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ORIGINAL PAPER

Buchwald–Hartwig amination reaction using supported palladium on phosphine-functionalized magnetic nanoparticles

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Abstract The supported palladium on phosphine-functionalized magnetic nanoparticles (Pd-PFMN) was found to be an efficient magnetically separable catalyst for the Buchwald–Hartwig amination reaction (BHAR) under solvent-free conditions. All of the reactions in the presence of Pd-PFMN catalyst afforded the corresponding products in good to excellent yields. The catalyst can be easily separated from the reaction mixture using an external magnetic field, and it can be reused at least five cycles without significant loss in its initial catalytic activity.

Keywords Buchwald–Hartwig amination reaction (BHAR) · Palladium · Phosphine-functionalized magnetic nanoparticles (PFMN) · Phosphorus ligands · Arylamines

Introduction

The Buchwald–Hartwig amination reaction (BHAR) is generally involved in the coupling of aryl halides with amines mediated by a suitable palladium catalyst to afford arylamines [1–3]. Arylamines are very important structural motif in organic synthesis due to their widespread applications in natural products, pharmaceuticals, agrochemicals, and advanced materials [4–7]. There are many chemicals and pharmaceutical intermediates with amine structural units, which are synthesized using the BHAR in the presence of a palladium catalyst system, representing the synthetic importance of this method in organic synthesis [8, 9]. Since the discovery of the BHAR (1995) [10, 11], a range of modifications for this reaction has been developed to increase the reaction efficacy [12, 13]. A survey in this field demonstrated that major advances have been obtained on developing new and more effective phosphorus ligands. The chemical structures of some of the used phosphorus ligands in BHAR are shown in Fig. 1 [14–19]. It should be mentioned that some of these ligands have been showed high activity in BHAR.

Despite the high activity of phosphorus ligands in metal-catalyzed organic reactions, they often suffer from some disadvantages, such as intrinsic toxicity, foul-smell, easy oxidization during reaction process, difficulty of extraction, tedious purification process, and lack of recoverability [20, 21]. Stabilization of these ligands on a recyclable support is one of the most important approaches to improve their applicability in organic reactions [22–24]. However, separation and recovery of these ligands on solid supports usually required filtration or centrifugation; therefore, the efficiency of the recovered ligands can be somewhat reduced. In the recent years, magnetic nanoparticles (MNPs) have attracted much attention because of their easy preparation, large surface area ratio, facile separation by use of magnetic force, and low toxicity and price [25].

Recently, in our research group, MNPs were functionalized using chlorodiphenylphosphine ($ClPPh_2$) and phosphine-functionalized magnetic nanoparticles (PFMN) as a recyclable phosphorus ligand were obtained [22]. Also, palladium (II) complex of PFMN ligand (Pd-PFMN) was prepared and its catalytic activity evaluated in the Heck reaction of chloroarenes. The results revealed that, this new catalyst showed high catalytic activity in the Heck reaction of chloroarenes [22]. This activity is attributed to the high reactivity of Pd complex involving phosphorus ligands and dispersible ability of MNPs in solution as a high surface

