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Supplementary information

Regulated synthesis of Zr-metal-organic frameworks with variable hole size and its influence on the performance of Novel MOF-based heterogeneous amino acid-thiourea catalyst

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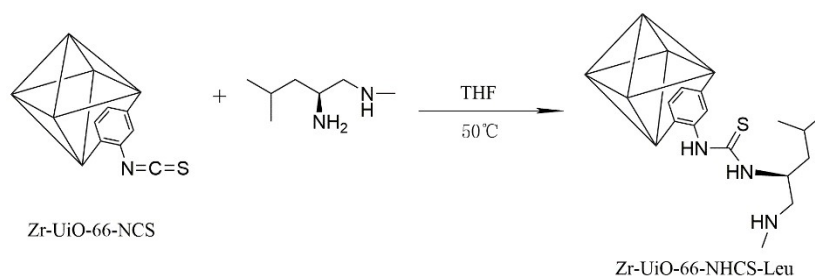
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Experiment section

Synthesis and characterization of catalysts

1. Synthesis of Zr-UiO-66-NHCS-Leu



In a 50 mL round-bottomed flask, 1.20 mmol of 2-amino-4-methylpentylmethylamine was dispersed in 20 mL of anhydrous tetrahydrofuran, and the required amount of Zr-UiO-66-NH₂ was added (1.00 mmol). The solution was stirred at 50°C for 24 h. Then, it was centrifuged, and the solid was washed with THF (3×10 mL) to obtain as a fine yellow powder after drying in vacuo at 50°C.

¹H NMR (500 MHz, Deuterium Oxide) δ 8.26 (d, *J* = 1.5 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 3.52-3.49 (m, 5H), 2.03 (s, 3H), 1.71 – 1.53 (m, 6H), 0.66-0.62 (m, 1H).

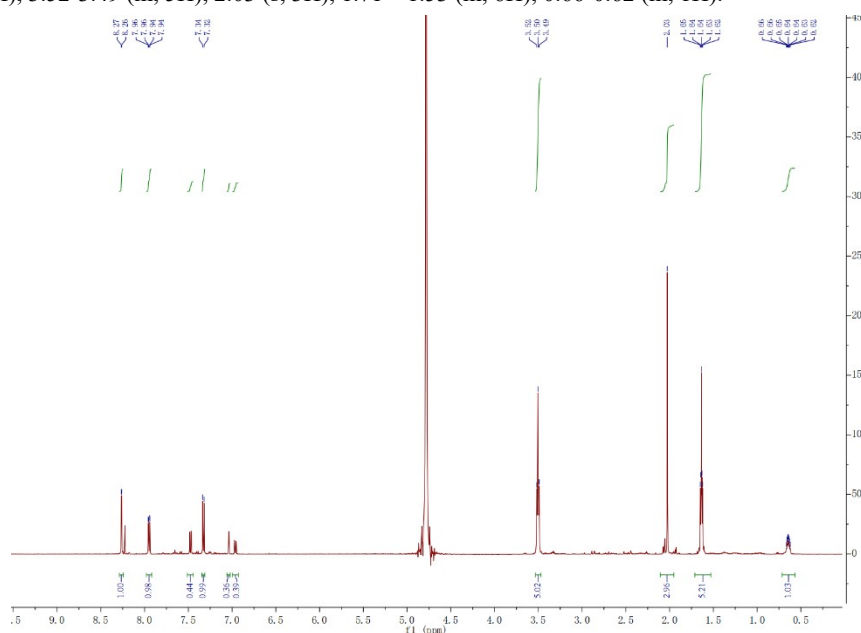
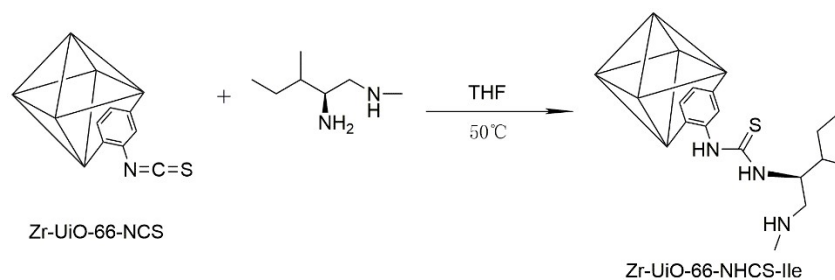


Fig. S1 Representative ¹H NMR spectrum of Zr-UiO-66-NHCS-Leu dissolved in NaOH-D₂O solution (ca. 64% modified). Unmodified Zr-UiO-66-NH₂ and functionalized linker were identified at a peak area of 6.9–8.5 ppm.

