Supporting Information

Efficient homogeneous-like enantioselective catalysis of bulky chiral spirocyclic phosphoric acid on polystyrene brushes grafted on SiO_2 nanospheres

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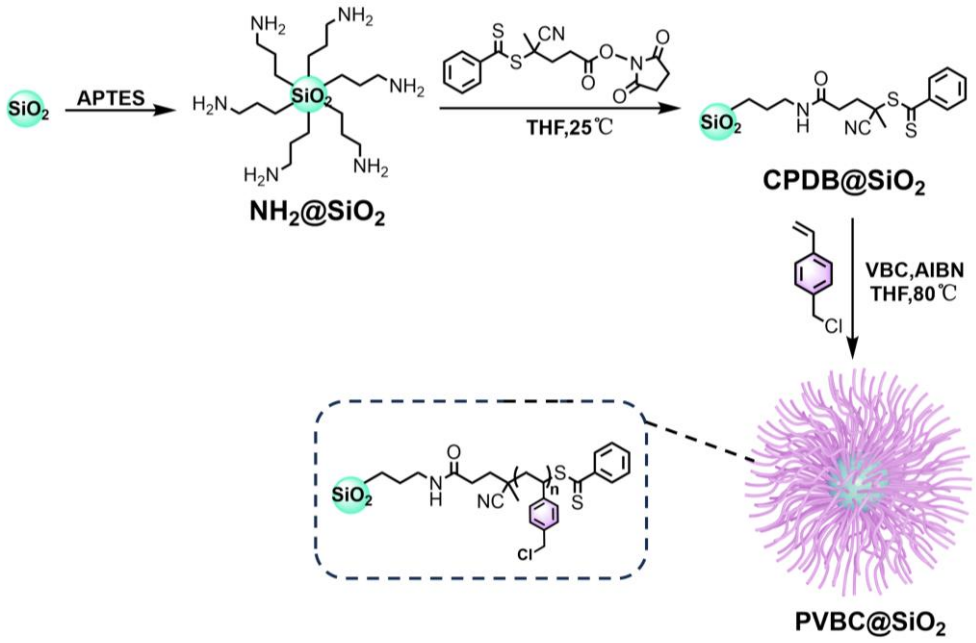
1. Preparation of raw materials

1.1 PVBC brushes grafted on SiO_2 nanoparticles (PVBC@SiO_2)



Scheme S1 Preparation route to PVBC brush grafted on SiO_2 nanoparticles (PVBC@SiO_2).

1.1.1 NH_2@SiO_2

In a 250 mL two-necked flask, anhydrous ethanol (110 mL), aqueous ammonia (5.7 mL, 25–28 wt%) were added, heated to 35°C, and then TEOS (3.8 mL, 17.0 mmol) in ethanol (8 mL) was slowly added dropwise. The reaction was allowed to be stirring for 24 h. Subsequently, 3-aminopropyltriethoxysilane (APTES, 2.4 mL, 8.6 mmol) was added dropwise and stirred for additional 12 h. The reaction mixture was cooled to room temperature naturally, and centrifuged (13000 rpm, 5 min). The isolated solid was washed with anhydrous ethanol (54 mL × 3) until the supernatant showed no color change with ninhydrin reagent. The solid was dried at 75°C for 6 h, yielding a white powdery solid NH_2@SiO_2 (1.15 g), which was stored for later use.

1.1.2 CPDB@SiO_2

In a 50 mL dry three-necked flask, a THF solution (10 mL) of CPDB (350 mg, 0.15 mmol) and a THF suspension (10 mL) of NH_2@SiO_2 (1.0 g) were added. The mixture was stirred at 25°C for 24 h. Subsequently, the mixed solvents of cyclohexane/ether (V/V = 4/1, 50 mL) were added, and the mixture was centrifuged (10000 rpm, 2 min). The isolated solid was added to THF (15 mL), stirred to form a suspension, and then precipitated with cyclohexane/ether (50 mL, V/V = 4/1), followed by centrifugation (10000 rpm, 2 min). This process was repeated until the supernatant

was colorless and transparent. The isolated solid was dried under vacuum for 6 h, yielding a light pink powdery solid CPDB@SiO_2 (900 mg), which was stored for later use.

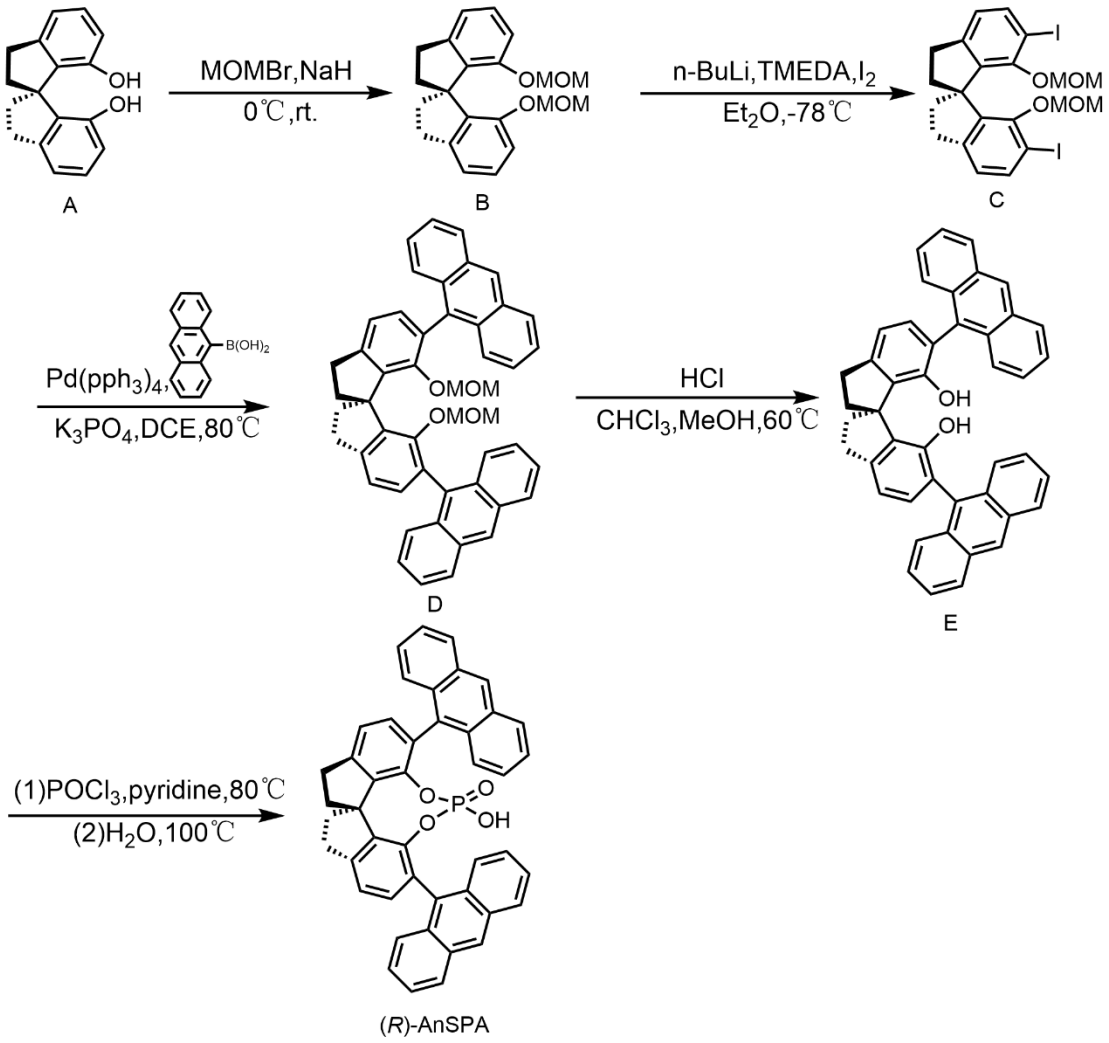
1.1.3 PVBC@SiO_2[1]

In a 25 mL dry Schlenk tube, CPDB@SiO_2 (350 mg) and THF (4.0 mL) were added and sonicated for 5 min to form a homogeneous suspension. Subsequently, vinylbenzyl chloride (VBC, 2.5 g, 18.04 mmol) and a THF solution (1 mL) of AIBN (8.3 mg) (0.05 mol L^{-1}, 270 μL) were added and sonicated for 5 min. The suspension was frozen with liquid nitrogen and then evacuated till the frozen solid became a suspension. This freeze-thaw cycle was repeated three times. The mixture was warmed to room temperature naturally, purged with N_2, sonicated for 10 min, heated to 80°C, and stirred for 36 h. The mixture was cooled to room temperature with an ice-water bath, centrifuged (10000 rpm, 5 min). The isolated solid was washed with THF (9 mL × 3), dried under vacuum at 75°C for 6 h, and ground to yield a light yellow powdery solid PVBC@SiO_2 (405 mg), which was stored for later use.

1.2 Synthesis of contrast HMPNs[2]

In a 100 mL three-necked flask fitted with a condenser, polyvinylpyrrolidone (PVP, 1.0 g, 9.0 mmol) and F-127 (0.3 g, 1.8 mmol) were added. The apparatus was evacuated and flushed with nitrogen three times. Ethanol (24 mL), styrene (2 mL, 1.80 mmol), and water (3 mL) were added in sequence and stirred for 5 min. An ethanol solution (1 mL) of azobisisobutyronitrile (AIBN, 5 mg, 0.03 mmol) was introduced, and the reaction was carried out at 70°C for 1 h. A aqueous solution (1 mL) of potassium persulfate (KPS, 35 mg, 0.13 mmol) was added, and the reaction was stirred for an additional 2 h. Next, an ethanol solution (5 mL) containing styrene (0.3 mL, 2.6 mmol), *p*-chloromethylstyrene (0.26 mL, 1.75 mmol), and divinylbenzene (DVB, 0.25 mL, 1.75 mmol) was added dropwise to the reaction mixture over 30 min, stirred for 22 h. The solid was separated by centrifugation (13,000 rpm, 5 min), washed successively with ethanol (20 mL), THF (20 mL × 2), and ethanol (20 mL), and dried at 75 °C for 6 h, affording HMPNs (500 mg).

1.3 Synthesis of AnSPA[3]



Scheme S2 Synthetic route to AnSPA.

(1) (*R*)-7,7′-bis(1-methoxymethoxy)-1,1′-spirobiindane (B)

In a three-necked flask, compound A (2 g, 8 mmol) and NaH (1.0 g, 40 mmol) were added and mixed with THF (25 mL) at 0°C, stirred for 3 h. Then a THF solution of MOMBr (1.6 mL, 19.2 mmol) was slowly added at 0°C and stirred at ambient temperature for 6 h. The mixture was quenched with water (10 mL) and extracted by ethyl acetate (30 mL). The organic layer was separated, washed with saturated NH_4Cl solution and brine, dried over $MgSO_4$. After the solvent was removed, the residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to yield a colorless liquid B (2.5 g, 94 % yield).

(2) (*R*)-6,6′-diiodo-7,7′-bis(1-methoxymethoxy)-1,1′-spirobiindane (C)

In an argon-filled three-necked flask, compound B (2.1 g, 6 mmol), tetramethylethylenediamine (TMEDA, 2.0 mL, 12.6 mmol) and ether (20 mL) were added and

stirred for 5 min. Then 2.2 M *n*-butyllithium (8.2 mL, 18 mmol) was added at -78°C and stirred at ambient temperature for 4 h. Next, the mixture was cooled to -78°C and an ether solution (25 mL) of iodine (4.6 g) was carefully added, warmed to ambient temperature and stirred overnight. After completion of the reaction, saturated Na_2SO_3 aqueous solution (100 mL) was carefully added and stirred for 1 h. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were dried over $MgSO_4$. After the solvent was removed, the residue was purified by column chromatography using mixed petroleum ether/ethyl acetate as eluents (*v/v* = 15:1) to yield white solid C (2.7 g, 75% yield).

(3) (*R*)-7,7'-Bis(methoxymethoxy)-6,6'-bis(9-anthracenyl)-1,1'-spirobiindane (D)

In a Schlenk tube filled with nitrogen, compound C (200 mg, 0.34 mmol), 9-anthraceneboronic acid (300 mg, 1.35 mmol), K_3PO_4 (573 mg, 2.7 mmol) and DME (3 mL) were added and stirred for 15 min to form a suspension. $Pd(PPh_3)_4$ (39 mg, 0.034 mmol) was added. The resulting mixture was degassed for 5 min and heated to 80 °C for 48 h. After the reaction, the mixture was cooled to ambient temperature, CH_2Cl_2 (10 mL) and H_2O (5 mL) were added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2, and the combined CH_2Cl_2 layers were concentrated. The residue was purified by column chromatography using mixed *n*-hexane and CH_2Cl_2 as eluents (*v/v* = 2:1), yielding white solid D (78 mg, 33% yield).

(4) (*R*)-6,6'-Bis(9-anthracenyl)-1,1'-spirobiindane-7,7'-diol (E)

In a three-necked flask, compound D (78 mg, 0.11 mmol) was dissolved in a mixed solvent of $CHCl_3$ (5 mL) and MeOH (5 mL), and concentrated HCl (1 mL) was added. The mixture was heated to 60°C and refluxed for 4 h. After cooling to room temperature, saturated $NaHCO_3$ was added. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were concentrated, and the residue was purified by column chromatography using mixed *n*-hexane and CH_2Cl_2 (*v/v* = 2:1) as eluents, yielding yellow solid E (61 mg, 90% yield).

(5) (*R*)-AnSPA

In a Schlenk tube, compound E (61 mg, 0.11 mmol), anhydrous pyridine (1.5 mL), and $POCl_3$ (98.5 mg, 0.64 mmol) were added at 0 °C, and the mixture was heated to 80 °C for 24 h. After the mixture was cooled to 0 °C, 1, 4-dioxane (2 mL) and H_2O (0.6 mL) were added, and the reaction was heated to 100°C for 48 h until the generated precipitate dissolved completely. The mixture

was cooled to room temperature, acidified with 10% HCl, and extracted with CH_2Cl_2 (20 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by column chromatography using CH_2Cl_2 and MeOH as eluents (*v*/*v* = 50:1–20:1). The product was dissolved in CH_2Cl_2 (50 mL) and thoroughly washed with aqueous HCl (4 mol L^{-1}) to remove salt impurities and ensure complete protonation of phenolic hydroxyl groups. The organic layer was separated and evaporated, and the residue was dried under vacuum for 24 h to afford **(*R*)-AnSPA** (59 mg, 80% yield).

2. Characterization

2.1 SEM and particle size distribution

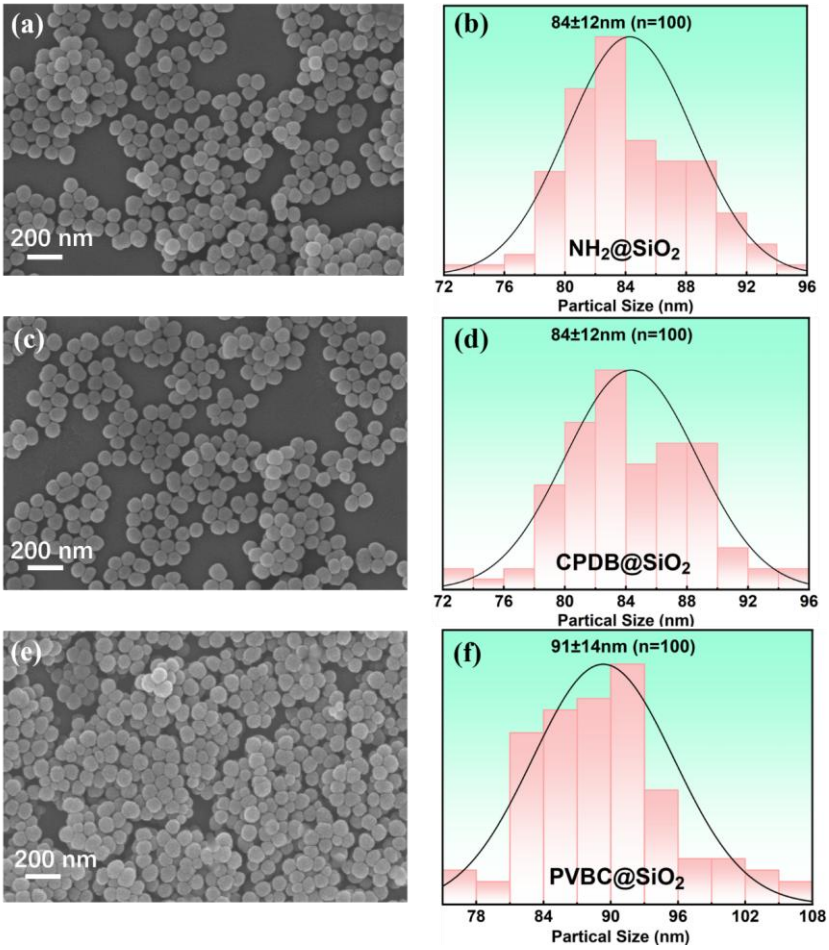


Fig. S1 SEM images and particle size distributions of $NH_2@SiO_2$ (a, b), CPDB@SiO_2 (c, d) and PVBC@SiO_2 (e, f).

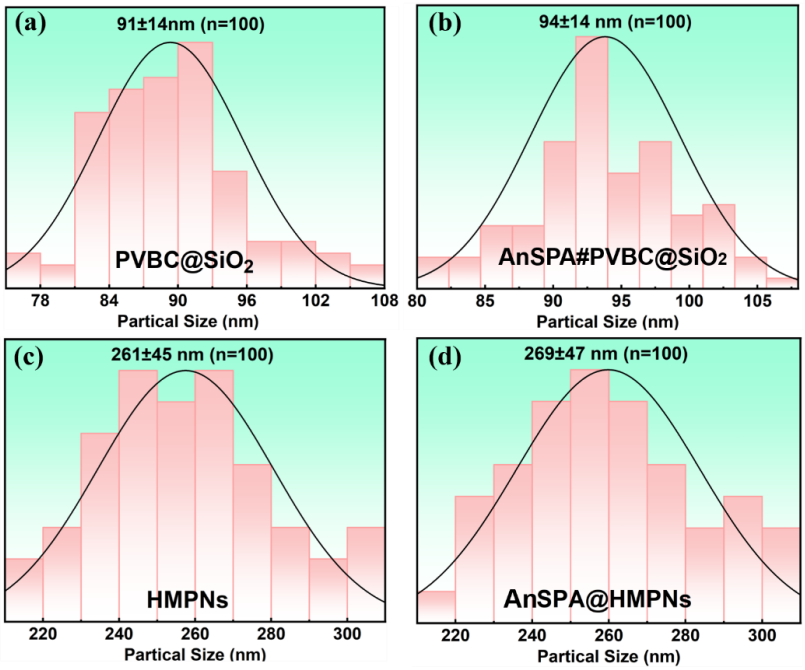


Fig. S2 Particle size distributions of PVBC@SiO_2 (a), AnSPA#PVBC@SiO_2 (b), HMPNs (c), AnSPA@HMPNs (d).

2.2 TEM and X-EDS elemental maps

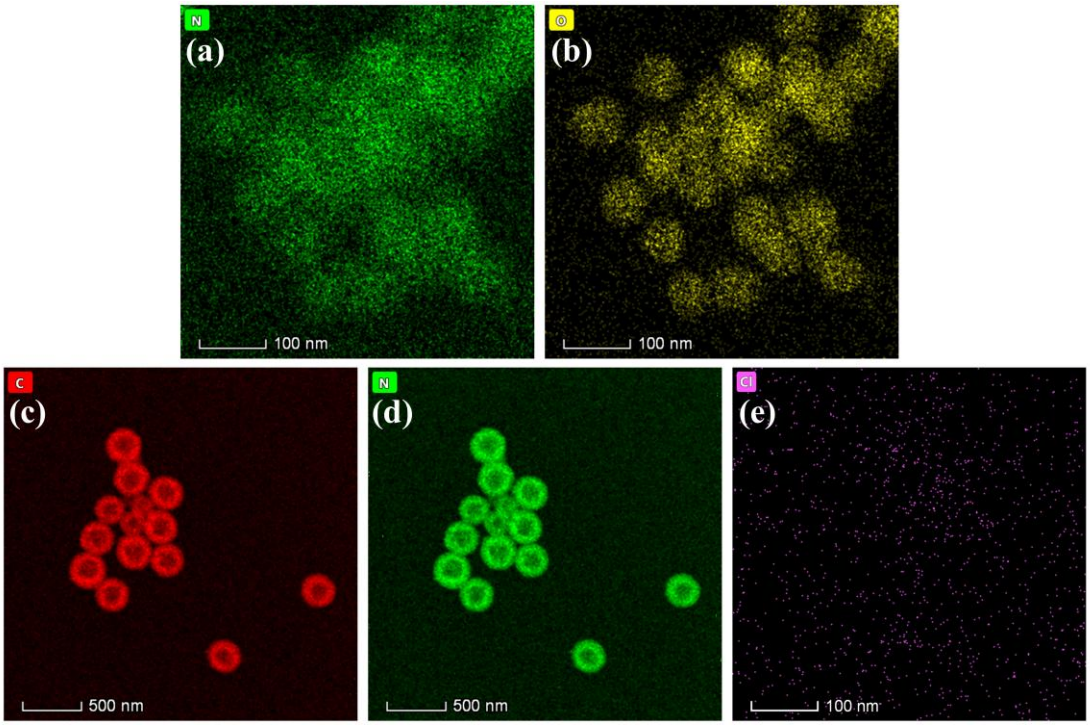


Fig. S3 X-EDS of AnSPA#PVBC@SiO_2: N (b), O (a) and AnSPA@HMPNs: C (c), N (d), Cl (e).

