



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

Name of the Student : SUBHENDU GHOSH

Roll Number : 166122017

Programme of Study : Ph.D.

Thesis Title: **Thermal(Photo) Induced Selective C–H Bond Functionalization/Oxidative Cyclization in Di-Nitrogen Benzenoid Heteroarenes**

Name of Thesis Supervisor(s) : Prof. Bhisma K. Patel

Thesis Submitted to the Department/ Center : Chemistry

Date of completion of Thesis Viva-Voce Exam : 22.04.2024

Keywords for description of Thesis Work : Metal catalysis, photo-catalysis, C–H bond functionalization, oxidative annulation, photo-physical application

SHORT ABSTRACT

This thesis demonstrates a number of thoughtful approaches for selective C–H functionalization and oxidative annulation strategies under thermal(photo) catalytic architectures. This thesis has been divided into five major chapters and extended toward a future perspective. **Chapter IA** gives a concise overview of Transition-metal catalyzed C–H functionalization and oxidative annulation (cyclization). Meanwhile, **Chapter IB** depicts the different photo-induced C–H functionalization and cyclization techniques. **Chapter II** demonstrates Ru(II)-catalyzed regioselective C–H/N oxidative annulation of 2-arylquinoxalines with internal alkynes. In this chapter, the synthesized quaternary annulated adducts are extensively scrutinized for detailed photo-physical applications. Such donor- π -acceptor type molecules exhibit Aggregation Enhanced Emission (AEE) in DMF/water solvent systems. Apart from this, such annulated adducts possess reversible mechanochromism. Such small quaternary salts are utilized for latent fingerprint detection (up to 2nd level). Furthermore, such luminogens serve as cellular imaging probes. **Chapter III** describes a solvent-switched regiodivergent C–H maleimidation on 2-arylimidazopyridines under Mn(I)-catalysis. This protocol enables selective C-H alkylation without the involvement of silver or oxidants. Before this work, Mn(CO)₅Br is known for the directed C-H functionalizations. In this chapter, a non-directed C–H metalation of Mn(CO)₅Br apart from the directed strategy has been revealed. **Chapter IV** offers the regioselective C-H maleimidation at the unattained C3-H site of 2-aryl quinoxalines. Herein, the non-directed Mn-catalysis enables the challenging C3-H activation over the usual *ortho* C–H activations. Besides these, the synthesized C3-maleimidated quinoxalines exhibit PIFA-promoted electron-drifted Spirocyclization at room temperature. Also, in the presence of Selector, the C3-maleimide quinoxalines undergo dehydrogenation of succinimides ring. **Chapter V** represents a reagent-less photo-induced auto-catalyzed oxygenation at sterically hindered C(sp³)-H site. This photochemical “reagent-less” solvent-dependent hydroxylation at Csp³-H and spiro-etherification involving C(sp³)-H/C(sp²)-H are unparalleled. Herein, the N-H tautomer of C3-maleimidated quinoxalines acts as a triplet sensitizer and transfers its energy to a triplet oxygen (³O₂) generating reactive singlet oxygen (¹O₂) which facilitates oxygenation reactions at the other C(sp³)-H sites within the molecule making it a true auto-sensitized process. This photo-oxygenation represents an illustration of a tautomer-assisted ¹O₂ uptake.