, resp.). Colorless oil. IR: 3460*m* (br.), 3080*w*, 3055*w*, 3025*m*, 2930*s*, 2850*s*, 2810*m*, 2235*w*, 1950*w*, 1800*w*, 1745*w*, 1705*w*, 1655*s*, 1490*w*, 1450*s*, 1415*s*, 1390*m*, 1375*m*, 1355*s*, 1300*m*, 1250*s*, 1215*s*, 1175*s*, 1130*m*, 1085*s*, 1070*s*, 1055*s*, 1025*m*, 1015*w*, 1005*w*, 975*m*, 950*m*, 930*m*, 905*m*, 870*m*, 850*m*, 820*s*, 785*m*, 760*m*, 730*s*, 710*m*, 700*s*, 680*m*, 660*m*. $^1$H-NMR (**19g**): 7.38–7.26 (*m*, 5 arom. H); 4.79 (br. *d*, *J* = 10.7, OH); 4.48, 4.45 (*AB*, *J* = 11.9, PhC*H*$_2$); 3.64 (br. *td*, *J* = 11.0, 3.7, C*H*(OH)); 3.49, 3.34 (*AB*, *J* = 13.0, SiCH$_2$); 2.48–2.41 (*m*, 1 H); 2.21 (*s*, MeC(O)); 1.86–1.67 (*m*, 3 H); 1.60–1.45 (*m*, 3 H); 1.35–1.19 (*m*, 1 H); 1.01 (*s*, *t*-Bu); 0.17 (*s*, MeSi). $^1$H-NMR (**19g′**): 7.38–7.28 (*m*, 5 arom. H); 4.62 (br. *d*, *J* = 10.7, OH); 4.44 (*s*, PhC*H*$_2$); 3.54 (br. *td*, *J* = 11.0, 3.8, C*H*(OH)); 3.37, 3.31 (*AB*, *J* = 13.0, SiCH$_2$); 2.48–2.41 (*m*, 1 H); 2.27 (*s*, MeC(O)); 1.86–1.67 (*m*, 3 H); 1.60–1.45 (*m*, 3 H); 1.35–1.19 (*m*, 1 H); 1.03 (*s*, *t*-Bu); 0.13 (*s*, MeSi). $^{13}$C-NMR (**19g**): 216.7 (*s*, CO); 138.3 (*s*, arom. C); 128.2, 127.7 (2*d*, 2 × 2 arom. C); 127.5 (*d*, arom. C); 77.4 (*t*, PhCH$_2$); 74.5 (*d*, CH(OH)); 61.2 (*t*, SiCH$_2$); 57.0 (*s*, Si*C*C(O)); 33.0, 31.7 (2*t*); 30.2 (*q*, *Me*C(O)); 28.6 (*q*, *Me*$_3$C); 25.3, 23.8 (2*t*); 19.7 (*s*, Me$_3$*C*); −7.8 (*q*, MeSi). $^{13}$C-NMR (**19g′**): 217.0 (*s*, CO); 138.3 (*s*, arom. C); 128.2, 127.7 (2*d*, 2 × 2 arom. C); 127.5 (*d*, arom. C); 77.4 (*t*, PhCH$_2$); 74.6 (*d*, CH(OH)); 61.1 (*t*, SiCH$_2$); 56.5 (*s*, Si*C*C(O)); 32.7, 31.5 (2*t*); 30.2 (*q*, *Me*C(O)); 28.6 (*q*, *Me*$_3$C); 25.3, 23.7 (2*t*); 19.7 (*s*, Me$_3$*C*); −8.5 (*q*, MeSi). CI-MS: 363 (30, [*M* + H]$^+$), 345 (100, [*M* + H − H$_2$O]$^+$), 256 (36), 142 (15), 125 (19). Anal. calc. for C$_{21}$H$_{34}$O$_3$Si (362.583): C 69.57, H 9.45; found: C 69.52, H 9.25.

