Abstract

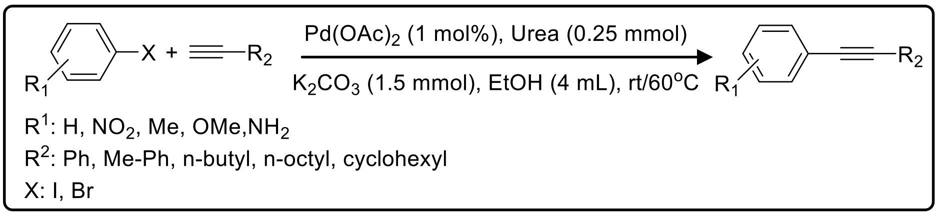
The present thesis describes a study on the development of some newer catalytic protocols for oxidative C_{sp2}-C_{sp2} and C_{sp2}-C_{sp} bond formation reactions considering greener reaction conditions. The main text of the thesis has been organized into six chapters.

Chapter 1: General Introduction

This chapter provides a brief introduction of the thesis which delivers a brief account of the history, importance and present status of the C-C bond forming reaction.

Chapter 2: Development of a mild and efficient methodology for palladium catalyzed Sonogashira cross coupling reaction

This chapter represents the utilization of urea as a mild and efficient promoter for palladium-catalyzed Sonogashira cross-coupling of aryl halides and terminal alkynes (Scheme 1). The $Pd(OAc)_2$/urea catalytic system is applicable to electronically diverse aryl iodides and terminal acetylenes at room temperature under copper and amine free condition using EtOH as the solvent medium. The system serves as an excellent alternative to various ligand assisting system avoiding hazardous chemical reagents and is readily accessible, inexpensive and highly flexible for both aromatic and aliphatic alkynes under mild reaction condition.

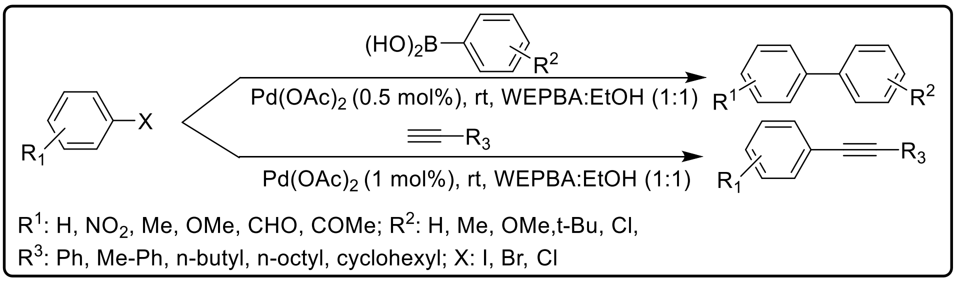


Scheme 1: $Pd(OAc)_2$/urea catalyzed Sonogashira coupling of aryl halides and terminal acetylenes.

Chapter 3: Studies of dual role of water extract of agro-waste ash in C_{sp2}-C_{sp2} and C_{sp2}-C_{sp} bond forming reaction

Section 3.1: *Analysis of water extract of papaya bark ash and its application as in situ base in ligand-free Suzuki-Miyaura and Sonogashira cross-coupling reaction*

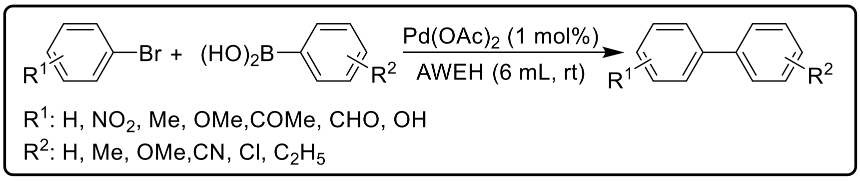
In this section, we have reported an efficient Suzuki-Miyaura and Sonogashira cross-coupling reaction using waste papaya bark to ash-water extract (WEPBA) as base as well as reaction medium (Scheme 2). The system develops an environmentally friendly *in situ* basic condition which in presence of $Pd(OAc)_2$ provides excellent cross-coupling under mild reaction condition. The water extract (WEPBA) along with alcoholic co-solvent results in *in situ* generation of Pd NPs. The papaya bark ash was characterized by EDX, ion chromatography and flame photometry to reveal the inherent basic nature of the extract. The generation of *in situ* Pd NPs was confirmed by TEM analysis. Moreover the catalytic system could be easily recovered by simple fractional separation and Suzuki Miyaura coupling can be reused for five consecutive cycles, with some loss in activity from 3rd cycle onwards.



