

143. Chiral Acylsilanes in Organic Synthesis

Diastereoselective 1,2-Additions to Racemic Alkoxyethyl-Substituted Acylsilanes

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The synthesis of the three alkoxyethyl-substituted acylsilanes **1–3** is described (*Schemes 1* and *2*). Their reactions with NaBH_4 as well as PhLi gave the corresponding alcohols with moderate to good diastereoisomeric induction (up to 78% de; see *Table*), depending upon the solvent used (*Scheme 3*). The results indicate that in Et_2O , the reactions with PhLi proceed *via* 6-membered chelates (see *C* in *Scheme 4*) leading to the products with high de's (74–78%). In THF, these chelates are not formed, and as a consequence, the additions take place with reversed and lower stereoselectivities (34–50% de).

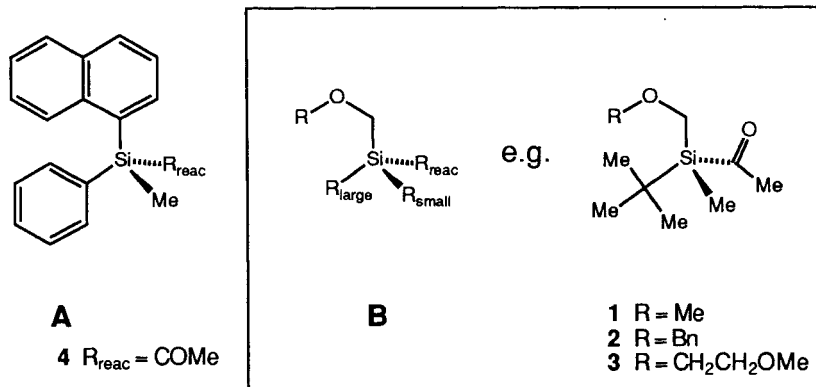
Introduction. – A major goal in modern synthetic organic chemistry is the efficient production of optically active materials. Great advances in this field have been made up to now [1]. Optically pure compounds have been prepared starting from prochiral precursors either by enantioselective or diastereoselective transformations using enantiomerically pure reagents, catalysts, or auxiliaries bearing in most cases their chirality on the C-skeleton.

In spite of the close relationship of Si- and C-atoms, and notwithstanding the heavy research activities in the field of organosilicon chemistry over the last years, only a few investigations concerning chirality transfer from Si to C have been undertaken [2–7]. The lack of a broader interest in such reactions might be due to the little promising results obtained so far using mostly the optically active methyl(naphth-1-yl)phenylsilyl group first introduced by *Sommer et al.* [8] as the chiral auxiliary (compounds of type **A**). We suppose, however, that the low ee's²⁾ and de's³⁾ observed in these reactions can be explained by the non-optimal nature of the chiral silyl system where the stereoselectivity depends mainly on the steric differences of a Me, a Ph, and a naphth-1-yl group. These differences, however, would be expected to be rather small [5a] [9]. For this reason, we started to study the use of compounds of type **B** bearing in addition to the reactive group (R_{reac}) and the two sterically differentiating groups (R_l = large, R_s = small) an alkoxy-methyl substituent. This novel type of molecules should be enabled to form rigid cyclic intermediates or transition states with cationic additives. As a result of their structures,

¹⁾ Part of the planned Ph.D. thesis of A. C., Universität Zürich.

²⁾ Enantiomeric excesses (ee) as low as 3.9–5.5% were found for *Lewis*-acid-promoted reductive allylations of dimethyl acetals with a chiral allylsilane [3b].

³⁾ The best diastereoisomeric excesses (de) reported so far are 14–53% for thiophilic additions of organometallic reagents to chiral silyl thiones [6b].

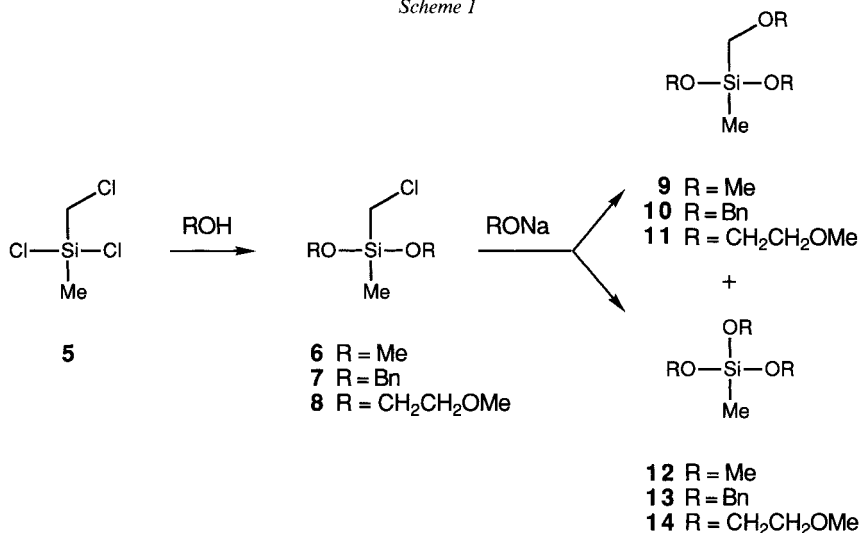


we assume that reactions with these compounds proceed with enhanced stereoselectivities.

We describe in this communication the synthesis of the three racemic acylsilanes **1–3** which are of type **B** and the diastereoselectivities obtained in their reactions with NaBH_4 and PhLi . The results will be compared with those obtained with racemic **4**, the corresponding acylsilane of type **A**.

Synthesis of the Racemic Acylsilanes 1–4. – The synthesis of the target acylsilanes **1–3** was achieved following modified literature procedures [10]. Reaction of dichloro(chloromethyl)methylsilane (**5**) with the appropriate alcohol (MeOH , BnOH , and 2-methoxyethanol) in pentane gave almost quantitatively the (chloromethyl)dialkoxysilanes **6–8** (Scheme 1). Treatment of these compounds with the corresponding sodium alkoxides afforded the alkoxymethyl derivatives **9–11** in 55–65%

Scheme 1



yields. Unexpectedly, the reactions of **7** and **8** gave, in addition to the desired compounds, considerable amounts of the corresponding (trialkoxymethyl)silanes **13** and **14**, respectively. Methyltrimethoxysilane (**12**) deriving from a similar side reaction was not found in the transformation **6** → **9**; the unsatisfactory yield (55%) in this reaction is mainly due to the high volatility of **9**.

It is known that a chloromethyl group at a Si-atom can be substituted *in toto* by the prolonged action of good 'Si-nucleophiles' (*i.e.* nucleophile towards Si) like alkoxides or halides [11]. It could be shown, however, that **13** and **14** are not only formed by this process, but also or rather by the corresponding substitution of the alkoxymethyl group of **10** and **11**, respectively. *E.g.*, the attempted distillative separation of a crude 85:15 mixture **11/14** (13 g; containing the corresponding alcohol and alkoxide as impurities) gave as a first fraction (3.3 g) **11/14** 82:18 and as residue (5.7 g) **11/14** 74:26 (GC evidence), *i.e.* at least 10% of the initially present **11** was transformed into **14** on distillation. Thus, prolonged treatment of **9–11** with alkoxides at elevated temperature were avoided by quenching the reaction mixtures with dry NH_4Cl followed by rapid distillation of the crude products under high vacuum.

