Electronic Supplementary Material (ESI) for Polymer Chemistry.
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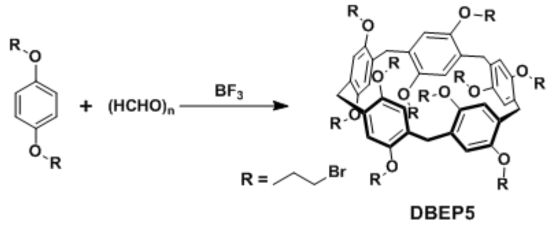
Electronic Supplementary Information

Pillar[5]arene-Based Chiral 3D Polymer Network for Heterogeneous Asymmetric Catalysis

Huangtianzhi Zhu, Bingbing Shi, Lina Gao, Yuezhou Liu, Pei-Ren Liu, Liqing Shangguan, Zhengwei Mao* and Feihe Huang*

1. Synthesis of DBEP5[S1]



Scheme S1. Synthetic route to **DBEP5**.

1,4-bis(2-bromoethoxy)benzene (20.0 g, 61.7 mmol) and paraformaldehyde (3.74 g, 123 mmol) was mixed in 600 mL of 1,2-dichloroethane, and $BF_3•OEt_2$ (7.79 mL, 98%, 61.7 mmol) was added. The reaction was monitored by TLC. 200 mL of water was added to quench the reaction. The organic layer was concentrated and purified through column chromatography using hexane:dichloromethane = 1:1 to obtain pure **DBEP5** as a white solid (6.01g, 29.1%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ(ppm): 6.91 (s, 10H), 4.22 (t, *J* = 5.6 Hz, 20H), 3.84 (s, 10H), 3.64 (t, *J* = 5.6 Hz, 20H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ(ppm): 149.66, 129.06, 116.04, 68.97, 30.79, 29.41.

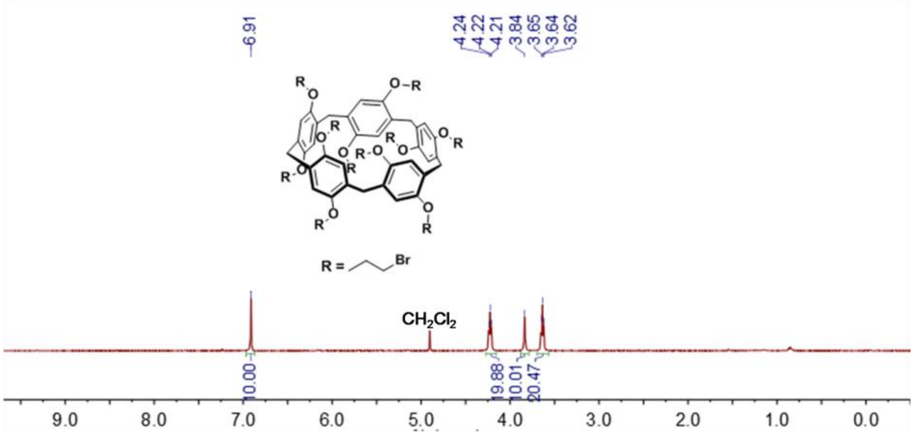


Fig. S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **DBEP5**.

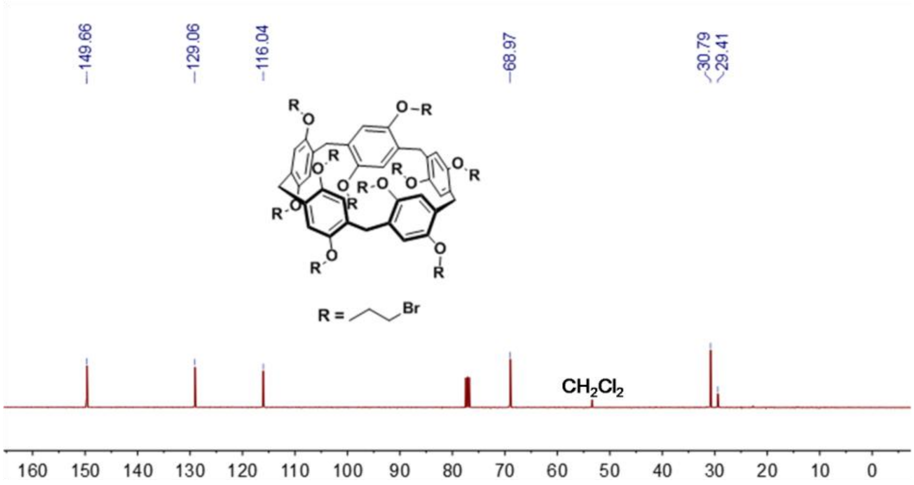
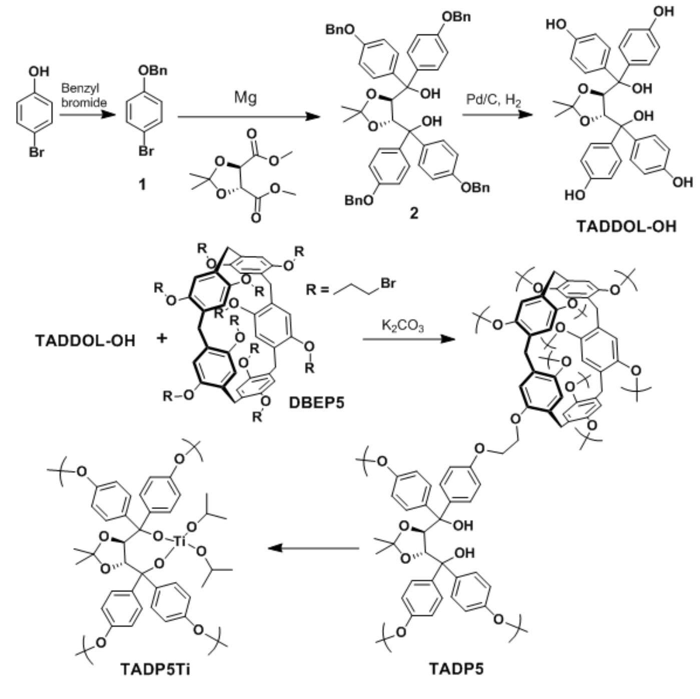


Fig. S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **DBEP5**.

2. Synthesis of TADP5 and TADP5Ti



Scheme S2. Synthetic route to **TADP5** and **TADP5Ti**.

Synthesis of compound **1**[S2]: To a solution of 4-bromophenol (10.0 g, 57.8 mmol) and benzyl bromide (14.0 g, 81.9 mmol) in acetonitrile (150 mL), K_2CO_3 (13.8 g, 100 mmol) was added under argon atmosphere. The mixture was stirred under reflux for 4 days. After that, the solvent was removed and crude product was purified through column chromatography on silica gel using hexane:ethyl acetate = 10:1 as the eluent to obtain pure **1** as a pale yellow oil (11.4 g, 75.6%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.34 (dd, J = 10.1, 7.9 Hz, 7H), 6.80 (d, J = 8.9 Hz, 2H), 4.96 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 157.95, 136.64, 132.39, 128.75, 128.22, 127.55, 116.78, 113.22, 70.26.

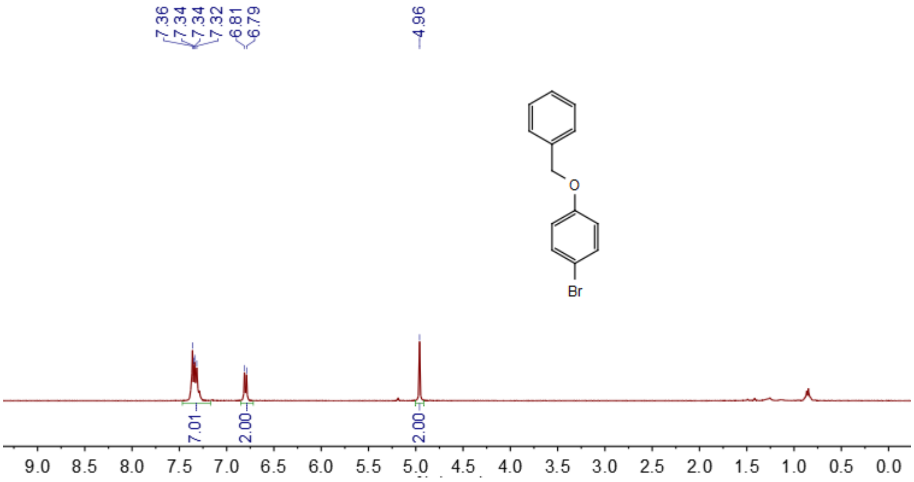


Fig. S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **1**.

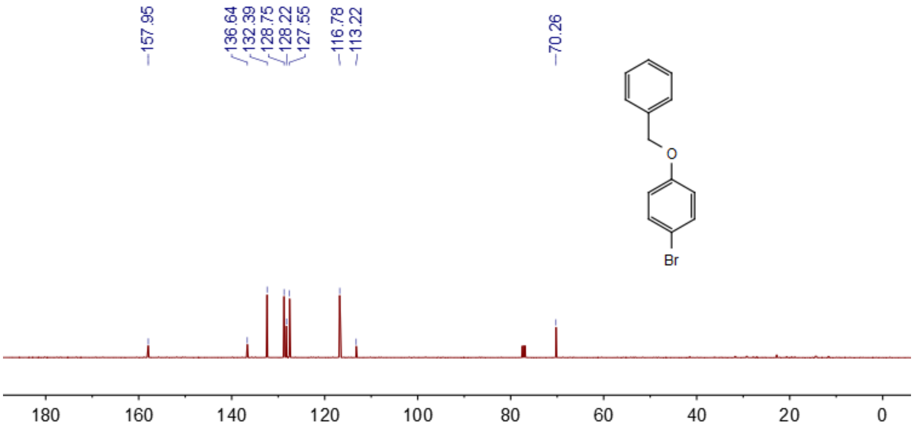


Fig. S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **1**.

Synthesis of compound **2**: Under protection of argon, magnesium (1.20 g, 50.0 mmol) and a piece of iodine were heated, followed by adding a few drops of compound **1** (11.4 g, 43.7 mmol) in 100 mL of anhydrous THF. After the Grignard reaction was triggered successfully, the solution of compound **1** in THF was added under reflux and stirred for 8 hours. The mixture was cooled to –12.0 ℃, and then (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylic acid dimethyl ester (2.00 g, 9.17 mmol) in 30.0 mL of anhydrous THF was added dropwise and reacted for 18 hours. After the reaction was quenched by NH_4Cl, the solvent was evaporated to get a residue, which was passed through column chromatrography on silica gel using hexane:ethyl acetate = 3:1 as the eluent to obtain a crude product, which was further recrystallized in ethanol to get pure product as a pale yellow solid (6.08 g, 74.5%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.49–7.27 (m, 26H), 7.23 (d, 2H), 6.93 (d, J = 8.8 Hz, 4H), 6.85 (d, J = 8.8 Hz, 4H), 5.04 (d, J

= 21.8 Hz, 8H), 4.47 (s, 2H), 3.98 (s, 2H), 1.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 157.97, 138.64, 137.02, 135.30, 129.74, 128.92, 128.59, 127.98, 127.74–127.28, 114.28, 113.54, 109.23, 81.10, 77.62, 69.97, 27.23. HRESIMS: *m*/*z* calcd for $[M - H]^-$ $C_{59}H_{53}O_8^-$, 889.3819, found 889.3774, error –5.1 ppm.

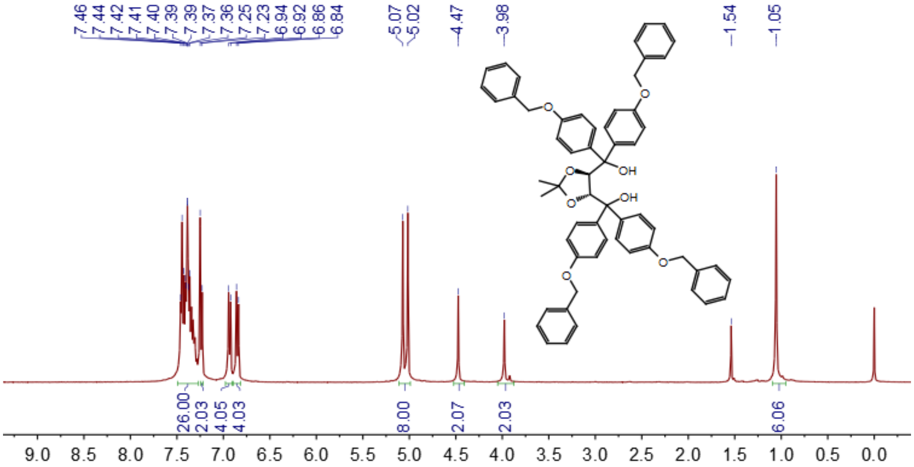


Fig. S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **2**.

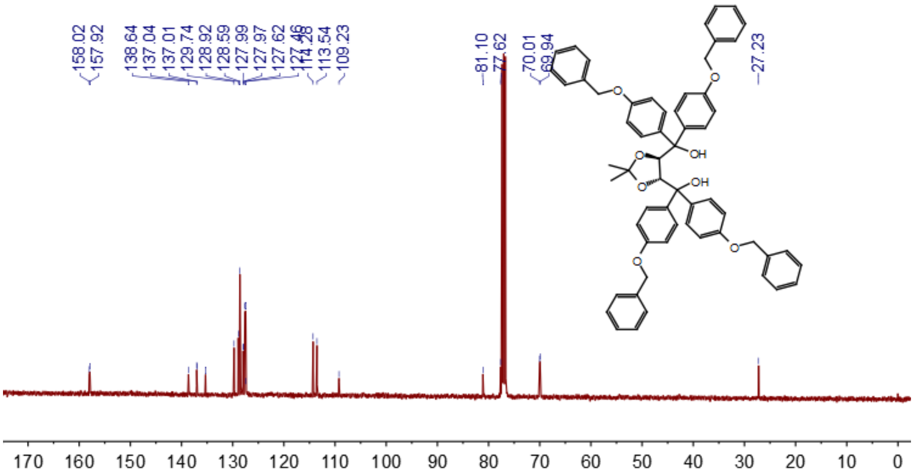


Fig. S6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **2**.

Synthesis of **TADDOL-OH**: To a solution of compound **2** (4.45g, 5.00 mmol) in 100 mL of ethyl acetate was added 3.00 g of Pd/C. The mixture was stirred in hydrogen atmosphere for 4 days. After that, undissolved solid was filtered, and the solvent was removed on a rotation evaporator to obtain pure **TADDOL-OH** as a pale yellow solid (2.62 g, 99%). ^{1}H NMR (400 MHz, acetone-d_6, 298 K) δ (ppm): 8.27 (d, J = 10.4 Hz, 4H), 7.40 (d, J = 8.6 Hz, 4H), 7.18 (d, J = 8.7 Hz, 4H), 6.80 (d, J = 8.6 Hz, 4H), 6.68 (d, J = 8.7 Hz, 4H), 6.28 (s, 2H), 4.42 (s, 2H), 1.00 (s, 6H). ^{13}C NMR (100 MHz, acetone-d_6, 298 K) δ (ppm): 157.15, 139.21, 135.29, 130.91, 130.06, 114.99, 114.47, 109.12, 82.70, 77.85, 27.48. HRESIMS: *m*/*z* calcd for $[M + Na]^+$ $C_{31}H_{30}O_8Na^+$, 553.1833, found 553.1838, error –1 ppm.

