

127. Chiral Acylsilanes in Organic Synthesis

Part 2¹⁾

The Role of the Solvent, the Organometallic Reagent, and the Nature of the Substrate for the Diastereoselectivity of 1,2-Additions to Racemic Alkoxyethyl-Substituted Acylsilanes

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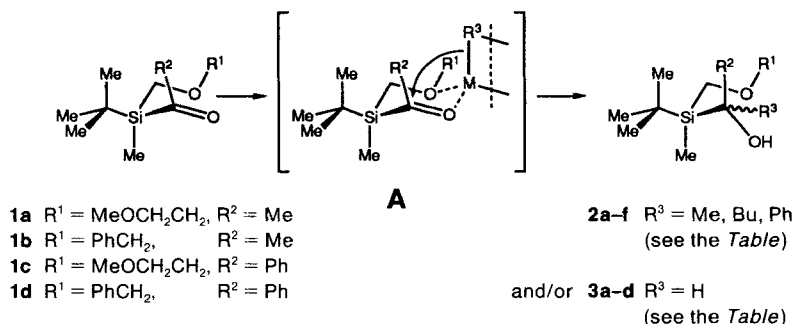
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(18.V.93)

The role of the solvent, the organometallic reagent, and the nature of the substrate for the diastereoselectivity of 1,2-additions to racemic alkoxyethyl-substituted acylsilanes was investigated with the acylsilanes **1a–d** by variation of the reaction parameters. The results obtained in this study support strongly the previously proposed preferred 'chelate-controlled' reaction path followed under several reaction conditions: highest stereoselectivities were obtained with the best chelating substrates reacting with the most *Lewis*-acidic organometallic reagents in the least donating solvents. It is shown that almost complete stereoselectivity can be obtained using optimal reaction conditions.

1. Introduction. – We reported in the previous communication on the synthesis of the acylsilanes **1a** and **1b** and on their reactions with NaBH₄ and PhLi [1]. Depending upon the solvent used, moderate-to-high diastereoselectivities were found for the corresponding 1,2-additions to the C=O group. The results indicated that in little-coordinating solvents such as Et₂O the transformations with PhLi proceed preferentially *via* six-membered chelates of the type **A** leading with high diastereoselectivities to the corresponding alcohols **2** or **3** (Scheme 1). Chelate intermediates of the type **A** were considered to be less favored in better coordinating solvents. Thus, the transformations lead to products

Scheme 1



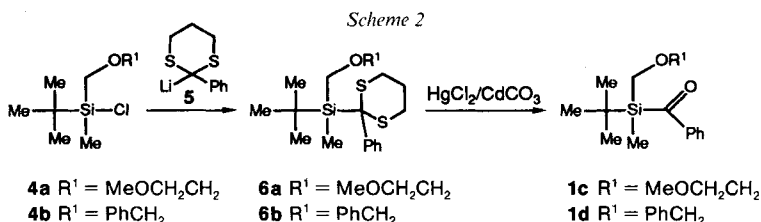
¹⁾ Part 1: [1].

²⁾ Part of the planned Ph. D. thesis of A. C., Universität Zürich.

deriving predominantly from an attack of the molecules in an open-chain form explaining the lower and reversed stereoselectivities found for the reactions performed in THF solution.

We were now interested to learn more about the dependence of the above transformations on several structure and process parameters with the aim to test our proposition of a competitive ‘chelate-controlled’/‘open-chain-controlled’ reaction course. Further, we intend to apply the newly gained insights to improve the diastereoselectivities of nucleophilic additions to chiral acylsilanes or of related processes. In the following, we present the results of a more thorough investigation of the role of the solvents, the organometallic reagents, and the nature of the substrate for the stereochemical outcome of 1,2-additions to chiral acylsilanes.

2. Results. – **2.1. Synthesis of the Racemic Acylsilanes **1c** and **1d**.** To study more profoundly the influence of the substrate structure on the reaction course of nucleophilic additions to chiral alkoxymethyl-substituted acylsilanes, it is necessary to vary not only the character of the alkoxymethyl substituent of such compounds but also the nature of the C=O moiety. The comparison of alkyl silyl ketones with aryl silyl ketones was expected to be especially informative with reference to the influence of the basicity of the carbonyl O-atom on the stereochemical outcome of the transformations. We synthesized, therefore, the phenyl silyl ketones **1c** and **1d** to compare the stereochemical results of their reactions with those obtained with **1a** and **1b**.



The racemic phenyl silyl ketones **1c** and **1d** were prepared in analogy to literature procedures [2][3] in two high-yielding steps, starting with chorosilanes **4a** and **4b**, synthesized from commercially available dichloro(chloromethyl)methylsilane as described in [1]. Replacement of the Cl-atoms in **4** by the 2-phenyl-1,3-dithiane-2-yl group by reaction with Li-dithiane **5** afforded the thioacetals **6a** and **6b** in 81 and 89% yield, respectively, and treatment of these compounds with $\text{HgCl}_2/\text{CdCO}_3$ in H_2O /acetone/toluene at reflux for several hours provided the desired products **1c** and **1d** in 87 and 83% yield.

Phenyl silyl ketones are of a characteristic yellow color (UV: $\lambda_{\text{max}} \approx 405$ (2.08), 421 (2.19), 441 (1.96)) and show in ^{13}C -NMR chemical shifts for the carbonyl C-atoms of $\delta \approx 234$ ppm, *ca.* 10 ppm upfield, compared to the absorptions of the carbonyl C-atoms of the corresponding methyl silyl ketones **1a** and **1b**. They show in EI-MS only negligible signals for the M^+ ions; in CI-MS with NH_3 as the reactant gas, however, $[M+1]^+$ and $[M+1+\text{NH}_3]^+$ ions are detected.

2.2. Addition of Organometallic Reagents to the Acylsilanes **1a–d.** The silyl ketones **1a–d** were treated with several organolithium and Grignard reagents under various conditions to deliver, in moderate-to-high chemical yields, the corresponding tertiary alcohols **2a–f** as mixtures of diastereoisomers (*cf.* Scheme 1). The conditions and results of these reactions are summarized in the Table.

Table. Results of the 1,2-Additions of Organometallic Reagents to Acylsilanes under Various Reaction Conditions

Entry	Substrate			Reaction conditions		Addition product			Reduction product		
	No.	R ¹	R ²	R ³ M	Solvent	No.	Yield [%]	de [%] ^{a)}	No.	Yield [%]	de [%] ^{a)}
1	1a	MeOCH ₂ CH ₂	Me	PhLi	Hexane	2a	82	83	—	—	—
2	1a	MeOCH ₂ CH ₂	Me	PhLi	Et ₂ O	2a	80	78	—	—	—
3	1a	MeOCH ₂ CH ₂	Me	PhLi	Et ₂ O/DME ^{b)}	2a	38	9	—	—	—
4	1a	MeOCH ₂ CH ₂	Me	PhLi	THF	2a	77	33	—	—	—
5	1a	MeOCH ₂ CH ₂	Me	PhLi	Et ₂ O/DMPU ^{b)}	2a	34	58	—	—	—
6	1a	MeOCH ₂ CH ₂	Me	PhMgBr	Et ₂ O	2a	64	89	—	—	—
7	1a	MeOCH ₂ CH ₂	Me	PhMgBr	THF	2a	41	66	—	—	—
8	1b	PhCH ₂	Me	PhLi	Hexane	2b	75	82	—	—	—
9	1b	PhCH ₂	Me	PhLi	Et ₂ O	2b	88	78	—	—	—
10	1b	PhCH ₂	Me	PhLi	Et ₂ O/DME ^{b)}	2b	35	44	—	—	—
11	1b	PhCH ₂	Me	PhLi	THF	2b	43	50	—	—	—
12	1b	PhCH ₂	Me	PhLi	Et ₂ O/DMPU ^{b)}	2b	30	60	—	—	—
13	1b	PhCH ₂	Me	PhMgBr	Et ₂ O	2b	67	43 ^{c)}	—	—	—
14	1b	PhCH ₂	Me	PhMgBr	THF	2b	75	46	—	—	—
15	1c	MeOCH ₂ CH ₂	Ph	MeLi	Et ₂ O	2a	95	75	—	—	—
16	1c	MeOCH ₂ CH ₂	Ph	MeLi	THF	2a	97	29	—	—	—
17	1c	MeOCH ₂ CH ₂	Ph	MeMgBr	Et ₂ O	2a	78	99	—	—	—
18	1c	MeOCH ₂ CH ₂	Ph	MeMgBr	THF	2a	98	99	—	—	—
19	1d	PhCH ₂	Ph	MeLi	Et ₂ O	2b	85	82	—	—	—
20	1d	PhCH ₂	Ph	MeLi	THF	2b	74	36	—	—	—
21	1d	PhCH ₂	Ph	MeMgBr	Et ₂ O	2b	98	97	—	—	—
22	1d	PhCH ₂	Ph	MeMgBr	THF	2b	98	97	—	—	—
23	1a	MeOCH ₂ CH ₂	Me	BuLi	Et ₂ O	2c	60	95	3a	32	82
24	1a	MeOCH ₂ CH ₂	Me	BuLi	THF	2c	50	82	3a	0	—
25	1a	MeOCH ₂ CH ₂	Me	BuMgBr	Et ₂ O	2c	68	96	3a	20	68
26	1a	MeOCH ₂ CH ₂	Me	BuMgBr	THF	2c	40	95	3a	8	50
27	1b	PhCH ₂	Me	BuLi	Et ₂ O	2d	56	60	3b	21	79
28	1b	PhCH ₂	Me	BuLi	THF	2d	52	44	3b	0	—
29	1b	PhCH ₂	Me	BuMgBr	Et ₂ O	2d	60	72	3b	20	33
30	1b	PhCH ₂	Me	BuMgBr	THF	2d	51	33	3b	34	9
31	1c	MeOCH ₂ CH ₂	Ph	BuLi	Et ₂ O	2e	57	78	3c	41	71
32	1c	MeOCH ₂ CH ₂	Ph	BuLi	THF	2e	83	29	3c	10	33
33	1c	MeOCH ₂ CH ₂	Ph	BuMgBr	Et ₂ O	2e	42	99	3c	50	98
34	1c	MeOCH ₂ CH ₂	Ph	BuMgBr	THF	2e	0	—	3c	79	60
35	1d	PhCH ₂	Ph	BuLi	Et ₂ O	2f	40	83	3d	44	43
36	1d	PhCH ₂	Ph	BuLi	THF	2f	46	65	3d	23	9
37	1d	PhCH ₂	Ph	BuMgBr	Et ₂ O	2f	53	94	3d	40	64
38	1d	PhCH ₂	Ph	BuMgBr	THF	2f	0	—	3d	72	17
39	1a	MeOCH ₂ CH ₂	Me	<i>t</i> -BuLi	Et ₂ O	—	—	—	3a	52	82
40	1b	PhCH ₂	Me	<i>t</i> -BuLi	Et ₂ O	—	—	—	3b	62	81

^{a)} The diastereoisomeric excesses (de's) were obtained from ¹H-NMR spectra of the crude products. The de's given in *italics* indicate the preferred formation of the 'open-chain-controlled' products.

