Electronic Supporting Information

Janus Colloid Surfactant Catalysts for *in Situ* Organic Reactions in Pickering Emulsion Microreactors

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Experimental Section

Materials. Styrene (St, 99%), polyvinylpyrrolidone (PVP) (Mn = 40,000 gmol$^{-1)}$, EtOH (anhydrous, 99.5%), poly(vinyl alcohol) (PVA, Mw = 13,000-23,000 gmol^{-1}, 87-89% hydrolyzed), ethylene glycol dimethacrylate (EGDMA, 98%), 1-hydroxycyclohexyl phenylketone (Irgacure 184, 99%), fluorescein isothiocyanate (FITC), Pluronic F-127 (Poloxamer 407), palladium acetyl acetonate ($Pd(acac)_2$, 99%), trioctylphosphine (TOP, 90%), polyethyleneimine solution (PEI, Mn = 60,000 gmol^{-1} by GPC, 50 wt% in H_2O), 4-methoxybenzylalcohol (4-MBOH, 98%) and silver (nanopowder, <150 nm particle size, 99% trace metals basis) were purchased from Sigma Aldrich (USA). 2, 2′-Azobis (isobutyronitrile) (AIBN, 98%) and vinyl acetate (VAc, 99%) were supplied from Junsei (Japan). Tetradecyl acrylate (TA) and oleylamine (OA, >50%) were purchased from TCI (Japan). All chemicals were reagent grades and used without further purification. Deionized doubled distilled water was used through the experiments.

Synthesis of JMPs. Poly (St-co-VAc) seed particles were synthesized by using the dispersion polymerization.[1] St (4 ml), VAc (1 ml), PVP (1.0 g) as a stabilizer, and AIBN (0.05 g) as an initiator were dissolved in EtOH (50 ml, 200 proofs) in a 100 ml round bottom flask. Nitrogen was purged for 5 min to remove oxygen in the reaction mixture. Then, the polymerization was carried out at 70 °C in an oil bath while stirring at 60 rpm for 48 h. After the polymerization, the particles were recovered by washing them repeatedly with EtOH and EtOH/water mixture (1/1, v/v) *via* centrifugation. Finally, the poly (St-co-VAc) particles were stored in the EtOH/water mixture (2/1, v/v). The concentration of the particles was set to 10 % by mass. The poly (St-co-VAc) seed particles were converted into poly (styrene-co-vinyl alcohol), poly (St-co-VA), by using the saponification, in which the reaction was conducted under basic conditions for 8 h at room temperature. Then, the poly (St-co-VA) seed particles were swollen with a mixture of TA, EGDMA, and Irgacure 184 in the presence of PVA (2 wt%) and Pluronic F127 (2 wt%) in an EtOH/water solution for 5 h at room temperature. The diameter of poly (St-co-VA) particles during swelling step increased, while maintaining their monodispersity of particle size. The monomers in the swollen particles were photo-polymerized by UV irradiation for 5 min at room temperature, which induced the phase separation between poly (St-co-VA) seed phase and secondary polymerized PTA phase. Poly (St-co-VA)/PTA JMPs were then washed repeatedly with a mixture of EtOH/water (1/1, v/v) to remove remaining monomers and additives.