2.3 Thermogravimetric analysis

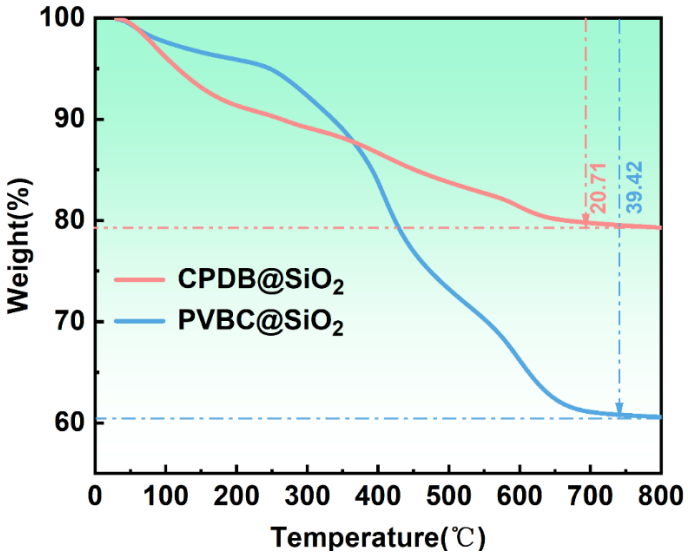


Fig. S4 Thermogravimetric curves of PVBC@SiO_2.

According to weight increment of organic moieties in the temperature range of 100–800 °C, the chloromethyl content in PVBC@SiO_2 was calculated to be 1.23 mmol g^{-1}.

2.4 Cleavage of PVBC brushes grafted on PVBC@SiO_2

In N_2-filled dry round-bottom flask (100 mL), PVBC@SiO_2 (250 mg) and anhydrous ethanol solution (50 mL) containing NH_4I (150 mg) were charged, sonicated for 2h, and heated to 75 °C. After being stirred for 2 h, hydrazine hydrate (500 mg) was added, stirred for 24 h, and cooled to room temperature. The solids was isolated by centrifugation and washed by THF (5 mL × 3). To the combined solutions, deionized water (150 mL) was added and extracted by $CHCl_3$ (20 mL × 3). The combined $CHCl_3$ phases were washed by deionized water (20 mL), filtered through filter head (0.22 um), and evaporated under reduced pressure, affording light yellow viscous oily liquid. The molecular weights (Mn) and polymer dispersity index (PDI) are determined using a Waters gel-permeation chromatograph (GPC) and listed in **Table S1**.

Table S1 Cleavage of SiO_2-grafted PVBC brushes

Sample	f_{SiO2} (%)	SiO_2 (nm)	Mn (10^4)	PDI	Grafting density (chain nm^{-2})
PVBC@SiO_2	60.58	84	2.56	1.84	0.47

2.5 Chloromethyl content in PVBC@SiO_2[4]

In a 25 mL dry three-necked flask filled with argon, $FeCl_3$ (20 mg, 0.12 mmol) and 10 mL of DCE mixture containing PVBC@SiO_2 (230 mg) were added, heated to certain temperature, and

stirred for 48 h. The isolated solids via centrifugation were washed with anhydrous ethanol (20 mL × 2) and HCl aqueous solution (20 mL × 4, 6 mol·L^{-1}) to remove $FeCl_3$, followed by deionized water (20 mL × 2) to pH = 7 and anhydrous ethanol (20 mL). Yellow solids (220 mg) were obtained under vacuum at 75 °C for 6 h. In a 10 mL round bottom flask, the obtained solids (220 mg) and THF (2 mL) were added, and ultrasonically irradiated for 10 min. Aqueous NaOH solution (5 mL, 1 mol L^{-1}) was added and heated to 40°C, stirred for 12 h. The mixture was cooled and centrifuged (1.3 × 10^4 rpm, 5 min). The supernatant was distilled under reduced pressure to remove THF. Deionized water (5 mL) was added, sonicated for 5 min, and filtered through a filter (0.22 μm). After the pH value was adjusted was added to neutral by diluted nitric acid, aqueous K_2CrO_4 solution (1 mL, 0.5% wt) was added. The titration with a standard $AgNO_3$ solution (0.1 mol L^{-1}) was immediately terminated when the color of solution became brick red color. The procedure was repeated three times, and the average consumed volume of $AgNO_3$ solution was obtained. Then the amounts of -CH_2Cl group in PVBC@SiO_2 at different temperatures were shown in **Fig. S5** and **Table S2**.

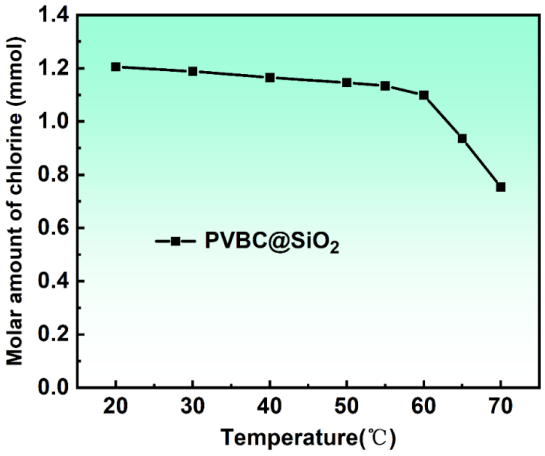


Fig. S5 The remaining amounts of chloromethyl in PVBC@SiO_2 at different temperatures by dealing with $FeCl_3$.

Table S2 Chloromethyl contents in **PVBC@SiO_2** dealt with $FeCl_3$ at different temperatures

Entry	Temperature (℃)	Volume of $AgNO_3$ solution(mL)[a]	Molar amount of chlorine (mmol g^{-1})
1	70	7.54	0.75
2	65	9.36	0.94
3	60	10.99	1.10
4	55	11.34	1.13
5	50	11.46	1.15

6	40	11.65	1.17
7	30	11.88	1.19
8	20	12.05	1.21

[a] Detected by titration with a burette.

2.6 Loading benzyl chloride moiety in HMPNs[4]

In round-bottom flask (10 mL), HMPNs (300 mg) and THF (2 mL) were charged and sonicated for 30 min. To the suspension, aqueous NaOH solution (5 mL, 1.0 mol L^{-1}) was added, heated to 40 °C for 12 h, evaporated under reduced pressure to remove THF, and filtered using filter head (0.22 μm). Diluted nitric acid was used to adjust the filtrate to pH = 7, and K_2CrO_4 (1 mL 0.5 %wt) was added. The obtained solution was titrated with standard $AgNO_3$ (0.1 mmol mL^{-1}) solution until brick red appears. This titration process was repeated three times. The content of benzyl chloride moiety in HMPNs was calculated to be 2.8 mmol g^{-1}.

2.7 Porous structure

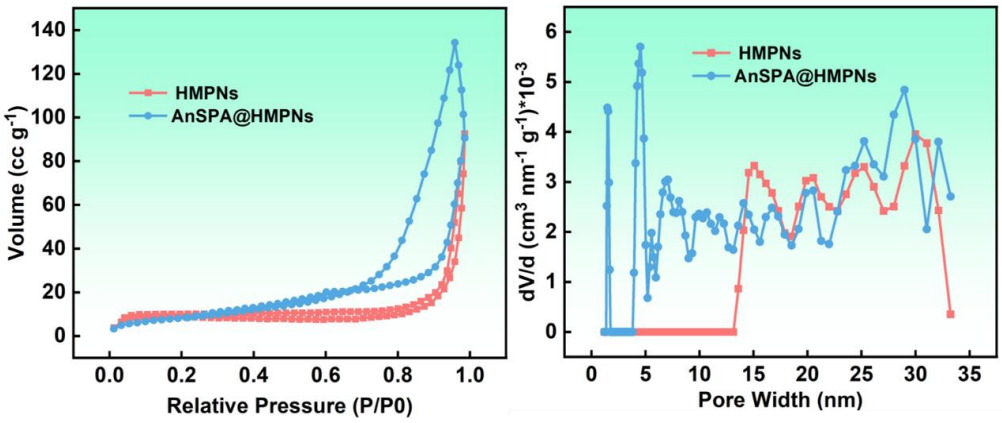


Fig. S6 N_2 adsorption-desorption isotherms (left) and pore size distributions (right) of HMPNs and AnSPA@HMPNs.

Table S3 Specific surface area, average pore size and pore volume of HMPNs and AnSPA@HMPNs [a]

Entry	Sample	Surface Area [b] (m^2 g^{-1})	Average Pore [c] (nm)	Pore Volume [d] (cc g^{-1})
1	HMPNs	34.8	1.65	0.14
2	AnSPA@HMPNs	28.4	2.93	0.21

[a] The samples were dried in vacuum at 473 K for 6 h, and isothermal adsorption-desorption analysis carried out at 77.4 K. [b] Based on BET method according to adsorbed N_2 volumes in the range of P/P_0 = 0.05–0.25. [c] Calculated using the QSDFT model (cylindrical pores model from adsorption branch). [d] Calculated using the Gurvich rule at P/P_0 =0.995.

The pore size distributions of HMPNs and AnSPA@HMPNs are obtained using quenched solid density functional theory (QSDFT). QSDFT for the pore size analysis of nanoporous materials is now available for many adsorption systems. This method allow one to calculate for a particular adsorptive/adsorbent pair a series of theoretical isotherms ($N(p/p_0, W)$ in pores of different widths for a given pore shape. The calculation of the pore size distribution function f(W) is based on a solution of the general adsorption isotherm (GAI) equation, which correlates the experimental adsorption isotherm $N(p/p_0)$ with the kernel of the theoretical adsorption or desorption isotherms $N(p/p_0,W)$. For this purpose, the GAI equation is expressed in the following form.

$$N(p/p^{o}) = \int_{W_{min}}^{W_{max}} N(p/p^{o}, W) f(W) dW$$

3. Volume of AnSPA

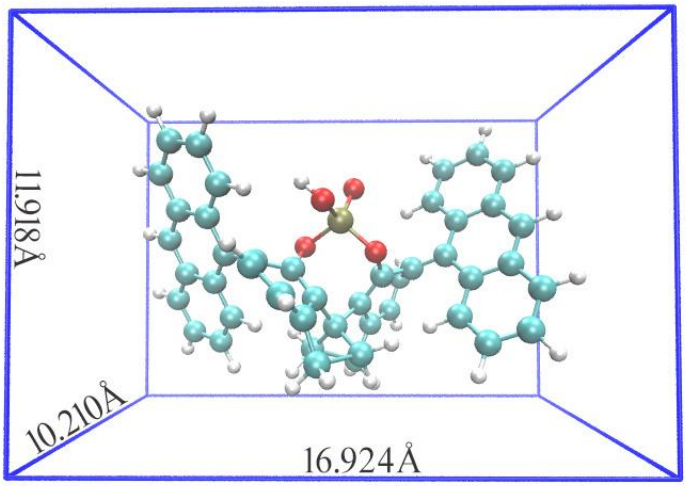


Fig. S7 Molecular volume of (*R*)-AnSPA.

4. Kinetics of reaction

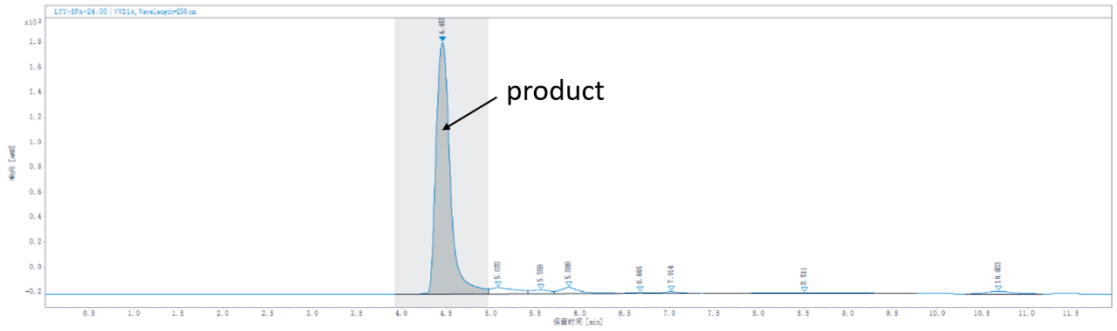


Fig. S8 HPLC spectrum of the reaction mixture in the enantioselective desymmetrization of 3-phenyl-3-hydroxy-1-oxocyclobutane with 6-ethoxy-2-mercaptobenzothiazole.

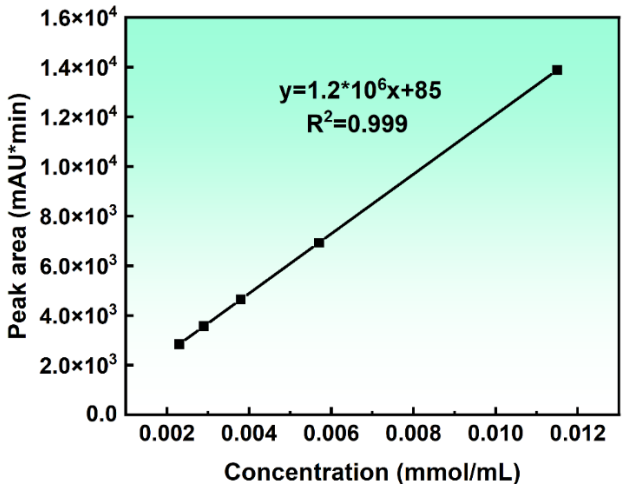
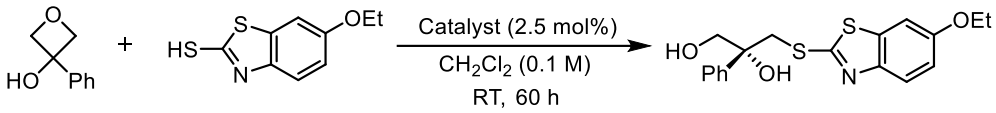


Fig. S9 Standard curve of peak area versus product concentration.

Table S4 Yields and enantioselectivities in the enantioselective desymmetrization of 3-phenyl-3-hydroxy-1-oxocyclobutane with 6-ethoxy-2-mercaptobenzothiazole promoted by various catalysts [a]



Sample / Time (h)	AnSPA#PVBC@SiO_2		AnSPA@HMPNs		PVBC@SiO_2		AnSPA	
	Yield (%)[b]	%ee[c]	Yield (%)[b]	%ee[c]	Yield (%)[b]	%ee[c]	Yield (%)[b]	%ee[c]
0	0	0	0	0	0	0	0	98
6	21	90	15	90	3	0	23	98
12	33	91	24	90	8	0	35	98
18	45	92	34	90	12	0	47	98
24	59	94	47	91	16	0	61	98
30	70	94	62	91	19	0	72	98
36	82	95	78	92	22	0	84	98
42	89	96	85	92	25	0	92	98
48	93	97	90	93	27	0	96	98
54	93	97	90	93	30	0	96	98
60	93	97	90	93	34	0	96	98

[a] Reaction conditions: 3-Phenyl-3-hydroxy-1-oxocyclobutane (0.1 mmol, 1.0 equiv.), 6-ethoxy-2-mercaptobenzothiazole (0.12 mmol, 1.2 equiv.), AnSPA#PVBC@SiO_2 (7 mg, 2.5 mol%), AnSPA@HMPNs (5 mg, 2.5 mol%), DCM (1 mL), 25 °C, 48 h. [b] Obtained by HPLC. [c] Determined by HPLC using Daicel Chiralpak AD-H column.

5. Characterization of products

(*R*)-7,7′-bis(1-methoxymethoxy)-1,1′-spirobiindane:[5] 95% yield as a colorless oil. $[\alpha]^{25}_{D}$ +23.1 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 6.99 (t, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 7.4 Hz, 2H), 6.66 (d, *J* = 8.1 Hz, 2H), 4.79 (d, *J* = 6.4 Hz, 2H), 4.73 (d, *J* = 6.4 Hz, 2H), 3.10 – 2.88 (m, 10H), 2.40 (dt, *J* = 12.7, 8.6 Hz, 2H), 2.13 (ddd, *J* = 12.7, 8.6, 4.1 Hz, 2H).

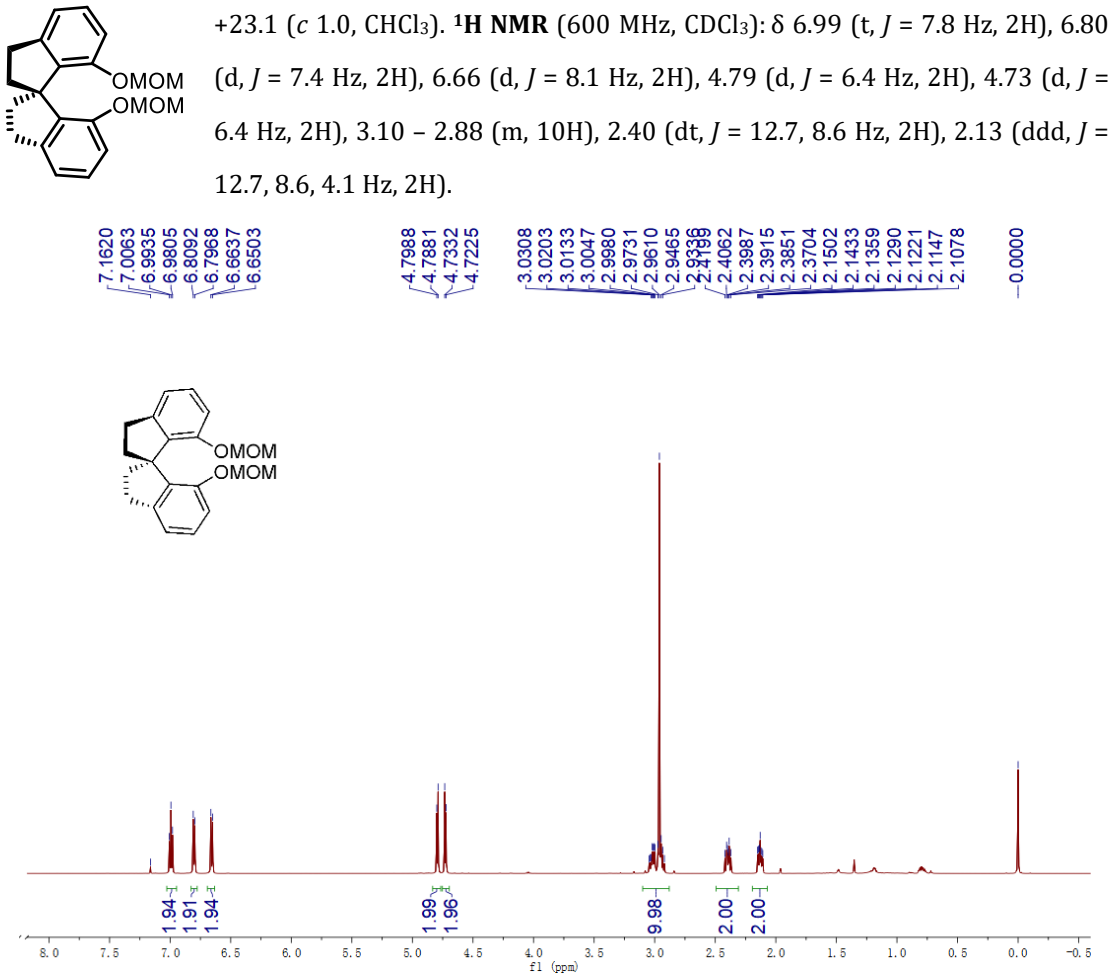
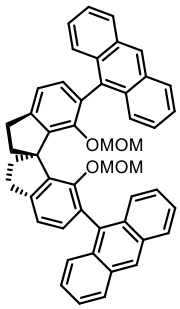


Fig. S10 ^{1}H NMR spectrum of (*R*)-7,7′-bis(1-methoxymethoxy)-1,1′-spirobiindane.

(*R*)-7,7'-Bis(methoxymethoxy)-6,6'-bis(9-anthracenyl)-1,1'-spirobiindane:[5] 33% yield as a white solid. $[\alpha]^{25}_{D}$: +326.2 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.40 (s, 2H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.89 (t, *J* = 8.8 Hz, 4H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.36 (dt, *J* = 14.5, 6.8 Hz, 4H), 7.12 – 7.06 (m, 2H), 7.04 (d, *J* = 7.4 Hz, 2H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.12 (t, *J* = 7.4 Hz, 2H), 4.30 (d, *J* = 5.8 Hz, 2H), 3.74 (d, *J* = 5.8 Hz, 2H), 3.23 – 3.15 (m, 3H), 3.03 (dd, *J* = 15.6, 8.6 Hz, 2H), 2.55 (t, *J* = 10.2 Hz, 2H), 2.47 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 6H).



