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Zinc (II) complex immobilized on the surface of magnetic nanoparticles modified with phenanthroline: A novel and efficient nanomagnetic reusable catalyst for cross-coupling reaction of aryl iodides with terminal aromatic alkynes

Indah Raya[a], Saade Abdalkareem Jasim[b], Adnan Hashim Abdulkadhim[c], Luay Hashem Abbud[d], and Himanshu Sharma[e]

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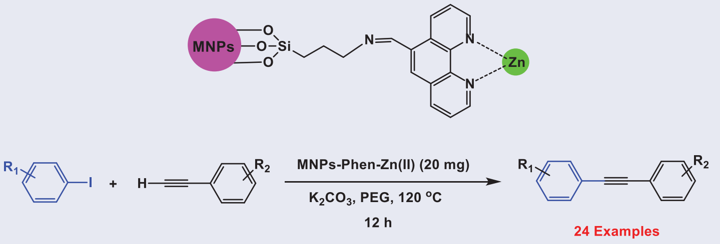
ABSTRACT

A novel and green nanomagnetic zinc catalyst were fabricated *via* the immobilization of zinc (II) complex on the surface of magnetic nanoparticles modified with phenanthroline (MNPs-Phen-Zn(II)). The structure of MNPs-Phen-Zn(II) nanomaterial was characterized by a series of spectroscopic techniques including FT-IR spectroscopy, SEM, TEM, EDX, XRD, VSM, and ICP-OES. The resulting zinc nanomagnetic catalyst was shown high catalytic activity for the synthesis of disubstituted alkynes *via* C(sp^2)–C(sp) cross-coupling reactions of alkynes with aryl iodides under eco-friendly conditions. To the best of our knowledge, it is the first report on the utilization of zinc nanomagnetic catalyst for the Sonogashira type cross-coupling reaction of alkynes with aryl iodides in the absence of added Pd and Cu sources. The simple preparation of the catalyst from commercially available materials, excellent chemoselectivity, easy separation of products, and straightforward recovery and reusability of the catalyst with unaltered activity make our procedure a green and practical method.

GRAPHICAL ABSTRACT



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KEYWORDS
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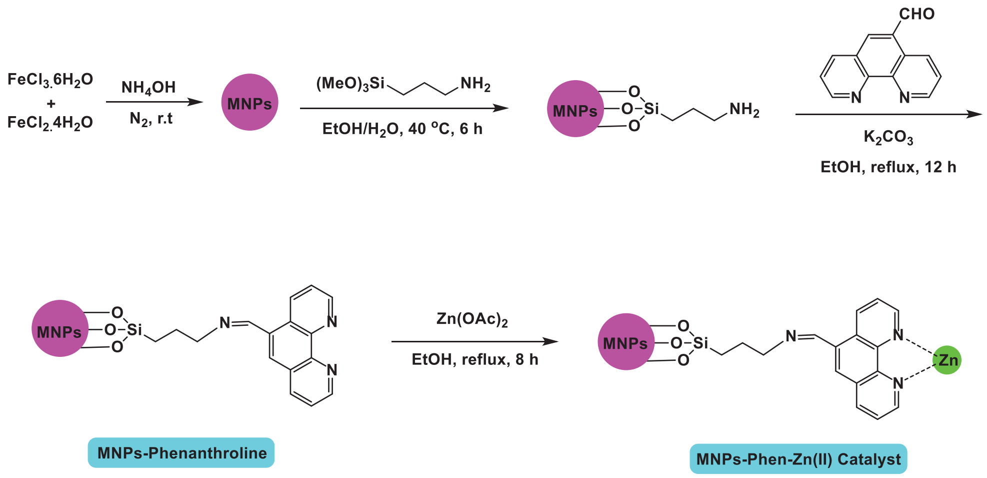
Introduction

One of the most important goals of chemists is to produce catalysts with high activity and efficiency, complete selectivity, the ability to separate and recover from the reaction mixture, low energy consumption, and long life.[1,2] Catalyst performance can be determined by controlling variables, such as size, structure, spatial and electron distribution, surface composition, thermal, and chemical stability.[3] With the introduction of nanotechnology into the catalyst industry, nanocatalysts have become more prominent. In most cases, these catalysts have shown remarkable properties and have found their way into industrial processes.[4,5] Research in the field of nanocatalysts has always been one of the most interesting topics in Nanochemistry and Green Chemistry.[6,7] Green Chemistry deals with healthy chemical reactions with safe products with maximum efficiency, and minimum consumption of matter and energy.[8–11] Nanocatalysts can lead us to this ideal. Today, magnetic nanoparticles have found a variety of applications due to properties, such as large specific surface area and simple separation with an external magnetic field.[12] The paramagnetic nature and insolubility of magnetic nanoparticles facilitate the separation of this catalyst from the reaction mixture by an external magnet.[13,14] The physical and chemical properties of magnetic nanoparticles largely depend on the method of synthesis and chemical structure.[15,16] In most cases, the particle size varies from 1 to 100 nanometers. In recent times, the utilization of magnetic nanoparticles in particular Fe_3O_4 nanoparticles as support for catalysis have received profound attention in organic synthesis.[15,17,18] A salient feature of magnetic nanoparticle-stabilized catalysts is that they are easily separated from the reaction medium using an external magnetic field, have high catalytic activity, and exhibit a high degree of chemical stability.[19–21]

