Enantioselective Synthesis of Di-, Tri-, and Tetrasubstituted Allenylsilanes

Boris K. Guintchin and Stefan Bienz*

Institute of Organic Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Received July 5, 2004

A number of differently substituted allenylsilanes were prepared by cuprate substitution of α-acetoxy- and α-mesyloxypropargylic silanes. The reactions were shown to proceed stereospecifically by the attack of the nucleophile *anti* to the leaving group.

Introduction

Allenes are versatile building blocks for organic synthesis. Their application is illustrated not only with regio- and stereoselective C,C-bond formations but also with the capability of chiral allenes to retain chiral information throughout synthetic transformations.[1] It is not surprising, therefore, that particular attention was given to the stereoselective synthesis and use of chiral allenes; some more recent examples are documented with references.[2] Of specific interest to us are allenylsilanes, which have been shown to react efficiently with several types of electrophiles in a regio- and stereospecific manner.[3] For instance, their addition to saturated aldehydes and ketones provides an enantioselective entry into homopropargylic alcohols,[4] and their reaction with α,β-unsaturated carbonyl compounds gives in the Danheiser reaction access to functionalized pentano-annulated products with high control of stereochemistry.[5]

Allenylsilanes are usually prepared by organocuprate substitution of γ-acetoxyalkynylsilanes[6] or, more recently, by silylcuprate substitution of O-mesyl propargylic alcohols.[4] Since we have stereospecific access to α-hydroxypropargylic silanes of type **2** through the stereocontrolled addition of acetylides to acylsilanes **1**,[7] we planned to prepare chiral allenylsilanes **4** by alkylcuprate substitution of α-acetoxypropargylic silanes of type **3** or related compounds (Scheme 1).

* To whom correspondence should be addressed. Tel: +41 1 635 42 45. E-mail: sbienz@oci.unizh.ch.

(1) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley-Interscience: New York, 1984; p 358.

(2) (a) Satoh, T.; Hanaki, N.; Kuramochi, Y.; Inoue, Y.; Hosoya, K.; Sakai, K. *Tetrahedron* **2002**, *58*, 2533. (b) Ogasawara, M.; Ikeda, H.; Nagano, T.; Hayashi, T. *J. Am. Chem. Soc.* **2001**, *123*, 2089. (c) Schultz-Fademrecht, C.; Wibbeling, B.; Froehlich, R.; Hoppe, D. *Org. Lett.* **2001**, *3*, 1221. (d) VanBrunt, M. P.; Standaert, R. F. *Org. Lett.* **2000**, *2*, 705. (e) Ohno, H.; Toda, A.; Fujii, N.; Takemoto, Y.; Tanaka, T.; Ibuka, T. *Tetrahedron* **2000**, *56*, 2811.

(3) (a) Fleming, I.; Waterson, D. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1809. (b) Fleming, I.; Terrett, N. K. *J. Organomet. Chem.* **1984**, *264*, 99. (c) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293. (d) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063.

(4) (a) Marshall, J. A.; Adams, N. D. *J. Org. Chem.* **1997**, *62*, 8976. (b) Marshall, J. A.; Maxson, K. *J. Org. Chem.* **2000**, *65*, 630.

(5) (a) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935. (b) Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989**, *37*, 57.

(6) Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390.

(7) Gassmann, S.; Guintchin, B.; Bienz, S. *Organometallics* **2001**, *20*, 1849.

Results and Discussion

Enantiomerically Enriched α-Hydroxypropargylic Silanes. For our investigation of the stereoselective S_N2' substitution of α-functionalized propargylic silanes, we have prepared the enantiomerically enriched α-hydroxypropargylic silanes **2a**−**d** shown in Scheme 1.

Starting with acetylsilane **1**, the two pairs of diastereomeric α-hydroxypropargylic silanes (*S*,*S*)-**2a**/(*R*,*S*)-**2a′** and (*S*,*S*)-**2b**/(*R*,*S*)-**2b′** were prepared with selectivities of 85:15 and 86:14, repectively (Scheme 2). The two pairs of epimers can be separated by chromatography, but we decided to proceed with the diastereomeric mixtures. This was advantageous for the stereochemical investigation of our subsequent transformations, where relative configurations and relative amounts of isomeric products were taken as the measure.

The reactions of acetylsilane **1** with the organometals were performed as previously reported:[7] the starting ketone **1** was precomplexed with 3 equiv of $MgBr_2$ and then treated at −78 °C with an excess of the respective lithium acetylide. As observed earlier, the use of Et_2O as the solvent gave the best stereochemical results. If, for instance, CH_2Cl_2 or THF was employed instead, either a significant loss or even reversal of selectivity was observed (ratios of approximately 60:40 and 40:60, respectively). Under the optimized reaction conditions, the nucleophiles predominantly attacked the *Si*-side of the carbonyl group of **1**, which was proven with products (*S*,*S*)-**2a**/(*R*,*S*)-**2a′**. These compounds were converted to the respective α-hydroxyallylsilanes (*S*,*S*)-**5a**/(*R*,*S*)-**5a′** and correlated to independently prepared samples of the same kind.[8]

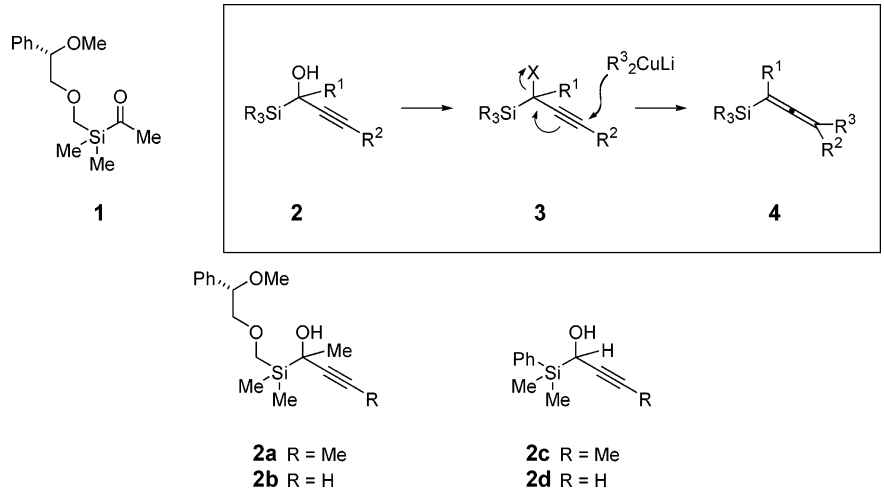
Enantiomerically enriched α-hydroxypropargylic silanes lacking the α-methyl group have not been efficiently accessible through the addition of acetylides to a chiral formylsilane related to **1**. As alternatives, resolution of racemic α-hydroxypropargylic silanes, e.g., (±)-**2c**/(±)-**2d**, or enantioselective reduction of the related unsaturated acylsilanes, i.e., **7c** and **7d**, was possible (Scheme 3). We have tested both methods.

For this purpose, racemic alcohols (±)-**2c** and (±)-**2d**, acetate (±)-**3c**, and ketones **7c** and **7d** were prepared from commercially available hydroxymethyl-substituted

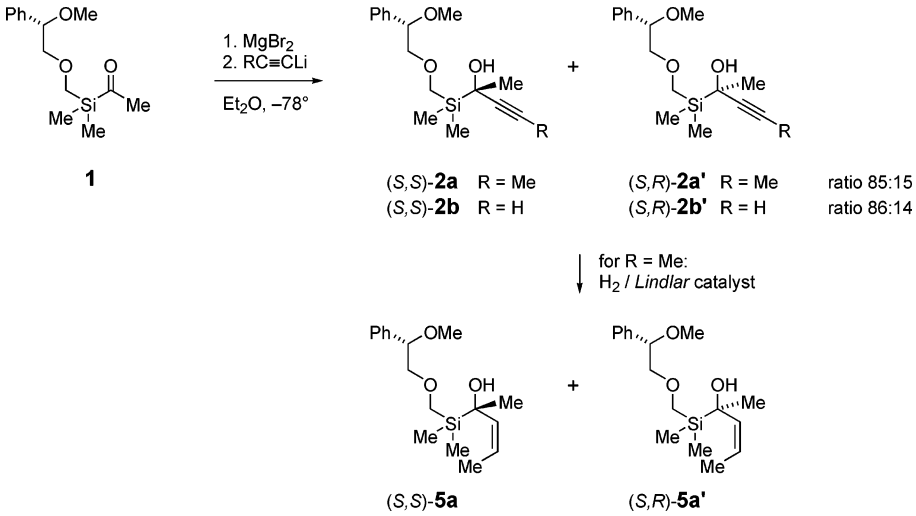
(8) Guintchin, B.; Bienz, S. *Tetrahedron* **2003**, *59*, 7527.

