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A chiral silyl ether as auxiliary for the asymmetric nucleophilic addition to α- and β-silyloxy carbonyl compounds

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Abstract—Chiral silicon groups, attached as protective group in proximity to a prostereogenic functionality by means of an ether linkage, can act, at least in specific cases, efficiently as stereochemical directors. The addition of Grignard reagents to α- and β-silyloxy carbonyl compounds (silyloxy is the stereogenic $(Me_3C)(BnOCH_2)MeSiO$-group) afforded the respective products with stereofacial selectivities of up to 92%. The source of the selectivities is discussed and their dependence upon structural parameters. The potential of the described principle might be increased by the structural optimization of the auxiliary group, which has not been performed yet.

1. Introduction

Silyl groups are well established protective groups in organic synthesis, particularly for alcohols but also for carboxylic acids and amines.[1] The silyl derivatives are easily prepared and cleaved, and their reactivities can usually be readily controlled with the appropriate choice of the groups attached to silicon. In the course of our ongoing investigation of the chiral [(benzyloxy)methyl]-(*tert*-butyl)methylsilyl group (**I**) as an auxiliary to control stereoselective processes,[2–5] we got interested in the combined use of **I** as a protective group and stereochemically directing auxiliary.

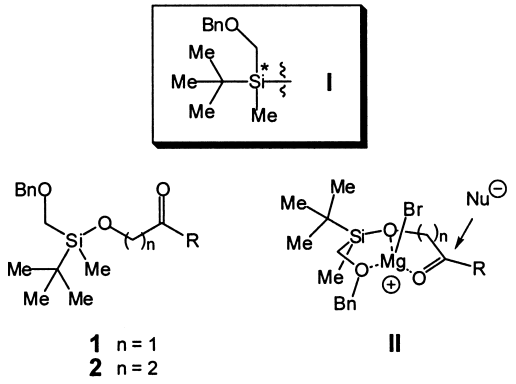

Figure 1. Silicon-based chiral moiety to be used as protective group and chiral auxiliary for nucleophilic additions to α- and β-hydroxy carbonyl compounds.

Keywords: chiral silicon; diastereoselectivity; chelate control; hydroxy carbonyl compound.

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For an initial investigation, we regarded racemic silyl ethers of α- and β-hydroxyketones and -aldehydes (compounds of type **1** and **2**, Fig. 1) as suitable substrates to study this bifunctional effect of the chiral silicon moiety. The addition of Grignard reagents to the carbonyl group of the compounds—performed under chelate-controlled condition in presence of a Lewis acid such as $MgBr_2$, which proved advantageous in related transformations[3,4,6]—was expected to proceed via tridentate transition structures of type **II**, affording the respective reaction products with high stereochemical control.

2. Results

A series of silylated compounds of type **1** and **2**, the starting materials for our investigation, were prepared with the readily available racemic chlorosilane **3**.[4] Silyl ethers **1b**,**d** were directly prepared from the commercial α-hydroxyketones **4b**,**d** by their treatment with the chlorosilane in presence of Et_3N and a catalytic amount of DMAP. Analogous monosilylation of 1,2-diol **5a** and 1,3-diols **6a**,**b**, using an excess of the alcohols, afforded the respective hydroxyethers **7a** and **8a**,**b**, and mild oxidation of the remaining alcohol functions under Swern conditions delivered aldehydes **1a** and **2a** and ketone **2b** (Scheme 1).

For the preparation of the substrates **1c**,**e** and **2c**–**e**, aldehydes **1a** and **2a** were used as the starting materials. Addition of the appropriate Grignard reagents to the carbonyl group of the two substrates gave rise to the respective alcohols **7c**,**e**/**7c′**,**e′** and **8c**–**e**/**8c′**–**e′**, which next were oxidized under Swern conditions to the desired ketones (Scheme 1).

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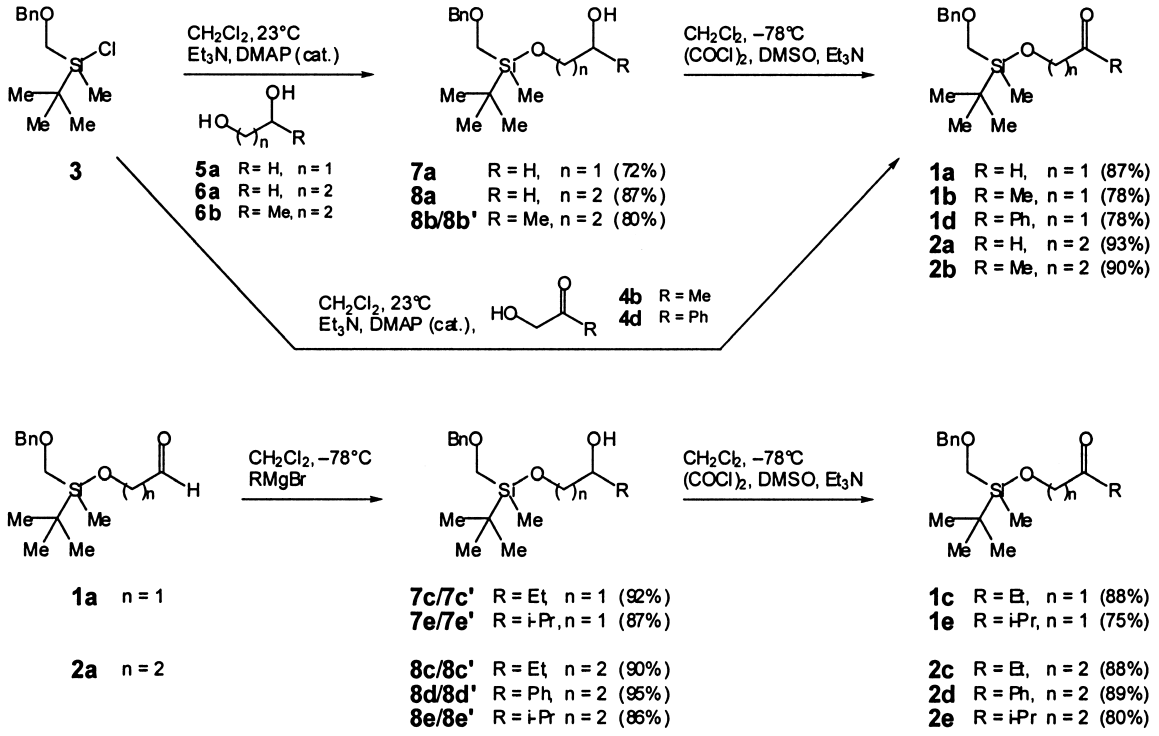
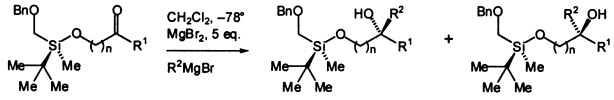


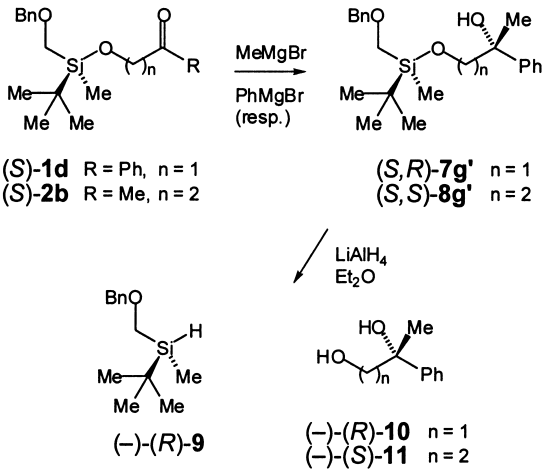
Scheme 1. Preparation of the silylated α- and β-silyloxy carbonyl compounds used as substrates.

Our investigation of the stereoselective addition of organometallic reagents to the carbonyl group of compounds **1a–e** and **2a–e** (Scheme in Table 1) started with the evaluation of the optimal reaction conditions. Ketone **1b** was thus treated with several organometallic species like PhLi, PhMgBr, and in situ prepared derivatives thereof, based on Ce(III), Cr(III), Zn(II), Cu(I), and other metal ions. The reactions were performed with or without pre-complexation of the ketone, using the respective metal salts as Lewis acids. Additionally, the reaction temperature (−30 to −100°C) as well as the solvent (pentane, CH_2Cl_2, Et_2O, THF) were varied. As in earlier investigations,[6] the use of Grignard reagents, combined with pre-complexation of the ketone with $MgBr_2$ in a little-donating solvent, turned out to

Table 1. Stereochemical results obtained with the addition of Grignard reagents to pre-complexed chiral α- and β-silyloxy carbonyl compounds



Entry	*n*	Starting material	R^1	R^2MgBr	*syn/anti* add. products	dr
1	1	**1a**	H	MeMgBr	**7b/7b′**	66:34
2	1	**1a**	H	EtMgBr	**7c/7c′**	60:40
3	1	**1a**	H	PhMgBr	**7d/7d′**	59:41
4	1	**1a**	H	*i*-PrMgBr	**7e/7e′**	53:47
5	1	**1a**	H	*t*-BuMgBr	**7f/7f′**	50:50
6	1	**1b**	Me	PhMgBr	**7g/7g′**	81:19
7	1	**1c**	Et	PhMgBr	**7h/7h′**	72:28
8	1	**1e**	*i*-Pr	PhMgBr	**7i/7i′**	53:47
9	1	**1d**	Ph	MeMgBr	**7g′/7g**	71:29
10	1	**1d**	Ph	EtMgBr	**7h′/7h**	66:34
11	1	**1d**	Ph	*i*-PrMgBr	**7i′/7i**	64:34
12	1	**1d**	Ph	*t*-BuMgBr	**7j′/7j**	52:48
13	2	**2a**	H	MeMgBr	**8b/8b′**	43:57
14	2	**2a**	H	EtMgBr	**8c/8c′**	37:63
15	2	**2a**	H	PhMgBr	**8d/8d′**	34:66
16	2	**2a**	H	*i*-PrMgBr	**8e/8e′**	36:64
17	2	**2b**	Me	PhMgBr	**8g/8g′**	13:87
18	2	**2c**	Et	PhMgBr	**8h/8h′**	16:84
19	2	**2e**	*i*-Pr	PhMgBr	**8i/8i′**	37:63
20	2	**2d**	Ph	MeMgBr	**8g′/8g**	25:75
21	2	**2d**	Ph	EtMgBr	**8h′/8h**	18:82
22	2	**2d**	Ph	*i*-PrMgBr	**8i′/8i**	20:80



Scheme 2. Proof of relative configurations by chemical correlation (major isomers only shown).

represent the best conditions. The addition of the Grignard reagents to the several carbonyl compounds was finally performed by carrying out the following standard procedure: the silyl ethers **1a–e** or **2a–e** were pre-complexed at −40°C in CH_2Cl_2 with 5 equiv. of $MgBr_2$ for 15 min and 3 equiv. of the Grignard reagents in Et_2O were added subsequently at −78°C. The reactions were quenched after approximately 2 h with aqueous NH_4Cl and delivered, after extraction and chromatography, the respective addition products, usually in high yields (80–95%). The stereochemical results of the transformations are summarized in Table 1.