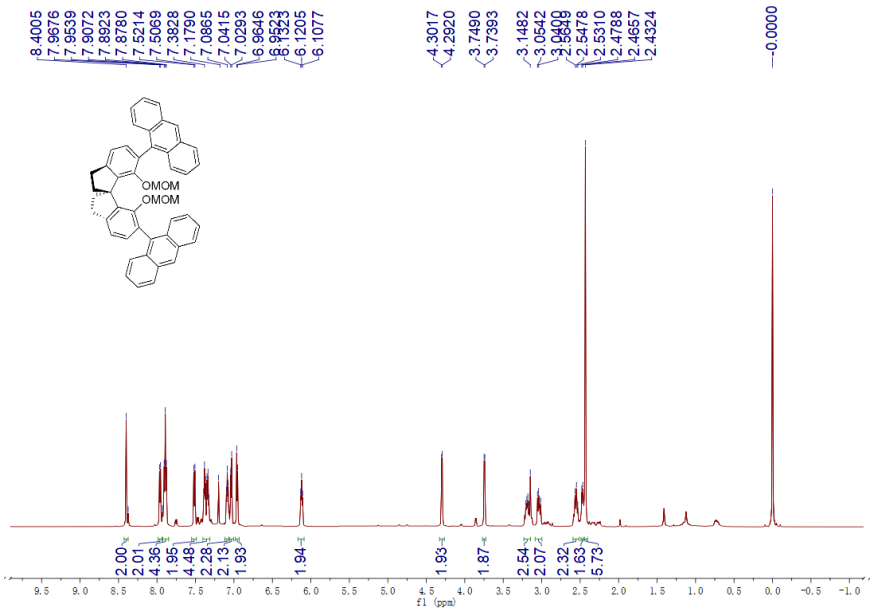
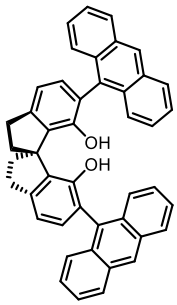


Fig. S11 ^{1}H NMR spectrum of (*R*)-7,7'-Bis(methoxymethoxy)-6,6'-bis(9-anthracenyl)-1,1'-spirobiindane

(*R*)-6,6'-Bis(9-anthracenyl)-1,1'-spirobiindane-7,7'-diol:[5] 90% yield as a white solid. $[\alpha]^{25}_{D}$: +372.1 (*c* 1.0, $CHCl_3$).**^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.43 (s, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.41 – 7.38 (m, 2H), 7.35 – 7.31 (m, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 7.4 Hz, 2H), 6.92 (d, *J* = 7.4 Hz, 2H), 6.42 – 6.37 (m, 2H), 4.51 (s, 2H), 3.22 – 3.14 (m, 2H), 3.07 (dd, *J* = 15.9, 8.7 Hz, 2H), 2.56 – 2.43 (m, 4H).



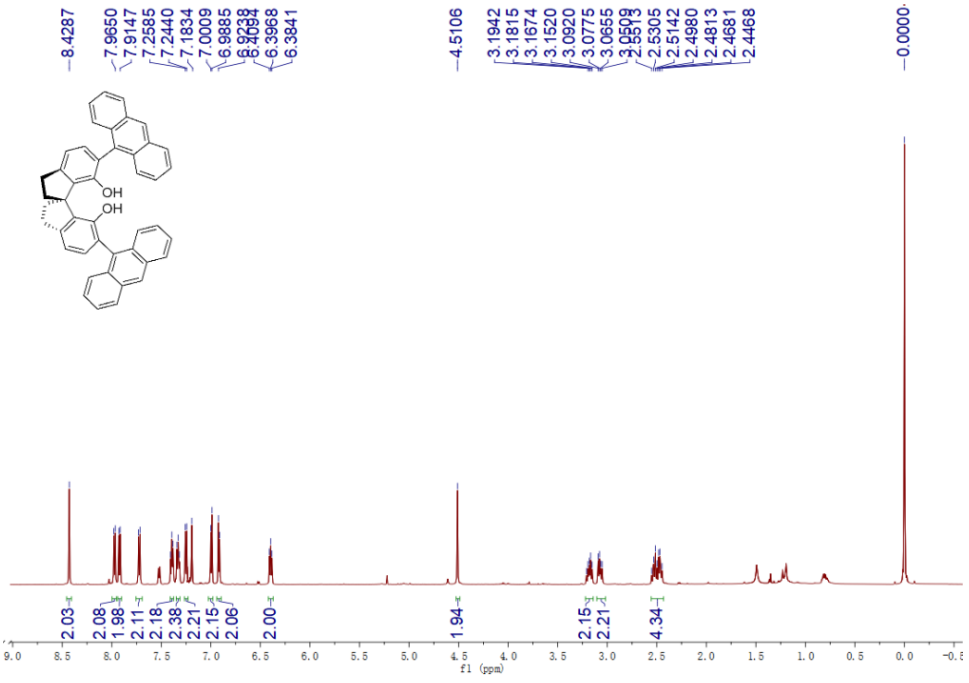
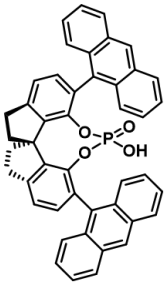


Fig. S12 ^{1}H NMR spectrum of (*R*)-6,6'-Bis(9-anthracenyl)-1,1'-spirobiindane-7,7'-diol.

(*R*)-6,6'-Bis(9-anthracenyl)-1,1'-spirobiindane-7,7'-diyl-hydrogenphosphate:[5] 80% yield as



a brown solid. $[\alpha]^{25}_{D}$: +445.0 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.01 (s, 2H), 7.77 (d, *J* = 6.2 Hz, 4H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.50 (s, 2H), 7.34 (s, 4H), 7.18 (d, *J* = 3.5 Hz, 2H), 7.11 - 7.01 (m, 4H), 6.74 (s, 2H), 4.05 (d, *J* = 7.1 Hz, 1H), 3.24 (dd, *J* = 21.1, 11.7 Hz, 2H), 2.99 (dd, *J* = 16.3, 7.7 Hz, 2H), 2.49 (s, 2H), 2.41 (d, *J*= 9.2 Hz, 2H). **^{13}C NMR** (151.0 MHz, Chloroform-*d*): δ 145.00, 139.31, 132.31, 131.15, 130.26, 129.75, 129.64, 128.60, 127.47, 127.10, 127.02, 126.25, 125.39, 124.80, 123.71, 123.66, 121.33, 59.21, 52.40, 37.89, 29.36.

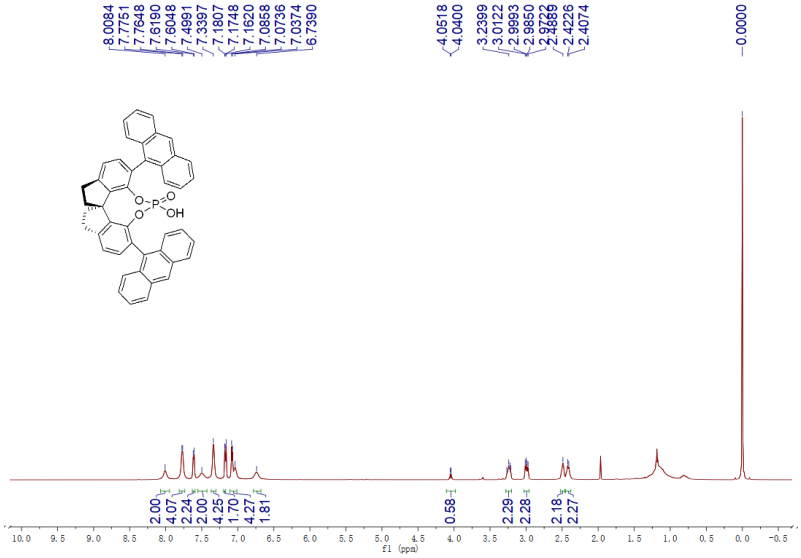


Fig. S13. ^{1}H NMR spectrum of (*R*)-6,6'-Bis(9-anthracenyl)-1,1'-spirobiindane-7,7'-diyl-hydrogenphosphate.

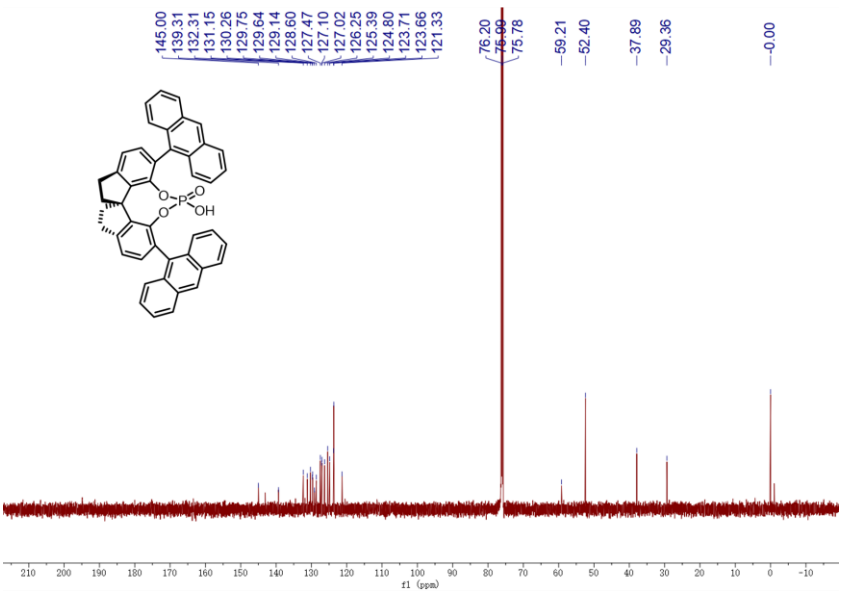


Fig. S14. ^{13}C NMR spectrum of (*R*)-6,6'-Bis(9-anthracenyl)-1,1'-spirobiindane-7,7'-diyl-hydrogenphosphate.

(*R*)-3-(Benzo[d]thiazol-2-ylthio)-2-phenylpropane-1,2-diol:[6] 89% yield, 97% ee as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.23 (dt, *J* = 14.3, 7.3 Hz, 2H), 5.36 (s, 1H), 3.90 (d, *J* = 11.6 Hz, 1H), 3.82 (d, *J* = 14.8 Hz, 1H), 3.73 – 3.65 (m, 2H), 3.23 (s, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*): δ 167.63, 151.34, 139.93, 133.96, 127.64, 127.01, 126.23, 125.25, 123.52, 120.09, 120.01, 62.66, 47.04, 34.91. **HPLC** analysis (Daicel Chiralpak AD-H column, hexane/*i*-PrOH =80/20, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{minor} = 12.1 min; t_{major} =13.6 min.

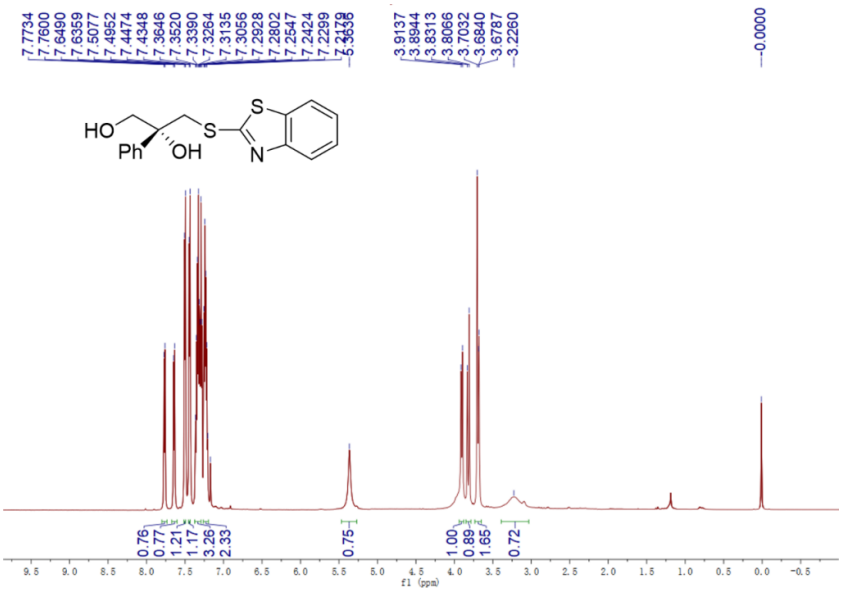


Fig. S15 ^{1}H NMR spectrum of (*R*)-3-(benzo[d]thiazol-2-ylthio)-2-phenylpropane-1,2-diol.

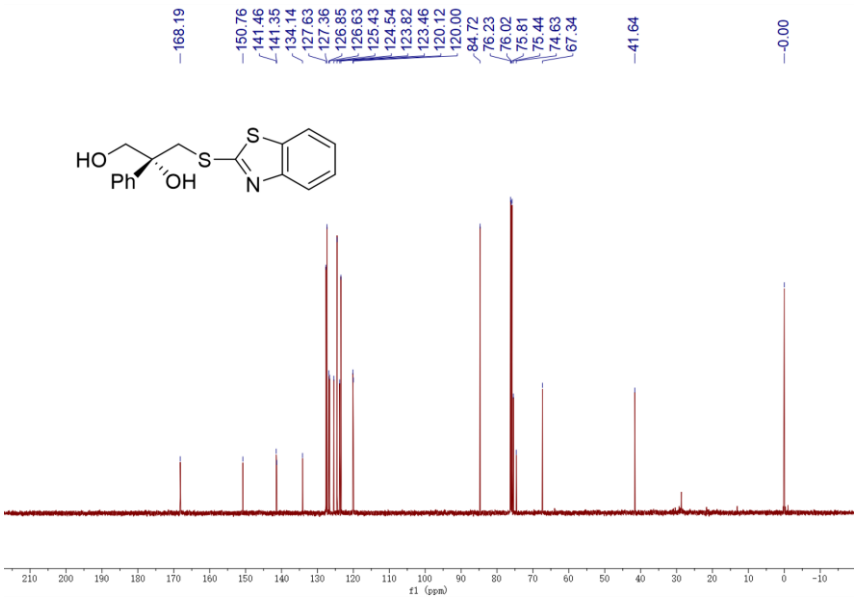
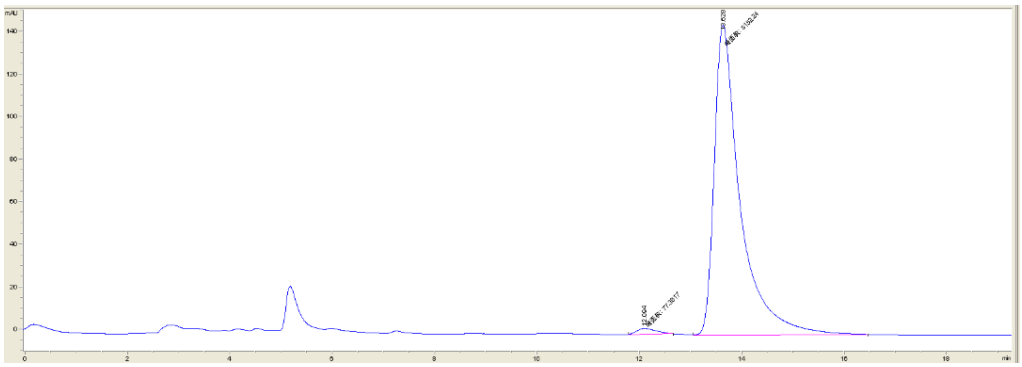
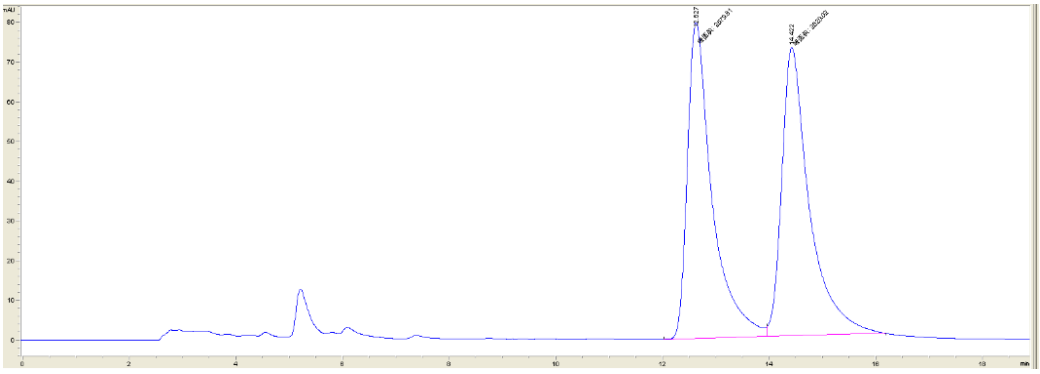


Fig. S16 ^{13}C NMR spectrum of (*R*)-3-(benzo[d]thiazol-2-ylthio)-2-phenylpropane-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	12.094	77.4	2.8	0.4573	0.619	1.479
2	13.628	5152.2	145.6	0.5896	0.486	98.521

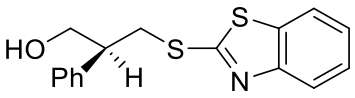
Fig. S17 HPLC spectrum of (*R*)-3-(benzo[d]thiazol-2-ylthio)-2-phenylpropane-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	12.627	2579.8	79.9	0.5389	0	49.613
2	14.422	2620	72.7	0.6033	0.548	50.387

Fig. S18 HPLC spectrum of racemic 3-(benzo[d]thiazol-2-ylthio)-2-phenylpropane-1,2-diol

(*S*)-3-(Benzo[d]thiazol-2-ylthio)-2-phenylpropan-1-ol:[6] 90% yield, 87% ee as a colorless oil.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.27 – 7.15 (m, 6H), 4.20 (s, 1H), 3.90 – 3.81 (m, 2H), 3.75 (dd, *J* = 14.1, 7.0 Hz, 1H), 3.64 (dd, *J* = 14.1, 5.5 Hz, 1H), 3.23 – 3.12 (m, 1H). **^{13}C NMR** (151 MHz, chloroform-*d*): δ 168.19, 150.76, 141.46, 141.35, 134.14, 127.63, 127.36, 126.85, 126.63, 125.43, 124.54, 123.82, 123.46, 120.12, 120.00, 84.72, 75.44, 74.63, 67.34, 41.64. **HPLC** analysis (Daicel Chiralpak AD-H column, hexane/*i*-PrOH =95/5, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{minor} = 28.6 min; t_{major} =40.5 min.

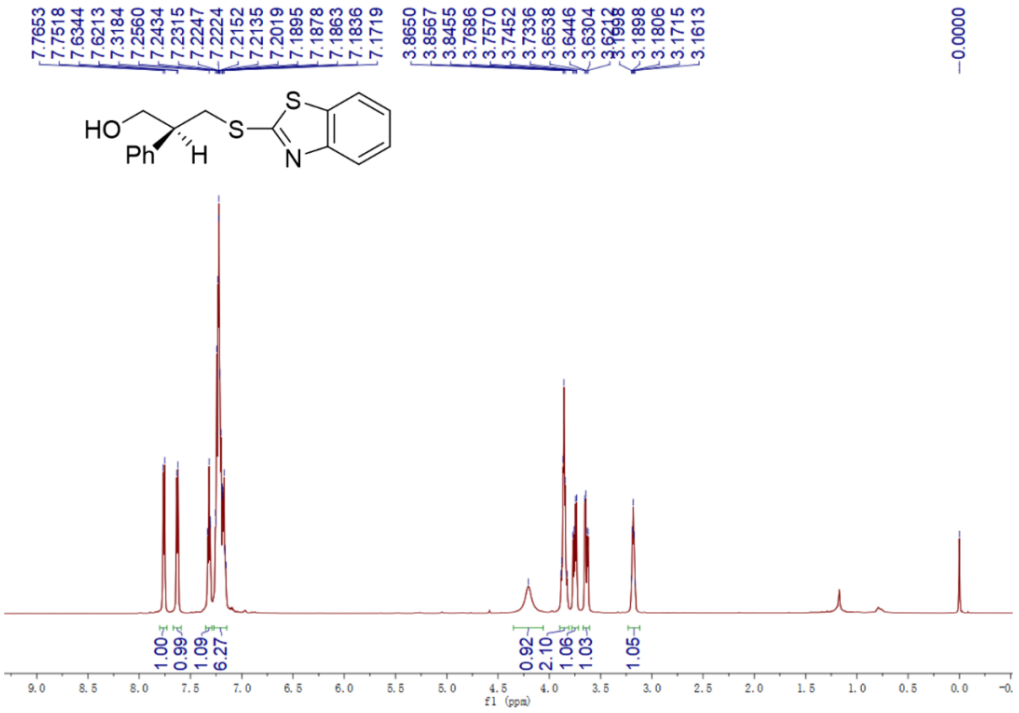


Fig. S19 ^{1}H NMR spectrum of (*S*)-3-(benzo[d]thiazol-2-ylthio)-2-phenylpropan-1-ol.

