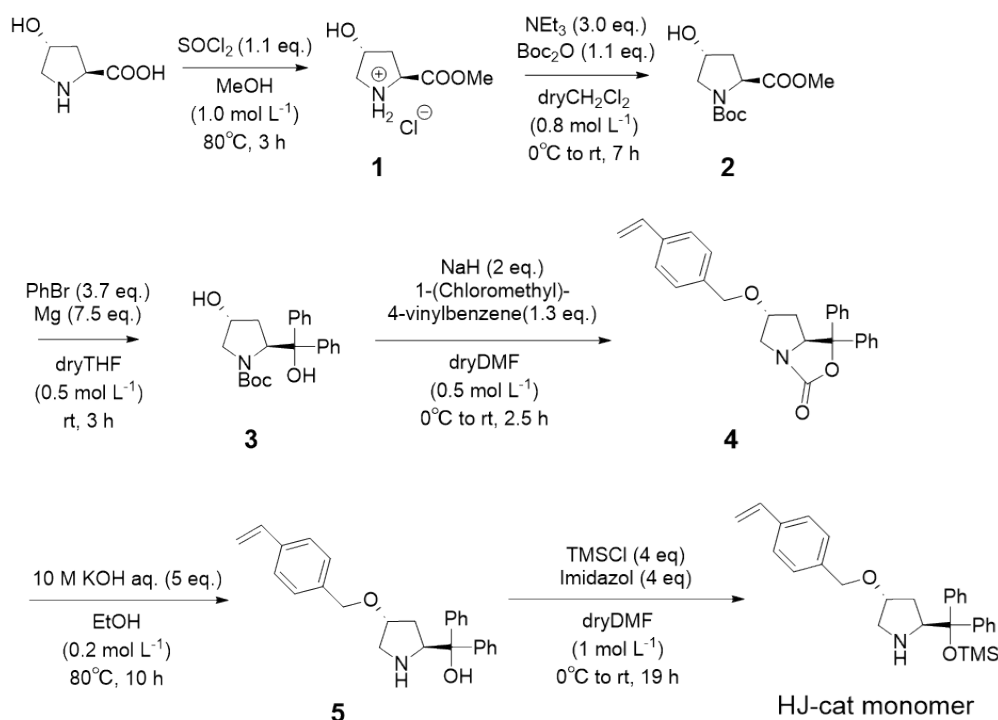


## Electronic Supplementary Information

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## 1. Synthesis of HJ-Cat Monomer<sup>[1]</sup>



### Compound 1:

A 2-L three-neck round-bottom flask was equipped with a magnetic stirring bar and dried with a heat gun under evacuation for 10 min. The flask was evacuated and backfilled with Ar three times. *trans*-4-Hydroxy-L-proline (30.0 g, 228.8 mmol, 1.0 eq) and MeOH (305 mL) were mixed in the flask. In an ice-water bath,  $\text{SOCl}_2$  (18.2 g, 251.7 mmol, 1.1 eq) was slowly added to the solution dropwise using a dropping funnel. Once the addition was completed, the ice-water bath was removed. The flask was heated in an oil bath at 80°C and continuously stirred for 3 h. After confirming the completion of the reaction by TLC, the reaction mixture was concentrated under reduced pressure. The residual  $\text{SOCl}_2$  was removed by azeotropic distillation with an excess of toluene. The crude mixture was used in the next reaction without further purification.

### Compound 2:

A 2-L three-neck round-bottom flask was equipped with a magnetic stirring bar. The flask was evacuated and backfilled with Ar three times. To a solution of **1** (crude mixture, 228.8 mmol, 1.0 eq) in dry  $\text{CH}_2\text{Cl}_2$  (285.9 mL) was added triethylamine (95.1 mL, 686.3 mmol, 3.0 eq) dropwise using a dropping funnel in an ice bath. Subsequently,  $\text{Boc}_2\text{O}$  (57.8 mL, 251.6 mmol, 1.1 eq) was added dropwise to the reaction mixture. The ice-water bath was removed and stirred at room temperature for 6 h. After confirming the completion of the reaction by TLC, the solution was quenched with aq. HCl (1 mol L<sup>-1</sup>) and aq.  $\text{NaHCO}_3$  (1 mol L<sup>-1</sup>). The

organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The crude mixture was used in the next reaction without further purification.