The ratios of the diastereomeric products **7b–j/7b′–j′** and **8b–i/8b′–i′** were determined by ^{1}H NMR spectroscopy on the crude mixtures (before chromatography), and the relative configurations of the products were determined pars pro toto with compounds **7g/7g′** and **8g/8g′** by chemical correlation (Scheme 2). For this purpose, enantiomerically enriched ketones (*S*)-**1d** and (*S*)-**2b** were prepared.[7] Their treatment with MeMgBr and PhMgBr, respectively, afforded the mixtures of the enantiomerically enriched addition products **7g′** and **8g′**, which delivered upon reduction with $LiAlH_4$ in a stereospecific process hydrosilane (−)-(*R*)-**9**[5] and the corresponding enantiomerically enriched diols (−)-(*R*)-**10**[8] and (−)-(*S*)-**11**.[9]

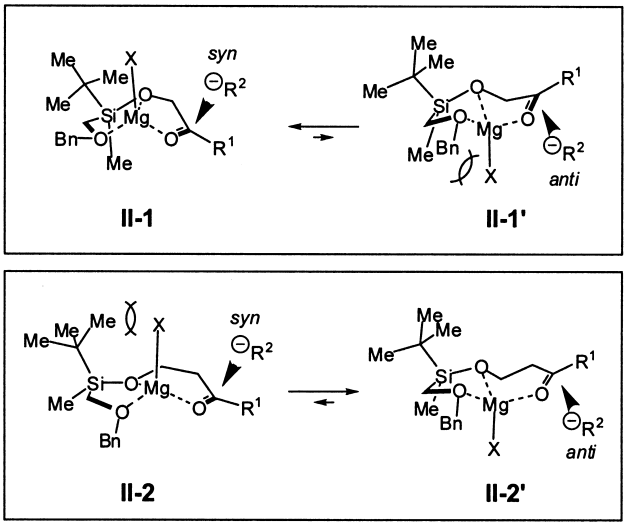


Figure 2. Proposed chelate structures for the two diastereotopic attacks (*syn* and *anti* to the *t*-Bu group) of the nucleophile to the carbonyl group of compounds of type **1** and **2**.

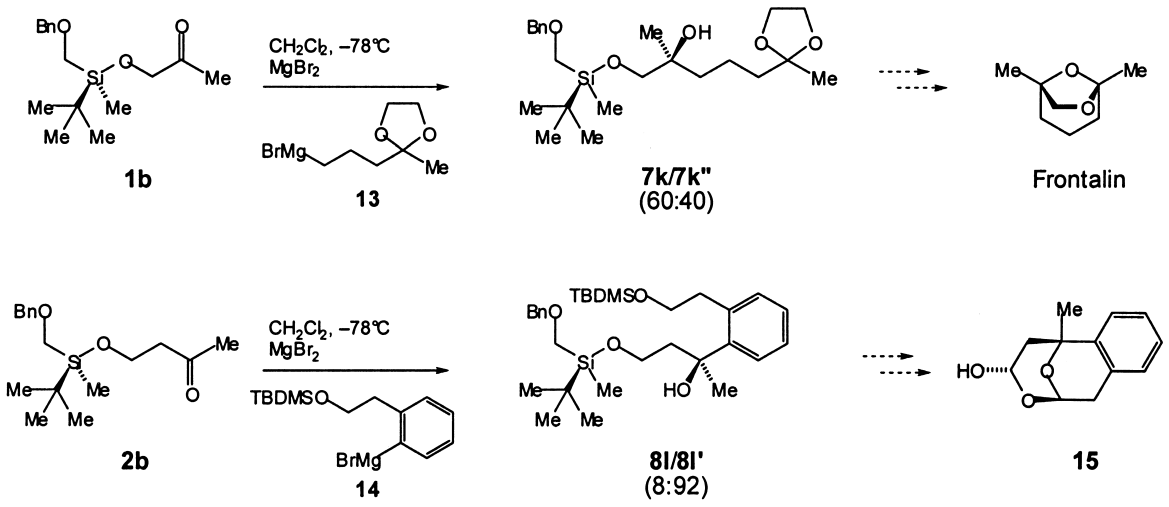
3. Discussion

Several trends can be extracted from the results presented in Table 1. (1) The π-facial selectivities obtained under the influence of the chiral auxiliary **I** are rather low and differ for the two types of substrates: compounds of type **1** prefer *syn*- and substrates of type **2** *anti*-attacks of the nucleophiles (*syn* and *anti* with respect to the *t*-Bu group in proposed complexes **II-1/II-1′** and **II-2/II-2′**, respectively, Fig. 2). (2) Highest selectivities were obtained with compounds of type **2**. (3) With the exception of the aldehydes **1a** and **2a**, increase in the size of the R^1 group is accompanied for both types of substrates with a decrease in stereoselectivity. (4) Expansion of the bulk of the nucleophile results in lowered selectivities for compounds of type **1** and slightly enhanced selectivities for compounds of type **2**.

The observed results can be explained to a great extent by scrutinizing the chelate structures **II-1/II-1′** and **II-2/II-2′**, proposed as competing initial arrangements leading to the two opposite sites of nucleophilic attack at the carbonyl C-atom for the two types of compounds (Fig. 2). Simple molecular models, and semi-empirical calculations (computed for R^1=Me and X=Br on the PM3 level), also suppose that complexes of type **II-1** for compounds **1** and complexes of type **II-2′** for compounds **2** are each thermodynamically favored over the related stereoisomeric complexes **II-1′** and **II-2**, respectively. This finding agrees well with the observed stereoselectivities, corresponding to preferred *syn*-attacks of the nucleophiles at the ketones of type **1** and *anti*-attacks at the carbonyl groups of the compounds of type **2**.

In addition, the dependence of the stereoselectivities upon the size of the group R^1—with the exception of the particular behavior of the aldehydes **1a** and **2a**—and the bulkiness of the incoming nucleophile R^2 can be explained with the chelate structures shown in Fig. 2. Increasing the size of R^1 would generally be expected to introduce additional steric strain into the complexes **II-1/II-1′** and **II-2/II-2′**, leading to their overall destabilization. Thus, with increasing bulk of R^1, alternative non-selective reaction paths via 'open-chained' transition structures could progressively become more important and could thus gradually compete with the 'chelate-controlled' processes (compare entries 6–8 and 17–19, respectively, for the two types of compounds). This would lead to a general loss of selectivity.

The explanation of the effects observed upon variation of the R^2 group is less straightforward. It might be assumed that transmetallation of R^2 to the chelated Mg^{2+} or formation of bimetallic intermediates is important for the observed selectivities. Only this way, the several transition structures related to the complexes **II-1/II-1′** and **II-2/II-2′**



Scheme 3. Stereoselective preparation of tertiary alcohols as potential precursors for frontalin and isocannabinol analogs (major isomers shown only; the drawings reflect but the relative configurations).

could 'sense' the steric bulk of the incoming nucleophile (formally variation in the size of the group X). The stereoselectivities should then be expected to increase for both types of substrates on increasing the size of R^2, because the complexes **II-1** and **II-1′** or **II-2** and **II-2′**, respectively, should be discriminated more efficiently. This effect is in fact found for substrates of type **2** (compare entries 13–16 and 20–23) but not for compounds of type **1**. For the latter substrates, the π-facial selectivity drops for larger R^2 groups (compare entries 1–5 and 20–23). This effect might again be explained with alternative, non-selective 'open-chain-controlled' processes becoming important specifically for compounds **1**. Such processes might dominate for compounds **1** rather than for compounds **2** due to the more condensed structures of complexes **II-1/II-1′** (as compared to **II-2/II-2′**), where the interactions of bulky R^2 (X) groups with the substituents at silicon could lead to considerable destabilization.

With the above results in hand, it is readily understood that the addition of Grignard reagent **13** to α-silyloxyketone **1b** leads to the alcohols **7k/7k′**, with low stereoselectivity only. Compounds **7k/7k′** are regarded as precursors of frontalin, the attracting pheromone of the pine beetle (Scheme 3),[10] which should be formed upon treatment of the protected dihydroxyketone with acid.[11] On the other hand, it is not surprising that the addition of Grignard reagent **14**, a sterically demanding *ortho*-substituted benzene derivative, to β-silyloxyketone **2b** led to the respective addition products **8l/8l′** with high stereoselectivity (dr 92:8). Access to products **8l/8l′** should allow the stereoselective synthesis of tricyclic framework **15** having structural similarity to isocannabinol by some simple functional group interconversions. Derivatives of **15** have shown interesting physiological properties (Scheme 3).[12]

4. Conclusion

In conclusion, it is shown with the above investigation that chiral silicon groups, brought into proximity to a prostereogenic functionality by means of an ether linkage, can act—at least in particular cases—efficiently as stereochemical directors. The potential of this principle might be increased by the structural optimization of the silicon auxiliary. This is a topic of our ongoing research.

