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Electronic Supplementary Information

Magnetically Recyclable Hollow Nanocomposite Catalyst for Heterogeneous Reduction of Nitroarenes and Suzuki Reaction

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Materials

Water was deionized by a Barnsted Nano Pure System. All chemicals were purchased from various companies (Aldrich, Fluka, and Samchun) and used without further purification.

Characterization

Transmission electron microscope (TEM) and HRTEM images were obtained using a JEOL EM-2010 microscope at an acceleration voltage of 200 kV. Inductivity coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu ICPS-7500 Japan) was used for the elemental analysis. X-ray photoelectron spectroscopy was performed to collect core level spectra of Pd (3d) and Rh (3d) using Al Kα source (Sigma probe, VG Scientifics). Powder X-ray diffraction was obtained with a Rigaku D/Max-3C diffractometer, equipped with a rotating anode and a Cu Kα radiation source (λ= 0.15418 nm). FE-SEM images were obtained on a Jeol JSM-6700F. The surface area and pore size was measured using micromeritics surface area measurement analyzer (ASAP 2000). Elemental analysis was performed by Elemental Analyzer using CHNS-932 (LECO Corp).

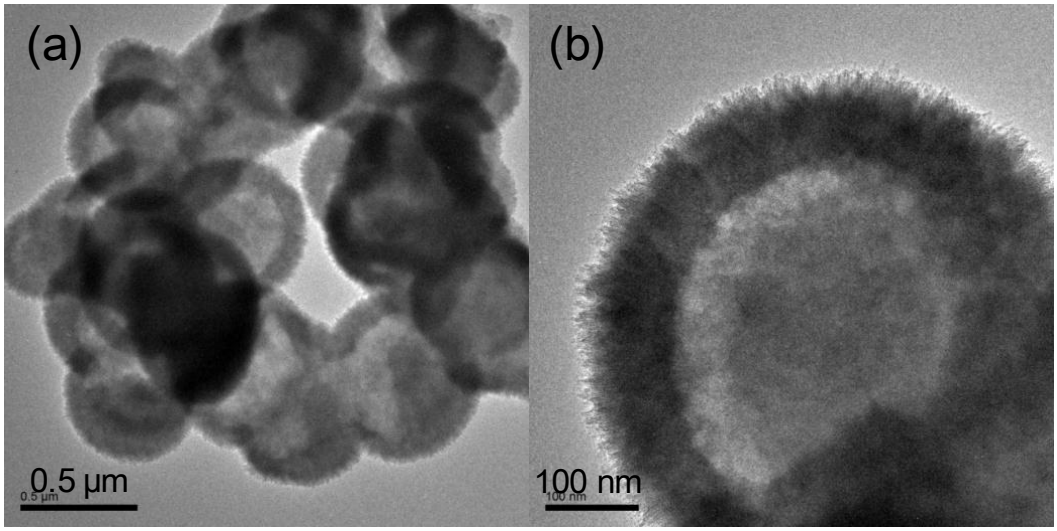

Figure S1. Low magnification (a) and high magnification (b) TEM images of hollow iron hydroxide nanostructures.

