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WILEY Applied Organometallic Chemistry

# Magnetic nanoparticle-tethered Schiff base-palladium(II): Highly active and reusable heterogeneous catalyst for Suzuki-Miyaura cross-coupling and reduction of nitroarenes in aqueous medium at room temperature

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#### **Funding information**

DST-SERB, India, Grant/Award Number: YSS/2015/000010; DST-Nanomission, India, Grant/Award Number: SR/NM/NS-20/2014 As a continuation of our efforts to develop new heterogeneous nanomagnetic catalysts for greener reactions, we identified a Schiff base-palladium(II) complex anchored on magnetic nanoparticles (SB-Pd@MNPs) as a highly active nanomagnetic catalyst for Suzuki-Miyaura cross-coupling reactions between phenylboronic acid and aryl halides and for the reduction of nitroarenes using sodium borohydride in an aqueous medium at room temperature. The SB-Pd@MNPs nanomagnetic catalyst shows notable advantages such as simplicity of operation, excellent yields, short reaction times, heterogeneous nature, easy magnetic work up and recyclability. Characterization of the synthesized SB-Pd@MNPs nanomagnetic catalyst was performed with various physicochemical methods such as attenuated total reflectance infrared spectroscopy, UV-visible spectroscopy, inductively coupled plasma atomic emission spectroscopy, energy-dispersive X-ray spectroscopy, field-emission scanning electron microscopy, transmission electron microscopy, powder X-ray powder diffraction, thermogravimetric analysis and Brunauer-Emmett-Teller surface area analysis.

#### KEYWORDS

magnetic nanoparticle, nanomagnetic catalyst, reduction of nitroarenes, Schiff base-palladium(II), Suzuki-Miyaura cross-coupling

# **1** | INTRODUCTION

The Suzuki–Miyaura cross-coupling reactions are some of the most extensively used C-C bond forming reactions in synthetic chemistry and have been utilized as an efficient method to obtain pharmaceutical drugs, complex natural products, engineering materials such as liquid crystals, molecular wires and conducting polymers.<sup>[1–9]</sup> Numerous catalysts have been developed for Suzuki–Miyaura cross-coupling reactions.<sup>[10–19]</sup> Among these, Schiff base-transition metal complexes have exhibited superior catalytic activities and several homogeneous catalysts have been developed.<sup>[20-23]</sup> Various organic amines have been used for the synthesis of numerous chemicals such as pesticides, agrochemicals, polymers, surfactants and dyestuffs.<sup>[24]</sup> The traditional methods for the synthesis of amines are based on the amination of functional groups such as H, F, Cl, Br, I, OH, etc. through the corresponding diazonium salts or the reduction of nitro compounds with homogeneous catalysts.<sup>[25-29]</sup> However,

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a major drawback of homogeneous catalysts is the difficulty of their recovery from the reaction medium for reuse. This problem is of environmental and economic concern in large-scale syntheses. Hence, huge efforts have been made for the design and development of various heterogeneous catalysts for Suzuki-Miyaura cross-coupling reactions and the reduction of nitroarenes. Numerous examples of heterogenization of Schiff base-transition metal complexes by immobilization onto various supports, such as zeolites,<sup>[30,31]</sup> polymers<sup>[32-34]</sup> and clays,<sup>[35]</sup> have been reported. Inorganic matrices show some advantages over organic supports, such as high thermal, chemical and mechanical stability.

The increasing demand for environment-friendly (greener) chemical processes has stimulated many researchers across the globe to develop heterogeneous catalysts, which can be recovered easily and reused effectively. Additionally, our efforts are targeted towards utilizing these catalysts to develop greener reactions, avoiding the use of organic solvents and high temperatures. Recently developed magnetically recyclable catalysts have proved to be promising, combining the advantages of high activities and facile recovery in heterogeneous catalytic processes.<sup>[36–38]</sup> In a continuation of our recent investigation of the application of magnetically recyclable catalysts in cross-coupling reactions,<sup>[39,40]</sup> herein we report the synthesis and characterization of a new nanomagnetic catalyst, a Schiff base-palladium(II) anchored complex on magnetic nanoparticles (SB-Pd@MNPs), for Suzuki-Miyaura cross-coupling of various aryl halides with phenylboronic acid and for the reduction of nitroarenes. The SB-Pd@MNPs nanomagnetic catalyst was structurally investigated using a combination of spectroscopic and microscopic techniques. Furthermore, the SB-Pd@MNPs nanomagnetic catalyst is shown to exhibit high catalytic activity in Suzuki-Miyaura cross-coupling reactions and in the reduction of nitroarenes in aqueous medium at room temperature. Additionally, the SB-Pd@MNPs nanomagnetic catalyst could be effortlessly separated from a reaction system using an external magnet, and could be reused in the next reaction cycle without significant loss of activity. The use of environmentally benign solvent water and reusable SB-Pd@MNPs nanomagnetic catalyst at ambient temperature makes our reaction procedure more fascinating for cross-coupling and reduction reactions. Thus, our research efforts have identified the perfect greener conditions to achieve high yields for Suzuki-Miyaura cross-coupling reactions as well as for reduction of nitroarenes. We hope our research findings will add great value to the catalysis and green chemistry research field.

#### 2 | EXPERIMENTAL

#### 2.1 | Materials

All solvents were purified according to standard methods prior to use. Unless otherwise stated, all reactions were performed under aerobic conditions in oven-dried glassware with magnetic stirring. FeCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O, ammonium hydroxide, 2-hydroxy-1-naphthaldehyde, 3-aminopropyltriethoxysilane, palladium(II) acetate, aryl halides, bases and phenylboronic acid were purchased from Sigma-Aldrich and were used without further purification. Heating was accomplished by either a heating mantle or silicone oil bath. Column chromatography was conducted with silica gel 230-400 mesh (Merck) and preparative TLC was carried out using 0.25 mm Merck TLC silica gel plates with UV light as a visualizing agent. Yields refer to chromatographically pure material. Concentration in vacuo refers to the removal of volatile solvent using a rotary evaporator attached to a dry diaphragm pump (10-15 mmHg) followed by pumping to a constant weight with an oil pump (<300 mTorr). All organic products were known and identified by comparison of their physical and spectral data with those of authentic samples.

### 2.2 | Instrumentation and Analyses

Attenuated total reflectance infrared (ATR-IR) spectra were recorded with a Bruker Alpha Eco-ATR spectrometer. UV-visible spectrophotometry was carried out with a Shimadzu UV-1800 A11454907691. Brunauer-Emmett-Teller (BET) surface areas were obtained by physisorption of nitrogen using a Microtrac BELSORP MAX instrument. The elemental palladium content of the nanomagnetic catalyst was determined with a Thermo Electron IRIS INTREPID II XSP DUO inductively coupled plasma atomic emission spectroscopy (ICP-AES) instrument. Transmission electron microscopy (TEM) images were obtained using a Jeol/JEM 2100 microscope. Field-emission scanning electron microscopy (FESEM) along with energy-dispersive X-ray spectroscopy (ESX) to observe morphology and determine elemental distributions, respectively, were conducted with a JEOL model JSM7100F. Thermogravimetric analysis (TGA) was carried out with a PerkinElmer Diamond TG/DTA with a heating rate of 10.0 °C min<sup>-1</sup>. Powder X-ray diffraction (XRD) patterns were obtained using a Bruker AXS D8 Advance. <sup>1</sup>H NMR spectra were recorded at 400 MHz, and are reported relative to deuterated chloroform (CDCl<sub>3</sub>;  $\delta$  = 7.27 ppm). <sup>1</sup>H NMR coupling constants (J) are reported in hertz (Hz) and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet),

m (multiplet). Liquid chromatography-mass spectra were recorded with an Agilent Technologies quadrupole LC-MS system.