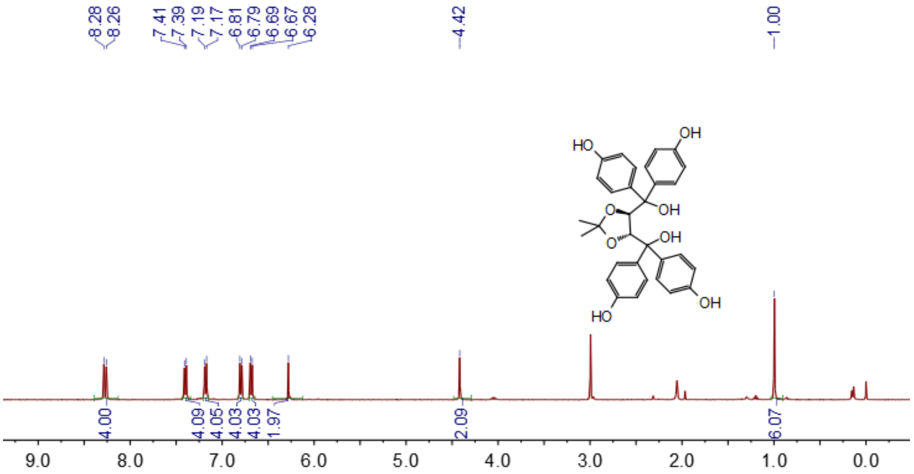


Fig. S7. ^{1}H NMR spectrum (400 MHz, acetone-d_6, 298 K) of **TADDOL-OH**.

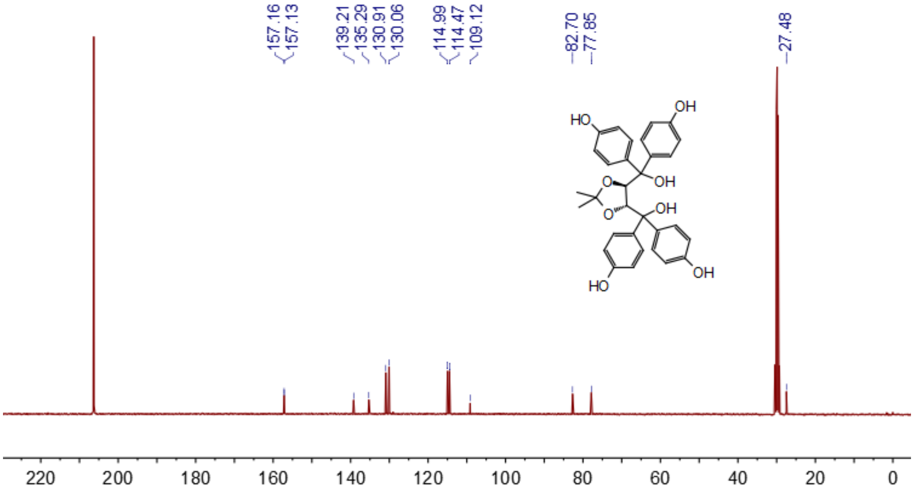


Fig. S8. ^{13}C NMR spectrum (100 MHz, acetone-d_6, 298 K) of **TADDOL-OH**.

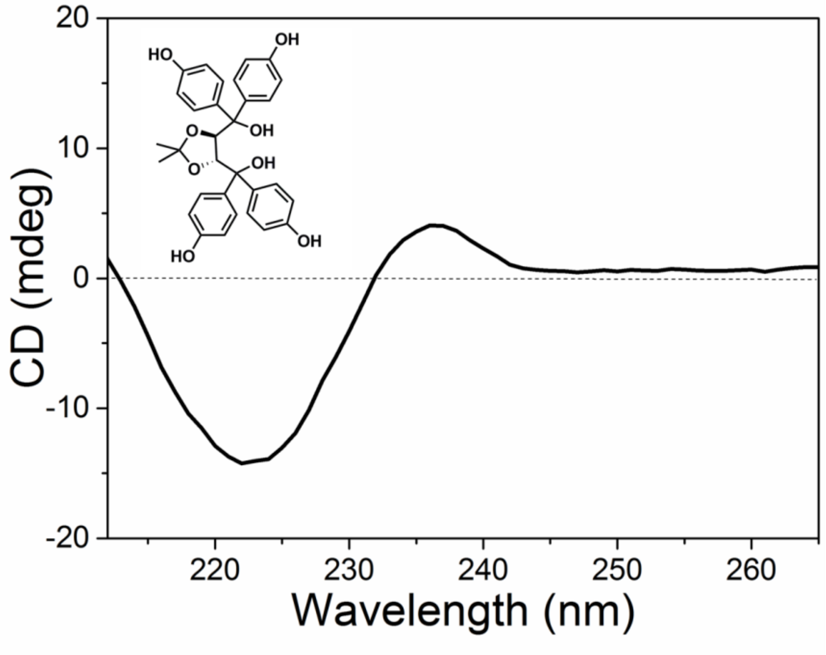


Fig. S9. CD spectrum of **TADDOL-OH** in methanol.

Synthesis of chiral cross-linking organic material **TADP5**: To a solution of **TADDOL-OH** (0.795 g, 1.50 mmol) in 30.0 mL of CH_3CN was added K_2CO_3 (3.00 g, 21.7 mmol) and **DBEP5** (1.00 g, 0.60 mmol). The mixture was stirred under reflux for 3 days. After that, the insoluble solid was filtered. The white solid was washed thoroughly with water, diluted HCl and acetone on ultrasound, and then dried in vacuum. The final product (0.704 g) is white, insoluble powder.

Preparation of **TADP5Ti**: Under protection of argon, **TADP5** (95.0 mg, ~0.140 mmol) was suspended in 1.50 mL of anhydrous toluene with vigorous stirring, and then 41.5 μL (0.140 mmol) of $Ti(O^{i}Pr)_4$ was added *via* syringe. After 4 hours stirring, insoluble solid was filtered, thoroughly washed with anhydrous toluene, and dried in vacuum to obtain a yellow solid. Due to the instability of organic titanate, **TADP5Ti** was susceptible to moisture and should be analyzed instantly.

3. Solid-state ^{13}C HPDEC MAS NMR spectra of TADP5.

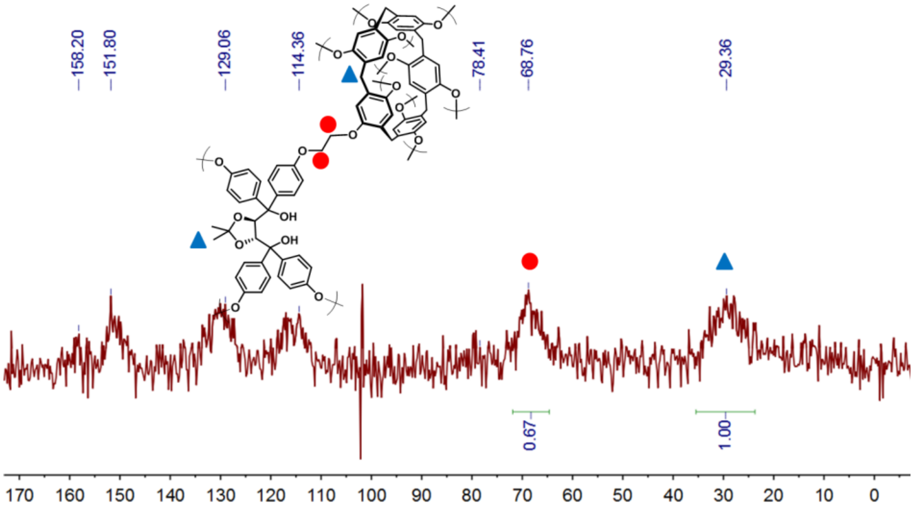


Fig. S10. Solid-state ^{13}C HPDEC MAS NMR spectrum of **TADP5**. The peaks at 29 ppm and 68 ppm were used for integrals. According to our calculation, the ratio between **TADDOL** unit and pillar[5]arene moiety is 7:1.

4. FT-IR spectra

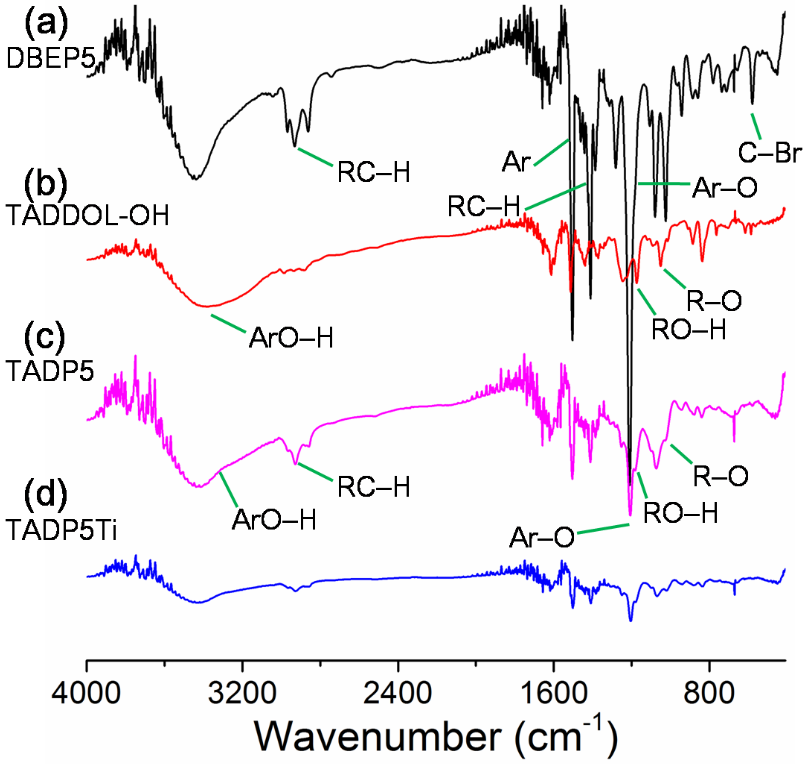


Fig. S11. FT-IR spectra (KBr pellet) of (a) **DBEP5**, (b) **TADDOL-OH**, (c) **TADP5**, and (d) **TADP5Ti**. Significant peaks are marked in the spectra ("Ar" and "R" denote aryl and alkyl groups, respectively.)

5. Thermogravimetric (TG) analysis

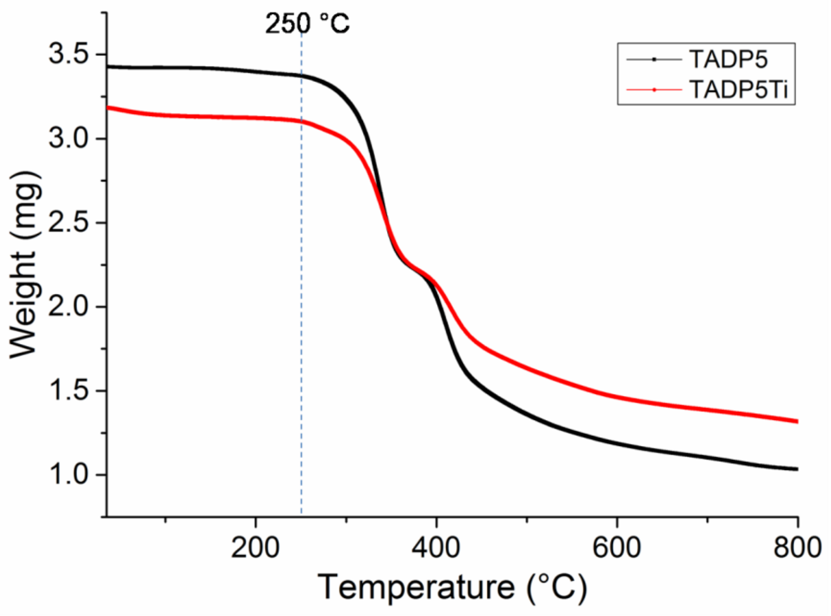


Fig. S12. TG analysis of **TADP5** (black line) and **TADP5Ti** (red line). From the data, we know that both two compounds are stable at 250 ℃.

6. Powder X-ray diffraction (XRD) analysis

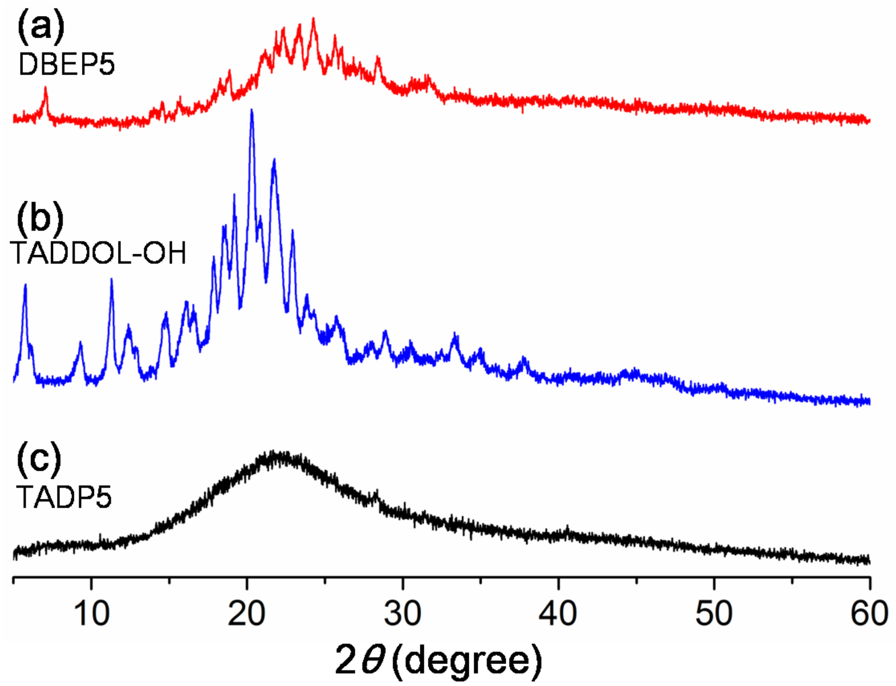
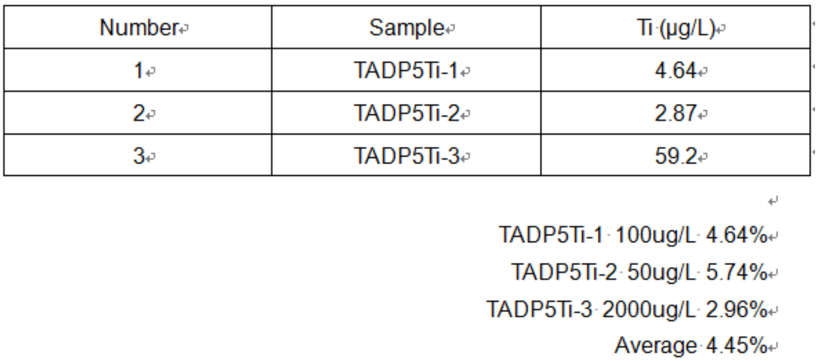


Fig. S13. Powder XRD analysis of (a) **DBEP5**, (b) **TADDOL-OH** and (c) **TADP5**.