10.1021/om049505e CCC: $27.50
Publication on Web 09/16/2004

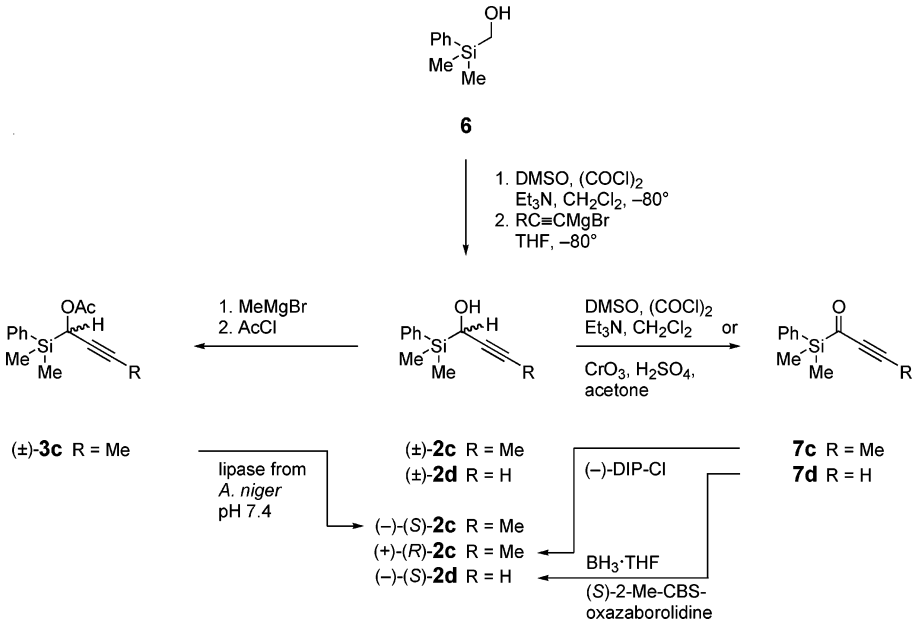
Scheme 1



Scheme 2

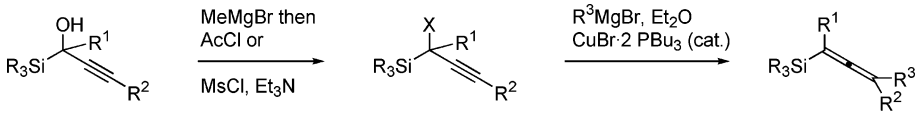


Scheme 3



silane **6**. Swern oxidation of **6** at −80 °C provided the corresponding formylsilane, which was directly treated with the respective Grignard acetylides to afford the desired racemic alcohols (±)-**2c** and (±)-**2d** in 62−63% yield. Swern oxidation of (±)-**2c** gave rise to acylsilane **7c** in 60% yield, while the same procedure applied to

Scheme 4



2 **3** **4**

(±)-**2d** delivered none of the desired product. Ketone **7d** was finally obtained in 88% yield by Jones oxidation, performed at −80 to −50 °C. Acetylation of alcohol (±)-**2c** afforded the respective acetate (±)-**3c**. As usual for α-hydroxysilanes that are prone to undergo Brook rearrangement, deprotonation was performed at low temperature with MeMgBr as the base, before it was quenched with AcCl.[9]

Resolution of the racemic alcohol (±)-**2c** or acetate (±)-**3c** was attempted by lipase-catalyzed acylation or hydrolysis, respectively. A number of lipases were tested for these reactions. While no acetylation was observed when (±)-**2c** was treated with vinyl acetates in the presence of lipases from *Pseudomonas fluorescens*, *Candida cylindracea*, *Aspergilus niger*, *Chromobacterium viskosum*, or hog pancreas, hydrolysis of (±)-**3c** with lipase of *A. niger* as the catalyst was at least partially successful. Treatment of acetate (±)-**3c** for 2 h in H_2O at pH 7.4 with the biocatalyst provided (−)-(*S*)-**2c** with an enantioselectivity (es) of 97% and a yield of 23%. Prolongation of the reaction time to 4 h, however, gave alcohol (−)-(*S*)-**2c** in slightly higher yield only (36%) but with the unsatisfactory stereoselectivity of merely 87%.

More successful than resolution was the enantioselective reduction of the ketones **7c** and **7d** (Scheme 3). Reaction of **7c** with (−)-B-chlorodiisopinocampheylborane ((−)-Ipc_2Cl)[10] gave alcohol (+)-(*R*)-**2c** in excellent 99% es and 94% yield. The same reaction performed with **7d**, however, was not successful: treatment of **7d** with (−)-DIP-Cl afforded solely degradation products. Alcohol (−)-(*S*)-**2d** was still obtained by reduction of ketone **7d** with BH_3·THF complex in the presence of the Corey−Bakshi−Shibata catalyst ((*S*)-2-methyl-CBS-oxazaborolidine[11]). When the reduction was performed with a catalytical amount of the chiral oxazaborolidine additive only, the enantiomerical purity of product (*S*)-**2d** was not satisfactory (81% es). However, when the transformation was carried out in the presence of a stoichiometric amount of the CBS reagent, the stereoselectivity increased to 98%. The absolute configurations and the enantiomeric ratios of the alcohols were determined by the Mosher method.[12]

Chiral Allenylsilanes by Substitution of α-Hydroxypropargylic Silane Derivatives. The enantiomerically enriched α-hydroxypropargylic silanes of type **2** were acylated to the respective α-acetoxypropargylic silanes of type **3** without loss of chiral information as described above (Scheme 4). Treatment of the acetates **3a**−**c** with $Ph_2CuMgBr$, prepared in situ from PhMgBr and a catalytical amount of $CuBr{\cdot}2PBu_3$, delivered, as expected, the corresponding Ph-substituted allenes **4a**−**c** (Scheme 4 and Table 1, entries 1−3). For compound (*R*)-**3c**, however, a considerable amount of alcohol (*R*)-**2c** (60%) was found in the product mixture, additionally to the desired allene (*P*)-**4c** (20% only). Alcohol (*R*)-**2c** was possibly re-formed from acetate (*R*)-**3c** by attack of the organometal at the carboxyl group. To avoid this side reaction, alcohols (*R*)-**2c** and (*S*)-**2d** were converted into the mesylates (*R*)-**3d** and (*S*)-**3e**, and reaction of these compounds with phenyl cuprate delivered the respective allenes in yields above 61 and 74%, respectively (Table 1, entries 4 and 5).

Table 1

entry	educt[a]	product[a]	yield[b] (%)	groups				
				R_3Si[c]	R^1	R^2	R^3	X
1	(*S*,*S*)-**3a**	(*S*,*M*)-**4a**	67	A	Me	Me	Ph	OAc
2	(*S*,*S*)-**3b**	(*S*,*M*)-**4b**	84	A	Me	H	Ph	OAc
3	(*R*)-**3c**	(*P*)-**4c**	20	B	H	Me	Ph	OAc
4	(*R*)-**3d**	(*P*)-**4c**	61	B	H	Me	Ph	OMs
5	(*S*)-**3e**	(*M*)-**4d**	74	B	H	H	Ph	OMs
6	(*S*,*S*)-**3a**	(*S*,*M*)-**4e**	79	A	Me	Me	Et	OAc
7	(*S*,*S*)-**3a**	(*S*,*M*)-**4f**	31	A	Me	Me	Bn	OAc
8	(*R*)-**3d**	(*P*)-**4g**	70	B	H	Me	Et	OMs
9	(*R*)-**3d**	(*P*)-**4h**	70	B	H	Me	Bn	OMs
10	(*S*)-**3e**	(*M*)-**4i**	69	B	H	H	Me	OMs
11	(*S*,*S*)-**3a**[d]	(*S*,*M*)-**4j**	11	A	Me	Me	Bu	OAc
		(*S*,*P*)-**4k**	66	66	66	66	H	H

[a] Major stereoisomer denoted only. [b] Yields refer to the mixtures of diastereomeric products that were obtained in different ratios depending on the diastereomeric composition of the starting materials. [c] A = (*S*)-[(2-methoxy-2-phenylethoxy)methyl](dimethyl)silyl, B = (dimethyl)(phenyl)silyl. [d] A stoichiometric amount of preformed Bu_2CuLi was used as the reagent.

The formation of the allenes proceeded with complete stereospecifity, transferring the centro-chiral information of the carbinol C atoms to the newly formed axis of chirality. The stereospecifity of the reactions is easiest followed with the transformation of the diasteromeric pairs of starting acetates (*S*,*S*)-**3a**/(*R*,*S*)-**3a′** and (*S*,*S*)-**3b**/(*R*,*S*)-**3b′**. Their reactions provided the two pairs of diastereomeric allenes (*S*,*M*)-**4a**/(*S*,*P*)-**4a′** and (*S*,*M*)-**4b**/(*S*,*P*)-**4b′**, which were directly distinguished and quantified by means of the $SiCH_2$ signals in the ^1H NMR spectra. Independently of the composition of the starting acetates, the product ratios always reflected the compositions of the diastereomeric mixtures of the starting materials. The absolute configurations of the major isomers of all chiral allenes were finally deduced with the Lowe−Brewster rules from the signs of the optical rotations of the compounds.[13] The formation of the *M*-configured allenes from the *S*-configured carbinols—or the *P*-configured products from the *R*-configured staring materials—allows the conclusion that the reactions proceed with remote attack of the nucleophiles *anti* to the leaving groups.

(9) Enev, V.; Stojanova, D.; Bienz, S. *Helv. Chim. Acta* **1996**, *79*, 391.

(10) (a) Soderquist, J. A.; Anderson, C. L.; Miranda, E. I.; Rivera, I.; Kabalka, G. W. *Tetrahedron Lett.* **1990**, *31*, 4677. (b) Sakagushi, K.; Mano, H.; Ohfune, Y. *Tetrahedron Lett.* **1998**, *39*, 4311.

(11) Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551.

(12) Gawley, R. E.; Aube, J. *Principles of Asymmetric Synthesis*; Pergamon Press: Oxford, 1996; Vol. 14, p 372.

(13) Lowe, G. *Chem. Commun.* **1965**, 411. Brewster, J. H. *Top. Stereochem.* **1967**, *2*, 1.

