Deprotection of Sulfonyl Aziridines

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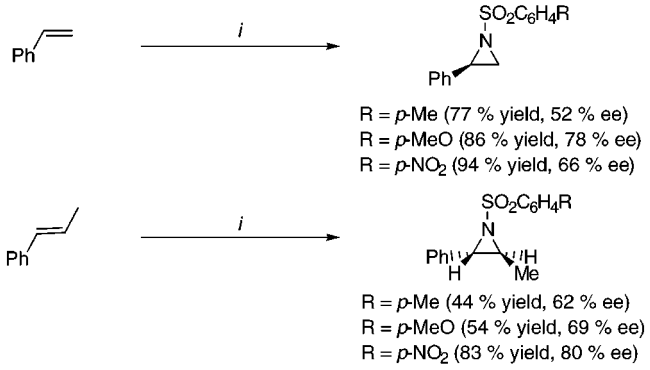
The deprotection of the chiral *N*-sulfonyl aziridines **1**−**3** has been studied under different desulfonylation conditions. Two methods for the efficient deprotection of 2-benzyl-, 2-phenyl-, and 2-carboxyl-*N*-sulfonylaziridines were found. The desulfonylation with lithium and a catalytic amount of di-*tert*-butyl biphenyl in THF at −78 °C led to the corresponding NH aziridines with yields up to 85%. Alternatively, the desulfonylation could be carried out with magnesium in methanol under ultrasonic conditions. The latter proved to be a very mild method and afforded the desulfonylated aziridines with yields up to 75%, even when the 2-phenyl substituted aziridine **2** was the studied substrate. Furthermore, in all the cases studied, no racemization was observed in the chiral center of the aziridines.

Introduction

Chiral aziridines are very useful intermediates in organic synthesis.[1] Their utilities as substrates, reagents, auxiliaries, and ligands have been demonstrated, and their preparation is an area of current interest.[2] Among the different routes to chiral nonracemic aziridines,[3] the asymmetric copper-catalyzed addition of nitrenoides to alkenes has a particularly high potential and has been intensively studied by different groups.[4] We have recently reported significant improvements of both enantioselectivity and chemical yield in this reaction by the use of nitrene precursors with different electronic properties.[5] In this way, it was found that the results with either [*N*-(4-methoxybenzenesulfonyl)imino]phenyliodinane or [*N*-(4-nitrobenzenesulfonyl)imino]phenyliodinane were, in all the cases studied, superior to those obtained with the previously used *p*-tolyl analogue (Scheme 1).

However, a major drawback with this method is the difficult removal of the *N*-sulfonyl group. Even though a wide variety of synthetic methods for the cleavage of the N−S bond are available,[6] considerably less attention has been devoted to the study of the desulfonylation of aziridines. Their high ring tension in combination with an electron-withdrawing group at the nitrogen makes them very vulnerable to undergo ring opening, and as a result, only a few examples of the deprotection of *N*-tosylaziridines have been reported.[7] However, none are general and without problems, which severely limits the scope of these procedures.[8] For instance, the method recently reported by Fukuyama for deprotection of nitrobenzene sulfonamides[9] invariably leads to ring opening products when applied to sulfonyl aziridines (Scheme 2).

Scheme 1[a]



[a] Key: (i) *p*-$RC_6H_4O_2SN$=IPh (1.5 equiv), CuOTf (5 mol %), *t*-Bu−Evans' bisoxazoline (6 mol %).

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(8) Good yields in the desulfonylation reactions were restricted to highly hindered 3-alkyl-2-aryl substituted *N*-(arenesulfonyl)aziridines.

(9) (a) Fukuyama, T.; Jow, Ch.-K.; Cheung, M. *Tetrahedron Lett.* **1995**, *36*, 6373. (b) Fukuyama, T.; Cheung, M.; Jow, Ch.-K.; Hidai, Y.; Kan, T. *Tetrahedron Lett.* **1997**, *33*, 5831. (c) Poor regioselectivities have been recently obtained in the deprotection of *N*-nosylate protected oxazolidines using Fukuyama's conditions: Wuts, P. G. M.; Northuis, J. M. *Tetrahedron Lett.* **1998**, *39*, 3889.

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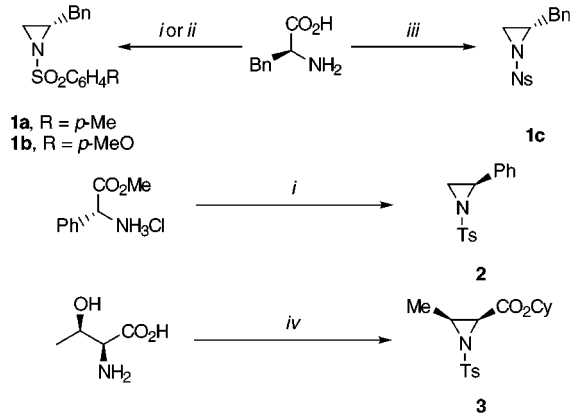
Scheme 2[a]

[a] Key: (i) PhSH (1 equiv), Et_3N (3 equiv), DMF, rt (92 %).

Scheme 3[a]



[a] Key: (i) (a) TsCl, Et_3N; (b) $LiAlH_4$; (c) TsCl, Et_3N; (60% for **2**, 87% for **1a**). (ii) (a) *p*-$MeOC_6H_4SO_2Cl$, Et_3N; (b) $LiAlH_4$; (c) TsCl, Et_3N; (70% for **1b**). (iii) (a) $LiAlH_4$; (b) *p*-$NO_2C_6H_4SO_2Cl$, Et_3N; (c) MsCl, Et_3N; (60%). (iv) (a) CyOH, $SOCl_2$, 80%; (b) TsCl, Et_3N, 100%; (c) DEAD, Ph_3P, 85%.

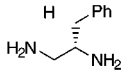
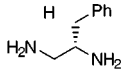
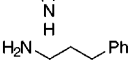
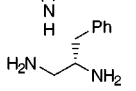
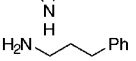
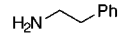
In this paper, we present our efforts to find a general yet mild method for the selective desulfonylation of aziridines that leaves the three-membered ring intact. Three different aziridines **1**−**3** (Scheme 3) have been studied, among them the 2-phenyl substituted aziridine **2**, which is particularly difficult to desulfonylate due to the presence of the labile benzylic C−N bond.

