

Supporting Information

Partially carbonized chiral polymer with Cu-bis(oxazoline) as efficient heterogeneous catalyst for asymmetric Henry reaction

Qingliang Chen,^a Feifei Bi,^a Jing Ye,^a Xiangke Guo,^a Yu Shen,^a Wen-Hua Zheng^{*,b} and Xuefeng Guo^{*,a,c,d}

a. Key Lab of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, Jiangsu, China.

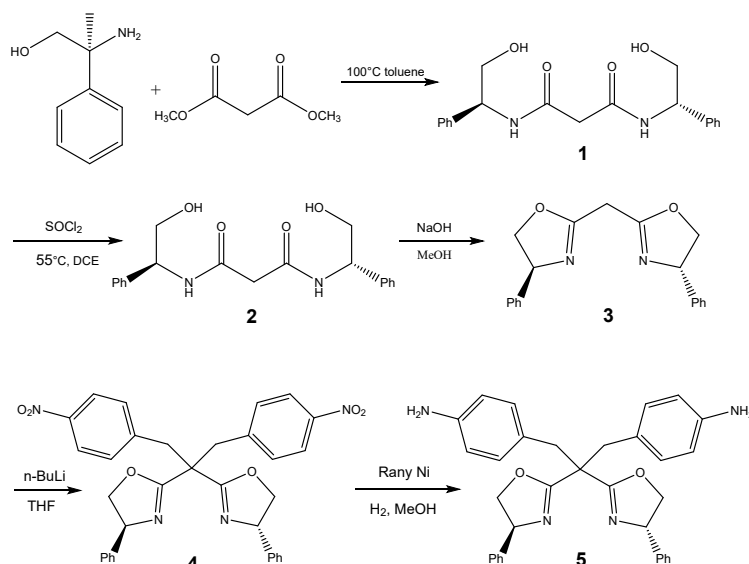
b. State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, Jiangsu, China.

c. Jiangsu Key Laboratory of Vehicle Emissions Control, Nanjing University, Nanjing 210023, China

d. Nanjing University-Yangzhou Institute of Chemistry and Chemical Engineering, Yangzhou 211900, China

1. Method

1.1 Synthesis of functionalized chiral monomer



Scheme 1 Synthetic method of functional chiral Bis(oxazoline) ligands.

(1) Preparation of Compound 1

L-Phenylglycinol (10 g) and anhydrous toluene were added into a 250 mL flask. Then 4.1 mL of methylmalonate was injected into the flask, the mixture was stirred at 100°C for 24 h. The white solid product 1 was obtained by cold filtration. After

washing with cold ethyl acetate and petroleum ether respectively, the pure product 1 was obtained with a yield of 97.8%.

(2) Preparation of Compound 2

Compound 1 (12.2 g) was added into a 250 mL flask with anhydrous DCE as solvent. Thionylchloride (5.2 mL) was added dropwise slowly into the flask and then stirred at 55°C for 4h. The solvent was removed and the crude product 2 was obtained.

(3) Preparation of Compound 3

Compound 2 (2.083 g) and NaOH (0.659 g) were added into a 250 mL flask with methanol (82 mL) as solvents. The resulting mixture was refluxed for 14 h at 100°C. The as-prepared product was monitored by TLC. Then the product was dissolved with dichloromethane. The organic phase was collected and washed with saturated NH₄Cl solution for three times. Finally, the product was purified by column chromatography on silica gel after the solvent was removed. The product 3 was obtained with a yield of 83.4%.

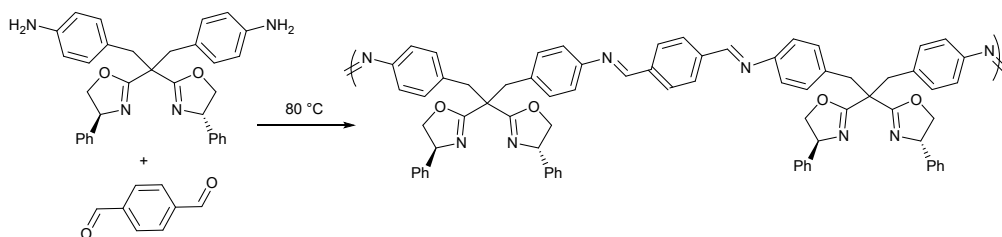
(4) Preparation of Compound 4

Compound 3 (0.3426 g) in anhydrous THF was injected into a dry bottle with a magnetic stirrer and cooled down to -55°C. n-BuLi (1.02 mL) was slowly injected into the bottle and stirred for 1 h at low temperature. Then, the anhydrous THF solution with 4-nitrobenzyl boronide (0.5323 g) was dropped into the bottle. The resulting mixture was refluxed at 95°C for 4h after the solution temperature returned to room temperature. The reaction was quenched by a little water. When the solvent was removed, the product was dissolved with dichloromethane and washed with water and saturated salt water, respectively. The product was purified by column chromatography on silica gel after the solvent was evaporated. The product 4 was obtained with a yield of 53%.

(5) Preparation of Compound 5

Raney Ni was added into the solution (Compound 4 (0.3413 g) in methanol and dichloromethane) and then reacted with H₂ for 12 h. The reaction was monitored by TLC. After the reaction was completed, the resulting residue was filtered and purified by recrystallization to afford the pure products.

1.2 Preparation of polymer



Scheme 2 The preparation of polymer.

