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A New Synthesis and Stereocontrolled Functionalization of Substituted Silacyclopent-3-enes†

Yannick Landais,*,‡ Cédrick Mahieux,‡ Kurt Schenk,§ and Sheetal S. Surange‡

Laboratoire de Chimie Organique et Organométallique, 351, Cours de la Libération, 33405 Talence Cedex, France, and Institut de cristallographie, Université de Lausanne, BPS Dorigny, CH-1015, Lausanne, Switzerland

y.landais@lcoo.u-bordeaux1.fr

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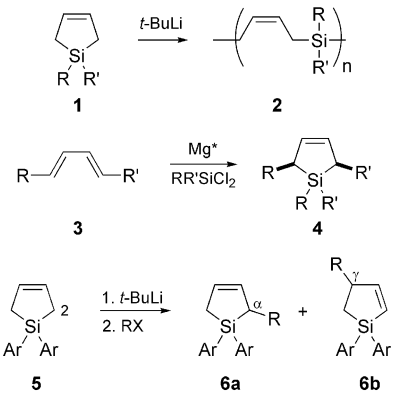
C2-Substituted silacyclopent-3-enes have been prepared in good yields in two steps starting from commercially available diallylsilane **9**. Coupling between carbanion of **9** and aldehydes or epoxides followed by ring-closing metathesis of the corresponding substituted diallylsilanes led to various silacyclopent-3-enes having a β- or a γ-hydroxysilane moiety. Dihydroxylation and epoxidation of the sila-cycle then led stereoselectively to polyhydroxylated silacyclopentanes. These processes were shown to occur with opposite topicity, offering a complementary and stereocontrolled access to diastereomeric polyols having up to five contiguous stereogenic centers.

Introduction

Silacyclopent-3-enes **1**, widely used as precursors of polymers **2**,[1] are attractive synthons which have rarely been exploited as building blocks in organic synthesis (Scheme 1).[2] Several practical routes have been described which led to the title compound as well as functionalized analogues in moderate to good yields.[3] For instance, silylation of dienes such as **3** with dichlorosilanes in the presence of magnesium is the most straightforward method to prepare **1** and analogues. Recently, Rieke[4] improved and extended the process using activated magnesium and showed that (2-butene-1,4-diyl)magnesium, generated from dienes **3**, reacted with dichlorosilanes to afford various polysubstituted silacyclopentenes (i.e., **4**) in good yields. Functionalization of the parent silacyclopentene **5** through direct alkylation has also been studied to access C2-substituted silacyclopent-3-enes. Unfortunately, the preferential attack of the silicon center by the base used to deprotonate **5** (generally *t*-BuLi) led to nucleophilic ring opening and subsequent polymerization of silacyclopentenes.[1,5] Chan et al.,[5] however, found that the presence of electron-rich substituents (Ar = *p*-(*t*-Bu)Ph) at the silicon center could prevent the attack of the lithium base on the heteroatom and thus limit the formation of polymeric material. Unfortunately, the addition of electrophiles onto the carbanion led to inseparable mixtures of α and γ isomers **6a**,**b** with poor regiocontrol. Therefore, although these methods offer a straightforward access to various types of silacyclopentenes, the number and nature of substituents allowed both on the ring and at the silicon center is rather limited. More generally, we noticed that there was no reliable methodology allowing the introduction of functionalized chain (possibly having stereogenic centers) in the α position (C2) relative to silicon.

SCHEME 1



* To whom correspondence should be addressed. Tel: + 33 5 57 96 22 89. Fax: +33 5 56 84 62 86.

† This paper is dedicated to Prof. Ian Fleming on the occasion of his retirement.

‡ Laboratoire de Chimie Organique et Organométallique.

§ Université de Lausanne.

(1) Brook, M. A. *Silicon in Organic, Organometallic and Polymer Chemistry*; J. Wiley & Sons: New York, 2000.

(2) For a recent functionalization of the parent unsubstituted silacyclopent-3-ene **1**, see: (a) Liu, D.; Kozmin, S. A. *Org. Lett.* **2002**, *4*, 3005−3007. (b) Liu, D.; Kozmin, S. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4757−4759.

(3) For a review, see: (a) Hermanns, J.; Schmidt, B. *J. Chem. Soc., Perkin Trans. 1* **1998**, 81−102. (b) Hermanns, J.; Schmidt, B. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2209−2230. (c) Mignani, S.; Damour, D.; Bastart, J.-P.; Manuel, G. *Synth. Commun.* **1995**, *25*, 3855−3862. (d) Mignani, S.; Barreau, M.; Damour, D.; Renaudon, A.; Dejean, V.; Manuel, G. *Synth. Commun.* **1998**, *28*, 1163−1174. (e) Matsumoto, K.; Yokoo, T.; Oshima, K.; Utimoto, K.; Abd. Rahman, N. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1694−1700. (f) Manuel, G.; Mazerolles, P.; Lesbre, M.; Pradel, J.-P. *J. Organomet. Chem.* **1973**, *61*, 147−165. (g) Weyenberg, D. R.; Toporcer, L. H.; Nelson, L. E. *J. Org. Chem.* **1968**, *33*, 1975−1982. (h) Dunoguès, J.; Arréguy, B.; Biran, C.; Calas, R.; Pisciotti, F. *J. Organomet. Chem.* **1973**, *63*, 119−131. (i) Manuel, G.; Mazerolles, P.; Florence, J. C. *J. Organomet. Chem.* **1971**, *30*, 5−19. (j) Sudo, T.; Asao, N.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 8919−8923.

(4) Rieke, R. D.; Xiong, H. *J. Org. Chem.* **1991**, *56*, 3109−3118.

(5) Horvath, R. F.; Chan, T. H. *J. Org. Chem.* **1987**, *52*, 4489−4494 and references therein.

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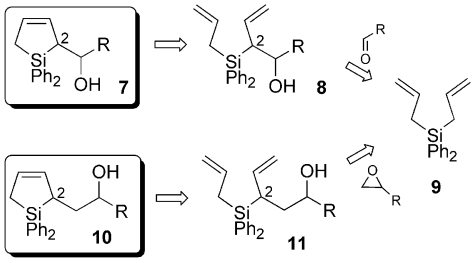
We wish to propose here a concise and practical route to C2-substituted silacylopent-3-enes as well as their elaboration into polyfunctionalized silacyclopentanes.[6] Our strategy is based on the ring-closing metathesis[7] of simple C2-substituted diallylsilanes such as **8** and **11**, available from the parent diallylsilane **9**.[8] It was anticipated from literature precedent that alkylation of **9** would not be regioselective (α- vs γ-alkylation).[9] Therefore, we turned our attention to the more reliable hydroxyalkylation developed by Reetz and Yamamoto,[10] based on the coupling of allyltitanate species with aldehydes. It was envisioned that this strategy would offer a stereocontrolled access to β-hydroxysilanes **8** having two stereogenic centers with defined stereochemistry. Moreover, in the event of an extension of the strategy to enantiopure series, an access to optically enriched β-hydroxysilanes would be at hand by simply using chiral nonracemic aldehydes. In parallel, silacyclopent-3-enes **10** should be available through ring-closing metathesis of homologous γ-hydroxysilanes **11**. The latter would be accessible by coupling of the carbanion generated from **9** with monosubstituted epoxides.[11] This approach is known to provide good regioselectivity in favor of the α-alkylation. As above, the method should be applicable in enantiopure series by using optically active epoxides.

Finally, synthons **7** and **10**, which are cyclic chiral allylsilanes, should be valuable intermediates for organic synthesis, providing that they can be functionalized in a stereocontrolled manner. Surprisingly, although the stereochemistry of electrophilic reactions onto chiral allylsilanes has been intensively studied in the past,[12] nothing has been reported on the stereochemistry of these processes applied to C2-substituted silacyclopentenes such as **7** or **10** (Scheme 2). The functionalization of these allylsilanes through dihydroxylation and epoxidation will be described and the stereochemical outcome of these reactions discussed.

Results and Discussions

Synthesis of Alcohols 8 and 11. β-Hydroxysilanes **8** were easily prepared by metalation of **9**, followed by transmetalation with Ti(O-*i*-Pr)$_4$ and coupling of the resulting allyltitanate intermediate with suitable aldehydes (Scheme 3).[10a−b,13] The deprotonation of **9** having phenyl substituents on the silicon center was found to be easy and could be carried out at −78 °C.[10b] We also noticed that better yields were obtained when transmetalation with Ti(O-*i*-Pr)$_4$ was carried out during 2 h at −78 °C. This strategy afforded alcohols **8a**−**d**,**f** in good yield after chromatography and in each case as a unique diastereomer (Table 1). X-ray structure determination of an advanced intermediate prepared from **8a** (vide infra) eventually showed that these β-hydroxysilanes had the anti configuration, in good agreement with earlier reports by Yamamoto.[10b] By analogy, we assumed that **8b**−**d**,**f** also have the anti configuration. This may be rationalized invoking a chairlike transition-state model (Figure 1) where the aldehyde is coordinated to titanium and bulky SiPh$_2$allyl and R groups occupy pseudoequatorial positions. Interestingly, when the one-pot protocol was ap-

SCHEME 2



SCHEME 3

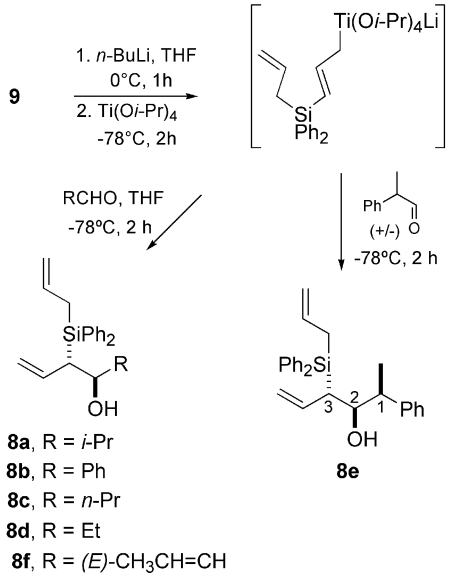


TABLE 1. Preparation of *anti*-β-Hydroxysilanes 8a−f (Scheme 3)

entry	alcohol	de[a] (%)	yield[b] (%)
1	**8a**	>98	83
2	**8b**	>98	68
3	**8c**	>98	78
4	**8d**	>98	50
5	**8e**	>98	52
6	**8f**	>98	60

[a] Estimated from 250 MHz ^{1}H NMR. [b] Yield after purification.

(6) For a preliminary account, see: Landais, Y.; Surange, S. S. *Tetrahedron Lett.* **2001**, *42*, 581−584.

(7) For recent reviews on olefin metathesis, see: (a) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413−4450. (b) Armstrong, S. K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 371−388. (c) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2036−2056.

(8) **9** is commercially available. For a synthesis, see: Nasiak, L. D.; Post, H. W. *J. Org. Chem.* **1959**, *24*, 489−492.

(9) (a) Li, L.-H.; Wang, D.; Chan, T. H. *Tetrahedron Lett.* **1991**, *32*, 2879−2882. (b) Chan, T. H.; Labrecque, D. *Tetrahedron Lett.* **1991**, *32*, 1149−1152. (c) Muchowski, J. M.; Naef, R.; Maddox, M. L. *Tetrahedron Lett.* **1985**, *26*, 5375−5378. (d) Koumaglo, K.; Chan, T. H. *Tetrahedron Lett.* **1984**, *25*, 717−720.

(10) (a) Reetz, M. T.; Wenderoth, B. *Tetrahedron Lett.* **1982**, *23*, 5259−5262. (b) Ikeda, Y.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 657−658. (c) Hodgson, D. M.; Wells, C. *Tetrahedron Lett.* **1992**, *33*, 4761−4762. (d) Shimizu, N.; Shibata, F.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3017−3018. (e) Sato, F.; Suzuki, Y.; Sato, M. *Tetrahedron Lett.* **1982**, *23*, 4589−4592. (f) Yamamoto, Y.; Saito, Y.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1326−1328.

