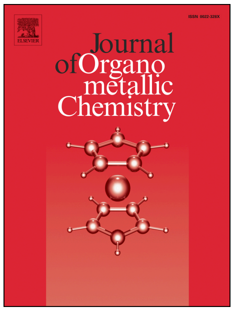

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PII: S0022-328X(17)30557-0
DOI: 10.1016/j.jorganchem.2017.09.037
Reference: JOM 20112

To appear in: *Journal of Organometallic Chemistry*

Received Date: 22 June 2017
Revised Date: 9 September 2017
Accepted Date: 24 September 2017

Please cite this article as: F. Panahi, F. Daneshgar, F. Haghighi, A. Khalafi-Nezhad, Immobilized Pd nanoparticles on silica-starch substrate (PNP-SSS): Efficient heterogeneous catalyst in Buchwald–Hartwig C–N cross coupling reaction, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2017.09.037.

Immobilized Pd Nanoparticles on Silica-Starch Substrate (PNP-SSS): Efficient Heterogeneous Catalyst in Buchwald–Hartwig C–N cross coupling reaction

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Abstract

An immobilized Pd nanoparticle on silica-starch substrate (PNP-SSS) is introduced as an efficient heterogeneous catalyst in Pd-catalyzed Buchwald–Hartwig C–N cross coupling reaction. A range of aryl amines were synthesized using reaction of aryl halides (chloride, bromide and iodide) and amines using PNP-SSS catalyst in good to excellent yields. The PNP-SSS catalyst shows high catalytic activity in C-N bond formation reaction and it is reusable in this reaction at least for five times without significant decreasing in its catalytic activity.

Keywords: Pd Nanoparticles, Silica-Starch Substrate, Heterogeneous Catalyst, Buchwald–Hartwig reaction, N-arylation, N-aryl amines

1. Introduction

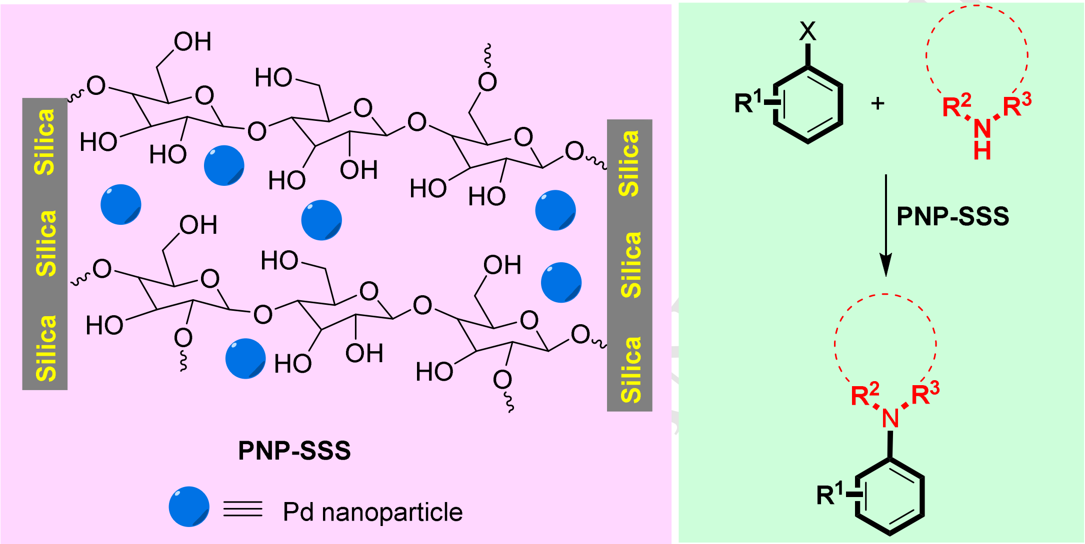
Palladium-catalyzed cross-coupling reactions have provided as a prevailing means for proficient carbon–carbon and carbon–heteroatom bond formations in the synthesis of pharmaceuticals, fine chemicals and advanced materials over the past decades **[1-3]**. Heterogeneous palladium catalysis has emerged in the synthetic area as a remarkably useful strategy in organic synthesis through Pd-catalyzed organic reactions **[4-6]**. Although wonderful advances in Pd-catalyzed carbon–carbon bond formation have been achieved, Pd-catalyzed carbon–heteroatom bond-forming processes have established considerably more challenging **[7-10]**.

The Pd-catalyzed C−N bond formation has emerged as an enormously common method for the preparation of aromatic amines **[11-13]**. Due to the widespread presence of *N*-aryl amines in natural products, pharmaceuticals, advanced materials, and ligands, the application of this method has been remarkably widespread. The continuous progress of ligands, catalysts and pre-catalysts since the first reports of Pd-catalyzed *N*-arylation reactions has afforded to enhancement of general and reliable procedures **[14-16]**. There are many attempts to find appreciate catalyst systems to accomplish Pd-catalyzed *N*-arylation reactions under heterogeneous conditions because recovery of the costly Pd metal is important and as well the production of uncontaminated product by Pd species is highly regarded by the industries. In this situation, different types of heterogeneous Pd-catalyst systems have been developed for Buchwald–Hartwig C–N cross coupling reaction **[17-23]**. Some of the reported palladium–catalyst systems for *N*-arylation reaction suffer from main drawbacks such as tedious and time-consuming work-up process, high cost and difficulty in synthesis of these catalyst systems. Reusability of the catalyst and more importantly leaching of Pd as an expensive metal, are other significant confronts. Development of high performance palladium-catalyzed systems and use of sustainable and environmentally benign reaction conditions for Buchwald–Hartwig C–N cross coupling reaction is highly considered in view point of both academic and industrial research **[24-26]**.

Use of naturally occurring substrate (NOSs) such as starch, cyclodextrins, cellulose, chitosan, agarose, pectin etc. are good candidate to be used as supports in order to provide an environmentally being and practical palladium catalysts systems. In addition to support role for NOSs, they can provide the reduction potential for a chemical process and acting as a reducing agent for the formation and stabilization of catalytically active metal nanoparticles **[27-33]**. These materials have received considerable attentions due to having potential in design of heterogeneous Pd catalyst systems with high reactivity and selectivity in environmentally benign/acceptable media. As well, NOSs are especially interesting, because they are inexpensive, conveniently available, environmentally benign, and structurally diverse.

