JOC Article

Stereoselective Synthesis of Optically Active Disilanes and Selective Functionalization by the Cleavage of Silicon−Naphthyl Bonds with Bromine

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Optically active disilanes with one chiral silicon center, (*R*)-1,2-dimethyl-1-(naphth-1-yl)-1,2,2-triphenyldisilane and (*R*)-1,2,2-trimethyl-2-(4-methoxynaphth-1-yl)-1-(naphth-1-yl)-1-phenyldisilane, were obtained by the reaction of (*S*)-methyl(naphth-1-yl)phenylchlorosilane (>99% ee) with methyldiphenylsilyllithium or by the reaction of methyldiphenylchlorosilane with optically active (*S*)-methyl(naphth-1-yl)phenylsilyllithium and by the reaction of (*S*)-methyl(naphth-1-yl)phenylchlorosilane (>99% ee) with dimethyl(4-methoxynaphth-1-yl)silyllithium. Under the optimized conditions, the reactions proceeded with almost complete inversion for the cholorosilanes and retention for the silyl anions. Optically active disilanes with two chiral centers, (1*R*,2*R*)-1,2-dimethyl-1,2-di(naphth-1-yl)-1,2-diphenyldisilane and (1*S*,2*S*)-1,2-di(4-methoxynaphth-1-yl)-1,2-dimethyl-1,2-diphenyldisilane, were obtained in high optical purity by the reactions of corresponding optically active halogenosilanes (Cl or F) with optically active silyllithiums. The silicon−silicon bond and the silicon−naphthyl bond of (*R*)-1,1,2-trimethyl-1,2-di(naphth-1-yl)-2-phenyldisilane and (1*R*,2*R*)-1,2-dimethyl-1,2-di(naphth-1-yl)-1,2-diphenyldisilane were cleaved without selectivity on bromination. The silicon−(4-methoxynaphth-1-yl) bond of (*R*)-1,2,2-trimethyl-2-(4-methoxynaphth-1-yl)-1-(naphth-1-yl)-1-phenyldisilane was regiospecifically cleaved, followed by the stereoselective cleavage of the remaining chiral silicon−naphthyl bond (94% inversion). Although the silicon−(4-methoxynaphth-1-yl) bonds of (1*S*,2*S*)-1,2-di(4-methoxynaphth-1-yl)-1,2-dimethyl-1,2-diphenyldisilane (>99% ee) were regioselectively cleaved without silicon−silicon bond scission, remarkable racemization could not be avoided during the one-pot reaction.

Introduction

Functionalized disilanes[1] are useful precursors to polymers composed of the regular alternating arrangement of a disilanylene and a π-electron system (poly(disilanylene-π-conjugated systems))[2] and also linear silicon−silicon catenative structures (oligo-[3] and polysilanes[4] including dendrimers[5]), which are of considerable interest because of their unique electrooptical properties due to the $\sigma-\sigma$ conjugation and σ conjugation along the polymer chain. The electronic structure of these polymers is easily changed by the change of $\sigma-\pi$ and σ conjugation caused by the conformational change of the mobile backbone and reflects in the thermochromism[6] and related phenomena. Thus, control of conformation of these polymers is of particular interest to develop many important applications of the polymers, which is one of the most challenging tasks.

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(1) (a) Tamao, K.; Kawachi, A.; Ito, Y. *Organometallics* **1993**, *12*, 580. (b) Tamao, K.; Kawachi, A.; Nakagawa, Y.; Ito, Y. *J. Organomet. Chem*. **1994**, *473*, 29. (c) Ackerhans, C.; Böttcher, P.; Müller, P.; Roesky, H. W.; Uson, I.; Schmidt, H.-G.; Noltemeyer, M. *Inorg. Chem*. **2001**, *40*, 3766. (c) Herzog, U.; Rheinwald, G. *J. Organomet. Chem*. **2002**, *648*, 220. (d) Wrackmeyer, B.; Milius, W.; Badshah, A. *J. Organomet. Chem*. **2003**, *656*, 97.

(2) (a) Ishikawa, M.; Matsusaki, K.; Naka, T.; Yokono, H. *J. Polym. Sci. Polym. Lett. Ed*. **1984**, *22*, 669. (b) Ohshita, J.; Matsuguchi A.; Furumori, K.; Hong, R.; Ishikawa, M.; Yamanaka, T.; Koike, T.; Shioya, J. *Macromolecules* **1992**, *25*, 2134. (c) Ishiwaka, M.; Sakamaoto, M.; Ishii, J.; Ohshita, J. *J. Polym. Sci. A: Polym. Chem*. **1993**, *31*, 3281. (d) Ohshita, J. Kanaya, D.; Watanabe, T.; Ishikawa, M. *J. Organomet. Chem*. **1995**, *489*, 165. (e) Fang, M.; Watanabe, A.; Matsuda, M. *Macromolecules* **1996**, *29*, 6807. (f) Ohshita, J.; Yamashita, A.; Hiraoka, T.; Shinpo, H.; Kunai, A.; Ishikawa, M. *Macromolecules* **1997**, *30*, 1540. (g) Maxka, J.; Teramae, H. *Macromolecules* **1999**, *32*, 7045. (h) Matsumi, N.; Umeyama, T.; Chujo, Y. *Macromolecules* **2001**, *34*, 3510. (i) Naka, K.; Uemura, T.; Chujo, Y. *J. Am. Chem. Soc*. **2001**, *123*, 6209. (j) Kawakami, Y.; Omote, M.; Imae, I.; Shirakawa, E. *Macromolecules* **2003**, *36*, 7461.

(3) (a) Plitt, H. S.; Michl, J. *Chem. Phy. Lett*. **1992**, *198*, 400. (b) Stüger, H. *J. Organomet. Chem*. **1993**, *458*. 1. (c) Yatabe, T.; Shimomura, M.; Kaito, A. *Chem. Lett*. **1996**, 551. (d) Obata, K.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 11345. (e) Yatabe, T.; Kaito, A.; Tanabe, Y. *Chem. Lett*. **1997**, 799. (f) Obata, K.; Kira, M. *Macromolecules* **1998**, *31*, 4666. (g) Fogarty, H. A.; Ottosson, C.; Michl, J. *J. Organomet. Chem*. **2000**, *556*, 105. (h) Tamao, K.; Tsuji, H.; Terada, M.; Asahara, M.; Yamaguchi, S.; Toshimitsu, A. *Angew. Chem., Int. Ed*. **2000**, *39*, 3287. (i) Tsuji, H.; Michl, J.; Tamao, K. *J. Organomet. Chem*. **2003**, *685*, 9. (j) Tsuji, H.; Terada, M.; Toshimitsu, A.; Tamao, K. *J. Am. Chem. Soc*. **2003**, *125*, 7486.