2. Synthesis of Zr-UiO-66-NHCS-Ile



In a 50 mL round-bottomed flask, 1.20 mmol of 3-amino-4-methylpentylmethylamine was dispersed in 20 mL of anhydrous tetrahydrofuran, and add the required amount of Zr-UiO-66-NH₂ was added (1.00 mmol). The

solution was stirred at 50°C for 24 h. Then, it was centrifuged, and the solid was washed with THF (3×10 mL) to obtain as a fine yellow powder after drying in vacuo at 50°C.

^1H NMR (500 MHz, Deuterium Oxide) δ 7.79 (s, 1H), 7.48 (d, J = 7.8 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.04 (m, 3H), 2.09 (s, 1H), 1.56 (s, 3H), 1.17 (m, 3H).

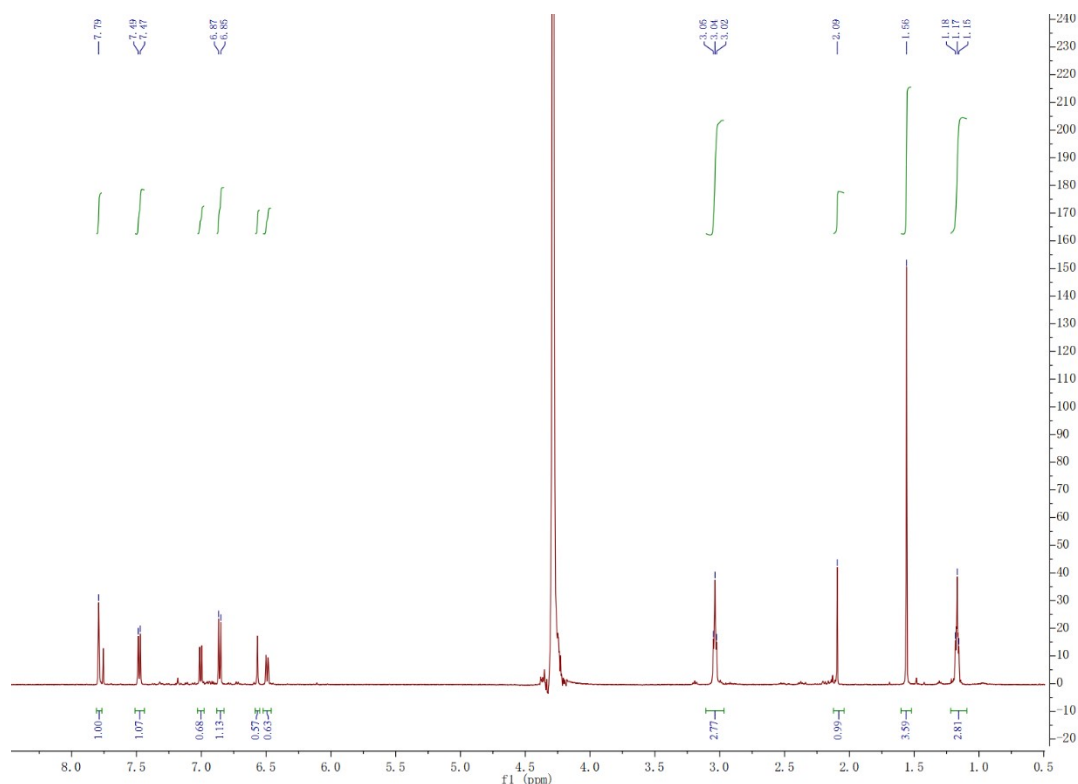
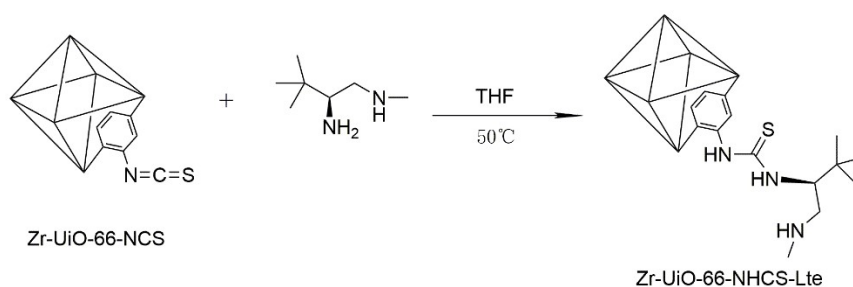


Fig. S2 Representative ^1H NMR spectrum of Zr-UiO-66-NHCS-IIe dissolved in NaOH- D_2O solution (ca. 43% modified). Unmodified Zr-UiO-66- NH_2 and functionalized linker were identified at a peak area of 6.8-8.0 ppm.

