Highly Stereoselective Ylide Aziridination of *N*-Sulfonylimines with Sulfonium Propargylides: A Simple Way To Synthesize Scalemic Acetylenylaziridines

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Under phase-transfer or low-temperature conditions, the ylide generated from diphenylsulfonium salt **2** readily reacts with *N*-sulfonylimines **1** to give acetylenylaziridines in excellent yields, but low to moderate cis/trans selectivity. When using *n*-BuLi as the base to generate the ylide at low termperature, product **3** with an intact silyl protecting group is obtained. *t*-BuOK, however, leads to desilylation product **4**. With Cs_2CO_3 as the base, dimethylsulfonium salts **6**, **21**, and **22** show much better cis/trans selectivity (>98:2) than diphenylsulfonium salt **2**. The asymmetric version of the above aziridination reaction using camphor-derived sulfonium salts **12**−**14** and **20** gives chiral aziridines with ee values up to 85%. Both (2*R*,3*S*)-(−)-**3** and (2*S*,3*R*)-(+)-**3** can be prepared from **12**/**20** or **13**/**14**, respectively. Ylides produced from telluronium salt **7** failed to react with imine **1a** at room temperature, but the reaction succeeded at low temperature. Arsonium ylides from **8** cannot react with *N*-sulfonylimines under both sets of conditions.

Introduction

The great synthetic utility of chiral aziridines stimulates the development of efficient methods for preparing this type of nitrogen-containing strained ring compounds.[1] Among various strategies[2] starting from prochiral C=C[3] and C=N[4] double bonds, the aziridination through the reaction of an imine with an ylide (i.e., ylide aziridination) has recently showed great promise in obtaining various functionalized aziridines by the results of Aggarwal,[5] our group,[6] and other laboratories[4,7] (although there were also a few other examples[8] earlier). Compared with other direct aziridinating reactions with a C=N double bond, e.g., the carbene approach,[4a−c] the aza-Darzens reaction,[4d,e] and the Lewis acid method,[4f] the present ylide approach has several advantages: (a) There are a wide range of ylide reagents from which to choose, most of them easily accessible. (b) A variety of substrates, either aromatic or aliphatic aldimines or ketimines, can be used. (c) The reaction conditions are generally mild, and the operations are simple. (d) The ylide precursor reagents are recyclable.

During the course of our studies on the reactivity of imines in developing imine-based synthetic methodologies,[6,9] we found that in contrast to the common *N*-aryl- or *N*-alkylimines, *N*-sulfonylimines showed extremely high reactivity toward semistabilized or stabilized sulfonium allylides. This has led to an efficient, convenient, and mild route to various vinylaziridines.[6] However, the trans/cis selectivity of these reactions was not satisfactory despite many efforts that had been made. Fortunately, when we extended these allylic ylide reagents to corresponding propargylic sulfonium ylides, exclusive cis selectivity was eventually achieved. On this basis, an efficient asymmetric ylide aziridination, which produced acetylenylaziridines, a type of new chiral aziridine derivative, was realized.[10] Herein, we report the full details of this new asymmetric aziridination.

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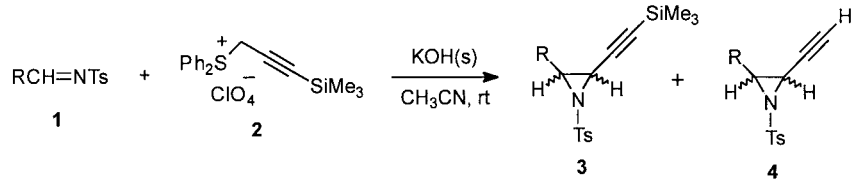
Table 1. Preparation of *N*-Sulfonylacetylenylaziridines 3 and 4 by Reaction of *N*-Sulfonylimines 1 and 3-(Trimethylsilyl)propargyldiphenylsulfonium Perchlorate (2) under Phase-Transfer Conditions[a]



Entry	Imines **1** R	Reaction time (min)	Silylated aziridines **3** yield,[b] %	Silylated aziridines **3** *cis*/*trans*[c]	Desilylated aziridines **4** yield,[b] %	Desilylated aziridines **4** *cis*/*trans*[c]
1	C_6H_5 (**1a**)	4	15 (**3a**)	40/60	78 (**4a**)	46/54
2	*p*-ClC_6H_4 (**1b**)	4	32 (**3b**)	63/37	66 (**4b**)	54/46
3	1-naphthyl (**1c**)	4	48 (**3c**)	49/51	50 (**4c**)	51/49
4	*o*-$MeOC_6H_4$ (**1d**)	6	75 (**3d**)	59/41	23 (**4d**)	72/28

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

Results and Discussion

Reaction of *N*-Sulfonylimines with Diphenylsulfonium 3-(Trimethylsilyl)propargylide. Among allylic, benzylic, and propargylic, these being three types of semistabilized sulfonium ylides, the last one has been least studied. The only known reaction of propargylic sulfonium ylide is the [2,3]-σ-rearrangement.[11] Commonly known ylide cyclization reactions including epoxidation, cyclopropanation, and aziridination with propargylic sulfonium ylides, to our knowledge, have not been previously reported, although the first two types of cyclization reactions have been realized with propargylides of other heteroatoms.[12] Considering the structural similarity between allylic and propargylic ylides (both belong to semistabilized ylides), we thought that they should show similar reactivity in many reactions. Therefore we prepared silylated propargylic sulfonium salt **2** and tested it in the previously reported ylide aziridination reaction in place of the corresponding allylic sulfonium salt.[6c] Some results from the reaction of diphenylsulfonium salt **2** with *N*-sulfonylimines **1** under solid−liquid phase-transfer conditions are summarized in Table 1.

Under solid−liquid phase-transfer conditions, ylides generated in situ from silylated propargylic diphenylsulfonium salt **2** rapidly reacted with *N*-sulfonylimines **1** to give the expected aziridination product **3** together with desilylated product **4**. Although the total yield (**3** + **4**) in all runs was nearly quantitative, the cis/trans selectivity was, as observed in earlier cases of aziridination using silylated allylic diphenylsulfonium salt,[6c] not high (ranging from 1:1 to 3:1 infavor of cis). To improve the utility of the present procedure, efforts were then made to improve the cis/trans selectivity by changing the reaction conditions—with preformed ylide and at low termperature.

Results from the reaction of imine **1b** with the preformed ylide **5** (generated from **2** with different bases) are presented in Table 2. Compared with the results obtained under phase-transfer conditions (entry 2 in Table 1), the cis/trans selectivity is significantly improved in some cases (entries 1 and 4−6 in Table 2). In addition, some interesting new phenomena were also observed: the silyl-retained aziridine **3b** was the only product in all cases on using Li^+-containing bases (entries 1−4 in Table 2), and the desilylated aziridine **4b** was the only product when using *t*-BuOK (entry 8 in Table 2). A mixture of both aziridines was obtained in other cases.

To further confirm the above observations, reactions with some other *N*-tosylarylaldimines were carried out using *n*-BuLi or *t*-BuOK as the base (Table 3). When using *n*-BuLi as the base, the silylated aziridines **3** were formed as the only products (entries 1−5 in Table 3), while using *t*-BuOK as the base, desilylated aziridines **4** became the sole products (entries 6−9 in Table 3). Yields were excellent in all cases, and the cis/trans selectivity was generally larger than 3:1. It is noteworthy that desilylated aziridines **4** are not easily accessible from simple propargylic ylides because their precursors (propargylsulfonium salts) easily isomerize into allenylsulfonium salt under basic conditions, rather than forming the corresponding ylides.[13] Therefore the direct formation of simple acetylenylaziridines **4** by using *t*-BuOK is synthetically useful. Although a plausible explanation for the above results is not available yet, it does not prevent us from preparing either silylated or desilylated products with good stereoselectivity just by using two different bases.

Up to now, an efficient aziridination of *N*-sulfonylimines with silylated propargylic sulfonium ylides has been successfully realized, and either silylated or de-

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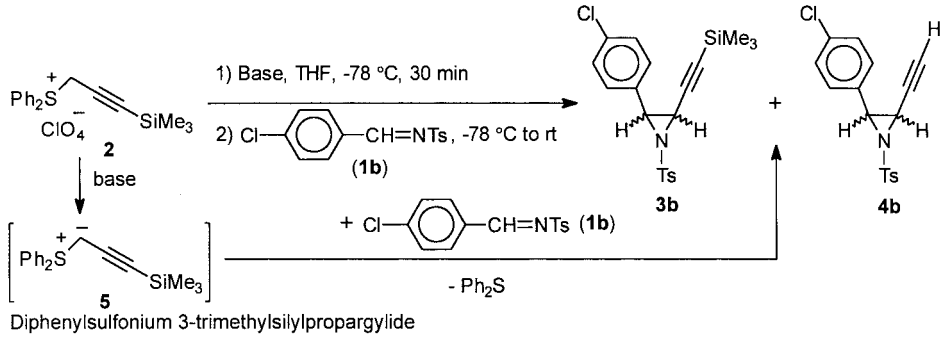
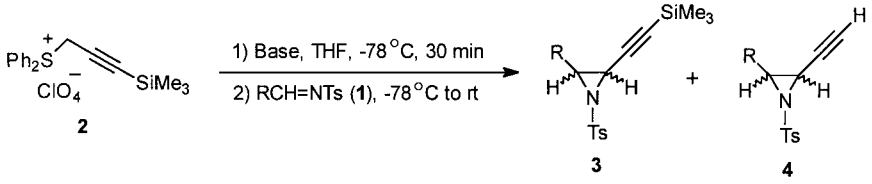
Table 2. Reaction of *N*-Sulfonylimines 1b with Preformed Diphenylsulfonium 3-(Trimethylsilyl)propargylide (5) Generated in Situ from 3-(Trimethylsilyl)propargyldiphenylsulfonium Perchlorate (2) with Different Bases[a]



Entry	Base	Silylated aziridine **3b**		Desilylated aziridine **4b**	
		yield,[b] %	*cis*/*trans*[c]	yield,[b] %	*cis*/*trans*[c]
1	*n*-BuLi	85	86/14	0	-
2	$LiN(SiMe_3)_2$	98	55/45	0	-
3	$LiBr+NaN(SiMe_3)_2$	65	54/46	trace	-
4	LDA	91	78/22	0	-
5	$NaN(SiMe_3)_2$	53	93/7	45	98/2
6	$KN(SiMe_3)_2$	42	80/20	41	86/14
7	NaH	26	65/35	48	36/64
8	*t*-BuOK	0	-	98	74/26

[a] All reactions were carried out in a ratio of imine:sulfonium salt:base = 1:1.2:1.2 at a 0.5-mmol scale in THF at −78 °C under N_2. [b] Isolated yields based on imine. [c] Determined by 300-MHz ^1H NMR analysis.

