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Sustainable and recyclable magnetic nanocatalyst of 1,10-phenanthroline Pd(0) complex in green synthesis of biaryls and tetrazoles using arylboronic acids as versatile substrates

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ARTICLE INFO	ABSTRACT
Keywords: 1, 10- Phenanthroline Palladium catalysis Magnetic core-shell Arylboronic acids Suzuki-Miyaura Tetrazol	A magnetic nanocatalyst was purveyed as a heterogeneous recoverable palladium-based catalyst anchored on green, sustainable and phosphine free support. Resulted $Fe_3O_4@SiO_2$ -Phen-Pd(0) nanocatalyst bearing powerful phenanthroline ligand was thoroughly characterized by physicochemical approaches like UV–vis, FT-IR, EDX, XRD, TGA, ICP, VSM, DLS, FESEM, and TEM analyses. After finding trustable data, the obtained magnetic catalyst was considered to be applied in the Suzuki-Miyaura type C-C couplings and getting corresponding tetrazoles using arylboronic acid derivatives as alternate precursors of aromatic halides and stupendous data were observed.

1. Introduction

The human health promotion and maintenance of the environment are "better to prevent than to cure". The concept of "sustainable development" was articulated from UN Commission on Environment and Development in 1987 (Brundtland Commission) to consider green chemistry in the fields of organic syntheses, processing, and using ecofriendly alternative chemicals [1]. To reach such context, nanotechnology has been reaped notable attentions in varies research fields including chemistry, environmental remediation, biomedical engineering, and biotechnology because of introducing unique properties of nanoparticles (NPs) belongings [2].

In the green chemistry point of view, nanotechnology is being considered to design more environmentally and economically sustainable and safe nano products with no creation health risk [3]. Among important chemicals in nanotechnology, the Fe_3O_4 -based nanoparticles have been found remarkable dignity due to their impressive superparamagnetic, simple synthesis and biochemical properties such as biodegradability, non-toxicity, and convenient separation from the reaction [2–4]. The deployment of such nanoparticles present extensive industrial and laboratory applications in drug delivery [4], hyperthermia [5], sensors [6], magnetic resonance imaging (MRI) [7,8], nanocomposites [9], bioseparations [10], therapeutic and medical usages [11], magnetic storage [12], and catalysts [13]. To stabilize the Fe₃O₄ nanoparticles and enhance their distribution, the utilization of which using silica (SiO₂) shell is of the most interests due to its stability, non-toxicity, and biocompatibility. The resultant magnetic core-shells have both advantages of magnetic core and sustainable shell [14,15]. As mentioned previously, this unique scaffold can be applied in the synthesis of magnetic catalyst to be performed in different organic processes especially in the synthesis of transition metal-based catalysts. The reactions such as Suzuki-Miyaura C-C couplings as so popular Csp²-Csp² bond formation reactions as well as getting tetrazole derivatives are attractive strategies in organic synthesis that have comprehensively applied palladium (Pd) based magnetic nanocatalysts [16–18].

These methodologies can introduce a vast library of pharmaceuticals including anticancer [19,20], antifungal [21,22], antibacterial [23,24], antitubercular [25,26], and antimalarial [27,28] compounds. Furthermore, nitrogen-rich heterocycles specifically tetrazoles are being attended as photosensitive reagents [29–35], ligands in coordination chemistry, constructing agents in metal-organic frameworks (MOFs) [36,37], valuable ligands in chiral catalysts in asymmetric reactions [38]. Some bioactive structures resulting from these strategies are shown in Fig. 1.

The synthesis of tetrazoles and the formation of C—C bonds by Suzuki-Miyaura C-C coupling reactions have recently attracted much attention and various preparative protocols have been introduced.

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Nevertheless, these protocols have some drawbacks such as harsh reaction conditions, using strong acidic catalysts, having tedious work-ups attributed to homogeneous catalyst, and applying non-reusable catalysts [39–42]. More importantly, some reports in the synthesis of Suzuki products and tetrazole derivatives considered catalysts bearing toxic phosphorous ligands [43,44] and it is the main motivation to accomplish such procedure using non-toxic catalysts free of phosphine ligands. For the first time and only approach in the literature, Vignesh et al. synthesized some tetrazoles directly from arylboronic acids using ONO pincer type palladium complex as a catalyst [44]. Arylboronic acids are of superior sources of aryl groups in Suzuki type C-C couplings as well as finding tetrazole derivatives owing to their stability, availability, high tolerance against various functional groups, and commonly, requirement of mild reaction conditions [45].

Noteworthy, the transition metal-catalyzed functionalization of aromatic C—H bonds obtains an efficient replacement to the cyanation reactions with metallic precursors of NaCN, KCN, CuCN, and ZnCN [46–48]. Hence, the development of the easy and accessible methodology for the cyanation of arylboronic acid compounds using NaCN is much desirable due to its robust properties, being cheap, water solubility, and unlike CuCN and TMSCN, it does not produce any undesirable waste [49].

An increasing demand for utilization environmentally benign process convinced us to design and develop a novel stable superparamagnetic heterogeneous phosphine ligand-free Pd complex of 1,10phenanthroline (Phen) as a bidentate nitrogen ligand, which has been widely used for preparation of various metal complexes [50]. Therefore, in ongoing of our research group, it was decided to prepare magnetic nanocatalyst of $Fe_3O_4@SiO_2$ -Phen-Pd(0) to be checked out its catalytic activity against one-pot multicomponent transformation of arylboronic acids to 5-substituted 1H-tetrazoles and biaryls through Suzuki cross coupling reaction, Scheme 1.

2. Experimental section

2.1. Chemical and instrumentation

All chemicals with high quality were prepared from Sigma-Aldrich and Merck. Determination of the monitoring the progress of reactions and purity of the substrate was accomplished by thin layer chromatography on silica gel polygram SILG/UV 254 plates. NMR spectra were recorded in CDCl3 and DMSO on Bruker Avance DPX250, DPX300, and DPX400 spectrometers, at 250, 300 and 400 MHz, respectively. FTIR spectrometer model Shimadzu FT-IR 8300 were considered to find FTIR measurements using KBr pellet. Melting points were measured by a micro melting point apparatus (electrothermal, BUCHI 510). The elemental analyses (C, H, N) were obtained using a Thermo Finnigan Flash EA-1112 CHNSO rapid elemental analyzer. X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8-Advance X-ray diffractometer using CuK α radiation ($\lambda = 1.5418$). Dynamic Light Scattering (DLS) using a HORIBA-LB550. The Brunauer-Emmett-Teller (BET) surface areas were obtained by using the nitrogen adsorptiondesorption isotherms determined at the temperature of liquid nitrogen on an automatic analyzer (Autosorb-iQ-MP, Quantachrome, USA). Field emission scanning electron microscopy (FE-SEM) characterization was operated on a Hitachi S-4160. Transmission Electron Microscopy (TEM) is performed on the Philips EM208 microscope, which operates at an accelerator voltage of 100 kV. Vibrating sample magnetometer (VSM) of magnetic nanocomposites were obtained using an instrument model BHV-55. The loading amount of palladium was measured by inductively coupled plasma (ICP, Varian, Vista- pro). A PerkinElmer device was used to get thermal gravimetric analysis (TGA) data. UV-vis spectra were obtained on a PerkinElmer Lambda 25 UV-vis spectrometer. The elements in the catalyst were investigated using an energy dispersive X-ray (EDX) spectroscopy accessory to the Philips scanning electron microscopy (SEM). Finally, the melting points and CHNS of products and their



Fig. 1. Some bioactive scaffolds have been obtained through Suzuki-Miyaura coupling reactions and the preparation of 5-substituted 1H- tetrazole derivative.



