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Microwave assisted and *in-situ* generated palladium nanoparticles catalysed desulfitative synthesis of cross-biphenyls from arylsulfonyl chlorides and phenylboronic acids

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ABSTRACT

A microwave assisted reaction protocol for Suzuki–Miyaura cross-coupling has been developed. Substituted arylboronic acids and arylsulfonyl chlorides coupled under microwave irradiation (MWI) to produce cross-biphenyls in high yields under aerobic condition. The principal advantage of this protocol is that formation of cross-biphenyls was achieved within shorter time along with desulfurization of arylsulfonyl chloride. *In-situ* generated Pd nanoparticles (NPs) act as catalyst in the reaction. Substituents like methyl, halogens, cyano, amino and t-butyl groups in arylboronic acids tolerate the reaction condition. Pd NPs could be reused several times under chosen reaction conditions without losing its activity significantly. The product formation and the role of the catalyst for the cross-coupling reaction has been rationalised with the help of a proposed mechanism. This reaction is one of the examples of *In-situ* generated Nanoparticles-catalyzed Organic Synthesis Enhancement (i-NOSE) approach. The approach derives its importance in terms of catalyst's (i) simple preparation method, (ii) stability under the chosen reaction condition, (iii) substrate specificity, (iv) simple filtration to recover the catalyst and (v) easy regeneracy which clearly indicate that the approach could be applicable for various types of catalytic transformations.

1. Introduction

In present scenario, biphenyls have secured its position as an important motif both in terms of academic research and industrial applications, Their importance has been demonstrated via their presence in many spheres of products of commercial and medicinal importance [1]. Further, cross-biphenyls are versatile intermediates in the synthesis of UV absorbers [2] and insecticides [3]. In recent times, synthesis of cross aryl derivatives has been achieved through carbon-hetero atom activation of selective compounds assisted by metal catalyst. Commonly, such cross-coupling reactions involve the catalyst of choice, palladium [4–10]. However, use of other transition metals like ruthenium etc. is also there in the literature [11-23]. In most cases, the Suzuki-Miyaura coupling reaction is adopted in order to synthesize biphenyls due to its simplicity and versatility. In line with this strategy, we applied Suzuki-Miyaura cross-coupling reaction to afford cross-biphenyls using arylboronic acid and arylsulfonyl chlorides in order to minimise the formation of biphenyls through homocoupling reaction. Traditionally, both aromatic and alkyl halides serve as excellent substrates to give access to cross-coupling products. However, these traditional substrates could be replaced by benzoic acids [24-26]. Of late, arylboronic acids [27,28] and aryl tosylates [28] have also been reported as excellent substrates for such type of reactions. Among them, one of the most promising and convenient alternatives is certainly substituted or unsubstituted $ArSO_2R$ derivatives, like $ArSO_2Na$ or $ArSO_2Cl$. Easy preparative methods, inexpensiveness, convenience handling to users associated with most of such members provide extra edge. Simple chlorination of sulfonic acids or sulfur containing substrates [29-33] afford $ArSO_2Cl$ derivatives. Alternatively, upon reduction, these chlorinated products yield $ArSO_2Na$ [34]. Occasionally, these coupling

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substrates during the reaction, opens up another door to yield regioisomers, which is an added advantage.

In a nutshell, these halogenated $ArSO_2R$ derivatives serve as attractive starting compounds for providing biaryls through breaking the C-S bond without affecting the substituents allowing further synthetic manipulations. Moreover, arylsulfonyl chlorides are very good desulfitative arylation reagents in biaryl synthesis [35].

Alternative strategies to produce cross-biphenyls involve use of harsh conditions like heating at more than 100 °C in presence of a strong base (e.g. KOH) for at least 20 h [34]. Vogel *et al.* [36] synthesized cross-biphenyls using palladium catalyst, Pd_2dba_3 (1.5 mol%) in the presence of a ligand (6 mol%) and Na_2CO_3, under refluxing condition for 35 h in THF (Scheme 1). Therefore, as a viable alternative, we tried to minimize the reaction time using aryl boronic acid, arylsulfonyl chlorides, a mild base and Pd NPs under MWI.

In our approach, we describe the synthesis of cross-biphenyls exploiting $Pd(OAc)_2$ as catalyst under MWI and ligand free condition. Notably, here, Pd NPs are the active catalysts, which are generated *in-situ*, took part in the reaction instead of bulk Pd, and resulted in an enhancement of the reaction in comparison to the bulk Pd. Instead of using some Pd complexes [36], the application of *in-situ* generated Pd NPs greatly enhanced the reaction with lower cost and less hazardous condition. Palladium salt was used together with reactants/starting materials and base in solvent. Pd NPs were generated *in-situ*, i.e. Pd(II) got converted to nano-Pd(0) under the reaction condition. Since, conventional catalysts are associated with drawbacks such as requirement of excess amount and potent polluter reagents, so, heterogeneously catalyzed methods are more preferable to carry out the reaction involving inexpensive, user friendly and non-polluting/less-polluting reagents. Therefore, there is a constant urge in this regard that set the focus of our work by unravelling the suitability of methods (MWI, weak base and less hazardous chemicals) which are environmentally friendly in the synthesis of biaryls. Accordingly, in line with these points, we pinpointed to develop cross-coupling reaction of arylboronic acid and arylsulfonyl chlorides in presence of *in-situ* generated Pd catalyst in polyethylene glycol (PEG) under MWI. There are earlier reports that introduced the synthesis of biaryls under MWI [37]. However; in those cases, larger amounts of chemicals and longer reaction times were required. Previously, Jiang et al. successfully utilized aryl fluorosulfates in Suzuki reaction in presence of Pd catalyst, the greenest solvent, water and strong base triethyl amine, that too under ligand free condition. Still, the reaction time was at least 2 h [38]. According to that report, cross-coupling reaction to cross-biphenyls yielded only 27–30% in presence of bases like K_2CO_3, Na_2CO_3 and Cs_2CO_3. On the contrary, in our protocol, 92% yield of biphenyl was achieved in presence of K_2CO_3 under MWI within 5 min. Few reports on Pd NPs catalysed Suzuki–Miyaura coupling reactions are available [39,40]. But, the reports did not emphasis on desulfurization. Here, in short, our effort lies in making the reaction greener by reducing the reaction time and temperature using catalyst, which is either non-polluting or less polluting. In fact, this is the need of the hour.