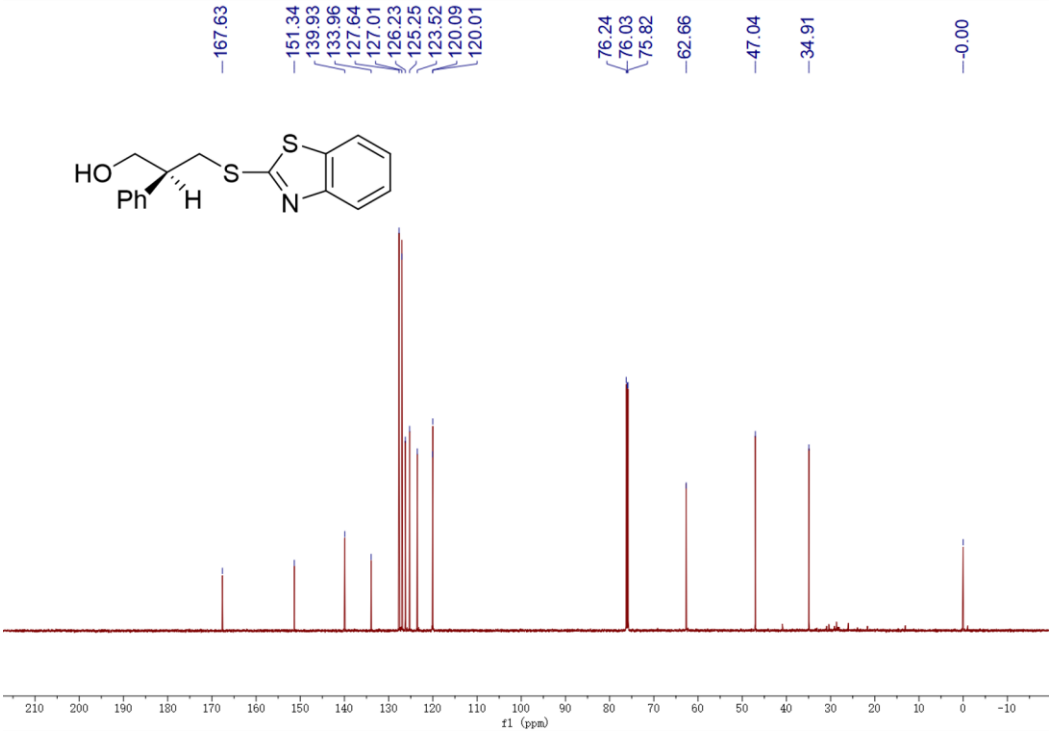
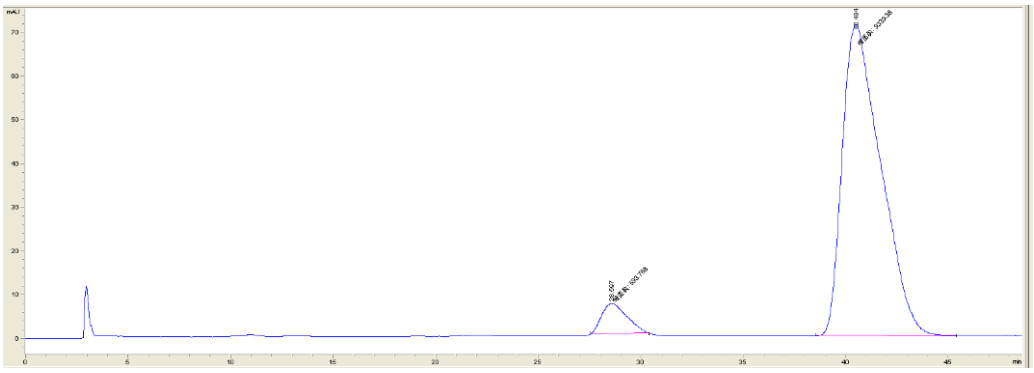
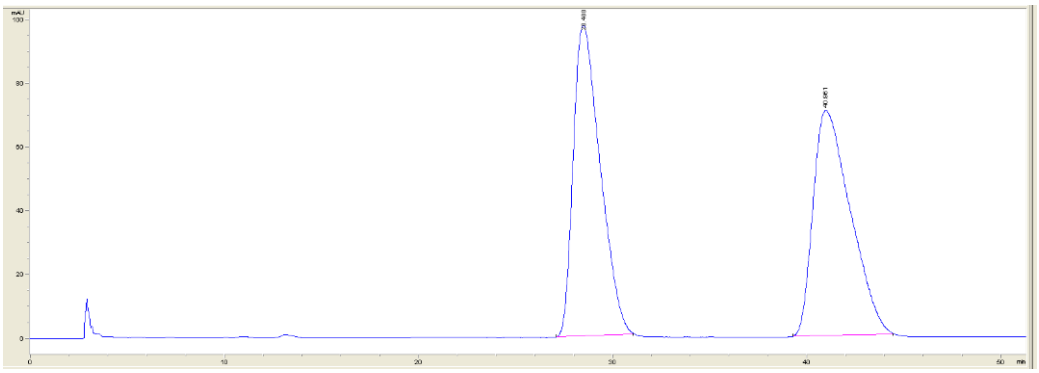


Fig. S20 ^{13}C NMR spectrum of (*S*)-3-(benzo[d]thiazol-2-ylthio)-2-phenylpropan-1-ol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	28.597	593.8	6.9	1.4372	0.696	5.978
2	40.494	9339.4	71.4	2.1811	0.537	94.044

Fig. S21 HPLC of (*S*)-3-(benzo[d]thiazol-2-ylthio)-2-phenylpropan-1-ol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	28.488	9434	97.6	1.3977	0.591	49.976
2	40.961	9443	70.7	1.7902	0.483	50.024

Fig. S22 HPLC of racemic 3-(benzo[d]thiazol-2-ylthio)-2-phenylpropan-1-ol.

(*S*)-2-((Benzo[d]thiazol-2-ylthio)methyl)-3,3,3-trifluoropropane-1,2-diol:[6] 93% yield, 97% ee as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 6.14 (s, 1H), 3.89 (d, *J* = 12.1 Hz, 1H), 3.78 (d, *J* = 12.2 Hz, 1H), 3.72 (d, J = 15.3 Hz, 1H), 3.60 (d, *J* = 15.3 Hz, 1H), 3.34 (s, 1H). **^{13}C NMR** (151 MHz, chloroform-*d*): δ 167.77, 150.40, 134.16, 125.67, 125.43, 124.20, 123.53, 120.25, 120.11, 61.44, 34.38. **HPLC** analysis (Daicel Chiralpak AD-H column, hexane/*i*-PrOH =90/10, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{minor} = 18.7 min; t_{major} =20.5 min.

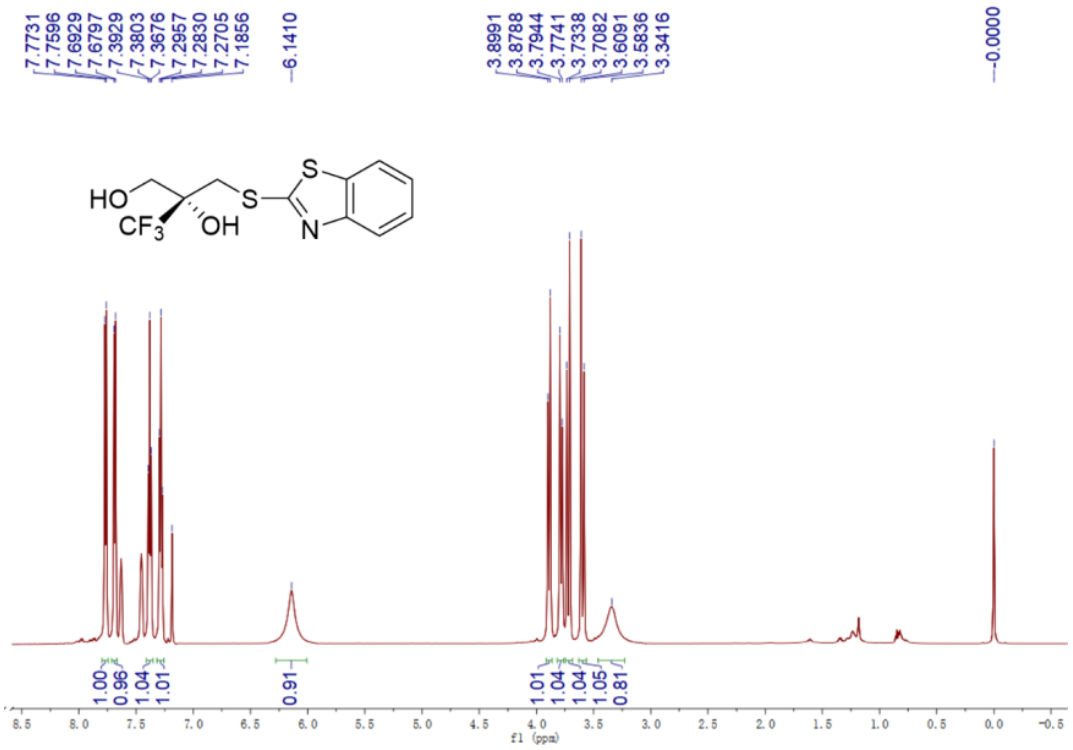


Fig. S23 ^{1}H NMR spectrum of (*S*)-2-((benzo[d]thiazol-2-ylthio)methyl)-3,3,3-trifluoropropane-1,2-diol.

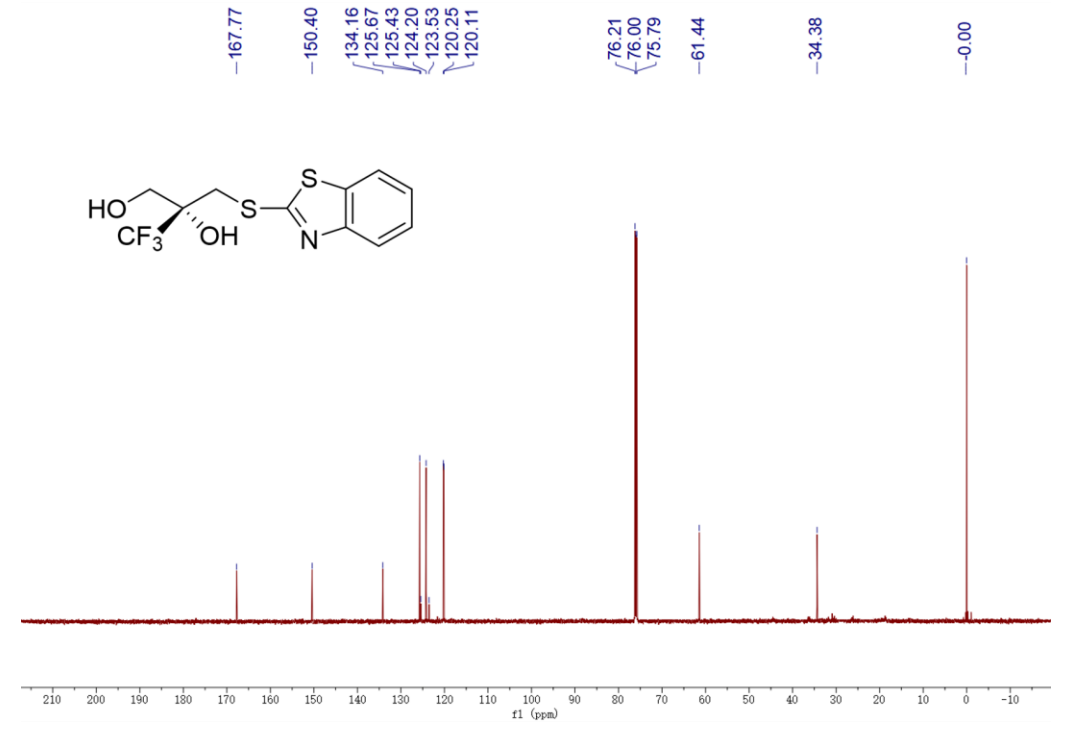
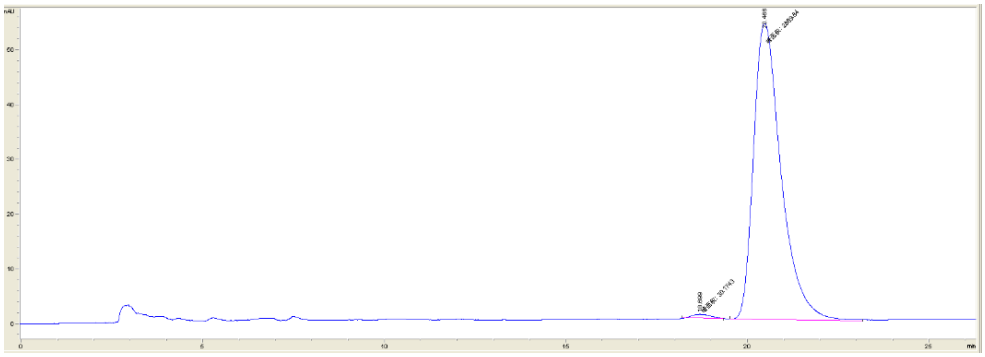
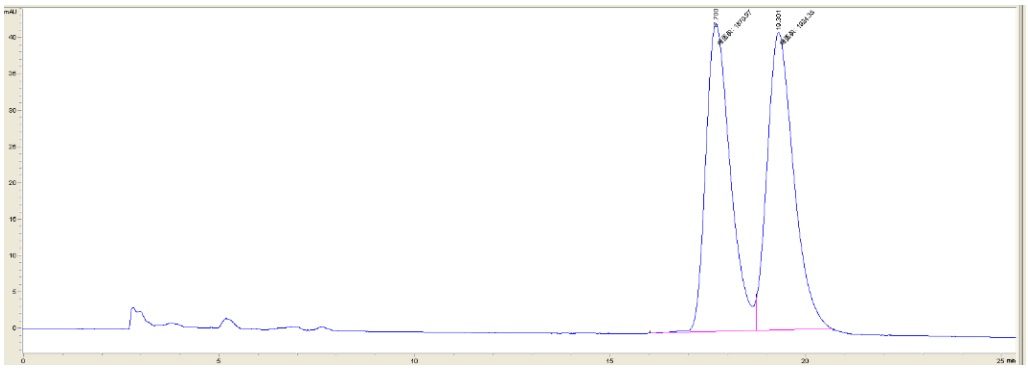


Fig. S24 ^{13}C NMR spectrum of (*S*)-2-((benzo[d]thiazol-2-ylthio)methyl)-3,3,3-trifluoropropane-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	18.699	30.2	0.77	0.649	0.76	1.040
2	20.466	2869.8	54.2	0.8829	0.642	98.960

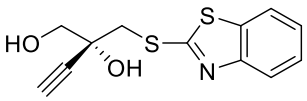
Fig. S25 HPLC of (*S*)-2-((benzo[d]thiazol-2-ylthio)methyl)-3,3,3-trifluoropropane-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	17.7	1871	42.4	0.7363	0	49.297
2	19.301	1924.4	41	0.7829	0.711	50.703

Fig. S26 HPLC of racemic 2-((benzo[d]thiazol-2-ylthio)methyl)-3,3,3-trifluoropropane-1,2-diol.

(*R*)-2-((Benzo[d]thiazol-2-ylthio)methyl)but-3-yne-1,2-diol: [6] 94% yield, 94% ee as a colorless oil.



^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 5.08 (s, 1H), 4.41 (s, 1H), 3.75 (d, J = 11.6 Hz, 1H), 3.67 (d, *J* = 14.6 Hz, 2H), 3.57 (d, *J* = 14.7 Hz, 1H), 2.49 (s, 1H). **^{13}C NMR** (151 MHz, chloroform-*d*): δ 168.00, 150.57, 134.03, 125.52, 123.96, 120.18, 119.96, 82.12, 73.66, 70.72, 65.82, 39.61. **HPLC** analysis (Daicel Chiralpak AD-H column, hexane/*i*-PrOH =80/20, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{minor} = 11.5 min; t_{major} =15.5 min.

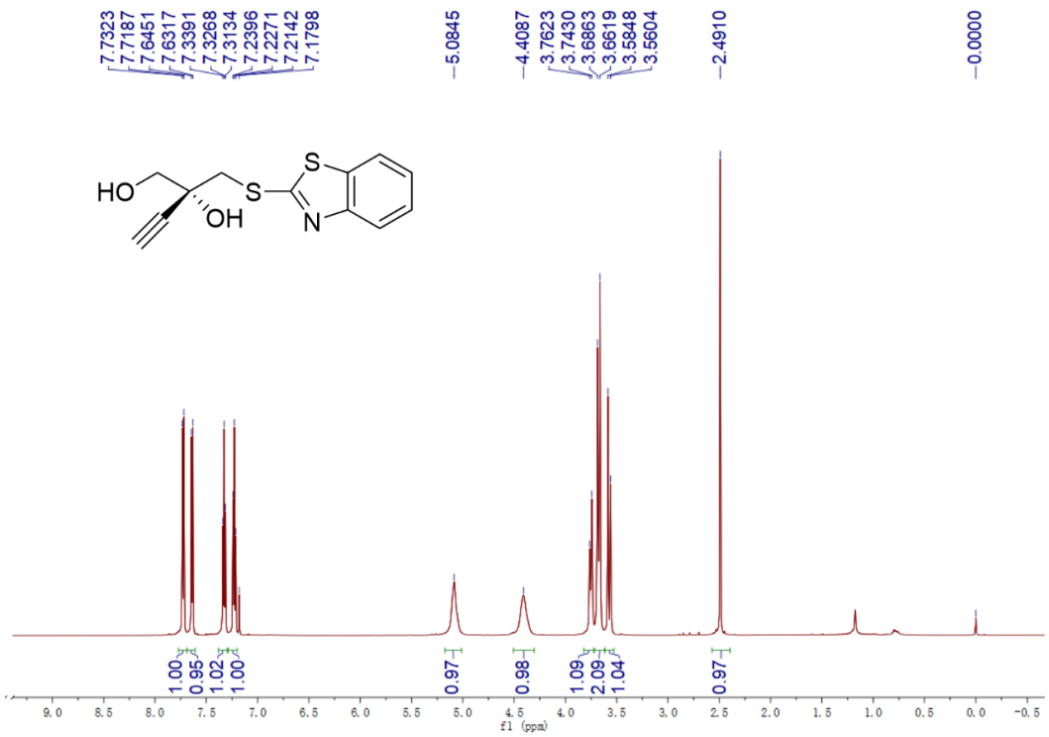


Fig. S27 ^{1}H NMR spectrum of (*R*)-2-((benzo[d]thiazol-2-ylthio)methyl)but-3-yne-1,2-diol.

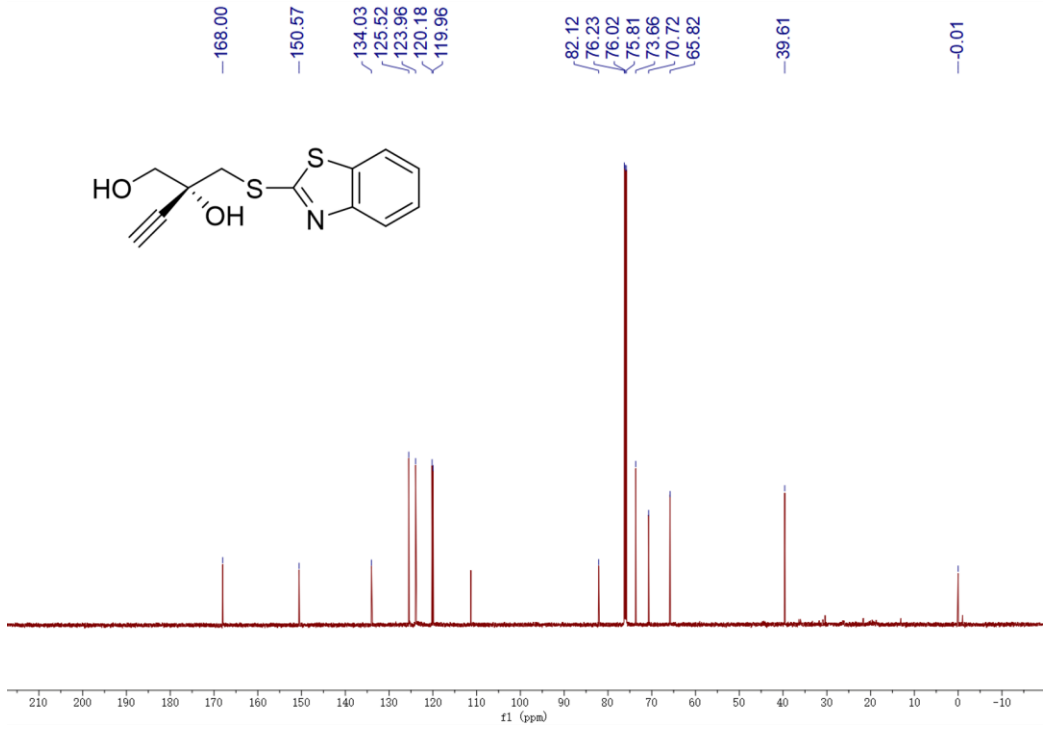
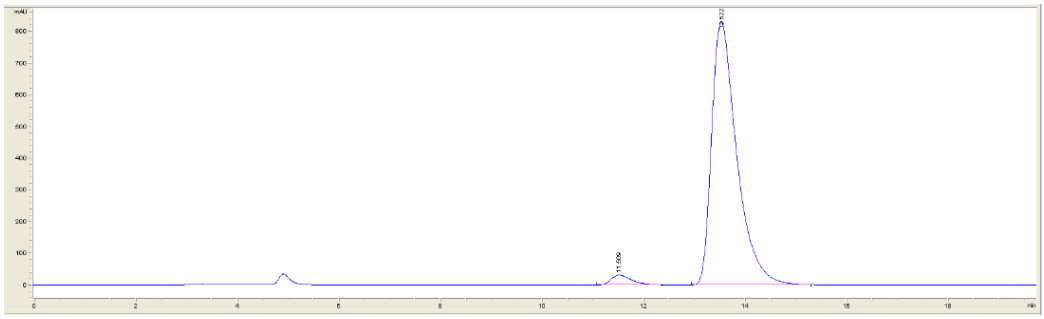
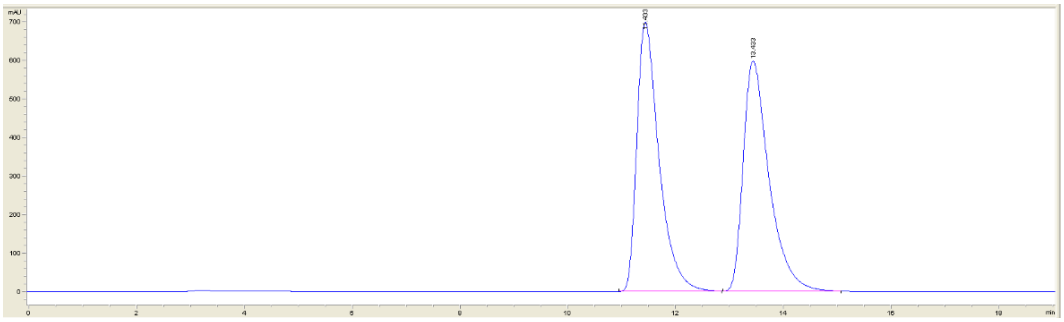


Fig. S28 ^{13}C NMR spectrum of (*R*)-2-((benzo[d]thiazol-2-ylthio)methyl)but-3-yne-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	11.509	868.1	31.2	0.4188	0.604	2.951
2	13.522	28550.5	830.5	0.5191	0.574	97.049

Fig. S29 HPLC of (*R*)-2-((benzo[d]thiazol-2-ylthio)methyl)but-3-yne-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	11.433	20040.6	699.4	0.4303	0.568	50.015
2	13.433	20028.4	598.5	0.5004	0.573	49.985

Fig. S30 HPLC of racemic 2-((benzo[d]thiazol-2-ylthio)methyl)but-3-yne-1,2-diol.

