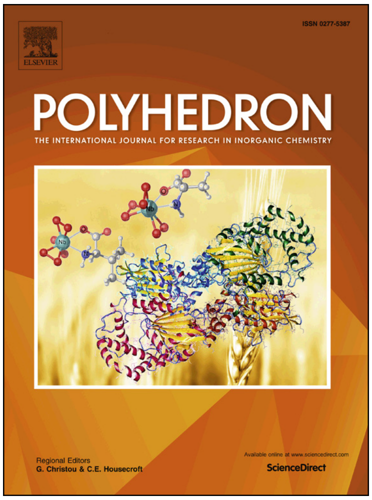

Synthesis of a new Pd(0)-complex supported on magnetic nanoparticles and study of its catalytic activity for Suzuki and Stille reactions and synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives

Taiebeh Tamoradi, Arash Ghorbani-Choghamarani, Mohammad Ghadermazi

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Synthesis of a new Pd(0)-complex supported on magnetic nanoparticles and study of its catalytic activity for Suzuki and Stille reactions and synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives

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Abstract

In the present work, we report synthesis of anchored palladium complex on functionalized Fe_3O_4 nanoparticles via simple and inexpensive procedure. The final nanohybrid compound was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray Diffraction(XRD), thermal gravimetric analysis (TGA) and vibrating sample magnetometer (VSM) measurements. The catalytic activity of Fe_3O_4-Serine-Pd as an efficient and reusable catalyst was investigated for Suzuki and Stille reactions and synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives. The heterogeneous catalyst could be easily separated by applying a simple magnet and reused several consecutive runs without appreciable change in its catalytic activity.

Keywords Magnetic nanoparticle, Palladium, 2,3-dihydroquinazolin-4(1H)-one, Suzuki, Stille.

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1. Introduction

The simplified recovery, reusability and the potential for incorporation in continuous reactors and microreactors are unique properties in organic synthesis, thus the major area of research is recently shifted toward more environment friendly catalysts [1-3]. In homogeneous systems it is complicated to recover the catalyst from the final reaction mixture; thus heterogeneous catalysts are used as supports. Heterogeneous catalysts have attracted a considerable attention in synthesis of organic compounds, because of their recovery by conventional filtration or centrifugation techniques. However, recovery and recycling of the heterogeneous catalysts are difficult because they require a tedious workup via filtration and the inevitable loss of solid in the recovery process [4-10]. Magnetic nanoparticles have recently proposed as ideal supports because of their multifunctional physical and chemical properties such as easy preparation and functionalization, high chemical activity, long catalytic life, large surface area ratio, excellent thermal and chemical stability, low price, less toxicity, high dispersion and easy separation via external magnet [11-22]. Furthermore, magnetic nanoparticles can be used as recoverable and reusable heterogeneous catalysts in Suzuki and Stille reactions and synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives [23-28]. 2,3-dihydroquinazolin-4(1H)-one derivatives are an important class of heterocyclic compounds in the production of industrially important chemicals and biological activities such as antitumor, antibiotic, antidefibrillatory, antipyretic, antihistamine, vasodilating behavior, analgesic, antihypertonic, diuretic and antidepressant [29,30]. Furthermore, the C-C coupling reactions are widely applied for the synthesis of the sartan family of hypertensive drugs, antimicrobial, fungicide boscalid, anti-proliferative, anti-inflammatory, anti-diabetic and analgesic applications [31-34]. In the present study, we prepared and characterized efficient and novel Fe_3O_4-Serine-Pd nanoparticles via simple work-up procedure and commercially available materials. Also, we will focus on the investigation of the catalytic activity of this heterogeneous nanocatalyst in Suzuki and Stille reactions and synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives.

2. Experimental

2.1. General remarks

All reactants used in this work are commercially available from Sigma-Aldrich and Merck chemical companies and used without further purification. The particle size and morphology of the samples were taken using SEM with a FESEM-TESCAN MIRA3, and also using TEM with a Zeiss-EM10C transmission electron microscope. VSM measurements were carried out in an external field up to 15kOe at several temperatures by a Vibrating Sample Magnetometer (VSM) MDKFD. The thermogravimetric analysis (TGA) curves were obtained on Shimadzu DTG-60 instrument. Powder X-ray diffraction (XRD) of Fe_3O_4-Serin-Pd(0) catalyst was collected using Co Kα radiation (λ= 1.78897 Å nm) with operating at 40 keV, and a cathode current of 40 Ma. IR spectra were recorded by KBr disc using a VRTEX 70 model BRUKER FT-IR spectrophotometer. The content of metal in the catalyst was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). Melting points were recorded by an Electrothermal 9100 apparatus.

2.2. Preparation of Fe_3O_4-Serine-Pd(0) nanocatalyst

Superparamagnetic nanoparticles were prepared by stirring 2.35 g of $FeCl_3.6H_2O$ and 0.86 g of $FeCl_2.4H_2O$ in 40 ml deionized distilled water under nitrogen gas at 80℃ and then adding 5 mL of NH_4OH solution into the reaction mixture. After stirring the mixture for 30 min, black precipitate was immediately formed. The black magnetite nanoparticles were separated by magnetic decantation, washed several times with deionized hot water and ethanol and dried in vacuum at 60℃. To prepare Fe_3O_4-Serine, 1 g of MNPs powder and 1.5 g of serine ligand were suspended in distilled water (30 mL) and refluxed for 20 h. Finally, Fe_3O_4-Serine was separated by an external magnet and washed with ethanol/water and dried in vacuum at 80℃. In the last step, Fe_3O_4-Serine-Pd(0) nanoparticles were afforded by mixing the Fe_3O_4-Serine (1 g) and $Pd(OAc)_2$ (0.5 g) in absolute ethanol (30 mL) and stirring under reflux for 16 h. Then Pd(II) ions reduced with $NaBH_4$ to give the Fe_3O_4-Serine-Pd(0).

