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A chiral (alkoxy)methyl-substituted silicon group as an auxiliary for the stereoselective cuprate addition to α,β-unsaturated ketones: synthesis of (−)-(*R*)-phenyl 2-phenylpropyl ketone

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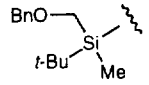
Abstract: The [(benzyloxy)methyl](*tert*-butyl)methylsilyl group was used as the chiral auxiliary to effect highly diastereoselective conjugate additions of organocuprates to enones. Thus, reaction of several R_2CuLi with α-silylated α,β-unsaturated ketones afforded the respective addition products with π-face selectivities of up to 99%. Starting with an optically active substrate, enantiomerically enriched (−)-(*R*)-phenyl 2-phenylpropyl ketone was prepared with virtually no loss of chiral information in a reaction sequence involving cuprate addition, hydrolysis, and removal of the silicon group. © 1997 Elsevier Science Ltd

Introduction

The conjugate addition of organocuprates and other organometallics to α,β-unsaturated ketones and carboxylic acid derivatives is widely used in organic synthesis for the preparation of specifically substituted carbonyl and carboxyl compounds.[1,2] In connection with the increasing importance of synthetic access to products of stereochemical integrity, the quest for stereoselective variations of this reaction started already some years ago. So far, a number of stereoselective transformations have been elaborated, including enantioselective processes that make use of chiral auxiliaries such as, *e.g.*, chiral sulfoxides[3–5] or chiral alkoxy[6,7] or alkylamino/amido[8–10] groups. Whereas 1,4-additions to chiral ester and amide derivatives of α,β-unsaturated carboxylic acids proceed often with high degrees of diastereoselectivity, the stereochemical success of reactions with α-auxiliary-substituted α,β-unsaturated ketones, particularly in the cases of acyclic enone systems, has yet remained rather modest.[3]

In this paper we present the use of the chiral silicon group **A** as the stereochemical director for reactions of organocuprates with α,β-unsaturated ketones. The group **A** has already provided high diastereoselectivities in chelate controlled 1,2-additions to acylsilanes[11,12] and, as shown below, proved equally potent as chiral auxiliary for stereoselective 1,4-additions.



A

Results and discussion

The model compounds of the type **5a,b** and the chiral α-silyl-substituted α,β-unsaturated ketones of the type **6a,b** used for this study have been prepared in a straightforward manner from the corresponding chlorosilanes **1** and **2** *via* the allylic alcohols of the type **3a,b** and **4a,b** (Scheme 1). The syntheses of the latter compounds has been described before.[13] Oxidation of the alcohols (*E*)-**3a,b** and (*E*)-**4a,b**

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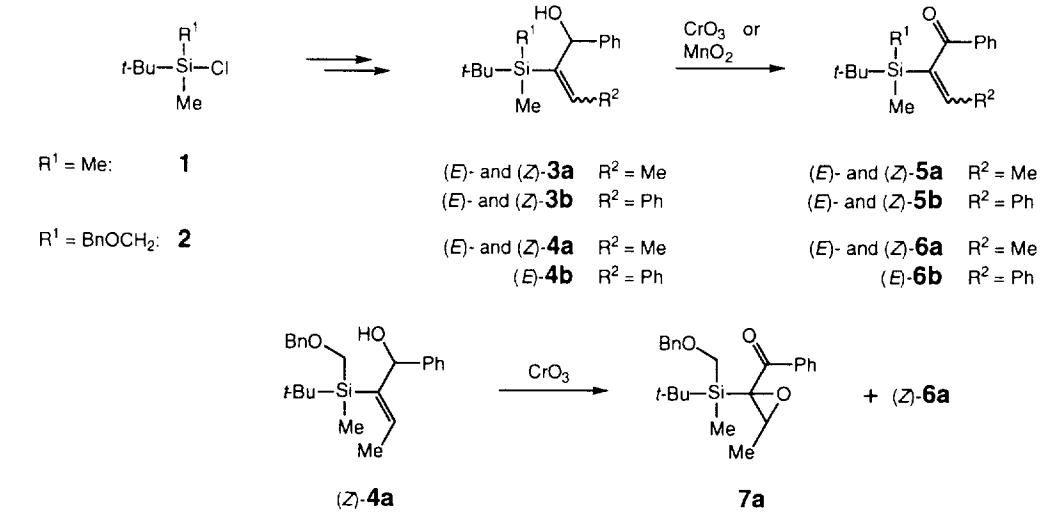
with *Jones* reagent[14] and of the alcohols (*Z*)-**3a,b** and (*Z*)-**4a**[15] with MnO_2 afforded the respective isomerically pure α,β-unsaturated ketones **5a,b** and **6a,b** in high yields. The use of milder oxidation conditions for the preparation of the (*Z*)-configured compounds **5a,b** and **6a** was neccessary because the reaction of the respective precursors, *e.g.*, (*Z*)-**4a**, with CrO_3 provided substantial amounts of over-oxidized α,β-epoxyketones, *e.g.*, **7a**. The reason for this peculiar behavior of the silyl-substituted (*Z*)-configured allyl alcohols is not known.



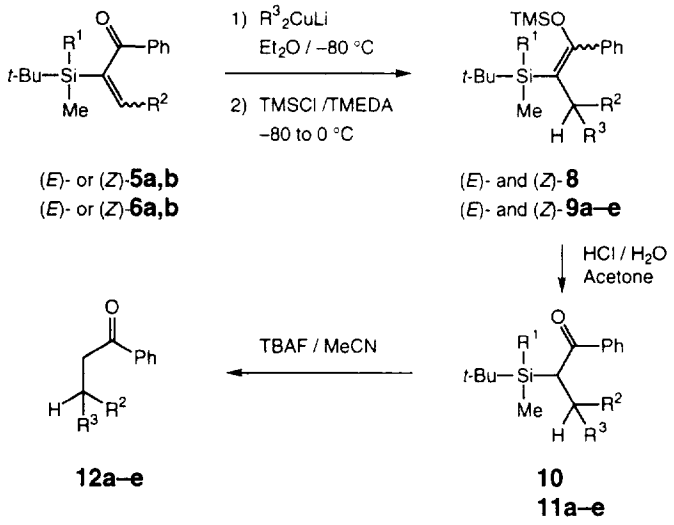
Scheme 1

The structures of the compounds **5** and **6**, particularly their double bond geometries, were ascertained by correlation with precursor molecules. Additionally, the vinylic protons show absorptions in the ^{1}H-NMR spectra characteristically different for the (*E*)- and (*Z*)-configured enones, the chemical shifts being moved towards lower fields for the latter compounds. Sound evidence for the assigned double bond geometries arose also from the values of $^3J(^{29}Si,^1H)$-coupling constants determined for the vicinal couplings of the vinylic Si- and H nuclei with the novel ACT-*J*-NMR experiment: [16] the (*Z*)-configured compounds displayed $^3J(^{29}Si, ^1H)_{trans}$-values of 13–15 Hz, the (*E*)-configured analogs $^3J(^{29}Si, ^1H)_{cis}$-values of 7–8 Hz. These values are characteristic for $^3J(^{29}Si,^1H)$-coupling constants of vinylsilanes of the given substitution patterns.[17]

Cuprate additions to α-silylated α,β-unsaturated ketones were initially tested and optimized with the achiral model compounds **5a,b**. Best results were obtained when the enones of the type **5** were treated at low temperature with the respective lithium diorganylcuprates, and when the resulting enolates were trapped as the silyl enol ethers (*E*)- or (*Z*)-**8** (Scheme 2, Table 1). Hydrolysis with aqueous H_2SO_4 in acetone provided the epimeric α-silylated ketones **10/10′**, which gave the desilylated ketone **12a** (R^2, R^3=Me, Ph) upon treatment with TBAF in MeCN.

It was imperative to capture the initially formed cuprate addition products as enol ethers: direct hydrolytic workup led to the formation of substantial amounts of oxidized silicon-free side products. The addition of *N,N,N′,N′*-tetramethylethylendiamine (TMEDA) to the enolate/TMSCl solution was neccessary to ensure complete silylation.

The reactions of the enones (*E*)-**5b** and (*Z*)-**5a,b** with approximately 1.5 equivalents of organocuprates and TMSCl to afford the silyl enol ethers of the type **8** were highly stereoselective: starting from the (*E*)-configured substrate (*E*)-**5b**, the respective (*E*)-configured enol ether **8** was obtained as the major product, and departing from the (*Z*)-configured starting materials (*Z*)-**5a,b**, the (*Z*)-configured products of the type **8** were formed with high preference[18] (Table 1). The selectivities probably reflect the preferred conformations of the starting materials, being most probably s-*cis* for (*E*)-**5a,b** and s-*trans*



For R^1, R^2, R^3, double bond configuration, and diastereoselectivities see the *Table*.

Scheme 2.

for (*Z*)-**5a,b**;[19] they are not considered to be the direct consequence of the double bond geometries of the enones. This assumption is important in connection with the interpretation of the stereoselectivities found in the cuprate additions performed with the chiral silicon compounds of the type **6**. Among the chiral starting materials **6a,b**, the ketones (*E*)-**6a** and (*Z*)-**6a** delivered the respective addition products (Si*R**,*S**,*Z*)-**9a–c** and (Si*R**,*R**,*Z*)-**9a–c** with high stereoselectivities, not only in respect to the newly formed stereogenic center at C(3) but also concerning the double bond configuration of the enol ether. The selectivities anent chiral induction of the reactions with the (*Z*)-configured compound were virtually complete whereas those of the transformations of the (*E*)-configured analog were slightly lower, though still satisfactory. The selectivities attained in the preparation of compounds of the type **9** starting from the phenyl-substituted (*E*)-**6b**, however, were disappointingly poor in all respects.

The high π-face selectivities of the cuprate additions to the enones (*E*)- and (*Z*)-**6a** were attributed to intermediary chelate-structures of the type **13a** (Scheme 3). It is assumed that such species are attacked by the copper reagents from the least hindered site, opposite to the *tert*-butyl group. This gives rise to (*Z*)-enolates of the type **14**, which are subsequently trapped by the silylating agent. In the case of (*Z*)-**6a**, the respective stereochemically crucial intermediate (*Z*)-**13a** should be formed particularly facile since negligible steric constraints are introduced into the structure. This is not the case with (*E*)-**6a**, where $A_{1,3}$ strain arises when the enone is forced from the preferred s-*cis* into the s-*trans* conformation. Therefore, it might be assumed that (*E*)-**6a** will not exclusively react *via* the highly organized intermediary (*E*)-**13a**, and this would thus account for the lower selectivities found with (*E*)-**6a** as the starting material. The still prominent diastereoselectivities obtained in the cuprate additions to (*E*)-**6a** show, however, that the $A_{1,3}$ strain in complex (*E*)-**13a** is not too high and can be mostly overcome by the returns of free energy attained by the formation of the chelate. With increasing size of a vinylic substituent positioned *cis* to the benzoyl group in compounds of the type (*E*)-**6**, though, increasing $A_{1,3}$ strain is introduced into a derived chelate structure of the type (*E*)-**13**. As a result, chelates of the type (*E*)-**13** should become less favorable and the stereoselectivities of conjugate additions must be expected to decrease. The poor stereochemical results of the reactions of organocuprates with (*E*)-**6b**, having the rather large phenyl group positioned *cis* to the benzoyl moiety, are in fact attributed to this effect.

That chelate intermediates of the type **13** might be important for the stereochemical course of the

Table 1. Organocuprate additions to enones of the type **5** and **6**, hydrolysis, and desilylation