### Compound 3:

A 3 L three-neck round-bottom flask was equipped with a magnetic stirring bar and dried with a heat gun under evacuation for 10 min. The flask was evacuated and backfilled with Ar three times. Mg (41.7 g, 1716.0 mmol, 7.5 eq),  $\text{I}_2$  (few particles), and dryTHF (460 mL) were added to the flask. Bromobenzene (88.6 mL, 846.5 mmol, 3.7 eq) was added dropwise using a dropping funnel. After completion of the addition, the reaction mixture was cooled in an ice-water bath. A solution of **2** (crude mixture, 228.8 mmol, 1.0 eq.) in dryTHF (307 mL) was added dropwise to the reaction mixture and continuously stirring for 3 h. After confirming the completion of the reaction by TLC, the reaction was quenched with HCl aq (6 mol  $\text{L}^{-1}$ , 572 mL). The aqueous layer was extracted with EtOAc three times. The combined organic layer was washed with sat. aq. NaCl, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The crude mixture was used in the next reaction without further purification.

### Compound 4:

A 1-L three-neck round-bottom flask was equipped with a magnetic stirring bar and dried with a heat gun under evacuation for 10 min. The flask was evacuated and backfilled with Ar three times. The flask was charged with NaH (6.2 g, 257.5 mmol, 2.2 eq) and cooled in an ice-water bath. A solution of **3** (crude mixture, 117.1 mmol, 1.0 eq) in dryDMF (234 mL) was added dropwise, followed by the addition of 1-(chloromethyl)styrene (141.0 mL, 152.2 mmol, 1.3 eq). The reaction mixture was continuously stirred for 2.5 h. After confirming the completion of the reaction by TLC, the reaction was quenched with aq. HCl (1 mol  $\text{L}^{-1}$ , 132 mL). The aqueous layer was extracted with EtOAc three times. The combined organic layer was washed with sat. aq. NaCl, dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure. The crude mixture was purified by normal-phase flash column chromatography (hexane/EtOAc = 19:1 to 3:1) to give a target compound as a brown and oily material (19.9 g, 81% yield in 4 steps).

**$^1\text{H NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  7.52 (m, 2H), 7.40-7.25 (m, 12H), 6.71 (dd,  $J = 17.6, 10.8$  Hz, 1H), 5.77-5.73 (m, 1H), 5.27-5.24 (m, 1H), 4.86 (q,  $J = 5.5$  Hz, 1H), 4.45 (s, 2H), 4.16-4.02 (m, 2H), 3.32 (dd,  $J = 12.8, 1.4$  Hz, 1H), 1.89 (dd,  $J = 12.8, 5.5$  Hz, 1H), 1.23-1.15 (m, 1H).

### Compound 5:

A 1-L two-neck round-bottom flask was charged with a solution of **4** (30.6 g, 74.3 mmol, 1.0 eq) in EtOH (372 mL). A solution of KOH (20.8 g, 371.6 mmol, 5.0 eq) in water (37.2 mL) was added to the reaction mixture. The reaction mixture was heated in an oil bath at  $80^\circ\text{C}$  and continuously stirred for 18 h. After confirming the completion of the reaction by TLC, the