2.3. General procedure for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones

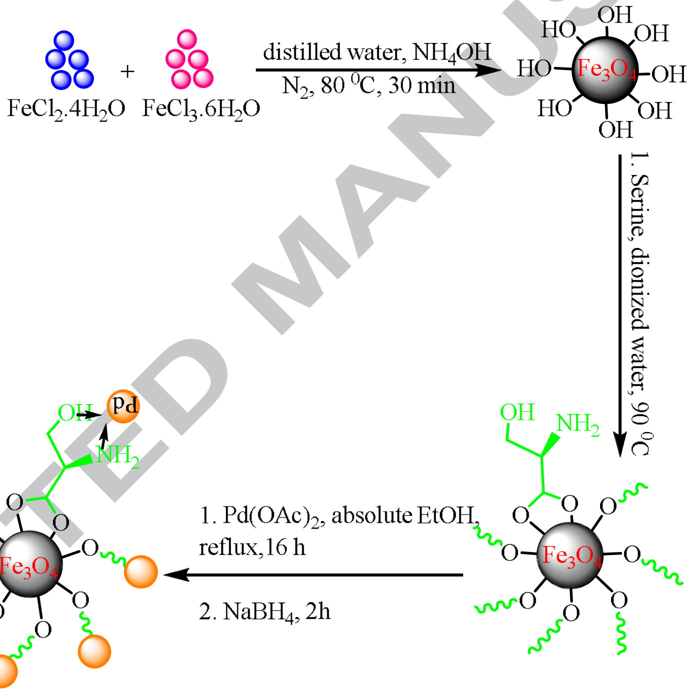
In a typical procedure, a mixture of aldehyde (1 mmol), 2-aminobenzamide (1 mmol) and Fe_3O_4-Serine-Pd(0) catalyst (0.007 g) in water (2 mL) was magnetically stirred in the reaction flask at room temperature. After the completion of the reaction indicated by TLC, the catalyst was separated by an external magnet and solvent was evaporated at 70 °C for reuse. Finally, a crude solid was obtained followed by crystallization from hot ethanol which prepared the pure product with excellent yield.

2.4. General procedure for synthesis of biphenyl derivatives

In a 5 ml round-bottom flask, to a mixture of arylhalide (1 mmol), phenylboronic acid (1 mmol)or triphenyltin chloride (0.5 mmol), Na_2CO_3 (3 mmol) and 2 ml of PEG, Fe_3O_4-Serine-Pd(0) (0.007 g) as catalyst was added; and the obtained mixture was heated at 100 °C for an appropriate time under stirring conditions. After the reaction was completed (monitored by TLC), the catalyst separated by an external magnet. Finally, the obtained organic layer was extracted with ethyl acetate to afford the pure biphenyl derivatives by removing solvent in good to high yield.

3. Results and discussion

In order to design and synthesize of a new and highly efficient catalyst system, the superparamagnetic nanoparticles (MNPs) were synthesized with chemical coprecipitation method [35-37]. Then, Fe_3O_4-Serine nanoparticles were obtained by the immobilization of serine on the surface of the synthesized magnetite nanoparticles via coordination bonding through hydroxyl group interaction. Afterward, Fe_3O_4-Serine-Pd(0) nanocatalyst was successfully achievedby reaction of $Pd(OAc)_2$ with the obtained Fe_3O_4-Serine ligand in ethanol under reflux condition (Scheme 1).



Scheme 1 General route for the fabrication of Fe_3O_4-Serine-Pd(0).

3.1. Catalyst characterization

The obtained Fe_3O_4-Serine-Pd(0) catalyst has been characterized by XRD, FT-IR, TEM, SEM, TGA, EDS, ICP and VSM techniques.

As shown in Fig. 1, the particle shape, the size distribution, surface morphology and fundamental physical properties of the Fe_3O_4 and Fe_3O_4-Serine-Pd(0) were investigated by Scanning Electron Microscopy (SEM). Therefore, it can be concluded that the synthesized materials are with uniform nanometer-sized particles. More importantly, no noticeable change in the surface morphology occurs upon the formation of Fe_3O_4-Serine-Pd(0) nanocatalyst.

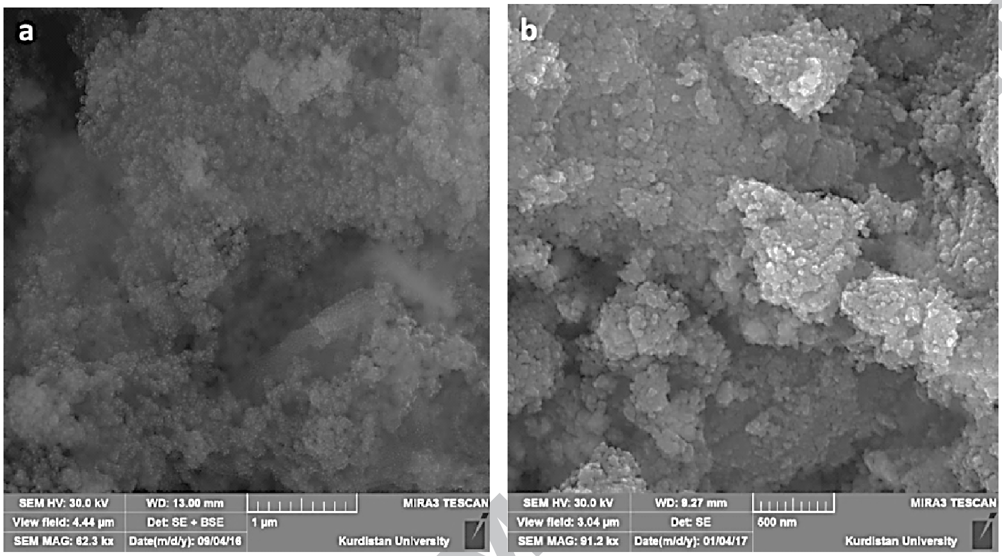


Fig. 1 SEM images of Fe_3O_4 (a) and Fe_3O_4-Serine-Pd(0) catalyst (b).

The presence of the kinds of elements in the synthesized Fe_3O_4-Serine-Pd(0) was investigated by the energy-dispersive X-ray spectroscopy (EDX) analysis. According to the database of the EDX pattern in Fig. 2, the presence of Fe, O, N, C and Pd specie in the obtained catalyst were verified. Also, the loading of Pd on the surface of the synthesized nanocatalyst was calculated by the ICP atomic emission spectroscopy technique. The exact amount of Pd loaded on modified magnetic nanoparticles is found to be 1.55mmol g^{-1}.

