



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title:

“Catalytic Asymmetric Synthesis of Cyclic Acetals and Dearomatization Reactions of Indoles & Naphthols”

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SHORT ABSTRACT

The contents of the present thesis entitled as “*Catalytic Asymmetric Synthesis of Cyclic Acetals and Dearomatization Reactions of Indoles & Naphthols*” have been divided into five chapters based on the results achieved from the experimental works performed during the entire course of the Ph.D. research programme.

Chapter I: Overview

Chapter I is divided in two parts. First part contains a brief discussion on asymmetric organocatalysis particularly, bifunctional thiourea and squaramide catalysis and chiral phosphoric acid. A brief description of Michael reaction is also presented here. And second part contains a brief discussion on dearomatization of arene systems mainly focused on indole and naphthol motifs.

Chapter II: Organocatalytic Asymmetric Synthesis of Cyclic Acetals with Spirooxindole Skeleton

In this chapter, a method for synthesizing a cyclic acetal with a spirooxindole structure asymmetrically using organocatalysis has been devised. This involves a domino reaction between isatin and γ -hydroxy enones. Among the catalysts tested, the bifunctional squaramide catalyst featuring an adamantyl motif exhibited the highest efficiency in promoting the cascade reaction. The cyclic acetal products are obtained with good to high yields, high enantioselectivities, and moderate diastereoselectivities.

Chapter III: Catalytic Asymmetric Dearomatization of 2,3-Disubstituted Indoles by a [4 + 2] Cycloaddition Reaction with In Situ Generated Vinylidene *ortho*-Quinone Methides (VQM)

A method for the enantioselective dearomatization of 2,3-disubstituted indoles through an organocatalytic intermolecular [4 + 2] cycloaddition reaction with in situ generated vinylidene *ortho*-quinone methide has been detailed. This protocol enables the efficient synthesis of a broad spectrum of polycyclic 2,3-fused indolines featuring vicinal quaternary carbon stereocenters, achieved with high yields and outstanding diastereo- and enantioselectivities.

Chapter IV: Organocatalytic Dearomative Spirocyclization Reaction of Enone-Tethered α - and β -Naphthols and Dearomatization Reaction of In Situ Generated Nitro-Olefin-Tethered α -Naphthols

In this study, we present a catalytic dearomative spirocyclization reaction involving novel substrates containing aryl/alkyl enone-tethered α - and β -naphthols, as well as a dearomatization reaction of in situ generated nitro-olefin-tethered α -naphthols. The resulting spirocarbocycles were obtained in moderate to good yields, showcasing high diastereoselectivities. Additionally, we introduced a preliminary catalytic asymmetric variant of this reaction. Furthermore, we explored a few applications such as hydrogenations and epoxidation reactions. Complementary to the experimental work, a theoretical study was conducted to elucidate the high diastereoselectivity observed in the triethylamine-catalyzed spirocyclization reaction.

Chapter V: Cooperative Iridium and Brønsted Acid Catalyzed Intramolecular Asymmetric Allylic Dearomatization of α - and β -Naphthols

A method for the asymmetric allylic dearomatization of novel substrates containing secondary racemic allyl alcohol-tethered α - and β -naphthols. Using iridium/Brønsted acid dual catalysis, the resulting naphthalenone spirocarbocycles were achieved in high yields and enantioselectivities with notable diastereoselectivities.