Optical Resolution and Epimerization of Fluorosilane Having an Optically Active Amino Group: A New, Convenient Access to Optically Active Silicon Compounds

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The diastereomeric (amino)fluorosilane **2** is prepared from the prochiral (1-naphthyl)-phenyldifluorosilane **5** with optically active bis[(*R*)-1-phenylethyl]amine (**3**). The two isomers of **2** can be easily separated due to their large solubility difference in CH_3NO_2. In addition, **2** undergoes epimerization at the silicon atom in the presence of a catalytic amount of AgF. Stereospecific methylation and the deamination−fluorination of **2** give the enantiomerically pure (1-naphthyl)phenylmethylfluorosilane (**1**).

Introduction

Since the pioneering work of Sommer from 1959 to the middle of the 1960s,[1] stereochemistry on a chiral silicon center in organic silicon compounds has received much attention.[2] Optically active silicon compounds have been obtained by optical resolution,[3] kinetic resolution,[4] or asymmetric synthesis.[5] Sommer's optical resolution method[1] using the (−)-menthoxy group involves separation of (±)-(1-naphthyl)phenylmethyl[(−)-menthoxy]silane by fractional crystallization. The introduction of the (−)-menthoxy group in the reaction of (1-naphthyl)phenylmethylmethoxysilane with (−)-menthol requires a high reaction temperature (135−145 °C) in the presence of KOH. Alternatively, Holt et al. developed a mild reaction of (1-naphthyl)phenylmethylsilane with (−)-menthol in the presence of Pd−C at room temperature.[6] The (−)-menthoxy group has also been used to resolve difunctional silanes,[3a−e] organosilicon compounds containing Si−Si and Si−Ge linkages,[3f,g] and cyclic organosilicon compounds.[3h−j] Optical resolution of α-amino organosilanes by use of (+)-tartaric acid has also been reported.[3k] Kinetic resolution has been achieved by partial reduction of racemic methoxysilanes[4a,b] with chiral complexes of lithium aluminum hydride and by alcoholysis of (1-naphthyl)phenylchlorosilane with (−)-menthol.[3b] Asymmetric synthesis has also been a way to optically active silicon compounds, which includes the reaction of prochiral bis(acetamido)silanes with optically active amino acids,[5b,c] alcoholysis of prochiral dihydrosilanes by use of an optically active alcohol and/or chiral catalyst,[5d,e] catalytic asymmetric hydrosilation of carbonyl compounds with prochiral dihydrosilanes,[5f−j] and reaction of dialkoxysilanes containing chiral alkoxy groups with organometals.[5k,l]

We report here a new, convenient access to optically active (1-naphthyl)phenylmethylfluorosilane (**1**) using an optically active amine. This method involves optical resolution and epimerization of {bis[(*R*)-1-phenylethyl]-amino}(1-naphthyl)phenylfluorosilane (**2**) and subsequent stereospecific methylation and deamination−fluorination as shown in Scheme 1. The introduction of the bis[(*R*)-1-phenylethyl]amino group onto the silicon induces a large solubility difference between the two diastereomers of **2**, resulting in easy separation of them.

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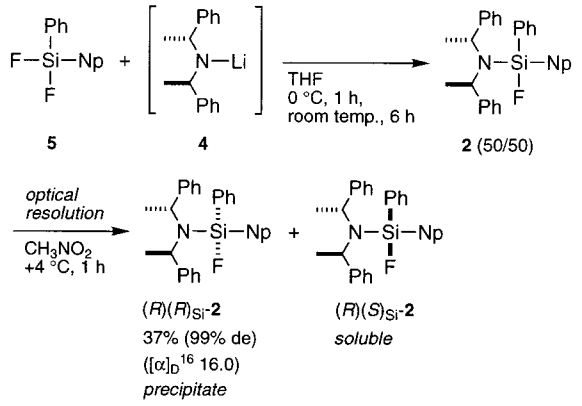
Scheme 1