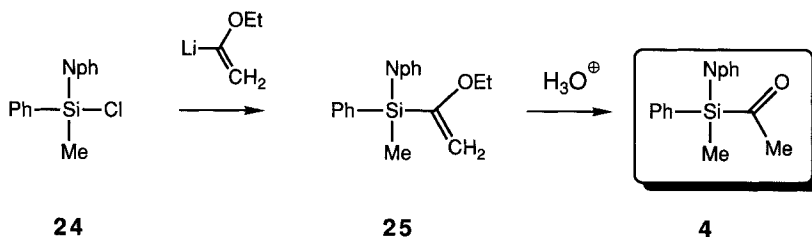
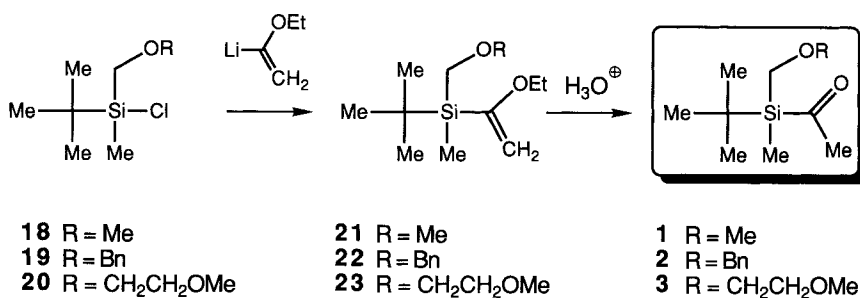
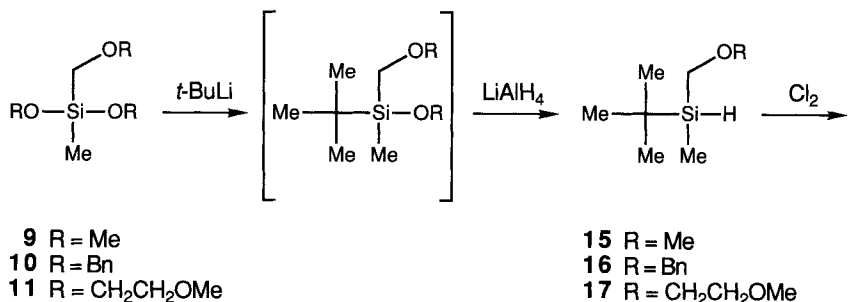
Direct conversion of **5** to **9–11** by reaction of **5** with the appropriate alcohol under basic conditions was not superior to the two-step procedure described above: *e.g.* the reaction of **5** with MeOH in the presence of Et_3N yielded only a complex and inseparable product mixture.

The racemic di(dealkoxy)silanes **15–17** were prepared in 61–81% yield from **9–11** by stepwise substitution using *t*-BuLi and LiAlH_4 (Scheme 2). Chlorination of **15–17** with Cl_2 gave almost quantitatively the chlorosilanes **18–20**, which in turn readily reacted with (1-ethoxyvinyl)lithium to the substitution products **21–23**. Finally, the desired acylsilanes **1–3** were obtained after acidic hydrolysis of the enol ethers in **19**, **27**, and 31% overall yield starting from **5** (6 steps). The reference acylsilane **4** was prepared in an analogous way from chlorosilane **24** [8] *via* **25** in 94% yield (Scheme 2).

The acylsilanes **1–3** are spectroscopically easily recognized: Their IR spectra show strong absorptions for the carbonyl groups at $1640\text{--}1650\text{ cm}^{-1}$ [12], and in the ^{13}C -NMR spectra, the signals for the carbonyl C-atoms attached to Si appear at $237.2\text{--}243.7\text{ ppm}$, clearly shifted to lower field compared to ketones or aldehydes [13]. The resonances for the MeCO (*q* at *ca.* 38 ppm), *t*-Bu (*q* at *ca.* 26.4 and *s* at *ca.* 16 ppm), and the MeSi groups (*q* at *ca.* -10 ppm) are recorded in the same regions for all three compounds. The ^1H -NMR spectra of **1–3** show each an *AB* pattern at $3.5\text{--}3.3\text{ ppm}$ ($J_{AB} \approx 13\text{ Hz}$) for the SiCH_2O groups and *s* at *ca.* 2.3, 0.95, and 0.2 ppm for the MeCO, the *t*-Bu, and the MeSi groups, respectively. In the EI-MS, the M^{+} are not observed, but the $[M - \text{COCH}_3]^+$ fragments are detected with intensities $> 50\%$.

Diastereoselective 1,2-Additions to the Acylsilanes 1–4. – The acylsilanes **1–4** were treated with PhLi and NaBH_4 to form the silyl-substituted tertiary alcohols **26–29** and secondary alcohols **30–33**, respectively, each as a mixture of diastereoisomers of yet unknown relative configurations at the two chiral centers (Scheme 3). Thus, treatment of **1–4** with PhLi gave the corresponding alcohol **26–29** with up to 78% diastereoselection, depending on the substrate and the solvent used (see Table). Generally, the transformations of the novel acylsilanes **1–3** showed distinctively higher stereoselectivities (34–78% de; Entries 1–3 and 5–7) than the reaction with the model compound **4** (20% de; Entries 4 and 8). Additionally, an interesting solvent effect was observed with **1–3**: the diastereoselectivities of the PhLi additions to these acylsilanes were reversed and to a considerable extent larger, when the additions were performed in Et_2O (Entries 1–3) rather

Scheme 2



Nph = naphth-1-yl

than in THF (*Entries 5–7*, preference for the other isomer). No such solvent effect could be observed in the corresponding additions to **4** (*Entries 4* and *8*). An explanation for this observation would be that the reactions of **1–3** with PhLi in these two solvents proceed *via* different transition states or intermediates, whereas the reaction of **4** follows in both solvents the same path.

Compounds **1–3** differ from **4** basically by possessing an alkoxymethyl substituent able to form a complex with cations. Hence, one can safely assume that the special behaviour of **1–3** in the two solvents is connected to this structural peculiarity. According

Scheme 3

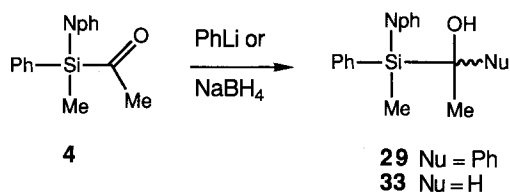
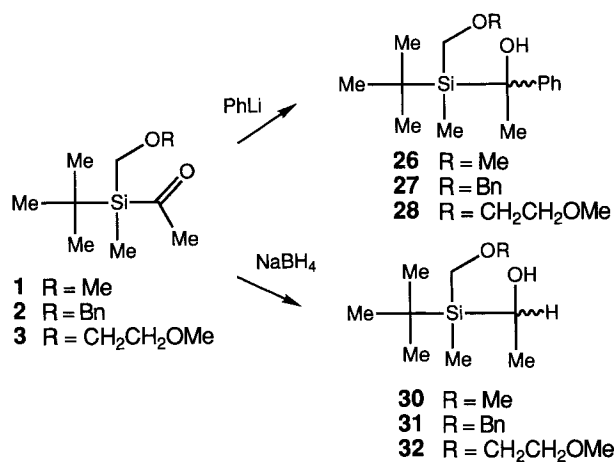


