JOC The Journal of Organic Chemistry

ARTICLE

pubs.acs.org/joc

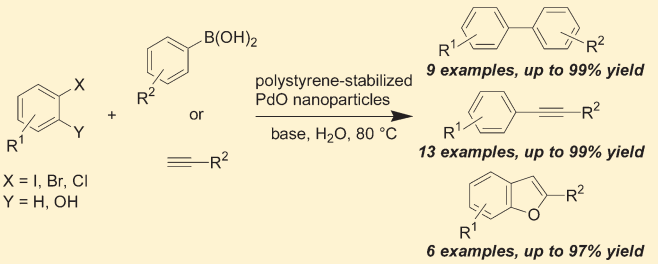
Linear Polystyrene-Stabilized Palladium Nanoparticles-Catalyzed C−C Coupling Reaction in Water

Atsushi Ohtaka,*[,†] Takuto Teratani,[†] Ryohei Fujii,[†] Kanako Ikeshita,[†] Takahiro Kawashima,[†] Koichi Tatsumi,[†] Osamu Shimomura,[†] and Ryôki Nomura*[,†,‡]

[†]Department of Applied Chemistry, Faculty of Engineering and [‡]Nanomaterials and Microdevices Research Center, Osaka Institute of Technology, 5-16-1 Ohmiya, Osaka, Osaka 535-8585, Japan

Supporting Information

ABSTRACT: Linear polystyrene-stabilized PdO nanoparticles (PS-PdONPs) were prepared in water by thermal decomposition of $Pd(OAc)_2$ in the presence of polystyrene. The immobilization degree of palladium was dependent on the molecular weight of polystyrene, while the size of the Pd nanoparticles was not. Linear polystyrene-stabilized Pd nanoparticles (PS-PdNPs) were also prepared using $NaBH_4$ and phenylboronic acid as reductants. The catalytic activity of PS-PdONPs was slightly higher than that of PS-PdNPs for Suzuki coupling reaction in water. PS-PdONPs exhibited high catalytic activity for Suzuki and copper-free Sonogashira coupling reactions in water and recycled without loss of activity.



1. INTRODUCTION

The efficiency of heterogeneous catalysis in organic synthesis[1] can be improved by employing nanosized catalysts because of their extremely small size and large surface-to-volume ratio. Recently, it has been demonstrated that palladium nanoparticles (PdNPs) as catalysts offer significant potential for a wide range of applications in organic synthesis.[2] PdNPs are typically formed in the presence of a protecting agent, because they tend to precipitate or aggregate and lose their catalytic activity. Popular protecting agents include tetraalkylammonium salts,[3] functionalized polymers,[4] dendrimers,[5] and ionic liquids.[6] The surface properties of these PdNPs and their catalytic activity are crucially controlled by the nature of these stabilizers.

The use of water instead of organic solvents, on the other hand, is of significant interest with respect to environmentally friendly organic synthesis.[7] Several research groups have developed PdNPs catalyzed reactions in water, including Suzuki coupling reaction,[8] Stille coupling reaction,[9] Heck reaction,[8a−d,10] Sonogashira coupling reaction,[8a,b,11] and π-allylic substitution.[12] However, recovery and reuse of the catalysts was difficult to achieve in these cases due to a significant loss of PdNPs during workup and/or morphology change (Ostwald ripening).[8k,13] In contrast, PdNPs stabilized by a hydrogel of poly(*N*-isopropylacrylamide-*co*-poly[2-methacrylic acid 3-(bis-carboxymethylamino)-2-hydroxypropyl ester] (PNIPAM-*co*-PMACHE),[14] e−shell poly(styrene-*co*-4-vinylpyridine) microspheres,[15] polyaniline,[16] poly(amidoamine)-based dendrimer captured in microporous polymer,[17] and fluorous ligands[18] have been demonstrated as easily reusable for Suzuki, Heck, and Sonogashira coupling reactions in water. On the other hand, Mayer et al. have reported that higher hydrophobicity of the latex type results in improved accumulation of Pd nanoparticles on its surface.[19] Kobayashi et al. described that the palladium catalyst would be immobilized by interaction between the π electrons of benzene rings of the polystyrene used as a polymer backbone and the vacant orbitals of the metal.[20] Encouraged by these results, we have investigated the immobilization of Pd nanoparticles onto polystyrene in water to develop a recyclable PdNPs catalyst system. Consequently, we found that PdO nanoparticles have only to be generated by thermal decomposition of $Pd(OAc)_2$[21] in the presence of polystyrene.[22] Here we report a simple method for preparation of linear polystyrene-supported palladium nanoparticles in water. Additionally, the catalytic activity of the resultant Pd nanoparticles is also discussed.

2. RESULTS AND DISCUSSION

2.1. Preparation and Characterization of PS-PdONPs and PS-PdNPs. Linear polystyrene-stabilized PdO nanoparticles (PS-PdONPs, **1a**) were prepared by thermal decomposition of $Pd(OAc)_2$ in the presence of polystyrene (M_n = 6.0 × 10^3).[23] The mixture of $Pd(OAc)_2$ and linear polystyrene was added to 1.5 mol·L^{-1} aqueous K_2CO_3 solution (Scheme 1).[24] After the mixture was stirred at 90 °C for 1 h, the color turned black. An X-ray diffraction (XRD) pattern of **1a** is presented in Figure 1a. Besides the broad diffraction with 2θ ranging from 12° to 28° ascribed to the polystyrene, five diffraction peaks assigned to PdO (JCPDS no. 41-1107, Figure 1b) are observed clearly. Figure 1c shows a transmission electron microscopy (TEM)

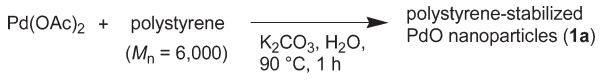
Received: March 8, 2011
Published: April 11, 2011

image of **1a**, which has a fairly uniform particle size of 2.3 ± 0.3 nm. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) revealed that **1a** contained an average of 2.5 mmol·g^{-1} of Pd.

Next, the effect of polystyrene on immobilization was investigated (Table 1). The loading of palladium decreased with an increase in the molecular weight of polystyrene (entries 1−5). In addition, the lowest palladium loading level was found for cross-linked polystyrene (entry 6). However, the precise reason is as yet unclear, and in fact the size of palladium nanoparticles was independent of the molecular weight and cross-linking (Figure 2).

Linear polystyrene-stabilized Pd nanoparticles (PS-PdNPs, **1a**′ and **1a**″) were also prepared using $NaBH_4$ and phenylboronic acid as reductants. An XRD pattern of PS-PdNPs is presented in Figure 3. In addition to the broad diffraction with 2θ ranging from 12° to 30° ascribed to polystyrene, five other diffraction peaks were assigned to the Pd nanoparticles (JCPDS no. 46-1043, Figure 3b). PS-PdNPs (**1a**′ and **1a**″) were examined by TEM, showing nanoparticles of about 4.1 ± 0.7 nm (Figure 4a) and 1.7 ± 0.2 nm (Figure 4b), respectively.

