Supporting Information

Harboring Organocatalysts in a Star-Shaped Block Copolymer for Micellar Catalysis and Emulsion Catalysis

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1. Materials and instruments.

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

^{1}H NMR spectra were recorded at 25 °C on a ADVANCE NEO 400 NMR spectrometer (Bruker, Germany)at 400 MHz.

Fourier transform infrared (FTIR) spectra were measured with a 6700 FT-IR spectrometer (Thermo Nicolet, USA) in the range of 400–4000 cm^{-1}.

Dynamic light scattering (DLS) measurements were recorded at 25 °C on a laser light scattering spectrometer (BI-200SM) equipped with a Zetasizer Nano ZS instrument (Malvern, UK). To prepare the samples, the polymers were dissolved in ethanol and then added to water to reach a final concentration of 0.05 mg/mL.

Transmission electron microscope (TEM) images were recorded on a Tecnai G2 F30 S-Twin electron microscope (FEI, Netherlands) with an accelerating voltage of 300 kV. The polymers were dissolved in ethanol and then added to water to form the micelles, which were dried at room temperature before the measurements.

Field emission scanning electron microscopy (FE-SEM) images were acquired on a HITACHI Regulus 8100 microscope (Hitachi, Japan). The samples were prepared by emulsifying a toluene and an aqueous agar solution (2 mg/mL) at 85 ℃, followed by cooling the emulsion to ambient temperature for a jellified water phase.

Emulsion images were acquired on an EVOS M5000 inverted fluorescence microscope (Thermo Scientific, USA).

The chiral-phase high-performance liquid chromatography (HPLC) was performed on the Primaide instrument (Hitachi, Japan) installed with a chiral column (CHIRALPAK® AD-H, 250 × 4.6 mm, 5 μm).

2. Synthesis.

2.1 Synthesis of chain transfer agent (CTA).

The chain transfer agent, 2-(((butylthio)carbonothioyl)thio)propanoic acid, was synthesized according to the previous method.[1] Potassium phosphate (11.76 g, 554 mmol) in 130 mL of acetone was stirred for 2 h, and a mixture of 1-butanethiol (5.05 g, 554 mmol) and carbon disulfide (4.22 g, 554 mmol) was added and stirred for 2 h. A solution of 2-bromo-2-methylpropionic acid (12.66 g, 554 mmol) in 20 mL of acetone was added dropwise to the stirred reaction over 30 min at 0 °C under an argon atmosphere. The mixture was further stirred overnight at 25 °C to obtain an orange slurry, which was resuspended in acetone and filtered to remove the salt. The solvent was removed under vacuum, and the residual was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 3/2 v/v, $R_f = 0.56$) to give the chain transfer agent as an oil yellow liquid.

2.2 Synthesis of the CTA-functionalized β-cyclodextrin.

The chain transfer agent (4.0 g, 16.8 mmol), β-cyclodextrin (1.36 g, 1.2 mmol) and 4-dimethylaminopyridine (DMAP, 0.37 g, 3.3 mmol) were dissolved in 100 mL of dimethylformamide (DMF). The dicyclohexylcarbodiimide (DCC, 4.13 g, 20 mmol) was then added to the mixture, which was stirred at 25 °C for overnight. The mixture was then filtrated, and the solvent was concentrated to 10 mL. Then dichloromethane (DCM, 100 mL) was added to precipitate the product, followed by washing with DCM for another two times to obtain the CTA-functionalized β-cyclodextrin as an orange solid.

2.3 Synthesis of N-octylmethacrylamide.

N-octylmethacrylamide was synthesized according to a previous publication.[2] Methacryloyl chloride (6 mL, 62 mmol) was dissolved in DCM (20 mL), and added dropwise to a mixture of octylamine (10.26 mL 62 mmol) and triethylamine (25.8 mL,

185 mmol) in DCM (100 mL) at 0 °C. The mixture was gradually warmed to ambient temperature and stirred for 20 hours before quenched with 100 mL water. The reaction solution was extracted two times with 100 mL of 2 M hydrochloric acid and two times with 100 mL of deionized water. The organic phase was collected and dried over anhydrous Na_2SO_4. The product, N-octylmethacrylamide, was obtained as colorless oil after removing the DCM under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (s, 1H), 5.66 (s, 1H), 5.30 (d, J = 1.3 Hz, 1H), 3.29 (dd, J = 13.3, 7.0 Hz, 2H), 1.95 (s, 3H), 1.52 (dd, J = 14.4, 6.8 Hz, 2H), 1.28 (d, J = 12.9 Hz, 10H), 0.87 (t, J = 6.8 Hz, 3H).

2.4 Synthesis of the star-shaped block copolymers.

Typically, the CTA-functionalized β-cyclodextrin (852 mg, 0.35 mmol), azodiisobutyronitrile (AIBN, 32.8 mg) and N-octylmethacrylamide were dissolved in 30 mL of DMF, which was bubbled with nitrogen for 30 min to remove the oxygen. The mixture was heated in an oil bath at 75 °C for 2 days. Then a mixture of N-isopropyl acrylamide (382 mg, 1.66 mmol) and AIBN (115 mg) in DMF was bubbled with nitrogen for 30 min and added to the reaction. After reaction at 75 °C for 2 days, the solvent was concentrated and the product was precipitated with water. The product was further purified two times by dissolving in DMF and precipitating in water, and polymer was obtained as a yellow solid after drying under vacuum.

