Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

Catalysis by Metal-Organic Framework: Proline and Gold functionalized MOFs for the Aldol and Three-Component Coupling Reactions

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Experimental section

1. Reagents and chemicals

2-Aminoterephthalic acid ($HO_2C-C_6H_3NH_2-CO_2H$, NH_2-BDC, >99%) and zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$, 98%) were purchased from Acros. Aldehydes (including aromatic aldehydes and aliphatic aldehydes), L-proline, and L-lactic acid were purchased from Alfa Aesar. Hexane (C_6H_{14}), diethyl amine ($(CH_3CH_2)_2NH$), and isopropanol (C_3H_8O) are HPLC reagents and were purchased from Fisher. $NaAuCl_4·2H_2O$ (99%) and AuCl (99.9%) were purchased from Aldrich. All other chemicals such as dimethylformamide (DMF), ethyl acetate ($CH_3COOCCH_3$, EtOAc), dimethyl sulfoxide ($(CH_3)_2SO$, DMSO), and acetone were purchased from Sinopharm chemical reagent Co. Ltd. All chemical materials purchased for synthesis were analytical regents (otherwise specified) and used without further purification.

2 Catalyst characterization

2.1 Optical microscopy and transmission electron microscope (TEM)

The crystal morphology of samples was observed on a DV320 optical microscope. TEM was used to determine the Au particle size and morphology of the gold functionalized CUP-1 samples. The specimens were prepared by grinding with a mortar and the resulting powder was then sonicated in ethanol to achieve good dispersion. The solution was dropped onto a holey carbon coated 300 mesh copper grid. The samples were dried and then analyzed with JEM-2010.

2.2 Powder X-ray diffraction (XRD) and single-crystal XRD

Powder XRD was performed on a Brüker D8 Advance diffractometer at 40 kV and 40 mA for CuKα, with a scan speed of 10°/min and a step size of 0.02° in 2θ. Single-crystal XRD was performed on a Smart CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at room temperature in the ω-2θ scan mode. A brown needle-shape crystal (0.15 x 0.10 x 0.10 mm) of CUP-1 was selected under polarizing optical microscope and glued on a glass fiber for the single-crystal XRD experiment. The number of collected reflections and independent reflections were 18531 and 6207, respectively, for CUP-1. The crystalline structure of CUP-1 was solved by direct methods and refined by full-matrix least squares using the SHELXTL package on the basis of F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were fixed at calculated positions and refined isotropically by using a riding mode. The final refinement including anisotropic thermal parameters of all non-hydrogen atoms converged to R1 = 0.0515 and wR2 = 0.1759R1. The theory powder XRD patterns of CUP-1 were simulated according to the program of Mercury. The crystal data were given in Table 1, and selected bond lengths and bond angles of the complexes are listed in Tables S1 and S2 of the supplementary data, respectively.

2.3 Nitrogen adsorption-desorption

N_2 adsorption-desorption measurment at liquid nitrogen temperature (–196 ^{o}C) was performed using Quantachrome. IRMOF-3, CUP-1, and their functionalized samples were outgassed at 50–60 ^{o}C for 13 h to remove loosely adsorbed species.

2.4 Inductively coupled plasma atomic emission spectroscopy

For elemental analysis, the samples were digested in a mixture of 1% HF and 1.25% H_2SO_4 (or aqua regia for gold content) and were analyzed with an inductively coupled plasma atomic emission spectroscopy (ICP-AES) Perkin Elmer Optima 7000 dv.

2.5 Thermogravimetric and differential thermal analysis (TG-DTA)

TG-DTA analyses were measured on a Mettler Toledo TGA/SDTA 851 instrument in flowing argon (50 mL min^{-1}) with a rate of 10 K min^{-1}. IRMOF-3 and L-proline functionalized IRMOF-3 and CUP-1 samples were vacuumed in a rotater at room temperature for 3 h before measurments. Specifically, gold functionalized CUP-1 samples were dried at 50 °C in an oven for 2 h before analysis.

2.6 Infrared spectrum (IR)

IR spectra (400–4000 cm^{-1}) of the IRMOF-3, CUP-1 and their modified samples were performed on a Nicolet Nexus 870 FTIR spectrometer. The sample (10 mg) was mixed with KBr (100 mg) to form a pellet for recording.

2.7 Temperature-programmed reduction (TPR)

Quantitative TPR was conducted from 25 to 600 °C on a homemade apparatus equipped with a thermal conductivity detector (TCD) with 5% H_2/Ar at a flow rate of 30 $mL \cdot min^{-1}$. Water was removed from the exit gas with a cold molecular sieve trap at –17 °C to avoid its interference with the TCD detector.

2.8 Solid state ^{13}C magic angle spinning nuclear magnetic resonance (MAS NMR)

The solid state ^{13}C MAS NMR spectra of IRMOF-3 and IRMOF-3-Pr(PM) were recorded at room temperature under MAS on a Bruker AV400 spectrometer. Before the measurements, the samples were pretreated at 150 °C for 12 h in flowing Ar to remove solvent and adsorbed water. The ^{13}C cross-polarization (CP) spectra were acquired by using a contact time of 5 ms and recycle time of 3 s. All spectra were recorded with a 7 mm Bruker BL-7 probe and at the sample spinning rate of 6 kHz. The ^{13}C spectra were referenced to tetramethylsilane at zero ppm.

2.9 Gas chromatograph-mass spectroscopy

Gas chromatograph-mass spectroscopy (GC-MS) was performed on Trace-DSQ (Thermal Finnigan) with the mass range of 1–1050 amu.

2.10 High pressure liquid chromatography

The high pressure liquid chromatography (HPLC) was performed on Agilent 1200 (UV detector: Agilent 1260; Wavelength: 220 nm).