Scheme 1. Application of Fe₃O₄@SiO₂- Phen-Pd(0) in Suzuki-Miyaura couplings and tetrazole formation reactions.

¹H NMR spectra were compared with literature values.

2.2. General procedure

2.2.1. The synthesis of 1, 10-phenanthroline-5, 6-dione (L2)

On the base of the literature report [51], a 200 mL double-neck round bottom flask was charged by 90 mL of H₂SO₄. The container was transferred to liquid nitrogen and simultaneously, it was maintained under inert nitrogen atmosphere. Then, 20 mmol of 1, 10-phenanthroline (L1) (3.65 g) and 208.8 mmol of KBr (24.85 g) were added to the vessel and allowed to the mixture to reach room temperature. After the appearance of orange solution, the concentrated HNO3 (50 mL) was carefully added dropwise until the solution color turns to red. Then, it was heated at 90 °C for 5 h under continuously mild stirring. After that, the crude was poured slowly in to 1 L of cooled water followed by neutralization by Na₂CO₃. The reaction mixture was extracted using CH₂Cl₂ to find white yellow organic layer. The obtained organic layer was dried over MgSO₄. The orange-yellow precipitate was observed after the evaporation of solvent under vacuum. Finally, the yield of pure 1, 10-phenanthroline-5,6-dione was calculated to be 91 % after recrystallization from EtOH.

2.2.2. The synthesis of 3a, 1H-imidazo [4,5-f][1,10]phenanthroline (L3)

Based on reported procedure in the literature [52], 5 mmol of 1, 10-phenanthroline-5,6-dione (1.05 g), 5.5 mmol of formaldehyde (37 wt.%), 16 ml glacial acetic acid, and 103.78 mmol of ammonium acetate (8 g) were surcharged to a flask and the resultant was let to be stirred under the reflux condition for 1 h. The mixture was then cooled down to room temperature, diluted with H₂O (10 mL), and neutralized by ammonia solution to attain cream residue. In the next, the precipitate was washed three times by acetone and water, respectively, and transferred to a desiccator to be dried. The recrystallization process from EtOH presented pure compound **3** in 88 % yield.

2.2.3. The synthesis of 1-butyl-3a, 11b-dihydro-1H-imidazo[4, 5-f] [1,10] phenanthroline (L4)

Accordingly [53], 0.67 g of as prepared structure L3 (3 mmol) was firstly dissolved in acetone and then, was treated by KOH (0.2 g, 3.6 mmol). Next, the resulted crude was stirred under the reflux conditions and after 1 h, 3 mmol of butyl iodide (0.34 mL) was subjoined to obtained mixture. This crude was kept on the reflux condition for 48 h with somehow vigorous stirring. The reaction progress was monitored by TLC and after the completion of reaction, the solvent was vaporized and the obtained residue was extra purified by dissolving in DCM followed by filtering off. Eventually, light brown precipitate (81 % yield calculated by GC) was observed by column chromatography (eluent: n-hexane: EtOAc /8:2) in 81 % yield. The approach of finding L4 is illustrated in Scheme 2.

2.2.4. Preparation of Fe₃O₄ NPs

As it has been reported previously [54], to a solution of 1 g of polyvinyl alcohol (PVA 15000) in 30 mL of deionized water, it was added 0.9 g of FeCl₂ (4.5 mmol) and 1.3 g of FeCl₃.6H₂O (4.8 mmol) at 80 °C, respectively. After stirring for 0.5 h, 1.0 mol/L of hexamethy-lenetetramine (HMTA) was poured into the solution dropwise to adjusted pH of the reaction medium on 10, and then, the mixture was heated for more 2 h at 60 °C to provide magnetic Fe₃O₄ NPs as a black solid residue. In the final step, Fe₃O₄ nanoparticles were regularly collected by a magnet, washed with H₂O and dried at 60 °C for 10 h.

2.2.5. Preparation of Fe₃O₄@SiO₂ core-shell

Routinely, Fe₃O₄ NPs (0.5 g) was dispersed in 5 mL of deionized H₂O with stirring at room temperature. Afterwards, this crude was treated by a solution of 0.2 mL of TEOS in ethanol (50 mL). Then, NaOH solution (5.0 mL, 10 wt%) was slowly added to the latter drop by drop and the resulting was let to be stirred for extra 30 min. Finally, Fe₃O₄@SiO₂ core-shells were accumulated magnetically, washed three times with H₂O/EtOH (1:1, 30 mL), and dried at 80 °C [55].

2.2.6. Preparation of Fe₃O₄@SiO₂-Cl

1.0 g of as prepared Fe₃O₄@SiO₂ NPs were dispersed ultrasonically in 20 mL of ethanol and the resulting mixture was treated by (3-chloropropyl)triethoxysilane (3 mmol, 0.7 mL). In continuous, the obtained solution was refluxed with stirring for 12 h to graft (3-chloropropyl) triethoxysilane on the surface of Fe₃O₄@SiO₂ NPs. The product, Fe₃O₄@SiO₂-Cl, was entirely collected by magnetic separation process, washed with a mixture of water and ethanol (3 × 30 mL) to rectify unreacted precursors and dried at 70 °C [54].

2.2.7. Preparation of Fe₃O₄@SiO₂-Phen (L5)

Subject to a simple method, 1 g of the synthesized $Fe_3O_4@SiO_2-Cl$ particles were interspersed in 20 mL of THF. The presented solution was augmented by 3 mmol of ligand L4 and the final mixture

was stirred for 12 h under the nitrogen atmosphere. The obtained **L5** scaffold was purified as the same as former step.

2.2.8. Preparation of Fe₃O₄@SiO₂-Phen-Pd (0) (L5-Pd)

Eventually, the magnetic nanocatalyst **L5-Pd** was synthesized by the addition of 5 mmol of Pd(OAc)₂ to the mixture of dispersed **L5** (1 g) in EtOH (20 mL) and the crude was stirred drastically for 6 h under the reflux condition. This ultimate magnetic nanocatalyst **L5-Pd** was wholly detached from the reaction medium, washed with H₂O: EtOH three



Scheme 2. The synthesis steps of the Fe₃O₄@SiO₂-Phen-Pd (0) Nanocatalyst.

times, and finally, dried at 70 °C. The synthetic pathway for synthesizing L5-Pd is illustrated in Scheme 2.

