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## Dendrimer-encapsulated Pd (0) nanoparticles immobilized on <sup>View Article Online</sup> nanosilica as a highly active and recyclable catalyst for the copperand phosphine free Sonogashira–Hagihara coupling reactions in water

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### Abstract

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This study demonstrates a new synthetic strategy for the preparation of porous SiO<sub>2</sub> for catalytic applications using natural and waste material from rice husk as the source of biosilica. Biogenic porous silica nanoparticles with a mean diameter of 45 nm were successfully prepared from rice husk (RH) biomass via a new multistep method. During the first step, sodium silicate is extracted from rice husk. Then, cetyl trimethylammonium bromide (CTAB), HCl, and HOAc were added into sodium silicate solution and the resulting mixture was sonicated. After the hydrothermal reaction, the collected samples were calcinated to get silica nanoparticles. Then, dendrimerencapsulated Pd (0) nanoparticles supported on nano-silica with surface amino groups were fabricated. These materials are prepared by sequestering palladium ions within dendrimers followed by chemical reduction to yield the corresponding zero-valent palladium nanoparticles. The synthesized nanostructures were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopic (XPS), Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA), dynamic light scattering (DLS), N<sub>2</sub> adsorption-desorption isotherm analysis, UV-Vis and elemental analysis. The morphologies of the catalyst were characterized using scanning (FE-SEM), and transmission electron microscopes (TEM). Also, its Pd content was determined by Inductively Coupled Plasma (ICP) analyzer. This catalytic system was used as an efficient catalyst for Sonogashira reaction of aryl halides with alkynes under copper and phosphine ligand-free conditions in water. The catalyst was regenerated for five cycles of reaction without any significant loss in its activity. Also, the analysis of the reaction mixture by the ICP technique showed the leaching of the catalyst was negligible.

## Keywords

Rice husk ash; Silica nanoparticles; Dendrimer-encapsulated nanoparticles; Sonogashira coupling reaction; Palladium nanoparticles; Reusable catalyst

## 1. Introduction

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Palladium catalyzed Sonogashira coupling reaction<sup>1-5</sup> and the hydroarylation of alkynes<sup>6,7</sup> are extremely powerful tools in organic synthesis and has been widely applied to various areas such as natural product synthesis, biologically active molecules and material science.<sup>1</sup>

<sup>14</sup> This reaction is generally co-catalyzed by Cu (I) and a phosphine ligand for palladium are also typically included.<sup>15-17</sup> An important side reaction encountered with the presence of a Cu (I) co-catalyst is the Glaser-type oxidative dimerization of the alkyne.<sup>18</sup> This side reaction is problematic when the terminal acetylenes are difficult to obtain. The use of other co-catalysts such as aluminum, boron, tin, zinc, AgOTf, and Ag<sub>2</sub>O have been developed to address this issue,<sup>19-21</sup> but additional steps are needed to make these agents. Furthermore many phosphine ligands are air sensitive and expensive, resulting in significant limits on their synthetic applications.<sup>22-25</sup>

Nowadays, environmental consciousness encourages more environmentally benign chemical processes. Along this line, industries have started implementing green chemistry practices such as waste prevention, using new heterogeneous catalysts and the use of less toxic solvents and reagents.<sup>26, 27</sup> Water is considered as an alternative to expensive, flammable and toxic organic solvents.<sup>28, 29</sup> The use of water as the reaction media has several benefits; water is a cheap and plentiful, nontoxic, nonflammable compound and is a green solvent. On the other hand, water with its chemical and physical properties imposes selectivity and reactivity in reactions conducted in this media which cannot be attained using organic solvents. In addition, in water, phase separation is facile because most of the organic compounds are not soluble in water therefore, can easily be separated from aqueous phase. However, the heat capacity of water is not favorable, which causes isolation and drying of the products sometimes difficult especially, when large scale operation is of concern.<sup>30-35</sup>

Dendrimers are a well-recognized class of precise macromolecules that should find multiple applications in energy conversion,<sup>36</sup> sensing,<sup>37-39</sup> molecular electronics,<sup>40, 41</sup> and catalysis.<sup>42</sup>

Biomedical applications of dendrimers include their use as contrast agents for magnetic resonance imaging,<sup>44</sup> as gene delivery vectors,<sup>45</sup> as antigen carriers and adjuvants in vaccine development,<sup>46</sup> and as targeting and drug delivery agents for diseases such as cancer.<sup>47-49</sup> Dendrimers are particularly well-suited for hosting metal nanoparticles for the following reasons: (1) the dendrimer templates themselves are of fairly uniform composition and nanoparticles are stabilized by encapsulation within the dendrimer, and therefore they do not agglomerate, <sup>50, 51</sup> (2) the dendrimer branches can be used as selective gates to control access of small molecules (substrates) to the encapsulated (catalytic) nanoparticles, <sup>52</sup> (3) the periphery can be tailored to control solubility of the hybrid nanocomposite and used as handles for facilitating linking to surfaces and other polymers.<sup>53</sup> Indeed, dendrimer composites represent an unusual case of the template and replica working in concert to exhibit functions that exceed those of the individual components.

Silica is a very important industrial material and is extensively used for a wide range of commercial applications such as catalyst supports, molecular sieves, resins, fillers in polymers, as well as in biomedical applications.<sup>54, 55</sup> In particular, silica nanoparticles with high surface area are of high interest to many key chemical applications.<sup>56, 57</sup> Development of non-toxic and rapid synthesis of low cost green catalysts from agricultural waste and biomass is growing field of interest. Rice husk ash (RHA) is a one of the major waste

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product of the rice milling industry and the silica content is known to be 94%.<sup>58</sup> Silicatice Online generated from RHA has been successfully used as a support material for various catalysis processes in the fine chemical industry.<sup>59, 60</sup> For these reasons, preparing an economically beneficial byproduct of silica nanoparticles from RH is an interesting topic. Therefore, in the present study, we report on the preparation of dendrimer-encapsulated Pd (0) nanoparticles immobilized on nanosilica (nSiO<sub>2</sub>-Dendrimer-Pd (0)) and their applications in the Sonogashira–Hagihara reaction without copper and phosphorous ligand in water under aerobic conditions, in which the dendrimer acted as a stabilizer and a recycling vehicle.

