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Stereocontrolled synthesis of tertiary silanes via optically pure 1,3,2-oxazasilolidine derivatives

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ABSTRACT

Optically pure 1,3,2-oxazasilolidine derivatives were synthesized from a chiral 1,2-amino alcohol. These heterocyclic compounds containing a stereogenic silicon atom produced tertiary silanes with excellent optical purity through successive reactions with Grignard reagents and diisobutylaluminum hydride. Stereochemical course of the reactions of the oxazasilolidine at the chiral silicon atom was elucidated based on the absolute configurations of the products and the substrate which were determined by chiral HPLC and X-ray crystallographic analyses.

1. Introduction

Optically active organosilicon compounds containing a stereogenic silicon atom have been studied for a wide range of applications, such as chiral auxiliaries [1], reagents [2], and resolving agents [3], drug candidates [4], stereoregulated polymers and their monomers [5]. Since these compounds retain unique properties that do not exist in the carbon-based counterparts, they have applications that are clearly differentiated from those of the carbon-based molecules (e.g., chiral auxiliaries that can be used as C–H or C–OH equivalents via substitution with F^- [1d] or the Tamao oxidation [1a], reagents for asymmetric hydrosilylations [2a,b,d,f], optically active polymers that retain flexibility, thermal stability, conductivity, nonlinear optical properties, etc. [5]).

However, the preparation of optically active organosilicon compounds is still a challenging task and mostly relies on the classical optical resolution of a single starting material, 1-NpPhMeSiOMen [1-Np = 1-naphthyl, Men = (−)-menthyl], which was developed by Sommer et al. [6] due to the lack of an efficient, versatile method to synthesize these compounds in a stereocontrolled manner. Although not a few methods have been developed to synthesize these compounds by using optical resolutions [6,7] or stereocontrolled reactions [8] and some of them provide the products with high optical purity [6,7,8a–g], none of these methods can provide a wide range of *Si*-stereogenic organosilicon compounds. With this background, we sought to develop a new versatile approach to synthesize optically active *Si*-stereogenic organosilicon compounds in a stereocontrolled manner. In this paper, we wish to describe the development of a versatile method that uses optically pure 1,3,2-oxazasilolidine derivatives as key intermediates to synthesize tertiary silanes with excellent optical purity.

2. Results and discussion

2.1. Synthetic strategy

The strategy of the present method is outlined in Scheme 1. Enantiopure 1,2-amino alcohols **1** are used as chiral sources and allowed to react with a prochiral silane derivative **2**, which has two leaving groups on its silicon atom, to synthesize 1,3,2-oxazasilolidine derivatives **3**. It is expected that the 1,3,2-oxazasilolidine key intermediates are formed with high stereoselectivity by an appropriate design of the 1,2-amino alcohol. Since Si–N bonds are more reactive toward nucleophiles than Si–O bonds in general [8f,g,9], an equimolar amount of a *C*-nucleophile would exclusively substitute the amino group on the chiral silicon atom of **3** to afford silyl ethers **4**. The silyl ethers **4** are expected to be useful as precursors of tertiary and quaternary silanes, or silyl ethers via nucleophilic attack of hydride, *C*-nucleophiles, or *O*-nucleophiles, respectively. In this study, we aimed to synthesize optically active tertiary silanes, which have much wider applications (e.g., monomers of stereoregular silicon-containing polymers [5a,b], reagents for asymmetric hydrosilylations [2a,b,d,f], and precursors of a variety of optically active organosilicon compounds via Si–H modifications [10]) than the other two potential targets. Phosphorus-based

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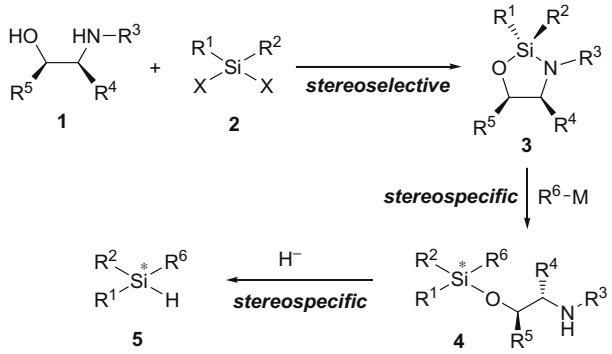


Scheme 1. Stereocontrolled synthesis of *Si*-stereogenic tertiary silanes **5** via 1,3,2-oxazasilolidine intermediates **3**.

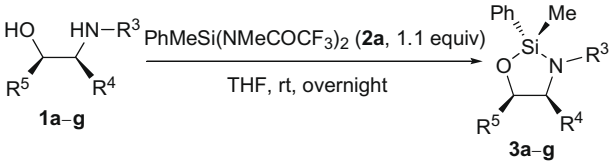
five-membered rings derived from chiral 1,2-amino alcohols (1,3,2-oxazaphospholidines) have been successfully used to synthesize optically pure organophosphorus compounds, such as ligands and biologically active compounds [11]. We have also developed a method to synthesize stereoregulated oligonucleotide analogues with *P*-modifications via 1,3,2-oxazaphospholidine intermediates [12]. These studies have also inspired the strategy of this study.

It has been reported that optically pure 1,3,2-oxazasilolidine derivatives (Fig. 1, **6**) were synthesized by using the corresponding amino acids, and used as precursors of optically active *Si*-stereogenic organosilicon compounds [8f,g]. However, a partial loss of optical purity occurred due to the epimerization of reaction intermediates. Silicon-containing heterocycles derived from C_2-symmetric diols **7** have also been developed and the successive nucleophilic substitutions at their silicon atoms afforded optically active silanes [8d,e]. However, stereoselectivity of the reactions was strongly dependent on the structure of nucleophiles because the stereoselectivity is controlled only by the stereoelectronic effects of **7** and the leaving ability of the two hydroxy groups at the silicon atoms is virtually the same. In contrast, a stoichiometric nucleophile is expected to substitute the amino group of the 1,3,2-oxazasilolidine **3** exclusively due to the significant difference in reactivity between the Si–N and Si–O bonds.