In our research group, silica-starch substrate (SSS) was synthesized using the reaction of starch and chlorine-functionalized silica and it was used as support for immobilization of Pd nanoparticles. In this way a heterogeneous Pd catalyst system (PNP-SSS) (Figure 1a) was synthesized and it was successfully used in C-C coupling reactions including Heck, Sonogashira **[34]** and Suzuki **[35]** in water media, while it was reusable for several times with approximately consistent catalytic activity.

In continuation of our program to develop heterogeneous palladium nanocatalysts and its application in Pd-catalyzed organic transformations **[34-39]**, we have disclosed a new, simple, and efficient method for Pd-catalyzed Buchwald–Hartwig C–N cross coupling reaction using PNP-SSS catalyst (Scheme 1).

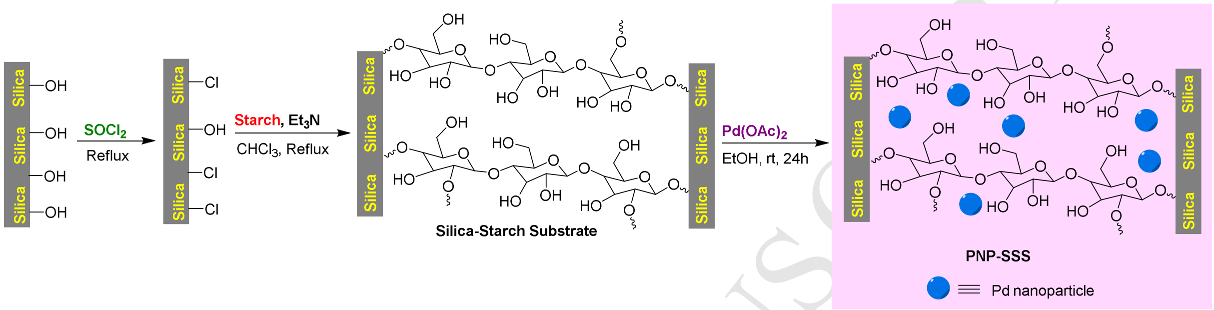


Scheme 1. A schematic representation structure of PNP-SSS catalyst and its application in Pd-catalyzed Buchwald–Hartwig C–N cross coupling reaction

This protocol possesses several advantages including using silica and starch as safe and cheep materials for preparation of support, absence of phosphine ligands and use of Pd nanoparticles as highly active catalyst species.

2. Results and Discussion

The PNP-SSS catalyst was synthesized based on our previous report **[34]**. The synthetic pathway toward synthesis of PNP-SSS catalyst is shown in Scheme 2.



Scheme 2. The synthetic route for the synthesis of PNP-SSS catalyst

First, silica was converted to silica chloride using its reaction with thionyl chloride ($SOCl_2$) under reflux conditions **[40]**. Starch was reacted with silica chloride material and it remained on the surface of silica covalently and produces a silica-modified substrate for stabilization of metal nanoparticles. Immobilization of Pd nanoparticles on the surface of silica-starch substrate (SSS) resulted in the production of a heterogeneous Pd catalyst system. This catalyst system has been fully characterized **[34]**. The TEM images of the fresh prepared catalyst system are shown in Figure 1a-c.

