A Direct Route to *C*-Vinylaziridines: Reaction of *N*-Sufonylimines with Allylic Ylides under Phase-Transfer Conditions or with Preformed Ylides at Low Temperature

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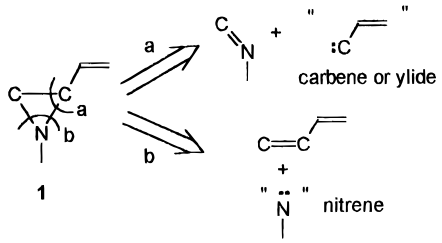
Received December 20, 1995⊗

Allylic sulfonium salts **3**, **5**, **7**, **11**, **12**, **13**, and arsonium salt **14** react with aromatic, heteroaromatic, and α,β-unsaturated *N*-sulfonylimines under solid−liquid phase-transfer conditions in the presence of KOH at room temperature to produce, respectively, vinyl-, (β-phenylvinyl)-, and [β-(trimethylsilyl)-vinyl]aziridines in excellent yields within several minutes. In some cases, pyrroline compound **9** is obtained as a minor product. This aziridination reaction has also been carried out with preformed ylides, generated from sulfonium salts **3**, **7**, arsonium salt **14**, and telluronium salts **15**, **16** with a base in THF at −78 °C. In most examples, quantitative yields were achieved. However, the *trans*/*cis* selectivity of the reaction was not high in either case. A semistable allylic sulfonium ylide, i.e., dimethylsulfonium 3-(trimethylsilyl)allylide, was found to not undergo an expected [2,3]-σ-rearrangement and so can also be used in this reaction.

Introduction

Because of their useful chemical reactivity, aziridines have seen extensive applications in organic synthesis.[1,2] Among the variously functionalized aziridines, vinylaziridine **1** has proven to be the most interesting, and many useful intermediates have derived from it through various transformations[3] and rearrangements.[4] However, methods for the preparation of vinylaziridines are few. A multistep sequence with low overall yields and troublesome operations has often been used.[3a,4a,d] Therefore, the development of practical and facile methods for preparing vinylaziridines is warranted. A retrosynthetic analysis of vinylaziridine reveals that paths a and b are two discrete disconnections of the nitrogen-containing three-membered ring (Scheme 1). For path b, desired chemoselectivity might be diminished when unsymmetric dienes are used.[5] Path a involves the reaction of an imine with a vinylcarbene or an allylic ylide. To our knowledge, no method using vinylcarbenes has been reported. For the allylic ylide route, two problems must first be solved: the activation of the imine[6] and the prevention of [2,3]-σ-rearrangement[7] of the allylide if sulfonium ylide is used. In our preliminary paper,[8] we reported an efficient method for preparing *N*-sulfonylvinylaziridines *via* an ylide route by very simple operations under extremely mild conditions. We disclose herein our detailed investigation of this reaction.

Scheme 1



Results and Discussion

Preparation of *N*-Sulfonylvinyl-, (β-Phenylvinyl)-, and [β-(Trimethylsilyl)vinyl]aziridines under Phase-Transfer Conditions. In contrast to the extensive research reported on ylide olefination, cyclopropanation, and epoxidation reactions,[9] aziridination *via* an ylide route has attracted little attention and only a few examples (limited to a methylene group transferring to C=N bond) have appeared in the literature.[10] This is due to the low reactivity of *N*-alkyl- oraryl-substituted imines

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⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1996.

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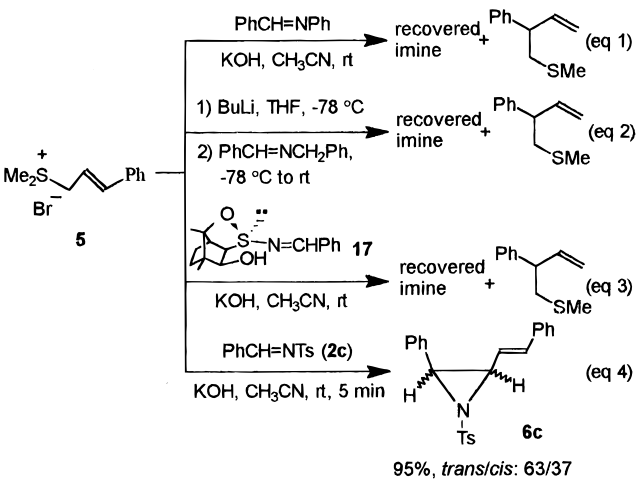
S0022-3263(95)02245-6 CCC: $12.00

Scheme 2



toward the attack of nucleophiles relative to that of carbonyl compounds and Michael acceptors, an activator being required in several instances.[11] Our success with asymmetric epoxidations by way of optically active sulfonium ylides under phase-transfer conditions[12] encouraged us to apply our ylides to the aziridination of imines, considering that aziridines are sometimes even more useful intermediates in the synthesis of nitrogen-containing biologically important substances.[1a,4b,c] In Scheme 2, the reaction of dimethylsulfonium cinnamylide, generated from salt **5**, with PhCH=NPh gave no sign of aziridine either under phase-transfer conditions (eq 1) or using a preformed ylide (eq 2). From both experiments, the recovered imine and the rearranged allylide were obtained. The same is true even for the more reactive sulfinimines (eq 3). It is the previously-mentioned two obstacles that make these ylide aziridination reactions unsuccessful. The former obstacle, i.e., the low reactivity of common imines, may be overcome by using activated imines. The atomic net charges of PhCHO, PhCH=NPh, and PhCH=NTs according to semiempirical AM1 calculations (HyperChem Release 3 from Hypercuban, Inc., and Autodesk, Inc., 1993) indicate that the qualitative order of electrophilicity is PhCH=NTs > PhCHO ≫ PhCH=NPh.[13] In addition, we observed that sulfonium salt **5** reacts with PhCHO in the presence of solid KOH in CH_3CN at room temperature to furnish the corresponding vinyloxirane in 74% yield within 30 min.[14] So, the reactive *N*-tosylimine **2c** might be a suitable candidate for our designed ylide aziridination reaction from the perspective of reactivity. The second obstacle, i.e., the [2,3]-σ-rearrangement of allylic sulfonium ylides, might be overcome by carrying out our reaction under solid−liquid phase-transfer conditions, considering that in our previous attempt to prepare vinyloxirane with sulfonium salt **5** the reaction of the dimethylsulfonium cinnamylide, generated *in situ* by the deprotonation of sulfonium salt **5** with KOH, with PhCHO to form an epoxide was much faster than the [2,3]-σ-rearrangement of the same ylide. We were lucky to find that the reaction of the activated imine, *N*-tosylimine **2c**, with dimethylcinnamylsulfonium bromide (**5**) is tremendously different from that of the unactivated imines, in the presence of KOH at room temperature. The reaction afforded vinylaziridine **6c** much more readily than we expected (eq 4 in Scheme 2).

In order to optimize the conditions for the reaction shown in eq 4 in Scheme 2, the effects of solvent and base on this reaction were investigated (Table 1).

Acetonitrile, dichloromethane, and tetrahydrofuran are suitable solvents for this reaction, acetonitrile being the best. Among various bases, solid KOH gave the highest yield. Under such conditions, the reaction proceeded so fast that no aldehyde from the hydrolysis of the imine was detected. Interestingly, even an organic base NEt_3 could be used in this reaction (entry 9 in Table 1).

Results from the reaction of *N*-sulfonylimines with dimethylallylsulfonium bromide (**3a**), diphenylallylsulfonium perchlorate (**3b**), dimethylcinnamylsulfonium bromide (**5**), [3-(trimethylsilyl)allyl]dimethylsulfonium bromide (**7a**), and [3-(trimethylsilyl)allyl]diphenylsulfonium perchlorate (**7b**) under the optimized condition are summarized in Table 2.