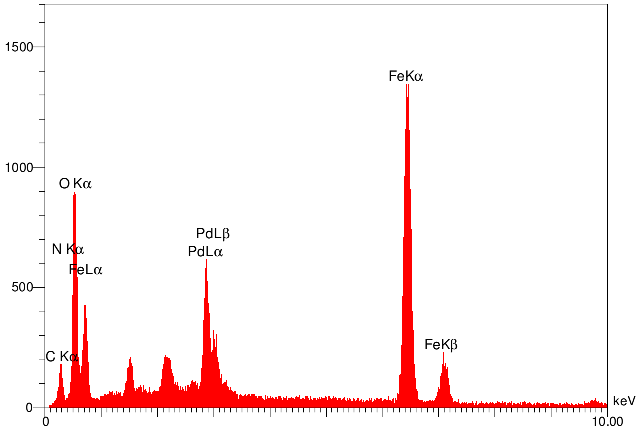


Fig.2 EDX pattern of Fe_3O_4-Serine-Pd(0).

TEM micrograph has been a suitable tool for determining the particle shape and size distribution. As it can be seen in Fig. 3, the magnetic cores of the nanoparticles were uniform in both shape and in size. It should be mentioned that the size of the Fe_3O_4-Serine-Pd(0) catalyst is around 15–25 nm.

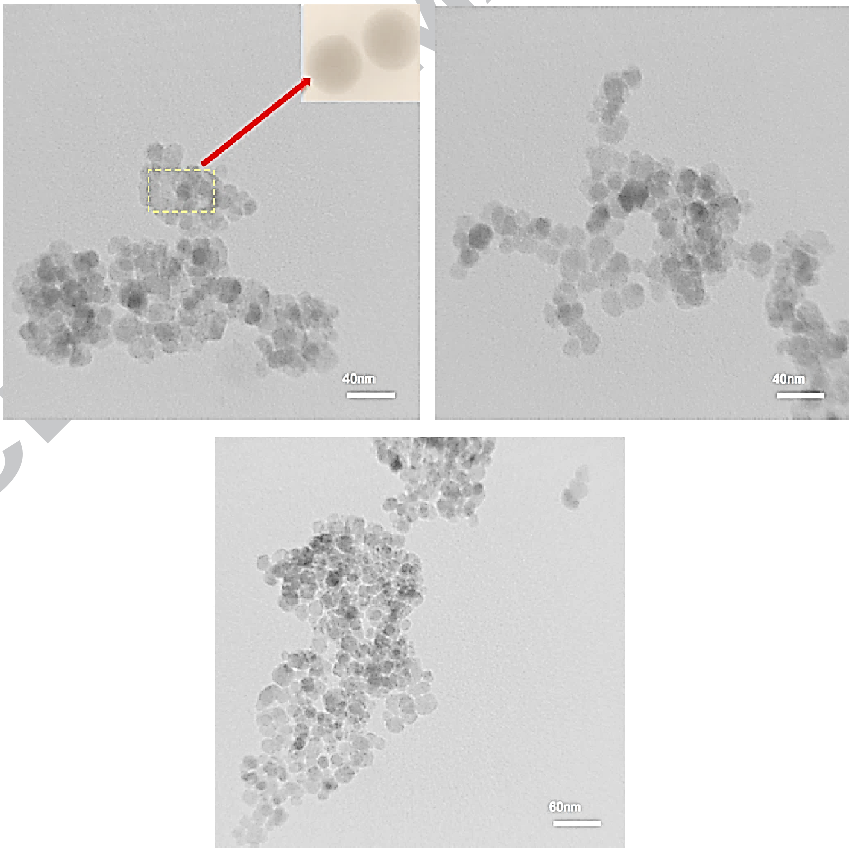


Fig. 3 TEM images of Fe_3O_4-Serine-Pd(0).

Also, to extend the scope of catalyst characterization, the X-ray diffraction analysis (XRD) pattern of Fe_3O_4-Serine-Pd(0) was investigated (Fig. 4). The XRD pattern of a standard Fe_3O_4 crystal indicated six characteristic peaks at (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) [38]. According to the Fig. 4, these peaks (2θ=30.17°, 35.5, 43.2°, 53.7°, 57.1° and 62.9°) can be assigned to the pure Fe_3O_4 nanoparticles. Also, a sequence of particular diffraction peaks (39.3°, 45.1° and 66.1°) confirmed the presence of Pd(0) in the prepared nanostructure.

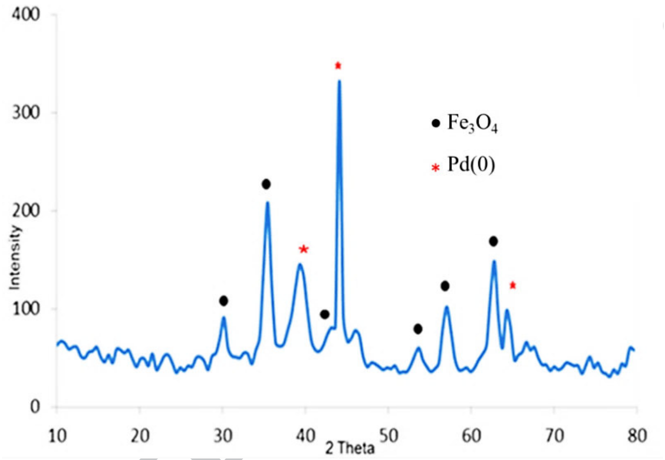


Fig. 4 XRD pattern of Fe_3O_4-Serine-Pd(0).

The existence of palladium complex on the surface of Fe_3O_4 nanoparticles was verified by FTIR studies. FTIR spectra for the pure Fe_3O_4 nanoparticles, Fe_3O_4-Serine and Fe_3O_4-Serine-Pd(0) are shown in Fig.5 in the 400–4000 cm^{-1}.The strong absorption at approximately 580 cm^{-1} in the Fe_3O_4, Fe_3O_4-Serine and Fe_3O_4-Serine-Pd(0) was exhibited which was attributed to the presence of Fe–O stretching vibration [39]. Absorption peaks at approximately 2840–2970cm^{-1} (C–H stretching vibration), absorption band at nearly 1390 cm^{-1} (C–N stretching vibration) and absorption peak at approximately 1690cm^{-1} (C=O stretching vibration) in the Fe_3O_4-Serine spectra is due to the coating of serine ligand on the surface of the synthesized magnetite nanoparticle. More importantly, the band near 1425 cm^{-1} of the Fe_3O_4-Serine is attributed to $\nu(NH_2)$ bending; this band is shifted to lower wavenumber in the spectrum of the

Fe_3O_4-Serine-Pd(0) due to the coordination of the amino group nitrogen atom to the metal ion [38]. Alo, FT-IR spectrum of Fe_3O_4-Serine exhibits a stretching band at 3489 cm^{-1} while in the Fe_3O_4-Serine-Pd(0) spectrum this band is shifted to lower frequency and appears at 3475 cm^{-1} indicating the formation of Pd–ligand bond [40].