2.2.9. General procedure for Suzuki-Miyaura coupling reaction

Aryl halide (1 mmol), 1.1 mmol of arylboronic acid and 2 mmol of K_2CO_3 were transferred to 10 mL round bottom flask as in addition to the addition of Fe_3O_4 @SiO₂-Phen-Pd(0) (5 mg, 0.17 mol% Pd) in 4 mL of EtOH/H₂O (1:1). The mixture was stirred at 50 °C for appropriate time and the progress of the reaction was checked out by TLC analysis. After finishing the reaction, the magnetic nanocatalyst was segregated from the reaction and the obtained crude was extracted using H₂O:DCM solution. Continuously, the organic layer was dried

over MgSO₄ and filtered off. The filtrate was concentrated by evaporation under vacuum and the residue was finally purified using flash chromatography by *n*-hexane / DCM (10:2) as eluent to detect desire product.

2.2.10. General procedure for synthesizing of 5-substituted 1H-tetrazole derivatives

To the same vessel containing 4 mL EtOH/H₂O (1:1), there were added all ingredients including arylboronic acid (1 mmol), KCN (3 mmol), NaN₃ (3 mmol), K₂CO₃ (2 mmol) and 4 mg of Fe₃O₄@SiO₂-Phen-Pd(0) (0.14 mol% Pd). This multicomponent one-pot reaction was refluxed under nitrogen in appropriate times. The reaction progress was monitored by TLC analysis and eventually, the inorganic impurities were taken away from the mixture after extracting with H₂O:DCM (1:1) mixture (3 × 50 mL). The organic layer was dried over anhydrous Na₂SO₄ and then, the filtrate was concentrated under vacuum to get crude residue. The pure outcomes were achieved in good to excellent yields using column chromatography with petroleum ether:DCM (10:2) as eluent.

3. Results and discussion

The 1, 10-phenanthroline complex of palladium (0) was anchored on Fe_3O_4 @SiO₂ nanospheres *via* the multistep procedure exhibited in Scheme 2.

The prepared catalyst was then examined by FT-IR (Fourier

transform infrared), powder XRD (X-ray diffraction), DLS (Dynamic light scattering), BET (Brunauer - Emmett - Teller), FE-SEM (Field emission scanning electron microscopy), TEM (Transmission electron microscopy), TGA (Thermogravimetric analysis), ICP (Inductively coupled plasma), VSM (Vibrating sample magnetometer), EDX (Energy dispersive X-ray), and UV-vis (Ultraviolet-visible spectroscopy). The FTIR was the first investigation for the characterization of Fe₃O₄, Fe₃O₄@SiO₂, 1-butyl-1*H*-imidazo[4,5f][1,10] phenanthroline (Phen), Fe₃O₄@SiO₂-Cl, Fe₃O₄@SiO₂-Phen, and Fe₃O₄@SiO₂-Phen-Pd(0) magnetic NPs, respectively (Fig. 2a-f). The peak at 581 cm⁻¹ can be depicted to the presence of Fe-O bonds in Fe₃O₄ and is clearly observed in the other spectrum that clarifies the stability of Fe₃O₄ MNPs in all synthetic steps (Fig. 2a, b, d-f). Moreover, the broad peak at 3424 cm⁻¹ is attributed to OH groups on Fe₃O₄ particles. Fe₃O₄@SiO₂ scaffolds were characterized by two well-known broad and intense bands at around 1080–1100 cm⁻¹ assigned to the presence of Si-O-Si asymmetric and symmetric vibrations in the silica shell (Fig. 2b,d-f). The successful preparation of 1-butyl-1*H*-imidazo[4,5-f][1,10] phenanthroline(Phen) is confirmed by the presence of specific absorbed peaks at 1455 cm⁻¹ (Bending vibrations of aliphatic C—H), 1673 cm⁻¹ (aromatic stretching of C=C), 1681 cm⁻¹ (stretching vibrations of C=N), and 2870-2970 cm^{-1} (CH- bonds stretching peaks) (Fig. 2c). The existence of vibrations at 610 $\rm cm^{-1}$ in Fig. 2d along with almost the same peaks in comparison with Fig. 2 a and b assured us from successful production of Fe₃O₄@SiO₂-Cl. In continues, the interaction between phenanthroline derivative and magnetic Fe₃O₄@SiO₂-Cl was supported by occurring (Fig. 2e). The characteristic peaks at 1461, 1671, 1689, 2874–2938, and 3405 cm⁻¹, which are allocated to bending vibrations of aliphatic C—H bonds, aromatic CC, CN== bond stretching vibrations, stretching peaks of C-H bonds, respectively, and also the absence of C-Cl absorption (Fig. 2e). At the end, the presence of the peak at 696 cm^{-1} in the Fe₃O₄@SiO₂-Phen-pd(0) NPs spectrum is attributed to formation of Pd-N bonds [56] as in addition to the other repetitious absorptions showed that magnetic nanocatalyst of Fe₃O₄@SiO₂-Phen-Pd(0), has been synthesized (Fig. 2f).

The crystalline structure of Fe₃O₄, Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-Phen-Pd(0) MNPs was investigated by XRD analyses (Fig. 3a-c). In the XRD patterns, the peaks at $2\theta = 30.7^{\circ}$, 35.6° , 43.3° , 53.1° , 56.9° and



Fig. 2. FT-IR spectra of (a) Fe_3O_4 , (b) Fe_3O_4 @SiO₂, (c) Phen, (d) Fe_3O_4 @SiO₂-Cl, (e) Fe_3O_4 @ SiO₂-Phen, and (f) Fe_3O_4 @SiO₂-Phen-Pd(0) NPs.



Fig. 3. XRD diffraction pattern of (a) Fe_3O_4 , (b) Fe_3O_4 @SiO₂, and (c) Fe_3O_4 @SiO₂-Phen-Pd(0) NPs.

62.3° with the Bragg reflections of (220), (311), (400), (422), (511), and (440), respectively, revealed the cubic spinel structure of Fe₃O₄ MNPs which agrees with the standard magnetite XRD spectra (JCPDS card no. 19-629) (Fig. 3a). Additionally, a decrease in the intensity of all diffraction peaks was observed as in addition to appearance of broad peak between $2\theta = 10^{\circ} \cdot 20^{\circ}$ owing to the presence of amorphous silica shell around magnetic particles in Fe₃O₄@SiO₂ NPs (Fig. 3b). The XRD pattern of Fe₃O₄@SiO₂-Phen-Pd(0) contains somehow the same reflections but in shorter peaks due to the presence of organic compounds beside amorphous silica(Fig. 3c). These data exhibit the excellent coating of Fe₃O₄ magnetic particles. Moreover, the mean crystal size of Fe₃O₄ particles (*D*) was calculated to be approximately 19 nm using the Debye-Scherrer equation (D= $K\lambda/\beta \cos\theta$).

