CHEMISTRY
A EUROPEAN JOURNAL

Stereoselective Synthesis of Highly Enantioenriched (*E*)-Allylsilanes by Palladium-Catalyzed Intramolecular Bis-Silylation: 1,3-Chirality Transfer and Enantioenrichment via Dimer Formation

Michinori Suginome,*[a, b] Taisuke Iwanami,[a] Yutaka Ohmori,[a] Akira Matsumoto,[a] and Yoshihiko Ito[a]

Abstract: Highly enantioenriched (*E*)-allylsilanes have been synthesized from optically active allylic alcohols on the basis of Pd-catalyzed intramolecular bis-silylation followed by highly stereospecific Si–O elimination reactions. The method involves three steps: 1) *O*-disilanylation of the allylic alcohols with chlorodisilanes, 2) intramolecular bis-silylation in the presence of a 1,1,3,3-tetramethylbutyl isocyanide/[Pd(acac)$_2$] (acac = acetylacetonate) catalyst at 110 °C, and 3) treatment of the reaction mixture with organolithium reagents. The overall transformation proceeds with nearly complete conservation of the enantiopurity of the starting allyl alcohols by transposition of the C=C bond. For instance, (*R*)-(*E*)-3-decen-2-ol (99.6–99.7 % *ee*) produced (*S*)-(*E*)-4-(organosilyl)-2-decene of 98.8–99.4 % *ee* for a variety of silyl groups, including Me_3Si, Me_2PhSi, *t*BuMe_2Si, Et_3Si, and *i*Pr_3Si. In the bis-silylation step, the initially formed *trans*-1,2-oxasiletanes immediately dimerize to stereoselectively give 1,5-dioxa-2,6-disilacyclooctanes, which are isolated in high yield by carrying out the reaction at 70 °C. The eight-membered ring compounds undergo thermal extrusion of (*E*)-allylsilanes in high yield at 110 °C, along with formation of 1,3-dioxa-2,5-disilacyclohexane derivatives. These in turn undergo a Peterson-type elimination by treatment with nucleophiles such as BuLi and PhLi to give the (*E*)-allylsilanes. All of the steps involved in the sequence proceed with extremely high stereoselectivity and stereospecificity, leading to almost complete 1,3-chirality transfer through the overall transformation. The dimerization step, which forms diastereomeric intermediates, allows the synthesis of a highly enantioenriched allylsilane (99.4 % *ee*) from an optically active allylic alcohol with lower enantiopurity (79.2 % *ee*) by enrichment of enantiopurity. A general method for the determination of the enantiomeric excesses of (*E*)-allylsilanes is also described in detail.

Keywords: asymmetric synthesis · dimerization · palladium catalyst · silicon · silylation

Introduction

Allylsilane is one of the most versatile reagents for stereoselective allylation reactions in organic synthesis, which has been utilized with a variety of electrophiles, such as carbonyl compounds activated by Lewis acids.[1] The synthetic usefulness of allylsilanes has also been demonstrated by Lewis acid catalyzed cycloaddition reactions[2] and metal-catalyzed carbosilylation reactions.[3] The configurational stability, which is due to the covalent nature of silicon–carbon bonds, is of major importance.[4] Thus, synthesis and isolation of regio- and stereochemically defined allylsilanes are readily achieved without any detectable allylic transposition, which would lead to nonselective allylations. In general, allylsilanes undergo electrophilic reaction selectively at the γ-position in an S_E2' fashion. Their synthetically useful features

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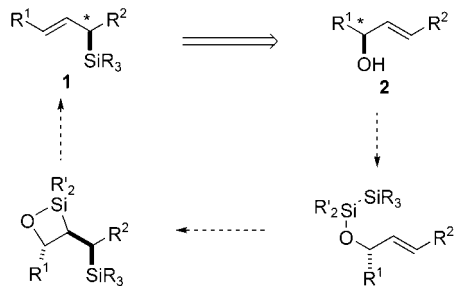
DOI: 10.1002/chem.200401031

have prompted the development of a number of preparative methods for achiral and racemic allylsilanes.[5]

In 1982, Hayashi and Kumada reported the synthesis and reactions of enantiomerically enriched allylsilanes, demonstrating the potential usefulness of such allylsilanes in asymmetric organic synthesis.[6,7] The chirality at the stereogenic allylic carbon atom bound to the silicon atom was stereoselectively transferred to the newly formed γ-stereogenic carbon center by the S_E2' reaction. Since then, methods for the synthesis of enantioenriched allylsilanes have been reported and utilized successfully for organic synthesis.[8–15] However, development of new synthetic methodologies for the preparation of enantiomerically pure allylsilanes are still desired for highly stereoselective organic synthesis.

We have developed a new stereoselective synthesis of organosilicon compounds by palladium-catalyzed intramolecular bis-silylation (IBS).[16,17] In particular, the IBS of homoallylic alcohols provided an efficient and stereoselective silicon–carbon bond-forming reaction, whose synthetic usefulness was demonstrated by the synthesis of stereodefined polyols.[18] In the course of the program, we became interested in the application of IBS to the synthesis of stereodefined allylsilanes, particularly those with high enantiopurity.[19]

Our strategy for the stereoselective synthesis of allylsilanes **1** is based on IBS with enantiomerically pure secondary allylic alcohols **2**, as outlined in Scheme 1. Introduction



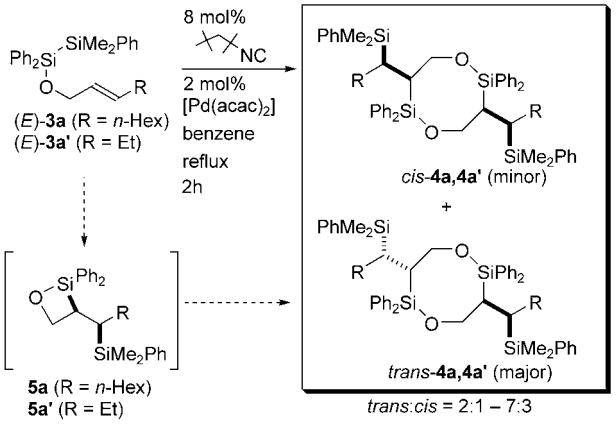
Scheme 1. A synthetic plan for allylsilanes from allylic alcohols by intramolecular bis-silylation and Peterson-type elimination.

of a disilanyl group on the hydroxy group of **2** is followed by palladium-catalyzed IBS, which may create two new Si–C bonds in a regio- and stereoselective manner. Subsequent Peterson-type elimination[20] from the four-membered oxasiletane intermediate is expected to produce allylsilanes with overall transposition of the starting C=C bond. To achieve a high level of chirality transfer from allylic alcohol to allylsilane, it is crucial to achieve high stereoselectivity and/or stereospecificity in the IBS as well as in the elimination step.

We herein describe in detail the IBS-based protocol for the synthesis of stereodefined allylsilanes with special emphasis on those with high enantiopurity.[21]

Results and Discussion

Intramolecular bis-silylation of achiral and racemic allylic alcohols: Disilanyl ether (*E*)-**3a**, which was prepared in high yield from (*E*)-2-nonen-1-ol and 1-chloro-1,1,2-triphenyl-2,2-dimethyldisilane[22] in the presence of triethylamine with a catalytic amount of 4-dimethylaminopyridine (DMAP), was allowed to react in the presence of a catalyst generated from $[Pd(acac)_2]$ (2 mol%) and 1,1,3,3-tetramethylbutyl isocyanide (*t*OcNC, 8 mol%) under reflux in benzene (Scheme 2). We chose this particular disilanyl group because



Scheme 2. IBS of disilanyl ethers derived from *prim*-allylic alcohols.

our previous study showed that the two phenyl groups on the silicon atom bound to the ether oxygen were crucial to achieve sufficient reactivity for addition to an internal C=C bond as well as to attain high stereoselectivity.[18b,d] The starting (*E*)-**3a** was completely consumed after 2 h, and a 1:2 mixture of two isomeric products **4a** (R = *n*-Hex) was isolated in high total yield (96%) by silica gel column chromatography. Although the major isomer was isolated in a diastereomerically pure form by washing the diastereomeric mixture with AcOEt, we could not establish the stereochemistry by spectroscopic analyses. Fortunately, we were able to identify the stereochemistry of **4a**′ (R = Et). Thus, the X-ray analysis of the major product isolated by recrystallization showed an eight-membered cyclic structure *trans*-**4a**′, which may be derived by dimerization of the initially formed oxasiletane **5a**′ (Figure 1). By analogy, it was presumed that *trans*-**4a**, which was derived by the dimerization of oxasiletane **5a** of opposite absolute configuration, was formed as the major isomer in the reaction of (*E*)-**3a**. On the other hand, the minor isomer may be assigned to *cis*-**4a**, which was formed by dimerization of oxasiletane with the same absolute configuration. The stereochemistry of the dimers clearly indicates that complete *cis* addition of the Si–Si bond across the C=C bond takes place during the IBS.

The eight-membered cyclic dioxadisilacyclooctanes were subjected to Peterson-type elimination using nucleophiles. Treatment of **4a** with a molar equivalent of *t*BuOK in THF

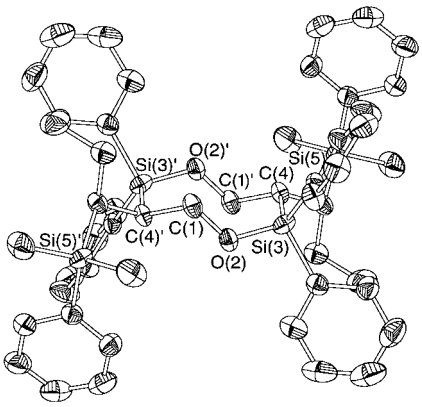
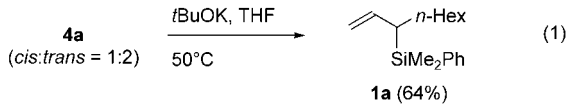


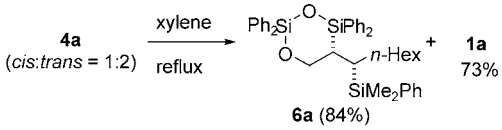
Figure 1. Crystal structure of *trans*-**4a**′. Selected bond lengths [Å] and angles [°]: O(2)–Si(3) 1.647(3), Si(3)–C(4) 1.896(4); C(1)-O(2)-Si(3) 124.7(3), O(2)-Si(3)-C(4) 110.4(2), Si(3)-C(4)-C(1)′ 111.6(3).

at 50 °C afforded allylsilane **1a** in moderate yield [Eq. (1)]. Several attempts at using other nucleophiles such as MeLi and *n*BuLi failed to give the desired allylsilane **1a**.

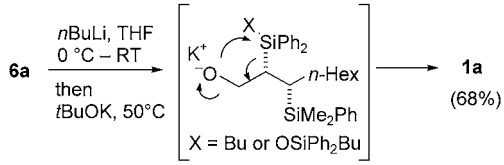


(1)

In the course of those examinations, we found that thermal ring contraction of the eight-membered ring took place at 140 °C in xylene. The disproportionation reaction cleanly afforded six-membered disiladioxane **6a** and allylsilane **1a** [Eq. (2)]. Furthermore, **6a** underwent Peterson-type elimination with *n*BuLi/*t*BuOK to give allylsilane **1a** [Eq. (3)].



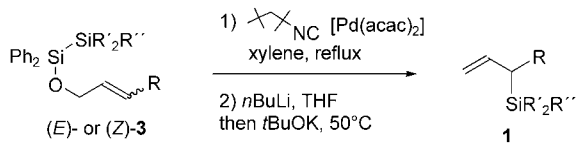
(2)



(3)

The combined yield of the allylsilane was greatly improved by carrying out the two steps in one pot. Thus, reaction of (*E*)-**3a** in the presence of [Pd(acac)$_2$]/*t*OcNC under reflux in xylenes provided a 1:1 mixture of **1a** and **6a**, which was then treated with *n*BuLi/*t*BuOK after replacement of the solvent with THF to give allylsilane **1a** in 90 % yield (Table 1, entry 1). This one-pot procedure was successfully applied to the synthesis of allylsilanes bearing other allylic

Table 1. One-pot synthesis of *sec*-allylsilanes from disilanyl ethers of primary allylic alcohols.

