

## Supporting Information

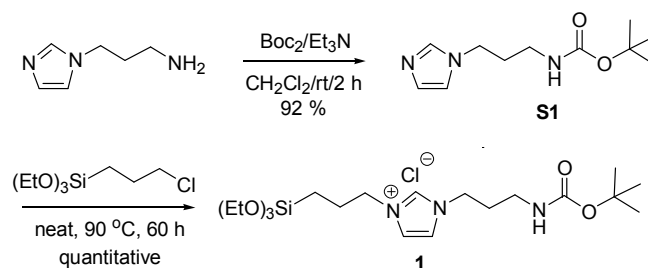
### Palladium nanoparticles captured onto spherical silica particles using a urea cross-linked imidazolium molecular band

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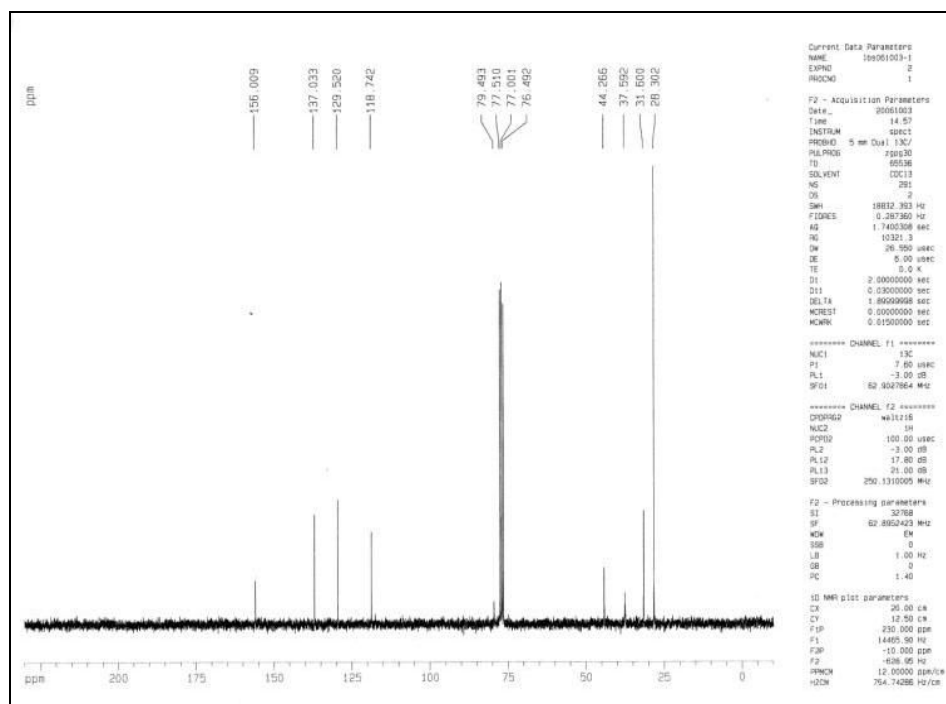
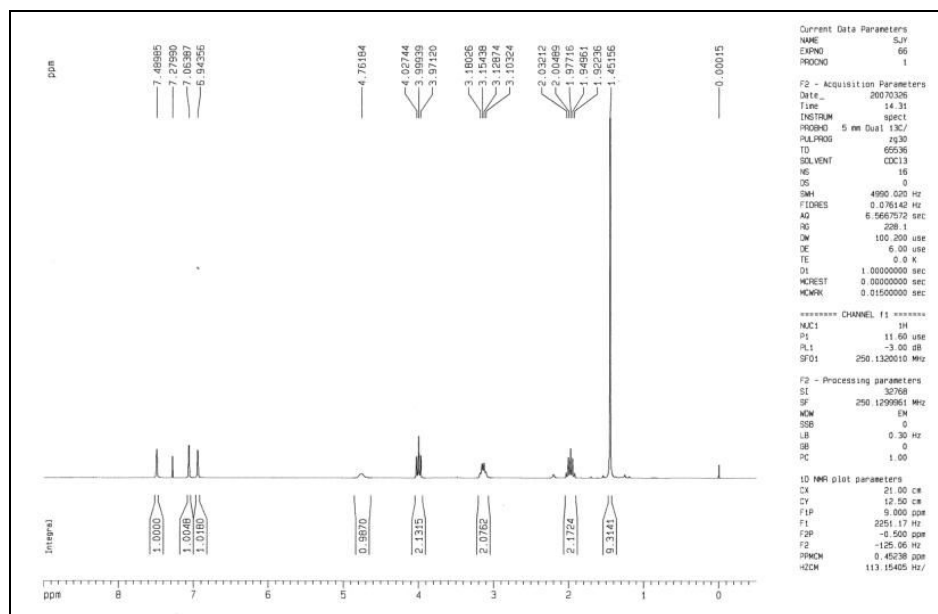
**General.** Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury VX300 NMR spectrometer (250 MHz) in given solvent. Chemical shifts were expressed in ppm with TMS as an internal standard ( $\delta = 0$  ppm) for  $^1\text{H}$  NMR, coupling constants ( $J$ ) are in Hz. All anhydrous solvents were dried prior to use: Methylene chloride and DMF were freshly distilled from calcium hydride. The purchased reagents are used as received without further purification. All manipulations involving air and moisture-sensitive compounds and reactions were carried out using standard Schlenk technique under nitrogen atmosphere. Inductive coupled plasma-atomic emission spectrometer (ICP-AES) analyses were conducted with Perkin Elmer (Optima-4300DV) and High Resolution Transmission Electron Microscope (HR-TEM) analyses were conducted with JEM-3010 (JEOL, 300Kv) at National center for inter-university research facilities in Seoul National University. X-Ray Photoelectron Spectrometer (XPS) analyses were conducted with ESCALAB 250 XPS spectrometer at Korea Basic Science Institute Busan Center. X-ray absorption near-edge structure (XANES) spectroscopy experiments were carried out at the Pd K-edge with the extended X-ray absorption fine structure (EXAFS) facility installed at the beam line 7C at the Pohang Accelerator Laboratory (PAL) in Korea. XANES data were collected at room temperature in a transmission mode using gas-ionization detectors. All the present spectra were calibrated by measuring the spectrum of Pd metal foil.