As shown in Scheme2, the target polymer was obtained through the condensation of amino and aldehyde. Compound 5 (0.3678 g) was dissolved into methanol (5 mL) and dichloromethane (3 mL). Meanwhile, terephthalaldehyde (0.0955 g) was dissolved into methanol (6 mL). The two kinds of solutions were added into polytetrafluoroethylene hydrothermal reactor. MgO powders were put into the solution and the resulting mixture was heat-treated at 80°C for 24 h. The polymer was purified by removing MgO with dilute acetic acid, and then washed with excessive ethanol while filtering. The obtained polymer was marked as CB.

1.3 Carbonization

In order to improve the stability of the catalyst, the sample was carbonized. Condition 1: the sample was heated at 180 °C for 12 h and marked as CB-180. Condition 2: the sample was heated to 200°C within 75 min and kept for 180 min under N₂, marked as CB-200. Condition 3: the sample was heated to 200°C within 75 min and kept for 180 min under N₂. Then, the temperature was increased to 350°C within 75 min and kept for 240 min. The as-prepared sample was marked as CB-350. Condition 4: the sample was heated to 200°C within 75 min and kept for 180 min under N₂. Then, the temperature was increased to 500°C within 180 min kept for 180 min. The as-prepared sample was marked as CB-500.

All samples were stirred for 12 h in room temperature using dilute acetic acid (volume ratio is 1:3 for acetic acid and water) to remove MgO. The samples were filtered and accompanied by washing with excessive water, and cleaned three times with ethanol. Finally, the samples were dried at 90°C for 24 h.

1.4 Partial carbonization materials loaded with copper

The copper is an excellent catalyst for Henry reaction. The loading steps of copper ion was as follows: 1.5 equivalent copper acetate and 1 equivalent carbonized compound mixed with ethanol were added into a flask and stirred at 55°C for 12 h. The product was filtered and washed with hot ethanol for three times, dried at 80°C for 12 h. The copper content of Cu-CB was 2.05 wt%, while that of Cu-CB-180 was 2.00 wt% (Analyzed by ICP-OES).

1.5 Catalytic reaction

Benzaldehyde (0.2 mmol) and catalyst loading with copper ions (0.02 g) were added into methanol (2 mL). Nitromethane (10 mmol) was dropped into the solution and stirred for 24 hours at room temperature. The crude products obtained by filtration when the reaction was finished and purified by column chromatography on silica gel.

2. Characterizations

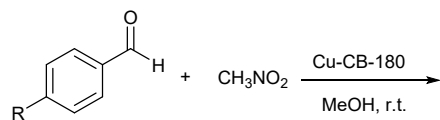
The samples were characterized by thermogravimetric analysis (TGA) with NETZSCH STA 449C (TA Instruments, Germany) in air atmosphere, the flow rate of the instrument is 60-80 mL/min and the temperature range from room temperature to 873 K. IR spectra were recorded using KBr pellets on a Thermo Nicolet FTIR spectrometer in the range of 4000 - 100 cm^{-1} . Transmission electron microscopy (TEM, JEOL JEM-1011, Japan) was used to observe the morphologies of all samples. HPLC analyses were performed on Shimadzu SPD-20A using Daicel Chiralpak OD-H Column, The enantiomeric ratio was determined by Daicel Chiralpak IC, Hexanes/IPA = 90:10, 1.0 mL/min, $\lambda = 220$ nm. Nitrogen isothermal adsorption and desorption measurements and analysis were performed on a Micromeritics ASAP 3020 instrument. Prior to testing, the samples to be tested were pretreated under vacuum at 90 °C for 24 h to remove possible adsorbed species on the surface, and finally the specific surface area and pore distribution of the tested samples were calculated by fitting with BET and BJH methods.

3. Supplementary Tables

Table S1 Catalytic performance of catalysts.

Entry	Catalyst	Experiment 1		Experiment 2		Experiment 3	
		Yield (%)	<i>ee</i> (%)	Yield (%)	<i>ee</i> (%)	Yield (%)	<i>ee</i> (%)
1	Cu-monomer	82.3	63	81.5	63	82.0	64
2	Cu-CB	82.4	65	82.6	65	81.8	66
3	Cu-CB-180	89.6	75	88.7	75	89.5	75
6	Cu-CB-200	68.5	50	68.1	50	65.7	54

Table S2 Catalytic performance of Cu-CB-180 with different substrates.



Entry	R	Yield (%)	ee (%)
1	4-OMe	61.5	67
2	4-NO ₂	91.3	45
3	4-Br	88.6	69

4. Supporting Figures

4.1 Thermogravimetric data

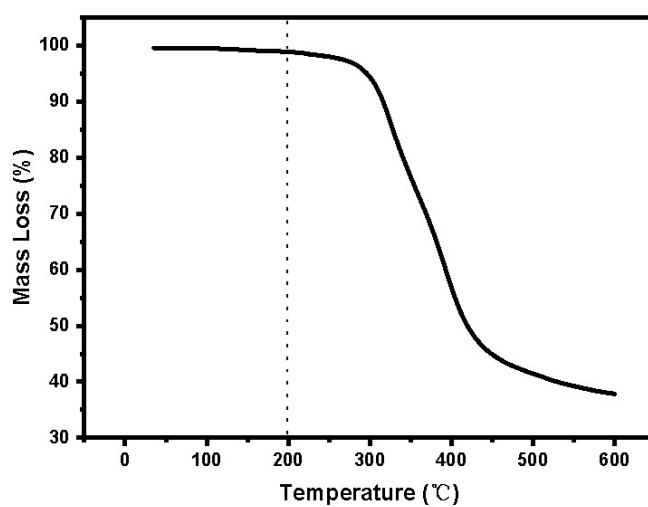


Figure S1 TG curves of CB.