A variety of allylic ylides, i.e., from the simplest dimethylsulfonium allylide to cinnamylide and silylated dimethylsulfonium allylide, and various *N*-sulfonylimines containing aromatic, heteroaromatic, and α,β-unsaturated moieties perform in this aziridination reaction. But, in the case of the α,β-unsaturated *N*-sulfonylimine (entry 19 in Table 2), we obtained a mixture of *N*-(benzenesulfonyl)-*trans*-2,3-bis(β-phenylvinyl)aziridine (*trans*-**6g**) and *N*-(benzenesulfonyl)-*cis*-4,5-diphenyl-4,5-dihydroazepine (**18**), which was derived from a rapid, room temperature Cope rearrangement of the *cis* isomer (*cis*-**6g**)[15] (Scheme 3).

The reaction was complete, usually within several minutes in almost quantitative yields in most examples. However, the *trans*/*cis* ratio of the product was rather low and needed to be improved. Attempts to improve the *trans*/*cis* selectivity of this reaction by introducing an *ortho*-substituent, such as a methoxy (entries 2, 11, 14, 21, and 25 in Table 2) or two chlorine atoms (entry 3 in Table 2) on the phenyl ring proved to be inefficient. The steric hindrance only diminished the yield and prolonged the reaction time (entry 3 in Table 2). A bulky α-naphthyl substituent on the imino carbon of *N*-tosylimine also failed to improve the *trans*/*cis* ratio of the product (entries 9, 12, 23, and 26 in Table 2). A possible mechanism for this reaction is shown in Scheme 4.

One proton α to the sulfur atom of sulfonium salt **I** is first extracted by the base to form an ylide **II**. Imine is then attacked by the ylidic carbon to produce a zwitterionic intermediate **III**. Sulfide is subsequently lost, furnishing vinylaziridine **IV**.

Several allylic sulfonium salts were employed to investigate the effect of ligands connected to the sulfur

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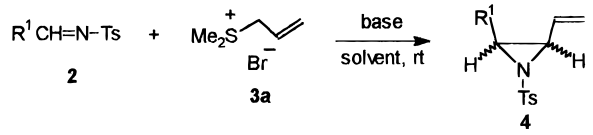
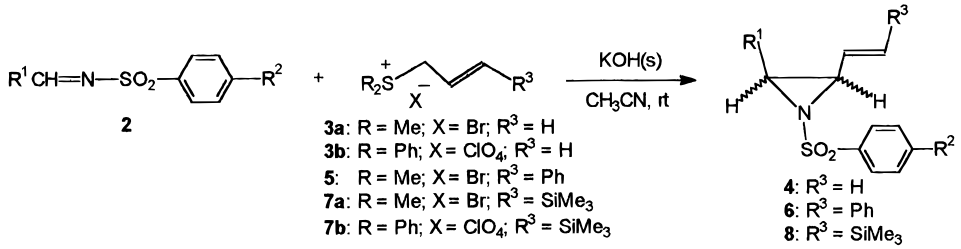
Table 1. Effects of Solvent and Base on the Ylide Aziridination of *N*-Sulfonylimines 2 with Dimethylallylsulfonium Bromide (3a) under Phase-Transfer Conditions[a]



entry	R^1	base/solvent	reaction time (min)	yield,[b] %	*trans*/*cis*[c]	recovered aldehyde,[d] %
1	phenyl	KOH/CH_3CN	5	93 (**4h**)	58/42	0
2	phenyl	KOH/CH_2Cl_2	6	83 (**4h**)	52/48	5
3	phenyl	KOH/THF	5	81 (**4h**)	66/34	9
4	*p*-chlorophenyl	KOH/CH_3CN	5	82 (**4g**)	47/53	0
5	*p*-chlorophenyl	$NaOH/CH_3CN$	15	63 (**4g**)	58/42	18
6	*p*-chlorophenyl	50% NaOH(aq)/CH_3CN	20	53 (**4g**)[e]	62/38	23
7	*p*-chlorophenyl	K_2CO_3/CH_3CN	55	71 (**4g**)	60/40	13
8	*p*-chlorophenyl	$KF.Al_2O_3/CH_3CN$	60	53 (**4g**)	63/37	22
9	*p*-chlorophenyl	NEt_3/CH_3CN	40	32 (**4g**)	61/39	37
10	*p*-chlorophenyl	$Ba(OH)_2.8H_2O/CH_3CN$	80	26 (**4g**)	59/41	56
11	*p*-chlorophenyl	$LiOH.H_2O/CH_3CN$	150	17 (**4g**)	56/44	62
12	*p*-chlorophenyl	$KF.2H_2O/CH_3CN$	300	14 (**4g**)	52/48	39

[a] All reactions were carried out under solid−liquid phase-transfer conditions at room temperature in a ratio of imine:sulfonium salt: base = 1:1.2:1.2 on a 0.5-mmol scale in a solvent. [b] Isolated yields based on imine. [c] Determined by 300 MHz ^{1}H-NMR analysis. [d] Produced by the hydrolysis of imine. [e] 18% of 2-(*p*-chlorophenyl)-3-vinyloxirane (*trans*/*cis*: 58/42) was isolated.

Table 2. Preparation of Vinyl-, (*β*-Phenylvinyl)-, and [*β*-(Trimethylsilyl)vinyl]aziridines 4, 6, or 8 by the Reaction of Sulfonium Salts 3, 5, or 7 and *N*-Sulfonylimines 2 under Phase-Transfer Conditions[a]

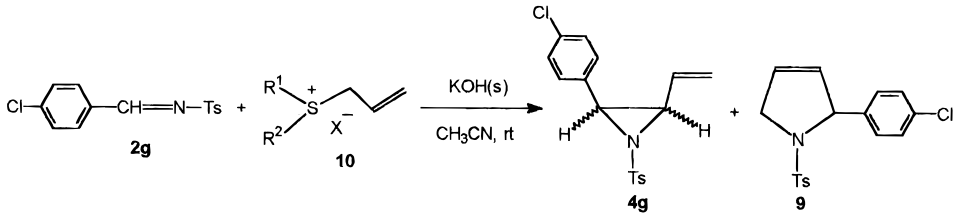


entry	R^1	R^2	R^3	R	X	reaction time (min)	yield,[b] %	*cis*/*trans*[c]
1	*p*-nitrophenyl	Me	H	Me	Br	5	54 (**4a**)	53/47
2	*o*-methoxyphenyl	Me	H	Me	Br	15	92 (**4b**)	61/39
3	2,6-dichlorophenyl	Me	H	Me	Br	80	36 (**4c**)[d]	56/44
4	3-pyridinyl	Me	H	Me	Br	5	82 (**4d**)[e]	65/35
5	*p*-methylphenyl	H	H	Me	Br	5	84 (**4e**)	34/66
6	*p*-methoxyphenyl	H	H	Me	Br	15	95 (**4f**)	45/55
7	*p*-chlorophenyl	Me	H	Me	Br	5	82 (**4g**)	53/47
8	phenyl	Me	H	Me	Br	5	93 (**4h**)	58/42
9	α-naphthyl	Me	H	Me	Br	30	75 (**4i**)	55/45
10	*p*-chlorophenyl	Me	H	Ph	ClO_4	5	69 (**4g**)	44/56
11	*o*-methoxyphenyl	Me	H	Ph	ClO_4	10	77 (**4b**)	27/73
12	α-naphthyl	Me	H	Ph	ClO_4	8	75 (**4i**)	46/54
13	*p*-nitrophenyl	Me	Ph	Me	Br	5	75 (**6a**)	51/49
14	*o*-methoxyphenyl	Me	Ph	Me	Br	10	96 (**6b**)	70/30
15	phenyl	Me	Ph	Me	Br	5	95 (**6c**)	63/37
16	*p*-methylphenyl	H	Ph	Me	Br	5	89 (**6d**)	75/25
17	*p*-methoxyphenyl	H	Ph	Me	Br	5	94 (**6e**)	57/43
18	*p*-chlorophenyl	Me	Ph	Me	Br	5	96 (**6f**)	52/48
19	*trans*-PhCH=CH	H	Ph	Me	Br	5	92 (**6g**)	64/36[f]
20	phenyl	Me	$SiMe_3$	Me	Br	4	97 (**8a**)	29/71
21	*o*-methoxyphenyl	Me	$SiMe_3$	Me	Br	18	96 (**8b**)	32/68
22	*p*-chlorophenyl	Me	$SiMe_3$	Me	Br	4	86 (**8c**)	42/58
23	α-naphthyl	Me	$SiMe_3$	Me	Br	20	93 (**8d**)	35/65
24	phenyl	Me	$SiMe_3$	Ph	ClO_4	4	85 (**8a**)	25/75
25	*o*-methoxyphenyl	Me	$SiMe_3$	Ph	ClO_4	12	97 (**8b**)	45/55
26	α-naphthyl	Me	$SiMe_3$	Ph	ClO_4	15	97 (**8d**)	29/71

