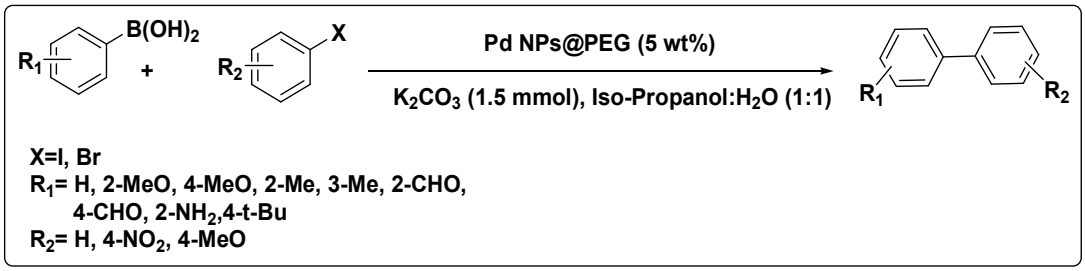
The main objective of the present thesis was to develop some green and efficient protocols for the synthesis of palladium and copper based nanoparticles (NPs) with the aim to reduce the use of hazardous chemicals. The characterizations of the synthesized NPs using various techniques are also a part of the thesis. After characterization the NPs, they are followed by implication in different types of carbon-carbon and carbon-nitrogen bond forming reactions viz Suzuki-Miyaura cross-coupling reaction, Sonogashira and Chan-Lam reaction. The main contents of the thesis have been divided into six chapters.

Chapter 1: General Introduction:

This chapter is to establish the basis with a general introduction and a brief review on literature relevant to the research topic, "**Studies on the development of palladium and copper based nanocatalysts for sustainable Suzuki-Miyaura, Sonogashira and Chan-Lam cross-coupling reaction**". An effort to describe the history, importance and present status of the C-C and C-N bond formation reaction, along with the importance of NPs and different methods employed for their synthesis are described here.

Chapter 2: Biosynthesis of poly(ethylene glycol)-supported palladium nanoparticles using *Colocasia esculanta (C. esculanta)* leaf extracts as reducing agent and their catalytic application in Suzuki-Miyaura cross-coupling reaction.

This chapter discusses the development of a simple and green method for the synthesis of poly(ethylene glycol) stabilized Pd NPs under ambient conditions from the aqueous extracts of *Colocasia esculanta* (*C. esculanta*) leaves. *C. esculanta* is locally known as "*kochu*" in Assam, a state in North-Eastern part of India and used in traditional systems of medicine by native people. The synthesized NPs showed very good catalytic activity towards Suzuki-Miyaura cross-coupling reaction for a wide variety of aryl halides and phenyl boronic acid substrates. The nanocatalysts were characterized by UV-visible spectroscopy, FT-IR, powder XRD and TEM analysis and also support our observation and results. The optimized reaction scheme is shown in Scheme 1:



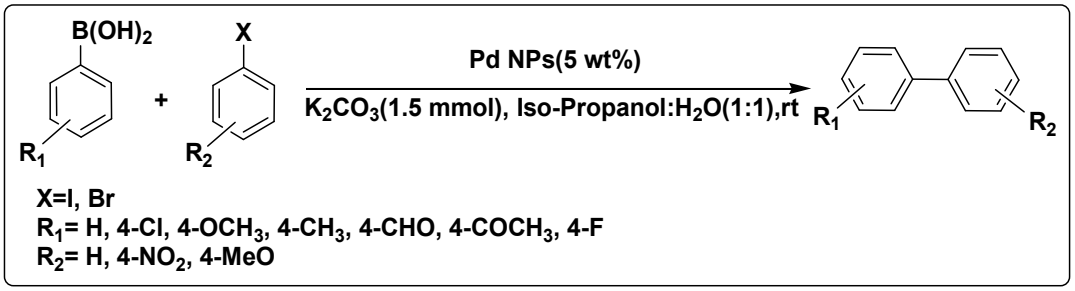
Scheme 1: Pd NPs@PEG catalyzed Suzuki-Miyaura reaction.