5. Experimental

5.1. General

Unless otherwise stated, manipulations were carried out under Ar in oven-dried glass equipment. For reactions, Et_2O was freshly distilled from Na with benzophenone ketyl as indicator; CH_2Cl_2 was freshly distilled from CaH_2; benzene (anal. grade) was stored over Na. All org. solvents were distilled prior to use. Anh. $MgBr_2$ was prepared from 1,2-dibromoethane and Mg in Et_2O. Extracts were washed with sat. aq. NH_4Cl solution and brine and were dried over $MgSO_4$. Solutions for workup procedures were prepared in deionized H_2O. Chromatography: Merck silica gel 60 (40–63 μm). Mp: Mettler FP5/FP52. IR spectra: neat liquid films between NaCl plates; Perkin–Elmer 297 or 781; in cm^{-1}, strong bands only. ^1H NMR spectra in $CDCl_3$; Bruker AC-300 (300 MHz), ARX-300 (300 MHz); δ in ppm rel. to $CHCl_3$ (δ 7.26), *J* in Hz. ^{13}C NMR spectra in $CDCl_3$; Bruker ARX-300 (75.5 MHz); δ in ppm rel. to $CDCl_3$ (δ 77.0); multiplicities from DEPT-135 and DEPT-90 experiments. Mass spectrometry (MS): Finnigan MAT 90 or Finnigan SSQ 700; chemical-ionization MS (CI-MS) with NH_3 as the reactant gas; quasi-molecular ions and characteristic fragments; in *m/z* (rel. %). Diastereomeric ratios (dr) were determined by ^1H NMR on the crude mixtures (before chromatography). The respective signals are marked with underlining.

5.2. General procedures

5.2.1. Swern oxidations. Oxalyl chloride (2.2 mmol) was added at −78°C in one portion to a stirred solution of dimethyl sulfoxide (4.4 mmol) in CH_2Cl_2 (20 mL). The resultant mixture was stirred for 30 min and a solution of an alcohol (2.0 mmol) in CH_2Cl_2 (2 mL) was added

dropwise via cannula. It was stirred for 30 min at −78°C, then Et_3N (10.0 mmol) was added dropwise, and after 10 min was allowed to warm to 23°C over a period of 15 min. Extraction with Et_2O and chromatography (hexane/Et_2O 10:3) provided the respective aldehyde or ketone.

5.2.2. Silylations of alcohols. To a stirred solution of [(benzyloxy)methyl](*tert*-butyl)chloro(methyl)silane (**3**,[4] 30.0 mmol) in CH_2Cl_2 (50 mL), Et_3N (35.0 mmol), DMAP (3.0 mmol), and an alcohol (90.0–150.0 mmol) were added at 0°C. The mixture was warmed to 23°C and stirred for 2 h. Extraction with Et_2O and chromatography (hexane/Et_2O 2:1) provided the respective silylether.

5.2.3. Grignard additions to the carbonyl compounds. A 2 M solution of $MgBr_2$ in Et_2O (5.0 mmol) was added to a stirred solution of a carbonyl compound (1.0 mmol) in CH_2Cl_2 (6 mL) at −40°C. After 15 min, it was cooled to −78°C and a 3 M solution of MeMgBr in Et_2O (3.0 mmol) was added dropwise via cannula. It was quenched after 2 h by the addition of sat. aq. NH_4Cl solution (2 mL). Extraction with Et_2O and chromatography (hexane/Et_2O 10:3) afforded the respective secondary or tertiary alcohols.

5.3. Aldehydes and ketones 1a–e and 2a–e

5.3.1. 2-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]oxy}-acetaldehyde (1a). According to general procedure given in Section 5.2.1, oxidation of **7a** (500 mg, 1.77 mmol) provided **1a** (432 mg, 1.54 mmol, 87%) as a colorless oil. IR: 2950, 2930, 2890, 2850, 1740, 1480, 1470, 1455, 1255, 1135br., 1100br., 830, 770, 735, 700. ^{1}H NMR: 9.67 (t, *J*=0.8 Hz, CHO); 7.37–7.25 (m, 5 arom. H); 4.45 (s, PhC*H*$_2$); 4.30 (d, *J*=0.8 Hz, SiOCH_2); 3.32, 3.23 (AB, *J*=13.3 Hz, SiCH_2); 0.96 (s, *t*-Bu); 0.16 (s, SiMe). ^{13}C NMR: 202.3 (d, CHO); 138.2 (s, arom. C); 128.3, 127.7 (2d, 2×2 arom. C); 127.6 (d, arom. C); 77.2 (t, Ph*C*H$_2$); 70.0 (t, SiOCH_2); 60.5 (t, SiCH_2); 26.0 (q, C*Me*$_3$); 18.1 (s, *C*Me$_3$); −7.9 (q, SiMe). CI-MS: 298 (100, $[M+NH_4]^+$); 281 (11, $[M+H]^+$). Anal. calcd for $C_{15}H_{24}O_3Si$ (280.44): C 64.24, H 8.63. Found: C 63.32, H 8.59.

5.3.2. 1-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-oxy}acetone (1b). According to general procedure given in Section 5.2.2, silylation of alcohol **4b** (7.37 g, 95.55 mmol, 3 equiv.) with **3** (8.81 g, 31.85 mmol, 1 equiv.) afforded **1b** (7.31 g, 24.83 mmol, 78%) as a colorless oil. IR: 2960, 2930, 2890, 2850, 1780, 1120br., 1080. ^{1}H NMR: 7.37–7.24 (m, 5 arom. H); 4.45 (s, SiOCH_2); 4.25 (s, PhCH_2); 3.32, 3.24 (AB, *J*=13.3 Hz, SiCH_2); 2.12 (s, COMe); 0.96 (s, *t*-Bu); 0.15 (s, SiMe). ^{13}C NMR: 209.0 (s, CO); 138.6 (s, arom. C); 128.3, 127.6 (2d, 2×2 arom. C); 127.5 (d, arom. C); 77.2 (t, Ph*C*H$_2$); 70.0 (t, SiOCH_2); 60.6 (t, SiCH_2); 26.0 (q, C*Me*$_3$); 25.9 (q, CO*Me*); 18.1 (s, *C*Me$_3$); −8.0 (q, SiMe). CI-MS: 312 (100, $[M+NH_4]^+$); 295 (26, $[M+H]^+$). Anal. calcd for $C_{16}H_{26}O_3Si$ (294.46): C 65.26, H 8.90. Found: C 64.96, H 9.01.

5.3.3. 1-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-oxy}butan-2-one (1c). According to general procedure given in Section 5.2.1, oxidation of **7c/7c′** (235 mg, 0.76 mmol) provided **1c** (206 mg, 0.67 mmol, 88%) as a colorless oil. IR: 2960, 2930, 2890, 2860, 1720, 1110br. ^{1}H NMR: 7.37–7.24 (m, 5 arom. H); 4.45 (s, SiOCH_2); 4.27 (s, PhCH_2); 3.32, 3.24 (AB, *J*=13.4 Hz, SiCH_2); 2.49 (q, *J*=7.3 Hz, CH_2Me); 1.03 (t, *J*=7.3 Hz, CH$_2$*Me*); 0.96 (s, *t*-Bu); 0.15 (s, SiMe). ^{13}C NMR: 211.6 (s, CO); 138.6 (s, arom. C); 128.2, 127.6 (2d, 2×2 arom. C); 127.5 (d, arom. C); 77.2 (t, Ph*C*H$_2$); 70.0 (t, SiOCH_2); 60.6 (t, SiCH_2); 31.5 (t, *C*H$_2$Me); 26.0 (q, C*Me*$_3$); 18.1 (s, *C*Me$_3$); 7.1 (q, CH$_2$*Me*); −8.0 (q, SiMe). CI-MS: 326 (100, $[M+NH_4]^+$); 309 (32, $[M+H]^+$). Anal. calcd for $C_{17}H_{28}O_3Si$ (308.49): C 66.19, H 9.15. Found: C 65.89, H 9.07.

5.3.4. 2-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-oxy}-1-phenylethan-1-one (1d). According to general procedure given in Section 5.2.2, silylation of 2-hydroxy-1-phenylethan-1-one (**4d**, 1.59 g, 11.67 mmol, 3 equiv.) with **3** (1.00 g, 3.89 mmol) afforded **1d** (1.08 g, 3.03 mmol, 78%) as a colorless oil. IR: 2950, 2930, 2890, 2850, 1705, 1150. ^{1}H NMR: 7.89–7.85 (m, 2 arom. H); 7.56–7.20 (m, 8 arom. H); 5.04 (s, SiOCH_2); 4.41 (s, PhCH_2); 3.37, 3.30 (AB, *J*=13.4 Hz, SiCH_2); 1.00 (s, *t*-Bu); 0.20 (s, SiMe). ^{13}C NMR: 197.2 (s, CO); 138.6, 134.9 (2s, 2 arom. C); 133.0 (d, arom. C); 128.5 (d, 2 arom. C); 128.1, 127.7, 127.5 (3d, 3×2 arom. C); 127.3 (d, arom. C); 77.2 (t, Ph*C*H$_2$); 67.7 (t, SiOCH_2); 61.1 (t, SiCH_2); 26.0 (q, C*Me*$_3$); 18.2 (s, *C*Me$_3$); −7.7 (q, SiMe). CI-MS: 374 (53, $[M+NH_4]^+$); 357 (79, $[M+H]^+$). Anal. calcd for $C_{21}H_{28}O_3Si$ (356.54): C 70.74, H 7.92. Found: C 70.05, H 7.94.

5.3.5. 1-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-oxy}-3-methylbutan-2-one (1e). According to general procedure given in Section 5.2.1, oxidation of **7e/7e′** (170 mg, 0.52 mmol) provided **1e** (150 mg, 0.46 mmol, 89%) as a colorless oil. IR: 2960, 2920, 2880, 2850, 1730, 1090br. ^{1}H NMR: 7.37–7.24 (m, 5 arom. H); 4.46 (s, SiOCH_2); 4.38 (s, PhCH_2); 3.33, 3.26 (AB, *J*=13.4 Hz, SiCH_2); 2.86 (sept., *J*=6.9 Hz, C*H*Me$_2$); 1.07 (d, *J*=6.9 Hz); 0.98 (s, *t*-Bu); 0.16 (s, SiMe). ^{13}C NMR: 213.6 (s, CO); 138.6 (s, arom. C); 128.2, 127.5 (2d, 2×2 arom. C); 127.4 (d, arom. C); 77.1 (t, Ph*C*H$_2$); 68.4 (t, SiOCH_2); 60.7 (t, SiCH_2); 36.0 (d, *C*HMe$_2$); 26.0 (q, C*Me*$_3$); 18.1 (s, *C*Me$_3$); 17.9 (q, CH*Me*$_2$); −8.0 (q, SiMe). CI-MS: 340 (100, $[M+NH_4]^+$); 323 (47, $[M+H]^+$). Anal. calcd for $C_{18}H_{30}O_3Si$ (322.52): C 67.03, H 9.38. Found: C 66.48, H 9.50.

