

### Article

# Pd-isatin Schiff base complex immobilized on $\gamma$ -Fe\_2O\_3 as a magnetically recyclable catalyst for the Heck and Suzuki cross-coupling reactions

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### 1. Introduction

Magnetic iron oxide nanoparticles have received a great deal of attention because of their unique physicochemical characteristics [1] and wide range of applications in protein separation [2], magnetic resonance imaging (MRI) [3,4], drug delivery [5,6], and as magnetic sensors [7] and in magnetic refrigeration [8]. Recent reports on the applications of magnetic nanoparticles (MNPs) have focused on their use as a promising support for the immobilization of homogeneous catalysts such as metal complexes for organic transformation [9]. The main interest in the synthesis of supported catalysts on MNPs is to have a quick and simple procedure for their reuse by using an external magnet [10]. This separation eliminates the necessity for tedious and time consuming laborious separation steps such as centrifugation or filtration and allows practical continuous catalysis [11]. Moreover, catalysts supported on MNPs

### ABSTRACT

A Pd-isatin Schiff base complex immobilized on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) was synthesized and characterized by Fourier transform infrared, scanning electron microscopy, high resolution transmission electron microscopy, X-ray diffraction, thermogravimetric gravimetric analysis, inductively-coupled plasma, X-ray photoelectron spectroscopy, and elemental analysis. It was used as a magnetically reusable Pd catalyst for the Heck and Suzuki cross-coupling reactions.

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show high catalytic activity, possess high thermal and mechanical stability and can be used for large scale production [12].

Transition metal-catalyzed carbon-carbon and carbon-heteroatom bond forming reactions [13] are powerful tools for advanced organic synthesis in both academic [14] and industrial laboratories [15]. In this area, Heck and Suzuki cross-coupling reactions are important strategies for the formation of carbon-carbon bonds. They are catalyzed by a homogeneous Pd catalyst [16]. The use of readily available starting materials, and simplicity and generality of the method make these cross-coupling reactions particularly attractive for the synthesis of a great variety of complex organic molecules such as drugs, fine chemicals, natural products, polymers, agrochemicals, and biologically active molecules [17,18]. However, these reactions suffer from problems associated with the separation and recovery of the homogeneous catalyst and high cost of Pd which may also result in undesirable metal contamination

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of the product. Therefore, to have an efficient recovery and recycling of the Pd catalyst, the immobilization of homogeneous Pd catalytic systems on different supports has been the subject of intense research [19,20]. Other challenge facing this field is the design of catalysts that are more robust and efficient using valuable ligands as stabilizers for Pd species [21]. In the past decades, the most common ligands used for these cross-coupling reactions have been the phosphine-based ones [22,23]. Since most of the phosphine-based ligands are air and/or moisture-sensitive, in recent years, several groups have tried to develop phosphine-free Pd complexes for the cross-coupling reactions [24-26]. However, the reported complexes have the drawbacks of requiring an excess of expensive ligands, multistep syntheses and inert conditions. Moreover, most of the reported methods are amenable only for the cross-coupling reactions of aryl iodides and bromides [27-29]. Therefore, it would be more beneficial if aryl chlorides, which are far cheaper and more available than other aryl halides, can be used for these cross-coupling reactions [30].

Isatin is a well-known natural product found in plants of genus Isatis and in Couropita guianancis aubl [31,32]. It has been isolated as a metabolic derivative of adrenaline in humans [33,34]. Isatin and its derivatives are unique members in the Schiff base family due to their pharmacological properties which include antibacterial [35], anticonvulsant [36], anti-HIV [37], antifungal [38] and antiviral activity [39]. Isatin Schiff bases readily coordinate with a wide range of transition metal ions, yielding stable metal complexes which exhibit interesting biological, clinical, and pharmacological properties [40]. Recently, we developed the synthesis of new heterogeneous catalysts based on magnetic nanoparticles [41-50]. In continuing this work, we have synthesized Pd-isatin Schiff base complex immobilized on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) and used it as an efficient, air- and moisture-stable and magnetically recoverable catalyst for the Heck and Suzuki cross-coupling reactions under solvent-free conditions [51].

### 2. Experimental

### 2.1. Synthesis

The chemicals were purchased from Merck Chemical Company.  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> MNPs were synthesized by a reported chemical co-precipitation technique using ferric and ferrous ions in alkali solution and with minor modifications [52,53]. FeCl<sub>2</sub>·4H<sub>2</sub>O (1.99 g) and FeCl<sub>3</sub>·6H<sub>2</sub>O (3.25 g) were dissolved in deionized water (30 mL) under an Ar atmosphere at room temperature. A NH<sub>4</sub>OH solution (0.6 mol/L, 200 mL) was added dropwise (drop rate = 1 mL/min) to the stirred mixture at room temperature to a reaction pH of 11. The resulting black dispersion was continuously stirred for 1 h at room temperature, and heated to reflux for 1 h to yield a brown dispersion. The MNPs were subsequently separated by a magnetic bar and washed with deionized water until they were neutral. The as-synthesized sample was heated at 2 °C/min to 250 °C and then kept in the furnace for 3 h to give a reddish-brown powder, i.e. γ-Fe<sub>2</sub>O<sub>3</sub> MNPs

The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (3.5 g) was sonicated in dry toluene (50 mL) for 30 min. 3-Aminopropyltriethoxysilane (3.5 mL, 13 mmol) was added to the dispersed  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in toluene under mechanical stirring. The mixture was slowly heated to 105 °C and kept at this temperature for 24 h. The solid was separated by an external magnet, washed three times with ethanol and dried under vacuum, and thus amino-functionalized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was obtained.

