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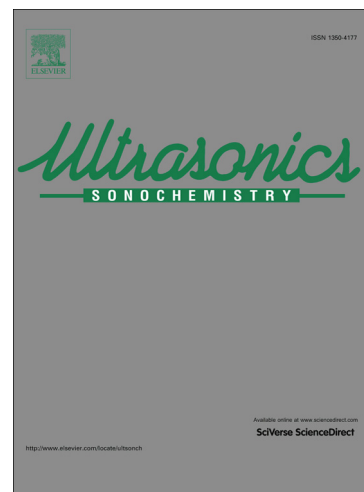
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Ultrasonic accelerated coupling reaction using magnetically recyclable bis (propyl malononitril) Ni complex nanocatalyst: a novel, green and efficient synthesis of biphenyl derivatives

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Abstract:

A novel, green and rapid sonochemical research to preparation of the biphenyls was carried out through the coupling reaction between various aryl halides and phenylboronic acid by using bis(propyl malononitrile) Ni (0) complex ($\text{NiFe}_2\text{O}_4@\text{SiO}_2\text{-BPMN-Ni}$) as an efficient nano catalyst. The catalyst can be recycled via an external magnet and reused several times without considerable loss of its catalytic activity. Compare to the previous works, this procedure has advantages such as easy workup, high yields of products, environmentally benign and short reaction times. The novel nickel catalyst prepared and characterized by FT-IR, XRD, SEM, EDX, TGA and VSM techniques.

Keywords: Heterogeneous catalyst, Coupling reaction, Ultrasound irradiation, Biphenyls, Nickel ferrite.

1. Introduction

At present, researchers know that the chemical effects of ultrasound irradiation are various and include considerable improvements in both stoichiometric and catalytic chemical reactions [1]. The cavitation phenomenon is driving force for sonochemistry, therefore a common requirement is that the reaction should be carried out in the liquid phase [2]. When liquid are affected by ultrasound irradiation, expansive and compressive acoustic waves makes alternately bubbles and develops the bubbles oscillate. In proper conditions, a bubble can overgrow and finally detonate, releasing the energy accumulated within the bubble in a very short time (with a heating and cooling rate of $>10^{10} \text{ K s}^{-1}$) [3]. The quick implosion of these bubbles in the liquids produces localized hot spots. The high local temperature and pressures provide desirable conditions for doing a large number of reactions [4]. Compared to traditional procedures which provides thermal energy in the macro environment, ultrasound irradiation is capable to activate many chemical organic reactions via providing the activation energy in micro system [5, 6]. Hence, an extensive diversity of chemical reactions can be carried out in shorter reaction times with higher yields and milder conditions under ultrasound irradiation compared to conventional methods [4]. Furthermore reduce of side products [7, 8], saving costs and energy, nontoxic and environmentally friendly solvent, are other advantages of sonochemistry [9, 10].

In recent years, magnetic nanoparticles have received significant attention due to their various applications in immobilize enzymes, bioactive polymers, transition metal catalysts and organocatalysts [11-13]. The surface of magnetic nanoparticles can be functionalized easily through proper surface modifications to enable the loading of a diversity of desirable functionalities [14].

Biaryl compounds have extensive application in many fields of organic chemistry. Suzuki and co-workers [15] first in 1979 reported one of the most applied procedure for the forming of carbon-carbon bonds involves Pd-catalyzed reactions between aryl halides and diverse organoboron compounds in the presence of a base, and it is usually referred to as the Suzuki coupling reaction [16]. Biaryl compounds has been applied to many fields, including natural compounds, bioactive products, UV absorbers, numerous polymers, agrochemicals and pharmaceutical intermediates, antioxidants, fine chemicals syntheses, and industrial applications [17]. Previously, the phosphine ligands have been applied to stabilize active palladium intermediates, and great effects have been reported for Pd-catalysed carbon-carbon coupling reactions. However, the oxygen and water sensitivity, expensive, toxicity and unrecoverable of these classes of ligands, prevents their usage in a diversity of synthetic applications [18]. Although using a Pd catalyst to develop the carbon-carbon cross coupling reaction is an appropriate and green procedure, it also has many drawbacks, such as the requirements of directing the group on the substrate to promote selectivity and low yields of products. Thus, the development of a novel method is still a notable aim for the coupling reactions. The advantages of this method are such as; mild, rapid, aerobic ligand less-based procedures using low catalyst loading, cheaper and environmentally friendly catalysts accessible, phosphine-free catalytic systems to overcome these difficulties. Nowadays, cross-coupling reactions catalyzed by other metals have been greatly prevalenced because these metals are accessible, cost-effective, and environmentally safe catalysts able to catalyze impressively the C-C coupling reactions [19-25].

The present research describes an ultrasound-assisted method that provides the efficient and simple preparation of biphenyls from phenylboronic acid and aryl halides using magnetically

BPMN-Ni complex. Furthermore, using the aforesaid procedure, catalyst separation becomes simpler and cost effective with an external magnetic field.

2. Experiment

2.1. Materials and Apparatus

All organic materials were purchased commercially from Sigma–Aldrich and Merck and were used without further purification.

FT-IR measurements were recorded on Magna 550 apparatus using with KBr plates. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 MHz spectrometers in the presence of tetramethylsilane as internal standard. A BANDELIN ultrasonic HD 3200 with probe model KE 76, with the diameter of 6 mm, was used to produce ultrasonic irradiation and homogenizing the reaction mixture. Transducer and probe converts electrical waves to mechanical vibrations and is consisted of backing, piezoelectric, matching, booster and Horn. Therefore, the induced frequency of probe to the reaction mixture is equal to 20 kHz. By changing the power of Tip the cavitations rate is displaced so that the Tip frequency under various amounts of power is constant. A thermal method was used for the calibration of ultrasonic power. Nanostructures were characterized using a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (Cu $K\alpha$, radiation, $\lambda = 0.154056$ nm), at a scanning speed of $2^\circ/\text{min}$ from 10° to 100° (2 θ). Scanning electron microscope (SEM) of nanoparticles and catalysts were recorded on a FESEM Hitachi S4160. Thermo gravimetric analysis (TGA) was performed on a mettler TA4000 system TG-50 at a heating rate of 10 K min^{-1} under N_2 atmosphere. The magnetic properties of nanoparticles have been measured with a vibrating sample magnetometer (VSM, PPMS-9T) at 300 K in Iran (Kashan University). Melting points was obtained with a Yanagimoto micro melting point apparatus and are uncorrected. The purity

determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

2.2. Catalyst preparation

2.3. General procedure for preparation of NiFe₂O₄ nanoparticles

Nickel ferrite nanoparticles (NiFe₂O₄) were synthesized by co-precipitation procedure, according to the reported method in the literature [26]. 3M solution of sodium hydroxide was added drop wise to salt solutions of 0.4M ferric chloride (FeCl₃.6H₂O) and 0.2M nickel chloride (NiCl₂.6H₂O). The pH of the solution was constantly monitored as the NaOH solution was added slowly. The reactants were stirred using a magnetic stirrer until the pH of solution was close to 13. Finally, 3 drops of oleic acid (as a surfactant) were added to the solution. The liquid-precipitate mixture was then brought to a reaction temperature of 80 °C and stirred for 40 min. The solutions were centrifuged and the precipitate was washed several times with double distilled water and ethanol to remove unwanted impurities and the excess surfactant from the synthesized sample. The sample was centrifuged for 15 min at 2000 rpm and then dried overnight at above 80 °C. The acquired substance was then grinded into a fine powder and then calcined for 10 h at 600 °C.

2.4. General procedure for preparation of nano-NiFe₂O₄@SiO₂ core-shell

The core-shell NiFe₂O₄@SiO₂ nanoparticles were obtained by a Stober method with minor modifications [27]. Generally, 100 mL of 75% ethanol/water solution containing the above obtained NiFe₂O₄ MNPs were transferred into a three-neck flask. After ultrasonic mixing for 10 min, under the N₂ atmosphere condition, 4 mL of tetraethoxysilane (TEOS) and 2 mL of

ammonia were added into NiFe_2O_4 MNPs suspension in turn under vigorous stirring. The reaction system was kept at 35 °C for 6 h. Consequently, the black precipitates, $\text{NiFe}_2\text{O}_4@ \text{SiO}_2$ MNPs, were washed with deionized water and ethanol for 3 times and dried at 80 °C for 10h.

2.5. General procedure for functionalization of $\text{NiFe}_2\text{O}_4@ \text{SiO}_2$ MNPs surfaces

To our knowledge, the surface of silica nanoparticles can be easily functionalized through the treatment with 3-iodopropyltriethoxysilane (3-IPTES). With vigorously stirring, 400 μL of 3-IPTES and 600 μL of ammonia were added slowly to 10 mL of $\text{NiFe}_2\text{O}_4@ \text{SiO}_2$ MNPs solution suspended in dry toluene. The solution was refluxed for 24 h under an inert atmosphere, filtered and washed subsequently with toluene, dichloromethane, and methanol, and dried under reduced pressure at 80 °C for 10 h. A mixture of 3-Iodopropyl functionalized MNPs was added to a suspension of K_2CO_3 (5 mmol) and malononitrile (5 mmol) in acetonitrile (30 ml). The mixture was refluxed for 48 h. Subsequently, the immobilization of metals (Ni, Co, Au, Fe and Ru) was carried out by their reduction in the presence of NaBH_4 as reducing agent, in absolute ethanol as the solvent system.

2.6. General procedure for the Suzuki-Miyaura coupling reaction

A vial equipped with a magnetic stirrer bar and a condenser was charged with aryl halide (1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2 mmol), catalyst (8 mol% Ni) and Water/ EtOH (1:1) (4 ml) and the reaction mixture was irradiated in ultrasonic apparatus. The reaction progress was followed using thin layer chromatography. After completion of the reaction, the mixture was cooled to room temperature, the catalyst was separated by an external magnet, and the product was extracted with ethyl acetate (15 ml) and dried over anhydrous MgSO_4 . The resulting solution was evaporated under vacuum to give the crude product. The separation of product by column

chromatography on silica gel using n-hexane or different mixtures of n-hexane, ethyl acetate as the eluents to afford the highly pure products (Table 4). The obtained pure products were characterized by physical methods and the IR, ^1H NMR and ^{13}C NMR spectra.

2.7. Spectral data for biphenyl derivatives:

1, 1'-Biphenyl. White solid; m.p.=70-72°C (Lit. [28] 68-70°C). IR (KBr)/ ν (cm^{-1}); 3058, 1433, 1072, 902, 729, 696. ^1H NMR (400 MHz, CDCl_3) δ : 7.35 (t, $J = 7.1$ Hz, 2H), 7.44 (t, $J = 7.4$ Hz, 4H), 7.60 (d, $J = 7.3$ Hz, 4H).

4-Methoxy-1, 1'-biphenyl. light yellow solid; m.p.=78-80°C (Lit. [28] 80-82°C). IR (KBr)/ ν (cm^{-1}); 1247, 1178, 1120, 1035, 833, 762, 697. ^1H NMR (400 MHz, CDCl_3) δ : 3.86 (s, 3H); 6.98-7.00 (d, $J = 8.4$ Hz, 2H); 7.47-7.43(t, $J = 7.2$ Hz, 1H), 7.60-7.55(t, $J = 7.4$ Hz, 2H), 7.60-7.55(t, $J = 8.2$ Hz, 4H).

(1, 1'-Biphenyl)-4-carbonitrile. White solid; m.p.=80-82°C (Lit. [28] 84-86°C). IR (KBr)/ ν (cm^{-1}); 844, 769, 722, 697. ^1H NMR (400 MHz, CDCl_3) δ : 7.42 (t, $J = 7.2$ Hz, 1H), 7.55 (t, $J = 7.6$ Hz, 2H), 7.60 (d, $J = 7.2$ Hz, 2H), 7.66-7.74 (m, 4H).

4-Nitro-1, 1'-biphenyl. Pale yellow solid; m.p.=112-114°C (Lit. [29] 113-115°C). IR (KBr)/ ν (cm^{-1}); 3077, 1599, 1520, 1345, 1122, 854, 740, 696. ^1H NMR (400 MHz, CDCl_3) δ : 7.46-7.48 (m, 1H), 7.50-7.52 (m, 2H), 7.61-7.66 (m, 2H), 7.69-7.49 (m, 2H), 8.29-8.31 (m, 2H).

