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Stereoselective Synthesis of 1,2,3-Triol Derivatives from α,β-Unsaturated Acylsilanes

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ABSTRACT: *The stereoselective synthesis of 1,2,3-triol derivatives having contiguous stereogenic centers from α,β-unsaturated acylsilanes* **1** *was described. The oxidation of an olefin moiety of* **1** *with osmium tetroxide proceeded smoothly to give the corresponding 2,3-syn-dihydroxyacylsilanes* **2**. *The protection of two hydroxy groups of* **2** *followed by a nucleophilic reaction to the silyl carbonyl group gave the corresponding silylated triol derivatives (***7** *and* **8***) with high stereoselectivity, depending on the kind of nucleophilic reagents. The deprotection for* **7** *and* **8** *and the following protodesilylation gave two isomers of possible four 1,2,3-triol derivatives. The stereoselective triol synthesis by asymmetric diolization of α-silylated allyl alcohols* **11** *derived by nucleophilic addition to* **1** *was also investigated.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 25:565–577, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21176

INTRODUCTION

Acylsilanes are a useful class of compounds in organic synthesis, and a number of methods for the preparation and the utilization of acylsilanes have been developed [1]. Especially, α,β-unsaturated acylsilanes are expected to be useful synthetic intermediates since three easily convertible functional groups, carbon–carbon double bond, carbonyl group, and silyl group, are presented in these compounds. Indeed, a number of synthetic processes using these functional groups of α,β-unsaturated acylsilanes have been reported [2]. For instance, α,β-unsaturated acylsilanes were used as starting materials to synthesize the various compounds, vinylcyclopropane-1,2-diols [2e], 3-cyclopentenols [2f], and (*Z*)-disubstituted silyl enol ethers [2b], stereoselectively. However, it has not been known the stereoselective synthesis of 1,2,3-triols from α,β-unsaturated acylsilanes. In this paper, the stereoselective synthesis of 1,2,3-triol derivatives having contiguous stereogenic centers from α,β-unsaturated acylsilanes as starting materials, using the feature of a silyl group as a directing group for a stereoselective reaction and a good leaving group, was described. Previously, we have reported the nucleophilic addition to β-methoxyacylsilane possessing stereogenic centers at the α and β positions (Scheme 1) [3a,b,d]. In this reaction, the silyl group acted as a directing group to obtain the high stereoselectivity, and the two diastereomers 1,2-*syn* isomer and 1,2-*anti* isomer were yielded at will with high stereoselectivity depending on the kind of nucleophiles and the reaction conditions [3a,d]. The reaction of β-methoxyacylsilane with methyllithium proceeded via 1,5-chelation intermediates **A** or **B**. The intermediate **B** is favored because of the steric repulsion between the silyl group and the substituent R^2 on the α position. Then, the methyl anion attacks the carbonyl group of **B** from a less-hindered site to afford the 1,2-*syn* isomer. On the other hand, in the reaction with trimethylaluminum, six-membered ring transition state **D** constructed

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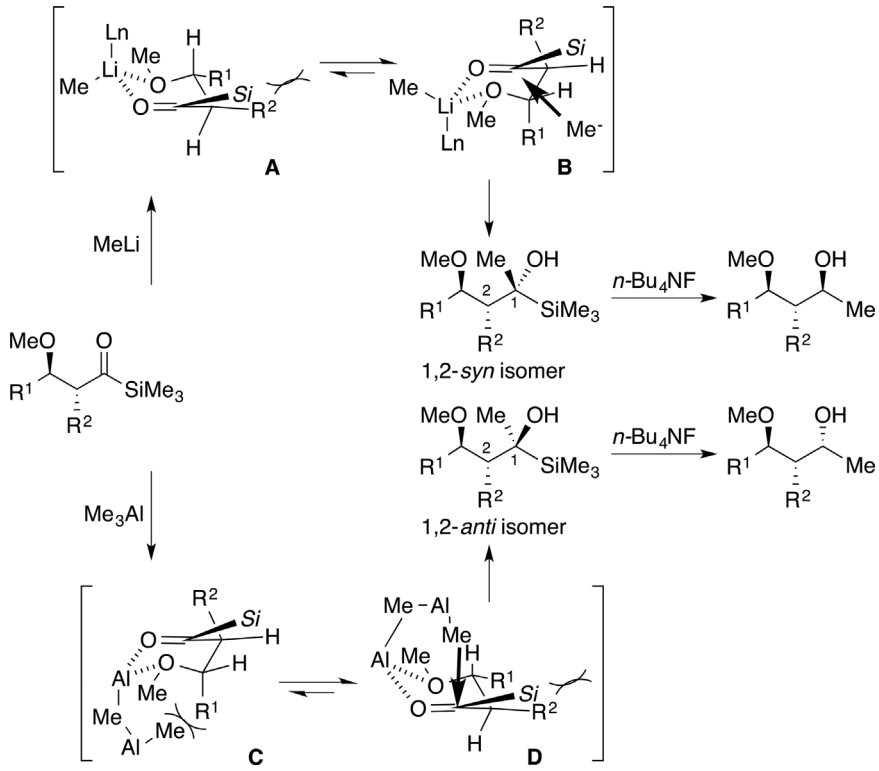
Dedicated to 77th birthday of Professor Renji Okazaki.

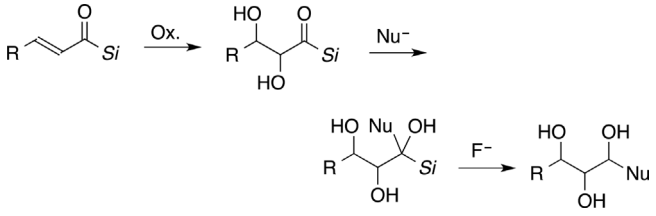


SCHEME 1 Stereocontrolled synthesis of 1,3-diol derivatives from β-methoxyacylsilanes.

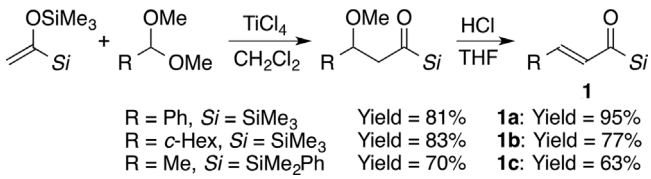
with two trimethylaluminum molecules and acylsilane seems to be favored compared to **C** by the less strain between the nucleophilic group and the substituent R^1 on the β position. As a result, 1,2-*anti* isomer is exclusively yielded. Furthermore, the protodesilylation of the resulting α-silylalcohols with tetrabutylammonium fluoride proceeded smoothly with complete retention of the configuration [3, 4]. Consequently, this method is thought to be a useful method for the stereoselective construction of 1,3-diol derivatives. Thus, we considered that a similar nucleophilic addition reaction to 2,3-dihydroxyacylsilane derived from the dihydroxylation of the alkene moiety of α,β-unsaturated acylsilane and the following protodesilylation give the corresponding 1,2,3-triol with high stereoselectivity (Scheme 2). Such 1,2,3-triol units having contiguous stereogenic centers are a very common pattern in the structure of many naturally occurring compounds; however, the facile stereoselective synthesis of desired isomers among four generable diastereomeric 1,2,3-triols was less well known [5]. So, our method will be useful for the stereoselective construction of 1,2,3-triol derivatives. In addition, another route to 1,2,3-triol, the nucleophilic addition reaction to α,β-unsaturated acylsilanes and the following dihydroxylation of the resulting α-silylated allyl alcohols, is also described.

RESULTS AND DISCUSSION

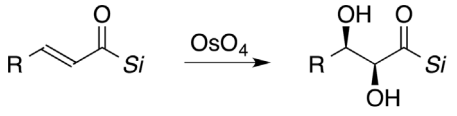
The preparation of α,β-unsaturated acylsilanes was accomplished by as follows (Scheme 3): The Mukaiyama aldol reaction of silyl enol ether derived from acetylsilanes with acetals [6] followed by the



SCHEME 2 Our synthetic strategy for constructing 1,2,3-triol.



SCHEME 3 Synthesis of α,β-unsaturated acylsilanes via the Mukaiyama aldol reaction.



R = Ph, *Si* = $SiMe_3$ — **2a**: Yield = 83%
R = *c*-Hex, *Si* = $SiMe_3$ — **2b**: Yield = 79%
R = Me, *Si* = $SiMe_2Ph$ — **2c**: Yield = 87%

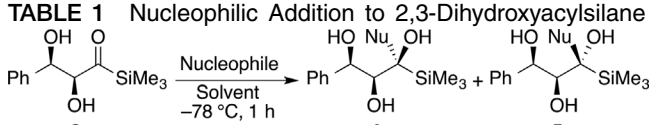
SCHEME 4 Synthesis of 2,3-*syn*-2,3-dihydroxyacylsilanes.

treatment of the resulting β-methoxyacylsilanes with hydrochloric acid in THF gave the desired (*E*)-α,β-unsaturated acylsilanes **1** with high stereoselectivity in good yields.