Table 3. Preparation of *N*-Sulfonyl-*β*-(trimethylsilyl)acetylenylaziridines 3 or 4 by Reaction of *N*-Sulfonylimines 1 with Preformed Diphenylsulfonium 3-(Trimethylsilyl)propargylide (5) Generated in Situ from 3-(Trimethylsilyl)propargyldiphenylsulfonium Perchlorate (2) with *n*-BuLi or *t*-BuOK[a]

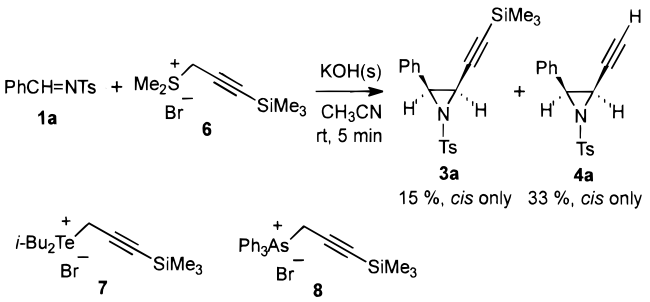


Entry	R	Base	Silylated aziridines **3**		Desilylated aziridines 4	
			Yield,[b] %	*cis*/*trans*[c]	Yield,[b] %	*cis*/*trans*[c]
1	C_6H_5 (**1a**)	*n*-BuLi	92	86/14	0	-
2	*p*-ClC_6H_4 (**1b**)	*n*-BuLi	85	86/14	0	-
3	1-naphthyl (**1c**)	*n*-BuLi	95	80/20	0	-
4	*o*-$MeOC_6H_4$(**1d**)	*n*-BuLi	98	89/11	0	-
5	*p*-$O_2NC_6H_4$ (**1e**)	*n*-BuLi	96	83/17	0	-
6	C_6H_5 (**1a**)	*t*-BuOK	0	-	81	67/33
7	*p*-ClC_6H_4 (**1b**)	*t*-BuOK	0	-	98	74/26
8	1-naphthyl (**1c**)	*t*-BuOK	0	-	88	76/24
9	o-$MeOC_6H_4$(**1d**)	*t*-BuOK	0	-	98	73/27

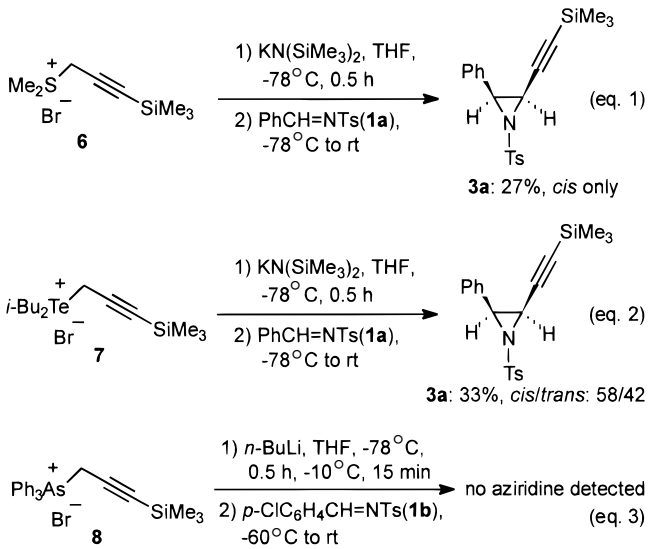
[a] All reactions were carried out in a ratio of imine:sulfonium salt:base = 1:1.2:1.2 at a 0.5-mmol scale in THF at −78 °C under N_2. [b] Isolated yields based on imine. [c] Determined by 300-MHz ^1H NMR analysis.

silylated acetylenylaziridines could be obtained in high yield. To our knowledge, the aziridination of imines with propargylic ylides has not been previously reported (except for our preliminary communication[10]), although corresponding epoxidation and cyclopropanation with propargylides of telluronium and arsonium are known.[12]

Scheme 1



Scheme 2



In addition, the product acetylenylaziridines are also a type of rarely reported functionalized aziridine derivatives.[14]

The above method suffered from several drawbacks: the difficulty in preparation of diphenylsulfonium salt **2** (silver salt is necessary and Ph_2S must be in great excess[15]), the requirements for low-temperature and moisture/oxygen-free conditions, and the unsatisfactory cis/trans selectivity (~3:1). To develop a more economic, convenient, and highly stereoselective method for preparing acetylenylaziridines and to explore the reactivity of propargylides of other heteroatoms with *N*-sulfonylimines, dimethylsulfonium salt **6** (much easier to prepare than the diphenyl counterpart) and telluronium and arsonium salts **7** and **8** were prepared and then tested in the reaction with imine **1a** (Scheme 1). Under the same reaction conditions as shown in Table 1, the reaction of **1a** with ylides generated from **6** gave aziridines **3a** and **4a** in 48% total yield as expected, together with significant amounts of side products. However, the stereoselectivity in this case is very high: only the cis isomer was formed. Telluronium salt **7** and arsonium salt **8** failed to react with imine **1a** under the same phase-transfer conditions.

Lowering the reaction temperature to suppress the side reactions and consequently to improve the yields was also attempted (Scheme 2). Similar to the results under the phase-transfer conditions, exclusive cis selectivity was again observed with sulfonium salt **6**, although the yield became even lower (eq 1 in Scheme 2). The ylides generated from telluronium salt **7** could also react with **1a** to afford silylated aziridine **3a** in 33% yield, but the stereoselectivity was almost lost (eq 2 in Scheme 2). Arsonium ylides from **8** still failed to proceed in the aziridination reaction with imine **1b**. In these runs, although the yields were not satisfactory, the desired high stereoselectivity was eventually achieved in two cases (Scheme 1 and eq 1 in Scheme 2).

Reaction of *N*-Sulfonylimines with Dimethylsulfonium 3-(Trimethylsilyl)propargylide. The very high cis/trans selectivity observed in the aziridination of *N*-sulfonylimines with **6** showed us its great potential as a stereoselective reagent for the preparation of acetylenylaziridines. Therefore, we next examined various bases and solvents (Table 4). We found that strong base (e.g., KOH) and polar solvent (e.g., CH_3CN) would cause side reactions and thus decrease the yields. Weak base (e.g., LiOH and K_2CO_3) and ethereal solvents (entries 4 and 5 in Table 4) would also decrease the yields because of hydrolysis of the imines. The best base/solvent combination for the reaction of *N*-sulfonylimines with **6** turned out to be Cs_2CO_3/CH_2Cl_2, with which both high yield and high stereoselectivity could be achieved (entry 9 in Table 4). Using the optimized conditions, a variety of substrates were examined. The results are listed in Table 5.

It was found that with all the examined 15 substrates, reaction was generally completed within 0.5−2.5 h. High yields were achieved in most cases, and very high cis selectivity was observed in all cases (with only one exception, entry 3 in Table 5). Various imines, including aromatic, heteroaromatic, α,β-unsaturated, and aliphatic aldimines, were all workable substrates for this reaction. Even with unreactive ketimine **1q**, high yield was still obtained (entry 15 in Table 5). Such a wide span of substrates is seldom seen in ylide epoxidation and cyclopropanation and never found in ylide aziridination. In addition, the very high cis/trans selectivity and the use of aliphatic sulfide to form a sulfonium salt (**6**) created the possibility of a chiral version for this reaction, which would lead to optically active acetylenylaziridines.

Reaction of *N*-Sulfonylimines with Camphor-Derived Chiral Sulfonium 3-(Trimethylsilyl)propargylide. The usefulness of chiral aziridines in the synthesis of biologically and medicinally important molecules prompted the development of efficient asymmetric aziridination methodologies.[2] Among various existing methods, asymmetric aziridination via an ylide route, although appearing very late and only a few examples[5,7,10] have been reported to date, has shown much promise in obtaining optically active functionalized aziridines. The very high cis/trans selectivity obtained in reactions using propargylic dimethylsulfonium salt **6** (see Table 5) and our previous experience in ylide epoxidation[16] encouraged us to transform the present aziridination into its asymmetric version.

