

# Chemoselective reduction of nitroarenes, *N*-acetylation of arylamines, and one-pot reductive acetylation of nitroarenes using carbon-supported palladium catalytic system in water

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# Abstract

Developing and/or modifying fundamental chemical reactions using chemical industry-favorite heterogeneous recoverable catalytic systems in the water solvent is very important. In this paper, we developed convenient, green, and efficient approaches for the chemoselective reduction of nitroarenes, *N*-acetylation of arylamines, and one-pot reductive acetylation of nitroarenes in the presence of the recoverable heterogeneous carbon-supported palladium (Pd/C) catalytic system in water. The utilize of the simple, effective, and recoverable catalyst and also using of water as an entirely green solvent along with relatively short reaction times and good-to-excellent yields of the desired products are some of the noticeable features of the presented synthetic protocols.

### Graphic abstract



**Keywords** Nitro reduction  $\cdot$  Amine  $\cdot$  Amine N-acetylation  $\cdot$  One-pot  $\cdot$  Nitro reductive acetylation  $\cdot N$ -Arylacetamide  $\cdot$  Heterogeneous catalyst  $\cdot$  Carbon-supported palladium catalytic system  $\cdot$  Pd/C

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Fig. 1 Examples of some drugs bearing aromatic and heteroaromatic amine and N-arylacetamide

# Introduction

Aromatic and heteroaromatic amines, and also *N*-arylacetamides are existed in the structure of various and valuable organic compounds, especially drugs such as amprenavir (HIV-protease inhibitor) [1], sparfloxacin (antibiotic) [2], lorlatinib (anti-cancer) [3], iclaprim (antibiotic) [4], trametinib (anti-cancer) [5], acetaminophen (analgesic) [6, 7], and many others (Fig. 1). In this regard, introducing novel, simple, and efficient protocols for the preparation of diverse amines and *N*-arylacetamides is of great and exceptional value.

The environment around us has been acutely affected by pollution caused by harmful chemical processes (especially in the industrial scales) in recent decades. Therefore, chemists have tried to minimize the detrimental consequences of chemical reactions by designing a series of protocols, which now are known as green chemistry principles. The reaction solvent is the most important decisive factor in the safety of the chemical processes, greenness, and cost-effectiveness [8–14]. Water has received significant attention as an entirely environmentally benign solvent considering it's harmless in contrast to many common hazardous organic solvents. In recent decades, water as a green, abundant, easily accessible, low-cost, and highly efficient reaction solvent has been successfully applied in various organic transformations [15–29]. Therefore, developing new chemical reactions and/or optimization of existing and classical synthetic methods based on water solvent are worthwhile.

In designing a new synthetic protocol, the catalyst has a fundamental role in the industrial and green chemistry point of view [30–34]. Heterogeneous catalytic systems, due to their respective and unique properties, especially for easy recoverability, are attractive in organic synthesis [35–39]. Among various heterogeneous catalytic systems, supported palladium catalysts are significant, well-known, and

practical in numerous organic transformations, even on industrial scales. Supported palladium on carbon (Pd/C) is one of the mentioned systems that has received a lot of attention in recent years. Up to now, numerous catalytic applications of Pd/C have been reported in various organic transformations, including selective reduction of non-aromatic C=C bonds [40–42], hydrogenation of 1,2-cyclohexenedicarboxylates to 1,2-cyclohexanedicarboxylates [43], one-step reduction of carbonyls to hydrocarbons [44], hydrogenation of nitriles [45, 46], chemoselective reductive amination of carbonyl compounds [47], hydrogenation of carbon dioxide (CO<sub>2</sub>) (preparation of formic acid) [48], *N*-methylation of nitroarenes and amines [49], amination of phenols [50], synthesis of  $\alpha$ -carbonyl- $\alpha$ '-amide sulfoxonium ylides [51], C–H bond functionalization of 1,2,3-triazoles [52], one-pot synthesis of 1,2-diaryl azaindoles [55], stereospecific hydrogenolysis of benzyl alcohols [56], synthesis of unsymmetrically substituted triarylamines through a dehydrogenative aromatization strategy [57], and many others.