Methyl (1, 1'-biphenyl)-4-carboxylate. White solid; m.p.=110-112°C (Lit. [28] 113-115°C). IR (KBr)/ ν (cm^{-1}); 698, 748, 856, 1113, 1186, 1283, 1719. ^1H NMR (400 MHz, CDCl_3) δ : 3.88 (s, 3H), 7.14(d, $J = 7.2$ Hz, 1H), 7.32-7.38 (t, $J = 7.4$ Hz, 2H), 7.43-7.50 (m, 4H), 7.84 (d, $J = 8.2$ Hz, 2H).

1-((1, 1'-Biphenyl)-4-yl) ethan-1-one. White solid, m.p=115-117°C; (Lit. [30] 117-119°C). IR (KBr)/ ν (cm^{-1}); 3031, 1681, 1600, 1359, 1263, 960, 842, 766. ^1H NMR (400 MHz, CDCl_3) δ : 2.67 (s, 3H); 7.42 (t, $J = 7.2$ Hz, 3H), 7.53 (d, $J = 7.2$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 8.02 (d, $J = 8.4$ Hz, 2H).

(1, 1'-Biphenyl)-4-carbaldehyde. White solid; m.p=61-63°C (Lit. [31] 62-65 °C). IR (KBr)/ ν (cm^{-1}); 2958, 2859, 1727, 1602, 1460, 846, 697. ^1H NMR (400 MHz, CDCl_3) δ : = 7.23 (t, $J = 7.0$ Hz, 1H), 7.44 (t, $J = 7.0$ Hz, 2H), 7.51 (d, $J = 7.9$ Hz, 2H), 7.66 (d, $J = 7.7$ Hz, 2H), 7.93 (d, $J = 7.7$ Hz, 2H), 10.05(s, 1H).

4-Methyl-1, 1'-biphenyl. White solid; m.p=40-42°C (Lit. [32] 41-43°C). IR (KBr)/ ν (cm^{-1}); 3027, 2926, 2859, 1599, 1567, 1522, 1456, 1381, 1340, 1072, 823, 749, 698, 481. ^1H NMR (400 MHz, CDCl_3) δ : 2.41 (s, 3H), 7.36-7.38 (m, 2H), 7.44-7.47 (m, 1H), 7.50-7.52 (m, 2H), 7.60-7.62 (m, 2H), 7.67-7.72 (m, 2H).

3-Methyl-1, 1'-biphenyl. Colorless liquid; (Lit. [29]). IR (KBr)/ ν (cm^{-1}); 3054, 3023, 2958, 2858, 1636, 1579, 1460, 1381, 1270, 1072, 882, 737, 727, 698, 617, 543. ^1H NMR (400 MHz, CDCl_3) δ : = 2.43 (s, 3H), 7.24 (d, $J = 8$ Hz, 1H) 7.36 (d, $J = 8.0$ Hz, 2H), 7.49 (m, 4H), 7.60 (q, $J = 8.0$ Hz, 2H).

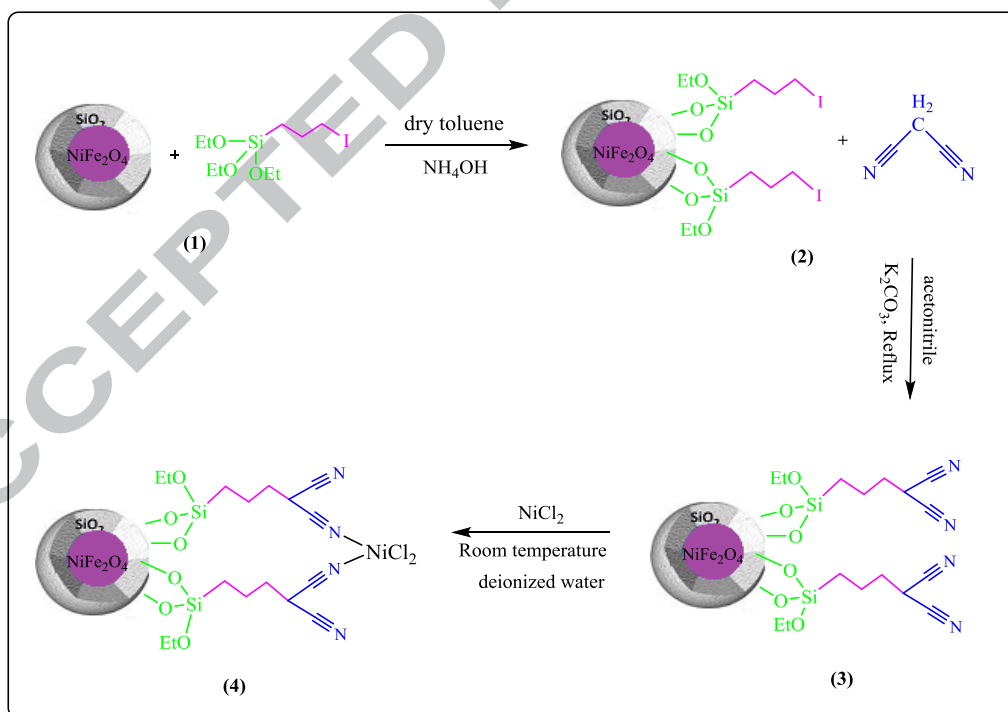
3-Chloro-1, 1'-biphenyl. Colorless transparent liquid; (Lit. [29]). IR (KBr)/ ν (cm^{-1}); 3049, 3023, 2914, 1375, 1489, 1457, 1418, 1122, 1068, 1040, 1015, 775, 747, 689. ^1H NMR (400 MHz, CDCl_3) δ : 7.35-7.39 (m, 3H), 7.52-7.56 (m, 3H), 7.70-7.72 (m, 3H).

p- Terphenyl. White solid; m.p=88-90°C (Lit. [32] 90-92°C). IR (KBr)/ ν (cm^{-1}); 1480, 1459, 1381, 1037, 837, 744. ^1H NMR (400 MHz, CDCl_3) δ : 7.35 (m, 2H), 7.44 (m, 4H), 7.60 (m, 8H).