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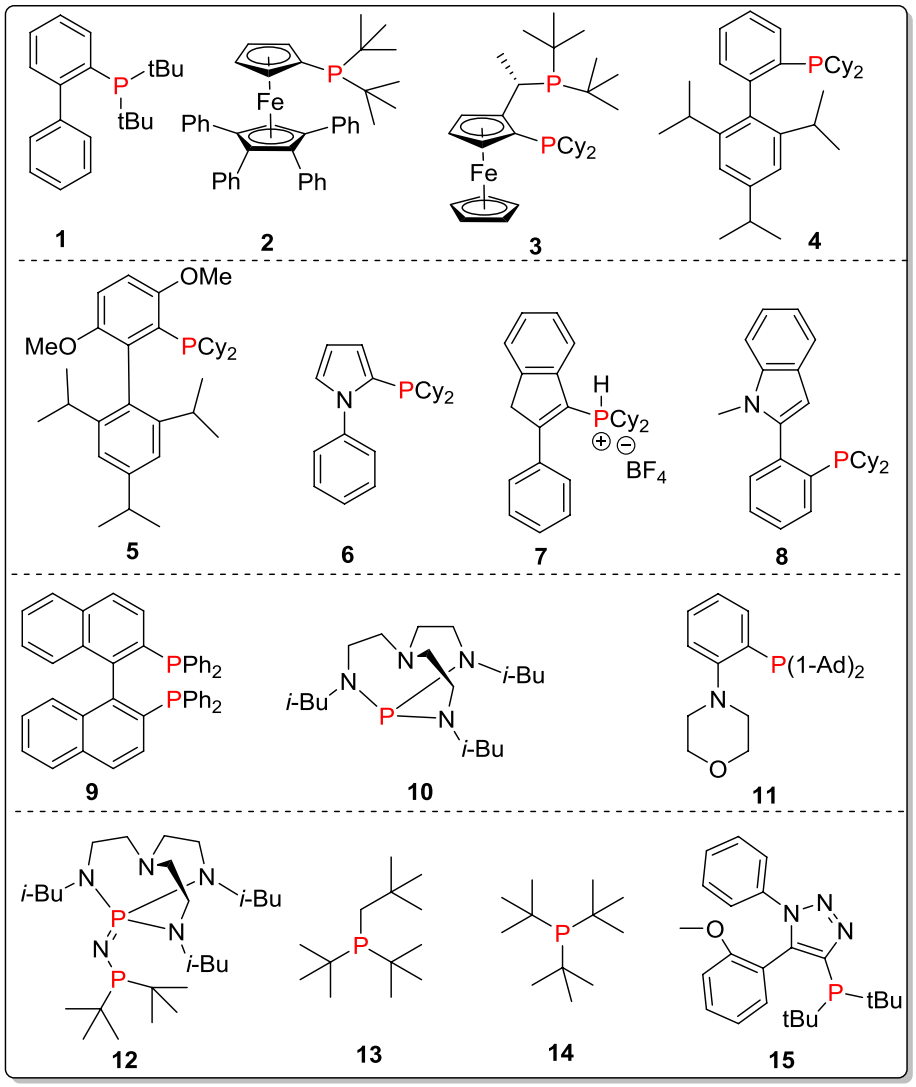


Fig. 1 The chemical structure of some of the used phosphorus ligands in Pd-catalyzed BHAR

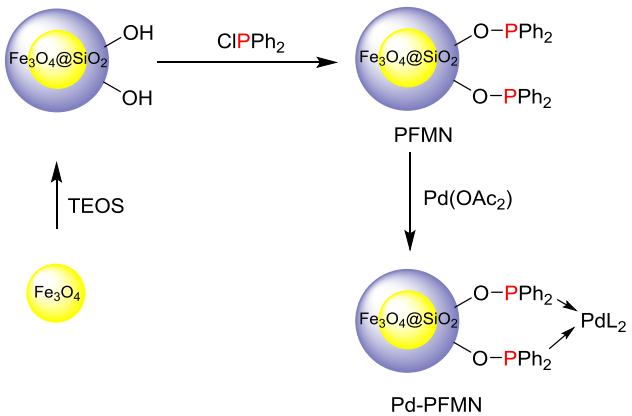
area support. Also, the application of this magnetically recyclable ligand was evaluated in Ru-catalyzed acceptor-less dehydrogenative coupling reaction of primary alcohols and 2-aminophenol for one-pot synthesis of benzoxazoles [23].

In the current study, in continuation of our previous work on heterogeneous palladium catalysts [22, 23, 26, 27], we would like to develop the synthetic practicality of Pd-PFMN catalyst by synthesis of some arylamines, using BHAR under heterogeneous and solvent-free conditions.

