




Short Communication

# Palladium nanoparticle biosynthesis via Yerba Mate (*Ilex paraguariensis*) extract: an efficient eco-friendly catalyst for Suzuki–Miyaura reactions

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## Abstract

This manuscript relates, for the first time, palladium nanoparticle production by bio-reduction using an *Ilex paraguariensis* aqueous extract. The solid obtained, PdISM, was used as a catalyst in Suzuki–Miyaura cross-coupling, composing a new eco-friendly, ligand-free, and low cost catalytic system. Excellent yields were obtained in the coupling of aryl iodides and bromides with phenylboronic acid. The same catalyst load was able to be recycled 3x.

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**Statement of Novelty** The merit of the manuscript is based on the use of a plant (*Ilex paraguariensis* - yerba mate), which is produced on a large scale in South America for the preparation of teas, in the biogenic synthesis of palladium nanoparticle. The search for more sustainable routes in the production of metallic nanoparticle has grown exponentially in the last ten years and, for the plant in question, the literature only shows one study for the synthesis of silver nanoparticle. On the other hand, palladium nanoparticle have a wide application as catalysts in the reactions of organic synthesis and, to date, there is no study using yerba mate as a bio-reducer in the synthesis of such nanostructures.

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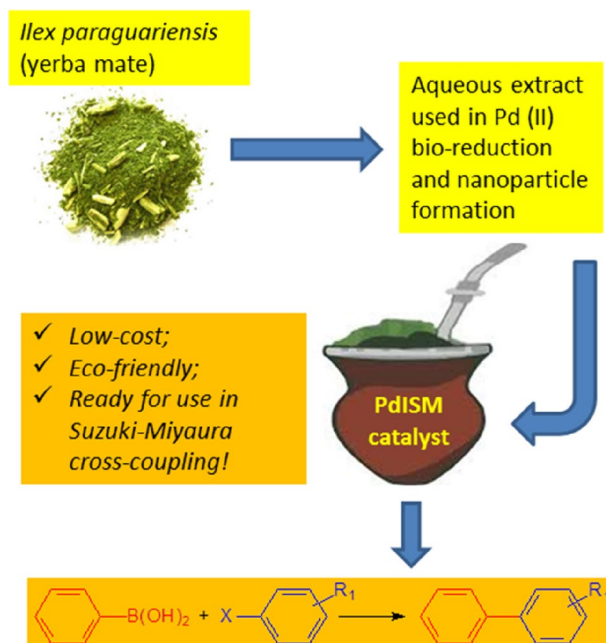
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## Graphical Abstract



**Keywords** Palladium nanoparticle · *Ilex paraguariensis* · Bio-synthesis · Suzuki–Miyaura cross-coupling

## 1 Introduction

Modern organic synthesis, via cross-coupling reactions, makes use of catalysts to minimize the number of steps involved and increase the reaction yield [1]. In this scenario, the use of palladium nanoparticles (Pd NPs) as a catalyst generally yields excellent results compared to other catalytic precursors with the same metal [2]. Fixed on the Suzuki–Miyaura reaction [3], one of the most studied catalytic cross-couplings, the use of Pd NPs is shown in several ways: employing the isolated solid [4] and the solid supported on polymeric films [5], on carbon-derived supports [6], on a magnetic solid [7], on biomass waste [8], and others. However, Pd is expensive and therefore the synthesis of Pd NPs is also expensive. Trying to minimize the costs and complexity of Pd NPs production, some research papers have reported excellent results in the bio-reduction of Pd salts with plant extracts [9–14]. The Pd NPs obtained by this route were tested in cross-coupling reactions and proved successful as catalysts, thus promoting a more eco-friendly synthesis. In order to enhance local biomass, the plant *Ilex paraguariensis* (yerba mate), a native plant from South America, proved to be potentially interesting for bio-reduction of Pd salts as it was already active for the production of silver nanoparticle [15]. Also, yerba mate

has a well-established production chain in the countries of Argentina, Brazil, Chile, Paraguay, Peru and Uruguay, due to its widespread use as tea [16], therefore, its acquisition is carried out in local commerce. The aqueous extract of yerba mate contains polyphenols, xanthines, alkaloids, flavonoids, vitamins and several minerals [17, 18], however, the reducing activity is attributed to the first two compounds listed [15, 19–21]. Given this scenario, in this paper we report, for the first time, the production of Pd NPs by bio-reduction using an *Ilex paraguariensis* aqueous extract. The technique used was innovative because it made use of sonication to avoid the agglomeration of nanometric structures. The solid, named PdISM, was produced at low cost and evaluated for Suzuki–Miyaura cross-coupling.

