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**FULL PAPER**

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# Biogenic synthesis of palladium nanoparticles using *Boswellia sarrata* and their applications in cross-coupling reactions

**Satyanarayan M. Arde** | **Gajanan S. Rashinkar** | **Sanjay N. Jadhav** | **Audumbar D. Patil** | **Rajashri S. Salunkhe**

Department of Chemistry, Shivaji University, Kolhapur, India

**Correspondence**
Rajashri S. Salunkhe, Department of Chemistry, Shivaji University, Kolhapur 416004, MS, India.
Email: rss234@rediffmail.com

A facile and green route for biogenic synthesis of palladium nanoparticles (PdNPs) using aqueous extract of nontoxic and renewable *Boswellia sarrata* leaves is reported. The as-synthesized PdNPs were systematically characterized by using ultraviolet (UV)–visible spectroscopy, X-ray diffraction analysis, scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. The PdNPs were crystalline and cubic in nature with average particle size of ~6 nm and successfully employed as heterogeneous catalyst in the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions. The PdNPs could be recycled up to five times with modest change in the catalytic activity.

**KEYWORDS**

*Boswellia sarrata*, Mizoroki-Heck reaction, palladium nanoparticles, reusability, Suzuki–Miyaura reaction

## 1 | INTRODUCTION

Admirable research has been progressed in cross-coupling reactions, which made great revolution in the organic transformation by developing simple and efficient protocols. Particularly, the transition metals like rhodium, ruthenium, nickel, and palladium have been frequently used for the development of highly efficient and mild protocols in the construction of carbon–carbon and carbon–heteroatom bonds.[1–4] Conceivably, the most successful development in this regard are Stille, Suzuki–Miyaura, Mizoroki–Heck, Sonogashira, Mukaiyama reactions, and so on. Among these, Suzuki–Miyaura cross-coupling reaction of aryl halides with aryl boronic acids is the most powerful carbon–carbon bond forming methodology for constructing biaryls in the toolbox of organic chemists. In addition to this, Mizoroki–Heck reaction is also the most fundamental palladium catalyzed carbon–carbon bond forming reaction that is used for the stereoselective synthesis of alkenes. Generally, both Suzuki–Miyaura and Mizoroki–Heck reactions are frequently catalyzed by using palladium complexes such as [Pd $(OAc)_2$], [Pd $(PPh_3)Cl_2$], and Pd $(dppf)Cl_2$ homogenous catalytic systems.[5,6] Amid various palladium catalysts for cross-coupling reactions, homogenous catalysts have been widely investigated, and less expensive heterogeneous catalysts have received less attention. However, in the last few years, the importance of palladium-based heterogeneous catalytic systems has received significant attention because of their facile recovery and reusability. Precedently, carbon,[7] magnetic materials,[8] silica,[9] hydroxyapatite,[10] zeolites,[11] Pd/DNA,[12,13] metal organic frameworks (MOFs),[14] organic polymers,[15] clays,[16] and bio-supports[17,18] have been employed for as support for this purpose. In the recent years, palladium nanoparticles (PdNPs) have garnered tremendous attention in heterogeneous catalysis due to their excellent catalytic activity.[19–25] In this regard, the green synthesis of PdNPs has attracted the vigil eye of attraction of nanotechnologists and material

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scientists, due to the growing environmental pollution caused by the conventional chemical methods.[26–31] Among various green recipes, biogenic synthesis of PdNPs[32–34] has recently emerged as an active area of research due to simplicity, cost-effectiveness, higher potential of reduction, and low toxic effect on human health as well as on the environment. Unfortunately, majority of earlier methods of plant-based reported catalysts[35a–d] often suffer from limitations like high reaction temperatures, high catalyst loadings, limited substrate scopes, and/or used of undesirable organic solvents as reaction, solid support, greater reaction time, and so on. Moreover, the biogenic reduction occurs at physiological conditions of temperature and pressure. In addition, the raw materials are easily available, and therefore, the reaction can be easily scaled up. Also, the reported plant-based PdNPs mostly tested for a single catalytic system, while their multifunctional potentiality remains largely underexplored. Thus, the appropriate selection of plant extract, which can bestow multifunctional role, namely, bio-reduction of Pd salts, aid in multiple catalytic reactions, and afford biological activities, is highly desirable. In this context, we would like to exploit a bio-resource, namely, *Boswellia sarrata* L. aqueous leaves extract for the synthesis of PdNPs. It comes under the family Burseraceae and is an evergreen middle-sized tree. It is mostly found in tropical part of Asia and Africa. In India, it is found in dry hilly woodland of Rajasthan, Madhya Pradesh, Bihar, Assam, Orissa, Telengana, and western Sahyadri hills of Maharashtra. The leaves, bark, and resins of *B. sarrata* L. contain strong aroma. The gum resin of this plant has been widely used in the treatment of cancer, skin disease, and urinary disorder, as analgesic, anti-inflammatory, and antipyretic properties.[36]

Considering aforementioned discussion, in present work, we describe a facile and environmentally friendly technique for the preparation of PdNPs using an aqueous extract of *B. sarrata* L. leaves as a bioreductant. Moreover, the phytomolecules present in *B. sarrata* L. extract are not only accountable for the reduction and progression of nanoparticles, but they were also found to perform as stabilizing agents. Furthermore, the green synthesized metallic PdNPs were used as a catalyst for Suzuki–Miyaura cross-coupling reaction in aqueous medium and Mizoroki–Heck reactions in DMF at moderate reaction conditions.

