JOC Article

Regio- and Stereospecific Synthesis of β-Sulfonamidodisulfides and β-Sulfonamidosulfides from Aziridines using Tetrathiomolybdate as a Sulfur Transfer Reagent‡

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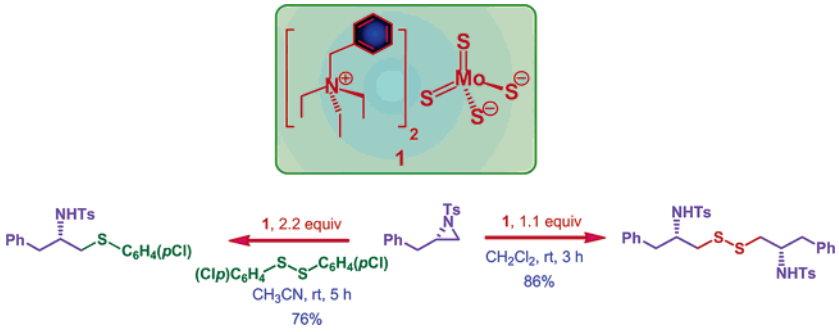
Received November 27, 2006



A comprehensive study of a general and effective one-step procedure for the synthesis of β-sulfonamidodisulfides directly from *N*-tosyl aziridines in a regio- and stereospecific manner under neutral conditions without the use of any Lewis acid or base has been reported. This methodology is extended to the synthesis of an optically pure cyclic seven-membered disulfide **29**. Synthesis of a variety of β-sulfonamidosulfides involving tandem, multistep reactions in one pot is also reported.

Introduction

Aziridines are versatile intermediates in organic synthesis because of their very high reactivity, ability to function as carbon electrophiles, and utility in the synthesis of biologically active natural products.[1] The most straightforward route for the synthesis of β-sulfonamidosulfides involves the regioselective ring-opening reaction of aziridines with thiols, and several other procedures have appeared in the literature.[2] The most common protocols used in the ring opening of aziridines with thiols are in the presence of Lewis acids such as $BF_3{\cdot}OEt_2$, $ZnCl_2$, $Cu(OTf)_2$, $Yb(OTf)_3$, $Ti(O^iPr)_4$, etc. and other Bronsted acids or bases. However, to the best of our knowledge there are not many reports for the synthesis of β-sulfonamidodisulfides from aziridines in a single-step process.[3] β-Sulfonamidodisulfide, which has disulfide bridge, is the most important structural motif in a wide range of biologically active peptides and proteins and plays an unique role in the conformation and formation of tertiary structure of peptides.[4] In a recent communication, we reported our results on the nucleophilic ring opening of various aziridines with benzyltriethylammonium tetrathiomolybdate[5] $[BnEt_3N]_2MoS_4$ (**1**) and demonstrated the utility of this methodology for the synthesis of a number of interesting sulfur heterocycles with high regio- and stereocontrol.[6] In continuation of our investigation into the utility of **1** in organic synthesis, herein we present details of a comprehensive study of a general

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‡ Dedicated to Professor K. Venkatesan on the occasion of his 75th birthday.

(1) (a) Tanner, D. *Angew. Chem., Int. Ed.* **1994**, *33*, 599−619. (b) Hu, X. E. *Tetrahedron* **2004**, *60*, 2701−2743. (c) McCoull, W.; Davis, F. A. *Synthesis* **2000**, *10*, 1347−1365.

(2) Wu, J.; Hou, X. L.; Dai, L. X. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1314−1317 and references therein.

(3) (a) Fulton, D. A.; Gibson, C. L. *Tetrahedron Lett.* **1997**, *38*, 2019−2022. (b) Hata, Y.; Watanabe, M. *Tetrahedron* **1987**, *43*, 3881−3888. (c) Poelert, M. A.; Hof, R. P.; Peper, N. C. M. W.; Kellogg, R. M. *Heterocycles* **1994**, *37*, 461−475.

(4) Thornton, J. M. *J. Mol. Biol.* **1981**, *151*, 261−287.

(5) Prabhu, K. R.; Devan, N.; Chandrasekaran, S. *Synlett* **2002**, 1762−1778.

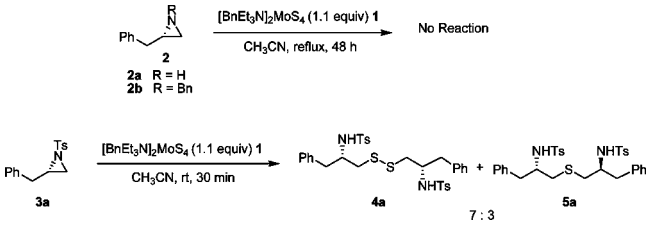
(6) Sureshkumar, D.; Koutha, S.; Chandrasekaran, S. *J. Am. Chem. Soc.* **2005**, *127*, 12760−12761.

10.1021/jo0624389 CCC: $37.00
Published on Web 02/23/2007

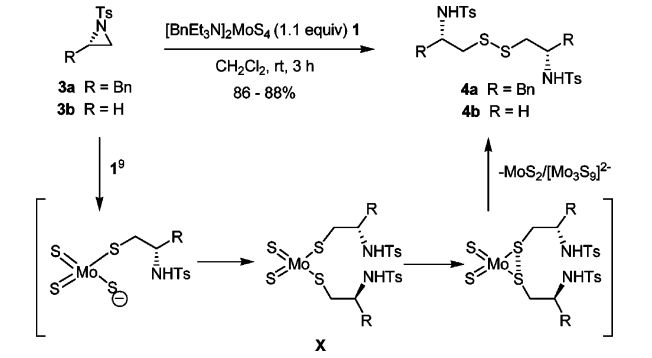
TABLE 1. Solvent Effect on the Ring Opening of *N*-Tosyl Aziridine 3a

entry	solvent	temp	time (h)	ratio **4a**:**5a**	yield (%)
1	THF	rt	48		
2	CH_3CN	rt	0.5	7:3	80
3	CH_3CN	−10 °C	5	8:2	83
4	CH_3CN	−20 °C	7	9:1	84
5	CH_3CN	−30 °C	8	9:1	84
6	CH_2Cl_2	rt	3	10:0	86
7	DMF	rt	0.25	7:3	81

SCHEME 1. Nucleophilic Ring Opening of Aziridines Using 1



SCHEME 2. Mechanism for Formation of *β*-Sulfonamidodisulfide 4

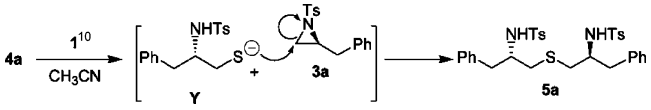


and effective one-step procedure for the synthesis of *β*-sulfonamidodisulfides **4** directly from *N*-tosyl aziridines **3** in a regio- and stereospecific manner under neutral conditions without the use of any Lewis acid or base. This methodology is extended to the synthesis of a cyclic seven-membered disulfide **29** and a variety of sulfonamidosulfides involving multistep, tandem reactions.

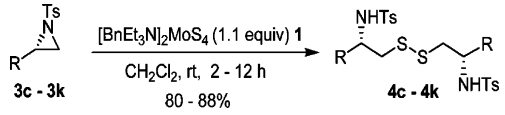
Results and Discussion

Reaction of Enantiopure *N*-Tosyl Aziridines with Tetrathiomolybdate 1. Whereas treatment of unactivated aziridines[7] **2a** and **2b** with **1** (1.1 equiv, CH_3CN, 28 °C, 48 h) failed to effect ring opening even under refluxing conditions, the activated *N*-tosyl aziridine[8] **3a** on reaction with **1** (1.1 equiv, CH_3CN, 28 °C, 0.5 h) underwent smooth and clean ring opening in a regiospecific manner to afford *β*-sulfonamidodisulfide **4a** and *β*-sulfonamidosulfide **5a** (7:3) in 80% yield (Scheme 1). To avoid the formation of **5a**, reaction conditions were optimized

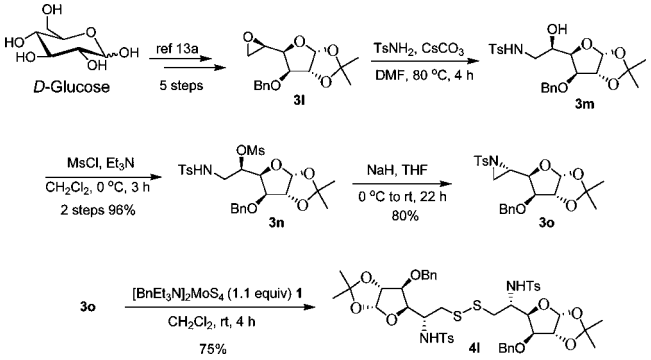
SCHEME 3. Mechanism for Formation of *β*-Sulfonamidosulfide 5a



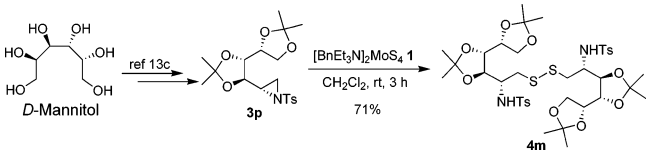
SCHEME 4. Regiospecific Ring Opening of Monosubstituted Aziridines 3



SCHEME 5. Regiospecific Ring Opening of D-Glucose-Derived Aziridine 3o with 1



SCHEME 6. Regiospecific Ring Opening of Carbohydrate-Derived Aziridine 3p with 1



using different solvent systems and reaction temperatures (Table 1). When the reaction was carried out in acetonitrile at −30 °C, **4a** and **5a** (9:1) were obtained in 84% yield. By switching the solvent from acetonitrile to dichloromethane (28 °C, 3 h), **4a** was obtained as the exclusive product in 86% yield.

It is reasonable to visualize the nucleophilic attack of reagent **1** on the aziridine **3a** at the less-substituted carbon center in a regiospecific manner followed by opening of the second aziridine ring to form an intermediate **X**. The intermediate **X** can then undergo an internal redox process[5,9,10] to form the *β*-sulfonamidodisulfide **4a** (Scheme 2). A tentative mechanism for the formation of *β*-sulfonamidosulfide **5a** is depicted in Scheme 3. Use of coordinating solvents such as acetonitrile accelerates the formation of *β*-sulfonamidodisulfide **4a** as well as reductive cleavage of the disulfide bond[10] by **1**, leading to the formation of thiolate intermediate **Y**, which further attacks aziridine **3a** in a regiospecific manner to furnish *β*-sulfonamidosulfide **5a**.