Results and Discussion

Synthesis of Chiral *N*-Sulfonylaziridines. Aziridines **1** and **2** are readily accessible from enantiomerically pure amino acids (or their esters) via either (a) *N*-sulfonylation reaction, reduction to the corresponding amino alcohols, and activation of the primary alcohol group with in situ aziridine ring closure[10] (for aziridines **1a**, **1b**, and **2**) or (b) direct reduction of the amino acid, followed by *N*-nosylation and *O*-mesylation with in situ aziridine ring closure[11] (for aziridine **1c**). Aziridine **3** was synthesized from L-threonine following a known procedure[12] (Scheme 3). The optical purity of tosyl aziridines **1a** and **2** was determined by HPLC analysis and found to be higher than 98% ee.

Desulfonylation Studies of Aziridines 1−3. For the study of the desulfonylation of aziridines **1**−**3**, five different N−S bond cleavage reactions were compared: metals in liquid ammonia,[6e,13] magnesium in methanol,[14] arene anion radicals,[6c,d] samarium iodide,[6h] and photoinduced electron transfer.[6i,j]

Table 1. Reduction of Aziridines 1−3 with Metal in Liquid Ammonia

Entry	Aziridine	Metal	Product no.	Product Structure	Yield (%)[a]
1	**1a**	Li	**4**		40
			5		20
2	**1b**	Li	**4**		32
			5		30
3	**3**	Li	-	*b*	-
4	**1a**	Na	**4**		8
			6		47
5	**1b**	Na	**4**		15
			5		30
6	**1c**	Na	**4**		13
			6		71
7	**2**	Na	**7**		85
8	**3**	Na	-	*b*	-
9	**1b**	Ca	**4**		20

[a] Isolated yield after flash chromatography (silica gel, ether/acetone). [b] Nonanalyzed complex mixture of compounds.

1. Desulfonylations with Metals in Liquid Ammonia. A series of experiments using dissolved metals in liquid ammonia[13] was carried out for the reduction of the 2-benzyl and 2-phenyl aziridines **1** and **2** and aziridine **3**. Lithium, with a high reducing ability, was tested first. Unfortunately, reduction of aziridines **1a** and **1b** with lithium powder (10 equiv) in liquid ammonia led to mixtures of the 1,2-diamine **5**, formed via a nucleophilic ring opening of the aziridine with the sodium amide desulfonylation process, and the corresponding NH aziridine **4** in variable ratios and in moderate yields (Table 1, entries 1 and 2). Reduction of aziridine **3** led to a complex mixture of compounds (entry 3). Because the reducing ability of metals dissolved in NH_3 follows the trend Li >K > Rb > Na > Ca,[15] we continued our experiments using sodium or an alkaline earth metal such as calcium which, due to its lower reduction potential, has offered good selectivites in the reduction of organic compounds bearing multifunctional groups.[13] However, these reductive systems also led to extensive ring opening formation and afforded the desulfonylated aziridines only in low yields (Table 1, entries 4 to 9).

2. Desulfonylations with Magnesium. Recently, excellent results in the reduction of alkyl sulfones have been achieved by using magnesium in methanol as the

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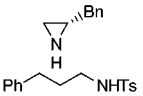
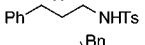
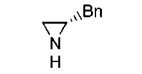
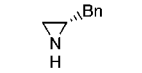
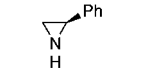
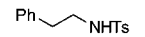
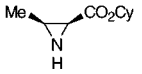
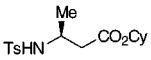
(13) (a) Takeda, Y.; Matsumoto, T.; Sato, F. *J. Org. Chem.* **1986**, *51*, 4731. (b) Hwu, J. R.; Wein, Y. S.; Leu, Y.-J. *J. Org. Chem.* **1996**, *61*, 1493.
(14) For the desulfonylation of *N*-sulfonylcarbamates using magnesium and ultrasound, see: Nyasse, B.; Grehn, L.; Ragnarsson, U. *Chem. Commun.* **1997**, 1017.
(15) Pleskov, V. A. *Zh. Fiz. Khim.* **1937**, *9*, 12; *Acta Physicochim. URSS* **1937**, *6*, 1.

Table 2. Reduction of Aziridines 1−3 with Mg in MeOH

Entry	Aziridine	Method[a]	Product no.	Product Structure	Yield (%)[b]
			1a	-	20
1	**1a**	A	**4**		55
			8		10[c]
2	**1a**	B	**4**		78[d]
3	**1b**	B	**4**		70[d]
4	**1c**	B	-	*e*	-
5	**2**	B	**9**		65[d]
			10		8
6	**3**	B	**11**		75[f]
			12		12

[a] Method A: reduction with Mg (5 equiv) in MeOH at rt; Method B: reduction with Mg (5 equiv) in MeOH under ultrasonic conditions. [b] Isolated yield after flash chromatography (silica gel, ether/acetone). [c] With 10 equiv of Mg, 20% of **8** together with 60% of desulfonylated aziridine **4** were obtained. [d] Enantiomeric excess for NH aziridines **4** and **9** was determined to be >98% after tosylation and HPLC analysis (WHELK-O, 1 mL/min hexane/*i*-PrOH, 95/5). [e] Nonanalyzed complex mixture of compounds. [f] Enantiomeric excess for NH aziridine **11** was determined to be >98% ee after tosylation and optical rotation analysis on the tosyl derivative.

cleaving agent.[16] However, this method has not been widely used, and only one example has been reported so far on the cleavage of a N−S bond (a *N*-tosyl protected indole).[17]

In the first experiments, aziridine **1a** was treated with 5 equiv of magnesium in dry methanol at room temperature (Table 2, entry 1). The reaction resulted in a fast consumption of the metal (ca. 40 min) and production of the NH aziridine, along with up to 20% of unreacted aziridine as well as 10% of ring opening product **8**. Using larger amounts of magnesium (10 equiv) gave full conversion of the starting material but also led to more extensive production of the *N*-tosylamine **8**. However, when the reaction was allowed to proceed under ultrasonic conditions[14] (5 equiv of magnesium in dry methanol), good yields of the corresponding desulfonylated aziridines were obtained (Table 2, entries 2 and 3). Unfortunatly, a complex yellow mixture of compounds was the result of the reaction when the *N*-nosyl aziridine **1c** was used, probably resulting from the reduction of the nitro group.[18]

We were particularly pleased to also find that the 2-phenyl substituted aziridine **2** gave a good yield of the NH aziridine. This is, to the best of our knowledge, the best result obtained so far for the desulfonylation of simple *N*-arenesulfonyl-2-phenylaziridines (Table 2, entry 5).

