Stereospecific C–N Bond Cleavage of 4-Silylated 1,2-Thiazetidine 1,1-Dioxides with $EtAlCl_2$ or $AlCl_3$: Formation of (*E*)-Vinylsulfonamides

Tetsuo IWAMA, Atsuko TAKAGI, and Tadashi KATAOKA*

Gifu Pharmaceutical University, 6–1, Mitahora-higashi 5-chome, Gifu 502–8585, Japan.
Received October 31, 1997; accepted December 26, 1997

Monosilylation of 1,2-thiazetidine 1,1-dioxides (β-sultams) 3 gave (3*R, 4*S**)-4-monosilyl-β-sultams 4 stereoselectively. Disilylated β-sultams 5 were obtained by the use of trimethylsilyl chloride. Treatment of 4-monosilyl-β-sultams 4 with $EtAlCl_2$ caused stereospecific C–N bond cleavage owing to β-cation stabilization of the silicon group to provide (*E*)-vinylsulfonamides (*E*)-7. (*E*)-α-Silylstyrylsulfonamides (*E*)-7j—l were generated in the reaction of 4,4-disilyl-β-sultams 5 with $EtAlCl_2$. Reaction of 4-silyl-β-sultams with $AlCl_3$ afforded *N*-dealkylated (*E*)-vinylsulfonamides in good yields. Reaction of (*E*)-α-silylstyrylsulfonamide (*E*)-10 with benzaldehyde in the presence of tetrabutylammonium fluoride and $BF_3 \cdot Et_2O$ provided the allylic alcohol (*E*)-12.**

Key words β-sultam; C–N bond cleavage; (*E*)-vinylsulfonamide

We previously reported the first success in stereospecific C–N bond cleavage of a β-sultam ring, by the reaction of 4-silylated 1,2-thiazetidine 1,1-dioxides (β-sultams) with $EtAlCl_2$ to form (*E*)-vinylsulfonamides.[1] Vinylsulfonamides have been used in various reactions, such as aziridine formation,[2] 1,3-dipolar cycloadditions,[3] Michael additions[4–9] and Diels–Alder reactions.[10,11] There are several reports on syntheses of vinylsulfonamides.[4,12–16] Recently Gennari and coworkers reported solution- and solid-phase syntheses of vinylogous sulfonamidopeptides with the aim of developing protease inhibitors and new drugs,[17,18] and Schwan and Refvik synthesized vinylsulfonamides by oxidation of vinylsulfenamides.[19,20]

In our previous papers, we showed that the C–S bond of a β-sultam ring bearing alkyl or aryl substituents at C-3 and C-4 was cleaved by a Lewis acid to give aryl ketones, aldehydes,[21] *trans*-1,2,3-oxathiazolidine 2-oxides and *cis*-aziridines.[22] In sharp contrast, reactions of 4-silyl-β-sultams with $EtAlCl_2$ caused C–N bond cleavage owing to the β-effect of silicon. There are several reports concerning C–N bond cleavage of a β-sultam ring;[23–26] however, these reactions are not stereospecific. This is the first report of stereospecific C–N bond cleavage of a β-sultam ring. Desilylated β-sultams were obtained without ring destruction from the reaction of 4-silylated β-sultams with tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF)–acetic acid.[27] On the other hand, use of $EtAlCl_2$ as a reagent resulted in ring opening with elimination of the silyl group. We present here a full account of the stereospecific C–N bond cleavage of 4-silylated β-sultams and formation of (*E*)-vinylsulfonamides.

Results and Discussion

Synthesis of β-Sultams by [2+2] Cycloaddition of Sulfenes and Imines β-Sultams **3** were prepared by the reaction of imines **1** and sulfonyl chlorides **2** (Chart 1, Table 1).[28,29] Methanesulfonyl chloride **2** ($R^3 = H$) was treated with an arylimine **1** in THF solution at room temperature for 3 d. A β-sultam was obtained in poor yield after immediate purification of the oily residue by silica gel column chromatography (entries 1, 3, method A). The oily residue gradually solidified on standing at room temperature for 7—10 d and was then purified by silica gel

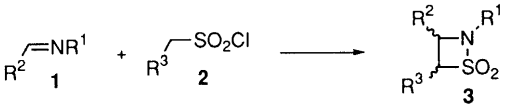

Chart 1

Table 1. Synthesis of β-Sultams **3** from Sulfonyl Chlorides **2** and Imines **1**

Entry	Method[a]	Time (d)	R^1	R^2	R^3	Products (%yield[b] *cis* : *trans*)
1	A	3	$^cC_6H_{11}$	Ph	H	**3a** (24)
2	B	3 then 10	$^cC_6H_{11}$	Ph	H	**3a** (59)
3	A	3	$^cC_6H_{11}$	*p*-MeC_6H_4	H	**3b** (27)
4	B	3 then 7	$^cC_6H_{11}$	*p*-MeC_6H_4	H	**3b** (58)
5	B	3 then 10	$^cC_6H_{11}$	*p*-$MeOC_6H_4$	H	**3c** (56)
6	B	3 then 8	$^cC_6H_{11}$	*p*-BrC_6H_4	H	**3d** (42)
7	C	2	$^cC_6H_{11}$	*tert*-Bu	H	**3e** (54)
8	C	3	$^cC_6H_{11}$	Ph	Me	**3f** (33, 53 : 47)[c]
9	C	3	$^cC_6H_{11}$	Ph	Et	**3g** (32, 61 : 39)[c]
10	D	3	^nBu	Ph	Ph	**3h** (83, 42 : 58)[c]
11	D	3	$^cC_6H_{11}$	*tert*-Bu	Ph	**3i** (18, 64 : 36)[d]

a) Method A: at room temperature for 3 d in THF followed by immediate purification; B: at room temperature for 3 d in THF followed by purification after allowing the residue to stand for 7—10 d at room temperature; C: at room temperature without solvent; D: at −20 °C to room temperature for 3 d in THF solution followed by immediate purification. *b*) Isolated yield. *c*) Separated ratio. *d*) An inseparable mixture. The ratio was determined by ^{1}H-NMR.

* To whom correspondence should be addressed.

chromatography. This method improved the yield (entries 2, 4—6, method B). 4-*tert*-Butyl-β-sultam **3e** was obtained in 54% yield from the reaction of methanesulfonyl chloride with *tert*-butylimine **1** (R^1 = cyclic C_6H_{11}, R^2 = *tert*-Bu) without solvent at room temperature (entry 7, method C). Treatment of ethane- or propanesulfonyl chloride with an arylimine without any solvent (method C) gave the 4-alkyl-β-sultam **3f** or **3g**, respectively, as a mixture of diastereomers (entries 8, 9). The 3,4-diphenyl-β-sultam **3h** was obtained in good yield as a mixture of diastereomers from the reaction of phenylmethanesulfonyl chloride with an arylimine at −20 °C to room temperature for 3 d (entry 10, method D). β-Sultams **3f—h** were used as a mixture of two isomers for the following silylation, although they were separable by silica gel column chromatography.

Synthesis of 4-Monosilyl- and 4,4-Disilyl-β-sultams 4-Monosilylated β-sultams were synthesized as shown in Chart 2. 4-Monosilylation of a β-sultam with trimethylsilyl chloride (TMSCl) is difficult since formation of an oversilylated product is unavoidable.[30] 4-Monosilyl-β-sultams **4a, b, d, e**, which possess (3*R**,4*S**)-configuration, were stereoselectively obtained from reactions using

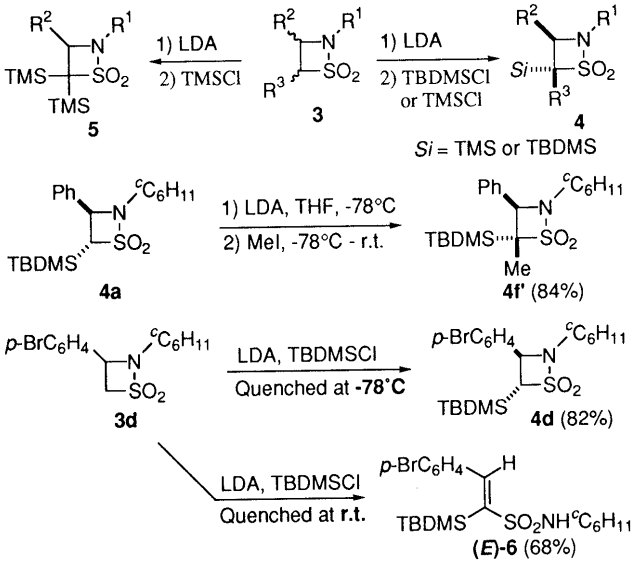

Chart 2

tert-butyldimethylsilyl (TBDMS) chloride as a silylating agent according to a procedure similar to that reported by Müller and co-workers[30] (Table 2, entries 1—4). Their configurations were determined from the ^{1}H-NMR spectra, and, for example, the ^{1}H-NMR spectrum of **4a** showed a pair of doublets at δ 3.80 and 4.08 with the coupling constant of 7.3 Hz due to the 3- and 4-hydrogens, respectively. The data are closely similar to those for a (3*R**,4*S**)-*N*-methyl derivative[30] and therefore show that the 3- and 4-substituents of **4a** have *trans*-geometry, namely the (3*R**,4*S**)-configuration. Silylation of 4-substituted β-sultams also proceeded stereoselectively to give the (3*R**,4*S**)-derivatives although the starting materials used were isomeric mixtures (entries 5—10).[27] In the ^{1}H-NMR spectrum of **4f** the signal of the 4-methyl group was observed at δ 1.05. This suggests that the methyl group is pseudoaxially oriented. If the methyl group were pseudoequatorially oriented, the signal should appear at lower field owing to the deshielding effect of the 3-phenyl group (compare the data for the starting materials, *cis*- and *trans*-**3f**). Silylation of **3i** was carried out twice (2.0 eq of lithium diisopropylamide (LDA) followed by 2.0 eq of TMSCl at −78 °C to room temperature for 16 h in THF) to give the 3-*tert*-butyl-4-trimethylsilyl-β-sultam **4i** in 54% crude yield (entry 10). Since β-sultams **4h, i** were unstable and desilylated during purification by silica gel column chromatography, they were used without purification for the following reactions. The β-sultam **4f'** was alternatively obtained in 84% yield by stereoselective methylation of **4a** according to a similar procedure to that reported by Müller and Otto.[27]

Possible mechanisms for stereoselective silylation and methylation are described in Chart 3. A tetrahedral carbanion I, which is more stable than the other carbanion II, is generated by deprotonation of a β-sultam **3** bearing a hydrogen or an alkyl group at C-4 (R^3 = H or alkyl). The steric hindrance of the R^2 substituent prevents approach of a bulky silylating agent to I, and silylation is achieved from the opposite face to R^2 *via* the less stable carbanion II to give a β-sultam possessing (3*R**,4*S**)-configuration. In the case of a 4-phenyl-β-sultam, deprotonation gives a nearly planar carbanion III which

Table 2. Synthesis of 4-Silylated β-Sultams **4** and **5**

Entry	Compd. No.	β-Sultam				Conditions	Product (%yield)[a]
		R^1	R^2	R^3	*Si* (*Si*Cl eq)		
1	**3a**	^{c}C$_6$H$_{11}$	Ph	H	TBDMS (1.5)	−78 °C, 2 h	**4a** (98)
2	**3b**	^{c}C$_6$H$_{11}$	*p*-MeC$_6$H$_4$	H	TBDMS (1.5)	−78 °C, 2 h	**4b** (93)
3	**3d**	^{c}C$_6$H$_{11}$	*p*-BrC$_6$H$_4$	H	TBDMS (1.5)	−78 °C, 2 h	**4d** (87)
4	**3e**	^{c}C$_6$H$_{11}$	*tert*-Bu	H	TBDMS (1.5)	−78 °C, 2 h	**4e** (92)
5	**3f**	^{c}C$_6$H$_{11}$	Ph	Me	TMS (2.0)	−78 °C—r.t., 18 h	**4f** (88)
6	**3f**	^{c}C$_6$H$_{11}$	Ph	Me	TBDMS (2.0)	−78 °C—r.t., 20 h	**4f'** (53)
7	**3g**	^{c}C$_6$H$_{11}$	Ph	Et	TMS (2.0)	−78 °C—r.t., 18 h	**4g** (72)
8	**3g**	^{c}C$_6$H$_{11}$	Ph	Et	TBDMS (2.0)	−78 °C—r.t., 22 h	**4g'** (44)
9	**3h**	^{n}Bu	Ph	Ph	TMS (2.0)	−78 °C—r.t., 18 h	**4h** (68)[c]
10[b]	**3i**	^{c}C$_6$H$_{11}$	*tert*-Bu	Ph	TMS (2.0)	−78 °C—r.t., 16 h	**4i** (54)[c]
11	**3a**	^{c}C$_6$H$_{11}$	Ph	H	TMS (3.0)	−78 °C—r.t., 20 h	**5a** (92)
12	**3c**	^{c}C$_6$H$_{11}$	*p*-MeOC$_6$H$_4$	H	TMS (3.0)	−78 °C—r.t., 20 h	**5c** (88)
13	**3d**	^{c}C$_6$H$_{11}$	*p*-BrC$_6$H$_4$	H	TMS (3.0)	−78 °C—r.t., 20 h	**5d** (84)

a) Isolated yield unless otherwise mentioned. *b*) Silylation was carried out twice. *c*) Crude yield.

is stabilized by high delocalization of the charge to the 4-phenyl and the sulfonamide groups.[31] A (3*R**,4*S**)-β-sultam **4** is stereoselectively obtained by kinetic silylation of III. On the other hand, the carbanion IV, which is generated from the 4-silyl-β-sultam **4a**, exists in the tetrahedral form and methylation occurs from the same face as the phenyl group due to the bulkiness of the TBDMS group, to produce **4f'**.