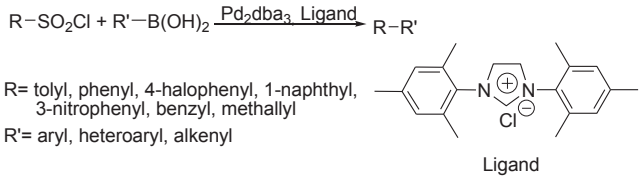
2. Results and discussion

Techniques and instrumentation like X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), particle size analyser, Scanning Electron Microscopy (SEM), EDAX and XPS were used for the characterization of *in-situ* generated Pd NPs. XRD profile (Fig. 1) recorded in the 2θ range of 20° to 70° of the synthesized Pd NPs supports the presence of the different characteristics peaks that could be indexed on the basis of JCPDS card no. 050681. This indexing confirmed that the material was face centered cubic (fcc) Pd. TEM (Fig. 2) shows that the Pd NPs formed are within ~ 45 to 55 nm diameter.

The approx. particle size (from particle size analyzer) lies within 50 to 70 nm (Fig. 3). The particle size indicated by this method was somewhat bigger compared to that obtained from TEM due to the agglomeration of individual Pd NPs. It clearly reveals lattice picture with approx. distance between two planes. Notably, in this case, PEG acts as a capping agent, which facilitates the one dimensional growth of Pd NPs. The surface morphologies of Pd NPs before and after the reaction were also studied by SEM (Figs. 4a and 4b). It is clear that the sharp crystals of Pd became rough upon the reaction, probably due to reaction happening on the surface.

The electronic state of the Pd catalyst was probed by high resolution XPS (X-ray photoelectron spectroscopy). XPS data of the Pd 3d core were taken with two samples of Pd catalyst: one before the reaction [Fig. 5(a)] and another after the first reaction cycle [Fig. 5(b)]. It was impossible to measure O 1 s line due to overlapping of this line with very intensive Pd 3p 3/2 photoelectron peak. There is no principal difference in Pd 3d spectra of the fresh catalyst and recovered catalyst and confirms that both Pd(II) and Pd(0) species are present. Binding energy (BE) values of 335.3 and 335.9 eV are consistent with that of Pd(0) and the BE values of 336.9 and 338.7 indicate the presence of the Pd(+2) states [41]. The surface layer of both samples consists of surface PdO (most probably), interface between PdO and metallic Pd. Fresh catalyst seems to have more PdO at the surface [Fig. 5(a)] than the recovered catalyst [Fig. 5 (b)]. However, the interface PdO/Pd(0) seems to be "thinner" in the case of fresh catalyst. Appearance of an oxide layer above the Pd NPs surface indicates the tendency toward oxidation [41]. This is also obvious as the reaction was carried out under aerobic condition. Similarity in XPS data (Pd 3d spectra) and differences in SEM images can be caused by: (a) dispersion of 1-D Pd NPs during reaction, or/and (b) "amorphization" of Pd NPs surface.

The *in-situ* generated Pd NPs were found to be efficient and heterogeneous, reusable catalyst in cross-coupling reaction of arylboronic acids and benzene sulfonyl chlorides under MWI. First of all, thermal reflux condition was imposed to perform the reaction in various solvents and temperature. It was observed that the maximum of 65% crossed biphenyl formed in methanol within 24 h (Table 1). Thermal reflux conditions were also tried in other solvents like PEG, but yield was still



Scheme 1. Suzuki-Miyaura cross-coupling reaction between substituted sulfonyl chlorides and boronic acids.

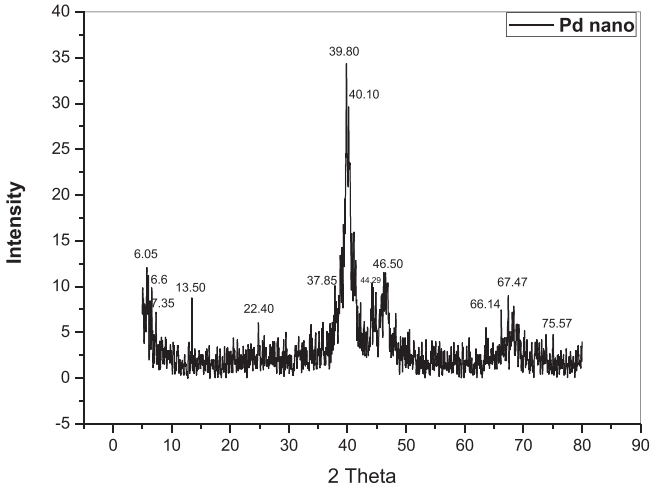


Fig. 1. Powder XRD pattern of fresh Pd NPs catalyst.

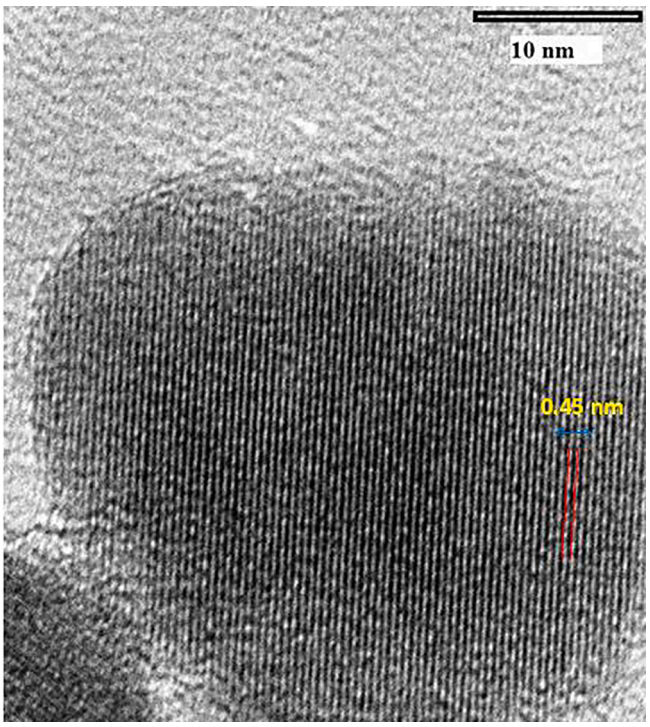


Fig. 2. HRTEM of synthesised Pd NPs catalyst.

