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TETRAHEDRON

Reactions of 1,2-Thiazetidine 1,1-Dioxides with Organometallics: β-Elimination and N-S Bond Cleavage

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Abstract: Reactions of 4-nonsubstituted β-sultams **1** with methyllithium gave only (*E*)-vinylsulfonamides **2**, whereas 2-aminoethyl sulfones **3** were obtained as minor products by use of methylmagnesium bromide. Reactions of 4-monosubstituted β-sultams **6** with organolithiums gave (*E*)-vinylsulfonamides **7** stereoselectively regardless of the configuration of 3- and 4-substituents. Treatment of 4,4-dimethyl-β-sultam **8a** with methylmagnesium bromide and methyllithium provided 2-aminoethyl sulfone **9** and bis-sulfone **10**, respectively, and isopropyl phenyl sulfone **11** was obtained by use of phenyllithium or phenylmagnesium bromide.

INTRODUCTION

1,2-Thiazetidine 1,1-dioxides (β-sultams) are the sulfonyl analogues of the β-lactam ring or the cyclized compounds of taurine. The chemistry of β-sultams has been widely investigated from both chemical and pharmacological points of view.[1-4] β-Lactams are stabilized by the π-bond overlap between the lone pair electrons of a nitrogen atom and the carbonyl group, and are much more stable than β-sultams.[5] The β-sultam ring consists of three different kinds of hetero single bonds, namely, C-N, C-S and N-S bonds, and β-sultams could be utilized as various synthetic equivalents as well as building blocks for the construction of other heterocycles.[1,2] We recently reported that selective cleavage of C-S or C-N bonds was achieved by reactions of β-sultams with Lewis acids to give ketones, aldehydes, *trans*-1,2,3-oxathiazolidine 2-oxides, *cis*-aziridines and (*E*)-vinylsulfonamides depending on C-3 and C-4 substituents of the β-sultam ring and on Lewis acids.[6-8] We intended to investigate the N-S bond cleavage of the β-sultam ring. The N-S bond is usually cleaved by hydrolysis or aminolysis with hetero nucleophiles.[1,2] Hydride reduction of β-sultams with sodium bis(2-methoxyethoxy)aluminum hydride (Vitride®) has provided 2-aminoethanethiol derivatives.[9] Otto and co-workers have reported that treatment of β-sultams with ^{n}BuLi underwent dimerization and rearrangement to produce dithiazine tetraoxide derivatives *via* the N-S bond cleavage.[10,11] This reaction proceeds *via* nucleophilic attack of a β-sultam carbanion to the sulfonyl group of another β-sultam molecule followed by intramolecular cyclization. We examined reactions of β-sultams with organometallics as a carbon nucleophile and found that organometallics worked as a base and/or a nucleophile to give (*E*)-vinylsulfonamides and/or sulfones, respectively, in contrast to the results reported by Otto and co-workers.[10,11]

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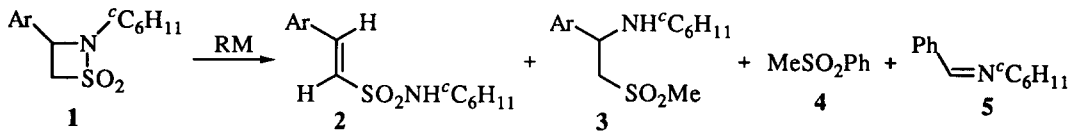
RESULTS AND DISCUSSION

First, we examined reactions of 4-nonsubstituted β-sultams **1** with methyllithium, phenyllithium and methylmagnesium bromide (Scheme 1, Table 1). The reaction of 3-phenyl-β-sultam **1a** with 1.2 equiv. of MeLi in tetrahydrofuran (THF) at 0°C for 2 h provided (*E*)-vinylsulfonamide **2a** in 70% yield by β-elimination together with 21% of the starting material (entry 1), and no dimerized product could be isolated.[10,11] β-Elimination proceeded smoothly at 0°C - room temperature by addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as a chelating reagent to give vinylsulfonamide **2a** in 84% yield as the sole product (entry 2). Treatment of β-sultam **1a** with 3.0 equiv. of MeLi and TMEDA at -78°C for 6 h resulted in recovery of the starting β-sultam (entry 3). The results suggest that a di-anion of a β-sultam is stable relative to a β-sultam mono-anion at low temperature and that reaction pathways are dependent on the amount of an organolithium and the reaction temperature. No reaction occurred by treatment of β-sultam **1a** with 3.0 equiv. of MeLi at -78°C for 1.5 h followed by raising the temperature to 0°C for 0.5 h. On the other hand, a β-sultam mono-anion, generated from **1a** and 1.2 equiv. of MeLi, underwent dimerization and rearrangement at -78°C for 6 h to give a dithiazine tetraoxide derivative in 34% yield.[10,11] MeMgBr worked partly as a nucleophile, and 2-aminoethylsulfone **3a** was provided in 8% yield as a minor product (entry 4). PhLi also acted both as a base and a nucleophile to give vinylsulfonamide **2a** (42%), methyl phenyl sulfone **4** (10%) and a trace amount of imine **5** (entry 5). Reactions of β-sultams **1b-d** with 1.2 equiv. of MeMgBr at room temperature gave similar results to the reaction of β-sultam **1a** (entries 7,9 and 10). Although 2-aminoethylsulfone **3b** was obtained in 21% yield as a major product together with 12% of vinylsulfonamide **2b**,



1 **2** **3** **4** **5**

Scheme 1

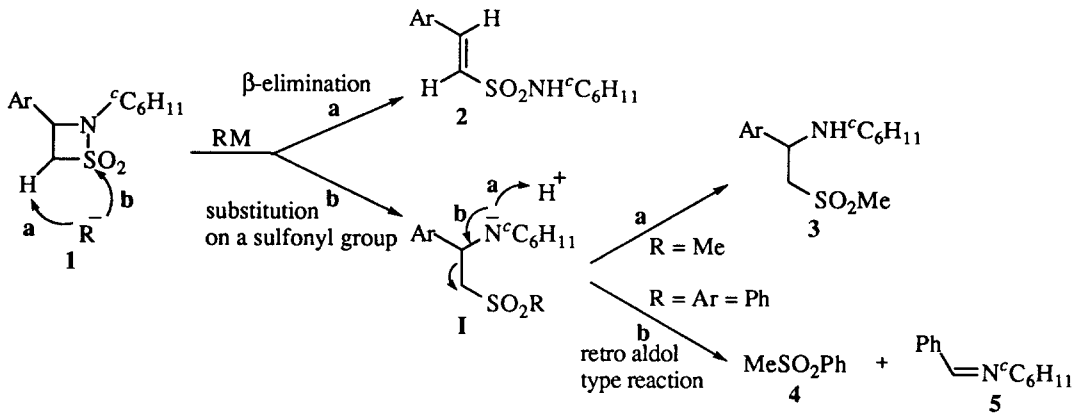
Table 1. Reactions of 4-Nonsubstituted β-Sultams **1** with Organometallics.

Entry	β-Sultam Compd No.	Ar	Conditions (eq.)	Products (%yield)[a]
1	**1a**	Ph	MeLi (1.2), THF, 0°C, 2h	**1a** (21), **2a** (70)
2			MeLi (1.2), TMEDA, THF, 0°C - r.t., 1 h	**2a** (84)
3			MeLi (3.0), TMEDA, THF, -78°C, 6 h	Recovery
4			MeMgBr (1.2), THF, r.t., 6 h	**2a** (67), **3a** (8)
5			PhLi (1.7), THF, 50°C, 30 min	**2a** (42), **4** (10), **5** (trace)
6	**1b**	*p*-$MeOC_6H_4$	MeMgBr (1.2), THF, 0°C, 2 h	**1b** (58), **2b** (12), **3b** (21)
7			MeMgBr (1.2), THF, r.t., 6 h	**2b** (75), **3b** (18)
8			MeMgBr (1.2), ether, r.t., 6 h	**2b** (78), **3b** (11)
9	**1c**	*p*-MeC_6H_4	MeMgBr (1.2), THF, r.t., 6 h	**2c** (68), **3c** (12)
10	**1d**	*o*-MeC_6H_4	MeMgBr (1.2), THF, r.t., 6 h	**2d** (72), **3d** (25)

[a] Isolated yield.

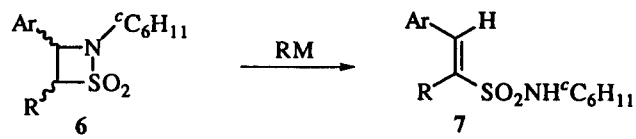
a considerable amount of the starting material was recovered in the reaction with MeMgBr at 0°C for 2 h (entry 6). No significant difference was observed by use of ether instead of THF (entries 7 and 8).