The literature survey shows that the reduction (or hydrogenation) of the nitro functional group in the presence of the Pd/C catalytic system is a fateful step in the multi-step synthesis of pharmaceutically interesting and agrochemical frameworks (Fig. 2) such as SB-235349 that is a key intermediate compound in the preparation of lotrafiban (oral platelet glycoprotein IIb/IIIa blocker) [58], telmisartan (antihypertensive medicine) [59], PF-4171455 (Toll-like receptor (TLR7) agonist) [60], and broflanilide (insecticide) [61], even in the scales of multi-gram and multi-kilogram.

Due to the importance of developing the Pd/C catalytic system in organic synthesis [62], and in continuation of our research program [63–70], we wish to report convenient, efficient, and environmentally benign strategies for the chemoselective reduction of aromatic nitro compounds (nitroarenes), *N*-acetylation of arylamines, and one-pot reductive acetylation of nitroarenes using mentioned efficacious recoverable heterogeneous catalytic system (Pd/C) in water (Fig. 3).

# **Results and discussion**

#### **Reduction of nitroarenes**

In the past decades, many protocols reported for the reduction of aromatic nitro compounds in the presence of the Pd/C catalytic system that most of them have some drawbacks [71–84]. To the best of our knowledge, the combination system of NaBH<sub>4</sub> and Pd/C for the reduction of an aromatic nitro compound was reported for the first time by Smith in 1987 (Fig. 4, section a) that carried out in methanol:water (60:5) under argon atmosphere [85]. In the same year and only a few months later, Petrini and co-workers described another strategy for the mentioned reaction in THF (Fig. 4, section b) [86]. In the Smith method, some (6%) of the hydrodehalogenated products were obtained, and also the protocol which was reported by Petrini et al. was not controllable, and the hydrodehalogenation process was wholly done along with nitro reduction. In this regard, we decided to introduce a new, efficient, and chemoselective strategy based on green chemistry principles in the reduction of

#### (a) Multi-step synthesis of SB-235349 as a key intermediate compound in the preparation of lotrafiban (ref. [58])



(b) Multi-step synthesis of telmisartan (ref. [59])



(c) Multi-step synthesis of PF-4171455 (ref. [60])



(d) Multi-step synthesis of broflanilide (ref. [61])



Fig. 2 Some examples of the application of the nitro functional group reduction using Pd/C catalytic system in the multi-step synthesis of pharmaceutically interesting and agrochemical frameworks

diverse aromatic nitro compounds using  $NaBH_4$  as a mild reducing agent and recoverable Pd/C catalyst. For this purpose, in the optimization step that the reduction of nitrobenzene (PhNO<sub>2</sub>) in the presence of NaBH<sub>4</sub> (2 mmol) and different amounts of Pd/C catalyst was under-investigated, we did our best to design the nitro reduction reaction in the water solvent (Table 1). On the other hand, we designed some control experiments to the investigation of reducing agent effect on the reduction of PhNO<sub>2</sub> in the presence of the Pd/C catalytic system (30 mg) in the reflux water Chemoselective reduction of nitroarenes, N-acetylation...



Fig. 3 Chemoselective reduction of nitroarenes, *N*-acetylation of arylamines, and one-pot reductive acetylation of nitroarenes using Pd/C catalytic system in water



Fig. 4 Previously reported protocols for the reduction of aromatic nitro compsounds with  $NaBH_4$  catalyzed by Pd/C

(Fig. 5). For this purpose, we used ammonium formate ( $NH_4HCO_2$ ), formic acid ( $HCO_2H$ ), and hydrazine monohydrate ( $NH_2NH_2\cdot H_2O$ ) as well-known and green reducing (or hydrogenating) agents. As exposed in Fig. 5, sodium borohydride is a perfectly effective reducer rather than others. After obtaining the optimal reaction conditions, we expanded our new protocol with various aromatic nitro compounds reduction. As shown in Table 2, all nitroarenes successfully converted to corresponding arylamines in good-to-excellent yields within approximately short