The stereospecific preparation of chiral allenylsilanes by substitution of α-hydroxypropargylic silanes is rather general, as is recognized with several further examples compiled in Table 1. The use of in situ prepared cuprates with catalytical amounts of Cu(I) salts, however, is crucial. If, for exampel, Bu_2CuLi was prepared separately and added to (*S*,*S*)-**3a**/(*R*,*S*)-**3a′** in stoichiometrical quantity, the respective allenes (*S*,*M*)-**4j**/(*S*,*P*)-**4j′** were obtained in only 11% yield, together with considerable amounts of reduction products (*S*,*P*)-**4k**/(*S*,*M*)-**4k′** (66%). Such reductions are not without precedence and are interpreted as processes typically involving Cu(III) species.[14] The use of the catalytic variation not only prevented the reductive pathway of the reactions to be followed but also eliminated the potential racemization of the products—a reaction occasionally observed with allenes in the presence of copper species.[15]

Conclusion

This article describes a flexible and general way for the preparation of differently substituted chiral allenylsilanes of high enantiomeric purities. The method is based on the stereoselective preparation of chiral α-hydroxypropargylic silanes and their stereospecific further conversion through organocopper(I)-mediated S_N2' reaction. A variety of di-, tri-, and tetrasubstituted allenylsilanes have been synthesized, and it was shown that the method thus provides an efficient tool for the preparation of a variety of allenylsilanes, ready to be used for subsequent stereoselective transformations.

Experimental Section

General Methods. Unless otherwise stated, manipulations were carried out under Ar in oven-dried glass equipment. For reactions, Et_2O and THF were freshly distilled from Na with benzophenone ketyl as indicator. Extracts were washed with saturated aqueous 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). IR spectra: neat liquid films between NaCl plates; Perkin-Elmer IR Spectrum One and Perkin-Elmer 781, in cm^{-1}. ^1H NMR spectra in $CDCl_3$; Bruker AC-300 (300 MHz); δ in ppm relative to $CHCl_3$ (δ 7.26), *J* in Hz. ^{13}C NMR spectra in $CDCl_3$; Bruker AC-300 (75.5 MHz); δ in ppm relative to $CDCl_3$ (δ 77.0); multiplicities from DEPT-135 and DEPT-90 experiments. ^{19}F NMR spectra in $CDCl_3$; Bruker AC-300 (282.4 MHz); δ in ppm relative to CCl_3F (δ 0.00). Mass spectrometry (MS): Finnigan MAT 90 or Finnigan SSQ 700. Chemical ionization mass spectrometry (CI-MS): NH_3 as the reactant gas; quasi-molecular ions and characteristic fragments; in *m*/*z* (rel %).

1. α-Hydroxypropargylic Silanes. 1.1. (2*S*,2′*S*)- and (2*R*,2′*S*)-2-{[(2-Methoxy-2-phenylethoxy)methyl]dimethylsilyl}pent-3-yn-2-ol ((*S*,*S*)-2a and (*R*,*S*)-2a′, respectively). A solution of $MgBr_2$ (1.07 mL, 1.07 mmol, of a 1 M solution in benzene/Et_2O (1:1)) was added at −80 °C to a solution of (*S*)-[(2-methoxy-2-phenylethoxy)methyl]dimethylsilyl methyl ketone (**1**[7]) (95 mg, 0.357 mmol) in Et_2O (5 mL), and it was stirred for 30 min. After addition of propynyllithium, freshly prepared from methylacetylene passing through a solution of BuLi (1.6 M in hexane, 1.10 mL, 1.78 mmol) in Et_2O (5.0 mL), the mixture was stirred for 1 h at −80 °C, slowly allowed to warm to −60 °C, and quenched by the addition of HCl (0.25 mL, 10% solution in H_2O). Extraction with Et_2O and chromatography (hexane/Et_2O, 8:2) afforded a mixture of (*S*,*S*)-**2a** and (*R*,*S*)-**2a′** (89 mg, 0.291 mmol, 81%, ratio 85:15) as a colorless oil. Spectral data from mixture. IR: 3465m, 2920m, 1100s, 845s, 700s. ^1H NMR (major): 7.38−7.27 (m, 5 arom. H); 4.33 (dd, *J* = 7.7, 4.2, PhC*H*); 3.64, 3.48 (AB of ABX, J_{AB} = 10.2, J_{AX} = 7.7, J_{BX} = 4.2, PhCHCH_2O); 3.52, 3.37 (AB, *J* = 12.7, SiCH_2O); 3.28 (s, *Me*O); 2.78 (br s, O*H*); 1.87 (s, *Me*CC); 1.42 (s, *Me*CSi); 0.14, 0.13 (2s, Me_2Si). ^1H NMR (minor): 7.38−7.27 (m, 5 arom. H); 4.33 (dd, *J* = 7.8, 3.8, PhC*H*); 3.62, 3.49 (AB of ABX, J_{AB} = 10.4, J_{AX} = 7.8, J_{BX} = 3.8, PhCHCH_2O); 3.53, 3.39 (AB, *J* = 12.6, SiCH_2O); 3.29 (s, *Me*O); 2.78 (br s, O*H*); 1.87 (s, *Me*CC); 1.44 (s, *Me*CSi); 0.16, 0.14 (2s, Me_2Si). ^{13}C NMR (major product only): 139.0 (s); 128.4 (d, 2 C); 127.9 (d); 126.9 (d, 2 C); 82.9 (s); 82.8 (d); 81.6 (s); 79.8, 63.8 (2t); 60.7 (s); 60.0, 25.4, 3.8, −6.9, −7.4 (5q). CI-MS: 324 (9); 289 (90); 257 (100). Anal. Calcd for $C_{17}H_{26}O_3Si$ (306.17): C 66.62, H 8.55. Found: C 66.71, H 8.39. The diastereomeric ratio of (*S*,*S*)-**2a** and (*R*,*S*)-**2a′** was deduced from the signals of their *Me*CSi groups (δ 1.42 for (*S*,*S*)-**2a** and 1.44 for (*R*,*S*)-**2a′**).

1.2. (2*S*,2′*S*)- and (2*R*,2′*S*)-2-{[(2-Methoxy-2-phenylethoxy)methyl]dimethylsilyl}but-3-yn-2-ol ((*S*,*S*)-2b and (*R*,*S*)-2b′, respectively). Analogously to section 1.1, **1** (348 mg, 1.31 mmol) was precomplexed with $MgBr_2$ (3.92 mmol, 3.92 mL of a 1 M solution in benzene/Et_2O (1:1)) and reacted with ethynyllithium (9.14 mmol), freshly prepared from acetylene passing through a solution of BuLi (1.6 m in hexane, 5.7 mL, 9.14 mmol) in Et_2O (10.0 mL), to give after a mixture of (*S*,*S*)-**2b** and (*R*,*S*)-**2b′** (272 mg, 0.93 mmol, 71%, ratio 86:14) as a yellowish oil. Spectral data from mixture. IR: 3470m, 3310w, 2960m, 2920m, 2900m, 2860m, 2820w, 1490w, 1450m, 1350w, 1250m, 1120s, 1095s, 1040m, 910w, 865m, 840s, 805m, 755m, 700s. ^1H NMR of major isomer ((*S*,*S*)-**2b**): 7.38−7.26 (m, 5 arom. H); 4.33 (dd, *J* = 7.9, 4.0, PhC*H*); 3.64, 3.49 (AB of ABX, J_{AB} = 10.2, J_{AX} = 7.9, J_{BX} = 4.0, PhCHCH_2O); 3.57, 3.40 (AB, *J* = 12.7, SiCH_2O); 3.35 (s, O*H*); 3.30 (s, *Me*O); 2.60 (s, CC*H*); 1.47 (s, *Me*CSi); 0.18, 0.15 (2s, Me_2Si). ^{13}C NMR of major isomer ((*S*,*S*)-**2b**): 138.8 (s); 128.4 (d, 2C); 128.0 (d); 126.9 (d, 2C); 88.1 (s); 82.4 (d); 79.8 (t); 73.4 (s); 63.6 (t); 60.4 (d); 56.9, 24.9, −7.6, −7.7 (4q). ^1H NMR of minor isomer ((*R*,*S*)-**2b′**): 7.38−7.26 (m, 5 arom. H); 4.46 (dd, *J* = 7.9, 3.8, PhC*H*); 3.62, 3.50 (AB of ABX, J_{AB} = 10.5, J_{AX} = 7.9, J_{BX} = 3.8, PhCHCH_2O); 3.58, 3.41 (AB, *J* = 12.7, SiCH_2O); 3.35 (s, O*H*); 3.28 (s, *Me*O); 2.59 (s, CC*H*); 1.49 (s, *Me*CSi); 0.19, 0.16 (2s, Me_2Si). ^{13}C NMR of minor isomer ((*R*,*S*)-**2b′**): 138.7 (s); 128.4 (d, 2C); 128.0 (d); 126.9 (d, 2C); 88.2 (s); 82.6 (d); 79.7 (t); 73.5 (s); 63.5 (t); 60.4 (d); 56.9, 25.0, −7.0, −7.1 (4q). CI-MS: 310 (17, $[M + NH_4]^+$), 275 (35), 261 (33), 243 (31), 141 (100, $C_7H_{13}OSi$). Anal. Calcd for $C_{16}H_{24}O_3Si$ (292.15): C 65.71, H 8.27. Found: C 65.50, H 8.10. Diastereomeric ratio of (*S*,*S*)-**2b** and (*R*,*S*)-**2b′** was deduced from the signals of their *Me*CSi groups (1.47 for (*S*,*S*)-**2b** and 1.49 for (*R*,*S*)-**2b′**).