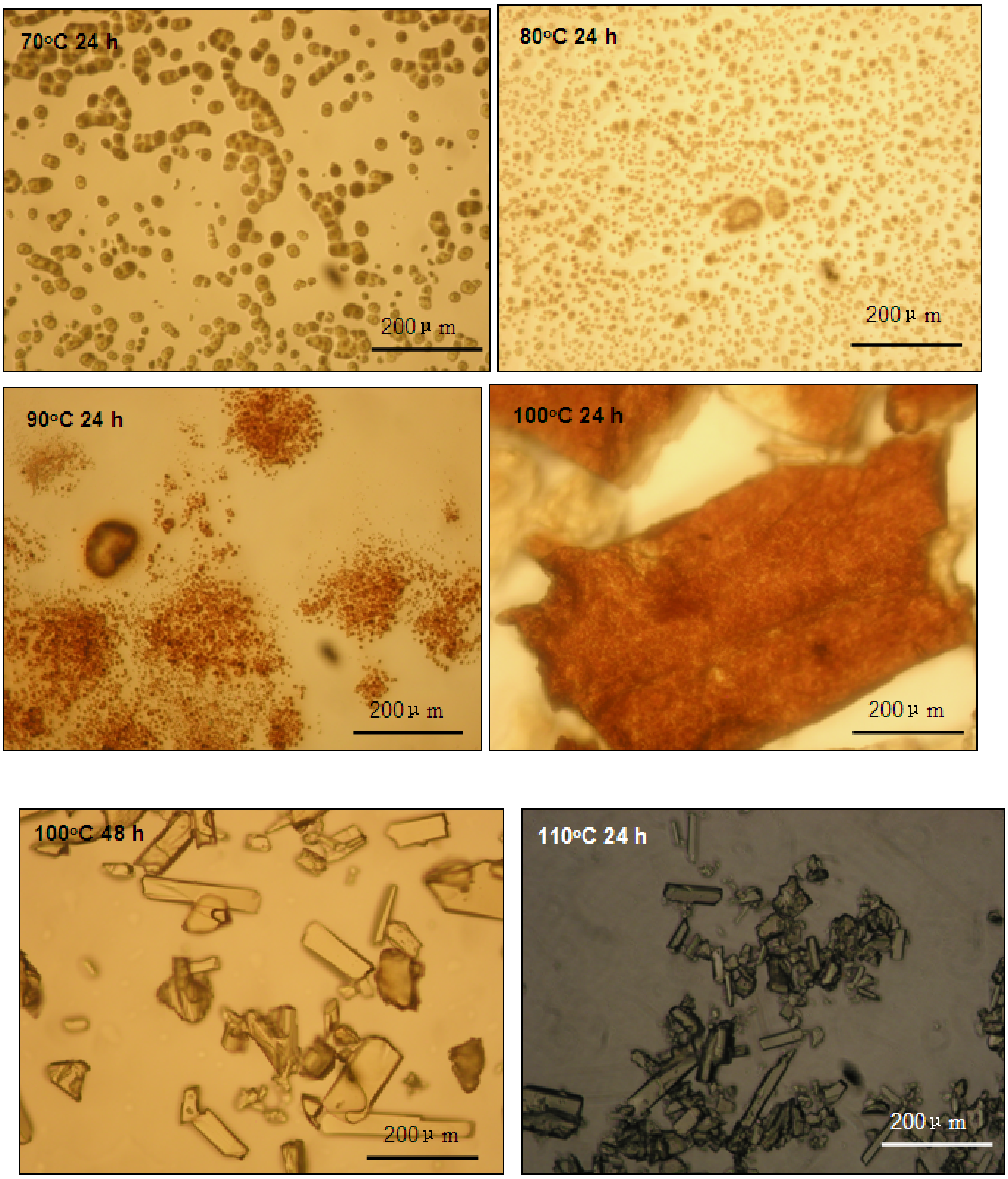
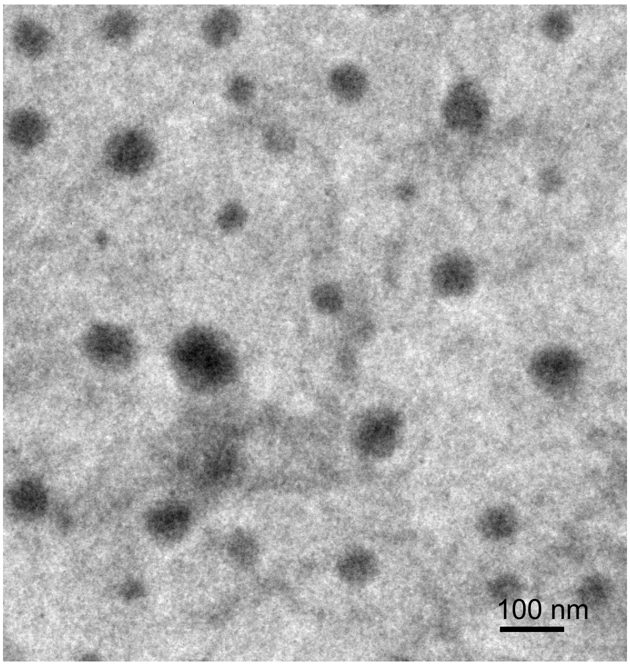


Fig. S1. Optical microscope images of the CUP-1 crystals with different crystallization temperature and time.



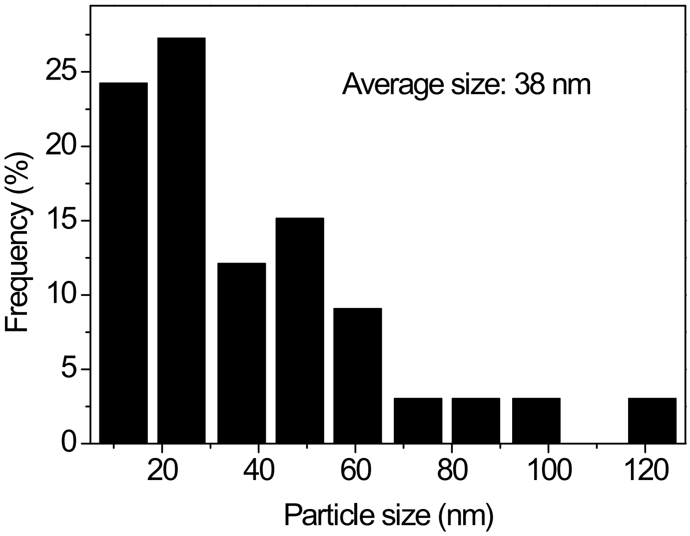


Fig. S2. TEM image and size distribution of gold in the recycled Au/CUP-1(PM) catalyst for the A^3 coupling reaction.