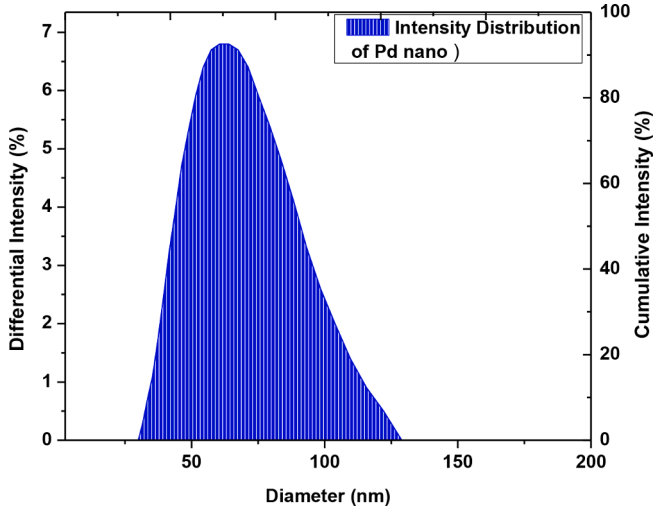


Fig. 3. Particle size distribution of Pd NPs.

poor. In the next approach, optimization of reaction conditions was attempted under MWI with identical catalyst concentration. Initially, phenylboronic acid and 4-nitrobenzenesulfonyl chlorides were selected as model substrates and a screening of solvent as well as base. Table 2 shows the summarized results. The effect of presence of various bases like K_2CO_3, Cs_2CO_3, Na_2CO_3 etc. as well as absence of a base in the reaction was also monitored. At first, we performed the above reaction in presence of Ni nano catalyst in different solvents like water, ethanol, PEG 400 & PEG 200. A maximum 15% of crossed biphenyl was observed in PEG 400 under 800 W of MWI. In the next trial, synthesis of crossed biphenyl was carried out over the *in-situ* generated Pd nano catalyst under various MW power and solvents (Table 2). In the absence of a base (Table 2, entry 5), formation of only a minor amount of the product was observed. Interestingly, compared to other bases, in the presence of K_2CO_3 base, the yield of the product was found to increase. Variation of

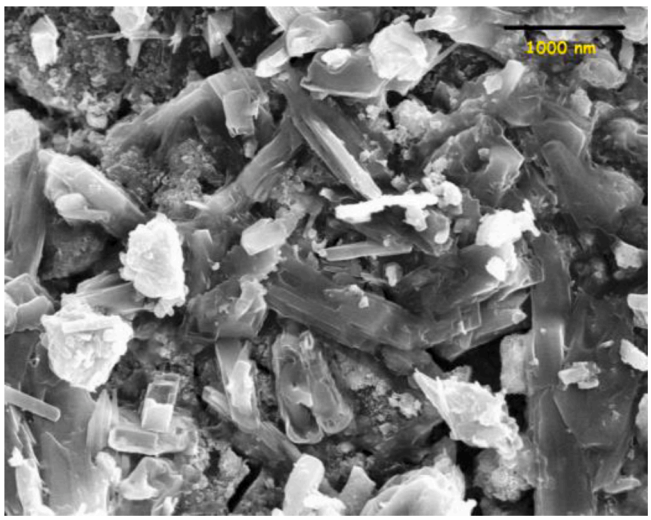


Fig. 4a. SEM of Pd NPs before reaction.

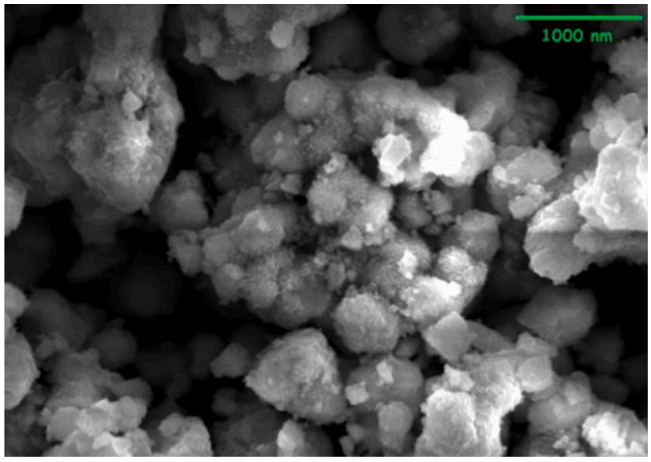


Fig. 4b. SEM of Pd NPs after reaction.

product yield with amount of base and solvent is given in the supplementary information.

At first, we performed the above reaction in presence of Ni nanocatalyst in different solvents like water, ethanol, PEG 400 & PEG 200. A maximum 15% of crossed biphenyl was observed in PEG 400 under 800 W of MWI. In the next trial, synthesis of crossed biphenyl was carried out over the *in-situ* generated Pd nanocatalyst under various microwave power and solvent (Table 2). In the absence of a base (Table 2, entry 5), formation of only a minor amount of the product was observed. Interestingly, compared to other bases, in the presence of K_2CO_3 base, the yield of the product of cross-biphenyl was found to increase.

As a result, K_2CO_3 was selected as the base of choice and MW power was varied. It was found that 640 W gave the best results. As a consequence, all consecutive experiments were conducted under MWI at 640 Watt in air. Again, different reaction times were investigated in the presence of K_2CO_3 and PEG in order to pin-point the optimized reaction condition. The maximum of 92% was obtained in presence of K_2CO_3 over *in-situ* generated Pd within 5 min (Table 2, entry 21).