Experimental

General

Chemicals were purchased from Merck to Aldrich chemical companies. All the chemicals and solvents were used



Scheme 1 Synthetic route for the preparation of Pd-PFMN catalyst

The Pd-PFMN catalyst has been fully characterized using some different microscopic and spectroscopic techniques [22]. For easier access a TEM, SEM image and XRD pattern of Pd-PFMN catalyst are shown in Fig. 2

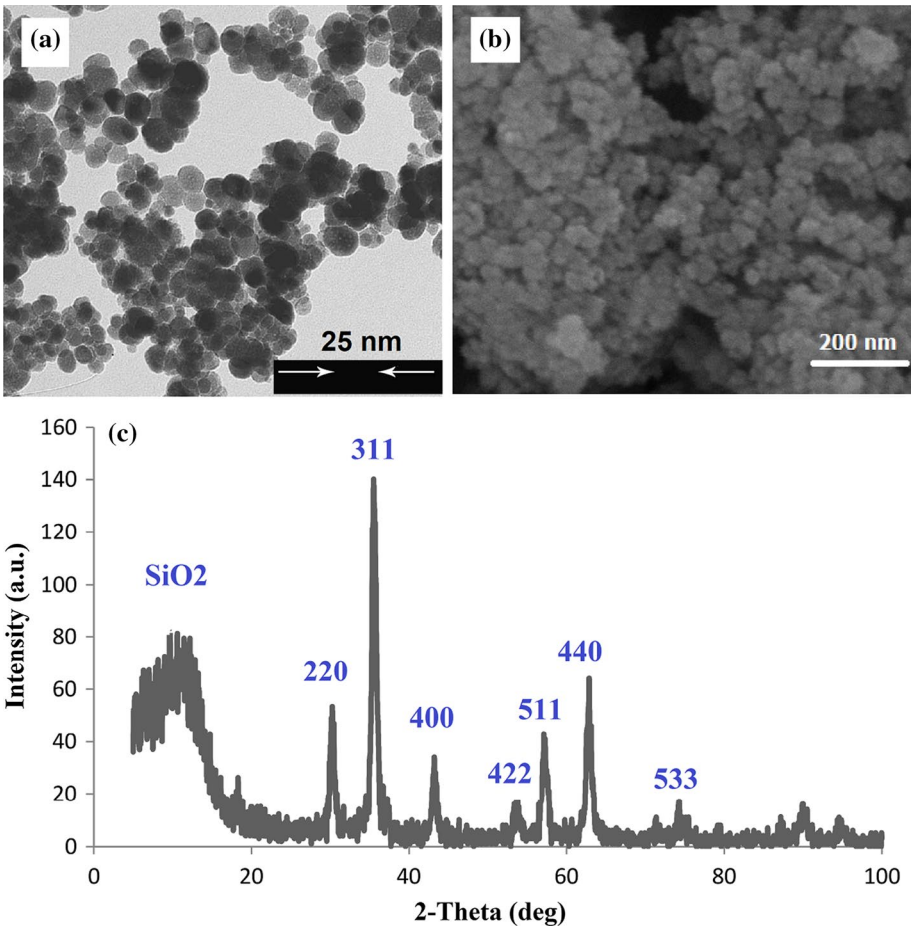


Fig. 2 **a** A TEM image, **b** a SEM image and **c** a XRD pattern of Pd-PFMN catalyst

as received without purification. Magnetic nanoparticles were prepared via the co-precipitation of Fe(III) and Fe(II) ions in the presence of sodium hydroxide based on previous report [28]. Fe_3O_4@SiO_2 nanoparticles were also prepared based on the literature procedure [28]. Pd-PFMN catalyst was prepared based on our previous report [22]. For recording ^{1}H-NMR and ^{13}C-NMR spectra we used a Brucker (250 MHz) Avance DRX, and samples were dissolved in pure deuterated DMSO-d_6 and $CDCl_3$ solvents with tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at 70 eV. FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer) was employed for characterization of the compounds. Melting points were determined in open capillary tubes in Barnstead Electrothermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates.