## 2 | EXPERIMENTAL

### 2.1 | General information

All reagents were purchased from Sigma-Aldrich and used without further purification. Fresh, green, and mature leaves of *Boswellia serrata* were collected from "Western Hill Region" of Maharashtra (India), and the taxonomic identification was done in Department of Botany, Shivaji University, Kolhapur (MS, India). The voucher specimen (SMA 001) was numbered and kept in research laboratory for further reference. The aqueous extract of *B. sarrata* leaves was freshly prepared using double distilled water. The ultraviolet (UV)–visible spectra were recorded over 200- to 800-nm range with UV-3600 PC UV–VIS NIR Spectrophotometer (Shimadzu). X-ray diffraction (XRD) patterns were recorded on Bruker AXS model D-8, (10–70° range, scan rate = $1^\circ\ \mathrm{min}^{-1}$) equipped with a monochromator and Ni-filtered Cu Kα radiation. Scanning electron microscopy (SEM) was performed using a HITACHI S-4800 instrument to study the morphology of PdNPs. The transmission electron microscopy (TEM) analysis was performed on a Jeol model JEM 1200 electron microscope operated at an accelerating voltage of 120 kV. The Energy-dispersive X-ray spectroscopy (EDS) was carried out on a DX-700HS spectrometer for elemental analysis. X-ray photoelectron spectroscopy (XPS) data of catalyst were collected on a VG scientific ESCA-3000 spectrometer using a non-monochromatized Mg K radiation (1,253.6 eV) at a pressure of about $1 \times 10^{-9}$ Torr (pass energy of 50 eV, electron takeoff angle 55°). Melting points were determined in an open capillary and found to be uncorrected. $^1$H NMR spectra were recorded at 300-MHz Bruker Avon spectrometer using $CDCl_3$ as solvent and TMS as an internal reference standard. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded on Thermo Scientific Neconet 6700 FTIR, in the range 4,000–400 $\mathrm{cm}^{-1}$. Mass spectra were performed on an Ultima Global spectrometer with an ESI source.

### 2.2 | Preparation of aqueous extract of *B. sarrata* leaves

Air-dried leaves of *B. serrata* were taken in mortar and crushed to fine powder. A mixture of fine powder of *B. serrata* leaves (5 g) and distilled water (200 mL) was heated at 90°C for 30 min. The mixture was cooled and filtered through Whatmann filter paper no. 41. The filtrate was diluted to 2 L by adding distilled water and used for the preparation of PdNPs.

### 2.3 | General procedure for the synthesis of PdNPs

A mixture of an aqueous solution of Pd $(OAc)_2$ (1 mM, 25 mL) and diluted aqueous extract of *B. sarrata* leaves (25 mL) was refluxed for 2 h in an oil bath. The resulting solution was centrifuged at 10,000 rpm for 20 min. Thus, obtained brown solid was washed with distilled water (3 × 10 mL) and dried under vacuum to get the desired PdNPs dried crystal powder.

## 2.4 | General procedure for the Suzuki–Miyaura cross-coupling reaction

Aryl halide (1.0 mmol), aryl boronic acid (1.1 mmol), $K_2CO_3$ (2 mmol), PdNPs (0.3 mol %), and 5 mL of water were stirred in Schlenk flask, equipped with a magnetic stir bar and a condenser at 60°C. Upon complete consumption of starting materials as determined by thin-layer chromatography (TLC) analysis, water (20 mL) was added, and the catalyst was separated out by centrifugation. The filtrate was extracted with diethyl ether (3 × 10 mL). The combined organic layers were collected, dried over anhydrous $Na_2SO_4$, concentrated in vacuum to afford desired product, and purified by column chromatography.

**TABLE 1** Effect of temperature on the synthesis of PdNPs

| Sr. no. | Solvent | Temperature | Reaction time | Reaction status |
|---|---|---|---|---|
| 1. | Water | 32°C (RT) | 24 h | No change in pale yellow color |
| 2. | Water | 50°C | 24 h | No change in pale yellow color |
| 3. | Water | 70°C | 3.5 h | Dark brown color |
| 4. | Water | 80°C | 2.5 h | Dark brown color |
| 5. | Water | Reflux | 2.0 h | Dark brown color |

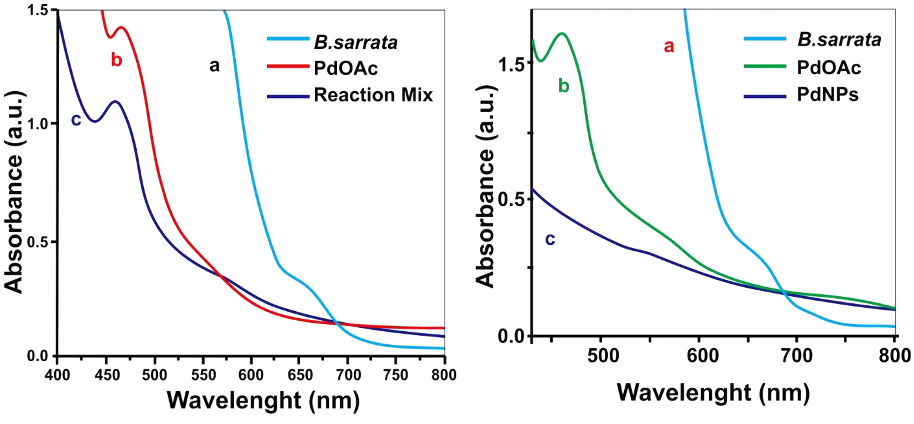
## 2.5 | General procedure for Mizoroki–Heck coupling reaction

Aryl halide (1.0 mmol), olefin compound (1.1 mmol), $K_2CO_3$ (2 mmol), PdNPs catalyst (0.3 mol %), and DMF (5 mL) were taken in Schlenk flask, which was equipped with a magnetic stir bar, septum, and a condenser. The flask was immersed in a heating bath and reaction mixture stirred at 110°C. Upon complete consumption of starting materials as determined by TLC analysis (petroleum ether:ethyl acetate, 8:2), catalyst was separated out by centrifugation, and the liquid mixture was extracted with diethyl ether (3 × 10 mL). The combined organic layer was collected, dried over anhydrous $Na_2SO_4$, and concentrated. The resulting compound was purified by column chromatography.