(S)-1-(Benzothiazol-2-ylthio)-3-hydroxypropan-2-yl-4-methyl-benzene sulfonate:[6] 86% yield, 90% ee as a colorless oil.**^{1}H NMR** (600 MHz, $CDCl_3$): δ7.74 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.23 (dd, *J* = 26.3, 8.0 Hz, 3H), 4.82 – 4.77 (m, 1H), 3.72 (dd, *J* = 12.7, 5.8 Hz, 1H), 3.64 (dt, *J* = 7.1, 4.1 Hz, 3H), 2.32 (s, 3H). **^{13}C NMR** (151 MHz, chloroform-*d*): δ 166.51, 166.49, 150.94, 144.15, 133.91, 132.16, 128.85, 126.90, 125.39, 123.81, 120.10, 120.06, 78.64, 59.87, 59.85, 32.36, 20.60. **HPLC** analysis (Daicel Chiralpak AD-H column, hexane/*i*-PrOH =90/10, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{major} = 28.0 min; t_{minor} =32.9 min.

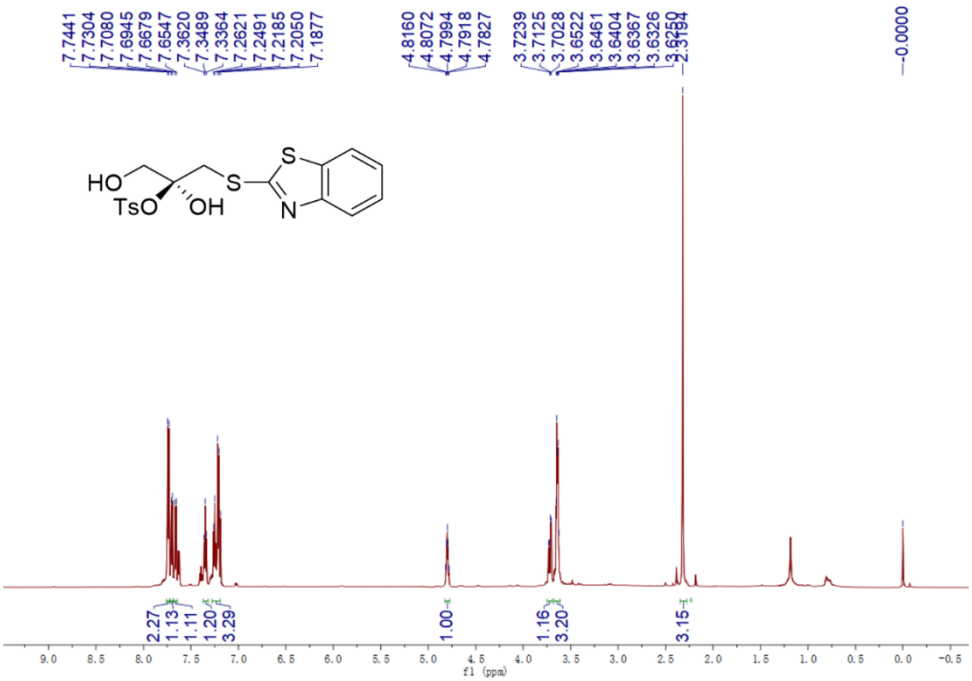


Fig. S31 ^{1}H NMR spectrum of (*S*)-1-(benzothiazol-2-ylthio)-3-hydroxypropan-2-yl-4-methyl-benzene sulfonate.

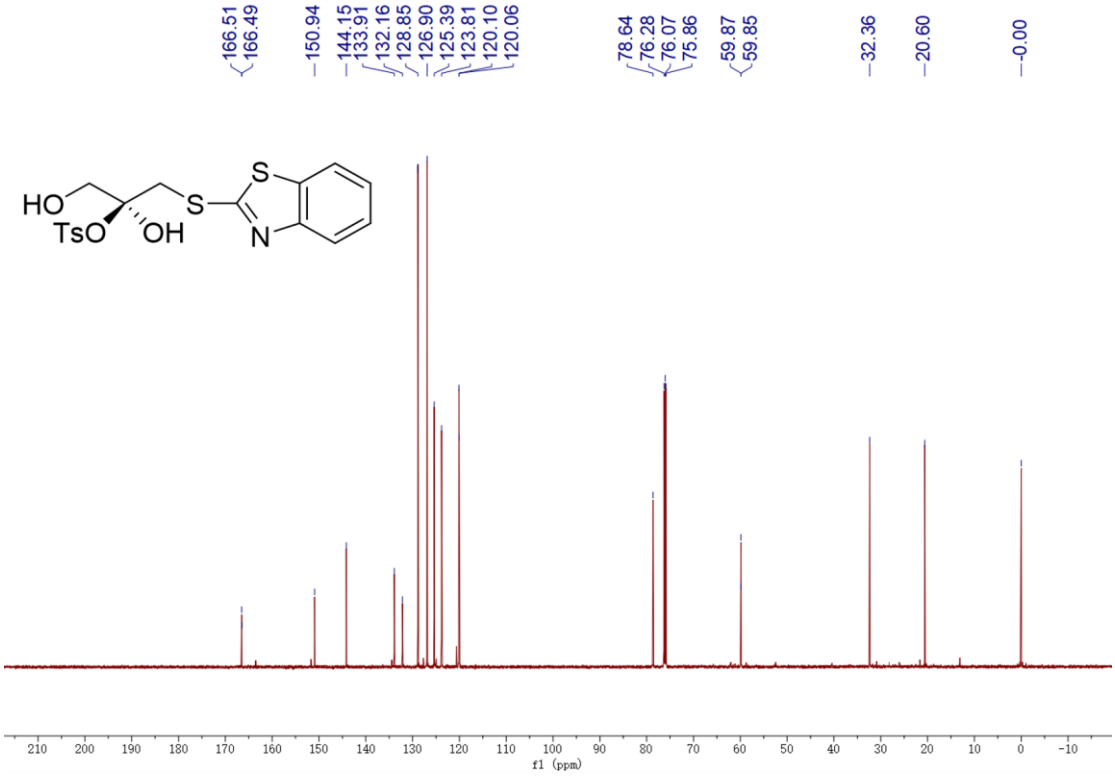
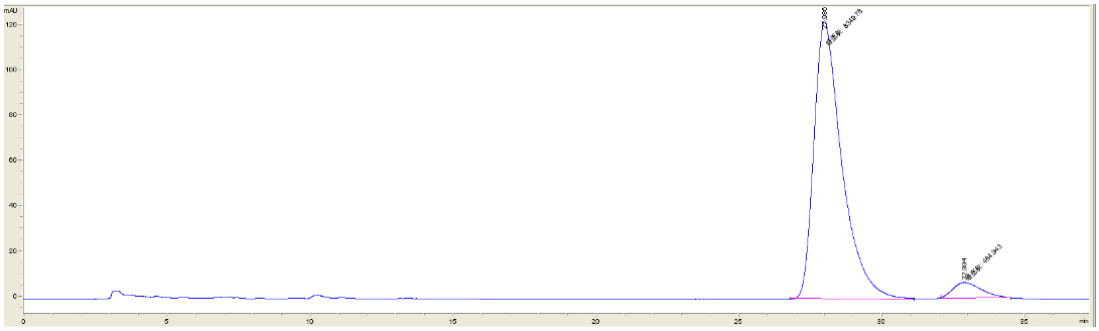
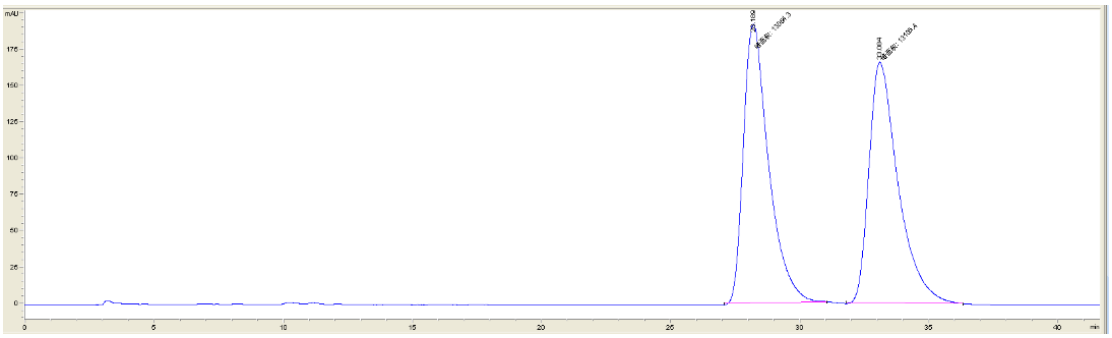


Fig. S32 ^{13}C NMR spectrum of (*S*)-1-(benzothiazol-2-ylthio)-3-hydroxypropan-2-yl-4-methyl-benzene sulfonate.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	27.986	8349.8	122.8	1.1334	0.584	94.725
2	32.884	464.9	6.8	1.134	0.687	5.275

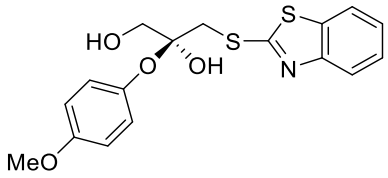
Fig. S33 HPLC of (*S*)-1-(benzothiazol-2-ylthio)-3-hydroxypropan-2-yl-4-methyl-benzene-sulfonate.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	28.189	13054.3	192.1	1.1323	0.615	49.902
2	33.064	13105.4	166.1	1.3147	0.559	50.098

Fig. S34 HPLC of racemic-1-(benzothiazol-2-ylthio)-3-hydroxypropan-2-yl-4-methyl-benzene-sulfonate.

(*S*)-3-(Benzo[d]thiazol-2-ylthio)-2-(4-methoxyphenoxy)propan-1-ol:[6] 94% yield, 95% ee as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 4.52 (t, *J* = 9.9 Hz, 1H), 4.12 (s, 1H), 3.87 – 3.75 (m, 3H), 3.69 (d, *J* = 11.9 Hz, 3H), 3.57 (dd, *J* = 14.6, 6.6 Hz, 1H). **^{13}C NMR** (151 MHz, chloroform-*d*): δ 167.15, 153.73, 151.23, 150.06, 134.09, 125.32, 123.67, 120.11, 117.03, 113.79, 76.92, 60.19, 54.69, 31.98. **HPLC** analysis (Daicel Chiralpak AD-H column, hexane/*i*-PrOH =90/10, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{minor} = 19.5 min; t_{major} =21.8 min.



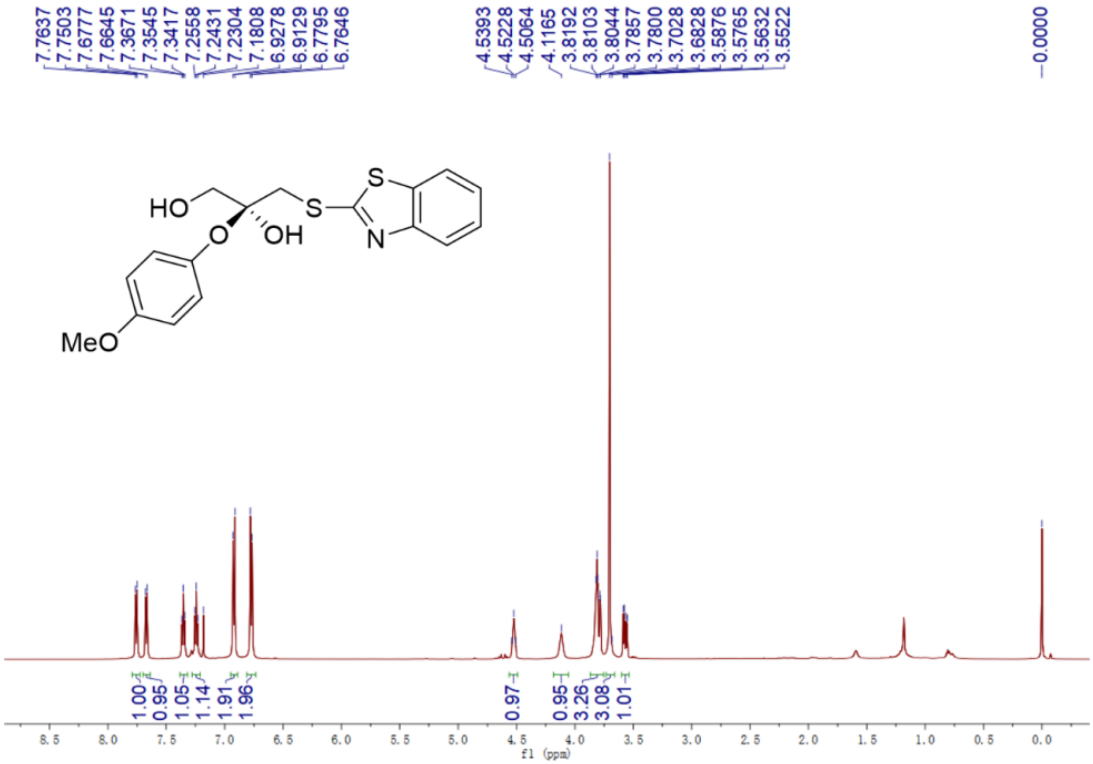


Fig. S35 ^{1}H NMR spectrum of (*S*)-3-(benzo[d]thiazol-2-ylthio)-2-(4-methoxyphenoxy)propan-1-ol.

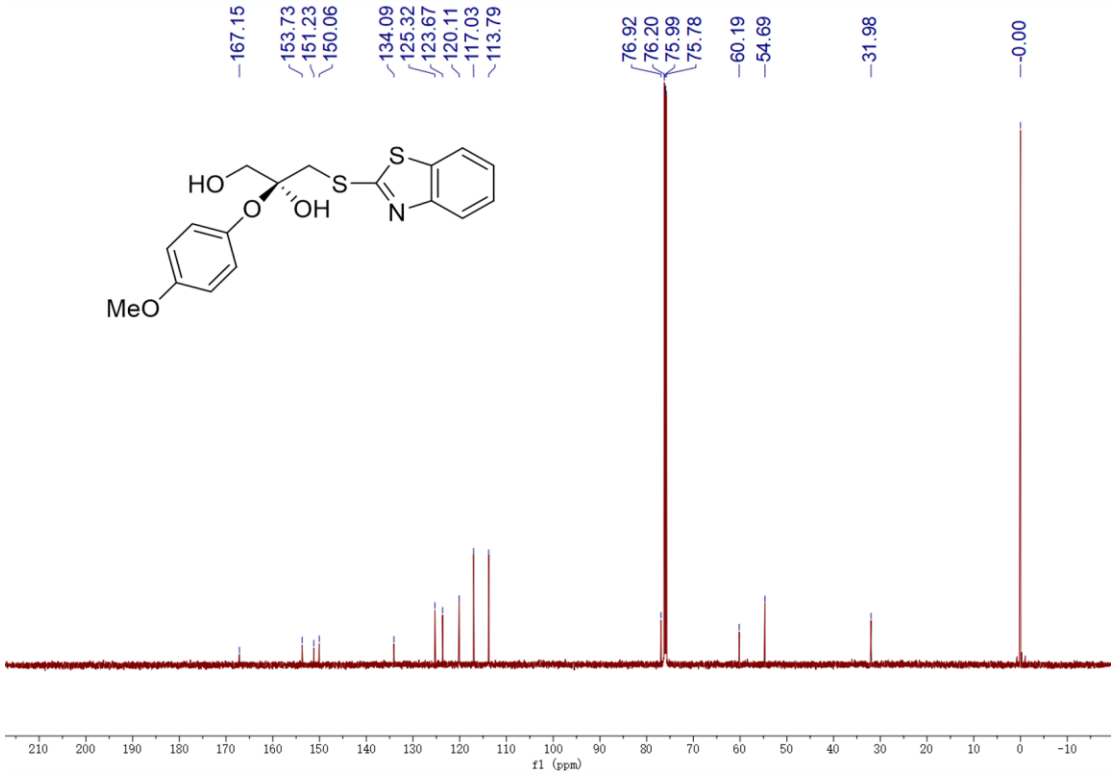
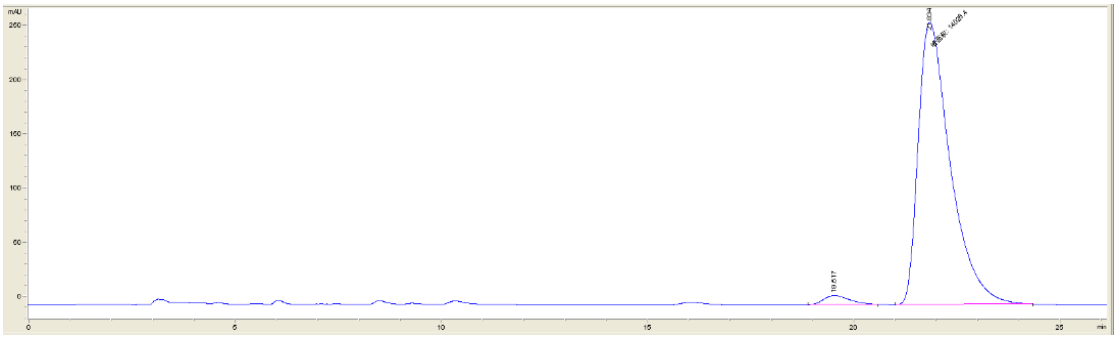
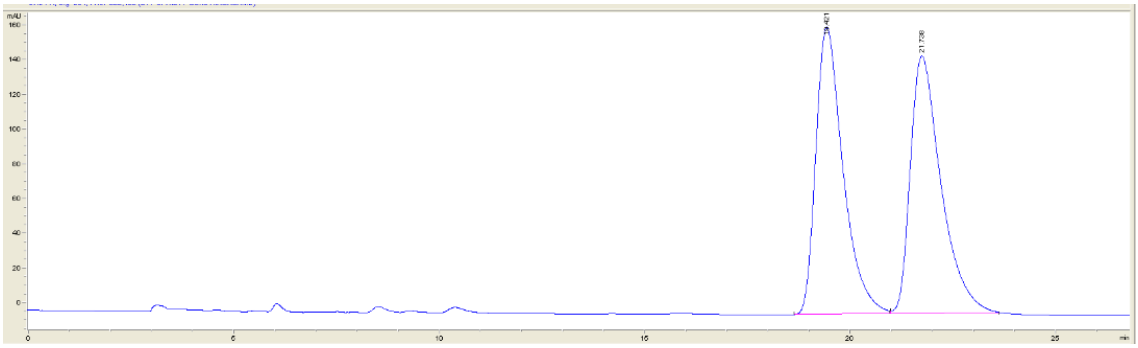


Fig. S36 ^{13}C NMR spectrum of (*S*)-3-(benzo[d]thiazol-2-ylthio)-2-(4-methoxyphenoxy)propan-1-ol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	19.517	377.8	8.5	0.5979	0.642	2.623
2	21.834	14026.4	259.7	0.9001	0.536	97.377

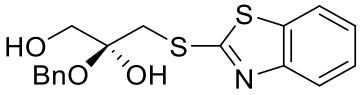
Fig. S37 HPLC of (*S*)-3-(benzo[d]thiazol-2-ylthio)-2-(4-methoxyphenoxy)propan-1-ol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	19.421	7646.3	165.7	0.6884	0.613	49.717
2	21.738	7733.4	148.6	0.7831	0.556	50.283

Fig. S38 HPLC of racemic 3-(benzo[d]thiazol-2-ylthio)-2-(4-methoxyphenoxy)propan-1-ol.