Results and Discussion

We have chosen an optically active amine, (+)-bis-[(*R*)-1-phenylethyl]amine (**3**),[7] as the resolving agent. The introduction of the amino group on silicon was successful under the mild conditions, as shown in Scheme 1. (1-Naphthyl)phenyldifluorosilane (**5**) was treated in THF with the lithium amide **4** prepared by deprotonation of **3** with *n*-butyllithium, affording a 1:1 diastereomeric mixture of (amino)fluorosilane **2** as an oily substance. Addition of CH_3NO_2 to the oily diastereomeric mixture of **2** induced precipitation of white crystals immediately. After the mixture stood for 1 h in a refrigerator, the precipitates were separated by filtration and washed with CH_3NO_2 to give one diastereomer of **2** in 37% yield with 99% diastereomeric excess (de), as determined by ^{1}H NMR spectroscopy. Similarly, addition of CH_3CN to **2** gave the identical diastereomer in 39% yield with 94% de. Washing the crystals with CH_3NO_2 several times or recrystallizing from hexane improves the purity to >99% de in each case. Thus, the optical resolution was quite readily achieved without long standing for fractional recrystallization.

The absolute configuration of the silicon center of the diastereomer was determined by X-ray crystallographic analysis, on the basis of the configuration of the bis-[(*R*)-1-phenylethyl]amino group. As shown in Figure 1, the configuration of the silicon is *R*, and hence this diastereomer is designated (*R*)(*R*)$_{Si}$-**2**.

We also found that **2** undergoes epimerization at the silicon atom in the presence of a catalytic amount of a fluoride source.[8] After examining several conditions, we found that AgF is most suitable as a fluoride source and CH_3CN is better than CH_3NO_2 as a solvent. The diastereomeric mixture of **2** prepared as above was treated with 0.05 molar equiv of AgF in CH_3CN at room temperature for 1 day and formed a white precipitate. After the solvent was removed, the residue was washed with CH_3NO_2 to give (*R*)(*R*)$_{Si}$-**2** of 96% de in 68% yield based on **5**, as shown in Scheme 2. Other fluoride sources, such as NaF, KF, $AgBF_4$, TBAF (tetrabutylammonium fluoride), and TASF (tris(dimethylamino)sulfonium trimethyldifluorosilicate), induced a similar epimerization in CH_3CN, but they concomitantly caused a deamination reaction of **2** to lower the yield of (*R*)-(*R*)$_{Si}$-**2** considerably. For example, in the presence of 0.05 molar equiv of NaF, (*R*)(*R*)$_{Si}$-**2** was obtained in 46% yield with >99% de after stirring at room temperature for 4 days. It is plausible that this epimerization proceeds via the pentacoordinate difluorosilicate **6** and that the equilibrium shifts from (*R*)(*S*)$_{Si}$-**2** to (*R*)(*R*)$_{Si}$-**2** due to the lower solubility of the latter in CH_3CN, as shown in Scheme 3. However, other pathways involving pseudorotation of pentacoordinate silicates or ligand exchange processes between penta- and/or hexacoordinate silicates cannot be excluded.[2]

The Si–F moiety in **2** was stereospecifically transformed into the Si–Me group. Thus, (*R*)(*R*)$_{Si}$-**2** (>99% de) was treated with methyllithium in THF at room temperature to afford {bis[(*R*)-1-phenylethyl]amino}[(*S*)-1-naphthyl]phenylmethylsilane ((*R*)(*S*)$_{Si}$-**7**) in 81% yield with retention of the configuration at the silicon, as shown in Scheme 4. The other diastereomer (*R*)(*R*)$_{Si}$-**7** was not detected in the reaction mixture by ^{1}H NMR analysis. The absolute configuration of the silicon center was determined again by X-ray crystallographic analysis, as shown in Figure 2. The retention of the config-

