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## 5. Overall conclusions:

### 5. 1. Conclusions from Chapter 2

Chapter 2 is based on the development of efficient Pd based catalysts for C-C bond formation reactions.

**Section 2.1.** In the section, we have described a rice straw ash promoted improved Suzuki-Miyaura cross-coupling reaction in *i*PrOH: water, catalyzed by *in-situ* generated Pd NPs.

The advantages presented by this method include:

- [a] We use a naturally abundant agro waste (Rice Straw Ash) as an *in-situ* base for the cross-coupling reaction and have identified the active metal oxide responsible for its basicity.
- [b] The biphasic solvent generates *in-situ* Pd NPs which is responsible for higher activity.
- [c] Better yields have been found with this method for both electron withdrawing and donating group substituted substrates than only in water extract of rice straw ash.
- [d] High temperature, expensive ligand external bases etc. have been avoided.

**Section 2.2.** Here, in this section, we have disclosed a methanol aided synthesis of Pd NPs decorated on montmorillonite K10 and successful utilization of the prepared catalyst in a base and aryl halide free Suzuki type cross-coupling reaction.

The main outcomes of the protocols are as follows:

- [a] The method is comprised of a simple solvent (methanol) assisted route for the synthesis of Pd NPs decorated on montmorillonite (K10) without using any external reducing agent.
- [b] The catalyst Pd NPs@ K10 has been synthesized at room temperature stirring method which avoids heat, ultrasonication etc.
- [c] The prepared catalyst has been applied in a base free Suzuki type cross-coupling reaction of aryldiazonium tetrafluoroborate and aryl boronic acids in water. The reaction completes within short reaction time.
- [d] Expensive and unfavorable ligands have been avoided.
- [e] The clay surface activates the boronic acid moiety and thus enhanced the reaction rate.

**Section 2.3.** This section demonstrates a room temperature ligand and Cu free Sonogashira cross-coupling reaction catalyzed by Pd NPs decorated on reduced graphene oxide.

It summarizes the following upshots:

[a] It is a ligand and Cu free protocol for Sonogashira cross-coupling reaction at room temperature.

[b] Room temperature synthesis of Pd NPs decorated on reduced graphene oxide has been accomplished.

[c] The catalyst is found to be reused up to five times without significant loss of yield.

### **5. 2. Conclusion from Chapter 3**

Chapter 3 is based on the development of mild and efficient method for C-N bond forming reaction.

**Section 3.1.** In this section, we have exemplified *N,N'*-dimethylurea/Cu(II) promoted room temperature methodology for *N*-arylation of anilines and imidazoles with aryl boronic acid.

The key findings of the methodology are listed below:

[a] A cheap and easily available ligand is used as a promoter.

[b] A naturally abundant waste material banana peel ash is utilized both as solvent and base for the reaction.

[c] The reactions have been performed at room temperature.

[d] The protocol avoids toxic solvents and external commercial bases.

[e] The reaction protocol takes shorter reaction time than most of the existing protocol for *N*-arylation.

**Section 3.2.** In this section, we have offered a room temperature *ipso*-nitration of aryl boronic acid catalyzed by molecular iodine which employs zirconium oxynitrate as a nitrating species.

The main conclusions of the methodology are listed below:

- [a] The reaction avoids harsh acid/oxidant.
- [b] It is a room temperature protocol and employed mild oxidant molecular iodine.
- [c] Non toxic nitrating species zirconium oxynitrate has been used.
- [d] DFT based calculations are also carried out to support the mechanism. Computational results shows that the reaction is thermodynamically favourable and we have identified transition states of the reaction pathway.
- [e] The reaction requires lesser time to complete than most of the existing methods and is successfully applicable to both aryl and heteroaryl moieties.

### **5. 3. Conclusion from Chapter 4**

The main premise of section 4 is to develop efficient methodology for *ipso*-hydroxylation of aryl boronic acids.

**Section 4.1.** In this section, we have focussed on an *ipso*-hydroxylation of aryl boronic acid catalyzed by bio-silica and hydrogen peroxide.

It derives the following conclusions:

- [a] We have developed a quick hydroxylation of arylboronic acid using a very minimum amount of mild oxidizing agent hydrogen peroxide.
- [b] A natural acidic catalyst bio-silica has been applied which has been found to be heterogeneous and reused up to sixth times.
- [c] Water is used as the solvent media for the reaction and yield of the reaction is excellent.
- [d] The green-ness of the protocol has been evaluated in terms of atom efficiency, E-factor, mass intensity etc. and proved to be a greener one than most of the previous outstanding methodology.

**Section 4.2.** This section involves the utilization of bio-catalyst Baker's yeast in *ipso*-hydroxylation of aryl boronic acid using hydrogen peroxide as an oxidant.

The central attraction of the methodology is described as follows:

- [a] Exploitation of a bio-catalyst in a useful organic transformation.

- [b] Application of a mild oxidising agent.
- [c] The reaction consumes short time for completion.
- [d] Expensive ligands and toxic solvents have been avoided.

### **Future scopes:**

- [a] To develop some efficient catalyst for dehydrogenative cross-coupling reaction.
- [b] To search some synthetic methodologies for desulphurization cum cross coupling reaction.
- [c] To establish some proficient protocols for C-H activation of arenes.
- [d] Emphasis may also be provided with regard to chirality.