2.2. Synthesis of optically active 1,3,2-oxazasilolidine derivatives

Firstly, the stereoselective synthesis of 1,3,2-oxazasilolidine derivatives was investigated. A variety of chiral 1,2-amino alcohols (Table 1, **1a**–**g**) were allowed to react with bis(*N*-methyl-2,2,2-trifluoroacetamido)methylphenylsilane **2a** in THF under anhydrous conditions. The prochiral silane **2a** was employed because it does not generate HCl upon reaction with amino alcohols and the resulting *N*-methyl-2,2,2-trifluoroacetamide can be removed *in vacuo* more easily than *N*-methylacetamide, which would be generated from bis(*N*-methylacetamido)methylphenylsilane, the starting material of **6** [8g,h]. Since the resultant 1,3,2-oxazasilolidine derivatives **3a**–**g** were extremely sensitive to moisture, crude **3a**–**g** were obtained upon removal of any volatile reagents under inert atmosphere, and analyzed by ^{1}H NMR to determine the diastereoselectivity of the reactions. The analysis showed that the desired oxazasilolidine derivatives **3a**–**g** were generated with modest to good diastereoselectivity (d.r. = 62:38–89:11) (Table 1). Oxazasilolidine derivatives having a substituent at the four-position were prone to give higher diastereoselectivity than those having a substituent at the five-position (entry 1 vs. 2, 3 vs. 4). Formation of an oxazasilolidine was not observed when a *p*-nitrophenyl group was used as the *N*-substituent of 1,2-amino alcohol (entry 7). To our surprise, when crude **3e** (d.r. = 89:11, entry 5) was washed with dry Et_2O, only the major diastereomer of **3e** remained as crystals and isolated in 64% yield (entry 6). An X-ray crystallographic analysis of the resultant **3e** showed that the absolute configuration of the chiral silicon atom was R_{Si} (Fig. 2). It should be noted that **3e** as well as the other oxazasilolidines were configurationally stable at r.t. but underwent epimerization at an elevated temperature. For example, d.r. of crude **3e** was lowered upon heating at 90 °C for 7 h in dry toluene (R_{Si}:S_{Si} = 60:40).

Table 1
Synthesis of 1,3,2-oxazasilolidines **3a**–**g**.



Entry	**1**	R^3	R^4	R^5	yield	R_{Si}:S_{Si} [a]
1	**a**	Ph	H	*i*-Pr	66%	62:38
2	**b**	Ph	*i*-Pr	H	66%	78:22
3	**c**	Ph	H	Ph	67%	80:20
4	**d**	Ph	Ph	H	90%	85:15
5	**e**	*p*-An[d]	Ph	H	90%	89:11
6	**e**	*p*-An[d]	Ph	H	64%	>99:1[c]
7	**f**	*p*-$NO_2C_6H_4$	Ph	H	–	–
8[b]	**g**	Ph	*t*-Bu	H	83%	80:20

[a] Determined by ^{1}H NMR.
[b] Racemic **1g** was used.
[c] Purified by precipitation from Et_2O.
[d] An = anisyl.

2.3. Nucleophilic substitution of 1,3,2-oxazasilolidine derivatives with Grignard reagents

Next, the diastereopure 1,3,2-oxazasilolidine **3e** thus obtained was allowed to react with a variety of Grignard reagents. Subsequent treatment of the products with Boc_2O and aqueous work-up afforded the desired silyl ethers **4a**–**g** with excellent diastereopurity (d.r. = 94:6–99:1, summarized in Table 2) in modest to good

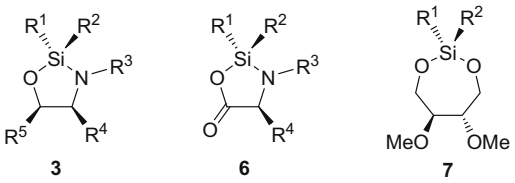


Fig. 1. Silicon-containing heterocyclic intermediates for asymmetric synthesis of silanes.

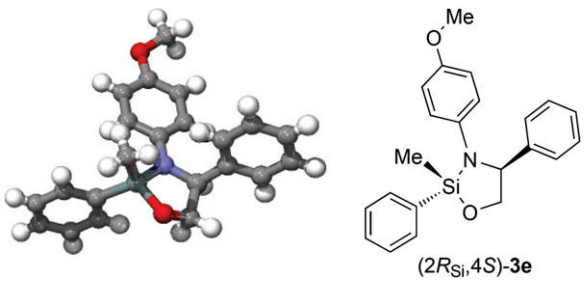
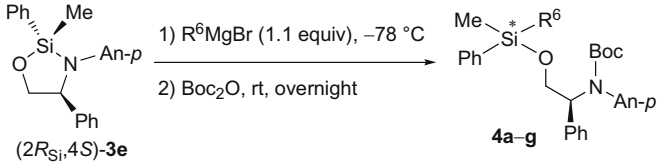


Fig. 2. X-ray crystal structure of ($2R_{Si}$,4*S*)-**3e**.

Table 2
Reaction of ($2R_{Si}$,4*S*)-**3e**[a] with Grignard reagents.