7. Inductively coupled plasma mass spectrometry (ICP-MS) analysis

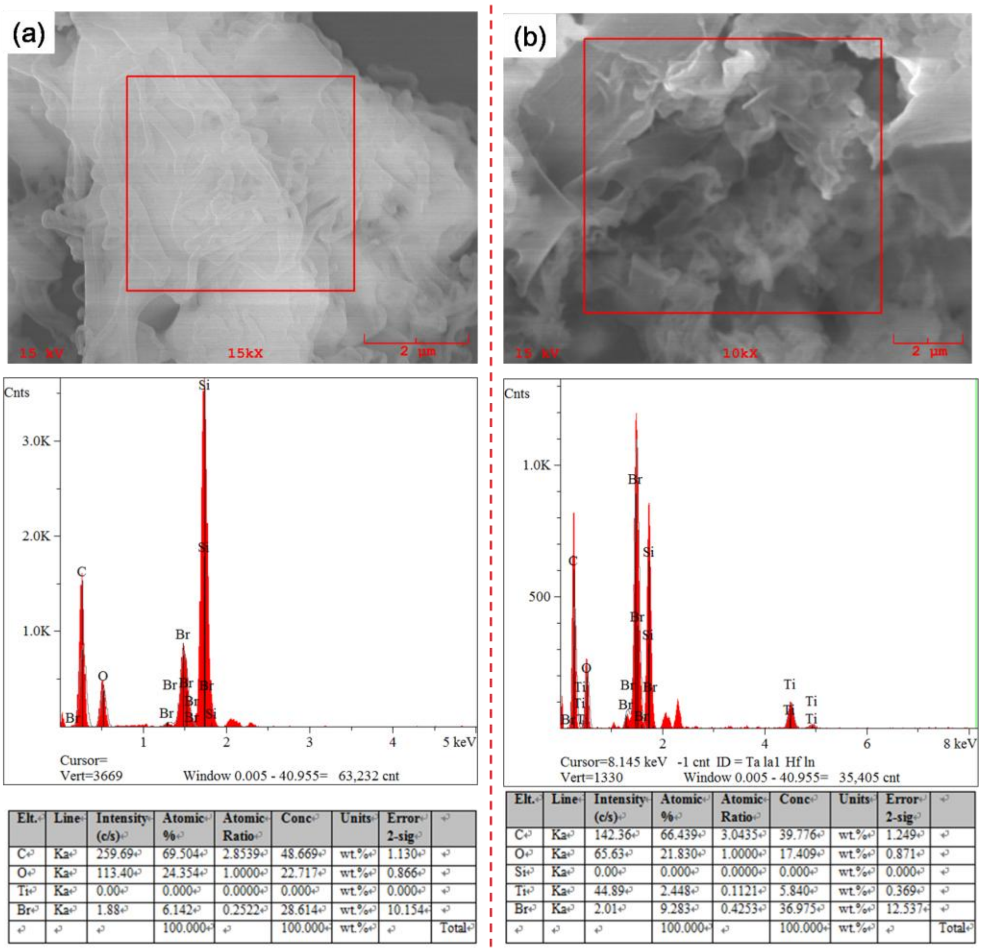


Number	Sample	Ti (μg/L)
1	TADP5Ti-1	4.64
2	TADP5Ti-2	2.87
3	TADP5Ti-3	59.2

TADP5Ti-1 100ug/L 4.64%
TADP5Ti-2 50ug/L 5.74%
TADP5Ti-3 2000ug/L 2.96%
Average 4.45%

Fig. S14. ICP-MS analysis of **TADP5Ti** for evaluating the content of titanium. 1.00 mg of **TADP5Ti** was dissolved in 1.00 mL of pure HNO_3 to form a transparent solution. The solution was diluted to 2000 μg/L, 100 μg/L and 50 μg/L for ICP-MS analysis. The average content of titanium was determined to be 4.45%.

8. Energy dispersive X-ray spectroscopy (EDX) analysis



Elt.	Line	Intensity (c/s)	Atomic %	Atomic Ratio	Conc	Units	Error 2-sig	
C	Ka	259.69	69.504	2.8539	48.669	wt.%	1.130	
O	Ka	113.40	24.354	1.0000	22.717	wt.%	0.866	
Ti	Ka	0.00	0.000	0.0000	0.000	wt.%	0.000	
Br	Ka	1.88	6.142	0.2522	28.614	wt.%	10.154	
			100.000		100.000	wt.%		Total

Elt.	Line	Intensity (c/s)	Atomic %	Atomic Ratio	Conc	Units	Error 2-sig	
C	Ka	142.36	66.439	3.0435	39.776	wt.%	1.249	
O	Ka	65.63	21.830	1.0000	17.409	wt.%	0.871	
Si	Ka	0.00	0.000	0.0000	0.000	wt.%	0.000	
Ti	Ka	44.89	2.448	0.1121	5.840	wt.%	0.369	
Br	Ka	2.01	9.283	0.4253	36.975	wt.%	12.537	
			100.000		100.000	wt.%		Total

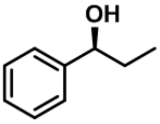
Fig. S15. EDX analysis of (a) **TADP5** and (b) **TADP5Ti**. The SEM images (top) show the areas for EDX analysis, the spectra (middle) show the analyzed elements, and the tables (bottom) show the approximate content of each element. The peaks of titanium indicate the titanium species were successfully loaded within the materials. The peaks of bromine are ascribed to the 2-bromoethyl group in **DBEP5**. The peaks of silicon come from the silicon wafer used in SEM.

9. Asymmetric addition reaction of $ZnEt_2$ to aryl aldehydes

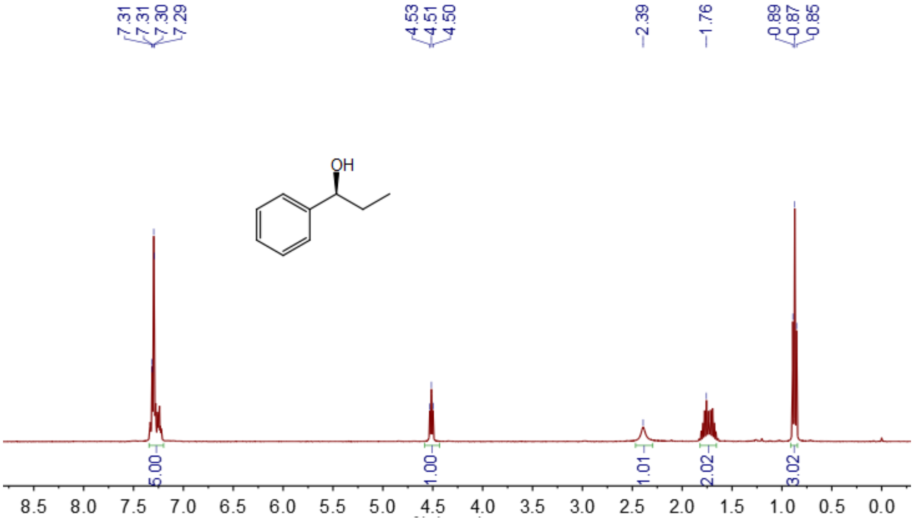
General procedure of asymmetric addition reaction: To a suspension of **TADP5** (95 mg, 0.14 mmol) in 1.5 mL of anhydrous toluene was added $Ti(O^{i}\text{-}Pr)_4$ (0.40 mL, 1.35 mmol) and the reaction mixture was stirred at room temperature for four hours in argon. After cooling to –30 ℃, aryl aldehyde (0.45 mmol) and $ZnEt_2$ (1.0 mL, 1.0 M in hexane, 1.0 mmol) were added carefully *via* a syringe. The mixture was stirred at –30 ℃ for 48 hours. 2.0 mL of diluted HCl and 1.0 mL of diethyl ether were added to quench the reaction. Undissolved polymer was filtered. Filtrate was dried and then purified on flash column chromatography on silica gel using hexane:ethyl acetate = 10:1 as the eluent to obtain pure 1-arylpropan-1-ol. The product was dissolved in isopropanol for chiral HPLC. The structure of product was analyzed by NMR spectroscopy.

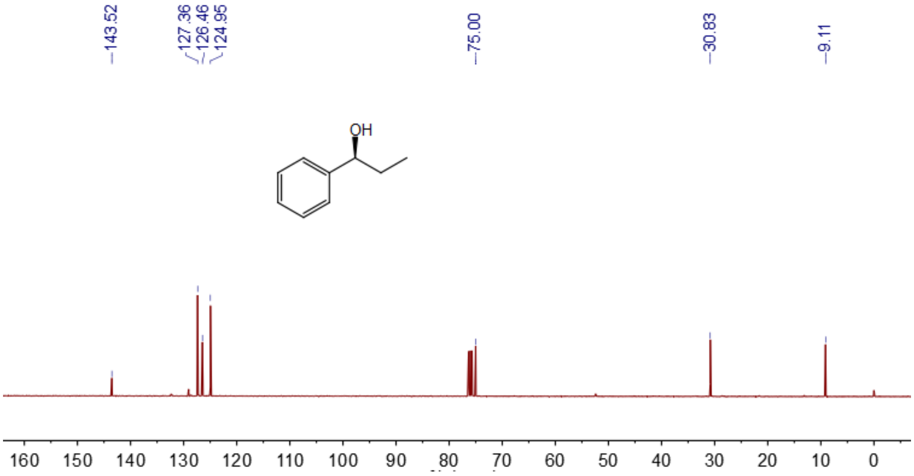
The racemic 1-arylpropan-1-ol was synthesized through a reported method:[S3] Under being catalyzed by 18-crown-6 and KI, a 1:1 mixture of (*R*)- and (*S*)-1-arylpropan-1-ol could be obtained by the addition reaction of $ZnEt_2$ to aryl aldehyde in good yield. The racemic product was used in chiral HPLC for comparison.

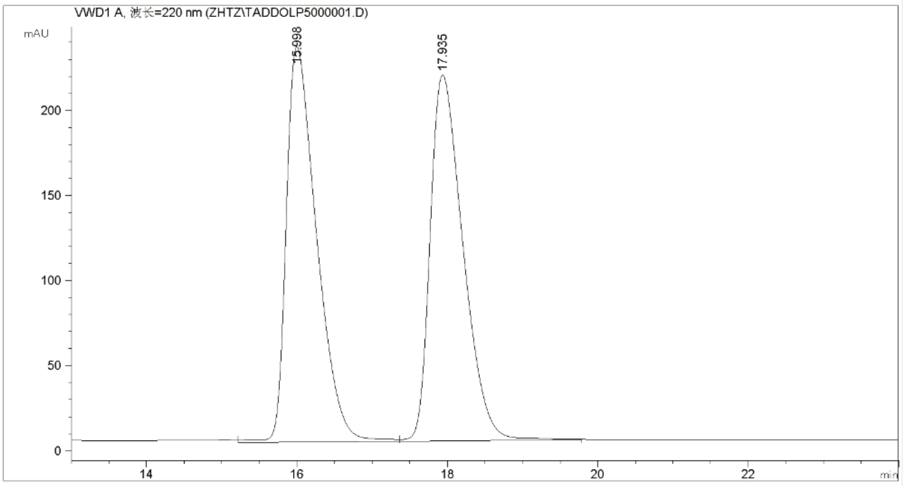
(*S*)-1-phenylpropan-1-ol



Colorless oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ(ppm): 7.30 (dd, *J* = 6.9, 1.2 Hz, 5H), 4.51 (t, *J* = 6.6 Hz, 1H), 2.39 (s, 1H), 1.76 (s, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ(ppm): 143.52, 127.36, 126.46, 124.95, 75.00, 30.83, 9.11. The enantiomeric excess was determined by chiral HPLC with Daicel chiral OD-H column at 220 nm: 25 ℃; hexane: iPrOH = 98:2; flow rate = 1.0 mL/min; *ee* = 94%.







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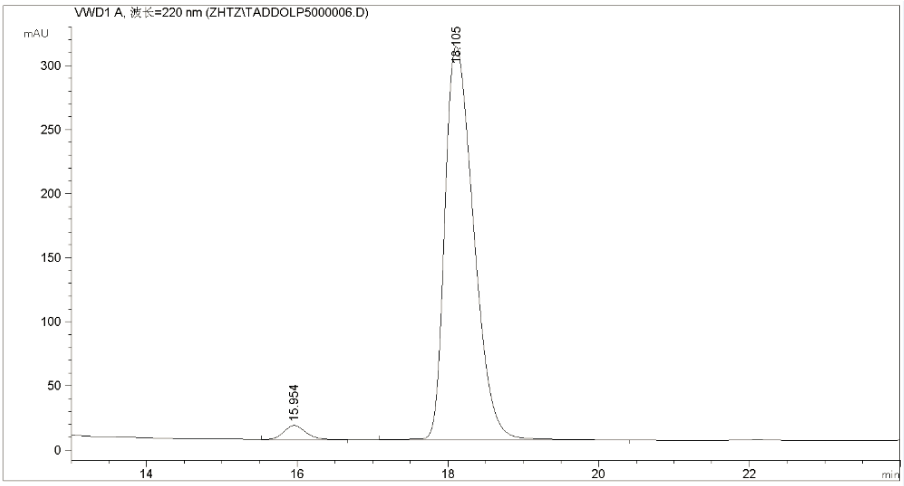

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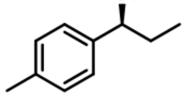
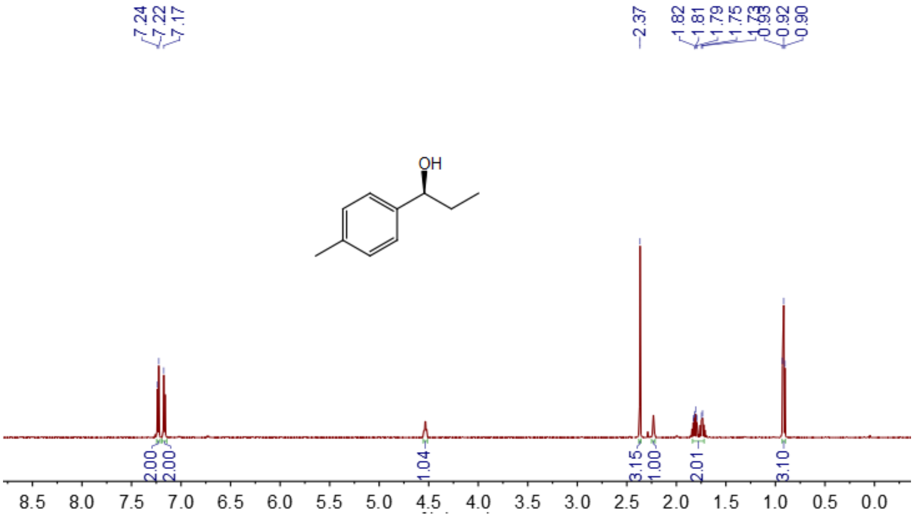
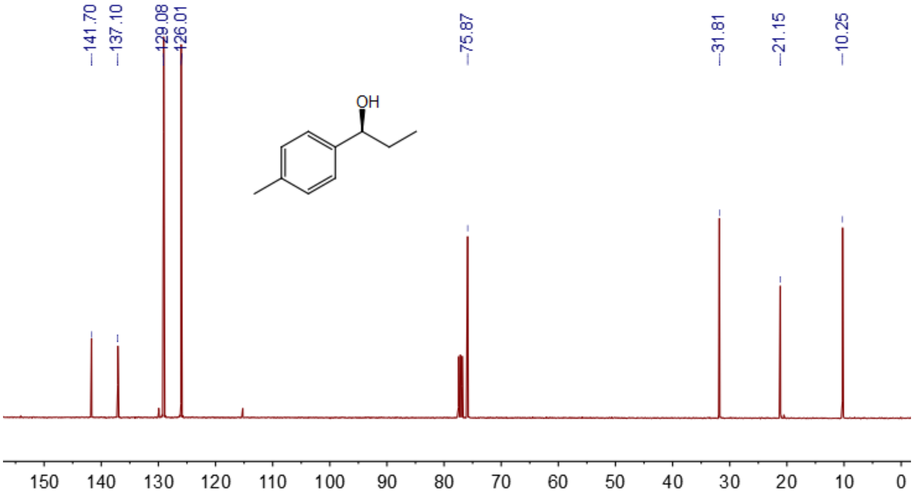
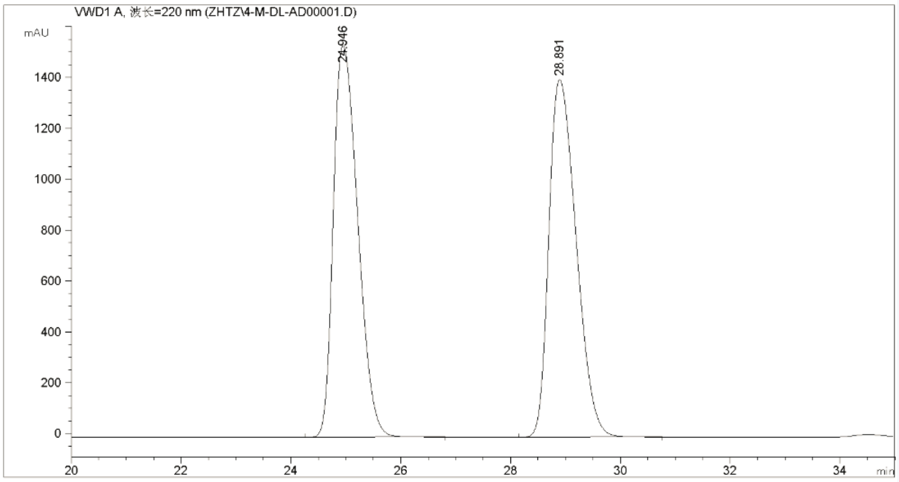
(*S*)-1-*p*-tolylpropan-1-ol