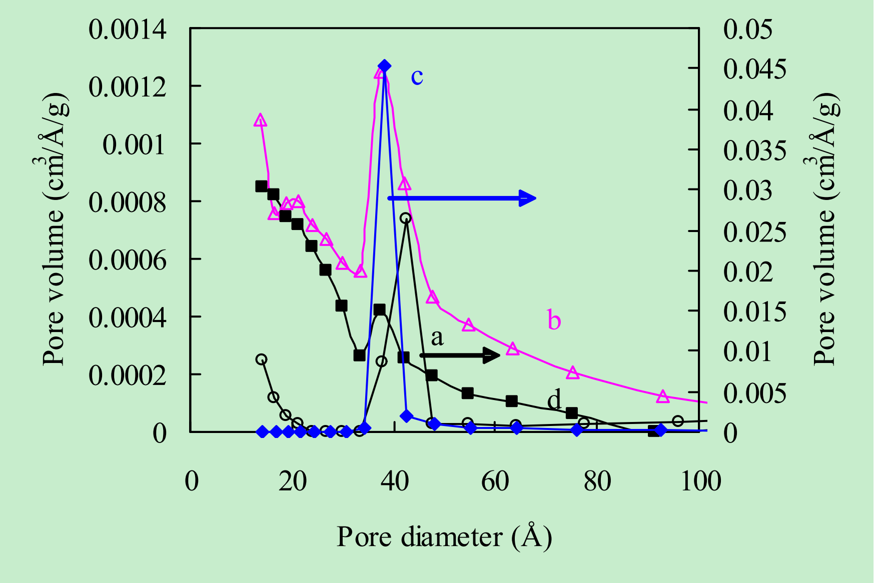


Fig. S3. Mesoporous diameter distribution determined by BJH desorption method on IRMOF-3 (a), IRMOF-3-Pr(OP) (b), IRMOF-3-Pr'(OP) (c), and CUP-1 (d) samples.

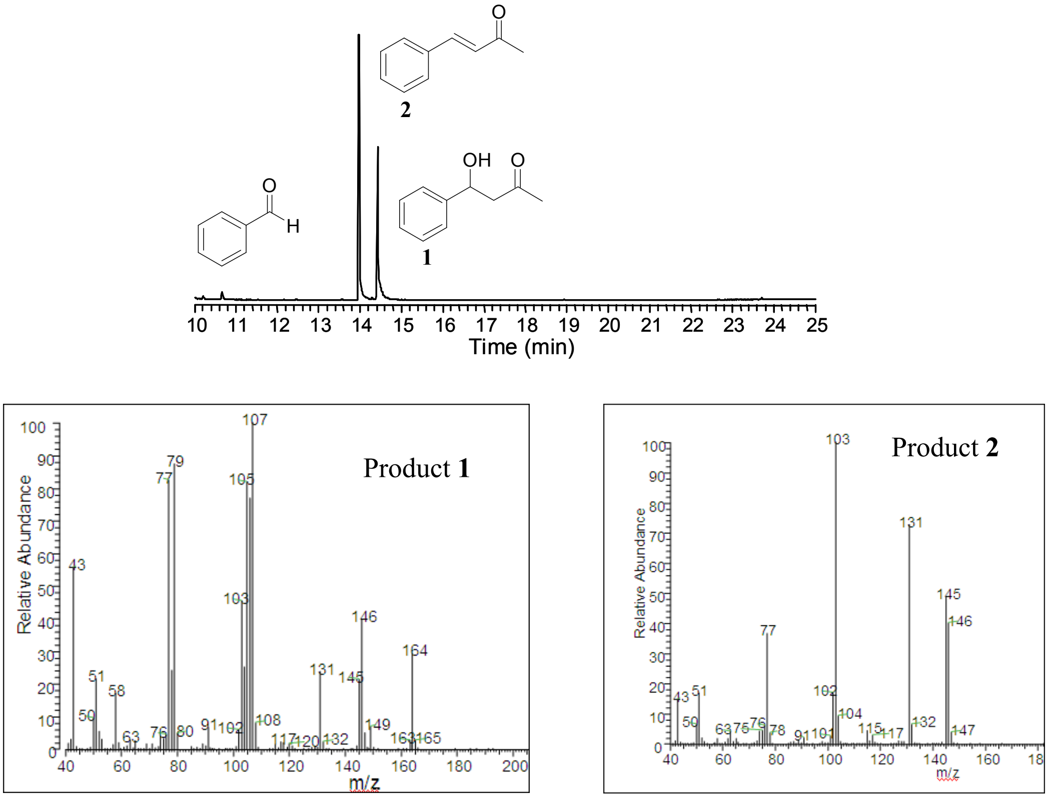


Fig. S4. GC-MS of product of **1** and **2.**

Table S1. Crystal data and structure refinement for CUP-1.

Chemical formula	Zn_2(atpt)(l-lac)(HCOO)
Empirical formula	$C_{12}H_{11}NO_9Zn_2$
Formula weight	443.96
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 10.3349(4) Å b = 11.8962(4) Å c = 20.2894(8) Å α=β=γ=90°
Volume	2494.50(16) $Å^3$
Z, Calculated density	4, 1.182 Mg/m^3
Absorption coefficient	1.953 mm^{-1}
F(000)	888
Crystal size	0.15 x 0.10 x 0.10 mm
Theta range for data collection	1.98-28.33°
Limiting indices	$-13 \le h \le 12$, $-11 \le k \le 15$, $-26 \le l \le 27$
Reflections collected / unique	18531 / 6207 R(int) = 0.0420
Completeness to theta = 28.33	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6207 / 0 / 222
Goodness-of-fit on F^2	1.062

Final R indices I>2σ(I)	R1 = 0.0515, wR2 = 0.1759
R indices (all data)	R1 = 0.0658, wR2 = 0.1879
Absolute structure parameter	0.07(3)
Largest diff. peak and hole	1.131 and -0.715 e.Å^{-3}

Table S2. Selected bond Lengths (Å) for Complexes Zn_2(atpt)(l-lac)(HCOO).

