INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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SHORT ABSTRACT

The contents of this thesis have been divided into five chapters based on the results of experimental works performed during the research period.

Chapter I is the introductory chapter of the thesis represents an overview of nitrile-triggered access to *N*-heterocycles under thermal and photochemical processes. This includes a brief discussion about transition-metal-catalyzed C–H/N and C–H/N–H oxidative alkyne annulations, alkyne insertion into the nitrile (–C≡N), thermal and visible-light mediated cascade addition/cyclization of the nitrile leading to the construction of diverse nitrogenous heterocycles through the formation of C–C and C–N bonds. ***Chapter II*** demonstrates a one-pot sequential synthesis of fused isoquinolines *via* intramolecular-cyclization/annulation and their photophysical investigations. The synthesis of fused isoquinolone, 4-oxo-2,6,7-triaryl-4*H*-pyrido[2,1-*a*]isoquinoline-3-carbonitrile was carried out from γ-ketomalononitriles and sequential addition of internal alkynes in the same pot. This one-pot process consisting of Cu(II)-catalyzed selective hydrolysis of a cyano group to an amide, dehydrative cyclization of the amide to a cyclic amide, aromatization of the cyclic amide to a 1,2-dihydropyridone and finally, the Ru(II)-catalyzed C–H/N–H annulation with an internal alkyne. This overall process is associated with the formation of one C–C, two C–N, two C=C and a C=O bonds leading to highly fluorescence active fused isoquinolone having emission in the green region (502–560) nm and absorption (λ_{max}) in the range of (454–490) nm. ***Chapter III***

illustrates a Pd(II)-catalyzed synthesis of furo[2,3-*b*]pyridines from β-ketodinitriles and alkynes *via* cyclization and N–H/C annulation. The participation of both the nitrile groups along with the concurrent construction of furan and pyridine rings through the formation of C–C, C=C, C–O, C–N, and C=N bonds are the important features. The control experiment reveals the formation of a 2-amino-3-cyano intermediate in the absence of alkyne and therefore this protocol could be further employed for the synthesis of 2,3-substituted quinoline-4-amine from 2-aminobenzonitriles. Terminal alkynes delivered one of the regioselective isomers whereas unsymmetrical internal alkyne provided either a single or a mixture of regioisomer depending on the nature of the substituents attached to the phenyl rings. Finally, a large-scale synthesis and a few post-synthetic functionalizations such as annulation, *o*-C–H activation, and cross-coupling reactions were demonstrated. ***Chapter IV*** describes the synthesis of aza-fused *N*-heterocycle having a benz-imidazopyridine scaffold *via* an addition-cyclization followed by an Ullmann-type C–N coupling between *o*-iodoanilines and γ-ketodinitriles. The synthesized fused imidazo-pyridines show excellent photoluminescence properties having emission maxima in the range of 502–533 nm and HOMO-LUMO energy gap of 3.49–3.57 eV. The prevalent existence of the core skeletons in medicinally pertinent compounds makes it synthetically useful. Beyond the synthesis, few post-synthetic functionalizations with the resulting molecules have been demonstrated. ***Chapter V*** describes the synthesis of 2,4,6-triarylnicotinonitriles and 2,5-diaryl-1*H*-pyrrole-3-carbonitriles *via* a Pd(II)-catalyzed coupling of arylboronic acid with γ-ketodinitriles and β-ketodinitriles respectively under mild reaction conditions followed by intramolecular cyclization of an intermediate formed after the regeneration of catalyst under acidic reaction conditions. The cascade reactions proceed in 1,2-dichloroethane solvent under visible-light irradiation, and the active catalyst is generated *in situ* in the presence of catalytic amounts of $Pd(OAc)_2$ and 2,2'-bipyridine. The targeted products, composed of a new C–C, a C–N, a C=N and two new C=C bonds, were isolated in good yields. The desired products possess nitrile moiety, which can be later functionalized to generate useful molecules for diverse applications.

Each of these chapters comprises of introduction, previous works, synthetic strategies of the corresponding *N*-heterocycles, present work, conclusion, experimental section, spectral data, a few representative ^{1}H NMR and ^{13}C{1H} NMR spectra, and references.