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Supporting Information

Pd-Nanodot Decorated MoS_2 Nanosheets as a Highly Efficient Photocatalyst for Visible-Light-Induced Suzuki-Miyaura Coupling Reaction

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Materials. Molybdenum disulfide (MoS_2) crystals were purchased from the SPI Supplies Division of STRUCTURE PROBE Inc. (West Chester, PA, USA). Ethanol (EtOH) and acetonitrile were purchased from DAEJUNG (Siheung, Korea). All other chemical reagents (potassium tetrachloropalladate (K_2PdCl_4), hexadecyltrimethyl-ammonium bromide (CTAB), L-ascorbic acid, sodium hydroxide (NaOH), tetrabutylammonium hydroxide 30-hydrate, phenyl-boronic acid, iodobenzene, biphenyl, potassium carbonate (K_2CO_3), triethanolamine (TEA), and potassium bromate ($KBrO_3$)) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and were used as received without further purification.

Characterization. Field Emission Transmission electron microscopy (FE-TEM; Titan G2 ChemiSTEM Cs Probe, FEI Company, Hillsboro, OR, USA) was performed with holey copper grid (C-flat®, Electron Microscopy Science, Hartfield, USA). Extinction spectra were obtained with a UV-visible spectrophotometer (8453E, Agilent, Santa Clara, CA, USA). The Raman and photoluminescence (PL) analyses were carried out with a Micro-PL & Raman spectrograph module (NOST, Seongnam, Korea) equipped with 532 nm laser system. The particle solution was placed on a SiO_2/Si substrate and the spectra were then acquired (5.0 sec exposure for acquisition of a single spectrum with 5.0 mW power reaching the sample). The thickness of MoS_2 was measured by atomic force microscopy (AFM; NX-10, ParkSystems, Suwon, Korea). The metal content in the materials was determined using Inductively Coupled Plasma (ICP)-mass (Varian 820-MS, Victoria, Australia). An ultrasonic bath (Bransonic CPX2800H-E, Emerson, St. Louis, Mo, USA) and ultrasonic processor (VC505, Sonics & Materials inc., Newtown, CT, USA) were used for dispersion of MoS_2. A Xe lamp (Ceramaxs, Waltham, USA) was used as the visible light (400−780 nm) source. A near-infrared (NIR) laser (Sanctity Laser SSL-808-6000-10TM-MF, Shanghai, China; 808 nm) was also used. The intensity of all light sources was measured by using a laser power meter (PM100USB, THORLABS, Newton, NJ, USA).

Calculation of TOF

$$TOF = \frac{[ideal\ amount\ of\ biphenyl\ (mol)\cdot yield\ (\%)]}{\left[\frac{theoretical\ mass\ of\ Pd}{Mw\ of\ Pd\left(\frac{g}{mol}\right)}\cdot reaction\ time\ (h)\right]}$$

or

$$TOF = \frac{[amount\ of\ substituted\ aryl\ halide\ (mol)\cdot conversion\ (\%)\cdot selectivity\ (\%)]}{\left[\frac{theoretical\ mass\ of\ Pd}{Mw\ of\ Pd\left(\frac{g}{mol}\right)}\cdot reaction\ time\ (h)\right]}$$