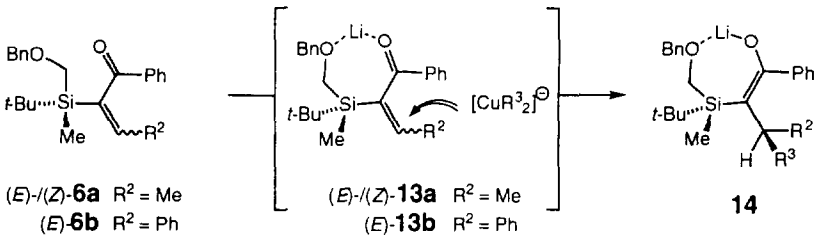
Starting Materials				Products							
Enone			Cuprate	Silyl Enol Ether		Silylated Ketone				Final Ketone	
No	R^1	R^2	R^3	No	yield (%)	No[b]	ratio	de[c] (%)	yield (%)[d]	No	yield (%)
(*E*)-**5a**	Me	Me	Ph	(*E*)-**8**/(*Z*)-**8** (2:1)[a]	76	**10/10'**	1 : 1	—	66	**12a**	82
(*Z*)-**5a**	Me	Me	Ph	(*E*)-**8**/(*Z*)-**8** (1:10)	91	**10/10'**	1 : 1	—	71	—	—
(*E*)-**5b**	Me	Ph	Me	(*E*)-**8**/(*Z*)-**8** (>40:1)	93	—	—	—	—	—	—
(*Z*)-**5b**	Me	Ph	Me	(*E*)-**8**/(*Z*)-**8** (1:6)	64	—	—	—	—	—	—
(*E*)-**6a**	$BnOCH_2$	Me	Ph	(Si*R**,*R**,*Z*)-**9a**/(Si*R**,*S**,*Z*)-**9a**	62	(Si*R**,3*R**)-**11a**/(Si*R**,3*S**)-**11a** (Si*R**,3*R**)-**11a'**/(Si*R**,3*S**)-**11a'**	0.5 : 93 0.5 : 6	98	79	**12a**	87
			Et	(Si*R**,*R**,*Z*)-**9b**/(Si*R**,*S**,*Z*)-**9b**	73	(Si*R**,3*R**)-**11b**/(Si*R**,3*S**)-**11b** (Si*R**,3*R**)-**11b'**/(Si*R**,3*S**)-**11b'**	5 : 31 / 5 : 59	80	85	**12b**	86
			Bu	(Si*R**,*R**,*Z*)-**9c**/(Si*R**,*S**,*Z*)-**9c**	73	(Si*R**,3*R**)-**11c**/(Si*R**,3*S**)-**11c** (Si*R**,3*R**)-**11c'**/(Si*R**,3*S**)-**11c'**	4 : 28 / 5 : 63	82	91	**12c**	89
(*Z*)-**6a**	$BnOCH_2$	Me	Ph	(Si*R**,*R**,*Z*)-**9a**/(Si*R**,*S**,*Z*)-**9a**	68	(Si*R**,3*R**)-**11a**/(Si*R**,3*S**)-**11a** (Si*R**,3*R**)-**11a'**/(Si*R**,3*S**)-**11a'**	20 : 2 78 : 0	96	94	—	—
			Et	(Si*R**,*R**,*Z*)-**9b**/(Si*R**,*S**,*Z*)-**9b**	78	(Si*R**,3*R**)-**11b**/(Si*R**,3*S**)-**11b** (Si*R**,3*R**)-**11b'**/(Si*R**,3*S**)-**11b'**	38 : 3 / 58 : 1	92	89	—	—
			Bu	(Si*R**,*R**,*Z*)-**9c**/(Si*R**,*S**,*Z*)-**9c**	93	(Si*R**,3*R**)-**11c**/(Si*R**,3*S**)-**11c** (Si*R**,3*R**)-**11c'**/(Si*R**,3*S**)-**11c'**	46 : 2.5 / 48 : 3.5	88	89	—	—
(*E*)-**6b**	$BnOCH_2$	Ph	Me	(Si*R**,*R**,*E*)-**9a**/(Si*R**,*R**,*Z*)-**9a** (Si*R**,*S**,*E*)-**9a**/(Si*R**,*S**,*Z*)-**9a**	75	(Si*R**,3*R**)-**11a**/(Si*R**,3*S**)-**11a** (Si*R**,3*R**)-**11a'**/(Si*R**,3*S**)-**11a'**	19 : 19 31 : 31	0	89	—	—
			Et	(Si*R**,*R**,*E*)-**9d**/(Si*R**,*R**,*Z*)-**9d** (Si*R**,*S**,*E*)-**9d**/(Si*R**,*S**,*Z*)-**9d**	89	(Si*R**,3*R**)-**11d**/(Si*R**,3*S**)-**11d** (Si*R**,3*R**)-**11d'**/(Si*R**,3*S**)-**11d'**	28 : 4 51 : 17	58	75	**12d**	77
			Bu	(Si*R**,*R**,*E*)-**9e**/(Si*R**,*R**,*Z*)-**9e** (Si*R**,*S**,*E*)-**9e**/(Si*R**,*S**,*Z*)-**9e**	59	(Si*R**,3*R**)-**11e**/(Si*R**,3*S**)-**11e** (Si*R**,3*R**)-**11e'**/(Si*R**,3*S**)-**11e'**	7 : 37 35 : 21	12	93	**12e**	73

a) This ratio cannot be compared directly to the ratios obtained with the other compounds of the type **5**. The reaction had to be performed in presence of a large excess of Ph_2CuLi (6 eq.) to ensure complete conversion of (*E*)-**5a**. This was not necessary for the other compounds that reacted to full conversion already with approx. 1.5 eq. of the organocuprate.

b) We were not able to determine the relative configurations of the stereogenic centers at C(2). Groups of compounds with or without the suffix '**'**' possess the same relative configuration at the stereogenic centers on the carbon framework (for the compounds of the type **11b,c/11b,c'** determined from similarities in the ^{1}H-NMR spectra).

c) Diastereomeric excess in respect to the stereogenic centers at silicon and C(3).

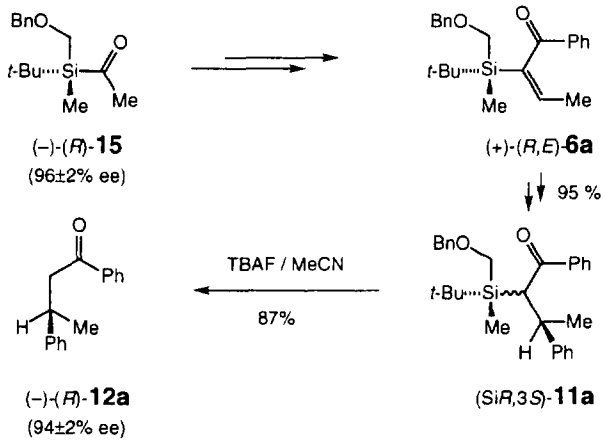
d) Higher overall yields were obtained when the enol ethers of the type **8** or **9** were *in situ* hydrolyzed upon their formation.



Scheme 3.

cuprate additions to (*E*)-**6a** and (*Z*)-**6a** is supported by the fact that exclusively the (*Z*)-configured enol ethers **9a–c** were formed. Evidently, and contradictory to the reactions with the achiral model compounds (*E*)-**5a,b** and (*Z*)-**5a,b**, a s-*trans* intermediate is involved not only in the transformation of the (*Z*)- but also of the (*E*)-configured **6a**. This seems not to be the case in the transformation of (*E*)-**6b**: since mixtures of four compounds were obtained after its treatment with cuprates and silylation, it must be assumed that the increased steric strain resulting from a conformational change from the s-*cis* to the s-*trans* form of (*E*)-**6b** could only partially be overcome. Reduced stereoselectivities were notably also obtained when the cuprate additions to any of the compounds of the type **6** were performed in the presence of a donating additive (like, *e.g.*, TMEDA or THF) that can compete as a ligand for complexation of the cations with the substrate and thus will disfavor the formation of the chelates of the type **13**.

The stereochemistry of the cuprate additions follows the course that is anticipated on the basis of the above mentioned 'chelate model'. This is secured by the result obtained from a reaction sequence starting with optically active substrate (+)-(*R,E*)-**6a**. Enantiomerically enriched (+)-(*R,E*)-**6a** (96±2% ee) was prepared from acetylsilane (−)-(*R*)-**15** (96±2% ee)[20,21] by a procedure described earlier.[13] The compound was treated with Ph_2CuLi and led, after direct hydrolysis of the intermediary silyl enol ether (Si*R*,3*S*,*Z*)-**9a**, in high yields to the respective mixtures of epimeric ketones (Si*R*,3*S*)-**11a/11a′** (Scheme 4). Desilylation, which was performed likewise with the racemic ketones of the type **11** and **11′** (giving racemic **12a–e**, Scheme 2, Table 1), was effected by treatment of (Si*R*,3*S*)-**11a/11a′** with TBAF in MeCN. The compound obtained this way in 83% overall yield (from (+)-(*R,E*)-**6b**) and in 94±2% ee was found to be (−)-(*R*)-phenyl 2-phenylpropyl ketone ((−)-(*R*)-**12a**), as assigned on the basis of its spectroscopic and chiroptic properties.[22] The configuration of the chiral center of (−)-(*R*)-**12a**, thus, corresponds to an attack of the cuprate to the *Re*-side of the π-system.



Scheme 4.

The formation of (−)-(*R*)-**12a** from (+)-(*R,E*)-**6a** does at this instance not only support the above proposed chelate model for the stereoselective conjugate cuprate addition to chiral α-silyl-substituted α,β-unsaturated ketones, but the synthesis of an acyclic β-chiral ketone in an enantiomeric excess of 94±2% by means of an auxiliary-assisted diastereoselective cuprate addition represents also one of the best examples of such a process. Thus, we have shown that the chiral silicon group **A** can efficiently be used as a stereochemical director in 'chelate-controlled' conjugate addition reactions.

Experimental

General remarks

Unless otherwise stated: all org. solvents were distilled prior to use. For the reactions, THF and Et_2O were dried over Na in presence of diphenylketyl; CH_2Cl_2 was dried over molecular sieves (3 Å). All reactions were carried out under an Ar atmosphere. Soln. of salts and acids for workup procedures were prepared in deionized H_2O. Extracts were dried ($MgSO_4$) and evaporated *in vacuo*. Chromatography: silica gel (SiO_2) Merck 60 (40–63 μm). M.p.: Mettler FP-5/FP-52. IR (neat): Perkin-Elmer 781; data in cm^{-1}. UV/VIS ($CHCl_3$): Perkin Elmer 555; λ_{max} in nm (lg ε). ^{1}H-NMR: at 300 MHz in $CDCl_3$; Bruker AC-300 or Bruker ARX-300; δ in ppm rel. to $CHCl_3$ (=7.26 ppm); *J* in Hz. ^{13}C-NMR: at 75.6 MHz in $CDCl_3$; Bruker ARX-300; δ in ppm rel. to $CDCl_3$ (=77.0 ppm); multiplicities from DEPT experiments. ^{29}Si-NMR: at 119.2 MHz in $CDCl_3$; Bruker ARX-600; δ in ppm rel. to $SiMe_4$ (=0.00 ppm). ^{19}F-NMR: at 564.5 MHz in $CDCl_3$; Bruker ARX-600; δ in ppm rel. to CCl_3F (=0.00 ppm). CI–MS (chemical ionization mass spectrometry) with NH_3 as the reactant gas; Finnigan SSQ 700 or Varian MAT 90; base peak and quasi-molecular ions only; data in *m/z*.

*1. Oxidation of the allylic alcohols of the type **3** and **4***

1.1. General procedures

A: To a soln. of the respective allylic alcohol in acetone (0.1 M) was added dropwise Jones reagent[14] until the color of the mixture remained persistently brown. It was diluted with H_2O, neutralized with sat. aq. $NaHCO_3$ soln., extracted with Et_2O, and chromatographed (SiO_2, hexane/EtOAc 25:1). *B*: To a soln. of the respective allylic alcohol in CH_2Cl_2 (0.1 M) was added MnO_2 (5 eq.), and the mixture was refluxed for 2 h. It was filtered, the solvent was evaporated, and the crude product chromatographed (SiO_2, hexane/EtOAc 25:1).

*1.2. (*E*)-1-[(*tert*-Butyl)dimethylsilyl]prop-1-enyl phenyl ketone (*E*)-**5a***

According to 1.1, procedure A: (*E*)-**3a**[13] (232 mg, 0.89 mmol) was converted to (*E*)-**5a** (201 mg, 0.77 mmol, 87%). IR: 3080*w*, 3060*w*, 3020*w*, 2959*s*, 2920*s*, 2880*s*, 2850*s*, 1655*s*, 1595*s*, 1575*s*, 1470*m*, 1460*m*, 1445*s*, 1410*m*, 1390*m*, 1370*m*, 1360*m*, 1345*s*, 1310*w*, 1245*s*, 1225*s*, 1170*s*, 1125*w*, 1070*w*, 1030*m*, 1015*s*, 1005*m*, 970*w*, 935*w*, 870*m*, 835*s*, 820*s*, 805*s*, 785*m*, 765*s*, 740*m*, 710*s*, 690*s*. UV/VIS: 242 (3.98). ^{1}H-NMR: 7.94–7.45 (*m*, 5 arom. H); 6.25 (*q*, *J*=6.7, HC=); 1.63 (*d*, *J*=6.7, MeC=); 0.91 (*s*, *t*-Bu); 0.05 (*s*, Me_2Si). ^{13}C-NMR: 202.3 (*s*, C=O); 145.3 (*s*, SiC=); 140.1 (*d*, HC=); 137.6 (*s*, arom. C); 133.1 (*d*, arom. C); 129.4, 128.8 (2*d*, 2×2 arom. C); 27.7 (*q*, *Me*$_3$C); 18.3 (*q*, *Me*CH); 18.0 (*s*, Me$_3$*C*); −5.5 (*q*, MeSi). CI–MS: 261 $[M+H]^+$.

*1.3. (*Z*)-1-[(*tert*-Butyl)dimethylsilyl]prop-1-enyl phenyl ketone (*Z*)-**5a***

According to 1.1, procedure B: (*Z*)-**3a**[13] (394 mg, 1.50 mmol) was converted to (*Z*)-**5a** (370 mg, 1.42 mmol, 95%). IR: 3070*w*, 3050*w*, 3020*w*, 2950*s*, 2920*s*, 2890*s*, 2850*s*, 1650*s*, 1595*s*, 1575*m*, 1465*m*, 1460*m*, 1445*s*, 1405*m*, 1390*m*, 1370*m*, 1340*w*, 1310*m*, 1250*s*, 1175*m*, 1155*w*, 1130*w*, 1070*w*, 1050*m*, 1035*w*, 1020*m*, 1005*m*, 955*w*, 935*w*, 905*w*, 870*w*, 835*s*, 825*s*, 800*s*, 760*s*, 740*w*, 730*w*, 705*s*. UV/VIS: 245 (4.02). ^{1}H-NMR: 7.82–7.39 (*m*, 5 arom. H); 6.57 (*q*, *J*=6.6, HC=); 1.99 (*d*, *J*=6.6, MeC=); 1.01 (*s*, *t*-Bu); 0.17 (*s*, Me_2Si). ^{13}C-NMR: 201.5 (*s*, C=O); 147.7 (*d*, HC=); 143.1 (*s*, SiC=); 138.2 (*s*, arom. C); 132.2 (*d*, arom. C); 129.9, 128.1 (2*d*, 2×2 arom. C); 27.2 (*q*, *Me*$_3$C); 18.8 (*q*, *Me*CH); 18.5 (*s*, Me$_3$*C*); −3.6 (*q*, MeSi). CI–MS: 261 $[M+H]^+$.