Synthesis of functional NPs. PVP-coated Fe_2O_3 NPs were synthesized according to a previously reported method.[2] Briefly, 0.0322 g of PVP was dissolved in 40 ml of distilled water and the resulting solution was heated up to 80 °C under vigorous mechanical stirring. Then, a mixture of 0.86 g of $FeCl_2 \cdot 4H_2O$ and 2.36 g of $FeCl_3 \cdot 6H_2O$ was added the PVP aqueous solution. The reaction mixture was purged continuously with nitrogen gas to get rid of oxygen. During this process, an orange-colored initial reaction solution gradually turned into a brownish-black colloidal dispersion. The reaction was conducted for 30 min at 80 °C. The produced colloidal dispersion was cooled down to room temperature and washed by addition of excess EtOH/water (1/1, v/v). The Fe_2O_3 NPs were re-dispersed and stored in EtOH. The zeta-potential of Fe_2O_3 NPs in water was detected by -10 mV (ELS-Z, Otsuka, Japan). The particle size of the nanoparticles was determined from analysis of TEM images. Pd NPs were synthesized according to the reported method in which TOP and OA were used as surfactants and solvents.[3] 0.1 g of $Pd(acac)_2$ was added into 1 mL of TOP to form an orange-colored Pd-metal complex. The complex solution was added to 10 mL of OA and heated slowly the reaction solution up to 250 °C, which turned gradually the color dark brown. After the reaction was completed, the dispersion of PD NPs was cooled to room temperature and washed by addition of excess EtOH. The Pd NPs were re-dispersed and stored in EtOH. The concentration of the Pd NPs was set to 1.8 wt/v%.

Site-specific patching of functional NPs on JMPs. To patch Fe_2O_3 NPs onto hydroxyl-functionalized bulb surface of JMPs, we dispersed 0.45g of JMPs in the solution of EtOH/water (9 ml, 5/4, v/v). Also, 0.045g of PEI was also prepared by dissolving it in 0.5 M NaCl solution (10 ml). Then, the PEI solution was added dropwise to the dispersion of JMPs at room temperature. After the addition of the PEI solution, the mixture was tumbled for 12 h with a rotation speed of 60 rpm at room temperature. The removal of remnant PEI was conducted by repeated centrifugation with a mixture of EtOH/water (1/1, v/v). Finally, PEI-coated JMPs were stored in EtOH/water (1/1, v/v) at room temperature. To give magnetic responsiveness to JMPs, we selectively patched Fe_2O_3 NPs onto the PEI-coated bulb surface. For this, a dispersion containing 1 wt% of Fe_2O_3 NPs was added dropwise to the dispersion of PEI-coated JMPs over 10 min while vigorously stirring the mixture at room temperature. Then, the mixture was tumbled for 12 h with a rotation speed of 60 rpm. After removal of excess Fe_2O_3 NPs by repeated centrifugation with EtOH/water (1/1, v/v), the Fe_2O_3 NPs-patchy JMPs were stored at room temperature. To give catalytic activity to JMPs, we patched catalytic NPs (Pd NPs and Ag NPs) onto the JMP surface. First, we dispersed 0.45g of Fe_2O_3 NPs-patchy JMPs in the solution of EtOH/water (9 ml, 5/4, v/v). Then, a dispersion containing 1 wt% of catalytic NPs was added dropwise to the dispersion of the Fe_2O_3 NPs-patchy JMPs over 10 min while gently stirring the mixture at room temperature. Then, the mixture was tumbled for 12 h with a rotation speed of 60 rpm. After removal of excess catalytic NPs by repeated centrifugation with EtOH/water (1/1, v/v), the JMP catalysts were stored at room temperature.

Preparation of JMP catalysts-stabilized Pickering emulsions. The water part was prepared by dispersing 1.3 wt% JMP catalysts. The composition of the emulsions is summarized in Table S1. First, a pre-emulsion was prepared via tumbling the mixture with the rotation speed of 60 rpm for 30 min at room temperature. The pre-emulsion was re-emulsified for 30 s by using a vortex mixer (Benchmark Scientific, BV202/EMD, US). This emulsification procedure produced JMPs-stabilized Pickering emulsions with the drop size of hundreds of micrometers. The Pickering emulsion produced was observed with a bright field microscope (3RS, Zeiss, Germany). The emulsion drop diameter was measured by analyzing the microscope image. After catalytic reactions for oxidation, amination and reductions, the product droplets were recovered by applying external magnet field. The product was then dissolved out with MeOH from the product droplets. The JMP catalysts attached to the magnet were further washed with MeOH and water three times and then dried at ambient temperature under vacuum.