Research on coupling reactions is one of the most important challenges in chemistry science in particular in organic synthesis.[22–24] Carbon-Carbon bond formation is one of the most fundamental and synthetically useful reactions in modern organic syntheses due to C–C bonds widely encountered in countless top-selling marketed drugs and many biologically active molecules and natural products.[24–26] The Sonogashira reaction is an important cross-coupling reaction in organic synthesis that has been used extensively for C–C bond formation.[27–30] The most common method for Sonogashira cross-coupling reactions involves reacting terminal acetylenes and aryl or alkenyl halides in the presence of Pd(0) and copper(I) catalysts with base.[31–33] Herein, we disclose a simple and efficient approach for the Sonogashira type cross-coupling reaction of alkynes with aryl iodides catalyzed by zinc nanomaterial in the absence of added Pd and Cu sources. In this method, the zinc complex immobilized on magnetic Fe_3O_4 nanoparticles as a catalyst suggested a series of advantages, such as magnetic separation, high stability, and excellent catalytic activity. To the best of our knowledge, it is the first report on the utilization of zinc nanomagnetic catalyst for the Sonogashira type cross-coupling reaction of alkynes with aryl iodides in the absence of added Pd and Cu sources.

Result and discussion

Details of the fabrication of zinc (II) complex immobilized on the surface of magnetic nanoparticles modified with phenanthroline (MNPs-Phen-Zn(II)) is shown in Scheme 1.



Scheme 1. Details of fabrication of MNPs-Phen-Zn(II) nanomaterial.

The structure of MNPs-Phen-Zn(II) nanomaterial was characterized by a series of spectroscopic techniques including FT-IR spectroscopy, SEM, TEM, EDX, XRD, VSM, TGA, ICP-OES, and AAS.

FT-IR Spectroscopy of MNPs-Phenanthroline and MNPs-Phen-Zn(II) nanomaterial is shown in Supplementary Figure 1. As shown in Supplementary Figure 1, a broad peak around 580 cm^{-1} is related to the stretching of the Fe–O bond. The existence of Zn in the structure of the catalyst was approved through stretching vibration of C=N bands that appeared at 1629 cm^{-1}, as this band shifts to a lower frequency (1613 cm^{-1}) due to the grafting of Zn (II) complex on the surface of MNPs-Phenanthroline.[34–36]

The morphology and size of MNPs-Phen-Zn(II) catalyst were determined by SEM and TEM analysis, as shown in Supplementary Figures 2 and 3. Both the SEM and TEM images demonstrate that the prepared magnetic nanoparticles are spherical, narrowly distributed, and well dispersed with an average size of <15 nm in diameter.

The elemental analysis of MNPs-Phen-Zn(II) catalyst was studied by Energy-Dispersive X-ray spectroscopy (EDX). As shown in Supplementary Figure 2, the EDX spectrum of MNPs-Phen-Zn(II) catalyst confirmed the presence of Fe, O, N, C, and Zn elements in the structure of the catalyst and proved that the magnetic nanoparticle has been successfully synthesized.

The magnetic property of MNPs-Phen-Zn(II) was checked using Vibrating Sample Magnetometer (VSM) technique at room temperature. The magnetization curve of MNPs-Phen-Zn(II) is illustrated in Supplementary Figure 4. According to the magnetization curves, the saturation of the MNPs-Phen-Zn(II) catalyst was about 35.21 emu/g. With superparamagnetic properties, the catalyst can be easily recovered by applying an external magnetic field.

The structure of MNPs-Phen-Zn(II) nanocatalyst was investigated by X-Ray Diffraction (XRD). The XRD pattern of MNPs-Phen-Zn(II) nanocatalyst is presented in Supplementary Figure 5. This analysis affirmed that the surface modification and conjugation of the Fe_3O_4 nanoparticles did not lead to phase change. Several characteristic peaks at $2\theta = 35.1$, 41.2, 50.6, 63.2, 67.3, and 74.6° were observed, which are assigned to the (220), (311), (400), (422), (511), and (440) crystallographic faces of magnetite (in good agreement with the standard Fe_3O_4 MNPs XRD spectrum reported in the literature).[37] Also, the crystal size was calculated according to Debye–Scherrer formula, and the mean crystal size of Fe_3O_4 NPs and MNPs-Phen-Zn(II), was obtained at 18.34 and 12.27 nm, respectively.

To determine the amount of Zn on the surface of the catalyst, the ICP-OES (Inductively coupled plasma-optical emission spectrometry) analysis was used which indicated that the exact amount of Zn, stabilized on the surface of MNPs-Phenanthroline, is found to be 21.18×10^{-5} mol/g.

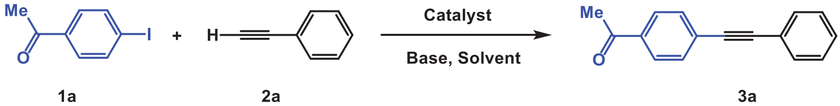
The XPS spectrum of the MNPs-Phen-Zn(II) nanocatalyst was successfully provided to characterize the oxidation state of the Zn species in the synthesized catalysts (Supplementary Fig. 6). An expanded scan demonstrated the presence of Zn^{2+} by the appearance of the sharp continues to peak at 1044.8 eV. In addition, the purity of Zn^{+2} species on the catalyst surface was confirmed by the absence of any other peaks in this area.