Camphor-derived chiral sulfonium salts **12**−**14** were easily prepared by reacting bromide **15** with sulfides **9**−**11**, respectively (Scheme 3).[16] We then used sulfonium salt **12** instead of dimethylsulfonium salt **6** to perform the reaction shown in Table 5. It was found that under the same conditions, ylides generated from chiral **12**

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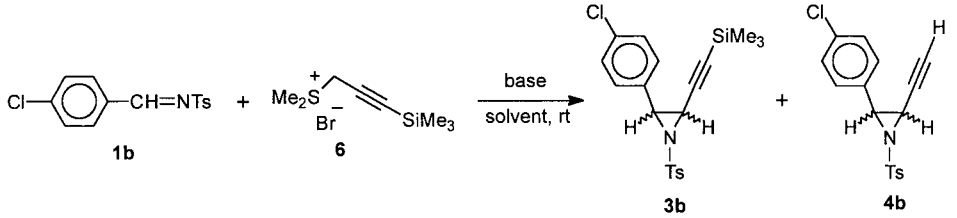
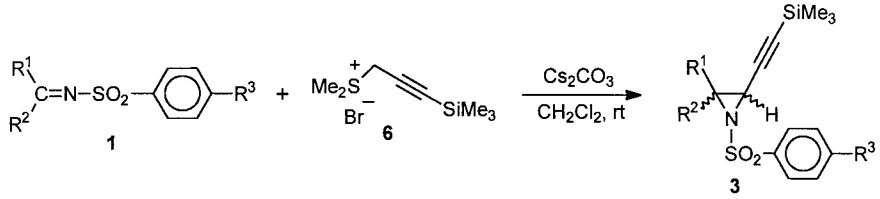
Table 4. Effects of Solvent and Base on Reaction of *N*-Sulfonylimines 1b and 3-(Trimethylsilyl)propargyldimethylsulfonium Bromide (6) under Solid−Liquid Phase-Transfer Conditions[a]



entry	Base/Solvent	Reaction time (min)	Silylated aziridine **3b** yield,[b] %	Silylated aziridine **3b** *cis*/*trans*[c]	Desilylated aziridine **4b** yield,[b] %	Desilylated aziridine **4b** *cis*/*trans*[c]
1	KOH/CH_3CN	6	10	>99/1	46	99/1
2	$LiOH.H_2O/CH_3CN$	90	7	96/4	0	-
3	Cs_2CO_3/CH_3CN	15	32	99/1	58	99/1
4	KOH/Et_2O	15	19	98/2	6	98/2
5	KOH/THF	6	0	-	16	99/1
6	KOH/CH_2Cl_2	12	38	>99/1	42	99/1
7	$KF.Al_2O_3/CH_2Cl_2$	150	41	98/2	25	99/1
8	K_2CO_3/CH_2Cl_2	150	42	>99/1	0	-
9	Cs_2CO_3/CH_2Cl_2	30	87	99/1	0	-

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

Table 5. Preparation of *N*-Sulfonyl-*β*-(trimethylsilyl)acetylenylaziridines 3 by Reaction of *N*-Sulfonylimines 1 and 3-(Trimethylsilyl)propargyldimethylsulfonium Bromide (6) under Phase-Transfer Conditions[a]

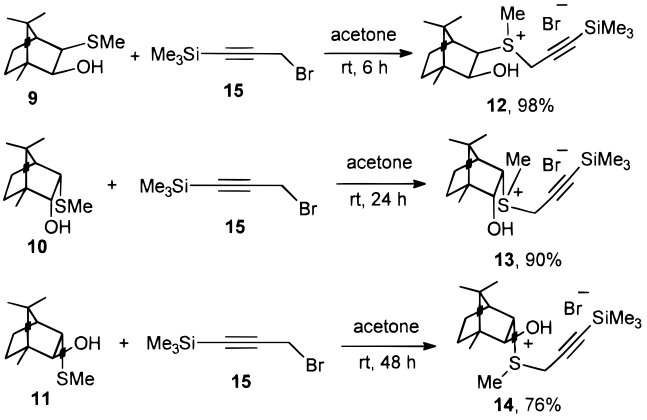


entry	R^1	R^2	R^3	reaction time (h)	yield,[b]	*cis*/*trans*[c]
1	C_6H_5 (**1a**)	H	Me	0.7	84 (**3a**)	>99/1
2	*p*-ClC_6H_4 (**1b**)	H	Me	0.5	87 (**3b**)	99/1
3	1-naphthyl (**1c**)	H	Me	1.0	73 (**3c**)[d]	93/7
4	*o*-$MeOC_6H_4$ (**1d**)	H	Me	0.7	80 (**3d**)	99/1
5	*p*-$O_2NC_6H_4$ (**1e**)	H	Me	0.7	54 (**3e**)	>99/1
6	3-pyridinyl (**1f**)	H	Me	0.7	74 (**3f**)	>99/1
7	*p*-MeC_6H_4 (**1g**)	H	H	0.5	88 (**3g**)	98/2
8	*p*-$MeOC_6H_4$ (**1h**)	H	Me	0.5	91 (**3h**)	>99/1
9	*p*-$AcOC_6H_4$ (**1i**)	H	Me	1.0	98 (**3i**)	>99/1
10	*p*-$MeSC_6H_4$ (**1j**)	H	Me	0.7	75 (**3j**)	>99/1
11	2-furyl (**1k**)	H	Me	0.5	86 (**3k**)	>99/1
12	*trans*-PhCH=CH (**1m**)	H	Me	0.5	78 (**3m**)	>99/1
13	cyclohexyl (**1n**)	H	Me	1.5	80 (**3n**)	>99/1
14	*t*-butyl (**1p**)	H	Me	2.5	98 (**3p**)	>99/1
15	Me (**1q**)	Me	Me	0.75	81 (**3q**)	-

[a] All reactions were carried out in a ratio of imine:sulfonium salt:Cs_2CO_3 = 1:1.2:1.2 at a 0.5-mmol scale in CH_2Cl_2 at room temperature. [b] Isolated yields based on imine. [c] Determined by 300-MHz ^{1}H NMR analysis. [d] 8% of desilylated product was also isolated. cis/trans: 95/5.

reacted smoothly with imines **1** to give optically active acetylenylaziridines (−)-**3** (Table 6) in high yields with excellent cis/trans selectivities (>98/2). The ee values, however, varied considerably (18−85%). Like the reac-

Scheme 3



tions with achiral sulfonium salt **6**, this asymmetric version had the same wide substrate span: it works well with not only aromatic imines but also aliphatic imines and ketimines. The highest ee (84.9%) was achieved with the imine (**1n**) derived from cyclohexanecarboxaldehyde (entry 13 in Table 6). Although the ee values obtained for many substrates were only moderate, we found that they could be improved by recrystallization. For example, the ee values of aziridines **3f**,**3r** were raised from 77.5% and 69.5% to 99.1% and 96.6%, respectively, by only a single recrystallization from *n*-hexane (entries 5 and 9 in Table 6). Although the above reaction was stoichiometric, the ylide precursor sulfide **9** could be easily recovered in >80% yields without losing its optical purity.

It is known that the reaction temperature usually has a pronounced effect on the enantioselectivity of a reaction. However, this does not seem to be the case here. With *p*-$ClC_6H_4CH{=}NTs$ (**1b**) as a model substrate, we ran the reaction at different temperatures (−78, −20, 0, and 25 °C and reflux temperature) and found that the ee values of the products fell in the range between 55.8% and 59.0%. Therefore, room temperature is later used as the "optimum temperature" for the asymmetric aziridination reaction.

The absolute configuration of phenylaziridine **3a** was determined as follows (Scheme 4): Aziridine (−)-**3a** was first desilylated to produce compound **16**, which was further converted by oxidation and esterification to (+)-**18**. On the basis of the known sign of optical rotation and absolute configuration of compound **18**,[4d] the configuration of (−)-**3a** is unambiguously assigned as 2*R*,3*S*. The configurations of other aziridines are deduced based on the signs of the optical rotations because of the structural similarity.

In our asymmetric epoxidation with chiral sulfonium ylides, we found that sulfides with an *exo*-sulfonium group and the ones with an *endo*-sulfonium group showed opposite asymmetric induction.[16] Does this phenomenon exist in the asymmetric aziridination? To find out, sulfonium salts **13** and **14** with an *endo*-sulfonium group were synthesized and used to replace *exo*-sulfonium salt **12** in the asymmetric aziridination reactions. Some results are summarized in Table 7. Just like sulfonium salt **12**, ylides produced from both **13** and **14** could smoothly aziridinate imine **1** to give **3** in excellent yields, with exclusive cis selectivity and moderate ee values, but this time all products possess a positive optical rotation. That means the absolute configuration of the product changed from the original 2*R*,3*S* (with sulfonium salt **12**) to 2*S*,3*R*. Opposite asymmetric induction was again achieved in aziridination, as observed in asymmetric epoxidation.[16]

To examine the asymmetric effect of other chiral sulfides, compound **19**[17] was synthesized and transformed to chiral sulfonium salt **20** (Scheme 5). However, when **20** was reacted with imine **1b** in the presence of Cs_2CO_3, only 32.5% (56% ee from salt **12**) ee was obtained. The lower ee may be attributed to the fact that the reacting site was far away from the chiral centers.

Reaction of *N*-Sulfonylimines with Other Propargyl-Type Sulfonium Ylides. In all the above aziridination reactions, the used ylides are various sulfonium 3-(trimethylsilyl)propargylides. From these reactions, both silylated and unsubstituted acetylenylaziridines can be highly efficiently prepared. There is still a problem to be answered: How about the scope of ylide reagents? Can other types of propargylic sulfonium ylides also be used? Thus phenyl-substituted sulfonium salt **21** and sulfonium salt containing an aliphatic long chain (**22**) were synthesized and utilized to perform an aziridination (Scheme 6). Under the same conditions as with other 3-(trimethylsilyl)propargylsulfonium salts, we found that the ylides produced from both **21** and **22** could react smoothly with imine **1b** to give aziridines **23** and **24** in 85% and 96% yields, respectively. However, the cis/trans selectivities (95/5 for **23** and 92/8 for **24**) were a little bit lower than that obtained with sulfonium salt **6** (99/1, entry 2 in Table 5). To examine the asymmetric induction, compound **25** was synthesized from chiral sulfide **9** and used to perform aziridination under the same conditions; only 31.1% ee (cf. 56% ee from salt **12**) was obtained (Scheme 7). The lower ee may be understood as a phenyl is smaller than a trimethylsilyl group.