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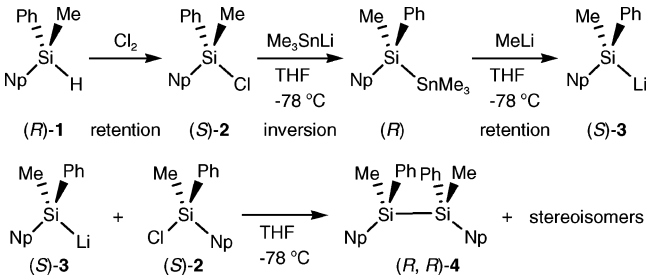
The conformation of a polymer is principally controlled by its stereoregularity and optical activity. Optically active functionalized disilanes with one chiral center or two chiral centers with C_2 symmetry will act as key intermediates to synthesize stereoregular and/or optically active silicon−silicon bond-containing polymers, as reported in the case of polysiloxane,[7] and the resulting polymers are expected to exhibit novel unique properties different from those without controlled stereoregularity. To realize such systems, it is essential to develop a selective functionalization of the optically active disilanes without cleavage of the silicon−silicon bond.

Silyllithiums[8] are useful reagents for the formation of silicon−silicon bonds. Although a great number of stereochemical studies have been carried out on substitution reactions at the chiral silicon center of optically active halogenosilanes with carbanions (alkyl- and aryllithium),[9] stereochemistry with silyl anions has received only little attention, probably because of the limitation of synthetically versatile methods to obtain optically active organosilylmetals.[10] Recently, we reported a successful preparation of configurationally stable naphthyl-substituted optically active silyllithium,[11] which is a powerful starting material to introduce a chiral silicon center to silicon−silicon bonds, and the spectral feature of optically active naphthyl-substituted disilanes having one or two chiral centers thus obtained was described.[12] We also reported the synthesis of both optically pure stereoisomers of chiral disilanes with one chiral center from a single antipode of the fluorosilane enantiomer as the starting material.[13]

SCHEME 1



In this article, we report an unambiguous determination of the absolute configuration of the products formed upon reaction of achiral chlorosilane with optically active silyllithium, or of optically active chlorosilane with achiral silyllithium by using X-ray analysis. We also report the synthesis of optically active functionalized disilanes and regio- and stereoselective functionalization of optically active disilanes by bromination.

Results and Discussion

We reported the synthesis and configurational stability of optically active methyl(naphth-1-yl)phenylsilyllithium **3** in THF at −78 °C prepared by tin−lithium exchange reaction of optically active methyl(naphth-1-yl)phenylsilylstannane derived from (*S*)-methyl(naphth-1-yl)phenylchlorosilane, (*S*)-**2** (<99% ee),[14] with methyllithium in THF at −78 °C.[11]

The absolute configuration of **3** was determined to be the (*S*)-form by the X-ray crystallographic analysis of the product (*R*,*R*)-1,2-dimethyl-1,2-di(naphth-1-yl)-1,2-diphenyldisilane (*R*,*R*)-**4**,[12(b)] obtained by the reaction of **3** with (*S*)-**2** assuming inversion and retention stereochemistry of chiral silicon centers of the chlorosilane (*S*)-**2** and silyllithium (*S*)-**3** in the formation of Si−Sn and Si−Si bonds, respectively, and retention of the chiral silicon center in the cleavage of the Si−Sn bond (Scheme 1). Although these seem reasonable assumptions,[10a] some contamination of stereoisomers of **4** formed in the synthesis of (*S*)-**3** and present in the reaction system made the conclusion a little obscure.

To exclude such uncertainty, the stereochemistry of the reaction of (*S*)-**2** (>99% ee) with an achiral methyldiphenylsilyllithium (product is **5a**) and that of an achiral methyldiphenylchlorosilane with optically active silyllithium **3** (90% ee) (product is **5b**) were investigated (Scheme 2).

Compound **5** was characterized as 1,2-dimethyl-1-(naphth-1-yl)-1,2,2-triphenyldisilane, and the configuration of **5a** and **5b** was proven to be the same by HPLC on an optically active stationary phase. The absolute configuration was determined as the (*R*)-form by X-ray analysis (see Figure 1 in Supporting Information).

The enantiomeric excess (ee) of **5a** is 99% and that of **5b** is 90% by HPLC, respectively. This clearly indicates the complete inversion of the chlorosilane and retention of the silyllithium at chiral silicon centers in the substi-

(4) For reviews, see: (a) Miller, R. D.; Michl, J. *Chem. Rev*. **1989**, *89*, 1359. (b) Jones, R. G.; Ando, W.; Chojnowski, J. *Silicon-Containing Polymers*; Kluwer Academic Publishers: Norwell, MA, 2000; Section 3. (c) Michl, J.; West, R. *Acc. Chem. Res*. **2000**, *33*, 821. (d) Fujiki, M. *Macromol. Rapid Commun*. **2001**, *22*, 539. (e) Fujiki, M.; Koe, J. R.; Terao, K.; Sato, T.; Teramoto, A.; Watanabe, J. *Polym. J*. **2003**, *35*, 297.

(5) (a) Lambert, J. B.; Pflug, J. L.; Stern, C. L. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 98. (b) Suzuki, H.; Kimata, Y.; Satoh, S.; Kuriyama, A. *Chem. Lett*. **1995**, *293*. (c) Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc*. **1995**, *117*, 4195.

(6) Bukalov, S. S.; Leites, L. A.; West, R. *Macromolecules* **2001**, *34*, 6003 and references therein.

(7) (a) Oishi, M.; Kawakami, Y. *Macromolecules* **2000**, *33*, 1960. (b) Oishi, M.; Moon, J.-Y.; Janvikul, W.; Kawakami, Y. *Polym. Int*. **2001**, *50*, 135.

(8) For recent reviews on silyl anion, see: (a) Kawachi, A.; Tamao, K. *Adv. Orgnomet. Chem*. **1995**, *38*, 1. (b) Lickiss, P. D.; Smith, C. M. *Coord. Chem. Rev*. **1995**, *145*, 75. (c) Sekiguchi, A.; Lee, V. Y.; Nanjo, M. *Coord. Chem. Rev*. **2000**, *210*, 11. (d) Belzner, J.; Dehnert, U. In *The Chemistry of Organic Silicon Compounds*; Apeloig, Y., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1998; Vol. 2, Chapter 14, p 779.

(9) For the excellent reviews on reaction mechanism of the nucleophilic substitution reaction at silicon, see: (a) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. Dynamic Stereochemistry at Silicon. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds., Wiley: Chichester, U.K., 1989; Vol. 1, Chapter 4, p 305. (b) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000; Part 1, p 115. (c) Sommer, L. H. In *Stereochemistry, Mechanism and Silicon*; McGraw-Hill: New York, 1965.