(S)-3-(Benzo[d]thiazol-2-ylthio)-2-(benzyloxy)propan-1-ol:[6] 95% yield, 96% ee as a



colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 (dt, *J* = 14.9, 7.3 Hz, 4H), 7.20 (dd, *J* = 13.6, 6.8 Hz, 2H), 4.60 (dd, *J* = 29.9, 11.8 Hz, 2H), 3.90 – 3.75 (m, 2H), 3.74 – 3.61 (m, 3H), 3.48 (dd, *J* = 14.4, 6.2 Hz, 1H). **^{13}C NMR** (151 MHz, chloroform-*d*): δ 167.21, 151.32, 136.86, 134.01, 127.48, 126.89, 126.82, 125.23, 123.53, 120.09, 120.04, 76.72, 70.80, 60.42, 32.62. **HPLC** analysis (Daicel Chiralpak AD-H column, hexane/*i*-PrOH =90/10, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{minor} = 14.5 min; t_{major} =16.2 min.

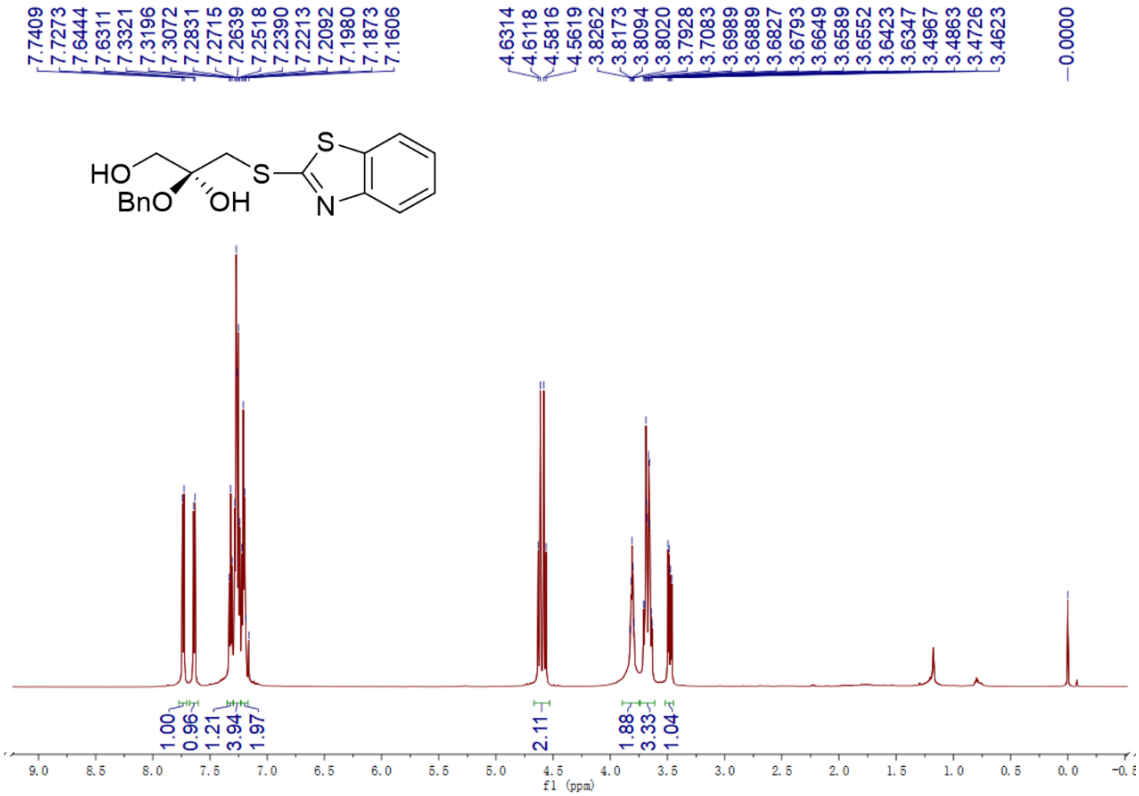


Fig. S39 ^{1}H NMR spectrum of (*S*)-3-(benzo[d]thiazol-2-ylthio)-2-(benzyloxy)propan-1-ol.

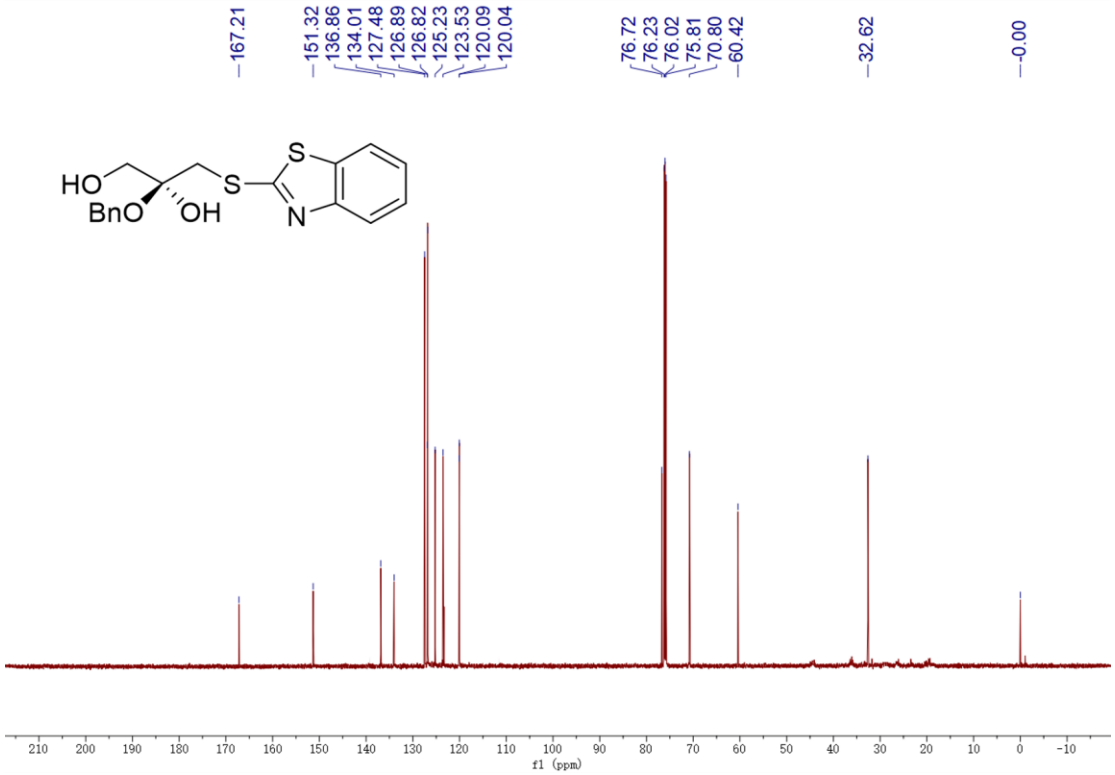
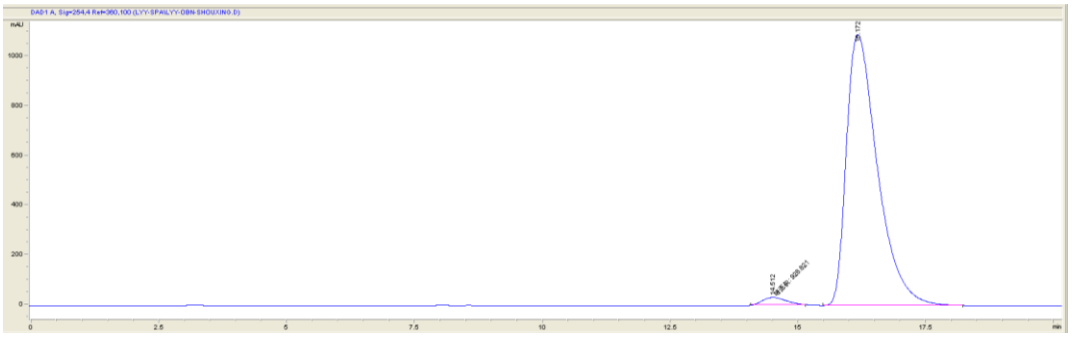
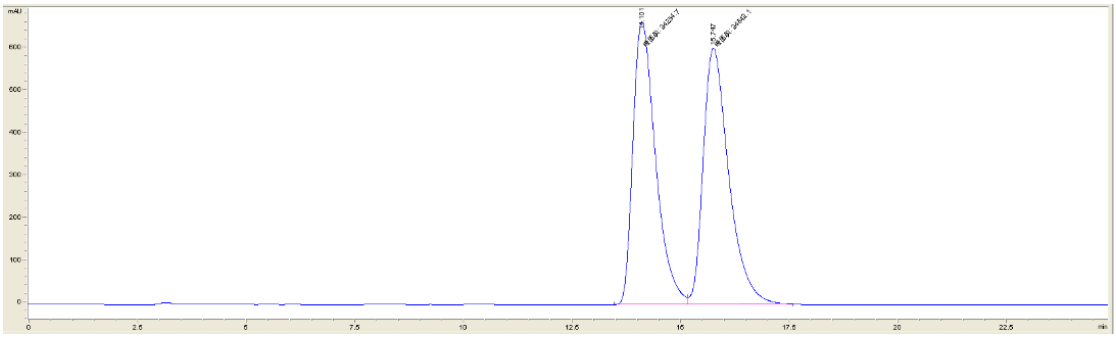


Fig. S40 ^{13}C NMR spectrum of (*S*)-3-(benzo[d]thiazol-2-ylthio)-2-(benzyloxy)propan-1-ol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	14.512	926.6	29.6	0.5216	0.797	1.964
2	16.172	46250.1	1090.6	0.6448	0.543	98.036

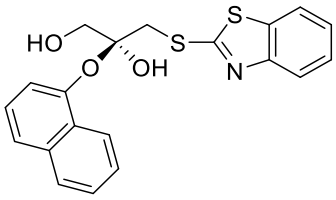
Fig. S41 HPLC of(*S*)-3-(benzo[d]thiazol-2-ylthio)-2-(benzyloxy)propan-1-ol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	14.101	24254.7	666.9	0.6062	0	49.402
2	15.747	24842.1	604.4	0.695	0.633	50.598

Fig. S42 HPLC of racemic 3-(benzo[d]thiazol-2-ylthio)-2-(benzyloxy)propan-1-ol

(*S*)-3-(Benzo[d]thiazol-2-ylthio)-2-(naphthalen-1-yloxy)propan-1-ol:[6] 93% yield, 94% ee as



a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.30 (m, 5H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 4.92 (s, 1H), 4.41 (s, 1H), 3.98 (dd, *J* = 18.9, 4.3 Hz, 3H), 3.70 (dd, *J* = 14.7, 6.3 Hz, 1H). **^{13}C NMR** (151 MHz, chloroform-*d*): δ 167.28, 151.66, 151.15, 134.06, 133.73, 126.51, 126.02, 125.51, 125.34, 125.23, 124.68, 124.44, 123.70, 123.45, 120.98, 120.28, 120.26, 120.11, 120.08, 111.07, 106.16, 75.60, 60.02, 32.29. **HPLC** analysis (Daicel Chiralpak AS-H column, hexane/*i*-PrOH =90/10, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{minor} = 11.8 min; t_{major} =13.0 min.

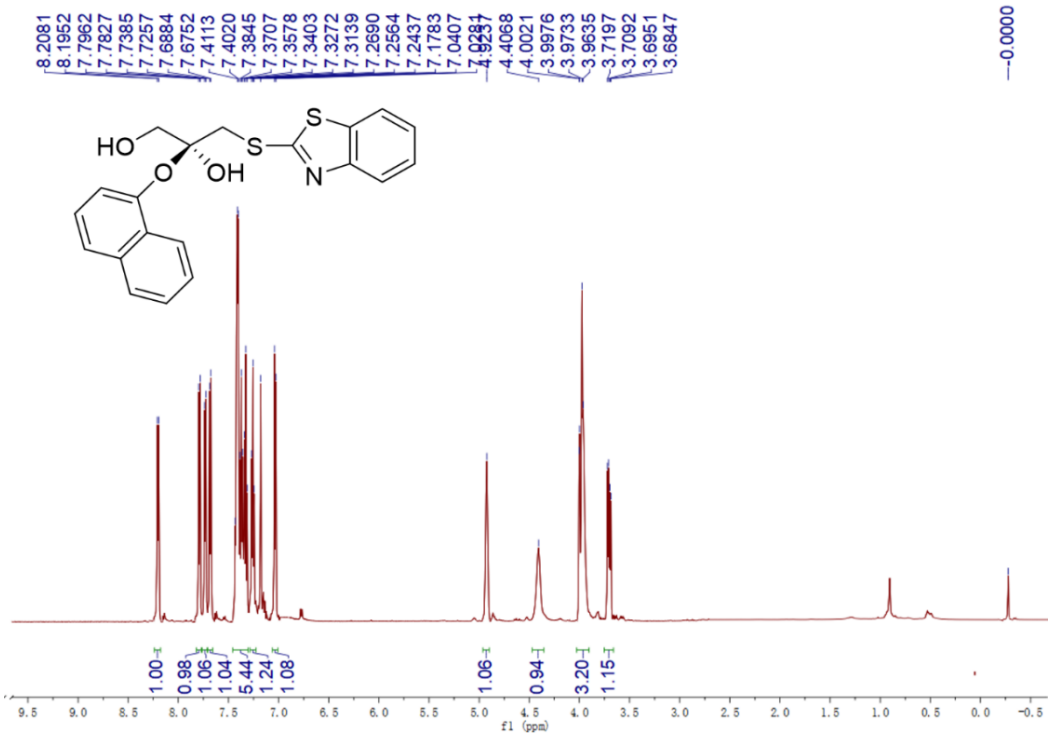


Fig. S43 ^{1}H NMR spectrum of (*S*)-3-(benzo[d]thiazol-2-ylthio)-2-(naphthalen-1-yloxy)propan-1-ol.

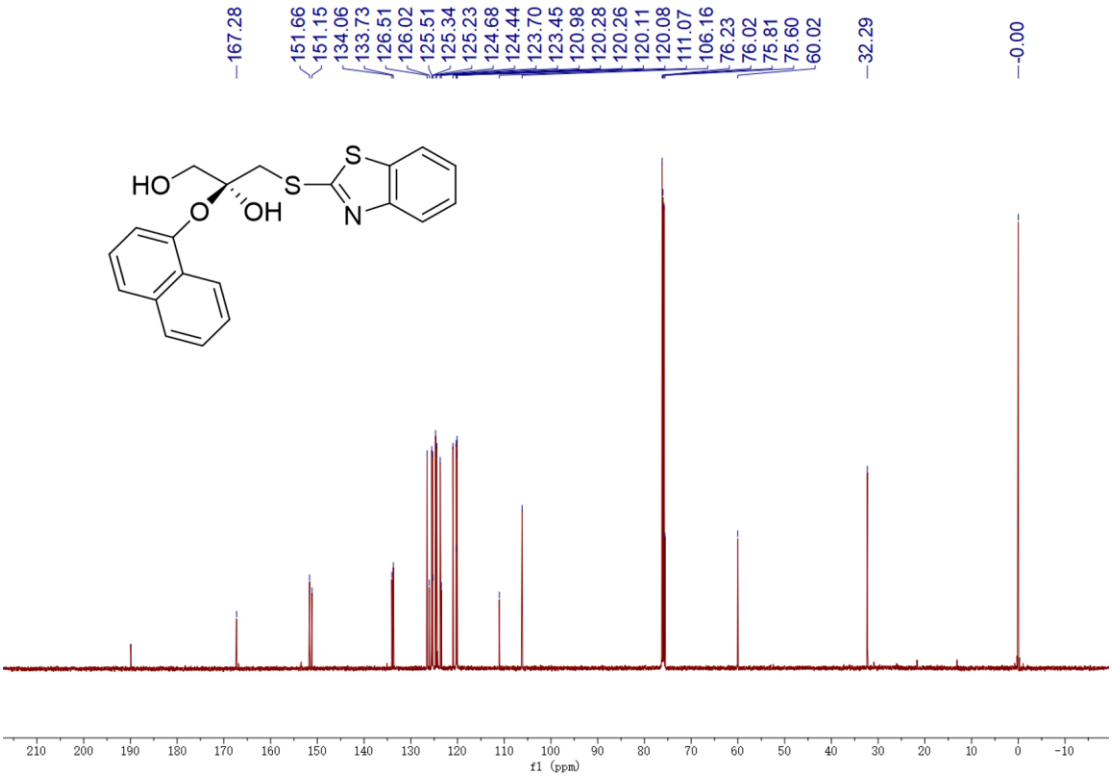
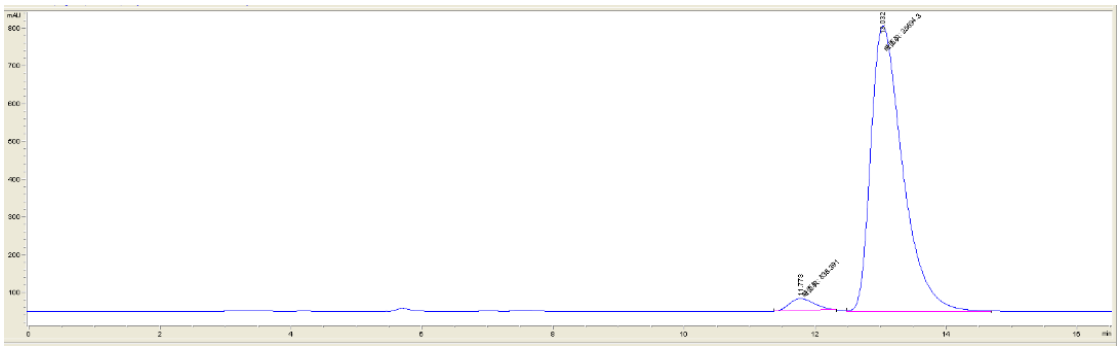
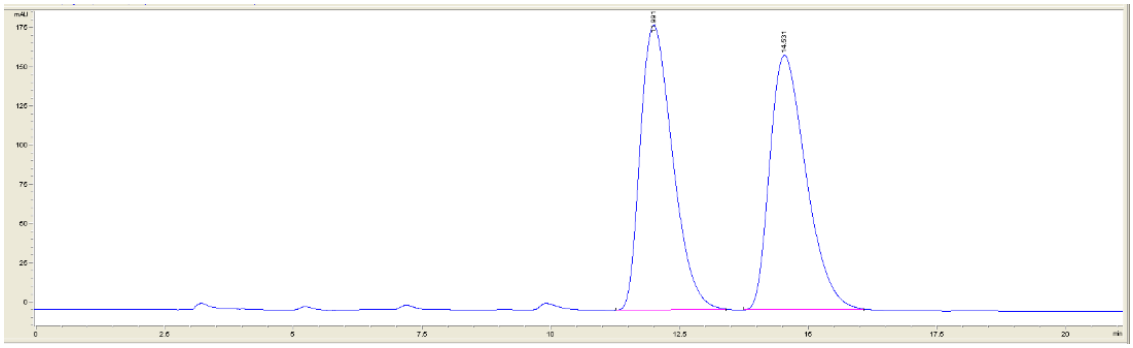


Fig. S44 ^{13}C NMR spectrum of (*S*)-3-(benzo[d]thiazol-2-ylthio)-2-(naphthalen-1-yloxy)propan-1-ol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	11.773	838.4	31.4	0.4455	0.732	3.160
2	13.032	25694. 3	757.1	0.5656	0.592	96.840

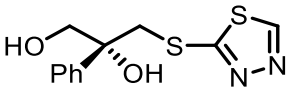
Fig. S45 HPLC of (*S*)-3-(benzo[d]thiazol-2-ylthio)-2-(naphthalen-1-yloxy)propan-1-ol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	11.991	7943.2	181.7	0.6819	0.657	49.944
2	14.531	7961. 1	162.4	0.7601	0.635	50.056

Fig. S46 HPLC of racemic 3-(benzo[d]thiazol-2-ylthio)-2-(naphthalen-1-yloxy)propan-1-ol.

(*R*)-3-((1,3,4-Thiadiazol-2-yl)thio)-2-phenylpropane-1,2-diol: [6] 72% yield, 88% ee as a



colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.89 (s, 1H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 4.74 (s, 1H), 3.92 (d, *J* = 14.4 Hz, 1H), 3.86 (dd, *J* = 11.2, 4.2 Hz, 1H), 3.74 (t, *J* = 11.6 Hz, 2H), 3.47 (s, 1H). **^{13}C NMR** (151 MHz, chloroform-*d*): δ 167.04, 150.92, 141.05, 127.43, 126.74, 124.52, 75.46, 67.65, 42.24. **HPLC** analysis (Daicel Chiralpak AD-H column, hexane/*i*-PrOH =90/10, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{major} = 47.5 min; t_{minor} =51.8 min.