Entry	**4**	R^6	solvent	Time[b] (h)	Yield[c] (%)	d.r.[d]
1	**a**	1-Np	THF	2	55	99:1
2[e]	**a**	1-Np	THF	2	60	1:99
3	**b**	*o*-$MeOC_6H_4$	THF	6	54	99:1
4	**c**	*o*-MeC_6H_4	THF	2	57	95:5
5	**c**	*o*-MeC_6H_4	THF–toluene (1:4, v/v)	6	53	99:1
6	**d**	CH_2 = CH	THF	2	44	96:4
7	**e**	CH_2 = $CHCH_2$	THF	2	21	94:6
8	**f**	Me_2C = CH	THF	2	59	96:4
9	**g**	mesityl	THF	2	43	95:5

[a] Diastereopure **3e** (d.r. > 99:1) was used.
[b] Reaction time for step 1.
[c] Isolated yield of **4a**–**g** from 1,2-amino alcohols **1e** (3 steps).
[d] Determined by ^{1}H NMR.
[e] (*R*)-2-(*p*-Methoxyanilino)-2-phenylethanol [(*R*)-**1e**] was used as the starting material.

total yields from the 1,2-amino alcohol (*S*)-**1e** (3 steps) [13,14]. As we expected, the Grignard reagents substituted the amino group on the silicon atom virtually exclusively. Each enantiomer of the 1,2-amino alcohol **1e** [(*R*)- and (*S*)-**1e**] afforded the corresponding diastereopure silyl ether (entries 1 and 2), though the absolute configurations of the silicon atoms could not be assigned at this point. The diastereopurity of the product was slightly improved when the reaction was conducted in a less-polar reaction medium (entries 4 and 5).

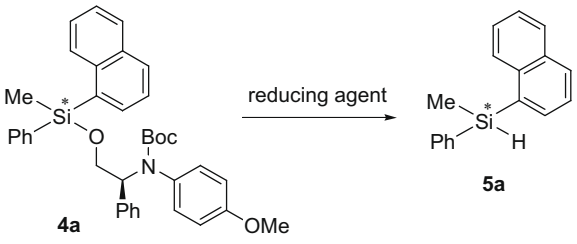
2.4. Synthesis of optically active Si-stereogenic tertiary silanes by reduction of silyl ethers

Next, we examined the synthesis of tertiary silanes by reduction of the diastereopure silyl ethers thus obtained. Lithium aluminum hydride (LAH) [6] and diisobutylaluminum hydride (DIBAL) [7a,15], both of which are known to reduce silyl ethers to tertiary silanes with *retention of configuration*, were employed. Diastereopure silyl ether **4a** was reduced under several different conditions (Table 3). The results showed that DIBAL gave the desired tertiary silane **5a** virtually stereospecifically, though an extended reaction at an elevated temperature was required (entry 4). Sterically less-hindered LAH gave the product with lower optical purity (entries 1 and 2). Chiral HPLC analysis (Daicel CHIRALCEL OD-H) [16] of the resultant **5a** showed that the absolute configuration of the silicon atom was R_{Si} [17]. Under these conditions, (R_{Si})- and (S_{Si})-methyl-1-naphthylphenylsilane [(R_{Si})- and (S_{Si})-**5a**], *o*-anisylmethylphenylsilane **5b**, methylphenyl(*o*-tolyl)silane **5c** were synthesized from the corresponding silyl ethers **4a**–**c** with excellent optical purity (Table 4). It should be noted that the relatively low-boiling tertiary silanes obtained from the silyl ethers **4d**–**f** could not be isolated from the solvent. The silyl ether **4g** did not give the corresponding tertiary silane under the same conditions probably due to the steric hindrance of the mesityl group on the silicon atom. Both enantiomers of **5a** were obtained with similar yields and optical purity. The major enantiomer of the resultant **5b** was eluted faster than the minor enantiomer under the same chiral HPLC analytical conditions, thus tentatively assigned as (R_{Si})-isomer. Every attempt to separate the enantiomers of **5c** by using chiral HPLC and GC resulted in failure. As described above, reductions of silyl ethers with DIBAL proceed with *retention of configuration* [7a,15]. It indicates that the absolute configuration of the silicon atom of **4a**, the precursor of (R_{Si})-**5a** is also (R_{Si}) and the reaction of the 1,3,2-oxazasilolidine ($2R_{Si}$,4*S*)-**3e** with Grignard reagents proceeded with *inversion of configuration* at the silicon atom.

2.5. Mechanism of stereoselective formation of 1,3,2-oxazasilolidine derivatives

In order to elucidate the mechanism of the stereoselective formation of 1,3,2-oxazasilolidine derivatives, we carried out several experiments described below. Firstly, the reactivity of **2a** toward the amino and the hydroxy groups of the 1,2-amino alcohols used in this study was investigated to determine whether the amino or the hydroxy group reacted with the silicon atom of **2a** first. Benzylphenylamine and methanol were used as model compounds of the amino and the hydroxy moieties of the 1,2-amino alcohols, respectively. Thus, **2a** was allowed to react with benzylphenylamine (2 equiv.) in $CDCl_3$, and the reaction was monitored by ^{1}H NMR to find that no nucleophilic substitution at the silicon atom occurred (Scheme 2). In contrast, addition of MeOH (2 equiv.) to

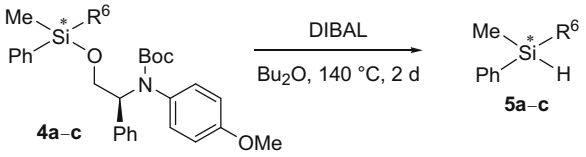
Table 3
Reduction of **4a**.



Entry	Reaction conditions	Yield (%)	R_{Si}:S_{Si}[a]
1	LAH (5 equiv.), THF, reflux, 1.5 h	50	82:18
2	LAH (3 equiv.), Bu_2O, 140 °C, 8 h	27	85:15
3	DIBAL (10 equiv.), hexane, reflux, 3 d	9	93:7
4	DIBAL (6 equiv.), Bu_2O, 140 °C, 2 d	37	98:2

[a] Determined by HPLC (Daicel CHIRALCEL OD-H, 0.46 × 25 cm, hexane, 0.4 mL/min).

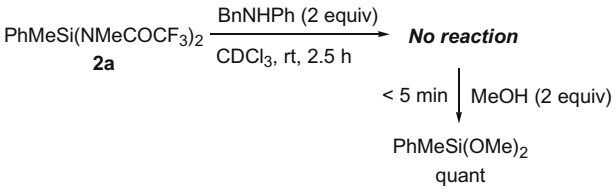
Table 4
Synthesis of tertiary silanes **5a–c**.