2.15. *(*SiR*,2R*,3R*)- and (*SiR*,2S*,3S*)-3-[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-2-hydroxyheptan-2-one* (**19h** and **19h′**, resp.). Colorless oil. IR: 3460*m* (br.), 3080*w*, 3055*w*, 3025*m*, 2955*s*, 2925*s*, 2850*s*, 2805*m*, 2730*w*, 1950*w*, 1870*w*, 1800*w*, 1670*s*, 1605*w*, 1585*w*, 1495*w*, 1460*s*, 1450*s*, 1430*m*, 1405*s*, 1390*m*, 1375*s*, 1365*s*, 1330*m*, 1250*s*, 1140*s*, 1105*s*, 1090*s*, 1070*s*, 1020*s*, 980*m*, 935*m*, 905*m*, 875*m*, 825*s*, 805*s*, 785*m*, 735*s*, 695*s*, 675*m*. $^1$H-NMR (**19h**; uncorr.): 7.50–7.36 (*m*, 5 arom. H); 4.55 (*s*, PhC*H*$_2$); 4.23 (*qd*, *J* = 6.4, 2.6, MeC*H*); 3.43, 3.22 (*AB*, *J* = 13.1, SiCH$_2$); 2.98 (*d*, *J* = 2.6, SiCH); 2.66, 2.49 (*AB* of *ABXX′*, $J_{AB}$ = 17.2, $J_{AX}$ = 8.9, $J_{AX'}$ = 6.3, $J_{BX}$ = 8.7, $J_{BX'}$ = 5.9, MeCH$_2$C*H*$_2$); 1.76–1.50 (*m*, MeC*H*$_2$); 1.37 (*d*, *J* = 6.4, *Me*CH); 1.14 (*s*, *t*-Bu); 0.97 (*t*, *J* = 7.4, *Me*CH$_2$); 0.26 (*s*, MeSi). $^1$H-NMR (**19h′**; uncorr.): 7.28–7.17 (*m*, 5 arom. H); 4.42, 4.37 (*AB*, *J* = 11.9, PhC*H*$_2$); 4.10–3.99 (*m*, MeC*H*); 3.36, 3.30 (*AB*, *J* = 13.0, SiCH$_2$); 2.71 (*d*, *J* = 1.6, SiCH); 2.51–2.22 (*m*, MeCH$_2$C*H*$_2$); 1.60–1.30 (*m*, MeC*H*$_2$); 1.16 (*d*, *J* = 5.9, *Me*CH); 0.90 (*s*, *t*-Bu); 0.82 (*t*, *J* = 7.4, *Me*CH$_2$); 0.00 (*s*, MeSi). $^{13}$C-NMR (**19h**): 216.7 (*s*, CO); 138.2 (*s*, arom. C); 128.2, 127.7 (2*d*, 2 × 2 arom. C); 127.6 (*d*, arom. C); 77.3 (*t*, PhCH$_2$); 67.9 (*d*, MeCH); 61.1 (*t*, SiCH$_2$); 49.5 (*d*, SiCH); 48.1 (*t*, MeCH$_2$CH$_2$); 27.4 (*q*, *Me*$_3$C); 24.5 (*q*, *Me*CH); 17.8 (*s*, Me$_3$*C*); 16.9 (*t*, MeCH$_2$); 13.7 (*q*, *Me*CH$_2$); −8.5 (*q*, MeSi). $^{13}$C-NMR (**19h′**): 215.9 (*s*, CO); 138.3 (*s*, arom. C); 128.2, 127.8 (2*d*, 2 × 2 arom. C); 127.5 (*d*, arom. C); 77.3 (*t*, PhCH$_2$); 67.8 (*d*, MeCH); 60.7 (*t*, SiCH$_2$); 50.4 (*d*, SiCH); 48.2 (*t*, MeCH$_2$CH$_2$); 27.4 (*q*, *Me*$_3$C); 24.3 (*q*, *Me*CH); 17.9 (*s*, Me$_3$*C*); 17.0 (*t*, MeCH$_2$); 13.8 (*q*, *Me*CH$_2$); −7.9 (*q*, MeSi). CI-MS: 368 (21, [*M* + NH$_4$]$^+$), 351 (100, [*M* + H]$^+$), 333 (65, [*M* + H − H$_2$O]$^+$), 307 (22), 256 (47), 238 (18).