(10) (a) Sommer, L. H.; Mason, R. *J. Am. Chem. Soc*. **1965**, *87*, 1619. (b) Colomer, E.; Corriu, R. J. P. *J. Chem. Soc., Chem. Commun*. **1976**, 176. (c) Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem*. **1977**, *133*. 159. (d) Stromann, C.; Hörnig, J.; Auer, D. *Chem. Commun*. **2002**, 766.

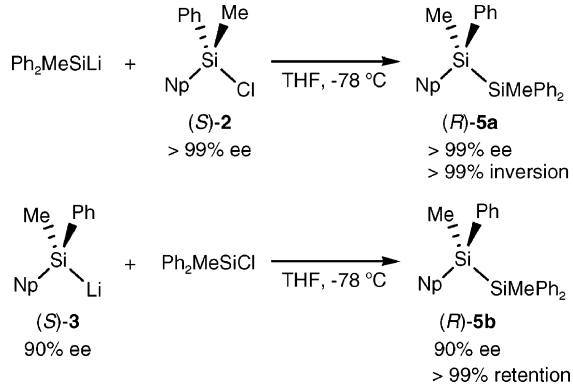
(11) Omote, M.; Tokita, T.; Shimizu, Y.; Imae, I.; Shirakawa, E.; Kawakami, Y. *J. Organomet. Chem*. **2000**, *611*, 20.

(12) (a) Oh, H. S.; Imae, I.; Kawakami, Y. *Chirality* **2003**, *15*, 231. (b) Oh, H. S.; Imae, I.; Kawakami, Y.; Raj, S. S.; Tamane, T. *J. Organomet. Chem*. **2003**, *685*, 35.

(13) Suzuki, K.; Kawakami, Y. *Organometallics* **2003**, *22*, 2367.

(14) (a) Sommer. L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc*. **1964**, *20*, 3271. (b) Sommer, L. H. *Angew. Chem., Int. Ed. Engl*. **1962**, *1*, 143. (c) Ashida, T.; Pepinsky, R.; Okaya, Y. *Acta Crystallogr*. **1963**, *16*, A48. (d) Okaya, Y. Ashida, T. *Acta Crystallogr*. **1996**, *20*, 461.

SCHEME 2



tution reactions, the same as the inversion stereochemistry of chlorosilane by alkyllithium.[9c]

To use thus produced optically active disilanes as starting materials for further synthesis of stereoregular polymers containing a disilane constitutional unit, stereoselective functionalization of the disilane is needed. One of the typical ways to functionalize oraganosilicon compounds is to introduce Br, Cl, and CF_3SO_3 (TfO) by the electrophilic cleavage reaction of the silicon−aromatic bonds. Unfortunately, when optically active (*R*)-1,2,2-trimethyl-1,2-di(naphth-1-yl)-1-phenyldisilane or (1*R*,2*R*)-1,2-dimethyl-1,2-di(naphth-1-yl)-1,2-diphenyldisilane (1*R*,2*R*)-**4** was treated with bromine, indiscriminate cleavage of silicon−naphthyl and silicon−silicon bonds[15] occurred. This result is similar to that by Sommer.[16] Selectivity of the cleavage of the silicon−naphthyl bond over the silicon−silicon bond must be given. Cleavage by TfOH gave completely racemized products at room temperature.

Kumada[17] and Stolberg[18] reported that the cleavage of a silicon−silicon bond having an electron-withdrawing substituent by halogen was remarkably slow. If we could selectively cleave the silicon−naphthyl bond by bromine by enhancing the reactivity of the silicon−naphthyl bond, we should be able to suppress the following cleavage of the silicon−silicon bond by the effect of the introduced bromo group on the silicon atom. Meanwhile, we reported that stereoselectivity (92% inversion, 84.5% optical purity of the product)[19] of the cleavage of the silicon−naphthyl bond of (*R*)-(+)-[(+)-menthoxy]methyl(naphth-1-yl)-phenylsilane by bromine in $CHCl_3$ at −64 °C can be improved (96% inversion, 91.3% optical purity of the product)[20] by the introduction of methoxy group at 4-position of naphthyl group.

To synthesize optically active disilane with one chiral center, a methoxy group was introduced into dimethyl-(naphth-1-yl)chlorosilane or dimethyl(naphth-1-yl)silyl-lithium. Reaction of dimethyl(4-methoxynaphth-1-yl)-chlorosilane with (*S*)-**3** (94% ee) in THF at −78 °C, by adding a THF solution of the chlorosilane to (*S*)-**3**, gave (*R*)-1,2,2-trimethyl-2-(4-methoxynaphth-1-yl)-1-(naphth-1-yl)-1-phenyldisilane (*R*)-**6** with 93% ee in 49% yield as a highly viscous colorless oil, indicating that the reaction proceeded in >99% retention of the silyl anion center (Scheme 3).

SCHEME 3

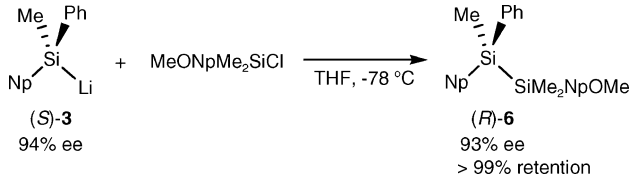
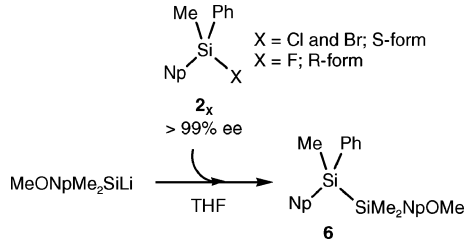


TABLE 1. Nucleophilic Substitution Reaction of Optically Active Halogenosilanes 2_X with Achiral Silyllithium under Various Conditions



entry	X	temp (°C)	solvent	yield (%)[b]	stereoselectivity (%)[c]
1	Cl	rt	THF	52	racemization
2		rt	Et_2O	46	77 (inversion)
3		rt	pentane	40	79 (inversion)
4		−78	THF	44	89 (inversion)
5		−78	Et_2O	49	96 (inversion)
6		−78	pentane	45	99 (inversion)
7	Br	rt	THF	40	racemization
8		rt	Et_2O	48	racemization
9		rt	pentane	35	72 (inversion)
10		−78	THF	38	racemization
11		−78	Et_2O	39	89 (inversion)
12		−78	pentane	37	90 (inversion)
13	F	rt	THF	37	80 (retention)
14		rt	Et_2O	39	84 (retention)
15		rt	pentane	39	81 (retention)
16		−78	THF	44	93 (inversion)
17		−78	Et_2O	40	93 (inversion)
18		−78	pentane	36	97 (inversion)

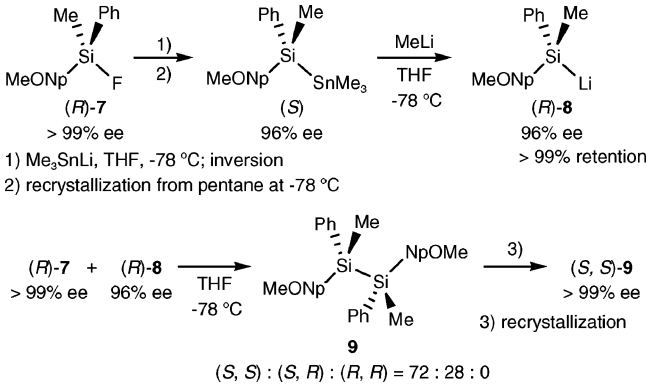
[a] Solution of $\mathbf{2_X}$ in each solvent (0.2 M, 2.5 mL) was added to the achiral silyllithium in THF (0.12 M, 5 mL). [b] Based on the achiral silyllithium. [c] Absolute configuration of **6** was determined by HPLC using a Daicel OD column.