As mentioned earlier, this represents one example of ***I-situ*** generated **N**anoparticle-catalyzed **O**rganic **S**ynthesis **E**nhancement (*i*-NOSE) approach. PEG 400 was used both as solvent as well as a size-capping agent upon formation of Pd NPs. A screening of different alkaline bases showed that K_2CO_3 was the preferred base as we observed highest yield of biphenyl in the presence of K_2CO_3. In fact, it was found that as

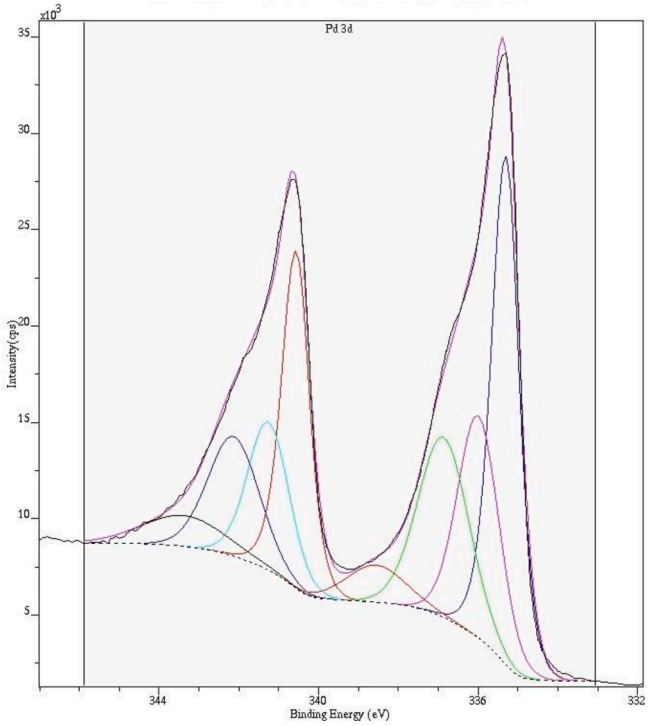


Fig. 5a. XPS spectra of the Pd catalyst (3d core) before the reaction.

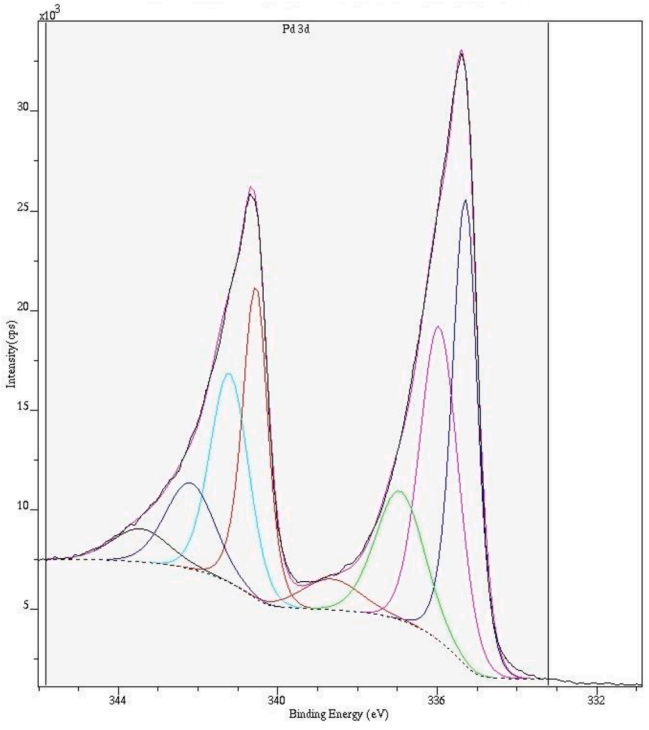
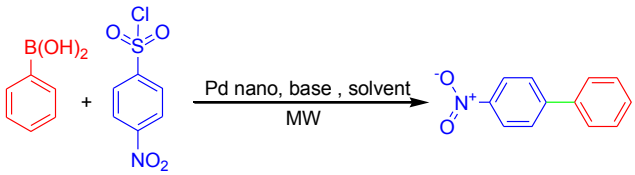


Fig. 5b. XPS spectra of the Pd catalyst (3d core) after the 1st cycle.

the amount of catalyst was increased to 2 mol%, the highest biphenyl yield was obtained. Any further increase in the catalyst concentration led to only marginal yield increase (Table 3). We also tried to carry out the reaction in the presence of PVA (poly vinyl alcohol) upon search for a better solvent and capping agent. As reported in table 3, it is clear that PEG 400 was a better solvent compared to PVA. Therefore, synthesis of cross-biphenyl was performed via coupling of arylboronic acid and benzenesulfonyl chlorides in presence of *in-situ* generated Pd NPs under air for 5 mins at 640 Watt of MWI. It was also observed that Pd NPs were very efficient in the reaction probably due to increased surface area relative to the bulk Pd.

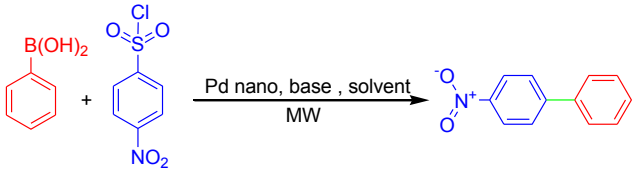
Table 1
Reaction under thermalreflux condition.[a]



Entry	Catalyst	Amount (mol%)	Solvent (2 mL)	Temperature (°C)	Time (h)	Yield[] (%)[b]
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

[a]*Reaction condition*: Arylboronic acid (1 mmol), arylsulfonyl acid (1 mmol), Pd NPs (1 mol%), K_2CO_3 (1.5 eqv.), [b]Isolated yield, [c]Characterization of all the compounds were performed by ^1H and ^{13}C NMR spectroscopy.

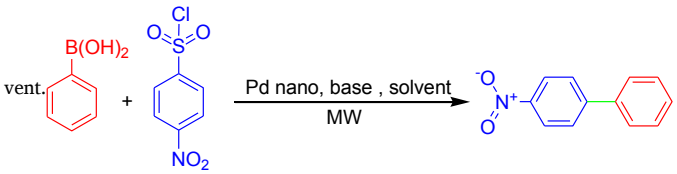
Table 2
Optimization of the reaction condition[a] in terms of MW power, reaction time and base of choice.