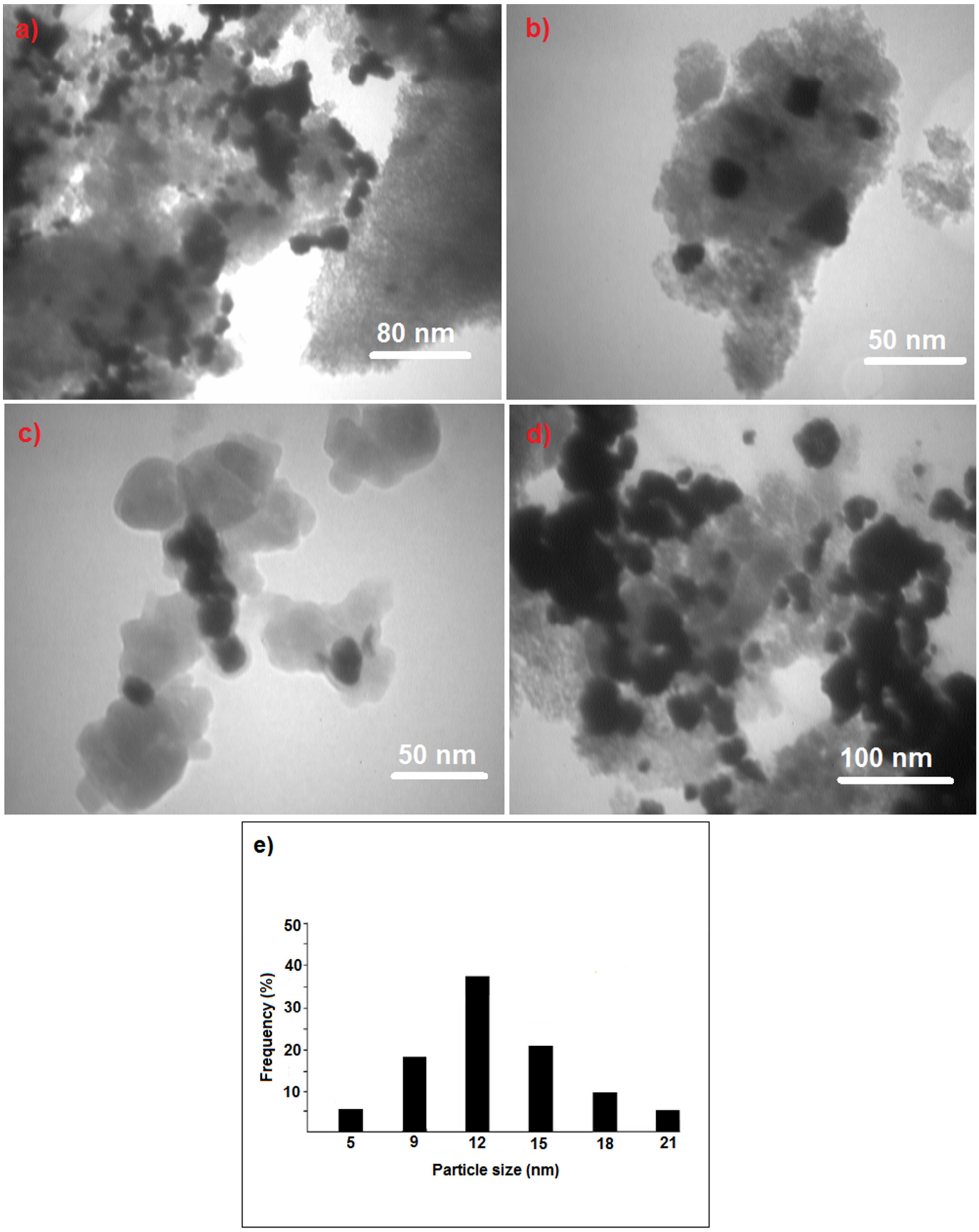


Figure 1. The TEM images of the fresh prepared PNP-SSS catalyst (a-c). The TEM image of reused PNP-SSS catalyst after five time of reusability (d). A histogram representing the size distribution of Pd nanoparticles in PNP-SSS catalyst (e)

The TEM images of the PNP-SSS with different magnifications are depicted in Figure 1. The TEM images of the PNP-SSS catalyst show nearly spherical Pd nanoparticles with an average particle size of ~12 nm. Images also show that the Pd nanoparticles with near spherical morphology are assembled onto the SSS with relatively good monodispersity. The palladium content of the catalyst was found to be 0.265 mmol per gram using ICP analysis.

The PNP-SSS catalyst system was successfully used in C-C bond formation reactions including Heck, Sonogashira and Suzuki in water as green solvents **[34,35]**. Our attempts on the application of this catalyst system in C-N bond formations in water solvent were failed and no satisfactory results were obtained. However, it was observed that the PNP-SSS catalyst has remarkable catalyst activity in DMF solvent and we decided to disclose these results in order to introduce an efficient, heterogeneous and simple catalyst system for application in C-N bond formation reactions.

In order to find optimized conditions for PNP-SSS catalyzed *N*-arylation of aryl halides with amines a model reaction including bromobenzene (**1a**) and morpholine (**2a**) was selected and different circumstances were checked (Figure 2).

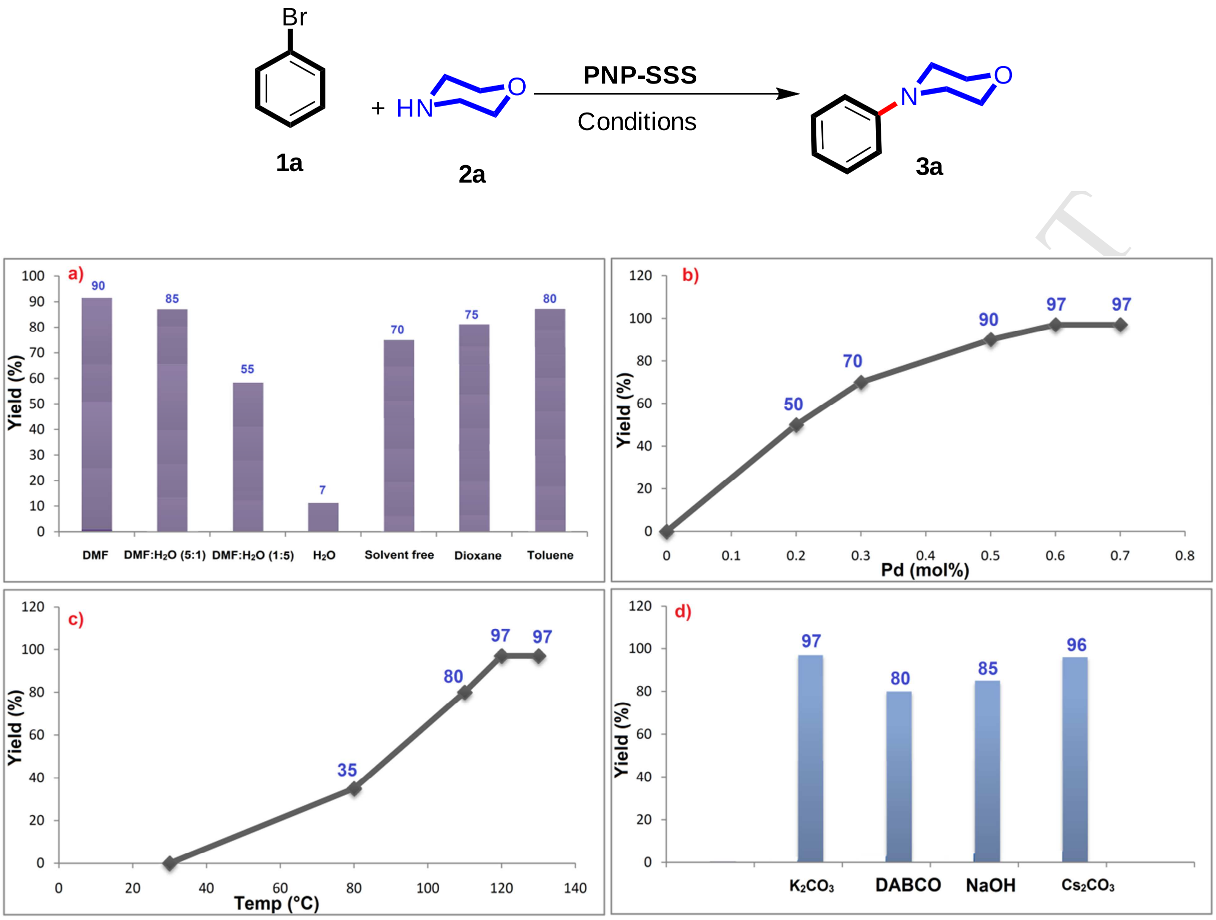
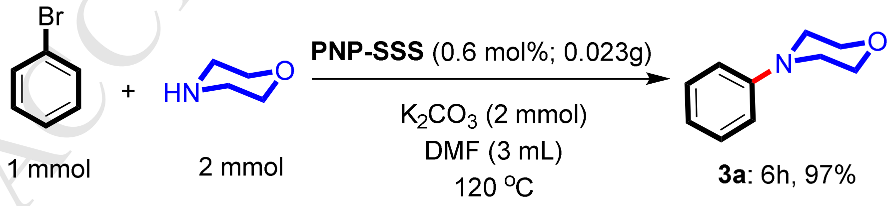


