Supporting Information for

“Click” Postsynthetic Modification of Metal–Organic Frameworks with Chiral Functional Adduct for Heterogeneous Asymmetric Catalysis

Wenting Zhu, Cheng He, Pengyan Wu, XiaoWu and Chunying Duan*

State Key Laboratory of Fine Chemicals, Dalian University of Technology Dalian, 116012, China. Email: cyduan@dlut.edu.cn

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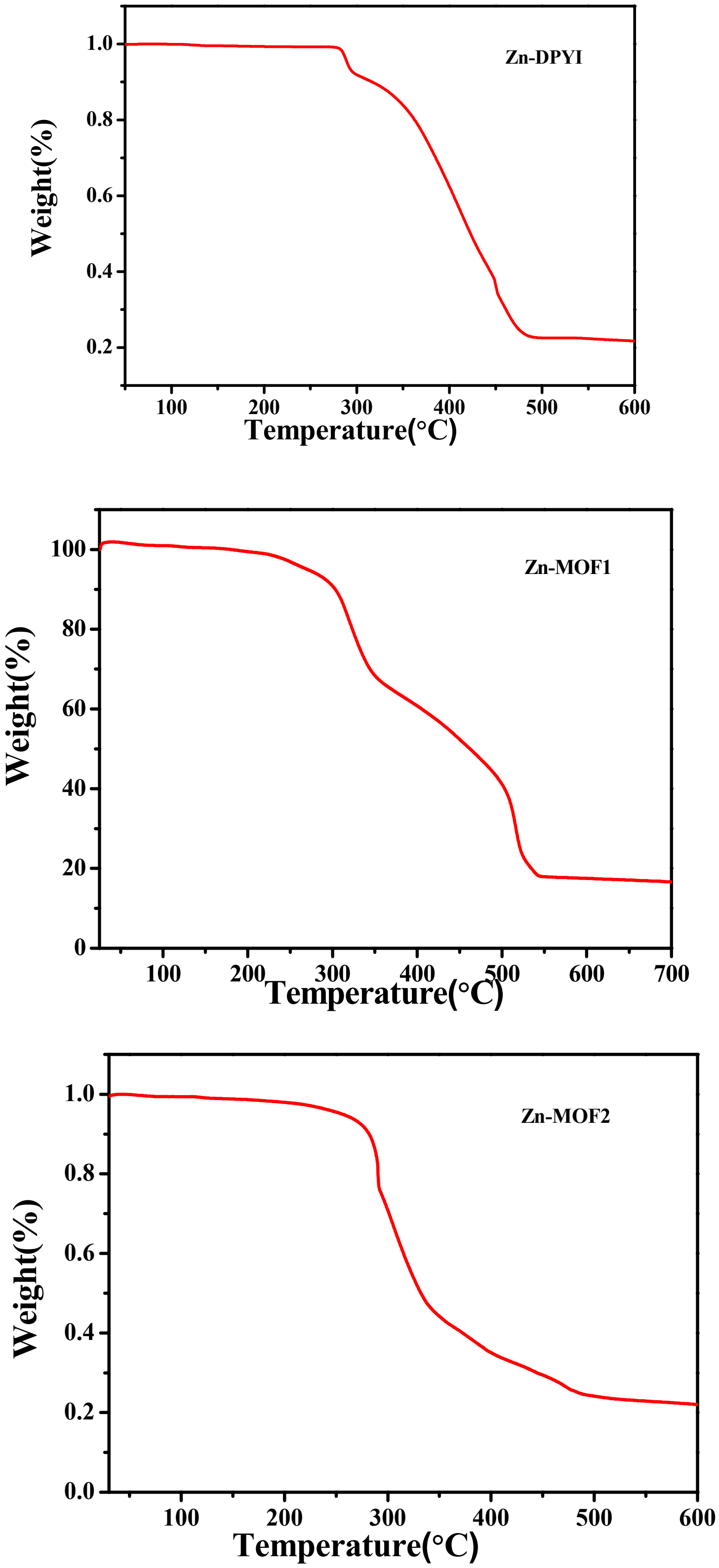
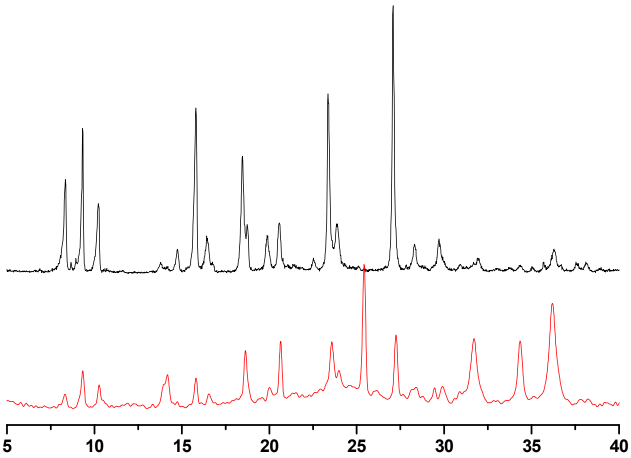
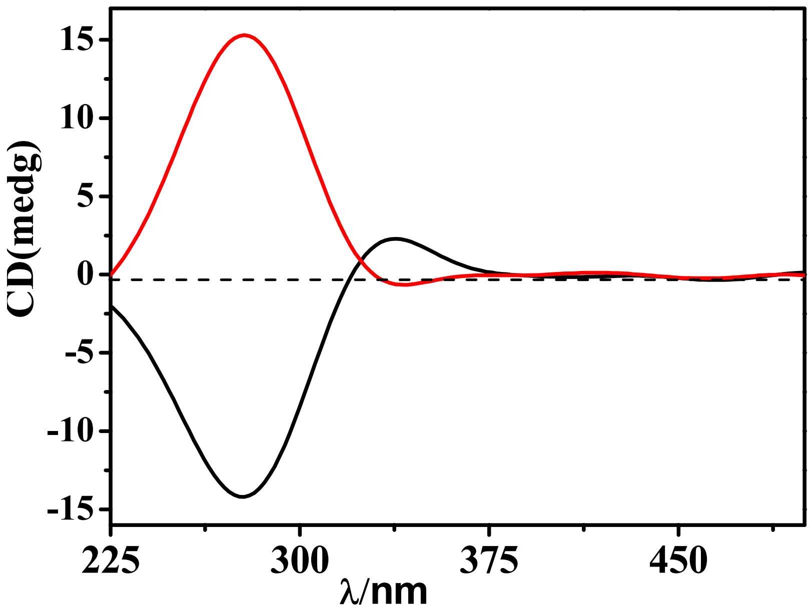