Scheme 1. Preparation of Polystyrene-Stabilized PdO Nanoparticles



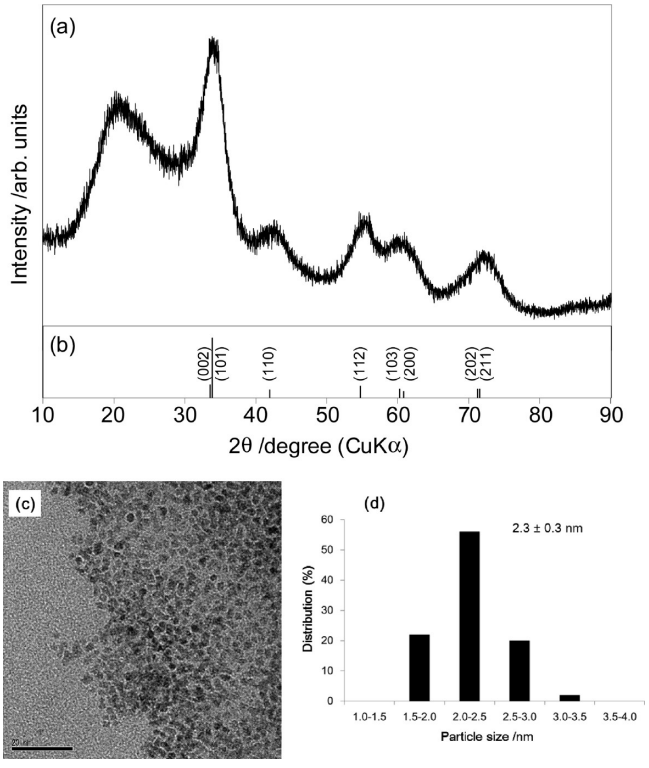


Figure 1. (a) XRD patterns of **1a**; (b) JCPDS data (no. 41-1107) for PdO; (c) TEM micrograph of **1a** (scale bar = 20 nm); (d) size distribution of **1a**.

2.2. Suzuki Coupling Reaction in Water. To test the potency of **1a** as a catalyst, the Suzuki coupling reaction of bromobenzene (**2a**) with 4-methylphenylboronic acid (**3a**) in 1.5 M KOH aqueous solution was examined as a test reaction (Table 2). The reaction proceeded efficiently at 80 °C for 1 h to give 4-methylbiphenyl (**4a**) in 99% yield (entry 1). More importantly, the workup was performed under organic solvent-free conditions where water was the only solvent used. When the reaction was completed, the reaction mixture was filtered with hot water. The catalyst was recovered on a filter, and the filtrate was cooled to room temperature to give **4a** quantitatively as colorless crystals in high purity. The reusability of the catalyst was also examined. The catalyst was recycled at least 10 times without any loss of activity. The average yield of **4a** in consecutive reactions promoted by the first through tenth recovered catalysts was 99%. No leaching of palladium into the reaction solutions occurred during the reaction, as confirmed by ICP-AES. ICP-AES analysis also revealed that quantitative recovery of palladium was achieved. Similar sizes of palladium nanoparticles were observed by TEM after the recycling experiments. However, the distribution was changed slightly, probable due to Ostwald ripening (Figure 5).

In contrast, the PS-PdNPs (**1a**′ and **1a**″) exhibited catalytic activities slightly lower than those of PS-PdONPs (entries 4 and 5), probably due to the presence of oxygen[25] and size effect.[13b] Neither Pd/C nor Pd/Al_2O_3 were effective catalysts under these reaction conditions (entries 6 and 7). Although a similar result was obtained with **1f**, the catalytic activity decreased in the third consecutive run as previously reported (entries 8 and 9).[8h] Given these results, the PS-PdONPs were determined to be the best catalyst for Suzuki coupling reaction in water.

The scope of the reaction was studied using various aryl halides and arylboronic acids (Table 3). Both the electron-rich and electron-deficient aryl bromides were reactive, affording the desired coupling products in high yields (entries 1−5). 2-Bromotoluene also underwent the Suzuki coupling reaction to give the corresponding product in 92% yield (entry 6). It is noteworthy that the reaction proceeded well and the catalyst could be recycled even with an aryl chloride (entry 9). However, the reaction of chlorobenzene (**2h**) with **3a** gave a low yield (entry 10).

2.3. Copper-Free Sonogashira Coupling Reaction with 1a in Water. The palladium-catalyzed reaction of aryl halides with terminal alkynes, known as Sonogashira coupling, is recognized as a powerful and reliable synthetic method for the formation of

Table 1. Preparation of PS-PdONPs Using Several Polystyrene

entry	polystyrene	PS-stabilized PdO nanoparticles	loading,[a] mmol·g^{-1}	size of Pd,[b] nm
1	linear (M_n = 6.0 × 10^3)	**1a**	2.5	2.3 ± 0.3
2	linear (M_n = 1.8 × 10^4)	**1b**	1.8	2.2 ± 0.3
3	linear (M_n = 3.8 × 10^4)	**1c**	1.5	2.2 ± 0.3
4	linear (M_n = 9.6 × 10^4)	**1d**	1.0	2.1 ± 0.2
5	linear (M_n = 4.3 × 10^5)	**1e**	0.4	2.2 ± 0.2
6	cross-linked (2% DVB)	**1f**	0.3	2.4 ± 0.2

[a] Determined by ICP-AES. [b] Determined by TEM.

dx.doi.org/10.1021/jo200485q |J. Org. Chem. 2011, 76, 4052–4060

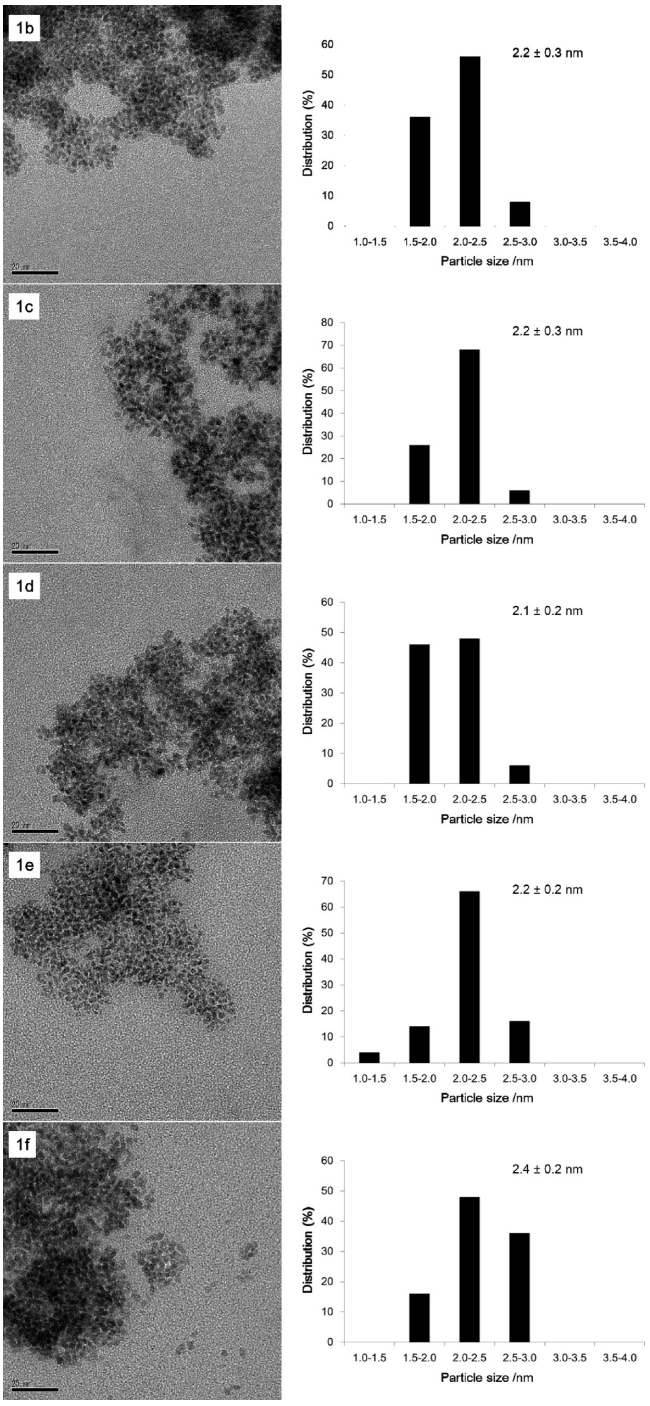


Figure 2. TEM micrographs and size distributions of **1b**−**1f** (scale bar = 20 nm).