Characterizations. The shape and morphology of the particles were observed with a bright-field microscope (Axio Vert. A1, Carl Zeiss, Germany). The Janus particle morphology was characterized with a fluorescent microscope (Axio Vert. A1, Carl Zeiss, Germany). In this case, hydroxyl groups on the surface of poly (St-co-VA) bulb was covalently labeled with FITC. NPs-patchy JMPs were observed with a scanning electron microscope (SEM, S-4800, Hitachi, Japan) and high-resolution transmission electron microscope (HR-TEM, JEN 2100F, JEOL, Japan). The diameter of particles was determined from direct analysis of SEM and TEM images. For these analyses, more than 100 particles were analyzed from EM images and the average was taken. Kinetic study of amination was conducted by using liquid chromatography (LC, Ultimate 3000, Thermo Scientific, USA), The purity of 4-MBA and oxidation progress of 4-MBOH were monitored by NMR spectrometry. ^{1}H-NMR spectra were recorded on a Bruker 400 MHz instrument (Bruker Biospin, Billerica, MA) using $CDCl_3$ as a solvent and were counterchecked with the literature data. The reduction reaction in the emulsion reactors was monitored *via* UV-Vis spectrometry (S-3100, SCINCO, USA) measurements at 250 nm and 400 nm, respectively. X-ray diffraction (D/MAX-2500/PC, Rigaku, Japan) was used to characterized the Ag NPs-patchy JMPs.

Experimental data

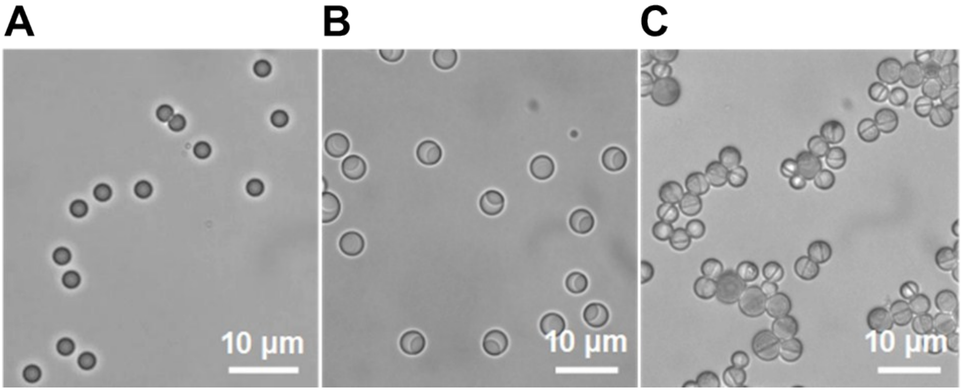


Figure S1. Bright-field microscopic images of (A) PS-co-PVA seed MPs, (B) TA swollen PS-co-PVA MPs, and (C) PS-co-PVA/PTA JMPs.