We next examined disilylation of the β-sultam **3d** with TBDMSCl as a silylating agent, since a TBDMS group is more effective for reaction of the silylated β-sultams with $EtAlCl_2$ than a TMS one (see the following section). Compound **3d** was treated with 3 eq of LDA followed by 3 eq of TBDMSCl at −78 °C in THF and the reaction mixture was quenched with saturated aqueous ammonium chloride at −78 °C to provide the monosilyl-β-sultam **4d** in 82% isolated yield. When the reaction of **3d** with TBDMSCl was carried out at room temperature, the ring-cleaved product (*E*)-**6** was formed in 68% yield by β-elimination of **4d** and no disilylated product was obtained. The geometry of (*E*)-**6** was determined by the nuclear Overhauser effect (NOE) technique (see Experimental). The failure of disilylation with TBDMSCl may be owing to the bulkiness of the TBDMS group, and so we next examined disilylation with less hindered TMSCl (Chart 2).[30] 4,4-Disilylated β-sultams **5** were prepared in high yields by treatment of **3** with LDA at −78 °C in THF followed by TMSCl at room temperature (Table 2, entries 11—13).

Reactions of 4-Silylated β-Sultams 4 and 5 with $EtAlCl_2$ 3-Aryl-4-monosilyl-β-sultams **4a, b, d** were treated with 2 eq of $EtAlCl_2$ in dry toluene at room temperature under a nitrogen atmosphere (Chart 4, Table 3) to provide stereospecifically (*E*)-styrylsulfonamides (*E*)-**7a**, **b**, **d** in good to high yields. All of the *vic*-olefinic protons of (*E*)-**7a, b, d** showed *trans J* values (15—16 Hz) in the ^{1}H-NMR spectra. Use of CH_2Cl_2 instead of toluene slowed down the reaction rate and 72 h was needed to complete the reaction (entry 2). Reaction of the 3-*tert*-butyl-β-sultam **4e** with 1.0 eq of $EtAlCl_2$ proceeded at 40 °C to give (*E*)-**7e** in 47% yield, together with the *N*-dealkylated (*E*)-vinylsulfonamide (*E*)-**8e** (entry 5) in 39% yield,[32,33] although only the starting material was

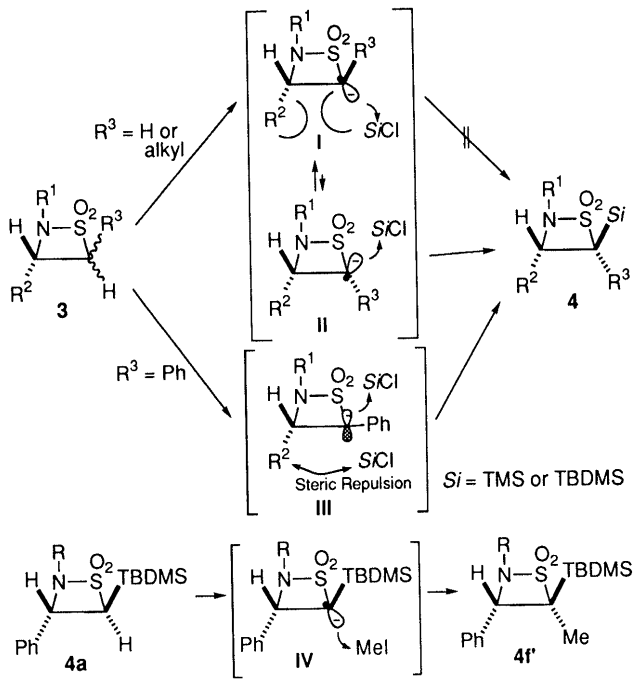

Chart 3

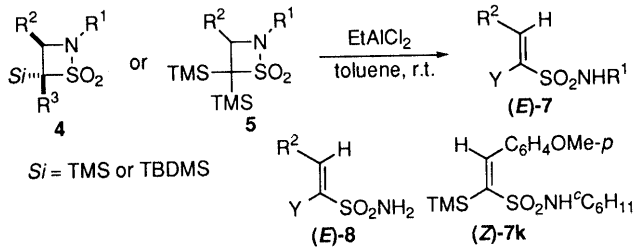

Chart 4

Table 3. Reactions of 4-Silylated β-Sultams **4** and **5** with $EtAlCl_2$

Entry	Compd. No.	4-Silyl-β-sultam				$EtAlCl_2$ (eq)	Time (h)	Product[a]	
		R^1	R^2	R^3	*Si*			Y	(%yield)[b]
1	**4a**	$^cC_6H_{11}$	Ph	H	TBDMS	2.0	26	H	(*E*)-**7a** (93)
2[c]	**4a**	$^cC_6H_{11}$	Ph	H	TBDMS	2.0	72	H	(*E*)-**7a** (89)
3	**4b**	$^cC_6H_{11}$	*p*-MeC_6H_4	H	TBDMS	2.0	24	H	(*E*)-**7b** (89)
4	**4d**	$^cC_6H_{11}$	*p*-BrC_6H_4	H	TBDMS	2.0	28	H	(*E*)-**7d** (91)
5[d]	**4e**	$^cC_6H_{11}$	*tert*-Bu	H	TBDMS	1.0	16	H	(*E*)-**7e** (47), (*E*)-**8e** (39)
6[d]	**4e**	$^cC_6H_{11}$	*tert*-Bu	H	TBDMS	1.5	23	H	(*E*)-**7e** (21), (*E*)-**8e** (65)
7	**4f**	$^cC_6H_{11}$	Ph	Me	TMS	4.0	24	Me	(*E*)-**7f** (64), **4f** (26)
8	**4f'**	$^cC_6H_{11}$	Ph	Me	TBDMS	2.0	24	Me	(*E*)-**7f** (92)
9	**4g**	$^cC_6H_{11}$	Ph	Et	TMS	4.0	24	Et	(*E*)-**7g** (70), **4g** (22)
10	**4g'**	$^cC_6H_{11}$	Ph	Et	TBDMS	2.0	24	Et	(*E*)-**7g** (93)
11[e]	**4h**	^nBu	Ph	Ph	TMS	2.0	30	Ph	(*E*)-**7h** (68), **3h** (12)
12[e]	**4i**	$^cC_6H_{11}$	*tert*-Bu	Ph	TMS	2.0	28	Ph	(*E*)-**7i** (54)
13	**5a**	$^cC_6H_{11}$	Ph	—	—	3.0	35	TMS	(*E*)-**7j** (89)
14[c,f]	**5a**	$^cC_6H_{11}$	Ph	—	—	2.0	8	TMS	(*E*)-**7j** (62), (*E*)-**8j** (38)
15[c]	**5a**	$^cC_6H_{11}$	Ph	—	—	2.0	72	TMS	(*E*)-**7j** (49), **5a** (43)
16	**5c**	$^cC_6H_{11}$	*p*-$MeOC_6H_4$	—	—	2.0	36	TMS	(*E*)-**7k** (71), (*Z*)-**7k** (21)
17	**5d**	$^cC_6H_{11}$	*p*-BrC_6H_4	—	—	2.0	34	TMS	(*E*)-**7l** (90)

a) The geometry was determined from the coupling constant between *vic*-olefinic protons in ^{1}H-NMR or by the NOE technique. *b*) Isolated yield. *c*) CH_2Cl_2 was used as a solvent instead of toluene. *d*) Reaction temperature: 40 °C. *e*) Crude materials (**4h**, **4i**) were used. *f*) $AlCl_3$ was used instead of $EtAlCl_2$.

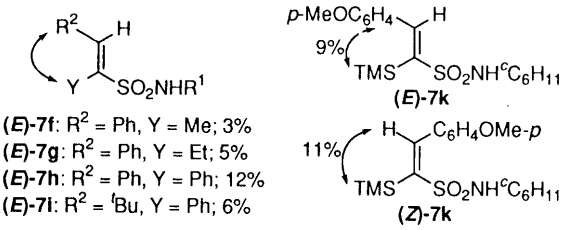

Fig. 1. NOE Experiments in Some Vinylsulfonamides 7

recovered when the reaction was carried out at room temperature. The low reactivity of the 3-*tert*-butyl-*β*-sultam **4e** should be due to weaker stabilization of the cationic intermediate by the *tert*-butyl group than by the aromatic groups. Use of an excess amount of $EtAlCl_2$ increased the yield of the *N*-dealkylated product (entry 6). Reactions of 4-substituted *β*-sultams **4f—i, f′, g′** also gave (*E*)-vinylsulfonamides (*E*)-**7f—i** stereospecifically. The geometry of (*E*)-**7f—i** was determined by the NOE technique (Fig. 1). A considerable amount of the starting materials was recovered from reactions of TMS-substituted *β*-sultams **4f, g** in spite of the use of 4.0 eq of $EtAlCl_2$ (entries 7—10). A TBDMS group was more effective than a TMS group, probably because of the increased distortion of a four-membered ring bearing a TBDMS substituent than that of a *β*-sultam ring having a TMS group. In the case of the 3,4-diphenyl-*β*-sultam **4h**, (*E*)-**7h** was obtained in 68% yield accompanied by the desilylated *β*-sultam **3h**, which may be formed by desilylation of unreacted starting material during purification by silica gel column chromatography.

(*E*)-Vinylsulfonamides (*E*)-**7** should be formed stereospecifically as follows (Chart 5). In the solution of a *β*-sultam **4**, conformation V is favored rather than VI, since both bulky aryl and silyl groups are pseudoequatorial.[27,30] The selective C–N bond cleavage is achieved by the coordination of $EtAlCl_2$ to the sulfonyl group to generate a cation intermediate VII stereospecifically owing to the neighboring group participation of silicon. The silyl group is eliminated from the cation VII without internal rotation to give (*E*)-**7**. As another possible pathway, the thermodynamically more stable product (*E*)-**7**, rather than (*Z*)-**7**, may be formed *via* a cationic intermediate VIII, without participation of silicon. Since a (3*R**,4*R**)-4-silyl-*β*-sultam could not be obtained because of the complete stereoselectivity of the silylation reaction, we examined reactions using 4,4-disilyl-*β*-sultams to determine the reaction mechanism.

(*E*)-*α*-Silylstyrylsulfonamide (*E*)-**7j** was obtained in 89% yield by treatment of the 4,4-disilyl-*β*-sultam **5a** with 3.0 eq of $EtAlCl_2$ for 35 h in toluene (Table 3, entry 13). Use of $AlCl_3$ instead of $EtAlCl_2$ shortened the reaction time; however, an *N*-dealkylated sulfonamide (*E*)-**8j** was formed in 38% yield as a by-product (entry 14). In the case of **5c**, the geometrical isomer (*Z*)-**7k** was formed in 21% yield together with (*E*)-**7k** in 71% yield (entry 16). (*E*)-**7l** was formed exclusively in the reaction of **5d** (entry 17).

