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Intramolecular Ene Reaction of Epoxyallylsilanes: Synthesis of Allyl- and Vinylsilane-Functionalized Cyclohexanols

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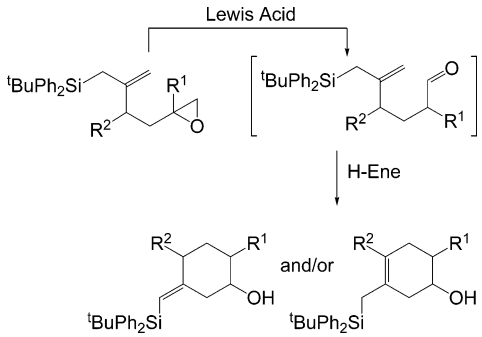

Epoxyallylsilanes bearing the bulky *tert*-butyldiphenylsilyl group undergo an uncommon tandem rearrangement−cyclization process upon treatment with Lewis acids. Two pathways for the carbonyl ene reaction are observed: one leading to allylsilane−cyclohexanols when the epoxyallylsilane (**28**−**31**) is nonsubstituted, 2-, or 4-monosubstituted and other leading to vinylsilane−cyclohexanols when the epoxyallylsilane (**24**−**27**) is 2,4-disubstituted or trisubstituted. An explanation for the observed regio- and stereoselectivity is advanced and a reliable mechanism proposed.

Introduction

Organosilicon compounds display a multitude of functions in organic synthesis.[1] The usefulness of these versatile building blocks in stereoselective reactions can be attributed both to their ability to react with electrophiles via selective formation of a carbocation β to the silyl group (the so-called β-effect) and to their stability toward a large number of functional groups and reaction conditions. Among them, allylsilanes have been widely recognized as valuable intermediates for the construction of ring systems, especially in the area of natural products synthesis.[2] Several groups have reported the synthesis of carbo- and heterocyclic compounds[3] by the Lewis acid promoted reaction of allylsilanes with carbonyl derivatives or related compounds (Sakurai−Hosomi reaction).[4]

Despite its synthetic potential, the cyclization of epoxyallylsilanes has not been widely explored. It has been reported that the stabilization of the incipient charge in the Lewis acid mediated intramolecular process overrides entropic and stereoelectronic factors. Thus, under Lewis acid conditions, nucleophilic substitution usually takes place at the most substituted carbon center of the epoxide[5] unless the presence of electron-withdrawing groups next to the epoxide destabilizes the developing carbocation.[6] Contrary to the normal 5-*exo*[7] or 6-*endo*[8] attack,[9] we have recently reported that the acid-catalyzed reaction of epoxyallylsilanes containing the phenyldimethylsilyl group follows an unusual rearrange-

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(3) Within others, see: (a) Barbero, A.; García, C.; Pulido, F. J. *Tetrahedron* **2000**, *56*, 2739. (b) Akiyama, T.; Yamanaka, M. *Synlett* **1996**, 1095. (c) Osumi, K.; Sugimura, H. *Tetrahedron Lett.* **1995**, *36*, 5789. (d) Panek, J. S.; Jain, N. F. *J. Org. Chem.* **1994**, *59*, 2674.

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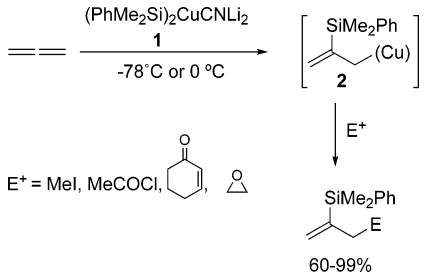
SCHEME 1



ment−cyclization process which leads to methylenecyclohexanols.[10] From previous work, it is clear that the behavior of the *tert*-butyldiphenylsilyl group is perceptively different from that observed for the phenyldimethylsilyl group.[11] In this paper, we report the acid-catalyzed cyclization reaction of allyl-*tert*-butyldiphenylepoxysilanes and we show their interesting reactivity pattern.

Epoxyallylsilanes have been previously prepared by Wittig reaction of an aldehyde with $Ph_3P{=}CHCH_2SiMe_3$ followed by epoxidation[12] and by cross-metathesis of alkenyl epoxides and allylsilanes.[13] Following our methodology,[10] we describe herein a new route for the synthesis of epoxyallylsilanes carrying the *tert*-butyldiphenylsilyl group by silylcupration of allene, followed by capture of the intermediate cuprate with enones and final formation of the epoxide via sulfur ylides.

Silylcupration of allene leads to the formation of intermediate cuprates, which react with electrophiles to afford either vinyl or allylsilanes.[2,14] The regiochemistry of the addition depends on various factors such as the nature of the cuprate, the substitution of the allene, the temperature of the reaction, and the nature of the silyl group. Thus, the reaction of 1,2-propadiene with higher order silylcyanocuprates **1** containing the phenyldimethylsilyl group gives, at any temperature between −78 and 0 °C, a vinylsilane−allylcuprate intermediate **2**, which readily reacts with a wide variety of electrophiles leading to the corresponding vinylsilanes (Scheme 1).

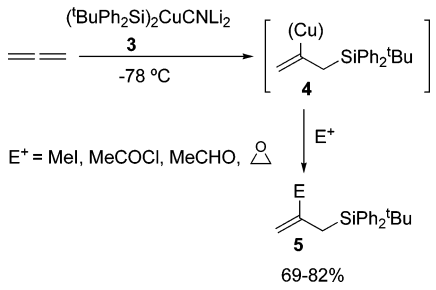
However, the silylcupration of allene, at −78 °C, using a bulkier silyl reagent as the higher order cuprate $(^tBuPh_2Si)_2CuCNLi_2$ **3**, gives rise to an allylsilane−vinylcuprate intermediate **4** where the steric hindrance of the silyl group forces it to the end of the allenic system (Scheme 2). This result is of interest since it opens a route for the synthesis of functionalized allylsilanes **5** (Scheme 2). The use of a lower order cuprate $^tBuPh_2SiCuCNLi$ **6** shows a similar regioselectivity pattern and offers the possibility of a cheaper methodology since just 1 equiv of silyllithium is required (Scheme 3).

Results and Discussion

Thus, *tert*-butyldiphenylsilylcuprate **6** readily adds to allene at −40 °C to give a vinylcopper intermediate **7**, which reacts smoothly with α,β-unsaturated carbonyl compounds **8**−**15** to afford after quenching with satd NH_4Cl compounds **16**−**23** in good yield. All the reactions (THF) were carried out in the presence of $BF_3{\cdot}OEt_2$ or TMSCl, which considerably increased the yields (Scheme 3, Table 1).