Table. Diastereoselectivity of the 1,2-Additions to Acylsilanes

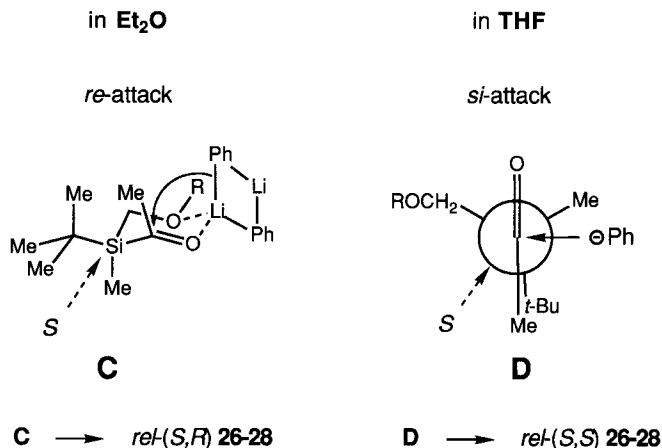
Entry	Substrate	Solvent	Reagent ^{a)}	Product ^{b)}	Diastereoisomer ratio ^{c)}	de [%]
1	1	Et ₂ O	PhLi	26	6.7:1	74
2	2	Et ₂ O	PhLi	27	8.1:1	78
3	3	Et ₂ O	PhLi	28	8.1:1	78
4	4	Et ₂ O	PhLi	29	1.5:1	20
5	1	THF	PhLi	26	1:2.6	44
6	2	THF	PhLi	27	1:3	50
7	3	THF	PhLi	28	1:2	34
8	4	THF	PhLi	29	1.5:1	20
9	1	THF	NaBH ₄	30	1.3:1	14
10	2	THF	NaBH ₄	31	1.4:1	16
11	3	THF	NaBH ₄	32	3:1	50
12	4	THF	NaBH ₄	33	1.1:1	4

^{a)} PhLi additions at $-100 \rightarrow 0^\circ$, NaBH₄ reductions at $-78 \rightarrow 0^\circ$.

^{b)} Chemical yields *ca.* 60%.

^{c)} Ratios were obtained from ¹H-NMR spectra of the crude products. Some mixtures of diastereoisomers were partially separated by chromatography.

^{d)} At $-78 \rightarrow 0^\circ$.



Scheme 4. Stereochemical Course of the PhLi Additions to **1-3** in Et₂O and THF.
Shown for a (*S*)-configured acylsilane.

to our expectations mentioned above, **1-3** could form in Et₂O with the lithium cation rigid six-membered chelates of type **C** which are anchored in their conformation by the *t*-Bu group (*Scheme 4*). A Ph group still bound to the Li-atom⁴⁾ should be transferred preferentially from the top side of these intermediates leading mainly to the *rel*-(*S,R*)-configured alcohols **26-28**. In THF, on the other hand, a complex of type **C** might be partially or completely broken as a consequence of the enhanced complexing ability of this solvent [15] [16]. Assuming that the rotation around the Si–C(carbonyl) bond is free, the stereochemical outcome of the PhLi addition to **1-3** should be predictable with the *Cram* rule. As outlined in *Scheme 4*, the attack of the nucleophile from the less hindered side of the carbonyl group in the ‘*Cram*’ conformation **D** would lead preferentially to the *rel*-(*S,S*)-alcohols **26-28** which are the products of reversed diastereoselectivity compared to the alcohols obtained *via C*. Because **4** does not possess a complexing substituent like **1-3**, no analogous solvent effect would be expected in its reaction with PhLi. In any solvent, the stereochemical outcome of the addition of a nucleophile should simply be the result of the least hindered attack to the carbonyl group of the compound in its most populated conformation.

The chelates of **1-3** with the Li⁺ ion in THF are presumably not altogether broken by the solvent: we find that the reaction of **3** (compared to **1** and **2**) in THF is accompanied by a distinct drop in selectivity. This is not expected on the basis of steric considerations because the three alkoxymethyl groups of **1-3** do not differ too much in size. However, due to the two O-atoms in its (2-methoxyethoxy)methyl group, the chelation capability of **3** is clearly better than that of **1** or **2**. Thus, the reaction of **3** in THF could proceed partially and to a greater extent than in the case of **1** and **2** *via* chelate **C** (with reversed selectivity) which would account for the lower stereoselectivity.

⁴⁾ PhLi exists in THF or Et₂O solution as a dimer [14], but the assumption that PhLi reacts in this form, as implied with **C** or **D** (*Scheme 4*), is not necessary for the explanation of the stereochemical outcome of the reactions.

We can further conclude from the stereochemical results obtained with **1–4** and PhLi in THF that the better selectivities found for **1–3** are the consequence of an improved steric relationship of the three nonreactive substituents at the Si-atom of these compounds (*t*-Bu, ROCH₂, and Me in **1–3** vs. naphth-1-yl, Ph, and Me in **4**). This result is valuable by itself and should encourage more investigations in optimizing chiral silyl auxiliaries by variation of the relative bulks of their substituents.

The NaBH₄ reductions of **1–4** gave similar results as the PhLi additions, yielding in THF the expected alcohols **30–33** as mixtures of diastereoisomers (*Scheme 3*). Although the diastereoselectivities in these reactions are lower than those obtained in the PhLi additions, the de's in the NaBH₄ reductions of **1–3** (14–50%; see *Entry 9–11, Table*) are again clearly higher than in the case of silane **4** (4%; *Entry 12*). Taking the results of the PhLi additions into account, the enhanced selectivities obtained in the NaBH₄ reductions of **1–3** compared to **4** could be the outcome of either reaction path mentioned above. However, in contrast to the PhLi additions in THF, the reductions with NaBH₄ in THF appear to proceed mainly *via* chelation intermediates similar to **C**. Acylsilane **3**, bearing the best chelating (2-methoxyethoxy)methyl group, shows the highest stereoselectivity (50% de; *Entry 11*) with NaBH₄ in THF, thus differing from the result with PhLi in THF. This high stereoselectivity is only expected if the degree of complexing ability of the acylsilanes is important. The preference for the NaBH₄ reductions to proceed *via* chelation even in THF as solvent is not surprising because the B-atom is a better *Lewis* acid than the Li-atom.

Conclusions. – As the relative configurations of the two chiral centers of the alcohols **26–29** and **30–33** are still unknown, unambiguous proof for the proposed reaction paths leading to these compounds still remains to be adduced. Undoubtedly, however, we can conclude from our experiments that alkoxymethyl-substituted silyl groups as chiral auxiliaries are superior to the methyl(naphth-1-yl)phenylsilyl group. The reactions of **1–3** not only gave addition products with up to 78% diastereoselectivity, which is the highest stereoselectivity obtained with chiral silanes⁵⁾ so far, but with these compounds, it is also possible to choose the direction of selectivity (attack on the *re*- or *si*-side of the prochiral carbonyl function) by selecting the appropriate reaction conditions.

The development of an easy access to enantiomerically pure acylsilanes, the improvement of the diastereoselectivities in their reactions with nucleophiles, and the use of these and other reactions for the synthesis of optically active C-frameworks are our objectives to achieve next. Corresponding investigations are in progress.

We thank the members of our analytical laboratories for their excellent services 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 professional discussions.

⁵⁾ *I.e.*, with silanes having a chiral Si-center. Better stereoselectivities (up to 95% de) were reported recently for the α -alkylation of benzylic silanes bearing a chiral substituent [17].

Experimental Part

1. *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 an inert gas (usually N₂). Soln. of salts and acids for workup procedures were prepared in deionized H₂O. Extracts were dried (MgSO₄) and evaporated *in vacuo*. Chromatography: silica gel *Merck 60* (40–63 µm) or *Merck LiChroprep Si 60* (40–63 µm) size *A* or *B* ('lobar'). M.p.: *Mettler FP-5/FP-52*. 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 isobutane; *Finnigan MAT 90* or *Varian MAT 711*; data in *m/z* (rel. %).