# 3 | RESULTS AND DISCUSSION

Initially, aqueous solution of Pd $(OAc)_2$ (1 mM) was treated with aqueous extract of *B. sarrata* leaves at room temperature. There was no formation of PdNPs even after prolonged reaction time of 24 h. Therefore, a series of experiments were undertaken in which the mixture was stirred at elevated temperatures. The formation of PdNPs was observed at and above 70°C with the best results obtained at reflux conditions (Table 1). The formation of PdNPs was easily identified by color change from pale yellow to dark brown and finally confirmed by UV–visible spectroscopy. The characteristic UV–visible absorption peak of Pd $(OAc)_2$ at 460 nm disappeared after color change clearly indicated the formation of PdNPs (Figure 1).

After the successful formation of PdNPs in aqueous extract of *B. sarrata* leaves, we investigated impact of various solvent systems such as acetone, water–acetone, ethyl alcohol, and water–ethyl alcohol, and the results are



(a) (b)

**FIGURE 1** UV–visible spectra of PdNPs (a) at room temperature (b) at reflux condition

**TABLE 2** Effect of solvent on the complete reduction of palladium as PdNPs at room temperature

| Sr. No. | Solvent | Reaction time | Color of the reaction mixture after addition of plant extract |
|---|---|---|---|
| 1. | Water | 24 h | No change in pale yellow color |
| 2. | Water: acetone (95:5) | 10 min | Dark brown color |
| 3. | Water: acetone (90:10) | 10 min | Dark brown color |
| 4. | Water: acetone (85:15) | 10 min | Dark brown color |
| 5. | Water: acetone (80:20) | 10 min | Dark brown color |
| 6. | Acetone | 08 min | Dark brown color |
| 7. | Water:ethyl alcohol (95:5) | 10 h | Dark brown color |
| 8. | Water:ethyl alcohol (90:10) | 10 h | Dark brown color |
| 9. | Ethyl alcohol | 09 h | Dark brown color |

summarized in Table 2. The formation of PdNPs was observed in all the investigated solvent systems with the best results in acetone as a solvent within short reaction time. We decided to employ water as a solvent for the synthesis of PdNPs as it is a green and ecofriendly solvent.

In all above experiments, plant extract was extracted in distilled water and kept constant for all reaction conditions. Further detailed characterization of biogenically synthesized PdNPs, water refluxed product was taken. After the completion of reaction, brown solution was centrifuged at 10,000 rpm in cooling centrifuge machine and washed thrice by distilled water and dried in vacuum.

FTIR (Figure 2) measurements were carried out to identify the possible biomolecules responsible for the reduction and stabilization of PdNPs synthesized by aqueous extract of *B. sarrata* leaves. The peaks at 1,736.53, 1,589.88, 1,365.96, 1,216.97, and 1,043.30 cm$^{-1}$ show the presence of higher esters of fatty acids, polyol, polyphenol, flavonoids, and hydroxyflavones like groups. The peak at 1,589.88 cm$^{-1}$ was assigned to C=C stretching vibration in aliphatic compounds, which may be characterized by the presence of high content of terpenoids and flavonoids. The peak 1,365.96 cm$^{-1}$ was due to deformation of $CH_2$ and $CH_3$ groups in aliphatic compounds.[37] The peaks at 1,216.97 cm$^{-1}$ arises most probably from the C–O groups of polyols such as hydroxyflavones and catechins.[37] The peak near

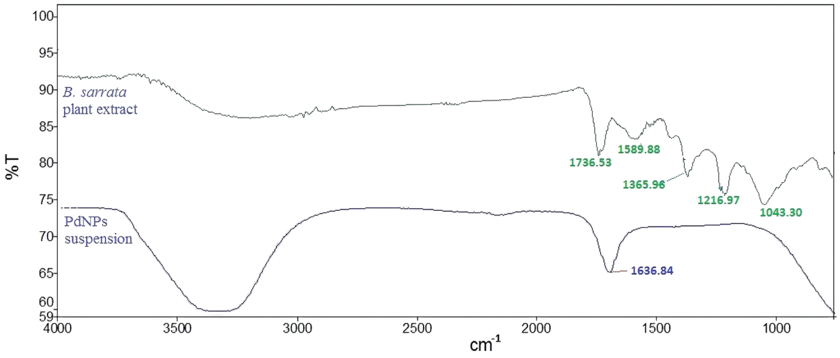
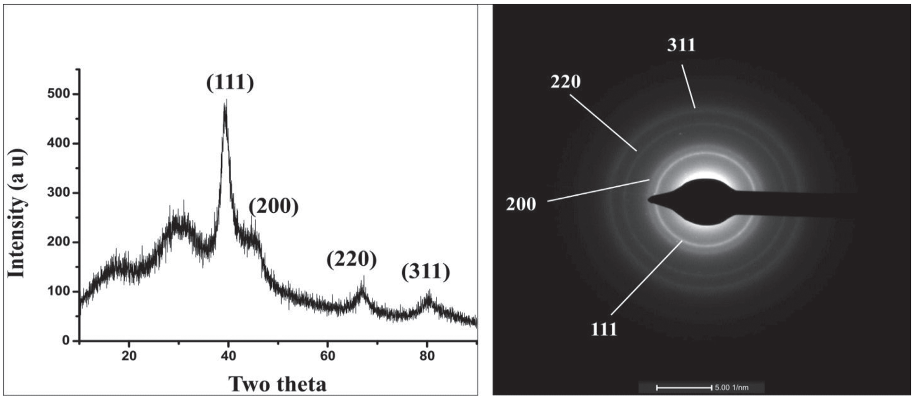


**FIGURE 2** FTIR analysis of aqueous extract of *B. sarrata* leaves and PdNPs suspension



**(a)** XRD pattern of PdNPs **(b)** SAED pattern of PdNPs

**FIGURE 3** (a) XRD pattern of PdNPs; (3b) SAED pattern of PdNPs

1,736.53 $\mathrm{cm}^{-1}$ is assigned for higher esters of fatty acids. The peaks present in '*B. sarrata* plant extract graph' at 1,736.53, 1,589.88, 1,365.96, 1,216.97 and 1,043.30 $\mathrm{cm}^{-1}$ are totally disappeared in 'PdNPs suspension graph' indicated that the polyols, hydroxyflavones, and terpenoid molecules are mainly responsible for the reduction of $\mathrm{Pd}^{++}$ ions.

