SUPPORTING INFORMATION

for

Role of the Cocatalyst in the Asymmetric Coupling of Racemic Epoxides with CO_2 using Multichiral Co(III) Complexes: Product Selectivity and Enantioselectivity

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Contents

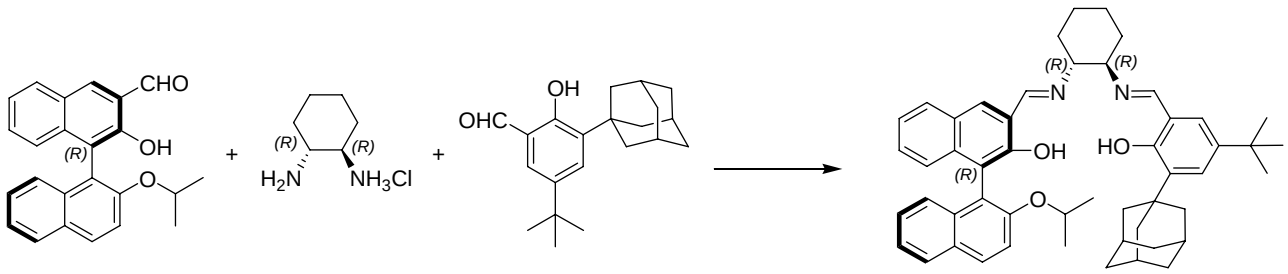
1. General information

All manipulations involving air- and/or water-sensitive compounds were carried out in glove box or under dry nitrogen using standard Schlenk techniques. Propylene oxide (PO) was refluxed over a mixture of KOH/CaH_2, and fractionally distilled under a nitrogen atmosphere prior to use. Other epoxides were purchased from Acros company and distilled under a nitrogen atmosphere from CaH_2 prior to use. Carbon dioxide (99.995%) was purchased from Dalian Institute of Special Gases and used as received.

^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 MHz type (^1H, 400 MHz; ^{13}C, 100 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ^1H NMR and against the solvent, chloroform-*d* at 77.0 ppm for ^{13}C NMR, respectively.

ESI/MS spectra of the complex and ligand in positive ion mode were carried out using a Micromass Q-Tof (Micromass, Wythenshawe, UK) mass spectrometer equipped with an orthogonal electrospray source (Z-spray) and referenced against the sample of $(m/z)^+$ = 574.3182 (Capillary = 2000 V, Sample cone = 20 V).

2. Synthesis of ligand

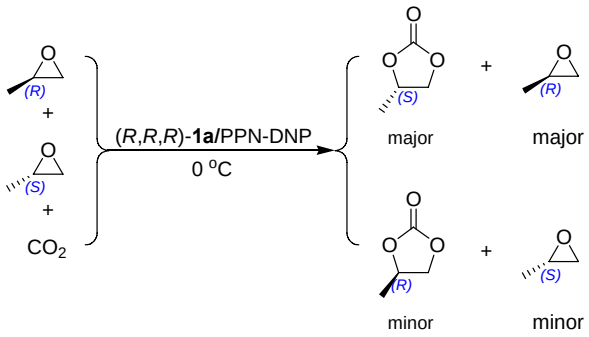


A flask was charged with (*R*,*R*)-1,2-diaminocyclohexane mono(hydrogen chloride) (0.15 g, 1.0 mmol), activated 5 Å molecular sieve (1.00 g), and anhydrous methanol (10 mL). 3-adamanyl-5-*tert*-butyl-2-hydroxybenzaldehyde (0.31 g, 1.0 mmol) was added in one portion and the reaction mixture was stirred at room temperature for 1 h. A solution of 3-formyl-2-hydroxy-2'-isopropoxy-1,1'-binaphthyl (0.36 g, 1.0 mmol) in anhydrous methylene chloride (10 mL) was then added to the reaction system, followed by the slow addition of triethylamine (0.14 mL, 1.0 mmol). After the reaction mixture was stirred at room temperature for an additional 4 h, all solvents and the excessive triethylamine were removed in *vacuo*. The residue was purified by column chromatography on silica gel using petrol ether/ethyl acetate (10:1) as the mobile phase to give the ligand as a bright yellow solid (0.48 g, 65%). $[\alpha]_D^{20}$ –193 (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 13.77 (s, 1H), 13.00 (s, 1H), 8.54 (s, 1H), 8.18 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.73–7.78 (m, 2H), 7.41 (t, J = 8.0 Hz, 1H), 7.05–7.29 (m, 7H), 6.87 (s, 1H), 4.33–4.39 (m, 1H), 3.36–3.41 (m, 1H), 3.20–3.25 (m, 1H), 2.19 (s, 6H), 2.09 (s, 3H), 1.50–2.04 (m, 14H), 1.18 (s, 9H), 1.01 (d, J = 6.0 Hz, 3H), 0.93 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 165.3, 158.3, 154.6, 154.1, 140.1, 136.8, 135.4, 134.1, 133.3, 129.8, 129.4, 128.6, 128.6, 128.1, 127.8, 127.3, 126.9, 126.4, 125.9, 125.6, 125.2, 123.8, 123.0, 121.7, 120.7, 118.7, 117.8, 117.5, 73.3, 72.8, 71.8, 40.4, 37.3, 34.2, 33.2, 32.9, 31.5, 29.5, 24.4, 24.3, 22.6, 22.5. HRMS (m/z) Calcd. for $[C_{51}H_{59}N_2O_3]^+$: 747.4526, found: 747.4573.