(*Z*)-*α*-Silylstyrylsulfonamide (*Z*)-**7k** would be formed as shown in Chart 5. A carbenium ion VII′, which is generated from a disilylated *β*-sultam **5** by a similar mechanism to that of the formation of VII, is rapidly transformed to

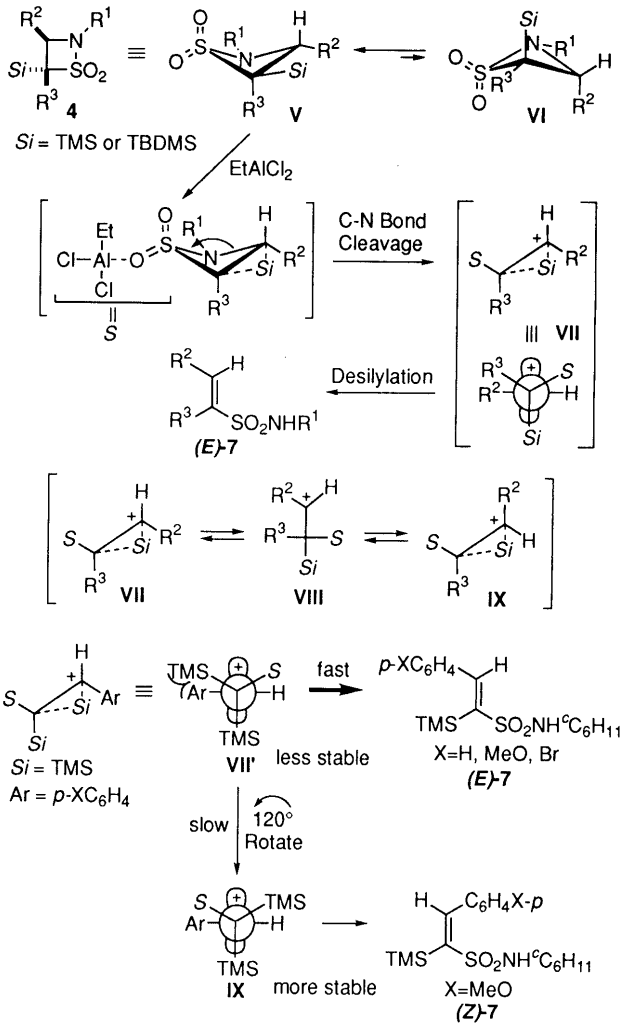

Chart 5

(*E*)-*α*-silylstyrylsulfonamides (*E*)-**7** stereospecifically. In the case of X = MeO the conjugation of the *p*-methoxy substituent stabilizes the intermediate VII′ enough to allow the internal 120° rotation of VII′, and a more stable conformer IX is partially generated to avoid the steric interaction between the silyl and aryl groups. The thermodynamically more stable (*Z*)-*α*-silylstyrylsulfonamide (*Z*)-**7k** is obtained by elimination of the silyl group, which is *anti*-coplanar with the vacant *p*-orbital of the cation. In the case of X = H or Br, stereospecific formation of (*E*)-styrylsulfonamides (*E*)-**7** is accomplished, since the *β*-silyl group is eliminated from the less stable VII′ before the internal rotation. These results suggest that the reactions proceed *via* the intermediate VII′, not VIII to give (*E*)-styrylsulfonamides stereospecifically owing to neighboring group participation of the silyl group.

Simultaneous Ring Destruction and *N*-Dealkylation of 4-Silyl-*β*-sultams with $AlCl_3$ Since the reaction of **5a** with $AlCl_3$ at room temperature for 8 h gave an *N*-dealkylated product as a by-product (Table 3, entry 14),[32,33] we examined simultaneous C–N bond cleavage and *N*-dealkylation of 4-silyl-*β*-sultams (Chart 6). Treatment of 3-phenyl-*β*-sultams **4a** and **4f′** with 3 eq of $AlCl_3$ in CH_2Cl_2 at room temperature provided *N*-dealkylated (*E*)-styrylsulfonamides (*E*)-**8a** and (*E*)-**8f**, respectively, in good yields. Reaction of the 3-*tert*-butyl-*β*-sultam **4e** under

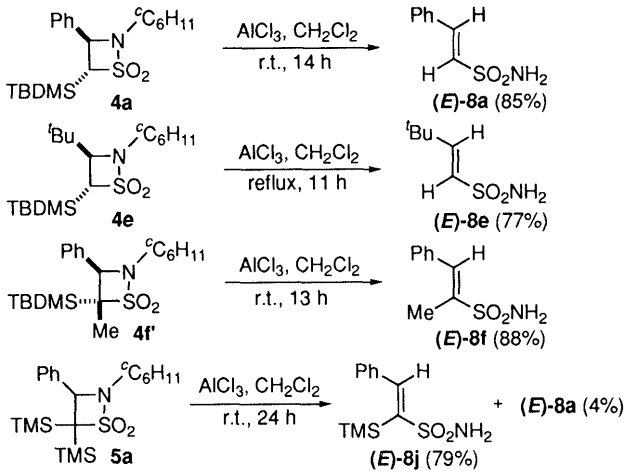

Chart 6

reflux in CH_2Cl_2 gave the (*E*)-vinylsulfonamide (*E*)-**8e** in 77% yield. The *N*-dealkylated (*E*)-α-silylsulfonamide (*E*)-**8j** was obtained from the 4,4-disilyl-β-sultam **5a** in 79% yield accompanied by a small amount of the α-desilylated vinylsulfonamide (*E*)-**8a** upon treatment at room temperature for 24 h. The coordination of $AlCl_3$ to a sulfonyl group may enhance the polarity of the C–N bond, favoring the *N*-dealkylation. However, the precise mechanism is not clear.

Reaction of (*E*)-α-Silylvinylsulfonamide with an Electrophile Vinylsilanes react with a variety of electrophiles, undergoing desilylation with retention of stereochemistry, and various types of vinylsilanes have been utilized as versatile synthetic intermediates.[34,35] However, α-silylvinylsulfonamides have not been studied, and we examined the reaction of α-silylvinylsulfonamide with benzaldehyde as an electrophile. The existence of an acidic proton of sulfonamides may cause proton transfer to a carbanion generated from α-silylvinylsulfonamides. Therefore, we wished to examine the reactions of *N*-methyl derivatives without an acidic proton. The starting material used was synthesized as shown in Chart 7. *N*-Methylation of (*E*)-**7k** with NaH and MeI in *N*,*N*-dimethylformamide (DMF) gave only the *N*-methylated desilylated product (*E*)-**9** quantitatively. The *N*,*N*-dialkylated α-silylvinylsulfonamide (*E*)-**10** was obtained in 45% yield by successive silylation, ring destruction and *N*-methylation of the β-sultam **3a**. Treatment of (*E*)-**10** with 1.5 eq of benzaldehyde and 1.2 eq of TBAF in the presence of molecular sieves gave only the desilylated product (*E*)-**9** (Chart 7). α-Hydroxymethylated vinylsulfonamide (*E*)-**12** was obtained in 36% yield from the reaction of the silylsulfonamide (*E*)-**10** with benzaldehyde and TBAF in the presence of molecular sieves and a catalytic amount of $BF_3 \cdot Et_2O$.

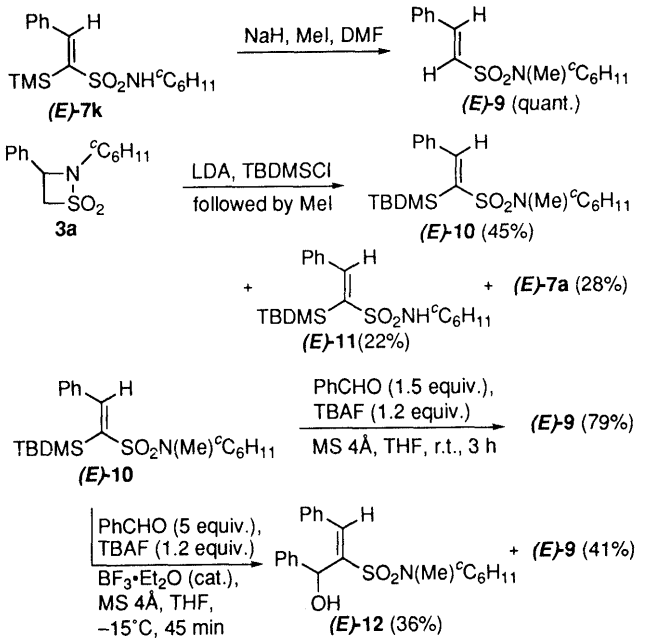

Chart 7

Experimental

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (NaCl) were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H-NMR spectra were recorded on a JEOL GX-270 (270 MHz) or a JEOL EX-400 (400 MHz) or JEOL EX-90 (90 MHz) spectrometer with tetramethylsilane as an internal standard. ^{13}C-NMR spectra and NOE were obtained on a JEOL EX-400 spectrometer with chloroform-*d* as an internal standard. The *J* values are given in Hz. Mass spectra (electron impact (EI) and FAB) were recorded on a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. Elemental analyses of new compounds were performed on a Yanaco CHN Corder MT-5. All chromatographic isolations were accomplished with either Kieselgel 60 (70—230 mesh) for column chromatography or Kieselgel 60 PF_{254} containing gypsum for preparative TLC.

Synthesis of β-Sultams by [2+2] Cycloaddition of Sulfenes and Imines. Method A, General Procedure To a stirred solution of methanesulfonyl chloride (0.77 ml, 10 mmol) in dry THF (5 ml) was added dropwise a solution of an imine (20 mmol) in dry THF (30 ml) at room temperature under nitrogen and the mixture was stirred at room temperature for 3 d. The precipitate was filtered off through Celite and the filtrate was evaporated under reduced pressure. Immediately, the residue was purified by column chromatography on silica gel with EtOAc–hexane (1 : 10—1 : 5 v/v).

Method B, General Procedure To a stirred solution of methanesulfonyl chloride (0.77 ml, 10 mmol) in dry THF (5 ml) was added dropwise a solution of an imine (20 mmol) in dry THF (30 ml) at room temperature under nitrogen and the mixture was stirred at room temperature for 3 d. The precipitate was filtered off through Celite and the filtrate was evaporated under reduced pressure. The residue was allowed to stand at room temperature for 7—10 d and purified by column chromatography on silica gel with EtOAc–hexane (1 : 10—1 : 5 v/v).

Method C, General Procedure A sulfonyl chloride (5 mmol) and an imine (10 mmol) were stirred without solvent at room temperature under nitrogen. The solidified reaction mixture was purified by column chromatography on silica gel with EtOAc–hexane (1 : 10—1 : 5 v/v).

Method D, General Procedure To a stirred solution of phenylmethanesulfonyl chloride (0.953 mg, 5 mmol) in dry THF (2.5 ml) was added dropwise a solution of imine (10 mmol) in dry THF (10 ml) under cooling with ice–NaCl under nitrogen, and the mixture was stirred at room temperature for 3 d. The precipitate was filtered off through Celite and the filtrate was evaporated under reduced pressure. Immediately, the residue was purified by column chromatography on silica gel with EtOAc–hexane (1 : 10—1 : 5 v/v).

2-Cyclohexyl-3-phenyl-1,2-thiazetidine 1,1-Dioxide (**3a**): Colorless prisms (CH_2Cl_2–hexane), mp 128—129 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.08—1.27 (4H, m), 1.42—1.74 (5H, m), 2.04 (1H, br d, *J* = 12.7 Hz), 3.20—3.28 (1H, m, NCH), 3.86 (1H, dd, *J* = 8.8, 15.1 Hz, 4-H), 4.34 (1H, dd, *J* = 7.81, 15.1 Hz, 4-H), 4.35 (1H, dd, *J* = 7.81, 8.8 Hz, 3-H), 7.27—7.43 (3H, m, ArH), 7.50—7.53 (2H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 24.0 (t), 24.2 (t), 25.3 (t), 30.2 (t), 31.6 (t), 49.1 (d), 56.8 (d), 65.9 (t), 126.5 (d), 128.8 (d), 129.0 (d), 139.0 (s); MS *m/z*: 265 (M^+, 7%), 104 (100); IR (KBr) cm^{-1}: 1310, 1140 (SO_2); *Anal.* Calcd for $C_{14}H_{19}NO_2S$: C, 63.37; H, 7.22; N, 5.28. Found: C, 63.34; H, 7.15; N, 5.34.

2-Cyclohexyl-3-(4-methylphenyl)-1,2-thiazetidine 1,1-Dioxide (**3b**):

Colorless prisms (CH_2Cl_2–hexane), mp 107—110 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.08—1.25 (4H, m), 1.43—1.71 (5H, m), 2.01 (1H, br d, J=12 Hz), 2.34 (3H, s, Me), 3.10—3.21 (1H, m, NCH), 3.81 (1H, dd, J=8, 15 Hz, 4-H), 4.30 (1H, dd, J=8, 15 Hz, 4-H), 4.31 (1H, t, J=8 Hz, 3-H), 7.18 (2H, d, J=7.8 Hz, ArH), 7.38 (2H, d, J=7.8 Hz, ArH); ^{13}C-NMR ($CDCl_3$) δ: 21.0 (q), 23.9 (t), 24.1 (t), 25.3 (t), 30.1 (t), 31.5 (t), 48.8 (d), 56.6 (d), 65.8 (t), 126.3 (d), 129.6 (d), 135.9 (s), 138.5 (s); MS m/z: 279 (M^+, 3%), 118 (100); IR (KBr) cm^{-1}: 1320, 1145 (SO_2); *Anal.* Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.52; H, 7.62; N, 5.03.