Entry	4	R^6	Yield (%)	R_{Si}: S_{Si}[a]
1	**a**	1-Np	37	98:2
2[b]	**a**	1-Np	41	3:97
3	**b**	*o*-$MeOC_6H_4$	68	97:3
4	**c**	*o*-MeC_6H_4	54	Not determined

[a] Determined by HPLC (Daicel CHIRALCEL OD-H, 0.46 × 25 cm, hexane, 0.4 mL/min).
[b] Silyl ether **4a** obtained from (*R*)-**1e** was used.

the mixture resulted in a quantitative formation of $PhMeSi(OMe)_2$ within 5 min. These experiments indicate that the hydroxy group of the 1,2-amino alcohol **1a–g** reacts with the silicon atom of **2a** first, and the following intramolecular nucleophilic attack of the amino group generates the oxazasilolidine derivative **3a–g**. To examine the relative reaction rates of the successive inter- and intramolecular nucleophilic attacks at the silicon atom, the reaction of **1e** with **2a** was carried out in dry THF-d_8 and monitored by ^1H NMR. The ^1H signals of the resultant $CF_3CONHMe$ at 2.96 and 2.95 ppm (methyl group) and that of **3e** at 5.17 ppm (5-H) were used for the quantitation. As shown in Fig. 3, the analysis showed that the first nucleophilic substitution, which was most likely by the hydroxy group of **1e** as depicted in Scheme 3, was completed within 30 min, whereas the second substitution reaction was significantly slow and required ca. 24 h, though the structure of the plausible reaction intermediate **8** could not be assigned due to the complexity of the reaction mixture.



Scheme 2. ^1H NMR analysis of reactivity of $PhMeSi(NMeCOCF_3)_2$ (**2a**) toward model compounds of amino and hydroxy groups of 1,2-amino alcohols.

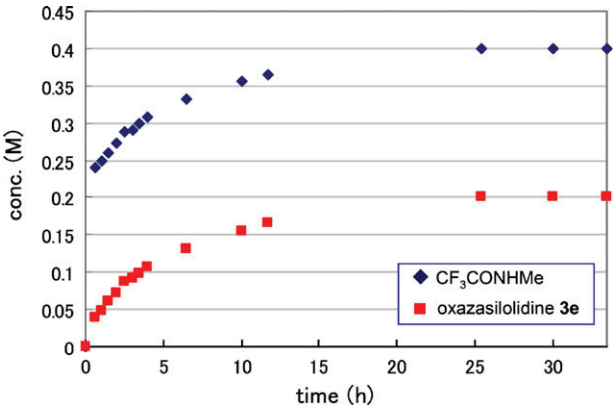
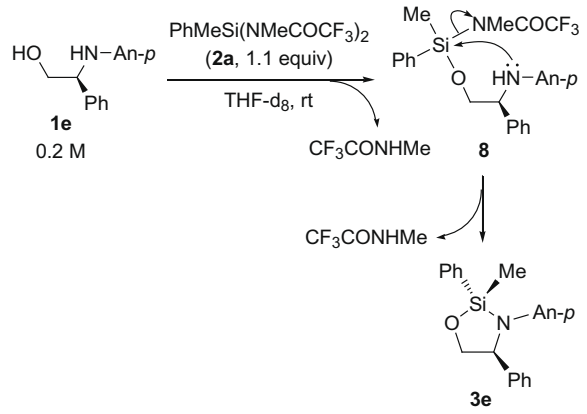


Fig. 3. Time course of formation of oxazasilolidine **3e** and accompanying generation of *N*-methyl-2,2,2-trifluoroacetamide.



Scheme 3. Formation of oxazasilolidine **3e** and generation of *N*-methyl-2,2,2-trifluoroacetamide via successive nucleophilic attacks of hydroxy and amino groups of **1e**.

Secondly, we heated the stereo-enriched oxazasilolidines **3a–g**, which were configurationally stable at r.t., in dry toluene under argon to find that all of these compounds underwent epimerization under these conditions as described above. It indicates that the (R_{Si})- and (S_{Si})-isomers of **3a–g** have similar thermodynamic stabil-

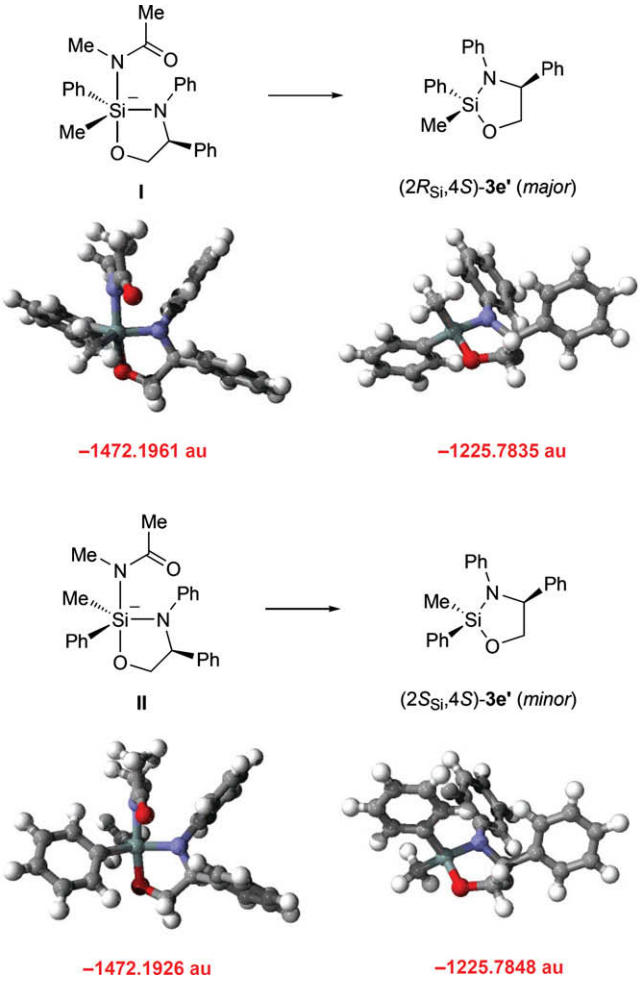


Fig. 4. Optimized structures and total energies of reaction intermediate and product models calculated at the HF/6-31G* level.