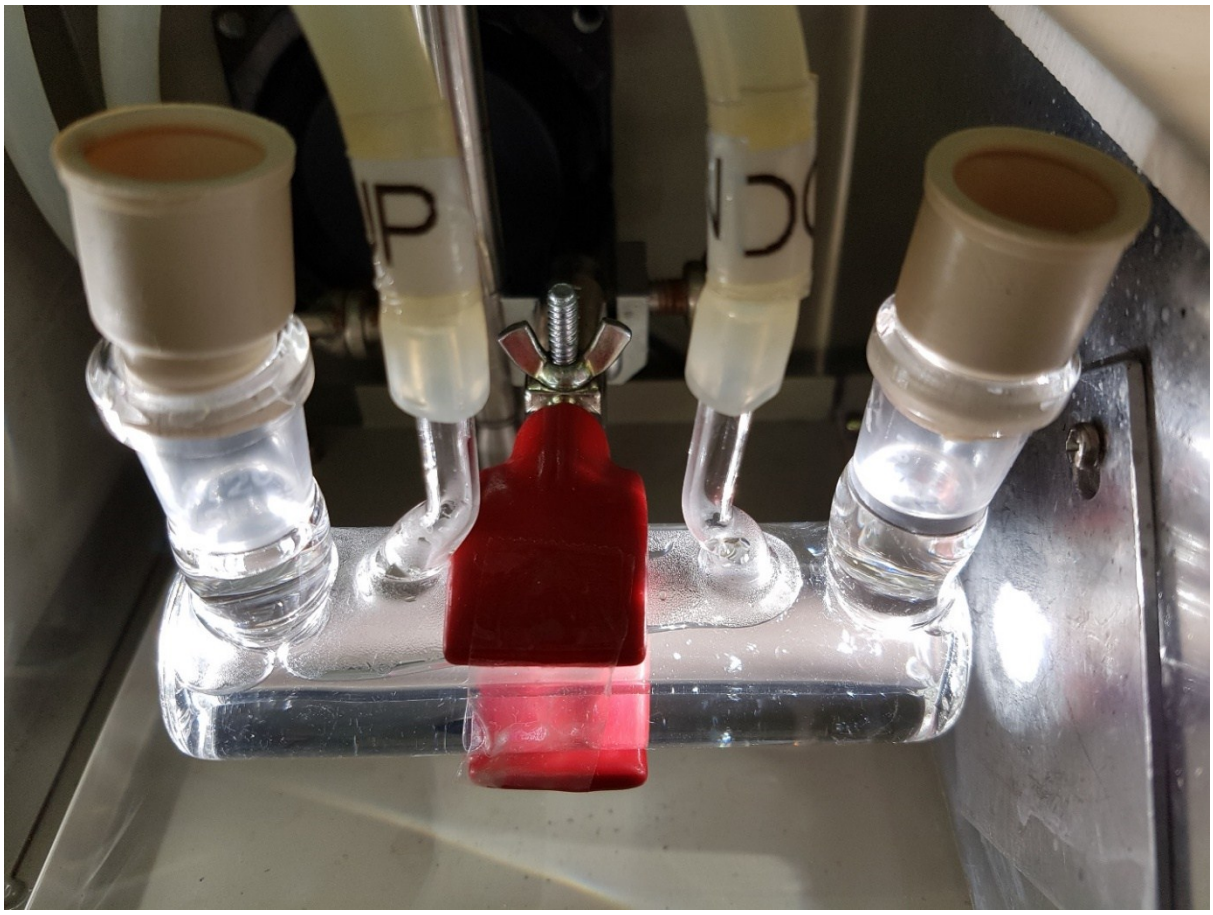

Figure S1. Instrumental setup for Suzuki-Miyaura coupling reaction. Light from the Xe lamp (400−780 nm) illuminates the reactor (Pyrex, 15 mL) with water circulation jacket.

