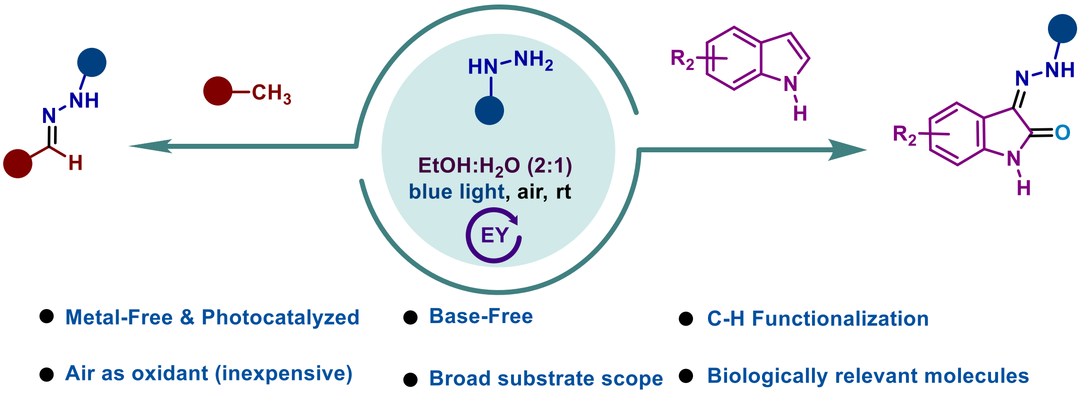
6.1 Summary and Conclusions

The main goal of this thesis is to design new synthetic methods for oxidative coupling utilizing visible light as a clean, eco-friendly, and renewable source of energy. Visible light photons are a traceless source of energy that carry out the reaction along with enhanced atom economy and green catalysis. The field of photoredox catalysis for C-H/S-H bond functionalization is rapidly expanding and has emerged as one of the extensively investigated areas for synthetic chemists. This thesis work focuses on developing novel photo-induced oxidative coupling methodologies for organic transformations *via* C-H/S-H functionalization in distinct ways.

The effective synthetic strategies for C-H/S-H functionalization are embodied in the thesis titled **" Photo-Induced Oxidative Coupling *via* C-H/S-H Functionalization ".** The thesis is divided into six chapters.

Chapter 1 provides an intricate elucidation of the significance of visible light in photochemical reactions, along with an exploration of the mechanisms governing these photochemical reactions. It also demonstrates several oxidative coupling reactions facilitated by photo-induced C-H/S-H functionalization. The subsequent four chapters outline the studies conducted and the resulting conclusions. Each chapter is self-contained and comprises an introduction, results and discussion, mechanism, experimental section, and references.

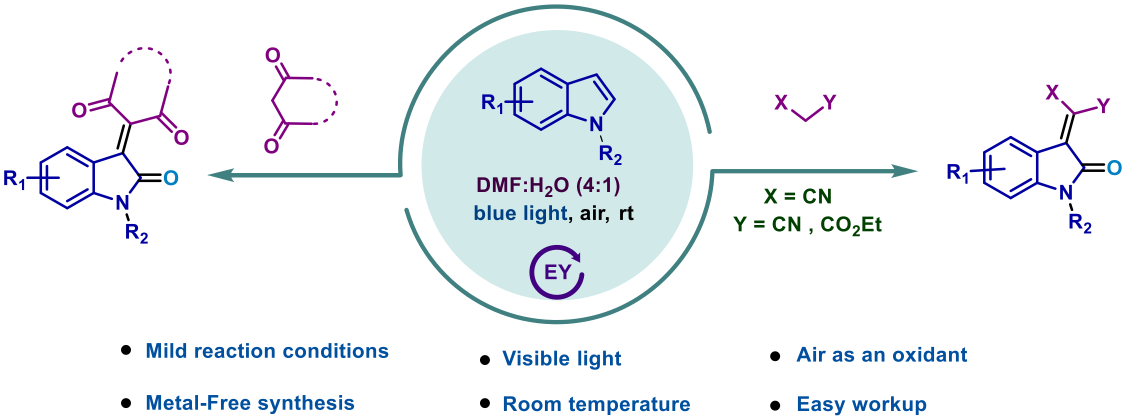
Chapter 2 describes a highly efficient, green, and metal-free method for synthesizing aryl hydrazones through oxidative C(sp^2)−H and C(sp^3)−H functionalization of indole and methyl arene to form C-N bonds under ambient air using organic photoredox catalysis at room temperature. With the aid of eosin Y, the C–H bonds of indole and methyl arenes were activated followed by coupling with arylhydrazines. The absence of metals, low cost, environmental friendliness, green solvent, non-toxicity, ease of handling, and utilization of renewable energy sources like visible light are some of this method’s primary advantages. The procedure was applied to a wide variety of substrates with good functional group compatibility, offering a creative way to make hydrazones from inexpensive and easily accessible raw materials (Scheme 6.1).