[a] All reactions were carried out under solid−liquid phase-transfer conditions at room temperature in a ratio of imine:sulfonium salt: KOH(s) = 1:1.2:1.2 on a 0.5-mmol scale in acetonitrile. [b] Isolated yields based on imine. [c] Determined by 300 MHz ^{1}H-NMR analysis. [d] 53% of imine was recovered. The yield could not be improved by lengthening the reaction time. [e] 16% of 2-(3-pyridinyl)-3-vinyloxirane (*trans*/*cis* = 2:1) from the reaction of ylide and aldehyde generated by the hydrolysis of imine was isolated. [f] This ratio refers to that of the rearranged product *N*-(benzenesulfonyl)-*cis*-4,5-diphenyl-4,5-dihydroazepine (**18**) and *N*-(benzenesulfonyl)-*trans*-2,3-bis(*β*-phenylvinyl)-aziridine (*trans*-**6g**).

atom of sulfonium salts in our ylide aziridination (Table 3). It was found that an increase in the bulkiness of the ligands on the sulfur atom did not improve the *trans*/*cis* selectivity of the reaction, but rather led to the formation

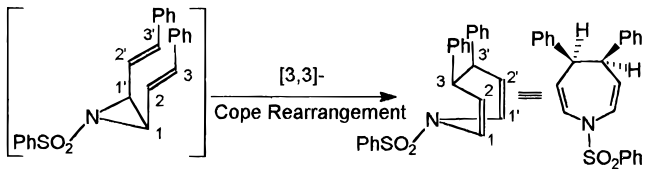
Table 3. Effect of Ligands on the Sulfur Atom in Allylic Sulfonium Salts on the Ylide Aziridination under Phase-Transfer Conditions[a]



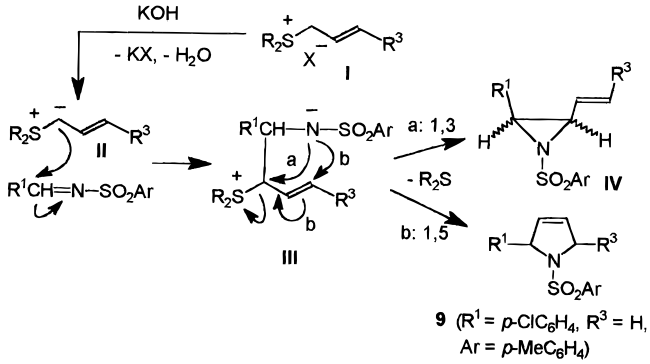
entry	sulfonium salt	reaction time (min)	4g yield,[b] %	4g *trans*/*cis*[c]	9, %
1	Me_2S^+ Br^- **3a**	4	82	53/47	0
2	Et_2S^+ Br^- **11**	2	41	55/45	25
3	Ph_2S^+ ClO_4^- **3b**	5	69	44/56	23
4	Me, Ph—S$^+$ ClO_4^- **12**	20	75	39/61	16
5	Me, S$^+$, OH, Br^- **13**	5	83	50/50	0

[a] All reactions were carried out under solid−liquid phase-transfer conditions at room temperature in a ratio of imine:sulfonium salt: KOH(s) = 1:1.2:1.2 on a 0.5-mmol scale in CH_3CN. [b] Isolated yields based on imine. [c] Determined by 300 MHz ^{1}H-NMR analysis.

Scheme 3



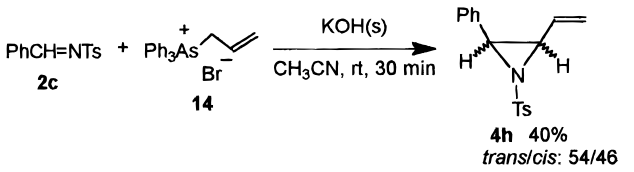
Scheme 4



of a pyrroline product **9** as a minor product (entries 2−4 in Table 3). Product **9** is thought to be formed by an intramolecular 1,5-elimination of the zwitterionic intermediate **III** in Scheme 4.

Several allylides of As, Te, and P have also been studied in our aziridination reaction. Allylic arsonium ylide generated *in situ* from allyltriphenylarsonium bromide (**14**) by KOH reacts with *N*-sulfonylimine **2c** to give vinylaziridine **4h** in moderate yield (Scheme 5). However, allylic telluronium (from **15**) and phosphorus (triphenylphosphonium allylide) ylides did not form an aziridine with *N*-sulfonylimine **2c**, but rather the hydrolyzed product, PhCHO, was recovered almost quantitatively. The obviously high reactivity of allylic sulfonium ylides, compared with the corresponding arsonium, telluronium, and phosphorus ylides, made them the best choice for the aziridination reaction.

Scheme 5



It is noteworthy that *N*-sulfonylimines have been reported to react with an oxosulfonium methylide $Me_2S(O)^+CH_2^-$ to give azetidines instead of aziridines.[16] In all of our reactions, no azetidine was detected. Recently, Matano et al.[17] found that triphenylbismuthonium 2-oxoalkylides reacted with *N*-sulfonylimines to form aziridinyl ketones.

Preparation of Vinylaziridines with Preformed Ylides at Low Temperature. Clearly, the *trans*/*cis* selectivity in forming the above-mentioned vinylaziridines under phase-transfer conditions is low. Efforts to improve the stereoselectivity of this reaction by exposure of *N*-sulfonylimines to preformed sulfonium, arsonium, and telluronium ylides have been made. Results are shown in Table 4.

Allylic sulfonium, arsonium, or telluronium salts in THF were treated with a base at −78 °C for 5−30 min to generate the corresponding ylides. Imines in THF were subsequently added to the ylide solution and allowed to warm to room temperature. Vinylaziridines were obtained after workup. Ylides generated from

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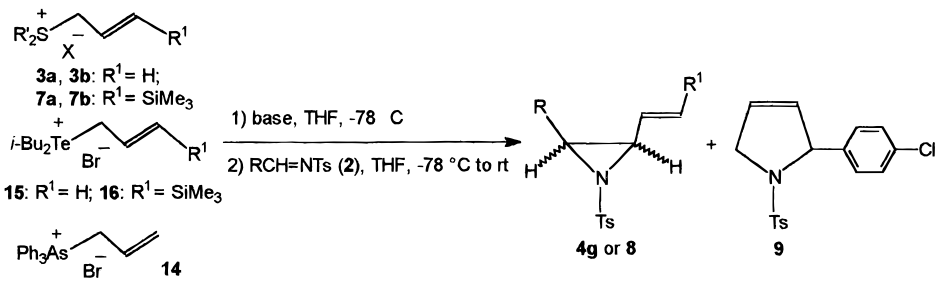
(17) Matano, Y.; Yoshimune, M.; Suzuki, H. *J. Org. Chem.* **1995**, *60*, 4663.