1.3. (±)-1-[(Dimethyl)(phenyl)silyl]but-2-yn-1-ol ((±)-2c). DMSO (3.00 mL, 42.50 mmol) was added at −80 °C to a stirred solution of oxalyl chloride (3.20 mL, 37.45 mmol) in CH_2Cl_2 (100 mL). After 10 min, a solution of [(dimethyl)(phenyl)silyl]methanol (4.152 g, 24.97 mmol) in CH_2Cl_2 (15 mL) was added dropwise, and after 15 min, the mixture was treated with Et_3N (4.1 mL, 92.55 mmol). After 5 min at −80 °C, a solution of propynylMgBr (0.5 M solution in THF, 100.0 mL, 50.0 mmol) was added. The mixture was allowed to warm to −60 °C and was stirred at this temperature for an additional 1 h. It was quenched with H_2O, and after extraction and chromatography (hexane/Et_2O, 10:2), (±)-**2c** (3.06 g, 14.98 mmol, 62%) was obtained as a yellowish oil. IR: 3420m,

(14) (a) Ortiz de Montellano, P. R. *J. Chem. Soc., Chem. Commun.* **1973**, 709. (b) Alexakis, A.; Marek, I.; Mangeney, P.; Normant, J. F. *Tetrahedron* **1991**, *47*, 1677. (c) Johnson, C. R.; Dhanoa, D. S. *J. Org. Chem.* **1987**, *52*, 1885. (d) Dollat, J. M.; Luche, J. L.; Crabbe, P. *J. Chem. Soc., Chem. Commun.* **1977**, 761.

(15) (a) Claesson, A.; Olsson, L. I. *J. Chem. Soc., Chem. Commun.* **1979**, 524. (b) Alexakis, A. *Pure Appl. Chem.* **1992**, *64*, 387. (c) Krause, N.; Purpura, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4355. (d) Chenier, J. H. B.; Howard, J. A.; Mile, B. *J. Am. Chem. Soc.* **1985**, *107*, 4190.

3070m, 3045w, 2980m, 2920w, 2240w, 1590w, 1430s, 1250s, 1115s, 1000w, 975m, 835s, 785s, 735s, 700s. ^{1}H NMR: 7.67−7.32 (m, 5 arom. H); 4.24 (q, J = 2.6, C*H*); 1.88 (d, J = 2.6, *Me*C); 1.73 (s br, *H*O); 0.44, 0.43 (2s, Me_2Si). ^{13}C NMR: 135.5 (s, arom. C); 134.3 (d, 2 arom. C); 129.6 (d, arom. C); 127.8 (d, 2 arom. C); 84.3, 79.2 (2s); 56.2 (d); 3.8, −5.5, −5.9 (3q). CI-MS: 222 (100, $[M + NH_4]^+$), 204 (22), 152 (15), 144 (12), 127 (10), 91 (44).

1.4. (−)-(*S*)-1-[(Dimethyl)(phenyl)silyl]but-2-yn-1-ol ((−)-(*S*)-2c). Lipase from *Aspergillus niger* (1.7 g, 194 U/g, Fluka) was added to a suspension of (±)-**3c** (1.7 g, 6.89 mmol) in a mixture of phosphate buffer (0.1 M, pH = 7.4, 136 mL) and MeOH (34 mL). The mixture was stirred at 23 °C for 2 h, filtered through Celite, and extracted with Et_2O. Chromatography (hexane/Et_2O, 10:3) gave (−)-(*S*)-**2c** (327 mg, 1.60 mmol, 23%, 97% er) as a yellowish oil. For spectral data see 1.3. $[\alpha]_D$ −76.0 ± 0.2 (*c* 1.17, $CHCl_3$, 94% ee). The enantiomeric ratio was determined by HPLC on a Chiralgel OB column (250 × 4.6 mm, Daicel Chemical Industrie, LTD.; UV detection at 254 nm; eluent hexane; flow rate 1 mL min^{-1}; retention times 17.9 min for (*S*)-**2c** and 18.1 min for (*R*)-**2c**) and by ^{19}F NMR of the (*S*)-Mosher ester derivatives[16] (−72.12 ppm for the major (*S*,*S*)- and −72.36 ppm for the minor (*R*,*S*)-isomer). The Mosher ester derivatives revealed also the absolute configurations at the carbinol C atoms. Relevant signals in the ^{1}H NMR: 5.47 (q, J = 2.6, SiC*H*, major (*S*,*S*)-derivative); 5.41 (q, J = 2.6, SiC*H*, minor (*R*,*S*)-derivative).

1.5. (+)-(*R*)-1-[(Dimethyl)(phenyl)silyl]but-2-yn-1-ol ((+)-(*R*)-2c). Ketone **7c** (300 mg, 1.48 mmol) was added dropwise at −35 °C to (−)-B-chlorodiisopinocampheylborane (523 mg, 1.63 mmol, (−)-Ipc$_2$BCl, Fluka) in THF (0.5 mL). After 3 h, the mixture was allowed to reach 23 °C, and THF and α-pinene were removed in vacuo (8 h at 0.2 Torr). The residue was dissolved in Et_2O (3.5 mL), diethanolamine (509 mg, 4.8 mmol) was added, and after 24 h, the mixture was filtered and the solid washed with pentane. Chromatography (hexane/Et_2O, 10:3) afforded (+)-(*R*)-**2c** (286 mg, 1.40 mmol, 94%, 99% er) as a yellowish oil. $[\alpha]_D$ +98.2 ± 0.2 (*c* 1.15, $CHCl_3$, 98% ee). For spectral data see 1.3; for the determination of enantiomeric ratio and absolute configuration see 1.4.

1.6. (±)-1-[(Dimethyl)(phenyl)silyl]prop-2-yn-1-ol ((±)-2d). Analogously to 1.3, [(dimethyl)(phenyl)silyl]methanol (5.00 g, 30.07 mmol) delivered after Swern oxidation, treatment with ethynylMgBr (0.5 M solution in THF, 120.0 mL, 60.00 mmol), and chromatography (hexane/Et_2O, 10:3) (±)-**2d** (3.61 g, 18.98 mmol, 63%) as a yellowish oil. IR: 3550m, 3420s, 3320s, 3080m, 3060m, 2970s, 2100w, 1595w, 1490w, 1435s, 1255s, 1170s, 1005s, 950m, 845s, 820s, 795s, 745s, 710s. ^{1}H NMR: 7.67−7.35 (m, 5 arom. H); 4.28 (d, J = 2.6, SiC*H*); 2.66 (d, J = 2.6, CC*H*); 1.48 (s br, O*H*); 0.47, 0.46 (2s, Me_2Si). ^{13}C NMR: 134.9 (s); 134.3 (d, 2C); 129.8 (d); 127.9 (d, 2C); 84.3 (s); 76.2, 55.9 (2d); −5.7, −6.0 (2q). CI-MS: 208 (100, $[M + NH_4]^+$), 130 (20), 91 (13).

1.7. (−)-(*S*)-1-[(Dimethyl)(phenyl)silyl]but-2-yn-1-ol ((−)-(*S*)-2d). Ketone **7d** (300 mg, 1.59 mmol) in THF (20 mL) was stirred with 0.3 g of activated molecular sieves (4 Å) for 1 h at 23 °C. The mixture was cooled to −30 °C, and (*S*)-2-methyl-CBS-oxazaborolidine (1.0 M solution in toluene, 1.6 mL, 1.6 mmol, Aldrich) was added, followed by a dropwise addition of BH_3-THF complex (1.0 M, 0.96 mL, 0.96 mmol). The mixture was stirred at −30 °C for 30 min, quenched with MeOH, extracted, and chromatographed (hexane/Et_2O, 10:3) to give (−)-(*S*)-**2d** (283 mg, 1.49 mmol, 93%, 98% er) as a yellowish oil. For spectral data see 1.6. $[\alpha]_D$ −55.0 ± 0.2 (*c* 1.0, $CHCl_3$, 96% ee). The enantiomeric purity was determined by ^{19}F NMR of the (*S*)-Mosher ester derivatives[16] (−72.15 ppm for the major (*S*,*S*)- and −72.34 ppm for the minor (*R*,*S*)-isomer). The Mosher ester derivatives revealed also the absolute configurations at the carbinol C atoms. Relevant signals in the ^{1}H NMR: 5.49 (q, J = 2.6, SiC*H*, major (*S*,*S*)-derivative); 5.43 (q, J = 2.6, SiC*H*, minor (*R*,*S*)-derivative).