## 2 Experimental section

### 2.1 Preparation of yerba mate aqueous extract

The *Ilex paraguariensis* sample was purchased locally (Picolo brand, lot 04,340,818) as it is a very widespread tea in the south of South America. In 10 g of sample were added 100 mL of deionized water. The mixture was placed in an 80 °C thermostatic bath and stirred for 20 min.

Subsequently, it was filtered, and the solution obtained was centrifuged for use in the electrochemical measurements or preparation of Pd NPs.

## 2.2 Electrochemical measurements

Aqueous solutions of the extracts containing potassium chloride (KCl)  $0.1 \text{ mol L}^{-1}$  as supporting electrolyte, were prepared for the analysis in a potentiostat apparatus (Metrohm Autolab, model PGSTAT302N). Calibration curves were constructed using ascorbic acid solutions also in water containing KCl  $0.1 \text{ mol L}^{-1}$ , and the antioxidant activity obtained by electrochemical methods were expressed in terms of equivalent of ascorbic acid. The cyclic voltammograms were obtained using scan rate =  $0.100 \text{ V s}^{-1}$ . The total charge under the anodic waves and the peak currents of the background signal (solvent + supporting electrode) were subtracted from the total charges under the anodic waves, and peak currents obtained for each sample were measured within the range of 0.0 to 0.8 V.

## 2.3 Preparation of Pd NPs

Pd NPs were obtained by bio-reduction of an  $\text{PdCl}_2$  aqueous solution with the *Ilex paraguariensis* aqueous extract by a sonication method (developed in this work).  $1 \text{ mM}$  of  $\text{PdCl}_2$  aqueous solution was prepared to be added to the yerba mate aqueous extract (ratio: 10 mL of extract to 100 mL of  $\text{PdCl}_2$  solution). The reduction of the  $\text{PdCl}_2$  solution was accomplished by using the 100 mL of  $1 \text{ mM}$   $\text{PdCl}_2$  solution which was placed in a burette to be slowly dripped into a beaker containing 10 mL of the *Ilex paraguariensis* aqueous extract. The beaker was placed in an ultrasonic bath (Cole-Parmer 08,895–31, USA), the apparatus was switched on at room temperature and dripped at low speed (1 drop every 5 s). After the addition of the  $\text{PdCl}_2$  solution was complete, the mixture remained under stirring in the apparatus for a further 24 h. The solution was washed with acetone until the green color was removed, and it was centrifuged to give a black precipitate. Yield: 112 mg of solid (PdISM).

## 2.4 Transmission electron microscopy analysis (TEM)

TEM analyses were performed using a JEOL JEM 1400 operated at 120 kV. The samples were prepared by deposition of the solid from an isopropanol suspension onto a carbon-coated copper grid at room temperature.

## 2.5 X-ray diffraction (XRD) analysis

The crystalline structure of the solid PdISM were obtained by X-ray diffraction (XRD) using a D500 Rigaku diffractometer (Siemens) operating at a scan rate of  $0.05^\circ \text{ s}^{-1}$  in the range of  $2\theta = 35\text{--}90^\circ$  using  $\text{CuK}_\alpha$  radiation ( $1.54056 \text{ \AA}$ ).

## 2.6 Fourier transform infrared spectroscopy (FT-IR)

FT-IR analysis was performed using a Shimadzu spectrophotometer (IR Prestige 21), combining 32 scans at a  $2 \text{ cm}^{-1}$  resolution. The sample was analysed as pellet with an approximate thickness and diameter of 2 mm and 5 mm, respectively. The sample mass dilution was performed with KBr.

## 2.7 Inductively coupled plasma optical emission spectrometry (ICP-OES)

A 50 mg sample of the solid obtained by bio-reduction via *Ilex paraguariensis* aqueous extract was decomposed using 4 mL of  $14.4 \text{ mol L}^{-1}$   $\text{HNO}_3$  and heating to  $100^\circ \text{C}$  (thermostatic bath), and was added to 10 mL with ultrapure water. The determination of metals in the sample was done by ICP-OES using a Spectro Ciros CCD (Spectro Analytical Instruments, Germany) simultaneous spectrometer equipped with a cross-flow pneumatic misting system, a double-step nebulization camera, and a quartz injector torch with 2.5 mm internal diameter. The plasma power was 1400 W and the argon flow rates were  $14 \text{ L min}^{-1}$  (plasma),  $1 \text{ L min}^{-1}$  (nebulizer), and  $1 \text{ L min}^{-1}$  (auxiliary). The wavelengths for the determinations were as follows: Al 396.152 nm, Ca 393.366 nm, Cu 324.754 nm, Fe 259.941 nm, K 766.491 nm, Mg 285.213 nm, Mn 257.611 nm, Na 588.995 nm, Ni 231.604 nm, P 213.618 nm, Pd 324.270 nm, S 182.034 nm, and Zn 206.191 nm.

