## RESEARCH



# Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) nanocomposite: a novel, efficient, and reusable heterogeneous catalyst for carbonylative preparation of *N*-aryl amides

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## Abstract

*N*-aryl amides hold significant importance in organic chemistry due to their widespread presence in pharmaceuticals, agrochemicals, and various bioactive compounds. As a result, catalysts and preparation methodologies for amide derivatives have long been a target of active investigation of interest. In the current work, a simple and accessible route was adopted for preparation of a magnetic catalyst [ $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd$  (0)] and then its catalysis in three-component amide synthesis via carbonylation reaction between aryl iodides and amines was examined. In experiments, its efficiency in producing a range of amides with high yields in a short and under mild conditions was unequivocally confirmed, and its efficiency in producing a range of amides with high yields of the desired compound ease in catalyst separation, high reusability of catalysts, mild reaction conditions, ease in accommodation of a range of substrates, and a thorough analysis for determination of the catalyst and produced compounds for characterization and purification have been taken as key features of this work.

**Keywords**  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  nanomaterial, Magnetic nanocatalyst, *N*-Aryl amides, High reusability, Azidation/carbonylation reactions

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## Introduction

N-aryl amides are key significant compounds in a variety of scientific areas [1, 2]. N-aryl amides have specific structures and multi-faceted functional capabilities that make them significant in a variety of areas of study [3, 4]. N-aryl amides form a fundamental constituent of the structure of thousands of drugs, amino acids, proteins, and bioactive compounds [3]. N-aryl amides' widespread use in drugs is significant, with many drugs featuring this functional group due to its stability and hydrogen bonding potential, a high value for biological activity [5, 6]. In organic and inorganic chemistry, N-aryl amides have a significant role in forming peptides and proteins, and serve as a fundamental bond in these basic biomacromolecules [7, 8]. In pharmacy, too, N-aryl amides have utility, with a high proportion of all approved drugs and drug candidates featuring at least one amide bond, a reflection of the key role played by this functional group in drug discovery and development [9–11]. Interaction between an amide and a biological target, including hydrogen bonding and N–H pKa, is of high value in new drug development [10].

However, their applications are not limited to organic chemistry; inorganic chemists use amides because of their chelating properties in providing a ligand, which makes them important in generating a variety of coordination complexes [12–14]. Therefore, the preparation of N-aryl amides is an important area of study, with work underway to develop increasingly efficient and environmentally friendly processes for their generation, a reflection of their usefulness in science and industry [15–17].

The formation of *N*-aryl amides through carbonylative processes is of high utility with its efficient incorporation of the carbonyl group (C=O) into the amide linkage [18, 19]. This method utilizes carbon monoxide, an abundant and cheap C1 source, in the presence of a catalyst, most often palladium, to drive the carbonylation of aryl halides with amines [20]. The reaction is



Scheme 1 Structurally detailed for the preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst

useful in that it tends to occur under mild reaction conditions, can exhibit high selectivity, and is tolerant to a variety of substrates [21, 22]. Besides, innovation in carbonylation processes has added an additional level of sustainability to this method, allowing for the use of environmentally friendly and economically feasible catalytic systems, which can make processes environmentally friendly and economically feasible [23–25]. *N*-aryl amide formation through carbonylative processes is a pillar skill of modern synthetic chemistry [26]. This reaction permits the preparation of complex and structurally diverse molecules with future utility in a variety of industries [27]. Multicomponent processes (MCRs) have a significant role in simplifying complex chemical syntheses by allowing several bonds to form in a single operational stage. Not only does this method enhance synthetic efficiency and atom economy but it also utilizes the magnetism of the catalyst for ease of catalyst recovery and reusability, in compliance with sustainable chemistry tenets. By combining the utility of an efficient catalyst with an efficient multicomponent reaction, such a strategy affords a powerful and flexible tool for the efficient preparation of amides, a feature of widespread utility in industries, including pharmaceuticals and materials science [28–34].