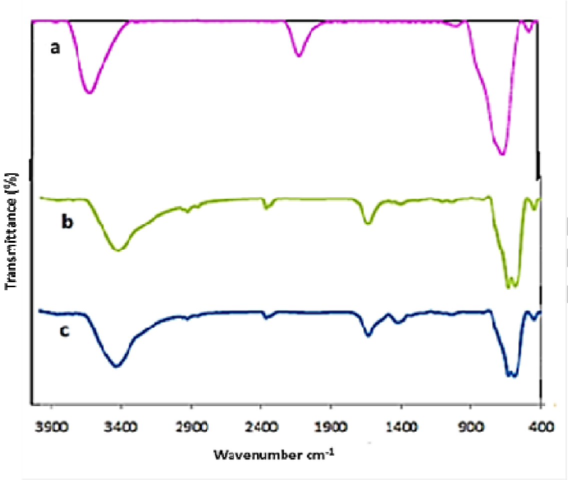


Fig. 5 FTIR spectrum for bare Fe_3O_4 nanoparticles (a), Fe_3O_4-Serine (b) and Fe_3O_4-Serine-Pd(0) (c).

The thermal stability of Fe_3O_4 and Fe_3O_4-Serine-Pd was studied by thermo-gravimetric analysis (TGA) (Fig. 6). In all samples the TGA curve shows the small amount of weight loss below 200 °C that is due to removal of the adsorbed water as well as dehydration of the surface OH groups [41]. The 28% weight loss in the range of 200-550 °C can be due to the decomposition of the organic layers on the surface of the synthesized magnetite nanoparticles. On the basis of this result, the well grafting of organic groups including Pd complex on the Fe_3O_4 is verified.

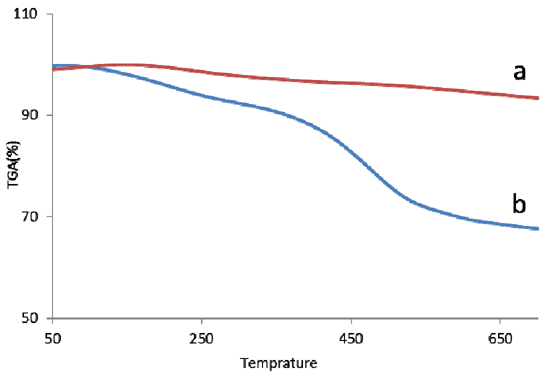


Fig. 6 The TGA diagrams of Fe_3O_4 (a) and Fe_3O_4-Serine-Pd(0) (b).

Vibrating sample magnetometer curves of the uncoated magnetic iron oxide (Fe_3O_4) and palladium complex coated Fe_3O_4 nanoparticles at room temperature were shown in Fig. 7. The saturation magnetization value (Ms) of the Fe_3O_4 and Fe_3O_4-Serine-Pd(0) nanoparticles were 73 and 45.6 emu g^{-1}, respectively. The magnetic saturation for Fe_3O_4 nanoparticles is higher than Fe_3O_4-Serine-Pd(0) that is due to the existence of nonmagnetic materials (palladium complex) on the surface of nanoparticles [36].

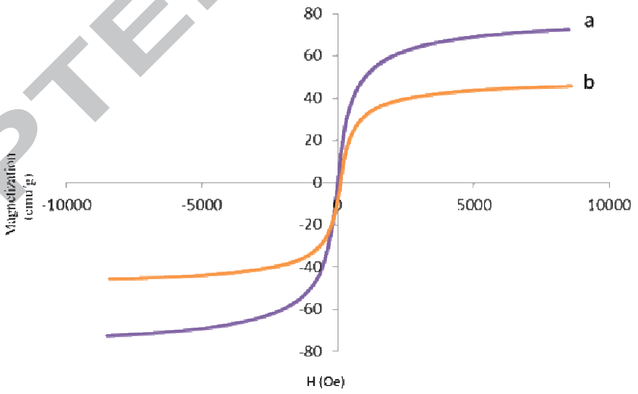
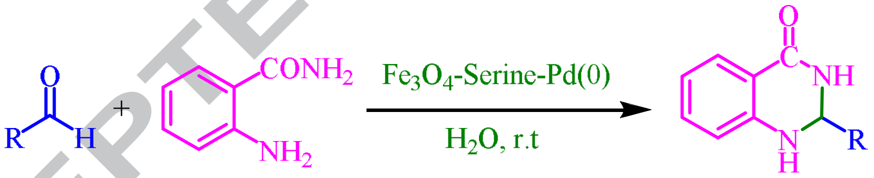


Fig. 7. Magnetization curves of Fe_3O_4 (a) and Fe_3O_4-Serine-Pd(0) (b) at room temperature.

3.2. Catalytic studies

After characterizing the Fe_3O_4-Serine-Pd(0), the catalytic activity of this nanocatalyst in organic reactions such as the preparation of 2,3-dihydroquinazolin-4(1H)-ones derivatives

(Scheme 2) and carbon–carbon bond formation using triphenyltin chloride or phenylboronic acid to obtain biphenyl derivatives (Scheme 4) was investigated. In search of the optimized reaction conditions for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones, the condensation of 4-chlorobenzaldehyde (1 mmol) with 2-aminobenzamide in in presence of Fe_3O_4-Serine-Pd(0) as catalyst was used as a model reaction. For assessing the generality of optimized reaction condition, the effect of various parameters such as solvent and catalyst concentration was investigated for the model reaction. During optimization of solvent, among solvents tested, the best results are obtained with water based on product yield (Table 1, entries 2–4). To investigate the effect of the catalyst concentration, different amounts of Fe_3O_4-Serine-Pd(0) were used (Table 1, entries 1–5). It should be mentioned that the reaction possess no desirable conversion in the absence of catalyst after 5 h (Table 1, entry 1). According to these results, 7 mg of Fe_3O_4-Serine-Pd(0) seems appropriate as the optimum amount of catalyst (Table 1, entry 3). The results of optimization were summarized using designed experiments in Table 1.



