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Ring-opening and -expansion of 2,2'-biaziridine: access to diverse enantiopure linear and bicyclic vicinal diamines

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Abstract

The chiral pool-derived 1,1'-ditosyl-2,2'-biaziridine has been established as a valuable building block for the divergent synthesis of enantiopure vicinal diamines. Efficient procedures for the regioselective ring opening of the biaziridine with oxygen, sulfur, nitrogen, and carbon nucleophiles are described. The strategic use of nucleophiles bearing pendant functionality allows further elaboration of the acyclic products to a variety of 2,2'-bicyclic-embedded diamines. Desymmetrization of the biaziridine has also been accomplished via the selective monoaddition of organocuprates.

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Ring-Opening and -Expansion of 2,2'-Biaziridine:Access to Diverse Enantiopure Linear and Bicyclic Vicinal Diamines

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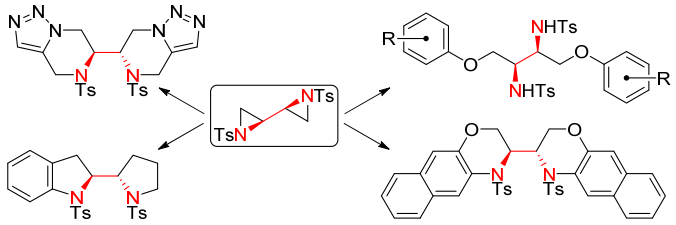
Graphical Abstract



ABSTRACT: The chiral pool-derived 1,1'-ditosyl-2,2'-biaziridine has been established as a valuable building-block for the divergent synthesis of enantiopure vicinal diamines. Efficient procedures for the regioselective ring opening of the biaziridine with oxygen, sulfur, nitrogen and carbon nucleophiles are described. The strategic use of nucleophiles bearing pendant functionality allows further elaboration of the acyclic products to a variety of 2,2'-bicyclic-embedded diamines. Desymmetrization of the biaziridine has also been accomplished via the selective mono-addition of organocuprates

The stereogenic vicinal diamine (Figure 1, red) is a ubiquitous structural unit in synthetic and medicinal chemistry.[1] In particular, this functional array occupies a privileged position in asymmetric catalysis, where it lies at the core of myriad natural and synthetic *N*-donor ligands,[2] organocatalysts[3] and *N*-heterocyclic carbenes.[4] Although other valuable classes of *N*-containing ligands (e.g. BOX, PyBOX) enjoy modularity from the amino-acid pool,[5] vicinal diamine-based catalysts rely extensively on commercially available fragments, most commonly **1** and **2** (Figure 1). To meet the increasing demand for diversity, a variety of methods have been developed to deliver these important motifs in homochiral form.[1a,b,6]

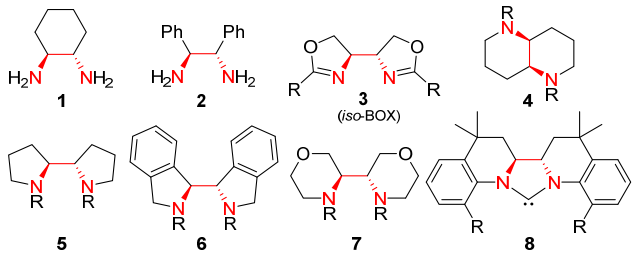
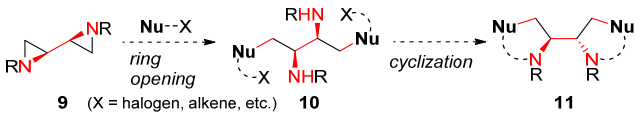


Figure 1. Exemplary stereogenic vicinal diamines.

One successful approach to achieve chirality transfer from vicinal diamines has been to embed the functional group within a semi-rigid bicyclic framework (e.g. **3-8**, Figure 1).[7] In particular, 2,2'-bridged scaffolds that preserve N(sp^3) hybridization (i.e. of type **5-8**) have proven effective with the bicyclic skeleton as the sole stereogenic element.[8] Despite the desirable properties of 2,2'-bicyclic diamines, synthetic access is not trivial, which has limited the opportunity for structural and electronic diversification beyond the commercially available bipyrrolidine (**5**). Although a number of syntheses have been investigated, the majority rely on classical resolution[8a,d,9] or chiral auxiliaries[10] to secure absolute stereochemical purity.