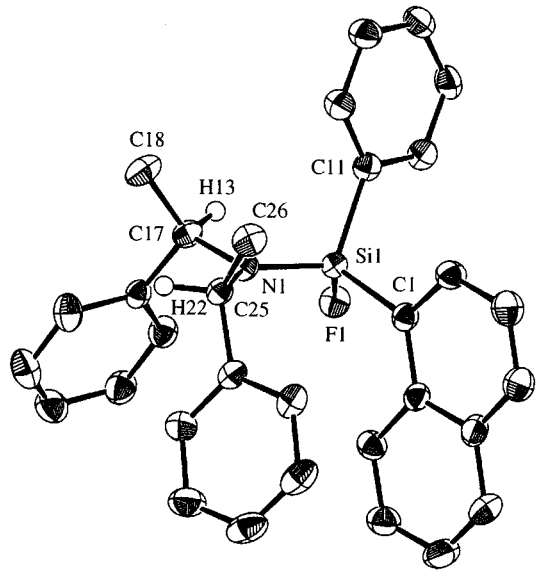
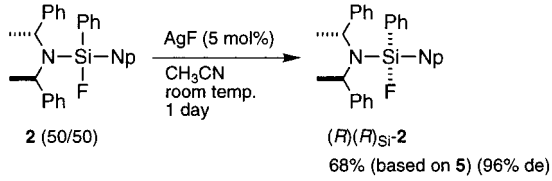
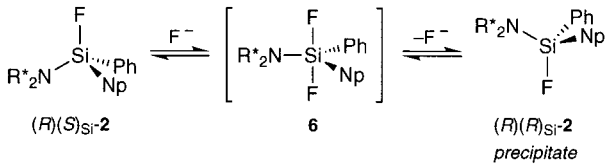


Figure 1. Crystal structure of (*R*)(*R*)$_{Si}$-**2**, shown at the 50% probability level. H atoms except for H13 and H22 are omitted for clarity.

Scheme 2



Scheme 3



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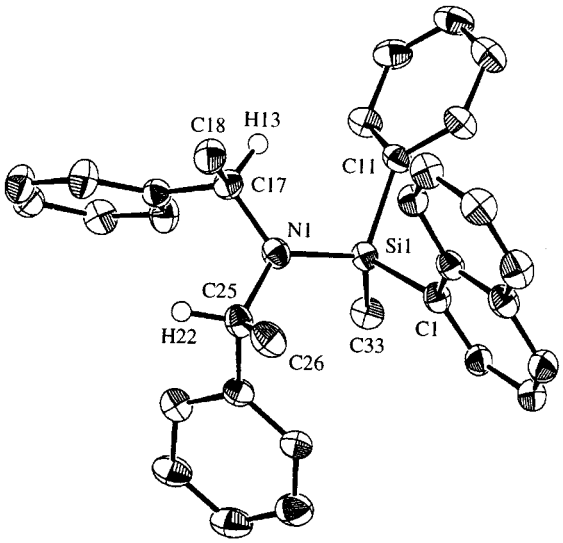
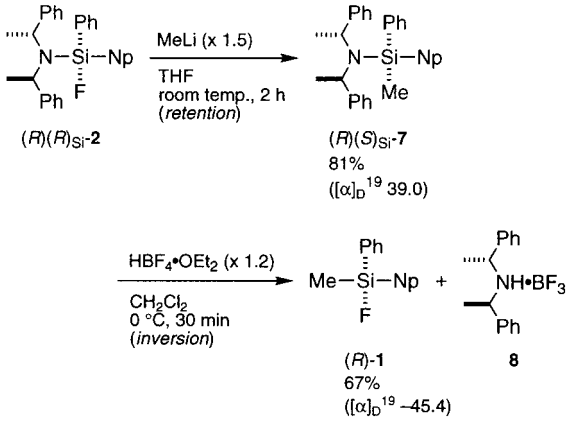


Figure 2. Crystal structure of $(R)(S)_{Si}$-**7**, shown at the 50% probability level. One of the three independent molecules is shown. H atoms except for H13 and H22 are omitted for clarity.

Scheme 4



uration is in agreement with the established preference of stereochemistry in the nucleophilic substitution of fluorosilanes with alkyllithiums.[2]

