



## Microwave-assisted Suzuki reaction catalyzed by Pd(0)–PVP nanoparticles

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### ABSTRACT

Suzuki cross-coupling reaction was successfully carried out in ethanol utilizing a palladium colloidal solution stabilized by polyvinylpyrrolidone (PVP). High isolated yields (75–97%) to biaryls were obtained using different bases, aryl halides, and aryl boronic acids with a small loading of the palladium catalyst. Pd(0)–PVP nanoparticles with 3–6 nm of medium diameter were prepared from Pd(OAc)<sub>2</sub> in the presence of the stabilizer PVP using methanol as the reducing agent.

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Transition-metal nanoparticles have attracted a great deal of attention in the last few years; their preparation, structure determination, and applications are topics of current interest.<sup>1,2</sup> An important field of application for nanoparticles is that of catalysis due to their large surface area.<sup>3–6</sup> In this regard the unique properties of these systems can lead to interesting applications in different types of reactions which include hydrogenations,<sup>7,8</sup> C–C couplings,<sup>9–11</sup> Fischer–Tropsch,<sup>12</sup> oxidations<sup>13</sup> etc. Metallic nanoparticles have been considered at the frontier between homogeneous and heterogeneous catalysis<sup>14</sup> allowing for a very high activity under mild conditions. Progress in nanocatalysis has been made in efficiency and selectivity of the reactions as well as in the recovery and reusability of the catalyst.

Palladium chemistry has emerged as one of the most prominent tools for the C–C bond formation with an increasing number of papers devoted to the cross-coupling reactions like Kumada,<sup>15</sup> Suzuki,<sup>16</sup> Stille,<sup>17</sup> Negishi,<sup>18</sup> and Hiyama<sup>19</sup> or to the Heck<sup>20</sup> and Sonogashira<sup>21</sup> couplings. The Suzuki cross-coupling reactions of arylboronic acids and aryl halides provide an effective synthetic route to biaryls, which are useful as precursors to pharmaceuticals, polymers, liquid crystals etc.<sup>22</sup> Although homogeneous palladium catalysis are usually effective in this reaction, their use often brings about the typical problems associated with all homogeneous catalysts, that is, separation of the catalyst from the reaction products and catalyst recovery. Water soluble polymers like polyvinylpyrrolidone (PVP) are effective stabilizers for nanoparticles and their utilities as stabilizers for palladium nanoparticles have been demonstrated in some opportunities in the literature.<sup>23</sup>

Properties of nanocatalysts are size dependent and it is well documented in the literature that the stability and size of nano-scaled colloidal particles strongly depend upon the method followed as well as the experimental conditions. Miyake and

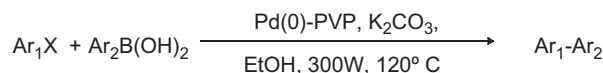
Teranishi,<sup>24</sup> for instance, prepared palladium nanoparticles from the reduction of H<sub>2</sub>PdCl<sub>4</sub> with alcohols as reducing agents of the Pd(II) species in the presence of PVP as the stabilizer. These authors reported that the amount of PVP, the kind, and concentration of the alcohol in the solvent play an important role on the control of the mean diameter of monodispersed Pd nanoparticles.

Microwave-assisted heating under controlled conditions has been proven as an invaluable technology for organic synthesis<sup>25</sup> and their application in several cases has led to acceleration of reactions, improvement of yields, and selectivities.<sup>26</sup> Our research group has already demonstrated the huge potential of this technique applied to palladium-catalyzed C–C bond couplings.<sup>20c,27</sup>

In this work, soluble Pd(0) nanoparticles stabilized by PVP were utilized as a catalyst in Suzuki reactions under microwave heating without phosphine ligands (Scheme 1).

Pd(0)–PVP nanoparticles were prepared following the procedure reported by Bradley et al.<sup>28,29</sup> using Pd(OAc)<sub>2</sub> as the palladium source and methanol as the reducing agent in the presence of polyvinylpyrrolidone as the stabilizer. After refluxing for 3 h, methanol was removed under reduced pressure and the residue was dissolved in ethanol or in acetonitrile. The brown solutions thus prepared were stable for months at room temperature without precipitation. Following this methodology, nanoparticles with a particle size ranging from 3 to 6 nm were obtained (Fig. 1). For comparison, Pd(0)–PVP nanoparticles were also prepared according to the Miyake et al.<sup>24</sup> methodology, in which ethanol was used as the reducing agent in the presence of PVP as the stabilizer and an acid solution of H<sub>2</sub>PdCl<sub>4</sub> was employed as the palladium source.

