Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Cellulose-supported hyper-crosslinked L-tryptophan as an efficient chiral catalyst support for improved catalytic performance

Yaodong Wang,[1] Yudan Wang,[1]Lijia Liu,[1,2*] Kexiao Sang,[1] Chunhong Zhang,[1,2] Guoxing Yang[3*]*

[1]Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin, 150001, China.

[2] Yantai Research Institute and Graduate School of Harbin Engineering University, Yantai, 264006, China;

[3]Daqing Petrochemical Research Center, Petrochemical Research Institute, PetroChina Corporation, Daqing 163000, China;

E-mail: yudanwang@hrbeu.edu.cn (Y. Wang); liulijia@hrbeu.edu.cn (L. Liu); ygx459@petrochina.com.cn (G. Yang)

Content

(B), HCP-SBA-15-(L)Trp (C), HCP-Zeolite-(L)Trp (D), HCP-PS-(L)Trp (E), HCP-Wood-(L)Trp (F) and HCP-cellulose-(L)Trp (G) (Co)**.**

Figure S9 EDS images of HCP-Silica-NH_2-(L)Trp (A), HCP-PS-(L)Trp (B) and HCP-cellulose-(L)Trp (C) (Ru)**.**

Figure S10 XPS of HCP-Cellulose-(L)Trp-Ru (A) and HCP-Cellulose-(L)Trp-Ru (5 cycles) (B)

Table S9 ICP-MS test data of hot filtration experiments

Table S10 ICP-MS test data of carrier

Table S11 Comparison with other heterogeneous catalysts

S2 High performance liquid chromatography of the product

S1 Experimental

S1.1 Chemicals and agents

Unless otherwise stated, all reagents were purchased from commercial sources and used without purification. All solvents used in the reactions were of analytical grade, carefully dried, and distilled before use. 4,4'-bis(chloromethyl)-1,1'-biphenyl, L-tryptophan, Dichloro(1,5-cyclooctadiene)ruthenium(II), anhydrous ferric chloride ($FeCl_3$), nitromethane and Dichlorobis(triphenylphosphine)cobalt(II) were purchased from Aladdin Chemical Co. Ltd. (Shanghai, China). 4-nitrobenzaldehyde, 4-bromo-2-hydroxybenzaldehyde, 4-methylbenzaldehyde, 4-bromobenzaldehyde, protocatechualdehyde, benzaldehyde and vanillin were purchased from Sahn Chemical Technology Co., Ltd. Amino silica gel and carboxyl silica gel (particle size:

3-10 μm, CAS: 112945-52-5) were purchased from Aladdin Chemical Co. Ltd. Molecular sieves (SBA-15), wood (made from fir) was purchased online. Polystyrene (Type：universality II, CAS: 9003-53-6) and zeolite (particle size < 10 μm, CAS: 1318-02-1) were purchased from Aladdin Chemical Co. Ltd.

S 1.2 Characterization

The 1H NMR spectra (500 MHz) were recorded using a Bruker AVANCE III-500 instrument at room temperature. IR spectra were obtained with a Perkin-Elmer FTIR-100 spectrophotometer. The characteristics were recorded using scanning electron microscope (Thermoscientific ApreoS LoVac, USA, SEM). Element content was analyzed using X-ray photoelectron spectroscopy (Thermo ESCALAB 250XI, USA, XPS). The morphology of the matrix in the catalyst was characterized by high-resolution transmission electron microscopy (Talos F200X G2, USA, HRTEM). The absolute configuration of products was determined by JASCO PU-2089 high performance liquid chromatograph (HPLC) system equipped with UV−vis (JASCO-UV-2070), circular dichroism (JASCO-CD-2095) detectors and a column of OD-H using a solution of hexane/2-propanol as eluent at a flow rate of 1.0 mL min^{-1}. A solution of product (1.00 mg mL^{-1}) was injected into the chromatographic system through an intelligent sampler (JASCO AS- 2055).

S 1.3 Preparation of cellulose

After vacuum for 20 min, the cut wood block (0.8 cm*0.8 cm) was placed in a round-bottom flask containing 400 mL NaClO solution (4 wt%), and then the solution pH was adjusted to 4.6 with HAc, followed by sonicated for 40 min. Delignification

was performed in an oil bath for 24 h at 100 ℃ (observe the color of the wood until it turns white). Subsequently, the treated wood was washed with H_2O until the pH of effluent was close to neutral, put into NaOH/H_2O solution (w/w, 8%) and extract 8 h at 80 ℃. After that, solvent exchange with EtOH/H_2O solution (20/80, 40/60, 60/40, 80/20, 100/0) to remove residual NaOH and freeze-dried. The product cellulose is obtained.

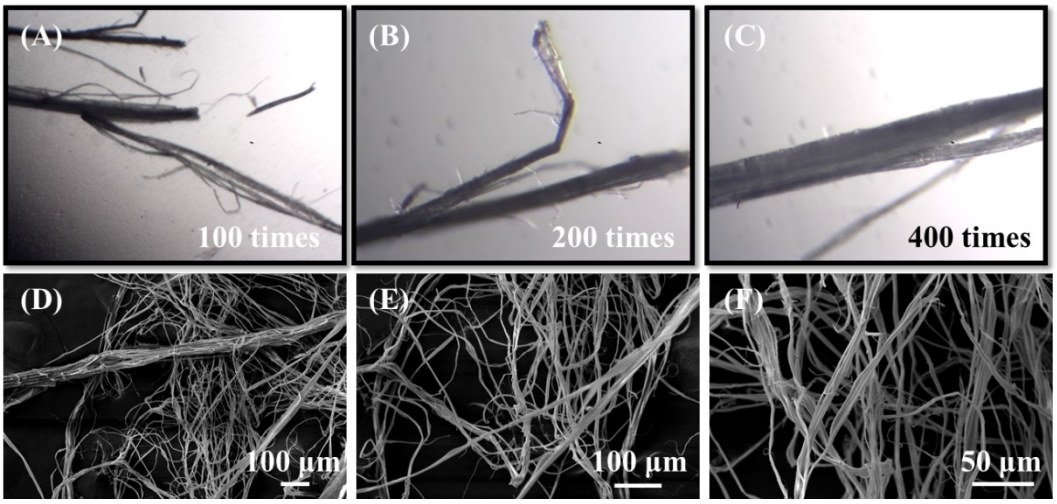


Figure S1 Optical microscope image (A-C) and SEM image of cellulose (D-F)

