

**Thesis Title-** Photoinduced regioselective C-C bond formation and transition metal catalyzed C-H activation

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## ABSTRACT

The thesis entitled “Photoinduced regioselective C–C bond formation and transition metal-catalyzed C-H activation” deals with the development of chemical reactions for the synthesis of heterocyclic molecules *via* a relatively greener approach. Visible light catalyzed selective construction of carbon–carbon bond has started to garner huge attention from chemists recently. The attractiveness of such selective photoreactions is attributed to the synthetic utility for the development of new reactions. We have developed regioselective C–C bond formation in heterocyclic compounds, which leads to the construction of analogues to biologically active molecules.

This dissertation comprises of five chapters. In the **first chapter**, the importance of photoredox catalysis, photophysical and electrochemical process and types of photocatalysts with emphasis on photoredox catalysis has been described. In the second part of the introduction chapter, discussions on various types of oxidative coupling reactions employed in C–C bond formation with the main emphasis on the dehydrogenative coupling of aromatic compounds is presented.

**Chapter two**, describes a metal-free and mild, photoinduced decarboxylative alkylation of coumarins at C4-position. Photoinduced single electron transfer has been initiated by utilizing the visible-light absorptivity of Eosin Y for a reductive generation of alkyl radicals from *N*-(acyloxy)-phthalimide esters. Depending on the nature of *N*-(acyloxy)-phthalimide esters (primary, secondary, and tertiary carboxylic acid derived), several saturated and unsaturated C4-alkylated coumarins were synthesized. To showcase the utility of the transformation for diversifying carboxylic acids containing natural-products and drugs, also have been used for the synthesis of coumarins derivative.

In **chapter three** development of Eosin Y catalyzed, photoinduced deaminative C4-position alkylation of coumarins *via* C-N bond activation has been reported. We have attempted to explore the reactivity of the radical intermediates generated by photocatalytic deaminative alkylpyridinium salts with 3-substituted coumarins and its analogues. Various secondary and benzylic amines derived pyridinium salts provided several exclusive unsaturated C-4 alkylated coumarins. Further, control experiments studies supported a radical based mechanism for the selective deaminative alkylation.

**Chapter four** deals with visible light-mediated regioselective functionalization of coumarins. This methodology offered selective functionalization of the benzo ring rather than a

heterocyclic ring of coumarins. Several tertiary carboxylic acids derived *N*-(acyloxy)phthalimide (NHPI) afforded exclusive C7-alkylated coumarins. Other carboxylic acid-containing drug derivative NHPI also provided corresponding coumarin products. All synthesized coumarin derivatives in this chapter are analogous to biological and pharmaceutical molecules.

In the **fifth chapter**, a transition metal-catalyzed regioselective, intramolecular, dehydrogenative cross-coupling reactions at the C5 and C2 position of pyrrole derivatives have been described for the synthesis of polyheterocyclic arenes, which is further divided into three subchapters.

In **chapter 5a**, we have disclosed a Cu-catalyzed, intramolecular dehydrogenative cross-coupling in 3-substituted and 3',4'-disubstituted pyrrole-azole systems. The site-selective C2-H activation of unsymmetrically substituted pyrroles in presence of C5 position has been successfully achieved in moderate to good yields for direct access to six- and seven-membered annulated pyrroles, which is an important scaffold, considering the wide biological activity of nitrogen-containing heterocycles.

**Chapter 5b** described the synthesis of polycyclic pyrrole-azole structures possessing fused six-membered and seven-membered rings *via* ligand-enabled, Pd-catalyzed, site-selective, intramolecular cross-couplings of *N*-substituted pyrrole-azoles. C5-H activation in the presence of a reactive C2-H remains a challenge that needs to be addressed and this was targeted to be resolved through the present approach by specifically generating the cyclized products with high selectivity. The featured methodology provides a novel disconnection for the synthesis of pyrrole containing alkaloids and medicinal compounds.

**Chapter 5c** deals a highly efficient and regioselective palladium-catalyzed annulation protocol for a series of linear and terminally substituted 1,2 and 1,3-diheteroaryl alkanes to corresponding polyheterocyclic arenes. Intramolecular oxidative coupling involving double C(sp<sup>2</sup>)-H bond functionalization provides feasible access to a bi-heteroaryl system annulated into a six-membered ring. The methodology is not only restricted to six-membered annulations but also extended to the synthesis of the seven-membered ring with bi-heteroaryl core.