Our initial investigation on the evaluation of the catalytic activity of Pd(0)–PVP nanoparticles started with the cross-coupling



**Scheme 1.** Pd(0)–PVP-catalyzed Suzuki reactions under MW.

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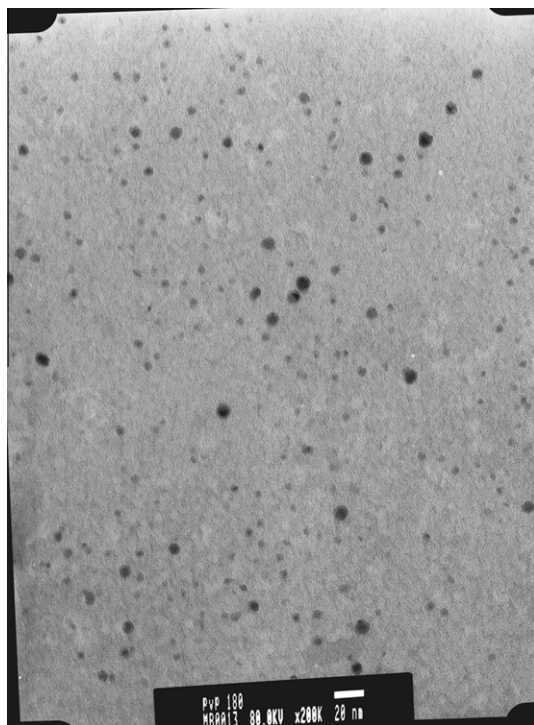
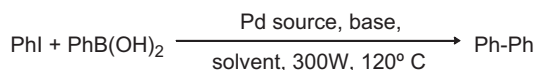


Figure 1. TEM image of the Pd(0)-PVP nanoparticles.

between phenylboronic acid and iodobenzene under microwave irradiation (Scheme 2, Table 1).

Our research group has previously reported that the solvent in which the nanoparticles were dissolved after the evaporation of methanol had a great influence on the coupling under conventional heating since Suzuki reaction was much faster in ethanol than in acetonitrile.<sup>30</sup> Under microwave heating, however, the use of both acetonitrile and ethanol led to a good yield of the coupling product (Table 1, entries 1 and 2). High turnovers and turnover frequencies could be obtained for the catalytic system using low loadings of palladium (0.005%, entries 5 and 6). Turnover frequencies were remarkably improved by employing dielectric heating when compared to those obtained under conventional heating (entry 4).<sup>30</sup> Under conventional heating with the Pd(0)-PVP prepared according to the Bradley and co-workers methodology,<sup>28</sup> quantitative yield to biphenyl was achieved in 4 h using 0.01% of the catalyst.<sup>30</sup> In the present work it can be observed that 0.005% of palladium and 7 min of microwave irradiation were enough for the obtainment of biphenyl in 99% yield. Catalytic activity of the pre-formed Pd(0)-PVP colloids in ethanol were comparable to that observed for Pd(OAc)<sub>2</sub> in ethanol and palladium could be easily recovered by the addition of ethyl ether to the reaction mixture in order to precipitate the PVP-stabilized palladium nanoparticles as well as the inorganics.

Pd(0)-PVP prepared according to Miyake and co-workers<sup>24</sup> procedure (ethanol/water, PVP, H<sub>2</sub>PdCl<sub>4</sub>) was also employed as a catalyst under microwave irradiation with ethanol as the solvent (entry 7, Table 1) in the same conditions utilized in the Suzuki coupling with Pd(0)-PVP prepared according to the Bradley and co-workers<sup>28</sup> procedure (methanol, Pd(OAc)<sub>2</sub>, PVP) (entry 6). Excellent yield (99%) to biphenyl was obtained in 7 min of the reac-



Scheme 2. Suzuki reaction between iodobenzene and phenylboronic acid.