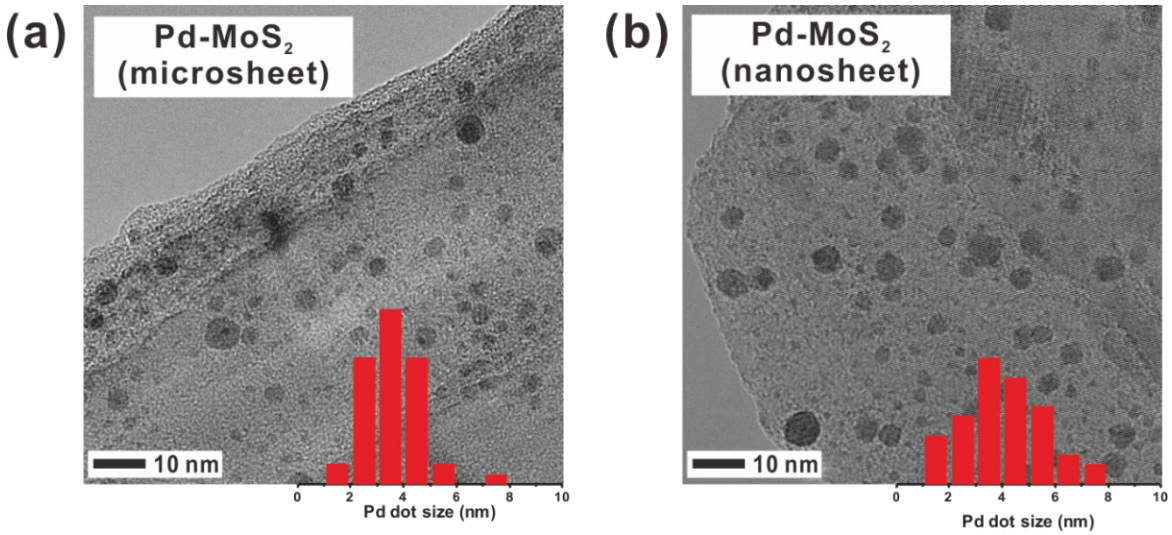

Figure S2. TEM images and Pd-nanodot size distribution of Pd-MoS_2 (a) microsheet and (b) nanosheet.

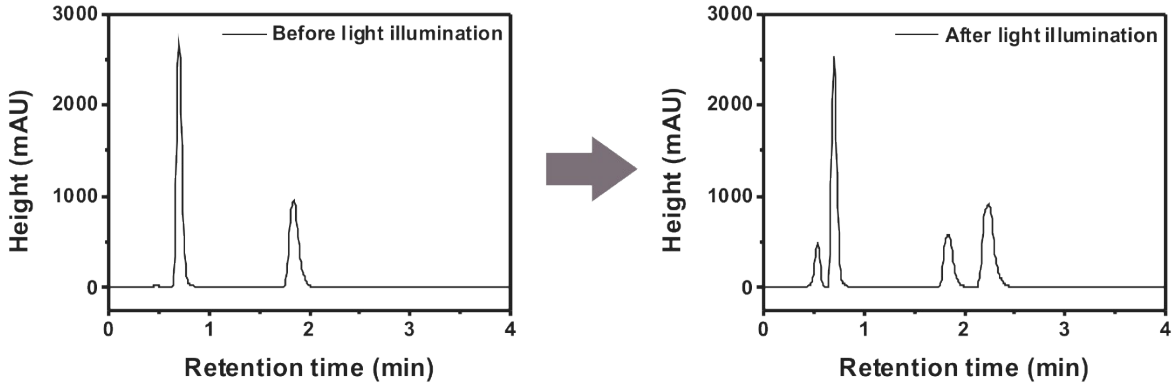

Figure S3. Representative chromatogram of the coupling reaction (retention time - phenyl boronic acid: 0.7 min, iodobenzene: 1.9 min, biphenyl (product): 2.3 min).

