ABSTRACT

Heterocyclic compounds have wide range of applications in the field of science such as medicine, pharmaceuticals and material chemistry. Transition metal-catalyzed C–H functionalization and oxidative annulation reaction plays pivotal role in the synthesis of heterocyclic motif in synthetic organic chemistry. The thesis entitled **"Synthesis and Functionalization of Heterocyclic Compounds *via* Palladium/Rhodium-Catalyzed Cross-Dehydrogenative Coupling Reactions"** deals with the synthesis and C–H bond fuctionalization of heterocyclic compounds using palladium/rhodium-catalyzed oxidative cross-dehydrogenative coupling reactions. The thesis is divided into four chapters.

The first chapter of the thesis gives a brief introduction of cross-dehydrogenative coupling reactions and pincer complexes. The synthesized new class of palladium complexes of NNN/CNN pincer ligands were characterized with the help of IR, NMR, HRMS, and single X-ray study. These complexes were found to be very efficient catalyst for the cross-dehydrogenative coupling reaction of thiophene, furan and benzothiazole derivatives with a wide range of heteroarenes such as *N*-methylbenzimidazole, *N*-methylimidazole, benzothiazole, and imidazo[1,2-*a*]pyridines and homo cross-dehydrogenative coupling reaction of thiophenes and benzothiazoles. The catalyst showed high functional group tolerance and only 1.0 mol % of the catalyst loading is required to achieve good yields in short reaction time

The second chapter of the thesis describes palladium(II)-catalyzed intramolecular cross-dehydrogenative coupling reaction for the synthesis of imidazopyridine-fused indoles *via* Knoevenagel condensation between active methylene azoles with *N*-substituted-1*H*-indole-2-carbaldehyde or *N*-substituted-1*H*-indole-3-carbaldehyde. A series of thirty-six compounds were synthesized by varying different substituent on substrate in good to excellent yield (23-94%). The method displayed broad functional group compatibility and was amiable for gram-scale synthesis. The developed strategy could further be utilized for the synthesis of aroyl substituted polycyclic heterocycles which could provide new class of medicinally important indole-based heterocycles.

The third chapter of the thesis describes rhodium-catalyzed oxidative annulation reactions. This chapter is divided into two parts: **Part A** presents Rh(III)-catalyzed oxidative [4 + 2] annulation of 2-arylimidazo[1,2-*a*]pyridines with maleimides to afford the benzo[*e*]pyrido[1',2':1,2]imidazo[4,5-*g*]isoindole derivatives in good to excellent yields. The obtained annulated products were further evaluated for photophysical studies and validated by

quantum chemical calculations. All the compounds are highly fluorescent with large Stokes shifts and moderate to high fluorescence quantum yield. The emission spectra of **13aa** was red-shifted with increasing polarity with no significant change in fluorescence in intensity. **Part B** presents Rh(III)-catalyzed oxidative annulation and spirocyclization of 2-arylindoles with maleimides giving pyrrolo[3,4-*c*]carbazole-1,3(2*H*,8*H*)-diones and spiro[isoindolo[2,1-*a*]indole-6,3'-pyrrolidine]-2',5'-diones frameworks in good to excellent yields. The protocol displayed broad functional group tolerance, high regioselectivity and is scalable. Interestingly, annulation of 2-pyrroleindoles with maleimides under standard conditions furnished isogranulatimide alkaloid analogues in moderate yields.

The fourth chapter of the thesis describes palladium–catalyzed weakly coordinating lactone directed C–H bond functionalization of 3-arylcoumarins with a wide range of functionalities as highlighted by prototypical methods for alkenylation, halogenation, fluoroalkoxylation, and hydroxylation. The protocol displayed broad substrate scope and furnished good to excellent yields of functionalized coumarins. The obtained *ortho*-hydroxylated products were further cyclized to afford coumastan derivatives in good yields. The developed method can be used for late-stage C–H functionalization under mild condition because lactone functionality under mild reaction conditions.

Finally, in the **fifth chapter** of the thesis, summary of the thesis work is presented along with that future scope of the research work.