Biogenically synthesized PdNPs were characterized by XRD analysis (Figure 3a). All the high-intensity reflections were observed at $2\theta = 39.524°$, $44.924°$, $66.812°$, and $80.782°$ corresponding to 111, 200, 220, and 311 planes. These are in good agreement with reported values (JCPDS file no. 00-001-1310). The analysis revealed that PdNPs are in the form of cubic nanocrystals. The full width at half maximum (FWHM) values measured for 111 plane of reflection were used with the Debye–Scherrer's equation $d = 0.9\ \lambda/\beta\cos\theta$. The average size of PdNPs was calculated as 7 nm, which is in accordance with the TEM image size (Figure 4c). Moreover, XRD pattern is in good agreement with the selected area electron diffraction pattern (SAED) (Figure 3b).

SEM was used for investigating surface morphology of biogenically synthesized PdNPs. The SEM images (Figure 4a) of PdNPs displayed less aggregated particles with spherical shape. The morphology and particle size of PdNPs were further confirmed by TEM and are displayed in Figure 4b,c. The analysis revealed size distribution with average size diameters of ~6 nm (Figure 4d).

The quantification of elemental palladium in PdNPs was confirmed by EDS. The PdNPs display an optical absorption peak at 2.4 KeV, which is typical absorption of metallic palladium nanocrystallites (Figure 5). The

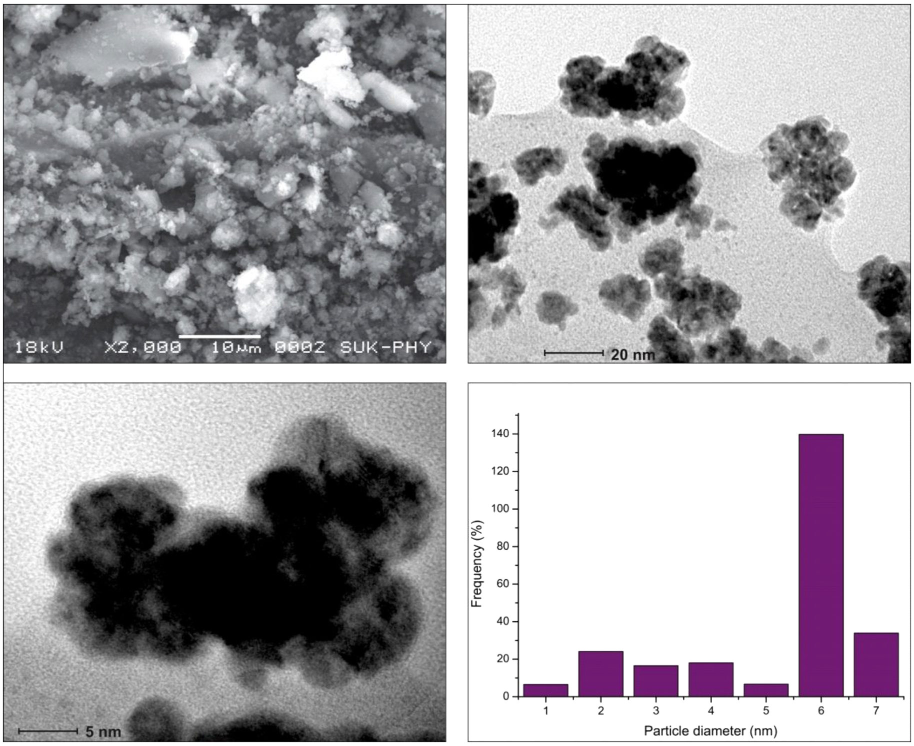


**FIGURE 4** (a) SEM image, (b,c) TEM image, (d) size distribution graph of biogenically synthesized PdNPs

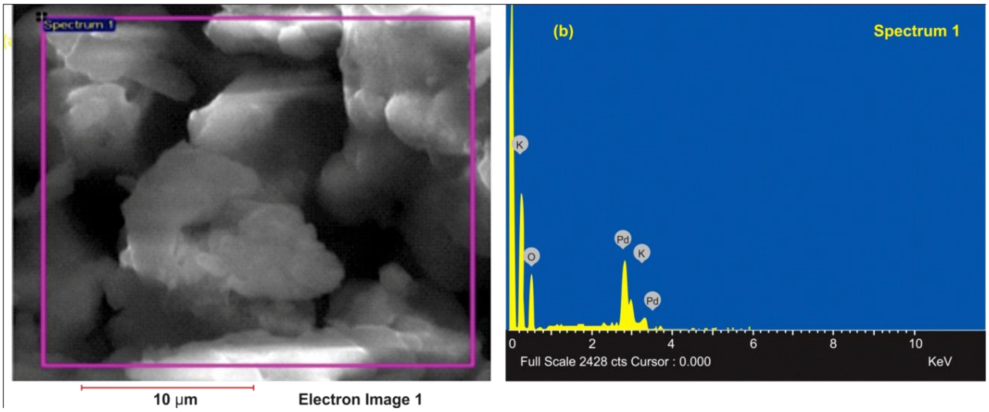
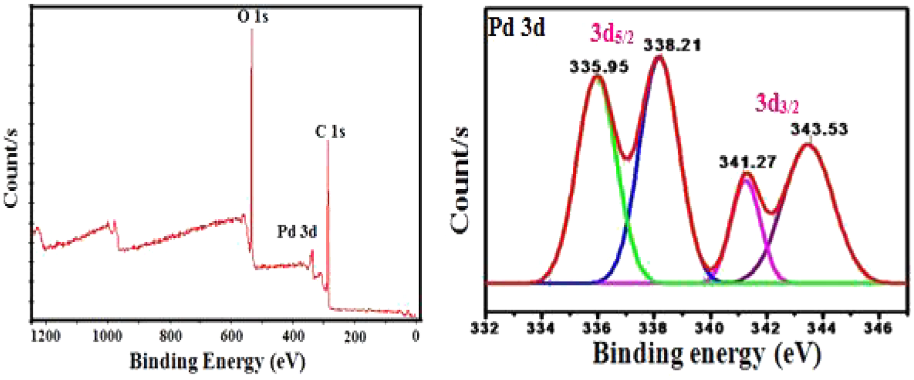


