

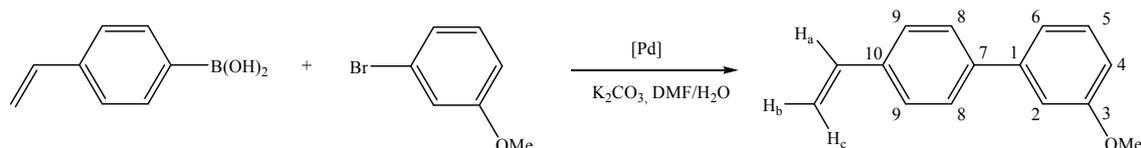
## Supplementary Material

### 1. Catalytic procedure for Suzuki reaction of 3-bromoanisole and 4-vinylboronic acid

In a typical catalytic reaction a three-neck flask was filled with boronic acid (0.2 g, 1.2 mmol),  $K_2CO_3$  (0.22 g, 1.6 mmol) and 15 mg Pd catalyst (Scheme S1) and three vacuum/ $N_2$  cycles (10 min/1 min) under stirring were applied to remove oxygen from the reaction atmosphere. In parallel, the solvent (DMF/ $H_2O$  95/5, 10 mL) and the aryl halide were mixed under nitrogen in a Schlenk tube, bubbling  $N_2$  inside the solution for 15 min to eliminate dissolved oxygen. Subsequently, this mixture was transferred to the three-neck flask with the solid mixture under  $N_2$ . The suspension was then heated to the corresponding temperature (using a condenser in the case of refluxing conditions) and stirred for 24 h. After this time, the solution was cooled to room temperature and the solvent was removed under vacuum.

The technique employed to quantitatively analyze the conversion of 3-bromoanisole and to identify the reaction product was gas chromatography (GC) with FID detector (Varian CP-3370) using a 15 m CP-SIL-8 column provided by Scharlau. To follow the changes of the halide concentration, an internal standard compound (1-octanol) was used. The calibration curve was prepared using concentration of halide in the range 0-500 ppm. The temperature conditions were: injector temperature: 240 °C, detector temperature: 250 °C, oven temperature program 130 °C (10 min); from 130 °C to 210 °C (with a ramp of 20 °C/min) and 210 °C (10 min). Operating under these conditions the retention times of the chemical species in solution were, DMF: 3.5 min, 1-octanol: 7.8 min, 3-bromoanisole: 12.0 min, 4-carboxyphenylboronic acid: 16.7 min, product 20.2 min. The tests were carried out in triplicate and the conversion of 3-bromoanisole for this reaction was  $41 \pm 1\%$ .

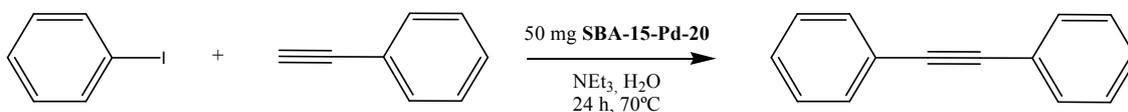
The purification of the product was achieved using a chromatographic column, charged with silica gel and the suitable eluent to separate the reaction product. The latter was chosen on the basis of tests carried out on thin layer chromatography (TLC). Hexane/dichloroethane (8/2) was used as the eluent solution. Solvent was removed from the solution containing the product with a rotavapor and the pale yellow solid obtained was dried overnight at 60 °C under vacuum. The product was characterized by  $^1H$ -NMR analysis, using  $CDCl_3$  as solvent.  $^1H$  NMR (500 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 3,90 (s, 3H, *OMe*), 5,31 (dd,  $^2J_{BC} = 1$  Hz y  $^3J_{BA} = 11$  Hz, 1H,  $CH=CH_2 \rightarrow H_b$ ), 5,82 (dd,  $^2J_{CB} = 1$  Hz y  $^3J_{CA} = 17,5$  Hz, 1H,  $CH=CH_2 \rightarrow H_c$ ), 6,79 (dd,  $^3J_{AB} = 11$  Hz y  $^3J_{AC} = 17,5$  Hz, 1H,  $CH=CH_2 \rightarrow H_a$ ), 6,92 (dd appears as a pseudo t, 1H, *H* en C6), 7,16 (pseudo t, 1H, *H* en C2), 7,22 (d, 1H, *H* en C4), 7,38 (m, 1H, *H* en C5), 7,51 (d,  $^3J = 8,0$  Hz, 2H, *H* en C9) y 7,59 (d,  $^3J = 8,0$  Hz, 2H, *H* en C8) ppm.  $^{13}C\{^1H\}$  NMR (500 MHz,  $CDCl_3$ , 25 °C):  $\delta$  = 55,3 (*OMe*), 112,70 y 112,73 (C2 y C4), 114,0 ( $CH=CH_2$ ), 119,5 (C6), 126,6 (C9), 127,3 (C8), 129,8 (C5), 136,4 y 136,8 (C1 y C7), 140,5 (C10), 142,3 ( $CH=CH_2$ ), 160,0 (C3) ppm.