The reactions of (*S*)-chloro-, (*S*)-bromo-, or (*R*)-fluoro-[methyl(naphth-1-yl)phenyl]silane ($\mathbf{2_x}$; X = Cl, Br, F, >99% ee)[14] with 1,1-dimethyl(4-methoxynaphth-1-yl)-silyllithium prepared in the same manner as for (*S*)-**3** were also carried out (Table 1).

It was found that racemization of (*S*)-$\mathbf{2_x}$ (X = Cl and Br) could be suppressed by decreasing the polarity of the solvent of (*S*)-$\mathbf{2_x}$ or by lowering the reaction temperature. Stereoselectivity with chlorosilane was higher than that with bromosilane, and (*R*)-**6** with 99% ee could be obtained in 45% yield for a pentane solution of (*S*)-$\mathbf{2_{Cl}}$ (entry 6). Fluorosilane (*R*)-$\mathbf{2_F}$ generally gave higher stereoselectivity at both room temperature and −78 °C (entries 13−18). The fact that the same configuration of **6** was derived from (*S*)-$\mathbf{2_x}$ (X = Cl and Br) and (*R*)-$\mathbf{2_F}$ at

(15) (a) Gilman, H.; Ingham, R. K.; Smith, A. G. *J. Org. Chem.* **1953**, *18*, 1743. (b) Kumada, M.; Shiina, K.; Yamaguchi, M. *Kogyo Kagaku Zasshi* **1954**, *57*, 230.
(16) Sommer, L. H.; Posbrough. K. T. *J. Am. Chem. Soc.* **1969**, *91*, 7067.
(17) Takeda, A.; Kumada, M.; Karama, K. *Nippon Kagaku Zasshi* **1957**, *78*, 999.
(18) (a) Stolberg, U. G. *Chem. Ber.* **1963**, *96*, 2798. (b) Stolberg, U. G. *Angew. Chem.* **1963**, *75*, 206.
(19) Kawakami, Y.; Takahashi, T.; Yada, Y.; Imae, I. *Polym. J.* **1998**, *30*, 1001.
(20) Oishi, M.; Kawakami, Y. *Org. Lett.* **1999**, *1*, 549.

SCHEME 4



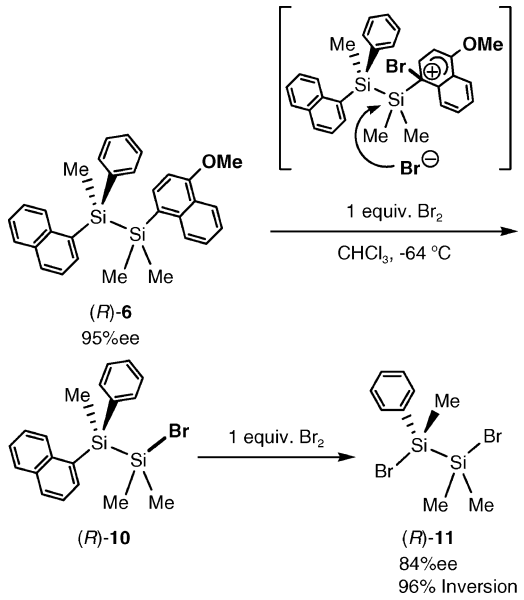
room temperature and the opposite configuration of **6** arose from (*R*)-$\mathbf{2_F}$ at −78 °C, evidenced by HPLC, indicates that the reaction of fluorosilane with the silyllithium proceeded with inversion of configuration of the chiral halogen silicon center at −78 °C and retention of configuration at room temperature.[13]

To get optically active functionalized disilane having two chiral centers (C_2-symmetric structure), we attempted to introduce a methoxy group into the optically active halogenosilane component. However, optically active (4-methoxynaphth-1-yl)-substituted chlorosilane is not easily accessible because of the cleavage of the silicon−(4-methoxynaphth-1-yl) bond in the chlorination step of (*S*)-methyl(4-methoxynaphth-1-yl)phenylsilane ((*S*); >99% ee) by chlorine gas. (*R*)-Fluoro(4-methoxynaphth-1-yl)methylphenylsilane (*R*)-**7** (>99% ee), obtained from (*S*)-(−)-[(−)-menthoxy](4-methoxynaphth-1-yl)methylphenylsilane (>99% ee)[20] with boron trifluoride/ether complex (BF_3·Et_2O) in toluene at 50 °C for 7 days, was used to synthesize optically active (*R*)-(4-methoxynaphth-1-yl)methylphenylsilyllithium (*R*)-**8** (96% ee)[21] by conversion to (*S*)-(4-methoxynaphth-1-yl)methylphenylsilylstannane (96% ee)[22] followed by the tin−lithium exchange reaction with methyllithium (Scheme 4).

The reaction between (*R*)-**7** (>99% ee) and (*R*)-**8** (96% ee) could give optically pure disilane with a methoxynaphthyl group on both silicon atoms, (*S*,*S*)-1,2-di(4-methoxynaphth-1-yl)-1,2-dimethyl-1,2-diphenyldisilane (*S*,*S*)-**9** ((*S*,*S*); > 99% ee), after purification by recrystallization from pentane at 0 °C to remove *meso*-**9** as a solid.[23]

Functionalization of methoxynaphthyl-substituted disilane by bromine was studied. Contrary to the indiscriminate cleavage seen for (*R*)-1,2,2-trimethyl-1,2-di-

SCHEME 5. Regio- and Stereoselective Cleavage of Silicon−Naphthyl Bonds of (*R*)-6 by Bromine



(naphth-1-yl)-1-phenyldisilane and (1*R*,2*R*)-**4**, the optically active 1,2-di(naphth-1-yl)-substituted disilanes, the reaction of (*R*)-**6**, having one methoxynaphthyl group, with 2 equiv of bromine in $CHCl_3$ at −64 °C gave (*R*)-1,2-dibromo-1,2,2-trimethyl-1-phenyldisilane (*R*)-**11** as the major product, evidenced by HPLC as the reduced hydorosilane[14(a)] 1,2,2-trimethyl-1-phenyldisialne **12**[24] by $LiAlH_4$ (Scheme 5).