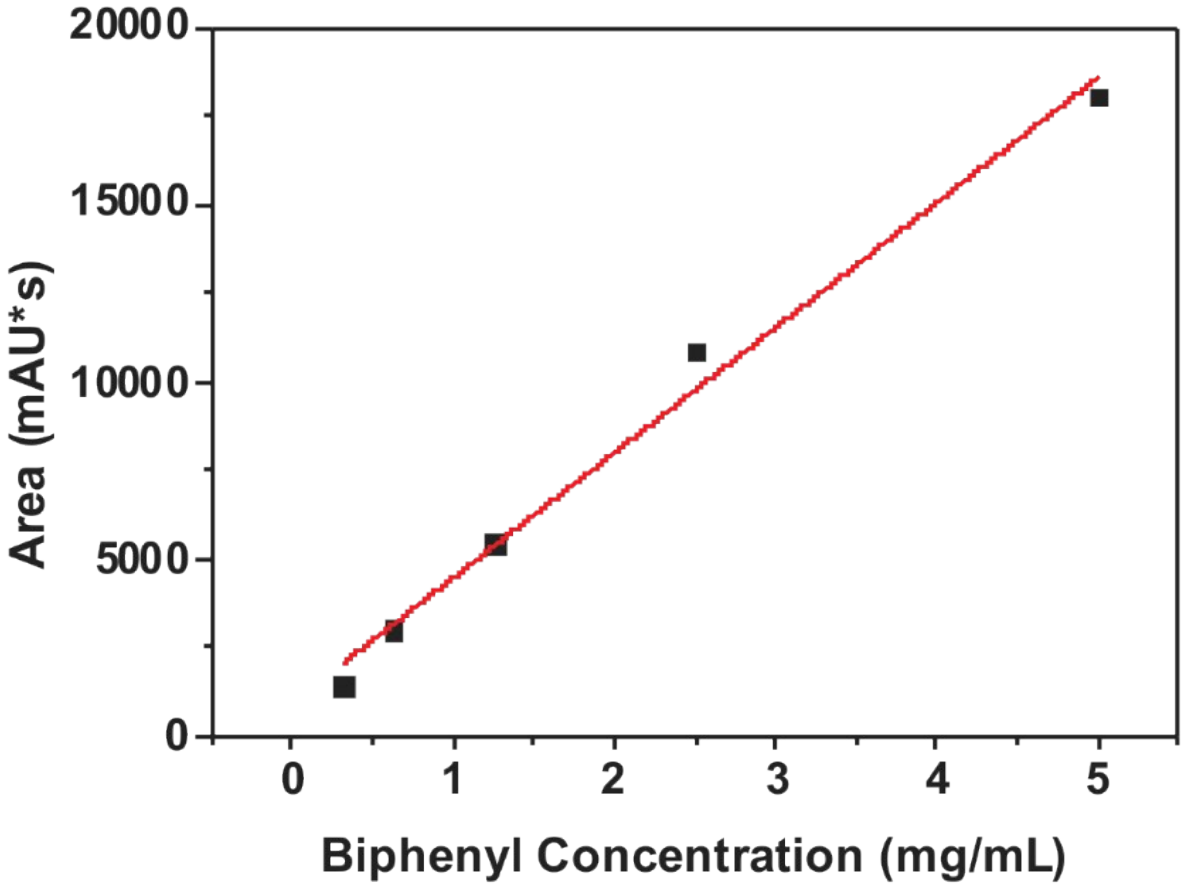

Figure S4. Calibration curve of biphenyl product for yield calculation.