2.16. *(*SiR*,2S*,3R*)- and (*SiR*,2R*,3S*)-3-[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-2-hydroxyheptan-2-one* (**19i** and **19i′**, resp.). Colorless oil. IR: 3410*m* (br.), 3085*m*, 3060*m*, 3030*m*, 2960*s*, 2930*s*, 2855*s*, 2810*m*, 1950*w*, 1870*w*, 1680*s*, 1570*m*, 1460*s*, 1425*s*, 1375*s*, 1365*s*, 1285*s*, 1245*s*, 1095*s*, 1070*s*, 1025*s*, 1005*m*, 970*m*, 940*m*, 900*m*, 875*m*, 825*s*, 805*s*, 775*m*, 740*s*, 700*s*, 670*m*. $^1$H-NMR (**19i**; uncorr.): 7.24–7.12 (*m*, 5 arom. H); 4.32, 4.30 (2*s*,

visible part of *AB*, PhC$H_2$); 4.28–4.18 (*m*, MeC*H*); 3.24, 3.03 (*AB*, *J* = 12.7, SiC$H_2$); 2.60 (*d*, *J* = 8.5, SiCH); 2.36, 2.20 (*AB* of *ABXX'*, $J_{AB}$ = 6.1, $J_{AX'}$ = 8.7, $J_{AX'}$ = 6.1, $J_{BX'}$ = 8.8, $J_{BX'}$ = 6.0, MeC$H_2$C$H_2$); 1.56–1.22 (*m*, MeC$H_2$); 1.05 (*d*, *J* = 6.1, *Me*CH); 0.85 (*s*, *t*-Bu); 0.71 (*t*, *J* = 7.4, *Me*C$H_2$); 0.00 (*s*, MeSi). $^1$H-NMR (**19i'**; uncorr.): 7.24–7.12 (*m*, 5 arom. H); 4.44 (*s*, PhC$H_2$); 4.26–4.18 (*m*, MeC*H*); 3.24, 3.03 (*AB*, *J* = 12.7, SiC$H_2$); 2.67 (*d*, *J* = 9.9, SiCH); 2.41–2.30, 2.26–2.15 (2*m*, MeC$H_2$C$H_2$); 1.56–1.22 (*m*, MeC$H_2$); 1.06 (*d*, *J* = 6.1, *Me*CH); 0.87 (*s*, *t*-Bu); 0.71 (*t*, *J* = 7.4, *Me*C$H_2$); 0.00 (*s*, MeSi). $^{13}$C-NMR (**19i**; $C_6D_6$; signals in arom. region not given): 211.7 (*s*, CO); 78.1 (*t*, PhC$H_2$); 68.8 (*d*, MeC*H*); 62.7 (*t*, SiC$H_2$); 53.7 (*d*, SiCH); 48.6 (*t*, MeC$H_2$C$H_2$); 28.3 (*q*, *Me*$_3$C); 25.0 (*q*, *Me*CH); 17.6 (*t*, MeC$H_2$); 14.3 (*q*, *Me*C$H_2$); −7.2 (*q*, MeSi). $^{13}$C-NMR (**19i'**; $C_6D_6$; signals in arom. region not given): 211.7 (*s*, CO); 78.1 (*t*, PhC$H_2$); 68.5 (*d*, MeC*H*); 61.4 (*t*, SiC$H_2$); 54.6 (*d*, SiCH); 48.4 (*t*, MeC$H_2$C$H_2$); 27.9 (*q*, *Me*$_3$C); 24.6 (*q*, *Me*CH); 17.4 (*t*, MeC$H_2$); 14.4 (*q*, *Me*C$H_2$); −7.5 (*q*, MeSi). CI-MS: 368 (7, $[M+NH_4]^+$), 351 (5, $[M+H]^+$), 333 (3, $[M+H-H_2O]^+$), 256 (100).

