PROJECT COMPLETION REPORT

Project entitled

Development of novel palladium based catalyst for Suzuki-Miyaura and Sonogashira reaction in aqueous solution

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By

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PROJECT COMPLETION REPORT

1. **Title of the Project:** "Development of novel palladium based catalyst for Suzuki– Miyaura and Sonogashira reaction in aqueous solution"
2. **Principal Investigator:** Dr. Anindita Dewan
3. **Mentor:** Dr. Pankaj Bharali
4. **Implementing Institution and other collaborating Institution(s):** Tezpur University and Dibrugarh University.
5. **Date of Commencement:** 21.03.2012
6. **Planned Date of Completion:** 20.03.2015
7. **Actual Date of Completion:** 20.03.2015
8. **Objectives as stated in the project proposal:**

   i) The main objective of the proposed research project is to develop palladium based catalyst for Suzuki-Miyaura and Sonogashira coupling using nitrogen based ligands under mild reaction conditions in aqueous solution.

   ii) Palladium based metal complexes will be synthesized using different types nitrogen based ligands and their catalytic activity in Suzuki-Miyaura and Sonogashira coupling reaction will be examined.

   iii) Immobilized palladium catalyst will be synthesized based on either ligand functionalized amorphous or ordered mesoporous silica for utilization in Suzuki-Miyaura and Sonogashira coupling.

   iv) Use of aryl chlorides as coupling partner in Suzuki-Miyaura and Sonogashira coupling.

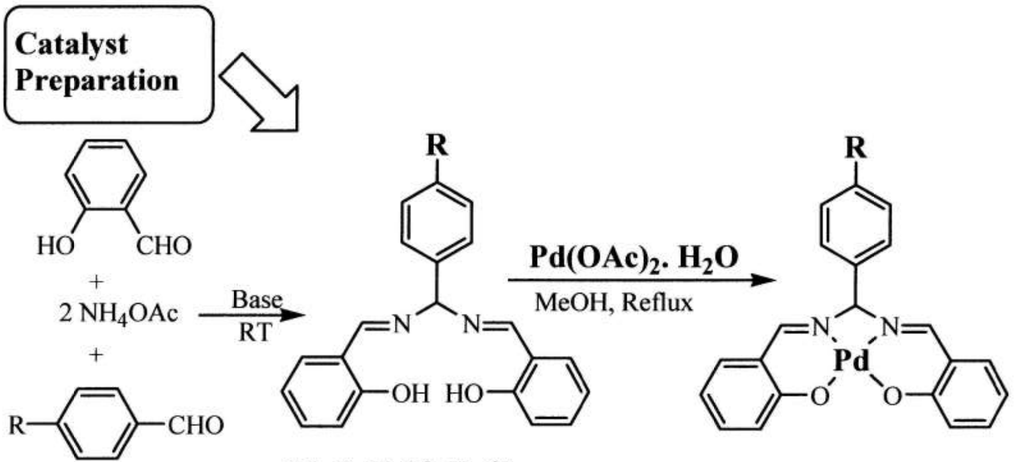
   v) Some biologically significant heterocyclic compounds will be synthesized utilizing these newly developed catalyst system.

9. **Deviation made from original objectives if any, while implementing the project and reasons thereof:** No any deviation

10. **Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams & photographs:**

Experiment 1:

a) We have synthesised and characterised novel palladium based shift based catalyst using nitrogen based ligands. The catalyst is very simple and the starting materials used are commercially available and cheap. The newly synthesized complexes were characterized by elemental analysis, IR, ^{1}H- and ^{13}C- NMR and mass spectral data.

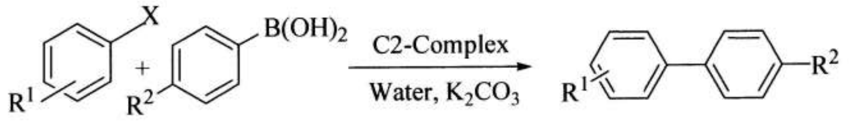


L1: R=H, L2: R=Cl,
L3: R=OCH$_3$, L4: R=NO$_2$

C1: R=H, C2: R=Cl,
C3: R=OCH$_3$, C4: R=NO$_2$

(Scheme 1)

b) This tetradentate Schiff base palladium complex (Scheme 1) was found to be efficient catalyst for Suzuki-Miyaura cross-coupling reactions of aryl halides with arylboronic acid in water at room temperature. Further the scope of this protocol has been extended to the Suzuki–Miyaura cross-coupling reaction of aryl chlorides with arylbronic acids. However, we were able to isolate 75% yield of the cross-coupling product by using i-PrOH as solvent.



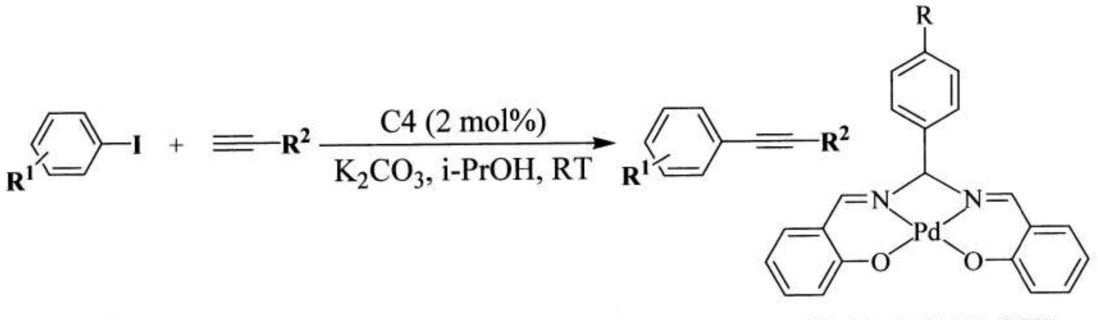
R^1= H, CH_3, OCH_3, NO_2, CHO, $COCH_3$
R^2= H, $C(CH_3)_3$, OCH_3, Cl
X = Br (*in water*)
X = Cl (*in isopropanol*)

(Scheme 2)

This work is published in ***Tetrahedron Letters*****, 2014,** 55, 1689-1692.