Bond	Length (Å)	Bond	Length (Å)
Zn(1)-O(1)	1.969（3）	Zn(2)-O(7)#1	1.976(5)
Zn(1)-O(3)	1.980(5)	Zn(2)-O(2)	2.136(4)
Zn(1)-O(8)#1	1.993(4)	Zn(2)-O(6)	2.145(5)
Zn(1)-O(4)	2.022(4)	O(7)-Zn(2)#3	1.976(5)
Zn(1)-O(2)	2.138(4)	O(8)-Zn(1)#3	1.993(4)
Zn(2)-O(1)#2	1.932(3)	O(1)-Zn(2)#4	1.932(3)
Zn(2)-O(5)	1.966(4)		

Table S3. Selected bond angles (°) for Zn_2(atpt)(l-lac)(HCOO).

Bond	Angles (°)	Bond	Angles (°)
O(1)-Zn(1)-O(3)	129.3(2)	O(1)#2-Zn(2)-O(6)	95.47(18)
O(1)-Zn(1)-O(8)#1	113.0(2)	O(5)-Zn(2)-O(6)	87.3(2)
O(3)-Zn(1)-O(8)#1	116.4(2)	O(7)#1-Zn(2)-O(6)	85.8(2)
O(1)-Zn(1)-O(4)	102.09(16)	O(2)-Zn(2)-O(6)	168.93(18)
O(3)-Zn(1)-O(4)	84.7(2)	C(8)-O(3)-Zn(1)	137.0(4)
O(8)#1-Zn(1)-O(4)	95.1(2)	C(8)-O(5)-Zn(2)	132.6(4)
O(1)-Zn(1)-O(2)	79.34(14)	C(12)-O(6)-Zn(2)	136.0(8)
O(3)-Zn(1)-O(2)	88.02(18)	C(1)-O(7)-Zn(2)#3	135.7(4)
O(8)#1-Zn(1)-O(2)	91.99(18)	C(1)-O(8)-Zn(1)#3	131.5(4)
O(4)-Zn(1)-O(2)	171.5(2)	C(10)-O(1)-Zn(2)#4	118.7(3)
O(1)#2-Zn(2)-O(5)	117.6(2)	C(10)-O(1)-Zn(1)	114.6(3)
O(1)#2-Zn(2)-O(7)#1	116.6(2)	Zn(2)#4-O(1)-Zn(1)	125.69(17)
O(5)-Zn(2)-O(7)#1	125.7(2)	C(9)-O(2)-Zn(2)	134.8(4)
O(1)#2-Zn(2)-O(2)	95.29(14)	C(9)-O(2)-Zn(1)	113.2(3)
O(5)-Zn(2)-O(2)	90.03(19)	Zn(2)-O(2)-Zn(1)	106.36(16)
O(7)#1-Zn(2)-O(2)	87.08(19)	C(9)#4-O(4)-Zn(1)	131.4(4)

Table S4. The Aldol reaction of benzaldehyde and acetone catalyzed by IRMOF-3-Pr(OP) at 60 °C for 72 h.[a]

Entry	Solvents [b]	Benzaldehyde:acetone molar ratio	Conv. (%)	S_1 (%)[c]
1	neat	1:10	57.6	12.8
2	DMF	1:2	30.1	15.5
3	DMF	1:10	60.0	22.3
4	DMF	1:20	54.5	18.5
5	DMSO	1:10	58.2	44.1
6	DMSO	1:20	52.8	78.7

[a] Reaction condition: IRMOF-3-Pr(OP): 20 mg.

[b] Solvent: 0.5 g.

[c] The selectivity of β-hydroxy carbonyl compound (**1**).

Entry 1 in Table 3. L-Proline catalysed benzaldehyde and acetone at 40 ^{o}C with 12 % ee.

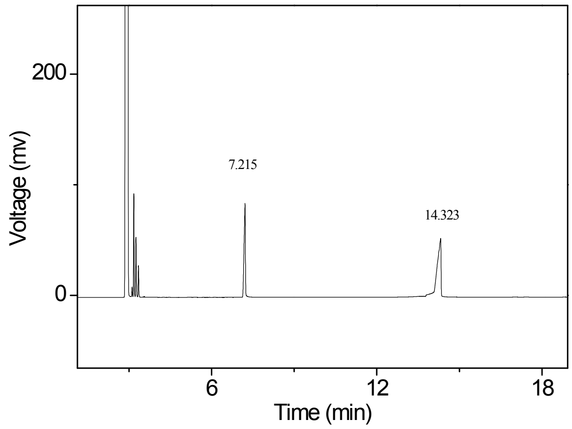


Figure 1A GC analysis of mixture.

Table 1A Result of GC analysis

RT (min.)	Substance
7.215	benzaldehyde
14.323	β-hydroxy carbonyl compound

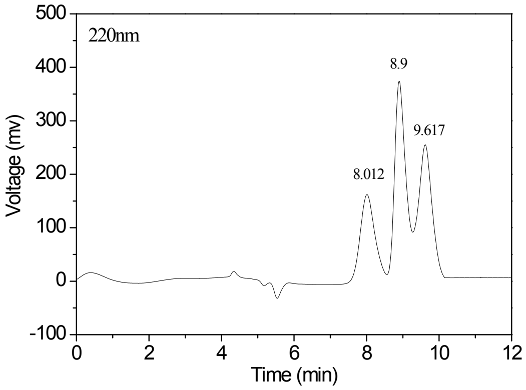


Figure 1B HPLC analysis of mixture.

Table 1B Result of HPLC analysis

Substance	RT (min)	Area (s*mv)	ee%
benzaldehyde	8.102	4786.1	
β-hydroxy carbonyl compound (enantiomer)	8.9	8704.8	12
β-hydroxy carbonyl compound (enantiomer)	9.617	6780.8	

Entry 7 in Table 3. Aldol reaction of benzaldehyde and acetone at RT on IRMOF-3-Pr(OP) with 98% ee.