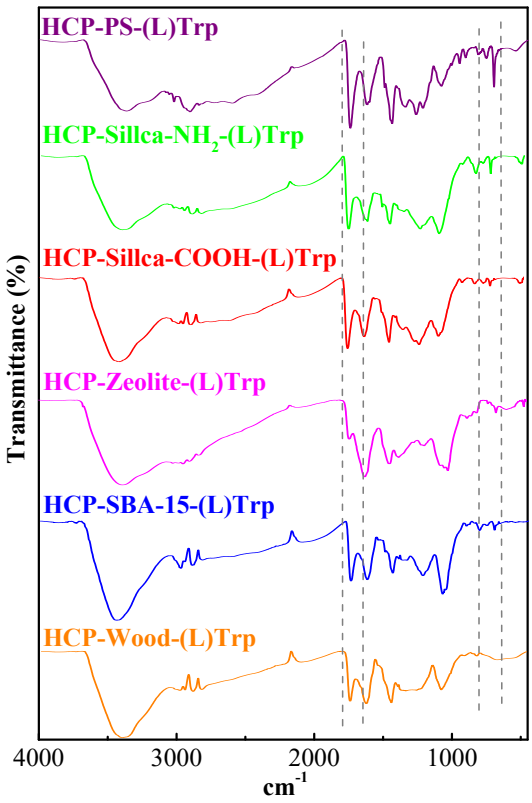


Figure S2 FT-IR spectra of HCP-PS-(L)Trp, HCP-Silica-NH_2-(L)Trp, HCP-Silica-COOH-(L)Trp, HCP-Zeolite-(L)Trp, HCP-SBA-15-(L)Trp and HCP-Wood-(L)Trp

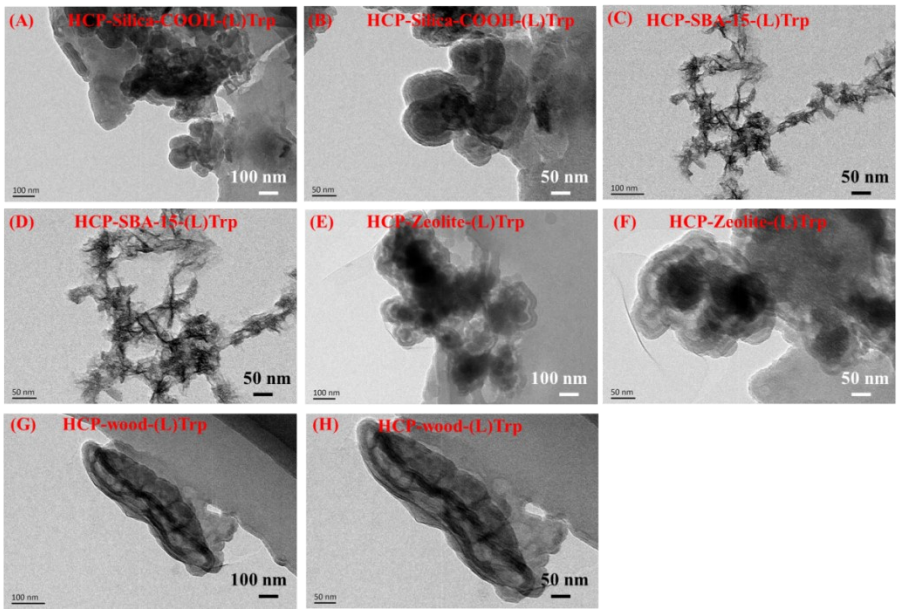


Figure S3 TEM images of HCP-Silica-COOH-(L)Trp (A B), HCP-SBA-15-(L)Trp (C D), HCP-Zeolite-(L)Trp (E F) and HCP-Wood-(L)Trp (G H)

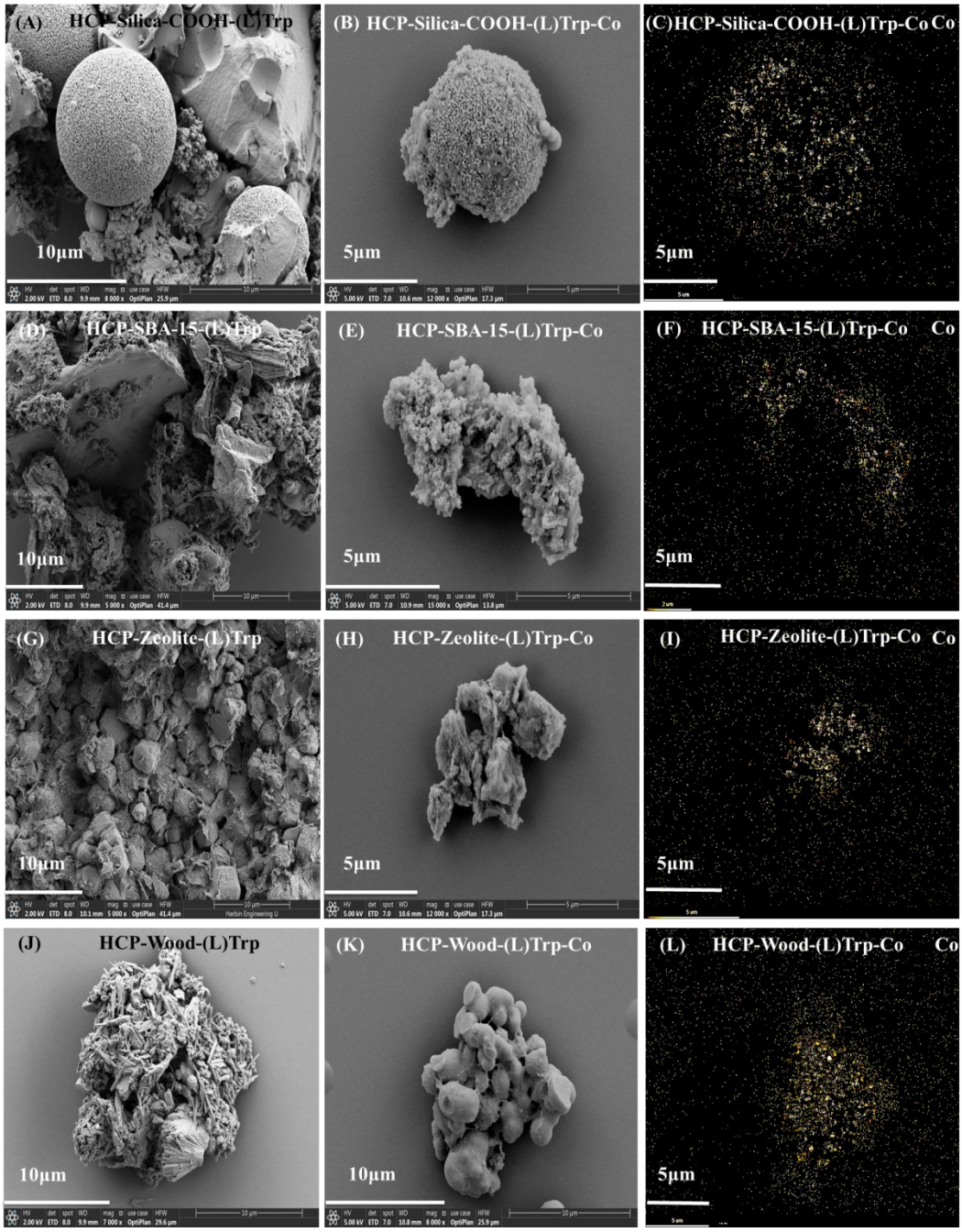


Figure S4 SEM and EDS images of HCP-Silica-COOH-(L)Trp-Co (A-C), HCP-SBA-15-(L)Trp-Co (D-F), HCP-Zeolite-(L)Trp-Co (G-I) and HCP-Wood-(L)Trp-Co (J-L)