The amino-functionalized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (3 g) was sonicated in absolute ethanol (50 mL) for 30 min. Isatin (0.19 g, 13 mmol) was added slowly to the sonicated mixture and stirred at 80 °C for 24 h. The resulting mixture was cooled to room temperature. The solid was separated by an external magnet, washed with ethanol and dried at 50 °C in oven under vacuum. The prepared sample denoted as isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

Isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (3.3 g) was added to a solution of palladium acetate (0.11 g) in dry acetone (30 mL). The reaction mixture was stirred at room temperature for 24 h. After stirring, the solid was separated by an external magnet, washed with acetone, ethanol and ether, and then dried in an oven at 90 °C overnight to give Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

### 2.2. Characterization

NMR spectra were recorded in ppm concentrations in CDCl<sub>3</sub> on a Bruker Avance DPX-400 instrument using TMS as internal standard. The purity of the products and progress of reaction were measured by TLC using silica gel polygram SILG/UV254 plates. Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. High resolution transmission electron microscopy (HRTEM) analysis was performed using a HRTEM microscope (Philips CM30). The morphology of the products was determined using a Hitachi Model S4160 scanning electron microscope (SEM) at an accelerating voltage of 15 kV. Thermogravimetric analysis (TGA) was performed using a Shimadzu thermogravimetric analyzer (TG-50). Elemental analysis was carried out on a Costech 4010 CHNS elemental analyzer. Power X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer or on a X'Pert Pro MPD diffractometer with Cu  $K_{\alpha}$  ( $\lambda$  = 0.154 nm) radiation. Surface analysis spectroscopy of the catalyst was performed on an ESCA/AES system. This system was equipped with a concentric hemispherical (CHA) electron energy analyzer (Specs model EA10 plus) suitable for X-ray photoelectron spectroscopy (XPS). The Pd content on the catalyst was detemined by OPTIMA 7300DV ICP analyzer.

### 2.3. Reaction

General procedure for the Heck cross-coupling reaction. A mixture of aryl halide (1 mmol), olefin (1.1 mmol),  $Et_3N$  (2 mmol) and catalyst (0.002 g, 0.5 mol%) was stirred at 100 °C for an appropriate time (Table 2). EtOAc (5 mL) was added to the reaction mixture. The catalyst was separated by an external magnet, washed with EtOAc, dried and reused for a consecutive run under the same reaction conditions. Evaporation of the solvent of the filtrate under reduced pressure gave the crude

products. The pure products were isolated by chromatography on silica gel eluted with *n*-hexane: EtOAc (50:1).

General procedure for the Suzuki cross-coupling reaction. A mixture of aryl halid (1 mmol), phenylboronic acid (1.1 mmol), Et<sub>3</sub>N (2 mmol) and catalyst (0.002 g, 0.5 mol%) was stirred at 100 °C for an appropriate time (Table 3). EtOAc (5 mL) was added to the reaction mixture. The catalyst was separated by an external magnet, washed with EtOAc, dried and reused for a consecutive run under the same reaction conditions. Evaporation of the solvent of the filtrate under reduced pressure gave the crude products. The pure products were isolated by chromatography on silica gel eluted with *n*-hexane:EtOAc (50:1).

### 2.4. Spectral data of representative compounds

(E)-Methyl cinnamate. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.74 (s, 3H), 6.38 (d, 1H, <sup>3</sup>*J* = 16.4 Hz), 7.31–7.33 (m, 3H), 7.45–7.47 (m, 2H), 7.63 (d, 1H, <sup>3</sup>*J* = 16.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  51.6, 117.7, 128.1, 128.9, 130.3, 134.3, 144.8, 167.3.

(E)-Methyl 2-methyl-3-phenylacrylate. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.15 (s, 3H), 3.83 (s, 3H), 7.21–7.41 (m, 5H), 7.92 (d, 1H, <sup>3</sup>*J* = 16.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  14.1, 52.0, 127.9, 129.6, 135.8, 138.9, 169.1.

(E)-Ethyl cinnamate. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.43 (t, 3H, <sup>3</sup>*J* = 8.0 Hz), 4.19 (q, 2H, <sup>3</sup>*J* = 8.0 Hz), 6.35 (d, 1H, <sup>3</sup>*J* = 16 Hz), 7.27–7.28 (m, 3H), 7.41–7.42 (m, 2H), 7.63 (d, 1H, <sup>3</sup>*J* = 16.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  14.2, 60.0, 118.2, 127.9, 128.7, 130.1, 134.3, 144.3, 166.6.

