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# A highly stable and active magnetically separable Pd nanocatalyst in aqueous phase heterogeneously catalyzed couplings

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## Abstract

An active and stable magnetically separable Pd nanocatalyst was prepared and characterized. The nanocatalyst exhibited excellent activities and reusabilities in aqueous phase processes including the *O*-arylation of phenols and Sonogashira cross-coupling reactions. The proposed protocol features mild reaction conditions and an extraordinary simplicity and efficiency using NaOH as base in water.

**Keywords:** Magnetite nanoparticles, Palladium, Sonogashira cross-coupling reaction, *O*-arylation of phenol, Water.

## 25 Introduction

26 The design of novel magnetically separable systems has attracted a great deal of attention in  
27 recent times as an interesting alternative to improve the efficient separation of heterogeneous  
28 (nano)catalysts from solutions upon reaction completion by applying a simple magnet, providing  
29 improved reusability in the designed systems as well as enhanced properties depending on the  
30 selected approach.<sup>1</sup> The combination of this concept with that of nanocatalysis holds a significant  
31 potential in the development of innovative systems with improved activities and selectivities in  
32 different chemistries due to the inherent advantages of nanocatalysts. Nanomaterial-based catalysts  
33 can indeed provide high specific surface area to volume ratio which enhances the contact between  
34 reactants and catalyst support and consequently increases the catalytic activity.<sup>2</sup> Although their  
35 higher surface area affords more active sites, their large surface energies make them unstable, with  
36 a significant tendency to agglomerate. In this regard, magnetic nanoparticles (MAGNPs) can offer  
37 very promising properties as catalyst supports due to their large specific surface areas and magnetic  
38 properties, which facilitate the separation of the catalyst upon reaction completion.<sup>3,4</sup> MAGNPs have  
39 been designed and widely employed as novel magnetically separated catalysts in traditional metal  
40 catalyzed reactions,<sup>5</sup> organocatalysis, and enzymatic catalysis.<sup>6</sup> MAGNPs of Fe<sub>3</sub>O<sub>4</sub> are particularly  
41 robust, chemically stable as well as readily available with an inherent low toxicity and cost. Their  
42 preparation is also generally very simple, making them an efficient and important alternative to  
43 conventional heterogeneous catalyst supports (e.g. silica, alumina). Most importantly,  
44 MAGNPs-supported catalyst can be conveniently separated from the final reaction mixture upon  
45 completion by using an external magnet without filtration.<sup>7,8</sup> The subsequent functionalisation of  
46 MAGNPs with a range of different chemical entities including metal complexes, functional groups  
47 and metal nanoparticles (e.g. Pd) has allowed the design of highly active and selective systems in a  
48 variety of catalytic applications.<sup>5, 6, 9</sup>

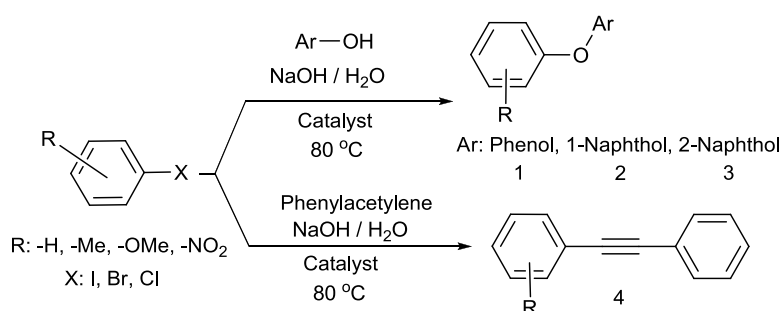
49 The Sonogashira reaction is probably one of the most straightforward and powerful  
50 transformations for the construction of C(sp<sup>2</sup>)-C(sp) bonds which can lead to conjugated acetylenic

51 compounds, an important class of molecules that have found applications in areas including natural  
52 products, pharmaceuticals, biologically active molecules, liquid crystalline materials, conducting  
53 polymers and molecular organic materials in nanomaterials.<sup>10</sup> The most commonly utilized catalytic  
54 systems for this reaction comprised palladium homogeneous catalysts including  $\text{PdCl}_2(\text{PPh}_3)_2$ ,  
55  $[\text{Pd}(\text{allyl})\text{Cl}]_2/\text{PPh}_3$ ,  $\text{PdCl}_2/\text{PPh}_3$ , or  $\text{Pd}(\text{PPh}_3)_4$  together with  $\text{CuI}$  as the co-catalyst and large amounts of  
56 amines as solvents or co-solvents.<sup>11</sup> However, the presence of  $\text{CuI}$  can result in the formation of  
57 diyne side products (via oxidative homocoupling of in situ generated  $\text{Cu(I)}$  acetylides)<sup>12</sup> and can also  
58 decrease the efficiency to cross-coupling products.<sup>13,14</sup> Furthermore, only limited success has to date  
59 been reported in the Sonogashira cross-coupling of alkynes with aryl chlorides. For these reasons,  
60 this field is still challenging and the development novel and greener protocols for the Sonogashira  
61 cross-coupling reaction are desirable. A range of homogeneous and heterogeneously catalyzed  
62 systems have been reported in past years with different results being obtained for a wide variety of  
63 conditions, catalysts and compounds. For more details, readers are kindly referred to recent  
64 literature reviews on the topic of the development of Sonogashira couplings in recent years.<sup>15</sup>

65 On the other hand, transition metal catalyzed coupling reactions of aryl halides and phenols  
66 (Ullman type reactions) are the most straightforward methods for the preparations of diaryl  
67 ethers.<sup>16</sup> Diaryl ethers are commonly found in a variety of important compounds including a number  
68 of pharmaceuticals, agrochemicals and polymers.<sup>17</sup> This linkage also appears in biologically active  
69 natural products such as mammalian hormone thyroxine and antibiotics.<sup>18</sup> In recent years, much  
70 progress has been achieved in  $\text{Cu/Pd}$ -catalyzed synthesis of diaryl ethers using aryl bromides and  
71 aryl iodides as aryl donors to couple with phenols providing excellent yields under mild conditions.<sup>19</sup>  
72 Additionally, other organometalloids such as organobismuth,<sup>20</sup> organotrifluoroborate reagents<sup>21</sup> and  
73 arylboronic acids<sup>22</sup> have extended this challenging field of research. However, in some cases the  
74 requirements of stoichiometric or greater quantities of copper at high temperatures (125-300 °C) in  
75 polar solvents (typically pyridine or DMF) compromised the environmental soundness of the  
76 protocol and often rendered it unsuitable for the construction of complex molecules.<sup>23</sup> Examples for

77 the coupling of aryl chlorides with phenols have also been rarely reported in the literature<sup>24</sup> but  
 78 there are some relevant examples of the use of magnetically separable Pd catalysts<sup>25</sup> and a Cu-free  
 79 system based on a charcoal supported Pd material.<sup>26</sup>

80 In this work, we present our approach based on the design of a water tolerant novel  
 81 Pd-containing magnetically separable system for C-O and C-C coupling reactions including the  
 82 Sonogashira coupling and the *O*-arylation of phenols in aqueous environments (Scheme 1).