Colorless oil, 91% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 (s, 2H), 4.53 (td, *J* = 6.8, 2.4 Hz, 1H), 2.37 (s, 3H), 2.23 (d, *J* = 2.4 Hz, 1H), 1.84 – 1.72 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ (ppm): 141.70, 137.10, 129.08, 126.01, 75.87, 31.81, 21.15, 10.25. The enantiomeric excess was determined by chiral HPLC with Daicel chiral AD-H column at 220 nm: 25 ℃; hexane:iPrOH = 99:1; flow rate = 1.0 mL/min; *ee* = 84%.







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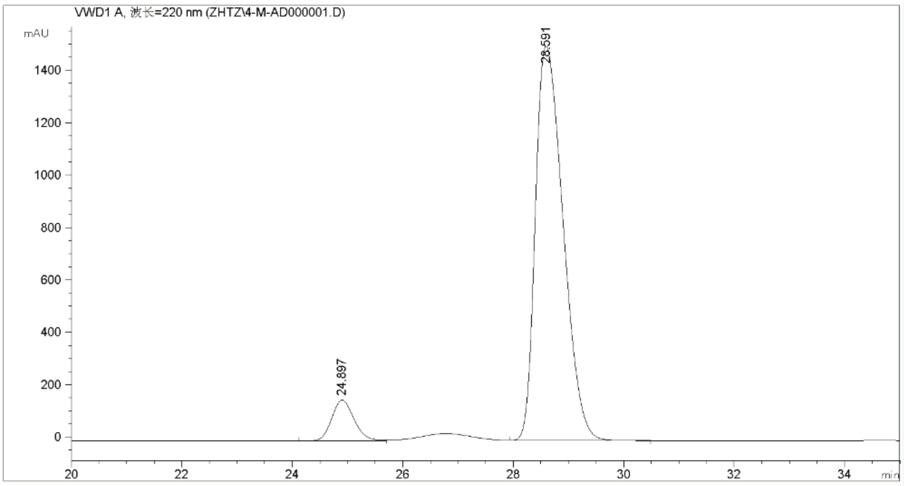

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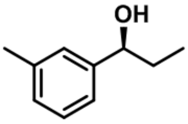
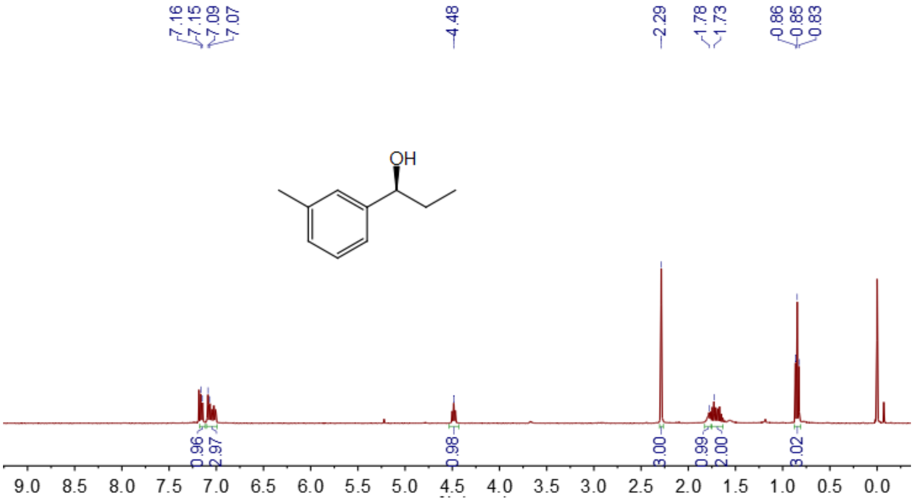
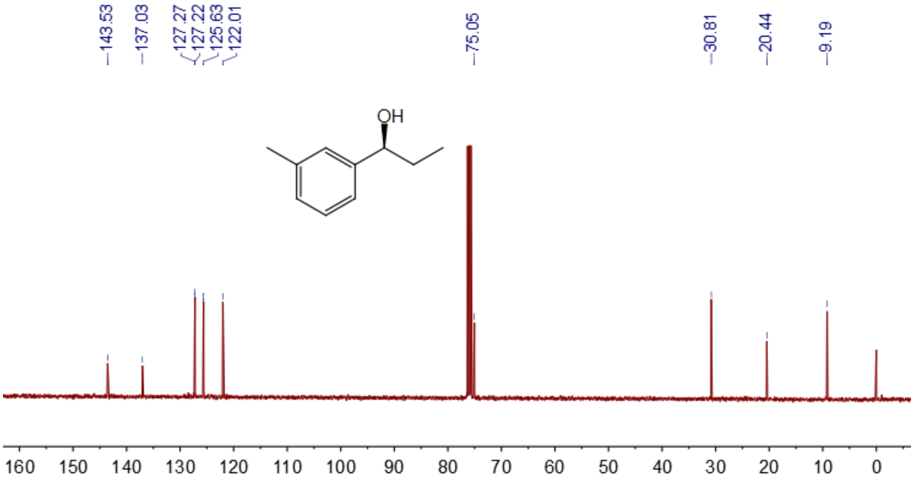
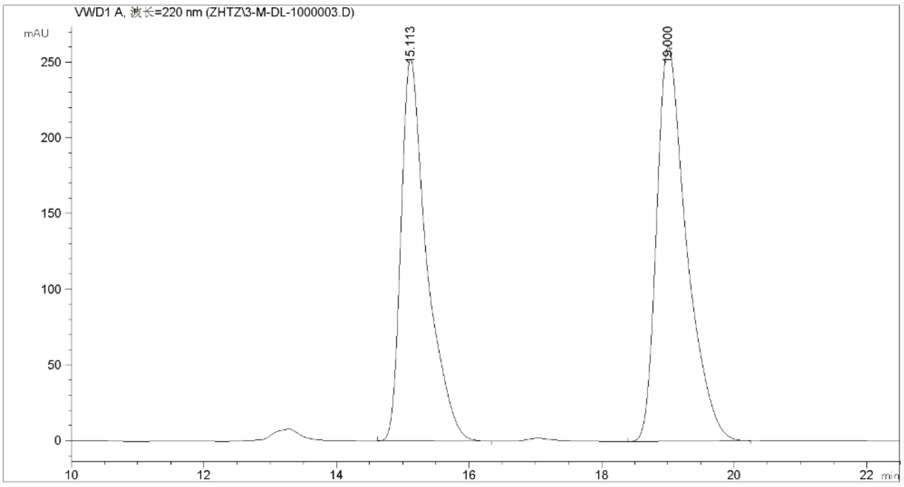


Colorless oil, 89% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 7.15 (d, J = 7.5 Hz, 1H), 7.08 (d, J = 8.6 Hz, 3H), 4.48 (s, 1H), 2.29 (s, 3H), 1.78 (s, 1H), 1.73 (s, 2H), 0.85 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ (ppm): 143.53, 137.03, 127.25, 125.63, 122.01, 75.05, 30.81, 20.44, 9.19. The enantiomeric excess was determined by chiral HPLC with Daicel chiral OD-H column at 220 nm: 25 ℃; hexane:iPrOH = 98:2; flow rate = 0.8 mL/min; *ee* = 88%.







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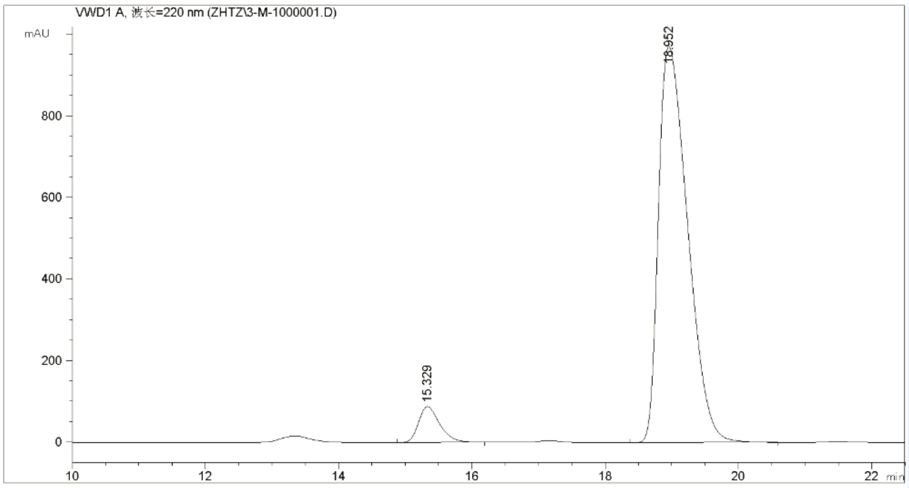
 #    [min]          [min]   mAU     *s     [mAU    ]       %
----|-------|----|-------|----------|----------|--------|
   1   15.113 BB     0.3965 6813.62646   252.41710   45.3552
   2   19.000 BB     0.4672 8209.17090   261.13058   54.6448
```



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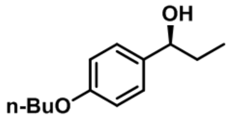
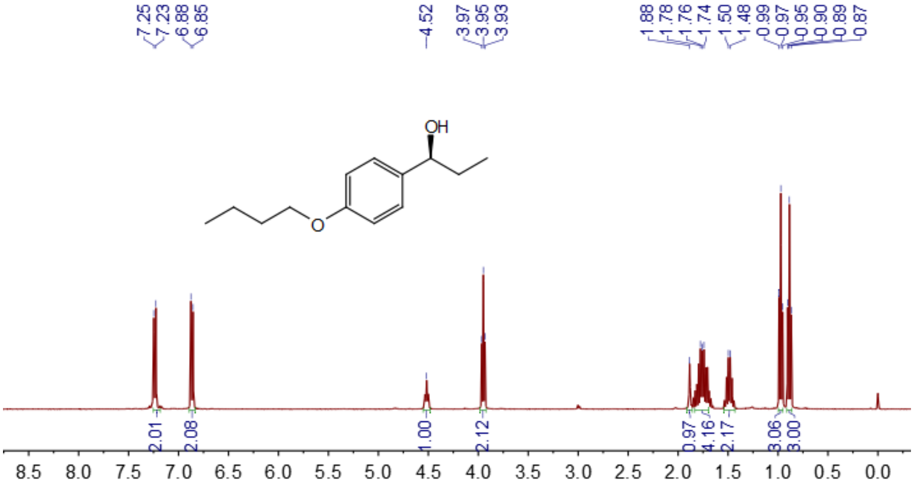
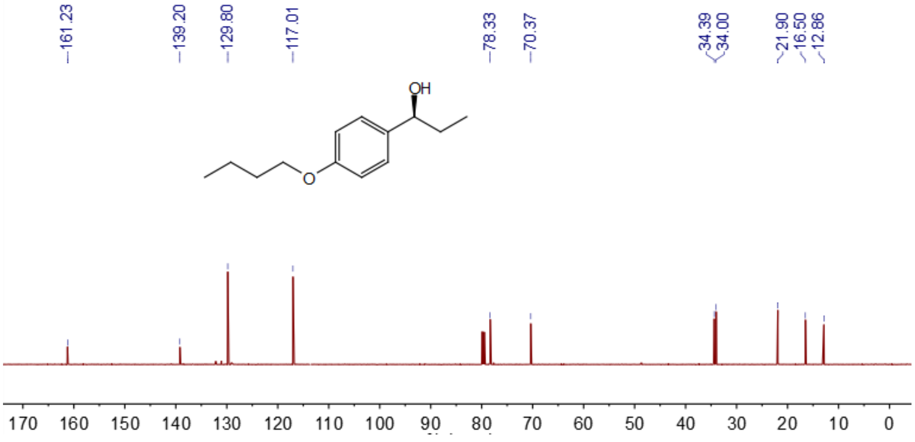
 峰  保留时间  类型   峰宽       峰面积         峰高       峰面积
 #    [min]          [min]   mAU     *s     [mAU    ]       %
----|-------|----|-------|----------|----------|--------|
   1   15.329 BB     0.3351 1942.61987    88.35589    6.1789
   2   18.952 VB     0.4795 2.94967e4    971.42786   93.8211
```

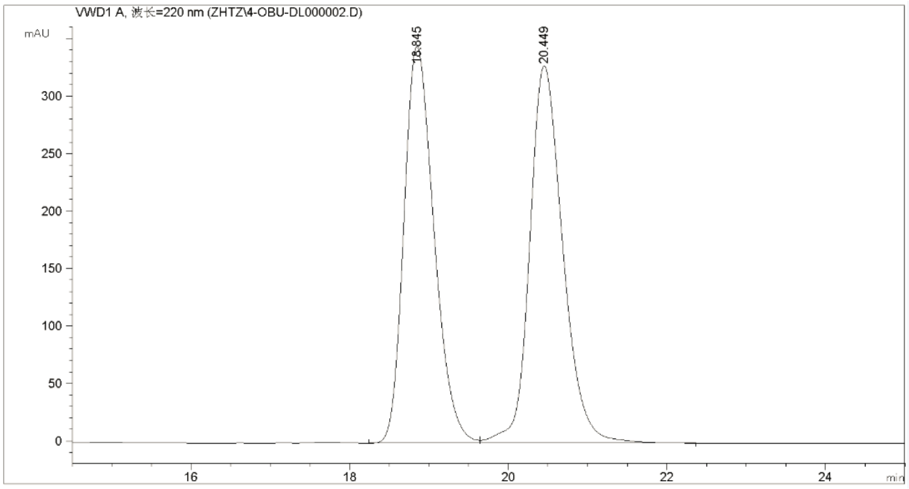
(*S*)-1-(4-butyloxylphenyl) propan-1-ol



Colorless oil, 83% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 7.24 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.52 (s, 1H), 3.95 (t, *J* = 6.5 Hz, 2H), 1.88 (s, 1H), 1.83 – 1.69 (m, 4H), 1.49 (d, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ (ppm): 161.23, 139.20, 129.80, 117.01, 78.33, 70.37, 34.39, 34.00, 21.90, 16.50, 12.86. The enantiomeric excess was determined by chiral HPLC with Daicel chiral OD-H column at 220 nm: 25 ℃; hexane:iPrOH = 98:2; flow rate = 0.8 mL/min; *ee* = 84%.