After characterization of MNPs-Phen-Zn(II) nanomaterial, the catalytic activity of zinc nanomagnetic catalyst was evaluated for the synthesis of disubstituted alkynes *via* C(sp^2)–C(sp) cross-coupling reactions of alkynes with aryl iodides under eco-friendly conditions. To find the standardized conditions for the Sonogashira type cross-coupling reaction of alkynes with aryl iodides, the model reaction of 4-iodoacetophenone (**1a**) with phenylacetylene (**2a**) was studied under different conditions, such as catalyst loading, solvent and base nature, and temperature. The model product (**3a**) was not seen in the absence of a zinc catalyst (Table 1, Entry 1–3). As seen in Table 1 (Entry 4–7), when the amount of catalyst increased, the reaction efficiency also increased. But catalytic amounts above 20 mg of MNPs-Phen-Zn(II) did not significantly affect the reaction progress (Table 1, Entry 8). Then the effect of several bases and solvents were studied to find the best conditions. The presence of base was very vital for these reactions because the model product was not seen in the absence of base (Table 1, Entry 14). Amongst tested solvents, the maximum yield was seen in PEG-400 at 120 °C (Table 1, Entry 20). Therefore, the utilization of 20 mg of MNPs-Phen-Zn(II) catalyst in K_2CO_3 (2 equiv.) in PEG-400 (3 mL) at 120 °C for 12 h was considered as the standardized conditions for the Sonogashira type cross-coupling reaction of alkynes with aryl iodides.

After optimization of the reaction conditions, the scope and generality of the Sonogashira type cross-coupling reaction were illustrated with respect to various aryl iodides and phenylacetylene derivatives. The results of these experiments are listed in Table 2. A variety of benzyl iodide derivatives containing electron-donating or electron-withdrawing functionalities and some heteroaromatic iodides underwent facile reactions giving very good to excellent yields. Aryl iodides with both electron-withdrawing and electron-releasing substituents on reaction with phenylacetylene derivatives afforded good to excellent yields of the target product indicating the absence of electronic effects in these reactions. We have also investigated the coupling of aryl bromides with acetylenes, which unfortunately proceeded with a very low yield of the target product.

The catalytic cyclic mechanism for cross-coupling reaction of aryl iodides with terminal aromatic alkynes in the presence of MNPs-Phen-Zn(II) is shown in Scheme 2 based on previously reported mechanism.[38]

Table 1. Optimization of reaction conditions for Sonogashira type cross-coupling reaction of alkynes with aryl iodides.[a]



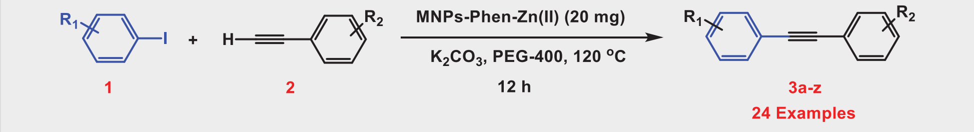
Entry	Catalyst (mg)	Base	Solvent (temperature)	Time (h)	Yield[b] (%)
1	—	K_3PO_4	1,4-dioxane (Reflux)	24	—
2	Fe_3O_4 MNPs(5)	K_3PO_4	1,4-dioxane (Reflux)	12	—
3	MNPs-Phenanthroline (5)	K_3PO_4	1,4-dioxane (Reflux)	12	—
4	MNPs-Phen-Zn(II) (5)	K_3PO_4	1,4-dioxane (Reflux)	12	66
5	MNPs-Phen-Zn(II) (10)	K_3PO_4	1,4-dioxane (Reflux)	12	71
6	MNPs-Phen-Zn(II) (15)	K_3PO_4	1,4-dioxane (Reflux)	12	77
7	MNPs-Phen-Zn(II) (20)	K_3PO_4	1,4-dioxane (Reflux)	12	82
8	MNPs-Phen-Zn(II) (25)	K_3PO_4	1,4-dioxane (Reflux)	12	82
9	MNPs-Phen-Zn(II) (20)	NaOH	1,4-dioxane (Reflux)	12	4
10	MNPs-Phen-Zn(II) (20)	KOH	1,4-dioxane (Reflux)	12	7
11	MNPs-Phen-Zn(II) (20)	K_2CO_3	1,4-dioxane (Reflux)	12	87
12	MNPs-Phen-Zn(II) (20)	Cs_2CO_3	1,4-dioxane (Reflux)	12	81
13	MNPs-Phen-Zn(II) (20)	Et_3N	1,4-dioxane (Reflux)	12	22
14	MNPs-Phen-Zn(II) (20)	—	1,4-dioxane (Reflux)	24	—
15	MNPs-Phen-Zn(II) (20)	K_2CO_3	DMF (Reflux)	12	84
16	MNPs-Phen-Zn(II) (20)	K_2CO_3	Toluene (Reflux)	12	49
17	MNPs-Phen-Zn(II) (20)	K_2CO_3	DMSO (Reflux)	12	51
18	MNPs-Phen-Zn(II) (20)	K_2CO_3	THF (Reflux)	12	32
19	MNPs-Phen-Zn(II) (20)	K_2CO_3	CH_3CN (Reflux)	12	63
20	**MNPs-Phen-Zn(II) (20)**	**K_2CO_3**	**PEG-400 (120 °C)**	**12**	**91**
21	MNPs-Phen-Zn(II) (20)	K_2CO_3	NMP (120 °C)	12	28
22	MNPs-Phen-Zn(II) (20)	K_2CO_3	SF(120 °C)	12	Trace
23	MNPs-Phen-Zn(II) (20)	K_2CO_3	EtOH (Reflux)	12	44
24	MNPs-Phen-Zn(II) (20)	K_2CO_3	Water (Reflux)	12	26
25	MNPs-Phen-Zn(II) (20)	K_2CO_3	PEG-400 (25 °C)	12	Trace
26	MNPs-Phen-Zn(II) (20)	K_2CO_3	PEG-400 (60 °C)	12	43
27	MNPs-Phen-Zn(II) (20)	K_2CO_3	PEG-400 (130 °C)	12	91
28	MNPs-Phen-Zn(II) (20)	K_2CO_3	PEG-400 (140 °C)	12	90
29	MNPs-Phen-Zn(II) (20)	K_2CO_3	PEG-400 (110 °C)	12	88
30	MNPs-Phen-Zn(II) (20)	—	PEG-400 (120 °C)	12	—