(E)-*n*-Butyl cinnamate. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.88 (t, 3H, <sup>3</sup>J = 7.6 Hz), 1.34–1.36 (m, 2H), 1.59–1.62 (m, 2H), 4.13 (t, 2H, <sup>3</sup>J = 6.8 Hz), 6.36 (d, 1H, <sup>3</sup>J = 16.0 Hz), 7.29–7.30 (m, 3H), 7.43–7.45 (m, 2H), 7.60 (d, 1H, <sup>3</sup>J = 16.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  13.7, 19.2, 30.8, 64.3, 118.2, 128.0, 128.8, 130.1, 134.4, 144.4, 166.8.

(E)-*n*-Butyl 3-(4-methoxyphenyl)acrylate. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.91 (t, 3H, <sup>3</sup>J =7.0 Hz), 1.35–1.40 (m, 2H), 1.60–1.62 (m, 2H), 3.72 (s, 3H), 4.13 (m, 2H, <sup>3</sup>J =7.0 Hz), 6.24 (d, 1H, <sup>3</sup>J = 16.0 Hz), 6.81 (d, 3H, <sup>3</sup>J = 4.8 Hz), 7.39 (d, 3H, <sup>3</sup>J = 4.2 Hz), 7.58 (d, 1H, <sup>3</sup>J = 16.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  13.6, 19.1, 30.7, 55.0, 64.0, 114.1, 115.5, 127.0, 129.5, 144.0, 161.2, 167.1.

(E)-*n*-Butyl 3-(4-chlorophenyl)acrylate. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.90 (t, 3H, <sup>3</sup>*J* = 7.2 Hz), 1.33–1.39 (m, 2H), 1.57–1.64 (m, 2H), 4.13 (t, 2H, <sup>3</sup>*J* = 6.8 Hz), 6.64 (d, 1H, <sup>3</sup>*J* = 16.0 Hz), 7.45 (d, 2H, <sup>3</sup>*J* = 8.0 Hz), 7.63 (d, 1H, <sup>3</sup>*J* = 16.0 Hz), 7.74 (d, 2H, <sup>3</sup>*J* = 8.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  13.7, 19.2, 30.7, 64.4, 118.8, 129.1, 129.4, 132.9, 136.0, 143.0, 166.7.

(E)-*n*-Butyl 3-(4-nitrophenyl)acrylate. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.92 (t, 3H, <sup>3</sup>*J* = 7.2 Hz), 1.35–1.44 (m, 2H), 1.62–1.69 (m, 2H), 4.17–4.24 (m, 2H), 6.53 (d, 1H, <sup>3</sup>*J* = 16.0 Hz), 7.63–7.68 (m, 3H), 8.20 (d, 2H, <sup>3</sup>*J* = 8.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  13.6, 19.1, 30.6, 64.7, 122.5, 124.0, 128.6, 140.5, 141.5, 148.3, 166.0.

(E)-*n*-Butyl 3-(4-cyanophenyl)acrylate. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.77 (t, 3H, <sup>3</sup>*J* = 7.0 Hz), 1.30–1.38 (m, 2H), 1.57–1.64 (m, 2H), 4.14 (t, 2H, <sup>3</sup>*J* = 6.8 Hz), 6.45 (d, 1H, <sup>3</sup>*J* = 16.0 Hz), 7.54

(d, 2H,  ${}^{3}J$  = 8.4 Hz), 7.57 (d, 1H,  ${}^{3}J$  = 15.2 Hz), 7.60 (d, 2H,  ${}^{3}J$  = 8.0 Hz);  ${}^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  13.5, 19.0, 30.5, 64.4, 113.0, 118.1, 121.6, 128.3, 132.4, 138.4, 141.8, 165.7.

(E)-1,2-Diphenylethene. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.18 (s, 2H), 7.33 (t, 2H, <sup>3</sup>*J* = 6.8 Hz), 7.42 (t, 4H, <sup>3</sup>*J* = 7.0 Hz), 7.58 (d, 4H, <sup>3</sup>*J* = 7.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  126.7, 127.8, 128.8, 137.4.

(E)-1-Methoxy-4-styrylbenzene. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.89 (s, 3H), 6.92 (d, 2H, <sup>3</sup>*J* = 8.4 Hz), 6.99 (d, 2H, <sup>3</sup>*J* = 16.4 Hz), 7.09 (d, 2H, <sup>3</sup>*J* = 16.0 Hz), 7.36 (t, 2H, <sup>3</sup>*J* = 7.6 Hz), 7.46–7.52 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  55.3, 114.1, 126.3, 126.6, 127.2, 127.8, 128.2, 128.7, 130.1, 137.7, 159.3.