## 2. Results and discussion

Initially, silica nanoparticles with narrow size distribution and high surface area were synthesized from rice husks (RHs). Scheme1 presents the procedure for the preparation of nSiO<sub>2</sub> stepwise.



Scheme 1 A possibly low-cost, energy-efficient and green production of nano SiO<sub>2</sub> from RHs.

Then, we reported the synthesis, characterization and stability of dendrimer-encapsulated Pd (0) nanoparticles immobilized on nanosilica with surface amino groups. These materials were prepared by sequestering palladium ions within dendrimers followed by chemical reduction to yield the corresponding zero valent palladium nanoparticles (Scheme 2).

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Scheme 2 Process for preparation of noble nanosilica dendritic polymer supported palladium nanoparticles (nSiO<sub>2</sub>-Dendrimer-Pd (0)).

Fig. 1 shows the FT-IR spectra of  $nSiO_2$ ,  $nSiO_2-NH_2$ , MA1- $nSiO_2$ ,  $NH_2$  (1)-MA1- $nSiO_2$  and  $NH_2$  (2)-MA2- $nSiO_2$  nanoparticles in the 500–4000 cm<sup>-1</sup> wave number range. In Fig. 1a, the distinguishing band at 1000-1150 cm<sup>-1</sup> is owing to the Si–O stretching frequency in Si–O–Si structure. The absorption band for H–O–H bending vibration in water is at 1620–1650 cm<sup>-1</sup>. Also, the spectrum shows a broad band around 3400 cm<sup>-1</sup>, which is owing to the adsorbed water molecules. Fig. 1b shows the FT-IR spectrum of  $nSiO_2$ – $NH_2$  nanoparticles; the peaks at 1000–1150, 1400–1410 and 1543 cm<sup>-1</sup> are attributed to Si–O–Si (asymmetric stretching), C–N (stretching vibration) and N–H (bending), respectively. Also, the presence of several bands with medium intensity in 2808–2985 and 3165–3386 cm<sup>-1</sup> region are allocated to C–H stretching of the propyl group and N–H stretching. Complete conversion of amine ( $nSiO_2$ - $NH_2$ ) to ester (MA1- $nSiO_2$ ) and ester (MA1- $nSiO_2$ ) to amide ( $NH_2$  (1)-MA1- $nSiO_2$ ) was proven by FT-IR spectra. Fig. 1c shows the FT-IR spectrum of MA1- $nSiO_2$  nanoparticles, the presence of absorbance at 2810-2985, 1735, 1387, 1250-1310, 1165-1205 and 1000-1150 cm<sup>-1</sup> are attributed to CH (stretching), C=O (ester stretching), CH<sub>3</sub> (bending), C-O (stretching), C-N (stretching) and Si-O-Si, respectively.

From the FT-IR spectra presented in Fig. 1d and e, the absorption peaks at 1641. cp<sup>ijerdArticle Online</sup> belonged to the stretching vibration mode of amide peaks in NH<sub>2</sub>(1)-MA1-nSiO<sub>2</sub> and NH<sub>2</sub>(2)-MA2-nSiO<sub>2</sub>. Also, the presence of vibration bands in 3400 (O-H stretching), 3150-3380 (N-H stretching), 2810-2985 (C-H stretching), 1460-1470 (CH<sub>2</sub> bending), 1165-1205 (C-N) and 1000-1150 cm<sup>-1</sup> (Si-O-Si stretching) demonstrates the existence of NH<sub>2</sub> (1)-MA1-nSiO<sub>2</sub> and NH<sub>2</sub> (2)-MA2-nSiO<sub>2</sub> nanoparticles in the spectrum (Fig. 1d and e). For finding the completion time of the amidation step, which is occurring by refluxing MA2-nSiO<sub>2</sub> ester and bis(3-aminopropyl) amine mixture in the presence of 5 mL methanol, the reaction progresses were monitored by FT-IR every one hour to observe the disappearance of ester peak (1735 cm<sup>-1</sup>) and appearance amide peak in1641 cm<sup>-1</sup> (Fig. 1B). After disappearance of prominent ester peak, which had been happened after 4 hours, refluxing was terminated.



**Fig.1** (A) FT-IR spectra: (a)  $nSiO_2$ , (b)  $nSiO_2$ -NH<sub>2</sub>, (c) MA1- $nSiO_2$ , (d) NH<sub>2</sub>(1)-MA1- $nSiO_2$  and (e) NH<sub>2</sub>(2)-MA2- $nSiO_2$  nanoparticles. (B) FT-IR monitoring conversion of MA2- $nSiO_2$  to NH<sub>2</sub>(2)-MA2- $nSiO_2$ .

The evidence of formation of Pd (0) nanoparticles into the porous nanospheres of  $NH_2$  (2)-MA2-nSiO<sub>2</sub> was obtained from powder XRD analysis (Fig. 2). The diffraction peak which appeared at about 25° in all of the structures was attributed to the amorphous silica gel. This observation proved that no essential changes in topological structure of the silica gel occurred during the grafting process. The XRD pattern of the nSiO<sub>2</sub>-Dendrimer-Pd(0) catalyst is consistent with the metallic Pd (0) data in the literature.<sup>61,62</sup> Fig. 2b shows the (111), (200), (220) and (311) crystallographic planes of the Pd (0) nanoparticles. Among the peaks observed, the intensity of (111) peak is the strongest, indicating that this plane was predominant crystal facet in nSiO<sub>2</sub>-Dendrimer-Pd(0). The size of Pd (0) nanoparticles was also determined from X-ray line broadening using Scherrer equation and the half width of the intense (111) plane reflection and the average size was found to be below 4 nm. The

calculated size matched approximately the size observed from TEM image. The same result was also obtained for the XRD pattern of the catalyst after its use in the Sonogashira– Hagihara coupling reaction between *p*-bromoacetophenone and phenylacetylene for five cycles (Fig. 2c). This reveals the excellent stability and recovery of the catalyst.



**Fig. 2** XRD patterns of (a) nanosilicate, (b)  $nSiO_2$ -Dendrimer-Pd(0) and (c)  $nSiO_2$ -Dendrimer-Pd(0) after five cycles of reaction between *p*-bromoacetophenone and phenylacetylene.