### 2.3 | Synthesis of Hydroxyl-Substituted Magnetic Nanoparticles (MNPs) (1)

MNPs (1) were synthesized from chemical coprecipitation of  $Fe^{3+}$  and  $Fe^{2+}$  ions with a molar ratio of 2:1. A mixture of  $FeCl_3 \cdot 6H_2O$  (4.70 g, 17.38 mmol) and  $FeCl_2 \cdot 4H_2O$  (1.73 g, 8.70 mmol) was dissolved in deionized water (80 ml) and the resultant solution was stirred for 30 min at 85 °C. Subsequently, ammonium hydroxide (15 ml) solution was added slowly with vigorous stirring at 85 °C to produce a black-coloured precipitate and stirring was continued for an additional 30 min. The obtained black-coloured MNPs were collected by magnetic decantation, washed repeatedly with deionized water until neutrality, further washed with ethanol (6 × 30 ml) and dried at 80 °C for 12 h.

# 2.4 | Synthesis of Amine-Functionalized Magnetic Nanoparticles (AFMNPs) (3)

Nanoparticles **1** (4.0 g) were suspended in an EtOH–H<sub>2</sub>O (2:1) mixture (140 ml) with ultrasonicating for 10 min. 3-Aminopropyltriethoxysilane (**2**; 16.43 g, 74.22 mmol) was added to the suspension and stirred at 40 °C for 20 h. Then the reaction mixture was cooled to room temperature. The obtained dark brown AFMNPs (**3**) were collected using a magnetic separator, washed with deionized water ( $2 \times 20$  ml) followed by ethanol ( $2 \times 20$  ml) and dried at 45 °C for 12 h.

### 2.5 | Synthesis of Magnetic Nanoparticle-Tethered Schiff Base (SB@MNPs) (5)

Nanoparticles **3** (4.0 g) were dispersed in toluene (60 ml) by ultrasonicating for 10 min. 2-Hydroxynapthaldehyde (**4**; 4.0 g, 23.23 mmol) was added in one portion to the reaction mixture and stirred at 110 °C for 24 h. Then the reaction mixture was cooled to room temperature. The obtained dark brown SB@MNPs was collected using an external magnetic field, washed with methanol (3  $\times$  20 ml) and dried at 45 °C for 12 h.

### 2.6 | Synthesis of Magnetic Nanoparticle-Supported Schiff Base–Palladium(II) Complex (SB-Pd@MNPs) (6)

To a solution of palladium(II) acetate (0.8 g,3.56 mmol) in ethanol (40 ml) was added **5** (3.5 g) and the reaction mixture was stirred at 78 °C for 12 h. Then the

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reaction mixture was cooled to room temperature. The resulting SB-Pd@MNPs as a dark brown solid was separated by magnetic decantation, washed with water (3  $\times$  20 ml) followed by ethanol (3  $\times$  20 ml) and dried at 45 °C for 12 h. The obtained yield of SB-Pd@MNPs nanaomagnetic catalyst was 3.81 g. In addition, the purity of the SB-Pd@MNPs nanaomagnetic catalyst was confirmed using various physicochemical methods.

# 2.7 | General Procedure for SB-Pd@MNPs-Catalysed Suzuki–Miyaura Cross-Coupling Reactions

To a mixture of aryl halide (0.27 mmol), phenylboronic acid (0.036 g, 0.30 mmol), SB-Pd@MNPs nanomagnetic catalyst (0.15 mol% Pd) and trisodium phosphate (0.098 g, 0.60 mmol) in an oven-dried round-bottomed flask was added EtOH-H<sub>2</sub>O (1:1, 10 ml) and the reaction mixture was stirred at room temperature for the required time. The progress of the reaction was monitored by TLC. After completion of the reaction, the SB-Pd@MNPs nanomagnetic catalyst was separated using a permanent magnet and dichloromethane (20 ml) was added. The dichloromethane layer was separated from the water layer using a separating funnel and dried with anhydrous magnesium sulfate. The dried dichloromethane layer was concentrated in vacuum, and the crude cross-coupled product was purified through column chromatography over silica gel using *n*-hexane and ethyl acetate as eluting solvents to obtain the desired purity. All the cross-coupled products were known molecules and were confirmed by comparing the melting point and <sup>1</sup>H NMR and mass spectroscopic data (see supporting information) with those of authentic samples.

# 2.8 | General Procedure for Reduction of Nitroarenes

In a typical reduction reaction, nitroarene (0.05 g) was mixed with the SB-Pd@MNPs nanomagnetic catalyst (0.05 mol% Pd) in water (10 ml) and the reaction mixture was stirred for 1 min at room temperature. Subsequently, NaBH<sub>4</sub> (3.0 mol) was added to the flask and the reaction mixture was vigorously stirred at room temperature for the required time. The progress of the reaction was checked through TLC. After completion of the reaction, the SB-Pd@MNPs nanomagnetic catalyst was separated using a permanent magnet and dichloromethane (20 ml) was added. The dichloromethane layer was separated from the water layer using a separating funnel and dried with anhydrous magnesium sulfate. The dried dichloromethane layer was concentrated in vacuum,

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and the crude reduced product was purified through column chromatography over silica gel using *n*-hexane and ethyl acetate as eluting solvents to afford the pure product. All the reduced products were known molecules and were confirmed by comparing the melting point and <sup>1</sup>H NMR and mass spectroscopic data (see supporting information) with those of authentic samples.

#### 2.9 | Procedure for Recovery of SB-Pd@MNPs Nanomagnetic Catalyst

After reaction completion, the SB-Pd@MNPs nanomagnetic catalyst was separated using a permanent magnet. The separated SB-Pd@MNPs nanomagnetic catalyst was then washed with water  $(2 \times 10 \text{ ml})$  followed by ethanol  $(2 \times 10 \text{ ml})$  and dried at 45 °C for 12 h. The dried SB-Pd@MNPs nanomagnetic catalyst was used for the next reaction run without further purification.

# 3 | RESULTS AND DISCUSSION

# 3.1 | Synthesis of SB-Pd@MNPs Nanomagnetic Catalyst

In continuation of our studies of the applications of palladium complexes immobilized on MNPs in organic transformations,<sup>[39,40]</sup> herein we report a simple and efficient green method for Suzuki–Miyaura cross-coupling between phenylboronic acid and a range of aryl halides containing iodo, bromo and chloro moieties and also for the reduction of nitroarenes in the presence of catalytic amounts of SB-Pd@MNPs nanomagnetic catalyst.