Then the dihydroxylation of an olefin moiety of **1** was carried out. The oxidation with osmium tetroxide [7] proceeded smoothly to give the corresponding 2,3-*syn*-dihydroxyacylsilanes **2** in high yields independent of the kind of the substituent on C-3 or silicon atom (Scheme 4). On the other hand, the epoxydation of an olefin moiety of **1** could not be achieved (Scheme 5). The oxidation of **1a** with *m*-CPBA [8] gave the complex mixture including desilylated compounds that was observed by NMR spectra. So, the protection of the silylcarbonyl group with ethylene glycol [9] and the following oxidation with *m*-CPBA was examined. Although the corresponding epoxide derivative was provided in good yield, the deprotection with protic acid also gave the desilylated complex mixture. As a consequence, 2,3-*anti*-dihydroxyacylsilane **3a** has not yet been obtained.

The nucleophilic addition of organometallic reagents to **2a** proceeded to afford the corresponding 1,2,3-triol derivatives in low yields. Furthermore, in these reactions, high diastereoselectivity observed in the similar reaction using β-alkoxyacylsilanes [3] was not accomplished. The representative results are shown in Table 1. The reaction of **2a** with alkyllithium gave the diastereomeric mixture with a slight

TABLE 1 Nucleophilic Addition to 2,3-Dihydroxyacylsilane



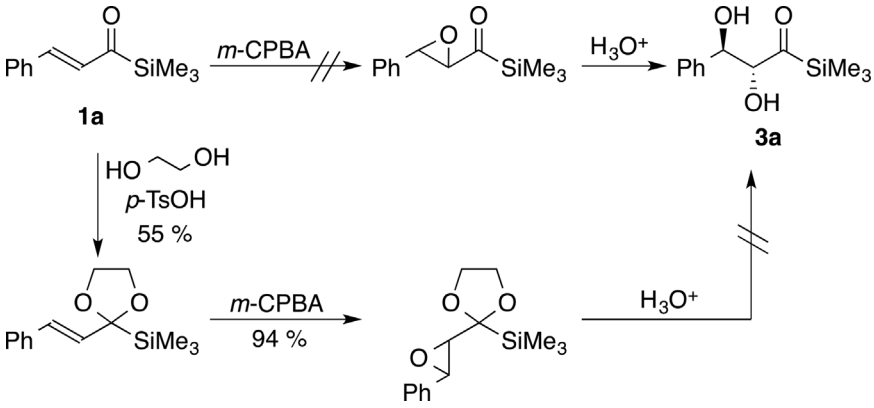
Entry	*Nucleophile*	*Solvent*	*Yield (%)*[a]	***4/5***[b]
1	MeLi	Et_2O	24	82:18
2	*n*-BuLi	Et_2O	13	64:36
3	Me_3Al	Toluene	60	42:58
4	MeLi[c]	CH_2Cl_2	16	28:72

Molar ratio; **2a**/RLi = 1:3, **2a**/Me_3Al = 1:4.
[a]Isolated yield.
[b]Determined by ^1H NMR analysis.
[c]An equimolar amount of $TiCl_4$ was used as an additive.

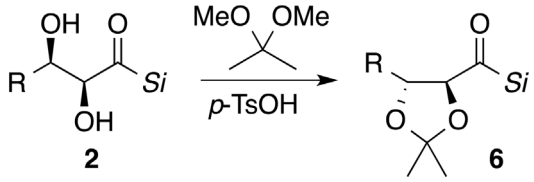
preference for 1,2-*syn* isomers **4**; however, that with trimethylaluminum proceeded with a little stereoselectivity. Meanwhile, 1,2-*anti* isomer **5** was preferentially yielded by the reaction with MeLi in the presence of titanium tetrachloride as an additive [10].

Since these low yield and stereoselectivity were attributed to undesirable chelation of a nucleophilic reagent with free hydroxyl groups on C-2 of **2**, the protection of two hydroxyl groups of **2** with acetone ketal in the presence of *p*-TsOH was performed [11], and then the corresponding dioxolanylacylsilane derivatives **6** were obtained in moderate-to-good yields (Scheme 6).

The nucleophilic addition of organometallic reagents to the silyl carbonyl group of **6** was carried out. The results are shown in Table 2. In all cases, the corresponding diastereomeric mixtures of silyl alcohol derivatives **7** and **8** were obtained. The reaction with methyllithium or phenyllithium in diethyl ether proceeded smoothly to afford **7** predominantly independent of the kind of the substituent on C-3 or silicon atom (entries 1–4). Similarly, high diastereoselectivity was observed in the reaction of **6a** with the Grignard reagent (entry 5). It should be noted



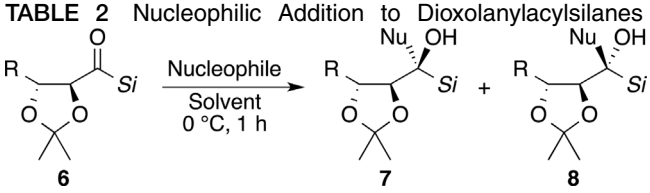
SCHEME 5 Approaches to the synthesis of 2,3-*anti*-2,3-dihydroxyacylsilane.



R = Ph, *Si* = $SiMe_3$ **6a**: Yield = 65%
R = *c*-Hex, *Si* = $SiMe_3$ **6b**: Yield = 65%
R = Me, *Si* = $SiMe_2Ph$ **6c**: Yield = 84%

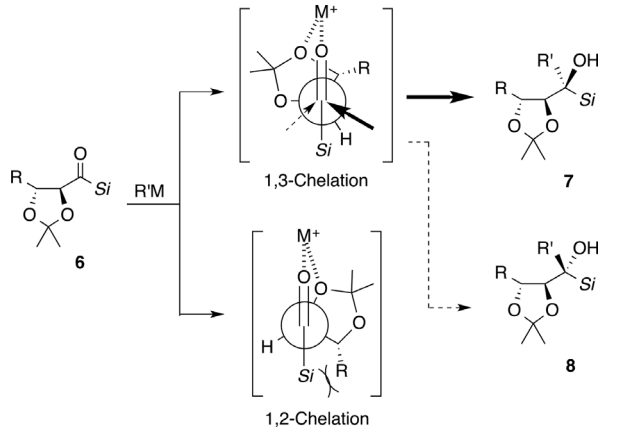
SCHEME 6 Protection of 2,3-dihydroxyacylsilanes.

TABLE 2 Nucleophilic Addition to Dioxolanylacylsilanes

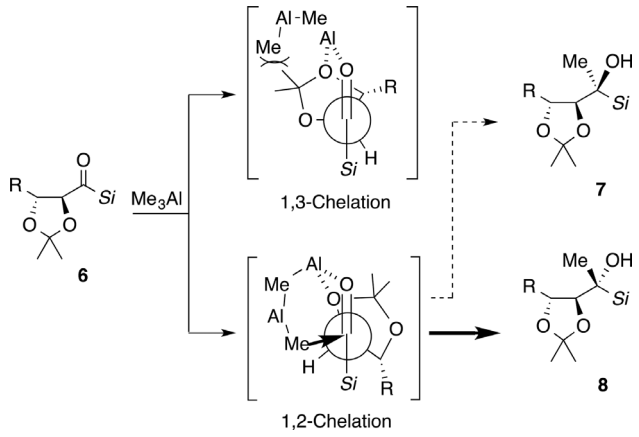


Entry	***6***	*Nucleophile*	*Solvent*	*Yield (%)*[a]	*Products*	***7/8***[b]
1	**6a**	MeLi	Et_2O	96	**7a, 8a**	93: 7
2	**6b**	MeLi	Et_2O	70	**7b, 8b**	93: 7
3	**6c**	MeLi	Et_2O	88	**7c, 8c**	95: 5
4	**6a**	PhLi[c]	Et_2O	97	**7d, 8d**	99: 1
5	**6a**	MeMgBr[c]	Et_2O	79	**7a, 8a**	98: 2
6	**6a**	Me_3Al	Toluene	91	**7a, 8a**	5:95
7	**6b**	Me_3Al	Toluene	85	**7b, 8b**	5:95
8	**6c**	Me_3Al	Toluene	98	**7c, 8c**	7:93

Molar ratio; **6**/RLi = 1:2, **6**/MeMgBr = 1:3, **6**/Me_3Al = 1:5.
[a]Isolated yield.
[b]Determined by ^1H NMR analysis.
[c]The reaction was carried out at –78°C.



SCHEME 7 Plausible mechanism of a reaction with organolithium or Grignard reagent.