Finally, the stereospecific deamination−fluorination reaction of $(R)(S)_{Si}$-**7** was achieved.[9] Treatment of (R)-$(S)_{Si}$-**7** with HBF_4·Et_2O in CH_2Cl_2 at 0 °C afforded the fluorosilane (R)-**1** together with the amine−boron trifluoride complex **8** (Scheme 4). The hexane-insoluble complex **8** was easily separated from the reaction mixture. From the filtrate, after recrystallization from pentane, (R)-**1** was obtained in 67% yield; $[\alpha]_D^{19} = -45.4$ ($c = 9.00$, Et_2O) (lit.[1b] $[\alpha]_D^{19} = -46.9$ ($c = 8.12$, Et_2O)). Several points deserve comment. (1) The deamination reaction proceeds with inversion of the configuration at silicon. (2) The strong protic acid HBF_4·Et_2O reacts with the amino group selectively, keeping the aryl groups intact.[10] A similar reaction of $(R)(S)_{Si}$-**7** with BF_3·Et_2O, which was reported to be an effective reagent for the conversion of the menthoxysilane to the corresponding fluorosilane (inversion),[1b] proceeded very slowly in Et_2O even under refluxing. (3) Other attempted deamination reactions using gaseous HCl, aqueous HCl solution, MeOH, and *t*-BuOH gave a racemic mixture of the corresponding chlorosilane, silanol, and alkoxysilanes, respectively. (4) The optically active amine **3** can be recovered from the complex **8** by treatment with aqueous KOH solution in 80% recovered yield.

Conclusion

We achieved a new, convenient access to optically active (1-naphthyl)phenylmethylfluorosilane (**1**) using an optically active amine through optical resolution, epimerization of {bis[(*R*)-1-phenylethyl]amino}(1-naphthyl)phenylfluorosilane (**2**), and the subsequent stereospecific methylation and deamination−fluorination reaction. This method can be an alternative to optical resolution using the (−)-menthoxy group, especially in terms of the easy separation of the diastereomers and the facile removal of the amino group. The scope and limitation of this method are currently under study.

Experimental Section

General Remarks. ^1H (270 MHz), ^{13}C (67.94 MHz), ^{11}B (86.68 MHz), ^{19}F (254.19 MHz), and ^{29}Si (53.67 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer. ^1H and ^{13}C chemical shifts were referenced to internal benzene-d_6 (^1H, δ 7.200 ppm), CD_2Cl_2 (^1H, δ 5.300 pm), and $CDCl_3$ (^{13}C, δ 77.00 ppm). ^{11}B chemical shifts were referenced to external BF_3·Et_2O (0 ppm). ^{19}F chemical shifts were referenced to external $CFCl_3$ (0 ppm). ^{29}Si chemical shifts were referenced to external tetramethylsilane (0 ppm). Optical rotations were measured with a JASCO DIP-370 digital polarimeter. Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer. Melting points were measured with a Yanaco MP-S3 apparatus and were uncorrected. Infrared spectra were recorded on a JASCO FT/IR-430 Fourier transform infrared spectrometer. The elemental analyses were performed at the Microanalysis Division of the Institute for Chemical Research, Kyoto University: analytical samples were purified by recrystallization.

(+)-Bis[(*R*)-1-phenylethyl]amine (**3**), which was claimed to be 99+% ee/GLC, with $[\alpha]_D^{20} = +199.0$ (neat), was purchased from Aldrich. *n*-Butyllithium in hexane was purchased from Wako Pure Chemical Industries. Methyllithium in Et_2O and AgF were purchased from Kanto Chemical Co., Inc. HBF_4·Et_2O (tetrafluoroboric acid−diethyl ether complex) was purchased from Aldrich. THF and Et_2O were distilled from sodium benzophenone ketyl or K/Na alloy under a nitrogen atmosphere. Hexane was distilled over sodium wire under nitrogen. Dichloromethane was distilled from CaH_2 under nitrogen. Acetonitrile was distilled from CaH_2 and then from P_2O_5 under nitrogen. Nitromethane was passed through an alumina column (ICN Alumina N, activity I) prior to use. (1-Naphthyl)-phenyldifluorosilane was prepared by fluorination of (1-naphthyl)phenyldichlorosilane with ZnF_2;[11] the former was prepared by reaction of phenyltrichlorosilane with naphthyllithium. All reactions were carried out under an inert atmosphere unless otherwise noted.