These mild reaction conditions are also compatible with other functional groups. For instance, reduction of carboxylate aziridine **3** provided a 75% yield of the desulfonylated aziridine **11** accompanied by only 12% of the ring opening product **12**.[19] This successful reduction of **3**, together with the results discussed before, clearly demonstrates the utility of this method in the desulfonylation of sensitive aziridines, not only because of the good selectivities obtained but also because no racemization of the chiral center on the aziridines could be detected in any case.[20]

3. Arene Radical Desulfonylations. It has previously been reported that the use of anion radicals derived from aromatic hydrocarbons (mainly naphthalene and anthracene) and alkaline metals such as Li or Na[21] leads to efficient cleavage of arenesulfonamides, but very few examples exist on the use of this methodology for the desulfonylation of aziridines.[22] Initial experiments using the *N*-tosylated aziridine **1a** as substrate revealed that the use of Li/naphthalene led to higher yields of desulfonylated aziridine than Na/naphthalene (Table 3, entries 1 and 2).

Even better results were obtained using an excess of lithium powder in the presence of a catalytic amount (10 mol %) of di-*tert*-butyl biphenyl (DTBB). To our surprise, not only substrates **1a** and **1b** gave very satisfactory results with yields up to 85% (Table 3, entries 3 and 4), but also the nosyl derivative **1c** and the aziridine **2** gave the desulfonylated products with acceptable yields (entries 5 and 6). Moreover, in the case of aziridine **2**, no ring opening products could be detected by ^{1}H NMR.[23] Again, all the cases studied presented no racemization in the chiral center of the desulfonylated aziridines.[20] However, in the case of aziridine **3**, the ring opening product **12** was isolated as the major component of a complex mixture of products (Table 3, entry 7).

4. Desulfonylations with SmI_2. Samarium(II) iodide is a powerful one-electron reducing agent capable of reducing a wide range of functional groups with a high degree of selectivity under neutral conditions. This mild reagent, however, has not been widely used for the deprotection of sulfonamides,[6g] and only two examples for the desulfonylation of *N*-tosylaziridines have been reported by Vedejs.[7c]

(16) Lee, G. H.; Choi, E. B.; Lee, E.; Pak, C. S. *Tetrahedron Lett.* **1993**, *34*, 4541.

(17) Yokoyama, Y.; Matsumoto, T.; Murakami, Y. *J. Org. Chem.* **1995**, *60*, 1486.

(18) *N*-(4-Aminobenzenesulfonyl)-(2*S*)-benzylaziridine could be isolated as one of the major components of the mixture.

(19) A similar regioselective ring opening process has been observed in the reduction with SmI_2 of aziridine-2-carboxylates: Molander, G. A.; Stengel, P. J. *Tetrahedron* **1997**, *53*, 8887.

(20) No racemization was observed (HPLC analysis, WHELK-O, 1 mL/min hexane/*i*-PrOH, 95/5) in the tosyl aziridines obtained after tosylation of the corresponding NH aziridines with tosyl chloride and Et_3N in CH_2Cl_2.

(21) For the reduction of arene sulfonamides using Na/naphthalene, see: (a) Ji, S.; Gortler, L. B.; Waring, A.; Battisti, A.; Bank, S.; Closson, W. D.; Wriede, P. *J. Am. Chem. Soc.* **1967**, *89*, 3311. (b) Sugimura, H.; Miura, M.; Yamada, N. *Tetrahedron: Asymmetry* **1997**, *8*, 4089. For the reduction of *N*-substituted tosylamides with lithium and a catalytic amount of naphthalene, see: Alonso, E.; Ramón, D. J., Yus, M. *Tetrahedron* **1997**, *53*, 14355.

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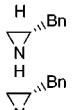
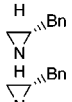
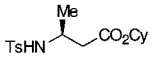
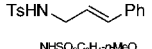
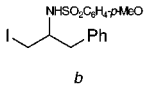
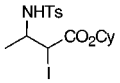
(23) For naphthalene-catalyzed reductive opening of aziridines with lithium, see: (a) Almena, J., Foubelo, F.; Yus, M. *Tetrahedron Lett.* **1993**, *34*, 1649. (b) Almena, J., Foubelo, F.; Yus, M. *J. Org. Chem.* **1994**, *59*, 3210.

Table 3. Arene-Catalyzed Reduction of Aziridines 1−3

Entry	Aziridine	Method[a]	Product no.	Product Structure	Yield (%)[b]
1	**1a**	A	**4**		50[c]
2	**1a**	A	**4**		73[d]
3	**1a**	B	**4**		83[d]
4	**1b**	B	**4**		85[d]
5	**1c**	B	**4**		55[d]
6	**2**	B	**9**		40[d]
7	**3**	B	**12**		25

[a] Method A: sodium or lithium metal (entries 1 or 2) (4 equiv) and a stoichiometric amount of naphthalene (4.5 equiv); Method B: lithium powder (8 equiv) and a catalytic amount of DTBB (10 mol % to the substrate).[b] Isolated yield after flash chromatography (silica gel, ether/acetone).[c] Ring opening products as well as starting material were detected on the crude reaction mixture. [d] Enantiomeric excess for NH aziridines **4** and **9** was determined to be >98% after tosylation and HPLC analysis (WHELK-O, 1 mL/min hexane/*i*-PrOH, 95/5).

Table 4. SmI_2 Reduction of Aziridines 1−3

Entry	Aziridine	Additive	Temp.	Product no.	Product Structure	Yield (%)[a]
1	**1a**	-	rt	**1a**	-	-
2	**1a**	DMPU	rt	**1a**	-	-
3	**1a**	DMPU	reflux	**13**		50
4	**1b**	DMPU	reflux	**14**		55
5	**2**	DMPU	reflux	-	*b*	-
6	**3**	*c*	rt	**15**		70

[a] Isolated yield after flash chromatography (silica gel, EtOAc/pentane). [b] No desulfonylated aziridine could be detected in the crude reaction mixture (see ref 7c). [c] Similar results were obtained with or without DMPU as additive.