1.2 Figure S2. Powder X-ray diffraction patterns of Zn−**DPYI** (black), Zn−**MOF1**(red).



1.2 Figure S3. The solid state spectra CD of *L*-**AMP** (red) and *D*-**AMP** (balck).



2. Catalysis experiments

Typical procedure for the aldol reaction using the catalyst in heterogeneous manner:

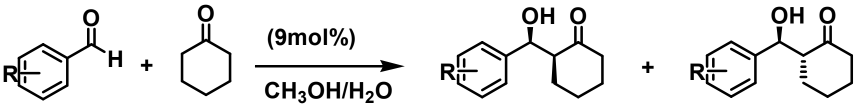
To a mixture of ketone (5mmol) and aromatic aldehyde (0.5mmol) catalyst (about 0.045mmol) was added and the resulting mixture was stirred at rt for seven days. After completion of the reaction, it was extracted with EtOAc (3×2mL). The combined organic extracts were dried over Na_2SO_4 and evaporated to dryness. Diastereoselectivity and conversion were determined by ^{1}H NMR analysis .The crude product was column chromatographed over silica gel (200–300 mesh) and Kromasil Lc-80 using SiO_2 chromatographic column to afford pure aldol product. The enantiomeric excess (ee) was determined by HPLC analysis. The catalyst was washed repeatedly with EtOAc (3×2mL), dried and reused when required.

2.1 Table S1 The conversion of heterogeneous the aldol reaction using the catalyst Zn–DPYI.

entry	Ar	**Conversion** (%)[b]
1	2-nitrophenyl	<10
2	3-nitropehnyl	12
3	4-nitrophenyl	<10

a: Reactions conditions: 25 °C for seven days in 1:1 solution of methanol and water using 0.5 mmol aldehyde and 5 mmol of cyclohexanones with the catalyst about 0.045 mmol (9% mol) and cocatalyst HAC 0.07mmol (14% mol) b: conversion based on aldehydes.

