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## Stereoselective synthesis of allyl ethers using $\alpha$ , $\beta$ -unsaturated acylsilanes

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ABSTRACT

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Keywords: α,β-Unsaturated acylsilane Silylvinylmethanol Allylic rearrangement Allyl ether Protodesilylation The reaction behavior of silylvinylmethanols with acid catalysts was investigated. The starting silylvinylmethanols 2 were prepared by the reaction of the corresponding  $\alpha,\beta$ -unsaturated acylsilanes 1 with organocerium reagents. The reaction of 2 with TsOH in methanol proceeded to give the corresponding silyl-substituted allyl ether derivatives 3 in high yields with good stereoselectivity. The silylvinylmethanols 2 having a *n*-alkyl or phenyl group on the carbinyl carbon reacted to afford the *E*-allyl derivatives selectively. On the other hand, the reaction of silylvinylmethanols possessing a *tert*-butyl group gave the *Z*-isomers exclusively. The following protodesilylation of the resulting allyl derivatives 3 proceeded with retention of configuration to provide the geometrically constrained allyl ethers 4.

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Z-Allyl ethers 4

#### Introduction

Acylsilanes will become useful synthetic intermediates due to specific properties of sterically congested and electrically positive silvl group and carbonyl group that is one of the most reactive organic functional groups.<sup>1</sup> We have currently investigated the newly synthetic methods for functionalized acylsilanes<sup>2</sup> and their synthetic utilities.<sup>3</sup> Especially, cyclopropyl silvl ketones have been conveniently synthesized<sup>2</sup> and utilized as a building block for the stereoselective synthesis of homoallyl derivatives by applying the specific properties of the silyl group as a good directing and leaving group (Scheme 1).<sup>3a</sup> Therefore our stereoselective synthetic route for Z-homoallyl derivatives is existing as a complementary method for the preparation of Ehomoallyl derivatives developed by Julia and co-workers (Scheme 2).<sup>4</sup> While this serviceable and useful method has not been applied to prepare Z-allyl derivatives that are homolog compounds of Z-homoallyl derivatives, there is a report to



Scheme 1. Synthesis and utilization of cyclopropyl silyl ketones.



Scheme 3. Geometrically defined synthesis of allyl ether derivatives. construct allyl alcohol possessing silyl group at the terminal vinyl carbon derived from  $\alpha$ -hydroxyalkenylsilane by similar type of reaction.<sup>5</sup> In this letter, stereoselective synthesis of Z-allyl ethers 4 using  $\alpha,\beta$ -unsaturated acylsilanes 1 by a sequence of reactions mentioned above is described (Scheme 3). Our synthetic method will be very helpful to prepare Z-allyl derivatives that have a great deal of potential in organic reactions (e.g. Claisen rearrangement,<sup>6</sup> Sharpless epoxidation<sup>7</sup>) to elaborate naturally occurring complex compounds.

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#### **Results and discussion**

The starting materials,  $\alpha$ , $\beta$ -unsaturated acylsilanes 1, are prepared by four routes I-IV as follows depending on the kind of terminal substituent group R (Scheme 4). The silylation of easily available  $\alpha$ , $\beta$ -unsaturated aldehydes 5 was carried out to obtain

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#### Tetrahedron



Scheme 4. Preparation of α,β-unsaturated acylsilanes 1.

the corresponding acylsilanes (route I). Since the direct conversion of aldehyde to silyl ketone is impossible, the umpolung of carbonyl group was employed by thioacetal formation.<sup>8</sup> The aldehydes 5 were quantitatively converted to thioacetals 6 by reaction with 1,3-propanedithiol and iodine.<sup>9</sup> These results were shown in Table 1. The deprotonation of resulting thioacetals 6 with n-butyllithium, followed by electrophilic reaction with chlorosilanes afforded 2-silylated 1,3dithiane derivatives 7 in high yields.<sup>10</sup> The deprotection of silvldithianes 7 with calcium carbonate and iodine provided the corresponding 1 having a phenyl group at terminal position (Entries 1 and 2).<sup>11</sup> However, similar deprotection of silyldithianes 7 possessing a terminal alkyl group gave the complex mixture (Entries 3 and 4). Then the nucleophilic silulation of  $\alpha,\beta$ -unsaturated aldehydes 5 with silulithium and the following oxidation of resulting silyl alcohols to prepare the desired acylsilanes 1 were investigated (Scheme 4, route II). The nucleophilic reaction of silyllithium, prepared from disilane with methyllithium, to 5 proceeded to give silyl alcohol 8 with moderate yield (Scheme 5).<sup>12</sup> However the reaction of **Table 1.** Preparation of  $\alpha$ ,  $\beta$ -unsaturated acylsilanes 1 via dithiane route