TEM, FE-SEM and DLS of the prepared nanoparticles were shown in Fig. 3. TEM image of nanosilicate shown in Fig. 3a, as illustrated particle size have a good agreement with DLS and FE-SEM results. Fig. 3d and f represent FE-SEM and size histogram of SiO<sub>2</sub> nanoparticles. These nanoparticles have nearly spherical morphology with a mean diameter of 45 nm. Surface functionalization of nanosilicate with dendritic polymer supported palladium caused nanoparticles aggregation and their size raised to about 55 nm. In TEM image of these particles Pd nanoparticles clearly were observed (Fig. 3b).

Also, to confirm occurrence of aggregation, if any, TEM analysis of the reused catalyst was performed (Fig. 3c). After five repeated Sonogashira–Hagihara reaction cycles, we did not observe significant change in the morphology of the catalyst, but some Pd particles might have aggregated onto the surfaces of the matrices. This may take place through the leaching/re-deposition processes during the catalytic reactions.

To investigate the size distribution of these nanoparticles, particle size histograms were prepared for  $nSiO_2$ ,  $nSiO_2$ -Dendrimer-Pd(0) and  $nSiO_2$ -Dendrimer-Pd(0) after five cycles (Fig. 3 f-h respectively) by DLS analysis. This size distribution was centered at a value of 45 nm for nanosilicate. The size distribution of Pd nanoparticles in  $nSiO_2$ -Dendrimer-Pd(0) and  $nSiO_2$ -Dendrimer-Pd(0) after five cycles were located about 4 and 5 nm, indicating that some palladium nanoparticles might have aggregated upon immobilization on nanosilicate.

However, all these observations indicated that the dendritic polymer was a good how article ligand for palladium nanoparticles.

The resulting Pd supported nanoparticles were characterized by UV–Vis spectroscopy to ascertain the complete conversion of Pd(II) to Pd(0). This was supported by the disappearance of the peak at around 420 nm (Fig. 4A).

In order to ascertain the chemical oxidation state as well as to ensure the complete reduction, the samples were characterized by XPS analysis (Fig. 4B). XPS was used to study not only the coordination of macromolecular ligand and metal ions but also the chemical state of palladium presenting in the supported catalysts. The XPS spectrum of the  $nSiO_2$ -Dendrimer-Pd( $\Pi$ ) revealed the presence of palladium in a +2 oxidation state with binding energies 336.2 eV  $(3d_{5/2})$  and 341.4 eV  $(3d_{3/2})$  (Fig. 4Ba).<sup>63</sup> For further confirmation, XPS analyses of the  $nSiO_2$ -Dendrimer-Pd( $\Pi$ ) after reduction with NaBH<sub>4</sub> (fresh nSiO<sub>2</sub>-Dendrimer-Pd(0)) and recycled nSiO<sub>2</sub>-Dendrimer-Pd(0) catalyst (five recycles) have been carried out to probe the change in oxidation state of palladium (Fig. 4Bb,c). As shown, the peaks located around 335.7 eV and 340.9 eV were assigned to the Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$  level in the Pd(0) metallic form in agreement with literature report.<sup>64</sup> The binding energy clearly showed the fact that the Pd nanoparticles in our catalyst contained only Pd(0) species. The above phenomena supported that the Sonogashira cross-coupling reaction proceeded via the traditional  $Pd^{0/Pd^{2+}}$  cycle but not via the  $Pd^{2+/Pd^{4+}}$  mechanism. Also, it indicated that there was a good interaction to make Pd more stable on the surface of NH<sub>2</sub>(2)-MA2-nSiO<sub>2</sub> nanoparticles. It was also well recognized that amino groups can suppress the agglomeration of Pd nanoclusters, and enhance the catalytic efficiency of Pd nanoparticles.<sup>62</sup>

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**Fig. 3** TEM images of (a) nanosilicate, (b)  $nSiO_2$ -Dendrimer-Pd(0) and (c)  $nSiO_2$ -Dendrimer-Pd(0) after five cycles; FE-SEM images of (d) nanosilicate and (e)  $nSiO_2$ -Dendrimer-Pd(0) nanoparticles; Particle size distribution results for (f) nanosilicate, (g)  $nSiO_2$ -Dendrimer-Pd(0) and (h)  $nSiO_2$ -Dendrimer-Pd(0) after five cycles.

Thermal stability of  $nSiO_2-NH_2$ , MA1- $nSiO_2$ ,  $NH_2(1)-MA1-nSiO_2$  and  $NH_2(2)_TMA22$  is  $SiO_{2G}^{int}$  nanoparticles was analyzed by TGA and thermograms were presented in Fig. 4C, respectively. The TGA plots of samples depicted a two-step thermal decomposition. The first step of weight loss was attributed to the removal of physically adsorbed solvent and surface hydroxyl groups, whereas, the main weight loss in the second step was due to the removal of organic moieties on the surface.

The surface of catalysis covered with  $NH_2$  groups has hydrophilic property and therefore the catalyst can be dispersed in water for a long time. As show in Fig. 4D, the catalyst has a good disparity for 35 min and this property attributed to well its catalytic activity.



**Fig. 4** (A) UV–Vis spectra of  $Pd(OAc)_2$ ,  $nSiO_2$ -Dendrimer- $Pd(\Pi)$  and  $nSiO_2$ -Dendrimer-Pd(0); (B) (a) XPS spectra of  $nSiO_2$ -Dendrimer- $Pd(\Pi)$ , (b)  $nSiO_2$ -Dendrimer-Pd(0) and (c)  $nSiO_2$ -Dendrimer-Pd(0) after five reaction cycles; (C) Thermogravimetric analysis of (a)  $nSiO_2$ - $NH_2$ , (b) MA1- $nSiO_2$ , (c)  $NH_2(1)$ -MA1- $nSiO_2$  and (d)  $NH_2(2)$ -MA2- $nSiO_2$  nanoparticles; (D) Photographs of catalyst dispersion in water.