Scheme 2. Synthesis of 2,3-dihydroquinazolin-4(1H)-ones.

Table 1
Optimization of various parameters for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones by Fe_3O_4-Serine-Pd(0) [a].

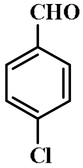
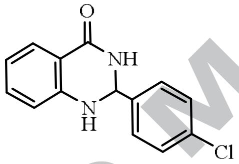
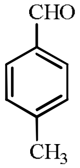
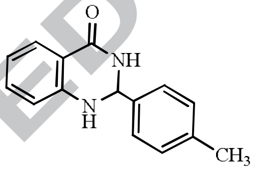
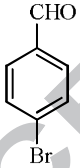
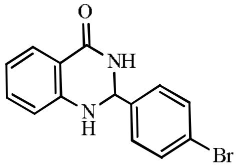
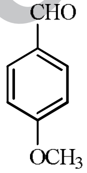
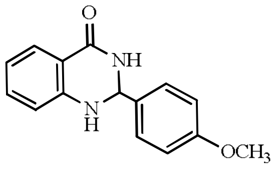
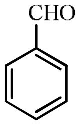
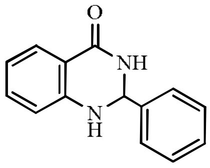
Entry	Solvent	Catalyst (mg)	Time (min)	Yield[b] (%)
1	H_2O	0	5h	Treac
2	H_2O	8	25	97
3	H_2O	7	25	96
4	H_2O	6	25	88
5	H_2O	5	25	81

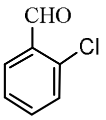
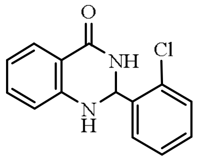
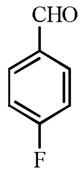
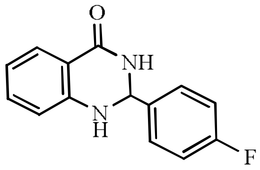
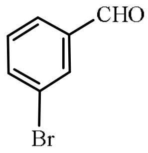
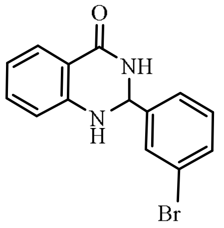
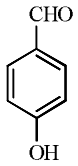
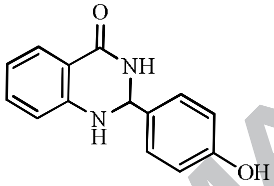
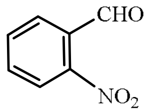
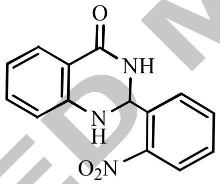
6	EtOH	7	25	70
7	EtOH/reflux	7	25	81
8	PEG	7	25	89
9	DMF	7	25	61

[a] Reaction conditions: 4-chlorobenzaldehyde (1 mmol) and 2-aminobenzamide (1 mmol) as a model reaction at room temperature.
[b] Yields refertoisolatedpureproduct.

As shown in Table 2, under the optimized reaction conditions, different aldehydes were tested for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones to give the products in good to excellent yields.

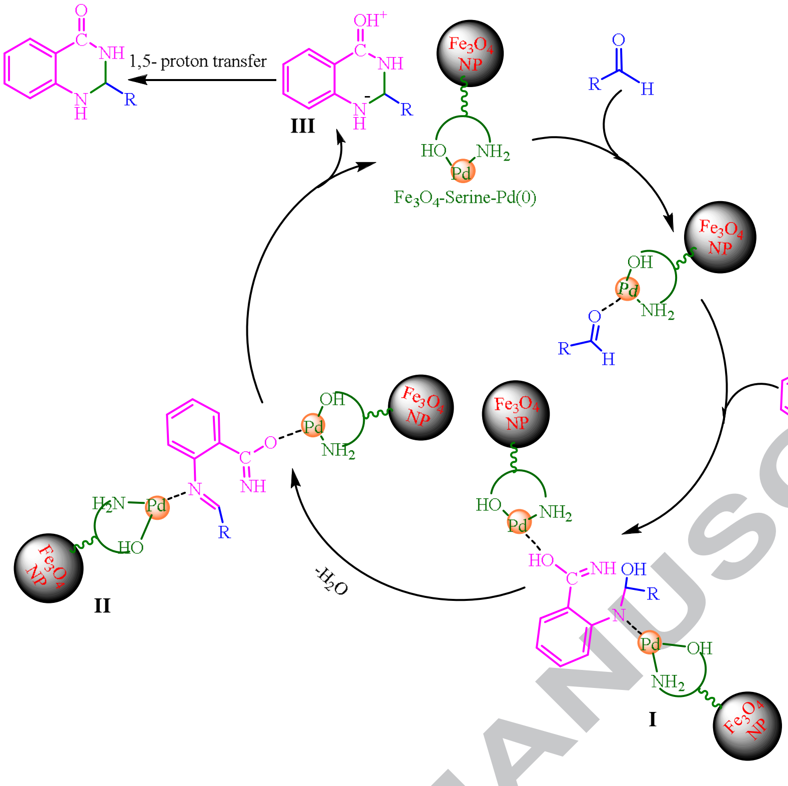
Table 2
Synthesis of 2,3-dihydroquinazolin-4(1H)-ones catalyzed by Fe_3O_4-Serine-Pd(0)[a].

Entry	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C) [Ref.]
1			25	96	202-204 [42]
2			50	98	228-232 [25]
3			35	93	197-200 [42]
4			55	94	190-1191 [25]
5			40	96	218-222 [43]

6			35	92	228-230 [44]
7			15	94	193-195 [42]
8			30	97	184-187 [16]
9			35	94	278-280 [43]
10			40	96	191–194 [43]

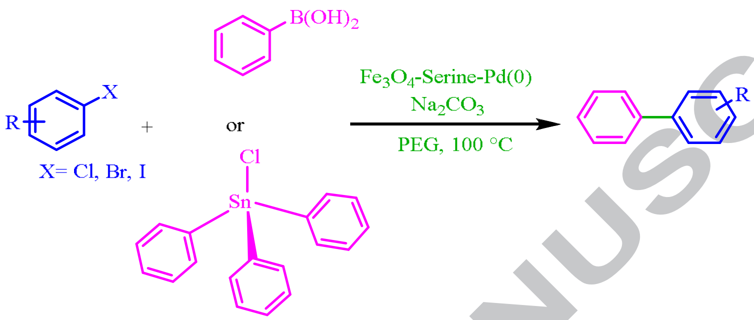
[a]Reaction conditions: aldehyde (1 mmol), 2-aminobenzamide (1 mmol), catalyst (0.007 g) in H_2O solvent (2 mL) at room temperature.
[b]Isolated yield.