cinnamaldehyde did not proceed well. Next, the silyl protection of allyl alcohol and the continuing retro-Brook rearrangement<sup>13</sup> to afford silyl alcohol were performed (route **III**). A sequence of reactions beginning with *E*-2-nonenol gives the corresponding silyl alcohols **8** in good yields, however 1,2-silyl migration of cynnamyloxysilane did not proceed (Table 2).<sup>12-14</sup> The Swern oxidation of the resulting 1-silyl-2-nonenols **8** provided the target acylsilanes **1** (Scheme 6).<sup>14a,15</sup> Since it was difficult to synthesize the compound **1** possessing a methyl group at the terminal position via routes **I–III**, this acylsilane was prepared by Mukaiyama aldol reaction<sup>16</sup> using silyl enol ether of acetylsilane



Scheme 5. Nucleophilic silulation of  $\alpha,\beta$ -unsaturated aldehyde 5 with silulithium.

F	о н 5	CHCl <sub>3</sub> r.t., 10 min	$\begin{array}{c} & & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ $	BuLi <u>SiCl</u> HF 0 °C, 2 h 1.5 h	$ \begin{array}{c}  S \\  S \\  S \\  S \\  S \\  S \\  THI  r.t.,  $	$F_{H_2O}$ $R$ $S_{I_2}$ $S_{I_2O}$ $S_{I_2$
	Entry	R	Yield of 6 (%) <sup>a</sup>	Si	Yield of 7 (%) <sup>a</sup>	Yield of $1 (\%)^{b}$
	1	Dh	> 00	SiMe <sub>3</sub>	>99	66
	2	FII	~99	SiMe <sub>2</sub> Ph	>99	39
	3	<i>п</i> -С <sub>6</sub> Н <sub>13</sub>	>99	SiMe <sub>2</sub> Ph	91	Complex mixture
	4	Ме	>99	SiMe <sub>2</sub> Ph	>99	Complex mixture
	<sup>a</sup> Crude	vield				

<sup>b</sup> Isolated yield.

Table 2. Synthesis of silyl alcohol 8 via retro-Brook rearrangement of silyl ehter 9

R´	∕∾∩н	<u><i>n</i>-BuLi</u> THF -78 to 0 °C 1 h	- <u>SiCl</u> THF -78 to 0 ℃ 2 h	OSi <u>t-B</u> 9 -78 to 3	ULi HF -30 °C 8 h	S
	Entry	R	Si	Yield of <b>9</b> (%) <sup>a</sup>	Yield of <b>8</b> (%) <sup>a</sup>	
	1	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	SiMe <sub>3</sub>	91	88	
	2	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	SiMe <sub>2</sub> Ph	>99	55	
	3	Ph	SiMe <sub>3</sub>	88	Complex mixture	

<sup>a</sup> Crude yield.



#### Scheme 6. Swern oxidation of silyl alcohol 8.

(route **IV**). The acetylsilane was easily enolized with LDA. Then the resulting enolate was trapped with chlorosilane to afford the silyl enol ether (Scheme 7).<sup>17</sup> The Mukaiyama aldol reaction of this enol ether with dimethyl acetal gave the corresponding  $\beta$ methoxyacylsilane in good yield,<sup>17,18</sup> and the following  $\beta$ elimination of methanol provided the desired propenyl silyl ketone **1**.<sup>17e</sup>



Scheme 7. Synthesis of  $\alpha$ , $\beta$ -unsaturated acylsilane 1 via Mukaiyama aldol reaction