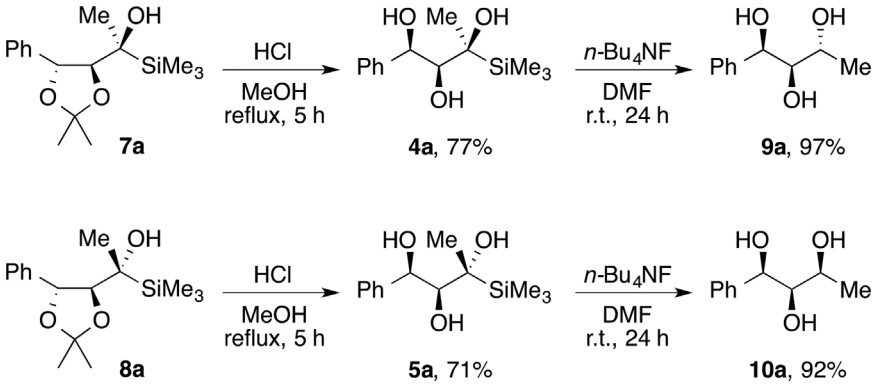
SCHEME 8 Plausible mechanism of reaction with trimethlaluminum.

that the other stereoisomeric products **8** were predominantly yielded in the reactions with trimethylaluminum as a nucleophilic reagent (entries 6–8). In these nucleophilic additions, the silyl group would act as a directing group for the synthesis of silylalcohols with high stereoselectivity, as mentioned above [3a].

It appears that these reactions proceeded as follows: In the reaction of **6** with organolithium reagents or Grignard reagent (Scheme 7), the 1,3-chelation model seems to be favored compared to the 1,2-chelation model by the less strain between silyl group and the substituent R group on C-3. The attack of nucleophile occurs from a less-hindered site to afford the silyl alcohol derivatives **7**. On the other hand, the reaction with trimethylaluminum proceeds via six-membered ring transition states (Scheme 8). In this case, the 1,2-chelation model seems to be favored compared to the 1,3-chelation model by the less strain between the six-membered ring and dioxolanyl ring. Then the silyl alcohol derivatives **8** are exclusively yielded.

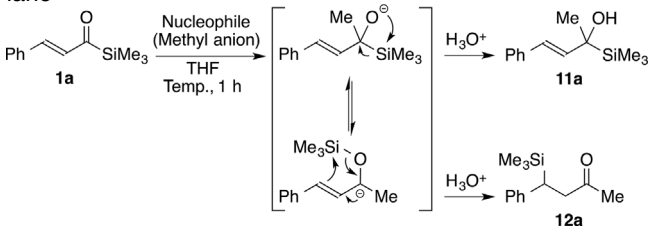
The deprotection of a cyclic ketal moiety of the resulting silyl alcohols **7a** and **8a** was successfully achieved to give the silylated triol derivatives **4a** and **5a** by the treatment with hydrochloric acid in methanol under reflux (Scheme 9) [12]. It is known that the protodesilylation of α-silylalcohols proceeds with complete retention of the configuration [4]. Thus, the protodesilylation of **4a** and **5a** with tetrabutylammonium fluoride was carried out and gave the corresponding 1,2,3-triols **9a** and **10a** in good yields, respectively. Consequently, two diastereoisomers (**9** and **10**) of 1,2,3-triol derivatives having the three contiguous stereogenic centers among four possible diastereomeric products were yielded with high stereoselectivity by a series of reactions starting from α,β-unsaturated acylsilanes.

Next, we tried out the other route to 1,2,3-triol. That is, the nucleophilic addition reaction to α,β-unsaturated acylsilanes and the following dihydroxylation of the resulting α-silylated allyl alcohols were studied.



SCHEME 9 Deprotection and following protodesilylation to 1,2,3-triols.

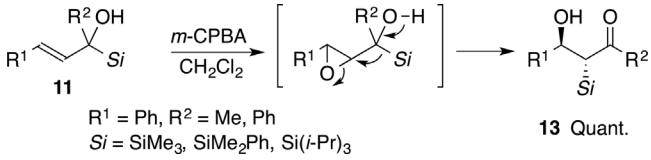
TABLE 3 Nucleophilic Addition to α,β-Unsaturated Acylsilane



Entry	*Nucleophile*	*Temperature (°C)*	*Product*	*Yield(%)*[a]
1	MeLi	0	**12a**	62
2	MeLi	−78	**11a**	51
3	MeMgI	−78	**11a**	94
4	$MeCeCl_2$	−78	**11a**	99

Molar ratio; **1a**/MeLi = 1:2, **1 a**/MeMgI = 1:4, **1a**/$MeCeCl_2$ = 1:6.
[a]Isolated yield.

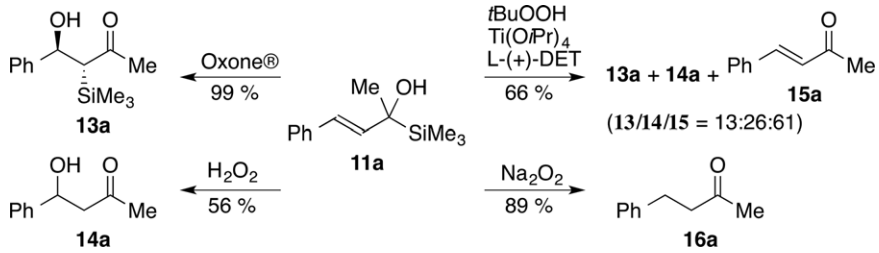
At first, the nucleophilic addition to α,β-unsaturated acylsilane was investigated. These results are shown in Table 3. The reaction of α,β-unsaturated acylsilane **1a** with methyllithium at 0°C proceeded to give β-silyl ketone derivative **12a**, and the desired silyl alcohol **11a** was not produced at all. It has been known that the nucleophilic addition of vinyllithium to acylsilanes affords the β-silyl ketones via the Brook rearrangement of the corresponding alkoxide intermediate and the following migration of the silyl group to β-position [13]. Because the reaction of **1a** with alkyllithium gave the similar alkoxide intermediate, the β-silyl ketone **12a** would be yielded via the Brook rearrangement of the above intermediate. In contrast, the exclusive formation of **11a** was achieved by the reaction at –78°C with methyllithium. The Brook rearrangement of the alkoxide intermediate would be prevented under low temperature. The yield was, however, remained moderate. On the other hand, the use of the Grignard reagent or organo cerium reagent [13, 14] made it feasible to generate **11a** quantitatively.



SCHEME 10 Oxidation of α-silylated allyl alcohols with *m*-CPBA.

To obtain the desired 2,3-*anti* triol derivatives, stereoselective epoxydation of the resulting α-silylated allyl alcohols **11** with several oxidants and the following hydrolysis reaction were carried out [15]. The treatment of α-silylated allyl alcohols **11** possessing various substituents and silyl groups with *m*-CPBA did not give the corresponding epoxides, but afforded the silyl-migrated compounds **13** with excellent 2,3-*anti* selectivity in quantitative yields (Scheme 10) [16]. In addition, the desired epoxides as the precursor compounds of 2,3-*anti* triol derivatives were not obtained at all by using the epoxidation reaction of **11a** with other oxidants, Sharpless–Katsuki asymmetric epoxidation reagents [17], Oxone® [18], hydrogen peroxide [19], sodium peroxide [20]. In these reactions, silyl-migrated or silyl-eliminated derivatives **13**–**16** were, respectively, yielded (Scheme 11).

In conclusion, the stereoselective synthesis of 1,2,3-triol derivatives having the three contiguous stereogenic centers from α,β-unsaturated acylsilanes has been investigated. The two isomers of possible four stereoisomers of 1,2,3-triol derivatives were synthesized by using the characteristic features of the silyl group with high stereoselectivity. However, synthetic routes to the other two isomers have not been established yet. Further studies are aimed at the synthesis of the other two isomers using α,β-unsaturated acylsilanes in our laboratory.



SCHEME 11 Oxidation of α-silylated allyl alcohol.

EXPERIMENTAL

General Procedures

IR spectra were recorded on a Horiba FTIR-720 or Shimadzu FTIR- 8300 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM EX-270, LA-400 or ECA-500 spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane (TMS) with reference to internal residual $CHCl_3$ (δ = 7.26) in $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ (δ = 77.0) as an internal standard. Coupling constants (J) were reported in hertz (Hz). Following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, br = broad, m = multiplet. Mass spectra were recorded on a JEOL JMS-700 or JMS-SX102A mass spectrometer. Melting points were measured on a Yanaco MP-J3 and were uncorrected. Analytical thin layer chromatography (TLC) was performed on precoated glass plates (Merck Kieselgel 60 F_{254}, layer thickness 0.25 mm). Visualization was accomplished with UV light (254 nm) and molybdophosphoric acid. Flash column chromatography was carried out using Kanto Chemical silica gel 60 N (40–50 mm). Preparative HPLC was performed on a JAI LC-908 and LC-918 chromatograph equipped with JAIGEL-1H and -2H and JAIGEL-SIL. GC analysis was performed on a Shimadzu GC-14B equipped with a CBP1-M25-O20 column (Shimadzu, 25 m $\times$ 0.22 mm, detector = FID) with a helium gas as a carrier. Unless otherwise noted, commercially available reagents were used without purification. All the solvents were distilled and stored over a drying agent. Methyllithium (1.3 M solution in diethylether), *n*-butyllithium (1.6 M solution in hexane), phenyllithium (1.1 M solution in cyclohexane), methyl magnesium bromide (1.0 M solution in tetrahydrofuran), and trimethylaluminum (1.0 M solution in hexane) were purchased from Kanto Chemical. All reactions were carried out under an argon atmosphere in dried glassware.