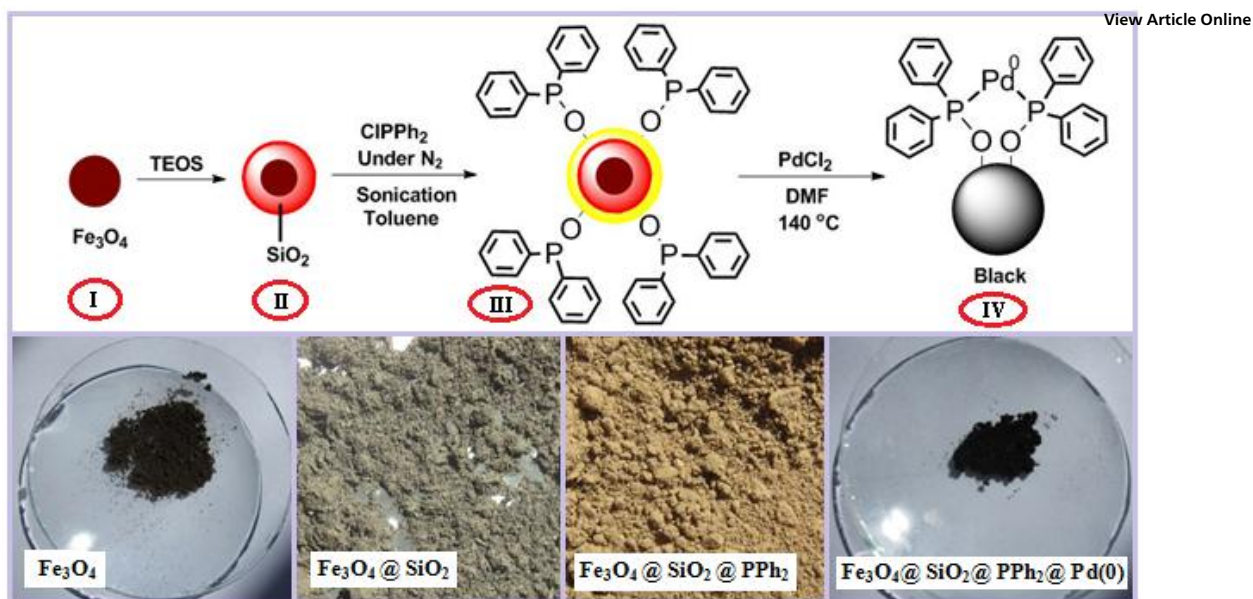


84 **Scheme 1.** *O*-Arylation of phenols and copper and amine-free Sonogashira reaction.

## 85 Results and discussion

86 **Results and discussion**

87  $\text{Fe}_3\text{O}_4$  particles (**I**) were prepared according to a previous report by Qu *et al.*<sup>9a</sup> and subsequently  
 88 coated with a layer of silica upon reaction with tetraethyl orthosilicate (TEOS). MAGNPS-Silica  
 89 core-shell materials (**II**) were then sonicated in toluene. Chlorodiphenylphosphine was immediately  
 90 added to the dispersed MAGNPS-Silica core-shell materials (**II**) under nitrogen atmosphere and the  
 91 intermediate material **III** was obtained. Finally, **III** was reacted with  $\text{PdCl}_2$  in DMF as solvent and  
 92 heated at  $140^\circ\text{C}$  to yield the final catalyst. A pictorial representation of the current synthesis has  
 93 been illustrated in Figure 1.