Experiment 2:

This similar catalytic system is also used in Sonogashira cross-coupling reaction of terminal acetylenes with aryl and vinyl halides at room temperature using isopropanol as solvent under copper free condition. The main catalytic species ie the Pd-complex was derived from Schiff base ligand N,N$'$-bis(salicylidene)-arylmethanediamine and Pd(OAc)2. Electronically diversified and sterically hindered aryl iodides underwent the smooth coupling reaction with electronically diversified aryl/alkyne acetylene to afford good to excellent yield of diaryl alkynes in isopropanol at room temperature.



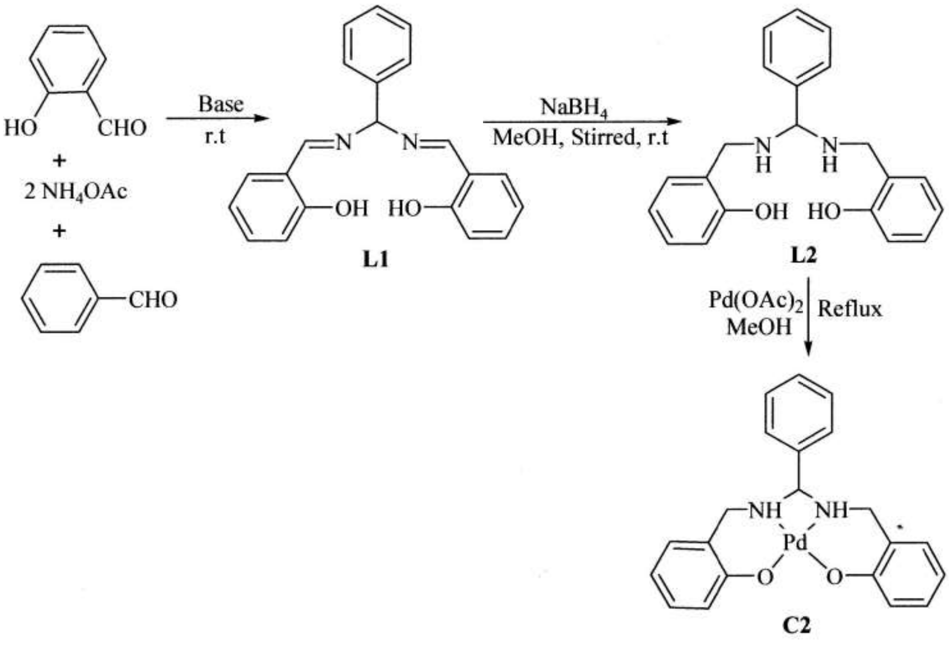
C1: R=H; C3: R=OCH_3
C2: R=Cl; C4: R=NO_2

(Scheme 3)

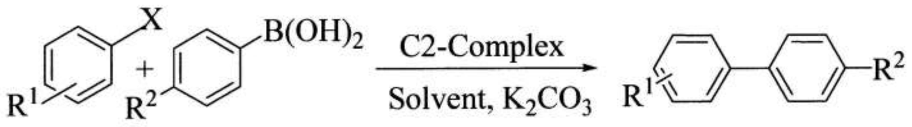
This work is accepted for publication in ***New J. Chem*****, 2015**

Experiment 3:

Again we have synthesised and characterized one novel palladium complexes with a previously reported tetradentate Schiff-base ligand N,N'-bis(salicylidene)-phenylmethanediamine (L1) and its reduced form (L2), ligand (Scheme 4). The new palladium complex C2 was prepared by refluxing methanolic solution of the corresponding tetradentate ligand L2 with equimolar amount of palladium acetate. The newly synthesized complex C2 were characterized by elemental analysis, IR, ^{1}H- and^{13} C-NMR and mass spectral data. Using this new catalyst here we developed a facil and efficient room temperature Suzuki-Miyaura cross-coupling reaction using greener solvent. The same catalytic system is also effective for Suzuki Miyaura Cross-Coupling reaction of less reactive aryl chlorides with aryl boronic acids. Since, there has been a tremendous rise in interest for employing aryl chloride as substrates for Suzuki-Miyaura cross-coupling, as they are easily accessible economical compared to their bromide and iodide counterparts.



(Scheme 4)



R^1= H, CH_3, OCH_3, NO_2, CHO, $COCH_3$

R^2= H, $C(CH_3)_3$, OCH_3, Cl

X = Br {iPrOH:Water(1:1), 0.2 mol% C2-Complex, RT}

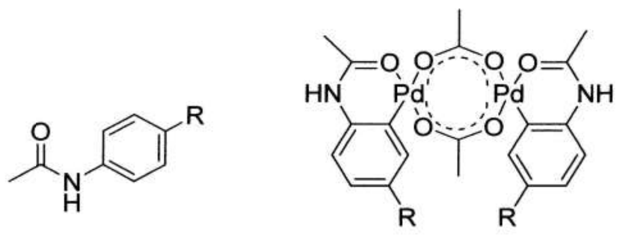
X = Cl (in isopropanol, 1mol% C2-complex, 50°C)

(Scheme 5)

This work is published in ***Bull. Korean Chem. Soc.*** **2014**, 35, 1855-1858.

Experiment 4:

Recently, nitrogen-containing ligands such as N-heterocyclic carbenes, amines and oxime have emerged as efficient ligands for Suzuki–Miyaura reaction with the potential to overcome most of the drawbacks of traditional phosphine ligands. Additionally, some common laboratory chemicals and reagents such as sodium sulfate, PEG and EDTA have been successfully utilized as promoters for the reaction. Acetanilide is a routinely used cheap laboratory chemical with immense potential as a ligand. Moreover, acetanilide derivatives are well-known precursors for palladacycles, which have wide applicability in various organic transformations such as orthoalkylation. We have synthesised three acetanilide-based palladacycles by using cheap, easily accessible and commercially available acetanilide derivatives, viz. N-phenylacetamide (L1), N-(4-chlorophenyl)acetamide (L2) and N- (4-methylphenyl)acetamide (L3) as palladacycle precursors (Scheme 5). This type of amide-based palladacycle can easily be synthesized within short reaction times under mild reaction conditions (Scheme 5).