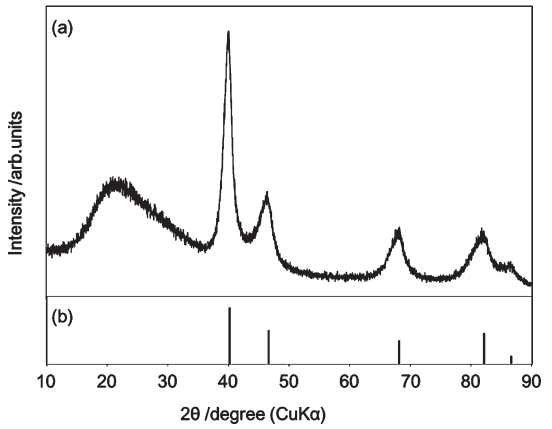


Figure 3. (a) XRD patterns of **1a**′. (b) JCPDS data (no. 46-1043) for Pd.

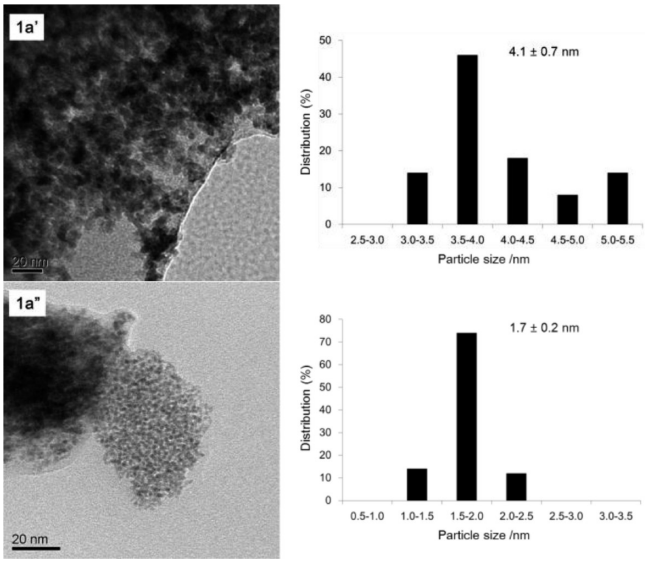
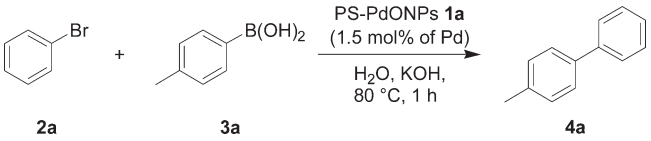


Figure 4. TEM micrographs and size distributions of **1a**′ and **1a**″ (scale bar = 20 nm).

substituted acetylenes.[26] Poly(ethylene glycol) (PEG)-stabilized PdNPs and *in situ* generated PdNPs have high catalyitc activity for the Sonogashira coupling reaction in water under copper-free conditions.[8b,11b] However, it is difficult to reuse the catalyst because the PdNPs are dispersed in water. Recently, Cacchi et al. have reported that perfluoro-tagged PdNPs immobilized on silica gel was reused many times for the Sonogashira coupling reaction in water under copper-free conditions.[18b] Our continuing interest in the catalytic utility of PS-PdONPs led us to examine the Sonogashira coupling in water with **1a** under copper-free conditions. Representative results are summarized in Table 4. The coupling of iodobenzene (**2i**) with phenylacetylene (**5a**) took place smoothly in water at 80 °C in the presence of 3 equiv of Et_3N and 1.5 mol % palladium of **1a** to give **6a** in 99% yield (entry 1). After the reaction, the catalyst **1a** was recovered and successively subjected to second through fifth runs of the coupling reaction under the same conditions to afford **6a** in 99%, 99%, 97%, and 98% yields, respectively (entries 2−5). ICP-AES analysis of the aqueous phases revealed barely detectable levels of palladium residue, although the size distribution of nanoparticles was changed slightly (Figure 6). Both electron-rich and electron-deficient aryl iodides were applicable, affording the desired coupling products in excellent yields (entries 6−9). Sterically hindered aryl iodides such as 2-iodotoluene (**2n**) and 1-iodonaphthalene (**2o**) also underwent the Sonogashira coupling with **5a** to give the corresponding products in 74% and 84% yields, respectively (entries 10 and 11). The coupling of various terminal alkynes bearing electron-withdrawing groups and electron-donating groups took place with **2i** to give the corresponding product in 99%, 91%, and 97% yields, respectively (entries

dx.doi.org/10.1021/jo200485q |*J. Org. Chem.* 2011, 76, 4052–4060

Table 2. Suzuki Coupling Reaction in Water



2a 3a 4a

entry	catalyst	run	yield (%)
1	**1a**	first run	99[a] (73)[b]
2		tenth run	99
3		first to tenth consecutive	av 99
4	**1a′**		99 (57)[b]
5	**1a″**		99 (49)[b]
6	Pd/C		61
7	Pd/Al_2O_3		52
S	**1f**	first run	99
9		3rd run	53

[a] Isolated by crystallization under organic solvent-free conditions. [b] Yield in parentheses refers to an experiment at 60 °C.

12−14). 1-Octyne (**5e**) and trimethylsilylacetylene (**5f**) reacted with **2i** to generate the corresponding products in good yields (entries 15 and 16). However, the reaction of **5a** with bromobenzene (**2a**) gave a low yield (entry 17).

2.4. Synthesis of Benzo[*b*]furan with 1a in Water. The Sonogashira coupling reaction of *o*-halophenols with terminal alkynes is an efficient procedure for the synthesis of benzo[*b*]furan derivatives. Pal et al. found that Pd/C was active for the synthesis of benzo[*b*]furan derivatives in water, although this method required a cocatalyst and phosphine ligand.[27] Uozumi et al. reported the preparation of benzo[*b*]furan derivatives using amphiphilic polystyrene-PEG resin-supported Pd catalyst under copper-free conditions although no recycling experiments was reported.[28] Ranu et al. developed a very simple method using *in situ* generated PdNPs.[11a] However, loss of activity was observed in recycling experiment due to agglomerization of PdNPs after each cycle.

PS-PdONPs proved to function efficiently for the Sonogashira coupling in water under copper-free conditions; therefore, our attention was turned to the synthesis of benzo[*b*]furan derivatives. The reaction of *o*-halophenol with 1.1 equiv of terminal alkyne was performed in the presence of **1a** (1.5 mol % of Pd) and 3 equiv of Et_3N in water (Table 5). The coupling of 2-iodophenol (**2p**) with phenylacetylene (**5a**) was accomplished in 20 h to afford 2-phenylbenzofuran (**7a**) in 97% yield (entry 1). In addition, the catalytic deactivation of reused **1a** was not observed at all (entries 2−5). ICP-AES analysis confirmed that no leaching of Pd into either the aqueous or organic solutions occurred. A TEM image of the recovered catalyst revealed a fairly uniform particle size (Figure 7). To establish the scope of the reaction, the reaction of various *o*-halophenols with terminal alkynes was next examined. The reaction of 4-ethynyltoluene (**5c**) and 4-ethynylanisole (**5d**) bearing electron-donating groups at their *para* positions gave the corresponding coupling products in 93% and 94% yields, respectively (entries 6 and 7). 1-Octyne (**5e**) and 1-ethynyl-4-fluorobenzene (**5g**) also underwent the reaction with **2p** under similar conditions to afford the corresponding benzofuran in 71% and 95% yields, respectively (entries 8 and 9). 4-Hydroxy-3-iodobiphenyl (**2q**) reacted with **5a** to generate 2,5-diphenylbenzofuran (**7f**) in 90% yield (entry 10).