**Scheme S1.** Suzuki C-C coupling reaction of 4-vinylphenylboronic acid and 3-bromoanisole

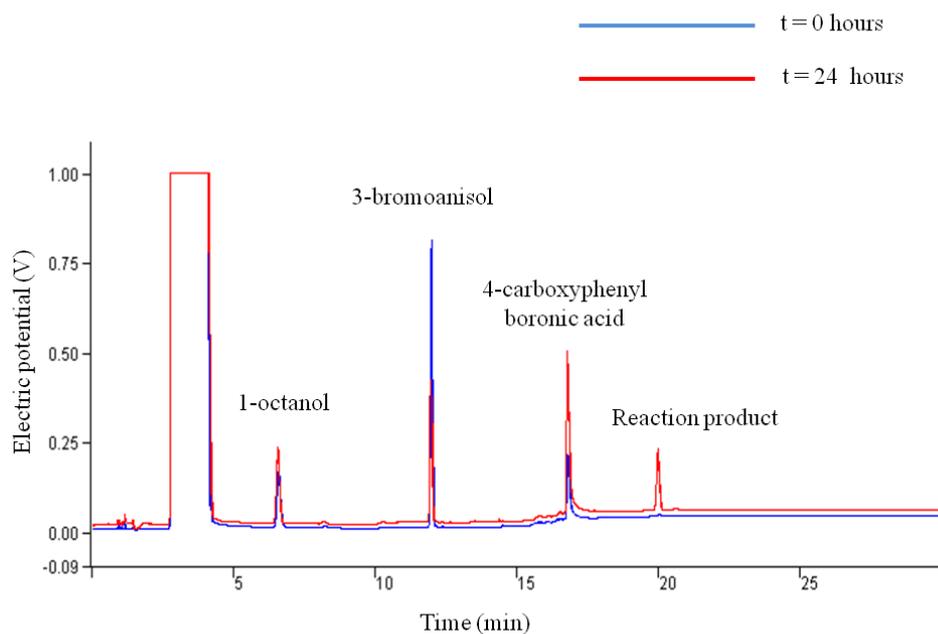
## 2. Catalytic procedure for Sonogashira reaction of iodobenzene and phenylacetylene

To a three-neck flask with stirring bar, iodobenzene (52.0 mg, 0.5 mmol), phenylacetylene (56.2 mg, 0.55 mmol), triethylamine (152 mg, 1.5 mmol), and H<sub>2</sub>O (10 mL). and 50 mg of **SBA-15-Pd-20** were added (Scheme S2). The reaction was then stirred at 70 °C for 24 hours and then slowly cooled to room temperature. Subsequently, the mixture was filtered and the filtrate extracted four times with diethylether. The combined organic extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The resulting product was purified by TLC (hexane/CH<sub>2</sub>Cl<sub>2</sub>) and analyzed by <sup>1</sup>H NMR observing the exclusive formation of diphenylacetylene, yield: 36%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.56-7.52 (m, 4 H), 7.36-7.33 (m, 6 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 131.2, 128.3, 128.2, 123.5, 89.2.



