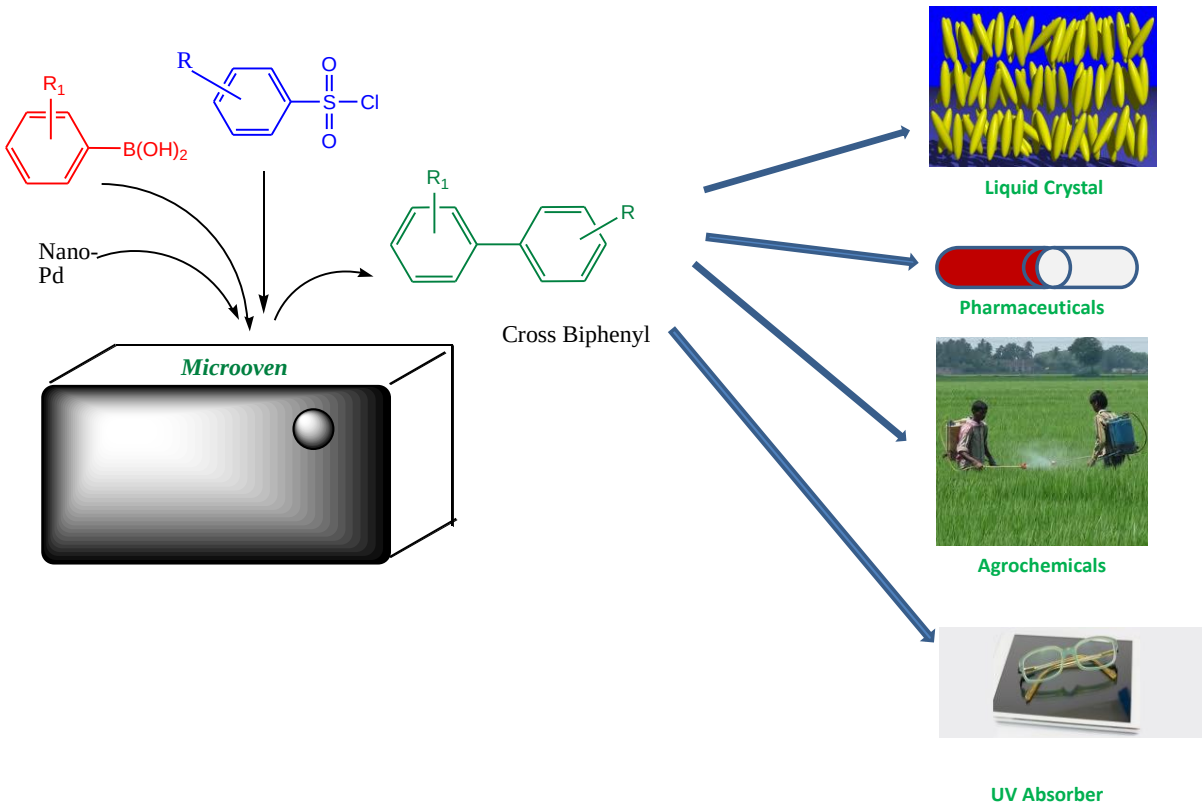
Chapter 4

Microwave irradiated and *in-situ* generated Pd nanoparticles catalysed synthesis of cross-biphenyls cum desulfurization using aryl sulfonyl chlorides and phenyl boronic acids



Chapter 4

4.1 Introduction

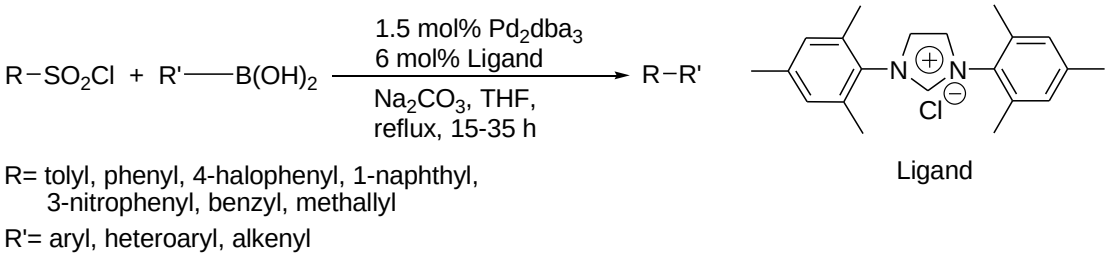
Interest in the chemistry of biphenyls is consistently expanding. The biaryl moiety is found to have application in several areas like pharmaceuticals, natural products, agrochemicals, ligands, conducting polymers, liquid crystals and advanced materials[1]. Cross biphenyls are versatile intermediates in the synthesis of the starting material of UV absorbers[2] and insecticide.[3] Now-a-days, the arylation of (cross) aromatics *via* metal catalyzed C−Cross bond activation provides an efficient access to the corresponding aryl- (cross) aryl derivatives. Palladium is the most widely used catalyst for such direct cross-coupling reactions[4−10] but, other transition metals like ruthenium etc. have also been used for this purpose.[11-23] To synthesize biphenyls generally Suzuki-Miyaura coupling reaction has been followed due to its simplicity of method. Here, we have tried Suzuki-Miyaura cross coupling reaction to produce cross biphenyls using arylboronic acid and arylsulfonyl chlorides minimising the formation of biphenyls through homocoupling reaction. Initially, alkyl- and especially aryl-halides were extensively used as the coupling partners for such reactions.