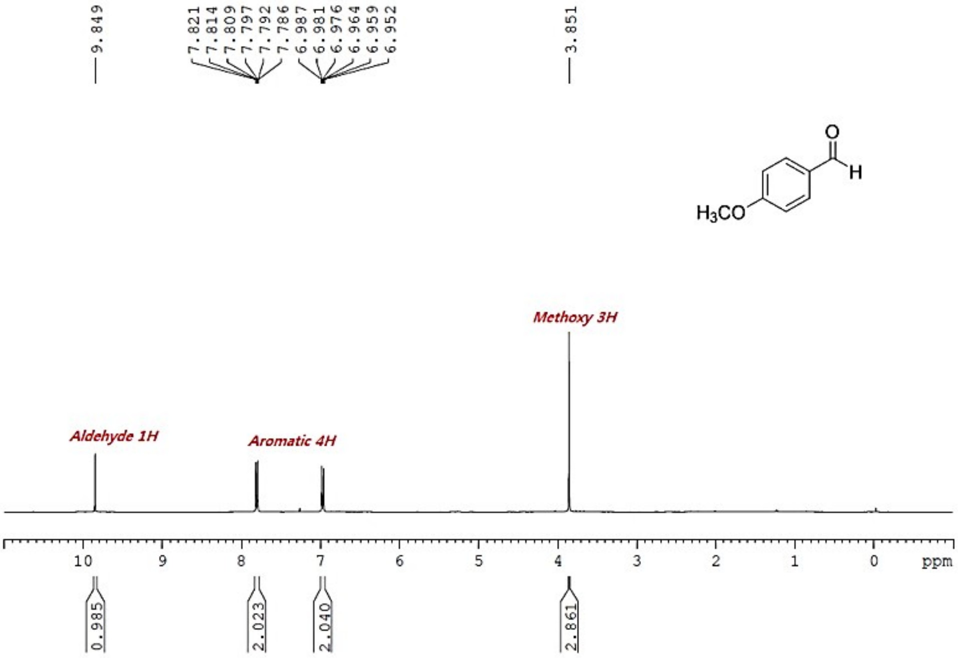


Figure S2. NMR spectra of 4-methoxybenzaldehyde.

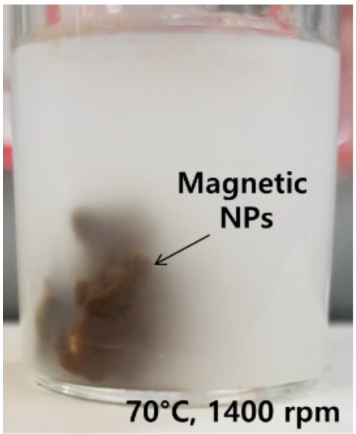


Figure S3. The catalytic oxidation of MBOH to MBA by using JMP catalysts at 70°C

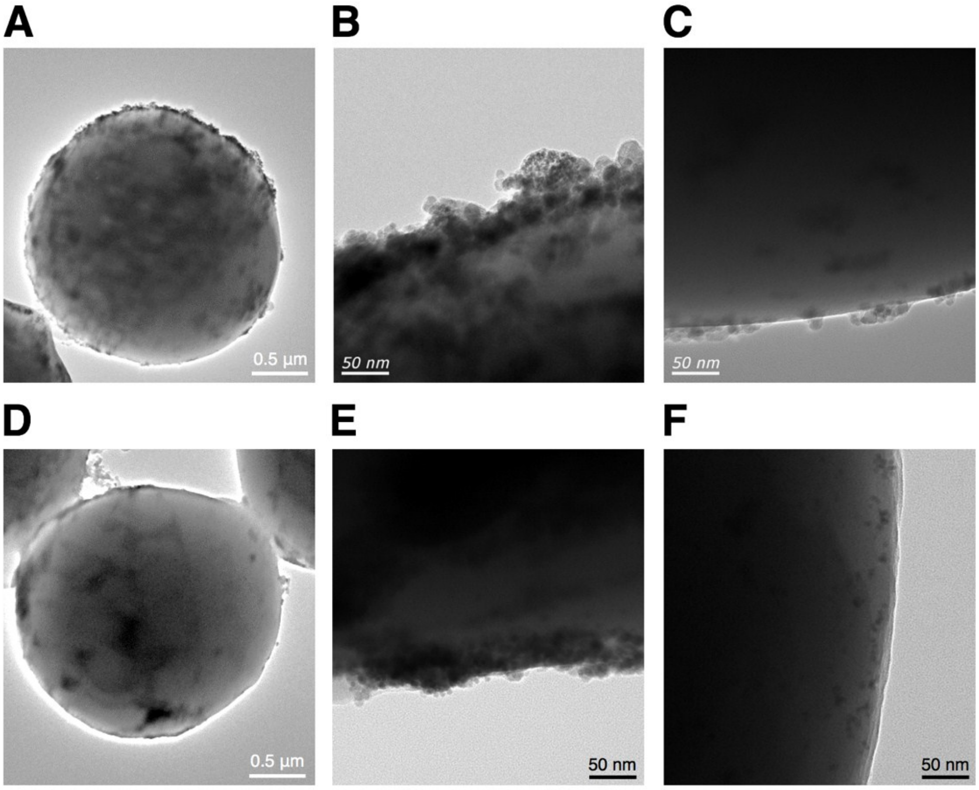


Figure S4. TEM images of JMP catalysts after repeated cycling of oxidation reaction: (A-C) 2 cycle and (D-F) 3 cycle. (A, D) JMP catalysts, (B, E) poly(St-co-VA) bulb, and (C, F) PTA bulb.