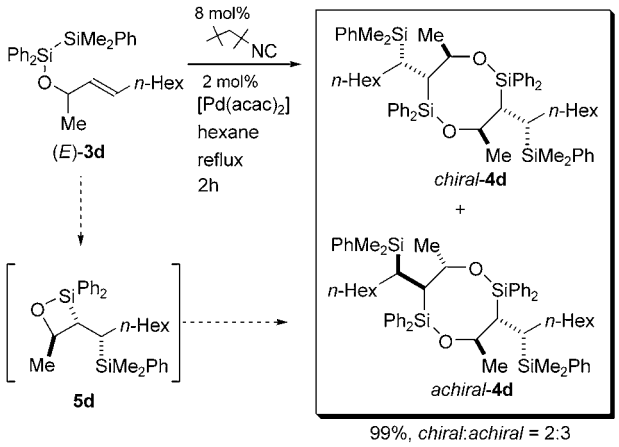


Entry	Disilanyl ether	R	SiR′$_2$R″	**1** (yield [%])[a]
1	(*E*)-**3a**	*n*-Hex	$SiMe_2Ph$	**1a** (90)
2	(*E*)-**3b**	*c*-Hex	$SiMe_2Ph$	**1b** (77)
3	(*E*)-**3c**	Ph	$SiEt_3$	**1c** (58)
4[b]	(*Z*)-**3a**	*n*-Hex	$SiMe_2Ph$	**1a** (68)

[a] Yields of isolated products. [b] PhLi was used for the second step instead of *n*BuLi.

substituents (Table 1, entries 2 and 3). Note that disilanyl allyl ether (*Z*)-**3a**, which has a *cis*-C=C bond, similarly underwent IBS and subsequent elimination to give **1a** in moderate yield when subjected to the one-pot procedure (Table 1, entry 4).

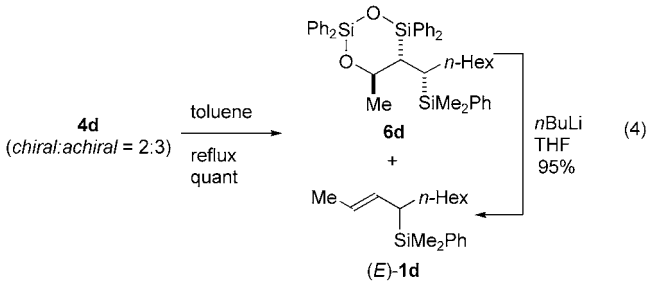
We then examined reactions of *sec*-allylic alcohols, which led to the synthesis of allylsilanes with an internal C=C bond. Our primary concern was diastereofacial selectivity of the IBS reaction. Disilanyl ether (*E*)-**3d**, prepared from racemic (*E*)-3-decen-2-ol, underwent IBS in the presence of [Pd(acac)$_2$]/*t*OcNC under reflux in hexane (ca. 70 °C) to give eight-membered ring dimers **4d** in quantitative yield as a mixture of two diastereomers (Scheme 3). This result indicated that IBS of (*E*)-**3d** proceeded with high stereoselectivity to produce diastereomerically pure *trans*-oxasiletane **5d** as a racemate, which then dimerized to give *chiral*-**4d** and *achiral*-**4d** in a ratio of 2:3.[23]



Scheme 3. IBS of disilanyl ethers derived from racemic *sec*-allylic alcohols.

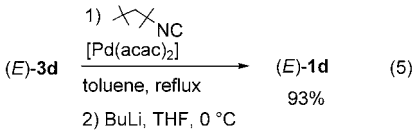
The dimers **4d** underwent thermal disproportionation more readily than the corresponding dimer **4a** obtained from the primary allylic alcohol. Thus, heating **4d** in refluxing toluene afforded disiladioxane **6d** and allylsilane (*E*)-**1d** quantitatively without formation of any stereoisomers of

each product [Eq. (4)]. This finding may unambiguously prove that the thermal extrusion of the allylsilane proceeds with almost complete stereospecificity for the *syn*-elimination. Treatment of the six-membered cyclic compound **6d** with *n*BuLi afforded (*E*)-**1d** in 95% yield by Peterson elimination.



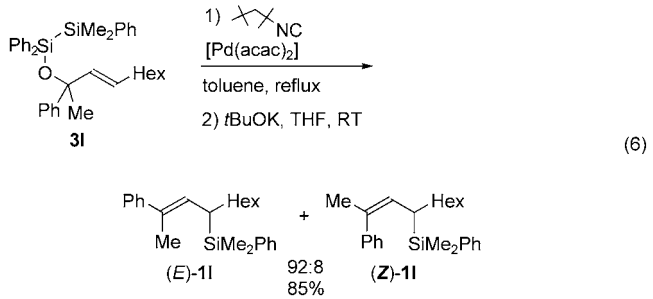
(4)

The one-pot procedure was found to be applicable to the synthesis of allylsilanes such as **1d** with an internal C=C bond. Thus, IBS of (*E*)-**3d** under reflux in toluene, followed by treatment of the crude reaction mixture with *n*BuLi in THF, gave allylsilane (*E*)-**1d** in 93% yield [Eq. (5)]. No *cis*-allylsilane was detected in the reaction mixture, suggesting high stereoselectivity of the bis-silylation step as well as complete stereospecificity of the elimination steps.



(5)

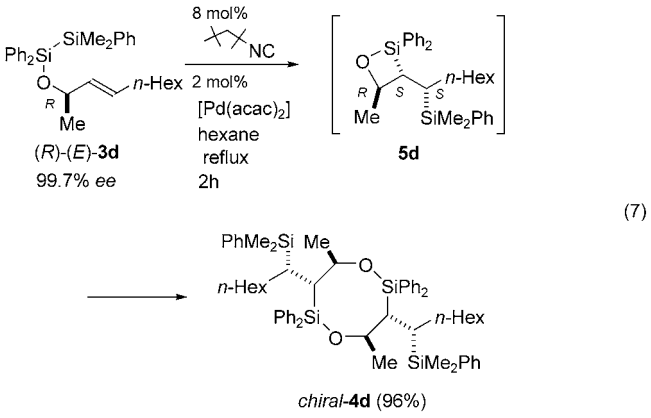
Reaction of the disilanyl ether **3l** of the chiral *tert*-allylic alcohol was also examined. IBS under toluene reflux followed by treatment with *t*BuOK afforded allylsilane (*E*)-**1l** and (*Z*)-**1l** in 85% yield as a 92:8 mixture of the two stereoisomers [Eq. (6)].



(6)

Synthesis of enantioenriched (*E*)-allylsilanes with 1,3-chirality transfer: It has thus far been established that the IBS of a chiral allylic alcohol creates two new silyl-bound stereogenic carbon centers in an oxasiletane in a highly diastereoselective fashion. Since one stereogenic center newly created at the α-silylalkyl substituent on the four-membered ring is retained in chiral allylsilanes after the elimination steps, highly stereoselective 1,3-transfer of chirality from the starting allylic alcohols to the produced allylsilanes was expected. We attempted to use highly enantioenriched allylic alcohols as starting materials, which were readily available by asymmetric synthesis.

Initially, we examined the IBS reactions of highly enantioenriched disilanyl ethers (*R*)-(*E*)-**3d** (99.7% *ee*) and (*R*)-(*Z*)-**3d** (96% *ee*) to confirm the stereochemical course in detail. IBS of (*R*)-(*E*)-**3d** in refluxing hexane afforded an eight-membered ring dimer in high yield [Eq. (7)]. We could detect only one isomer assignable to enantiopure *chiral*-**4d** in the reaction mixture. Likewise, IBS of (*R*)-(*Z*)-**3d** provided *chiral*-**ent-4d** in high yield, essentially as a single isomer under the same reaction conditions [Eq. (8)]. The structures of both eight-membered ring products, *chiral*-**4d** and *chiral*-**ent-4d**, were confirmed by single-crystal X-ray analyses (Figures 2 and 3). It is interesting to note that the transannular Si–O distances (2.86–2.96 Å) in *chiral*-**4d** and *chiral*-**ent-4d** are significantly shorter than the sum of the van der Waals radii (ca. 3.4 Å), which is responsible for the facile thermal ring contraction. The requirement of a relatively



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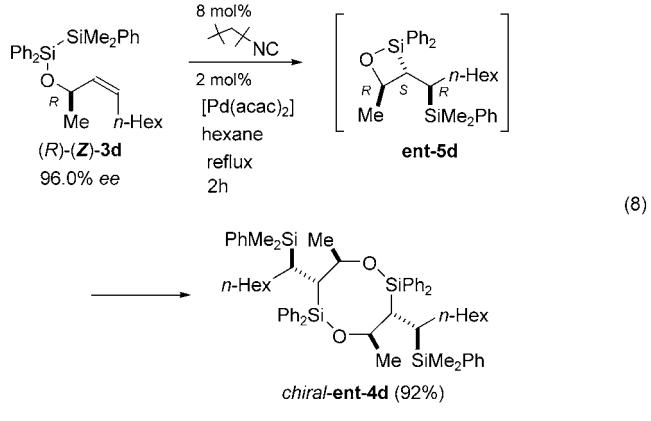

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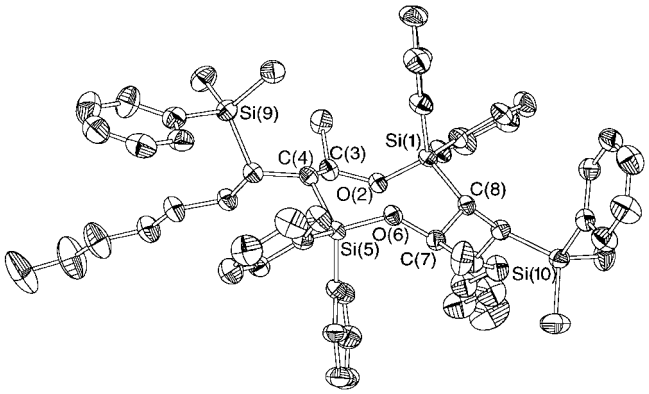


Figure 2. Crystal structure of *chiral*-**4d**. Selected bond lengths [Å] and angles [°]: Si(1)–O(2) 1.645(4), Si(1)–C(8) 1.911(5), Si(5)–O(6) 1.655(4), Si(5)–C(4) 1.889(5); Si(1)-O(2)-C(3) 134.9(4), O(2)-Si(1)-C(8) 109.1(2), Si(5)-O(6)-C(7) 126.6(4), C(4)-Si(5)-O(6) 106.5(3).

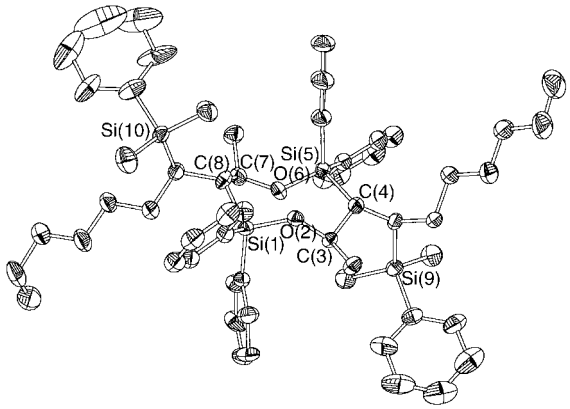
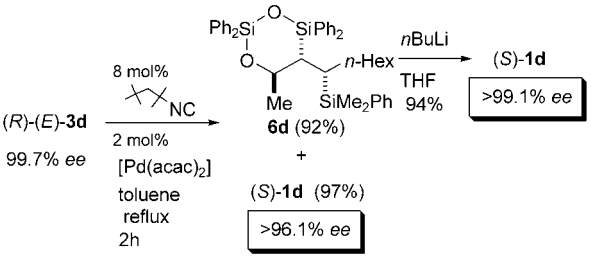


Figure 3. Crystal structure of *chiral*-**ent-4d**. Selected bond lengths [Å] and angles [°]: Si(1)–O(2) 1.647(4), Si(1)–C(8) 1.920(6), Si(5)–O(6) 1.636(5), Si(5)–C(4) 1.888(6), Si(1)-O(2)-C(3) 126.8(3), O(2)-Si(1)-C(8) 106.0(3), Si(5)-O(6)-C(7) 133.8(4), O(6)-Si(5)-C(4) 109.5(3).

high temperature in the thermal ring contraction of **4a**, which is derived from the primary allylic alcohol, may be attributed to the slightly deviated conformation of the eight-membered ring, in which the longer transannular Si–O distance (3.41 Å) was observed in the X-ray crystal structure (Figure 1). The two compounds, *chiral*-**4d** and *chiral*-**ent-4d**, have the same stereochemistry with respect to the substituents in the eight-membered ring, but differ in the configuration at the α-silylalkyl substituents. This result undoubtedly establishes the extremely high diastereofacial selectivity as well as perfect stereospecificity for *cis*-addition of the Si–Si bond across the C=C bond, which leads to the formation of *trans*-oxasiletanes **5d** and **ent-5d** from the starting (*E*)- and (*Z*)-alkenes, respectively.