Figure 2. Optimization reaction conditions for *N*-arylation using PNP-SSS catalyst. The reaction model was bromobenzene and morpholine. Reaction conditions: PhBr (**1a**; 1.0 mmol), morpholine (**2a**; 2.0 mmol), base (2.0 mmol), solvent (3.0 mL). All yields are isolated product. a) Optimization of solvent: maximum yield of product was obtained in DMF solvent. The temperatures for solvents were as following: DMF (120 °), DMF:H_2O (100 °C), H_2O (reflux), solvent free (110 °C), dioxane (105-110 °C) and toluene (105-110 °C). b) Optimization amount of catalyst loading: about 0.6 mol% of Pd (23 mg of catalyst) was recognized as optimum. c) Temperature optimization: among temperature tested

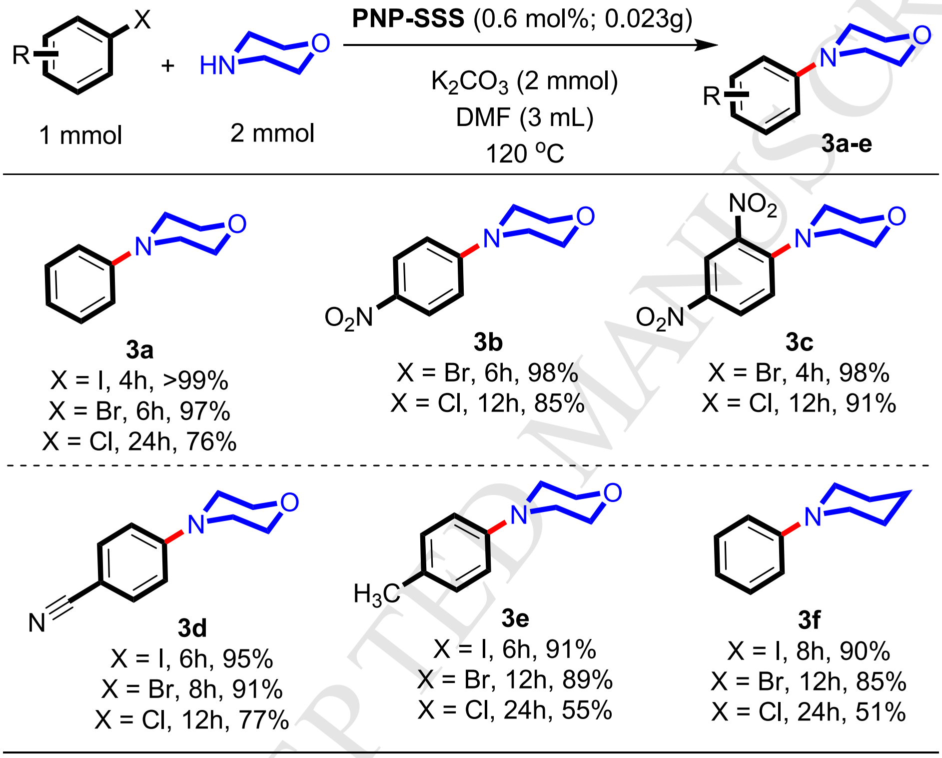
maximum yield of product was observed at 120 °C. d) To find best base: among base tested potassium carbonate was distinguished as the best base.

After selection of model reaction, the reaction media was changed and DMF:H_2O was used as solvent, however, in spite of our exception, it was observed that by increasing the fraction of water the reaction yield decreased significantly so that in pure water no product was observed (Figure 2a). Under solvent free conditions about 70% of product was isolated. In other solvents including toluene and dioxane the reaction no improvement in reaction outcome was observed. Thus, DMF was selected as the reaction media. As shown in Figure 2b, no product was observed in the absence of catalyst. In the presence of only 0.5 mol% of catalyst about 90% of coupling product was obtained in DMF solvent at 120 °C. Subsequently, the catalyst loading was changed and 0.6 mol% of catalyst was selected as optimum. By decreasing the reaction temperature, reaction yield was decreased significantly and 120 °C was selected as optimized temperature (Figure 2c). Some other bases was also checked and no superiority was observed in comparison with K_2CO_3 (Figure 2d). Thus, the optimized conditions for *N*-arylation of aryl halides using PNP-SSS as catalyst are shown in Scheme 3.