The TGA results were summarized in Table.1. The observed organic weight losses for  $nSiO_2-NH_2$ , MA1-nSiO<sub>2</sub>, NH<sub>2</sub>(1)-MA1-nSiO<sub>2</sub> and NH<sub>2</sub>(2)-MA2-nSiO<sub>2</sub> were 6.71%, 11.10%, 13.69% and 43.28%, respectively. On the basis of these values, the theoretical conversion was 42% for  $nSiO_2-NH_2 \longrightarrow MA1-nSiO_2$ , 77% for MA1-nSiO<sub>2</sub>  $\longrightarrow NH_2(1)-MA1-nSiO_2$  and 62% for  $NH_2(1)-MA1-nSiO_2 \longrightarrow NH_2(2)-MA2-nSiO_2$  (Table.1).

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Sample	ample Organic [wt%] <sup>a</sup>		Yield [%]	
nSiO <sub>2</sub> -NH <sub>2</sub>	6.710	1.15	-	
MA1-nSiO <sub>2</sub>	11.108	0.48	42	
NH <sub>2</sub> (1)-MA1-nSiO <sub>2</sub>	13.693	0.37	77	
NH <sub>2</sub> (2)-MA2-nSiO <sub>2</sub>	43.284	0.23	62	

 Table 1 Thermogravimetric analysis (TGA) results.

<sup>a</sup> Organic weight lose percent in range 150 °C to 600 °C

A summary of the elemental analysis and TGA data was included in Table 2. A good agreement was observed between elemental analysis and TGA data for these conversions.

**Table 2** TGA and elemental analysis (EA) results for the synthesis of nano silica dendritic polymer supported palladium nanoparticles.

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Sample		C(%)	H(%)	N(%)	Total(%) <sup>a</sup>
nSiO NH	TGA (wt%)	4.158	0.925	1.619	6.710
IISIO <sub>2</sub> -INH <sub>2</sub>	EA (wt%)	4.702	1.049	1.920	7.671
MA1 = SO	TGA (wt%)	6.375	0.966	0.676	8.016
	EA (wt%)	6.145	1.018	0.761	7.924
	TGA (wt%)	8.062	1.471	3.135	12.668
$NH_2(1)$ -MAT-IISIO <sub>2</sub>	EA (wt%)	7.613	1.456	3.788	12.857
	TGA (wt%)	25.314	4.491	9.844	39.649
$NH_2(2)$ -MA2-IISIO <sub>2</sub>	EA (wt%)	25.934	4.685	9.831	40.450
a  Total(%) = C% + H% + N%					

 $N_2$  adsorption-desorption isotherm analysis provided information on the specific surface area and porosity of the prepared samples. The specific surface area values, the average pore diameter (according to BJH method) and total pore volume were listed in Table 3. According to the BET isotherm, the active surface area of  $nSiO_2$ ,  $NH_2(1)$ -MA1- $nSiO_2$ ,  $NH_2(2)$ -MA2- $nSiO_2$ ,  $nSiO_2$ -Dendrimer-Pd(0) and catalyst after five recycling was estimated at 430.5, 380.1, 350.2, 347.2 and 340.8 m<sup>2</sup>/g, respectively (Table 3).

Catalyst/Cycle Specific surface Pore volume Average pore Entry  $(cm^3/g)$ area  $(m^2/g)$ reusability radius (nm) 1 nSiO<sub>2</sub> 430.5 0.771.81 2  $NH_2(1)$ -MA1-nSiO<sub>2</sub> 380.1 0.71 1.85 3 NH<sub>2</sub>(2)-MA2-nSiO<sub>2</sub> 350.2 0.65 1.92 347.2 0.62 1.95 4 nSiO<sub>2</sub>-Dendrimer-Pd(0)  $nSiO_2$ -Dendrimer-Pd(0)/(5)<sup>b</sup> 340.8 0.57 2.00 5

**Table 3** BET results of  $nSiO_2$ ,  $NH_2(1)$ -MA1- $nSiO_2$ ,  $NH_2(2)$ -MA2- $nSiO_2$ ,  $nSiO_2$ -Dendrimer-Pd(0) and  $nSiO_2$ -Dendrimer-Pd(0) after five cycles.<sup>a</sup>

<sup>a</sup> Calculated by the BJH method.

<sup>b</sup> BET surface areas for the catalyst after 5 times recycling.

Determination of Pd content was performed by Inductively Coupled Plasma (ICP) analyzer. According to the ICP analysis, the Pd content in the  $nSiO_2$ -Dendrimer-Pd(0) nanoparticles was determined to be 0.17 mmol/g. This amount showed that the catalyst has a high ability to accommodate palladium nanoparticles. To explore the catalytic activity, the

Sonogashira–Hagihara cross coupling reaction of aryl halides with alkynes  $was_{0}$  conducted  $S_{5G}$  with these nanoparticles (Scheme 3).



Scheme 3 Sonogashira–Hagihara coupling in the presence of nSiO<sub>2</sub>-Dendrimer-Pd(0).

Initial studies were performed on the reaction of *p*-bromoacetophenone with phenylacetylene as a model reaction and the effects of different solvents, temperature, bases and amount of catalyst were studied (Table 4). The best result was achieved by carrying out the reaction of *p*-bromoacetophenone and phenylacetylene with mole ratio 1:1.1 in the presence of 0.085 mol% of Pd in H<sub>2</sub>O under reflux condition (Table 4, entry 17). Use of a higher amount of catalysts did not improve the yield (Table 4, entries 11, 12) while a decrease in the amount of catalyst provided a lower yield of the corresponding product (Table 4, entries 9 and 10). In the absence of catalyst, the reaction did not proceed even after a long reaction time (24 h) (Table 4, entry 8). Furthermore, the effect of solvent was examined by running the model reaction in common organic solvents such as THF, H<sub>2</sub>O, EtOH, MeOH, EtOH/H<sub>2</sub>O under reflux conditions, and DMF/H<sub>2</sub>O and DMF at 100 °C (Table 4, entries 17-23) and excellent yields of the product were observed in H<sub>2</sub>O (Table 4, entry 17).

The effect of temperature was studied by carrying out the model reaction at different temperatures in  $H_2O$  in the presence of  $Et_3N$  and the best results were obtained under reflux conditions (Table 4, entry 17).