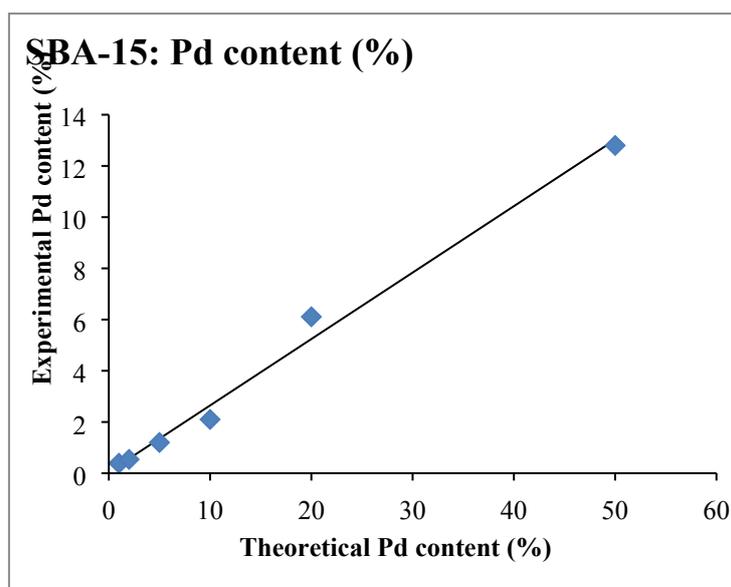
**Scheme S2.** Sonogashira reaction of iodobenzene and phenylacetylene

### 3. GC analysis

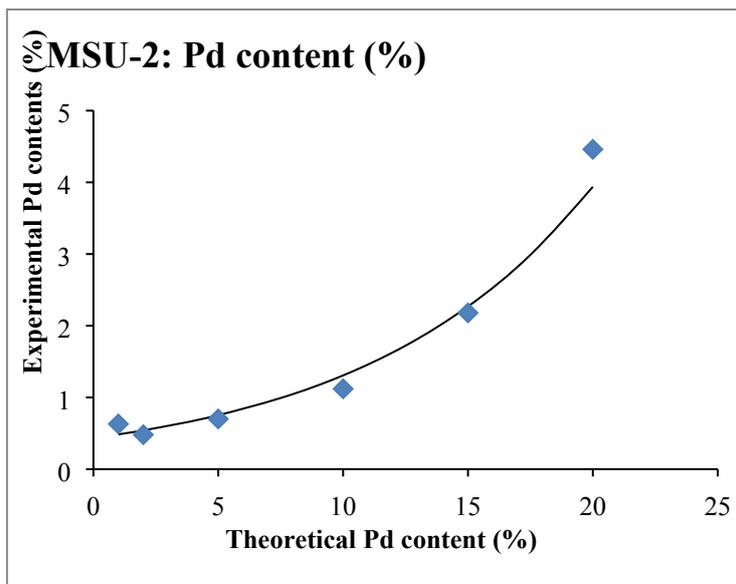


**Figure S1.** Example of a GC chromatogram of the mixture in the catalytic reaction of 4-carboxyphenyl boronic acid and 3-bromoanisole