The oxoallylsilanes thus obtained were treated with dimethylsulfonium methylide to give in good yield the corresponding epoxides **24**−**31** (Table 2). Compounds **24**, **26**, **27**, and **31** were isolated as mixtures of diastereomers in almost equimolar ratio (Table 2). For compound **24**, both diastereomers (**24a** and **24b**) could be separated by chromatography and their relative *R*/*S* configuration assigned. In the other cases, they were used as a mixture

SCHEME 2



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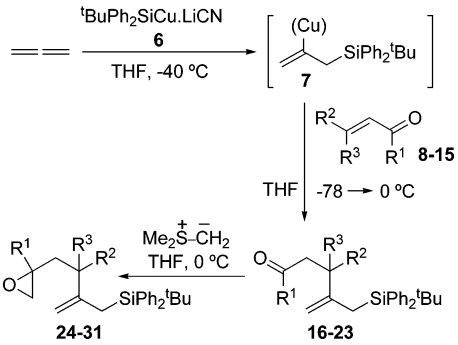

TABLE 1. Synthesis of Oxoallylsilanes

entry	oxo compd	activant	R^1	R^2	R^3	oxoallylsilane	yield (%)
1	**8**	$BF_3{\cdot}OEt_2$	Me	Ph	H	**16**	85
2	**9**	$BF_3{\cdot}OEt_2$	Me	Me	Me	**17**	90
3	**10**	$BF_3{\cdot}OEt_2$	Et	Me	H	**18**	89
4	**11**	$BF_3{\cdot}OEt_2$	Me	*i*-Pr	H	**19**	88
5	**12**	TMSCl	Et	H	H	**20**	88
6	**13**	TMSCl	Me	H	H	**21**	90
7	**14**	TMSCl	H	H	H	**22**	90
8	**15**	TMSCl	H	Me	H	**23**	80

TABLE 2. Synthesis of Epoxyallylsilanes

entry	oxoallylsilane	R^1	R^2	R^3	epoxyallylsilane	yield (%)
1	**16**	Me	Ph	H	**24**	74[a]
2	**17**	Me	Me	Me	**25**	78
3	**18**	Et	Me	H	**26**	68[a]
4	**19**	Me	*i*-Pr	H	**27**	65[a]
5	**20**	Et	H	H	**28**	75
6	**21**	Me	H	H	**29**	72
7	**22**	H	H	H	**30**	72
8	**23**	H	Me	H	**31**	70[a]

[a] Diastereomeric ratio (*R**,*R**)/(*R**,*S**) approximately 1:1.

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(10) Barbero, A.; Castreño, P.; Pulido, F. J. *Org. Lett.* **2003**, *5*, 4045.
(11) (a) Barbero, A.; Castreño, P.; García, C.; Pulido, F. J. *J. Org. Chem.* **2001**, *66*, 7723. (b) Barbero, A.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I.; Sánchez, A. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1525.
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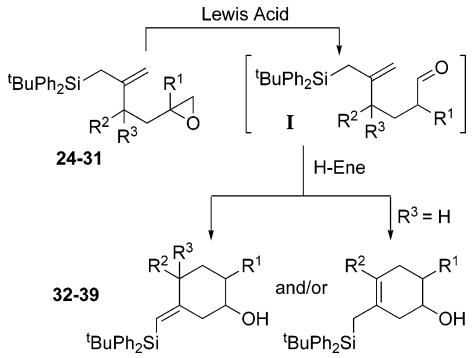
SCHEME 4

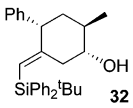
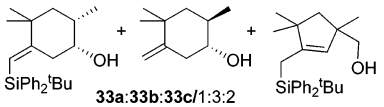
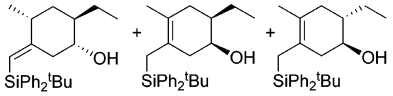
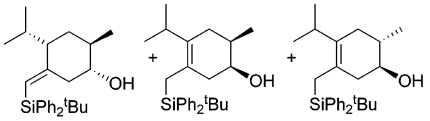
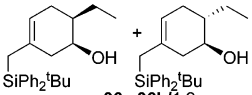
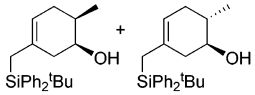
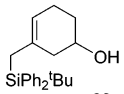
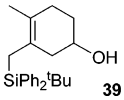


of diastereomeric epoxides in the subsequent cyclization, which apparently does not represent a limitation since it was verified that both diastereomers **24a** and **24b** lead separately to the same result.

As we noted previously for epoxyallylsilanes bearing the phenyldimethylsilyl group,[10] the reaction of compounds **24**−**31**, in the presence of a Lewis acid, occurs through a rearrangement−cyclization process, where the first stage involves Lewis acid promoted isomerization of the epoxy group to an aldehyde **I** and the second stage occurs by intramolecular ene reaction between the oxo group and the allylsilane unit (Scheme 4). To our knowledge, this is the first time that this sequential type of process has been observed[15] in the acid-catalyzed cyclization of epoxyallylsilanes. The former observation allows us to assert that rearrangement of these epoxides occur much faster than nucleophilic substitution on the epoxy group. Moreover, the fact that the Lewis acid cyclization of **24a** or **24b** gives the same result seems to indicate that the reaction proceeds through common intermediates and, in consequence, that rearrangement to the aldehyde takes place prior to cyclization. The degree of concertedness between the two steps is still uncertain.[16] Surprisingly, the presence of the *tert*-butyldiphenylsilyl group introduces another special feature in these epoxyallylsilane cyclizations, when compared with the phenyldimethylsilyl series,[10] since the hindered silyl group is maintained along the whole process. Recently, Alcaide et al.[17] described the preparation of six-membered rings by Lewis acid promoted carbonyl−ene cyclization, and we previously reported the intramolecular ene reaction of oxoallylsilanes containing the *tert*-butyldiphenylsilyl group.[11a]

The regioselectivity of the cyclization depends dramatically upon the substitution of the epoxyallylsilane. Thus, nonsubstituted and 2- or 4-monosubstituted epoxyallylsilanes **28**−**31** give exclusively allylsilanes **36**−**39**, upon treatment with Lewis acids (Table 3, entries 5−8). However, 2,4-disubstituted epoxyallylsilanes **24**−**27** give either mixtures of vinylsilanes and allylsilanes or exclusively vinylsilanes (Table 3, entries 1−4). The only example in which we found some of the normal product (**33c)** of 5-exo attack, predicted by the Baldwin rules, is

