Electronic Supplementary Information for

Hollow structural effect of microporous organicatalytic polymers with pyrrolidines: Dramatic enhancement of catalytic performance

Kyoungil Cho,[a] Jin Yoo,[a] Hyeong-Wan Noh,[b] Sang Moon Lee,[c] Hae Jin Kim,[c] Yoon-Joo Ko,[d] Hye-Young Jang,*[b] and Seung Uk Son*[a]

[a]*Department of Chemistry and Department of Energy Science, Sungkyunkwan University, Suwon 16419, Korea*

[b]*Division of Energy Systems Research, Ajou University, Suwon 16499, Korea*

[c]*Korea Basic Science Institute, Daejeon 34133, Korea*

[d]*Laboratory of Nuclear Magnetic Resonance, National Center for Inter-University Research Facilities(NCIRF), Seoul National University, Seoul 08826, Korea*

Experimental Sections

Transmission (TEM) and scanning electron microscopy (SEM) images were obtained using a JEOL 2100F unit and a FE-SEM (JSM6700F), respectively. The N_2 adsorption-desorption isotherms were measured at 77K using a BELSORP II-mini equipment. The pore size analysis was conducted based on the DFT method. PXRD patterns were obtained using a Rigaku MAX-2200 (filtered Cu-Ka radiation). Infrared absorption spectra of materials in KBr pellets were obtained using a Bruker VERTEX 70 FT-IR spectrometer. The solid phase ^{13}C-NMR spectroscopy (CPTOSS) was conducted using a 500 MHz Bruker ADVANCE II NMR spectrometer at the NCIRF of Seoul National University utilizing a 4 mm magic angle spinning probe. The spinning rate was 5 kHz. ^{1}H and ^{13}C NMR spectra were obtained by 400 MHz and 500 MHz Varian spectrometers. Elemental analysis was conducted using a CE EA1110 instrument. High resolution mass spectrum was obtained using a JEOL JMS 700 high resolution mass spectrometer at the KBSI. The enantioselectivity was measured using an Agilent HPLC 1100 and PerkinElmer 343 plus polarimeter. Thermogravimetric analysis (TGA) was conducted using a STA7200 Thermal Analysis System (Hitachi).

Synthetic procedure for H-MOP-P

Silica spheres with a diameter of 310 ± 20 nm were prepared by the Stöber method in the literature.[1] In our work, the following procedures were applied. In a 500 mL flask, tetraethyl orthosilicate (14 mL), ethanol (200 mL), water (18 mL), and ammonia solution (28~30%, 7 mL) were added. The reaction mixture was stirred for 2.5 h at room temperature. The powder was separated by centrifugation, washed with ethanol, and dried under vacuum.

Tetrakis(4-ethynylphenyl)adamantane is a known compound and was prepared by the synthetic procedures in the literature.[2] In our work, the following procedures were applied. 1-Bromoadamantane (9.0 g, 42 mmol) was dissolved in benzene (80 mL). The solution was placed in an ice bath and t-butylbromide (14 mL, 125 mmol) was added. Then $AlCl_3$ (0.56 g, 4.2 mmol) was added. The temperature of reaction mixture increased to room temperature. The generated HCl gas was quenched using NaOH solution. The reaction mixture was heated at 90 ^{o}C for 4 h. After being cooled to room temperature, the reaction mixture was poured into ice water. After adding benzene (40 mL), the aqueous part was removed using a separatory funnel. The solid (tetraphenyladamantane) in the organic part was collected by filtration and was purified using a Soxhlet extractor using chloroform. 1,3,5,7-

Tetraphenyladamantane (6.0 g, 14 mmol) was added to chloroform (190 mL) in a 250 mL flask. Ground iodine powder (7.3 g, 29 mmol) and [bis(trifluoroacetocyl)iodo]benzene (12 g, 29 mmol) were added. The mixture was stirred for 30 min at room temperature. Ground iodine (7.3 g, 29 mmol) was added and the mixture was stirred for 2 h at room temperature. The [bis(trifluoroacetocyl)iodo]benzene (12 g, 29 mmol) was added and the mixture was stirred overnight at room temperature. The solution was treated with 5% $Na_2S_2O_4$ solution, water, and brine. The separated chloroform solution was dried with $MgSO_4$ and the solvent was evaporated. The solid, tetrakis(4-iodophenyl)adamantane was purified via recrystallization in chloroform/methanol. In a 250 mL Schlenk flask, tetrakis(4-iodophenyl)adamantane (4.0 g, 4.2 mmol), trimethylsilylacetylene (3.0 mL, 21 mL), $(PPh_3)_2PdCl_2$ (0.29 g, 0.42 mmol), CuI (97 mg, 0.51 mmol), diisopropylamine (60 mL), and toluene (140 mL) were added. The reaction mixture was heated at 90 ^oC for 10 h. After the mixture was cooled to room temperature, the solvent was evaporated. The crude product was dissolved in chloroform, filtered, and dried with $MgSO_4$. After the solvent was evaporated, the product, tetrakis(4-trimethylsilylethynylphenyl)adamantane was purified by recrystallization in chloroform/methanol. Tetrakis(4-trimethylsilylethynylphenyl)adamantane (3.1 g, 3.8 mmol), K_2CO_3 (4.1 g, 31 mmol), methanol (200 mL), and THF (200 mL) were added to a 500 mL flask. The mixture was stirred for 10 h at room temperature. After the solvent was evaporated, the crude product was dissolved in chloroform and the organic part was extracted with brine and dried with $MgSO_4$. After the solvent was evaporated, the product, tetrakis(4-ethynylphenyl)adamantane was purified via recrystallization in methanol.