ity, and the preferential formation of the (R_{Si})-isomers of the oxazasilolidine derivatives **3a–g** was kinetically controlled. *Ab initio* molecular orbital calculations also supported the kinetic control. Thus, we used a model structure of the oxazasilolidine **3e**, in which the *N*-methyl-2,2,2-trifluoroacetamido group at the silicon atom and the *p*-anisyl group at the amino group were replaced with an *N*-methylacetamido group and a phenyl group, respectively, for simplicity, and calculated the optimized structures and total energies of the two diastereomers [(2R_{Si},4*S*)- and (2S_{Si},4*S*)-**3e′**] and the corresponding five-coordinated intermediates (**I** and **II**) (Fig. 4). The calculations showed that (2S_{Si},4*S*)-**3e′**, the model for the *minor* isomer of **3e**, was a little more stable than (2R_{Si},4*S*)-**3e′** (ΔE = 0.83 kcal/mol), while the intermediate **I**, which corresponds to (2R_{Si},4*S*)-**3e′**, was significantly more stable than the intermediate **II** (ΔE = 2.21 kcal/mol), indicating that the major isomer of the oxazasilolidine **3e** was generated through an intermediate corresponding to **I** under kinetic conditions.

3. Conclusion

In conclusion, 1,3,2-oxazasilolidine derivatives proved to be useful to synthesize *Si*-stereogenic tertiary silanes with excellent optical purity through successive reactions with Grignard reagents and a hydride reducing agent. A study on the oxazasilolidine ring formation processes indicated that the oxazasilolidine rings were formed via the fast nucleophilic attack of the hydroxy group of 1,2-amino alcohols and subsequent slow intramolecular cyclization by the nucleophilic attack of the amino group. The stereochemical course of the ring formation was kinetically controlled. Considering that the stereoselectivity of the reaction between the oxazasilolidine and Grignard reagents was virtually independent of the substituent introduced to the stereogenic silicon atom and the resultant silyl ethers are expected to produce quaternary silanes and other silyl ethers via subsequent reaction with *C*- and *O*-nucleophiles, the method developed in this study would expand the availability of optically active *Si*-stereogenic organosilicon compounds.

4. Experimental

4.1. General information

All NMR spectra were recorded on a Varian Mercury 300. ^{1}H NMR spectra were obtained at 300 MHz with tetramethylsilane (TMS) (δ 0.0) as an internal standard in $CDCl_3$ unless otherwise noted. ^{13}C NMR spectra were obtained at 75 MHz with $CDCl_3$ as an internal standard (δ 77.0) in $CDCl_3$. ^{29}Si NMR spectra were obtained at 60 MHz with tetramethylsilane (TMS) (δ 0.0) as an internal standard in $CDCl_3$. Chemical ionization (CI) mass spectra were recorded on a Shimadzu GCMS-QP5050A mass spectrometer. ESI mass spectra were recorded on an Applied Biosystems QSTAR. HPLC was carried out using a Daicel CHIRALCEL OD-H (0.46 × 25 cm). The X-ray intensities were collected with a Rigaku MERCURY CCD system and the crystal structure was solved with the SHELXL-97 program [18]. Silica gel column chromatography was carried out using Kanto silica gel 60 N (spherical, neutral, 63−210 μm) or NH silica gel (Fuji Silysia Chemical Inc., DM1020 100–200 mesh). Dry THF and ether were prepared by distillation from sodium benzophenone ketyl under argon prior to use. Other dry organic solvents were prepared by appropriate procedures. The other organic solvents were reagent grade and used as received. *Ab initio* molecular orbital calculations were carried out using the Spartan'04 [19] on a Dell Inc. PRECISION 650 workstation. Geometry optimizations and single-point energy calculations were carried out at the HF/6-31G* level.

4.2. Synthesis of bis(N-methyl-2,2,2-trifluoroacetamido)methylphenylsilane (**2a**)

N-Methyl-2,2,2-trifluoroacetamide (10.4 g, 82 mmol) was dissolved in dry THF (40 mL) under argon and dried over MS 4A overnight. The solution was cooled to 0 °C and a 2.64 M solution of BuLi in hexane (32 mL, 84 mmol) was added dropwise. The mixture was then stirred at r.t. for 1 h, refluxed for 1 h, and cooled to r.t. Dichloromethylphenylsilane (6.5 mL, 40 mmol) was then added dropwise, and the mixture was stirred for 2 h at 50 °C. The resultant precipitate was removed by filtration through a glass filter under argon, and the filtrate was concentrated under reduced pressure. The residue was purified by distillation under reduced pressure (bp 55–65 °C/30 Pa) to afford **2a** (10.5 g, 28 mmol, 70%) as a colorless liquid. A mixture of trifluoroacetamide rotamers. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72–7.40 (5H, m), 3.14–2.97 (6H, m), 0.90, 0.85, 0.77 (3H, s, s, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9 (q, $^2J_{CF}$ = 38.0 Hz), 140.7 (q, $^2J_{CF}$ = 38.9 Hz), 134.0, 133.4, 132.2, 131.6, 131.3, 130.3, 129.3, 128.6, 128.5, 128.4, 116.8 (q, $^1J_{CF}$ = 274 Hz), 116.7 (q, $^1J_{CF}$ = 273 Hz), 115.9 (q, $^1J_{CF}$ = 285 Hz), 115.6 (q, $^1J_{CF}$ = 284 Hz), 34.7, 34.5, −2.8, −3.1, −3.4. ^{29}Si NMR (60 MHz, $CDCl_3$) δ −13.3, −21.1. CI-MS: *m*/*z* 372 $[M]^+$. ESI-HRMS: *m*/*z* calcd for $C_{13}H_{15}F_6N_2O_2Si^+$ $[(M+H)^+]$ 373.0801, found 373.0828.