2.5 Synthesis of adamantane-modified trans-4-hydroxy-L-proline.

1-Adamantane carboxylic acid (3.6 g, 20 mmol), oxalyl chloride (5.04 mL, 100 mmol, 5eq.) were dissolved in 100 mL of DCM, followed by adding a catalytic amount of DMF dropwise to initiate the reaction for 4 h. The solvents were removed under vacuum and the residuals were redissolved in 10 mL of trifluoroacetic acid, which was added dropwise to a solution of trans-4-hydroxy-L-proline (2.6 g, 20 mmol, 1 eq.) in trifluoroacetic acid. The reaction was finished 2 hours later by concentrating the solvent to 5 mL under vacuum, after which 200 mL of petroleum ether was added to precipitate the crude product. Another two times purification was done by dissolving the crude

product in 5 mL trifluoroacetic acid and precipitating in 200 mL petroleum ether. The product was finally obtained dried as white powder after drying under vacuum.

2.6 Synthesis of Fluorescein isothiocyanate isomer I labeled 1-adamantylamine (Ad-FITC):

Fluorescein isothiocyanate isomer I labeled 1-adamantylamine was synthesized according to the previous method.[3] Fluorescein isothiocyanate isomer I (FITC, 50.0 mg, 0.642 mmol) was dissolved in 2 mL of anhydrous DMF. To this solution 2 mL of triethylamine was added. Subsequently, 1-adamantylamine (Ad, 30.0 mg, 0.642 mmol) was added and stirred at room temperature for 12 hours under a nitrogen atmosphere. The concentrated solution was extracted with DCM/water, and the organic layer was collected. The solvent was removed under vacuum to obtain the crude product which was purified by silica gel column chromatography (ethanol: ethyl acetate, 2:1, v/v) to yield fluorescein isothiocyanate isomer I labeled 1-adamantylamine (Ad-FITC, 70% yield) as a light-orange powder. ^{1}H NMR (400 MHz, DMSO): δ 10.12 (s, 2H), 9.68 (s, 1H), 8.31 (d, J = 1.8 Hz, 1H), 7.69 (dd, J = 8.4, 2.0 Hz, 1H), 7.58 (s, 1H), 7.14 (d, J = 8.3 Hz, 1H), 6.66 (d, J = 2.1 Hz, 2H), 6.58 (d, J = 8.8 Hz, 2H), 6.55 (dd, J = 8.7, 2.2 Hz, 2H), 2.25 (s, 6H), 2.06 (s, 3H), 1.64 (s, 6H).

3. Evaluation of the catalytic performance.

3.1 Micellar catalysis for asymmetric Aldol reaction.

Typically, the star-shaped polymer (2 mg) was dissolved in 0.1 mL ethanol which was added in 0.9 mL water to form the micelles. Afterwards, Ad-pro (0.005 mmol, 0.3 mg, 0.05 eq.) or an equal amount of free L-proline, and *p*-nitrobenzaldehyde (0.1 mmol, 15.1 mg, 1 eq.) were added into the system. Cyclohexanone (0.6 mmol, 62.1 μL, 6 eq.) was added to initiate the reaction. The reaction mixture was placed in the shaker at 25 °C, 400 rpm for 48 h. The reaction mixture was extracted with ethyl acetate and dried with Na_2SO_4. After removing the solvents under vacuum, the obtained product was dissolved in 500 μL $CDCl_3$ for ^{1}H NMR analysis to determine the diastereoselectivity

and conversion. The enantiomeric excess (*ee*) was determined by a chiralphase HPLC with the mobile phase of isopropanol: hexane = 10 :90.

The enantiomeric excess (*ee*) values of target component were calculated according to **Eqn. S1** based on the corresponding peak areas.

$$\%ee = \left(\frac{[R] - [S]}{[R] + [S]}\right) \times 100 \qquad \textbf{Eqn. S1}$$

[R]: the peak area of one enantiomer

[S]: the peak area of the other enantiomer

3.2 Emulsion catalysis for asymmetric Aldol reaction.

The emulsions were prepared by adding water to the toluene phase containing 20 mg/mL polymers, followed by sonication for emulsification. The water-to-oil ratios (W/O ratio) were tailored from 9:1 to 1:9 to investigate their influence on the emulsion stability and morphology. After emulsification, Ad-pro (0.005 mmol, 0.3 mg, 0.05 eq.) and p-nitrobenzaldehyde (0.1 mmol, 15.1 mg, 1 eq.) were added into the system. Cyclohexanone (0.6 mmol, 62.1 μL, 6 eq.) was added to initiate the reaction. The emulsions were placed in the shaker at 25 °C, 400 rpm for 48 h. The product was extracted with ethyl acetate and dried with Na_2SO_4. After removing the solvents under vacuum, the obtained product was subjected to ^{1}H NMR and HPLC analysis.