Upon heating in refluxing toluene, (*R*)-(*E*)-**3d** afforded disiladioxane **6d** and allylsilane (*S*)-**1d** in high total yield [Eq. (9)]. The six-membered cyclic **6d**, which was separated from (*S*)-**1d** and isolated, was subjected to treatment with *n*BuLi, affording (*S*)-**1d** in high yield. Enantiomeric excesses of both samples of the allylsilane were determined to be 96.1 and 99.1 % *ee*.[24] The absolute configuration of the allylsilane was determined to be *S*, suggesting highly enantioenriched allylsilane was produced with nearly complete 1,3-chirality transfer through the expected stereochemical course.



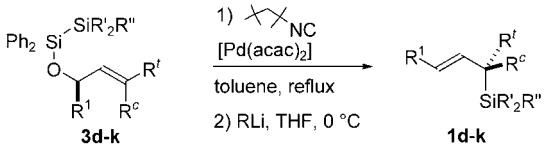
(9)

Application of the one-pot method to the synthesis of the highly enantioenriched allylsilane was also successful. Thus, IBS of (*R*)-(*E*)-**3d** in refluxing toluene followed by treatment with *n*BuLi afforded (*S*)-**1d** of 99.1 % *ee* in 90 % yield (Table 2, entry 1). In good agreement with the stereoselective formation of **ent-5d** in IBS in refluxing hexane, (*R*)-(*Z*)-**3d** afforded (*R*)-**1d** in good yield with nearly complete 1,3-chirality transfer (Table 2, entry 2). Results of the synthesis of a series of highly enantioenriched allylsilanes by the one-pot procedure are summarized in Table 2. Allylsilanes with a variety of silyl groups and allyl groups were successfully prepared with >99 % conservation of enantiopurity of the starting allylic alcohols. Moreover, except for the TIPS derivative (Table 2, entry 6), yields were generally high. These results demonstrate the synthetic usefulness of the new protocol for the preparation of highly enantioenriched allylsilanes.

Stereochemical course: The highly stereoselective 1,3-transfer of chirality from the allylic alcohol to the allylsilane is primarily attributed to the highly stereoselective IBS, which exclusively produces *trans*-oxasiletane **5**. As we previously proposed, the bis-silylation may proceed through a bis(silyl)palladium(II) intermediate, which is formed by oxidative addition of the Si–Si bond to the palladium(0) complex ligated by *tert*-alkyl isonitrile. It is presumed that the bis(silyl)palladium(II) intermediate formed from the disilanyl ether of the allylic alcohol is able to adopt two conformations in the cyclization step, depicted as **A** and **B** in Scheme 4, in which the R^1 group at the stereogenic center is at the pseudo equatorial or axial position, respectively. The IBS reaction may exclusively proceed via the intermediate **A**, since the cyclization via intermediate **B** may be unfavorable because of steric repulsion between the R^1 group and the phenyl group on the silicon atom. Accordingly, the *trans* four-membered ring product *trans*-**5** is obtained with high stereoselectivity.

Subsequent dimerization may be driven by an intermolecular Lewis acid–base interaction between the ether oxygen atom and the silicon atom in the four-membered ring, of which the respective basicity and acidity may be enhanced

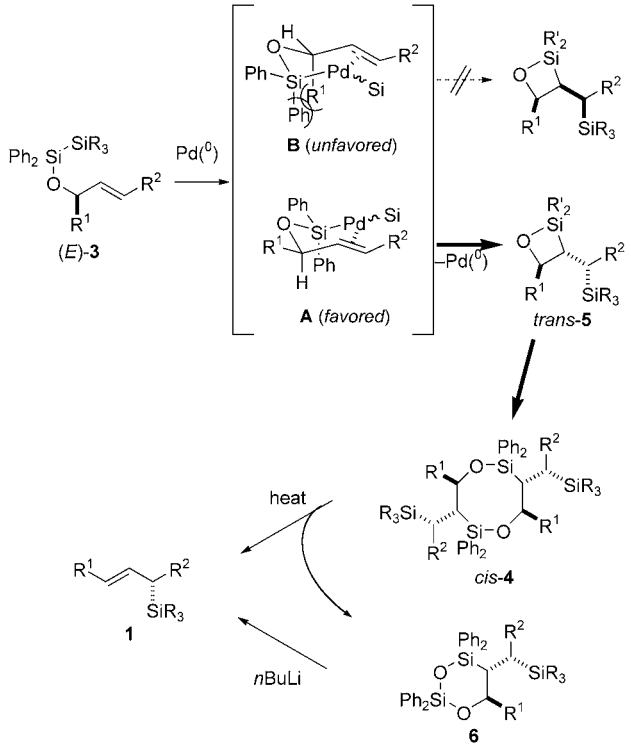
Table 2. One-pot synthesis of enantioenriched (*E*)-allylsilanes[a].



3d-k 1d-k

Entry	**3** (*ee* [%])[b]	R″R′$_2$Si	R^1	R^t	R^c	**1** (yield [%])[c]	*ee* [%][d]	ce [%][e]
1	(*R*)-(*E*)-**3d** (99.7)	PhMe$_2$Si	Me	*n*-Hex	H	(*S*)-**1d** (90)	99.1	99.4
2[f]	(*R*)-(*Z*)-**3d** (96.0)	PhMe$_2$Si	Me	H	*n*-Hex	(*R*)-**1d** (84)	95.4	99.4
3	(*R*)-(*E*)-**3e** (99.6)	Me$_3$Si	Me	*n*-Hex	H	(*S*)-**1e** (81)	99.1	99.4
4	(*R*)-(*E*)-**3f** (99.6)	*t*BuMe$_2$Si	Me	*n*-Hex	H	(*S*)-**1f** (82)	99.4	99.8
5	(*R*)-(*E*)-**3g** (99.6)	Et$_3$Si	Me	*n*-Hex	H	(*S*)-**1g** (94)	99.2	99.6
6	(*R*)-(*E*)-**3h** (99.6)	*i*Pr$_3$Si	Me	*n*-Hex	H	(*S*)-**1h** (62)	98.8	98.8
7	(*S*)-(*E*)-**3i** (>99.0)	PhMe$_2$Si	Ph	*n*-Hex	H	(*S*)-**1i** (99)	98.7	>98.7
8	(*S*)-(*E*)-**3j** (99.8)	PhMe$_2$Si	*c*-Hex	*n*-Hex	H	(*S*)-**1j** (96)	99.0	99.3
9	(*R*)-(*E*)-**3k** (98.2)	PhMe$_2$Si	Me	Ph	H	(*R*)-**1k** (92)	98.1	99.9

[a] Unless otherwise noted, the bis-silylations were carried out in the presence of [Pd(acac)$_2$] (2 mol%) and 1,1,3,3-tetramethylbutyl isocyanide (8 mol%) under reflux in toluene. After replacement of the solvent with THF, *n*BuLi in hexane was added at 0°C. [b] Enantiomeric excesses of the corresponding allylic alcohols determined by HPLC. [c] Yields of isolated products. [d] Enantiomeric excesses determined by hydroboration method (see main text). [e] Conservation of enantiopurity (*ee* of **1**/*ee* of **3**). [f] PhLi was used instead of *n*BuLi.

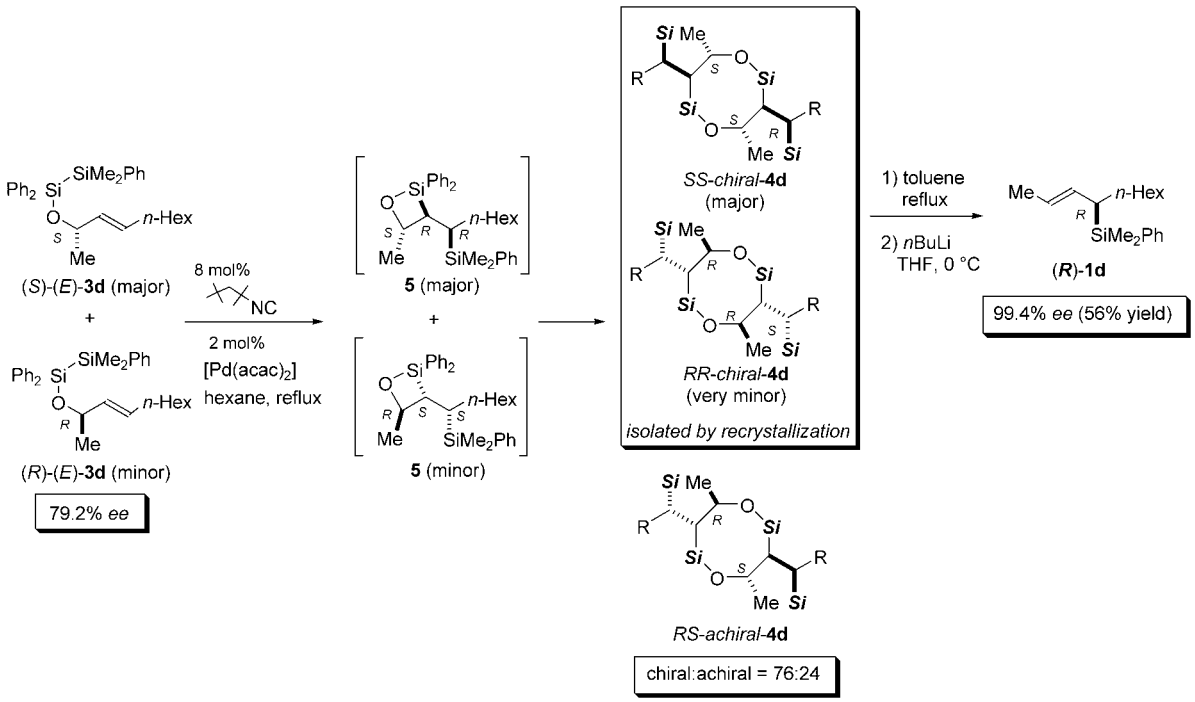


Scheme 4. Stereochemical course of the sequence from (*E*)-**3** to **1**.

by the ring strain. This dimerization mechanism involving Si–O bond cleavage may be supported by the fact that no racemization took place during synthesis of the allylsilanes. Subsequent elimination reactions, such as ring contraction of **4** and nucleophile-induced reaction of **6**, proceed in a perfect *syn* fashion. Although the mechanism for the latter elimination has been well documented in the literature,[25] the present study showed that the thermal extrusion of allylsilane from dioxadisilacyclooctane **4** also proceeded with highly stereospecific *syn*-elimination.

Enrichment of the enantiomeric excesses through dimerization: It is commonly accepted that the *ee* of the product does not exceed the *ee* of the starting material in asymmetric syntheses involving chirality transfer. Although crystalline products with incomplete enantiopurity may be purified by preferential recrystallization to produce enantiopure materials, there is no way to enrich the enantiopurity of nonsolid materials. Indeed, this was true for our protocol for the one-pot synthesis of enantioenriched allylsilanes. In principle, however, it would still be possible to enrich enantiopurity through the chirality transfer process, if it involves the formation of diastereomeric intermediates that are isolable and purifiable.[26] The present reaction sequence involves the formation of isolable diastereomeric intermediates, the chiral and achiral eight-membered cyclic dimers **4**. Therefore, isolation of the chiral isomer in a pure state may lead to the production of allylsilanes with higher *ee* values than those of the allyl alcohols used as starting materials. Indeed, the degree of enrichment of enantiopurity can be roughly estimated by a simple calculation based on the assumption that the dimerization of *trans*-oxasiletane **5** takes place randomly.[27] Using enantioenriched allyl alcohol containing x% *S* enantiomer (and $(100-x)$% *R* enantiomer), IBS and subsequent dimerization provides two enantiomers, *SS-chiral*-**4** and *RR-chiral*-**4**, along with *RS-achiral*-**4** (Scheme 5). The ratio of *SS*- to *RR*- and *RS*-**4** is calculated to be x^2:$(100-x)^2$:$2x(100-x)$. Removal of the achiral dimer *RS*-**4** by recrystallization leaves the chiral dimers, which contain the *SS*- and *RR*-enantiomers in a ratio of at least x^2:$(100-x)^2$. The ratio is maintained in the enantioenriched allylsilanes produced by the subsequent elimination reactions. For instance, allylsilanes of 99.4% *ee* and 97.6% *ee* can be obtained from enantioenriched allyl alcohols of 90.0% *ee* ($x = 95.0$) and 80.0% *ee* ($x = 90.0$), respectively, according to the calculation.