The N₂ adsorption-desorption isotherms were taken to examine the porous structure and surface area of the NPs. The measured specific surface areas were 473.2, 423.7 and 389.3 m²/g for Fe₃O₄, Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-Phen-Pd(0), respectively, and the mean pore diameter was determined by BET analysis to be 20.1 nm (Table 1). In addition, Scherrer equation was applied to get the mean particle sizes of synthesized nanoparticles in each step. The sizes were obtained to be 13.7, 16.3, and 19 nm for Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@SiO₂-Phen-Pd(0), respectively (Table 1).

The morphology and size of synthesized magnetic nanoparticles are of the main goals in the synthesis of such particles. As illustrated in Fig. 4, the FESEM (Fig. 4a-c) and DLS analyses of nanoparticles (Fig. 4d–f) present the abiding shape of these nanoparticles indicating the stability of synthesized particles in such conditions. The size of nanoparticles is in good harmony with the results had been provided from XRD investigations. The increasing trend in the particle size can also be followed by DLS measurements in which the mean particle size was increased in each step (Fig. 4d–f).

TEM (Fig. 5a-c) images of Fe $_3O_4$, Fe $_3O_4$ @SiO $_2$ and Fe $_3O_4$ @SiO $_2$ -Phen-Pd(0)

MNPs exhibit spherical shape and the clear core-shell structure of nanoparticles (Fig. 5c).

The stability and magnetic capability of final nanomagnetic catalyst were pursued using TGA (between 0–600 °C) and VSM analyses (Fig. 6). As it can be observed, the first weight loss was occurred at around 110 °C in TGA curve resulting from the elimination of absorbed water and some solvents (Fig. 6A) [57]. In continue, the other weigh loses observed were related to the organic constructing compounds of magnetic nanocatalyst up to 600 °C, which are totally equal to only 29 % weight loss that is significantly snazzy. This information presents the sustainable structure of synthesized nanocatalyst and its applicability in higher temperatures which are suitable for industrial processes.

Based on the magnetization curves, no hysteresis in samples was obtained with the saturation magnetization values of 70.7, 49.6, and 24.8 emu/g for Fe₃O₄, Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-Phen-Pd(0) respectively, which disclose the superparamagnetic character of magnetic particles. The reductions in magnetization properties of Fe₃O₄@-SiO₂ and Fe₃O₄@SiO₂-Phen-Pd (0) nanoparticles attributes to silica shell and the organic layers. However, the magnetic strength of final nanocatalysts is enough to be entirely separated from the reaction media using an external magnet (Fig. 6Ba-c).

Table 1

Some properties of Fe₃O₄, Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-Phen-Pd(0) NPs.

Sample	Fe ₃ O ₄ crystal structure	Specific surfacearea (m²/ g) ^a	Magnetite particlesize (nm) ^b
Fe ₃ O ₄	Cubic spinel	473.2	13.7
Fe ₃ O ₄ @SiO ₂	Cubic spinel	423.7	16.3
Fe ₃ O ₄ @SiO ₂ -	Cubic spinel	389.3	19
Phen-Pd(0)			

^a Calculated using the BJH method.

^b Calculated using the Scherrer equation based on XRD patterns.



Fig. 4. FE-SEM images of (a) Fe_3O_4 , (b) $Fe_3O_4@SiO_2$, and (c) $Fe_3O_4@SiO_2$ -Phen-Pd (0); and size distributions of (d) Fe_3O_4 , (e) $Fe_3O_4@SiO_2$, and (f) $Fe_3O_4@SiO_2$ -Phen-Pd (0) NPs.



Fig. 5. TEM images of (a) Fe₃O₄, (b) Fe₃O₄@SiO₂, and (c) Fe₃O₄@SiO₂-Phen-Pd (0) NPs.



Fig. 6. (A) TGA spectrum of $Fe_3O_4@SiO_2$ -Phen-Pd(0) NPs; (B) magnetic hysteresis curves of (a) Fe_3O_4 (b) Fe_3O_4 @SiO_2 and (c) $Fe_3O_4@SiO_2$ -Phen-Pd(0) NPs; (C) catalyst ability for effective recovery at the end of reactions by an external magnetic field.

Inductively coupled plasma atomic emission spectrometry (ICP-MS) analysis was taken to evaluate the exact content of decorated Pd particles in the $Fe_3O_4@SiO_2$ -Phen-Pd(0) magnetic nanocatalyst structure. As a result, the anchored Pd particles were measured to be 0.33 mmol in 1 g

of MNPs.



Fig. 7. (A) UV-Vis spectra (B) EDX spectrum of Fe₃O₄@SiO₂-Phen -Pd (0).

Fe₃O₄@SiO₂–Phen–Pd(0) NPs were studied and shown in Fig. 7A. The presence of two absorption bands in the range of 225–305 nm are attributed to π → π *transitions Phen ring [58a]. The disappearance of the peak at around 400–430 nm which belongs to Pd (II) species, demonstrates the complete conversion of Pd (II) to Pd(0) [58b]. Energy dispersive spectroscopy (EDX) is a useful method to characterize the elemental profile of compounds. Therefore, the EDX analysis, which can obtain further indication for anchoring palladium complex on the surface of Fe₃O₄@SiO₂, was performed. The EDX spectrum of Fe₃O₄@SiO₂–Phen–Pd(0) shows the presence of Fe₃O₄@SiO₂-Phen-Pd(0) shows the presence of Fe₃O₄@SiO₂-Phen-Pd(0) MNPs (Fig. 7B).

With the full characterization data in hand, the catalytic ability of magnetic nanocatalyst was considered in Suzuki-Miyaura C-C coupling reaction and the synthesis of variety of different tetrazoles. Firstly, the optimized reaction parameters were found for Suzuki-Miyaura couplings in the reaction between bromobenzene and phenylboronic acid as a test reaction. As summarized in Table 2, a library of solvents, bases, various temperatures, reaction times, and catalyst amounts were employed. Different protic and aprotic solvents were applied (Table 2, entries 1-7) and the best efficiency was observed in EtOH/H2O as solvent (Table 2, entry 4). In ongoing, varies amounts of the synthesized magnetic nanocatalyst were applied (Table 2, entries 8-11) and surprisingly, only 5 mg of which (0.17 mol% of pd) triggered the reaction (Table 2, entry 10). Noteworthy, no more yield was obtained with more amounts of catalyst. Among the bases applied, K₂CO₃ exhibited highest efficiency (Table 2, entry 10). The Suzuki-Miyaura reaction is somehow temperature sensitive in which different temperatures exhibit different results. So, the model reaction was explored in diverse temperatures to find the best one and as it cited in (Table 2, entries 10, 17-19), not better data were achieved in higher and lower temperatures than 50 $^\circ\mathrm{C}$ (Table 2, entries 10, 18, and 19). Finally, the reaction time was subjected to study be investigated and checking out the reaction progress revealed that 1.5 h is enough to get the best result (Table 2, entry 22). Thereupon, the optimized conditions were found to be using EtOH/H₂O as solvent, in the presence of 5 mg of catalyst (0.17 mol% of pd), K₂CO₃, 50 °C, and 1.5 h reaction time.