3. Enantiomeric excess of propylene carbonate at multiple conversions

Table S1 Enantioselective Coupling of Propylene Oxide with CO_2 at various reaction time points[a]

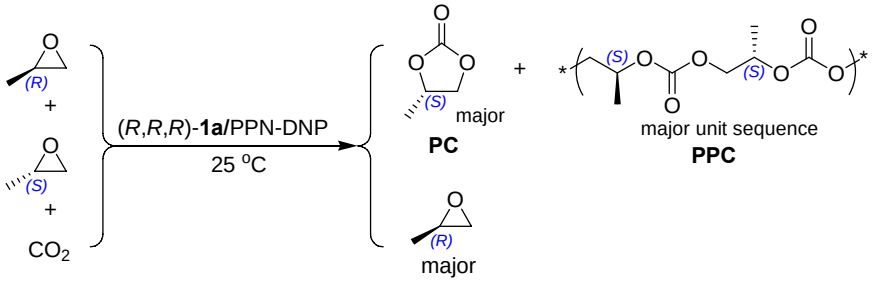


Entry	Time (h)	Conversion (%)	PC *ee* (%)[b]	k_{rel}[c]
1	5	15	94.5	41.6
2	9	26	93.4	40.2
3	12	35	91.8	40.6
4	18	47	88.2	38.4

[a] The reaction was performed in neat *racemic* propylene oxide (7.0 mL, 100 mmol), CO_2 (0.5~0.6 equiv) catalyzed by complex (*R*,*R*,*R*)-**1a** and PPN-DNP under 0 °C in a 75 mL autoclave. The molar ratio of epoxide to (*R*,*R*,*R*)-**1a** is 2000/1, and the molar ratio of PPN-DNP to (*R*,*R*,*R*)-**1a** is 200/1. Selectivity for cyclic carbonate in all systems is 100% based on ^{1}H NMR spectroscopy of the crude product. [b] *ee* is the enantiomeric excess of the propylene carbonate and determined by chiral GC. [c] $k_{rel} = \ln[(1 - c)(1 - ee)]/\ln[(1 - c)(1 + ee)]$, where *c* is the conversion and *ee* is the enantiomeric excess of the recovered epoxide.

4. Effect of the molar ratio of propylene oxide to (R,R,R)-1a on the product selectivity and enantioselectivity

Table S2 Enantioselective Coupling of *Racemic* Propylene Oxide with CO2[a]

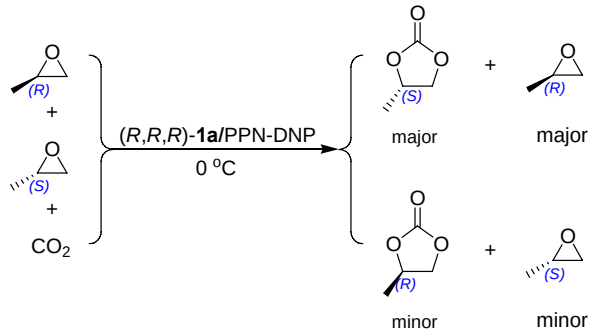


Entry	[PO]/[**1a**]	Time (h)	Conversion (%)	PC/PPC (%)[b]	PC *ee* (%)[c]	k_{rel}[d]
1	2000	2	45	91/9	86.2	27.6
2	5000	4	38	90/10	88.1	27.1
3	10000	12	46	93/7	86.0	29.1
4	20000	24	42	98/2	88.5	31.6

[a] The reaction was performed in neat *racemic* propylene oxide (7.0 mL, 100 mmol), CO_2 (0.5~0.6 equiv) catalyzed by complex (*R*,*R*,*R*)-**1a** and PPN-DNP under 25 °C in a 75 mL autoclave. The molar ratio of PPN-DNP to (*R*,*R*,*R*)-**1a** is 200/1. [b] Selectivity for cyclic carbonate over the polycarbonate in all systems is determined by ^{1}H NMR spectroscopy of the crude product. [c] *ee* is the enantiomeric excess of the propylene carbonate and determined by chiral GC. [d] $k_{rel} = \ln[(1 - c)(1 - ee)]/\ln[(1 - c)(1 + ee)]$, where *c* is the conversion and *ee* is the enantiomeric excess of the recovered epoxide.

5. Catalyst Recycling Experiments

Table S3 Enantioselective Coupling of *Racemic* Propylene Oxide with Carbon Dioxide Using Recovered Binary System of (*R*,*R*,*R*)-**1a** and PPN-DNP[a]



Entry	Time (h)	Conversion (%)	PC *ee* (%)[c]	k_{rel}[d]
1 st	12	35	91.8	40.6
2 nd[b]	12	33	92.5	40.3
3 rd[b]	12	30	93.1	41.4
4 th[b]	15	34	92.1	38.9

[a] The reaction was performed in neat *racemic* propylene oxide (7.0 mL, 100 mmol), CO_2 (0.5~0.6 equiv) catalyzed by complex (*R*,*R*,*R*)-**1a** and PPN-DNP under 0 °C in a 75 mL autoclave. The molar ratio of epoxide to (*R*,*R*,*R*)-**1a** is 2000/1, and the molar ratio of PPN-DNP to (*R*,*R*,*R*)-**1a** is 200/1. Selectivity for cyclic carbonate in all systems is 100% based on ^{1}H NMR spectroscopy of the crude product. [b] The binary system of (*R*,*R*,*R*)-**1a** and PPN-DNP was recovered by distillation of reaction mixture under reduced pressure. [c] *ee* is the enantiomeric excess of the propylene carbonate and determined by chiral GC. [d] $k_{rel} = \ln[(1 - c)(1 - ee)]/\ln[(1 - c)(1 + ee)]$, where *c* is the conversion and *ee* is the enantiomeric excess of the recovered epoxide.

6. Studying the coordination of complex $^{n}Bu_4NN_3$ to (R,R,R)-1b by FTIR spectroscopy

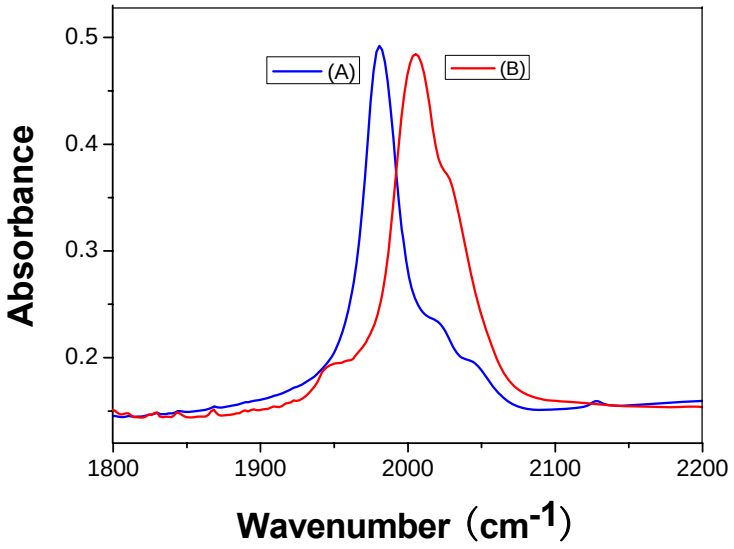


Figure S1. Infrared spectra of CH_2Cl_2 solutions of (A) cobalt salen azide complex, (B) the complex **1b** in the present of 2 equiv of $^{n}Bu_4NN_3$.