4.3. Synthesis of (2R_{Si},4*S*)-2-methyl-3-(*p*-methoxyphenyl)-2,4-diphenyl-1,3,2-oxazasilolidine [(2R_{Si},4*S*)-**3e**]. A general procedure for the synthesis of 1,3,2-oxazasilolidine derivatives **3a–g**

(*S*)-2-(*p*-Methoxyanilino)-2-phenylethanol [(*S*)-**1e**] (0.243 g, 1.0 mmol) was dried by repeated coevaporations with dry toluene and dissolved in freshly distilled THF (2.0 mL) under argon. The solution was slowly added dropwise to a stirred solution of **2a** (0.409 g, 1.1 mmol) in freshly distilled THF (3.0 mL) under argon at r.t. The resultant mixture was stirred at r.t. under argon overnight. The mixture was then concentrated to dryness under reduced pressure, and residual *N*-methyl-2,2,2-trifluoroacetamide was removed *in vacuo* to afford crude **3e** (0.328 g, 0.90 mmol, 90%). D.r. (R_{Si}:S_{Si}) of the crude **3e** was 89:11 (^{1}H NMR). The crude product was washed with freshly distilled Et_2O (3 × 1 mL) with a syringe under argon and dried *in vacuo* to afford (2R_{Si},4*S*)-**3e** (0.233 g, 0.64 mmol, 64%) as colorless crystals. D.r. (R_{Si}:S_{Si}) > 99:1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63–7.19 (10H, m), 6.66–6.39 (4H, m), 4.95 (1H, dd, *J* = 3.6, 6.3 Hz), 4.59 (1H, dd, *J* = 6.3, 9.3 Hz), 4.06 (1H, dd, *J* = 3.6, 9.9 Hz), 3.62 (3H, s), 0.92 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0, 142.2, 139.2, 134.4, 134.2, 130.8, 128.7, 128.2, 127.2, 126.3, 116.9, 114.5, 72.2, 61.5, 55.4, −2.8. ^{29}Si NMR (60 MHz, $CDCl_3$) δ 4.4. CI-MS: *m*/*z* 361 $[M]^+$. ESI-HRMS: *m*/*z* calcd for $C_{22}H_{24}NO_2Si^+$ $[(M + H)^+]$ 362.1571, found 362.1575.

4.4. Synthesis of methyl-1-naphthylphenyllsilyl ether **4a**. A general procedure for the synthesis of **4a–g**

(*S*)-2-(*p*-Methoxyanilino)-2-phenylethanol [(*S*)-**1e**] (0.243 g, 1.0 mmol) was dried by repeated coevaporations with dry toluene and dissolved in freshly distilled THF (2.0 mL) under argon. The solution was slowly added dropwise to a stirred solution of **2a** (0.409 g, 1.1 mmol) in freshly distilled THF (3.0 mL) under argon at r.t. The resultant mixture was stirred at r.t. under argon overnight. The mixture was then concentrated to dryness under reduced pressure, and residual *N*-methyl-2,2,2-trifluoroacetamide was removed *in vacuo* to afford crude **3e**, which was washed with freshly distilled Et_2O (3 × 1 mL) with a syringe under argon and dried *in vacuo* to afford diastereopure **3e** as colorless crystals. The diastereopure **3e** was dissolved in freshly distilled THF (4.0 mL) under argon and the solution was cooled to −78 °C. A freshly prepared solution of 1-naphthylmagnesium bromide in

dry THF (0.5 M) (2.2 mL, 1.1 mmol) was added dropwise, and the mixture was stirred for 2 h at −78 °C. Di-*tert*-butyl dicarbonate (0.46 mL, 2.0 mmol) was added, and the mixture was allowed to warm to r.t. and stirred for 1 h. A 0.3 M phosphate buffer solution (pH 7.4) (10 mL) was then added, and the mixture was extracted with Et_2O (4 × 10 mL). The organic layers were combined and washed with a 0.3 M phosphate buffer solution (pH 7.4) (10 mL). The aqueous layers were combined and extracted with Et_2O (10 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated to dryness under reduced pressure. The residue was purified by NH silica gel column chromatography (20 g of NH silica gel, 0–1.5% AcOEt in hexane) to afford **4a** (0.325 g, 0.55 mmol, 55%) as a colorless foam. D.r. = 99:1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (1H, d, J = 8.4 Hz), 7.89 (1H, d, J = 8.1 Hz), 7.84 (2H, t, J = 7.2 Hz), 7.47–7.08 (11H, m), 6.81–6.59 (6H, m), 4.65 (1H, t, J = 7.8 Hz), 4.34 (2H, m), 3.72 (3H, s), 1.41 (9H, s), 0.72 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 153.3, 139.7, 137.6, 137.1, 136.8, 135.3, 135.0, 134.3, 133.7, 133.4, 130.5, 129.2, 129.1, 128.8, 128.7, 127.7, 127.5, 127.3, 125.6, 125.4, 125.1, 113.4, 81.8, 66.8, 60.5, 55.3, 27.7, 0.4. ^{29}Si NMR (60 MHz, $CDCl_3$) δ −5.6. CI-MS: m/z 589 $[M]^+$. ESI-HRMS: m/z calcd for $C_{37}H_{40}NO_4Si^+$ $[(M+H)^+]$ 590.2721, found 590.2695. The enantiomer of **4a** (0.354 g, 0.60 mmol, 60%) was also obtained as a colorless foam from (*R*)-2-(*p*-methoxyanilino)-2-phenylethanol [(*R*)-**1e**] (0.243 g, 1.0 mmol) according to the same procedure (Table 2, entry 2). D.r. = 1:99. NMR and CI-MS spectra were identical to those of **4a**. ESI-HRMS: m/z calcd for $C_{37}H_{40}NO_4Si^+$ $[(M+H)^+]$ 590.2721, found 590.2701.