2. *(Chloromethyl)dimethoxy(methyl)silane (6).* To a soln. of 16.35 g (0.10 mol) of dichloro(chloromethyl)methylsilane (**5**) in 200 ml of pentane at –30° were added dropwise 9.75 ml (0.24 mmol) of MeOH. A stream of N₂ was passed through the soln. to remove HCl. It was stirred at 23° for 2 h and fractionally distilled *via* a *Vigreux* column (83°/120 mbar): 13.01 g (84%) of **6**. Colorless liquid. IR (film): 2945*m*, 2845*m*, 1460*w*, 1400*w*, 1265*m*, 1195*m*, 1090*s*, 850*s*, 805*s*, 695*m*. ¹H-NMR: 3.57 (*s*, 2 MeO); 2.79 (*s*, SiCH₂Cl); 0.26 (*s*, MeSi). ¹³C-NMR: 50.1 (*q*, 2 MeO); 25.7 (*t*, SiCH₂Cl); –7.7 (*q*, MeSi). GC/EI-MS: 154 (< 1, *M*⁺), 105 (100, [*M* – CH₂Cl]⁺), 75 (50), 59 (18). Anal. calc. for C₄H₁₁ClO₂Si (154.57): C 31.06, H 7.17, Cl 22.92; found: C 30.80, H 7.10, Cl 22.83.

3. *(Chloromethyl)bis(benzyloxy)methylsilane (7).* As described for **6**, from 10.0 g (61.2 mmol) of **5** in 100 ml of pentane, and 15.5 g (144 mmol) of benzyl alcohol (3 h at 0° and at 7 h 23°; b.p. 90°/2·10⁻⁴ mbar): 18.1 g (96%) of **7**. Colorless liquid. IR (film): 3060*m*, 3030*m*, 2930*m*, 2870*m*, 2730*w*, 1950*w*, 1870*w*, 1810*w*, 1610*w*, 1585*w*, 1495*m*, 1452*s*, 1380*s*, 1305*w*, 1260*s*, 1210*s*, 1180*w*, 1090*s*, 1070*s*, 1030*s*, 870*s*, 840*s*, 805*s*, 730*s*, 695*s*, 620*m*. ¹H-NMR: 7.40–7.29 (*m*, 10 arom. H); 4.85 (*s*, 2 PhCH₂O); 2.82 (*s*, SiCH₂Cl); 0.35 (*s*, MeSi). ¹³C-NMR: 139.7 (*s*, 2 arom. C); 128.2 (*d*, 4 arom. C); 127.3 (*d*, 2 arom. C); 126.5 (*d*, 4 arom. C); 65.1 (*t*, 2 PhCH₂O); 26.8 (*t*, SiCH₂Cl); –6.14 (*q*, MeSi). CI-MS: 305 (43, [*M* – I]⁺), 271 (13), 269 (20), 231 (15), 229 (44), 217 (14), 215 (37), 182 (14), 181 (100), 179 (47). Anal. calc. for C₁₆H₁₉ClO₂Si (306.87): C 62.63, H 6.24, Cl 11.55; found: C 58.80, H 6.44, Cl 11.02.

4. *(Chloromethyl)bis(2-methoxyethoxy)methylsilane (8).* As described for **6**, from 43.6 g (267 mmol) of **5** in 300 ml of pentane at 0° and 50.7 g (667 mmol) of 2-methoxyethanol (23° overnight, then evaporation of solvents; b.p. 63–65°/5·10⁻² mbar): 59.9 g (92%) of **8**. Colorless liquid. IR (film): 2935*s*, 2885*s*, 2845*m*, 2725*w*, 1455*m*, 1400*w*, 1370*w*, 1295*m*, 1260*m*, 1200*m*, 1145*s*, 1100*s*, 1030*m*, 960*s*, 845*s*, 800*s*. ¹H-NMR: 3.81–3.78 (*t*-like *m*, 2 CH₂OSi); 3.40–3.37 (*t*-like *m*, 2 MeOCH₂); 3.26 (*s*, 2 MeO); 2.72 (*s*, SiCH₂Cl); 0.18 (*s*, MeSi). ¹³C-NMR: 72.9 (*t*, 2 MeOCH₂); 61.9 (*t*, 2 CH₂OSi); 57.9 (*q*, 2 MeO); 26.2 (*t*, SiCH₂Cl); –7.0 (*q*, MeSi). EI-MS: 227 (2, [*M* – CH₃]⁺), 193 (100, [*M* – CH₂Cl]⁺), 169 (26), 167 (69), 149 (24), 139 (6), 125 (14), 123 (39), 105 (94), 97 (10), 95 (26), 75 (10), 45 (17). Anal. calc. for C₈H₁₉ClO₄Si (242.78): C 39.58, H 7.89, Cl 14.60; found: C 39.71, H 7.79, Cl 14.86.

5. *Dimethoxy(methoxymethyl)methylsilane (9).* A mixture of dry MeOH (5 ml) and Na (890 mg, 31.8 mmol) was stirred at 23° until the Na was completely dissolved. Then 4.91 g (31.8 mmol) of neat **6** were added dropwise, heated to reflux for 8 h, and stirred at 23° overnight. The mixture was filtered and the filtrate distilled fractionally *via* a *Vigreux* column (70–72°/130 mbar): 2.60 g (55%) of **9**. Colorless liquid. IR (film): 2970*m*, 2940*m*, 2840*m*, 2810*m*, 1465*w*, 1450*w*, 1420*w*, 1260*m*, 1190*m*, 1090*s*, 935*m*, 855*s*, 820*s*, 800*s*, 740*m*. ¹H-NMR: 3.56 (*s*, 2 MeOSi); 3.36 (*s*, MeOCH₂); 3.16 (*s*, SiCH₂O); 0.18 (*s*, MeSi). ¹³C-NMR: 62.8 (*t*, SiCH₂O); 62.6 (*q*, MeOCH₂); 49.9 (*q*, 2 MeOSi); –7.1 (*q*, MeSi). GC/EI-MS: 150 (2, *M*⁺), 135 (24, [*M* – Me]⁺), 105 (100, [*M* – CH₂OMe]⁺), 95 (5), 75 (50), 59 (21). Anal. calc. for C₅H₁₄O₃Si (150.25): C 39.97, H 9.39; found: C 39.35, H 9.06.

6. *Bis(benzyloxy)[(benzyloxy)methyl]methylsilane (10).* A dispersion of NaH (1.65 g, 60% in oil, 42 mmol) was washed with pentane and the resultant solid suspended in 90 ml of THF. While stirring and cooling with ice, 4.4 g (41 mmol) of benzyl alcohol were added. After the evolution of H₂ ceased, the mixture was stirred at 23° for another 3 h. Then 12.0 g (39 mmol) of **7** were added dropwise at 0°. The mixture was allowed to warm slowly to 23° and after 6 h (GC: 80% of desired **10** and 20% of **13**), the reaction was quenched with an excess of NH₄Cl (dried at 60°/10⁻² mbar for 6 h). THF was evaporated, and the products were taken up into pentane and decanted from the salts. The solvent was evaporated and the residue distilled rapidly (bulb-to-bulb, 130°/10⁻⁴ mbar): 10.2 g of a 4:1 mixture of **10** (corresp. to 55%) and methyltris(benzyloxy)silane (**13**). This mixture was not separated and used directly for the transformation of **10** into **16**. Data of **10** (from **10/13**): ¹H-NMR: 7.35 (*m*, arom. H); 4.84 (*s*, 2

PhCH₂OSi); 4.50 (s, PhCH₂OCH₂); 3.26 (s, SiCH₂O); 0.29 (s, MeSi). CI-MS: 377 (100, [M – 1]⁺), 287 (41), 197 (28).