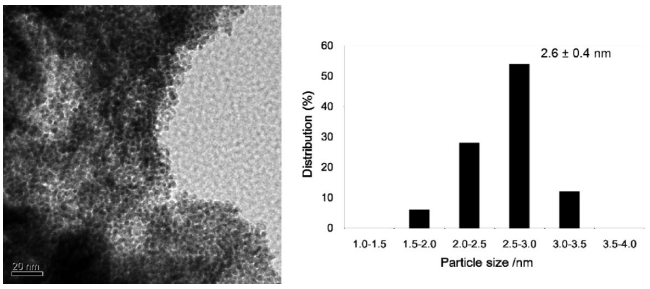


Figure 5. TEM micrographs and size distributions of **1a** after recycling experiments (scale bar = 20 nm).

3. CONCLUSION

In summary, a highly efficient heterogeneous palladium catalyst for Suzuki and copper-free Sonogashira coupling reactions in water was prepared with a simple procedure. The immobilization degree of palladium was dependent on the molecular weight of polystyrene, while the size of the nanoparticles was not. The polystyrene-supported PdO nanoparticles were easily recycled with no loss of activity. ICP-AES analysis confirmed that no palladium was leached into either the aqueous or organic solutions and that the recovery of palladium was achieved quantitatively. However, the size distribution of nanoparticles was changed slightly, which suggests that Ostwald ripening occurred during the reaction.

4. EXPERIMENTAL SECTION

4.1. Preparation of PS-PdONPs (1a). To a screw-capped vial with a stirring bar were added 9.0 mg of polystyrene (85 μmol of styrene unit), $Pd(OAc)_2$ 5.5 mg (25 μmol), and 1.5 M aqueous K_2CO_3 solution (3 mL). After stirring at 90 °C for 1 h, the reaction mixture was filtered with hot water. Subsequently, the polystyrene-stabilized Pd nanoparticles were washed with hot water (5 × 1.0 mL) and acetone (5 × 1.0 mL).

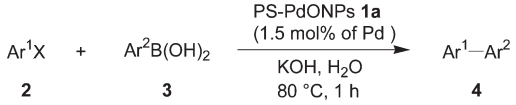
4.2. Preparation of PS-PdNPs by Reduction with $NaBH_4$ (1a′). To a screw-capped vial with a stirring bar were added 1.8 mg of polystyrene (17 μmol of styrene unit), $Pd(OAc)_2$ 1.0 mg (5 μmol), and water (1 mL). After adding an ethanol solution of $NaBH_4$ (0.01 mol·L^{-1}) dropwise, the mixture was stirring at 25 °C for 1 h, and then the aqueous solution was decanted. Subsequently, the polystyrene-stabilized Pd nanoparticles were washed with water (5 × 1.0 mL) and acetone (5 × 1.0 mL).

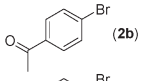
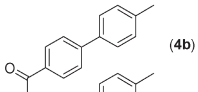
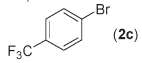
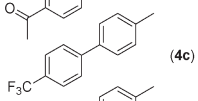
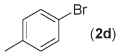
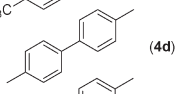
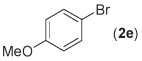
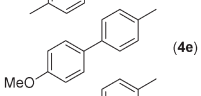
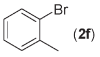
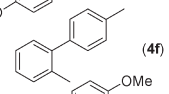
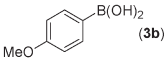
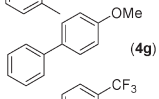
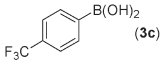
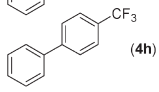
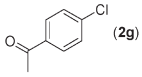
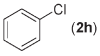
4.3. Preparation of PS-PdNPs by Reduction with Phenylboronic Acid (1a″). To a screw-capped vial with a stirring bar were added 1.8 mg of polystyrene (17 μmol of styrene unit), $Pd(OAc)_2$ 1.0 mg (5 μmol), phenylboronic acid 9.1 mg (0.75 mmol), and water (1 mL). After stirring at 90 °C for 1 h, the aqueous solution was decanted. Subsequently, the polystyrene-stabilized Pd nanoparticles were washed with water (5 × 1.0 mL) and acetone (5 × 1.0 mL).

4.4. Determination of Loading of the Palladium. **1a** (2.9 mg) was placed in a screw-capped vial, and then was added 13 M nitric acid (5 mL). The mixture was heated at 80 °C to dissolve completely. After cooling to room temperature, the solution was adjusted to 50 mL by water and then the amount of Pd metal was measured by ICP-AES analysis (15.3 ppm). The amount of Pd in **1b**−**1f**, **1a′**, and **1a″** was as follows: **1b**, 11.1 ppm; **1c**, 9.38 ppm; **1d**, 6.12 ppm; **1e**, 2.53 ppm; **1f**, 1.56 ppm; **1a′**, 15.5 ppm; **1a″**, 15.5 ppm.

4.5. Typical Procedures for Suzuki Coupling Reaction. To a screw-capped vial with a stirring bar were added 0.5 mmol of bromobenzene, 0.75 mmol of *p*-methylphenylboronic acid, **1a** (2.9 mg, 1.5 mol % of Pd), and 1.5 M aqueous KOH solution (1 mL). After stirring at 80 °C for 1 h, the reaction mixture was filtered with hot water. Subsequently, the

Table 3. Suzuki Coupling Reaction of Various Aryl Halides with Arylboronic Acids in Water



Entry	Ar^1X	$Ar^2B(OH)_2$	product	Yield (%)
1	**2a**	**3a**	**4a**	99
2	 (**2b**)	**3a**	 (**4b**)	99
3	 (**2c**)	**3a**	 (**4c**)	92
4	 (**2d**)	**3a**	 (**4d**)	89
5	 (**2e**)	**3a**	 (**4e**)	92
6	 (**2f**)	**3a**	 (**4f**)	92
7	**2a**	 (**3b**)	 (**4g**)	99
8	**2a**	 (**3c**)	 (**4h**)	70
9	 (**2g**)	**3a**	**4b**	99[a] (99)[b]
10	 (**2h**)	**3a**	**4a**	6[c]

[a] Reaction time = 12 h. [b] Yield in parentheses refers to a second set of experiment. [c] Reaction time = 20 h.

catalyst was washed with hot water (5 × 1.0 mL). The filtrate was cooled to room temperature to afford crystals of 4-methylbiphenyl. The recovered **1a** was dried in vacuo and reused. Furthermore, the amount of Pd metal in the recovered **1a** determined by ICP-AES analysis was 15.3 ppm.

4-Methylbiphenyl (***4a***)[8f]. ^{1}H NMR ($CDCl_3$) δ 7.60−7.55 (m, 2 H), 7.50−7.47 (m, 2 H), 7.43−7.39 (m, 2 H), 7.33−7.29 (m, 1 H), 7.25−7.20 (m, 2 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 141.1, 138.3, 136.9, 129.4, 128.7, 128.7, 126.9, 21.1. CAS registry number: 644-08-6.

4-Acetyl-4′-methylbiphenyl (***4b***)[29]. ^{1}H NMR ($CDCl_3$) δ 8.02 (d, J = 8.7 Hz, 2 H), 7.67 (d, J = 8.7 Hz, 2 H), 7.53 (d, J = 8.4 Hz, 2 H), 7.27 (d, J = 8.4 Hz, 2 H), 2.63 (s, 3 H), 2.41 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.8, 145.7, 138.2, 136.9, 135.5, 129.7, 128.9, 127.1, 126.9, 26.6, 21.2. CAS registry number: 5748-38-9.

4-Methyl-4′-(trifluoromethyl)biphenyl (***4c***)[8f]. ^{1}H NMR ($CDCl_3$) δ 7.67 (m, 4 H), 7.50 (d, J = 8.4 Hz, 2 H), 7.28 (d, J = 8.4 Hz, 2 H), 2.41 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.6, 138.1, 136.8, 129.7, 129.2 (q, J = 32.3 Hz), 127.2, 127.1, 125.6 (q, J = 4.2 Hz), 124.3 (q, J = 271.7 Hz), 21.1. CAS registry number: 97067-18-0.