1-Phenylnaphthalene. Colorless oil; (Lit. [33]). IR (KBr)/ ν (cm^{-1}); 3056, 2957, 1593, 1487, 1072, 1022, 910, 801, 778. ^1H NMR (400 MHz, CDCl_3) δ : 7.48(m, 3H), 7.55 (m, 6H), 7.91 (d, $J= 8.0$ Hz, 1H), 7.96 (d, $J= 7.6$ Hz, 2H).

3. Results and discussion

Nickel ferrite nanoparticles were prepared by using co-precipitation procedure, according to the procedure reported in the literature [26]. The synthetic pathway for preparation of the catalyst is shown in Scheme 1. In order to characterize the catalyst structure, the synthesized nano catalyst was characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectra, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), vibrating sample magnetometer (VSM), and also, thermo-gravimetric analysis (TGA) techniques.



Scheme 1. Synthesis of the NiFe₂O₄@BPMN-Ni (0) catalyst.

3.1 Characterization results of NiFe₂O₄@ BPMN-Ni

The powder XRD pattern of the nickel ferrite nanoparticles is shown in Figure 1. All of the characteristics peaks of NiFe₂O₄ are present in the diffraction pattern and the diffraction peaks match with standard XRD pattern (JCPDS file no. 03-0875). According to the Debye–Scherrer equation, the average particle sizes of the as-synthesized nano NiFe₂O₄ were calculated and the results show that the nano NiFe₂O₄ was obtained with an average diameter of 30 nm.

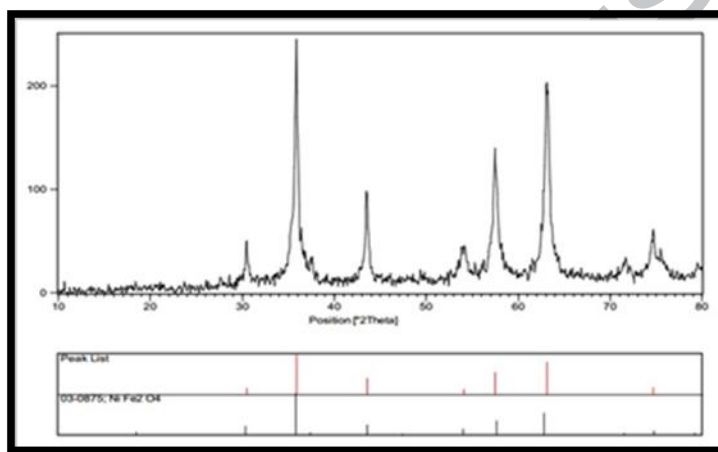


Fig. 1. The X-ray diffraction patterns of calcinated NiFe₂O₄.

Figure 2 shows the FT-IR spectrum of NiFe₂O₄ NPs, NiFe₂O₄@SiO₂, NiFe₂O₄@SiO₂-(CH₂)₃-I and NiFe₂O₄@BPMN in the range 400–4000 cm⁻¹. The spectrum presents characteristic bands at 3415, 2920, 1620, 597 and 421 cm⁻¹. The bands at 3415 and 1620 cm⁻¹ can be assigned to the stretching modes of absorbed water. The band at 2920 cm⁻¹ shows the presence of trace amounts of CO₂. The band at 597 cm⁻¹ is attributed to the vibration of Fe–O bonds. The characteristic band at 421 cm⁻¹ can be assigned to metal vibrations of Ni–O bonds. In all three spectra, the revealed peaks of NiFe₂O₄ were observed at 421–601 cm⁻¹, which could be attributed to the characteristic absorption of Fe–O and Ni–O bonds. In NiFe₂O₄@SiO₂

spectrum, NiFe₂O₄@SiO₂-NH₂ spectrum and final catalyst spectrum the intense peaks at 1091, 1095, 1096 cm⁻¹ was derived from the Si-O-Si stretching vibrations. These peaks proved that SiO₂ has coated the surface of NiFe₂O₄. In NiFe₂O₄@SiO₂-(CH₂)₃-I spectrum, the characterized peaks at 591 cm⁻¹ could be attributed to the C-I stretching vibrations. Moreover, the peak at 2945 cm⁻¹ is related to stretching vibration of CH₂, the peak at 1466 cm⁻¹ is related to bending vibration of CH₂. These described peaks confirmed that NiFe₂O₄@SiO₂-(CH₂)₃-I is prepared. The FT-IR spectrum of NiFe₂O₄@BPMN showed absorption bands at 2225 cm⁻¹; cyano, 2910 cm⁻¹ (C-H).