A Typical Procedure for the Preparation of α,β-Unsaturated Acylsilanes **1**

To a stirred solution of titanium tetrachloride (10.4 g, 55 mmol) in dichloromethane (150 mL) at –78°C, a solution of acetal (55 mmol) in dichloromethane was added slowly. The resulting reaction mixture was stirred, and then acylsilane silyl enol ether (55 mmol) in dichloromethane was added. After stirring for 2 h, methanol (10 mL) was added and the reaction mixture was allowed to warm to ambient temperature and then poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with hexane for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 20:1 hexane–ethyl acetate as the eluent to give β-methoxyacylsilane derivatives in 70–81% yields as pale yellow oil.

3-Methoxy-3-phenyl-1-trimethylsilyl-1-propanone. IR (neat) 3086, 3063, 3029, 2955, 2926, 1644, 1453, 1248, 1105, 842 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.26–7.35 (m, 5H), 4.67 (dd, J = 8.6 Hz, 4.3 Hz, 1H), 3.24 (dd, J = 16.2 Hz, 8.6 Hz, 1H), 3.17 (s, 3H), 2.67 (dd, J = 16.2 Hz, 4.3 Hz, 1H), 0.12 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 240.5, 138.9, 132.2, 128.8, 126.5, 82.3, 56.6, 55.0, –2.7. HRMS calcd for $C_{13}H_{20}O_2Si$ (M^+) 236.1233, found 236.1230.

3-Cyclohexyl-3-methoxy-1-trimethylsilyl-1-propanone. IR (neat) 2926, 2853, 1643, 1456, 1250, 1096, 847 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.56 (ddd, J = 7.9 Hz, 4.1 Hz, 4.1 Hz, 1H), 3.25 (s, 3H), 2.90 (dd, J = 16.2 Hz, 7.9 Hz, 1H), 2.51 (dd, J = 16.2 Hz, 4.0 Hz, 1H), 1.73–0.99 (m, 11H), 0.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 247.1, 79.9, 57.3, 49.2, 41.2, 28.2, 28.0, 26.2, 26.0, 25.9, –3.6. HRMS calcd for $C_{13}H_{26}O_2Si$ (M^+) 242.1702, found 242.1705.

3-Methoxy-1-dimethylphenylsilyl-1-butanone. IR (neat) 2970, 2930, 1643, 1460, 1429, 1373, 1250, 1194, 1111, 1088 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$):

δ 7.56–7.38 (m, 5H), 3.74 (m, 1H), 2.94 (dd, J = 16.3 Hz, 5.9 Hz, 1H), 2.51 (dd, J = 16.3 Hz, 4.0 Hz, 1H), 1.04 (d, J = 6.2 Hz, 3H), 0.49 (s, 3H), 0.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 245.6, 134.2, 133.9, 129.8, 128.1, 72.1, 55.9, 55.0, 19.3, –4.9, –5.0. HRMS calcd for $C_{13}H_{20}O_2Si$ (M^+) 236.1233, found 236.1241.

To a stirred solution of β-methoxyacylsilane (1 mmol) in THF (10 mL) at 25–40°C, an aqueous solution of HCl (1.0 M, 2.5 mL) was added slowly. The resulting reaction mixture was stirred, and then acylsilane silyl enol ether (55 mmol) in dichloromethane was added. After completion of the reaction evidenced by GC (usually after being stirred for 3–44 h), brine was then added, and the resulting mixture was separated. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with saturated aq. $NaHCO_3$ and brine for three times, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 10:1 hexane–ethyl acetate as the eluent to give α,β-unsaturated acylsilane derivatives in 63–95% yields as pale yellow oil.

*(E)-3-Phenyl-1-trimethylsilyl-2-propen-1-one (***1a***).* IR (neat) 3028, 2958, 2900, 1703, 1639, 1622, 1579, 1562, 1494, 1250 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.38–7.25 (m, 6H), 6.90 (d, J = 16.5 Hz, 1H), 0.32 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 235.9, 142.7, 134.6, 131.0, 130.2, 128.7, 128.0, –2.2. HRMS calcd for $C_{12}H_{16}OSi$ (M^+) 204.0970, found 204.0971.

*(E)-3-Cyclohexyl-1-trimethylsilyl-2-propen-1-one (***1b***).* IR (neat) 2928, 2853, 1638, 1593, 1448, 1250, 980, 845 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.68 (dd, J = 16.3 Hz, 6.6 Hz, 1H), 6.16 (dd, J = 16.3 Hz, 1.3 Hz, 1H), 1.79–1.14 (m, 11H), 0.25 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 236.9, 153.9, 133.7, 40.7, 31.7, 25.8, 25.6, –1.9. HRMS calcd for $C_{12}H_{22}OSi$ (M^+) 210.1440, found 210.1440.

*(E)-1-dimethylphenylsilyl-2-buten-1-one (***1c***).* IR (neat) 3069, 2966, 1639, 1585, 1429, 1283, 1248, 1186, 1111, 970, 837 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.56–7.37 (m, 5H), 6.6 (m, 1H), 6.24 (dt, J = 8.4 Hz, 1.6 Hz, 1H), 1.73 (m, 3H), 0.49 (s, 3H), 0.48 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 233.9, 144.5, 137.8, 135.4, 133.8, 129.6, 128.0, 18.4, –3.7. HRMS calcd for $C_{12}H_{16}OSi$ (M^+) 204.0970, found 204.0961.

General Procedure for the Dihydroxylation of α,β-Unsaturated Acylsilanes **1**

To a solution of α,β-unsaturated acylsilane (5 mmol) in pyridine (25 mL) at room temperature, osmium tetroxide (1.4 g, 5.5 mmol) was added slowly. After stirring for 1 h, water (25 mL), sodium hydrogen sulfite (2.4 g, 23 mmol), and pyridine (25 mL) was added and the reaction mixture was stirred for 1 h, and then the aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel using 2:1 hexane–ethyl acetate as the eluent to give 2,3-*syn*-dihydroxyacylsilane derivatives **2** in 79–87% yields as pale yellow oil.

*2,3-syn-2,3-Dihydroxy-3-Phenyl-1-trimethylsilyl-1-propanone (***2a***).* IR (neat) 3438, 2950, 2901, 1703, 1643, 1593, 1495, 1452, 1248 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.39–7.29 (m, 5H), 5.20 (d, J = 2.0 Hz, 1H), 4.50 (d, J = 2.0 Hz, 1H), 0.30 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 244.5, 141.0, 128.8, 128.2, 126.4, 84.1, 72.0, 2.8. HRMS calcd for $C_{12}H_{18}O_3Si$ (M^+) 238.1025, found 238.1029.

*2,3-syn-3-Cyclohexyl-2,3-dihydroxy-1-trimethylsilyl-1-propanone (***2b***).* IR (neat) 3369, 2903, 2855, 1638, 1389, 1250, 1115, 849 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.44 (dd, J = 3.8 Hz, 1.1 Hz, 1H), 4.07 (d, J = 3.8 Hz, 1H), 3.77 (t, J = 9.4 Hz, 1H), 2.05–0.99 (m, 11H), 0.29 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 244.2, 81.0, 74.4, 29.6, 29.4, 26.3, 25.9, 25.8, –2.7. HRMS calcd for $C_{12}H_{24}O_3Si$ (M^+) 244.1495, found 244.1503.

*2,3-syn-2,3-Dihydroxy -1-dimethylphenylsilyl-1-butanone (***2c***).* IR (neat) 3433, 3070, 2974, 1639, 1429, 1379, 1252, 1111, 1088, 989, 912 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.58–7.40 (m, 5H), 4.16 (dq, J = 6.4 Hz, 1.6 Hz, 1H), 4.09 (d, J = 1.8 Hz, 1H), 1.19 (d, J = 6.5 Hz, 3H), 0.58 (s, 3H), 0.55 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 243.5, 134.0, 133.5, 130.1, 128.2, 84.4, 66.2, 20.1, –4.3, –4.6. HRMS calcd for $C_{12}H_{18}O_3Si$ (M^+) 238.1025, found 238.1021.

General Procedure for the Nucleophilic Reaction to Dihydroxyacylsilanes **2a**

To a solution of dihydroxyacylsilane **2** (0.5 mmol) in a solvent (10 mL) at –78°C, a solution of nucleophilic reagent was added slowly. After stirring for 1 h, methanol (1 mL) was added and the reaction mixture was allowed to warm to ambient

temperature and then poured into brine. The aqueous layer was extracted with diethyl ether for three times. The combined organic layer was then washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 10:1 hexane–ethyl acetate as the eluent to give silyltriol derivatives **4** and **5** in 13–60% yields as pale yellow oil.