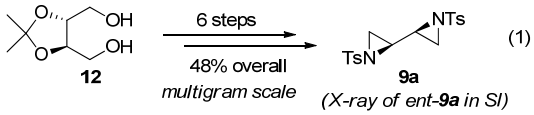
With a view towards greater molecular diversity, we became interested in developing a *de novo* synthetic route to 2,2'-bicyclic diamines in which the requisite vicinal stereocenters could be translated from the chiral pool. Enantiospecific access to bipyrrolidine **5** and bimorpholine **7** from tartaric acid has been demonstrated,[11,12] however, these multistep procedures require upstream chain-elongation and, inherently, are not readily amenable to analogue iteration. Thus, in our search for a chiral pool preparation with an advanced point of divergence, we turned our attention to the tartrate-derived biaziridine **9**, which constitutes the lowest homologue of a 2,2'-bicyclic-diamine (Scheme 1). Based on the abundance of methods for the formal ring-expansion of mono-aziridines via tandem ring opening/closure,[13] we envisioned that **9** would provide a divergent entry to remotely-functionalized diamines **10**, which could be doubly cyclized to target homologues **11**.



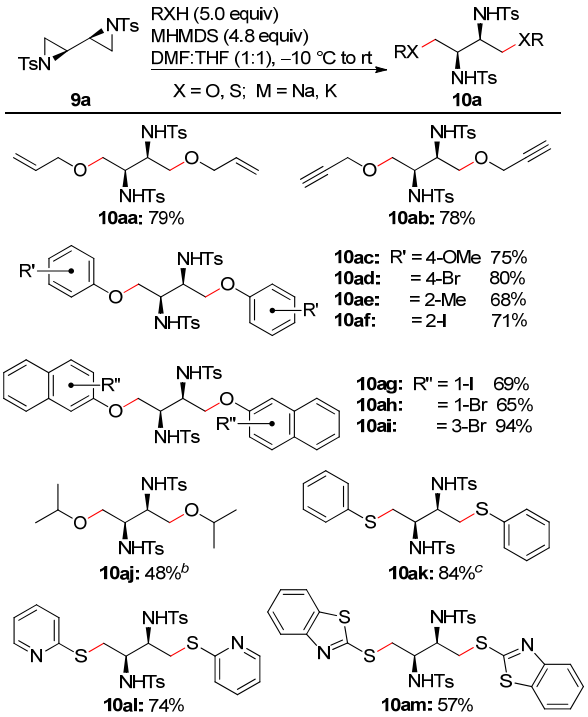
Scheme 1. Proposed Route to 2,2'-Bicyclic Diamines

Despite several reports on the preparation of *N*-protected 2,2'-biaziridines,[14] their application in the context of vicinal diamine assembly has remained essentially unexplored.[15] As such, the initial focus of this investigation became establishing procedures for the regioselective ring opening of **9**. Full evaluation of the nucleophile scope was also of importance, as the ring opening itself presents the opportunity to rapidly unveil novel chiral diamines with a flexible linear core; a structural feature observed in numerous bioactive diamines.[1a]

Our choice of *N*-protecting group was influenced by a previous reaction from our laboratory which ruled out carbamate activation due to undesired intramolecular *N*-acylation during ring opening.[16] The tosyl (Ts) group was selected by virtue of its broad nucleophile compatibility and well documented performance in aziridine ring openings.[17] Thus, both enantiomers of the biaziridine (**9a** and *ent*-**9a**) were prepared on a multi-gram scale from the tartrate-derived commercially available diols **12** and *ent*-**12**, respectively (eq 1). Our procedure was modified from the original report,[14b] resulting in a significant increase in overall yield (48% over 6 steps).[18] Notably, **9a** is a bench-stable solid, enabling confirmation of the absolute configuration (*ent*-**9a**) by X-ray crystallographic analysis.