Entry	Catalyst (2 mol%)	Solvent (2 mL)	Base (1.5 eqv.)	MW power (Watt)	Time (min)	Yield (%)[b,c]
	Ni NPs	Water	K_2CO_3	800	5	0
	Ni NPs	Ethanol	K_2CO_3	800	5	0
	Ni NPs	PEG 400	K_2CO_3	800	5	15
	Ni NPs	PEG 200	K_2CO_3	800	5	10
	Pd NPs	PEG 400	Nil	800	5	20
	Pd NPs	PEG 400	K_2CO_3	800	5	94
	Pd NPs	PEG 400	Cs_2CO_3	800	5	97
	Pd NPs	PEG 400	Na_2CO_3	800	5	76
	Pd NPs	PEG 300	K_2CO_3	800	5	62
	Pd NPs	PEG 200	K_2CO_3	800	5	55
	Pd NPs	PEG 400	K_2CO_3	640	5	92
	Pd NPs	PEG 400	Cs_2CO_3	640	5	95
	Pd NPs	PEG 400	Na_2CO_3	640	5	80
	Pd NPs	PEG 400	K_2CO_3	480	5	65
	Pd NPs	PEG 400	Cs_2CO_3	480	5	72
	Pd NPs	PEG 400	Na_2CO_3	480	5	58
	Pd NPs	PEG 400	K_2CO_3	640	1	27
	Pd NPs	PEG 400	K_2CO_3	640	2	53
	Pd NPs	PEG 400	K_2CO_3	640	3	78
	Pd NPs	PEG 400	K_2CO_3	640	4	86
	Pd NPs	**PEG 400**	**K_2CO_3**	**640**	**5**	**92**
	Pd NPs	PEG 400	K_2CO_3	640	6	92
	Pd NPs	PEG 400	K_2CO_3	640	7	92
	Pd NPs	PEG 400	K_2CO_3	640	10	93
	Pd NPs	PEG 400	K_2CO_3	640	20	94

[a] *Reaction condition*: Arylboronic acid (1.5 mmol), arylsulfonyl chloride (1 mmol).
[b] Isolated yield.
[c] Characterisation of all the compounds were performed by ^1H and ^{13}C NMR spectroscopy.

Table 3
Optimization of reaction condition[a] in terms of the catalyst, base and solvent.



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

[a]*Reaction condition*: K_2CO_3 (1.5 eqv.), arylboronic acid (1.5 mmol), arylsulfonyl chloride (1 mmol), PEG 400 (2 mL), [b]Isolated yield, [c]Characterisation of all the compounds were performed by ^1H and ^{13}C NMR spectroscopy.

Moreover, in case of bulk Pd, cross-biphenyls were obtained in poor yields (Fig. 6).

The versatility and generality of the synthesis strategy were investigated after pin-pointing of the optimized reaction conditions. As evident upon looking at Table 4, good to excellent yields of the products were obtained with differently substituted majority of the arylboronic acids and benzenesulfonyl chlorides (Table 4). Phenylboronic acids/arylsulfonyl chlorides that contain electron-withdrawing groups afforded cross-coupling products in good to excellent yields (88–92%; Table 4, entries 6–10 and 16–18). Nonetheless, electron donating groups attached phenylboronic acids/arylsulfonyl chlorides also afforded good yields (84–88%) of the desired products (Table 4, entries 2–5 and 11–15). However, bulky methoxypyridine group attached arylboronic acid was reluctant to undergo cross-coupling reaction. After carefully inspecting the results, we observed good to excellent yields of the products for arylboronic acids having diverse substituents both at *meta*- and *para*-positions. Steric effect might be responsible for the lower yields of products in case of *ortho*-substituted arylboronic acids. Good selectivity of the products were observed for *p*-methoxyphenyl boronic acid and *p*-methoxyphenylsulfonyl chlorides (85% isolated yield, Table 4, entry 14).

Sheldon Test

The Sheldon test [42] was performed to ensure whether synthesis of cross-biphenyl catalyzed by Pd was truly heterogeneous or some Pd was leaching out to the filtrate. For that, when the reaction (Table 5) was ~ 53% complete, the reaction mixture was subjected to filtration to separate out and collect the Pd catalyst. The filtrate so collected was subjected to the same reaction condition but, this time in absence of Pd catalyst. After continuing the reaction for another 6 h we ended up with no indication of formation of any product. The filtrate of the reaction mixture and the filtrate of Pd solution in water were analyzed for any metal impurity that might be present with atomic absorption spectroscopy. These experiments confirmed that there was no metal leaching out in to the filtrate which in turn clearly supported the hypothesis of heterogeneously catalyzed reaction.Table 6.

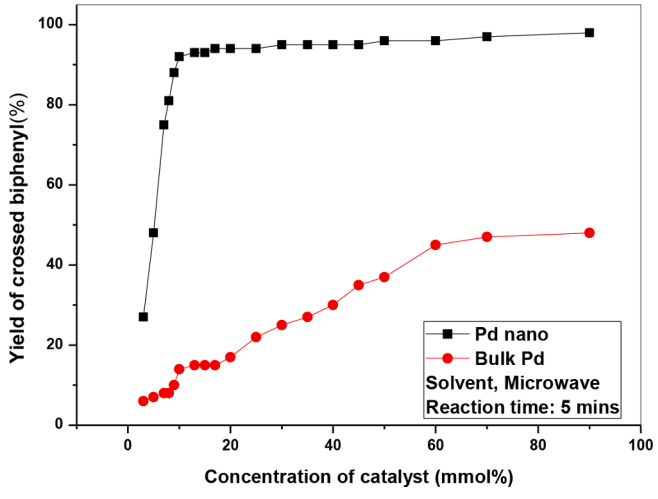


Fig. 6. Comparison of the performances of Pd NPs *vs* bulk Pd counterpart.