7. Studying the weak coordination of MTBD to (R,R,R)-1b by UV-Vis spectroscopy

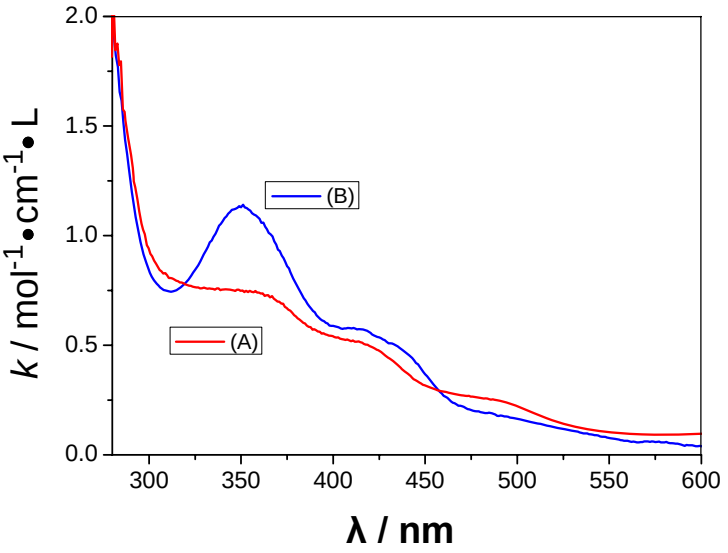


Figure S2. Ultraviolet spectra of CH_2Cl_2 solutions of (A) the complex **1b**, (B) after addition of 2 equiv of MTBD.

8. Monitoring the selectivity of cyclic/polymeric products by in situ infrared spectroscopy

To a stirred mixture of complex **2** (21.3 mg, 0.025 mmol, 1 equiv.) and appropriate $^{n}Bu_4N$-DNP or $^{n}Bu_4NCl$ were dissolved in propylene oxide (3.5 mL, 50 mmol, 2000 equiv.) to form red-brown solution in a nitrogen atmosphere. The mixture solution was charged into a pre-dried 75 mL autoclave equipped with a sampling valve under a CO_2 atmosphere. The autoclave was pressurized to CO_2 (2.0 MPa). Then, the reaction mixture was transfer into the infrared cell (25 um thickness) with 2.0 MPa CO_2. Typical data obtained for the formation of cyclic carbonates and polycarbonates as monitored in the C=O region by infrared spectroscopy every 2 min.

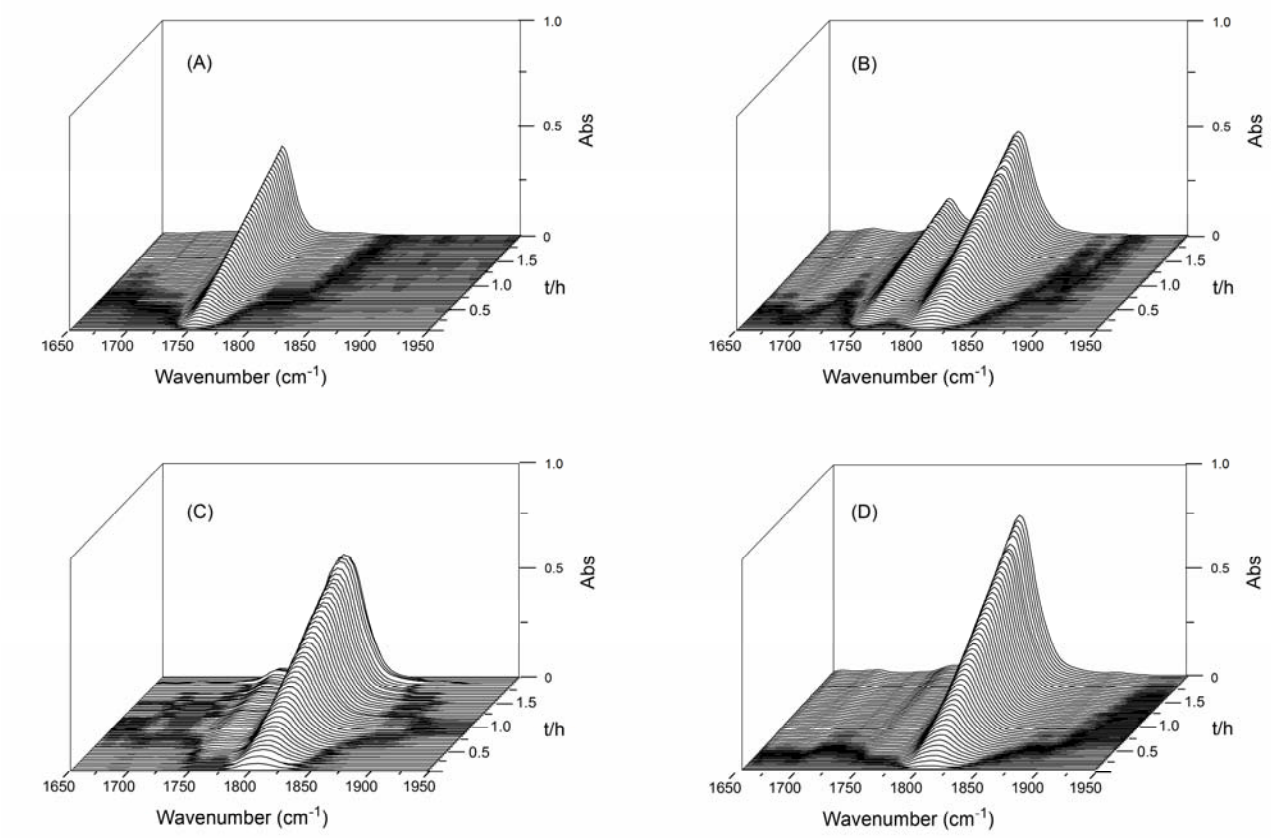


Figure S3 In situ infrared monitoring of the coupling of PO with CO_2 catalyzed by complex **2** and $^{n}Bu_4NCl$. The molar ratio of **2** to $^{n}Bu_4NCl$ is (A) 1:1; (B) 1:5; (C) 1:10 and (D) 1:20.