5.3.6. 3-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]oxy}-propanal (2a). According to general procedure given in Section 5.2.1, oxidation of **8a** (928 mg, 3.13 mmol) provided **2a** (860 mg, 2.91 mmol, 93%) as a colorless oil. IR: 2950, 2930, 2880, 2850, 1725, 1090, 1070, 835, 775, 735, 700. ^{1}H NMR: 9.78 (t, *J*=2.3 Hz, CHO); 7.37–7.25 (m, 5 arom. H); 4.48 (s, PhCH_2); 4.10–4.06 (m, SiOCH_2); 3.29, 3.23 (AB, *J*=13.3 Hz, SiCH_2); 2.61–2.56 (m, CH_2CHO); 0.91 (s, *t*-Bu); 0.14 (s, SiMe). ^{13}C NMR: 202.1 (d, CHO); 138.7 (s, arom. C); 128.2, 127.6 (2d, 2×2 arom. C); 127.4 (d, arom. C); 77.1 (t, Ph*C*H$_2$); 60.2 (t, SiOCH_2); 58.0 (t, SiCH_2); 46.5 (t, *C*H$_2$CHO); 26.0 (q, C*Me*$_3$); 18.1 (s, *C*Me$_3$); −8.0 (q, SiMe). CI-MS: 312 (100, $[M+NH_4]^+$); 295 (10, $[M+H]^+$). Anal. calcd for $C_{16}H_{26}O_3Si$ (294.46): C 65.26, H 8.90. Found: C 64.93, H 9.08.

5.3.7. 4-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-oxy}butan-2-one (2b). According to general procedure given in Section 5.2.1, oxidation of **8b/8b′** (710 mg, 2.28 mmol) provided **2b** (635 mg, 2.05 mmol, 90%) as a colorless oil. IR: 2960, 2930, 2880, 2860, 1715, 1100, 1075. ^{1}H NMR: 7.37–7.24 (m, 5 arom. H); 4.47 (s, PhC*H*$_2$); 3.97 (t, *J*=6.3 Hz, SiOC*H*$_2$); 3.28, 3.23 (AB, *J*=13.3 Hz, SiC*H*$_2$); 2.62 (t, *J*=6.3 Hz, OCH$_2$C*H*$_2$); 2.14 (s, COMe); 0.91 (s, *t*-Bu); 0.12 (s, SiMe). ^{13}C NMR: 208.0 (s, CO); 138.8 (s, arom. C); 128.2, 127.5 (2d, 2×2 arom. C); 127.4 (d, arom. C); 77.1 (t, Ph*C*H$_2$); 60.7 (t, SiOCH$_2$); 59.4 (t, SiCH$_2$); 46.5 (t, OCH$_2$*C*H$_2$); 30.7 (q, CO*Me*); 26.0 (q, C*Me*$_3$); 18.1 (s, *C*Me$_3$); −8.1 (q, SiMe). CI-MS: 326 (100, [M+NH$_4$]$^+$); 309 (61, [M+H]$^+$). Anal. calcd for $C_{17}H_{28}O_3Si$ (308.49): C 66.19, H 9.15. Found: C 66.17, H 9.18.

5.3.8. 1-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-oxy}pentan-3-one (2c). According to general procedure given in Section 5.2.1, oxidation of **8c/8c′** (210 mg, 0.65 mmol) provided **2c** (184 mg, 0.57 mmol, 88%) as a colorless oil. IR: 2960, 2930, 2880, 2860, 1715, 1100, 1070. ^{1}H NMR: 7.37–7.24 (m, 5 arom. H); 4.47 (s, PhC*H*$_2$); 3.97 (t, *J*=6.3 Hz, SiOC*H*$_2$); 3.28, 3.23 (AB, *J*=13.1 Hz, SiC*H*$_2$); 2.60 (t, *J*=6.3 Hz, OCH$_2$C*H*$_2$); 2.43 (q, *J*=7.2 Hz, C*H*$_2$Me); 1.02 (t, *J*=7.2 Hz, CH$_2$*Me*); 0.91 (s, *t*-Bu); 0.12 (s, SiMe). ^{13}C NMR: 210.5 (s, CO); 138.8 (s, arom. C); 128.2, 127.5 (2d, 2×2 arom. C); 127.4 (d, arom. C); 77.1 (t, Ph*C*H$_2$); 60.7 (t, SiOCH$_2$); 59.5 (t, SiCH$_2$); 45.3 (t, OCH$_2$*C*H$_2$); 36.9 (t, *C*H$_2$Me); 26.0 (q, C*Me*$_3$); 18.1 (s, *C*Me$_3$); 7.5 (q, CH$_2$*Me*); −8.1 (q, SiMe). CI-MS: 340 (100, [M+NH$_4$]$^+$); 323 (96, [M+H]$^+$). Anal. calcd for $C_{18}H_{30}O_3Si$ (322.52): C 67.03, H 9.37. Found: C 66.87, H 9.19.

5.3.9. 3-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-oxy}-1-phenylpropan-1-one (2d). According to general procedure given in Section 5.2.1, oxidation of **8d/8d′** (295 mg, 0.79 mmol) provided **2d** (261 mg, 0.70 mmol, 89%) as a colorless oil. IR: 2950, 2930, 2880, 2860, 1680, 1100, 1075. ^{1}H NMR: 7.96–7.93 (m, 2 arom. H); 7.58–7.23 (m, 8 arom. H); 4.46 (s, PhC*H*$_2$); 4.15 (t, *J*=6.5 Hz, SiOC*H*$_2$); 3.30–3.18 (m, SiCH$_2$ and OCH$_2$C*H*$_2$); 0.89 (s, *t*-Bu); 0.12 (s, SiMe). ^{13}C NMR: 236.9 (s, CO); 138.8, 137.3 (2s, 2 arom. C); 133.0 (d, arom. C); 128.5 (d, 2 arom. C); 128.2 (d, 4 arom. C); 127.5 (d, 2 arom. C); 127.3 (d, arom. C); 77.1 (t, Ph*C*H$_2$); 60.7 (t, SiOCH$_2$); 59.8 (t, SiCH$_2$); 41.7 (t, OCH$_2$*C*H$_2$); 26.1 (q, C*Me*$_3$); 18.2 (s, *C*Me$_3$); −8.0 (q, SiMe). CI-MS: 388 (53, [M+NH$_4$]$^+$); 371 (100, [M+H]$^+$). Anal. calcd for $C_{22}H_{30}O_3Si$ (370.56): C 71.31, H 8.16. Found: C 70.99, H 7.97.

5.3.10. 1-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-oxy}-4-methylpentan-3-one (2e). According to general procedure given in Section 5.2.1, oxidation of **8e/8e′** (170 mg, 0.50 mmol) provided **2e** (135 mg, 0.40 mmol, 80%) as a colorless oil. IR: 2960, 2930, 2880, 2850, 1720, 1090. ^{1}H NMR: 7.37–7.23 (m, 5 arom. H); 4.48 (s, PhC*H*$_2$); 3.97 (t, *J*=6.3 Hz, SiOC*H*$_2$); 3.28, 3.23 (AB, *J*=16.6 Hz, SiC*H*$_2$); 2.66 (t, *J*=6.3 Hz, OCH$_2$C*H*$_2$); 2.59 (sept., *J*=7.0 Hz, COC*H*Me$_2$); 1.07 (d, *J*=7.0 Hz); 0.91 (s, *t*-Bu); 0.12 (s, SiMe). ^{13}C NMR: 213.3 (s, *C*O); 138.8 (s, arom. C); 128.2, 127.5 (2d, 2×2 arom. C); 127.3 (d, arom. C); 77.1 (t, Ph*C*H$_2$); 60.7 (t, SiOCH$_2$); 59.4 (t, SiCH$_2$); 43.2 (t, OCH$_2$*C*H$_2$); 41.4 (d, *C*HMe$_2$); 26.0 (q, C*Me*$_3$); 18.1 (s, *C*Me$_3$); 17.8 (q, CH*Me*$_2$); −8.1 (q, SiMe). CI-MS: 354 (100, [M+NH$_4$]$^+$); 337 (34, [M+H]$^+$). Anal. calcd for $C_{19}H_{32}O_3Si$ (336.54): C 67.81, H 9.58. Found: C 67.62, H 9.54.

5.4. Alcohols 7a–l and 8a–l

5.4.1. 2-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]oxy}-ethanol (7a). According to general procedure given in Section 5.2.2, silylation of ethylene glycol (**5a**, 0.79 mL, 12.60 mmol, 5 equiv.) with **3** (648 mg, 2.52 mmol) afforded **7a** (513 mg, 1.81 mmol, 72%) as a colorless oil. IR: 3420br., 2930, 2850, 1470, 1460, 1450, 1255, 1100br., 935, 830, 775, 735, 700. ^{1}H NMR: 7.38–7.26 (m, 5 arom. H); 4.50 (s, PhC*H*$_2$); 3.82 (t, *J*=4.4 Hz, SiOC*H*$_2$); 3.72–3.57 (m, C*H*$_2$OH); 3.33, 3.21 (AB, *J*=13.2 Hz, SiC*H*$_2$); 2.78 (br.s, OH); 0.92 (s, *t*-Bu); 0.16 (s, SiMe). ^{13}C NMR: 138.1 (s, arom. C); 128.3, 127.8 (2d, 2×2 arom. C); 127.6 (d, arom. C); 77.2 (t, Ph*C*H$_2$); 65.5 (t, SiOCH$_2$); 64.0 (t, CH$_2$OH); 60.5 (t, SiCH$_2$); 26.0 (q, C*Me*$_3$); 18.1 (s, *C*Me$_3$); −8.0 (q, SiMe). CI-MS: 300 (100, [M+NH$_4$]$^+$); 283 (5, [M+H]$^+$). Anal. calcd for $C_{15}H_{26}O_3$ Si (282.46): C 63.79, H 9.28. Found: C 63.58, H 9.27.