4,4′-Dimethylbiphenyl (***4d***)[30]. ^{1}H NMR ($CDCl_3$) δ 7.47 (d, J = 8.1 Hz, 4 H), 7.23 (d, J = 8.1 Hz, 4 H), 2.38 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 138.2, 136.7, 129.4, 126.8, 21.1. CAS registry number: 613-33-2.

4-Methoxy-4′-methylbiphenyl (***4e***)[8f]. ^{1}H NMR ($CDCl_3$) δ 7.51 (d, J = 9.0 Hz, 2 H), 7.45 (d, J = 8.1 Hz, 2 H), 7.22 (d, J = 8.1 Hz, 2 H), 6.96 (d, J = 9.0 Hz, 2 H), 3.84 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.9, 137.9, 136.3, 133.7, 129.4, 127.9, 126.6, 114.2, 55.3, 21.0. CAS registry number: 53040-92-9.

2,4′-Dimethylbiphenyl (***4f***)[31]. ^{1}H NMR ($CDCl_3$) δ 7.25−7.20 (m, 8 H), 2.40 (s, 3 H), 2.28 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 141.8, 140.0, 136.4, 135.4, 130.2, 129.8, 129.0, 128.7, 127.0, 125.7, 21.27, 20.5. CAS registry number: 611-61-0.

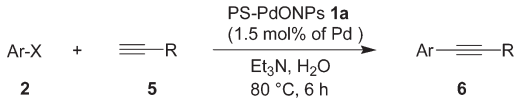
4-Methoxybiphenyl (***4g***)[8f]. ^{1}H NMR ($CDCl_3$) δ 7.58−7.51 (m, 4 H), 7.42 (t, J = 7.6 Hz, 2 H), 7.31 (t, J = 7.6 Hz, 1 H), 6.98 (d, J = 8.7 Hz, 2 H), 3.85 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 159.1, 140.7, 133.7, 128.6, 128.0, 126.6, 126.6, 114.2, 55.3. CAS registry number: 613-37-6.

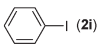
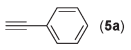
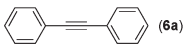
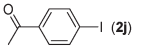
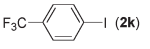
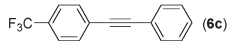
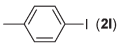
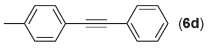
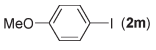
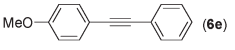
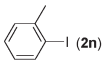
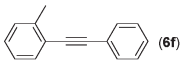
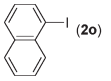
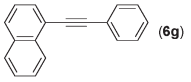
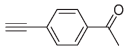
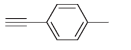
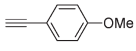
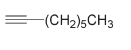
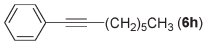
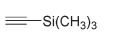
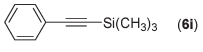
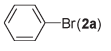
4-Trifluoromethylbiphenyl (***4h***)[8f]. ^{1}H NMR ($CDCl_3$) δ 7.76−7.68 (m, 4 H), 7.68−7.58 (m, 2 H), 7.51−7.38 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.7, 139.7, 129.3 (q, J = 32.3 Hz), 129.0, 128.2, 127.6, 127.4, 127.3, 125.6 (q, J = 3.2 Hz), 124.3 (q, J = 272.1 Hz). CAS registry number: 398-36-7.

4.6. Typical Procedures for Sonogashira Coupling Reaction. To a screw-capped vial with a stirring bar were added iodobenzene (52.0 mg, 0.5 mmol), phenylacetylene (56.2 mg, 0.55 mmol), **1a** (2.9 mg, 1.5 mol % of Pd), triethylamine (152 mg, 1.5 mmol), and H_2O (1.0 mL). After stirring at 80 °C for 6 h, the reaction mixture was cooled to room temperature by immediately immersing the vial in water (∼20 °C) for about 10 min. Subsequently, the aqueous phases were removed, and recovered catalyst was washed with H_2O (5 × 3.0 mL) and diethyl ether (5 × 3.0 mL), which were then added to the aqueous phase. The aqueous phase was extracted eight times with diethyl ether. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The recovered **1a** was dried in vacuo and reused. The resulting product was purified by PTLC (hexane/CH_2Cl_2) and analyzed by ^{1}H NMR.

dx.doi.org/10.1021/jo200485q |*J. Org. Chem.* 2011, 76, 4052–4060

Table 4. Sonogashira Coupling Reaction of Various Aryl Halides with Alkynes in Water



Entry	Ar-X	Alkyne	Product	Yield (%)
1	 (**2i**)	 (**5a**)	 (**6a**)	99
2				(2nd run) 99
3				(3rd run) 99
4				(4th run) 97
5				(5th run) 98
6	 (**2j**)	**5a**	 (**6b**)	99
7	 (**2k**)	**5a**	 (**6c**)	99
8	 (**2l**)	**5a**	 (**6d**)	99
9	 (**2m**)	**5a**	 (**6e**)	93
10	 (**2n**)	**5a**	 (**6f**)	74
11	 (**2o**)	**5a**	 (**6g**)	84
12	**2i**	 (**5b**)	**6b**	99
13	**2i**	 (**5c**)	**6d**	91
14	**2i**	 (**5d**)	**6e**	97
15	**2i**	 (**5e**)	 (**6h**)	80
16	**2i**	 (**5f**)	 (**6i**)	74
17	 (**2a**)	**5a**	**6a**	49[a]

[a] Reaction was carried out at 90 °C for 24 h.

Diphenylacetylene (***6a***)[26c]. ^{1}H NMR ($CDCl_3$) δ 7.56−7.52 (m, 4 H), 7.36−7.33 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 131.2, 128.3, 128.2, 123.42, 89.3. CAS registry number: 501-65-5.

4′-(Phenylethynyl)acetophenone (***6b***)[26c]. ^{1}H NMR ($CDCl_3$) δ 7.95 (d, J = 8.1 Hz, 2 H), 7.62 (d, J = 8.1 Hz, 2 H), 7.61−7.55 (m, 2 H), 7.38−7.35 (m, 3 H), 2.62 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.3, 136.1, 131.7, 131.7, 128.8, 128.4, 128.3, 128.2, 122.6, 92.7, 88.6, 26.6. CAS registry number: 1942-31-0.

1-Phenyl-2-(p-trifluoromethylphenyl)acetylene (***6c***)[26c]. ^{1}H NMR ($CDCl_3$) δ 7.65−7.54 (m, 6 H), 7.39−7.35 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 131.8, 131.7, 129.9 (q, J = 34 Hz), 128.8, 128.4, 127.1, 125.7, 125.3 (q, J = 3.2 Hz), 122.5, 91.7, 87.9. CAS registry number: 370-99-0.

1-Phenyl-2-(p-tolyl)acetylene (***6d***)[26c]. ^{1}H NMR ($CDCl_3$) δ 7.54−7.49 (m, 2 H), 7.43 (d, J = 8.1 Hz, 2 H), 7.37−7.30 (m, 3 H), 7.14 (d, J = 8.1 Hz, 2 H), 2.36 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 138.4, 131.5, 131.4, 129.1, 128.3, 128.0, 123.4, 120.1, 89.5, 88.7, 21.5. CAS registry number: 185817-85-0.

1-(p-Methoxyphenyl)-2-phenyl acetylene (***6e***)[26c]. ^{1}H NMR ($CDCl_3$) δ 7.53−7.45 (m, 4 H), 7.37−7.26 (m, 3 H), 6.88 (d, J = 9.0 Hz, 2 H), 3.82 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.3, 88.0, 55.3. CAS registry number: 7380-78-1.