*1-Phenyl-3-trimethylsilylbutane-1,2,3-triol (**4a**, **5a**).* Compound **4a**: IR (neat) 3313, 3065, 3020, 2959, 1605, 1495, 1452, 1249 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.39–7.25 (m, 5H), 5.09 (s, 1H), 3.72 (s, 1H), 3.59 (d, $J = 6.1$ Hz, 1H), 2.29 (d, $J = 6.1$ Hz, 1H), 1.98 (s, 1H), 1.31 (s, 3H), 0.21 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 141.6, 128.5, 127.6, 125.8, 77.5, 75.0, 70.8, 22.5, –3.0. HRMS calcd for $C_{13}H_{22}O_2Si$ (M^+) 254.1338, found 254.1332.

Compound **5a**: IR (neat) 3365, 3020, 2961, 1647, 1541, 1508, 1248 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.36–7.25 (m, 5H), 5.02 (brs, 1H), 3.91 (brs, 1H), 3.52 (brs, 1H), 1.29 (s, 3H), 0.19 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 141.3, 128.4, 127.5, 125.9, 77.6, 73.4, 72.0, 21.2, –2.9. HRMS calcd for $C_{13}H_{22}O_2Si$ (M^+) 254.1338, found 254.1333.

*1-Phenyl-3-trimethylsilylheptane-1,2,3-triol (**4b**, **5b**).* Compound **4b**: IR (neat) 3371, 3063, 3028, 2957, 2934, 2903, 2872, 1452, 1249 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.40–7.27 (m, 5H), 5.12 (s, 1H), 4.02 (s, 1H), 3.75 (d, $J = 6.6$ Hz, 1H), 2.21 (d, $J = 6.6$ Hz, 1H), 1.94 (s, 1H), 1.29–1.23 (m, 6H), 0.89 (t, $J = 6.8$ Hz, 3H), 0.26 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 141.5, 128.4, 127.6, 125.7, 77.5, 74.3, 74.2, 37.6, 27.0, 23.5, 14.0, –1.8. HRMS calcd for $C_{16}H_{28}O_2Si$ (M^+) 296.1808, found 296.1818.

Compound **5b**: IR (neat) 3420, 3028, 2957, 2932, 2901, 2862, 1452, 1248 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.39–7.26 (m, 5H), 5.23 (s, 1H), 3.91 (brs, 1H), 3.72 (d, $J = 6.3$ Hz, 1H), 2.36 (d, $J = 6.4$ Hz, 1H), 1.44–1.25 (m, 6H), 0.97 (t, $J = 6.9$ Hz, 3H), 0.13 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 141.3, 128.5, 127.5, 125.8, 75.8, 74.9, 73.3, 36.7, 27.0, 23.7, 14.0, –1.9. HRMS calcd for $C_{16}H_{28}O_2Si$ (M^+) 296.1808, found 296.1807.

Protection of the Carbonyl Group of α,β-Unsaturated Acylsilane **1a**

To a stirred solution of acylsilane **1a** (8.16 g, 40 mmol) in benzene (100 mL), - ethylene glycol (2.73 g, 44 mmol) and *p*-TsOH (83 mg, 0.46 mmol) were added. After stirring under reflux for 6 h, the reaction mixture was cooled to ambient temperature and extracted with 10% sodium hydroxide solution (200 mL). The organic layers were washed with brine, dried over anhydrous potassium carbonate, and concentrated in vacuo. The residue was purified by recrystallization from *t*-butyl alcohol to give 1,3-dioxane derivative in 55% yield as a white solid.

(E)-2-Styryl-1-trimethylsilyl-1,3-dioxolane. Mp 115.6°C. IR (neat) 3028, 2962, 2891, 1248, 1122, 987 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.40–7.23 (m, 5H), 6.56 (d, $J = 16.0$ Hz, 1H), 6.10 (d, $J = 16.0$ Hz, 1H), 3.93 (ddd, $J = 6.3$ Hz, 3.1 Hz, 1.9 Hz, 2H), 3.86 (ddd, $J = 6.4$ Hz, 3.1 Hz, 1.9 Hz, 2H), 0.10 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 136.6, 129.6, 129.3, 128.4, 127.4, 126.4, 108.4, 64.5, –4.1. HRMS calcd for $C_{14}H_{20}O_2Si$ (M^+) 248.1233, found 248.1238.

Epoxydation of (E)-2-Styryl-1-trimethylsilyl-1,3-dioxolane

To a stirred solution of (*E*)-2-styryl-1-trimethylsilyl-1,3-dioxolane (248 mg, 1 mmol) in dichloromethane (15 mL), - *m*-chloroperbenzoic acid (259 mg, 1.5 mmol) dissolved in dichloromethane was added. After stirring at room temperature for 13 h, the reaction mixture was poured into 10% solution of sodium sulfite to destroy any excess peroxide. The organic layer was then washed with saturated aq. $NaHCO_3$ and brine for three times, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 5:1 hexane–ethyl acetate as the eluent to give 1,3-dioxane derivative in 94% yield as pale yellow oil.

2-(3-Phenyloxiran-2-yl)-2-trimethylsilyl-1,3-dioxolane. IR (neat) 3031, 2964, 2895, 1654, 1560, 1252, 993 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.45–7.32 (m, 5H), 4.21–4.14 (m, 2H), 4.02–3.86 (m, 3H), 3.14 (d, $J = 2.0$ Hz, 1H), 0.22 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 136.9, 128.3, 127.8, 125.2, 105.3, 66.5, 65.5, 64.8, 55.0, –4.0. HRMS calcd for $C_{14}H_{20}O_3Si$ (M^+) 264.1182, found 264.1179.

General Procedure for the Protection of Hydroxy Groups of Dihydroxyacylsilanes **2**

To a solution of dihydroxyacylsilane **2** (5.8 mmol) in acetone (50 mL), 2,2-dimethoxypropane (5.2 g, 51 mmol) and *p*-TsOH (128 mg, 0.75 mmol) were added. After stirring at room temperature for 21 h, the reaction mixture was poured into cooled saturated aq. $NaHCO_3$. The mixture was extracted with diethyl ether for three times. The organic layer was then washed with brine, dried over potassium carbonate, and concentrated in vacuo. The residue was

purified by column chromatography on a silica gel 10:1 hexane–ethyl acetate as the eluent to give dioxolanylacylsilane derivatives **6** in 65–84% yields as pale yellow oil.

*4,5-anti-2,2-Dimethyl-5-phenyl-1,3-dioxolan-4-yltrimethylsilylmethanone (**6a**).* IR (neat) 3029, 2988, 2901, 1651, 1496, 1452, 1380, 1249, 1068 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.40–7.27 (m, 5H), 5.00 (d, J = 7.6 Hz, 1H), 4.21 (d, J = 7.6 Hz, 1H), 1.55 (s, 3H), 1.53 (s, 3H), 0.26 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 245.1, 138.7, 128.3, 127.8, 126.3, 110.3, 91.4, 78.0, 26.6, 26.4, –1.9. HRMS calcd for $C_{15}H_{22}O_3Si$ (M^+) 278.1338, found 278.1342.

*4,5-anti-5-Cyclohexyl-2,2-dimethyl-1,3-dioxolan-4-yltrimethylsilylmethanone (**6b**).* IR (neat) 2988, 2928, 2855, 1649, 1450, 1381, 1248, 1211 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 4.07 (d, J = 3.8 Hz, 1H), 3.77 (dd, J = 5.6 Hz, 3.8 Hz, 1H), 2.05–0.99 (m, 11H), 0.29 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 264.1, 109.4, 87.9, 80.6, 41.1, 29.5, 28.3, 26.7, 26.5, 26.3, 26.0, 25.8, –2.3. HRMS calcd for $C_{15}H_{28}O_3Si$ (M^+) 284.1808, found 284.1799.

*4,5-anti-2,2,5-Trimethyl-1,3-dioxolan-4-yldimethylphenylsilylmethanone (**6c**).* IR (neat) 3068, 2986, 2934, 1645, 1429, 1379, 1248, 1173, 1096, 1061, 839 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.58–7.37 (m, 5H), 4.16 (dq, J = 4.5 Hz, 1.8 Hz, 1H), 4.09 (d, J = 1.8 Hz, 1H), 1.37 (s, 3H), 1.27–1.25 (m, 3H), 1.19 (s, 3H), 0.58 (s, 9H), 0.58 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 243.8, 134.2, 134.2, 129.7, 127.8, 109.4, 91.3, 72.9, 27.0, 26.1, 18.2, –3.7, –4.4. HRMS calcd for $C_{15}H_{22}O_3Si$ (M^+) 278.1338, found 278.1330.

General Procedure for the Nucleophilic Reaction to Dioxolanylacylsilane Derivatives **6**

Method for Using the Organolithium Reagent or Grignard Reagent as a Nucleophilic Reagent. To a solution of dioxolanylacylsilanes **6** (0.4 mmol) in ether (10 mL) at -0°C, a solution of nucleophilic reagent was added slowly. After stirring for 1 h, methanol (1 mL) was added and the reaction mixture was allowed to warm to ambient temperature and then poured into brine. The aqueous layer was extracted with diethyl ether for three times. The combined organic layer was then washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 10:1 hexane-ethyl acetate as the eluent to give silyl alcohol derivatives **7** and **8** in 70–97% yields as pale yellow oil.