TABLE 3. Acid-Catalyzed Cyclization of Epoxyallylsilanes

Entry	Epoxyallylsilane	Products	Yield (%)
1	**24**	 **32**	75
2	**25**	 **33a**:**33b**:**33c**/1:3:2	74
3	**26**	 **34a**:**34b**:**34c**/1:2:3	70
4	**27**	 **35a**:**35b**:**35c**/1:2:3	67
5	**28**	 **36a**:**36b**/1:2	70
6	**29**	 **37a**:**37b**/1:2	70
7	**30**	 **38**	76
8	**31**	 **39**	71

[a] Cyclization conditions: $BF_3{\cdot}OEt_2$, DCM, 0 °C.

for the 2,4,4-trisubstituted epoxyallylsilane **25**. Obviously, **33c** is formed by cyclization of the cation primarily formed by ring opening of the epoxide before the rearrangement to the aldehyde. The stereoisomers collected in Table 3 could be adequately separated by flash chromatography. The structural assignments of the different products were established by means of careful ^{1}H, COSY, and NOESY studies and X-ray analysis.

From the classical mechanistic standpoint, it is generally agreed that the concerted ene reaction of allylsilanes[18] involves a highly asynchronous transition state featuring a well-developed C−C bond prior to a relatively late proton transfer toward the oxygen.[19] Consequently, the ene transition state has dipolar character, and the silyl group, which enhances the nucleophilicity of the double bond, is also a powerful force for the stabilization of the partial positive charge at the β-carbon atom.

(15) Products of epoxide rearrangement have been obtained in a similar cyclization reaction: Xiao, X.-Y.; Park, S.-K.; Prestwich, G. D. *J. Org. Chem.* **1988**, *53*, 4869.

(16) We were not able to isolate or detect aldehydes resulting from isomerization of the starting epoxyallylsilane.

(17) Alcaide, B.; Pardo, C.; Rodriguez-Ranera, C.; Rodriguez-Vicente, A. *Org. Lett.* **2001**, *3*, 4205.

(18) (a) Monti, H.; Laval, G.; Feraud, M. *Eur. J. Org. Chem.* **1999**, *8*, 1825. (b) Dumeunier, R.; Leclercq, C.; Marko, E. *Tetrahedron Lett.* **2002**, *43*, 2307.

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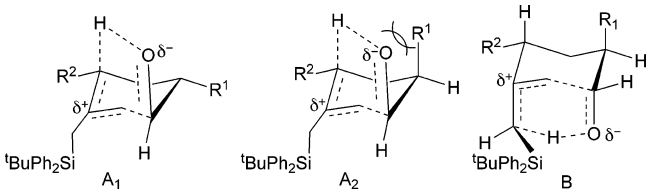
SCHEME 5



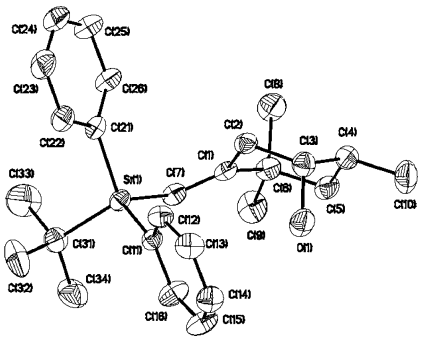


FIGURE 1. X-ray crystal structure of (*E*)-(1*R**,2*S**)-5-*tert*-butyldiphenylsilylmethylene-2,4,4-trimethylcyclohexanol.

Three transition states $\mathbf{A_1}$, $\mathbf{A_2}$, and **B** may account for all of the observed compounds (Scheme 5). In the case of the 2- or 4-monosubstituted epoxyallylsilanes, a simple examination of the molecular structure shows that the completion of the H-ene reaction is favored by a well-positioned endocyclic axial hydrogen, with the 2- or 4-substituent occupying an equatorial position in a chairlike transition state $\mathbf{A_1}$ (R^1 or R^2 = H). This is an energetically favored transition state since the endocyclic axial C−H bond and the σ C−Si bond are both coplanar to the empty carbon p-orbital, and therefore, the β-C−Si bond hyperconjugation is not perturbed. Formation preferential of *trans* products (**36b** and **37b**) should be a consequence of the difference of energy between transition states $\mathbf{A_1}$ and $\mathbf{A_2}$, the latter being more crowded.

However, for 2,4-disubstituted epoxyallylsilanes (R^1 and $R^2 \neq$ H) there are two possible pathways for the ene reaction, depending on the stereochemistry of the intermediate aldehyde **I**. Thus, for the pseudo-*cis* stereoisomer, both substituents in the 2- and 4-position will be equatorial, and then the transition state $\mathbf{A_1}$ will be still favored since there is an appropriate pseudoaxial hydrogen in the allylic position. However, for the pseudo-*trans* stereoisomer, where one of the substituents (the bulkier) will be equatorial and the other will be axial, there is competitiveness between two energetically close transition states $\mathbf{A_2}$ and **B**. Thus, in the transition state $\mathbf{A_2}$ the hyperconjugation effect is not perturbed but there is an unfavorable sterical interaction with the 2-substituent in axial. On the contrary, in the transition state **B** the hydrogens of the exocyclic α-silylated position are both accessible to the carbonyl group without steric repulsion, but the β-C−Si bond hyperconjugation is seriously perturbed since the required coplanarity is lost.

Moreover, the selective formation of *E*-vinylsilanes (**32**, **33a 34a**, and **35a**) indicates that, in the transition state **B**, the bulky silyl group attains an orientation anti to the 4-substituent for minimal steric repulsions (Scheme 5); in this way, only one of the methylene hydrogens α to silicon is selectively transferred, just the one in close proximity with the negative part of the enophile. Stereochemistry has been corroborated by X-ray analysis of **33a** (Figure 1).

Conclusions

In summary, epoxyallylsilanes containing the bulky *tert*-butyldiphenylsilyl group undergo, upon treatment with Lewis acid, a sequential rearrangement−cyclization process, which leads stereoselectively to allyl- and vinylsilane functionalized cyclohexanol derivatives. The low electrofugacity of the *tert*-butyldiphenylsilyl group compared with other silyl groups is responsible for the formation of silicon containing cyclic products. Formally, the cyclization follows an ene mechanism, through a chairlike transition state of type **A** or **B**, leading to the formation of either allyl- or vinylsilanes depending upon the structure of the starting epoxyallylsilane.

Experimental Section

Silylcupration of Allene. Preparation of Intermediate 7. A solution of *tert*-butyldiphenylsilyllithium[11b] (6 mmol) in THF was added by syringe to a stirred suspension of copper(I) cyanide (6 mmol) in THF at 0 °C. After 30 min at this temperature, the solution of *tert*-butyldiphenylsilylcopper **6** (6 mmol) was cooled at −40 °C and a slight excess of allene was added from a balloon. The mixture was stirred for 1 h and then used immediately.