Table 4. Preparation of Vinylaziridine 4g and [*β*-(Trimethylsilyl)vinyl]aziridines 8 by the Reaction of Allylic or Silylated Allylic Sulfonium, Arsonium, and Telluronium Ylides and *N*-Sulfonylimines at −78 °C[a]



					4g or 8		
entry	R	R^1	salt	base	yield,[b] %	*trans*/*cis*[c]	**9**, %
1	*p*-ClC_6H_4	H	**3a**	*n*-BuLi	32 (**4g**)	59/41	0
2	*p*-ClC_6H_4	H	**3a**	$KN(SiMe_3)_2$	35 (**4g**)	61/39	0
3	*p*-ClC_6H_4	H	**14**	$LiN(SiMe_3)_2$	25 (**4g**)	70/30	10
4	*p*-ClC_6H_4	H	**14**	$KN(SiMe_3)_2$	21 (**4g**)	54/46	15
5	*p*-ClC_6H_4	H	**15**	LiBr + $KN(SiMe_3)_2$	57 (**4g**)	55/45	0
6	*p*-ClC_6H_4	H	**15**	$KN(SiMe_3)_2$	79 (**4g**)	45/55	0
7	*p*-ClC_6H_4	H	**3b**	*n*-BuLi	68 (**4g**)	41/59	23
8	*p*-ClC_6H_4	H	**3b**	$LiN(SiMe_3)_2$	83 (**4g**)	41/59	12
9	*p*-ClC_6H_4	H	**3b**	$KN(SiMe_3)_2$	61 (**4g**)	35/65	17
10	*p*-ClC_6H_4	$SiMe_3$	**16**	$KN(SiMe_3)_2$	39 (**8c**)	33/67	
11	*p*-ClC_6H_4	$SiMe_3$	**7b**	*n*-BuLi	97 (**8c**)	37/63	
12	*p*-ClC_6H_4	$SiMe_3$	**7b**	$LiN(SiMe_3)_2$	98 (**8c**)	42/58	
13	*p*-ClC_6H_4	$SiMe_3$	**7b**	$NaN(SiMe_3)_2$	98 (**8c**)	39/61	
14	*p*-ClC_6H_4	$SiMe_3$	**7b**	$KN(SiMe_3)_2$	98 (**8c**)	45/55	
15	*p*-ClC_6H_4	$SiMe_3$	**7a**	*n*-BuLi	95 (**8c**)	61/39	
16	*p*-ClC_6H_4	$SiMe_3$	**7a**	$LiN(SiMe_3)_2$	92 (**8c**)	67/33	
17	*p*-ClC_6H_4	$SiMe_3$	**7a**	$NaN(SiMe_3)_2$	92 (**8c**)	59/41	
18	*p*-ClC_6H_4	$SiMe_3$	**7a**	$KN(SiMe_3)_2$	98 (**8c**)	29/71	
19	*o*-$MeOC_6H_4$	$SiMe_3$	**7a**	$KN(SiMe_3)_2$	98 (**8b**)	22/78	
20	α-naphthyl	$SiMe_3$	**7a**	$KN(SiMe_3)_2$	98 (**8d**)	64/36	
21	α-naphthyl	$SiMe_3$	**7a**	$NaN(SiMe_3)_2$	98 (**8d**)	73/27	

[a] All reactions were carried out at −78 °C in a ratio of imine:salt:base = 1:1.2:1.2 on a 0.5-mmol scale in THF. [b] Isolated yields based on imine. [c] Determined by 300 MHz ^{1}H-NMR analysis.

sulfonium salt **3a**, because of a known [2,3]-*σ*-rearrangement,[7] and arsonium salt **14**, due to the relatively low reactivity, gave low yields (entries 1−4 in Table 4). Ylides from telluronium salt **15** and from sulfonium salt **3b** reacted with *N*-tosylimines to form the desired aziridines in reasonable yields (entries 5−9 in Table 4). However, the *trans*/*cis* ratio of the product remained almost the same as that obtained from phase-transfer reactions, even in the presence of lithium ion (entries 1, 3, 5, 7, 8, 11, 12, 15, and 16 in Table 4), which is known to play an important role in the control of the stereochemistry in ylide chemistry.[18] In some cases, pyrroline product **9** was produced as a minor product (entries 3, 4, and 7−9 in Table 4), the combined total yields still being very high.

Considering that good stereoselectivity has never been achieved in ylide epoxidation[7a,19] and ylide cyclopropanation[7a] with the simplest sulfonium,[7a,19a,b] arsonium,[19c,d] and telluronium[19e,g] allylides, we tried to improve the *trans*/*cis* selectivity by using a bulky trimethylsilyl-substituted allylide. It was not efficient either through a telluronium ylide (entry 10 in Table 4) or through sulfonium ylides, although quantitative yields were achieved in all examples with sulfonium ylides (entries 11−21 in Table 4). It is noteworthy that the ylide generated from sulfonium salt **7a** did not undergo the expected [2,3]-*σ*-rearrangement. This ylide could stand for several hours at −78 °C without significant change. Its extreme stability to rearrangement and its transformable $SiMe_3$ may make the dimethylsulfonium 3-trimethylsilylated allylide a very useful reagent for preparing vinyloxiranes, vinylcyclopropanes, and vinylaziridines.

Conclusions

A method for preparing *N*-sulfonylvinylaziridines *via* an ylide route, which may be regarded as the simplest direct way to this kind of potentially useful compound for organic synthesis, is reported. Allylic sulfonium salts **3**, **5**, and **7** reacted with aromatic, heteroaromatic, and α,*β*-unsaturated *N*-sulfonylimines in CH_3CN with KOH as the base at room temperature to produce, respectively, vinyl-, (*β*-phenylvinyl)-, and [*β*-(trimethylsilyl)vinyl]aziridines in excellent yields. Generally, the reaction was complete within several minutes. This aziridination reaction has also been carried out with preformed ylides,

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generated from sulfonium salts **3** and **7**, arsonium salt **14**, and telluronium salts **15** and **16** with a base in THF at low temperature. In most examples, quantitative yields were achieved. Since the tosyl group can be cleaved by well-known procedures,[20] and the vinylaziridines can be easily transformed to many very useful synthetic intermediates, the value of this direct method is apparent.

Experimental Section

Materials and General Procedure. All reagents and solvents, unless otherwise specified, are commercially available and used without further purification. THF was distilled immediately prior to use from sodium/benzophenone ketyl under nitrogen. All *N*-sulfonylimines **2** were prepared according to literature method[21] in reasonable yields. Sulfonium salts **3a**, **5**, **7a**, **11**, and **13** were prepared by the reaction of corresponding allylic bromides with sulfides in a small amount of acetone at rt in excellent yields. Sulfonium salts **3b**, **7b**, and **12** were obtained by a literature procedure[7a] except that $AgClO_4$ was used instead of $AgBF_4$. Arsonium salt **14** was prepared by the reaction of Ph_3As and allyl bromide.[19c] Telluronium salts **15** and **16** were prepared by the reaction of *i*-Bu_2Te[22] with allyl bromide or 3-(trimethylsilyl)allyl bromide,[23] respectively, without solvent at room temperature in quantitative yields.[24] Sulfinimine **17**[25] was obtained according to a literature procedure.

General Procedure for Aziridination under Solid−Liquid Phase-Transfer Conditions. A 25-mL flask containing a magnetic stirring bar was charged with imine (**2**, 1.0 equiv), sulfonium salt (**3**, **5**, **7**, **11**, **12**, or **13**, 1.2 equiv) or arsonium salt **14** (1.2 equiv) and acetonitrile (4 mL, reagent grade; it need not be dried before use). Powdered potassium hydroxide (1.2 equiv) was subsequently added under stirring. After the reaction was complete according to TLC, the reaction mixture was filtered on a short neutral Al_2O_3 column to remove inorganic salts. The filtrate was concentrated and chromatographed on a neutral Al_2O_3 column with a mixture of light petroleum (60−90 °C), ethyl acetate, and NEt_3 (8 :1 :1) as the eluent to give pure product.