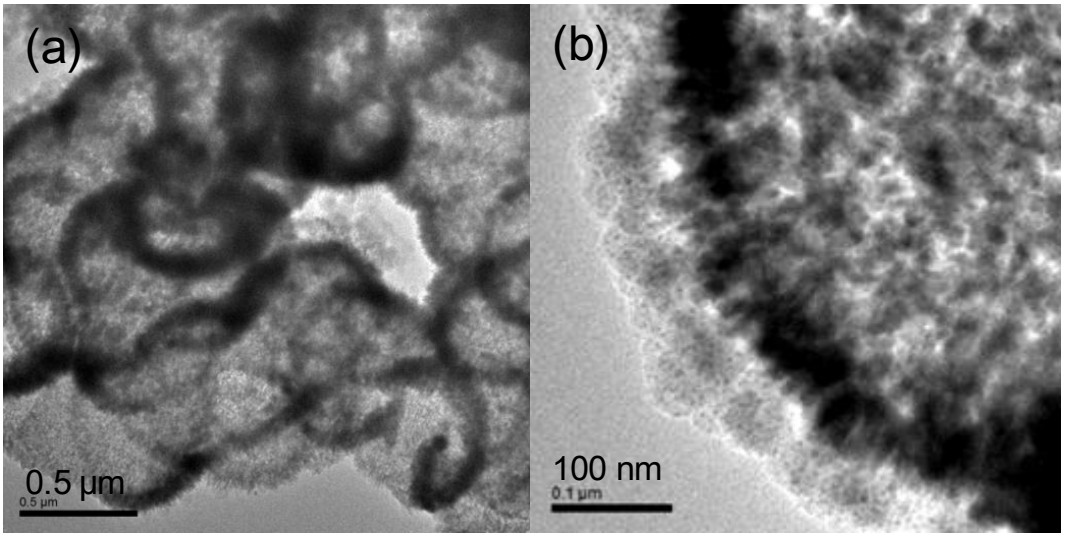

Figure S2. Low magnification (a) and high magnification (b) TEM images of the hollow nanocomposite Pd catalysts.

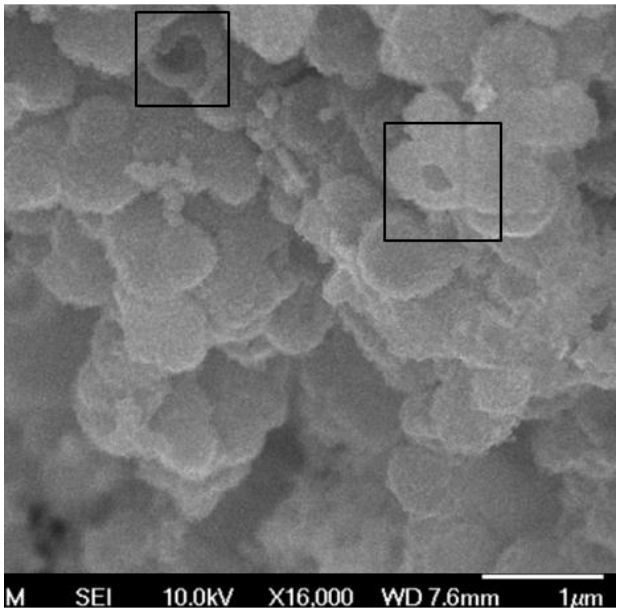

Figure S3. SEM image of magnetically recyclable hollow nanocomposite catalyst.

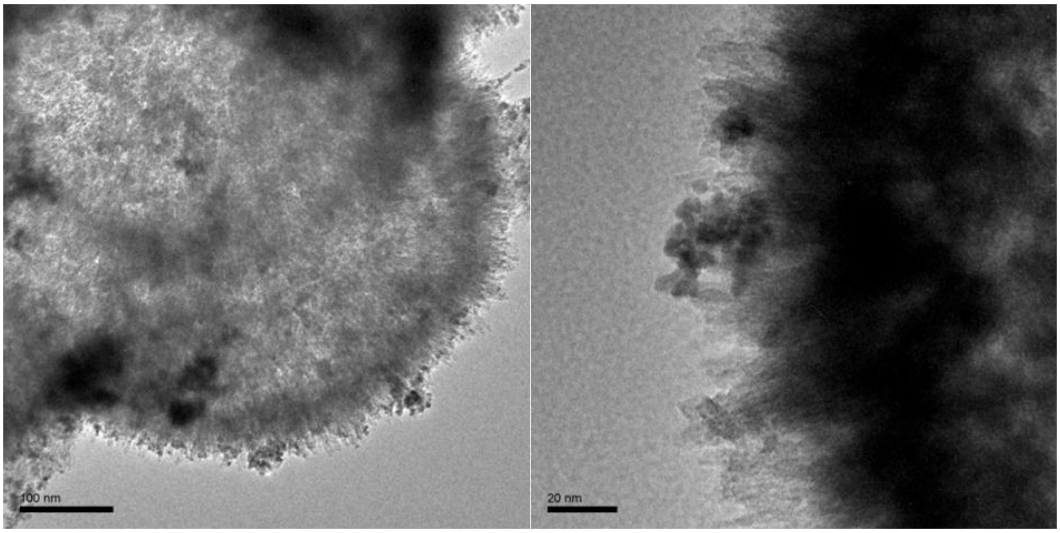

Figure S4. TEM image of Pd NPs loaded on hollow nanocomposite without carbon.