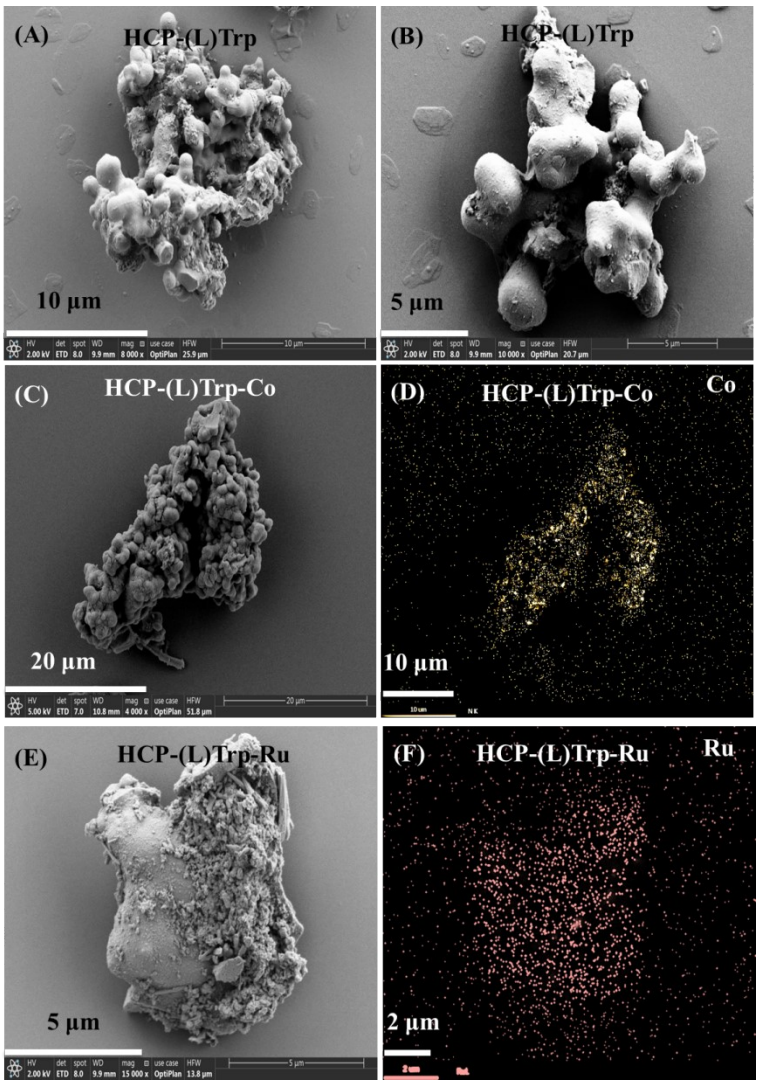


Figure S5 SEM and EDS images of HCP-(L)Trp , HCP- (L)Trp-Co and HCP-(L)Trp-Ru

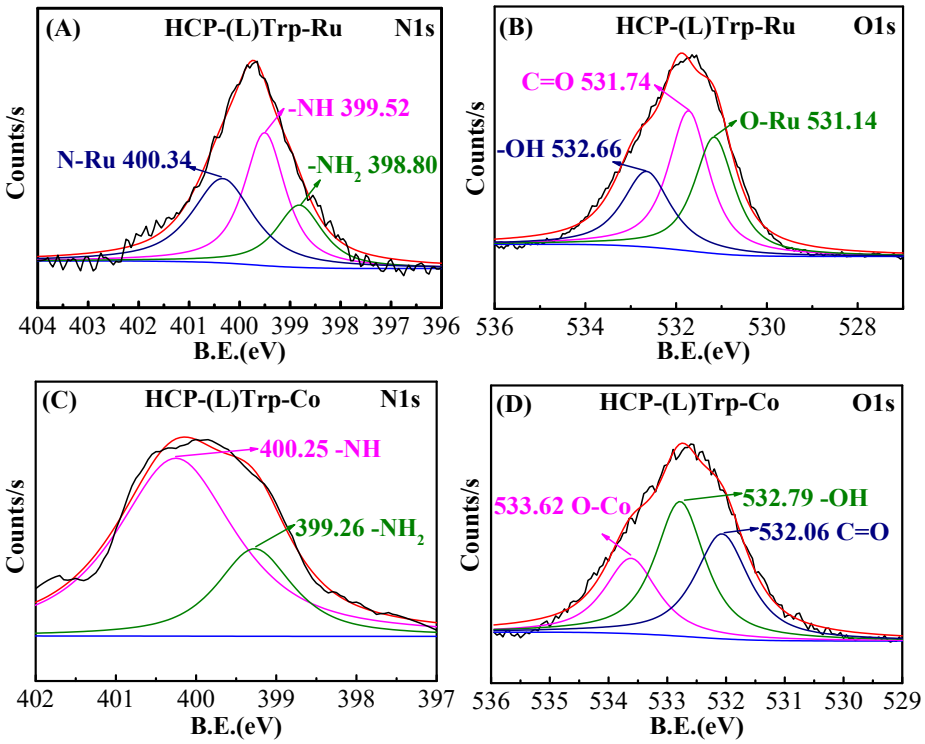
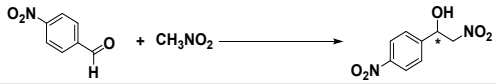


Figure S6 XPS of HCP- (L)Trp-Co and HCP- (L)Trp-Ru

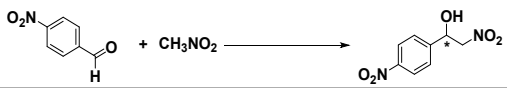
Table S1 Different catalysts catalyze the Henry reaction[a]



Entry	Catalyst	Time (d)	solvent	Yield (%)[b]	*ee* (%)[c]
1	HCP-Trp-Ru	1	$CHCl_3$	93	80
2	HCP-Trp-Ru	2	$CHCl_3$	99	81
3	HCP-Trp-Ru	3	$CHCl_3$	99	82

[a] The reaction was performed with nitromethane (0.6 mmol), paranitroanisole (0.5 mmol), catalyst (10 mg) at 25 °C. [b] Isolated yields. [C] For R enantiomer, determined by chiral HPLC analysis (Chiralpak OD) with hexane/isopropanol (90/10, v/v) as the eluent, ee for S isomer.