1.4. (E)*-1-[(*tert*-Butyl)dimethylsilyl]-2-phenylethenyl phenyl ketone* (E)*-**5b***

According to 1.1, procedure A: (*E*)-**3b**[13] (113 mg, 0.35 mmol) was converted to (*E*)-**5b** (98 mg, 0.30 mmol, 87%). IR: 3080*w*, 3050*m*, 3020*m*, 2950*s*, 2930*s*, 2890*m*, 2880*m*, 2850*s*, 1700*m*, 1650*s*, 1595*m*, 1580*m*, 1490*w*, 1465*m*, 1469*m*, 1445*m*, 1410*w*, 1390*m*, 1360*m*, 1315*m*, 1280*w*, 1265*m*, 1250*m*, 1230*s*, 1200*m*, 1175*m*, 1070*w*, 1045*m*, 1005*m*, 935*m*, 925*m*, 900*m*, 880*m*, 835*s*, 820*s*, 710*s*. UV/VIS: 247 (4.30). ^{1}H-NMR: 7.81–7.04 (*m*, 10 arom. H); 6.98 (*s*, HC=); 0.91 (*s*, *t*-Bu); 0.07 (*s*, Me_2Si). ^{13}C-NMR: 202.1 (*s*, C=O); 145.2 (*s*, arom. C); 141.3 (*d*, HC=); 138.6 (*s*, SiC=); 136.3 (*s*, arom. C); 132.8 (*d*, arom. C); 129.1, 128.7 (2*d*, 2×2 arom. C); 128.3, 128.2 (2*d*, 2×2 arom. C); 128.1 (*d*, arom. C); 26.7 (*q*, *Me*$_3$C); 18.1 (*s*, Me$_3$*C*); −5.7 (*q*, Me_2Si). CI–MS: 323 $[M+H]^+$.

1.5. (Z)*-1-[(*tert*-Butyl)dimethylsilyl]-2-phenylethenyl phenyl ketone* (Z)*-**5b***

According to 1.1, procedure B: (*Z*)-**3b**[13] (220 mg, 0.68 mmol) was converted to (*Z*)-**5b** (187 mg, 0.58 mmol, 86%). IR: 3080*w*, 3060*m*, 3020*w*, 2950*s*, 2930*s*, 2890*m*, 2850*s*, 1655*s*, 1595*m*, 1580*m*, 1485*m*, 1470*m*, 1460*m*, 1445*m*, 1405*w*, 1390*w*, 1360*w*, 1310*m*, 1250*s*, 1235*s*, 1205*w*, 1175*m*, 1160*w*, 1115*w*, 1060*m*, 1025*m*, 1005*w*, 1000*w*, 935*w*, 910*m*, 870*w*, 835*s*, 820*s*, 790*w*, 760*s*, 750*s*, 735*m*, 700*s*. UV/VIS: 245 (4.20). ^{1}H-NMR: 7.78–7.11 (*m*, 10 arom. H); 7.33 (*s*, HC=); 0.69 (*s*, *t*-Bu); −0.27 (*s*, Me_2Si). ^{13}C-NMR: 201.7 (*s*, C=O); 149.6 (*d*, HC=); 145.2 (*s*, arom. C); 138.1 (*s*, SiC=); 137.7 (*s*, arom. C); 132.6 (*d*, arom. C); 130.1, 128.3 (2*d*, 2×2 arom. C); 128.2 (*d*, arom. C); 127.9, 127.8 (2*d*, 2×2 arom. C); 27.6 (*q*, *Me*$_3$C); 18.1 (*s*, Me$_3$*C*); −2.8 (*q*, Me_2Si). CI–MS: 323 $[M+H]^+$.

1.6. (±)-(E)*- and* (+)-(R,E)*-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}prop-1-enyl phenyl ketone* (E)*-**6a** and* (+)-(R,E)*-**6a***

According to 1.1, procedure A: (*E*)-**4a**[13] (440 mg, 1.20 mmol) or (*R,E*)-(−)-**4a** (320 mg, 0.87 mmol) was converted to (*E*)-**6e** (430 mg, 1.17 mmol, 98%) or (*R,E*)-(+)-**6a** (295 mg, 0.81 mmol, 93%). $[\alpha]_D^{23}$=13.0 (c=1.7, THF), for (+)-(*R,E*)-**6a**. IR: 3080*w*, 3060*w*, 3020*w*, 2950*s*, 2920*s*, 2880*m*, 2850*s*, 1660*s*, 1590*m*, 1575*m*, 1490*w*, 1460*m*, 1445*m*, 1410*w*, 1390*w*, 1375*m*, 1360*m*, 1345*m*, 1310*w*, 1265*m*, 1250*m*, 1230*s*, 1170*m*, 1105*m*, 1095*m*, 1070*m*, 1030*m*, 1015*m*, 1000*m*, 980*m*, 935*m*, 900*w*, 865*m*, 825*s*, 810*m*, 780*m*, 765*m*, 735*m*, 720*m*, 695*s*. UV/VIS: 245 (4.03). ^{1}H-NMR: 7.85–7.12 (*m*, 10 arom. H); 6.25 (*q*, *J*=6.8, HC=); 4.22 (*s*, PhCH_2O); 3.19 (*s*, $SiCH_2O$); 1.51 (*d*, *J*=6.8, MeC=); 0.86 (*s*, *t*-Bu); 0.01 (*s*, MeSi). ^{13}C-NMR: 201.5 (*s*, C=O); 142.6 (*s*, arom. C); 141.1 (*d*, HC=); 138.7 (*s*, SiC=); 137.4 (*s*, arom. C); 132.8 (*d*, arom. C); 129.2, 128.4 (2*d*, 2×2 arom. C); 128.1, 127.4 (2*d*, 2×2 arom. C); 127.2 (*d*, arom. C); 77.0 (*t*, PhCH_2O); 60.5 (*t*, $SiCH_2O$); 27.0 (*q*, *Me*$_3$C); 18.1 (*q*, *Me*C=); 17.7 (*s*, Me$_3$*C*); −8.5 (*q*, MeSi). CI–MS: 367 $[M+H]^+$.

1.7. (Z)*-1-{(Benzyloxy)methyl](*tert*-butyl)methylsilyl}prop-1-enyl phenyl ketone* (Z)*-**6a***

According to 1.1, procedure B: (*Z*)-**4a**[13] (300 mg, 0.82 mmol) was converted to (*Z*)-**6a** (291 mg, 0.80 mmol, 97%). IR: 3080*w*, 3060*m*, 3020*m*, 2950*s*, 2920*s*, 2890*m*, 2850*s*, 2810*m*, 1725*w*, 1700*m*, 1650*s*, 1595*m*, 1575*m*, 1490*w*, 1470*m*, 1460*m*, 1445*m*, 1390*m*, 1375*m*, 1360*m*, 1345*w*, 1310*m*, 1250*s*, 1200*w*, 1175*m*, 1155*w*, 1130*w*, 1105*m*, 1090*m*, 1070*s*, 1055*m*, 1035*w*, 1025*m*, 1005*w*, 975*w*, 935*w*, 905*m*, 879*w*, 830*s*, 825*s*, 805*m*, 770*m*, 760*s*, 735*s*, 705*s*. UV/VIS: 243 (4.09). ^{1}H-NMR: 7.69–7.02 (*m*, 10 arom. H); 6.53 (*q*, *J*=7.1, HC=); 4.20 (*s*, PhCH_2O); 3.31, 3.25 (*AB*, J_{AB}=12.6, $SiCH_2O$); 1.89 (*d*, *J*=7.1, MeC=); 0.94 (*s*, *t*-Bu); 0.19 (*s*, MeSi). ^{13}C-NMR: 201.3 (*s*, C=O); 149.6 (*d*, HC=); 141.5 (*s*, arom. C); 138.7 (*s*, SiC=); 138.3 (*s*, arom. C); 131.9 (*d*, arom. C); 129.9, 128.0 (2*d*, 2×2 arom. C); 127.9, 127.4 (2*d*, 2×2 arom. C); 127.1 (*d*, arom. C); 77.1 (*t*, PhCH_2O); 61.3 (*t*, $SiCH_2O$); 27.7 (*q*, *Me*$_3$C); 18.9 (*q*, *Me*CH); 18.5 (*s*, Me$_3$*C*); −6.2 (*q*, MeSi). CI–MS: 367 $[M+H]^+$.

1.8. (E)*-1-[[(Benzyloxy)methyl](*tert*-butyl)methylsilyl]-2-phenylethenyl phenyl ketone* (E)*-**6b***

According to 1.1, procedure A: (*E*)-**4b**[13] (400 mg, 0.93 mmol) was converted to (*E*)-**6b** (380 mg, 0.89 mmol, 95%). IR: 3080*w*, 3060*m*, 3020*m*, 2950*s*, 2930*s*, 2880*m*, 2850*s*, 2810*m*, 1700*m*, 1650*s*,

1595*m*, 1580*m*, 1570*m*, 1490*w*, 1470*m*, 1460*m*, 1445*m*, 1390*w*, 1380*m*, 1360*m*, 1310*w*, 1280*w*, 1250*m*, 1225*s*, 1200*m*, 1170*m*, 1155*w*, 1105*m*, 1090*m*, 1070*m*, 1050*m*, 1020*m*, 1005*w*, 980*w*, 940*w*, 930*w*, 900*w*, 880*w*, 825*m*, 780*m*, 765*m*, 745*m*, 735*m*, 695*s*. UV/VIS: 247 (4.25). ^{1}H-NMR: 7.86–7.05 (*m*, 15 arom. H); 7.05 (*s*, HC=); 4.32 (*s*, PhCH_2O); 3.38, 3.33 (*AB*, J_{AB} =13.1, SiCH_2O); 0.99 (*s*, *t*-Bu); 0.13 (*s*, MeSi). ^{13}C-NMR: 201.9 (*s*, C=O); 142.8 (*s*, arom. C); 142.4 (*d*, HC=); 138.6 (*s*, SiC=); 136.6, 136.3 (2*s*, 2 arom. C); 132.7, 129.2, 128.9, 128.2, 128.1, 127.4, 127.2 (7*d*, 15 arom. C); 77.1 (*t*, PhCH_2O); 60.4 (*t*, SiCH_2O); 27.1 (*q*, *Me*$_3$C); 18.2 (*s*, Me$_3$*C*); −8.5 (*q*, MeSi). CI–MS: 429 $[M+H]^+$.

2. Preparation of the cuprates

2.1. Ph_2CuLi, Bu_2CuLi, and Me_2CuLi

The respective organolithium reagent (2 eq., commercial) was added to a suspension of CuI (20 mg/ml) in Et_2O at −50°C. The temperature was slowly raised to 0°C (30 min), and stirring was continued for an additional 2 h.

2.2. Et_2CuLi

t-BuLi (1 eq., 1.7 M in hexane) was added dropwise to a soln. of EtI in Et_2O (0.3–0.4 M) at −78°C. The temperature was slowly raised to 23°C and stirring was continued for 2 h. The resulting soln. was dropwise added at −50°C to a suspension of CuI (0.5 eq., 20 mg/ml) in Et_2O, the temperature was slowly raised to 0°C (30 min), and stirring was continued for an additional 2 h.

*3. Cuprate additions to the silylated enones of the type **5** and **6***

3.1. General procedure

To a soln. of cuprate reagent (5–10 M in Et_2O) at −80°C were subsequently added TMSCl (2 eq.) and the respective ketone (0.2–0.5 eq.). The temperature was raised to 0°C over a period of 30 min., and the mixture was stirred for 1 h. TMEDA (2 ml) was added and stirring continued for an additional 30 min. It was quenched with sat. aq. NH_4Cl soln. at 0°C, extracted with Et_2O, and chromatographed (SiO_2, hexane/CH_2Cl_2 5:1).

*3.2. (E)- and (Z)-2-{(tert-Butyl)dimethylsilyl}-1-(trimethylsiloxy)-1,3-diphenylbut-1-ene (E)-**8** and (Z)-**8***

According to 3.1, (*E*)-**5a** (150 mg, 0.58 mmol) was reacted with Ph_2CuLi (4.18 mmol) and TMSCl (1 ml, 8.36 mmol) to give an inseparable mixture of (*E*)-**8** and (*Z*)-**8** (180 mg, 76%, (*E*)-**8**/(*Z*)-**8**=2:1 determined by ^{1}H-NMR). Likewise, (*Z*)-**5a** (90 mg, 0.35 mmol) gave with Ph_2CuLi (0.69 mmol) and TMSCl (0.1 ml, 0.79 mmol) (*Z*)-**8** (129 mg, 0.31 mmol, 91%); (*E*)-**5b** (150 mg, 0.47 mmol) gave with Me_2CuLi (0.56 mmol) and TMSCl (0.14 ml, 0.94 mmol) (*E*)-**8** (180 mg, 0.44 mmol, 93%); (*Z*)-**5b** (100 mg, 0.31 mmol) gave with Me_2CuLi (0.46 mmol) and TMSCl (0.1 ml, 0.80 mmol) a mixture of (*E*)-**8** and (*Z*)-**8** (82 mg, 0.20 mmol, 64%, (*E*)-**8**/(*Z*)-**8**=1:6); (*Z*)-**5b** (112 mg, 0.35 mmol) gave with Me_2CuLi (2.00 mmol) and TMSCl (0.55 ml, 4.38 mmol) a mixture of (*E*)-**8** and (*Z*)-**8** (110 mg, 0.27 mmol, 77%, (*E*)-**8**/(*Z*)-**8**=1:2).

Data of (*E*)-**8** (colorless oil). IR: 3080*w*, 3050*w*, 3020*w*, 2950*s*, 2920*s*, 2870*s*, 2850*s*, 1610*m*, 1585*s*, 1485*m*, 1460*m*, 1440*m*, 1405*w*, 1385*w*, 1375*w*, 1365*w*, 1355*w*, 1325*w*, 1305*w*, 1260*s*, 1250*s*, 1190*w*, 1135*s*, 1110*m*, 1095*m*, 1070*w*, 1055*w*, 1030*w*, 1005*w*, 990*w*, 935*w*, 920*w*, 885*m*, 850*s*, 840*s*, 820*s*, 810*s*, 785*m*, 775*s*, 765*s*, 725*m*, 700*s*. ^{1}H-NMR: 7.48–7.12 (*m*, 10 arom. H); 3.64 (*q*, *J*=7.0, Ph(Me)C*H*); 1.69 (*d*, *J*=7.0, Ph(*Me*)CH); 0.92 (*s*, *t*-Bu); −0.37, −0.42 (2*s*, Me$_2$Si); −0.44 (*s*, Me$_3$Si). ^{1}H,^{1}H-NOE: irrad. at −0.44, responsive signals at 7.48–7.47, 7.30–7.12, and 3.64. ^{13}C-NMR: 157.5 (*s*, Ph*C*=); 146.6, 139.5 (2*s*, 2 arom. C); 129.8, 127.3, 126.9, 126.8, 126.4, 123.9 (6*d*, 10 arom. C); 115.7 (*s*, SiC=); 38.4 (*d*, Ph(Me)CH); 27.1 (*q*, *Me*$_3$C); 18.5 (*q*, Ph(*Me*)CH); 18.1 (*s*, Me$_3$*C*); 0.0 (*q*, Me$_3$Si); −4.5, −4.9 (2*q*, Me$_2$Si). CI–MS: 411 $[M+H]^+$.