The products **2-5** are formed as described in Scheme 2. (*E*)-Vinylsulfonamides **2** are obtained by abstraction of a *pseudoequatorial* proton of C^4 when an organometallic acts as a base.[12,13] Nucleophilic attack of an organometallic towards the sulfonyl group caused ring-opening with the N-S bond fission to provide an amide intermediate **I**, which follows two pathways: one is formation of 2-aminoethylsulfones **3** by protonation of the amide **I** during work-up in the cases of R = Me. The other route is the retro aldol type reaction of the amide **I** to give methyl phenyl sulfone **4** and imine **5** in the case of R = Ph. The difference may be due to steric bulkiness of the methyl- and phenylsulfonyl groups.



Scheme 2

Next, we examined reactions of 4-monosubstituted β-sultams **6** (Scheme 3, Table 2). In all cases no products, which would be formed by nucleophilic substitution of an organometallic to the sulfonyl group, were isolated. The higher acidity of a C^4-proton (benzylic proton) of 4-phenyl-β-sultams **6** than that of 4-nonsubstituted β-sultams **1** would work advantageously for deprotonation and β-elimination. Reactions of 3,4-diphenyl derivative ***cis*-6a** with MeLi below room temperature resulted in isomerization to compound ***trans*-6a** and formation of (*E*)-vinylsulfonamide **7a** (entries 1 and 2), and reactions of β-sultam ***trans*-6a** under the same conditions gave the compound **7a** in lower yields (entries 7 and 8). The reaction rate of β-elimination was considerably accelerated by addition of TMEDA, and vinylsulfonamide **7a** was obtained in high yield at 0°C for 1 h (entry 3). Vinylsulfonamide **7a** was also obtained in good yields by refluxing in THF for 1.5 h (entries 4 and 9). Although treatment with PhLi at 50°C for 30 min afforded 82% of vinylsulfonamide **7a** (entry 5), only isomerised product ***trans*-6a** was formed from the reaction with MeMgBr at 0°C for 13 h (entry 6). MeLi gave a better result than MeMgBr for β-elimination (compare entries 2 and 6). 3-*p*-Methoxyphenyl β-sultams **6b** provided (*E*)-vinylsulfonamide **7b** in good yields regardless of the configuration of 3- and 4-substituents (entries 10 and 11). Compound **7c** was obtained in 44% yield from the reaction of 3-(2-thienyl)-β-sultam ***cis*-6c** and MeLi at room temperature (entry 12) although the reaction of 4-ethyl-β-sultam ***cis*-6d** with MeLi at room temperature provided a small amount of compound **7d** and 67% of isomerised β-sultam ***trans*-6d** (entry 13). The greater reactivity of 4-phenyl-β-sultams **6a-c** than that of 4-ethyl derivative ***cis*-6d** towards β-elimination would be owing to formation of more stabilized stilbene derivatives by conjugation with



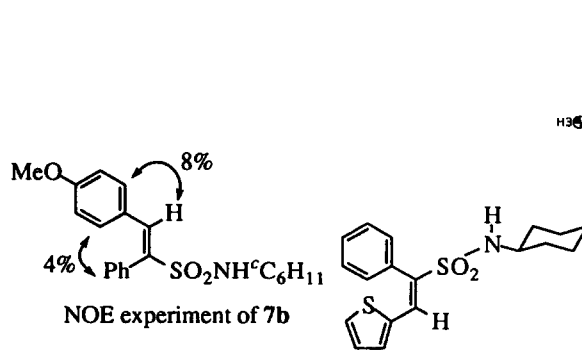
Scheme 3

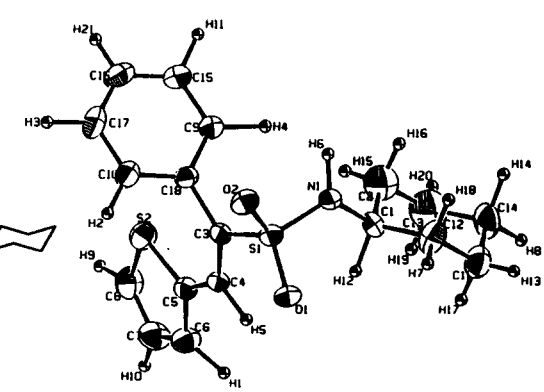
Table 2. Reactions of 4-Monosubstituted β-Sultams **6** with Organometallics.

Entry	β–Sultam Compd No.	Ar	R	Conditions (eq.)	Products (%yield)[a]
1	***cis*-6a**	Ph	Ph	MeLi (1.2), THF, -78°C - r.t., 8 h	***trans*-6a** (50), **7a** (44)
2				MeLi (1.2), THF, -10°C, 4 h	***trans*-6a** (63), **7a** (28)
3				MeLi (1.2), TMEDA, THF, 0°C - r.t., 1 h	**7a** (86)
4				MeLi (1.5), THF, reflux, 1.5 h	**7a** (84)
5				PhLi (1.7), THF, 50°C, 30 min	**7a** (82)
6				MeMgBr (1.5), THF, 0°C, 13 h	***trans*-6a** (89)
7	***trans*-6a**	Ph	Ph	MeLi (1.2), THF, -78°C - r.t., 8 h	***trans*-6a** (54), **7a** (35)
8				MeLi (1.2), THF, -10°C, 4 h	***trans*-6a** (70), **7a** (20)
9				MeLi (1.5), THF, reflux, 1.5 h	**7a** (78)
10	***cis*-6b**	*p*-$MeOC_6H_4$	Ph	MeLi (1.5), THF, reflux, 1.5 h	**7b** (68)
11	***trans*-6b**	*p*-$MeOC_6H_4$	Ph	MeLi (1.5), THF, reflux, 1.5 h	**7b** (76)
12	***cis*-6c**	2-Thienyl	Ph	MeLi (1.5), THF, r.t., 6 h	**7c** (44)
13	***cis*-6d**	Ph	Et	MeLi (1.5), THF, r.t., 6 h	***trans*-6a** (67), **7d** (11)

[a] Isolated yield.

an aromatic ring. The geometry of (*E*)-vinylsulfonamides **7** was determined by NOE measurements and X-ray crystallographic analysis (Fig. 1).

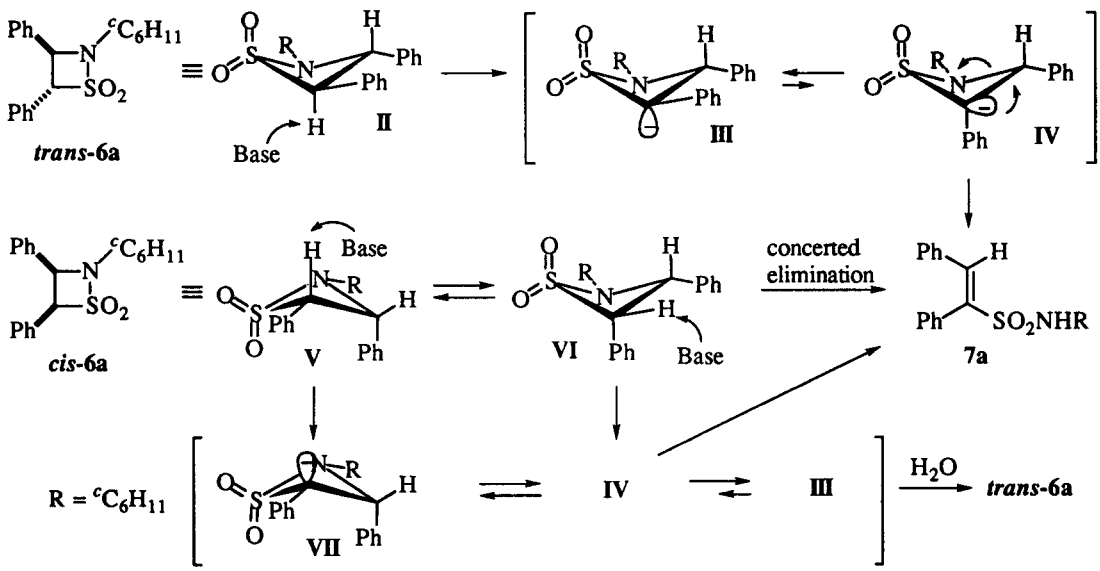




ORTEP drawing of **7c**

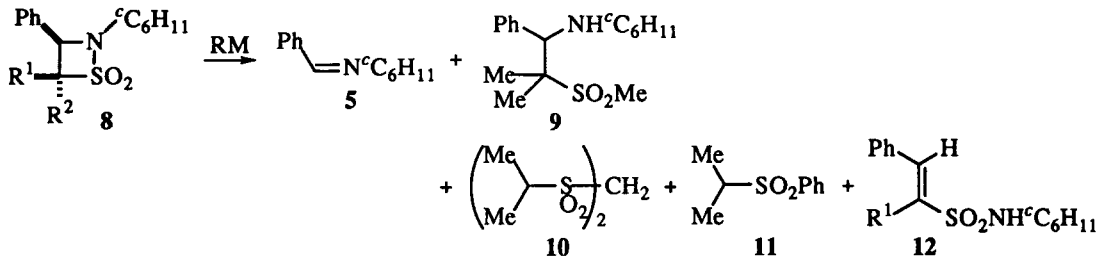
Fig. 1. Structure determination of vinylsulfonamides **7**

(*E*)-Selective formation of vinylsulfonamides and the difference in reactivity between 3,4-diphenyl-β-sultams ***cis***- and ***trans***-**6a** would be explained as illustrated in Scheme 4. Compound ***trans***-**6a** exists in a conformer **II** in solution, in which two phenyl groups are *pseodoequatorially* oriented,[14-16] and a carbanion **III** is generated by deprotonation with a base. β-Elimination proceeds *via* another less stable carbanion **IV**, in which the p-orbital of the anion and the C-N bond are in *anti*-periplanar relationship, to give an (*E*)-vinylsulfonamide stereoselectively. On the other hand, *cis*-β-sultam would exist in both conformers **V** and **VI**. (*E*)-Vinylsulfonamide **7a** is formed by deprotonation of an *axial*-proton of the conformer **V** *via* a carbanion **VII** followed by conversion to the carbanion **IV**. In addition, concerted β-elimination of the conformer **VI** is achieved by abstraction of a *pseudoequatorial* proton to provide the compound **7a**, and the *cis*-isomer gives a slightly better result than the *trans*-isomer. β-Sultam ***trans***-**6a** is obtained by isomerization of the carbanion **IV** to the most stable carbanion **III** and protonation of **III** during work-up.