Initial studies were focused on the reaction of the tosyl protected aziridine **1a** using 6 equiv of SmI_2[24] in THF at room temperature. As can be seen in Table 4, entries 1 and 2, even upon addition of *N*,*N*-dimethylpropyleneurea (DMPU) as a cosolvent[25] only unreacted starting material was recovered from the reaction. On the contrary, running the reaction in refluxing THF indeed resulted in the consumption of the starting material, but sulfonamide **13** was the only isolated product in a 50% yield (Table 4, entry 3). Similary, reaction of aziridines **1b** and **3** with SmI_2 produced the ring opening iododerivatives **14** and **15** in moderate yields (Table 4, entries 4 and 6). This highly regioselective ring opening reaction with SmI_2 is currently under investigation in our group.[26] Aziridine **2** only produced a mixture of compounds in which the desulfonylated aziridine could not be detected.[7c]

Table 5. Photolysis of Aziridines 1[a]

Entry	Aziridine	Donor	Reductant	Filter	Product
1	**1a**	-	-	quartz	*b*
2	**1a**	-	-	pyrex	s. material
3	**1a**	veratrol[c]	-	pyrex	s. material
4	**1b**	veratrol[c]	-	pyrex	s. material
5	**1c**	veratrol[c]	-	pyrex	s. material
6	**1a**	veratrol	NH_2NH_2	pyrex	*d*
7	**1a**	veratrol	$NaBH_4$	pyrex	*d*
8	**1a**	veratrol	AA	pyrex	*d*

[a] In a typical experiment, a 10 mM solution of the aziridine (1 equiv), a donor (3 equiv), and the corresponding reductant (10−15 equiv) in 95% EtOH were irradiated during 24 h with a low-pressure mercury lamp under nitrogen. When donors were used, a pyrex filter was applied to cut off the light below 300 nm. [b] Photodegradation products were obtained. [c] Similar results were obtained when 1,4-dimethoxynaphthalene was used as a donor. [d] Nonanalyzed mixture of ring opening products.

5. Photodesulfonylations. In recent years, the use of protecting groups for which the regeneration of the protected function can be accomplished by photochemical means has become an attractive field in organic synthesis.[27] In addition, the potential of sulfonamides as photolabile protecting groups for the amino function has been recently investigated.[6h,28]

Initial experiments on aziridine **1a**, with irradiation below 300 nm in aqueous ethanol, led only to photodegradation products (Table 5, entry 1). When the reaction was carried out with UV light of wavelength longer than 300 nm (Pyrex filter), the electron-accepting tosyl group remained unchanged even in the presence of longer wavelength electron-donating chromophores such as veratrol or 1,4-dimethoxynaphthalene (Table 5, entries 2 and 3).

We have also studied the nosyl and *p*-methoxybenzenesulfonamide protecting groups in aziridines **1b** and **1c** as potentially photoremovable protecting groups. In spite of the different absorption pattern shown by these groups, only unreacted starting material was recovered from the reaction (Table 5, entries 4 and 5). The use of coreductants (hydrazine, $NaBH_4$, and ascorbic acid) together with electron-donating chromophores led only to ring opening adducts (Table 5, entries 6−8).

Conclusions

In conclusion, we have shown that chiral *N*-sulfonyl aziridines can be efficiently deprotected using magnesium under ultrasonic conditions or lithium in the presence of a catalytic amount of DTBB. The former method appears to be more general for the substrates studied, including

(24) For the preparation of SmI_2, see: Molander, G. A.; Kenny, C. *J. Org. Chem.* **1991**, *56*, 1439.

(25) Additives such as DMPU, HMPA, and TMEDA are usually used to increase the reduction potential of SmI_2. See ref 17 and Shabangi, M.; Sealy, J. M.; Fuchs, J. R.; Flowers, R. A., II. *Tetrahedron Lett.* **1998**, *39*, 4429.

(26) Alonso, D. A.; Andersson, P. G. Unpublished results.

(27) Pillai, V. N. R. *Synthesis* **1980**, 1.

(28) (a) Pincock, J. A.; Jurgens, A. *Tetrahedron Lett.* **1979**, *12*, 1029. (b) Epling, G. A., Walker, M. E. *Tetrahedron Lett.* **1982**, *23*, 3843. (c) Hamada, T.; Nishida, A., Yonemitsu, O. *J. Am. Chem. Soc.* **1986**, *108*, 140. (d) Art, J. F.; Kestemont, J. P.; Soumillon, J. Ph. *Tetrahedron Lett.* **1991**, *32*, 1425.

the 2-phenyl substituted aziridine, which is very difficult to deprotect due to the presence of the benzylic C−N bond. In addition, the mild reaction conditions tolerate different functionalization on the aziridine ring. Finally, it is also important to note that in all the cases studied no racemization of the chiral center of the aziridines was observed.

Experimental Section

For general experimental information see ref 29. Flash cromatography was preformed on silica gel (Matrex 60A, 37−70 μm). When mentioned, deactivated silica gel means that it was treated with 5% Et_3N in pentane and the column was eluted with the same solvent mixture until the eluent was basic according to pH paper. TLC was preformed on precoated plates, SIL G-60 UV_{254}, purchased from Macherey−Nagel. When mentioned, deactivated silica gel means that the TLC plate was eluted with 5% Et_3N in pentane and dried before application of the sample. HPLC analysis was carried out using a chiral column (WHELK-O), using a 254 nm UV detector and a flow rate of 1 mL/min of hexane/*i*-PrOH, 95/5. For the Mg in methanol reductions under ultrasonic conditions, magnesium powder (Aldrich, −50 mesh 99+%) and a 35 kHz, 120−240 W (Elma, type T 570/H) ultrasonic bath were used. Li powder, Ca granules (ca. 6 mesh 99%), Na lump in kerosene, Sm (ingot, 99.9%), and anhydrous MeOH (99.8%) were all purchased from Aldrich Co. A low-pressure mercury lamp (ACE Glass) was used for the photochemical desulfonylations.