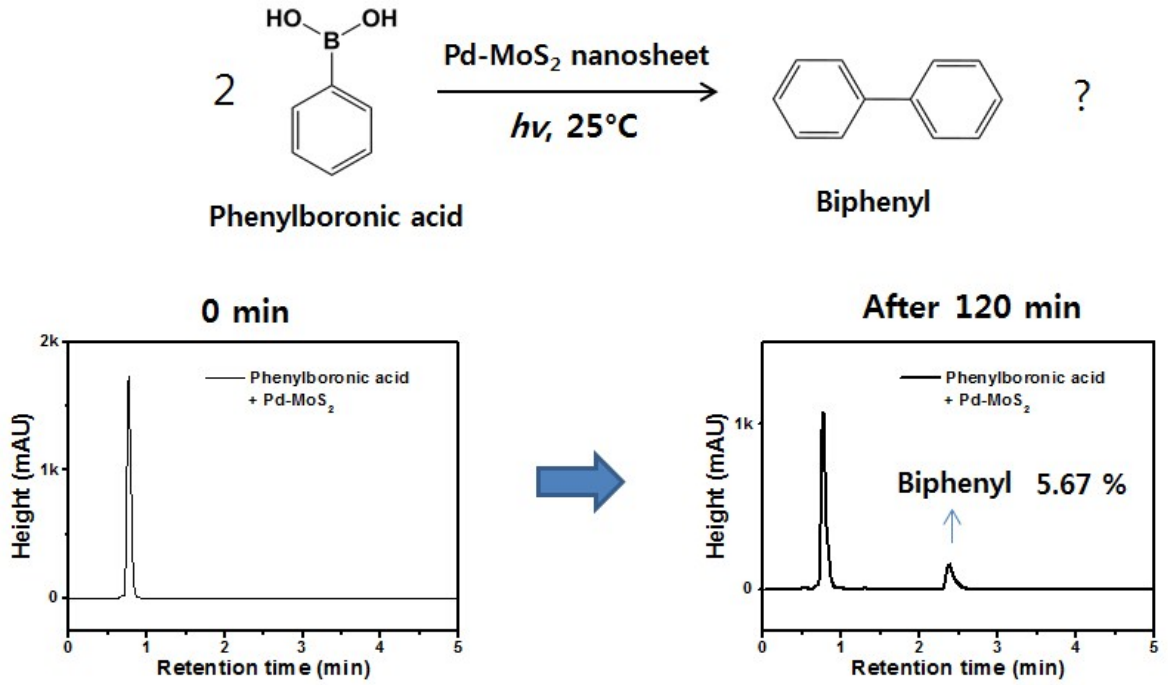

Figure S5. The HPLC chromatogram of phenylboronic acid self-coupling reactions in the presence of Pd-MoS_2 nanosheets with Xe-lamp illumination.

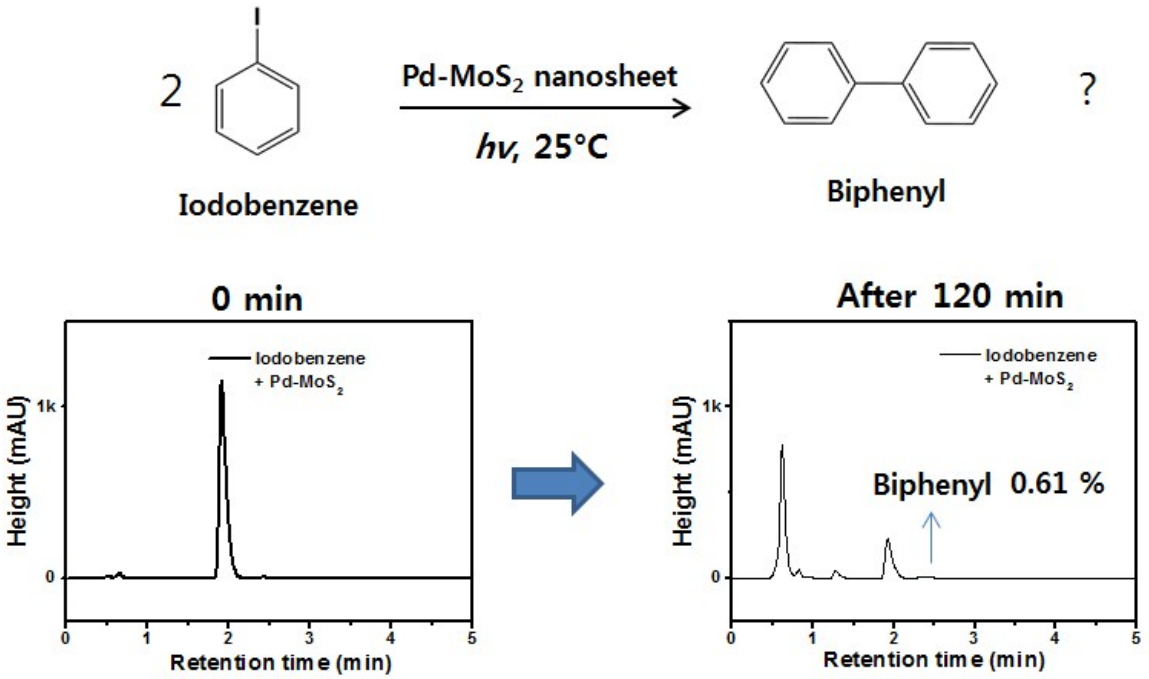

Figure S6. The HPLC chromatogram of iodobenzene self-coupling reactions in the presence of Pd-MoS_2 nanosheets with Xe-lamp illumination.