7. *Bis(2-methoxyethoxy)[(2-methoxyethoxy)methyl]methylsilane (11)*. As described for **10**, from NaH (7.2 g, 60% in oil, 182 mmol) in 400 ml of THF, 15.1 g (199 mmol) of 2-methoxyethanol, and 40.0 g (165 mmol) of **8** (quenching after 3 h (GC: 85% of desired **11** and 15% of **14**); b.p. 140–150°/10^{–3} mbar): 37.9 g of a 8:2 mixture of **11** (corresp. to 65%) and *methyltris(2-methoxyethoxy)silane (14)*. The bulk of this mixture was used directly for the transformation of **10** into **16**, and a sample was repeatedly distilled (bulb-to-bulb, gradient 74–64°/10^{–3} mbar) to give clean **11** (98% by GC). IR (film): 2925s, 2880s, 2820s, 2720w, 1455m, 1400w, 1365w, 1295m, 1200m, 1135s, 1100s, 1025m, 965m, 845s, 795s. ¹H-NMR: 3.90–3.89 (t-like m, 2 SiOCH₂); 3.60–3.47 (m, 4 OCH₂); 3.36 (s, 2 MeO); 3.35 (s, MeO); 3.25 (s, SiCH₂O); 0.21 (s, MeSi). ¹³C-NMR: 73.5 (t, MeOCH₂); 73.0 (t, 2 MeOCH₂); 71.0 (t, SiCH₂OCH₂); 61.4 (t, 2 SiOCH₂); 61.1 (t, SiCH₂O); 57.9 (q, 3 MeO); –6.2 (q, MeSi). EI-MS: 207 (13, [M – OCH₂CH₂OMe]⁺), 193 (100, [M – CH₂OCH₂CH₂OMe]⁺), 149 (19), 135 (6), 119 (19), 105 (100), 91 (27), 89 (11), 77 (7), 75 (27), 61 (15), 45 (18), 40 (38). Anal. calc. for C₁₁H₂₆O₆Si (282.41): C 46.78, H 9.28; found: C 46.74, H 9.17.

8. *(tert-Butyl)(methoxymethyl)methylsilane (15)*. To a soln. of 1.95 g (13.0 mmol) of **9** in 30 ml of Et₂O at 0° were added 10 ml (14 mmol) of 1.4M *t*-BuLi in pentane. After 30 min, 495 mg (13 mmol) of LiAlH₄ were added, and stirring was continued for another 2 h. The mixture was poured on ice/10% HCl soln., extracted with Et₂O, and the extract washed with sat. NH₄Cl soln., brine, and H₂O. The solvent was removed by distillation *via* a Vigreux column at 100 mbar, and the residue was distilled (96–97°/400 mbar): 1.54 g (81%) of **15**. Colorless liquid. IR (film): 2950s, 2930s, 2890s, 2855s, 2805m, 2115s (Si–H), 1460m, 1445w, 1420w, 1390w, 1360w, 1250m, 1215w, 1175w, 1105s, 1005w, 935m, 860s, 825m, 810w. ¹H-NMR: 3.69–3.58 (m, H–Si); 3.35 (s, MeO); 3.28, 3.22 (AB of ABX, J_{AB} = 13.1, J_{AX} = 2.4, J_{BX} = 3.0, SiCH₂O); 0.95 (s, *t*-Bu); 0.08 (d, J = 3.7, MeSi). ¹³C-NMR: 62.9 (q, t, MeO, SiCH₂O); 26.9 (q, Me₃C); 15.6 (s, Me₃C); –10.4 (q, MeSi). EI-MS: 145 (4, [M – 1]⁺), 143 (9), 119 (6), 115 (11), 111 (15), 105 (51), 91 (6), 75 (100), 73 (29), 69 (65), 59 (10), 57 (18), 55 (24), 45 (11), 43 (29). Anal. calc. for C₇H₁₈OSi (146.31): C 57.47, H 12.40; found: C 56.96, H 12.41.

9. *[(Benzyloxy)methyl](tert-butyl)methylsilane (16)*. As described for **15**, from 9.52 g (25.0 mmol) of **10** in 100 ml of Et₂O, 21 ml (29 mmol) of 1.4M *t*-BuLi, and 1.10 g (29.0 mmol) of LiAlH₄ (stirring continued for 4.5 h). The solvent was evaporated and the residue chromatographed (SiO₂, AcOEt/hexane 1:20) and distilled (bulb-to-bulb, 80–85°/10^{–4} mbar): 3.40 g (61%) of **16**. Colorless liquid. IR (film): 3060w, 3030w, 2950s, 2930s, 2860s, 2810m, 2740w, 2710w, 2110s (Si–H), 1740w, 1610w, 1580w, 1495m, 1470s, 1460s, 1430m, 1380m, 1360m, 1250s, 1200m, 1090s, 1070s, 1030m, 1010m, 980w, 940m, 900m, 880s, 860s, 830m, 810m, 735s, 700s. ¹H-NMR: 7.40–7.29 (m, 5 arom. H); 4.51 (s, PhCH₂O); 3.71 (m, H–Si); 3.23, 3.19 (AB of ABX, J_{AB} = 13.0, J_{AX} = 2.4, J_{BX} = 2.8, SiCH₂O); 0.98 (s, *t*-Bu); 0.38 (d, J = 3.7, MeSi). ¹³C-NMR: 138.8 (s, arom. C); 128.2 (d, 2 arom. C); 127.6 (d, 2 arom. C); 127.4 (d, arom. C); 77.0 (t, PhCH₂O); 60.1 (t, SiCH₂O); 27.2 (q, Me₃C); 15.9 (s, Me₃C); –9.9 (q, MeSi). EI-MS: 222 (3, M⁺), 221 (12), 191 (5), 166 (15), 165 (100), 163 (15), 135 (12), 91 (47). Anal. calc. for C₁₃H₂₂OSi (222.40): C 70.27, H 9.97; found: C 70.54, H 9.77.

10. *(tert-Butyl)[(2-methoxyethoxy)methyl]methylsilane (17)*. To a soln. of 10.0 g (80% by GC, corresp. to 28.4 mmol) of **11** in 125 ml of Et₂O at 0° were added 20.0 ml (28 mmol) of 1.4M *t*-BuLi in pentane followed by 1.3 g (34 mmol) of LiAlH₄. The mixture was stirred for another 2 h, poured on ice/10% HCl soln., and extracted with Et₂O to give, after evaporation, chromatography ('lobar' B, hexane/AcOEt 150:4), and distillation (bulb-to-bulb, 90–110°/20 mbar) 3.43 g (64%) of **17**. Colorless oil. IR (film): 2960s, 2935s, 2890s, 2870s, 2720w, 2120s (Si–H), 1465m, 1395w, 1365w, 1245m, 1200m, 1135s, 1105s, 1030w, 1010w, 985w, 940w, 860s, 830m. ¹H-NMR: 3.71–3.65 (m, H–Si); 3.60–3.45 (m, OCH₂CH₂O); 3.28 (s, MeO); 3.28, 3.21 (AB of ABX, J_{AB} = 13.1, J_{AX} = 2.4, J_{BX} = 3.0, SiCH₂O); 0.95 (s, *t*-Bu); 0.09 (d, J = 3.8, MeSi). ¹³C-NMR: 74.1 (t, MeOCH₂); 71.4 (t, SiCH₂OCH₂); 60.7 (t, SiCH₂O); 58.4 (q, MeO); 26.7 (q, Me₃C); 15.4 (s, Me₃C); –10.5 (q, MeSi). EI-MS: 133 (100, [M – (*t*-Bu)]⁺), 119 (3), 105 (12), 103 (6), 91 (21), 89 (63), 77 (37), 75 (48), 73 (28), 61 (29), 59 (77), 45 (10), 43 (17). Anal. calc. for C₉H₂₂O₂Si (190.36): C 56.79, H 11.65; found: C 56.57, H 11.64.