Data of (*Z*)-**8** (colorless oil). ^{1}H-NMR: 7.61–7.12 (*m*, 10 arom. H); 3.53 (*q*, *J*=7.2, Ph(Me)C*H*); 1.33 (*d*, *J*=7.2, Ph(*Me*)CH); 0.95 (*s*, *t*-Bu); 0.16 (*s*, MeSi); −0.07 (*s*, Me$_3$Si); −0.44 (*s*, MeSi). ^{1}H,^{1}H-

NOE: irrad. at −0.07, responsive signals at 0.95, 0.16, and −0.44. ^{13}C-NMR: 158.0 (*s*, PhC=); 145.5, 138.1 (2*s*, 2 arom. C); 127.4, 126.8, 126.5, 126.4, 125.9, 125.8 (6*d*, 10 arom. C); 117.3 (*s*, SiC=); 38.1 (*d*, Ph(Me)CH); 27.4 (*q*, *Me*$_3$C); 18.3 (*q*, Ph(*Me*)CH); 17.4 (*s*, Me$_3$*C*); 0.0 (*q*, Me$_3$Si); −3.1, −3.6 (2*q*, Me$_2$Si). CI–MS: 411 $[M+H]^+$.

*3.3. (Si*R*,R*,E)-, (Si*R*,S*,E)-, (Si*R*,R*,Z)-, and (Si*R*,S*,Z)-2-{[(benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-(trimethylsiloxy)-1,3-diphenylbut-1-ene (Si*R*,R*,E)-**9a**, (Si*R*,S*,E)-**9a**, (Si*R*,R*,Z)-**9a**, and (Si*R*,S*,Z)-**9a***

According to 3.1, (*E*)-**6a** (100 mg, 0.27 mmol) was reacted with Ph_2CuLi (1.64 mmol) and TMSCl (0.4 ml, 3.17 mmol); (*Z*)-**6a** (70 mg, 0.19 mmol) with Ph_2CuLi (0.77 mmol) and TMSCl (0.3 ml, 2.37 mmol); and (*E*)-**6b** (80 mg, 0.19 mmol) with Me_2CuLi (0.37 mmol) and TMSCl (0.1 ml, 0.88 mmol); to give inseparable mixtures of (Si*R**,*R**,*E*)-**9a**, (Si*R**,*S**,*E*)-**9a**, (Si*R**,*R**,*Z*)-**9a**, and (Si*R**,*S**,*Z*)-**9a** of the compositions and in the yields given in Table 1. (Data of (Si*R**,*R**,*E*)-**9a**, (Si*R**,*S**,*E*)-**9a** not given, since these compounds arose only as components in the mixture of all four compounds of the type **9a**.)

Data of (Si*R**,*R**,*Z*)-**9a** (from (*Z*)-**6a**, slightly contaminated with (Si*R**,*S**,*Z*)-**9a**): IR: 3080*w*, 3060*w*, 3020*w*, 2960*s*, 2930*s*, 2890*s*, 2850*s*, 1605*m*, 1485*s*, 1460*m*, 1455*m*, 1440*m*, 1410*w*, 1390*w*, 1375*w*, 1360*w*, 1265*s*, 1250*s*, 1200*w*, 1195*w*, 1115*s*, 1080*s*, 1070*s*, 1050*w*, 1035*w*, 1025*m*, 1020*m*, 1000*w*, 975*w*, 960*m*, 935*m*, 920*w*, 905*m*, 870*s*, 840*s*, 825*s*, 785*m*, 775*m*, 760*s*, 745*s*, 735*s*, 700*s*. ^{1}H-NMR: 7.75–7.08 (*m*, 15 arom. H); 4.58, 4.52 (*AB*, J_{AB}=12.2, PhCH_2O); 3.58 (*q*, *J*=7.2, Me(Ph)C*H*); 3.56, 3.50 (*AB*, J_{AB}=12.5, SiCH$_2$O); 1.41 (*d*, *J*=7.2, *Me*(Ph)CH); 1.08 (*s*, *t*-Bu); −0.05 (*s*, MeSi); −0.38 (*s*, Me$_3$Si). ^{1}H,^{1}H-NOE: irrad. at −0.38, responsive signals at 7.75–7.08, 4.58, 4.52, 3.56, 3.50, 1.08, and −0.05. ^{13}C-NMR: 158.5 (*s*, PhC=); 145.2, 138.2, 137.7 (3*s*, 3 arom. C); 128.1, 127.4, 126.6, 126.5, 126.3, 126.1, 125.9, 125.7, 123.7 (9*d*, 15 arom. C); 115.5 (*s*, SiC=); 75.6 (*t*, PhCH$_2$O); 61.9 (*t*, SiCH$_2$O); 37.7 (*d*, Me(Ph)*C*H); 27.6 (*q*, *Me*$_3$C); 18.3 (*q*, *Me*(Ph)CH); 17.4 (*s*, Me$_3$*C*); 0.0 (*q*, Me$_3$Si); −7.2 (*q*, MeSi). CI–MS: 517 $[M+H]^+$.

Data of (Si*R**,*S**,*Z*)-**9a** (from (*E*)-**6a**, slightly contaminated with (Si*R**,*R**,*Z*)-**9a**): IR: 3080*w*, 3050*w*, 3020*m*, 2960*s*, 2920*s*, 2880*s*, 2850*s*, 2810*w*, 1605*m*, 1585*s*, 1485*m*, 1455*m*, 1410*w*, 1390*w*, 1375*w*, 1360*w*, 1265*s*, 1250*s*, 1200*w*, 1140*w*, 1115*s*, 1085*s*, 1070*s*, 1055*w*, 1040*w*, 1025*m*, 1020*m*, 1000*w*, 980*w*, 960*m*, 935*w*, 920*w*, 910*m*, 870*s*, 840*s*, 835*s*, 805*m*, 785*m*, 775*m*, 750*s*, 735*s*, 700*s*. ^{1}H-NMR: 7.33–7.10 (*m*, 15 arom. H); 4.20 (*s*, PhCH_2O); 3.54–3.47 (*m*, Me(Ph)C*H*); 2.84, 2.78 (*AB*, J_{AB}=12.7, SiCH$_2$O); 1.33 (*d*, *J*=7.2, *Me*(Ph)CH); 0.97 (*s*, *t*-Bu); 0.18 (*s*, MeSi); −0.11 (*s*, Me$_3$Si). ^{1}H,^{1}H-NOE: irrad. at −0.11, responsive signals at 7.33–7.10, 2.78, 2.84, 0.97, and 0.18. ^{13}C-NMR: 158.3 (*s*, PhC=); 145.1, 138.1, 137.7 (3*s*, 3 arom. C); 128.1, 127.7, 126.8, 126.7, 126.5, 126.3, 126.1, 126.0, 123.8 (9*d*, 15 arom. C); 116.6 (*s*, SiC=); 75.4 (*t*, PhCH$_2$O); 61.8 (*t*, SiCH$_2$O); 37.9 (*d*, Me(Ph)*C*H); 27.5 (*q*, *Me*$_3$C); 18.0 (*q*, *Me*(Ph)CH); 17.5 (*s*, Me$_3$*C*); 0.0 (*q*, Me$_3$Si); −6.6 (*q*, MeSi). CI–MS: 517 $[M+H]^+$.

*3.4. (Si*R*,R*,Z)- and (Si*R*,S*,Z)-2-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-3-methyl-1-(trimethylsiloxy)-1-phenylpent-1-ene (Si*R*,R*,Z)-**9b** and (Si*R*,S*,Z)-**9b***

According to 3.1, (*E*)-**6a** (100 mg, 0.37 mmol) was reacted with Et_2CuLi (1.64 mmol) and TMSCl (0.9 ml, 7.04 mmol); and (*Z*)-**6a** (100 mg, 0.27 mmol) with Et_2CuLi (1.10 mmol) and TMSCl (0.6 ml, 4.80 mmol); to give inseparable mixtures of (Si*R**,*R**,*Z*)-**9b** and (Si*R**,*S**,*Z*)-**9b** in the yields given in Table 1.

Data of (Si*R**,*R**,*Z*)-**9b** (from (*Z*)-**6a**, slightly contaminated with (Si*R**,*S**,*Z*)-**9b**): IR: 3060*w*, 3030*w*, 2960*s*, 2920*s*, 2890*s*, 2950*s*, 2810*w*, 1605*m*, 1575*s*, 1485*m*, 1460*m*, 1440*m*, 1410*w*, 1390*w*, 1375*m*, 1360*w*, 1310*w*, 1265*s*, 1250*s*, 1200*w*, 1170*w*, 1140*w*, 1100*s*, 1035*w*, 1025*m*, 1010*w*, 1000*w*, 980*m*, 965*w*, 950*w*, 920*w*, 905*w*, 875*s*, 840*s*, 825*s*, 785*s*, 760*m*, 735*s*, 700*s*. ^{1}H-NMR: 7.37–7.15 (*m*, 10 arom. H); 4.56, 4.50 (*AB*, J_{AB}=12.2, PhCH_2O); 3.56, 3.43 (*AB*, J_{AB}=12.7, SiCH$_2$O); 1.99–1.96 (*m*,

Et(Me)C*H*); 1.38–1.21, 1.09–1.06 (2*m*, MeCH_2); 1.05 (*s*, *t*-Bu); 0.89 (*d*, *J*=7.1, Et(*Me*)CH); 0.72 (*t*, *J*=7.4, *Me*CH_2); 0.32 (*s*, MeSi); −0.18 (*s*, Me_3Si). ^{1}H,^{1}H-NOE: irrad. at −0.18, responsive signals at 7.37–7.15, 4.56, 4.50, 3.56, 3.43, 1.05, and 0.32; irrad. at 1.05, responsive signals at 7.37–7.15, 4.56, 4.50, 3.56, 3.43, 0.32, and −0.18. ^{13}C-NMR: 157.2 (*s*, Ph*C*=); 138.5, 138.3 (2*s*, 2 arom. C); 128.3 (*d*, arom. C); 126.8, 126.5 (2*d*, 2×2 arom. C); 126.4 (*d*, arom. C); 126.1, 125.7 (2*d*, 2×2 arom. C); 116.4 (*s*, SiC=); 75.6 (*t*, Ph*C*H_2O); 62.3 (*t*, Si*C*H_2O); 36.5 (*d*, Et(Me)*C*H); 28.7 (*t*, Me*C*H_2); 27.4 (*q*, *Me*$_3$C); 19.9 (*q*, Et(*Me*)CH); 17.7 (*s*, Me_3*C*); 11.9 (*q*, *Me*CH_2); 0.0 (*q*, Me_3Si); −6.2 (*q*, MeSi). CI–MS: 469 $[M+H]^+$.

Data of (Si*R**,*S**,*Z*)-**9b** (from (*Z*)-**6a**, slightly contaminated with (Si*R**,*R**,*Z*)-**9b**): IR: 3060*w*, 3020*m*, 2950*s*, 2920*s*, 2890*s*, 2850*s*, 2810*m*, 1610*m*, 1570*s*, 1485*m*, 1460*m*, 1440*m*, 1410*w*, 1390*w*, 1375*m*, 1365*m*, 1310*w*, 1265*s*, 1250*s*, 1200*w*, 1170*w*, 1140*w*, 1100*s*, 1070*s*, 1025*m*, 1010*w*, 1000*w*, 985*m*, 950*w*, 920*w*, 905*w*, 875*s*, 840*s*, 825*s*, 780*s*, 760*m*, 735*s*, 700*s*. ^{1}H-NMR: 7.36–7.14 (*m*, 10 arom. H); 4.54, 4.48 (*AB*, J_{AB}=12.2, Ph*C*H_2O); 3.51, 3.40 (*AB*, J_{AB}=12.7, Si*C*H_2O); 1.98–1.94 (*m*, Et(Me)*C*H); 1.35–1.13 (*m*, MeCH_2); 1.04 (*s*, *t*-Bu); 0.87 (*d*, *J*=7.1, Et(*Me*)CH); 0.71 (*t*, *J*=7.4, *Me*CH_2); 0.31 (*s*, MeSi); −0.19 (*s*, Me_3Si). ^{1}H,^{1}H-NOE: irrad. at −0.19, responsive signals at 7.36–7.14, 4.54, 4.48, 3.51, 3.40, 1.04, and 0.31. ^{13}C-NMR: 157.3 (*s*, Ph*C*=); 138.5, 138.2 (2*s*, 2 arom. C); 128.4 (*d*, arom. C); 126.8, 126.5 (2*d*, 2×2 arom. C); 126.4 (*d*, arom. C); 126.1, 125.7 (2*d*, 2×2 arom. C); 116.7 (*s*, SiC=); 75.6 (*t*, Ph*C*H_2O); 62.4 (*t*, Si*C*H_2O); 36.5 (*d*, Et(Me)*C*H); 28.5 (*t*, Me*C*H_2); 27.3 (*q*, *Me*$_3$C); 19.9 (*q*, Et(*Me*)CH); 17.6 (*s*, Me_3*C*); 11.9 (*q*, *Me*CH_2); 0.0 (*q*, Me_3Si); −6.3 (*q*, MeSi). CI–MS: 469 $[M+H]^+$.