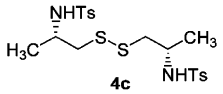
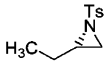
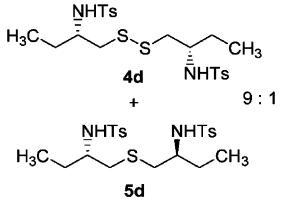
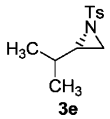
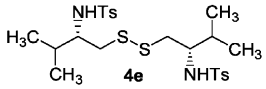
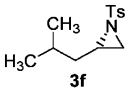
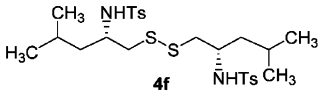
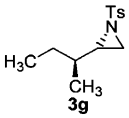
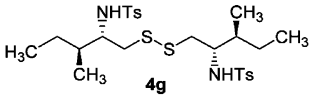
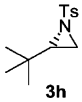
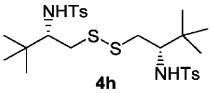
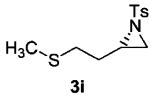
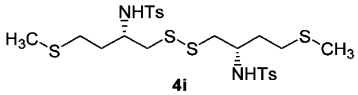
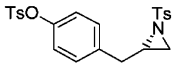
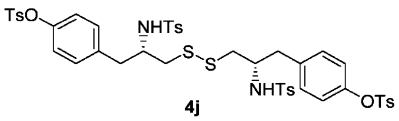
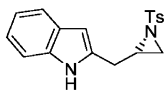
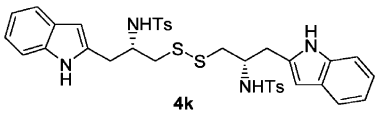
(7) (a) Bates, G. S.; Varelas, M. A. *Can. J. Chem.* **1980**, *58*, 2562−2566. (b) Lohray, B. B.; Gao, Y.; Sharpless, K. B. *Tetrahedron Lett.* **1989**, *30*, 2623−2626. (c) Berry, M. B.; Craig, D. *Synlett* **1992**, 41−44. (d) Bieber, L. W.; De Araujo, M. C. F. *Molecules* **2002**, *7*, 902−906.

(8) It has been tested with other protecting groups (activating groups) such as Boc and Cbz, but the reaction took more time (20 h) in the case of Boc and in the case of Cbz the reaction was incomplete even after 88 h. The *N*-Boc-protected 2,3-disubstituted aziridines failed to undergo ring opening with **1**.

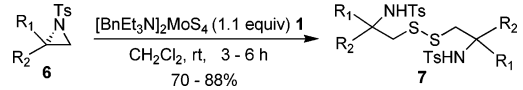
(9) (a) Kruhlak, N. L.; Wang, M.; Boorman, P. M.; Parvez, M. *Inorg. Chem.* **2001**, *40*, 3141−3148. (b) Boorman, P. M.; Wang, M.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1995**, 999−1000.

(10) (a) Pan, W. H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459−460. (b) Coyle, C. L.; Harmer, M. A.; George, G. N. Daage, M.; Stiefel, E. I. *Inorg. Chem.* **1990**, *29*, 14−19. and references therein. (c) Prabhu, K. R.; Sivanand, P.; Chandrasekaran, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4316−4319.

TABLE 2. Synthesis of Enantiopure β-Sulfonamidodisulfides

Entry	Aziridines	Enantiopure β-sulfonamidodisulfides	Time (h)	Yield (%)
1	 **3c**	 **4c**	2	80
2	 **3d**	 **4d** + **5d** 9 : 1	2	86
3	 **3e**	 **4e**	4	88
4	 **3f**	 **4f**	4	83
5	 **3g**	 **4g**	3	85
6	 **3h**	 **4h**	5	80
7	 **3i**	 **4i**	4	78
8	 **3j**	 **4j**	3	74
9	 **3k**	 **4k**	12	65

SCHEME 7. Regiospecific Ring Opening of 2,2-Disubstituted Aziridines



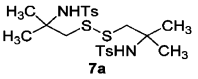
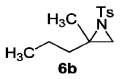
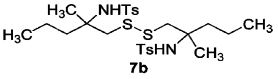
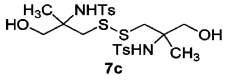
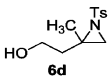
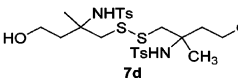
The mildness of reaction conditions and the excellent yields of products obtained encouraged us to examine the scope and generality of the present methodology. The results are summarized in Table 2. Starting from optically active aziridines[7c] (**3c**−**k**) enantiopure β-sulfonamidodisulfides (**4c**−**k**) were obtained in good to excellent yields (Scheme 4). In the reaction of **3d** with **1**, although **4d** was the major product, a small amount of monosulfide **5d** was also formed. The structure of monosulfide **5d** was confirmed by X-ray analysis.[11]

In order to use these *N*-tosyl-β-sulfonamidodisulfides for further transformations, attempts were made to deprotect the *N*-tosyl group[12] in the presence of disulfide bond, but the results have not been satisfactory.

Synthesis of Carbohydrate-Derived β-Sulfonamidodisulfides. To expand the scope of this methodology to the study of other aziridines having different functionality and complexity, D-glucose-derived aziridine **3o** was synthesized from the epoxide **3l**[13a] in three steps (Scheme 5). D-Glucose- and D-mannitol-derived aziridines[13] **3o** and **3p** were treated with **1** (1.1 equiv, CH_2Cl_2, 28 °C) to afford the corresponding disulfides **4l** and **4m**, respectively, in good yields (Schemes 5 and 6). These

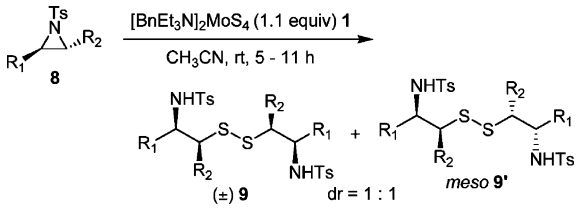
(11) CCDC 631951 (**5d**), CCDC 631952 (**7a**), CCDC 631953 (**7c**), CCDC 631954 (**9a**), CCDC 631955 (**9b**), CCDC 288572 (**9c**), CCDC 631956 (**11a**), CCDC 631957 (**14**), CCDC 631958 (**32**), CCDC 631959 (**36**), and CCDC 631960 (**44**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallography Data Centre via www.ccdc.cam.ac.uk/data request/cif.

TABLE 3. Synthesis of β-Substituted β-Sulfonamidodisulfides

Entry	2,2-Disubstituted Aziridines	β-Substituted β-sulfonamidodisulfide[a]	Time (h)	Yield (%)
1	 **6a**	 **7a**	3	88
2	 **6b**	 **7b**	6	82
3	 **6c**	 **7c**	5	74
4	 **6d**	 **7d**	4	70

[a] Isolated as a mixture (1:1) of diastereomers except in the case of **7a**.

SCHEME 8. Regio- and Stereospecific Ring Opening of 2,3-Disubstituted Aziridines 8



enantiopure disulfide derivatives have the potential to be used as chiral ligands in diethyl zinc addition to aldehydes.[14]

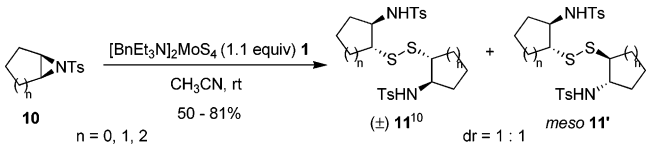
Reaction of Disubstituted *N*-Tosyl Aziridines with Tetrathiomolybdate 1. When this methodology was applied to the reaction of 2,2-disubstituted aziridines **6**, nucleophilic attack[15] occurred exclusively at the unsubstituted carbon atom to form β-sulfonamidodisulfides **7** (dr = 1:1) as expected (Scheme 7). As depicted in Table 3, a series of β-substituted β-sulfonamidodisulfides **7** could be synthesized in a straightforward manner, allowing some interesting structural diversity. Using this strategy we have demonstrated the synthesis of α-methyl cystinol derivative **7c** and α-methyl homo cystinol derivative **7d** in a single step from the corresponding aziridines[16] **6c** and **6d**, respectively, in good yields (Table 3, entries 3 and 4). The structures of compound **7a** and **7c** were confirmed by single-crystal X-ray analysis.[11]

Reaction of 2,3-Disubstituted Aziridines with 1. To demonstrate the stereospecificity in the ring opening of 2,3-disubstituted aziridines with **1**, *meso*-*N*-tosyl-2,3-diethylaziridine **8a**[17] was treated with **1** (1.1 equiv, CH_3CN, 28 °C, 8 h) to afford exclusively the *anti*-β-sulfonamidodisulfides **9a** and **9a′** as a diastereomeric mixture (dr = 1:1) in 79% yield. (Scheme 8). In the case of (±)-*trans*-*N*-tosyl-2,3-diethylaziridine **8b**,[17] *syn*-β-sulfonamidodisulfides **9b** and **9b′** were obtained as a diastereomeric mixture (dr = 1:1) in 82% yield under the same reaction conditions (Table 4). Stereospecificity of this reaction was confirmed by single-crystal X-ray analysis of **9a** and **9b**.[11]

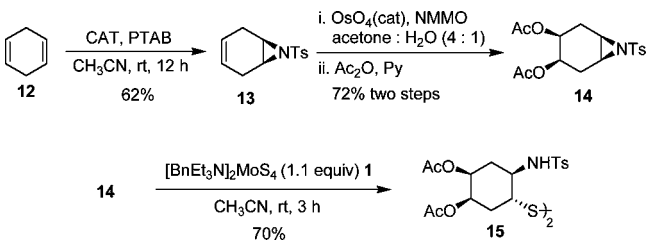
To assess the regio- and stereospecificity together in the same substrate, (±)-*cis*-*N*-tosyl-2-isopropyl-3-methylaziridine **8c** was treated with **1** (1.1 equiv, CH_3CN, 28 °C, 11 h) to afford exclusively the *anti*-β-sulfonamidodisulfides **9c**[11] and **9c′** as a diastereomeric mixture (dr = 1:1) in 80% yield.[6] In the case of (±)-*trans*-*N*-tosyl-2-isopropyl-3-methylaziridine **8d**, the *syn*-β-sulfonamidodisulfides[6] **9d** and **9d′** were obtained as a diastereomeric mixture (dr = 1:1) in 85% yield under the same reaction conditions. Here, tetrathiomolybdate **1** attacks the aziridines **8c** and **8d** at the less-hindered C2 carbon site in a S_N2 fashion with regio- and stereocontrol and with complete inversion (Table 4, entries 3 and 4).