5.4.2. (2*R,Si*R**)- and (2*S**,Si*R**)-1-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}propan-2-ol (7b and 7b′).** According to general procedure given in Section 5.2.3, **1a** (250 mg, 0.89 mmol) gave upon treatment with MeMgBr **7b/7b′** (235 mg, 0.79 mmol, 89%, ratio 66:34, Entry 1 of Table 1) as a colorless oil. Data from mixture. IR: 3430br., 2960, 2930, 2860, 1090br. ^{1}H NMR (signals of **7b′** are given in italics): 7.31–7.18 (m, 5 arom. H); 4.43 (s, PhC*H*$_2$); 4.81–3.61 (m, SiOCH$_2$);); 3.44–3.11 (m, SiCH$_2$ and C*H*OH); 2.85 (br.s, OH); 1.05, *1.02* (2d, *J*=6.5 Hz, CHOH*Me*); 0.87, *0.86* (2s, *t*-Bu); *0.07*, 0.08 (2s, SiMe). ^{13}C NMR: 138.3, *138.2* (2s, arom. C); 128.2 (d, 2 arom. C); 127.7 (d, 2 arom. C); 127.5 (d, arom. C); 77.1 (t, Ph*C*H$_2$); *69.8*, 69.3 (2t, SiOCH$_2$); *68.1*, 68.0 (2d, CHOH); 60.4 (t, SiCH$_2$); 26.1, *25.8* (2q, C*Me*$_3$); 18.3, *18.0* (2q, CHOH*Me*); 18.2 (s, *C*Me$_3$); −8.0, *−8.1* (2q, SiMe). CI-MS: 314 (100, [M+NH$_4$]$^+$); 297 (21, [M+H]$^+$). Anal. calcd for $C_{16}H_{28}O_3Si$ (296.48): C 64.82, H 9.52. Found: C 64.52, H 9.47.

5.4.3. (2*R,Si*R**)- and (2*S**,Si*R**)-1-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}butan-2-ol (7c and 7c′).** According to general procedure given in Section 5.2.3, **1a** (248 mg, 0.88 mmol) gave upon treatment with EtMgBr **7c/7c′** (247 mg, 0.79 mmol, 90%, ratio 60:40, Entry 2 of Table 1) as a colorless oil. Data from mixture. IR: 3450br., 2955, 2930, 2855, 1090br. ^{1}H NMR (signals of **7c′** are given in italics): 7.31–7.18 (m, 5 arom. H); *4.44*, 4.43 (2s, PhC*H*$_2$); 3.74–3.40 (m, SiOCH$_2$ and C*H*OH); 3.27–3.12 (m, SiCH$_2$); 2.95 (br.s, OH); 1.45–1.32 (m, C*H*$_2$Me); 0.92–0.84 (m, CH$_2$*Me* and *t*-Bu); *0.09*, 0.08 (2s, SiMe). ^{13}C NMR: 138.3 (s, arom. C); 128.2, 127.7 (2d, 2×2 arom. C); 127.5 (d, arom. C); 77.1 (t, Ph*C*H$_2$); 73.3 (d, CHOH); *68.2*, 67.7 (t, SiOCH$_2$); 60.4 (t, SiCH$_2$); 26.1 (q, C*Me*$_3$); 26.0 (t, *C*H$_2$Me); 18.1 (s, *C*Me$_3$); 10.0 (q, CH$_2$*Me*); −8.0 (q, SiMe). CI-MS: 328 (100, [M+NH$_4$]$^+$); 311 (11,

$[M+H]^+$). Anal. calcd for $C_{17}H_{30}O_3Si$ (310.51): C 65.76, H 9.74. Found: C 66.39, H 9.83.

5.4.4. (1*R,Si*R**)- and (1*S**,Si*R**)-2-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}-1-phenylethanol (7d and 7d′).** According to general procedure given in Section 5.2.3, **1a** (245 mg, 0.87 mmol) gave upon treatment with PhMgBr **7d/7d′** (249 mg, 0.70 mmol, 80%, ratio 59:41, Entry 3 of Table 1) as a colorless oil. Data from mixture. IR: 3440br., 2930, 2860, 1100br., 1070, 700. ^{1}H NMR (signals of **7d′** are given in italics): 7.31–7.15 (m, 10 arom. H); 4.75–4.68 (m, C*H*OH); 4.48–4.42 (m, PhCH_2); 3.87–3.78, 3.65–3.53 (m, SiOCH_2 and OH); 3.29–3.13 (m, SiCH_2); 0.87 (s, *t*-Bu); *0.10*, 0.09 (2s, SiMe). ^{13}C NMR: 140.6, *140.4* (2s, arom. C); 138.2, *138.0* (2s, arom. C); 128.3, 128.1 (2d, 2×2 arom. C); 127.9, *127.8* (2d, arom. C); 127.8 (d, 2 arom. C); 127.6 (d, arom. C); 126.2 (d, 2 arom. C); 77.2 (t, Ph*C*H_2); 74.4 (d, CHOH); *70.1*, 69.7 (2t, SiOCH_2); 60.2 (t, SiCH_2); 26.1, *25.9* (2q, C*Me*$_3$); 18.2, *18.1* (2s, *C*Me$_3$); −7.8, *−8.1* (2q, SiMe). CI-MS: 376 (100, $[M+NH_4]^+$); 358 (57, $[M+NH_4-H_2O]^+$). Anal. calcd for $C_{21}H_{30}O_3Si$ (358.55): C 70.35, H 8.43. Found: C 70.16, H 8.55.

5.4.5. (2*R,Si*R**)- and (2*S**,Si*R**)-1-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}-3-methylbutan-2-ol (7e and 7e′).** According to general procedure given in Section 5.2.3, **1a** (258 mg, 0.92 mmol) gave upon treatment with *i*-PrMgBr **7e/7e′** (256 mg, 0.79 mmol, 86%, ratio 53:47, Entry 4 of Table 1) as a colorless oil. Data from mixture. IR: 3450br., 2960, 2930, 2860, 1100br., 1070. ^{1}H NMR (signals of **7e′** are given in italics): 7.31–7.18 (m, 5 arom. H); *4.44*, 4.43 (2s, PhCH_2); 3.75–3.72, 3.59–3.48 (m, SiOCH_2); 3.26–3.13 (m, C*H*OH and SiCH_2); 2.95 (s, OH); 1.70–1.56 (m, C*H*Me$_2$; 0.92–0.82 (m, CH*Me*$_2$ and *t*-Bu); 0.09, *0.08* (2s, SiMe). ^{13}C NMR: *138.3*, 138.2 (2s, arom. C); 128.2, 127.7 (2d, 2×2 arom. C); 127.5 (d, arom. C); 77.1 (t, Ph*C*H_2); 76.7 (d, CHOH); 66.6, *66.2* (2t, SiOCH_2); 60.3 (t, SiCH_2); 30.6 (d, *C*HMe$_2$); 26.0 (q, C*Me*$_3$); 18.7, *18.3* (2q, CH*Me*$_2$) 18.5, *18.1* (2s, *C*Me$_3$); −8.0 (q, SiMe). CI-MS: 342 (100, $[M+NH_4]^+$); 325 (7, $[M+H]^+$). Anal. calcd for $C_{18}H_{32}O_3$ Si (324.54): C 66.62, H 9.94. Found: C 66.42, H 9.93.

5.4.6. (2*R,Si*R**)- and (2*S**,Si*R**)-1-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}-3,3-dimethylbutan-2-ol (7f and 7f′).** According to general procedure given in Section 5.2.3, **1a** (248 mg, 0.88 mmol) gave upon treatment with *t*-BuMgBr **7f/7f′** (242 mg, 0.70 mmol, 80%, ratio 50:50, Entry 5 of Table 1) as a colorless oil. Data from mixture. IR: 3450br., 2950, 2930, 2860, 1110, 1070. ^{1}H NMR (signals of one of the isomers are given in italics): 7.38–7.25 (m, 5 arom. H); 4.50, *4.49* (2s, PhCH_2); 3.88–3.83, 3.62–3.53 (m, SiOCH_2); 3.33– 3.16 (m, C*H*OH and SiCH_2); 2.86 (br.s, OH); 0.94, *0.93*, *0.91*, 0.90 (4s, 2×*t*-Bu); 0.15 (s, SiMe). ^{13}C NMR: 138.4 (s, arom. C); 128.2, 127.7 (2d, 2×2 arom. C); 127.5 (d, arom. C); *78.9*, 78.8 (2d, CHOH); 77.2 (t, Ph*C*H_2); *65.0*, 64.7 (2t, SiOCH_2); 60.4 (t, SiCH_2); 33.4, *33.3* (2s, CH(OH)*C*Me$_3$); 26.1 (2q, 2×C*Me*$_3$); 18.2, *18.1* (2s, *C*Me$_3$); −7.88 (q, SiMe). CI-MS: 356 (100, $[M+NH_4]^+$); 339 (8, $[M+H]^+$). Anal. calcd for $C_{19}H_{34}O_3Si$ (338.56): C 67.41, H 10.12. Found: C 66.88, H 9.96.