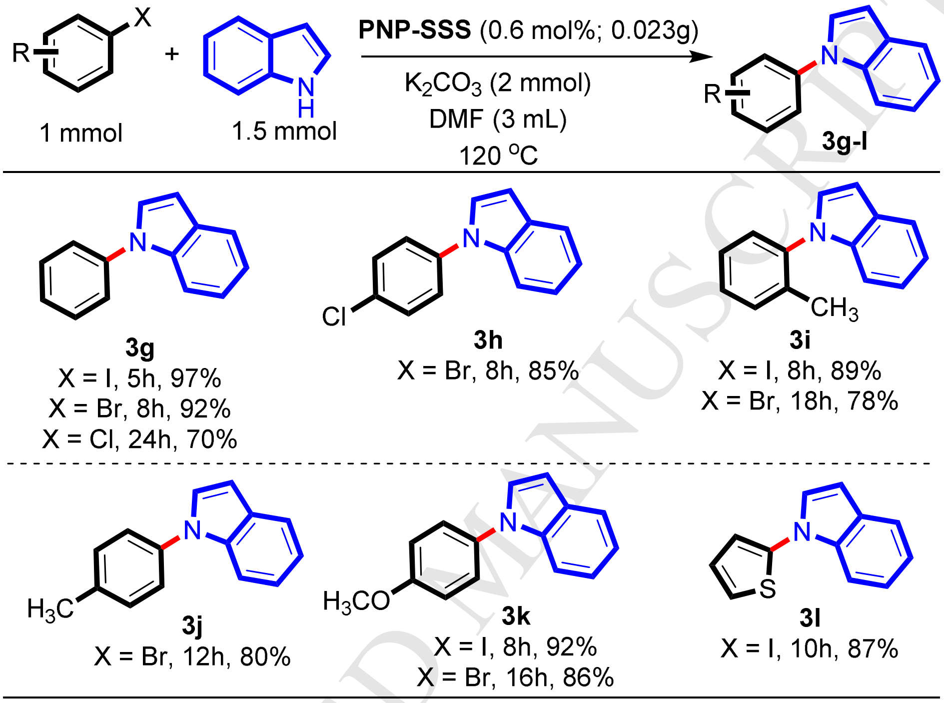
Scheme 3. Optimized condition for *N*-arylation of aryl halides using PNP-SSS catalyst

After optimization study, the generality and scope of this method was evaluated in synthesis of diverse aryl amines using reaction of different aryl halides and amines. Since morpholine is one of the biologically important molecules, first, some other morpholine and piperidine based aryl amines were synthesized under optimized conditions (Scheme 4).



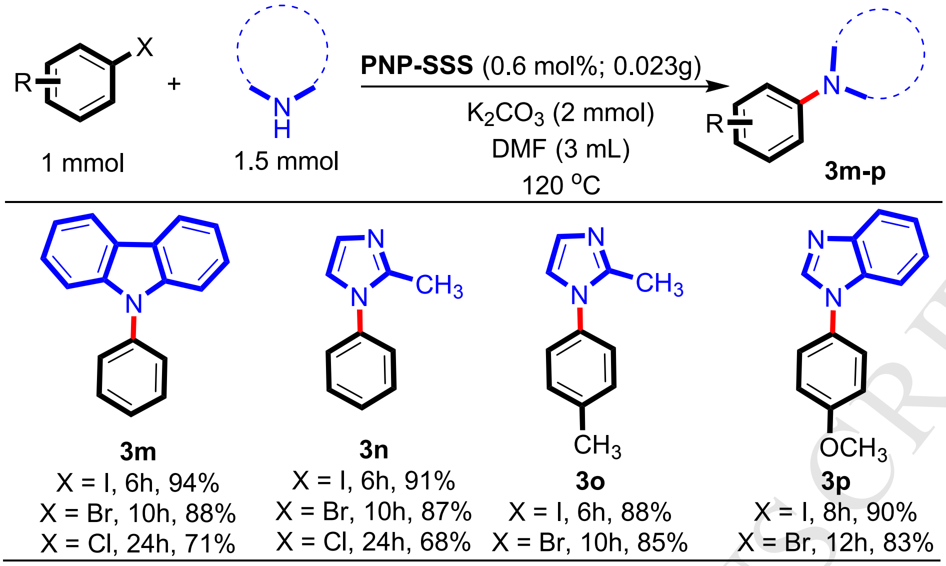
Scheme 4. Synthesis of some *N*-aryl substituted morpholine derivatives using PNP-SSS catalyst under optimized conditions

As shown in Scheme 4, it is possible to synthesize diverse derivatives of morpholine with aryl halides (iodide, bromide and chloride) bearing both electron-withdrawing (**3b-d**) and electron-donating (**3e**) groups using our synthetic methodology in good to excellent yields. Then, indole was used as amine coupling partner and some derivatives were synthesized in good to excellent yields (Scheme 5). The condition used are same morpholine with this difference that 1.5 equivalent of indole was necessary for this conversion.



Scheme 5. Synthesis of some *N*-aryl indole derivatives using PNP-SSS catalyst

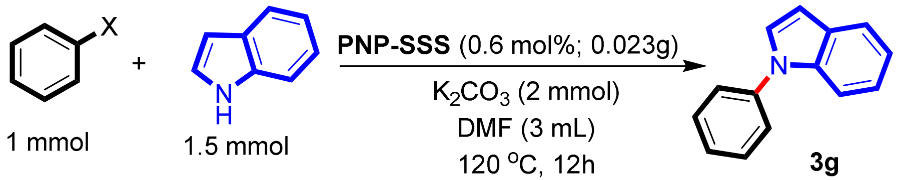
As shown in Scheme 5, the PNP-SSS catalyst is highly efficient for *N*-arylation of indole and aryl halides. The reaction yields for aryl iodides are more than aryl bromide and chlorides. Good yields for aryl bromides were obtained which is suitable for synthetic approaches because aryl bromides are less expensive than aryl iodides. We decided to use other *N*-heterocycles in order to evaluate the catalytic applicability of PNP-SSS in synthesis of other *N*-aryl substituted heterocycles (Scheme 6).



Scheme 6. *N*-arylation of aryl halides using different *N*-heterocyclic compounds.

In this part carbazole, imidazole and benzimidazole were used as amine component in coupling with aryl halides (Scheme 6).

Results demonstrate that our synthetic methodology is suitable for synthesis of different *N*-aryl amines using selection of desired *N*-heterocyclic compounds. The catalytic applicability of PNP-SSS catalyst was evaluated in *N*-arylation of aryl C-O electrophiles such as triflates, tosylates and mesylates and results demonstrate that these coupling partners especially triflates are also active in this reaction (Scheme 7).