Preparation of {Bis[(*R*)-1-phenylethyl]amino}[(*R*)-1-naphthyl]phenylfluorosilane ($(R)(R)_{Si}$-2). To a solution of amine **3** (900 mg, 4.0 mmol) in THF (5.0 mL) was added *n*-butyllithium in hexane (1.6 M, 2.5 mL, 4.0 mmol) at 0 °C over 20 min. After the mixture was stirred for a further 20 min, a yellow solution of lithium amide **4** was obtained. To

(9) Stereochemical aspects of the reactions of the silicon−nitrogen bond: (a) Sommer, L. H.; Citron, J. D.; Frye, C. L. *J. Am. Chem. Soc.* **1964**, *86*, 5684. (b) Sommer, L. H.; Citron, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 5797.

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the solution was added (1-naphthyl)phenyldifluorosilane (**5**; 1.10 g, 4.0 mmol) in THF (3.0 mL) at 0 °C over 30 min. The reaction mixture was stirred at that temperature for 1 h and at room temperature for 6 h. Trimethylchlorosilane (0.5 mL, 4.0 mmol) was added dropwise to the reaction mixture at room temperature. (Note: Treatment of the reaction mixture with trimethylchlorosilane made the isolation of **2** easier; otherwise, the excess lithium amide caused some decomposition of **2**.) After the mixture was stirred for 1 h, the solvent was removed. The residue was diluted with benzene (10 mL) and filtered. The filtrate was concentrated to give crude **2** as a viscous substance. The oily residue was dissolved in CH_3NO_2 (1.0 mL) under sonication and stored in a refrigerator for 1 h to afford $(R)(R)_{Si}$-**2** (695 mg, 37% yield, 99% de) as a white precipitate. Concentration of the mother liquor gave the other crude diastereomer $(R)(S)_{Si}$-**2** (1.27 g, ca. 80% de) as a yellow liquid. For epimerization (see below), the liquid was stirred in CH_3CN (5.3 mL) in the presence of AgF (17 mg, 0.13 mmol) at room temperature for 1 day, during which time white precipitates gradually deposited. The solvent was evaporated. The residue was triturated with CH_3NO_2 (2 mL) and filtered. The filter cake was dissolved in THF (10 mL) and filtered to remove insoluble AgF. The filtrate was concentrated to give $(R)(R)_{Si}$-**2** (442 mg, 24% yield, >99% de) as a white solid. The combined yield was 61%. $[\alpha]_D^{16} = 16.0$ ($c = 3.00$, $CHCl_3$). Mp: 133.5−135.0 °C. ^{1}H NMR (C_6D_6): δ 1.63 (d, $J = 7.0$ Hz, 6 H), 4.61 (q, $J = 7.0$ Hz, 2H), 6.95−7.43 (m, 16H), 7.63−7.71 (m, 4H), 7.91 (dd, $J = 6.8$ and 1.1 Hz, 1H), 8.78 (d, $J = 8.1$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 21.49, 53.51, 124.89, 125.61, 125.97, 126.63, 127.49, 127.67, 127.82, 128.14, 128.66, 129.06, 129.09, 129.70, 131.05, 132.22, 132.49, 133.26, 133.84, 134.18, 134.93, 134.97, 136.41, 136.48, 136.68, 143.81, 143.86. ^{29}Si NMR ($CDCl_3$): δ −18.2 (d, $^1J_{Si-F} = 286$ Hz). ^{19}F NMR (C_6D_6): δ −138.30. MS: *m/e* 475 (M^+, 22), 460 ($M^+ - Me$, 31), 251 ($M^+ - (PhMeHC)_2N$, 36), 105 ($PhMeHC^+$, 100). Anal. Calcd for $C_{32}H_{30}NFSi$: C, 80.80; H, 6.36; N, 2.95. Found: C, 81.08; H, 6.33; N, 2.91.

Epimerization of $(R)(S)_{Si}$-2 to $(R)(R)_{Si}$-2. The crude diastereomeric 1:1 mixture of **2**, prepared as described above from **5** (1.10 g, 4.0 mnol) and the lithium amide **4**, was stirred in CH_3CN (8.0 mL) in the presence of AgF (25 mg, 0.20 mmol) at room temperature for 1 day. The solvent was evaporated. The residue was triturated with CH_3NO_2 (5 mL) and filtered. The filter cake was dissolved in THF (10 mL) and the solution filtered to remove insoluble AgF. The filtrate was concentrated to give $(R)(R)_{Si}$-**2** (1.29 g, 68% yield, 96% de) as a white solid.