(11) Schaumann, E.; Kirschning, A. *Tetrahedron Lett.* **1988**, *29*, 4281−4284.

(12) (a) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063−2192. (b) Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989**, *37*, 57−575.

(13) Direct coupling of the allyllithium species with aldehydes led exclusively to the γ-product.

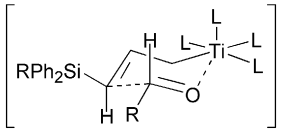
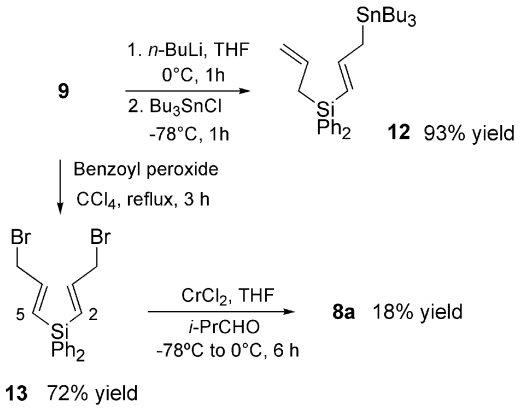


FIGURE 1.

SCHEME 4



plied to chiral racemic phenylpropionaldehyde, β-hydroxysilane **8e** (entry 5, Table 1) was formed as a single diastereomer having three stereogenic centers in a syn-anti relative configuration. The relative stereochemistry at C1 and C2, determined by X-ray crystallography on an advanced intermediate (vide infra), is consistent with an approach of the allyltitanate toward phenylpropionaldehyde following a Felkin−Anh transition-state model.[10a−b]

We also considered the preparation of the complementary *syn*-β-hydroxysilane series starting from an allylstannane[10f] instead of an allyltitanate. These are known to give syn diastereomers with a high level of stereocontrol.[10f] Metalation of **9** with *n*-BuLi followed by reaction of the resulting carbanion with Bu_3SnCl effectively furnished the required acid-sensitive allylstannane **12** in good yield (Scheme 4). Unfortunately, all our attempts to couple **12** with an aldehyde in the presence of Lewis acids such as BF_3-OEt_2 or $Sc(OTf)_3$ failed. We also investigated the double functionalization of **9** in order to get access to C2−C5-disubstituted silacyclopent-3-enes. In our first approach, we carried out a bis-lithiation of **9**, transmetalation with $Ti(O\text{-}i\text{-}Pr)_4$, and then reaction with isobutyraldehyde. Unfortunately, under these conditions, only the "mono" β-hydroxysilane **8a** was obtained in 38% yield. A second approach was then tested, involving the preparation of a bis-allylbromide such as **13** which was expected to couple with the aldehyde via an allylchromium intermediate.[10c] Again, only **8a** was formed in low yield, without traces of the expected bis-β-hydroxysilane.

Alcohols **11a**−**c** and **14a**−**c** were prepared through metalation of **9** with *n*-BuLi, followed by coupling of the resulting carbanion with racemic monosubstituted epoxides (Scheme 5).[11] This resulted in the formation of the expected γ-hydroxysilanes as a separable mixture of diastereomers **11** and **14** with generally poor stereocontrol (Table 2). Under these conditions, regiocontrol of the alkylation was satisfying, since less than 10% of the γ-isomer was formed which could easily be discarded by chromatography. The relative configuration of the major isomer **11b** was obtained from X-ray structure determination of an advanced intermediate (vide infra) and was

SCHEME 5

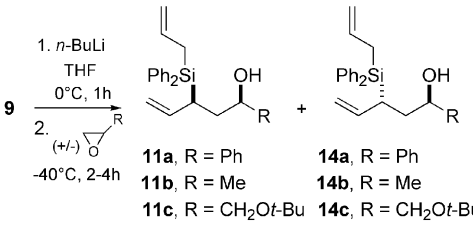
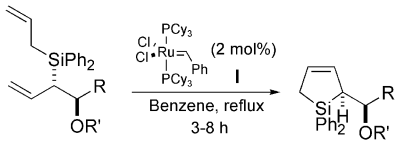


TABLE 2. Preparation of γ-Hydroxysilanes 11 and 14 (Scheme 5)

alcohols	R	ratio **11**/**14**[a] (%)	yield[b] (%)
11a, **14a**	Ph	60:40	77
11b, **14b**	Me	68:32	70
11c, **14c**	CH_2Ot-Bu	64:36	70

[a] Estimated from 250 MHz ^{1}H NMR. [b] Overall yield after purification.

SCHEME 6



15a, R = *i*-Pr, R' = Ac
15b, R = *n*-Pr, R' = Ac
8a, R = *i*-Pr, R' = H
8b, R = Ph, R' = H
8d, R = Et, R' = H
8e, R = CHMePh, R' = H
7a, R = *i*-Pr, R' = Ac
7b, R = *n*-Pr, R' = Ac
7c, R = *i*-Pr, R' = H
7d, R = Ph, R' = H
7e, R = Et, R' = H
7f, R = CHMePh, R'= H

found to be syn. Although we did not establish firmly the relative configuration for the other alcohols, we assumed by analogy that in each case the major isomer has the syn configuration.

Ring-Closing Metathesis of Alcohols 8 and 11−14. With our diallylsilanes **8**, **11**, and **14** in hand, we then investigated their ring-closing metathesis using Grubbs first-generation catalyst **I** (Scheme 6).[7] Our preliminary attempts were carried out on the acetate protected alcohols **15a**,**b**[14] in benzene under reflux.[15] The desired silacyclopent-3-enes **7a**,**b** were thus obtained in less than 3 h in good yield after purification by chromatography on silica gel (entries 1 and 2, Table 3).[16] We also observed that alcohol protection was not required since ring-closing metathesis of **8a**,**b** and **8d**,**e** in the presence of catalyst **I** led to the free hydroxy silacyclopent-3-enes **7c**−**f** in excellent yields and high purity (entries 3−6, Table 3). However, RCM of **8a**−**e** required slightly longer reaction times than their protected analogues **15a**,**b**.

Under the same conditions, diallylsilane **8f** led to a cyclized product in which the crotyl methyl group had

(14) Alcohols **8a**, **8c,** and **8f** were easily acetylated using Ac_2O and 4-DMAP in CH_2Cl_2 for 3−18 h at rt to afford **15a**−**c** in 74%, 79%, and 81% yield, respectively.

(15) Much lower yields were obtained when the reaction was carried out in CH_2Cl_2 under reflux.

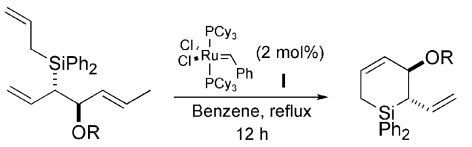
(16) The synthesis of nonsubstituted 1-silacyclopent-3-enes **1** through RCM using a tungsten catalyst has been reported. Poor to excellent results (8−90% yield) were obtained depending on the nature of the substituents at the silicon center. See: (a) Leconte, M.; Pagano, S.; Mutch, A.; Lefebvre, F.; Basset, J. M. *Bull. Soc. Chim. Fr.* **1995**, *132*, 1069−1071. (b) Ahmad, I.; Falck-Pedersen, M. L.; Undheim, K. *J. Organomet. Chem.* **2001**, *625*, 160−172.

TABLE 3. Ring-Closure Metathesis of 8a−e and 15a,b (Scheme 6)

entry	diene	product	time (h)	yield[a] (%)
1	**15a**	**7a**	3	88
2	**15b**	**7b**	3	95
3	**8a**	**7c**	6	93
4	**8b**	**7d**	8	78
5	**8d**	**7e**	6	75
6	**8e**	**7f**	8	74

[a] Yield after purification.

SCHEME 7



8f, R = H
15c, R = Ac

16, R = H (57%)
17, R =Ac (61%)

TABLE 4. Ring-Closing Metathesis of γ-Hydroxysilanes 11a−c and 14a−c (Scheme 8)

entry	diene	product	time (h)	yield[a] (%)
1	**11a**	**10a**	18	75
2	**11b**	**10b**	16	77
3	**11c**	**10c**	36	66
4	**14a**	**10d**	7	84
5	**14b**	**10e**	30	78
6	**14c**	**10f**	7	72
7	**11a**	**10a**	3	78[b]

[a] Yield after purification. [b] Grubbs catalyst II (1.5 mol %).

disappeared. Extensive NMR studies (COSY, INADEQUATE) finally showed unambiguously that RCM on **8f** and **15c** led preferentially to the six-membered silacycles **16** and **17**, albeit in moderate yield (Scheme 7).[17]

The ring-closing metathesis was then extended to γ-hydroxysilanes **11a−c** and **14a−c** (Table 4, Scheme 8). As above, cyclization using Grubbs catalyst **I** gave the corresponding silacyclopent-3-enes **10a−f** in good yields. However, the reaction was more sluggish than with β-hydroxysilanes, requiring longer period of reflux and larger amount of catalyst (4−10 mol % instead of 2 mol %). Grubbs catalyst **II**[18] led to a slight improvement leading to completion of the reaction in less than 4 h (Table 4, entry 7). The slower rate of cyclization, as compared with β-hydroxysilane analogues, may indicate that the free hydroxy group coordinates to the ruthenium carbene and thus slows down the cyclization.[19] Relative configuration of **10b** was obtained from X-ray diffraction study, which also allowed the assignment of the configuration of **11b**.

Electrophilic Functionalization of C2-Substituted Silacyclopent-3-enes. Functionalization of chiral allylsilanes using electrophilic reagents has been extensively investigated over the last 20 years, and general trends have emerged, providing reliable models to predict

SCHEME 8

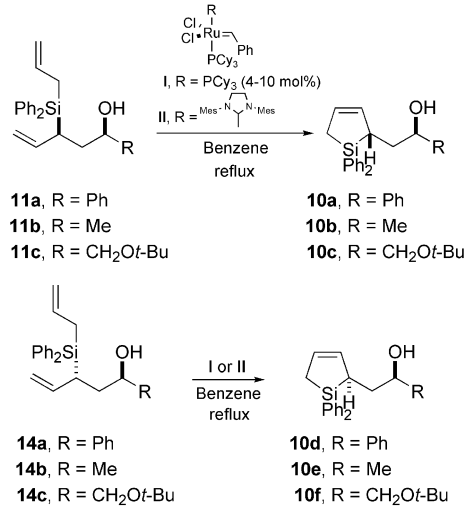


TABLE 5. Dihydroxylation of Silacyclopentenes 7 (Scheme 9)

entry	allylsilane	diol	trans/cis ratio[a]	yield[b] (%)
1	**7c**	**18a**	80:20	84
2	**7d**	**18b**	84:16	quant[c]
3	**7f**	**18c**	79:21	63[c]
4	**7b**	**18d**	76:24	70

[a] Estimated from ^{1}H NMR of the crude reaction mixture. [b] Yield after purification of the diols. [c] Crude yield of the diols.

the stereochemical outcome of these processes.[12] Surprisingly, nothing has been reported on the stereochemistry of electrophilic reactions of cyclic allylsilanes such as C2-substituted silacylopent-3-enes (i.e., **7** and **10**). Silacyclopent-3-enes react like allylsilanes in the presence of electrophiles, providing addition and SE_2' products.[3i] Therefore, one may expect in these processes a transfer of the chiral information from the C2-allylic stereogenic center to the prochiral olefin moiety. It may be anticipated that in such rigid systems stereofacial differentiation should be governed by the size and nature of the R group at the allylic stereogenic center (Figure 2). We thus investigated the epoxidation and dihydroxylation reactions of precursors **7** and **10**, which should lead to highly functionalized polyols systems, valuable intermediates for organic synthesis.

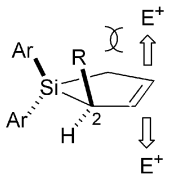


FIGURE 2.