The synthetic pathway for the SB-Pd@MNPs nanomagnetic catalyst described in this work is outlined in Scheme 1. Initially, **1** was prepared via chemical co-precipitation from a 2:1 molar ratio of  $Fe^{3+}$  and  $Fe^{2+}$  with ammonium hydroxide as base. Then, **3** was prepared by the functionalization of **1** with **2** in EtOH–H<sub>2</sub>O mixture at 40 °C. In the next step, **5** was synthesized from the reaction between **4** and **3** in toluene at 110 °C. Finally, **5** was



SCHEME 1 Synthetic route to (a) MNPs (1) and (b) SB-Pd@MNPs nanomagnetic catalyst (6)

treated with palladium(II) acetate in ethanol at 78 °C to afford the desired SB-Pd@MNPs nanomagnetic catalyst (**6**).

# 3.2 | Spectroscopic and Microscopic Characterization

#### 3.2.1 | ATR-IR spectroscopy

All the synthesized compounds were structurally characterized using the ATR-IR spectroscopic technique. Figure 1 displays ATR-IR spectra of MNPs, AFMNPs, SB@MNPs and SB-Pd@MNPs nanomagnetic catalyst. The strong absorption peak at 556  $\text{cm}^{-1}$  is attributed to Fe-O bond stretching and the broad peak at around  $3000-3500 \text{ cm}^{-1}$  represents the O-H stretching vibrations of MNPs (Figure 1a).<sup>[39,40]</sup> The ATR-IR spectrum of AFMNPs (Figure 1b) displays a characteristic peak of Si--O at 1007 cm<sup>-1</sup> and stretching vibrations of aliphatic C-H bonds at 2901 cm<sup>-1</sup>, which confirms that 3-aminopropyltriethoxysilane is successfully grafted on the surface of MNPs.<sup>[39,40]</sup> In the ATR-IR spectrum of SB@MNPs, a new band is observed at1630 cm<sup>-1</sup> due to the C=N stretch of the imine group and another new band at around 1405 cm<sup>-1</sup> is assigned to the aromatic C=C stretch (Figure 1c). These bands demonstrate that 2-hydroxynaphthaldehyde has been successfully grafted onto the AFMNPs.<sup>[41,42]</sup> The ATR-IR spectrum of the SB-Pd@MNPs nanomagnetic catalyst reveals typical bands at 2906, 1437, 1009 and 558 cm<sup>-1</sup> attributed to aliphatic C-H stretching, aromatic C=C stretching, Si--O stretching and O--H stretching vibrations (Figure 1 d).<sup>[39,40]</sup> The band due to (C=N) in the SB@MNPs spectrum is observed at 1630 cm<sup>-1</sup> and is shifted to lower wavenumber of 1619 cm<sup>-1</sup> in the SB-Pd@MNPs spectrum indicating coordination of SB@MNPs through imine nitrogen to palladium (Figure 1d).<sup>[41,42]</sup> Figure 2(b,c) shows the ATR-IR spectra of five-times-recycled SB-Pd@MNPs nanomagnetic catalyst from Suzuki-Miyaura cross-coupling reaction and ten-times-recycled SB-Pd@MNPs nanomagnetic catalyst from reduction of nitroarenes. Results show that recycled SB-Pd@MNPs nanomagnetic catalyst from both reactions is intact except for some slight shift in the peak positions.

#### 3.2.2 | Thermogravimetric analysis

The thermal stability of MNPs and the SB-Pd@MNPs nanomagnetic catalyst was investigated using TGA under nitrogen atmosphere from 40 to 740 °C at a rate of 10 °C min<sup>-1</sup>. Figure 3(a) shows a weight loss of 3% at 40–110 °C which corresponds to removal of hydroxyl groups present on the surface of the MNPs. On the other



**FIGURE 1** ATR-IR spectra of (a) MNPs, (b) AFMNPs, (c) SB-MNPs and (d) SB-Pd@MNPs nanomagnetic catalyst



**FIGURE 2** ATR-IR spectra of SB-Pd@MNPs nanomagnetic catalyst: (a) freshly prepared, (b) recycled after Suzuki–Miyaura reaction and (c) recycled after reduction reaction



**FIGURE 3** TGA curves of (a) MNPs and (b) SB-Pd@MNPs nanomagnetic catalyst

hand, the SB-Pd@MNPs nanomagnetic catalyst shows weight loss in two stages (Figure 3(b)). In the first stage, a weight loss of up to 3% is observed in the range 40–110 °C which is due to hydroxyl groups and physically adsorbed solvent molecules present on the surface of MNPs. A weight loss of up to 7% is found in the second stage at 110–600 °C which is due to the thermal decomposition of organic moieties anchored on the surface of MNPs. Therefore, on the basis of the TGA results, attachment of the Schiff base–palladium(II) complex on the surface of MNPs is confirmed.<sup>[43,44]</sup> In addition, from the TGA results, it is clear that the SB-Pd@MNPs nanomagnetic catalyst is stable up to 220 °C which in turn allows the usage of this SB-Pd@MNPs nanocatalyst in reactions carried out at temperatures up to 200 °C.

#### 3.2.3 | BET surface area analysis

The surface functionalization of MNPs and the SB-Pd@MNPs nanomagnetic catalyst was investigated using BET surface area analysis. The nitrogen adsorption and desorption isotherms for MNPs and the SB-Pd@MNPs nanomagnetic catalyst are shown in Figure 4. The SB-Pd@MNPs nanomagnetic catalyst exhibited a type-II isotherm. The amount of nitrogen adsorbed on MNPs is high compared to that on the SB-Pd@MNPs nanomagnetic catalyst. The surface area of bare MNPs is 77.47 m<sup>2</sup> g<sup>-1</sup> which is decreased to 48.18 m<sup>2</sup> g<sup>-1</sup> upon the formation of the SB-Pd@MNPs nanomagnetic catalyst. The decrease in surface area reveals the successful functionalization of



**FIGURE 4** Nitrogen adsorption-desorption curves for (a) MNPs and (b) SB-Pd@MNPs nanomagnetic catalyst

MNPs with the Schiff base–palladium(II) complex, which is evident from the BET data.<sup>[39,40,45]</sup>

#### 3.2.4 | TEM analysis

TEM was used to obtain direct information regarding the morphology and structure of the synthesized nanoparticles. TEM images of MNPs, SB-Pd@MNPs nanomagnetic catalyst and recycled SB-Pd@MNPs nanomagnetic catalyst are shown in Figure 5. MNPs are spherical in nature and the size of the nanoparticles varies from 7 to 10 nm (Figure 5a). After immobilization of the Schiff basepalladium(II) complex on the surface of MNPs, the size increases to 10-20 nm with quasi-spherical morphology (Figure 5b). In addition, dark magnetic core present inside the SB-Pd@MNPs nanomagnetic catalyst particles can be clearly seen in the TEM image. Furthermore, the recycled SB-Pd@MNPs nanomagnetic catalyst did not show much change in morphology after being reused five times in Suzuki–Miyaura cross-coupling reaction (Figure 5c).<sup>[46–48]</sup> Moreover, the selected area electron diffraction (SAED) pattern (Figure 5d) of the SB-Pd@MNPs nanomagnetic catalyst reveals the material is polycrystalline in nature.