General procedure for BHAR catalyzed by the Pd-PFMN catalyst

In a conical flask (10 mL) a mixture of aryl halide (1 mmol), amine (3 mmol), K_2CO_3 (2 mmol), and Pd-PFMN catalyst (0.06 g, 1.2 mol%) was stirred for 24 h. Afterward, the mixture was cooled down to room temperature and the catalyst was magnetically separated from the reaction mixture and washed with diethyl ether (2 × 10 mL) followed by deionized and oxygen-free water (2 × 10 mL). The reused catalyst was dried for the next run. The aqueous phase was extracted with diethyl ether (2 × 10 mL) and the combined organic phases were dried over Na_2SO_4. The products were purified by column chromatography (hexane/ethyl acetate) to obtain the desired purity.

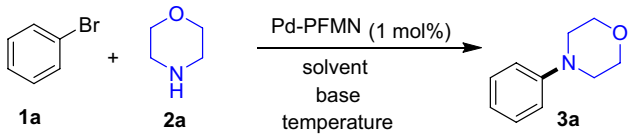
4-Phenylmorpholine (3a)

Yield: 94 %, 152 mg. ^{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, 73.52; H, 8.00; N, 8.51.

4-(4-Nitrophenyl)morpholine (3b)

Yield: 95 %, 198 mg. ^{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

Table 1 Studies of various conditions for the BHAR between bromobenzene and morpholine using Pd-PFMN catalyst



Entry	Solvent	Base	T (°C)	Yield (%)[a]
1	DMF	*t*-BuOK	120	0[b]
2	DMF	*t*-BuOK	120	87
3	DMF	Cs_2CO_3	120	75
4	DMF	K_2CO_3	120	71
5	DMF	*t*-BuOK	130	89
6	DMSO	*t*-BuOK	120	54
7	DMSO	KOH	120	61
8	DMSO	K_2CO_3	120	58
9	DMSO	Cs_2CO_3	120	61
10	Toluene	*t*-BuOK	Reflux	35
11	Toluene	K_2CO_3	Reflux	33
12	–	K_2CO_3	120	94[c]
13	–	Cs_2CO_3	120	93[c]
14	–	*t*-BuOK	120	92[c]
15	–	K_2CO_3	100	88[c]
16	–	K_2CO_3	130	96[c]
17	–	K_2CO_3	120	90[d]
18	–	K_2CO_3	120	95[e]

Reaction conditions: bromobenzene (1 mmol), morpholine (1.2 mmol), solvent (5 mL), base (2 mmol)

[a] Isolated yield

[b] No catalyst used

[c] 3 mmol of morpholine was used

[d] 2 mmol of morpholine was used

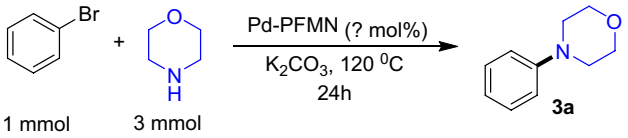
[e] 4 mmol of morpholine was used

(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 $C_{10}H_{12}N_2O_3$(208.2): C, 57.69; H, 5.81; N, 13.45. Found: C, 57.61; H, 5.76; N, 13.40.

4-(2,4-Dinitrophenyl) morpholine (3c)

Yield: 98 %, 248 mg. ^{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 $C_{10}H_{11}N_3O_5$ (253.2): C, 47.43; H, 4.38; N, 16.60. Found: C, 47.37; H, 4.31; N, 16.57.

Table 2 Optimization of catalyst loading for the synthesis of 4-phenylmorpholine using Pd-PFMN catalyst



Entry	Pd-PFMN (mol%)	Yield (%)[a]
1	1.0	94
2	1.2	96
3	1.5	96
4	0.8	89

Reaction conditions: bromobenzene (1 mmol), morpholine (3 mmol), K_2CO_3 (2 mmol)

[a] Isolated yield

4-Morpholinobenzonitrile (3d)

Yield: 91 %, 171 mg. ^{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 $C_{11}H_{12}N_2O$ (188.2): C,70.19; H,6.43; N, 14.88. Found: C, 70.12; H, 6.38; N, 14.82.