Disilanyl ether (*S*)-(*E*)-**3d** was prepared from the corresponding allylic alcohol with 79.2% *ee* and subjected to IBS under reflux in hexane. A 76:24 mixture of *chiral*-**4d** (*SS* and *RR*) and *achiral*-**4d** (*RS*) was obtained by silica gel chromatography. Fortunately, *chiral*-**4d** could be isolated by recrystallization from Et$_2$O/EtOH. The pure *chiral*-**4d** was then heated in refluxing toluene and treated with *n*BuLi as described above. Consequently, allylsilane (*R*)-**1d** of

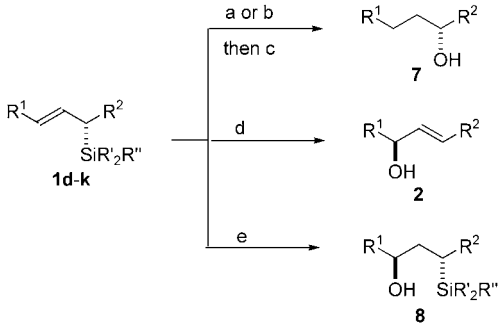


Scheme 5. Synthesis of enantiopure allylsilane (*R*)-**1d** from (*S*)-(*E*)-**3d** of 79.2 % *ee* by enrichment of enantiopurity (Si = $SiMe_2Ph$).

99.4 % *ee* was isolated in 56 % overall yield from (*S*)-(*E*)-**3d** of 79.2 % *ee*.

This result demonstrates that allylic alcohols with only moderate *ee* values are sufficient for the production of almost enantiopure allylsilanes. The minor enantiomer of the starting disilanyl ether **3d** is accumulated predominantly in *achiral*-**4d**, resulting in the formation of *chiral*-**4d** with nearly perfect enantiomeric excess. Though the observed *ee* (99.4 %) for the allylsilane prepared from (*S*)-(*E*)-**3d** of 79.2 % *ee* was unexpectedly higher than the calculated value (97.3 % *ee*), this may be due to preferential crystallization of the major enantiomer (*SS-chiral*-**4d**) during the recrystallization. These enrichment processes may be especially valuable in cases where optically pure allylic alcohols are not easily accessible.

Determination of enantiomeric excesses: Since chiral HPLC analysis provides the most reliable determination of enantiomeric excesses of highly enantioenriched compounds, optically active allylsilanes obtained by our protocol were subjected to some stereospecific transformations for the purpose of making them amenable to chiral HPLC analysis (Scheme 6). Allylsilane (*S*)-**1d**, which was prepared from (*R*)-(*E*)-**3d** of 99.7–99.9 % *ee*, was hydrogenated in the presence of Pd/C followed by oxidation of the Si–C bond under the Tamao condition to give 4-decanol (**7d**).[28] To our surprise, a chiral HPLC analysis of the corresponding 3,5-dinitrophenylcarbamate showed only 30 % *ee* (Table 3, entry 1). We suppose that the decrease in *ee* did not arise from inefficient 1,3-chirality transfer, but from racemization during the transformation prior to the analysis. Indeed, hydrogenation



Scheme 6. Transformations of enantioenriched allylsilanes for determination of enantiomeric excesses. Reagents and conditions: a) H_2, Pd/C, AcOEt; b) $TsNHNH_2$, Et_3N, dioxane, reflux; c) CF_3CO_2H, 50 °C, then KHF_2, $KHCO_3$, MeOH, THF, 50 °C; d) *m*CPBA, CH_2Cl_2, −78 – 0 °C, then AcOH, MeOH; e) 9-BBN, THF, 50 °C, then H_2O_2, NaOH aq, 50 °C.

Table 3. Enantiomeric excesses of alcohols **2**, **7**, and **8** derived from enantioenriched allylsilane (*S*)-**1d** by transformations outlined in Scheme 6.

Entry	*ee* of **3d**[a] [%]	Path[b]	Produced alcohol	Yield [%]	*ee* [%]	ce[c] [%]
1	99.7	***a***, ***c***	**7d**	52	30.4	30.5
2	99.9	***b***, ***c***	**7d**	49	97.3	97.4
3	99.9	***d***	**2d**	50	96.8	96.9
4	99.7	***e***	**8d**	85	99.1	99.4

[a] Enantiomeric excess of (*R*)-(*E*)-**3d** employed for the synthesis of (*S*)-**1d**. [b] The alphabetical designations correspond to those in Scheme 6. [c] Conservation of enantiopurity.

of the C=C bond with diimide instead of Pd-catalyzed hydrogenation led to the formation of **7d** with 97.3% *ee* (Table 3, entry 2). Reaction of (*S*)-**1d** with *m*CPBA was also attempted. Although slight racemization may have taken place during the transformation, allylic alcohol (*S*)-(*E*)-**2d** (96.8% *ee*) was obtained in moderate yield (entry 3). The absolute configuration of (*S*)-**1d** was unambiguously established by the chiral HPLC analysis of allyl alcohol (*E*)-**2d** obtained by the *m*CPBA oxidation. Indeed, the analysis of (*E*)-**2d** showed the absolute configuration of (*S*), which was opposite to that for the starting (*R*)-(*E*)-**2d**, indicating that the absolute configuration of (*S*) of the allylsilane **1d** is in accord with the reported stereochemical course for the *m*CPBA reaction of allylsilanes.[29] The highest *ee*, which may inevitably be the most accurate value, was attained by regio- and stereoselective hydroboration of (*S*)-**1d** with 9-BBN,[30] which gave *anti*-4-silyldecan-2-ol **8d** in good yield on treatment with basic hydrogen peroxide (Table 3, entry 4). The *ee* (99.1% *ee*) measured by the HPLC analysis showed that the enantiopurity of the starting allylic alcohol was almost completely conserved in the allylic silane obtained.

The method for *ee* determination was generally applied to all enantioenriched allylsilanes **1d–k** described thus far. The hydroboration method generally showed higher, or more accurate, enantiopurity than the other methods examined. The hydroboration-oxidation sequence is advantageous over other methods in that essentially no racemization takes place during the transformation and a wide range of allylsilanes, including those with bulky silyl groups such as *tert*-butyldimethylsilyl (TBDMS) and triisopropyl silyl (TIPS), can be evaluated. The transformation using Tamao oxidation or *m*CPBA oxidation was not applicable for the *ee* determination of allylsilanes with bulky trialkylsilyl groups such as **1f** and **1h**.

Conclusion

We have established a new synthetic route to highly enantioenriched allylsilanes from allylic alcohols by stereoselective IBS followed by stereospecific elimination reactions. For the conversion of allylic alcohols to allylsilanes starting with the corresponding disilanyl ethers, which are easily prepared from allylic alcohols and disilanyl chloride, the following simple operations are carried out in one flask: 1) IBS in refluxing toluene in the presence of the palladium–isonitrile catalyst and 2) treatment of the reaction mixture with *n*BuLi (or PhLi). Highly enantioenriched (*E*)-allylsilanes were thus obtained with nearly complete stereoconservation of the enantiomeric excess of the starting allylic alcohols. Moreover, even from allylic alcohols with about 80% *ee*, enantioenriched allylsilanes with higher than 99% *ee* are available through isolation and recrystallization of the eight-membered dimeric intermediates. The present method will open up new possibilities for the application of enantioenriched allylsilanes in stereoselective organic synthesis. The synthetic utility of the method has been demonstrated by the synthesis of highly enantioenriched, functionalized allylsilanes including those supported on a polymer resin.[31,32]

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-2000 (7.0 T magnet) or a JEOL JNM 400 (11.7 T magnet) spectrometer at ambient temperature. ^{1}H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C NMR spectra were obtained with complete proton decoupling. IR spectra were obtained on a Hitachi 270–30 spectrometer. High-resolution mass spectra were recorded on a JEOL JMS HX-110 spectrometer. Optical rotations were measured on a Perkin–Elmer 243 polarimeter.

Solvents were distilled from the indicated drying agents: benzene ($LiAlH_4$), toluene ($LiAlH_4$), xylenes (CaH_2), hexanes (Na), THF (Na/benzophenone). [Pd(acac)$_2$] (Mitsuwa), *n*BuLi (Mitsuwa), *t*BuOK (Nacalai), *m*CPBA (80%, Nacalai), and 9-BBN (Aldrich) were purchased from commercial sources and used as received. Chlorodisilanes ($ClPh_2Si-SiR'_2R''$) were prepared by the reactions of $(Et_2N)Ph_2SiLi$ with $ClSiR'_2R''$ in THF, followed by treatment with AcCl in the same reaction vessel.[22] (*E*)-Allylic alcohols were prepared by the reactions of the corresponding propargylic alcohols with sodium bis(methoxyethoxy)aluminum hydride (Red-Al) in toluene. (*Z*)-Allylic alcohols were prepared from the corresponding propargylic alcohols by hydromagnesation using *i*BuMgCl in the presence of [Cp_2TiCl_2] followed by hydrolysis.[33] Highly enantioenriched allylic alcohols were obtained with Sharpless kinetic resolution using [Ti(O*i*Pr)$_4$] with L-(+)-diisopropyl tartrate at −20 °C.[34] Enantiomeric excesses of the allylic alcohols were determined by chiral HPLC analysis. Disilanyl ethers of the allylic alcohols were prepared from the corresponding chlorodisilanes and the alcohols in the presence of Et_3N (1.5 equiv) and 4-(dimethylamino)pyridine (0.02 equiv) in THF at room temperature.

IBS of (*E*)-3a in refluxing benzene (Scheme 2): A mixture of [Pd(acac)$_2$] (1.3 mg, 4.2×10^{-3} mmol) and 1,1,3,3-tetramethylbutyl isocyanide (12×10^{-3} mL, 66×10^{-3} mmol) was stirred for 10 min under nitrogen at room temperature. Benzene (0.4 mL) and (*E*)-**3a** (101 mg, 0.22 mmol) were added to the catalyst mixture. The mixture was stirred for 2 h under reflux. Evaporation of the solvent followed by silica gel column chromatography (hexane only to hexane/ether = 50:1) afforded a mixture of *cis*- and *trans*-**4a** (97 mg, 96%). The major isomer, *trans*-**4a**, was isolated in diastereomerically pure form by washing the mixture with EtOAc. *trans*-**4a**: ^{1}H NMR ($CDCl_3$): δ = 0.26 (s, 6H), 0.33 (s, 6H), 0.55–1.11 (m, 22H), 0.78 (t, J = 7.2 Hz, 6H), 2.23–2.31 (m, 2H), 3.70–3.82 (m, 4H), 7.16–7.49 ppm (m, 30H); ^{13}C NMR ($CDCl_3$): δ = −2.8, −2.4, 13.9, 22.5, 23.2, 27.0, 28.0, 29.5, 30.7, 31.5, 63.2, 127.3, 127.8, 128.8, 129.3, 129.7, 134.0, 134.8, 135.0, 135.8, 136.0, 139.7 ppm. *cis*-**4a**: ^{1}H NMR ($CDCl_3$): δ = 0.01 (s, 6H), 0.07 (s, 6H), 0.55–1.38 (m, 22H), 0.75 (t, J = 7.2 Hz, 6H), 1.91–1.98 (m, 2H), 3.90 (dd, J = 6.3, 10.8 Hz, 2H), 4.05 (t, J = 10.8 Hz, 2H), 7.17–7.69 ppm (m, 30H). A mixture of the *cis* and *trans* isomers isolated by silica gel column chromatography was subjected to elemental analysis; elemental analysis calcd (%) for $C_{58}H_{76}O_2Si_4$: C 75.92, H 8.35; found: C 75.76, H 8.33.

