INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: **Harnessing the Nitrile Functionality to Heterocycles via Thermal and Photochemical Strategies**

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SHORT ABSTRACT

The Ph.D. thesis, ***"Harnessing the Nitrile Functionality to Heterocycles via Thermal and Photochemical Strategies,"*** focuses on the synthesis of biologically relevant heterocycles and is divided into five chapters, including an introduction.

Chapter I titled *An Overview of Accessing N-Heterocycles via Thermal and Photochemical Approaches*, provides a comprehensive summary of transition-metal-catalyzed and photochemical strategies for synthesizing *N*-heterocycles utilizing the nitrile (C≡N) functionality. This chapter explores key methodologies, including transition-metal-catalyzed addition and addition/cyclization reactions, alkyne insertion into nitriles (C≡N), and photochemical cascade processes for accessing *N*-heterocycles.

Chapter II describes a solvent-controlled, regio-divergent Pd(II)-catalyzed cascade addition/cyclization of (*E*)-2-(1,3-diarylallylidene)malononitriles with arylboronic acids under visible-light irradiation. Using 2,2,2-trifluoroethanol (TFE) or ethanol (EtOH) as solvents, the reaction selectively yields *Z*-alkenylated quinolines or pyridines, respectively. The active catalyst, [$L_2Pd(0)$], acts as an exogenous photosensitizer, enabling efficient synthesis of 2,4,6-triarylnicotinonitriles and (*Z*)-2-aryl-4-styrylquinoline-3-carbonitriles.

Chapter III demonstrates a Pd(II)-catalyzed three-component synthesis of 2,4,6-triarylfuro[2,3-*d*]pyrimidines from β-ketodinitriles, boronic acids, and aldehydes. Both nitrile groups participate to construct the furo-pyrimidine scaffold, forming C–C, C=C, C–O, C–N, and C=N bonds. The products exhibit excellent photoluminescence properties (absorption: 348–387 nm; emission: 468–533 nm). The synthetic utility of the protocol was further demonstrated through a few postsynthetic manipulations.

Chapter IV highlights a Pd(II)-catalyzed synthesis of furo[2,3-*b*]pyrrolo[2,3-*d*]pyridines from β-ketodinitriles and buta-1,3-diynes via dual annulative cyclization. Both nitrile groups participate to construct three heterocycles (furan, pyrrole, and pyridine) in one pot, forming C–C, C=C, C–O, C–N, and C=N bonds. The synthetic utility of the protocol was further demonstrated through a few post-synthetic manipulations.

Chapter V details a visible/solar-light-induced electron-donor-acceptor (EDA)-mediated radical cyclization of (*E*)-2-(1,3-diarylallylidene)malononitriles with thiophenols, forming poly-functionalized pyridines. The EDA complex absorbs light, generating a thiol radical that initiates the cyclization through C–S and C–N bond formation.