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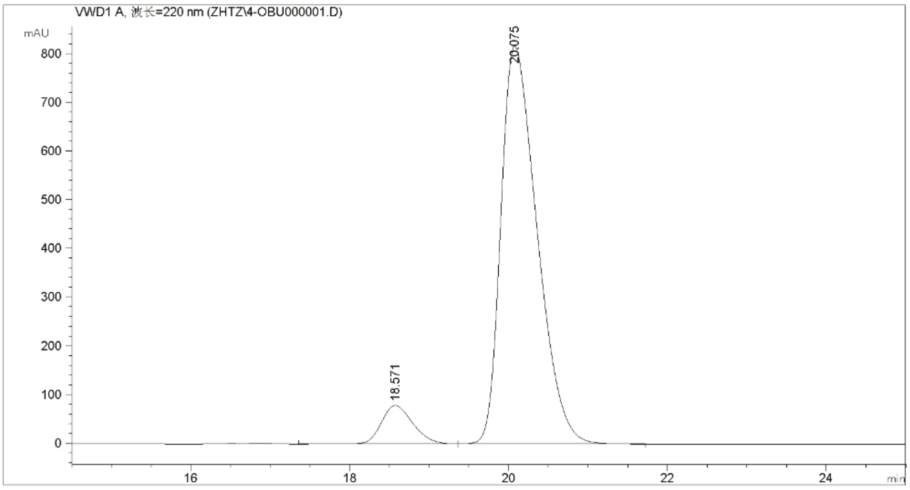
峰  保留时间  类型  峰宽      峰面积        峰高         峰面积
 #    [min]          [min]  mAU    *s    [mAU    ]         %
----|-------|----|-------|----------|----------|--------|
   1  18.845 VV    0.4082 9110.30371  345.36377  48.7475
   2  20.449 VB    0.4448 9578.44043  328.68134  51.2525
```



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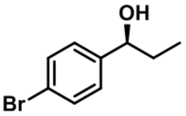
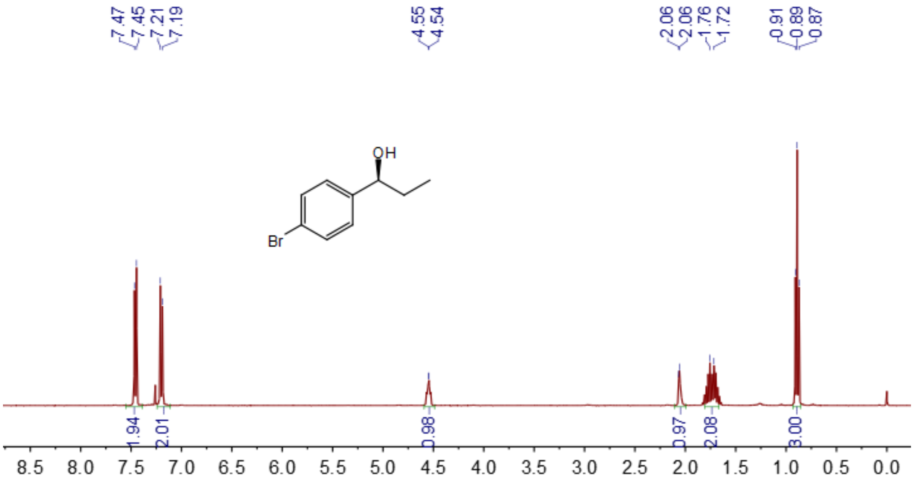
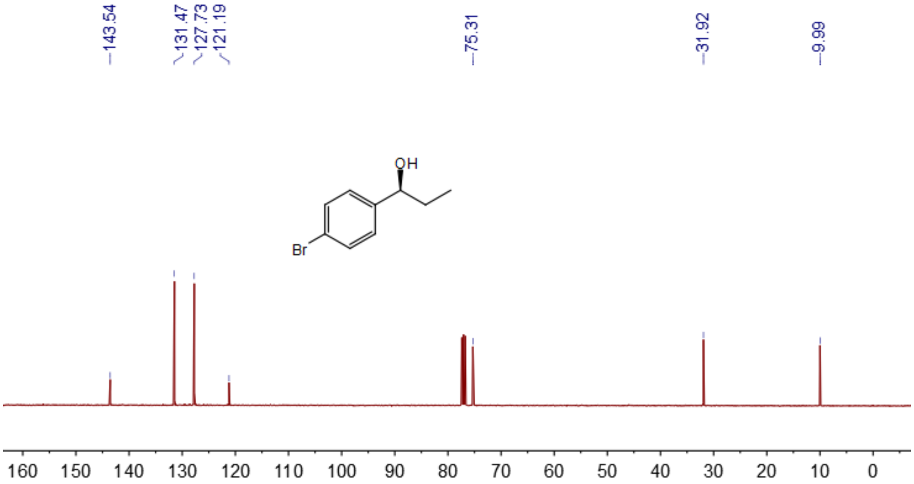
峰  保留时间  类型  峰宽      峰面积        峰高         峰面积
 #    [min]          [min]  mAU    *s    [mAU    ]         %
----|-------|----|-------|----------|----------|--------|
   1  18.571 VV    0.4292 2237.58936   79.76981   7.9465
   2  20.075 VB    0.4892 2.59205e4   817.77545  92.0535
```

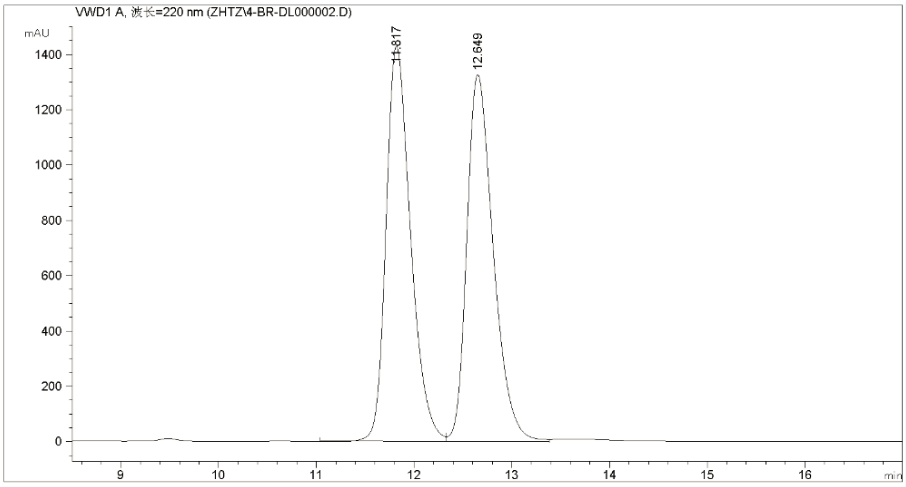
(*S*)-1-(4-bromophenyl) propan-1-ol



Colorless oil, 90% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 7.46 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.55 (d, *J* = 2.7 Hz, 1H), 2.06 (d, *J* = 2.9 Hz, 1H), 1.74 (d, *J* = 16.1 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ (ppm): 143.54, 131.47, 127.73, 121.19, 75.31, 31.92, 9.99. The enantiomeric excess was determined by chiral HPLC with Daicel chiral OD-H column at 220 nm: 25 ℃; hexane:iPrOH = 97:3; flow rate = 1.0 mL/min; *ee* = 88%.







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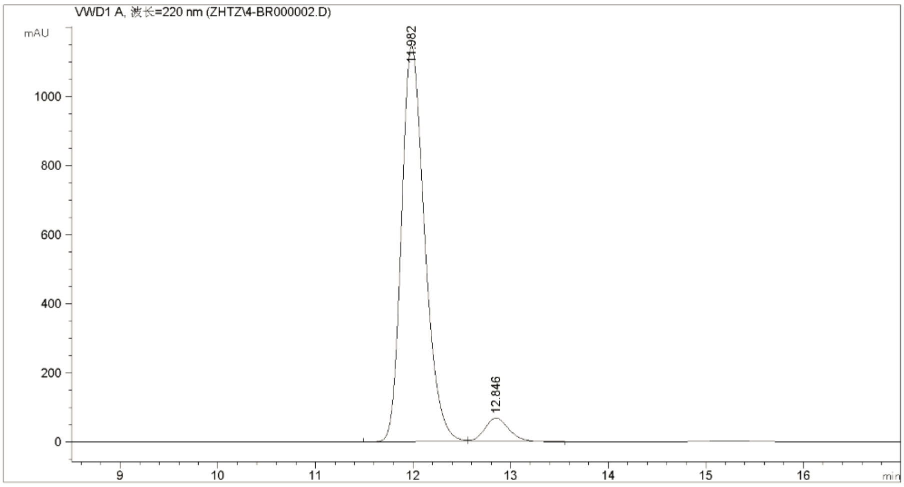
峰  保留时间  类型   峰宽      峰面积        峰高        峰面积
 #    [min]          [min]   mAU    *s    [mAU    ]        %
----|-------|----|-------|----------|----------|--------|
  1   11.817  VV     0.2664 2.49743e4  1429.89087  50.0441
  2   12.649  VV     0.2877 2.49303e4  1326.76965  49.9559
```



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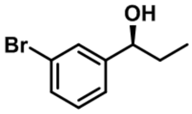
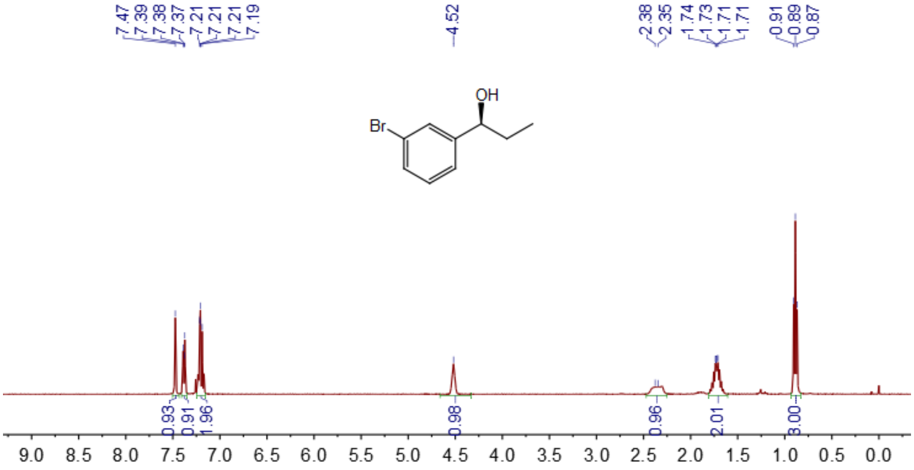
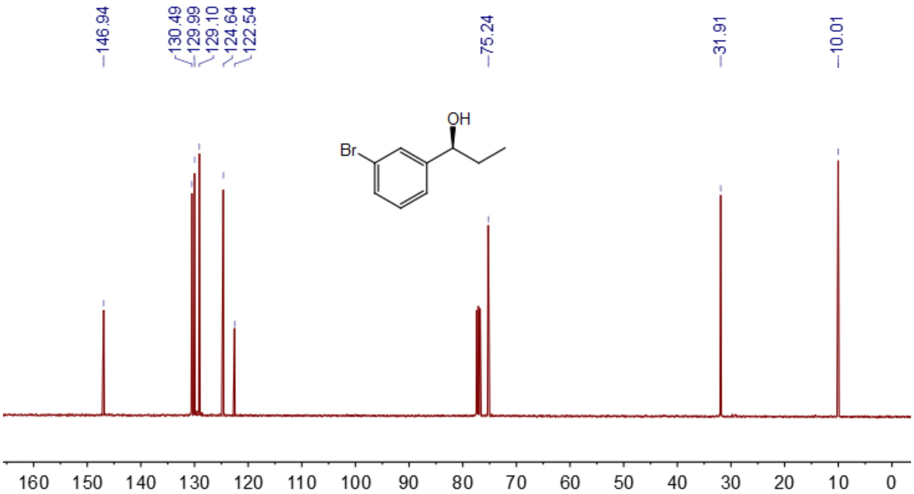
峰 保留时间 类型  峰宽      峰面积       峰高        峰面积
#   [min]        [min]   mAU    *s    [mAU    ]       %
----|-------|----|-------|----------|----------|--------|
  1  11.982 BV    0.2519 1.88946e4  1146.65076  93.9509
  2  12.846 VB    0.2694 1216.54541   69.11926   6.0491
```

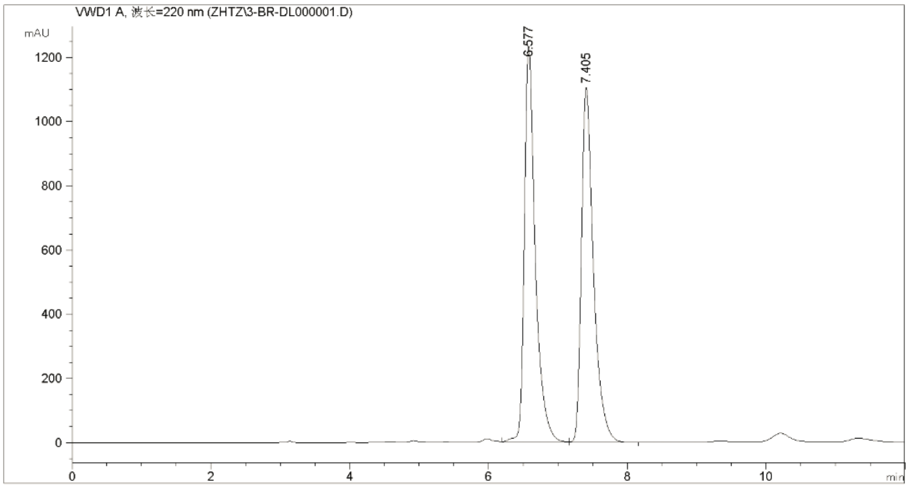
(*S*)-1-(3-bromophenyl) propan-1-ol



Colorless oil, 92% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 7.47 (s, 1H), 7.41 – 7.35 (m, 1H), 7.20 (dd, *J* = 5.9, 4.6 Hz, 2H), 4.52 (s, 1H), 2.36 (d, *J* = 12.3 Hz, 1H), 1.72 (dd, *J* = 9.0, 1.4 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ (ppm): 146.94, 130.49, 129.99, 129.10, 124.64, 122.54, 75.24, 31.91, 10.01. The enantiomeric excess was determined by chiral HPLC with Daicel chiral OD-H column at 220 nm: 25 ℃; hexane:iPrOH = 97:3; flow rate = 1.0 mL/min; *ee* = 95%.