Our preliminary studies started with the dihydroxylation of precursors **7b−d**,**f** using modified Sharpless conditions,[20] i.e., quinuclidine as an achiral ligand. In each case, a pair of diastereomers was formed in high yield with reasonable diastereoselectivity (Table 5, Scheme 9). Major diols **18b** and **18c** were found to be poorly

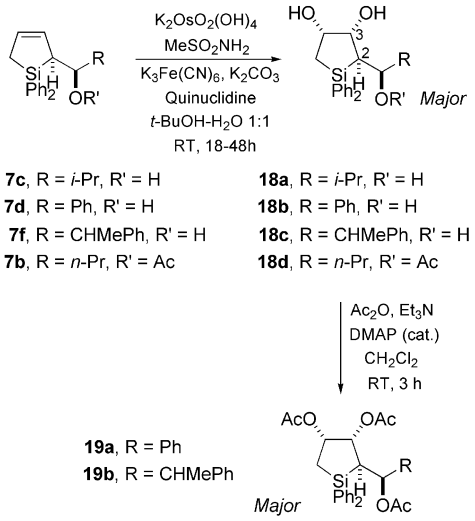
(17) A five-membered ring structure was first proposed in the preliminary communication.[6]

(18) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956.

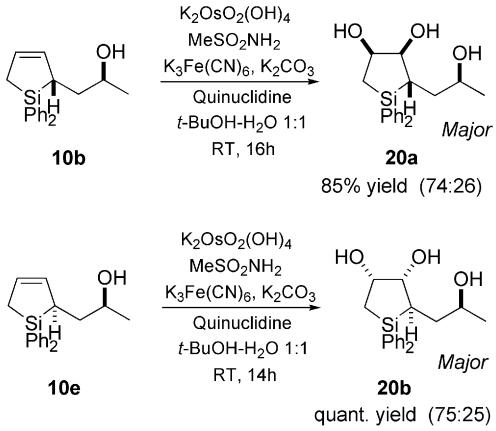
(19) Furstner, A.; Langemann, K. *J. Am. Chem. Soc.* **1997**, *119*, 9130−9136.

(20) Kolb, H. C.; vanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483−2547.

SCHEME 9



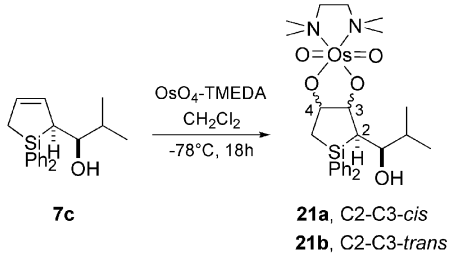
SCHEME 10



soluble, so they were characterized as their triacetates **19a**,**b**. The presence of an acetate on the acyclic chain (i.e., **7b**) instead of a hydroxy group had no effect on the diastereocontrol (entry 4). Changing quinuclidine for Sharpless chiral ligands did not improve the stereoselectivity. Interestingly, most diastereomers could be isolated by chromatography and were found to be remarkably stables. X-ray crystallographic studies on the major diastereomer **18a**, issued from the dihydroxylation of **7c**, not only confirmed the anti relative configuration for the β-hydroxysilane precursor **8a** (Scheme 3), but also indicated that the osmium reagent approached preferentially anti relative to the chain at C2 to afford majoritarely the C2−C3-trans product. We assumed that the dihydroxylation on closely related analogues **7d**, **7f**, and **7b** occurred with the same stereochemistry.

Silacyclopentenes **10b** and **10e** were dihydroxylated under the same conditions as above to give the desired diols **20a** and **20b** (major isomer shown) in good yield with a diastereomeric ratio similar to those obtained with silacyclopentenes **7a**−**f** (Scheme 10). The stereochemistry of the major isomers of **20a** and **20b** was not determined since both compounds could not be isolated pure through chromatography.[21] A C2−C3-trans stereochemistry was, however, assigned by analogy with that of **18a**−**d**.

SCHEME 11



We also investigated the possibility to access, from **7**, to diastereomeric diols having the complementary C2−C3-cis stereochemistry (resulting from a syn dihydroxylation relative to the chain at C2), using a method recently introduced by Donohoe et al.[22] Association of a strongly coordinating solvent such as TMEDA to OsO_4 was reported to generate an osmium complex where the electron density at oxygen was increased. Such a complex was shown to lead, through hydrogen bonding, to a reversal of topicity during dihydroxylation of allylic alcohols. It was effectively shown that the title reagent gave high syn diastereocontrol as compared to usual Upjohn conditions, which are known to provide anti stereoselectivity. Treatment of **7c** with a stoechiometric amount of OsO_4 in the presence of TMEDA (1 equiv) led after hydrolysis (Na_2SO_3) to the formation of a mixture of two compounds, which were not the expected diols. ^{1}H and ^{13}C NMR showed that TMEDA was present in the structure, which strongly supported the formation of a diastereomeric mixture of osmates (Scheme 11). ^{13}C chemical shift for C3 and C4 carbons in the 93−96 ppm range instead of the expected 72−75 ppm reinforced this hypothesis. Fortunately, it turned out that **21a**,**b** gave, upon recrystallization, suitable crystals for X-ray structure determination. The structure is that of the *syn*-osmate **21a**, but the crude reaction mixture was composed of a 55:45 ratio of both diastereomers **21a**,**b** (as measured from ^{1}H NMR). Forcing hydrolysis conditions did not allow us to isolate the diols in good yield (<20%), due to the sensitivity of our silicon precursors toward hydrolytic medium. However, we have shown that the use of Donohoe's conditions may reverse, at least partially, the sense of stereoinduction, leading to larger amount of the syn diol. The incomplete reversal of stereoinduction in our case may be attributed to the occurrence of an homoallylic instead of an allylic hydroxy group, which is too far remote form the reacting olefin to direct efficiently the electrophilic reagent onto the syn face. Isolation of osmates **21a**,**b** as well as the X-ray crystallography of **21a** is noteworthy and constitutes one of the few examples of such structures in the literature.[23]

A solution to the problem of stereocontrolled access to C2−C3-cis diastereomer eventually emerged when we

(21) All attempts to separate the mixture of diastereomers by chromatography through silica gel led to decomposition.

(22) (a) Donohoe, T. J.; Moore, P. R.; Waring, M. J.; Newcombe, N. J. *Tetrahedron Lett.* **1997**, *38*, 5027−5030. (b) Donohoe, T. J.; Blades, K.; Moore, P. R.; Waring, M. J.; Winter, J. J. G.; Helliwell, M.; Newcombe, N. J.; Stemp, G. *J. Org. Chem.* **2002**, *67*, 7946−7956. (c) Donohoe, T. J. *Synlett* **2002**, 331−333.

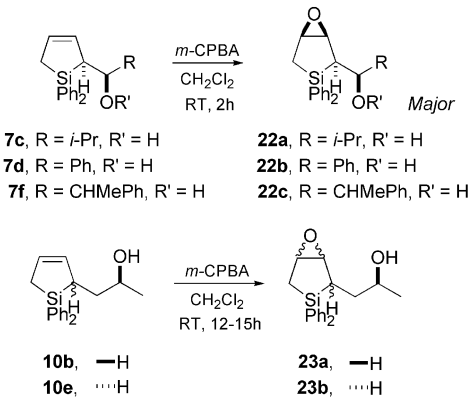
(23) (a) Corey E. J.; Sarshar, S.; Azimioara, M. D.; Newbold, R. C.; Noe, M. C. *J. Am. Chem. Soc.* **1996**, *118*, 7851−7852. (b) Donohoe, T. J.; Johnson, P. D.; Cowley, A.; Keenan, M. *J. Am. Chem. Soc.* **2002**, *124*, 12934−12935.

TABLE 6. Epoxidation of Silacyclopentenes (Scheme 12)

entry	Allylsilane	diol	cis/trans ratio[a]	yield[b] (%)
1	**7c**	**22a**	88:12	69
2	**7d**	**22b**	93:7	66
3	**7f**	**22c**	90:10	66
4	**10b**	**23a**	60:40[c]	78
5	**10e**	**23b**	65:35[c]	98

[a] Estimated from ^{1}H NMR of the crude reaction mixture. [b] Yield after purification. [c] Stereochemistry not determined.

SCHEME 12



investigated the epoxidation of silacyclopentenes **7b**, **7d**, and **7f**. Epoxidation of these allylsilanes in the presence of *m*-CPBA led to the desired epoxides **22a**−**c** (major isomer shown) in good yields with slightly better diastereocontrol than that observed during dihydroxylation (Table 6, Scheme 12). Interestingly, the diastereomers could be separated by chromatography over silica gel and were found to be much more stable than their acyclic analogues, which tend to open in the presence of trace of acid.[24] This unusual stability may be explained by the conformation of the cyclic epoxide in which the C−Si bond is perpendicular to the epoxide C−O bond and thus is not properly aligned for the Peterson elimination to occur. This can be observed on X-ray structure of major epoxide **22c**, which also demonstrates that the epoxidation of **7f** has occurred syn relative to the chain at C2 and thus with reversal of topicity as compared with the dihydroxylation. It also confirmed the syn-anti relative configuration of diallylsilane precursor **8e** (Scheme 3). The stereochemistry of other epoxides **22a**,**b** was assigned by analogy to **22c**. Epoxidation of the homologous γ-hydroxysilanes **10b** and **10e** was also performed and was found to be slower and much less stereoselective (vide infra).

Transition-State Models for Dihydroxylation and Epoxidation of Silacyclopentenes. As mentioned above, dihydroxylation and epoxidation of C2-substituted silacyclopent-3-enes **7** and **10** proceed surprisingly with reversal of topicity. This may be rationalized by invoking two transition-state models as drawn in Figure 3 (dihydroxylation and epoxidation of **7c**). For dihydroxylation, OsO_4 would approach anti relative to the sterically hindered C2-chain from the less crowded face (Figure 3,

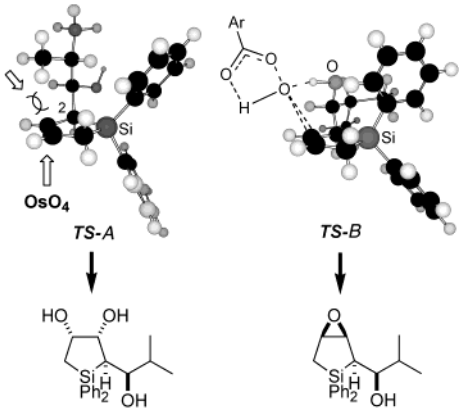


FIGURE 3.

TS-A). The substantial amount of C2−C3-cis diols (up to 20%), resulting from a syn dihydroxylation of precursors **7**, may also be indicative of a competitive directing effect of the acyclic OH group. OsO_4−quinuclidine is not as good an hydrogen acceptor as OsO_4−TMEDA but may, however, hydrogen bond to a certain extent to the homoallylic OH group, which would lead to the contrasteric C2−C3-cis product.[22b] The reversal of topicity with *m*-CPBA may be ascribed to the known tendency of this reagent to give hydrogen bonds with alcohols. This has been used many times in the stereocontrolled epoxidation of chiral allylic alcohols and is also operative, although less efficiently, with homoallylic alcohols.[25] It is likely that in our case the homoallylic alcohol directs the peracid to the top face, thus providing high level of syn stereoselectivity through a cyclic transition state model (Figure 3, ***TS-B***). The low stereocontrol observed during epoxidation of **10b** and **10e** may be rationalized by the γ-position of the hydroxy group (bishomoallylic), which is too far remote from the double bond to efficiently direct the peracid on the top face of the olefin. Finally, when comparing transition state models ***TS-A*** and ***TS-B*** (Figure 3) with those proposed for systems having an "external" silicon group,[12] it appears that in sila-cycles, the exocyclic chain at C2 mainly controls the stereochemistry of electrophilic processes, the silicon group having no major steric influence. Electron-rich σ_{C-Si} bonds are not "conjugated" with the allylic π-orbital and therefore are not expected to influence to a major extent the double bond reactivity during these processes.[12,26] In turn, the perpendicular arrangement between the σ_{C-Si} and C−O bonds contributes to the unusual stability of the epoxidation products **22a**−**c**.[24] It is worth noting that epoxidation of closely related cyclopent-2-ene methanol with *m*-CPBA led to a 4:1 ratio in favor of the cis product, thus indicating further that in our system the silicon group has little influence on the stereochemistry of the epoxidation reaction.[27]

(24) (a) Roush, W. R.; Grover, P. T.; Lin, X. *Tetrahedron Lett.* **1990**, *31*, 7563−7566. (b) Roush, W. R.; Grover, P. T. *Tetrahedron Lett.* **1990**, *31*, 7567−7570. (c) Roush, W. R.; Grover, P. T. *Tetrahedron* **1992**, *48*, 1981−1998. (d) Landais, Y.; Parra-Rapado, L. *Tetrahedron Lett.* **1996**, *37*, 1205−1208.