The preparation of silyl-substituted allyl alcohols 2 by nucleophilic addition of organocerium reagents<sup>19</sup> to the resulting 1 was examined.<sup>17d,e,20</sup> Acylsilanes 1 were treated with organocerium reagents at -78 °C in THF as shown in Table 3. The reaction proceeded to afford the corresponding silyl alcohols 2 in moderate to high yields, accompanied by the formation of  $\beta$ silyl ketones 10 as by-product. In these reactions, the selectivity on the formation of 2 and 10 was affected by the bulkiness of nucleophilic groups (R'). The reaction using methyl or phenylcerium reagent as nucleophiles predominantly gave silyl alcohols 2 independent of the kind of substituent of acylsilanes 1 (Entries 1, 4, 5, 9, 10, 12, and 13). Though the rate of production of  $\beta$ -silyl ketones was increased with increasing of the bulkiness of nucleophilic groups (Entries 1-3, and 5-8). The plausible reaction mechanism of nucleophilic addition to acylsilanes is proposed as shown in Scheme  $8.^{20,21}$  First, the attack of nucleophilic group occurs to yield alkoxy anion species A. When R' is a small group, the following hydrolysis proceeds to afford silyl alcohols 2, whereas R' is a bulky group, the Brook rearrangement<sup>22</sup> also goes to form carbanion **B** in order to avoid the steric repulsion between R' and bulky silyl group on quaternary carbon. In the case of the intermediate A having a phenyl group as R', the phenyl group acts as a small group since it has a strainless planear structure. After the resonance with the ally anion C, 1,4-migration of silvl group and the following hydrolysis of **D** proceed to give  $\beta$ -silyl ketones 10.

	B			. <sub>В</sub> ́	R' OH Si Si + B	o I B'
		1	лпг, <del>-</del> 76 С, 211		2	10
	Entry	R	Si	R'	Total yield (%) <sup>a</sup>	2/10 <sup>b</sup>
	1	Ph	SiMe <sub>3</sub>	Me	99	>99/1
	2	Ph	SiMe <sub>3</sub>	<i>n</i> -Bu	50	87/13
	3	Ph	SiMe <sub>3</sub>	t-Bu	60	62/38
	4	Ph	SiMe <sub>3</sub>	Ph	74	>99/1
	5	Ph	SiMe <sub>2</sub> Ph	Ме	55	>99/1
	6	Ph	SiMe <sub>2</sub> Ph	<i>n</i> -Bu	22	85/15
	7	Ph	SiMe <sub>2</sub> Ph	<i>s</i> -Bu	39	54 <sup>c</sup> /46
7	8	Ph	SiMe <sub>2</sub> Ph	<i>t</i> -Bu	35	47/53
	9	Ph	SiMe <sub>2</sub> Ph	Ph	70	>99/1
	10	Me	SiMe <sub>2</sub> Ph	Me	80	>99/1
	11	Me	SiMe <sub>2</sub> Ph	<i>n</i> -Bu	47	87/13
	12	Me	SiMe <sub>2</sub> Ph	Ph	58	>99/1
	13	<i>п</i> -С <sub>6</sub> Н <sub>13</sub>	SiMe <sub>3</sub>	Me	61	>99/1
	14	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	SiMe <sub>3</sub>	t-Bu	39	65/35

Table 3. Nucleophilic addition reaction with organocerium reagents

Molar ratio; 1/R'CeCl<sub>2</sub>=1:6.

R'CeCl<sub>2</sub> was generated by the reaction of R'Li with CeCl<sub>3</sub>.

<sup>a</sup> Isolated yield.

<sup>b</sup> Determined by <sup>1</sup>H NMR analysis.

<sup>c</sup> Diasteromer mixture was obtained (51:49).

Tetrahedron



Scheme 8. Plausible reaction pathway of nucleophilic addition.

Table 4. Rearrangement reaction of silvl alcohols 2 with TsOH

			4	TsOH	_	MeO R'	2
	R	~~	Si MeC	OH, Temp., Ti	ime	R Si	
	2	2				3	
Entry	R	R'	Si	Temp. (°C)	Time (h)	Yield (%) <sup>a</sup>	$E/Z^{b}$
1	Ph	Me	SiMe <sub>3</sub>	0	0.5	93	76/24
2	Ph	<i>n</i> -Bu	SiMe <sub>3</sub>	0	0.5	96	93/7
3	Ph	t-Bu	SiMe <sub>3</sub>	r.t.	2.0	65	2/98
4	Ph	Ph	SiMe <sub>3</sub>	0	2.0	75	96/4
5	Ph	Me	SiMe <sub>2</sub> Ph	0	0.5	80	91/9
6	Ph	<i>n</i> -Bu	SiMe <sub>2</sub> Ph	0	0.5	>99	89/11
7	Ph	<i>s</i> -Bu	SiMe <sub>2</sub> Ph	r.t.	1.0	81	32/68
8	Ph	t-Bu	SiMe <sub>2</sub> Ph	r.t.	2.0	47	4/96
9	Ph	Ph	SiMe <sub>2</sub> Ph	r.t.	1.0	76	97/3
10	Me	Me	SiMe <sub>2</sub> Ph	0	0.5	77	85/15
11	Me	<i>n</i> -Bu	SiMe <sub>2</sub> Ph	0	0.5	77	64/36
12	Me	Ph	SiMe <sub>2</sub> Ph	0	2.0	91	97/3
13	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	Me	SiMe <sub>3</sub>	0	0.5	68	78/22
14	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	t-Bu	SiMe <sub>3</sub>	r.t.	10.0	79	2/98