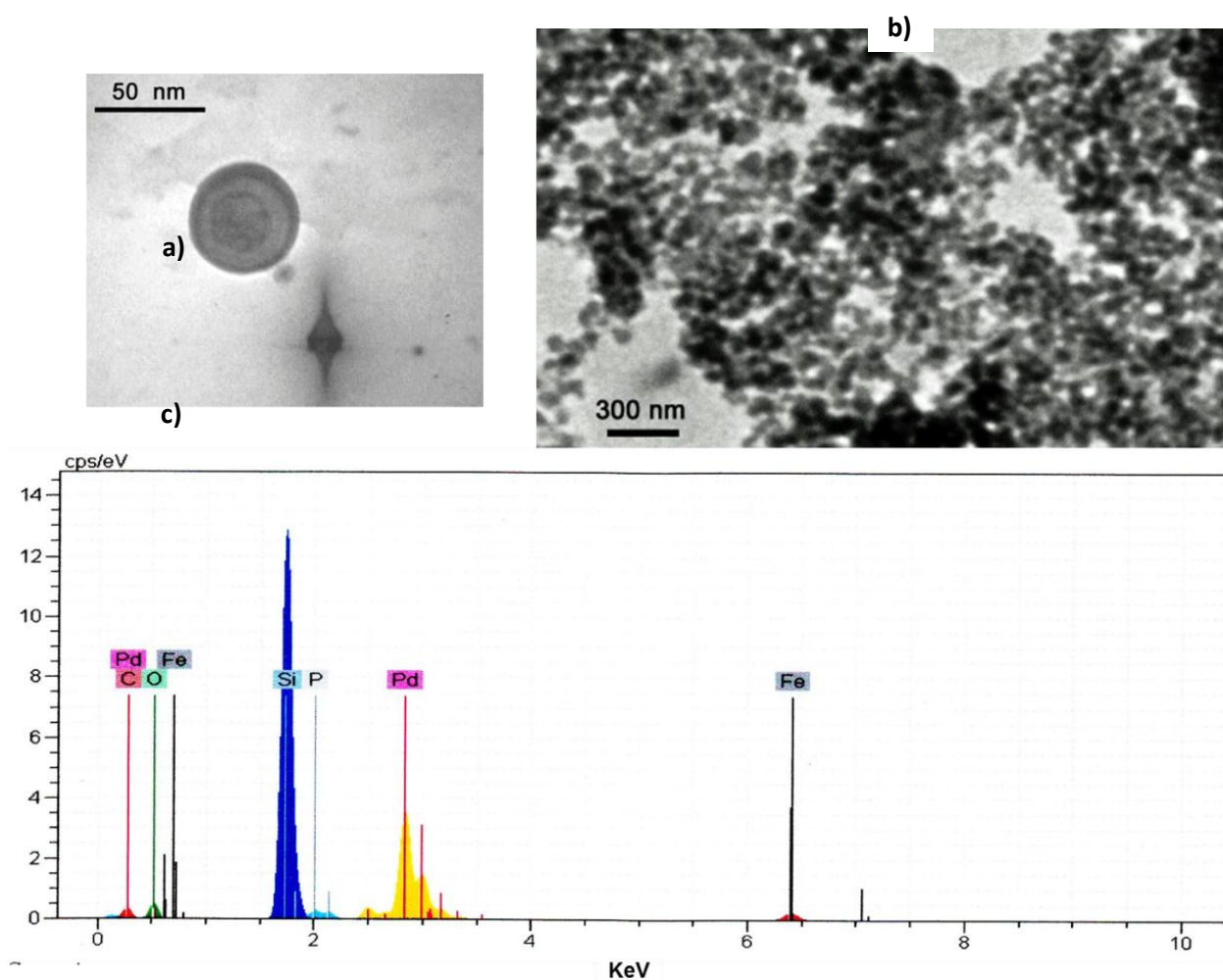


**Figure 1.** Stepwise preparation of the magnetically separable system

Transmission electron microscopy (TEM) images of the synthesized catalyst were recorded and depicted in Figure 2a and 2b. According to these images, the catalyst was approximately 50 nm in size (Figure 2a). EDX from the obtained nanomaterials (Figure 2a) provided the presence of the expected elements in the structure of the catalyst, namely iron, oxygen, silicon, phosphorus, carbon and palladium (Figure 2c).

The phase and purity of the different stepwise synthesized materials in this work (from magnetite  $\{\text{Fe}_3\text{O}_4\}$  to final catalyst  $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PPh}_2@\text{Pd}(0)\}$ ) have been determined by XRD patterns (shown in Figure 2). XRD pattern of  $\text{Fe}_3\text{O}_4$  exhibited peaks at  $2\theta = 18.3, 30.2, 35.6, 43.3, 53.6, 57.3, 62.8$  and  $74.2^\circ$  corresponding to diffraction lines (111), (220), (311), (400), (422), (511) and (440), respectively. The diffraction peaks in this pattern can be well indexed to the cubic spinel phase of  $\text{Fe}_3\text{O}_4$ , in good agreement with literature data (JCPDS 01-1111) (Figure 3a). Silica coated magnetite particles  $\{\text{Fe}_3\text{O}_4@\text{SiO}_2\}$  exhibited an XRD broadened pattern due to its non-crystalline nature at  $2\theta = 20-29^\circ$  and also  $30.2, 35.6, 43.3, 53.6, 57.3, 62.8$  and  $74.2^\circ$  which corresponded to a  $\text{Fe}_3\text{O}_4$  structure (Figure 3b). Upon addition of the phosphorus ligands to  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , a much broadened diffraction pattern to that of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  was observed (Figure 3c). Finally, the addition of palladium to

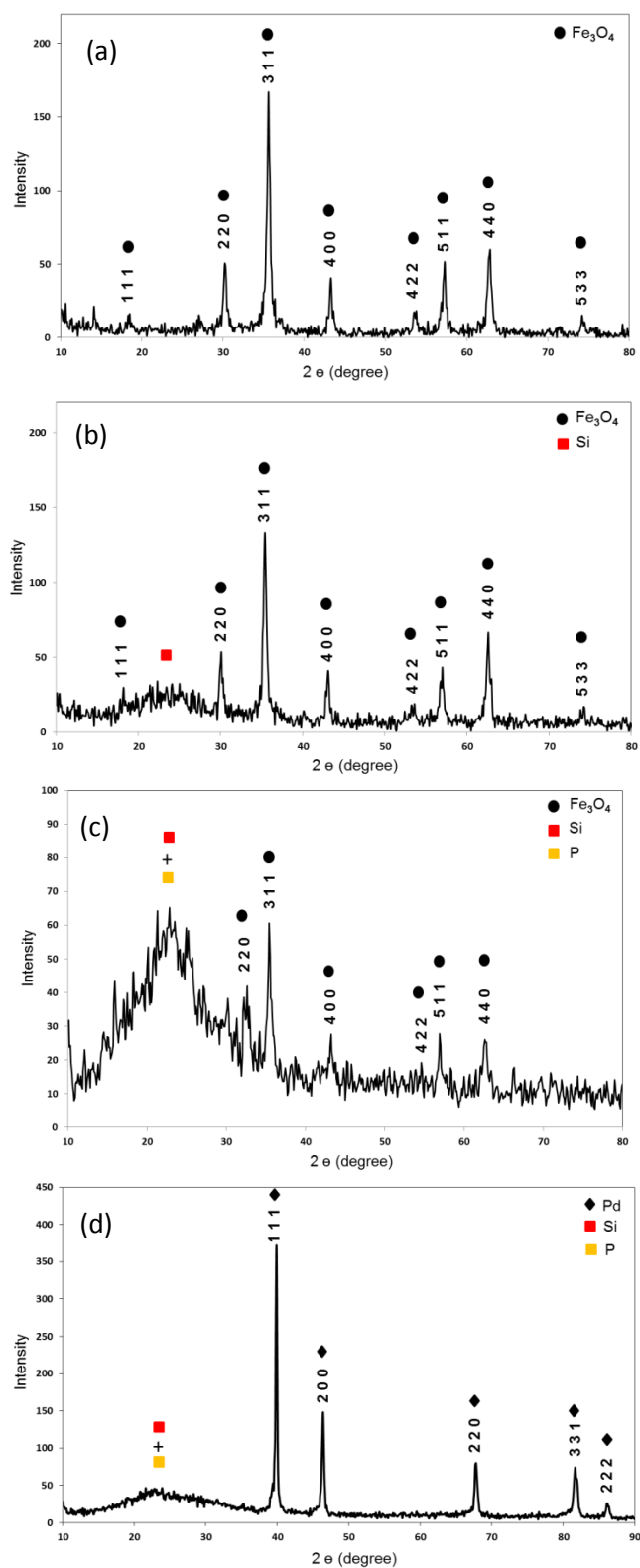
111  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PPh}_2$  gave rise to lines at  $2\theta = 39.9, 46.4, 67.7, 81.6$  and  $86.1^\circ$  oriented along (111),  
112 (200), (220), (311), and (222) diffraction lines, respectively. No peaks due to impurities were  
113 detected, indicating the high purity of the catalyst (Figure 3d). The lattice constant measured for the  
114 sample is  $a = 3.907 \text{ \AA}$ . The miller-indices and lattice constant of the catalyst  
115  $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PPh}_2@\text{Pd}(0)\}$  were found to be in agreement with values reported in the  
116 JCPDS 87-0643 card.