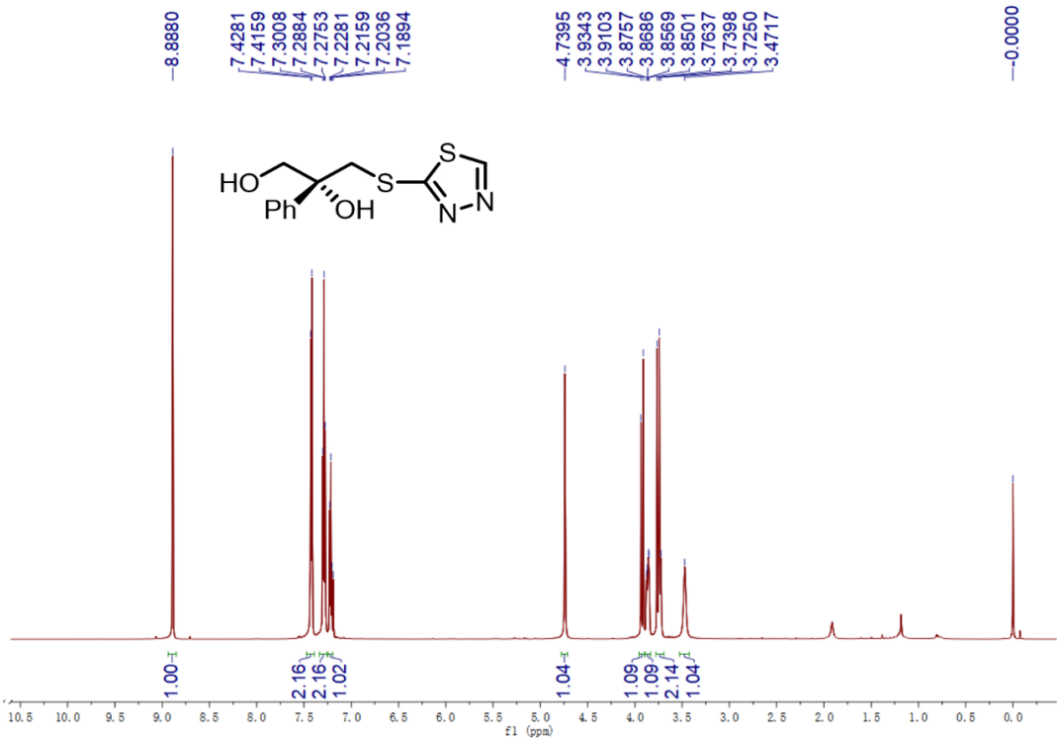


Fig. S47 ^{1}H NMR spectrum of (*R*)-3-((1,3,4-thiadiazol-2-yl)thio)-2-phenylpropane-1,2-diol.

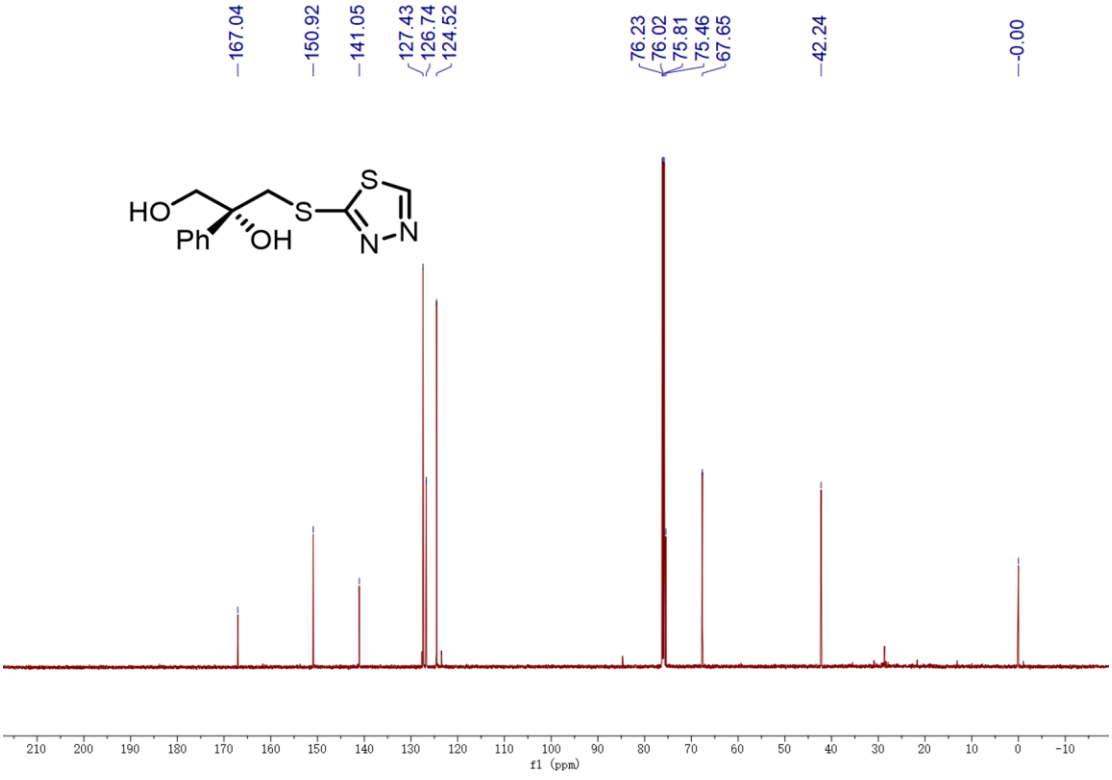
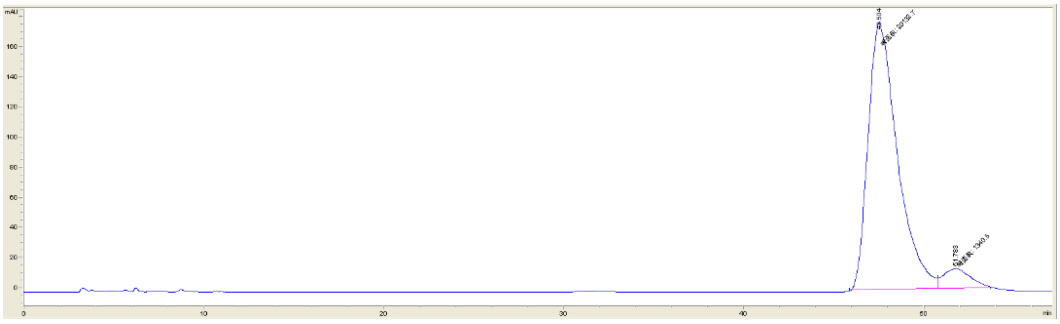
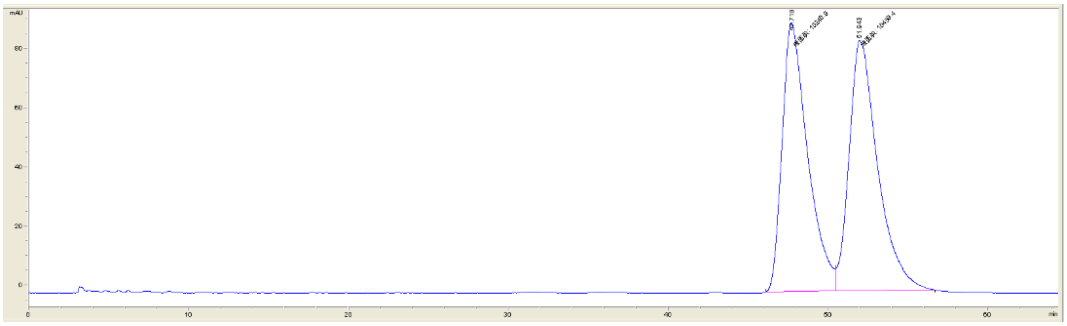


Fig. S48 ^{13}C NMR spectrum of (*R*)-3-((1,3,4-thiadiazol-2-yl)thio)-2-phenylpropane-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	47.504	20132.7	177.7	1.8884	0	93.757
2	51.783	1340. 5	13.1	1.7109	0.844	6.243

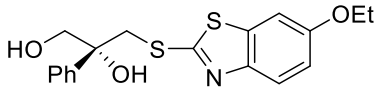
Fig. S49 HPLC of (*R*)-3-((1,3,4-thiadiazol-2-yl)thio)-2-phenylpropane-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	47.719	10246.9	90.8	1.8812	0	49.487
2	51.943	10459.4	84.6	2.0606	0.549	50.513

Fig. S50 HPLC of racemic 3-((1,3,4-thiadiazol-2-yl)thio)-2-phenylpropane-1,2-diol.

(*R*)-3-((6-Ethoxybenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol:[6] 93% yield, 97% ee



as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.1 Hz, 1H), 7.08 (s, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 3.97 (q, *J* = 6.8 Hz, 2H), 3.91 (d, *J* = 11.5 Hz, 1H), 3.78 (d, J = 14.8 Hz, 1H), 3.67 (dd, *J* = 17.8, 13.4 Hz, 2H), 1.35 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, chloroform-*d*): δ 164.77, 155.71, 145.23, 141.62, 135.48, 127.32, 126.55, 124.55, 120.46, 114.61, 103.84, 75.40, 67.37, 63.13, 41.80, 13.76. **HPLC** analysis (Daicel Chiralpak AD-H column, hexane/*i*-PrOH =80/20, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{minor} = 19.4 min; t_{major} =27.1 min.

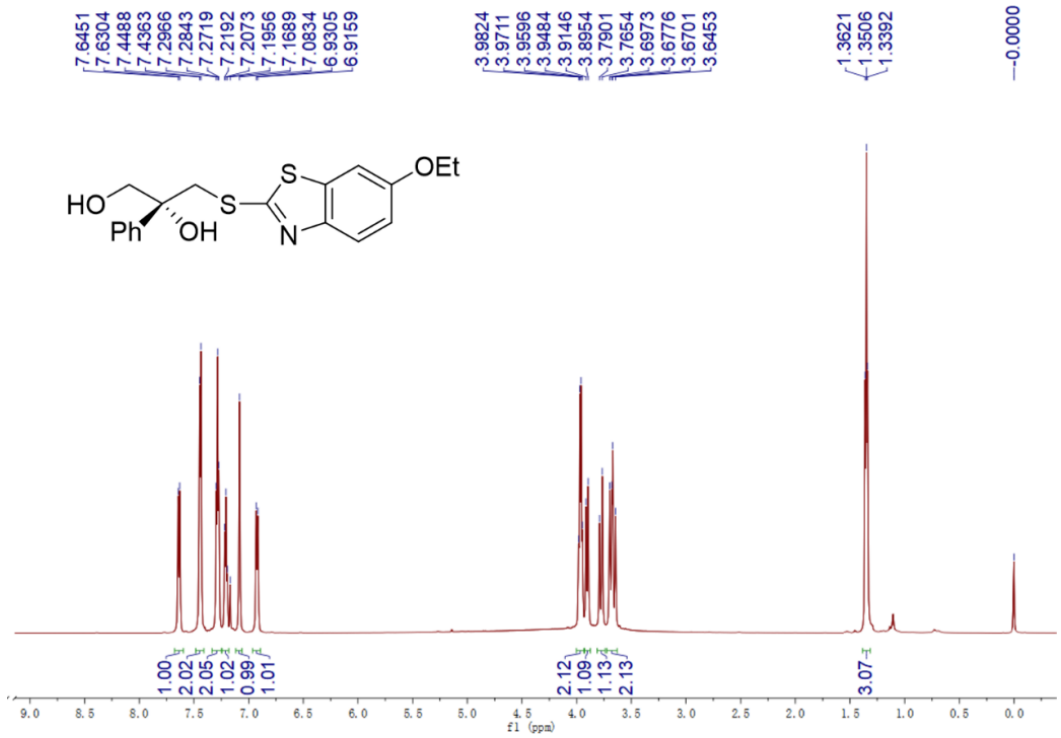


Fig. S51 ^{1}H NMR spectrum of (*R*)-3-((6-ethoxybenzo[d]thiazol-2-yl)thio)-2-phenylpropane--1,2-diol.1,2-diol.

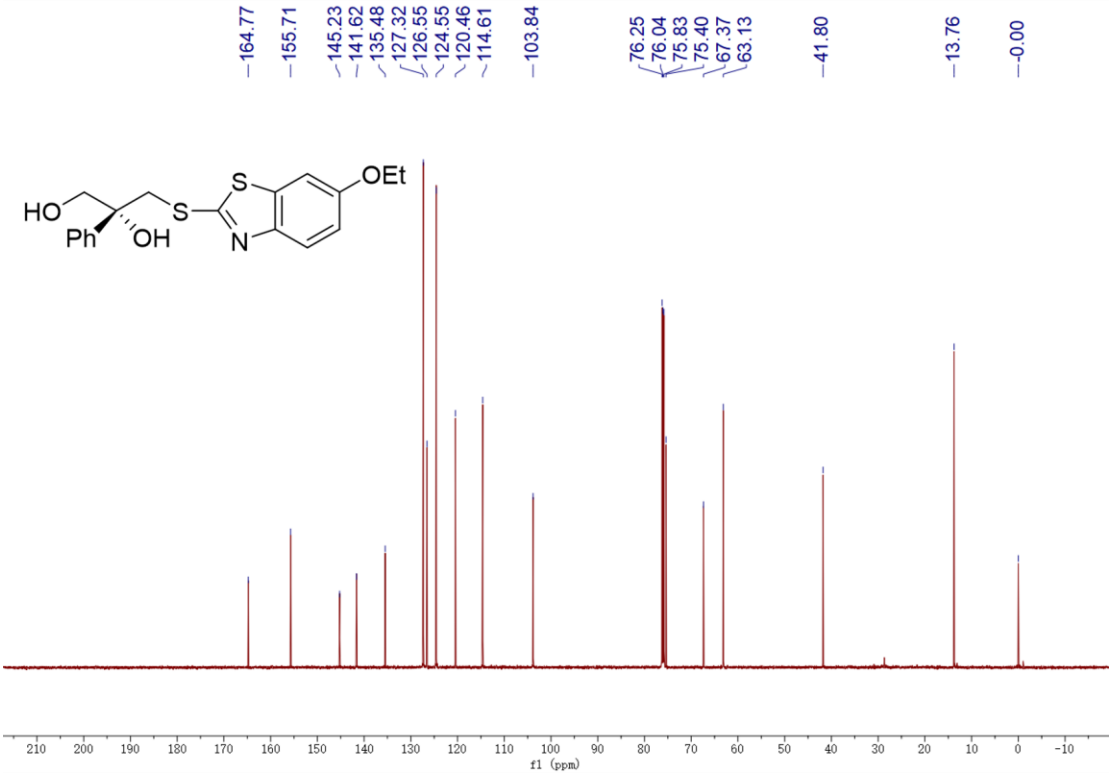
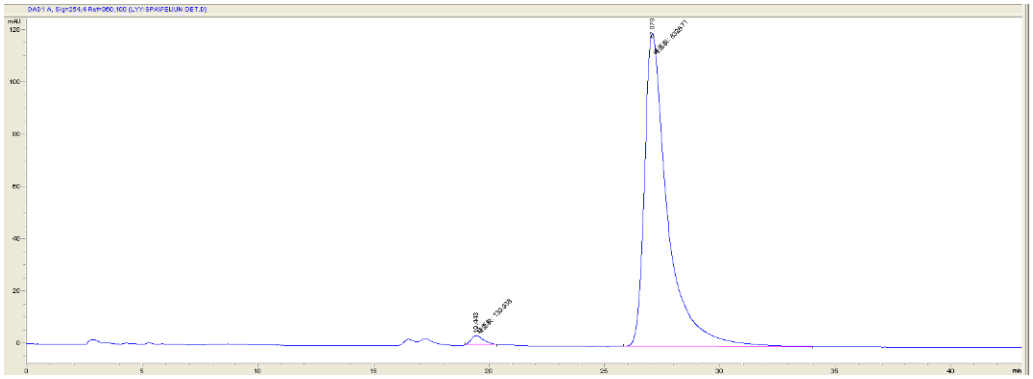
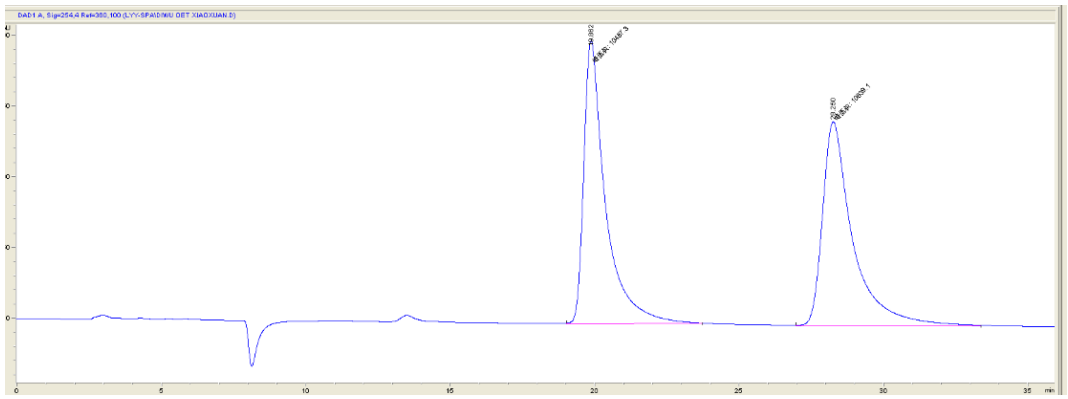


Fig. S52 ^{13}C NMR spectrum of (*R*)-3-((6-ethoxybenzo[d]thiazol-2-yl)thio)-2-phenylpropane--1,2-diol.1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	19.443	130.9	3.5	0.6311	0.743	1.548
2	27.07	8326.7	119.4	1.1618	0.511	98.452

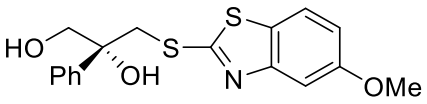
Fig. S53 HPLC of (*R*)-3-((6-ethoxybenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	19.862	10487.3	200.1	0.8735	0.481	49.641
2	28.25	10639.1	144.6	1.2261	0.523	50.359

Fig. S54 HPLC of racemic 3-((6-ethoxybenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol**.**

(*R*)-3-((5-Methoxybenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol:[6] 93% yield,



95 %ee as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 14.3, 8.2 Hz, 3H), 7.33 – 7.26 (m, 3H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 3.92 (d, *J* = 11.5 Hz, 1H), 3.82 (d, *J* = 14.9 Hz, 1H), 3.79 (s, 3H), 3.69 (t, *J* = 12.8 Hz, 2H). **^{13}C NMR** (151 MHz, chloroform-*d*): δ 169.06, 158.21, 152.00, 141.54, 127.37, 126.62, 125.74, 124.53, 120.32, 113.78, 102.90, 75.41, 67.38, 54.67, 41.77. **HPLC** analysis (Daicel Chiralpak AS-H column, hexane/*i*-PrOH =80/20, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{major} = 14.9min; t_{minor} =20.4 min.

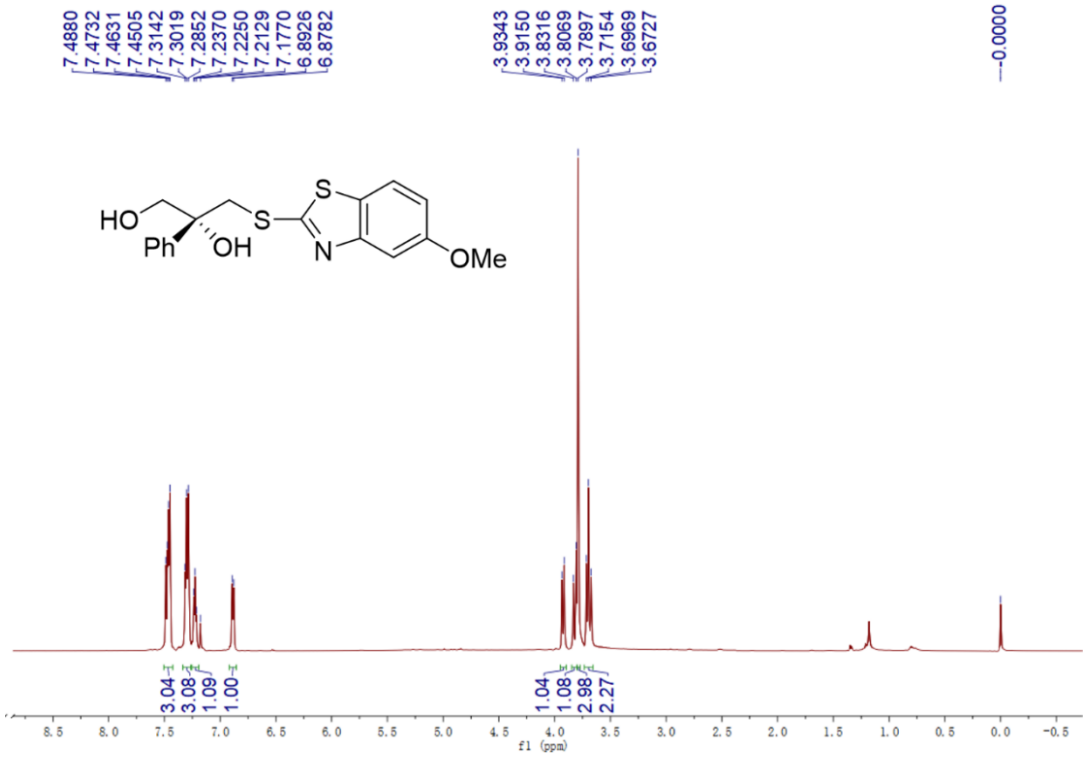


Fig S55 ^{1}H NMR spectrum of (*R*)-3-((5-methoxybenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol.