1-Phenyl-2-(o-tolyl)acetylene (***6f***)[26c]. ^{1}H NMR ($CDCl_3$) δ 7.56−7.48 (m, 3 H), 7.38−7.31 (m, 3 H), 7.24−7.14 (m, 3 H), 2.52 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 140.2, 131.8, 131.5, 129.4, 128.3, 128.1, 125.6, 123.5, 123.0, 93.3, 88.3, 20.7. CAS registry number: 14635-91-7.

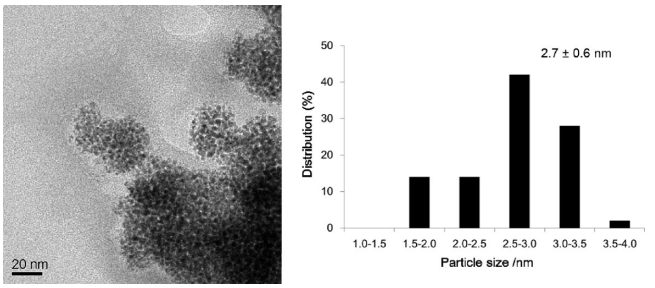
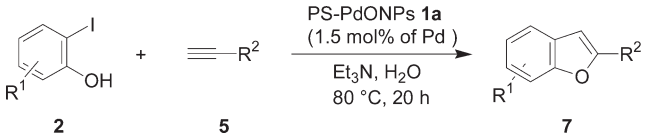


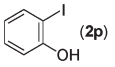
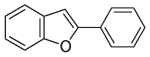
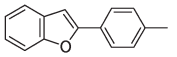
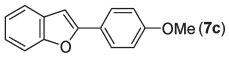
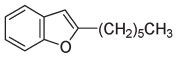
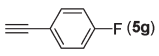
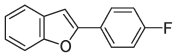
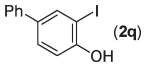
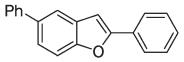
Figure 6. TEM micrographs and size distributions of **1a** after Sonogashira coupling reaction (scale bar = 20 nm).

dx.doi.org/10.1021/jo200485q |*J. Org. Chem.* 2011, 76, 4052–4060

Table 5. Synthesis of Benzo[*b*]furans in Water



2 5 7

Entry	Ar-I	Alkyne	Product	Yield (%)
1	 (**2p**)	**5a**	 (**7a**)	97
2				(2nd run) 96
3				(3rd run) 96
4				(4th run) 97
5				(5th run) 97
6	**2p**	**5c**	 (**7b**)	93
7	**2p**	**5d**	 (**7c**)	94
8	**2p**	**5e**	 (**7d**)	71
9	**2p**	 (**5g**)	 (**7e**)	95
10	 (**2q**)	**5a**	 (**7f**)	90

1-(1-Naphthyl)-2-phenyl acetylene (***6g***)[26c]. ^{1}H NMR ($CDCl_3$) δ 8.45 (d, J = 7.5 Hz, 1 H), 7.85 (t, J = 8.1 Hz, 2 H), 7.77 (dd, J = 7.2 Hz, 1.2 Hz, 1 H), 7.67−7.63 (m, 2 H), 7.60 (dt, J = 6.9 Hz, 1.5 Hz, 1 H), 7.53 (dt, J = 6.9 Hz, 1.5 Hz, 1 H), 7.45 (dd, J = 8.4 Hz, 7.2 Hz, 1 H), 7.43−7.35 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 133.3, 133.2, 131.7, 130.4, 128.8, 128.4, 128.3, 128.2, 126.8, 126.4, 126.2, 125.3, 123.4, 120.9, 94.3, 87.5. CAS registry number: 4044-57-9.

1-Phenyl-1-octyne (***6h***)[26d]. ^{1}H NMR ($CDCl_3$) δ 7.41−7.37 (m, 2 H), 7.29−7.25 (m, 3 H), 2.40 (t, J = 7.2 Hz, 2 H), 1.75−1.29 (m, 8 H), 0.91 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 131.5, 128.1, 127.4, 124.1, 90.5, 80.5, 31.4, 28.7, 28.6, 22.6, 19.4, 14.1. CAS registry number: 16967-02-5.

1-Phenyl-2-(trimethylsilyl)acetylene (***6i***)[32]. ^{1}H NMR ($CDCl_3$) δ 7.51−7.45 (m, 2 H), 7.33−7.28 (m, 3 H), 0.25 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 131.9, 128.5, 128.2, 123.1, 105.1, 94.1, −0.03. CAS registry number: 13735-81-4.

4.7. Typical Procedures for Synthesis of Benzo[*b*]furan. To a screw-capped vial with a stirring bar were added 2-iodophenol (110 mg, 0.5 mmol), phenylacetylene (56.2 mg, 0.55 mmol), **1a** (2.9 mg, 1.5 mol % of Pd), triehtylamine (152 mg, 1.5 mmol), and H_2O (1.0 mL). After stirring at 80 °C for 20 h, the reaction mixture was cooled to room temperature by immediately immersing the vial in water (~20 °C) for about 10 min. Subsequently, the aqueous phases were removed, and recovered catalyst was washed with H_2O (5 × 3.0 mL) and diethyl ether (5 × 3.0 mL), which were then added to the aqueous phase. The aqueous phase was extracted eight times with diethyl ether. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The recovered **1a** was dried in vacuo and reused. The resulting product was purified by PTLC (hexane/CH_2Cl_2) and analyzed by ^{1}H NMR.

2-Phenylbenzofuran (***7a***)[33]. ^{1}H NMR ($CDCl_3$) δ 7.87 (d, J = 7.2 Hz, 2 H), 7.58 (d, J = 7.6 Hz, 1 H), 7.52 (d, J = 7.6 Hz, 1 H), 7.45 (t, J = 7.2 Hz, 2 H), 7.33 (t, J = 7.2 Hz, 1 H), 7.28 (t, J = 7.2 Hz, 1 H), 7.23 (t, J = 7.2 Hz, 1 H), 7.03 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.9, 154.8, 132.5, 130.4, 129.2, 128.8, 128.5, 128.4, 124.9, 124.2, 122.9, 120.9, 111.2, 101.3. CAS registry number: 1839-72-1.

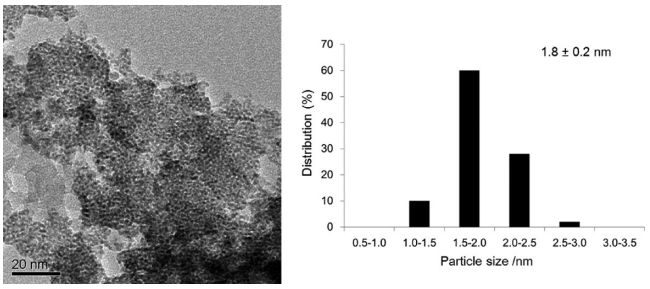


Figure 7. TEM micrographs and size distributions of **1a** after the synthesis of 2-phenylbenzofuran (scale bar = 20 nm).

2-(4-Methylphenyl)benzofuran (***7b***)[33]. ^{1}H NMR ($CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2 H), 7.55 (d, J = 8.1 Hz, 1 H), 7.49 (d, J = 8.1 Hz, 1 H), 7.28−7.17 (m, 4 H), 6.97 (s, 1H), 2.40 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.1, 154.7, 138.6, 129.5, 129.3, 127.7, 124.8, 124.0, 122.8, 120.7, 111.1, 100.5, 21.4. CAS registry number: 25664-48-6.

2-(4-Methoxyphenyl)benzofuran (***7c***)[33]. ^{1}H NMR ($CDCl_3$) δ 7.80 (d, J = 9.0 Hz, 2 H), 7.57−7.48 (m, 2 H), 7.28−7.18 (m, 2 H), 6.98 (d, J = 9.0 Hz, 2 H), 6.89 (s, 1 H), 3.86 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 159.9, 156.0, 154.7, 129.5, 126.4, 123.7, 123.3, 122.8, 120.5, 114.2, 111.0, 99.6, 55.3. CAS registry number: 19234-04-9.