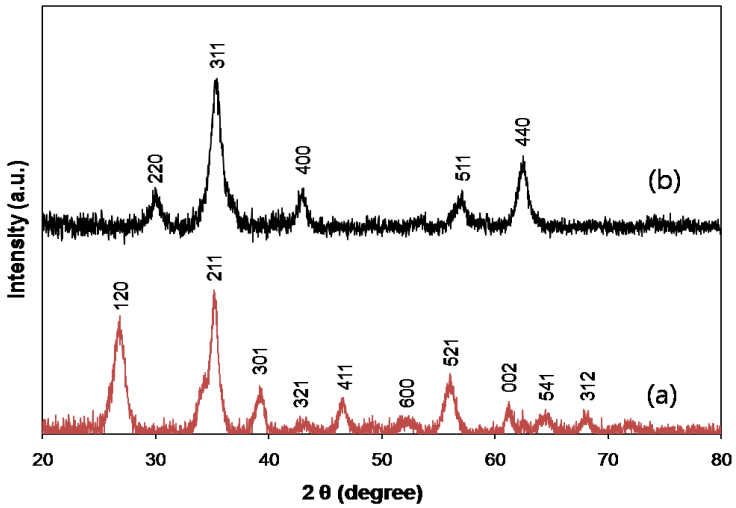

Figure S5. XRD pattern of (a) hollow iron hydroxide (β-FeOOH), and (b) magnetically recyclable hollow nanocomposite catalyst.

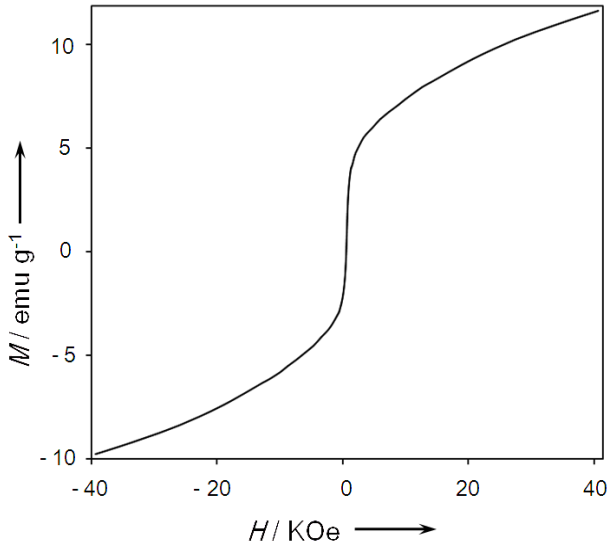

Figure S6. Field-dependent magnetization of the hollow nanocomposite catalyst at 300 K.

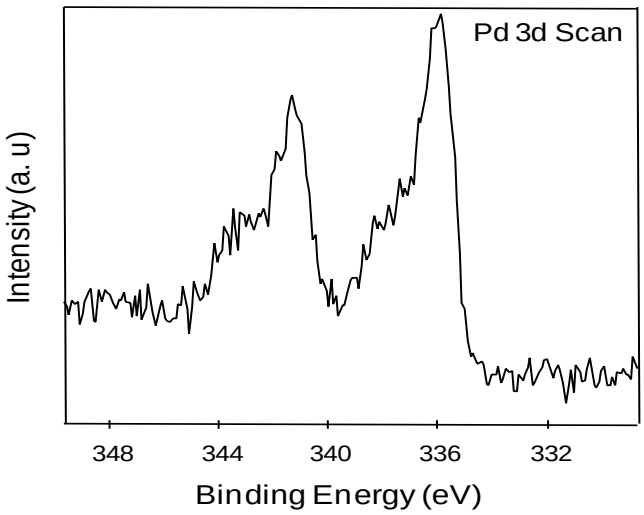

Figure S7. XPS analysis of Pd 3d scan for magnetically recyclable hollow nanocomposite Pd catalyst.