***N*-Tosyl-2-(*p*-nitrophenyl)-3-vinylaziridine (4a).** *cis*-**4a**: ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3 H), 3.69 (dd, J = 6.6, 7.1 Hz, 1 H), 4.13 (d, J = 7.3 Hz, 1 H), 5.17−5.24 (m, 2 H), 5.39−5.47 (m, 1 H), 7.27−7.43 (m, 4 H), 7.89 (dd, J = 1.7, 8.3 Hz, 2 H), 8.12 (dd, J = 2.7, 4.4 Hz, 2 H); MS m/z 345 (M^+ + 1, 3.3), 344 (M^+, 1.2), 189 (100), 173 (3.7), 149 (39), 115 (9.7), 103 (22), 91 (17), 77 (2.8), 65 (9); HRMS calcd for $C_{17}H_{16}N_2O_4S$ (M^+) 344.0831, found 344.0807. *trans*-**4a**: ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3 H), 3.29 (dd, J = 3.9, 9.6 Hz, 1 H), 4.11 (d, J = 3.9 Hz, 1 H), 5.16−5.63 (m, 2 H), 6.34 (ddd, J = 2.8, 7.0, 10.0 Hz, 1 H), 7.27−7.43 (m, 4 H), 7.83 (dd, J = 1.8, 6.7 Hz, 2 H), 8.15 (dd, J = 2.0, 4.7 Hz, 2 H).

***N*-Tosyl-2-(*o*-methoxyphenyl)-3-vinylaziridine (4b).** *cis*-**4b**: ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 3.65 (dd, J = 4.5, 7.3 Hz, 1 H), 3.77 (s, 3 H), 4.20 (d, J = 7.3 Hz, 1 H), 5.11 (dd, J = 2.0, 10.1 Hz, 1 H), 5.25 (m, 1 H), 5.35−5.42 (m, 1 H), 6.77−6.85 (m, 2 H), 7.13−7.32 (m, 4 H), 7.88 (dd, J = 1.6, 6.7 Hz, 2 H); MS m/z 330 (M^+ + 1, 5.8), 329 (M^+, 0.8), 210 (10.7), 174 (100), 155 (11.4), 137 (33), 107 (27), 91 (34), 77 (9.5), 65 (13), 56 (16); HRMS calcd for $C_{18}H_{19}NO_3S$ (M^+) 329.1086, found 329.1048. *trans*-**4b**: ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3 H), 3.25 (dd, J = 4.2, 9.5 Hz, 1 H), 3.77 (s, 3 H), 4.34 (d, J = 4.3 Hz, 1 H), 5.45 (d, J = 10.5 Hz, 1 H), 5.55 (d, J = 16.8 Hz, 1 H), 6.35 (ddd, J = 7.1, 9.9, 16.9 Hz, 1 H), 6.77−6.85 (m, 2 H), 7.13−7.32 (m, 4 H), 7.85 (d, J = 8.4 Hz, 2 H).

***N*-Tosyl-2-(2,6-dichlorophenyl)-3-vinylaziridine (4c).** *cis*-**4c**: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 3.76 (dd, J = 6.6, 6.7 Hz, 1 H), 4.07 (d, J = 7.0 Hz, 1 H), 5.09 (dd, J = 2.0, 9.9 Hz, 1 H), 5.18−5.29 (m, 1 H), 5.35 (dd, J = 2.1, 16.9 Hz, 1 H), 7.09−7.14 (m, 1 H), 7.19−7.23 (m, 2 H), 7.27−7.36 (m, 2 H), 7.90 (dd, J = 1.8, 8.3 Hz, 2 H); MS m/z 370 (1.89), 369 (0.87), 368 (M^+, 2.82), 214 (72), 213 (16), 212 (100), 174 (53), 173 (10), 172 (78), 136 (12), 123 (10), 91 (29), 65 (16); HRMS calcd for $C_{17}H_{15}Cl_2NO_2S$ (M^+) 367.0201, found 367.0169. *trans*-**4c**: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 3.50 (dd, J = 4.5, 9.6 Hz, 1 H), 4.12 (d, J = 4.5 Hz, 1 H), 5.52 (d, J = 10.3 Hz, 1 H), 5.65 (d, J = 16.8 Hz, 1 H), 6.30 (ddd, J = 9.9, 9.9, 16.9 Hz, 1 H), 7.09−7.14 (m, 1 H), 7.19−7.23 (m, 2 H), 7.27−7.36 (m, 2 H), 7.88 (dd, J = 1.9, 8.3 Hz, 2 H).

***N*-Tosyl-2-(3-pyridinyl)-3-vinylaziridine (4d).** *cis*-**4d**: ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3 H), 3.67 (dd, J = 6.9, 7.0 Hz, 1 H), 4.05 (d, J = 6.9 Hz, 1 H), 5.19−5.31 (m, 2 H), 5.41−5.47 (m, 1 H), 7.19−7.90 (m, 6 H), 8.46−8.51 (m, 2 H); MS m/z 301 (M^+ + 1, 3.9), 300 (M^+, 2.6), 261 (9), 171 (23), 155 (37), 139 (8.7), 107 (25), 91 (100), 77 (8.5), 65 (27); HRMS calcd for $C_{16}H_{16}N_2O_2S$ (M^+) 300.0932, found 300.0894. *trans*-**4d**: ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 3.33 (dd, J = 4.0, 9.7 Hz, 1 H), 4.06 (d, J = 3.6 Hz, 1 H), 5.51 (d, J = 10.3 Hz, 1 H), 5.60 (d, J = 16.9 Hz, 1 H), 6.35 (ddd, J = 7.1, 9.8, 16.9 Hz, 1 H), 7.19−7.90 (m, 6 H), 8.46−8.51 (m, 2 H).

***N*-(Benzenesulfonyl)-2-(*p*-methylphenyl)-3-vinylaziridine (4e).** *cis*-**4e**: ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 3.62 (dd, J = 7.2, 7.2 Hz, 1 H), 4.07 (d, J = 7.2 Hz, 1 H), 5.19−5.31 (m, 2 H), 5.39−5.46 (m, 1 H), 7.06−7.08 (m, 4 H), 7.42−7.61 (m, 3 H), 8.0 (dd, J = 1.4, 7.3 Hz, 2 H); MS m/z 300 (M^+ + 1, 4), 196 (2.5), 158 (100), 143 (5), 129 (4), 118 (58), 103 (3.9), 91 (10), 77 (19), 65 (4), 51 (7); HRMS calcd for $C_{17}H_{17}NO_2S$ (M^+) 299.0980, found 299.1024. *trans*-**4e**: ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 3.32 (dd, J = 4.1, 9.6 Hz, 1 H), 4.03 (d, J = 4.2 Hz, 1 H), 5.46 (d, J = 10.0 Hz, 1 H), 5.55 (d, J = 16.9 Hz, 1 H), 6.31 (ddd, J = 7.1, 9.9, 17.0 Hz, 1 H), 7.06−7.08 (m, 4 H), 7.42−7.61 (m, 3 H), 7.95 (dd, J = 1.9, 5.6 Hz, 2 H).