Table 1 Optimization experiments for the reduction of  $PhNO_2$  to aniline with  $NaBH_4$  catalyzed by Pd/C in water





Fig. 5 Control experiments

reaction times (4–15 min). On the other hand, in our method, hydrodehalogenation process was not occurred on the reduction of 3-bromonitrobenzene and 2-chloro-5-nitrobenzaldehyde (Table 2, entries 18 and 19). Also, the reduction of acetamide and carboxylic acid moieties were not possible (Table 2, entries 27 and 28). Unfortunately, molecules with the complexity of nitro and carbonyl functional groups did not show any selectivity in the reduction process and both of the mentioned groups were reduced (Table 2, entries 12, 14, 16, 19, 21, 23, and 25). As shown in Table 2 (entries 13, 15, 17, 20, 22, 24, and 26), in these cases, both of the aldehyde and ketone groups reduced to corresponding alcohols easier and faster than reduction of nitro functional group.

Based on our observation, experimental results, and the Pd/C catalytic behavior, we demonstrated a plausible reaction mechanism for the reduction of aromatic nitro compounds to corresponding arylamines using  $NaBH_4$  catalyzed by Pd/C in water

År NaBH₄ / H₂O / Reflux År 4-15 min 83-93%								
Entry	Substrate	Product	Molar Ratio <sup>a</sup>	Pd/C (mg)	Time (min)	Yield <sup>b</sup> (%)		
1	NO <sub>2</sub>	NH <sub>2</sub>	1:2	30	7	93		
2	NO <sub>2</sub> CH <sub>3</sub>	NH <sub>2</sub> CH <sub>3</sub>	1:2	30	8	84		
3	NO <sub>2</sub> NHNH <sub>2</sub>	NH <sub>2</sub> NHNH <sub>2</sub>	1:3.5	47	10	89		
4	NO <sub>2</sub> OH	NH <sub>2</sub> OH	1:3.5	30	8	86		
5	NO₂ → J	N H2 OH	1:3.5	30	12	89		
6°	NO <sub>2</sub> OH	NH <sub>2</sub> OH	1:2	30	9	90		
7°	NO <sub>2</sub> OH	NH <sub>2</sub> OH	1:2	30	7	87		

Table 2Reduction of nitroarenes using NaBH4 catalyzed by Pd/C in water $NO_2$ (7 wt%) Pd/C $NH_2$ 

Entry	Substrate	Product	Molar Ratio <sup>a</sup>	Pd/C (mg)	Time (min)	Yield <sup>b</sup> (%)
8	NO2 H	Z D D	1:2	30	7	90
9°	NO <sub>2</sub> NH <sub>2</sub>	NH <sub>2</sub> NH <sub>2</sub>	1:2	30	4	83
10°	NO <sub>2</sub>	NH <sub>2</sub>	1:2	30	6	88
11°		NH <sub>2</sub> NH <sub>2</sub>	1:2	30	4	89
12	NO <sub>2</sub> O H	NH <sub>2</sub> OH H	1:3	30	5	85
13	NO <sub>2</sub> O H	NO <sub>2</sub> OH	1:0.5	12	3	88
14	NO <sub>2</sub> H O	NH <sub>2</sub> H H OH	1:3	30	11	86

# Table 2 (continued)

Table 2 (continued)