^{b)} Five equiv. of co-solvent were added to the solution prior to the PhLi addition.

^{c)} A hitherto structurally unknown Si-containing side-product was formed; this de is, therefore, not reliable.

Some transformations, namely the reactions of the compounds **1a–d** with BuLi, BuMgBr, and *t*-BuLi, led not only to the expected alkyl addition products **2** but also to the corresponding secondary alcohols **3a–d**, resulting from formal hydride reduction of

the C=O group. The yields of these side products and the stereochemical results of the reductions are also summarized in the *Table*.

3. Discussion. – 3.1. *The Role of the Solvent.* The stereochemical outcome of nucleophilic additions to alkoxyethyl-substituted acylsilanes shows a strong dependence on the reaction medium. We already concluded from our preliminary findings – as mentioned before – that in little-coordinating solvents like Et₂O a ‘chelate-controlled’ reaction path *via* an intermediate of the type **A** is preferred, whereas in more basic environments – as a consequence of the competing stabilization of the cation by solvation – a non-chelated ‘open-chain-controlled’ [4] reaction course is predominantly followed. On the basis of this model, it is assumed that the use of less coordinating solvents than Et₂O should even more favor the ‘chelate-controlled’ reaction path and, thus, enhance the diastereoselectivities of organometallic additions to chiral acylsilanes in these solvents. On the other hand, the admixture of better coordinating co-solvents to Et₂O, like DME or DMPU, should disfavor the formation of chelates of the type **A** and, therefore, lower or even reverse the stereoselectivities of the reactions. In fact, these expected solvent effects could be established with our investigation.

Pars pro toto, the stereochemical outcome of the PhLi additions to the methyl silyl ketones **1a** and **1b** in different solvent systems are visualized in *Fig. 1*. The stereoselectivi-

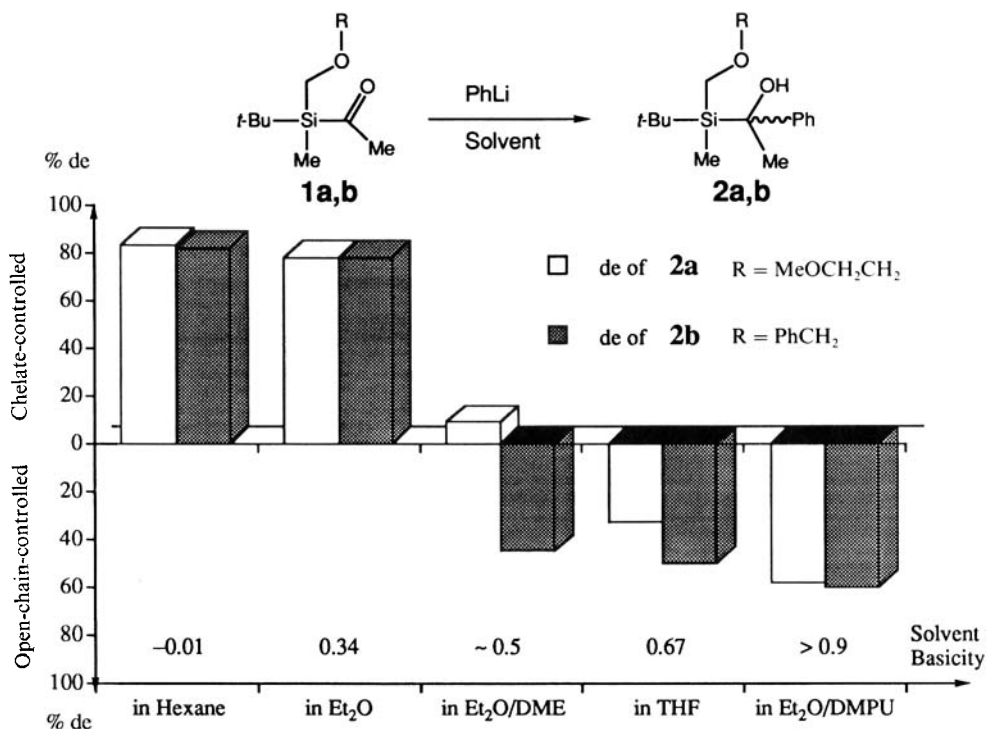


Fig. 1. Selectivity dependence on the nature of the solvent: stereochemical outcomes of the 1,2-additions of PhLi to **1a** and **1b** as a function of the solvent basicity. The de's in favor of the ‘open-chain-controlled’ products are indicated below the x-axis.

ties of these transformations – characterized by the diastereoisomeric excesses (de) of the corresponding major product isomer – are delineated as columns in the graph, arranged in the order of increasing solvent basicity. The de's in favor of the 'open-chain-controlled' products are drawn towards the negative direction of the ordinate.

The basicities (B values) of the solvents (hexane: -0.01 ; Et_2O : 0.34 ; DME: 0.50 ; THF: 0.67) are quoted from a communication by Swain *et al.* [5] where the free energy changes due to solvent were fitted for a number of reactions by the function $aA + bB + c$, with A (anion-solvating tendency) and B (cation-solvating tendency = basicity) depending on only the solvent and a, b , and c depending on solely the reaction. The given B values have to be understood relative to two of the trivial scale-setting subsidiary conditions $B = 0$ for heptane and $B = 1$ for H_2O set for the evaluation of the constants A, B, a, b , and c . The B values for the Et_2O /DME mixture used in the above experiments is estimated to be approximately the same as for DME alone (~ 0.5 , no change in selectivity using higher DME concentrations was found), and the basicity of the Et_2O /DMPU mixture is judged to exceed 0.9 , based on the B values of other well-coordinating aprotic dipolar solvents such as DMF (0.93), HMPTA (1.07), and DMSO (1.08).

It can easily be recognized from the graph in *Fig. 1* that, along with the increasing basicity of the solvent system, the 'chelate-controlled' reaction path becomes less important. In an Et_2O /DME solvent mixture³⁾ – perceptible on the preferred formation of the hitherto minor product isomer – even the alternative 'open-chain-controlled' reaction course begins to dominate for the reaction with the benzyloxymethyl-substituted silane **1b**. In the same solvent system, the corresponding (2-methoxyethoxy)methyl-substituted compound **1a** still yields with a small preference the 'chelate-controlled' reaction product, but the corresponding 'selectivity flip' is found for this starting silane, too, when the more-donating solvent THF is used.

In the two solvent systems Et_2O /DME and THF, the selectivity differences of the PhLi additions to the acylsilanes **1a** and **1b** – deriving from rather small differences in the chelation abilities of the two compounds (see discussion later) – are most pronounced, indicating real competitions of the two proposed reaction paths in these solvents. In hexane or in Et_2O /DMPU solution, on the other hand, practically no selectivity differences are observed for the reactions of **1a** and **1b**, implying pure reaction mechanisms to be followed in these solvents. In the nonbasic hexane, the 'chelate-controlled' reaction path is strongly preferred, more or less independent from small structural differences of the substrate, whereas in the well donating Et_2O /DMPU mixture – equally independent from small structural substrate variations – the non-chelated 'open-chain-controlled' reaction path predominates.

In agreement with the observed solvent dependence of the PhLi additions to the acetylsilanes **1a** and **1b**, a remarkable decrease in selectivity was also noticed for all other 1,2-addition reactions with **1a–d**, when the solvent was changed from Et_2O to the more basic THF (*cf.* the *Table*). Thus, in all cases, the stereoselectivities obtained in 1,2-addition reactions to the $\text{C}=\text{O}$ group of chiral alkoxymethyl-substituted acylsilanes are highest, when nonbasic solvents assisting the formation of chelates of the type **A** are used.

3.2. The Role of the Organometallic Reagent. It seems evident that the tendency to form intermediary chelates of the type **A** in the transformations of the acylsilanes **1** to the

³⁾ The reaction could not be performed in pure DME at standard conditions (-90°) because of solidification of the solvent. Five equiv. of DME in Et_2O was used instead. It was found that the addition of more DME did not alter the stereochemical outcome of the reaction, indicating no further increase of solvent basicity.

alcohols **2** would not only be a function of the solvent basicity but also of the nature of the attacking organometallic reagent and the substrate. The higher the ability of a substrate is to chelate a particular reagent or the better complexed a reagent can be by a given substrate, the more 'chelate-controlled' reaction should be observed. To test the role of the metal portion of the attacking organometallic reagents for the selectivity of nucleophilic additions to the acylsilanes **1**, the reactions with organosodium, organopotassium, organotitanium, and *Grignard* reagents were examined. With the organoalkali reagents a successive decrease in 'chelate-controlled' selectivity was expected in the order $\text{RLi} > \text{RNa} > \text{RK}$ (R = alkyl or aryl) according to the decreasing heat of solvation found for $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ in several solvents (*cf. e.g.* [6]). For the reactions with *Grignard* and organotitanium reagents increased selectivities – compared to those obtained with Li reagents – were anticipated as a consequence of the increased *Lewis* acidity of the metal cations.