Molar ratio; 2/TsOH/MeOH=1:3:40.

<sup>a</sup> Isolated yield. <sup>b</sup> Determined by <sup>1</sup>H NMR analysis.

Then, treatment of silyl-substituted allyl alcohols **2**, derived from the above nucleophilic reaction, with TsOH in methanol was carried out.<sup>3a</sup> The allylic rearrangement proceeded to give silyl-substituted allyl ethers **3** stereoselectively. The results are summarized in Table 4. The yields of allyl derivatives **3** were generally reasonable, irrespective of the substituents on the terminal or the carbinyl carbon except in the presence of *t*-butyl group. It is noteworthy that the stereoselectivity of these reactions was significantly influenced by the bulkiness of the substituents on the carbinyl carbon. The reaction of silyl alcohols **2** having a *n*-alkyl or phenyl group on the carbinyl carbon afforded the *E*-isomer selectively (Entries 1, 2, 4, 5, 6, 9, 10, 11, 12, and 13). On the other hand, the alcohols **2** possessing a *s*- or *t*-alkyl group on that reacted to yield the corresponding *Z*-isomer with high stereoselectivity (Entries 3, 7, 8, and 14). These results suggest that the stereochemistry of allylic rearrangement of the silyl-substituted allyl alcohols **2** is dependent on the steric repulsion between substituents, silyl group on the carbinyl carbon and the terminal group of alkene moiety. Thus, the following mechanism for the reaction is proposed (Scheme 9). The acid protonates at the oxygen atom of the starting alcohol and allyl cation species  $\mathbf{E}^{23}$  is formed. When *Si* group is larger than R' (*n*-alkyl or phenyl), the formation of *trans*-allylic cation **F** is favored compared to *cis*-allylic cation **G** due to the less strain between R' group and terminal substituent **R**. As a consequence, *E*-silylalkene is formed selectively. In contrast, in the case of the reaction using silyl-substituted allyl alcohols having a *s*- or *t*-alkyl group on the carbinyl carbon, *trans*-allylic cation **F** is disfavored by the steric repulsion between *s*- or *t*-alkyl group, that is bulky compared with silyl





group, and terminal group R. Although the *Si* group is also bulky, the long Si–C single bond reduces the effective steric hindrance.<sup>24</sup> As a result, the reaction of silyl alcohols possessing a *s*- or *t*-alkyl group leads to *Z*-silylalkene with high stereoselectivity by way of *cis*-allylic cation **G**.

It is known that the protodesilylation of vinylsilane proceeds with complete retention of the configuration.<sup>25</sup> Thus, protodesilylation of the resulting *E*- and *Z*-silyl-substituted allyl derivatives **3** was examined and the results are shown in Tables 5 and 6. Treatment of *E*- and *Z*-**3** with tetrabutylammonium fluoride (TBAF) in hexamethylphosphoric triamide at 80 °C gave the corresponding *Z*- and *E*-protodesilylated compounds **4**, respectively. While the reaction of vinylsilane possessing an aryl group on silicon atom proceeded smoothly, the reactivity of desilylation of vinyltrialkylsilane was low.<sup>25a,b</sup> Unfortunately, the reaction of vinylsilanes having a phenyl group on the  $\alpha$  carbon

Table 5. Protodesilylation of E-vinylsilanes 3 with n-Bu<sub>4</sub>NF

	MeO	R'	<i>n</i> -Bu₂	ţNF	MeO R'		
	R	Si	HMPA, 80	°C, Time	R		
	E-3	3			Z-4		
Entry	R	R'	Si	Time (h)	Yield (%) <sup>a</sup>	E/Z <sup>b</sup>	
1	Ph	Me	SiMe <sub>3</sub>	2.0	13	0/100	
2	Ph	Me	SiMe <sub>2</sub> Ph	2.5	45	0/100	
3	Ph	<i>n</i> -Bu	SiMe <sub>2</sub> Ph	4.5	62	0/100	

Molar ratio; 3/n-Bu<sub>4</sub>NF=1:5.