Entry	Substrate	Product	Molar Ratio <sup>a</sup>	Pd/C (mg)	Time (min)	Yield <sup>b</sup> (%)
15			1:0.5	12	2	89
16°	NO <sub>2</sub>	NH <sub>2</sub> HO H	1:3	30	6	83
17		NO <sub>2</sub> HO	1:0.5	12	2	88
18	NO <sub>2</sub> Br	NH <sub>2</sub> Br	1:2	30	12	90
19°		NH <sub>2</sub> H H Cl OH	1:3	30	14	85
20	NO <sub>2</sub> H Cl O	H H CI OH	1:0.5	12	0.833	88
21°	NO <sub>2</sub> O CH <sub>3</sub>	NH <sub>2</sub> OH HCH <sub>3</sub>	1:3	30	5	85

Entry	Substrate	Product	Molar Ratio <sup>a</sup>	Pd/C (mg)	Time (min)	Yield <sup>b</sup> (%)
22	NO <sub>2</sub> O CH <sub>3</sub>	NO <sub>2</sub> OH H CH <sub>3</sub>	1:1.5	24	1	85
23°	NO <sub>2</sub> CH <sub>3</sub>	NH <sub>2</sub> H CH <sub>3</sub> OH	1:3	30	6	87
24	NO <sub>2</sub> CH <sub>3</sub>	NO <sub>2</sub> H CH <sub>3</sub> OH	1.1.5	24	10	80
25°	NO <sub>2</sub> OCH <sub>3</sub>	HO CH <sub>3</sub>	1:3	30	15	88
26	NO <sub>2</sub> CH <sub>3</sub>	HO CH <sub>3</sub>	1:1.5	24	1	85
27°	NO <sub>2</sub> HN <sub>C</sub> CH <sub>3</sub>	NH <sub>2</sub> HN <sub>C</sub> CH <sub>3</sub>	1:3	30	14	89
28	NO <sub>2</sub> O OH	NH <sub>2</sub> O OH	1:3	30	2	88

 Table 2 (continued)

Table 2	(continued)
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Entry	Substrate	Product	Molar Ratio <sup>a</sup>	Pd/C (mg)	Time (min)	Yield <sup>b</sup> (%)
29°	NO <sub>2</sub> NO <sub>2</sub>	NH <sub>2</sub> NH <sub>2</sub>	1:3	30	7	88
30	NO <sub>2</sub>	NH <sub>2</sub>	1:3	30	8	92

<sup>a</sup>Substrate: NaBH<sub>4</sub>

<sup>b</sup>Yields refer to isolated pure products

<sup>c</sup>In these reactions, NaBH<sub>4</sub> was added portion-wisely

(Scheme 1). Notably, by seeing the production of hydrogen gas  $(H_2)$  inside the reaction vessel, we believe that produced  $H_2$  diffused in the reaction environment and then activated on the Pd surface of the mentioned catalytic system to form H–Pd–H species, which was one of the fundamental steps in the mentioned reduction reaction process.

#### **N-Acetylation of arylamines**

The *N*-acetylation of amines [87, 88], which is one of the famous reactions in organic synthesis, has perpetually been employed as a straightforward and sturdy tool for the protection of amine functional groups in multi-step syntheses and also in the preparation of strategic acetamide-containing organic frameworks. It is worthy to note that efforts to develop this relatively simple and basic chemical reaction are still ongoing. In the past two decades, various *N*-acetylation methods based on diverse catalytic systems such as niobium<sup>V</sup> chloride (NbCl<sub>5</sub>) [89], bismuth ferrite (BiFeO<sub>3</sub>) [90], P(4-VPH)ClO<sub>4</sub> [91], ZnAl<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub> [92], trimethylsilyl chloride-potassium iodide (TMSCl-KI) [93], SiO<sub>2</sub>/PDA-SO<sub>3</sub>H [94], dialuminium nickel tetraoxide (NiAl<sub>2</sub>O<sub>4</sub>) [95], Ni<sub>2</sub>(BDC)<sub>2</sub>(DABCO) [96], Fe<sub>3</sub>O<sub>4</sub>@PEG [97], Fe<sub>3</sub>O<sub>4</sub>@ Chitosan-TCT-Salen-Cu<sup>II</sup> [98], and many others have been reported.