Reaction of Intermediates 7 with α,β-Unsaturated Carbonyl Compounds. $BF_3{\cdot}OEt_2$ or TMSCl (6 mmol) was added at −78 °C to the solution previously prepared and the mixture stirred for an additional period of 10 min. The aldehydes or ketones **8**−**15** (6 mmol) in THF were slowly dropped in at −78 °C and stirred at this temperature for 1 h. After gentle warming to 0 °C, the mixture was quenched with saturated ammonium chloride solution and extracted twice with ether. The organic layer was dried ($MgSO_4$), evaporated, and chromatographed to give the corresponding products **16**−**23** (Table 1). Compounds **16**,[3a] **17**,[11a] and **18**[11a] were previously described.

5-*tert*-Butyldiphenylsilylmethyl-4-isopropylhex-5-en-2-one (19): colorless oil; IR (neat, cm^{-1}) 1715, 1630; ^{1}H NMR ($CDCl_3$) δ 7.75−7.45 (m, 10H), 4.66 (s, 1H), 4.56 (s, 1H), 2.39−2.20 (m, 4H), 2.12 (d, *J* = 16 Hz, 1H), 1.91 (s, 3H), 1.78−1.67 (m, 1H), 1.04 (s, 9H, ^{t}Bu-Si), 0.77 (d, *J* = 6.8 Hz, 3H), 0.73 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 208.2, 147.1, 136.2, 134.6, 134.3, 129.0, 127.4, 112.8, 48.8, 44.4, 29.8, 29.7, 27.8, 20.8, 18.8, 18.5. Anal. Calcd for $C_{26}H_{36}SiO$: C, 79.53; H, 9.24. Found: C, 79.88; H, 9.51.

6-*tert*-Butyldiphenylsilylmethylhept-6-en-3-one (20): colorless oil; IR (neat, cm^{-1}) 1716, 1636, 1106, 736; ^{1}H NMR ($CDCl_3$) δ 7.61−7.42 (m, 10H), 4.65 (s, 1H), 4.54 (s, 1H), 2.29−2.18 (m, 4H), 2.22 (s, 2H), 1.91 (t, *J* = 7.7 Hz, 2H), 1.09 (s, 9H, ^{t}Bu-Si), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 211.0, 145.6, 136.1, 134.6, 129.1, 127.4, 109.8, 40.5, 35.4, 32.3, 27.7, 20.6, 18.5, 7.7. Anal. Calcd for $C_{24}H_{32}SiO$: C, 79.06; H, 8.85. Found: C, 79.39; H, 9.11.

5-*tert*-Butyldiphenylsilylmethylhex-5-en-2-one (21): colorless oil; IR (neat, cm^{-1}) 1717, 1627, 1105, 910; ^{1}H NMR ($CDCl_3$) δ 7.74−7.39 (m, 10H), 4.73 (s, 1H), 4.60 (s, 1H), 2.31−2.28 (m, 4H), 1.97−1.95 (m, 2H), 1.95 (s, 3H), 1.15 (s, 9H, ^{t}Bu-Si); ^{13}C NMR ($CDCl_3$) δ 208.2, 145.4, 136.2, 134.6, 129.2, 127.5, 109.9, 41.8, 32.2, 29.5, 27.8, 20.6, 18.6. Anal. Calcd for $C_{23}H_{30}SiO$: C, 78.80; H, 8.63. Found: C, 79.15; H, 8.94.

4-*tert*-Butyldiphenylsilylmethylpent-4-enal (22): colorless oil; IR (neat, cm^{-1}) 1726, 1636, 1105; ^{1}H NMR ($CDCl_3$) δ 9.40 (t, *J* = 2.0, 1H), 7.64−7.45 (m, 10H), 4.72 (s, 1H), 4.56 (s, 1H), 2.27 (td, *J* = 7.3 and 2.0 Hz, 2H), 2.24 (s, 2H), 1.96 (t, *J* = 7.3 *Hz*, 2H), 1.11 (s, 9H, ^{t}Bu-Si); ^{13}C NMR ($CDCl_3$) δ 202.3,

144.9, 136.1, 134.4, 129.2, 127.5, 110.3, 41.5, 30.3, 27.7, 20.6, 18.5. Anal. Calcd for $C_{22}H_{28}SiO$: C, 78.51; H, 8.39. Found: C, 79.85; H, 8.91.

4-*tert*-Butyldiphenylsilylmethyl-3-methylpent-4-enal (23): colorless oil; ^{1}H NMR ($CDCl_3$) δ 9.20 (s, 1H), 7.69−7.37 (m, 10H), 4.71 (s, 1H), 4.59 (s, 1H), 2.24−2.15 (m, 3H), 2.23 (s, 2H), 1.09 (s, 9H, ^{t}Bu-Si), 0.89 (d, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 202.8, 149.7, 136.2, 134.5, 129.2, 127.7, 109.5, 49.5, 35.1, 27.8, 19.5, 18.9, 18.5. Anal. Calcd for $C_{23}H_{30}SiO$: C, 78.80; H, 8.63. Found: C, 79.18; H, 8.98.

Synthesis of Epoxyallylsilanes. To a solution of trimethylsulfonium iodide (1 mmol) in dry THF (5 mL) was added dropwise BuLi (1 mmol, 1.6 M BuLi in hexanes) and the mixture stirred for 5 min at 0 °C. Then a solution of the oxoallylsilane (0.8 mmol) in THF (1 mL) was added. After the solution was stirred for an additional 30 min at 0 °C and 1 h at rt, brine (10 mL) was added and the mixture extracted with ether, dried, and evaporated to dryness. The residue was purified by chromatography to give epoxyallylsilanes **24**−**31**. Compounds **24**, **26**, **27**, and **31** were isolated as mixtures (∼1:1) of diastereomers. In the case of compound **24**, both diastereomers (**24a** and **24b**) could be cleanly separated by chromatography and their relative *R*/*S* configuration assigned by comparison with the analogous compound bearing the $PhMe_2Si$ group,[10] the latter unequivocally identified by X-ray characterization.[10]

(2*R,4*R**)-5-*tert*-Butyldiphenylsilylmethyl-2-methyl-4-phenyl-1,2-epoxyhex-5-ene (24a):** colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.72−6.98 (m, 15H), 4.93 (s, 1H), 4.89 (s, 1H), 2.82−2.78 (m, 1H), 2.34 (d, J = 14.2 Hz, 1H), 2.12−2.05 (m, 1H), 2.04 (d, J = 4.3 Hz, 1H), 1.86 (d, J = 14.2 Hz, 1H), 1.70 (d, J = 4.3 Hz, 1H), 1.51−1.40 (m, 1H), 1.11 (s, 9H, ^{t}Bu-Si), 0.91(s, 3H); ^{13}C NMR ($CDCl_3$) δ 148.8, 142.7, 136.5, 136.3, 134.9, 134.5, 129.3, 129.2, 128.2, 128.1, 127.6, 127.5, 126.6, 109.2, 55.7, 54.5, 48.7, 42.2, 27.7, 20.6, 19.9, 18.6; MS *m*/*z* 383 ($M^+ - {}^t$Bu), 199.