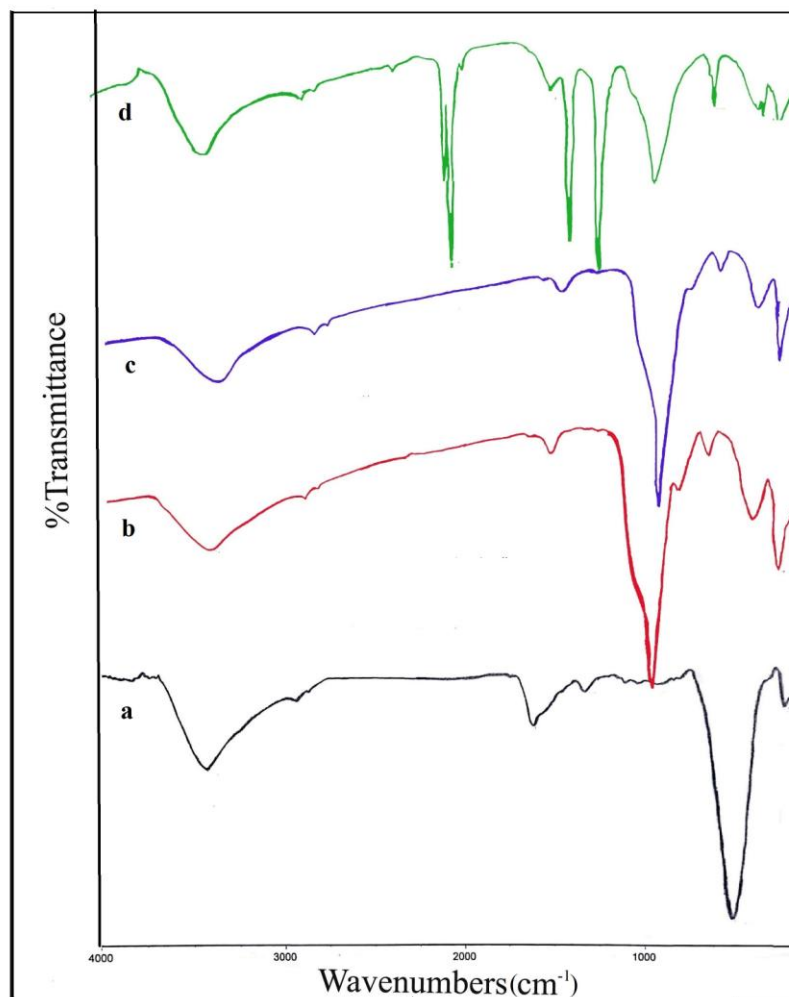


Fig. 2. FT-IR spectrum of a) NiFe₂O₄ NPs, b) NiFe₂O₄@SiO₂, c) NiFe₂O₄@SiO₂-(CH₂)₃-I and d) NiFe₂O₄@BPMN.

Figure 3 shows the SEM image of NiFe₂O₄ and final catalyst, in that the spherical morphology with an average diameter of about 50 nm for NiFe₂O₄ and 60 nm for catalyst was observed. Elemental analysis was also performed. The results show that the nanoparticles have a uniform size and spherical shape respectively as shown in Figure 3A and 3B.

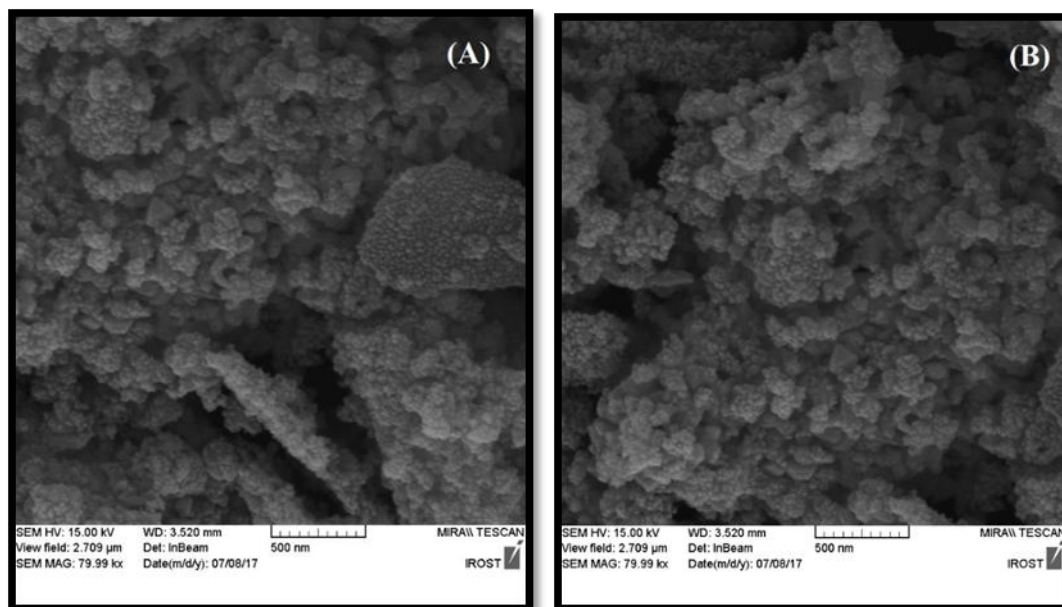
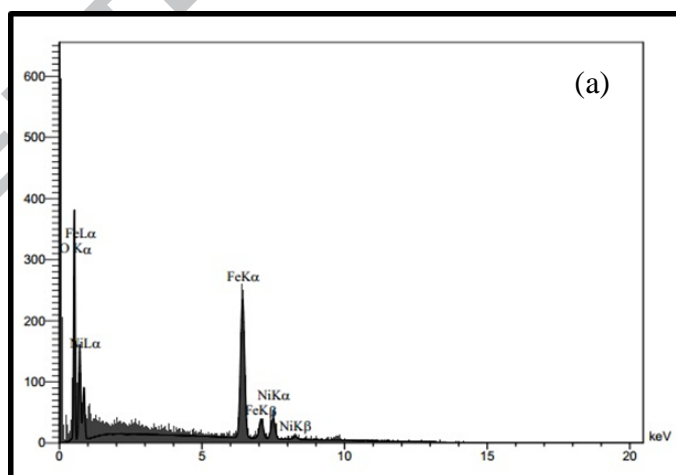


Fig. 3. SEM images of (A) NiFe₂O₄ nanoparticles and (B) NiFe₂O₄@BPMN-Ni

Figure 4 shows the EDX spectra of NiFe₂O₄ and Ni complex supported on NiFe₂O₄ nanoparticles. The results showed the presence of C, N, O, Si, Cl, Fe, and Ni in the composites, which confirmed that the Ni complex was loaded into NiFe₂O₄ nanoparticles.



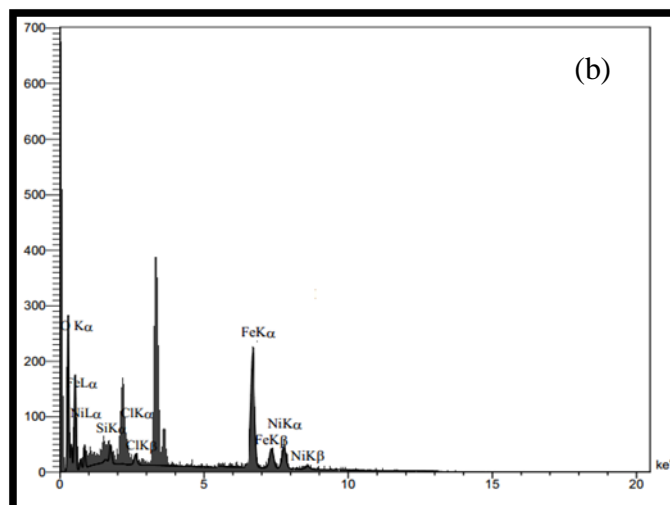


Fig.4. EDX spectrum of the (a) NiFe_2O_4 nanoparticles and (b) NiFe_2O_4 @BPMN-Ni

Magnetic properties of NiFe_2O_4 nanoparticles and NiFe_2O_4 @BPMN were investigated with VSM at room temperature (Figure 5). Magnetization of samples could be completely saturated at high fields of up to 1.0 T and the saturation magnetization of samples decreased from 35 to 10 emu g^{-1} . Furthermore, this consequence shows that the magnetization property reduces via coating and functionalization. Therefore these results confirm that the catalysts can be simply separated and recycled by an external magnetic field.