In recent years, various alternative coupling partners, such as benzoic acids,[24-26] arylboronic acids,[27,28] or aryl tosylates,[29] have been successfully used to prepare cross biphenyls. Among them, one of the most promising and convenient types is certainly substituted or unsubstituted $ArSO_2R$ derivatives, such as $ArSO_2Na$ or $ArSO_2Cl$. Principal advantages of these substrates are that most of them are easy to prepare, commercially available and safe handling. $ArSO_2Cl$ derivatives can be easily synthesized from sulfonic acids or sulfur substrates by chlorination,[30-34] and $ArSO_2Na$ can be prepared by the reduction of the corresponding $ArSO_2Cl$.[38]Another important advantage of such coupling partners is that, in some cases, they give access to alternative regioisomers. Moreover, the use of halo-substituted $ArSO_2R$ derivatives produces biaryls without cleavage of the Ar−Br or Ar−I bonds, allowing further transformations. The reaction also gives products with desulfurization of arylsulfonyl chlorides which inhibits environmental pollution to be happened due to sulphur containing substance. To the best of our knowledge, there is no report on the synthesis of cross-biphenyls with desulfurization of sulfonyl chlorides. The method can be taken for degrading sulphur containing organic substance as a precautionary step towards environmental pollution.

Parts of this chapter are communicated in an international journal

Sulphur can cause so many problems in our environment and it can harm to human beings including other living beings.[35] Bacteria use deposited sulfur from soil as a food or energy source and they produce hydrogen sulfide gas as a byproduct of their metabolic functions. Water that contains hydrogen sulfide is easily recognizable by its bad odour. Consuming sulphur containing water is not so much health risk, but it can be unappetizing.[36] Short-term exposures to high concentration of sulfur dioxide can be life-threatening. Exposure to 100 ppm of sulfur dioxide is considered immediately dangerous to life and health of both animal & human beings. Previously miners who breathed sulfur dioxide released from underground copper mine developed burning problems of the nose and throat, breathing difficulties and severe obstructions. Long-term exposure to persistent levels of sulfur dioxide may have fatal affect on our health. It has been observed that Lung function in some workers exposed to 0.4–3.0 ppm of sulfur dioxide for 20 years or more is disrupted so much. Additionally, asthmatics are sensitive to the respiratory effects of low concentrations (0.25 ppm) of sulfur dioxide.[37]

Some of the researchers used harsh condition like heating more than 100 ^{0}C in presence of strong acid (e.g. KOH) for at least 20 h to produce cross biphenyls.[38] Pierre Vogel *et al.*[39] synthesized cross-biphenyls using complex palladium catalyst under refluxing condition for 35 h in THF (Scheme 1). In our approach, we have tried to minimize the reaction time using mild base and Pd NPs under greener microwave irradiation technique.



Scheme 4.1: Palladium-catalyzed Suzuki-Miyaura cross-couplings of sulfonyl chlorides and boronic acids[39]

We have used *in-situ* generated Pd NPs as catalyst and microwave irradiation (MWI) techniques to prepare cross biphenyls. Instead of using some Pd complexes,[38,39] use of *in-situ* generated Pd greatly favoured the reaction with less environmental pollution in terms of cost and hazardous effect. Conventional catalysts

are required in a large excess and they significantly contribute to increase environmental pollution. Consequently, there is a need for efficient and heterogeneous catalytic methods for this reaction involving inexpensive, easily handled and non-polluting reagents.

The main objective of this work is to reveal the synthetic utility of environmentally benign techniques (MWI, use of weak base and less hazardous chemicals) for the formation of biaryl derivatives. For these reasons, we focused our efforts on developing a rapid, microwave-assisted cross-coupling of arylboronic acid and arylsulfonyl chlorides in presence of *in-situ* generated Pd NPs catalyst. There is report on the synthesis of the biaryls under MWI techniques.[40] Moreover, that method involves use of more chemicals and time. On the other hand, Biao Jiang *et al.* reported the palladium-catalyzed, ligand-free Suzuki reaction in water using aryl fluorosulfates in presence of strong base triethyl amine and the reaction took at least 2 h of time.[41] According to that report, coupling reaction to synthesize cross biphenyl yields only 27-30% in presence of bases like K_2CO_3, Na_2CO_3 and Cs_2CO_3. Whereas, we could realize 92% yield of in presence of K_2CO_3 under MWI within 5 mins. Our aim is to achieve a reduction in the reaction times as well as to design an environmentally benign procedure avoiding use of the polluting commonly used homogeneous catalyst.