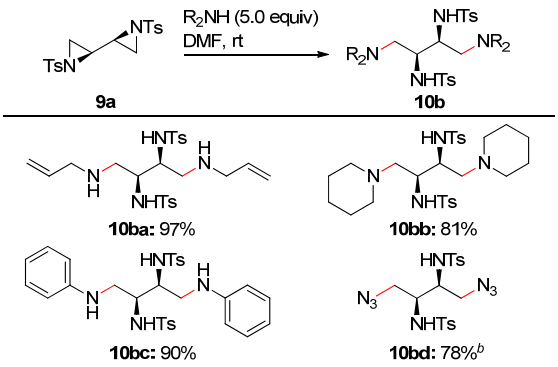


Initial investigations into the ring opening of **9a** utilized *O*- and *S*-nucleophiles in the form of alkoxides and thiolates (Scheme 2). These conditions were chosen over Lewis acid activation[17,19] to ensure attack at the terminal carbons and preservation of the vicinal diamine moiety. Conveniently, the ring opening could be performed at ambient temperature, although excess nucleophile was necessary to minimize competing oligomerization and/or decomposition of **9a**. Under the standard conditions, primary, phenyl and naphthyl alcohols performed well, giving the desired ethers **10aa-ai** in 65-94% yield. The method appears insensitive to electronic effects, with 4-OMe- and 4-BrPh substrates exhibiting comparable reactivity. *Ortho*-substitution of phenyl and naphthyl substrates was tolerated in the form of a methyl group and halogens, although slight decreases in yield occurred. The use of a secondary alkoxide provided **10aj** in a moderate 48% yield, accompanied by $TsNH_2$ as the only other identifiable material. The latter could have resulted from hydrolysis (during aqueous work-up) of enamides formed via competing elimination.[20] A small survey of (hetero)aryl thiolates was also performed, providing **10ak-am** in acceptable to good yield (57-84%).



Scheme 2. Ring Opening of **9a** with Alcohols and Thiols. [a] Reactions performed with 0.13 mmol of **9a** ($[\mathbf{9a}]_0$ = 0.06 M). Alkyl alcohols and thiols: M = Na. Aryl alcohols: M = K. Yields are of isolated product. [b] Corrected yield based on partial co-elution with $TsNH_2$. c 3.0 equiv of RXH used.

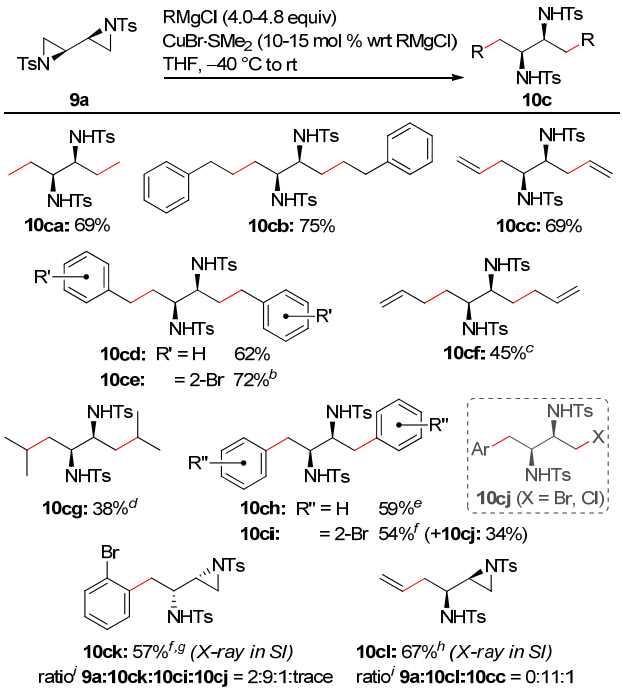
Next, we briefly investigated a new entry to chiral products containing the 1,2,3,4-tetramine functional group. Not surprisingly,[17,21] linear, cyclic and phenyl (anilino) amines were all alkylated cleanly by **9a** at room temperature, without additives, to afford the desired tetramines **10ba-bc** in 81-97% yield (Scheme 3). Additionally, the versatile azide functionality was introduced using $TMSN_3$ and catalytic fluoride ion.[22]



Scheme 3. Ring Opening of **9a** with Amines. [a] Reactions performed with 0.13 mmol of **9a** ($[\mathbf{9a}]_0$ = 0.13 M). Yields are of isolated product. [b] Conditions: $TMSN_3$ (5.0 equiv), TBAF (10 mol %), THF, 0 °C to rt.