4-(4-(Trifluoromethyl)phenyl)morpholine (3e)

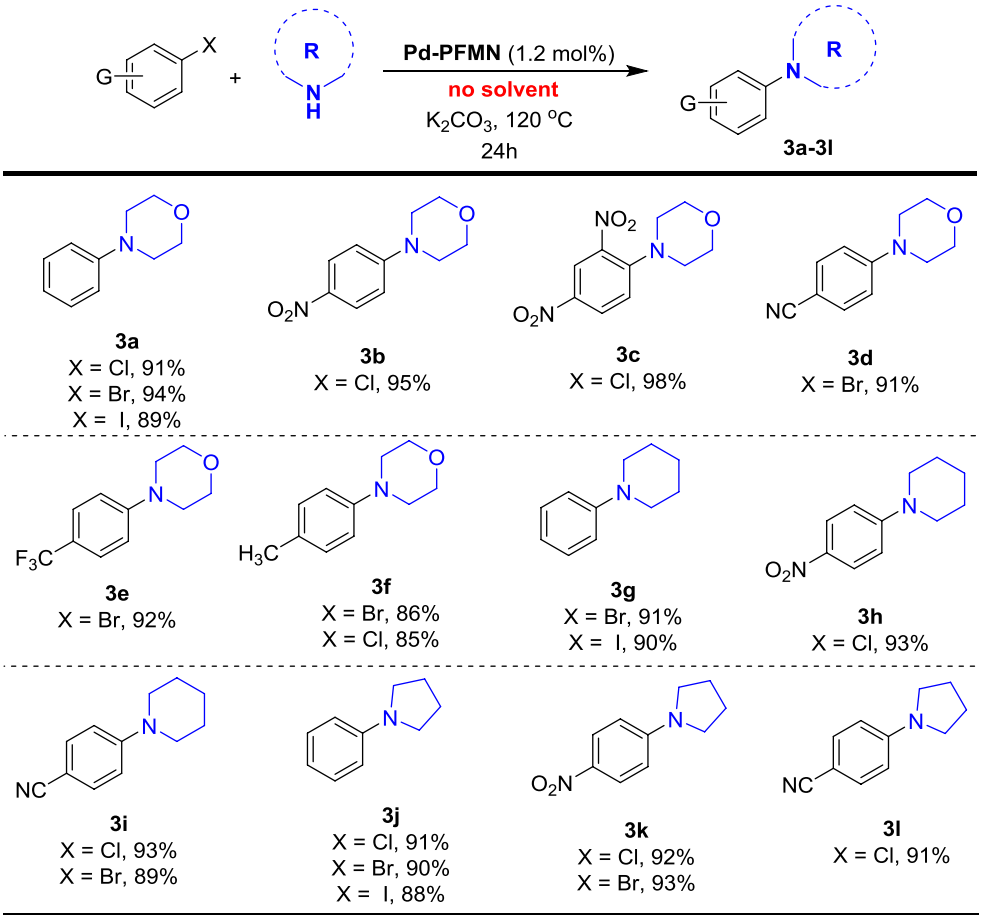
Yield: 92 %, 212 mg. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.22–3.25 (m, 4H), 3.85–3.88 (m, 4H), 8.92 (d, J = 3.5 Hz, 2H), 7.49–7.53 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 48.3, 66.8, 114.4, 120.59 (q, J = 32.3 Hz), 123.0, 126.62 (q, J = 3.7 Hz), 153.5. Anal. Calcd for $C_{11}H_{12}F_3NO$ (231.22): C, 57.14; H, 5.23; F, 24.65; N, 6.06. Found: C, 57.06; H, 5.17; N, 5.98.