Reaction of Cyclic Aziridines with 1. This methodology was then extended to study the reaction of aziridines derived from cyclic systems. Reaction of aziridines **10** with **1** (1.1 equiv, CH_3CN, 28 °C, 0.5−48 h, room temperature) led to facile ring opening in a stereospecific manner to afford *trans*-β-sulfonamidodisulfides **11** and **11′** as a diastereomeric mixture (dr = 1:1) in very good yields (Scheme 9). Although the reaction of aziridine **10a** was very fast (0.5 h), in the case of aziridines **10b** and **10c** the reaction was much slower (2 and 12 h, respectively). Interestingly, treatment of **1** with bicyclic aziridine **10d** derived from cyclooctene did not yield any product even after 48 h. This reactivity trend may be attributed to the puckered nature of bicyclic aziridine **10d**; with increasing size of the bicyclic aziridine ring, the nucleophilic attack at the aziridine ring becomes more difficult. To demonstrate selective opening of aziridine ring in the presence of epoxide, aziridino-epoxides[18] **10f**−**10h** were synthesized from the corresponding 1,4-cyclic dienes using a Sharpless aziridination[16] (1,4-diene, 3 mmol; CAT, 3.3 mmol; PTAB, 0.3 mmol; 15 mL CH_3CN, room temperature, 12 h) followed by epoxidation using *m*-CPBA as an epoxidation reagent.[17] Treatment of aziridino-epoxides **10f**−**10h** with **1** (1.1 equiv, CH_3CN, room temperature), re-

SCHEME 9. Stereospecific Ring Opening of Aziridines 10



SCHEME 10. Stereospecific Ring Opening of Cyclic Aziridine 14



(12) (a) Roemmele, R. C.; Rapoport, H. *J. Org. Chem.* **1988**, *53*, 2367−2371. (b) Opalka, C. J.; D'Ambra, T. E.; Faccone, J. J.; Bodson, G.; Cossement, E. *Synthesis* **1995**, 766−768. (c) Kudav, D. P.; Samant, S. P.; Hosangadi, B. D. *Synth. Commun.* **1987**, *17*, 1185−1187.

(13) (a) Epoxide **3l** was prepared from D-glucose in five steps through a known procedure: *Methods in Carbohydrate Chemistry*; Academic Press: New York, 1963; Vol. II, p 190. (b) Atsushi, E.; Toshiyuki, K.; Tohru, F. *Synlett* **1999**, *7*, 1103−1105. (c) Mao, H.; Joly, G. J.; Peters, K.; Hoornaert, G. J.; Compernolle, F. *Tetrahedron* **2001**, *57*, 6955−6967.

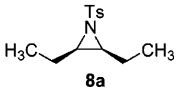
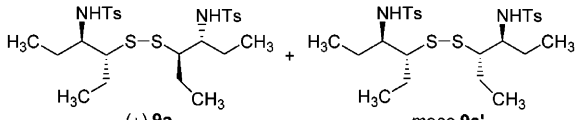
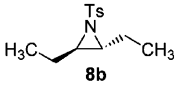
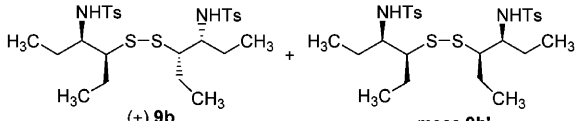
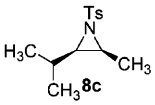
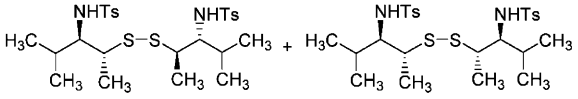
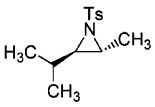
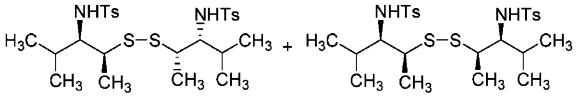
(14) (a) Kang, J.; Kim, D. S.; Kim, J. I. *Synlett* **1994**, *10*, 842−4. (b) Braga, L. B.; Milani, P.; Paixao, M. W.; Zeni, G.; Rodrigues, O. E. D.; Alves, E. F. *Chem. Commun.* **2004**, 2488−2489. (c) Braga, A. L.; Luedtke, D. S.; Wessjohann, L. A.; Paixao, M. W.; Schneider, P. H. *J. Mol. Catal. A: Chem.* **2005**, *229*, 47−50.

(15) Stamm, H.; Assithianakis, P.; Buchholz, B.; Weiss, R. *Tetrahedron Lett.* **1982**, *23*, 5021−5024.

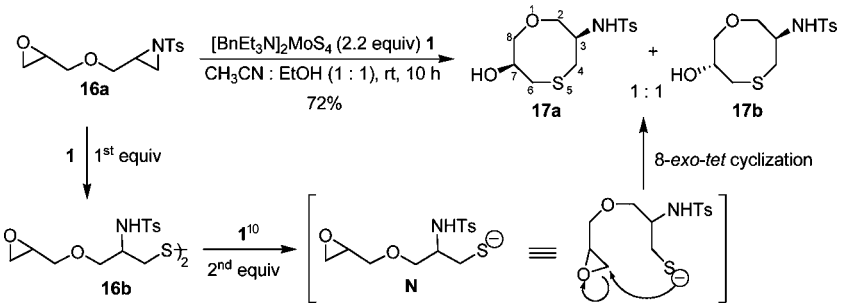
(16) Jeong, J. U.; Tao, B.; Sagasser, I.; Henniges, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1998**, *120*, 6844−6845.

(17) Iwamoto, K.; Kajima, M.; Chatani, N.; Murai, S. *J. Org. Chem.* **2001**, *66*, 169−174.

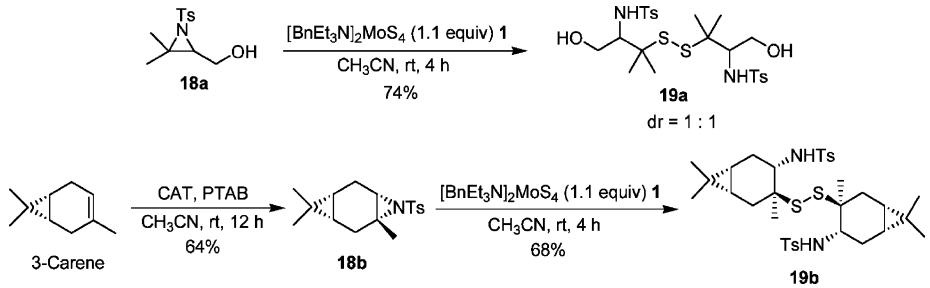
TABLE 4. Synthesis of Disubstituted β-Sulfonamidodisulfides by Regio- and Stereospecific Ring Opening of 2,3-Disubstituted Aziridines 8

Entry	2,3-Disubstituted Aziridines	β-Sulfonamidodisulfides	Time (h)	Yield (%)
1	 **8a**	 (±) **9a** + *meso* **9a'** dr = 1 : 1	8	79
2	 **8b**	 (±) **9b** + *meso* **9b'** dr = 1 : 1	6	82
3	 **8c**	 (±) **9c** + *meso* **9c'** dr = 1 : 1	11	80
4	 **8d**	 (±) **9d** + *meso* **9d'** dr = 1 : 1	5	85

SCHEME 11. Tandem Aziridine Opening−Disulfide Formation−Reduction−Cyclization in One Pot



SCHEME 12. Regio- and Stereospecific Ring Opening of Trisubstituted Aziridines

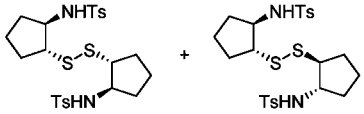
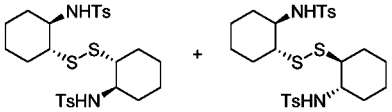
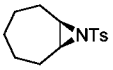
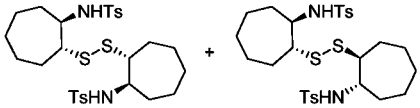
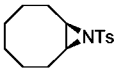
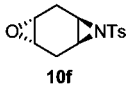
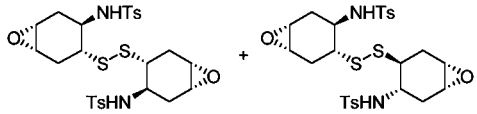
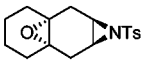
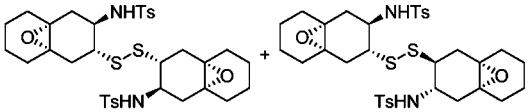
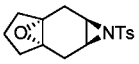
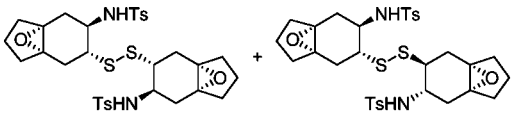


sulting in the exclusive formation of products **11f−11h**, respectively, in good yields (Table 5). The epoxide ring was left untouched under the reaction conditions. In continuation of these studies, aziridine **14**[11] was synthesized starting from 1,4-cyclohexadiene by aziridination followed by dihydroxylation[19] and subsequent acetylation (Scheme 10). Reaction of **14** with **1** (1.1 equiv, CH_3CN, room temperature, 3 h) furnished hydroxy-protected *trans*-β-sulfonamidodisulfide **15** as a diastereomeric mixture (dr = 1:1) in 70% yield (Scheme 10).

These studies could be further extended to the ring opening of both the aziridine and epoxide rings with **1** in the same molecule in a tandem, one-pot operation. Accordingly, (±)-aziridino-epoxide **16a** was synthesized from allyl glycidyl ether by Sharpless aziridination.[16] Treatment of **16a** with **1** (2.2 equiv, CH_3CN/EtOH; 1:1, room temperature, 10 h) resulted in the formation of **17a** and **17b** (1:1 ratio) in 72% yield. A tentative mechanism for the tandem aziridine and epoxide ring opening[20]

(18) Sureshkumar, D.; Maity, S.; Chandrasekaran, S. *J. Org. Chem.* **2006**, *71*, 1653−1657.