Also, the coupling of *p*-bromoacetophenone and phenylacetylene was carried out in  $H_2O$  with the nSiO<sub>2</sub>-Dendrimer-Pd(0) catalyst under reflux conditions in the presence of 2 equiv of different bases. The most effective base proved to be triethylamine as seen in the representative results summarized in Table 4. The coupling with K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, K<sub>3</sub>PO<sub>4</sub>, piperidine, NaOAc and Cs<sub>2</sub>CO<sub>3</sub> gave 1,2-diphenylethyne was resulted in 57%, 48%, 21%, 39%, 87%, 81% and 61% yield, respectively (Table 4, entries 1-7).

Entry	Solvent	Catalyst	Base	Temp.	Time	Yield <sup>b</sup>
		(mol% Pd)		(°C)	(h)	(%)
1	H <sub>2</sub> O	0.085	K <sub>2</sub> CO <sub>3</sub>	Reflux	4	57
2	$H_2O$	0.085	$Na_2CO_3$	Reflux	4	48
3	$H_2O$	0.085	NaOH	Reflux	4	21
4	$H_2O$	0.085	$K_3PO_4$	Reflux	4	39
5	$H_2O$	0.085	Piperidine	Reflux	4	87
6	$H_2O$	0.085	NaOAc	Reflux	4	81
7	$H_2O$	0.085	$Cs_2CO_3$	Reflux	4	61
8	$H_2O$	0.0	Et <sub>3</sub> N	Reflux	24	0
9	$H_2O$	0.04	Et <sub>3</sub> N	Reflux	10	48
10	$H_2O$	0.06	Et <sub>3</sub> N	Reflux	6	55
11	$H_2O$	0.12	Et <sub>3</sub> N	Reflux	4	92
12	$H_2O$	0.17	Et <sub>3</sub> N	Reflux	4	94
13	$H_2O$	0.085	Et <sub>3</sub> N	R.T	12	34
14	$H_2O$	0.085	Et <sub>3</sub> N	60	12	48
15	$H_2O$	0.085	Et <sub>3</sub> N	80	6	81
16	$H_2O$	0.085	Et <sub>3</sub> N	90	4	85
17	$H_2O$	0.085	Et <sub>3</sub> N	Reflux	4	94
18	THF	0.085	Et <sub>3</sub> N	Reflux	6	16
19	DMF	0.085	Et <sub>3</sub> N	100	3	93
20	EtOH	0.085	Et <sub>3</sub> N	Reflux	6	82
21	MeOH	0.085	Et <sub>3</sub> N	Reflux	6	57
22	$EtOH/H_2O(1/1)$	0.085	Et <sub>3</sub> N	Reflux	6	89
23	$DMF/H_2O(1/1)$	0.085	Et <sub>3</sub> N	100	3	94

**Table 4** Optimization of the reaction parameters such as amount of catalyst, solvent, temperature  $p_{DC4}^{\text{nline}}$  and base on the reaction of *p*-bromoacetophenone with phenylacetylene<sup>a</sup>

<sup>a</sup>Reactions were run in 2 mL solvent with 1 mmol *p*-bromoacetophenone, 1.1 mmol phenylacetylene, and 2 mmol base.

<sup>b</sup> Isolated yield.

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With these results in hand, we then decided to investigate the effect of reagent molar ratio on the efficiency of reaction. Interestingly, in this study, it was found that increasing the phenylacetylene: *p*-bromoacetophenone molar ratio from 1.1:1 to 1.2:1 or 1.4:1 resulted in a significant drop in reaction rate (Fig. 5a). This finding might be related to the formation of polymer or oligomer by-products from excess of phenylacetylene used in the reaction mixture that would be deposited on the surface of the nanoparticles, which was able to diminish the activity of the immobilized palladium catalyst.<sup>66, 67</sup>

The results of the interactions between three independent variables (time, temperature, catalyst amount) and dependent variable (reaction yield) were shown in Fig. 5b, c, d.



**Fig. 5** (a) Effect of phenylacetylene: *p*-bromoacetophenone molar ratio on reaction conversions; (b) The interaction effect of time and catalyst amount on reaction yield; (c) The interaction effect of temperature and catalyst amount on reaction yield; (d) The effects of time and temperature on reaction yield.

Employing the optimized reaction conditions, a range of aryl iodides, bromides and chlorides with various substituent groups were examined in the Sonogashira coupling reaction in the presence of  $nSiO_2$ -Dendrimer-Pd(0) catalytic system in water. The results were summarized in Table 5. As expected, the reaction of aryl iodides bearing electron donating groups went to completion in longer reaction times (Table 5, entries 2-5) than those with electron-withdrawing groups (Table 5, entries 6-10). The coupling reaction of phenyl acetylene with both electron-releasing and electron withdrawing aryl bromides afforded the desired products in high yields (Table 5, entries 12-27). Among the substrates, sterically hindered 2-bromoanisole, 2-bromotoluene and 2-bromobenzaldehyde were also successfully coupled with phenylacetylene (Table 5, entries 13, 16 and 21). Also, 3-bromopyridine, 5-bromopyrimidine and 3-bromothiophene led to the corresponding arylated alkynes in good yields (Table 5, entries 25-27). Although aryl chlorides were not as reactive as iodide and bromide counterparts but they underwent Sonogashira reaction in the present of nSiO<sub>2</sub>-Dendrimer-Pd(0) nanoparticles and provided the title products in medium to high yields (Table 5, entries 28-33). Moreover, aryl iodides, bromides and chlorides also underwent Sonogashira coupling reactions with 1-octyne under similar conditions to afford the corresponding products in high yields (Table 5, entries 34-39). Also, 1-ethynyl-1cyclohexanol reacted efficiently with chlorobenzene and provided excellent yield of the desired product (Table 5, entry 40).