### 4. Plots of palladium loading reactions

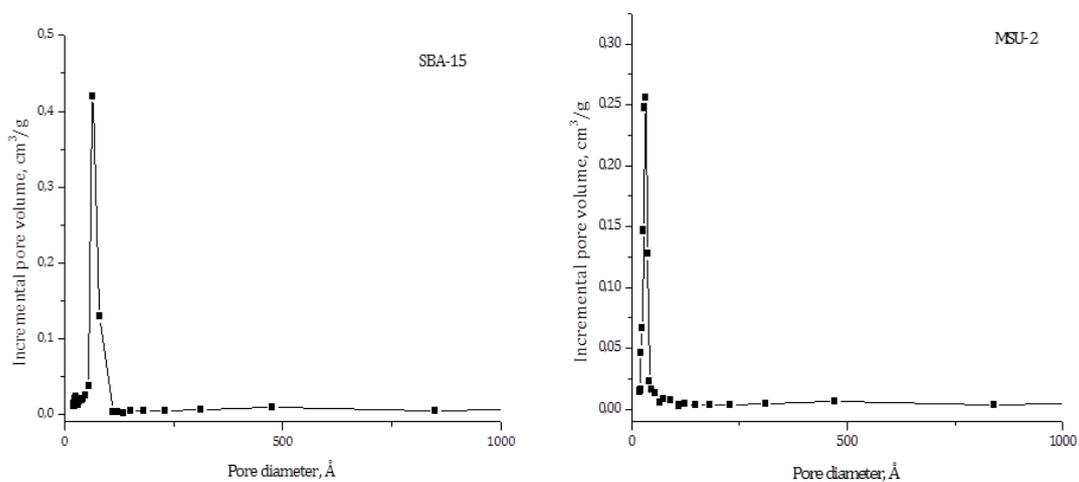


**Figure S2.** Plot for Pd-loading reactions using SBA-15.



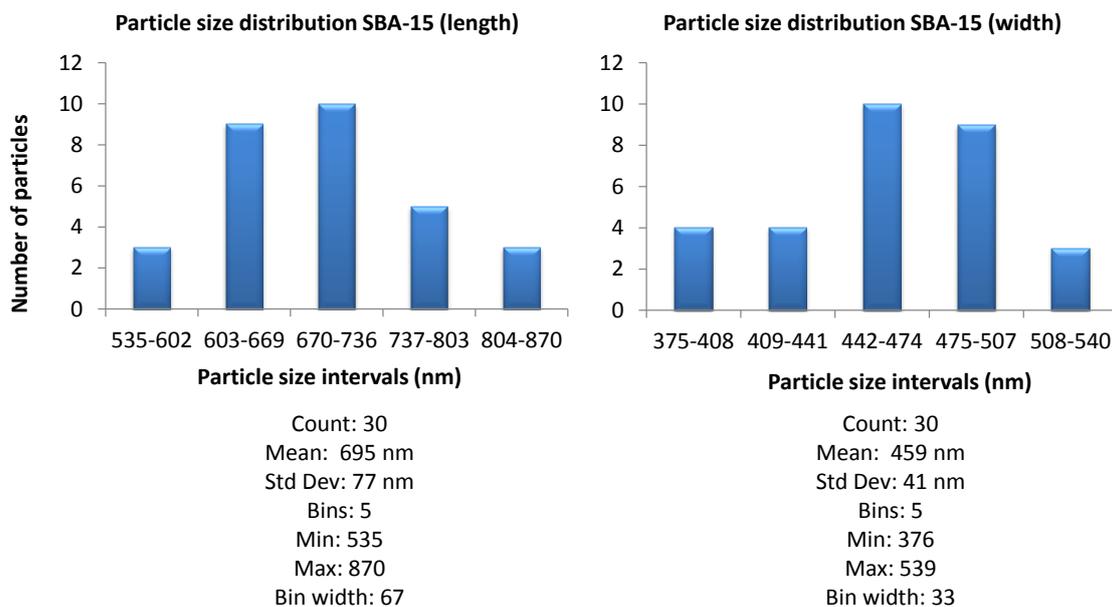
**Figure S3.** Plot for Pd-loading reactions using MSU-2.