(2*R,4*S**)-5-*tert*-Butyldiphenylsilylmethyl-2-methyl-4-phenyl-1,2-epoxyhex-5-ene (24b):** colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.67−7.01 (m, 15H), 4.82 (s, 1H), 4.80 (s, 1H), 2.88 (dd, J = 10.2 and 4.7 Hz, 1H), 2.27 (d, J = 4.8 Hz, 1H), 2.23 (d, J = 14.6 Hz, 1H), 2.20 (d, J = 4.8 Hz, 1H), 1.95 (dd, J = 13.9 and 10.2 Hz, 1H), 1.86 (d, J = 14.6 Hz, 1H), 1.72 (dd, J = 13.9 and 4.7 Hz, 1H), 1.03 (s, 9H, ^{t}Bu-Si), 0.77 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 148.8, 143.0, 136.4, 136.3, 134.8, 134.5, 129.2, 128.4, 128.3, 127.5, 126.5, 109. 8, 56.2, 53.1, 49.4, 41.2, 27.8, 21.5, 18.9, 18.6; MS *m*/*z* 383 ($M^+ - {}^t$Bu), 199. Anal. Calcd for $C_{30}H_{36}SiO$: C, 81.76; H, 8.23. Found: C, 82.15; H, 8.51.

5-*tert*-Butyldiphenylsilylmethyl-2,4,4-trimethyl-1,2-epoxyhex-5-ene (25): colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.73−7.27 (m, 10H), 4.79 (s, 1H), 4.67 (s, 1H), 2.63 (d, J = 4.9 Hz, 1H), 2.54 (dd, J = 4.9 and 1.1 Hz, 1H), 2.16 (s, 2H), 2.07 (dd, J = 14.3 and 1.1 Hz, 1H), 1.45 (d, J = 14.3 Hz, 1H), 1.33 (s, 9H, ^{t}Bu-Si), 1.06 (s, 3H), 1.03 (s, 3H), 1.01 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 151.0, 136.2, 134.6, 134.5, 129.0, 127.4, 112.4, 55.9, 54.9, 47.3, 39.8, 28.5, 27.9, 27.5, 22.2, 18.5, 12.8. Anal. Calcd for $C_{26}H_{36}SiO$: C, 79.53; H, 9.24. Found: C, 79.85; H, 9.58.

(2*R,4*R**)- and (2*R**,4*S**)-5-*tert*-butyldiphenylsilylmethyl-2-ethyl-4-methyl-1,2-epoxyhex-5-ene (26):** colorless oil; IR (neat, cm^{-1}) 1635, 1428, 1105; ^{1}H NMR ($CDCl_3$) δ **26a** 7.67−7.27 (m, 10H), 4.62 (s, 1H), 4.60 (s, 1H), 2.46 (d, J = 4.8 Hz, 1H), 2.35 (d, J = 4.8 Hz, 1H), 2.27 (d, J = 14.7 Hz, 1H), 2.10 (d, J = 14.7 Hz, 1H), 1.90−1.80 (m, 1H), 1.50−1.31 (m, 4H), 1.07 (s, 9H, ^{t}Bu-Si), 0.84 (d, J = 6.6 Hz, 3H), 0.77 (t, J = 7.5 Hz, 3H), **26b** 4.63 (s, 1H), 4.58 (s, 1H), 2.52 (d, J = 4.8 Hz, 1H), 2.44 (d, J = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ **26a** 151.1, 136.3, 136.2, 134.7, 134.5, 129.1, 127.4, 108.9, 59.2, 51.3, 40.2, 37.0, 27.9, 26.3, 19.5, 18.7, 18.5, 9.1, **26b** 108.5, 59.0, 53.1, 40.1, 26.1, 19.1, 18.9, 8.5. Anal. Calcd for $C_{26}H_{36}SiO$: C, 79.53; H, 9.24. Found: C, 79.87; H, 9.51.

(2*R,4*R**)- and (2*R**,4*S**)-5-*tert*-butyldiphenylsilylmethyl-2-methyl-4-isopropyl-1,2-epoxyhex-5-ene (27):** colorless oil; IR (neat, cm^{-1}) 1636, 1105; ^{1}H NMR ($CDCl_3$) δ **27a** 7.77−7.27 (m, 10H), 4.73 (s, 1H), 4.62 (s, 1H), 2.44 (d, J = 4.6 Hz, 1H), 2.30 (d, J = 4.6 Hz, 1H), 2.15 (d, J = 16.4 Hz, 1H), 2.06 (d, J = 16.4 Hz, 1H), 1.90−1.58 (m, 3H), 1.31−1.23 (m, 1H), 1.04 (s, 3H), 1.02 (s, 9H, ^{t}Bu-Si), 0.81 (d, J = 6.9 Hz, 3H), 0.74 (d, J = 6.9 Hz, 3H), **27b** 4.72 (s, 1H), 4.60 (s, 1H), 2.42 (d, J = 4.8 Hz, 1H), 2.38 (d, J = 4.8 Hz, 1H), 2.03 (d, J = 16.0 Hz, 1H), *1*.06 (s, 3H), 0.72 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ **27a** 146.4, 136.2, 136.1, 134.3, 129.1, 127.4, 113. 6, 56.5, 53.8, 50.6, 36.1, 29.8, 27.8, 20.9, 20.7, 18.9, 18.4, 17.8, **27b** 113.4, 55.1, 53.1, 49.6, 35.4, 29.3, 21.6, 20.5, 19.2, 17.6. Anal. Calcd for $C_{27}H_{38}SiO$: C, 79.74; H, 9.42. Found: C, 80.09; H, 9.74.