117  
118 **Figure 2.** (a) Core-shell structure of the catalyst (b) Transmission electron microscopy (TEM) of the catalyst (c)  
119 Energy-dispersive X-ray spectroscopy (EDX) of the catalyst

120

121



122 **Figure 3.** XRD patterns of (a)  $\text{Fe}_3\text{O}_4$  (b)  $\text{Fe}_3\text{O}_4@SiO_2$  (c)  $\text{Fe}_3\text{O}_4@SiO_2@PPh_2$  (d)  $\text{Fe}_3\text{O}_4@SiO_2@PPh_2@Pd(0)$

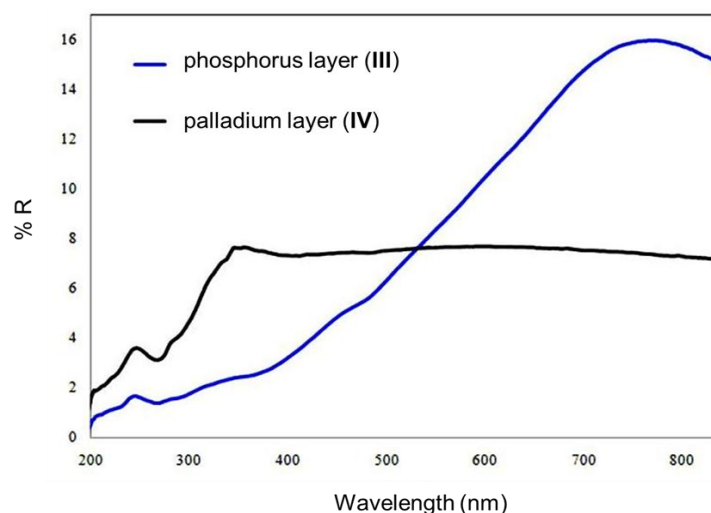
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124 The average crystallite size  $D$  for the designed  $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PPh}_2@\text{Pd}(0)\}$  catalyst was calculated  
125 using the Debye–Sherrer formula  $D = K\lambda / (\beta \cos \theta)$ , with  $\lambda$  being the X-ray wavelength,  $K$  is the  
126 Scherrer constant,  $\beta$  the peak width of half-maximum, and  $\theta$  is the Bragg diffraction angle.

127 The average size of the catalyst thus obtained from this equation was found to be ca. 52 nm, in good  
128 agreement to that observed in the transmission electron micrograph (TEM) studies. ICP/MS analysis  
129 of the catalyst showed that the Pd content was ca. 1.5 wt% Pd in the systems.

130 UV-DRS studies within the range of 200–850 nm were subsequently conducted to visualise the  
131 presence of Pd(0) in the materials. Figure 4 depicts the two curves obtained for materials III  
132 (phosphorus layer) and IV (supported Pd material). The final nanocatalyst  $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PPh}_2@\text{Pd}(0)\}$   
133 exhibited a broad band which could be attributed to Pd(0) in the structure, in good agreement with  
134 previous studies.<sup>27</sup> These findings were also corroborated in XPS investigations (Figure 5) in which  
135 two peaks could be observed related to Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  of Pd(0) at 335.2 and 340.2 eV.<sup>28</sup>

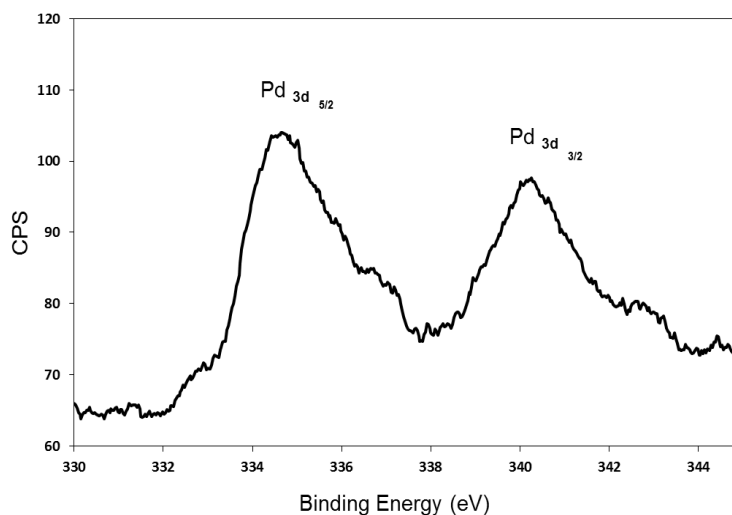


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137 **Figure 4.** UV-DRS spectra of the third layer (Blue) and fourth layer (Pd(0), Black) in the magnetite  
138 catalyst.