Synthesis of Aziridines 1a and 1b. To a cooled (0 °C) solution of (*S*)-phenylalanine (5 g, 30 mmol) in CH_2Cl_2 (50 mL) and Et_3N (2.5 equiv, 75 mmol) was added portionwise *p*-toluenesulfonyl chloride (1 equiv, 30 mmol) (for aziridine **1a**) or *p*-methoxysulfonyl chloride (1 equiv, 30 mmol) (for aziridine **1b**), and the reaction was stirred at room temperature for 12 h. The reaction mixture was then washed with water (3 × 50 mL), and the organic phase was dried ($MgSO_4$) and concentrated under vacuo to give the corresponding *N*-protected-(*S*)-phenylalanines. $LiAlH_4$ (2 equiv) was added portionwise under a nitrogen atmosphere to a cooled (0 °C) solution in dry THF of these compounds (1 equiv), and the reactions were stirred at room temperature for 12 h and then quenched following a literature procedure.[30] Then, *p*-toluenesulfonyl chloride (1 equiv) was added portionwise to a cooled (0 °C) solution of the obtained amino alcohols (1 equiv) in CH_2Cl_2 (60 mL) and Et_3N (2 equiv), and the reactions were stirred at room temperature for 12 h. The reactions were then hydrolyzed with water and extracted three times with CH_2Cl_2 (50 mL). The combined organic phases were dried ($MgSO_4$) and concentrated to give the corresponding crude aziridines which were purified by flash chromatography (silica gel, pentane/EtOAc, 5/1) and recrystallized from EtOAc/pentane to afford the pure compounds as white solids (87% yield for **1a**; 70% for **1b**).

***N*-Tosyl-(2*S*)-benzylaziridine (1a)**:[10] R_f 0.78 (pentane/EtOAc, 3/1); mp 94−95 °C (pentane/EtOAc); $[\alpha]^{25}_D$ 17.8 (*c* 1.82, $CHCl_3$); IR (KBr, cm^{-1}) 1316 and 1159; ^1H NMR δ 2.16 (1 H, d, J = 4.4 Hz), 2.42 (3 H, s), 2.68 (1 H, dd, J = 14.4, 7.2 Hz), 2.71 (1 H, d, J = 6.8 Hz), 2.81 (1 H, dd, J = 14.4, 5.2 Hz), 2.95 (1 H, m), 7.00−7.08, 7.12−7.18 (5 H, 2m), 7.20 and 7.69 (2 H each, 2d, J = 8.4 Hz); ^{13}C NMR δ 21.5, 32.7, 37.4, 41.1, 126.4, 127.7, 128.3, 128.6, 129.5, 134.8, 136.9, and 144.2; MS (EI) *m*/*z* (rel intensity) 288 (M^+ + 1, 17), 287 (M^+, 15), 155 (27), 133 (10), 132 (100), 130 (28), 117 (33), 116 (28), 105 (77), 104 (17), 103 (14), 91 (47), 79 (20), and 51 (12); t_R 15.31 min [17.47 min for (*R*) enantiomer].

***N*-(4-Methoxybenzenesulfonyl)-(2*S*)-benzylaziridine (1b)**: R_f 0.59 (pentane/EtOAc, 3/1); mp 84−85 °C (EtOAc); $[\alpha]^{25}_D$ 9.6 (*c* 1.02, $CHCl_3$); IR (KBr, cm^{-1}) 1326, 1262, and 1158; ^1H NMR δ 2.15 (1 H, d, J = 4.4 Hz), 2.67 (1 H, dd, J = 14.4, 7.2 Hz), 2.69 (1 H, d, J = 6.8 Hz), 2.82 (1 H, dd, J = 14.4, 4.8 Hz), 2.93 (1 H, m), 3.87 (3 H, s), 6.86, 7.72 (2 H each, 2d, J = 8.8 Hz) 7.00−7.08, and 7.12−7.20 (5 H, 2m); ^{13}C NMR δ 32.7, 37.5, 41.1, 55.6, 114.1, 126.5, 128.4, 128.7, 129.3, 130.0, 137.1, and 163.4; MS (EI) *m*/*z* (rel intensity) 304 (M^+ + 1, 11), 303 (M^+, 18), 171 (22), 132 (100), 131 (22), 130 (23), 123 (10), 117 (33), 116 (17), 115 (14), 105 (70), 103 (16), 91 (14), 79 (17), and 77 (15). Anal. Calcd for $C_{16}H_{17}NO_3S$: C, 63.35; H, 5.65; N, 4.62. Found: C, 63.21; H, 5.77; N, 4.55.

***N*-Nosyl-(2*S*)-benzylaziridine (1c).** Nosyl chloride (17 g, 77 mmol) was added in portions at 0 °C to (*S*)-phenylalaninol (11.6 g, 77 mmol), prepared by reduction with $LiAlH_4$ of (*S*)-phenylalanine in THF at 0 °C (95% yield), and Et_3N (43 mL, 306 mmol) in dry CH_2Cl_2 (400 mL). The resulting mixture was stirred for 1 h at room temperature. Then, mesityl chloride (6 mL, 77 mmol) was added dropwise while the reaction mixture was cooled with an ice bath. The mixture was stirred for an additional 2 h at 0 °C and then kept at −20 °C overnight. The cold mixture was washed with water (3 × 300 mL), and the organic phase was dried ($MgSO_4$) to give, after evaporation of the solvent, crude aziridine **1c**. Recrystallization from EtOAc/CH_2Cl_2 afforded pure **1c** as a yellow solid in a 60% yield: R_f 0.73 (pentane/EtOAc, 3/1); mp decomp after 130 °C (EtOAc); $[\alpha]^{25}_D$ −10 (*c* 0.25, acetone); IR (KBr, cm^{-1}) 1527, 1355, 1332, 1309, and 1165; ^1H NMR δ 2.30 (1 H, d, J = 4.4 Hz), 2.48 (1 H, dd, J = 14.4, 8.8 Hz), 2.88 (1 H, d, J = 6.8 Hz), 2.95−3.10 (2 H, m), 6.90−7.0, 7.04−7.12 (5 H, 2m), 7.87 and 8.15 (2 H each, 2d, J = 8.8 Hz); ^{13}C NMR δ 33.3, 37.5, 42.8, 124.0, 126.7, 128.5, 128.6, 129.0, 136.8, 143.5, and 150.4; MS (EI) *m*/*z* (rel intensity) 318 (M^+, 14), 132 (17), 131 (30), 130 (100), 117 (37), 116 (65), 115 (12), 105 (47), 104 (22), and 91 (20). Anal. Calcd for $C_{15}H_{14}N_2O_4S$: C, 56.59; H, 4.43; N, 8.80. Found: C, 56.50; H, 4.31; N, 8.95.