4.2 HPLC data

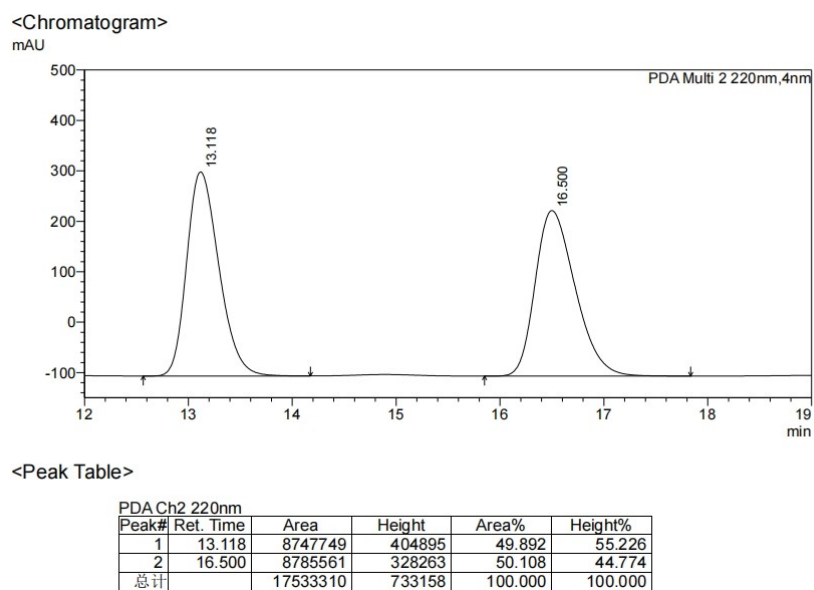


Figure S2 HPLC data of the racemization product of Henry reaction.

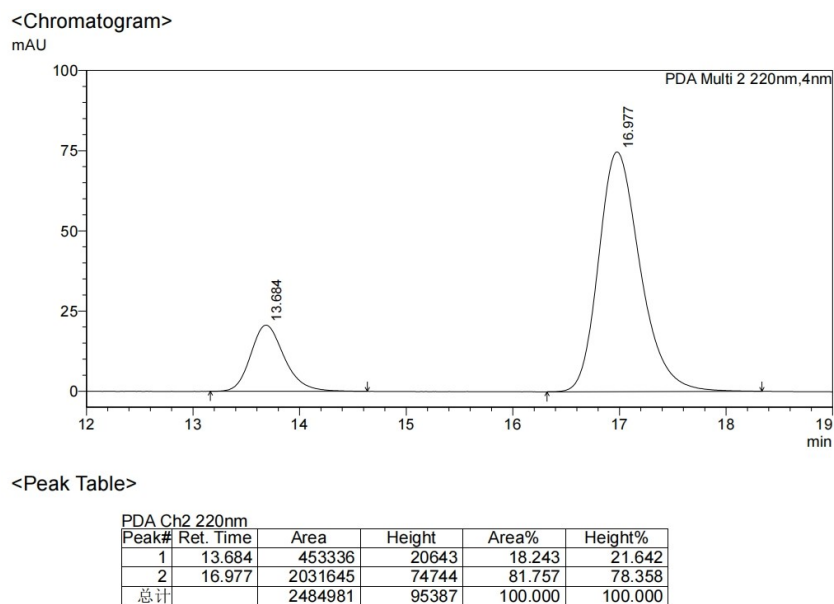
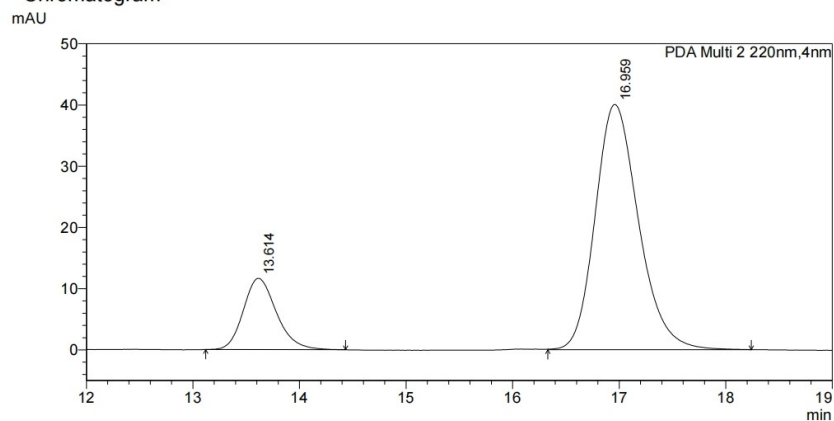


Figure S3 HPLC data of monomer catalyst (Experiment 1).