2. α-Acetoxy- and α-Mesyloxypropargylic Silanes. 2.1. (1*S*,2′*S*)- and (1*R*,2′*S*)-1-{[(2-Methoxy-2-phenylethoxy)methyl]dimethylsilyl}-1-methylbut-2-ynyl Acetate ((*S*,*S*)-3a and (*R*,*S*)-3a′, respectively). MeMgBr (3.0 M in Et_2O, 0.29 mL, 0.87 mmol) was added at −80 °C to a solution of (*S*,*S*)-**2a** and (*R*,*S*)-**2a′** (188 mg, 0.61 mmol, dr 85:15) in Et_2O (10.0 mL). After 10 min, AcCl (97 μL, 1.37 mmol) was added, and the previously formed precipitate dissolved almost completely. The mixture was slowly allowed to warm to 23 °C (ca. 2 h), and the stirring was continued for another 30 min. Quenching with saturated aqueous $NaHCO_3$ solution, extraction with Et_2O, and chromatography (hexane/Et_2O, 15:2) gave a mixture of (*S*,*S*)-**3a** and (*R*,*S*)-**3a′** (169 mg, 0.47 mmol, ratio 85:15, 79%) as a yellowish oil. Spectral data from mixture. IR: 2970w, 2930w, 2820w, 1730s, 1370m, 1370m, 1265s, 1230s, 1200m, 1115s, 1095s, 1045m, 1015m, 935w, 840m, 760m, 700s. ^{1}H NMR of major isomer (*S*,*S*)-**3a**: 7.37−7.24 (m, 5 arom. H); 4.34 (dd, J = 7.3, 4.2, PhC*H*); 3.65, 3.45 (AB of ABX, J_{AB} = 10.4, J_{AX} = 7.3, J_{BX} = 4.2, PhCHCH_2O); 3.38, 3.34 (AB, J = 13.1, SiCH_2O); 3.30 (s, *Me*O); 1.98 (s, *Me*CO_2); 1.86 (s, CC*Me*), 1.58 (s, *Me*CSi); 0.16, (s, Me_2Si). ^{13}C NMR of major isomer (*S*,*S*)-**3a**: 170.2 139.6 (2s); 128.3 (d, 2C); 127.7 (d); 126.9 (d, 2C); 83.8 (s); 82.9 (d); 79.7 (t); 79.3, 68.9 (2s); 63.0 (t); 57.0, 22.9, 21.5, 3.9, −6.2, −6.3 (6q). CI-MS: 366 (13, $[M + NH_4]^+$), 306 (47), 289 (61), 257 (100), 223 (27), 155 (59). Anal. Calcd for $C_{19}H_{28}O_4Si$ (348.18): C 65.48, H 8.10. Found: C 65.30, H 8.01.

2.2. (1*S*,2′*S*)- and (1*R*,2′*S*)-1-{[(2-Methoxy-2-phenylethoxy)methyl]dimethylsilyl}-1-methylprop-2-ynyl Acetate ((*S*,*S*)-3b and (*R*,*S*)-3b′, respectively). Analogously to 2.1, transformation of (*S*,*S*)-**2b** and (*R*,*S*)-**2b′** (111 mg, 0.38 mmol, dr 86:14) gave a mixture of (*S*,*S*)-**3b** and (*R*,*S*)-**3b′** (103 mg, 0.31 mmol, dr 86:14, 82%) as a yellow oil. Spectral data from mixture. IR: 3200w, 3020w, 2970m, 2930m, 2890m, 2820m, 1735s, 1490w, 1450m, 1370m, 1250s, 1125s, 1095s, 1120s, 1095s, 1040m, 935w, 910w, 845s, 760m, 730m, 700s. ^{1}H NMR of major isomer (*S*,*S*)-**3b**: 7.38−7.24 (m, 5 arom. H); 4.33 (dd, J = 7.3, 4.3, PhC*H*); 3.65, 3.46 (AB of *ABX*, J_{AB} = 10.4, J_{AX} = 7.3, J_{BX} = 4.3, PhCHCH_2O); 3.39, 3.36 (AB, J = 13.1, SiCH_2O); 3.30 (s, *Me*O); 2.68 (s, CC*H*); 2.01 (s, *Me*CO_2), 1.64 (s, *Me*CSi); 0.191, 0.186 (2s, Me_2Si). ^{13}C NMR of major isomer (*S*,*S*)-**3b**: 170.1, 139.35 (2s); 128.3 (d, 2C); 127.7 (d); 126.9 (d, 2C); 84.0 (s); 82.6 (d); 79.6 (t); 75.82 (s); 67.72 (d); 62.4 (t); 57.1, 22.3, 21.5, −6.5, −6.7 (5q). ^{1}H NMR of minor isomer (*R*,*S*)-**3b′**: 7.38−7.24 (m, 5 arom. H); 4.34 (d*d*, J = 7.3, 4.3, PhC*H*); 3.66, 3.45 (AB of ABX, J_{AB} = 10.4, J_{AX} = 7.3, J_{BX} = 4.3, PhCHCH_2O); 3.42, 3.33 (AB, J = 13.2, SiCH_2O); 3.30 (s, *Me*O); 2.69 (s, CC*H*); 2.00 (s, *Me*CO_2), 1.62 (s, *Me*CSi); 0.19, (s, Me_2Si). ^{13}C NMR of minor isomer (*R*,*S*)-**3b′**: 170.1, 139.37 (2s); 128.3 (d, 2C); 127.7 (d); 126.9 (d, 2C); 84.0 (s); 82.6 (d); 79.6 (t); 75.77 (s); 67.70 (d); 62.4 (t); 57.1, 22.3, 21.5, −6.5, −6.7 (5q). CI-MS: 352 (8, $[M + NH_4]^+$), 275 (53), 243 (54), 141 (100, $C_7H_{13}OSi$). Anal. Calcd for $C_{18}H_{26}O_4Si$ (334.48): C 64.64, H 7.83. Found: C 64.76, H 7.82.

2.3. (±)- and (+)-(*R*)-1-[(Dimethyl)(phenyl)silyl]but-2-ynyl Acetate ((±)-3c and (+)-(*R*)-3c). Analogously to 2.1, transformation of (±)-**2c** or (+)-(*R*)-**2c** (1.40 g, 6.83 mmol, 99% er) gave (±)-**3c** or (+)-(*R*)-**3c** (1.70 g, 6.83 mmol, 99% er, 100%) as a yellowish oil. For (+)-(*R*)-**3c** $[\alpha]_D$ +117.8 ± 0.2 (*c* 1.19, $CHCl_3$, 98% ee). IR: 3070w, 3050w, 2960w, 2920w, 2220w, 1735s, 1430m, 1370m, 1300w, 1250s, 1230s, 1145w, 1115m, 1015m, 960w, 835m, 790m, 735m, 700m. ^{1}H NMR: 7.62−7.32 (m, 5 arom. H); 5.34 (q, J = 2.6, SiC*H*); 2.01 (s, OC*Me*); 1.85 (d, J = 2.6, C*Me*); 0.44, 0.43 (2s, Me_2Si). ^{13}C NMR: 170.5, 134.8 (2s); 134.1 (d, 2C); 129.7 (d); 127.7 (d, 2C); 84.2, 75.6 (2s); 58.2 (d); 20.8, 3.8, −5.3, −5.5 (4q). CI-MS: 264 (26, $[M + NH_4]^+$), 204 (22), 191 (100), 169 (28), 134 (15). Anal. Calcd for $C_{14}H_{18}O_2Si$ (246.38): C 68.25, H 7.36. Found: C 68.36, H 7.32.

2.4. (+)-(*R*)-1-[(Dimethyl)(phenyl)silyl]but-2-ynyl Methanesulfonate ((+)-(*R*)-3d). Et_3N (0.140 mL, 1.0 mmol) and

(16) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.

MsCl (70 μL, 0.90 mmol) were successively added to a stirred solution of (+)-(*R*)-**2c** (150 mg, 0.734 mmol, 99% er) in CH_2Cl_2 (5 mL) at −80 °C. After 30 min, it was quenched with saturated aqueous $NaHCO_3$ solution, extracted with Et_2O, and chromatographed (hexane/Et_2O, 10:3) to give (+)-(*R*)-**3d** (173 mg, 0.612 mmol, 99% er, 84%) as a yellowish oil. $[\alpha]_D$ +113.2 ± 0.2 (*c* 1.16, $CHCl_3$, 98% ee). IR: 3060w, 3010w, 2950w, 2900w, 2210w, 1420m, 1350s, 1245m, 1165s, 1140w, 1110m, 990w, 965m, 900s, 810s, 725m, 690m. ^{1}H NMR: 7.63−7.35 (m, 5 arom. H); 5.08 (q, *J* = 2.6, C*H*); 3.01 (s, S*Me*); 1.89 (d, *J* = 2.6, C*Me*); 0.49 (s, Me_2Si). ^{13}C NMR: 134.2 (d, 2C); 133.6 (s); 130.1 (d); 127.9 (d, 2C); 88.4, 74.1 (2s); 67.2 (d); 39.1, 3.8, −5.7, −5.8 (4q). CI-MS: 300 (98, $[M + NH_4]^+$), 204 (45), 170 (100), 153 (52), 91 (34).

2.5. (−)-(*S*)-1-[(Dimethyl)(phenyl)silyl]prop-2-ynyl Methanesulfonate ((−)-(*S*)-3e). Analogously to 2.4, transformation of (−)-(*S*)-**2d** (100 mg, 0.525 mmol, 98% er) gave (−)-(*S*)-**3e** (130 mg, 0.484 mmol, 98% er, 92%) as a yellowish oil. $[\alpha]_D$ −30.3 ± 0.2 (*c* 2.8, $CHCl_3$, 96% ee). IR: 3270m, 3070w, 3025w, 2960w, 2210w, 1425m, 1350s, 1250s, 1170s, 1110s, 970m, 910s, 810s, 725s, 690s. ^{1}H NMR: 7.65−7.35 (m, 5 arom. H); 5.10 (d, *J* = 2.6, SiC*H*); 3.03 (s, S*Me*); 2.85 (d, *J* = 2.6, CC*H*); 0.53 (2s, Me_2Si). ^{13}C NMR: 134.2 (d, 2C); 132.9 (s); 130.3 (d); 128.0 (d, 2C); 79.9 (d); 78.8 (s); 65.7 (d); 39.1 (q); −5.9 (q, 2C). CI-MS: 286 (100, $[M + NH_4]^+$), 170 (12), 152 (12).