5.4.7. (2*R,Si*R**)- and (2*S**,Si*R**)-1-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}-2-phenylpropan-2-ol (7g and 7g′).** According to general procedure given in Section 5.2.3, **1b** (100 mg, 0.34 mmol) and **1d** (134 mg, 0.38 mmol) gave upon treatment with PhMgBr and MeMgBr, respectively, **7g/7g′** (120 mg, 0.32 mmol, 94%, ratio 76:24, and 125 mg, 0.33 mmol, 88%, ratio 29:71, Entries 6 and 9 of Table 1) as colorless oils. **7g** and **7g′** were separated by chromatography (hexane/Et_2O 10:3). Data of **7g**: IR: 3460, 2950, 2930, 2880, 2860, 1100br., 1080, 1070, 700. ^{1}H NMR: 7.45–7.20 (m, 10 arom. H); 4.48 (s, PhCH_2); 3.83, 3.77 (AB, *J*=9.9 Hz, SiOCH_2); 3.53 (s, OH); 3.24, 3.17 (AB, *J*=13.5 Hz, SiCH_2); 1.47 (s, COH*Me*); 0.86 (s, *t*-Bu); 0.06 (s, SiMe). ^{13}C NMR: 145.6 (s, arom. C); 138.4 (s, arom. C); 128.3 (d, 2 arom. C); 127.9 (d, 2 arom. C); 127.7, 127.5 (2d, 2 arom. C); 126.6 (d, 2 arom. C); 125.2 (d, 2 arom. C); 77.2 (t, Ph*C*H_2); 74.4 (s, COH); 72.2 (t, SiOCH_2); 60.4 (t, SiCH_2); 26.0 (q, C*Me*$_3$); 25.7 (q, COH*Me*); 18.1 (s, *C*Me$_3$); −8.1 (q, SiMe). CI-MS: 372 (65, $[M+NH_4-H_2O]^+$); 355 (100, $[M+H-H_2O]^+$). Data of **7g′**: IR: 3460, 2950, 2930, 2880, 2860, 1100br., 1080, 1070, 700. ^{1}H NMR: 7.44–7.19 (m, 10 arom. H); 4.49 (s, PhCH_2); 3.73, (s, SiOCH_2); 3.64 (s, OH); 3.21, 3.14 (AB, *J*=13.5 Hz, SiCH_2); 1.57 (s, COH*Me*); 0.90 (s, *t*-Bu); 0.10 (s, SiMe). ^{13}C NMR: 145.4 (s, arom. C); 138.3 (s, arom. C); 128.3 (d, 2 arom. C); 128.0 (d, 2 arom. C); 127.8, 127.6 (2d, 2 arom. C); 126.7 (d, 2 arom. C); 125.2 (d, 2 arom. C); 77.2 (t, Ph*C*H_2); 74.3 (s, COH); 72.4 (t, SiOCH_2); 60.3 (t, SiCH_2); 25.9 (q, C*Me*$_3$); 25.7 (q, COH*Me*); 18.1 (s, *C*Me$_3$); −8.1 (q, SiMe). CI-MS: 372 (65, $[M+NH_4-H_2O]^+$); 355 (100, $[M+H-H_2O]^+$). Anal. calcd for $C_{22}H_{32}O_3Si$ (372.59): C 70.92, H 8.66. Found: C 69.25, H 8.51.

5.4.8. (2*R,Si*R**)- and (2*S**,Si*R**)-1-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}-2-phenylbutan-2-ol (7h and 7h′).** According to general procedure given in Section 5.2.3, **1c** (232 mg, 0.75 mmol) and **1d** (207 mg, 0.58 mmol) gave upon treatment with PhMgBr and EtMgBr, respectively, **7h/7h′** (249 mg, 0.50 mmol, 86%, ratio 72:28, and 197 mg, 0.51 mmol, 88%, ratio 34:66, Entries 7 and 10 of Table 1) as colorless oils. Data from mixture. IR: 3440, 2950, 2930, 2880, 2860, 1460, 1100, 1080br., 700. ^{1}H NMR (signals of **7h** are given in italics): 7.29–7.05 (m, 10 arom. H); 4.35 (s, PhCH_2); 3.75–3.61 (m, SiOCH_2); 3.21 (br.s, OH); 3.13–2.98 (m, SiCH_2); 1.90–1.56 (m, CH_2Me); 0.78, *0.74* (2s, *t*-Bu); 0.66–0.60 (m, CH$_2$*Me*); −0.02, *−0.07* (2s, SiMe). ^{13}C NMR: *143.9*, 143.7, 138.2 (3s, 2 arom. C); 128.2, 127.8, 127.7 (3d, 3×2 arom. C); 127.5, 126.4 (2d, 2 arom. C); 125.6 (d, 2 arom. C); 77.1 (t, Ph*C*H_2); 76.8 (s, COH); *71.8*, 71.6 (2t, SiOCH_2); 60.3 (t, SiCH_2); *31.1*, 30.8 (2t, *C*H$_2$Me); 26.0 (q, C*Me*$_3$); 18.1 (s, *C*Me$_3$); 7.6 (q, CH$_2$*Me*); −8.1 (q, SiMe). CI-MS: 404 (16, $[M+NH_4]^+$); 386 (100, $[M+NH_4-H_2O]^+$); 369 (54, $[M+H-H_2O]^+$). Anal. calcd for $C_{23}H_{34}O_3Si$ (386.61): C 71.46, H 8.86. Found: C 71.42, H 8.94.

5.4.9. (2*R,Si*R**)- and (2*S**,Si*R**)-1-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}-3-methyl-2-phenyl-butan-2-ol (7i and 7i′).** According to general procedure given in Section 5.2.3, **1e** (221 mg, 0.69 mmol) and **1d** (134 mg, 0.38 mmol) gave upon treatment with PhMgBr and *i*-PrMgBr, respectively, **7i/7i′** (206 mg, 0.52 mmol, 75%, ratio 53:47, and 108 mg, 0.29 mmol, 77%, ratio

34:64, Entries 8 and 11 of Table 1) as colorless oils. Data from mixture. IR: 3450, 2960, 2930, 2880, 2860, 1470, 1100br., 1090, 700. ^{1}H NMR (signals of **7i** are given in italics): 7.29–7.08 (m, 10 arom. H); *4.37*, 4.34 (2s, PhCH_2); 3.97–3.81 (m, SiOCH_2); 3.16 (br.s, OH); 3.07–2.96 (m, SiCH_2); 2.04–1.90 (m, CHMe$_2$; 0.82–0.67 (m, CHMe_2 and *t*-Bu); −0.01, −*0.09* (2 s, SiMe). ^{13}C NMR: *143.6*, 143.2, 138.0 (3s, 2 arom. C); 127.8, 127.3 (2d, 2×2 arom. C); 127.0, 125.9 (2d, 2 arom. C); 125.8, 125.6 (2d, 2×2 arom. C); 78.0 (s, COH); 76.7 (t, PhCH$_2$); 68.8 (t, SiOCH_2); 59.9 (t, SiCH_2); *34.8*, 34.7 (2d, CHMe$_2$); 25.5 (q, CMe_3); 17.6, *17.2* (2s, CMe$_3$); 16.5 (q, CHMe_2); −8.5, −*8.7* (2q, SiMe). CI-MS: 418 (6, [M+NH$_4$]$^+$); 400 (16, [M+NH$_4$−H$_2$O]$^+$); 383 (100, [M+H−H$_2$O]$^+$). Anal. calcd for $C_{24}H_{36}O_3Si$ (400.63): C 71.95, H 9.06. Found: C 71.04, H 8.97.

5.4.10. (2*R,Si*R**)- and (2*S**,Si*R**)-1-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]oxy}-3,3-dimethyl-2-phenylbutan-2-ol (7j and 7j′).** According to general procedure given in Section 5.2.3, **1d** (124 mg, 0.35 mmol) gave upon treatment with *t*-BuMgBr **7j/7j′** (78 mg, 0.19 mmol, 54%, ratio 48:52, Entry 12 of Table 1) as a colorless oil. Data from mixture. IR: 3450, 2950, 2930, 2850, 1135, 1090, 1070, 840, 830, 700. ^{1}H NMR (signals of **7j** are given in italics): 7.28–7.00 (m, 10 arom. H); 4.34–4.12 and 3.95–3.91 (m, PhCH_2 and SiOCH_2); *3.31*, 3.04 (2br.s, OH); 3.01–2.87 (m, SiCH_2); 0.76 (s, *t*-Bu); *0.60*, 0.58 (2 s, Si*t*-Bu); −0.04, −*0.13* (2 s, SiMe). ^{13}C NMR: 143.5, *138.6*, 138.0 (3s, 2 arom. C); 128.7, 127.8 (2d, 2×2 arom. C); 127.6 (d, arom. C); 126.8, 126.1 (2d, 2×2 arom. C); 126.1 (d, arom. C); *80.2*, 79.9 (2s, COH); 77.2 (t, PhCH$_2$); 66.5 (t, SiOCH_2); 60.5 (t, SiCH_2); 36.8 (s, CMe$_3$); 26.2, 25.8 (2q, CMe_3 and SiCMe_3); 17.9 (s, SiCMe$_3$); −7.9, −*8.2* (2q, SiMe). CI-MS: 432 (26, [M+NH$_4$]$^+$); 414 (19, [M+NH$_4$−H$_2$O]$^+$); 397 (100, [M+H−H$_2$O]$^+$). Anal. calcd for $C_{25}H_{38}O_3Si$ (414.66): C 72.41, H 11.58. Found: C 72.13, H 9.24.

5.4.11. (2*R,Si*R**)- and (2*S**,Si*R**)-1-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]oxy}-2-methyl-5-(2-methyl-1,3-dioxolan-2-yl)pentan-2-ol (7k and 7k′).** According to general procedure given in Section 5.2.3, **1b** (295 mg, 1.00 mmol) gave upon treatment with 3-(2-methyl-1,3-dioxolan-2-yl) prop-1-yl magnesium bromide (**13**)[13] **7k/7k′** (360 mg, 0.85 mmol, 85%, ratio 60:40) as a colorless oil. Data from mixture. IR: 3460, 2960, 2930, 2860, 1380, 1250, 1100, 1070, 840. ^{1}H NMR (signals of **7k′** are given in italics): 7.37–7.24 (m, 5 arom. H); 4.48 (s, PhCH_2); 3.97–3.87 (m, OCH$_2$CH$_2$O); 3.54, 3.48 (AB, *J*=9.9 Hz, SiOCH_2); 3.28, 3.20 (AB, *J*=13.4 Hz, SiCH_2); 2.40 (br.s, OH); 1.66–1.39 (m, (CH$_2$)$_3$); 1.31 (s, Me); *1.12*, 1.09 (2s, COHMe); 0.92 (s, *t*-Bu); 0.13 (s, SiMe). ^{13}C NMR: 137.2 (s, arom. C); 128.2, 127.7 (2d, 2×2 arom. C); 127.5 (d, arom. C); 110.1 (s, OCO); 77.1 (t, PhCH$_2$); 72.4, *72.3* (2s, COH); *71.1*, 71.0 (2t, SiOCH$_2$) 64.6 (t, OCH$_2$CH$_2$O); *63.7*, 60.4 (2t, SiCH_2); 39.8, 38.7, *37.9*(3t, CH$_2$CH$_2$$CH_2$); 26.0 (q, C$Me_3$); 23.7, *23.1*, 22.8 (3t, COHMe and Me); 18.5 (s, CMe$_3$); *18.3*, 18.2 (2t, CH$_2$$CH_2CH_2$); −8.2 (q, SiMe). CI-MS: 363 (67, [M−C$_2$H$_5$O$_2$]$^+$); 267 (100). Anal. calcd for $C_{23}H_{40}O_5Si$ (424.65): C 65.05, H 9.49. Found: C 62.41, H 9.05.