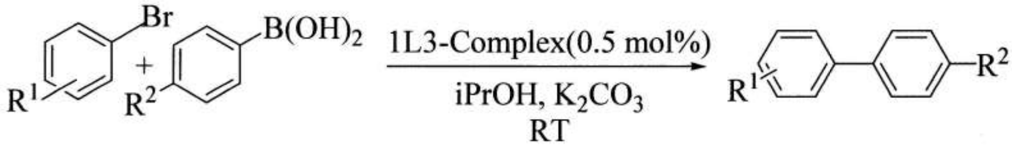


R= H; L_1
R= Cl; L_2
R= CH_3; L_3

R= H; 1L1
R= Cl; 1L2
R= $CH_3$1L3,

(Scheme 5)

Among these three 1L3 acetanilide-palladacycle was found to be efficient catalyst for Suzuki-Miyaura cross-coupling reactions of aryl halides with arylboronic acid in isopropanol at room temperature. It is very efficient in case of activated aryl bromide at very low catalyst loading.

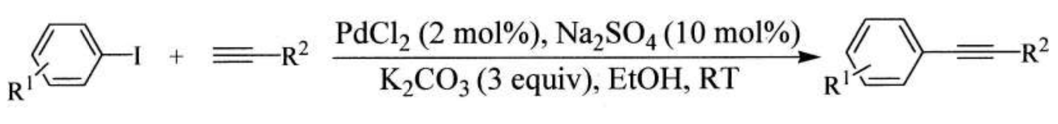


(Scheme 6)

This work is published in ***Appl. Organometal. Chem.*** **2014**, 28, 230–233.

Experiment 5:

We have also developed a Na_2SO_4 promoted efficient procedure for the Sonogashira cross coupling reaction of aryl iodides with aryl acetylenes at room temperature under ligand and copper free condition. The innocuous nature and rate enhancing effect of these salts makes them a suitable alternate for ligands in the Pd-catalyzed Sonogashira cross coupling reaction.



(Scheme 7)

This work is published in ***RSC Adv.,*** **2015**, 5, 16–19.

Experiment 6:

Again we have also want to develope environment friendly method for Suzuki cross-coupling reaction of aryl bromides and phenylboronic acid derivatives catalyzed by in situ-generated Pd(0) nanoparticles in pure water, at room temperature with excellent yields using starch as soluble polymer without any conventional ligand.

The generation of Pd nanoparticles has been monitored by the UV/Vis absorption spectroscopy as shown in figure 1.

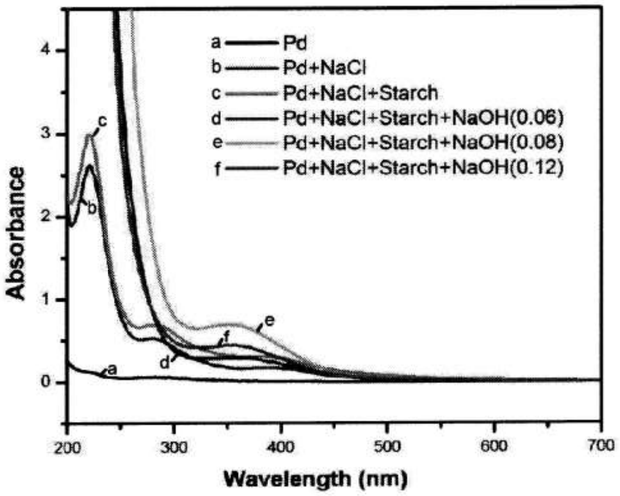
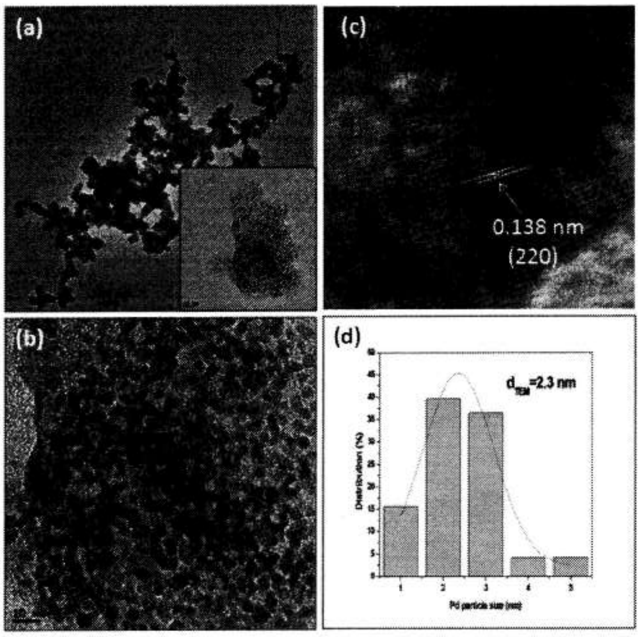


Figure 1

The two absorption peaks at 225 and 275 nm were observed that could be assigned to the ligand-to-metal charge transfer band of the complex $Na_2Pd(OAc)_2Cl_2$ (fig 1, b). However no any changes of absorption peak in UV-Vis was observed after addition of starch (fig 1, c). Interestingly on addition of NaOH to the aqueous solution of $Na_2Pd(OAc)_2Cl_2$, showed disappearance of two peaks appeared at 225 nm and 275 nm and appearance of a new absorption band, which may be assigned to the Pd nanoparticles (fig 1, d). Several test reactions were carried out using different amounts Pd(OAc)2, NaOH and starch to find the optimised reaction conditions (fig 1, d, e, f).