The reactions of the acetylsilanes **1a** and **1b** with PhNa and PhK, however, were not successful. After acidic workup, only starting silanes and decomposition products were obtained. Evidently, the reagents did not add to the C=O group of the acylsilanes but – due to their high basicity – they deprotonated the ketones to form the corresponding enolates. In fact, these enolates could be trapped with benzaldehyde as an electrophile leading to aldol-type products. The reactions of **1a** and **1b** with several phenyl titanium reagents failed as well. Either no reaction was observed (at -90°), or the silanes were completely decomposed (at $\geq -30^\circ$).

Only the additions of *Grignard* reagents to the silanes **1a–d** lead successfully to the alcohols **2**. As expected, the stereoselectivities of all reactions with PhMgBr, MeMgBr, or BuMgBr were distinctively higher than those obtained in the transformations using the corresponding Li reagents. As a matter of fact, the highest stereoselectivities at all with formation of the major isomer in up to $> 99\%$ de have been obtained using *Grignard* reagents. Exemplarily, the results of the butyl additions in Et_2O and THF are delineated graphically in *Fig. 2*. The background columns in the graph, representing the de's of the BuMgBr additions, are in all cases higher (towards the 'chelate-controlled' product) than the columns in the foreground, visualizing the de's achieved using Li compounds. Comparing the stereochemical outcomes of the reactions of a particular starting material with the two organometallic reagents in the two solvents used, the selectivity differences are more pronounced in the better coordinating THF than in Et_2O . The reaction, again, shows more sensitivity to structural parameters – this time varied in the reagent – in the more donating solvent where the competition of the 'chelate-controlled' and the 'open-chain-controlled' reaction paths is more important.

The stereoselectivity of the organometallic additions seems not to depend crucially on the bulkyness of the attacking carbanoid nucleophile but more on the state of aggregation of the organometallic reagent. For instance, the additions of MeLi and BuLi in Et_2O – both reagents exist as tetramers in this solvent – to **1c** (*Entries 15 and 31*; 75 and 78% de, respectively) and **1d** (*Entries 19 and 35*; 82 and 83% de) afforded almost the same stereochemical results, whereas the reaction of PhLi – which is dimeric in Et_2O – compared to that of BuLi gave distinctively lower selectivity with **1a** (*Entries 2 and 23*; 78 and 95% de) and higher selectivity with **1b** (*Entries 9 and 27*; 78 and 60% de). Our limited interpretation of these results, however, should not be overvalued: as a consequence of the fact that solutions of organolithium compounds, analogously to solutions of *Grignard*

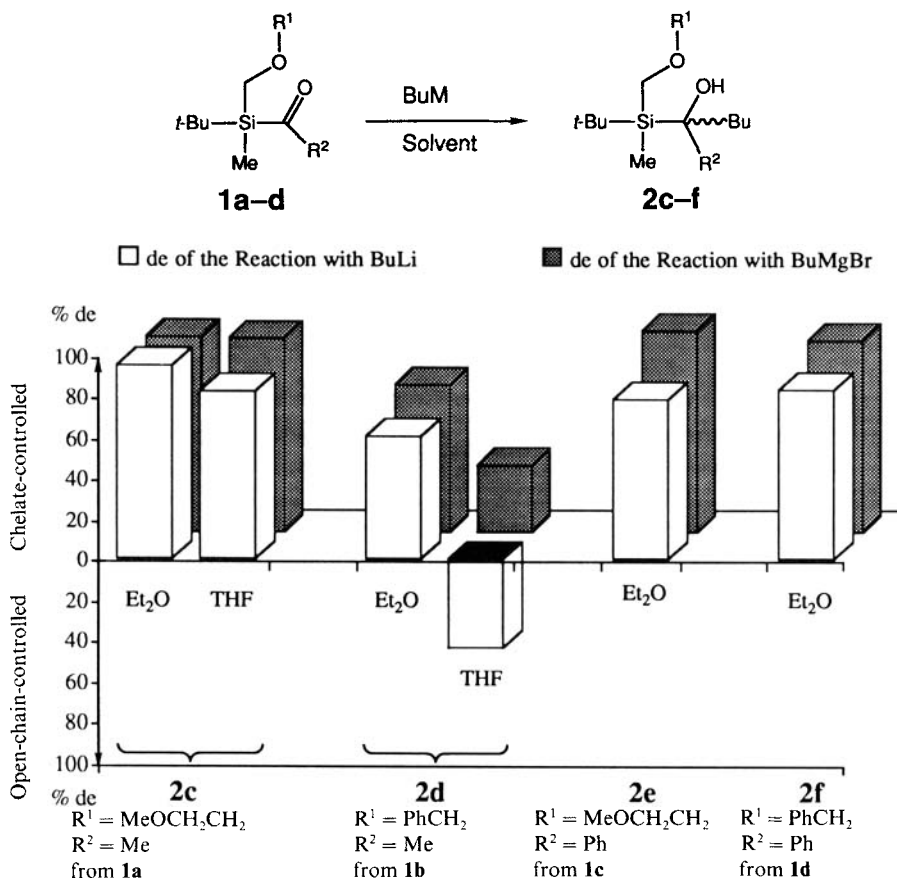


Fig. 2. Selectivity dependence on the nature of the organometallic reagent: comparison of the stereochemical outcomes of the 1,2-additions of BuLi and BuMgBr to **1a-d**

reagents, are complex dynamic-equilibrium systems [7], it is far from certain what exactly the aggregation state of the organometallic species in the transition state of the reaction is. It is to note at this point, too, that it was not possible to investigate in more detail the selectivity dependence of the reactions on steric factors of the reagent. The treatment of the acylsilanes **1a-d** with bulkier organometallic reagents – like *t*-BuLi – yielded solely the corresponding reduction products **3a-d** along with recovered starting material.

3.3. The Role of the Substrate Structure. It has been already mentioned earlier that it would be reasonable to find the preferred formation of ‘chelate-controlled’ products in nucleophilic additions to the chiral acylsilanes **1a-d** paralleling the degree of the substrate abilities to chelate a given reagent. However, such tendencies – expressed, *e.g.*, as complex stability constants – are not accessible for our silanes, and they could not be reliably established without performing laborious experiments and/or calculations. Yet, we were confident to qualitatively assign relative complexing abilities on the basis of the structural peculiarities of the silanes compared. It seemed evident in analogy to, *e.g.*, [8] that metal complexes of the (2-methoxyethoxy)methyl-substituted acylsilanes **1a** and **1c** would be

more stable than those of the corresponding (benzyloxy)methyl-substituted silanes **1b** and **1d**, which possess one coordinating O-atom less in their structures. Analogously, the benzoylsilanes **1c** and **1d** were assumed to be better complexing agents than the corresponding acetylsilanes **1a** and **1b** because of the higher basicity of the carbonyl O-atom of conjugated ketones (*cf. e.g.* [9] [10]). The selectivities obtained in the reactions of the organometallic compounds with **1a–d**, shown graphically in *Fig. 3* for the addition of the Bu group, confirmed to a great extent that these simple reflections were reasonable. The reactions of **1a–d** with *Grignard* reagents showed indeed the expected relative stereochemical outcomes: higher selectivities were found for the (2-methoxyethoxy)methyl-substituted acylsilanes **1a** and **1c**, each compared with the corresponding (benzyloxy)methyl-substituted silane **1b** and **1d**, and increased selectivities were observed for the benzoylsilanes **1c** and **1d** compared with the corresponding acetylsilanes **1a** and **1b**.

Some results diverging from our expectations were obtained with the organolithium reagents. Comparing the BuLi additions to the acetylsilanes **1a** and **1b** or to the (benzyl-

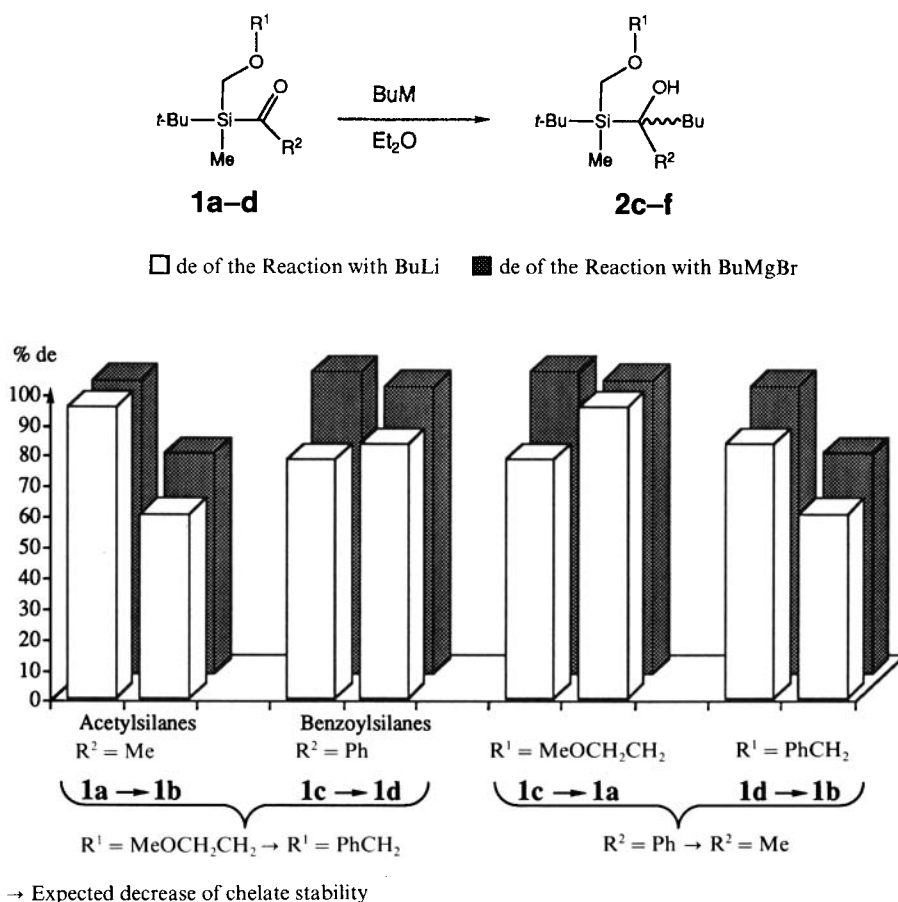


Fig. 3. Selectivities obtained from the 1,2-additions of BuLi and BuMgBr to **1a–d** in Et₂O

oxy)methylated silanes **1d** and **1b**, the corresponding stereoselectivities are still higher for the first of the two compounds each, as expected, but comparing the reactions of the benzoylsilanes **1c** and **1d** or of the (2-methoxyethoxy)methyl-substituted acylsilanes **1c** and **1a**, an unexpected lower selectivity is noticed for the corresponding first – expectedly more chelating – acylsilane **1c**.