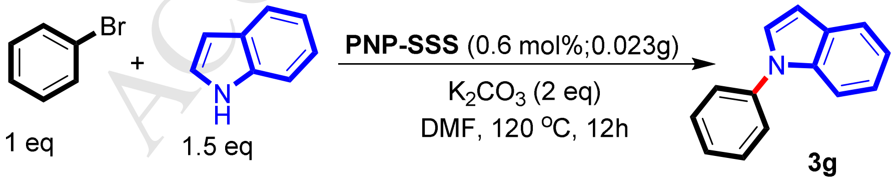


X	I	Br	OTf	Cl	OMs	OTs
Yield (%)	98	92	91	65	64	45

Scheme 7. Application of PNP-SSS catalyst in *N*-arylation of aryl C-O electrophiles and their comparison with aryl halides

Also we decided to investigate the catalytic applicability of PNP-SSS catalyst in a gram-scale *N*-arylation process. Thus bromobenzene (10 mmol) was reacted with indole (15 mmol) using PNP-SSS (0.6 mol%) catalyst and 90% of product (**3g**) was isolated.

The level of recyclability of the PMP-SSS catalyst for *N*-arylation reaction was also investigated by use of *N*-arylation reaction of bromobenzene with indole under optimized conditions. When the reaction was complete, the catalyst was separated from the reaction mixture using a simple filtration and was then washed with hot ethanol and next water. The recycled catalyst was dried in oven and used for the next run. The recycled catalyst could be reused 5 times without a remarkable decrease in its catalytic activity (Scheme 8).



Run	1	2	3	4	5
Yield (%)	92	91	91.5	90	89

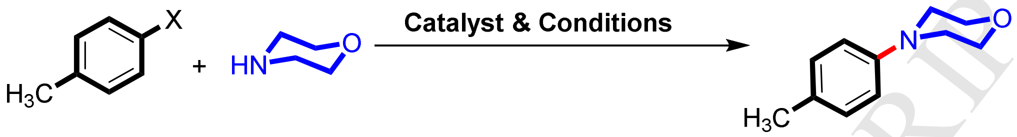
Scheme 8. The catalyst reusability test of PNP-SSS catalyst in N-arylation reaction

In order to show that the catalyst activity of the PNP-SSS catalyst did not change significantly during the reaction process, the Pd content of catalyst after 5 cycles of reusability was investigated using the ICP analysis method and the results show that only about 0.7% of Pd was lost (1.6 ppm). Also, the TEM image of catalyst after 5 times of reusability show that the morphology and size of catalyst not changed significantly, although some aggregation after 5 times of reusability is observable for catalyst (Figure 1d). These results are in good agreement with the reactivity obtained from PNP-SSS catalyst after each recovery.

To confirm this point that the activity originated from the supported palladium nanoparticles on the silica starch–substrate and not from leached Pd, we did the following test. When the reaction between bromobenzene and indole was completed, the hot filtration accomplished, the obtained aqueous solution from the filtrate was analyzed with ICP. The ICP analysis of the aqueous solution showed that only 0.2% of Pd was lost from silica-starch substrate.

In order to demonstrate the applicability of PNP-SSS catalyst in *N*-arylation reaction, a comparison with some other reported palladium catalysts is presented in Table 1. As shown in Table 1, our catalyst system is comparable with the reported homogeneous and heterogeneous catalysts in efficiency.

Table 1. Comparison of Buchwald-Hartwig C-N cross coupling reaction of PNP-SSS catalyst with other catalytic systems



Entry	Catalyst & conditions	X	Time (h)	Yield (%)[a]	TON[b]	TOF[c]	Ref.
1	PNP-SSS (0.6 mol%), K_2CO_3, DMF, 120 °C	Cl	24	55	92	3.8	This work
2	PNP-SSS (0.6 mol%), K_2CO_3, DMF, 120 °C	Br	12	89	148	12.4	This work
3	PNP-SSS (0.6 mol%), K_2CO_3, DMF, 120 °C	I	6	91	152	25.3	This work
4	Pd/C (1.0 mol%), K_2CO_3, DMF, 120 °C	Cl	24	40	40	1.7	This work
5	PFG-Pd (1.7 mol%), NaO*t*Bu, 110 °C	Br	12	88	51.7	4.3	[19]
6	Pd-PFMN (1.2 mol% Pd), K_2CO_3, 120 °C	Cl	24	85	71	3.0	[20]
7	$Pd_2(dba)_3$ (0.5 mol%), phosphine ligand (1 mol%), NaO-*t*-Bu, toluene, 100 °C	Cl	20	89	178	8.9	[51]
8	$Pd(dba)_2$ (1 mol%), phosphine ligand (2 mol%), NaO-*t*-Bu, DME, 120 °C, under N_2	Cl	24	93	93	3.9	[52]

9	Pd(OAc)2 (1 mol%), Polymer-supported dialkylphosphinobiphenyl ligand (1.3 mol%), NaO-*t*-Bu, toluene, 80 °C	Cl	20	90	90	4.5	[53]
10	$Pd(OAc)_2$ (1 mol%), phosphine ligand (2 mol%), KOH, toluene, 90 °C	Cl	20	97	97	4.8	[54]
11	$Pd(dba)_2$ (0.5 mol%), phosphine ligand (1 mol%), NaO-*t*-Bu, toluene, 110 °C	Cl	20	97	194	9.7	[55]

[a] Isolated Yield. [b] TON = mol product/mol catalyst. [c] TOF = TON/h.

3. CONCLUSION

In conclusion, we have established a practical palladium-catalyzed N-arylation method which permits us to convert aryl halides and amines (or heteroaryls) to *N*-aryl amines in good to excellent yields. The immobilized Pd-nanoparticles on silica-starch substrate were used as heterogeneous Pd nanocatalyst for this transformation. The synthetic route for the preparation of PNP-SSS catalyst is simple and starting materials are cheap and available. The PNP-SSS catalyst shows high catalytic activity in the synthesis of aryl amines using the reaction of NH containing compounds and aryl halides. A range of arylamines were synthesized using PNP-SSS catalyst under optimized conditions. The PNP-SSS catalyst was reusable at least for 5 times without considerable decreasing in its catalytic activity.