3. Synthesis of Zr-UiO-66-NHCS-Lte



In a 50 mL round-bottomed flask, 1.20 mmol of 2-amino-3,3-dimethylbutylmethylamine was dispersed in 20 mL of anhydrous tetrahydrofuran, and the required amount of Zr-UiO-66- NH_2 was added (1.00 mmol). The solution was stirred at 50°C for 24 h. Then, it was centrifuged, and the solid was washed with THF (3×10 mL) to obtain as a fine yellow powder after drying in vacuo at 50°C.

^1H NMR (500 MHz, Deuterium Oxide) δ 8.33 (d, J = 1.4 Hz, 1H), 8.01 (dd, J = 7.8, 1.4 Hz, 1H), 7.40 (d, J = 7.8 Hz, 1H), 2.69 (s, 2H), 2.52 (s, 1H), 2.10 (m, 12H).

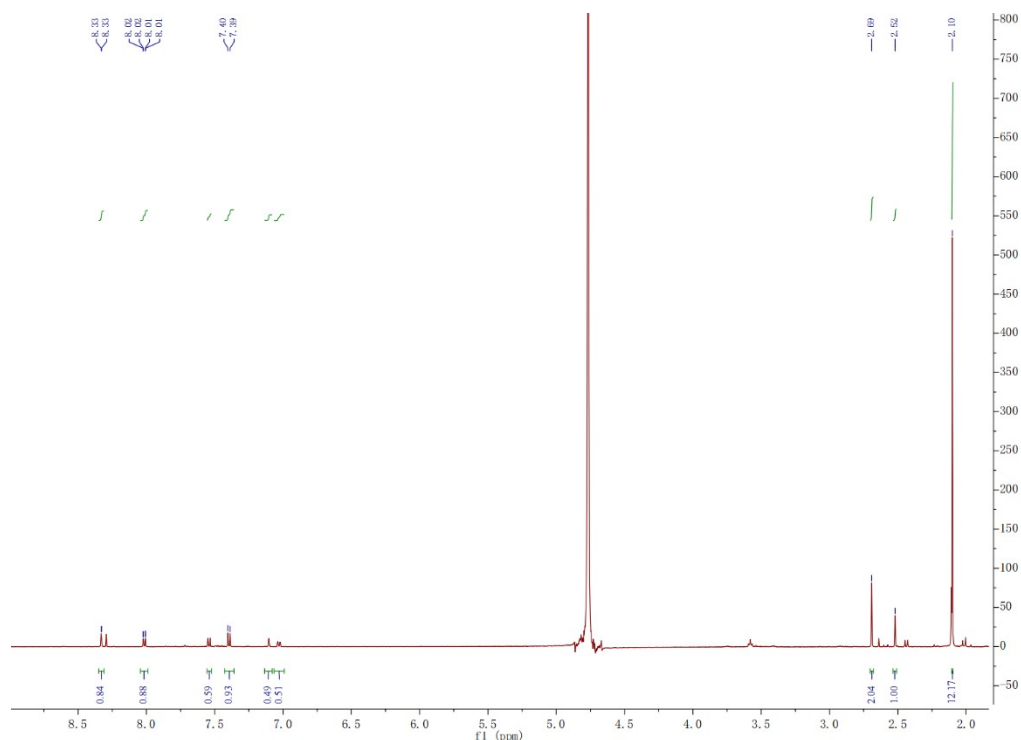
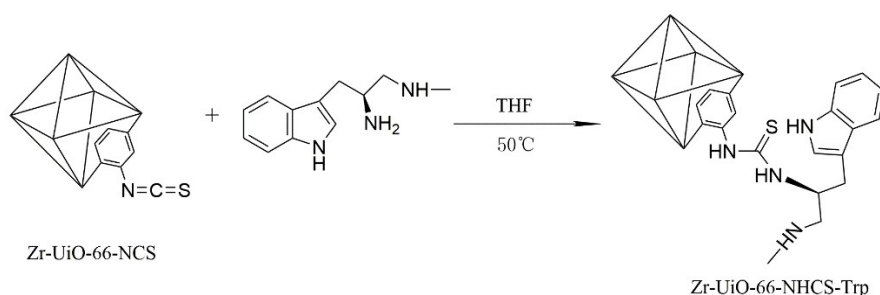


Fig. S3 Representative ^1H NMR spectrum of Zr-UiO-66-NHCS-Lte dissolved in NaOH- D_2O solution (ca. 42% modified). Unmodified Zr-UiO-66- NH_2 and functionalized linker were identified at a peak area of 6.9–8.5 ppm.

