INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: Organocatalytic Asymmetric Acyl Transfer Reactions and the Synthesis of C-C and C-N Atropisomers.

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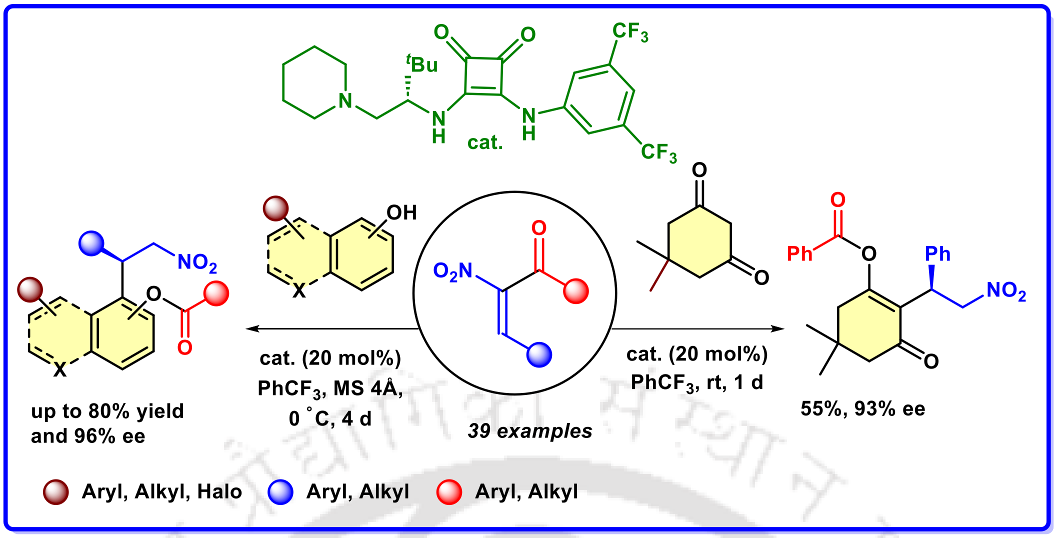
SHORT ABSTRACT

The contents of the present thesis entitled as "***Organocatalytic Asymmetric Acyl Transfer Reaction and the Synthesis of C-C and C-N Atropisomers***" have been divided into six chapters based on the results achieved from the experimental works performed during the entire course of the PhD research programme.

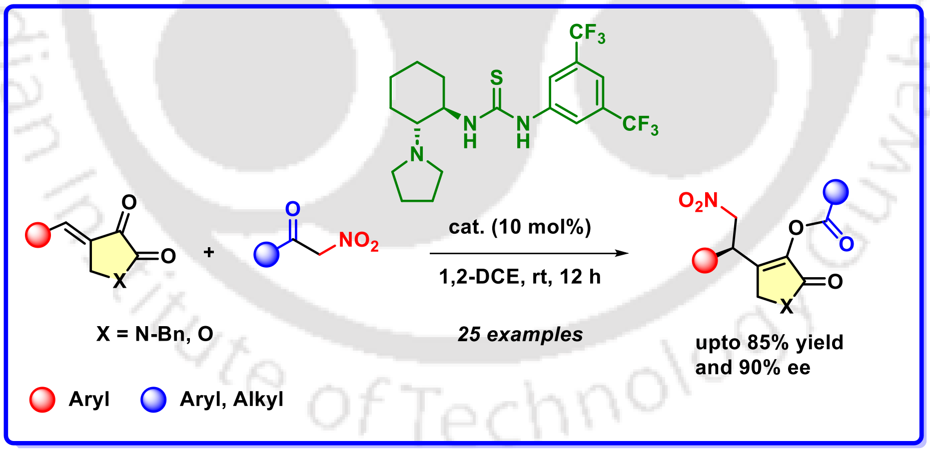
Chapter 1 is of two parts, first part contains a brief overview of asymmetric synthesis, details organocatalytic mechanistic approaches and in part two describes the details study about the atropisomer.

