



# Palladium supported on bis(indolyl)methane functionalized magnetite nanoparticles as an efficient catalyst for copper-free Sonogashira-Hagihara reaction

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## ABSTRACT

A novel heterogeneous catalyst based on palladium nanoparticles supported on 3,3'-bisindolyl(4-hydroxyphenyl)methane functionalized magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles was synthesized, characterized and used as catalyst for Sonogashira-Hagihara reaction. The alkylation of a variety of aryl iodides and aryl bromides with terminal alkynes was carried out at 60 °C under copper and phosphane-free conditions using *N,N*-dimethyl acetamide as solvent, DABCO as base and low Pd loadings (0.18 mol%) under air. In the case of aryl chlorides, the reaction was carried out at 120 °C in the presence of tetra-*n*-butylammonium bromide (TBAB) and 0.36 mol% of Pd catalyst. The heterogeneous palladium catalyst introduced in this study is recoverable by an external magnet and it can be used for seven consecutive runs without a significant loss in catalytic activity.

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## 1. Introduction

The palladium catalyzed carbon–carbon bond forming reactions are of great importance in modern synthetic organic chemistry [1]. Among well-known carbon–carbon coupling reactions, the Sonogashira-Hagihara cross-coupling stands out as a unique method enabling the coupling between (sp) carbon and (sp<sup>2</sup>) carbon atoms [2–9]. The reaction products containing such bonds have found applications in a wide range of synthetic reactions such as biologically active compounds and pharmaceuticals [10–12]. Palladium catalyzed Sonogashira-Hagihara alkylation reaction can be performed either in the presence of copper as co-catalyst or under copper-free conditions. The presence of copper increases the reactivity of the acetylene by the formation of a copper acetylide. However, the formation of undesired homo-coupling byproducts is usually observed (Glaser coupling reaction) [13,14]. Thus, the design and synthesis of active palladium catalysts for Sonogashira-

Hagihara reaction under copper free and mild reaction conditions are highly desirable [15–24].

Due to difficulties in the removal of metal contaminants of coupling reaction products under homogeneous conditions, many heterogeneous palladium catalysts for Sonogashira-Hagihara reaction have also been developed in recent years [2,25–29]. However, despite great developments in this field, heterogeneous catalysts are also difficult to separate from the reaction mixture by standard laboratory methods such as filtration and centrifugation. In this regard, magnetic nanoparticles with large ratio of surface area to volume, superparamagnetic behavior and low toxicity have proven to be an excellent supports for the stabilization of palladium nanoparticles (NPs) [30–36]. Variety of ligands such as those containing phosphane or nitrogen functional groups have been used for the modification of  $\text{Fe}_3\text{O}_4$  nanoparticles. However, phosphane-based ligands are air and/or moisture sensitive, poisonous, unrecoverable and degradable at elevated temperatures which limits their large scale application in industrial level chemistry [37–39]. We have recently introduced two novel and efficient phosphane-free magnetic nanoparticles which supported palladium catalysts for Suzuki-Miyaura coupling reaction in water [40,41]. However, to date, a few magnetite nanoparticles supported

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palladium catalysts have been prepared and successfully used in the Sonogashira-Hagihara coupling reaction [42–50].

We envisaged that supporting a 3,3'-bisindolyl(4-hydroxyphenyl)methane ligand to magnetite nanoparticles coated with silica gel would be an adequate and simple way to coordinate and stabilize Pd nanoparticles. Herein, we report the synthesis of a new and highly active palladium catalyst supported on functionalized magnetite nanoparticles for Sonogashira-Hagihara reaction under copper and phosphane-free conditions.

## 2. Experimental section

### 2.1. General

All chemicals were purchased from Sigma-Aldrich, Acros and Merck companies and were used without further purification. Magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles were prepared according to a previously reported method in the literature [51,52]. Synthesis of 3,3'-Bisindolyl(4-hydroxyphenyl)methane was carried out by the modification of the published literature procedure [53].  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{DMSO}-d_6$  and  $\text{CDCl}_3$  at room temperature on a Bruker 400 MHz spectrometer and referenced internally using TMS as internal standard. Thermogravimetric analysis (TGA) was conducted from room temperature to  $700^\circ\text{C}$  in an oxygen, sure flow using a NETZSCH STA 409 PC/PG instrument. Transmission Electron Microscopy was carried out by JEOL model JEM-1400 Plus working at 120 kV with a LaB6 filament. Magnetic measurements were performed using vibration sample magnetometry VSM, (MDK Co. Kashan, Iran) analysis. FT-IR spectra were recorded on a Bruker Vector 22 instrument. Energy dispersive X-ray analysis (EDX) results were obtained using Carl Zeiss Sigma instrument. Adsorption-desorption analyses were recorded using BELSORP-max instrument. The content of copper and palladium in the catalyst was determined using Varian atomic absorption spectrometry.

### 2.2. Synthesis of silica-coated $\text{Fe}_3\text{O}_4$ nanoparticles (SMNP)

$\text{Fe}_3\text{O}_4$  (1.0 g) was sonicated in ethanol (200 mL) for 30 min at room temperature. Then, to the resulting suspension were added tetraethyl orthosilicate (TEOS, 2.0 mL) and aqueous ammonia (25%) (6.0 mL) and the mixture was stirred for 24 h at room temperature. The obtained silica-coated  $\text{Fe}_3\text{O}_4$  nanoparticles were separated by an external magnet and washed with distilled water ( $3 \times 10$  mL) and ethanol ( $3 \times 10$  mL) and dried under vacuum.