4. Synthesis of Zr-UiO-66-NHCS-Trp



In a 50 mL round-bottomed flask, 1.20 mmol of α -aminoindolylpropylmethylamine was dispersed in 20 mL of anhydrous tetrahydrofuran, and the required amount of Zr-UiO-66- NH_2 was added (1.00 mmol). The solution was stirred at 50°C for 24 h. Then it was centrifuged, and the solid was washed with THF (3×10 mL) to obtain as a fine yellow powder after drying in vacuo at 50°C .

^1H NMR (500 MHz, Chloroform- d) δ 8.33 (s, 1H), 7.64 (d, $J = 7.8$ Hz, 1H), 7.37 (d, $J = 8.1$ Hz, 1H), 7.26 (s, 1H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 7.08 – 6.99 (m, 1H), 5.78 (s, 1H), 5.18 (s, 1H), 4.40 (s, 1H), 3.31 (m, 1H), 3.19 – 3.10 (m, 1H), 2.96 (s, 1H), 2.81 (s, 3H), 2.67–2.65 (m, 3H).

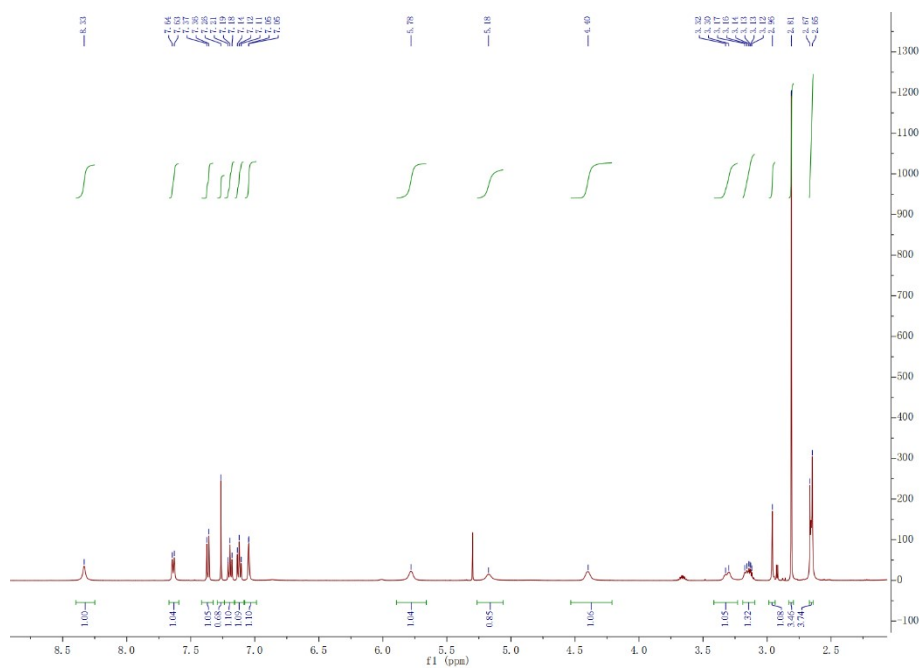
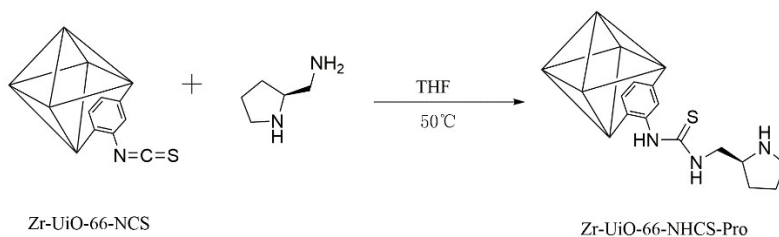


Fig. S4 Representative ^1H NMR spectrum of Zr-UiO-66-NHCS-Trp dissolved in NaOH- D_2O solution (ca. 50% modified). Unmodified Zr-UiO-66- NH_2 and functionalized linker were identified at a peak area of 7.0–8.5 ppm.