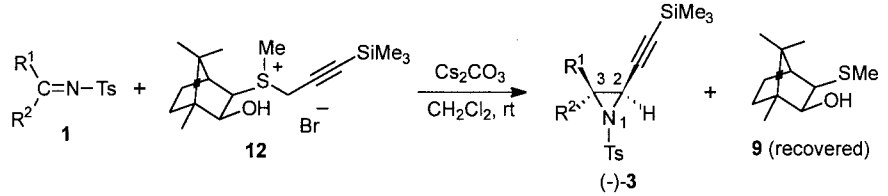
Exclusive cis selectivity was achieved by the reaction of *N*-sulfonylimines with proparglic sulfonium ylides under phase-transfer conditions. This may be explained by an intermediate formed by [2 + 2]-cycloaddition of imines and ylide (Scheme 8). The [2 + 2]-cycloaddition is the rate-determining step. Due to steric hindrance, only trans intermediate **III** was formed. Then intramolecular trans elimination of Me_2S gave *cis*-aziridines. This is similar to epoxidation and olefination reactiona of carbonyl compounds with telluronium ylides[18a] and phosphine ylides. [18b]

Until now, four types of acetylenylaziridines could be efficiently prepared, i.e., unsubstituted and trimethylsilyl-, aryl-, and alkyl-substituted ones. The last type of acetylenylaziridine is especially noteworthy. It lets us believe that our present aziridination strategy may be developed into a general methodology for synthesizing various substituted *N*-sulfonylacetylenylaziridines and may really become a synthetically useful reaction. Studies on the reactivities of the above acetylenylaziridines and exploration of the possibility to use the present aziridination method in organic synthesis are now in progress in our laboratory.

(17) Furukawa, N.; Sugihara, Y.; Fujihara, H. *J. Org. Chem.* **1989**, *54*, 4222.

(18) (a) Zhou, Z.-L.; Huang, Y.-Z.; Shi, L.-L.; Hu, J. *J. Org. Chem.* **1992**, *57*, 6598. (b) Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 2823 and references therein.

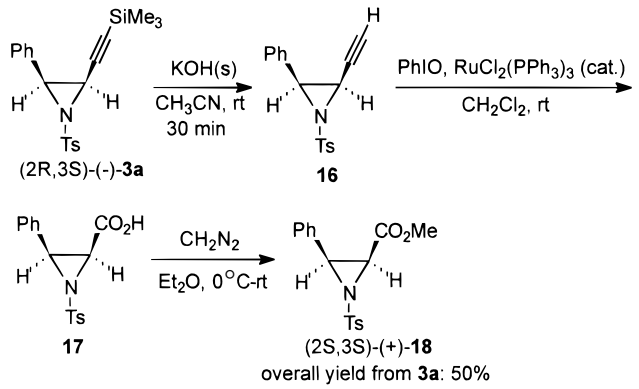
Table 6. Preparation of (−)-*N*-Tosyl-*β*-(trimethylsilyl)acetylenylaziridines 3 by Asymmetric Aziridination Reaction of *N*-Sulfonylimines 1 and D-(+)-Camphor-Derived Sulfonium Salt 12 under Phase-Transfer Conditions[a]



entry	R^1	R^2	reaction time (h)	yield,[b] %	*cis*/*trans*[c]	ee,[d] %	config[f]
1	C_6H_5 (**1a**)	H	5.0	85 (**3a**)	>99/1	50.5	2R,3S
2	*p*-ClC_6H_4 (**1b**)	H	5.0	92 (**3b**)	98/2	56.0	(2R,3S)
3	*o*-$MeOC_6H_4$ (**1d**)	H	5.5	90 (**3d**)	99/1	18.4	(2R,3S)
4	*p*-$O_2NC_6H_4$ (**1e**)	H	4.0	54 (**3e**)	>99/1	26.8	(2R,3S)
5	3-pyridinyl (**1f**)	H	4.0	85 (**3f**)	>99/1	77.5 (99.1[e])	(2R,3S)
6	*p*-$MeOC_6H_4$ (**1h**)	H	3.5	98 (**3h**)	>99/1	47.0	(2R,3S)
7	*p*-$AcOC_6H_4$ (**1i**)	H	4.0	87 (**3i**)	>991	50.0	(2R,3S)
8	*p*-$MeSC_6H_4$ (**1j**)	H	4.0	90 (**3j**)	>99/1	47.6	(2R,3S)
9	*p*-FC_6H_4 (**1r**)	H	3.0	89 (**3r**)	>99/1	69.5 (96.6[e])	(2R,3S)
10	*p*-BrC_6H_4 (**1s**)	H	3.0	95 (**3s**)	>99/1	49.2	(2R,3S)
11	2-furyl (**1k**)	H	3.5	87 (**3k**)	>99/1	36.0	(2R,3S)
12	*trans*-PhCH=CH (**1m**)	H	3.5	88 (**3m**)	>99/1	44.3	(2R,3S)
13	cyclohexyl (**1n**)	H	2.5	81 (**3n**)	>99/1	84.9	(2R,3S)
14	*t*-butyl (**1p**)	H	4.0	92 (**3p**)	>99/1	40.8	(2R,3S)
15	Me (**1q**)	Me	3.0	95 (**3q**)	-	67.4	(2R)

[a] All reactions were carried out in a ratio of imine:sulfonium salt:Cs_2CO_3 = 1:1.2:1.2 at a 0.5-mmol scale in CH_2Cl_2 at room temperature. Sulfide **9** was recovered in >80% yields without losing the optical purity after workup in all cases. [b] Isolated yields based on imine. [c] Determined by 300-MHz ^1H NMR analysis. [d] Determined by chiral HPLC on a Chiralcel OD column or a Chiralpak AD column. [e] The ee values refer to those after single recrystallization from *n*-hexane. [f] Determined by chemical transformations (see the Experimental Section). The configuration in parentheses is estimated by analogy with phenylacetylenylaziridine **3a**.

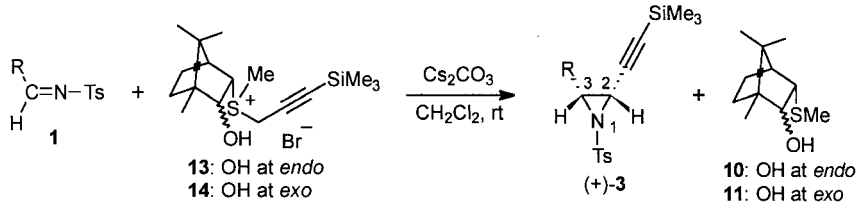
Scheme 4



Conclusions

A highly stereoselective ylide aziridination based on the reaction of *N*-sulfonylimines with various propargylic ylides has been described. Simple unsubstituted propargylic sulfonium ylides cannot be prepared by the basic deprotonation of the corresponding sulfonium salt due to the isomerization of precursor propargylic salt into allenic salt and therefore cannot be used directly to react with imines. Both preformed (low-temperature conditions) or in situ-formed (phase-transfer conditions) diphenylsulfonium 3-(trimethylsilyl)propargylide (**5**) can react with *N*-sulfonylimines **1** to give silylated and/or desilylated acetylenylaziridines in excellent yields with low to moderate cis/trans selectivity. The cis/trans ratios of products obtained under low-temperature conditions are generally better than those obtained under phase-transfer conditions. In low-temperature reactions, when using *n*-BuLi as the base to generate ylides, silylated products **3** were obtained exclusively, while employing *t*-BuOK as the base led to desilylated aziridines **4** as the only products. The stereoselectivity of the present aziridination was greatly improved by using dimethylsulfonium 3-(trimethylsilyl)propargylide. A cis/trans ratio of >99/1 was achieved in most cases. Under Cs_2CO_3/CH_2Cl_2−rt conditions, in situ-generated dimethylsulfonium 3-(trimethylsilyl)propargylide can react with a variety of substituted *N*-sulfonylaldimines and -ketimines to give silylated acetylenylaziridines in excellent yields. When using camphor-derived sulfonium salts **12**−**14** and **20**, an efficient asymmetric aziridination with varying ee values (up to 85%) was realized. Opposite asymmetric induction was just achieved when using sulfonium salt **12** or **20** and **13** or **14**. It allows either (2*R*,3*S*)-(−)-**3** or (2*S*,3*R*)-(+)-**3** to be prepared. 3-Phenyl- or 3-alkyl-substituted propargylsulfonium salts can also be used to perform the above aziridination. Among sulfonium, telluronium, and arsonium (three types of propargylides), sulfonium ylides are the most efficient reagents to effect aziridination of *N*-sulfonylimines and the arsonium ones are the worst ones.