Scheme 4

We carried out reactions of 4,4-disubstituted β-sultams lacking a β-hydrogen which is responsible for β-elimination (Scheme 5, Table 3). The reaction of dimethyl-β-sultam **8a** was very slow, probably due to steric hindrance of the two methyl groups, and 2-aminoethylsulfone **9** was obtained in 79% yield accompanied with a small amount of the starting sultam by use of 8.0 equiv. of MeMgBr at room temperature for 23 h (entry 1). The reaction with 2.0 equiv. of MeLi at room temperature was complicated, and only small amounts of products **5**,**9** and **10** were isolated (entry 2). The reaction proceeded smoothly by addition of 2.0 equiv. of MeLi into the refluxing solution of sultam **8a** in THF to give bis-sulfone **10** in high yield (entry 3). Treatment with 8.0 equiv. of PhMgBr at room temperature provided isopropyl phenyl sulfone **11** in 95% yield together with 5% of imine **5** (entry 4). Sulfone **11** was also obtained by use of PhLi (entry 5). Use of a cuprate and a cerium reagent[11] resulted in recovery of sultam **8a** (entries 6 and 7). 2-Aminoethylsulfone **9** was provided in 45% yield together with 41% of the starting sultam **8a** by use of MeMgBr-$LiClO_4$ (entry 8).[18,19] Starting materials



Scheme 5

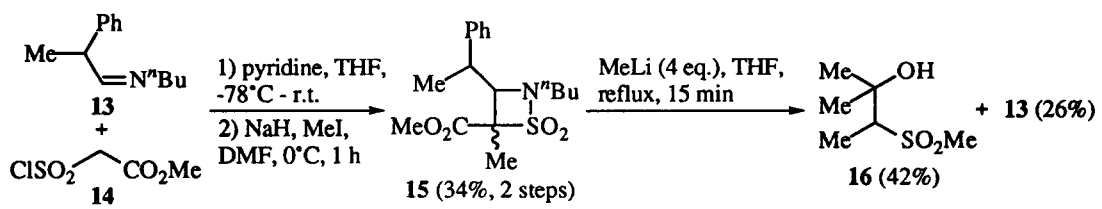
Table 3. Reactions of 4,4-Disubstituted β-Sultams **8** with Organometallics.

Entry	β-Sultam Compd No.	R^1	R^2	Conditions (eq.)	Products (%yield)[a]
1	**8a**	Me	Me	MeMgBr (8.0), THF, r.t., 23 h	**8a** (5), **9** (79)
2				MeLi (2.0), THF, r.t., 6 h	**5** (trace), **9** (5), **10** (17)
3				MeLi (2.0), THF, reflux, 1 h	**5** (36), **10** (87)
4				PhMgBr (8.0), THF, r.t., 24 h	**5** (3), **11** (95)
5				PhLi (2.0), THF, 50°C, 2 h	**5** (8), **8a** (31), **11** (62)
6				MeMgBr/CuI (2.0/1.0), THF, 0°C - r.t., 21 h	Recovery
7				MeMgBr/$CeCl_3$ (1.5/1.5), THF, 0°C - r.t., 18 h	Recovery
8				MeMgBr (4.0), $LiClO_4$ (1.0), PhH-ether, r.t., 20 h	**8a** (41), **9** (45)
9	**8b**	TMS	TMS	MeMgBr (8.0), THF, r.t., 40 h	**8b** (91), **12b** (4)
10	**8c**	Me	TBDMS	MeMgBr (8.0), THF, r.t., 20 h	**8c** (92), **12c** (7)

[a] Isolated yield.

8b,c were almost completely recovered accompanied with trace amounts of desilylated (*E*)-vinylsulfonamides **12b,c** even by use of 8.0 equiv. of MeMgBr at room temperature because steric hindrance of the bulky silyl groups prevented nucleophilic attack of MeMgBr to the sulfonyl group (entries 9 and 10).

The reaction of β-sultamcarboxylic acid ester **15** was examined (Scheme 6). The β-sultam **15** was synthesized in 34% overall yield by [2+2] cycloaddition of imine **13** and sulfonyl chloride **14** by reference to the literature,[20] followed by methylation of the inseparable mixture of products with MeI. 2-Hydroxypropylsulfone **16** was obtained in 42% yield together with 26% of imine **13** by treatment of **15** with 4 equiv. of MeLi under refluxing in THF for 15 min.



Scheme 6

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 were recorded on a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. Elemental analyses of new compounds were performed by a Yanaco CHN Corder MT-5. All chromatographic isolations were accomplished with either Kieselgel 60 (Merck) or BW-127ZH (Fuji Silysia) for column chromatography or Kieselgel 60 PF_{254} containing gypsum (Merck) for TLC.

Synthesis of β-Sultams by [2+2] Cycloaddition of Sulfonyl Chlorides and Imines

Method A, general procedure. To a stirred solution of methanesulfonyl chloride (0.77 cm^3, 10 mmol) in dry THF (5 cm^3) was added dropwise a solution of imine (20 mmol) in dry THF (30 cm^3) at room temperature under nitrogen and the mixture was stirred at room temperature for 3 days. 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 days and purified by column chromatography on silica gel and eluted with EtOAc–hexane (1:10 -1:5 v/v).

Method B, general procedure. To a stirred solution of phenylmethanesulfonyl chloride (0.953 mg, 5 mmol) in dry THF (2.5 cm^3) was added dropwise a solution of imine (10 mmol) in dry THF (10 cm^3) under cooling with ice-NaCl under nitrogen and the mixture was stirred at room temperature for 3 days. 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 and eluted with EtOAc–hexane (1:10 -1:5 v/v).

Method C, general procedure. A sulfonyl chloride (5 mmol) and an imine (10 mmol) was stirred without solvent at room temperature under nitrogen. After standing at room temperature for 3 days, the solidified reaction mixture was purified by column chromatography on silica gel and eluted with EtOAc–hexane (1:10 -1:5 v/v).

2-Cyclohexyl-3-phenyl-1,2-thiazetidine 1,1-dioxide (1a) Prepared by Method A, yield 59%, colorless prisms (CH_2Cl_2-hexane), mp 128-129°C; ^{1}H NMR ($CDCl_3$) δ: 1.08-1.27 (4 H, m), 1.42-1.74 (5 H, m), 2.04 (1 H, br d, *J* = 12.7 Hz), 3.20-3.28 (1 H, m, NCH), 3.86 (1 H, dd, *J* = 8.8 and 15.1 Hz, 4-H), 4.34 (1 H, dd, *J* = 7.81 and 15.1 Hz, 4-H), 4.35 (1 H, dd, *J* = 7.81 and 8.8 Hz, 3-H), 7.27-7.43 (3 H, m, ArH), 7.50-7.53 (2 H, 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 (EI) *m/z* (rel. int. %): 265 (7, M^+), 104 (100); IR ν_{max} (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-methoxyphenyl)-1,2-thiazetidine 1,1-dioxide (1b) Prepared by Method A, yield 56%, colorless prisms (CH_2Cl_2-hexane), mp 80-82°C; ^{1}H NMR ($CDCl_3$) δ: 1.10-1.28 (4 H, m), 1.43-1.73 (5 H, m), 2.01 (1 H, br d, *J* = 12.7 Hz), 3.19-3.22 (1 H, m, NCH), 3.82 (3 H, s, OMe), 3.83 (1H,

dd, J = 8 and 14 Hz, 4-H), 4.31 (1 H, dd, J = 8 and 14 Hz, 4-H), 4.32 (1 H, t, J = 8 Hz, 3-H), 6.91 (2 H, d, J = 8.8 Hz, ArH), 7.42 (2 H, 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 (EI) *m/z* (rel. int. %): 295 (2, M^+), 134 (100); IR ν_{max} (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.