<sup>a</sup> Isolated yield.

<sup>b</sup> Determined by <sup>1</sup>H NMR analysis.

Table 6. Protodesilylation of Z-vinylsilanes 3 with n-Bu<sub>4</sub>NF

	MeO	Si	<i>n</i> -Bu₄N	IF	MeO	
	R	<sup></sup> R'	HMPA, 80 °	C, Time	R R	
	Z-3				E-4	
Entry	R	R'	Si	Time (h)	Yield (%) <sup>a</sup>	E/Z <sup>b</sup>
1	Ph	t-Bu	SiMe <sub>3</sub>	4.0	27	100/0
2	Ph	<i>s</i> -Bu	SiMe <sub>2</sub> Ph	2.5	68	100/0
3	Ph	<i>t</i> -Bu	SiMe <sub>2</sub> Ph	2.5	61	100/0
4	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	<i>t</i> -Bu	SiMe <sub>3</sub>	3.0	77	100/0

Molar ratio; 3/n-Bu<sub>4</sub>NF=1:5.

<sup>a</sup> Isolated yield.

<sup>b</sup> Determined by <sup>1</sup>H NMR analysis.

Table 7. Reaction of vinylsilanes 3 having a phenyl group with n-Bu<sub>4</sub>NF

Me	Ç PI	h	<i>n</i> -Bu₄NF	MeO		MeO
R′		`SiMe₂Ph	HMPA, 80 °C,	Time R	<sup>~</sup> Ph <sup>+</sup>	R Ph
	E-3			4		11
-	Entry	R	Time (h)	Total yield (%) <sup>a</sup>	4/11	<i>E/Z</i> ratio of 4 <sup>b</sup>
	1	Me	1.0	62	100/0	52/48
	2	Ph	2.0	45	18/82	100/0
-	M	olar ratio; 3	3/ <i>n</i> -Bu₄NF=1:5.			

<sup>a</sup> Isolated yield.

<sup>b</sup> Determined by <sup>1</sup>H NMR analysis.

gave the isomeric mixture of allyl derivatives **4** (Table 7, Entry 1). The reason for this unexpected reaction is not yet understood. In addition, that of vinylsilane having another phenyl group on the  $\gamma$  carbon afforded vinyl ether **11** preferentially that was derived by isomerization from allyl derivatives **4** (Entry 2).

#### Conclusion

In conclusion, acid-catalyzed allylic rearrangement of silvlvinylmethanols 2 has been described. The silvlvinylmethanols 2 reacted with TsOH in methanol to afford the corresponding allyl ethers 3 in high yields with good stereoselectivity, depended on the substituents on the carbinyl carbon. The silvlvinvlmethanols 2 having a *n*-alkyl or phenvl group reacted to afford the *E*-allyl derivatives **3** selectively. On the other hand, the reaction of silvlvinylmethanols possessing a tert-butyl group gave Z-isomers exclusively. The following protodesilylation of the resulting allyl derivatives 3 proceeded with retention of configuration. Thus, it was achieved that the regioselective formation of Z and E-allyl ethers derivatives 4, respectively. Further studies are aimed at expanding the scope of these reactions, and introduction of other functional group instead of silyl group and the following allylic rearrangement reaction are now in progress in our laboratory. The results will be reported in due course.