***N*-Tosyl-(2*R*)-phenylaziridine (2).**[31] The procedure for the synthesis of this compound was similar to that used for the synthesis of aziridine **1a** but started from (*R*)-phenylglycine methyl ester hydrochloride (60% yield): R_f 0.89 (pentane/EtOAc, 3/1); mp 92−93 °C (ether); $[\alpha]^{24}_D$ −80.25 (*c* 0.8, $CHCl_3$); IR (KBr, cm^{-1}) 1323 and 1159; ^1H NMR δ 2.38 (1 H, d, J = 4.4 Hz), 2.43 (3 H, s), 2.98 (1 H, d, J = 7.2 Hz), 3.78 (1 H, dd, J = 7.2, 4.4 Hz), 7.20−7.34 (7 H, m), and 7.87 (2 H, d, J = 8.0 Hz); ^{13}C NMR δ 21.5, 35.8, 40.9, 126.4, 127.8, 128.1, 128.4, 129.6, 134.8, 134.9, and 144.5; MS (EI) *m*/*z* (rel intensity) 275 (M^+ + 2, 24), 274 (M^+ + 1, 100), 226 (13), 209 (12), 205 (21), 194 (11), 193 (66), 181 (13), 165 (12), 162 (21), 118 (30), 92 (10), 91 (42), and 90 (11); t_R 15.20 min [13.70 min for (*S*) enantiomer].

Cyclohexyl (3*S*)-Methyl-*N*-*p*-toluenesulfonylaziridin-(2*S*)-carboxylate (3). L-Threonine cyclohexyl ester hydrochloride (24 g), prepared by reaction of L-threonine (15 g, 124 mmol) with $SOCl_2$ (248 mmol) in cyclohexanol under reflux for 2 h, was tosylated with *p*-toluenesulfonyl chloride (23.6 g) and Et_3N (372 mmol) in CH_2Cl_2 (100 mL) for 12 h to give *N*-*p*-toluenesulfonyl-L-threonine cyclohexyl ester (80% yield). DEAD (186 mmol) was then added dropwise to a cooled (0 °C) and stirred mixture of the above ester and PPh_3 (186 mmol) in THF (200 mL), and the mixture was stirred for 15 h at room temperature. The mixture was evaporated under reduced pressure, and the residual oil was purified by flash chromatography on silica gel (pentane/EtOAc, 7/1) to yield **3** as a white solid (85% yield) which could be recrystallized from 2,2,4-trimethylpentane: R_f 0.49 (pentane/EtOAc, 5/1); $[\alpha]^{25}_D$ −35 (*c* 0.37, $CHCl_3$); IR (KBr, cm^{-1}) 1735, 1274, 1228, and 1109; ^1H NMR δ 1.17−1.83 (13 H, 2m with d at 1.28, J = 7.6 Hz), 2.40 (3 H, s), 3.08 (1 H, m), 3.30 (1 H, d, J = 10.0 Hz), 4.75 (1 H, m), 7.30 and 7.81 (4 H, 2d, J = 8.3 Hz); ^{13}C NMR δ 12.0, 21.5, 23.26, 23.30, 25.0, 31.2, 39.8, 41.5, 74.1, 127.8, 129.6, 134.3, 144.7, and 164.9; MS (EI) *m*/*z* (rel intensity) 339 (M^+ + 2, 27), 338 (M^+ + 1, 100), 256 (21), 139 (27), 100 (48), 91 (23), 83 (12), and 55 (18). Anal. Calcd for $C_{17}H_{23}NO_4S$: C, 60.51; H, 6.87; N, 4.15. Found: C, 60.25; H, 7.03; N, 4.06.

Ring Opening Reaction of 1c under Fukuyama's Conditions. A a solution of aziridine **1c** (50 mg, 0.16 mmol)

(29) Bedekar, A. V.; Koroleva, E. B.; Andersson, P. G. *J. Org. Chem.* **1997**, *62*, 2518.

(30) Micovic, V. M.; Mihailovic, M. L. *J. Org. Chem.* **1953**, *18*, 1190.

(31) Toshimitsu, A.; Abe, H.; Hirosawa, Ch., Tamao, K. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3465.

in dry DMF (3 mL) was added to a suspension of K_2CO_3 (65 mg, 0.48 mmol) and thiophenol (20 μL, 0.16 mmol) in DMF (3 mL). The reaction mixture was stirred for 12 h and extracted with ether and water. The organic phase was washed with water (3 × 10 mL), dried ($MgSO_4$), and evaporated to afford the crude ring opening product. Purification by flash chromatography (silica gel, pentane/EtOAc, 4/1) afforded the pure yellow product in a 92% yield.

***N*-[(2*S*)-3-Phenyl-1-thiophenoxypropyl]-4-methylbenzenesulfonamide**: R_f 0.53 (pentane/EtOAc, 3/1); $[\alpha]^{25}_D$ −69.2 (*c* 0.5, $CHCl_3$); IR (neat, cm^{-1}) 3252, 1531, 1347, and 1160; ^1H NMR δ 2.71 (1 H, dd, J = 14.0, 8.0 Hz), 2.95 (1 H, dd, J = 14.0, 6.8 Hz), 3.08 (1 H, dd, J = 14.0, 5.6 Hz), 3.22 (1 H, dd, J = 14.0, 4.8 Hz), 3.48 (1 H, m), 4.95 (1 H, br d, J = 7.2 Hz), 6.92 (2 H, d, J = 6.4 Hz), 7.58, 8.02 (2 H each, 2d, J = 8.8 Hz), 7.10−7.30 (8 H, m). ^{13}C NMR δ 38.8, 40.1, 55.2, 124.2, 127.0, 127.2, 128.2, 129.0, 129.38, 129.42, 129.8, 134.8, 136.6, 145.3, and 149.9; MS (EI) *m*/*z* (rel intensity) 429 (M^+ + 1, 26), 428 (M^+, 45), 305 (17), 227 (32), 136 (11), 135 (100), 124 (37), 120 (13), 119 (91), 118 (33), 117 (25), 91 (18), and 89 (11). Anal. Calcd for $C_{21}H_{20}N_2O_4S_2$: C, 58.86; H, 4.70; N, 6.54. Found: C, 58.73; H, 4.79; N, 6.72.