1,4-Bis(trimethylsilylethynyl)-2,5-dibrombenzene is a known compound and was prepared by the synthetic procedures in the literature.[3] In our work, the following procedures were applied. 1,4-Dibromo-2,5-diiodobenzene (10 g, 20.5 mmol), trimethylsilylacethylene (5.8 mL, 41 mmol), $(PPh_3)_2PdCl_2$ (0.40 g, 0.57 mmol), CuI (0.23 g, 1.2 mmol), diisopropylamine (60 mL), and benzene (100 mL) were added to a 250 mL flask. The reaction mixture was stirred for 1 h at room temperature. After water (150 mL) was added, the product was extracted using ether. The organic part was dried with $MgSO_4$. After the solvent being evaporated, the 1,4-bis(trimethylsilylethynyl)-2,5-dibrombenzene was separated via column chromatography using hexane as an eluent.

For the preparation of H-MOP-A, silica sphere (0.30 g), $(PPh_3)_2PdCl_2$ (8.4 mg, 0.012 mmol), and CuI (2.3 mg, 0.012 mmol) were added to triethylamine (30 mL) in a flame-dried 50 mL Schlenk flask. The mixture was sonicated for 1 h at room temperature. Tetrakis(4-ethynylphenyl)adamantane (64.4 mg, 0.120 mmol) and 1,4-bis(trimethylsilylethynyl)-2,5-dibrombenzene (0.103 g, 0.240 mmol) were added. The reaction mixture was heated at 80 ^oC for 2 d and then cooled to room temperature. The powder was retrieved by centrifugation, washed with dichloromethane, acetone and methanol, and dried under vacuum. The powder was added to a 50 mL Falcon tube. The mixture of HF aqueous solution (45%), water (15 mL), and methanol (10 mL) was added. *Caution: HF is an extremely dangerous reagent and should be handled with specialized gloves in a well-ventilated hood.* The reaction mixture was stirred for 2 h at room temperature. The powder (H-MOP-A) was separated by centrifugation, washed with water and methanol, and dried under vacuum.

For the preparation of H-MOP-PBoc, *N*-Boc-2-azidomethylpyrrolidine was prepared by the synthetic procedure

in the literature.[4] In our work, the following procedure was applied. (S)-proline (7.5 g, 65 mmol), NaOH solution (1 M, 130 mL), and dioxane (33 mL) were added to a 250 mL flask. At 0°C, di-t-butyldicarbonate (17 mL, 74 mmol) wad added dropwise for 20 min. The mixture was stirred for 30 min at 0°C and then, stirred overnight at room temperature. After the organic solvent being evaporated, the pH of aqueous solution was controlled to 2.0 by adding sulfuric acid. The product, *N*-Boc-proline was extracted with chloroform and brine. The organic part was dried with Na_2SO_4 and the solvent was evaporated. *N*-Boc-proline (9.2 g, 43 mmol) was dissolved in THF (40 mL). The mixture was cooled to 0°C. Borane-THF complex (26 mL, 2.0 M) was added slowly. The mixture was stirred at room temperature and heated at 60 °C for 4 h. After being cooled to room temparture, the mixture was poured into ice water. The product, *N*-Boc-prolinol was extracted with ethylacetate and brine. The organic part was dried with Na_2SO_4 and the solvent was evaporated. *N*-Boc-prolinol (13 g, 63 mmol), methylene chloride (300 mL), and pyridine (22 mL) were added to a 500 mL flask. At 0°C, *p*-tosylchloride (14 g, 76 mmol) was added. The mixture was stirred overnight at room temperature and was poured into ice water. The product, *N*-Boc-prolinol tosylate was extracted using methylene chlrodie, 10% HCl, and brine. The organic part was dried with $MgSO_4$ and the solvent was evaporated. *N*-Boc-prolinol tosylate was purified via column chromatography using a 4:1 mixture of hexane and ethylacetate as an eluent. *N*-Boc-prolinol tosylate (3.0 g, 8.4 mmol) was dissolved in DMSO (70 mL). Sodium azide (1.2 g, 19 mmol) was added. The mixture was heated at 70 °C for 24 h and was cooled to room temperature. The product, *N*-Boc-azidomethylpyrrolidine was extracted using ether, water, and brine. The organic part was dried with Na_2SO_4 and filtered. The solvent was evaporated and the product was dried under vacuum. *Caution: N-Boc-2-azidomethylpyrrolidine should be kept in a refrigerator.*