**Table 5** Sonogashira–Hagihara coupling of different aryl halides with alkynes in wate  $\frac{1}{10.1059}$  ( $\frac{1}{10.1059}$ ) ( $\frac{1}{10.1059}$ 

R	X + =	$-R_1 \xrightarrow{\text{nSiO}_2\text{-Dendrimer-Pd}(0)} Et_3N, H_2O, 90\text{-}100^{\circ}C \rightarrow$	R			R <sub>1</sub>
Entry	Aryl halide	Product	Time (h)	Yield (%) <sup>b</sup>	TON <sup>c</sup>	$TOF (h^{-1})^d$
1			1	96	1130	1130
2	MeO	MeO-	2	91	1070	535
3	Me	Me	2	93	1094	547
4	но	но-	2	88	1035	517.5
5			2	90	1058	529
6	MeOC	MeOC-	1	94	1106	1106
7	F <sub>3</sub> CI	F <sub>3</sub> C	1	93	1094	1094
8	Cl		1.5	89	1047	698
9	Br	Br-	2	87	1024	512
10	O <sub>2</sub> N I		0.75	97	1141	1521
	I	Ph				
11			2	92	1082	541
12	Br		4	94	1106	276.5

13	OMe Br	OMe	7	88	DOI: 10.103 1035	View Article Onli 19/C5CY01455 148
14	MeO	MeO-	8	85	1000	125
15	Me	Me-	8	83	976	122
16	Me Br	Me	6	86	1012	169
17	HO	но-	8	82	964	120.5
18	MeOC	MeOC	4	94	1106	276.5
19	F <sub>3</sub> C Br	F <sub>3</sub> C	3	92	1082	361
21	CHO Br	CHO	4	90	1058	265
22	Cl-Br		6	91	1070	178
23	NC Br		4	93	1094	273.5
24	O <sub>2</sub> N Br		3	95	1118	373
25	N= Br		8	90	1059	132
26	N N Br		8	92	1082	135
27	S Br	$s \rightarrow = \langle  \rangle$	10	90	1058	106
28			12	78	918	76.5

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$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	2
$40 \qquad \qquad$	5.5

<sup>a</sup> Reactions were performed with ArX (1 mmol), alkyne (1.1 mmol),  $Et_3N$  (2 mmol), catalyst (0.085 mol% of Pd) in H<sub>2</sub>O (2 mL) under reflux conditions.

<sup>b</sup> Isolated yield.

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<sup>c</sup> TON= mmol of products/mmol of catalyst.

<sup>d</sup> TOF= TON/time.

To test the worth of the present work in comparison with some of reported catalysts in the literature, the data on Sonogashira coupling reaction between iodobenzene with phenylacetylene was summarized in Table 6, these study appeared  $nSiO_2$ -Dendrimer-Pd(0) performs its catalytic role in lower amount , shorter reaction time and give higher yield of the desired product in water as non-toxic solvent. Using Dendrimer-encapsulated Pd(0) was led to higher yield and lower reaction time in compare to Dendrimer-encapsulated Pd(0)

supported on silica (Table 6, entries 11,12). Also, from Table 6, it was seen that present of the online catalyst exhibited higher yields and higher turnover numbers (TOFs) compared to the other reported system (Entry 13).

**Table 6** Comparison of catalytic activity of the present catalyst with the other reported catalysts in the Sonogashira coupling reaction between iodobenzene and phenylacetylene.

Entry	Catalyst	Conditions	Time (h)	Yield (%)	TON	TOF ( $h^{-1}$ )	Ref.
1	Pd(0)/MCoS-1 (0.2 mol% Pd)	Et <sub>2</sub> N/H <sub>2</sub> O/90 °C	6	94	470	78	[68]
2	Pd-LHMS-3 (0.524 mol% Pd)	Hexamine/H <sub>2</sub> O/Reflux	10	85	162	16.2	[69]
3	Si-PVI-Pd (0.5 mol% Pd)	DMF/K <sub>2</sub> CO <sub>3</sub> /120 °C	1.25	93	186	148.8	[70]
4	NHC-palladium complex (1 mol% Pd)	DMSO/K <sub>3</sub> PO <sub>4</sub> /100 °C	1	81	81	81	[71]
5	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /Schiff base/Pd(II) (0.5 mol%)	DMF/K2CO3/90 °C	1	93	186	186	[72]
6	I-Pd (300 mg, 0.1 mmol Pd)	CH <sub>3</sub> CN/Et <sub>3</sub> N/Reflux	24	80	8	0.33	[73]
7	Nano Pd@Fe <sub>3</sub> O <sub>4</sub> (1 mol% Pd)	DMF/piperidine/110 °C	24	83	83	3.46	[74]
8	Pd/MgLa (1 mol% Pd)	DMF/ Et <sub>3</sub> N/80 °C	10	90	90	9	[75]
9	Nano Pd/AT-Mont (0.07 mol%)	CH <sub>3</sub> CN, Et <sub>3</sub> N, 82 °C	3	90	1285	428	[76]
10	[PdCl(SeCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> )] <sub>2</sub> (3 mol% Pd)	Dioxane/ Et <sub>3</sub> N/100 °C	12	92	31	2.6	[77]
11	Dendrimer-encapsulated Pd(0) (0.25 mol% Pd)	$Et_3N/~H_2O/90~^{o}C$	1.5	93	372	248	This work
12	Dendrimer-encapsulated Pd(0) supported on silica (0.5 mol% Pd)	Et <sub>3</sub> N/ H <sub>2</sub> O/90 °C	2.5	84	168	67.2	This work
13	nSiO <sub>2</sub> -Dendrimer-Pd(0) (0.085 mol% Pd)	Et <sub>3</sub> N/ H <sub>2</sub> O/90 °C	1	96	1130	1130	This work

The reusability and recovery of the catalyst are important issues, especially when the reactions use solid catalysts. For the recycling study, Sonogashira coupling reactions were performed separately between iodobenzene (1 mmol) and *p*-bromoacetophenone (1 mmol) with phenylacetylene (1.1 mmol) in the presence of the catalyst (0.085 mol% of Pd) and triethylamine (2 mmol) in water (2 mL) under reflux conditions at 90 and 100 °C respectively as test models (Fig. 6a). After the first cycle of the reaction, the catalyst was recovered by centrifugation and then washed thoroughly with diethyl ether, followed by water to remove triethylamine and finally by dichloromethane. Then, the recovered catalyst was dried under vacuum at 70 °C. The performance of the recycled catalyst in Sonogashira coupling reaction up to six successive runs was shown in Fig. 6a. These bar diagrams clearly suggest that the desired products were obtained in high yields without distinct deterioration in catalytic activity. We also decided to perform the kinetic studies to estimate the reaction rates at different cycles. For this purpose we selected the reaction of pbromoacetophenone and phenylacetylene in the presence of  $nSiO_2$ -Dendrimer-Pd(0) under optimized conditions to evaluate the reactivity of catalyst at different time at every cycle. The results were summarized in (Fig. 6b).