2-Cyclohexyl-3-(4-methylphenyl)-1,2-thiazetidine 1,1-dioxide (1c) Prepared by Method A, yield 58%, colorless prisms (CH_2Cl_2-hexane), mp 107-110°C; ^{1}H NMR ($CDCl_3$) δ: 1.08-1.25 (4 H, m), 1.43-1.71 (5 H, m), 2.01 (1 H, br d, J = 12 Hz), 2.34 (3 H, s, Me), 3.10-3.21 (1 H, m, NCH), 3.81 (1 H, dd, J = 8 and 15 Hz, 4-H), 4.30 (1 H, dd, J = 8 and 15 Hz, 4-H), 4.31 (1 H, t, J = 8 Hz, 3-H), 7.18 (2 H, d, J = 7.8 Hz, ArH), 7.38 (2 H, 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 (EI) *m/z* (rel. int. %): 279 (3, M^+), 118 (100); IR ν_{max} (KBr)/cm^{-1}: 1320 and 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-(2-methylphenyl)-1,2-thiazetidine 1,1-dioxide (1d) Prepared by Method A, yield 63%, colorless prisms (from EtOAc-hexane), mp 112-115°C; ^{1}H NMR ($CDCl_3$) δ: 1.09-1.27 (4 H, m), 1.49-1.59 (4 H, m), 1.73 (1 H, br d, J = 12 Hz), 2.08 (1 H, br d, J = 12 Hz), 2.33 (3 H, s, Me), 3.21-3.24 (1 H, m, 1'-H), 3.72 (1 H, dd, J = 6.3 and 12.2 Hz, 4-H), 4.35 (1 H, dd, J = 7.8 and 12.2 Hz, 4-H), 4.55 (1 H, dd, J = 6.3 and 7.8 Hz, 3-H), 7.13 (1 H, d, J = 7 Hz, ArH), 7.21 (1 H, t, J = 7 Hz, ArH), 7.27 (1 H, t, J = 7 Hz, ArH), 7.75 (1 H, d, J = 7 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ: 18.9 (q), 24.1 (t), 24.4 (t), 25.3 (t), 30.2 (t), 31.8 (t), 45.3 (d), 57.1 (d), 64.6 (t), 125.6 (d), 126.8 (d), 128.1 (d), 130.5 (d), 134.5 (s), 136.9 (s); MS (EI) *m/z* (rel. int. %): 279 (1, M^+), 118 (100); IR ν_{max} (KBr) cm^{-1}: 1315, 1150 (SO_2); *Anal.* Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.28; H, 7.70; N, 4.99.

***trans*-2-Cyclohexyl-3,4-diphenyl-1,2-thiazetidine 1,1-dioxide (*trans*-6a)** Prepared by Method B, yield 31%, colorless prisms (from EtOAc-hexane), mp 139-144°C; ^{1}H NMR ($CDCl_3$) δ: 1.18–1.39 (4 H, m), 1.60-1.83 (5 H, m), 2.20 (1 H, br d, J = 12.2 Hz), 3.36-3.41 (1 H, m, 1'-H), 4.48 (1 H, d, J = 6.8 Hz, 3-H), 5.13 (1 H, d, J = 6.8 Hz, 4-H), 7.15-7.54 (10 H, m, ArH); ^{13}C NMR ($CDCl_3$) δ: 24.2 (t), 24.4 (t), 25.3 (t), 30.5 (t), 32.0 (t), 57.0 (d), 58.2 (d), 82.9 (d), 126.4 (d), 128.6 (s), 128.8 (d), 128.9 (d), 129.0 (d), 129.2 (d), 129.5 (d), 138.1 (s); MS (EI) *m/z* (rel. int. %): 341 (22, M^+), 83 (100); IR ν_{max} (KBr) cm^{-1}: 1310, 1170 (SO_2); *Anal.* Calcd for $C_{20}H_{23}NO_2S$: C, 70.35; H, 6.79; N, 4.10. Found: C, 70.09; H, 6.74; N, 3.98.

***cis*-2-Cyclohexyl-3,4-diphenyl-1,2-thiazetidine 1,1-dioxide (*cis*-6a)** Prepared by Method B, yield 45%, colorless prisms (from EtOAc-hexane), mp 186-191°C; ^{1}H NMR ($CDCl_3$) δ: 1.14-1.39 (4 H, m), 1.59-1.83 (5 H, m), 2.22(1 H, br d, J = 12.2 Hz), 3.33-3.41 (1 H, m, 1'-H), 4.95 (1 H, d, J = 8.8 Hz, 3-H), 5.70 (1 H, d, J = 8.8 Hz, 4-H), 7.06-7.25 (10 H, m, ArH); ^{13}C NMR ($CDCl_3$) δ: 24.4 (t), 24.8 (t), 25.4 (t), 31.0 (t), 31.9 (t), 55.1 (d), 57.2 (d), 79.6 (d), 127.5 (d), 127.8 (d), 127.9 (d), 128.0 (d), 128.4 (s), 128.6 (d), 130.0 (d), 135.0 (s); MS (EI) *m/z* (rel. int. %): 341 (15, M^+), 194 (100); IR ν_{max} (KBr) cm^{-1}: 1308, 1175 (SO_2); *Anal.* Calcd for $C_{20}H_{23}NO_2S$: C, 70.35; H, 6.79; N, 4.10. Found: C, 70.41; H, 6.84; N, 4.11.

***trans*-2-Cyclohexyl-3-(4-methoxyphenyl)-4-phenyl-1,2-thiazetidine 1,1-dioxide (*trans*-6b)** Prepared by Method B, yield 23%, colorless prisms (from EtOAc-hexane), mp 110-112°C; ^{1}H NMR ($CDCl_3$) δ: 1.13-1.30 (4 H, m), 1.53-1.77 (5 H, m), 2.11 (1 H, br d, J = 12.7 Hz), 3.28-3.33 (1 H, m, 1'-H), 3.79 (3 H, s, OMe), 4.38 (1 H, d, J = 6.8 Hz, 3-H), 5.04 (1 H, d, J = 6.8 Hz, 4-H), 6.88 (2 H, d, J = 8.3 Hz, ArH), 7.38-7.44 (7 H, m, ArH); ^{13}C NMR ($CDCl_3$) δ: 24.2 (t), 24.4 (t), 25.4 (t), 30.5 (t), 32.0 (t), 55.3(q), 56.9 (d), 58.0 (d), 82.9 (d), 114.3 (d), 127.7 (d), 128.7 (s), 128.9 (d), 129.2 (d), 129.5 (d), 129.9 (s), 160.0 (s); MS (EI) *m/z* (rel. int. %): 371 (13, M^+), 216 (100); IR ν_{max} (KBr) cm^{-1}: 1300, 1170 (SO_2); *Anal.* Calcd for $C_{21}H_{25}NO_3S$: C, 67.90; H, 6.78; N, 3.77. Found: C, 67.72; H, 6.83; N, 3.76.

***cis*-2-Cyclohexyl-3-(4-methoxyphenyl)-4-phenyl-1,2-thiazetidine 1,1-dioxide (*cis*-6b)** Prepared by Method B, yield 35%, colorless prisms (from EtOAc-hexane), mp 131-134°C; ^{1}H NMR ($CDCl_3$) δ: 1.14-1.35 (4 H, m), 1.57-1.83 (5 H, m), 2.19 (1 H, br d, J = 12.2 Hz), 3.31-3.37 (1 H, m, 1'-H), 3.69 (3 H, s, OMe), 4.91 (1 H, d, J = 8.8 Hz, 3-H), 5.65 (1 H, d, J = 8.8 Hz, 4-H), 6.69 (2 H, d, J = 8.8 Hz, ArH), 7.10-7.20 (7 H, m, ArH); ^{13}C NMR ($CDCl_3$) δ: 24.5 (t), 24.8 (t), 25.4 (t), 31.0 (t), 31.9 (t), 54.9 (q), 55.1 (d), 57.0 (d), 79.6 (d), 113.4 (d), 126.8 (s), 128.0 (d), 128.6 (d), 128.8 (d), 130.0 (d), 159.3 (s), aromatic methine and quaternary carbons are overlapped; MS (EI) *m/z* (rel. int. %): 371 (20, M^+), 216 (100); IR ν_{max} (KBr) cm^{-1}: 1320, 1165 (SO_2); *Anal.* Calcd for $C_{21}H_{25}NO_3S$: C, 67.90; H, 6.78; N, 3.77. Found: C, 67.89; H, 6.83; N, 3.81.