5. Synthesis of Zr-UiO-66-NHCS-Pro



In a 50 mL round-bottomed flask, 1.20 mmol of Pyrrolidine-2-methylamine was dispersed in 20 mL of anhydrous tetrahydrofuran, and the required amount of Zr-UiO-66- NH_2 was added (1.00 mmol). The solution was stirred at 50°C for 24 h. Then, it was then centrifuged, and the solid was washed with THF (3×10 mL) to obtain as a fine yellow powder after drying in vacuo at 50°C .

^1H NMR (500 MHz, Deuterium Oxide) δ 8.35 (s, 1H), 8.03 (d, $J = 7.7$ Hz, 1H), 7.43 – 7.35 (m, 1H), 2.89 – 2.77 (m, 1H), 2.69 – 2.54 (m, 2H), 2.48 – 2.35 (m, 1H), 1.94-1.93 (m, 1H), 1.77-1.70 (m, 1H), 1.60 – 1.51 (m, 3H).

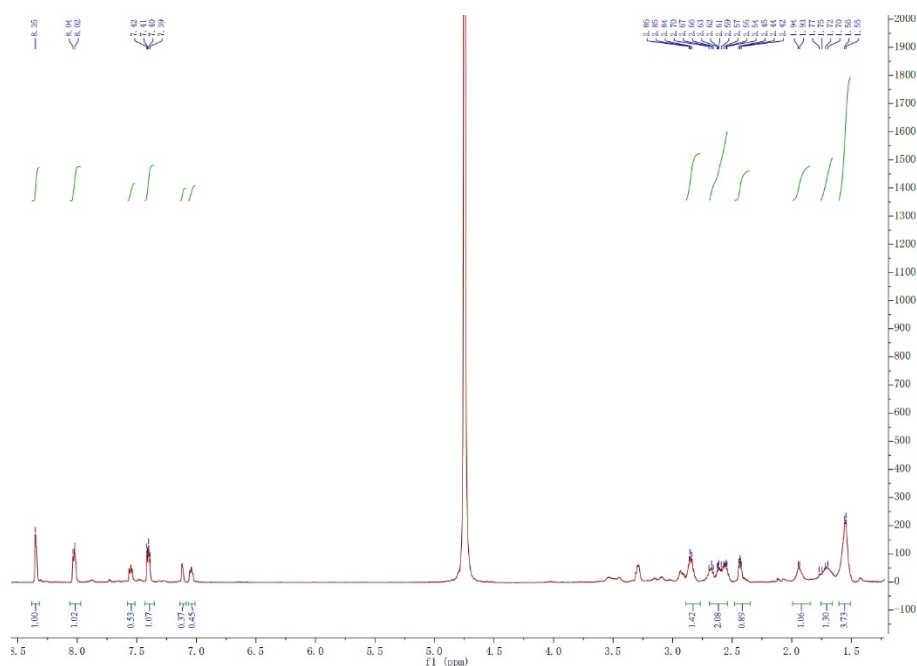
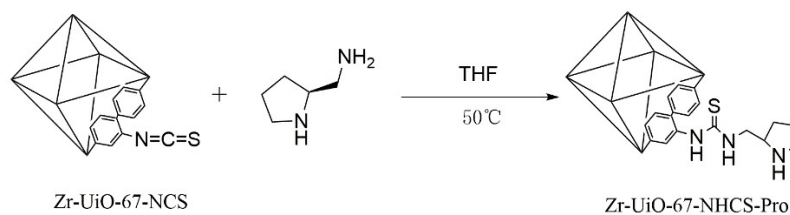


Fig. S5 Representative ^1H NMR spectrum of Zr-UiO-66-NHCS-Pro dissolved in NaOH- D_2O solution (ca. 67 % modified). Unmodified Zr-UiO-66- NH_2 and functionalized linker were identified at a peak area of 7.0–8.5 ppm.

6. Synthesis of Zr-UiO-67-NHCS-Pro



In a 50 mL round-bottomed flask, 1.20 mmol of Pyrrolidine-2-methylamine was dispersed in 20 mL of anhydrous tetrahydrofuran, and the required amount of Zr-UiO-67- NH_2 was added (1.00 mmol). The solution was stirred at 50°C for 24 h. Then, it was then centrifuged, and the solid was washed with THF (3×10 mL) to obtain as a fine yellow powder after drying in vacuo at 50°C .