4. Experimental

4.1. General

Chemicals and all reagents and solvents were obtained from commercial suppliers and used without further purification. The PNP-SSS catalyst was prepared using our previous method reported in the literature **[34]**. The known products were characterized by comparison of their spectral and physical data with those reported in the literature. ^{1}HNMR (250 MHz) and ^{13}C NMR (62.5 MHz) spectra were recorded on a Brucker Avance DPX-250 spectrometer in deuterated chloroform ($CDCl_3$) solution with tetramethylsilane (TMS) as an internal standard. Chemical shifts were reported in ppm (δ), and coupling constants in Hz (J). Fourier-transform infrared (FT-IR) spectroscopy with a Shimadzu FTIR-8300 spectrophotometer was employed for characterization of the products. Melting points were determined in open capillary tubes using a Barnstead electro-thermal 9100BZ circulating oil melting point apparatus. Transmission electron microscopy (TEM) was obtained using a TEM apparatus (CM-10-Philips, 100 kV) for characterization of the catalyst. The amount of Pd supported on PNP-SSS catalyst was measured using an ICP analyzer (Varian, Vista-pro) and atomic absorption spectroscopy. The reaction monitoring was carried out on silica gel analytical sheets and column chromatography was carried out on column of silica gel. Thin layer chromatography was carried out on silica gel 254 analytical sheets obtained from Fluka.

4.2. General procedure for Buchwald–Hartwig C–N cross coupling reaction using PNP-SSS catalyst

Aryl halide (1.0 mmol), amine (1.5-2.0 mmol), PNP-SSS (0.6 mol%; 0.023g), K_2CO_3 (2 mmol), and DMF (3.0 mL) was placed in a 25 mL flask equipped with a magnetic stirring bar and heated at 120 °C under nitrogen gas. The reaction was then monitored by TLC until the consumption of aryl halide was detected. After completion of the reaction 5 mL of water and 5 mL of ethyl acetate were added to the reaction mixture. The organic solution was extracted and dried over anhydrous Na_2SO_4. After removing of organic solvent the crude product was obtained. For further purification the chromatography technique was used.

4.3. Spectral data for synthesized compounds

4-Phenylmorpholine (3a). White solid; mp = 53-55 °C (Lit: 51-54 °C) **[41].** ^{1}H-NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) = 3.13-3.16 (m, 4H), 3.83-3.87 (m, 4H), 6.85-6.92 (m, 3H), 7.24-7.29 (m, 2H). ^{13}C-NMR (62.5 MHz, $CDCl_3$/TMS): δ (ppm) = 49.5, 66.6, 116.2, 119.9, 129.5, 151.0. Anal. calcd. for $C_{10}H_{13}NO$ (163.22): C 73.59, H 8.03, N 8.58. Found: C 73.50, H 7.94, N 8.51.

4-(4-Nitrophenyl)morpholine (3b). White solid; mp = 151-153 °C (Lit: °C: 152) **[42].** ^{1}H-NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) = 3.28-3.32 (m, 4H), 3.77-3.81 (m, 4H), 6.71-6.77 (m, 2H), 8.01-8.07 (m, 2H). ^{13}C-NMR (62.5 MHz, $CDCl_3$/TMS): δ (ppm) = 47.1, 66.3, 112.6, 125.8, 138.9, 155.0. Anal. calcd. for $C_{10}H_{12}N_2O_3$ (208.22): C 57.69, H 5.81, N 13.45. Found: C 57.62, H 5.73, N 13.38.

4-(2,4-Dinitrophenyl) morpholine (3c). Yellow solid; mp = 119-120 °C (Lit: 117-118 °C) **[43].** ^{1}H-NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) = 3.18-3.21 (m, 4H), 3.78-3.82 (m, 4H), 7.04 (d, *J* = 9.2 Hz, 1H), 8.22 (dd, *J* = 7.3, 2.4 Hz, 1H), 8.64 (d, *J* = 2.0 Hz, 1H). ^{13}C-NMR (62.5 MHz, $CDCl_3$/TMS): δ (ppm) = 50.8, 66.1, 119.1, 124.7, 128.3, 140.1, 149.7 (2C). Anal. calcd. for $C_{10}H_{11}N_3O_5$ (253.21): C 47.43, H 4.38, N 16.60. Found: C 47.35, H 4.31, N 16.52.

4-Morpholinobenzonitrile (3d). Colorless solid; mp = 75-77 °C (Lit: 74-76 °C) **[44]**. ^{1}H-NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) = 3.25-3.29 (m, 4H), 3.82-3.86 (m, 4H), 6.82-6.88 (m, 2H), 7.47-7.53 (m, 2H). ^{13}C-NMR (62.5 MHz, $CDCl_3$/TMS): δ (ppm) = 47.2, 66.4, 100.9, 114.0, 119.8, 133.5, 152.9. Anal. calcd. for $C_{11}H_{12}N_2O$ (188.23): C 70.19, H 6.43, N 14.88. Found: C 70.12, H 6.36, N 14.81.

4-(*p*-Tolyl)morpholine(3e). Colorless solid; mp = 44 °C (Lit: 40-42 °C) **[45]**. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 2.27 (s, 3H), 3.10-3.13 (m, 4H), 3.85-3.89 (m, 4H), 6.85 (d, *J* = 3.7 Hz, 2H), 7.07 (d, *J* = 4.0 Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 20.3, 49.6, 65.8, 116.0, 129.6, 129.7, 149.0. Anal. calcd. for $C_{11}H_{15}NO$ (177.25): C 74.54, H 8.53, N 7.90. Found: C 74.38, H 8.36, N 7.75.

1-phenylpiperidine (3f). Colorless oil, **[46]**. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.58-1.81 (m, 6H), 3.17-3.19 (4H), 3.83-3.87 (m, 1H), 6.96-6.99 (m, 2H), 7.23-7.31 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 24.3, 25.9, 50.7, 116.6, 119.2, 128.9, 152.2. Anal. Calcd for $C_{11}H_{15}N$ (161.25): C, 81.94; H, 9.38; N, 8.69. Found: C, 81.85; H, 9.30; N, 8.61.