- Metal-Free & Photocatalyzed
- Air as oxidant (inexpensive)
- Base-Free
- Broad substrate scope
- C-H Functionalization
- Biologically relevant molecules

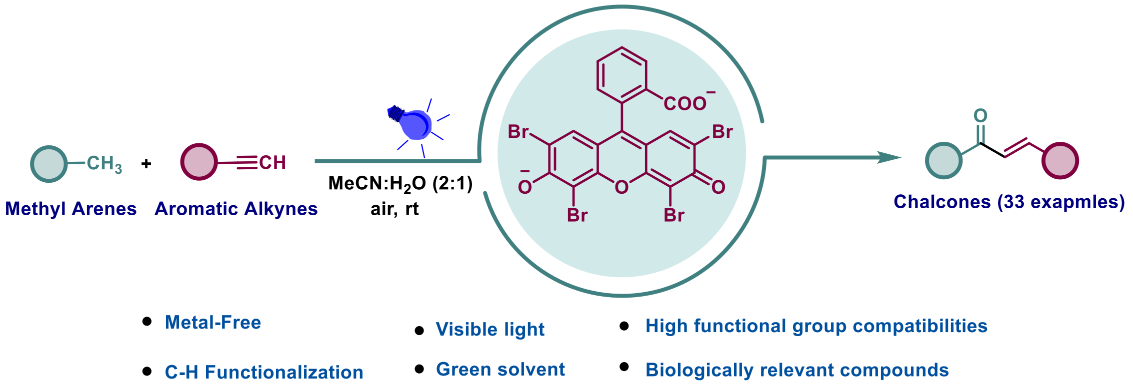
Scheme 6.1 Synthesis of aryl hydrazones

Chapter 3 describes a visible light-mediated oxidative coupling of indoles and active methylene compounds including malononitrile, ethylcyanoacetate, dimedone, and barbituric acid for the formation of C-C unsaturated bonds using eosin Y as a metal-free photocatalyst. This new approach generates isatin *in situ* via a photochemical oxidation of indole using ambient air; then accomplishing comparable coupling reactions. In this work, only one molecule of malononitrile, ethyl cyanoacetate, or dimedone reacts with one molecule of indole, but, in contrast, two molecules of barbituric acid react with one molecule of indole. The reaction occurs efficiently under milder conditions and virtually in assessable yield of the desired coupling products. This approach displays outstanding functional group compatibility with both electron-donating and electron-withdrawing indole (Scheme 6.2).



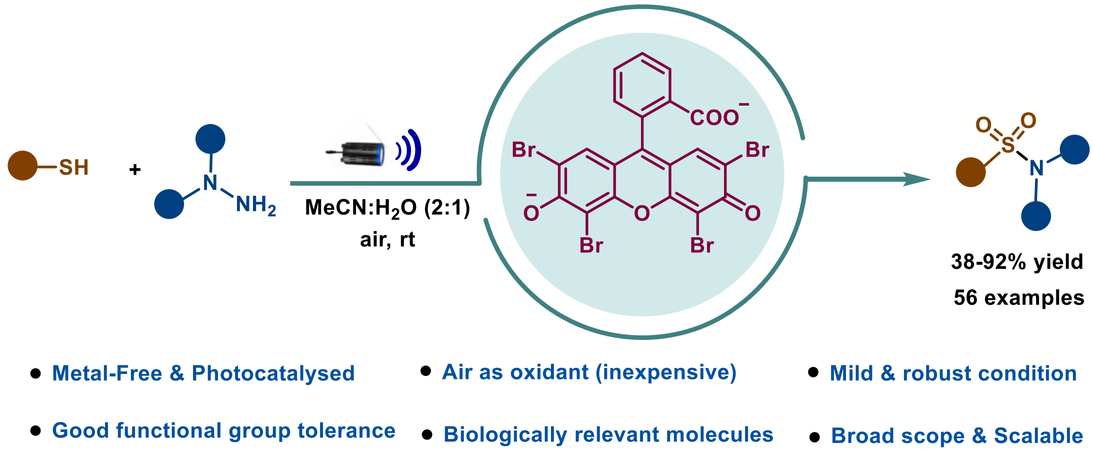
Scheme 6.2 Synthesis of C-C unsaturated bonds

Chapter 4 describes the first method for hydroacylating terminal alkynes employing C(sp^3)-H functionalized methyl arenes as the acylating agent using metal-free photoredox catalysis in a more environmentally friendly solvent. This protocol synthesizes α, β-unsaturated ketones i.e. chalcones using eosin Y as an organic photocatalyst and ambient air as an oxidant under blue LED irradiation. With high atom efficiency, use of green solvents, metal-free nature, environmental friendliness, and visible light as a renewable energy source, this method is compatible with biologically active molecules (Scheme 6.3).



Scheme 6.3 Hydroacylation of alkynes with methyl arenes

Chapter 5 describes a metal-free, environment-friendly photoredox-catalyzed sulfonylation of phenylhydrazines using thiols, employing MeCN:H_2O as a green solvent and eosin Y as a photoredox catalyst. Compared to the conventional synthetic methods of sulfonamides, the appealing part of the current method is the employment of thiols instead of sulfonyl chlorides as the sulfur sources, which is more step-economical. This method produces sulfonamide in good to excellent yield with a broad substrate scope and a good functional group compatibility, including a wide range of biologically active compounds(Scheme 6.4).



Scheme 6.4 Synthesis of sulfonamides

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.

6.2 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 fundamental 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. We are hopeful that the creation of new organo photocatalytic system can be used for selectively targeting stronger C−H bonds, particularly primary (1°) or secondary (2°) bonds.

4. Organo photocatalytic C-H/S-H functionalization has emerged as a pivotal and potent approach in organic synthesis and can be used for synthesizing enantioselective natural products as well as bioactive molecules.

5. We remain hopeful that the outcomes of our methodologies will furnish synthetic chemists with a unique set of tools for crafting diverse and privileged scaffolds in the realm of drug discovery.