^1H NMR (500 MHz, Deuterium Oxide) δ 7.74-7.72 (m, 3H), 7.52 (d, $J = 8.3$ Hz, 2H), 7.19 – 7.15 (m, 1H), 2.78-2.72 (m, 1H), 2.63 – 2.47 (m, 2H), 2.35-2.32 (m, 2H), 2.03 (s, 1H), 1.65-1.60 (m, 1H), 1.51 – 1.40 (m, 2H), 1.11 – 0.99 (m, 1H).

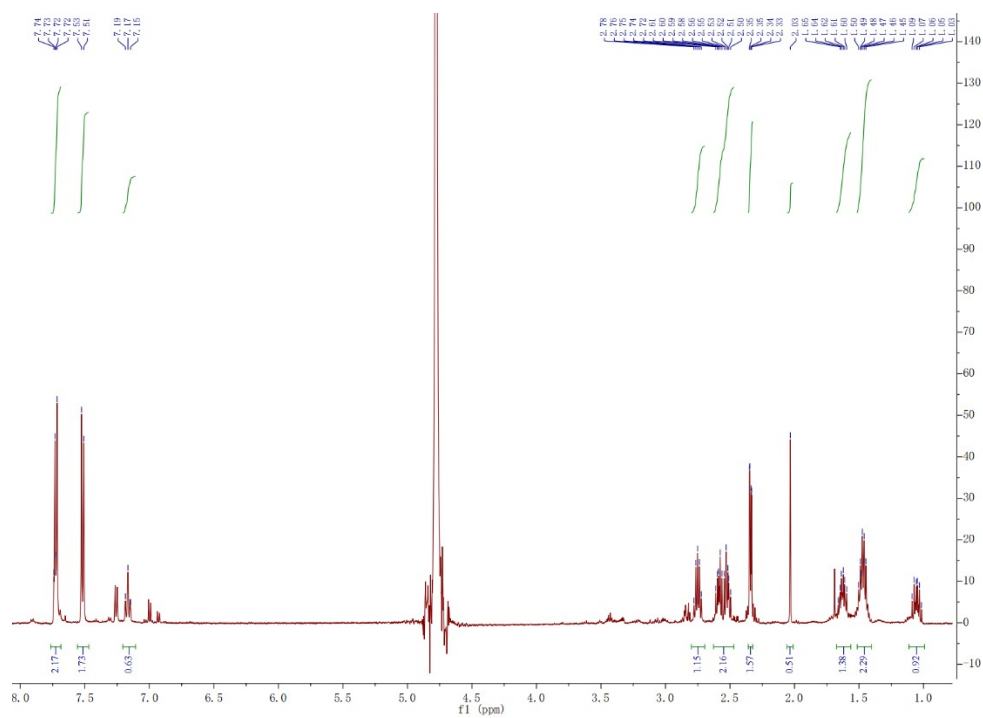


Fig. S6 Representative ^1H NMR spectrum of Zr-UiO-67-NHCS-Pro dissolved in NaOH- D_2O solution (ca. 63 % modified). Unmodified Zr-UiO-67- NH_2 and functionalized linker were identified at a peak area of 7.0–8.0 ppm.