The particle size and shape of the in situ generated palladium nanoparticles were further characterized by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) measurements (Figure 2). Figure 2(a) presents the global TEM image of in situ generated Pd nanoparticles. It could be observed from the TEM image that Pd nanoparticles preferentially crystallize in spherical shape. Closer view of the TEM image at higher resolution demarcate that very fine spherical nanoparticles of Pd are homogeneously distributed (inset of Figure 2(a)). A representative HRTEM image as shown in Figure 2(b) reveals that nearly monodisperse spherical Pd nanoparticles with an average particle size of ~3-4 nm were obtained. Figure 2(c) confirms the presence of crystal plans with the lattice 'd' spacing of 0.138 nm which corresponds to the (220) plane of Pd-nanoparticles.



It is worth to mention that the system exhibit excellent catalytic activity for coupling unreactive aryl bromide with phenylboronic acid in pure water at room temperature. The efficiency of this in situ-generated Pd(0) nanoparticles as catalyst was evaluated by coupling reaction of 4-methoxybromobenzene (1 mmol) and phenylboronic acid (1.2 mmol) as the model substrate. After gating the optimized reaction condition, we have study the scope and limitations of the current procedure using a wide array of electronically diverse aryl bromides with arylboronic acids (Table 1).

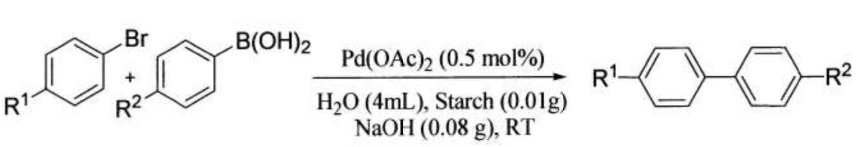
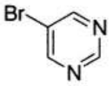
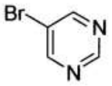
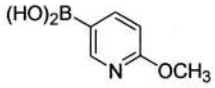


Table:1 Suzuki-Miyaura reaction of aryl bromides with different arylboronic acids.

Entry	**R^1**	**R^2**	**Time(h)**	**Yield (%)^C**
1	H	H	4	98
2	H	OMe	4	95
3	H	Cl	5	95
4	H	t-Butyl	5	95
5	4-NO_2	H	8	98^b
6	4-NO_2	OMe	8	85^b
7	4-NO_2	Cl	8	80^b
8	4-OMe	H	3	98
9	4-OMe	OMe	3	95
10	4-OMe	Cl	3	95
11	2-OMe	H	4	98
12	4-CH_3	H	3	95
13	4-CH_3	OMe	3	95
14	4-CH_3	t-Butyl	5	90
15	4-CH_3	Cl	5	95
16	4-OCH	H	8	90^b
17	4-OCH	OMe	8	90^b
18	4-OCH	Cl	8	85^b
19	4-OCCH_3	H	8	90
20	4-OCCH_3	OMe	8	90
21	4-OCCH_3	Cl	8	85
22		H	8	90
23			8	85

^{a}Reaction Conditions: arylbromobenzene(1 mmol), phenylboronic acid (1.2 mmol), Pd$(OAc)_2$ (0.5 mol%), NaOH (1 mmol), water (4mL), 25°C, in air. ^{b} EtOH (0.25 mL) was used as co-solvent for solubility. ^{c} Isolated yield.

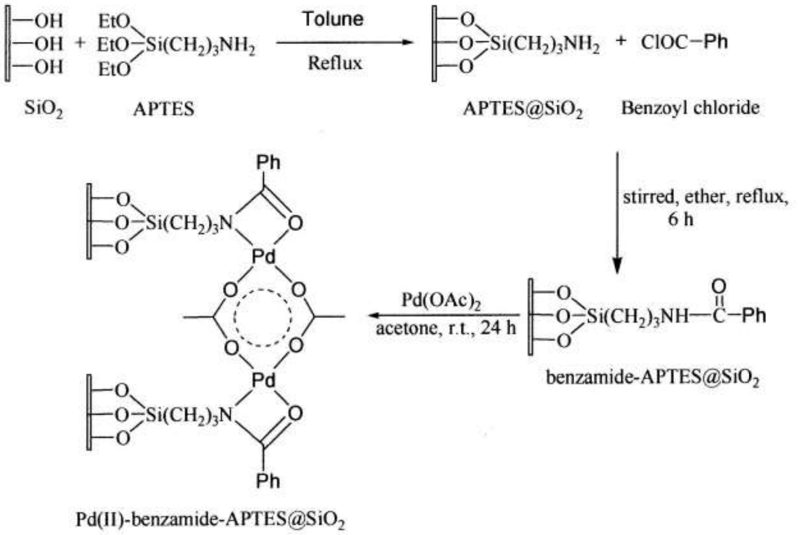
In conclusion, here we have developed a simple and efficient protocol for Suzuki-Miyaura cross coupling reaction in pure water with excellent yield in presence of low catalyst loading at room temperature. In our work this can be possible only due to in situ formation of palladium nanoparticles.

This work is communicated to **Green Chemistry.**

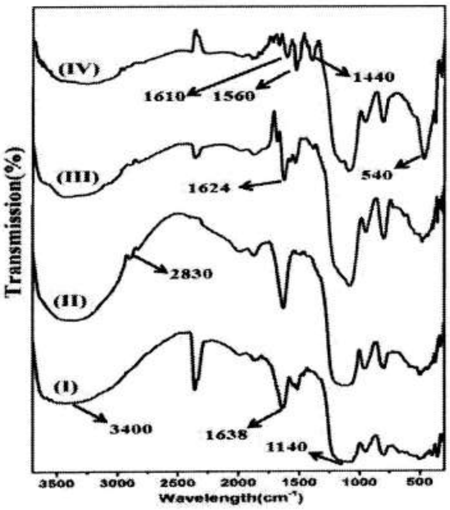
Experiment 7:

In recent years heterogeneous catalyst systems have been found to be some of the most effective tools for various types of reactions. Among these, Pd-based catalyst systems have attracted wide attention owing to their excellent catalytic activity in cross-coupling reactions like Suzuki–Miyaura, Sonogashira, Heck and Tsuji–Trost reactions. However homogenous cataly from the commercial point of view, lack of possibility of reus st for recycling from the reaction mixture. So use of supported or impregnated heterogeneous Pd catalyst will obviously be a better alternative. Herein we synthesised and characterized a new heterogeneous and reusable catalyst for Suzuki-Miyaura cross-coupling reaction at room temperature in green solvent.