Table 4
Pd NPs catalysed cross-coupling reaction of arylboronic acids and arylsulfonyl chloride under aerobic condition.[a]

Entry	R	R_1	Products	Yield (%)[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	4,4́-difluorobiphenyl	91
8	3-NH_2	H	3-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-2́-methylbiphenyl	85
13	4-OCH_3	3-CH_3	4-methoxy-3́-methylbiphenyl	86
14	4-OCH_3	4-OCH_3	4,4́-Dimethoxybiphenyl	85
15	4-OCH_3	4-CHO	4-formyl-4́-methoxybiphenyl	86
16	H	4-NO_2	4-Nitrobiphenyl	92
17	4-OCH_3	4-NO_2	4-Methoxy-4́-nitrobiphenyl	88
18	4-*tert*-butyl	4-NO_2	4-*tert*-butyl-4́-nitrobiphenyl	89

[a]*Reaction condition*: Arylboronic acid (1.5 mmol), arylsulfonyl chloride (1 mmol), Pd NPs (1.5 mol%), K_2CO_3 (1.5 eqv.), PEG 400 (2 mL), MWI. [b]Isolated yield, [c]Characterised by ^1H and ^{13}C NMR spectroscopy.

Reusability of catalyst

At the end of reaction, filtration separated out the catalyst from the reaction medium which was then washed repeatedly with ethyl acetate & dry ethanol. Heating the washed catalyst at 120 °C for 2 h followed by room temperature drying under vacuum resulted the activated catalyst paving the way for its reuse in the next run. Fig. 7 demonstrates the result of these reusability tests. It was observed that cross-biphenyl formed with a decrease in product yield in subsequent cycles. This may be due to the agglomeration of the NPs and the release of salt byproducts during the reaction that might retard the progress of the coupling reaction [43]. Maintaining all the chosen reaction parameters and performing the reaction on 7.95 g scale (0.1 mol) afforded 90%

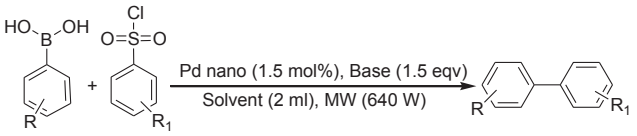
yield of the product. This yield is at par with the small scale reactions and showed that the reaction could be efficiently scaled up to a certain degree.

Table 5
Sheldon test results.[a]

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

[a]*Reaction condition*: Arylboronic acid (1.5 mmol), arylsulfonyl acid (1 mmol), Pd NPs (1.5 mol%), K_2CO_3 (1.5 eqv.), PEG 400 (2 mL), MWI. [b]Isolated yield. [c]Characterisation of all the compounds were performed by ^1H and ^{13}C NMR spectroscopy.

Table 6
Reusability of Pd NPs catalyst.



Entry	Catalyst	Cycle run	Yield (%)
1	Pd NPs	1st	92
2	Pd NPs	2nd	90
3	Pd NPs	3rd	87
4	Pd NPs	4th	83
5	Pd NPs	5th	80

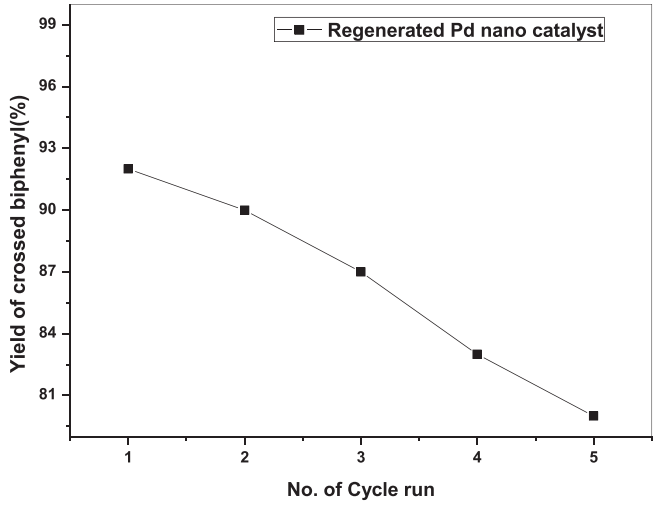


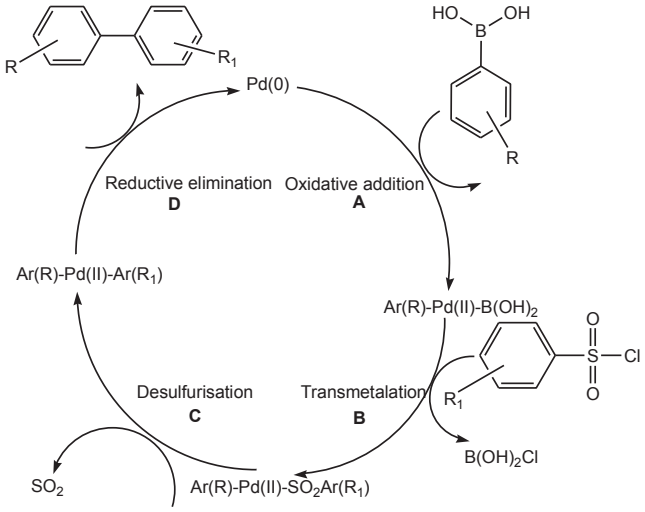
Fig. 7. Reusability of Pd NPs catalyst.

3. Comparison of methods

Our method is very much effective for aryl substrates, not found suitable for substrates having heterocycles. But, use of low amount of catalyst and microwave irradiaion are prime advantage of this work over others. As per report by other researchers, Suzuki-Miyaura cross-coupling of aryl sulfonyl chlorides and aryl trifluoroborates works with heterocyclic substrates. Heterocycles generally interact with boronic acid during course of reaction due to presence of reactive nitrogen, oxygen or other heteroatoms. Probably, this is the reason behind non-suitability of heterocyclic coupling partners for the reaction with boronic acids. A similar desulfonative reaction is the coupling of aryl trifluoroborates with arylsulfonyl chlorides catalyzed by Pd [44]. Which is effective for stronger electron donating/ withdrawing ligand and yield is poor for aryl compounds having weaker ligands and requires higher amount of Pd catalyst (5 mol%), conventional heating in solvents like DMSO, THF, Diglyme, DME, NMP and Acetonitrile. However, our methodology is applicable for common aryl compounds having weak/ moderate electron donating/withdrawing substituents, requires lesser amount of nano catalyst (1.5 mol%), microwave irradiation which is a greener mode of heating and greener solvent like PEG.