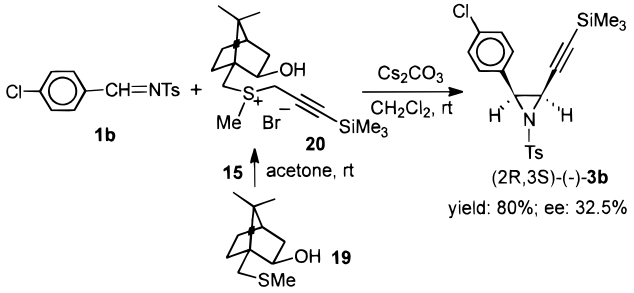
Table 7. Preparation of (+)-*N*-Sulfonyl-*β*-(trimethylsilyl)acetylenylaziridines 3 by Asymmetric Aziridination Reaction of *N*-Sulfonylimines 1 and D-(+)-Camphor-Derived Sulfonium Salts 13 and 14 under Phase-Transfer Conditions[a]



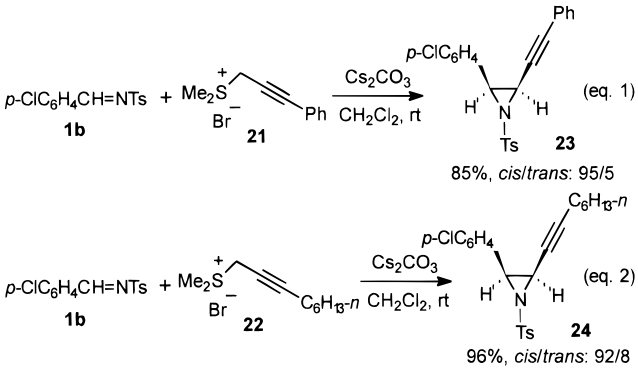
entry	R	sulfonium salt	time (h)	yield,[b] %	ee,[c] %	config[d]
1	C_6H_5 (**1a**)	**13**	3.0	88 (**3a**)	25.7	2S,3R
2	*p*-ClC_6H_4 (**1b**)	**13**	3.0	92 (**3b**)	21.3	(2S,3R)
3	*o*-$MeOC_6H_4$ (**1d**)	**13**	3.5	92 (**3d**)	22.0	(2S,3R)
4	3-pyridinyl (**1f**)	**13**	2.5	85 (**3f**)	56.3	(2S,3R)
5	cyclohexyl (**1n**)	**13**	4.0	90 (**3n**)	51.9	(2S,3R)
6	C_6H_5 (**1a**)	**14**	3.5	89 (**3a**)	14.0	2S,3R
7	*o*-$MeOC_6H_4$ (**1d**)	**14**	3.5	90 (**3d**)	14.0	(2S,3R)
8	3-pyridinyl (**1f**)	**14**	3.0	82 (**3f**)	41.9	(2S,3R)
9	cyclohexyl (**1n**)	**14**	4.5	89 (**3n**)	39.2	(2S,3R)

[a] All reactions were carried out in a ratio of imine:sulfonium salt:Cs_2CO_3 = 1:1.2:1.2 at a 0.5-mmol scale in CH_2Cl_2 at room temperature. Sulfide **10** or **11** was recovered in >80% yields without losing the optical purity after workup in all cases. [b] Isolated yields based on imine. The cis/trans ratio in all cases was >99/1. [c] Determined by chiral HPLC on a Chiralcel OD column or a Chiralpak AD column. All ee values belong to the major products. [d] Determined by chemical transformations (see the Experimental Section). The configuration in parentheses is estimated by comparison with the phenyl analogue.

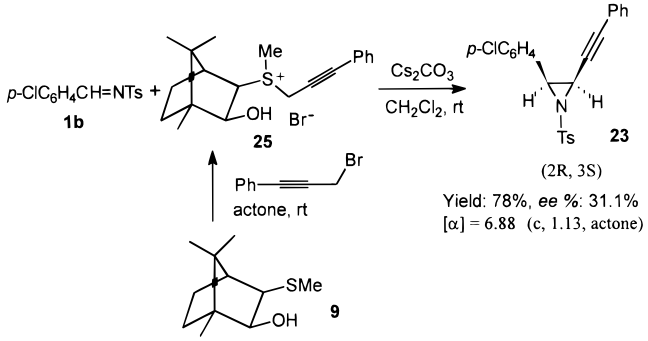
Scheme 5



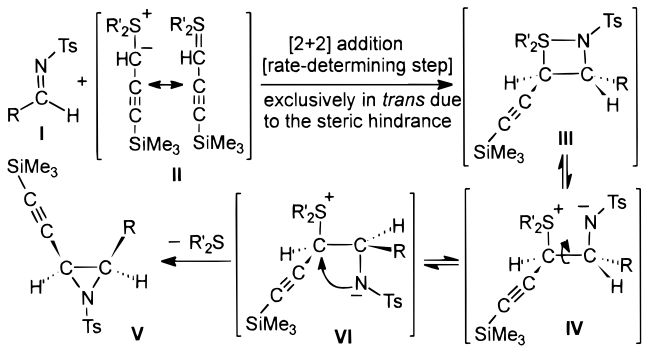
Scheme 6



Scheme 7



Scheme 8



Experimental Section

Materials and General Procedure. All reagents and solvents, unless otherwise specified, are from commercial sources and used without further purification. THF was distilled immediately prior to use from sodium/benzophenone ketyl under nitrogen. All *N*-sulfonylimines **1** were prepared according to the literature method.[19] Compound **15** was prepared by a well-established method.[20] Sulfonium salts **6**, **12**−**14**, **20**, and **25** were prepared by the reaction of corresponding bromides with sulfides in the presence of a small amount of acetone at room temperature. Sulfonium salt **2** was obtained following a literature procedure[15] except for using $AgClO_4$ instead of $AgBF_4$. Arsonium salt **8** was prepared by the reaction of Ph_3As with 3-bromo-1-(trimethylsilyl)propyne (**15**).[21] Telluronium salts **7** was prepared by the reaction of *i*-Bu_2Te[22] with compound **15** without solvent at room temperature.[23] Chiral sulfides **9**−**11** were synthesized according to

(19) (a) Love, B. E.; Raje, P. S.; Williams, T. C., II. *Synlett* **1994**, 493. (b) Jennings, W. B.; Lovely, C. J. *Tetrahedron Lett.* **1988**, *29*, 3725.
(20) Jones, T. K.; Denmark, S. E. *Org. Synth.* **1990**, *7*, 524.
(21) Ousset, J. B.; Mioskowski, C.; Solladie, G. *Tetrahedron Lett.* **1983**, *24*, 4419.

our previous paper.[16] Compound **19** were prepared according to Furukawa's method.[17]

Analysis of Enantiomeric Excess. Chromatographic separations were achieved using a liquid chromatograph constructed from the following components: a Waters M510 pump operating at 0.7 mL/min, a M440 UV detector (Waters, UV 254 nm), a Rheodyne M 7725 injector, and 250- × 4.6-mm i.d. Chiralpak and Chiralcel OD columns (Chiral Technologies). The detector output was stored and reprocessed using a Perkin-Elmer Nelson 1022. The temperature was about 20 °C. **3a**: Chiralpak AD, hexane/*i*-PrOH (100/1.5); 20.3 min (2*R*,3*S*), 21.8 min (2*S*,3*R*). **3b**: Chiralcel OD, hexane/*i*-PrOH (100/2.5); 13.8 min (2*R*,3*S*), 16.7 min (2*S*,3*R*). **3d**: Chiralpak AD, hexane/*i*-PrOH (100/2.5); 16.4 min (2*R*,3*S*), 20.9 min (2*S*,3*R*). **3e**: Chiralcel OD, hexane/*i*-PrOH (100/2.5); 35.3 min (2*R*,3*S*), 44.9 min (2*S*,3*R*). **3f**: Chiralcel OD, hexane/*i*-PrOH (100/2.5); 17.3 min (2*R*,3*S*), 23.8 min (2*S*,3*R*). **3h**: Chiralpak AD, hexane/*i*-PrOH (90/10); 11.5 min (2*R*,3*S*), 13.1 min (2*S*,3*R*). **3i**: Chiralpak AD, hexane/*i*-PrOH (80/20); 9.5 min (2*R*,3*S*), 13.9 min (2*S*,3*R*). **3j**: Chiralpak AD, hexane/*i*-PrOH (90/10); 15.4 min (2*R*,3*S*), 19.6 min (2*S*,3*R*). **3k**: Chiralpak AD, hexane/*i*-PrOH (100/2.5); 15.6 min (2*R*,3*S*), 17.3 min (2*S*,3*R*). **3m**: Chiralcel OD, hexane/*i*-PrOH (100/1.0); 20.8 min (2*R*,3*S*), 25.8 min (2*S*,3*R*). **3b**: Chiralcel OD, hexane/*i*-PrOH (100/2.5); 13.8 min (2*R*,3*S*), 16.7 min (2*S*,3*R*). **3n**: Chiralpak AD, hexane/*i*-PrOH (100/2.5); 7.6 min (2*R*,3*S*), 11.9 min (2*S*,3*R*). **3p**: Chiralpak AD, hexane/*i*-PrOH (100/0.5); 16.9 min (2*R*,3*S*), 18.2 min (2*S*,3*R*). **3q**: Chiralpak AD, hexane/*i*-PrOH (100/1.0); 12.2 min (2*R*), 13.8 min (2*S*). **3r**: Chiralcel OD, hexane/*i*-PrOH (100/2.5); 13.1 min (2*R*,3*S*), 15.7 min (2*S*,3*R*). **3s**: Chiralcel OD, hexane/*i*-PrOH (100/2.5); 14.0 min (2*R*,3*S*), 16.3 min (2*S*,3*R*). **23**: Chiralcel OD, hexane/*i*-PrOH (80/20); 14.5 min (2*R*,3*S*), 18.3 min (2*S*,3*R*).

General Procedure for Aziridination under Solid−Liquid Phase-Transfer Conditions. A 25-mL flask containing a magnetic stirring bar was charged with imines **2** (1.0 equiv), sulfonium salts **2**, **6**−**8**, **12**−**14**, **20**, or **25** (1.2 equiv), or arsonium salts **8** (1.2 equiv) and solvent (CH_3CN, Et_2O, THF, or CH_2Cl_2, 3 mL, reagent grade; it need not be dried before use). Powdered inorganic base (KOH, K_2CO_3, $LiOH·H_2O$, Cs_2CO_3, or $KF·Al_2O_3$, 1.2 equiv) was subsequently added with stirring. After reaction was complete according to TLC, the reaction mixture was filtered through a short silica gel column to remove the inorganic salts. The filtrate was concentrated and chromatographed on a silica gel column eluting with a mixture of light petroleum (bp 60−90 °C), ethyl acetate, and NEt_3 (8:1:1) to give pure products (chiral sulfides were also recovered). The results are shown in Tables 1, 4−7.