Table S2 Effects of solvents on catalytic properties[a]



Entry	Catalyst	Time (h)	solvent	Yield (%)[b]	*ee* (%)[c]
1	HCP-Trp-Ru(10mg)	48	MeOH	97	82
2	HCP-Trp-Ru(10mg)	48	$CHCl_3$	99	83
3	HCP-Trp-Ru(10mg)	48	Toluene	96	74
4	HCP-Trp-Ru(10mg)	48	CH_2Cl_2	90	71

[a] The reaction was performed with nitromethane (0.6 mmol), paranitroanisole (0.5 mmol), HCP-Trp-Ru (10 mg) at 25 °C. [b] Isolated yields. [C] For R enantiomer, determined by chiral HPLC analysis (Chiralpak OD) with hexane/isopropanol (90/10, v/v) as the eluent, ee for S isomer.

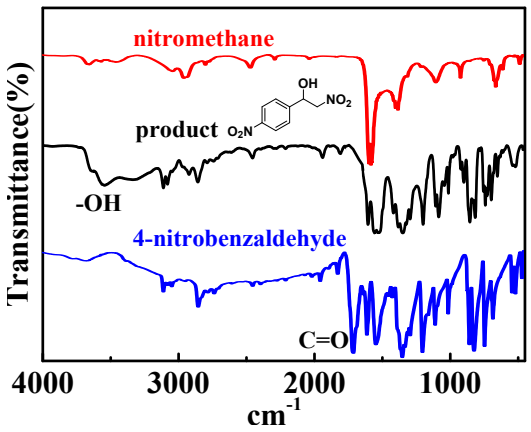
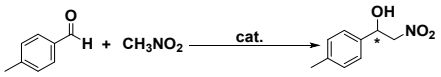
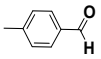
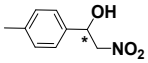


Figure S7 Henry reaction infrared spectrum

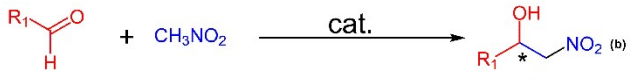
Table S3 Effect of template dosage on catalytic performance[a]

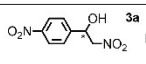
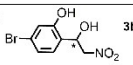
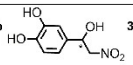
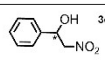
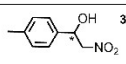
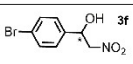
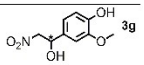


Entry	Reactant 1	product	Catalyst[b]	Yield (%)[c]	*ee* (%)[d]
1			HCP-PS(00%)-(L)Trp-Co	99	81
2			HCP-PS(10%)-(L)Trp-Co	97	70
3			HCP-PS(20%)-(L)Trp-Co	99	75
4			HCP-PS(25%)-(L)Trp-Co	97	84
5			HCP-PS(30%)-(L)Trp-Co	99	77

[a] The reaction was performed with nitromethane (0.6 mmol), p-Tolualdehyde (0.5 mmol), Catalyst (10 mg) and $CHCl_3$(0.6 mL) at 25 °C. Reaction time was 48 hours. [b] Matrix content wt% = (Matrix / (Matrix + chiral ligand)) x100 wt% [c] Isolated yields. [d] For enantiomer, determined by chiral HPLC analysis (Chiralpak OD) with hexane/isopropanol (90/10, v/v) as the eluent, ee for S isomer.

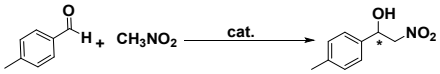
Table S4 Performance test of the catalyst supports[a]



	 3a	 3b	 3c	 3d	 3e	 3f	 3g
HCP-Silica-COO -(L)Trp-Co	73% ee 97% yield	———	———	17% ee 97% yield	65% ee 89% yield	———	———
HCP-SBA-15 -(L)Trp-Co	71% ee 95% yield	———	79% ee 99% yield	———	71% ee 99% yield	———	91% ee 94% yield
HCP-Zeolite-(L)Trp-Co	97% ee 94% yield	99% ee 97% yield	97% ee 99% yield	33% ee 98% yield	79% ee 99% yield	73% ee 38% yield	———
HCP-Wood -(L)Trp-Co	83% ee 94% yield	95% ee 98% yield	90% ee 98% yield	30% ee 97% yield	81% ee 97% yield	93% ee 72% yield	95% ee 92% yield

(a)The reaction was performed with nitromethane (0.6 mmol), Reactant 1 (0.5 mmol), Catalyst (10 mg) and $CHCl_3$ (0.6 mL) at 25 °C. Reaction time was 48 hours. (b) For enantiomer, determined by chiral HPLC analysis (Chiralpak OD) with hexane/isopropanol (90/10, v/v) as the eluent,ee for S isomer. Note: the horizontal line indicated that the catalyst has no catalytic effect under current conditions.

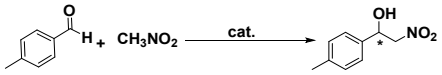
Table S5 Reuse of catalysts[a]



Entry	Catalyst	Yield (%)[b]	*ee* (%)[c]
1	HCP-Cellulose-(L)Trp-Ru	97	95
2	Recycle2	95	94
3	Recycle3	94	95
4	Recycle4	96	93
5	Recycle5	92	88
6	Recycle6	80	89
7	Recycle7	75	90
8	Recycle8	60	88
9	Recycle9	64	87
10	Recycle10	50	86

[a] The reaction was performed with nitromethane (0.6 mmol), p-Tolualdehyde (0.5 mmol), Catalyst (10 mg) and $CHCl_3$(0.6 mL) at 25 °C. Reaction time was 48 hours. [b] Isolated yields. [C] For R enantiomer, determined by chiral HPLC analysis (Chiralpak OD) with hexane/isopropanol (90/10, v/v) as the eluent, ee for S isomer.

Table S6 Blank experimental results[a]



Entry	Catalyst	Yield (%)[b]	*ee* (%)[c]
1	HCP-Silica-NH_2-(L)Trp	5	82
2	HCP-PS-(L)Trp	-	-
3	HCP-Cellulose-(L)Trp	-	-

[a] The reaction was performed with nitromethane (0.6 mmol), p-Tolualdehyde (0.5 mmol), Catalyst (10 mg) and $CHCl_3$(0.6 mL) at 25 °C. Reaction time was 48 hours. [b] Isolated yields. [C] For R enantiomer, determined by chiral HPLC analysis (Chiralpak OD) with hexane/isopropanol (90/10, v/v) as the eluent, ee for S isomer.