*3.5. (Si*R*,R*,Z*)- and (Si*R*,S*,Z*)-2-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-3-methyl-1-(trimethylsiloxy)-1-phenylhept-1-ene (Si*R*,R*,Z*)-**9c** and (Si*R*,S*,Z*)-**9c***

According to 3.1, (*E*)-**6a** (100 mg, 0.27 mmol) was reacted with Bu_2CuLi (0.81 mmol) and TMSCl (0.25 ml, 1.97 mmol); and (*Z*)-**6a** (104 mg, 0.28 mmol) with Bu_2CuLi (0.57 mmol) and TMSCl (0.2 ml, 1.34 mmol); to give inseparable mixtures of (Si*R**,*R**,*Z*)-**9c** and (Si*R**,*S**,*Z*)-**9c** in the yields given in Table 1.

Data of (Si*R**,*R**,*Z*)-**9c**: IR: 3060*w*, 3030*w*, 2950*s*, 2920*s*, 2850*s*, 2810*w*, 1605*w*, 1580*s*, 1485*m*, 1460*m*, 1440*m*, 1410*w*, 1390*w*, 1375*m*, 1360*w*, 1265*s*, 1250*s*, 1200*w*, 1135*w*, 1100*s*, 1070*s*, 1025*m*, 1010*w*, 1000*w*, 980*w*, 920*w*, 900*m*, 890*m*, 860*s*, 849*s*, 830*s*, 785*s*, 760*m*, 730*m*, 700*s*. ^{1}H-NMR: 7.39–7.12 (*m*, 10 arom. H); 4.55, 4.50 (*AB*, J_{AB}=12.2, Ph*C*H_2O); 3.54, 3.41 (*AB*, J_{AB}=12.6, Si*C*H_2O); 2.35–1.99 (*m*, Bu(Me)*C*H); 1.43–1.02 (*m*, Me(*C*H_2)$_3$); 1.03 (*s*, *t*-Bu); 0.87 (*d*, *J*=7.1, Bu(*Me*)CH); 0.79 (*t*, *J*=6.8, *Me*CH_2); 0.30 (*s*, MeSi); −0.20 (*s*, Me_3Si). ^{1}H,^{1}H-NOE: irrad. at −0.20, responsive signals at 7.39–7.12, 4.55, 4.50, 3.54, 3.41, 1.03, and 0.30. ^{13}C-NMR: 157.0 (*s*, Ph*C*=); 138.4, 138.3 (2*s*, 2 arom. C); 128.3 (*d*, arom. C); 126.8, 126.5 (2*d*, 2×2 arom. C); 126.4 (*d*, arom. C); 126.1, 125.7 (2*d*, 2×2 arom. C); 116.7 (*s*, SiC=); 75.6 (*t*, Ph*C*H_2O); 62.3 (*t*, Si*C*H_2O); 35.7 (*t*, Pr*C*H_2); 34.7 (*d*, Me(Bu)*C*H); 29.3 (*t*, Et*C*H_2); 27.4 (*q*, *Me*$_3$C); 21.5 (*t*, Me*C*H_2); 20.2 (*q*, Bu(*Me*)CH); 17.6 (*s*, Me_3*C*); 12.8 (*q*, *Me*CH_2); 0.0 (*q*, Me_3Si); −6.1 (*q*, MeSi). CI–MS: 497 $[M+H]^+$.

Data of (Si*R**,*S**,*Z*)-**9c**: IR: 3060*w*, 3020*w*, 2950*s*, 2920*s*, 2890*s*, 2850*s*, 1605*w*, 1580*s*, 1485*w*, 1460*m*, 1440*m*, 1410*w*, 1385*w*, 1375*m*, 1360*w*, 1310*w*, 1265*s*, 1250*s*, 1135*w*, 1100*s*, 1070*s*, 1025*m*, 1010*w*, 1000*w*, 980*w*, 920*w*, 905*m*, 890*m*, 860*s*, 840*s*, 825*s*, 780*s*, 760*m*, 730*s*, 600*s*. ^{1}H-NMR: 7.32–7.10 (*m*, 10 arom. H); 4.50, 4.45 (*AB*, J_{AB}=6.1, Ph*C*H_2O); 3.48, 3.36 (*AB*, J_{AB}=12.7, Si*C*H_2O); 2.03–1.99 (*m*, Bu(Me)*C*H); 1.27–1.02 (*m*, Me(*C*H_2)$_3$); 1.01 (*s*, *t*-Bu); 0.84 (*d*, *J*=7.1, Bu(*Me*)CH); 0.76 (*t*, *J*=6.9, *Me*CH_2); 0.27 (*s*, MeSi); −0.15 (*s*, Me_3Si). ^{1}H,^{1}H-NOE: irrad. at −0.15, responsive signals at 7.32–7.10, 4.50, 4.45, 3.48, 3.36, 1.01, and 0.27. ^{13}C-NMR: 157.1 (*s*, Ph*C*=); 138.5, 138.2 (2*s*, 2 arom. C); 128.3 (*d*, arom. C); 126.8, 126.5 (2*d*, 2×2 arom. C); 126.4 (*d*, arom. C); 126.1, 125.7 (2*d*, 2×2 arom. C); 116.9 (*s*, SiC=); 75.6 (*t*, Ph*C*H_2O); 62.4 (*t*, Si*C*H_2O); 35.5 (*t*, Pr*C*H_2); 34.6 (*d*, Bu(Me)*C*H); 29.5 (*t*, Et*C*H_2); 27.3 (*q*, *Me*$_3$C); 21.4 (*t*, Me*C*H_2); 20.3 (*d*, Bu(*Me*)CH); 17.6 (*s*, (Me)$_3$*C*); 12.8 (*q*, *Me*CH_2); 0.0 (*q*, Me_3Si); −6.2 (*q*, MeSi). CI–MS: 497 $[M+H]^+$.

*3.6. (Si*R*,R*,E)-, (Si*R*,S*,E)-, (Si*R*,R*,Z)-, and (Si*R*,S*,Z)-2-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-(trimethylsiloxy)-1,3-diphenylpent-1-ene (Si*R*,R*,E)-**9d**, (Si*R*,S*,E)-**9d**, (Si*R*,R*,Z)-**9d**, and (Si*R*,S*,Z)-**9d***

According to 3.1, (*E*)-**6b** (80 mg, 0.19 mmol) was reacted with Et_2CuLi (0.62 mmol) and TMSCl (0.1 ml, 0.88 mmol) to give (Si*R**,*R**,*E*)-**9d**, (Si*R**,*S**,*E*)-**9d**, (Si*R**,*R**,*Z*)-**9d**, and (Si*R**,*S**,*Z*)-**9d** (91 mg, 0.17 mmol, 89%) as an inseparable mixture. ^{1}H-NMR: rather complex; indicates the presence of the title structures. Structural proof is given with the derived products of the type **11d**.

*3.7. (Si*R*,R*,E)-, (Si*R*,S*,E)-, (Si*R*,R*,Z)-, and (Si*R*,S*,Z)-2-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-1-(trimethylsiloxy)-1,3-diphenylhept-1-ene Si*R*,R*,E)-**9e**, (Si*R*,S*,E)-**9e**, (Si*R*,R*,Z)-**9e**, and (Si*R*,S*,Z)-**9e***

According to 3.1, (*E*)-**6b** (80 mg, 0.19 mmol) was reacted with Bu_2CuLi (0.37 mmol) and TMSCl (0.1 ml, 0.88 mmol) to give (Si*R**,*R**,*E*)-**9e**, (Si*R**,*S**,*E*)-**9e**, (Si*R**,*R**,*Z*)-**9e**, and (Si*R**,*S**,*Z*)-**9e** (63 mg, 0.11 mmol, 59%) as an inseparable mixture. ^{1}H-NMR: rather complex; indicates the presence of the title structures. Structural proof is given with the derived products of the type **11e**.

4. Hydrolysis of the enol ethers of the type 8 and 9

4.1. General procedure

To a soln. of the respective silyl enol ether in acetone (approx. 0.1 M) was added conc. H_2SO_4 (2–3 drops to 1.5 ml). The mixture was diluted with H_2O, neutralized with aq. $NaHCO_3$ soln., extracted with Et_2O, and chromatographed (SiO_2, hexane/EtOAc 25:1).

*4.2. (1-[(tert-Butyl)dimethylsilyl]-2-phenylpropyl phenyl ketones **10** and **10′***

According to 4.1, compounds of the type **8** gave equal amounts of the epimeric compounds **10** (first eluting) and **10′** (second eluting) as colorless oils in 66–71% yield. The relative configurations of the stereogenic centers could not be elaborated.

Data of **10** (colorless oil): IR: 3080*w*, 3060*w*, 3020*m*, 2950*s*, 2920*s*, 2890*m*, 2880*m*, 2850*s*, 1655*s*, 1595*m*, 1575*m*, 1490*m*, 1460*m*, 1445*m*, 1410*w*, 1390*w*, 1360*w*, 1350*m*, 1330*m*, 1305*w*, 1285*s*, 1275*s*, 1250*m*, 1215*m*, 1205*m*, 1180*m*, 1155*w*, 1140*w*, 1070*m*, 1025*w*, 1015*w*, 1000*s*, 990*s*, 930*w*, 905*w*, 895*w*, 835*s*, 820*s*, 805*s*, 770*m*, 760*s*, 745*s*, 720*m*, 700*s*, 690*s*. ^{1}H-NMR: 7.82–7.15 (*m*, 10 arom. H); 3.78 (*d*, *J*=8.2, SiCH); 3.56–3.46 (*m*, Me(Ph)C*H*); 1.36 (*d*, *J*=6.8, *Me*(Ph)CH); 0.67 (*s*, *t*-Bu) −0.07, −0.17 (2*s*, Me_2Si). ^{13}C-NMR: 203.8 (*s*, C=O); 147.2, 130.2, (2*s*, 2 arom. C); 132.2, 128.4, 128.3, 127.4, 126.3 (5*d*, 10 arom. C); 45.2 (*d*, SiCH); 41.3 (*d*, Me(Ph)*C*H); 27.0 (*q*, *Me*$_3$C); 22.4 (*q*, *Me*(Ph)CH); 17.9 (*s*, Me$_3$*C*); −5.2, −5.4 (2*q*, Me_2Si). CI–MS: 339 $[M+H]^+$.

Data of **10′** (colorless crystals): M.p. 116–118°C (from oil). IR ($CHCl_3$): 3080*w*, 3060*w*, 3020*w*, 2969*s*, 2930*s*, 2890*m*, 2880*m*, 2850*s*, 1660*s*, 1595*m*, 1580*m*, 1490*w*, 1460*m*, 1450*m*, 1445*m*, 1410*w*, 1390*w*, 1375*w*, 1360*m*, 1330*s*, 1280*s*, 1260*s*, 1190*m*, 1180*m*, 1120*m*, 1090*s*, 1015*s*, 1000*s*, 985*m*, 935*w*, 900*m*, 830*s*, 700*s*. ^{1}H-NMR: 7.69–6.97 (*m*, 10 arom. H); 3.80 (*d*, *J*=11.2, SiCH); 3.63–3.53 (*m*, Me(Ph)C*H*); 1.43 (*d*, *J*=7.0, *Me*(Ph)CH); 0.94 (*s*, *t*-Bu) 0.20, −0.04 (2*s*, Me_2Si). ^{13}C-NMR: 203.3 (*s*, C=O); 147.7, 139.4, (2*s*, 2 arom. C); 132.0, 128.1, 128.0, 126.9, 125.7 (5*d*, 10 arom. C); 46.8 (*d*, SiCH); 40.9 (*d*, Me(Ph)*C*H); 27.5 (*q*, *Me*$_3$C); 24.0 (*q*, *Me*(Ph)CH); 18.2 (*s*, Me$_3$*C*); −3.7, −5.0 (2*q*, Me_2Si). CI–MS: 339 $[M+H]^+$.

*4.3. (Si*R*,3R*)- and (Si*R*,3S*)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-2-phenylpropyl phenyl ketones (Si*R*,3R*)-**11a**, (Si*R*,3S*)-**11a**, (Si*R*,3R*)-**11a′**, and (Si*R*,3S*)-**11a′***

According to 4.1, compounds of the type **9a** gave inseparable mixtures of epimeric compounds (Si*R**,3*R**)-**11a**/(Si*R**,3*S**)-**11a** (first eluting) and of (Si*R**,3*S**)-**11a′**/(Si*R**,3*S**)-**11a′** (second eluting) as colorless oils. Yields, diastereomeric ratios, and diastereomeric excesses (in respect to the stereogenic centers at silicon and C(3)), see Table 1. Likewise, (−)-(Si*R*,3*S*)-**11a** (296 mg, 0.67 mmol,

84%) and (+)-(Si*R*,3*S*)-**11a′** (38 mg, 0.09 mmol, 11%) were obtained from (+)-(Si*R*,*S*,*Z*)-**6a** (290 mg, 0.79 mmol) by reaction with Ph_2CuLi (6 eq.) according to 3.1 and direct hydrolysis according to 4.1.

Data of (Si*R**,3*R**)-**11a** (from (*Z*)-**6a**, slightly contaminated with (Si*R**,3*S**)-**11a**): IR: 3080*w*, 3060*w*, 3020*m*, 2960*s*, 2920*s*, 2880*m*, 2750*s*, 2710*w*, 1655*s*, 1595*m*, 1525*m*, 1490*m*, 1460*m*, 1445*s*, 1390*w*, 1380*m*, 1360*m*, 1350*m*, 1325*m*, 1010*w*, 1285*m*, 1265*s*, 1250*s*, 1220*s*, 1205*s*, 1180*m*, 1155*w*, 1090*s*, 1070*s*, 1025*m*, 1020*s*, 1000*m*, 990*m*, 935*w*, 905*w*, 820*s*, 800*m*, 660*s*, 645*s*, 635*s*, 700*s*. ^{1}H-NMR: 7.87–7.16 (*m*, 15 arom. H); 4.11, 4.05 (*AB*, J_{AB}=11.9, PhCH_2O); 3.99 (*d*, *J*=7.9, SiCH); 3.63–3.50 (*m*, Me(Ph)C*H*); 3.14, 2.95 (*AB*, J_{AB}=12.9, $SiCH_2O$); 1.37 (*d*, *J*=6.9, *Me*(Ph)CH); 0.82 (*s*, *t*-Bu); 0.13 (*s*, MeSi). ^{13}C-NMR: 203.6 (*s*, C=O); 147.0, 140.0, 138.8 (3*s*, 3 arom. C); 132.1, 128.4, 128.3, 128.1, 127.9, 127.3, 127.0, 126.3 (8*d*, 15 arom. C); 76.7 (*t*, PhCH_2O); 61.0 (*t*, $SiCH_2O$); 43.6 (*d*, SiCH); 40.9 (*d*, Me(Ph)*C*H); 27.5 (*q*, *Me*$_3$C); 22.2 (*q*, *Me*(Ph)CH); 18.1 (*s*, Me$_3$*C*); −8.3 (*q*, MeSi). CI–MS: 445 $[M+H]^+$.