Scheme 2: Suzuki-Miyaura and Sonogashira cross-coupling of aryl halides with aryl boronic acids and terminal alkynes using $Pd(OAc)_2$/WEPBA.

Section 3.2: *Extraction of base from naturally abundant aquatic biomass and its implication in palladium catalyzed Suzuki-Miyaura cross-coupling reaction*

This section describes the development of another non-conventional base using a naturally abundant waste aquatic biomass, *Eichhornia crassipes* (Common name: Water Hyacinth). Low temperature combustion of the dried mass of *Eichhornia crassipes* imparts inherent basicity in water. The system serves as an excellent alternative base and solvent system for palladium catalyzed Suzuki-Miyaura cross-coupling reaction of aryl halides and aryl boronic acids at room temperature (Scheme 3). The basicity of the AWEH (Ash Water Extract of water Hyacinth) may be due to the formation of corresponding metal oxides and hydroxide in water. The distribution of metal contents in its ash was characterised by Energy Dispersive X-ray (EDX) analysis.

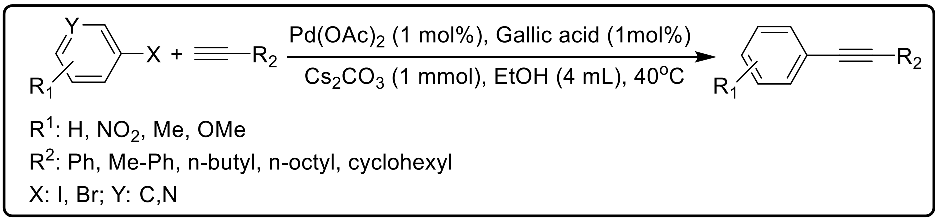


Scheme 3: Pd(OAc)$_2$/AWEH catalyzed Suzuki-Miyaura cross-coupling reaction of aryl halides with aryl boronic acid.

Chapter 4: Development of sustainable methodologies for generation of *in situ* Pd NPs and investigation of catalytic activity in C_{sp2}-C_{sp2} and C_{sp2}-C_{sp} bond forming reaction

Section 4.1: *Gallic acid assisted in situ generation of Pd NPs and its catalytic application in Sonogashira cross-coupling reaction*

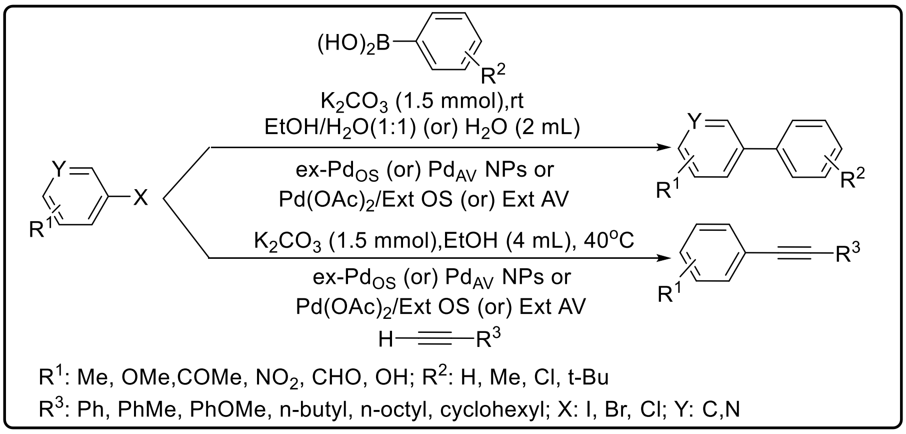
In this section we present a non-toxic naturally abundant phytochemical, gallic acid for *in situ* generation of Pd(0) NP. The method provides an efficient alternative route for Sonogashira coupling reaction under mild reaction condition (Scheme 4).The catalytic system displayed excellent reactivity for diverse range of substrates including less reactive aryl bromides. The formation of the Pd NPs was confirmed by performing UV/Vis spectroscopy, powder XRD analysis and their size and morphology were determined by transmission electron microscopy (TEM). Further the *in situ* generated Pd NPs can be reused for four consecutive cycles without much loss in its catalytic activity.