Proposed reaction mechanism

At this moment, we are not clear about how the reaction progresses. However, based on literature [38,45] and certain observations a plausible mechanism is being proposed for this cross-coupled reaction (Scheme 2). These observations are: (1) the different experiments and analyses carried out confirmed that the species which is active is the Pd (0); (2) air is very much important and plays a key role; (3) active participation of the partner carrying negative charge and (4) already well established *trans*-metalation due to presence of boronic acid. As per



Scheme 2. Probable mechanism of cross-coupling reaction.

Scheme 2, in the first step, Pd(0) forms complex with arylboronic acid via oxidative addition. Then, it undergoes transmetalation reaction that yields Pd-arylsulfonyl intermediate eliminating boronic acid complex. Finally, desulfurization and reductive elimination are responsible to afford the product, cross-biphenyl. Simultaneously, Pd(

4. Conclusions

In conclusion, we have successfully demonstrated an *in-situ* generated Pd NPs catalyzed MW assisted desulfitative synthesis of cross-biphenyls using arylsulfonyl chlorides and phenylboronic acid. Under MWI, the reaction time was significantly shortened and unnecessary heating/thermal refluxing could be avoided. This represents an example of *i*-NOSE approach for biphenyl synthesis. The reaction is greener in the sense that it occurs under aerobic condition in a solvent which is cheap and affordable. Moreover, base used is a very mild one. Suitable efficacy, recoverability, regeneration and reusability more than four times without any significant loss of activity are the strength of this catalyst. Our protocol provides an edge over conventional Suzuki cross-coupling in terms of superior selectivity and complements the existing established methods.

5. Experimental section

5.1. General information

A conical flask, other glasswares and a Microwave synthesis system from Catalyst^{TM} systems (model CAT-2R) equipped with an internal temperature probe were used in experimental set up for synthesizing the hetero-biphenyl and Pd NPs. All the chemicals and reagents were utilized as received from the manufacturers. No attempt was made to purify them. In all the experiments, water was employed which was distilled twice prior to use. Cu Kα radiation ($\lambda = 0.154$ nm) of an X-ray diffractometer was used for the analysis of phase of the Pd NPs. SEM was used to study the morphology of the NPs. The particle size of Pd NPs was measured using a TEM and size distribution of Pd NPs was carried out with a particle size analyzer. Presence of elements in the sample was determined with the help of EDX analysis. A melting point apparatus provided the melting points of all products and no correction was done to those values. ^{1}H and ^{13}C NMR spectra were recorded in both 600 and a 400 MHz spectrophotometer in $CDCl_3$. Chemical shifts (δ ppm) are reported with reference to the internal standard, tetramethylsilane (TMS, $\delta = 0.00$ ppm). The couplings between the ^{1}H nuclei are provided in the form of coupling constants (J Hertz). Progress of the reactions was

monitored by thin-layer chromatography (TLC) using aluminium sheets precoated with silica gel. Visualization of TLC plates was accomplished with UV lamp or I2 stain. Column chromatography (Stationary phase: 200–300 mesh, silica gel) was performed to separate the components from the mixture. Products were characterized with the help of ^{1}H and ^{13}C NMR spectroscopic data along with a comparision of these data with the literature one.

5.2. Synthesis procedure

A mixture of Pd (1.5 mol%), arylsulfonyl chloride (1 mmol), arylboronic acid (1.5 mmol) and potassium carbonate (1.5 eqv.) in PEG 400 (2 mL) were taken in a conical flask and whole system was investigated under microwave irradiation (MWI) for 5 min at 70 °C in air. After the reaction, the mixture was taken in a separating funnel with some amount of double distilled water and ethyl acetate. The separated organic layer was collected, concentrated under vacuum and finally silica gel column chromatography (mobile phase: ethyl acetate/hexane, 1:10) was performed to furnish the purified product.

5.3. Characterization data of the products:

Adopting the procedure described above all the following compounds was synthesized.

Biphenyl (Table 4**, entry 1)** [46]**:** Colourless solid; yield: 141.87 mg (92%); m.p. 69–70 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 7.69–7.68 (m, 4H), 7.54–7.51 (m, 4H), 7.44–7.42 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ 141.4, 128.9, 127.4, 127.3 ppm.

2-methylbiphenyl (Table 4**, entry 2)** [47]**:** Colourless oil; yield: 141.29 mg (84%); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 7.26–7.24 (m, 9H), 2.05 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 140.5, 134.7, 128.7, 128.2, 126.1, 124.4, 18.7 ppm.

3-methylbiphenyl (Table 4**, entry 3)** [47]**:** Colourless oil; yield: 148.02 mg (88%); b.p. 271 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 7.39–7.37 (m, 4H), 7.37–7.31 (m, 2H), 7.31–7.30 (m, 2H), 7.31 (m, 1H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 140.3, 137.2, 127.5, 126.9, 126.8, 123.2, 20.5 ppm.

4-methylbiphenyl (Table 4**, entry 4)** [47]**:** Colourless solid, yield: 142.97 mg (85%); m.p. 45–47 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 7.60–7.48 (m, 4H), 7.45–7.38 (m, 4H), 7.37–7.30 (m, 1H), 1.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 137.6, 132.6, 131.7, 130.3, 128.5, 128.4, 128.3, 127.5, 123.4, 89.5, 31.0 ppm.

4-ethylbiphenyl (Table 4**, entry 5)** [48]**:** Colourless solid, yield: 163.74 mg (87%); m.p. 34–35 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 7.50–7.48 (m, 4H), 7.25–7.23 (m, 5H), 2.68–2.65 (m, 2H), 1.28–1.24 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 143.1, 138.6, 128.3, 127.0, 29.8, 28.6 ppm.

2,4-difluorobiphenyl (Table 4**, entry 6)** [49]**:** Colourless solid; yield: 171.17 mg (90%); m.p. 63–66 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 7.58–7.43 (m, 6H), 7.01–6.95 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ 163.3, 161.6, 160.6, 159.0, 135.1, 131.6, 129, 128.7, 127.9, 125.5, 111.7, 104.5 ppm.

