

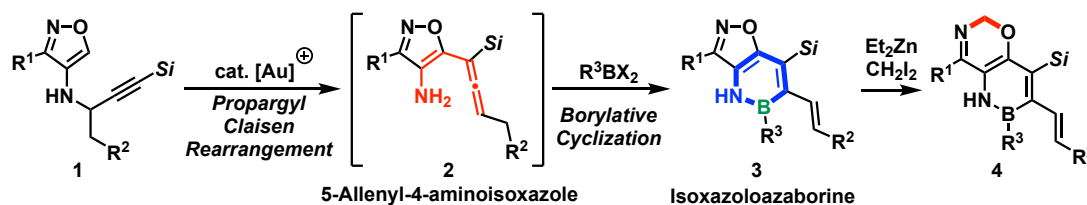
Synthesis of Isoxazoloazaborines via Gold(I)-Catalyzed Propargyl Aza-Claisen Rearrangement/Borylative Cyclization Cascade and Methylene Insertion of Zinc Carbenoid into N-O Bond of Isoxazoles

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Heterocycles containing boron and nitrogen atoms in their ring systems, represented by 1,2-azaborine as a BN isostere of benzene, have recently attracted much attention in various research fields.¹⁾ Although recent synthetic studies have yielded numerous BN-embedded polycyclic aromatic compounds, there are still few examples of heteroarene-fused 1,2-azaborines because of the limited synthetic approaches to the ring system. In general, heteroarene-fused 1,2-azaborines have been synthesized by treating 2-aminostyrenes with electrophilic boron agents.

Recently, we reported the synthesis of 5-allenyl-4-aminoisoxazoles **2** by cationic gold(I) catalyzed propargyl aza-Claisen rearrangement of 4-*N*-propargylaminoisoxazoles **1**.²⁾ Although the allenic amine intermediates have been considered to be generated by conventional propargyl aza-Claisen rearrangement, they had never been used in further reactions because of their rapid intramolecular cyclization.³⁾ Herein, we report the synthesis of an unprecedented BN-heterocycle, isoxazoloazaborine **3** using 5-allenyl-4-aminoisoxazole **2**. The adjacent amino group and allene moiety of isoxazole **2** were successfully engaged in electrophilic borylative cyclization to give fused azaborine **3**. This is the first report of 1,2-azaborine synthesis utilizing allene functionality. Moreover, studies on derivatization of product **3** led us to find ring-expansion of isoxazoles through N-O bond insertion of zinc carbenoid to give oxazine-fused azaborine **4**.⁴⁾



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