2-Cyclohexyl-3-(4-methoxyphenyl)-1,2-thiazetidine 1,1-Dioxide (**3c**): Colorless prisms (CH_2Cl_2–hexane), mp 80—82 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.10—1.28 (4H, m), 1.43—1.73 (5H, m), 2.01 (1H, br d, J=12.7 Hz), 3.19—3.22 (1H, m, NCH), 3.82 (3H, s, OMe), 3.83 (1H, dd, J=8, 14 Hz, 4-H), 4.31 (1H, dd, J=8, 14 Hz, 4-H), 4.32 (1H, t, J=8 Hz, 3-H), 6.91 (2H, d, J=8.8 Hz, ArH), 7.42 (2H, d, J=8.8 Hz, ArH); ^{13}C-NMR ($CDCl_3$) δ: 23.8 (t), 23.9 (t), 25.1 (t), 29.9 (t), 31.3 (t), 48.4 (d), 55.0 (q), 56.4 (d), 65.7 (t), 114.1 (d), 127.5 (d), 130.7 (s), 159.7 (s); MS m/z: 295 (M^+, 2%), 134 (100); IR (KBr) cm^{-1}: 1315, 1145 (SO_2); *Anal.* Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74. Found: C, 60.78; H, 7.16; N, 4.77.

3-(4-Bromophenyl)-2-cyclohexyl-1,2-thiazetidine 1,1-Dioxide (**3d**): Colorless prisms (CH_2Cl_2–hexane), mp 118—121 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.05—1.27 (4H, m), 1.42—1.73 (5H, m), 2.03 (1H, br d, J=13.2 Hz), 3.20—3.25 (1H, m, NCH), 3.81 (1H, dd, J=4.4, 10.7 Hz), 4.29—4.37 (2H, m), 7.40 (2H, d, J=8.3 Hz, ArH), 7.53 (2H, d, J=8.3 Hz, ArH); ^{13}C-NMR ($CDCl_3$) δ: 24.0 (t), 24.2 (t), 25.3 (t), 30.3 (t), 31.7 (t), 48.5 (d), 56.9 (d), 65.7 (t), 122.8 (s), 128.5 (d), 132.2 (d), 138.2 (s); MS m/z: 343 (M^+, 10%), 182 (100); IR (KBr) cm^{-1}: 1315, 1150 (SO_2); *Anal.* Calcd for $C_{14}H_{18}BrNO_2S$: C, 48.84; H, 5.27; N, 4.07. Found: C, 49.07; H, 5.29; N, 4.04.

3-*tert*-Butyl-2-cyclohexyl-1,2-thiazetidine 1,1-Dioxide (**3e**): Colorless needles (CH_2Cl_2–hexane), mp 108—109 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.99 (9H, s, *tert*-Bu), 1.11—1.26 (3H, m), 1.66—1.87 (5H, m), 2.06—2.09 (1H, m), 2.17—2.21 (1H, m), 3.01—3.09 (1H, tt, J=4, 12 Hz, NCH) 3.42 (1H, dd, J=5.9, 7.8 Hz, 3-H), 3.71 (1H, dd, J=5.9, 12.2 Hz, 4-H), 3.85 (1H, dd, J=7.8, 12.2 Hz, 4-H); ^{13}C-NMR ($CDCl_3$) δ: 25.3 (t), 25.5 (t), 25.9 (q), 26.1 (t), 28.7 (t), 31.1 (t), 33.9 (s), 51.9 (d), 58.3 (d), 58.5 (t); MS m/z: 245 (M^+, 6%), 83 (100); IR (KBr) cm^{-1}: 1300, 1150 (SO_2); *Anal.* Calcd for $C_{12}H_{23}NO_2S$: C, 58.74; H, 9.45; N, 5.71. Found: C, 58.51; H, 9.57; N, 5.73.

2-Cyclohexyl-4-methyl-3-phenyl-1,2-thiazetidine 1,1-Dioxide (**3f**): The *trans* Isomer: Colorless prisms (EtOAc–hexane), mp 104—106 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.03—1.31 (4H, m), 1.47—1.65 (4H, m), 1.53 (3H, d, J=6.8 Hz, Me), 1.71—1.75 (1H, m), 2.07—2.09 (1H, m), 3.17—3.22 (1H, m, NCH), 3.74 (1H, d, J=6.8 Hz, 3-H), 4.00 (1H, quintet, J=6.8 Hz, 4-H), 7.27—7.49 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 11.5 (q), 24.1 (t), 24.3 (t), 25.3 (t), 30.4 (t), 31.9 (t), 57.0 (d), 58.5 (d), 73.9 (d), 126.4 (d), 128.7 (d), 129.0 (d), 138.4 (s); MS m/z: 279 (M^+, 8%), 117 (100); IR (KBr) cm^{-1}: 1300, 1140 (SO_2); *Anal.* Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.40; H, 7.64; N, 5.03.

The *cis* Isomer: Colorless prisms (EtOAc–hexane), mp 119—120 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.03 (3H, d, J=7.3 Hz, Me), 1.10—1.30 (4H, m), 1.46—1.74 (5H, m), 2.08—2.11 (1H, m), 3.22—3.27 (1H, m, NCH), 4.50 (1H, dq, J=8.3, 7.3 Hz, 4-H), 4.58 (1H, d, J=8.3 Hz, 3-H), 7.27—7.40 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 10.7 (q), 24.3 (t), 24.6 (t), 25.4 (t), 30.8 (t), 31.9 (t), 53.1 (d), 56.6 (d), 68.6 (d), 127.6 (d), 128.4 (d), 135.3 (s); MS m/z: 279 (M^+, 9%), 117 (100); IR (KBr) cm^{-1}: 1310, 1140 (SO_2); *Anal.* Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.42; H, 7.67; N, 5.07.

2-Cyclohexyl-4-ethyl-3-phenyl-1,2-thiazetidine 1,1-Dioxide (**3g**): The *trans* Isomer: Colorless prisms (EtOAc–hexane), mp 74—75 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.02 (3H, t, J=7.3 Hz, Me), 1.02—1.27 (4H, m), 1.45—1.74 (5H, m), 1.86—1.95 (1H, m), 2.05—2.17 (2H, m), 3.16—3.22 (1H, m, NCH), 3.81 (1H, d, J=6.3 Hz, 3-H), 3.86—3.92 (1H, m, 4-H), 7.27—7.49 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 11.6 (q), 21.2 (t), 24.1 (t), 24.3 (t), 25.3 (t), 30.3 (t), 31.9 (t), 56.8 (d), 57.2 (d), 80.5 (d), 126.5 (d), 128.6 (d), 128.9 (d), 139.0 (s); MS m/z: 293 (M^+, 10%), 117 (100); IR (KBr) cm^{-1}: 1310, 1140 (SO_2); *Anal.* Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90; N, 4.77. Found: C, 65.37; H, 7.95; N, 4.85.

The *cis* Isomer: Colorless prisms (EtOAc–hexane), mp 83—84 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.86 (3H, t, J=7.3 Hz, Me), 1.04—1.29 (5H, m), 1.43—1.77 (6H, m), 2.05—2.08 (1H, m), 3.21—3.26 (1H, m, NCH), 4.29 (1H, ddd, J=5.3, 7.4, 8.8 Hz, 4-H), 4.56 (1H, d, J=8.8 Hz, 3-H), 7.27—7.40 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 11.8 (q), 19.9 (t), 24.3 (t), 24.6 (t), 25.4 (t), 30.8 (t), 31.9 (t), 53.0 (d), 56.4 (d), 75.7 (d), 127.6 (d), 128.4 (d), 135.7 (s); MS m/z: 293 (M^+, 6%), 117 (100); IR (KBr) cm^{-1}: 1310, 1140 (SO_2); *Anal.* Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90; N, 4.77. Found: C, 65.37; H, 7.86; N, 4.79.

2-*n*-Butyl-3,4-diphenyl-1,2-thiazetidine 1,1-Dioxide (**3h**): The *trans* Isomer: Colorless prisms (CH_2Cl_2–hexane), mp 93—95 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, t, J=7.3 Hz, Me), 1.44—1.55, 1.64—1.80 (each 2H, m, CH_2CH_2), 2.94—3.01, 3.37—3.44 (each 1H, m, NCH_2), 4.39 (1H, d, J=6.8 Hz, 3-H), 5.25 (1H, d, J=6.8 Hz, 4-H), 7.42—7.54 (10H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 13.4 (q), 20.1 (t), 30.1 (t), 45.9 (t), 59.9 (d), 82.7 (d), 126.5 (d), 128.4 (s), 128.8 (d), 128.9 (d), 129.0 (d), 129.5 (d), 136.2 (s); MS m/z: 315 (M^+, 35%), 57 (100); IR (KBr) cm^{-1}: 1305, 1160 (SO_2); *Anal.* Calcd for $C_{18}H_{21}NO_2S$: C, 68.54; H, 6.71; N, 4.44. Found: C, 68.34; H, 6.70; N, 4.34.

The *cis* Isomer: Colorless prisms (CH_2Cl_2–hexane), mp 105—106 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.02 (3H, t, J=7.3 Hz, Me), 1.52—1.64, 1.75—1.88 (each 2H, m, CH_2CH_2), 3.00—3.08, 3.46—3.52 (each 1H, m, NCH_2), 4.86 (1H, d, J=8.8 Hz, 3-H), 5.77 (1H, d, J=8.8 Hz, 4-H), 7.15—7.26 (10H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 13.6 (q), 20.3 (t), 30.4 (t), 46.6 (t), 57.3 (d), 80.0 (d), 127.1 (d), 127.8 (d), 127.9 (d), 128.1 (d), 128.2 (s), 128.6 (d), 130.0 (d), 133.6 (s); MS m/z: 315 (M^+, 37%), 91 (100); IR (KBr) cm^{-1}: 1305, 1158 (SO_2); *Anal.* Calcd for $C_{18}H_{21}NO_2S$: C, 68.54; H, 6.71; N, 4.44. Found: C, 68.69; H, 6.79; N, 4.45.

3-*tert*-Butyl-2-cyclohexyl-4-phenyl-1,2-thiazetidine 1,1-Dioxide (**3i**): Colorless needles as a mixture of diastereomers (*trans*:*cis*=1.8:1 by ^{1}H-NMR) (CH_2Cl_2–hexane); ^{1}H-NMR ($CDCl_3$) δ: 0.85 (9H, s, Me×3, *cis*), 0.98 (9H, s, Me×3, *trans*), 1.15—1.26 (total 8H, m), 1.65—1.86 (total 8H, m), 2.16—2.31 (total 4H, m), 3.13—3.16 (total 2H, m, NCH), 3.59 (1H, d, J=6 Hz, 3-H, *trans*), 3.86 (1H, d, J=8.3 Hz, 3-H, *cis*), 4.96 (1H, d, J=6 Hz, 4-H, *trans*), 5.32 (1H, d, J=8.3 Hz, 4-H, *cis*), 7.33—7.42, 7.61 (total 10H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 25.5 (t, *trans*), 25.6 (t, *cis*), 25.7 (t, *trans*), 25.8 (t, *cis*), 26.4 (t, *trans*), 26.7 (q, *trans*), 27.8 (t, *cis*), 27.9 (q, *cis*), 28.9 (t, *cis*), 31.8 (t, *trans*), 32.0 (s, *trans*), 34.9 (t, *trans*), 35.1 (t, *cis*), 58.6 (d, *trans*), 58.9 (d, *cis*), 60.0 (d, *cis*), 61.0 (d, *trans*), 75.7 (d, *trans*), 78.6 (d, *cis*), 128.2 (d), 129.1 (d), 129.2 (d), 129.4 (d), 129.7 (d), 129.9 (s), 130.9 (s), 131.7 (d); MS m/z: 321 (M^+, 1%), 118 (100); IR (KBr) cm^{-1}: 1300, 1160 (SO_2); *Anal.* Calcd for $C_{18}H_{27}NO_2S$: C, 67.25; H, 8.47; N, 4.36. Found: C, 67.08; H, 8.49; N, 4.41.

Synthesis of 4-Monosilyl-β-sultams 4a—e. General Procedure To a solution of LDA (2 mmol, prepared from 2 mmol of diisopropylamine (0.26 ml) and 2 mmol of *n*-BuLi in hexane) in dry THF (10 ml) was added dropwise a solution of a β-sultam (1 mmol) in THF (2—4 ml) at −78 °C under nitrogen. After 30 min, a solution of TBDMSCl (226 mg, 1.5 mmol) in THF (1—2 ml) was added dropwise to it and the whole was stirred at −78 °C for 2 h. Saturated aqueous NH_4Cl (4 ml) was added to the reaction mixture at −78 °C and the organic layer was separated. The aqueous layer was extracted twice with EtOAc (10 ml). The organic layer and the extracts were combined, washed with saturated aqueous NaCl (20 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc–hexane (1:50—1:20 v/v).