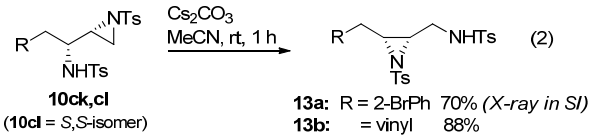
C−C bond formations with terminal *N*-sulfonyl aziridines have recently been achieved via Suzuki and Negishi cross-couplings, however these processes are either not highly regioselective[23] or are limited to aryl nucleophiles.[24] Thus we opted for the traditional copper catalyzed Kumada coupling conditions.[17] Under our optimized protocol (Scheme 4), primary alkyl, vinyl and benzyl Grignard reagents coupled smoothly with **9a**, giving **10ca-ce** in moderate to good yields (62-75%). The allyl carbanion was an unexpectedly troublesome substrate; in addition to **10cf**, we consistently observed at least two products, of which only one could be identified, being $TsNH_2$. In this instance, we favor

β-hydride elimination from the assumed Cu(III)-alkyl intermediate[25] as a means to the latter.[24] Using the secondary isopropyl Grignard, previously unseen olefinic side products emerged. These could be alleviated using an equimolar quantity of the copper salt and a lower reaction temperature,[26] although decomposition of **9a** was still the prevailing pathway. With phenyl Grignard reagents, C−C bond formation occurred satisfactorily, but a significant side product **10cj** was produced from halide addition to the second aziridine.[27] In the case of the 2-bromophenyl analogue, **10cj** was isolated (34%) and characterized as a ~2:1 mixture of bromide/chloride adducts.[28] No halide di-addition products were observed from these reactions.



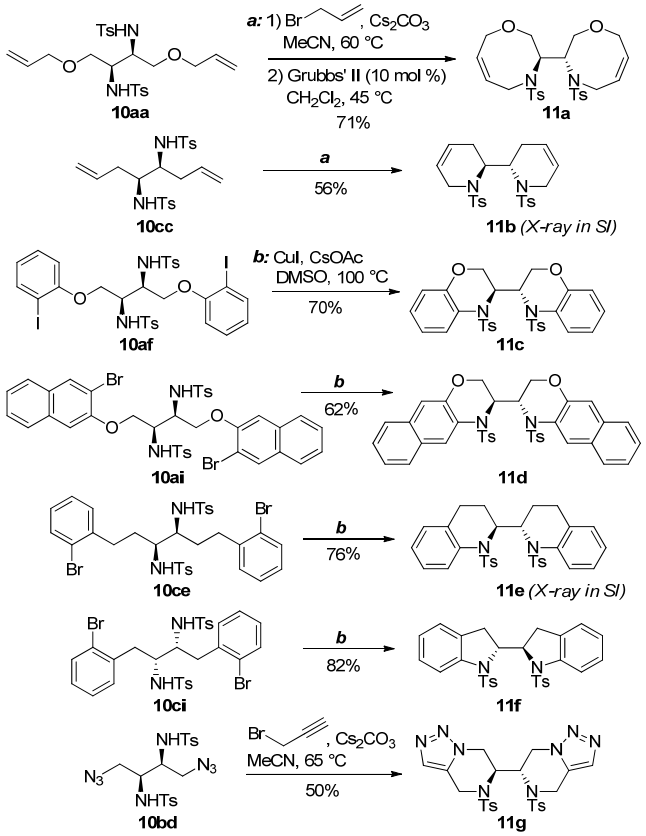
Scheme 4. Ring Opening of **9a** with Grignard Reagents. [a] Reactions performed with 0.13-0.51 mmol of **9a** ([**9a**]0 = 0.03-0.08 M). Yields are of isolated product. [b] RMgBr used. [c] Corrected yield based on co-elution with $TsNH_2$. [d] 100 mol % CuBr·SMe2, −78 °C to rt. [e] Corrected yield based on partial co-elution with **10cj**. [f] *ent*-**9a** used. [g] 3.0 equiv RMgCl, −40 °C to −10 °C, 7 h. [h] 2.3 equiv RMgCl, −40 °C to −10 °C, 4 h. [i] Determined by ^{1}H NMR analysis of the crude reaction mixture.