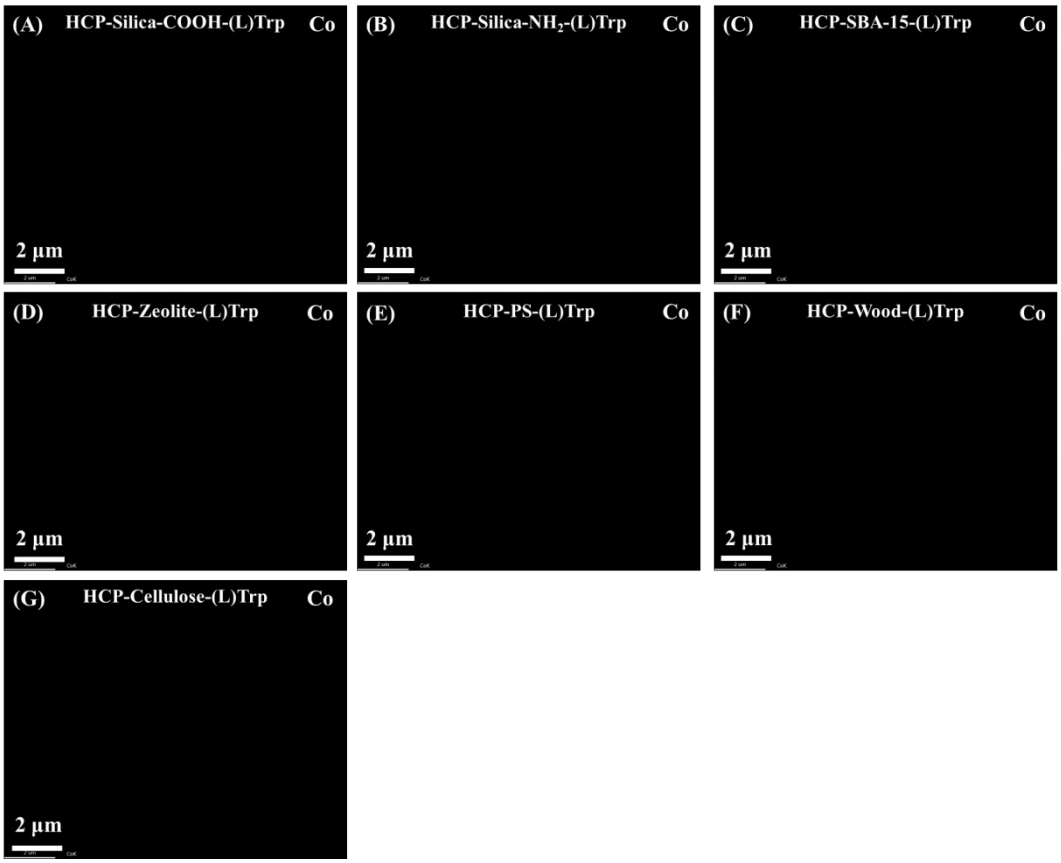


Figure S8 EDS images of HCP-Silica-COOH-(L)Trp (A), HCP-Silica-NH_2-(L)Trp (B), HCP-SBA-15-(L)Trp (C), HCP-Zeolite-(L)Trp (D), HCP-PS-(L)Trp (E), HCP-Wood-(L)Trp (F) and HCP-cellulose-(L)Trp (G) (Co)**.**

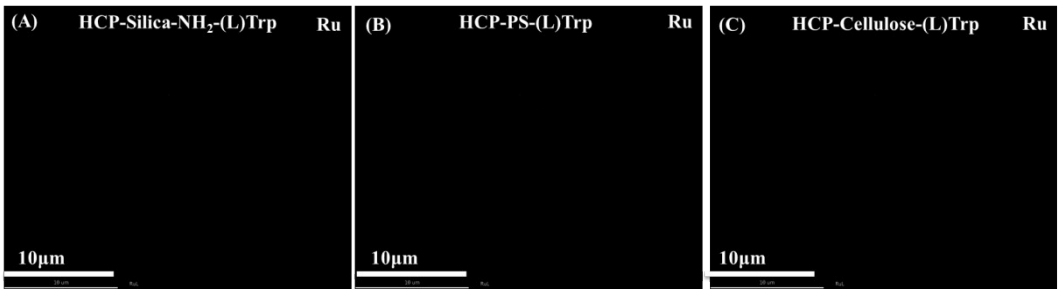


Figure S9 EDS images of HCP-Silica-NH_2-(L)Trp (A), HCP-PS-(L)Trp (B) and HCP-cellulose-(L)Trp (C) (Ru)**.**

Table S7 Chlorine content in catalyst support

Entry	Catalyst support	Cl2p (%)
1	HCP-(L)Trp	0.40
2	HCP-Cellulose-(L)Trp	0.67
3	HCP-Silica-COOH-(L)Trp	0.46
4	HCP-Silica-NH_2-(L)Trp	0.43
5	HCP-SBA-15-(L)Trp	0.47
6	HCP-Zeolite Powder-(L)Trp	0.49
7	HCP-PS-(L)Trp	0.78
8	HCP-Wood-(L)Trp	0.68

Determined by X-ray photoelectron spectroscopy analysis.

Table S8 The content of active metal in the catalyst

Entry	Catalyst	metallic element concentration (mg/L)[a]	metallic element mass (mg)[b]	mass percent (%)[c]
1	HCP-(L)Trp-Ru	5.1020	0.051020	5.1020
2	HCP-Cellulose-(L)Trp-Ru	5.1269	0.051269	5.1269
3	HCP-Cellulose-(L)Trp-Ru (Recycle5)	5.1239	0.051239	5.1239
4	HCP-(L)Trp-Co	0.3434	0.003434	0.3434
5	HCP-Silica-COOH-(L)Trp-Co	0.3635	0.003635	0.3635
6	HCP-Silica-NH_2-(L)Trp-Co	0.3433	0.003433	0.3433
7	HCP-SBA-15-(L)Trp-Co	0.3420	0.003420	0.3420
8	HCP-Zeolite Powder-(L)Trp-Co	0.3496	0.003496	0.3496
9	HCP-PS-(L)Trp-Co	0.3458	0.003458	0.3458
10	HCP-Wood-(L)Trp-Co	0.3485	0.003485	0.3485
11	HCP- Cellulose -(L)Trp-Co	0.3495	0.003495	0.3495

Test condition: [a] 1mg of sample was weighed and dissolved in concentrated nitric acid with assistance of ultrasound. After complete dissolution, the solution was diluted to 10mL with deionized water. The concentration of metal ions in the solution was determined by ICP-AES.