2-Hexylbenzofuran (***7d***)[34]. ^{1}H NMR ($CDCl_3$) δ 7.51−7.39 (m, 2 H), 7.23−7.14 (m, 2 H), 6.37−6.36 (m, 1 H), 2.76 (t, J = 7.5 Hz, 2 H), 1.74 (tt, J = 7.5 Hz, 7.5 Hz, 2 H), 1.45−1.22 (m, 6 H), 0.92−0.86 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 159.8, 154.6, 129.0, 123.0, 122.3, 120.1, 110.7, 101.7, 31.6, 28.9, 28.4, 27.6, 22.6, 14.1. CAS registry number: 39195-67-0.

dx.doi.org/10.1021/jo200485q |*J. Org. Chem.* 2011, 76, 4052–4060

*2-(4-Fluorophenyl)benzofuran (**7e**)*[33]. ^{1}H NMR ($CDCl_3$) δ 7.87−7.81 (m, 2 H), 7.60−7.56 (m, 1 H), 7.53−7.50 (m, 1 H), 7.32−7.21 (m, 2 H), 7.17−7.11 (m, 2 H), 6.98 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 164.5, 161.2, 154.8, 126.8, 126.7, 124.3, 123.0, 120.9, 116.0, 115.7, 111.1, 101.0. CAS registry number: 69976-38-1.

*2,5-Diphenylbenzofuran (**7f**)*[35]. ^{1}H NMR ($CDCl_3$) δ 7.88 (d, J = 7.5 Hz, 2 H), 7.78−7.75 (m, 1 H), 7.65−7.33 (m, 10 H), 7.06 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 154.5, 141.6, 136.6, 130.4, 129.7, 128.8, 128.7, 128.6, 128.5, 127.4, 126.9, 124.9, 124.0, 119.4, 111.3, 101.5. CAS registry number: 121045-39-4.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Copies of ^{1}H NMR and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +81-6-6954-4729. Fax: +81-6-6957-2135. E-mail: otaka@chem.oit.ac.jp; nomura@chem.oit.ac.jp.

■ ACKNOWLEDGMENT

We are grateful to the Nanomaterials and Microdevices Research Center (NMRC) of OIT for financial and instrumental support. This work was supported by the Joint Studies Program (2010) of the Institute for Molecular Science. We wish to thank Prof. Uozumi for general discussions. We also thank Dr. G. Hamasaka, Dr. T. Shinagawa, and Dr. Y. Kashiwagi for assistance with TEM, ICP-AES, and XRD measurements.

■ REFERENCES

(1) (a) Kirschning, A. *Top. Curr. Chem.* **2004**, *242*, 1.(b) Diederich, F.; Stang, P. J. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, 1999.

(2) (a) Astruc, D. *Inorg. Chem.* **2007**, *46*, 1884. (b) Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852. (c) Moreno-Mañas, M.; Pleixats, R. *Acc. Chem. Res.* **2003**, *36*, 638.

(3) (a) Adak, L.; Chattopadhyay, K.; Ranu, B. C. *J. Org. Chem.* **2009**, *74*, 3982. (b) Dey, R.; Chattopadhyay, K.; Ranu, B. C. *J. Org. Chem.* **2008**, *73*, 9461. (c) Liu, J.; Deng, Y.; Wang, H.; Zhang, H.; Yu, G.; Wu, B.; Zhang, H.; Li, Q.; Marder, T. B.; Yang, Z.; Lei, A. *Org. Lett.* **2008**, *10*, 2661. (d) Reetz, M. T.; de Vries, J. G. *Chem. Commun.* **2004**, 1559.

(4) (a) Niembro, S.; Shafir, A.; Vallribera, A.; Alibés, R. *Org. Lett.* **2008**, *10*, 3215. (b) Bernini, R.; Cacchi, S.; Fabrizi, G.; Forte, G.; Niembro, S.; Petrucci, F.; Pleixats, R.; Prastaro, A.; Sebastián, R. M.; Soler, R.; Tristany, M.; Vallribera, A. *Org. Lett.* **2008**, *10*, 561. (c) Abu-Reziq, R.; Wang, D.; Post, M.; Alper, H. *Chem. Mater.* **2008**, *20*, 2544. (d) Jiang, X.; Wei, G.; Zhang, X.; Zhang, W.; Zheng, P.; Wen, F.; Shi, L. J. Mol. Catal. A: Chem **2007**, *277*, 102. (e) Park, C. M.; Kwon, M. S.; Park, J. *Synthesis* **2006**, 3790. (f) Li, P.; Wang, L.; Li, H. *Tetrahedron* **2005**, *61*, 8633. (g) Houdayer, A.; Schneider, R.; Billaud, D.; Ghanbaja, G.; Lambert, J. *Appl. Organometal. Chem.* **2005**, *19*, 1239.

(5) (a) Astruc, D. *Tetrahedron: Asymmetry* **2010**, *21*, 1041. (b) Weir, M. G.; Knecht, M. R.; Frenkel, A. I.; Crooks, R. M. *Langmuir* **2010**, *26*, 1137. (c) Badetti, E.; Caminade, A.-M.; Majoral, J.-P.; Moreno-Mañas, M.; Sebastián, R. M. *Langmuir* **2008**, *24*, 2090. (d) Diallo, A. K.; Ornelas, C.; Salmon, L.; Aranzaes, J. R.; Astruc, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8644.

(6) (a) Kovtunov, K. V.; Zhivonitko, V. V.; Kiwi-Minsker, L.; Koptyug, I. V. *Chem. Commun.* **2010**, 5764. (b) Liu, G.; Hou, M.; Song, J.; Jiang, T.; Fan, H.; Zhang, Z.; Han, B. *Green Chem.* **2010**, *12*, 65. (c) Sawant, A. D.; Raut, D. G.; Darvatkar, N. B.; Desai, U. V.; Salunkhe, M. M. *Catal. Commun.* **2010**, *12*, 273. (d) Hu, Y.; Yang, H.; Zhang, Y.; Hou, Z.; Wang, X.; Qiao, Y.; Li, H.; Feng, B.; Huang, Q. *Catal. Commun.* **2009**, *10*, 1903. (e) Yang, X.; Fei, Z.; Zhao, D.; Ang, W. H.; Li, Y.; Dyson, P. J. *Inorg. Chem.* **2008**, *47*, 3292.

(7) (a) Lamblin, M.; Nassar-Hardy, L.; Hierso, J.-C.; Fouquet, E.; Felpin, F.-X. *Adv. Synth. Catal.* **2010**, *352*, 33. (b) Yan, N.; Xiao, C.; Kou, Y. *Coord. Chem. Rev.* **2010**, *254*, 1179.(c) Grieco, P. A. *Organic Synthesis in Water*; Blackie Academic & Professional: London, 1998. (d) Leadbeater, N. E. *Chem. Commun.* **2005**, 2881. (e) Li, C. J. *Chem. Rev.* **2005**, *105*, 3095.