Scheme 4: Gallic acid derived Pd NPs catalyzed Sonogashira cross-coupling reaction of aryl halides with terminal alkynes.

Section 4.2: *Application of plant extract towards NOSE approach: A comparative study of catalytic activity in C_{sp2}-C_{sp2} and C_{sp2}-C_{sp} cross-coupling reaction*

This section discloses the use of plant extract as reducing and stabilizing agents for generation of NPs. A comparative study of reduction of Pd(II) ion using *Ocimum sanctum* leaf extract (Ext OS) and *Aloe vera* extract (Ext AV) has been taken into account. The catalytic effect of both the *in situ* and *ex situ* condition was examined in Suzuki-Miyaura and Sonogashira cross-coupling reaction (Scheme 5). The system serves as a reliable alternative to conventional methodologies for NPs synthesis and maintains a green synthetic pathway avoiding hazardous chemical reagents and tolerates broad substrate scope. The structural and morphological characteristics of the NPs are examined by UV-visible spectroscopy, FTIR spectroscopy, X-ray diffraction and transmission electron microscopy analyses.

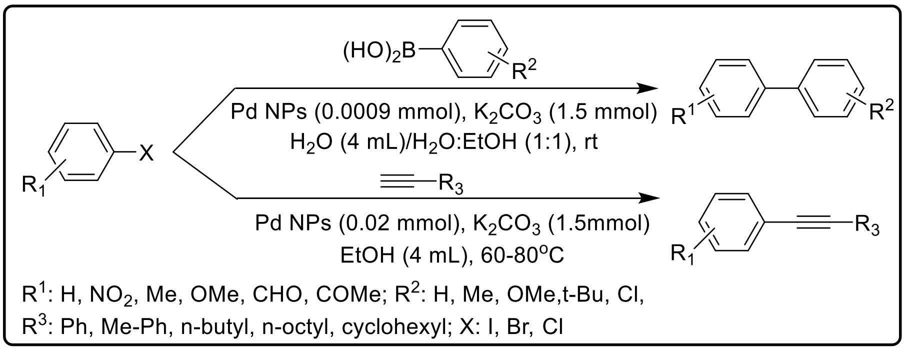


Scheme 5: Pd NPs catalyzed Suzuki-Miyaura and Sonogashira cross-coupling reaction of aryl halides with aryl boronic acid and terminal alkynes.

Chapter 5: Development of green methodology for the synthesis of reusable metal NPs using agro-waste and its application in oxidative C_{sp2}-C_{sp2} and C_{sp2}-C_{sp} bond forming reaction

Section 5.1: *Synthesis of efficient Pd NPs using papaya peel and its implication in Suzuki and Sonogashira cross-coupling reaction*