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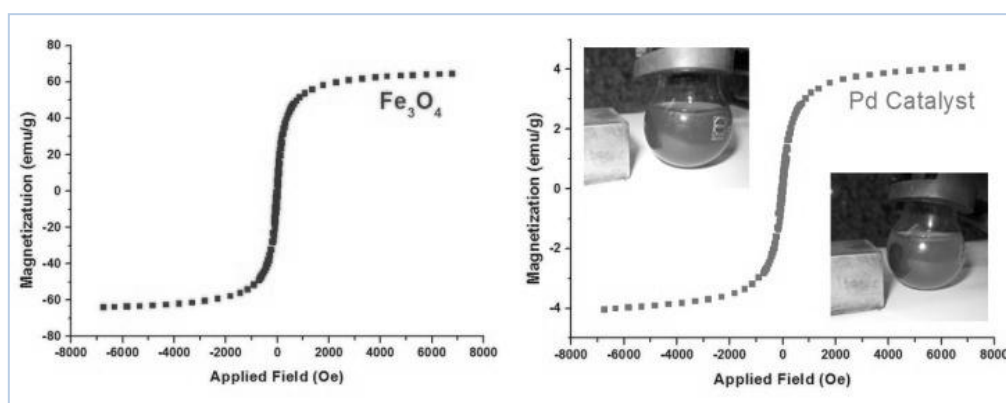


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142

**Figure 5.** XPS spectra of the catalyst.

143 Figure 6 shows the magnetic properties of the catalyst in comparison with  $\text{Fe}_3\text{O}_4$  that were  
 144 investigated at room temperature using a vibrating sample magnetometer (VSM). Based on  
 145 magnetization curves, the magnetization is saturated up to 4 emu/g at an applied field of 7000 Oe,  
 146 with an almost insignificant coercivity. The insert figures in the right image indicate the magnetic  
 147 properties of the catalyst allow a facile separation from the reaction mixture and subsequent  
 148 redispersion into solution without any appreciable aggregation in successive reaction runs.<sup>8b</sup>



149

**Figure 6.** The vibrating sample magnetometer (VSM) of the catalyst in comparison with  $\text{Fe}_3\text{O}_4$ .

151

152 The activity of the catalyst was subsequently investigated upon characterisation in the  
 153 Sonogashira reaction as well as in the *O*-arylation of phenols with less activated aryl halides  
 154 (X = Cl, Br). Starting with the Sonogashira coupling, the reaction of phenylacetylene with  
 155 bromobenzene was studied as test process for optimisation. Blank runs provided negligible activity  
 156 to the cross-coupling product in the absence of catalyst. The effect of catalyst loading in the reaction  
 157 was firstly investigated and different quantities of catalyst ranging from 0.002 to 0.010 g were  
 158 tested. The best results were obtained using 0.005 g catalyst (ESI). No significant improvement in  
 159 reaction results was observed by further increasing the quantity of catalyst in the reactions. A series  
 160 of bases including NaOH, K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> and Et<sub>3</sub>N were then screened, with optimum results  
 161 obtained using aqueous NaOH (up to 93% isolated yield at 80 °C, Table 1). No homocoupling product  
 162 was observed under the investigated conditions. Additionally, to study the effect of solvents in the  
 163 reaction, we examined a range of solvents in comparison with water (e.g. EtOH, DMF, DMSO, PEG  
 164 and toluene) for the model reaction. Gratifyingly, results obtained with alternative solvents to water  
 165 did not provide any improved yields under the investigated conditions (Table 2).

**Table 1.** Effect of different bases in the catalytic activity of {Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PPh<sub>2</sub>@Pd(0)} in the Sonogashira reaction at 80 °C<sup>[a]</sup>

Entry	Base	Amount of the Catalyst [g]	Time (min)	Isolated yield [%]
1	NaOH	0.005	33	93
2	K <sub>2</sub> CO <sub>3</sub>	0.005	43	89
3	Cs <sub>2</sub> CO <sub>3</sub>	0.005	35	93
4	Et <sub>3</sub> N	0.005	120	Trace
5	NaOH	---	240	---

[a] Reaction conditions: Bromobenzene (1mmol), Phenylacetylene (1 mmol), Water (5 ml) and 1.5 eq Base.

166 The scope of the reaction was subsequently expanded to several substrates including a range of  
 167 more challenging aryl chlorides (Table 3). Results summarized in Table 3 clearly demonstrate that  
 168 the protocol was amenable to various substrates (bromo- and chloro-derivatives) and substituents,  
 169 providing very good to excellent yields to products even in the case of less activated substrates (e.g.  
 170 1-chloro-4-methoxybenzene), with relatively short times of reaction in the range of 0.5 - 6 h.

**Table 2.** Effect of different solvents in the catalytic activity of {Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PPh<sub>2</sub>@Pd(0)} in the Sonogashira reaction at 80 °C<sup>[a]</sup>

Entry	Solvent	Temp [°C]	t [min]	Isolated yield [%]
1	H <sub>2</sub> O	80	33	93
2	EtOH	80	40	90
3	DMF	80	60	81
4	DMSO	80	60	83
5	PEG	80	80	69
6	Toluene	80	120	40

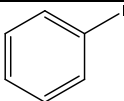
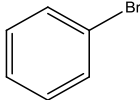
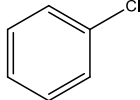
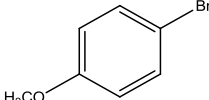
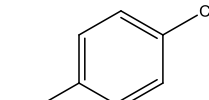
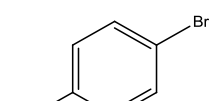
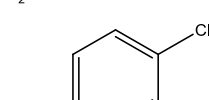
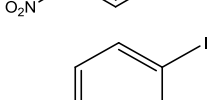
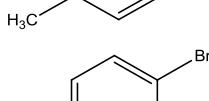
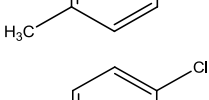
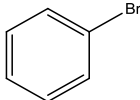
[a] Reaction conditions: Catalyst (0.005 g), Bromobenzene (1mmol), Phenylacetylene (1 mmol), 1.5 mmol NaOH and Solvent (5 ml).