H-MOP-A (84 mg), *N*-Boc-2-azidomethylpyrrolidine (0.19 g, 0.84 mmol). CuI (32 mg, 0.17 mmol), diisopropylamine (0.30 mL, 1.7 mmol), THF (3 mL), and DMF (1.5 mL) were added to a flame-dried Schlenk flask. The reaction mixture was heated at 60 °C for 1 d under argon and then, was cooled to room temperature. The powder (H-MOP-Pboc) was retrieved by centrifugation, washed with 5% NaEDTA solution, dichlromethane, acetone, and methanol, and dried under vacuum.

For the preparation of H-MOP-P, H-MOP-PBoc (0.30 g) was added to a mixture of dichlromethane (22 mL) and trifluoroacetic acid (15 mL) in a 40 mL Schlenk flask. The reaction mixture was stirred for 1 d at room temperature. The powder (H-MOP-P) was retrieved by centrifugation, washed with THF, THF(2% TEA), methanol, and acetone, and dried under vacuum.

Synthetic procedure for MOP-P

For the preparation of nonhollow MOP-A, MOP-PBoc, and MOP-P, the synthetic procedures of H-MOP-A were applied without using silica templates. *Caution: HF is an extremely dangerous reagent and should be handled with specialized gloves in a well-ventilated hood.*

Experimental procedure for oranocatalytic reactions

We followed the procedures of organocatalytic reactions in the literature.[5] The pyrrolidine contents in H-MOP-P and MOP-P were calculated as 1.28 and 0.95 mmol/g based on elemental analysis, respectively. H-MOP-P or MOP-P (2, 6, or 10 mol% pyrrolidines for cinamaldehyde), cinamaldehyde (0.25 mmol), malonate (0.75 mmol),

benzoic acid (9.2 mg, 0.075 mmol), DMF (0.62 mL), and water (0.62 mL) were added to an 8 mL vial. The mixture was stirred for 3 d at room temperature under air. The catalysts were retrieved by centrifugation, washed with methylene chloride, THF, methanol, ethylacetate, and acetone, dried under vacuum, and reused for the recycling tests. There were no any thermal pre-activation steps of H-MOP-P before reaction and between cycles. The organic part was extracted with ethylacetate. After the solvent in the mixture was evaporated, the crude product was purified via column chromatography. All products in Table 1 are known compounds and the ^{1}H NMR spectra of products matched well with those reported in the literature.[5,6] The product of entry 1: ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 2.87-2.97 (m, 2H), 3.50 (s, 3H), 3.73 (d, J = 9.8 Hz, 1H), 3.74 (s, 3H), 4.00-4.05 (m, 1H), 7.21-7.31 (m, 5H), 9.59 (s, 1H) ppm. The product of entry 2: ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 1.00 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H), 2.85-2.96 (m, 2H), 3.70 (d, J = 10.0 Hz, 1H), 3.94 (q, J = 7.1 Hz, 2H), 3.99-4.05 (m, 1H), 4.20 (q, J = 7.1 Hz, 2H), 7.23-7.27 (m, 5H), 9.60 (s, 1H) ppm. The product of entry 4: ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 2.82-3.93 (m, 2H), 3.52 (s, 3H), 3.69 (d, J = 9.4 Hz, 1H), 3.74 (s, 3H), 3.77 (s, 3H), 4.13-4.17 (m, 1H), 7.44 (d, J = 8.7 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 9.63 (s, 1H) ppm. The product of entry 5: ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 2.91-2.95 (m, 2H), 3.54 (s, 3H), 3.71 (d, J = 9.7 Hz, 1H) 3.74 (s, 3H), 3.99-4.03 (m, 1H), 7.18 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 9.60 (s, 1H) ppm. The product of entry 6: ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 2.86-2.98 (m, 2H), 3.54 (s, 3H), 3.70 (d, J = 9.6 Hz, 1H) 3.74 (s, 3H), 3.97-4.02 (m, 1H), 7.12 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 9.60 (s, 1H) ppm. The product of entry 7: ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 2.97-3.10 (m, 2H), 3.55 (s, 3H), 3.76 (s, 3H), 3.79 (d, J = 9.6 Hz, 1H), 3.95-4.00 (m, 1H), 6.81 (d, J = 8.7 Hz, 2H), 7.14 (d, J = 8.7 Hz, 2H), 9.58 (s, 1H) ppm.