(E)-1-Chloro-4-styrylbenzene. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): *δ* 7.07 (s, 2H), 7.28–7.39 (m, 5H), 7.43–7.46 (m, 2H), 7.50–7.52 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *δ* 127.7, 128.5, 128.8, 129.0, 129.9, 130.0, 130.4, 134.3, 136.9, 138.1.

(E)-4-Styrylbenzonitrile. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.09 (d, 1H, <sup>3</sup>*J* = 16.0 Hz), 7.22 (d, 1H, <sup>3</sup>*J* = 16.0 Hz), 7.31–7.34 (t, 1H, <sup>3</sup>*J* = 4.0 Hz), 7.38–7.41 (t, 2H, <sup>3</sup>*J* = 4.0 Hz), 7.54 (d, 2H, <sup>3</sup>*J* = 7.2 Hz), 7.58 (d, 2H, <sup>3</sup>*J* = 8.4 Hz), 7.64 (d, 2H, <sup>3</sup>*J* = 8.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  111.7, 120.2, 127.8, 128.0, 128.1, 129.8, 130.0, 133.5, 133.6, 137.4, 142.9.

(E)-1-Nitro-4-styrylbenzene. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.06–7.18 (m, 1H), 7.40–7.45 (m, 4H), 7.49–766 (m, 4H), 8.15–8.26 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  125.2, 127.4, 128.0, 128.2, 130.0, 134.4, 137.3, 145.0, 147.8.

Biphenyl. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.46 (t, 2H, <sup>3</sup>*J* = 7.2 Hz), 7.56 (t, 4H, <sup>3</sup>*J* = 8.0 Hz), 7.72 (d, 4H, <sup>3</sup>*J* = 6.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  127.2, 127.3, 128.8, 141.3.

4-Methoxybiphenyl. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.83 (s, 3H), 6.99 (d, 2H, <sup>3</sup>*J* = 8.8 Hz), 7.31 (t, 1H, <sup>3</sup>*J* = 7.2 Hz), 7.43 (t, 2H, <sup>3</sup>*J* = 8.0 Hz), 7.55 (t, 4H, <sup>3</sup>*J* = 8.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  56.5, 115.3, 127.8, 127.9, 129.3, 129.9, 134.9, 142.0, 160.3.

4-Chlorobiphenyl. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.31–7.49 (m, 5H), 7.51–7.57 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 128.1, 128.7, 129.3, 129.5, 130.0, 130.2, 140.8, 141.1.

4-Nitrobiphenyl. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.43–7.52 (m, 3H), 7.62–7.64 (m, 2H), 7.73–7.76 (m, 2H), 8.29–8.30 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  125.2, 128.5, 128.9, 130.0, 130.3, 139.9, 148.2, 148.7.

4-Cyanobiphenyl. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.41–7.51 (m, 3H), 7.56–7.60 (m, 2H), 7.68–7.74 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  112.0, 120.1, 128.3, 128.8, 129.8, 130.2, 133.7, 140.3, 146.8.

### 3. Results and discussion

## 3.1. Synthesis and characterization of Pd-isatin Schiff base-γ-Fe<sub>2</sub>O<sub>3</sub>

Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was synthesized by the steps shown in Scheme 1. First,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was reacted with 3-aminopropyltriethoxysilane to obtain amino-functionalized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The reaction of the amino-functionalized MNPs with isatin produced isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Finally, the supported Pd catalyst was obtained by the reaction of dissolving palladium (II) acetate in methanol with the above synthesized isatin



Scheme 1. Synthesis of Pd-isatin Schiff base-γ-Fe<sub>2</sub>O<sub>3</sub>.

Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The synthesized Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was characterized by FT-IR, SEM, HRTEM, XRD, TGA, ICP, XPS and elemental analysis.

The FT-IR spectra of amino-functionalized y-Fe<sub>2</sub>O<sub>3</sub>, isatin Schiff base-y-Fe<sub>2</sub>O<sub>3</sub>, and Pd-isatin Schiff base-y-Fe<sub>2</sub>O<sub>3</sub> are shown in Fig. 1. The band at 550-670 cm<sup>-1</sup> was assigned to the stretching vibration of the Fe-O bond in these compounds. The peaks at 1085, 3438, 3480, and 2869-2906 cm-1 in amino-functionalized y-Fe<sub>2</sub>O<sub>3</sub> corresponded to C-N, N-H and C-H stretching modes of the alkyl chain, respectively. The N-H bending mode appeared at 1631 cm<sup>-1</sup>. For isatin Schiff base-y-Fe<sub>2</sub>O<sub>3</sub>, new bands were observed at 1455, 1608, and 1718 cm<sup>-1</sup>, which were due to the C=C, C=N, and C=O stretching vibrations, respectively. These bands proved that isatin had been successfully reacted with amino-functionalized y-Fe<sub>2</sub>O<sub>3</sub>. The N-H stretching band of the amide group in isatin overlapped the broad O-H band, which was found at 3390 cm<sup>-1</sup>. Over the Pd-isatin Schiff base-y-Fe<sub>2</sub>O<sub>3</sub>, the C=N and C=O stretching frequencies were shifted to the lower wavenumbers (1600, 1704 cm<sup>-1</sup>), which showed the successful coordination of nitrogen and oxygen to the metal center.