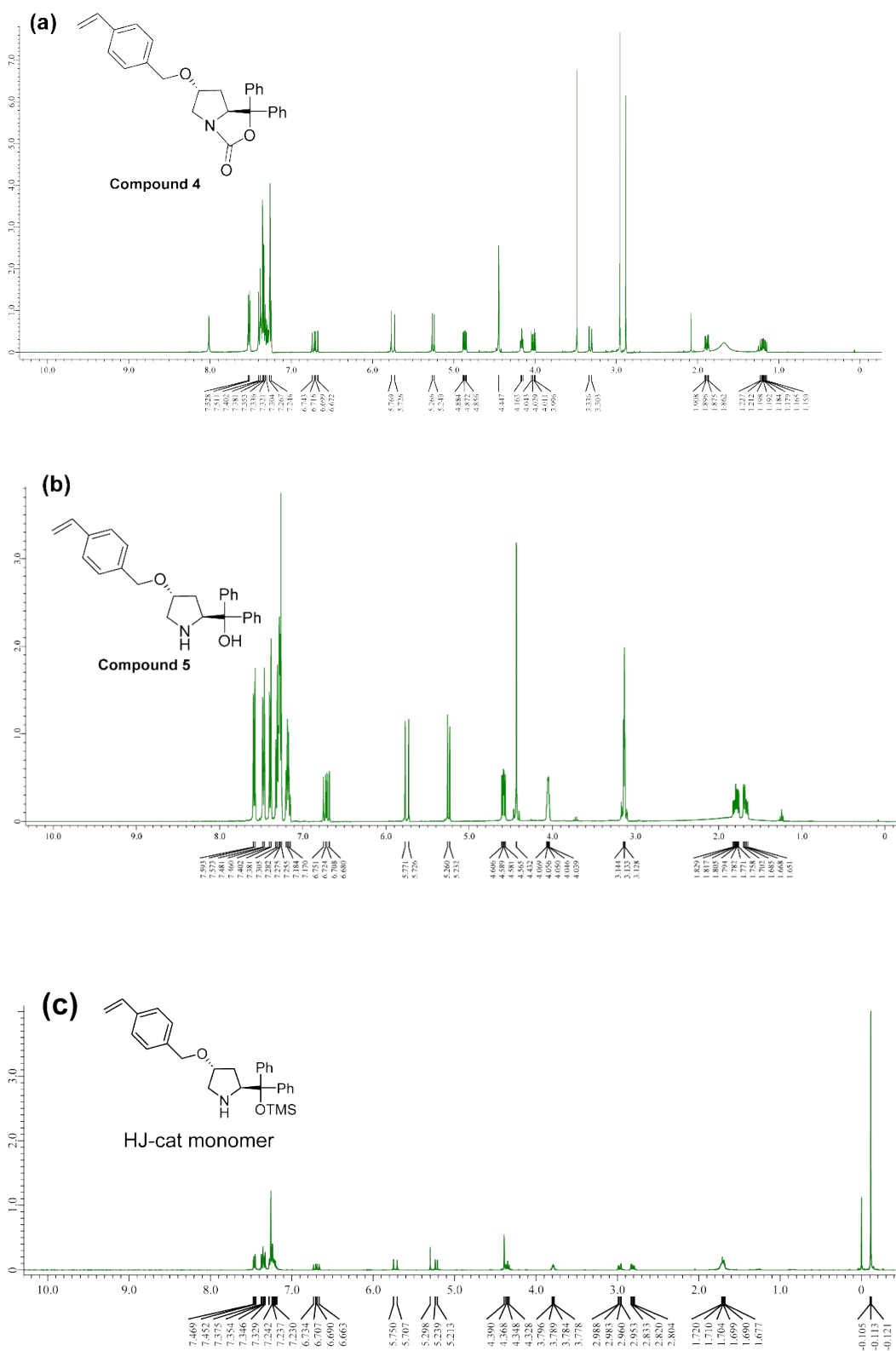
reaction mixture was cooled to room temperature, and sat. aq.  $\text{NH}_4\text{Cl}$  (530 mL) was added to quench the reaction. EtOH was removed under reduced pressure, and the aqueous layer was extracted with EtOAc three times. The combined organic layer was washed with sat. aq. NaCl., dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The crude mixture was purified by recrystallization from EtOH to give a target compound as a white and powdered crystal (26.2 g, 92% yield).