TABLE 5. Synthesis of *trans*-*β*-Sulfonamidodisulfides

Entry	Cyclic aziridines	Cyclic *β*-sulfonamidodisulfides	Time (h)	Yield (%)
1	 **10a**	 (±) **11a**[11] dr = 1 : 1 *meso* **11a'**	0.5	81
2	 **10b**	 (±) **11b** dr = 1 : 1 *meso* **11b'**	2	68
3	 **10c**	 (±) **11c** dr = 1 : 1 *meso* **11c'**	12	50
4	 **10d**	No reaction	48	-
5	 **10e**	No reaction	48	-
6	 **10f**	 (±) **11f** dr = 1 : 1 *meso* **11f'**	2	78
7	 **10g**	 (±) **11g** dr = 1 : 1 *meso* **11g'**	3	76
8	 **10h**	 (±) **11h** dr = 1 : 1 *meso* **11h'**	2	70

with **1** followed by cyclization to form **17a** and **17b** is presented in Scheme 11. In the first stage, the reaction of **16a** with **1** leads to **16b** resulting from the aziridine ring opening. The intermediate disulfide **16b** undergoes reductive cleavage with **1**[10] to form the thiolate **N**, which then undergoes 8-*exo*-*tet*-cyclization to give the products.

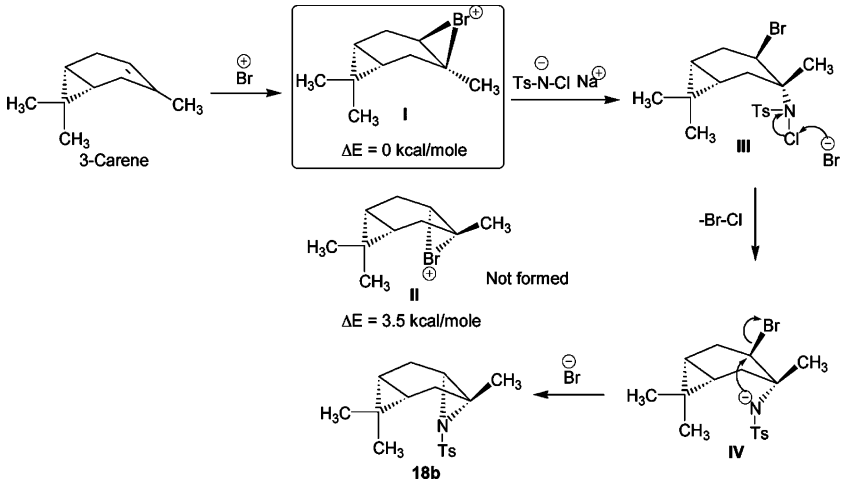
Reaction of 2,2,3-Trisubstituted Aziridines with 1. Next, we studied the ring opening of 2,2,3-trisubstituted aziridines **18** with **1**. The reaction of aziridine **18a** with **1** (1.1 equiv, CH_3CN, room temperature, 4 h) gave a diastereomeric mixture of **19a** in 74% yield (Scheme 12). This product resulted from aziridine ring opening with **1** at the more hindered site[21] to form a quaternary carbon center. The structure of this product is supported by the ^1H NMR where the -NH proton appears as a doublet. In order to extend this methodology, we synthesized an optically pure trisubstituted aziridine[22] **18b** from Δ^3-carene using the Sharpless procedure (Scheme 12). Since formation of bromonium ion is the first step in the Sharpless aziridination procedure,[16] in the case of Δ^3-carene the formation of bromonium ion **I** occurs selectively in a *trans*-fashion and Chloramine-T opens up the bromonium ion **I** from the α-face followed by Br-Cl elimination to generate intermediate **IV**,

(19) (a) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, *23*, 1973−1976. (b) VanRheenen, V.; Cha, D. Y.; Hartley, W. M. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 342. (c) Maras, A.; H. Secen, H.; Sutbeyaz, Y.; Balci, M. *J. Org. Chem.* **1998**, *63*, 2039−2041. (d) Mehta, G.; Ramesh, S. S.; Bera, M. K. *Chem. Eur. J.* **2003**, *9*, 2264−2272.

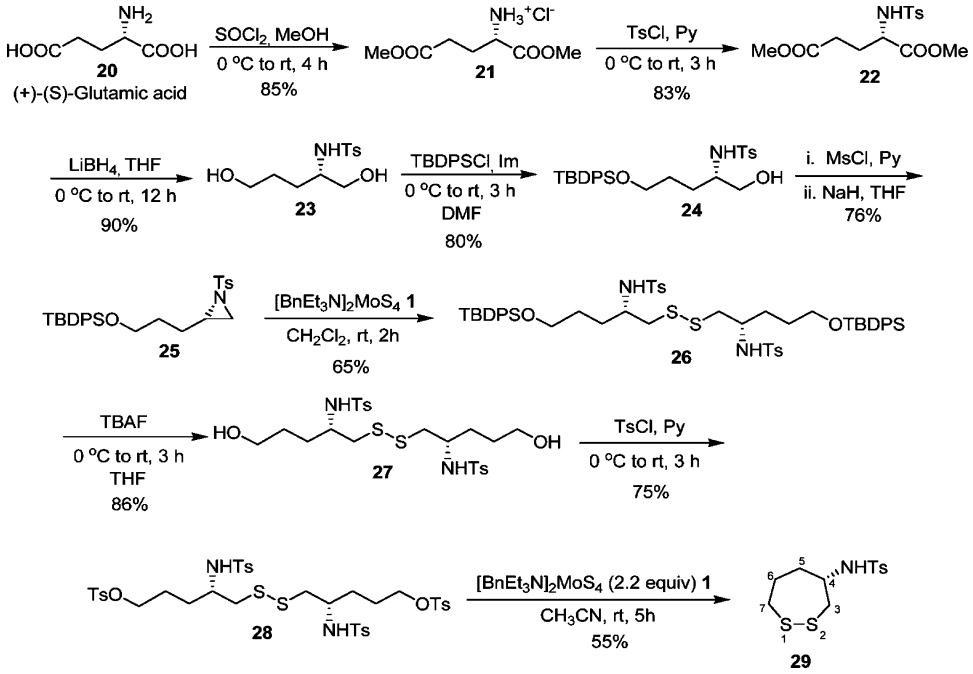
(20) Devan, N.; Sridhar, P. R.; Prabhu, K. R.; Chandrasekaran, S. *J. Org. Chem.* **2002**, *6*, 9417−9420.

(21) (a) Li, P.; Forbeck, E. M.; Evans, C. D.; Joullie, M. M. *Org. Lett.* **2006**, *8*, 5105−5107. (b) Lin, P.; Bellos, K.; Stamm, H.; Onistschenko, A. *Tetrahedron* **1992**, *48*, 2359−2372.

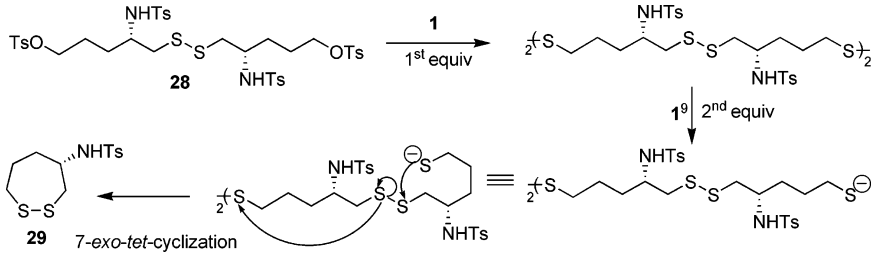
SCHEME 13. Tentative Mechanism for Formation of *cis*-Aziridino-carene by Sharpless Aziridination



SCHEME 14. Synthesis of Seven-Membered Cyclic Disulfide from L-Glutamic Acid



SCHEME 15. Tentative Mechanism for Formation of 29



which upon intramolecular substitution forms *cis*-aziridino-carene **18b**. In the catalytic cycle, formation of *trans*-bromonium ion **I** is 3.5 kcal/mol more stable than the corresponding *cis*-bromonium ion, which then leads to the formation of **18b** (Scheme 13).[23] Treatment of **18b** with **1** (1.1 equiv, CH_3CN, room temperature, 4 h) led to the formation of disulfide **19b** in 68% yield via regio- and stereospecific ring opening from the more hindered site as in the case of **18a**. A detailed study of the mechanism of ring opening of trisubstituted aziridines with **1** is under investigation.

Synthesis of Seven-Membered Cyclic Disulfide 29 from L-Glutamic Acid 20. This methodology was then extended to

(22) Handy, S. T.; Ivanow, A.; Czopp, M. *Tetrahedron Lett.* **2006**, *47*, 1821−1823.

(23) DFT calculations were carried out on intermediates **I** and **II** using B3LYP method and the 6-31.G(d) level basis set using *Guassian 98*.

SCHEME 16. Synthesis of *β*-Sulfonamidosulfide Involving Tandem, Multistep Reactions

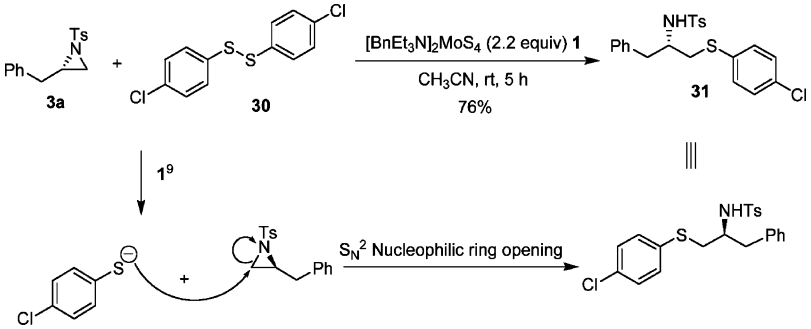
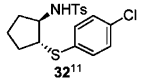
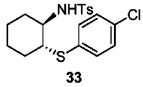
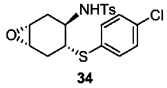
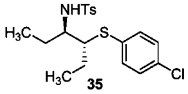
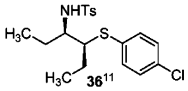
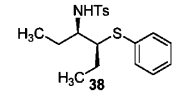
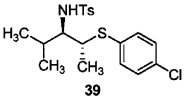
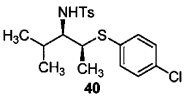
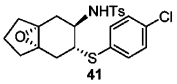
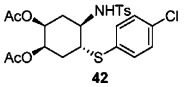
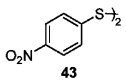
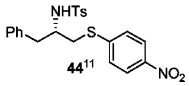


TABLE 6. Synthesis of *β*-Sulfonamidosulfides by Tandem, Multistep Reaction Mediated by 1

