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Synergistic Copper-TEMPO catalysis of intermolecular vicinal diamination of styrenes

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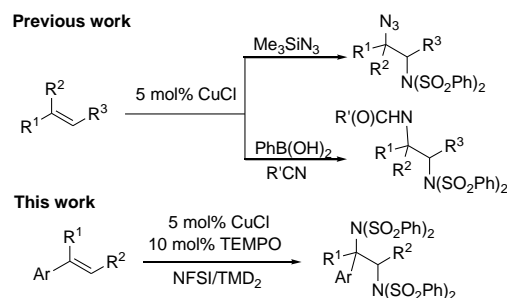
ABSTRACT

A copper-catalyzed, 2,2,6,6-tetramethyl piperidine *N*-oxy radical-assisted intermolecular diamination of styrenes with *N*-fluorobenzenesulfonimide has been developed. The current protocol proved amenable to a diverse array of styrenes via cascade radical addition to readily afford synthetically useful aromatic vicinal diamines with exclusive diastereoselectivity.

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Vicinal diamines are highly important functional groups in a wide range of bioactive compounds and natural products. In addition, functionalized 1,2-diamines have been broadly applied as chiral ligands and auxiliaries.¹ As a result, considerable efforts have been directed toward the development of efficient methods for their synthesis.^{2,3} Transition metal-catalyzed diamination of amino-tethered alkenes has become the most popular approach because it is currently the most efficient and shortest route for the practical synthesis of 1,2-diamines.⁴ In addition, the groups of Chemler and Michael independently established a method for accessing vicinal diamine-containing heterocycles via the copper- and palladium-catalyzed oxidative diamination of anchored amino alkenes using electron-deficient sulfonamides, anilines or *N*-fluorobenzenesulfonimide (NFSI) as secondary intermolecular aminative coupling sources.^{5,6} These two oxidative transformations are of interest because high levels of enantioselectivities can be introduced into the heterocycle frameworks in the presence of suitable chiral auxiliaries.^{4,6} In addition to these remarkable achievements, Shi and coworkers developed a copper- or palladium-catalyzed enantioselective intermolecular alkene diamination that uses diaziridines as the oxidative nitrogen sources and provides an advanced solution for circumventing the inherently more challenging intermolecular version of this reaction.^{4,7} Furthermore, Múniz reported the chiral hypervalent iodine-mediated asymmetric diamination of alkenes, which represents another straightforward route to the direct, intermolecular installation of two amino groups across a double bond.³

NFSI has recently been widely employed as an oxidative nitrogen source in transition metal-catalyzed amination reactions.^{6,8} The ability to easily produce the electrophilic bisulfonamidyl radical ($\cdot\text{N}(\text{SO}_2\text{Ph})_2$) via the oxidative addition of Cu with NFSI provides an opportunity to use a cascade radical reaction to conduct the vicinal aminative difunctionalization of alkenes or alkynes (Scheme 1).⁹ Among these remarkable achievements, the Cu(I)-catalyzed intermolecular aminoazidation and diamination of alkenes to incorporate azidosilane and reaction solvents have also been realized through the formation of Si-F or B-F bonds in the second amination step.^{9e,f} This conceptually inspired us to further explore the utility of NFSI in the field of aminative difunctionalization of alkenes. Herein, we report a new Cu(I)-catalyzed intermolecular diamination of styrenes that employs NFSI as the sole nitrogen source and hexamethyldisilane (HMD) as an external fluoride radical scavenger, with the assistance of the reductive 2,2,6,6-tetramethyl piperidine *N*-oxy radical (TEMPO).¹⁰



Scheme 1. Copper-catalyzed vicinal diamination of alkenes.

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