Given the importance of this transformation, we tried to introduce an efficient and environmentally benign method for the *N*-acetylation of arylamines using the Pd/C catalytic system. For the optimization process, which was investigated on the *N*-acetylation of aniline (PhNH<sub>2</sub>), all the reactions were done in water as a green solvent using one mmol of acetic anhydride (Ac<sub>2</sub>O) as an acetylating agent in the presence of a various amount of the Pd/C catalyst (Table 3). After the optimization process, the scope and limitations of the mentioned reaction are explored by various arylamines. As shown in Table 4, all the *N*-acetylation



**Scheme 1** Plausible mechanism for the reduction of nitroarenes to arylamines using NaBH<sub>4</sub> catalyzed by Pd/C in water

 Table 3 Optimization experiments for the N-acetylation of aniline in the presence of the Pd/C catalytic system in water



reactions were performed in relatively short reaction times along with good-toexcellent yields of the desired products. On the other hand, under optimized reaction conditions, the benzylic alcohol group was not converted to the corresponding benzyl acetate, which shows the chemoselectivity of the presented method (Table 4, entries 13 and 14). Furthermore, an acceptable mechanism for this transformation is depicted in Scheme 2.

#### One-pot reductive acetylation of nitroarenes

In organic synthesis and green chemistry, omitting one or more of the synthetic steps in preparing target compound(s) is extremely important. One-pot synthetic approaches are an excellent choice for this purpose due to their several extraordinary benefits, especially reduction in the number of tedious work-up, extraction, and purification steps [99-105]. On the other hand, the transformation of toxic, waste, and cheap substances into strategic molecules is more desirable. Not only aromatic nitro compounds are toxic [106–110], but also are low-price than arylamines. Based on stated reasons, introducing novel, efficient, and environmentally benign protocols for the straightforward one-pot reductive acetylation of nitroarenes in order to the preparation of the substituted N-arylacetamides are valuable. In this research work, we successfully developed a novel, green, efficient, and convenient strategy for the mentioned one-pot reaction by merely combining the reaction conditions that have been obtained from the reduction of nitroarenes (Table 3) and N-acetylation of arylamines (Table 4). As shown in Table 5, the mentioned chemoselective one-pot reductive acetylation protocol performed upon diverse aromatic nitro compounds in satisfactory yields of the desired *N*-arylacetamide.

	NH <sub>2</sub> (7 v I Ar Ac	vt%) Pd/C (24 mg) $\stackrel{\text{NH}}{\underset{2}{\sim}0}$ / H <sub>2</sub> O / Reflux Ar	COCH <sub>3</sub>		
Entry	Substrate	Product	Molar Ratio <sup>a</sup>	Time (min)	Yield <sup>b</sup> (%)
1	NH <sub>2</sub>	NHCOCH <sub>3</sub>	1:1	2	88
2	NH <sub>2</sub> Br	NHCOCH <sub>3</sub> Br	1:1	13	82
3	NH <sub>2</sub> Br	NHCOCH <sub>3</sub>	1:1	10	84
4	NH <sub>2</sub> CI	NHCOCH <sub>3</sub>	1:1	10	84
5	CI		1:2	7	87
6	CI CI	CI CI	1:2	10	86

Table 4 *N*-Acetylation of arylamines using  $Ac_2O$  catalyzed by Pd/C in water  $NH_2$  (7 wt%) Pd/C (24 mg)  $NHCOCH_3$ 

Table 4 (continued)

Entry	Substrate	Product	Molar Ratio <sup>a</sup>	Time (min)	Yield <sup>b</sup> (%)
7	CI	CI	1:1.5	15	87
8	CI CH <sub>3</sub>	CI CI	1:1	15	85
9	CH <sub>3</sub>	CH <sub>3</sub> CH <sub>3</sub> CI	1:1.5	5	85
10	CH <sub>3</sub>	CH <sub>3</sub> CH <sub>3</sub>	1:1	10	85
11	NH <sub>2</sub> CH <sub>3</sub>	NHCOCH <sub>3</sub>	1:1	5	88
12	CH <sub>3</sub> CH <sub>3</sub>	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	1:1	8	85