172  
 173 The magnetically separable catalyst was subsequently tested in the *O*-arylation of phenols. The  
 174 reaction of bromobenzene with phenol was chosen as model reaction. Blank runs gave no  
 175 conversion to products in the absence of catalyst. Aqueous NaOH media was also found to be the  
 176 best choice (Table 4), selected as optimum, as poor activities were obtained in other solvents  
 177 (Table 5). Catalyst loading studies were also conducted (see ESI for full details). Under optimized  
 178 conditions (2 hours, 0.005 g of catalyst, 80 °C), quantitative conversion of bromobenzene to target  
 179 product was obtained, with a 90 % of isolated yield. Similarly to the Sonogashira reaction, the  
 180 versatility of the protocol was clearly proved when a range of aryl halides were successfully converted  
 181 to target products in very good yields in times of reaction in the 1.5-15 h range. Naphthols could also  
 182 be conveniently coupled to bromobenzene and chlorobenzene in good yields.

183 To investigate the truly heterogeneous nature of the protocols and thus any potential palladium  
 184 leaching, ICP/MS results proved no detected any palladium leaching in the filtrate (<0.05 ppm) upon  
 185 reaction completion, which indicates the high stability of the prepared catalyst. In order to know  
 186 whether the reaction takes place at the surface of solid Pd as a truly heterogeneous reaction or any  
 187 Pd-leached species act as homogeneous catalyst, the hot filtration test was conducted at 80°C in a  
 188 similar way to that previously recommended and reported.<sup>29</sup>

189

**Table 3.** Investigations of the scope of substrates in the Pd-catalyzed Sonogashira cross-coupling reaction

Entry <sup>[a]</sup>	Aryl Halide	Product	t [min]	Yield <sup>[b]</sup> (%)
1		<b>4a</b>	15	91
2		<b>4b</b>	33	93
3		<b>4c</b>	55	85
4		<b>4d</b>	180	95
5		<b>4e</b>	360	77
6		<b>4f</b>	25	90
7		<b>4g</b>	90	88
8		<b>4h</b>	65	93
9		<b>4i</b>	90	90
10		<b>4j</b>	250	70
11 <sup>[c]</sup>		<b>4b</b>	35	>90

[a] Reaction conditions: Aryl Halide (1 mmol), phenylacetylene (1 mmol), water (5 mL), NaOH (1.5 mmol) and catalyst (0.005 g, containing  $17 \times 10^{-4}$  g, 0.015 mmol of Pd)  
 [b] Yields of purified products.  
 [c] Hot filtration test (run corresponding to fresh substrates added to the recovered catalyst from entry 2 in a new reaction under identical conditions at 80°C).

**Table 4.** Effect of different bases in Pd-catalyzed O-arylation of phenols <sup>[a]</sup>

Entry	Base	Amount of the Catalyst [g]	t [h]	Isolated yield [%]
1	NaOH	0.005	2	90
2	K <sub>2</sub> CO <sub>3</sub>	0.005	3	90
3	Cs <sub>2</sub> CO <sub>3</sub>	0.005	2.5	90
4	Et <sub>3</sub> N	0.005	4	Trace
5	NaOH	---	6	---

[a] Reaction conditions: Bromobenzene (1mmol), Phenol (1 mmol), Water (5 ml) and 1.5eq Base, 80°C.

190  
191

192 In the light of these premises, the Sonogashira cross-coupling reaction for bromobenzene and  
 193 phenylacetylene in the presence of the catalyst in H<sub>2</sub>O at 80 °C was performed for 5 min and  
 194 then the catalyst was immediately removed from the reaction mixture with a magnet. In this  
 195 step, isolated yield of reaction product showed a 28% conversion to product. In the next step,  
 196 the reaction mixture (without the catalyst) was further reacted under stirring at 80 °C for 12  
 197 hours. After this time, the reaction did not progress any further (conversion ca. 30%).  
 198 Comparatively, the isolated catalyst from the hot filtration reaction provided >90% isolated  
 199 yield after 33 min when fresh reagents were added in a new reaction run (Table 3, entry 11).  
 200 These findings indicate that the reaction has mainly been catalyzed by the heterogeneous  
 201 system. A similar result was obtained in the case of the O-arylation of phenols (Table 6, entry  
 202 11).

203

**Table 5.** Effect of Different Solvents in the Pd- catalyzed O-arylation of phenols<sup>[a]</sup>

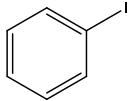
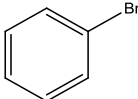
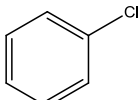
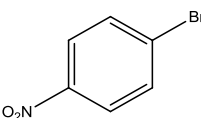
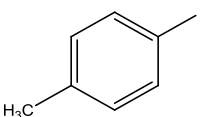
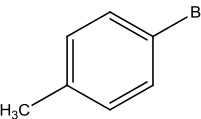
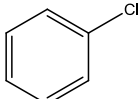
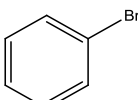
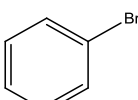
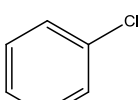
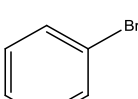
Entry	Solvent	Temp [°C]	t [h]	Isolated yield [%]
1	H <sub>2</sub> O	80	2	90
2	EtOH	80	2.5	88
3	DMF	80	3	85
4	DMSO	80	3	83
5	PEG	80	4	75
6	Toluene	80	5	30

[a] Reaction conditions: Catalyst (0.005 g), Bromobenzene (1mmol), Phenol (1 mmol), 1.5 mmol NaOH and Solvent (5 mL).

204

205

**Table 6.** Palladium-supported onto phosphorus silica magnetite catalyzed O-arylation of phenols.

Entry <sup>[a]</sup>	Aryl Halide	Ar-OH	Product	t [h]	Yield <sup>[b]</sup> [%]
1		Phenol	<b>1a</b>	1.5	93
2		Phenol	<b>1b</b>	2	90
3		Phenol	<b>1c</b>	3.5	83
4		Phenol	<b>1d</b>	1.5	88
5		Phenol	<b>1e</b>	5	90
6		Phenol	<b>1f</b>	7	80
7		1-Naphthol	<b>2a</b>	9	72
8		1-Naphthol	<b>2b</b>	7	70
9		2-Naphthol	<b>3a</b>	10	60
10		2-Naphthol	<b>3b</b>	15	60
11 <sup>[c]</sup>		Phenol	<b>1b</b>	2	>90