Chapter 2 In this chapter, highlights the α-nitro-α, β-unsaturated ketones as efficient electrophilic acyl transfer reagents, and they were employed in Friedel−Crafts as well as in Michael reactions. This strategy features broad substrate scope (39 examples), high atom economy, as well as α-nitro-α, β-unsaturated ketones as efficient electrophilic acyl transfer reagents in asymmetric cascade reactions for the first time. The desired acyl transfer products of these reactions were obtained in high yields with high to excellent enantioselectivities with *t*-leucine-derived squaramide catalyst under mild reaction conditions. Few applications including a synthesis of the isoxazoline motif have been demonstrated.



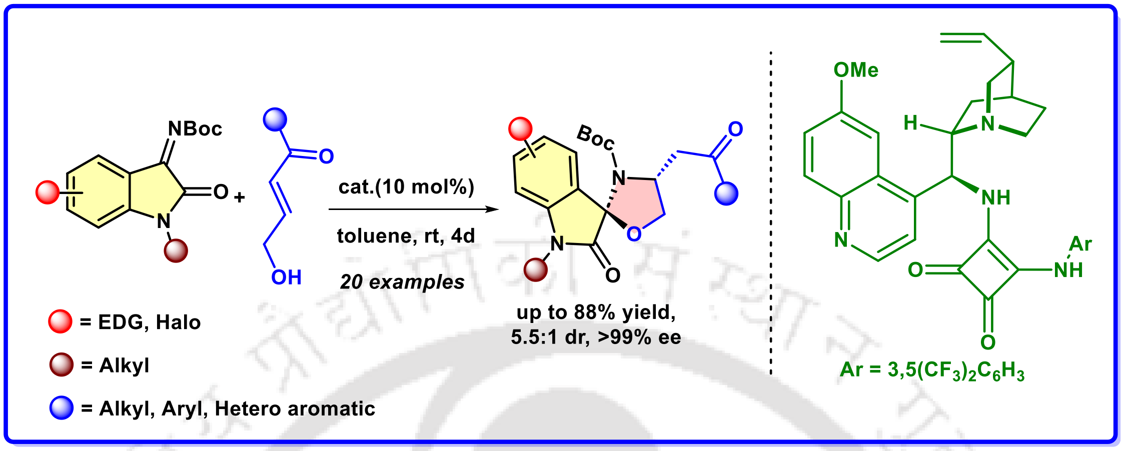
Scheme 1

Chapter 3 represents an organocatalytic asymmetric Michael/acyl transfer reaction between α-nitroketones and 4-arylidenepyrrolidine-2,3-diones is reported. A bifunctional thiourea catalyst was found to be effective for this reaction. With 10 mol % of the catalyst, good results were attained for a variety of 1,5-dihydro-2H-pyrrol-2-ones under mild reaction conditions.



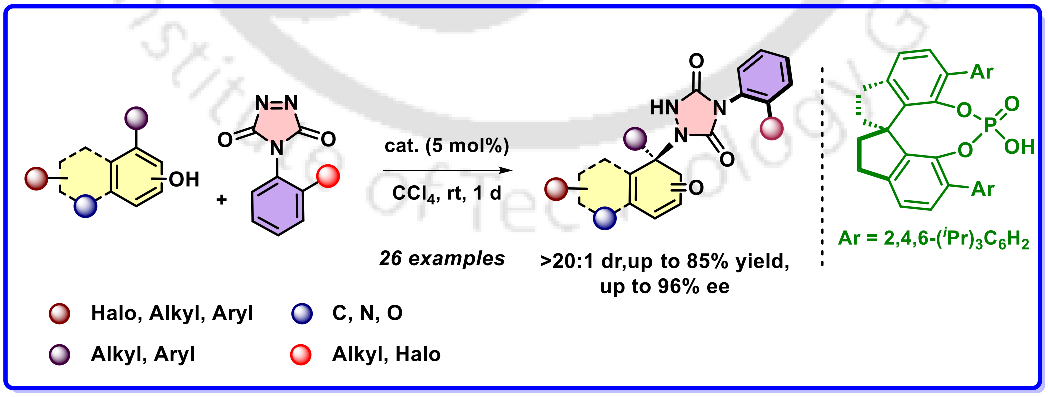
Scheme 2

Chapter 4 describes the first organocatalytic asymmetric synthesis of spirooxindole embedded oxazolidines has been developed via a domino reaction involving hemiaminal formation, followed by an unprecedented *aza*-Michael reaction between isatin derived *N*-Boc ketimines and *γ*-hydroxy enones. A quinine derived bifunctional squaramide catalyst was found to be efficient for this reaction, and the products were obtained in good diastereoselectivity and with high enantioselectivity.