Table 4 (continued)

<sup>a</sup>Substrate: Ac<sub>2</sub>O

<sup>b</sup>Yields refer to isolated pure products



Scheme 2 Acceptable mechanism for the N-acetylation of arylamines using  $Ac_2O$  catalyzed by Pd/C in water

# Experimental

#### Reagents, samples, and apparatus

Chemicals were purchased from the Merck, Fluka, and Sigma-Aldrich chemical companies and directly used without any purification step. Melting points were determined on an Electrothermal 9200 apparatus. Infrared spectra were recorded on a Nexus 670 Thermo Nicolet Fourier transform infrared spectrometer and measured as KBr discs. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance spectrometer at 300 MHz in CDCl<sub>3</sub> with tetramethylsilane (TMS) as an internal standard.

# General procedure for the reduction of nitroarenes to arylamines catalyzed by Pd/C

For example, in a round-bottom flask (15 mL) equipped with a magnetic stirrer, a mixture of PhNO<sub>2</sub> (1 mmol, 0.123 g) and H<sub>2</sub>O (2 mL) was prepared. Then, (7 wt%) Pd/C (30 mg) was added, and the mixture was stirred. At the next step, NaBH<sub>4</sub> (2 mmol, 0.076 g) was added, and the resulting mixture continued to stir at reflux for 7 min. After completion of the reaction (monitored by thin-layer

NO <sub>2</sub> (7 wt%) Pd/C NHCOCH <sub>3</sub>								
, År 1) NaBH₄ / H₂O / Reflux År 2) <mark>Ac₂O / H₂O / Reflux 79-89%</mark> 8-20 min								
Entry	Substrate	Product	Molar Ratio <sup>a</sup>	Pd/C (mg)	Time (min)	Yield <sup>b</sup> (%)		
1	NO <sub>2</sub>	NHCOCH <sub>3</sub>	1:2:1	30	9	88		
2	CH <sub>3</sub>	CH3	1:2:1	30	15	88		
3	NO <sub>2</sub> OH	NHCOCH <sub>3</sub> OCOCH <sub>3</sub>	1:3.5:2	30	13	85		
4	NO <sub>2</sub> OH	NHCOCH <sub>3</sub>	1:3.5:2	30	18	88		
5°	NO <sub>2</sub> OH	NHCOCH <sub>3</sub> OH	1:2:1	30	15	87		
6°	NO <sub>2</sub> OH	OH	1:2:1	30	12	86		
7	NO <sub>2</sub>	NHCOCH <sub>3</sub>	1:2:1	30	12	87		



Entry	Substrate	Product	Molar Ratio <sup>a</sup>	Pd/C (mg)	Time (min)	Yield <sup>b</sup> (%)
8°	NO <sub>2</sub> NH <sub>2</sub>	NHCOCH <sub>3</sub> NHCOCH <sub>3</sub>	1:2:2	30	12	80
9°	NO <sub>2</sub>	NHCOCH <sub>3</sub>	1:2:2	30	10	81
10°	NO <sub>2</sub> NH <sub>2</sub>	NHCOCH <sub>3</sub>	1:2:2	30	8	89
11°	NO <sub>2</sub> O H	CH <sub>3</sub> COHN OH	1:3:1	30	12	86
12	NO <sub>2</sub> H	NHCOCH <sub>3</sub> H H OH	1:3:1	30	13	85
13°	NO <sub>2</sub>	HO H	1:3:1	30	10	89
14°		NHCOCH <sub>3</sub> H H CI OH	1:3:2	30	20	89