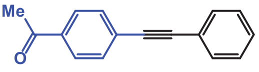
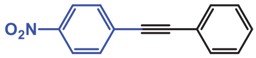
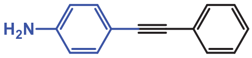
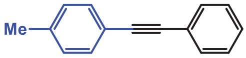
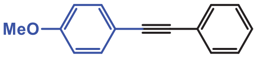
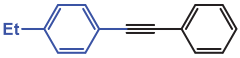
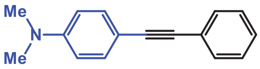
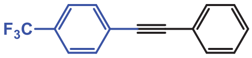
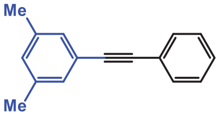
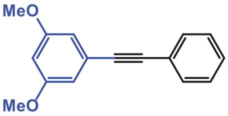
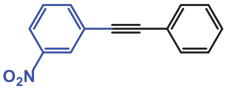
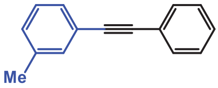
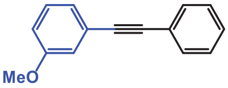
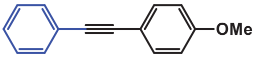
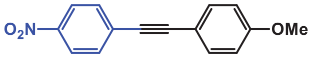
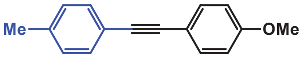
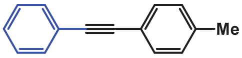
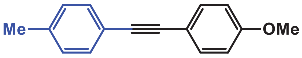
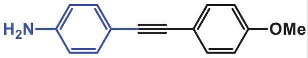
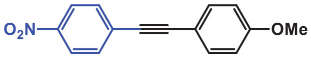
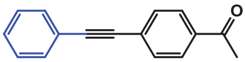
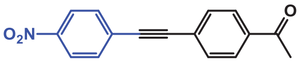
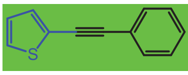
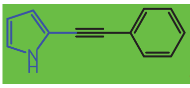
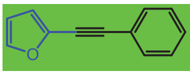
[a] Reaction conditions: alkyne (1 mmol), aryliodide (1.1 mmol), Base (2 equiv.), catalyst, Solvent (3 ml).
[b] Isolated yield.
Bold values represent standardized condition.

The reusability of the catalyst is one of the most important advantages and makes it beneficial for commercial applications. Recycling and reusability of the MNPs-Phen-Zn(II) catalyst were also examined upon the synthesis of the model product (**3a**) *via* the reaction of 4-iodoacetophenone (**1a**) with phenylacetylene (**2a**) under standardized conditions. After finishing each run, 3 ml hot ethyl acetate was added to the reaction mixture and stirred and heated to dissolve the crude product. 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 a decrease in the product yield. The results of reusability studies, summarized in Supplementary Figure 7, indicated that the MNPs-Phen-Zn(II) catalyst was stable and reusable seven times without any significant loss of activity and even after the seven runs.

The magnetization curve of reused MNPs-Phen-Zn(II) after 7 runs is illustrated in Supplementary Figure 8. According to the magnetization curves, the saturation of the MNPs-Phen-Zn(II) catalyst was about 35.21 emu/g. Scanning Electron Microscope

Table 2. Scope of Sonogashira type cross-coupling reactions of alkynes with aryl iodides catalyzed by MNPs-Phen-Zn(II) nanomaterial.[a,b]



 91% (3a)	 94% (3b)	 83% (3c)
 96% (3d)	 80% (3e)	 83% (3f)
 78% (3g)	 95% (3h)	 91% (3i)
 88% (3j)	 84% (3k)	 82% (3l)
 91% (3m)	 81% (3n)	 83% (3o)
 86% (3p)	 89% (3q)	 80% (3r)
 83% (3s)	 82% (3t)	 86% (3u)
 88% (3x)	 93% (3y)	 95% (3z)
 91% (3aa)	 88% (3ab)	 90% (3ac)
 91% (3ad)	 87% (3ae)	 83% (3af)

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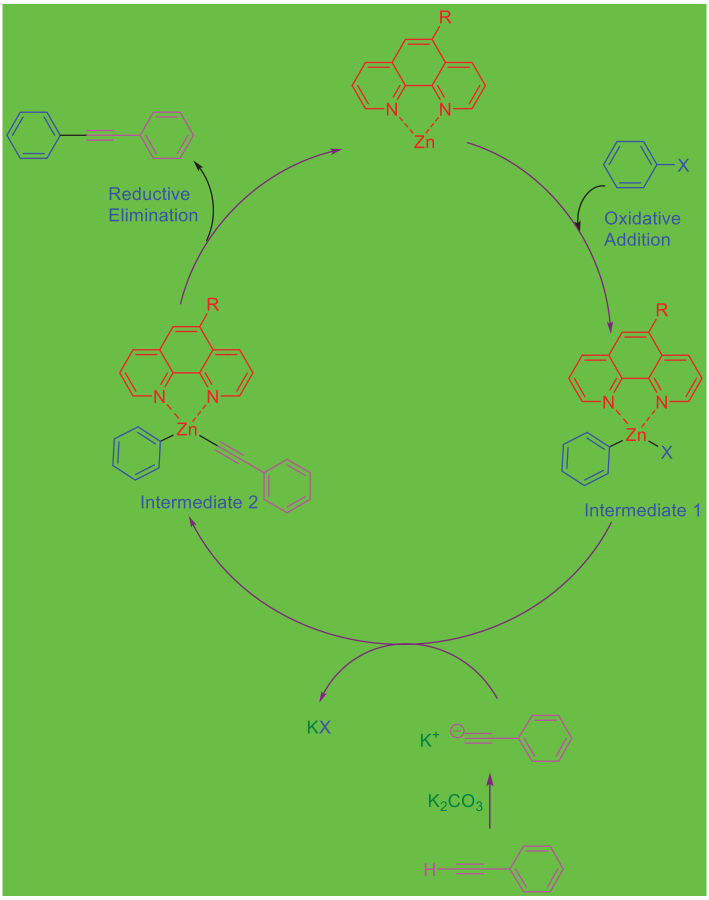
[a] Reaction conditions: alkyne (1 mmol), aryliodide (1.1 mmol), K_2CO_3 (2 equiv.), MNPs-Phen-Zn(II) nanomaterial catalyst (20 mg), PEG-400 (3 ml), 120 °C, 12 h.