## 2.8 Suzuki–Miyaura cross-couplings

### 2.8.1 Experimental

All reactions were conducted under a nitrogen atmosphere in a Schlenk reactor. Bases and solvents were purchased from Synth (Brazil). Phenylboronic acid and aryl halides were purchased from Sigma-Aldrich (Brazil). All chemicals were used without further purification. NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer. Mass spectra were obtained on a GC/MS PerkinElmer Clarus 600 T (EI, 70 eV) equipped with a 30 m capillary DB-5 column with a dimethylpolysiloxane stationary phase. Gas chromatography was performed on a

PerkinElmer Clarus 400 GC equipped with a flame ionisation detector (FID) and a 30 m capillary column with a dimethylpolysiloxane stationary phase.

### 2.8.2 Typical procedure for the Suzuki–Miyaura cross-coupling reaction

A Schlenk reactor was charged with base (2 mmol), phenylboronic acid (187 mg, 1.5 mmol), aryl halide (1 mmol), 2 mg of catalysts (~0.5 mol% of Pd using PdISM), undecane (internal standard, 10  $\mu$ L), and solvent (3 mL). The reaction mixture was stirred at 100 °C until complete. The solution was then allowed to cool to room temperature, taken up in ether (20 mL) and washed with aqueous NaOH (1 M, 5 mL) and brine (2  $\times$  5 mL). The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuum; then the crude material was purified by flash chromatography on silica gel. The corresponding biaryl products were characterised by <sup>1</sup>H and <sup>13</sup>C NMR, and by GC–MS.

**4-Methylbiphenyl** [5]. White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.58–7.56 (m, 2H), 7.48 (d,  $J$  = 8.1 Hz, 2H), 7.42–7.39 (m, 2H), 7.32–7.28 (m, 1H), 7.23 (d,  $J$  = 7.8 Hz, 2H), 2.38 (s, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 141.1, 138.3, 137.0, 129.4, 128.7, 127.0, 126.9, 21.1 ppm. GC–MS (IE, 70 eV)  $m/z$  (%): 168 (100, M+), 167 (75), 165 (30), 152 (27), 153 (19), 83 (19), 82 (17), 169 (12).

**4-Aminobiphenyl** [24]. Orange solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.54–7.51 (d,  $J$  = 7.1 Hz, 2H), 7.42–7.36 (m, 4H), 7.27–7.23 (m, 1H), 6.74–6.71 (m, 2H), 3.66 (s, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 145.8, 141.1, 131.5, 128.6, 127.9, 126.3, 126.2, 115.3 ppm. GC–MS (IE, 70 eV)  $m/z$  (%): 169 (100, M+), 168 (20), 167 (14), 170 (13), 84 (12), 83 (11), 141 (10), 115 (9).

**Biphenyl** [5]. White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.59–7.57 (m, 4H), 7.44–7.40 (m, 4H), 7.34–7.31 (m, 2H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 141.2, 128.7, 127.2, 127.1 ppm. GC–MS (IE, 70 eV)  $m/z$  (%): 154 (100, M+), 153 (43), 152 (29), 76 (19), 155 (12), 151 (9), 77 (9), 115 (7).

**4-Cyanobiphenyl** [5]. White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.72–7.66 (m, 4H), 7.59–7.56 (m, 2H), 7.50–7.39 (m, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 145.6, 139.1, 132.5, 129.0, 128.6, 127.7, 127.2, 118.9, 110.8 ppm. GC–MS (IE, 70 eV)  $m/z$  (%): 179 (100, M+), 178 (25), 151 (17), 180 (14), 76 (14), 89 (11), 177 (8), 152 (8).

**4-Methoxybiphenyl** [5]. White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.56–7.51 (m, 4H), 7.43–7.39 (m, 2H), 7.31–7.28 (m, 1H), 6.97 (d,  $J$  = 8.8 Hz, 2H), 3.84 (s, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3 ppm. GC–MS (IE, 70 eV)  $m/z$  (%): 184 (100, M+), 141 (69), 169 (68), 115 (53), 139 (19), 185 (17), 76 (13), 63 (12).