Preparation of *trans*-4a′ (for an X-ray analysis): According to the same procedure as that for IBS of (*E*)-**3a** to make **4a**, the eight-membered cyclic **4a′** (73% in total, a 7:3 mixture of two stereoisomers) was prepared from (*E*)-**3a′**. From the stereoisomeric mixture, *trans*-**4a′** was isolated by recrystallization (EtOH/Et_2O). *trans*-**4a′**: ^{1}H NMR ($CDCl_3$): δ = 0.28 (s, 6H), 0.33 (t, J = 7.4 Hz, 6H), 0.34 (s, 6H), 0.75–1.18 (m, 6H), 2.28 (dd, J = 10.3, 5.2 Hz, 2H), 3.67–3.87 (m, 4H), 7.16–7.58 ppm (m, 30H); ^{13}C NMR ($CDCl_3$): δ = −2.9, −2.2, 15.1, 20.7, 25.0, 27.0, 63.0, 127.3, 127.7, 128.8, 129.2, 129.6, 134.0, 134.7, 134.9, 135.7, 135.9,

139.5 ppm; elemental analysis calcd (%) for $C_{50}H_{60}O_2Si_4$: C 74.57, H 7.51; found C 74.31, H 7.65.

Reaction of 4a with *t*BuOK [Eq. (1)]: Compound **4a** (50 mg, 0.055 mmol) was added to a solution of *t*BuOK (25 mg, 0.22 mmol) in THF (0.5 mL) at room temperature. The mixture was heated at 50 °C for 6 h. The reaction mixture was cooled and aqueous NH_4Cl (saturated) was added. Extractive workup followed by silica gel column chromatography (hexane) afforded **1a** (18 mg, 64 %).

Thermal ring contraction of 4a [Eq. (2)]: A solution of **4a** (a mixture of the *cis* and *trans* isomers, 48 mg, 0.052 mmol) in xylene (0.4 mL) was heated at 140 °C for 3 h. The solvent was stripped off under vacuum. A ^{1}H NMR spectrum of the crude mixture showed clean formation of **6a** and **1a**. Silica gel column chromatography afforded **1a** (10 mg, 73 %) and **6a** (29 mg, 84 %). **6a**: ^{1}H NMR ($CDCl_3$): δ = 0.38 (s, 3H), 0.41 (s, 3H), 0.53–1.40 (m, 14H), 2.24 (t, J = 7.2 Hz, 1H), 4.32 (d, J = 7.2 Hz, 2H), 7.21–7.92 ppm (m, 25H); ^{13}C NMR ($CDCl_3$): δ = −2.7, −1.7, 14.0, 22.5, 24.5, 29.1, 29.5, 29.8, 30.9, 31.4, 64.6, 127.6, 127.8, 127.9, 128.0, 128.9, 129.9, 130.2, 130.5, 133.4, 133.8, 134.4, 134.5, 134.57, 134.61, 134.9, 135.5, 139.3 ppm; elemental analysis calcd (%) for $C_{41}H_{48}O_2Si_3$: C 74.94, H 7.36; found: C 74.71, H 7.34.

Reaction of 6a with *n*BuLi/*t*BuOK [Eq. (3)]: *n*BuLi (1.5 M in hexane, 0.11 mL, 0.17 mmol) was added to a solution of **6a** (51 mg, 7.8×10^{-2} mmol) in THF (0.5 mL) at 0 °C. The mixture was stirred as it warmed from 0 °C to room temperature over 1.5 h. *t*BuOK (18 mg, 0.16 mmol) and THF (0.2 mL) at room temperature were added to the mixture, which was stirred at 50 °C for 15 h. Extractive workup followed by silica gel column chromatography (hexane) afforded **1a** (14 mg, 68 %).

General procedure for one-pot synthesis of allylsilanes 1a–c (Table 1): A mixture of [Pd(acac)$_2$] (2.7 mg, 8.9×10^{-3} mmol) and 1,1,3,3-tetramethylbutyl isocyanide (2.3×10^{-2} mL, 0.13 mmol) was stirred for 10 min under nitrogen at room temperature. Xylene (0.7 mL) and disilanyl ether **3a–c** (0.45 mmol) were added to the catalyst mixture. The mixture was stirred for 10 h under reflux. After stripping the volatile materials off under vacuum, THF (0.7 mL) was added to the residue. The solution was cooled to 0 °C and *n*BuLi (0.30 mL, 1.50 M in hexane, 0.45 mmol) was added; the mixture was stirred for 1.5 h at room temperature. *t*BuOK (51 mg, 0.45 mmol) at room temperature was added to the mixture, which was then stirred at 50 °C for 12 h. Addition of aqueous NH_4Cl (saturated) to the mixture and extractive workup with ether followed by column chromatography on silica gel (hexane) afforded (*E*)-allylsilanes **1a–c**.

3-(Dimethylphenylsilyl)-1-nonene (1a): ^{1}H NMR ($CDCl_3$): δ = 0.26 (s, 3H), 0.27 (s, 3H), 0.85 (t, J = 6.6 Hz, 3H), 1.04–1.50 (m, 10H), 1.67–1.81 (m, 1H), 4.75–4.92 (m, 2H), 5.58 (dt, J = 16.9, 9.8 Hz, 1H), 7.31–7.57 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ = −5.2, −4.4, 14.1, 22.7, 28.4, 29.1, 29.2, 31.8, 34.4, 112.4, 127.6, 128.9, 134.0, 137.9, 139.9 ppm; elemental analysis calcd (%) for $C_{17}H_{28}Si$: C 78.38, H 10.83; found: C 78.49, H 11.10.

3-Cyclohexyl-3-(dimethylphenylsilyl)-1-propene (1b): ^{1}H NMR ($CDCl_3$): δ = 0.28 (s, 3H), 0.30 (s, 3H), 0.91–1.29 (m, 5H), 1.37–1.77 (m, 7H), 4.79 (dd, J = 16.7, 2.2 Hz, 1H), 4.90 (dd, J = 10.3, 2.2 Hz, 1H), 5.71 (dt, J = 16.7, 10.3 Hz, 1H), 7.30–7.57 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ = −3.5, −2.8, 26.2, 26.7, 31.3, 34.1, 38.4, 42.2, 113.7, 127.5, 128.7, 133.9, 137.8, 139.0 ppm; elemental analysis calcd (%) for $C_{17}H_{26}Si$: C 79.00, H 10.14; found: C 78.80, H 10.10.

IBS of racemic (*E*)-3d in refluxing hexanes (Scheme 3): [Pd(acac)$_2$] (6.9 mg, 2.3×10^{-2} mmol) was placed in a Schlenk flask and tetramethylbutyl isocyanide (15×10^{-3} mL, 8.6×10^{-2} mmol) was added. The mixture was stirred for 10 min at room temperature. Hexane (5.0 mL) and (±)-(*E*)-**3d** (501 mg, 1.1 mmol) were added to the dark red mixture at room temperature and it was stirred under reflux for 1 h. The solvent was stripped off under vacuum and the residue was subjected to silica gel column chromatography (hexane/ether = 100:1) to give **4d** (493 mg, 98 %) as a viscous oil. **4d** (a mixture of *chiral*-**4d** and *achiral*-**4d**): ^{1}H NMR ($CDCl_3$): δ = −0.30 (s, 6H; *chiral*-**4d**), −0.04 (s, 6H; *chiral*-**4d**), 0.19 (s, 6H; *achiral*-**4d**), 0.26 (s, 6H; *achiral*-**4d**), 0.30–1.40 (m, 34H; *chiral*-**4d** and 34H; *achiral*-**4d**), 1.75 (d, J = 11.1 Hz, 2H; *chiral*-**4d**), 2.18 (d, J = 9.6 Hz, 2H; *achiral*-**4d**), 4.11 (dq, J = 9.6, 6.0 Hz, 2H; *achiral*-**4d**), 4.54 (dq, J = 11.1, 6.3 Hz, 2H; *chiral*-**4d**), 6.88–6.96 (m, 4H; *chiral*-**4d**), 7.07–7.59 (m, 18H; *chiral*-**4d** and 26H; *achiral*-**4d**), 7.65–7.73 (m, 4H; *achiral*-**4d**), 7.78–7.86 (m, 4H; *chiral*-**4d**), 7.92–7.99 ppm (m, 4H; *chiral*-**4d**); ^{13}C NMR ($CDCl_3$): δ = −4.2, −2.9, −1.7, −1.3, 14.0, 22.0, 22.5, 23.0, 25.6, 26.2, 27.9, 28.2, 29.4, 29.6, 30.2, 30.4, 31.3, 31.6, 33.7, 36.7, 69.6, 71.3, 127.2, 127.3, 127.46, 127.52, 127.7, 128.2, 128.4, 129.0, 129.4, 129.5, 129.7, 133.7, 133.9, 135.4, 136.0, 136.5, 137.4, 137.9, 140.6, 140.8 ppm; elemental analysis calcd (%) for $C_{60}H_{80}O_2Si_4$: C 76.21, H 8.53; found: C 75.96, H 8.70. See below for spectral data for diastereomerically pure *chiral*-**4d**.

Thermal ring contraction of 4d and subsequent Peterson elimination of 6d [Eq. (4)]: Compound **4d** (100 mg, 1.06×10^{-1} mmol) in toluene (0.4 mL) was heated under reflux for 1 h. The solvent was stripped off under vacuum, and the residual oil was dissolved in THF (0.5 mL). The reaction mixture was cooled (0 °C), *n*BuLi (212×10^{-3} mL, 1.50 M in hexane, 3.18×10^{-1} mmol) was added, and the mixture was stirred for 20 min. Addition of saturated NH_4Cl (aq.) to the mixture at 0 °C was followed by extraction with Et_2O and subsequent drying over $MgSO_4$. Silica gel column chromatography (hexane) gave (*E*)-**1d** (56 mg, 95 %).

IBS of enantioenriched (*R*)-(*E*)-3d giving *chiral*-4d [Eq. (7)]: Hexane (0.4 mL) and (*R*)-(*E*)-**3d** (99.7 % ee, 99 mg, 2.1×10^{-1} mmol) were added to a catalyst mixture prepared from [Pd(acac)$_2$] (1.3 mg, 4.2×10^{-3} mmol) and 1,1,3,3-tetramethylbutyl isocyanide (2.0 M in toluene, 8.5×10^{-3} mL, 17×10^{-3} mmol). The mixture was stirred for 1 h under reflux. After stripping the volatile materials off under vacuum, the residue was subjected to silica gel column chromatography (hexane/ether = 100:1) to give *chiral*-**4d** (95 mg, 96 %). ^{1}H NMR ($CDCl_3$): δ = −0.30 (s, 6H), −0.04 (s, 6H), 0.46–1.36 (m, 34H), 1.76 (d, J = 10.8 Hz, 2H), 4.55 (dq, J = 10.8, 6.0 Hz, 2H), 6.89–6.96 (m, 4H), 7.07–7.28 (m, 6H), 7.30–7.50 (m, 12H), 7.79–7.86 (m, 4H), 7.93–8.01 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): δ = −4.2, −1.7, 14.0, 22.0, 22.5, 25.5, 27.9, 29.4, 30.2, 31.3, 36.7, 71.3, 127.3, 127.5, 128.1, 129.4, 129.5, 133.6, 136.0, 136.5, 137.3, 137.8, 140.8 ppm; elemental analysis calcd (%) for $C_{60}H_{80}O_2Si_4$: C 76.21, H 8.53; found: C 76.00, H 8.77.