(3*R**,4*S**)-4-(*tert*-Butyldimethylsilyl)-2-cyclohexyl-3-phenyl-1,2-thiazetidine 1,1-Dioxide (**4a**): Colorless needles (EtOAc–hexane), mp 165—169 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.10 (3H, s, SiMe), 0.34 (3H, s, SiMe), 0.80 (9H, s, *tert*-Bu), 0.96—1.29 (4H, m), 1.40—1.71 (5H, m), 1.98—2.01 (1H, m), 3.17—3.24 (1H, m, NCH), 3.80 (1H, d, J=7.3 Hz, 3-H), 4.08 (1H, d, J=7.3 Hz, 4-H), 7.26—7.54 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: −6.9 (q), −6.7 (q), 16.3 (s), 23.9 (t), 24.1 (t), 25.4 (t), 26.4 (q), 30.1 (t), 31.7 (t), 52.1 (d), 57.0 (d), 68.3 (d), 127.1 (d), 128.6 (d), 128.8 (d), 140.0 (s); MS m/z (FAB): 380 (M^++1, 54%), 154 (100); IR (KBr) cm^{-1}: 1300, 1160 (SO_2); *Anal.* Calcd for $C_{20}H_{33}NO_2SSi$: C, 63.28; H, 8.76; N, 3.69. Found: C, 62.83; H, 8.71; N, 3.67.

(3*R**,4*S**)-4-(*tert*-Butyldimethylsilyl)-2-cyclohexyl-3-(4-methylphenyl)-1,2-thiazetidine 1,1-Dioxide (**4b**): Colorless prisms (EtOAc–hexane), mp 115—118 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.10 (3H, s, SiMe), 0.33 (3H, s, SiMe), 0.81 (9H, s, *tert*-Bu), 0.96—1.29 (4H, m), 1.39—1.71 (5H, m), 1.98—2.04 (1H, m), 2.35 (3H, s, ArMe), 3.17—3.22 (1H, m, NCH), 3.79 (1H, d, J=7.3 Hz, 3-H), 4.06 (1H, d, J=7.3 Hz, 4-H), 7.16 (2H, d, J=8 Hz, ArH), 7.40 (2H, d, J=8 Hz, ArH); ^{13}C-NMR ($CDCl_3$) δ: −6.9 (q), −6.7 (q), 16.3 (s), 21.2 (q), 24.0 (t), 24.1 (t), 25.4 (t), 26.4 (q), 30.1 (t), 31.7 (t), 51.9 (d), 56.9 (d), 68.2 (d), 127.0 (d), 129.5 (d), 136.9 (s), 138.4 (s); MS m/z: 393 (M^+, 1%) , 336 (100); IR (KBr) cm^{-1}: 1300, 1150 (SO_2); *Anal.* Calcd for $C_{21}H_{35}NO_2SSi$: C, 64.07; H, 8.96; N, 3.56.

Found: C, 63.95; H, 8.99; N, 3.54.

(3*R**,4*S**)-3-(4-Bromophenyl)-4-*tert*-butyldimethylsilyl-2-cyclohexyl-1,2-thiazetidine 1,1-Dioxide (**4c**): Colorless prisms (CH_2Cl_2–hexane), mp 106—108 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.10 (3H, s, SiMe), 0.34 (3H, s, SiMe), 0.82 (9H, s, *tert*-Bu), 0.95—1.29 (4H, m), 1.38—1.71 (5H, m), 1.97—2.04 (1H, m), 3.17—3.23 (1H, m, NCH), 3.75 (1H, d, J=7 Hz, 3-H), 4.06 (1H, d, J=7 Hz, 4-H), 7.43 (2H, d, J=8 Hz, ArH), 7.50 (2H, d, J=8 Hz, ArH); ^{13}C-NMR ($CDCl_3$) δ: −6.94 (q), −6.89 (q), 16.2 (s), 23.8 (t), 24.0 (t), 25.3 (t), 26.3 (q), 30.1 (t), 31.6 (t), 51.3 (d), 56.9 (d), 68.2 (d), 122.5 (s), 128.7 (d), 132.0 (d), 139.2 (s); MS *m/z*: 457 (M^+, 0.4%), 402 (100); IR (KBr) cm^{-1}: 1300, 1160 (SO_2); *Anal.* Calcd for $C_{20}H_{32}BrNO_2SSi$: C, 52.39; H, 7.03; N, 3.05. Found: C, 52.20; H, 7.07; N, 3.08.

(3*R**,4*S**)-3-*tert*-Butyl-4-(*tert*-butyldimethylsilyl)-2-cyclohexyl-1,2-thiazetidine 1,1-Dioxide (**4e**): Colorless prisms (EtOAc–hexane), mp 143—147 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.06 (3H, s, SiMe), 0.26 (3H, s, SiMe), 0.85—1.26 (5H, m), 1.00 (18H, s, *tert*-Bu × 2), 1.49—1.82 (3H, m), 2.00 (1H, br d, J=12 Hz), 2.14 (1H, br d, J=12 Hz), 3.06—3.11 (1H, m, NCH), 3.21 (1H, d, J=4.9 Hz, 3-H), 3.64 (1H, d, J=4.9 Hz, 4-H); ^{13}C-NMR ($CDCl_3$) δ: −6.7 (q), −4.4 (q), 16.6 (s), 25.4 (t), 25.5 (t), 26.2 (t), 26.8 (q), 27.0 (q), 29.7 (t), 31.0 (t), 35.4 (s), 53.6 (d), 58.6 (d), 59.9 (d); MS *m/z* (FAB): 360 (M^++1, 10%), 185 (100); IR (KBr) cm^{-1}: 1295, 1160 (SO_2); *Anal.* Calcd for $C_{18}H_{37}NO_2SSi$: C, 60.11; H, 10.37; N, 3.89. Found: C, 59.88; H, 10.42; N, 3.98.

Methylation of the β-Sultam 4a To a solution of LDA (2 mmol, prepared from 2 mmol of diisopropylamine (0.26 ml) and 2 mmol of *n*-BuLi in hexane) in dry THF (10 ml) was added dropwise a solution of the β-sultam **4a** (380 mg, 1 mmol) in THF (2—4 ml) at −78 °C under nitrogen. After 30 min, MeI (0.19 ml, 3 mmol) was added dropwise to it and the whole was stirred at room temperature for 26 h. Saturated aqueous NH_4Cl (4 ml) was added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted twice with EtOAc (10 ml). The organic layer and the extracts were combined, washed with saturated aqueous NaCl (20 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc–hexane (1 : 50—1 : 20 v/v) to give the β-sultam **4f′** (331 mg, 84%).

Synthesis of 4-Monosilyl-β-sultams 4f—i. General Procedure To a solution of LDA (2 mmol, prepared from 2 mmol of diisopropylamine (0.26 ml) and 2 mmol of *n*-BuLi in hexane) in dry THF (10 ml) was added dropwise a solution of a β-sultam (1 mmol) in THF (2—4 ml) at −78 °C under nitrogen. After 30 min, a solution of a silyl chloride (2 mmol) in THF (1—2 ml) was added dropwise to it and the whole was stirred at room temperature for an appropriate time. Saturated aqueous NH_4Cl (4 ml) was added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted twice with EtOAc (10 ml). The organic layer and the extracts were combined, washed with saturated aqueous NaCl (20 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc–hexane (1 : 50—1 : 20 v/v).

(3*R**,4*S**)-2-Cyclohexyl-4-methyl-3-phenyl-4-(trimethylsilyl)-1,2-thiazetidine 1,1-Dioxide (**4f**): Colorless prisms (CH_2Cl_2–hexane), mp 179—181 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.29 (9H, s, $SiMe_3$), 1.05 (3H, s, 4-Me), 1.09—1.30 (4H, m), 1.35—1.72 (5H, m), 1.99—2.04 (1H, m), 3.17—3.26 (1H, m, NCH), 4.45 (1H, s, 3-H), 7.30—7.36 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: −2.8 (q), 13.8 (q), 24.2 (t), 24.6 (t), 25.4 (t), 30.9 (t), 31.9 (t), 55.3 (d), 56.0 (d), 68.2 (s), 127.7 (d), 128.3 (d), 128.5 (d), 136.2 (s); MS *m/z*: 351 (M^+, 23%), 186 (100); IR (KBr) cm^{-1}: 1295, 1155 (SO_2); *Anal.* Calcd for $C_{18}H_{29}NO_2SSi$; C, 61.49; H, 8.31; N, 3.98. Found: C, 61.22; H, 8.22; N 4.01.

(3*R**,4*S**)-4-(*tert*-Butyldimethylsilyl)-2-cyclohexyl-4-methyl-3-phenyl-1,2-thiazetidine 1,1-Dioxide (**4f′**): Colorless prisms (CH_2Cl_2–hexane), mp 148—151 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.23 (3H, s, SiMe), 0.42 (3H, s, SiMe), 1.00 (9H, s, *tert*-Bu), 1.21 (3H, s, 4-Me), 1.04—1.28 (4H, m), 1.37—1.74 (5H, m), 1.96—2.04 (1H, m), 3.16—3.22 (1H, m, NCH), 4.49 (1H, s, 3-H), 7.34—7.43 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: −6.1 (q), −5.7 (q), 15.3 (q), 18.0 (s), 24.1 (t), 24.5 (t), 25.4 (t), 27.9 (q), 30.8 (t), 31.7 (t), 55.7 (d), 55.9 (d), 69.3 (s), 128.2 (d), 128.4 (d), 128.5 (d), 135.7 (s); MS *m/z*: 393 (M^+, 1%), 272 (100); IR (KBr) cm^{-1}: 1300, 1155 (SO_2); *Anal.* Calcd for $C_{21}H_{35}NO_2SSi$: C, 64.07; H, 8.96; N, 3.56. Found: C, 63.79; H, 9.00; N, 3.51.

(3*R**,4*S**)-2-Cyclohexyl-4-ethyl-3-phenyl-4-(trimethylsilyl)-1,2-thiazetidine 1,1-Dioxide (**4g**): Colorless prisms (EtOAc–hexane), mp 122—123 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.36 (9H, s, $SiMe_3$), 0.87—1.30 (6H, m), 1.01 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 1.39—1.69 (4H, m), 1.89—2.17 (2H, m), 3.15—3.24 (1H, m, NCH), 4.48 (1H, s, 3-H), 7.26—7.36 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: −0.8 (q), 12.0 (q), 24.3 (t), 24.7 (t), 24.8 (t), 25.5 (t), 31.0 (t), 31.9 (t), 55.8 (d), 56.2 (d), 73.5 (s), 127.7 (d), 128.2 (d), 128.4 (d), 136.3 (s); MS *m/z*: 365 (M^+, 12%), 186 (100); IR (KBr) cm^{-1}: 1300, 1155 (SO_2); *Anal.* Calcd for $C_{19}H_{31}NO_2SSi$: C, 62.42; H, 8.55; N, 3.83. Found: C, 62.26; H, 8.56; N, 3.90.

(3*R**,4*S**)-4-(*tert*-Butyldimethylsilyl)-2-cyclohexyl-4-ethyl-3-phenyl-1,2-thiazetidine 1,1-Dioxide (**4g′**): Colorless prisms (EtOAc–hexane), mp 97—98 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.45 (3H, s, SiMe), 0.46 (3H, s, SiMe) 0.93 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 1.02 (9H, s, *tert*-Bu), 1.05—1.78 (10H, m), 1.92—1.95 (1H, m), 2.13 (1H, dq, J=14, 7 Hz, $C\underline{H}_2CH_3$), 3.16—3.22 (1H, m, NCH), 4.57 (1H, s, 3-H), 7.27—7.48 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: −4.6 (q), −3.2 (q), 12.4 (q), 18.7 (s), 24.0 (t), 24.3 (t), 24.4 (t), 25.4 (t), 27.9 (q), 30.8 (t), 31.4 (t), 54.5 (d), 56.4 (d), 74.9 (s), 128.3 (d), 128.5 (d), 129.0 (d), 135.4 (s); MS *m/z*: 407 (M^+, 1%), 286 (100); IR (KBr) cm^{-1}: 1295, 1150 (SO_2); *Anal.* Calcd for $C_{22}H_{37}NO_2SSi$: C, 64.81; H, 9.15; N, 3.44. Found: C, 65.04; H, 9.22; N, 3.49.

Synthesis of 4,4-Disilyl-β-sultams 5. General Procedure To a solution of LDA (3 mmol, prepared from 3 mmol of diisopropylamine (0.39 ml) and 3 mmol of *n*-BuLi in hexane) in dry THF (10 ml) was added dropwise a solution of a β-sultam (1 mmol) in THF (2—4 ml) at −78 °C under nitrogen. After 30 min, a solution of TMSCl (326 mg, 3 mmol) in THF (1—2 ml) was added dropwise to it and the whole was stirred at room temperature for an appropriate time. Saturated aqueous NH_4Cl (4 ml) was added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted twice with EtOAc (10 ml). The organic layer and the extracts were combined, washed with saturated aqueous NaCl (20 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc–hexane (1 : 50—1 : 20 v/v).