The next step is using perceived optimized conditions to scrutiny the reaction scope in which a wide spread various of aromatic alides (I, Br and Cl) and arylboronic acids have been adverted (Table 3). It was observed that almost all purified products were achieved in excellent yields in TOFs point of view, but aryl iodides are more reactive than aryl bromides and the latter are more reactive that aryl chlorides (Table 3). Interestingly, both electron-releasing groups and electron-withdrawing groups on arylboronic acids structure presented good to excellent yield with slightly better result for electron-withdrawing groups

Table 2

Evaluation of reaction parameters in the Suzuki-Miyaura reaction between phenylboronic acid and bromobenzene. $^{\rm a}$

Br + (HO) ₂ B- → Fe ₃ O ₄ @SiO ₂ -Phen-Pd(0) Reaction conditions						
entry	catalyst (mg/ mol% of Pd)	solvent	base	temp. (°C)	time (h)	yield (%) ^b
1	10/0.33	H ₂ O	K ₂ CO ₃	50	2	66
2	10/0.33	EtOH	K ₂ CO ₃	50	2	86
3	10/0.33	DMF	K ₂ CO ₃	50	2	91
4	10/0.33	EtOH/H2O	K ₂ CO ₃	50	2	90
		(1:1)				
5	10/0.33	DMF/H ₂ O (1:1)	K ₂ CO ₃	50	2	89
6	10/0.33	DMSO	K ₂ CO ₃	50	2	90
7	10/0.33	Toluene	K ₂ CO ₃	50	2	57
8	_	EtOH/H2O	K ₂ CO ₃	Reflux	24	_
		(1:1)	2 0			
9	3/0.1	EtOH/H ₂ O	K ₂ CO ₃	50	2	60
		(1:1)	2 0			
10	5/0.17	EtOH/H ₂ O	K ₂ CO ₃	50	2	94
		(1:1)				
11	7/0.23	EtOH/H ₂ O	K ₂ CO ₃	50	2	86
		(1:1)				
12	5/0.17	EtOH/H ₂ O	-	Reflux	24	Trace
		(1:1)				
13	5/0.17	EtOH/H ₂ O	Na ₂ CO ₃	50	2	71
		(1:1)				
14	5/0.17	EtOH/H ₂ O	K ₃ PO ₄	50	2	80
		(1:1)				
15	5/0.17	EtOH/H ₂ O	NaOAc	50	2	82
		(1:1)				
16	5/0.17	EtOH/H ₂ O	Et ₃ N	50	2	84
		(1:1)				
17	5/0.17	EtOH/H ₂ O	K ₂ CO ₃	r.t	24	61
		(1:1)				
18	5/0.17	EtOH/H ₂ O	K_2CO_3	40	24	77
		(1:1)				
19	5/0.17	EtOH/H ₂ O	K_2CO_3	60	3	90
		(1:1)				
20	5/0.17	EtOH/H ₂ O	K ₂ CO ₃	50	1	55
		(1:1)				
21	5/0.17	EtOH/H ₂ O	K ₂ CO ₃	50	1.5	96
	E (0.1E	(1:1)	<i>v</i> , co	50	0.5	
22	5/0.17	EtOH/H ₂ O	K_2CO_3	50	2.5	92
		(1:1)				

 a Reaction conditions: phenylboronic acid (1.1 mmol), bromobenzene (1 mmol), Fe_3O_4@SiO_2-Phen -Pd (0), solvent (4 mL), base (2 mmol). b Isolated yield.

Table 3

Suzuki coupling reaction of arylboronic acids with aromatic halides in the presence of Fe₃O₄@SiO₂-Phen-Pd (0) NPs.^a

Fe₃O₄@SiO₂-Phen-Pd(0) Ar-Ar Ar-X + (HO)₂B-Ar' EtOH/H2O, K2CO3, 50 °C MeO Br (3b) (3c) (3a) $X = I: 0.7 h, 97 \%^{d}, TOF = 815.1 (h^{-1})$ $X = I: 1.4 h, 92 \%^{d}, TOF = 386. (h^{-1})$ $X = I: 1.3 h, 92 \%^{d}, TOF = 416.3(h^{-1})$ Br: 1.5 h, 96 % ^d, TOF = 376.5 (h⁻¹) Br: 2.8 h, 89 % ^d, TOF = 187 (h⁻¹) Cl: 15 h, Br: 2.5 h, 90 % ^d, TOF = 211.8 (h⁻¹) Cl: 12 h, 66 % d tof = 32.4 (h⁻¹) 63 % ^d. TOF = 24.7 (h⁻¹) Cl: 12 h, 65 % ^d, TOF = 32 (h⁻¹) O₂N² NC (3d) (3c)(3f) $X = I: 0.5 h, 98 \%^{d}, TOF = 1153 (h^{-1})$ $X = I: 1.3 h, 92 \%^{d}, TOF = 416.3 (h^{-1})$ $X = I: 1.5 h, 94 \% d, TOF = 368.6 (h^{-1})$ Br: 1.2 h, 95 % ^d, TOF = 465.7 (h^{-1}) Br: 2.5 h, 90 % d , TOF = 211.8 (h⁻¹) Br: 3 h, 90 % ^d, TOF = 176.5 (h^{-1}) Cl: 10 h, 83 % ^d, TOF = 48.8 (h⁻¹) Cl: 12 h, 65 % ^d, TOF = 32 (h⁻¹) Cl: 12 h, 75 % ^d, TOF = 36.8 (h⁻¹) Me Me O₂N (3 g) (3 h) (3i) $X = I: 0.6 h, 96 \%^{d}, TOF = 941.2 (h^{-1})$ $X = I: 2 h, 90 \% d, TOF = 267.7 (h^{-1})$ $X = I: 3 h, 88 \%^{d}, TOF = 172.6 (h^{-1})$ Br: 1.5 h, 91 % ^d, TOF = 357 (h⁻¹) Cl: 11 h, 77 % ^d, TOF = 41.2 (h⁻¹) Br: 3.5 h, 83 % ^d, TOF = 139.5 (h⁻¹) Br: 4 h, 80 % ^d, TOF = 117.6 (h⁻¹) Cl: 15 h, 68 % ^d, TOF = 26.7 (h⁻¹) Cl: 13 h, 70 % ^d, TOF = 31.7 (h⁻¹) MeO H₂N (3 j) (3k) (31) $X = I: 3.5 h, 84 \% d, TOF = 141.2 (h^{-1})$ $X = I: 3.1 h, 88 \%^{d}, TOF = 167 (h^{-1})$ $X = I: 3.5 h, 85 \%^{d}, TOF = 144.5 (h^{-1})$ Br: 4.5 h, 78 % ^d, TOF = 102 (h⁻¹) Cl: 15 h, 64 % ^d, TOF = 25.1 (h⁻¹) Br: 4.2 h, 81 % ^d, TOF = 113.4 (h⁻¹) Cl: 15 h, 69 % ^d, TOF = 27 (h⁻¹) Br: 4.3 h, 77 % ^d, TOF = 105.3 (h⁻¹) Cl: 14 h, 62 % ^d, TOF = 26 (h⁻¹) H₂C CE₂ MeO -CE₂ -CF₂ (3 m) (3n) (30) $X = I: 4 h, 80 \%^{d}, TOF = 117.6 (h^{-1})$ $X = I: 1.5 h, 92 \%^{d}, TOF = 360.8 (h^{-1})$ $X = I: 1.7 h, 90 \%^{d}, TOF = 311.4 (h^{-1})$ Br: 5 h, 72 % ^d, TOF = 84.7 (h⁻¹) Cl: 16 h, 60 % ^d, TOF = 22.1 (h⁻¹) Br: 2.2 h, 89 % ^d, TOF = 238 (h⁻¹) Br: 2.6 h, 84 % ^d, TOF = 190 (h⁻¹) Cl: 11 h, 66 % ^d, TOF = 36.3 (h⁻) Cl: 13 h, 61 % ^d, TOF = 27.6 (h⁻¹) (3q) (3p) (3 r) $X = I: 1.6 h, 91 \%^{d}, TOF = 344.6 (h^{-1})$ $X = I: 3.2 h, 91 \%^{d}, TOF = 167.3 (h^{-1})$ $X = I: 3.5 h, 90 \%^{d}, TOF = 151.3(h^{-1})$ Br: 2.3 h, 82 % ^d, TOF = 210 (h^{-1}) Br: 4 h, 88 % ^d, TOF = 129.4 (h^{-1}) Br: 4.2 h, 87 % ^d, TOF = 122 (h⁻¹) Cl: 12 h, 60 % ^d, TOF = 29.4 (h^{-1}) -CF₃ (3 s) (3 t) (3 u) X= I: 3 h, 89 % $^{\rm d}$, TOF = 174.5 (h $^{-1}$) $X = I: 1.8 h, 90 \%^{d}, TOF = 294.1 (h^{-1})$ X^{b} = I: 3 h, 84%^d, TOF = 82.4 (h⁻¹) Br: 4.2 h, 83 % ^d, TOF = 116.2 (h^{-1}) Br: 2.1 h, 86 % d , TOF = 241 (h⁻¹) Br: 4 h, 75 $\%^d$, TOF = 55.2 (h⁻¹) CaF (3v) (3x) w $X^{b} = I: 2.4 h, 88\%^{d}, TOF = 108(h^{-1})$ $X^c = Cl: 5 h, 83\%^d, TOF = 32.6 (h^1)$ $X^{c} = Cl: 5 h, 80\%^{d}, TOF = 31.4 (h^{-1})$ Br: 3.2 h, 83 $\%^d$, TOF = 76.3 (h⁻¹)