***N*-Tosyl-3-phenyl-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3a).** *cis*-**3a**: ^{1}H NMR ($CDCl_3$/TMS) δ −0.02 (s, 9 H), 2.43 (s, 3 H), 3.62 (d, J = 6.78 Hz, 1 H), 3.94 (d, J = 6.89 Hz, 1 H), 7.25−7.34 (m, 7 H), 7.88 (d, J = 8.22 Hz, 2 H); EIMS *m*/*z* (relative intensity) 370 (M^+ + 1, 1.3), 354 (2.5), 243 (1.4), 214 (100), 199 (2.9), 173 (0.6), 159 (5.7), 155 (2.5), 111 (3.2), 97 (3.9), 91 (11), 83 (10), 73 (3), 65 (4.6). Anal. Calcd for $C_{20}H_{23}NO_2SSi$: C, 65.00; H, 6.27; N, 3.79. Found: C, 65.13; H, 5.77; N, 3.75. *trans*-**3a**: ^{1}H NMR ($CDCl_3$/TMS) δ 0.24 (s, 9 H), 2.61 (s, 3 H), 3.12 (d, J = 4.01 Hz, 1 H), 4.14 (d, J = 4.01 Hz, 1 H), 7.25−7.34 (m, 7 H), 7.89 (d, J = 8.22 Hz, 2 H).

***N*-Tosyl-3-phenyl-2-acetylenylaziridine (4a).** *cis*-**4a**: ^{1}H NMR ($CDCl_3$) δ 2.07 (d, J = 1.92 Hz, 1 H), 2.40 (s, 3 H), 3.62 (dd, J = 1.69, 6.80 Hz, 1 H), 3.99 (d, J = 6.88 Hz, 1 H), 7.15−7.34 (m, 7 H), 7.88 (d, J = 8.17 Hz, 2 H); MS *m*/*z* 297 (M^+, 0.1), 217 (0.7), 182 (0.7), 142 (100), 115 (37), 104 (0.6), 91 (8.7), 89 (6), 77 (2), 69 (1), 65 (6.6); HRMS calcd for $C_{10}H_8N$ (M^+ − Ts) 142.0657, found 142.0652. *trans*-**4a**: ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3 H), 2.62 (d, J = 2.08 Hz, 1 H), 3.17 (dd, J = 2.07, 4.01 Hz, 1 H), 4.15 (d, J = 4.01 Hz, 1 H), 7.15−7.34 (m, 7 H), 7.88 (d, J = 8.17 Hz, 2 H).

***N*-Tosyl-3-(*p*-chlorophenyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3b).** *cis*-**3b**: ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 2.44 (s, 3 H), 3.62 (d, J = 6.85 Hz, 1 H), 3.90 (d, J = 6.93 Hz, 1 H), 7.26 (m, 4 H), 7.34 (d, J = 8.33 Hz, 2 H), 7.86 (d, J = 8.26 Hz, 2 H); MS *m*/*z* 406 (3.7), 404 (11), 267 (2), 250 (37), 248 (100), 179 (3), 163 (5.8), 139 (4), 123 (6), 111 (13.3), 91 (21), 83 (50), 69 (22), 47 (3); HRMS calcd for $C_{13}H_{15}ClNSi$ (M^+ − Ts) 248.0662, found 248.0623. Anal. Calcd for $C_{20}H_{22}ClNO_2SSi$: C, 59.46; H, 5.49; N, 3.47. Found: C, 59.42; H, 5.45; N, 3.79. *trans*-**3b**: ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 9 H), 2.44 (s, 3 H), 3.10 (d, J = 3.9 Hz, 1 H), 4.10 (d, J = 3.9 Hz, 1 H), 7.26 (m, 4 H), 7.34 (m, 2 H), 7.86 (m, 2 H).

***N*-Tosyl-3-(*p*-chlorophenyl)-2-acetylenylaziridine (4b).** *cis*-**4b**: ^{1}H NMR ($CDCl_3$) δ 2.07 (d, J = 1.9 Hz, 1 H), 2.44 (s, 3 H), 3.61 (dd, J = 1.89, 6.86 Hz, 1 H), 3.95 (d, J = 6.89 Hz, 1 H), 7.28 (m, 4 H), 7.35 (d, J = 8.26 Hz, 2 H), 7.88 (d, J = 8.26 Hz, 2 H); MS *m*/*z* 333 (M^+ (^{37}Cl), 0.4), 332 (M^+ (^{35}Cl), 1.33), 241 (0.54), 178 (39), 176 (100), 151 (11), 149 (32), 141 (5.4), 114 (6), 91 (9), 75 (1.4), 65 (5.4), 51 (1); HRMS calcd for $C_{10}H_7ClN$ (M^+ − Ts) 176.0267, found 176.0272. Anal. Calcd for $C_{17}H_{14}ClNO_2S$: C, 61.53; H, 4.25; N, 4.22. Found: C, 61.25; H, 4.11; N, 4.01. *trans*-**4b**: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 2.62 (d, J = 2.16 Hz, 1 H), 3.20 (dd, J = 2.17, 3.97 Hz, 1 H), 4.17 (d, J = 3.97 Hz, 1 H), 7.30 (m, 4 H), 7.38 (d, J = 8.27 Hz, 2 H), 7.93 (d, J = 8.27 Hz, 2 H).

***N*-Tosyl-3-(1-naphthyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3c).** *cis*-**3c**: ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 2.73 (s, 3 H), 4.18 (d, J = 6.67 Hz, 1 H), 4.82 (d, J = 6.84 Hz, 1 H), 7.55−7.85 (m, 6 H), 8.15−8.18 (m, 2 H), 8.26−8.31 (m, 2 H), 8.39 (m, 1 H); MS *m*/*z* 420 (M^+ + 1, 2.1), 302 (0.8), 264 (100), 249 (10), 228 (1.3), 192 (3.2), 166 (7), 141 (6), 115 (1.6), 91 (6.6), 73 (21), 65 (3), 45 (0.6); HRMS calcd for $C_{17}H_{18}NSi$ (M^+ − Ts) 264.1209, found 264.1213. Anal. Calcd for $C_{24}H_{25}NO_2SSi$: C, 68.69; H, 6.01; N, 3.34. Found: C, 68.78; H, 5.72; N, 2.98. *trans*-**3c**: ^{1}H NMR ($CDCl_3$) δ 0.62 (s, 9 H), 2.74 (s, 3 H), 3.50 (d, J = 4.32 Hz, 1 H), 5.00 (d, J = 4.27 Hz, 1 H), 7.55−7.85 (m, 6 H), 8.07 (m, 2 H), 8.26−8.31 (m, 2 H), 8.42 (m, 1 H).

***N*-Tosyl-3-(1-naphthyl)-2-acetylenylaziridine (4c).** *cis*-**4c**: ^{1}H NMR ($CDCl_3$) δ 1.81 (d, J = 1.63 Hz, 1 H), 2.45 (s, 3 H), 3.86 (dd, J = 1.66, 6.58 Hz, 1 H), 4.52 (d, J = 6.77 Hz, 1 H), 7.14−7.59 (m, 6 H), 7.79−8.09 (m, 5 H); MS *m*/*z* 348 (M^++1, 1.8), 282 (0.5), 269 (0.2), 192 (100), 177 (4), 165 (46), 153 (3.8), 141 (24), 127 (4.7), 115 (7), 91 (15), 77 (1.7), 65 (7.5), 51 (1.3); HRMS calcd for $C_{14}H_{10}N$ (M^+ − Ts) 192.0813, found 192.0809. Anal. Calcd for $C_{21}H_{17}NO_2S$: C, 72.60; H, 4.93; N, 4.03. Found: C, 72.01; H, 4.55; N, 3.69. *trans*-**4c**: ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3 H), 2.71 (d, J = 2.16 Hz, 1 H), 3.19 (dd, J = 2.11, 3.91 Hz, 1 H), 4.70 (d, J = 4.22 Hz, 1 H), 7.14−7.59 (m, 6 H), 7.79−8.09 (m, 5 H).

***N*-Tosyl-3-(*o*-methoxyphenyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3d).** *cis*-**3d**: ^{1}H NMR ($CDCl_3$) δ −0.04 (s, 9 H), 2.42 (s, 3 H), 3.66 (d, J = 7.04 Hz, 1 H), 3.81 (s, 3 H), 4.28 (d, J = 6.98 Hz, 1 H), 6.80−6.99 (m, 2 H), 7.22−7.34 (m, 4 H), 7.93 (dd, J = 1.47, 8.26 Hz, 2 H); MS *m*/*z* 400 (M^+ + 1, 0.98), 244 (100), 229 (3.2), 214 (2.2), 187 (2.5), 138 (3), 111 (1.4), 91 (7), 73 (3); HRMS calcd for $C_{14}H_{18}NOSi$ (M^+ − Ts) 244.1158, found 244.1163. Anal. Calcd for $C_{21}H_{25}NO_3SSi$: C, 63.12; H, 6.31; N, 3.51. Found: C, 63.28; H, 6.47; N, 3.29. *trans*-**3d**: ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 2.42 (s, 3 H), 3.16 (d, J = 4.30 Hz, 1 H), 3.81 (s, 3 H), 4.44 (d, J = 4.26 Hz, 1 H), 6.80−6.99 (m, 2 H), 7.22−7.34 (m, 4 H), 7.89 (d, J = 8.33 Hz, 2 H).