Method for Using Trimethylaluminum as a Nucleophilic Reagent. To a solution of dioxolanylacylsilanes **6** (0.4 mmol) in toluene (10 mL) at -0°C, a 1.0 M solution of trimethylaluminum (2 mL, 2 mmol) in hexane was added slowly. After stirring for 1 h, the reaction mixture was poured into saturated aq. NH_4Cl. The aqueous layer was extracted with diethyl ether for three times. The combined organic layer was then washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 10:1 hexane–ethyl acetate as the eluent to give silyl alcohol derivatives **7** and **8** in 85–98% yields as pale yellow oil.

*1-(2,2-Dimethyl-5-phenyl-1,3-dioxolan-4-yl)-1-trimethylsilylethan-1-ol (**7a**, **8a**).* Compound **7a**: IR (neat) 3503, 3031, 2986, 1460, 1456, 1371, 1246, 1169, 1059 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.45–7.32 (m, 5H), 4.93 (d, J = 8.4 Hz, 1H), 4.10 (d, J = 8.4 Hz, 1H), 1.51 (s, 3H), 1.48 (s, 3H), 1.19 (s, 3H), 0.06 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 138.6, 128.4, 128.1, 127.6, 108.2, 88.1, 78.3, 66.3, 27.3, 27.2, 20.8, –3.1. HRMS calcd for $C_{16}H_{26}O_3Si$ (M^+) 294.1651, found 294.1644.

Compound **8a**: IR (neat) 3464, 3035, 2984, 1427, 1377, 1250, 1215, 1175, 1117, 1061 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.45–7.29 (m, 5H), 5.11 (d, J = 8.4 Hz, 1H), 4.04 (d, J = 8.4 Hz, 1H), 1.51 (s, 3H), 1.48 (s, 3H), 0.85 (s, 3H), 0.06 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 139.0, 128.3, 128.1, 127.9, 107.8, 87.1, 77.0, 65.0, 27.4, 27.2, 19.6, –3.3. HRMS calcd for $C_{16}H_{26}O_3Si$ (M^+) 294.1651, found 294.1657.

*1-(5-Cyclohexyl-2,2-dimethyl-1,3-dioxolan-4-yl)-1-trimethylsilylethan-1-ol (**7b**, **8b**).* Compound **7b**: IR (neat) 3490, 2983, 1457, 1373, 1247, 1170, 1071 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 3.93 (d, J = 7.6 Hz, 1H), 3.76 (dd, J = 7.6 Hz, 4.0 Hz, 1H), 1.79–1.18 (m, 11H), 1.38 (s, 3H), 1.35 (s, 3H), 1.23 (s, 3H), 0.10 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 107.5, 83.1, 80.5, 66.1, 40.2, 31.4, 27.6, 27.5, 26.8, 26.7, 26.5, 26.3, 21.2, –3.1. HRMS calcd for $C_{16}H_{32}O_3Si$ (M^+) 300.2121, found 300.2120.

Compound **8b**: IR (neat) 3482, 2986, 1451, 1372, 1251, 1171, 1082 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 3.97 (dd, J = 6.9 Hz, 4.1 Hz, 1H), 3.90 (d, J = 7.1 Hz, 1H), 1.77–1.18 (m, 11H), 1.39 (s, 3H), 1.34 (s, 3H), 1.08 (s, 3H), 0.08 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 107.6, 82.8, 79.2 65.7, 41.2, 31.6, 27.8, 27.5, 26.9, 26.8, 26.5, 26.3, 19.8, –3.0. HRMS calcd for $C_{16}H_{32}O_3Si$ (M^+) 300.2121, found 300.2125.

*1-(2,2,5-Trimethyl-1,3-dioxolan-4-yl)-1-dimethylphenylsilylethan-1-ol (**7c**, **8c**).* Compound **7c**: IR

(neat) 3483, 3053, 2984, 1456, 1369, 1248, 1171, 1059, 918 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.63–7.34 (m, 5H), 3.98 (dq, $J = 8.1$ Hz, 5.9 Hz, 1H), 3.60 (d, $J = 8.1$ Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H), 1.23–1.06 (m, 3H), 0.41 (s, 3H), 0.40 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 136.1, 134.5, 129.2, 127.6, 107.4, 87.4, 72.3, 66.1, 27.1, 20.9, 19.9, 0.10, –4.6. HRMS calcd for $C_{16}H_{26}O_3Si$ (M^+) 294.1651, found 294.1656.

Compound **8c**: IR (neat) 3462, 3049, 2984, 1458, 1427, 1377, 1250, 1175, 1117, 1061, 980, 868 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.61–7.34 (m, 5H), 4.20 (dq, $J = 7.8$ Hz, 5.9 Hz, 1H), 3.50 (d, $J = 7.8$ Hz, 1H), 1.36 (s, 3H), 1.34 (s, 3H), 1.23 (d, $J = 5.9$ Hz, 1H), 1.06 (s, 3H), 0.40 (s, 3H), 0.39 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 136.1, 134.5, 129.2, 127.0.41 (s, 3H), 0.40 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 136.3, 134.3, 129.1, 127.4, 107.2, 87.1, 70.6, 64.7, 27.1, 20.8, 19.5, –4.6, –5.0. HRMS calcd for $C_{16}H_{26}O_3Si$ (M^+) 294.1651, found 294.1655.

*2,2-Dimethyl-5-phenyl-1,3-dioxolan-4-ylphenyltrimethylsilylmethanol (***7d***).* IR (neat) 3539, 3032, 2977, 1590, 1483, 1445, 1371, 1246, 1069, 1026, 843 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.53–7.25 (m, 10H), 4.63 (d, $J = 8.4$ Hz, 1H), 4.39 (d, $J = 8.4$ Hz, 1H), 1.55 (s, 3H), 1.52 (s, 3H), 0.06 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 143.5, 141.1, 138.1, 128.7, 128.6, 128.4, 127.7, 127.2, 127.1, 127.0, 125.7, 124.8, 108.2, 87.4, 78.6, 71.3, 27.3, 27.0, –3.3. HRMS calcd for $C_{21}H_{28}O_3Si$ (M^+) 356.1808, found 356.1811.

Deprotection of Silyl Alcohol Derivatives **7a** *and* **8a**

To a stirred solution of *trimethylsilylethanol* **7a** or **8a** (147 mg, 0.5 mmol) in methanol (16 mL), an aqueous solution of HCl (1.0 M, 2.5 mL) was added slowly. The resulting mixture was heated to reflux. Acetone and methanol were slowly distilled. Additional methanol (2 mL) and an aqueous solution of HCl (0.5 M, 1.1 mL) were added, and the mixture was stirred at room temperature for 5 h. The mixture was diluted with saturated sodium bicarbonate solution and extracted with ether for three times. The organic layer was then washed with brine for three times, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 2:1 hexane–ethyl acetate as the eluent to give silyl substituted triol derivatives **4a** or **5a** in 71–77% yields as pale yellow oil.

Protodesilylation of Silyltriol Derivatives **4a** *and* **5a**

To a stirred solution of *trimethylsilyltriol* **4a** or **5a** (127 mg, 0.5 mmol) in DMF (10 mL), tetrabutylammonium fluoride (653 mg, 2.5 mmol) was added slowly. After stirring for 24 h, the reaction mixture was poured into brine. The aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel using 2:1 hexane–ethyl acetate as the eluent to give triol derivatives **9a** or **10a** in 92–97% yields as pale yellow oil.

*3-Methyl-1-phenylbutane-1,2,3-triol (***9a***, **10a***).* Compound **9a**: IR (neat) 3367, 3018, 2931, 2859, 1495, 1454, 1379, 1197, 1056, 1011 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.35–7.24 (m, 5H), 4.71 (d, $J = 5.9$ Hz, 1H), 3.65 (dq, $J = 6.5$ Hz, 2.7 Hz, 1H), 3.40 (dd, $J = 5.9$ Hz, 2.7 Hz, 1H), 1.14 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.5, 128.5, 127.3, 126.1, 76.9, 75.5, 71.5, 22.6. HRMS calcd for $C_{11}H_{16}O_3Si$ (M^+) 196.1099, found 196.1101.

Compound **10a**: IR (neat) 3362, 3021, 2933, 2860, 1458, 1380, 1196, 1055 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.33–7.16 (m, 5H), 4.96 (d, $J = 3.2$ Hz, 1H), 3.93 (m, 1H), 3.66 (m, 1H), 1.20 (d, $J = 6.1$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 140.9, 128.6, 127.8, 126.2, 76.9, 73.9, 73.3, 22.7. HRMS calcd for $C_{11}H_{16}O_3Si$ (M^+) 196.1099, found 196.1097.

General Procedure for the Nucleophilic Reaction to α,β-Unsaturated Acylsilane **1a**

To a solution of acylsilane **1a** (0.5 mmol) in THF (10 mL), a solution of a nucleophilic reagent was added slowly. After stirring for 1 h, methanol (1 mL) was added and the reaction mixture was allowed to warm to ambient temperature and then poured into brine. The aqueous layer was extracted with diethyl ether for three times. The combined organic layer was then washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 10:1 hexane–ethyl acetate as the eluent to give silyl alcohol derivative **11a** in 51–99% yields or β-silyl ketone derivative **12a** in 62% yield as pale yellow oil.