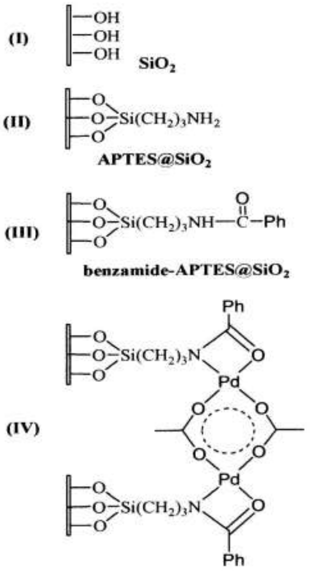
Catalyst preparation:



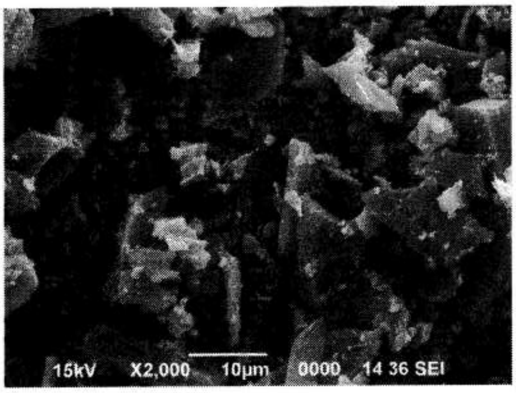
The newly synthesized Pd(II)-benzamide-APTES@SiO_2 catalyst characterized by elemental analysis, IR, ESR and SEM data.

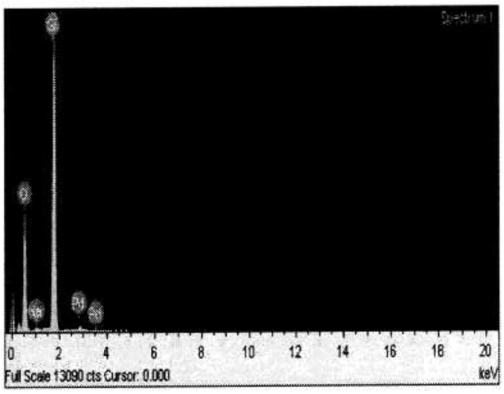


FTIR-spectra



Pd(II)-benzamide-APTES@SiO$_2$





SEM image of Pd(II)-benzamide-APTES@SiO$_2$

EDX analysis of Pd(II)-benzamide-APTES@SiO$_2$

This heterogeneous catalytic system exhibit excellent catalytic activity for coupling aryl halides with phenylboronic acid at room temperature in isopropanol/water as solvent system. The efficiency of this catalyst was evaluated by coupling reaction of 4-methoxybromobenzene (1 mmol) and phenylboronic acid (1.2 mmol) as the model substrate. After gating the optimized reaction condition, we have study the scope and limitations of the current procedure using a wide array of electronically diverse aryl bromides with arylboronic acids (Table 1).

So We have developed a mild and efficient protocol for the Suzuki–Miyaura cross-coupling reaction at room temperature under aerobic conditions using 0.43 mol% Pd(II)-benzamide-APTES@SiO_2. The catalyst system was found to be effective for a wide array of functionalized aryl halides and arylboronic acids. The application of aqueous solvent in our protocol and the reusability of the catalyst are significant advantages compared to other existing catalyst systems for the Suzuki reaction.

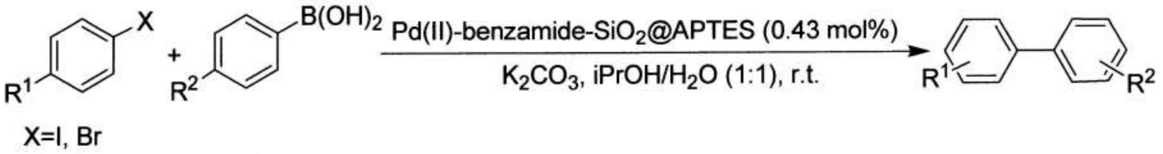


Table 1: Suzuki-Miyaura reaction of aryl bromides and iodides with different arylboronic acids.

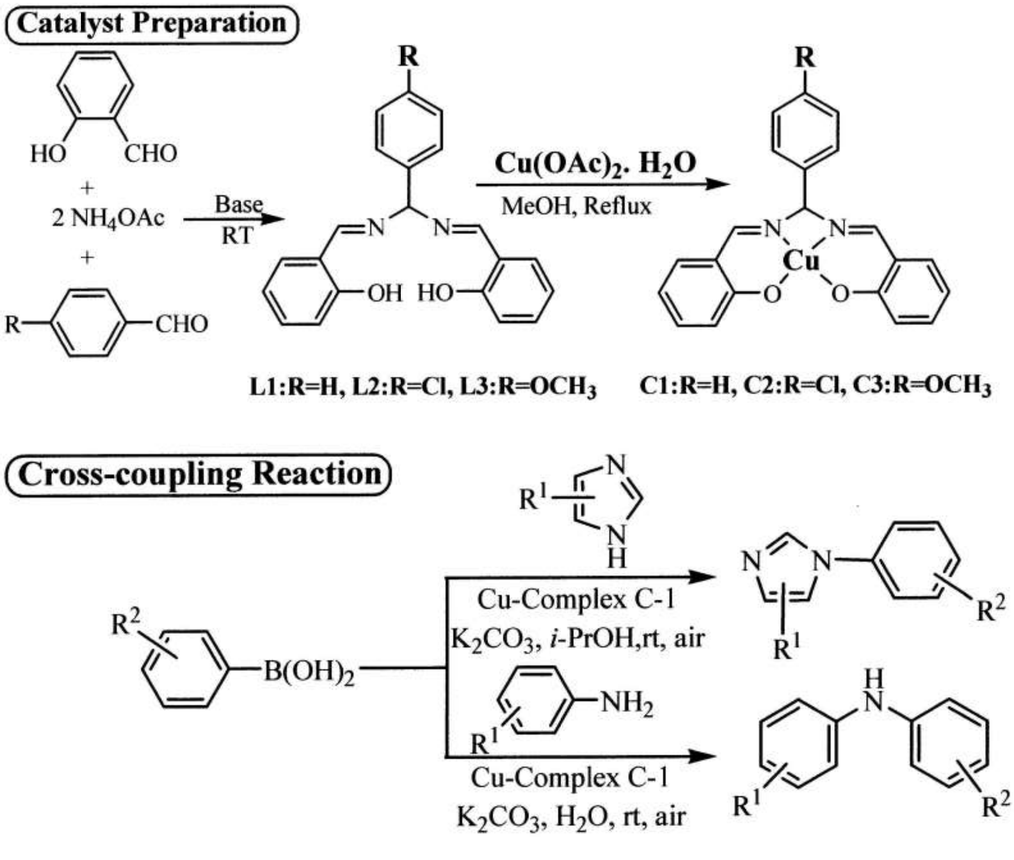
Entry	R¹	R²	Time (h)	Yield (%)
1	NO_2	H	3.5	99
2	NO_2	F	4	96
3	NO_2	OCH_3	6	94
4	OCH_3	H	2.5	98
5	OCH_3	F	3.5	94
6	OCH_3	OCH_3	4.5	92
7	CHO	H	7	90
8	CHO	OCH_3	4.5	97
9	CHO	F	6	95
10	$COCH_3$	H	4	95
11	$COCH_3$	OCH_3	6	93
12	$COCH_3$	F	7	90
13	H	H	1	100
14	H	OCH_3	2.5	97
15	H	F	3.5	95