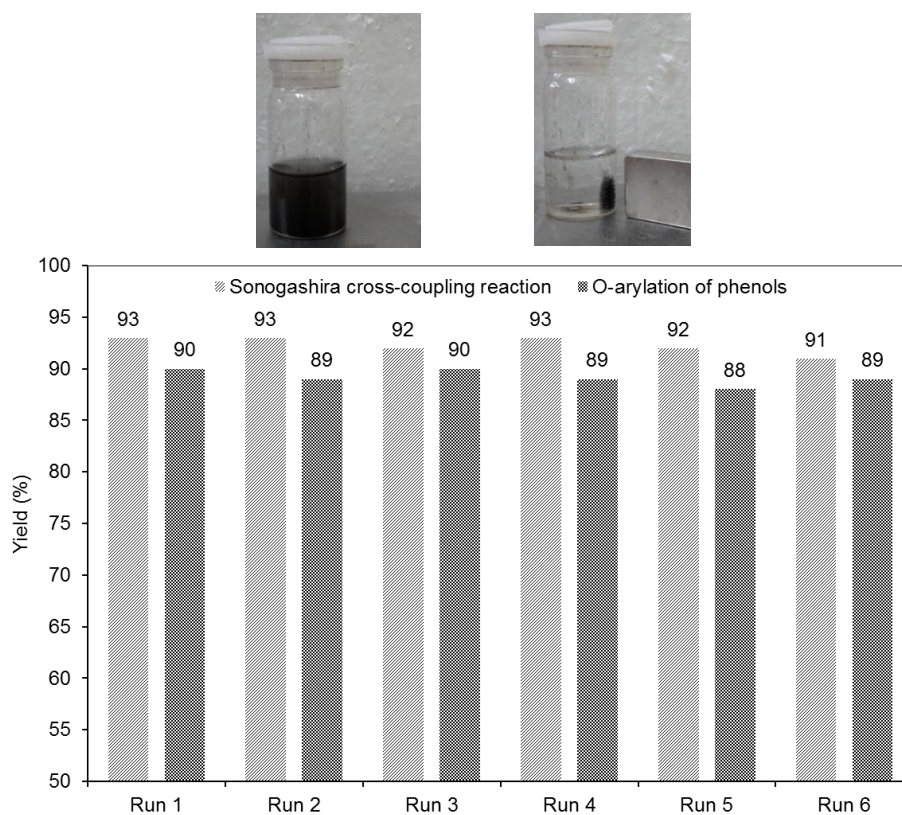
[a] Reaction condition: Aryl Halide (1mmol), Ar-OH (1mmol), water (5 mL), NaOH (1.5 mmol) and catalyst (0.005 g, containing  $17 \times 10^{-4}$  g, 0.015 mmol of Pd), 80°C.

[b] Yields of purified products.

[c] Hot filtration test (run corresponding to fresh substrates added to the recovered catalyst from entry 2 in a new reaction under identical conditions at 80°C).

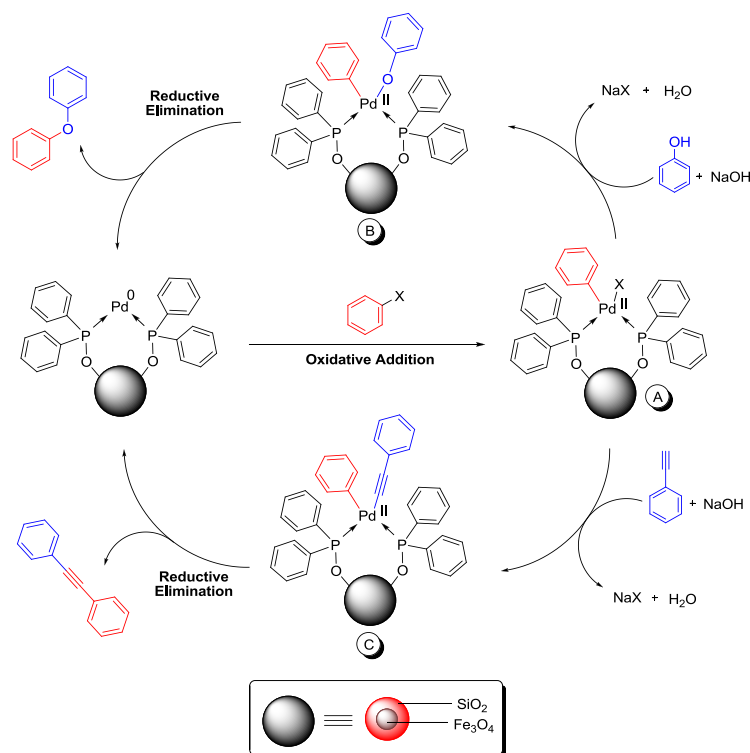
207 Apart from the magnetic isolation and separation of the catalyst upon reaction completion, the  
208 additional possibility to reuse the catalyst several cycles was also studied. Results depicted in Figure  
209 7 confirm that the magnetically separable Pd catalyst could be recycled and reused several times (up  
210 to 6 uses) without any appreciable loss of its initial catalytic activity regardless of the type of  
211 coupling.

212 A schematic representation of the proposed catalytic routes for both types of couplings has been  
213 summarized in Scheme 2. In a first step, the active palladium catalyst reacts with the aryl halide in an  
214 oxidative addition to produce Pd<sup>II</sup> intermediate (complex A) in both couplings. Such intermediate  
215 could react with phenylacetylene (Sonogashira reaction) or phenol (*O*-arylation) in the presence of  
216 NaOH as a base to render intermediates B or C. Finally, these complexes undergo reductive  
217 elimination to afford the expected products, regenerating the catalyst at the same time, which can  
218 be further used in another cycle.



219 **Figure 7.** The catalytic activity and reusability of the Pd-magnetically separable catalyst





220

221 **Scheme 2.** Proposed reaction mechanisms for the Pd-catalysed Sonogashira reaction (bottom part of the

222 mechanism) and O-arylation of phenols (top part of the mechanism).