2.2 Table S2. Study on Recycling of compound Zn–MOF1 catalyst for the Aldol reactions[a]:



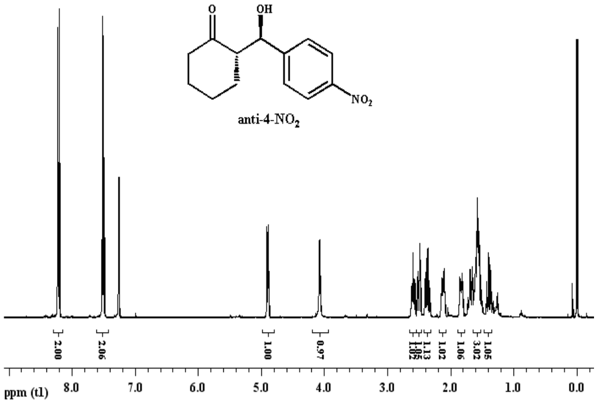
Entry	*Conversion (%)*	*ee (%)*[a]
1	*75*	*70*
2	*66*	*66*
3	*62*	*65*

Reactions conditions were same with those in Table s2.

a: Value represents the *anti* isomer.

2.3 Anti-2-(Hydroxy-(p-nitrophenyl)methyl)cyclohexan-1-one[1]

^{1}H NMR (400MHz, $CDCl_3$): δ = 8.23,8.21 (d, 2H), 7.53,7.51 (d, 2H), 4.92,4.90 (d, 1H), 4.08 (s, 1H), 2.62–2.59 (m, 1H), 2.53–2.49 (m, 1H), 2.42–2.30 (m, 1H), 2.17–2.08 (m, 1H), 1.86–1.82 (m, 1H), 1.61–1.50 (m, 3H), 1.44-1.33 (m, 1H).



Catalyzed by Zn-MOF1: Enantiomeric excess was determined by HPLC with a Chiralpak AD–H column (hexane/2-propanol=90:10), 254 nm, 1mL/min, tR1= 57.116 min (minor), tR2 = 75.654 min (major).

Peak results

Peak	Ret Time(min)	Width(min)	Area (mAU)	Area （%）
1	57.116	1.7927	2570.1	14.7683
2	75.654	2.6274	14832.7	85.2317

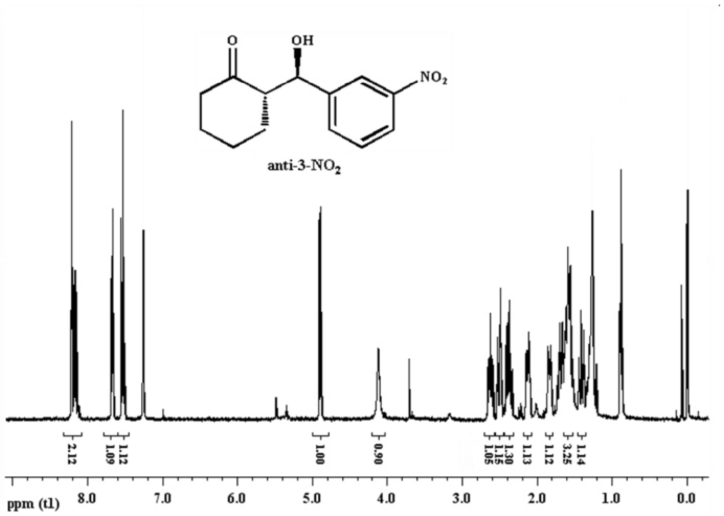
Catalyzed by Zn-MOF2: Enantiomeric excess was determined by HPLC with a Chiralpak AD–H column (hexane/2-propanol=90:10), 254 nm, 1mL/min, tR1= 51.586 min (major), tR2= 68.169 min (minor).

Peak results

Peak	Ret Time(min)	Width(min)	Area (mAU)	Area （%）
1	51.586	2.3406	187121.9	86.3812
2	68.169	2.927	29501.6	13.6188

2.4 Anti-2-(Hydroxy-(*m*-nitrophenyl)methyl)cyclohexan-1-one[2]

^{1}H NMR (400MHz, CDCl$_3$): δ = 8.21–8.15 (m, 2H), 7.68, 7.66 (d, 1H), 7.55-7.51 (m, 1H), 4.91,4.89 (d, 1H), 4.12 (s, 1H), 2.66–2.60 (m, 1H), 2.53–2.49(m, 1H), 2.42–2.33 (m, 1H), 2.15–2.08 (m, 1H), 1.86–1.79 (m, 1H), 1.66-1.52(m, 3H),1.44-1.37 (m, 1H).



Catalyzed by Zn-MOF1: Enantiomeric excess was determined by HPLC with a Chiralpak AD–H column (hexane/2-propanol=92:8), 210 nm, 1 mL/min, t_{R1} = 51.644 min (major), t_{R2} = 66.431 min (minor).