***trans*-2-Cyclohexyl-3-(2-thienyl)-4-phenyl-1,2-thiazetidine 1,1-dioxide (*trans*-6c)** Prepared by Method B, yield 25%, colorless prisms (from EtOAc-hexane), mp 158-161°C; ^{1}H NMR ($CDCl_3$) δ: 1.15-1.42 (4 H, m), 1.54-1.78 (4 H, m), 1.85 (1 H, br d, J = 12 Hz), 2.12 (1 H, br d, J = 12 Hz), 3.30-3.37 (1 H, m, 1'-H), 4.73 (1 H, d, J = 6 Hz, 3-H), 5.21 (1 H, d, J = 6 Hz, 4-H), 6.94 (1 H, dd, J = 3 and 5 Hz, ArH), 7.07 (1 H, dd, J = 1 and 3 Hz, ArH), 7.31 (1 H, dd, J = 1 and 5 Hz, ArH), 7.37-7.45 (5 H, m, ArH); ^{13}C NMR ($CDCl_3$) δ: 24.3 (t), 24.6 (t), 25.4 (t), 30.4 (t), 31.8 (t), 54.2 (d), 57.0 (d), 83.3 (d), 125.9 (d), 126.3 (d), 127.1 (d), 128.5 (s), 129.0 (d), 129.1 (d), 129.7 (d), 142.1 (s); MS (EI) *m/z* (rel. int. %): 347 (25, M^+), 200 (100); IR ν_{max} (KBr) cm^{-1}: 1320, 1170 (SO_2); *Anal.* Calcd for $C_{18}H_{21}NO_2S_2$: C, 62.22; H, 6.09; N, 4.03. Found: C, 62.29; H, 6.11; N, 3.98.

***cis*-2-Cyclohexyl-3-(2-thienyl)-4-phenyl-1,2-thiazetidine 1,1-dioxide (*cis*-6c)** Prepared by Method B, yield 39%, colorless prisms (from EtOAc-hexane), mp 149-152°C; ^{1}H NMR ($CDCl_3$) δ: 1.16-1.41 (3 H, m), 1.42-1.50 (1 H, m), 1.57-1.67 (2 H, m), 1.76-1.80 (2 H, m), 1.91 (1 H, br d, J = 12 Hz), 2.17 (1 H, br d, J = 12 Hz), 3.36-3.43 (1 H, m, 1'-H), 5.18 (1 H, d, J = 8 Hz, 3-H), 5.65 (1 H, d, J = 8 Hz, 4-H), 6.81 (1 H, dd, J = 3 and 5 Hz, ArH), 6.95 (1 H, d, J = 3 Hz, ArH), 7.09 (1 H, d, J = 5 Hz, ArH), 7.16-7.24 (3 H, m, ArH), 7.26-7.31 (2 H, m, ArH); ^{13}C NMR ($CDCl_3$) δ: 24.5 (t), 24.9 (t), 25.4 (t), 31.0 (t), 31.8 (t), 51.8 (d), 57.1 (d), 79.8 (d), 125.9 (d), 126.8 (d), 126.9 (d), 128.0 (d), 128.2 (s), 128.9 (d), 129.9 (d), 138.7(s); MS (EI) *m/z* (rel. int. %): 347 (20, M^+), 200 (100); IR ν_{max} (KBr) cm^{-1}: 1320, 1160 (SO_2); *Anal.* Calcd for $C_{18}H_{21}NO_2S_2$: C, 62.22; H, 6.09; N, 4.03. Found: C, 62.47; H, 6.24; N, 4.14.

***trans*-2-Cyclohexyl-4-ethyl-3-phenyl-1,2-thiazetidine 1,1-dioxide (*trans*-6d)** Prepared by Method C, yield 20%, colorless prisms (EtOAc-hexane), mp 74-75°C; ^{1}H NMR ($CDCl_3$) δ: 1.02 (3 H, t, J =

7.3 Hz, Me), 1.02-1.27 (4 H, m), 1.45-1.74 (5 H, m), 1.86-1.95 (1 H, m), 2.05-2.17 (2 H, m), 3.16-3.22 (1 H, m, NCH), 3.81 (1 H, d, J = 6.3 Hz, 3-H), 3.86-3.92 (1 H, m, 4-H), 7.27-7.49 (5 H, 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 (EI) *m/z* (rel. int. %): 293 (10, M^+), 117 (100); IR ν_{max} (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.

***cis*-2-Cyclohexyl-4-ethyl-3-phenyl-1,2-thiazetidine 1,1-dioxide (*cis*-6d)** Prepared by Method C, yield 12%, colorless prisms (EtOAc-hexane), mp 83-84°C; ^{1}H NMR ($CDCl_3$) δ: 0.84 (3 H, t, J = 7.3 Hz, Me), 1.04-1.29 (5 H, m), 1.43-1.77 (6 H, m), 2.05-2.08 (1 H, m), 3.21-3.26 (1 H, m, NCH), 4.29 (1 H, ddd, J = 5.3, 7.4 and 8.8 Hz, 4-H), 4.56 (1 H, d, J = 8.8 Hz, 3-H), 7.27-7.40 (5 H, 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), 128.5 (d), 135.7 (s), aromatic methine and quaternary carbons are overlapped; MS (EI) *m/z* (rel. int. %): 293 (6, M^+), 117 (100); IR ν_{max} (KBr)/cm^{-1}: 1340, 1145 (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.

Synthesis of 4,4-Dimethyl-β-sultam 8a

To a solution of LDA (3 mmol, prepared from 3 mmol of diisopropylamine (0.39 cm^3) and 3 mmol of ^{n}BuLi in hexane) in dry THF (10 cm^3) was added dropwise a solution of β-sultam **1a** (265 mg, 1 mmol) in THF (2-4 cm^3) at -78°C under nitrogen. After 30 min., MeI (0.19 cm^3, 3 mmol) was added dropwise to it and the whole was stirred at room temperature for 12 h. Saturated aqueous NH_4Cl (4 cm^3) was added to the reaction mixture and the organic layer was separated. The water layer was extracted twice with EtOAc (10 cm^3). The organic layer and the extracts were combined, washed with saturated aqueous NaCl (20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with EtOAc–hexane (1:10 v/v) to give 272 mg (93%) of 2-cyclohexyl-4,4-dimethyl-3-phenyl-1,2-thiazetidine 1,1-dioxide **8a**, colorless prisms (from EtOAc-hexane), mp 108-110°C; ^{1}H NMR ($CDCl_3$) δ: 1.08 (3 H, s, Me), 1.10-1.31 (4 H, m), 1.49-64 (4 H, m), 1.64 (3 H, s, Me), 1.72-1.75 (1 H, m), 2.12-2.15 (1 H, m), 3.16-3.22 (1 H, m, 1'-H), 4.07 (1 H, s, 3-H), 7.33-7.41 (5 H, m, ArH); ^{13}C NMR ($CDCl_3$) δ: 19.2 (q), 22.2 (q), 24.4 (t), 24.8 (t), 25.4 (t), 31.0 (t), 32.1 (t), 57.0 (d), 62.3 (d), 75.3 (s), 127.1 (d), 128.5 (d), 135.5 (s), two aromatic methine carbons are overlapped; MS (EI) *m/z* (rel. int. %): 293 (10, M^+), 186 (100); IR ν_{max} (KBr) cm^{-1}: 1310, 1130 (SO_2); *Anal.* Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90; N, 4.77. Found: C, 65.21; H, 7.93; N, 4.74.

Synthesis of 4,4-Disilyl-β-sultam 8b

To a solution of LDA (3 mmol, prepared from 3 mmol of diisopropylamine (0.39 cm^3) and 3 mmol of ^{n}BuLi in hexane) in dry THF (10 cm^3) was added dropwise a solution of β-sultam (265 mg, 1 mmol) in THF (2-4 cm^3) at -78°C under nitrogen. After 30 min., a solution of TMSCl (326 mg, 3 mmol) in THF (1-2 cm^3) was added dropwise to it and the whole was stirred at room temperature for an appropriate time. Saturated aqueous NH_4Cl (4 cm^3) was added to the reaction mixture and the organic layer was separated. The water layer was extracted twice with EtOAc (10 cm^3). The organic layer and the extracts were combined, washed with saturated aqueous NaCl (20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with EtOAc–hexane (1:50 -1:20 v/v).

2-Cyclohexyl-3-phenyl-4,4-bis(trimethylsilyl)-1,2-thiazetidine 1,1-dioxide (8b) Yield 92%, colorless prisms (EtOAc-hexane), mp 83-84°C; ^{1}H NMR ($CDCl_3$) δ: -0.07 (9 H, s, $SiMe_3$), 0.42 (9 H, s, $SiMe_3$), 1.09-1.27 (4 H, m), 1.51-1.74 (5 H, m), 2.11-2.15 (1 H, m), 3.19-3.24 (1 H, m, NCH), 4.60 (1 H, s, 3-H), 7.29-7.43 (5 H, 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), two aromatic methine carbons are overlapped; MS (EI) *m/z* (rel. int. %): 409 (21, M^+), 186 (100); IR ν_{max} (KBr)/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.