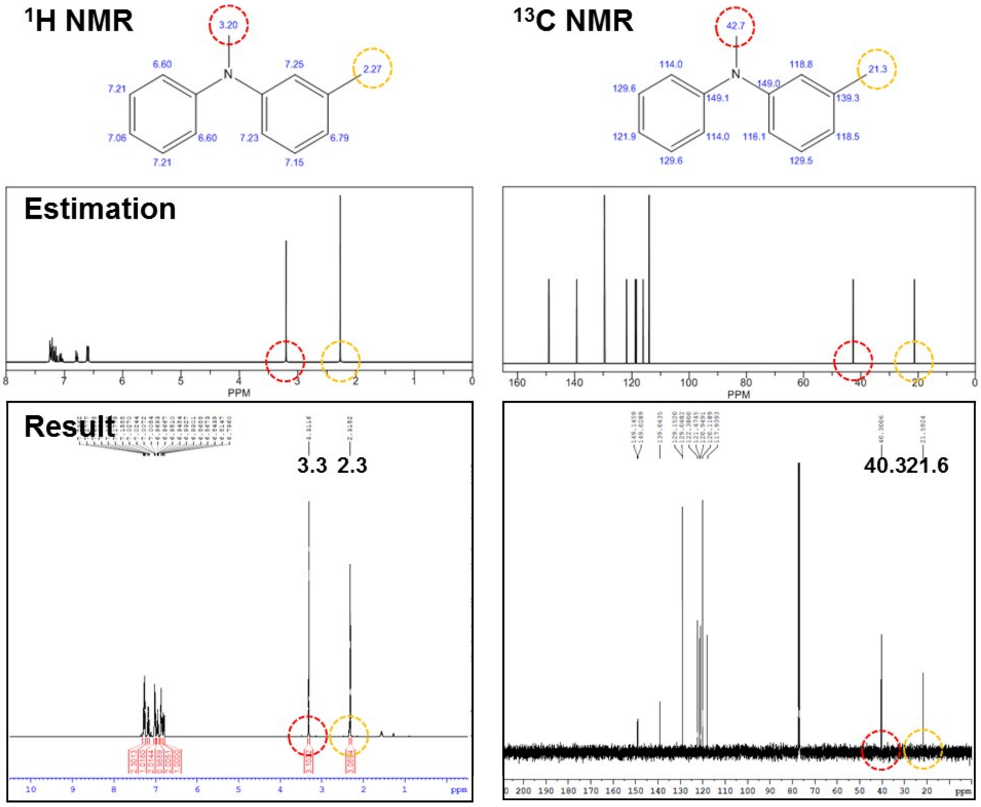


Figure S5. ^{1}H NMR and ^{13}C NMR spectroscopic data of MPT purified using a flash column chromatography.