[b] metallic element mass in the samples = metallic element concentration x volume of solution.

[c] mass percent of metallic element in the materials = (metallic element mass / weight) x100%

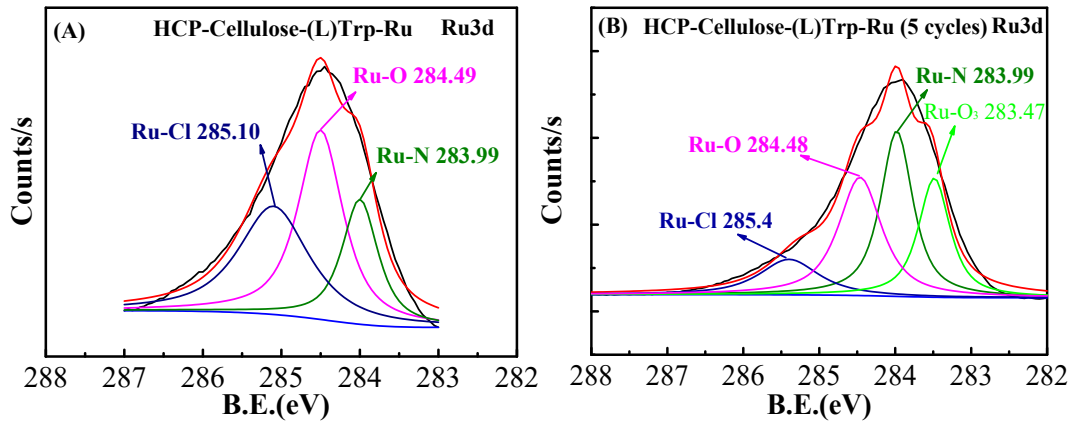


Figure S10 XPS of HCP-Cellulose-(L)Trp-Ru (A) and HCP-Cellulose-(L)Trp-Ru (5 cycles) (B)

Table S9 ICP-MS test data of hot filtration experiments

Entry	Catalyst	metallic element concentration (μg/L)[a]	metallic element mass (μg)[b]	dissolution rate[c]
1	HCP-(L)Trp-Ru	2.112	0.02112	0.04%
2	HCP-Cellulose-(L)Trp-Ru	1.421	0.01421	0.03%
3	HCP-(L)Trp-Co	0.612	0.00612	0.18%
4	HCP-Silica-COOH-(L)Trp-Co	0.414	0.00414	0.11%
5	HCP-Silica-NH_2-(L)Trp-Co	0.571	0.00517	0.15%
6	HCP-SBA-15-(L)Trp-Co	0.609	0.00609	0.18%
7	HCP-Zeolite Powder-(L)Trp-Co	0.626	0.00626	0.18%
8	HCP-PS-(L)Trp-Co	0.410	0.00410	0.12%
9	HCP-Wood-(L)Trp-Co	0.303	0.00303	0.09%
10	HCP- Cellulose -(L)Trp-Co	0.217	0.00217	0.06%

Test condition: [a] 1mg sample was stirred in deionized water (5 mL) at 50℃for 24h, then the solution was diluted to 10mL with deionized water. The concentration of metal ions in the solution was determined by ICP-MS;

[b] metallic element mass in the samples = metallic element concentration x volume of solution.

[c] (Dissolved metal/total amount of metal) X100 wt%

Table S10 ICP-MS test data of carrier

Entry	Carrier	metallic element concentration (μg /L)[a]	metallic element mass (μg)[b]	mass percent (%)[c]
1	HCP-(L)Trp	3.910(Fe)	0.0391	0.0039
2	HCP-Cellulose-(L)Trp	5.189(Fe)	0.0519	0.0052
3	HCP-Silica-COOH-(L)Trp	4.333(Fe)	0.0433	0.0043
4	HCP-Silica-NH_2-(L)Trp	4.145(Fe)	0.0415	0.0041
5	HCP-SBA-15-(L)Trp	3.849(Fe)	0.0385	0.0038
6	HCP-Zeolite Powder-(L)Trp	4.043(Fe)	0.0404	0.0040
7	HCP-PS-(L)Trp	3.567(Fe)	0.0357	0.0036
8	HCP-Wood-(L)Trp	4.832(Fe)	0.0483	0.0048

Test condition: [a] 1mg of sample was weighed and dissolved in concentrated nitric acid with assistance of ultrasound. After complete dissolution, the solution was diluted to 10mL with deionization. The concentration of metal ions in the solution was determined by ICP-MS.

[b] metallic element mass in the samples = metallic element concentration x volume of solution.

[c] mass percent of metallic element in the materials = (metallic element mass / weight) x100%

Table S11 Comparison with other heterogeneous catalysts

reaction	references	catalysts	reported ee and yield	this experiment
Henry reaction	37 Chiral Ni-Schiff Base Complexes inside Zeolite-Y and Their Application in Asymmetric Henry Reaction: Effect of Initial Activation with Microwave Irradiation	Ni^{2+}-L1@NaY (heterogeneous)	ee 46-83% yield 54-92%	ee 90-99% yield 90-99%
	38 Chiral enhancement in the confined space of zeolites for the asymmetric synthesis of b-hydroxy nitroalkanes	Cu-Y-1a ((1S,2S)-N1,N2-Bis(3-chlorobenzyl)cyclohexane-1,2-diamine 1a) (heterogeneous)	ee 57-94% yield 57-97%	
	39 Chiral enhancement in the confined space of zeolites for the asymmetric synthesis of b-hydroxy nitroalkanes	Cu^{2+}-Y-CD (heterogeneous)	ee 30-88% yield 48-94%	

S2 High performance liquid chromatography of the product

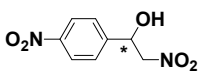
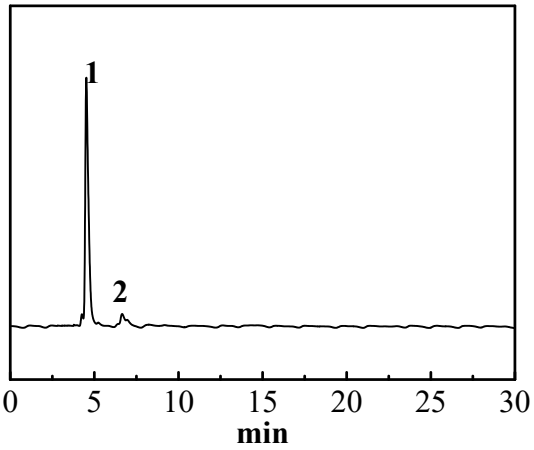
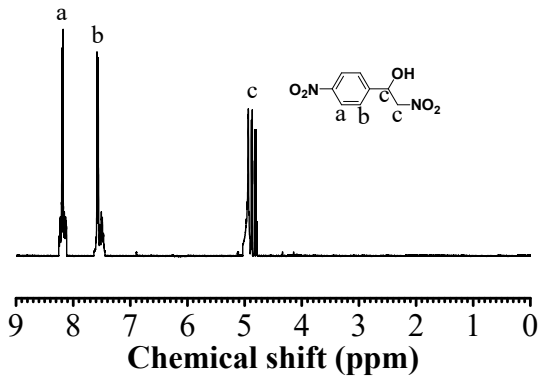