Stepwise addition of 1 equiv of bromine to **6** gave 2-bromo-1,2,2-trimethyl-1-(naphth-1-yl)-1-phenyldisilane **10** as the only product by the selective cleavage of the silicon−methoxynaphthyl bond. Addition of another 1 equiv of bromine to **10** gave **11** as the major product. Electrophilic attack on the naphthyl group by bromo cation was preferentially enhanced over the attack on the silicon−silicon bond by the introduction of methoxy group as electron-donating substituent at the 4-position of the naphthyl group. The attack of bromo anion on the silicon atom linked to the methoxynaphthyl group[20,25] led to the selective elimination of the methoxynaphthyl group from **6** to give **10** by the first 1 equiv of bromine. Once monobromodisilane **10** was produced, the electron-withdrawing bromo group introduced on one silicon atom of the disilane suppressed the cleavage of the silicon−silicon bond, and the remaining silicon−naphthyl bond was selectively cleaved to give **11**. The regioselective cleavage reaction of the silicon−naphthyl bonds of (*R*)-**6** ((*R*); 95% ee) afforded (*R*)-**11** in 68% yield with 84% ee

(21) Configuration of **8** (96% ee) was stable at −78 °C for at least 3 h. Absolute configuration of **8** was determined as (*R*)-form after hydrolysis to hydrosilane (retention) by the comparison of its HPLC with (*R*)-(4-methoxynaphth-1-yl)methylphenylsialne prepared by the reduction of (*S*)-(−)-[(−)-menthoxy](4-methoxynaphth-1-yl)methylsialne with $LiAlH_4$ (retention).[14a] The fact indicated the inversion stereochemistry of fluorosilane (*R*)-**7** with stanyllithium in THF.

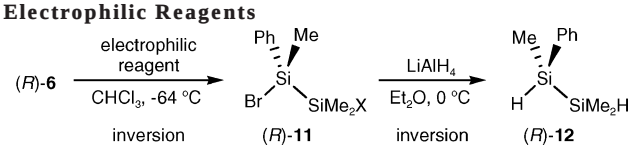
(22) Optically pure (*R*)-MeONpMePhSiSnMe$_3$ (96% ee) was obtained as a colorless viscous oil by the reaction of (*R*)-**7** (>99% ee) with Me_3SnLi in THF and recrystallization from pentane at −78 °C to remove *rac*-MeONpMePhSiSnMe$_3$. Although stereochemistry crossover from inversion to retention of configuration in the substitution reaction of optically active fluorosilane with achiral silyllithium was observed by changing temperature, solvents, and additives,[13] stereochemistry of the reaction of (*R*)-**7** with the stanyllithium was not affected by these factors and proceeded with 85% inversion of configuration.

(23) The stereoisomer ratio of **9** was found to be (*S*,*S*):(*S*,*R*):(*R*,*R*) = 72:28:0 by ^{1}H NMR and HPLC based on the inversion and retention stereochemistry of the chiral silicon centers of attacked fluorosilane and attacking silyllithium at −78 °C, respectively. Stereoselectivity in this reaction was low, probably because the stereoisomer **9** was produced by the reaction between remaining optically active silylstannane and produced (*R*)-**8**.

(24) (a) Corey, J. Y.; Zhu, X.-H.; Bedard, T. C.; Lange, L. D. *Organometallics* **1991**, *10*, 924. (b) Corey, J. Y.; Zhu, X.-H. *Organometallics* **1992**, *11*, 672. (c) Corey, J. Y.; Kraichely, D. M.; Huhmann, J. L.; Braddock-Wilking, J.; Lindeberg, A. *Organometallics* **1995**, *14*, 2704. (d) Rosenberg, L.; Davis, C. W.; Yao, J. *J. Am. Chem. Soc.* **2001**, *123*, 5120.

(25) Eaborn, C.; Steward, O. W. *Proc. Chem. Soc.* **1963**, 59.

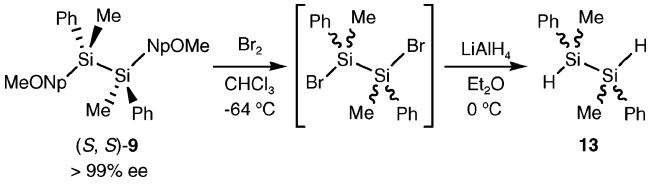
TABLE 2. Functionalization of (*R*)-6 by Various Electrophilic Reagents



entry	electrophilic reagent	temp (°C)	% ee (*R*)-**6**	% ee (*R*)-**12**	stereoselectivity (%)[a]
1	Br_2	−64	95	84	94 (inversion)
2	ICl	−64	96	77	90 (inversion)
3	IBr	−64	92	64	85 (inversion)
4	TfOH	−64	99	racemic	racemization
5	TfOH	0	78	racemic	racemization
6	Cl_2[b]	0	99		

[a] The absolute configuration of **12** was determined by HPLC using a Daicel OD column. [b] This reaction was carried out in CCl_4.

SCHEME 6



estimated by HPLC after reduction with $LiAlH_4$. Thus, the stereochemistry of the cleavage reaction of the silicon−naphthyl bond by bromine is evaluated as a 94% inversion process (Table 2, entry 1).

Other electrophilic reagents were also investigated as summarized in Table 2. Iodine monochloride and bromine monochloride could give the product under the same condition, but the stereoselectivity was lower than that by bromine. Trific acid gave the racemic products under the same or even milder condition. Chlorine gas afforded a mixture of products through the indiscriminate cleavage reaction of the silicon−silicon and silicon−naphthyl bonds.

Functionalization of optical pure **9** ((*S*,*S*); > 99% ee) with 2 equiv bromine under the same reaction condition of **6** gave only the desired 1,2-dimethyl-1,2-diphenyldisilane **13** after the reduction with $LiAlH_4$ (Scheme 6).

This cleavage reaction is also regiospecific for the silicon−methoxynaphthyl bond over the silicon−silicon bond. However, remarkable racemization in this reaction was observed even with 1 equiv of bromine. Contrary to the cleavage of (*R*)-**6** by bromine, where stepwise reaction seemd to occur and good stereoselectivity was attained, the cleavage of (*S*,*S*)-**9** may proceed under the influence of two equivalent oxygen atoms on each naphthyl group complexing with bromo cation, and the stereoselection has been changed. Further improvement of the stereochemistry is still needed by studying the reaction conditions to obtain stereospecificity, for instance, the synthesis starting from (1*S*,2*S*)-1-(4-methoxynaphth-1-yl)-2-(naphth-1-yl)-1,2-dimethyl-1,2-diphenyldisilane, which is considered to proceed in a stepwise manner.