The SEM image of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> showed the uniformity and spherical morphology of the MNPs (Fig. 2).

The size and structure of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> were determined using HRTEM. The results demonstrated the



**Fig. 1.** FT-IR spectra of amino-functionalized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (1), isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (2), and Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (3).

spherical shape of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with an average diameter of 12 nm (Fig. 3). The black spots with an average diameter of 2 nm were attributed to supported Pd.

As shown in Fig. 4, six characteristic diffraction peaks ( $2\theta = 30.4^{\circ}, 35.7^{\circ}, 43.4^{\circ}, 53.8^{\circ}, 57.3^{\circ}, and 63.0^{\circ}$ ) corresponding to the (220), (311), (400), (422), (511) and (440) reflections, respectively, of inverse spinel  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs were observed. This indicated that the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs mostly existed in the face centered



Fig. 2. SEM image of Pd-isatin Schiff base-y-Fe<sub>2</sub>O<sub>3</sub>.



Fig. 3. HRTEM images of Pd-isatin Schiff base-y-Fe<sub>2</sub>O<sub>3</sub>.



Fig. 4. XRD pattern of Pd-isatin Schiff base-γ-Fe<sub>2</sub>O<sub>3</sub>.

cubic structure. The XRD pattern of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> showed a weak peak at (2 $\theta$  = 39.4°) which correspond to the (111) reflection of supported Pd.

The thermal behavior of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was investigated by TGA. As shown in Fig. 5, the weight loss at 180 °C was related to the loss of adsorbed water. There was also a significant weight loss of 13.92% from 200 to 800 °C, which was related to the decomposition of the isatin Schiff base ligand and organic components located on the surface of the MNPs.

The loading amount of the Pd-complex on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was also quantified by elemental analysis, and it was 0.31 mmol/g based on the nitrogen and carbon amounts (0.86% and 3.95%, respectively).

The Pd content of Pd-isatin Schiff  $base-\gamma-Fe_2O_3$  was determined by ICP. The ICP analysis showed that 0.28 mmol of Pd was anchored on 1.0 g of Pd-isatin Schiff  $base-\gamma-Fe_2O_3$ .

The XPS spectrum of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is shown in Fig. 6. The observed peaks at 337.6 (3 $d_{5/2}$ ) and 342.1 eV (3 $d_{3/2}$ ) corresponded to Pd in the +2 oxidation state. No peaks corresponding to Pd<sup>0</sup> was detected.

# 3.2. Catalytic activity of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> for the Heck and Suzuki cross-coupling reactions

The Heck cross-coupling reaction of iodobenzene and *n*-butyl acrylate in the presence of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (0.5 mol%) was chosen as a model reaction for optimizing the reaction parameters such as the base and solvent at 100 °C



Fig. 5. TGA of Pd-isatin Schiff base-γ-Fe<sub>2</sub>O<sub>3</sub>.



Fig. 6. XPS spectrum of Pd-isatin Schiff base-γ-Fe<sub>2</sub>O<sub>3</sub>.

(Table 1). The model reaction was examined in different solvents such as DMF,  $H_2O$  and toluene at 100 °C, and in refluxing EtOH and CH<sub>3</sub>CN (Table 1, entries 1–5). The best yield was obtained in DMF (Table 1, entry 1). To try to avoid the use of toxic and expensive organic solvents, the reaction was also studied under solvent-free conditions (Table 1, entry 6). It was observed that the cross-coupling reaction gave a high yield of the corresponding product in 0.5 h under the solvent-free conditions. Among the studied bases, Et<sub>3</sub>N showed the best results for this reaction in terms of reaction time and yield (Table 1, entries 6–9). The effect of the reaction temperature was also studied. It was found that the reaction time increased and yield of the desired product decreased when the temperature was reduced from 100 to 80 °C (Table 1, entry 10). Increasing the

#### Table 1

Heck cross-coupling reaction of iodobenzene with n-butyl acrylate under different conditions.

Entry	Iodobenzene:	Daaa	Colorent	Time	Yield <sup>a</sup>
	n-Butyl acrylate	Base	Solvent	(h)	(%)
1	1:1.1	Et₃N	DMF	0.5	95
2	1:1.1	$Et_3N$	$H_2O$	0.5	63
3	1:1.1	Et₃N	Toluene	0.5	51
4	1:1.1	Et₃N	EtOH	0.5	84
5	1:1.1	$Et_3N$	CH₃CN	0.5	59
6	1:1.1	$Et_3N$	—	0.5	95
7	1:1.1	K <sub>2</sub> CO <sub>3</sub>	—	0.5	73
8	1:1.1	КОН	—	0.5	42
9	1:1.1	NaOAc	—	0.5	64
10 <sup>b</sup>	1:1.1	Et₃N	—	0.5	90
11 <sup>c</sup>	1:1.1	Et₃N	—	0.5	95
12	1:1.1	_	—	24	trace
13 <sup>d</sup>	1:1.1	$Et_3N$	—	24	trace
14 e	1:1.1	Et₃N	—	24	trace
15 f	1:1.1	Et₃N	—	24	trace
16 g	1:1.1	$Et_3N$	—	1	64

Reaction conditions: Et\_3N 2 equivalents, Pd-isatin Schiff base- $\gamma\text{-}Fe_2O_3$  0.5 mol%, 100 °C.