Table S1. Parameters of chiral-phase HPLC methodology for analyzing the components in the asymmetric aldol reactions of cyclohexanone and various arylaldehydes.

Mobile phase			Column	Analysis result	
n-hexane [vol. %]	isopropanol [vol. %]	Hold [min]		components	t_R [min]
90	10	40	HPLC column CHIRALPAK® AD-H, 250 × 4.6 mm, 5 µm	nitroPhCHO	18.2
				$P_{syn\ (2R,\ 1'R)}$	20.6
				$P_{syn\ (2S,\ 1'S)}$	23.0
				$P_{anti\ (2S,\ 1'R)}$	27.8
				$\mathbf{P_{anti\ (2R,\ 1'S)}}$	**30.6**

Detector: UV = 220 nm; T: 25 °C; flowrate: 1.0 mL/min.
nitroPhCHO: *p*-nitrobenzaldehyde
P: 2-[hydroxy-(4-nitrophenyl) methyl] cyclohexan-1-one

4. Supplementary figures.

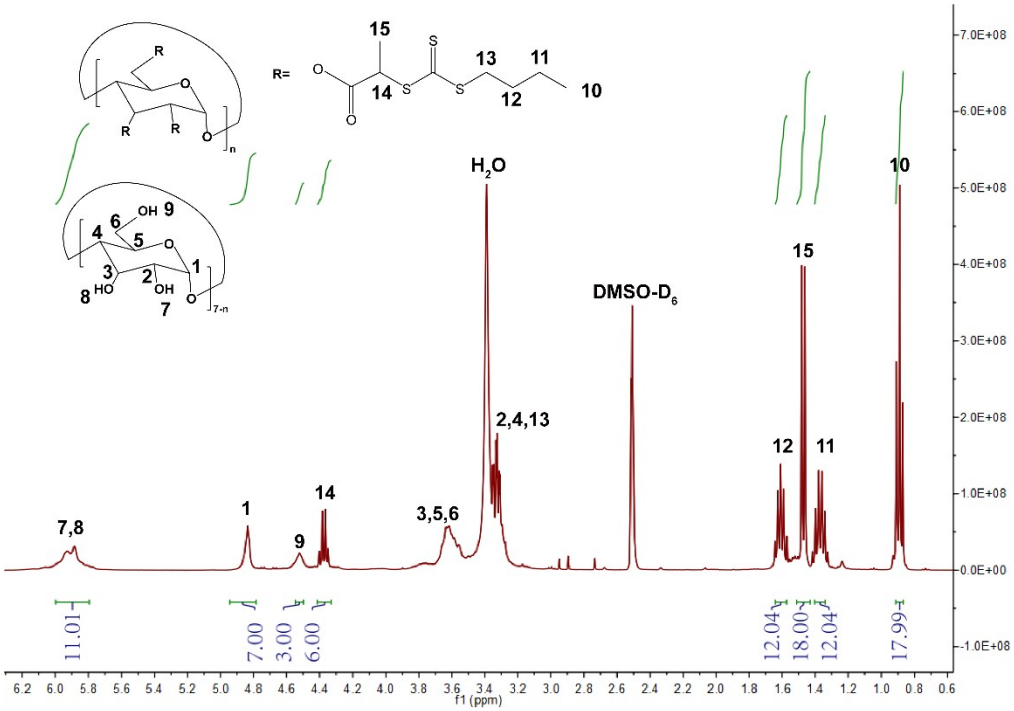


Figure S1. [1]H NMR spectrum of CTA-modified β-cyclodextrin.