^a Reaction conditions: arylboronic acid (1.1 mmol), aromatic halide (1 mmol), Fe₃O₄@SiO₂-Phen-Pd(0) (5 mg, 0.1 mol% Pd), K₂CO₃ (2 mmol), EtOH/H₂O (1:1, 4 mL), 50 °C.

^b Reaction conditions: 2.2 mmol of arylboronic acid, 1 mmol of aromatic halide, Fe₃O₄@SiO₂-Phen-Pd(0) (10 mg, 0.34 mol% Pd), 4 mmol of K₂CO₃, EtOH/H₂O (1:1,

10 mL), and 60 °C.

^c Reaction conditions: 3.5 mmol of arylboronic acid, 1 mmol of aromatic halide, Fe₃O₄@SiO₂-Phen-Pd(0) (15 mg, 0.51 mol% Pd), 7 mmol of K₂CO₃, EtOH/H₂O (1:1, 20 mL), and 60 °C.

^d Isolated yield.



Table 4

Entry	Catalyst	Condition	Time (h)	Yield (%)	TOF (h ⁻¹)	Ref.
1	Pd-Fe ₃ O ₄ (0.1 mol %)	DME/H ₂ O (3:1)/ K ₂ CO ₃ / reflux	48	92	19.2	[59]
2	C/Co@PNIPAM- PPh ₂ -Pd(3 mol%)	Toluene/ H ₂ O (2:1)/ K ₂ CO ₃ /85 °C	16	99	2.1	[60]
3	Fe ₃ O ₄ -Bpy-Pd (OAc) ₂ (0.5 mol%)	Toluene∕ K₂CO₃∕80 °C	6	99	33	[61]
4	Co/C-ROMPgel immobilized Pd- complex (1.1 mol %)	THF/H ₂ O (1:2)/ Na ₂ CO ₃ /65 °C	2	96	44	[62]
5	Fe@FexOy/Pd (0.5 mol%)	EtOH/H ₂ O (1:1)/ K ₂ CO ₃ /r.t	2	98	98	[63]
6	Xerogel g1-MNPs (1 mol%)	CH ₃ OH/ Na ₂ CO ₃ /60 °C	2	99	49.5	[64]
7	Pd@Mag-MSN (1 mol%)	CH ₂ Cl ₂ ∕ K ₂ CO ₃ ∕80 °C	6	85	14	[65]
8	Pd(0)-ZnFe ₂ O ₄ (4.62 mol%)	EtOH/ K ₂ CO ₃ / Reflux	4	92	5	[66]
9	Pd–MWCNT (0.3 mol%)	MeOH, NaOAc/ Reflux	2	95	158	[67]
10	Pd–Fe ₃ O ₄ @IM (1 mol%)	H ₂ O/ K ₂ CO ₃ /70 °C	5	75	15	[68]
11	Fe ₃ O ₄ @MCM- 41@Pd-SPATB (1.26 mol%)	PEG/ K ₂ CO ₃ /100 °C	1	90	142.8	[69]
12	Pd0-AmP-SMC (0.2 mol%)	EtOH/H ₂ O (1:1)/ K ₂ CO ₃ /90 °C	5	84	98.8	[70]
13	Fe ₃ O ₄ @SiO ₂ - Phen-Pd(0) (0.17 mol% Pd)	EtOH/H ₂ O (1:1)/ K ₂ CO ₃ /50	1.5	96	376.5	This work



Scheme 3. Plausible mechanism of Suzuki-Miyaura coupling reaction.