#### Synthesis of 1-[(*N*-*tert*-butoxycarbonyl)aminopropyl]-3-(3-triethoxysilylpropyl)imidazolium chloride **1**.

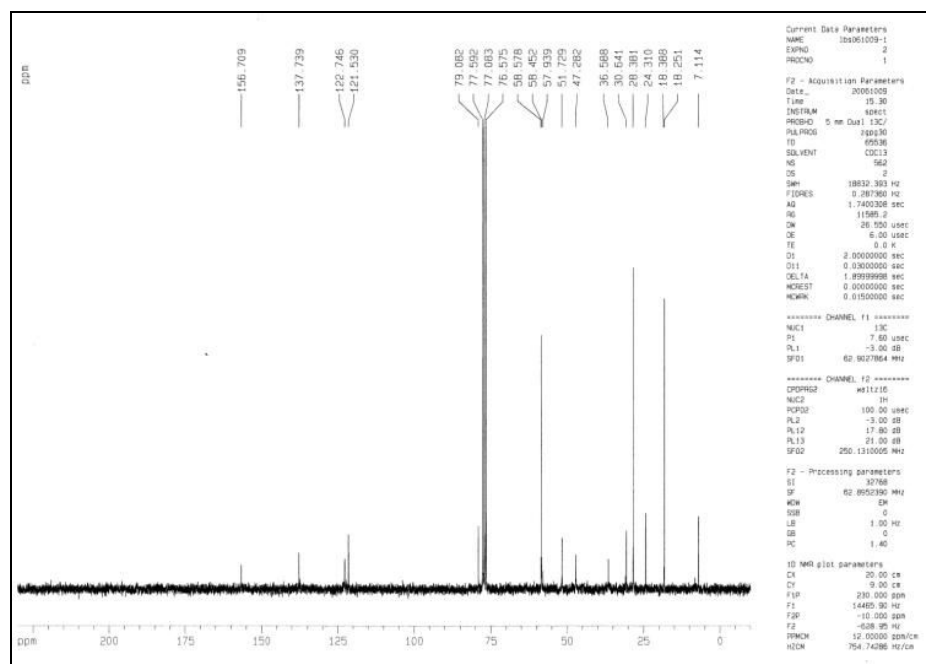
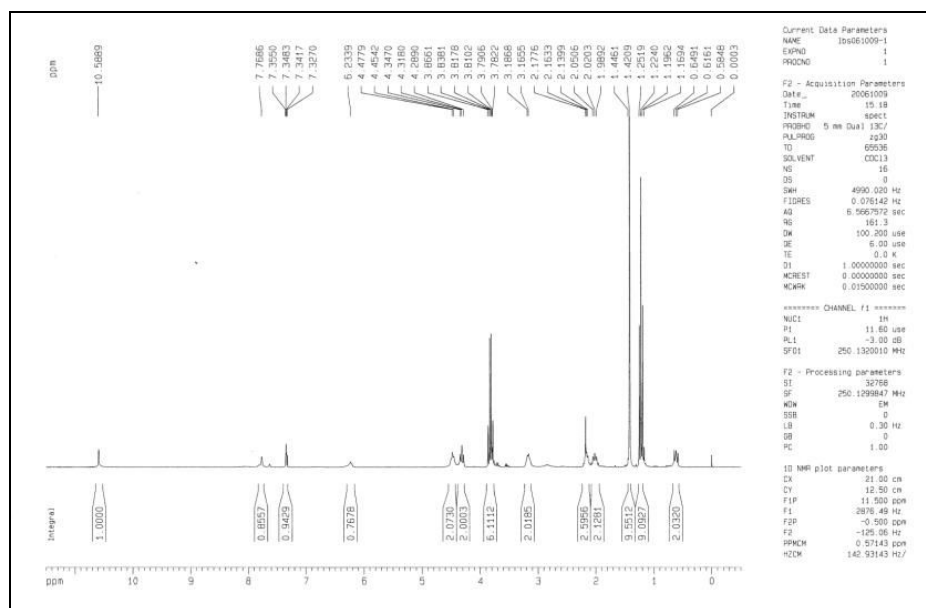


**1-[(*N*-*tert*-butoxycarbonyl)aminopropyl]imidazole **S1**:** To a solution of 1-(3-aminopropyl)imidazole (1.0 g, 8.2 mmol) in anhydrous methylene chloride (9.0 mL) was added triethylamine (1.14 mL, 8.2

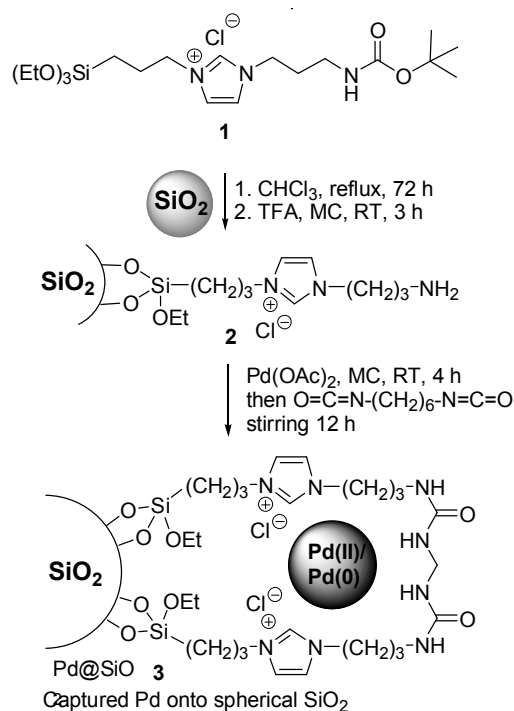
mmol) and excess  $\text{Boc}_2\text{O}$  (2.0 mL) at room temperature. The reaction mixture was stirred for 2 h, and the solvent was evaporated under reduced pressure. The resulting brown residue was purified by column chromatography on silica-gel (petroleum ether/EtOAc = 4/1) to give 1-[(*N*-tert-butoxycarbonyl)aminopropyl]imidazole **S1** (1.65 g, 92%) as a colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.45 (s, 9H), 1.98 (tt,  $J=6.9$  Hz, 2H), 3.13 (dt,  $J=6.4, 6.5$  Hz, 2H), 3.99 (t,  $J=7.0$  Hz, 2H), 4.76 (bs, 1H), 6.94 (s, 1H), 7.06 (s, 1H), 7.49 (s, 1H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.3, 31.6, 37.6, 44.3, 79.5, 118.7, 129.5, 137.0, 156.1 ppm.



