

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

Keigo Suzuki, Yusuke Kawakami,* Devadasan Velmurugan,[†] and Takashi Yamane[‡]

Graduate School of Materials Science, Japan Advanced Institute of Science & Technology [JAIST], Asahidai 1-1, Tatsunokuchi, Ishikawa 923-1292, Japan, Department of Crystallography & Biophysics, University of Madras Guindy Campus, Chennai 600 025 India, and Department of Biotechnology, School of Engineering, Nagoya University, Furo-cho, Chikusa Nagoya 464-8603, Japan

kawakami@jaist.ac.jp

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Optically active disilanes with one chiral silicon center, (R)-1,2-dimethyl-1-(naphth-1-yl)-1,2,2triphenyldisilane and (R)-1,2,2-trimethyl-2-(4-methoxynaphth-1-yl)-1-(naphth-1-yl)-1-phenyldisilane, triphenyldisilane, triphwere 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 silvl anions. Optically active disilanes with two chiral centers, (1R,2R)-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-1,2diphenyldisilane, 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 (1R,2R)-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-(4methoxynaphth-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 disilanes¹ are useful precursors to polymers composed of the regular alternating arrangement of a disilarlylene and a π -electron system (poly- $(disilarly lene - \pi - conjugated systems))^2$ and also linear silicon-silicon catenative structures (oligo-³ and polysilanes⁴ including dendrimers⁵), which are of considerable interest because of their unique electrooptical properties due to the σ - σ 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 thermochromism⁶ 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.

^{*} To whom correspondence should be addressed. Fax: +81-761-51-1635.

[†] University of Madras Guindy Campus.

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 ¹ Nagoya University.
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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.

Silvllithiums⁸ 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

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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-

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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 CF₃SO₃ (TfO) by the electrophilic cleavage reaction of the silicon-aromatic bonds. Unfortunately, when optically active (R)-1,2,2trimethyl-1,2-di(naphth-1-yl)-1-phenyldisilane or (1R,2R)-1,2-dimethyl-1,2-di(naphth-1-yl)-1,2-diphenyldisilane (1R, 2*R*)-**4** was treated with bromine, indiscriminate cleavage of silicon-naphthyl and silicon-silicon bonds¹⁵ 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.

Kumada¹⁷ and Stolberg¹⁸ 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 of (R)-(+)-[(+)-menthoxy]methyl(naphth-1-yl)bond 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)silyllithium. Reaction of dimethyl(4-methoxynaphth-1-yl)- JOC Article



TABLE 1. Nucleophilic Substitution Reaction ofOptically Active Halogenosilanes 2_X with AchiralSilyllithium under Various Conditions



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

^{*a*} Solution of $\mathbf{2}_{\mathbf{X}}$ 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.

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).

The reactions of (*S*)-chloro-, (*S*)-bromo-, or (*R*)-fluoro-[methyl(naphth-1-yl)phenyl]silane (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)- 2_x (X = Cl and Br) could be suppressed by decreasing the polarity of the solvent of (S)- 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)- 2_{Cl} (entry 6). Fluorosilane (R)- 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)- 2_x (X = Cl and Br) and (R)- 2_F at

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(S, S): (S, R): (R, R) = 72 : 28 : 0

room temperature and the opposite configuration of **6** arose from (*R*)-**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-1vl)methylphenylsilane (>99% ee)²⁰ with boron trifluoride/ ether complex (BF_3 ·Et₂O) 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 tinlithium 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(4methoxynaphth-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-diSCHEME 5. Regio- and Stereoselective Cleavage of Silicon–Naphthyl Bonds of (*R*)-6 by Bromine



(naphth-1-yl)-1-phenyldisilane and (1R,2R)-**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 CHCl₃ 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 LiAlH₄ (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 electronwithdrawing bromo group introduced on one silicon atom of the disilane suppressed the cleavage of the siliconsilicon 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 LiAlH₄ (retention).^{14a} The fact indicated the inversion stere-ochemistry of fluorosilane (*R*)-**7** with stanyllithium in THF.

⁽²²⁾ Optically pure (*R*)-MeONpMePhSiSnMe₃ (96% ee) was obtained as a colorless viscous oil by the reaction of (*R*)-7 (>99% ee) with Me₃-SnLi in THF and recrystallization from pentane at -78 °C to remove *rac*-MeONpMePhSiSnMe₃. 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 ¹H 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**.

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

 Electrophilic Reagents

(<i>R</i>)-6	electrophilic reagent	Ph Me		LiAIH ₄	Me Ph	
	CHCl ₃ , -64 °C	Br	SiMe₂X	Et ₂ O, 0 °C	H SiMe₂H	
	inversion	(<i>R</i>)- 11		inversion	(<i>R</i>)- 12	
	electrophilic	temp	% ee	% ee	stereoselectivity	
entry	reagent	(°C)	(R)- 6	(<i>R</i>)- 12	(%) ^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 CCl₄.

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 LiAlH₄ (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 stereo-chemistry is still needed by studying the reaction conditions to obtain stereospecificity, for instance, the synthesis starting from (1S,2S)-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 MePh₂SiLi 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-1yl)phenylsilane (0.745 g, 3 mmol, >99% ee) in CCl₄ (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 Et₂O, and dried over anhydrous MgSO₄. 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 ($t_{\rm R}$) = 28.2 min; (S)-(-)-5 $t_{\rm R}$ = 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, cyclohexaně). ¹H ŇMR & 0.68 (s, 3H, -SiPh₂CH₃), 0.797 (s, 3H, -SiNpPhCH₃), 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). ¹³C 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. ²⁹Si NMR δ -21.15, -22.26. Anal. Calcd for C₃₀H₂₈Si₂: C, 81.02; H, 6.35. Found: C, 81.00; H, 6.49.