Table 5

Evaluation of the reaction parameters for the synthesis of 5-phenyl 1H-tetrazole.^a

	B(OH) ₂ + ^{NaN₃} Fe ₃ KCN	O ₄ @SiO ₂ -Phen-Pd(0) Reaction Conditions ^a		7	
Entry	Molar ratio:	Catalyst	Reaction	Time	Yield
-	Phenylboronic acid / NaNa/KCN	amount (mg/ mol% of Pd	conditions	(h)	(%) ^b
	,	(0))			
1	1:3:3	5/0.17	MeOH/	3	45
			Reflux		
2	1:3:3	5/0.17	EtOH/	3	35
0	1.0.0	E /0.17	Reflux	0	40
3	1:3:3	5/0.17	CH ₃ CN/ Reflux	3	43
4	1:3:3	5/0.17	H ₂ O/Reflux	3	47
5	1:3:3	5/0.17	EtOH/H ₂ O	3	90
			(1:1)/Reflux		
6	1:3:3	5/0.17	Dioxane/	8	30
_	100	E (0.15	Reflux		=0
7	1:3:3	5/0.17	PEG/100 °C	3	78
0	1:5:5	5/0.1/	(1.1)/90 °C	3	83
9	1:3:3	5/0.17	DMF/110 °C	3	90
10	1:3:3	5/0.17	DMF/H ₂ O	3	89
			(1:1)/100 °C		
11	1:3:3	5/0.17	NMP/120 °C	4	63
12	1:3:3	5/0.17	DMSO/110	3	65
10	100	E (0.15	°C		00
13	1:3:3	5/0.17	Ethylene	1.5	89
14	1:3:3	5/0.17	THF/Reflux	8	40
15	1:3:3	5/0.17	Solvent-	8	20
			free/110 °C		
16	1:1:1	5/0.17	EtOH/H ₂ O	3	48
			(1:1)/Reflux		
17	1:2:2	5/0.17	EtOH/H ₂ O	3	76
10	1.4.4	E /0 17	(1:1)/Reflux	2	0.4
18	1:4:4	5/0.1/	(1.1)/Reflux	3	64
19	1:3:3	None	EtOH/H ₂ O	24	Trace
			(1:1)/Reflux		
20	1:3:3	2/0.07	EtOH/H ₂ O	8	47
			(1:1)/Reflux		
21	1:3:3	4/0.14	EtOH/H ₂ O	3	93
	100	<i>c</i> (0.0	(1:1)/Reflux	-	
22	1:3:3	6/0.2	$EtOH/H_2O$	5	88
23	1.3.3	4/0.14	FtOH/HaO	1	55
20	1.0.0	., 0.1 1	(1:1)/Reflux	-	55
24	1:3:3	4/0.14	EtOH/H ₂ O	1.5	87
			(1:1)/Reflux		
25	1:3:3	4/0.14	EtOH/H ₂ O	2	97
			(1:1)/		
26	1.0.0	4 /0.14	Reflux	9.5	05
20	1.3:3	4/0.14	EIUH/H2U (1.1)/Reflux	2.5	90
			(1.1)/ 101104		

 $^{\rm a}$ Reaction conditions: Phenylboronic acid (1.0 mmol), $\rm K_2CO_3$ (2 mmol), $\rm NaN_3$ (3 mmol), KCN (3 mmol), solvent (4 mL).

^b Isolated yield.

(Table 3, entries 3n-3o). The existences of aromatic halides with electron-withdrawing groups were let to the better result in comparison with ones with electron-releasing groups (Table 3, entries 3d-3 g). For expanding of the applicability of this approach, heteroaryl halides were also employed and all of them undergo efficiently the Suzuki reactions and provided high to excellent yields but in higher temperature (Table 3, entries3p and 3 u-3x).

To ascertainment the capability of applied nanocatalyst, the application of that to accomplish the Suzuki coupling between bromobenzene and phenylboronic was selected to be compared with the literature reports (Table 4). As it can be observed in Table 4, the most of catalysts published catalyze the C-C cross coupling reaction to prepare biphenyl

Table 6

Catalyzed one-pot synthesis of 5-substituted 1H-tetrazoles with Fe $_3O_4@SiO_2$ -Phen-Pd (0) in water/ethanol.^a



 a Reaction conditions: arylboronic acid (1 mmol), $\rm K_2CO_3$ (2 mmol), KCN (3 mmol), NaN_3 (3 mmol), Fe_3O_4@SiO_2-Phen-Pd(0) (4 mg, 0.14 mol% Pd,), EtOH/ $\rm H_2O$ (1:1, 4 mL), Reflux.

^b Isolated yield.

at higher temperatures, in toxic solvents, and using larger amounts of catalysts after longer reaction times in lower yields with significantly low TOFs (Table 4, entries 1–12).

In consonance with, the plausible mechanism is proposed in Scheme 3. The oxidative addition is the first step, which can be carried out on the catalyst A to reach the intermediate B. After getting unstable structure C in situ, resulting from the treatment of arylboronic acid with hydroxyl ions, the transmetalation step is happened and both intermediated E and F would be apperceived. The final product G is obtained after passing reductive elimination step and eventually, Pd (0)-based magnetic

Table 7

Catalytic performance of two Pd-based catalysts in the one-pot reaction for conversion of 4- methoxy phenylboronic acid to 5-(4-methoxyphenyl)-1H-tetrazole.

MeO	B(OH) ₂	MeO	N N N N N N N N N N N N N N N N N N N			
Entry	Catalyst	Condition	Time (h)	Yield (%) ^a	TOF (h ⁻¹)	Ref.
1	Pd(II)-ONO Pincer(PPh ₃) (0.1 mol% Pd)	DMSO/H₂O (1:1)/KOH/90 °C, NaN₃, NH₄HCO₃	6	86	143	[44]
2	Fe ₃ O ₄ @SiO ₂ - Phen-Pd(0) (0.14 mol% Pd)	EtOH/H ₂ O (1:1)/K ₂ CO ₃ / Reflux, NaN ₃ , KCN	1.5	92	438	This work

^a Isolated yield.

nanocatalyst will be produced to take part in consecutive runs.

4. The synthesis of tetrazoles

Attractive results associated to the successful C—C bond formation using Suzuki-Miyaura coupling reaction by Fe₃O₄@SiO₂-Phen-Pd(0) magnetic nanocatalyst caused strong tendency to check out the applicability of such nanocatalyst in the production of a library of tetrazoles starting from arylboronic acids, as novel alternatives precursors. Inspiring from reported data in the literature [44], the reaction among phenylboronic acid, NaN₃, and KCN as a model reaction, was approved to find optimized reaction conditions (Table 5). As shown in Table 5, a group of solvents were firstly perused (Table 5, entries 1–15) and using EtOH/H₂O and DMF displayed the best results (Table 5, entries 5 and 9).



Scheme 4. Proposed mechanism of the direct transformation of arylboronic acids to the corresponding tetrazoles.