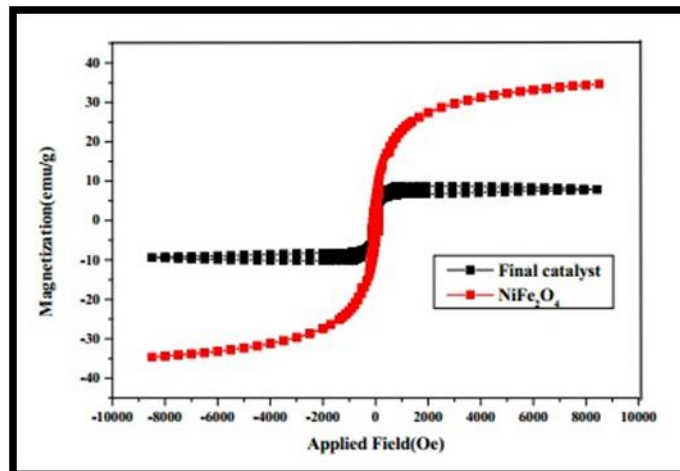


Fig. 5. The VSM curve of NiFe₂O₄ nanoparticles and NiFe₂O₄@BPMN-Ni.

The thermal stability of the magnetic nanocatalyst was investigated using thermogravimetric analysis (TGA) to confirm the presence of various groups on the surface of the NPs and the related curves are displayed in Figure 6. The initial small weight loss from the catalyst below 200 °C which could be assigned to the loss of bound water or physically adsorbed solvent. The weight loss observed (30%) at 250–650 °C in TGA curve of NiFe₂O₄@BPMN is mainly related to the decomposition of organic groups grafted to the NiFe₂O₄ surface. These results show that catalyst is stable up to 250 °C and can be used in organic synthesis.

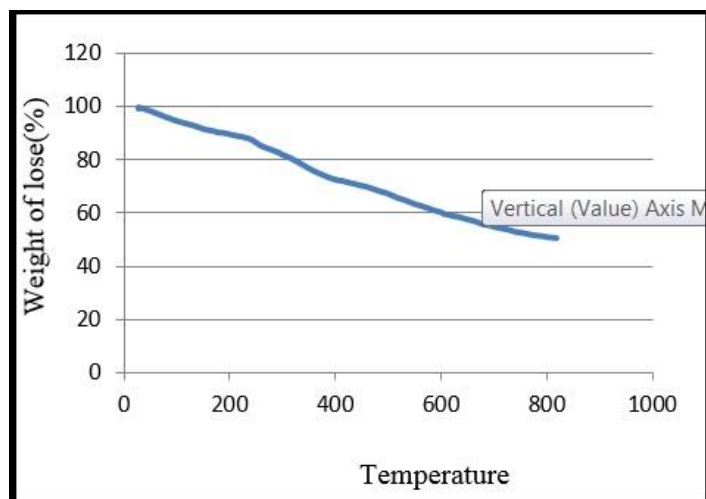


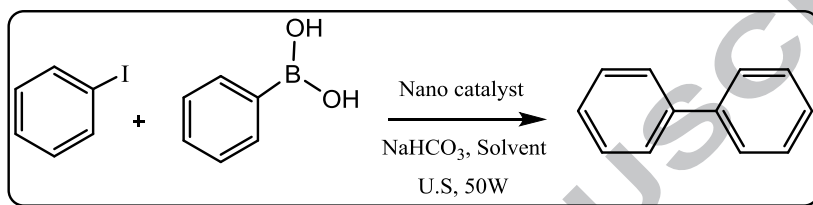
Fig. 6. TGA curve of NiFe₂O₄@BPMN-Ni.

3.2. Investigation of catalyst activity

To investigate the catalytic efficiency of the nanocatalyst and to characterize optimal conditions for Suzuki-Miyaura coupling reaction, iodobenzene and phenylboronic acid was selected as model reagents and were studied under different factors such as type and amount of catalyst, solvent, bases and the effect of ultrasound irradiation and the results are listed in Tables 1, 2 and 3. At first, we investigated performance of the several metals in Suzuki-Miyaura reaction. After screening a various catalyst containing Ni, Co, Au, Fe and Ru complex, it has been found that the NiFe₂O₄@BPMN-Ni is the most effective catalyst for the sonochemically preparation of biphenyl derivatives. Therefore, NiFe₂O₄@BPMN-Ni complex was used for further investigations. Then several solvents such as DMF, EtOH, CH₃CN, DMSO and H₂O/EtOH (1:1) were checked. The examination of solvent was displayed that H₂O/EtOH (1:1) was the best solvent for the coupling reaction of phenylboronic acid and aryl halide compounds (Table 1, entry 9). Afterwards, the activity of the catalyst in different amounts on the reaction was studied. The reviews showed that in the presence of 8 mol% of the NiFe₂O₄@BPMN-Ni catalyst, the yield developed sharply to 93% (Table 1, entry 9).

In continues, to obtain the appropriate base for the reaction, we examined diverse bases, among the different bases screened, K_2CO_3 was found to be the excellent base for this reaction (Table 2, entry 7).

Table 1. Optimization of solvent and catalytic system for the formation of biphenyl derivatives^a.