**FIGURE 5** EDS spectrum of biogenically synthesized PdNPs



(a) (b)

**FIGURE 6** (a) Full survey XPS analysis; (b) highlighted XPS spectrum of biogenically synthesized PdNPs

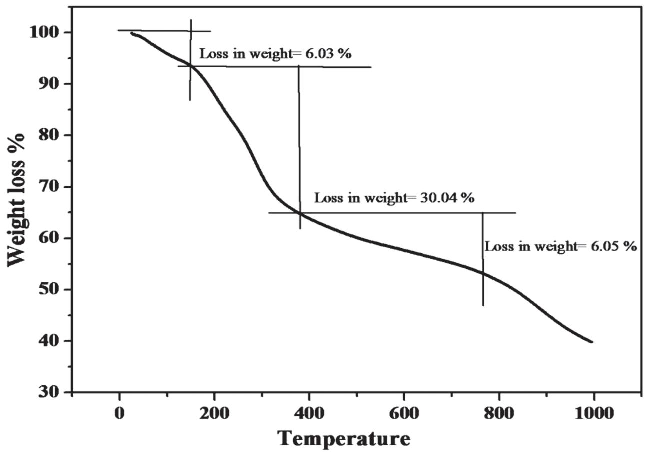
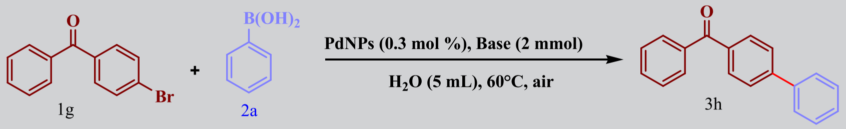


**FIGURE 7** TGA analysis of biogenically synthesized PdNPs

total weight percentage of palladium in PdNPs is found to be 39.75%.

XPS analysis was conducted to examine the comprehensive picture in terms of quantity and chemical state of biogenically synthesized PdNPs. Full survey XPS analysis (Figure 6a) displayed peaks at 286.08, 337.08, and 535.08 eV corresponding to C 1s, Pd 3d, and O 1s respectively. Scanning of Pd 3d (Figure 6a) shows (core spectrum) double peaks with binding energies at 335.95 and 341.27 eV corresponding to two chemical states of the Pd as Pd $3d_{5/2}$ and Pd $3d_{3/2}$ indicating $Pd^0$ whereas 338.21 eV and 343.53 eV values indicating oxidative $Pd^{2+}$ ions. Quantitative comparison in the fitting peak area of $Pd^0$ and $Pd^{2+}$ indicates that the oxidation degree of Pd is reduced with decreasing Pd percentage as shown in the Figure 6b.

**TABLE 3** Screening of bases for Suzuki–Miyaura coupling reaction[a]



| Entry | Base (mmol) | Time (min) | Yield (%)[b] |
|---|---|---|---|
| 1 | $Et_3N$ | 85 | 62 |
| 2 | NaOAc | 65 | 82 |
| 3 | n-$Pr_3N$ | 75 | 61 |
| 4 | t-BuOK | 60 | 78 |
| 5 | Pyridine | 80 | 66 |
| 6 | DABCO | 65 | 72 |
| 7 | $K_3PO_4$ | 55 | 92 |
| 8 | $Na_2CO_3$ | 40 | 90 |
| 9 | $K_2CO_3$ | 35 | 95 |

[a] Reaction conditions: 4-bromobenzopheneone (1.0 mmol), phenyl boronic acid (1.1 mmol), in the presence of catalytic amount of PdNPs, base (2.0 mmol), water (5 mL), at 60°C under air.

[b] Isolated yields.

**TABLE 4** Optimization of catalyst for Suzuki–Miyaura coupling reaction[a]

| Entry | Catalyst (mol %) | Temp. (°C) | Time (min) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | 0.1 | 60 | 60 | 60 |
| 2 | 0.2 | 60 | 45 | 82 |
| 3 | 0.3 | 60 | 35 | 95 |
| 4 | 0.4 | 60 | 35 | 95 |
| 5 | 0.5 | 60 | 35 | 95 |
| 6 | 0.3 | r.t. | 70 | 40 |
| 7 | 0.3 | 50 | 45 | 82 |
| 8 | 0.3 | 80 | 35 | 94 |

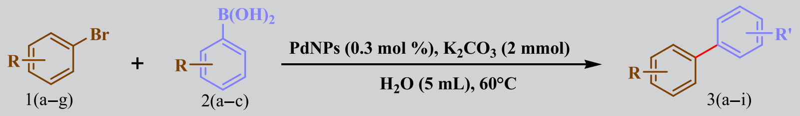
[a] Reaction conditions: 4-bromobenzopheneone (1.0 mmol), phenyl boronic acid (1.1 mmol), PdNPs (mol %), $K_2CO_3$ (2.0 mmol), water (5 mL), at 60°C under air.
[b] Isolated yields.