Data of (Si*R**,3*R**)-**11a′** (from (*Z*)-**6a**, slightly contaminated with (Si*R**,3*S**)-**11a′**): IR: 3080*w*, 3060*m*, 3020*m*, 2960*s*, 2930*s*, 2880*s*, 2850*s*, 2810*w*, 1660*s*, 1595*m*, 1575*m*, 1490*m*, 1465*m*, 1455*s*, 1445*s*, 1404*w*, 1390*w*, 1380*m*, 1360*m*, 1325*m*, 1280*m*, 1260*s*, 1210*m*, 1190*m*, 1180*m*, 1155*m*, 1090*s*, 1070*s*, 1025*m*, 1015*m*, 1000*m*, 985*w*, 935*w*, 905*m*, 830*s*, 805*m*, 785*m*, 760*s*, 700*s*. ^{1}H-NMR: 7.94–6.94 (*m*, 15 arom. H); 4.31 (*s*, PhCH_2O); 3.89 (*d*, *J*=11.1, SiCH); 3.71–3.60 (*m*, Me(Ph)C*H*); 3.32, 3.22 (*AB*, J_{AB}=12.9, $SiCH_2O$); 1.45 (*d*, *J*=7.0, *Me*(Ph)CH); 0.97 (*s*, *t*-Bu); 0.12 (*s*, MeSi). ^{13}C-NMR: 203.3 (*s*, C=O); 147.5, 139.2, 138.6 (3*s*, 3 arom. C); 131.9, 128.2, 128.1, 128.0, 127.5, 127.3, 127.0, 125.8 (8*d*, 15 arom. C); 77.0 (*t*, PhCH_2O); 61.0 (*t*, $SiCH_2O$); 46.3 (*d*, SiCH); 41.0 (*d*, Me(Ph)*C*H); 27.8 (*q*, *Me*$_3$C); 23.7 (*q*, *Me*(Ph)CH); 18.7 (*s*, Me$_3$*C*); −6.4 (*q*, MeSi). CI–MS: 445 $[M+H]^+$.

Data of (−)-(Si*R*,3*S*)-**11a** (from (*R*,*E*)-**6a**, slightly contaminated with (Si*R*,3*R*)-**11a**): $[\alpha]_D^{23}$=−13.8 (c=1.0, THF). IR: 3080*w*, 3060*m*, 3020*m*, 2960*s*, 2930*s*, 2880*s*, 2850*s*, 2810*m*, 1660*s*, 1595*m*, 1575*m*, 1490*m*, 1460*m*, 1450*s*, 1445*s*, 1430*w*, 1390*w*, 1380*m*, 1360*m*, 1350*m*, 1330*m*, 1310*w*, 1285*m*, 1265*s*, 1250*s*, 1205*s*, 1180*m*, 1155*w*, 1090*m*, 1070*s*, 1025*m*, 1000*s*, 995*s*, 935*w*, 905*m*, 825*s*, 805*s*, 780*m*, 760*s*, 750*s*, 735*s*, 700*s*. ^{1}H-NMR: 7.87–7.11 (*m*, 15 arom. H); 4.24, 4.18 (*AB*, J_{AB}=11.9, PhCH_2O); 4.01 (*d*, *J*=8.5, SiCH); 3.66–3.56 (*m*, Me(Ph)C*H*); 2.97, 2.64 (*AB*, J_{AB}=12.8, $SiCH_2O$); 1.33 (*d*, *J*=6.9, *Me*(Ph)CH); 0.76 (*s*, *t*-Bu) 0.13 (*s*, MeSi). ^{13}C-NMR: 203.8 (*s*, C=O); 146.9, 139.9, 138.8 (3*s*, 3 arom. C); 132.3, 128.5, 128.3, 128.1, 127.4, 127.2, 126.3 (7*d*, 15 arom. C); 76.9 (*t*, PhCH_2O); 60.7 (*t*, $SiCH_2O$); 43.2 (*d*, SiCH); 41.1 (*d*, Me(Ph)*C*H); 27.5 (*q*, *Me*$_3$C); 22.5 (*q*, *Me*(Ph)CH); 18.2 (*s*, Me$_3$*C*); −8.3 (*q*, MeSi). CI–MS: 445 $[M+H]^+$.

Data of (+)-(Si*R*,3*S*)-**11a′** (from (*R*,*E*)-**6a**, slightly contaminated with (Si*R*,3*R*)-**11a′**): $[\alpha]_D^{23}$=33.6 (c=1.2, THF). IR: 3080*w*, 3060*w*, 3020*m*, 2960*s*, 2920*s*, 2850*s*, 2810*w*, 1725*w*, 1685*w*, 1660*s*, 1595*m*, 1580*m*, 1490*m*, 1470*m*, 1450*s*, 1445*s*, 1390*w*, 1375*m*, 1360*m*, 1325*m*, 1280*m*, 1260*s*, 1210*m*, 1190*m*, 1180*m*, 1155*w*, 1090*s*, 1070*s*, 1025*m*, 1015*m*, 1000*m*, 985*m*, 935*w*, 900*w*, 830*s*, 800*m*, 790*m*, 760*s*, 735*s*, 700*s*. ^{1}H-NMR: 7.69–6.91 (*m*, 15 arom. H); 4.29, 4.23 (*AB*, J_{AB}=11.8, PhCH_2O); 3.94 (*d*, *J*=11.2, SiCH) 3.66–3.55 (*m*, Me(Ph)C*H*); 3.30, 3.13 (*AB*, J_{AB}=12.8, $SiCH_2O$); 1.44 (*d*, *J*=6.8, *Me*(Ph)CH); 1.04 (*s*, *t*-Bu); 0.11 (*s*, MeSi). ^{13}C-NMR: 203.0 (*s*, C=O); 147.3, 139.2, 138.6 (3*s*, 3 arom. C); 131.8, 128.0, 127.9, 127.8, 127.4, 127.1, 127.0, 126.0 (8*d*, 15 arom. C); 76.9 (*t*, PhCH_2O); 61.7 (*t*, $SiCH_2O$); 45.6 (*d*, SiCH); 41.1 (*d*, Me(Ph)*C*H); 28.0 (*q*, *Me*$_3$C); 23.7 (*q*, *Me*(Ph)CH); 18.6 (*s*, Me$_3$*C*); −7.5 (*q*, MeSi). CI–MS: 445 $[M+H]^+$.

*4.4. (Si*R**,3*R**)- and (Si*R**,3*S**)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-2-methylbutyl phenyl ketones (Si*R**,3*R**)-11b, (Si^{R}*,3^{S}*)-11b, (Si^{R}*,3^{R}*)-11b′, and (Si*R**,3*S**)-11b′*

According to 4.1, compounds of the type **9b** gave inseparable mixtures of (Si*R**,3*R**)-**11b**, (Si*R**,3*S**)-**11b**, (Si*R**,3*R**)-**11b′**, and (Si*R**,3*S**)-**11b′** as colorless oils. Yields, diastereomeric ratios, and diastereomeric excesses (in respect to the stereogenic centers at silicon and C(3)), see Table 1.

Data of mixture (Si*R**,3*R**)-**11b**/(Si*R**,3*R**)-**11b′** (from (*Z*)-**6a**, slightly contaminated with (Si*R**,3*S**)-**11b**/(Si*R**,3*S**)-**11b′**): IR: 3080*w*, 3060*m*, 3030*m*, 2960*s*, 2930*s*, 2850*s*, 2810*m*, 1730*w*,

1660*s*, 1595*m*, 1575*m*, 1490*w*, 1460*s*, 1445*s*, 1430*m*, 1410*w*, 1390*m*, 1380*m*, 1360*m*, 1320*m*, 1300*w*, 1280*m*, 1255*s*, 1210*s*, 1205*s*, 1180*m*, 1155*m*, 1095*s*, 1070*s*, 1035*m*, 1000*m*, 990*m*, 935*w*, 905*m*, 825*s*, 805*s*, 780*m*, 735*s*, 700*s*. ^{1}H-NMR (major two isomers): 7.87–7.83, 7.43–7.04 (2*m*, 10 arom. H); 4.23, 4.05, 4.01 (*s* and *AB*, J_{AB}=12.2, PhCH_2O); 3.62, 3.44 (2*d*, *J*=5.6, 7.9, SiCH); 3.19, 3.11, 3.14, 2.89 (2*AB*, J_{AB}=12.9, 12.9, SiCH_2O); 2.23–2.10, 2.07–1.98 (2*m*, Et(Me)C*H*); 1.55–1.39, 1.20–1.05 (2*m*, MeCH_2); 1.00, 0.99 (2*d*, *J*=6.8, 6.8, Et(*Me*)CH); 0.91, 0.81 (2*s*, *t*-Bu); 0.81, 0.72 (2*t*, *J*=7.8, 7.4, *Me*CH_2); 0.03, 0.00 (2*s*, MeSi). ^{13}C-NMR (major two isomers): 204.0, 203.5 (2*s*, C=O); 140.1, 139.9, 138.8, 138.7 (4*s*, 2 arom. C); 132.2, 132.1, 128.4, 128.3, 128.2, 128.1, 128.0, 127.5, 127.2, 127.0 (10*d*, 10 arom. C); 77.9, 76.8 (2*t*, PhCH_2O); 61.6, 61.1 (2*t*, SiCH_2O); 44.0, 41.3 (2*d*, SiCH); 36.4, 36.2 (2*d*, Et(Me)*C*H); 31.1, 29.2 (2*t*, MeCH_2); 27.7 (*q*, *Me*$_3$C); 20.1, 18.6 (2*q*, *Me*CH); 18.4, 18.2 (2*s*, Me$_3$*C*); 12.2, 11.7 (2*q*, *Me*CH_2); −6.8, −8.3 (2*q*, MeSi). ^{29}Si-NMR: 4.92, 4.26, 4.25, 3.87 (ratio 3:38:58:1). CI–MS: 397 $[M+H]^+$.

Data of mixture (Si*R**,3*S**)-**11b**/(Si*R**,3*S**)-**11b′** (from (*E*)-**6a**, slightly contaminated with (Si*R**,3*R**)-**11b**/(Si*R**,3*R**)-**11b′**): IR: 3080*w*, 3060*m*, 3020*m*, 2960*s*, 2920*s*, 2850*s*, 2810*m*, 1660*s*, 1595*m*, 1575*m*, 1490*w*, 1460*s*, 1445*s*, 1430*m*, 1390*m*, 1380*m*, 1360*m*, 1320*m*, 1275*m*, 1250*s*, 1210*s*, 1180*m*, 1155*w*, 1105*m*, 1090*m*, 1070*s*, 1025*m*, 1000*m*, 990*m*, 935*w*, 905*m*, 825*m*, 805*m*, 780*m*, 730*s*, 700*s*. ^{1}H-NMR (major two compounds): 7.93–7.90, 7.51–7.11 (2*m*, 10 arom. H); 4.36, 4.17, 4.12 (*s* and *AB*, J_{AB}=12.0, PhCH_2O); 3.61, 3.58 (2*d*, *J*=6.0, 7.7, SiCH); 3.31, 3.23, 3.23, 3.02 (2*AB*, J_{AB}=13.0, 13.0, SiCH_2O); 2.25–2.09 (*m*, Et(Me)C*H*); 1.70–1.50 1.30–1.12 (2*m*, MeCH_2); 1.05 1.03 (2*d*, *J*=6.7, 6.7, Et(*Me*)CH); 0.97, 0.87 (2*s*, *t*-Bu); 0.89, 0.81 (2*t*, *J*=5.9, 7.3, *Me*CH_2); 0.08, 0.07 (2*s*, MeSi). ^{13}C-NMR (major two compounds): 203.9, 203.6 (2*s*, C=O); 140.1, 139.9, 138.8, 138.7 (4*s*, 2 arom. C); 132.2, 132.1, 128.3, 128.2, 128.1, 128.0, 128.5, 127.3, 127.0 (9*d*, 10 arom. C); 77.1, 76.8 (2*t*, PhCH_2O); 61.7, 61.0 (2*t*, SiCH_2O); 43.4, 42.1 (2*d*, SiCH); 36.2 (*d*, Et(Me)*C*H); 31.0, 28.8 (2*t*, MeCH_2); 27.9, 27.7 (2*q*, *Me*$_3$C); 20.1, 18.7 (2*q*, *Me*CH); 18.4, 18.3 (2*s*, Me$_3$*C*); 12.1, 11.7 (2*q*, *Me*CH_2); −7.3, −7.9 (2*q*, MeSi). ^{29}Si-NMR: 4.92, 4.26, 4.25, 3.87 (ratio 59:5:5:31). CI–MS: 397 $[M+H]^+$.

*4.5. (Si*R**,3*R**)- and (Si*R**,3*S**)-1-{[(Benzyloxy)methyl](tert-butyl)methylsilyl}-2-methylhexyl phenyl ketones (Si*R**,3*R**)-**11c**, (Si*R**,3*S**)-**11c**, (Si*R**,3*R**)-**11c′**, and (Si*R**,3*S**)-**11c′***

According to 4.1, compounds of the type **9c** gave inseparable mixtures of (Si*R**,3*R**)-**11c**, (Si*R**,3*S**)-**11c**, (Si*R**,3*R**)-**11c′**, and (Si*R**,3*S**)-**11c′** as colorless oils. Yields, diastereomeric ratios, and diastereomeric excesses (in respect to the stereogenic centers at silicon and C(3)), see Table 1.