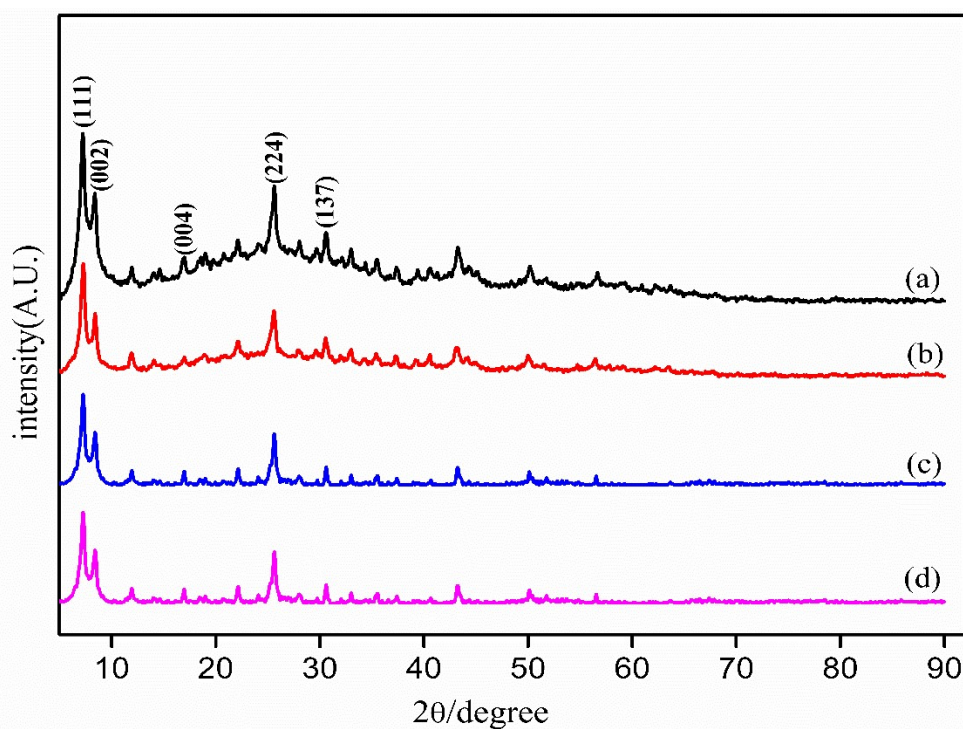


Fig. S7 PXRD patterns of different catalysts. (a) Zr-UiO-66-NHCS-Leu. (b) Zr-UiO-66-NHCS-Ile. (c) Zr-UiO-66-NHCS-Lte. (d) Zr-UiO-66-NHCS-Trp. (e) Zr-UiO-66-NHCS-Pro.

Catalysis of aldol reaction

$$ee = \frac{Area_{max} - Area_{min}}{Area_{max} + Area_{min}}$$

In a typical catalytic run, 30 mg of Zr-UiO-66-NHCS-Pro which corresponds to 0.05 mmol of proline moiety, was suspended in a solution of p-nitro-benzaldehyde (30 mg, 0.20 mmol) in acetone (1 mL). The suspension was allowed to react at room temperature and monitored by thin layer chromatography (TLC). After two days, the p-nitro-benzaldehyde was vanished from TLC. Then, the suspension was centrifuged. The solid catalyst was washed by CH₂Cl₂ (3×1 mL); the organic phases were combined and separated by TLC. Then, after concentration, a pale-yellow solid was obtained. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 5.27 (m, 1H), 2.86 (m, 2H), 2.23 (s, 3H) and it was analyzed by HPLC (AS-H column, hexane: isopropanol = 70:30, 1 mL/min, 254 nm) to obtain enantiomeric excess (ee).

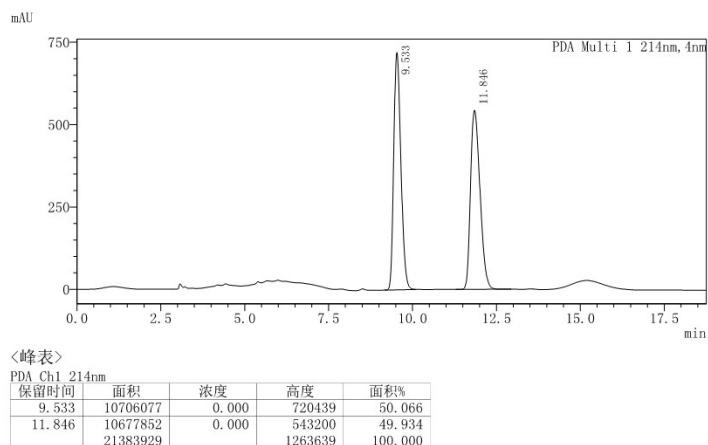


Fig. S8 HPLC of racemic modification.

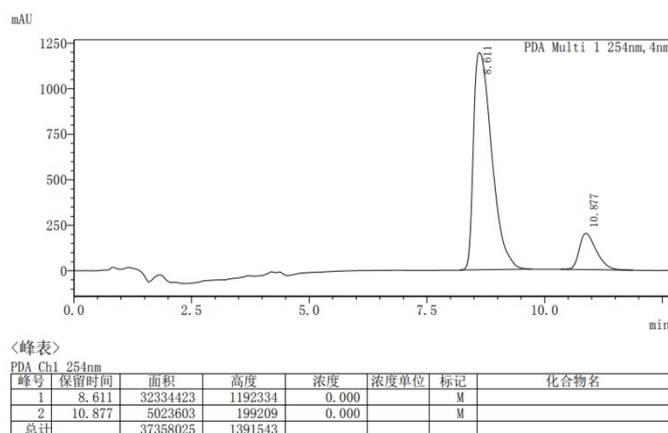


Fig. S9 Typical HPLC trace for the aldol reaction catalyzed by Zr-UiO-66-NHCS-Pro (cycle 1, 83% yield, 73% ee).