9. ^{1}H NMR and ^{13}C NMR spectra of the ligand

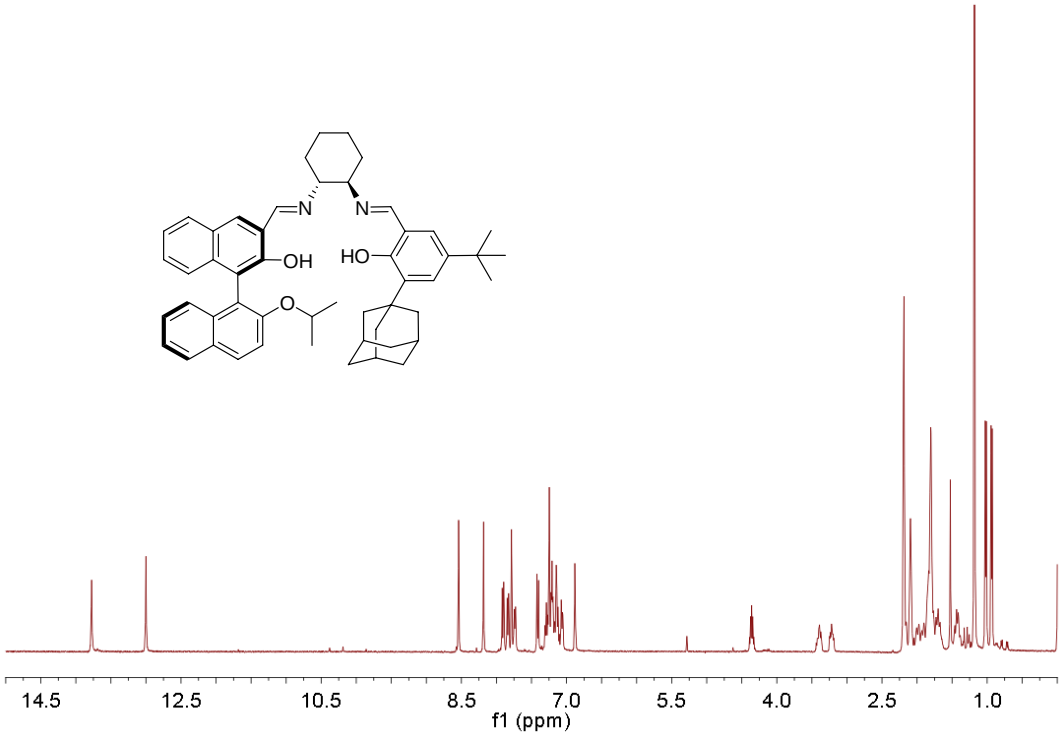


Figure S4. ^{1}H NMR spectrum of the ligand

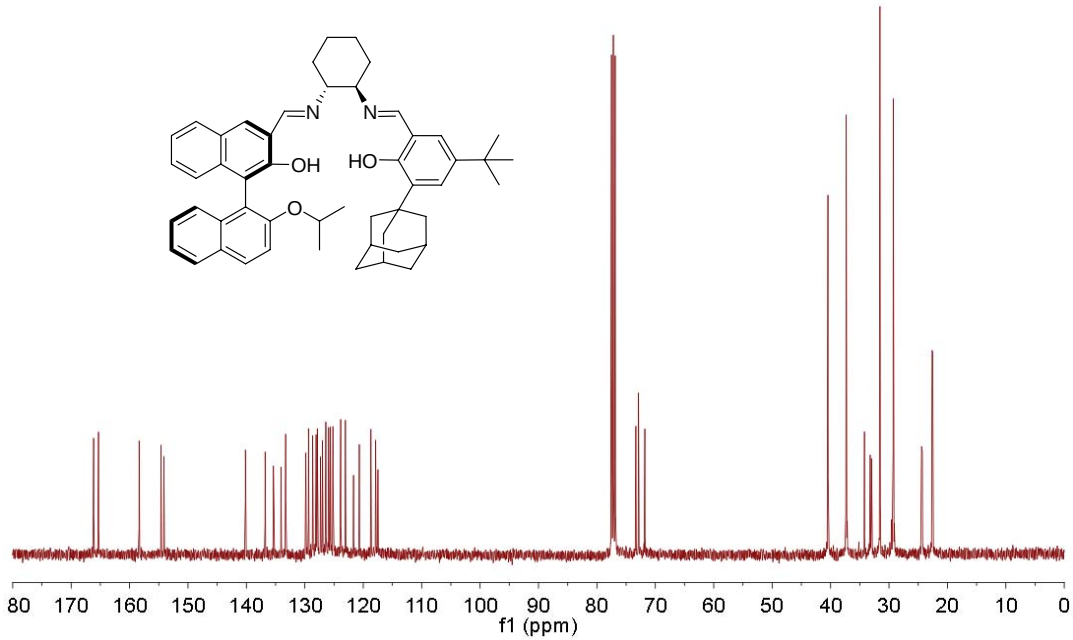


Figure S5. ^{13}C NMR spectrum of the ligand