4.4.1. o-Anisylmethylphenylsilyl ether (*4b*)

The silyl ether **4b** (0.310 g, 0.54 mmol, 54%) was synthesized as a white foam from (*S*)-2-(*p*-methoxyanilino)-2-phenylethanol [(*S*)-**1e**] (0.243 g, 1.0 mmol) according to the general procedure shown above. The treatment of the oxazasilolidine **3e** with *o*-anisyl Grignard reagent was performed for 6 h. D.r. = 99:1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (2H, d, J = 6.3 Hz), 7.42–7.14 (8H, m), 6.96–6.82 (4H, m), 6.68–6.55 (4H, m), 4.68 (1H, t, J = 7.5 Hz), 4.43–4.37 (2H, m), 3.76 (3H, s), 3.71 (3H, s), 1.37 (9H, s), 0.51 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 156.8, 153.4, 140.0, 137.6, 137.6, 133.5, 131.5, 128.9, 128.9, 127.6, 127.3, 127.0, 124.5, 120.5, 113.0, 109.6, 81.6, 67.2, 59.9, 55.0, 54.6, 27.6, −0.7. ^{29}Si NMR (60 MHz, $CDCl_3$) δ −6.7. CI-MS: m/z 569 $[M]^+$. ESI-HRMS: m/z calcd for $C_{34}H_{40}NO_5Si^+$ $[(M+H)^+]$ 570.2670, found 570.2656.

4.4.2. Methylphenyl(o-tolyl)silyl ether (*4c*)

The silyl ether **4c** (0.291 g, 0.53 mmol, 53%) was synthesized as a white foam from (*S*)-2-(*p*-methoxyanilino)-2-phenylethanol [(*S*)-**1e**] (0.243 g, 1.0 mmol) according to the general procedure shown above. The treatment of the oxazasilolidine **3e** with *o*-tolyl Grignard reagent was performed for 6 h in dry THF–dry toluene (1:4, v/v). D.r. = 99:1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.65 (1H, m), 7.64–7.13 (11H, m), 6.80–6.76 (4H, m), 6.65–6.62 (2H, m), 4.59 (1H, t, J = 7.2 Hz), 4.35 (2H, m), 3.72 (3H, s), 2.35 (3H, s), 1.42 (9H, s), 0.60 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 153.4, 144.4, 139.9, 138.0, 137.3, 135.2, 135.0, 133.4, 130.2, 129.8, 128.9, 128.6, 127.8, 127.4, 127.2, 124.8, 113.3, 81.8, 66.8, 60.3, 55.2, 27.7, 23.5, 0.2. ^{29}Si NMR (60 MHz, $CDCl_3$) δ −5.8. CI-MS: m/z 553 $[M]^+$. ESI-HRMS: m/z calcd for $C_{34}H_{40}NO_4Si^+$ $[(M+H)^+]$ 554.2721, found 554.2709.

4.4.3. Methylphenylvinylsilyl ether (*4d*)

The silyl ether **4d** (0.217 g, 0.44 mmol, 44%) was synthesized as a colorless oil from (*S*)-2-(*p*-methoxyanilino)-2-phenylethanol [(*S*)-**1e**] (0.243 g, 1.0 mmol) according to the general procedure shown above. D.r. = 96:4. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63–7.60 (2H, m), 7.38–7.31 (3H, m), 7.20–7.12 (3H, m), 6.81–6.77 (2H, m), 6.62–6.43 (5H, m), 6.10 (1H, dd, J = 3.6, 14.7 Hz), 5.76 (1H, dd, J = 3.6, 20.4 Hz), 4.64 (1H, t, J = 7.5 Hz), 4.40–4.31 (2H, m), 3.72 (3H, s), 1.48 (9H, m), 0.35 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 153.5, 139.6, 137.1, 137.0, 134.8, 134.0, 133.7, 129.3, 128.4, 127.8, 127.6, 127.1, 113.2, 81.9, 66.3, 59.7, 55.2, 27.8, −2.8. ^{29}Si NMR (60 MHz, $CDCl_3$) δ −10.0. CI-MS: m/z 489 $[M]^+$. ESI-HRMS: m/z calcd for $C_{29}H_{36}NO_4Si^+$ $[(M+H)^+]$ 490.2408, found 490.2412.

4.4.4. Allylmethylphenylsilyl ether (*4e*)

The silyl ether **4e** (0.108 g, 0.21 mmol, 21%) was synthesized as a colorless oil from (*S*)-2-(*p*-methoxyanilino)-2-phenylethanol [(*S*)-**1e**] (0.243 g, 1.0 mmol) according to the general procedure shown above. D.r. = 94:6. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65–7.62 (2H, m), 7.42–7.35 (3H, m), 7.20–7.09 (3H, m), 6.70–6.50 (6H, m), 5.73 (1H, m), 4.88–4.80 (2H, m), 4.54 (1H, t, J = 7.5 Hz), 4.36–4.24 (2H, m), 3.74 (3H, s), 1.95 (2H, m), 1.48 (9H, s), 0.28 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 153.5, 139.3, 137.2, 134.6, 134.5, 134.1, 129.4, 128.4, 127.7, 127.1, 114.0, 113.2, 81.9, 66.2, 59.5, 55.2, 27.7, 23.2, −3.6. ^{29}Si NMR (60 MHz, $CDCl_3$) δ −3.7. CI-MS: m/z 503 $[M]^+$. ESI-HRMS: m/z calcd for $C_{30}H_{38}NO_4Si^+$ $[(M+H)^+]$ 504.2565, found 504.2542.