Table S2, Entry 4 (S). The product is yellow liquid. HCP-Trp-Ru is the catalyst. Reaction time 30 min, enantiomeric excess: 81%; Chiral HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol =90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR_1 (major) =4.525 min, tR_2 =6.650 min. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.76-5.03 (m, 2H, CH_2), 4.90 (m, 1H, CH), 7.59 (m, 2H, Ar-H), 8.19 (m, 2H, Ar-H).



	time/min	area%

1	4.525	90.534
2	6.650	9.466



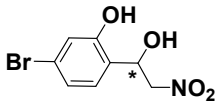
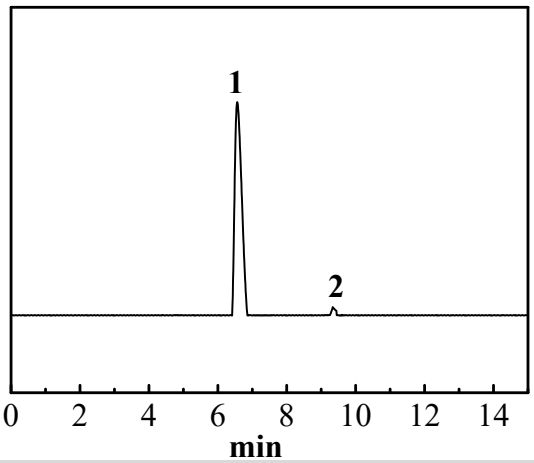
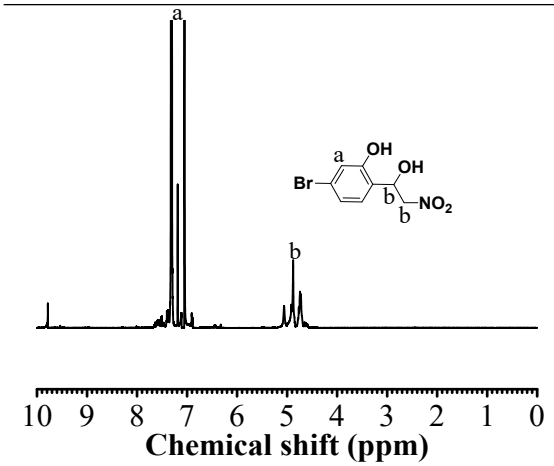


Table 2, 3b (S). The product is yellow liquid. HCP-Trp-Co is the catalyst. Reaction time 15 min, enantiomeric excess: 95%; Chiral HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol =90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR_1 (major) =6.567 min, tR_2 =9.217 min. ^1H NMR (500 MHz, $CDCl_3$, δ): 4.67-5.14 (m, 2H, CH_2), 4.91 (m, 1H, CH),6.99-7.42 (m, 3H, Ar-H).



	time/min	area%
1	6.567	97.072
2	9.217	2.928



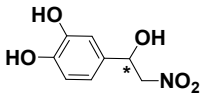
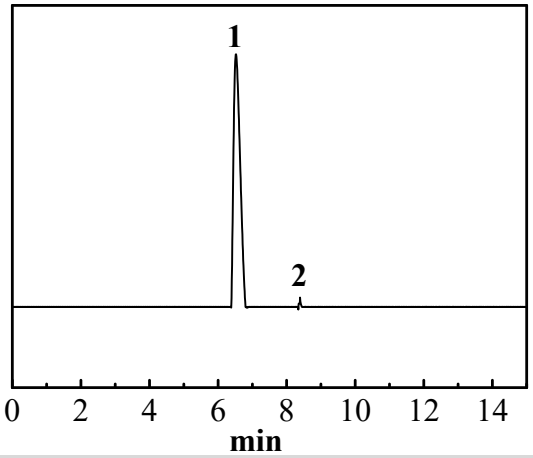
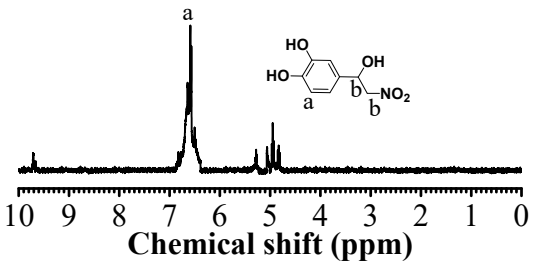


Table S4, 3c (S). The product is yellow liquid. HCP-Zeolite-(L)Trp-Co is the catalyst. Reaction time 15 min, enantiomeric excess: 97%; Chiral HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol =90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR_1 (major) =6.525 min, tR_2 =8.392 min. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.77-5.18 (m, 2H, CH_2), 4.95 (m, H, CH), 6.38-6.86 (m, 3H, Ar-H).



	time/min	area%
1	6.525	98.916
2	8.392	1.084



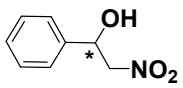
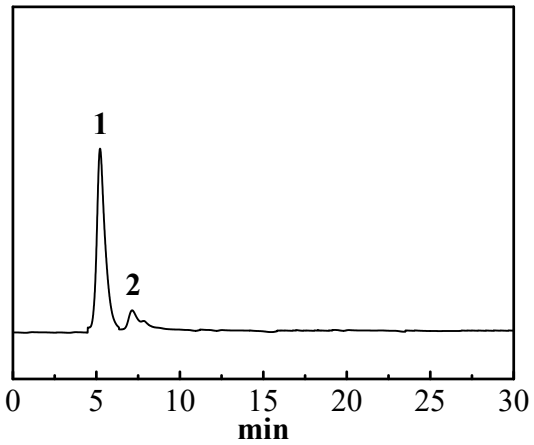
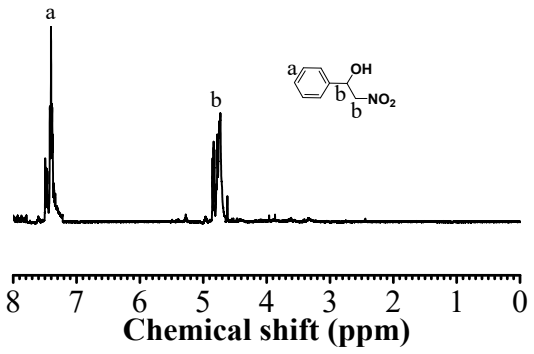


