Ring-Opening of Aziridines by Pendant Sulfamates Allows for Regioselective and Stereospecific Preparations of Vicinal Diamines

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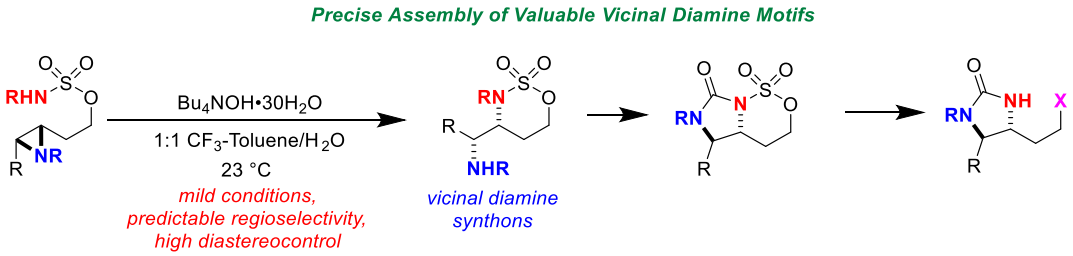
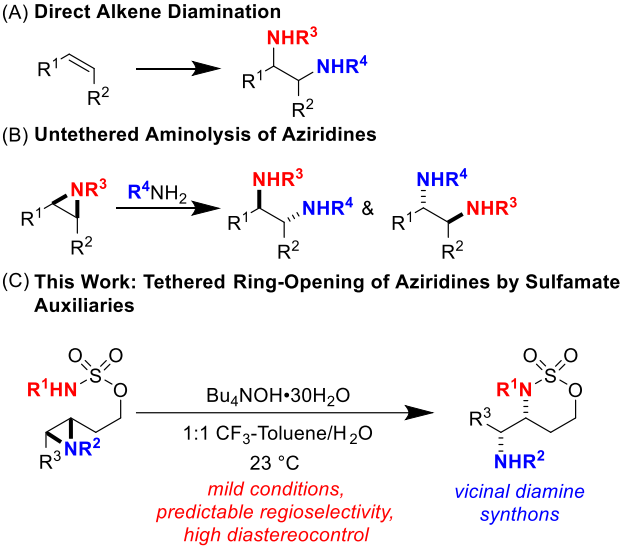
Supporting Information Placeholder



ABSTRACT: The ring-opening of aziridines by pendant sulfamates is a viable strategy for the rapid preparation of vicinal diamines. Our reaction is compatible with both di-substituted *cis* and *trans* aziridines; unsubstituted, *N*-alkyl, and *N*-aryl sulfamates engage effectively. In all cases examined, the cyclization reaction is perfectly regioselective and stereospecific. Once activated, the product oxathiazinane heterocycles can be ring-opened with a diverse range of nucleophiles.

Vicinal diamines (1,2-diamines) are well-represented in molecules of value, including those used as medicines, ligands, and agrochemicals.[1-7] Given their importance to multiple areas of synthetic chemistry, it is no surprise that numerous protocols have been invented for their construction.[8-39] Diamination of olefins[40-45] and untethered (intermolecular) aminolysis[46-48] of aziridines are common strategies for accessing these motifs (**Scheme 1**). The direct diamination of olefins is a powerful approach for the construction of vicinal diamines, as it installs both nitrogens in a single synthetic step; some limitations of existing protocols include harsh reaction conditions, limited substrate scope, and issues with regioselectivity and stereoselectivity. Intermolecular aminolysis of aziridines has also been studied in numerous contexts, but, depending on the substrate and reaction conditions, intractable mixtures of regioisomeric products can result. In contrast to the first two approaches, aminolysis of aziridines utilizing detachable tethers has hardly been explored for the synthesis of 1,2-diamines (**Scheme 1**).[49] As part of a larger program on olefin-functionalization[50-52] and ring-opening of aziridines[53, 54] and epoxides,[55-57] our laboratory is very interested in using sulfamate tethers as convenient *N*-nucleophiles. Here, we present a mild protocol for the intramolecular ring opening of aziridines by pendant sulfamates, which allows for regioselective and stereospecific syntheses of a variety of vicinal diamines. Further, we demonstrate that the product oxathiazinanes are convenient synthons for an array of polyfunctional targets.

