

## ABSTRACT

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**Title:** "Design and Development of Bis-azo Based Homogeneous 3d-Metal Catalysts for Auto-Tandem Annulation of N-Heterocycles via Oxidative Dehydrogenation"

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The thesis entitled "**Design and Development of Bis-azo Based Homogeneous 3d-Metal Catalysts for Auto-Tandem Annulation of N-Heterocycles via Oxidative Dehydrogenation**" presents a glimpse on recent advances in the field of ligand  $\pi$  radical chemistry derived from tailor-made poly aza chelates. The thesis comprises of five chapters.

**Chapter 1** contains a general introduction of concise literature review of sustainable approaches in transition-metal catalysis for the activation and functionalization of small organic molecules and physical methods, computational details and equipment used for the characterization of compounds.

**Chapter 2** highlights the development and application of an air- and moisture-stable zinc catalyst,  $[\text{Zn}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})\text{Cl}_2]$ , enables selective  $\alpha$ -alkylation of ketones (14 examples) and quinoline synthesis (32 examples) via acceptorless dehydrogenative coupling (ADC) and N-annulation under mild conditions. Utilizing borrowing hydrogen (BH) methodology, the reactions achieve up to 93% yield with high turnover numbers ( $\sim 10^4$ ).

**Chapter 3** demonstrates highly efficient Ni-catalyzed [3 + 2 + 1] annulation for C–N/C–C bond formation, enabling the scalable synthesis of *s*-triazines and pyrimidines from amidines and alcohols/phenyl acetylenes. This method, effective for 76 substrates, achieves higher turnover numbers than previous homogeneous catalysts.

**Chapter 4** contains a nickel-metalloradical-catalyzed, eco-friendly method for poly-substituted pyridine synthesis via microwave-assisted, solvent-free [2 + 2 + 1 + 1] annulation, achieving 68–93% yields. The catalyst facilitates alcohol dehydrogenation and ring aromatization via SET pathways, generating only benign byproducts. This cost-effective approach follows green chemistry principles, offering high efficiency with an E-factor of 0.3–0.5.

**Chapter 5** presents a Cu(II)-catalyzed approach for dehydrogenative coupling of secondary alcohols or ketones with 2-amino primary alcohols through Friedländer annulation, achieving high yields and selectivity. This penta-coordinated  $\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$ -ligated Cu(II) catalyst enables a superior TON, with mechanistic studies indicating an initial Cu-catalyzed alcohol dehydrogenation followed by condensation, producing only benign byproducts ( $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$ ).

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