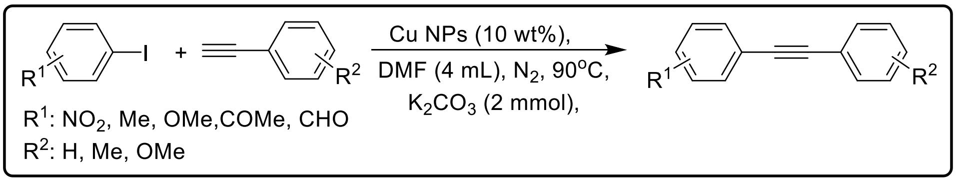
This chapter focuses on the utilization of agro-waste for synthesis of Pd NPs without the assistance of any conventional strategies and investigation of its catalytic application in Suzuki-Miyaura and Sonogashira cross-coupling reaction. The catalyst shows excellent activity for coupling reaction of aryl halides with organoboron compounds and terminal alkynes under mild condition (Scheme 6). The Pd NPs are characterized by SEM, EDX, TEM, BET and Powder XRD analysis.



Scheme 6: Pd NPs catalyzed Suzuki-Miyaura cross-coupling of aryl halides and aryl boronic acid and Sonogashira cross-coupling reaction of aryl halides and terminal alkynes.

Section 5.2: *Synthesis of copper NPs using papaya peel extract and its catalytic activity towards Sonogashira cross-coupling reaction*

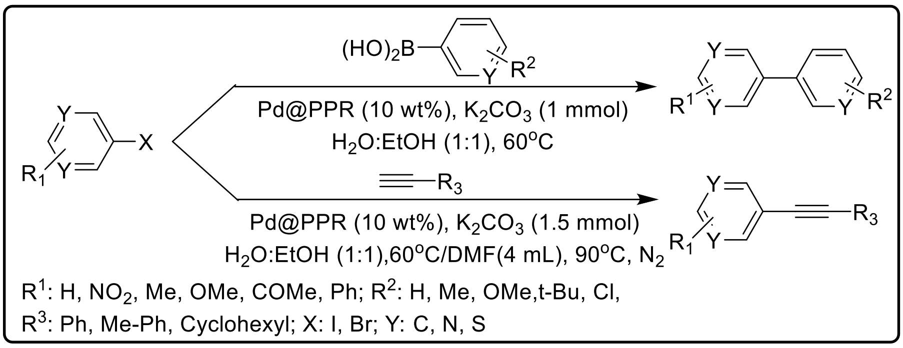
In this section, a facile, inexpensive and eco-friendly method for synthesis of copper NPs has been developed using papaya peel extract. A Cu_2O/Cu NPs has been synthesized by hydrothermal method without the assistance of any reducing agents. The catalytic activity of the Cu_2O/Cu NPs was examined for palladium free Sonogashira type cross-coupling reaction of aryl iodides and phenylacetylenes (Scheme 7). The reaction affords good to excellent yield of disubstituted alkynes. The synthesized NP was characterized by UV/Vis Spectroscopy, FTIR, Powder XRD, SEM, EDX, TEM and BET analysis.



Scheme 7: Cu_2O/Cu NPs catalyzed Pd free Sonogashira cross-coupling reaction of aryl halides and terminal alkynes.

Chapter 6: Synthesis of mesoporous cellulose matrices: Its application as a heterogeneous support for Pd NPs and study of its catalytic activity in C_{sp2}-C_{sp2} and C_{sp2}-C_{sp} cross coupling reaction

This chapter focuses on the development of mesoporous biodegradable cellulose matrix using waste fruit peel and corresponding fabrication with *in situ* generated Pd NPs using the same fruit peel residue without use of any external chemical reducing agent (Scheme 8).



Scheme 8: Heterogeneous Pd NPs catalyzed Suzuki-Miyaura and Sonogashira cross-coupling reaction.

The activity of the catalytic system has been investigated in C_{sp2}-C_{sp2} and C_{sp2}-C_{sp} cross-coupling reaction. Moreover this chapter shows a significant difference in the structural morphology of cellulose matrices with conventional acid treated method and microwave assisted method. The catalytic system is well characterized by FTIR, Powder XRD, TEM, SEM, EDX and BET analysis.