*4-Phenyl-2-trimethylsilyl-3-buten-1-ol (***11a***).* IR (neat) 3443, 3026, 2957, 2899, 1599, 1493, 1448, 1248, 1059 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.19 (m, 5H), 6.41 (d, $J = 16.2$ Hz, 1H), 6.37 (d,

J = 16.2 Hz, 1H), 1.40 (s, 3H), 0.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 136.6, 128.4, 126.7, 126.0, 125.0, 69.0, 24.8, –4.4. HRMS calcd for $C_{13}H_{20}OSi$ (M^+) 220.1283, found 220.1281.

4-Phenyl-2-dimethylphenylsilyl-2-propen-1-ol (**11b**), 4-Phenyl-2-triisopropylsilyl-3-buten-1-ol (**11c**), and 1,3-diphenyl-1-trimethylsilyl-3-buten-1-ol (**11d**) were synthesized in a manner similar to those for **11a** described above, in the yield of 81, 84, and 74%, respectively, as pale yellow oil.

Compound **11b**: IR (neat) 3439, 3025, 2961, 1599, 1577, 1492, 1448, 1248, 1115 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.19 (m, 10H), 6.36 (d, J = 16.0 Hz, 1H), 6.31 (d, J = 16.0 Hz, 1H), 1.36 (s, 3H), 0.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 135.9, 135.5, 134.2, 129.4, 128.2, 127.4, 126.5, 125.8, 125.1, 68.9, 24.8, –6.1. HRMS calcd for $C_{18}H_{22}OSi$ (M^+) 282.1440, found 282.1442.

Compound **11c**: IR (neat) 3450, 3026, 2945, 2866, 1600, 1493, 1448, 1252, 1115 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.16 (m, 5H), 6.48 (d, J = 15.8 Hz, 1H), 6.44 (d, J = 15.8 Hz, 1H), 1.50 (s, 3H), 1.37–1.05 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 137.6, 128.5, 126.7, 126.0, 123.7, 71.8, 28.3, 19.2, 11.0. HRMS calcd for $C_{19}H_{32}OSi$ (M^+) 304.2222, found 304.2225.

Compound **11d**: IR (neat) 3433, 3028, 2959, 1599, 1578, 1493, 1248, 1067 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.13 (m, 10H), 6.93 (d, J = 15.6 Hz, 1H), 6.60 (d, J = 15.6 Hz, 1H), 0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 137.6, 134.3, 128.5, 128.4, 128.3, 127.0, 126.6, 125.9, 124.2, 75.0, –4.1. HRMS calcd for $C_{18}H_{22}OSi$ (M^+) 282.1440, found 282.1443.

4-Phenyl-4-trimethylsilylbutan-2-one (**12a**). IR (neat) 3024, 2955, 2897, 1717, 1601, 1578, 1495, 1450, 1248, 1115 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.00 (m, 5H), 2.97–2.91 (m, 1H), 2.74–2.62 (m, 2H), 2.03 (s, 3H), 0.06 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.0, 142.5, 128.1, 127.2, 124.6, 43.8, 31.5, 29.7, –3.2. HRMS calcd for $C_{13}H_{20}OSi$ (M^+) 220.1283, found 220.1287.

*General Procedure for the Reaction of Silyl Alcohols **11** with m-CPBA*

To a solution of silyl alcohol (1 mmol) in dichloromethane (15 mL) at room temperature, *m*-CPBA (336 mg, 1.5 mmol) was added. After completion of the reaction evidenced by GC (usually after being stirred for 1.5–24 h), a saturated sodium hydrogen carbonate solution was added, and then the aqueous layer was extracted with diethyl ether for three times. The combined organic layers were washed with saturated sodium bicarbonate solution and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel using 10:1 hexane–ethyl acetate as the eluent to give 3–hydroxy-2-silylpropan-1-one derivatives **13** in quantitative yield as pale yellow oil.

3-Hydroxy-4-phenyl-3-trimethylsilylbutan-2-one (**13a**). IR (neat) 3429, 3030, 2957, 2899, 1692, 1454, 1420, 1252, 1057 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.32–7.19 (m, 5H), 4.96 (d, J = 5.7 Hz, 1H), 3.04 (d, J = 5.7 Hz, 1H), 1.99 (s, 3H), 0.03 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 212.4, 144.1, 128.4, 127.3, 125.7, 73.7, 56.5, 31.4, –1.7. HRMS calcd for $C_{13}H_{20}O_2Si$ (M^+) 236.1233, found 236.1234.

3-Hydroxy-4-phenyl-3-dimethylphenylsilylbutan-2-one (**13b**). IR (neat) 3379, 3048, 2900, 1669, 1611, 1577, 1495, 1450, 1256, 1119, 1058 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.54–7.20 (m, 10H), 4.96 (brs, 1H), 4.23 (brd, 1H), 3.23 (d, J = 4.6 Hz, 1H), 1.72 (s, 3H), 0.45 (s, 3H), 0.40 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 197.5, 142.6, 132.1, 129.6, 128.4, 127.8, 127.4, 127.2, 126.2, 72.9, 55.5, 26.5, 0.0. HRMS calcd for $C_{18}H_{22}O_2Si$ (M^+) 298.1389, found 298.1392.

3-Hydroxy-4-phenyl-3-triisopropylsilylbutan-2-one (**13c**). IR (neat) 3447, 3026, 2945 2868, 1670, 1601, 1582, 1493, 1450, 1234, 1163, 1057 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.38–7.17 (m, 5H), 5.29 (d, J = 10.5 Hz, 1H), 4.97 (d, J = 10.5 Hz, 1H), 3.24 (s, 1H), 1.92 (s, 3H), 1.41–1.34 (m, 3H), 1.25–1.13 (m, 18H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 215.0, 145.5, 128.1, 126.7, 124.8, 72.4, 50.6, 34.1, 18.7, 11.9. HRMS calcd for $C_{19}H_{32}O_2Si$ (M^+) 320.2172, found 320.2170.

3-Hydroxy-1,3-diphenyl-2-trimethylsilylpropan-2-one (**13d**). IR (neat) 3452, 3029, 2947, 2901, 1689, 1491, 1450, 1257, 1056 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.77–7.19 (m, 10H), 5.21 (d, J = 4.6 Hz, 1H), 3.94 (d, J = 4.6 Hz, 1H), 0.01 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$): δ 205.2, 144.8, 138.9, 132.7, 128.6, 128.1, 127.6, 126.0, 125.6, 74.1, 50.4, –1.5. HRMS calcd for $C_{18}H_{22}O_2Si$ (M^+) 298.1389, found 298.1392.

General Procedure for the Oxidation of Silyl Alcohol **11a**

Method for using Oxone® as an oxidant. To a solution of silyl alcohol **11a** (220 mg, 1 mmol) in ethyl

acetate (5 mL) at room temperature, a sodium bicarbonate solution (420 mg, 5 mmol, 5 mL) was added. Then an aqueous oxone solution (oxone 923 mg, 1.5 mmol, 6.4 mL) and acetone (732 μL, 10 mmol) were added. After stirring for 1 h, the reaction mixture was separated and then the aqueous layer was extracted with diethyl ether for three times. The combined organic layer was then washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 10:1 hexane–ethyl acetate as the eluent to give hydroxysilylpropanone derivative **13a** in quantitative yield.

Method for Using Hydrogen Peroxide as an Oxidant. To a solution of silyl alcohol **11a** (220 mg, 1 mmol) in methanol (10 mL) at room temperature, acetonitrile (165 mg, 4 mmol), 30% hydrogen peroxide (456 mg, 4 mmol), and phosphate buffer (8.7 mmol KH_2PO_4 and 30.4 mmol $Na_2HPO_4/kg{\cdot}H_2O$, 250 μL) were added. After stirring for 24 h, the reaction mixture was added brine and then extracted with diethyl ether for three times. The combined organic layer was then washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 10:1 hexane–ethyl acetate as the eluent to give β-hydroxy ketone derivative **14a** in 56% yield as pale yellow oil.

Method for Sharpless–Katsuki Asymmetric Epoxidation Reagents as an Oxidant. To a solution of titanium isopropoxide (355μL, 1.2 mmol) at –18°C, diethyl-L-tartarate (248 mg, 1.2 mmol) was added. After stirring for 5 min, the reaction mixture was added silyl alcohol **11a** (220 mg, 1 mmol) and *tert*-butyl hydroperoxide(219 μL, 1.2 mmol) and then stirred at ambience temperature for 1 h. Then 10% tartaric acid solution was added and stirred for 30 min. The reaction mixture was separated, and then the aqueous layer was extracted with diethyl ether for three times. The combined organic layer was then washed with brine, and concentrated in vacuo. The residue was added diethyl ether (10 mL) and 1 N sodium hydroxide solution at 0°C. After stirring for 30 min, a saturated ammonium chloride solution was added, and then the aqueous layer was extracted with diethyl ether for three times. The combined organic layer was then washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 10:1 hexane–ethyl acetate as the eluent to give the mixture of **13a**, **14a,** and 4-phenyl-3-buten-2-one **15a** (13:26:61) in 66% yield as pale yellow oil.