**1-[(*N*-*tert*-butoxycarbonyl)aminopropyl]-3-(3-triethoxysilylpropyl)imidazolium chloride 1:** An equivalent molar mixture of 3-chloropropyltriethoxysilane (1.0 mL, 4.44 mmol) and 1-[(*N*-*tert*-butoxycarbonyl)aminopropyl]imidazole **S1** (1.0 g, 4.44 mmol) was stirred for 60 h at 90 °C under N<sub>2</sub> atmosphere. The reaction mixture was cooled to room temperature and dried under vacuum to give the desired 1-[(*N*-*tert*-butoxycarbonyl)aminopropyl]-3-(3-triethoxysilylpropyl)imidazolium chloride **1** (2.0 g, 99%) as a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.61 (m, 2H), 1.22 (t, *J*=7.0 Hz, 9H), 1.42 (s, 9H), 2.02 (m, 2H), 2.14 (m, 2H), 3.17 (m, 2H), 3.83 (q, *J*=7.0 Hz, 6H), 4.32(t, *J*=7.3 Hz, 2H), 4.48 (t, *J*=6.0 Hz, 2H), 6.23(bs, 1H), 7.35 (s, 1H), 7.77 (s, 1H), 10.59 (s, 1H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 7.1, 18.3, 24.3, 28.4, 30.6, 36.6, 47.3, 51.7, 58.5, 79.1, 121.5, 122.7, 137.7, 156.7 ppm.



**Representative procedure for the preparation of captured palladium particles onto spherical silica particles (Pd@SiO<sub>2</sub> 3)**



1-(3-*N*-*tert*-Butoxycarbonylamino)propyl)-3-(triethoxysilyl)propyl)imidazolium chloride **1** (4.5 mL) was added to a suspension of spherical SiO<sub>2</sub> (4.5 g) in chloroform (30 mL). The resulting mixture was refluxed for 72 h under nitrogen atmosphere. After cooling to room temperature, the SiO<sub>2</sub> particles were separated and washed 4 times with dichloromethane by repeated (10,000 rpm, 500 sec), and dried under vacuum at room temperature to give *N*-Boc protected aminoimidazolium-functionalized SiO<sub>2</sub> particles (4.5 g) as white solid. For the deprotection of *N*-Boc group, to a suspension of *N*-Boc protected aminoimidazolium-functionalized SiO<sub>2</sub> particles (0.5 g) in dry methylene chloride (8.0 mL) was added trifluoro acetic acid (0.8 mL) at room temperature. After 3 h stirring gently, the SiO<sub>2</sub> particles separated by centrifuge and washed successively with 10% Et<sub>3</sub>N/CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and dichloromethane (50 mL x 5) and dried under vacuum to give Boc deprotected aminoimidazolium-functionalized SiO<sub>2</sub> particles **2** (0.5 g). Elemental analysis SiO<sub>2</sub> particles **2** indicated 0.238 mmol/g of aminopropylimidazolium moiety was incorporated. In order to capture palladium particles onto spherical SiO<sub>2</sub> particles, to a suspension of aminoimidazolium-functionalized SiO<sub>2</sub> particles (0.36 g) in dry dichloromethane (5.0 mL) was added Pd(OAc)<sub>2</sub> (36 mg). After the stirring gently for 4 h at room temperature, 1,6-diisocyanatohexane (20 mg) was added and stirred 12 h further. The SiO<sub>2</sub> particles were separated by centrifugation and washed several times with dichloromethane to remove unreacted diisocyanatohexane and uncaptured Pd(OAc)<sub>2</sub>. After drying under vacuum at room temperature, the Pd@SiO<sub>2</sub> composites subjected to ICP-AES analysis, which indicated 6.846 x 10<sup>-2</sup> mmol/g of Pd captured onto the silica particles.