Preparation of {Bis[(*R*)-1-phenylethyl]amino}[(*S*)-1-naphthyl]phenylmethylsilane ($(R)(S)_{Si}$-7). To a solution of $(R)(R)_{Si}$-**2** (1.43 g, 3.0 mmol) in THF (6.0 mL) was added methyllithium in Et_2O (1.14 M, 4.0 mL, 4.5 mmol) at 0 °C over 30 min. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 2 h. The solvent was evaporated. The residue was diluted with benzene (10 mL) and the solution filtered. The filtrate was concentrated. The remaining solid was recrystallized from hexane to give $(R)(S)_{Si}$-**7** (1.14 g, 81% yield) as colorless crystals. $[\alpha]_D^{19} = 39.0$ ($c = 1.00$, $CHCl_3$). Mp: 124.0−125.0 °C. ^{1}H NMR (C_6D_6): δ 0.66 (s, 3H), 1.65 (d, $J = 6.8$ Hz, 6H), 4.72 (q, $J = 6.8$ Hz, 2H), 6.90−7.42 (m, 21H), 7.61−7.75 (m, 4H), 8.09 (dd, $J = 7.0$ and 1.4 Hz, 1H), 8.34 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 2.21, 21.75, 53.80, 124.85, 125.07, 125.19, 126.34, 127.48, 127.58, 128.03, 128.79, 128.91, 129.65, 130.17, 133.53, 135.58, 136.21, 136.73, 137.10, 139.05, 145.14. ^{29}Si NMR ($CDCl_3$): δ −6.3. MS: *m/e* 471 (M^+, 30), 456 ($M^+ - Me$, 45), 352 (59), 247 ($M^+ - (PhMeHC)_2N$, 69), 105 ($PhMeHC^+$, 100). Anal. Calcd for $C_{33}H_{33}NSi$: C, 84.03; H, 7.05; N, 2.97. Found: C, 84.15; H, 7.17; N, 2.84.

Preparation of (*R*)-(1-naphthyl)phenylmethylfluorosilane ((*R*)-1). To a solution of $(R)(R)_{Si}$-**7** (2.50 g, 5.3 mmol) in CH_2Cl_2 (12 mL) was added $HBF_4 \cdot Et_2O$ (1.1 mL, 6.4 mmol) at 0 °C over 10 min. The reaction mixture was stirred at 0 °C for 30 min. The solvent was evaporated. The residue was diluted with pentane (50 mL) and the solution filtered to remove the amine−boron trifluoride **8**. The filtrate was concentrated to leave solids, which were recrystallized from pentane several times to give (*R*)-**1** as colorless crystals: first crop (329 mg), $[\alpha]_D^{16} = -45.4$ ($c = 9.00$, Et_2O); second crop (435 mg), $[\alpha]_D^{18} = -44.2$ ($c = 9.00$, Et_2O); third crop (182 mg), $[\alpha]_D^{19} = -43.8$ ($c = 8.60$, Et_2O) (lit.[1b] $[\alpha]_D^{19} = -46.9$ ($c = 8.12$, Et_2O)) (67% yield in total). Mp: 67.0−68.0 °C (lit.[1b] mp: 67.5−68.0 °C). ^{1}H NMR (CD_2Cl_2): δ 0.89 (d, $J = 7.6$ Hz, 3 H), 7.35−7.99 (m, 12H). ^{13}C NMR ($CDCl_3$): δ −1.20, −0.97, 125.01, 125.79, 126.40, 128.05, 128.10, 128.93, 130.60, 131.36, 132.11, 132.33, 133.24, 133.96, 134.70, 134.77, 134.93, 136.53. ^{29}Si NMR ($CDCl_3$): δ −10.9 (d, $^1J_{Si-F} = 281$ Hz). ^{19}F NMR (C_6D_6): δ −162.17. MS: *m/e* 266 (M^+, 100), 251 ($M^+ - Me$, 94), 173 (34), 139 ($M^+ - Naph$, 7).