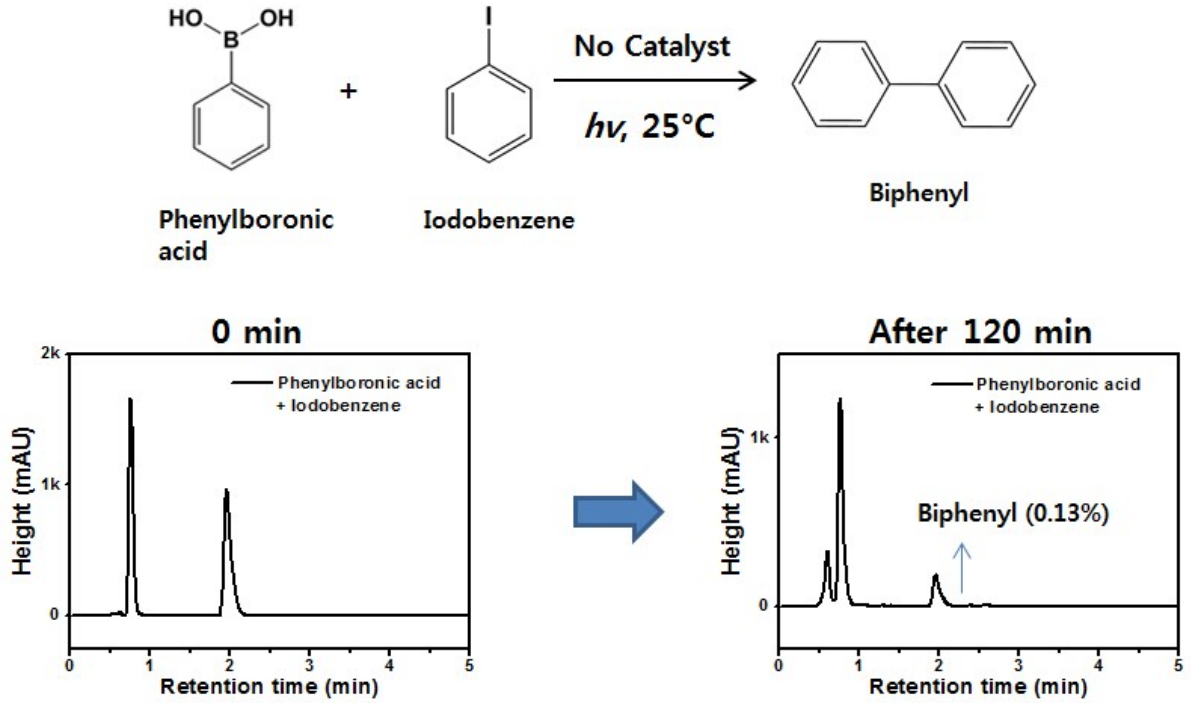

Figure S7. The HPLC chromatogram of phenylboronic acid and iodobenzene cross-coupling reactions in the absence of Pd-MoS_2 nanosheest with Xe-lamp illumination.

