**INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI**
**SHORT ABSTRACT OF THESIS**

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Programme of Study : **Ph.D.**

Thesis Title: **Designing SNS and NNO Donor Ni and Co Complexes Toward (De)hydrogenative Alcohol Activation: A Sustainable Approach to C-C and C-N Bond Construction**

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Key words for description of Thesis Work **: ACCEPTORLESS DEHYDROGENATION, BORROWING HYDROGEN**

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**SHORT ABSTRACT**


The present thesis entitled "**Designing SNS and NNO Donor Ni and Co Complexes Toward (De)hydrogenative Alcohol Activation: A Sustainable Approach to C-N and C-N Bond Construction**" is divided into five chapters. The first chapter primarily focused on a brief discussion of the concept outline such as Acceptorless Dehydrogenation, Borrowing Hydrogen approach, Metal-Ligand Cooperation, etc. The Chapter 2 to 5 discuss on development of Nickel and Cobalt complexes and its catalytic application toward various alcohol activation reaction.

## Chapter 1: Alcohols: A Sustainable Application in Organic Synthesis

This chapter provides a comprehensive overview of the necessity of biomass feedstock-based starting materials for various chemical syntheses. Alcohol is one of the important components of renewable resources i.e., lignocellulosic biomass. Concerning on the diverse advantages of alcohol, chemists explored alcohol in organic synthesis in various manners which is discussed comprehensively. The chapter focus on the reactivity of alcohol for various C-C and C-N bond construction via "Acceptorless Dehydrogenation" and "Borrowing Hydrogen" approach.

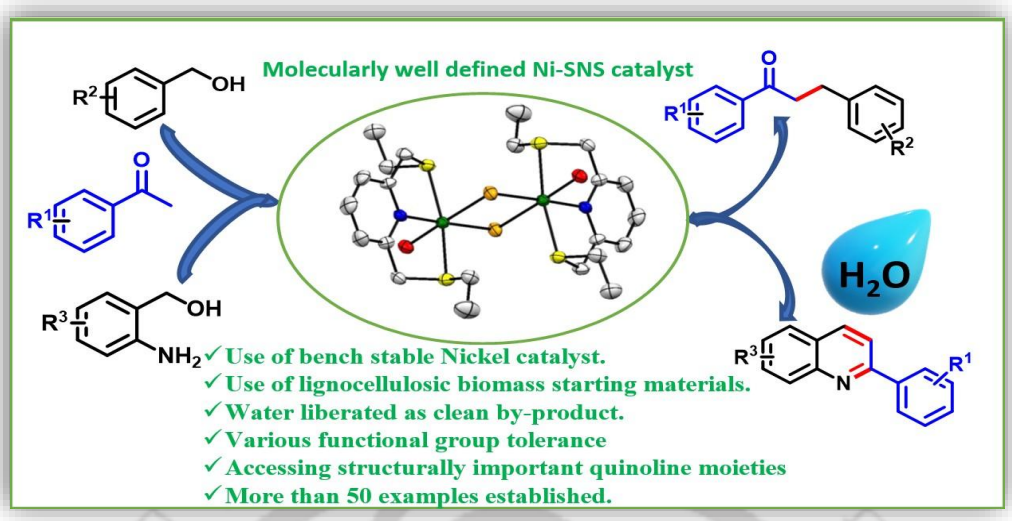
Moreover, the importance of Cobalt and Nickel based catalysis most importantly with respect to the activation of alcohol is discussed in details.

**Aim of the Thesis:**

The present objective of the thesis is designing a non-phosphine based ligand system, synthesizing from cheap and readily available starting materials. The synthesized ligand is then reacted with 3d Nickel and Cobalt metal precursors. The synthesized nickel and cobalt complexes are characterized using single crystal XRD and mass spectrometry. Further, these complexes are applied for alcohol activation followed by the construction of various C-C and C-N bonds.