(25) Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307−1370.

(26) Theoretical studies have shown that in allylsilanes, ground-state interactions between alkene π-orbital and the coplanar C−Si bond raises the HOMO of the allylsilane and thus make it more reactive towards electrophiles, see: Kahn, S. D.; Pau, C. F.; Chamberlin, A. R.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 650−663.

(27) Morizawa, Y.; Nakayama, T.; Matsumura, Y.; Uchida, K.; Yasuda, A. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2714−2719.

Conclusion

In summary, we reported here a stereoselective access to polyhydroxylated silacyclopent-3-enes in only three steps, starting from commercially available diallylsilane **9**. A careful choice of oxidants, during the functionalization of the allylsilane moiety, may be used to access complementary sets of diastereomeric polyols. Levels of stereocontrol are generally good and are of preparative value since diastereomers can be easily isolated in pure form by a simple chromatography. The structures of major diastereomers have been determined unambiguously by X-ray diffraction studies, allowing the drawing of transition state models ***TS-A*** and ***TS-B*** for dihydroxylation and epoxidation processes. It is also worth noticing that the strategy can easily be extended to enantiopure series by using chiral nonracemic aldehydes and epoxides in the first step. Tartrate-[24a−c,28] and pinane-based[29] allylboranes might also be used in this context. Further elaboration through regioselective Peterson elimination[30] and/or C−Si bond oxidation[2,31] should lead to polyhydroxylated skeletons having up to five stereocontrolled contiguous stereogenic centers. Work along these lines is now underway and will be reported in due course.

Experimental Section

General Remarks. ^{1}H NMR spectra were measured at 200 or 250 MHz. ^{13}C NMR spectra were measured at 50 and 63 MHz using $CDCl_3$ as an internal reference unless otherwise stated. Low- and high-resolution mass spectra were recorded using either electronic impact (EI) with an ionization potential of 70 eV or LSIMS with ionization potential of 35 keV (matrix: 3-nitrobenzyl alcohol). Elemental analyses were performed by the service central d'analyze, Vernaison, CNRS, France. Silica gel 60 (70−200 μm) was used for column chromatography. All anhydrous and inert atmosphere reactions were performed with oven-dried glass apparatus under nitrogen atmosphere. THF, ether, benzene, and petroleum ether were distilled from sodium and benzophenone. CH_2Cl_2 was distilled from CaH_2.

General Procedure for the Preparation of β-Hydroxysilane 8a−f from 9. (3*R,4*S**)-4-(Allyldiphenylsilyl)-2-methylhex-5-en-3-ol (8a).** To a stirred solution of diallyldiphenylsilane **9** (528 mg, 2.0 mmol) in dry THF (5.0 mL) was added dropwise at 0 °C a 2.5 M solution of *n*-BuLi in hexane (0.8 mL, 2.0 mmol) under a nitrogen atmosphere. The resulting deep yellow solution was stirred for 1 h at 0 °C and then cooled to −78 °C. Ti(O-*i*-Pr)$_4$ (0.59 mL, 2.0 mmol) was added and the reaction mixture stirred for 1 h at −78 °C. Freshly distilled isobutyraldehyde (0.18 mL, 2.0 mmol) in dry THF (2.0 mL) was then added dropwise at −78 °C, and stirring was continued for 2 h at −78 °C. The reaction mixture was then quenched with aq NH_4Cl and allowed to warm to rt. The organic layer was decanted and the aqueous layer extracted with ether. The combined extracts were washed with brine and dried ($MgSO_4$), and the solvents were concentrated in vacuo. The crude product was purified by chromatography through silica gel (petroleum ether−EtOAc 95:5) giving **8a** as an oil (558 mg, 83%). R_f = 0.46 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3417, 1625, 1427, 1216, 1109 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.64 (m, 5H), 7.4 (m, 5H), 5.84 (m, 2H), 5.0 (m, 4 H), 3.52 (m, 1H), 2.68 (dd, J = 10, 4 Hz, 1H), 2.28 (d, J = 8 Hz, 2H), 1.72 (m, 1H), 1.48 (d, J = 5 Hz, 1H), 0.92 (d, J = 5 Hz, 3H), 0.88 (d, J = 5 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 135.7, 134.3, 134.2, 129.5, 127.8, 127.7, 116.3, 114.8, 77.0, 37.0, 32.8, 20.3, 19.0. MS (EI) *m*/*z*: 223, 199 (100), 183.1, 145. Anal. Calcd for $C_{22}H_{28}SiO$: C, 78.51; H, 8.39. Found: C, 78.55; H, 8.72.

(1*R,2*S**)-2-(Allyldiphenylsilyl)-1-phenylbut-3-en-1-ol (8b).** Compound **8b** was obtained as a colorless oil (68%). R_f = 0.52 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3563, 1627, 1602, 1453, 1427 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.6 (m, 5H), 7.4 (m, 5H), 7.28 (m, 5 H), 5.98 (m, 1H), 5.84−5.6 (m, 1H), 5.08−4.78 (m, 5H), 2.71 (dd, J = 10, 5 Hz, 1H), 2.0 (d, J = 8 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.8, 135.8, 135.7, 134.3, 134.0, 133.9, 133.5, 129.6, 129.5, 128.1, 127.8, 127.4, 126.3, 117.6, 114.9, 42.3, 20.3. MS (EI) *m*/*z*: 223, 199 (100), 183, 145.

(3*S,4*R**)-3-(Allyldiphenylsilyl)hept-1-en-4-ol (8c).** Compound **8c** was obtained as an oil (78%). R_f = 0.51 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3582, 1627, 1427, 1215, 1109 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.6 (m, 4H), 7.36 (m, 6H), 5.97−5.62 (m, 2H), 5.12−4.8 (m, 4H), 3.86 (m, 1H), 2.4 (dd, J = 11, 4 Hz, 1H), 2.2 (dd, J = 8, 2 Hz, 2H), 1.3 (m, 5H), 0.8 (t, J = 7 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 135.7, 134.5, 134.1, 133.9, 129.5, 129.5, 127.8, 127.7, 116.9, 114.8, 39.4, 39.2, 20.4, 19.1, 13.9. MS (EI) *m*/*z*: 223, 199 (100), 183, 145. Anal. Calcd for $C_{22}H_{28}OSi$: C, 78.51; H, 8.39; Si, 8.35. Found: C, 78.48; H, 8.40; Si, 8.24.

(3*R,4*S**)-4-(Allyldiphenylsilyl)hex-5-en-3-ol (8d).** Compound **8d** was obtained as a colorless oil (50%). R_f = 0.53 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3456, 2964, 1628, 1428, 1258, 1108 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.56 (m, 4H), 7.38 (m, 6H), 6.02 (dt, J = 17.4, 10.4 Hz, 1H), 5.89 (dd, J = 16.9, 10.1 Hz, 1H), 5.09 (m, 4H), 3.88 (m, 1H), 2.60 (dd, J = 10.5, 3.7 Hz, 1H), 2.35 (d, J = 7.9 Hz, 2H), 1.73 (d, J = 4.3 Hz, 1H), 1.57 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 135.8, 134.6, 134.4, 134.3, 134.1, 129.7, 129.6, 128.0, 127.9, 117.0, 115.0, 72.8, 39.0, 30.1, 20.6, 10.6. MS (EI) *m*/*z*: 223, 199 (100), 183, 145.

(2*S,3*R**,4*S**)-4-(Allyldiphenylsilyl)-2-phenylhex-5-en-3-ol (8e).** Compound **8e** was obtained as an oil (52%). R_f = 0.51 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3581, 1626, 1493, 1427, 1217 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.6 (m, 2H), 7.4 (m, 11H), 7.1 (m, 2H), 6.0 (m, 1H), 5.67 (m, 1H), 5.18 (dd, J = 8, 2 Hz, 1H), 4.85 (m, 3H), 4.0 (m, 1H), 2.9 (m, 1H), 2.32 (dd, J = 10.7, 1.6 Hz, 1H), 2.2 (m, 2H), 1.5 (d, J = 4.9 Hz, 1H, exchangeable with D_2O), 1.25 (d, J = 7 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 144.7, 135.7, 135.6, 133.9, 133.8, 133.6, 129.7, 129.5, 128.4, 128.0, 127.7, 126.5, 117.5, 114.8, 75.9, 45.0, 36.3, 20.2, 18.7. MS (EI) *m*/*z*: 376, 352, 319, 251, 223 (100).

(*E*)-(3*S,4*R**)-3-(Allyldiphenylsilyl)hepta-1,5-dien-4-ol (8f).** Compound **8f** was obtained as an oil (60%). R_f = 0.42 (petroleum ether−EtAOc 6:4). IR ($CHCl_3$): ν_{max} 3582, 1627, 1589, 1519, 1487, 1428, 1378, 1215 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.6 (m, 4H), 7.4 (m, 6H), 6.0−5.65 (m, 2H), 5.48 (m, 2H), 5.18−4.84 (m, 4H), 4.28 (t, J = 6 Hz, 1H), 2.5 (dd, J = 10, 6 Hz, 1H), 2.21 (d, J = 8 Hz, 2H), 1.75 (br s, 1H), 1.56 (d, J = 5 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 135.7, 135.2, 134.0, 133.5, 129.5, 129.4, 127.7, 127.6, 127.4, 117.4, 114.9, 72.5, 40.9, 20.7, 17.5. MS (EI) *m*/*z*: 223, 199 (100), 183, 145. Anal. Calcd for $C_{22}H_{26}OSi$: C, 78.99; H, 7.83. Found: C, 78.79; H, 7.95.

General Procedure for the Preparation of γ-Hydroxysilanes 11a−c and 14a−c from 9. (1*R,3*S**)-3-(Allyldiphenylsilyl)-1-phenylpent-4-en-1-ol (11a) and (1*R**,3*R**)-3-(Allyldiphenylsilyl)-1-phenylpent-4-en-1-ol (14a).** To a solution of diallydiphenylsilane **9** (2.64 g, 10 mmol) in anhydrous THF (30 mL) was added dropwise under stirring at 0 °C a 1.6 M solution of *n*-BuLi in hexane (7.5 mL, 12 mmol). The orange solution was maintained at this temperature under

(28) Roush, W. R.; Walts, A. E.; Hoong, L. K. *J. Am. Chem. Soc.* **1985**, *107*, 8186−8190.

(29) (a) Ramachandran, P. V. *Aldrichim. Acta* **2002**, *35*, 23−35. (b) Barrett, A. G. M.; Malecha, J. W. *J. Org. Chem.* **1991**, *56*, 5243−5245.

(30) Ager, D. J. *Org. React.* **1990**, *38*, 1−223.