11. *Chloro(tert-butyl)(methoxymethyl)methylsilane (18)*. Through a soln. of 685 mg (4.69 mmol) of **15** in 4 ml of CCl₄ at –30° was passed Cl₂ (g) until a greenish yellow color persisted. Excess of Cl₂ was removed with a stream of N₂, the solvent was evaporated, and the residue distilled (bulb-to-bulb, 100–110°/400 mbar) to give 762 mg

⁶⁾ We found for several of our silanes the [M – 1]⁺ base peak in the CI-MS. Investigations to explain this unusual observation are in progress.

(99%) of **18** as a colorless liquid which was directly used for the substitution reaction to **21**. ¹H-NMR: 3.37 (s, MeO); 3.37, 3.30 (AB, J_{AB} = 13.4, SiCH₂O); 1.01 (s, *t*-Bu); 0.41 (s, MeSi).

12. *Chloro[(benzyloxy)methyl](tert-butyl)methylsilane (19)*. As described for **18**, from 500 mg (2.25 mmol) of **16** in 4 ml of CCl₄, and Cl₂ (b.p. 80°/10⁻⁴ mbar): 538 mg (92%) of **19**. Colorless liquid. IR (film): 3060w, 3030w, 2960s, 2930s, 2890m, 2810w, 1700w, 1495w, 1470m, 1460m, 1455m, 1430w, 1380w, 1360w, 1255s, 1205w, 1070s, 1005m, 940w, 905w, 830s, 780s, 735s, 700s. ¹H-NMR: 7.36–7.29 (m, 5 arom. H); 4.52 (s, PhCH₂O); 3.43, 3.33 (AB, J_{AB} = 13.3, SiCH₂O); 1.03 (s, *t*-Bu); 0.44 (s, MeSi). ¹³C-NMR: 138.3 (s, arom. C); 128.3 (d, 2 arom. C); 127.6 (d, 2 arom. C); 77.0 (t, PhCH₂O); 61.7 (t, SiCH₂O); 25.7 (q, Me₃C); 19.1 (s, Me₃C); –4.2 (q, MeSi). EI-MS: 257 (2, M^{+}), 255 (5), 221 (4), 199 (8), 181 (10), 179 (8), 165 (4), 163 (11), 135 (6), 65 (100), 63 (36), 57 (75). Anal. calc. for C₁₃H₂₁ClOSi (256.85): C 60.79, H 8.24, Cl 13.80; found: C 60.73, H 8.01, Cl 14.00.

13. *Chloro(tert-butyl)[(2-methoxyethoxy)methyl]methylsilane (20)*. As described for **18**, from 3.00 g (15.8 mmol) of **17** in 10 ml of CCl₄, and Cl₂ (b.p. 100°/1.5 mbar): 3.50 g (98%) of **20**. Colorless liquid. IR (film): 2960s, 2930s, 2890s, 2870s, 1465m, 1390w, 1365m, 1260m, 1200w, 1105s (br.), 940w, 840m, 790m, 700m, 610m. ¹H-NMR: 3.77–3.51 (m, OCH₂CH₂O); 3.48, 3.38 (AB, J_{AB} = 13.4, SiCH₂O); 3.37 (s, MeO); 0.42 (s, MeSi). ¹³C-NMR: 74.4 (t, MeOCH₂); 71.7 (t, SiCH₂OCH₂); 63.0 (t, SiCH₂O); 58.9 (q, MeO); 25.5 (q, Me₃C); 19.0 (s, Me₃C); –4.4 (q, MeSi). CI-MS: 267 (5), 259 (16), 257 (20), 225 (48), 223 (100, $[M - 1]^{+}$), 189 (59, $[M - Cl]^{+}$), 169 (8), 167 (26, $[M - (t\text{-Bu})]^{+}$). Anal. calc. for C₉H₂₁ClO₂Si (224.81): C 48.04, H 9.42, Cl 15.77; found: C 47.73, H 9.16, Cl 16.03.

14. *(tert-Butyl)(1-ethoxyethenyl)(methoxymethyl)methylsilane (21)*. To a soln. of 1.19 g (16.5 mmol) of ethyl vinyl ether in 15 ml of THF at –78° were added 10.7 ml (15 mmol) of 1.4M *t*-BuLi in pentane. The mixture was warmed to 0° until the yellow precipitate dissolved and the soln. discolored (ca. 5 min). After recooling to –78°, 680 mg (4.13 mmol) of neat **18** were added and stirred for 1 h, while the mixture was allowed to warm slowly to 0°. Quenching with sat. NH₄Cl soln., extraction with Et₂O, and distillation (bulb-to-bulb, 100°/20 mbar) gave 775 mg (87%) of **21**. Colorless liquid. IR (film): 3090w, 2955s, 2930s, 2895s, 2805m, 1585s, 1460m, 1445m, 1420w, 1380m, 1310m, 1250m, 1215s, 1180w, 1150w, 1105s, 1050s, 1010w, 970m, 935m, 860m, 830s, 775s, 720w, 680w. ¹H-NMR: 4.68 (d, J = 1.8, 1 H, CH₂=C); 4.33 (d, J = 1.8, 1 H, CH₂=C); 3.69 (q, J = 7.0, CH₃CH₂O); 3.35 (s, MeO); 3.30 (s, SiCH₂O); 1.26 (t, J = 7.0, CH₃CH₂O); 0.95 (s, *t*-Bu); 0.14 (s, MeSi). EI-MS: 187 (7, $[M - Et]^{+}$), 159 (39, $[M - (t\text{-Bu})]^{+}$), 145 (15), 133 (100), 119 (32), 105 (28), 103 (98), 91 (61), 89 (71), 77 (24), 75 (28), 73 (12), 61 (24), 59 (28), 57 (25), 45 (10), 43 (13), 41 (14). Anal. calc. for C₁₁H₂₄O₂Si (216.40): C 61.06, H 11.18; found: C 61.34, H 11.14.