**$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  7.58 (d,  $J$  = 8.2 Hz, 2H), 7.47 (d,  $J$  = 8.2 Hz, 2H), 7.39 (d,  $J$  = 8.2 Hz, 2H), 7.32-7.26 (m, 6H), 7.18 (dd,  $J$  = 13.3, 7.3 Hz, 2H), 6.72 (dd,  $J$  = 17.4, 11.0 Hz, 1H), 5.75 (d,  $J$  = 17.4 Hz, 1H), 5.25 (d,  $J$  = 11.0 Hz, 1H), 4.59 (dd,  $J$  = 9.8, 6.6 Hz, 1H), 4.43 (s, 2H), 4.07-4.03 (m, 1H), 3.14-3.13 (m, 2H), 1.83-1.76 (m, 1H), 1.68 (q,  $J$  = 6.6 Hz, 1H).

HJ-cat monomer:

A 30-mL glass vial was charged with a solution of **5** (3.0 g, 7.8 mmol, 1.0 eq) and imidazole (2.1 g, 31.1 mmol, 4.0 eq) in dryDMF (7.8 mL). The reaction mixture was cooled in an ice-water bath followed by addition of TMSCl (4.0 mL, 31.1 mmol, 4.0 eq) dropwise. After removing the ice-water bath, the reaction mixture was continuously stirred for 19 h. After confirming the completion of the reaction by TLC, the reaction was quenched with aq. phosphate buffer (pH 7.0, 10.7 mL) in the ice-water bath. The aqueous layer was extracted with EtOAc four times. The combined organic phase was washed with sat. aq. NaCl., dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The crude mixture was purified by normal-phase flash column chromatography (hexane/EtOAc = 2:98 to 1:4) to give a target compound as a yellow and oily material (1.8 g, 50% yield).

**$^1\text{H-NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  7.47-7.44 (m, 2H), 7.35 (dd,  $J$  = 10.7, 7.5 Hz, 4H), 7.28-7.20 (m, 9H), 6.70 (dd,  $J$  = 17.4, 10.7 Hz, 1H), 5.73 (d,  $J$  = 17.4 Hz, 1H), 5.30-5.21 (m, 2H), 4.39 (s, 2H), 4.35 (t,  $J$  = 7.5 Hz, 1H), 3.80-3.78 (m, 1H), 2.99-2.79 (m, 2H), 1.72-1.68 (m, 2H), -0.11 (t, 9H).



**Fig. S1.**  $^1\text{H}$  NMR spectra of (a) **Compound 4**, (b) **Compound 5**, and (c) **HJ-cat monomer** (400 MHz,  $\text{CDCl}_3$ ).

## 2. Characterization of MPG

**Table S1.** Yields and Loading of HJ-Cat Monomer in the **MPG**<sup>a</sup>

entry	X (wt%)	yield (%)	[HJ-cat] (mmol g <sup>-1</sup> ) <sup>b</sup>	Incorporation ratio of HJ-cat (%) <sup>c</sup>
<b>MPG20</b>	20	90	0.28	106
<b>MPG40</b>	40	93	0.25	116
<b>MPG60</b>	60	91	0.23	126
<b>MPG40'</b>	40	90	0.26	118

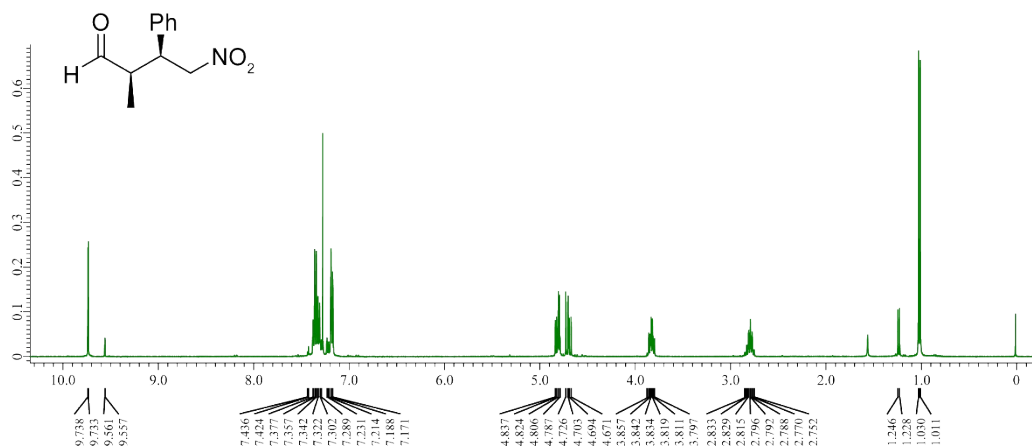
<sup>a</sup>Conditions: DVB (X wt%), styrene (90-X wt%), HJ-cat monomer (10 wt%), monomer = 300 mg, toluene/1-decanol (30:70 w/w, 700 mg), AIBN (1 wt% with respect to the monomers), 70°C, 72 h. <sup>b</sup>Based on the feed ratio of monomers, theoretical loading of HJ-cat on the **MPG** was calculated and compared.