This chapter also explains reaction parameters and substrate scope of this methodology with wide varieties of electronically diverse substrates. Recyclability issue is also addressed here. The detail experimental procedure of the performed reactions, results and the supporting data of the prepared compounds (physical data, spectroscopic data etc.) are also covered in this chapter.

<u>Chapter 3:</u> A green synthesis of palladium nanoparticles by *Sapindus mukorossi* (*S. mukorossi*) seed extracts and its application in efficient room temperature Suzuki-Miyaura cross-coupling reaction.

This chapter castes light on a simple and green method for the synthesis of Pd NPs using an aqueous extract of *Sapindus mukorossi* seed extract. No external stabilizer is added in this method. The synthesized palladium nanocatalysts were characterized using different techniques like UV-visible spectroscopy, powder XRD, EDX and TEM analysis which supported our results. The EDX analysis of seed powder indicates the presence of element potassium (K) in addition to carbon (C) and oxygen (O). However, the amount of potassium (K) is very low (0.69%) compared to C (63.92%) and O (35.39%). Further, flame photometry technique also confirms the low amount of K (460.5 ppm), which suggests that the metals don't have any role in the overall properties of the seed extracts. The synthesized Pd NPs were applied efficiently to room temperature Suzuki-Miyaura cross-coupling reaction as shown in scheme 2.

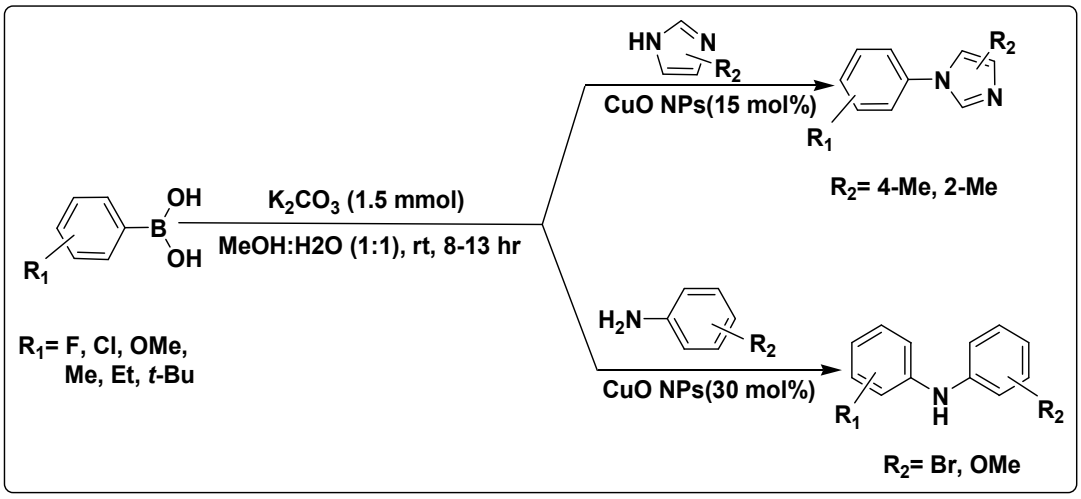
The substrate scope of this method with wide varieties of electronically diverse substrates along with the detailed experimental procedure, results and discussion on the outcomes and the supporting data (physical data, spectroscopic data etc.) of the prepared compounds are included in this chapter. Recyclability of the catalyst was also studied.



Scheme 2: Pd NPs catalyzed Suzuki-Miyaura reaction.

<u>Chapter 4:</u> Copper oxide nanoparticles as a mild and efficient catalyst for *N*-arylation of imidazole and aniline at room temperature.

In this chapter, an efficient protocol for *N*-arylation of aniline and imidazole with aryl boronic acid as coupling partner catalyzed by CuO NPs at room temperature is presented. The optimized reaction protocol is shown in scheme 3. The CuO NPs were synthesized by using a simple thermal refluxing technique. The as synthesized NPs were characterized by FT-IR spectroscopy, powder TGA, XRD, SEM, EDX, TEM, XPS and BET surface area analysis which supported our observations and result. The detailed experimental procedure as well as the substrates scope of this method is included in this chapter. Products were characterized by melting point determination, spectroscopic data etc. Also, the catalytic system was found to be recyclable up to 5th run without significant loss of catalytic activity.