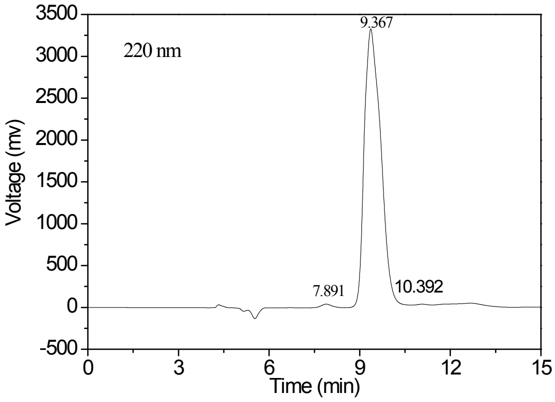


Figure 2 HPLC analysis of mixture

Table 2 Result of HPLC analysis

Substance	RT (min)	Area (s*mv)	ee%
benzaldehyde	7.891	3696	
β-hydroxy carbonyl compound (enantiomer)	9.367	124800	98
β-hydroxy carbonyl compound (enantiomer)	10.392	881	

Entry 8 in Table 3. Aldol reaction of benzaldehyde and acetone on IRMOF-3-Pr(OP) at 40 ^{o}C with 73% ee.

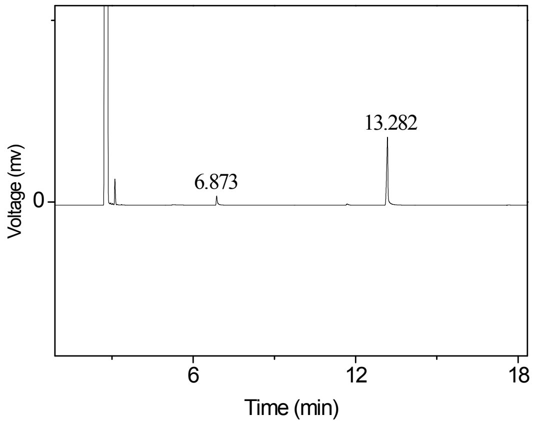


Figure 3A GC analysis of mixture.

Table 3A Result of GC analysis

RT (min)	Substance
6.873	benzaldehyde
13.282	β-hydroxy carbonyl compound

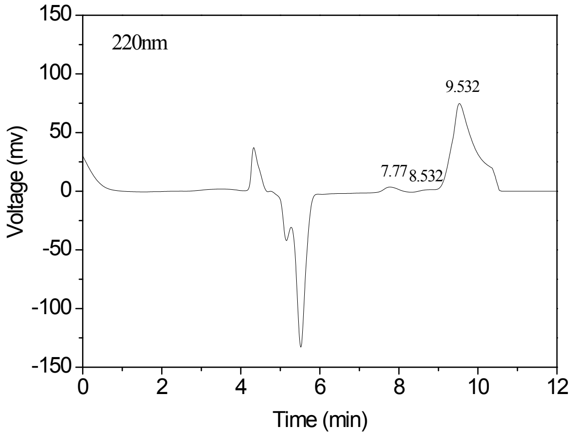


Figure 3B HPLC analysis of mixture.

Table 3B Result of HPLC analysis

Substance	RT (min)	Area (s*mv)	ee%
benzaldehyde	7.77	143	
β-hydroxy carbonyl compound (enantiomer)	8.532	130.0	73.3
β-hydroxy carbonyl compound (enantiomer)	9.532	845.1	

Entry 9 in Table 3. Aldol reaction of benzaldehyde and acetone on IRMOF-3-Pr(OP) at 60 °C with 10% ee.

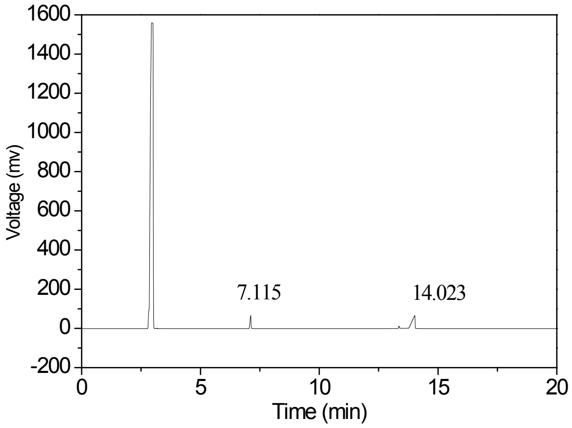


Figure 4A GC analysis of mixture.

Table 4A Result of GC analysis

RT (min)	Substance
7.115	benzaldehyde
14.023	β-hydroxy carbonyl compound

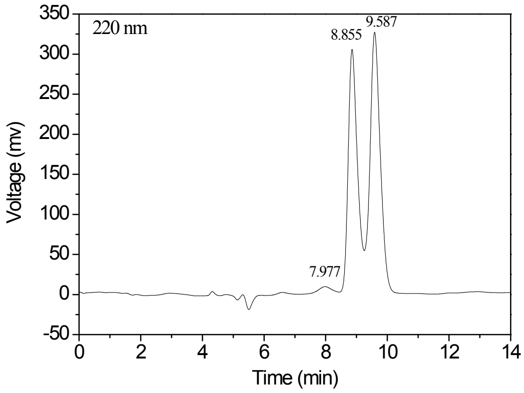


Figure 4B HPLC analysis of mixture.

Table 4B Result of HPLC analysis

Substance	RT (min)	Area (s*mv)	ee%
benzaldehyde	7.977	332	
β-hydroxy carbonyl compound (enantiomer)	8.855	6136	10
β-hydroxy carbonyl compound (enantiomer)	9.587	7532	

Entry 10 in Table 3. Aldol reaction of 4-nitrobenzaldehyde and acetone on IRMOF-3-Pr(OP) at 60 °C with 89% ee.

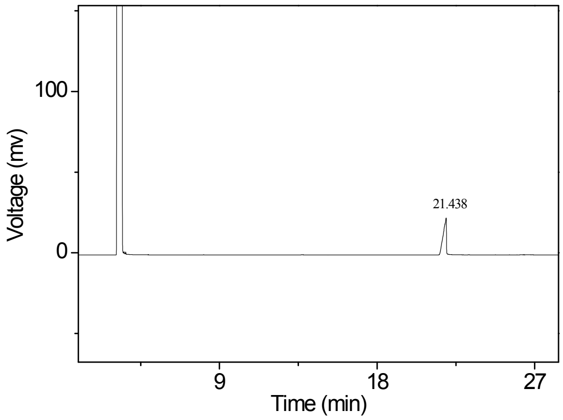


Figure 5A GC analysis of mixture.