Peak results

Peak	Ret Time(min)	Width(min)	Area (mAU)	Area (%)
1	51.644	2.1233	51352.5	82.2903
2	66.431	2.2171	11051.6	17.7097

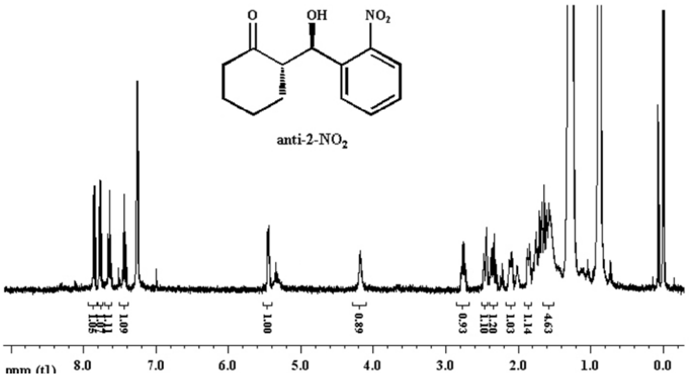
Catalyzed by Zn-MOF2: Enantiomeric excess was determined by HPLC with a Chiralpak AD–H column (hexane/2-propanol=92:8), 210 nm, 1 mL/min, t_{R1} = 55.312 min (minor), t_{R2} = 70.265 min (major).

Peak results

Peak	Ret Time(min)	Width(min)	Area (mAU)	Area (%)
1	55.312	2.1762	19942.5	17.8229
2	70.265	2.9805	91949.8	82.1771

2.5 Anti-2-(Hydroxy-(o-nitrophenyl)methyl)cyclohexan-1-one[1]

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.87, 7.84 (d, 1H), 7.79, 7.77 (d, 1H), 7.66-7.62 (m, 1H), 7.45-7.43(m, 1H), 5.46, 5.44 (d, 1H), 4.18 (s, 1H), 2.77–2.73(m, 1H), 2.48–2.44 (m, 1H), 2.40-2.30 (m, 1H), 2.14-2.06 (m, 1H), 1.90-1.81 (m, 1H), 1.66–1.52(m, 4H).



Catalyzed by Zn-MOF1: Enantiomericexcess was determined by HPLC with a Chiralpak AD–H column (hexane/ 2-propanol = 95/5), 254nm, 1mL/min, t_{R1} =80.233 min (major), t_{R2} = 85.589 min (minor).

Peak results

Peak	Ret Time(min)	Width(min)	Area (mAU)	Area (%)
1	80.233	2.7147	15652.5	73.7532
2	85.589	2.5999	5570.3	26.2468

Catalyzed by Zn-MOF2: Enantiomericexcess was determined by HPLC with a Chiralpak AD–H column (hexane/ 2-propanol = 95/5), 254nm, 1mL/min, t_{R1} =71.871 min (minor), t_{R2} = 77.743 min (major).

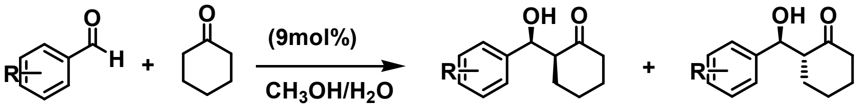
Peak results

Peak	Ret Time(min)	Width(min)	Area (mAU)	Area (%)
1	71.871	2.274	5382.1	13.6598
2	77.743	3.0048	34019	86.3402

2.6 The procedure for the aldol reaction using the catalyst in homogeneous manner:

To a mixture of ketone (5mmol) and aromatic aldehyde (0.5mmol) was added L- or D-**AMP** (0.045mmol) and cocatalyst HAC 0.07mmol (14% mol). The resulting mixture was stirred at rt for seven days. After completion of the reaction, it was evaporated to dryness and the crude product was directly column chromatographed over silica gel (200-300 mesh) to afford pure aldol product. The enantiomeric excess (e.e.) was determined by HPLC analysis.

Table S3. Study on aldol reaction catalyzed by AMP in homogeneous manner.



Entry	*R*	*Conversion (%)*		*ee (%)[a]*	
		L-AMP	*D-AMP*	*L-AMP*	*D-AMP*
1	*2-NO_2*	*17*	*12*	*<10*	*<10*
2	*3-NO_2*	*45*	*50*	*29*	*24*
3	*4-NO_2*	*40*	*41*	*26*	*34*

Reactions conditions were same with those in Table S2.

a: Value represents the *anti* isomer.

3. References:

1. Rodriguez, B.; Rantanen, T.; Bolm, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 6924-6926.
2. Wu, Y. Y.; Zhang, Y. Z.; Yu, M. L.; Zhao, G.; Wang, S. W. *Org. Lett.* **2006**, *8*, 4417-4420.