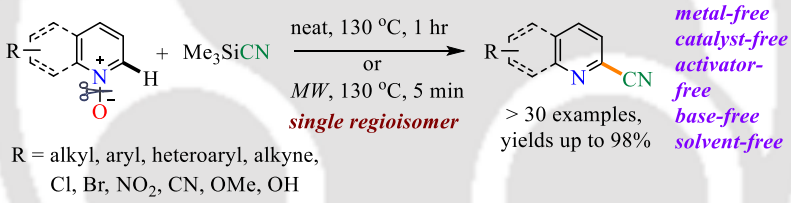
Abstract

The present thesis, entitled "***Selective C-H and C-C Bond Functionalization of Benzo-Fused N-Heteroaromatic Compounds***" is divided into five chapters based on the results obtained from the experimental works during the course of PhD research period.

Chapter-1 includes a brief introduction about the importance of C-H activation process for *N*-heterocyclic compounds, the problems associated with the classical processes and a short account of the literature reports for C-H activation involving *N*-oxide chemistry to solve the above shortcomings by both conventional and green chemistry protocols.

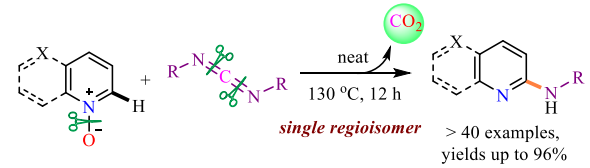
Each of the following chapters contains an introduction, previous literature reports, present results and discussion, experimental section and references. The spectral data for the newly synthesized molecules are provided in the **Annexure I-IV**.

Chapter 2 reports the regioselective deoxygenative C2-cyanation of quinoline *N*-oxides with trimethylsilyl cyanide (TMSCN) under a completely metal-, activator-, catalyst- and solvent-free condition using both conventional heating and microwave irradiation methods. The reaction is both regio- and chemoselective and the mechanistic investigations revealed the dual role of TMSCN as the cyanation agent as well as an activator. Late-stage cyanation of bio-active molecules quinine and (±)-*α*-tocopherol modified quinoline derivative is also demonstrated. Notably, the product gets sublimated during the reaction and thus, can be easily isolated, avoiding any aqueous work-up.



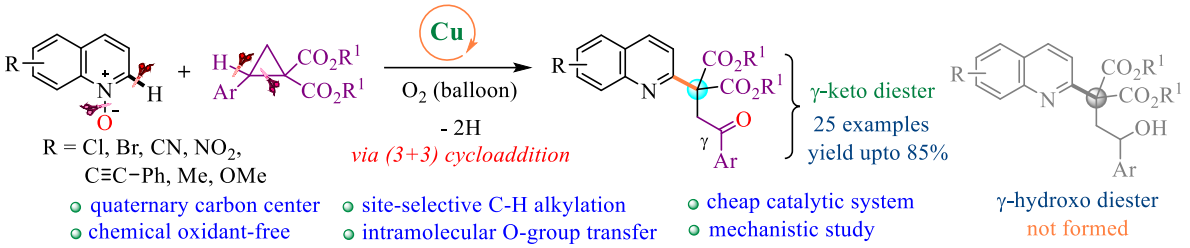
- *excellent regioselectivity*
- *shorter reaction time, no aqueous work up*
- *late-stage functionalization of pharmaceuticals*

Chapter 3 describes the regioselective deoxygenative C2-amination of quinoline *N*-oxides with carbodiimides under completely metal-, activator- and catalyst-free conditions to give both aryl- and alkylaminated quinolines. The protocol supports a wide range of functional groups and bulky arylamino groups also can be introduced under the reaction conditions. The protocol can be extended to late-stage amination of bio-active molecules like anti-malarial drug quinine, tryptamine, and (±)-α-tocopherol modified quinolines effectively. It also includes the possible mechanistic pathway derived from both experimental works and theoretical calculations. The present protocol displays impressive figures for different green matrix parameters and produces only CO_2 as a co-product, which could be trapped easily.



- *catalyst-, activator-, base- and solvent free*
- *one-pot direct C-H amination protocol*
- *excellent selectivity*
- *CO_2 trapping experiment*
- *high atom economoy*
- *low E-factor*
- *late-stage functionalization of pharmaceuticals*

Chapter 4 reports the copper-catalysed deoxygenative alkylation of quinoline *N*-oxides with donor-acceptor cyclopropanes to introduce a tertiary alkyl motif at the C2-position of quinoline. This work uses molecular oxygen as a benign oxidant and supports a range of functional groups. The mechanistic pathway has been investigated using both experimental and theoretical calculations which shows the involvement of a possible radical pathway.



Chapter 5 demonstrates DIBAL-H mediated reductive cleavage of C(sp^3)-C(sp^2) bond in *N*-heteroaryl *γ*-ketodiester compounds to give biologically relevant *β*-ketodiester motifs. DIBAL-H works both as a Lewis acid and a hydride donor. Theoretical calculations have been performed to investigate the possible mechanistic pathway which shows that 2 equivalents of DIBAL-H are required for one equivalent of the *N*-heteroarene compound.