***N*-Tosyl-3-(*o*-methoxyphenyl)-2-acetylenylaziridine (4d).** *cis*-**4d**: ^{1}H NMR ($CDCl_3$) δ 1.97 (d, J = 2.00 Hz, 1 H), 2.43 (s, 3 H), 3.64 (dd, J = 1.99, 6.95 Hz, 1 H), 3.83 (s, 3 H), 4.27 (d, J = 6.95 Hz, 1 H), 6.80−6.92 (m, 2 H), 7.21−7.35 (m, 4 H), 7.88−7.92 (m, 2 H); MS *m*/*z* 328 (M^+ + 1, 2.2), 173 (15), 172 (100), 157 (4.4), 145 (14), 115 (5), 102 (3.4), 91 (14), 77 (2.5), 66 (16), 51 (2.2); HRMS calcd for $C_{11}H_{10}NO$ (M^+ − Ts) 172.0762, found 172.0720. *trans*-**4d**: ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3 H), 2.60 (d, J = 2.16 Hz, 1 H), 3.14 (dd, J = 2.18, 4.24 Hz, 1 H), 3.82 (s, 3 H), 4.43 (d, J = 4.16 Hz, 1 H), 6.80−6.92 (m, 2 H), 7.21−7.35 (m, 4 H), 7.88−7.92 (m, 2 H).

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***N*-Tosyl-3-(*p*-nitrophenyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3e).** *cis*-**3e**: ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 9 H), 2.45 (s, 3 H), 3.69 (d, J = 7.01 Hz, 1 H), 4.00 (d, J = 6.90 Hz, 1 H), 7.36 (d, J = 8.37 Hz, 2 H), 7.50 (dd, J = 1.93, 6.94 Hz, 2 H), 7.88 (dd, J = 1.78, 8.39 Hz, 2 H), 8.16 (dd, J = 1.78, 6.74 Hz, 2 H); MS *m*/*z* 399 (0.8), 342 (0.9), 259 (100), 231 (1.6), 204 (4.7), 187 (1.6), 171 (3), 155 (4.4), 139 (2.7), 111 (13), 97 (9), 91 (19), 83 (35.4), 65 (7.7), 43 (4.6); HRMS calcd for $C_{13}H_{15}N_2O_2Si$ (M^+ − Ts) 259.0903, found 259.0877.

***N*-Tosyl-3-(*p*-nitrophenyl)-2-acetylenylaziridine (4e).** *cis*-**4e**: ^{1}H NMR ($CDCl_3$) δ 2.08 (d, J = 2.0 Hz, 1 H), 2.43 (s, 3 H), 3.68 (dd, J = 2.03, 6.97 Hz, 1 H), 4.01 (d, J = 6.90 Hz, 1 H), 7.36 (d, J = 8.22 Hz, 2 H), 7.50 (d, J = 8.74 Hz, 2 H), 7.87 (d, J = 8.27 Hz, 2 H), 8.15 (d, J = 8.71 Hz, 2 H); MS *m*/*z* 343 (M^+ + 1, 0.6), 342 (M^+, 0.5), 259 (27.5), 243 (1.6), 187 (100), 171 (5.5), 155 (5.7), 141 (21.5), 129 (2.6), 114 (13), 102 (4), 91 (25), 65 (15), 51 (3.4); HRMS calcd for $C_{10}H_7N_2O_2$ (M^+ − Ts) 187.0508, found 187.0509.

***N*-Tosyl-3-(3-pyridinyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3f).** *cis*-**3f**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 2.45 (s, 3 H), 3.68 (d, J = 6.77 Hz, 1 H), 3.95 (d, J = 6.84 Hz, 1 H), 7.26 (m, 1 H), 7.35 (d, J = 8.16 Hz, 2 H), 7.65 (m, 1H), 7.88 (d, J = 8.34 Hz, 2 H), 8.56 (m, 2 H); MS *m*/*z* 371 (M^+ + 1, 0.1), 355 (0.2), 260 (0.3), 233 (0.6), 228 (1.3), 215 (100), 200 (3.8), 187 (1.9), 160 (5.6), 130 (1.6), 111 (7.4), 97 (7.8), 91 (21), 83 (29), 65 (8.3), 55 (2.5), 43 (4.5). Anal. Calcd for $C_{19}H_{22}N_2O_2SSi$: C, 61.58; H, 5.98; N, 7.56. Found: C, 61.87; H, 6.00; N, 7.71.

***N*-(Benzenesulfonyl)-3-(*p*-methylphenyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3g).** *cis*-**3g**: ^{1}H NMR ($CDCl_3$) δ −0.08 (s, 9 H), 2.22 (s, 3 H), 3.55 (d, J = 6.68 Hz, 1 H), 3.86 (d, J = 6.87 Hz, 1 H), 7.00 (d, J = 8.04 Hz, 2 H), 7.14 (m, 2 H), 7.40−7.55 (m, 3 H), 7.91 (m, 2 H); MS *m*/*z* 370 (M^+ + 1, 1.34), 354 (1.8), 228 (100), 213 (4.8), 198 (2), 186 (1.6), 173 (13.7), 159 (2.4), 135 (2.7), 111 (3.9), 97 (9), 83 (21), 77 (18), 69 (2.7), 59 (3.6), 51 (6); HRMS calcd for $C_{20}H_{23}NO_2SSi$ (M^+) 369.1219, found 369.1190.

***N*-Tosyl-3-(*p*-methoxyphenyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3h).** *cis*-**3h**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 2.38 (s, 3 H), 3.58 (d, J = 6.93 Hz, 1 H), 3.73 (s, 3 H), 3.88 (d, J = 6.82 Hz, 1 H), 6.80 (d, J = 8.70 Hz, 2 H), 7.22−7.30 (m, 4 H), 7.84 (d, J = 8.23 Hz, 2 H); MS *m*/*z* 400 (M^+ + 1, 0.2), 244 (100), 229 (4.2), 214 (2.7), 202 (3), 189 (14.4), 149 (2.6), 121 (3.7), 111 (3.7), 97 (6.7), 91 (18), 83 (18.5), 73 (10.7), 65 (6.9), 55 (2); HRMS calcd for $C_{14}H_{18}NOSi$ (M^+ − Ts) 244.1158, found 244.1164.

***N*-Tosyl-3-(*p*-acetoxyphenyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3i).** *cis*-**3i**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 2.26 (s, 3 H), 2.43 (s, 3 H), 3.62 (d, J = 6.76 Hz, 1 H), 3.91 (d, J = 6.84 Hz, 1 H), 7.01 (d, J = 8.60 Hz, 2 H), 7.21−7.34 (m, 4 H), 7.86 (d, J = 8.27 Hz, 2 H); MS *m*/*z* 428 (M^+ + 1, 0.1), 272 (55), 230 (100), 215 (2.7), 188 (1.5), 175 (10.7), 149 (3), 111 (3.7), 97 (5.3), 91 (11.6), 83 (15.8), 73 (5.5), 65 (4.5), 55 (1.6), 43 (4.5); HRMS calcd for $C_{15}H_{18}NO_2Si$ (M^+ − Ts) 272.1107, found 272.1103.

***N*-Tosyl-3-(*p*-methylthiophenyl)-2-(*β*-(trimethylsilyl)-acetylenyl)aziridine (3j).** *cis*-**3j**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 2.44 (s, 3 H), 2.46 (s, 3 H), 3.60 (d, J = 6.86 Hz, 1 H), 3.88 (d, J = 6.83 Hz, 1 H), 7.17 (d, J = 8.46 Hz, 2 H), 7.23 (d, J = 8.90 Hz, 2 H), 7.32 (d, J = 8.16 Hz, 2 H), 7.86 (d, J = 8.22 Hz, 2 H); MS *m*/*z* 416 (M^+ + 1, 1.1), 400 (0.8), 260 (100), 245 (2.5), 213 (8.8), 205 (8.6), 188 (2.0), 155 (3.7), 137 (3), 126 (2.6), 111 (3), 97 (5), 91 (19), 83 (13.5), 77 (2.3), 73 (6.3), 65 (8), 55 (1.7); HRMS calcd for $C_{14}H_{18}NSSi$ (M^+ − Ts) 260.0929, found 260.0916.

***N*-Tosyl-3-(2-furyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3k).** *cis*-**3k**: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 2.44 (s, 3 H), 3.63 (d, J = 6.85 Hz, 1 H), 3.96 (d, J = 6.76 Hz, 1 H), 6.32 (dd, J = 1.83, 3.32 Hz, 1 H), 6.42 (d, J = 3.23 Hz, 1 H), 7.32−7.37 (m, 3 H), 7.86 (dd, J = 1.61, 8.27 Hz, 2 H); MS *m*/*z* 360 (M^+ + 1, 2.0), 359 (M^+, 0.9), 204 (100), 177 (4.1), 155 (2.3), 139 (3.5), 111 (2), 97 (2.5), 91 (13), 83 (2.7), 77 (1.2), 65 (7.2); HRMS calcd for $C_{11}H_{14}NOSi$ (M^+ − Ts) 204.0845, found 204.0861.

***N*-Tosyl-3-(*β*-phenylvinyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3m).** *cis*-**3m**: ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9 H), 2.44 (s, 3 H), 3.55−3.58 (m, 2 H), 6.02 (m, 1 H), 6.79 (d, J = 16.04 Hz, 1 H), 7.26−7.36 (m, 7 H), 7.86 (dd, J = 1.52, 8.26 Hz, 2 H); MS *m*/*z* 395 (M^+, 0.8), 240 (100), 224 (10), 210 (4.4), 185 (7.6), 168 (8), 155 (3.8), 149 (9.3), 115 (63), 91 (22), 73 (45.6), 65 (6.2); HRMS calcd for $C_{15}H_{18}NSi$ (M^+ − Ts) 240.1209, found 240.1230.