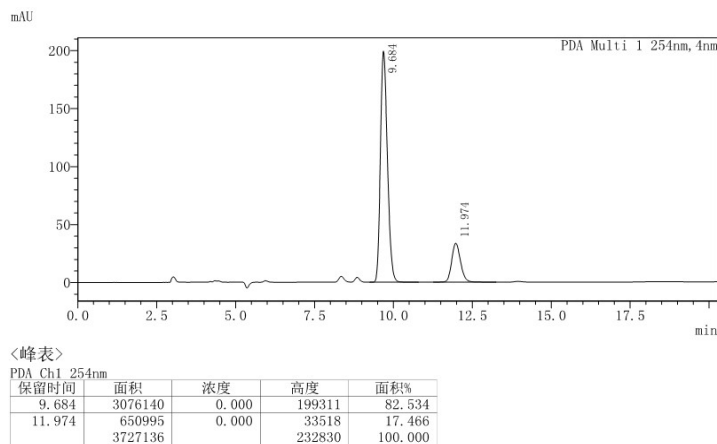
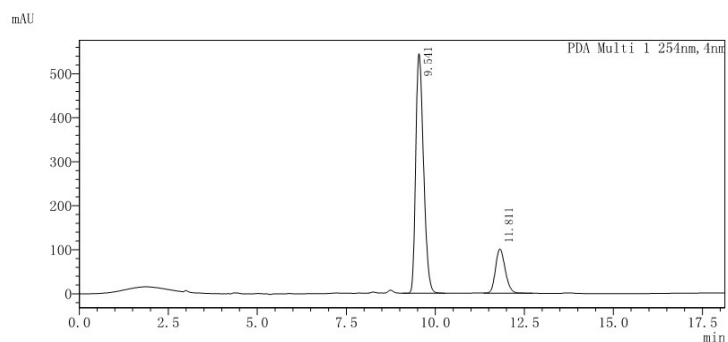


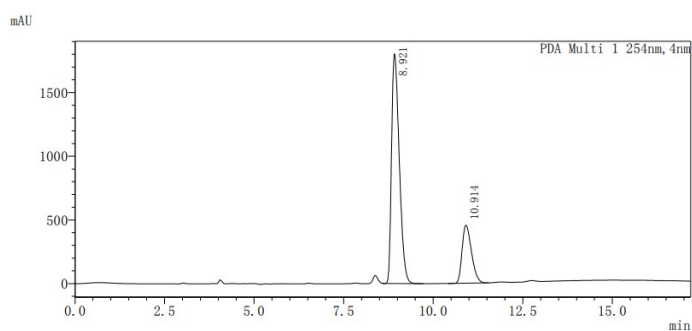
Fig. S10 Typical HPLC trace for the aldol reaction catalyzed by Zr-UiO-66-NHCS-Pro (cycle 2, acetone, 68% yield, 65% ee).



<峰表>

保留时间	面积	浓度	高度	面积%
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11.811	1896427	0.000	100246	18.546
	10225563		644696	100.000

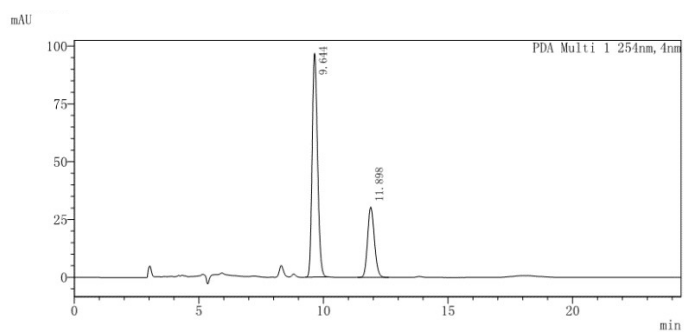
Fig. S11 Typical HPLC trace for the aldol reaction catalyzed by Zr-UiO-66-NHCS-Pro (cycle 3, 65% yield, 63% ee).



<峰表>

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.921	27021724	1800593	0.000		M	
2	10.914	8306958	455464	0.000		M	
总计		35328681	2256057				

Fig. S12 Typical HPLC trace for the aldol reaction catalyzed by Zr-UiO-66-NHCS-Pro (cycle 4, 60% yield, 54% ee).



<峰表>

保留时间	面积	浓度	高度	面积%
9.644	1452475	0.000	96797	71.677
11.898	573936	0.000	30324	28.323
	2026411		127121	100.000

Fig. S13 Typical HPLC trace for the aldol reaction catalyzed by Zr-UiO-66-NHCS-Pro (cycle 5, 55% yield, 43% ee).