Silane **1c** evidently represents the exception within the row of the four compounds **1a–d**. The reason for its different behavior towards BuLi is not known. We assume, however, that steric interactions of the large groups in a tridentate complex of the type **A** decrease markedly its stability, and coordinating the lithium cation with all three O-atoms of the silane **1c** might be less favorable. The stability of the corresponding Mg complex of the type **A** should be less decreased because of the more stable Mg–O bonds associated with the higher *Lewis* acidity of the metal cation.

3.4. Formation of the Reduction Products 3a–d. Treatment of the acylsilanes **1a–d** with butyl organometallic reagents afforded, in addition to the desired tertiary alcohols **2c–f**, the secondary alcohols **3a–d** with up to 80% yield and with moderate-to-high stereoselectivities. Whereas the reduction of sterically hindered ketones with bulky alkyl *Grignard* reagents is well known [11–13], we were surprised to find the corresponding reaction also with organolithium reagents⁴). The amounts of reduction product formed with the Li compounds are characteristically lower than those produced by action of organomagnesium reagents – as can be recognized from the results summarized in the *Table* – but with up to 62% yield (for the reaction of **1b** with *t*-BuLi), they can not be ignored.

The stereoselectivities of the reduction reactions show dependencies on reaction and structural parameters paralleling to some extent those observed for the addition reactions, indicating similar mechanisms to be followed. For example, the diastereoselectivities increase generally with decreasing solvent basicity. However, a behavior diverging from the expectations for a ‘chelate-controlled’ reaction is found for these transformations, too. The stereodifferentiation grows with increasing acidity of the metal portion of the organometallic reagent in the additions to the benzoylsilanes **1c** and **1d** but decreases slightly in the additions to the acetylsilanes **1a** and **1b**. An increase of stereoselectivity was also observed, when the reactions of the acetylsilanes **1a** and **1b** or the benzoylsilanes **1c** and **1d** were compared, but a slight decrease of selectivity was recognized comparing the reactions of the benzoylsilanes with those of the acetylsilanes.

4. Conclusion. – The present investigation clearly demonstrates that the stereoselectivities of 1,2-addition reactions to the C=O group of chiral alkoxyethyl-substituted acylsilanes depend crucially on process and structure parameters. The best stereochemical results with a given substrate were obtained, when *Grignard* reagents were used as the organometallic reaction partners, and the transformations were carried out in Et₂O as a little-donating solvent (up to 99% de, cf. *Entries 17 and 33 of the Table*). These findings not only support the proposed ‘chelate-controlled’ reaction path but also allow the statement that chiral alkoxyethyl-substituted silyl groups can be used efficiently for the transfer of chiral information from a Si-atom to an adjacent C-atom. With optically active acylsilanes as the starting compounds, enantiomerically enriched C-frameworks

⁴) Decomposition of THF to lithium butanolate – corresponding to a formal hydride reduction, too – was observed by action of ‘aged’ BuLi [14]. We checked our reactions with ‘fresh’ BuLi, which does not show the corresponding THF decomposition, and found still reduction of the silanes.

should be accessible using the above described transformation. The synthesis of enantiomerically pure silanes is our objectives to achieve next.

We thank the members of our analytical laboratories for their excellent services, Mr. A. Guggisberg for his many helpful advises, and the Swiss National Science Foundation for financial support. We are especially grateful to Prof. Dr. M. Hesse who provided us with laboratory space, equipment, and regular occasions for discussions.

Experimental Part

General. Unless otherwise stated: all org. solvents were distilled prior to use. For the reactions, THF and Et₂O were dried over Na-ketyl, pentane, and hexane over CaH₂. All reactions were carried out under Ar. Soln. of salts and acids for workup were prepared in deionized H₂O. Extracts were dried (Na₂SO₄) and evaporated *in vacuo*. Chromatography: silica gel Merck 60 (40–63 µm). M.p.: Mettler FP-5/FP-52. UV/VIS Spectra: Perkin-Elmer (model 555, 190–900 nm); maxima ($\lambda_{\max}$) in nm (log ϵ). IR Spectra: Perkin-Elmer 781; data in cm⁻¹. ¹H-NMR: at 300 MHz in CDCl₃; Bruker AC-300; δ in ppm rel. to CHCl₃ (= 7.26 ppm), *J* in Hz. ¹³C-NMR: at 50.4 MHz in CDCl₃; Varian XL-200; δ in ppm rel. to CDCl₃ (= 77.0 ppm); multiplicities from DEPT experiments. MS: EI (electron impact) at 70 eV, CI (chemical ionization) with ammonia; Finnigan MAT 90 or Varian MAT 711; data in *m/z* (rel. %).

1. Synthesis of the Benzoysilanes. – 1.1. 2-[(*tert*-Butyl)[(2-methoxyethoxy)methyl]methylsilyl]-2-phenyl-1,3-dithiane (**6a**). A soln. of 18.8 g (96.0 mmol) of 2-phenyl-1,3-dithiane in 6 ml of THF was treated with 55 ml (88 mmol) of 1.6M BuLi in pentane at –40°. The mixture was allowed to warm to 0° within 2 h and was stirred for another 3 h. After dropwise addition of 17.2 g (76.8 mmol) of chloro(*tert*-butyl)[(2-methoxyethoxy)methyl]methylsilane (**4a**) the stirring was continued for an additional 12 h at 23°. Quenching with sat. NH₄Cl soln., extraction with Et₂O, and chromatography (hexane/AcOEt 20:1) gave 23.9 g (81%) of **6a** as a colorless liquid. IR (film): 3060w, 3010w, 2930s, 2900s, 2860s, 2820w, 2710w, 1590w, 1480s, 1470s, 1460s, 1440s, 1420m, 1410m, 1390m, 1360m, 1340w, 1310w, 1270m, 1250s, 1200m, 1130s, 1100s, 1030m, 1010m, 980w, 930m, 910m, 890m, 870w, 830s, 800s, 790m, 760m, 720m, 700s, 680w. ¹H-NMR: 7.99–7.96 (*m*, 2 arom. H); 7.39–7.34 (*m*, 2 arom. H); 7.20–7.15 (*m*, arom. H); 3.58–3.44 (*m*, CH₂OCH₂CH₂O); 3.35 (*s*, MeO); 2.86–2.70, 2.41–2.34 (*2m*, 2 SCH₂); 2.09–1.82 (*m*, SCH₂CH₂); 0.85 (*s*, *t*-Bu); 0.22 (*s*, MeSi). ¹³C-NMR: 140.5 (*s*, arom. C); 130.0 (*d*, 2 arom. C); 128.3 (*d*, 2 arom. C); 125.4 (*d*, arom. C); 74.5 (*t*, MeOCH₂); 71.7 (*t*, SiCH₂OCH₂); 60.7 (*t*, SiCH₂O); 59.0 (*q*, MeO); 38.4 (*s*, PhC); 27.9 (*q*, Me₃C); 25.11, 25.10, 25.0 (*3t*); 19.9 (*s*, Me₃C); –9.9 (*s*, MeSi). CI-MS: 385 (36, [*M* + 1]⁺), 309 (100), 189 (12). Anal. calc. for C₁₉H₃₂O₂S₂Si (384.680): C 59.33, H 8.38, S 16.67; found: C 59.45, H 8.48, S 16.89.

1.2. 2-[(*Benzyloxy*)methyl](*tert*-butyl)methylsilyl]-2-phenyl-1,3-dithiane (**6b**). As described for **6a**, from 174.0 mg of 2-phenyl-1,3-dithiane in 6 ml of THF, 0.52 ml (0.73 mmol) of 1.4M *t*-BuLi in pentane, and 150.0 mg (0.58 mmol) of chloro[*benzyloxy*]methyl(*tert*-butyl)methylsilane (**4b**), after chromatography (hexane/AcOEt 20:1): 214.5 mg (89%) **6b**. Colorless liquid. IR (film): 3050w, 3020w, 2920s, 2895s, 2850s, 1950w, 1660w, 1590w, 1490w, 1470m, 1460m, 1440m, 1420m, 1410w, 1390w, 1380w, 1360w, 1310w, 1270w, 1250m, 1200w, 1180w, 1150w, 1090s, 1070s, 1030m, 1010w, 980w, 930m, 910w, 885w, 830s, 800s, 785m, 760m, 730s, 700s. ¹H-NMR: 7.98–7.96 (*m*, 2 arom. H); 7.37–7.25 (*m*, 6 arom. H); 7.20–7.15 (*m*, 2 arom. H); 4.46 (*s*, PhCH₂O); 3.48 (*s*, SiCH₂O); 2.86–2.70, 2.42–2.35 (*2m*, 2 SCH₂); 2.05–1.83 (*m*, SCH₂CH₂); 0.86 (*s*, *t*-Bu); 0.23 (*s*, MeSi). ¹³C-NMR: 140.5, 139.0 (2s, arom. C); 130.1 (*d*, 2 arom. C); 128.3 (*d*, 2 arom. C); 128.1 (*d*, 2 arom. C); 127.3 (*d*, 2 arom. C); 127.1, 125.5 (2*d*, arom. C); 77.0 (*t*, PhCH₂O); 60.0 (*t*, SiCH₂O); 38.5 (*s*, CPh); 28.0 (*q*, Me₃C); 25.2, 25.1, 25.0 (*3t*); 20.0 (*s*, Me₃C); –9.7 (*q*, MeSi). CI-MS: 417 (33, [*M* + 1]⁺), 311 (100). Anal. calc. for C₂₃H₃₂OS₂Si (416.725): C 66.29, H 7.74, S 15.39; found: C 66.51, H 7.80, S 15.62.

