

Thesis title: Photochemical Methods for the Synthesis of Protected Amines

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Abstract in English

Constructing C-N bond remains highly relevant in modern organic synthesis, as it enables the introduction of ubiquitous nitrogen-containing heterocycles. Owing to their basicity, nucleophilicity, and dipole character, these structures are valuable in pharmaceutical and agrochemical industries. The synthesis of amines is essential because they occur in several biologically important processes. In classical chemistry, transition metal-catalysis is a well-established strategy to furnish C-N bonds. However, such approaches often do not meet sustainable requirements.

Along this line, photochemistry enables to perform reactions with the use of light source and open new synthetic routes to the compounds that are unavailable under thermal conditions. Along this line, *N*-Aminopyridinium salts recently gained more attention as amination reagents which can easily generate an electrophilic nitrogen-centered radical precursors by reductive cleavage of the N-N bond. The resulting radicals offer broad synthetic potential.

The main goal of my PhD dissertation was to investigate novel reactivity of photochemically generated nitrogen-centered radicals and aziridines for the formation of C-N and C-C bonds, leading to amines and their derivatives.

Three publications are included as part of my doctoral thesis. The first publication reports photochemical γ -amidation of α,β -unsaturated carbonyl compounds using amidyl radicals derived from *N*-aminopyridinium salt. The robustness of this method was demonstrated with a broad substrate scope, generally high yields, and successful application to biologically relevant compounds.

The second paper further describes the utility of amidyl radicals from *N*-aminopyridinium salts to functionalize pyridine moieties. It shows the use of *N*-aminopyridinium salts and Zincke imine intermediates to peripheral editing of pyridine at C3-position under photochemical conditions. The new C-N bond occurs predominantly at C3 position, however, changing substituent at C2 position (aryl to alkyl) changes the regioselectivity. These experimental observations are supported by DFT calculations.

The final publication discusses photochemical ring-opening of epoxides and aziridines using native vitamin B₁₂ in micellar medium, yielding alcohol and amines in moderate to high yields and with high regioselectivity.

In conclusion, I have developed new methods for C-N bond-forming reactions via generation of reactive radical intermediates under photochemical conditions, contributing with novel approaches towards more sustainable and efficient amine synthesis.