**Procedure for the immobilization of palladium particles onto unmodified spherical silica particles**

(Pd@unmodified SiO<sub>2</sub>). To a suspension of unfunctionalized SiO<sub>2</sub> particles (0.60 g) in dry dichloromethane (10.0 mL) was added Pd(OAc)<sub>2</sub> (60 mg), and the resulting suspension was stirred for 12 h. The SiO<sub>2</sub> particles were separated by centrifugation and washed several times with dichloromethane to remove unbound Pd(OAc)<sub>2</sub>. After drying under vacuum at room temperature, the Pd@un-modified SiO<sub>2</sub> composites subjected to ICP-AES analysis, which indicated 2.44 x 10<sup>-2</sup> mmol/g of Pd captured onto the silica particles.

**Suzuki-Miyaura Coupling reaction.** To a solution of 4-bromoacetophenone (55.8 mg, 0.27 mmol), phenylboronic acid (39.0 mg, 0.30 mmol), CsCO<sub>3</sub> (116.3 mg, 0.36 mmol) in dimethylformamide (1.6 mL) was added Pd@SiO<sub>2</sub>-**3** (197.2 mg, 5 mol%, based on palladium content), and the reaction mixture stirred at 130 °C for 18 h. The reaction mixture was filtered through a membrane filter (0.2 μm porosity) and the filter cake was washed with methylene chloride first, and subsequently washed with water/methanol (3:7, v/v), and methanol to recover the captured Pd@SiO<sub>2</sub>-**3**, which was used for the next run after drying under vacuum at room temperature. The water/methanol filtrate was evaporated, and extracted with ethyl acetate. The methylene chloride filtrate and ethyl acetate were combined. Evaporation under reduced pressure and purification by short silica column chromatography gave 4-phenylacetophenone (52 mg, 95% yield). The same reactions were conducted with Pd deposited onto amine-functionalized SiO<sub>2</sub> **2** (Pd@SiO<sub>2</sub>-**2**) and un-modified SiO<sub>2</sub> (Pd@SiO<sub>2</sub>-unmodified), and the recycling results and the Pd contents in the recovered Pd@SiO<sub>2</sub>-**3**, Pd@SiO<sub>2</sub>-**2**, Pd@SiO<sub>2</sub>-unmodified and in the reaction mixture determined by ICP-AES are summarized in Table S1.

Table S1.

entry	catalyst	runs	yield	Loss of wt% Pd mmol/g (before/after)	Pd in reaction mixture
1	Pd@SiO <sub>2</sub> - <b>3</b>	1	> 95	6.85x10 <sup>-2</sup> /5.04 x 10 <sup>-2</sup> (26%)	375 ppm
2		2	> 95	5.04x10 <sup>-2</sup> /4.94 x 10 <sup>-2</sup> (2.0%)	10 ppm
3		3	> 95	4.94x10 <sup>-2</sup> /4.83x10 <sup>-2</sup> (2.0%)	7 ppm
4		4	> 95	-	-
5		5	> 95	-	-
6	Pd@SiO <sub>2</sub> - <b>2</b>	1	> 95	4.04x10 <sup>-2</sup> /2.19x10 <sup>-2</sup> (46%)	649 ppm
7		2	68%	2.19x10 <sup>-2</sup> /1.70x10 <sup>-2</sup> (23%)	170 ppm
	Pd@SiO <sub>2</sub> -unmodified	1	> 95	2.44x10 <sup>-2</sup> /0.15x10 <sup>-2</sup> (94%)	-