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# PTED MANUSCRIPT

### Table 1. Preparation of $\alpha$ , $\beta$ -unsaturated acylsilanes 1 via dithiane route

o ∩∎	о <u>(</u> SH, I				CaCO <sub>3</sub> , I₂ O	
R 5	<sup>∼</sup> H CHCl <sub>3</sub> r.t., 10 m	in 6	THF 0 °C 0 °C, 1.5 h	c, 2 h R Si 7	THF/H <sub>2</sub> O R S r.t., 20 h 1	í -
Entry	R	Yield of $6^{a}$ (%	) Si	Yield of $7^{a}$ (%)	Yield of $1^{b}$ (%)	
1	Dh	> 00	SiMe <sub>3</sub>	>99	66	
2	FII	299	SiMe <sub>2</sub> Ph	>99	39	
3	$n-C_6H_{13}$	>99	SiMe <sub>2</sub> Ph	91	Complex mixture	
4	Me	>99	SiMe <sub>2</sub> Ph	>99	Complex mixture	
<sup>a</sup> Crude yiel	ld.					
<sup>b</sup> Isolated yi	ield.					
1~~0	H <u></u>	→ SiCl THF C -78 to 0 °C 2 h	9 -78	t-BuLi THF to -30 °C 8 3 h	Si	9
Entry	R	Si Y	(%) Yield of <b>9</b> <sup>a</sup>	Yield of <b>8</b> <sup>a</sup> (%)		
1	$n-C_6H_{13}$	SiMe <sub>3</sub> 9	1	88		
2	$n-C_6H_{13}$	SiMe <sub>2</sub> Ph >	.99	55		
3	Ph	SiMe <sub>3</sub> 8	8	Complex mixture		
<sup>a</sup> Crude yiel Table 3.	ld. Nucleoph	ilic addition r	reaction with o	rganocerium rea	gents	
R		CeCl₂ 78 °C, 2 h R	R' OH Si +		*	

### Table 2. Synthesis of silyl alcohol 8 via retro-Brook rearrangement of silyl ehter 9

<b>₽</b> ∕∕~	`OH <u></u>	<i>Si</i> Cl THF -78 to 0 °C 2 h	• R OSi 9	t-BuLi         Of           THF         R           -78 to -30 °C         8           3 h         8
Entry	R	Si	Yield of $9^a$ (%)	Yield of $8^{a}$ (%)
1	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	SiMe <sub>3</sub>	91	88
2	$n-C_6H_{13}$	$SiMe_2Ph$	>99	55
3	Ph	SiMe <sub>3</sub>	88	Complex mixture

### Table 3. Nucleophilic addition reaction with organocerium reagents

	` <i>Si</i> ────────────────────────────────────	CeCl₂ ⁄8 °C, 2 h		OH Si Si + R	0 
Entry	R	Si	R'	Total yield <sup>a</sup> (%)	2/10 <sup>b</sup>
1	Ph	SiMe <sub>3</sub>	Me	90	>99/1
2	Ph	SiMe <sub>3</sub>	n-Bu	50	87/13
3	Ph	SiMe <sub>3</sub>	t-Bu	60	62/38
4	Ph	SiMe <sub>3</sub>	Ph	74	>99/1
5	Ph	SiMe <sub>2</sub> Ph	Me	55	>99/1
6	Ph	SiMe <sub>2</sub> Ph	n-Bu	22	85/15
7	Ph	SiMe <sub>2</sub> Ph	s-Bu	39	54°/46
8	Ph	SiMe <sub>2</sub> Ph	t-Bu	35	47/53
9	Ph	SiMe <sub>2</sub> Ph	Ph	70	>99/1
10	Me	SiMe <sub>2</sub> Ph	Me	80	>99/1
11	Me	SiMe <sub>2</sub> Ph	<i>n</i> -Bu	47	87/13
12	Me	SiMe <sub>2</sub> Ph	Ph	58	>99/1
13	$n-C_{6}H_{13}$	SiMe <sub>3</sub>	Me	61	>99/1
14	$n-C_6H_{13}$	SiMe <sub>3</sub>	t-Bu	39	65/35

Molar ratio; 1/R'CeCl<sub>2</sub>=1:6.

 $R'CeCl_2$  was generated by the reaction of R'Li with  $CeCl_3$ .

<sup>a</sup> Isolated yield.

<sup>b</sup>Determined by <sup>1</sup>H NMR analysis.

<sup>c</sup>Diastereomer mixture was obtained (51:49).