As a catalyst for chemical processes, stabilised palladium over magnetic nanoparticles of  $Fe_3O_4$  possesses numerous advantages [35–37]. For one, nanoparticles, with a high surface area, have increased activity for catalysts, allowing for accelerated and efficient reaction [38–40]. Iron nanoparticles' magnetism simplifies catalyst separation and its reuse, minimizing loss and being both cost-effective and environmentally friendly [41]. In addition, supported palladium is increased in its stability and can be reused with little loss in activity [42–44]. Due to its property, it is an economically and environmentally friendly option for a variety of industrial processes [45–47].

In addition, the use of such catalysts provides the possibility of improving the selectivity of reactions, which helps in increasing the desired products [48, 49]. Therefore, such technology is a major advance in the field of catalysis, as it combines the catalytic properties of palladium with the ease of its separation by an external magnet from the reaction medium [50–53].

In this study, we offer a new and effective technique for creating a range of *N*-aryl amides. A magnetic catalyst [Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd (0)] is used in this process, which enables carbonylation reactions between aromatic iodides and aromatic amines. This strategy is distinct since it is predicated on ecologically favorable circumstances, rendering it a viable and resource-efficient choice.

## Experimental

All the materials for this work were purchased from Fisher and Merck. The reagents and solvents obtained from Sigma-Aldrich, Fluka, or Merck were used without further purification. We monitored the reactions using thin-layer chromatography (TLC) and performed column chromatography using Merck silica gel (230–400 mesh). Additionally, we recorded <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra using a Bruker DRX-400 spectrometer at 400 and 100 MHz, respectively.

## General approach for preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/ DI(S-NH)-Pd(0) nanocatalyst

Initially, magnetic  $Fe_3O_4$  nanoparticles were synthesized following a previously established protocol [56]. Subsequently, 1 g of  $Fe_3O_4$  was dispersed in 100 mL of water through ultrasonication for 1 h. These nanoparticles are then coated with a silica shell by reacting with tetraethyl orthosilicate (TEOS) and polyethylene glycol (PEG) in



catalyst

ethanol under basic conditions (NH<sub>3</sub>, H<sub>2</sub>O) for 24 h at room temperature, yielding Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. While stirring at ambient temperature, 3 mmol of 3,4-dihydroxybenzoic acid was introduced into the Fe<sub>3</sub>O<sub>4</sub> suspension, and the resulting mixture was stirred under reflux conditions for 8 h. Next, the disulfide-containing organic ligand 2,2'-disulfanediyldianiline is synthesized (by reaction of 2-aminobenzenethiol with mixture of hydrogen peroxide in ethanol at room temperature after in 2 h). This ligand is then reacted with 4-chloromethyl-3,5-dihydroxybenzoic acid (DHB) to form the DHB/DI(S-NH) ligand, which is subsequently anchored onto the  $Fe_3O_4@$ SiO<sub>2</sub> nanoparticles by reacting in ethanol under reflux for 8 h, resulting in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH). Finally, the palladium catalyst is immobilized onto the support by reacting Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH) (2 mmol) with PdCl2 (5 mmol) was added to a suspension of 1 g of ultrasonically dispersed Fe<sub>3</sub>O<sub>4</sub>@BA/Amine MNPs in 100 mL of ethanol, and the mixture was refluxed for 12 h. The Pd(II) is then reduced to Pd(0) using NaBH<sub>4</sub> (2 mmol) in ethanol, yielding the final Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) nanocatalyst. The resulting material consists of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles functionalized with the DHB/DI(S-NH) ligand, which in turn coordinates Pd(0) atoms, creating the catalytically active sites, product was





Fig. 2 SEM images of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) Nano composite at varying magnification measurements

magnetically separated, washed with hot water and ethanol, and dried at room temperature.

## General approach for preparation of N-aryl amides catalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0)

A solution was prepared by combining aryl iodides (0.4 mmol), Mo(CO)<sub>6</sub> (0.6 mmol), aromatic amines (0.4 mmol), KOAc (1.5 equiv), and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst (7 mol%) in PEG (3 mL). The resulting mixture was then stirred at 100 °C for 4 h. After the reaction, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst was easily separated using an external magnet. The reaction mixture was then cooled to room temperature, and 30 mL of water was added. The mixture was then extracted three times with 30 mL portions of EtOAc. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, followed by concentration under vacuum. The resulting residue was purified using silica gel column chromatography with a petroleum ether/ethyl acetate eluent system, yielding pure amide products with high yields. The structure of the amide products was confirmed through <sup>1</sup>H NMR and <sup>13</sup>C NMR analysis (Inserted in Supplementary File).

