INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

Name of the Student : MONURANJAN KONWAR

Roll Number : 186122020

Programme of Study : Ph.D.

Thesis Title: **Annulated Quinoline- and Quinoxaline-Functionalized NHC- Ru(II)-Complexes: Catalytic Evaluation towards the C-H Bond Activation, Oxidation of Olefins and Annulation Reactions**

Name of Thesis Supervisor(s) : Dr. Animesh Das

Thesis Submitted to the Department/ Center : Chemistry

Date of completion of Thesis Viva-Voce Exam : 28-01-2025

Key words for description of Thesis Work : Imidazo[1,5-*a*]quinoline, Imidazo[1,5-*a*]quinoxaline, C–H activation, Olefin oxidation, Photophysical property

---

SHORT ABSTRACT

The present thesis, entitled ***"Annulated Quinoline- and Quinoxaline-Functionalized NHC- Ru(II)-Complexes: Catalytic Evaluation towards the C-H Bond Activation, Oxidation of Olefins and Annulation Reactions"*** is divided into five chapters based on the results obtained from the experimental works performed during the complete course of the PhD research period.

Chapter 1 contains a brief overview of the diverse and rich chemistry of cyclometalated complexes. The synthesis, properties, reactivity, and application of these cyclometalated complexes in the catalytic fields are elaborately discussed. Especially the basic properties of C_{NHC}^C type ruthenacyclo complexes, their mechanism in catalytic reactions, and potential applications have been briefly presented.

Each of the following chapters (Chapter 2 to Chapter 5) contains an introduction, previous literature reports, present results and discussion, experimental section, and references along with the characterization data of the products including spectral data of the newly synthesized molecules.

Chapter 2 reports a new rigid π-conjugated fused imidazo[1,5-*a*]quinoline (ImQ)-based cyclometalated ruthenium complex and its catalytic utility for selective oxidation of *N*-substituted tetrahydroquinolines to lactams. In the presence of α-methyl or reactive α-methylene C–H bonds, cyclic-α-methylene C–H bonds were selectively oxidized. This methodology has been successfully utilized in the late-stage functionalization and diversification of pharmaceuticals. The mechanistic study demonstrates that high-valent Ru(VI)-*cis*-dioxo species plays an important role in controlling selectivity. Detailed experimental and theoretical studies have been carried out to elucidate the reaction mechanism with the help of the deuterium kinetic isotope effect, kinetic Hammett studies, and DFT studies.

Chapter 3 demonstrates a highly efficient imidazo[1,5-*a*]quinoline (ImQ) and imidazo[1,5-*a*]quinoxaline (ImQx)-based cyclometalated ruthenium catalysts for olefin oxidation reactions. A strong *σ*-donating ability of both the carbanion donor site and NHC, paired with the rigid backbone and redox activity of ruthenium provided exceptionally high catalytic activity and a long lifetime for oxidative cleavage of olefin to the carbonyl compounds. Complex shows outperforming state-of-the-art systems reach turnover frequencies of 720000 h^{-1} and turnover numbers of several million. The catalyst tolerates numerous functional groups and applies to challenging biomass, natural products, sugar, amino acid, and fatty acid-derived substrates. Based on kinetic studies, thermodynamic activation parameters, and DFT study, the mechanistic finding demonstrated that [3+2] cycloaddition reaction is the key step in the oxidation process. The effect of the by-product $NaIO_3$ in the unprecedented catalytic efficiency has been disclosed for the first time herein.

Chapter 4 describes the reactivity of the ImQ-based cyclometalated Ru(II)-complex **Ru-1**. The complex **Ru-1** is found as a key intermediate in the catalytic oxidative annulation reaction of imidazo[1,5-*a*]quinolin-2-ium salts with alkynes *via N*-heterocyclic carbene-directed C–H activation. Molecular oxygen has been explored as an economic and clean oxidant, an alternative to metal oxidants. The current protocol exhibits a wide range of substrate scope including bioactive (±)-*α*-tocopherol derivatives. Moreover, most of the products show strong fluorescence properties indicating their potential for making new light-emitting materials. Based on several control experiments, deuterium-kinetic isotope effect, and thermodynamic activation parameters the mechanistic finding demonstrated that fused imidazo-[1,5-*a*]quinolin-2-ium C(2)−H bond cleavage is the rate-determining step and ruling out the possibility of reductive elimination for controlling the rate of reaction. Furthermore, DFT calculation is also performed to support the proposed mechanism.

Chapter 5 reports a Ru(II)-catalyzed oxidative annulation of imidazo[1,5-*a*]quinoline with alkynes *via* double C−H activation to produce highly functionalized quinolizines where the key to the successful conversion is the addition of carboxylic acid as an additive. This reaction featured high efficiency and a relatively wide substrate scope, further has been successfully utilized in the late-stage functionalization and diversification of annulated products. The reaction is highly chemoselective and regioselective. In addition, the use of biomass-derived solvent as a reaction medium, the catalyst can be recycled after five reaction cycles without loss of catalytic activity. Interestingly, most of the annulated products exhibit intense fluorescence emission at a broad range and their photophysical property could be tuned by restricting the intramolecular motion in aqueous media and showing AIE-active properties.