The enantioselectivity in Table 1 was measured following the procedures in the literature.[5,6] As guided in the literature,[5,6a] the unstable aldehyde products were converted to enones by reaction with Ph_3P=CHCOPh and then, ee values were measured by HPLC analysis. For the conversion, Ph_3P=CHCOPh (88 mg, 0.25 mmol) and aldehyde product (malonate adduct, 0.23 mmol) were dissolved in methylene chloride (1.5 mL) in a 10 mL one-neck flask. The mixture was stirred for 10 h at 60 ^{o}C. After being cooled to room temperature, the crude product was extracted with ethylacetate and water. The organic part was dried with $MgSO_4$ and the solvent was evaporated. The enone products were purified by column chromatography and were characterized by ^{1}H NMR and high resolution mass spectroscopy. The enone product of entry 1: ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 2.68 (m, 1H), 2.77 (m, 1H), 3.47 (s, 3H), 3.64 (td, J = 10.2, 4.5 Hz, 1H), 3.77 (d, J = 10.5 Hz, 1H), 3.78 (s, 3H), 6.67-6.77 (m, 2H), 7.20-7.25 (m, 3H), 7.29-7.32 (m, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.72 (dd, J = 8.3, 1.3 Hz, 2H) ppm, HR-MS: calc. [M^+] for $C_{22}H_{22}O_5$, 366.1467; found 366.1470. The enone product of entry 2: ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 0.96 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H), 2.64 (m, 1H), 2.76 (m, 1H), 3.58 (m, 1H), 3.72 (d, J = 10.6 Hz, 1H), 3.89 (q, J = 7.2 Hz, 2H), 4.22 (q, J = 7.2 Hz, 2H), 6.67-6.77 (m, 2H), 7.22 (m, 3H), 7.30 (m, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.71 (dd, J = 8.3, 1.2 Hz, 2H) ppm, HR-MS: calc. [M^+] for $C_{24}H_{26}O_5$, 394.1780; found 394.1782. The enone product of entry 4: ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 2.64 (m, 1H), 2.75 (m, 1H), 3.49 (s, 3H), 3.59 (td, J = 10.2, 4.5 Hz, 1H), 3.71 (d, J = 10.3 Hz, 1H), 3.77 (s, 6H), 6.68-6.77 (m, 2H), 6.83 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 8.7 Hz, 2H), 7.41 (t, J = 7.7 Hz, 2H),

7.52 (t, J = 7.4 Hz, 1H), 7.74 (dd, J = 8.3, 1.3 Hz, 2H) ppm, HR-MS: calc. [M^+] for $C_{23}H_{24}O_6$, 396.1573; found 396.1573. The enone product of entry 5: ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 2.63 (m, 1H), 2.77 (m, 1H), 3.50 (s, 3H), 3.62 (td, J = 10.1, 4.5 Hz, 1H), 3.72 (d, J = 10.3 Hz, 1H), 3.78 (s, 3H), 6.68-6.75 (m, 2H), 7.15 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.74 (dd, J = 8.3, 1.2 Hz, 2H) ppm, HR-MS: calc. [M^+] for $C_{22}H_{21}O_5Cl$, 400.1078; found 400.1081. The enone product of entry 6: ^{1} H-NMR ($CDCl_3$, 500 MHz): δ = 2.63 (m, 1H), 2.77 (m, 1H), 3.51 (s, 3H), 3.61 (td, J = 10.1, 4.5 Hz, 1H), 3.73 (d, J = 10.3 Hz, 1H), 3.78 (s, 3H), 6.68-6.75 (m, 2H), 7.10 (d, J = 8.4 Hz, 2H), 7.43 (m, 4H), 7.54 (t, J = 7.4 Hz, 1H), 7.73 (dd, J = 8.3, 1.3 Hz, 2H) ppm, HR-MS: calc. [M^+] for $C_{22}H_{21}O_5Br$, 444.0572; found 444.0575. The enone product of entry 7: ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 2.70 (m, 1H), 2.83 (m, 1H), 3.52 (s, 3H), 3.76-3.81 (m, 5H), 6.69-6.78 (m, 2H), 7.40 (m, 4H), 7.54 (t, J = 7.4 Hz, 1H), 7.77 (dd, J = 8.4, 1.3 Hz, 2H), 8.18 (d, J = 8.8 Hz, 2H) ppm, HR-MS: calc. [M^+] for $C_{22}H_{21}O_7N$, 411.1318; found 411.1316.