Entry	Aziridines	Disulfides	Time (h)	*β*-Sulfonamidosulfides	Yield (%)
1	**10a**	**30**	4	 **32**[11]	65
2	**10b**	**30**	6	 **33**	71
3	**10f**	**30**	5	 **34**	66
4	**8a**	**30**	8	 **35**	68
5	**8b**	**30**	4	 **36**[11]	70
6	**8b**	 **37**	6	 **38**	70
7	**8c**	**30**	7	 **39**	68
8	**8d**	**30**	6	 **40**	72
9	**10h**	**30**	5	 **41**	68
10	**14**	**30**	3	 **42**	71
11	**3a**	 **43**	4	 **44**[11]	62

the synthesis of disulfide **29**, a potential radiation-protection drug[24] starting from (+)-(*S*)-glutamic acid using tetrathiomolybdate **1** as sulfur transfer reagent (Scheme 14). L-Glutamic acid **20** was converted into dimethyl glutamate amine hydrochloride **21**, which was further converted into tosylamino derivative **22** followed by reduction using $LiBH_4$ in THF for 12 h to furnish (*S*)-2-tosylamino-1,5-pentanediol **23**.[25] Selective protection of the hydroxyl group at C-5 of the amino diol **23** using TBDPSCl furnished the protected amino alcohol **24**,[26] which upon mesylation followed by cyclization afforded aziridine **25** in good yield. Aziridine **25** was converted into *β*-sulfonamidodisulfide **26** in 65% yield using **1** as sulfur transfer reagent. Deprotection of **26** using TBAF gave diol **27**, which was further converted into ditosylate **28**. Treatment of ditosylate **28** with **1** (2.2 equiv, CH_3CN, 28 °C, 5 h) afforded (−)-(*S*)-1,2-dithiepane-4-amino derivative **29** in 55% yield (Scheme 14). A tentative mechanism for the reaction ditosylate **28** with **1** to form dithiepane derivative **29** is presented in Scheme 15.

Synthesis of *β*-Sulfonamidosulfides: Tandem Disulfide Cleavage−Aziridine Ring Opening. Finally, we have demonstrated cleavage of disulfide bonds assisted by **1** and the use of masked thiolate for the synthesis of *β*-sulfonamidosulfides involving multistep reactions in a one-pot operation (Scheme 16). It has been shown earlier that disulfide bonds are cleaved in the presence of **1**, involving an induced redox reaction.[10] The results of tandem cleavage of disulfide bonds assisted by **1** followed by aziridine ring opening to provide *β*-sulfonamidosulfides are summarized in Table 6. Thus, in the reaction of disulfide **30** with **1** (2.2 equiv, CH_3CN, 28 °C, 3 h) followed by the addition of aziridine **3a**, the corresponding *β*-sulfonamidosulfide **31** was obtained as the only product in good yield. Treatment of *trans*-aziridino-epoxide **10f** with *p*-chloro diphenyl disulfide **30** with **1** under similar conditions gave selectively aziridine-opened *trans*-*β*-sulfonamidosulfide **34** without affecting the epoxide ring. Finally, to assess the regio- and stereospecificity together in the same substrate, *cis*-aziridine **8c** was treated with disulfide **30** in the presence of **1** to afford exclusively the *anti*-*β*-sulfonamidosulfide **39** in 68% yield. In the case of *trans*-aziridine **8d**, the *syn*-*β*-sulfonamidosulfide **40** was obtained in 72% yield under the same reaction condition. Solid-state structure and stereochemistry of compounds **32**, **36**, and **44** were confirmed by X-ray crystallography.[11]

Conclusion

In summary, tetrathiomolybdate **1** provides an easy access to *β*-sulfonamidodisulfides from aziridines in regio- and stereospecific ring-opening processes under neutral conditions without the use of any Lewis acid or base. Selective aziridine ring opening in the presence of epoxide has also been demonstrated to provide epoxy-*β*-sulfonamidodisulfides from the aziridino-epoxides. We have achieved the construction of eight-membered ring system **17** from aziridino-epoxide **16a** by

(24) Herbrandson, H. F.; Wood, R. H. *J. Med. Chem.* **1969**, *12*, 620−624.

(25) (a) Grabowski, S.; Armbruster, J.; Prinzbach, H. *Tetrahedron Lett.* **1997**, *38*, 5485−5488. (b) Kang, S. H.; Hwang, Y. S.; Youn, J. H. *Tetrahedron Lett.* **2001**, *42*, 7599−7603.

(26) Wipf, P.; Graham, T. H. *J. Org. Chem.* **2001**, *66*, 3242−3245.

performing both aziridine and epoxide ring opening in one pot and also the synthesis of optically pure cyclic seven-membered disulfide **29** from L-glutamic acid. Additionally, a number of β-sulfonamidosulfides were synthesized in a tandem, multistep process in a one-pot operation.

Experimental Section

Synthesis of D-Glucose-Derived Aziridine 3o. The mesylate **3n**[13b] (0.271 g, 0.5 mmol) was dissolved in dry THF and cooled to 0 °C, followed by the addition of a suspension of freshly washed (hexanes) sodium hydride (60% dispersion in mineral oil, 0.160 g, 4.0 mmol) in THF (3 mL). After 22 h, the reaction mixture was evaporated onto SiO_2, and chromatography on SiO_2 (ethyl acetate/hexanes, 1:9) yielded **3o** as a colorless oil. R_f = 0.50 (EtOAc/hexanes, 1:1). Yield: 0.178 g, 80%. $[\alpha]^{27}_D = -60.00$ (c = 1.0, $CHCl_3$). IR (neat) ν_{max}: 1520, 1451, 1329, 1171, 1041, 670 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.1 Hz, 2H), 7.37−7.29 (m, 7H), 5.91 (d, J = 3.9 Hz, 1H), 4.70 (d, J = 12.2 Hz, 1H), 4.57 (d, J = 3.9 Hz, 1H), 4.46 (d, J = 12.2 Hz, 1H), 3.87 (d, J = 3.7 Hz, 1H), 3.74 (dd, J = 7.4, 3.7 Hz, 1H), 3.18−3.17 (m, 1H), 2.60 (d, J = 7.3 Hz, 1H), 2.42 (s, 3H), 2.03 (d, J = 4.6 Hz, 1H), 1.39 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 136.9, 134.7, 129.5, 128.5, 128.2, 128.0, 127.9, 111.8, 105.4, 82.2, 81.8, 80.6, 71.8, 38.9, 28.9, 26.7, 26.1, 21.6. HRMS m/z: calcd for $C_{23}H_{27}NO_6SNa^+$ [M + Na^+] 468.1457, found 468.1461.

General Procedure for Ring Opening of Mono- and 2,2-Disubstituted Aziridines with Benzyltriethylammonium Tetrathiomolybdate 1. To a stirred solution of appropriate aziridine (0.50 mmol) in CH_2Cl_2 (3 mL) was added benzyltriethylammonium tetrathiomolybdate **1** (0.335 g, 0.55 mmol) at room temperature (28 °C). After completion of the reaction (TLC, 2−6 h) the solvent was removed in vacuo, and the black residue was extracted with CH_2Cl_2/Et_2O (1:4, 5 × 20 mL) and filtered through Celite pad. The filtrate was concentrated, and the crude product was purified by flash column chromatography on silica gel (230−400 mesh, eluting with hexanes/ethyl acetate 9:1) to obtain the corresponding β-sulfonamidodisulfides in good yield.

β-Sulfonamidodisulfide 4a. R_f = 0.60 (EtOAc/hexanes, 3:7). Yield: 0.138 g, 86%. $[\alpha]^{27}_D = -80.32$ (c = 12.6, CH_2Cl_2). IR (neat) ν_{max}: 3263, 1329, 1158, 815, 666 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, J = 8.1 Hz, 2H), 7.21−7.16 (m, 5H), 6.99−6.96 (m, 2H), 5.11 (d, J = 7.8 Hz, 1H), 3.76−3.66 (m, 1H), 2.99 (dd, J = 13.8, 4.8 Hz, 1H), 2.90 (dd, J = 13.8, 6.3 Hz, 1H), 2.75−2.66 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.2, 136.9, 136.4, 129.6, 129.3, 128.6, 126.9, 126.7, 54.3, 43.2, 39.2, 21.5. HRMS m/z: calcd for $C_{32}H_{36}N_2O_4S_4Na^+$ [M + Na^+] 663.1456, found 663.1466. Anal. Calcd for $C_{32}H_{36}N_2O_4S_4$: C, 59.97; H, 5.66; N, 4.39; S, 20.01. Found: C, 60.12; H, 5.84; N, 4.58; S, 20.32.

β-Sulfonamidodisulfide 4l. R_f = 0.60 (EtOAc/hexanes, 1:1). Yield: 0.179 g, 75%. $[\alpha]^{27}_D = +16.00$ (c = 1.0, $CHCl_3$). IR (neat) ν_{max}: 3280, 1513, 1455, 1324, 1160, 1074, 1029, 665 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, J = 8.1 Hz, 2H), 7.41−7.30 (m, 3H), 7.26−7.20 (m, 4H), 5.71 (d, J = 3.6 Hz, 1H), 5.22 (d, J = 5.4 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 3.9 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.31 (dd, J = 7.2, 3.3 Hz, 1H), 3.95 (d, J = 3.3 Hz, 1H), 3.87 (q, J = 6.0 Hz, 1H), 3.02 (dd, J = 14.4, 6.3 Hz, 1H), 2.83 (dd, J = 14.4, 4.5 Hz, 1H), 2.38 (s, 3H), 1.43 (s, 1H), 1.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.2, 137.1, 136.7, 129.4, 128.7, 128.2, 127.8, 127.4, 116.1, 111.9, 104.5, 81.9, 81.5, 78.6, 71.4, 52.3, 40.7, 26.7, 26.2, 21.5. HRMS m/z: calcd for $C_{46}H_{56}N_2O_{12}S_4K^+$ [M + K^+] 995.2353, found 995.2373.

β-Sulfonamidodisulfide 4m. R_f = 0.70 (EtOAc/hexanes, 1:1). Yield: 0.153 g, 71%. $[\alpha]^{27}_D = +36.00$ (c = 1.0, $CHCl_3$). IR (neat) ν_{max}: 3278, 1373, 1336, 1159, 1070, 846, 669 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 5.10 (d, J = 9.9 Hz, 1H), 4.31 (d, J = 7.8 Hz, 1H), 4.10−4.06 (m, 1H), 3.98 (dd, J = 13.2, 7.5 Hz, 1H), 3.86−3.76 (m, 1H), 3.71 (dd, J = 8.7, 6.0 Hz, 1H), 3.59 (t, J = 7.8 Hz, 1H), 2.60 (d, J = 7.8 Hz, 1H), 2.43 (s, 3H), 1.41 (s, 3H), 1.38 (s, 3H), 1.33 (s, 1H), 1.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.6, 137.9, 129.8, 127.1, 109.8, 109.7, 77.8, 77.4, 76.8, 67.7, 51.9, 39.5, 27.0, 26.9, 26.2, 25.2, 21.5. HRMS m/z: calcd for $C_{38}H_{56}N_2O_{12}S_4K^+$ [M + K^+] 899.2353, found 899.2336.