Table 1  
Suzuki reaction between iodobenzene and phenylboronic acid

	Conditions	Y <sup>a</sup> (%)	TOF (h <sup>-1</sup> )
1	0.1% Pd(0)-PVP, K <sub>2</sub> CO <sub>3</sub> , EtOH, 12 min	>99	2.6 × 10 <sup>3</sup>
2	0.1% Pd(0)-PVP, K <sub>2</sub> CO <sub>3</sub> , MeCN, 12 min	96	2.5 × 10 <sup>3</sup>
3	0.025% Pd(0)-PVP, K <sub>2</sub> CO <sub>3</sub> , EtOH, 12 min	>99	1.0 × 10 <sup>4</sup>
4	0.01% Pd(0)-PVP, K <sub>2</sub> CO <sub>3</sub> , EtOH, 12 min	>99	2.6 × 10 <sup>4</sup> (1.3 × 10 <sup>3</sup> ) <sup>b</sup>
5	0.005% Pd(0)-PVP, K <sub>2</sub> CO <sub>3</sub> , EtOH, 12 min	>99	5.2 × 10 <sup>4</sup>
6	0.005% Pd(0)-PVP, K <sub>2</sub> CO <sub>3</sub> , EtOH, 7 min	99	4.4 × 10 <sup>5</sup>
7	0.005% Pd(0)-PVP <sup>c</sup> , K <sub>2</sub> CO <sub>3</sub> , EtOH, 7 min	99	4.4 × 10 <sup>5</sup>

Conditions: iodobenzene (1.0 mmol); PhB(OH)<sub>2</sub> (1.1 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), % Pd w/w with respect to iodobenzene, 2.0 mL EtOH, P = 300 W, 120 °C, sealed tube.<sup>32</sup>

<sup>a</sup> GC-MS yield with respect to iodobenzene, normalized areas.

<sup>b</sup> Conventional heating, 4 h, 80 °C.

<sup>c</sup> Prepared according to the Miyake and co-workers methodology (H<sub>2</sub>PdCl<sub>4</sub>, ethanol as reducing agent, PVP as stabilizer).

tion.<sup>30</sup> Palladium black precipitation was not observed at the end of the reaction when the Pd(0)-PVP prepared according to the Bradley and co-workers' methodology was employed. When the nanoparticles prepared according to Miyake and co-workers<sup>24</sup> procedure were utilized however, palladium black precipitation was observed at the end of the reaction under microwave heating. Similar observations were made by El-Sayed and co-workers when they employed this catalyst under conventional heating.<sup>31</sup> These authors attributed this precipitation to the low stability of these nanoparticles under high temperatures. The Pd-PVP nanoparticles employed in this work (PVP/Pd = 101, 3–6 nm in ethanol) displayed a superior stability at the same time as excellent activities could be achieved with this catalyst.

Antunes and co-workers<sup>27</sup> also employed the Miyake and co-workers nanoparticles in the Suzuki coupling under microwave irradiation (0.2 mol % Pd-PVP, K<sub>2</sub>CO<sub>3</sub>, 15 mL of 40% EtOH/water, 220 W). These researchers<sup>26</sup> obtained biphenyl quantitatively in 40 min of irradiation (TOF = 750/h). In the present work, using the same catalyst (Table 1, entry 7), biphenyl was obtained in excellent yield (99%) with 0.005% (mol %) of palladium in 7 min of irradiation (4.4 × 10<sup>5</sup>/h).

In the majority of the reaction time, potency was maintained between 60 and 70 W and temperature in 120 °C. The temperature and potency profile for the reactions under microwave irradiation are shown in Figure 2.

The excellent results obtained in the cross-coupling of iodobenzene with phenylboronic acid under microwave heating encour-