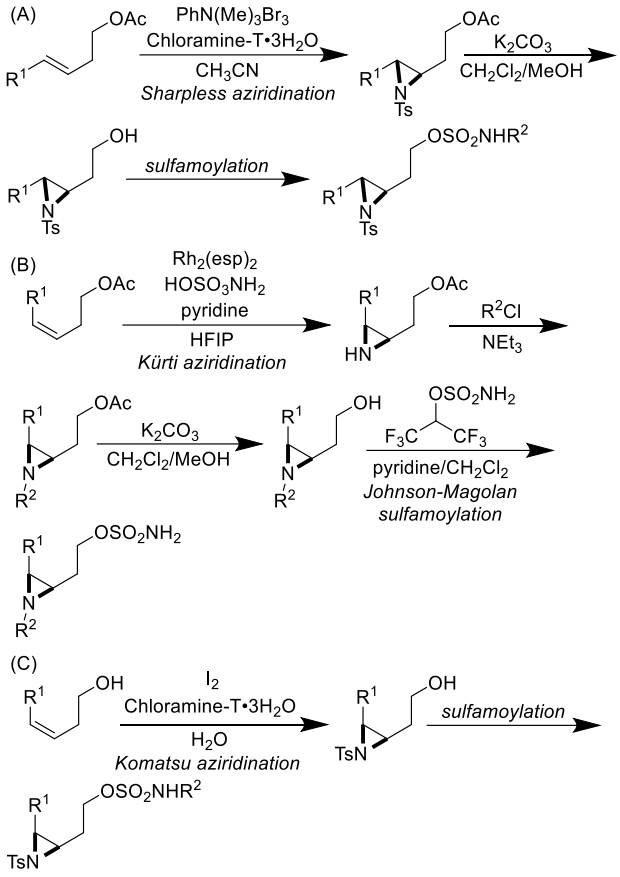
Scheme 1. Current strategies to access vicinal diamines inspire our own efforts.



Before we could begin exploring our envisioned intramolecular ring-opening of aziridines by tethered sulfamates, we had to develop robust protocols for starting material preparation (**Scheme 2**). While epoxy-sulfamates can be readily synthesized by *m*CPBA epoxidation of the corresponding alkene, alkenyl sulfamates were resistant to several existing aziridination protocols.[58-60] Fortunately, alkenyl alcohols and alkenyl

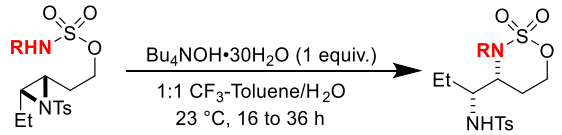
acetates were amenable to aziridination using Sharpless (**Scheme 2A**),[58] Kürti (**Scheme 2B**),[59] or Komatsu[61, 62] (**Scheme 2C**) reactions. In the case of aziridine acetates (**Scheme 2A** and **2B**), carefully monitored hydrolysis gave aziridine alcohols, which were then converted into the corresponding sulfamates.[63, 64]

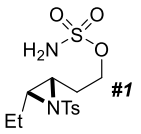
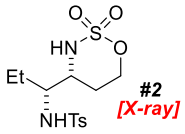
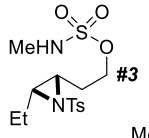
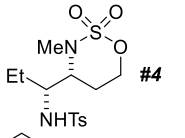
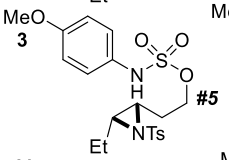
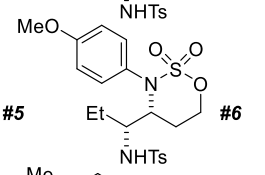
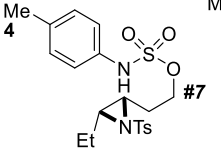
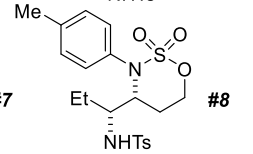
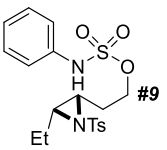
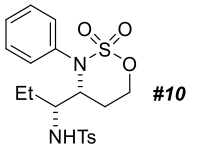
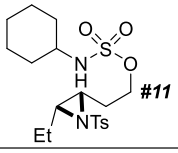
Scheme 2. Representative preparation of aziridine sulfamate substrates.