**4-Nitrobiphenyl** [5]. Brown solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.30 (d,  $J$  = 9.0 Hz, 2H), 7.74 (d,  $J$  = 9.0 Hz, 2H),

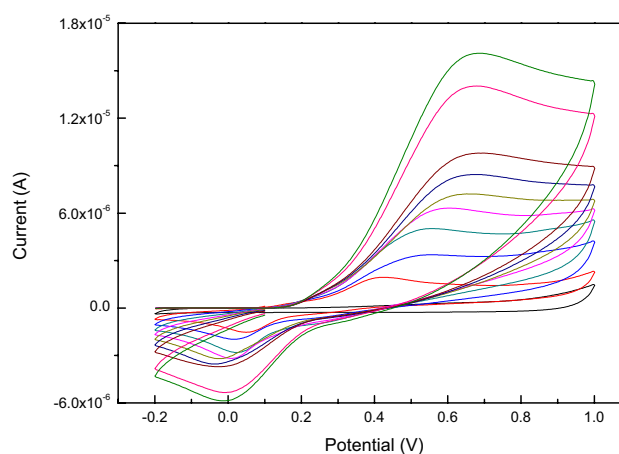
7.64–7.61 (m, 2H), 7.52–7.43 (m, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 147.6, 147.1, 138.8, 129.2, 128.9, 127.8, 127.4, 124.1 ppm. GC–MS (IE, 70 eV)  $m/z$  (%): 152 (100), 199 (58, M+), 169 (53), 151 (34), 141 (24), 153 (22), 115 (17), 76 (15).

## 3 Results and discussion

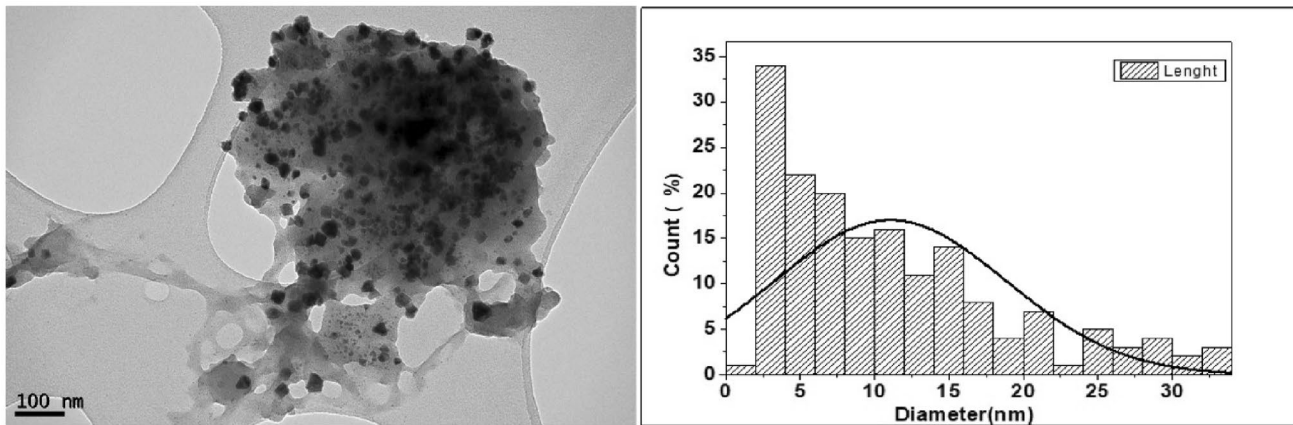
Initially, the verification of the reducing activity of the aqueous extract of yerba mate was evaluated by cyclic voltammetry in different concentrations (Fig. 1).

In Fig. 1 it is observed that the *Ilex paraguariensis* extract shows an oxidation peak in the range of 0.40–0.70 V, indicating the presence of reducing substances. Also, the increase of the anodic peak currents can be observed as a function of the higher concentration of the extract. In this case, ascorbic acid was used as the standard antioxidant, for which cyclic voltammograms were obtained for solutions in different concentrations. Ascorbic acid presented oxidation peak at 0.47 V, and the currents obtained presented linearity as a function of the concentration according to the equation [Ascorbic Acid] = 20,695.85  $i_{ap}$  + 0.00103 ( $i_{ap}$  = anodic peak current, in Amperes), in the concentration range of 0.0 to 0.5 mg mL<sup>-1</sup>, with  $R^2$  = 0.9962. Using the calibration curve to determine the total antioxidant activity of the stock solution of *Ilex paraguariensis* extract (1 mg/10 mL), antioxidant activity equivalent to 3.45 mg of ascorbic acid per milliliter.