### 5. Pore size distribution of SBA-15 and MSU-2

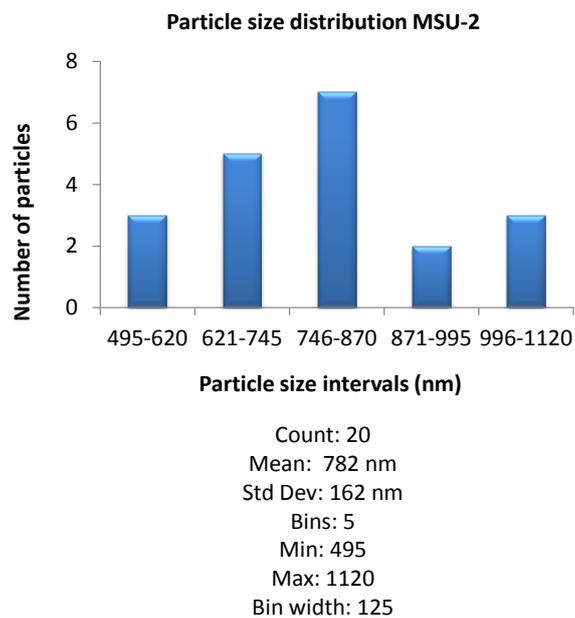


**Figure S4.** Pore size distribution for SBA-15 and MSU-2

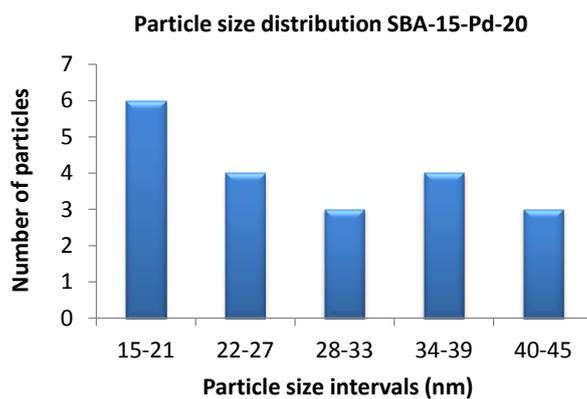
## 6. Particle Size analysis of TEM images



**Figure S5.** Particle size distribution for SBA-15 (from TEM images using ImageJ software).

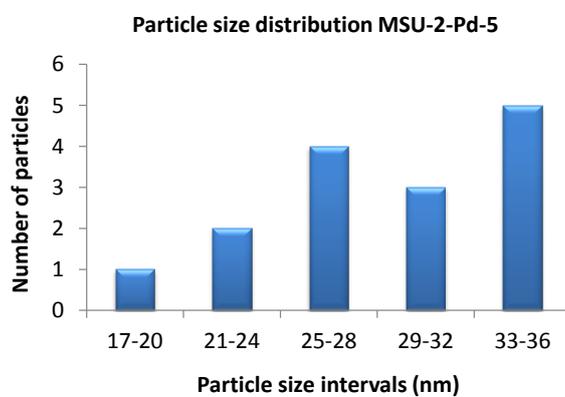


**Figure S6.** Particle size distribution for MSU-2 (from TEM images using ImageJ software)



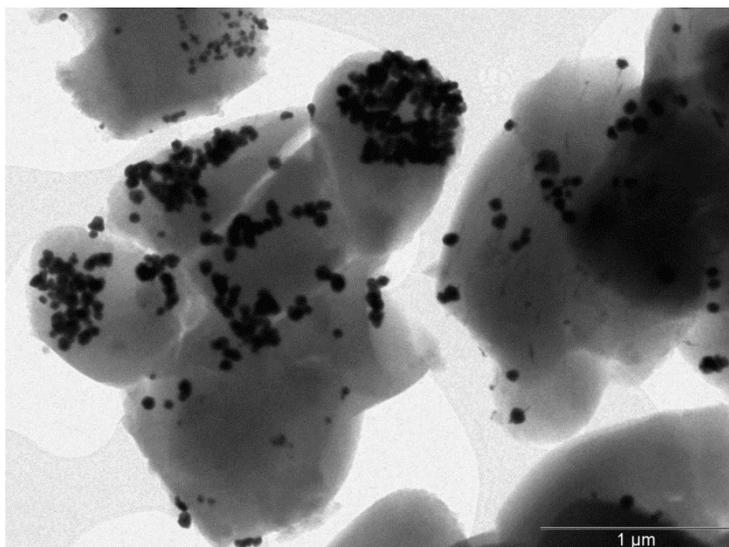
Count: 20  
 Mean: 29 nm  
 Std Dev: 9 nm  
 Bins: 5  
 Min: 16  
 Max: 45  
 Bin width: 6

**Figure S7.** Particle size distribution for palladium nanoparticles in **SBA-15-Pd-20** (from TEM images using ImageJ software)



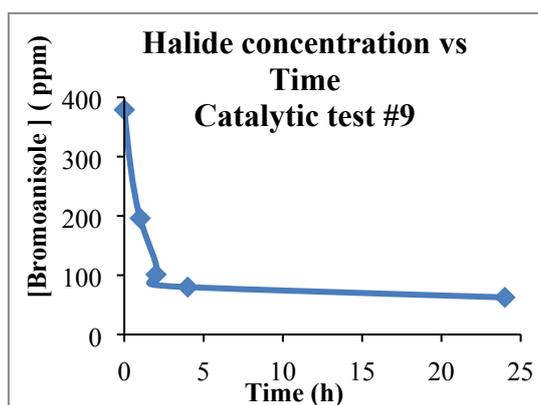
Count: 15  
 Mean: 28 nm  
 Std Dev: 5 nm  
 Bins: 5  
 Min: 17  
 Max: 36  
 Bin width: 4