Table 5A Result of GC analysis

RT (min)	Substance
21.438	β-hydroxy carbonyl compound

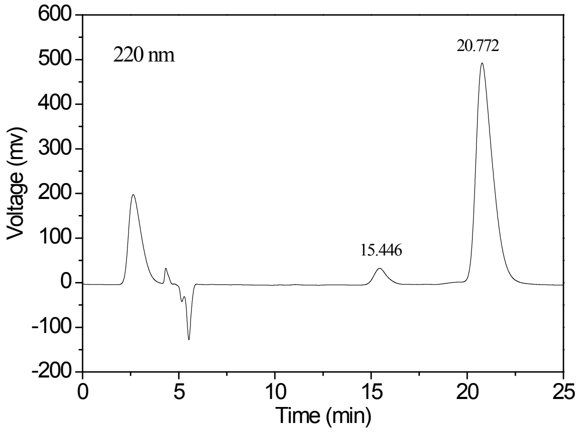


Figure 5B HPLC analysis of mixture.

Table 5B Result of HPLC analysis

Substance	RT (min)	Area (s*mv)	ee%
β-hydroxy carbonyl compound (enantiomer)	15.446	1757	89
β-hydroxy carbonyl compound (enantiomer)	20.772	309115	

Entry 11 in Table 3. Aldol reaction of 3-chlorobenzaldehyde and acetone on IRMOF-3-Pr(OP) at 60 °C with 88% ee.

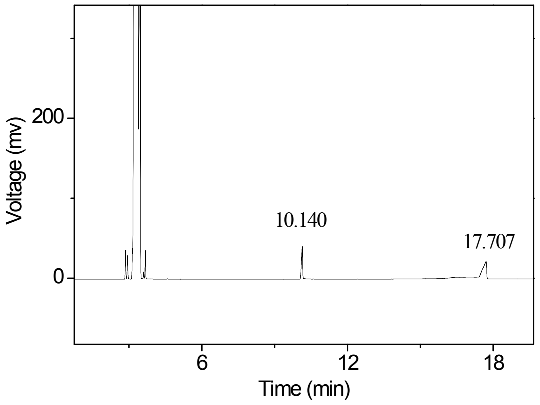


Figure 6A GC analysis of mixture.

Table 6A Result of GC analysis

RT (min)	Substance
10.140	3-chlorobenzaldehyde
16.640	α,β-unsaturated carbonyl compound
17.707	β-hydroxy carbonyl compound

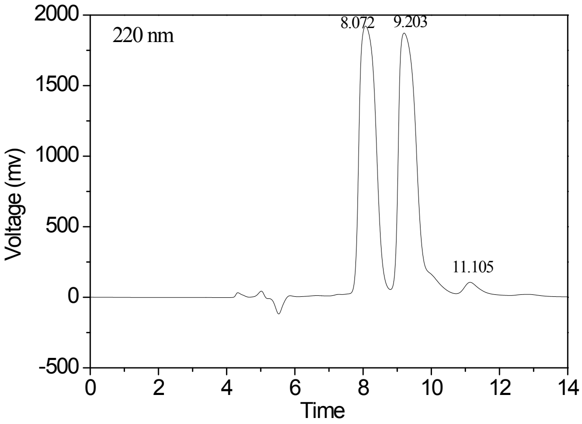


Figure 6B HPLC analysis of mixture.

Table 6B Result of HPLC analysis

Substance	RT (min)	Area (s*mv)	ee%
3-chlorobenzaldehyde	8.072	62793	
β-hydroxy carbonyl compound (enantiomer)	9.203	62521	88
β-hydroxy carbonyl compound (enantiomer)	11.105	3884	

Entry 12 in Table 3. Aldol reaction of n-octaldehyde and acetone on IRMOF-3-Pr(OP) at 60 °C with 28% ee.

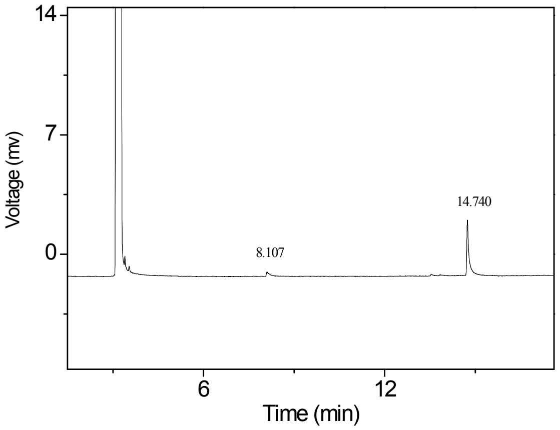


Figure 7A GC analysis of mixture.

Table 7A Result of GC analysis

RT (min)	Substance
8.107	n-octaldehyde
14.740	β-hydroxy carbonyl compound

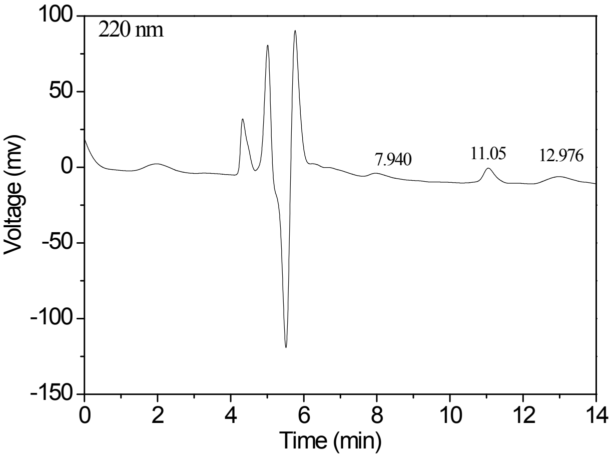


Figure 7B HPLC analysis of mixture.

Table 7B Result of HPLC analysis

Substance	RT (min)	Area (s*mv)	ee%
n-octaldehyde	7.940	132	
β-hydroxy carbonyl compound (enantiomer)	11.05	232	28
β-hydroxy carbonyl compound (enantiomer)	12.976	411	

Entry 13 in Table 3. Aldol reaction of cyclohexanecarboxaldehyde and acetone on IRMOF-3-Pr(OP) at 60 °C with 52% ee.