β-Sulfonamidodisulfide 7c. R_f = 0.30 (EtOAc/hexanes, 1:1). Yield: 0.102 g, 74%. Mp: 156 °C. IR (neat) ν_{max}: 3456, 3289, 1512, 1443, 1312, 1223, 1212, 1165, 667 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-d_6, 1:1 mixture of diastereomers): δ 7.79 (d, J = 8.1 Hz, 4H), 7.31 (d, J = 8.1 Hz, 4H), 5.54 (s, 1H), 5.52 (s, 1H), 3.61−3.57 (m, 4H), 3.12 (dd, J = 27.6, 13.5 Hz, 4H), 2.78 (bs, 2H), 2.43 (s, 6H), 1.12 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$/DMSO-d_6, 1:1 mixture of diastereomers): δ 142.2, 140.1, 128.9, 126.1, 66.4, 59.8, 59.7, 47.3, 20.8, 19.5, 19.4. HRMS m/z: calcd for $C_{22}H_{32}N_2O_6S_4Na^+$ [M + Na^+] 571.1041, found 571.1038. Anal. Calcd for $C_{22}H_{32}N_2O_6S_4$: C, 48.15; H, 5.88; N, 5.10; S, 23.37. Found: C, 48.24; H, 5.81; N, 5.28; S, 23.42.

General Procedure for the Synthesis of Aziridines.[16] To a mixture of an appropriate olefin (3 mmol) and $TsNClNa.3H_2O$ (CAT) (0.930 g, 3.3 mmol) in CH_3CN (15 mL) was added phenyltrimethylammonium tribromide (PTAB) (0.113 g, 0.3 mmol) at 28 °C. After 12 h of vigorous stirring, the reaction mixture was concentrated, filtered through a short column of silica gel, and eluted with 10% EtOAc in hexanes. After evaporation of solvent, the resultant solid was purified by flash column chromatography to yield the corresponding aziridine.

***cis*-2,3-Diethyl-*N*-tosyl Aziridine 8a.** R_f = 0.7 (EtOAc/hexanes, 3:7). Yield: 0.486 g, 64%. Mp: 78 °C. IR (neat) ν_{max}: 1334, 1162, 948, 716, 682 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 2.78−2.71 (m, 2H), 2.44 (s, 1H), 1.58−1.32 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.2, 135.4, 129.5, 128.0, 46.7, 21.6, 20.0, 11.6. HRMS m/z: calcd for $C_{13}H_{19}NO_2SNa^+$ [M + Na^+] 276.1034, found 276.1036. Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53; S, 12.66. Found: C, 61.75; H, 7.59; N, 5.66; S, 12.78.

***trans*-2,3-Diethyl-*N*-tosyl Aziridine 8b.** R_f = 0.8 (EtOAc/hexanes, 3:7). Yield: 0.516 g, 68%. Mp: 122 °C. IR (neat) ν_{max}: 1321, 1159, 937, 711, 696 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 2.64−2.58 (m, 2H), 2.43 (s, 3H), 1.79−1.69 (m, 4H), 0.93 (t, J = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7, 137.9, 129.4, 127.4, 50.9, 23.2, 21.5, 11.7. HRMS m/z: calcd for $C_{13}H_{19}NO_2SNa^+$ [M + Na^+] 276.1034, found 276.1031. Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53; S, 12.66. Found: C, 61.82; H, 7.61; N, 5.71; S, 12.62.

***cis*-*N*-Tosyl-aziridino-carene 18b.** R_f = 0.60 (EtOAc/hexanes, 3:7). Yield: 0.586 g, 64%. $[\alpha]^{27}_D = +36.00$ (c = 1.0, $CHCl_3$). IR (neat) ν_{max}: 1450, 1321, 1157, 1091, 923, 815 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 3.03 (dd, J = 7.8, 3.9 Hz, 1H), 2.42 (s, 3H), 2.28 (q, J = 8.7 Hz, 1H), 2.11 (dd, J = 15.6, 8.6 Hz, 1H), 1.76 (s, 3H), 1.19 (dd, J = 15.6, 6.4 Hz, 1H), 0.98 (s, 3H), 0.85−0.79 (m, 1H), 0.78 (s, 3H), 0.66−0.57 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.3, 138.3, 129.3, 126.9, 51.2, 46.9, 28.3, 27.7, 21.5, 20.5, 19.1, 19.0, 18.9, 18.8, 15.6. HRMS m/z: calcd for $C_{17}H_{23}NO_2SNa^+$ [M + Na^+] 328.1347, found 328.1348.

General Procedure for Ring Opening of 2,3-Disubstituted Aziridines with 1. To a well-stirred solution of appropriate aziridine (0.50 mmol) in CH_3CN (6 mL) was added **1** (0.335 g, 0.55 mmol) at once, and the mixture was stirred at room temperature (28 °C) for 5−11 h. The solvent was evaporated under reduced pressure, and the black residue was extracted with CH_2Cl_2/Et_2O (1:5, 3 × 10 mL) and filtered through a Celite pad. The filtrate was concentrated, and the residue was purified by flash column chromatography on silica gel to give β-sulfonamidodisulfides in good yields.

***anti*-*β*-Sulfonamidodisulfide 9c and 9c′.** R_f = 0.30 (EtOAc/hexanes, 3:7). Yield: 0.090 g, 80%. Mp: 157 °C. IR (neat) ν_{max}: 3285, 1507, 1456, 1323, 1238, 1201, 1157, 899, 826, 753, 667 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 7.78 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 4H), 5.09 (d, J = 9.3 Hz, 1H), 4.72 (d, J = 9.3 Hz, 1H), 3.25 (m, 2H), 3.16 (m, 2H), 2.41 (s, 6H), 1.92 (m, 2H), 1.31 (d, J = 6.6 Hz, 3H), 1.19 (d, J = 7.8 Hz, 3H), 0.83 (d, J = 7.8 Hz, 3H), 0.78 (d, J = 6.6 Hz, 6H), 0.71 (d, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 143.1, 143.0, 138.7, 138.6, 129.4, 126.9, 63.8, 63.7, 49.7, 30.2, 21.5, 20.9, 18.9, 18.3. HRMS *m*/*z*: calcd for $C_{26}H_{40}$ $N_2O_4S_4Na^+$ [M + Na^+] 595.1769, found 595.1776. Anal. Calcd for $C_{26}H_{40}N_2O_4S_4$: C, 54.51; H, 7.04; N, 4.89; S, 22.39. Found: C, 54.71; H, 7.27; N, 5.18; S, 22.13.

***syn*-*β*-Sulfonamidodisulfide 9d and 9d′.** R_f = 0.45 (EtOAc/hexanes, 3:7). Yield: 0.096 g, 85%. Mp: 142 °C. IR (neat) ν_{max}: 3288, 1512, 1463, 1323, 1239, 1207, 1159, 905, 828, 754, 668 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 7.76 (d, J = 8.4 Hz, 4H), 7.28 (d, J = 8.4 Hz, 4H), 4.61 (d, J = 9.9 Hz, 1H), 4.57 (d, J = 9.6 Hz, 1H), 3.37 (m, 2H), 2.89 (m, 2H), 2.41 (s, 6H), 1.97 (m, 2H), 1.20 (d, J = 6.9 Hz, 6H), 0.86 (d, J = 6.9 Hz, 6H), 0.77 (d, J = 5.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 143.1, 138.6, 129.4, 127.1, 127.0, 62.4, 62.3, 50.5, 50.4, 30.0, 29.9, 21.5, 20.6, 20.5, 17.9, 17.8, 17.7, 17.6. HRMS *m*/*z*: calcd for $C_{26}H_{40}$ $N_2O_4S_4Na^+$ [M + Na^+] 595.1769, found 595.1780. Anal. Calcd for $C_{26}H_{40}N_2O_4S_4$: C, 54.51; H, 7.04; N, 4.89; S, 22.39. Found: C, 54.62; H, 7.24; N, 5.03; S, 22.23.

***β*-Sulfonamidodisulfide 11a and 11a′.** R_f = 0.30 (EtOAc/hexanes, 1:1). Yield: 0.110 g, 81%. Mp: 156 °C. IR (neat) ν_{max}: 3268, 1447, 1323, 1159, 1092, 813, 667 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 7.81 (d, J = 8.1 Hz, 4H), 7.31 (d, J = 8.1 Hz, 4H), 5.32 (d, J = 6.6 Hz, 1H), 5.11 (d, J = 6.0 Hz, 1H), 3.59−3.50 (m, 2H), 3.17−3.08 (m, 2H), 2.43 (s, 6H), 2.21−2.05 (m, 2H), 1.99−1.85 (m, 2H), 1.67−1.26 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 143.5, 143.4, 137.6, 137.4, 129.7, 129.6, 127.3, 127.2, 60.5, 59.4, 56.5, 55.4, 31.9, 31.8, 30.6, 30.3, 21.8, 21.7, 21.5. HRMS *m*/*z*: calcd for $C_{24}H_{32}N_2O_4S_4Na^+$ [M + Na^+] 563.1143, found 563.1158. Anal. Calcd for $C_{24}H_{32}N_2O_4S_4$: C, 53.30; H, 5.96; N, 5.18; S, 23.72. Found: C, 53.51; H, 5.86; N, 5.33; S, 23.89.