5-*tert*-Butyldiphenylsilylmethyl-2-ethyl-1,2-epoxyhex-5-ene (28): colorless oil; IR (neat, cm^{-1}) 1636, 1463, 1105, 820; ^{1}H NMR ($CDCl_3$) δ 7.69−7.34 (m, 10H), 4.67 (s, 1H), 4.58 (s, 1H), 2.43 (d, J = 4.6 Hz, 1H), 2.28 (d, J = 4.6 Hz, 1H), 2.22 (s, 2H), 1.67−1.58 (m, 4H), 1.35 (q, J = 7.6 Hz, 2H), 1.10 (s, 9H, ^{t}Bu-Si), 0.79 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 146.3, 136.1, 134.7, 129.1, 127.4, 109. 4, 59.8, 51.9, 33.1, 31.9, 27.7, 26.7, 20.7, 18.5, 8.7. Anal. Calcd for $C_{25}H_{34}SiO$: C, 79.31; H, 9.05. Found: C, 79.69; H, 9.34.

5-*tert*-Butyldiphenylsilylmethyl-2-methyl-1,2-epoxyhex-5-ene (29): colorless oil; IR (neat, cm^{-1}) 1633, 1425, 1106, 906; ^{1}H NMR ($CDCl_3$) δ 7.71−7.36 (m, 10H), 4.71 (s, 1H), 4.61 (s, 1H), 2.41 (d, J = 4.8 Hz, 1H), 2.35 (d, J = 4.8 Hz, 1H), 2.25 (s, 2H), 1.71−1.36 (m, 4H), 1.12 (s, 9H, ^{t}Bu-Si), 1.07 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 146.2, 136.2, 134.7, 129.1, 127.5, 109.5, 56.7, 53.6, 34.8, 33.5, 27.8, 20.7, 20.6, 18.6. Anal. Calcd for $C_{24}H_{32}SiO$: C, 79.06; H, 8.85. Found: C, 79.39; H, 9.14.

5-*tert*-Butyldiphenylsilylmethyl-1,2-epoxyhex-5-ene (30): colorless oil; IR (neat, cm^{-1}) 1630, 1440, 1110, 705; ^{1}H NMR ($CDCl_3$) δ 7.70−7.27 (m, 10H), 4.71 (s, 1H), 4.64 (s, 1H), 2.68−2.60 (m, 2H), 2.28−2.25 (m, 1H), 2.25 (s, 2H), 1.82−1.71 (m, 2H), 1.57−1.38 (m, 2H), 1.11 (s, 9H, ^{t}Bu-Si); ^{13}C NMR ($CDCl_3$) δ 145.8, 136.2, 134.7, 129.1, 127.5, 110.1, 51.9, 47.0, 34.2, 30.5, 27.8, 20.4, 18.6. Anal. Calcd for $C_{23}H_{30}SiO$: C, 78.80; H, 8.63. Found: C, 79.13; H, 8.94.

(2*R,4*R**)- and (2*R**,4*S**)-5-*tert*-Butyldiphenylsilylmethyl-4-methyl-1,2-epoxyhex-5-ene (31):** colorless oil; IR (neat, cm^{-1}) 1633, 1426, 1105, 788; ^{1}H NMR ($CDCl_3$) δ **31a** 7.78−7.26 (m, 10H), 4.66 (s, 2H), 2.69−2.61 (m, 2H), 2.36 (dd, J = 5.0 and 3.1 Hz, 1H), 2.32−2.23 (m, 2H), 1.96−1.20 (m, 3H), 1.11 (s, 9H, ^{t}Bu-Si), 0.93 (d, J = 7.0 Hz, 3H), **31b** 4.71 (s, 1H), 4.69 (s, 1H); ^{13}C NMR ($CDCl_3$) δ **31a** 150.4, 136.2, 134.5, 129.0, 127.4, 109.1, 51.2, 46.7, 39.0, 38.4, 27.8, 19.5, 18.5, 18.4, **31b** 109.0, 50.9, 47.5, 38.2, 38.1, 19.1. Anal. Calcd for $C_{24}H_{32}SiO$: C, 79.06; H, 8.85. Found: C, 79.41; H, 9.17.

Cyclization of Epoxyallylsilanes. $BF_3{\cdot}OEt_2$ (1.4 mmol) was slowly added to a solution of **24**−**31** (1 mmol) in DCM (10 mL) under nitrogen at 0 °C. After the mixture was slowly stirred for 30 min at this temperature, brine was added and the mixture extracted with ether. The organic layer was dried over $MgSO_4$, the solvent was evaporated, and the residue was purified by chromatography. Compound **33b** was already described.[10]

(*E*)-(1*R,2*R**,4*S**)-5-*tert*-Butyldiphenylsilylmethylene-2-methyl-4-phenylcyclohexanol (32):** colorless oil; IR (neat, cm^{-1}) 3560, 3450, 1610, 1430, 1100; ^{1}H NMR ($CDCl_3$) δ 7.81−7.72 (m, 4H), 7.47−7.35 (m, 11H), 5.84 (s, 1H), 3.82−3.80 (m, 1H), 2.94 (ddd, J = 12.5, 9.1 and 4.1 Hz, 1H), 2.44 (dd, J = 10.1 and 4.5 Hz, 1H), 2.22 (dd, J = 13.2 and 4.1 Hz, 1H), 1.80 (dd, J = 13.2 and 9.1 Hz, 1H), 1.68−1.57 (m, 2H), 1.04 (s, 9H), 0.99 (d, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 161.5, 142.1, 136.0, 135.3, 129.1, 128.4, 127.7, 127.6, 127.5, 126.0, 120.2, 75.6, 50.6, 40.5, 35.8, 34.1, 27.3, 18.2, 17.9; MS *m*/*z* 441 (M^+), 423 ($M^+ - H_2O$), 239 ($Ph_2{}^t$BuSi), 199. Anal. Calcd for $C_{30}H_{36}OSi$: C, 81.76; H, 8.23. Found: C, 82.07; H, 8.57.

(*E*)-(1*R,2*S**)-5-*tert*-Butyldiphenylsilylmethylene-2,4,4-trimethylcyclohexanol (33a):** white crystals; mp 88−89 °C; IR (neat, cm^{-1}) 3560, 1590, 1420, 1100; ^{1}H NMR ($CDCl_3$) δ 7.81−7.37 (m, 10H), 5.92 (s, 1H), 3.45−3.39 (m, 1H), 2.20 (d, J = 3.1 Hz, 2H), 1.85−1.72 (m, 1H), 1.51 (t, J = 13.0 Hz, 1H), 1.28 (s, 3H), 1.20 (s, 3H), 1.23−1.14 (m, 1H), 1.01 (s, 9H), 0.84

(d, J = 6.7 Hz, 3H), 0.09 (d, J = 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 165.9, 136.6, 136.1, 135.7, 134.5, 129.0, 127.9, 127.6, 115.0, 71.9, 42.9, 39.8, 39.0, 32.0, 29.5, 27.6, 27.3, 18.1, 17.8; MS *m/z* 335 ($M^+ - {}^t$Bu), 317 ($M^+ - {}^t$Bu $- H_2O$), 239 ($Ph_2{}^t$BuSi).

