

Abstract

Synthesis of Heterocycles of Biological Interests via Metal Catalyzed Cyclizations of Acetylenic Compounds

Submitted by: **Sukanya De**

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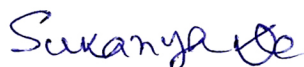
In view of the immense importance of heterocycles in various fields, efforts are made for their construction. In this thesis, few elegant methods are reported for the synthesis of some nitrogen and oxygen containing heterocycles of biological interests via Pd(II)- and Fe(III)-catalyzed cyclizations of acetylenic substrates as described briefly below.

In **Chapter 1**, an atom-economic general synthesis of 10,15-dihydro-9*H*-dibenzo[5,6:7,8]cycloocta[1,2-*b*]indol-10-ols and 15-tosyl-9*H*-dibenzo[5,6:7,8]cycloocta[1,2-*b*]indol-10(15*H*)-one have been developed via a Pd(II)-catalyzed cascade cyclizations of 2-(biphenylethynyl)anilines tethered to an aldehyde or cyano group. The reaction proceeds via amino-palladation of the alkyne followed by nucleophilic addition onto the aldehyde/cyano group. Nevertheless, subsequent treatment of the former products with *p*-TsOH.H₂O provided easy access to cyclooctatetraenes (COT) fused at three double bonds. The hallmarks of the synthesis are high yield (up to 95%), atom-economy, tolerance towards functional groups and formation of two new rings (i.e., cyclooctatriene and indole).

In **Chapter 2**, Fe(III)-catalyzed unprecedented cascade reactions have been developed for the general synthesis of spiro-indenyl 1,4-benzoxazines and 2-(2,2-diarylvinyl)quinoxalines from *O*-propargyl-*N*-tosyl-amino phenols and *N*-propargyl-*N*-tosyl-amines, respectively via intramolecular cyclization reaction. The use of simple substrates and environmentally benign low cost catalyst, broad substrate scope, tolerance of diverse functional groups and substrate- controlled product divergence makes the methodology inherently attractive and greener.

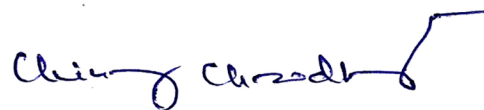
In **Chapter 3**, a general synthesis of 4-(2,2-diarylvinyl)quinolines and 4-(2,2-diarylvinyl) 2*H*-chromenes have been reported through Fe(III)-catalyzed intramolecular annulations of homopropargyl amines and ethers, respectively. Mechanistically, the reaction proceeds through an intramolecular *Friedel-Crafts reaction* (IMFC) resulting in an allene intermediate which readily isomerizes into 1,3-diene by iron catalyst. The reactions constitute the fast intramolecular assembly taking place under one-pot and diverse substrates were found to be compatible.

In **Chapter 4**, a one-pot synthesis of benzo[*g*]indoles is reported via palladium(II)-catalyzed cascade reactions of ene-yne substrates carrying cyano/aldehyde group. The reactions involve successive hetero- and benz-annulations via *trans*-aminopalladation onto alkyne, followed by 1,2-addition to cyano/aldehyde group. The hallmarks of the reactions are operationally simple, compatible with a range of functional groups and atom-economical in nature.



Signature of Candidate

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Signature of Supervisor with Seal

Date: 8/12/2022

Dr. Chinmay Chowdhury
Chief Scientist & Deputy Head
Organic & Medicinal Chemistry Division
Indian Institute of Chemical Biology
4, Raja S. C. Mullick Road
Kolkata - 700 032