Methylation of 4-(ᵗButyldimethylsilyl)-2-cyclohexyl-3-phenyl-β-sultam

To a solution of LDA (2 mmol, prepared from 2 mmol of diisopropylamine (0.26 cm^3) and 2 mmol of ^{n}BuLi in hexane) in dry THF (10 cm^3) was added dropwise a solution of 2-cyclohexyl-4-(ᵗbutyldimethylsilyl)-3-phenyl-β-sultam (380 mg, 1 mmol) in THF (2-4 cm^3) at -78°C under nitrogen. After 30 min., MeI (0.19 cm^3, 3 mmol) was added dropwise to it and the whole was stirred at room temperature for 26 h. Saturated aqueous NH_4Cl (4 cm^3) was added to the reaction mixture and the organic layer was separated. The water layer was extracted twice with EtOAc (10 cm^3). The organic layer and the extracts were combined, washed with saturated aqueous NaCl (20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with EtOAc–hexane (1:50 -1:20 v/v) to give 331 mg (84%) of 4-(ᵗbutyldimethylsilyl)-2-cyclohexyl-4-methyl-3-phenyl-1,2-thiazetidine 1,1-dioxide (**8c**), colorless prisms (CH_2Cl_2-hexane), mp 148-151°C; ^{1}H NMR ($CDCl_3$) δ: 0.23 (3 H, s, SiMe), 0.42 (3 H, s, SiMe), 1.00 (9 H, s, ᵗBu), 1.21 (3 H, s, 4-Me), 1.04-1.28 (5 H, m), 1.37-1.74 (4 H, m), 1.96-2.04 (1 H, m), 3.16-3.22 (1 H, m, NCH), 4.49 (1 H, s, 3-H), 7.34-7.43 (5 H, 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 (EI) *m/z* (rel. int. %): 393 (1, M^+), 272 (100); IR ν_{max} (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.

Synthesis of 4-Methoxycarbonyl-4-methyl-β-sultam 15

To a solution of an imine **13** (947 mg, 5 mmol) and pyridine (0.6 cm^3, 7.5 mmol) in THF (20 cm^3) was added dropwise a solution of a sulfonyl chloride **14** (1.29 g, 7.5 mmol) at -78°C under nitrogen. After 30 min., the suspension was allowed to warm gradually to room temperature. Saturated aqueous NH_4Cl (10 cm^3) and water (10 cm^3) was added to the reaction mixture and the organic layer was separated. The water layer was extracted twice with ether (30 cm^3). The organic layer and the extracts were combined, washed with saturated aqueous NaCl (30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with EtOAc–hexane (1:10 v/v) to give a β-sultam containing uncharacterized products. The crude β-sultam and MeI (0.47 cm^3, 7.5 mmol) were dissolved in DMF (15 cm^3) and treated with NaH (60% in mineral oil, 240 mg, 6 mmol) at 0°C for 2 h. Water (30 cm^3) was added to the reaction mixture and the whole was extracted twice with EtOAc (30 cm^3). The extracts were washed with saturated aqueous NaCl (30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with EtOAc–hexane (1:10 v/v) to give 577 mg (34%) of 2-butyl-4-methoxycarbonyl-4-methyl-3-(α-methylbenzyl)-1,2-thiazetidine 1,1-dioxide **15**, colorless prisms (from CH_2Cl_2-hexane), mp 72-79°C; ^{1}H NMR ($CDCl_3$) δ: 0.96 (3 H, t, J = 7.3 Hz, CH_2CH_3), 1.30 (3 H, s, Me), 1.37 (3 H, d, J = 7 Hz, $CHCH_3$), 1.45 (2 H, sextet, J = 7.3 Hz, CH_2CH_3), 1.67-1.79 (2 H, m,

$CH_2CH_2CH_2$), 3.03 (1 H, ddd, J = 7, 9 and 13 Hz, NCH_2), 3.14 (1H, d, J = 10 Hz, 3-H), 3.38 (1 H, ddd, J = 6, 9 and 13 Hz, NCH_2), 3.67 (1 H, dq, J = 10 and 7 Hz, $CHCH_3$), 3.75 (3 H, s, OMe), 7.08 (2 H, d, J = 7 Hz, ArH), 7.23 (1 H, t, J = 7 Hz, ArH), 7.29 (2 H, t, J = 7 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ: 13.7 (q), 193.0 (q), 20.4 (t), 20.9 (q), 31.0 (t), 40.7 (d), 49.3 (t), 53.0 (q), 66.6 (d), 80.7 (s), 127.4 (d), 127.5 (d), 128.7 (d), 141.9 (s), 165.6 (s); MS (FAB) *m/z* (rel. int. %): 340 (62, $M^+ + 1$), 154 (100); IR ν_{max} (KBr) cm^{-1}: 1735 (C=O), 1320, 1145 (SO_2), 1245 (C-O); *Anal.* Calcd for $C_{17}H_{25}NO_4S$: C, 60.15; H, 7.42; N, 4.13. Found: C, 60.04; H, 7.45; N, 3.94.

Reactions of β-Sultams with Organometallics

General procedure. To a solution of a β-sultam (0.5 mmol) in THF (2 cm^3) was added dropwise an organometallic compound at an appropriate temperature. After an appropriate time, the reaction was quenched by addition of saturated aqueous NH_4Cl (1 cm^3), and water (5 cm^3) was added to the reaction mixture (in the cases of refluxing reactions, the reactions were quenched after cooling to room temperature). The whole was extracted twice with EtOAc (10 cm^3) (if needed, the whole was filtered through celite in order to remove an inorganic precipitate before extraction). The extracts were washed with saturated aqueous NaCl (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by TLC on silica gel and eluted with EtOAc–hexane (1:10 – 1:1 v/v). The reaction conditions and yields are summarized in Tables 1-3.

(*E*)-*N*-Cyclohexyl-2-phenylvinylsulfonamide (2a) Colorless prisms (CH_2Cl_2-hexane), mp 110-113°C; ^1H NMR ($CDCl_3$) δ: 1.13-1.36 (5 H, m), 1.54-1.57 (1 H, m), 1.68-1.71 (2 H, m), 1.95-1.97 (2 H, m), 3.21-3.23 (1 H, m, NCH), 4.67 (1 H, br s, NH), 6.80 (1 H, d, J = 15.6 Hz, 1-H), 7.34-7.42 (3 H, m, ArH), 7.47 (1 H, d, J = 15.6 Hz, 2-H), 7.44-7.50 (2 H, 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 (EI) *m/z* (rel. int. %): 265 (16, M^+), 144 (100); IR ν_{max} (KBr)/cm^{-1}: 3270 (NH), 1320, 1145 (SO_2); HRMS (EI) Calcd for $C_{14}H_{19}NO_2S$: 265.1136. Found: 265.1150.

2-Cyclohexylamino-2-phenylethyl methyl sulfone (3a) Light yellow oil; ^1H NMR ($CDCl_3$) δ: 1.08-1.27 (5 H, m), 1.54-1.66 (5 H, m), 2.01 (1 H, br d, J = 11 Hz), 2.26-2.33 (1 H, m, 1'-H), 2.88 (3 H, s, SO_2Me), 3.12 (1 H, dd, J = 4 and 15 Hz, SCH_2), 3.33 (1 H, dd, J = 9 and 15 Hz, SCH_2), 4.41 (1 H, dd, J = 4 and 9 Hz, CH), 7.27-7.45 (5 H, m, ArH); ^{13}C NMR ($CDCl_3$) δ: 24.8 (t), 25.2 (t), 26.3 (t), 32.8 (t), 34.8 (t), 42.9 (q), 54.0 (d), 54.8 (d), 63.8 (t), 126.7 (d), 129.1 (d), 131.3 (d), 139.1 (s); MS (EI) *m/z* (rel. int. %): 281 (15, M^+), 104 (100); IR ν_{max} (NaCl) cm^{-1}: 3340 (NH), 1300, 1135 (SO_2); HRMS (EI) Calcd for $C_{15}H_{23}NO_2S$: 281.1449. Found: 281.1162.

(*E*)-2-(4-Methoxyphenyl)vinylsulfonamide (2b) Colorless prisms (from EtOAc-hexane), mp 112-115°C; ^1H NMR ($CDCl_3$) δ: 1.14-1.35 (5 H, m), 1.55 (1 H, br d, J = 12 Hz), 1.68-1.71 (2 H, m), 1.96 (2 H, br d, J = 9 Hz), 3.20-3.22 (1 H, m, 1'-H), 3.84 (3 H, s, OMe), 4.52 (1 H, d, J = 4 Hz, NH), 6.63 (1 H, d, J = 15 Hz, 2-H), 6.92 (2 H, d, J = 8 Hz, ArH), 7.42 (1 H, d, J = 15 Hz, 1-H), 7.43 (2 H, d, J = 9 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ: 24.7 (t), 25.1 (t), 34.3 (t), 52.5 (d), 55.4 (q), 114.4 (d), 123.9 (d), 125.3 (s), 129.8 (d), 140.3 (d), 161.6 (s); MS (EI) *m/z* (rel. int. %): 295 (16, M^+), 134 (100); IR ν_{max} (KBr) cm^{-1}: 3280 (NH), 1320, 1150 (SO_2); *Anal.* Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74. Found: C, 61.07; H, 7.20; N, 4.76.