(*R*)-5 from MePh₂SiCl and (*S*)-3. (*R*)-Methyl(naphth-1yl)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 Et₂O 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 Et₂O, and dried over anhydrous MgSO₄. 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 MeONpMe₂SiCl and (*S*)-3. To a solution of (*S*)-3, prepared from (*R*)-methyl(1naphthyl)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 Et₂O, dried over anhydrous MgSO₄, 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. [α]²⁵_D = +13.99 (c = 1.0, cyclohexane). ¹H 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). ¹³C 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. ²⁹Si NMR δ –20.85 (overlapped). Anal. Calcd for C₃₀H₃₀OSi₂: C, 77.87; 6.53. Found: C, 77.23; H, 6.66.

(*R*)-6 from MeONpMe₂SiLi 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 Et₂O 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 $(S)^{-}(-)^{-}[(-)^{-}menthoxy](4-methox$ ynaphth-1yl)methylphenylsilane (>99% ee)²⁰ (11.7 g, 27 mmol, >99% de) in toluene (60 mL) was added freshly distilled BF₃. Et₂O (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 BF₃·Et₂O 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 $t_{\rm R} = 90.0$ min; (R)-(-)-7 $t_{\rm R} = 107$ min. $[\alpha]^{27}_{\rm D} = 12.25$ (c = 0.97, cyclohexane). ¹H NMR δ 0.85 (d, J = 7.4 Hz, 3H, $-\text{Si}CH_3$), 4.03 (s, 3H, $-NpOCH_3$), 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). $^{13}\mathrm{C}$ NMR δ –1.25 (d, J = 17.3 Hz), 55.48, 103.15, 122.62, 123.18 (d, J = 15.4Hz), 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. ²⁹Si NMR δ 10.47 (d, J = 280.0 Hz). Anal. Calcd for C₁₈H₁₇OSiF: 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 (4methoxynaphth-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). [α]²⁷_D = -28.13 (c = 1.21, cyclohexane). (*R*)-(+) $t_{\rm R}$ = 28.2 min, (*S*)-(-) $t_{\rm R}$ = 31.3 min. ¹H NMR δ 0.089 (s, 9H, $-Sn(CH_3)_3$), 0.849 (s, 3H, $-SiCH_3$, 4.02 (s, 3H, $-NpOCH_3$), 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). ¹³C 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. $^{29}\mathrm{Si}$ NMR δ -7.19. Anal. Calcd for C21H26OSiSn: 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)-1,2diphenyldisialne (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 Et₂O, 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*,*Š*); >99% ee) as a colorless solid. $[\alpha]^{27}_{D} = -9.689 \ (c = 1.01, \text{ cyclohexane}). \ (S, S)-(-)-9 \ t_{R} = 100$ min, (R, R)-(+)-9 $t_{\rm R} = 146$ min. ¹H NMR δ 0.79 (s, 6H, $(-SiCH_3)_2$), 3.98 (s, 6H, $(-NpOCH_3)_2$), 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). $^{13}\mathrm{C}$ NMR δ -2.399 (SiCH₃, 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 $C_{36}H_{34}O_2\text{-}$ Si₂: C, 77.93; H, 6.18. Found: C, 77.44; H, 6.20.

Addition of hexane (10 mL) to diastereo-9 from rac-(4methoxynaphth-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: ¹H NMR & 0.83 (s, 6H, (-SiCH₃)₂), 3.98 (s, 6H, $(-NpOCH_3)_2$), 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). ¹³C NMR δ –2.002 (SiCH₃, 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. ²⁹Si NMR δ –20.55. Anal. Calcd for C₃₆H₃₄O₂Si₂: 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 CHCl₃ solution) was added dropwise to (R)-6 (0.234 g, 0.5 mmol, (R); 95% ee) in CHCl₃ (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)-1224 after the reduction with LiAlH₄ (0.04 g, 1.1 mmol) in Et₂O (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 $t_{\rm R}$ = 13.05 min, (S)-(+)-12 $t_{\rm R}$ = 14.32 min. ¹H NMR δ 0.20, 0.22 (two d, 6H, HSiMe₂, J_{SiHCH} = 4.5 Hz), 0.47 (d, 3H, PhHSiMe, $J_{SiHCH} = 4.6$ Hz), 3.87 (d septet, 1H, Me₂SiH, J_{SiHCH} = 4.5 Hz, J_{SiHSiH} = 2.2 Hz), 4.32 (dq, 1H, MePhSiH, J_{SiHCH} = 4.6 Hz, $J_{\text{SiHSiH}} = 2.2$ Hz), 7.21–7.72 (m, 5H, aromatic). ¹³C NMR δ -7.47, -6.13, 127.73, 127.81, 128.70, 134.60. EI-MS (m/e) 180 (M⁺), 165 ([M - CH₃]⁺), 135 ([M - 3CH₃]⁺), 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 CHCl₃ solution). The product was identified as reduced product, 1,2-dimethyl-1,2-diphenyldisilane. ¹H 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). ¹³C NMR δ –7.65, –7.44, 127.94, 128.98, 134.73, 134.85. EI-MS (*m/e*) 242 (M⁺), 197 ([M – 3CH₃]⁺), 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

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,

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(28) *CrystalStructure 3.6.0*, Crystal Structure Analysis Package; Rigaku and Rigaku/MSC (2000-2004), 9009 New Trails Dr., The Woodlands, TX 77381. a = 10.015(2), b = 14.070(2), c = 17.975(3) Å, V = 2532.8(7) Å³, 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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