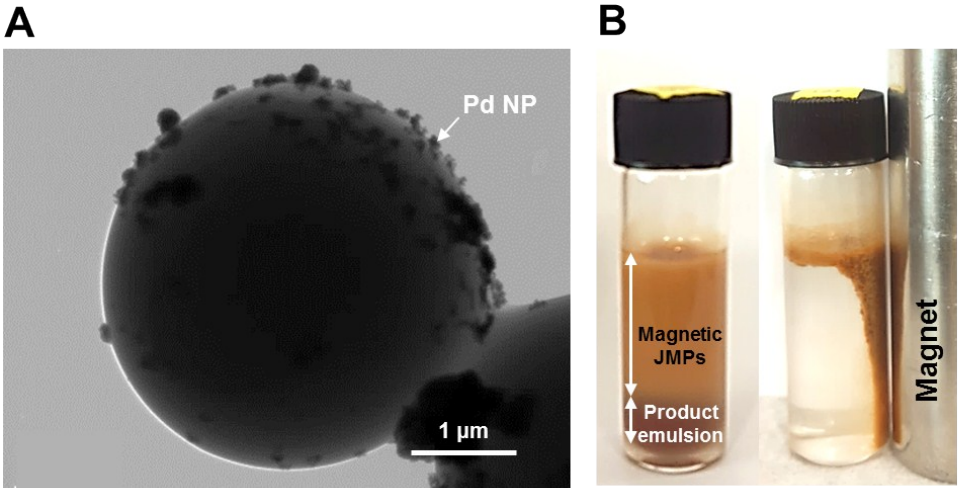


Figure S6. (A) TEM image of a Pd-patchy JMP. (B) Recovery of MPT Pickering emulsion droplets with aids of Fe_2O_3-patchy JMPs in response to the applied magnetic field.

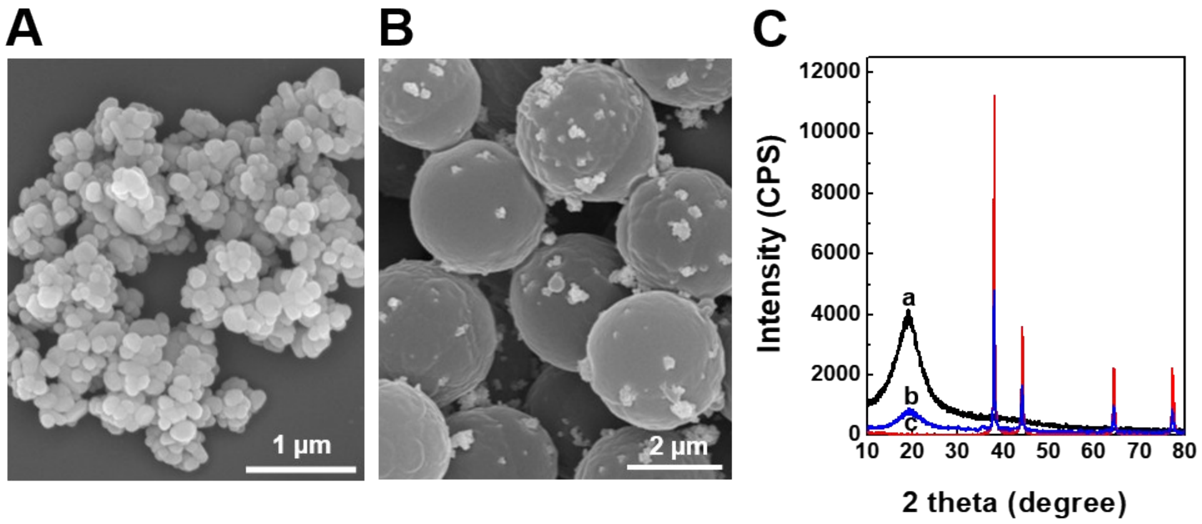


Figure S7. SEM images of (A) Ag NPs and (B) Ag NPs-patchy JMPs. Ag NPs/JMPs=1/5 (w/w). (C) XRD spectra of JMPs (a), Ag NPs-patchy JMP catalysts (b), and Ag NPs (c).