This work is communicated in ***Tetrahedron Letters.***

Experiment 8:

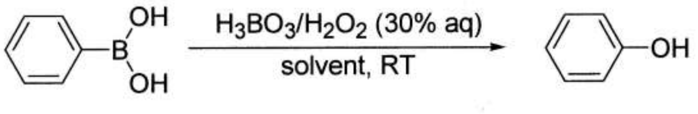
Some other related work

a. Like tetradentate Schiff base palladium complex, we have synthesised Cu-based catalyst using the same nitrogen based ligands and used this catalyst for Chan-Lam type coupling reaction in water at room temperature.



This work is published in ***Tetrahedron Letters*, 2014**, 31-35

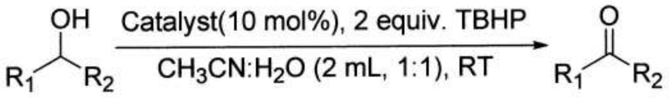
b. We have also developed a boric acid catalysed ipso-hydroxylation of arylboronic acid to phenol using aqueous hydrogen peroxide as an oxidizing agent and ethanol as a solvent at room temperature



This work is published in ***Heteroatom Chem.* 2014**, 127-130.

c. Again we have developed a vanadium based catalyst system for the oxidation of primary and secondary alcohols to aldehydes or ketones by using tert-butyl hydroperoxide as oxidizing agent and vanadyl sulfate as catalyst at room temperature.

The versatility of the catalytic protocol is studied with wide variety of substrates. The catalytic system could be reused successfully until the sixth run without either significant loss of yield or extension of the reaction time. Use of aqueous solvent, no ligands and reusability of catalyst are some major advantages of the present protocol.



This work is published in ***Tetrahedron Letters*, 2014**, 5029-5032

11. Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject:

Recently, there is a renewed interest in using green chemistry principles in the field of research addressing current requirements in synthetic chemistry and catalysis. Green chemistry is the design, development and implementation of chemical products and processes to reduce the use and generation of substances hazardous to human health and the environment. Nowadays, the development of the field of green chemistry through organic reactions conducted in water has become one of the most exciting research endeavours for organic chemists. Actually, water is an attractive alternative to traditional organic solvents because it is inexpensive, non-flammable, non-toxic, and environmentally sustainable by alleviating the problem of pollution by organic solvents. Also, water is an attractive solvent for metal-catalyzed reactions, such as Suzuki–Miyaura couplings. Furthermore, from the commercial point of view, lack of possibility of reuse of such costly homogeneous catalysts makes their widespread or industrial use less viable. So by using supported or impregnated heterogeneous catalyst will obviously be a better alternative.

12. Conclusions summarising the achievements and indication of scope for future work:

(a) Room temperature Suzuki-Miyaura reaction has been carried out in aqueous medium using novel palladium based Schiff base catalyst using nitrogen based ligands.

(b) Using the same catalyst Sonogashira cross-coupling reaction has been carried out at room temperature using isopropanol as solvent.

(c) We have also synthesised and characterized another novel palladium based Schiff base complexes by reducing tetradentate Schiff-base ligand N,N'-bis(salicylidene)-phenylmethanediamine. This catalyst also found to be very effective for Suzuki Miyaura Cross-Coupling reaction of less reactive aryl chlorides with aryl boronic acids at room temperature.

(d) A novel amide-based palladacycle catalysed Suzuki-Miyaura reaction has been carried out at room temperature under mild reaction conditions

(e) Na_2SO_4 promoted Pd-catalysed Sonogashira cross coupling reaction of aryl iodides with aryl acetylenes at room temperature under ligand and copper free condition has been carried out.

(f) In situ generated palladium nanoparticle catalysed Suzuki-Miyaura cross coupling reaction in pure water at room temperature has been developed.

(g) Reusable silica supported heterogeneous Pd-catalyst was found to be effective for the Suzuki reaction of functionalized aryl halides and arylboronic acids at room temperature under mild reaction condition.

(h) A mild and efficient methodology has been developed for Chan-Lam type coupling reaction using copper based Schiff base catalyst.

(i) A simple, efficient and environmentally benign boric acid catalysed hydroxylation of arylboronic acid has been developed using aqueous hydrogen peroxide as an oxidizing agent.

(j) We have also developed a vanadium based catalyst system for the oxidation of primary and secondary alcohols to aldehydes or ketones by using tert-butyl hydroperoxide as oxidizing agent and vanadyl sulfate as catalyst at room temperature.