2.17. *(*E*)-1-Phenylpent-3-en-2-one* (**24c**). Colorless oil. IR: 3080*w*, 3055*m*, 3025*m*, 2965*m*, 2930*m*, 2910*m*, 2845*w*, 1950*w*, 1875*w*, 1800*w*, 1690*s*, 1665*s*, 1625*s*, 1600*m*, 1580*m*, 1490*s*, 1450*s*, 1440*s*, 1410*m*, 1370*m*, 1335*m*, 1325*m*, 1315*m*, 1295*s*, 1210*m*, 1185*s*, 1155*m*, 1125*m*, 1090*m*, 1070*m*, 1030*m*, 1000*w*, 970*s*, 950*m*, 935*m*, 865*w*, 825*w*, 755*m*, 735*s*, 700*s*, 660*m*. $^1$H-NMR (uncorr.): 7.26–7.09 (*m*, 5 arom. H); 6.84 (*dq*, *J* = 15.7, 6.9, MeC*H*); 6.07 (*dq*, *J* = 15.7, 1.6, MeCH=C*H*); 3.72 (*s*, PhC$H_2$); 1.78 (*dd*, *J* = 6.9, 1.6, Me). $^{13}$C-NMR: 197.3 (*s*, CO); 143.6 (*d*, MeCH); 134.6 (*s*, arom. C); 130.9, 129.4 (2*d*, 2 × 2 arom. C); 128.7 (*d*, arom. C); 126.8 (*d*, MeCH=*C*H); 47.6 (*t*, PhC$H_2$); 18.3 (*q*, Me). CI-MS: 178 (100, $[M+NH_4]^+$), 161 (5, $[M+H]^+$).

2.18. *[(Benzyloxy)methyl](*tert*-butyl)methylsilanol* (**25b**). Slightly yellow oil. IR: 3400*s* (br.), 3085*m*, 3060*m*, 3030*m*, 2950*s*, 2930*s*, 2880*s*, 2850*s*, 2810*m*, 2735*w*, 2710*w*, 2240*w*, 1945*w*, 1870*w*, 1800*w*, 1710*w*, 1600*w*, 1585*w*, 1495*m*, 1460*s*, 1430*m*, 1380*m*, 1360*s*, 1300*w*, 1255*s*, 1205*m*, 1090*s*, 1070*s*, 1030*m*, 1010*m*, 980*m*, 940*m*, 905*s*, 830*s*, 805*s*, 775*s*, 735*s*, 700*s*, 680*s*. $^1$H-NMR: 7.38–7.25 (*m*, 5 arom. H); 4.49 (*s*, PhC$H_2$); 3.50, 3.46 (*AB*, *J* = 7.0, SiC$H_2$); 1.98 (br. *s*, OH); 0.94 (*s*, *t*-Bu); 0.14 (*s*, MeSi). $^{13}$C-NMR: 138.5 (*s*, arom. C); 128.3, 127.7 (2*d*, 2 × 2 arom. C); 127.5 (*d*, arom. C); 77.1 (*t*, PhC$H_2$); 61.4 (*t*, SiC$H_2$); 25.8 (*q*, *Me*$_3$C); 17.8 (*s*, Me$_3$*C*); −6.0 (*q*, MeSi). CI-MS: 256 (100, $[M+NH_4]^+$), 239 (8, $[M+H]^+$).