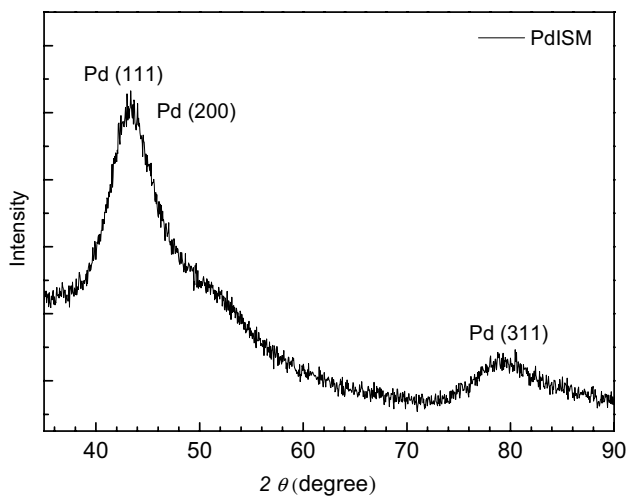
After confirming the reducing activity of the aqueous extract of yerba mate, the study continued with the production of Pd NPs. For this, a solution of PdCl<sub>2</sub> was slowly added to the aqueous extract of yerba mate by a



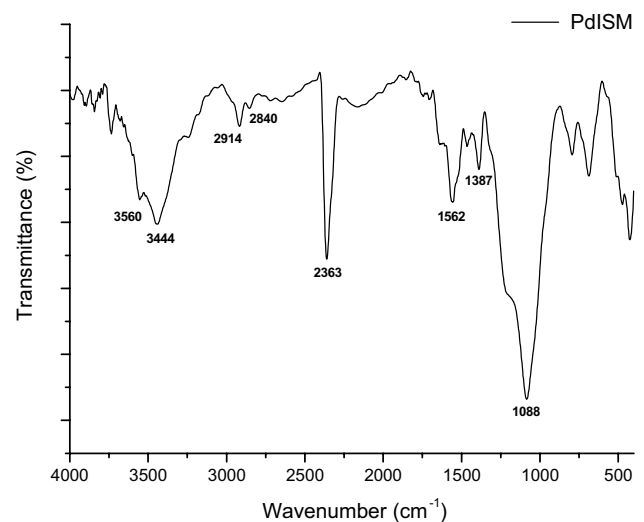
**Fig. 1** Cyclic voltammograms of aqueous solutions of the aqueous extract of yerba mate at concentrations of 0.00, 1.00, 1.96, 2.91, 3.84, 4.76, 5.66, 7.40, 9.09, and 10.71 mg mL<sup>-1</sup>, in KCl 0.1 mol L<sup>-1</sup>, sweep speed = 100 mV s<sup>-1</sup>



**Fig. 2** TEM micrograph of the solid PdISM (left) and a histogram (right) illustrating the particle size distribution



**Fig. 3** X-ray diffractogram of the PdISM catalyst



**Fig. 4** FT-IR spectrum of PdISM catalyst

sonication method (see Experimental section). The gradual color change of the solution from reddish orange to black indicated the formation of Pd NPs. After purification of the obtained solid, it was called PdISM and properly characterized. PdISM was evaluated by TEM indicating nanostructures (Fig. 2).

Figure 2 illustrates that sonication avoids total agglomeration of nanostructures, resulting in diameters compatible with other publications dealing with bio-reduction of palladium [8–14, 22]. Continuing the characterization of the solid, the crystalline nature of the PdISM catalyst was determined using XRD (Fig. 3).

Figure 3 shows the characteristic peaks of Pd, being a face-centred cubic (fcc) structure similar to other studies involving Pd NPs bio-synthesis [9, 11, 13, 23]. The diffractogram shows considerably wide peaks, which is a good indication of the nanometric characteristic of crystals

or crystallites. The Pd peaks corresponding to the (111) and (200) planes, which are coupled, and the (311) plane appear in the diffractogram (JCPDS N° 89–4897). It is possible that this sample also contains Pd, Mg and Mn oxides/hydroxides, elements in greater concentration in the solid PdISM.

Following the investigation, the FT-IR analysis was conducted in order to assess the presence of organic compounds from the yerba mate linked to PdISM (Fig. 4).