<Chromatogram>

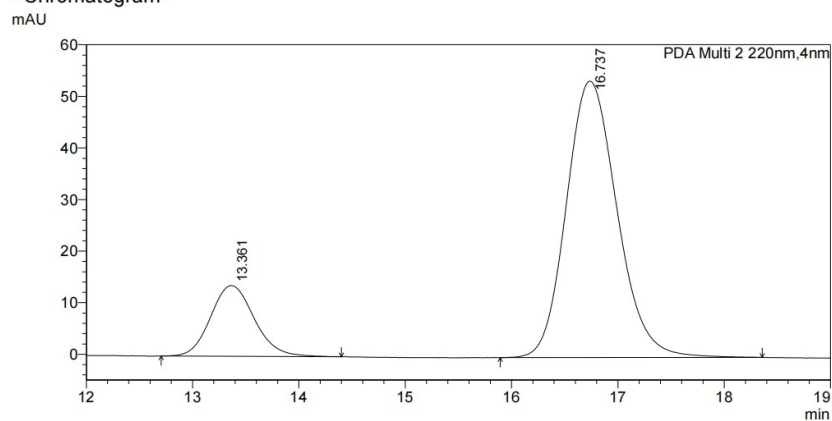


<Peak Table>

PDA Ch2 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.614	252377	11650	18.186	22.523
2	16.959	1135364	40075	81.814	77.477
总计		1387740	51725	100.000	100.000

Figure S4 HPLC data of monomer catalyst (Experiment 2).

<Chromatogram>

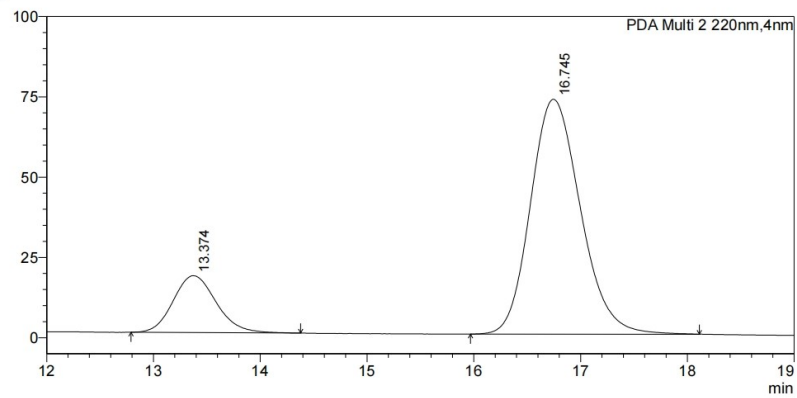


<Peak Table>

PDA Ch2 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.361	392513	13723	18.063	20.387
2	16.737	1780453	53590	81.937	79.613
总计		2172965	67313	100.000	100.000

Figure S5 HPLC data of monomer catalyst (Experiment 3).

<Chromatogram>
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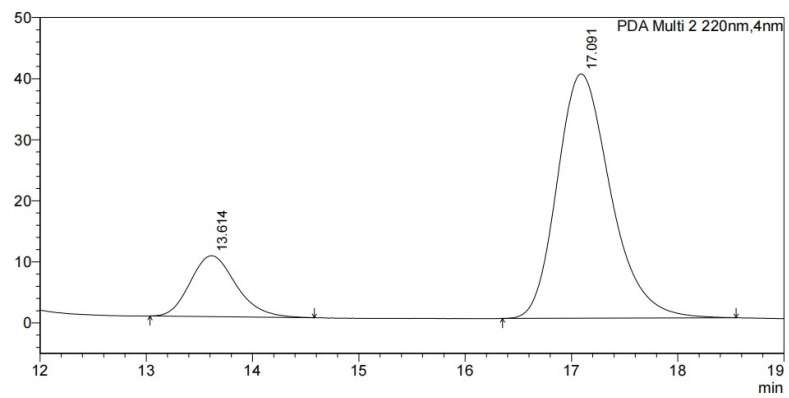


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PDA Ch2 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.374	497245	17731	17.304	19.519
2	16.745	2376286	73108	82.696	80.481
总计		2873531	90839	100.000	100.000

Figure S6 HPLC data of Cu-CB (Experiment 1).

<Chromatogram>
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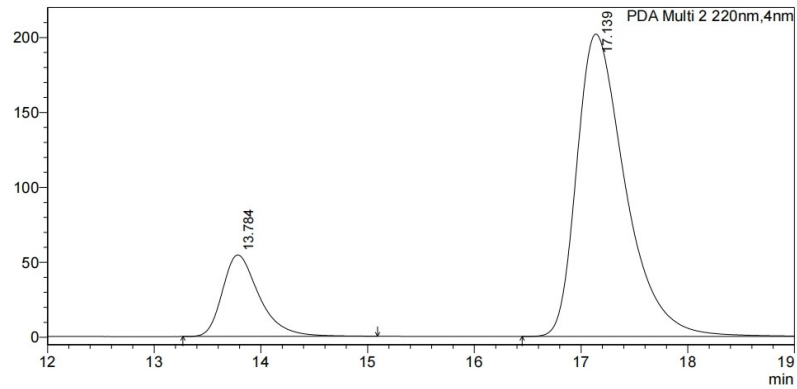


<Peak Table>

PDA Ch2 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.614	299605	9979	17.625	19.958
2	17.091	1400314	40022	82.375	80.042
总计		1699919	50002	100.000	100.000

Figure S7 HPLC data of Cu-CB (Experiment 2).