2.19. *1-[(*R**,*R**)-1-[(*tert*-Butyl)dimethylsilyl]-2-hydroxy-3-oxocyclohexyl]-2-phenylethanone* (**26**). Colorless oil. IR ($CHCl_3$): 3480*m* (br.), 3080*w*, 3060*w*, 3025*m*, 2955*s*, 2930*s*, 2855*s*, 1720*s*, 1675*s*, 1600*w*, 1585*w*, 1495*m*, 1465*s*, 1450*s*, 1395*m*, 1380*m*, 1365*m*, 1345*m*, 1315*m*, 1275*m*, 1255*s*, 1230*m*, 1180*m*, 1155*s*, 1110*s*, 1080*s*, 1035*m*, 1015*m*, 970*w*, 930*w*, 880*w*, 860*m*, 835*s*, 820*s*, 810*s*, 780*m*, 770*s*, 725*s*, 695*s*. $^1$H-NMR (uncorr.): 7.33–7.19 (*m*, 3 arom. H); 7.11–7.08 (*m*, 2 arom. H); 4.33 (br. *s*, 1 H); 4.10–4.00 (*m*, 1 H); 3.97, 3.55 (*AB*, *J* = 17.4, PhC$H_2$); 2.68–2.61 (*m*, 1 H); 2.55–2.48 (*m*, 1 H); 2.42–2.30 (*m*, 1 H); 2.06–1.93 (*m*, 2 H); 1.65–1.48 (*m*, 1 H); 1.06 (*s*, *t*-Bu); 0.27, 0.25 (2*s*, $Me_2$Si). $^{13}$C-NMR: 210.1, 209.5 (2*s*, 2 CO); 133.9 (*s*, arom. C); 129.9, 128.3 (2*d*, 2 × 2 arom. C); 126.8 (*d*, arom. C); 77.9 (*d*, CH(OH)); 59.9 (*s*, Si*C*C(O)); 48.5 (*t*, PhC$H_2$); 39.1, 30.6 (2*t*); 28.4 (*q*, *Me*$_3$C); 25.1 (*t*); 19.8 (*s*, Me$_3$*C*); −5.0, −5.4 (2*q*, $Me_2$Si). CI-MS: 364 (9, $[M+NH_4]^+$), 347 (15, $[M+H]^+$), 329 (100, $[M+H-H_2O]^+$).

**3. (*SiR**,*3R**,*4S**)-3-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-4-[(4-bromophenyl)carbamoyloxy]pentan-2-one** (= *(*SiR**,*1S**,*2R**)-2-[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-1-methyl-3-oxobutyl (4-Bromobutyl)carbamate)*. To a soln. of **19b** (51.2 mg, 0.16 mmol) in hexane (2 ml) at 23°, 4-bromophenyl isocyanate (62.9 mg, 0.32 mmol) was added. The mixture was refluxed for 2 h, sat. aq. $NH_4Cl$ soln. was added at 23°. Workup and FC (hexane/$Et_2O$ 12:1) afforded (4-bromophenyl)carbamate derivative of **19b** (59.5 mg, 0.11 mmol, 72%). Colorless needles. M.p. 90.5–90.6° (hexane). IR ($CHCl_3$): 3670*w* (br.), 3430*m*, 2930*m*, 2850*m*, 1730*s*, 1690*s*, 1595*s*, 1505*s*, 1395*m*, 1355*w*, 1305*m*, 1280*w*, 1240*w*, 1175*m*, 1120*s*, 1070*s*, 1030*m*, 1005*m*, 985*w*, 960*w*, 935*w*, 905*w*, 885*w*, 825*m*. $^1$H-NMR (uncorr.): 7.31–7.06 (*m*, 9 arom. H); 6.38 (br. *s*, NH); 5.27–5.18 (*dq*, *J* = 8.0, 6.2, MeC*H*); 4.35, 4.27 (*AB*, *J* = 11.9, PhC$H_2$); 3.18, 3.03 (*AB*, *J* = 13.0, SiC$H_2$); 3.07 (*d*, *J* = 8.0, SiCH); 2.07 (*s*, MeC(O)); 1.29 (*d*, *J* = 6.2, *Me*CH); 0.93 (*s*, *t*-Bu); 0.00 (*s*, MeSi). CI-MS: 537/539 (5, $[M+NH_4]^+$), 520/522 (1, $[M+H]^+$), 436/438 (40), 359 (12), 305 (100), 171 (14), 119 (13), 102 (96).

**4. Crystal Structure Determination of 18d, 18f, and 18g, and of the (4-Bromophenyl)carbamate of 19b**[7]. All measurements were conducted on a *Rigaku AFC5R* diffractometer fitted to a 12-kW rotating anode generator. The intensities of three standard reflections, which were measured after every 150 reflections, remained stable throughout each data collection. The intensities were corrected for *Lorentz* and polarization effects, but not for

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[7] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Center* as supplementary publication no. CCDC-106601 (**18d**), 106602 (**18f**), 106603 (**18g**), and 106604 ((4-bromophenyl)carbamate of **19b**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fac: +44-(0)1223-336033; email: deposit@ccdc.cam.ac.uk).

