Photomediated Nitrogen Ring Walk: A New Strategy for Substitution Pattern Alteration.

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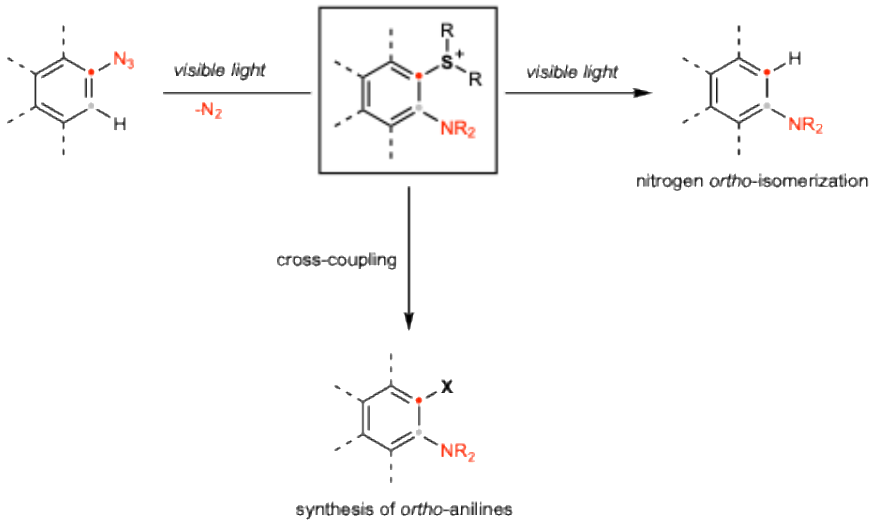
The substitution pattern of a benzenoid ring affects acidity (Hammett), molecular shape (flat, rod-like, or spherical), and redox potential, all of which influence a molecule's interaction with its environment, including biological targets. Alteration of such substitution patterns can significantly impact the function of small molecules or polymeric building blocks.

In this presentation, I will introduce a novel synthetic strategy that enables the formal migration of nitrogen functionality around a benzenoid ring. This approach facilitates the late-stage alteration of aromatic substitution patterns, which typically originate from natural feedstocks or synthetic routes dominated by nucleophilic and electrophilic aromatic substitution chemistry. Such methodologies could be highly valuable for drug discovery, where late-stage alterations of aromatic substitution patterns are currently rare. Specifically, the transformation involves scrambling a nitrogen functionality with its adjacent hydrogen atom, resulting in a 1,2-nitrogen migration *via* the photorearrangement of an aryl azide. The key intermediates generated can also be further functionalized through cross-coupling reactions, broadening the utility of this strategy for the preparation of a wide array of *ortho*-substituted anilines.



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