4.4.5. Methyl-2-methylpropen-1-ylphenylsilyl ether (*4f*)

The silyl ether **4f** (0.306 g, 0.59 mmol, 59%) was synthesized as a colorless oil from (*S*)-2-(*p*-methoxyanilino)-2-phenylethanol [(*S*)-**1e**] (0.243 g, 1.0 mmol) according to the general procedure shown above. D.r. = 96:4. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.60 (2H, m), 7.34–7.28 (3H, m), 7.18–7.07 (3H, m), 6.72–6.69 (2H, m), 6.63–6.53 (4H, m), 5.60 (1H, bs), 4.64 (1H, t, J = 7.2 Hz), 4.40–4.29 (2H, m), 3.72 (3H, s), 1.91 (3H, s), 1.67 (3H, s), 1.45 (9H, s), 0.35 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 154.5, 153.5, 139.7, 139.0, 135.4, 134.7, 133.8, 129.0, 128.5, 127.6, 127.6, 126.9, 121.2, 113.1, 81.7, 66.5, 59.5, 55.1, 29.7, 27.7, 23.9, −0.6. ^{29}Si NMR (60 MHz, $CDCl_3$) δ −13.0. CI-MS: m/z 517 $[M]^+$. ESI-HRMS: m/z calcd for $C_{31}H_{40}NO_4Si^+$ $[(M+H)^+]$ 518.2721, found 518.2725.

4.4.6. Mesitylmethylphenylsilyl ether (*4g*)

The silyl ether **4g** (0.248 g, 0.43 mmol, 43%) was synthesized as a colorless foam from (*S*)-2-(*p*-methoxyanilino)-2-phenylethanol [(*S*)-**1e**] (0.243 g, 1.0 mmol) according to the general procedure shown above. D.r. = 95:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–7.10 (8H, m), 6.88–6.79 (6H, m), 6.71–6.68 (2H, m), 4.62 (1H, t, J = 7.5 Hz), 4.32 (2H, d, J = 7.8 Hz), 3.76 (3H, s), 2.27 (3H, s), 2.24 (6H, s), 1.40 (9H, s), 0.58 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 153.4, 145.8, 143.0, 139.7, 139.3, 135.3, 133.9, 133.8, 129.8, 129.4, 128.8, 128.1, 127.8, 127.5, 127.3, 113.5, 81.8, 69.6, 67.0, 60.8, 55.3, 27.7, 25.4, 21.0, 5.9. ^{29}Si NMR (60 MHz, $CDCl_3$) δ −8.2. CI-MS: m/z 581 $[M]^+$. ESI-HRMS: m/z calcd for $C_{36}H_{44}NO_4Si^+$ $[(M+H)^+]$ 582.3034, found 582.3011.

4.5. Synthesis of (R_{Si})-methyl-1-naphthylphenyllsilane [(R_{Si})-*5a*]. A general procedure for the synthesis of tertiary silanes *5a–c*

Methyl-1-naphthylphenyllsilyl ether **4a** (0.236 g, 0.40 mmol) was dried by repeated coevaporations with dry toluene and dissolved in dry Bu_2O (5.0 mL) under argon. A 1 M solution of diisobutylaluminum hydride in hexane (2.8 mL, 2.8 mmol) was added dropwise at r.t., and the mixture was stirred at 140 °C for 2 d. The mixture was cooled to r.t. and diluted with Et_2O (10 mL). A 1 M HCl aqueous solution (10 mL) was carefully added and the mixture was extracted with Et_2O (3 × 10 mL). The organic layers were combined, washed with saturated NaCl aqueous solutions (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (15 g of silica gel, hexane) to afford (R_{Si})-**5a**

(37.2 mg, 0.15 mmol, 37%) as colorless crystals. ^{1}H NMR spectrum was identical to the data in the literature [8d]. Enantiomer ratio was determined to be (R_{Si})-**5a**:(S_{Si})-**5a** = 98:2 by chiral HPLC analysis (Daicel CHIRALCEL OD-H, 0.46 × 25 cm, hexane, 0.4 mL/min).

4.5.1. (S_{Si})-Methyl-1-naphthylphenyllsilane ((S_{Si})-*5a*)

(S_{Si})-Methyl-1-naphthylphenyllsilane (S_{Si})-**5a** (40.4 mg, 0.16 mmol, 41%) was synthesized as colorless crystals from (S_{Si})-methyl-1-naphthylphenyllsilyl ether [(S_{Si})-**4a**] (0.236 g, 0.40 mmol) according to the general procedure shown above. ^{1}H NMR spectrum was identical to the data in the literature [8d]. Enantiomer ratio was determined to be (R_{Si})-**5a**:(S_{Si})-**5a** = 3:97 by chiral HPLC analysis (Daicel CHIRALCEL OD-H, 0.46 × 25 cm, hexane, 0.4 mL/min).

4.5.2. o-Anisylmethylphenylsilane (*5b*)

o-Anisylmethylphenylsilane **5b** (31.2 mg, 0.14 mmol, 68%) was synthesized as a colorless liquid from the *o*-anisylmethylphenylsilyl ether **4b** (0.114 g, 0.20 mmol) according to the general procedure shown above. ^{1}H NMR spectrum was identical to the data in the literature [20]. Enantiomer ratio was determined to be (R_{Si})-**5b**:(S_{Si})-**5b** = 97:3 by chiral HPLC analysis (Daicel CHIRALCEL OD-H, 0.46 × 25 cm, hexane, 0.4 mL/min). The assignment of the absolute configuration is tentative.

4.5.3. Methylphenyl(o-tolyl)silane (*5*)

Methylphenyl(*o*-tolyl)silane **5c** (22.9 mg, 0.11 mmol, 54%) was synthesized as a colorless liquid from the methylphenyl(*o*-tolyl)silyl ether **5c** (0.111 g, 0.20 mmol) according to the general procedure shown above. ^{1}H NMR spectrum was identical to the data in the literature [20]. Enantiomer ratio could not be determined by chiral HPLC analysis.

5. Supplementary material

CCDC 701477 contains the supplementary crystallographic data for (2R_{Si},4*S*)-**3e**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[14] To determine the d.r. by ^{1}H NMR, the silyl ethers **4a–g** with a lower d.r. were synthesized as follows: crude **3e** was heated at 90 °C for 2 h in dry toluene under argon to epimerize. The resultant oxazasilolidine **3e** with a lower d.r. (R_{Si}:S_{Si} = ca. 80:20) was used to synthesize silyl ethers **4a–g**, which were obtained with d.r. of 72:28–84:16.

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