<sup>a</sup> Isolated yield.

<sup>b</sup>Temperature: 80 °C.

<sup>c</sup>Catalyst: Pd-isatin Schiff base-γ-Fe<sub>2</sub>O<sub>3</sub> (1 mol%).

<sup>d</sup> No catalyst.

eCatalyst: γ-Fe<sub>2</sub>O<sub>3</sub> (0.04 g).

fCatalyst: Pd(OAc)2.

gCatalyst: Pd(OAc)<sub>2</sub>/γ-Fe<sub>2</sub>O<sub>3</sub> (1 mol%).

molar ratio of the catalyst to 1 mol% did not have any significant effects on the progress of the reaction (Table 1, entry 11). A trace amount of the desired product was formed after 24 h in the absence of the catalyst or the base (Table 1, entries 12 and 13). These results showed the importance of the catalyst and the base for this reaction. The cross-coupling reactions did not take place in the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Pd(OAc)<sub>2</sub> even after 24 h (Table 1, entries 14 and 15). The catalytic activity of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was higher than that of Pd-supported  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> [Pd(OAc)<sub>2</sub>/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>] as a catalyst (Table 1, entry 16).

Then, the reaction of a variety of aryl halides with olefins in the presence of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (0.5 mol%) and Et<sub>3</sub>N at 100 °C under solvent-free conditions was investigated. The results of this study are collected in Table 2. As expected, the catalyst demonstrated excellent efficiency in the reaction of aryl iodides with alkyl acrylates and gave the corresponding products in high yields (Table 2, entries 1–6). Aryl bromides underwent the reaction with *n*-butyl acrylate to afford the desired products in good to high yields (Table 2, entries 7–9). It is important to note that Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was successfully applied as a catalyst for the reaction of aryl chlorides with *n*-butyl acrylate (Table 2, entries 10–12). The reaction of aryl iodides, bromides and chlorides with styrene also proceeded well (Table 2, entries 13–20).

Following this initial success in the Heck cross-coupling reaction, we investigated the application of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in the Suzuki reaction. As shown in Table 3, various aryl iodides, bromides and chlorides containing elec-

### Table 2

Heck cross-coupling reaction of olefins with aryl halides in the presence of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> as a catalyst at 100 °C.

$R'$ Pd-isatin Schiff base- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> (0.5mol%)				
R		Et <sub>3</sub> N, 100 °C, solvent-free	R	∠
Entry	محمد المعانيات	Olafin	Time	Isolated
Епиу	Aryrnande	Olelill	(h)	yield (%)
1	PhI	CH <sub>2</sub> =CH <sub>2</sub> -CO <sub>2</sub> Me	0.5	95
2	PhI	CH <sub>2</sub> =C(Me)-CO <sub>2</sub> Me	0.5	90
3	PhI	CH <sub>2</sub> =CH-CO <sub>2</sub> Et	0.5	92
4	PhI	CH2=CH-CO2Bun	0.5	95
5	4-MeOC <sub>6</sub> H <sub>4</sub> I	CH2=CH-CO2Bun	4	87
6	4-ClC <sub>6</sub> H <sub>4</sub> I	CH2=CH-CO2Bun	0.75	90
7	PhBr	CH2=CH-CO2Bun	7	63
8	4-O2NC6H4Br	CH2=CH-CO2Bun	2	64
9	4-NCC <sub>6</sub> H <sub>4</sub> Br	CH2=CH-CO2Bun	5	90 *
10	PhCl	CH2=CH-CO2Bun	0.5	82 *
11	4-O2NC6H4Cl	CH2=CH-CO2Bun	0.5	90 *
12	4-NCC <sub>6</sub> H <sub>4</sub> Cl	CH2=CH-CO2Bun	2	90 *
13	PhI	PhCH=CH <sub>2</sub>	1	93
14	4-MeOC <sub>6</sub> H <sub>4</sub> I	PhCH=CH <sub>2</sub>	4	89
15	4-ClC <sub>6</sub> H <sub>4</sub> I	PhCH=CH <sub>2</sub>	2	90
16	PhBr	PhCH=CH <sub>2</sub>	4	77 *
17	4-NC-C <sub>6</sub> H <sub>4</sub> -Br	PhCH=CH <sub>2</sub>	6	63
18	$4-O_2N-C_6H_4Br$	PhCH=CH <sub>2</sub>	5	71
19	PhCl	PhCH=CH <sub>2</sub>	4	60 *
20	4-O2NC6H4Cl	PhCH=CH <sub>2</sub>	6	70 *

Reaction conditions: aryl halide 1 mmol, olefin 1.1 mmol,  $Et_3N$  2 mmol, catalyst 0.5 mol% (\* 1.5 mol%). The products were characterized by comparison of their physical properties with the authentic samples [54–58].