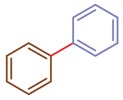
**TABLE 5a** TON and TOF values for the Suzuki–Miyaura reaction

| Sr. no. | Products | TON | TOF ($min^{-1}$) |
|---|---|---|---|
| 1 | **3a** | 317 | 7.92 |
| 2 | **3b** | 267 | 4.45 |
| 3 | **3c** | 313 | 6.95 |
| 4 | **3d** | 300 | 4.00 |
| 5 | **3e** | 307 | 5.11 |
| 6 | **3f** | 317 | 9.05 |
| 7 | **3g** | 313 | 4.81 |
| 8 | **3h** | 317 | 9.05 |
| 9 | **3i** | 313 | 7.82 |

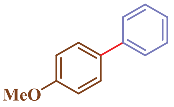
Abbreviations: TOF, turnover frequency; TON, turnover number.

**TABLE 5** The Suzuki–Miyaura reaction of various aryl bromides and phenyl boronic acids[a] with an isolated yield[b]

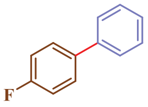




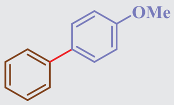
**3a (95 % yield, 40 min)**



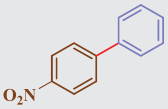
**3b (80 % yield, 60 min)**



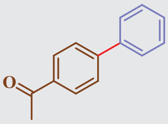
**3c (94 % yield, 45 min)**



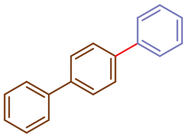
**3d (90 % yield, 75 min)**



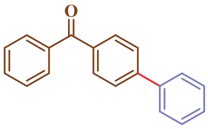
**3e (92 % yield, 60 min)**



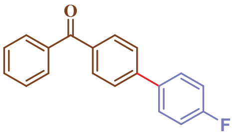
**3f (95 % yield, 35 min)**



**3g (94 % yield, 65 min)**



**3h (95 % yield, 35 min)**



**3i (94 % yield, 40 min)**

[a] Reaction conditions: arylbromides (1 mmol), arylboronic acids (1.1 mmol), PdNPs (0.3 mol %), $K_2CO_3$ (2 mmol), water (5.0 mL), at 60°C in air.
[b] Isolated yields.

The thermal profile of biogenically synthesized PdNPs was investigated by using thermal gravimetric analysis (TGA) (Figure 7). The thermogram displayed initial weight loss of 6.03% up to 160°C due to evaporation of water or moisture. The combined weight loss of 30.04% in the range 160–400°C and 6.05% in the range 400–780°C is attributed to the degradation of volatile organic materials loosely bound on the surface of the PdNPs.

After the successful formation and characterization of biogenically synthesized PdNPs, we explored their catalytic activity in Suzuki–Miyaura and Mizoroki–Heck reactions. To begin with, we investigated the catalytic activity of PdNPs in Suzuki–Miyaura cross-coupling reaction. The cross-coupling between 4-bromo benzophenone (1 mmol) and phenyl boronic acid (1.1 mmol) in the presence of PdNPs in water was chosen as a model reaction for optimization of reaction conditions. Initially, the influence of nature of bases was investigated by performing model reaction with various organic and inorganic bases in water at 60°C. It was observed that inorganic bases are more effective (Table 3, entries 7–9) as compared with organic bases (Table 3, entries 1–6). The results revealed $K_2CO_3$ as a promising base for the effective cross-coupling (Table 3, entry 9).

Next, we investigated the effect of amount of PdNPs on the model reaction, and results are summarized in Table 4. The model reaction afforded 60% of corresponding product with loading of 0.1 mol % of PdNPs (Table 4, entry 1). Increasing the quantity to 0.3 mol % increased the yield significantly to 95% (Table 4, entries 2 and 3). However, further increase in the catalyst quantity beyond to 0.3 mol % did not have quantitative effect on the yield of the product (Table 4, entries 4 and 5). The efficiency of reaction was affected

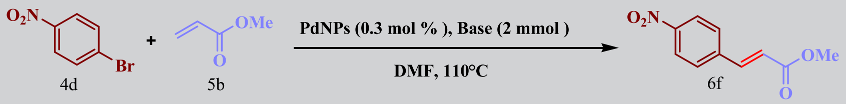
**TABLE 7** Effect of solvent for Mizoroki–Heck reaction[a]

| Entry | Solvent | Temp. (°C) | Time (min) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | $CH_3CN$ | 110 | 70 | 30 |
| 2 | DMF | 110 | 35 | 92 |
| 3 | DCM | 110 | 65 | 35 |
| 4 | THF | 110 | 15 | 78 |
| 5 | Toluene | 110 | 70 | 10 |
| 6 | 95% EtOH | 30 | 70 | Nil |
| 7 | 95% EtOH | 50 | 70 | 10 |
| 8 | 95% EtOH | 70 | 70 | 30 |
| 9 | 95% EtOH | 90 | 50 | 80 |
| 10 | 95% EtOH | 110 | 40 | 90 |
| 11 | Water | 110 | 70 | Nil |

[a] Reaction conditions: 4-nitro bromobenzene (1.0 mmol), methyl acrylate (1.1 mmol), PdNPs (0.3 mol %), $K_2CO_3$ (2.0 mmol), DMF (5 mL), at 110°C under air.

[b] Isolated yields.