15. *[(Benzyloxy)methyl](tert-butyl)(1-ethoxyethenyl)methylsilane (22)*. As described for **21**, from 350 mg (4.86 mmol) of ethyl vinyl ether in 5 ml of THF, 3.9 ml (5.4 mmol) of 1.4M *t*-BuLi in pentane, and 400 mg (1.56 mmol) of neat **19** (stirring for 2 h; b.p. 90°/10⁻⁴ mbar): 428 mg (94%) of **22**. Colorless liquid. IR (film): 3080w, 3060w, 3030w, 2960s, 2930s, 2860s, 1740w, 1580m, 1495w, 1470m, 1460m, 1450m, 1380m, 1360m, 1250m, 1215s, 1110m, 1090m, 1070m, 1050s, 1010w, 970m, 940w, 900w, 860m, 830s, 790s, 770s, 730s, 700s. ¹H-NMR: 7.35–7.29 (m, 5 arom. H); 4.68 (d, J = 1.9, 1 H, CH₂=C); 4.51 (d, J = 3.0, PhCH₂O); 4.35 (d, J = 1.9, 1 H, CH₂=C); 3.70 (q, J = 7.0, CH₃CH₂O); 3.37, 3.40 (AB, J_{AB} = 13.0, SiCH₂O); 1.27 (t, J = 7.0, CH₃CH₂O); 0.96 (s, *t*-Bu); 0.17 (s, MeSi). ¹³C-NMR: 166.5 (s, SiC(OEt)=CH₂); 139.1 (s, arom. C); 128.2 (d, 2 arom. C); 127.5 (d, 2 arom. C); 127.3 (d, arom. C); 96.0 (t, CH₂=C); 77.0 (t, PhCH₂O); 61.8 (t, SiCH₂O); 60.1 (t, CH₃CH₂O); 27.1 (q, Me₃C); 16.6 (s, Me₃C); 14.5 (q, CH₃CH₂O); –9.3 (q, MeSi). EI-MS: 292 (3, M^{+}), 265 (12), 249 (30), 235 (14), 223 (12), 222 (16), 221 (84), 209 (12), 195 (17), 191 (27), 181 (57), 179 (43), 174 (13), 173 (100), 165 (38), 151 (25), 149 (39), 135 (21), 133 (7), 75 (18), 73 (23), 65 (20), 57 (10). Anal. calc. for C₁₇H₂₈O₂Si (292.49): C 69.81, H 9.65; found: C 70.01, H 9.81.

16. *(tert-Butyl)(1-ethoxyethenyl)[(2-methoxyethoxy)methyl]methylsilane (23)*. As described for **21**, from 4.50 g (62.4 mmol) of ethyl vinyl ether in 50 ml of THF, 39 ml (54.6 mmol) of 1.4M *t*-BuLi in pentane, and 3.50 g (15.6 mmol) of **20** (after warming slowly to 23°, stirring at 23° for another 2 h). Quenching with ice/sat. NH₄Cl soln., extraction with hexane, and filtration through a plug of silica gel gave, after distillation (bulb-to-bulb, 110–120°/0.1 mbar), 3.60 g (89%) of **23**. Colorless liquid. IR (film): 3100w, 2985s, 2965s, 2935s, 2860s, 2820m, 2720w, 1585s, 1465s, 1390m, 1380m, 1365s, 1255m, 1220s, 1135m, 1110s, 1065s, 1015w, 970s, 865m, 835s. ¹H-NMR: 4.65, 4.33 (2d, J = 1.9, CH₂=C); 3.68 (q, J = 7.0, CH₃CH₂O); 3.61–3.48 (m, OCH₂CH₂O); 3.42, 3.35 (AB, J_{AB} = 13.1, SiCH₂O); 3.36 (s, MeO); 1.26 (t, J = 7.0, CH₃CH₂O); 0.95 (s, *t*-Bu); 0.13 (s, MeSi). ¹³C-NMR: 166.3 (s, SiC(OEt)=CH₂); 95.8 (t, CH₂=C); 74.5 (t, CH₃CH₂O); 71.7 (t, SiCH₂OCH₂); 61.6, 61.1 (2t, SiCH₂O, MeOCH₂); 58.9 (q, MeO); 26.9 (q, Me₃C); 16.4 (s, Me₃C); 14.4 (q, CH₃CH₂O); –9.6 (q, MeSi). EI-MS: 217 (4), 203 (78, $[M - (t\text{-Bu})]^{+}$), 189 (5), 177 (8), 157 (16), 133 (21), 119 (42), 113 (14), 105 (19), 103 (62), 91 (49), 89 (54), 77 (18), 75

(48), 73 (12), 61 (18), 59 (31), 58 (34), 43 (100). Anal. calc. for $C_{13}H_{28}O_3Si$ (260.45): C 59.95, H 10.84; found: C 60.19, H 10.70.

17. *[(tert-Butyl)(methoxymethyl)methylsilyl] Methyl Ketone (1)*. A soln. of 719.7 mg (3.33 mmol) of **21** in 5 ml of acetone and 0.5 ml of 10% HCl soln. was stirred for 30 min at 23°, and an excess of NaOAc was added. The solvent was evaporated, H_2O added, and the mixture extracted with Et_2O . Chromatography (SiO_2 , hexane/ Et_2O 15:1) followed by distillation (bulb-to-bulb, 100°/130 mbar) gave 363.8 mg (58%) of **1** (low yield because of low vapor pressure of **1**; product loss upon removal of the solvents). Colorless liquid. IR (film): 2930s, 2890m, 2860s, 2810m, 1640s (C=O), 1465m, 1435w, 1425w, 1365w, 1340m, 1250m, 1215w, 1175w, 1135m, 1105s, 1010w, 930m, 830s, 780s, 720w, 690m. 1H -NMR: 3.40, 3.33 (AB, J_{AB} = 13.1, $SiCH_2O$); 3.35 (s, MeO); 2.31 (s, MeCO); 0.96 (s, *t*-Bu); 0.22 (s, MeSi). ^{13}C -NMR: 237.2 (s, CO); 63.1 (q, MeO); 62.1 (t, $SiCH_2O$); 37.9 (q, MeCO); 26.4 (q, Me_3C); 16.4 (s, Me_3C); -10.2 (q, MeSi). EI-MS: 173 (4, $[M - Me]^+$), 145 (53, $[M - COMe]^+$), 117 (3), 103 (31), 89 (100), 85 (8), 75 (63), 61 (12), 59 (48), 45 (9), 43 (13). Anal. calc. for $C_9H_{20}O_2Si$ (188.35): C 57.39, H 10.70; found: C 57.42, H 10.51.

18. *[(Benzyloxy)methyl](tert-butyl)methylsilyl] Methyl Ketone (2)*. As described for **1**, from 1.00 g (3.42 mmol) of **22** in 2 ml of acetone, 0.5 ml of 10% HCl soln. (15 min stirring), and excess NaOAc (b.p. 80°/10⁻⁴ mbar): 858 mg (95%) of **2**. Colorless liquid. IR (film): 3060w, 3030w, 2960s, 2930s, 2860s, 2810m, 1640s (C=O), 1495w, 1460m, 1430w, 1410w, 1380w, 1360m, 1340m, 1250m, 1200w, 1140m, 1090s, 1070s, 1030w, 1010w, 980w, 935w, 905w, 828s, 805m, 778s, 735s, 698s, 665w. 1H -NMR: 7.30–7.29 (m, 5 arom. H); 4.51 (s, $PhCH_2O$); 3.45, 3.39 (AB, J_{AB} = 13.0, $SiCH_2O$); 2.32 (s, MeCO); 0.98 (s, *t*-Bu); 0.24 (s, MeSi). ^{13}C -NMR: 244.3 (s, CO); 138.8 (s, arom. C); 128.2 (d, 2 arom. C); 127.5 (d, 2 arom. C); 127.4 (d, arom. C); 77.0 (t, $PhCH_2O$); 60.1 (t, $SiCH_2O$); 27.2 (q, Me_3C); 15.9 (s, Me_3C); -9.9 (q, MeSi). EI-MS: 264 (4, M^+), 249 (33), 221 (27), 173 (5), 151 (9), 149 (35), 135 (27), 73 (9), 65 (81), 63 (17), 57 (100), 43 (72). Anal. calc. for $C_{15}H_{24}O_2Si$ (264.44): C 68.13, H 9.15; found: C 68.32, H 9.30.