Our laboratory has previously explored the ring-opening of epoxides and aziridines using both sulfamate[55] and di-*tert*-butylsilanol tethers.[53, 54, 56, 57] It is noteworthy that while di-*tert*-butylsilanol epoxides and aziridines cyclize efficiently when treated with Lewis acids or Brønsted acids, the corresponding sulfamate substrates do not react well under these conditions. With epoxy-sulfamates, treatment with aqueous base gave clean and reproducible reactivity.[55] Analogously, when aziridine sulfamate **1** was stirred with 1 equivalent of $Bu_4NOH•30H_2O$ in a 1:1 mixture of CF_3-toluene/H_2O at room temperature, oxathiazinane **2** formed in an excellent yield of 82% (**Scheme 3**, **Entry 1**). A crystal structure of **2** allowed us to unambiguously assign its identity and relative stereochemistry **(CCDC: 2274209)**. We wished to study the effect of adding substituents to the sulfamate nitrogen. Replacing H with a Me group did not dramatically affect the efficiency of cyclization (**Scheme 3**, **Entry 2**). With bulkier substituents such as *p*-methoxy-phenyl (**Scheme 3**, **Entry 3**), the yield of cyclization dropped, and the reaction time had to be extended by 16 h. We note that the mass balance of the reaction was excellent and was comprised of product and unreacted starting material. Cyclization reactions with *p*-methyl-phenyl and phenyl sulfamates were similarly efficient (**Scheme 3**, **Entries 4**–**5**). In contrast, *N*-cyclohexyl sulfamate **11** was completely resistant to cyclization (**Scheme 3**, **Entry 6**).

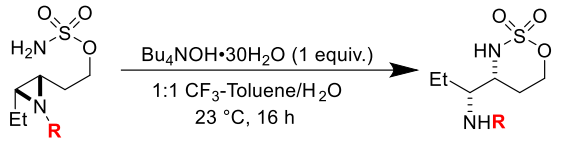
Scheme 3. Structure-reactivity relationship with various sulfamate esters.

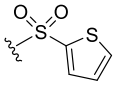
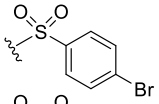
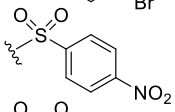
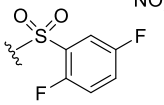
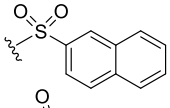
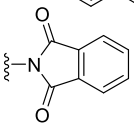


Entry	Substrate	Product	Isolated Yield
1	 #1	 #2 [X-ray]	82%
2	 #3	 #4	70%
3	 #5	 #6	56%
4	 #7	 #8	48%
5	 #9	 #10	45%
6	 #11	No Reaction	———

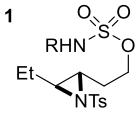
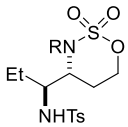
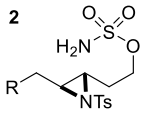
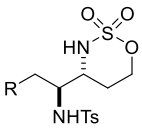
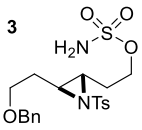
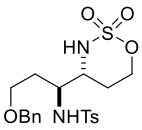
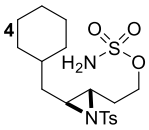
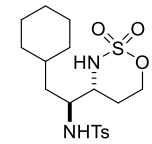
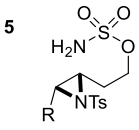
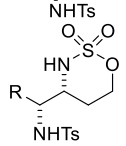
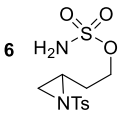
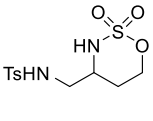
We next examined the effect of varying the substituent on the aziridine nitrogen (**Scheme 4**). In general, to successfully engage, the aziridine had to be "activated" with an electron-withdrawing group. A variety of such moieties were well tolerated, including methanesulfonyl, 2-thiophenesulfonyl, 4-bromophenylsulfonyl, 4-nitrobenzenesulfonyl, 2,5-difluorobenzenesulfonyl, and 2-naphthalenesulfonyl groups (**Scheme 4**, **Entries 1**–**6**). Tosyl groups can be difficult to remove from amines, often requiring harsh reagents like lithium aluminum hydride or dissolving metal conditions with poor functional group compatibility. In contrast, nitrobenzenesulfonyl (nosyl) groups are much more amenable to removal, often with room temperature treatment with thiolate nucleophiles; thus, we were pleased that nosylated aziridines were fully compatible with our optimized protocol. There was no productive reaction with *N*-phthalimido-aziridine substrate **24**; only decomposition of starting material was observed (**Scheme 4**, **Entry 7**). We hypothesize that the known instability of phthalimide protecting groups in a basic milieu underlies this.