2-Cyclohexylamino-2-(4-methoxyphenyl)ethyl methyl sulfone (3b) Colorless prisms (from EtOAc-hexane), mp 67-69°C; ^{1}H NMR ($CDCl_3$) δ: 1.10-1.16 (5 H, m), 1.54-1.69 (4 H, m), 1.99-2.01 (1 H, m), 2.09 (1 H, br s, NH), 2.29-2.33 (1 H, m, 1'-H), 2.86 (3 H, s, SO_2Me), 3.20 (1 H, dd, *J* = 4.4 and 14.7 Hz, SCH_2), 3.40 (1 H, dd, *J* = 8.8 and 14.7 Hz, SCH_2), 3.82 (3 H, s, OMe), 4.43 (1 H, dd, *J* = 4.4 and 8.8 Hz, CH), 6.91 (2 H, d, *J* = 8 Hz, ArH), 7.28 (2 H, d, *J* = 8 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ: 24.5 (t), 24.9 (t), 25.9 (t), 32.2(t), 34.3 (t), 42.7 (q), 53.4(d), 54.2 (d), 55.3 (q), 62.1 (t), 114.4 (d), 128.0 (d), 133.0 (s), 159.4 (s); MS (EI) *m/z* (rel. int. %): 311 (6, M^+), 134 (100); IR ν_{max} (KBr) cm^{-1}: 3330 (NH), 1300, 1130 (SO_2); *Anal.* Calcd for $C_{16}H_{25}NO_3S$: C, 61.71; H, 8.09; N, 4.50. Found: C, 61.84; H, 8.13; N, 4.43.

(*E*)-*N*-Cyclohexyl-2-(4-methylphenyl)vinylsulfonamide (2c) Colorless prisms (CH_2Cl_2-hexane), mp 108-110°C; ^{1}H NMR ($CDCl_3$) δ: 1.15-1.31 (5 H, m), 1.53-1.58 (1 H, m), 1.68-1.72 (2 H, m), 1.94-1.96 (2 H, m), 2.38 (3 H, s, Me), 3.21 (1 H, br s, NCH), 4.59 (1 H, d, *J* = 7.8 Hz, NH), 6.73 (1 H, d, *J* = 15 Hz, 1-H), 7.20 (2 H, d, *J* = 8 Hz, ArH), 7.38 (2 H, d, *J* = 8 Hz, ArH), 7.44 (1 H, 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 (EI) *m/z* (rel. int. %): 279 (25, M^+), 158 (100); IR ν_{max} (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.

2-Cyclohexylamino-2-(4-methylphenyl)ethyl methyl sulfone (3c) Colorless oil; ^{1}H NMR ($CDCl_3$) δ: 1.04-1.15 (5 H, m), 1.53-1.64 (5 H, m), 2.00 (1 H, br d, *J* = 11 Hz), 2.26-2.32 (1 H, m, 1'-H), 2.35 (3 H, s, Me), 2.89 (3 H, s, SO_2Me), 3.14 (1 H, dd, *J* = 3.9 and 14.7 Hz, SCH_2), 3.31 (1 H, dd, *J* = 9.3 and 14.7 Hz, SCH_2), 4.41 (1 H, dd, *J* = 3.9 and 9.3 Hz, CH), 7.17 (2 H, d, *J* = 8 Hz, ArH), 7.20 (2 H, d, *J* = 8 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ: 21.4 (q), 24.8 (t), 25.3 (t), 26.3 (t), 32.8 (t), 34.9 (t), 43.0 (q), 53.6 (d), 54.8 (d), 62.7 (t), 126.9 (d), 130.0 (d), 138.0 (s), 139.0 (s); MS (EI) *m/z* (rel. int. %): 295 (33, M^+), 202 (100); IR ν_{max} (NaCl) cm^{-1}: 3340 (NH), 1300, 1140 (SO_2); HRMS (EI) Calcd for $C_{16}H_{25}NO_2S$: 295.1606. Found: 295.1584.

(*E*)-*N*-Cyclohexyl-2-(2-methylphenyl)vinylsulfonamide (2d) Colorless prisms (from EtOAc-hexane), mp 97-100°C; ^{1}H NMR ($CDCl_3$) δ: 1.15-1.38 (5 H, m), 1.54-1.56 (1 H, m), 1.66-1.73 (2 H, m), 1.96-1.99 (2 H, m), 2.43 (3 H, s, Me), 3.22-3.27 (1 H, m, 1'-H), 4.22 (1 H, d, *J* = 7.3 Hz, NH), 6.67 (1 H, d, *J* = 15.1 Hz, 1-H), 7.22-7.26 (2 H, m, ArH), 7.31(1 H, t, *J* = 7 Hz, ArH), 7.46 (1 H, d, *J* = 7 Hz, ArH), 7.74 (1 H, d, *J* = 15.1 Hz, 2-H); ^{13}C NMR ($CDCl_3$) δ: 19.8 (q), 24.7 (t), 25.1 (t), 34.4 (t), 52.6 (d), 126.5 (d), 126.6 (d), 127.6 (d), 130.4 (d), 130.9 (d), 131.8 (s), 137.7 (s), 138.3 (d); MS (EI) *m/z* (rel. int. %): 279 (18, M^+), 43 (100); IR ν_{max} (KBr) cm^{-1}: 3250 (NH), 1310, 1165 (SO_2); *Anal.* Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.65; H, 7.64; N, 5.11.

2-Cyclohexylamino-2-(2-Methylphenyl)ethyl methyl sulfone (3d) Light yellow oil; ^{1}H NMR ($CDCl_3$) δ: 1.07-1.22 (5 H, m), 1.26 (1 H, br s, NH), 1.53-1.63 (4 H, m), 1.98 (1 H, br d, *J* = 11 Hz), 2.19-2.28 (1 H, m, 1'-H), 2.40 (3 H, s, Me), 2.94 (3 H, s, SO_2Me), 3.05 (1 H, dd, *J* = 3.4 and 14.6 Hz, SCH_2), 3.23 (1 H, dd, *J* = 9 and 14.6 Hz, SCH_2), 4.74 (1 H, dd, *J* = 3.4 and 9 Hz, CH), 7.17-7.26 (3 H, m, ArH), 7.36 (1 H, d, *J* = 7.3 Hz, ArH); ^{13}C NMR ($CDCl_3$) δ: 19.6 (q), 24.9 (t), 25.3 (t), 26.3 (t), 33.1 (t),

35.0 (t), 43.1 (q), 50.3 (d), 53.8 (d), 61.9 (t), 125.6 (d), 127.0 (d), 127.9 (d), 131.3 (d), 135.7 (s), 140.1 (s); MS (EI) *m/z* (rel. int. %): 295 (18, M^+), 116 (100); IR ν_{max} (NaCl) cm^{-1}: 3300 (NH), 1295, 1125 (SO_2); HRMS (EI) Calcd for $C_{16}H_{25}NO_2S$: 295.1606. Found: 295.1590.

(*E*)-*N*-Cyclohexyl-1,2-diphenylvinylsulfonamide (7a) Colorless prisms (from EtOAc-hexane), mp 105-113°C; ^1H NMR ($CDCl_3$) δ: 1.10-1.31 (5 H, m), 1.51-1.58 (1 H, m), 1.64-1.65 (2 H, m), 1.86-1.90 (2 H, m), 3.11-3.15 (1 H, m, 1'-H), 4.09 (1 H, br s, NH), 7.04 (2 H, d, *J* = 8 Hz, ArH), 7.16 (2 H, t, *J* = 8 Hz, ArH), 4.23 (1 H, t, *J* = 8 Hz, ArH), 7.42 (5 H, s, ArH), 7.70 (1 H, s, olefinic H); ^{13}C NMR ($CDCl_3$) δ: 24.7 (t), 25.2 (t), 34.1 (t), 53.0 (d), 128.4 (d), 129.0 (d), 129.2 (d), 129.5 (d), 130.3 (d), 130.7 (d), 132.0 (s), 133.2 (s), 136.4 (d), 140.4 (s); MS (EI) *m/z* (rel. int. %): 341 (24, M^+), 179 (100); IR ν_{max} (KBr) cm^{-1}: 3295 (NH), 1320, 1145 (SO_2); *Anal.* Calcd for $C_{20}H_{23}NO_2S$: C, 70.35; H, 6.79; N, 4.10. Found: C, 70.38; H, 6.95; N, 4.04.

(*E*)-*N*-Cyclohexyl-2-(4-methoxyphenyl)-1-phenylvinylsulfonamide (7b) Light yellow oil; ^1H NMR ($CDCl_3$) δ: 1.10-1.31 (5 H, m), 1.52-1.55 (1 H, m), 1.64-1.67 (2 H, m), 1.89 (2 H, br d, *J* = 12.4 Hz), 3.09-3.14 (1 H, m, 1'-H), 3.74 (3 H, s, OMe), 4.01 (1 H, d, *J* = 6.4 Hz, NH), 6.69 (2 H, d, *J* = 9 Hz, ArH), 6.98 (2 H, d, *J* = 9 Hz, ArH), 7.43 (5 H, s, ArH), 7.64 (1 H, s, olefinic H); ^{13}C NMR ($CDCl_3$) δ: 24.7 (t), 25.2 (t), 34.1 (t), 52.9 (d), 55.2 (q), 113.9 (d), 125.6 (s), 129.0 (d), 129.1 (d), 130.8 (d), 132.0 (d), 132.3 (s), 136.2 (d), 137.6 (s), 160.6 (s); MS (EI) *m/z* (rel. int. %): 371 (43, M^+), 209 (100); IR ν_{max} (NaCl) cm^{-1}: 3300 (NH), 1310, 1145 (SO_2); HRMS (EI) Calcd for $C_{21}H_{25}NO_3S$: 371.1555. Found: 371.1539.