Synthesis of Aziridine Derivative 14. OsO_4 (4 mg, 1 mol %) and 50% aqueous solution of *N*-methylmorpholine *N*-oxide (NMMO) (260 μL, 0.56 mmol) were added to a solution of aziridine **13**[16] (272 mg, 1.09 mmol) in acetone/water (4:1, 5 mL) at 0 °C, and the resulting pale yellow reaction mixture was stirred at room temperature for 4 h, before quenching with solid $NaHSO_3$. The resulting mixture was diluted with ethyl acetate (10 mL) and filtered through Celite, and the filtrate was concentrated under reduced pressure. The crude residue was dissolved in pyridine (5 mL), and acetic anhydride (246 μL, 2.61 mmol) was added slowly at 0 °C. After the reaction mixture stirred for 3 h at room temperature, pyridine was removed under reduced pressure, diluted with diethyl ether (25 mL), and washed with 1 N cold hydrochloric acid. The residue was subjected to column chromatography over silica gel (20% ethyl acetate/hexanes) to afford the aziridine **14** as colorless crystals. R_f = 0.60 (EtOAc/hexanes, 3:7). Yield: 0.287 g, 72%. Mp: 122 °C. IR (neat) ν_{max}: 1749, 1246, 1168, 1048, 666 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 4.90 (t, J = 5.4 Hz, 2H), 2.98 (s, 2H), 2.45 (s, 3H), 2.17 (d, J = 5.1 Hz, 4H), 2.0 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 170.2, 144.4, 135.5, 129.6, 127.5, 67.5, 36.7, 25.4, 21.6, 20.9. HRMS *m*/*z*: calcd for $C_{17}H_{21}NO_6SNa^+$ [M + Na^+] 390.0987, found 390.0998. Anal. Calcd for $C_{17}H_{21}NO_6S$: C, 55.57; H, 5.76; N, 3.81; S, 8.73. Found: C, 55.62; H, 5.83; N, 3.96; S, 8.97.

Synthesis of *β*-Sulfonamidodisulfide 15. To a well-stirred solution of aziridine **14** (0.184 g, 0.50 mmol) in CH_3CN (6 mL) was added tetrathiomolybdate **1** (0.335 g, 0.55 mmol) at once, and the mixture was stirred at room temperature (28 °C) for 3 h. The solvent was evaporated under reduced pressure, and the black residue was extracted with CH_2Cl_2/Et_2O (1:5, 3 × 10 mL) and filtered through a Celite pad. The filtrate was concentrated, and the residue was purified by flash column chromatography on silica gel to give *β*-sulfonamidodisulfide **15** as colorless oil in good yield. R_f = 0.70 (EtOAc/hexanes, 1:1). Yield: 0.140 g, 70%. IR (neat) ν_{max}: 3281, 1743, 1446, 1369, 1246, 1159, 1041, 663 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 7.78 (d, J = 8.1 Hz, 4H), 7.34 (d, J = 8.1 Hz, 4H), 5.58 (d, J = 7.2 Hz, 1H), 5.43 (d, J = 6.9 Hz, 1H), 5.18 (bs, 2H), 4.95−4.88 (m, 2H), 3.51 (bs, 2H), 3.38 (bs, 2H), 2.44 (s, 6H), 2.30−2.07 (m, 2H), 2.08−2.02 (m, 16H), 1.79−1.62 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 170.1, 170.0, 169.7, 169.6, 143.8, 137.8, 129.9, 126.9, 69.0, 67.6, 67.5, 49.9, 31.8, 21.6, 21.5, 20.9, 20.8. HRMS *m*/*z*: calcd for $C_{34}H_{44}N_2O_{12}S_4Na^+$ [M + Na^+] 823.1675, found 823.1675.

Synthesis of 3-(Tosylamino)-1,5-oxathiocan-7-ol 17. To a stirred solution of aziridino-epoxide **16a** (0.141 g, 0.50 mmol) in CH_3CN/EtOH (1:1; 5 mL) was added tetrathiomolybdate **1** (0.669 g, 1.1 mmol) at room temperature (28 °C). After completion of the reaction (TLC, 10 h) the solvent was removed in vacuo, and the black residue was extracted with CH_2Cl_2/Et_2O (1:4, 5 × 20 mL) and filtered through a Celite pad. The filtrate was concentrated, and the crude product was purified by flash column chromatography on silica gel (230−400 mesh, eluting with hexanes/ethyl acetate 8:2) to obtain compounds **17a** and **17b** as a diastereomeric mixture (1:1). R_f = 0.70 (EtOAc/hexanes, 1:1). Yield: 0.114 g, 72%. IR (neat) ν_{max}: 3466, 3273, 1415, 1326, 1158, 1091, 1033, 814, 664 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 7.77−7.73 (m, 4H), 7.31 (d, J = 8.1 Hz, 4H), 5.71 (d, J = 9.6 Hz, 1H), 5.17 (d, J = 9.6 Hz, 1H), 3.98 (dd, J = 12.3, 3.3 Hz, 4H), 3.89−3.81 (m, 2H), 3.77 (dd, J = 11.1, 4.5 Hz, 2H), 3.66−3.61 (m, 2H), 3.56−3.41 (m, 4H), 3.03 (dd, J = 15.3, 6.6 Hz, 2H), 2.91−2.59 (m, 8H), 2.43 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 143.7, 143.6, 138.1, 137.8, 129.9, 129.8, 126.9, 126.8, 75.9, 74.6, 74.1, 72.2, 70.3, 67.9, 52.7, 51.7, 40.2, 40.0, 39.1, 38.5, 21.5. HRMS *m*/*z*: calcd for $C_{13}H_{19}NO_4S_2Na^+$ [M + Na^+] 340.0653, found 340.0658.

Synthesis of Δ^3-Carene Derived *β*-Sulfonamidodisulfide 19b. To a well-stirred solution of *cis*-Δ^3-carene derived aziridine **18b** (0.50 mmol) in CH_3CN (6 mL) was added **1** (0.335 g, 0.55 mmol) at once, and the mixture was stirred at room temperature (28 °C) for 4 h. The solvent was evaporated under reduced pressure, and the black residue was extracted with CH_2Cl_2/Et_2O (1:5, 3 × 10 mL) and filtered through a Celite pad. The filtrate was concentrated, and the residue was purified by flash column chromatography on silica gel to give *β*-sulfonamidodisulfide **19b** as colorless oil in good yield. R_f = 0.60 (EtOAc/hexanes, 3:7). Yield: 0.115 g, 68%. $[\alpha]^{27}_D$ = +46.00 (c = 1.0, $CHCl_3$). IR (neat) ν_{max}: 3280, 1455, 1321, 1159, 813, 669 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.49 (d, J = 8.7 Hz, 1H), 3.39 (dd, J = 14.7, 8.7 Hz, 1H), 2.44 (s, 3H), 2.25 (dd, J = 14.7, 7.5 Hz, 1H), 2.05−1.96 (m, 1H), 1.18 (s, 3H), 1.06−0.86 (m, 2H), 0.98 (s, 3H), 0.93 (s, 3H), 0.70−0.54 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 137.4, 129.7, 127.3, 55.6, 54.7, 30.6, 28.1, 25.8, 24.6, 21.6, 20.9, 18.6, 18.5, 15.3. HRMS *m*/*z*: calcd for $C_{34}H_{48}N_2O_4S_4Na^+$ [M + Na^+] 699.2395, found 699.2382.

***N*1-[(1*S*)-4-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxy-1-(hydroxymethyl)butyl]-4-methyl-1-benzene Sulfonamide 24.** To a solution of amino diol[25] **23** (1 g, 3.7 mmol) in DMF (25 mL) held at 0 °C under argon were successively added imidazole (0.548 g, 8.0 mmol) and *tert*-butyldiphenylsilyl chloride (1.1 mL, 4.1 mmol). After 30 min of stirring at 0 °C, the mixture was warmed to room temperature and stirred for additional 3 h. The reaction solution was diluted with ethyl acetate (30 mL) and water (30 mL). The layers were separated, and the aqueous phase was extracted with ethyl acetate (2 × 30 mL). The organic extracts were combined and washed with water (2 × 30 mL). The resulting residue was

purified by flash chromatography on silica gel (ethyl acetate/hexanes 2:8) to afford compound **24** as a colorless oil. $R_f = 0.40$ (EtOAc/hexanes, 1:9). Yield: 1.51 g, 80%. $[\alpha]^{27}_D = -16.00$ ($c = 2.0$, $CHCl_3$). IR (neat) ν_{max}: 3502, 3262, 1328, 1162, 672 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.62−7.59 (m, 5H), 7.43−7.35 (m, 7H), 4.83 (d, $J = 7.8$ Hz, 1H), 3.57−3.45 (m, 4H), 3.25−3.19 (m, 1H), 2.38 (s, 3H), 1.77 (bs, 3H), 1.55−1.22 (m, 4H), 1.02 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.5, 137.5, 135.5, 133.6, 130.8, 129.7, 127.7, 127.1, 64.9, 63.1, 55.4, 28.3, 28.1, 26.8, 21.5, 19.1. HRMS *m/z*: calcd for $C_{28}H_{37}NO_4SSiNa^+$ [M + Na^+] 534.2110, found 534.2126.

(2*S*)-2-(3-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxypropyl)-1-[(4-methylphenyl)sulfonyl]azirane 25. To a solution of amido alcohol **24** (1 g, 1.96 mmol) in dry CH_2Cl_2 (15 mL) were slowly added pyridine (0.48 mL, 5.9 mmol) followed by mesyl chloride (0.23 mL, 2.9 mmol) at 0 °C. The mixture was stirred at 20 °C for 3 h. The reaction mixture was diluted with 30 mL of diethyl ether followed by washing with cold HCl (1 N, 2 × 20). The aqueous layer was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and evaporated to afford a crude residue. It was dissolved in dry THF and cooled to 0 °C followed by the addition of a suspension of freshly washed (hexanes) sodium hydride (60% dispersion in mineral oil, 0.157 g, 4.0 mmol) in THF (3 mL). After 3 h, the reaction mixture was evaporated onto SiO_2, and chromatography on SiO_2 (ethyl acetate/hexanes, 1:9) yielded **25** as a colorless oil. $R_f = 0.70$ (EtOAc/hexanes, 2:8). Yield: 0.739 g, 76%. $[\alpha]^{27}_D = -152.00$ ($c = 1.0$, $CHCl_3$). IR (neat) ν_{max}: 1324, 1162, 1110, 819, 703 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, $J = 8.1$ Hz, 2H), 7.63−7.60 (m, 2H), 7.42−7.29 (m, 8H), 3.58 (t, $J = 6.0$ Hz, 2H), 2.76−2.68 (m, 1H), 2.63 (d, $J = 7.2$ Hz, 1H), 2.42 (s, 3H), 2.06 (d, $J = 4.5$ Hz, 1H), 1.75−1.64 (m, 1H), 1.58−1.32 (m, 3H), 1.02 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.4, 135.5, 135.2, 133.8, 129.6, 127.9, 127.6, 62.9, 40.2, 33.8, 29.6, 27.8, 26.8, 21.6, 19.2. HRMS *m/z*: calcd for $C_{28}H_{35}NO_3SSiNa^+$ [M + Na^+] 516.2005, found 516.2032.