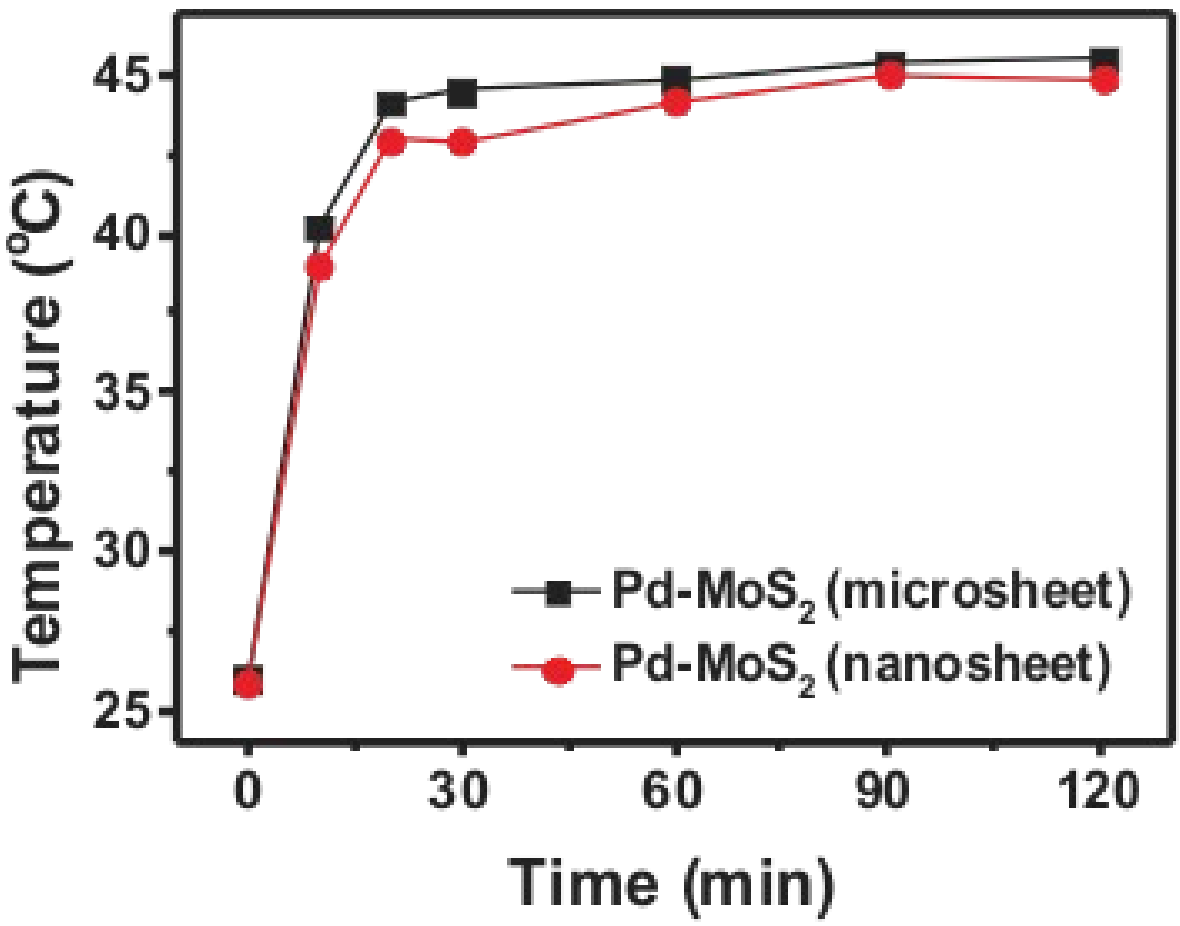

Figure S8. Changes of solution temperature during the Suzuki-Miyaura coupling reaction with Xe lamp illumination in the presence of Pd-MoS_2 microsheets or Pd-MoS_2 nanosheets.

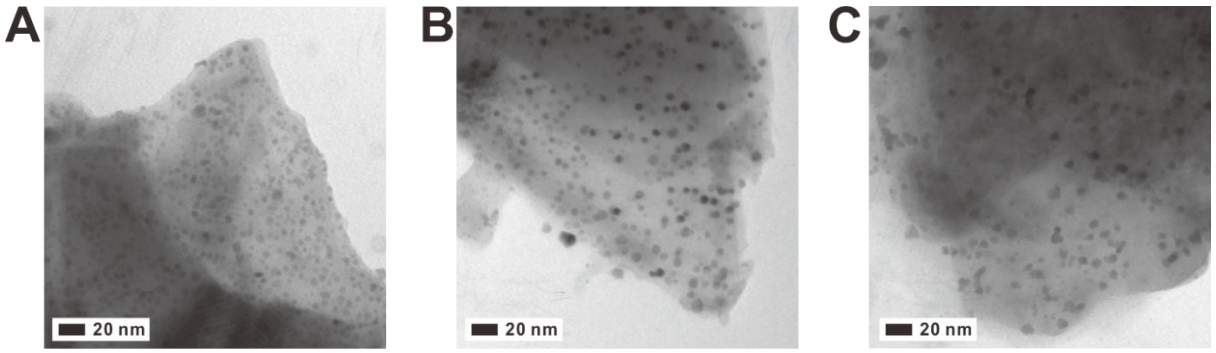

Figure S9. TEM images of recycled Pd-MoS_2 nanosheets after Suzuki-Miyaura coupling reaction (1^{st} (A), 2^{nd} (B), 3^{rd} cycle (C)).