Conclusion

The stereochemistry of the nucleophilic substitution reaction of optically active halogenosilane by optically active silyllithium was elucidated as inversion and retention for attacked and attacking chiral silicon, respectively, by X-ray crystallographic analysis. Optically active bis(naphth-1-yl)-substituted disilanes having one or two chiral silicon centers were successfully synthesized by the substitution reactions from the combination of optically active halogenosilanes and silyllithiums. Stepwise cleavage of the silicon−naphthyl bonds of the disilaneby bromine proceeded regio- and stereoselectively for the disilane with a 4-methoxy group on one naphthyl group by the suppression of the cleavage of the silicon−silicon bond. Although regioselectivity could be controlled, the stereochemistry of the cleavage of bis(4-methoxynaphth-1-yl)-substituted disilane could not be controlled.

Experimental Section

(*R*)-1,2-Dimethyl-1-(naphth-1-yl)-1,2,2-triphenyldisilane (*R*)-5 from $MePh_2SiLi$ and (*S*)-2. Methyldiphenylsilyllithium was prepared by adding methyldiphenylchlorosilane (0.7 g, 3 mmol) dropwise to a lithium dispersion (0.1 g, 15 mmol) in dry THF (6 mL). The solution was stirred at room temperature for 2 h and filtered in an argon atmosphere. To this solution was added dropwise during 10 min at −78 °C (*S*)-methyl(naphth-1-yl)phenylchlorosilane (*S*)-**2$_{Cl}$** in pentane (6 mL), prepared by the chlorination of (*R*)-methyl(naphth-1-yl)phenylsilane (0.745 g, 3 mmol, >99% ee) in CCl_4 (6 mL) with chlorine gas at 0 °C, and following removal of the solvent and excess chlorine gas the mixture was stirred at the temperature for 30 min. The resulting solution was poured into 1 N HCl solution, extracted with Et_2O, and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a solid as crude product. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (40/1) as eluent (R_f = 0.29) to give (*R*)-**5** as a colorless solid (0.18 g, 14% yield). The enantiomeric excess of (*R*)-**5** was determined as 99% ee by HPLC analysis: (*R*)-(+)-**5** retention time (t_R) = 28.2 min; (*S*)-(−)-**5** t_R = 31.3 min. Recrystallization of (*R*)-**5** (> 99% ee) with pentane at room temperature afforded (*R*)-**5** as a crystal suitable for X-ray analysis. Mp 115 °C. $[\alpha]^{24}_D$ = +15.23 (*c* = 1.05, cyclohexane). ^{1}H NMR δ 0.68 (s, 3H, −SiPh$_2$*CH*$_3$), 0.797 (s, 3H, −SiNpPh*CH*$_3$), 7.07−7.103 (m, 1H, aromatic), 7.21−7.24 (m, 6H, aromatic), 7.27−7.39 (m, 11H, aromatic), 7.68−7.71 (m, 2H, aromatic), 7.81 (d, *J* = 8.2 Hz, 1H, aromatic), 7.85 (d, *J* = 8.2 Hz, 1H, aromatic). ^{13}C NMR δ −3.61, −2.54, 125.13, 125.38, 125.40, 127.78 (overlapped), 127.81, 128.74, 128.79, 128.89, 128.90, 129.35, 130.12, 133.44, 134.69, 135.10, 135.26, 135.30, 136.13, 136.69, 136.71, 137.14, 137.32. ^{29}Si NMR δ −21.15, −22.26. Anal. Calcd for $C_{30}H_{28}Si_2$: C, 81.02; H, 6.35. Found: C, 81.00; H, 6.49.

(*R*)-5 from $MePh_2SiCl$ and (*S*)-3. (*R*)-Methyl(naphth-1-yl)phenylsilyltrimethylstannane (0.19 g, 0.5 mmol, 90% ee) in THF (2.5 mL) was added to a solution of methyllithium (0.6 mL as 1.04 M Et_2O solution, 0.64 mmol) in THF (1.25 mL) at −78 °C during 10 min, and the mixture was stirred for 20 min. To the resulting solution of (*S*)-**3** was added methyldiphenylchlorosilane (0.12 g, 0.52 mmol) in THF (2.5 mL) during 10 min. The reaction mixture was stirred at −78 °C for 30 min, and the resulting mixture was poured into 1 N HCl, extracted with Et_2O, and dried over anhydrous $MgSO_4$. Similar workup and purification as the procedure above gave (*R*)-**5** (0.072 g, 32% yield, 90% ee) as a colorless solid. The compound gave reasonable analytical data.

(*R*)-1,2,2-Trimethyl-2-(4-methoxynaphth-1-yl)-1-(naphth-1-yl)-1-phenyldisilane (*R*)-6 from $MeONpMe_2SiCl$ and (*S*)-3. To a solution of (*S*)-**3**, prepared from (*R*)-methyl(1-naphthyl)phenylsilyltrimethylstannane (0.4 g, 0.98 mmol, 93% ee) in THF (20 mL), was added dimethyl(4-methoxynaphth-1-yl)chlorosilane (0.76 g, 3.0 mmol) in THF (20 mL). The resulting solution was poured into a 1 N HCl solution,

extracted with Et_2O, dried over anhydrous $MgSO_4$, and purified by silica gel column chromatography with hexane/toluene = 10:1− 10:2 to give 0.22 g (49%) of a highly viscous oil. $[\alpha]^{25}_D = +13.99$ (c = 1.0, cyclohexane). ^{1}H NMR δ 0.51 (s, 3H, NpOMeSi*Me*), 0.59 (s, 3H, NpOMeSi*Me*), 0.74 (s, 3H, NpSi*Me*), 4.00 (s, 3H, NpO*Me*), 6.76−6.77 (d, J = 7.8 Hz, 1H), 6.99−7.02 (m, 1H), 7.13−7.16 (m, 1H), 7.27−7.45 (m, 8H), 7.56−7.57 (d, J = 7.8 Hz, 1H), 7.59−7.61 (m, 2H), 7.80−7.83 (t, J = 7.8 Hz, 3H), and 8.22−8.24 (d, J = 8.2 Hz, 1H). ^{13}C NMR δ −2.32, −1.04, −0.96, 55.38, 103.44, 122.22, 124.66, 125.20 (overlapped), 125.32, 125.63, 127.81, 128.42, 128.62 (overlapped), 128.70, 129.26, 129.81, 133.35, 133.81, 134.42, 135.08, 135.29, 135.40, 137.19, 137.97, 138.03, 156.68. ^{29}Si NMR δ −20.85 (overlapped). Anal. Calcd for $C_{30}H_{30}OSi_2$: C, 77.87; 6.53. Found: C, 77.23; H, 6.66.