### 2.3. Procedure for the preparation of $\text{Cl@SiO}_2@\text{Fe}_3\text{O}_4$ (1)

Dry SMNP powder (1.0 g) was mixed with dry toluene (50 mL) to produce a homogeneously mixed solution. This mixture was sonicated for 30 min prior to the addition of (3-chloropropyl) trimethoxysilane (7.0 mmol, 1.27 mL). The resulting mixture was refluxed for 24 h under argon atmosphere. Then, the reaction mixture was subjected to magnetic separation and the resulting powder was washed sequentially with distilled water ( $3 \times 10$  mL) and ethanol ( $3 \times 10$  mL) and finally dried under vacuum.

### 2.4. Procedure for the preparation of compound (2)

Compound 1 (500 mg) was sonicated and dispersed separately in dry toluene (20 mL) for 30 min. In a separate experiment, sodium hydride (1.2 mmol, 27 mg) was added to prepared 3,3'-bisindolyl(4-hydroxyphenyl)methane (1 mmol, 330 mg) under argon and the resulting mixture was added to the flask containing compound 1. The reaction mixture was stirred at  $100^\circ\text{C}$  for 24 h under argon

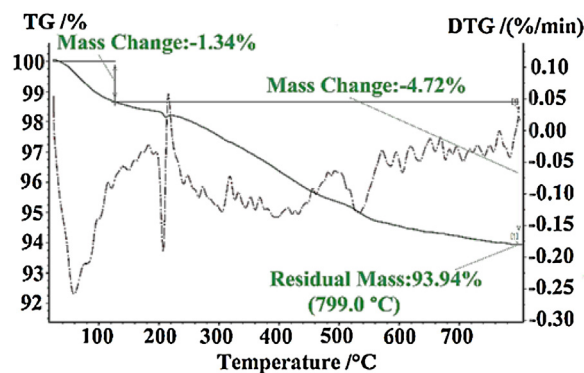


Fig. 1. Thermogravimetric diagram of  $\text{Cl@SiO}_2@\text{Fe}_3\text{O}_4$ .

atmosphere. Then, the reaction mixture was cooled to room temperature and bis indole functionalized magnetic nanoparticles (2) were subjected to magnetic separation. The isolated product was washed sequentially with ethanol ( $2 \times 10$  mL) and dried under vacuum for 24 h.

### 2.5. Procedure for the preparation of $\text{Pd@bisindole@SiO}_2@\text{Fe}_3\text{O}_4$

Compound 2 (400 mg) was sonicated in dichloromethane (10.0 mL) for 30 min at room temperature. Then,  $\text{Pd}(\text{OAc})_2$  (0.09 mmol, 20 mg) was added and the mixture was stirred for 24 h at room temperature under argon atmosphere. Then, the reaction mixture was subjected to magnetic separation and the isolated material was washed sequentially with distilled water ( $3 \times 10$  mL) and ethanol ( $3 \times 10$  mL). Drying under vacuum for 24 h provided compound  $\text{Pd@bisindole@SiO}_2@\text{Fe}_3\text{O}_4$  as a black powder.

### 2.6. General procedure for the Sonogashira-Hagihara reaction

Aryl halide and a terminal alkyne, with an equivalent molar ratio of 1.0–1.5, were added to a mixture of  $\text{Pd@bisindole@SiO}_2@\text{Fe}_3\text{O}_4$  (0.18 mmol, 20 mg) and DABCO (2.0 mmol, 224 mg) in a flask and 2 mL DMA was added. The reaction mixture was stirred at  $60^\circ\text{C}$  for aryl iodides and aryl bromides. The reaction temperature was set to  $120^\circ\text{C}$  for aryl chlorides and 1 mmol TBAB was also added. The progress of the reaction was monitored by gas chromatography. After completion of the reaction, distilled water (2 mL) was added to the reaction mixture and the crude product was extracted with ethyl acetate ( $3 \times 5.0$  mL). The crude product was further purified by column chromatography using *n*-hexane and ethyl acetate as eluents.

## 3. Results and discussion

The catalyst preparation steps are summarized in Scheme 1. Briefly,  $\text{Fe}_3\text{O}_4$  nanoparticles were prepared in a co-precipitation step based on the procedure of Massart et al. using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  salts [51]. The obtained  $\text{Fe}_3\text{O}_4$  NPs were coated with a thin layer of silica using tetraethyl orthosilicate to produce core/shell  $\text{Fe}_3\text{O}_4$  NPs (SMNP) [52]. The presence of a sharp peak in the IR spectrum around  $1091\text{ cm}^{-1}$  (Fig. 1, supporting information) confirmed the formation of Si–O–Fe bonds.  $\text{SiO}_2@\text{Fe}_3\text{O}_4$  core/shell nanospheres were allowed to react with 3-chloropropyltrimethoxysilane to afford chloro-functionalized magnetic NPs ( $\text{Cl@SiO}_2@\text{Fe}_3\text{O}_4$ ). In the next step, NaH was used as base to deprotonate the hydroxyl group of the prepared 3,3'-bisindolyl(4-hydroxyphenyl)methane. Then,  $\text{Cl@SiO}_2@\text{Fe}_3\text{O}_4$  was added to afford 3,3'-bisindolyl(4-hydroxyphenyl)methane functionalized  $\text{Fe}_3\text{O}_4$  NPs ( $\text{bisindole@SiO}_2@\text{Fe}_3\text{O}_4$  NPs). In the final step,

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