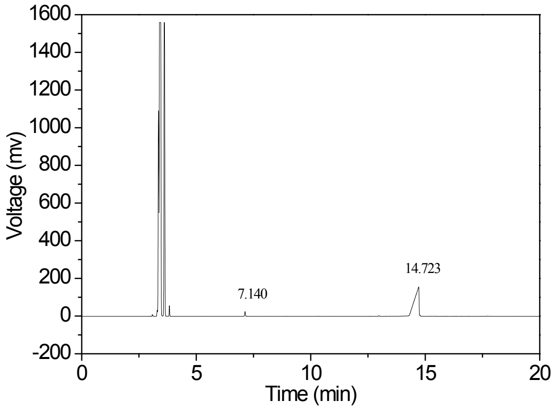


Figure 8A GC analysis of mixture.

Table 8A Result of GC analysis

RT (min)	Substance
7.140	cyclohexanecarboxaldehyde
14.723	β-hydroxy carbonyl compound

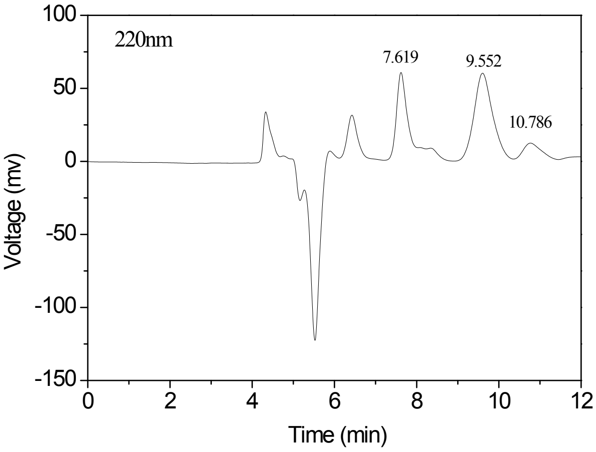


Figure 8B HPLC analysis of mixture.

Table 8B Result of HPLC analysis

Substance	RT (min)	Area (s*mv)	ee%
cyclohexanecarboxaldehyde	7.619	841	
β-hydroxy carbonyl compound (enantiomer)	9.552	1112	52
β-hydroxy carbonyl compound (enantiomer)	10.786	353	

Entry 14 in Table 3. Aldol reaction of benzaldehyde and acetone on IRMOF-3-Pr(PM) at RT with 93% ee.

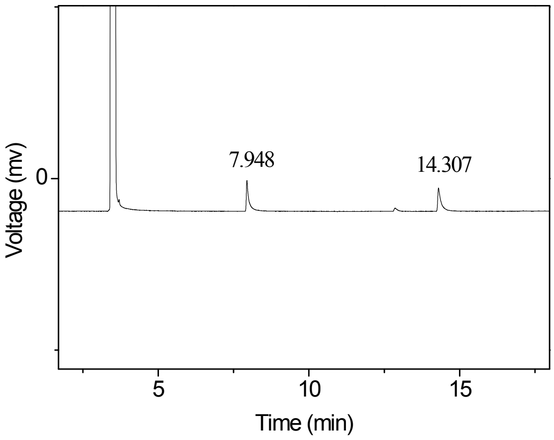


Figure 9A GC analysis of mixture.

Table 9A Result of GC analysis

RT (min)	Substance
7.948	benzaldehyde
14.307	β-hydroxy carbonyl compound

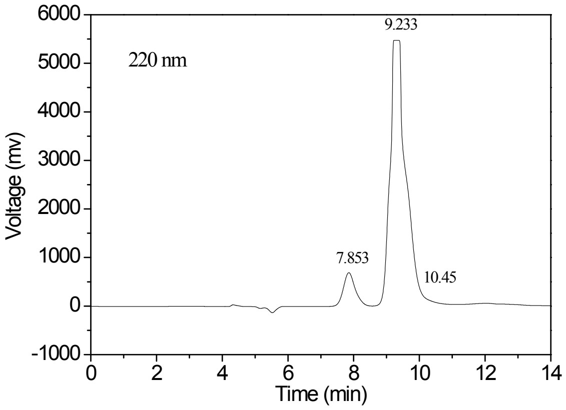


Figure 9B HPLC analysis of mixture.

Table 9B Result of HPLC analysis

Substance	RT (min)	Area (s*mv)	ee%
benzaldehyde	7.853	18757	
β-hydroxy carbonyl compound (enantiomer)	9.233	191298	93
β-hydroxy carbonyl compound (enantiomer)	10.45	6657	

Entry 15 in Table 3. Aldol reaction of benzaldehyde and acetone on IRMOF-3-Pr(PM) at 40 °C with 33% ee.

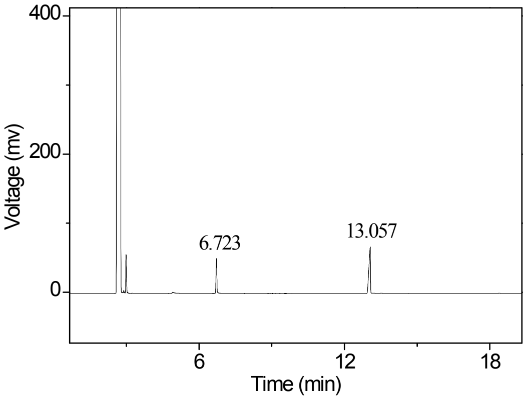


Figure 10A GC analysis of mixture.

Table 10A Result of GC analysis

RT (min)	Substance
6.723	benzaldehyde
13.057	β-hydroxy carbonyl compound

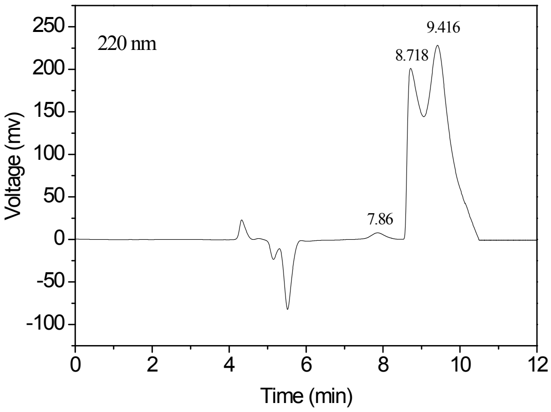


Figure 10B HPLC analysis of mixture.