4-(*p*-Tolyl)morpholine (3f)

Yield: 86 % 150 mg. ^{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, 74.45; H, 8.44; N, 7.79.

1-Phenylpiperidine (3g)

Yield: 91 %, 146 mg. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.58–1.81 (m, 6H), 3.17–3.19 (4H), 3.83–3.87



Scheme 2 Products of BHAR between different aryl halides and amines using Pd-PFMN catalyst. Reaction conditions: aryl halide (1 mmol), amine (3 mmol), K_2CO_3 (2 mmol). All yields are isolated yields

(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-(4-Nitrophenyl) piperidin (3h)

Yield: 93 %, 191 mg. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.65–1.69 (m, 4H), 3.41–3.44 (m, 4H), 6.76–6.80 (m, 2H), 8.06–8.11 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 24.2, 25.1, 48.3, 112.1, 126.1, 137.2, 154.9. Anal.Calcd. for $C_{11}H_{14}N_2O_2$ (206.24): C, 64.06; H, 6.84; N, 13.5. Found: C, 63.99; H, 6.78; N, 13.42.

4-(Piperidin-1-yl)benzonitrile (3i)

Yield: 93 %, 172 mg. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.65 (m, 6H), 3.32 (m, 4H), 6.81–6.86 (m, 2H), 7.44–7.48 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 24.2, 25.2, 48.4, 101, 6, 107.9, 114.0, 133.5, 160.8.Anal.Calcd. for $C_{12}H_{14}N_2$ (186.26): C, 77.38; H, 7.58; N, 15.04. Found: C, 77.31; H, 7.52; N, 14.96.

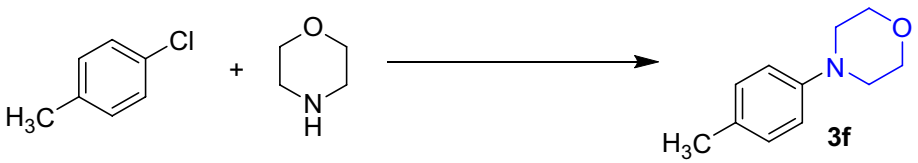
1-Phenylpyrrolidine (3j)

Yield: 91 %, 133 mg. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 2.02–2.07 (m, 4H), 3.32–3.37 (m, 4H), 6.62–6.72 (m, 3H), 7.26–7.31 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) = 25.3, 47.5, 111.5, 115.2, 129.0, 147.8. Anal. Calcd for $C_{10}H_{13}N$ (147.22): C, 81.58; H, 8.90; N, 9.51. Found: C, 81.48; H, 8.80; N, 9.42.

1-(4-Nitro-phenyl)-pyrrolidine (3k)

Yield: 93 %, 178 mg. ^{1}H-NMR (250 MHz, $CDCl_3$/TMS) δ (ppm) = 2.04–2.10 (m, 4H), 3.37–3.42 (m, 4H), 6.46 (dd, J = 9.32, 1.63 Hz, 2H), 8.11 (dd, J = 9.3, 1.7 Hz, 2H). ^{13}C-NMR (62.5 MHz, $CDCl_3$/TMS): δ (ppm) = 25.4, 47.9, 110.4, 126.3, 138.4, 139.4, 163.0. Anal. Calcd. for $C_{10}H_{12}N_2O_2$ (192.21): C, 62.49; H, 6.29; N, 14.57. Found: C, 62.41; H, 6.22; N, 14.23.