## **Results and discussion**

The  $Fe_3O_4@SiO_2$ -DHB/DI(S-NH)-Pd(0) nanomaterial was prepared by a straightforward procedure in Scheme 1. First,  $Fe_3O_4$  nanoparticles are prepared by a co-precipitation reaction of  $FeCl_2 \cdot 4H_2O$  and  $FeCl_2 \cdot 6H_2O$ in water under a  $N_2$  atmosphere at 80 °C for 1 h followed by NH<sub>4</sub>OH treatment. Then, an outer silica layer is coated on these nanoparticles by reaction with tetraethyl orthosilicate (TEOS) and polyethylene glycol (PEG) in ethanol under basic conditions (NH<sub>3</sub>, H<sub>2</sub>O) at room temperature for 24 h to give Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>.

Next, the disulfide-containing organic ligand 2, 2'-disulfanediyldianiline is synthesized. This ligand is then reacted with 4-chloromethyl-3, 5-dihydroxybenzoic acid (DHB) to form the DHB/DI(S-NH) ligand, which is subsequently anchored onto the Fe3O4@SiO2 nanoparticles by reacting in ethanol under reflux for 8 h, resulting in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH).

Lastly, the palladium catalyst is supported onto the support through reaction of  $Fe_3O_4@SiO_2-DHB/DI(S-NH)$  with  $PdCl_2$  in refluxing ethanol for 12 h. The NaBH<sub>4</sub> then reduces the Pd(II) to form Pd(0), and the final nanocatalyst,  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$ , is produced. Product is nanoparticles of  $Fe_3O_4@SiO_2$ that have been functionalized with DHB/DI(S-NH).

The nanomaterial  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$ was thoroughly characterized using various spectroscopic tools. FT-IR spectra were obtained from the synthesized  $Fe_3O_4$  NPs,  $Fe_3O_4@SiO_2$ ,  $Fe_3O_4@SiO_2-DHBC$ ,  $Fe_3O_4@SiO_2-DHB/DI(S-NH)$ , and  $Fe_3O_4@SiO_2-DHB/$ DI(S-NH)-Pd(0) catalyst, and the results are presented in Fig. 1. The spectrum provided valuable insights, confirming the successful formation of the samples. Notably, the presence of the Fe–O bond was established by a distinct peak at around 582 cm<sup>-1</sup>, while the broad peak at





Fig. 3 TEM images and particles size histogram of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) nanocomposite



Fig. 4 TGA and BET analyses of  $Fe_3O_4@SiO_2$ -DHB/DI(S-NH)-Pd(0) nanocomposite



Fig. 5 Elemental mapping and EDX analysis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) nanocomposite



Fig. 6 XRD patterns and VSM spectrums of Fe<sub>3</sub>O<sub>4</sub> NPs and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst



Scheme 2 Preparation of N-(p-tolyl)benzamide (product 4a) in the absence of Fe<sub>3</sub>O<sub>4</sub>@BA-Imid-Pyrim-Pd(0) nanocatalyst

3300 cm<sup>-1</sup> indicated the presence of OH groups on the nanoparticles' surface. Furthermore, the peaks around 2800 cm<sup>-1</sup> suggested the presence of bonding aromatic C–H groups. Additionally, the peak at 1620 cm<sup>-1</sup> indicated the formation of a C–N bond, signifying the bonding of the ligand with the palladium metal.