[b] Isolated yield.



Scheme 2. Mechanism of the Zn-catalyzed Sonogashira reaction.

(SEM) of MNPs-Phen-Zn(II) nanocatalyst after 7 runs are shown in Supplementary Figure 8. The SEM image illustrates that these particles are of nearly spherical morphology with a mean diameter of about 10–20 nm. ICP-OES was employed to determine the exact Zn content of nanomaterial (after seven times), which was found to be 21.03×10^{-5} mol/g.

Comparison

The comparative study of different protocols for the synthesis of the model product (**3a**) *via* the reaction of 4-iodoacetophenone (**1a**) with phenylacetylene (**2a**) is illustrated in Table 3. Though the effectiveness of our catalyst is very better than of literature reports, they have utilized either harsh conditions, more time, elevated temperature, or conventional heating as an energy source.

Conclusion

In this paper, we reported (for the first time) the utilization of zinc nanomagnetic catalyst for the Sonogashira type cross-coupling reaction of alkynes with aryl iodides in the

Table 3. Comparative study of different protocols for cross-coupling reaction of aryl iodides with terminal aromatic alkynes.

Entry	Catalyst	Time (h)	Yield (%)	References
1	PdO/C	20	81	[39]
2	Cu(phen)(PPh_3)Br	24	85	[40]
3	$PdCl_2(PPh_3)_2$	1.5	87	[41]
4	Pd-phosphine ylide complex	24	64	[42]
5	MNPs-Phen-Zn(II)	12	95	Present work

absence of added Pd and Cu sources. zinc nanomagnetic catalyst was successfully fabricated *via* the immobilization of zinc (II) complex on the surface of magnetic nanoparticles modified with phenanthroline (MNPs-Phen-Zn(II)) and was well characterized by a series of spectroscopic techniques including FT-IR spectroscopy, SEM, TEM, EDX, XRD, VSM, and ICP-OES. The resulting zinc nanomagnetic catalyst was shown high catalytic activity for the synthesis of disubstituted alkynes *via* C(sp^2)–C(sp) cross-coupling reactions of alkynes with aryl iodides under eco-friendly conditions. The present method is efficient in terms of yield, catalyst toxicity, reaction conditions, and catalyst loading. The simplicity of this reaction protocol makes it a feasible alternative to the traditional Sonogashira cross-coupling reaction.

Experimental

Chemicals were purchased from Fisher and Merck companies. The reagents and solvents used in this work were obtained from Sigma–Aldrich, Fluka, or Merck companies and used without further purification. The infrared spectra (IR) of samples were recorded in KBr disks using NICOLET impact 410 spectrometers. ^{1}HNMR and ^{13}CNMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz, respectively. Nanostructures were characterized using a Holland Philips X'Pert X-ray powder diffraction (XRD) diffractometer (Co Kα, radiation = 0.154056 nm), at a scanning speed of $2^\circ\ \text{min}^{-1}$ from 10 to 80°. A scanning electron microscope (SEM) was performed on an FEI Quanta 200 SEM operated at a 20 kV accelerating voltage. The thermogravimetric analysis (TGA) curves are recorded using a PL-STA 1500 device manufactured by Thermal Sciences. The magnetic measurements were carried out in a vibrating sample magnetometer (VSM, BHV-55, Riken, Japan) at room temperature.

Preparation of the magnetic Fe_3O_4-nanoparticles

The mixture of $FeCl_3.6H_2O$ (5.838 g, 0.0216 mol) and $FeCl_2.4H_2O$ (2.147 g, 0.0108 mol) was dissolved in 100 mL of deionized water in a three-necked bottom (250 mL) under N_2 atmosphere. After that, under rapid mechanical stirring, 10 ml (Ammonia solution for example 28%) was added into the solution within 30 min with vigorous mechanical stirring. After being rapidly stirred for 30 min, the resultant black dispersion was heated to 80 °C for 30 min. The obtained black precipitate was isolated by magnetic decantation, washed with double-distilled water until neutrality, and further washed twice with ethanol and dried at room temperature.

Preparation of the Fe_3O_4@SiO_2

Then the obtained Fe_3O_4 MNPs (2 g) were dispersed in 20 mL of water by sonication for 30 min, and then 2-propanol (200 mL) was added to the reaction mixture. The reaction mixture was stirred using a magnetic stirrer at room temperature. Under continuous stirring, PEG-400 (5.36 g), water (20 mL), ammonia solution (10 mL, 28 wt.%), and 2 mL of tetraethyl orthosilicate (TEOS) were respectively added into the suspension and continuously reacted for 30 h under stirring at room temperature.[21] Then the product (Fe_3O_4@SiO_2) was isolated with an external magnet and washed two times with ethanol and distilled water.