(8) (a) Senra, J. D.; Malta, L. F. B.; da Costa, M. E. H.; Michel, R. C.; Aguiar, L. C. S.; Simas, A. B. C.; Antunes, O. A. C. *Adv. Synth. Catal.* **2009**, *351*, 2411. (b) Sawoo, S.; Srimani, D.; Dutta, P.; Lahiri, R.; Sakar, A. *Tetrahedron* **2009**, *65*, 4367. (c) Zheng, P.; Zhang, W. *J. Catal.* **2007**, *250*, 324. (d) Bhattacharya, S.; Srivastava, A.; Sengupta, S. *Tetrahedron Lett.* **2005**, *46*, 3557. (e) Saha, D.; Chattopadhyay, K.; Ranu, B. C. *Tetrahedron Lett.* **2009**, *50*, 1003. (f) Liu, L.; Zhang, Y.; Wang, Y. *J. Org. Chem.* **2005**, *70*, 6122. (g) Sin, E.; Yi, S.-S.; Lee, Y.-S. *J. Mol. Catal. A: Chem.* **2010**, *315*, 99. (h) Lyubimov, S. E.; Vasil'ev, A. A.; Korlyukov, A. A.; Ilyin, M. M.; Pisarev, S. A.; Matveev, V. V.; Chalykh, A. E.; Zlotin, S. G.; Davankov, V. A. *React. Funct. Polym.* **2009**, *69*, 755. (i) Zhang, M.; Zhang, W. *J. Phys. Chem. C* **2008**, *112*, 6245. (j) Wei, G.; Zhang, W.; Wen, F.; Wang, Y.; Zhang, M. *J. Phys. Chem. C* **2008**, *112*, 10827. (k) Beletskaya, I. P.; Kashin, A. N.; Khotina, I. A.; Khokhlov, A. R. *Synlett* **2008**, 1547. (l) Wang, L.; Cai, C. *J. Mol. Catal. A: Chem.* **2009**, *306*, 97. (m) Samba Sivudu, K.; Mallikarjuna Reddy, N.; Nagendra Prasad, M.; Mohana Raju, K.; Murali Mohan, Y.; Yadav, J. S.; Sabitha, G.; Shailaja, D. *J. Mol. Catal. A: Chem.* **2008**, *295*, 10.

(9) (a) Bernechea, M.; de Jesús, E.; López-Mardomingo, C.; Terreros, P. *Inorg. Chem.* **2009**, *48*, 4491. (b) Garcia-Martinez, J. C.; Lezutekong, R.; Crooks, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 5097.

(10) (a) Qiao, K.; Sugimira, R.; Bao, Q.; Tomida, D.; Yokoyama, C. *Catal. Commun.* **2008**, *9*, 2470. (b) Ranu, B. C.; Chattopadhyay, K. *Org. Lett.* **2007**, *9*, 2409. (c) Jiang, J.-Z.; Cai, C. *J. Colloid Interface Sci.* **2006**, *299*, 938.

(11) (a) Saha, D.; Dey, R.; Ranu, B. C. *Eur. J. Org. Chem.* **2010**, 6067. (b) Liang, B.; Dai, M.; Chen, J.; Yang, Z. *J. Org. Chem.* **2005**, *70*, 391.

(12) Ranu, B. C.; Chattopadhyay, K.; Adak, L. *Org. Lett.* **2007**, *9*, 4595.

(13) (a) Narayanan, R.; El-Sayed, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 8340. (b) Li, Y.; Boone, E.; El-Sayed, M. A. *Langmuir* **2002**, *18*, 4921. (c) Imre, A.; Beke, D. L.; Gonitier-Moya, E.; Szabó, I. A.; Gillet, E. *Appl. Phys. A: Mater. Sci. Process.* **2000**, *71*, 19.

(14) Wang, Y.; Zhang, J.; Zhang, W.; Zhang, M. *J. Org. Chem.* **2009**, *74*, 1923.

(15) Wen, F.; Zhang, W.; Wei, G.; Wang, Y.; Zhang, J.; Zhang, M.; Shi, L. *Chem. Mater.* **2008**, *20*, 2144.

(16) (a) Gallon, B. J.; Kojima, R. W.; Kaner, R. B.; Diaconescu, P. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 7251. (b) Kantam, M. L.; Roy, M.; Roy, S.; Sreedhar, B.; Madhavendra, S. S.; Choudary, B. M.; Lal De, R. *Tetrahedron* **2007**, *63*, 8002.

(17) Ogasawara, S.; Kato, S. *J. Am. Chem. Soc.* **2010**, *132*, 4608.

(18) (a) Boffi, A.; Cacchi, S.; Ceci, P.; Cirilli, R.; Fabrizi, G.; Prastaro, A.; Niembro, S.; Shafir, A.; Vallribera, A. *ChemCatChem* **2011**, *3*, 347. (b) Bernini, R.; Cacchi, S.; Fabrizi, G.; Forte, G.; Petrucci, F.; Prastaro, A.; Niembro, S.; Shafir, A.; Vallribera, A. *Org. Biomol. Chem.* **2009**, *7*, 2270.

(19) Mayer, A. B.; Mark, J. E. *Angew. Makromol. Chem.* **1999**, *268*, 52.

(20) (a) Nishio, R.; Sugiura, M.; Kobayashi, S. *Chem. Asian J.* **2007**, *2*, 983. (b) Inasaki, T.; Ueno, M.; Miyamoto, S.; Kobayashi, S. *Synlett* **2007**, 3209. (c) Hagio, H.; Sugiura, M.; Kobayashi, S. *Org. Lett.* **2006**, *8*, 375. (d) Nishio, R.; Sugiura, M.; Kobayashi, S. *Org. Lett.* **2005**, *7*, 4831. (e) Okamoto, K.; Akiyama, R.; Yoshida, H.; Yoshida, T.; Kobayashi, S. *J. Am. Chem. Soc.* **2005**, *127*, 2125. (f) Okamoto, K.; Akiyama, R.; Kobayashi, S. *Org. Lett.* **2004**, *6*, 1987.

(21) Reetz, M. T.; de Vries, J. G. *Chem. Commun.* **2004**, 1559.

(22) (a) Teratani, T.; Ohtaka, A.; Kawashima, T.; Shimomura, O.; Nomura, R. *Synlett* **2010**, 2271. (b) Ohtaka, A.; Teratani, T.; Fujii, R.; Ikeshita, K.; Shimomura, O.; Nomura, R. *Chem. Commun.* **2009**, 7188.

(23) Narrow molecular weight distribution standards for gel permeation chromatographic (GPC) analysis.

(24) The role of K_2CO_3 is likely an electrostatic stabilization. Indeed, immobilization failed in the absence of K_2CO_3. See ref 20c.
(25) Similar results have been reported. (a) Liu, C.; Yang, W. *Chem. Commun.* **2009**, 6267. (b) Han, W.; Liu, C.; Jin, Z.-L. *Org. Lett.* **2007** *9*, 4005.
(26) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467. (b) Sonogashira, K. *J. Organomet. Chem.* **2002**, *653*, 46. (c) Suzuka, T.; Okada, Y.; Ooshiro, K.; Uozumi, Y. *Tetrahedron* **2010**, *66*, 1064. (d) Yi, C.; Hua, R. *J. Org. Chem.* **2006**, *71*, 2535.
(27) Pal, M.; Subramanian, V.; Yeleswarpu, K. R. *Tetrahedron Lett.* **2003**, *44*, 8221.
(28) Uozumi, Y.; Kobayashi, Y. *Heterocycles* **2003**, *59*, 71.
(29) Chow, W. K.; So, C. M.; Lau, C. P.; Kwong, F. Y. *J. Org. Chem.* **2010**, *75*, 5109.
(30) Nising, C. F.; Schmid, U. K.; Nieger, M.; Bräse, S. *J. Org. Chem.* **2004**, *69*, 6830.
(31) Hohiya, N.; Shimoda, M.; Yoshikawa, H.; Yamashita, Y.; Shuto, S.; Arisawa, M. *J. Am. Chem. Soc.* **2010**, *132*, 7270.
(32) Nishihara, Y.; Saito, D.; Tanemura, K.; Noyori, S.; Takagi, K. *Org. Lett.* **2009**, *11*, 3546.
(33) Faragó, J.; Kotschy, A. *Synthesis* **2009**, 85.
(34) Ackermann, L.; Kaspar, L. T. *J. Org. Chem.* **2007**, *72*, 6149.
(35) Bates, C. G.; Saejueng, P.; Murphy, J. M.; Venkataraman, D. *Org. Lett.* **2002**, *4*, 4727.