Although the basis for the apparent attenuation in the rate of the second carbanion addition is not yet well understood, these observations lead us to envisage the possibility of desymmetrizing **9a** by mono-ring opening. By reducing the equivalents of the carbanion and restricting the reaction temperature, high selectivity was obtained for the mono-addition of both 2-bromophenyl- and vinyl Grignard reagents (Scheme 4, **10ck**,**cl**). Interestingly, these isolated mono-aziridines were found to undergo a base-induced stereospecific aza-Payne-type rearrangement,[29] affording internal isomers **13** (eq 2).[30]



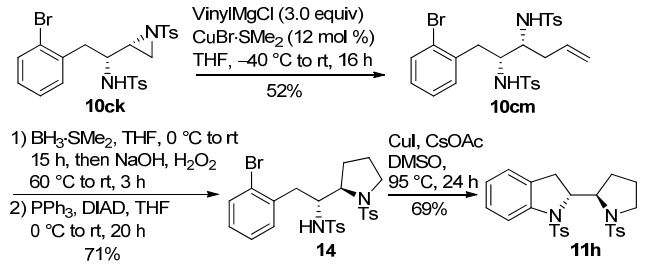
With an extensive collection of conformationally flexible vicinal diamines on hand, we proceeded to examine ring-closure reactions (Scheme 5). Linear diamines **10aa** and **10cc** were submitted to an *N*-allylation/ring closing metathesis sequence, affording **11a** and **11b** with alkene handles conveniently retained for further manipulation. Buchwald-Hartwig cyclization of halo-

functionalized aryl substrates could be affected using an inexpensive combination of CuI and CsOAc,[31] giving **11c-f** in good yields (62-82%).[32] As found with related monocyclic amides,[31] an excess of CuI was required to ensure adequate reaction rates. Additionally, *N*-propargylation of diazide **10bd** triggered a thermal intramolecular Huisgen cycloaddition to provide the triazole-fused skeleton **11g**. To demonstrate the utility of a desymmetrized product, aziridine **10ck** was subjected to a second cross-coupling reaction to install a pendant alkene (Scheme 6). Subsequent hydroboration/oxidation and regioselective intramolecular Mitsunobu alkylation provided **14**, which was further cyclized under the standard copper protocol to give **11h**, bearing electronically differentiated nitrogens.



Scheme 5. Cyclization of Ring-Opened Products **10**

Notably, with the exception of **11f**, all enantiopure cyclized products (Schemes 5 and 6) constitute novel bi-heterocyclic scaffolds.[33] The parent *N*-H form of *ent*-**11f** has been reported previously,[16] while (*N*-H)-**11e** has only been obtained prior in racemic and *meso* forms.[34]

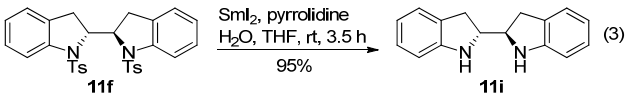


Scheme 6. Synthesis of Asymmetric Bicyclic Diamine **11h**

As anticipated, all evidence pertaining to the stereochemical purity of the products pointed conclusively to a complete chirality transfer from the biaziridine. The universal absence of (*meso*-

)diastereoisomers in the NMR spectra of all crude materials served as primary evidence against epimerization under the basic ring opening/cyclization conditions. In addition, X-ray crystallographic analysis of products **10ck**, **10cl**, **11b**, **11e** and **13a** identified a homochiral crystal lattice of the expected configuration in each case.[18] Representative ring-opened products **10ab** and **10bc** were also subjected to analytical chiral HPLC, together with their enantiomers prepared from *ent*-**9a**, which revealed ≥99% *ee* for all four samples.[18]

Double deprotection of a representative diamine **11f** proceeded smoothly with SmI_2[35] to give **11i** in 95% yield (eq 3). As expected, NMR and chiral HPLC analyses (relative to *ent*-**11i**)[16] revealed a single stereoisomer.



(3)

In summary, we have developed a chiral pool approach to the synthesis of enantiopure vicinal diamines based on the ring opening of 2,2'-biaziridine. Installation of the diamino functionality into this strained ring system was found to provide a reactive electrophile for the addition of both heteroatom- and carbon-based fragments, allowing late stage divergence (from tartaric acid) to an array of 1,2-diamines in short order. The utility of several acyclic products was demonstrated by their elaboration to a set of five-to-eight membered biaziridine homologues, encompassing oxygenated and olefin-containing backbones with fused (hetero)aryl rings as additional rigidifying/electron tuning elements. Potential applications of the vicinal diamines described herein in asymmetric catalysis are now under investigation in our laboratory.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, NMR spectra, HPLC traces and X-ray structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

[#]These authors contributed equally.

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(32) At current, cyclization of the 1-halonapthyl isomer (**10ag,ah**) under the CuI/CsOAc thermal conditions has been unsuccessful.
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