

The present thesis describes a study on development of some newer catalytic protocols for oxidative C-C and C-heteroatom bond formation reactions. The main text of the thesis has been organized into five chapters. The Chapter 1 provides the introduction of the thesis which delivers a brief account of the importance and the present developments relevant to this field. Chapter 2 offers newer experimental results on C-C bond formation reaction and it is subdivided into three sections containing three different works of C-C coupling reactions. Chapter 3 and 4 include results of C-N and C-O bond formation reactions, both the chapters are subdivided into two sections respectively having some singular works in each of the sections and lastly the chapter 5 summarizes the overall conclusion and future scope.

Chapter 1: General Introduction:

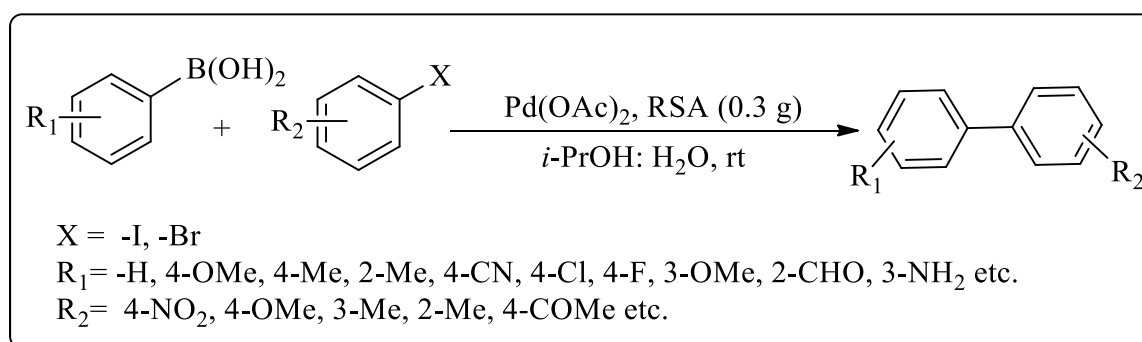
Chapter 1 is a brief introduction to C-C and C-heteroatom bond formation reaction. This chapter is a modest effort to describe the history, importance and present status of the stated bond formation reactions. Since the mid of last century, these bond formation reactions have been occupying a central attraction in the domain of synthetic organic chemistry because of their immense application in varieties of areas like pharmaceutical, natural products chemistry, catalysis etc. On the other hand, they also afford very important role in developing a new generation of resourcefully recognized organic materials having original electronic and mechanical properties. Thereby, synthetic chemists have been found to pay more attention towards this field to develop some efficient methodology with low cost, avoiding harsh reaction condition which gives confidence us to carry out the work.

Chapter 2: Development of Efficient Pd Based Catalysts for C-C Bond Formation Reactions:

Section 2.1

Improved Suzuki-Miyaura cross-coupling reaction in Rice Straw Ash: Evidence for enhancing effect in water: i-propanol with in-situ generated Pd NPs.

In this chapter, we present an improved Suzuki–Miyaura cross-coupling reaction in RSA (Rice Straw Ash). We found that, although the reaction can be run in neat water, but, use of alcoholic co-solvent dramatically enhances the yield and generates *in-situ* Pd NPs during the reaction (**Scheme 1**). The Pd NPs are characterized by TEM and powder XRD analysis. The RSA is characterized by EDX, flame photometry, and Ion-Exchange chromatography to reveal a broad range of active metal species. The chemical analysis reports of ash shows the presence of oxides of K, Na and Ca, which probably in the presence of water produces the corresponding hydroxides responsible for the observed basicity.