***N*-(Benzenesulfonyl)-2-(*p*-methoxyphenyl)-3-vinylaziridine (4f).** *cis*-**4f**: ^{1}H NMR ($CDCl_3$) δ 3.60 (dd, J = 7.2, 7.2 Hz, 1 H), 3.73 (s, 3 H), 4.05 (d, J = 7.2 Hz, 1 H), 5.16−5.58 (m, 3 H), 6.75−6.81 (m, 2 H), 7.07−7.14 (m, 2 H), 7.43−7.61 (m, 3 H), 8.0 (d, J = 7.9 Hz, 2 H); MS m/z 316 (M^+ + 1, 50), 227 (6.7), 196 (10), 174 (100), 160 (34), 147 (9), 137 (34), 122 (6.5), 109 (7.8), 91 (6.5), 77 (38), 56 (11); HRMS calcd for $C_{17}H_{17}NO_3S$ (M^+) 315.0929, found 315.0939. *trans*-**4f**: ^{1}H NMR ($CDCl_3$) δ 3.32 (dd, J = 4.2, 9.6 Hz, 1 H), 3.73 (s, 3 H), 4.02 (d, J = 4.2 Hz, 1 H), 5.16−5.58 (m, 2 H), 6.3 (ddd, J = 2.7, 7.2, 10.0 Hz, 1 H), 6.75−6.81 (m, 2 H), 7.07−7.14 (m, 2 H), 7.43−7.61 (m, 3 H), 7.93 (dd, J = 1.4, 7.9 Hz, 2 H).

***N*-Tosyl-2-(*p*-chlorophenyl)-3-vinylaziridine (4g).** *cis*-**4g**: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 3.61 (dd, J = 7.1, 7.1 Hz, 1 H), 4.03 (d, J = 7.1 Hz, 1 H), 5.18−5.30 (m, 2 H), 5.40−5.16 (m, 1 H), 7.09−7.17 (m, 2 H), 7.21−7.35 (m, 4 H), 7.88 (d, J = 8.3 Hz, 2 H); MS m/z 336 (0.76), 335 (0.50), 334 (1.87), 333 (0.31), 294 (1.4), 210 (6.2), 178 (100), 155 (10), 138 (58), 125 (2.7), 115 (8.5), 91 (20), 65 (8.4), 51 (2). Anal. Calcd for $C_{17}H_{16}ClNO_2S$: C, 61.20; H, 4.83; N, 4.20. Found: C, 61.13; H, 4.65; N, 4.44. *trans*-**4g**: ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3 H), 3.26 (dd, J = 4.1, 9.7 Hz, 1 H), 4.01 (d, J = 4.3 Hz, 1 H), 5.49 (d, J = 10.2 Hz, 1 H), 5.57 (d, J = 16.9 Hz, 1 H), 6.32 (ddd, J = 9.9, 10.0, 17.0 Hz, 1 H), 7.09−7.17 (m, 2 H), 7.21−7.35 (m, 4 H), 7.83 (d, J = 8.3 Hz, 2 H).

***N*-Tosyl-2-phenyl-3-vinylaziridine (4h).** *cis*-**4h**: ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 3.61 (dd, J = 7.3, 8.4 Hz, 1 H), 4.07 (d, J = 8.4 Hz, 1 H), 5.14−5.28 (m, 2 H), 5.39 (m, 1 H), 7.15−7.32 (m, 7 H), 7.88 (d, J = 8.2 Hz, 2 H); MS m/z 300 (M^+ + 1, 1.2), 299 (M^+, 0.36), 260 (0.56), 155 (2.8), 144 (100), 128 (1.5), 115 (9.9), 104 (62.6), 91 (18), 77 (7.4), 65 (8.8), 51 (3). Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68. Found: C, 67.74; H, 5.75; N, 4.94. *trans*-**4h**: ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3 H), 3.30 (dd, J = 4.1, 9.6 Hz, 1 H), 4.04 (d, J = 4.2 Hz, 1 H), 5.45

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(d, J = 16.9 Hz, 1 H), 5.54 (d, J = 16.9 Hz, 1 H), 6.33 (ddd, J = 7.1, 9.9, 17.0 Hz, 1 H), 7.15−7.32 (m, 7 H), 7.83 (d, J = 8.2 Hz, 2 H).

***N*-Tosyl-2-(α-naphthyl)-3-vinylaziridine (4i).** *cis*-**4i**: ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3 H), 3.87 (dd, J = 7.3, 7.5 Hz, 1 H), 4.51 (d, J = 7.2 Hz, 1 H), 4.98−5.16 (m, 2 H), 5.41 (dd, J = 1.4, 16.9 Hz, 1 H), 7.24−7.51 (m, 6 H), 7.80−7.83 (m, 2 H), 7.92−7.98 (m, 3 H); MS m/z 349 (M^+, 0.56), 210 (1.37), 194 (100), 179 (2.5), 165 (11), 154 (47), 139 (6.8), 127 (10), 115 (3.6), 102 (0.6), 91 (10), 77 (1.5), 65 (5). Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found: C, 71.96; H, 5.16; N, 3.72. *trans*-**4i**: ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3 H), 3.30 (dd, J = 4.3, 9.8 Hz, 1 H), 4.58 (d, J = 4.3 Hz, 1 H), 5.55 (d, J = 10.5 Hz, 1 H), 6.54 (ddd, J = 10.0, 10.0, 17.0 Hz, 1 H), 7.1 (d, J = 7.1 Hz, 1 H), 7.24−7.51 (m, 5 H), 7.70−7.74 (m, 2 H), 7.92−7.98 (m, 3 H).

***N*-Tosyl-2-(*p*-nitrophenyl)-3-(*trans*-β-phenylvinyl)aziridine (6a).** *cis*-**6a**: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 3.86 (dd, J = 7.5, 7.8 Hz, 1 H), 4.19 (d, J = 7.3 Hz, 1 H), 5.50 (dd, J = 8.1, 15.9 Hz, 1 H), 6.75 (d, J = 15.9 Hz, 1 H), 7.13−7.47 (m, 9 H), 7.91 (d, J = 8.3 Hz, 2 H), 8.16 (d, J = 6.6 Hz, 2 H); MS m/z 420 (M^+, 5.4), 278 (5), 265 (100), 244 (7), 219 (30), 191 (7), 155 (12), 139 (19), 115 (50), 91 (51), 77 (11), 65 (19); HRMS calcd for $C_{23}H_{20}N_2O_4S$ (M^+) 420.1144, found 420.1125. *trans*-**6a**: ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 3.43 (dd, J = 3.9, 9.4 Hz, 1 H), 4.22 (d, J = 4.0 Hz, 1 H), 6.71 (dd, J = 9.5, 15.8 Hz, 1 H), 6.82 (d, J = 15.8 Hz, 1 H), 7.13−7.47 (m, 9 H), 7.84 (d, J = 8.3 Hz, 2 H), 8.16 (d, J = 6.8 Hz, 2 H).

***N*-Tosyl-2-(*o*-methoxyphenyl)-3-(*trans*-β-phenylvinyl)aziridine (6b).** *cis*-**6b**: ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3 H), 3.77 (s, 3 H), 3.84 (dd, J = 7.8, 7.7 Hz, 1 H), 4.28 (d, J = 7.3 Hz, 1 H), 5.56 (dd, J = 8.2, 15.9 Hz, 1 H), 6.79 (d, J = 16.3 Hz, 1 H), 7.14−7.46 (m, 11 H), 7.91 (dd, J = 1.8, 6.9 Hz, 2 H); MS m/z 405 (M^+, 0.71), 250 (100), 235 (5.7), 191 (1.1), 178 (1.6), 134 (4.5), 115 (38), 91 (22), 77 (4), 65 (6), 51 (2.4). Anal. Calcd for $C_{24}H_{23}NO_3S$: C, 71.08; H, 5.72; N, 3.45. Found: C, 70.82; H, 5.48; N, 3.11. *trans*-**6b**: ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3 H), 3.39 (dd, J = 4.3, 8.8 Hz, 1 H), 3.81 (s, 3 H), 4.45 (d, J = 4.2 Hz, 1 H), 6.74 (dd, J = 9.3, 15.6 Hz, 1 H), 6.85 (d, J = 15.5 Hz, 1 H), 7.14−7.46 (m, 11 H), 7.86 (d, J = 8.3 Hz, 2 H).