<Chromatogram>
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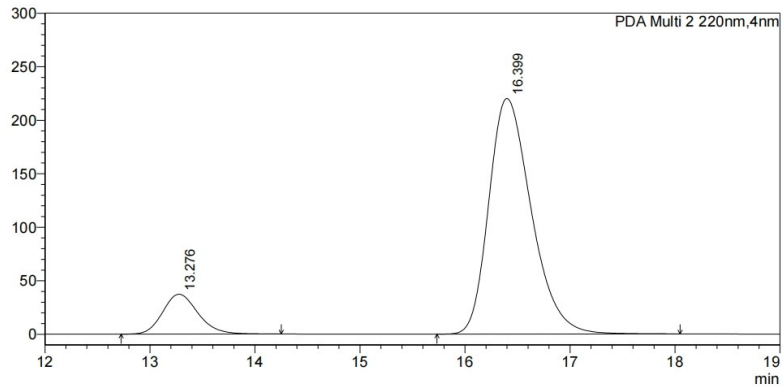


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PDA Ch2 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.784	1304767	54356	16.961	21.221
2	17.139	6387842	201780	83.039	78.779
总计		7692609	256136	100.000	100.000

Figure S8 HPLC data of Cu-CB (Experiment 3).

<Chromatogram>
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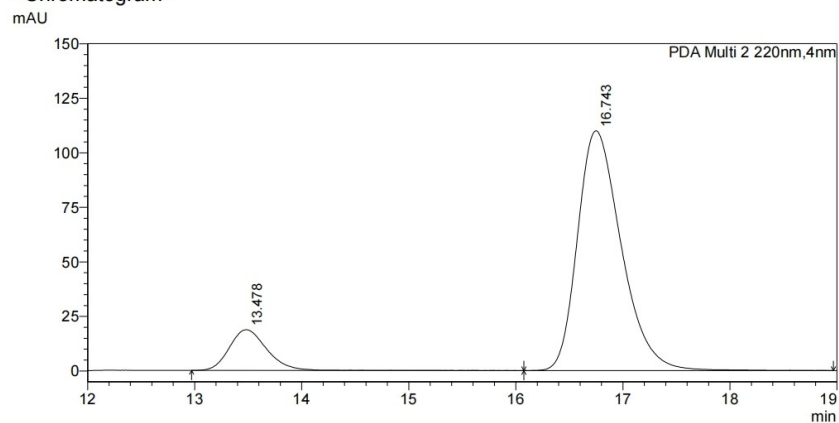


<Peak Table>

PDA Ch2 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.276	871016	37213	12.330	14.462
2	16.399	6193423	220093	87.670	85.538
总计		7064439	257306	100.000	100.000

Figure S9 HPLC data of Cu-CB-180 (Experiment 1).

<Chromatogram>

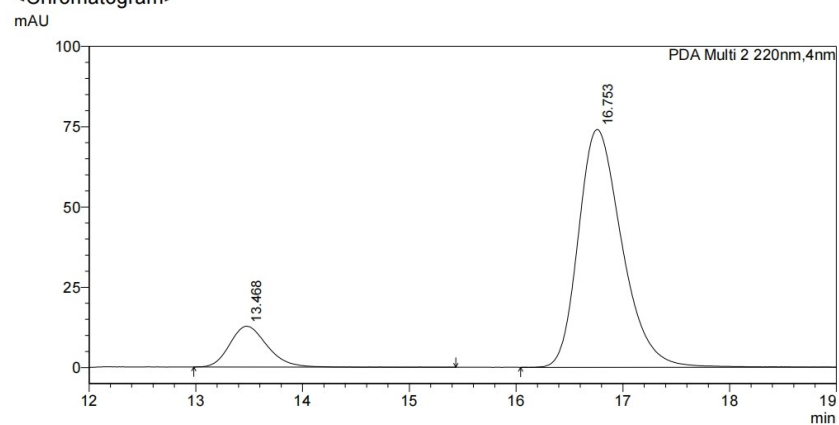


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Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.478	462719	19077	12.704	14.538
2	16.743	3179524	112144	87.296	85.462
总计		3642243	131221	100.000	100.000

Figure S10 HPLC data of Cu-CB-180 (Experiment 2).

<Chromatogram>

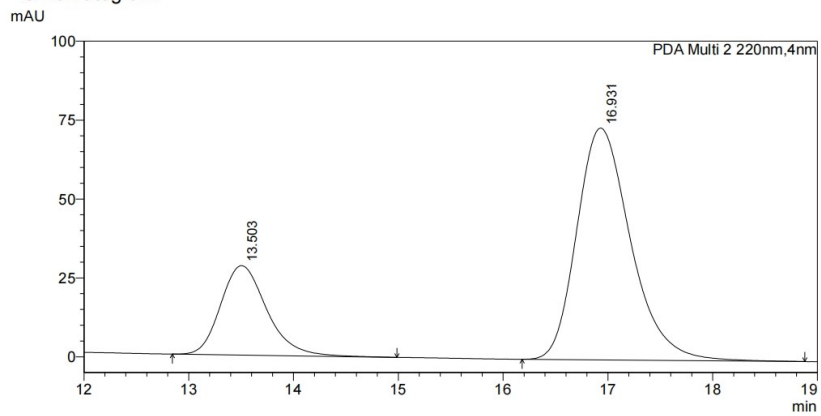


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Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.468	314888	12983	12.804	14.658
2	16.753	2144474	75591	87.196	85.342
总计		2459362	88574	100.000	100.000

Figure S11 HPLC data of Cu-CB-180 (Experiment 3).

