# *Ph.D. DISSERTATION DEFENSE*

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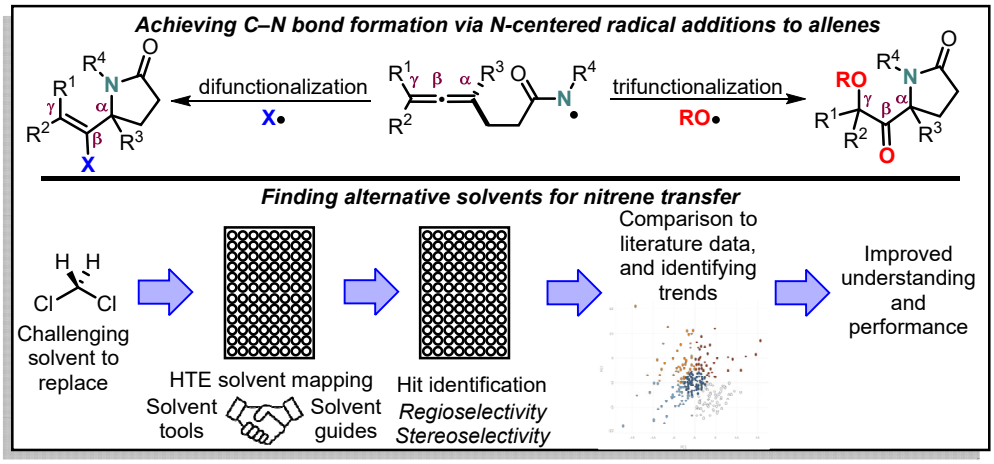
## Investigating the Mechanistic Aspects of Radical-Mediated Di- and Trifunctionalization of Allenes and Utilizing HTE to Identify Solvent Alternatives for Nitrene Transfer.

Schomaker Group
Thursday, August 11th, 2:15 pm
Room 9341 or on Zoom

The prevalence of carbon-nitrogen (C–N) bonds in natural products, materials and pharmaceuticals, highlights the need for mild and selective amination conditions. Approaches describing the construction of C–N bonds through nitrogen-centered radical additions to allenes are scarce in the literature. Allenes offer several attractive features, including potential for selective amidation at three distinct sites via judicious choice of precursor or radical source, the opportunity for axial-to-point chirality transfer, and productive trapping of vinyl or allyl radical intermediates to diversify functionality in the products. The first half of this work describes (1) development of a novel amidyl radical cyclization with allenes resulting in γ-lactams with appended olefins and (2) achieving radical-mediated allene trifunctionalization and providing insights into the impact of allene substitution pattern.

Carbon–nitrogen bonds can alternatively be formed via amination of C–H bonds or aziridination of π-bonds through nitrene transfer. Solvents typically employed in nitrene transfer are typically those found in reactive chemistry, including benzene, chlorinated solvents and acetonitrile. However, these solvents possess health and environmental drawbacks and thus alternatives are needed. Solvent screens are utilized in the second portion of this work to (1) identify suitable replacements for chlorinated solvents in nitrene transfer, (2) study relationships between various solvent parameters and experimental results to support or refute our computationally proposed explanations for the unusual tunable selectivity observed with silver catalysis and (3) understand the key differences between silver and traditional metals (Rh, Mn, Fe) often employed for nitrene transfer.

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