Scheme 1: RSA promoted Suzuki-Miyaura cross-coupling reaction

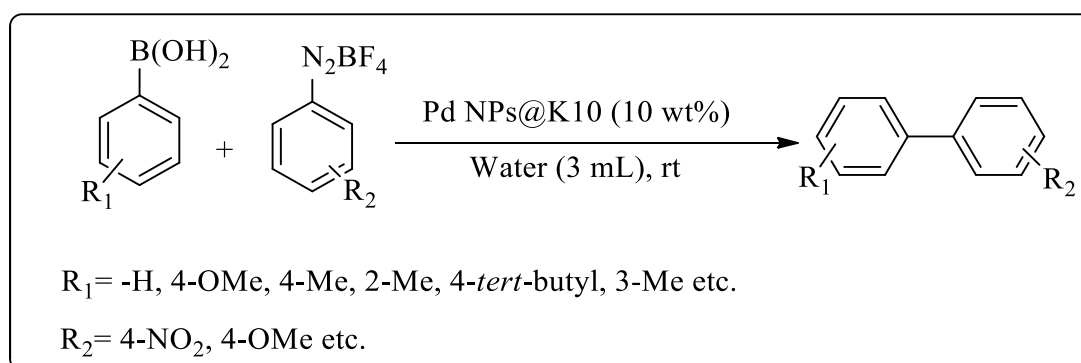
The systematic investigations of different reaction parameters and substrate scope of this method is included in the chapter. Besides this, the detail experimental procedure of the performed reactions, results and discussion, outcomes and the supporting data of the synthesized compounds are also the part of this chapter.

Section 2.2

External reducing agent free facile synthesis of Pd NPs decorated on Montmorillonite K10 and its implication in Suzuki type cross-coupling reaction under base free condition.

In this chapter, we discuss methanol aided synthesis of Pd NPs decorated on Montmorillonite K10 and its implication in Suzuki type cross-coupling reaction under base free condition.

Here, an efficient catalyst Pd NPs decorated on Montmorillonite K10 is prepared by simply stirring Pd(OAc)₂ in methanol at room temperature without using any external reducing agent. The catalyst shows excellent activity for Suzuki type cross coupling reaction between aryldiazonium salt and arylboronic acid under ligand and base free conditions within short reaction time (**Scheme 2**). The catalyst is well characterized by techniques like SEM, EDX, TEM, BET and Powder XRD etc. The reaction pathway is found to be greener because it is associated with aqueous reaction medium, base free reaction condition, room temperature and reusable heterogeneous catalyst.



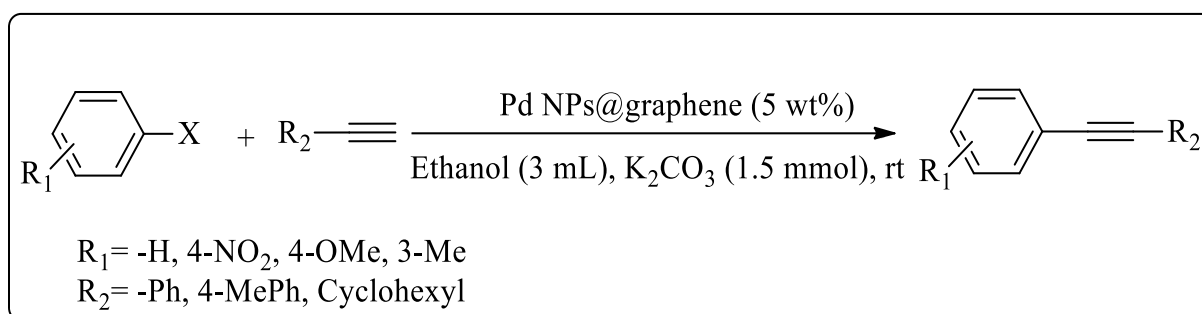
Scheme 2: Pd NPs@K 10 catalyzed Suzuki type cross-coupling reaction in water

Section 2.3

A room temperature ligand and copper free Sonogashira cross-coupling reaction catalyzed by Pd NPs decorated on reduced graphene oxide.

In this chapter, we disclose an efficient room temperature methodology for copper and ligand free protocol for Sonogashira cross-coupling reaction catalyzed by Pd NPs decorated on reduced graphene oxide. The catalyst shows excellent catalytic activity towards the said coupling reaction which is well characterized by HR-TEM, SEM, XRD, XPS, FT-IR etc. and can be reused up to fifth cycle with almost constant yield of the desired product.

The drawing superiority of this protocol is that the reaction completes within short reaction time under ligand and copper free condition and it avoids harsh reaction conditions (**Scheme 3**).