Figure 4 shows that the PdISM has FT-IR spectrum similar to the aqueous extract of yerba mate obtained by Arreche and coworkers [15]. The obtained bands can be correlated to the compounds present in the plant extract, mainly polyphenols and xanthenes: hydroxyls groups ( $3560\text{--}3544\text{ cm}^{-1}$ ), aliphatic C-H bonds ( $2914\text{--}2840\text{ cm}^{-1}$ ), carbonyl group ( $1562\text{ cm}^{-1}$ ),  $\delta_{\text{C-H}}$  ( $1387\text{ cm}^{-1}$ ), and  $\nu_{\text{C-O}}$  ( $1088\text{ cm}^{-1}$ ). The band observed at  $2363\text{ cm}^{-1}$  indicates

a possible contamination of the sample by CO<sub>2</sub> during the FT-IR analysis. Thus, based on the FT-IR data, it can be inferred that the phenolic hydroxyl groups present in the extract of yerba mate play an important role in the reduction of Pd(II) cations and [9, 11, 13, 23], together with the carbonyl groups, has a possible action consortium in the stabilization of Pd NPs [24].

ICP-OES analysis was also performed on the prepared PdISM sample, and it showed that only 29% of the weight was formed by Pd. This result was consistent with the literature [23]. To better elucidate the composition of PdISM, a scan of other elements was performed (Table 1).

Table 1 showed that the composition of PdISM found is very similar to the composition of *Ilex paraguariensis* determined in dry leaves marketed for the preparation of teas [21].

Thus, with the actual knowledge about the composition of PdISM, the catalytic activity of the solid obtained was tested in the Suzuki–Miyaura reaction of phenylboronic acid with 4-bromotoluene (Scheme 1, Table 2). The catalytic systems employed were guided by previous work of our research group and excelled by the use of the eco-friendly reagents [24–26].

The results outlined in Table 2 indicate that the best result (entry 3<sup>a</sup>) was obtained when K<sub>2</sub>CO<sub>3</sub> was used as the base and ethanol as the solvent. Reaction yield decreased with reduction of catalyst amount (entry 3<sup>b</sup>), temperature (entry 3<sup>c</sup>), and reaction time (entry 3<sup>d</sup>), showing that the reaction conditions of entry 3<sup>a</sup> are optimized. On the other hand, the PdISM catalyst did not tolerate apolar solvents like dioxane

**Table 1** Results for determination of other elements in the PdISM sample by ICP-OES

Entry	Element	Concentration (µg g <sup>-1</sup> )	Standard deviation (± µg g <sup>-1</sup> )
1	Al	1187	32
2	Ca	8213	324
3	Cu	66.3	1.7
4	Fe	1257	25
5	K	6155	157
6	Mg	16,930	282
7	Mn	4102	22
8	Na	391	10
9	Ni	50.2	3.1
10	S	2913	86
11	Zn	248	3

**Table 2** Optimization of reaction conditions for the Suzuki–Miyaura cross-coupling of PdISM with phenylboronic acid and 4-bromotoluene<sup>a</sup>

Entry	Solvent	Base	Yield (%)
1	Ethanol	K <sub>3</sub> PO <sub>4</sub>	69
2	Ethanol	CsF	53
3	Ethanol	K <sub>2</sub> CO <sub>3</sub>	97 (95) 66 <sup>b</sup> 41 <sup>c</sup> 70 <sup>d</sup> 0 <sup>e</sup>
4	Dioxane	K <sub>3</sub> PO <sub>4</sub>	29
5	Dioxane	CsF	31
6	Dioxane	K <sub>2</sub> CO <sub>3</sub>	42
7	DMF	K <sub>3</sub> PO <sub>4</sub>	55
8	DMF	CsF	58
9	DMF	K <sub>2</sub> CO <sub>3</sub>	67

<sup>a</sup>Reaction conditions: 4-bromotoluene (1 mmol), phenylboronic acid (1.5 mmol), PdISM catalyst (2 mg, 0.5 mol% of Pd), base (2 mmol), solvent (3 mL), undecane (10 µL), 24 h, 100 °C, yields determined by GC (average of two runs). The isolated yield is stated in parentheses

<sup>b</sup>PdISM catalyst (1 mg, 0.25 mol% of Pd)