***N*-Tosyl-3-cyclohexyl-2-(*β*-(trimethylsilyl)acetylenyl)-aziridine (3n).** *cis*-**3n**: ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9 H), 0.95−1.79 (m, 11 H), 2.44 (s, 3 H), 2.56 (dd, J = 6.83, 9.45 Hz, 1 H), 3.34 (d, J = 7.02 Hz, 1 H), 7.33 (d, J = 7.86 Hz, 2 H), 7.82 (d, J = 8.26 Hz, 2 H); MS *m*/*z* 376 (M^+ + 1, 1.6), 360 (1.5), 220 (100), 204 (12), 192 (2.7), 178 (2.6), 155 (5.5), 152 (26), 138 (12), 126 (95.5), 111 (8.5), 95 (57), 91 (34), 73 (51), 67 (18), 55 (13.8); HRMS calcd for $C_{13}H_{22}NSi$ (M^+ − Ts) 220.1522, found 220.1547.

***N*-Tosyl-3-(*tert*-butyl)-2-(*β*-(trimethylsilyl)acetylenyl)-aziridine (3p).** *cis*-**3p**: ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 0.92 (s, 9 H), 2.43 (s, 3 H), 2.51 (d, J = 7.4 Hz, 1 H), 3.25 (d, J = 7.25 Hz, 1 H), 7.33 (d, J = 8.05 Hz, 2 H), 7.83 (d, J = 8.26 Hz, 2 H); MS *m*/*z* 350 (M^+ + 1, 0.5), 334 (0.8), 280 (2), 264 (1.3), 228 (0.7), 194 (100), 178 (2.9), 155 (5), 149 (6), 126 (20), 110 (4), 100 (5.5), 96 (16), 91 (22), 83 (10.5), 77 (1.7), 73 (78), 69 (27), 65 (7.6), 57 (6.4), 43 (5.4); HRMS calcd for $C_{11}H_{20}NSi$ (M^+ − Ts) 194.1365, found 194.1381.

***N*-Tosyl-3,3-dimethyl-2-(*β*-(trimethylsilyl)acetylenyl)-aziridine (3q):** ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 1.41 (s, 3 H), 1.73 (s, 3 H), 2.41 (s, 3 H), 3.39 (s, 1 H), 7.30 (d, J = 8.19 Hz, 2 H), 7.82 (d, J = 8.27 Hz, 2 H); MS *m*/*z* 322 (M^+ + 1, 0.68), 306 (1.5), 166 (100), 155 (2), 149 (4.2), 138 (11.5), 109 (4.8), 97 (20.7), 91 (14), 83 (12), 73 (16), 68 (14), 65 (7), 59 (5); HRMS calcd for $C_9H_{16}NSi$ (M^+ − Ts) 166.1052, found 166.1031.

***N*-Tosyl-3-(*p*-fluorophenyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3r).** *cis*-**3r**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 2.44 (s, 3 H), 3.61 (d, J = 6.98 Hz, 1 H), 3.92 (d, J = 6.81 Hz, 1 H), 6.98 (m, 2 H), 7.26−7.36 (m, 4 H), 7.87 (d, J = 8.27 Hz, 2 H); MS *m*/*z* 388 (M^+ + 1, 0.1), 372 (0.65), 253 (0.5), 232 (100), 217 (3.9), 202 (1.6), 177 (13), 160 (3.1), 155 (2), 133 (2.5), 111 (9.3), 97 (6.9), 91 (14), 83 (32), 77 (2), 65 (6.8); HRMS calcd for $C_{13}H_{15}FNSi$ (M^+ − Ts) 232.0957, found 232.0945.

***N*-Tosyl-3-(*p*-bromophenyl)-2-(*β*-(trimethylsilyl)acetylenyl)aziridine (3s).** *cis*-**3s**: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 2.44 (s, 3 H), 3.63 (d, J = 6.62 Hz, 1 H), 3.88 (d, J = 6.89 Hz, 1 H), 7.19 (dd, J = 1.94, 6.63 Hz, 2 H), 7.34 (m, 2 H), 7.42 (dd, J = 1.97, 6.55 Hz, 2 H), 7.86 (dd, J = 1.81, 6.57 Hz, 2 H); MS *m*/*z* 448 ($M^+(^{81}Br)$, 0.2), 446 ($M^+(^{79}Br)$, 0.2), 432 (0.6), 430 (0.6), 294 (100), 292 (95), 279 (2.7), 277 (2.6), 239 (8), 237 (8.2), 213 (4.6), 198 (3), 183 (2.5), 155 (4.4), 149 (4), 139 (4.4), 111 (12), 97 (9.9), 91 (18), 83 (39), 77 (2), 65 (7); HRMS calcd for $C_{13}H_{15}NSiBr^{79}$ (M^+ − Ts) 292.0157, found 292.0233; calcd for $C_{13}H_{15}NSiBr^{81}$ (M^+ − Ts) 294.0136, found 294.0165.

***N*-Tosyl-3-(*p*-chlorophenyl)-2-(phenylacetylenyl)aziridine (23).** *cis*-**23**: ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3 H), 3.88 (d, J = 6.66 Hz, 1 H), 4.05 (d, J = 6.77 Hz, 1 H), 7.10−7.40 (m, 11 H), 7.92 (d, J = 8.25, 2 H); MS *m*/*z* 254 ($M(^{37}Cl)$ − Ts, 100), 252 ($M(^{35}Cl)$ − Ts, 35), 225 (32.2), 189 (18.2), 115 (13.0), 91 (27.3), 65 (14.9); HRMS calcd for $C_{16}H_{21}Cl^{35}N$ (M^+ − Ts) 252.0580, found 252.2582. *trans*-**23**: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 3.35 (d, J = 3.90 Hz, 1 H), 4.22 (d, J = 3.99 Hz, 1 H), 7.10−7.40 (m, 11 H), 7.92 (d, J = 8.20, 2 H).

***N*-Tosyl-3-(*p*-chlorophenyl)-2-(*n*-hexylacetylenyl)aziridine (24).** *cis*-**24**: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3 H), 1.05−1.40 (m, 2 H), 1.98 (m, 2 H), 2.50 (s, 3 H), 3.63 (d, t, J = 6.73, 1.60 Hz, 1 H), 3.90 (d, J = 6.96 Hz, 1 H), 7.27 (m, 4 H), 7.33 (d, J = 8.32 Hz, 2 H), 7.87 (d, J = 8.23 Hz, 2 H); MS *m*/*z* 418 (M^+ + 2, 7.80), 416 (M^+, 3.09), 260 (100), 125 (7.64), 91 (13.2), 65 (5.1); HRMS calcd for $C_{23}H_{26}Cl^{35}NO_2S$ (M^+) 252.1451, found 416.1467. *trans*-**24**: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3 H), 1.05−1.40 (m, 2 H), 1.98 (m, 2 H), 2.51 (s, 3 H), 3.12 (d, t, J = 3.98, 1.60 Hz, 1 H), 4.03 (d, J = 3.98 Hz, 1 H), 7.27 (m, 4 H), 7.33 (d, J = 8.32 Hz, 2 H), 7.87 (d, J = 8.23 Hz, 2 H).

General Procedure for Aziridination at −78 °C. A solution of the base (*n*-BuLi in hexanes, $LiN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $KN(SiMe_3)_2$, $NaN(SiMe_3)_2$ + LiBr, LDA, NaH, or

t-BuOK in THF, 1.2 equiv) was added dropwise to a solution of a sulfonium (**2** or **6**), telluronium (**7**), or arsonium (**8**) in 6 mL of THF at −78 °C under nitrogen. The mixture was stirred for 5−30 min (5 min for **6**, 30 min for others), and imine (1.0 equiv) in 4 mL of 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 the inorganic salt. The filtrate was concentrated and chromatographed on a silica gel column with petroleum ether (60−90 °C) and ethyl actate (4/1) as the eluent to give pure product. The results are shown in Tables 2 and 3.

Determination of Absolute Configuration of Aziridine (−)-*cis*-3a. Silylated aziridine (−)-*cis*-**3a** (369 mg, 1 mmol) and powdered KOH (56 mg, 1 mmol) were stirred in 4 mL of CH_3CN at room temperature. After completion of the reaction (about 30 min), the reaction mixture was filtered and evaporated to leave a white solid (**16**) (291 mg, 98% yield). It was pure enough for further use. Acid **17** was prepared according to the literature procedure:[24] PhIO (490 mg, 2.23 mmol) in 8 mL of CH_2Cl_2 was added to 2 mL of a CH_2Cl_2 solution of $RuCl_2(PPh_3)_3$ (18 mg). After stirring for 2 min, a CH_2Cl_2 solution of compound **16** (245 mg, 0.82 mmol, in 2 mL of solvent) was added. The reaction mixture was further stirred for 24 h. After workup according to the literature procedure,[24] solid acid **17** was obtained in 79% yield (206 mg). It was treated with CH_2N_2 in ether at 0 °C for 12 h to give ester **18** in 64% yield: $[\alpha]^{20}_D = +15.3$ ($c = 2.0$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ 2.44 (s, 3 H, CH_3), 3.49 (s, 3 H, OCH_3), 3.70 (d, $J = 7.5$ Hz, 1 H), 4.11 (d, $J = 7.4$ Hz, 1 H), 7.29 (m, 5 H), 7.35 (d, $J = 8.0$ Hz, 2 H), 7.92 (d, $J = 8.1$ Hz, 2 H). By comparison of the optical rotations with the known compound, (+)-**18** should have a configuration of 2*S*,3*S*,[7d] and therefore, the absolute configuration of (−)-*cis*-**3a** is unambiguously assigned as 2*R*,3*S*.

(24) Müller, P.; Godoy, J. *Helv. Chim. Acta* **1981**, *64*, 2531.

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Supporting Information Available: Copies of NMR spectra (24 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.

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