2-Cyclohexyl-3-phenyl-4,4-bis(trimethylsilyl)-1,2-thiazetidine 1,1-Dioxide (**5a**): Colorless prisms (EtOAc–hexane), mp 83—84 °C; ^{1}H-NMR ($CDCl_3$) δ: −0.07 (9H, s, $SiMe_3$), 0.42 (9H, s, $SiMe_3$), 1.09—1.27 (4H, m), 1.51—1.74 (5H, m), 2.11—2.15 (1H, m), 3.19—3.24 (1H, m, NCH), 4.60 (1H, s, 3-H), 7.29—7.43 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 1.0 (q), 1.3 (q), 24.3 (t), 24.9 (t), 25.4 (t), 30.8 (t), 32.0 (t), 55.4 (d), 57.7 (d), 67.9 (s), 127.5 (d), 128.3 (d), 137.2 (s); MS *m/z*: 409 (M^+, 21%), 186 (100); IR (NaCl) cm^{-1}: 1300, 1150 (SO_2); *Anal.* Calcd for $C_{20}H_{35}NO_2SSi_2$: C, 58.63 ; H, 8.61 ; N, 3.42. Found: C, 58.88 ; H, 8.62; N, 3.38.

2-Cyclohexyl-3-(4-methoxyphenyl)-4,4-bis(trimethylsilyl)-1,2-thiazetidine 1,1-Dioxide (**5c**): Colorless prisms (CH_2Cl_2–hexane), mp 95—98 °C; ^{1}H-NMR ($CDCl_3$) δ: −0.05 (9H, s, $SiMe_3$), 0.40 (9H, s, $SiMe_3$), 1.08—1.32 (4H, m), 1.47—1.74 (5H, m), 2.08—2.09 (1H, m), 3.15—3.24 (1H, m, NCH), 3.82 (3H, s, OMe), 4.55 (1H, s, 3-H), 6.88 (2H, d, J=8 Hz, ArH), 7.32 (2H, d, J=8 Hz, ArH); ^{13}C-NMR ($CDCl_3$) δ: 1.1 (q), 1.5 (q), 24.4 (t), 25.0 (t), 25.5 (t), 30.9 (t), 32.1 (t), 55.0 (d), 55.3 (q), 57.6 (d), 68.0 (s), 113.6 (d), 128.8 (d), 129.2 (s), 159.6 (s); MS *m/z*: 439 (M^+, 11%), 216 (100); IR (KBr) cm^{-1}: 1300, 1150 (SO_2); *Anal.* Calcd for $C_{21}H_{37}NO_3SSi_2$: C, 57.36; H, 8.48; N, 3.19. Found: C, 57.21; H, 8.52; N, 3.18.

3-(4-Bromophenyl)-2-cyclohexyl-4,4-bis(trimethylsilyl)-1,2-thiazetidine 1,1-Dioxide (**5d**): Colorless prisms (CH_2Cl_2–hexane), mp 95—96 °C; ^{1}H-NMR ($CDCl_3$) δ: −0.05 (9H, s, $SiMe_3$), 0.40 (9H, s, $SiMe_3$), 1.10—1.31 (4H, m), 1.48—1.74 (5H, m), 2.09—2.12 (1H, m), 3.16—3.21 (1H, m, NCH), 4.52 (1H, s, 3-H), 7.31 (2H, d, J=8 Hz, ArH), 7.49 (2H, d, J=8 Hz, ArH); ^{13}C-NMR ($CDCl_3$) δ: 1.1 (q), 1.5 (q), 24.4 (t) , 24.9 (t), 25.5 (t), 30.9 (t), 32.2 (t), 55.0 (d), 57.7 (d), 68.1 (s), 122.2 (s), 129.3 (d), 131.5 (d), 136.7 (s); MS *m/z*: 487 (M^+, 9%), 73 (100); IR (KBr) cm^{-1}: 1300, 1145 (SO_2); *Anal.* Calcd for $C_{20}H_{34}BrNO_2SSi_2$: C, 49.16; H, 7.01; N, 2.87. Found: C, 49.00; H, 7.06; N, 2.90.

Silylation of the β-Sultam 3d with *tert*-Butyldimethylsilyl Chloride. Method A To a solution of LDA (3 mmol, prepared from 3 mmol of diisopropylamine (0.39 ml) and 3 mmol of *n*-BuLi in hexane) in dry THF (10 ml) was added dropwise a solution of the β-sultam **3d** (344 mg, 1 mmol) in THF (2—4 ml) at −78 °C under nitrogen. After 30 min, a solution of TBDMSCl (452 mg, 3 mmol) in THF (1—2 ml) was added dropwise to it and the whole was stirred at −78 °C for 3 h. Saturated aqueous NH_4Cl (4 ml) was added to the reaction mixture at −78 °C and the organic layer was separated. The aqueous layer was extracted twice with EtOAc (10 ml). The organic layer and the extracts were combined, washed with saturated aqueous NaCl (20 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column

chromatography on silica gel with EtOAc–hexane (1 : 50—1 : 20 v/v) to give the β-sultam **4d** (376 mg, 82%).

Method B To a solution of LDA (3 mmol, prepared from 3 mmol of diisopropylamine (0.39 ml) and 3 mmol of *n*-BuLi in hexane) in dry THF (10 ml) was added dropwise a solution of the β-sultam **3d** (344 mg, 1 mmol) in THF (2—4 ml) at −78 °C under nitrogen. After 30 min, a solution of TBDMSCl (452 mg, 3 mmol) in THF (1—2 ml) was added dropwise to it and the whole was stirred at room temperature for 15 h. Saturated aqueous NH_4Cl (4 ml) was added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted twice with EtOAc (10 ml). The organic layer and the extracts were combined, washed with saturated aqueous NaCl (20 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc–hexane (1 : 10—1 : 5 v/v) to give (*E*)-2-(4-bromophenyl)-1-(*tert*-butyldimethylsilyl)-*N*-cyclohexylethenylsulfonamide ((*E*)-**6**, 312 mg) in 68% yield: Colorless prisms (EtOAc–hexane), mp 102—106 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.06 (6H, s, SiMe × 2), 0.88 (9H, s, *tert*-Bu), 1.19—1.39 (5H, m), 1.57—1.75 (3H, m), 1.96—2.03 (2H, m), 3.20—3.21 (1H, m, NCH), 4.18 (1H, d, J = 7.8 Hz, NH), 7.06 (2H, d, J = 8.3 Hz, ArH), 7.48 (2H, d, J = 8.3 Hz, ArH), 8.33 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: −1.6 (q), 18.1 (s), 24.8 (t), 25.2 (t), 27.9 (q), 34.3 (t), 52.7 (d), 122.5 (s), 129.5 (d), 131.1 (d), 135.1 (s), 146.2 (s), 151.6 (d); MS *m/z* (FAB): 458 (M^+ + 1, 76%), 402 (100); IR (KBr) cm^{-1}: 3300 (NH), 1295, 1150 (SO_2); *Anal.* Calcd for $C_{20}H_{32}BrNO_2SSi$: C, 52.39; H, 7.03; N, 3.05. Found: C, 52.42; H, 6.99; N, 3.08. NOE experiments showed *E*-geometry; 2% NOE was observed between the aromatic protons and the *tert*-butyl group, and 2% NOE was also observed between the aromatic protons and the methyl groups of the TBDMS group.

Reactions of 4-Silyl-β-sultams with $EtAlCl_2$. General Procedure To a stirred solution of a 4-silylated β-sultam (0.1 mmol) in dry toluene (1 ml) was added dropwise 2.0 eq of $EtAlCl_2$ in hexane at room temperature under nitrogen. The reaction mixture was stirred at room temperature for an appropriate time and saturated aqueous $NaHCO_3$ (3 ml) was added to it. The inorganic precipitate was filtered off through Celite and washed with EtOAc (5 ml). The organic layer was separated, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane–EtOAc (4 : 1 v/v)) to give an (*E*)-vinylsulfonamide.

(*E*)-*N*-Cyclohexyl-2-phenylethenylsulfonamide ((*E*)-**7a**): Colorless prisms (CH_2Cl_2–hexane), mp 110—113 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.13—1.36 (5H, m), 1.54—1.57 (1H, m), 1.68—1.71 (2H, m), 1.95—1.97 (2H, m), 3.21—3.23 (1H, m, NCH), 4.67 (1H, br s, NH), 6.80 (1H, d, J = 15.6 Hz, 1-H), 7.34—7.42 (3H, m, ArH), 7.47 (1H, d, J = 15.6 Hz, 2-H), 7.44—7.50 (2H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 24.7 (t), 25.1 (t), 34.3 (t), 52.6 (d), 126.5 (d), 128.1 (d), 129.0 (d), 130.6 (d), 132.7 (s), 140.4 (d); MS *m/z*: 265 (M^+, 16%), 144 (100); IR (KBr) cm^{-1}: 3270 (NH), 1320, 1145 (SO_2); HR-MS. Calcd for $C_{14}H_{19}NO_2S$: 265.1136. Found: 265.1150.

(*E*)-*N*-Cyclohexyl-2-(4-methylphenyl)ethenylsulfonamide ((*E*)-**7b**): Colorless prisms (CH_2Cl_2–hexane), mp 108—110 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.15—1.31 (5H, m), 1.53—1.58 (1H, m), 1.68—1.72 (2H, m), 1.94—1.96 (2H, m), 2.38 (3H, s, Me), 3.21 (1H, br s, NCH), 4.59 (1H, d, J = 7.8 Hz, NH), 6.73 (1H, d, J = 15 Hz, 1-H), 7.20 (2H, d, J = 8 Hz, ArH), 7.38 (2H, d, J = 8 Hz, ArH), 7.44 (1H, d, J = 15 Hz, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 21.4 (q), 24.7 (t), 25.1 (t), 34.3 (t), 52.5 (d), 125.4 (d), 128.1 (d), 129.7 (d), 130.0 (s), 140.5 (d), 141.1 (s); MS *m/z*: 279 (M^+, 25%), 158 (100); IR (KBr) cm^{-1}: 3290 (NH), 1315, 1145 (SO_2); *Anal.* Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.36; H, 7.59; N, 5.05.

(*E*)-2-(4-Bromophenyl)-*N*-cyclohexylethenylsulfonamide ((*E*)-**7d**): Colorless prisms (EtOAc–hexane), mp 132—133 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.13—1.32 (5H, m), 1.54—1.57 (1H, m), 1.69—1.72 (2H, m), 1.93—1.96 (2H, m), 3.18—3.22 (1H, m, NCH), 4.77 (1H, d, J = 8 Hz, NH), 6.79 (1H, d, J = 15.6 Hz, 2-H), 7.34 (2H, d, J = 8.3 Hz, ArH), 7.40 (1H, d, J = 15.6 Hz, 2-H), 7.53 (2H, d, J = 8.3 Hz, ArH); ^{13}C-NMR ($CDCl_3$) δ: 24.6 (t), 25.1 (t), 34.2 (t), 52.6 (d), 124.9 (s), 127.3 (d), 129.5 (d), 131.6 (s), 132.2 (d), 139.0 (d); MS *m/z*: 343 (M^+, 21%), 222 (100); IR (KBr) cm^{-1}: 3270 (NH), 1320, 1150 (SO_2); *Anal.* Calcd for $C_{14}H_{18}BrNO_2S$: C, 48.84; H, 5.27; N, 4.07. Found: C, 48.60; H, 5.22; N, 4.07.

(*E*)-2-*tert*-Butyl-*N*-cyclohexylethenylsulfonamide ((*E*)-**7e**): Colorless needles (EtOAc–hexane), mp 58—59 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.93—1.46 (6H, m), 1.10 (9H, s, *tert*-Bu), 1.63—1.96 (4H, m), 3.09 (1H, br s, NCH), 4.82 (1H, d, J = 7.7 Hz, NH), 6.10 (1H, d, J = 15.3 Hz, 1-H), 6.74 (1H, d, J = 15.3 Hz, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 24.6 (t), 25.0 (t), 28.4 (q), 33.5 (s), 34.0 (t), 52.4 (d), 125.4 (d), 153.9 (d); MS *m/z*: 245 (M^+, 29%), 202 (100); IR (KBr) cm^{-1}: 3300 (NH), 1320, 1140 (SO_2); *Anal.* Calcd for $C_{12}H_{23}NO_2S$: C, 58.74; H, 9.45; N, 5.71. Found: C, 58.48; H, 9.41; N, 5.74.