4.2 Results and Discussions

4.2.1 Characterization

Palladium catalyst is well characterized with the help of TEM, SEM, EDAX, particle size analyzer and XRD. The typical XRD profile in the 2θ range of 20^o to 70^o of the synthesized palladium, shows the presence of the different characteristics peaks and could be indexed on the basis of JCPDS card no. 050681 (Figure 4.1). Matching with the JCPDS file revealed that the material was face centered cubic (fcc) palladium. High Resolution TEM image shows that the palladium NPs are within the diameter ~45 to 55 nm (Figure 4.2). It clearly reveals lattice picture with approx. distance between two planes. Thus, for the present case, in all probability, Polyethylene glycol (PEG) acts as a capping agent (please see section 4.2.2) which facilitates the one dimensional growth of Pd NPs. The surface morphologies of Pd NPs before and after reaction were determined by SEM images (Figures 4.3a and 4.3b respectively).

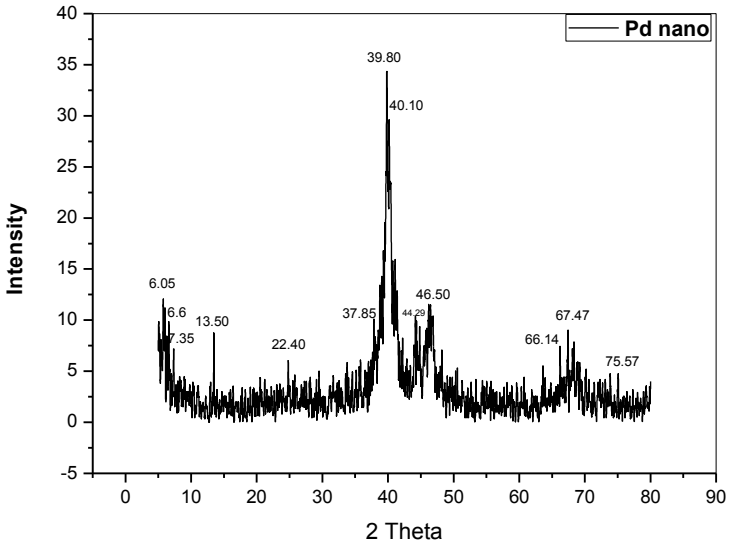


Figure 4.1: Powder XRD pattern of fresh Pd NPs catalyst

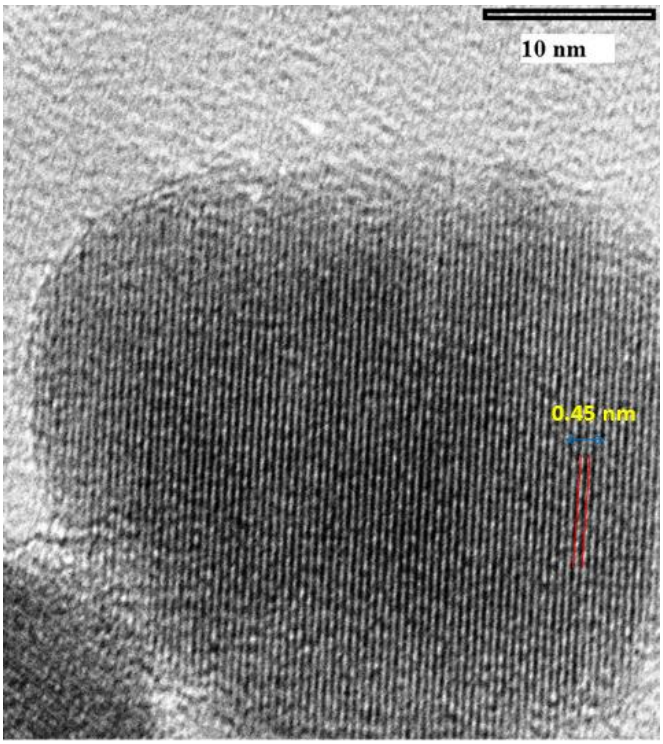


Figure 4.2: HRTEM image of Pd NPs

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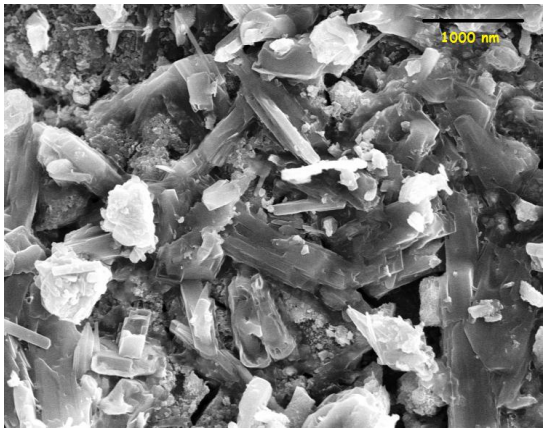


Figure 4.3(a): SEM image of Pd NPs before the reaction

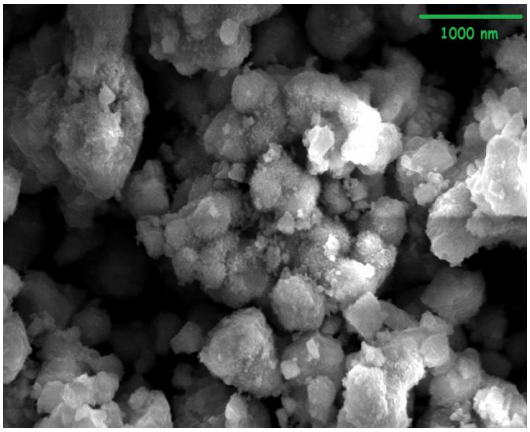


Figure 4.3(b): SEM image of Pd NPs after the reaction

The approx. particle size from particle size analyzer was also obtained and that was within 50 to 70 nm (Figure 4.4). However, the particle size from particle size analyzer is somewhat bigger compared to that found from TEM is due to agglomeration of individual Pd NPs.