(31) (a) Fleming, I. *Chemtracts: Organic Chemistry* **1996**, 1−64. (b) Landais, Y.; Jones, G. *Tetrahedron* **1996**, *52*, 7599−7662. (c) Tamao, K. *Advances in Silicon Chemistry*; JAI Press, Inc.: Greenwich, CT, 1996; Vol. 3, p 1.

rapid stirring during 1 h. The reaction mixture was then cooled to −78 °C, and styrene oxide (1.32 g, 11 mmol) was added dropwise. The reaction mixture was allowed to warm to −40 °C, and stirring was continued for 3 h at this temperature. The reaction mixture was then quenched with an aq NH_4Cl solution, and the organic layer was decanted. The aqueous layer was extracted with ether, the combined extracts were washed with brine and dried over $MgSO_4$, and the solvents were evaporated in vacuo. The crude residue was purified by flash chromatography through silica gel (petroleum ether−EtOAc 9:1), affording the corresponding γ-hydroxysilane as a separable 60:40 mixture of two diastereoisomers **11a** (major) (1.91 g, 50%) and **14a** (minor) (1.04 g, 27%) as pale yellow oils. **11a**. R_f = 0.22 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3574, 2920, 1628, 1492, 1428, 1260 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.58−7.33 (m, 15H), 5.88 (m, 2H), 5.06 (m, 4H), 4.88 (m, 1H), 2.80 (m, 1H), 2.11 (d, J = 7.8 Hz, 2H), 1.96 (m, 1H), 1.68 (m, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 143.6, 138.7, 135.6, 135.5, 134.1, 133.4, 133.0, 129.6, 128.6, 127.9, 127.7, 126.6, 125.4, 124.4, 114.9, 114.7, 74.6, 37.8, 28.4, 19.4. MS (LSIMS, Na) m/z: 407 $[M + Na]^+$ (13), 376 (11), 367, 325, 224 (22), 223 $[Si(CH_2CH{=}CH_2)Ph_2]^+$ (100), 221. HRMS: calcd for $C_{26}H_{28}OSiNa$ $[M + Na]^+$ 407.180714, found 407.179970. **14a**. R_f = 0.35 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3444, 2971, 1627, 1492, 1454, 1262, 1110 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.53−7.25 (m, 15H), 5.75 (m, 2H), 5.06 (m, 4H), 4.72 (m, 1H), 2.80 (m, 1H), 2.11 (d, J = 7.9 Hz, 2H), 1.96 (m, 1H), 1.68 (m, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 145.1, 138.2, 135.6, 135.5, 134.3, 134.2, 133.5, 129.9, 19.40, 129.37, 128.3, 127.8, 127.6, 127.2, 125.5, 114.9, 114.7, 72.0, 38.1, 27.5, 19.5. MS (LSIMS, Na) m/z: 407 $[M + Na]^+$ (32), 376, 367 $[M - OH\cdot]^+$, 325 $[367 - CH_2{=}CHCH_2\cdot]^+$, 305, 237, 224 (22), 223 $[Si(CH_2CH{=}CH_2)Ph_2]^+$ (100), 221. HRMS: calcd for $C_{26}H_{28}OSiNa$ $[M + Na]^+$ 407.180714, found 407.179510. Anal. Calcd for $C_{26}H_{28}OSi$: C, 81.20; H, 7.34; Si, 7.30. Found: C, 81.11; H, 7.29; Si, 7.00.

(2*S,4*S**)-4-(Allyldiphenylsilyl)hex-5-en-2-ol (11b) and (2*S**,4*R**)-4-(Allyldiphenylsilyl)hex-5-en-2-ol (14b).** Compounds **11b** (49%), and **14b** (21%) were obtained as pale yellow oils. **11b**. R_f = 0.31 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3582, 2969, 1628, 1428, 1261, 1110 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.41−7.37 (m, 10H), 5.76 (m, 2H), 4.96 (m, 4H), 3.89 (m, 1H), 2.39 (m, 1H), 2.20 (d, J = 7.9 Hz, 2H), 1.69 (m, 2H), 1.17 (d, J = 6.1 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 139.4, 139.0, 136.0, 135.9, 135.7, 134.5, 133.9, 133.7, 133.5, 130.01, 130.00, 129.8, 124.2, 115.3, 114.7, 69.1, 38.5, 30.0, 22.7, 19.9, 22.7. MS (LSIMS, Na) m/z: 345 $[M + Na]^+$ (3), 281 $[M - CH_2{=}CHCH_2\cdot]^+$ (5), 223 $[Si(CH_2CH{=}CH_2)Ph_2]^+$ (57), 199 $[(Ph)_2SiOH]^+$ (100), 181 (20), 163 (19), 145 (35). HRMS: calcd for $C_{21}H_{26}OSiNa$ $[M + Na]^+$ 345.165064, found 345.164245. **14b**. R_f = 0.44 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3583, 2969, 1628, 1487, 1428, 1262, 1110 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.53−7.35 (m, 10H), 5.71 (m, 2H), 4.95 (m, 4H), 3.85 (m, 1H), 2.68 (m, 1H), 2.14 (d, J = 7.9 Hz, 2H), 1.65 (m, 2H), 1.16 (d, J = 6.1 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 139.5, 138.8, 136.0, 135.9, 134.0, 133.9, 133.8, 133.5, 130.0, 129.9, 128.2, 128.1, 115.3, 115.0, 69.2, 38.2, 30.1, 22.7, 20.0. MS (LSIMS, Na) m/z: 345 $[M + Na]^+$ (6), 281 (7), 239 (5), 224 (12), 223 $[SiPh_2(CH_2CH{=}CH_2)]^+$ (53), 199 $[(Ph)_2SiOH]^+$ (100), 183 (47), 163 (17), 145 (20). HRMS: calcd for $C_{21}H_{26}OSiNa$ $[M + Na]^+$ 345.165064, found 345.164374.

(2*R,4*S**)-4-(Allyldiphenylsilyl)-1-*tert*-butoxyhex-5-en-2-ol (11c) and (2*R**,4*R**)-4-(Allyldiphenyl-silyl)-1-*tert*-butoxyhex-5-en-2-ol (14c).** Compounds **11c** (58%) and **14c** (12%) were obtained as pale yellow oils. **11c**. R_f = 0.32 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3449, 2973, 1957, 1629, 1486, 1428, 1258, 1111 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.57 (m, 4H), 7.37 (m, 6H), 5.85 (m, 2H), 5.02 (m, 2H), 4.91 (m, 2H), 3.77 (br s, 1H), 3.41 (dd, J = 8.6, 3.0 Hz, 1H), 3.27 (m, 1H), 2.37 (m, 1H), 2.18 (d, J = 7.9 Hz, 2H), 1.65 (m, 2H), 1.22 (s, 9H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$): δ 136.0, 135.7, 134.4, 130.9, 129.8, 128.2, 124.1, 129.7, 129.40, 129.38, 127.7, 115.2, 114.9, 73.1, 70.5, 66.3, 33.4, 29.1, 28.7, 19.9. MS (LSIMS, Na) m/z: 417 $[M + Na]^+$ (19), 376 $[M - H_2O]^+$ (6), 297 (34), 241 (25), 223 $[Si(CH_2CH{=}CH_2)Ph_2]^+$ (100), 219 (44). HRMS: calcd for $C_{25}H_{34}O_2SiNa$ $[M + Na]^+$ 417.222579, found 417.222716. **14c**. R_f = 0.42 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3452, 2974, 1628, 1491, 1427, 1248, 1111 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.63 (m, 4H), 7.42 (m, 6H), 5.79 (m, 2H), 5.01 (m, 2H), 1.20 (s, 9H), 4.88 (m, 2H), 3.80 (m, 1H), 3.17 (dd, J = 8.6, 3 Hz, 1H), 3.14 (t, J = 8.6 Hz, 1H), 2.85 (t, J = 10.3 Hz, 1H), 2.72 (br s, 1H), 2.18 (d, J = 7.9 Hz, 2H), 1.78 (m, 1H), 1.40 (m, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 138.3, 135.7, 135.6, 134.3, 133.6, 133.5, 133.4, 129.7, 129.40, 129.38, 127.75, 127.70, 127.67, 114.8, 114.7, 72.9, 68.7, 66.5, 32.1, 27.5, 26.7, 19.7. MS (LSIMS, Na) m/z: 417 $[M + Na]^+$ (11), 376 $[M - H_2O]^+$, 297 (34), 241 (37), 223 $[Si(CH_2CH{=}CH_2)Ph_2]^+$ (59), 199 $[(Ph)_2SiOH]^+$ (100). HRMS: calcd for $C_{25}H_{34}O_2SiNa$ $[M + Na]^+$ 417.222579, found 417.222681.

General Procedure for Acetylation of β-Hydroxysilanes 8a, 8c, and 8f. Acetic Acid (1*R,2*S**)-2-(Allyldiphenylsilyl)-1-isopropylbut-3-enyl Ester (15a).** To a stirred solution of **8a** (400 mg, 1.2 mmol) in dry CH_2Cl_2 (5.0 mL) were added acetic anhydride (0.22 mL, 2.4 mmol), NEt_3 (0.33 mL, 2.4 mmol), and a catalytic amount of 4-DMAP. The resulting mixture was then stirred at rt under nitrogen for 18 h and was treated with saturated aq $NaHCO_3$ solution. The organic layer was decanted and the aqueous layer extracted with ether. The combined extracts were washed with brine and dried over $MgSO_4$, and the solvents were concentrated in vacuo. The crude product was purified by chromatography through silica gel (petroleum ether−EtOAc 95:5) affording **15a** as a thick oil (336 mg, 74%). IR ($CHCl_3$): ν_{max} 1722, 1627, 1487, 1428, 1372, 1241, 1216 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.4 (m, 10 H), 6.04−5.6 (m, 2H), 5.6−4.82 (m, 5H), 2.68 (dd, J = 11, 2 Hz, 1H), 2.19 (m, 2H), 1.84 (m, 1H), 1.36 (s, 3H), 0.86 (d, J = 6.6 Hz, 3H), 0.75 (d, J = 6.6 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 135.7, 135.5, 134.0, 133.6, 133.41, 129.5, 129.3, 127.7, 127.6, 116.6, 115.1, 76.5, 34.7, 31.7, 20.4, 20.1, 18.8. MS (EI) m/z: 241 (100), 223, 199, 183, 105, 74, 59.

General Procedure for Ring-Closing Metathesis of β- and γ-Hydroxysilanes. Acetic Acid (1*R,2*S**)-1-(1,1-Diphenyl-2,5-dihydro-1*H*-silol-2-yl)-2-methylpropyl Ester (7a).** To a stirred solution of acetate **15a** (292 mg, 0.77 mmol) in dry benzene (7.0 mL) was added Grubbs catalyst **I** (2 mol %, 12.7 mg, 0.015 mmol) under nitrogen. The black reaction mixture was refluxed until consumption of **15a**. Reaction was found to be complete after 3.0 h under reflux. After completion, benzene was removed in vacuo, and the residue was purified by chromatography through silica gel (petroleum ether−EtOAc 95:5) giving **7a** as a colorless oil (240 mg, 88%). R_f = 0.48 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 1726, 1611, 1486, 1428, 1370, 1251 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.65 (m, 2H), 7.53 (m, 2H), 7.4 (m, 6H), 6.15 (m, 1H), 5.86 (m, 1H), 4.9 (dd, J = 10, 3 Hz, 1H), 2.68 (m, 1H), 2.1−1.98 (m, 1H), 1.94 (s, 3H), 1.88−1.77 (m, 1H), 1.61 (m, 1H), 0.88 (d, J = 7 Hz, 3H), 0.61 (d, J = 7 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 135.3, 134.5, 134.3, 133.0, 132.6, 131.6, 129.9, 129.8, 128.2, 128.1, 78.9, 31.9, 30.5, 20.8, 20.1, 17.3, 16.1. MS (EI) m/z: 290, 241 (100), 199, 181, 105, 43.