Preparation of MNPs_APTMS

The obtained Fe_3O_4@SiO_2 nanoparticles (1.5 g) were dispersed in 250 mL ethanol/water (volume ratio, 1:1) by sonication for 30 min, and then (3-Aminopropyl)triethoxysilane (APTMS) (2.5 mL) was added to the mixture reaction. The reaction mixture was stirred using mechanical stirring under an N_2 atmosphere at 40 °C for 6 h then, the nanoparticles were re-dispersed in ethanol by sonication for 5 times and separated through magnetic decantation. The nanoparticles product (Fe_3O_4@SiO_2_APTMS) was dried at room temperature.[22]

Preparation of MNPs-phenanthroline

The MNPs_amine (2.2 g) was dispersed in EtOH (50 mL) by ultrasonic bath for 10 min. Potassium carbonate (1 mmol) and Phenanthroline (1.8 g) were added and stirred at reflux temperature for 18 h under an N_2 atmosphere. Then, the prepared MNPs-Phenanthroline nanocomposite was separated by magnetic decantation and washed three times with ethanol to remove the unattached substrates. The resulting product was dried at room temperature.

Preparation of the MNPs-Phen-Zn(II) catalyst

In the last step, $Zn(OAc)_2$ (6 mmol) was added to MNPs-Phenanthroline (2.5 g) in ethanol 98% (50 mL) and the resultant mixture was stirred under reflux for 8 h. Finally, the synthesized nanosolid (MNPs-Phen-Zn(II)) was separated by magnetic decantation. The nanomagnetic catalyst was washed several times with ethanol 98% and dried under vacuum at room temperature.

Typical experimental procedure for the Sonogashira type cross-coupling reaction of alkynes with aryl iodides

A dry sealed tube was charged with 1.1 mmol of aryl iodides and 2 equiv. of K_2CO_3 (276 mg). To the above mixture was added 1 mmol of phenyl acetylene derivatives, 20 mg of MNPs-Phen-Zn(II) catalyst, and 3 mL of PEG-400 under nitrogen. The sealed tube was heated in an oil bath which was preheated to 120 °C and the reaction mixture was stirred under the same conditions for 12 h and the progress of the reaction was monitored by TLC. The reaction mixture was then cooled and extracted with ethyl acetate (3 × 15 ml) and the catalyst was separated by an external magnet; the ethyl acetate layer was washed with distilled water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure in a rotary evaporator. The crude residue was purified by column chromatography using hexane–EtOAc (49:1) as the eluent to get the target products.

All the products reported here are known compounds and the spectroscopic data matched literature values.[28–30]

References

[1] Kaur, H.; Garg, N. Interactive Effects of Zinc-Arbuscular Mycorrhizal (AM) Fungi on Cadmium Uptake, Rubisco, Osmolyte Synthesis and Yield in *Cajanus cajan* (L.) Millsp. *Int. J. Sustain. Agric. Res.* **2021**, *8*, 17–42. DOI: 10.18488/journal.70.2021.81.17.42.

[2] Lakshman, M. Fe_3O_4@SiO_2-Pip-SA Nanocomposite: A Novel and Highly Efficient Reusable Acidic Catalyst for Synthesis of Rhodanine Derivatives. *J. Synth. Chem.* **2022**, *1*, 48–51. DOI: 10.22034/jsc.2022.149234.

[3] Mikhailov, O. V.; Chachkov, D. V. Novel Oxidation Degree-Zn + 3 in the Macrocyclic Compound with Trans-di[Benzo]Porphyrazine and Fluoride Ligand: Quantum-Chemical Consideration. *ECB.* **2020**, *9*, 160–163. DOI: 10.17628/ecb.2020.9.160-163.

[4] Bakhshkandi, R.; Ghoranneviss, M. Investigating the Synthesis and Growth of Titanium Dioxide Nanoparticles on a Cobalt Catalyst. *JRSET.* **2020**, *7*, 1–3. DOI: 10.24200/jrset.vol7iss4pp1-3.

[5] Gharibzadeh, F.; Vessally, E.; Edjlali, L.; et al. A DFT Study on Sumanene, Corannulene and Nanosheet as the Anodes in Li – Ion Batteries. *Iran. J. Chem. Chem. Eng.* **2020**, *39*, 51–62. DOI: 10.30492/ijcce.2020.106867.3568.

[6] Netam, a.; Bhargava, V.; Singh, R.; Sharma, P. Physico-Chemical Characterization of Ayurvedic Swarna Bhasma by Using SEM, EDAX, XRD and PSA. *J. Complement. Med. Res.* **2021**, *12*, 204. DOI: 10.5455/jcmr.2021.12.02.23.

[7] Gupta, S. Sulfuric Acid Heterogenized on Magnetic Nanoparticles Functionalized with Glycerol Catalyzed Synthesis of 2, 3-Dihydroquinazoline-4(1*H*)-Ones. *J. Synth. Chem.* **2022**, *1*, 37–41. DOI: 10.22034/jsc.2022.149222.

[8] Nair, K.; Velmurugan, R.; Sukumaran, S. Influence of Polylactic Acid and Polycaprolactone on Dissolution Characteristics of Ansamycin-Loaded Polymeric Nanoparticles: An Unsatisfied Attempt for Drug Release Profile. *J. Pharm. Negative Results* **2020**, *11*, 23. DOI: 10.4103/jpnr.JPNR_26_19.

[9] Mohan, R.; Ganapathy, K.; Rama, A. Brain Tumour Classification of Magnetic Resonance Images Using a Novel CNN Based Medical Image Analysis and Detection Network in Comparison with VGG16. *J. Popul. Ther. Clin. Pharmacol.* **2022**, *28*, e113–e125. DOI: 10.47750/jptcp.2022.873.

[10] Blagojević, D.; Lazić, D.; Kešelj, D.; et al. Determining the Content of Silicon Dioxide in Bauxites Using X-Ray Fluorescence Spectrometry. *Iran. J. Chem. Chem. Eng.* **2019**, *38*, 115–125.