## Chapter 2: Well-defined Ni-SNS Complex Catalysed Borrowing Hydrogenative α-Alkylation of Ketones and Dehydrogenative Synthesis of Quinolines

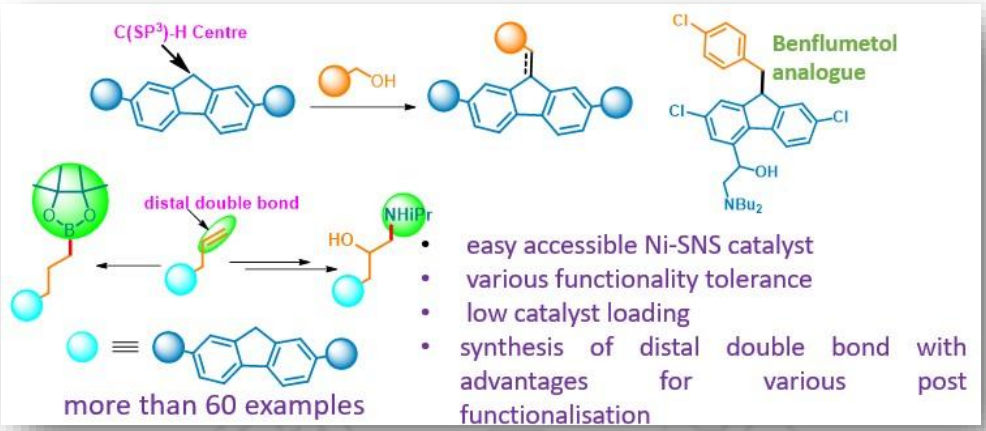
The "Borrowing Hydrogen" (BH) method for C-alkylation reactions using alcohol as alkylating agents is an important synthetic transformation. In this respect, designing cheap and bench-stable earth-abundant metal catalysts for borrowing hydrogen transformation is a key challenge to be witnessed. This chapter presents the synthesis, and characterisation of non-phosphine and bench-stable SNS-Ni complexes and successfully applied for C-alkylation of ketone enolates to α-alkylated ketones. Primary alcohol with different functional groups and various heteroaromatic alcohols are well tolerated. Moreover, the presence of both isolated and conjugated unsaturation in the substrates was well tolerated in the present catalytic protocols. The present catalyst system was efficiently applied to gram scale synthesis along with the calculating green chemistry metrics. The present protocol was also extended successfully for the synthesis of biologically important quinoline moieties. Finally, various control experiments and deuterium-labelled experiments suggest that the reaction proceeds via a non-radical borrowing hydrogen pathway.




**R. Sharma**, A. Mondal, A. Samanta, N. Biswas, B. Das and D. Srimani *Adv. Synth. Catal.* **2022**, *364*, 2429–2437.

## Chapter 3: A strategic approach for Csp3–H functionalization of 9H-fluorene: an acceptorless dehydrogenation and borrowing hydrogen approach

9H-Fluorene constitutes an important class in chemistry, featuring its significance both in material chemistry, showcasing the properties of optical devices, and in medicinal chemistry. Moreover, the alkylation in 9$^{th}$ position of 9H-fluorene is very important and from the context of borrowing hydrogen chemistry, it was much less explored. This chapter describes the selective synthesis of both alkylated and alkenylated fluorenes using a single SNS ligand-derived nickel complex. The protocol was employed for a wide range of substrates, including substituted fluorenes and various alcohols including aliphatic alcohols with a distal double bond. To expand the synthetic utility, an antimalarial drug analogue, benflumetol, was synthesized, and various post-modifications of alkylated fluorene to its corresponding epoxides, amino alcohol, and boronate ester were demonstrated. Control experiments and kinetic profile diagram depict that the reaction works via an unsaturated intermediate and prove the involvement of borrowing hydrogen approach.