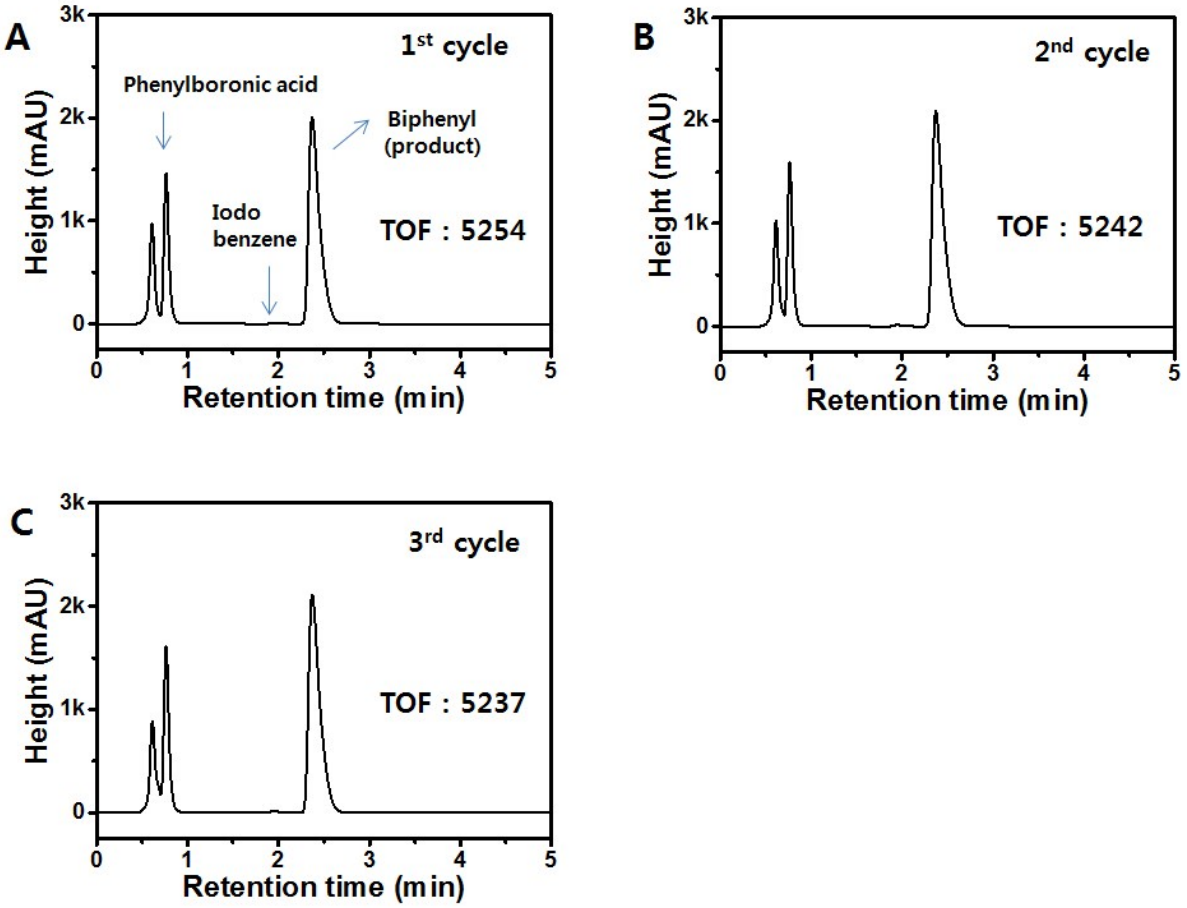

Figure S10. HPLC chromatogram of C-C coupling reactions obtained with fresh Pd-MoS_2 nanosheets (1st (A)) or recycled Pd-MoS_2 nanosheets (2nd (B), 3rd cycle (C)).

References

[S1] H. F. Dong, S. S. Tang, Y. S. Hao, H. Z. Yu, W. H. Dai, G. F. Zhao, Y. Cao, H. T. Lu, X. J. Zhang and H. X. Ju, *Acs. Appl. Mater. Inter.*, 2016, **8**, 3107-3114.

[S2] X. Huang, Z. Y. Zeng, S. Y. Bao, M. F. Wang, X. Y. Qi, Z. X. Fan and H. Zhang, *Nat. Comm.*, 2013, **4**, 1444.