#### 3.2.5 | FESEM analysis

To obtain more information about the surface morphology of freshly prepared SB-Pd@MNPs nanomagnetic catalyst and recycled SB-Pd@MNPs nanomagnetic catalyst after use in Suzuki–Miyaura cross-coupling reaction, FESEM analysis was carried out. FESEM images are shown in Figure 6. The FESEM image of freshly prepared SB-Pd@MNPs (Figure 6a) shows that nanoparticles are distributed uniformly and of nanometre size with spherical morphology.<sup>[49–51]</sup> After five recycles in Suzuki–Miyaura cross-coupling reaction, the surface morphology of the SB-Pd@MNPs nanomagnetic catalyst remains almost same as that of fresh freshly prepared SB-Pd@MNPs nanomagnetic catalyst as shown in Figure 6(b).

#### 3.2.6 | EDX analysis

In order to confirm the existence of each element present in the newly synthesized SB-Pd@MNPs nanomagnetic catalyst, EDX was employed. The EDX spectrum (Figure 7) of the SB-Pd@MNPs nanomagnetic catalyst shows characteristic signals corresponding to C, N, O, Si, Fe and Pd atoms which evidence the attachment of Schiff base–palladium(II) complex on the surface of MNPs.<sup>[52]</sup> Elemental mapping of the SB-Pd@MNPs nanomagnetic catalyst was carried out to understand the distribution of elements as shown in Figure 8. From elemental mapping data it is clear that all the elements are distributed evenly. -WILEY Organometallic Chemistry



**FIGURE 5** TEM images of (a) MNPs, (b) SB-Pd@MNPs nanomagnetic catalyst and (c) five-times-recycled SB-Pd@MNPs nanomagnetic catalyst in Suzuki–Miyaura cross-coupling reaction. (d) SAED pattern of SB-Pd@MNPs nanomagnetic catalyst 8 of 21 WILEY Organometallic Chemistry



**FIGURE 6** FESEM images of (a) SB-Pd@MNPs nanomagnetic catalyst and (b) five-times-recycled SB-Pd@MNPs nanomagnetic catalyst in Suzuki–Miyaura cross-coupling reaction

![](_page_7_Figure_3.jpeg)

FIGURE 7 EDX spectrum of SB-Pd@MNPs nanomagnetic catalyst

#### 3.2.7 | ICP-AES analysis

In addition, the exact quantity of palladium loaded on the SB-Pd@MNPs nanomagnetic catalyst was determined using ICP-AES analysis. This analysis shows a loading of

11.43% (w/w) of palladium on the SB-Pd@MNPs nanomagnetic catalyst.

#### 3.2.8 | XRD analysis

The crystalline structure of MNPs and the SB-Pd@MNPs nanomagnetic catalyst was determined using the powder XRD technique. The diffraction patterns of MNPs and SB-Pd@MNPs nanomagnetic catalyst are shown in Figure 9. The XRD pattern of bare MNPs (Figure 9a) shows diffraction peaks at  $2\theta$  of  $30.09^\circ$ ,  $35.59^\circ$ ,  $43.07^\circ$ , 53.43°, 57.37° and 62.90° corresponding to the crystal planes of (220), (311), (400), (422), (511) and (440), which confirms cubic spinel structure of MNPs. Figure 9(b) depicts the XRD pattern of the SB-Pd@MNPs nanomagnetic catalyst which shows that the phase remains unaltered even after the functionalization of MNPs which is in good agreement with the TEM images. Diffraction peaks at  $2\theta$  of 39.99° and 43.14° corresponding to the crystal planes of (111) and (200) show the presence of palladium in the SB-Pd@MNPs nanomagnetic catalyst.<sup>[53,54]</sup>

#### 3.2.9 | UV-visible spectroscopy

The UV–visible spectra of MNPs and the SB-Pd@MNPs nanomagnetic catalyst in water are shown in Figure 10. The spectra of MNPs and the SB-Pd@MNPs nanomagnetic catalyst display bands at 386 and 322 nm. The band shift from 386 to 322 nm suggests the successful surface functionalization of MNPs.<sup>[55,56]</sup>

# 3.3 | Catalytic Activity of SB-Pd@MNPs in Suzuki-Miyaura Cross-Coupling Reactions

After full characterization of the synthesized SB-Pd@MNPs nanomagnetic catalyst with spectroscopic and microscopic methods, its catalytic potential was investigated as a magnetically separable nanomagnetic catalyst in Suzuki-Miyaura cross-coupling reactions. The Suzuki-Miyaura cross-coupling reaction is one of the most important methods for C-C bond formation in organic transformations. The Suzuki-Miyaura crosscoupling reaction is used in various organic reactions and therefore it now belongs to an essential set of palladium-catalysed cross-coupling reactions. Thus, the catalytic potential of the synthesized SB-Pd@MNPs nanomagnetic catalyst was explored in Suzuki-Miyaura cross-coupling reactions. The reaction conditions were optimized for a model Suzuki-Miyaura cross-coupling reaction of 4-bromobenzonitrile with phenylboronic acid as shown in Scheme 2.

![](_page_8_Figure_1.jpeg)

FIGURE 8 Elemental mapping of SB-Pd@MNPs nanomagnetic catalyst

![](_page_8_Figure_3.jpeg)

**FIGURE 9** XRD patterns of (a) MNPs and (b) SB-Pd@MNPs nanomagnetic catalyst

Recently, worldwide significant research efforts have been devoted to the replacement of organic solvents (flammable, non-biodegradable and toxic) in chemical reactions by green solvents (non-toxic, cheap, bio-renewable and non-flammable). Thus, ethanol and water were given high priority as solvents during process optimization. The reaction conditions were optimized for model reaction in the presence of SB-Pd@MNPs nanomagnetic

![](_page_8_Figure_6.jpeg)

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**FIGURE 10** UV-visible spectra of (a) MNPs and (b) SB-Pd@MNPs nanomagnetic catalyst

catalyst as presented in Table 1. The preliminary outcome revealed that using Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O base, EtOH-H<sub>2</sub>O (1:1) solvent and 0.15 mol% Pd of SB-Pd@MNPs nanomagnetic catalyst at room temperature for 4 h resulted in the highest yield (Table 1, entry 7). The catalytic potential of the SB-Pd@MNPs nanomagnetic catalyst with varying base, solvent, temperature, time and catalyst ratio was also studied for the model reaction, with the results presented in Tables 2–6, respectively.

![](_page_9_Figure_0.jpeg)

**TABLE 1** Optimization of conditions for Suzuki–Miyaura cross-coupling model reaction in presence of SB-Pd@MNPs nanomagnetic catalyst<sup>a</sup>

Entry	Base	Solvent	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>
1	K <sub>2</sub> CO <sub>3</sub>	EtOH	RT	3.0	45
2	Na <sub>2</sub> CO <sub>3</sub>	EtOH	RT	3.0	62
3	Na <sub>2</sub> CO <sub>3</sub>	EtOH-H <sub>2</sub> O (1:1)	RT	3.0	75
4	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH	RT	10.0	45
5	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	H <sub>2</sub> O	RT	7.5	65
6	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	DMF	RT	3.0	—
7	$Na_3PO_4 \cdot 12H_2O$	EtOH-H <sub>2</sub> O (1:1)	RT	4.0	94
8	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	5.0	94
9	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	40	4.0	90
10	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	50	4.0	92
11	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	70	4.0	92

<sup>a</sup>Reaction conditions: 4-bromobenzonitrile (1.0 mmol), phenylboronic acid (1.1 mmol), SB-Pd@MNPs nanomagnetic catalyst (0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (10 ml) in air.