Scheme 4. Structure-reactivity relationship with various aziridine *N*-substituents.



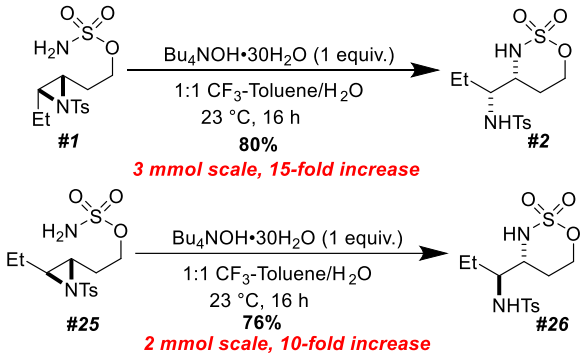
Entry	R		Isolated Yield
1		(***#12***, ***#13***)	83%
2		(***#14***, ***#15***)	85%
3		(***#16***, ***#17***)	76%
4		(***#18***, ***#19***)	73%
5		(***#20***, ***#21***)	80%
6		(***#22***, ***#23***)	58%
7		(***#24***)	No Product

Scheme 5. Substrate scope.

Entry	Substrate	Product		Isolated Yield[a]
1			(***#25***, ***#26***) R = H	***[X-ray]*** 75%
			(***#27***, ***#28***) R = cy-hex	***[X-ray]*** 78%
2			(***#29***, ***#30***) R = Ph	83%
			(***#31***, ***#32***) R = *p*-Br-C_6H_4	90%
			(***#33***, ***#34***) R = *m*-CF_3-C_6H_4	89%
			(***#35***, ***#36***) R = 1-naphthyl	90%
3			(***#37***, ***#38***)	70%
4			(***#39***, ***#40***)	72%
5			(***#41***, ***#42***) R = C_4H_9	65%
			(***#43***, ***#44***) R = CH_3	93%
6			(***#45***, ***#46***)	61%

[a]Reaction conditions: $Bu_4NOH•30H_2O$ (1 equiv.)/1:1 CF_3-toluene:H_2O /23 °C, 16 h

Scheme 6. Cyclization scales well with both *cis*- and *trans*-aziridine sulfamate substrates.