#### Table 3

Suzuki cross-coupling reaction of phenylboronic acid with aryl halides in the presence of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> as a catalyst at 100 °C.

R $X + H$ $H$ $H$	$D_{D}B = \frac{Pd\text{-isatin Schiff base-}\gamma\text{-}}{Et_3N, 100 \text{ °C, solution}}$	Fe <sub>2</sub> O <sub>3</sub> (0.5mol%) vent-free	$ \qquad \qquad$
Entry	Aryl halide	Time (min)	Isolated yield (%)
1	PhI	30	95
2	4-MeOC <sub>6</sub> H <sub>4</sub> I	180	93
3	4-ClC <sub>6</sub> H <sub>4</sub> I	45	86
4	PhBr	45	90 *
5	4-MeOC <sub>6</sub> H <sub>4</sub> Br	45	70 *
6	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br	270	97
7	4-NCC <sub>6</sub> H <sub>4</sub> Br	90	60
8	PhCl	270	90 *
9	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Cl	60	93 *
10	4-NCC <sub>6</sub> H <sub>4</sub> Cl	120	76 *

Reaction conditions: aryl halide 1 mmol, phenylboronic acid 1.1 mmol,  $Et_3N$  2 mmol, catalyst 0.5 mol% (\* 1.5 mol%). Products were characterized by comparison of their physical properties with reference samples [59,60].

tron-donating and electron-withdrawing groups underwent the cross-coupling reaction with phenylboronic acid to produce the corresponding products in good to high yields.

### 3.3. Recycling of the catalyst

In Fig. 7, the results of the recycling of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> for five consecutive runs of the halobenzenes (iodo, bromo and chloro) with *n*-butyl acrylate (Heck reaction) and phenylboronic acid (Suzuki reaction) are presented. After each run, EtOAc was added to the reaction mixture and the catalyst was separated by an external magnet, washed with



**Fig. 7.** Reusability of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> as a magnetically recyclable heterogeneous catalyst for the Heck (halobenzenes with *n*-butyl acrylate) (a) and Suzuki (halobenzenes with phenylboronic acid (b) cross-coupling reactions at 100 °C in 0.5 h.

### Table 4

Catalytic activity of Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> compared with some catalysts reported for the Heck (*n*-butyl acrylate with aryl halides) and Suzuki (phenylboronic acid with aryl halides) coupling reactions.

En- try	Coupling reaction	Catalyst (mol%)	Halide	Conditions	Time (h)	Yield <sup>a</sup> (%)	[Ref.]
1	Heck	POCOP b (0.3)	I, Br, Cl	K <sub>2</sub> CO <sub>3</sub> , DMF, 100 °C	1.5, 6, 24	94, 85, 67 <sup>c</sup>	[61]
2	Heck	Pd/DIAION HP20 (0.2)	Ι	Bu <sub>3</sub> N, DMA, 100 °C	4	95	[62]
3	Heck	[Pd(L)Cl <sub>2</sub> ] d (0.5)	Br	K <sub>2</sub> CO <sub>3</sub> , DMF, 110 °C	24	75	[63]
4	Heck	Bis(oxamato)palladate(II) complex e (1)	Br	Et <sub>3</sub> N, <i>n</i> -Bu <sub>4</sub> NBr, 120 °C	0.5	99	[64]
5	Heck	SMNPs-supported 4,5-diazafluroen-9-one-Pd f (0.2)	Ι	DABCO, Solvent-free, 140 °C	2	92	[65]
6	Heck	Pd-DABCO-γ-Fe <sub>2</sub> O <sub>3</sub> (1, 3, 3)	I, Br, Cl	Et <sub>3</sub> N, Solvent-free, 100 °C	0.5, 7, 24	92, 83, 43 <sup>g</sup>	[45]
7	Heck	γ-Fe <sub>2</sub> O <sub>3</sub> -acetamidine-Pd (0.12)	I, Br, Cl	Et <sub>3</sub> N, DMF, 100 °C	1, 0.5, 24	94, 69, 0	[47]
8	Heck	Pd-isatin Schiff base-γ-Fe <sub>2</sub> O <sub>3</sub> (0.5, 0.5, 1.5)	I, Br, Cl	Et <sub>3</sub> N, Solvent-free, 100 °C	0.5, 7, 0.5	95, 63, 82	this work
7	Suzuki	Pd-BOX <sup>h</sup> (2)	Ι	K <sub>2</sub> CO <sub>3</sub> , DMF, 70 °C	6	100	[66]
8	Suzuki	SiO <sub>2</sub> -pA-Cyan-Cys-Pd <sup>i</sup> (0.5)	I, Br, Cl	K <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 100 °C	5, 5.5, 6	95, 88, 52	[67]
9	Suzuki	NHC-Pd(II) complex <sup>1</sup> (0.2)	I, Br, Cl	K <sub>3</sub> PO <sub>4</sub> .3H <sub>2</sub> O, H <sub>2</sub> O, TBAB, 40 °C	5, 6, 13	98, 90, 87	[68]
$10^{b}$	Suzuki	Bis(oxamato)palladate(II) complex k (5)	I, Br	Et <sub>3</sub> N, <i>n</i> -Bu <sub>4</sub> NBr, 120 °C	2	78, 65 <sup>1</sup>	[64]
11 <sup>c</sup>	Suzuki	Pd <sub>3</sub> (dba) <sup>m</sup> (1)	Br, Cl	K <sub>3</sub> PO <sub>4</sub> , THF, 80 °C	24	77.7, 0.9 <sup>1</sup>	[69]
12	Suzuki	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> -acetamidine-Pd (0.12)	I, Br, Cl	Et <sub>3</sub> N, DMF, 100 °C	0.5, 0.5, 10	96, 96, 41	[47]
13 <sup>d</sup>	Suzuki	Pd-isatin Schiff base- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> (0.5, 1.5, 1.5)	I, Br, Cl	Et <sub>3</sub> N, Solvent-free, 100 °C	0.5, 0.75, 4.5	95, 90, 90	this work