<sup>b</sup>Isolated yield after separation by column chromatography; average of two runs.

Entry	Base	Solvent	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>
1	Na <sub>2</sub> CO <sub>3</sub>	EtOH-H <sub>2</sub> O (1:1)	RT	4.0	80
2	K <sub>2</sub> CO <sub>3</sub>	EtOH-H <sub>2</sub> O (1:1)	RT	4.0	85
3	NaOH	EtOH-H <sub>2</sub> O (1:1)	RT	4.0	37
4	КОН	EtOH-H <sub>2</sub> O (1:1)	RT	4.0	30
5	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> 0 (1:1)	RT	4.0	94
6	KF	EtOH-H <sub>2</sub> O (1:1)	RT	4.0	32
7	$Cs_2CO_3$	EtOH-H <sub>2</sub> O (1:1)	RT	4.0	85
8	Triethylamine	EtOH-H <sub>2</sub> O (1:1)	RT	4.0	59

TABLE 2 Suzuki-Miyaura cross-coupling model reaction using SB-Pd@MNPs nanomagnetic catalyst with various bases<sup>a</sup>

<sup>a</sup>Reaction conditions: 4-bromobenzonitrile (1.0 mmol), phenylboronic acid (1.1 mmol), SB-Pd@MNPs nanomagnetic catalyst (0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (10 ml) in air.

<sup>b</sup>Isolated yield after separation by column chromatography; average of two runs.

### 3.4 | Effect of Base on Suzuki–Miyaura Cross-Coupling Reaction

The catalytic potential of the SB-Pd@MNPs nanomagnetic catalyst was studied in the model reaction using various bases: Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaOH, KOH, Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O, KF, Cs<sub>2</sub>CO<sub>3</sub> and triethylamine (Table 2; Figure 11a). Among the bases employed, Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O showed good conversion rate (Table 2, entry 5) and bases Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaOH, KOH, KF, Cs<sub>2</sub>CO<sub>3</sub> and trimethylamine resulted in lesser conversion (Table 2, entries 1–4 and 6–8).

### 3.5 | Effect of Solvent on Suzuki–Miyaura Cross-Coupling Reaction

with phenylboronic acid

The catalytic activity of the SB-Pd@MNPs nanomagnetic catalyst in the model reaction was investigated using various solvents, namely  $H_2O$ , EtOH, MeOH, dimethylformamide (DMF), tetrahydrofuran (THF), toluene, acetone, acetonitrile (CH<sub>3</sub>CN), dichloromethane (DCM), isopropyl alcohol (IPA) and EtOH–H<sub>2</sub>O (1:1) mixture. The results are presented in Table 3 and Figure 11(b). It is clear that the SB-Pd@MNPs nanomagnetic catalyst worked well with polar solvents

TABLE 3 Suzuki-Miyaura cross-coupling model reaction in presence of SB-Pd@MNPs nanomagnetic catalyst with various solvents<sup>a</sup>

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Entry	Base	Solvent	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>
1	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	МеОН	RT	4.0	60
2	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH	RT	4.0	70
3	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	H <sub>2</sub> O	RT	4.0	30
4	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	CH <sub>3</sub> CN	RT	4.0	_
5	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	Acetone	RT	4.0	_
6	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	THF	RT	4.0	_
7	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	Toluene	RT	4.0	26
8	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	DCM	RT	4.0	_
9	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	DMF	RT	4.0	_
10	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	IPA	RT	4.0	_
11	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	4.0	94

<sup>a</sup>Reaction conditions: 4-bromobenzonitrile (1.0 mmol), phenylboronic acid (1.1 mmol), SB-Pd@MNPs nanomagnetic catalyst (0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (10 ml) in air.

<sup>b</sup>Isolated yield after separation by column chromatography; average of two runs.

Entry	Base	Solvent	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>
1	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	0	4.0	30
2	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	15	4.0	40
3	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	4.0	94
4	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	40	4.0	90
5	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	50	4.0	92
6	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	60	4.0	92
7	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	70	4.0	92

TABLE 4 Suzuki-Miyaura cross-coupling model reaction using SB-Pd@MNPs nanomagnetic catalyst at various temperatures<sup>a</sup>

<sup>a</sup>Reaction conditions: 4-bromobenzonitrile (1.0 mmol), phenylboronic acid (1.1 mmol), SB-Pd@MNPs nanomagnetic catalyst (0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (10 ml) in air.

<sup>b</sup>Isolated yield after separation by column chromatography; average of two runs.

Entry	Base	Solvent	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>
1	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	1.0	73
2	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	2.0	81
3	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	3.0	87
4	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	4.0	94
5	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O(1:1)	RT	5.0	94
6	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	6.0	93

TABLE 5 Suzuki-Miyaura cross-coupling model reaction using SB-Pd@MNPs nanomagnetic catalyst at various time intervals<sup>a</sup>

<sup>a</sup>Reaction conditions: 4-bromobenzonitrile (1.0 mmol), phenylboronic acid (1.1 mmol), SB-Pd@MNPs nanomagnetic catalyst(0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (10 ml) in air.

<sup>b</sup>Isolated yield after separation by column chromatography; average of two runs.

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TABLE 6 Suzuki-Miyaura cross-coupling model reaction using various SB-Pd@MNPs nanomagnetic catalyst ratios<sup>a</sup>

Entry	Base	Solvent	Temperature (°C)	Pd (mol%)	Yield (%) <sup>b</sup>
1	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	0.025	50
2	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	0.05	75
3	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	0.075	80
4	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	0.10	85
5	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	0.125	88
6	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	0.15	94
7	$Na_3PO_4 \cdot 12H_2O$	EtOH-H <sub>2</sub> O (1:1)	RT	0.175	94
8	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	0.20	94

<sup>a</sup>Reaction conditions: 4-bromobenzonitrile (1.0 mmol), phenylboronic acid (1.1 mmol), base (2.2 mmol) and solvent (10 ml) in air.

<sup>b</sup>Isolated yield after separation by column chromatography; average of two runs.

![](_page_11_Figure_5.jpeg)

FIGURE 11 Plots depicting yields of Suzuki–Miyaura cross-coupling products against varying (a) base, (b) solvent, (c) temperature, (d) time and (e) catalyst ratio

like MeOH, EtOH,  $H_2O$  and EtOH $-H_2O$  mixture (Table 3, entries 1–3 and 11). Furthermore, the model reaction in EtOH $-H_2O$  (1:1) mixture gave the highest yield (Table 3, entry 11).