Data of mixture (Si*R**,3*R**)-**11c**/(Si*R**,3*R**)-**11c′** (from (*Z*)-**6a**, slightly contaminated with (Si*R**,3*S**)-**11c**/(Si*R**,3*S**)-**11c′**): IR: 3080*w*, 3060*w*, 3020*w*, 2950*s*, 2920*s*, 2850*s*, 1655*s*, 1595*m*, 1575*m*, 1490*w*, 1465*m*, 1445*m*, 1375*m*, 1360*m*, 1340*w*, 1325*w*, 1275*m*, 1250*m*, 1220*m*, 1210*m*, 1180*m*, 1155*w*, 1105*m*, 1090*m*, 1070*s*, 1025*w*, 1000*m*, 995*m*, 935*w*, 905*w*, 825*m*, 800*m*, 780*m*, 735*s*, 695*s*. ^{1}H-NMR (major two isomers): 7.90–7.86, 7.48–7.06 (2*m*, 10 arom. H); 4.27, 4.06 (2*s*, PhCH_2O); 3.64, 3.48 (2*d*, *J*=5.6, 7.6, SiCH); 3.23, 3.14, 3.14, 2.91 (2*AB*, J_{AB}=12.8, 12.8, SiCH_2O); 2.30–2.21, 2.20–2.16 (2*m*, Bu(Me)C*H*); 1.53–1.03 (*m*, Me(CH_2)$_3$); 1.04, 1.02 (2*d*, *J*=4.5, 4.7, *Me*CH); 0.95, 0.84 (2*s*, *t*-Bu); 0.78, 0.76 (2*t*, *J*=5.1, 4.8 *Me*CH_2); 0.07, 0.04 (2*s*, MeSi). ^{13}C-NMR (major two isomers): 204.0, 203.6 (*s*, C=O); 140.2, 139.9, 138.7, 138.6 (4*s*, 2 arom. C); 132.2, 132.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.5, 127.2, 127.0 (10*d*, 10 arom. C); 77.0, 76.8 (2*t*, PhCH_2O); 61.6, 61.1 (2*t*, SiCH_2O); 44.2, 41.7 (2*d*, SiCH); 38.1, 36.2 (2*t*, PrCH_2); 34.6 (*d*, Me(Bu)*C*H); 29.9, 29.7 (2*t*, EtCH_2); 27.8, 27.7 (2*q*, *Me*$_3$C); 22.7 (*t*, MeCH_2); 20.7, 19.1 (2*q*, *Me*CH); 18.4, 18.2 (2*s*, Me$_3$*C*); 14.0 (*q*, *Me*CH_2); −6.8, −8.2 (2*q*, MeSi). ^{29}Si-NMR: 4.93, 4.28, 4.24, 3.89 (ratio 2.5:46:48:3.5). CI–MS: 425 $[M+H]^+$.

Data of mixture (Si*R**,3*S**)-**11c**/(Si*R**,3*S**)-**11c′** (from (*E*)-**6a**, slightly contaminated with (Si*R**,3*R**)-**11c**/(Si*R**,3*R**)-**11c′**): IR: 3080*w*, 3060*m*, 3020*m*, 2850*s*, 2820*s*, 2790*s*, 2810*m*, 1660*s*, 1595*m*, 1575*m*, 1490*w*, 1460*s*, 1445*s*, 1375*m*, 1360*m*, 1320*m*, 1275*m*, 1250*s*, 1220*m*, 1210*m*, 1180*m*,

1155*w*, 1090*m*, 1070*s*, 1025*m*, 1000*m*, 995*m*, 935*w*, 905*w*, 825*s*, 800*m*, 780*m*, 695*s*. ^{1}H-NMR (major two compounds): 7.93–7.89, 7.49–7.11 (2*m*, 10 arom. H); 4.36, 4.16, 4.12 (*s* and *AB*, *J*=11.5, PhCH_2O); 3.59, 3.57 (2*d*, *J*=6.1, 7.8, SiCH); 3.31, 3.24, 3.23, 3.02 (2*AB*, J_{AB}=12.9, 12.9, SiCH_2O); 2.26–2.19, (*m*, Bu(Me)C*H*); 1.55–1.19 (*m*, Me(CH_2)$_3$); 1.05, 1.03 (2*d*, *J*=5.7, 6.7, *Me*CH); 0.97, 0.88 (2*s*, *t*-Bu); 0.83, 0.81 (2*t*, *J*=6.8, 7.6, *Me*CH_2); 0.08, 0.06 (2*s*, MeSi). ^{13}C-NMR (major two compounds): 203.9, 203.7 (*s*, C=O); 140.1, 140.0, 138.8, 138.7 (4*s*, 2 arom. C); 132.2, 132.1, 128.3, 128.24, 128.2, 128.1, 128.0, 127.5, 127.3, 127.1 (10*d*, 10 arom. C); 77.1, 76.8 (2*t*, PhCH_2O); 61.7, 61.0 (2*t*, SiCH_2O); 43.6, 42.3 (2*d*, SiCH); 38.1, 35.9 (2*t*, PrCH_2); 34.7, 34.5 (2*d*, Bu(Me)C*H*); 29.9, 29.8 (2*t*, EtCH_2); 27.9, 27.7 (2*q*, *Me*$_3$C); 22.7 (*t*, MeCH_2); 20.8, 19.2 (2*q*, *Me*CH); 18.4, 18.3 (2*s*, Me$_3$*C*); 14.0 (*q*, *Me*CH_2); −7.3, −7.9 (2*q*, MeSi). ^{29}Si-NMR: 4.93, 4.28, 4.24, 3.89 (ratio 63:5:4:28). CI–MS: 425 [*M*+H]$^+$.

*4.6. (Si*R**,3R*)- and (Si*R**,3S*)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-2-phenylbutyl phenyl ketones (Si*R**,3R*)-**11d**, (Si*R**,3S*)-**11d**, (Si*R**,3R*)-**11d′**, and (Si*R**,3S*)-**11d′***

According to 4.1, compounds **9d** (91 mg, 0.17 mmol, 89%) gave inseparable mixtures of epimeric (Si*R**,3*R**)-**11d**/(Si*R**,3*S**)-**11d** (25 mg, 0.05 mmol, 32%, first eluting, ratio 5:1, determined by ^{1}H-NMR) and of (Si*R**,3*R**)-**11d′**/(Si*R**,3*S**)-**11d′** (32 mg, 0.07 mmol, 41%, second eluting, ratio 1.6:1, determined by ^{1}H-NMR).

Data of (Si*R**,3*R**)-**11d**/(Si*R**,3*S**)-**11d** (as a mixture): IR: 3080*w*, 3060*m*, 3020*m*, 2980*s*, 2930*s*, 2850*s*, 2810*m*, 1660*s*, 1595*m*, 1575*m*, 1490*m*, 1460*m*, 1450*s*, 1445*s*, 1430*w*, 1390*w*, 1375*m*, 1360*m*, 1325*m*, 1310*w*, 1290*w*, 1260*s*, 1250*s*, 1215*m*, 1200*m*, 1180*m*, 1155*w*, 1140*w*, 1105*m*, 1090*s*, 1070*s*, 1025*m*, 1010*m*, 1000*m*, 985*m*, 960*w*, 935*w*, 905*w*, 860*m*, 830*m*, 800*m*, 780*m*, 755*m*, 740*s*, 700*s*. ^{1}H-NMR: 7.94–7.82, 7.56–7.12 (2*m*, 15 arom. H); 4.20, 4.14, 4.11, 4.05 (2*AB*, J_{AB}=11.9, 9.3, PhCH_2O); 4.05, 4.02 (2*d*, *J*=9.3, 10.6, SiCH); 3.35–3.25 (*m*, Ph(Et)C*H*); 3.13, 2.97, 2.90, 2.47 (2*AB*, J_{AB}=12.9, 12.8, SiCH_2O); 1.90–1.77, 1.70–1.57 (2*m*, MeCH_2); 0.79, 0.75 (2*s*, *t*-Bu) 0.59, 0.57 (2*t*, *J*=5.9, 7.2 *Me*CH_2); −0.02, −0.07 (2*s*, MeSi). ^{13}C-NMR: 204.1, 204.0 (2*s*, C=O); 144.1, 139.9, 138.8 (3*s*, 3 arom. C); 132.4, 132.2, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.4, 127.3, 127.2, 126.4 (12*d*, 15 arom. C); 76.8, 76.7 (2*t*, PhCH_2O); 61.0, 60.1 (2*t*, SiCH_2O); 48.7, 48.6 (2*d*, SiCH); 44.3, 43.1 (2*d*, Ph(Et)C*H*); 29.2, 28.7 (2*t*, MeCH_2); 27.6 (*q*, *Me*$_3$C); 18.3, 18.1 (2*s*, Me$_3$*C*); 12.3 (*q*, *Me*CH_2); −8.4 (*q*, *Me*Si). CI–MS: 459 [*M*+H]$^+$.

Data of (Si*R**,3*R**)-**11d′** and (Si*R**,3*S**)-**11d′** (as a mixture): IR: 3080*m*, 3060*s*, 3020*s*, 2950*s*, 2920*s*, 2850*s*, 2810*m*, 1655*s*, 1595*m*, 1575*m*, 1490*m*, 1460*s*, 1450*s*, 1430*m*, 1405*m*, 1390*m*, 1375*m*, 1360*m*, 1320*m*, 1300*m*, 1255*s*, 1215*m*, 1185*m*, 1155*m*, 1105*m*, 1090*s*, 1070*s*, 1025*m*, 1010*m*, 1000*m*, 975*m*, 930*m*, 920*m*, 900*m*, 845*m*, 835*m*, 800*m*, 780*m*, 765*m*, 735*m*, 700*s*. ^{1}H-NMR: 7.68–7.62, 7.42–6.95 (2*m*, 15 arom. H); 4.33, 4.31, 4.25 (*s* and *AB*, J_{AB}=12.0, PhCH_2O); 4.00, 3.93 (2*d*, *J*=11.1, 11.0, SiCH); 3.39–3.24 (*m*, Ph(Et)C*H*); 3.34, 3.24, 3.31, 3.14 (2*AB*, J_{AB}=12.9, 12.8, SiCH_2O); 2.15–1.99, 1.70–1.58 (2*m*, MeCH_2); 1.05, 0.98 (2*s*, *t*-Bu) 0.75, 0.66 (2*t*, *J*=12.3, 7.4 *Me*CH_2); 0.10 (*s*, MeSi). ^{13}C-NMR: 203.1, 202.8 (2*s*, C=O); 144.6, 144.4, 139.4, 138.6 (4*s*, 3 arom. C); 131.8, 128.6, 128.5, 128.3, 128.2, 128.1, 128.9, 127.9, 127.7, 127.5, 127.4, 127.3, 127.1, 125.7 (14*d*, 15 arom. C); 77.1, 76.9 (2*t*, PhCH_2O); 61.8, 61.0 (2*t*, SiCH_2O); 48.4, 48.2 (2*d*, SiCH); 45.9, 45.0 (2*d*, Ph(Et)CH); 29.7, 29.1 (2*t*, MeCH_2); 28.1, 27.8 (*q*, *Me*$_3$C); 18.7, 18.1 (2*s*, Me$_3$*C*); 12.3, 12.2 (2*q*, *Me*CH_2); −6.3, −7.6 (*q*, MeSi). CI–MS: 459 [*M*+H]$^+$.

*4.7. (Si*R**,3R*)- and (Si*R**,3S*)-1-{[(Benzyloxy)methyl](*tert*-butyl)methylsilyl}-2-phenylhexyl phenyl ketones (Si*R**,3R*)-**11e**, (Si*R**,3S*)-**11e**, (Si*R**,3R*)-**11e′**, and (Si*R**,3S*)-**11e′***

According to 4.1, compounds **9e** (63 mg, 0.11 mmol, 59%) gave inseparable mixtures of epimeric (Si*R**,3*R**)-**11e**/(Si*R**,3*S**)-**11e** (17 mg, 0.03 mmol, 27%, first eluting, ratio 8:1, determined by ^{1}H-NMR) and of (Si*R**,3*R**)-**11e′** and (Si*R**,3*S**)-**11e′** (36 mg, 0.07 mmol, 66%, second eluting, ratio 3:1, determined by ^{1}H-NMR).

Data of (Si*R**,3*R**)-**11e**/(Si*R**,3*S**)-**11e** (as a mixture): IR: 3080*m*, 3060*m*, 3020*m*, 2950*s*, 2930*s*, 2850*s*, 2810*m*, 1665*s*, 1595*m*, 1580*m*, 1490*m*, 1465*s*, 1450*s*, 1445*s*, 1410*w*, 1390*w*, 1375*m*, 1360*m*, 1325*m*, 1300*w*, 1275*m*, 1259*s*, 1205*m*, 1185*m*, 1155*w*, 1105*m*, 1090*s*, 1070*s*, 1025*m*, 1000*m*, 985*m*, 935*w*, 905*m*, 825*s*, 800*m*, 780*m*, 765*s*, 735*s*, 700*s*. ^{1}H-NMR (major isomer): 7.80–7.77, 7.45–7.10 (2*m*, 15 arom. H); 4.10, 4.03 (*AB*, J_{AB}=11.9, PhCH_2O); 3.97 (*d*, *J*=8.1, SiCH); 3.35–3.28 (*m*, Ph(Bu)C*H*); 3.09, 2.94 (*AB*, J_{AB}=12.9, SiCH_2O); 1.83–1.64 (*m*, PrCH_2); 1.21–0.80 (*m*, Me(CH_2)$_2$); 0.78 (*s*, *t*-Bu) 0.71 (*t*, *J*=7.4, *Me*CH_2); −0.08 (*s*, *Me*Si). ^{13}C-NMR (major isomer): 203.8 (*s*, C=O); 144.8, 140.0, 138.8 (3*s*, 3 arom. C); 132.1, 128.4, 128.3, 128.2, 127.9, 127.3, 127.0, 126.4 (8*d*, 15 arom. C); 76.6 (*t*, PhCH_2O); 61.0 (*t*, SiCH_2O); 46.7 (*d*, SiCH); 44.0 (*d*, Ph(Bu)*C*H); 35.3 (*t*, PrCH_2); 30.3 (*t*, EtCH_2); 27.5 (*q*, *Me*$_3$C); 22.4 (*t*, MeCH_2); 15.2 (*s*, Me$_3$*C*); 13.9 (*q*, *Me*CH_2); −8.2 (*q*, MeSi). CI–MS: 487 [*M*+H]$^+$.