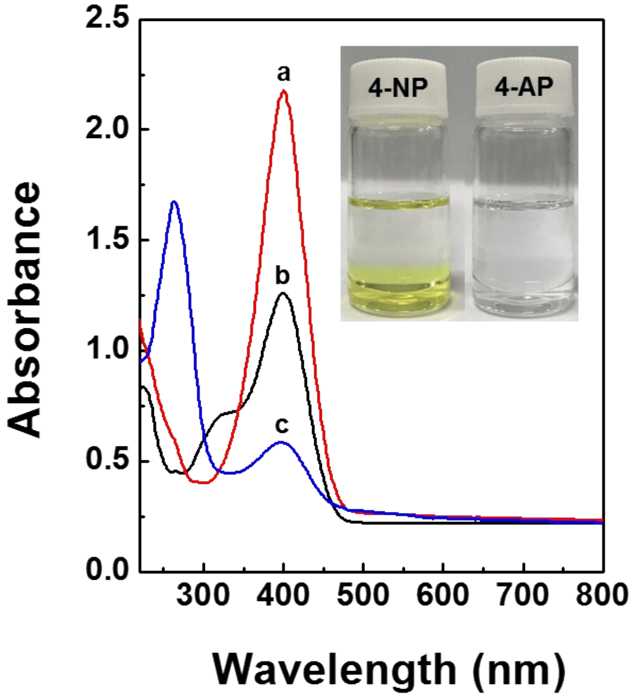
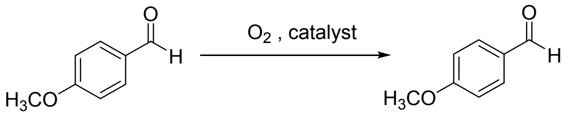


Figure S8. UV-vis spectra of 4-NP (a), 4-NPL (b), and 4-AP (c). The inset shows the color change from yellow (4-NP) to transparent (4-AP) by the reduction reaction.

Table S1. The composition and type of emulsions used for organic reactions

Organic reaction	Dispersion phase	Continuous phase	Emulsion type
Oxidation	4-MBOH (5 vol%)	Water (95 vol%)	Reactant-in-water
Amination	3-BT, MA (5 vol%)	Water (95 vol%)	Reactant-in-water
Reduction	Water (95 vol%)	Hexadecane (5 vol%)	Water-in-reactant

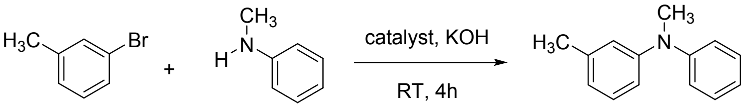
Table S2. Oxidation reaction



Entry	Catalyst (mol%)	Temp (°C)	Time (h)	Yield (%)	TON (mol/mol)[a]	TOF (h^{-1})[b]
1	0.16	50	16	63	394	24.6
2	1.60	50	20	67	42	2.1
3	3.20	50	18	70	20	1.1
4	0.16	rt	16	35	279	17.4

[a] TON (turnover number): reactant moles converted/catalyst moles. [b] TOF (turnover frequency): TON/reaction time.

Table S3. Amination reaction



Entry	Catalyst	mol%	Time (h)	Yield (%)	TON (mol/mol)[a]	TOF (h^{-1})[b]
1	$[(\pi\text{-allyl})PdCl]_2$	0.5	4	46	92	23.0
2	$[(\pi\text{-allyl})PdCl]_2$ with TBAB	0.5	4	75	150	37.5
3	$[(\pi\text{-allyl})PdCl]_2$ with neat JMPs	0.5	4	63	126	31.5
4	Pd NPs-patchy JMPs only	0.5	4	0	0	0
5	$[(\pi\text{-allyl})PdCl]_2$ with Pd NPs-patchy JMPs	0.5	4	93	186	46.5
6	$[(\pi\text{-allyl})PdCl]_2$ with Pd NPs- and Fe_2O_3 NPs-patchy JMPs	0.5	4	32	64	16

[a] TON (turnover number): reactant moles converted/catalyst moles. [b] TOF (turnover frequency): TON/reaction time

References

1. J. W. Kim, J. Cho, J. Cho, B. J. Park, Y. J. Kim, K. H. Choi and J. W. Kim, *Angew. Chem. Int. Ed.* **2016**, *128*, 4585-4589.
2. H. Y. Lee, N. H. Lim, J. A. Seo, S. H. Yuk, B. K. Kwak, G. Khang, H. B. Lee and S. H. Cho, *J. Biomed. Mater. Res. B. Appl. Biomater.*, **2006**, *79*, 142-150.
3. S. W. Kim, J. Park, Y. Jang, Y. Chung, S. Hwang, T. Hyeon and Y. W. Kim, *Nano Lett.*, **2003**, *3,* 1289-1291.