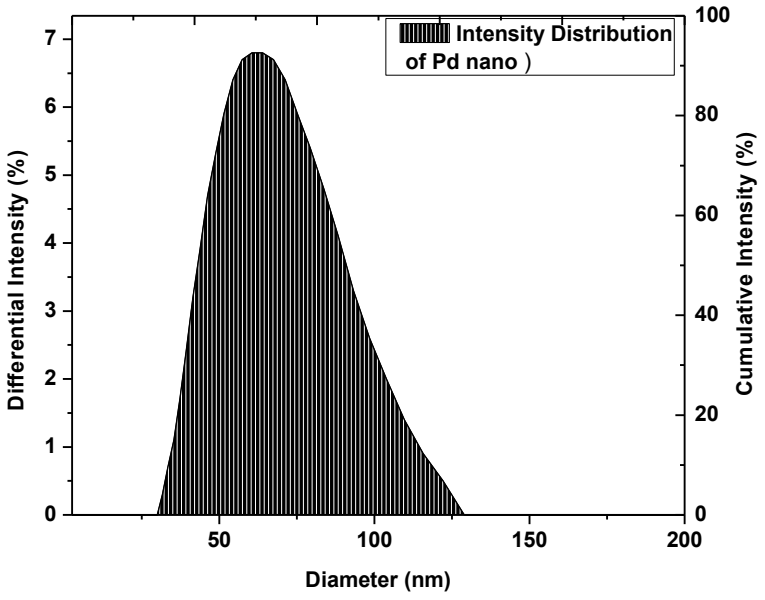


Figure 4.4: Particle size distribution of Pd NPs

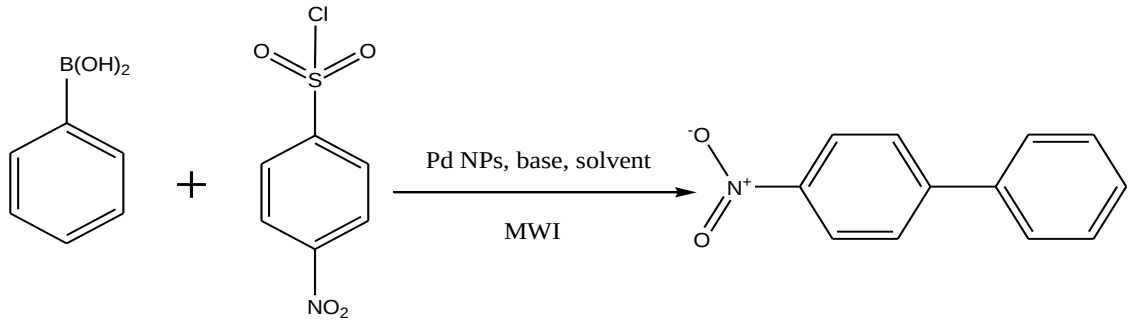
4.2.2 Synthesis

Palladium NPs were synthesized as follows:

Palladium chloride and PEG-400 were taken in a silica crucible and subjected to MWI for 5 mins at 800 W. After completion of reaction, the reaction mixture was

taken out and worked-up well. Palladium NPs were confirmed from particle size analyzer as well as other instrumental techniques.

Here, *in-situ* generated Pd NPs catalysed cross-coupling of arylboronic acids and benzenesulfonyl chlorides under MWI in air is reported. To the best of our knowledge, Microwave irradiated/assisted synthesis of cross-biphenyls cum desulfurization using arylsulfonyl chlorides and phenylboronic acids has not been reported so far. Pd was found to be an efficient and heterogeneous, reusable catalyst. First of all, the reaction was carried out in refluxing condition varying solvent and temperature. We have taken phenylboronic acid and *p*-nitrosulfonyl chlorides as the model substrates (Scheme 4.2) and it was found to have a maximum of 65% yield of cross-biphenyls in presence of Pd NPs and methanol within 24 h (Table 4.1).



Scheme 4.2: Model reaction for the synthesis of cross biphenyls

Table 4.1: Hetero-coupling reaction under thermal reflux condition

Entry	Catalyst	mol%	Solvent (2 mL)	Temperature (℃)	Time (h)	Yield [a,b,c] (%)
1	Ni NPs	10	Methanol	120	36	25
2	Pd NPs	2	Methanol	120	24	58
3	Pd NPs	2	Methanol	120	24	65
4	Pd NPs	2	PEG 400	120	20	62
5	Pd NPs	2	PEG 400	80	20	62
6	Pd NPs	2	PEG 400	45	36	60

Reaction condition: [a]Arylboronic acid (1 mmol), [a]Arylsulfonyl acid (1 mmol), Pd NPs (1 mol%), K_2CO_3 (1.5 eqv.), [b]Isolated yield, [c]All the compounds are characterized by ^1H and ^{13}C NMR spectroscopy.