Table 3 Comparison of the results of the synthesis of 4-(*p*-tolyl)Morpholine using BHAR catalyzed by Pd-PFMN and other reported methods



Entry	Reaction conditions	Time (h)	Yield (%)[a]	TON[b]	TOF (h^{-1})[c]	References
1	Pd-PFMN (1.2 mol% Pd), K_2CO_3, 120 °C	24	85	71	3.0	This work
2	$Pd_2(dba)_3$ (1 mol%), 2 (2 mol%), NaO-*t*-Bu, toluene, 70 °C	27	98	98	3.6	[3]
3	$Pd_2(dba)_3$ (0.1 mol%), 2 (2 mol%), NaO-*t*-Bu, toluene, 100 °C	19	92	920	48.4	[3]
4	$Pd_2(dba)_3$ (0.5 mol%), 10 (1 mol%), NaO-*t*-Bu, toluene, 100 °C	20	89	178	8.9	[14]
5	$Pd(dba)_2$ (1 mol%), 7 (2 mol%), NaO-*t*-Bu, DME, 120 °C, under N_2	24	93	93	3.9	[19]
6	$Pd(OAc)_2$ (0.5 mol%), 12 (1 mol%), NaO-*t*-Bu, toluene, 80 °C	1	97	194	194	[30]
7	$Pd(OAc)_2$ (1 mol%), Polymer-supported dialkylphosphinobiphenyl ligand (1.3 mol%), NaO-*t*-Bu, toluene, 80 °C	20	90	90	4.5	[31]
8	$Pd(OAc)_2$ (1 mol%), 1 (2 mol%), KOH, toluene, 90 °C	20	97	97	4.8	[32]
10	$Pd(OAc)_2$ (1 mol%), 13 (1 mol%), NaO-*t*-Bu, toluene, 50 °C	2	89	89	44.5	[33]
11	$Pd(dba)_2$ (0.5 mol%), 15 (1 mol%), NaO-*t*-Bu, toluene, 110 °C	20	97	194	9.7	[34]
12	$PdCl_2$/3 (0.5 mol%), NaO-*t*-Bu, DME, 110 °C	48	90	180	3.7	[35]

[a] Isolated Yield

[b] TON = mol product/mol catalyst

[c] TOF = TON/h

4-(Pyrrolidin-1-yl) benzonitrile (3l)

Yield: 91 %, 156 mg. ^{1}H-NMR (250 MHz, $CDCl_3$/TMS) δ (ppm) = 2.01–2.06 (m, 4H), 3.29–3.34 (m, 4H), 6.49 (dd, *J* = 6.9, 2.0 Hz, 2H), 7.43 (dd, *J* = 6.9, 2.1 Hz, 2H). ^{13}C-NMR (62.5 MHz, $CDCl_3$/TMS): δ (ppm) = 25.4, 47.5, 103.7, 111.4, 119.2, 132.9, 133.4, 147.1. Anal.Calcd. for $C_{11}H_{12}N_2$ (172.23): C, 76.71; H, 7.02; N, 16.27. Found: C, 76.65; H, 6.97; N, 16.21.

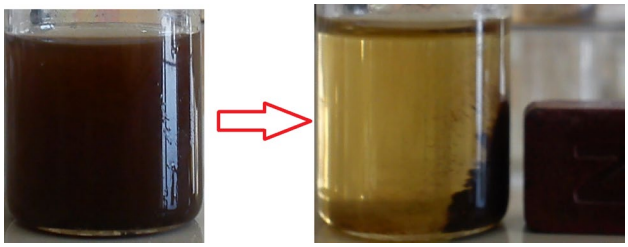
Results and discussion

The heterogeneous Pd-PFMN catalyst was prepared based on our previous procedure in three-step process as shown in Scheme 1 [22].

According to TEM image (Fig. **2a**), the average diameter of the catalyst particles based on the proposed procedure is estimated to be about 10 nm. The SEM image of Pd-PFMN catalyst (Fig. **2b**), show that the catalyst particles are regular in shape and possess near spherical morphology with relatively good monodispersity. This image also established the point that the Pd-PFMN were created with near sphere-shaped morphology. According to the XRD patterns of Pd-PFMN catalyst (Fig. **2c**), the strongest peaks of the XRD pattern correspond to SiO_2, demonstrating the core–shell structure of material. The peaks are indexed as the (220), (311), (400), (422), (511), (440), and (533) planes of the Fe_3O_4 nanoparticle [22]. The Pd-PFMN catalyst was applied in the BHAR to evaluate the catalytic performance in this process. To assess the catalytic reactivity of the Pd-PFMN catalyst, the BHAR between bromobenzene (**1a**) and morpholine (**2a**) was selected as simple model substrate and optimization study is shown in Table 1.