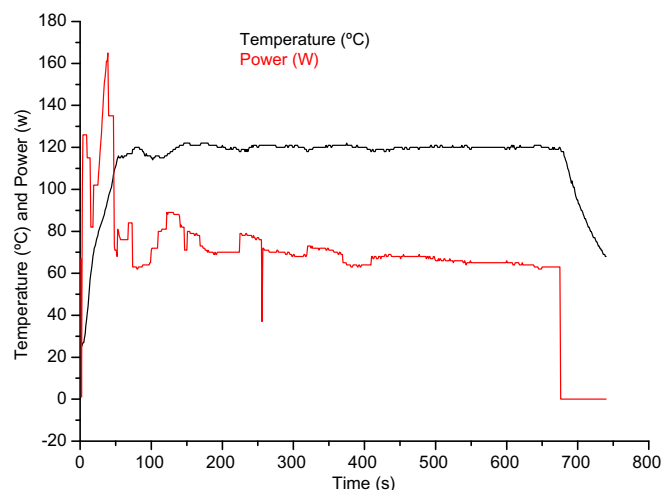


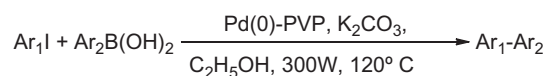
Figure 2. Temperature and potency profile for the microwave-assisted Suzuki reactions catalyzed by Pd(0)-PVP.

aged us to further screen other aryl halides and boronic acids as coupling partners (Table 2, Scheme 3).

Very good yields were achieved in the cross-coupling reactions catalyzed by Pd(0)–PVP under microwave irradiation with several aryl iodides.<sup>32</sup> Electron-deficient iodides (entries 5 and 6, Table 2) and the electron-rich ones afforded the corresponding biphenyls in very good yields. Good results were also obtained in the presence of an electron withdrawer like fluorine in the aryl boronic acid. Reaction between 2-furanboronic acid and iodobenzene afforded the corresponding biaryl in poor yield (entry 7, Table 2). Smith et al.<sup>33</sup> have reported that transmetalation is the limiting rate step of the reaction between boronic acids and iodoarenes. As in this case a large amount of biphenyl (17%) was detected, it is probable that the palladium(II) complex, generated after the quick oxidative addition of iodobenzene to the catalytic active palladium(0) species, became susceptible to the homocoupling, because the furanyl group was not readily transferred to this complex.

Although a good isolated yield (90%) was achieved in the coupling of phenylboronic acid with 4-iodoanisole (entry 2), the same was not observed for the reaction between this boronic acid and iodoanilines (entries 10 and 11). The amino group deactivated the aryl iodide to a greater extent than did the methoxy group. These results can be attributed to the higher basicity of the nitrogen atom compared to oxygen. Furthermore, amines are good ligands for transition metals and can inhibit the cycle steps where available sites are necessary. Increasing the catalyst loading from 0.005% to 0.025% (entry 11, Table 2), 2-phenylaniline could be obtained in 80% yield.

Attempts to further investigate the scope and limitations of the Pd(0)–PVP catalysts, aryl bromides were also employed in the cou-



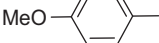
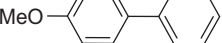
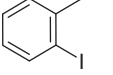
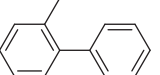

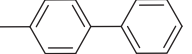
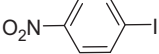
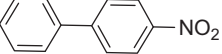
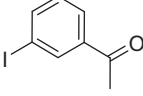
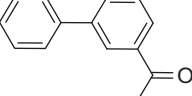
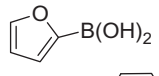
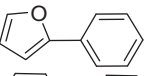
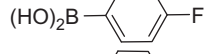
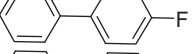
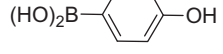
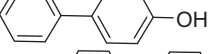
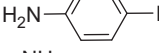
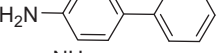

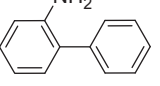
**Scheme 3.** Suzuki coupling between aryl halides and arylboronic acids catalyzed by Pd(0)–PVP.

pling reaction with phenylboronic acids under microwave heating (Scheme 4, Table 3). Yields of these reactions reflected the reactivity of the aryl bromides toward the oxidative addition. These results were consistent with the previous Letter by Smith et al.<sup>33</sup> that oxidative addition is the rate limiting step for the coupling of aryl bromides. Good yields were achieved when bromobenzene (87%) and 4-bromoacetophenone (79%) were used as electrophiles with 0.025% of palladium. However, the coupling with the electron rich 4-bromoanisole furnished the corresponding 4-methoxybiphenyl in poor yield (43%).

After the reaction, product could be easily isolated by precipitating the nanoparticles together with the inorganics present in the reaction mixture by the addition of diethyl ether.