5.4.12. 3-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]oxy}propanol (8a). According to general procedure given in Section 5.2.2, silylation of propane-1,3-diol (**6a**, 1.48 g, 19.45 mmol, 5 equiv.) with **3** (1.00 g, 3.89 mmol) afforded **8a** (1.01 g, 3.38 mmol, 87%) as a colorless oil. IR: 3400br., 2950, 2930, 2880, 2850, 1090, 1070, 835, 775, 735, 700. ^{1}H NMR: 7.38–7.25 (m, 5 arom. H); 4.49 (s, PhCH_2); 3.93–3.89 (m, SiOCH_2); 3.81–3.74 (m, CH_2OH); 3.31, 3.23 (AB, *J*=13.2 Hz, SiCH_2); 2.69 (t, *J*=5.7 Hz, OH); 1.80–1.72 (m, OCH$_2$CH_2); 0.93 (s, *t*-Bu); 0.13 (s, SiMe). ^{13}C NMR: 138.4 (s, arom. C); 128.3 (d, 2 arom. C); 127.8 (d, arom. C); 127.5 (d, 2 arom. C); 77.2 (t, PhCH$_2$); 62.4 (t, SiOCH_2); 61.2 (t, CH$_2$OH); 60.4 (t, SiCH_2); 34.3 (t, OCH$_2$$CH_2$); 26.1 (q, C$Me_3$); 18.1 (s, CMe$_3$); −8.0 (q, SiMe). CI-MS: 314 (100, [M+NH$_4$]$^+$); 297 (74, [M+H]$^+$). Anal. calcd for $C_{16}H_{28}O_3Si$ (296.48): C 64.82, H 9.52. Found: C 64.29, H 9.65.

5.4.13. (2*S,Si*R**)- and (2*R**,Si*R**)-4-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]oxy}butan-2-ol (8b and 8b′).** According to general procedure given in Section 5.2.2, silylation of (±)-butane-1,3-diol (**6b**, 1.23 g, 13.65 mmol, 5 equiv.) with **3** (700 mg, 2.73 mmol) afforded **8b/8b′** (760 mg, 2.46 mmol, 90%, ratio 1:1). Analogous to Section 5.3.2, **2a** (100 mg, 0.34 mmol) gave upon treatment with MeMgBr **8b/8b′** (90 mg, 0.29 mmol, 85%, ratio 43:57, Entry 13 of Table 1). Colorless oils; data from mixture. IR: 3420br., 2960, 2930, 2850, 1090. ^{1}H NMR (signals of **8b** are given in italics): 7.37–7.25 (m, 5 arom. H); 4.49 (s, PhCH_2); 4.06–3.81 (m, SiOCH_2 and CHOH); 3.33–3.20 (m, SiCH_2 and OH); 1.67–1.60 (m, OCH$_2$CH_2); 1.18 (d, *J*=6.1 Hz, CHOHMe); 0.93 (s, *t*-Bu); *0.14*, 0.13 (2s, SiMe). ^{13}C NMR: *138.5*, 138.4 (2s, arom. C); 128.6 (d, 2 arom. C); 127.7, *127.6* (2d, 2 arom. C); 127.5 (d, arom. C); 77.1 (t, PhCH$_2$); *67.4*, 67.0 (2d, CHOH); *62.9*, 62.4 (2t, SiOCH_2); 60.4, *60.2* (2t, SiCH_2); 40.3 (t, OCH$_2$$CH_2$); *26.1*, 26.0 (2q, C$Me_3$); *23.3*, 23.2 (2q, CHOHMe); *18.1*, 18.0 (2s, CMe$_3$); −*8.0*, −8.2 (2q, SiMe). CI-MS: 328 (100, [M+NH$_4$]$^+$); 311 (88, [M+H]$^+$). Anal. calcd for $C_{17}H_{30}O_3Si$ (310.51): C 65.76, H 9.74. Found: C 65.56, H 9.61.

5.4.14. (3*S,Si*R**)- and (3*R**,Si*R**)-1-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]oxy}pentan-3-ol (8c and 8c′).** According to general procedure given in Section 5.2.3, **2a** (100 mg, 0.34 mmol) gave upon treatment with EtMgBr **8c/8c′** (96 mg, 0.30 mmol, 88%, ratio 37:63, Entry 14 of Table 1) as a colorless oil. Data from mixture. IR: 3450br., 2960, 2930, 2860, 1080. ^{1}H NMR (signals of **8c** are given in italics): 7.37–7.24 (m, 5 arom. H); 4.49 (s, PhCH_2); 4.03–3.82 (m, SiOCH_2); 3.79–3.68 (m, CHOH); 3.34–3.21 (m, SiCH_2 and OH); 1.73–1.40 (m, OCH$_2$CH_2 and CH_2Me); 0.97– 0.90 (m, CH$_2$$Me$); 0.93 (s, *t*-Bu); *0.14*, 0.13 (2s, SiMe). ^{13}C NMR: 138.5 (s, arom. C); 128.3, 127.7 (2d, 2×2 arom. C); 127.5 (d, arom. C); 77.2 (t, PhCH$_2$); *72.7*, 72.3 (d, CHOH); *63.1*, 62.6 (t, SiOCH_2); 60.5, *60.3* (2t, SiCH_2); 38.1 (t, OCH$_2$$CH_2$); 30.2 (t, CH$_2$Me); 26.1 (q, CMe_3); *18.1*, 18.0 (s, CMe$_3$); 10.0, *9.9* (2q, CH$_2$$Me$); −*8.0*, −8.1 (2q, SiMe). CI-MS: 342 (54, [M+NH$_4$]$^+$); 325 (100, [M+H]$^+$). Anal. calcd for $C_{18}H_{32}O_3Si$ (324.53): C 66.62, H 9.94. Found: C 66.37, H 10.03.

5.4.15. (1*R,Si*R**)- and (1*S**,Si*R**)-3-{[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]oxy}-1-phenylpropanol (8d and 8d′).** According to general procedure given in Section 5.2.3, **2a** (100 mg, 0.34 mmol) gave upon treatment with PhMgBr **8d/8d′** (120 mg, 0.32 mmol, 95%, ratio

34:66, Entry 15 of Table 1) as a colorless oil. Data from mixture. IR: 3420br., 2950, 2930, 2880, 2860, 1090, 1070, 700. ^{1}H NMR (signals of **8d** are in given italics): 7.39–7.20 (m, 10 arom. H); 4.99–4.93 (m, C*H*OH); 4.50 (s, PhCH_2); 4.03–3.85 (m, SiOCH_2); 3.67 (br.s, OH); 3.36–3.18 (m, SiCH_2); 2.00–1.90 (m, OCH$_2$CH_2); 0.96 (s, *t*-Bu); *0.16*, 0.15 (2s, SiMe). ^{13}C NMR: 144.7 (s, arom. C); 138.4 (s, arom. C); 128.3 (d, 4 arom. C); 127.8 (d, 2 arom. C); 127.5, 127.1 (2d, 2 arom. C); 125.8 (d, 2 arom. C); 77.2 (t, Ph*C*H$_2$); *73.3*, 72.9 (2d, CHOH); *62.5*, 62.1 (2t, SiOCH$_2$); 60.4, *60.3* (2t, SiCH$_2$); 40.9 (t, OCH$_2$*C*H$_2$); 26.1 (q, C*Me*$_3$); 18.0 (s, *C*Me$_3$); *−8.0*, −8.1 (2q, SiMe). CI-MS: 390 (18, [M+NH$_4$]$^+$); 237 (90); 117 (100). Anal. calcd for $C_{22}H_{32}O_3Si$ (372.58): C 70.92, H 8.66. Found: C 70.87, H 8.56.

5.4.16. (3*R,Si*R**)- and (3*S**,Si*R**)-1-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}-4-methylpentan-3-ol (8e and 8e′).** According to general procedure given in Section 5.2.3, **2a** (100 mg, 0.34 mmol) gave upon treatment with *i*-PrMgBr **8e/8e′** (100 mg, 0.30 mmol, 87%, ratio 36:64, Entry 16 of Table 1) as a colorless oil. Data from mixture. IR: 3480br.m, 2950, 2930, 2860, 1080. ^{1}H NMR (signals of **8e** are given in italics): 7.37–7.24 (m, 5 arom. H); 4.49 (s, PhCH_2); 4.10–3.82 (m, SiOCH_2); 3.60–3.52 (m, C*H*OH); 3.35–3.16 (m, SiCH_2 and OH); 1.72–1.53 (m, OCH$_2$CH_2 and C*H*Me$_2$; 0.93 (s, *t*-Bu); 0.89 (d, *J*=8 Hz, CH*Me*$_2$); *0.15*, 0.14 (2s, SiMe). ^{13}C NMR: 138.5 (s, arom. C); 128.2, 127.7 (2d, 2×2 arom. C); 127.5 (d, arom. C); 77.2 (t, Ph*C*H$_2$); *76.2*, 75.9 (2d, CHOH); *63.4*, 63.0 (2t, SiOCH$_2$); 60.5, *60.4* (2t, SiCH$_2$); 35.4 (t, OCH$_2$*C*H$_2$); 33.7 (d, *C*HMe$_2$); 26.1 (q, C*Me*$_3$); 18.5, *17.8* (2q, CH*Me*$_2$) *18.1*, 18.0 (2s, *C*Me$_3$); *−8.0*, −8.1 (2q, SiMe). CI-MS: 356 (26, [M+NH$_4$]$^+$); 339 (100, [M+H]$^+$). Anal. calcd for $C_{19}H_{34}O_3Si$ (338.56): C 67.41, H 10.12. Found: C 67.17, H 10.21.