(+)-Bis[(*R*)-1-phenylethyl]amine−Boron Trifluoride (8). Mp: 214.0−216.0 °C. ^{1}H NMR (CD_2Cl_2): δ 1.68 (d, $J = 7.0$ Hz, 6H), 1.75 (broad, 1H), 3.93 (q, $J = 7.0$ Hz, 2H), 7.26−7.50 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 20.54, 57.61, 127.42, 129.49, 129.72, 134.48. ^{29}Si NMR ($CDCl_3$): δ −0.92. ^{19}F NMR ($CDCl_3$): δ −145.75. ^{11}B NMR ($BF_3 \cdot Et_2O$): δ −0.9. MS: *m/e* 225 ($M^+ - BF_3$, 5), 251 ($M^+ - Me$, 94), 173 (34), 105 ($PhMeHC^+$, 100).

Recovery of (+)-Bis[(*R*)-1-phenylethyl]amine (3). To a solution of **8** (586 mg, 2.0 mmol) in THF (10 mL) was added slowly a 1 M KOH aqueous solution (10 mL) at room temperature. After it was stirred at that temperature for 20 min, the reaction mixture was extracted with Et_2O (30 mL × 3). The combined organic layer was dried with K_2CO_3 and filtered. The filtrate was concentrated and distilled bulb-to-bulb (109−115 °C/0.5 mmHg, bath temperature) to give **3** (360 mg, 80% yield). $[\alpha]_D^{16} = 170$ ($c = 3.00$, cyclohexane) (for the purchased sample, $[\alpha]_D^{17} = 168$ ($c = 3.00$, cyclohexane)).

X-ray Structure Determinations for $(R)(R)_{Si}$-2 and $(R)(S)_{Si}$-7. Crystal Data for $(R)(R)_{Si}$-2: $C_{32}H_{30}NSiF$; $M_r = 475.68$; Rigaku RAXIS-IV imaging plate area detector; crystal size 0.40 × 0.40 × 0.30 mm; monoclinic, space group $P2_1$ (No. 4), $Z = 2$; $a = 9.1573(5)$ Å, $b = 15.1602(8)$ Å, $c = 9.5858(5)$ Å; $\beta = 109.897(3)°$; $V = 1251.3199$ Å^3, $D_{calcd} = 1.262$ g/cm^3; $\mu = 1.23$ cm^{-1} (Mo Kα, $\lambda = 0.710\ 70$ Å); $F(000) = 504.00$; $T = 193$ K; $2\theta_{max} = 55.1°$. The structure analysis is based on 2842 reflections, 2712 of which are observed ($I > 3.00\sigma(I)$), and 325 parameters. The structure was solved by direct methods and refined by full-matrix least squares on $|F|^2$: $R = 0.034$, $R_w = 0.050$; goodness of fit indicator 1.27; maximum/minimum peak in final difference map +0.24/−0.30 e/Å^3.

Crystal Data for $(R)(S)_{Si}$-7: $C_{33}H_{33}NSi$; $M_r = 471.72$; Rigaku RAXIS-IV imaging plate area detector; crystal size 0.50 × 0.30 × 0.30 mm; triclinic, space group $P1$ (No. 1), $Z = 3$; $a = 14.8474(3)$ Å, $b = 14.8549(3)$ Å, $c = 10.8778(2)$ Å; $\beta = 104.073(2)°$; $V = 1954.39(10)$ Å^3, $D_{calcd} = 1.202$ g/cm^3; $\mu = 1.1$ cm^{-1} (Mo Kα, $\lambda = 0.710\ 70$ Å); $F(000) = 756.00$; $T = 273$ K; $2\theta_{max} = 55.1°$. The structure analysis is based on 8083 reflections, 7729 of which are observed ($I > 3.00\sigma(I)$), and 959 parameters. The structure was solved by direct methods and refined by full-matrix least squares on $|F|^2$: $R = 0.047$, $R_w = 0.088$; goodness of fit indicator 1.71; maximum/minimum peak in final difference map +0.35/−0.43 e/Å^3.

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Supporting Information Available: Listings of crystal data, X-ray experimental details, atomic coordinates, thermal parameters, bond lengths, and bond angles for the compounds $(R)(R)_{Si}$-**2** and $(R)(S)_{Si}$-**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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