3-*tert*-Butyldiphenylsilylmethyl-1,4,4-trimethylcyclopent-2-enylmethanol (33c): colorless oil; IR (neat, cm^{-1}) 3560, 1590,1420, 1100; ^{1}H NMR ($CDCl_3$) δ 7.76−7.65 (m, 4H), 7.45−7.32 (m, 6H), 4.47 (s, 1H), 3.03−2.89 (m, 2H), 1.97 (dd, J = 17.0 and 1.8 Hz, 1H), 1.90 (dd, J = 17.0 and 1.1 Hz, 1H), 1.70 (d, J = 13.1 Hz, 1H), 1.34 (d, J = 13.1 Hz, 1H), 1.05 (s, 3H), 1.03 (s, 3H), 1.01 (s, 9H), 0.77 (s, 3H), 0.50−0.42 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 148.7, 135.9, 134.6, 134.2, 130.3, 129.2, 127.6, 127.5, 70.5, 48.7, 48.3, 48.0, 29.5, 28.1, 27.7, 24.8, 18.5, 6.5. Anal. Calcd for $C_{26}H_{36}OSi$: C, 79.53; H, 9.24. Found: C, 79.87; H, 9.56.

(*E*)-(1*R,2*R**,4*R**)-5-*tert*-Butyldiphenylsilylmethylene-2-ethyl-4-methylcyclohexanol (34a):** colorless oil; IR (neat, cm^{-1}) 3500, 3450, 1610, 1430, 1105; ^{1}H NMR ($CDCl_3$) δ 7.80−7.70 (m, 4H), 7.45−7.36 (m, 6H), 5.73 (s, 1H), 3.03−2.95 (m, 1H), 2.66−2.56 (m, 1H), 2.08 (dd, J = 13.6 and 4.2 Hz, 1H), 1.94 (dd, J = 13.6 and 8.8 Hz, 1H), 1.75−1.57 (m, 3H), 1.51−1.29 (m, 3H), 1.21 (d, J = 7.0 Hz, 3H), 1.01 (s, 9H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 164.4, 135.9, 135.4, 129.0, 127.6, 127.5, 114.8, 73.7, 40.2, 39.8, 39.6, 35.3, 27.2, 24.1, 19.6, 18.0, 11.2. Anal. Calcd for $C_{26}H_{36}OSi$: C, 79.53; H, 9.24. Found: C, 79.91; H, 9.51.

(1*S,6*R**)-3-*tert*-Butyldiphenylsilylmethyl-6-ethyl-4-methylcyclohex-3-enol (34b):** colorless oil; IR (neat, cm^{-1}) 3430, 1430, 1105; ^{1}H NMR ($CDCl_3$) δ 7.69−7.60 (m, 4H), 7.45−7.27 (m, 6H), 3.67−3.58 (m, 1H), 2.20 (d, J = 15.5 Hz, 1H), 2.12 (d, J = 15.5 Hz, 1H), 2.10−2.03 (m, 1H), 1.84−1.62 (m, 4H), 1.41 (s, 3H), 1.35−1.18 (m, 3H), 1.11 (s, 9H), 0.83 (t, J = 7.3, 3H); ^{13}C NMR ($CDCl_3$) δ 136.1, 135.0, 134.4, 129.0, 127.2, 123.7, 123.1, 67.5, 40.6, 39.8, 33.0, 27.5, 24.3, 19.6, 18.3, 16.4, 11.5. Anal. Calcd for $C_{26}H_{36}OSi$: C, 79.53; H, 9.24. Found: C, 79.87; H, 9.56.

(1*S,6*S**)-3-*tert*-Butyldiphenylsilylmethyl-6-ethyl-4-methylcyclohex-3-enol (34c):** colorless oil; IR (neat, cm^{-1}) 3370, 1430, 1105; ^{1}H NMR ($CDCl_3$) δ 7.70−7.61 (m, 4H), 7.45−7.27 (m, 6H), 3.22−3.11 (m, 1H), 2.12 (s, 2H), 2.06−1.90 (m, 2H), 1.76−1.66 (m, 1H), 1.54−1.44 (m, 2H), 1.33 (s, 3H), 1.31−1.20 (m, 3H), 1.11 (s, 9H), 0.83 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 136.2, 135.0, 129.0, 127.4, 127.1, 123.9, 123.3, 70.9, 41.7, 40.5, 35.3, 27.6, 24.1, 19.2, 18.3, 16.6, 11.0.

(*E*)-(1*R,2*R**,4*S**)-5-*tert*-Butyldiphenylsilylmethylene-2-methyl-4-isopropylcyclohexanol (35a):** colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.80−7.65 (m, 4H), 7.45−7.30 (m, 6H), 5.81 (s, 1H), 3.48−3.39 (m, 1H), 2.10 (dd, J = 15.2 and 3.2 Hz, 1H), 2.07−1.97 (m, 2H), 1.89−1.77 (m, 1H), 1.71−1.49 (m, 2H), 1.11−1.07 (m, 2H), 1.02 (s, 9H), 0.99 (d, J = 6.5 Hz, 6H), 0.85 (d, J = 6.5 Hz, H); ^{13}C NMR ($CDCl_3$) δ 161.2, 136.2, 135.1, 129.0, 127.6, 120.1, 71.8, 56.3, 39.0, 31.0, 30.5, 27.3, 26.8, 22.2, 21.0, 18.1, 17.6. Anal. Calcd for $C_{27}H_{38}OSi$: C, 79.74; H, 9.42. Found: C, 80.11; H, 9.71.

(1*S,6*R**)-3-*tert*-Butyldiphenylsilylmethyl-4-isopropyl-6-methylcyclohex-3-enol (35b):** colorless oil; IR (neat, cm^{-1}) 3430, 1610, 1427, 1105; ^{1}H NMR ($CDCl_3$) δ 7.82−7.65 (m, 4H), 7.45−7.29 (m, 6H), 3.51−3.45 (m, 1H), 2.62 (sept, J = 6.8 Hz, 1H), 2.15 (d, J = 14.3 Hz, 1H), 2.05 (d, J = 14.3 Hz, 1H), 1.95−1.69 (m, 4H), 1.54−1.43 (m, 2H), 1.09 (s, 9H), 0.98 (d, J = 6.3 Hz, 3H), 0.83 (d, J = 6.8 Hz, 3H), 0.71 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 136.3,134.9, 134.5, 132.2, 129.1, 127.2, 121.5, 69.4, 40.3, 32.6, 29.4, 27.6, 26.7, 20.0, 19.7, 18.3, 16.3, 15.4. Anal. Calcd for $C_{27}H_{38}OSi$: C, 79.74; H, 9.42. Found: C, 80.07; H, 9.76.