<sup>a</sup> Isolated yield.

<sup>b</sup> POCOP: Bisphosphinite PCP-pincer palladium complex.

<sup>c</sup>*n*-Bu<sub>4</sub>NBr was used as an additive.

<sup>d</sup>L: 1-benzyl-4-phenylthiomethyl.

<sup>e</sup>Bis(oxamato)palladate(II) complex: (n-Bu<sub>4</sub>N)<sub>2</sub>[Pd(2-Mepma)<sub>2</sub>].4H<sub>2</sub>O.

<sup>f</sup>SMNPs: Silica-coated magnetite nanoparticles.

<sup>g</sup> Conversion.

<sup>h</sup>Pd-BOX: Palladium-bis(oxazoline) complex.

<sup>1</sup>SiO<sub>2</sub>-pA-Cyan-Cys-Pd: Propylamine-cyanuric-cysteine palladium complex immobilized onto silica.

<sup>1</sup>NHC-Pd (II): [1,1-(hexylene-1,6-diyl)bis(3-n-butylbenzimidazol-2-ylidene)][PdCl<sub>2</sub>(CH<sub>3</sub>CN)]<sub>2</sub>.

<sup>k</sup>Bis(oxamato)palladate(II) complexes: (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Pd(2-Mepma)<sub>2</sub>].4H<sub>2</sub>O.

<sup>1</sup>Determined by GC.

 $^{m}Pd_{3}(dba): N_{3}P_{3}(O-C_{6}H_{4}-p-P(C_{6}H_{5})_{2})_{5}(O-C_{6}H_{4}-p-C_{6}H_{4}-p-O(CH_{2})_{3}Si(OCH_{3})_{3}.$ 

EtOAc, dried and re-used for a consecutive run under the same reaction conditions. Although no significant loss of the catalytic activity was observed for Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in these reactions, the amount of Pd leached from the heterogeneous catalyst was determined by ICP. It was found that less than 1 ppm of the total amount of the original Pd species was lost during the reaction.

A comparison of the activity of various Pd catalysts with Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in the Heck and Suzuki coupling reactions published in the literature is listed in Table 4. It shows that Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> displayed good catalytic activity for the Heck and Suzuki reactions, but compared with the other catalysts, the advantage was not remarkable, and some of the other catalytic systems were much better. However, our procedure provides significant advantages in terms of a catalyst simply prepared from an inexpensive ligand and it was active with different halobenzenes (iodo, bromo and chloro) with desirable yields. More importantly, among the supported Pd catalysts, our catalyst supported on magnetic nanoparticles can be easily separated from the reaction mixture by an external magnet.

### 4. Conclusions

We developed a novel, practical and economical heterogeneous catalytic system for the Heck and Suzuki cross-coupling reactions by using Pd-isatin Schiff base- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> as a phosphine-free Pd catalyst. The synthesis of this magnetically reusable catalyst from commercially available starting materials, its good to high yields of the products, and simple and convenient method for the separation and reuse of the catalyst are the advantages of this catalytic system for C-C bond formation by the reaction of aryl halides (iodides, bromides and chlorides) with olefins and phenylboronic acid.

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### Graphical Abstract

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Pd-isatin Schiff base complex immobilized on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> as a magnetically recyclable catalyst for the Heck and Suzuki cross-coupling reactions

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A Pd-isatin Schiff base complex immobilized on  $\gamma\text{-}Fe_2O_3$  was synthesized and characterized, and used as a magnetically reusable Pd catalyst for the Heck and Suzuki cross-coupling reactions.

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