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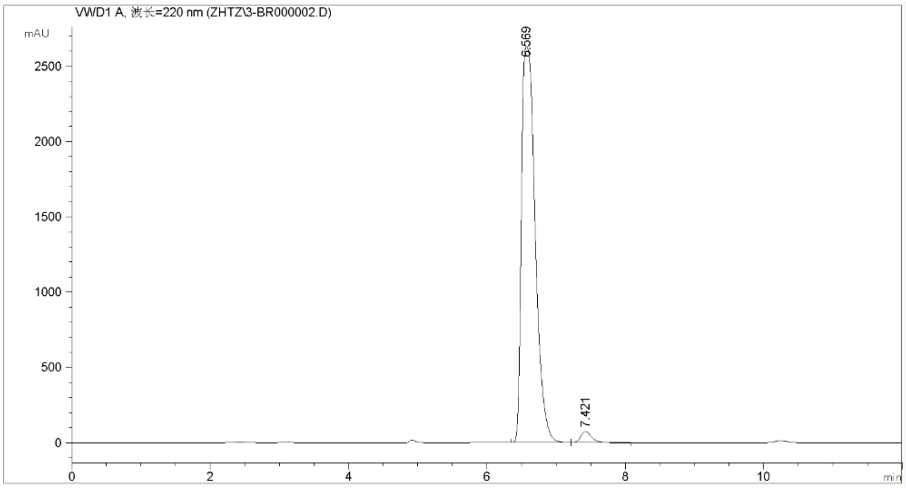
峰  保留时间  类型   峰宽       峰面积        峰高         峰面积
 #   [min]          [min]    mAU     *s    [mAU     ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.577  VV    0.1631  1.35679e4  1235.32275  50.3970
   2   7.405  VB    0.1816  1.33541e4  1106.50684  49.6030
```



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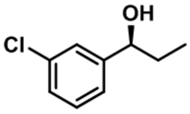
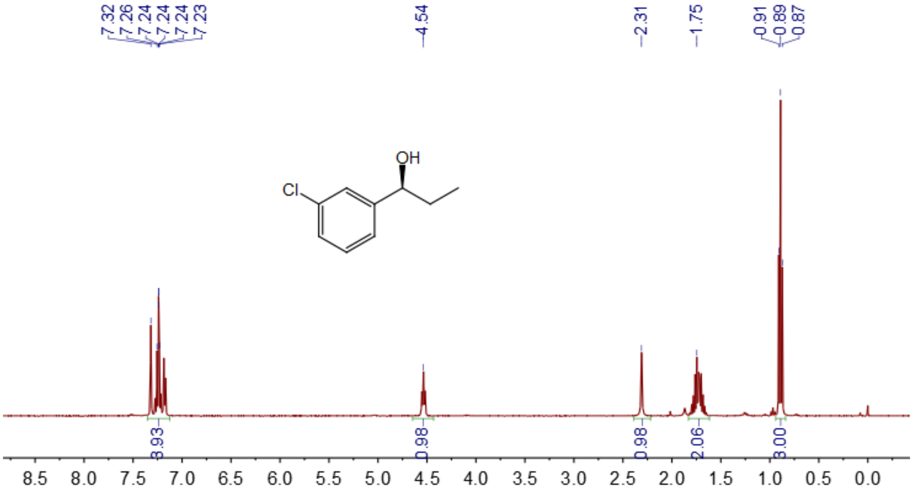
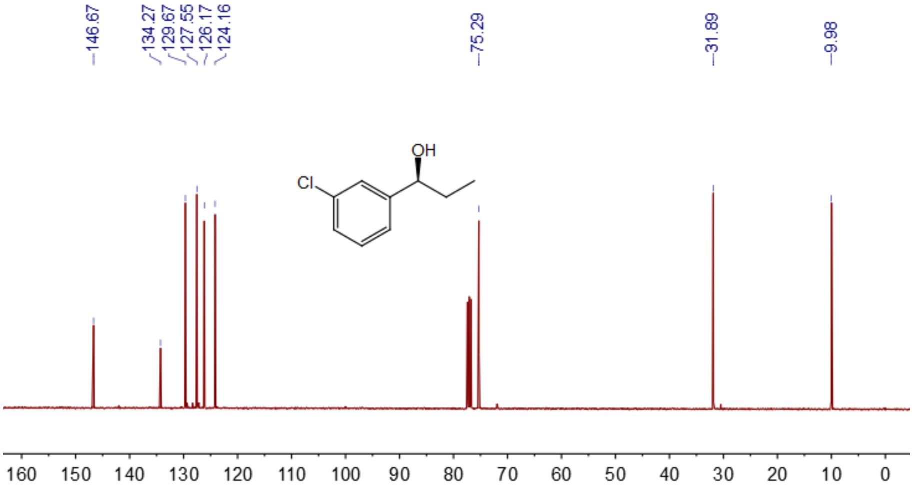
峰  保留时间  类型   峰宽       峰面积        峰高         峰面积
 #   [min]          [min]    mAU     *s    [mAU     ]      %
----|-------|----|-------|----------|----------|--------|
   1   6.569  VV    0.2147  3.63080e4  2633.29858  97.6278
   2   7.421  VB    0.1725  882.21826    76.46769   2.3722
```

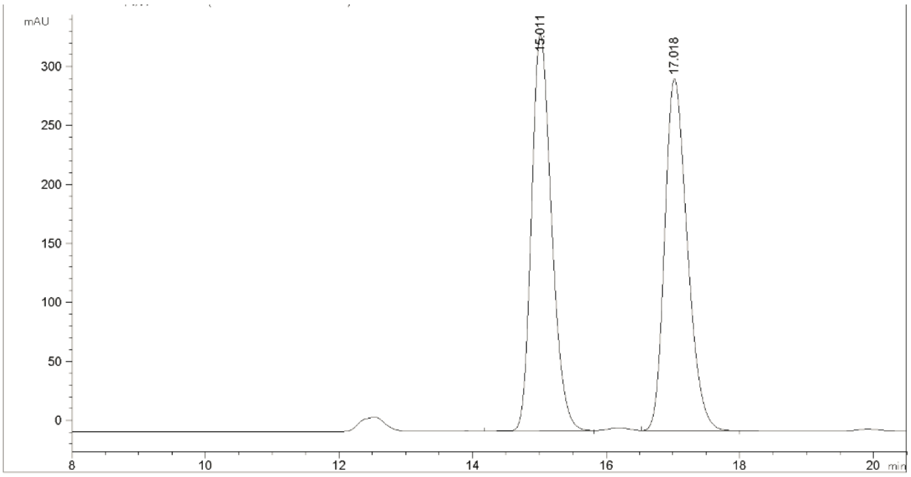
(*S*)-1-(3-chlorophenyl) propan-1-ol



Colorless oil, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.35–7.13 (m, 4H), 4.54 (s, 1H), 2.31 (s, 1H), 1.75 (s, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 146.67, 134.27, 129.67, 127.55, 126.17, 124.16, 75.29, 31.89, 9.98. The enantiomeric excess was determined by chiral HPLC with Daicel chiral OD-H column at 220 nm: 25 ℃; hexane:iPrOH = 98:2; flow rate = 1.0 mL/min; *ee* = 93%.







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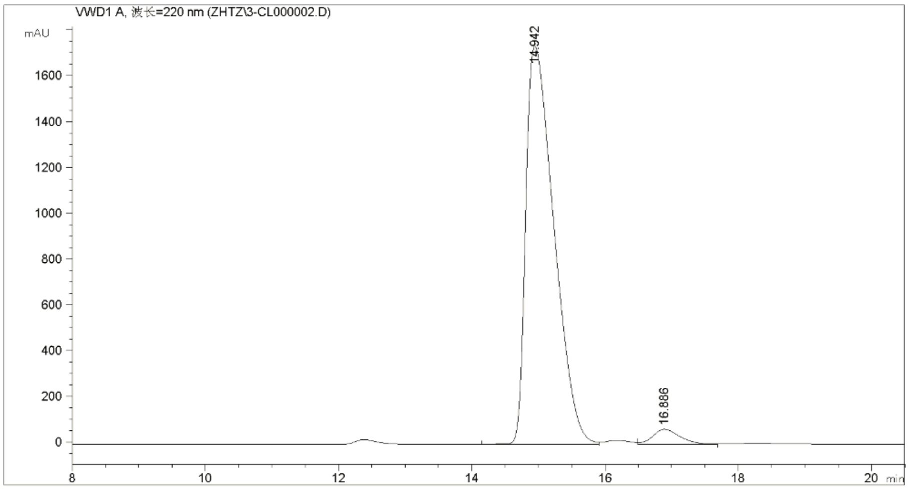
峰  保留时间  类型   峰宽       峰面积        峰高         峰面积
 #    [min]          [min]   mAU    *s    [mAU    ]        %
----|-------|----|-------|----------|----------|--------|
   1  15.011 VV     0.3218 7055.92920  336.49625  50.0311
   2  17.018 VB     0.3626 7047.16016  298.71158  49.9689
```



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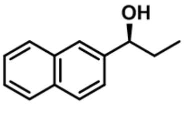
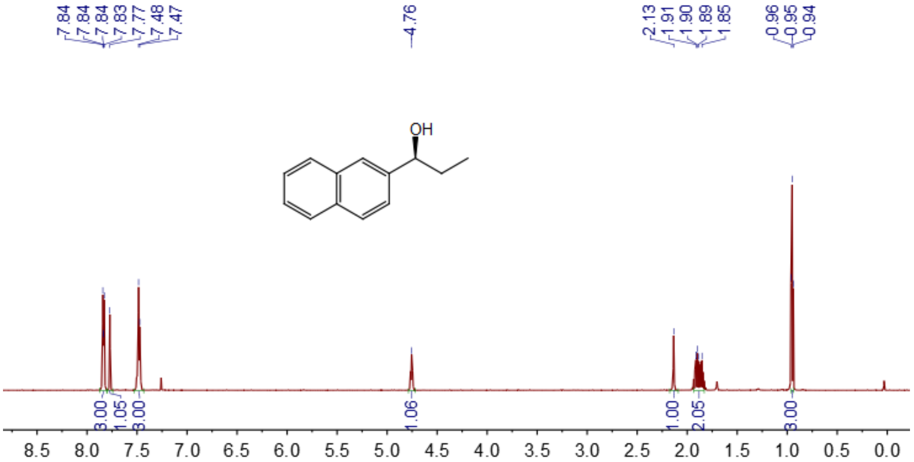
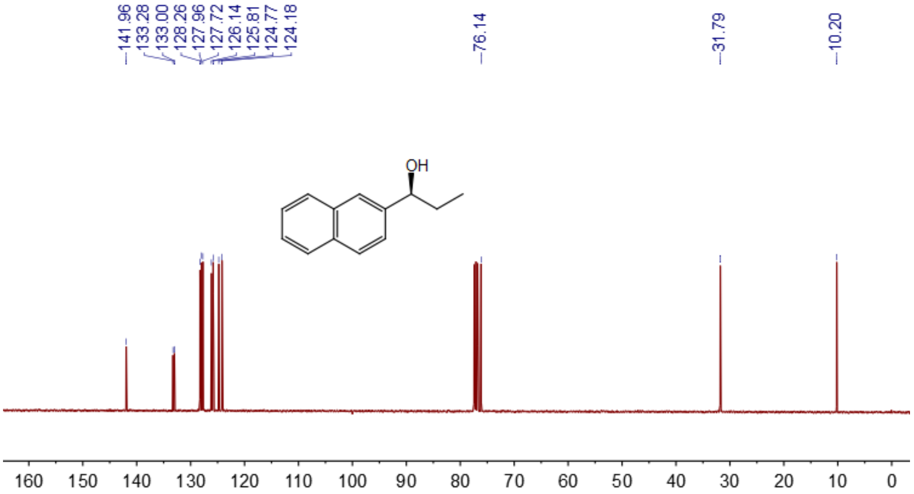
峰  保留时间  类型   峰宽       峰面积        峰高         峰面积
 #    [min]          [min]   mAU    *s    [mAU    ]        %
----|-------|----|-------|----------|----------|--------|
   1  14.942 VV     0.4523 5.09194e4 1738.98767  96.4366
   2  16.886 VB     0.4244 1881.48926   66.27860   3.5634
```

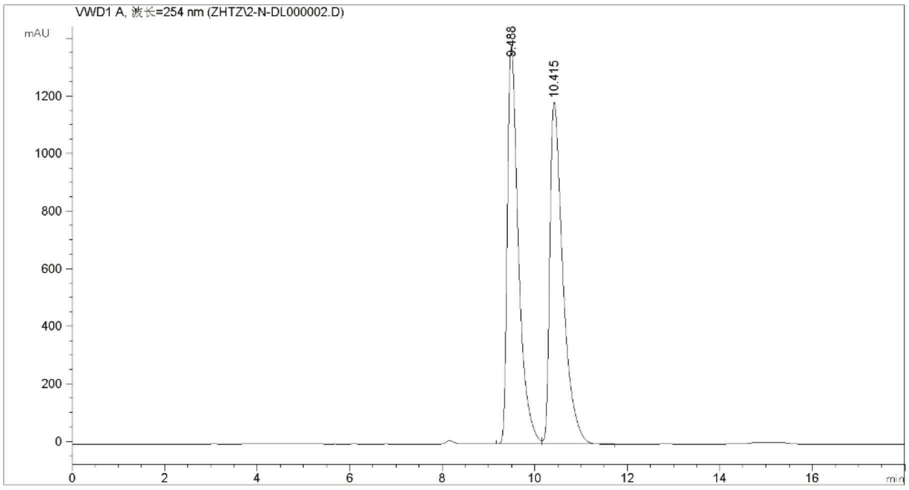
(*S*)- 1-(naphthalen-2-yl) propan-1-ol



Yellow solid, 92% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 7.84 (dd, *J* = 4.8, 3.6 Hz, 3H), 7.77 (s, 1H), 7.48 (d, *J* = 7.0 Hz, 3H), 4.76 (s, 1H), 2.13 (s, 1H), 1.89 (dd, *J* = 21.6, 14.3 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ (ppm): 141.96, 133.28, 133.00, 128.26, 127.96, 127.72, 126.14, 125.81, 124.77, 124.18, 76.14, 31.79, 10.20. The enantiomeric excess was determined by chiral HPLC with Daicel chiral OD-H column at 254 nm: 25 ℃; hexane:iPrOH = 90:10; flow rate = 1.0 mL/min; *ee* = 96%.