3. Allenes. 3.1. (*M*,*S*)- and (*P*,*S*)-[(2-Methoxy-2-phenylethoxy)methyl](dimethyl)(1-methyl-3-phenylbuta-1,2-dienyl)silane ((*M*,*S*)-4a and (*P*,*S*)-4a′, respectively). To a solution of (*S*,*S*)-**3a**/(*R*,*S*)-**3a′** (50 mg, 0.143 mmol, dr. 85:15) in Et_2O (1 mL) was added a solution of $CuBr{\cdot}2PBu_3$ (1 M solution in Et_2O, 14 μL, 0.014 mmol). The mixture was cooled to −50 °C, and PhMgBr (3 M solution in Et_2O, 0.10 mL, 0.30 mmol) was rapidly added. The temperature was allowed to rise slowly to 0 °C, and the reaction mixture was quenched with saturated aqueous NH_4Cl solution and chromatographed (hexane/Et_2O, 20:1) to deliver a mixture of (*M*,*S*)-**4a** and (*P*,*S*)-**4a′** (35 mg, 0.095 mmol, 67%, ratio 85:15) as a colorless oil. Spectral data from mixture. $[\alpha]_D$ −58.6 ± 0.2 (*c* 0.8, Et_2O). IR: 3080w, 3060w, 3020w, 2950s, 2920s, 2860s, 2820m, 1945s, 1590m, 1490s, 1450m, 1350m, 1245m, 1115s, 1095s, 1060m, 1020m, 1000w, 900m, 835s, 800m, 750s, 700s, 690s. ^{1}H NMR of major isomer (*M*,*S*)-**4a** (C_6D_6) 7.48−7.00 (m, 10 arom. H); 4.29 (dd, *J* = 7.1, 4.6, PhC*H*); 3.69, 3.46 (AB of ABX, J_{AB} = 10.1, J_{AX} = 7.1, J_{BX} = 4.6, PhCHCH_2O); 3.26, 3.16 (AB, *J* = 12.8, SiCH_2O); 3.15 (s, *Me*O); 2.00 (s, PhC*Me*); 1.79 (s, SiC*Me*); 0.17, (s, Me_2Si). ^{13}C NMR of major isomer (*M*,*S*)-**4a** (C_6D_6): 207.0, 140.6, 138.7 (3s); 128.6 (d, 2C); 128.5 (d, 2C); 127.8 (d); 127.3 (d, 2C); 126.1 (d); 125.6 (d, 2C); 95.1, 92.3 (2s); 83.50 (d); 80.54, 64.60 (2t); 56.97, 16.56, 15.57, −4.5, −4.6 (5q). ^{1}H NMR of minor isomer (*P*,*S*)-**4a′** (C_6D_6): 7.48−7.00 (m, 10 arom. H); 4.29 (dd, *J* = 7.1, 4.6, PhC*H*); 3.69, 3.47 (AB of ABX, J_{AB} = 10.1, J_{AX} = 7.1, J_{BX} = 4.6, PhCHCH_2O); 3.25, 3.17 (AB, *J* = 12.8, SiCH_2O); 3.14 (s, *Me*O); 2.00 (s, PhC*Me*); 1.79 (s, SiC*Me*); 0.17 (s, Me_2Si). ^{13}C NMR of minor isomer (*P*,*S*)-**4a′**(C_6D_6): 207.0, 140.6, 138.7 (3s); 128.6 (d, 2C); 128.5 (d, 2C); 127.8 (d); 127.3 (d, 2C); 126.1 (d); 125.6 (d, 2C); 95.1, 92.3 (2s); 83.48 (d); 80.51, 64.57 (2t); 56.95, 16.53, 15.54, −4.5, −4.6 (5q). CI-MS: 384 (100, $[M + NH_4]^+$), 247 (57), 232 (35), 219 (53). The diastereomeric ratio of (*M*,*S*)-**4a** and (*P*,*S*)-**4a′** was deduced from the signals of their SiCH_2O groups.

3.2. (*M*,*S*)- and (*P*,*S*)-[(2-Methoxy-2-phenylethoxy)methyl](dimethyl)(1-methyl-3-phenylpropa-1,2-dienyl)silane ((*M*,*S*)-4b and (*P*,*S*)-4b′, respectively). Analogously to 3.1, (*S*,*S*)-**3b**/(*R*,*S*)-**3b′** (50 mg, 0.161 mmol, ratio 86:14), treated with PhMgBr, gave a mixture of (*M*,*S*)-**4b** and (*P*,*S*)-**4b′** (48 mg, 0.136 mmol, 84%, ratio 86:14) as a colorless oil. Spectral data from mixture. $[\alpha]_D$ −87.6 ± 0.2 (*c* 0.9, $CHCl_3$). IR: 3080w, 3060w, 3020w, 2860m, 2820w, 1925s, 1730w, 1600w, 1495w, 1450m, 1250m, 1120s, 1100s, 1025w, 930m, 840s, 800m, 755s, 700s, 690s. ^{1}H NMR of major isomer (*M*,*S*)-**4b** (C_6D_6): 7.31−6.96 (m, 10 arom. H); 5.86 (q, *J* = 2.8, CCC*H*); 4.27 (dd, *J* = 7.1, 4.4, PhC*H*); 3.66, 3.45 (AB of ABX, J_{AB} = 10.1, J_{AX} = 7.0, J_{BX} = 4.5, PhCHCH_2O); 3.25, 3.16 (AB, *J* = 12.8, SiCH_2O); 3.14 (s, *Me*O); 1.77 (d, *J* = 2.8, PhC*Me*); 0.17, 0.16 (2s, Me_2Si). ^{13}C NMR of major isomer (*M*,*S*)-**4b** (C_6D_6): 207.0, 140.4, 136.2 (3s); 128.9, 125.5 (2d, 2C); 127.8 (d); 127.3, 126.5 (2d, 2C); 126.3 (d); 94.0 (s); 89.3, 83.4 (2d); 80.43, 64.4 (2t); 56.9, 15.5, −4.7, −4.8 (4q). ^{1}H NMR of minor isomer (*P*,*S*)-**4b′** (C_6D_6): 7.31−6.96 (m, 10 arom. H); 5.85 (q, *J* = 2.8, CCC*H*); 4.27 (dd, *J* = 7.0, 4.5, PhC*H*); 3.66, 3.45 (AB of ABX, J_{AB} = 10.2, J_{AX} = 7.0, J_{BX} = 4.5, PhCHCH_2O); 3.24, 3.17 (AB, *J* = 13.1, SiCH_2O); 3.13 (s, *Me*O); 1.77 (d, *J* = 2.8, PhC*Me*); 0.17, 0.16 (2s, Me_2Si). ^{13}C NMR of minor isomer (*P*,*S*)-**4b′** (C_6D_6): 207.0, 140.5, 136.2 (3s); 128.9, 125.5 (2d, 2C); 127.8 (d); 127.3, 126.5 (2d, 2C); 126.3 (d); 94.0 (s); 89.4, 83.4 (2d); 80.39, 64.4 (2t); 56.9, 15.5, −4.7, −4.8 (4q). CI-MS: 370 (100, $[M + NH_4]^+$), 321 (56), 223 (47), 120 (44). Anal. Calcd for $C_{22}H_{28}O_2Si$ (352.54): C 74.95, H 8.01. Found: C 74.80, H 8.11. The diastereomeric ratio of (*M*,*S*)-**4b** and (*P*,*S*)-**4b′** was deduced from the signals of their SiCH_2O groups.

3.3. (+)-(*P*)-(Dimethyl)(phenyl)(3-phenylbuta-1,2-dienyl)silane ((+)-(*P*)-4c). From (+)-(*R*)-3c. Analogously to 3.1, (+)-(*R*)-**3c** (150 mg, 0.609 mmol, er 98%), treated with PhMgBr, gave (+)-(*P*)-**4c** (32 mg, 0.121 mmol, 20%) as a colorless oil ($[\alpha]_D$ +390.6 ± 0.2 (*c* 0.5, Et_2O)) and (+)-(*R*)-**2c** (77 mg, 0.362 mmol, 60%).

From (+)-(*R*)-3d. Analogously to 3.1, (+)-(*R*)-**3d** (214 mg, 0.758 mmol, er 99%), treated with PhMgBr, gave (+)-(*P*)-**4c** (122 mg, 0.463 mmol, 61%, 99% er) as a colorless oil. $[\alpha]_D$ +390.7 ± 0.2 (*c* 1.1, Et_2O). IR: 3060w, 3010w, 2940m, 2920s, 1920s, 14900m, 1420m, 1365w, 1135m, 1240s, 1110s, 1060m, 1020w, 990w, 900w, 830s, 810s, 780s, 725s, 685s. ^{1}H NMR (C_6D_6): 7.72−7.12 (m, 10 arom. H); 5.46 (q, *J* = 3.7 C*H*); 2.07 (d, *J* = 3.7 C*Me*); 0.41, 0.40 (2s, Me_2Si). ^{13}C NMR (C_6D_6): 211.7, 138.5, 137.3 (3s); 133.6 (d, 2C); 129.2 (d) 128.3, 127.8 (2d, 2C); 125.8 (d); 125.1 (d, 2C); 94.2 (s); 84.0 (d); 16.0 (q); −2.1 (q, 2C). CI-MS: 282 (34, $[M + NH_4]^+$), 265 (34), 226 (35), 204 (23), 152 (100), 91 (43). The determination of the enantiomeric ratios was done by GC (column type: WCOT Fused Silia; stationary phase: CP-Chirasil, Dex CB; column length: 25 m; inside diameter: 0.25 mm, outside diameter: 0.36 mm; film thickness: 0.25 um; Varian); carrier gas: H_2, 40 kPa; temperature program: 20 min isotherm at 120 °C then gradient 1 deg min^{-1} to 160 °C; retention times: 50.7 min for (+)-(*P*)-**4c** and 51.1 min for (−)-(*M*)-**4c**.