Thermal reflux method was followed for other solvents like PEG (table 4.1, entries 4-6), but yield was still poor. Then, optimization of reaction conditions under MWI has been carried out taking same amount of catalyst. Initially, phenylboronic acid and 4-nitro-benzenesulfonyl chlorides were selected as model substrates (Scheme 4.2) with variation of solvent as well as base with the aim of optimizing the yield and the results are summarized in Table 4.2.

Table 4.2: Optimization of the reaction condition for microwave oven power, time and base

Entry	Catalyst (2 mol%)	Solvent (2 mL)	Base (1.5 eqv.)	Power of Microwave oven (W)	Time (min)	Yield[a,b,c] (%)
1	Ni NPs	Water	K_2CO_3	800	5	0
2	Ni NPs	Ethanol	K_2CO_3	800	5	0
3	Ni NPs	PEG400	K_2CO_3	800	5	15
4	Ni NPs	PEG200	K_2CO_3	800	5	10
5	Pd NPs	PEG400	Nil	800	5	20
6	Pd NPs	PEG400	K_2CO_3	800	5	94
7	Pd NPs	PEG400	Cs_2CO_3	800	5	97
8	Pd NPs	PEG400	Na_2CO_3	800	5	76
9	Pd NPs	PEG300	K_2CO_3	800	5	62
10	Pd NPs	PEG200	K_2CO_3	800	5	55
11	Pd NPs	PEG400	K_2CO_3	640	5	92
12	Pd NPs	PEG400	Cs_2CO_3	640	5	95
13	Pd NPs	PEG400	Na_2CO_3	640	5	80
14	Pd NPs	PEG400	K_2CO_3	480	5	65
15	Pd NPs	PEG400	Cs_2CO_3	480	5	72
16	Pd NPs	PEG400	Na_2CO_3	480	5	58
17	Pd NPs	PEG400	K_2CO_3	640	1	27
18	Pd NPs	PEG400	K_2CO_3	640	2	53
19	Pd NPs	PEG400	K_2CO_3	640	3	78
20	Pd NPs	PEG400	K_2CO_3	640	4	86
21	**Pd NPs**	**PEG400**	**K_2CO_3**	**640**	**5**	**92**
22	Pd NPs	PEG400	K_2CO_3	640	6	92
23	Pd NPs	PEG400	K_2CO_3	640	7	92
24	Pd NPs	PEG400	K_2CO_3	640	10	93
25	Pd NPs	PEG400	K_2CO_3	640	20	94

Reaction condition: [a]Arylboronic acid (1.5 mmol), [a]Arylsulfonyl chloride (1 mmol) [b]Isolated yield, [c]All the compounds are characterized by ^1H and ^{13}C NMR spectroscopy.

The reaction has been performed in presence of various alkaline compounds like K_2CO_3, Cs_2CO_3, Na_2CO_3 etc. as well as absence of base. Firstly, we have performed the above reaction in presence of Ni NPs catalyst varying solvents like water, ethanol, PEG 400 & PEG 200. Maximum 15% of cross biphenyls were found in presence of PEG 400 under MWI (800 W). Then the synthesis of cross biphenyls has been carried out in presence of *in-situ* generated Pd NPs catalyst varying microwave power and solvent (Table 4.2). Very less amount of product was found in the absence of a base (Table 4.2, entry 5). The yield of the cross biphenyls was found to increase in case of potassium carbonate base. Keeping K_2CO_3 fixed, microwave power was varied and optimum result was found at 640 W. Therefore, subsequently, all the reactions were conducted under MWI (640 W) in air. Again, the reaction was subjected to time variation in presence of K_2CO_3 and PEGs in order to get optimized reaction condition. Maximum of 92% product was found in presence of K_2CO_3, and *in-situ* generated Pd NPs catalyst within 5 mins (Table 4.2, entry 21). The reaction is one of the examples of ***I****n-situ* generated **N**anoparticle-catalyzed **O**rganic **S**ynthesis **E**nhancement (***i*-NOSE**) approach. Based on this observations, finally, we have chosen PEG-400 as solvent cum size capping agent for the formation of Pd NPs. The reaction was performed varying different alkaline bases in methanol solvent at room temperature and yield of the biphenyls was found to increase in K_2CO_3.

The biphenyls yield was also found to increase rapidly with an increase in the amount of catalyst. Pd or nano catalyst was taken in mol% and it was found that as the amount of catalyst was increased to 1.5 mol% (Table 4.3, entry 2), biphenyl formation was optimum and further addition of the catalyst had no significant effect on the yield (Table 4.3, entry 1).

The reaction has been performed in presence of PVA (poly vinyl acetate) in order to find the better solvent cum capping agent. From Table 4.3, it is clear that PEG-400 is better solvent compared to PVA. Thus, synthesis of cross biphenyls was performed via coupling of arylboronic acid and benzenesulfonyl chlorides in presence of *in-situ* generated Pd NPs catalyst under air for 5 mins at 640 W. It has also been observed that Pd NPs were very efficient to catalyze cross coupling of arylboronic acid with arylsulfonyl chlorides probably due to their higher surface area compared to their bulk counterpart.