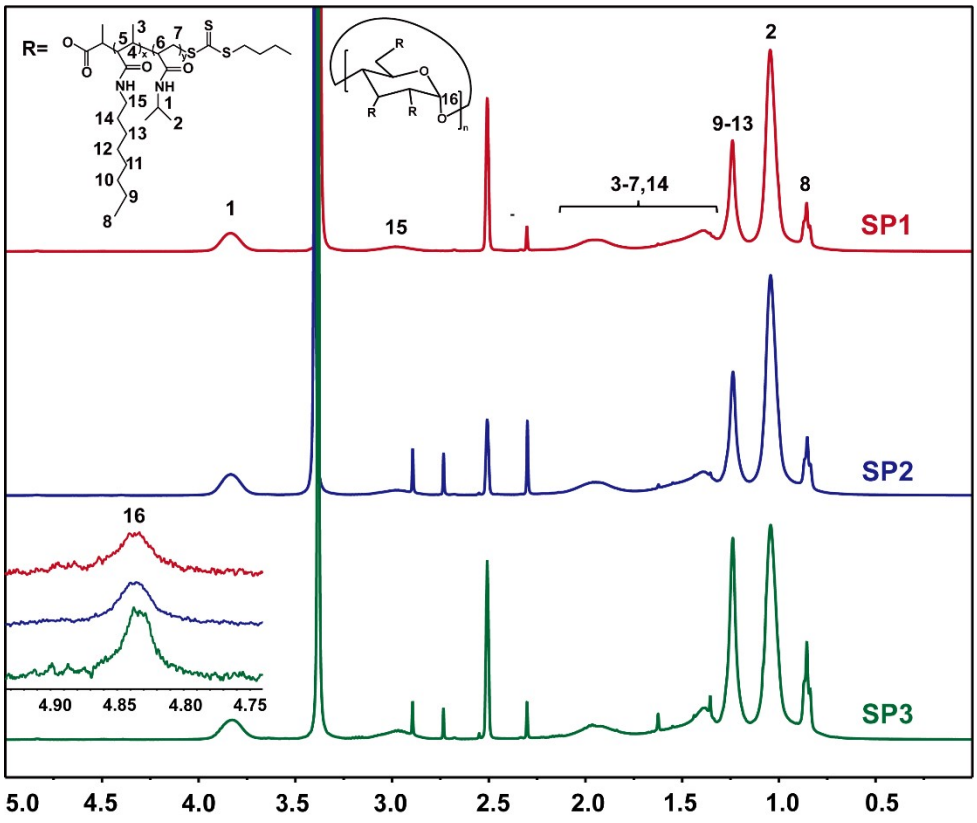


Figure S2. [1]H NMR spectra of SP1, SP2, and SP3.

