# Visible-Light Mediated Synthesis of Nitrogen and Sulfur Containing Compounds: A Greener Approach

**THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF DEGREE**

DOCTOR OF PHILOSOPHY

By

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# Chapter-6

# Summary and conclusion

## 6.1 Summary and Conclusions

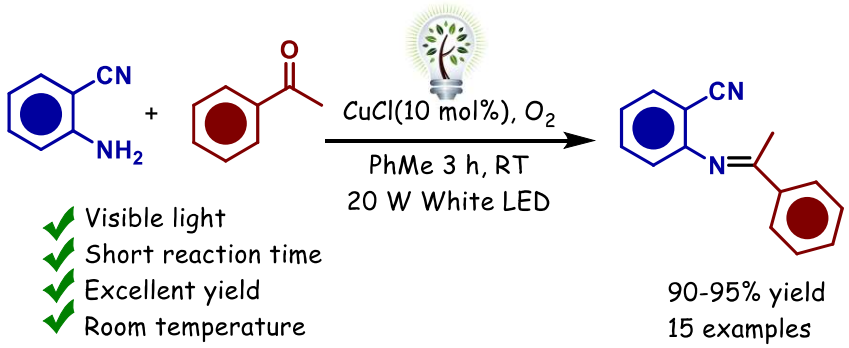
The primary purpose of this thesis is to develop new synthetic strategies employing visible light as a renewable, sustainable, and benign source of energy. Light irradiation provides enough energy to perform the reaction without the disadvantages of thermal activation, such as high temperatures or harsh conditions. This thesis work focuses on developing novel visible-light-mediated organic transformation strategies for the synthesis of Nitrogen and Sulfur-containing compounds in distinct ways.

The effective green synthesis of nitrogen and sulfur-containing compounds is embodied in the thesis titled **"Visible Light Mediated Synthesis of Nitrogen and Sulfur-Containing Compounds: A Greener Approach".** The thesis's is divided into six chapters.

**Chapter 1** provides a detailed explanation of visible light, its importance, and visible light-mediated synthesis of nitrogen and sulfur-containing compounds. The following four chapters describe the studies and conclusions (Chapters 2 to 5). Each chapter, which is complete in itself, consists of an introduction, results and discussion, mechanism, experimental section, and references.

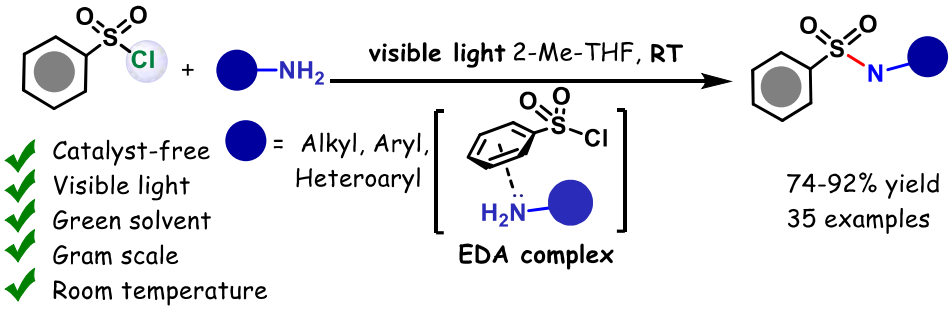
**Chapter 2** describes a simple, green eco-friendly, highly efficient, inexpensive process for Schiff's bases from 2-amino benzonitrile and acetophenone derivatives at room temperature using CuCl as a photoredox catalyst under visible light. The inexpensive nature of the catalyst, no use of exogenous photosensitizer, and the energy efficiency under visible light irradiation make this process a green alternative to existing thermal

methodologies. The current procedure escapes the traditional chromatography and purification process and provides the product with excellent yields of 95% compared to conventional methods. The approach was also validated on gram scale synthesis. (Scheme 6.1).