Entry	Substrate	Product	Molar Ratio <sup>a</sup>	Pd/C (mg)	Time (min)	Yield <sup>b</sup> (%)
15°	CH <sub>3</sub>	H H OH	1:3:2	30	14	79
16°	NO <sub>2</sub>	HCOCH3 HOCH3	1:3.25:2	47	14	79
17°	NO <sub>2</sub> NHCOCH <sub>3</sub>	NHCOCH <sub>3</sub>	1:3:2	30	18	80
18°	NO <sub>2</sub> NO <sub>2</sub>	NHCOCH <sub>3</sub>	1:3:3	40	12	87
19	NO <sub>2</sub>	NHCOCH <sub>3</sub>	1:2:2	30	12	85

Table 5 (continued)

<sup>a</sup>Substrate: NaBH<sub>4</sub>:Ac<sub>2</sub>O

<sup>b</sup>Yields refer to isolated pure products

<sup>c</sup>In these reactions, NaBH<sub>4</sub> was added portion-wisely

chromatography (TLC) using CCl<sub>4</sub>:ether (5:2) as an eluent), the mixture was cooled to room temperature, and the mentioned catalytic system was separated by filtration. The reaction mixture was extracted with dichloromethane (DCM)  $(3 \times 5 \text{ mL})$  and then dried over anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>). Finally, the solvent was evaporated under reduced pressure to afford the pure liquid aniline in 93% yield.

# General procedure for the N-acetylation of arylamines catalyzed by Pd/C

To the synthesis of *N*-phenylacetamide (acetanilide) as a representative example, a mixture of aniline (1 mmol, 0.093 g) and H<sub>2</sub>O (2 mL) was prepared in a round-bottom flask (15 mL), which equipped with a magnetic stirrer. Then, Pd/C (24 mg) was added into the reaction environment, and the resulting mixture was stirred at reflux. Next, Ac<sub>2</sub>O (1 mmol, 0.102 g) was added to the prepared mixture followed by stirring for 2 min at reflux. After completion of the acetylation reaction (monitored by TLC using *n*-hexane:EtOAc (5:1) as an eluent), the mixture was cooled to room temperature, and the Pd/C catalyst was separated by filtration. Then, the reaction mixture was extracted with DCM ( $3 \times 5$  mL) and then dried over Na<sub>2</sub>SO<sub>4</sub>. Finally, evaporation of the solvent under reduced pressure afforded the pure acetanilide in 88% yield.

# General procedure for the one-pot reductive acetylation of nitroarenes catalyzed by Pd/C

As an example, PhNO<sub>2</sub> (1 mmol, 0.123 g) was mixed with 2 mL of H<sub>2</sub>O in a 15 mL round-bottom flask equipped with a magnetic stirrer. Then, Pd/C (30 mg) was added, and the mixture was stirred. Next, NaBH<sub>4</sub> (2 mmol, 0.075 g) was added, and the resulting mixture was stirred under reflux conditions for 7 min. After completion of the reduction reaction, acetic anhydride (1 mmol, 0.102 g) was added to the reaction mixture, followed by stirring for an additional 2 min at reflux. Afterward, the mixture was cooled to room temperature, and the Pd/C catalyst was separated by filtration. Then, the reaction mixture was extracted with DCM (3×5 mL) and then dried over Na<sub>2</sub>SO<sub>4</sub>. Finally, evaporation of the solvent under reduced pressure afforded the pure acetanilide in 88% yield.

# Conclusion

In summary, we have tried to develop convenient, environmentally benign, and efficient methodologies for the chemoselective reduction of nitroarenes, *N*-acetylation of arylamines, and one-pot reductive acetylation of nitroarenes in the presence of the recoverable heterogeneous carbon-supported palladium (Pd/C) catalytic system in water. Due to the utilizing of the simple, capable, and recoverable catalyst, along with using water as a green solvent, relatively short reaction times, good-to-excellent yields of the desired products, all three introduced synthetic strategies can apply to the chemical industry.

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#### Declarations

Conflict of interest The authors declare no conflict of interest.

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