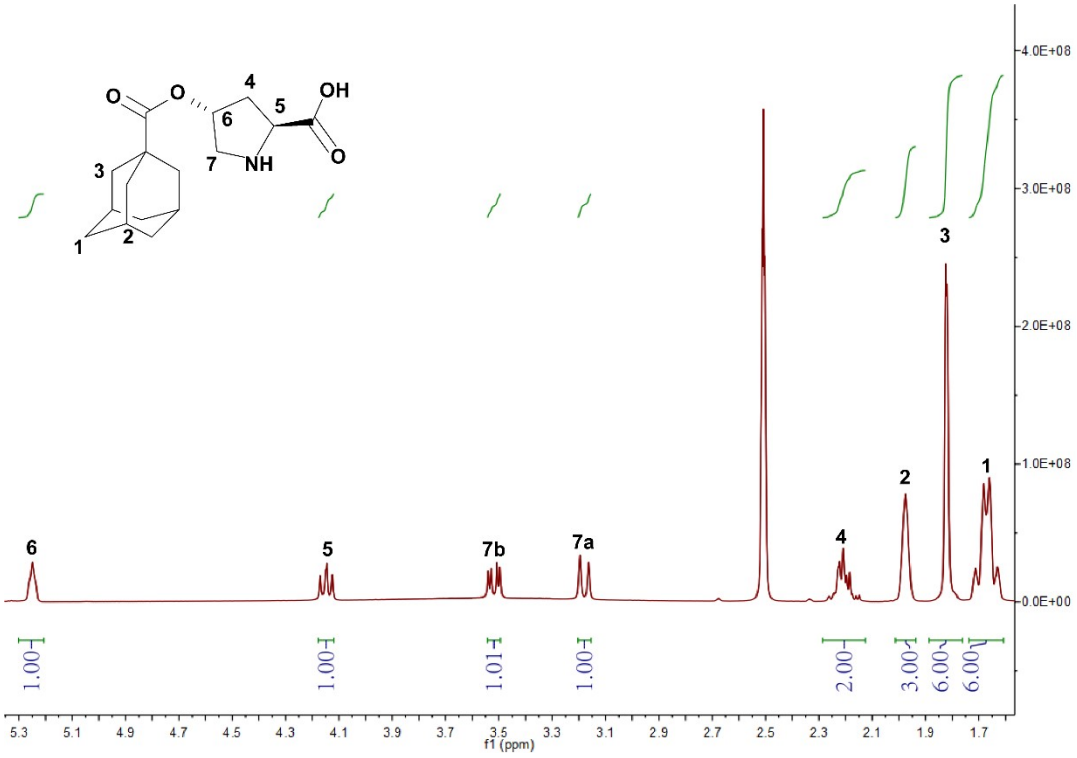
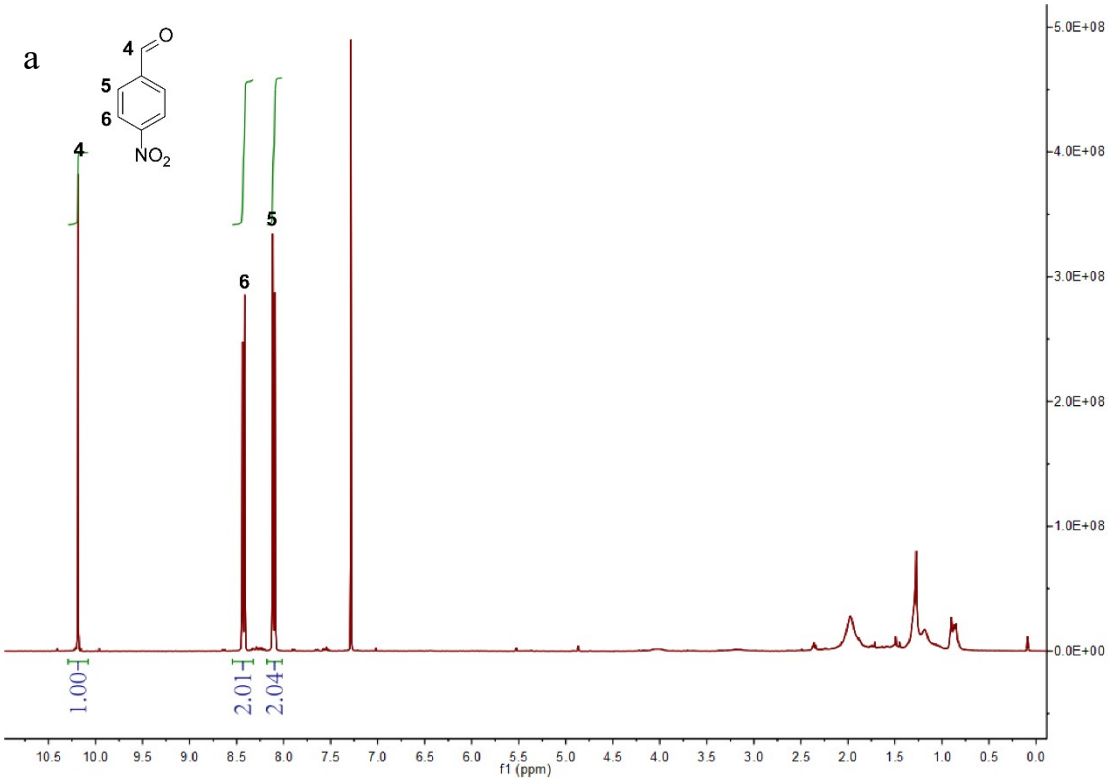