<Chromatogram>

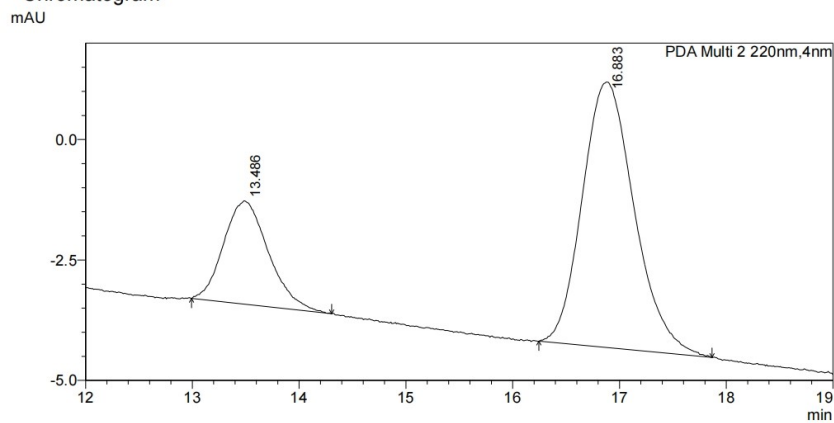


<Peak Table>

PDA Ch2 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.503	869115	28359	24.876	27.855
2	16.931	2624690	73451	75.124	72.145
总计		3493805	101809	100.000	100.000

Figure S12 HPLC data of Cu-CB-200 (Experiment 1).

<Chromatogram>

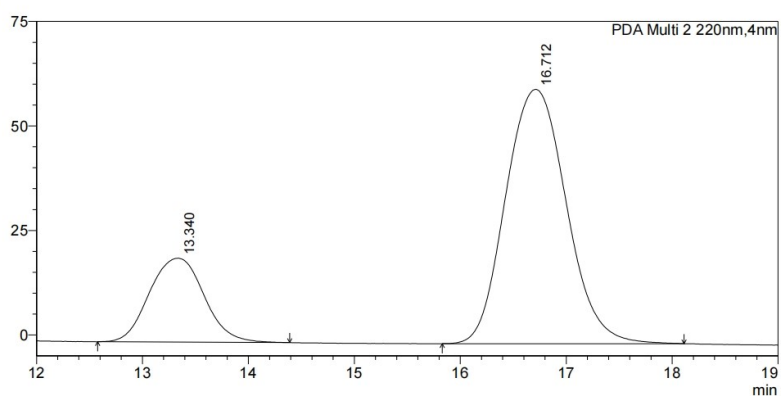


<Peak Table>

PDA Ch2 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.486	62529	2148	25.093	28.042
2	16.883	186662	5511	74.907	71.958
总计		249191	7659	100.000	100.000

Figure S13 HPLC data of Cu-CB-200 (Experiment 2).

<Chromatogram>
mAU



<Peak Table>

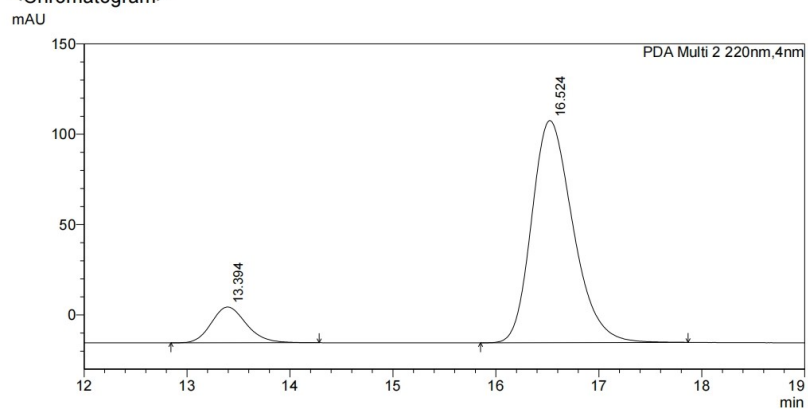
PDA Ch2 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.340	719905	20069	22.915	24.806
2	16.712	2421730	60834	77.085	75.194
总计		3141635	80904	100.000	100.000

Figure S14 HPLC data of Cu-CB-200 (Experiment 3).



Figure S15 HPLC data for recycling of Cu-CB-180 (Cycle 1).

<Chromatogram>

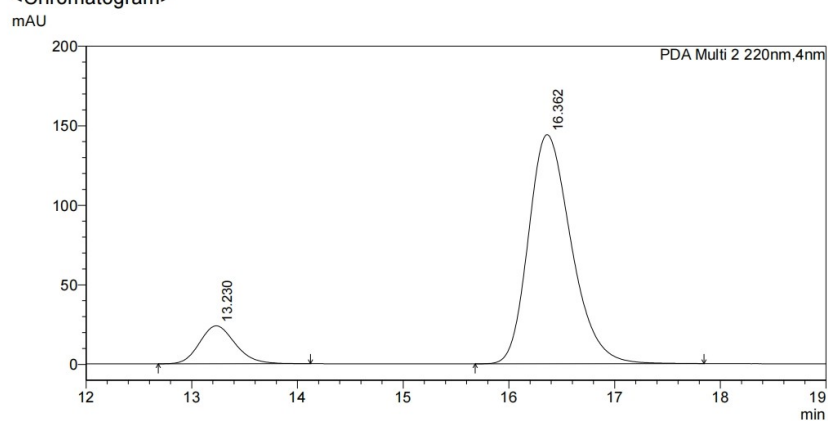


<Peak Table>

PDA Ch2 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.394	469813	19789	12.048	13.864
2	16.524	3429549	122950	87.952	86.136
总计		3899362	142739	100.000	100.000

Figure S16 HPLC data for recycling of Cu-CB-180 (Cycle 2).