The major enantiomers were confirmed based on the negative rotation angle values of aldehyde product (malonate adduct). HPLC conditions in our work were as follows. The product of entry 1: Chiralpak AS-H, *i*-PrOH/hexane = 20/80, flow rate = 0.5 mL/min, λ = 254 nm, t_{minor} = 34.14 min, t_{major} = 37.55 min, ee = 66%. The product of entry 2: Chiralpak AS-H, *i*-PrOH/hexane = 20/80, flow rate = 0.5 mL/min, λ = 210 nm, t_{major} = 23.03 min, t_{minor} = 24.65 min, ee = 66%. The product of entry 4: Chiralpak AS-H, *i*-PrOH/hexane = 20/80, flow rate = 0.5 mL/min, λ = 210 nm, t_{major} = 42.52 min, t_{minor} = 46.79 min, ee = 48%. The product of entry 5: Chiralpak AS-H, *i*-PrOH/hexane = 20/80, flow rate = 0.7 mL/min, λ = 254 nm, t_{minor} = 25.28 min, t_{major} = 27.14 min, ee = 81%. The product of entry 6: Chiralcel OD-H, *i*-PrOH/hexane = 10/90, flow rate = 0.5 mL/min, λ = 254 nm, t_{major} = 53.35 min, t_{minor} = 70.17 min, ee = 83%. The product of entry 7: Chiralpak AS-H, *i*-PrOH/hexane = 20/80, flow rate = 0.5 mL/min, λ = 254 nm, t_{minor} = 48.44 min, t_{major} = 51.69 min, ee = 92%.

A model homogeneous catalyst [(*S*)-4-phenyl-1-(pyrrolidin-2-ylmethyl)-1*H*-1,2,3-triazole] in Fig. S4a was prepared by the synthetic procedures in the literature.[7] 1H-NMR data of the compound matched well with those in the literature.[7] ^{1} H-NMR ($CDCl_3$, 500 MHz) : δ = 1.50-1.57 (m, 1H), 1.72-1.86 (m, 2H), 1.96-2.04 (m, 1H), 2.69 (br, 1H), 2.99 (t, J = 6.8 Hz, 2H), 3.69 (qd, J = 7.5, 4.5 Hz, 1H), 4.30 (dd, J = 13.6, 8.0 Hz, 1H), 4.48 (dd, J = 13.6, 4.4 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H) , 7.41 (t, J = 7.7 Hz, 2H) , 7.82 (d, J = 7.2 Hz, 2H) , 7.96 (s, 1H) ppm.

References

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Fig. S1 PXRD patterns of H-MOP-A, H-MOP-PBoc, H-MOP-P, MOP-A, MOP-PBoc, and MOP-P showing amorphous characteristic.

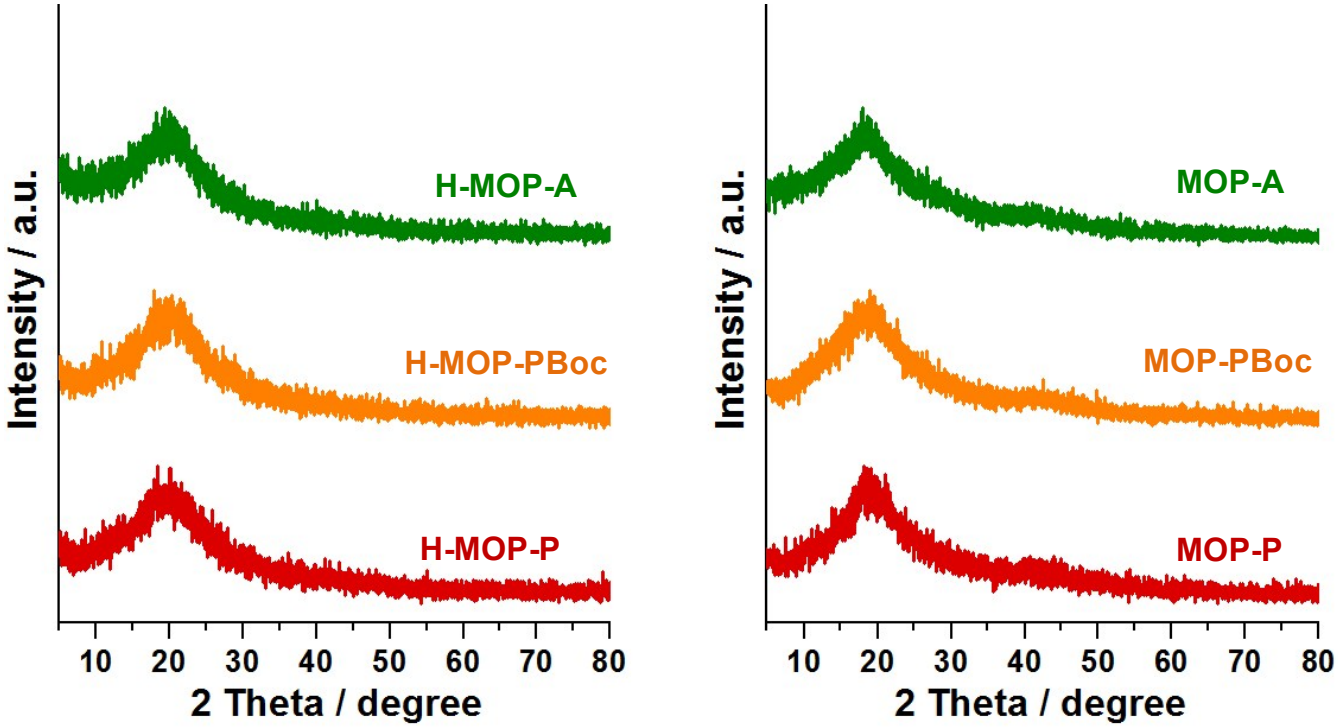
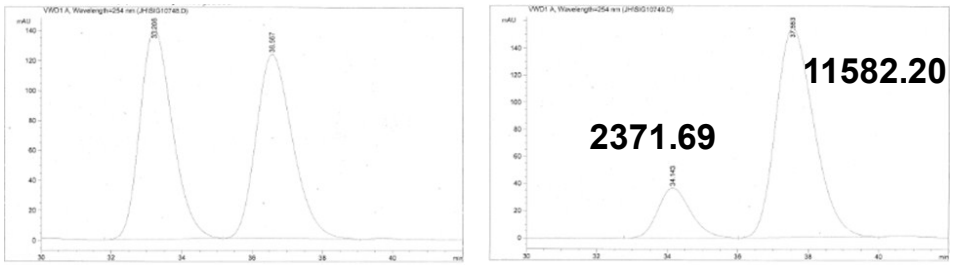