***N*-Tosyl-2-phenyl-3-(*trans*-β-phenylvinyl)aziridine (6c).** *cis*-**6c**: ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3 H), 3.80 (dd, J = 7.9, 7.8 Hz, 1 H), 4.14 (d, J = 7.1 Hz, 1 H), 5.59 (dd, J = 8.5, 16.1 Hz, 1 H), 6.74 (d, J = 15.5 Hz, 1 H), 7.15−7.42 (m, 12 H), 7.91 (dd, J = 1.4, 6.7 Hz, 2 H); MS m/z 375 (M^+, 0.82), 220 (100), 204 (2.6), 191 (2.8), 178 (1.8), 165 (1.7), 139 (2.8), 115 (67), 104 (9.3), 91 (31), 77 (4.8), 65 (7.8), 51 (2.3). Anal. Calcd for $C_{23}H_{21}NO_2S$: C, 73.57; H, 5.64; N, 3.73. Found: C, 73.37; H, 5.44; N, 3.32; HRMS calcd for $C_{16}H_{14}N$ (M^+ − Ts) 220.1126, found 220.1134. *trans*-**6c**: ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3 H), 3.44 (dd, J = 4.1, 9.4 Hz, 1 H), 4.16 (d, J = 4.1 Hz, 1 H), 6.66 (dd, J = 9.3, 15.8 Hz, 1 H), 6.80 (d, J = 15.4 Hz, 1 H), 7.15−7.42 (m, 12 H), 7.84 (d, J = 8.4 Hz, 2 H).

***N*-(Benzenesulfonyl)-2-(*p*-methylphenyl)-3-(*trans*-β-phenylvinyl)aziridine (6d).** *cis*-**6d**: ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3 H), 3.81 (dd, J = 7.9, 7.9 Hz, 1 H), 4.13 (d, J = 7.2 Hz, 1 H), 5.62 (dd, J = 8.4, 16.0 Hz, 1 H), 6.73 (d, J = 15.7 Hz, 1H), 6.99−7.60 (m, 12 H), 8.03 (d, J = 8.0 Hz, 2 H); MS m/z 376 (M^+ + 1, 12), 375 (M^+, 30), 260 (39), 234 (100), 219 (23), 202 (6), 156 (4), 141 (13), 115 (15), 105 (7.6), 91 (9.6), 77 (34), 65 (3.5); HRMS calcd for $C_{23}H_{21}NO_2S$ (M^+) 375.1293, found 375.1314. *trans*-**6d**: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 3.48 (dd, J = 4.2, 9.0 Hz, 1 H), 4.15 (d, J = 4.3 Hz, 1 H), 6.69 (dd, J = 9.0, 15.8 Hz, 1 H), 6.78 (d, J = 15.8 Hz, 1 H), 6.99−7.60 (m, 12 H), 7.94 (d, J = 8.2 Hz, 2 H).

***N*-(Benzenesulfonyl)-2-(*p*-methoxyphenyl)-3-(*trans*-β-phenylvinyl)aziridine (6e).** *cis*-**6e**: ^{1}H NMR ($CDCl_3$) δ 3.76 (s, 3 H), 3.79 (dd, J = 8.4, 8.4 Hz, 1 H), 4.13 (d, J = 8.4 Hz, 1 H), 5.62 (dd, J = 8.4, 16.0 Hz, 1 H), 6.79 (d, J = 16.1 Hz, 1H), 7.12−7.56 (m, 12 H), 8.03 (d, J = 7.0 Hz, 2 H); MS m/z 391 (M^+, 11), 317 (6), 276 (21), 250 (100), 223 (25), 191 (9), 178 (23), 165 (11), 145 (13), 135 (46), 115 (34), 105 (19), 91 (23), 77 (62), 65 (8), 51 (18); HRMS calcd for $C_{23}H_{21}NO_3S$ (M^+) 391.1242, found 391.1284. *trans*-**6e**: ^{1}H NMR ($CDCl_3$) δ 3.47 (dd, J = 4.3, 9.3 Hz, 1 H), 3.76 (s, 3 H), 4.13 (d, J = 4.0 Hz, 1 H), 6.68 (dd, J = 9.6, 16.1 Hz, 1 H), 6.78 (d, J = 16.1 Hz, 1 H), 7.12−7.56 (m, 12 H), 7.95 (d, J = 8.8 Hz, 2 H).

***N*-Tosyl-2-(*p*-chlorophenyl)-3-(*trans*-β-phenylvinyl)aziridine (6f).** *cis*-**6f**: ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3 H), 3.79 (dd, J = 7.7, 7.8 Hz, 1 H), 4.09 (d, J = 7.4 Hz, 1 H), 5.54 (dd, J = 8.4, 16.1 Hz, 1 H), 6.74 (d, J = 16.0 Hz, 1 H), 7.14−7.45 (m, 11 H), 7.83 (d, J = 8.3 Hz, 2 H); MS m/z 409 (M^+, 16), 294 (38), 254 (100), 219 (69), 202 (9), 155 (36), 140 (14), 115 (26), 91 (57), 77 (8), 65 (14); HRMS calcd for $C_{23}H_{20}ClNO_2S$ (M^+) 409.0903, found 409.0926. *trans*-**6f**: ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 3.40 (dd, J = 4.4, 9.6 Hz, 1 H), 4.11 (d, J = 4.2 Hz, 1 H), 5.63 (dd, J = 9.4, 15.8 Hz, 1 H), 6.80 (d, J = 15.9 Hz, 1 H), 7.14−7.45 (m, 11 H), 7.90 (d, J = 8.3 Hz, 2 H).

***N*-(Benzenesulfonyl)-2-(*trans*-β-phenylvinyl)-3-(*trans*-β-phenylvinyl)aziridine (6g).** *trans*-**6g**: ^{1}H NMR ($CDCl_3$) δ 3.63 (dd, J = 3.1, 10.9 Hz, 2 H), 6.24 (dd, J = 10.8, 15.9 Hz, 2 H), 6.79 (d, J = 15.8 Hz, 2 H), 6.55 (d, J = 7.3 Hz, 2 H), 7.01−7.51 (m, 11 H), 7.95 (d, J = 9.0 Hz, 2 H); MS m/z 387 (M^+, 2.1), 272 (10.5), 246 (100), 231 (4), 202 (2.6), 168 (6.6), 130 (12), 115 (45), 103 (4.4), 91 (19), 77 (19), 51 (4.6); HRMS calcd for $C_{24}H_{21}NO_2S$ (M^+) 387.1293, found 387.1276.

***N*-(Benzenesulfonyl)-*cis*-4,5-diphenyl-4,5-dihydroazepine (18)**: ^{1}H NMR ($CDCl_3$) δ 3.77 (d, J = 5.9 Hz, 2 H), 5.23 (dd, J = 6.0, 9.4 Hz, 2 H), 6.84 (d, J = 9.6 Hz, 2 H), 7.01−7.51 (m, 13 H), 7.91 (d, J = 7.6 Hz, 2 H).