Table 2, 3d (S). The product is yellow liquid. HCP-Cellulose-(L)Trp-Co is the catalyst. Reaction time 15 min, enantiomeric excess: 87%; Chiral HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol =90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR_1 (major) =5.242 min, tR_2 =7.130 min. ^1H NMR (500 MHz, $CDCl_3$, δ): 4.61-4.95 (m, 2H, CH_2), 4.90 (s, 1H, CH), 7.20-7.55 (m, 5H, Ar-H).



	time/min	area%
1	5.242	93.555
2	7.130	6.445



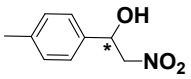
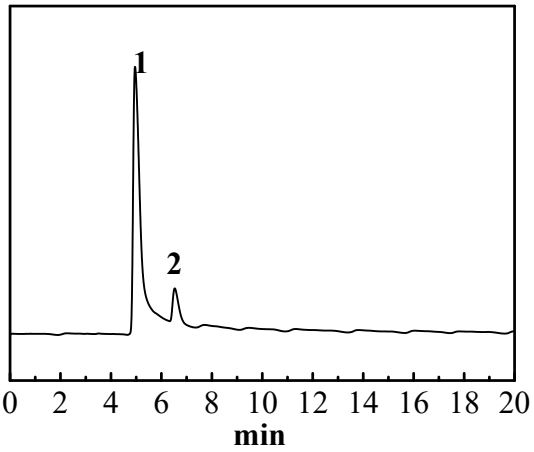
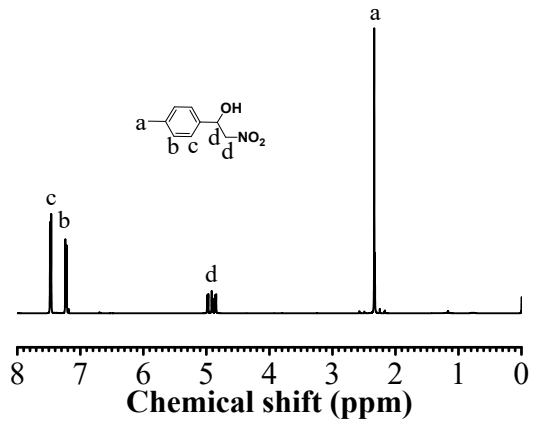


Table 2, 3e (S). The product is yellow liquid. HCP-(L)Trp-Co is the catalyst. Reaction time 20 min, enantiomeric excess: 81%; Chiral HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol =90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR_1 (major) =4.958 min, tR_2 =6.525 min. ^1H NMR (500 MHz, $CDCl_3$, δ): 2.33 (m, 3H, CH_3), 4.77-5.02 (m, 2H, CH_2), 4.90 (m, H, CH), 7.22 (m, 2H, Ar-H), 7.47 (m, 2H, Ar-H).



	time/min	area%
1	4.958	90.546
2	6.525	9.454



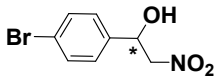
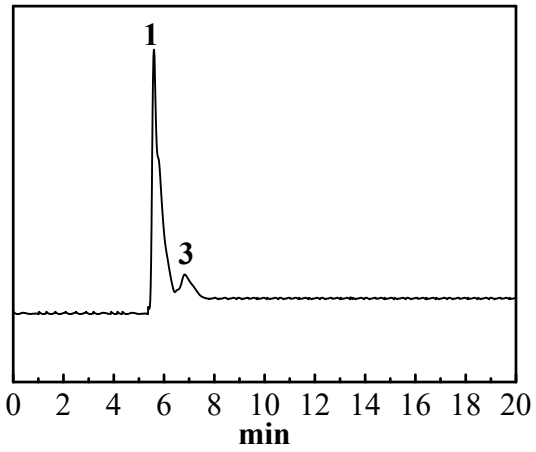
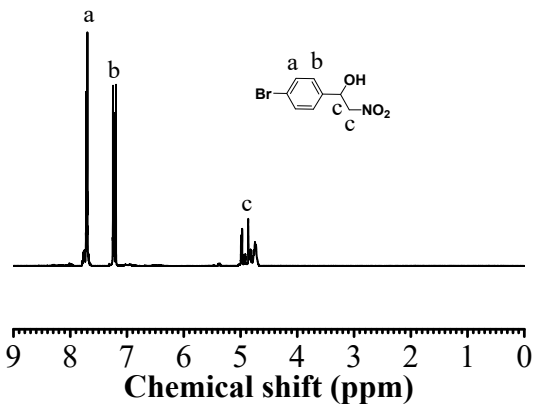


Table 2, 3f (S). The product is yellow liquid. HCP-Silica-NH_2-(L)Trp-Co is the catalyst. Reaction time 20 min, enantiomeric excess: 83%; Chiral HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol =90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR_1 (major) =5.600 min, tR_2 =6.8175 min. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.65-5.01 (m, 2H, CH_2), 4.95 (s, 1H, CH), 7.21 (m, 2H, Ar-H), 7.68 (m, 2H, Ar-H).



	time/min	area%
1	5.600	91.970
2	6.817	8.030



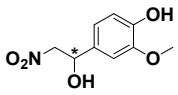
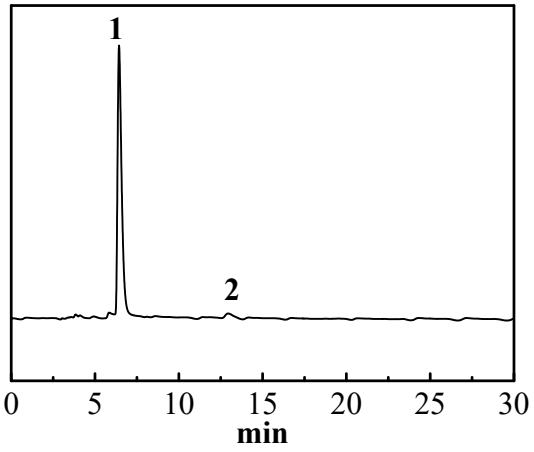


Table 2, 3g (S). The product is yellow liquid. HCP-PS-(L)Trp-Co is the catalyst. Reaction time 30 min, enantiomeric excess: 93%; Chiral HPLC analysis: Daicel Chiralpak OD-H, hexane/iso-propanol =90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: tR_1 (major) =6.433 min, tR_2 =12.942 min. ^1H NMR (500 MHz, $CDCl_3$, δ): 3.93(m, 3H, CH_3), 4.77-5.08 (m, 2H, CH_2), 4.95 (m, H, CH), 6.71-6.88 (m, 3H, Ar-H).



	time/min	area%
1	6.433	96.291
2	12.942	3.709