10. ^{1}H NMR and ^{13}C NMR spectra of the complex (R,R,R)-1a

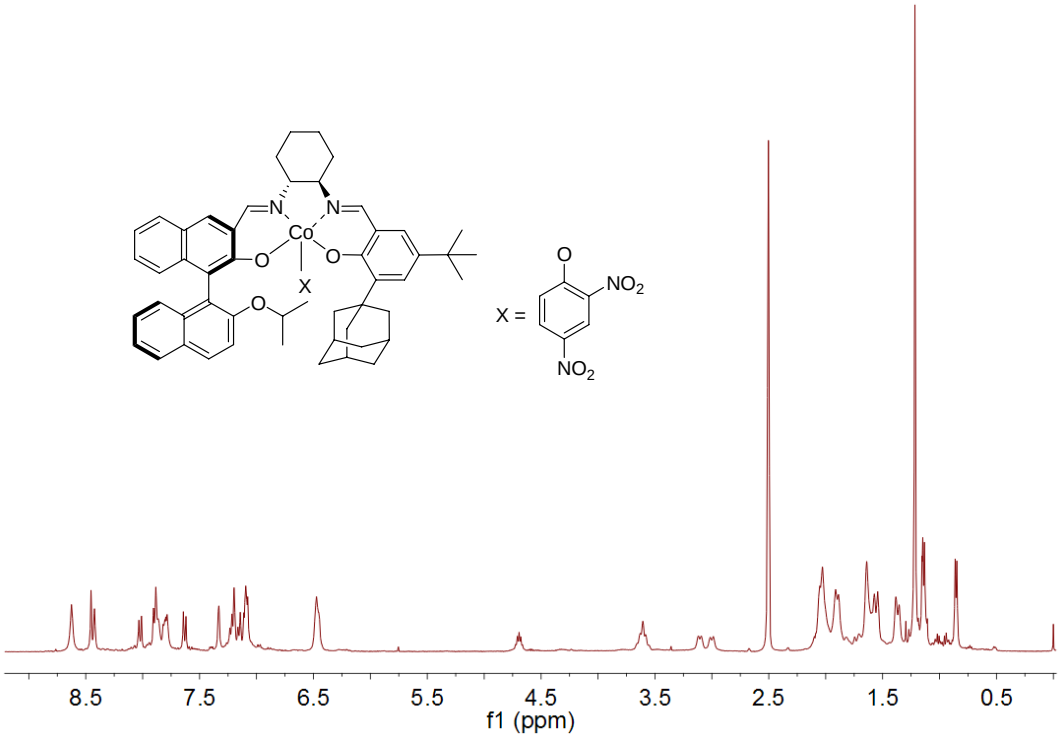


Figure S6. ^{1}H NMR spectrum of the complex (*R*,*R*,*R*)-**1a**

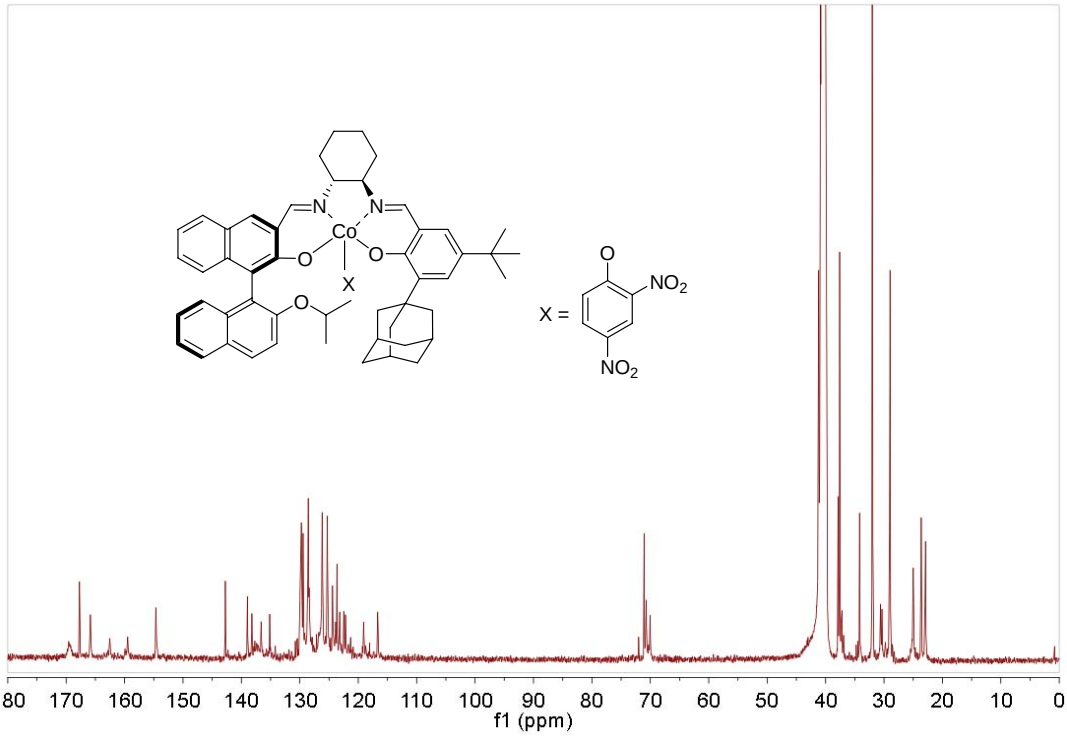
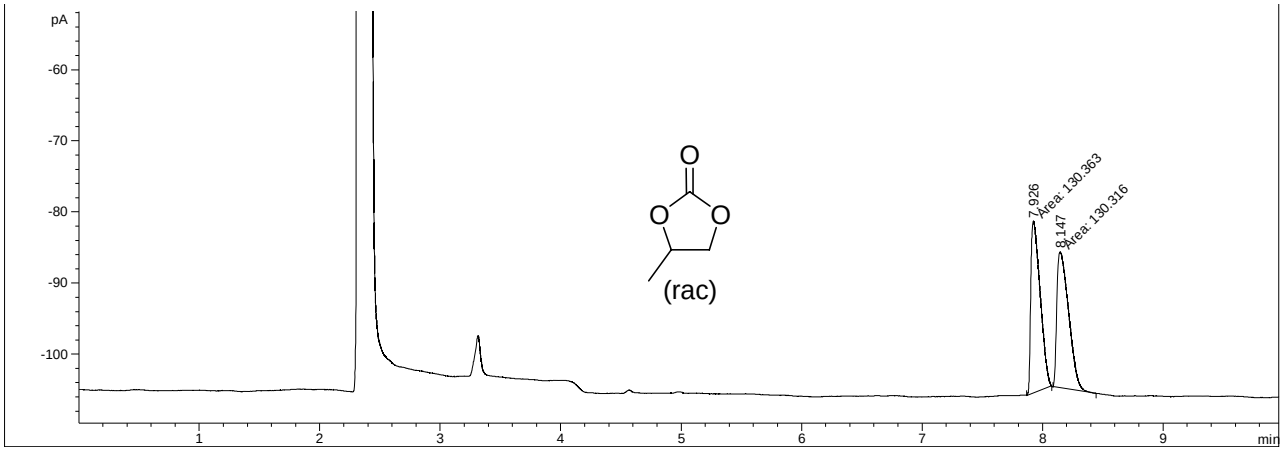