Fig. S2 Chromatograms for the enantioselectivity values in the Table 1 and Fig.5a.

Entry 1 in Table 1



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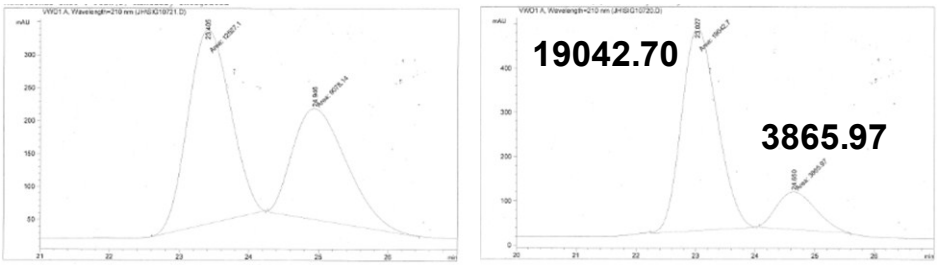
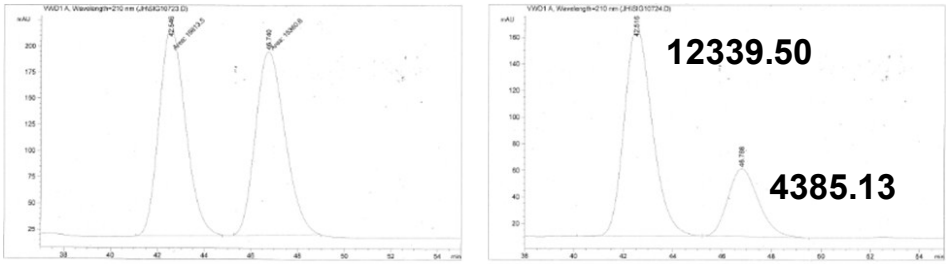
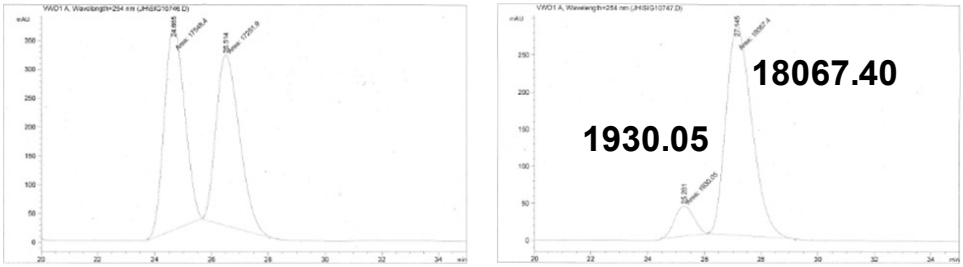