Data of (Si*R**,3*R**)-**11e′** and (Si*R**,3*S**)-**11e′** (as a mixture): IR: 3080*w*, 3060*m*, 3020*m*, 2950*s*, 2930*s*, 2850*s*, 2810*m*, 1660*s*, 1595*m*, 1580*m*, 1490*m*, 1465*m*, 1450*m*, 1445*m*, 1390*w*, 1375*m*, 1360*m*, 1325*m*, 1300*w*, 1280*m*, 1250*m*, 1215*m*, 1200*m*, 1180*m*, 1165*w*, 1090*m*, 1070*m*, 1025*w*, 1000*m*, 940*w*, 905*w*, 825*m*, 800*m*, 780*m*, 735*m*, 700*s*. ^{1}H-NMR: 7.67–7.61, 7.41–6.94 (2*m*, 15 arom. H); 4.33, 4.26 (2*s*, PhCH_2O); 3.98, 3.92 (2*d*, *J*=11.3, 11.0, SiCH); 3.48–3.34 (*m*, Ph(Bu)C*H*); 3.34, 3.24, 3.24, 3.12 (2*AB*, J_{AB}=13.0, 12.8, SiCH_2O); 2.06–1.95, 1.69–1.56 (2*m*, PrCH_2); 1.31–1.10 (*m*, Me(CH_2)$_2$); 1.05, 0.98 (2*s*, *t*-Bu) 0.81, 0.76 (2*t*, *J*=7.4, 7.2, *Me*CH_2); 0.11, 0.10 (2*s*, MeSi). ^{13}C-NMR: 203.2, 202.9 (2*s*, C=O); 145.0, 144.8, 139.4, 138.6 (4*s*, 3 arom. C); 131.8, 128.2, 128.0, 127.9, 127.7, 127.6, 127.4, 127.3, 127.1, 125.7 (10*d*, 15 arom. C); 77.1, 76.9 (2*t*, PhCH_2O); 61.9, 61.0 (2*t*, SiCH_2O); 46.7, 46.5 (2*d*, SiCH); 46.1, 45.2 (2*d*, Ph(Bu)*C*H); 36.6, 36.5 (2*t*, PrCH_2); 29.9, 29.8 (2*t*, EtCH_2); 28.0, 27.9 (2*q*, *Me*$_3$C); 22.6 (*t*, MeCH_2); 18.6 (*s*, Me$_3$*C*); 15.2, 14.0 (2*q*, *Me*CH_2); −6.2, −7.6 (2*q*, MeSi). CI–MS: 487 [*M*+H]$^+$.

*5. Removal of the silicon groups of compounds of the type **10** and **11***

5.1. General procedure

To a soln. of the respective α-silylated ketone in CH_3CN (0.1 M) was added TBAF (4 eq., 1 M in THF). The mixture was stirred for 1 h and diluted with H_2O. It was extracted with Et_2O and chromatographed (SiO_2, hexane/EtOAc 25:1).

*5.2. (±)- and (−)-(*R*)-Phenyl 2-phenylpropyl ketone (±)-**12a** and (−)-(*R*)-**12a***

According to 5.1, a mixture of all racemic isomeric compounds of the type **10** (159 mg, 0.47 mmol) gave (±)-**12a** (86 mg, 0.38 mmol, 82%) as a colorless oil. Likewise, a mixture of all racemic compounds of the type **11** (170 mg, 0.38 mmol) gave (±)-**12a** (75 mg, 0.33 mmol, 87%) (oil), and (−)-(Si*R*,3*S*)-**11a** (170 mg, 0.38 mmol) gave (−)-(*R*)-**12a** (75 mg, 0.33 mmol, 87%) as a colorless solid. M.p.: 45–50°C (oil for (−)-(*R*)-**12a**,[22] 45–48°C for (+)-(*S*)-**12a**[23]). $[\alpha]_D^{23}$=−12.4 (c=1.4, CCl_4)(−14.8 (c=1.2, CCl_4) for (−)-(*R*)-**12a**,[22] +13.3 (c=2.8, CCl_4) for (+)-(*S*)-**12a**[23]). IR: 3080*m*, 3050*m*, 3020*s*, 2960*s*, 2920*m*, 2870*m*, 1685*s*, 1595*s*, 1580*m*, 1490*m*, 1445*s*, 1400*m*, 1360*m*, 1310*m*, 1270*s*, 1215*s*, 1200*s*, 1175*m*, 1155*w*, 1100*w*, 1075*w*, 1020*m*, 990*s*, 935*w*, 905*w*, 875*w*, 840*w*, 835*w*, 790*w*, 755*s*, 700*s*. ^{1}H-NMR: 7.98–6.96 (*m*, 10 arom. H); 3.55–3.42 (*m*, Me(Ph)C*H*); 3.28, 3.16 (*AB* of *ABX*, J_{AB}=16.4, J_{AX}=8.2, J_{BX}=5.7, PhCOCH_2); 2.51 (*d*, *J*=6.9, *Me*CH). ^{13}C-NMR: 199.0 (*s*, C=O); 146.5, 137.2 (2*s*, 2 arom. C); 132.9, 128.5, 128.0, 126.8, 126.2 (5*d*, 10 arom. C); 47.0 (*t*, PhCO*C*H$_2$); 35.5 (*d*, Me*C*H); 15.2 (*q*, *Me*CH). CI–MS: 242 [*M*+NH_4]$^+$.

The enantiomeric excess of (−)-(*R*)-**12a** was determined by means of the Mosher method:[24] (−)-(*R*)-**12a** (160 mg, 0.71 mmol) was reduced with $LiAlH_4$ (32 mg, 0.84 mmol) in Et_2O (5 ml) to give two isomeric alcohols (ratio *ca.* 1:1, 94%), which were separated by chromatography (SiO_2, hexane/EtOAc 25:1). The first eluting isomer (20 mg, 0.09 mmol) was transferred into the respective Mosher ester (20 mg, 0.05 mmol, 61%) by treatment with (−)-(*R*)-α-methoxy-α-trifluoromethylphenylacetic acid chloride (112 mg, 0.44 mmol) in the presence of Et_3N. ^{19}F-NMR: 71.42, 71.91 (ratio 97:3).

5.3. 2-Methylbutyl phenyl ketone ***12b***

According to 5.1, a mixture of all compounds of the type **11b** (243 mg, 0.61 mmol) gave **12b** (93 mg, 0.53 mmol, 86%) as a colorless oil. IR: 3080*w*, 3060*m*, 3020*w*, 2960*s*, 2920*s*, 2870*s*, 1690*s*, 1595*m*, 1580*m*, 1470*m*, 1445*s*, 1405*m*, 1360*s*, 1320*m*, 1280*m*, 1260*m*, 1205*s*, 1180*m*, 1155*w*, 1100*w*, 1075*w*, 1015*m*, 1000*m*, 995*w*, 965*w*, 930*w*, 915*w*, 890*w*, 840*w*, 825*w*, 780*w*, 750*s*, 690*s*. ^{1}H-NMR: 7.78–7.24 (*m*, 5 arom. H); 2.76, 2.55 (*AB* of *ABX*, J_{AB}=15.7, J_{AX}=7.9, J_{BX}=5.7, PhCOCH_2); 1.96–1.85 (*m*, Me(Et)C*H*); 1.32–0.98 (*m*, MeCH_2); 0.77 (*d*, *J*=6.7, *Me*CH); 0.74 (*t*, *J*=7.4, *Me*CH_2). ^{13}C-NMR: 200.4 (*s*, C=O); 137.4 (*s*, arom. C); 132.7 (*d*, arom. C); 128.4, 128.0 (2*d*, 2×2 arom. C); 45.5 (*t*, PhCO*C*H$_2$); 31.3 (*d*, Me(Et)*C*H); 29.6 (*t*, Me*C*H$_2$); 19.4 (*q*, *Me*CH); 11.3 (*q*, *Me*CH_2). CI–MS: 194 $[M+NH_4]^+$.

5.4. 2-Methylhexyl phenyl ketone ***12c***

According to 5.1, a mixture of all compounds of the type **11c** (261 mg, 0.62 mmol) gave **12c** (112 mg, 0.55 mmol, 89%) as a colorless oil. IR: 3080*w*, 3060*w*, 3020*w*, 2950*s*, 2920*s*, 2870*s*,, 2850*s*, 1690*s*, 1595*m*, 1580*m*, 1460*m*, 1445*s*, 1405*w*, 1375*m*, 1360*m*, 1315*w*, 1280*m*, 1250*w*, 1215*m*, 1190*w*, 1180*m*, 1155*w*, 1100*w*, 1070*w*, 1000*m*, 940*w*, 910*w*, 890*w*, 840*w*, 770*w*, 750*s*, 690*s*. ^{1}H-NMR: 7.78–7.23 (*m*, 5 arom. H); 2.76, 2.55 (*AB* of *ABX*, J_{AB}=15.8, J_{AX}=7.9, J_{BX}=5.7, PhCOCH_2); 2.00–1.93 (*m*, Me(Bu)C*H*); 1.24–0.99 (*m*, Me(CH_2)$_3$); 0.77 (*d*, *J*=6.7, *Me*CH); 0.76–0.68 (*m*, *Me*CH_2). ^{13}C-NMR: 200.4 (*s*, C=O); 137.4 (*s*, arom. C); 132.7 (*d*, arom. C); 128.4, 128.0 (2*d*, 2×2 arom. C); 45.9 (*t*, PhCO*C*H$_2$); 36.8 (*t*, Pr*C*H$_2$); 29.7 (*d*, Me(Bu)*C*H); 29.2 (*t*, Et*C*H$_2$); 22.8 (*t*, Me*C*H$_2$); 19.9 (*q*, *Me*CH); 14.0 (*q*, *Me*CH_2). CI–MS: 222 $[M+NH_4]^+$.

5.6. Phenyl 2-phenylbutyl ketone ***12d***

According to 5.1, a mixture of all compounds of the type **11d** (50 mg, 0.11 mmol) gave **12d** (20 mg, 0.08 mmol, 77%) as a colorless oil. IR: 3080*m*, 3060*m*, 3020*m*, 2960*s*, 2920*s*, 2870*m*, 1725*w*, 1690*s*, 1595*m*, 1580*m*, 1490*m*, 1445*s*, 1405*m*, 1375*m*, 1365*m*, 1350*m*, 1330*m*, 1315*m*, 1280*m*, 1245*m*, 1210*m*, 1200*m*, 1180*m*, 1155*w*, 1100*w*, 1070*w*, 1115*m*, 975*m*, 950*w*, 925*w*, 905*w*, 840*w*, 785*w*, 750*s*, 700*s*. ^{1}H-NMR: 7.94–7.16 (*m*, 10 arom. H); 3.30–3.23 (2*m*, Ph(Et)C*H* and PhCOCH_2); 1.88–1.59 (*m*, MeCH_2); 0.82 (*t*, *J*=7.3, *Me*CH_2). ^{13}C-NMR: 199.1 (*s*, C=O); 144.6, 137.2 (2*s*, 2 arom. C); 132.8, 128.4, 128.3, 128.0, 127.6 (5*d*, 5×2 arom. C); 45.5 (*t*, PhCO*C*H$_2$); 43.0 (*d*, Ph(Et)*C*H); 29.1 (*t*, Me*C*H$_2$); 12.0 (*q*, *Me*CH_2). CI–MS: 256 $[M+NH_4]^+$.

5.7. Phenyl 2-phenylhexyl ketone ***12e***

According to 5.1, a mixture of all compounds of the type **11e** (50 mg, 0.10 mmol) gave **12e** (20 mg, 0.08 mmol, 73%) as a colorless oil. IR: 3080*m*, 3050*m*, 3020*s*, 3000*m*, 2950*s*, 2920*s*, 2850*s*, 1725*w*, 1690*s*, 1595*s*, 1580*m*, 1490*m*, 1465*m*, 1445*m*, 1405*m*, 1365*m*, 1350*m*, 1330*m*, 1315*m*, 1285*m*, 1270*m*, 1250*m*, 1215*m*, 1200*m*, 1180*m*, 1155*w*, 1110*w*, 1070*m*, 1020*m*, 975*m*, 940*w*, 930*w*, 905*w*, 885*w*, 870*w*, 840*w*, 750*s*, 725*m*, 700*s*. ^{1}H-NMR: 7.95–7.15 (*m*, 10 arom. H); 3.38–3.31 (*m*, Ph(Bu)C*H*); 3.29–3.21 (*m*, PhCOCH_2); 1.80–1.58 (*m*, Pr*C*H$_2$); 1.35–1.07 (*m*, Me(CH_2)$_2$); 0.83 (*t*, *J*=7.2, *Me*CH_2). ^{13}C-NMR: 198.9 (*s*, C=O); 144.7, 137.0 (2*s*, 2 arom. C); 132.5, 128.2, 128.1, 128.0, 127.2 (5*d*, 5×2 arom. C); 45.7 (*t*, PhCO*C*H$_2$); 41.0 (*d*, Ph(Bu)*C*H); 35.7 (*t*, Pr*C*H$_2$); 29.3 (*t*, Et*C*H$_2$); 22.3 (*t*, Me*C*H$_2$); 13.6 (*q*, *Me*CH_2). CI–MS: 284 $[M+NH_4]^+$.

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