In light of this, SEM and TEM analyses were taken from the synthesized  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  nanocatalyst (Figs. 2 and 3). SEM and TEM photographs

of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst clearly showed that the particles are spherical; spherical particles are uniformly distributed, and their average size is approximately 15–30 nm. The average particle size is measured at 20.32 nm, indicating a relatively narrow size distribution. This suggests that there is minimal variation in particle dimensions, with most of the particles exhibiting a similar size. The consistency in size may have implications for their behavior and interaction in various

1 0.4 mm	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Product 4a
Entry	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -DHB/DI(S-NH)-Pd(0) nanocatalyst (mol%)	Yield (%) <sup>a</sup>
1	3 mol%	63%
2	4 mol%	77%
3	5 mol%	82%
4	6 mol%	85%
5	7 mol%	88%
6	8 mol%	88%
7	10 mol%	88%

Table 1 Effect of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) nanocatalyst in the model reaction (product 4a)

<sup>a</sup> Yields referred to isolated products

<sup>b</sup> Conditions: lodobenzene (0.4 mmol), 4-methyl aniline(0.4 mmol), Mo(CO)<sub>6</sub> (0.6 mmol) and solvent (1 mL)



Scheme 3 Preparation of N-(p-tolyl)benzamide (product 4a) in the absence of base

applications, emphasizing the homogeneity of the particle sample.

In the TGA analysis of the synthesized  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  nanocatalyst, Approximately 22% of the overall weight was lost., as illustrated in Fig. 4. The solvent and (OH) groups are responsible for the 7% weight loss below 250 °C. In comparison, the weight loss of about 15% in the temperature range of 250 to 750 °C is due to the decomposition of functional groups and palladium stabilized on  $Fe_3O_4$  NPs. In addition to these findings, Fig. 4 also presents the N<sub>2</sub> adsorption and

desorption isotherms and the pore size distribution curve for the  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  material. These results reveal a porous structure within the  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  composite. Upon analysis using the BJH method, the calculated pore size was determined to be 20 nm, with the majority of the pores located in the mesopore region, a finding consistent with the TEM result. Furthermore, the specific surface area of the  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  microspheres, determined through BET analysis, was 130.6 m<sup>2</sup> g<sup>-1</sup>. This mesoporous structure is advantageous as it contributes

## Table 2 Effect of base in the model reaction (product 4a)

1 U 0.4 mmol	H2N     7 mol%       +     Me       2     0.4 mmol       Mo(CO)6       0.6 mmol	⇒ O Me C Product 4a
Entry	Base	Yield (%) <sup>a</sup>
1	K <sub>2</sub> CO <sub>3</sub>	88%
2	Na <sub>2</sub> CO <sub>3</sub>	81%
3	КОН	72%
4	DBU	43%
5	Et <sub>3</sub> N	69%
6	КОАс	92%
7	K <sub>3</sub> PO <sub>4</sub>	34%
8	t-BuOK	39%

<sup>a</sup> Yields referred to isolated products

<sup>b</sup> Conditions: lodobenzene (0.4 mmol), 4-methyl aniline(0.4 mmol), Mo(CO)<sub>6</sub> (0.6 mmol) and solvent (1 mL)

to an increased specific surface area, ultimately enhancing the material's catalytic performance.

The analyzed  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$ nanocatalyst was examined using two powerful spectroscopic techniques, Energy Dispersive X-ray Spectroscopy (EDX) and elemental mapping. The detailed analysis, as seen in Fig. 5, confirmed the presence of the critical elements Fe, O, Si, C, N, and Pd in the complex catalyst structure of Fe3O4@SiO2-DHB/DI(S-NH)-Pd(0). Detailed analysis is unequivocal evidence of successful catalyst synthesis. In addition, inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis confirms the results by the presence of  $1.24 \times 10-3$  mol/g of palladium within the catalyst structure.

The XRD patterns of synthesized  $Fe_3O_4$  NPs and  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  nanocatalysts are represented in Fig. 6. X-ray diffraction (XRD) of the nanocatalyst showed several peaks closely resembling

previously documented samples in the literature [51]. It proves that, even with metal stabilization and surface modification, the structure of magnetic  $Fe_3O_4$  nanoparticles did not change. To explore the magnetism of the  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  catalyst, the VSM spectra of Fe3O4 NPs and  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  catalyst are represented in Fig. 6. The  $Fe_3O_4$  NPs showed a high magnetism property (70.247 emu/g). Nevertheless, with a postmodification of the surface of Fe3O4 NPs and metal stabilization with palladium, its magnetism property showed a decrement. As seen in Fig. 6, even with a nanocatalyst of  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$ , its magnetism character showed a high value (49.126).