[11] Saied, S. M.; Mohammed, S. J.; Khaleel, B. T.; Saleh, M. Y. Comparative Studies between Conventional Techniques and Green Chemistry to Synthesis of Novel Piperidinium Salts Ionic Liquids (PBSILs). *J. Chem. Heal. Risks* **2021**, *11*, 451–456. DOI: 10.22034/JCHR.2021.686640.

[12] Zouaoui, E. H.; Djamel, N.; Wan Ba Karim Ghani, W. A.; Amokarane, S. High-Pressure CO_2 Adsorption onto Nax Zeolite: Effect of Li^+, K^+, Mg^{2+}, and Zn^{2+} and Equilibrium Isotherms Study. *Iran. J. Chem. Chem. Eng.* **2021**, *40*, 1195–1215. DOI: 10.30492/ijcce.2020.40342.

[13] Riedel, W.; Thum, L.; Möser, J.; Fleischer, V.; Simon, U.; Siemensmeyer, K.; Schnegg, A.; Schomäcker, R.; Risse, T.; Dinse, K.-P.; et al. Magnetic Properties of Reduced and Reoxidized Mn-Na_2WO_4/SiO_2: A Catalyst for Oxidative Coupling of Methane (OCM). *J. Phys. Chem. C* **2018**, *122*, 22605–22614. DOI: 10.1021/acs.jpcc.8b07386.

[14] Heydari, Z.; Bahadorikhalili, S.; Ranjbar, P. R.; Mahdavi, M. DABCO-Modified Super-Paramagnetic Nanoparticles as an Efficient and Water-Compatible Catalyst for the Synthesis of Pyrano[3,2-*c*:5,6-*c*′]Dichromene-6,8-Dione Derivatives under Mild Reaction Conditions. *Appl. Organomet. Chem.* **2018**, *32, e4561*. DOI: 10.1002/aoc.4561.

[15] Jahangirian, H.; Lemraski, E. G.; Webster, T. J.; Rafiee-Moghaddam, R.; Abdollahi, Y. A Review of Drug Delivery Systems Based on Nanotechnology and Green Chemistry: Green Nanomedicine. *Int. J. Nanomedicine* **2017**, *12*, 2957–2978. DOI: 10.2147/IJN.S127683.

[16] Veisi, H.; Ghorbani, F. Iron Oxide Nanoparticles Coated with Green Tea Extract as a Novel Magnetite Reductant and Stabilizer Sorbent for Silver Ions: Synthetic Application of Fe_3O_4@Green Tea/Ag Nanoparticles as Magnetically Separable and Reusable Nanocatalyst for Reduction of 4. *Appl. Organomet. Chem.* **2017**, *31*, e3711. DOI: 10.1002/aoc.3711.

[17] Krishnan, S. G.; Pua, F.-L.; Zhang, F. A Review of Magnetic Solid Catalyst Development for Sustainable Biodiesel Production. *Biomass Bioenergy* **2021**, *149*, 106099. DOI: 10.1016/j.biombioe.2021.106099.

[18] Zhou, S.-M.; Wang, G.-Z.; Chen, H.-F.; et al. Research Progress on Heterogeneous Persulfate-Based Catalytic Materials. *Xiandai Huagong/Modern Chem. Ind.* **2020**, *40*, 20–25. DOI: 10.16606/j.cnki.issn0253-4320.2020.10.005.

[19] Xu, Y.; Cao, M.; Zhang, Q. Recent Advances and Perspective on Heterogeneous Catalysis Using Metals and Oxide Nanocrystals. *Mater. Chem. Front.* **2021**, *5*, 151–222. DOI: 10.1039/D0QM00549E.

[20] Geng, W.; Wang, L.; Yang, X.-Y. Nanocell Hybrids for Green Chemistry. *Trends Biotechnol.* **2022**, *40*, In Press. DOI: 10.1016/j.tibtech.2022.01.012.

[21] Masunga, N.; Mmelesi, O. K.; Kefeni, K. K.; Mamba, B. B. Recent Advances in Copper Ferrite Nanoparticles and Nanocomposites Synthesis, Magnetic Properties and Application in Water Treatment: Review. *J. Environ. Chem. Eng.* **2019**, *7*, 103179. DOI: 10.1016/j.jece.2019.103179.

[22] Gholinejad, M. Palladium Nanoparticles Supported on Agarose-Catalyzed Heck-Matsuda and Suzuki-Miyaura Coupling Reactions Using Aryl Diazonium Salts. *Appl. Organometal. Chem.* **2013**, *27*, 19–22. DOI: 10.1002/aoc.2932.

[23] Sharma, R. K.; Katiyar, D. Recent Advances in Transition-Metal-Catalyzed Synthesis of Coumarins. *Synthesis* **2016**, *48*, 2303–2322. DOI: 10.1055/s-0035-1560450.

[24] Taheri Kal Koshvandi, A.; Heravi, M. M.; Momeni, T. Current Applications of Suzuki–Miyaura Coupling Reaction in the Total Synthesis of Natural Products: An Update. *Appl. Organometal. Chem.* **2018**, *32*, e4210. DOI: 10.1002/aoc.4210.

[25] Floriani, C. Metal-Carbon and Carbon-Carbon Bond Formation from Small Molecules and One Carbon Functional Groups. *Pure Appl. Chem.* **1982**, *54*, 59–64. DOI: 10.1351/pac198254010059.

[26] Miyaura, N. Cross-Coupling Reaction of Organoboron Compounds via Base-Assisted Transmetalation to Palladium(II) Complexes. *J. Organomet. Chem.* **2002**, *653*, 54–57. DOI: 10.1016/S0022-328X(02)01264-0.