Entry	Solvent	Catalytic system (mol %)	Yield ^b (%)
1	DMF	NiFe ₂ O ₄ @ BPMN-Au (10%)	74
2	DMF	NiFe ₂ O ₄ @ BPMN-Co (10%)	65
3	DMF	NiFe ₂ O ₄ @ BPMN - Ni (10%)	89
4	DMF	NiFe ₂ O ₄ @ BPMN - Fe (10%)	42
5	DMF	NiFe ₂ O ₄ @ BPMN - Ru (10%)	35
6	CH ₃ CN	NiFe ₂ O ₄ @ BPMN - Ni (10%)	78
7	H ₂ O / EtOH (1:1)	NiFe ₂ O ₄ @ BPMN - Ni (10%)	93
8	DMSO	NiFe ₂ O ₄ @ BPMN - Ni (10%)	82
9	H ₂ O / EtOH (1:1)	NiFe ₂ O ₄ @ BPMN - Ni (8%)	93
10	H ₂ O / EtOH (1:1)	NiFe ₂ O ₄ @ BPMN - Ni (6%)	88

^a Reactions conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol), NaHCO₃ (2 mmol), ^b Isolated yield

Table 2. Optimization of reaction in the presence of different bases ^a

Entry	Solvent	Base	Base amount (mmol)	Yield ^b
1	H ₂ O / EtOH (1:1)	K ₃ PO ₄	2	65
2	H ₂ O / EtOH (1:1)	NEt ₃	2	67
3	H ₂ O / EtOH (1:1)	K ₂ CO ₃	2	99
4	H ₂ O / EtOH (1:1)	KOH	2	76
5	H ₂ O / EtOH (1:1)	NaHCO ₃	2	89
6	H ₂ O / EtOH (1:1)	Na ₂ CO ₃	2	72
7	H ₂ O / EtOH (1:1)	K ₂ CO ₃	1.5	99
8	H ₂ O / EtOH (1:1)	K ₂ CO ₃	1	94

^a Reactions conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol), Ultrasonic irradiation (50 W), H₂O / EtOH (1:1) NiFe₂O₄@ BPMN - Ni (8%), ^b Isolated yield.

In next step of this research, the power of the ultrasonic irradiation was optimized. The coupling reaction was performed under different powers of ultrasound irradiation. It was found that the appropriate and effective power of ultrasound for this reaction to be 55 watt (Table 3, entry 5).

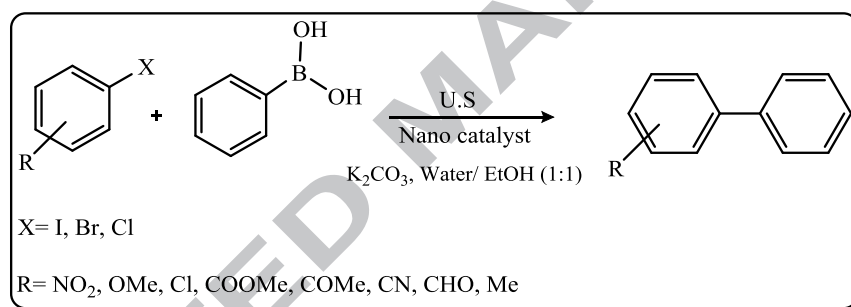
Table 3. Study of the ultrasonic irradiation effect on the Suzuki cross-coupling ^a

Entry	Power (w)	Time (min)	Yield (%) ^b
1	silent	120	-
2	35	50	58
3	40	46	76
4	45	41	82
5	50	35	91

6	55	28	99
7	60	28	99

^a Reactions conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol), NiFe₂O₄@BPMN - Ni (8%) and K₂CO₃ (1.5 mmol) in Water/ EtOH (1:1), ^b Isolated yield.

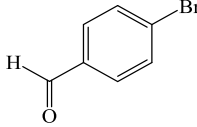
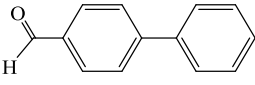
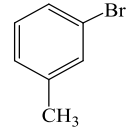
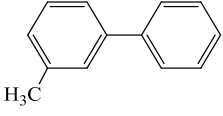
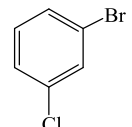
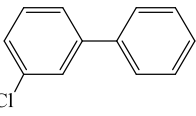
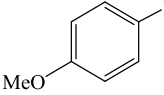
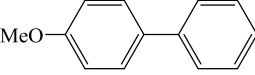
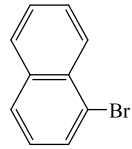
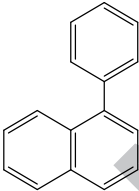
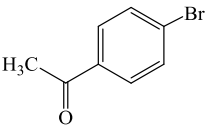

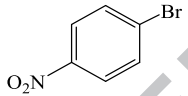
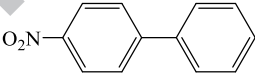
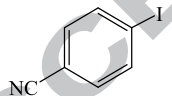
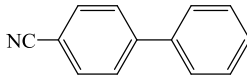
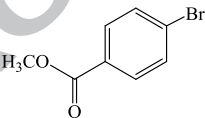
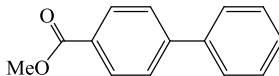
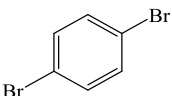

With the optimal reaction condition in hands, a broad range of structurally diverse aryl halides were reacted with phenylboronic acid in the presence of 8 mol% of NiFe₂O₄@BPMN-Ni catalyst and 3 mmol K₂CO₃ with water as solvent under ultrasonic irradiation and the results are showed in Table 4. As shown in Table 4, in the presence of Ni nanocatalyst, excellent product yields were achieved in shorter reaction times under ultrasound irradiation.

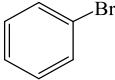
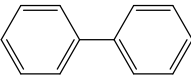
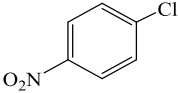
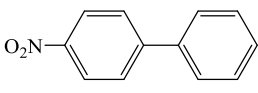
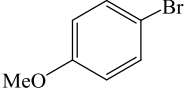
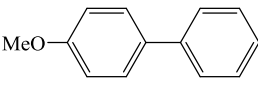
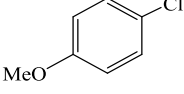
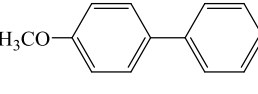


Scheme 2. Suzuki-Miyaura cross-coupling using the NiFe₂O₄@BPMN-Ni complex.

Table 4. Suzuki-Miyaura cross-coupling of aryl halides and phenylboronic acid catalyzed by NiFe₂O₄@BPMN-Ni ^a

Entry	Aryl halide	Product	Time (min)	Yield ^b (%)
1			28	99
2			51	90

3			25	97
4			50	93
5			37	95
6			40	97
7			43	96
8			37	97
9			35	98
10			25	98
11			38	95
12			35	97

13			48	98
14			73	90
15			50	92
16			80	82

^a Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol), NiFe₂O₄@BPMN-Ni (8%) and K₂CO₃ (1.5 mmol), ^b Isolated yield.