1.3. {(*tert*-Butyl)[(2-methoxyethoxy)methyl]methylsilyl} Phenyl Ketone (**1c**). A soln. of 23.9 g (62.2 mmol) of **6a** in 50 ml of acetone was added while stirring to a suspension of 108 g (400 mmol) of HgCl₂ and 27.5 g (160 mmol) of CdCO₃ in a mixture of 50 ml of H₂O, 130 ml of acetone, and 500 ml of toluene. After heating to reflux for 2 h the solvents were evaporated *in vacuo*, the residue dissolved in Et₂O, washed with H₂O and brine to give, after chromatography (hexane/Et₂O, gradient: 20:1 → 15:1), 15.9 g (87%) of **1c** as a bright yellow liquid. UV (hexane): $\lambda_{\max}$ 202 (4.17), 252 (4.09), 402 (2.08), 421 (2.19), 441 (1.97). IR (film): 3060w, 2960s, 2930s, 2895s, 2860s, 2820s, 2720w, 1970w, 1610s, 1590s, 1575s, 1470s, 1460s, 1405w, 1390m, 1365s, 1340w, 1305m, 1250s, 1210s, 1170m, 1160m, 1130s, 1100s, 1040m, 1025m, 1010m, 985w, 940m, 870m, 830s, 810s, 780s, 765s, 720m, 690s, 670m. ¹H-NMR: 7.92–7.89 (*m*, 2 arom. H); 7.55–7.43 (*m*, 3 arom. H); 3.62–3.51 (*m*, CH₂OCH₂CH₂O); 3.36 (*s*, MeO); 0.10 (*s*, *t*-Bu);

0.39 (s, MeSi). ^{13}C -NMR: 237.2 (s, CO); 142.4 (s, arom. C); 132.4 (d, arom. C); 128.3 (d, 2 arom. C); 127.6 (d, 2 arom. C); 74.5 (t, MeOCH_2); 71.5 (t, $\text{SiCH}_2\text{OCH}_2$); 61.0 (t, SiCH_2O); 58.7 (q, MeO); 26.9 (q, Me_3C); 17.0 (s, Me_3C); -8.1 (q, MeSi). CI-MS (C_4H_{10}): 295 (100, $[M + 1]^+$), 189 (5, $[M - \text{COPh}]^+$), 121 (4). Anal. calc. for $\text{C}_{16}\text{H}_{26}\text{O}_3\text{Si}$ (294.470): C 65.26, H 8.90; found: C 65.42, H 9.00.

1.4. $\{[(\text{Benzyloxy})\text{methyl}]/(\text{tert-butyl})\text{methylsilyl}\}$ Phenyl Ketone (**1d**). As described for **1c**, from 214.0 mg (0.51 mmol) of **6b**, 680 mg (2.54 mmol) of HgCl_2 , and 176.0 mg (1.0 mmol) of CdCO_3 in 0.5 ml of H_2O , 1 ml of acetone, and 5 ml of toluene (reflux 4 h), after chromatography (hexane/ Et_2O 20:1): 138.5 mg (83%) of **1d**. Bright yellow liquid. UV (hexane): λ_{max} 207 (4.29), 252 (4.05), 407 (2.08), 421 (2.19), 442 (1.96). IR (film): 3050m, 3020m, 2950s, 2920s, 2880s, 2850s, 2800m, 2740w, 1955w, 1810w, 1720w, 1700w, 1610s, 1590s, 1570s, 1490m, 1470s, 1460s, 1440s, 1390m, 1380m, 1360m, 1310w, 1250m, 1210s, 1170m, 1090s, 1070s, 1025m, 1005m, 1000w, 975w, 930m, 900w, 820s, 800s, 780s, 760s, 730s. ^1H -NMR: 7.90–7.87 (m, 2 arom. H); 7.55–7.41 (m, 3 arom. H); 7.37–7.41 (m, 5 arom. H); 4.52 (s, PhCH_2O); 3.56 (s, SiCH_2O); 0.99 (s, *t*-Bu); 0.40 (s, MeSi). ^{13}C -NMR: 234.2 (s, CO); 142.5, 138.2 (2s, arom. C); 132.5 (d, arom. C); 128.4 (d, 2 arom. C); 128.1 (d, 2 arom. C); 127.7 (d, 2 arom. C); 127.5 (d, 2 arom. C); 127.4 (d, arom. C); 77.1 (t, PhCH_2O); 60.1 (t, SiCH_2O); 27.0 (q, Me_3C); 17.1 (s, Me_3C); -7.8 (q, MeSi). CI-MS: 344 (6, $[M + 1 + \text{NH}_3]^+$), 327 (100, $[M + 1]^+$). Anal. calc. for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{Si}$ (326.515): C 73.57, H 8.03; found: C 73.61, H 7.81.

2. Addition of Organometallic Reagents to the Acylsilanes. – 2.1. General Procedure. The acylsilane dissolved in the respective solvent (ca. 1.5–2.5M) was treated with 1.2 equiv. of the corresponding organometallic reagent (BuLi: 1.6M in pentane (Fluka), *t*-BuLi: 1.4M in pentane (Fluka); MeLi: 1.6M in Et_2O (Fluka); PhLi: 2.0M in cyclohexane/ Et_2O 7:3 (Fluka); MeMgBr: 3.0M in Et_2O (Aldrich); BuMgBr and PhMgBr: freshly prepared from the corresponding bromide in the appropriate ether (0.7–1.1M) at -100° , until no further reaction could be detected by TLC (1 min to 2 h). Quenching with sat. NH_4Cl soln., extraction with Et_2O , washing with H_2O and brine gave, after evaporation, a mixture of crude addition products **2** and/or reduction products **3**. This mixture was analyzed by ^1H -NMR (reference signals: s for the *t*-Bu and/or s for the Me group attached to the Si-atom) to determine the ratio of the diastereoisomers given in the Table. The crude products were chromatographed (hexane/ AcOEt 20:1) to afford pure **2** and/or **3**, in some cases separated into the diastereoisomers, as colorless oils in the yields summarized in the Table.

2.2. 1- $\{[(\text{tert-Butyl})]/(2\text{-methoxyethoxy})\text{methyl}\}\text{methylsilyl}\}$ -1-phenylethanol (**2a**). Characteristics of first eluting, major isomer of Entries 1–3, 6, 7: IR (film): 3460s (br.), 3050w, 3010w, 2950s, 2920s, 2880s, 2850s, 2710w, 1685w, 1600m, 1490m, 1470m, 1460m, 1445m, 1390m, 1360m, 1250m, 1195m, 1130s, 1090s, 1060m, 1030m, 980w, 935w, 910w, 890w, 865w, 825s, 780w, 770w, 750w, 730w, 700s. ^1H -NMR: 7.41–7.15 (m, 5 arom. H); 4.05 (s, OH); 3.66–3.47 (m, $\text{OCH}_2\text{CH}_2\text{O}$); 3.46, 3.22 (AB, $J_{AB} = 12.5$, SiCH_2O); 3.43 (s, MeO); 1.77 (s, $\text{C}(\text{OH})\text{Me}$); 0.93 (s, *t*-Bu); 0.01 (s, MeSi). ^{13}C -NMR: 148.1 (s, arom. C); 127.2 (d, 2 arom. C); 125.1 (d, arom. C); 124.9 (d, 2 arom. C); 74.7 (t, MeOCH_2); 71.5 (t, $\text{SiCH}_2\text{OCH}_2$); 70.8 (s, $\text{SiC}(\text{OH})$); 62.1 (t, SiCH_2O); 58.8 (q, MeO); 27.8 (q, Me_3C); 26.6 (q, $\text{C}(\text{OH})\text{Me}$); 18.0 (s, Me_3C); -10.1 (q, MeSi). CI-MS: 328 (3, $[M + 1 + \text{NH}_3]^+$), 206 (23), 189 (90, $[M - \text{C}(\text{OH})(\text{Me})(\text{Ph})]^+$). Anal. calc. for $\text{C}_{17}\text{H}_{30}\text{O}_3\text{Si}$ (310.513): C 65.76, H 9.74; found: C 66.00, H 9.85.