Table 4.3: Optimization of reaction condition for the catalyst, base and solvent

Entry	Catalyst	Catalyst (mol%)	Solvent (2 mL)	Base (1.5 eqv.)	Time (min)	Yield[a,b,c] (%)
1.	Pd NPs	2	PEG	K_2CO_3	5	93
2.	**Pd NPs**	**1.5**	**PEG**	**K_2CO_3**	**5**	**92**
3.	Pd NPs	1.0	PEG	K_2CO_3	5	67
4.	Pd NPs	0.5	PEG	K_2CO_3	5	48
5.	Pd NPs	2.0	PVA	K_2CO_3	5	64
6.	**Pd NPs**	**1.5**	**PVA**	**K_2CO_3**	**5**	**55**
7.	Pd NPs	1.0	PVA	K_2CO_3	5	45
8.	Pd NPs	0.5	PVA	K_2CO_3	5	26

Reaction condition: [a]Arylboronic acid (1.5 mmol) and Arylsulfonyl chloride (1 mmol), [b]Isolated yield, [c]All the compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy.

It was also observed that bulk Pd was able to produce cross-biphenyls with poor yield (Figure 4.5). Whenever, bulk Pd was used more than 10 times of nano Pd, the cross biphenyls yield remained poor compared to NPs-catalyzed products. It is noteworthy to mention that NPs have various unique properties which can be purposefully used in many spheres of practical application.

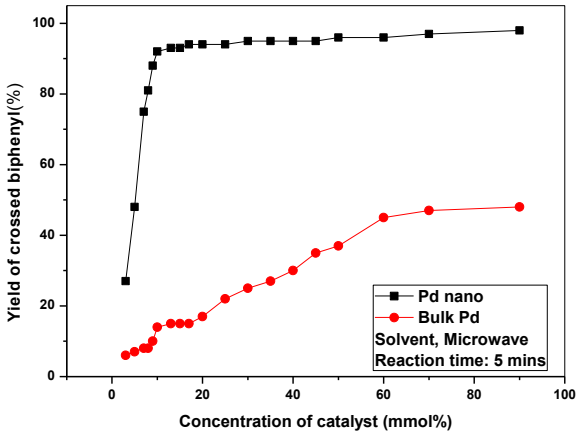
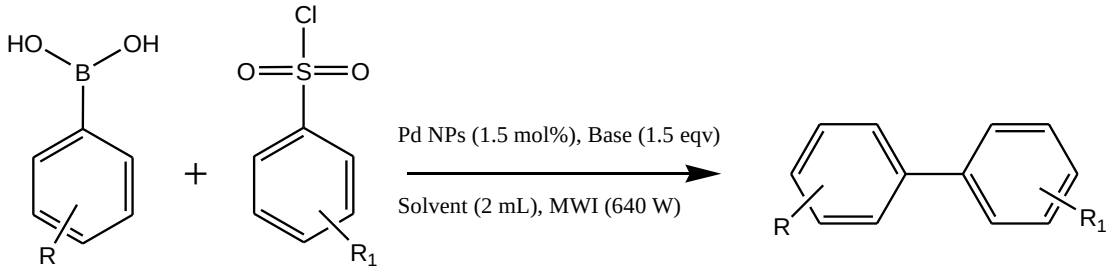


Figure 4.5: Comparison of catalytic performance of Pd NPs *vs* bulk Pd counterpart

Having defined the optimized reaction conditions, we investigated the scope of the Pd NPs catalyzed cross coupling reaction between arylboronic acids and

arylsulfonyl chlorides (Scheme 4.3) incorporating diversely substituted phenylboronic acid and substituted sulfonylchlorides has been represented in Table 4.4.



Scheme 4.3: General representative scheme for synthesis of cross biphenyls

Table 4.4: Pd NPs catalysed aerobic cross-coupling reaction of Aryl boronic acids

Entry	R	R_1	Products	Yield[a,b,c] (%)
1	H	H	Biphenyl	92
2	2-CH_3	H	2-Methylbiphenyl	84
3	3-CH_3	H	3-Methylbiphenyl	88
4	4-CH_3	H	4-Methylbiphenyl	85
5	4-CH_3-CH_2-	H	4-Ethylbiphenyl	87
6	2,4-difluoro	H	2,4-Difluorobiphenyl	90
7	4-fluoro	4-fluoro	4,4´-Difluorobiphenyl	91
8	3-NH_2	H	4-Aminobiphenyl	90
9	4-CN	H	4-Cyanobiphenyl	89
10	4-CHO	H	4-Formylbiphenyl	89
11	4-OCH_3	H	4-Methoxybiphenyl	87
12	4-OCH_3	2-CH_3	4-Methoxy-2´-methylbiphenyl	85
13	4-OCH_3	3-CH_3	4-Methoxy-3´-methylbiphenyl	86
14	4-OCH_3	4-OCH_3	4,4´-Dimethoxybiphenyl	85
15	4-OCH_3	4-CHO	4-Formyl-4´-methoxybiphenyl	86
16	H	4-NO_2	4-Nitrobiphenyl	92
17	4-OCH_3	4-NO_2	4-Methoxy-4´-nitrobiphenyl	88
18	4-*tert*-butyl	4-NO_2	4-*tert*-butyl-4´-nitrobiphenyl	89

Reaction condition: [a]Arylboronic acid (1.5 mmol), Arylsulfonyl acid (1 mmol), Pd NPs (1.5 mol%), K_2CO_3 (1.5 eqv.), PEG (2 ml), MWI, [b]Isolated yield, [c]All the compounds are characterized by ^1H and ^{13}C NMR spectroscopy.