**Figure S8.** Particle size distribution for palladium nanoparticles in **MSU-2-Pd-5** (from TEM images using ImageJ software)

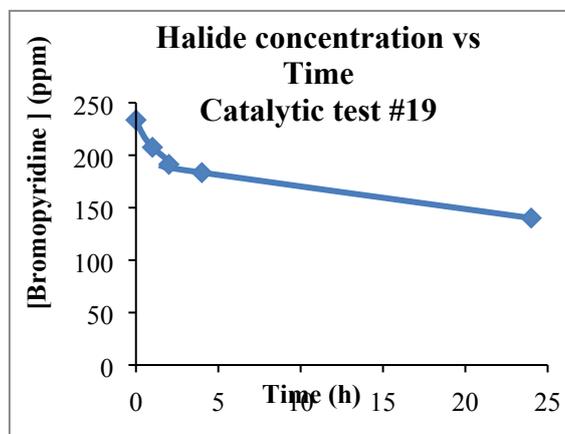


**Figure S9.** TEM image of SBA-15-Pd-50 after a catalytic reaction at 110 °C.

#### 7. Halide concentration vs Time plot for some catalytic tests

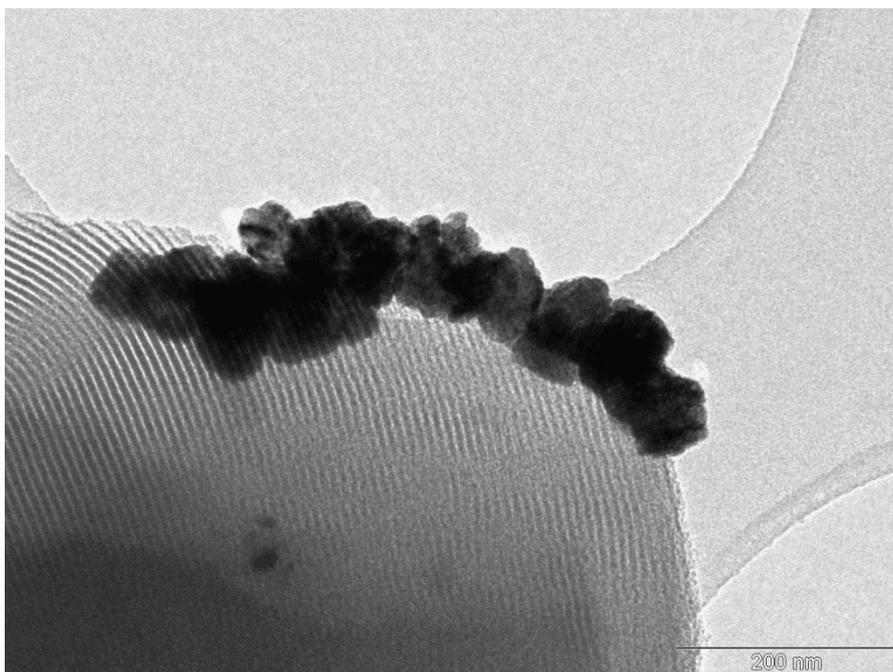


**Figure S10.** Halide concentration vs time in catalytic test #9



**Figure S11.** Halide concentration vs time in catalytic test #19

## 8. TEM analysis and experimental data in recyclability tests



**Figure S12.** TEM image of SBA-15-Pd-50 after the first catalytic cycle in recyclability tests

**Table S1.** Final quantities of reactants used in the different recyclability tests

	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
3-bromoanisole	327.2 mg	310.9 mg	294.5 mg	278.2 mg	261.8 mg
4-carboxyphenylboronic acid	432.8 mg	412.9 mg	390.5 mg	368.1 mg	348.2 mg
K <sub>2</sub> CO <sub>3</sub>	480.9 mg	458.8 mg	434.0 mg	409.1 mg	387.0 mg
DMF/H <sub>2</sub> O 95/5	65 mL	62 mL	59 mL	55 mL	52 mL
Catalyst	1.0 g	0.95 g	0.90 g	0.85 g	0.80 g