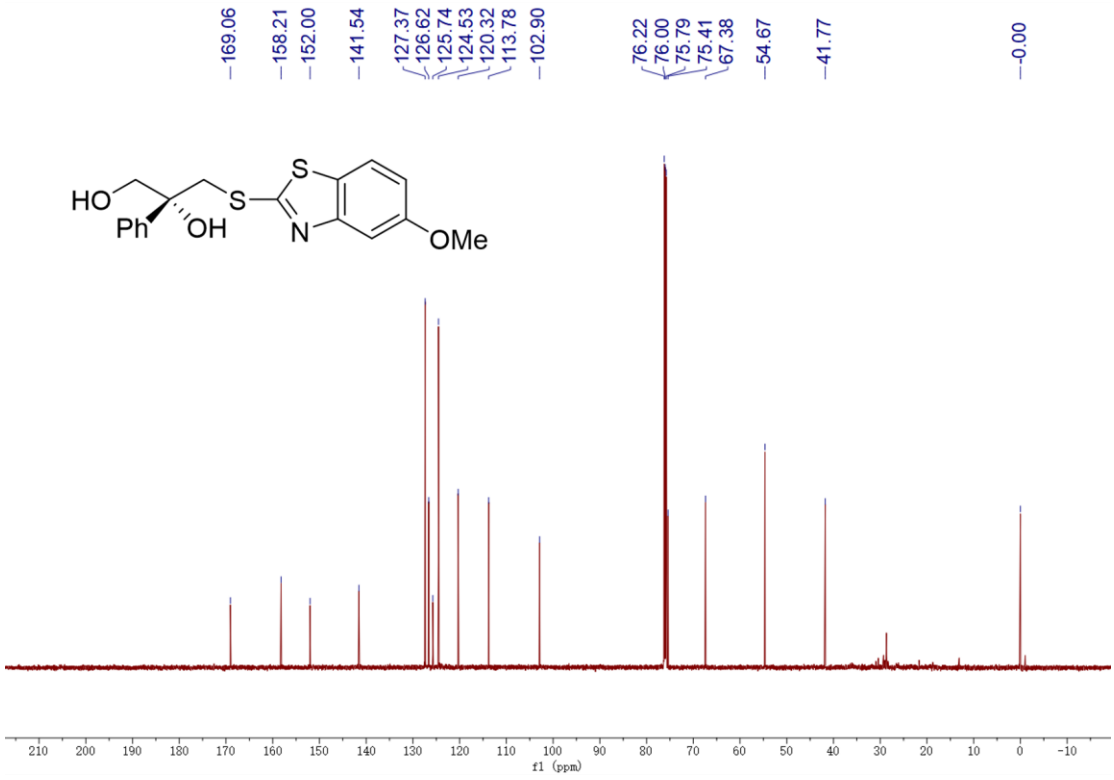
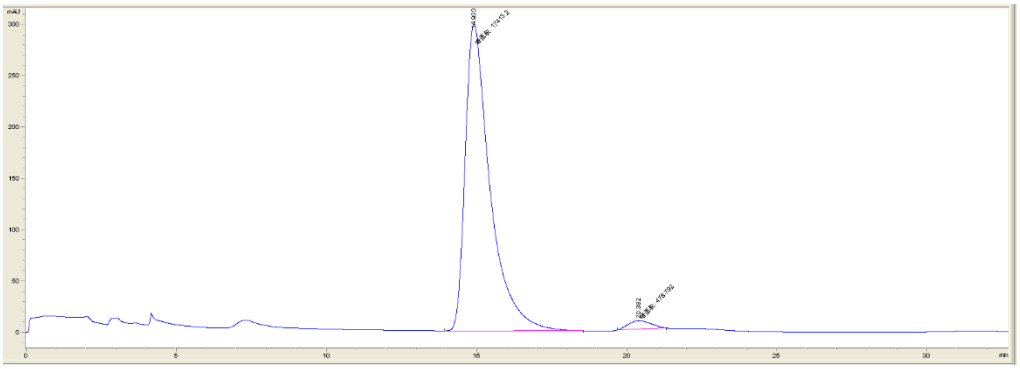
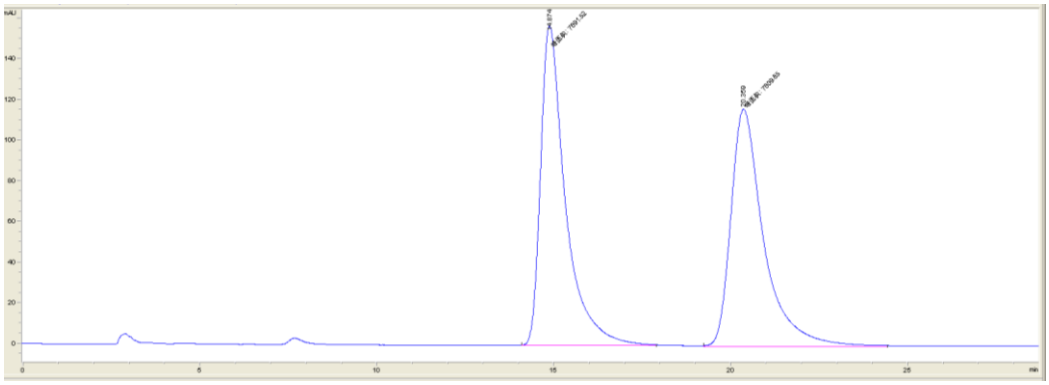


Fig S56 ^{13}C NMR spectrum of (*R*)-3-((5-methoxybenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	14.903	17413.2	299.8	0.9681	0.523	97.324
2	20.382	478.8	8.7	0.9178	0.808	2.676

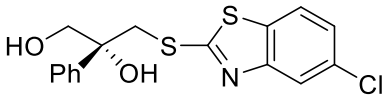
Fig. S57 HPLC of (*R*)-3-((5-methoxybenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	14.874	7691.5	157.5	0.8139	0.532	50.267
2	20.359	7609.9	117	1.0844	0.601	49.733

Fig. S58 HPLC of racemic 3-((5-methoxybenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol.

(*R*)-3-((5-Chlorobenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol:[6] 96% yield, 99% ee



as a colorless oil.**^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.9 Hz, 2H), 5.07 (s, 1H), 3.88 (dd, *J* = 24.3, 13.1 Hz, 2H), 3.71 (d, *J* = 14.1 Hz, 2H), 3.55 (s, 1H). **^{13}C NMR** (151 MHz, chloroform-*d*): δ 170.37, 151.62, 141.30, 132.40, 131.61, 127.42, 126.71, 124.50, 124.19, 120.72, 119.98, 75.44, 67.47, 41.67. **HPLC** analysis (Daicel Chiralpak OD-H column, hexane/*i*-PrOH =95/5, flow rate 1.0 mL min^{-1}, 280 nm, 30 °C): t_{minor} = 39.0 min; t_{major} =45.7 min.

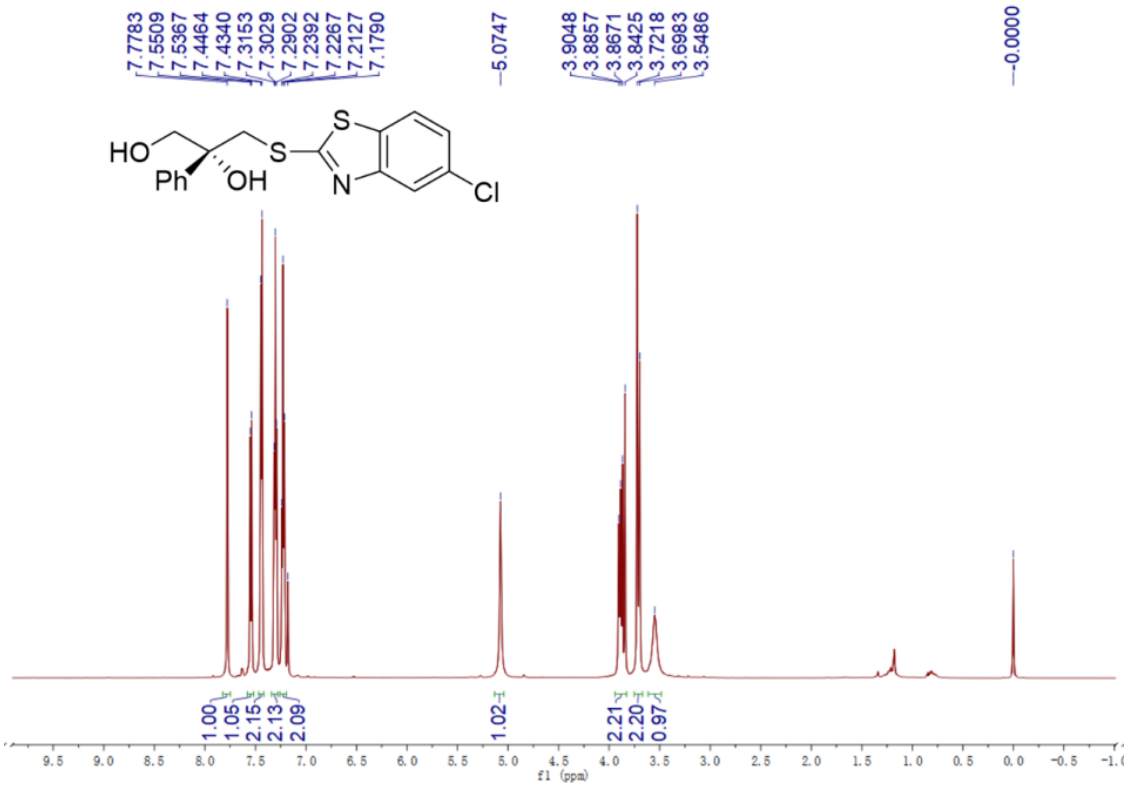


Fig. S59 ^{1}H NMR spectrum of (*R*)-3-((*5*-chlorobenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol.

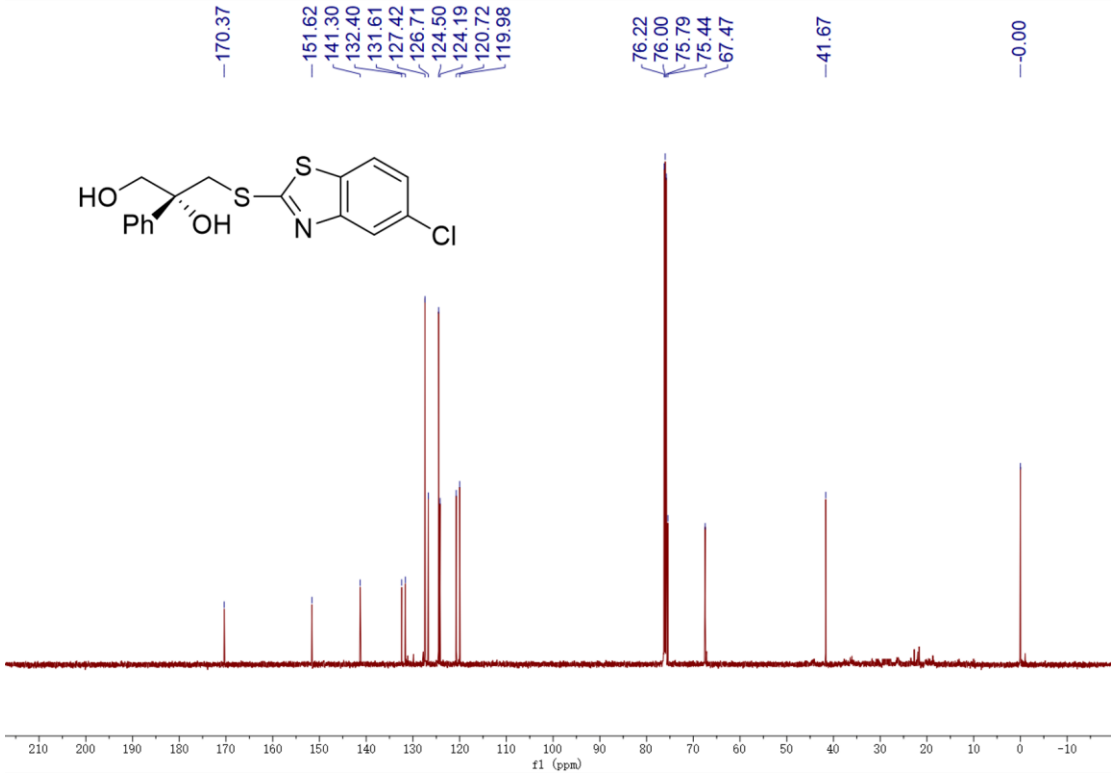
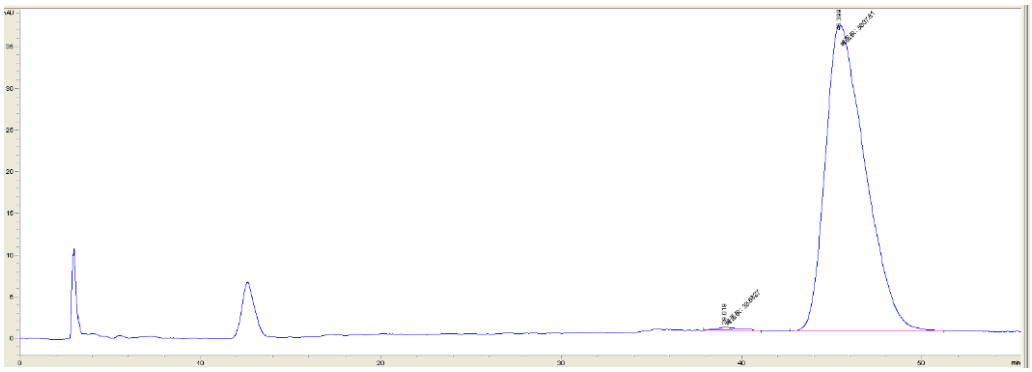
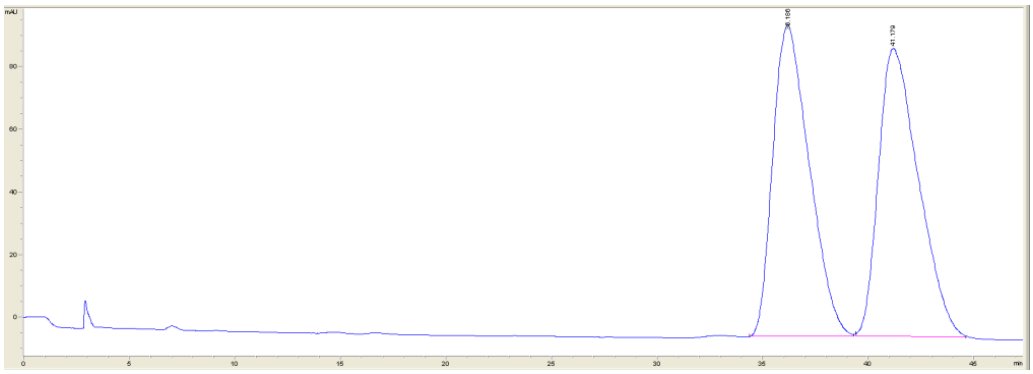


Fig. S60 ^{13}C NMR spectrum of (*R*)-3-((*5*-chlorobenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	39.019	36.7	0.4	1.5469	0.38	0.650
2	45.699	5607.8	36.7	2.5499	0.541	99.350

Fig. S61 HPLC of (*R*)-3-((5-chlorobenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol.



Entry	Time[min]	Area[mAU*s]	Height[mAU]	Width[min]	Symmetry factor	Area%
1	36.180	11963.6	99.7	1.6481	0.648	49.639
2	41.179	12137.5	92.1	1.7273	0.552	50.361

Fig. S62 HPLC of racemic 3-((5-chlorobenzo[d]thiazol-2-yl)thio)-2-phenylpropane-1,2-diol.

6. Reaction of (*R*)-AnSPA with (chloromethyl)pentamethylbenzene

In a dry argon-filled Schlenk tube (25 mL), (*R*)-AnSPA (66.7 mg, 0.1 mmol), 2,3,4,5,6-pentamethylbenzyl chloride (19.6 mg, 0.1 mmol) and DCE (10 mL) were added. The resulting mixture was heated to 60 °C and stirred for 36 h. After being cooled to room temperature, DCE was removed under reduced pressure. The residue was purified by column chromatography using mixed solvents of CH_2Cl_2 and MeOH as eluents (*v*/*v* = 50:1), yielding a white solid (20 mg, 24 %). ^{1}H NMR spectra of the white solid and (*R*)-AnSPA are shown in Fig.S63.

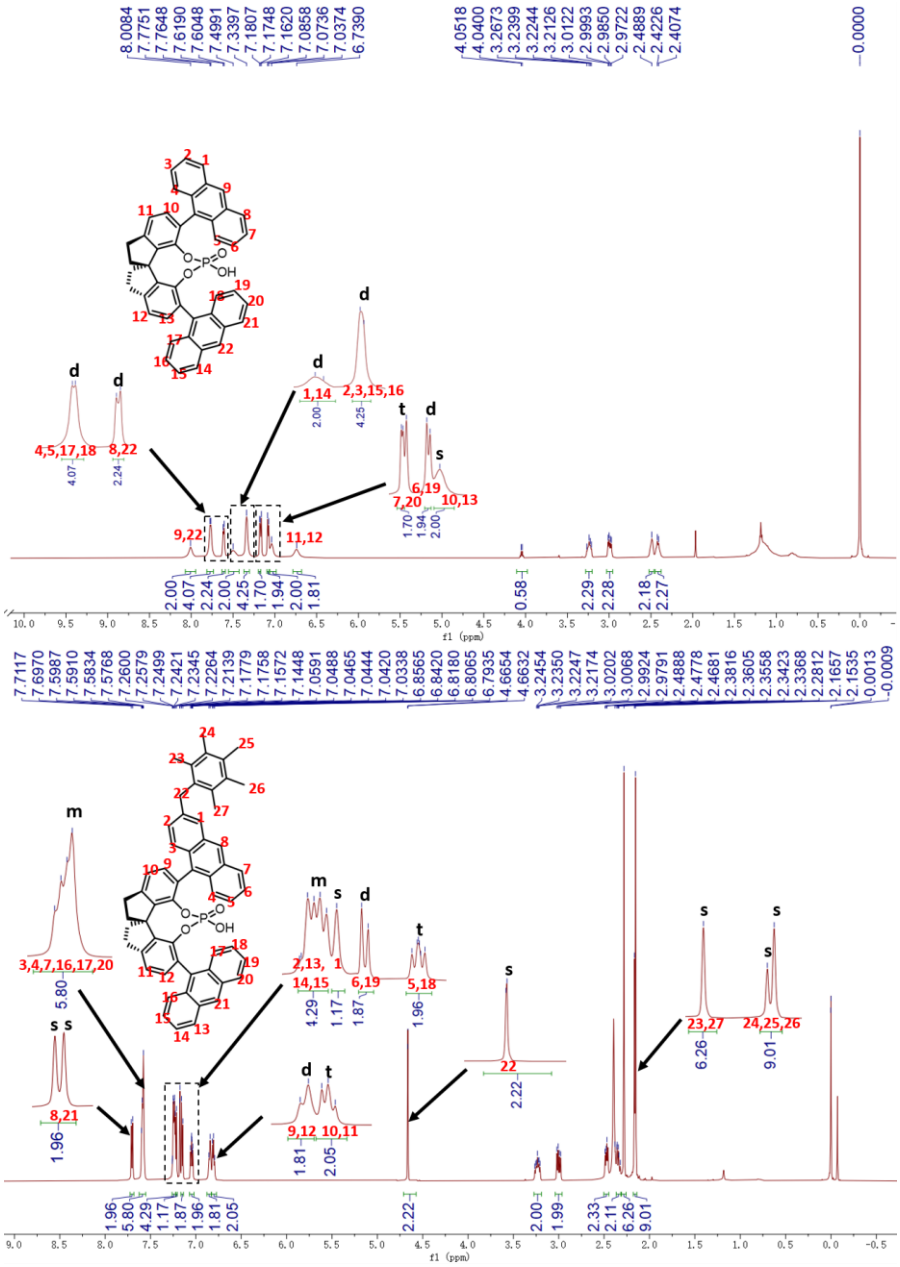


Fig. S63 ^{1}H NMR spectrum of (*R*)-AnSPA (a) and molecule obtained by the reaction of (*R*)-AnSPA with (chloromethyl)pentamethylbenzene (b).

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