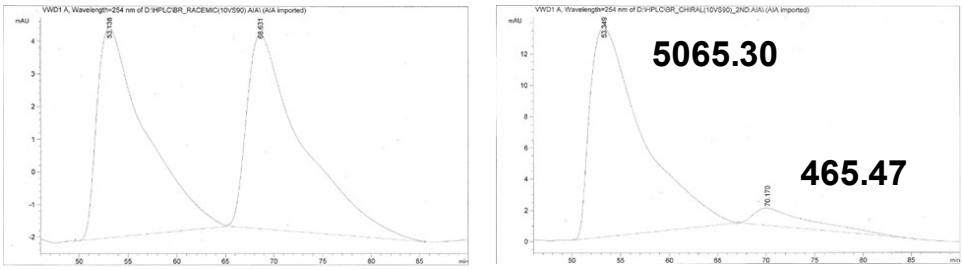
Entry 4 in Table 1



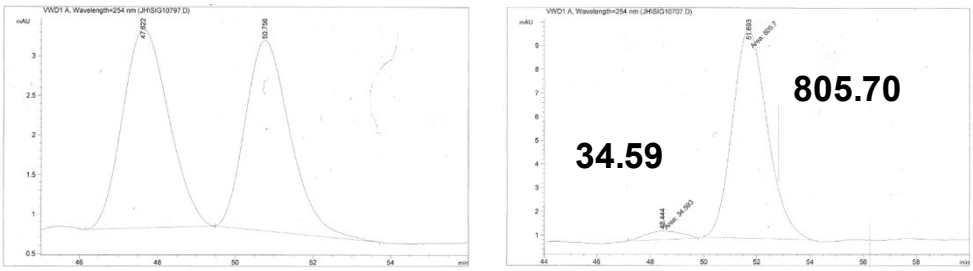
Entry 5 in Table 1



Entry 6 in Table 1



Entry 7 in Table 1



Entry 7 in Table 1 and recycling test in Fig. 5a

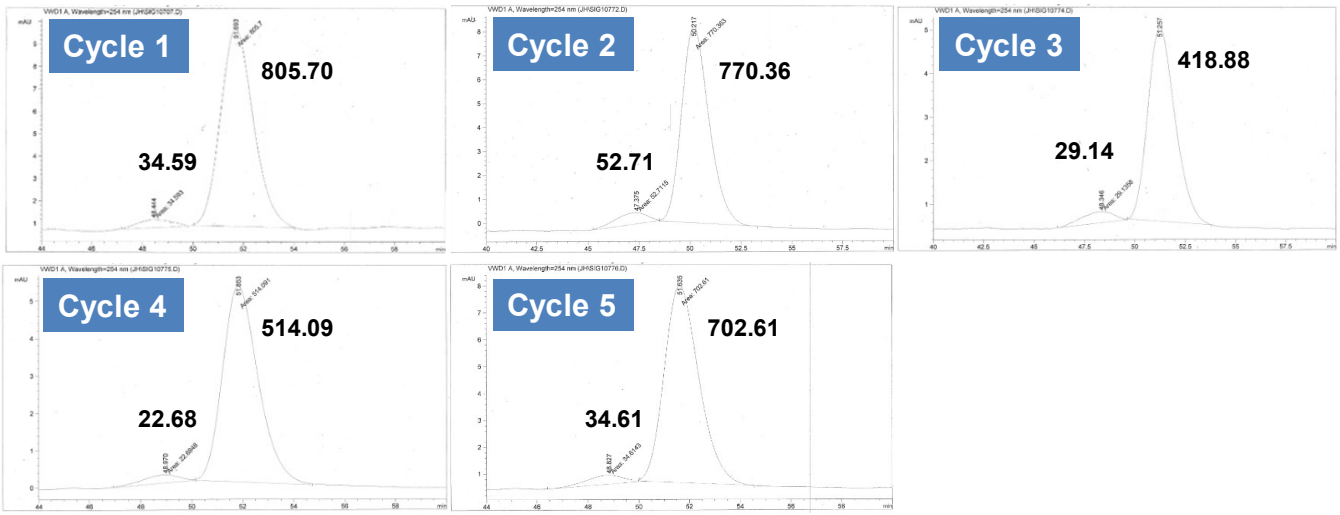


Fig. S3 (a) SEM images of H-MOP materials prepared using various amount ratios of tetrakis(4-ethynylphenyl)methane to silica template. For the H-MOP materials denoted as 0.30, 0.40, 0.60, and 1.20 mmol/g in SEM images, the 0.12 mmol of tetrakis(4-ethynylphenyl)methane and 0.40, 0.30, 0.20, and 0.10 g silica templates were used, respectively. (b) TEM images of H-MOP materials prepared using the relative amount ratios of 0.60, and 1.20 mmol/g (tetrakis(4-ethynylphenyl)methane to silica template). (c) The conversion yields of 4-nitrocinamaldehyde by H-MOP-P, H-MOP-P-0.60, H-MOP-P-1.20, and MOP-P. The reaction conditions were 10 mol% pyrrolidines, 4-cinamaldehyde (0.25 mmol), dimethyl malonate (0.75 mmol), benzoic acid (0.075 mmol), DMF/H_2O (1:1, 1.2 mL), room temperature, and 12 h. H-MOP-P and MOP-P are materials described in text. H-MOP-P-0.60 and H-MOP-P-1.20 are materials prepared using the 0.20 and 0.10 g silica templates, respectively, and 0.12 mmol of tetrakis(4-ethynylphenyl)methane, respectively.