A plausible reaction mechanism for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones derivatives in the presence of Fe_3O_4-Serine-Pd(0) as catalyst is shown in Scheme 3. As shown in this scheme, anhydride is activated. Then, an intermediate (I) is formed by the N-nucleophilic attacks of amine on the carbonyl. In following, the imine intermediate II is obtained. Also, after activation of imine in this intermediate by metal, intermediate III could be generated by intramolecular nucleophilic attack of the amide nitrogen on activated imine group. Finally, 1,5-proton transfer occurred to yield the final product [45].



Scheme 3 Proposed mechanism for the synthesis of quinazolinones.

In continuation of this research work, the catalytic activity of Fe_3O_4-Serine-Pd(0) was evaluated in the synthesis of biphenyl compounds through the reaction of aryl halides with phenylboronic acid or triphenyltin chloride. In the preliminary stage of investigation, the Suzuki cross-coupling reaction was done between iodobenzene (1mmol) and phenylboronic acid (1mmol) to optimize the reaction conditions, including catalyst amount, solvent, base and temperature. Initially, our studies focused on the effects of various solvents such as DMF, PEG, EtOH, DMSO and H_2O (Table 3, entries 1–5). Finally, among the tested solvents, PEG was obtained as the best solvent based on product yield. Subsequently, we investigated the effect of various bases such as K_2CO_3, Na_2CO_3, KOH, NaOH and Et_3N in the model reaction (Table 3, entries 6–10). Among the examined bases, the best result is obtained for Na_2CO_3 as an excellent base for this reaction. The reported result in Table 3 showed that the amount of base was also important in the synthesis of biphenyls. Subsequently, we explored the effect of the amount of catalyst to obtain the best operative experimental conditions. It should be mentioned that 0.007 g of Fe_3O_4-Serine-Pd(0) catalyst and 3 mmol of Na_2CO_3 as the base were evaluated in the selection of an optimized conditions for the C-C coupling reaction (Table 3, entries 6). The results of this investigation are summarized in Table 3.



Scheme 4 General scheme for the Suzuki and Stille reactions catalysed by Fe_3O_4-Serine-Pd(0).

Table 3

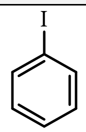
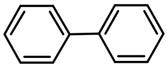
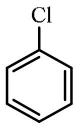
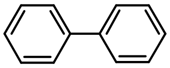
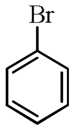
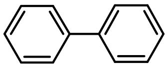
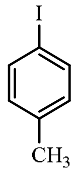
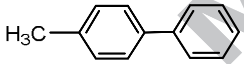
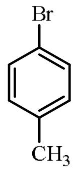
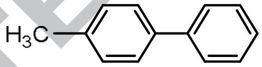
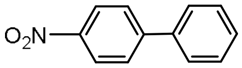
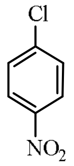
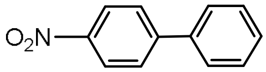
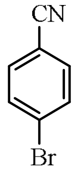
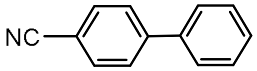
Optimization of various parameters for synthesis of biphenyl catalysed by Fe_3O_4-Serine-Pd(0).

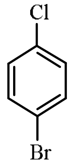
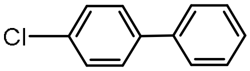
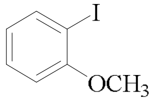
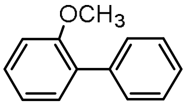
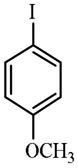
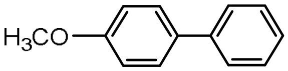
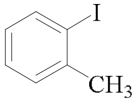
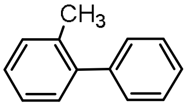
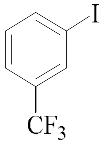
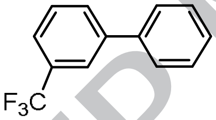
Entry	Solvent	Base	Time (min)	Catalyst (mg)	Base (mmol)	Temp. (°C)	Yield[a] (%)
1	DMSO	Na_2CO_3	20	7	3	80	43
2	EtOH	Na_2CO_3	20	7	3	80	34
3	H_2O	Na_2CO_3	20	7	3	80	42
4	DMF	Na_2CO_3	20	7	3	80	63
5	PEG	Na_2CO_3	20	7	3	80	84
6	PEG	Na_2CO_3	20	7	3	100	97
7	PEG	K_2CO_3	20	7	3	100	74
8	PEG	KOH	20	7	3	100	61
9	PEG	NaOH	20	7	3	100	53
10	PEG	Et_3N	20	7	3	100	58
11	PEG	Na_2CO_3	20	6	3	100	85
12	PEG	Na_2CO_3	20	5	3	100	80
13	PEG	Na_2CO_3	20	8	3	100	98
14	PEG	Na_2CO_3	20	7	2	100	86
15	PEG	Na_2CO_3	20	7	4	100	98
16	PEG	Na_2CO_3	24 h	-	3	100	N.R

[a] Isolated yield.

In continuation of this work on the applications of Fe_3O_4-Serine-Pd(0), we also explored the catalytic activity of Fe_3O_4-Serine-Pd(0) for the Suzuki cross-coupling reaction of phenylboronic acid with a wide range of aryl halides under the optimized reaction condition in high to excellent yields in a short reaction time. The results are summarized in Table 4.