**TABLE 6** Screening of various bases for Mizoroki–Heck reaction[a]



| Entry | Base (mmol) | Time (min) | Yield (%)[b] |
|---|---|---|---|
| 1 | $K_3PO_4$ | 60 | 80 |
| 2 | NaOAc | 45 | 82 |
| 3 | $K_2CO_3$ | 35 | 92 |
| 4 | $Et_3N$ | 30 | 78 |
| 5 | n-$Pr_3N$ | 55 | 81 |
| 6 | t-BuOK | 70 | 79 |
| 7 | Pyridine | 80 | 78 |
| 8 | DABCO | 55 | 77 |
| 9 | $Na_2CO_3$ | 40 | 90 |

[a] Reaction conditions: 4-nitro bromobenzene (1.0 mmol), methyl acrylate (1.1 mmol), PdNPs (0.3 mol %), base (2.0 mmol), DMF (5 mL), at 110°C under air.

[b] Isolated yields.

**TABLE 8** Screening of amount of catalyst for Mizoroki–Heck reaction[a]

| Entry | Catalyst (mol %) | Time (min) | Yield (%)[b] |
|---|---|---|---|
| 1 | 0.1 | 45 | 60 |
| 2 | 0.2 | 40 | 82 |
| 3 | 0.3 | 35 | 92 |
| 4 | 0.4 | 35 | 92 |
| 5 | 0.5 | 35 | 92 |

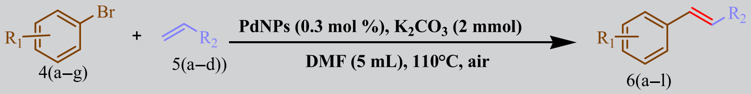
[a] Reaction conditions: 4-nitro bromobenzene (1.0 mmol), methyl acrylate (1.1 mmol), PdNPs (mol %), $K_2CO_3$ (2.0 mmol), DMF (5 mL), at 110°C under air.
[b] Isolated yields.

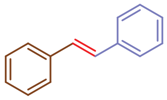
by temperature, and maximum product yield was noted at 60°C (Table 4, entries 6–8).

After optimization of reaction conditions, the scope and generality of the protocol were investigated by reacting various aryl bromides with aryl boronic acids, and the results are summarized in Table 5. In all the cases, the reactions proceeded smoothly affording cross-coupling products in good to excellent yields, which lighten the generality of the protocol.

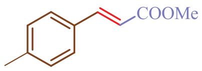
Inspired by success of biogenically synthesized PdNPs in Suzuki–Miyaura reaction, we decided to extend the protocol for Mizoroki–Heck reaction. Accordingly, reaction between 4-nitro bromobenzene and methyl acrylate

**TABLE 9** The Mizoroki–Heck reaction of various aryl halides and olefinic compounds over PdNPs catalyst[a] with an isolated yield[b]

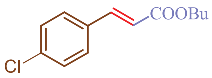




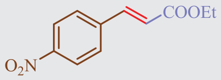
**6a**, 90 % Yield, 35 min



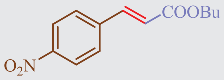
**6b**, 85 % Yield, 65 min



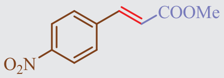
**6c**, 90 % Yield, 50 min



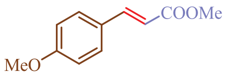
**6d**, 92 % Yield, 30 min



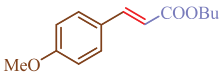
**6e**, 89 % Yield, 40 min



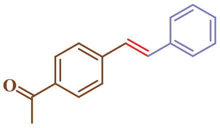
**6f**, 92 % Yield, 35 min



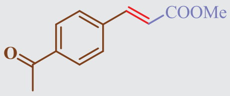
**6g**, 85 % Yield, 60 min



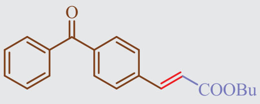
**6h**, 86 % yield, 70 min



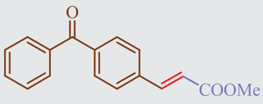
**6i**, 90 % Yield, 50 min



**6j**, 81 % Yield, 55 min



**6k**, 88 % Yield, 80 min



**6l**, 90 % Yield, 50 min

[a] Reaction conditions: 4-nitro bromobenzene (1.0 mmol), methyl acrylate (1.1 mmol), PdNPs (mol %), $K_2CO_3$ (2.0 mmol), DMF (5 mL), at 110°C under air.
[b] Isolated yields.

using PdNPs in DMF at 110°C was chosen as a model reaction for optimization of reaction conditions. In order to evaluate the effects of base, various bases were screened for model reaction (Table 6). The results revealed $K_2CO_3$ as the best base for the model reaction as the corresponding product was obtained in quantitative yield within short reaction time (Table 6, entry 3).

In order to evaluate the effects of solvent, various protic and aprotic solvents were screened for model reaction (Table 7). The results revealed DMF as the best solvent for the model reaction (Table 7, entry 2) as corresponding product was obtained in quantitative yield within short reaction time. To study the effect of temperature, the model reaction was carried out at different heating conditions. As expected, when the reaction temperature was increased from 25°C to 110°C, the reaction time was decreased significantly affording excellent yield of corresponding product (Table 7, entries 6–10), indicating that temperature is a crucial factor.

**TABLE 10** TON and TOF values for the Mizoroki–Heck reaction

| Sr. no. | Products | TON | TOF ($min^{-1}$) |
|---|---|---|---|
| 1 | **6a** | 300 | 8.57 |
| 2 | **6b** | 283 | 4.35 |
| 3 | **6c** | 300 | 6.00 |
| 4 | **6d** | 307 | 10.23 |
| 5 | **6e** | 297 | 7.22 |
| 6 | **6f** | 307 | 8.77 |
| 7 | **6g** | 283 | 4.71 |
| 8 | **6h** | 286 | 4.08 |
| 9 | **6i** | 300 | 6.00 |
| 10 | **6j** | 270 | 4.90 |
| 11 | **6k** | 293 | 3.66 |
| 12 | **6l** | 300 | 6.00 |

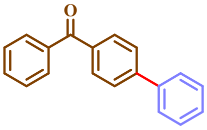
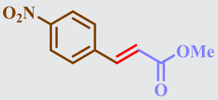
Abbreviations: TOF, turnover frequency; TON, turnover number.