As evident from Table 4.4, most of the phenylboronic acids with a variety of substituents and substituted benzenesulfonyl chlorides gave the products in good to

excellent yields under the optimum reaction conditions. Phenylboronic acids/arylsulfonyl chlorides having electron-withdrawing groups like nitro, cyano, fluoro, diifluoro, and formyl groups gave corresponding cross-coupling products in good yields (88–92%, Table 4.4, Entries 6-10 and 16–18).

Phenylboronic acids/arylsulfonyl chlorides bearing methyl, ethyl, *tert*-butyl, methoxy etc. groups provided desired products in 84–88% yields (Table 4, Entries 2–5 and 11-15). It was observed that arylboronic acid bearing bulky methoxypyridine group was reluctant to undergo cross-coupling reaction. Careful inspection of the results revealed that *para*- and *meta*-substituted arylboronic acids give biaryls in good to excellent yields. Lower yield of crossed biphenyls was obtained for *o*-substituted arylboronic acids which may be attributed to steric effects. As for example, the reaction of *p*-methoxyphenyl boronic acid and *p*-methoxyphenyl sulfonylchlorides, isolated yield of the desired product 4,4'-dimethoxybiphenyl was in 85% (Table 4.4, Entry 14), demonstrating good selectivity.

4.2.3 Sheldon Test

The Sheldon test[42] was performed to ensure whether synthesis of cross-biphenyls catalyzed by Pd NPs was truly heterogeneous or some Pd leached out to the filtrate. The reaction was carried out under the optimized conditions and the palladium NPs catalyst was filtered from the reaction mixture at ~53% of cross biphenyls formation (Table 4.5).

Table 4.5: Sheldon test

Catalyst	Time (mins)	Yield (%)	Time (mins)	Yield[a,b,c] (%)
Pd NPs	0.5	17	-	-
Pd NPs	1	25	-	-
Pd NPs	2	53	(53 + 360) =413	53
Pd NPs	3	77	-	-
Pd NPs	4	84	-	-
Pd NPs	5	92	-	-

Reaction condition: [a]Arylboronic acid (1.5 mmol), Arylsulfonyl acid (1 mmol), Pd NPs (1.5 mol%), K_2CO_3 (1.5 eqv.), PEG (2 mL), MWI, [b]Isolated yield, [c]All the compounds were characterized by ^1H and ^{13}C NMR spectroscopy.

After removal of Pd catalyst, the filtrate was further subjected to reaction condition for an additional 6 h and no further biphenyls product was found. The absence of metal leaching was also confirmed from atomic absorption spectroscopy

analysis of the filtrate from the reaction mixture and also of the filtrate from a stirred solution of Pd in water under identical reaction conditions. Thus, the atomic absorption spectroscopic data clearly demonstrated that Pd was truly heterogeneous in nature.

4.2.4. Reusability of catalyst

Reusability of the Pd NPs catalyst was investigated for real application of synthesized products (Cross biphenyls). After completion of the reaction, the catalyst was recovered by filtration and washed with ethyl acetate & dry ethanol. After washing, catalyst was heated at 120 °C for 2 h and activated under vacuum at room temperature. The material was reused for the subsequent cycles and the results are presented in Figure 4.6.