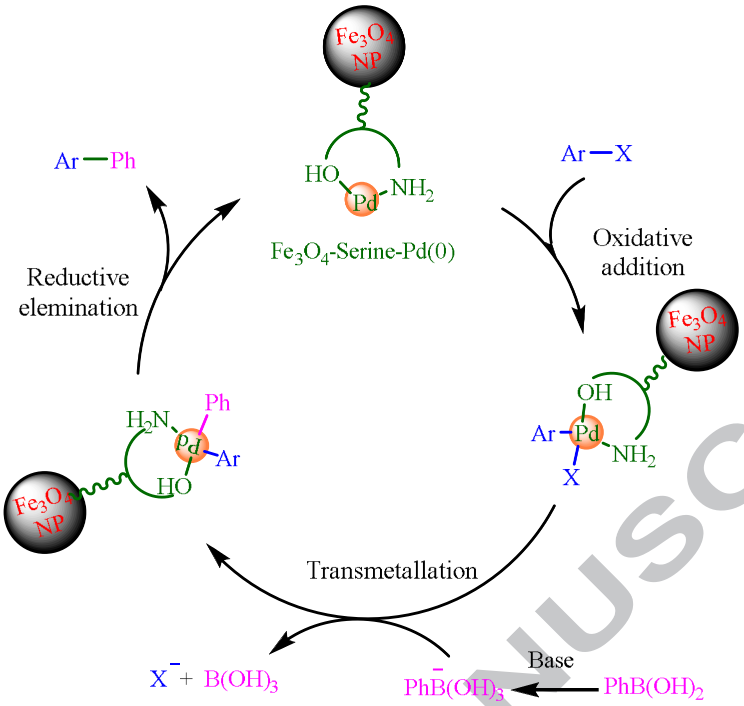
Table 4
C–C coupling of aryl halides with phenylboronic acid in the presence of Pd Fe_3O_4-Serine-Pd(0) [a].

Entry	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C) [Ref.]
1			20	98	66-69 [18]
2			95	94	68-71 [18]
3			40	96	69 [18]
4			15	93	45 [46]
5			30	98	46-48[46]
6			60	97	113-116[46]
7			75	96	115-118 [18]
8			90	93	78-81 [46]

9			70	95	78 [46]
10			90	96	Oil [43]
11			100	92	84–86 [46]
12			120	97	Oil [43]
13			30	97	Oil [43]

[a] Reaction conditions: iodobenzene (1 mmol), phenylboronic acid (1 mmol), base (3 mmol), Fe_3O_4-Serine-Pd(0) (0.007 g), solvent (2 mL) at 110 °C.
[b] Isolated yield.

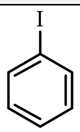
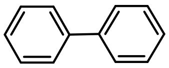
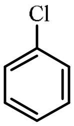
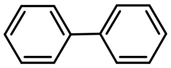
Catalytic cycle for this C–C bond formation reaction in the presence of Fe_3O_4-Serine-Pd(0) was shown in Scheme 5 [47].

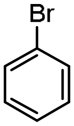
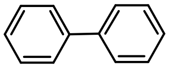
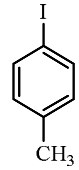
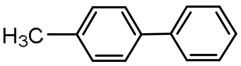
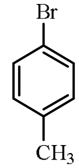
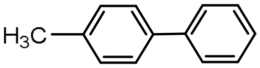
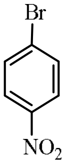
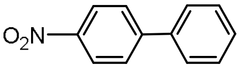
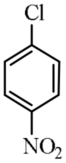
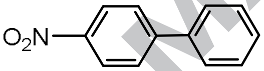
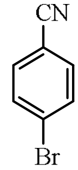
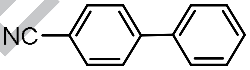
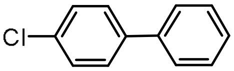
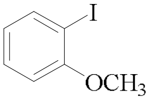
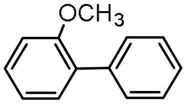


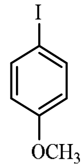
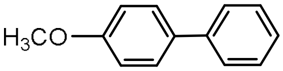
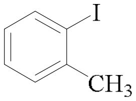
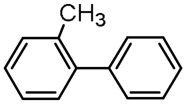
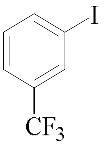
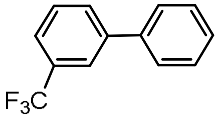
Scheme 5 Mechanism of the palladium-catalyzed Suzuki reaction.

Also in order to investigate the behavior of the catalyst in the Stille reaction, under the optimized reaction condition, the biphenyl compounds were successfully synthesized through the reaction of the different aryl halides with triphenyltin chloride in high to excellent yields in a short reaction time. The results are shown in Table 5.

Table 5
C–C coupling of aryl halides with phenylboronic acid in the presence of Pd-Fe_3O_4-Serine-Pd(0) [a].

Entry	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C) [Ref.]
1			35	95	68 [18]
2			110	93	66-69 [18]

3			45	94	71 [18]
4			30	98	45-48 [46]
5			45	96	47 [46]
6			65	96	110-112 [18]
7			80	97	113-115 [46]
8			85	98	80-83 [46]
9			60	93	76-79 [46]
10			80	92	Oil [43]

11			90	94	85–87 [46]
12			110	98	Oil [43]
13			45	93	Oil [43]

[a] Reaction conditions: iodobenzene (1 mmol), triphenyltin chloride (0.5 mmol), base (3 mmol), Fe_3O_4-Serine-Pd(0) (0.007 g), solvent (2 mL) at 110 °C.
[b] Isolated yield.

In order to examine the efficiency of the procedures presented, we compared the results of synthesis of 2-Phenyl-2,3-dihydroquinazolin-4(1H)-one (entries 1-9) and Suzuki reaction (entries 10-14) in the presence of new catalyst with previously reported catalysts in the literature. The results of this comparison indicated shorter reaction time and higher yield of the Fe_3O_4-Serine-Pd(0) catalyst than the well-known catalyst from the literature. Noticeably, the Fe_3O_4-Serine-Pd(0) catalyst is superior in terms of stability, commercially available materials, ease of operation and easy separation than the previously reported ones.

Table 6 Comparison of Fe_3O_4-Serine-Pd(0) catalyst with reported catalysts for Suzuki reaction and synthesize of 2-Phenyl-2,3-dihydroquinazolin-4(1H)-one.