1-Phenyl-*1H*-indole (3g). Colorless oil, **[47]**. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.62 – 7.59 (m, 1H), 7.51 – 7.05 (m, 9H), 6.60 – 6.59 (m, 1H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) 139.9, 135.9, 129.6, 129.4, 128.0, 126.5, 124.4, 122.4, 121.2, 120.4, 110.5, 103.6. Anal. calcd. for $C_{14}H_{11}N$ (193.25): C 87.01, H 5.74, N 7.25. Found: C 86.93, H 5.74, N 7.16.

1-(4-Chlorophenyl)-*1H*-indole (3h). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.63 – 7.59 (m, 1H), 7.45 – 7.09 (m, 8H), 6.62 – 6.60 (m, 1H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) 145.2, 138.4, 132.0, 129.8, 129.4, 127.7, 125.5, 122.6, 121.3, 120.6, 110.3, 104.0. Anal. calcd. for $C_{14}H_{10}ClN$ (227.69): C 73.85, H 4.43, N 6.15. Found: C 73.77, H 4.38, N 6.09.

1-(*o*-Tolyl)-*1H*-indole (3i). Colorless oil, **[47]**. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.64 – 7.61 (m, 1H), 7.31 – 6.95 (m, 8H), 6.61 – 6.59 (m, 1H), 1.99 (s, 3H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) 140.5, 134.4, 131.2, 129.8, 128.7, 128.2, 128.1, 126.8, 122.0, 121.2, 120.8, 119.8, 110.5, 102.4, 17.6. Anal. calcd. for $C_{15}H_{13}N$ (207.28): C 86.92, H 6.32, N 6.76. Found: C 86.86, H 6.25, N 6.71.

1-(*p*-Tolyl)-1H-indole (3j). Colorless oil, **[47]**. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.64 – 7.59 (m,1H), 7.48 – 7.05 (m, 8H), 6.62 – 6.59 (m, 1H), 2.36 (s, 3H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) 136.8, 136.3, 135.0, 130.1, 129.1, 128.1, 124.3, 122.2, 121.0, 120.2, 110.5, 103.2, 21.0. Anal. calcd. for $C_{15}H_{13}N$ (207.28): C 86.92, H 6.32, N 6.76. Found: C 86.83, H 6.24, N 6.67.

1-(4-Methoxyphenyl)-1H-indole (3k). White solid; mp = 59-60 °C (Lit: 60-61 °C) **[48].** ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.59 – 7.55 (m, 1H), 7.33 – 6.85 (m, 8H), 6.55 – 6.52 (m, 1H), 3.72 (s, 3H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm): 158.3, 136.4, 132.9, 129.4, 128.4, 126.0, 122.2, 121.1, 120.2, 114.8, 110.5, 103.0, 55.6. Anal. calcd. for $C_{15}H_{13}NO$ (223.28): C 80.69, H 5.87, N 6.27. Found: C 80.60, H 5.81, N 6.22.

1-(Thiophen-2-yl)-1H-indole (3l). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.60 – 7.45 (m, 2H), 7.22 – 6.96 (m, 6H), 6.60 – 6.58 (m, 1H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm): 141.1, 129.3, 127.2, 126.0, 125.0, 122.8, 121.6, 121.0, 120.8, 120.4, 110.6, 104.1. Anal. calcd. for $C_{12}H_9NS$ (199.27): C 72.33, H 4.55, N 7.03. Found: C 72.27, H 4.49, N 6.96.

9-Phenyl-9H-carbazole (3m). White solid; mp = 94-96 °C (Lit: 95-97 °C) **[49]**. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 8.09 – 8.06 (m, 2H), 7.57 – 7.17 (m, 11H). ^{13}C-NMR (62.5 MHz,

$CDCl_3$) δ (ppm) 140.9, 137.7, 129.8, 127.4, 127.1, 125.9, 123.3, 120.3, 119.9, 109.8. Anal. calcd. for $C_{18}H_{13}N$ (243.31): C 88.86, H 5.39, N 5.76. Found: C 88.81, H 5.33, N 5.70.

2-Methyl-1-phenyl-*1H*-imidazole (3n). Colorless oil, **[50]**. ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.44-7.18 (m, 5H), 6.95-6.92 (m, 2H), 2.28 (s, 3H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm): 144.7, 137.9, 129.5, 128.2, 127.4, 125.5, 120.6, 13.6. Anal. calcd. for $C_{10}H_{10}N_2$ (158.20): C 75.92, H 6.37, N 17.71. Found: C 75.85, H 6.31, N 17.64.

2-Methyl-1-(*p*-tolyl)-*1H*-imidazole (3o). ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.28-7.14 (m, 4H), 6.99 (d, *J* = 10.0 Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm): 143.1, 138.8, 135.9, 130.0, 127.3, 125.3, 121.2, 21.1, 13.6. Anal. calcd. for $C_{11}H_{12}N_2$ (172.23): C 76.71, H 7.02, N 16.27. Found: C 76.64, H 6.95, N 16.21.

1-(4-Methoxyphenyl)-1H-benzo[d]imidazole (3p). Pale yellow solid; mp = 100-102 °C (Lit: °C: 99-101) **[44].** ^1H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.92 (s, 1H), 7.50 – 7.24 (m, 6H), 7.11 – 7.06 (m, 2H), 3.89 (s, 3H). ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) 156.6, 144.7, 140.6, 135.2, 134.0, 125.8, 123.7, 122.9, 120.3, 115.1, 110.5, 55.6. Anal. calcd. for $C_{14}H_{12}N_2O$ (224.26): C 74.98, H 5.39, N 12.49. Found: C 74.90, H 5.33, N 12.41.

Acknowledgment

Financial supports from the research councils of Shiraz University and Amirkabir University of Technology are gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data related to this article can be found at

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Highlights

- Use of immobilized PNP-SSS catalyst in Buchwald–Hartwig C–N cross coupling reaction
- Coupling of different amines and aryl halides using catalytic amount of PNP-SSS
- 5 times reusability of PNP-SSS catalyst in Buchwald–Hartwig coupling reaction
- Introduction of an efficient catalyst for C-N coupling reaction prepared from abundant, cheap and available starting materials