**Fig. 6** (a) Recycling of the catalyst in Sonogashira coupling reaction of iodobenzene (black) and p-bromoacetophenone (gray) with phenylacetylene; (b)The kinetics plot of Sonogashira coupling reaction of p-bromoacetophenone with phenylacetylene at different runs.

To determine the exact Pd species responsible for the observed reactions and to measure the extent of Pd leaching after the reactions, we used the hot filtration test.<sup>78-80</sup> In a typical experiment, *p*-bromoacetophenone (1.0 mmol), phenylacetylene (1.1 mmol), catalyst (0.085 mol%), triethyl amine (2.0 mmol) and water (2 mL) were taken in a round-bottom flask and stirred under reflux conditions at 100 °C for 1.5 h. After cooling down the reaction mixture to room temperature, the solid was separated by centrifugation and washed with dichloromethane (10 mL). The conversion of *p*-bromoacetophenone to the corresponding product was measured by GC to be 51%. Then, the organic phase was removed under vacuum and the reaction was carried out at 100 °C. Continuation of the reaction showed 54% conversion (GC) after 12 h. This result showed that the amount of leaching of the catalyst into the reaction mixture should be low and confirmed that the catalyst acts heterogeneously in the reaction.

To measure the degree of leaching of Pd from the heterogeneous catalyst, the catalyst was removed by centrifugation after the reaction of *p*-bromoacetophenone with phenylacetylene was completed and the palladium content of the filtrate was determined by ICP. The amount of palladium leaching after the first run was determined to be only 0.3%, and after five repeated recycling was 2.8%, which showed the average amount of leaching of palladium per cycle was around 0.4%.

#### 3. Conclusion

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In summary, it was reported here a novel route for isolation of silica components from rice husk and synthesized a novel kind of dendrimer-encapsulated Pd(0) nanoparticles immobilized on nanosilica with surface amino groups. The surface and morphological of these nanoparticles were evaluated. The FT-IR and TGA results demonstrated the formation of dendritic polymer in the presence of the SiO<sub>2</sub> NPs. Both TEM and FE-SEM indicated that the silica nanoparticles have been well coated with dendrimer-encapsulated Pd(0). The crystallite size obtained from X-ray line profile fitting was comparable with the particle size obtained from TEM. It was shown that  $nSiO_2$ -Dendrimer-Pd(0) is an efficient, recyclable,

stable catalyst and strongly active in coupling reactions of aryl halides with termin@cscy01455G alkynes under copper and phosphine ligand-free conditions in water. In addition to these attractive properties of the catalyst, providing excellent yields in short reaction times and simplicity of operation make this method a facile tool in Sonogashira cross coupling reaction. In addition, the excellent catalytic performance in water and the easy preparation, thermal stability and separation of the catalyst make it a good heterogeneous system and a useful alternative to other heterogeneous palladium catalysts.

### 4. Experimental

#### 4.1. General

Chemical materials were purchased from the Merck Chemical Company in high purity. All other chemicals are analytical grade and used without further purification. Infrared spectra (500–4000 cm<sup>-1</sup>) were recorded on a Shimadzu FTIR-8300 spectrophotometer. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance DPX 250 MHz Spectrometer in CDCl<sub>3</sub> or DMSO- $d_6$  solvents using TMS as an internal standard reference. Transmission electron microscope (TEM) images were obtained on a Philips EM208 with an accelerating voltage of 100 Kv and field emission scanning electron microscopy (FE-SEM) images were obtained on HITACHI S-4160. Dynamic light scattering (DLS) were recorded on a HORIBA-LB550. TGA thermograms were recorded on an instrument of Perkin Elmer with N<sub>2</sub> carrier gas and the rate of temperature change of 20 °C min<sup>-1</sup>. X-ray powder diffraction (XRD) spectra were taken on a Bruker AXS D8advance X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda$ = 1.5418). High resolution X-ray photoelectron spectroscopy (XPS) measurements were conducted with a XR3E2 (VG Microtech) twin anode X-ray source using AlKα=1486.6 eV. UV spectra (PerkinElmer, Lambda 25, UV/Vis spectrometer) were used to ensure the complete conversion of Pd(II) to Pd(0). BET surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2000 instrument at 196 °C. Gas chromatography-mass spectrometry (GC-MS) was performed on a 430 GC (Varian, USA). The Pd contents in the catalysts before and after the cross coupling reactions were determined using Inductive Coupled Plasma (ICP) Optical Emission Spectroscopy (Varian Vista-MPX CCD Simultaneous ICP-OES) and ICP Mass Spectrometry (ICP-MS, Varian 820-MS). The C, H, N and S elemental analyses were carried out by the using a Thermofinigan Flash EA-1112 CHNSO rapid elemental analyzer. Melting points were determined with a Buchi 510 instrument in open capillary tubes and are uncorrected. All products were identified by comparison of their spectral data and physical properties with those of the authentic sample and all yields refer to isolated products.

# 4.2. Synthesis of dendrimer-encapsulated Pd(0) nanoparticles immobilized on nanosilica ( $nSiO_2$ -Dendrimer-Pd(0))

4.2.1. The Preparation of Silica nanoparticles from rice husk ash (nSiO<sub>2</sub>)

4.2.1.1. The Preparation of Sodium Silicate from rice husk ash

The rice husk was washed with water and ethanol for several time to remove dist and others contaminants and dried at 100 °C for 12 h. The pure RH is burnt inside a muffle furnace and heating at 400 °C for 1 h and then held at 750 °C for 2 h. For extraction of silica from rice husk ash, 5.0 g of RHA was added to 300 mL of 1.0 M HNO<sub>3</sub> sloution and stirred for about 10 h at room temprature. The resulting white powder was filtered and washed three times with ethanol and dried at 70 °C for 6 h. The SiO<sub>2</sub> extracted (3 g) was mixed with 2 g of the NaOH and heated at 650 °C for 2 h. The resulting powder was dissolved in 500 ml water and the solution was filtered and the residue was washed with 50 ml boiling water. The filtrate is a solution of sodium silicate.