4,4′-difluorobiphenyl (Table 4**, entry 7)** [50]**:** Colourless solid; yield: 172.9 mg (91%); m.p. 89–91 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 7.50 (dd, 4H, J = 5.4 Hz), 7.13 (t, 4H, J = 8.4 Hz) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ 163.4, 161.7, 136.5, 128.7, 128.6, 115.9, 115.7 ppm.

3-aminobiphenyl (Table 4**, entry 8)** [51]**:** Colourless solid; yield: 152.29 mg (90%); m.p. 30–33 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 7.63 (d, 2H, J = 6 Hz), 7.48 (t, 2H, J = 7.8 Hz), 7.40 (t, 1H, J = 7.2 Hz), 7.29 (t, 1H, J = 7.8 Hz), 7.07 (d, 1H, J = 7.2 Hz), 6.95 (s, 1H), 6.72 (d, 1H, J = 6 Hz), 3.73 (s, broad, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ 146.8, 12.4, 141.4, 129.7, 128.7, 127.3, 127.2, 117.0, 114.2, 113.9 ppm.

4-cyanobiphenyl (Table 4**, entry 9)** [52]**:** Colourless solid; yield: 159.50 mg (89%); m.p. 86–87 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 7.60 (q, 4H, J = 8.4 Hz), 7.46 (t, 2H, J = 7.2 Hz), 7.40 (q, 3H, J = 7.8 Hz) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ 141.1, 140.3, 129.0, 128.9, 128.5, 127.9, 127.7, 127.2, 118.0, 23.2 ppm.

4-formylbiphenyl (Table 4**, entry 10)** [53]**:** Colourless solid; yield: 162.22 mg (89%); m.p. 57–59 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 9.97 (s, 1H), 8.02 (d, 1H, J = 7.2 Hz), 7.57 (t, 1H, J = 8.4 Hz), 7.45–7.38 (m, 5H), 7.34 (d, 2H, J = 6.6 Hz) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ 192.0, 145.7, 137.6, 133.5, 133.4, 130.6, 130.1, 128.4, 128.0, 127.6, 127.4, 30.7 ppm.

4-methoxybiphenyl (Table 4**, entry 11)** [52]**:** Colourless solid; yield: 160.28 mg (87%); m.p. 87–89 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ 7.59 (q, 4H, J = 7.8 Hz), 7.45 (t, 2H, J = 7.8 Hz), 7.34 (t, 1H, J = 7.2 Hz), 7.02 (d, 2H, J = 8.4 Hz), 3.87 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ 159.2, 140.9, 133.8, 128.9, 128.4, 128.3, 126.8, 114.3 ppm.

4-methoxy-2′-methylbiphenyl (Table 4**, entry 12**) [54]: Colorless oil; yield: 168.52 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 7.53–7.50 (m, 2H), 7.36–7.30 (m, 3H), 7.25–7.20 (m, 1H), 6.98–6.95 (m, 2H), 3.84 (m, 3H), 2.40 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 159.1, 140.8, 138.6, 133.9, 128.7, 128.2, 127.6, 127.4, 123.9, 114.2, 55.4, 21.6 ppm.

4-methoxy-3′-methylbiphenyl (Table 4**, entry 13**) [55]: Colourless solid; yield: 170.50 mg (86%); m.p. 51 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 7.52–7.49 (m, 2H), 7.35–7.28 (m, 3H), 7.14–7.08 (m, 1H), 6.97–6.94 (m, 2H), 3.83 (m, 3H), 2.40 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 159.1, 140.9, 138.3, 133.9, 128.7, 128.2, 127.6, 127.5, 123.9, 114.2, 55.4, 21.6 ppm.

4,4′-dimethoxybiphenyl (Table 4**, entry 14**) [46]: Colourless solid; yield: 182.12 mg (85%); m.p. 171–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 7.48–7.46 (m, 4H), 6.96–6.94 (m, 4H), 3.83 (s, 6H) ppm; ^{13}C NMR (100 MHz, CDCl3, 25 °C, TMS): δ 158.7, 133.5, 127.8, 114.2, 55.4 ppm.

4-formyl-4′-methoxybiphenyl (Table 4**, entry 15**) [56]: Colourless solid; yield: 182.52 mg (86%); m.p. 99–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 10.0 (s, 1H), 7.94–7.92 (m, 2H), 7.73–7.71 (m, 2H), 7.02–7.00 (m, 2H), 3.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 192.0, 159.2, 134.7, 130.4, 128.5, 127.1, 114.5, 55.4 ppm.

4-nitrobiphenyl (Table 4**, entry 16**) [52]: Colourless solid; yield: 183.27 mg (92%); m.p. 114–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 8.31–8.29 (m, 2H), 7.75–7.73 (m, 2H), 7.62–7.58 (m, 2H), 7.32–7.26 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 129.2, 127.8, 127.4, 124.2 ppm.

4-methoxy-4′-nitrobiphenyl (Table 4**, entry 17**) [46]: Yellow solid; yield: 201.72 mg (88%); m.p. 97–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 8.01–7.99 (m, 2H), 7.65–7.63 (m, 2H), 7.59–7.57 (m, 2H), 7.01–6.99 (m, 2H), 3.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 197.0, 159.2, 145.4, 135.3, 129.0, 128.4, 126.7, 114.5, 26.7 ppm.

4-*tert*-butyl-4′-nitrobiphenyl (Table 4**, entry 18**) [57]: Pale yellow solid; yield: 228.02 mg (89%); m.p. 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 8.29–8.27 (m, 2H), 8.74–8.72 (m, 2H), 7.59–7.51 (m, 4H), 1.37 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 152.3, 147.5, 146.9, 135.8, 127.6, 127.1, 126.2, 124.1, 34.8, 31.3 ppm.

6. Associated content:

Supporting information: Optimisation of reaction with respect to amount of base and solvent, copies of ^{1}H and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.

CRediT authorship contribution statement

Prasanta Kumar Raul: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization.

Abhijit Mahanta: Validation. **Raju K.Borah:** Validation. **Utpal Bora:** Resources. **Ashim Jyoti Thakur:** Supervision, Conceptualization, methodology, Validation, Formal analysis, Writing - Review & Editing, Project administration. **Jyri-Pekka Mikkola:** Formal analysis. **Andrey Shchukarev:** Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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