***N*-Tosyl-2-phenyl-3-[β-(trimethylsilyl)vinyl]aziridine (8a).** *cis*-**8a**: ^{1}H NMR ($CDCl_3$) δ −0.04 (s, 9 H), 2.43 (s, 3 H), 3.63 (dd, J = 7.6, 7.0 Hz, 1 H), 4.01 (d, J = 7.3 Hz, 1 H), 5.41 (dd, J = 7.3, 18.71 Hz, 1 H), 6.12 (d, J = 18.5 Hz, 1 H), 7.15−7.34 (m, 7 H), 7.89 (d, J = 8.3 Hz, 2 H); MS m/z 372 (M^+ + 1, 0.32), 228 (0.8), 218 (6), 217 (22), 216 (100), 200 (18), 149 (9.4), 113 (4.3), 91 (19), 85 (7), 73 (47), 59 (11). Anal. Calcd for $C_{20}H_{25}NO_2SSi$: C, 64.65; H, 6.78; N, 3.77. Found: C, 64.28; H, 6.84; N, 3.38. *trans*-**8a**: ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9 H), 2.40 (s, 3 H), 3.27 (dd, J = 4.0, 9.0 Hz, 1 H), 4.08 (d, J = 4.1 Hz, 1 H), 6.21 (d, J = 18.4 Hz, 1 H), 6.42 (dd, J = 8.9, 18.3 Hz, 1 H), 7.15−7.34 (m, 7 H), 7.82 (d, J = 8.3 Hz, 2 H).

***N*-Tosyl-2-(*o*-methoxyphenyl)-3-[β-(trimethylsilyl)vinyl]aziridine (8b).** *cis*-**8b**: ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 2.51 (s, 3 H), 3.81 (dd, J = 7.2, 7.2 Hz, 1 H), 3.85 (s, 3 H), 4.27 (d, J = 7.3 Hz, 1 H), 5.52 (dd, J = 7.3, 18.8 Hz, 1 H), 6.20 (d, J = 19.2 Hz, 1 H), 6.89−6.93 (m, 2 H), 7.22 (d, J = 7.4 Hz, 1 H), 7.31−7.44 (m, 3 H), 8.01 (d, J = 8.2 Hz, 2 H); MS m/z 319 (2), 268 (6), 267 (23), 266 (83), 246 (100), 231 (6.2), 216 (7.2), 139 (10), 113 (4), 91 (31), 73 (68), 59 (10), 45 (6). Anal. Calcd for $C_{21}H_{27}NO_3SSi$: C, 62.80; H, 6.78; N, 3.49. Found: C, 62.57; H, 6.58; N, 3.64. *trans*-**8b**: ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9 H), 2.49 (s, 3 H), 3.40 (dd, J = 4.1, 9.1 Hz, 1 H), 3.88 (s, 3 H), 4.54 (d, J = 4.0 Hz, 1 H), 6.34 (d, J = 18.6 Hz, 1 H), 6.61 (dd, J = 9.0, 18.7 Hz, 1 H), 6.89−6.93 (m, 2 H), 7.12 (d, J = 7.0 Hz, 1 H), 7.31−7.44 (m, 3 H), 7.95 (d, J = 8.3 Hz, 2 H).

***N*-Tosyl-2-(*p*-chlorophenyl)-3-[β-(trimethylsilyl)vinyl]aziridine (8c).** *cis*-**8c**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 2.50 (s, 3 H), 3.71 (dd, J = 7.2, 7.1 Hz, 1 H), 4.05 (d, J = 7.2 Hz, 1 H), 5.48 (dd, J = 7.1, 18.6 Hz, 1 H), 6.21 (d, J = 18.5 Hz, 1 H), 7.18−7.23 (m, 2 H), 7.28−7.42 (m, 4 H), 7.96 (dd, J = 1.4, 6.7 Hz, 2 H); MS m/z 254 (3), 253 (11), 252 (48), 251 (25), 250 (100), 236 (3.8), 234 (7.6), 199 (8), 169 (3.6), 149 (12), 139 (5.5), 121 (13), 91 (19), 85 (12), 73 (64), 65 (7.8), 59 (20), 45 (8). Anal. Calcd for $C_{20}H_{24}ClNO_2SSi$: C, 59.16; H, 5.96; N, 3.45. Found: C, 59.14; H, 5.90; N, 3.68. *trans*-**8c**: ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 9 H), 2.47 (s, 3 H), 3.32 (dd, J = 4.2, 9.1 Hz, 1 H), 4.13 (d, J = 4.1 Hz, 1 H), 6.31 (d, J = 18.4 Hz, 1 H), 6.50 (dd, J = 9.0, 18.5 Hz, 1 H), 7.18−7.23 (m, 2 H), 7.28−7.42 (m, 4 H), 7.90 (dd, J = 1.6, 6.6 Hz, 2 H).

***N*-Tosyl-2-(α-naphthyl)-3-[β-(trimethylsilyl)vinyl]aziridine (8d).** *cis*-**8d**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 2.68 (s, 3 H), 4.20 (dd, J = 7.4, 7.3 Hz, 1 H), 4.77 (d, J = 7.2 Hz, 1 H), 5.55 (dd, J = 7.5, 18.7 Hz, 1 H), 6.40 (d, J = 18.7 Hz, 1 H), 7.47−7.63 (m, 4 H), 7.73−7.81 (m, 2 H), 7.99−8.02 (m, 1 H), 8.06−8.12 (m, 1 H), 8.18−8.30 (m, 3 H); MS m/z 268 (8.4), 267 (30), 266 (100), 250 (12), 193 (4.6), 168 (7.6), 139 (10.4), 127 (2.7), 113 (3.4), 91 (14), 73 (59), 59 (10), 45 (5.4); HRMS calcd for $C_{17}H_{20}NSi$ (M^+ − Ts) 266.1365, found 266.1339. *trans*-**8d**: ^{1}H NMR ($CDCl_3$) δ 0.48 (s, 9 H), 2.66 (s, 3 H), 3.61 (dd, J = 4.2, 9.2 Hz, 1 H), 4.95 (d, J = 4.1 Hz, 1 H), 6.57 (d, J

= 18.4 Hz, 1 H), 6.96 (dd, J = 9.2, 18.4 Hz, 1 H), 7.47−7.63 (m, 4 H), 7.73−7.81 (m, 2 H), 7.99−8.02 (m, 1 H), 8.06−8.12 (m, 1 H), 8.18−8.30 (m, 3 H).

***N*-Tosyl-2-(*p*-chlorophenyl)-3-pyrroline (9):** ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 4.29 (m, 1 H), 4.34 (ddd, J = 2.3, 4.8, 14.6 Hz, 1 H), 5.48 (ddd, J = 2.2, 4.7, 5.3 Hz, 1 H), 5.61 (ddd, J = 2.2, 4.4, 6.2 Hz, 1 H), 5.80 (ddd, J = 2.0, 4.0, 6.2 Hz, 1 H), 7.17−7.26 (m, 6 H), 7.52 (dd, J = 1.6, 6.6 Hz, 2 H); MS m/z 336 (6.8), 335 (5), 334 (19), 333 (4.7), 222 (52), 180 (33), 178 (100), 155 (30), 143 (23), 115 (24), 91 (45), 75 (2.8), 65 (13), 51 (2); HRMS calcd for $C_{17}H_{16}ClNO_2S$ (M^+) 333.0590, found 333.0559.

General Procedure for Aziridination at −78 °C. A solution of the base (*n*-BuLi in hexanes, $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, or LiBr (1.2 equiv) + $NaN(SiMe_3)_2$ in THF, 1.2 equiv) was added dropwise to a solution of a sulfonium (**3a**, **3b**, **7a**, **7b**), telluronium (**15**, **16**), or arsonium (**14**) salt in 6 mL of THF at −78 °C under N_2. The mixture was stirred for 5−30 min (5 min for **3a**, 30 min for others), and imine (1.0 equiv) in 4 mL THF was subsequently added. The reaction mixture was then allowed to warm to room temperature within 2−3 h. The reaction mixture was filtered on a short neutral Al_2O_3 column to hydrolyze the excess active species and remove inorganic salts. The filtrate was concentrated and chromatographed on a neutral Al_2O_3 column with a mixture of light petroleum (60−90 °C), ethyl acetate, and NEt_3 (8:1:1) as the eluent to give pure product.

Acknowledgment. Financial support from the National Natural Foundation of China and Chinese Academy of Sciences is gratefully acknowledged.

Supporting Information Available: Copies of NMR spectra (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO952245D