Entry	Catalyst	Substrate	Time (min)	Condition	Yield (%)[a]
1	GSA@MNPs	4-Chlorobenzaldehyde	50	Ethanol, reflux	87 [48]
2	2-(N-Morpholino)ethanesulfo	4-Chlorobenzaldehyde	180	Ethanol, 60˚C	89 [49]

	nic acid				
3	[Bmim]PF6	4-Chlorobenzaldehyde	40	Ionic liquid, 75 °C	90 [50]
4	Yb(OTf)$_3$	4-Chlorobenzaldehyde	120	EtOH, r.t	94 [51]
5	Boehmite-SSA	4-Chlorobenzaldehyde	50	EtOH, 80 °C	98 [52]
6	PdCl2	4-Chlorobenzaldehyde	270	THF, reflux	86 [53]
7	Fe_3O_4-SA-PPCA	4-Chlorobenzaldehyde	110	EtOH, 50 °C	91 [25]
8	$CuCl_2/Fe_3O_4$-TEDETA	4-Chlorobenzaldehyde	60	EtOH, reflux	95 [20]
9	Fe_3O_4-Serine-Pd(0)	4-Chlorobenzaldehyde	25	H_2O, r.t	96 [this work]
10	PANI–Pd	Iodobenzene	240	K2CO3, 1,4-dioxane–H2O (1:1), 95°C	91 [54]
11	Pd-MPTAT-1	Iodobenzene	480	NaOH, DMF–H_2O (1:5), 85°C	95 [55]
12	Pd NPs	Iodobenzene	720	H2O, KOH, 100°C	95 [56]
13	NHC–Pd(II) complex	Iodobenzene	720	THF, Cs_2CO_3, 80°C	88 [57]
14	Fe_3O_4-Serine-Pd(0)	Iodobenzene	20	PEG, Na_2CO_3, 100,	98 [this work]

[a]Isolated yields.

To investigate the activity constancy of the catalyst, catalytic reusability of Fe_3O_4-Serine-Pd(0) was investigated for Suzuki reaction and synthesis of 2,3-dihydroquinazolin-4(1H)-one under the optimized reaction conditions in the model reaction (Fig.8). In this procedure, the catalyst successfully reused several continuous cycles without noticeable change in its catalytic activity, which clearly demonstrates the practical recyclability of this catalyst. After completion of the reaction, the catalyst was magnetically recovered, washed with ethyl acetate several times and dried at 60 °C and reused for the next run. The weight loss of catalyst in the operation for recovery and/or deactivation of the catalyst may have led to decrease in the product yield.

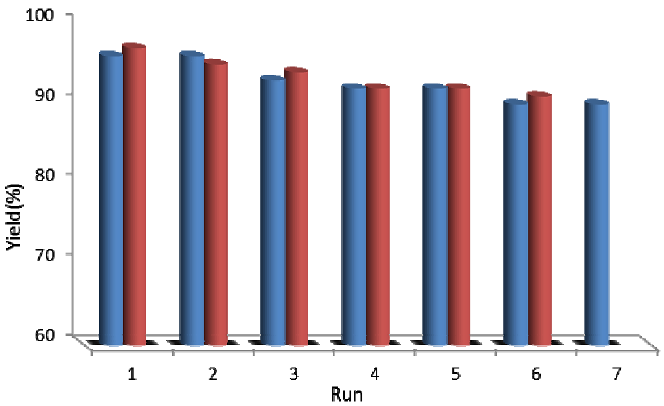


Fig. 8 Reusability of Fe_3O_4-Serine-Pd(0) in the synthesis of 2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one (blue column) and 4-nitro-1,1-biphenyl (red column).

4. Conclusions

In summary, a magnetically recoverable palladium catalyst was prepared by simple and versatile procedure as a novel catalyst and characterized using several techniques such as FTIR, XRD, SEM, EDX, ICP-OES, TEM, VSM and TGA, and then investigated its catalytic performance in Suzuki and Stille reactions and synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives. In these reactions, this nanohybrid compound represents the attractive features including high yield , operational simplicity, short reaction time, environmental friendliness, and recyclability of the magnetic catalyst, as well as the ability to tolerate a wide variety of substitutions in the reagents.

Acknowledgment

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Graphical Abstract - Synopsis

The present work describes the synthesis of a new palladium complex immobilized on Fe_3O_4 nanostructure as efficient catalyst for Suzuki and Stille reactions and synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives. Characterization of the prepared nanostructure was performed by FT-IR, SEM, TEM, EDX, ICP-OES, XRD, TGA and VSM. Use of green medium, easy separation, excellent reusability of the nanocatalyst, and short reaction time are outstanding advantages of this method.

Graphical abstract

Synthesis of a new Pd(0)-complex supported on magnetic nanoparticles and study of its catalytic activity for Suzuki and Stille reactions and synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives

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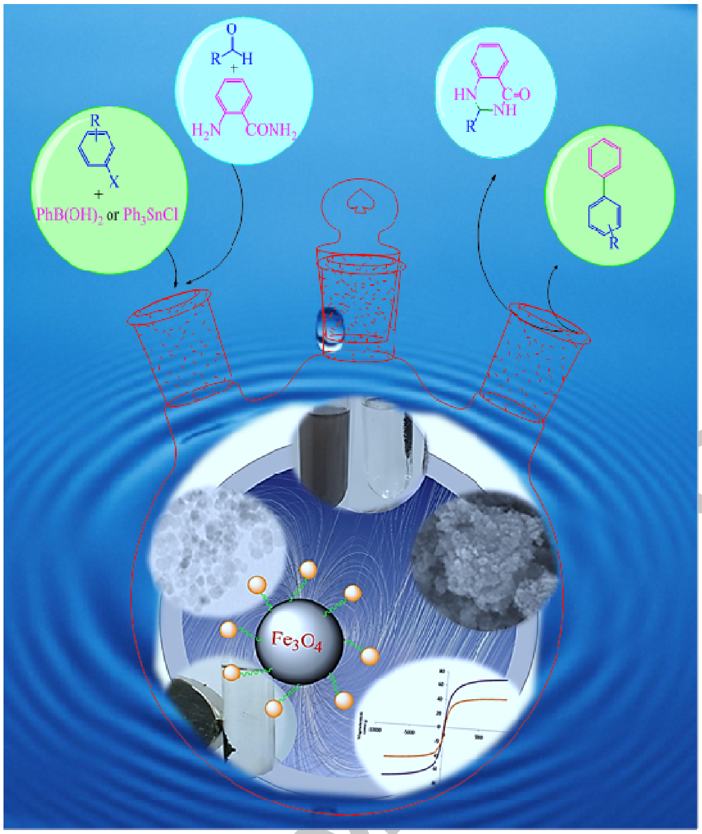
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X
+
PhB(OH)$_2$ or Ph$_3$SnCl
O
R
H
+
H$_2$N
CONH$_2$
HN
C=O
NH
R
R
Fe$_3$O$_4$