13. New Observations:

(a) This tetradentate Schiff base palladium complex can be easily synthesised at room temperature.

(b) It is efficient catalyst for Suzuki-Miyaura, Sonogashira cross-coupling reaction under mild reaction condition.

(c) Another amide-based palladium complex found to be an efficient catalyst for Suzuki-Miyaura reaction at room temperature under aqueous condition.

(d) The innocuous nature and rate enhancing effect of simple inorganic salts like Na_2SO_4 makes it suitable alternate for ligands in the Pd-catalyzed reaction. So under ligand and copper free condition, Na_2SO_4 can promote Sonogashira cross coupling reaction at room temperature in presence of very small amount of $Pd(OAc)_2$ as catalyst.

(e) There is growing interest to develop alternative green and eco-friendly routes for the synthesis of nanomaterials with control size and morphology in single synthetic steps with minimum chemical waste in environmentally friendly solvents. Palladium nanoparticles (PdNPs) as catalyst attracted much attention in Suzuki Miyaura cross coupling reactions due to the unique properties arise at nanoscale. Here we have able to develope environment friendly method for Suzuki cross-coupling reaction of aryl bromides and phenylboronic acid derivatives catalyzed by in situ-generated Pd(0) nanoparticles in pure water, at room temperature with excellent yields using starch as soluble polymer without any conventional ligand.

(f) Heterogeneous catalysis is widely used in industrial applications because of the facile costly catalyst separation, which often results in lower operating costs in compare to homogeneous catalyst. Herein we synthesised and characterized a new heterogeneous reusable catalyst for Suzuki-Miyaura cross-coupling reaction at room temperature in green solvent.

(g) Cu-based Schiff base catalyst a mild and efficient catalyst for the Chan-Lam type cross coupling reaction in water, which has versatile synthetic utility.

(h) We have developed a simple and facile one-pot synthetic method of ipso-hydroxylation of aryl boronic acids to the corresponding phenol.

14. Innovations: Suzuki-Miyaura, Sonogashira, Chan-Lam type cross-coupling, oxidation of alcohol and Hydroxylation reaction has been carried out at room temperature using green solvent.

15. Application Potential:

a. Immediate: Use of green solvent in Suzuki-Miyaura and Sonogashira cross-coupling reaction. In most of the methods developed for Suzuki-Miyaura and Sonogashira cross-coupling reaction are performed in organic solvent, but from environmental and economic point of view, the use of water as a solvent in the carbon-carbon bond formation reactions are extremely interesting because water is a cheap, readily available and environmentally friendly solvent.

b. Long Term: A remarkable amount of progress can be achieved toward solving the long-standing challenge of developing readily available and additives for Suzuki-Miyaura and Sonogashira cross coupling reactions using appropriate choice of catalyst.

16. S&T benefits accrued:

a. List of Research publications

S No	**Authors**	**Title of paper**	**Name of the Journal**	**Volume**	**Pages**	**Year**
1	**Anindita Dewan***, Utpal Bora, Geetika Borah	A simple and efficient tetradentate Schiff base derived palladium complex for Suzuki–Miyaura reaction in water	Tetrahedron Letters	55	1689–1692	2014
2	**Anindita Dewan***	A Highly Efficient and Inexpensive Palladium-Salen Complex for Room Temperature Suzuki-Miyaura Reaction	Bull. Korean Chem. Soc.	35	1855-1858	2014
3	**Anindita Dewan**, Zenith Buragohain, Manoj Mondal, Gayatri Sarmah, Geetika Borah Utpal Bora,*	Acetanilide palladacycle: an efficient catalyst for room-temperature Suzuki–Miyaura crosscoupling reaction	Appl. Organometal. Chem.	28	230–233	2014

4	Ankur Gogoi, **Anindita Dewan,*** Geetika Borah Utpal Bora*	A palladium salen complex: an efficient catalyst for the Sonogashira reaction at room temperature	New J. Chem DOI: 10.1039/c4nj01822b			Accepted 24th February 2015
5	Ankur Gogoi, **Anindita Dewan,** Utpal Bora*	A highly efficient copper and ligand free protocol for the room temperature Sonogashira reaction	RSC Adv.	5	16–19	2015
6	Ankur Gogoi, Gayatri Sarmah, **Anindita Dewan**, Utpal Bora*	Unique copper–salen complex: an efficient catalyst for N-arylations of anilines and imidazoles at room temperature	Tetrahedron Letters	55	31–35	2014
7	Kongkona Gogoi, **Anindita Dewan**, Ankur Gogoi, Geetika Borah, Utpal Bora*	Boric Acid as Highly Efficient Catalyst for the Synthesis of Phenols from Arylboronic Acids	Heteroatom Chemistry	25	127-130	2014
8	Gayatri Sarmah, Saitanya K.	An efficient and reusable vanadium based	Tetrahedron Letters	55	5029–5032	2014

	Bharadwaj, **Anindita Dewan,** Ankur Gogoi, Utpal Bora*	catalytic system for room temperature oxidation of alcohols to aldehydes and ketones				

b. Manpower trained on the project

i) Ph.D. produced: No

ii) Other Technical Personnel trained: No

c. Patents taken, if any: No

17. Financial Position:

S No	Financial Position/ Budget Head	Funds Sanctioned	Expenditure	% of Total cost
1.	Salaries/ Manpower costs	1st Year:5,50,000/-	12,74,677/-	
2.	Equipment	2nd Year:10,60,000/-	1,94,826/-	
3.	Supplies & Materials	3rd Year: 6,00,000/-	3,50,127/-	
4.	Contingencies		73,482/-	
5.	Travel		37,313/-	
6.	Overhead Expenses		2,62,500/-	
7.	Others, if any			
	Total	22,10,000/-	21,92,925/-	99.22%

18. Procurement/ Usage of Equipment

a)

S No	Name of Equipment	Make/ Model	Cost (FE/ Rs)	Date of Installation	Utilisation Rate (%)	Remarks regarding maintenance / breakdown
1	Electric Balance	ML-204 Mettler-Toledo	1,20,000/-		95.87%	They are all in good condition
2	Laptop	Dell Vostro 3450	46,707/-			
3	Printer	HP Lsser Jet 1020 Plus	6,951/-			
4	Scanner	HP Scanjet G2410	3,999/-			
5	Quickheal Total Security		3,900/-			
6	Vacuum Pump Oil Free		10,191/-			

b) Plans for utilising the equipment facilities in future

Currently research scholars are using these equipments. Again I will apply another new project and so for this I will use these equipment.