Figure S7. ^{13}C NMR spectrum of the complex (*R*,*R*,*R*)-**1a**

11. Determination of enantiomeric purity of various substrates or products.

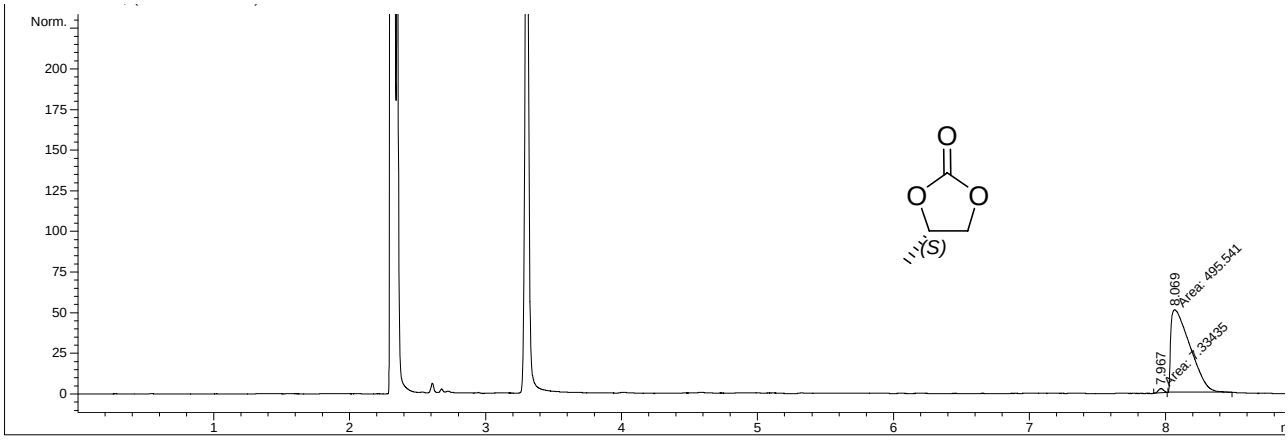
Enantiomeric excesses (ee's) were determined by capillary GC analysis using an Agilent 6890 Series II Gas Chromatograph with N_2 as a carrier gas or by chiral HPLC analysis using an Agilent 1150 HPLC. The following GC columns were employed: 2,6-dibutyl-3-butyryl-β-Cyclodex-B (30 m x 0.25 mm id x 0.25 μm film; Advanced Separation Technologies, Inc.) set at a column head pressure of 13 psi, Cyclodex-B (30 m x 0.25 mm id x 0.25 μm film; J&W Scientific) set at a column head pressure of 10 psi. The following HPLC columns were employed: Chiracel OD-H (Daicel Inc., 25 cm x 0.46 cm i.d.), Whelk-O 1 (Regis Technologies Inc., 25 cm x 0.46 cm i.d.).

(*S*)-propylene carbonate: The ee of the resulting propylene oxide was determined to be 97.1% by chiral GC analysis (2,6-dibutyl-3-butyryl-β-Cyclodex-B, 160 °C, isothermal, t_R(minor) = 7.97 min, t_R(major) = 8.07 min).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.926	MM	0.0898	130.36259	24.18311	50.00896
2	8.147	MM	0.1136	130.31590	19.12234	49.99104
Totals :				260.67850	43.30544	

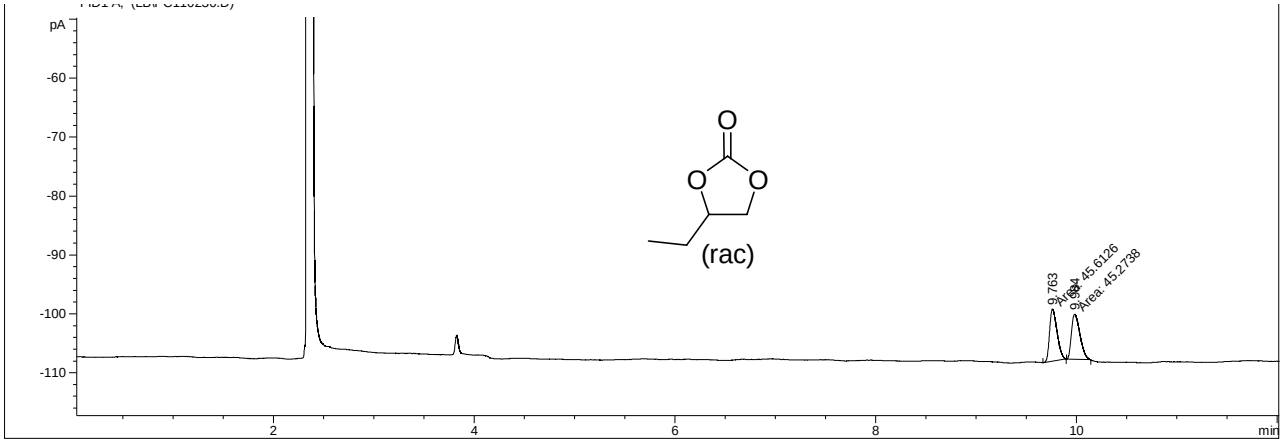
Figure S8. The chiral GC analysis of racemic propylene carbonate



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.967	MM	0.0294	7.33435	4.89735	1.45848
2	8.069	MM	0.1639	495.54097	48.99463	98.54151
Totals :				502.87532	53.89195	

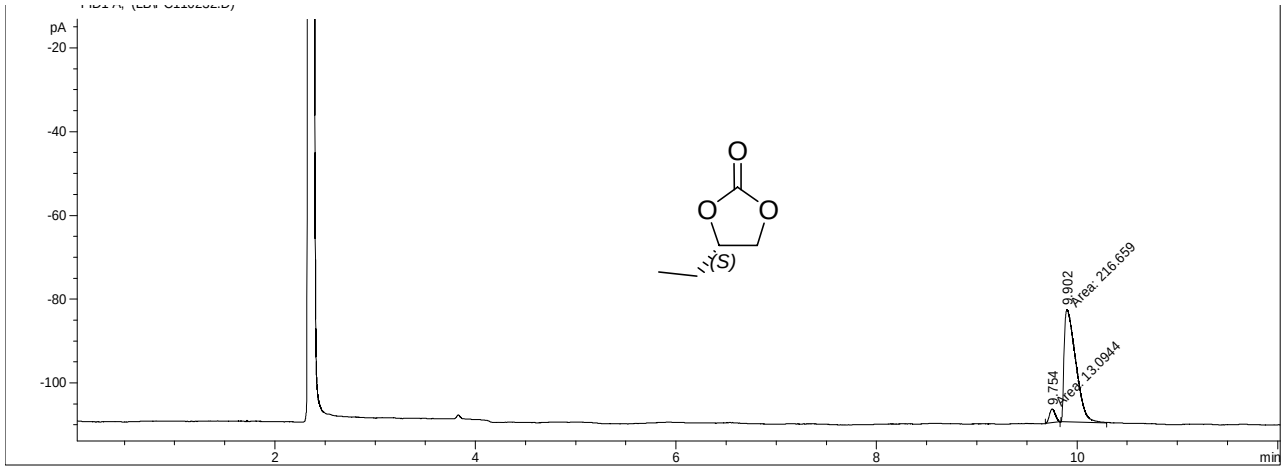
Figure S9. The chiral GC analysis of (*S*)-configuration-enriched propylene carbonate