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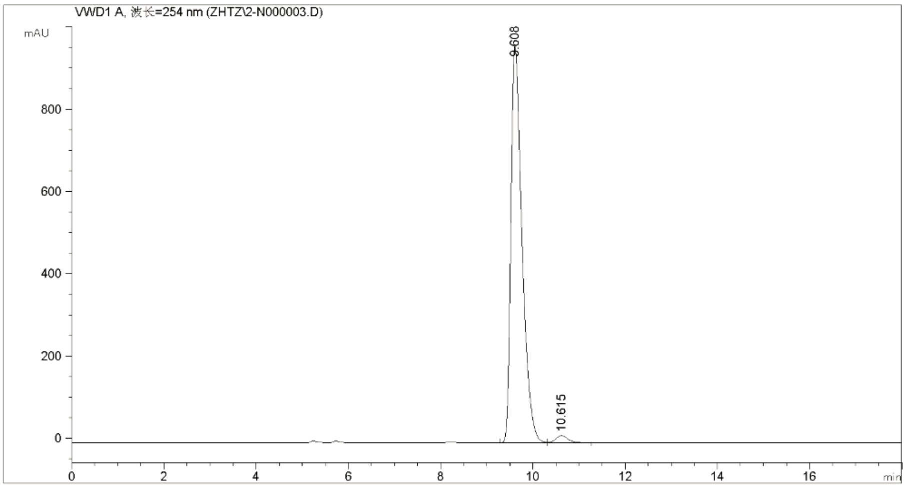
 峰  保留时间  类型   峰宽      峰面积       峰高       峰面积
 #    [min]          [min]   mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.488 VV     0.2524 2.31985e4 1383.44226 49.8235
   2  10.415 VB     0.2946 2.33628e4 1189.62500 50.1765
```



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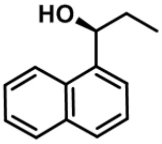
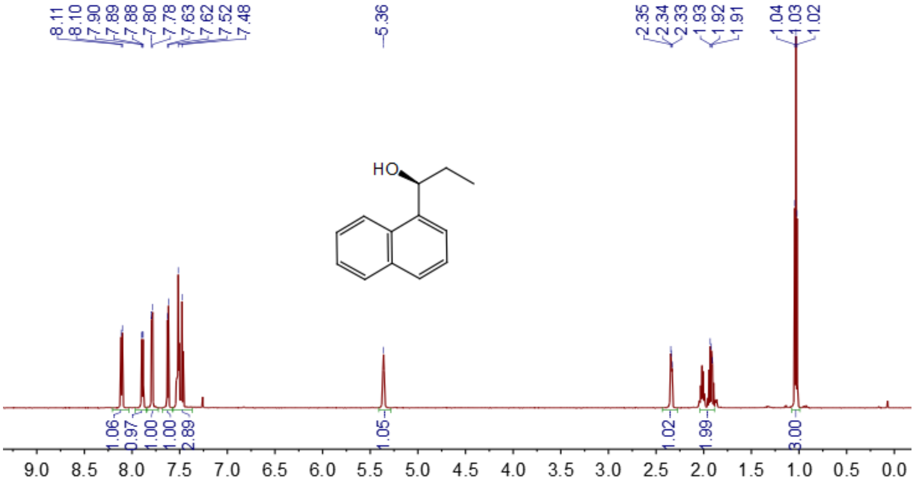
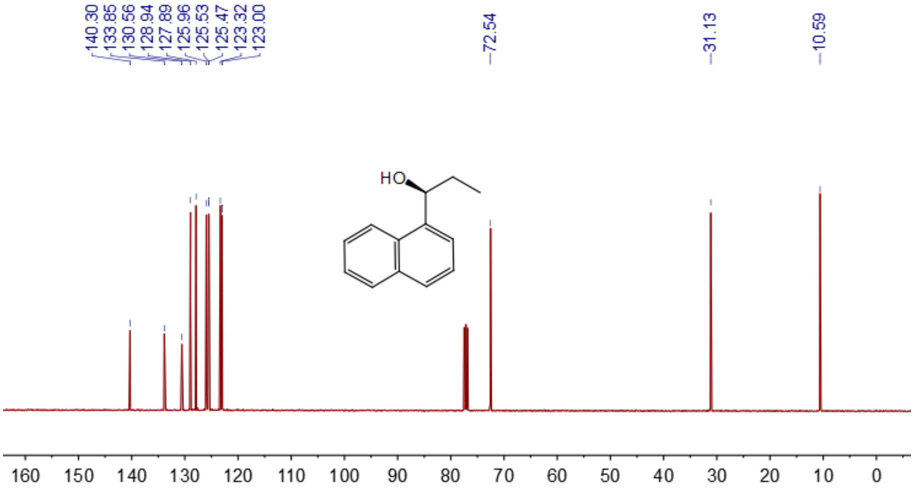
峰  保留时间 类型  峰宽      峰面积       峰高        峰面积
 #   [min]        [min]  mAU    *s    [mAU    ]        %
----|-------|----|-------|----------|----------|--------|
  1    9.608 BV    0.2535 1.61427e4   964.41589  98.0278
  2   10.615 VB    0.2798  324.77551   17.56066   1.9722
```

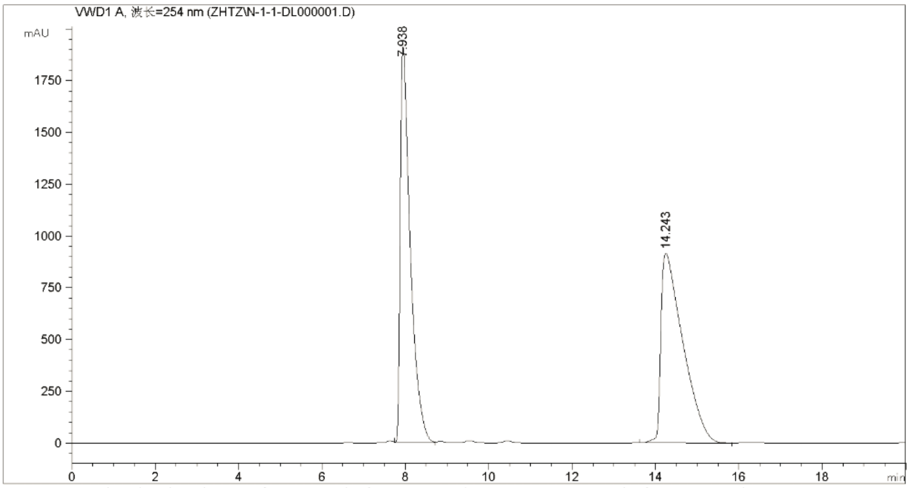
(*S*)- 1-(naphthalen-1-yl) propan-1-ol



Yellow oil, 85% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 8.11 (d, J = 8.0 Hz, 1H), 7.97–7.84 (m, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 7.1 Hz, 1H), 7.50 (d, J = 23.7 Hz, 3H), 5.36 (s, 1H), 2.44–2.27 (m, 1H), 2.04–1.89 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ (ppm): 140.30, 133.85, 130.56, 128.94, 127.89, 125.96, 125.50 (d, J = 6.0 Hz), 123.32, 123.00, 72.54, 31.13, 10.59. The enantiomeric excess was determined by chiral HPLC with Daicel chiral OD-H column at 254 nm: 25 ℃; hexane:iPrOH = 90:10; flow rate = 1.0 mL/min; *ee* = 86%.







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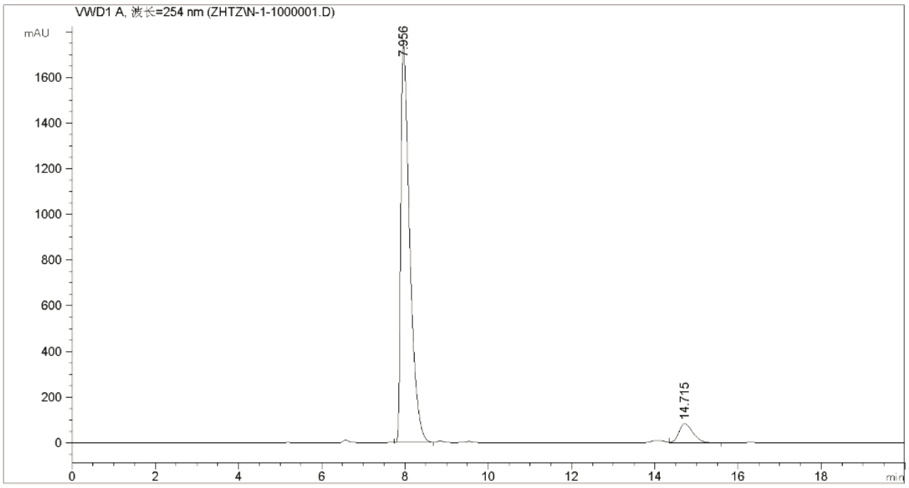
峰  保留时间  类型   峰宽      峰面积       峰高        峰面积
 #   [min]          [min]   mAU    *s    [mAU    ]      %
----|--------|----|-------|----------|----------|--------|
  1    7.938  VV    0.2488 3.22866e4  1917.72559  48.9328
  2   14.243  VB    0.5260 3.36949e4   917.52094  51.0672
```



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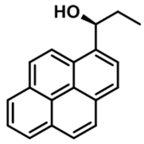
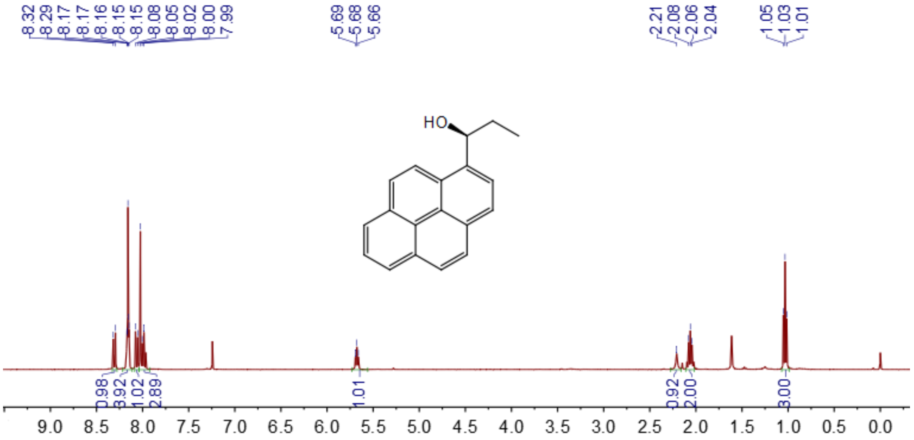
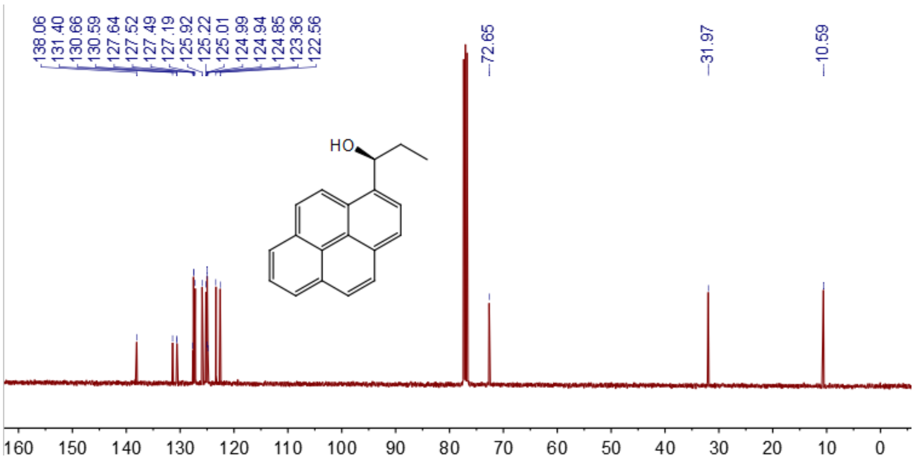
峰  保留时间  类型   峰宽      峰面积       峰高        峰面积
 #   [min]          [min]   mAU    *s    [mAU    ]      %
----|--------|----|-------|----------|----------|--------|
  1    7.956  VV    0.2265 2.61583e4  1738.85535  92.9302
  2   14.715  VB    0.3666 1990.03064   83.57822   7.0698
```

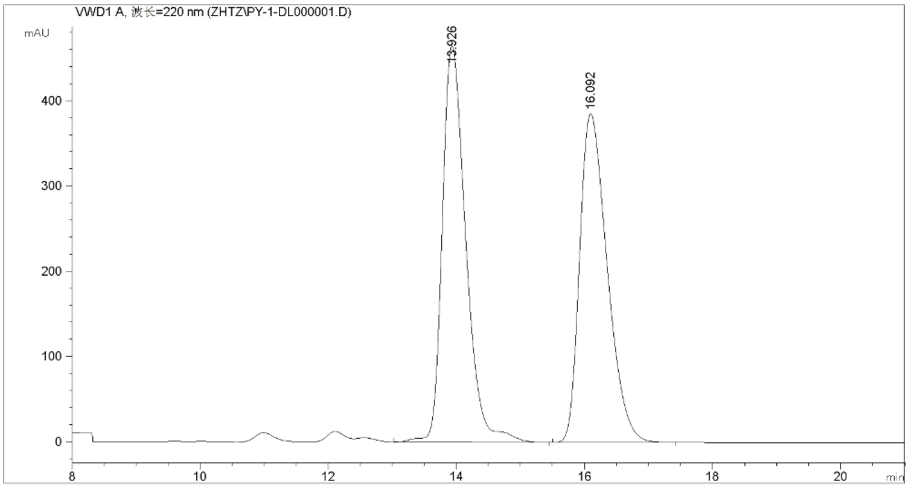
(*S*)-1-(pyren-1-yl) propan-1-ol



Yellow solid, 81% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 8.31 (d, J = 9.3 Hz, 1H), 8.22–8.11 (m, 4H), 8.07 (d, J = 9.3 Hz, 1H), 8.04–7.92 (m, 3H), 5.68 (t, J = 6.4 Hz, 1H), 2.21 (s, 1H), 2.11–2.02 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ (ppm): 138.06, 131.40, 130.63, 127.55, 127.19, 125.92, 125.22, 124.95, 123.36, 122.56, 72.65, 31.97, 10.59. The enantiomeric excess was determined by chiral HPLC with Daicel chiral OD-H column at 220 nm: 25 ℃; hexane:iPrOH = 90:10; flow rate = 1.0 mL/min; *ee* = 82%.







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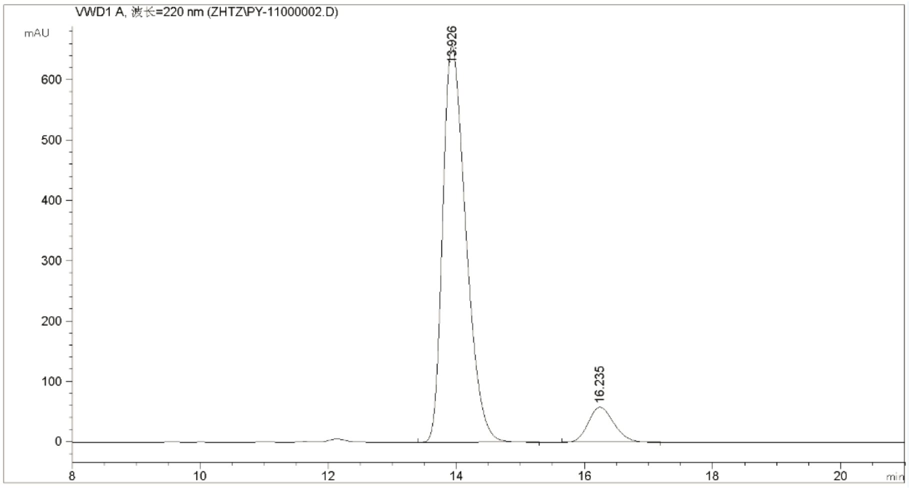
峰  保留时间  类型   峰宽        峰面积        峰高        峰面积
 #    [min]          [min]   mAU    *s    [mAU    ]         %
----|-------|----|-------|----------|----------|--------|
   1  13.926 VB    0.3910 1.18679e4    464.95300  50.7225
   2  16.092 BB    0.4622 1.15298e4    385.78293  49.2775
```



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峰  保留时间  类型   峰宽        峰面积        峰高        峰面积
 #    [min]          [min]   mAU    *s    [mAU    ]         %
----|-------|----|-------|----------|----------|--------|
   1  13.926 BB    0.3896 1.65413e4    657.54730  90.9713
   2  16.235 BB    0.4379 1641.69214    58.26885   9.0287
```

8. Recycle experiments of TADP5.

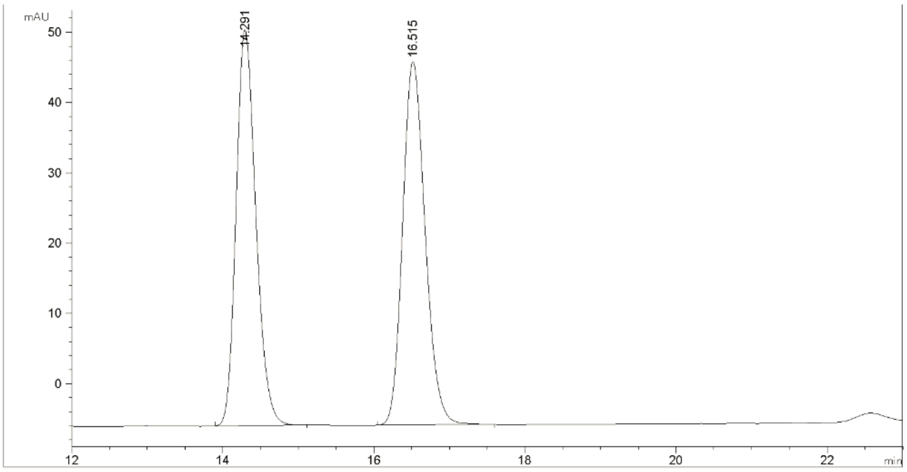
General procedure of recycle experiments: After the reaction was quenched by diluted HCl and ethyl ether, the insoluble solid was filtered. The solid was washed thoroughly with diluted HCl, acetone and toluene to eliminate metal salts or organic residuals, followed by dried in vacuum. The dried solid was reloaded with titanate in a new run. After each run, the product was isolated through column chromatography and dissolved in isopropanol for chiral HPLC analysis. The results were summarized as follows.