Acetic Acid (1*R,2*S**)-1-(1,1-Diphenyl-2,5-dihydro-1*H*-silol-2-yl)-2-butyl Ester (7b).** Compound **7b** was obtained as a colorless oil (95%). R_f = 0.46 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 1610, 1589, 1428, 1373, 1242, 1215 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.7−7.35 (m, 10H), 6.17 (m, 1H), 5.91 (m, 1H), 4.97 (td, J = 9, 4 Hz, 1H), 2.6 (m, 1H), 2.14−2.0 (m, 1H), 1.94 (s, 3H), 1.91−1.78 (m, 1H), 1.6−0.9 (m, 6H), 0.6 (t, J = 7 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 170.8, 135.3, 135.0, 134.57, 133.4, 132.6, 131.9, 129.9, 129.9, 128.2, 128.1, 75.5, 36.9, 35.6, 21.1, 18.7, 17.4, 13.4. MS (LSIMS, Na) m/z: 291, 243, 242, 241 (100), 235, 228. Anal. Calcd for $C_{22}H_{26}O_2Si$: C, 75.42; H, 7.42; Si, 8.0. Found: C, 75.30; H, 7.49; Si, 8.30.

(1*R)-1-((2*S**)-1,1-Diphenyl-2,5-dihydro-1*H*-silol-2-yl)-2-methylpropan-2-ol (7c).** Compound **7c** was obtained as a brown oil (93%). R_f = 0.41 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3582, 1606, 1486, 1428, 1386, 1366, 1259, 1216 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.6 (m, 4H), 7.4 (m, 6H), 6.3 (m, 1H), 6.1 (m, 1H), 3.35 (t, J = 5.8 Hz, 1H), 2.59 (m, 1H), 2.1 (m, 1H), 2.1 (m, 1H), 1.7 (m, 2H), 1.33 (br s, 1 H), 0.91 (d, J = 6.4 Hz, 3H), 0.82 (d, J = 6.7 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 135.5, 134.8, 133.6, 131.9, 129.8, 129.7, 128.1, 128.0, 77.6, 34.9, 33.2, 20.1, 17.7, 16.7. MS (EI) *m*/*z*: 279, 263, 245, 199, 181, 158, 139, 105, 77.

(*R)-((2*S**)-1,1-Diphenyl-2,5-dihydro-1*H*-silol-2-yl)phenylmethanol (7d).** Compound **7d** was obtained as a brown oil (78%). R_f = 0.55 (petroleum ether−EtOAc 8:2). IR ($CHCl_3$): ν_{max} 3440, 1606, 1428, 1397, 1306, 1216, 1114 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.36 (m, 13H), 7.06 (m, 2H), 6.32 (m, 1H), 6.2 (m, 1H), 4.76 (d, J = 10 Hz, 1H), 2.8 (m, 1H), 2.16−1.8 (m, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 144.5, 135.4, 134.9, 134.4, 133.9, 132.9, 132.8, 129.8, 129.6, 128.2, 127.9, 127.4, 126.3, 74.8, 40.3, 17.2. MS (EI) *m*/*z*: 342 $[M]^+$, 288, 236, 199 (100), 181, 158, 128, 105, 77. HRMS: calcd for $C_{23}H_{22}OSi$ 342.143994, found 342.144162. Anal. Calcd for $C_{23}H_{22}SiO$: C, 80.70; H, 6.43. Found: C, 80.46; H, 6.43.

(1*R)-1-((2*S**)-1,1-Diphenyl-2,5-dihydro-1*H*-silol-2-yl)-propan-1-ol (7e).** Compound **7e** was obtained as a brown oil (75%). R_f = 0.41 (petroleum ether−EtOAc 9:1). IR ($CDCl_3$): ν_{max} 3583, 1626, 1428, 1397, 1306, 1216, 1108 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.62−7.43 (m, 10H), 6.26 (m, 2H), 3.79 (m, 1H), 2.36 (m, 1H), 2.21 (m, 2H), 1.48 (m, 2H), 1.73 (t, J = 7.3 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 136.3, 135.1, 134.8, 134.7, 132.9, 130.6, 129.7, 129.6, 129.3, 74.2, 33.1, 21.0, 11.0. MS (LSIMS, Na) *m*/*z*: 317 $[M + Na]^+$ (28), 277 $[M - OH^\bullet]^+$ (100), 235 $[M - CH_3CH_2CHOH^\bullet]^+$ (39), 215 (20). HRMS: calcd for $C_{19}H_{22}OSiNa$ 317.133764, found 317.133875.

(2*S,3*R**)-((2*S**)-1,1-Diphenyl-2,5-dihydro-1*H*-silol-2-yl)-2-phenylpropan-1-ol (7f).** Compound **7f** was obtained as a brown oil (74%). R_f = 0.68 (petroleum ether−EtOAc 8:2). IR ($CHCl_3$): ν_{max} 3405, 1713, 1597, 1493, 1428, 1378, 1217, 1114 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.8 (m, 2H), 7.7 (m, 2H), 7.53 (m, 6H), 7.4 (m, 3H), 7.0 (m, 2H), 6.4 (m, 1H), 6.28 (m, 1H), 3.9 (t, J = 5.8 Hz, 1H), 2.93 (m, 1H), 2.61 (m, 1H), 2.27−2.15 (m, 1H), 1.98−1.86 (m, 1H), 1.7 (br s, 1H), 1.45 (d, J = 7.4 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 145.1, 135.4, 134.8, 133.8, 133.1, 132.2, 129.9, 129.6, 128.4, 128.2, 128.0, 127.4, 126.2, 76.8, 44.7, 34.4, 16.9, 15.7. MS (EI) *m*/*z*: 370 $[M]^+$, 265, 237, 199, 128, 105 (100), 91, 77. HRMS: calcd for $C_{25}H_{26}OSi$ 370.175294, found 370.176618. Anal. Calcd for $C_{25}H_{26}OSi$: C, 81.08; H, 7.02; Si, 7.56. Found: C, 81.19; H, 6.95; Si, 7.11.

(2*R,3*S**)-1,1-Diphenyl-2-vinyl-1,2,3,6-tetrahydr-silin-3-ol (16).** Compound **16** was obtained as a yellow gum (57%). R_f = 0.46 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3383, 1694, 1628, 1590 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.8−7.3 (m, 10H), 6.0 (m, 1H), 5.87−5.64 (m, 2H), 5.1 (m, 2H), 4.37 (d, J = 10.4 Hz, 1H), 2.47 (t, J = 10.4 Hz, 1H), 1.85 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 136.1, 135.5, 135.0, 134.4, 133.6, 129.9, 128.0, 127.97, 127.86, 127.80, 125.6, 117.0, 70.0, 39.9, 11.3. MS (LSIMS, Na) *m*/*z*: 292 $[M]^+$, 291, 275, 259, 222, 215, 213.

(1*R,3*S**)-2-(1,1-Diphenyl-2,5-dihydro-1*H*-silol-2-yl)-1-phenylethan-1-ol (10a).** γ-Hydroxysilane **11a** (216 mg, 5.62 mmol) was subjected to the standard ring-closing metathesis conditions described above (10 mol % of Grubbs catalyst **I** was used) to afford after purification by column chromatography through silica gel (petroleum ether−EtOAc 98:2) **10a** as a colorless oil (130 mg, 75%). R_f = 0.27 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3582, 3396, 2976, 1609, 1492, 1428, 1262, 1114 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.73−7.20 (m, 15H), 6.00 (m, 2H), 4.48 (m, 1H), 2.55 (m, 1H), 2.00 (m, 1H), 1.89 (d, J = 7.8 Hz, 2H), 1.66 (m, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 145.1, 137.0, 135.4, 135.3, 134.8, 134.5, 130.1, 129.7, 128.3, 128.1, 128.0, 127.3, 125.3, 74.5, 41.3, 26.6, 17.3. MS (LSIMS, Na) *m*/*z*: 379 $[M + Na]^+$ (35), 352 $[379 - OH^\bullet]^+$ (25), 339 $[M - OH^\bullet]^+$ (90), 319 (41), 277 (34), 261 (64), 235 (100), 223 $[Si(CH_2{-}CH{=}CH_2)Ph_2]^+$ (57), 221 (56). HRMS: calcd for $C_{24}H_{24}OSiNa$ $[M + Na]^+$ 379.149414, found 379.150497.

Preparation of 10a Using Grubbs Catalyst II. γ-Hydroxysilane **11a** (402 mg, 1.1 mmol) was subjected to the standard ring-closing metathesis conditions described above (1.5 mol % of Grubbs catalyst **II** was used) to afford after purification by column chromatography through silica gel (petroleum ether−EtOAc 98:2) **10a** as a colorless oil (290 mg, 78%). All spectoscopic data were in good agreement with those of the material obtained during ring-closure metathesis of **11a** with Grubbs catalyst **I**.

(2*S,4*S**)-1-(1,1-Diphenyl-2,5-dihydro-1*H*-silol-2-yl)propan-2-ol (10b).** γ-Hydroxysilane **11b** (601 mg, 1.86 mmol) was subjected to the standard ring-closing metathesis conditions described above (4 mol % of Grubbs catalyst **I** was used) to afford after purification by column chromatography through silica gel (petroleum ether−EtOAc 98:2) **10b** as white crystals (421 mg, 77%). Mp: 143−146 °C (petroleum ether−ether). R_f = 0.66 (petroleum ether−EtOAc 8:2). IR ($CHCl_3$): ν_{max} 3576, 2976, 1609, 1492, 1428, 1262, 1114 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.57−7.35 (m, 10H), 5.98 (m, 2H), 3.66 (q, J = 6.1 Hz, 1H), 2.44 (m, 1H), 1.85 (m, 2H), 1.45 (m, 2H), 1.01 (d, J = 6.1 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 137.3, 136.7, 135.7, 135.5, 130.4, 130.1, 130.0, 128.4, 128.3, 68.2, 40.8, 26.8, 24.2, 17.3. MS (LSIMS, Na) *m*/*z*: 317 $[M + Na]^+$ (55), 293 $[M - H^\bullet]^+$ (20), 277 $[M - OH^\bullet]^+$ (39), 259 (20), 249 (25), 235 (59), 223 $[Si(CH_2{-}CH{=}CH_2)Ph_2]^+$ (100). HRMS: calcd for $C_{19}H_{22}OSiNa$ $[M + Na]^+$ 317.133764, found 317.133270.

(2*R,4*S**)-1-*tert*-Butoxy-3-(1,1-diphenyl-2,5-dihydro-1*H*-silol-2-yl)propan-2-ol (10c).** γ-Hydroxysilane **11c** (307 mg, 0.78 mmol) was subjected to the standard ring-closing metathesis conditions described above (8 mol % of Grubbs catalyst **I** was used) to afford after purification by column chromatography through silica gel (petroleum ether−EtOAc 98:2) **10c** as a colorless oil (178 mg, 66%). R_f = 0.32 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3413, 2925, 1610, 1489, 1428, 1365, 1259, 1114 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.74 (m, 4H), 7.40 (m, 6H), 6.02 (m, 2H), 3.57 (m, 1H), (m, 1H), 3.02 (dd, J = 8.6, 3.0 Hz, 1H), 2.97 (t, J = 8.6 Hz, 1H), 2.53 (m, 2H), 2.53 (br s, 1H), 1.92 (m, 2H), 1.12 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 137.3, 135.24, 135.19, 134.1, 129.7, 129.6, 129.5, 128.0, 127.7, 73.0, 70.9, 65.7, 34.7, 27.5, 26.2, 17.1. MS (LSIMS, Na) *m*/*z*: 389 $[M + Na]^+$ (93), 319 (58), 259 (39), 241 (45), 233 (75), 223 $[Si(CH_2CH{=}CH_2)Ph_2]^+$ (100), 219 (47), 215 (61). HRMS: calcd for $C_{23}H_{30}O_2SiNa$ $[M + Na]^+$ 389.191279, found 389.191764.