(*E*)-2-*tert*-Butylethenylsulfonamide ((*E*)-**8e**): Colorless needles (EtOAc–hexane), mp 70—72 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.11 (9 H, s, *tert*-Bu), 4.97 (2H, s, NH_2), 6.30 (1H, d, J = 15.1 Hz, 1-H), 6.79 (1H, d, J = 15.1 Hz, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 28.4 (q), 33.7 (s), 126.3 (d), 153.8 (d); MS *m/z*: 163 (M^+, 1%), 61 (100); IR (KBr) cm^{-1}: 3350, 3290 (NH), 1335 1140 (SO_2); *Anal.* Calcd for $C_6H_{13}NO_2S$: C, 44.15; H, 8.03; N, 8.58. Found: C, 44.39; H, 8.06; N, 8.45.

(*E*)-*N*-Cyclohexyl-1-methyl-2-phenylethenylsulfonamide ((*E*)-**7f**): Colorless prisms (CH_2Cl_2–hexane), mp 124—125 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.15—1.37 (5H, m), 1.55—1.71 (3H, m), 1.94—1.96 (2H, m), 2.24 (3H, s, Me), 3.19—3.20 (1H, m, NCH), 4.35 (1H, d, J = 7.8 Hz, NH), 7.26—7.44 (5H, m, ArH), 7.56 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 13.3 (q), 24.7 (t), 25.2 (t), 34.2 (t), 52.6 (d), 128.6 (d), 128.9 (d), 129.4 (d), 134.2 (s), 136.0 (d), 136.5 (s); MS *m/z*: 279 (M^+, 27%), 117 (100); IR (KBr) cm^{-1}: 3270 (NH), 1310, 1155 (SO_2); *Anal.* Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.50; H, 7.63; N, 5.04.

(*E*)-*N*-Cyclohexyl-1-ethyl-2-phenylethenylsulfonamide ((*E*)-**7g**): Colorless prisms (EtOAc–hexane), mp 114—116 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.14—1.39 (3H, m), 1.31 (3H, t, J = 7 Hz, $CH_2\underline{CH}_3$), 1.56—1.77 (5H, m), 1.93—1.97 (2H, m), 2.65 (2H, q, J = 7 Hz, $C\underline{H}_2CH_3$), 3.13—3.26 (1H, m, NCH), 4.15 (1H, d, J = 7.8 Hz, NH), 7.29—7.48 (5H, m, ArH), 7.55 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 13.9 (q), 20.7 (t), 24.8 (t), 25.2 (t), 34.3 (t), 52.6 (d), 128.8 (d), 129.0 (d), 129.2 (d), 134.0 (s), 136.2 (d), 142.3 (s); MS *m/z*: 293 (M^+, 21%), 91 (100); IR (KBr) cm^{-1}: 3270 (NH), 1310, 1155 (SO_2); *Anal.* Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90; N, 4.77. Found: C, 65.47; H, 7.96; N, 4.86.

(*E*)-*N*-*n*-Butyl-2,3-diphenylethenylsulfonamide ((*E*)-**7h**): Yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 7.3 Hz, Me), 1.30 (2H, sextet, J = 7.3 Hz, CH_2), 1.46 (2H, quintet, J = 7.3 Hz, CH_2), 2.98 (2H, q, J = 7.3 Hz, NCH_2), 4.05 (1H, t, J = 7.3 Hz, NH), 7.04 (2H, d, J = 7 Hz, ArH), 7.12—7.26 (4H, m, ArH), 7.39—7.45 (4H, m, ArH), 7.70 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 13.5 (q), 19.7 (t), 31.9 (t), 43.1 (t), 128.4 (d), 129.2 (d), 129.3 (d), 129.6 (d), 130.3 (d), 130.4 (d), 132.0 (s), 133.0 (s), 137.2 (d), 139.0 (s); MS *m/z*: 315 (M^+, 14%), 57 (100); IR (NaCl) cm^{-1}: 1305, 1160 (SO_2); *Anal.* Calcd for $C_{18}H_{21}NO_2S$: C, 68.54; H, 6.71; N, 4.44. Found: C, 68.34; H, 6.70; N, 4.34.

(*E*)-2-*tert*-Butyl-*N*-cyclohexyl-1-phenylethenylsulfonamide ((*E*)-**7i**): Light yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 0.94 (9H, s, *tert*-Bu), 1.09—1.38 (6H, m), 1.66—1.70 (2H, m), 1.91—1.94 (2H, m), 3.04—3.09 (1H, m, NCH), 3.78 (1H, d, J = 6.4 Hz, NH), 6.91 (1H, s, 2-H), 7.32—7.40 (5H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ: 24.7 (t), 25.2 (t), 30.2 (q), 34.1 (t), 34.4 (s), 53.0 (d), 127.8 (d), 128.8 (d), 129.6 (s), 131.6 (d), 139.1 (s), 148.7 (d); MS *m/z*: 321 (M^+, 7%), 118 (100); IR (KBr) cm^{-1}: 1300, 1160 (SO_2); *Anal.* Calcd for $C_{18}H_{27}NO_2S$: C, 67.25; H, 8.47; N, 4.36. Found: C, 67.12; H, 8.58; N, 4.39.

(*E*)-*N*-Cyclohexyl-2-phenyl-1-(trimethylsilyl)ethenylsulfonamide ((*E*)-**7j**): Colorless prisms (CH_2Cl_2–hexane), mp 92—93 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.14 (9H s, $SiMe_3$), 1.16—1.40 (5H , m), 1.58—1.61 (1H, m), 1.71—1.75 (2H, m), 1.98—2.01 (2H, m), 3.22—3.27 (1H, m, NCH), 4.06 (1H, d, J = 7.8 Hz, NH), 7.22—7.26 (2H, m, ArH), 7.36—7.38 (3 H, m, ArH), 8.28 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 0.8 (q), 24.8 (t), 25.2 (t), 34.3 (t), 52.7 (d), 128.0 (d), 128.2 (d), 128.7 (d), 136.1 (s), 145.9 (s), 151.7 (d); MS *m/z*: 337 (M^+, 5%), 73 (100); IR (KBr) cm^{-1}: 3290 (NH), 1145, 1305 (SO_2); *Anal.* Calcd for $C_{17}H_{27}NO_2SSi$: C, 60.49; H, 8.06; N, 4.15. Found: C, 60.60; H, 8.19; N, 4.23.

(*E*)-2-Phenyl-1-(trimethylsilyl)ethenylsulfonamide ((*E*)-**8j**): Colorless prisms (CH_2Cl_2–hexane), mp 129.5—132 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.17 (9H, s, $SiMe_3$), 4.64 (2H, s, NH_2), 7.24—7.26 (2H, m, ArH), 7.36—7.38 (3H, m, ArH), 8.37 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 0.7 (q), 128.1 (d), 128.3 (d), 128.9 (d), 135.7 (s), 146.5 (s), 151.4 (d); MS *m/z*: 255 (M^+, 11%), 74 (100); IR (KBr) cm^{-1}: 3375, 3250 (NH), 1290, 1140 (SO_2); *Anal.* Calcd for $C_{11}H_{17}NO_2SSi$: C, 51.73; H, 6.71; N, 5.48. Found: C, 51.79; H, 6.81; N, 5.20.

(*E*)-*N*-Cyclohexyl-2-(4-methoxyphenyl)-1-(trimethylsilyl)ethenylsulfonamide ((*E*)-**7k**): Colorless needles (CH_2Cl_2–hexane), mp 95—98 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.20 (9H, s, $SiMe_3$), 1.14—1.42 (5H, m), 1.57—1.74 (3H, m), 1.96—2.00 (2H, m), 3.18—3.28 (1H, m, NCH), 3.84 (3H, s, OMe), 3.99 (1H, d, J = 7.3 Hz, NH), 6.90 (2H, d, J = 8.8 Hz, ArH), 7.22 (2H, d, J = 8.8 Hz, ArH), 8.20 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 1.1

(q), 25.0 (t), 25.4 (t), 34.5 (t), 52.8 (d), 55.5 (q), 113.8 (d), 128.3 (s), 130.3 (d), 143.8 (s), 151.9 (d), 160.4 (s); MS *m/z*: 367 (M^+, 3%), 204 (100); IR (KBr) cm^{-1}: 3300 (NH), 1295, 1135 (SO_2); *Anal.* Calcd for $C_{18}H_{29}NO_3SSi$: C, 58.82; H, 7.95; N, 3.81. Found: C, 58.85; H, 7.93; N, 3.88.

(*Z*)-*N*-Cyclohexyl-2-(4-methoxyphenyl)-1-(trimethylsilyl)ethenylsulfonamide ((*Z*)-**7k**): Colorless needles (CH_2Cl_2–hexane), mp 137—142 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.35 (9H, s, $SiMe_3$), 0.78—1.33 (6H, m), 1.46—1.56 (4H, m), 2.87—2.91 (1H, m, NCH), 3.85 (3H, s, OMe), 4.06 (1H, J=6.4 Hz, NH), 6.91 (2H, d, J=8.8 Hz, ArH), 7.18 (1H, s, 2-H), 7.64 (2H, d, J=8.8 Hz, ArH); ^{13}C-NMR ($CDCl_3$) δ: −0.5 (q), 24.4 (t), 25.2 (t), 33.4 (t), 52.8 (d), 55.4 (q), 114.1 (d), 127.7 (s), 131.1 (d), 145.9 (d), 146.0 (s), 160.5 (s); MS *m/z*: 367 (M^+, 4%), 204 (100); IR (KBr) cm^{-1}: 3340 (NH), 1170, 1300 (SO_2); *Anal.* Calcd for $C_{18}H_{29}NO_3SSi$: C, 58.82; H, 7.95; N, 3.81. Found: C, 58.67; H, 7.96; N, 3.86.

(*E*)-2-(4-Bromophenyl)-*N*-cyclohexyl-1-(trimethylsilyl)ethenylsulfonamide ((*E*)-**7l**): Colorless needles (CH_2Cl_2–hexane), mp 126—128 °C; ^{1}H-NMR ($CDCl_3$) δ: 0.15 (9H, s, $SiMe_3$), 1.13—1.39 (5H, m), 1.58—1.60 (1H, m), 1.71—1.75 (2H, m), 1.96—2.04 (2H, m), 3.21—3.27 (1H, m, NCH), 4.05 (1H, d, J=7.3 Hz, NH), 7.11 (2H, d, J=8 Hz, ArH), 7.52 (2H, d, J=8 Hz, ArH), 8.16 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 0.9 (q), 24.8 (t), 25.2 (t), 34.3 (t), 52.8 (d), 123.0 (s), 129.7 (d), 131.5 (d), 134.9 (s), 146.9 (s), 150.2 (d); MS *m/z*: 415 (M^+, 1%), 254 (100); IR (KBr) cm^{-1}: 3300 (NH), 1310, 1140 (SO_2); *Anal.* Calcd for $C_{17}H_{26}BrNO_2SSi$: C, 49.03; H, 6.29; N, 3.36. Found: C, 49.05; H, 6.33; N, 3.35.

Reactions of 4-Silyl-β-sultams with $AlCl_3$. General Procedure To a stirred solution of a 4-silylated β-sultam (0.1 mmol) in dry CH_2Cl_2 (1 ml) was added 3.0 eq of $AlCl_3$ (40 mg, 0.3 mmol) at 0 °C under nitrogen. The reaction mixture was stirred at room temperature or under reflux for an appropriate time and saturated aqueous $NaHCO_3$ (3 ml) was added to it. The inorganic precipitate was filtered off through Celite and washed with CH_2Cl_2 (5 ml). The organic layer was separated, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane–EtOAc (2 : 1 v/v)) to give an *N*-dealkylated (*E*)-vinylsulfonamide.

(*E*)-2-Phenylethenylsulfonamide ((*E*)-**8a**): Colorless leaves (CH_2Cl_2), mp 129—136 °C; ^{1}H-NMR ($CDCl_3$) δ: 4.75 (2H, brs, NH_2), 6.92 (1H, d, J=15.6 Hz, 1-H), 7.40—7.45 (3H, m, ArH), 7.48—7.50 (2H, m, ArH), 7.54 (1H, d, J=15.6 Hz, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 127.1 (d), 128.3 (d), 129.1 (d), 130.9 (d), 132.4 (s), 140.7 (d); MS *m/z*: 183 (M^+, 53%), 102 (100); IR (KBr) cm^{-1}: 3330, 3240 (NH), 1310, 1160 (SO_2); *Anal.* Calcd for $C_8H_9NO_2S$: C, 52.44; H, 4.95; N, 7.64. Found: C, 52.72; H, 5.14; N, 7.29.

(*E*)-1-Methyl-2-phenylethenylsulfonamide ((*E*)-**8f**): Colorless leaves (CH_2Cl_2), mp 136—138 °C; ^{1}H-NMR ($CDCl_3$) δ: 2.32 (3H, s, Me), 4.71 (2H, brs, NH_2), 7.37—7.44 (5H, m, ArH), 7.60 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 13.3 (q), 128.7 (d), 129.0 (d), 129.4 (d), 133.8 (s), 135.4 (d), 137.3 (s); MS *m/z*: 197 (M^+, 33%), 116 (100); IR (KBr) cm^{-1}: 3330, 3240 (NH), 1320, 1155 (SO_2); *Anal.* Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62; N, 7.10. Found: C, 54.94; H, 5.75; N, 6.80.