**Table S2.** Median Pore Sizes ( $D_{\text{median}}$ ), Specific Surface Areas ( $S_v$ ), and Porosities in Dry State ( $\epsilon_{\text{dry}}$ ) of the **MPG**<sup>a</sup>

	$D_{\text{median}}$ (nm)	$S_v$ (m <sup>2</sup> g <sup>-1</sup> )	$\epsilon_{\text{dry}}$ (%)
<b>MPG20</b>	2190	98	82
<b>MPG40</b>	800	17	81
<b>MPG60</b>	340	29	82
<b>MPG40'</b>	25450	1	81

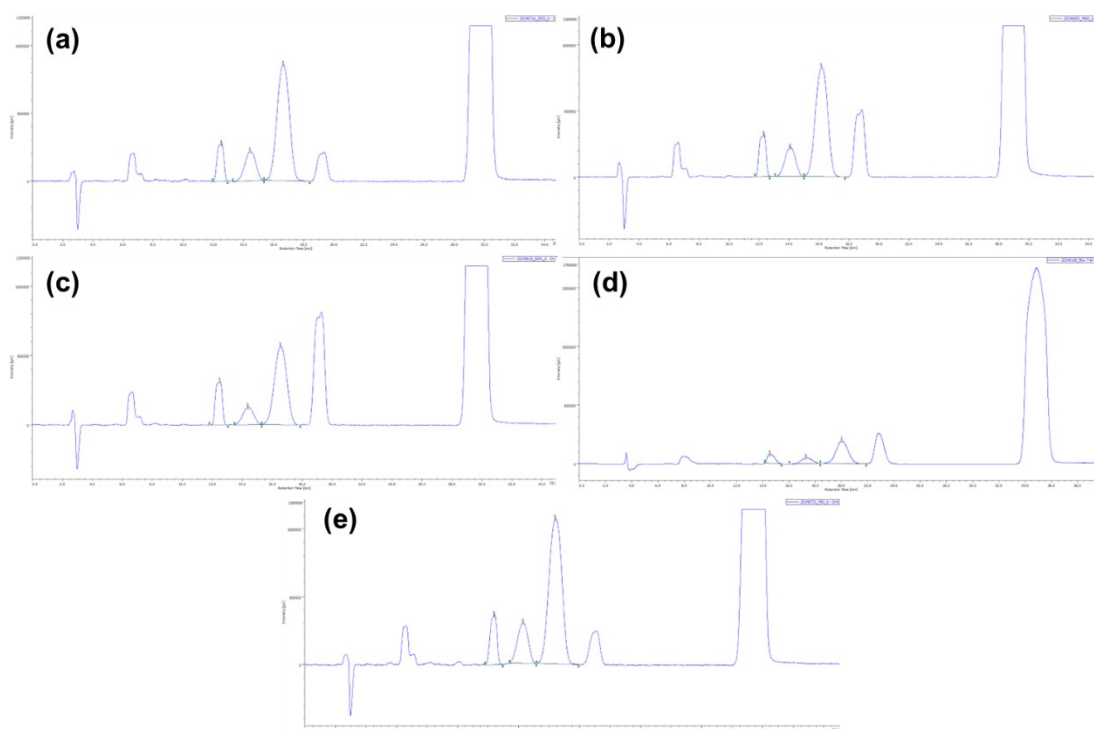
<sup>a</sup>Determined using mercury intrusion porosimetry.