#### Table 4. Rearrangement reaction of silyl alcohols 2 with TsOH

R'	он	TsO	н	MeO R'					
R	Si N	MeOH, Ten	np., Time	R	Si				
2				3					
Entry	R	R'	Si	Temp. (°C)	Time (h)	Yield <sup>a</sup> (%)	$E/Z^{\circ}$		
1	Ph	Me	SiMe <sub>3</sub>	0	0.5	93	76/24		
2	Ph	<i>n</i> -Bu	SiMe <sub>3</sub>	0	0.5	96	93/7		
3	Ph	<i>t</i> -Bu	SiMe <sub>3</sub>	r.t.	2.0	65	2/98		
4	Ph	Ph	SiMe <sub>3</sub>	0	2.0	75	96/4		
5	Ph	Me	SiMe <sub>2</sub> Ph	0	0.5	80	91/9		
6	Ph	<i>n</i> -Bu	SiMe <sub>2</sub> Ph	0	0.5	>99	89/11		
7	Ph	s-Bu	SiMe <sub>2</sub> Ph	r.t.	1.0	81	32/68		
8	Ph	<i>t</i> -Bu	SiMe <sub>2</sub> Ph	r.t.	2.0	47	4/96		
9	Ph	Ph	SiMe <sub>2</sub> Ph	r.t.	1.0	76	97/3		
10	Me	Me	SiMe <sub>2</sub> Ph	0	0.5	77	85/15		
11	Me	<i>n</i> -Bu	SiMe <sub>2</sub> Ph	0	0.5	77	64/36	67	
12	Me	Ph	SiMe <sub>2</sub> Ph	0	2.0	91	97/3		
13	$n-C_6H_{13}$	Me	SiMe <sub>3</sub>	0	0.5	68	78/22	/	
14	$n-C_6H_{13}$	<i>t</i> -Bu	SiMe <sub>3</sub>	r.t.	10.0	79	2/98		
Iolar rati	o; <b>2</b> /TsOH/N	AeOH=1:3	3:40.						
Isolated	yield.					<b>•</b>			
Determin	ed by <sup>1</sup> H NM	/IR analysi	is.						

## Table 5. Protodesilylation of *E*-vinylsilanes 3 with *n*-Bu<sub>4</sub>NF

MeO R'		<i>n</i> -Bu₄NF		MeO	R' 1	
R	Si Si	HMPA	, 80 °C, Time	R		
E-3				<i>Z</i> -4		
Entry	R	R'	Si	Time (h)	Yield <sup>a</sup> (%)	$E/Z^{b}$
1	Ph	Me	SiMe <sub>3</sub>	2.0	13	0/100
2	Ph	Me	SiMe <sub>2</sub> Ph	2.5	45	0/100
3	Ph	<i>n-</i> Bu	SiMe <sub>2</sub> Ph	4.5	62	0/100

Molar ratio; 3/n-Bu<sub>4</sub>NF=1:5.

<sup>a</sup> Isolated yield.

<sup>b</sup>Determined by <sup>1</sup>H NMR analysis.

MeO	Si	<i>n</i> -Bu₄NF		MeO		
R	R' HM	IPA, 80 °C	, Time	R	I	
Z-3				E-4		
Entry	R	R'	Si	Time (h)	Yield <sup>a</sup> (%)	$E/Z^{b}$
1	Ph	t-Bu	SiMe <sub>3</sub>	4.0	27	100/0
2	Ph	s-Bu	SiMe <sub>2</sub> Ph	2.5	68	100/0
3	Ph	t-Bu	SiMe <sub>2</sub> Ph	2.5	61	100/0
4	$n-C_{6}H_{13}$	t-Bu	SiMe <sub>3</sub>	3.0	77	100/0

## Table 6. Protodesilylation of Z-vinylsilanes 3 with *n*-Bu<sub>4</sub>NF

Molar ratio; 3/n-Bu<sub>4</sub>NF=1:5.

<sup>a</sup> Isolated yield.

<sup>b</sup>Determined by <sup>1</sup>H NMR analysis.

### **Table 7.** Reaction of vinylsilanes **3** having a phenyl group with *n*-Bu<sub>4</sub>NF

MeO	Ph	<i>п</i> -Ві	u <sub>4</sub> NF MeO		MeO	
R	SiMe <sub>2</sub> l	Ph HMPA, 8	O °C, Time R ∕	∽ Ph <sup>+</sup>	R	
E	-3			4	11	
Entry	R	Time (h)	Total yield <sup>a</sup> (%	) 4/11	$E/Z$ ratio of $4^{\mathrm{b}}$	
1	Me	1.0	62	100/0	52/48	
2	Ph	2.0	45	18/82	100/0	
Molar ra	atio; <b>3</b> / <i>n</i> -Bu	u <sub>4</sub> NF=1:5.				
<sup>a</sup> Isolate	d yield.					
<sup>b</sup> Determ	nined by <sup>1</sup> H	NMR analys	sis.			
				$<$ $\checkmark$		
1						
	-					

#### Highlights

· Geometrically defined allyl ether derivatives have been synthesized.

Accepted • The silyl group acted as a directing group and a good leaving group.

acylsilanes were described.