(*S*)-1,2-butylene carbonate: The ee of the resulting 1,2-butylene oxide was determined to be 88.5% by chiral GC analysis (2,6-dibutyl-3-butyryl-β-Cyclodex-B, 160 °C, isothermal, t_R(minor) = 9.75 min, t_R(major) = 9.90 min).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	9.736	MM	0.0870	45.61259	8.86383	50.18638
2	9.984	MM	0.0970	45.27380	7.69940	49.81362
Totals :				90.88639	16.56323	

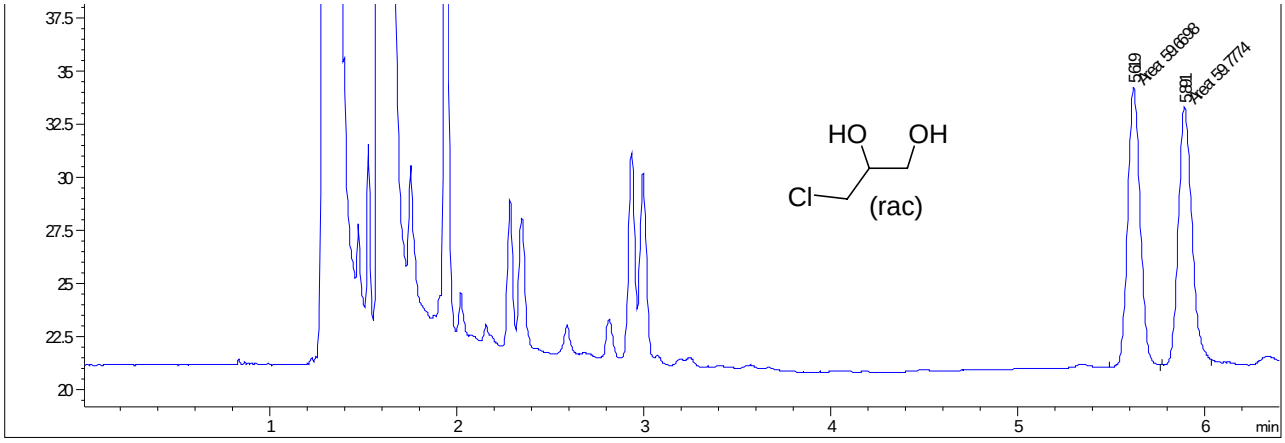
Figure S10. The chiral GC analysis of racemic 1,2-butylene carbonate



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	9.754	MM	0.0704	13.09441	3.41533	5.74379
2	9.902	MM	0.1311	216.65883	26.67322	94.25621
Totals :				229.75324	30.08853	

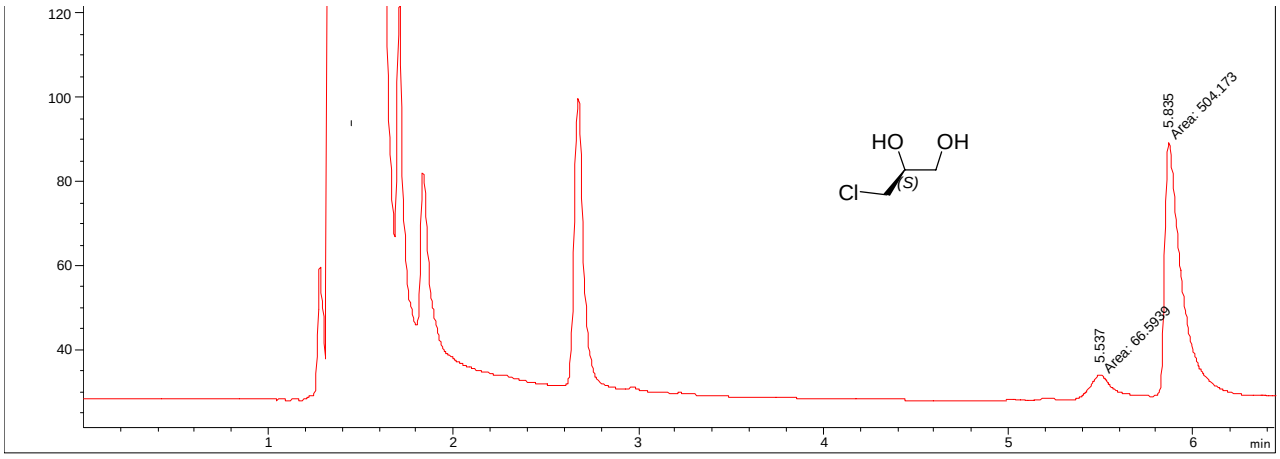
Figure S11. The chiral GC analysis of (*S*)-configuration-enriched 1,2-butylene carbonate

(*S*)-4-(chloromethyl)-1,3-dioxolan-2-one: The ee of the resulting 4-(chloromethyl)-1,3-dioxolan-2-one was determined to be 77.3% by chiral GC analysis of the diol derivative form hydrolysis with 1M NaOH (Cyclodex-B, 80 ^{o}C, isothermal, t_R(minor) = 5.54 min, t_R(major) = 5.84 min) .