### 3. Continuous-flow Michael addition



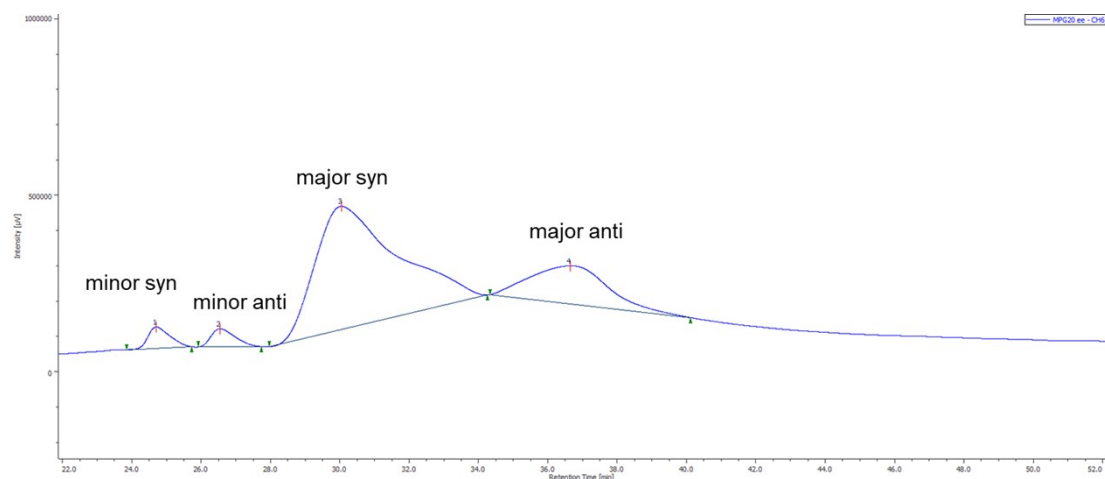
**Fig. S2.**  $^1\text{H}$  NMR spectrum of product in Michael addition (400 MHz,  $\text{CDCl}_3$ ).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  9.74 (d,  $J = 1.8$  Hz, syn isomer, 1H), 9.56 (d,  $J = 1.8$  Hz, anti isomer, 1H), 7.44-7.30 (m, 4H), 7.20 (dd,  $J = 16.9, 6.9$  Hz, 2H), 4.84-4.67 (m, 2H), 3.88-3.80 (m, 1H), 2.85-2.75 (m, 1H), 1.24 (d,  $J = 7.2$  Hz, anti isomer, 3H), 1.02 (d,  $J = 7.6$  Hz, syn isomer, 3H).



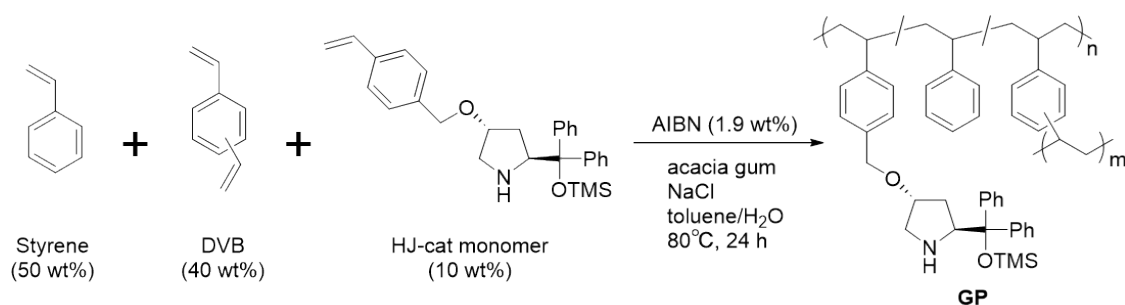
**Fig. S3.** Reverse-phase HPLC charts of elution after Michael addition with (a) **MPG20**, (b) **MPG40**, (c) **MPG60**, (d) **MPG40'**, and (e) **GP** at 6 CV. Conditions: mobile phase = acetonitrile/water (60:40 v/v) containing 0.1 vol% trifluoroacetic acid at  $1 \text{ mL min}^{-1}$ . Retention time: 12.5 min (nitrobenzene), 14.5 min (product, anti isomer), 16.5 min (product, syn isomer).