<Chromatogram>

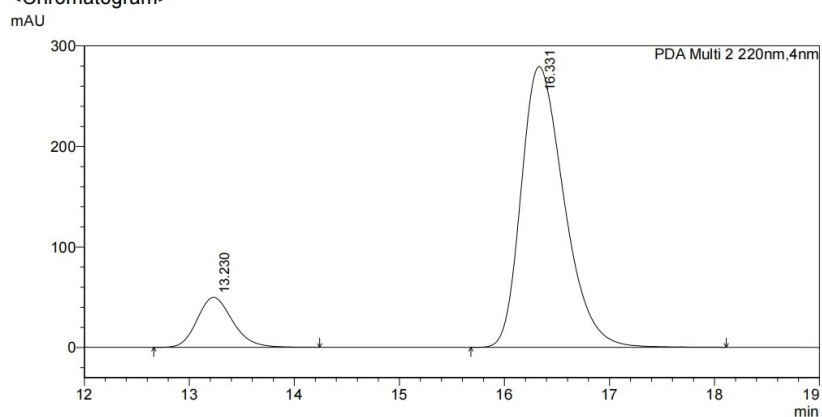


<Peak Table>

PDA Ch2 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.230	560224	23829	12.152	14.193
2	16.362	4049896	144062	87.848	85.807
总计		4610120	167891	100.000	100.000

Figure S17 HPLC data for recycling of Cu-CB-180 (Cycle 3).

<Chromatogram>

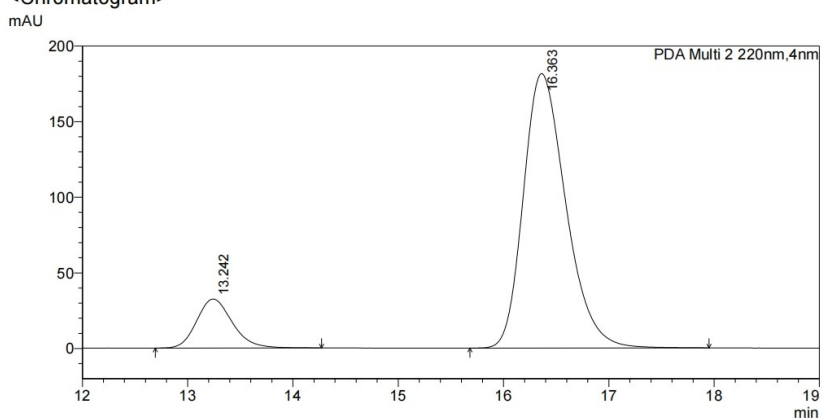


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.230	1164176	49618	12.800	15.081
2	16.331	7930792	279385	87.200	84.919
总计		9094968	329003	100.000	100.000

Figure S18 HPLC data for recycling of Cu-CB-180 (Cycle 4).

<Chromatogram>

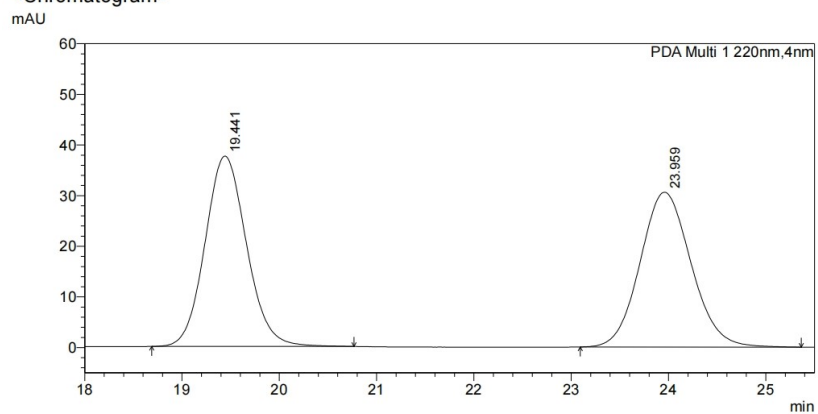


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.242	759067	32388	12.966	15.140
2	16.363	5095057	181543	87.034	84.860
总计		5854124	213931	100.000	100.000

Figure S19 HPLC data for recycling of Cu-CB-180 (Cycle 5).

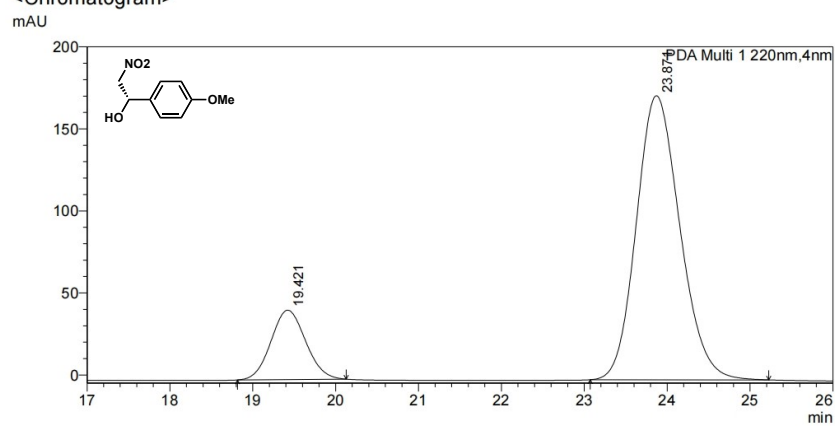
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<Peak Table>

PDA Ch1 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	19.441	1114462	37584	50.014	55.143
2	23.959	1113824	30573	49.986	44.857
总计		2228287	68156	100.000	100.000