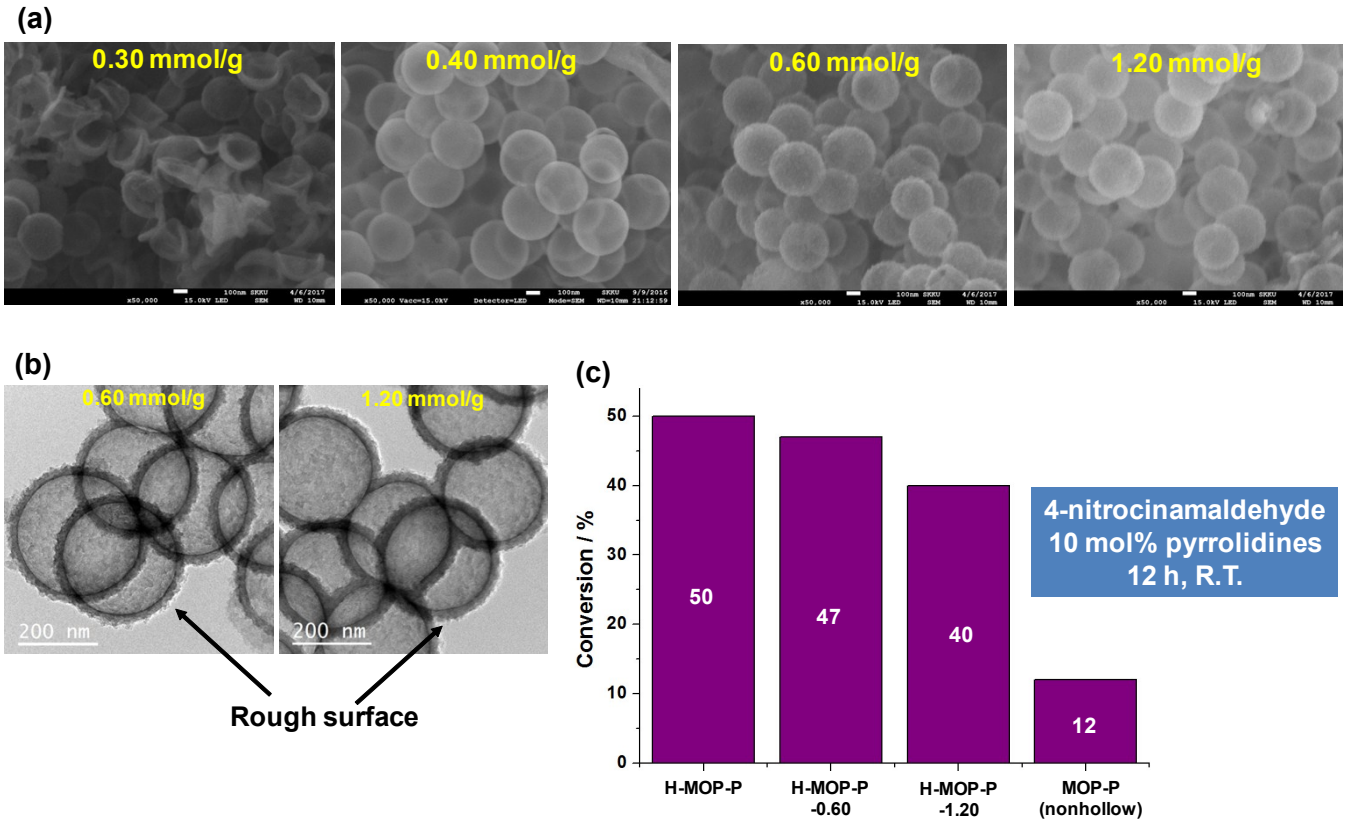


Fig. S4 (a) The model homogeneous catalyst, (*S*)-4-phenyl-1-(pyrrolidin-2-ylmethyl)-1*H*-1,2,3-triazole was prepared by the click reaction of (S)-2-azidomethylpyrrolidine with phenylacetylene. It is a known compound (Refer to ref. 19 in text). (b) Chromatograms for the enantioselectivity value of the dimethyl malonate addition to 4-nitrocinamaldehyde catalyzed by a homogeneous catalyst (10 mol%). The reaction conditions were homogeneous catalysts (10 mol%), 4-nitrocinamaldehyde (0.25 mmol), dimethyl malonate (0.75 mmol), benzoic acid (0.075 mmol), DMF/H_2O (1:1, 1.2 mL), room temperature, and 12 h. (c) TGA curve of H-MOP-P. (d) SEM images of H-MOP-P recovered after reactions at 50 °C and 70 °C for 12 h. (e) The conversion yields and enantioselectivity (the major product was a R enantiomer for all cases) of the dimethyl malonate addition to 4-nitrocinamaldehyde by H-MOP-P and a homogeneous catalysts. For the reactions at 50 oC and 70 oC, the reaction conditions were H-MOP-P (10 mol% pyrrolidines), 4-nitrocinamaldehyde (0.25 mmol), dimethyl malonate (0.75 mmol), benzoic acid (0.075 mmol), DMF/H_2O (1:1, 1.2 mL), 50 °C or 70 °C, and 12 h.