# 3.6 | Effect of Temperature on Suzuki-Miyaura Cross-Coupling Reaction

To explore the catalytic activity of our new SB-Pd@MNPs nanomagnetic catalyst at varying temperatures, the model

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**TABLE 7** Suzuki–Miyaura cross-coupling reactions between aryl halides and phenylboronic acid catalysed by SB-Pd@MNPs nanomagnetic catalyst<sup>a</sup>

	$R_1$ + (HO) <sub>2</sub> B-	$\frac{\text{SB-Pd}@\text{MNPs}, \text{Na}_3\text{PO}_4\text{-}12\text{H}_2\text{O}}{\text{EtOH:H}_2\text{O}(1\text{-}1\text{)}, \text{RT}} R_1$	$\rightarrow \frown $	
Entry	Aryl halide	Product	Time (h)	Yield (%) <sup>b</sup>
1	NC	NC	4	94
2	HO O Br	HOTO	3	71
3	HO	но	3	81
4	Br H O		15	75
5	H Br	H	15	72
6	O Br		22	84
7	HOBR	но	2.5	89
8	H <sub>3</sub> C	H <sub>3</sub> C	0.5	43
9	o Br	, C	0.5	56
10	O <sub>2</sub> N Br	O <sub>2</sub> N	1	88
11	H	н	0.5	85
12	H <sub>2</sub> N Br	H <sub>2</sub> N	22	87

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	$R_1$ + (HO) <sub>2</sub> B-	$\frac{\text{SB-Pd}@\text{MNPs}, \text{Na}_3\text{PO}_4\text{-}12\text{H}_2\text{O}}{\text{EtOH:H}_2\text{O}(1:1), \text{RT}} R_1$	$\rightarrow \rightarrow$	
Entry	Aryl halide	Product	Time (h)	Yield (%) <sup>b</sup>
13	F F	F	1	22
14	Br O		22.5	81
15	→	$\rightarrow$	0.5	74
16	HOCI	но	22.5	60
17	CI	y C	17	68
18	OH Cl	OH	23	Trace
19	O OH Cl	O OH	24	Trace
20			0.5	95

<sup>a</sup>Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol), SB-Pd@MNPs nanomagnetic catalyst (0.15 mol% Pd), base (2.2 mmol) and EtOH-H<sub>2</sub>O (10 ml) in air.

<sup>b</sup>Isolated yield after separation by column chromatography; average of two runs.

reaction was carried out at different temperatures as presented in Table 4 (Figure 11c). Results show high catalytic activity at room temperature (Table 4, entry 3) and above (Table 4, entries 4-7); hence the preferred reaction temperature for the model reaction is room temperature (Table 4, entry 3). On the other hand, below room temperature the yields were less (Table 4, entries 1 and 2).

#### 3.7 | Effect of Time on Suzuki-Miyaura **Cross-Coupling Reaction**

To understand the effect of time, the model reaction was conducted for various time intervals with the SB-Pd@MNPs nanomagnetic catalyst (Table 5; Figure 11d). It is clear from the results obtained that the yield increased with increasing time (Table 5, entries 1-4) and further yield improvement was not observed after a time period of 4 h (Table5, entries 5 and 6). Therefore, 4 h is the optimum time period required for the maximum yield (Table 5, entry 4).

### 3.8 | Effect of Catalyst Ratio on Suzuki-**Miyaura Cross-Coupling Reaction**

Catalyst ratio plays an important role in the Suzuki-Miyaura cross-coupling reaction. In order to investigate the effect of the quantity of catalyst, various catalyst ratios of 0.025, 0.05, 0.075, 0.10, 0.125, 0.15, 0.175 and 0.20 mol% of Pd were used in the model reaction (Table 6; Figure 11 e). Increase in catalyst ratio resulted in increased yield up to 0.15 mol% of Pd (Table 6, entries 1-6) and further increase in the catalyst ratio did not increase the yield (Table 6, entries 7 and 8). Hence, 0.15 mol% of Pd is the

best catalyst ratio required for the maximum yield (Table 6, entry 6).

### 3.9 | Suzuki-Miyaura Cross-Coupling Reactions of Aryl Halides

To explore the scope of the Suzuki-Miyaura crosscoupling reaction, various aryl halides were reacted with phenylboronic acid catalysed by SB-Pd@MNPs nanomagnetic catalyst using the aforementioned optimized conditions and the results are presented in Table 7. The obtained results reveal that variously substituted aryl bromides, aryl chlorides and aryl iodide are converted into the corresponding products in good to excellent yields. Aryl halides with both electronwithdrawing and electron-donating groups were subjected to the reaction. The results show that all aryl halides gave good to excellent yields, but the steric effect played an important role in conversion of aryl halide to product. Nevertheless, aryl chloride (Table 7, entries 16-18) reacted more slowly than aryl bromide (Table 7, entries 1-5, 7-11, 13 and 15) and aryl iodide (Table 7, entry 20) derivatives. Overall, these results confirmed that the SB-Pd@MNPs nanomagnetic catalyst is highly active towards Suzuki-Miyaura cross-coupling reactions. Also, the selectivity of the SB-Pd@MNPs nanomagnetic catalyst

![](_page_14_Figure_4.jpeg)

SCHEME 3 Proposed mechanism of Suzuki-Miyaura reaction

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was confirmed by the presence of a negligible amount of the homocoupled product obtained. For additional clarification on selectivity, Suzuki–Miyaura cross-coupling reactions were carried out without aryl halides under optimized conditions. The biphenyl homocoupled product obtained was in a trace amount, which indicated that the SB-Pd@MNPs nanomagnetic catalyst is highly selective.<sup>[57,58]</sup> A plausible mechanism for our newly investigated SB-Pd@MNPs nanomagnetic catalyst is illustrated in Scheme 3 which delivers the C-C coupling products via possible mechanistic intermediates (**I–III**).<sup>[13]</sup>

#### 3.10 | Catalyst Recyclability and Leaching in Suzuki–Miyaura Cross-Coupling Reactions

Catalyst recycling is important from industrial, economic and environmental points of view. Hence, the SB-Pd@MNPs nanomagnetic catalyst was studied in the We successfully recovered model reaction. the SB-Pd@MNPs nanomagnetic catalyst after cross-coupling reaction by applying an external magnetic field, washing with ethanol and water and drying. The recovered SB-Pd@MNPs nanomagnetic catalyst can be reused for up to five cycles without loss of catalytic activity (Table 8). After five recycles, a decrease in catalytic activity was observed (Figure 12; Table 8). The ATR-IR spectrum (Figure 2b), TEM image (Figure 5c) and FESEM image (Figure 6b) of five-times-recycled SB-Pd@MNPs nanomagnetic catalyst were obtained. No change in the morphology was observed through the TEM image after recycling up to five tomes which is further confirmed by the FESEM image. Furthermore, the ATR-IR spectrum shows that the SB-Pd@MNPs nanomagnetic catalyst is intact after recycling.

Leaching of palladium is a serious problem for supported palladium catalysts, and prevents catalyst separation and recycling. Hence, leaching study was done for magnetic separation of the SB-Pd@MNPs nanomagnetic

Entry	Base	Solvent	Temperature (°C)	Catalyst run	Yield (%) <sup>b</sup>
1	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	Fresh	94
2	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	1st recycle	94
3	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	2nd recycle	93
4	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	3rd recycle	92
5	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	4th recycle	92
6	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	EtOH-H <sub>2</sub> O (1:1)	RT	5th recycle	90

TABLE 8 Recyclability of the SB-Pd@MNPs nanomagnetic catalyst in model reaction<sup>a</sup>

<sup>a</sup>Reaction conditions: 4-bromobenzonitrile (1.0 mmol), phenylboronic acid (1.1 mmol), SB-Pd@MNPs nanomagnetic catalyst (0.15 mol% Pd), base (2.2 mmol) and solvent in air.