Figure S3. ^{1}H NMR spectrum of adamantane-modified 4-hydroxy-L-proline (Ad-pro).



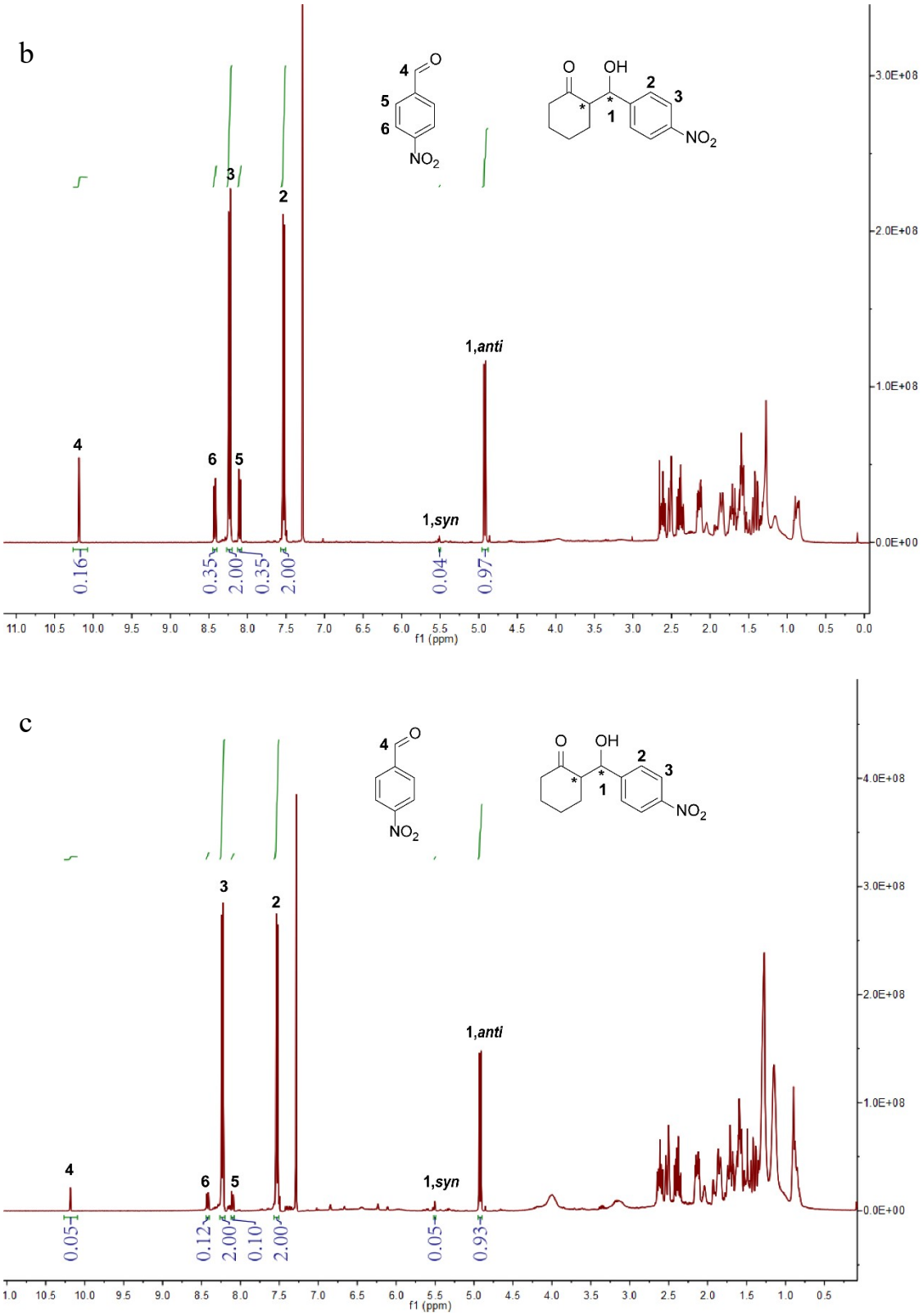


Figure S4. ^{1}H NMR spectra of the Aldol reactions in (a) SP2 micelle with 4-hydroxy-L-proline, (b) SP2 micelle with Ad-pro and (c) SP2 emulsion with Ad-pro at the W/O ratio of 7:3. ^{1}H NMR (400 MHz, $CDCl_3$), δ_{syn} = 5.49, δ_{anti} = 4.90.

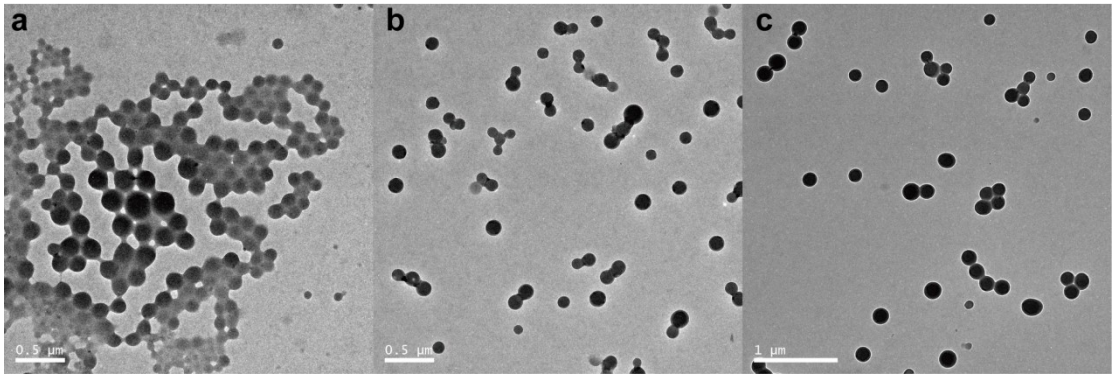


Figure S5. TEM images of the micelles assembled by the (a) SP1, (b) SP2 and (c) SP3 star-shaped polymers.

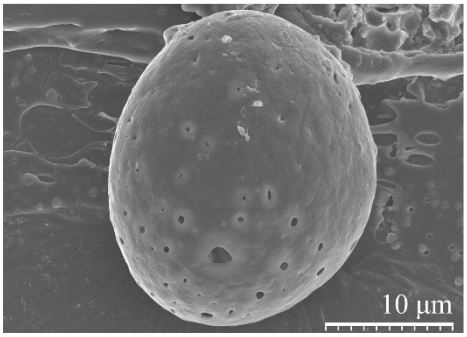


Figure S6. SEM images of jellified emulsion droplets.

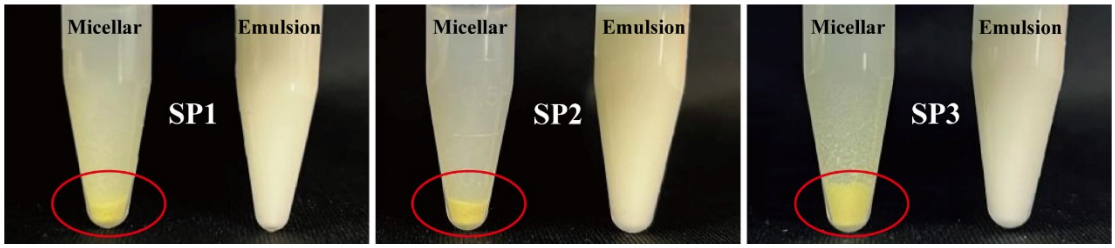


Figure S7. The solubility of substrates in micellar catalysis and emulsion catalysis. From left to right are SP1, SP2 and SP3.

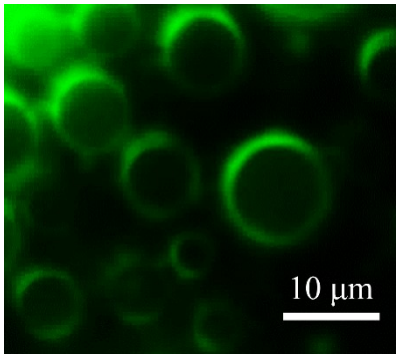


Figure S8. Ad-FITC labeled emulsion under fluorescent microscopy.