In summary, microwave irradiation improved the reaction rates of the Suzuki cross-couplings between arylboronic acids and aryl halides catalyzed by Pd(0)–PVP. The corresponding biaryls could be obtained in good yields (75–97%) and short times (12 min) from aryl iodides and in 43–87% yield from the aryl bromides. Products could be easily isolated precipitating the nanoparticles and the inorganics present in the reaction mixture by adding diethyl ether. As far as we are aware, our system exhibits significant advantages as remarkably higher turnover numbers (up to 10<sup>4</sup> to 10<sup>5</sup>/h in 12 min × 750/h in 40 min) were attained for the coupling of aryl iodides and bromides.

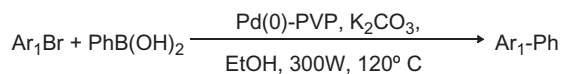
**Table 2**  
Microwave-assisted Suzuki reaction with aryl iodides

Entry	Boronic acid	Aryl halide	Product	Yield <sup>b</sup> (%) (Y)
1	PhB(OH) <sub>2</sub>	PhI	Ph–Ph	83 (>99)
2	PhB(OH) <sub>2</sub>			90 (>99)
3	PhB(OH) <sub>2</sub>			97 (99)
4	PhB(OH) <sub>2</sub>			92 (>99)
5	PhB(OH) <sub>2</sub>			85 (>99)
6	PhB(OH) <sub>2</sub>			94
7		PhI		34 <sup>b</sup>
8		PhI		94 (>99)
9		PhI		75 (>99)
10	PhB(OH) <sub>2</sub>			<0.01
11	PhB(OH) <sub>2</sub>			80 <sup>b,c</sup>

<sup>a</sup> Reaction conditions: Ar<sub>1</sub>I (1.0 mmol), Ar<sub>2</sub>B(OH)<sub>2</sub> (1.1 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), 0.005% Pd(0)–PVP, EtOH (2.0 mL), sealed tube, 300 W, 12 min. Isolated yields.

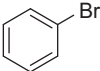
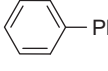
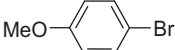
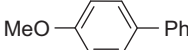
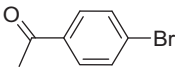
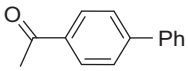
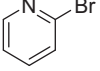
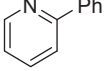
<sup>b</sup> GC–MS yield.

<sup>c</sup> 0.025% of Pd(0)–PVP.



Scheme 4. Pd(0)-PVP-catalyzed Suzuki reactions under MW.

**Table 3**  
Suzuki couplings between aryl bromides and phenylboronic acid

	Ar <sub>1</sub> Br	Product	Yield <sup>a</sup> (%)
1			87
2			43
3			79
4			60

Conditions: aryl iodide (1.0 mmol), arylboronic acid (1.1 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), ethanol (2 mL), 0.01% Pd with respect to the mass of the aryl bromide.

<sup>a</sup> GC-MS yield with respect to the consumption of the aryl halide by normalization of the areas.