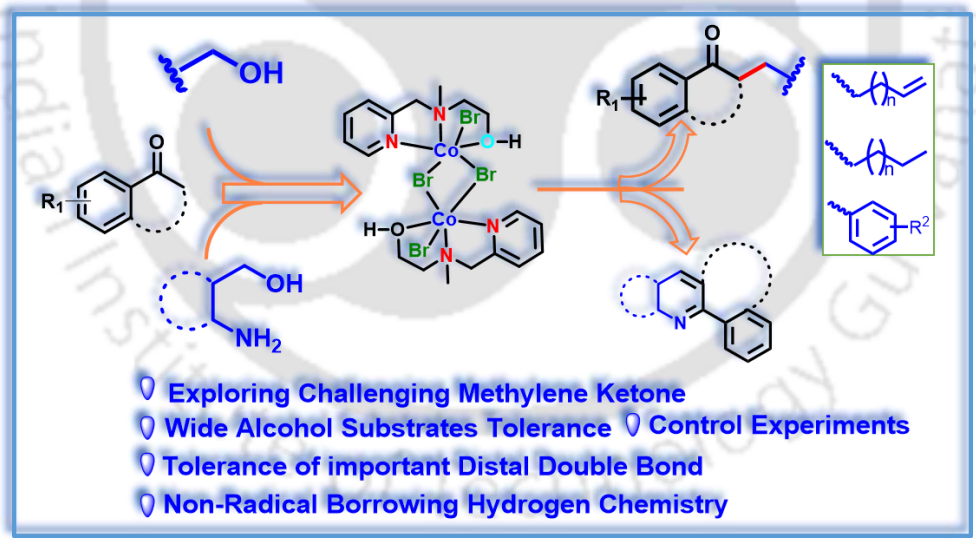

**R. Sharma**, A. Mondal, A. Samanta and D. Srimani, *Catal. Sci. Technol.*, **2023**, *13*, 611.

## Chapter 4: Unveiling the Potential of SNS-Ni Complex for Establishing C-N Bonds: An Approach Toward Chemoselectivity

Recent research has focused a lot on using the Borrowing Hydrogen (BH) approach to react amines with alcohols to convert a C-O bond into a C-N bond. However, the notion of chemoselectivity in BH-mediated N-alkylation of amines, has rarely been studied. This chapter demonstrates the application of synthesized SNS-Ni complex toward constructing various C-N bonds via the coupling of diverse amines with varieties of alcohols. Delightfully, the catalytic protocol also activates challenging C4-C16 aliphatic alcohols. Aryl amino alcohols are selectively N-alkylated with different alcohols while keeping the OH group intact in the amino alcohol portion. Furthermore, without reducing the distal unsaturation, the catalytic technique was also successfully employed for chemoselective N-alkylation of different fatty alcohols. The preliminary mechanistic investigation suggests alkylation occurs via a non-radical “Borrowing Hydrogen” pathway.


**R. Sharma**, A. Mondal, S. Maji and D. Srimani, *Organometallics*, **2024**, *43*, 2697–2702.

## Chapter 5: Exploring the Potential of Non-Phosphine Cobalt System for the Alcohol Activation: Expedition of C-C and C-N Bond Formation

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Non-phosphine Cobalt complexes are much less explored in "Acceptorless Dehydrogenation" and "Borrowing Hydrogen" chemistry. Most importantly the cobalt chemistry is not explored exclusively for C-alkylation of methylene ketones. This chapter focused on the development of NNO-Co complexes. The potential of the synthesized complexes was explored for the C-alkylation

of challenging methylene ketones. The protocol displays a wide range of functional group tolerance. Important substrates including aliphatic alcohols bearing distal double bonds couples with ketones effectively. In addition, the protocol is also efficient toward multi-substituted quinoline synthesis. Moreover, the catalyst was also applied for the C-alkylation of N-heteroarenes. The control experiments discard the involvement of radical pathways and the complex acts as a homogeneous catalyst. Deuterium scrambling experiments prove the involvement of Borrowing Hydrogen chemistry.