(1*R,3*R**)-2-(1,1-Diphenyl-2,5-dihydro-1*H*-silol-2-yl)-1-phenylethan-1-ol (10d).** γ-Hydroxysilane **14a** (839 mg, 2.2 mmol) was subjected to the standard ring-closing metathesis conditions described above (4 mol % of Grubbs catalyst **I** was used) to afford after purification by column chromatography through silica gel (petroleum ether−EtOAc 98:2) **10d** as a colorless oil (661 mg, 84%). R_f = 0.29 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3575, 2925, 1616, 1493, 1428, 1390, 1262, 1112 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.61−7.18 (m, 15H), 6.06 (m, 2H), 4.67 (dd, J = 8.85, 4.9 Hz, 1H), 2.42 (m, 1H), 1.89 (d, J = 7.8 Hz, 2H), 1.66 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 145.3, 136.6, 135.8, 135.5, 135.4, 134.2, 130.7, 130.1, 130.0, 128.8, 128.3, 127.8, 126.3, 74.5, 41.2, 26.7, 17.3. MS (LSIMS, Na) *m*/*z*: 379 $[M + Na]^+$ (21), 339 $[M - OH^\bullet]^+$ (74), 319 (49), 277 (23), 261 (64), 235 (100), 223 $[Si(CH_2CH{=}CH_2)Ph_2]^+$ (38), 221 (48). HRMS: calcd for $C_{24}H_{24}OSiNa$ $[M + Na]^+$ 379.149414, found 379.149391.

(2*S,4*R**)-1-(1,1-Diphenyl-2,5-dihydro-1*H*-silol-2-yl)-propan-2-ol (10e).** γ-Hydroxysilane **14b** (640 mg, 1.98 mmol) was subjected to the standard ring-closing metathesis conditions described above (8 mol % of Grubbs catalyst **I** was used) to afford after purification by column chromatography through silica gel (petroleum ether−EtOAc 98:2) **10e** as a colorless oil (452 mg, 78%). R_f = 0.56 (petroleum ether−EtOAc 8:2). IR ($CHCl_3$): ν_{max} 3582, 2921, 1606, 1486, 1428, 1373, 1261, 1113

cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.67−7.35 (m, 10H), 6.05 (m, 2H), 3.81 (m, 1H), 2.36 (m, 1H), 1.92 (m, 2H), 1.48 (m, 2H), 1.12 (d, J = 6.1 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 136.3, 135.5, 134.6, 130.6, 129.6, 129.0, 128.2, 127.9, 68.0, 41.4, 26.3, 23.2, 17.1. MS (LSIMS, Na) m/z: 317 $[M + Na]^+$ (23), 293 $[M - H^\bullet]^+$ (15), 277 $[M - OH^\bullet]^+$ (41), 259 (35), 249 (26), 235 (71), 223 $[Si(CH_2CH{=}CH_2)Ph_2]^+$ (100). Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53; Si, 9.54. Found: C, 77.27; H, 7.54; Si, 9.80.

(2*R,4*R**)-1-*tert*-Butoxy-3-(1,1-diphenyl-2,5-dihydro-1*H*-silol-2-yl)propan-2-ol (10f).** γ-Hydroxysilane **14c** (138 mg, 0.35 mmol) was subjected to the standard ring-closing metathesis conditions described above (4 mol % of Grubbs catalyst **I** was used) to afford after purification by column chromatography through silica gel (petroleum ether−EtOAc 98:2) **10f** as a colorless oil (93 mg, 72%). R_f = 0.36 (petroleum ether−EtOAc 9:1). IR ($CHCl_3$): ν_{max} 3569, 2973, 1605, 1486, 1428, 1364, 1257, 1114 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.69 (m, 2H), 7.53 (m, 2H), 7.38 (m, 6H), 6.09 (br s, 2H), 3.80 (m, 1H), 3.27 (dd, J = 8.6, 3.0 Hz, 1H), 3.07 (t, J = 8.6 Hz, 1H), 2.58 (m, 2H), 2.50 (br s, 1H), 1.93 (m, 2H), 1.16 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 136.8, 135.8, 135.5, 134.5, 130.5, 130.0, 128.8, 128.4, 128.3, 73.5, 70.5, 66.9, 35.2, 28.0, 25.4, 17.2. MS (LSIMS, Na) m/z: 389 $[M + Na]^+$ (22), 335 (8), 319 (7), 241 (10), 233 (31), 215 (14), 199 $[(Ph)_2SiOH]^+$ (100), 183 (21), 165 (13), 154 (22), 139 (45). HRMS: calcd for $C_{23}H_{30}O_2SiNa$ $[M + Na]^+$ 389.191279, found 389.190882.

General Procedure for the Dihydroxylation of Silacyclopent-3-enes. (2*R,3*S**,4*R**)-2-((1*R**)-1-Hydroxy-2-methylpropyl)-1,1-diphenylsilolane-3,4-diol (18a).** To the dihydroxylation mixture prepared by mixing $K_3Fe(CN)_6$ (306 mg, 0.93 mmol), K_2CO_3 (129 mg, 0.93 mmol), quinuclidine (0.32 mg, 0.0029 mmol), and $K_2OsO_4{\cdot}2H_2O$ (1.06 mg, 0.0029 mmol) in a 1:1 solution of *t*-BuOH and water (2.0 mL) was added after 5 min methanesulfonamide (20.0 mg, 0.21 mmol). The resulting orange solution was cooled to 0 °C, and then silacyclopentene **7c** (67 mg, 0.21 mmol) in *t*-BuOH (1.0 mL) was added at 0 °C. Water (1.0 mL) was added to maintain the 1:1 ratio with *t*-BuOH, and the reaction mixture was slowly allowed to warm to rt under stirring. After completion of the reaction (1 h, TLC), the mixture was cooled to 0 °C, quenched carefully with sodium sulfite (312 mg), and then stirred for 0.75 h. The aqueous layer was extracted several times with EtOAc. The combined extracts were washed by brine and dried over anhydrous $MgSO_4$, and the solvents were concentrated in vacuo to give a solid residue. Triol **18a** was obtained as a 80:20 mixture of two diastereomers, which were separated by column chromatography through silica gel (petroleum ether−EtOAc 98:2) (91 mg, 84%). **18a** (major). R_f = 0.54 (petroleum ether−EtOAc 4:6). Mp: 172−174 °C (CH_2Cl_2−petroleum ether). IR ($CHCl_3$): ν_{max} 3438, 1601, 1520, 1428, 1215, 1151, 1111 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.7 (m, 2H), 7.4 (m, 8H), 4.48 (m, 1H), 4.36 (br s, 1H), 4.22 (dd, J = 10, 3 Hz, 1H), 3.74 (d, J = 12 Hz, 1H), 2.69 (br s, 1H), 2.09 (t, J = 10 Hz, 1H), 1.6 (m, 1H), 1.4 (m, 2H), 0.75 (d, J = 7 Hz, 3H), 0.65 (d, J = 7 Hz, 3H). ^{13}C NMR (50 MHz, acetone-d_6): δ 136.2, 136.1, 130.4, 130.4, 128.8, 128.7, 82.2, 78.4, 74.0, 46.0, 34.3, 21.1, 18.6, 14.8. MS (EI) m/z: 299, 237, 199 (100), 181, 165, 139, 105, 77. Anal. Calcd for $C_{20}H_{26}O_3Si$ C, 70.17; H, 7.60. Found: C, 70.15; H, 7.63. **18a** (minor). R_f = 0.14 (petroleum ether−EtOAc 4:6). IR ($CHCl_3$): ν_{max} 3331, 1428, 1323, 1215 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.6 (m, 4H), 7.38 (m, 6H), 4.5 (t, J = 4 Hz, 1H), 4.1 (m, 1H), 3.8 (dd, J = 8, 3 Hz, 1H), 3.23 (br s, 1H), 2.3 (br s, 1H), 1.82 (dd, J = 8, 3 Hz, 1H), 1.6 (m, 3H), 0.85 (d, J = 8 Hz, 3H), 0.7 (d, J = 6.4 Hz, 3H). ^{13}C NMR (50 MHz, acetone-d_6): δ 137.1, 137.0, 136.0, 135.5, 130.5, 130.4, 129.2, 128.6, 77.1, 75.7, 72.7, 39.8, 33.9, 22.0, 20.6. MS (EI) m/z: 299, 237, 225, 199 (100), 181, 139, 105.

Acetic Acid (2*R,3*S**,4*R**)-4-Acetoxy-2-((*R**)-acetoxyphenylmethyl)-1,1-diphenylsilolan-3-yl Ester (19a).** Following the general protocol reported above for **7c**, silacyclopentene **7d** (1.27 g, 3.71 mmol) afforded after 48 h the corresponding triols **18b** as a 84:16 mixture of two diastereomers (R_f = 0.50 and 0.25, petroleum ether−EtOAc 4:6) (1.36 g, quantitative yield), which were directly acetylated without further purification. To a stirred solution of the above crude triol **18b** (1.33 g, 3.53 mmol) in dry CH_2Cl_2 (9.0 mL) were added acetic anhydride (1.67 mL, 17.65 mmol), Et_3N (2.47 mL, 17.6 mmol), and a catalytic amount of 4-DMAP. The resulting reaction mixture was stirred at rt under nitrogen for 3 h and then treated with a saturated aq $NaHCO_3$ solution. The dichloromethane layer was separated, and the aqueous layer was extracted with ether. The combined extracts were washed with brine and dried over $MgSO_4$, and the solvents were concentrated in vacuo to afford the two diastereomers of **19a** as a white solid (1.55 g, 83%). Major triacetate of **19a** crystallized out from EtOH. Mp: 184−186 °C (EtOH). R_f = 0.50 (petroleum ether−EtOAc 3:7). IR ($CHCl_3$): ν_{max} 1736, 1588, 1495, 1428, 1373 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.52−7.08 (m, 13H), 6.87 (br d, J = 7.1 Hz, 2H), 5.94 (d, J = 9.8 Hz, 1H), 5.68−5.53 (m, 2H), 2.74 (t, J = 9.8 Hz, 1H), 1.98 (s, 3H), 1.84 (s, 3 H), 1.82 (s, 3H), 1.61 (t, J = 3.9 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1, 169.7, 139.7, 135.4, 134.6, 131.8, 130.2, 129.7, 128.1, 128.0, 127.8, 127.7, 127.1, 77.6, 76.2, 74.9, 34.6, 21.0, 20.9, 20.8, 15.5. MS (EI) m/z: 382, 365, 305, 241 (100), 223, 199, 181, 160. Anal. Calcd for $C_{29}H_{30}O_6Si$: C, 69.30; H, 6.02; Si, 5.59. Found: C, 69.10; H, 6.04; Si, 5.80.

Acetic Acid (2*R,3*S**,4*R**)-4-Acetoxy-2-((1*R**,2*S**)-1-acetoxy-2-phenylpropyl)-1,1-diphenylsilolan-3-yl Ester (19b).** Following the general protocol, triol **18c** was obtained as a 79:21 mixture of two diastereomers (R_f = 0.51 and 0.27, petroleum ether−EtOAc 4:6) (63%), which were directly acetylated to afford acetate **19b** as a white solid (85%). The major triacetate of **19b** crystallized from EtOH. **19b**: R_f = 0.42 (petroleum ether−EtOAc 7:3). Mp: 157−158 °C (EtOH). IR ($CHCl_3$): ν_{max} 3424, 3019, 1736, 1640, 1428, 1373 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.63−7.36 (m, 10H), 7.18−7.11 (m, 3H), 6.71−6.63 (m, 2H), 5.68−5.61 (m, 1H), 5.41 (dd, J = 8.8, 2.7 Hz, 1H), 5.26 (dd, J = 8.2, 4.9 Hz, 1H), 2.9−2.77 (m, 1H), 2.44 (t, J = 8.5 Hz, 1H), 2.03 (s, 3H), 1.83 (s, 3H), 1.79 (s, 3H), 1.68−1.42 (m, 2H), 1.23 (d, J = 7.3 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1, 170.0, 169.7, 143.5, 135.7, 134.7, 131.6, 130.4, 129.9, 128.5, 128.1, 128.0, 127.4, 126.4, 77.8, 76.3, 74.5, 43.0, 30.2, 21.0, 20.8, 20.7, 15.6, 14.6. MS (EI) m/z: 425, 365, 323, 263, 241 (100), 223, 199, 181. Anal. Calcd for $C_{31}H_{34}O_6Si$: C, 70.16; H, 6.46; Si, 5.29. Found: C, 70.01; H, 6.48; Si, 5.60.