(1*S,6*S**)-3-*tert*-Butyldiphenylsilylmethyl-4-isopropyl-6-methylcyclohex-3-enol (35c):** colorless oil; IR (neat, cm^{-1}) 3420, 1425, 1105; ^{1}H NMR ($CDCl_3$) δ 7.65−7.55 (m, 4H), 7.45−7.30 (m, 6H), 3.15−3.05 (m, 1H), 2.54 (sept, J = 6.8 Hz, 1H), 2.13 (d, J = 14.4 Hz, 1H), 2.11−2.02 (m, 1H), 2.05 (d, J = 14.4 Hz, 1H), 1.97−1.75 (m, 3H), 1.50−1.40 (m, 2H), 1.10 (s, 9H), 0.89 (d, J = 6.3 Hz, 3H), 0.71 (d, J = 6.8 Hz, 3H), 0.56 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 136.2, 134.9, 134.7, 132.2, 129.0, 127.2, 122.8, 72.6, 41.1, 35.3, 30.3, 29.2, 27.6, 19.9, 19.6, 18.3, 17.5, 15.6.

(1*S,6*R**)-3-*tert*-Butyldiphenylsilylmethyl-6-ethylcyclohex-3-enol (36a):** colorless oil; IR (neat, cm^{-1}) 3580, 3470, 1550, 1470, 1105; ^{1}H NMR ($CDCl_3$) δ 7.69−7.58 (m, 4H), 7.48−7.31 (m, 6H), 5.33−5.29 (m, 1H), 3.68−3.59 (m,1H), 2.11 (s, 2H), 1.98−1.85 (m, 2H), 1.76−1.62 (m, 2H), 1.36−1.11 (m, 4H) 1.06 (s, 9H), 0.82 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 136.2, 134.7, 134.5, 130.9, 129.1, 127.4, 120.6, 67.6, 39.6, 38.9, 27.7, 26.7, 24.2, 20.5, 18.4, 11.6. Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.67; H, 9.36.

(1*S,6*S**)-3-*tert*-Butyldiphenylsilylmethyl-6-ethylcyclohex-3-enol (36b):** colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.70−7.61 (m, 4H), 7.45−7.30 (m, 6H), 5.20 (s, 1H), 3.30−3.20 (m, 1H), 2.09 (s, 2H), 1.93−1.82 (m, 2H), 1.71−1.49 (m, 4H), 1.30−1.19 (m, 2H), 1.06 (s, 9H), 0.80 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 136.2, 134.7, 131.6, 129.0, 127.4, 120.1, 70.7, 40.6, 39.3, 28.6, 27.7, 24.0, 20.5, 18.4, 11.1. Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.62; H, 9.31.

(1*S,6*R**)-3-*tert*-Butyldiphenylsilylmethyl-6-methylcyclohex-3-enol (37a):** colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.70−7.55 (m, 4H), 7.45−7.30 (m, 6H), 5.26 (s, 1H), 3.51−3.47 (m, 1H), 2.14 (d, J = 15.2 Hz, 1H), 2.07 (d, J = 15.2 Hz, 1H), 1.98−1.83 (m, 2H), 1.71−1.52 (m, 4H), 1.05 (s, 9H), 0.80 (d, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 136.2, 134.7, 134.6, 130.8, 129.1, 127.4, 120.4, 69.6, 39.1, 31.8, 29.1, 27.6, 20.6, 18.4, 16.4. Anal. Calcd for $C_{24}H_{32}OSi$: C, 79.06; H, 8.85. Found: C, 79.41; H, 9.14.

(1*S,6*S**)-3-*tert*-Butyldiphenylsilylmethyl-6-methylcyclohex-3-enol (37b):** colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.69−7.59 (m, 4H), 7.45−7.32 (m, 6H), 5.16 (s, 1H), 3.17−3.09 (m, 1H), 2.08 (s, 2H), 2.09−1.99 (m, 2H), 1.94−1.82 (m, 2H), 1.65−1.52 (m, 2H), 1.06 (s, 9H), 0.83 (d, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 136.2, 134.8, 134.7, 132.0, 129.0, 127.4, 120.1, 72.5, 39.5, 34.5, 32.3, 27.7, 20.5, 18.4, 17.3. Anal. Calcd for $C_{24}H_{32}OSi$: C, 79.06; H, 8.85. Found: C, 79.37; H, 9.09.

3-*tert*-Butyldiphenylsilylmethylcyclohex-3-enol (38): colorless oil; IR (neat, cm^{-1}) 3350, 1430, 1100; ^{1}H NMR ($CDCl_3$) δ 7.75−7.65 (m, 4H), 7.45−7.31 (m, 6H), 5.18 (s, 1H), 3.71−3.63 (m, 1H), 2.24−2.14 (m, 1H), 2.15 (s, 2H), 1.91−1.68 (m, 4H), 1.56−1.47 (m, 1H), 1.39−1.27 (m, 1H), 1.11 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 136.2, 134.9, 134,8, 134.7, 129.1, 127.4, 118.0, 66.4, 34.4, 30.9, 29.1, 27.7, 20.8, 18.4. Anal. Calcd for $C_{23}H_{30}OSi$: C, 78.80; H, 8.63. Found: C, 79.15; H, 8.96.

3-*tert*-Butyldiphenylsilylmethyl-4-methylcyclohex-3-enol (39): colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.65−7.55 (m, 4H), 7.45−7.30 (m, 6H), 3.69−3.61 (m, 1H), 2.16 (d, J = 15.0 Hz, 1H), 2.08 (d, J = 15.0 Hz, 1H), 2.06−1.99 (m, 1H), 1.85−1.63 (m, 5H), 1.53−1.44 (m, 1H), 1.33 (s, 3H), 1.09 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 136.2, 134.9, 134.8, 129.0, 127.2, 126.6, 121.2, 66.9, 40.5, 31.0, 29.9, 27.6, 19.8, 18.3, 16.6. Anal. Calcd for $C_{24}H_{32}OSi$: C, 79.06; H, 8.85. Found: C, 79.41; H, 9.11.

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Supporting Information Available: Crystallographic data collection parameters for compound **33a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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