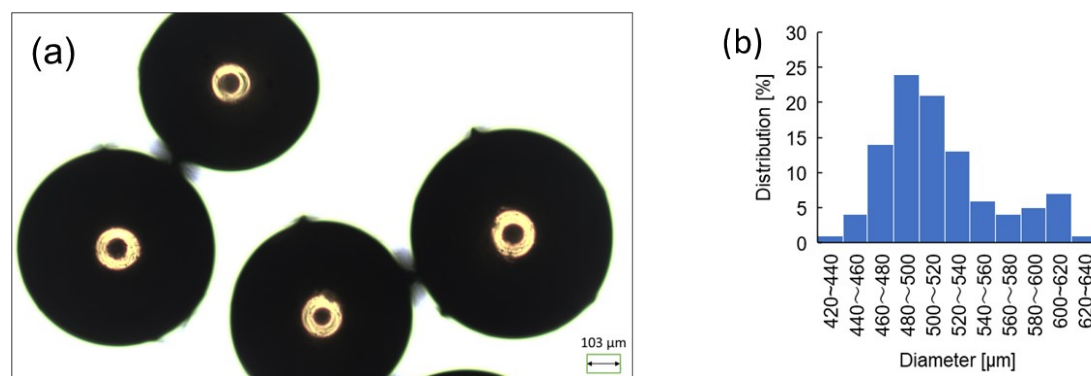


**Fig. S4.** Chiral HPLC chart of product in the Michael addition with **MPG20**. Conditions: mobile phase = 2-propanol/hexane (6.2:93.8 v/v) at 0.75 mL min<sup>-1</sup>. Retention time: 24.7 min (product, minor syn isomer), 26.5 min (product, minor anti isomer), 30.3 min (product, major syn isomer), 27.0 min (product, major anti isomer).

#### 4. Preparation of GP<sup>[2]</sup>



A solution of acacia gum (2.4 g) and NaCl (1.5 g) in water (60 mL) was placed in a 500-mL round-bottom flask equipped with a magnetic stirring bar. The aqueous (continuous) phase was degassed by purging with N<sub>2</sub> for more than 30 min. On the other hand, styrene (750 mg, 50 wt%), divinylbenzene (600 mg, 40 wt%), HJ-cat monomer (150 mg, 10 wt%), and AIBN (29 mg, 1 wt% with respect to total monomer) were completely dissolved in toluene (3 mL), and the monomer solution was degassed by purging with N<sub>2</sub> for more than 30 min. The organic (dispersed) phase containing the monomers was injected rapidly into the continuous phase under stirring at 300 rpm. The reaction mixture was continuously stirred at 80°C for 24 h. After cooling to room temperature, the mixture was filtered, washed successively with H<sub>2</sub>O, MeOH, THF, and toluene, and dried in vacuo to give gel particles (**GP**) as brown solids (949 mg, 63% yield). The obtained **GPs** were passed through a series of sieves, and those with 420–640 μm diameter were used (Fig. S1) for further experiments. Based on the EA for N element, the loading of HJ-cat on the **GPs** was estimated to be 0.29 mmol g<sup>-1</sup>.



**Fig. S5.** (a) The microscopic image of the **GPs**. (b) Diameter distribution of the sieved **GPs**.

## 5. References

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- [2] T. Iwai, T. Harada, K. Hara, M. Sawamura, *Angew. Chem. Int. Ed.* **2013**, *52*, 12322–12326.