IBS of enantioenriched (*R*)-(*Z*)-3d giving *chiral*-ent-4d [Eq. (8)]: According to the same procedure as that for the preparation of *chiral*-**4d**, *chiral*-**ent-4d** (92 mg, 92 %; eluent for column chromatography: hexane/ether = 80:1) was synthesized from (*R*)-(*Z*)-**3d** (96.0 % *ee*, 100 mg, 2.1×10^{-1} mmol). ^{1}H NMR ($CDCl_3$): δ = −0.23 (s, 6H), −0.20 (s, 6H), 0.46–1.34 (m, 34H), 1.89 (d, J = 5.4 Hz, 2H), 4.38–4.64 (m, 2H), 6.93 (d, J = 6.6 Hz, 4H), 7.07–7.22 (m, 6H), 7.38–7.56 (m, 12H), 7.86 (d, J = 6.9 Hz, 4H), 7.96–8.03 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): δ = −4.3, −1.3, 13.9, 22.5, 24.1, 25.5, 28.8, 29.6, 31.4, 31.6, 39.1, 74.6, 127.3, 127.4, 127.5, 128.2, 129.4, 129.5, 133.6, 136.1, 137.1, 137.5, 138.6, 140.7 ppm; elemental analysis calcd (%) for $C_{60}H_{80}O_2Si_4$: C 76.21, H 8.53; found: C 75.92, H 8.65.

Step-by-step synthesis of (*S*)-1d from (*R*)-(*E*)-3d [Eq. (9)]: Toluene (0.4 mL) and disilanyl ether (*R*)-(*E*)-**3d** (99.7 % ee, 103 mg, 0.22 mmol) were added to the catalyst mixture of [Pd(acac)$_2$] (1.3 mg, 4.2×10^{-3} mmol) and 1,1,3,3-tetramethylbutyl isocyanide (8.4×10^{-3} mL, 1.7×10^{-2} mmol). The mixture was stirred for 3 h under reflux. After stripping the volatile materials off under vacuum, the residue was subjected to a short column of Florisil (hexane/ether = 4:1) to give a mixture of **1d** and **6d**. These were separated by HPLC (hexane/EtOAc = 10:1) to give **1d** (27 mg, 49 %) and **6d** (62 mg, 46 %). Enantiomeric excess of **1d** was determined to be 96.1 % *ee* (absolute configuration of *S*) after transformation to **7d** by diimide reduction (see below). Compound **6d** was dissolved in THF (0.5 mL) and treated with *n*BuLi (1.52 M in hexane, 0.20 mL, 0.30 mmol) at 0 °C for 15 min. Extractive workup followed by column chromatography on silica gel afforded **1d** (24 mg, 94 % based on **6d**). The *ee* was determined to be 99.1 % (absolute configuration of *S*) according to the same determination procedure as above.

General procedure for the one-pot synthesis of enantioenriched allylsilanes 1d–k (Table 2): Toluene (0.4 mL) and disilanyl ether **3d–k** (0.45 mmol) were added to the catalyst mixture of [Pd(acac)$_2$] (1.3 mg, 4.2×10^{-3} mmol) and 1,1,3,3-tetramethylbutyl isocyanide (2.9×10^{-3} mL, 1.7×10^{-2} mmol). The mixture was stirred for 1 h under reflux. After stripping the volatile materials off under vacuum, THF (0.5 mL) was added to the residue. *n*BuLi (1.37 M in hexane, 0.24 mL, 0.33 mmol) or

PhLi (for the reaction of (*Z*)-**3d** (entry 2 in Table 3), 1.0 M in cyclohexane, 0.33 mL, 0.33 mmol) was added to the solution cooled at 0 °C; the mixture was stirred for 15 min at 0 °C. Addition of aqueous NH_4Cl (saturated) to the mixture and extractive workup with ether followed by column chromatography on silica gel (hexane) afforded (*E*)-allylsilanes **1d–k**.

(*S*)-(*E*)-4-(Dimethylphenylsilyl)-2-decene ((*S*)-1d): *ee* > 99.1 %; $[\alpha]_D^{22}$ = +3.8 (c = 2.2, benzene); ^{1}H NMR ($CDCl_3$): δ = 0.25 (s, 3H), 0.27 (s, 3H), 0.87 (t, *J* = 6.4 Hz, 3H), 1.03–1.71 (m, 14H), 5.11–5.32 (m, 2H), 7.32–7.41 (m, 3H), 7.45–7.56 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = −5.1, −4.2, 14.1, 18.1, 22.7, 29.0, 29.1, 29.3, 31.8, 32.5, 123.0, 127.5, 128.7, 132.0, 134.1, 138.4 ppm; elemental analysis calcd (%) for $C_{18}H_{30}Si$: C 78.75, H 11.02; found: C 78.68, H 11.00.

(*S*)-(*E*)-4-(Trimethylsilyl)-2-decene ((*S*)-1e): *ee* > 99.0 %; $[\alpha]_D^{22}$ = +18.6 (c = 2.5, benzene); ^{1}H NMR ($CDCl_3$): δ = −0.06 (s, 9H), 0.88 (t, *J* = 6.4 Hz, 3H), 1.03–1.44 (m, 11H), 1.66 (d, *J* = 4.7 Hz, 3H), 5.09–5.32 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = −3.1, 14.1, 18.1, 22.7, 29.0, 29.3, 29.4, 31.9, 33.0, 122.2, 132.6 ppm; elemental analysis calcd (%) for $C_{13}H_{28}Si$: C 73.50, H 13.28; found: C 73.22, H 13.15.

(*S*)-(*E*)-4-(*tert*-Butyldimethylsilyl)-2-decene ((*S*)-1f): *ee* > 99.4 %; $[\alpha]_D^{22}$ = −3.2 (c = 2.6, benzene); ^{1}H NMR ($CDCl_3$): δ = −0.10 (s, 3H), −0.08 (s, 3H), 0.89 (s, 9H), 0.91 (t, *J* = 8.0 Hz, 3H), 1.03–1.62 (m, 11H), 1.65 (d, *J* = 4.6 Hz, 3H), 5.12–5.31 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = −7.1, −7.0, 14.1, 17.6, 18.0, 22.7, 27.3, 29.2, 29.3, 29.8, 31.2, 31.9, 122.4, 133.4 ppm; elemental analysis calcd (%) for $C_{16}H_{34}Si$: C 75.50, H 13.46; found: C 75.48, H 13.49.

(*S*)-(*E*)-4-(Triethylsilyl)-2-decene ((*S*)-1g): *ee* > 99.2 %; $[\alpha]_D^{22}$ = −2.4 (c = 2.7, benzene); ^{1}H NMR ($CDCl_3$): δ = 0.46–0.59 (m, 6H), 0.83–1.00 (m, 12H), 1.03–1.67 (m, 14H), 5.11–5.32 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 2.3, 7.6, 14.1, 18.1, 22.7, 29.2, 29.5, 30.3, 31.9, 121.9, 133.0 ppm; elemental analysis calcd (%) for $C_{16}H_{34}Si$: C 75.50, H 13.46; found: C 75.44, H 13.50.

(*S*)-(*E*)-4-(Triisopropylsilyl)-2-decene ((*S*)-1h): *ee* > 98.8 %; $[\alpha]_D^{22}$ = −16.3 (c = 2.4, benzene); ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 3H), 0.98–1.84 (m, 35H), 5.13–5.42 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 11.2, 14.1, 18.0, 19.1, 22.7, 29.2, 29.7, 29.8, 30.0, 31.9, 122.3, 133.6 ppm; elemental analysis calcd (%) for $C_{19}H_{40}Si$: C 76.94, H 13.59; found: C 76.67, H 13.74.

(*S*)-(*E*)-3-(Dimethylphenylsilyl)-1-phenyl-1-nonene ((*S*)-1i): *ee* > 98.7 %; $[\alpha]_D^{22}$ = +23.9 (c = 2.6, benzene); ^{1}H NMR ($CDCl_3$): δ = 0.32 (s, 3H), 0.33 (s, 3H), 0.86 (t, *J* = 6.6 Hz, 3H), 1.07–1.64 (m, 10H), 1.91 (dt, *J* = 9.2, 3.7 Hz, 1H), 6.03 (dd, *J* = 15.8, 9.2 Hz, 1H), 6.19 (d, *J* = 15.8 Hz, 1H), 7.12–7.58 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): δ = −4.9, −4.2, 14.0, 22.6, 29.1, 29.6, 31.7, 34.0, 125.6, 126.2, 127.9, 128.4, 129.0, 132.9, 134.1, 137.8, 138.5 ppm; elemental analysis calcd (%) for $C_{23}H_{32}Si$: C 82.07, H 9.58; found: C 81.90, H 9.65.

(*S*)-(*E*)-1-Cyclohexyl-3-(dimethylphenylsilyl)-1-nonene ((*S*)-1j): *ee* > 99.0 %; $[\alpha]_D^{22}$ = +4.8 (c = 2.7, benzene); ^{1}H NMR ($CDCl_3$): δ = 0.25 (s, 3H), 0.26 (s, 3H), 0.87 (t, *J* = 6.6 Hz, 3H), 0.93–1.48 (m, 15H), 1.55–1.78 (m, 6H), 1.83–2.01 (m, 1H), 5.04–5.25 (m, 2H), 7.30–7.38 (m, 3H), 7.44–7.53 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = −5.0, −4.3, 14.1, 22.6, 26.2, 26.3, 28.9, 29.0, 29.1, 31.8, 32.4, 33.6, 33.7, 41.1, 127.5, 128.3, 128.7, 134.1, 135.1, 138.5 ppm; elemental analysis calcd (%) for $C_{23}H_{38}Si$: C 80.62, H 11.18; found: C 80.47, H 11.19.

(*R*)-(*E*)-1-(Dimethylphenylsilyl)-1-phenyl-2-butene ((*R*)-1k): *ee* > 98.1 %; $[\alpha]_D^{22}$ = −13.7 (c = 2.4, benzene); ^{1}H NMR ($CDCl_3$): δ = 0.22 (s, 3H), 0.25 (s, 3H), 1.66 (dd, *J* = 6.3, 1.5 Hz, 3H), 3.06 (d, *J* = 9.8 Hz, 1H), 5.35 (ddq, *J* = 15.0, 6.3, 0.9 Hz, 1H), 5.75 (ddq, *J* = 15.0, 9.8, 1.5 Hz, 1H), 6.88–7.41 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): δ = −4.7, −4.3, 18.1, 42.4, 124.0, 124.5, 127.4, 128.1, 129.0, 129.9, 134.3, 137.1, 142.4 ppm; elemental analysis calcd (%) for $C_{18}H_{22}Si$: C 81.14, H 8.32; found: C 81.38, H 8.57.

Synthesis of 4-(dimethylphenylsilyl)-2-phenyl-2-decene (1l) [Eq. (6)]: A mixture of [Pd(acac)$_2$] (1.1 mg, 3.6×10^{-3} mmol) and 1,1,3,3-tetramethylbutyl isocyanide (7.3×10^{-3} mL, 1.5×10^{-2} mmol) was stirred for 10 min under nitrogen at room temperature. Toluene (0.4 mL) and disilanyl ether **3l** (94 mg, 0.17 mmol) were added to the catalyst mixture. The mixture was stirred for 5 h under reflux. After stripping the volatile materials off under vacuum, THF (0.5 mL) was added to the residue, followed by *t*BuOK (19 mg, 0.17 mmol) at room temperature. The mixture was stirred at room temperature for 6 h. Addition of aqueous NH_4Cl (saturated) to the mixture and extractive workup with ether followed by column chromatography on silica gel (hexane) afforded **1l** (51 mg, 85 %, *E*/*Z* = 92:8). The isomers were separated by HPLC (hexane). (*E*)-**1l**: ^{1}H NMR ($CDCl_3$): δ = 0.32 (s, 3H), 0.36 (s, 3H), 0.88 (t, *J* = 6.6 Hz, 3H), 1.09–1.69 (10H), 1.86 (d, *J* = 1.3 Hz, 3H), 2.14 (dt, *J* = 11.2, 3.0 Hz, 1H), 5.60 (dd, *J* = 11.2, 1.3 Hz, 1H), 7.18–7.44 (m, 8H), 7.50–7.60 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = −5.0, −4.3, 14.1, 16.2, 22.7, 29.1, 29.9, 30.1, 30.2, 31.8, 125.4, 126.0, 127.6, 128.1, 128.9, 130.9, 132.6, 134.0, 138.0, 144.5 ppm; elemental analysis calcd (%) for $C_{24}H_{34}Si$: C 82.22, H 9.77; found: C 82.34, H 9.93.