<sup>c</sup>Temperature = 50 °C

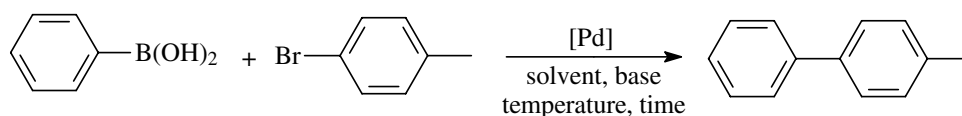
<sup>d</sup>Time = 16 h. <sup>e</sup>Without catalyst

(entries 4–6), and the use of DMF yielded only modest results (entries 7–9). The result obtained with PdISM catalyst was successful, and represented a Suzuki–Miyaura cross-coupling reaction that was free of phosphine ligands and quaternary ammonium salts. The catalytic system is sustainable due to the "green" method of obtaining PdISM as well as the use of eco-friendly reagents (ethanol and K<sub>2</sub>CO<sub>3</sub>). When the same reaction was repeated without catalyst (entry 3<sup>e</sup>), obviously, no formation of 4-methylbiphenyl was observed. These data confirmed the catalytic efficiency of PdISM.

With the actual knowledge about the composition of PdISM, the scope of its use in the Suzuki–Miyaura reaction was increased by varying aryl halides and/or functional groups on the aromatic ring (Table 3).

Table 3 shows the efficiency of PdISM in the development of a catalytic system for Suzuki–Miyaura cross-coupling without auxiliary ligands. Excellent yields for the coupling of aryl iodides were observed in extremely short reaction times; for example, the coupling reaction of phenylboronic acid with 4-iodoaniline occurred in only 15 min (entry 1). The catalytic system tolerated both electron-donating and electron-withdrawing groups on the aromatic ring (*para* position) of the

**Scheme 1.** The Suzuki–Miyaura cross-coupling reaction investigated in this study



**Table 3** Suzuki–Miyaura cross-coupling of phenylboronic acid with different aryl halides catalyzed by PdISM<sup>a</sup>

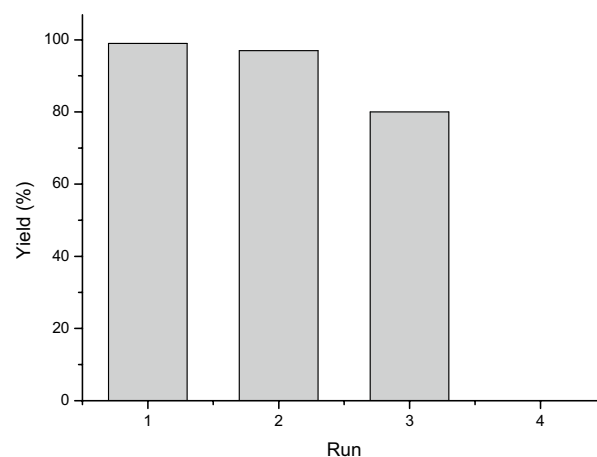
Entry	ArX	Time (h)	Yield (%)	TON	TOF
1	4-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I	0.25	99	198	792
2	PhI	1	96	192	192
3	4-MeC <sub>6</sub> H <sub>4</sub> I	1	94	188	188
4	4-NCC <sub>6</sub> H <sub>4</sub> Br	20	93	186	9
5	PhBr	24	99	198	8
6	4-MeC <sub>6</sub> H <sub>4</sub> Br	24	97 35 <sup>b</sup>	194 70	8 3
7	4-MeOC <sub>6</sub> H <sub>4</sub> Br	24	91	182	8
8	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Cl	24	11	22	1
9	4-F <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> Cl	24	Traces	–	–
10	PhCl	24	Traces	–	–
11	4-MeOC <sub>6</sub> H <sub>4</sub> Cl	24	No reaction	–	–

<sup>a</sup>Reaction conditions: ArX (1 mmol), phenylboronic acid (1.5 mmol), PdISM catalyst (2 mg, 0.5 mol% of Pd), K<sub>2</sub>CO<sub>3</sub> (2 mmol), ethanol (3 mL), 100 °C, isolated yields (average of two runs). Time not optimized. TON: turnover number, yield of product/per mol of Pd. TOF: turnover frequency, TON/time of reaction (h)