First, the model reaction was checked in the absence of the catalyst in dimethylformamide (DMF) in the presence of potassium *tert*-butoxide (*t*-BuOK), and no product was detected after 24 h (Table 1, entry 1). The Pd-PFMN catalyst was used in DMF for the reaction between bromobenzene and morpholine, as 4-phenylmorpholine (**3a**) was obtained with 87 % isolated yield (Table 1, entry 2). The reaction was also checked in the presence of carbonate bases, but no significant difference in activity was observed (Table 1, entries 3 and 4). When temperature increased to 130 °C, compound **3a** was obtained with 89 % isolated yield (Table 1, entry 5). Also, in the DMSO solvent, the reaction was not improved (Table 1, entries 6–9). The reaction was checked in toluene, but less than 40 % yield of product was obtained (Table 1, entries 10 and 11). A remarkable yield of product was obtained under

Table 4 Reusability of Pd-PFMN catalyst in the BHAR



Entry	Yield of product (%)	Recovery of catalyst (%)
1	94	>99
2	93	98
3	91	>97
4	90	97
5	88	96

Reaction conditions: bromobenzene (1 mmol), morpholine (3 mmol), Pd-PFMN (1.2 mol%), K_2CO_3 (2 mmol) and 120 °C

solvent-free conditions (Table 1, entries 12–16). Thus, solvent-free as the best condition was recognized for the BHAR in the presence of Pd-PFMN catalyst. Afterwards, the catalyst quantity was optimized and 1.2 mol% (0.06 g) [22] of catalyst selected as optimum amount (Table 2).

Accordingly, the BHAR was properly carried out under solvent-free condition in the presence of 1.2 mol% Pd-PFMN catalyst.

It is noteworthy that the Pd-PFMN is a magnetic recyclable catalyst and can easily be separated from the reaction mixture by simple external field attraction. In view of the fact that the Pd-PFMN catalyst was an efficient and reusable catalyst for the BHAR, its catalytic activity was evaluated with other substrates (Scheme 2).

As shown in Scheme 2, the BHAR of a variety of aryl halides proceeded smoothly to furnish the desired products with good to excellent yields. The generality of this protocol was observed by the application of a wide range of aryl halides under the same reaction conditions. The structural diversity of this reaction was investigated using different cyclic aliphatic amines, leading to the formation of arylamines.

In order to demonstrate the applicability of Pd-PFMN catalyst in BHAR, a comparison with some other reported homogeneous and heterogeneous palladium catalysts is presented in Table 3. As shown in Table 3, our catalyst system is comparable with the reported homogeneous and heterogeneous catalysts in efficiency and is compatible with the environment [29–35].

For sensible applications of this heterogeneous catalyst, the level of reusability was also evaluated in the reaction between bromobenzene and morpholine. The recycled catalyst could be reused for at least five times without any treatment (Table 4).

The ICP analysis of the catalyst after five cycles of reusability showed that only a very small amount of the Pd metal (about 1.8 % of Pd) was removed from the substrate. The results confirmed that the supported Pd on the PFMN substrate provides the high catalytic activity without leaching of a significant quantity of Pd.

Conclusions

The catalytic activity of the supported palladium on phosphine-functionalized magnetic nanoparticles (Pd-PFMN) as a magnetic recyclable palladium catalyst was investigated in Buchwald–Hartwig amination reaction. This catalyst system has some advantages with the respect to yield, solvent, and wastes generated when compared to the currently in use BHAR methods. Reusability (five times) and easy workup (catalyst can be separated from reaction mixture using an external magnetic field) were two other advantages of this catalyst system. Using Pd-PFMN catalyst, a range of arylamines was synthesized in good to excellent yields.

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