

## ABSTRACT

The thesis entitled “**Photoinduced Regio-/Stereoselective C-C/C-X Bond Formation**” is divided into five chapters which are mainly focused with development of chemical reactions by illuminating the intricacies of visible light, unlocking the secret of photoinduced reaction in performing unconventional reactions. Chapter one describes the importance of visible light, photocatalysis for selective C-C and C-X bond formation. In chapter two describes the efficient application of naturally abundant carboxylic acid in alkylation. Chapter three realizes the importance of visible light for synthesizing C-Se bond formation. Chapter four describes an unconventional site-selective trifluoromethylation/perfluoroalkylation *via* visible light. Finally, chapter five, realizes the concept of diastereoselective and enantioselective photoinduced alkylation.

**Chapter 1:** Discloses the brief concept of photochemistry to understand the molecular dynamics. In addition, chirality and its role in day-to-day life, emphasis on asymmetric catalysis *via* photoinduction has been described. Moreover, achiral photocatalysis induced *via* single bifunctional catalysis or dual catalysis and its proof of concept has been elaborated along with their photophysical properties.

**Chapter 2:** Herein, we have unraveled a metal-free, photochemical protocol for C-4 alkylation of 2-iminochromene has been reported by employing naturally abundant chemical feedstock aliphatic carboxylic acid. Importantly, our catalytic system efficiently tolerates range of carboxylic acids including bioactive acids such as gemfibrozil, etc. The developed protocol yields selective C-4 alkylation under photo redox condition to access C-4 alkylated 2-iminochromene in high yields. We believe that this protocol amplifies the potential of organic photo-redox catalytic processes for C-4 alkylation of imines, providing an opportunity for further investigation of the core.

**Chapter 3:** Discloses a visible light mediated novel metal-free, oxidant free phosphoric acid catalysed method for the synthesis of selenyl NHCbz-Tryptamine/3-methyl indole. This protocol for direct C-2 selenation strategy, under environmental benign conditions by reaction of tryptamine/3-methyl indole and diphenylselenide, allows access to a wide range of 2-aryl selenyl NHCbz-tryptamines/3-methyl indole. An experimental investigation using UV-Vis, cyclic voltammetry, and controlled experiments sheds insight into the plausible mechanism.

**Chapter 4:** Unconventional regioselective trifluoromethylation/perfluoroalkylation for aromatic C-H bond in presence of multifarious reactive sites has been described, this chapter has been further divided into two subchapters.

**Chapter 4a:** The task of reinventing and installing trifluoromethyl group via radical pathway has attracted attention recently. However, functionalization of C-H bonds of benzocore of alkylidene malononitrile is still a challenge. In this study we have developed facile visible light-driven- metal free *para* selective trifluoromethylation/perfluoroalkylation of aryl/alkylidene malononitriles. The dual pronged strategy appears to be critical for achieving desirable reactivity and selectivity for broad range of substrates including drugs stapled substrates.

**Chapter 4b:** Herein, a highly regioselective photocatalyzed protocol for aromatic C-7 selective C-H trifluoromethylation/perfluoroalkylation of coumarins is presented. The reaction undergoes a radical type of nucleophilic substitution instead of a radical type electrophilic substitution owing to the benzocore activation as a result of lowering the LUMO. The reaction was found to be extremely general and versatile as demonstrated by its applicability to a wide range of substrates giving exclusive C-7 trifluoromethylated product.

**Chapter 5:** In this chapter, we have disclosed the work which encompasses a stereoselective alkylation, with the focus on diastereoselective photoinduced alkylation (chapter 5a) and enantioselective alkylation (chapter 5b).

**Chapter 5a:** Herein, we have developed a mild, metal-free, diastereoselective protocol for the synthesis of C-4 alkylated coumarins. The incorporation of (-) Phenyl-menthol, is the key for diastereoselective addition. Furthermore, the protocol is compatible for range of carboxylic acid including secondary and tertiary derived NHPI esters. We believe that the developed methodology offers a powerful approach for post-synthetic modification route for generating various new chiral class of highly functionalized small molecules.

**Chapter 5b:** Herein, we report the copper catalysed enantioselective deaminative alkylation with glycine derivatives. Key for success was the chiral phosphine-Cu complex formed in-situ which not only acts as a photocatalyst but also plays a pivotal role in inducing stereoselectivity. Experimental and spectroscopic mechanistic studies provide key insight for the plausible mechanism and stereo induction. These findings open avenues for the development of chiral unnatural amino acids thus offering a de-nova strategy for enantioenriched  $sp^3$ - $sp^3$  linkage via deaminative strategy.