<sup>b</sup>Isolated yield after separation by column chromatography.

![](_page_15_Figure_1.jpeg)

**FIGURE 12** Recycling efficiency of SB-Pd@MNPs nanomagnetic catalyst in Suzuki–Miyaura cross-coupling reaction of 4-bromobenzonitrile and phenylboronic acid

catalyst after 30 min of reaction time, and the same reaction was additionally continued for more than 4 h and was observed through TLC. Further conversion was not observed and the isolated yield was around 65%. This proved that leaching of the SB-Pd@MNPsnanomagnetic catalyst did not occur perhaps because of the specific nature of the designed catalyst.

#### 3.11 | Comparison of Catalysts

Table 9 presents a comparison of results for the SB-Pd@MNPs nanomagnetic catalyst with those for other catalysts for the Suzuki–Miyaura cross-coupling reaction. Comparison of the results demonstrates a better catalytic activity of SB-Pd@MNPs nanomagnetic catalyst at room temperature in aqueous medium (EtOH–H<sub>2</sub>O (1:1)) for

Suzuki–Miyaura cross-coupling reactions.<sup>[59–70]</sup> Some of the main benefits of the SB-Pd@MNPs nanomagnetic catalyst are: (i) use of green solvents, (ii) short reaction times, (iii) mild reaction conditions, (iv) excellent selectivity, (v) ability to easily remove the catalyst from reaction mixture and (vi) reusability for subsequent reactions. In addition, the SB-Pd@MNPs nanomagnetic catalyst can be prepared using inexpensive chemicals under aerobic conditions, which do not require a sophisticated setup.

#### 3.12 | Activity of SB-Pd@MNPs Nanomagnetic Catalyst in Reduction of Nitroarenes

In continuation of our investigation of the catalytic activity and application of the newly synthesized SB-Pd@MNPs nanomagnetic catalyst, we next studied its catalytic effect in the reduction of nitroarenes. To optimize the reaction conditions, reduction of nitrobenzene to amine was used as a model reaction (Scheme 4). Conditions such as catalyst ratio, amount of reducing agent (NaBH<sub>4</sub>), solvent, temperature and time were investigated. As expected, target product could not be detected in the absence of the SB-Pd@MNPs nanomagnetic catalyst. The best results were achieved by carrying out the reaction with 3.0 equivalents of reducing agent, water as solvent (10 ml) and 0.05 mol% Pd of SB-Pd@MNPs

![](_page_15_Figure_9.jpeg)

**SCHEME 4** Catalytic activity of SB-Pd@MNPs nanomagnetic catalyst in reduction of nitrobenzene

TABLE 9 Comparison of results for SB-Pd@MNPs nanomagnetic catalyst with those for other catalysts in model reaction

Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)	Ref.
1	Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> -NH <sub>2</sub> /SA/Pd	Toluene	100	1	76	[59]
2	Pd/Fe <sub>3</sub> O <sub>4</sub> @charocoal	DMF-H <sub>2</sub> O (4:1)	100	4	99	[60]
3	Iron oxide-Pd complex	DMF	50	12	77	[61]
4	Palladacycle adduct catalyst	Dioxane	100	12	93	[62]
5	Pd/CoFe <sub>2</sub> O <sub>4</sub>	DMF	100	1	99	[63]
6	C/Co@PNIPAM	Toluene– $H_2O(2:1)$	85	16	99	[64]
7	Pd/phosphine catalyst (6-G <sub>0</sub> )	THF-H <sub>2</sub> O (2:5)	60	14	95	[65]
8	Co/C-ROMP gel Pd	THF-H <sub>2</sub> O (1:2)	65	12	92	[66]
9	MUA-Pd	DMF	90	1	99	[67]
10	Catalyst-C4	CH <sub>3</sub> CN	80	16	91	[68]
11	Pd-SB@MWCNTs	DMF-H <sub>2</sub> O (1:1)	60	3	97	[69]
12	Pd-Fe <sub>3</sub> O <sub>4</sub> NCS	DME-H <sub>2</sub> O (3:1)	Reflux	24	81	[70]
13	SB-Pd@MNPs	EtOH-H <sub>2</sub> O (1:1)	RT	4	94	Present work

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**TABLE 10** Optimization f conditions for reduction reaction of nitrobenzene with sodium borohydride in presence of SB-Pd@MNPs nanomagnetic catalyst<sup>a</sup>

Entry	Solvent	NaBH <sub>4</sub> (mol)	Pd (mol%)	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>
1	H <sub>2</sub> O	2	—	RT	4.0	—
2	H <sub>2</sub> O	2	0.1	RT	2.5	25
3	THF-H <sub>2</sub> O	2	0.1	50	1.0	_
4	THF-H <sub>2</sub> O	4	_	RT	24.0	_
5	THF-H <sub>2</sub> O	4	0.1	RT	0.16	75
6	THF-H <sub>2</sub> O	3	0.1	RT	0.16	86
7	THF-H <sub>2</sub> O	3	0.05	RT	0.33	72
8	H <sub>2</sub> O	3	0.1	RT	0.033	92
9	H <sub>2</sub> O	3	0.05	RT	0.033	92

<sup>a</sup>Reaction conditions: nitrobenzene (1.0 mmol) and solvent (10 ml).

<sup>b</sup>Isolated yield after separation by column chromatography; average of two runs.

	$R_1$ NO <sub>2</sub> SB	B-Pd@MNPs, NaBH <sub>4</sub> Water, RT	IH <sub>2</sub>	
Entry	Nitroarene	Product	Time (h)	Yield (%) <sup>b</sup>
1		NH <sub>2</sub>	0.03	92
2		H-O-NH2	0.03	68
3	$H \xrightarrow{NO_2} O$	H O NH2	0.03	67
4	Br-V-NO2	Br-NH2	2.5	Trace
5		NH <sub>2</sub> NH <sub>2</sub>	0.03	88
6	O <sub>2</sub> N-	H <sub>2</sub> N-NH <sub>2</sub>	0.03	86
7	NO <sub>2</sub>	NH <sub>2</sub>	18	62
8	Br NO <sub>2</sub>	Br NH <sub>2</sub>	7	Trace
9		HO NH <sub>2</sub>	0.03	31
10	O <sub>2</sub> N NO <sub>2</sub>	H <sub>2</sub> N NH <sub>2</sub>	0.03	92

 TABLE 11
 Nitroarene reduction catalysed by SB-Pd@MNPs nanomagnetic catalyst<sup>a</sup>

<sup>a</sup>Reaction conditions: nitroarene (1.0 mmol), NaBH<sub>4</sub> (3.0 mmol), SB-Pd@MNPs nanomagnetic catalyst (0.05 mol% Pd), and water (10 ml). <sup>b</sup>Isolated yield after separation by column chromatography; average of two runs.