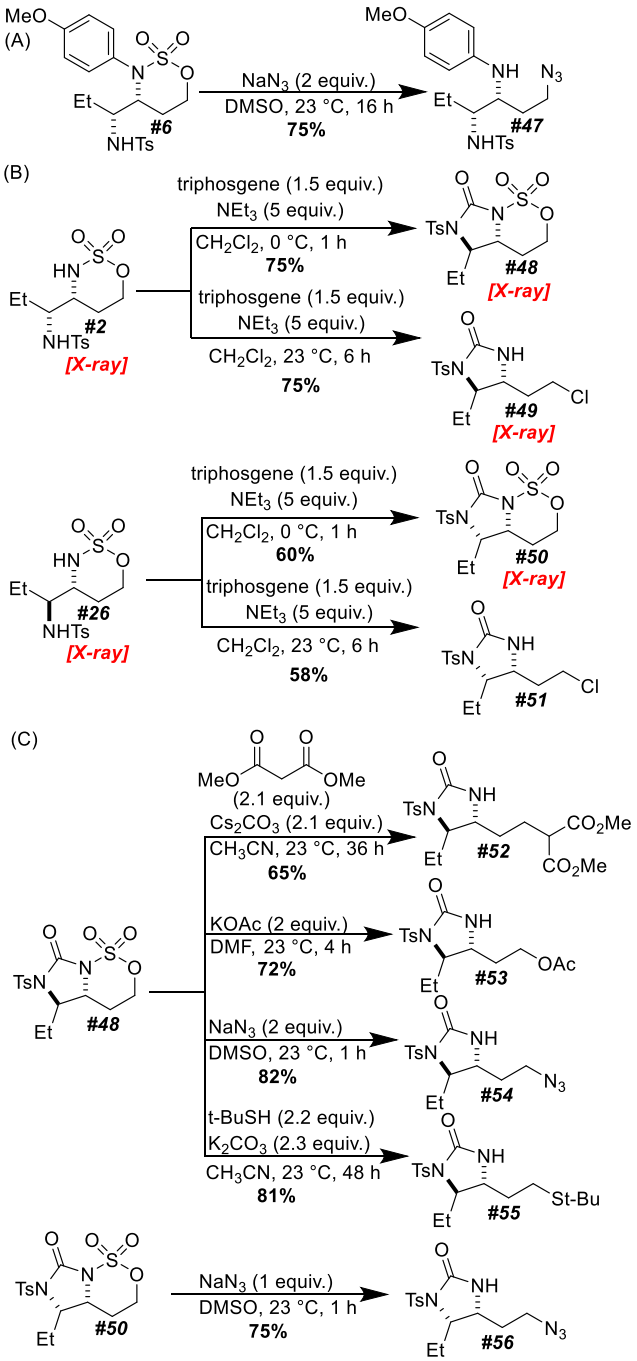
With all substrates tested (**Scheme 5**), the cyclization was perfectly regioselective and stereospecific. In all cases, the pendant sulfamate auxiliary cleaved the aziridine with 6-*exo*-selectivity to give 6-membered oxathiazinane heterocycles bearing vicinal diamines. *Trans*-aziridine sulfamate starting materials gave products with an *erythro*-configuration; conversely, *cis*-aziridine sulfamates gave products with a *threo*-configuration. With our optimized protocol, *cis*, *trans*, and terminal aziridine sulfamates were competent cyclization substrates but, in some instances, with differing reactivity. For example, *cis*-aziridine *N*-cyclohexyl sulfamate **11** (**Scheme 3**) gave no reaction, even with extended reaction times; in sharp contrast, *trans*-aziridine *N*-cyclohexyl sulfamate **27** cyclized efficiently (**Scheme 5**, **Entry 1**). Crystal structures of products **26** (**CCDC: 2277022**) and **28** (**CCDC: 2277021**) allowed for unambiguous determination of relative stereochemistry. The identities of other products were assigned by analogy. Multi-fold increases in scale were tolerated without erosion of yield or selectivity (**Scheme 6**).

The oxathiazinane products could be ring-opened with a variety of nucleophiles, allowing for the rapid transformation of these heterocycles into value-added products (**Scheme 7**). For example, stirring **6** with NaN_3 at room temperature formed azide **47**, which is a triamine surrogate (**Scheme 7A**). When **2** was reacted with triphosgene and NEt_3 at 0 °C, bicyclic oxathiazinane urea **48** formed in good yield (**Scheme 7B**). The reactions conditions had to be carefully controlled; when the reaction was warmed to room temperature, chloride **49** was the exclusive product. Crystal structures of **48** (**CCDC: 2277025**) and **49** (**CCDC: 2277024**) have allowed us to confirm identity and relative stereochemistry. Similar reactions with **26** allowed for formation of products **50** (**CCDC: 2279638**) and **51**, which are epimers of **48** and **49** (**Scheme 7B**). Bicyclic oxathiazinane ureas **48** and **50** could be ring-opened with a diverse array of nucleophiles, allowing for the facile construction of C–C, C–O, C–N, and C–S linkages (**Scheme 7C**).

In summary, we have shown that the ring-opening of aziridines by pendant sulfamates is a viable strategy for the preparation of vicinal diamines. Our reaction is compatible with both *cis* and *trans* di-substituted aziridines; unsubstituted, *N*-alkyl, and *N*-aryl sulfamates engaged effectively. In all cases examined, the cyclization reaction was perfectly regioselective and stereospecific. The product oxathiazinane heterocycles could be activated and ring-opened with a diverse range of

nucleophiles.

Scheme 7. Product oxathiazinane heterocycles are amenable to further functionalization.



Given the importance of vicinal diamines to multiple areas, this strategy is a welcome addition to existing protocols.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, reasoning for structural assignments, NMR spectra, and crystallographic information

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