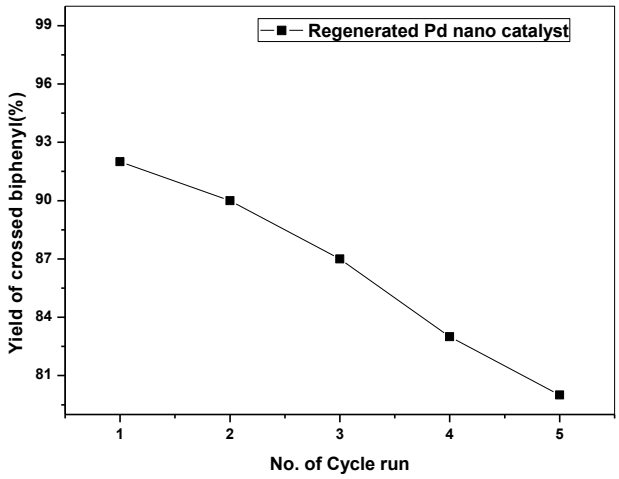


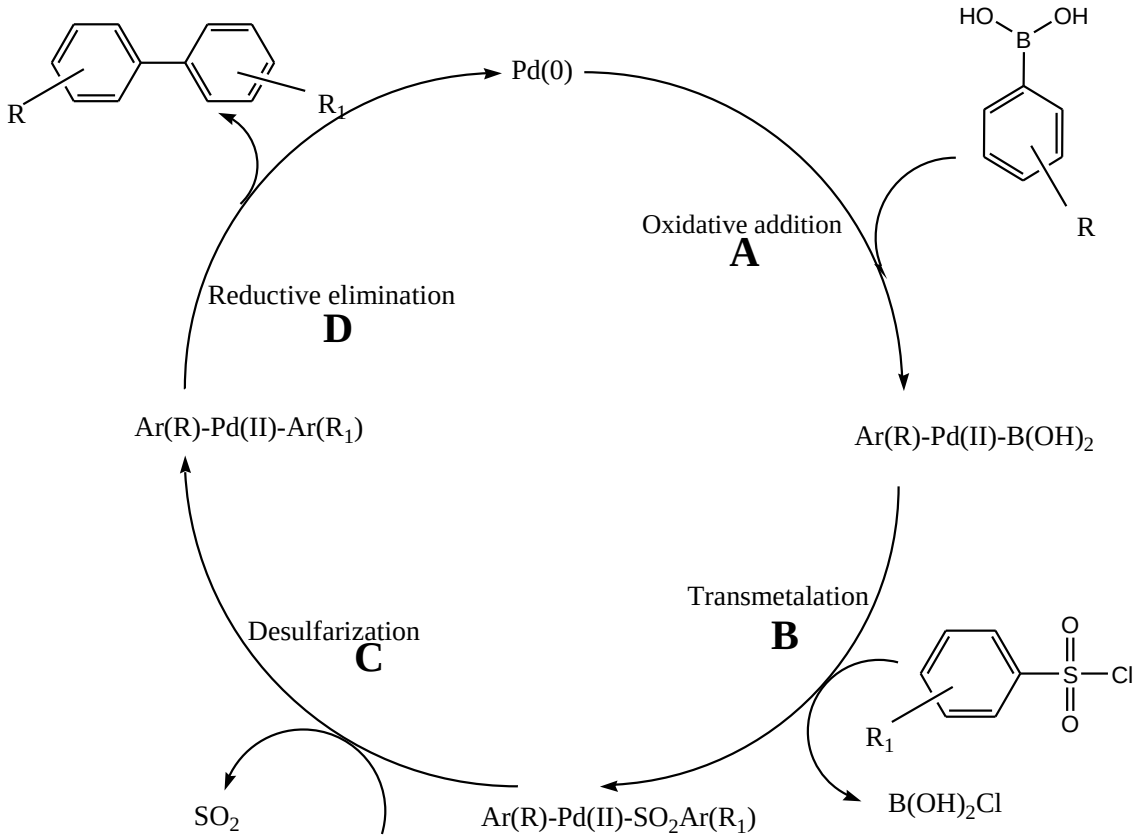
Figure 4.6: Reusability of Pd NPs catalyst

It was observed that cross-biphenyls formed with a minor loss of product yield even after five times of catalyst reuse. To demonstrate the potential utility of this method for preparative purposes, the reaction was also carried out under the optimized reaction conditions on 7.95 g scale (0.1 mol), giving 90% yield which are comparable to those obtained for a small scale reaction.

4.2.5. Plausible mechanism

The mechanism of the palladium-catalyzed cross-coupling reaction is not obvious at the present stage. Here, we have proposed a probable mechanism based on

predicted mechanism reported by some other researchers.[43] The following observations may be useful to predict the mechanism: (1) Pd is catalytically active in the cross-coupling, (2) air is critical to the reaction, (3) the negative counterpart plays an important role and (4) *trans*-metalation due to presence of boronic acid. On the basis of these observations and the proposed mechanisms in the literature,[41] possible catalytic cycle is depicted in Scheme 4.4.



Scheme 4.4: Probable mechanism of cross-coupling reaction

During the cross-coupling reaction, in the first step, Pd(0) forms complex with arylboronic acid *via* oxidative addition. Then, it undergoes trans-metalation reaction to form palladium-arylsulfonyl intermediates eliminating boronic acid complexes. Finally, it undergoes desulfurization followed by reductive elimination to give the desired cross-biphenyls and Pd(0) catalyst is regenerated. The catalyst again takes part in the reaction and complete cycles are repeated for continuous formation of desired product.

4.3 Conclusions

In conclusion, we have successfully developed microwave assisted synthesis of cross-biphenyls using arylsulfonyl chlorides and phenylboronic acid as well as desulfurization of sulfonyl derivatives. By using MWI technology, we have reduced the reaction time as well as unnecessary heating/thermal refluxing. *In-situ* generated Pd NPs are able to transform arylboronic acid and arylsulfonyl chlorides to un-symmetrical biaryls which is an example of *i*-**NOSE** approach. The cross-coupling reaction proceeds in economical, cheapest and easily available solvent under extremely mild conditions: in presence of air, very mild base and MWI. The synthesized Pd NPs remain in same condition even after performing the catalytic reaction. The catalyst is efficient, easily recoverable and reusable more than four times without losing its activity. This work reveals a new cheap and fast procedure to synthesize un-symmetrical biaryls in a relatively environmentally friendly manner. The good selectivity of cross-coupling over the Suzuki cross-coupling reaction shows potential application in synthesis of biphenyls.

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