Further, the effect of amount of PdNPs was investigated (Table 8). It is observed that with increasing the amount of PdNPs from 0.1 to 0.3 mol% dramatically enhanced the yield of corresponding product (Table 8, entries 1–3). However, further increase from 0.3 to 0.5 mol % did not significantly improved the yield. Thus, among the different quantity of PdNPs catalyst, 0.3 mol % proved to be the best affording desired product in 30 min with 92% yield in DMF at 110°C (Table 8, entry 3).

After optimization of reaction conditions, the scope and generality of the protocol were investigated by reacting variety of substituted and nonsubstituted aryl bromides with olefins under the optimized reaction conditions. In all the cases, Mizoroki–Heck reactions proceeded effectively furnishing desired products in excellent yields within 30–80 min (Tables 9 and 10).

For practical applications of heterogeneous systems, the lifetime of the catalyst and its level of reusability are important features. The recyclability of PdNPs was investigated with Suzuki–Miyaura reaction of 4-bromobenzophenone and phenyl boronic acid and Mizoroki–Heck reaction of 4-nitro bromobenzene with methyl acrylate. After first cycle, PdNPs were recovered by centrifugation and extensively washed with water, dichloromethane, and acetone. The PdNPs were dried under vacuum before performing the reusability test, and the results are summarized in Table 11 as well as shown in graph. We were delighted to note that PdNPs could be effectively reused for five consecutive runs without appreciable decrease in the yield of corresponding products. The graphical representation of recyclability of PdNPs

**TABLE 11** Recyclability of catalyst in Suzuki–Miyaura and Mizorokii–Heck reactions

| Entry | | Cycle | Time (min) | Yield (%) |
|---|---|---|---|---|
| 1 |  | 1 | 35 | 95 |
| | | 2 | 40 | 92 |
| | | 3 | 50 | 90 |
| | | 4 | 65 | 86 |
| | | 5 | 80 | 83 |
| 2 |  | 1 | 35 | 92 |
| | | 2 | 40 | 88 |
| | | 3 | 60 | 85 |
| | | 4 | 90 | 81 |
| | | 5 | 100 | 78 |

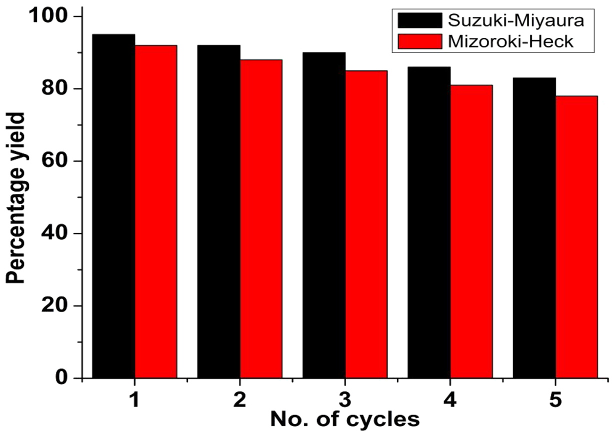


**FIGURE 8** The graphical representation of recyclability of PdNPs catalyst

catalyst with respect to Suzuki–Miyaura and Mizoroki–Heck reactions has given below (Figure 8).

The leaching study revealed that, larger size of cubic nanocrystals whose size more than 20 nm are more stable and shows lower leaching property. Whereas, smaller cubic nanocrystals whose size less than 20 nm shows greater catalytic activity with greater leaching property.[38] To assess the PdNPs leaching from catalyst during the reaction, we performed the hot filtration test for Suzuki–Miyaura reaction of 4-bromo benzophenone and phenyl boronic acid. The reaction was stopped after 20 min and then the hot filtrate was transferred to another flask containing base and water at 60°C. Upon further heating of the catalyst free solution for 3.5 h, no considerable progress was observed. Moreover, using AAS, the same reaction solution at the midpoint of completion indicated that no significant quantities of PdNPs were lost to the reaction liquors during the process. Also, the PdNPs catalyst was used for five runs and showed modest change in catalytic activity with increased time period with each run. This is due to the smaller size of PdNPs (∼6 nm).

## 4 | CONCLUSION

In conclusion, we have developed rapid, green, eco-friendly, and simple strategy for the synthesis of PdNPs by using aqueous extract of *B. sarrata* leaves as a reducingv and stabilizing agent without adding external reducing agent or surfactant template. The average particle size of PdNPs was characterized by TEM analysis and found to be ∼6 nm. The crystalline nature of PdNPs was confirmed by XRD and SAED analysis. XPS results confirmed the formation of metallic PdNPs. The biogenically synthesized PdNPs were used as efficient heterogeneous catalyst in Suzuki–Miyaura and Mizoroki–Heck reactions. The PdNPs could be recycled up to five cycles with modest change in catalytic activity. The developed protocol provides an unprecedented reactivity pattern, economically attractive and environmentally benign alternative route for the production of various biaryl and alkene derivatives.

## Data availability statement

Data were available on request from the authors.

## AUTHOR CONTRIBUTIONS

**Satyanarayan Arde:** Conceptualization; data curation; formal analysis; methodology; resources. **Gajanan Rashinkar:** Supervision. **Sanjay Jadhav:** Data curation; formal analysis. **Audumbar Patil:** Formal analysis. **Rajashri Salunkhe:** Conceptualization; data curation; methodology; supervision.

## ORCID

*Satyanarayan M. Arde* https://orcid.org/0000-0002-9732-8269

*Gajanan S. Rashinkar* https://orcid.org/0000-0002-7200-5260

*Sanjay N. Jadhav* https://orcid.org/0000-0002-3792-5889

*Audumbar D. Patil* https://orcid.org/0000-0002-8299-9326

*Rajashri S. Salunkhe* https://orcid.org/0000-0001-9352-1769

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## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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