Acetic Acid (1*R)-1-((2*S**,3*S**,4*R**)-3,4-Dihydroxy-1,1-dihydroxy-1,1-diphenylsilolan-2-yl)butyl Ester (18d).** Following the general protocol, triol **18d** was isolated as a 76:24 mixture of two diastereomers (70%). **18d** (major). R_f = 0.35 (petroleum ether−EtOAc 1:1). Mp: 129−132 °C (EtOH). IR ($CHCl_3$): ν_{max} 3528, 1729, 1589, 1428, 1374, 1215, 1112 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.7 (m, 2H), 7.4 (m, 8H), 5.15 (m, 1H), 4.45 (m, 1H), 4.2 (m, 1H), 2.62 (d, J = 3.1 Hz, 1H), 2.46 (br s, 1H), 2.14 (dd, J = 11.3, 9.5 Hz, 1H), 2.03 (s, 3H), 1.55−0.84 (m, 6H), 0.5 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 171.0, 135.4, 135.1, 134.0, 133.8, 133.0, 130.1, 129.9, 128.3, 128.2, 79.9, 76.1, 74.2, 37.5, 35.9, 21.5, 18.2, 17.8, 13.1. MS (EI) m/z: 241, 225, 199 (100), 181. Anal. Calcd for $C_{22}H_{28}O_4Si$: C, 68.75; H, 7.29. Found: C, 68.66; H, 7.34. **18d** (minor). R_f = 0.44 (petroleum ether−EtOAc 1:1). IR ($CHCl_3$): ν_{max} 3462, 3018, 1701, 1428, 1260, 1145, 1116 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.7 (m, 4H), 7.5 (m, 3H), 7.4 (m, 3H), 5.06 (m, 1H), 4.26 (br s, 1H), 4.09−3.95 (m, 2H), 2.63 (br s, 1H), 2.11 (s, 3H), 1.83 (dd, J = 11.3, 2.7 Hz, 1H), 1.75−1.5 (m, 2H), 1.4−0.9 (m, 4H), 0.49 (t, J = 7 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 135.7, 134.9, 134.1, 133.9, 132.1, 129.7, 129.6, 127.8, 127.7, 74.7, 74.0, 73.9, 39.1, 36.7, 20.8, 19.9, 18.6, 12.5.

Dihydroxylation of Silacyclopentene 7c with OsO_4−TMEDA. Osmates 21a,b. To a solution of **7c** (109 mg, 0.35 mmol) and TMEDA (59 μL, 0.39 mmol) in anhydrous CH_2Cl_2, precooled at −78 °C, was added a 1.97 M solution of OsO_4 (0.19 mL, 0.37 mmol) in anhydrous CH_2Cl_2. The solution turned deep red and then black. The solution was stirred until

complete consumption of starting material (1.5 h; TLC analysis). Sodium sulfite (600 mg, 12 equiv) was then added and the stirring maintained for 0.75 h. The solution was then filtered and washed with a 10% NaOH solution. The aqueous layer was extracted with EtOAc, and the combined extracts were poured into brine, dried over $MgSO_4$, and the solvent removed under reduced pressure to afford the osmate complex as a 55:45 mixture of diastereomers **21a** and **21b**. $R_f = 0.54$ (petroleum ether−EtOAc 3:7) for both diastereomers. Mp: 191−193 °C (ether−EtOAc). IR ($CDCl_3$) ν_{max} 3414, 2929, 2253, 1794, 1474, 1428, 1383, 1110 cm^{-1}. **21a**. ^1H NMR (250 MHz, $CDCl_3$): δ 7.75−7.19 (m, 10H), 5.16 (t, $J = 4$ Hz, 1H), 4.40 (dd, $J = 10$, 4.3 Hz, 1H), 4.30 (br s, 1H), 3.86 (m, 1H), 3.60−3.35 (m, 4H), 3.30−3.10 (s, 12H), 2.88 (m, 1H), 2.37 (m, 1H), 1.95−1.85 (m, 1H), 1.68−1.52 (m, 1H), 0.79 (d, $J = 6.41$ Hz, 3H), 0.65 (d, $J = 6.41$ Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 136.6, 135.9, 135.8, 135.4, 135.3, 134.9, 133.9, 131.0, 129.6, 129.4, 129.3, 129.1, 128.1, 127.7, 127.3, 97.6, 96.7, 93.3, 92.1, 77.9, 77.7, 77.1, 76.6, 76.3, 64.8, 64.7, 64.2, 52.1, 51.9, 51.7, 51.5, 51.4, 34.1, 33.9, 33.7, 33.6, 20.9, 20.7, 17.8, 17.1, 16.6, 14.6. **21b**. ^1H NMR (250 MHz, $CDCl_3$): δ 7.75−7.19 (m, 10H), 5.11 (m, 1H), 4.40 (m, 1H), 3.92 (br s, 1H), 3.60−3.35 (m, 4H), 3.30−3.10 (s, 12H), 2.06 (m, 1H), 1.95−1.85 (m, 1H), 1.68−1.52 (m, 2H), 0.97 (d, $J = 6.71$ Hz, 3H), 0.85 (d, $J = 6.71$ Hz, 3H).

General Procedure for Epoxidation of Silacyclopentenes. (1*R)-1-((2*R**,3*R**,4*S**)-3,3-Diphenyl-6-oxa-3-silabicyclo[3.1.0]hex-2-yl)-2-methylpropan-1-ol (22a).** To a stirred solution of silacyclopentene **7c** (1.54 g, 5.0 mmol) in dry CH_2Cl_2 (15.0 mL) under nitrogen was added *m*-CPBA (2.58 g, 15.0 mmol) at 0 °C. The reaction was slowly allowed to warm to rt, stirred for 2 h, and treated with saturated aq Na_2CO_3. The organic layer was decanted, and the aqueous layers were extracted with EtOAc. The combined extracts were washed with brine and dried over $MgSO_4$, and the solvents were concentrated in vacuo to afford **22a** as a 88:12 mixture of two diastereomers, which were separated by chromatography through silica gel (petroleum ether−EtOAc 8:2) (1.12 g, 69%). **22a** (major). $R_f = 0.32$ (petroleum ether−EtOAc 8:2). IR ($CHCl_3$): ν_{max} 3448, 2964, 1428, 1383, 1186, 1110 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.6 (m, 4H), 7.4 (m, 6H), 3.79−3.61 (m, 2H), 2.29 (dd, $J = 10.4$, 2.1 Hz, 1H), 1.98−1.67 (m, 2H), 1.62−1.44 (m, 2H), 0.91 (d, $J = 7.0$ Hz, 3H, CH_3), 0.66 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 136.2, 135.0, 129.8, 129.7, 128.2, 123.7, 74.9, 59.6, 57.0, 34.4, 32.9, 20.7, 16.6, 14.8. MS (LSIMS, Na) *m*/*z*: 347 $[M + Na]^+$ (100), 319, 308, 307, 281, 259, 229, 225. **22a** (minor). $R_f = 0.34$ (petroleum ether−EtOAc 8:2). IR ($CHCl_3$): ν_{max} 2965, 1600, 1524, 1472, 1428, 1112 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.6 (m, 4H), 7.4 (m, 6H), 3.71 (s, 2H), 3.33 (m, 1H), 2.32 (d, $J = 3.7$ Hz, 1H), 1.9−1.66 (m, 3H), 1.3 (br s, 1H), 0.91 (d, $J = 2.4$ Hz, 3H), 0.88 (d, $J = 2.15$ Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 135.51, 135.46, 129.9, 129.4, 128.2, 127.6, 76.5, 58.5, 32.6, 31.2, 19.7, 18.8, 14.4.

(1*R)-1-((2*R**,3*R**,4*S**)-3,3-Diphenyl-6-oxa-3-silabicyclo[3.1.0]hex-2-yl)phenylmethanol (22b).** Following the general epoxidation procedure, **22b** was obtained as a 93:7 mixture of two diastereomers (66%). **22b** (major). $R_f = 0.25$ (petroleum ether−EtOAc 8:2). Mp: 156−158 °C (*i*-PrOH). IR ($CHCl_3$): ν_{max} 3422, 1588, 1491, 1454, 1428 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.45−7.1 (m, 10H), 6.88−6.76 (m, 5H), 4.85 (d, $J = 10.8$ Hz, 1H), 4.0−3.92 (m, 1H), 3.78−3.7 (m, 1H), 2.8 (br s, 1H), 2.43 (dd, $J = 10.8$, 1.95 Hz, 1H), 1.93−1.54 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.7, 135.4, 129.7, 129.3, 128.2, 128.0, 127.7, 127.0, 125.4, 72.5, 58.6, 58.3, 35.7, 14.3. MS (EI) *m*/*z*: 278, 251, 224, 198 (100), 183, 138. **22b** (minor). $R_f = 0.25$ (petroleum ether−EtOAc 8:2). IR ($CHCl_3$): ν_{max} 3430, 3069, 1588, 1427, 1379 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.6−7.2 (m, 15H), 4.9 (d, $J = 4.7$ Hz, 1H), 3.72 (br s, 1H), 3.57 (d, $J = 2.7$ Hz, 1H), 2.5 (d, $J = 4.7$ Hz, 1H), 1.9−1.6 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.8, 136.6, 134.6, 133.6, 129.7, 129.6, 129.3, 128.2, 127.9, 127.6, 127.5, 126.8, 73.8, 59.7, 56.9, 39.6, 16.2. MS (EI) *m*/*z*: 314, 237, 225, 199 (100), 183, 165, 13. Anal. Calcd for $C_{23}H_{22}O_2Si$: C, 77.05; H, 6.19; Si, 7.83. Found: C, 76.98; H, 6.25; Si, 7.75.

(1*R,2*S**)-1-((2*R**,3*R**,4*S**)-3,3-Diphenyl-6-oxa-3-silabicyclo[3.1.0]hex-2-yl)-2-phenylpropan-1-ol (22c).** Following the general epoxidation procedure, **22c** was obtained as a 90:10 mixture of two diastereomers (66%). **22c** (major). $R_f = 0.48$ (petroleum ether−EtOAc 8:2). Mp: 158−159 °C (*i*-PrOH). IR ($CHCl_3$): ν_{max} 3425, 3018, 1428, 1215, 1140, 1110 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.73−7.58 (m, 4H), 7.51−7.37 (m, 6H), 7.17−7.1 (m, 3H), 6.62−6.54 (m, 2H), 3.99−3.88 (m, 1H), 3.82−3.75 (m, 1H), 3.71−3.64 (m, 1H), 2.83−2.69 (m, 1H), 2.32 (dd, $J = 5.9$, 2.2 Hz, 1H), 1.91 (br d, $J = 16$ Hz, 1H), 1.71 (d, $J = 3.95$ Hz, 1H), 1.53 (dd, $J = 16$, 2.2 Hz, 1H), 1.34 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 136.5, 134.8, 129.8, 128.2, 128.1, 128.0, 127.2, 126.1, 60.0, 56.7, 43.6, 33.2, 16.6, 12.2. MS (EI) *m*/*z*: 281, 263, 237, 225, 199 (100), 181, 155, 143. Anal. Calcd for $C_{25}H_{26}O_2Si$: C, 77.68; H, 6.78; Si, 7.27. Found: C, 77.48; H, 6.89; Si, 7.45.

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Supporting Information Available: Preparation and characterization for compounds **12**, **13**, **15b**,**c**, **17**, **20a**,**b**, and **23a**,**b**. ^1H and ^{13}C NMR spectra for compounds **7a**,**c**−**d**, **8a**−**e**, **10b**,**e**, **11a**−**c**, **12**, **13**, **14a**−**c**, **15a**,**b**, **16**, **19b**, **20a**, **21a**, and **22c**. X-ray crystallographic data for compounds **10b**, **18a**, **21a**, and **22c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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