absorption. The structures of **18d** and **18f** were solved by direct methods using SHELXS86 [29], which revealed the positions of all non-H-atoms. The structures of **18g** and of the (4-bromophenyl)carbamate of **19b** were solved by *Patterson* methods using SHELXS86 and DIRDIF 92 [30], respectively, which yielded the positions of the heavy atoms. All remaining non-H-atoms were located in *Fourier* expansions of the *Patterson* solutions. The non-H-atoms were refined anisotropically except for the disordered C-atoms of the minor orientation of **18g** (see below), which were refined isotropically. All H-atoms of **18d** and **18f** were located in difference electron-density maps, and their positions were refined together with individual isotropic displacement parameters. For **18g** and for the (4-bromophenyl)carbamate of **19b**, the H-atoms bonded to O or N, resp., were fixed in the positions indicated by a difference electron-density map, and the remaining H-atoms were fixed in geometrically calculated positions with a C–H distance of 0.95 Å. Each H-atom of **18b** and the H-atom bonded to C(11) of the (4-bromophenyl)carbamate of **19b** was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of the atom to which it was bonded. Individual isotropic temp. factors were refined for all other H-atoms of the (4-bromophenyl)carbamate of **19b**. All refinements were carried out on *F* using full-matrix least-squares procedures which minimized the function $\sum w(|F_o|-|F_c|)^2$, where $1/w=[\sigma^2(F_o)+(0.005F_o)^2]$. The data

Table 3. *Crystallographic Data for* **18d**, **18f**, *and* **18g** *and for (4-Bromophenyl)carbamate of* **19b**

| | **18d** | **18f** | **18g** | (4-Bromophenyl)-carbamate of **19b** |
|---|---|---|---|---|
| Crystallized from | hexane | hexane | EtOH | hexane |
| Empirical formula | $C_{12}H_{26}O_2Si$ | $C_{17}H_{28}O_2Si$ | $C_{20}H_{32}O_2Si$ | $C_{25}H_{34}BrNO_4Si$ |
| Formula weight | 230.42 | 292.49 | 332.56 | 520.54 |
| Crystal color, habit | colorless, prism | colorless, needle | colorless, prism | colorless, prism |
| Crystal dimensions [mm] | 0.20 × 0.25 × 0.38 | 0.15 × 0.23 × 0.50 | 0.25 × 0.45 × 0.45 | 0.15 × 0.18 × 0.38 |
| Diffractometer | *Rigaku AFC5R* | *Rigaku AFC5R* | *Rigaku AFC5R* | *Rigaku AFC5R* |
| Radiation, wavelength [Å] | Mo$K_\alpha$, 0.71069 | Mo$K_\alpha$, 0.71069 | Mo$K_\alpha$, 0.71069 | Mo$K_\alpha$, 0.71069 |
| Crystal temp. [K] | 173(1) | 173(1) | 173(1) | 173(1) |
| Scan type | $\omega/2\theta$ | $\omega/2\theta$ | $\omega/2\theta$ | $\omega$ |
| Crystal system | monoclinic | triclinic | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ | $P2_1/c$ |
| *Z* | 4 | 4 | 4 | 4 |
| Reflections for cell determination | 25 | 25 | 25 | 23 |
| $2\theta$ Range for cell determination [°] | 29–38 | 24–26 | 36–40 | 20–35 |
| Unit cell parameters *a* [Å] | 10.126(2) | 10.929(1) | 13.483(4) | 10.438(4) |
| *b* [Å] | 11.771(2) | 20.469(5) | 16.204(5) | 10.299(5) |
| *c* [Å] | 12.101(2) | 8.242(2) | 9.419(5) | 25.465(2) |
| $\alpha$ [°] | 90 | 95.23(3) | 90 | 90 |
| $\beta$ [°] | 100.87(1) | 104.05(2) | 107.70(3) | 96.31(1) |
| $\gamma$ [°] | 90 | 86.86(2) | 90 | 90 |
| *V* [Å$^3$] | 1416.5(4) | 1780.1(8) | 1960(1) | 2721(2) |
| *F*(000) | 512 | 640 | 728 | 1088 |
| $D_x$ [g cm$^{-3}$] | 1.080 | 1.091 | 1.127 | 1.270 |
| $\mu$(Mo$K_\alpha$) [mm$^{-1}$] | 0.149 | 0.132 | 0.127 | 1.587 |
| $2\theta_{(max)}$ [°] | 55 | 50 | 55 | 55 |
| Total reflections measured | 3596 | 6610 | 4864 | 6969 |
| Symmetry-independent reflections | 3249 | 6251 | 4508 | 6267 |
| Reflections used ($I>2\sigma(I)$) | 2050 | 4745 | 3098 | 2668 |
| Parameters refined | 240 | 585 | 246 | 322 |
| *R* | 0.0421 | 0.0400 | 0.0750 | 0.0489 |
| *wR* | 0.0350 | 0.0386 | 0.0729 | 0.0376 |
| Goodness of fit *s* | 1.785 | 1.696 | 3.082 | 1.589 |
| Secondary extinction coefficient | – | – | $1.3(2)\cdot10^{-6}$ | – |
| Final $\Delta_{max}/\sigma$ | 0.0004 | 0.0005 | 0.0001 | 0.0001 |
| $\Delta\rho$ (max; min) [e Å$^{-3}$] | 0.31; −0.21 | 0.25; −0.21 | 0.37; −0.41 | 0.58; −0.68 |
| $\sigma(d(C-C))$ [Å] | 0.003–0.004 | 0.003–0.004 | 0.004–0.03 | 0.006–0.008 |