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## References and notes

- Sergeev, G. B. In *Nanochemistry*; Elsevier: Amsterdam, 2006; pp 1–6.
- El-Sayed, M. A. *Acc. Chem. Res.* **2001**, *34*, 257–264.
- Rao, C. N. R.; Kulkarni, G. U.; Thomas, P. J.; Edwards, P. P. *Chem. Soc. Rev.* **2000**, *29*, 27–35.
- Astruc, D. In *Nanoparticles and Catalysis*; Wiley-VCH: Weinheim, 2008; Vol. 1, pp 1–48.
- Aiken, J. D., III; Finke, R. G. J. *Mol. Catal. A: Chem.* **1999**, *145*, 1–44.
- Grunes, J.; Zhu, J.; Somorjai, G. A. *Chem. Commun.* **2003**, 2257–2260.
- Mukherjee, D. J. *Nanopart. Res.* **2008**, *10*, 429–436.
- Alonso, F.; Riente, P.; Sirvent, J. A.; Yus, M. *Appl. Catal. A: Gen.* **2010**, *378*, 42–51.
- Calò, V.; Nacci, A.; Monopoli, A.; Montigelli, F. *J. Org. Chem.* **2005**, *70*, 6040–6044.
- Trzeciak, A. M.; Ziólowski, J. J. *Coord. Chem. Rev.* **2007**, *251*, 1281–1293.
- Gniewek, A.; Trzeciak, A. M.; Ziólowski, J. J.; Kepiński, L.; Wrzyszczyk, J.; Tylus, W. *J. Catal.* **2005**, *229*, 332–343.
- Silva, D. O.; Scholten, J. D.; Gelesky, M. A.; Teixeira, S. R.; Santos, A. C. B.; Souza-Aguiar, E. F.; Dupont, J. *ChemSusChem* **2008**, *1*, 291–294.
- Ishida, T.; Watanabe, H.; Bebeko, T.; Akita, T.; Haruta, M. *Appl. Catal. A: Gen.* **2010**, *377*, 42–46.
- Astruc, D.; Lu, F.; Aranzas, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852–7872.
- Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374–4376.
- (a) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513–519; (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147–168.
- (a) Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992–4998; (b) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *98*, 508–524.
- Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729–6731.
- Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918–920.
- (a) Heck, R. F.; Nolley, J. P. *J. Org. Chem.* **1972**, *37*, 2320–2322; (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009–3066; (c) Martins, D. L.; Alvarez, H. M.; Aguiar, L. C. S.; Antunes, O. A. C. *Lett. Org. Chem.* **2007**, *4*, 253–255.
- (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467–4470; (b) Chinchilla, R.; Nájera, C. *Chem. Rev.* **2007**, *107*, 874–922.
- Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.
- (a) Roy, P. S.; Bagchi, J.; Bhattacharya, S. K. *Transit. Met. Chem.* **2009**, *34*, 447–453; (b) Zhang, Y.; Yu, J.; Liu, H. *J. Colloid Interface Sci.* **2007**, *313*, 503–510.
- Teranishi, T.; Miyake, M. *Chem. Mater.* **1998**, *10*, 594–600.
- Kappe, C. O. *Angew. Chem., Int. Ed.* **2004**, *43*, 6250–6284.
- (a) Nilson, P.; Olofson, K.; Larhed, M. *Top. Curr. Chem.* **2006**, *266*, 103–144; (b) Appukkuttan, P.; Eycken, E. V. *Eur. J. Org. Chem.* **2008**, 1133–1155.
- Souza, A. L. F.; Silva, L. C.; Oliveira, B. L.; Antunes, O. A. C. *Tetrahedron Lett.* **2008**, *49*, 3895–3898.
- Bradley, J. S.; Millar, J. M.; Hill, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 4016–4017.
- 2.5 g of PVP (40,000 Da) was added to 150 mL of methanol and stirred until the total solubilization of the polymer. To this solution, Pd(OAc)<sub>2</sub> was added and the resulting mixture was immersed in a pre-heated oil bath at 85 °C, under constant stirring for 3.0 h. Next, methanol was removed in a rotary evaporator and the Pd(0)-PVP nanoparticles were transferred quantitatively to a 25 mL volumetric flask.
- Martins, D.L.; Alvarez, H. M.; Aguiar, L. C. S. Suzuki reactions catalyzed by Pd(0)-PVP nanoparticles under conventional heating and ultrasound irradiation—the Letter has been submitted for reviewing.