Method for Using Sodium Peroxide as an Oxidant. To a solution of silyl alcohol **11a** (220 mg, 1 mmol) in ethanol (10 mL) at room temperature, sodium peroxide (312 mg, 4 mmol) was added. After stirring at 45°C for 40 min, the reaction mixture was allowed to cool to 35°C and stirred for 1 h. Then 0.01 M hydrochloric acid solution was added at ambience temperature, the reaction mixture was separated and then the aqueous layer was extracted with diethyl ether for three times. The combined organic layer was then washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on a silica gel 10:1 hexane–ethyl acetate as the eluent to give 4-phenylbutan-2-one **16a** in 89% yield as pale yellow oil.

REFERENCES

[1] For recent reviews on synthesis and reaction of acylsilanes, see (a) Brook, M. A. Silicon in Organic, Organometallic, and Polymer Chemistry; Wiley: New York, 2000; (b) Page, P. C. B.; McKenzie, M. J. Product Subclass 25: Acylsilanes. In Science of Synthesis; Fleming, I., Ed.; Thieme: Stuttgart, Germany, 2001; Vol. 4, pp. 513–568; (c) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A. J Organomet Chem 1998, 567, 181–189; (d) Qi, H.; Curran, D. P. In Acyl Silicon, Germanium, or Boron Functions. Comprehensive Organic Functional Group Transformations: Synthesis: Carbon with Two Attached Heteroatoms with at Least One Carbon-to-Heteroatom Multiple Link, Katrizky, A. R., Meth-Cohn, O., Rees, C. W., Moody, C. J., (Eds.); Pergamon: Oxford, UK, 1995; Vol. 5, pp. 409–433, Ch. 5.09; (e) Cirillo, P. F.; Panek, J. S. Org Prep Proced Int 1992, 24, 553–582.

[2] (a) Page, P. C. B.; McKenzie, M. J.; Klair, S. S.; Rosenthal, S. In The Chemistry of Organic Silicon Compounds; Rappoport, Z., Apeloig, Y., (Eds.); Wiley: New York, 1998; Vol. 2, pp. 1599–1665, Ch. 27; (b) Tsubouchi, A.; Sasaki, N.; Enatsu, S.; Takeda, T. Tetrahedron Lett 2013, 54, 1264–1267; (c) Sasaki, M.; Oyamada, K.; Takeda, K. J Org Chem 2010, 75, 3941–3943; (d) Takeda, K. Yakugaku Zasshi 2007, 127, 1399–1418; (e) Takeda, K.; Nakatani, J.; Nakamura, H.; Sako, K.; Yoshii, E.; Yamaguchi, K. Synlett 1993, 841–843; (f) Takeda, K.; Fujisawa, M.; Makino, T.; Yoshii, E. J Am Chem Soc 1993, 115, 9351–9352.

[3] (a) Honda, M.; Mikami, Y.; Sanjyo, T.; Segi, M.; Nakajima, T. Chem Lett 2005, 34, 1432–1433; (b) Honda, M.; Ohkura, N.; Saisyo, S.-I.; Segi, M.; Nakajima, T. Tetrahedron 2003, 59, 8203–8212; (c) Honda, M.; Nakajima, T.; Okada, M.; Ymaguchi, K.; Suda, M.; Kunimoto, K.-K.; Segi, M. Tetrahedron Lett 2011, 52, 3740–3742; (d) Honda, M. and Segi, M. J Synth Org Chem Jpn 2010, 68, 601–613; (e) Honda, M.; Mita, T.; Nishizawa, T.; Sano, T.; Segi, M. and Nakajima, T. TetrahedronLett 2006, 47, 5751–5754; (f) Honda, M.; Naitou, T.; Hoshino, H.; Takagi, S.; Segi, M. and Nakajima, T. Tetrahedron Lett 2005, 46, 7345–7348; (g) Honda, M.; Yamamoto, Y.; Tsuchida, H.; Segi,

M.; Nakajima, T. Tetrahedron Lett 2005, 46, 6465–6468; (h) Honda, M.; Iwamoto, R.; Nogami, Y.; Segi, M. Chem Lett 2005, 3x4, 466–467; (i) Honda, M.; Oguchi, W.; Segi, M.; Nakajima, T. Tetrahedron 2002, 58, 6815–6823.

[4] For reports on protodesilylation of α-silylalcohols with complete retention of the configuration, see (a) Nakada, M.; Urano, Y.; Kobayashi, S.; Ohno, M. J Am Chem Soc 1988, 110, 4826–4827; (b) Nakada, M.; Urano, Y.; Kobayashi, S.; Ohno, M. Tetrahedron Lett 1994, 35, 741–744.

[5] For recent examples of synthesis of 1,2,3-triol derivatives, but they are not stereocontrolled synthesis, see (a) Mukerjee, P.; Abid, M.; Schroeder, F. C. Org Lett 2010, 12, 3986–3989; (b) Alp, C.; Atmaca, U.; Çelik, M.; Gültekin, M. S. Synlett 2009, 2765–2768; (c) Dunlap, N. K.; Drake, J.; Ward, A.; Salyard, T. L. J.; Martin, L. J Org Chem 2007, 73, 2928–2930; (d) Fujino, A.; Asano, M.; Yamaguchi, H.; Shirasaka, N.; Sakoda, A.; Ikunaka, M.; Obata, R.; Nishiyama, S.; Sugai, T. Tetrahedron Lett 2007, 48, 979–983.

[6] (a) Honda, M.; Oguchi, W.; Segi, M.; Nakajima, T. Tetrahedron 2002, 58, 6815–6823; (b) Sato, T.; Arai, M.; Kuwajima, I. J Am Chem Soc 1977, 99, 5827–5828.

[7] For reviews on osmylation reaction, see (a) Français, A.; Bedel, O.; Haudrechy, A. Tetrahedron 2008, 64, 2495–2524; (b) Donohoe, T. J. Oxidation and Reduction in Organic Synthesis; Oxford University Press: New York, 2000.

[8] Valente, V. R.; Wolfhagen, J. L. J Org Chem 1966, 31, 2509–2512.

[9] Daignault, R. A.; Eliel, E. L. Org Synth Coll. Vol. V, 1973, 303–305.

[10] Fujisawa, T.; Ukaji, Y.; Funabora, M.; Yamashita, M.; Sato, T. Bull Chem Soc Jpn 1990, 63, 1894–1897.

[11] Huber, P.; Bratovanov, S.; Bienz, S.; Syldatk, C.; Pietzsch, M. Tetrahedron: Asymmetry 1996, 7, 69–78.

[12] Mash, E. A.; Nelson, K. A.; Deusen, S. V.; Hemperly, S. B. Org Synth Coll, Vol. VIII, 1993, 155–161.

[13] (a) Enda, J.; Kuwajima, I. J Am Chem Soc 1985, 107, 5495–5501; (b) Kato, M.; Mori, A.; Oshino, H.; Enda, J.; Kobayashi, K.; Kuwajima, I. J Am Chem Soc 1984, 106, 1773–1778; (c) Bonini, B. F.; Comes-Franchini, M.; Fochi, M.; Mazzanti, G.; Ricci, A.; Varchi, G. Synlett 2000, 1688–1690.

[14] Imamoto, T.; Suguira, Y.; Takiyama, N. Tetrahedron Lett 1984, 25, 4233–4236.

[15] For review on directed epoxidation of allylic alcohols, see Hoveyda, A. H.; Evans, D. A.; Fu, G. C. Chem Rev 1993, 93, 1307–1370.

[16] Fässler, J.; Enev, V.; Bienz, S. Helv Chim Acta 1999, 82, 561–587.

[17] For reviews on Sharpless-Katsuki asymmetric epoxidation, see (a) Johnson, R. A.; Sharpless, K. B. In Comprehensive Organic Synthesis, Trost, B. M.; Fleming, I., (Eds.); Pergamon Press: New York, 1991; Vol. 7, pp. 389–436; (b) Johnson, R. A.; Sharpless, K. B. In Catalytic Asymmetric Synthesis, Ojima, I., (Ed.); VCH: New York, 1993; pp. 103–158; (c) Katsuki, T.; Martin, V. S. Org React 1996, 48, 1–300.

[18] For report on epoxidation of olefins using oxone, see Hashimoto, N.; Kanda, A. Org Proc Res Dev 2002, 6, 405–406.

[19] For report on epoxidation with H_2O_2 in buffer, see Ogata, Y.; Sawaki, Y. Tetrahedron 1964, 20, 2065–2068.

[20] Yamashita, M.; Reddy, K. V.; Rao, L. N.; Haritha, B.; Maeda, M.; Suzuki, K.; Totsuka, H.; Takahashi, M.; Oshikawa, T. Tetrahedron Lett 2003, 44, 2339–2341.