223 **Conclusions**

224 A novel and efficient Pd-containing phosphorus silica magnetite [Fe<sub>3</sub>O<sub>4</sub> @ SiO<sub>2</sub> @ PPh<sub>2</sub> @ Pd (0)] has  
 225 been developed as highly active and stable nanocatalyst for aqueous phase coupling reactions,  
 226 namely the *O*-arylation of phenols with aryl halides [ArX (X= Cl, Br and I)] and the Sonogashira  
 227 coupling reaction under mild conditions. The salient features of the proposed methodology include  
 228 high efficiency, generality and simplicity which lead to high yields, a cleaner reaction profile and easy  
 229 recyclability of the highly stable heterogeneous catalyst by a simple magnet. The applicability of the  
 230 current systems is currently under investigation in related chemistries which will be reported in due  
 231 course.

232

233

## 234 **Experimental**

### 235 **Characterization methods**

236 The structure of the magnetite nanocatalyst was characterized by FT-IR, UV-VIS (DRS), XRD, XPS,  
237 EDAX, TEM and VSM analysis. NMR spectra were recorded with a Bruker Avance 250 spectrometer  
238 ( $^1\text{H}$ NMR 250 MHz and  $^{13}\text{C}$ NMR 62.9 MHz) in pure deuterated chloroform with tetramethylsilane  
239 (TMS) as the internal standard. Transmission electron microscope, TEM (ZEISS EM900) was also used  
240 to obtain TEM images. The crystallographic structure of synthesized materials was determined by an  
241 X-ray diffractometer ITAL STRUCTURES model APD2000 with applying Cu K $\alpha$  radiation wavelength  
242 (0.15405 nm), and at 2 $\theta$  range of 10° to 90°. XPS spectrum was acquired by VG and consisted of a  
243 twin anode XR3E2 x-ray source. Magnetic measurements were carried out in a vibrating sample  
244 magnetometer (VSM - 4 inch, Daghigh Meghnatis Kashan Co., Kashan, Iran) at room temperature.  
245 The elemental analysis of the catalyst using energy-dispersive X-ray spectroscopy technique (EDAX,  
246 Röntec QX2) was calculated to obtain direct data for the elemental composition of the layers and  
247 elementals. Infrared spectrum of layers is recorded by Perkin Elmer PE-1600-FTIR. Ultraviolet diffuse  
248 reflectance spectroscopy (UV-DRS, V-670, JASCO spectrometer) of the catalyst was recorded within  
249 the range of 200–900 nm. The metal content in the materials was determined using Inductively  
250 Coupled Plasma (ICP) in a Philips PU 70000 sequential spectrometer equipped with an Echelle  
251 monochromator (0.0075 nm resolution) couple with mass spectrometry. Samples were digested in  
252  $\text{HNO}_3$  and subsequently analysed by ICP at the SCAI in Universidad de Cordoba.

253

### 254 **Catalyst preparation**

255 Initially,  $\text{Fe}_3\text{O}_4$  (magnetite phase) was prepared by adding 3 mL  $\text{FeCl}_3$  (2 mol  $\text{L}^{-1}$  dissolved in 2 mol  $\text{L}^{-1}$   
256  $\text{HCl}$ ) to 10.33 mL double distilled water followed by a dropwise addition of 2 mL  $\text{Na}_2\text{SO}_3$  (1 mol  $\text{L}^{-1}$ ) in  
257 1 min under magnetic stirring. Upon solution color changing from red to light yellow, 80 mL  $\text{NH}_3\cdot\text{H}_2\text{O}$

258 solution ( $0.85 \text{ mol L}^{-1}$ ) were added under vigorous stirring. After 15 min, the magnetite precipitate (I)  
259 was washed to  $\text{pH} < 7.5$  by distilled water and separated with a magnet.<sup>8d, 9a</sup> To a mixture containing  
260 1 g of  $\text{Fe}_3\text{O}_4$  (I), 20 mL water, 80 mL ethanol, 3 mL ammonia and 3 mL tetraethyl orthosilicate (TEOS)  
261 were added under reflux to obtain MAGNPS-Silica core-shell materials (II).<sup>30</sup> 1 g of prepared particles  
262 (II) were sonicated in 5 mL toluene and then 2 mL of  $\text{ClPPH}_2$  was added under nitrogen atmosphere  
263 (to remove the produced HCl) for 4 hours to give III. The amount of active phase of phosphorus  
264 layer, measured according to a previously reported method,<sup>31</sup> was 4 mmol per gram of material.  
265 Finally, 1 g of compound III was reacted with 0.727 g of  $\text{PdCl}_2$  (4.2 mmol) in 8 mL DMF at  $140 \text{ }^\circ\text{C}$  for  
266 12 hours to give the final catalyst IV as a black powder.

### 267 **General procedure for the Sonogashira cross-coupling reaction**

268 A round-bottomed flask (10 mL) was charged with aryl halide derivatives (1 mmol) and  
269 phenylacetylene (1 mmol) in water (5 mL). NaOH (1.5 mmol) and the catalyst (0.005 g, containing  $17$   
270  $\times 10^{-4}$  g, 0.015 mmol of Pd) were then added and the final mixture connected to a reflux condenser.  
271 The reaction mixture was stirred for the required period of time at  $80 \text{ }^\circ\text{C}$  to reaction completion, as  
272 monitored by TLC. The final reaction mixture was then cooled at room temperature, the catalyst  
273 easily collected by means of a magnet to be reused in subsequent reactions and the residue of the  
274 reaction extracted with  $\text{Et}_2\text{O}$  ( $3 \text{ mL} \times 5 \text{ mL}$ ). The ethereal solution was evaporated to afford the  
275 desired product in an almost pure state. For further purification, has been performed by using  
276 column chromatography over silica gel that eluted with *n*-hexane/ethyl acetate (10:1) to give the  
277 pure biphenyl compounds.

### 278 **General procedure for the O-arylation of phenols**

279 A round-bottomed flask (10 mL) was charged with phenol derivatives (1 mmol) and aryl halides  
280 (1 mmol) in water (5 mL). NaOH (1.5 mmol) and the catalyst (0.005 g, containing  $17 \times 10^{-4}$  g, 0.015  
281 mmol of Pd) were then added and the final mixture connected to a reflux condenser. The reaction

282 mixture was stirred for 1.5-15 hours at 80 °C to reaction completion, as monitored by TLC, and then  
283 cooled at room temperature; the catalyst was removed from the solution using a magnet and the  
284 final residue of the reaction subsequently purified by column chromatography over silica gel using  
285 *n*-hexane/ethyl acetate (13:1).

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