- Li, Y.; Hong, X. M.; Collard, D. M.; El-Sayed, M. A. *Org. Lett.* **2000**, *2*, 2385–2388.
- In a typical experiment, a pyrex tube equipped with a magnetic stirrer was charged with 0.276 g of K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), 2.0 mL of ethanol, 0.22 mL of Pd(0)-PVP solution (0.1% Pd with respect to the iodobenzene mass), iodobenzene, (1.0 mmol) and phenylboronic acid (1.1 mmol). This tube was sealed and the content was subjected to the focused microwave irradiation at 300 W for 12 minutes (2.0 min ramping + 10 min) with 120 °C as the general final temperature. Then, the reaction mixture was cooled to room temperature and diluted with 8.0 mL of diethyl ether and stirred until the nanoparticles and the inorganics precipitation. Organic phase was analyzed by GC-MS (GCMS-QP2010PlusShimadzu). Afterward, the mixture was passed through a Celite pad, washed with ether, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent evaporated at reduced pressure. Products were analyzed by GC-MS and <sup>1</sup>H RMN.<sup>34</sup>
- Smith, G. B.; Dezeny, G. C.; Hugues, D. L.; King, A. O.; Verhoeven, T. R. *J. Org. Chem.* **1994**, *59*, 8151–8156.
- Biphenyl**: white solid *m/z* (EI) 154 (100), 153 (40), 128 (5), 102 (4), 76 (28), 51 (7). **2-phenyltoluene** *m/z* (EI) 168 (100), 153 (45), 128 (7), 63 (9), 51 (6). **4-phenyltoluene**: white solid *m/z* (EI) 168 (100), 162 (60), 152 (20), 91 (19), 63 (21), 51 (17); *d<sub>c</sub>* (50 MHz, CDCl<sub>3</sub>) 141.26, 138.46, 137.71, 129.56, 128.79, 127.07, 21.77. **4-methoxybiphenyl**: white solid—*d<sub>H</sub>* (200 MHz CDCl<sub>3</sub>) 7.6–7.22 (7H, m), 7.01 (2H, d, *J* 10 Hz), 3.87 (3H, s); *d<sub>c</sub>* (50 MHz, CDCl<sub>3</sub>) 159.2, 140.85, 133.78, 128.73, 128.17, 126.69, 114.25, 55.32; *n<sub>max</sub>* (KBr) 3303, 2908, 2836, 1606, 1523, 1488, 1251, 1053, 834, 760, 688 cm<sup>-1</sup>; *m/z* (EI) 184 (100), 169 (55), 141 (55), 115 (70), 89 (18), 76 (28), 63 (28). **4-nitrobiphenyl**: yellow solid—*d<sub>H</sub>* (200 MHz CDCl<sub>3</sub>) 8.25 (2H, d, *J* 8 Hz), 8.15 (2H, d, *J* 8 Hz), 7.65 (2H, d, *J* 6 Hz), 7.56–7.28 (3H, m); *d<sub>c</sub>* (50 MHz, CDCl<sub>3</sub>) 147.7, 147.1, 138.9, 129.2, 129.0, 127.9, 127.5, 124.2; *n<sub>max</sub>* (KBr) 3036, 3038, 1597, 1514, 1345, 853, 740 cm<sup>-1</sup>; *m/z* (EI) 199 (72), 169 (41), 152 (100), 127 (12), 115 (19), 76 (22), 46 (<2). **2-phenylfuran** *m/z* (EI) 144 (99), 115 (98), 89 (16), 63 (11), 51 (8). **4-fluorobiphenyl**: white solid—*d<sub>H</sub>* (200 MHz CDCl<sub>3</sub>) 7.6–7.10 (9H, m); *d<sub>c</sub>* (50 MHz, CDCl<sub>3</sub>) 163.75 and 161.30, 140.32, 137.44 and 137.38, 128.87 and 128.66, 128.82, 127.07, 115.15 and 114.77; *n<sub>max</sub>* (KBr) 3080, 3062, 3040, 1592, 1520, 1487, 1239, 1196, 1164, 837, 759, 687, 558, 486; *m/z* (EI) 172 (100), 146 (5), 133 (5), 85 (14). **3-phenylacetophenone**: yellow oil—*d<sub>H</sub>* (200 MHz CDCl<sub>3</sub>) 8.21 (1H, s), 7.96 (1H, d, *J* 8 Hz), 7.82 (1H, d, *J* 8 Hz), 7.67–7.30 (6H, m), 2.68 (3H, s); *d<sub>c</sub>* (50 MHz, CDCl<sub>3</sub>) 198.26, 141.84, 140.29, 137.75, 131.85, 129.26, 129.14, 129.02, 127.91, 127.29, 127.07, 26.84; *n<sub>max</sub>* (KBr) 3060, 3032, 1684, 1599, 1452, 1419, 1357, 1235, 803, 758, 697, 589. **4-phenylacetophenone**: white solid *m/z* (EI) 196 (50), 181 (100), 152 (60), 76 (75), 43 (36). **4-hydroxybiphenyl**: white solid *d<sub>H</sub>* (200 MHz CDCl<sub>3</sub>) 7.59–7.28 (7H, m), 6.93 (2H, d, *J* 10 Hz); *m/z* (EI) 170 (100), 141 (35), 115 (35). **2-phenylpyridine**: *m/z* (EI) 155 (100), 127 (19), 77 (21), 63 (5), 51 (15).