collection and refinement parameters for each compound are listed in *Table 3*. Neutral atom-scattering factors for non-H-atoms were taken from [31] and the scattering factors for H-atoms from [32]. Anomalous dispersion efects were included in $F_c$ [33] the values for $f'$ and $f''$ were taken from [34]. All calculations were performed using the TEXSAN [35] crystallographic software package.

*Specific Remarks.* The molecules of racemic **18d** are linked to infinite one-dimensional chains by intermolecular H-bonds between the OH group and the C=O O-atom of a neighboring molecule.

The crystal of racemic **18f** contains two independent molecules in the asymmetric unit. The major differences between the molecules are twists about the C(4)–C(5) and C(5)–C(6) bonds by *ca.* 29 and 33°, resp. The orientation of the O–H bond is also different in the two molecules because each independent molecule shows a H-bond to a different O-atom of a neighboring molecule, namely the OH O-atom in molecule B and the C=O O-atom in molecule A. The H-bonds link the molecules into infinite one-dimensional. ⋯ A ⋯ B ⋯ A ⋯ B ⋯ chains.

The structure of racemic **18g** exhibits disorder in the (*t*-Bu)$Me_2$Si chain and the cyclohexane ring, in which the OH group occupies alternately both sites in $\alpha$-position to C(1). Two positions were defined for the OH group, C(6) and the atoms of the (*t*-Bu)$Me_2$Si group. The central C-atom of the *t*-Bu group is common to both orientations. The relative site occupancies of the two orientations are 0.802 : 0.198. Some of the bond lengths and angles in the disordered region have quite poor agreement with the normally expected geometry, especially for the minor conformation and in the *t*-Bu group; however, the overall structural features and connectivity are clearly defined. Poor bond angles for the minor orientation of the cyclohexane ring suggest that the ring may contain additional disorder, but additional electron density could not be detected. The major conformation exhibits an intramolecular H-bond between the OH group and the C=O O-atom. The situation for the minor conformations is unclear because the location of the OH H-atom is probably unreliable due to the very weak electron density; the minor conformation possibly forms intermolecular H-bonds involving the same atoms.

In the racemic (4-bromophenyl)carbamate of **19b**, the displacement ellipsoids of some atoms in both phenyl rings and the Br-atom are unusually elongated. The pattern of these distortions is irregular and cannot, therefore, be explained in terms of thermal vibration within the crystal. It is presumably the effect of some systematic error in the data, possibly arising from the crystal quality. The crystals that were examined were weakly diffracting, and broadened peak profiles attested to the imperfect quality of the crystals. The molecules are linked in infinite one-dimensional chains by intermolecular H-bonds between the amide NH group and the C=O O-atom of a neighboring molecule.

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