Single-crystal X-ray studies: Single crystals were mounted on glass fibers. Intensity data collections were carried out with a Mac Science MXC3 diffractometer using graphite-monochromated $Cu_{K\alpha}$ (λ = 1.54178 Å) radiation at 293 K. Intensity data were collected using w/2q scans and corrected for Lorentz-polarization and for absorption by an analytical function. Details of crystal and data collection parameters are shown in Table 4.

Table 4. Summary of crystallographic data.

	trans-**4a′**	**4d**	**ent-4d**
recryst. solvent	Et_2O/EtOH	CH_2Cl_2/MeOH	EtOH/MeOH
formula	$C_{50}H_{60}O_2Si_4$	$C_{60}H_{80}O_2Si_4$	$C_{60}H_{80}O_2Si_4$
crystal size [mm]	0.25×0.25×0.35	0.20×0.40×0.40	0.20×0.30×0.50
FW	805.40	945.60	945.60
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (no. 2)	*P*21 (no. 4)	*P*1 (no. 1)
a [Å]	10.120 (3)	19.730(4)	11.381(3)
b [Å]	13.925 (4)	11.524(3)	11.802(5)
c [Å]	17.787 (6)	13.380(3)	12.401(4)
α [°]	74.32 (3)		112.01(3)
β [°]	76.98 (3)	106.86(2)	104.22(2)
γ [°]	81.91 (3)		100.79(3)
V [Å^3]	2343 (1)	2911.330078(1)	1422.9(8)
Z	2	2	1
ρ_{calcd} [g cm^{-3}]	1.14	1.078	1.103
$2\theta_{max}$ [°]	130	125	125
μ [cm^{-1}]	14.530	12.279	12.562
independent refl.	7845	5012	4616
observed refl.	5662	4651	4260
no. of parameters	694	672	672
GOF	1.22	0.933	0.806
*R*1	0.0517	0.056	0.056
w*R*2	0.0531	0.071	0.072

Structure solutions and refinements were carried out with the program package CrystanG (Mac Science). All non-hydrogen atoms were refined anisotropically by full-matrix least squares. All hydrogen atoms were included in the refinement at the calculated positions (0.96 Å) with isotropic thermal parameters. CCDC-252165 (*trans*-**4a′**), CCDC-252164 (**4d**), and CCDC-252163 (ent-**4d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of highly enantioenriched (*R*)-1d from (*S*)-(*E*)-3d with lower enantiopurity (Scheme 5): Hexane (2 mL) and (*S*)-(*E*)-**3d** (79.2 % ee, 505 mg, 1.1 mmol) at room temperature were added to the catalyst mixture prepared from [Pd(acac)$_2$] (6.7 mg, 2.2×10^{-2} mmol) and 1,1,3,3-tetramethylbutyl isocyanide (15×10^{-3} mL, 8.6×10^{-2} mmol). The reaction mixture was stirred under reflux for 1 h. After evaporation of volatile materials, the resultant residual oil was passed through a short Florisil column

and purified by recrystallization (Et_2O/EtOH×2) to afford **4d** (294 mg, 58%). Compound **4d** (103 mg, 0.11 mmol) was dissolved in toluene (0.4 mL) and stirred under reflux for 1 h. After replacement of the solvent with THF (0.5 mL), *n*BuLi (240×10^{-3} mL, 1.37 M in hexane, 0.33 mmol) was added to the reaction mixture at 0°C. After stirring for 10 min at 0°C, saturated NH_4Cl (aq.) was added to the mixture at 0°C. Extractive workup with Et_2O followed by silica gel column chromatography (hexane) gave (*R*)-**1d** (99.4% *ee*, 57 mg, 96%).

General procedure for the determination of enantiomeric excesses: 9-BBN (242 mg, 2.0 mmol) was added to a solution of **1** (0.19 mmol) in THF (2 mL); the mixture was stirred at 50°C for 2 h. Aqueous NaOH (3 M, 0.34 mL) and 30% hydrogen peroxide (2.0 mL) were then added at 0°C. After stirring for 1 h at 50°C, excess hydrogen peroxide was quenched by aqueous sodium thiosulfate at room temperature. Extraction with ether followed by silica gel column chromatography afforded the corresponding silylalkanols.

(2*S*,4*S*)-4-(Dimethylphenylsilyl)decan-2-ol (8d): ^{1}H NMR ($CDCl_3$): δ = 0.26 (s, 3H), 0.27 (s, 3H), 0.78–0.94 (m, 4H), 1.06 (d, J = 6.0 Hz, 3H), 1.12–1.46 (m, 11H), 1.47 (dt, J = 2.1, 6.0 Hz, 2H), 3.70 (sextet, J = 6.0 Hz, 1H), 7.30–7.35 (m, 3H), 7.46–7.51 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = −4.3, −3.9, 14.0, 21.9, 22.6, 23.1, 29.1, 29.6, 30.5, 31.7, 40.0, 67.5, 127.8, 128.9, 133.9, 139.0 ppm; elemental analysis calcd (%) for $C_{18}H_{32}OSi$: C 73.90, H 11.03; found: C 73.63, H 10.95.

(2*S*,4*S*)-4-(Trimethylsilyl)decan-2-ol (8e): ^{1}H NMR ($CDCl_3$): δ = −0.04 (s, 9H), 0.52–0.60 (m, 1H), 0.85 (t, J = 6.3 Hz, 3H), 1.14 (d, J = 6.0 Hz, 3H), 1.22–1.52 (m, 12H), 3.83 ppm (sextet, J = 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = −2.4, 14.0, 22.3, 22.6, 23.2, 29.1, 29.8, 30.4, 31.7, 39.9, 67.7 ppm; HRMS (FAB) calcd for [MH^+-H_2O] (M: $C_{13}H_{30}OSi$): 213.2039; found 213.2036.

(2*S*,4*S*)-4-(*tert*-Butyldimethylsilyl)decan-2-ol (8f): ^{1}H NMR ($CDCl_3$): δ = 0.06 (s, 6H), 0.67–0.84 (m, 1H), 0.88 (t, J = 7.2 Hz, 3H), 0.90 (s, 9H), 1.18 (d, J = 9.0 Hz, 3H), 1.20–1.40 (m, 10H), 1.47–1.57 (m, 3H), 3.85 ppm (sextet, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = −6.5, −6.1, 14.1, 17.6, 20.0, 22.7, 23.0, 27.4, 29.3, 29.9, 30.9, 31.8, 40.5, 67.8 ppm; elemental analysis calcd (%) for $C_{16}H_{36}OSi$: C 70.51, H 13.31; found; C 70.66, H 13.59.

(2*S*,4*S*)-4-(Triethylsilyl)decan-2-ol (8g): ^{1}H NMR ($CDCl_3$): δ = 0.55 (q, J = 8.0 Hz, 6H), 0.63–0.80 (m, 1H), 0.88 (t, J = 6.7 Hz, 3H), 0.95 (t, J = 8.0 Hz, 9H), 1.17 (d, J = 6.6 Hz, 3H), 1.20–1.61 (m, 13H), 3.85 ppm (sextet, J = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 2.7, 7.7, 14.1, 19.6, 22.7, 23.1, 29.8, 29.9, 30.7, 31.8, 40.4, 67.8 ppm; HRMS (FAB) calcd for [MH^+-H_2O] (M: $C_{16}H_{36}OSi$): 255.2508; found 255.2506.

(2*S*,4*S*)-4-(Triisopropylsilyl)decan-2-ol (8h): ^{1}H NMR ($CDCl_3$): δ = 0.80–1.65 (m, 17H), 0.88 (t, J = 8.0 Hz, 3H), 1.09 (s, 18H), 1.20 (d, J = 6.1 Hz, 3H), 3.81–4.01 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 11.3, 14.1, 19.2, 19.3, 19.6, 22.7, 30.1, 31.77, 31.80, 32.0, 42.2, 68.2 ppm; HRMS (FAB) calcd for [MH^+-H_2O] (M: $C_{19}H_{42}OSi$): 297.2978; found 297.2974.

(1*R*,3*S*)-3-(Dimethylphenylsilyl)-1-phenylnonan-1-ol (8i): ^{1}H NMR ($CDCl_3$): δ = 0.24 (s, 3H), 0.25 (s, 3H), 0.78–0.91 (m, 4H), 1.14–1.39 (m, 9H), 1.44–1.56 (m, 1H), 1.64 (d, J = 3.0 Hz, 1H), 1.79 (t, J = 6.6 Hz, 2H), 4.55 (dt, J = 3.0, 6.6 Hz, 1H), 7.14–7.19 (m, 2H), 7.22–7.39 (m, 6H), 7.40–7.46 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = −4.6, −3.7, 14.0, 21.5, 22.6, 29.0, 29.7, 30.4, 31.7, 39.3, 74.0, 126.2, 127.6, 127.8, 128.4, 128.9, 133.9, 139.0, 144.6 ppm; elemental analysis calcd (%) for $C_{23}H_{34}OSi$: C 77.90, H 9.66; found C 78.09, H 9.86.

(1*R*,3*S*)-1-Cyclohexyl-3-(dimethylphenylsilyl)nonan-1-ol (8j): ^{1}H NMR ($CDCl_3$): δ = 0.28 (s, 3H), 0.29 (s, 3H), 0.73–1.77 (m, 25H), 0.86 (t, J = 8.0 Hz, 3H), 3.14–3.28 (m, 1H), 7.30–7.37 (m, 3H), 7.46–7.54 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = −4.3, −3.7, 14.0, 21.9, 22.6, 26.1, 26.4, 26.5, 26.8, 29.0, 29.46, 29.54, 30.8, 31.7, 34.6, 43.2, 75.3, 127.8, 128.9, 133.9, 139.4 ppm; elemental analysis calcd (%) for $C_{23}H_{40}OSi$: C 76.60, H 11.18; found: C 76.33, H 11.20.

(1*S*,3*R*)-4-(Dimethylphenylsilyl)-4-phenylbutan-2-ol (8k): ^{1}H NMR ($CDCl_3$): δ = 0.16 (s, 3H), 0.24 (s, 3H), 1.04 (d, J = 6.0 Hz, 3H), 1.68 (ddd, J = 13.8, 7.8, 3.3 Hz, 1H), 2.10 (dt, J = 7.8, 13.8 Hz, 1H), 2.25 (dd, J = 13.8, 3.3 Hz, 1H), 3.62 (tq, J = 6.0, 7.8 Hz, 1H), 6.94 (d, J = 7.5 Hz, 2H), 7.07 (tt, J = 7.5, 1.5 Hz, 1H), 7.18 (t, J = 7.5 Hz, 2H), 7.27–7.39 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ = −5.6, −4.2, 22.2, 33.8, 67.9, 124.8, 127.7, 127.8, 128.3, 129.2, 134.2, 137.2, 142.3 ppm; HRMS (FAB) calcd for [MH^+-H_2O] (M: $C_{18}H_{24}OSi$): 267.1569; found 267.1567.

Attempted transformations for *ee* determination: *Pd/C catalyzed hydrogenation followed by Tamao oxidation*: Allylsilane **1d** (26 mg, 0.096 mmol) was added to a suspension of Pd/C (5%, 24 mg) in AcOEt (0.6 mL) at room temperature under H_2. The mixture was stirred at room temperature for 1 h. The palladium catalyst was filtered off through Celite. Evaporation of the solvent left almost pure hydrogenation products. The flask containing the crude material was filled with nitrogen. To this was added trifluoroacetic acid (0.5 mL) at room temperature; the mixture was stirred at 50°C for 1 h. The acid was stripped off under vacuum and MeOH (0.2 mL), KHF_2 (30 mg, 0.38 mmol), TBAF (1 M in THF, 0.20 mL), 30% hydrogen peroxide (0.12 mL), and $KHCO_3$ (81 mg, 0.81 mmol) were added to the residue. The mixture was stirred at 50°C for 30 min and then treated with aqueous sodium thiosulfate. Extraction with ether followed by silica gel column chromatography (hexane/ether = 3:1) and subsequent purification with HPLC (hexane/ether = 8:1) afforded (*S*)-decan-4-ol (11 mg, 74%).

Diimide reduction followed by Tamao oxidation: A mixture of allylsilane **1** (0.036 mmol), tosyl hydrazide (67 mg, 0.36 mmol), and triethylamine (0.05 mL, 0.36 mmol) in 1,4-dioxane (0.4 mL) was heated for 8 h under reflux. The cooled mixture was subjected to preparative TLC to give a hydrogenated product in high yield. The crude material was subjected to hydrogen peroxide oxidation by the same procedure as for Pd/C hydrogenation. Enantiomeric excesses of the obtained alcohols were determined by chiral HPLC.