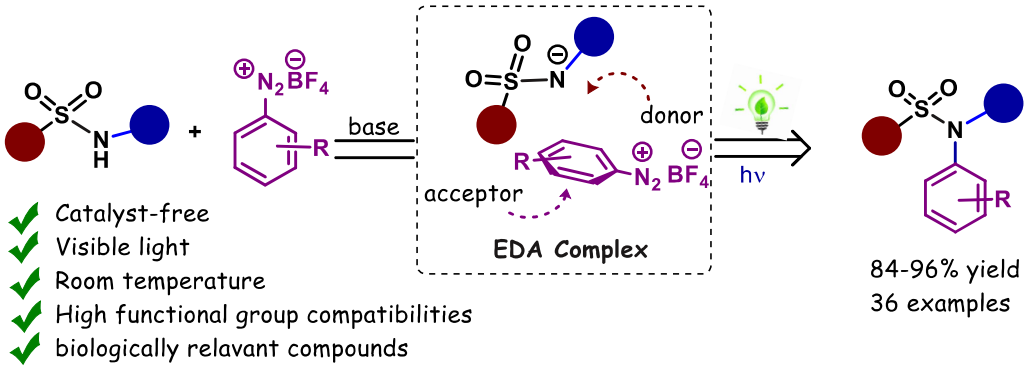

**Scheme 6.1** Synthesis of Schiff's base

**Chapter 3** describes a synthesis of sulfonamide at room temperature without external photocatalyst, base, and transition metals, using 2-MeTHF as the green solvent. This new approach is recognized as an environmentally friendly and efficient visible light-triggered and EDA complex-promoted sulfonation of amine. This reaction is also valid for the gram-scale synthesis of sulfonamide using a simple reaction setup and validated for sunlight. (Scheme 6.2)



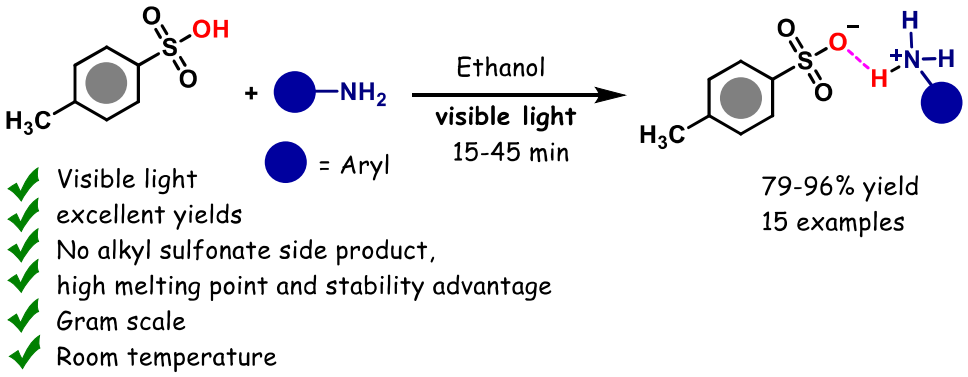

**Scheme 6.2** Synthesis of sulfonamide

**Chapter 4** describes the direct formation of N-aryl sulfonamide which is more effective because it is free from genotoxic and undesirable potential impurities. The photoexcitation of aryl(hetero)diazonium salt and sulfonamide enabled this strategy under visible light irradiation through an EDA complex used to generate a one-step synthesis without a catalyst. The approach tolerated various functional groups of primary sulfonamide and (hetero)aryl diazonium salt frequently found in modern medications and pharmacological intermediates. This method also enabled the direct arylation of secondary sulfonamide. The mechanistic study showed that the formation of electron donor-acceptor EDA complex and sulfonamide radical rapidly interact with aryl radical intermediate through radical coupling to generate the desired product. (Scheme 6.3)




**Scheme 6.3** Synthesis of N-aryl sulfonamide

**Chapter 5** describes a mild, catalyst-free, green, and environment-friendly protocol for the visible-light-initiated synthesis of amine-sulfonate salts at room temperature. The prepared thermally stable and irreversible amine sulfonate salts are extremely useful in the pharmaceutical industry. Mechanistic investigations reveal that the reaction occurs in visible light, and there is no formation of genotoxic sulfonate ester as a side product. (Scheme 6.4)




**Scheme 6.4** Synthesis of amine-sulfonate salt

All the demonstrated protocols in the thesis are superior to most of the existing protocols in terms of reaction condition and yield. Innocuous reagents, convenient procedure, and high yield make these methods more attractive in organic synthesis. Hence, the developed methodologies will find wide applications in organic synthesis.

**Scope for Further Work**

1. The power of visible light induced chemical reaction has long piqued the interest of chemist. Because of chemical reactivity of electronically excited molecules not from fundamemtal ground state, photochemistry has the potential to unlock reaction manifolds that are not accessible via traditional thermal pathways.

2. We should investigate how this can be extended to ions and carbenes since the majority of known visible-light photocatalytic processes go through radical intermediates. Future advancements in photocatalysis have a lot of potential.

3. The synthesized compounds Schiff base, sulphonamides and N-aryl sulfonamides derivatives may further used for biological activities such as anti-inflammatory, antimicrobial, antiviral, antibacterial, anti cancer etc.

4. Further, explore the Schiff base, from 2-amino benzonitrile(2-Aminobenzonitrile is a versatile synthon for the construction of nitrogen heterocycles) as a surrogate for the construction of some privileged heterocycles such as 2-amino Quinoline, Quinozoline, amino indole etc.

5. In the pharmaceutical industry, more than half of the top drugs are given as salt form to optimize the pharmaceutical, physicochemical, therapeutic, active pharmaceutical ingredients and processing properties of ionizable drug substances so the prepared thermally stable and irreversible amine sulfonate salts are extremely useful in the pharmaceutical industry.