[27] Aly, H. M. Synthesis of Bifunctional Thieno[3,2-*c*]Pyrazole, Pyrazolothieno[2,3-*d*] Pyrimidin Derivatives and Their Antimicrobial Activities. *J. Iran. Chem. Soc.* **2016**, *13*, 999–1009. DOI: 10.1007/s13738-016-0813-2.

[28] Mio, M. J. How the Principles of Green Chemistry Changed the Way Organic Chemistry Labs Are Taught at the University of Detroit Mercy. *Phys. Sci. Rev.* **2017**, *2*, 1–5. DOI: 10.1515/psr-2016-0077.

[29] Adib, M.; Yasaei, Z.; Karimi-Nami, R.; Khakyzadeh, V.; Veisi, H. Facile Preparation of Highly Stable and Active Hybrid Palladium Nanoparticles: Effectual, Reusable and Heterogeneous Catalyst for Coupling Reactions. *Appl. Organometal. Chem.* **2016**, *30*, 748–752. DOI: 10.1002/aoc.3499.

[30] Wilson, M.; Kore, R.; Fraser, R. C.; Beaumont, S. K.; Srivastava, R.; Badyal, J. P. S. Recyclable Palladium Catalyst Cloths for Carbon-Carbon Coupling Reactions. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *520*, 788–795. DOI: 10.1016/j.colsurfa.2017.01.050.

[31] Chinchilla, R.; Nájera, C. The Sonogashira Reaction: A Booming Methodology in Synthetic Organic Chemistry. *Chem. Rev.* **2007**, *107*, 874–922. DOI: 10.1021/cr050992x.

[32] Govan, J.; Gun'ko, Y. K. Recent Advances in the Application of Magnetic Nanoparticles as a Support for Homogeneous Catalysts. *Nanomaterials* **2014**, *4*, 222–241. DOI: 10.3390/nano4020222.

[33] Amblard, F.; Cho, J. H.; Schinazi, R. F. Cu(l)-Catalyzed Huisgen Azide-Alkyne 1,3-Dipolar Cycloaddition Reaction in Nucleoside, Nucleotide, and Oligonucleotide Chemistry. *Chem. Rev.* **2009**, *109*, 4207–4220. DOI: 10.1021/cr9001462.

[34] Taheri, N.; Heidarizadeh, F.; Kiasat, A. A New Magnetically Recoverable Catalyst Promoting the Synthesis of 1,4-Dihydropyridine and Polyhydroquinoline Derivatives via the Hantzsch Condensation under Solvent-Free Conditions. *J. Magn. Magn. Mater.* **2017**, *428*, 481–487. DOI: 10.1016/j.jmmm.2016.09.099.

[35] Tamoradi, T.; Ghorbani-Choghamarani, A.; Ghadermazi, M. 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(1*H*)-One Derivatives. *Polyhedron* **2018**, *145*, 120–130. DOI: 10.1016/j.poly.2018.01.016.

[36] Soleimani, E.; Naderi Namivandi, M.; Sepahvand, H. $ZnCl_2$ Supported on $Fe_3O_4@SiO_2$ Core–Shell Nanocatalyst for the Synthesis of Quinolines via Friedländer Synthesis under Solvent-Free Condition. *Appl. Organometal. Chem.* **2017**, *31*, e3566. DOI: 10.1002/aoc.3566.

[37] Ali Ghasemzadeh, M.; Elyasi, Z.; Azimi-Nasrabad, M.; Mirhosseini-Eshkevari, B. Magnetite Nanoparticles-Supported APTES as a Powerful and Recoverable Nanocatalyst for the Preparation of 2-Amino-5,10-Dihydro-5,10-Dioxo-4*H*-Benzo[*g*]Chromenes and Tetrahydrobenzo[*g*]Quinoline-5,10-Diones. *Comb. Chem. High Throughput Screen.* **2017**, *20*, 64–76. DOI: 10.2174/1386207319666161223121612.

[38] Thankachan, A. P.; Abi, T. G.; Sindhu, K. S.; Anilkumar, G. Experimental and Mechanistic Exploration of Zn-Catalyzed Sonogashira-Type Cross-Coupling Reactions. *ChemistrySelect* **2016**, *1*, 3405–3412. DOI: 10.1002/slct.201600668.

[39] Rossy, C.; Majimel, J.; Delapierre, M. T.; Fouquet, E.; Felpin, F.-X. On the Peculiar Recycling Properties of Charcoal-Supported Palladium Oxide Nanoparticles in Sonogashira Reactions. *Appl. Catal. A Gen.* **2014**, *482*, 157–162. DOI: 10.1016/j.apcata.2014.05.019.

[40] Gujadhur, R. K.; Bates, C. G.; Venkataraman, D. Formation of Aryl–Nitrogen, Aryl–Oxygen, and Aryl–Carbon Bonds Using Well-Defined Copper(I)-Based Catalysts. *Org. Lett.* **2001**, *3*, 4315–4317. DOI: 10.1021/ol0170105.

[41] Komáromi, A.; Tolnai, G. L.; Novák, Z. Copper-Free Sonogashira Coupling in Amine–Water Solvent Mixtures. *Tetrahedron Lett.* **2008**, *49*, 7294–7298. DOI: 10.1016/j.tetlet.2008.10.037.

[42] Sabounchei, S. J.; Ahmadi, M. An Efficient Protocol for Copper- and Amine-Free Sonogashira Reactions Catalyzed by Mononuclear Palladacycle Complexes Containing Bidentate Phosphine Ligands. *Catal. Commun.* **2013**, *37*, 114–121. DOI: 10.1016/j.catcom.2013.03.028.