Reaction with mCPBA: A solution of mCPBA (80%, 69 mg, 0.32 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise to a mixture of (*S*)-**1d** (80 mg, 0.29 mmol) and $NaHCO_3$ (24 mg, 0.29 mmol) in CH_2Cl_2 (1.0 mL) at −78°C. The mixture was stirred at 0°C for 1 h. After evaporation of the solvent, MeOH (1.2 mL) and acetic acid (0.2 mL) were added to the mixture at room temperature. After the mixture had been stirred for 20 min at room temperature, organic material was extracted with diethyl ether and washed with aqueous NaOH (5 M, three times) and water. The organic phase was dried over $MgSO_4$. After evaporation, the residual oil was subjected to silica gel column chromatography (hexane/diethyl ether = 1:1) to give an 86:14 mixture of (*S*)-(*E*)-3-decen-2-ol and (*R*)-(*Z*)-3-decen-2-ol (23 mg, 50%).

Acknowledgment

This work was supported by Grant-in-Aids from the Ministry of Education, Science, Sports and Culture, Japan. T. I. acknowledges fellowship support of the Japan Society for the Promotion of Science for Japanese Young Scientists.

[1] A. Hosomi, H. Sakurai, *Tetrahedron Lett.* **1978**, *19*, 2589. Reviews: I. Fleming, J. Dunogues, R. Smithers, *Org. React.* **1989**, *37*, 57; J. S. Panek in *Comprehensive Organic Synthesis*, *Vol. 1* (Ed.: B. M. Trost), Pergamon, Oxford, **1991**, p. 579.

[2] [3+2] cycloadditions: a) H.-J. Knölker, P. G. Jones, J.-B. Pannek, *Synlett* **1990**, 429; b) H.-J. Knölker, R. Graf, *Synlett* **1994**, 131; c) J. S. Panek, N. F. Jain, *J. Org. Chem.* **1993**, *58*, 2345; d) J. S. Panek, R. Beresis, *J. Org. Chem.* **1993**, *58*, 809; [2+2] cycloadditions: e) G. P. Brengel, C. Rithner, A. I. Meyers, *J. Org. Chem.* **1994**, *59*, 5144; f) T. Akiyama, M. Kirino, *Chem. Lett.* **1995**, 723. For the closely related cycloaddition with allenylsilanes, see: g) R. L. Danheiser, D. J. Carini, *J. Org. Chem.* **1980**, *45*, 3927.

[3] a) S. H. Yeon, B. W. Lee, B. R. Yoo, M.-Y. Suk, I. N. Jung, *Organometallics* **1995**, *14*, 2361; b) E. Yoshikawa, V. Gevorgyan, N. Asao, Y. Yamamoto, *J. Am. Chem. Soc.* **1997**, *119*, 6781; c) M. Yamaguchi, T. Sotokawa, M. Hirama, *Chem. Commun.* **1997**, 743; d) K. Imamura, E. Yoshikawa, V. Gevorgyan, Y. Yamamoto, *J. Am. Chem. Soc.* **1998**, *120*, 5339.

[4] W. R. Roush in *Comprehensive Organic Synthesis*, *Vol. 2* (Ed.: B. M. Trost), Pergamon, Oxford, **1991**, p. 1.
[5] T. K. Sarkar, *Synthesis* **1990**, 969 and 1101; T. K. Sarkar, *Sci. Synth.* **2002**, *4*, 837.
[6] T. Hayashi, M. Konishi, M. Kumada, *J. Am. Chem. Soc.* **1982**, *104*, 4963; T. Hayashi, M. Konishi, M. Kumada, *J. Org. Chem.* **1983**, *48*, 281.
[7] C. E. Masse, J. S. Panek, *Chem. Rev.* **1995**, *95*, 1293.
[8] Asymmetric cross-coupling of α-(silyl)alkyl Grignard reagents to alkenyl bromides in the presence of chiral ferrocenylphosphine–palladium complexes: a) T. Hayashi, M. Konishi, H. Ito, M. Kumada, *J. Am. Chem. Soc.* **1982**, *104*, 4962; b) T. Hayashi, M. Konishi, Y. Okamoto, K. Kabeta, M. Kumada, *J. Org. Chem.* **1986**, *51*, 3772.
[9] Wittig olefination of enantioenriched α-silylaldehydes: V. Bhushan, B. B. Lohray, D. Enders, *Tetrahedron Lett.* **1993**, *34*, 5067.
[10] Regioselective nucleophilic substitution of enantioenriched allylic esters and carbamates with (organosilyl)cuprates: a) I. Fleming, A. P. Thomas, *J. Chem. Soc. Chem. Commun.* **1986**, 1456; b) I. Fleming, D. Higgins, N. J. Lawrence, A. P. Thomas, *J. Chem. Soc. Perkin Trans. 1* **1992**, 3331.
[11] Claisen rearrangement of enantioenriched allylic alcohols: a) K. Mikami, T. Maeda, N. Kishi, T. Nakai, *Tetrahedron Lett.* **1984**, *25*, 5151; b) M. A. Sparks, J. S. Panek, *J. Org. Chem.* **1991**, *56*, 3431.
[12] Asymmetric hydrosilation of 1,3-dienes: a) T. Hayashi, S. Hengrasmee, Y. Matsumoto, *Chem. Lett.* **1990**, 1377; b) T. Hayashi, Y. Matsumoto, I. Morikawa, Y. Ito, *Tetrahedron: Asymmetry* **1990**, *1*, 151, and references therein.
[13] Asymmetric reduction of allyl carbonates: T. Hayashi, H. Iwamura, Y. Uozumi, *Tetrahedron Lett.* **1994**, *35*, 4813.
[14] Asymmetric silylation of allyl chlorides: T. Hayashi, A. Ohno, S.-j. Lu, Y. Matsumoto, E. Fukuyo, K. Yanagi, *J. Am. Chem. Soc.* **1994**, *116*, 4221.
[15] Other preparation of enantioenriched allylsilanes: M. J. C. Buckle, I. Fleming, S. Gil, *Tetrahedron Lett.* **1992**, *33*, 4479.
[16] a) M. Suginome, Y. Ito, *J. Chem. Soc. Dalton Trans.* **1998**, 1925; b) M. Suginome, Y. Ito, *J. Synth. Org. Chem. Jpn.* **1997**, *55*, 1041; c) Y. Ito, M. Suginome, M. Murakami, *J. Org. Chem.* **1991**, *56*, 1948; d) M. Murakami, H. Oike, M. Sugawara, M. Suginome, Y. Ito, *Tetrahedron* **1993**, *49*, 3933; e) M. Murakami, M. Suginome, K. Fujimoto, Y. Ito, *Angew. Chem.* **1993**, *105*, 1542; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1473; f) M. Suginome, A. Matsumoto, Y. Ito, *J. Org. Chem.* **1996**, *61*, 4884; g) M. Suginome, A. Takama, Y. Ito, *J. Am. Chem. Soc.* **1998**, *120*, 1930.
[17] T. K. Sarkar, S. A. Haque, A. Basak, *Angew. Chem.* **2004**, *116*, 1441; *Angew. Chem. Int. Ed.* **2004**, *43*, 1417.
[18] a) M. Murakami, P. G. Andersson, M. Suginome, Y. Ito, *J. Am. Chem. Soc.* **1991**, *113*, 3987; b) M. Murakami, M. Suginome, K. Fujimoto, H. Nakamura, P. G. Andersson, Y. Ito, *J. Am. Chem. Soc.* **1993**, *115*, 6487; c) M. Suginome, Y. Yamamoto, K. Fujii, Y. Ito, *J. Am. Chem. Soc.* **1995**, *117*, 9608; d) M. Suginome, A. Matsumoto, K. Nagata, Y. Ito, *J. Organomet. Chem.* **1995**, *499*, C1; e) M. Suginome, S. Matsunaga, T. Iwanami, A. Matsumoto, Y. Ito, *Tetrahedron Lett.* **1996**, *37*, 8887; f) M. Suginome, H. Nakamura, Y. Ito, *Tetrahedron Lett.* **1997**, *38*, 555.
[19] See ref. [18b] for some attempts at IBS of allylic alcohols with terminal C=C bonds.
[20] D. J. Peterson, *J. Org. Chem.* **1968**, *33*, 780.
[21] For preliminary reports of this article, see: M. Suginome, A. Matsumoto, Y. Ito, *J. Am. Chem. Soc.* **1996**, *118*, 3061; M. Suginome, T. Iwanami, A. Matsumoto, Y. Ito, *Tetrahedron: Asymmetry* **1997**, *8*, 859.
[22] The requisite chlorodisilanes were readily prepared by the reaction of (diethylamino)diphenylsilyllithium with the corresponding tri(organo)chlorosilanes followed by treatment with acetyl chloride. a) K. Tamao, A. Kawachi, Y. Ito, *J. Am. Chem. Soc.* **1992**, *114*, 3989–3990; b) K. Tamao, A. Kawachi, Y. Nakagawa, Y. Ito, *J. Organomet. Chem.* **1994**, *473*, 29–34; Review: c) K. Tamao, A. Kawachi, *Adv. Organomet. Chem.* **1995**, *38*, 1–58.
[23] One isomer, *chiral*-**4d**, possesses a C_2 axis passing through the center of the eight-membered ring, while *achiral*-**4d** has an inversion center at the center of the ring.
[24] The *ee* determination was carried out according to the procedure that includes reduction of the C=C bond with diimide followed by oxidation of the Si–C bond as described below.
[25] For discussion of the mechanism of the Peterson elimination, see: a) T. Kawashima, N. Iwama, R. Okazaki, *J. Am. Chem. Soc.* **1992**, *114*, 7598; b) K. Naganuma, T. Kawashima, R. Okazaki, *Chem. Lett.* **1999**, 1139, and references therein.
[26] a) J. P. Vigneron, M. Dhaenens, A. Horeau, *Tetrahedron* **1973**, *29*, 1055; b) V. Rautenstrauch, *Bull. Soc. Chim. Fr.* **1994**, *131*, 515.
[27] In reality, the dimerization took place with slight preference for the achiral dimer as shown in Scheme 3.
[28] a) K. Tamao, T. Kakui, M. Akita, T. Iwahara, R. Kanatani, J. Yoshida, M. Kumada, *Tetrahedron* **1983**, *39*, 983; b) K. Tamao, N. Ishida, T. Tanaka, M. Kumada, *Organometallics* **1983**, *2*, 1694. Review: c) K. Tamao, *Adv. Silicon Chem.* **1996**, *3*, 1–62.
[29] a) I. Fleming, N. K. Terrett, *Tetrahedron Lett.* **1983**, *24*, 4153; b) T. Hayashi, Y. Okamoto, K. Kabeta, T. Hagihara, M. Kumada, *J. Org. Chem.* **1984**, *49*, 4224.
[30] I. Fleming, N. J. Lawrence, *J. Chem. Soc. Perkin Trans. 1* **1992**, 3309.
[31] M. Suginome, T. Iwanami, Y. Ito, *J. Org. Chem.* **1998**, *63*, 6096. M. Suginome, T. Iwanami, Y. Ito, *Chem. Commun.* **1999**, 2537; M. Suginome, T. Iwanami, A. Yamamoto, Y. Ito, *Synlett* **2001**, 1042; M. Suginome, Y. Ito, *J. Organomet. Chem.* **2003**, *685*, 218.
[32] M. Suginome, T. Iwanami, Y. Ito, *J. Am. Chem. Soc.* **2001**, *123*, 4356.
[33] F. Sato, H. Ishikawa, H. Watanabe, T. Miyake, M. Sato, *J. Chem. Soc. Chem. Commun.* **1981**, 718.
[34] V. S. Martin, S. S. Woodard, T. Katsuki, Y. Yamada, M. Ikeda, K. B. Sharpless, *J. Am. Chem. Soc.* **1981**, *103*, 6237; Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune, K. B. Sharpless, *J. Am. Chem. Soc.* **1987**, *109*, 5765.

Received: October 12, 2004
Published online: March 3, 2005

