INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title:
Organocatalytic Enantioselective Synthesis of Aza-Spirooxindoles and Construction of Quaternary Stereocenters by Desymmetrization Reactions

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SHORT ABSTRACT

The contents of the present thesis entitled as "***Organocatalytic Enantioselective Synthesis of Aza-Spirooxindoles and Construction of Quaternary Stereocenters by Desymmetrization Reactions***" 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 on enantioselective merged gold/organocatalysis. And second part contains a brief discussion on construction of quaternary stereocenters by desymmetrization reactions.

Chapter II: Sequential Organo and Metal Catalyzed Reaction Between 3-Pyrrolyloxindoles and Linear Nitroenynes: Access to Cyclic Aza-Spirooxindoles

An asymmetric Michael addition/hydroarylation reaction sequence, catalyzed by a sequential catalytic system consisting of a squaramide and a combination of silver and gold salts, provides a new series of cyclic aza-spirooxindole derivatives in excellent yields (up to 94%) and high diastero- and enantioselectivities (up to 7:1 dr, up to >99% ee). Computational study has also been performed.

Chapter III: Organocatalytic Asymmetric Synthesis of C-N Atropisomers with Pyrrole, Oxindole and Succinimide Scaffold

Organocatalytic desymmetric Michael addition of 3-pyrrolyloxindole with prochiral N-aryl maleimides was used to create an asymmetric synthesis of C-N atropisomers with pyrrole, oxindole, and succinimide moities. High

diasteroselectivities and enantioselectivities (>20:1 dr, up to >99% ee) were obtained for the C-N atropisomers in acceptable yields. Additionally, the C-N rotational energy barrier has been determined.

Chapter IV: Organocatalytic Asymmetric Desymmetrization of Cyclopentene-1,3- diones via Formal Diaza-ene Reaction with Donor–Acceptor Hydrazones

Here in, we disclose a catalytic asymmetric desymmetrization of cyclopentene-1,3-diones through formal diaza-ene reaction/tautomerization with donor-acceptor hydrazones. It was found that H8-TRIP chiral phosphoric acid worked well for this process. Chiral cyclopentane 1,3-diones embedded with the hydrazone motif were obtained in good to high yields with excellent diastereo- and good to high enantioselectivities. The scope of the reaction was broad, and some synthetic application, such as chiral pyrazole synthesis have been shown.

Chapter V: Catalytic Asymmetric Desymmetrizing [4+2] Cycloaddition/Base Mediated Oxidative Aromatization Sequence: *De Novo* Synthesis of Isobenzofuranone Embedded Chiral Arenes

Asymmetric desymmetrizing [4+2] cycloaddition/base-mediated oxidative aromatization reaction between β-methyl cinnamaldehydes and spirophthalide 2,5-cyclohexadienones has been developed here. The reaction progressed through the formation of an in situ chiral dienamine intermediate resulting in densely functionalised spirocyclic isoben-zofuranone embedded chiral arenes with high yields and excellent enantioselectivities. Additionally, a twofold desymmetrization reaction was carried out, yielding products with high enantioselectivities.