3.4. (−)-(*M*)-(Dimethyl)(phenyl)(3-phenylpropa-1,2-dienyl)silane ((−)-(*M*)-4d). Analogously to 3.1, (−)-(*S*)-**3e** (95 mg, 0.354 mmol, 98% er), treated with PhMgBr, gave (−)-(*M*)-**4d** (66 mg, 0.264 mmol, 74%) as a colorless oil. $[\alpha]_D$ −222.2 ± 0.2 (*c* 1.07, Et_2O). IR: 3060w, 3020w, 2960w, 1925s, 1600w, 1495m, 1455m, 1430m, 1370w, 1250m, 1180m, 1115m, 910w, 860m, 835s, 820s, 785m, 770m, 730m, 700s. ^{1}H NMR (C_6D_6): 7.52−6.89 (m, 10 arom. H); 5.83 (d, *J* = 6.9, PhC*H*); 5.44 (d, SiC*H*); 0.30, 0.28 (2s, Me_2Si). ^{13}C NMR (C_6D_6): 212.0, 138.2, 135.1 (3s); 134.0 (d, 2C); 129.6 (d); 129.0 (d, 2C); 128.2 (d); 126.5 (d, 4C); 89.0, 86.0 (2d); −2.1, −2.2 (2q). CI-MS: 268 (100, $[M + NH_4]^+$), 190 (11), 152 (42).

3.5. (*M*,*S*)- and (*P*,*S*)-(1,3-Dimethylpenta-1,2-dienyl)[(2-methoxy-2-phenylethoxy)methyl](dimethyl)silane ((*M*,*S*)-4e and (*P*,*S*)-4e′, respectively). Analogously to 3.1, (*S*,*S*)-**3a**/(*R*,*S*)-**3a′** (50 mg, 0.140 mmol, ratio 85:15), treated with EtMgBr, gave a mixture of (*M*,*S*)-**4e** and (*P*,*S*)-**4e′** (36 mg, 0.11 mmol, 79%, ratio could not be determined since the two products are impossible to differentiate by NMR) as a colorless oil. Spectral data from mixture. $[\alpha]_D$ +33.5 ± 0.2 (*c* 1.0, Et_2O). IR: 3065w, 3030w, 2960s, 2930s, 2890s, 2860s, 2820m, 1945s, 1495w, 1455s, 1360m, 1320w, 1250s, 1200w, 1120s, 1105s, 1030w, 1000w, 920m, 840s, 815m, 760m, 700s. ^{1}H NMR (C_6D_6): 7.34−7.05 (m, 5 arom. H); 4.32 (dd, *J* = 7.1, 4.8, PhC*H*); 3.73, 3.50 (AB of ABX, J_{AB} = 10.3, J_{AX} = 7.1, J_{BX} = 4.8, PhCHCH_2O); 3.28, 3.19 (AB, *J* = 12.6, SiCH_2O); 3.16 (s, *Me*O); 1.96−1.79 (m, MeCH_2C); 1.76 (s, SiC*Me*); 1.65 (s,

EtC*Me*); 1.0 (t, J = 7.3); 0.20, 0.19 (2s, Me_2Si). ^{13}C NMR (C_6D_6): 205.3, 140.7 (2s); 128.5 (d, 2C); 127.8 (d); 127.3 (d, 2C); 95.1, 89.9 (2s); 83.6 (d); 80.6, 64.8 (2t); 57.0 (q); 26.9 (t), 18.7, 16.5, 12.8 (3q), −4.5 (q, 2C). CI-MS: 336 (100, $[M + NH_4]^+$), 287 (32), 240 (38), 223 (45), 219 (18), 120 (37). Anal. Calcd for $C_{19}H_{30}O_2Si$ (318.53): C 71.64, H 9.49. Found: C 71.77, H 9.27.

3.6. (*M*,*S*)- and (*P*,*S*)-(1,3-Dimethyl-4-phenylbuta-1,2-dienyl)[(2-methoxy-2-phenylethoxy)methyl](dimethyl)silane ((*M*,*S*)-4f and (*P*,*S*)-4f′, respectively). Analogously to 3.1, (*S*,*S*)-**3a**/(*R*,*S*)-**3a′** (50 mg, 0.143 mmol, ratio 85:15), treated with BnMgBr, gave a mixture of (*M*,*S*)-**4f** and (*P*,*S*)-**4f′** (17 mg, 0.045 mmol, 31%, ratio could not be determined since the two products are impossible to differentiate by NMR) as a colorless oil. Spectral data from mixture. $[\alpha]_D$ +8.0 ± 0.2 (*c* 0.5, Et_2O). IR: 3090w, 3060w, 3030w, 2960m, 2920s, 2890s, 2860s, 2820m, 1945s, 1495m, 1455m, 1365m, 1245m, 1120s, 1100s, 1030w, 950w, 845s, 760m, 740m, 700s. ^{1}H NMR (C_6D_6): 7.44−6.86 (m, 10 arom. H); 4.31 (dd, J = 6.9, 4.6, PhC*H*); 3.73, 3.50 (AB of ABX, J_{AB} = 10.1, J_{AX} = 6.9, J_{BX} = 4.6, PhCHCH_2O); 3.28−3.09 (m, 4H, SiCH_2O, PhCH_2); 3.15 (s, *Me*O); 1.71 (s, BnC*Me*); 1.62 (s, SiC*Me*); 0.15 (s, Me_2Si). ^{13}C NMR (C_6D_6): 206.4,140.6, 140.5 (3s); 129.4, 128.5, 128.4 (3d, 2C); 127.8 (d); 127.3 (d, 2C); 126.4 (d); 93.3, 89.4 (2s); 83.5 (d); 80.5, 64.7 (2t); 57.0 (q); 41.2 (t); 18.2, 16.3, −4.5, −4.6 (4q). CI-MS: 398 (100, $[M + NH_4]^+$), 349 (25), 240 (10), 223 (33), 219 (58), 120 (27).

3.7. (+)-(*P*)-(Dimethyl)(3-methylpenta-1,2-dienyl)-(phenyl)silane ((+)-(*P*)-4g). Analogously to 3.1, (+)-(*R*)-**3d** (138 mg, 0.489 mmol, 99% er), treated with EtMgBr, gave (+)-(*P*)-**4g** (74 mg, 0.348 mmol, 70%) as a colorless oil. $[\alpha]_D$ +13.3 ± 0.2 (*c* 0.54, Et_2O). IR: 3070w, 3050w, 2970s, 2940m, 2170w, 1945m, 1430m, 1355w, 1295w, 1250m, 1120m, 1055w, 1000w, 940w, 845s, 830s, 785s, 735s, 700m. ^{1}H NMR (C_6D_6): 7.69−7.16 (m, 5 arom. H); 5.15 (m, C*H*); 1.94−1.70 (m, CH_2); 1.60 (d, J = 3.6, C*Me*); 0.98 (t, J = 7.4, CH_2*Me*); 0.35 (s, Me_2Si). ^{13}C NMR (C_6D_6): 210.4, 139.2 (2*s*); 134.1 (d, 2C); 129.3 (d); 128.1 (d, 2C); 94.3 (s); 81.7 (d); 26.4 (t); 18.0, 12.6 (2q); −1.9 (q, 2C). CI-MS: 266 (100), 250 (85), 232 (64, $[M + NH_4]^+$), 220 (47), 152 (87).

3.8. (+)-(*P*)-(Dimethyl)(3-methyl-4-phenylbuta-1,2-dienyl)(phenyl)silane ((+)-(*P*)-4h). Analogously to 3.1, (+)-(*R*)-**3d** (415 mg, 1.47 mmol, 99% er), treated with BnMgBr, gave (+)-(*P*)-**4h** (285 mg, 1.03 mmol, 70%) as a colorless oil. $[\alpha]_D$ +36.8 ± 0.2 (*c* 1.06, Et_2O). IR: 3060w, 3020m, 2950w, 2910w, 2850w, 1945m, 1600w, 1490m, 1450m, 1430m, 1355m, 1245m, 1110m, 1070w, 1025w, 995w, 835s, 820s, 780s, 730s, 700m. ^{1}H NMR (C_6D_6): 7.53−6.96 (m, 10 arom. H); 5.07 (m, C*H*); 3.22−3.07 (m, CH_2); 1.57 (d, J = 3.7, C*Me*); 0.32, 0.31 (2s, Me_2Si). ^{13}C NMR (C_6D_6): 211.0, 140.0, 138.9 (3s); 134.1 (d); 129.3 (d, 2C); 128.6 (d); 128.5, 128.1 (2d, 2C); 126.4, 126.2 (2d); 92.5 (s); 81.1 (d); 40.5 (t), 17.7, −1.9, −2.0 (3q). CI-MS: 296 (66, $[M + NH_4]^+$), 218 (100), 152 (40).

3.9. (−)-(*M*)-(Buta-1,2-dienyl)(dimethyl)(phenyl)silane ((−)-(*M*)-4i). Analogously to 3.1, (−)-(*S*)-**3e** (56 mg, 0.209 mmol, 98% er), treated with BnMgBr, gave (−)-(*M*)-**4i** (27 mg, 0.143 mmol, 69%) as a colorless oil. $[\alpha]_D$ −17.1 ± 0.2 (*c* 0.9, Et_2O). IR: 3080m, 3060m, 2960m, 2930m, 2900m, 2860w, 1940s, 1600w, 1430s, 1365s, 1250s, 1200m, 1115s, 860s, 835s, 815s, 785s, 730s, 700s. ^{1}H NMR (C_6D_6): 7.57−6.17 (m, 5 arom. H); 5.08 (dd, J = 6.9, 4.0, MeC*H*); 4.72 (quint., J = 7.0, SiC*H*); 1.5 (dd, J = 4.0, 7.0, CH*Me*); 0.343, 0.338 (2s, Me_2Si). ^{13}C NMR (C_6D_6): 212.6, 138.8 (2s); 134.1 (d, 2C); 129.4 (d); 128.1 (d, 2C); 80.9, 78.7 (2d); 13.1, −2.10, −2.13 (3q). CI-MS: 222 (41), 220 (100), 206 (93, $[M + NH_4]^+$), 152 (52), 128 (16).