Characteristics of second eluting, major isomer of Entries 4, 5, 15–18: IR (film): 3460s (br.), 3050w, 3010w, 2950s, 2920s, 2880s, 2850s, 2710w, 1685w, 1600m, 1490m, 1470m, 1460m, 1445m, 1390m, 1360m, 1250m, 1195m, 1130s, 1090s, 1060m, 1030m, 980w, 935w, 910w, 890w, 865w, 825s, 780w, 770w, 750w, 730w, 700s. ^1H -NMR: 7.42–7.12 (m, 5 arom. H); 4.26 (s, OH); 3.66–3.56 (m, $\text{OCH}_2\text{CH}_2\text{O}$); 3.59, 3.47 (AB, $J_{AB} = 12.7$, SiCH_2O); 3.28 (s, MeO); 1.69 (s, $\text{C}(\text{OH})\text{Me}$); 0.69 (s, *t*-Bu); 0.12 (s, MeSi). ^{13}C -NMR: 148.3 (s, arom. C); 127.8 (d, 2 arom. C); 125.1 (d, arom. C); 124.5 (d, 2 arom. C); 74.8 (t, MeOCH_2); 71.6 (t, $\text{SiCH}_2\text{OCH}_2$); 70.5 (s, $\text{SiC}(\text{OH})$); 62.6 (t, SiCH_2O); 58.9 (q, MeO); 28.6 (q, $\text{C}(\text{OH})\text{Me}$); 27.3 (q, Me_3C); 18.0 (s, Me_3C); -9.0 (q, MeSi). CI-MS: 328 (10, $[M + 1 + \text{NH}_3]^+$), 310 (100, $[M - \text{OH} + \text{NH}_3]^+$), 206 (10), 189 (55, $[M - \text{C}(\text{OH})(\text{Me})(\text{Ph})]^+$). Anal. calc. for $\text{C}_{17}\text{H}_{30}\text{O}_3\text{Si}$ (310.513): C 65.76, H 9.74; found: C 66.02, H 9.71.

2.3. 1- $\{[(\text{Benzyloxy})\text{methyl}]/(\text{tert-butyl})\text{methylsilyl}\}$ -1-phenylethanol (**2b**). Characteristics of first eluting, major isomer of Entries 8, 9, 14: IR (film): 3450s (br.), 3080w, 3020w, 2950s, 2920s, 2850s, 2740w, 2710w, 1750w, 1600m, 1490m, 1470m, 1460m, 1450m, 1445m, 1430w, 1380m, 1310m, 1250m, 1200w, 1175w, 1155w, 1085s, 1065s, 1025m, 1005w, 935w, 910w, 895m, 825s, 805m, 785m, 745s, 715m, 700s. ^1H -NMR: 7.40–7.28 (m, 9 arom. H); 7.25–7.12 (m, arom. H); 4.55, 4.50 (AB, $J_{AB} = 11.8$, PhCH_2O); 3.83 (s, OH); 3.41, 3.18 (AB, $J_{AB} = 12.6$, SiCH_2O); 1.76 (s, $\text{C}(\text{OH})\text{Me}$); 0.90 (s, *t*-Bu); 0.01 (s, MeSi). ^{13}C -NMR: 148.2, 137.5 (2s, arom. C); 128.4 (d, 2 arom. C); 127.9 (d, 2 arom. C); 127.8 (d, 3 arom. C); 125.1 (d, arom. C); 124.4 (d, 2 arom. C); 77.7 (t, PhCH_2O); 70.6 (s, $\text{SiC}(\text{OH})$); 61.3 (t, SiCH_2O); 28.8 (q, $\text{C}(\text{OH})\text{Me}$); 27.4 (q, Me_3C); 18.1 (s, Me_3C); -9.0 (q, MeSi). CI-MS: 343 (10, $[M + 1]^+$), 342 (34, $[M - \text{OH} + \text{NH}_3]^+$), 326 (28), 325 (100, $[M - \text{OH}]^+$), 281 (18), 256 (21), 238 (36). Anal. calc. for $\text{C}_{21}\text{H}_{30}\text{O}_2\text{Si}$ (342.558): C 73.63, H 8.83; found: C 73.51, H 8.56.

Characteristics of second eluting, major isomer of *Entries 10–12, 19–22*: IR (film): 3450s (br.), 3080w, 3020w, 2950s, 2920s, 2850s, 2740w, 2710w, 1750w, 1600m, 1490m, 1470m, 1460m, 1450m, 1445m, 1430w, 1380m, 1310m, 1250m, 1200w, 1175w, 1155w, 1085s, 1065s, 1025m, 1005w, 935w, 910w, 895m, 825s, 805m, 785m, 745s, 715m, 700s. ¹H-NMR: 7.41–7.27 (*m*, 9 arom. H); 7.17–7.11 (*m*, arom. H); 4.56 (*s*, PhCH₂O); 4.22 (*s*, OH); 3.53, 3.42 (*AB*, *J*_{AB} = 12.9, SiCH₂O); 1.65 (*s*, C(OH)Me); 0.70 (*s*, *t*-Bu); 0.01 (*s*, MeSi). ¹³C-NMR: 148.1, 137.7 (2s, arom. C); 128.4 (*d*, 2 arom. C); 127.9 (*d*, 2 arom. C); 127.8 (*d*, arom. C); 127.7 (*d*, 2 arom. C); 125.3 (*d*, arom. C); 125.0 (*d*, 2 arom. C); 77.7 (*t*, PhCH₂O); 71.0 (*s*, SiC(OH)); 61.0 (*t*, SiCH₂O); 27.9 (*q*, Me₃C); 26.9 (*q*, C(OH)Me); 18.2 (*s*, Me₃C); –9.9 (*q*, MeSi). CI-MS: 343 (2, [*M* + 1]⁺), 342 (15, [*M* – OH + NH₃]⁺), 325 (100, [*M* – OH]⁺). Anal. calc. for C₂₁H₃₀O₂Si (342.558): C 73.63, H 8.83; found: C 73.55, H 8.67.

2.4. 2-[(*tert*-Butyl)[(2-methoxyethoxy)methyl]methylsilyl]hexan-2-ol (**2c**). Obtained as a mixture of diastereoisomers. IR (film, *Entry 25*): 3490m (br.), 2950s, 2920s, 2890s, 2850s, 2700w, 1640w, 1465s, 1390m, 1365m, 1245m, 1195m, 1130s, 1095s, 1010m, 980w, 930w, 920w, 850m, 825s, 800m, 780m, 765m, 710m, 690w, 660w. ¹H-NMR (major isomer of *Entries 23–26*, from spectrum of mixture): 3.59–3.39 (*m*, OCH₂CH₂O, SiCH₂O); 3.15 (*s*, OH); 3.35 (*s*, MeO); 1.67–1.23 (*m*, CH₂CH₂CH₂); 1.33 (*s*, C(OH)Me); 0.97 (*s*, *t*-Bu); 0.91 (*t*, *J* = 7.1, CH₂Me); 0.09 (*s*, MeSi). ¹H-NMR (minor isomer of *Entries 23–26*, signal relevant for the determination of the *de*, from spectrum of mixture): 0.20 (*s*, MeSi). ¹³C-NMR (major isomer of *Entries 23–26*, from spectrum of mixture): 74.8 (*t*, MeOCH₂); 71.6 (*t*, SiCH₂OCH₂); 67.3 (*s*, SiC(OH)); 62.7 (*t*, SiCH₂O); 58.9 (*q*, MeO); 40.0 (*t*, C(OH)CH₂); 27.9 (*q*, Me₃C); 25.1 (*q*, C(OH)Me); 24.1, 23.5 (2*t*); 17.6 (*s*, Me₃C); 14.1 (*q*, CH₂Me); –9.5 (*q*, MeSi). CI-MS (*Entry 25*): 308 (3, [*M* + 1 + NH₃]⁺), 291 (2, [*M* + 1]⁺), 290 (3), 206 (30, [*M* – C(OH)(Bu)(Me) + NH₃]⁺), 189 (100, [*M* – C(OH)(Bu)(Me)]⁺). Anal. calc. for C₁₅H₃₄O₃Si (290.522): C 62.02, H 11.80; found (*Entry 25*): C 62.22, H 11.79.

2.5. 2-[(*Benzoyloxy*)methyl](*tert*-butyl)methylsilyl]hexan-2-ol (**2d**). Obtained as a mixture of diastereoisomers. IR (film, *Entry 30*): 3480m (br.), 3050w, 3020w, 2950s, 2920s, 2850s, 1495w, 1465m, 1450m, 1430w, 1380m, 1360m, 1250m, 1200w, 1135w, 1105m, 1085m, 1065s, 1025w, 1005w, 920w, 900w, 850w, 825m, 785w, 760w, 735m, 710w. ¹H-NMR (major isomer of *Entries 27, 29, 30*, from spectrum of mixture): 7.37–7.28 (*m*, 5 arom. H); 4.51, 4.46 (*AB*, *J*_{AB} = 11.9, PhCH₂O); 3.50, 3.33 (*AB*, *J*_{AB} = 12.6, SiCH₂O); 3.05 (*s*, OH); 1.65–1.13 (*m*, CH₂CH₂CH₂); 1.31 (*s*, C(OH)Me); 0.97 (*s*, *t*-Bu); 0.9 (*t*, *J* = 7.1, CH₂Me); 0.08 (*s*, MeSi). ¹H-NMR (major isomer of *Entry 28*, signal relevant for the determination of the *de*, from spectrum of mixture): 0.07 (*s*, MeSi). ¹³C-NMR (major isomer of *Entries 27, 29, 30*, from spectrum of mixture): 137.8 (*s*, arom. C); 128.3 (*d*, 2 arom. C); 127.7 (*d*, 2 arom. C); 127.6 (*d*, arom. C); 77.6 (*t*, PhCH₂O); 67.5 (*s*, SiC(OH)); 61.5 (*t*, SiCH₂O); 40.0 (*t*, C(OH)CH₂); 28.0 (*q*, Me₃C); 25.1 (*q*, C(OH)Me); 24.1, 23.5 (2*t*); 17.7 (*s*, Me₃C); 14.1 (*q*, CH₂Me); –9.5 (*q*, MeSi). CI-MS (*Entry 30*): 340 (30, [*M* + 1 + NH₃]⁺), 323 (18, [*M* + 1]⁺), 238 (100, [*M* – C(OH)(Bu)(Me) + NH₃]⁺). Anal. calc. for C₁₉H₃₄O₃Si (322.568): C 70.75, H 10.62; found (*Entry 30*): C 70.91, H 10.77.