(*R*)-6 from MeONpMe$_2$SiLi and 2$_X$ (X = Cl, Br, (*S*)-form; X = F, (*R*)-form). To (4-methoxynaphth-1-yl)dimethysilyllithium, prepared from dimethyl(4-methoxynaphth-1-yl)silyltrimethylstannane (0.19 g, 0.5 mmol) and methyllithium (0.6 mL as 1.04 M Et_2O solution, 0.62 mmol) in THF at −78 °C was slowly added **2$_X$** (0.5 mmol, X = Cl, Br, F, >99% ee) in pentane (2.5 mL) at the designated temperature during 30 min, and the mixture was stirred for 60 min. Similar workup as above gave the product, which gave reasonable analytical data.

(*R*)-Fluoro(4-methoxynaphth-1-yl)methylphenylsilane (*R*)-7. To a solution of (*S*)-(−)-[(−)-menthoxy](4-methoxynaphth-1yl)methylphenylsilane (>99% ee)[20] (11.7 g, 27 mmol, >99% de) in toluene (60 mL) was added freshly distilled BF_3·Et_2O (7.8 g, 55 mmol) at room temperature, and the mixture was heated at 50 °C for 7 days. After the removal the solvent and excess BF_3·Et_2O under reduced pressure, the residue was distilled (0.18 Torr, 130−140 °C) to give the mixture of (−)-menthol and **7**. Recrystallization of the mixture from pentane at −78 °C gave **7** as a colorless crystal. Further recrystallization of **7** in pentane at 0 °C for several times gave 1.16 g (>99% ee, 13%) and 1.84 g (80% ee, 25%) of **7** as colorless crystal. The absolute configuration was determined as the (*R*)-form by the comparison of its HPLC profile with (*S*)- and (*R*)-fluoro(naphth-1-yl)methylphenylsilane.[14a] (*S*)-(+)-**7** t_R = 90.0 min; (*R*)-(−)-**7** t_R = 107 min. $[\alpha]^{27}_D = 12.25$ (c = 0.97, cyclohexane). ^{1}H NMR δ 0.85 (d, J = 7.4 Hz, 3H, −Si*CH*$_3$), 4.03 (s, 3H, −Np*OCH*$_3$), 6.85 (d, J = 7.8 Hz, 1H, aromatic), 7.36−7.40 (m, 2H, aromatic), 7.42−7.50 (m, 3H, aromatic), 7.61−7.65 (m, 2H, aromatic), 7.72 (d, J = 7.8 Hz, 1H, aromatic), 7.94−7.98 (m, 1H, aromatic), 8.32−8.35 (m, 1H, aromatic). ^{13}C NMR δ −1.25 (d, J = 17.3 Hz), 55.48, 103.15, 122.62, 123.18 (d, J = 15.4 Hz), 125.17, 125.72, 126.92, 127.83, 128.04, 130.44, 134.00, 135.35 (d, J = 17.3 Hz), 135.74 (d, J = 3.8 Hz), 137.72. ^{29}Si NMR δ 10.47 (d, J = 280.0 Hz). Anal. Calcd for $C_{18}H_{17}OSiF$: C, 72.94; H, 5.78. Found: C, 72.77; H, 5.824.

(*S*)-(4-Methoxynaphth-1-yl)methylphenylsilyltrimethylstananne. This compound was synthesized similarly to (4-methoxynaphth-1-yl)dimethylsilylstannnane from (*R*)-**7** (1.0 g, 3.4 mmol, >99%ee). After evaporation of volatile materials, hexane was added, and the mixture was vigorously stirred at 0 °C to make *rac*-silylstannane precipitate as a colorless powder. After hexane was removed, the residue was purified by column chromatography over silica gel with hexane/ethyl acetate (80/1) as eluent (R_f = 0.38) to give (*S*)-**7** as a viscous colorless oil (0.92 g, 62%, (*S*); >96.4% ee). $[\alpha]^{27}_D = -28.13$ (c = 1.21, cyclohexane). (*R*)-(+) t_R = 28.2 min, (*S*)-(−) t_R = 31.3 min. ^{1}H NMR δ 0.089 (s, 9H, −Sn(*CH*$_3$)$_3$), 0.849 (s, 3H, −Si*CH*$_3$), 4.02 (s, 3H, −NpO*CH*$_3$), 6.82 (d, J = 7.8 Hz, 1H, aromatic), 7.295−7.49 (m, 7H, aromatic), 7.579 (d, J = 7.8 Hz, 1H, aromatic), 7.81 (d, 1H, J = 8.2 Hz, aromatic), 8.316 (d, J = 7.8 Hz, 1H, aromatic). ^{13}C NMR δ −10.84, −1.49, 55.15, 103.26, 122.37, 124.69, 125.41, 125.55, 126.01, 127.703, 127.949, 128.48, 134.46, 135.16, 137.62, 138.519, 156.91. ^{29}Si NMR δ −7.19. Anal. Calcd for $C_{21}H_{26}OSiSn$: C, 57.17; H, 5.94. Found: C, 57.11; H, 5.97.

Racemic (4-methoxynaphth-1-yl)methylphenylsilylstananne was prepared in the same way.

(*S,S*)-1,2-Dimethyl-1,2-di(4-methoxynaphth-1-yl)-1,2-diphenyldisialne (*S,S*)-9. To (*R*)-**8** from (*S*)-(4-methoxynaphth-1-yl)methylphenylsilylstananne (1.3 g, 2.95 mmol, 96% ee) was slowly added (*R*)-**7** (0.87 g, 2.95 mmol, >99% ee) in THF (15 mL) at −78 °C, and the reaction system was stirred for 30 min at the temperature. Decomposition with 1 N HCl, extraction with Et_2O, concentration, and addition of hexane led to the precipitation of *meso*-**9** as a colorless solid at 0 °C. The crude product from the solution was purified by column chromatography (hexane/ethyl acetate = 40/1, R_f = 0.22) to give (*S,S*)-**9** (0.70 g, 43%, (*S,S*); >99% ee) as a colorless solid. $[\alpha]^{27}_D = -9.689$ (c = 1.01, cyclohexane). (*S, S*)-(−)-**9** t_R = 100 min, (*R, R*)-(+)-**9** t_R = 146 min. ^{1}H NMR δ 0.79 (s, 6H, (−Si*CH*$_3$)$_2$), 3.98 (s, 6H, (−NpO*CH*$_3$)$_2$), 6.67 (d, J = 7.8 Hz, 2H, aromatic), 7.02−7.05 (m, 2H, aromatic), 7.17−7.24 (m, 4H, aromatic), 7.30−7.36 (m, 6H, aromatic), 7.47 (s, 2H, aromatic). 7.66 (d, 2H, J = 8.7 Hz, aromatic), 7.67 (d, 2H, J = 7.8 Hz, aromatic), 8.25 (d, J = 8.2 Hz, 2H, aromatic). ^{13}C NMR δ −2.399 (Si*CH*$_3$, *S*, *S*), 55.37, 103.400, 122.28, 124.74, 125.45, 125.84, 125.92, 127.71, 128.61, 128.98, 135.27, 137.15, 137.84, 138.13, 157.04. ^{29}Si NMR δ −20.29. Anal. Calcd for $C_{36}H_{34}O_2Si_2$: C, 77.93; H, 6.18. Found: C, 77.44; H, 6.20.