Scheme 3: A room temperature copper and ligand free Sonogashira cross-coupling reaction

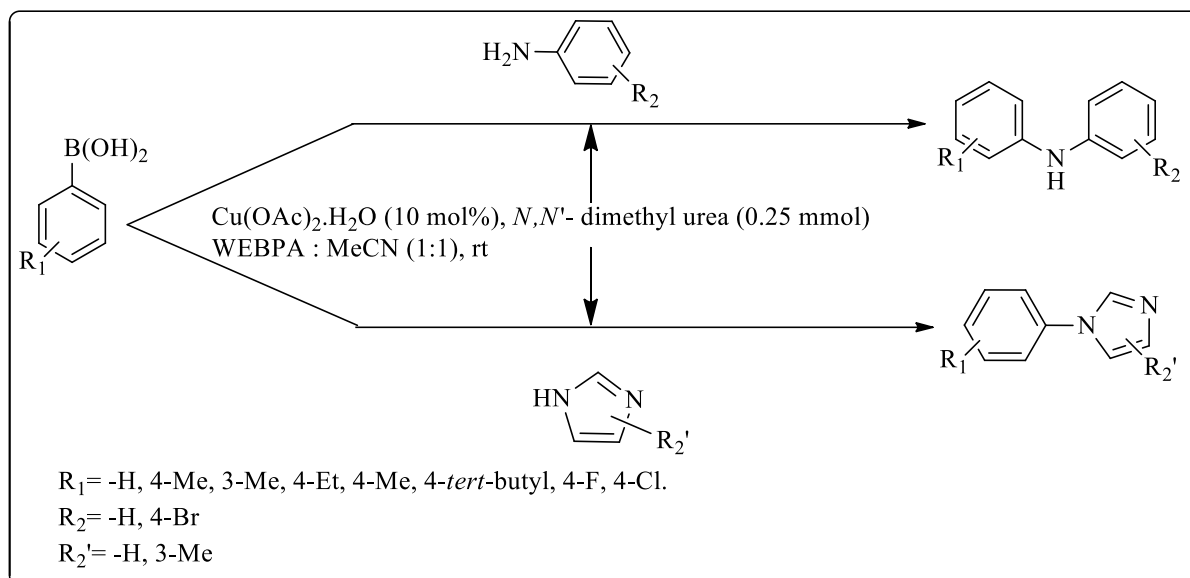
Chapter 3: Development of Mild and Efficient Protocols for C-N Bond Formation

Reactions:

Section 3.1

***N,N'*-dimethyl urea/ Cu(II) as an excellent promoter for room temperature N-arylation of aniline and imidazole in 'WEBPA': MeCN.**

In this chapter, we present an efficient room temperature protocol for *N*-arylation of imidazole and aniline with arylboronic acid as coupling partner reaction in which agro waste 'WEBPA' (Water Extract of Banana Peel Ash) acts as both base and solvent (**Scheme 4**). Moreover, we use *N,N'*-dimethyl urea as an excellent promoter for the reaction which is an easily available, cheap and non-toxic reagent. The central attraction of the protocol is that the reaction completes within short reaction time and it employs environmentally benign agro-waste as solvent and base.

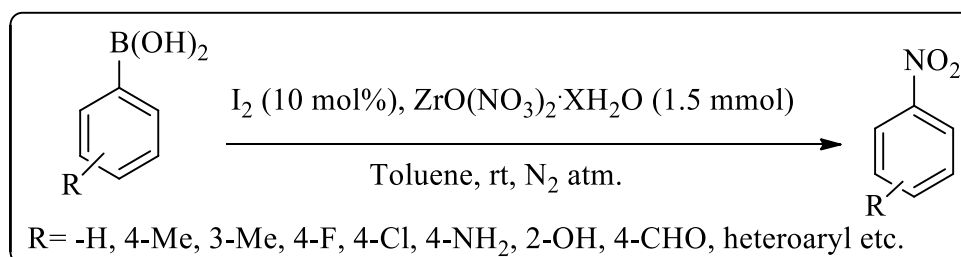


Scheme 4: *N,N'*-dimethyl urea/ Cu(II) promoted *N*-arylation of aniline and imidazole with arylboronic acid

Section 3.2

Molecular iodine catalyzed ipso-nitration of arylboronic acid at room temperature with zirconium oxynitrate: A theoretical and experimental investigation.