2.6. 1-[(*tert*-Butyl)[(2-methoxyethoxy)methyl]methylsilyl]-1-phenylpentan-1-ol (**2e**). Obtained as a mixture of diastereoisomers. IR (film, *Entry 33*): 3460s (br.), 3050w, 3020w, 2950s, 2920s, 2895s, 2850s, 2710w, 1950w, 1800w, 1750w, 1600m, 1490m, 1460s, 1445s, 1390m, 1375m, 1360m, 1250s, 1220m, 1195m, 1130s, 1090s, 1030m, 1010w, 980w, 960w, 930m, 890w, 860m, 825s, 805m, 795m, 750w, 700s. ¹H-NMR (major isomer of *Entries 31–33*, from spectrum of mixture): 7.37–7.10 (*m*, 5 arom. H); 3.99 (*s*, OH); 3.65–3.55 (*m*, OCH₂CH₂O); 3.59, 3.49 (*AB*, *J*_{AB} = 12.6, SiCH₂O); 3.39 (*s*, MeO); 2.07–2.00 (*m*, C(OH)CH₂); 1.48–0.85 (*m*, CH₂CH₂Me); 0.81 (*t*, *J* = 7.3, CH₂Me); 0.67 (*s*, *t*-Bu); 0.09 (*s*, MeSi). ¹H-NMR (minor isomer of *Entries 31–33*, signals relevant for the determination of the *de*, from spectrum of mixture): 0.94 (*s*, *t*-Bu); –0.05 (*s*, MeSi). ¹³C-NMR (major isomer of *Entries 31–33*, from spectrum of mixture): 145.8 (*s*, arom. C); 127.8 (*d*, 2 arom. C); 124.9 (*d*, 2 arom. C); 124.7 (*d*, arom. C); 74.8 (*t*, MeOCH₂); 73.3 (*s*, SiC(OH)); 71.6 (*t*, SiCH₂OCH₂); 62.9 (*t*, SiCH₂O); 58.9 (*q*, MeO); 39.2 (*t*, C(OH)CH₂); 27.3 (*q*, Me₃C); 23.3, 23.2 (2*t*); 18.1 (*s*, Me₃C); 14.0 (*q*, CH₂Me); –8.9 (*q*, MeSi). CI-MS (*Entry 33*): 370 (2, [*M* + 1 + NH₃]⁺), 352 (5), 206 (90, [*M* – C(OH)(Bu)(Ph) + NH₃]⁺), 189 (100, [*M* – C(OH)(Bu)(Ph)]⁺). Anal. calc. for C₂₀H₃₆O₃Si (352.594): C 68.13, H 10.29; found (*Entry 33*): C 68.13, H 10.35.

2.7. 1-[(*Benzoyloxy*)methyl](*tert*-butyl)methylsilyl]-1-phenylpentan-1-ol (**2f**). Obtained as a mixture of diastereoisomers. IR (film, *Entry 37*): 3450s (br.), 3060w, 3020w, 2950s, 2920s, 2850s, 2810w, 1600w, 1490m, 1465s, 1450s, 1445s, 1390m, 1380m, 1360m, 1250s, 1200w, 1110m, 1080m, 1065s, 1025m, 1010m, 930w, 900w, 860w, 825m, 800m, 790m, 740m, 700s. ¹H-NMR (major isomer of *Entries 35–37*, from spectrum of mixture): 7.41–7.10 (*m*, 10 arom. H); 4.60, 4.52 (*AB*, *J*_{AB} = 11.8, PhCH₂O); 4.01 (*s*, OH); 3.52, 3.45 (*AB*, *J*_{AB} = 12.8, SiCH₂O); 2.08–1.86 (*m*, C(OH)CH₂); 1.42–1.14 (*m*, CH₂CH₂Me); 0.81 (*t*, *J* = 7.3, CH₂Me); 0.68 (*s*, *t*-Bu); 0.06 (*s*, MeSi). ¹H-NMR (minor isomer of *Entries 35–37*, signals relevant for the determination of the *de*, from spectrum of mixture): 0.97 (*s*, *t*-Bu); 0.16 (*s*, MeSi). ¹³C-NMR (major isomer of *Entries 35–37*, from spectrum of mixture): 145.7, 137.5 (2s, arom. C); 128.3 (*d*, 2 arom. C); 127.9 (*d*, 2 arom. C); 127.7 (*d*, 3 arom. C); 124.8 (*d*, 2 arom. C); 124.7 (*d*, arom. C); 77.6 (*t*, PhCH₂O); 67.8 (*s*, SiC(OH)); 61.4 (*t*, SiCH₂O); 39.2 (*t*, C(OH)CH₂); 27.3 (*q*, Me₃C); 23.3, 23.1 (2*t*); 18.1 (*s*,

Me_3C); 14.0 (*q*, CH_2Me); -9.0 (*q*, MeSi). CI-MS (*Entry* 37): 402 (8, $[\text{M} + 1 + \text{NH}_3]^+$), 384 (9), 367 (23), 346 (7), 321 (75), 304 (10), 238 (100, $[\text{M} - \text{C}(\text{OH})(\text{Bu})(\text{Ph}) + \text{NH}_3]^+$). Anal. calc. for $\text{C}_{24}\text{H}_{36}\text{O}_2\text{Si}$ (384.639): C 74.94, H 9.43; found (*Entry* 37): C 74.97, H 9.35.

2.8. 1- $\{(\text{tert-Butyl})[(2\text{-methoxyethoxy})\text{methyl}]\text{methylsilyl}\}\text{ethanol}$ (**3a**). Obtained as a mixture of diastereoisomers. Complete set of spectra from a sample mixture obtained by reduction of **1a** with NaBH_4 . IR (film): 3420s (br.), 2940s, 2920s, 2890s, 2880s, 2700w, 1720w, 1470s, 1460s, 1430m, 1390m, 1360s, 1305m, 1245s, 1195m, 1130s, 1090s, 1030s, 1005m, 975m, 930w, 880m, 860w, 820s, 800m, 770m, 730m, 690w. $^1\text{H-NMR}$ (major isomer of *Entries* 23, 25, 26, 39, from spectrum of mixture): 3.68 (*q*, $J = 7.6$, $\text{CH}(\text{OH})\text{Me}$); 3.58–3.48 (*m*, $\text{OCH}_2\text{CH}_2\text{O}$); 3.49, 3.33 (*AB*, $J_{AB} = 12.8$, SiCH_2O); 3.35 (*s*, MeO); 2.53 (*s*, OH); 1.41 (*d*, $J = 7.6$, $\text{CH}(\text{OH})\text{Me}$); 0.97 (*s*, *t*-Bu); 0.05 (*s*, MeSi). $^1\text{H-NMR}$ (minor isomer of *Entries* 23, 25, 26, 39, signals relevant for the determination of the de, from spectrum of mixture): 0.95 (*s*, *t*-Bu); 0.02 (*s*, MeSi). $^{13}\text{C-NMR}$ (major isomer of *Entries* 23, 25, 26, 39, from spectrum of mixture): 74.5 (*t*, MeOCH_2); 71.5 (*t*, $\text{SiCH}_2\text{OCH}_2$); 61.9 (*t*, SiCH_2O); 60.8 (*q*, MeO); 58.7 (*d*, $\text{SiCH}(\text{OH})$); 27.2 (*q*, Me_3C); 20.4 (*q*, $\text{C}(\text{OH})\text{Me}$); 16.8 (*s*, Me_3C); -10.4 (*q*, MeSi). CI-MS: 252 (100, $[\text{M} + 1 + \text{NH}_3]^+$), 235 (20, $[\text{M} + 1]^+$). Anal. calc. for $\text{C}_{11}\text{H}_{26}\text{O}_3\text{Si}$ (234.414): C 56.36, H 11.18; found: C 55.21, H 11.09.

2.9. 1- $\{(\text{Benzyloxy})\text{methyl}\}(\text{tert-butyl})\text{methylsilyl}\}\text{ethanol}$ (**3b**). Characteristics of first eluting, major isomer of *Entries* 27, 29, 40: IR (film): 3420s (br.), 3060w, 3020w, 2950s, 2920s, 2880s, 2850s, 2800m, 1495w, 1470s, 1460s, 1450s, 1430m, 1380m, 1360m, 1300w, 1250m, 1200w, 1090s, 1070s, 1030s, 1005m, 975m, 935w, 900w, 885m, 825s, 800m, 780m, 765m, 730s, 695s. $^1\text{H-NMR}$: 7.38–7.28 (*m*, 5 arom. H); 4.50 (*s*, PhCH_2O); 3.78 (*q*, $J = 7.5$, $\text{CH}(\text{OH})\text{Me}$); 3.50, 3.38 (*AB*, $J_{AB} = 12.6$, SiCH_2O); 3.16 (*d*, $J = 4.1$, OH); 1.32 (*d*, $J = 7.5$, $\text{CH}(\text{OH})\text{Me}$); 0.95 (*s*, *t*-Bu); 0.01 (*s*, MeSi). $^{13}\text{C-NMR}$: 137.8 (*s*, arom. C); 128.3 (*d*, 2 arom. C); 127.6 (*d*, 3 arom. C); 77.5 (*t*, PhCH_2O); 61.1 (*t*, SiCH_2O); 58.7 (*d*, $\text{SiCH}(\text{OH})$); 27.0 (*q*, Me_3C); 20.3 (*q*, $\text{C}(\text{OH})\text{Me}$); 16.5 (*s*, Me_3C); -10.9 (*q*, MeSi). CI-MS: 284 (100, $[\text{M} + 1 + \text{NH}_3]^+$), 267 (35, $[\text{M} + 1]^+$). Anal. calc. for $\text{C}_{15}\text{H}_{26}\text{O}_2\text{Si}$ (266.459): C 67.62, H 9.84; found: C 67.40, H 9.56.