Table 10B Result of HPLC analysis

Substance	RT (min)	Area	ee%
benzaldehyde	7.86	234	
β-hydroxy carbonyl compound (enantiomer)	8.718	4687	33
β-hydroxy carbonyl compound (enantiomer)	9.416	9303	

The A^3 coupling reactions

Entry 4 in Table 4

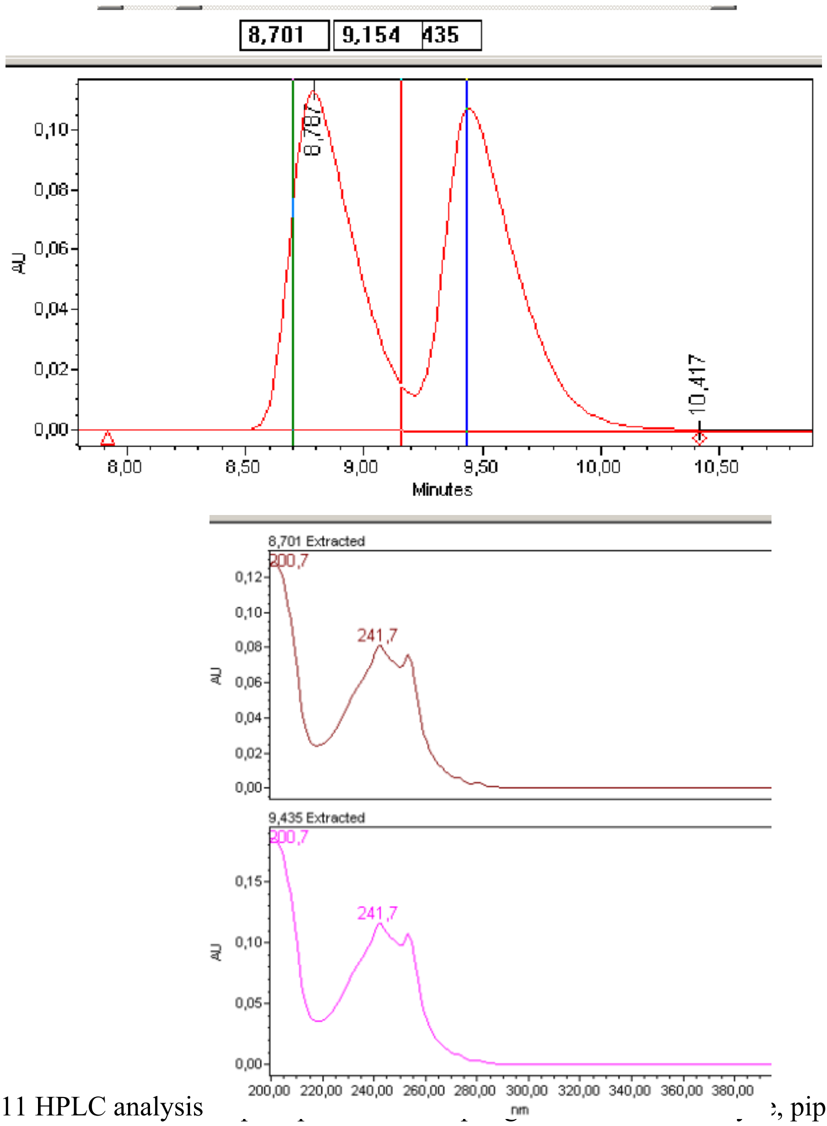


Figure 11 HPLC analysis , piperidine, and phenylacetylene over Au/CUP-1(PM) at 100 °C

Table 11 Result of HPLC analysis

Substance	RT (min)	Area (mv*s)	ee%
N-(1,3-diphenyl-2-propynyl)piperidine (enantiomer)	8.701	2520	6
N-(1,3-diphenyl-2-propynyl)piperidine (enantiomer)	9.435	2240	

Entry 5 in Table 4

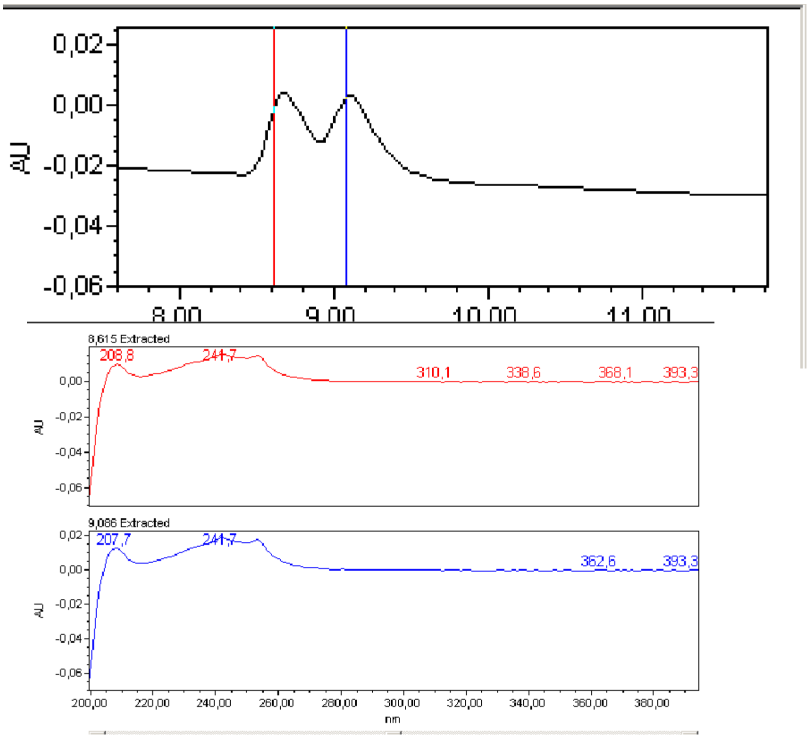


Figure 12 HPLC analysis of pure product of coupling reaction benzaldehyde, piperidine, and phenylacetylene over Au/CUP-1(PM) at 120 °C

Table 12 Result of HPLC analysis

Substance	RT (min)	Area (mv*s)	ee%
N-(1,3-diphenyl-2-propynyl)piperidine (enantiomer)	8.715	375	4
N-(1,3-diphenyl-2-propynyl)piperidine (enantiomer)	9.256	345	