General Procedure for Dissolved Metal Reductions. A suspension in dry THF (15 mL) of the corresponding metal (Li, Na or Ca) (10 or 2 equiv) was dissolved in liquid ammonia at −78 °C under an argon atmosphere in a three-necked flask equipped with a dry acetone-cooled Dewar condenser. To this blue solution was added the aziridine (0.5 mmol) solved in dry THF (3 mL), and the reaction was kept at −78 °C with stirring for 45 min (4 h for the reactions with Ca). Brine (10 mL) was then added cautiously to the reaction flask, followed by the addition of CH_2Cl_2 (10 mL). The ammonia in the solution was then allowed to evaporate, and the reaction mixture was extracted with two more portions of CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated. The residue was then purified by flash chromatography (deactivated silica gel, ether/acetone) to provide the corresponding products.

(2*S*)-Benzylaziridine (4):[32] R_f 0.35 (acetone); t_R = 10.25 min; $[\alpha]^{24}_D$ −7.7 (*c* 1.82, $CHCl_3$); IR (film, cm^{-1}) 3254; ^1H NMR δ 0.80 (1 H, m), 1.45 (1 H, d, J = 3.6 Hz), 1.82 (1 H, br d, J = 5.6 Hz), 2.16−2.25 (1 H, m), 2.65 (1 H, dd, J = 14.8, 6.4 Hz), 2.80 (1 H, dd, J = 14.8, 6.0 Hz), and 7.20−7.35 (5 H, m); ^{13}C NMR δ 24.8, 30.9, 40.0, 126.3, 128.3, 128.7, and 139.0; MS (EI) *m*/*z* (rel intensity) 133 (M^+, 25), 132 (69), 118 (17), 117 (17), 104 (39), 103 (40), 92 (18), 91 (100), 89 (28), 78 (39), 77 (49), 65 (26), 63 (26), 62 (20), 56 (28), 51 (51), and 50 (39).

(*S*)-Benzylethylenediamine (5): R_f 0.22 (pentane/EtOAc, 3/1); t_R = 11.40 min; IR (film, cm^{-1}) 3385; ^1H NMR δ 1.80 (1 H, dd, J = 6.0, 2.8 Hz), 1.99 (1 H, dd, J = 8.4, 2.4 Hz), 2.31 (1 H, m), 2.60 (1 H, dd, J = 14.8, 6.4 Hz), 2.74 (1 H, dd, J = 14.8, 7.2 Hz), 6.01 (1 H, br s), 7.22−7.35 (5 H, m); ^{13}C NMR δ 37.1, 37.5, 43.4, 126.4, 128.5, 128.7, and 138.4; MS (EI) *m*/*z* (rel intensity) 132 (M^+ − 15, 40), 130 (27), 118 (18), 117 (100), 105 (37), 104 (81), 103 (38), 92 (11), 91 (71), 79 (17), 78 (40), 77 (16), and 65 (17).

General Procedure for Magnesium Reductions. To a suspension of Mg (40 mg, 1.6 mmol) in anhydrous MeOH (3 mL) was added a solution of the corresponding aziridine (0.3 mmol) in anhydrous MeOH (2 mL). The resulting suspension was stirred or sonicated (methods A and B in Table 2) for 30 min until comsumption of the starting material (reaction minitored by TLC) was complete. The reaction was then diluted with brine (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The organic layer was dried over $MgSO_4$ and evaporated. The resulting residue was purified by flash chromatography (deactivated silica gel) to yield pure products **4** and **8**−**12**.

***N*-(3-Phenylpropyl)-toluene-4-sulfonamide (8)**:[33] All the physical and spectroscopic data were in complete agreement with the reported ones.

(2*R*)-Phenylaziridine (9):[34] R_f 0.35 (EtOAc); t_R = 9.34 min; $[\alpha]^{20}_D$ −31.5 (*c* 1.4, $CHCl_3$); IR (film, cm^{-1}) 3303; ^1H NMR δ 1.50 (1 H, br s), 1.81 (1 H, d, J = 3.2 Hz), 2.21 (1 H, d, J = 6.0 Hz), 3.02 (1 H, m), and 7.15−7.40 (5 H, m); ^{13}C NMR δ 29.2, 32.1, 125.6, 126.7, 128.2, and 140.7; MS (EI) *m*/*z* (rel intensity) 119 (M^+, 15), 118 (100), 117 (25), 91 (36), 89 (17), 65 (12), 63 (13), and 51 (13).

***N*-(2-Phenylethyl)toluene-4-sulfonamide (10)**:[35] All the physical and spectroscopic data were in complete agreement with the reported ones.

Cyclohexyl (3*S*)-Methyl-1-aziridin-(2*S*)-carboxylate (11): R_f 0.26 (pentane/EtOAc, 1/1); t_R 13.05 min; $[\alpha]^{24}_D$ +15.3 (*c* 1, $CHCl_3$); IR (film, cm^{-1}) 3419, 1722, and 1202; ^1H NMR δ 1.20−1.60 (10 H, m with d at 1.27, J = 6.0 Hz), 1.65−1.95 (2 H each, 2m), 2.26 (1 H, m), 2.58 (1 H, br d, J = 6.0 Hz), and 4.82 (1 H, m); ^{13}C NMR δ 12.9, 23.6, 23.7, 25.2, 31.5, 31.7, 33.5, 35.1, 73.8, and 170.2; MS (EI) *m*/*z* (rel intensity) 184 (M^+ + 1, <1), 101 (38), 83 (76), 56 (24), 55 (100), and 54 (10). Anal. Calcd for $C_{17}H_{25}NO_4S$: C, 60.15; H, 7.42; N, 4.13. Found: C, 60.10; H, 7.30; N, 4.29.

Cyclohexyl (3*S*)-(*p*-Toluenesulfonamido)butanoate (12): R_f 0.64 (pentane/EtOAc, 3/1); IR (film, cm^{-1}) 3600−3050, 1725, 1332, 1161, and 1091; ^1H NMR δ 1.14 (3 H, d, J = 6.8 Hz), 1.20−1.40, 1.64−1.84 (10 H, 2m), 2.37 (2 H, d, J = 5.6 Hz), 2.42 (3 H, s), 3.68 (1 H, m), 4.71 (1 H, m), 5.19 (1 H, br d, J = 8.0 Hz), 7.29 and 7.75 (2 H each, 2d, J = 8.0 Hz); ^{13}C NMR δ 21.0, 21.5, 23.7, 25.4, 31.47, 31.55, 40.8, 46.7, 73.3, 127.0, 129.7, 138.1, 143.3, and 170.6; MS (EI) *m*/*z* (rel intensity) 341 (M^+ + 2, 35), 340 (M^+ + 1, 84), 322 (12), 274 (49), 258 (12), 242 (16), 240 (17), 220 (21), 198 (79), 184 (53), 155 (39), 102 (100), and 91 (29).