3.10. (*M*,*S*)- and (*P*,*S*)-(1,3-Dimethyl-4-hepta-1,2-dienyl)[(2-methoxy-2-phenylethoxy)methyl](dimethyl)silane ((*M*,*S*)-4j and (*P*,*S*)-4j′, respectively) and (*M*,*S*)- and (*P*,*S*)-[(2-Methoxy-2-phenylethoxy)methyl](dimethyl)(1-methyl-4-buta-1,2-dienyl)silane ((*M*,*S*)-4k and (*P*,*S*)-4k′, respectively). BuLi (1.6 M in Et_2O, 10.15 mL, 16.24 mmol) was added dropwise at −50 °C to a suspension of CuI (1.55 mg, 8.12 mmol) in Et_2O (39 mL). The temperature was slowly raised to 0 °C (30 min), and the stirring was continued for an additional 2 h. The solution was cooled to −80 °C, and a solution of **3a**/(*R*,*S*)-**3a′** (283 mg, 0.812 mmol, ratio 85:15) in Et_2O (3 mL) was added slowly. The temperature was raised to 0 °C over a period of 30 min, and the mixture was stirred for 1 h. It was quenched with saturated aqueous NH_4Cl solution at 0 °C, extracted with Et_2O, and chromatographed (hexane/Et_2O, 20:1) to give a mixture of (*M*,*S*)-**4j** and (*P*,*S*)-**4j′** (30 mg, 0.087 mmol, 11%, ratio could not be determined since the two products are impossible to differentiate by NMR) and a mixture of (*M*,*S*)-**4k** and (*P*,*S*)-**4k′** (155 mg, 0.534 mmol, 66%, ratio could not be determined since the two products are impossible to differentiate by NMR), each as a colorless oil. Spectral data for (*M*,*S*)-**4j** and (*P*,*S*)-**4j′**. IR: 3020w, 2960s, 2920s, 2860s, 1940m, 1730w, 1450m, 1245m, 1115s, 1100s, 755m, 700s. ^{1}H NMR: 7.38−7.24 (m, 5 arom. H); 4.35 (dd, J = 7.4, 4.2, PhC*H*); 3.64, 3.44 (AB of ABX, J_{AB} = 10.5, J_{AX} = 7.4, J_{BX} = 4.2, PhCHCH_2O); 3.31 (s, *Me*O); 3.27, 3.19 (AB, J = 13.0, SiCH_2O); 1.92−1.83 (m, CH_2C); 1.63 (s, *Me*CHC); 1.61 (s, *Me*CSi); 1.41−1.25 (m, MeCH_2CH_2C); 0.93−0.85 (m, *Me*CH_2); 0.08 (s, Me_2Si). ^{13}C NMR: 205.1, 139.7 (2s); 128.3 (d, 2C); 127.7 (d); 126.9 (d, 2C); 92.9, 88.4 (2s); 82.9 (d); 79.7, 64.6 (2t); 57.2 (q); 33.3, 30.0, 22.4 (3t); 18.6, 16.1, 14.0 (3q); −4.7 (q, 2C). CI-MS: 364 (58, $[M + NH_4]^+$), 315 (23), 240 (26), 223 (100, $C_{12}H_{19}O_2Si$), 120 (95). Anal. Calcd for $C_{21}H_{34}O_2Si$ (346.23): C 72.78, H 9.89. Found: C 72.98, H 9.78. Spectral data for (*M*,*S*)-**4k** and (*P*,*S*)-**4k′**. IR: 3030w, 2920s, 2860s, 1935m, 1730w, 1495m, 1455m, 1250m, 1200w, 1130s, 1100s, 975w, 840s, 810m, 760m, 700s. ^{1}H NMR: 7.38−7.24 (m, 5 arom. H); 4.75−4.64 (m, C*H*CC); 4.35 (dd, J = 7.4, 4.2, PhC*H*); 3.64, 3.45 (AB of ABX, J_{AB} = 10.5, J_{AX} = 7.4, J_{BX} = 4.2, PhCHCH_2O); 3.31 (s, *Me*O); 3.28, 3.22 (AB, J = 13.0, SiCH_2O); 1.65 (d, J = 2.9, *Me*CHC); 1.58 (d, J = 6.9, *Me*CSi); 0.09 (s, Me_2Si). ^{13}C NMR: 207.4, 139.6 (2s); 128.2 (d, 2C); 127.6 (d); 126.9 (d, 2C); 88.5 (s); 82.9 (d); 79.7 (t); 78.7 (d); 64.3 (t); 57.1, 15.8, 13.7 (3q); −4.9 (q, 2C). CI-MS: 308 (19, $[M + NH_4]^+$), 240 (14), 223 (100, $C_{12}H_{19}O_2Si$), 120 (59).

4. Auxiliary Compounds. 4.1. (2*S*,2′*S*,*Z*)- and (2*R*,2′*S*,*Z*)-2-{[(2-Methoxy-2-phenylethoxy)methyl](dimethyl)silyl}-pent-3-en-2-ol (5a and 5b, respectively). A solution of (*S*,*S*)-**3a**/(*R*,*S*)-**3a′** (50 mg, 0.16 mmol, ratio 85:15) in hexane (10 mL) was stirred under H_2 (1 atm) and in the presence of Lindlar catalyst (14 mg) for 40 min at 23 °C. The catalyst was removed by filtration and the solvent evaporated to give a mixture of **5a**/**5b** (50 mg, 0.16 mmol, ratio 85:15, 100%). The spectra of the products were in agreement with those of **5a**/**5b** obtained directly from **1** and propenyllithium.[7]

4.2. 1-[(Dimethyl)(phenyl)silyl]but-2-yn-1-one (7c). DMSO (0.59 mL, 8.32 mmol) was added to a stirred solution of oxalyl chloride (0.63 mL, 7.34 mmol) in CH_2Cl_2 (15 mL) at −80 °C. After 10 min, a solution of (±)-**3c** (1.0 g, 4.89 mmol) in CH_2Cl_2 (5 mL) was added dropwise, and after 15 min, Et_3N (2.5 mL, 18.11 mmol) followed. Extraction with Et_2O and chromatography (hexane/Et_2O, 10:1) gave **7c** (0.596 g, 2.95 mmol, 60%) as a yellowish oil. IR: 3090w, 3070w, 2210s, 1600s, 1440m, 1260m, 1155m, 1120s, 1010w, 850s, 820s, 795s, 750s, 710s, 665s. ^{1}H NMR: 7.62−7.34 (m, 5 arom. H); 2.04 (s, C*Me*); 0.55 (s, Me_2Si). ^{13}C NMR: 224.0 (s); 134.1 (d, 2C); 133.4 (s); 129.9 (d); 127.9 (d, 2C); 99.8, 84.0 (2s); 4.3 (q); −5.1 (q, 2C). CI-MS: 220 (100, $[M + NH_4]^+$), 202 (49), 142 (50).

4.3. 1-[(Dimethyl)(phenyl)silyl]prop-2-yn-1-one (7d). Jones reagent (1.90 mL, 5.07 mmol) was added dropwise at −80 °C to a stirred solution of (±)-**3d** (814 mg, 4.28 mmol). The mixture was allowed to slowly warm to −50 °C. It was quenched with saturated aqueous $NaHCO_3$ solution, and after extraction with Et_2O and chromatography (hexane/Et_2O, 10:1), **7d** (709 mg, 3.76 mmol, 88%) was obtained as a yellowish oil. IR: 3370m, 3070w, 3050w, 2960w, 2070s, 1730w, 1605s, 1460m, 1250s, 1115s, 1020m, 950m, 840s, 815s, 790s, 740s, 710s, 700s. ^{1}H NMR: 7.62−7.35 (m, 5 arom. H); 3.81 (s, C*H*);

0.58 (2s, Me_2Si). ^{13}C NMR: 224.1 (s); 134.2 (d, 2C); 132.6 (s); 130.3 (d); 128.1 (d, 2C); 86.7 (d); 84.3 (s); −5.3 (q, 2C). CI-MS: 206 (100, $[M + NH_4]^+$).

Acknowledgment. We would like to express our thanks to the members of the analytical laboratories of our institute and the Swiss National Science Foundation for their generous financial support.

Supporting Information Available: ^{1}H NMR spectra as proof of purity for compounds (±)-**2c**, (±)-**2d**, (+)-(*R*)-**3d**, (−)-(*S*)-**3e**, (*M*,*S*)-**4a**/(*P*,*S*)-**4a′**, (+)-(*P*)-**4c**, (−)-(*M*)-**4d**, (*M*,*S*)-**4f**/(*P*,*S*)-**4f ′**, (+)-(*P*)-**4g**, (+)-(*P*)-**4h**, (−)-(*M*)-**4i**, (*M*,*S*)-**4k**/(*P*,*S*)-**4k′**, **7c**, and **7d** that were not characterized by elemental analyses due to their volatility or high reactivity, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049505E