#### 4.2.1.2. The Preparation of Silica nanoparticles from Sodium Silicate

Acetic acid (4 mL) was added to the solution of 2 g Cetyl trimethylammonium bromide in 50 mL of 2 M HCl and then the resltant solution was strirred for 2 h. At 60 °C, this solution was added dropwise under vigorous stirring to 30 mL of the sodium silicate solution (10 % w/w), which has been obtained in the above procedure and stirred for 30 min at room temperature before using. The formed powder was filtered by centrifugation and washed with deionized water and ethanol several times. Then, 50 mL of deionized water was added in the washed sediment. The pH of the obtained mixture was adjusted to 2 with 2 M HCl and sonicated for 1 h with high-intensity ultrasound simultaneously before being transferred into a hydrothermal reaction. After the hydrothermal reaction at 150 °C for 24 h, the collected samples were separated by centrifugation, washed, dried in air, and then calcinated at 650 °C for 2 h to get silica nanoparticles.

# 4.2.2. Preparation of functionalized $SiO_2$ nanoparticle with 3-(triethoxysilyl)-propylamine ( $nSiO_2$ - $NH_2$ )

Nano SiO<sub>2</sub> (1 g) was added to the solution of 3-(triethoxysilyl) propylamine (2 mmol, 0.352 g) in ethanol (5 mL) and the resultant mixture was under reflux for 12 h under nitrogen atmosphere. After refluxing, the mixture was cooled to room temperature and the solid product was separated by centrifugation, washed with ethanol and water to remove unreacted species and dried at 80 °C for 6 h.

#### 4.2.3. Preparation of MA1-nSiO<sub>2</sub>

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Nano SiO<sub>2</sub>-NH<sub>2</sub> (1 g) was added to the stirred solution of methyl acrylate (MA) (5 mmol, 0.42 g) in methanol (5 mL). The final mixture was stirred at room temperature for 24 hours. Then, the solid material was separated by centrifugation, washed with hot methanol for 6 h in a Soxhlet apparatus to remove the unreacted starting materials and then finally dried in a vacuum oven at 60 °C.

### 4.2.4. Preparation of Nano Silica Supported Dendritic Polymer (NH<sub>2</sub>(1)-MA1-nSiO<sub>2</sub>)

To a slurry of MA1-nSiO<sub>2</sub> (1 g) in methanol (5 mL) was added bis(3-aminopropyly and the Galine (10 mmol, 1.2 mL). The reaction mixture was refluxed with continuous stirring under inert atmosphere for 4 h or irradiated with CEM Discovery Microwave at 200 W for 120 minute. Temperature was kept approximately at bulk temperature 120 °C during microwave irradiation. Final product was separated by centrifugation, washed with hot methanol for 6 h in a Soxhlet apparatus to remove the unreacted starting materials and then dried in a vacuum oven at 60 °C.

#### 4.2.5. Preparation of Nano Silica Supported Dendritic Polymer (NH<sub>2</sub>(2)-MA2-nSiO<sub>2</sub>)

A well stirred solution of MA (10 mmol, 0.84 g) in methanol (10 mL) was added to the stirred solution of  $NH_2(1)$ -MA1-nSiO<sub>2</sub> (1 g). The final mixture was stirred at room temperature for 24 hours. Then, the solid material (MA2-nSiO<sub>2</sub>) was separated by centrifugation, washed with hot methanol for 6 h in a Soxhlet apparatus to remove the unreacted starting materials and then finally dried in a vacuum oven at 60 °C. Then, bis(3-aminopropyl) amine (20 mmol, 2.4 mL) was added to a stirred solution of MA2-nSiO<sub>2</sub> (1 g) in 10 mL methanol. The final mixture was refluxed with continuous stirring under inert atmosphere for 4 h or irradiated with CEM Discovery Microwave at 200 W for 120 minute at 120 °C. Final product was separated by centrifugation, washed with hot methanol for 6 h in a Soxhlet apparatus to remove the unreacted starting materials and then dried in a vacuum oven at 60 °C.

## **4.2.6.** Preparation of Nano-Silica Supported Dendritic Polymer Palladium Nanoparticles (nSiO<sub>2</sub>-Dendrimer-Pd(0))

A mixture of  $Pd(OAc)_2$  (200 mg, 0.9 mmol) and  $NH_2(2)$ -MA2-nSiO<sub>2</sub> (1 g) was mixed in 10 mL of deionized water and stirred at room temperature for 4 h. After that, the solid was separated by centrifugation, washed with deionized water. This separation and wash process was repeated three times. Then, the resulting solid was redispersed in deionized water, and 0.4 mL of freshly prepared NaBH<sub>4</sub> (0.25 M) aqueous solution was added and stirred for 1 h. The reaction started immediately and the color changed from light green to black, due to conversion of Pd(II) into Pd(0) nanoparticles. The black solid mass was washed with distilled water for several times and then dried in a desiccator for 6 h. The sample thus prepared was designated as  $nSiO_2$ -Dendrimer-Pd(0) and stored in airtight bottle for further use.

#### 4.3. General procedure for the Sonogashira reaction using nSiO<sub>2</sub>-Dendrimer-Pd(0)

In a typical reaction, in 5mL round-bottomed flask equipped with a condenser, a mixture of aryl halide (1.0 mmol), alkyne (1.1 mmol), triethyl amine (2.0 mmol), H<sub>2</sub>O (2 mL) and catalyst (0.085 mol% of Pd) was subjected to reflux condition under an air atmosphere with vigorous stirring for an appropriate time. Progress of the reaction was monitored by GC analysis at different time interval of the reaction. After the completion of the reaction, the reaction mixture was cooled to room temperature and the solid was separated by centrifugation and washed with methanol (2×10 mL). The filtrate was collected and the

solvent was removed under vacuum. The residue was extracted with dichloromethane  $145G_{145G}$  three times (3×10 mL). The organic phase was dried over sodium sulfate, and concentrated under a reduced pressure. The resulted crude material was purified by flash column chromatography on silica gel.

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## **Graphical abstract**



Recyclable dendrimer-encapsulated Pd(0) nanoparticles immobilized on nanosilica in the Sonogashira–Hagihara reaction under copper(I) and phosphine ligand-free conditions in water