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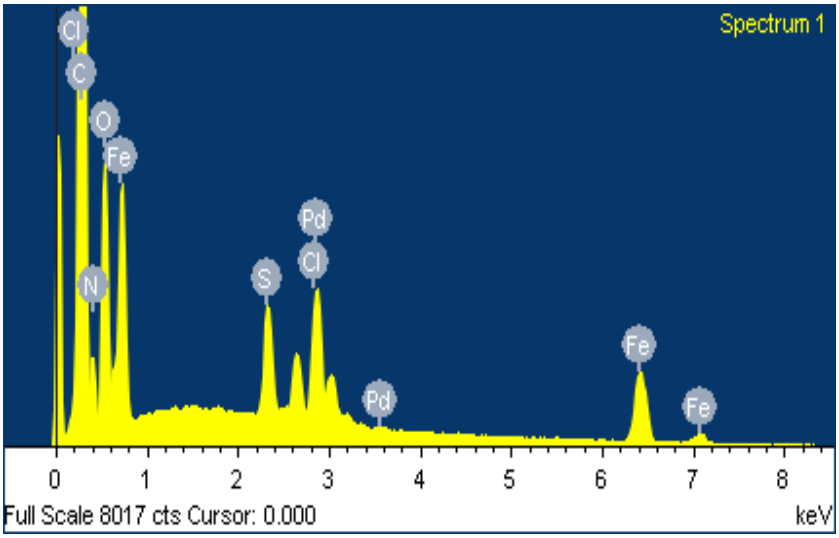


Figure S8. EDX spectrum of magnetically recyclable hollow nanocomposite Pd catalyst.

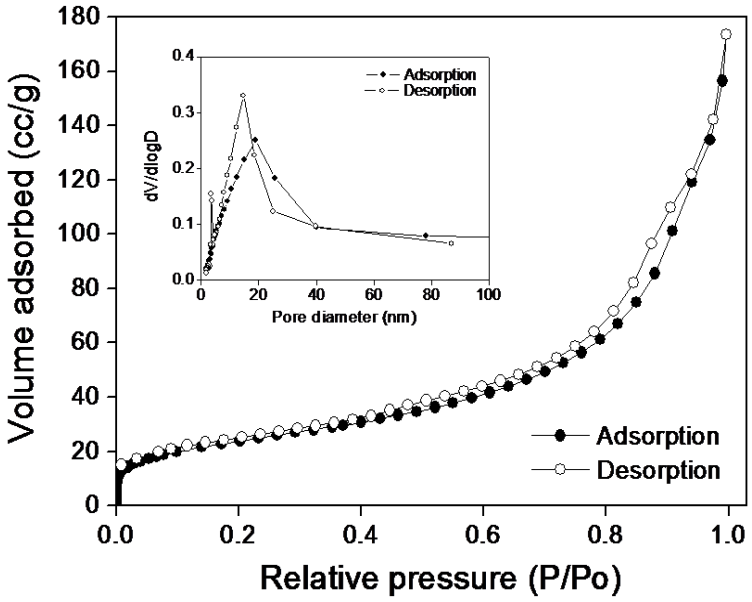


Figure S9. N_2 adsorption/desorption isotherms of magnetically recyclable hollow nanocomposite catalyst. The inset shows pore size distribution.

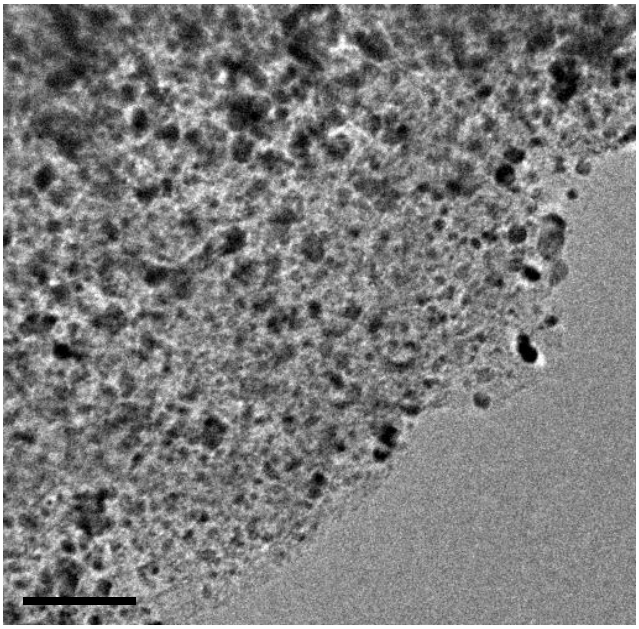


Figure S10. TEM image of commercially available Pd/C catalyst.