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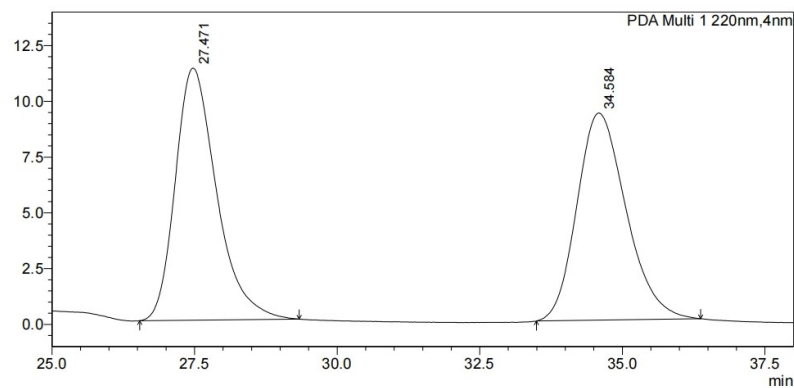
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PDA Ch1 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	19.421	1230226	42308	16.276	19.632
2	23.871	6328201	173191	83.724	80.368
总计		7558427	215498	100.000	100.000

Figure S20 HPLC data of various substrates catalyzed by Cu-CB-180.

<Chromatogram>

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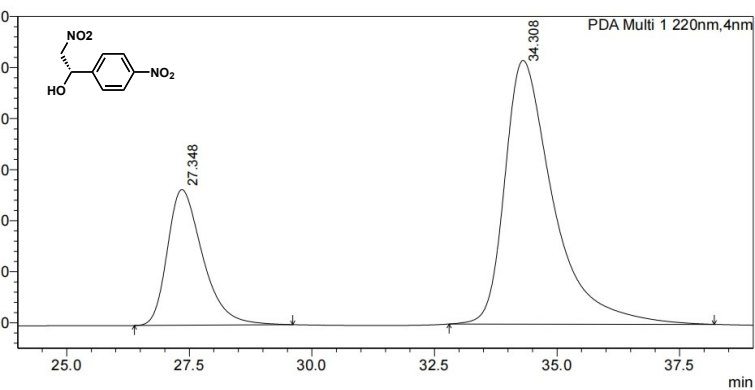


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%	Height%
1	27.471	569620	11302	50.582	54.885
2	34.584	556508	9290	49.418	45.115
总计		1126128	20592	100.000	100.000

<Chromatogram>

mAU

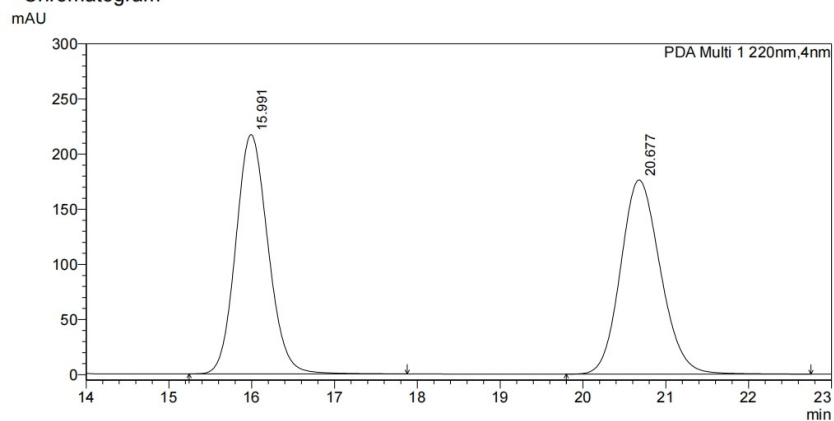


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%	Height%
1	27.348	1334846	26576	27.276	33.968
2	34.308	3558917	51663	72.724	66.032
总计		4893763	78239	100.000	100.000

Figure S21 HPLC data of various substrates catalyzed by Cu-CB-180.

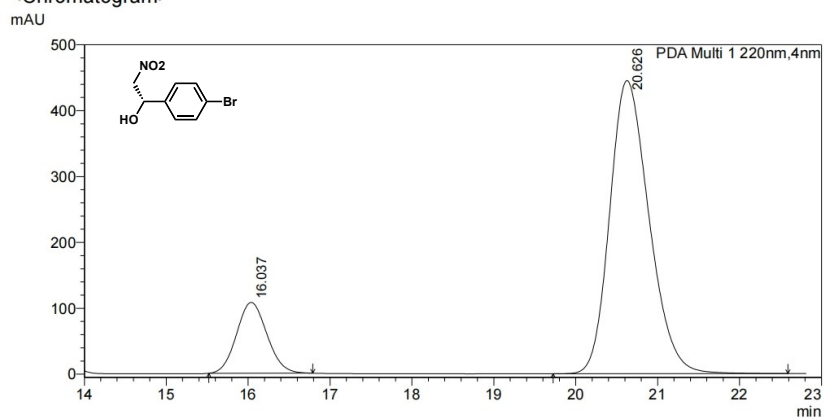
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<Peak Table>

PDA Ch1 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.991	5878873	217089	49.953	55.215
2	20.677	5889822	176082	50.047	44.785
总计		11768695	393171	100.000	100.000

<Chromatogram>



<Peak Table>

PDA Ch1 220nm					
Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.037	2775612	107443	15.753	19.446
2	20.626	14843934	445064	84.247	80.554
总计		17619546	552506	100.000	100.000

Figure S22 HPLC data of various substrates catalyzed by Cu-CB-180.