## **Catalytic investigation**

We conducted a series of template reactions using iodobenzene, 4-methyl aniline, and  $Mo(CO)_6$  to identify the

1 U 0.4 mmol	$H_2N$ $+$ $B_2$ $2$ $0.4 \text{ mmol}$ $Mo(CO)_6$ $0.6 \text{ mmol}$ $7 \text{ mol\%}$ $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$ $KOAc, Solvent °C, 4 \text{ h}$	Product 4a
Entry	Solvent (°C)	Yield (%) <sup>a</sup>
1	DMF (100 °C)	88%
2	$H_2O$ (Reflux)	42%
3	EtOH (Reflux)	83%
4	Toluene (100 °C)	37%
5	Dioxane (100 °C)	51%
6	MeCN (Reflux)	85%
7	Anisole (100 °C)	90%
8	Solvent-Free (100 °C)	7%
9	PEG (100 °C)	97%

<sup>a</sup> Yields referred to isolated products

<sup>b</sup> Conditions: lodobenzene (0.4 mmol), 4-methyl aniline(0.4 mmol), Mo(CO)<sub>6</sub> (0.6 mmol) and solvent (1 mL)

ideal conditions for synthesizing amides. We systematically assessed the impact of catalysts, solvents, and bases on the reactions. Initially, when the reaction was carried out without the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst and with potassium carbonate base in DMF solvent, no product 4a was observed after 24 h (Scheme 2). However, introducing the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst successfully synthesized the model product 4a with high yields. Further investigation revealed that 7 mol% of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst was the optimal amount for amide synthesis (Table 1, Entry 5). Subsequent tests without a base in the presence of the optimal amount of the catalyst did not yield product 4a (Scheme 3). Consequently, we explored the impact of various organic bases and determined that KOAc was the most practical base for the reaction (Table 2, Entry 6). Finally, using the optimal amount of the catalyst and KOAc base, we screened the model reaction in different solvents to determine the best conditions for amide synthesis (Table 3). The results demonstrated that the highest yield was achieved when PEG was employed as the solvent at 100 °C (Table 3, Entry 9).

Under optimal conditions, using 7 mol% of  $Fe_3O_4@$ SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst in the presence of KOAc in PEG at 100 °C for 4 h, we evaluated the effectiveness of the system in synthesizing various derivatives of amides through the reaction of different aryl iodides and aromatic amines (Table 4). Despite the presence of substitutions on the phenyl ring in aryl iodides and anilines, all amide products were synthesized with high efficiency. The results indicated that having electrondonating substituents on the ring made the reaction



Table 4 Scope of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) nanocatalyst in synthesis of *N*-aryl amides

## Table 4 (continued)

<sup>a</sup> Yields referred to isolated products

<sup>b</sup> Conditions: Iodobenzene (0.4 mmol), 4-methyl aniline(0.4 mmol), Mo(CO)<sub>6</sub> (0.6 mmol) and solvent (1 mL)



**Scheme 4** Suggested mechanism for synthesis of amides [preparation of *N*-(*p*-tolyl)benzamide (product 4a) as a model reaction] catalyzed by  $Fe_3O_4@SiO_7-DHB/DI(S-NH)-Pd(0)$  nanocomposite



Fig. 7 Recyclability-results of the  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  nanocatalyst for synthesis of N-(p-tolyl) benzamide (product 4a)

easier and allowed for the synthesis of products with higher yields. The physical properties of all the obtained products aligned with those reported in previous methods. NMR analysis was used to confirm the structure of the amide products, and it confirmed the successful preparation of all amide derivatives.