***N*1-((1*S*)-4-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxy-1-[((2*S*)-5-[1-(*tert*-butyl)-1,1-diphenylsilyl]oxy-2-[(4-methylphenyl)sulfonyl]-aminopentyl)disulfanyl]methylbutyl)-4-methyl-1-benzenesulfonamide 26.** To a stirred solution of aziridine **25** (0.247 g, 0.50 mmol) in CH_2Cl_2 (3 mL) was added benzyltriethylammonium tetrathiomolybdate **1** (0.335 g, 0.55 mmol) at room temperature (28 °C). After completion of the reaction (TLC, 2 h) the solvent was removed in vacuo, and the black residue was extracted with CH_2Cl_2/Et_2O (1:4, 5 × 20 mL) and filtered through a Celite pad. The filtrate was concentrated, and the crude product was purified by flash column chromatography on silica gel (230−400 mesh, eluting with hexanes/ethyl acetate 9:1) to obtain the corresponding β-sulfonamidodisulfide **26** as a colorless oil. $R_f = 0.50$ (EtOAc/hexanes, 2:8). Yield: 0.171 g, 65%. $[\alpha]^{27}_D = -50.00$ ($c = 1.0$, $CHCl_3$). IR (neat) ν_{max}: 3276, 1532, 1093, 853, 775, 663 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.61 (d, $J = 8.1$ Hz, 4H), 7.43−7.35 (m, 6H), 7.25−7.21 (m, 2H), 5.08 (d, $J = 8.1$ Hz, 1H), 3.48 (t, $J = 6.0$ Hz, 1H), 2.97 (dd, $J = 13.5$, 3.9 Hz, 1H), 2.69 (dd, $J = 13.5$, 6.6 Hz, 1H), 2.36 (s, 3H), 1.73−1.14 (m, 5H), 1.02 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.3, 137.8, 135.5, 133.7, 129.7, 127.7, 127.1, 63.1, 53.1, 44.3, 29.7, 28.2, 26.9, 21.5, 19.2. HRMS *m/z*: calcd for $C_{56}H_{72}N_2O_6S_4Si_2Na^+$ [M + Na^+] 1075.3709, found 1075.3736.

***N*1-((1*S*)-4-Hydroxy-1-[((2*S*)-5-hydroxy-2-[(4-methylphenyl)-sulfonyl]aminopentyl)disulfanyl] methylbutyl)-4-methyl-1-benzenesulfonamide 27.** To a solution of **26** (0.250 g, 0.24 mmol) in THF (3 mL) kept at 0 °C under argon was added a solution of tetra-*n*-butylammonium fluoride (1.0 M) in THF (0.25 mL, 1 equiv). After stirring for 15 min at 0 °C, the reaction mixture was gradually allowed to attain room temperature over 3 h. It was then diluted with EtOAc (0.56 mL) and washed with water (2 × 10 mL). The organic phase was dried over $MgSO_4$ and evaporated to dryness. The resultant oily residue was purified by flash chromatography on silica gel (EtOAc/hexanes, 3:7) to afford the diol **27** as a colorless oil. $R_f = 0.50$ (EtOAc/hexanes, 1:1). Yield: 0.118 g, 86%. $[\alpha]^{27}_D = -49.00$ ($c = 1.0$, $CHCl_3$). IR (neat) ν_{max}: 3513, 3272, 1321, 1153, 663 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 5.83 (bs, 1H), 3.53−3.46 (m, 3H), 2.91 (dd, $J = 15.0$, 4.2 Hz, 1H), 2.71 (dd, $J = 15.0$, 6.6 Hz, 1H), 2.42 (s, 3H), 2.33 (bs, 1H), 1.75−1.67 (m, 1H), 1.56−1.40 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.5, 137.6, 129.7, 127.1, 62.1, 53.2, 44.2, 29.9, 27.9, 21.6. HRMS *m/z*: calcd for $C_{24}H_{36}N_2O_6S_4Na^+$ [M + Na^+] 599.1354, found 599.1368.

(4*S*)-4-[(4-Methylphenyl)sulfonyl]amino-5-[((2*S*)-2-[(4-methylphenyl)sulfonyl]amino-5-[(4-methyl phenyl)sulfonyl]oxypentyl)disulfanyl]pentyl-4-methyl-1-benzenesulfonate 28. To a solution of diol **27** (0.115 g, 0.20 mmol) in pyridine (2 mL) cooled to 0 °C was added DMAP (5 mg, 0.04 mmol) and *p*-toluenesulfonyl chloride (0.084 g, 0.44 mmol). After stirring for 15 min at 0 °C and 3 h at room temperature, the solution was diluted with diethyl ether (50 mL) and washed with water (5 mL), cold 1 M HCl (2 × 5 mL), saturated $NaHCO_3$ (5 mL), and water (5 mL). The organic phase was dried over $MgSO_4$ and concentrated in vacuo. Chromatography on silica gel (10% EtOAc/hexanes) gave the ditosylate **28** as a colorless oil in high purity. $R_f = 0.60$ (EtOAc/hexanes, 3:7). Yield: 0.133 g, 75%. $[\alpha]^{27}_D = -41.00$ ($c = 1.0$, $CHCl_3$). IR (neat) ν_{max}: 3278, 1311, 1156, 669 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, $J = 8.1$ Hz, 2H), 7.73 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 5.17 (d, $J = 7.8$ Hz, 1H), 3.88 (dd, $J = 11.1$, 5.4 Hz, 2H), 3.42 (m, 1H), 2.81 (dd, $J = 14.1$, 4.5 Hz, 1H), 2.58 (dd, $J = 14.1$, 6.6 Hz, 1H), 2.45 (s, 3H), 2.42 (s, 3H), 1.68−1.58 (m, 2H), 1.47−1.36 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.9, 143.7, 137.6, 132.8, 129.9, 129.8, 127.8, 127.0, 69.8, 52.7, 44.2, 29.4, 24.6, 21.6, 21.5. HRMS *m/z*: calcd for $C_{38}H_{48}N_2O_{10}S_6Na^+$ [M + Na^+] 907.1531, found 907.1572.

Synthesis of (*S*)-1,2-Dithiepane-4-amino Derivative 29. To a well-stirred solution of ditosylate **28** (0.13 g, 0.15 mmol) in CH_3CN (6 mL) was added **1** (0.2 g, 0.33 mmol) at once, and the mixture was stirred at room temperature (28 °C) for 5 h. The solvent was evaporated under reduced pressure, and the black residue was extracted with CH_2Cl_2/Et_2O (1:5, 3 × 10 mL) and filtered through a Celite pad. The filtrate was concentrated, and the residue was purified by flash column chromatography on silica gel to give **29** as colorless oil. $R_f = 0.70$ (EtOAc/hexanes, 3:7). Yield: 0.025 g, 55%. $[\alpha]^{27}_D = -16.00$ ($c = 1.0$, $CHCl_3$). IR (neat) ν_{max}: 3268, 1331, 1136, 659 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 4.86 (d, $J = 9.6$ Hz, 1H), 3.85−3.75 (m, 1H), 2.91 (dd, $J = 14.1$, 4.2 Hz, 1H), 2.83−2.69 (m, 3H), 2.44 (s, 3H), 2.16−2.04 (m, 1H), 2.16−1.75 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.6, 137.9, 129.8, 126.9, 54.2, 47.5, 36.3, 32.9, 22.9, 21.5. HRMS *m/z*: calcd for $C_{12}H_{17}NO_2S_3Na^+$ [M + Na^+] 326.0319, found 326.0310.

Synthesis of β-Sulfonamidosulfide 34. To a well-stirred solution of appropriate disulfide **30** (0.5 mmol) in CH_3CN (8 mL) was added **1** (0.609 g, 1.0 mmol) at once, the mixture was stirred at room temperature (28 °C) for 2 h, and to this was added aziridine **10f** (0.133 g, 0.5 mmol). After completion of the reaction (TLC, 3 h) the solvent was evaporated under reduced pressure, and the black residue was extracted with CH_2Cl_2/Et_2O (1:5, 3 × 10 mL) and filtered through a Celite pad. The filtrate was concentrated, and the residue was purified by flash column chromatography on silica gel to give β-sulfonamidosulfide **34** as colorless oil in good yield. $R_f = 0.50$ (EtOAc/hexanes, 3:7). Yield: 0.135 g, 66%. IR (neat) ν_{max}: 3248, 1336, 1145, 642 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$/DMSO-d_6): δ 7.72 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.27−7.22 (m, 4H), 6.39 (d, $J = 6.0$ Hz, 1H), 3.57 (bs, 1H), 3.23−3.20 (m, 1H), 3.03−2.94 (m, 1H), 2.78−2.58 (m, 2H), 2.45 (s, 3H), 2.42−2.40 (m, 1H), 2.36 (td, $J = 13.2$, 4.2 Hz, 1H), 1.41−1.18 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$/DMSO-d_6): δ 143.0, 138.2, 135.5, 135.1, 134.2, 129.9, 129.3, 128.8, 69.9, 54.9, 52.3,

48.8, 39.8, 38.4, 21.4. HRMS *m*/*z*: calcd for $C_{19}H_{20}ClNO_3S_2Na^+$ [M + Na^+] 432.0471, found 432.0483.

β-Sulfonamidosulfide 38. R_f = 0.60 (EtOAc/hexanes, 3:7). Yield: 0.127 g, 70%. IR (neat) ν_{max}: 3256, 1462, 1382, 1133, 818, 755, 664 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, J = 8.4 Hz, 2H), 7.29−7.18 (m, 7H), 4.97 (d, J = 9.9 Hz, 1H), 3.48−3.39 (m, 1H), 2.85 (td, J = 7.8, 3.3 Hz, 1H), 1.61 (t, J = 7.2 Hz, 3H), 1.57−1.26 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.1, 138.3, 135.6, 131.2, 129.6, 129.0, 128.3, 126.9, 58.3, 57.8, 27.2, 22.9, 21.5, 12.3, 10.7. HRMS *m*/*z*: calcd for $C_{19}H_{25}NO_2S_2Na^+$ [M + Na^+] 386.1224, found 386.1213.

Acknowledgment. D.S. thanks CSIR, New Delhi for a senior research fellowship, and S.C.N. thanks DST, New Delhi for a JC Bose National Fellowship and for CCD X-ray facility.

Supporting Information Available: Experimental procedures; ^1H, ^{13}C, and DEPT spectra for all new compounds; and X-ray structures of compounds **5d**, **7a**, **7c**, **9a**, **9b**, **9c**, **11a**, **14**, **32**, **36**, and **44** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0624389