(*E*)-*N*-Cyclohexyl-1-phenyl-2-(2-thienyl)vinylsulfonamide (7c) Colorless needles (from CH_2Cl_2-hexane), mp 133-135°C; ^1H NMR ($CDCl_3$) δ: 1.09-1.33 (5 H, m), 1.54-1.57 (1 H, m), 1.66-1.71 (2 H, m), 1.92-1.95 (2 H, m), 3.11-3.18 (1 H, m, 1'-H), 4.12 (1 H, d, *J* = 6.4 Hz, NH), 6.94 (1 H, dd, *J* 3 and 5 Hz, ArH), 7.14 (1 H, d, *J* = 3 Hz, ArH), 7.22 (1 H, d, *J* = 5 Hz, ArH), 7.41-7.44 (2 H, m, ArH), 7.45-7.53 (3 H, m, ArH), 7.86 (1 H, s, olefinic H); ^{13}C NMR ($CDCl_3$) δ: 24.7 (t), 25.2 (t), 34.1 (t), 52.9 (d), 126.7 (d), 129.2 (d), 129.8 (d), 130.1 (d), 130.3 (s), 131.2 (d), 133.3 (d). 136.7 (s), 137.0 (s), two aromatic methine carbons are overlapped; MS (EI) *m/z* (rel. int. %): 347 (39, M^+), 184 (100); IR ν_{max} (KBr) cm^{-1}: 3290 (NH), 1320, 1150 (SO_2); *Anal.* Calcd for $C_{18}H_{21}NO_2S_2$: C, 62.22; H, 6.09; N, 4.03. Found: C, 62.21; H, 6.02; N, 4.09.

(*E*)-*N*-Cyclohexyl-1-ethyl-2-phenylvinylsulfonamide (7d) Colorless prisms (EtOAc-hexane), mp 114-116°C; ^1H NMR ($CDCl_3$) δ: 1.14-1.39 (3 H, m), 1.31 (3 H, t, *J* = 7 Hz, CH_2CH_3), 1.56-1.77 (5 H, m), 1.93-1.97 (2 H, m), 2.65 (2 H, q, *J* = 7 Hz, CH_2CH_3), 3.13-3.26 (1 H, m, NCH), 4.15 (1 H, d, *J* = 7.8 Hz, NH), 7.29-7.48 (5 H, m, ArH), 7.55 (1 H, 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 (EI) *m/z* (rel. int. %): 293 (21, M^+), 91 (100); IR ν_{max} (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*-Cyclohexyl-2-phenyl-1-(trimethylsilyl)vinylsulfonamide (12b) Colorless prisms (CH_2Cl_2-hexane), mp 92-93°C; ^1H NMR ($CDCl_3$) δ: 0.14 (9 H, s, $SiMe_3$), 1.16-1.40 (5 H , m), 1.58-1.61 (1

H, m), 1.71-1.75 (2 H, m), 1.98-2.01 (2 H, m), 3.22-3.27 (1 H, m, NCH), 4.06 (1 H, d, J = 7.8 Hz, NH), 7.22-7.26 (2 H, m, ArH), 7.36-7.38 (3 H, m, ArH), 8.28 (1 H, 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 (EI) *m/z* (rel. int. %): 337 (5, M^+), 73 (100); IR ν_{max} (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*)-*N*-Cyclohexyl-1-methyl-2-phenylvinylsulfonamide (12c) Colorless prisms (CH_2Cl_2-hexane), mp 124-125°C; ^{1}H NMR ($CDCl_3$) δ: 1.15-1.37 (5 H, m), 1.55-1.71 (3 H, m), 1.94-1.96 (2 H, m), 2.24 (3 H, s, Me), 3.19-3.20 (1 H, m, NCH), 4.35 (1 H, d, J = 7.8 Hz, NH), 7.26-7.44 (5 H, m, ArH), 7.56 (1 H, 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 (EI) *m/z* (rel. int. %): 279 (27, M^+), 117 (100); IR ν_{max} (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.

2-Cyclohexylamino-1,1-dimethyl-2-phenylethyl methyl sulfone (9) Colorless needles (from $CHCl_3$-hexane), mp 130-133°C; ^{1}H NMR ($CDCl_3$) δ: 1.05 and 1.41 (each 3 H, s, Me x 2), 1.02-1.10 (5 H, m), 1.47-1.66 (5 H, m), 1.99-2.02 (1 H, m), 2.15-2.21 (1 H, m, 1'-H), 3.15 (3 H, s, SO_2Me), 4.33 (1 H, s, CH), 7.24-7.37 (5 H, m, ArH); ^{13}C NMR ($CDCl_3$) δ: 16.0 (q), 20.2 (q), 24.6 (t), 25.0 (t), 26.0 (t), 32.3 (t), 35.0 (t), 39.5 (q), 54.2 (d), 62.1 (d), 66.6 (s), 127.7 (d), 128.3 (d), 139.9 (s), two aromatic methine carbons are overlapped; MS (EI) *m/z* (rel. int. %): 309 (1, M^+), 188 (100); IR ν_{max} (KBr) cm^{-1}: 3330 (NH), 1280, 1100 (SO_2); *Anal.* Calcd for $C_{17}H_{27}NO_2S$: C, 65.98; H, 8.79; N, 4.53. Found: C, 65.83; H, 8.95; N, 4.51.

Isopropyl isopropylsulfonylmethyl sulfone (10) Colorless prisms (from EtOAc-hexane), mp 128-130°C; ^{1}H NMR ($CDCl_3$) δ: 1.44 (12 H, d, J = 6.8 Hz, Me x 4), 3.85 (2 H, septet, J = 6.8 Hz, CH x 2), 4.46 (2 H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ: 15.1 (q), 54.1 (d), 63.1 (t); MS (EI) *m/z* (rel. int. %): 228 (1, M^+), 80 (100); IR ν_{max} (KBr) cm^{-1}: 1320, 1120 (SO_2); *Anal.* Calcd for $C_7H_{16}O_4S_2$: C, 66.82; H, 7.06. Found: C, 36.86; H, 7.06.

2-Hydroxy-1,2-dimethylpropyl methyl sulfone (16) Light yellow oil ; ^{1}H NMR ($CDCl_3$) δ: 1.35 (3 H, s, Me), 1.44 (3 H, d, J = 7.3 Hz, CHC*H*$_3$), 1.46 (3 H, s, Me), 2.97 (3 H, s, SO_2Me), 3.16 (1 H, q, J = 7.3 Hz, C*H*CH$_3$), 3.65 (1 H, br s, OH); ^{13}C NMR ($CDCl_3$) δ: 12.3 (q), 25.5 (q), 30.0 (q), 42.2 (q), 68.4 (d), 72.8 (s); MS (FAB) *m/z* (rel. int. %): 167 (14, M^+ + 1), 154 (100); IR ν_{max} (NaCl) cm^{-1}: 3500 (OH), 1290, 1120 (SO_2); HRMS (FAB) Calcd for $C_6H_{14}O_3S$ + H: 167.0738. Found: 167.0694.

X-Ray Study of (*E*)-*N*-Cyclohexyl-1-phenyl-2-(2-thienyl)vinylsulfonamide 7c

Colorless needles were mounted on a glass fiber and transferred to the diffractometer.

Crystal Data. $C_{18}H_{21}NO_2S_2$, M = 347.49, orthorhombic, a = 19.592(4), b = 18.732(3), c = 9.780(3) Å, V = 3589(2) Å^3 (from setting angles of 24 centred reflections with 30.62 < 2θ < 36.72°, λ = 0.71069 Å, T = 296 K), space group Pbca (# 61), Z = 8, D_c = 1.286 g cm^{-3}, colorless needles 0.40 x 0.36 x 0.30 mm, μ(Mo-Kα) = 2.92 cm^{-1}.

Data Collection and Processing. Rigaku AFC-5R four-circle diffractometer with 12kW rotating anode generator, $\varpi/2\theta$ scans with ϖ scan width $(1.26 + 0.30 \tan \theta)^{\circ}$, graphite-monochromated Mo-Kα X-radiation; 4632 reflections measured to $2\theta_{max} = 55^{\circ}$, giving 1992 which were retained in all calculations. No crystal decay was observed and no corrections were applied for absorption.

Structure Solution and Refinement. Automatic direct method[21] (all non-H atoms). Full-matrix least-squares refinement[22] with all non-H atoms anisotropic. The weighting scheme $w = 4Fo^2/\sigma^2(Fo^2)$ gave satisfactory agreement analyses. Final $R = 0.047$, $R_w = 0.051$, $S = 2.36$ for 198 refined parameters. The final ΔF synthesis showed no peaks above ± 0.65 e/Å^{-3}.

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