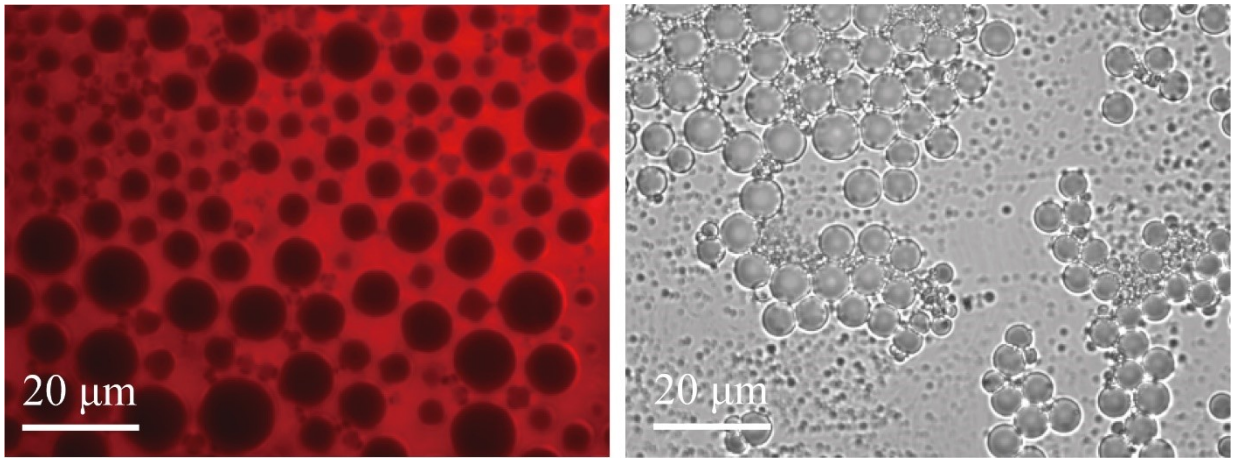


Figure S9. Emulsions under fluorescent and optical microscopy.

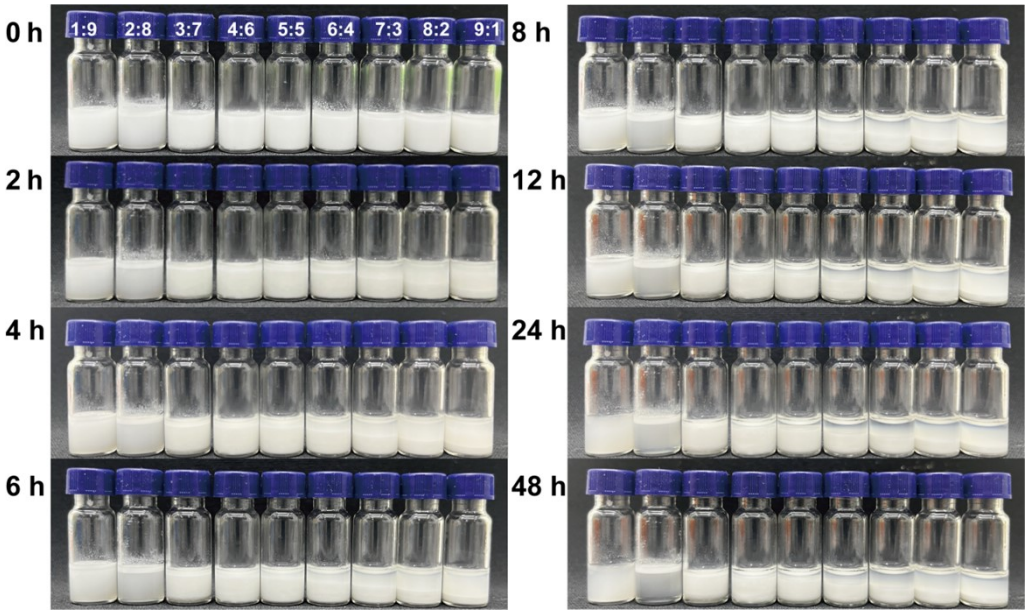


Figure S10. Emulsion stability with different water-to-oil ratios at different times.