Addition of hexane (10 mL) to *diastereo*-**9** from *rac*-(4-methoxynaphth-1-yl)methylphenylsilylstananne (0.62 g, 1.41 mmol) and *rac*-**7** (0.42 g, 1.42 mmol) at room temperature led to the precipitation of *meso*-**9** as a white solid (0.25 g, 0.45 mmol, 32%). Further addition of hexane (10 mL) to the residue at 0 °C gave *dl*-**9** as colorless solid (0.14 g, 0.26 mmol, 18%). *meso*-**9**: ^{1}H NMR δ 0.83 (s, 6H, (−Si*CH*$_3$)$_2$), 3.98 (s, 6H, (−NpO*CH*$_3$)$_2$), 6.70 (d, J = 7.8 Hz, 2H, aromatic), 7.05−7.09 (m, 2H, aromatic), 7.17−7.20 (m, 4H, aromatic), 7.28−7.37 (m, 6H, aromatic), 7.47 (s, 2H, aromatic), 7.69 (d, 2H, J = 7.8 Hz, aromatic), 7.71 (d, 2H, J = 8.2 Hz, aromatic), 8.29 (d, J = 8.2 Hz, 2H, aromatic). ^{13}C NMR δ −2.002 (Si*CH*$_3$, *meso*), 55.37, 103.42, 122.299, 124.73, 125.202, 125.859, 125.91, 127.62, 128.56, 129.04, 135.19, 137.103, 137.93, 138.16, 157.06. ^{29}Si NMR δ −20.55. Anal. Calcd for $C_{36}H_{34}O_2Si_2$: C, 77.93; H, 6.18. Found: C, 77.51; H, 6.20. *dl*-**9**: Analytical data are basically the same as those for (*S,S*)-**9**.

Cleavage of (*R*)-6 by Bromine and Successive Reduction to (*R*)-1,2,2-Trimethyl-1-phenyldisilane (*R*)-12. Bromine (1.0 mL, 0.49 M $CHCl_3$ solution) was added dropwise to (*R*)-**6** (0.234 g, 0.5 mmol, (*R*); 95% ee) in $CHCl_3$ (5 mL) for 10 min, and the mixture was stirred at −64 °C for 60 min. Formation of (*R*)-1,2-dibromo-1,1,2-trimethyl-2-phenyldisilane was evidenced as (*R*)-1,1,2-trimethyl-2-phenyldisilane (*R*)-**12**[24] after the reduction with $LiAlH_4$ (0.04 g, 1.1 mmol) in Et_2O (5 mL) at 0 °C. The crude products, after the solution was filtrated and concentrated, were separated by preparative HPLC with hexane to afford (*R*)-**6** (0.061 g, 68%, 84% ee). (*R*)-(−)-**12** t_R = 13.05 min, (*S*)-(+)-**12** t_R = 14.32 min. ^{1}H NMR δ 0.20, 0.22 (two d, 6H, HSi*Me*$_2$, J_{SiHCH} = 4.5 Hz), 0.47 (d, 3H, PhHSi*Me*, J_{SiHCH} = 4.6 Hz), 3.87 (d septet, 1H, Me$_2$Si*H*, J_{SiHCH} = 4.5 Hz, J_{SiHSiH} = 2.2 Hz), 4.32 (dq, 1H, MePhSi*H*, J_{SiHCH} = 4.6 Hz, J_{SiHSiH} = 2.2 Hz), 7.21−7.72 (m, 5H, aromatic). ^{13}C NMR δ −7.47, −6.13, 127.73, 127.81, 128.70, 134.60. EI-MS (*m/e*) 180 (M^+), 165 ([M − CH_3]$^+$), 135 ([M − 3CH_3]$^+$), 121 ([MePhSi]$^+$).

Cleavage of (*S,S*)-9 by Bromine. (*S,S*)-**9** (0.277 g, 0.5 mmol, (*S,S*); >99% ee) at −64 °C for 20 min was similarly treated with bromine (2.2 mL, 0.46 M $CHCl_3$ solution). The product was identified as reduced product, 1,2-dimethyl-1,2-diphenyldisilane. ^{1}H NMR δ 0.43 (d, 6H, Si*Me*, J_{CHSiH} = 4.7 Hz), 4.41 (q, 2H, Si*H*, J = 4.7 Hz), 7.20−7.70 (m, 10H, aromatic). ^{13}C NMR δ −7.65, −7.44, 127.94, 128.98, 134.73, 134.85. EI-MS (*m/e*) 242 (M^+), 197 ([M − 3CH_3]$^+$), 121 ([MePhSi]$^+$), 105 ([SiPh]$^+$).

X-ray Structure Determination of (*R*)-5. A single crystal was obtained by recrystallization from hexane. Measurement was made by Rigaku RAXIS-RAPID Imaging Plate, T = 296

K. The structure was solved by direct methods (SIR92)[26] and expanded using Fourier techniques (DIRDIF99):[27] 4630 reflections measured with 2θ in the range 6.3−143.5, 4606 unique reflections; 3218 with $I > 3\sigma(I)$; refinement by full matrix least-squares methods; anisotropic thermal parameters for all non-H atoms in the final cycles; H atoms were refined on a riding model in their ideal geometric positions; Flack parameter −0.00(3); $R = 0.034$, and $wR = 0.037$. All calculations were performed using the CrystalStructure[28,29] crystallographic software package.

Crystallographic Data for (*R*)-5. (*R*)-1,2-dimethyl-2-(naphth-1-yl)-1,1,2-triphenyldisilane: $C_{30}H_{28}Si_2$, $M = 444.72$, $a = 10.015(2)$, $b = 14.070(2)$, $c = 17.975(3)$ Å, $V = 2532.8(7)$ Å^3, orthorhombic, space group $P2_12_12_1$ (No. 19), $Z = 4$, μ(Cu Kα) = 13.67 cm^{-1}, $\lambda = 1.54187$ Å.

Additional Crystallographic Data. CCDC 233409 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033.

Supporting Information Available: Crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters for (*R*)-**5**, and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M., Polidori, G., and Camalli, M. J. *Appl. Crystallogr.* **1994**, *27*, 435.

(27) Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., de Gelder, R., Israel, R.; Smits, J. M. M. *The DIRDIF-99 Program System*, Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands 1999.

(28) *CrystalStructure 3.6.0*, Crystal Structure Analysis Package; Rigaku and Rigaku/MSC (2000−2004), 9009 New Trails Dr., The Woodlands, TX 77381.

(29) *CRYSTALS*, Issue 10; Watkin, D. J., Prout, C. K. Carruthers, J. R., Betteridge, P. W.; Chemical Crystallography Laboratory: Oxford, U.K., 1996.