5.4.17. (2*R,Si*R**)- and (2*S**,Si*R**)-4-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}-2-phenylbutan-2-ol (8g and 8g′).** According to general procedure given in Section 5.2.3, **2b** (150 mg, 0.48 mmol) and **2d** (50 mg, 0.13 mmol) gave upon treatment with PhMgBr and MeMgBr, respectively, **8g/8g′** (168 mg, 0.43 mmol, 90%, ratio 13:87, and 48 mg, 0.12 mmol, 92%, ratio 75:25, Entries 17 and 20 of Table 1) as colorless oils. Data from mixture. IR: 3490, 2950, 2930, 2880, 2860, 1470, 1090, 1070, 700. ^{1}H NMR (signals of **8g** are given in italics): 7.45–7.18 (m, 10 arom. H); 4.53, *4.52* (2s, OH); *4.44*, 4.38 (2s, PhCH_2); 3.88–3.59 (m, SiOCH_2); 3.21–3.08 (m, SiCH_2); 2.19–1.98 (m, OCH$_2$CH_2); 1.52 (s, COH*Me*); 0.91 (s, *t*-Bu); 0.06, *0.01* (2s, SiMe). ^{13}C NMR: 147.9 (s, arom. C); 138.6 (s, arom. C); 128.2 (d, 2 arom. C); 128.0, 127.6 (2d, 2×2 arom. C); 127.4, 126.2 (2d, 2 arom. C); 125.0 (d, 2 arom. C); 76.9 (t, Ph*C*H$_2$); 75.2 (s, COH); 61.8 (t, SiOCH_2); 60.1 (t, SiCH_2); 43.5 (t, OCH$_2$*C*H$_2$); 31.2 (q, COH*Me*); 26.0 (q, C*Me*$_3$); 17.9 (s, *C*Me$_3$); −8.5 (q, SiMe). CI-MS: 404 (100, [M+NH$_4$]$^+$); 386 (52, [M+NH$_4$−H$_2$O]$^+$). Anal. calcd for $C_{23}H_{34}O_3Si$ (386.60): C 71.46, H 8.86. Found: C 71.27, H 8.80.

5.4.18. (3*R,Si*R**)- and (3*S**,Si*R**)-1-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}-3-phenylpentan-3-ol (8h and 8h′).** According to general procedure given in Section 5.2.3, **2c** (150 mg, 0.46 mmol) and **2d** (50 mg, 0.13 mmol) gave upon treatment with PhMgBr and EtMgBr, respectively, **8h/8h′** (166 mg, 0.41 mmol, 90%, ratio 16:84, and 48 mg, 0.12 mmol, 89%, ratio 82:18, Entries 18 and 21 of Table 1) as colorless oils. Data from mixture. IR: 3490, 2950, 2930, 2880, 2850, 1470, 1085, 1050, 700. ^{1}H NMR (signals of **8h** are given in italics): 7.42–7.18 (m, 10 arom. H); 4.43 (s, OH); 4.37 (s, PhCH_2); 3.88–3.54 (m, SiOCH_2); 3.19–3.04 (m, SiCH_2); 2.23–1.70 (m, OCH$_2$CH_2 and CH_2Me); 0.90 (s, *t*-Bu); 0.75 (t, CH$_2$*Me*); 0.05, *0.02* (2s, SiMe). ^{13}C NMR: 146.1, 138.6 (2s, 2 arom. C); 128.2, 127.8, 127.5 (3d, 3×2 arom. C); 127.4, 126.0 (2d, 2 arom. C); 125.7 (d, 2 arom. C); 77.7 (s, COH); 76.9 (t, Ph*C*H$_2$); 61.7 (t, SiOCH_2); 60.1 (t, SiCH_2); 42.2 (t, OCH$_2$*C*H$_2$); 36.6 (t, *C*H$_2$Me); 26.0 (q, C*Me*$_3$); 17.9 (s, *C*Me$_3$); 7.53 (q, CH$_2$*Me*); −8.5 (q, SiMe). CI-MS: 418 (8, [M+NH$_4$]$^+$); 256 (50); 145 (100). Anal. calcd for $C_{24}H_{36}O_3Si$ (400.63): C 71.95, H 9.06. Found: C 72.33, H 8.81.

5.4.19. (3*S,Si*R**)- and (3*R**,Si*R**)-1-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}-4-methyl-3-phenyl-pentan-3-ol (8i and 8i′).** According to general procedure given in Section 5.2.3, **2e** (100 mg, 0.30 mmol) and **2d** (50 mg, 0.13 mmol) gave upon treatment with PhMgBr and *i*-PrMgBr, respectively, **8i/8i′** (110 mg, 0.26 mmol, 88%, ratio 37:63, and 49 mg, 0.11 mmol, 87%, ratio 80:20, Entries 19 and 22 of Table 1) as colorless oils. Data from mixture. IR: 3490, 2960, 2930, 2880, 2860, 1470, 1090, 1075, 705. ^{1}H NMR (signals of **8i** are given in italics): 7.39–7.17 (m, 10 arom. H); *4.41*, 4.37 (2s, PhCH_2); 4.23 (s, OH); 3.83–3.45 (m, SiOCH_2); 3.19–2.97 (m, SiCH_2); 2.36–2.24 (m, C*H*Me$_2$; 1.96–1.86 (m, OCH$_2$CH_2); 0.99 (d, *J*=6.5 Hz, CH*Me*); 0.87 (s, *t*-Bu); 0.69 (d, *J*=6.5 Hz, CH*Me*); 0.01, *−0.09* (2s, SiMe). ^{13}C NMR: 145.8, 138.7 (2s, 2 arom. C); 128.2, 127.6 (2d, 2×2 arom. C); 127.5, 127.3 (2d, 2 arom. C); 126.2, 125.9 (2d, 2×2 arom. C); 79.5 (s, COH); 76.8 (t, Ph*C*H$_2$); 61.9 (t, SiOCH_2); *60.3*, 60.1 (2t, SiCH_2); 39.4 (t, OCH$_2$*C*H$_2$); 38.9 (d, *C*HMe$_2$); 26.0 (q, C*Me*$_3$); 17.9 (s, *C*Me$_3$); 17.3, *16.7* (2q, CH*Me*$_2$); −8.5 (q, SiMe). CI-MS: 432 (8, [M+NH$_4$]$^+$); 159 (100). Anal. calcd for $C_{25}H_{38}O_3Si$ (414.66): C 72.41, H 9.24. Found: C 72.44, H 9.06.

5.4.20. (2*R,Si*R**)- and (2*S**,Si*R**)-4-{[[(Benzyloxy)-methyl](*tert*-butyl)methylsilyl]oxy}-2-[2-(2-{[*tert*-butyl-(dimethyl)silyl]oxy}ethyl)phenyl]butan-2-ol (8l and 8l′).** According to general procedure given in Section 5.2.3, **2b** (200 mg, 0.65 mmol) gave upon treatment with Grignard reagent **14**, prepared from {[(2-bromophenyl)ethyl]oxy}-(*tert*-butyl)dimethylsilane,[14] recovered **2b** (130 mg, 0.42 mmol, 65%) and **8l/8l′** (60 mg, 0.11 mmol, 17% (74% based on consumed **2b**) ratio 8:92) as colorless oils. Data from mixture. IR: 3480, 2960, 2920, 2880, 2850, 1470, 1460, 1255, 1090, 835, 775. ^{1}H NMR (signals of **8l** are given in italics): 7.45–7.12 (m, 9 arom. H); 4.66 (s, OH); *4.45*, 4.41 (2s, PhCH_2O); 3.92–3.68 (m, CH_2CH$_2$Ph and SiOCH_2); 3.30–2.98 (m, SiCH_2 and CH_2Ph); 2.28–2.06 (m, COHCH_2); 1.60 (s, COH*Me*); 0.91, 0.84 (2, 2×*t*-Bu); 0.09, *0.05* (2s, SiMe); −0.02, *−0.03* (2s, SiMe$_2$). ^{13}C NMR: 145.8, 138.7, 136.3 (3s, 3 arom. C); 131.9, 128.2, 127.5, 127.3, 126.6, 125.9 (6d, 9 arom. C); 75.7 (t, Ph*C*H$_2$O); 75.6 (s, COH); 65.4, 61.5, *60.5*, 60.4 (3t, SiOCH$_2$, SiCH$_2$

and CH_2CH_2Ph); 44.5, 37.1 (2t, OCH_2CH_2 and CH_2Ph); 30.8 (q, COH*Me*); 26.1, 25.9 (2q, 2×C*Me*$_3$); 18.4, 18.0 (2s, 2×*C*Me$_3$); −5.4 (q, $SiMe_2$); −8.5 (q, SiMe). CI-MS: 545 (86, $[M+H]^+$); 544 (100, $[M+NH_4-H_2O]^+$). Anal. calcd for $C_{31}H_{52}O_4Si_2$ (544.91): C 68.33, H 9.62. Found: C 68.40, H 9.51.

5.5. Proof of relative configurations

5.5.1. (−)-(*R*)-2-Phenylpropan-1,2-diol ((−)-(*R*)-10). According to general procedure given in Section 5.2.3, (*S*)-**1d**[7] (90 mg, 0.25 mmol) was treated with MeMgBr. After workup without chromatography, the crude mixture of **7g/7g′** was dissolved in Et_2O (2 mL), $LiAlH_4$ (10 mg, 0.25 mmol, 1 equiv.) was added at −30°C, and it was stirred for 3 h. After warming to −10°C, dilute aq. H_2SO_4 was added to neutral pH. It was extracted with Et_2O and chromatographed (hexane/Et_2O 2:1) to afford (−)-(*R*)-**10** (33 mg, 0.22 mmol, 87%, $[\alpha]_D=-5.3$ (*c* 1.40, Et_2O), lit.: $[\alpha]_D=-8.6$ (*c* 1.18, Et_2O)[8]) as a colorless oil.

5.5.2. (−)-(*S*)-3-Phenylbutan-1,3-diol ((−)-(*S*)-11). According to general procedure given in Section 5.2.3, (*S*)-**2b** (115 mg, 0.30 mmol) was treated with PhMgBr. After workup without chromatography, the crude mixture of **8g/8g′** was dissolved in Et_2O, $LiAlH_4$ (11 mg, 0.30 mmol, 1 equiv.) was added at −30°C, and it was stirred for 3 h. After warming to −10°C, dilute aq. H_2SO_4 was added to neutral pH. It was extracted with Et_2O and chromatographed (hexane/Et_2O 2:1) to afford (−)-(*S*)-**9** (42 mg, 0.25 mmol, 85%, $[\alpha]_D=-23.2$ (*c* 0.76, benzene), lit.: of (+)-(*R*)-**11**, $[\alpha]_D=+65.2$ (*c* 0.41, benzene)[9] as a colorless oil.

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