19. *[(tert-Butyl)(2-methoxyethoxy)methyl]methylsilyl] Methyl Ketone (3)*. As described for **1**, from 465 mg (1.80 mmol) of **23**, 0.5 ml of 10% HCl soln. in 4 ml of acetone (15 min stirring), and excess NaOAc (no chromatography; b.p. 100–120°/0.1 mbar): 375 mg (90%) of **3**. Colorless liquid. IR (film): 2950s, 2930s, 2890s, 2860s, 2810m, 2715w, 1640s (C=O), 1465m, 1430w, 1410w, 1365m, 1340m, 1250m, 1195m, 1135s, 1100s, 1025w, 1010w, 980w, 940w, 865w, 830s, 780s. 1H -NMR: 3.58–3.45 (m, OCH_2CH_2O); 3.48, 3.41 (AB, J_{AB} = 13.1, $SiCH_2O$); 2.31 (s, MeCO); 0.95 (s, *t*-Bu); 0.21 (s, MeSi). ^{13}C -NMR: 244.3 (s, CO); 74.5 (t, $MeOCH_2$); 71.4 (t, $SiCH_2OCH_2$); 60.1 (t, $SiCH_2O$); 58.5 (q, MeO); 37.8 (q, MeCO); 26.4 (q, Me_3C); 16.3 (s, Me_3C); -10.2 (q, MeSi). EI-MS: 189 (28, $[M - COMe]^+$), 145 (2), 103 (22), 91 (12), 89 (100), 77 (7), 75 (47), 61 (9), 59 (35), 45 (7), 43 (10), 41 (5). Anal. calc. for $C_{11}H_{24}O_3Si$ (232.40): C 56.85, H 10.41; found: C 57.09, H 10.67.

20. *(1-Ethoxyethenyl)methyl(naphth-1-yl)phenylsilane (25)*. As described for **21**, from 4.10 g (56.6 mmol) of ethyl vinyl ether in 50 ml of THF, 35 ml (50.0 mmol) of 1.4M *t*-BuLi in pentane, and 4.00 g (14.2 mmol) of **24** (after warming slowly to 23°, stirring at 23° for another 30 min). Quenching with ice/sat. NH_4Cl soln., extraction with hexane, and distillation (bulb-to-bulb, 130–140°/6 · 10⁻⁵ mbar) gave 4.52 g (100%) of **25**. Colorless highly viscous oil. IR (film): 3050m, 2975m, 2925m, 2900m, 2870m, 1950w, 1890w, 1825w, 1580s, 1500m, 1475w, 1455w, 1440w, 1430m, 1380m, 1355w, 1320w, 1305w, 1250m, 1215s, 1145m, 1110s, 1090w, 1050s, 1025w, 970s, 860s, 825s, 790s, 735s, 700s, 680m. 1H -NMR: 8.07 (d, J = 8.3, arom. H); 7.92 (d, J = 8.2, arom. H); 7.86 (d, J = 7.9, arom. H); 7.76–7.73 (m, arom. H); 7.65–7.61 (m, 2 arom. H); 7.49–7.33 (m, 6 arom. H); 4.87, 4.41 (2d, J = 1.8, C=CH₂); 3.85 (q, J = 7.0, CH_3CH_2O); 1.30 (t, J = 7.0, CH_3CH_2O); 0.84 (s, MeSi). ^{13}C -NMR: 166.7 (s, $SiC(OEt)=CH_2$); 137.2 (s, arom. C); 135.9 (d, arom. C); 135.8 (s, arom. C); 135.1 (d, 2 arom. C); 133.4, 133.1 (2s, arom. C); 130.4, 129.3, 129.2, 128.7 (4d, arom. C); 127.8 (d, 2 arom. C); 125.4, 125.3, 125.1 (3d, arom. C); 98.2 (t, $CH_2=C$); 62.5 (t, CH_3CH_2O); 14.5 (q, CH_3CH_2O); -3.2 (q, MeSi). EI-MS: 318 (11, M^+), 303 (3), 289 (9), 274 (7), 259 (7), 247 (100, $[M - 71]^+$), 231 (9), 215 (9), 202 (9), 183 (6), 169 (22), 167 (11), 165 (17), 155 (6), 137 (12), 121 (5), 105 (5). Anal. calc. for $C_{21}H_{22}OSi$ (318.50): C 79.20, H 6.96; found: C 78.76, H 6.96.

21. *Methyl [Methyl(naphth-1-yl)phenylsilyl] Ketone (4)*. As described for **1**, from 3.98 g (12.52 mmol) of **25** in 5 ml of acetone, 2 ml of 10% HCl soln. (10 min stirring), and excess NaOAc. The Et_2O extract was washed with sat. $NaHCO_3$ soln., brine, and H_2O to give, after filtration through a plug of silica gel followed by distillation (bulb-to-bulb, 130–140°/10⁻⁴ mbar), 3.41 g (94%) of **4**. Slightly yellow highly viscous oil which crystallized upon standing at 23° for some days. M.p. (hexane) 56.4–58.1°. IR (film): 3050m, 2960m, 2900w, 1950w, 1890w, 1825w, 1720w, 1645s (C=O), 1590w, 1500m, 1485w, 1430s, 1405m, 1340m, 1320w, 1250m, 1220w, 1190w, 1145m, 1130m, 1110s, 1025w, 980m, 825s, 785s, 740s, 720s, 700s, 685m, 660w. 1H -NMR: 8.00 (d, J = 8.2, arom. H); 7.94–7.91 (m, arom. H); 7.82–7.77 (m, 2 arom. H); 7.67–7.64 (m, 2 arom. H); 7.56–7.38 (m, 6 arom. H); 2.35 (s, MeCO); 0.92 (s, MeSi). ^{13}C -NMR: 243.7 (s, CO); 136.8 (s, arom. C); 135.7 (d, arom. C); 134.9 (d, 2 arom. C); 133.3, 132.9 (2s, arom.

C); 131.0 (*d*, arom. C); 130.7 (*s*, arom. C); 129.9, 129.0 (2*d*, arom. C); 128.1 (*d*, 2 arom. C); 127.8, 126.2, 125.7, 125.1 (4*d*, arom. C); 36.5 (*q*, MeCO); –4.3 (*q*, MeSi). EI-MS: 289 (4, [*M* – 1]⁺), 275 (34), 247 (100, [*M* – COMe]⁺), 231 (7), 221 (9), 202 (8), 169 (22), 167 (11), 162 (12), 155 (7), 139 (5), 127 (7). Anal. calc. for C₁₉H₁₈OSi (290.44): C 78.57, H 6.25; found: C 78.30, H 6.52.

22. *General Procedure for the NaBH₄ Addition to 1–4.* A soln. of acylsilane in THF (*ca.* 0.20–0.25M) was cooled to –78°, treated with 1.0 mol-equiv. of NaBH₄, stirred at –78° for 2 h, and allowed to warm to 23° within 2 h. The reaction was quenched at –78° with 10% HCl soln., the mixture extracted with Et₂O, the extract dried and evaporated, and the residue analyzed by ¹H-NMR: ratio of the diastereoisomers, see *Table*.

23. *General Procedure for the PhLi Addition to 1–4.* A soln. of acylsilane in THF or Et₂O (*ca.* 1.5–2.5M) was cooled to –100°, treated with 1.2 mol-equiv. of PhLi (2M in cyclohexane/Et₂O 7:3), and stirred at –100° for 30 min. After quenching with sat. NH₄Cl soln. and extraction with Et₂O, the extract was dried and evaporated and the residue analyzed by ¹H-NMR: ratio of diastereoisomers, see *Table*.

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