<sup>b</sup>PdCl<sub>2</sub> as catalyst (0.5 mol% of Pd)

aryl iodides and furnished the cross-coupled products without evidence of parallel reactions like homocoupling of phenylboronic acid (entries 1–3). The reactivity of the ArBr was similar to that of the aryl iodides but with a longer reaction time (entries 4–7). Entry 6 shows the superiority of the PdISM catalyst when compared to the commercial salt (PdCl<sub>2</sub>); the corresponding product was obtained in almost 3 × higher yield. The ArCl test in the Suzuki–Miyaura cross-coupling is always done to seek a positive result that will actually attest to the competence of the catalytic system, because such halides present great difficulty in making the oxidative addition in the coordinating sphere of Pd (first stage of the catalytic cycle). In the study presented, it is observed that only an activated ArCl (entry 8) achieved a reaction yield where it was possible to isolate the biphenyl, although the yield was low. The other aryl chlorides tested or reacted in the order of trace (entries 9–10) or did not promote the reaction (entry 11). In this study, the TON and TOF values were calculated and proved to be superior (see entry 1) to other catalytic systems that employ similar conditions (conventional heating and the same amount of catalyst) [24–26].

In order to compare the results obtained in Table 3 with other studies using the bio-synthesis of palladium nanoparticles, the 4-bromotoluene reaction (entry 6<sup>a</sup>) was chosen. Thus, observing the isolated yield in 4-methylbiphenyl (97%), it can be noted that the catalytic system employing PdISM catalyst is superior, in this regard, to the others that employ *Hibiscus sabdariffa* L. flower extract (90%) [23], *Rosa canina* fruit extract (92%) [11], and *Stachys lavandulifolia* herbal tea extract (96%)



**Fig. 5** Yields obtained after 15 min of reaction time in repeated runs of the Suzuki–Miyaura cross-coupling of phenylboronic acid with 4-iodoaniline in ethanol using K<sub>2</sub>CO<sub>3</sub> as the base and the same load of PdISM catalyst

[13] for the production of Pd NPs. On the other hand, another report that uses black tea leaves (*Camellia sinensis*) extract for the bio-reduction of Pd was shown to be superior in the production of 4-methylbiphenyl (98%) [9]. Obviously, each catalytic system has its pros and cons due to the large number of items that must be observed: reaction, Pd load, solvent, base, temperature, time, versatility and availability of biomass used in the synthesis of Pd NPs. Thus, focusing on the results obtained and the availability of biomass, it can be said that the catalytic system reported in this manuscript is among those with potential technological use.

Although the catalyst under study is not supported, it is necessary to evaluate its reusability. Thus, an investigation of the recycling capability of PdISM was conducted with the reaction of 4-iodoaniline with phenylboronic acid (Table 3, entry 1). In the first run, 99% yield was obtained within 15 min. After the first run, 20 mL of Et<sub>2</sub>O was added in a Schlenk reactor to extract the organic compounds. The K<sub>2</sub>CO<sub>3</sub> and PdISM remaining in the reactor were loaded into another reaction. The same procedure was repeated in the other runs. The performance of PdISM in the recycling study can be seen in Fig. 5.

As shown in Fig. 5, PdISM showed excellent catalytic activity up to the third run (second recycle). Already in the fourth run, no formation of the coupling product was observed. Although the number of recycles is low, it is worth remembering that the catalyst was not supported and no type of stabilizer was used to avoid the agglomeration of the Pd NPs. In this sense, during the fourth run was observed the formation of Pd black deposited in the reactor, this is a strong indication of the catalytic active species agglomeration.

In order to evaluate the use of the catalytic system developed with PdISM on a gram scale, the 4-bromotoluene reaction was reevaluated (Table 3, entry 6<sup>a</sup>). Thus, the reaction was conducted with an increase of 10 × in the quantities of reagents and base (20 mmol of K<sub>2</sub>CO<sub>3</sub>, 15 mmol of phenylboronic acid, 10 mmol of 4-bromotoluene, and 20 mg of catalyst), 10 mL of ethanol maintaining the same time and temperature. The average result of two runs indicated 89% isolated yield in 4-methylbiphenyl, confirming the robustness of the developed catalytic system.

## 4 Conclusion

In conclusion, in this work it was shown, for the first time, the use of *Ilex paraguariensis* extract in the bio-reduction of Pd salts to obtain nanometric structures. In addition, the route used was innovative by making use of sonication. The solid obtained, PdISM, was used as a catalyst in Suzuki–Miyaura cross-coupling, composing a new eco-friendly, ligand-free, and low-cost catalytic system. Excellent yields were obtained in the coupling of aryl iodides and bromides with phenylboronic acid. The same catalyst load was able to be recycled 3x. In addition, the PdISM catalyst was able to conduct the reaction of 4-bromotoluene on the gram scale, maintaining a very good performance. Our group continues the study by enabling PdISM support on polymeric films and studying the true catalytically active species.

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## Compliance with ethical standards

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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