![](_page_17_Figure_0.jpeg)

**SCHEME 5** Proposed mechanism for reduction of nitroarene using NaBH<sub>4</sub> catalysed by SB-Pd@MNPs nanomagentic catalyst

Entry	Solvent	Catalyst (mol%)	Time (h)	Temp. (°C)	Catalyst run	Yield (%) <sup>b</sup>
1	H <sub>2</sub> O	0.05	0.033	RT	Fresh	92
2	H <sub>2</sub> O	0.05	0.033	RT	1st recycle	92
3	H <sub>2</sub> O	0.05	0.033	RT	2nd recycle	92
4	H <sub>2</sub> O	0.05	0.033	RT	3rd recycle	92
5	H <sub>2</sub> O	0.05	0.033	RT	4th recycle	92
6	H <sub>2</sub> O	0.05	0.033	RT	5th recycle	92
7	H <sub>2</sub> O	0.05	0.033	RT	6th recycle	92
8	H <sub>2</sub> O	0.05	0.033	RT	7th recycle	91
9	H <sub>2</sub> O	0.05	0.033	RT	8th recycle	91
10	H <sub>2</sub> O	0.05	0.033	RT	9th recycle	91
11	H <sub>2</sub> O	0.05	0.033	RT	10th recycle	91

 TABLE 12
 Recyclability of SB-Pd@MNPs nanomagnetic catalyst in nitrobenzene reduction<sup>a</sup>

<sup>a</sup>Reaction conditions: nitrobenzene (1.0 mmol), NaBH<sub>4</sub> (3.0 mmol), SB-Pd@MNPs nanomagnetic catalyst (0.05 mol% Pd), and water.

<sup>b</sup>Isolated yield after separation by column chromatography; average of two runs.

nanomagnetic catalyst at room temperature in 2 min. The results are presented in Table 10.

catalyst through possible mechanistic intermediates (I-IV) is given in Scheme 5.<sup>[71]</sup>

### 3.13 | Reduction of Various Nitroarenes

Using the aforementioned optimized reaction conditions, next we examined the utility of the SB-Pd@MNPs nanomagnetic catalyst for reaction of nitroarenes containing both electron-withdrawing and electron-releasing groups. As evident from Table 11, our method is reasonably good and can be applied to several types of nitroarenes. In all cases, this procedure gives the desired products in good to excellent conversion rate and yield. Reduction of nitrobenzene to aniline shows 100% conversion in 2 min (Table 11, entry 1). Additionally, steric hindrance of the substituent influenced the product yield (Table 11, entries 2, 3, 7 and 9). These results confirm that the synthesized SB-Pd@MNPs nanomagnetic catalyst can act as an excellent catalyst in reduction of nitroarenes. A proposed mechanism for the reduction of nitroarene using NaBH<sub>4</sub> catalysed by SB-Pd@MNPs nanomagentic

![](_page_17_Figure_10.jpeg)

**FIGURE 13** Recycling efficiency of SB-Pd@MNPs nanomagnetic catalyst in nitroarene reduction reaction

TABLE 13 Comparison of results for SB-Pd@MNPs nanomagnetic catalyst with those of other catalysts in nitroarene reduction reaction

Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%) <sup>b</sup>	Ref.
1	Pd catalyst	THF-H <sub>2</sub> O	RT	3.0	85	[72]
2	NaBH <sub>4</sub> /Ni(OAc) <sub>2</sub> .4H <sub>2</sub> O	CH <sub>3</sub> CN-H <sub>2</sub> O	RT	0.33	92	[73]
3	PMHS/Ni(acac) <sub>2</sub>	Dioxane	100	3.0	84	[74]
4	Pd complex	МеОН	50	12.0	95	[75]
5	Pd/C, NH <sub>2</sub> NH <sub>2</sub> .H <sub>2</sub> O	МеОН	80	0.083	97	[76]
6	Pd/C	EtOAc	80	0.166	85	[77]
7	RuCl <sub>2</sub> (PPh <sub>3</sub> )	Dioxane	60	16.0	96	[78]
8	1,1-Dioctyl-4,4-BPDB	MeOH	RT	3.0	83	[29]
9	SB-Pd@MNPs	H <sub>2</sub> 0	RT	0.033	92	Present work

# 3.14 | Catalyst Recyclability in Nitroarene Reduction

One of the most important factors in catalysis is catalyst recovery and recycling. The newly synthesized SB-Pd@MNPs nanomagnetic catalyst was successfully recovered by applying an external magnetic field, washing with ethanol and distilled water and drying at 45 °C for 12 h. Further, the recovered catalyst was reused for reduction of nitrobenzene to aniline under the optimized conditions, and it was observed that there was no change in catalytic activity up to 10 recycles in the reduction of nitrobenzene with NaBH<sub>4</sub> (Table 12; Figure 13). Recycled SB-Pd@MNPs nanomagnetic catalyst was characterized using ATR-IR analysis, and the spectrum shows that the SB-Pd@MNPs nanomagnetic catalyst is intact after recycling (Figure 2c).

#### 3.15 | Comparison of Catalysts

In comparison with other catalysts used for nitroarene reduction, the as-synthesized SB-Pd@MNPs nanomagnetic catalyst is more efficient (Table 13). Reaction solvent, temperature, time and yield are the important factors in view of efficiency. As is evident from Table 13, the reported catalysts require various organic solvents, high temperature, longer reaction time and low yield for nitroarene reduction.<sup>[29,72-78]</sup>

#### 4 | CONCLUSIONS AND FUTURE SCOPE

A new reusable SB-Pd@MNPs nanomagnetic catalyst was successfully prepared and characterized using ATR-IR and UV-visible spectroscopies, TGA, BET analysis, TEM, FESEM, EDX, ICP-AES and XRD. We developed green procedures for Suzuki-Miyaura cross-coupling reactions and reduction of nitroarenes using this new SB-Pd@MNPs nanomagnetic catalyst. Notably, the SB-Pd@MNPs nanomagnetic catalyst shows good to excellent catalytic activity in both Suzuki-Miyaura cross-coupling reactions and reduction of nitroarenes in aqueous medium at room temperature. The main advantages of the SB-Pd@MNPs nanomagnetic catalyst are simplicity, selectivity, eco-friendliness and ease of recovery using an external magnetic field. The recovered catalyst can be reused for a minimum of five recycles without significant loss of catalytic activity in Suzuki-Miyaura cross-coupling and ten recycles in the case of nitroarene reduction. Thus, novel Schiff base-palladium complexes can be prepared and immobilized on magnetic nanoparticles following the above discussed protocol for the development of greener methodologies for various organic transformations such as Mizoroki-Heck reaction, Sonogashira-Hagihara coupling reaction and oxidation reactions in addition to Suzuki-Miyaura cross-coupling reactions and nitroarene reduction.

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#### ACKNOWLEDGEMENTS

The authors thank DST-Nanomission, India (SR/NM/NS-20/2014), DST-SERB, India (YSS/201S/000010) and Jain University, India for financial support.

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How to cite this article: Manjunatha K, Koley TS, Kandathil V, et al. Magnetic nanoparticletethered Schiff base–palladium(II): Highly active and reusable heterogeneous catalyst for Suzuki– Miyaura cross-coupling and reduction of nitroarenes in aqueous medium at room temperature. *Appl Organometal Chem.* 2018;e4266. https://doi.org/10.1002/aoc.4266

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