Name and Signature with Date

a. Anindita Dewan
23/04/15
(Principal Investigator)

b. PBharali 23/04/15
(Mentor) Pankaj Bharali.

STATEMENT OF EXPENDITURE

1. **Sanction Order No and Date:** No.SR/WOS-A/CS-78/2011(G) dtd.23/02/2012
2. **Total Project Cost:** 23,10,000/-
3. **Revised Project Cost** (if applicable):
4. **Date of Commencement:** 20/03/2012
5. **Grant received in each year:**
    - a. 1st Year: **5,50,000/- (Released during the financial year 2011-12)**
    - b. No fund was released during the financial year 2012-13
    - c. 2nd Year: **10,60,000/- (Released during the financial year 2013-14)**
    - d. 3rd Year:6,00,000/-**(Released during the financial year 2014-15)**
    - e. Interest, if any: Nil
    - **f. Total (a+b+c+d): 22,10,000/-**

STATEMENT OF EXPENDITURE

To be submitted financial year wise

(i.e. DOS* to 31st March of that financial year 01-04-2014 till 31.03.2015)

S No	Sanctioned Heads	Sanctioned Cost	Grant received	Expenditure Incurred				Total Expenditure VIII=IV + V + VI+VII	Balance as on (date) III(b) – VIII =	Requirement of Funds upto 31st March next year	Remarks (if any)
				1st Year [DOS to 31st March 2012) (IV)	2nd Year (1st April to 31st March 2012-13) (V)	3rd Year & so on (1st April to 31st March 2013-14) (VI)	4th Year & so on (1st April to 31th March 2014-15 (VII)				
(I)	(II)	(III)(a)	(III)(b)						(IX)		
1.	**Fellowship**	12,60,000/-	22,10,000/-	-	3,99,677/-	4,55,000/-	4,20,000/-	12,74,677/-	17,075/-		Unspent balance Rs 17,075/- on 31/03/15
2.	**Consumables**	4,00,000/-		-	1,12,739/-	-	2,37,388/-	3,50,127/-			
3.	**Travel**	75,000/-		-	-	37,313/-	-	37,313/-			
4.	**Contingencies**	75,000/-		-	24,984/-	7,526/-	40,972/-	73,482/-			
5.	**Others, if any**			-	-		-	-			
6.	**Equipment**	2,00,000/-		-	1,84,635/-		10,191/-	1,94,826/-			
7.	**Overhead expenses**	3,00,000/-		-	-	2,00,000/-	62,500/-	2,62,500/-			
8.	**Total**	**23,10,000/-**		-	7,22,035/-	6,99,839/-	77,1051/-	21,92,925/-			

Anindita Dewan

Name and Signature of Principal Investigator:

Date: 23/04/15

28/4/15

Signature of Competent financial authority: __________

(with seal) Date: __________

Finance Officer
Tezpur University

*** DOS – Date of Start of Project:20-03-2012**

Note :

1. Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under that head, without prior approval of DST i.e. Figures in Column (VIII) should not exceed corresponding figures in Column (III)
2. Utilisation Certificate for each financial year ending 31st March has to be enclosed along with request for carry-forward permission to the next financial year.

UTILISATION CERTIFICATE (2 COPIES)
FOR THE FINANCIAL YEAR - (ENDING 31ST MARCH, 2014-15)

1. **Title of the Project:** "*Development of novel palladium based catalyst for Suzuki Miyaura and Sonogashira reaction in aqueous solution*"

2. **Name of the Institution:** Tezpur University

3. **Principal Investigator:** Dr. Anindita Dewan

4. **Department of Science & Technology Sanction Order No & Date of sanctioning the project:** No.SR/WOS-A/CS-78/2011(G) dtd.23/02/2012

5. **Carry forward amount brought from the previous Financial year**
   i. Amount :1,88,126/-
   ii. Letter No :
   iii. Date :

6. **Amount received during the current financial year**
   i. Amount : 6,00,000/-
   ii. Letter/Order No :SR/WOS- A/CS-78/2011
   iii. Date : 22/08/2014

7. **Interest earned from previous grant** Amount : Nil

8. **Total amount that was available for expenditure during the financial year (Sr. No. 5+6+7)** Rs. 7,88,126/-

9. **Actual Expenditure incurred during the financial year (upto 31st March)** Rs.7,71,051/-

10. **Balance amount available at the end of the financial year (Sr. No. 8-9):** Rs. 17,075/-

11. **Unspent balance refunded, if any (please give details of cheque no etc.):** Rs. 17,075/-

12. **Amount to be carried forward to the next financial year (if applicable):**

UTILISATION CERTIFICATE

Certified that out of Rs 6,00,000/- (Six lacks only) of grants-in-aid sanctioned during the year 2014-15 in favour of Registrar, Tezpur University vid SERB order No. SR/WOS-A/CS-78/2011 dated 22/08/2014 and Rs 1,88,126/- (One lack eighty eight thousand one hundred twenty six only) on account of unspent balance of the previous year, a sum of Rs 7,88,126/- (Seven lacks eighty eight thousand one hundred twenty six only) has been utilised for the purpose of purchasing minor equipment, consumable, contingency and fellowship for which it was sanctioned and that the balance of Rs. 17,075/- (Seventeen thousand seventy five only) remaining unutilised at the end of the year has been surrendered to Government (vide DD No ________ dated ________)

Anindita Dewan
Signature of PI

Date 23/04/15

Signature of Registrar/ Head
(with seal)
Registrar
Tezpur University
Date

28/4/15
Signature of Accounts Officer
(with seal)
Finance Officer
Tezpur University
Date