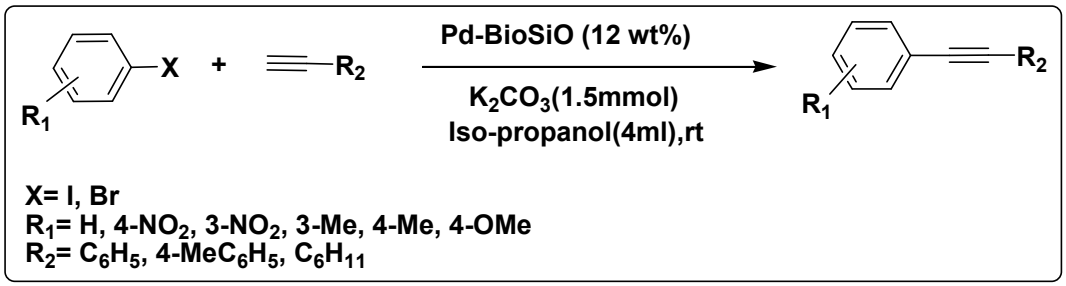
Scheme 3: CuO NPs catalyzed *N*-arylation of aniline and imidazole.

Chapter 5: Synthesis of Pd NPs decorated on biosilica: An efficient catalyst for C–C bond formation reaction.

Section 5.1: Facile synthesis of Pd NPs with the aid of methanol decorated on biosilica: An excellent catalyst for ligand and copper free Sonogashira cross-coupling reaction at room temperature.

In this section of the chapter 5, Methanol aided synthesis of Pd NPs decorated on biosilica and its successive implication in copper free Sonogashira cross-coupling reaction at room temperature are described.

Pd NPs decorated on biosilica was synthesized by simply stirring $Pd(OAc)_2$ in methanol at room temperature. No external reducing agent was added during the process. Excellent catalytic activity was shown by the catalyst for copper and ligand free Sonogashira coupling of terminal alkynes with aryl iodides/bromides at room temperature (scheme 4). Characterization of the catalyst was carried out by EDX, TEM, BET and Powder XRD analysis. The detailed experimental procedure applied results and discussion on the outcomes and the supporting data of the prepared compounds (melting point, spectroscopic data etc.) are included in this chapter.

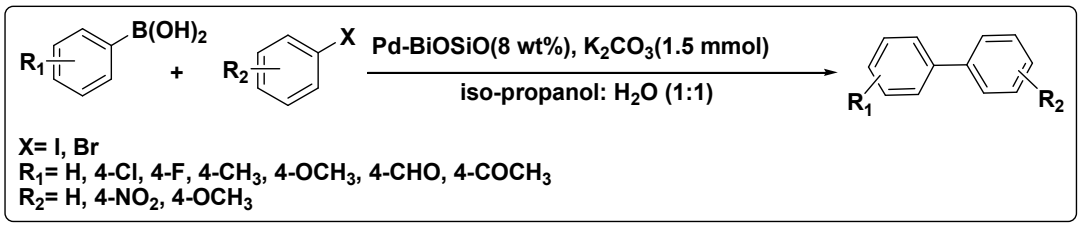


Scheme 4: Sonogashira cross-coupling reaction.

Section 5.2: Reducing agent free, simple and facile synthesis of Pd NPs decorated on biosilica and its implication in ligand free Suzuki-Miyaura cross-coupling reaction at room temperature.

In this section, the same catalyst (mentioned in section 5.1 above) has been reported for an efficient room temperature Suzuki–Miyaura reaction between aryl halides and phenyl

boronic acid substrates under ligand free reaction conditions and found that the catalyst shows excellent result. The reaction scheme after optimizing the catalyst, base and solvent is shown below (scheme 5).



Scheme 5: Suzuki-Miyaura cross-coupling reaction.

The detailed experimental procedure, results and discussion on the outcomes and the supporting data of the compounds (melting point determination, spectroscopic data etc.) that were prepared are included in this chapter.

Chapter 6: Conclusions and future scope:

This chapter highlights and summarizes all the results obtained in the preceding chapters. The general outcomes of each previously discussed chapter are also discussed here. Based on the findings mentioned in the preceding chapters, the future prospects of the existing works are also projected here.