We have proposed a detailed mechanism for the synthesis of amides using the preparation of N-(p-tolyl) benzamide (product 4a) as a model reaction; this process is catalyzed by the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) nanocomposite, as illustrated in Scheme 4. The proposed catalytic cycle, outlined in Scheme 4, initiates with the oxidative addition of an aryl iodide to the palladium(0) species, generating a Pd(II) intermediate (A). This step is crucial for the subsequent nucleophilic addition reactions. Intermediate A then reacts with an amine, potentially through a concerted or stepwise mechanism, leading to the formation of another Pd(II) species (B) and the target amide product (4a). A key feature of this catalytic system is the use of  $Mo(CO)_6$  as a CO source under heat, which facilitates the reductive elimination of the active Pd(0) species from the Fe<sub>3</sub>O<sub>4</sub>@BA-Imid-Pyrim-Pd(0) nanocomposite, regenerating the catalyst for subsequent cycles. This regeneration is accompanied by



Fig. 8 SEM and TEM images of the reused Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst



Fig. 9 FT-IR, XRD spectrums of fresh and reused Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst

the release of CO, which likely coordinates to the palladium, promoting the reductive elimination. The magnetic separability of the catalyst simplifies product purification and allows for catalyst recovery and reuse, aligning with green chemistry principles.

The recovery of catalysts from chemical processes is crucial to sustainable and environmentally friendly chemistry. In this study, we examined the potential for reusing the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) nanocatalyst in the production of product 4a. The Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst was easily separated from the reaction mixture using an external magnet and was then washed with ethyl acetate for reuse. Remarkably, our results demonstrated that the Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>-DHB/DI(S-NH)-Pd(0) catalyst maintained its catalytic efficiency over eight successive reuse cycles, as illustrated in Fig. 7. In addition, thorough spectroscopic analysis, i.e., SEM, TEM, FT-IR, XRD, and ICP-OES, confirmed that reused catalyst structure (Figs. 8, 9), morphology, and Pd content remained almost constant compared to the fresh state  $(1.24 \times 10^{-3} \text{ mol/g})$  and only a tiny amount was reduced  $(1.23 \times 10^{-3} \text{ mol/g})$  after 8 times, indicating its robustness and potential for sustainable use.

To showcase the effectiveness of this approach, we compared the results obtained from the synthesis of N-aryl amides using our method with those reported in the literature (see Table 5). Our findings illustrate that our method possesses multiple noteworthy advantages. These include the use of a recyclable and green



Table 5 Comparison of the results of this method with reported methods for synthesis of N-aryl amides

catalyst, conducting reactions in an optimum period of time, achieving high product yields, and carrying out reactions at mild conditions following the principles of green chemistry.

## Conclusion

This paper presents a novel protocol for the synthesis of various amides. This strategy is based on the threecomponent carbonylation reaction of aryl iodides and aromatic amines by the nanocatalyst  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  as a magnetically recoverable catalyst. This approach is not only general and efficient but also environmentally compatible. Several techniques well studied the structure of this nanocatalyst, and the successful synthesis of  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  nanocatalyst was confirmed. The results of VSM analysis confirmed the high properties of magnetic nanocatalyst both before and after recovery. Various aryl iodides readily participated in the carbonylation reaction alongside aromatic amines, facilitated by the  $Fe_3O_4@SiO_2-DHB/DI(S-NH)-Pd(0)$  catalyst. This resulted in synthesizing the desired amide products with highly impressive yields.

## Abbreviations

- TEM Transmission electron microscopy
- SEM Scanning electron microscopy
- FT-IR Fourier-Transform Infrared Spectroscopy
- TGA Thermogravimetric analysis
- VSM Vibrating sample magnetometry
- XRD X-ray diffraction
- PEG Polyethylene glycol
- BET Brunauer–Emmett–Teller
- EDX Energy-dispersive X-ray
- ICP-OES Inductively coupled plasma optical emission spectroscopy

## **Supplementary Information**

The online version contains supplementary material available at https://doi. org/10.1186/s13065-025-01440-2.

Supplementary Material 1.

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#### Author contributions

Ahmed M. H. Abudken Help in doing laboratory works and taking analyses. Lina Saadi Help in doing laboratory works and taking analyses. Radwan ALI Help in writing papers, doing laboratory works and taking analyses. Mosstafa Kazemi The main author of the article, Project manager, Supervisor.

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This published article and its supplementary information files include all data generated or analyzed during this study.

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#### **Competing interests**

The authors declare no competing interests.

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