Reaction of the α-Silylvinylsulfonamide (*E*)-7k with NaH and MeI To a suspension of NaH (60% in paraffin oil, 24 mg, 0.6 mmol) in DMF (2 ml) was added the vinylsulfonamide (*E*)-**7k** (184 mg, 0.5 mmol) in several portions at 0 °C. MeI (0.04 ml, 0.6 mmol) was added to it and the whole was stirred at room temperature for 1 h. The reaction mixture was poured into water (10 ml) and the whole was extracted with EtOAc (10 ml × 2). The extracts were washed with saturated aqueous NaCl (10 ml × 2), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane–EtOAc (4 : 1 v/v)) to give (*E*)-*N*-cyclohexyl-*N*-methyl-2-phenylethenylsulfonamide ((*E*)-**9**, 140 mg) in quantitative yield: Colorless prisms (EtOAc–hexane), mp 86—88 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.00—1.49 (6H, m), 1.62—1.82 (4H, m), 2.76 (3H, s, NMe), 3.71—3.78 (1H, m, NCH), 6.65 (1H, d, J=16 Hz, 1-H), 7.39—7.50 (5H, m, ArH), 7.48 (1H, d, J=16 Hz, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 25.2 (t), 25.7 (t), 28.3 (q), 30.9 (t), 56.6 (d), 124.5 (d), 128.0 (d), 129.0 (d), 130.5 (d), 132.9 (s), 140.6 (d); MS *m/z*: 279 (M^+, 34%), 158 (100); IR (KBr) cm^{-1}: 1330, 1145 (SO_2); *Anal.* Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.48; H, 7.58; N, 4.99.

Synthesis of *N,N*-Dialkyl-α-silylethenylsulfonamide (*E*)-10 To a solution of LDA (3 mmol, prepared from 3 mmol of diisopropylamine (0.39 ml) and 3 mmol of *n*-BuLi in hexane) in dry THF (10 ml) was added dropwise a solution of the β-sultam **3a** (265 mg, 1 mmol) in THF (2—4 ml) at −78 °C under nitrogen. After 30 min, a solution of TBDMSCl (226 mg, 1.5 mmol) in THF (1—2 ml) was added dropwise to it and the whole was stirred at room temperature for 12 h. MeI (0.2 ml, 3 mmol) was added to the reaction mixture and the whole was stirred at room temperature for 24 h. Saturated aqueous NH_4Cl (4 ml) was added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted twice with EtOAc (10 ml). The organic layer and the extracts were combined, washed with saturated aqueous NaCl (20 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane–EtOAc (4 : 1 v/v)) to give the *N*-methylated (*E*)-vinylsulfonamide (*E*)-**10** (178 mg, 45%) from the first fraction, the (*E*)-α-silylvinylsulfonamide (*E*)-**11** (85 mg, 22%) from the second fraction and the vinylsulfonamide (*E*)-**7a** (73 mg, 28%) from the third fraction.

(*E*)-1-(*tert*-Butyldimethylsilyl)-*N*-cyclohexyl-*N*-methyl-2-phenylethenylsulfonamide ((*E*)-**10**): Yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 0.04 (6H, s, SiMe × 2), 0.89 (9H, s, *tert*-Bu), 1.28—1.75 (6H, m), 1.82—1.85 (4H, m), 2.78 (3H, s, Me), 3.67—3.79 (1H, m, NCH), 7.19—7.21 (2H, m, ArH), 7.32—7.37 (3H, m, ArH), 8.25 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: −1.8 (q), 18.2 (s), 25.5 (t), 26.0 (t), 28.0 (q), 28.5 (q), 30.8 (t), 56.2 (d), 127.9 (d), 128.3 (d), 136.3 (s), 144.9 (s), 152.6 (d); MS *m/z* (FAB): 394 (M^+ + 1, 59%), 336 (100); IR (NaCl) cm^{-1}: 1310, 1120 (SO_2); *Anal.* Calcd for $C_{21}H_{35}NO_2SSi$: C, 64.07; H, 8.96; N, 3.56. Found: C, 63.80; H, 8.96; N, 3.55.

(*E*)-1-(*tert*-Butyldimethylsilyl)-*N*-cyclohexyl-2-phenylethenylsulfonamide ((*E*)-**11**): Yellow oil; ^{1}H-NMR ($CDCl_3$) δ: 0.06 (6H, s, SiMe × 2), 0.90 (9H, s, *tert*-Bu), 1.16—1.40 (5H, m), 1.58—1.78 (3H, m), 2.00—2.02 (2H, m), 3.22—3.24 (1H, m, NCH), 4.11 (1H, br s, NH), 7.19—7.21 (2H, m, ArH), 7.32—7.37 (3H, m, ArH), 8.46 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: −1.7 (q), 17.9 (s), 24.8 (t) , 25.2 (t), 28.0 (q), 34.3 (t), 52.7 (d), 127.8 (d), 127.9 (d), 128.3 (d), 136.2 (s), 145.3 (s), 153.2 (d); MS *m/z* (FAB): 380 (M^+ + 1, 89%), 322 (100); IR (NaCl) cm^{-1}: 3300 (NH), 1315, 1125 (SO_2); *Anal.* Calcd for $C_{20}H_{33}NO_2SSi$: C, 63.28; H, 8.76; N, 3.70. Found: C, 63.19; H, 8.92; N, 3.67.

Reactions of α-Silylvinylsulfonamide (*E*)-10 with Benzaldehyde A solution of TBAF (1 M solution in THF, 0.24 ml, 0.24 mmol) in THF (1 ml) was dried with molecular sieves 4 Å (100 mg, activated by heating with a burner for several hours followed by cooling under reduced pressure) with stirring for 24 h. Benzaldehyde (32 mg, 0.3 mmol) was added to it followed by addition of (*E*)-**10** (79 mg, 0.2 mmol) in THF (1 ml) at room temperature. After 3 h, the reaction mixture was poured into water (10 ml) and extracted twice with EtOAc (10 ml). The extracts were washed with saturated aqueous NaCl (15 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane–acetone (5 : 1 v/v)) to give the desilylated product (*E*)-**9** (44 mg, 79%).

A solution of TBAF (1 M solution in THF, 0.24 ml, 0.24 mmol) in THF (1 ml) was dried with molecular sieves 4 Å (150 mg, activated by heating with a burner for several hours followed by cooling under reduced pressure) with stirring for 24 h. Benzaldehyde (107 mg, 1 mmol) and 1 drop of $BF_3 \cdot Et_2O$ were added to it, followed by addition of (*E*)-**10** (79 mg, 0.2 mmol) in THF (1 ml) under cooling with ice–NaCl (−15 °C). After 45 min, the reaction mixture was poured into water (10 ml) and extracted twice with EtOAc (10 ml). The extracts were washed with saturated aqueous NaCl (15 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane–acetone (5 : 1 v/v)) to give the desilylated product (*E*)-**9** (23 mg, 41%) and allyl alcohol (*E*)-**12** (28 mg, 36%).

(*E*)-*N*-Cyclohexyl-1-(1-hydroxyphenylmethyl)-*N*-methyl-2-phenylethenylsulfonamide ((*E*)-**12**): Colorless prisms (EtOAc–hexane), mp 131—135 °C; ^{1}H-NMR ($CDCl_3$) δ: 1.22—1.47 (5H, m), 1.60—1.79 (5H, m), 2.47 (3H, s, Me), 3.52—3.58 (1H, m, NCH), 3.88 (1H, d, J=10 Hz, OH), 6.01 (1H, d, J=10 Hz, OCH), 7.25—7.48 (10H, m, ArH), 7.77 (1H, s, 2-H); ^{13}C-NMR ($CDCl_3$) δ: 25.3 (t), 25.8 (t), 27.8 (q), 30.7 (t), 56.7 (d), 69.3 (d), 125.8 (d), 127.5 (d), 128.3 (d), 128.7 (d), 129.1 (d), 129.4 (d), 133.1 (s), 139.9 (d), 140.7 (s), 142.7 (s); MS *m/z*: 385 (M^+, 0.4%), 208 (100); IR (KBr) cm^{-1}: 3460 (OH), 1285, 1130 (SO_2); *Anal.* Calcd for $C_{22}H_{27}NO_3S$: C, 68.54; H, 7.06; N, 3.63. Found: C, 68.38; H, 7.23; N, 3.52.

Acknowledgments This work was supported in part by Grants-in-Aid for Scientific Research (No. 08304037 and 09771915) from the Ministry of Education, Science, Sports, and Culture.

References

1) Kataoka T., Iwama T., Takagi A., *Tetrahedron Lett.*, **37**, 2257—2260 (1996).
2) Aumaitre G., Chanet-Ray J., Durand J., Vessière R., Lonchambon G., *Synthesis*, **1983**, 816—821 .
3) Chanet-Ray J., Vessière R., Zéroual A., *Heterocycles*, **26**, 101—108 (1987).
4) Distler H., *Angew. Chem.*, **77**, 291—302 (1965).
5) Hasegawa K., Hiraoka S., *Bull. Chem. Soc. Jpn.*, **45**, 1567—1568 (1972).
6) Hasegawa K., Sasaki T., Hiraoka S., *Bull. Chem. Soc. Jpn.*, **46**, 696—698 (1973).
7) Maindron M., Lacoste J., Vessiere R., *J. Photochem. Photobiol., A: Chem.*, **44**, 303—315 (1988).
8) Morris J., Wishka D. G., *J. Org. Chem.*, **56**, 3549—3556 (1991).
9) Tsuge H., Takumi K., Nagai T., Okano T., Eguchi S., Kimoto H., *Tetrahedron*, **53**, 823—838 (1997).
10) Metz P., Seng D., Fröhlich R., Wibbeling B., *Synlett*, **1996**, 741—742
11) Tsuge H., Nagai T., Okano T., Eguchi S., Kimoto H., *Synlett*, **1996**, 1106—1108.
12) Matlack A. S., *J. Org. Chem.*, **23**, 729—731 (1958).
13) Oliver J. E., DeMilo A. B., *Synthesis*, **1975**, 321—322.
14) Mladenova M., Gaudemar-Bardone F., *Phosphorus Sulfur*, **62**, 257—267 (1991).
15) Baudin J.-B., Julia S. A., Wang Y., *Synlett*, **1992**, 911—913.
16) Lube A., Neumann W. P., Niestroj M., *Chem. Ber.*, **128**, 1195—1198 (1995).
17) Gennari C., Salom B., Potenza D., Williams A., *Angew. Chem. Int. Ed. Engl.*, **33**, 2067—2069 (1994).
18) Gennari C., Nestler H. P., Salom B., Still C., *Angew. Chem. Int. Ed. Engl.*, **34**, 1763—1765 (1995).
19) Schwan A. L., Refvik M. D., *J. Chem. Soc., Chem. Commun.*, **1995**, 1949—1950.
20) Refvik M. D., Schwan A. L., *J. Org. Chem.*, **61**, 4232—4239 (1996).
21) Kataoka T., Iwama T., *Tetrahedron Lett.*, **36**, 245—248 (1995).
22) Kataoka T., Iwama T., *Tetrahedron Lett.*, **36**, 5559—5562 (1995).
23) Atkins J. G. M., Burgess E. M., *J. Am. Chem. Soc.*, **89**, 2502—2503 (1967).
24) Furukawa J., Kobayashi S., Saegusa T., *Polym. Bull.*, **21**, 421—426 (1989).
25) Schwenkkraus P., Otto H.-H., *Justus Liebigs Ann. Chem.*, **1994**, 251—257.
26) Merkle S., Otto H.-H., *Arch. Pharm.*, **327**, 657—660 (1994).
27) Müller M., Otto H.-H., *Arch. Pharm.*, **324**, 15—17 (1991).
28) Hiraoka T., Kobayashi T., *Bull. Chem. Soc. Jpn.*, **48**, 480—483 (1975).
29) Grunder E., Leclerc G., *Synthesis*, **1989**, 135—137.
30) Müller M., Meyle E., Paulus E. F., Plagge H., Otto H.-H., *Justus Liebigs Ann. Chem.*, **1989**, 975—983.
31) Grunder E., Leclerc G., Ehrhardt J.-D., *J. Heterocycl. Chem.*, **26**, 1781—1785 (1989).
32) Lacey R. N., *J. Chem. Soc.*, **1960**, 1633—1639.
33) Catt J. D., Matier W. L., *J. Org. Chem.*, **39**, 566—568 (1974).
34) Colvin E., "Silicon in Organic Synthesis," Butterworths, London, 1981.
35) Fleming I., Dunoguès J., Smithers R., *Org. React.*, **37**, 57—575 (1989).