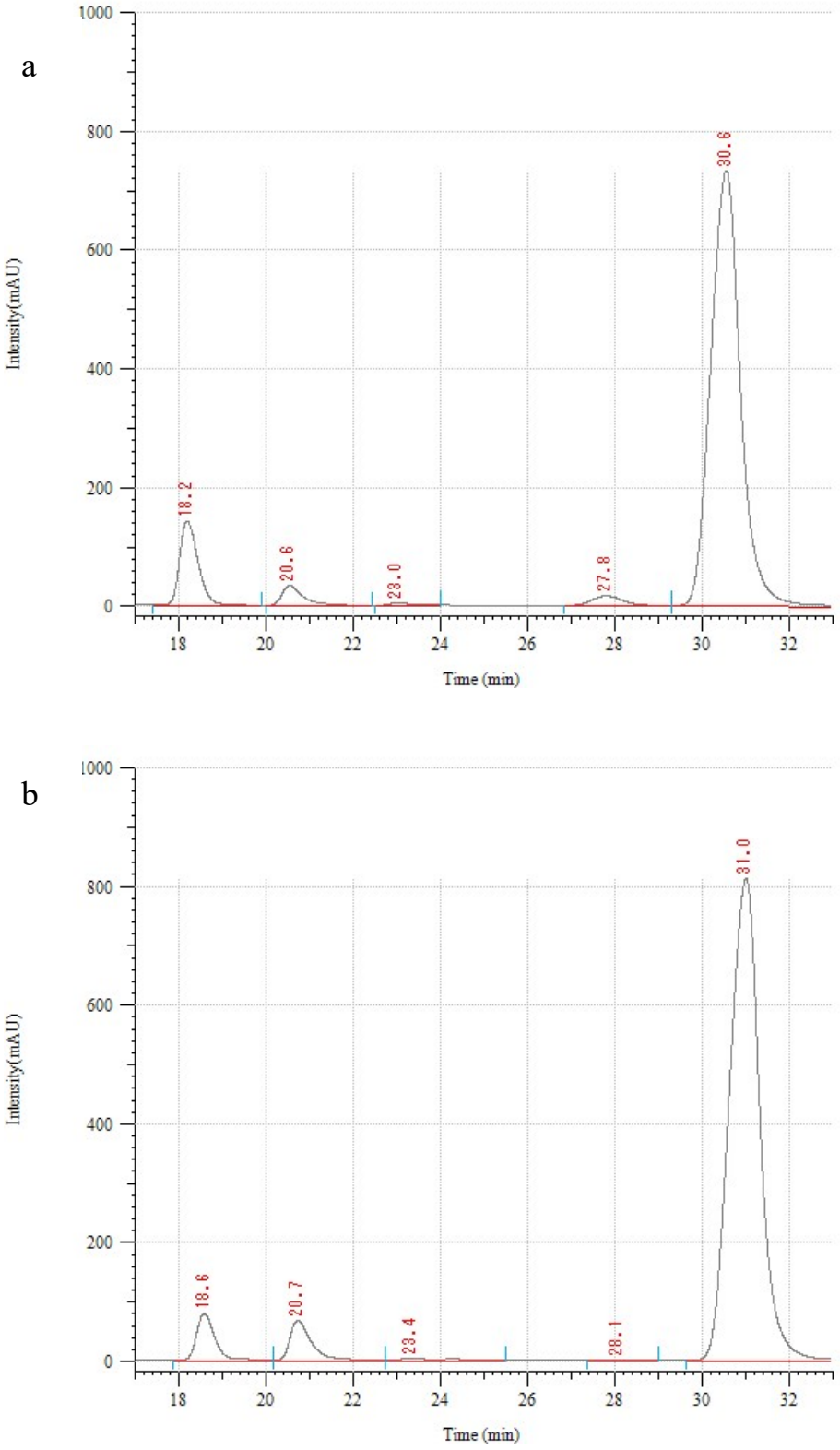


Figure S11. HPLC spectra of the Aldol reactions in (a) SP2 micelles and (b) SP2 emulsions with Ad-pro at W/O ratio of 7:3. (R.T. $_{syn\ (2R,1'R)}$ = 20.6 min, R.T. $_{syn\ (2S,1'S)}$ = 23.0 min, R.T. $_{anti\ (2S,\ 1'R)}$ = 27.8 min, R.T. $_{\boldsymbol{anti\ (2R,\ 1'S)}}$ = 30.6 min).

Table S2. SP1 emulsion catalysis for Aldol reaction

entry	W/O ratio	conv. [%]	*anti:syn*
1	9:1	94.5	96:4
2	8:2	91.5	95:5
3	7:3	86.0	95:5
4	6:4	82.4	94:6
5	5:5	69.0	94:6
6	4:6	59.8	93:7
7	3:7	55.1	93:7
8	2:8	45.1	94:6
9	1:9	50.5	94:6

Table S3. SP3 emulsion catalysis for Aldol reaction

entry	W/O ratio	conv. [%]	*anti:syn*
1	9:1	97.1	95:5
2	8:2	93.7	94:6
3	7:3	91.3	93:7
4	6:4	77.8	92:8
5	5:5	83.5	92:8
6	4:6	73.4	93:7
7	3:7	76.6	93:7
8	2:8	60.6	91:9
9	1:9	49.8	90:10

References：

1. Swift, T.; Swanson, L.; Geoghegan, M.; Rimmer, S., The pH-Responsive Behaviour of Poly(acrylic acid) in Aqueous Solution is Dependent on Molar Mass. *Soft Matter* **2016,** *12* (9), 2542-2549.

2. Ritter, H.; Schwarz-Barac, S.; Stein, P., Cyclodextrins in Polymer Synthesis: Two-Step Reaction to Aliphatic Poly(methacrylimide) Foams by Thermal Treatment of Copolymers Obtained from Cyclodextrin Complexes of tert-Butyl Methacrylate and Various N-Alkyl Methacrylamides. *Macromolecules* **2003,** *36* (2), 318-322.

3. Demirci, S.; Kinali-Demirci, S.; VanVeller, B., Controlled Supramolecular Complexation of Cyclodextrin-Functionalized Polymeric Ionic Liquid Brushes. *ACS Appl. Polym. Mater.* **2020,** *2* (2), 751-757.