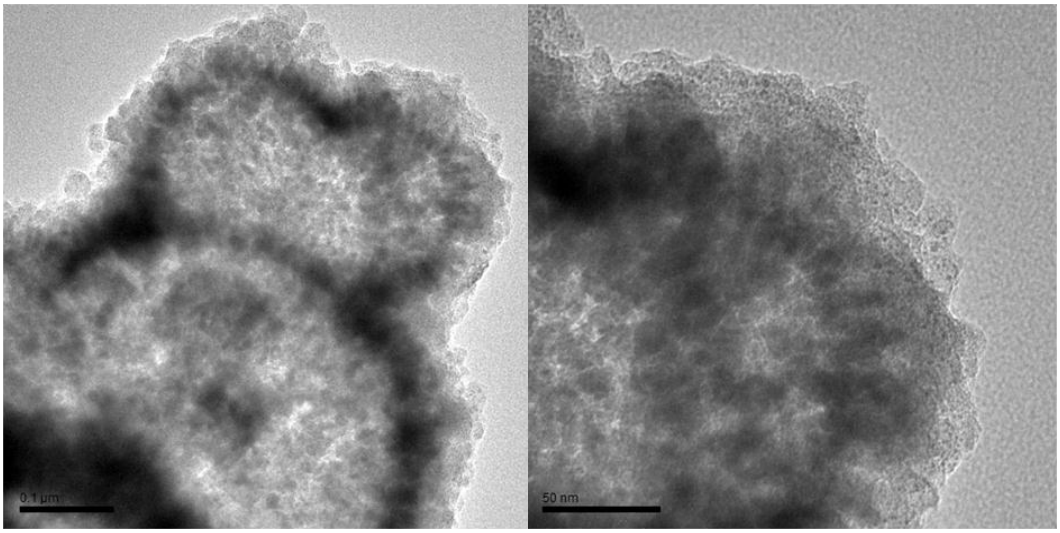


Figure S11. TEM image of magnetically recyclable hollow nanocomposite Rh catalyst.

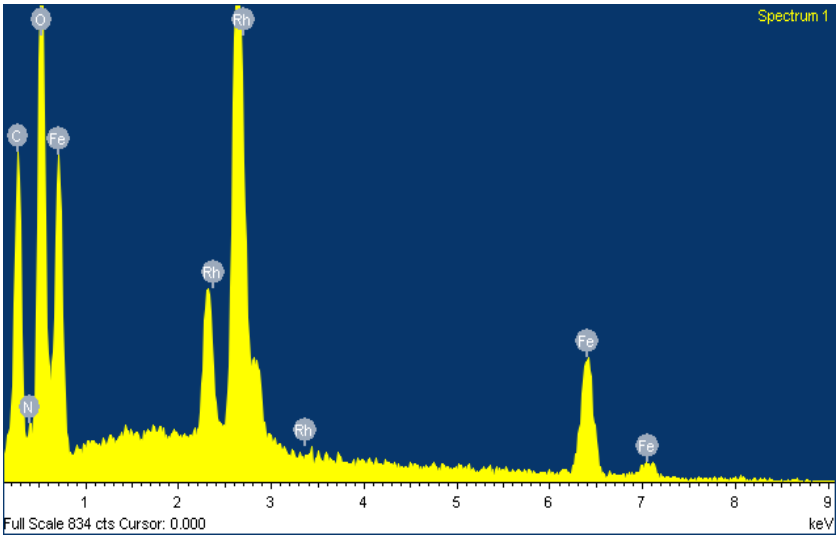


Figure S12. EDX spectrum of magnetically recyclable hollow nanocomposite Rh catalyst.

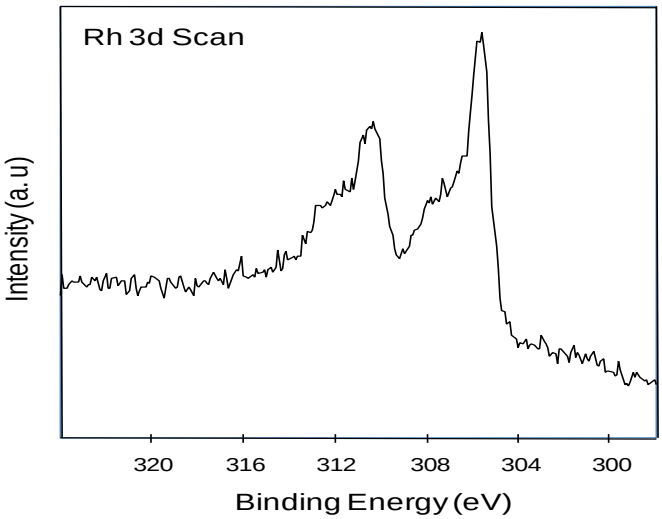


Figure S13. XPS analysis of Rh 3d scan for magnetically recyclable hollow nanocomposite Rh catalyst.