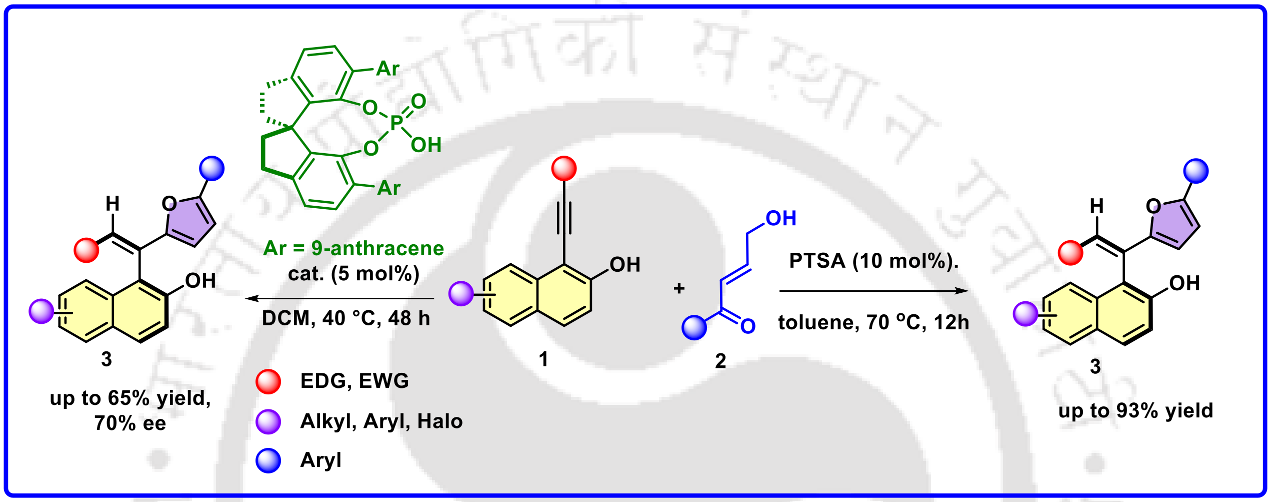
Scheme 3

Chapter 5 demonstrates a catalytic asymmetric dearomatization reaction of β-naphthols with 4-aryl-1,2,4-triazole-3,5-diones. A chiral phosphoric acid with spiro motif was found to be effective for this reaction. The chiral urazole embedded naphthalenones having both axial and central chirality were obtained in good to high yields (70–85%) with high diastereo- and enantioselectivities (up to >20:1, 96% ees), having C-N rotational energy barrier 31.54 kaclmol^{-1} and $t^{1/2}_{25\ ^{\circ}\mathrm{C}}$=589.8 years. The scope of the reaction was broad and few applications including a bromo-amination reaction have been demonstrated.



Scheme 4

Chapter 6 demonstrate the synthesis of furan embedded styrene atropisomer *via* the reaction between 1-(aryl-ethynyl)-naphthalen-2-ol and γ-hydroxyenone. With a catalytic quantity of PTSA, the styrene derivatives were produced with moderate to good yields, and in high diastereoselectivities. Moderate enantioselectivities up to (70% ee) were achieved with chiral phosphoric acid. Few applications such as triazole formation and cross-coupling reactions have been demonstrated. C-C rotational energy barrier 30.1 kaclmol^{-1} and $t_{1/2}^{25\,°C}$ = 21.2 years.



Scheme 5

Each of these chapters contain introduction, previous reported works, present result and discussion, experimental section, references, along with characterization data of products including few selective spectral data. Overall, this thesis demonstrates some new and efficient approaches for organocatalytic asymmetric acyl transfer reaction and the synthesis of C-C and C-N atropisomers.