However, in green point of view, the mixture of EtOH/H₂O (1:1) was selected to be utilized as a green solvent for the rest of more investigations (Table 5, entry 5). The effect of the molar ratios of KCN and NaN₃ relative to phenylboronic acid was also investigated (Table 5, entries 16-18). The best yield of 5-phenyl 1H-tetrazole was produced with a 1:3:3 M ratio of phenylboronic acid relative to KCN and NaN₃ (Table 5, entry 5). Then, the catalyst amount was optimized (Table 5, entries 19-22) and maximum efficiency was achieved when 4 mg of nanocatalyst (0.14 mol% of Pd) was loaded into the reaction mixture (Table 5, entry 21). Accordingly, the yield of the desired product, 5-phenyl 1H-tetrazole, was declined in the presence of lower and higher amount than 4 mg of the magnetic nanocatalyst (Table 5, entries 20 and 22). Finally, the reaction time effect was considered on the preparation of 5-phenyl 1H-tetrazole and best catalyst efficiency was obtained after 2 h (Table 5, entry 25). Consequently, the best conditions were found using 4 mg of nanocatalyst (0.14 mol% of Pd) in EtOH/H₂O (1:1) as solvent under reflux was chosen as the best conditions for the rest of study and 2 h of reaction time.

As the same as the previous survey on the application of arylboronic acids in Suzuki type coupling reactions, we have pursued the applicability of such starting materials in the preparation of 5-substituted 1H- tetrazoles in the presence of $Fe_3O_4@SiO_2$ -Phen-Pd(0) magnetic nanocatalyst as indexed in Table 6. Variety of arylboronic acids with electronreleasing groups and electron-withdrawing groups carried out the preparation of 5-substituted 1H-tetrazoles in high to excellent yields in range of 1.5–6 h (Table 6) under reflux condition in EtOH/H₂O (1:1). In general, arylboronic acids with electron releasing substitution are more reactive than electron-withdrawing one. Ortho isomers of arylboronic acids undergo usually the reaction in longer reaction times and in lower yields (Table 6, entries 4 and 8) probably due to ortho steric effect. Phenethyl boronic acid as an aliphatic boronic acid provides the related tetrazole in lower yield at longer time than arylboronic acids (Table 6, entry 16). Polynuclear arylboronic acids are transformed to the desired tetrazole in comparable yields to arylboronic acids but in longer reaction time (Table 6, entries 14–16).

Finally, we compared the capability of the synthesized nanocatalyst in the synthesis of 5-(4-methoxyphenyl)-1H-tetrazole with the only report published in the literature using arylboronic acids (Table 7). As can be seen, the ONO pincer type Pd(II) complex bearing toxic ligand of triphenylphosphine catalyzes preparation of 5-(4-methoxy phenyl)-1Htetrazole in aqueous solution of DMSO as toxic solvent at higher temperatures and longer reaction time in lower yield with significantly low



Fig. 8. A) Recyclability of the catalyst in the synthesis of a) 1,1'-biphenyl and b) 5-phenyl-1H-tetrazole; B), C) DLS and FE- SEM images of $Fe_3O_4@SiO_2$ -Phen -Pd (0) nanoparticles after eight reaction cycles in the synthesis of 1,1'-biphenyl in model reaction.



Fig. 9. EDX spectrum of the reused catalyst.

TOF. It is noteworthy, there are significant differences between the two catalysts in terms of the recovery and reusability, previous report is recovered by centrifuge and reused just for four runs while the present nanomagnetic catalyst is separated from the media reaction by an external magnet and reused for eight cycles.

In Scheme 4 it is illustrated how the products are produced using arylboronic acid precursors inspiring from the reported data in the literature [44]. Firstly, the Pd-based nanocatalyst **A** is treated with activated boronic acid **B**, potassium trihydroxy(pheny)borate, to give the sigma complex of palladium(II) **C** through transmetalation reaction. In the next step, the scaffold **D**, which is produced from the reaction KCN with **C**, is converted to **F** via the reaction of **E** with NaN₃. An intramolecular 1,3-dipolar cycloaddition reaction transform **F** to **G** which, in turn, is hydrolyzed to the 5-substituted-1*H*-tetrazole **H** and regenerate magnetic nanocatalyst **A** to begin another cycle of reaction.

Recyclability is a very important aspect of catalyst applications, economically and environmentally, in laboratory and industry. Therefore, recyclability of $Fe_3O_4@SiO_2$ -Phen-Pd(0) nanocatalyst was tested on the both model reactions. Due to supermagnetic behavior of the catalyst, in a typical approach, the catalyst was taken away from the reaction media, washed with the mixture of EtOH:H₂O (1:1) to remove unreacted chemical reagents, and reused directly in the next run without further purification. It was interestingly observed that this potent catalyst presents catalytic properties at least for 8 consecutive cycles (Fig. 8A).

Fig. 8B and C exhibit DLS and FE-SEM analyses of the isolated nanocatalyst after the 8th run for the synthesis of 1,1'-biphenyl in the model reaction in which the spherical morphology as well as the size distributions of nanoparticles confirm the stability of catalyst in shape and applicability. Substantially, the hydrodynamic diameter of Fe₃O₄@SiO₂-Phen-Pd (0) after eight runs is illustrated in Fig. 8B, the mean diameter of Fe₃O₄@SiO₂-Phen-Pd 0) and the centered particle size was calculated to be 41 nm, which is somehow larger than the fresh catalyst particles. The EDX analysis was also taken on the recovered catalyst after eight runs. This analysis displayed clearly the existence of the main catalyst components of the fresh catalyst such as Fe, Pd, Si, O, N, C and Cl (Fig. 9).

Continuously, the hot filtration test was exploited to determine if the leaching of absorbed Pd particles from the surface of the magnetic support in to the reaction media is responsible for the progress of model reactions. Adapted from common procedure had already been reported [71], the nanocatalyst was separated completely from the reaction magnetically and after passing half time of model reaction times (0.75 h for Suzuki couplings and 1 h for tetrazole process). Afterwards, the liquid phases were allowed to be stirred under optimized conditions and as expected, no progress in both reactions was observed by TLC and GC analyses revealing that the leaching of Pd particles are ignorable and

mainly, the supported catalytic Pd(0) is responsible in the process of getting products. The ICP analysis was finally studied and it demonstrates that the leaching amounts of Pd particles are only around 1.1% and 0.92% after passing 8th run in tetrazole and Suzuki reactions, respectively. All achievements proposed the efficient and impressive coverage of Pd(0) by magnetic support and the negligible leaching amount of active palladium particles.

5. Conclusions

In summary, green, unflinching and sustainable nanocatalyst Fe_3O_4 @SiO₂-Phen-Pd(0) was synthesized and entirely characterized in this reports. This excellent recoverable catalyst was applied in the both Suzuki-Miyaura and tetrazole reactions starting from arylboronic acids as superior sources of aryl groups and significant results were observed in TOFs and recyclability points of views which are mostly important in the laboratory and industrial applications. The nanocatalyst was separated 8 times and reused in subsequent cycles with no diminution in its activity.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Nastaran Bagherzadeh: Investigation, Visualization, Methodology, Writing - original draft, Validation, Data curation. Ali Reza Sardarian: Conceptualization, Resources, Project administration, Funding acquisition, Writing - review & editing. Hassan Eslahi: Methodology, Writing original draft, Validation, Data curation, Resources, Supervision.

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Appendix A. Supplementary data

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