Characteristics of second eluting, major isomer of *Entry* 30: IR (film): 3420s (br.), 3060w, 3020w, 2950s, 2920s, 2880s, 2850s, 2800m, 1495w, 1470s, 1460s, 1450s, 1430m, 1380m, 1360m, 1300w, 1250m, 1200w, 1090s, 1070s, 1030s, 1005m, 975m, 935w, 900w, 885m, 825s, 800m, 780m, 765m, 730s, 695s. $^1\text{H-NMR}$: 7.38–7.28 (*m*, 5 arom. H); 4.48 (*s*, PhCH_2O); 3.71 (*q*, $J = 7.5$, $\text{CH}(\text{OH})\text{Me}$); 3.46, 3.29 (*AB*, $J_{AB} = 12.7$, SiCH_2O); 2.34 (*d*, $J = 4.1$, OH); 1.40 (*d*, $J = 7.5$, $\text{CH}(\text{OH})\text{Me}$); 0.98 (*s*, *t*-Bu); 0.06 (*s*, MeSi). $^{13}\text{C-NMR}$: 138.2 (*s*, arom. C); 128.3 (*d*, 2 arom. C); 127.6 (*d*, 2 arom. C); 127.5 (*d*, arom. C); 77.5 (*t*, PhCH_2O); 60.9 (*t*, SiCH_2O); 60.5 (*d*, $\text{SiCH}(\text{OH})$); 27.4 (*q*, Me_3C); 20.6 (*q*, $\text{C}(\text{OH})\text{Me}$); 16.9 (*s*, Me_3C); -10.3 (*q*, MeSi). CI-MS: 284 (100, $[\text{M} + 1 + \text{NH}_3]^+$), 267 (10, $[\text{M} + 1]^+$), 221 (8). Anal. calc. for $\text{C}_{15}\text{H}_{26}\text{O}_2\text{Si}$ (266.459): C 67.62, H 9.84; found: C 65.98, H 9.41.

2.10. $\{(\text{tert-Butyl})[(2\text{-methoxyethoxy})\text{methyl}]\text{methylsilyl}\}\text{phenylmethanol}$ (**3c**). Characteristics of first eluting, major isomer of *Entries* 31–34: IR (KBr): 3420s (br.), 3050w, 3020w, 2920s, 2880s, 2850s, 2810m, 1720w, 1700w, 1600w, 1490w, 1470m, 1460m, 1450m, 1430w, 1390w, 1360m, 1310w, 1250m, 1195w, 1130s, 1105s, 1090s, 1035m, 1010m, 980w, 935w, 910w, 860m, 840s, 825s, 805m, 795m, 770m, 755w, 730w, 700s. $^1\text{H-NMR}$: 7.31–7.14 (*m*, 5 arom. H); 4.81 (*d*, $J = 4.1$, $\text{CH}(\text{OH})$); 3.62–3.52 (*m*, $\text{OCH}_2\text{CH}_2\text{O}$); 3.32 (*s*, OH); 3.43, 3.25 (*AB*, $J_{AB} = 12.7$, SiCH_2O); 3.39 (*s*, MeO); 0.83 (*s*, *t*-Bu); 0.11 (*s*, MeSi). $^{13}\text{C-NMR}$: 144.3 (*s*, arom. C); 128.0 (*d*, 2 arom. C); 125.6 (*d*, arom. C); 125.4 (*d*, 2 arom. C); 74.7 (*t*, MeOCH_2); 71.6 (*t*, $\text{SiCH}_2\text{OCH}_2$); 68.6 (*s*, $\text{SiCH}(\text{OH})$); 61.9 (*t*, SiCH_2O); 58.9 (*q*, MeO); 27.0 (*q*, Me_3C); 17.3 (*s*, Me_3C); -10.3 (*q*, MeSi). CI-MS: 314 (51, $[\text{M} + 1 + \text{NH}_3]^+$), 296 (73), 278 (26), 261 (100), 247 (74). Anal. calc. for $\text{C}_{16}\text{H}_{28}\text{O}_3\text{Si}$ (296.486): C 64.82, H 9.52; found: C 64.80, H 9.71.

Characteristics of second eluting, minor isomer of *Entries* 31–34: IR (film): 3420s (br.), 3050w, 3020w, 2920s, 2880s, 2850s, 2810m, 1720w, 1700w, 1600w, 1490w, 1470m, 1460m, 1450m, 1430w, 1390w, 1360m, 1310w, 1250m, 1195w, 1130s, 1105s, 1090s, 1035m, 1010m, 980w, 935w, 910w, 860m, 840s, 825s, 805m, 795m, 770m, 755w, 730w, 700s. $^1\text{H-NMR}$: 7.32–7.13 (*m*, 5 arom. H); 4.79 (*s*, $\text{CH}(\text{OH})$); 3.61, 3.39 (*AB*, $J_{AB} = 12.6$, SiCH_2O); 3.51 (*s*, OH); 3.65–3.54 (*m*, $\text{OCH}_2\text{CH}_2\text{O}$); 3.40 (*s*, MeO); 0.99 (*s*, *t*-Bu); 0.07 (*s*, MeSi). $^{13}\text{C-NMR}$: 144.3 (*s*, arom. C); 128.0 (*d*, 2 arom. C); 125.7 (*d*, 2 arom. C); 125.6 (*d*, arom. C); 74.8 (*t*, MeOCH_2); 71.5 (*t*, $\text{SiCH}_2\text{OCH}_2$); 67.9 (*d*, $\text{SiCH}(\text{OH})$); 62.0 (*t*, SiCH_2O); 58.9 (*q*, MeO); 27.0 (*q*, Me_3C); 17.0 (*s*, Me_3C); -9.9 (*s*, MeSi). CI-MS: 314 (100, $[\text{M} + 1 + \text{NH}_3]^+$), 296 (87, $[\text{M} - \text{OH} + \text{NH}_3]^+$), 286 (13), 278 (12), 264 (20), 261 (19), 247 (22). Anal. calc. for $\text{C}_{16}\text{H}_{28}\text{O}_3\text{Si}$ (296.486): C 64.82, H 9.52; found: C 64.73, H 9.70.

2.11. $\{(\text{Benzyloxy})\text{methyl}\}(\text{tert-butyl})\text{methylsilyl}\}\text{phenylmethanol}$ (**3d**). Characteristics of first eluting, major isomer of *Entries* 35–38: IR (film): 3420s (br.), 3050w, 3020w, 2950s, 2920s, 2880s, 2850s, 2800m, 1940w, 1870w, 1800w, 1720w, 1595w, 1535w, 1490m, 1465m, 1460m, 1450m, 1430m, 1400m, 1385m, 1375m, 1360s, 1330m, 1320m, 1300m, 1275w, 1245m, 1200w, 1150w, 1105m, 1090s, 1070s, 1025m, 1000m, 930w, 900w, 825s, 790m, 770m, 740s, 730s, 700s. $^1\text{H-NMR}$: 7.40–7.27 (*m*, 9 arom. H); 7.25–7.13 (*m*, arom. H); 4.84 (*d*, $J = 4.0$, $\text{CH}(\text{OH})$); 4.48 (*s*, PhCH_2O); 3.38, 3.17 (*AB*, $J_{AB} = 12.8$, SiCH_2O); 3.06 (*s*, OH); 0.87 (*s*, *t*-Bu); 0.07 (*s*, MeSi). $^{13}\text{C-NMR}$: 144.2, 137.6

(2s, arom. C); 128.4 (*d*, arom. C); 128.0 (*d*, 3 arom. C); 127.7 (*d*, 2 arom. C); 127.2 (*d*, arom. C); 125.6 (*d*, 2 arom. C); 125.3 (*d*, arom. C); 77.6 (*t*, PhCH₂O); 68.0 (*d*, SiCH(OH)); 60.6 (*t*, SiCH₂O); 27.1 (*q*, Me₃C); 17.0 (*s*, Me₃C); –10.5 (*s*, MeSi). CI-MS: 346 (40, [*M* + 1 + NH₃]⁺), 311 (100, [*M* – OH]⁺), 286 (36). Anal. calc. for C₂₀H₂₈O₂Si (328.531): C 73.12, H 8.59; found: C 73.26, H 8.51.

Characteristics of second eluting, minor isomer of *Entries 35–38*: IR (film): 3420s (br.), 3050w, 3020w, 2950s, 2920s, 2880s, 2850s, 2800m, 1940w, 1870w, 1800w, 1720w, 1595w, 1535w, 1490m, 1465m, 1460m, 1450m, 1430m, 1400m, 1385m, 1375m, 1360s, 1330m, 1320m, 1300m, 1275w, 1245m, 1200w, 1150w, 1105m, 1090s, 1070s, 1025m, 1000m, 930w, 900w, 825s, 790m, 770m, 740s, 730s, 700s. ¹H-NMR: 7.44–7.24 (*m*, 9 arom. H); 7.20–7.12 (*m*, arom. H); 4.79 (*d*, *J* = 4.0, CH(OH)); 4.55 (*s*, PhCH₂O); 3.95 (*d*, *J* = 4.0, OH); 3.48, 3.36 (*AB*, *J*_{AB} = 12.4, SiCH₂O); 0.99 (*s*, *t*-Bu); 0.07 (*s*, MeSi). ¹³C-NMR: 144.2, 137.8 (2s, arom. C); 128.3 (*d*, arom. C); 128.0 (*d*, 3 arom. C); 127.6 (*d*, arom. C); 127.2 (*d*, arom. C); 125.6 (*d*, 2 arom. C); 125.3 (*d*, 2 arom. C); 77.4 (*t*, PhCH₂O); 68.5 (*d*, SiCH(OH)); 60.8 (*t*, SiCH₂O); 27.2 (*q*, Me₃C); 17.3 (*s*, Me₃C); –9.9 (*s*, MeSi). CI-MS: 346 (19, [*M* + 1 + NH₃]⁺), 311 (100, [*M* – OH]⁺), 286 (18). Anal. calc. for C₂₀H₂₈O₂Si (328.531): C 73.12, H 8.59; found: C 72.93, H 8.62.

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