When the reaction was performed under ultrasonic irradiation to give excellent yields of products in very short reaction times. Ultrasonic irradiation differs from traditional energy sources. Ultrasound improves the organic reactions in a solution via increase the number of active cavitation bubbles and the size of the individual bubbles, both of which are expected to result in higher maximum collapse temperature and accelerated respective reaction.

In order to illustrate the merit of this proposed research, we compared the obtained results with the recently reported works. For this purpose, the reactions of iodobenzene and phenylboronic acid using 8 mol% of Ni complex in water under ultrasonic irradiation in the presence of 3 mmol of K₂CO₃ were chosen as a model reaction and the comparison was performed on the basis of reaction conditions, reaction time and obtained yields (Table 5). The properties of this research which make it exclusiveness than the other previously reported procedures, are mild reaction condition, environmentally benign, simple recycle of the nano catalyst by an external magnet, reusability of the catalyst for seven times without considerable loss of catalytic activity, excellent yields of biphenyls and very short reaction times.

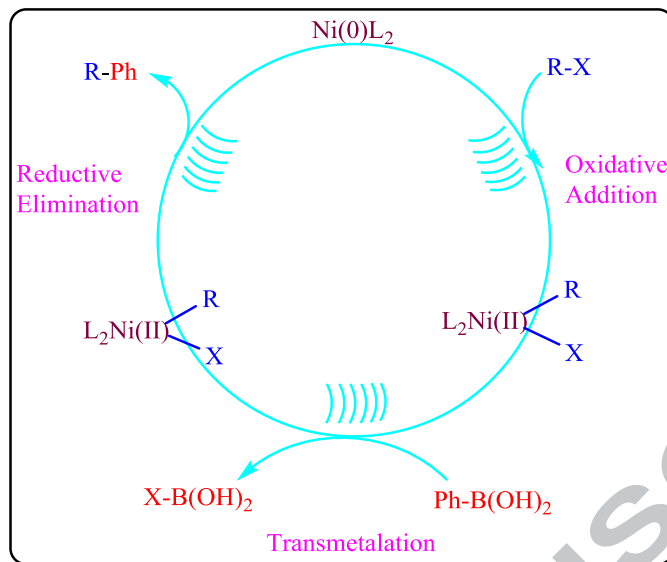
Table 5. Comparison the reaction results of 4-methoxy-1, 1'-biphenyl in this research and various reports in the literature.

Entry	Reaction Condition	Time	Yield (%) ^a	ref
1	NiFe ₂ O ₄ @ BPMN-Ni (0). US/55W	40 (min)	97	This work
2	Pd-Ni alloy, 100°C	12 (h)	92	[34]
3	S-S-Pd, 20KHz (US)	3 (h)	92	[35]
4	PAPT-stablized gold nanoparticles, 80°C	4 (h)	92	[36]
5	Ni (0)/MWCNTs, K ₃ PO ₄ , 100 °C	4 (h)	93	[37]

^a Isolated yield.

3.3. The proposed reaction mechanism

The proposed mechanism for the formation of biphenyl derivatives is demonstrated in Scheme 2. Actually, the catalytic cycle consists of three steps: (1) oxidative addition, (2) transmetalation, and (3) reductive elimination. The oxidative addition step is generally considered as the rate-determining step (RDS) (Scheme 2). This coupling reaction is efficiently performed on the high nanoparticle surface and also by the cavitation phenomenon of ultrasound irradiation. As shown in the steps, it is highly probable that the aryl halide compounds have been activated through placing Ni complex in nano catalyst between their carbon and halogen atoms. Thus the notable roles of NiFe₂O₄@BPMN-Ni nanocatalyst are activation of aryl halides and efficient development of the reaction on its high surface area.



Scheme 3. Proposed mechanism for Suzuki reaction

3.4. Catalyst Reusability

The recyclability of the $\text{NiFe}_2\text{O}_4\text{@BPMN-Ni}$ complex as a heterogeneous catalyst was investigated in the coupling of iodobenzene and phenylboronic acid using 8 mol% of catalyst in water under ultrasonic irradiation in the presence of 3 mmol of K_2CO_3 . After completion of the reaction, the catalytic system was separated from the reaction mixture using an external magnet and the residual catalyst was washed with ethanol several times, dried and reused in subsequent reactions. As can be seen after seven cycles, the catalyst was demonstrated approximately the same activity and led to the corresponding product in high yields (Figure 7).

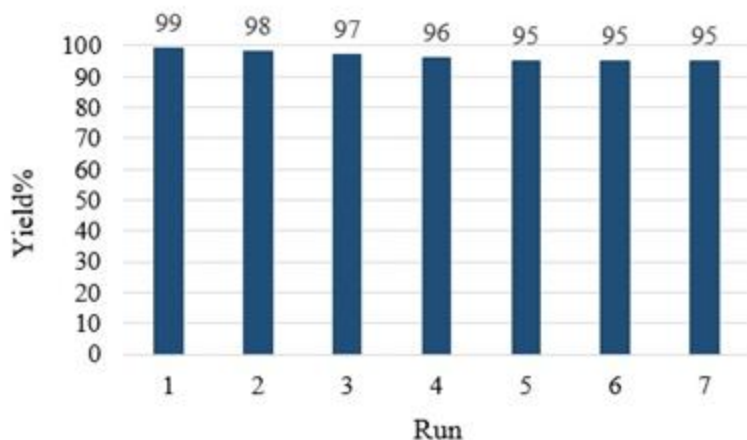


Fig. 7. Reusability of catalyst for the synthesis of biphenyl.

4. Conclusion

In the current study an advanced, convenient and mild procedure introduced for the synthesis of biphenyl compounds through condensation of phenylboronic acid and aryl halides using highly efficient and magnetically recyclable nanocatalyst under ultrasound irradiation. This novel sonochemically approach provides several advantages including green process, mild reaction conditions, easy recoverability and reusability up to seven times for the nanocatalyst, excellent yields of various biphenyl derivatives and short reaction times.

Acknowledgments

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Graphical abstract:

Ultrasonic accelerated coupling reaction using magnetically recyclable bis(propyl molononitril) Ni complex nanocatalyst: a novel, green and efficient synthesis of biphenyl derivatives