Table S1. Evaluation of recyclability of **TADP5**.

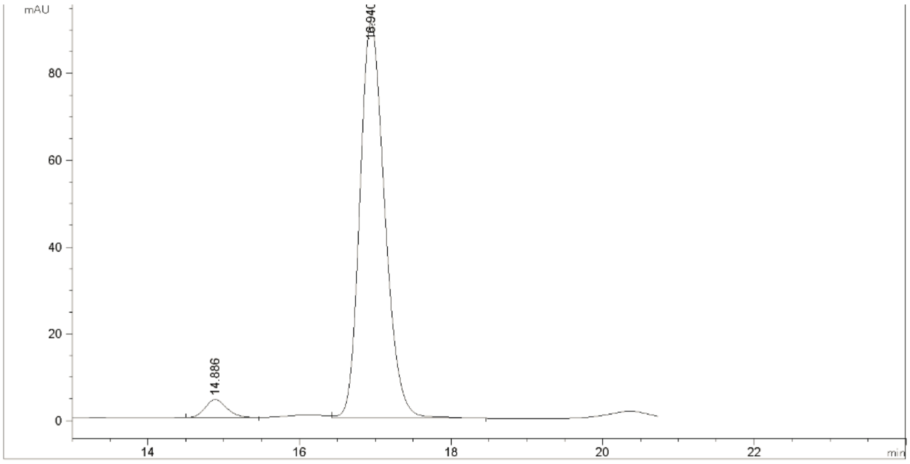
Run[a]	Yield[b] [%]	*ee*[c] [%]
1	88	94
2	89	92
3	85	89
4	85	92
5	83	91
6	80	85

[a] Reaction condition is the same as the general condition. [b] Isolated yield. [c] Determined by chiral HPLC.

Chiral HPLC data of each run: Daicel chiral OD-H column at 220 nm; 28 ℃; hexane:iPrOH = 98:2; flow rate = 1.0 mL/min.



```
峰  保留时间 类型   峰宽       峰面积        峰高       峰面积
 #   [min]         [min]   mAU    *s    [mAU    ]       %
----|-------|----|-------|----------|----------|--------|
   1  14.291 BB     0.2793 1025.23962   56.33960  48.8735
   2  16.515 BB     0.3206 1072.50220   51.71668  51.1265
```



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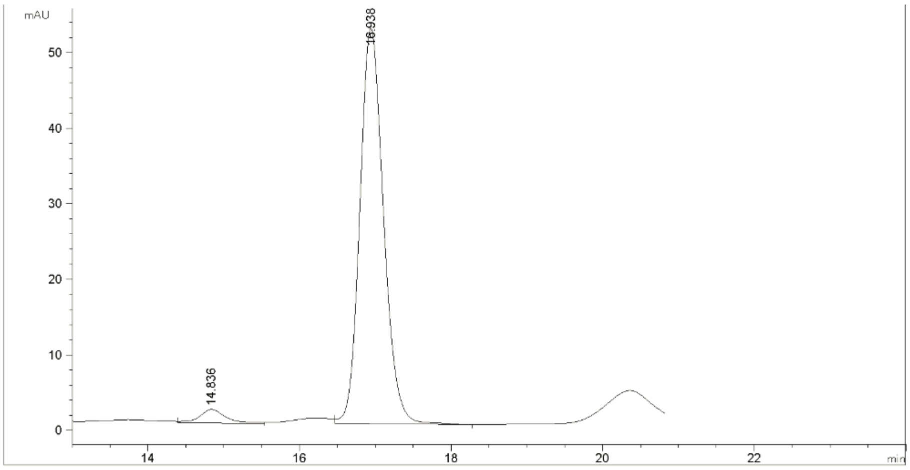
峰  保留时间  类型   峰宽       峰面积          峰高        峰面积
 #    [min]          [min]   mAU    *s    [mAU    ]        %
----|-------|----|-------|----------|----------|--------|
  1  14.886 BV     0.3124   86.89630    4.23138   3.9986
  2  16.940 VB     0.3544 2086.24976   91.12978  96.0014
```



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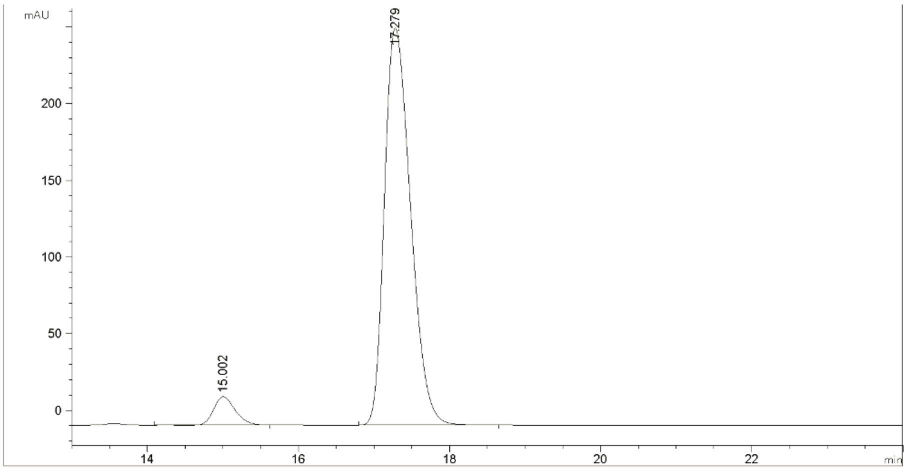
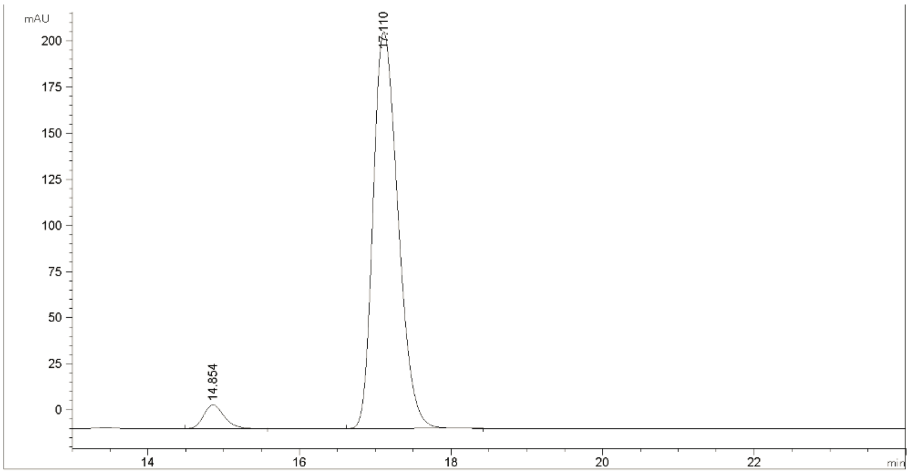
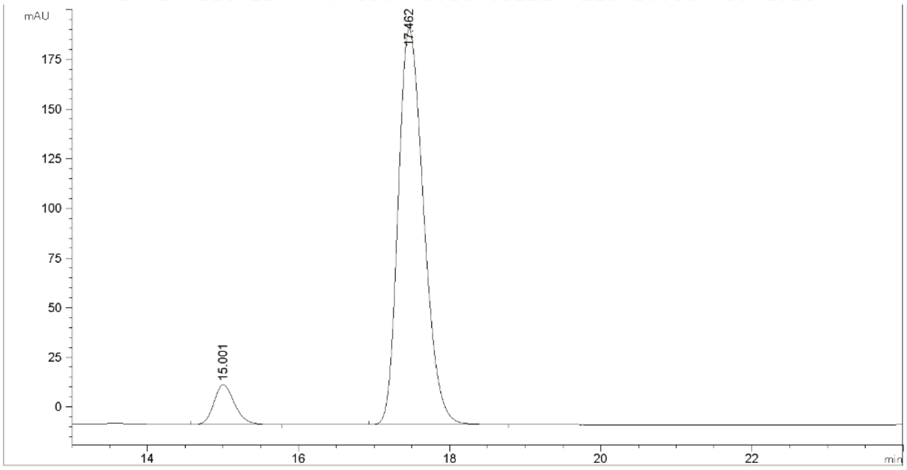
峰  保留时间  类型   峰宽       峰面积          峰高        峰面积
 #    [min]          [min]   mAU    *s    [mAU    ]        %
----|-------|----|-------|----------|----------|--------|
  1  14.836 VV     0.3625   45.94350    1.85017   3.8782
  2  16.938 VB     0.3350 1138.71997   52.42113  96.1218
```



```
峰  保留时间  类型   峰宽       峰面积          峰高        峰面积
 #    [min]          [min]   mAU    *s    [mAU    ]        %
----|-------|----|-------|----------|----------|--------|
  1  15.002 BV     0.3050  372.02710   18.69544   5.6362
  2  17.279 BB     0.3796 6228.65820  258.96466  94.3638
```



```
峰 保留时间 类型  峰宽      峰面积       峰高       峰面积
 #   [min]         [min]  mAU    *s    [mAU   ]        %
----|-------|----|-------|----------|----------|--------|
  1  14.854 BB    0.2909  244.87070   12.92790   4.7471
  2  17.110 BB    0.3567 4913.49121  215.16933  95.2529
```



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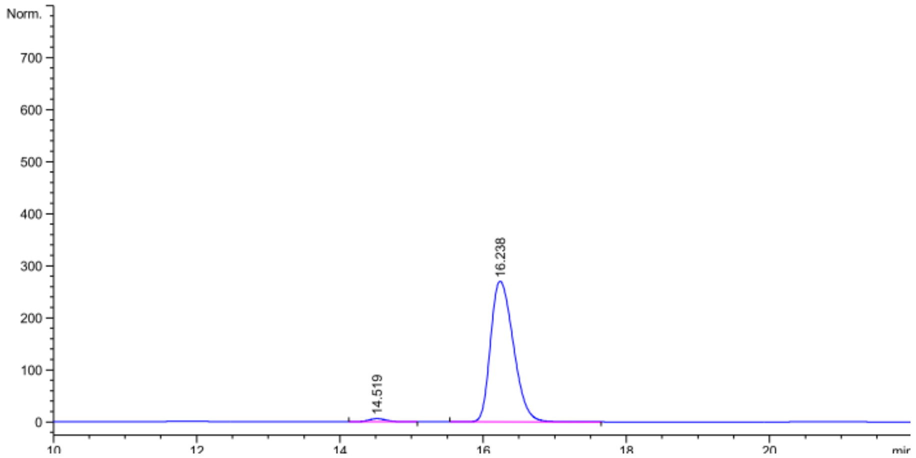
峰 保留时间 类型  峰宽      峰面积       峰高       峰面积
 #   [min]         [min]  mAU    *s    [mAU   ]        %
----|-------|----|-------|----------|----------|--------|
  1  15.001 VB    0.2943  380.59122   20.04922   7.5305
  2  17.462 BB    0.3668 4673.43457  199.24849  92.4695
```

10. Comparison of the heterogeneous catalyst and the homogeneous catalyst

TADDOL was used as a homogeneous catalyst for the addition reaction between benzaldehyde and diethyl zinc under the same conditions. The isolated yield of (*S*)-1-phenylpropan-1-ol was 89% and the *ee* value was determined to be 96% using chiral HPLC (Daicel chiral OD-H column at 220 nm: 25 ℃; hexane: iPrOH = 98:2; flow rate = 1.0 mL/min).



```
峰  保留时间  类型   峰宽      峰面积       峰高       峰面积
 #    [min]          [min]   mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------|
  1  14.519 BV     0.2657  109.87308    6.35605   1.8002
  2  16.238 VB     0.3519 5993.38086  270.25763  98.1998
```

The reactions catalyzed by **TADP5Ti** and **TADDOL**/Ti^{IV} were monitored in a certain time in order to study the kinetic profiles of the two reactions. The results were shown below.

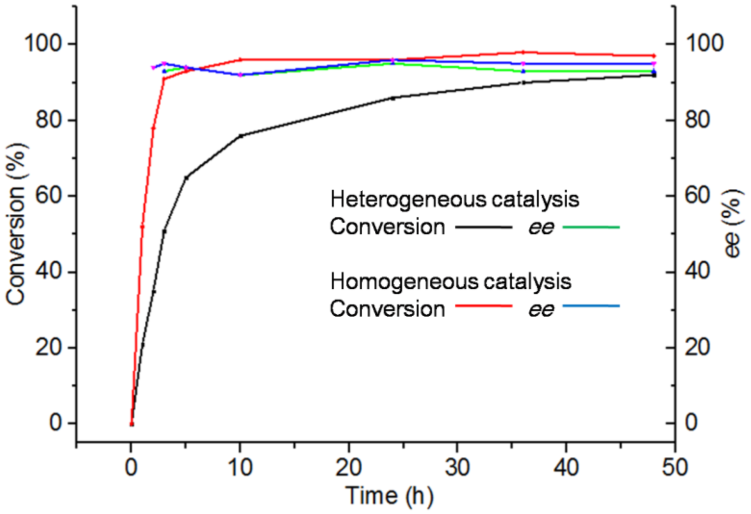


Fig. S16 Kinetic profiles of the reactions catalyzed by the heterogeneous catalyst and homogeneous catalyst.

From the studies of kinetic properties, we observed that the heterogeneous catalyst had some small flaws compared with homogeneous catalyst. Our polymer had slightly lower activity and enantioselectivity under the same reaction conditions. However, our heterogeneous catalyst is recyclable, which is an important advantage.

References

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S2. W.-J. Hu, X.-L. Zhao, M.-L. Ma, F. Guo, X.-Q. Mi, B. Jiang and K. Wen, *Eur. J. Org. Chem.* 2012, **7**, 1448.

S3. T. Werner, M. Bauer, A. M. Riahi and H. Schramm, *Eur. J. Org. Chem.* 2014, 4876.