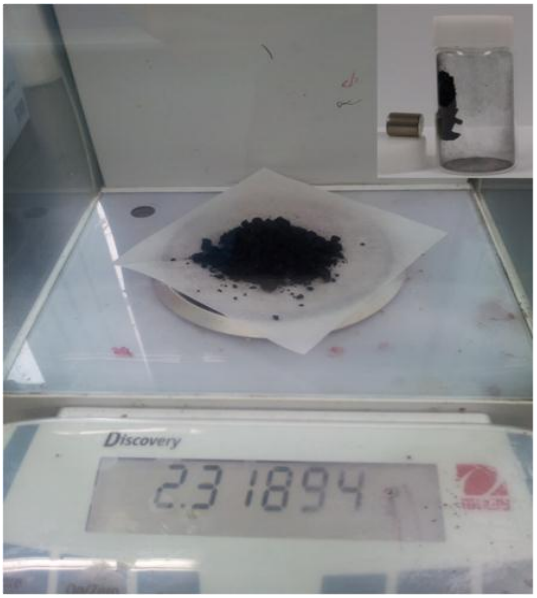
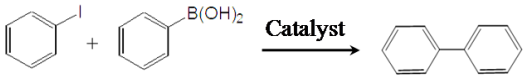


Figure S14. Photograph of scale up synthesis for magnetically recyclable hollow nanocomposite Pd catalyst.

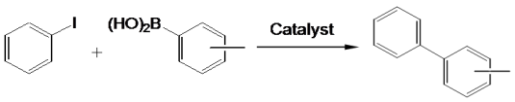
Table S1. Effect of solvents on the Suzuki reaction of iodobenzene and phenylboronic acid.[a]

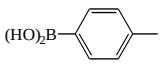
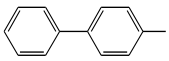
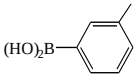
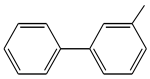
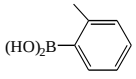
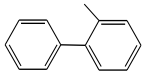
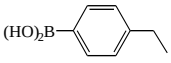
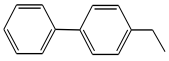
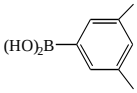
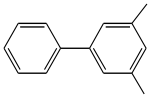


Entry	Solvent	Time (h)	T (^{o}C)	Yield (%)[b]
1	DMF/H_2O (3:1)	1.5	100	97
2	DMF/H_2O (2:1)	1.5	100	85
3	DMF/H_2O (1:1)	1.5	100	70
4	DMA/H_2O (3:1)	1.5	100	93
5	DMF	1.5	100	35
6	DMA	1.5	100	25
7	H_2O	1.5	100	0

[a] Reaction conditions: 0.5 mmol iodobenzene, phenylboronic acid (0.6 mmol), Pd catalyst (1 mol %), K_2CO_3 (1.5 mmol), solvent 10 ml, 100 °C.
[b] The yields were determined by GC-MS with respect to an internal standard (decane).

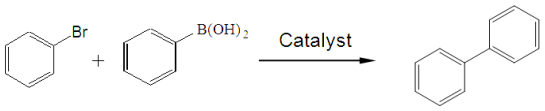
Table S2. Heterogeneous Suzuki cross-coupling reaction of aryl iodide with arylboronic acids. [a]



Entry	Arylboronic acid	Product	Yield (%)[b]
1			96
2			95
3			91
4			94
5			91

[a] Aryl iodide (0.5 mmol), aryl boronic acid (0.6 mmol), Pd catalyst (1 mol %), K_2CO_3 (1.5 mmol), DMF : H_2O (3:1), 100 °C, 1.5 h.
[b] Yields were determined by gas chromatography mass spectrometry (GC-MS) analysis using internal standard (decane).

Table S3. Magnetic separation and recycling of the catalyst in Suzuki cross-coupling reaction. [a]



Cycle	1st	2nd	3rd	4th	5th
Yield of product[b]	97	94	91	89	87

[a] Reaction conditions: 0.5 mmol bromobenzene, phenylboronic acid (0.6 mmol), Pd catalyst (1 mol %), K_2CO_3 (1.5 mmol), DMF/H_2O (3:1), 100 °C, 4 h.
[b] The yields were determined by GC-MS with respect to an internal standard (decane).