In this chapter, we disclose a facile method for *ipso*-nitration of arylboronic acid at room temperature catalyzed by molecular iodine using zirconium oxynitrate as nitrating species (Scheme 5).



Scheme 5: Molecular iodine catalyzed *ipso*-nitration of arylboronic acid

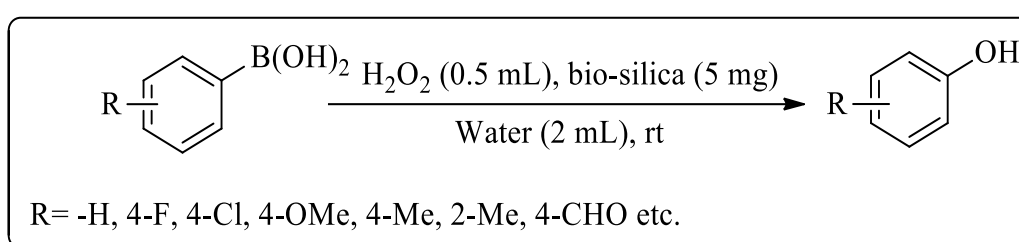
The protocol is applicable to electronically diverse aryl and hetero arylboronic acid moieties under mild reaction conditions with good to excellent isolated yields. Furthermore, theoretical investigation has been performed for the same titled reaction and reaction profiles are modeled using modern density functional theory (DFT). DFT based results support the experimentally observed results.

Chapter 4: Development of Efficient Protocols for *Ips*-Hydroxylation of Arylboronic Acid:

Section 4.1

A mild and efficient ipso-hydroxylation of arylboronic acid catalyzed by bio-silica.

In this chapter, we present bio-silica as an efficient heterogeneous catalyst for room temperature *ipso*-hydroxylation of arylboronic acid. In this protocol, we use mild oxidant aqueous hydrogen peroxide in minimal amount and bio-silica as catalyst. The recyclability of the catalyst is also evaluated and could be reused up to sixth consecutive cycles without a significant loss in catalytic activity. The reaction proceeds smoothly in water and completed within very short reaction time (**Scheme 6**).

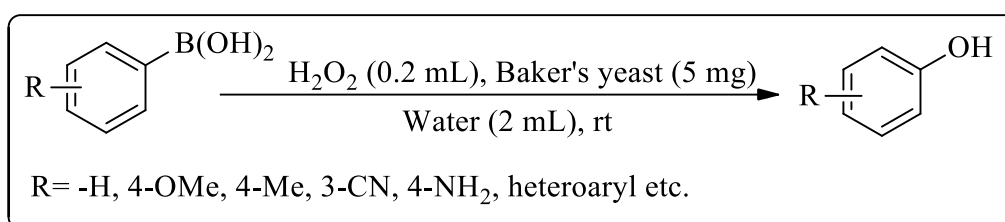


Scheme 6: *Ips*-hydroxylation of arylboronic acid catalyzed by bio-silica

Section 4.2

Baker's yeast as an efficient reusable bio catalyst for oxidative hydroxylation of aryl/heteroarylboronic acid.

In this chapter, we describe a room temperature *ipso*-hydroxylation of arylboronic acid catalyzed by efficient bio-catalyst Baker's yeast in presence of minimum amount of H₂O₂ (Scheme 7).



Scheme 7: Baker's yeast catalyzed *ipso*-hydroxylation of arylboronic acid

The recyclability of the bio-catalyst is also evaluated and can be reused up to sixth times without significant loss of percentage yield. The reaction protocol is advantageous than most of the existing methodologies as all the reactions were carried out in ligand, base and organic solvent free conditions within short reaction time.

Chapter 5: Conclusions and Future Scopes:

This chapter describes overall conclusions of the thesis summarizing the outcomes of the experiments performed along with the future scope of the work.