General Procedure for Metal/Naphthalene Reductions. To a cooled (−78 °C) green suspension of the corresponding metal (Na or Li, 1.44 mmol) and naphthalene (208 mg, 1.62 mmol) in dry THF (4 mL) was added the corresponding aziridine (0.36 mmol) under argon, and the mixture was stirred for 45 min at the same temperature. Then, the reaction was hydrolyzed with brine (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated. The resulting residue was purified by flash chromatography (deactivated silica gel, ether/acetone) to yield the corresponding pure products.

General Procedure for Reactions with Li and a Catalytic Amount of DTBB. To a cooled (−78 °C) green suspension of Li powder (15 mg, 2.16 mmol) and DTBB (6 mg, 0.011 mmol) in dry THF (4 mL) was slowly added (ca. 1 h) the corresponding aziridine (0.22 mmol) under argon, and the mixture was stirred for 60 min at the same temperature. Then, the reaction was hydrolyzed with brine (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated. The resulting residue was purified by flash chromatography (deactivated silica gel, ether/acetone) to yield the corresponding pure products.

General Procedure for SmI_2 Reductions. To a 0.1 M solution of SmI_2[24] (2.5 equiv for aziridine **3**, 6 equiv for aziridines **1a**, **1b**, and **2**) in dry THF was added a THF solution of the corresponding aziridines at 0 °C. The reaction mixture was then stirred at room temperature (aziridine **3**) or refluxed with 6 equiv of DMPU as cosolvent (for aziridines **1a**, **1b**, and **2**) for 15 h, quenched with brine (15 mL), and extracted with CH_2Cl_2 (3 × 15 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated. The resulting residue was purified by flash chromatography (deactivated silica gel) to yield pure products **13**−**15**.

***N*-[3-Phenyl-(2*E*)-propenyl]-4-methylbenzenesulfonamide (13):**[36] mp 109−110 °C (EtOAc); IR (KBr, cm^{-1}) 3386, 1330, and 1160; ^1H NMR δ 2.42 (3 H, s), 3.78 (2 H, dd, J = 6.2, 5.0 Hz), 4.67 (1 H, br s), 6.04 (1 H, dt, J = 16.0, 6.2 Hz), 6.46 (1 H, d, J = 16.0 Hz), 7.20−7.32 (7 H, m), and 7.78 (2 H, d, J = 8.0 Hz); ^{13}C NMR δ 21.5, 45.6, 124.1, 126.4, 127.2, 128.0,

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128.6, 129.8, 133.1, 136.1, 137.1, and 143.6; MS (EI) *m*/*z* (rel intensity) 287 (M^+, 7), 133 (12), 132 (100), 130 (68), 115 (22), 105 (52), 104 (14), 91 (61), 77 (26), and 65 (36).

***N*-[2-(1-Iodo-3-phenylpropyl)]-4-methoxyphenylsulfonamide (14)**: R_f 0.53 (pentane/EtOAc, 3/1); IR (film, cm^{-1}) 3278, 1330, 1260, and 1155; ^1H NMR δ 2.75 (1 H, dd, J = 13.8, 6.0 Hz), 2.82 (1 H, dd, J = 13.8, 6.8 Hz), 3.17−3.23 (3 H, m), 3.87 (3 H, s), 4.72 (1 H, br d, J = 7.2 Hz), 6.89, 7.67 (2 H each, 2d, J = 8.8 Hz), 7.03−7.08, and 7.18−7.24 (5 H, 2 m); ^{13}C NMR δ 13.4, 41.1, 54.1, 55.6, 114.2, 127.1, 128.8, 129.1, 131.7, 136.1, and 162.9; MS (EI) *m*/*z* (rel intensity) 432 ($M^+ + 1$, <1), 340 (12), 237 (11), 171 (39), 148 (11), 144 (11), 142 (13), 131 (13), 130 (28), 125 (18), 123 (100), 122 (10), 121 (17), 117 (61), 115 (44), 107 (35), 105 (12), 91 (54), 79 (14), and 77 (38). Anal. Calcd for $C_{16}H_{18}INO_3S$: C, 44.56; H, 4.21; N, 3.25. Found: C, 44.74; H, 4.40; N, 3.37.

Cyclohexyl 2-Iodo-3-(*p*-toluenesulfonamido)butanoate (15): R_f 0.78 (pentane/EtOAc, 3/1); IR (film, cm^{-1}) 3270, 1730, 1330, and 1150; ^1H NMR δ 1.20−1.58 (9 H, m with d at 1.30, J = 6.8 Hz), 1.60−1.85 (4 H, m), 2.42 (3 H, s), 3.50 (1 H, m), 4.43 (1 H, d, J = 5.2 Hz), 4.71 (1 H, m), 5.12 (1 H, br d, J = 8.0 Hz), 7.30 and 7.76 (2 H each, 2 d, J = 8.0 Hz); ^{13}C NMR δ 19.2, 21.5, 23.3, 23.4, 25.2, 26.5, 30.6, 31.1, 52.3, 74.7, 127.1, 129.7, 137.5, 143.6, and 168.6; MS (EI) *m*/*z* (rel intensity) 466 ($M^+ + 1$, 18), 199 (11), 198 (100), 155 (30), and 91 (10). Anal. Calcd for $C_{17}H_{24}INO_4S$: C, 43.88; H, 5.20; N, 3.01. Found: C, 44.04; H, 5.15; N, 2.98.

General Photolysis Procedure of Aziridines 1. A 10 mM solution of the aziridine (1 equiv), a donor (3 equiv), and the corresponding reductant (10−15 equiv) in 95% aqueous EtOH was irradiated with a low-pressure mercury lamp (ACE Glass) under nitrogen for 24 h. When donors were used, a Pyrex filter was applied to cut off the light below 300 nm. The reaction mixture was concentrated under vacuum to afford crude reaction products which were characterized by ^1H NMR.

Supporting Information Available: Copies of NMR spectra of **1b**, **1c**, and **3** (6 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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