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.619	MM	0.1215	59.66980	11.8564	49.95496
2	5.891	MM	0.1456	59.77741	10.1944	50.04504
Totals :				119.44721	20.0508	

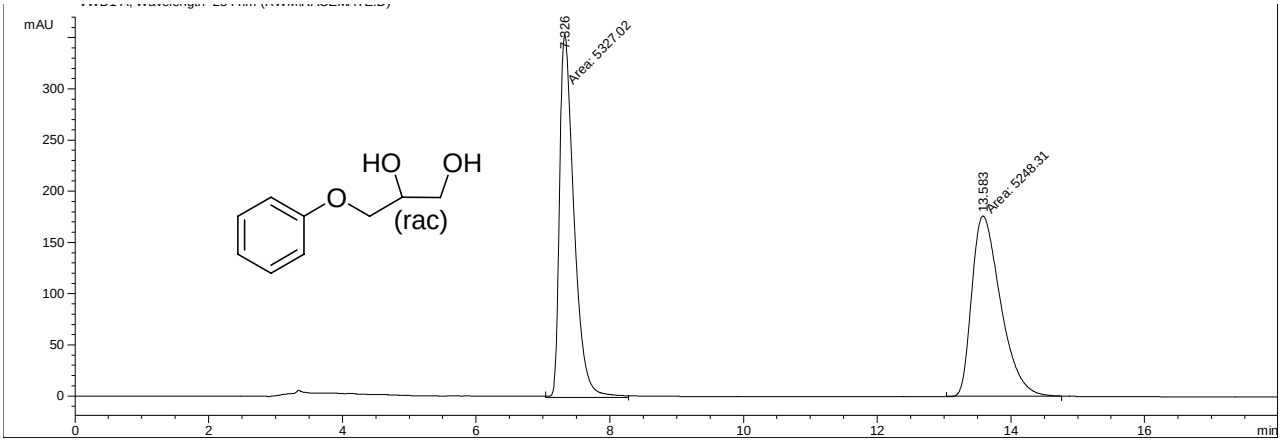
Figure S12. The chiral GC analysis of racemic 3-chloropropane-1,2-diol



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.537	MM	0.1467	66.59392	9.0437	11.35096
2	5.835	MM	0.1654	504.17261	48.5674	88.64904
Totals :				570.76653	57.6111	

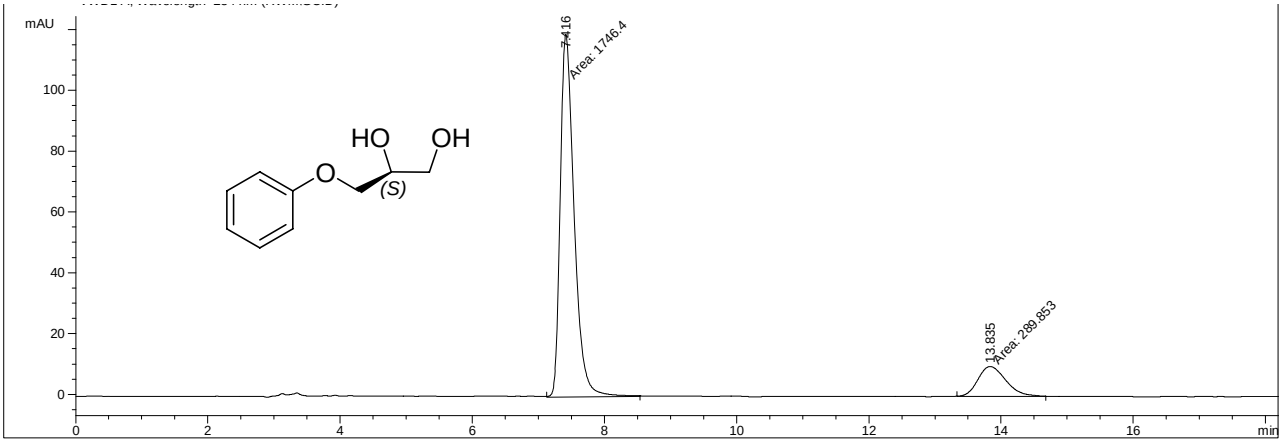
Figure S13. The chiral GC analysis of (*S*)-configuration-enriched 3-chloropropane-1,2-diol

(*S*)-4-(phenoxymethyl)-1,3-dioxolan-2-one: The ee of the resulting 4-(chloromethyl)-1,3-dioxolan-2-one was determined to be 72.4% by chiral HPLC analysis of the diol derivative from hydrolysis with 1 M NaOH (OD-H, 8:2 hexane:*i*-PrOH, t_R(major) = 7.42 min, t_R(minor) = 13.84 min) .



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.326	BB	0.2253	5327.02078	353.21173	50.62725
2	13.583	BB	0.4603	5248.31016	176.46399	49.37274
Totals :				1.05220e4	529.67572	

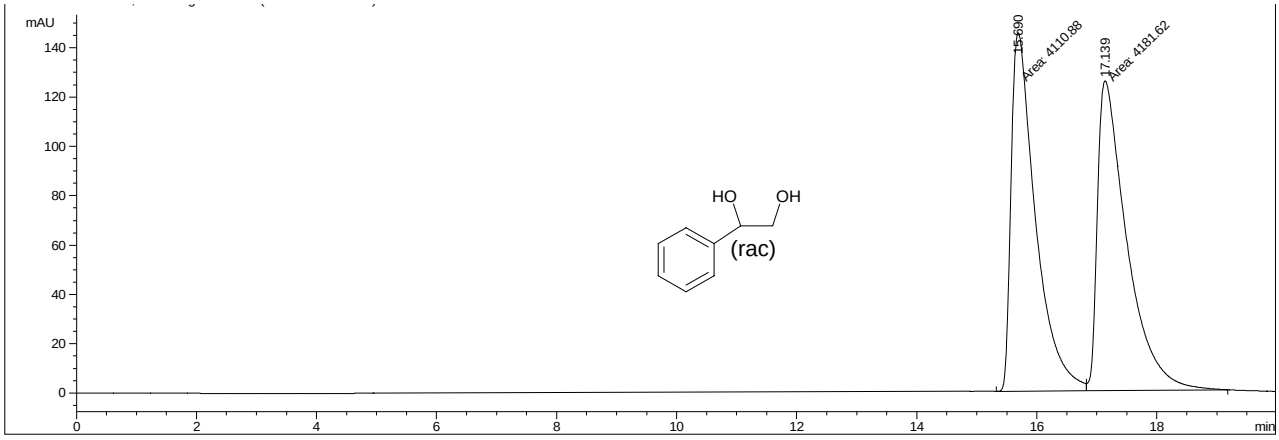
Figure S14. The chiral HPLC analysis of racemic 3-phenoxypropane-1,2-diol



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.416	PB	0.2208	1746.40681	118.97120	86.18541
2	13.835	BB	0.4531	289.85336	9.85969	13.81459
Totals :				2036.26017	128.83089	

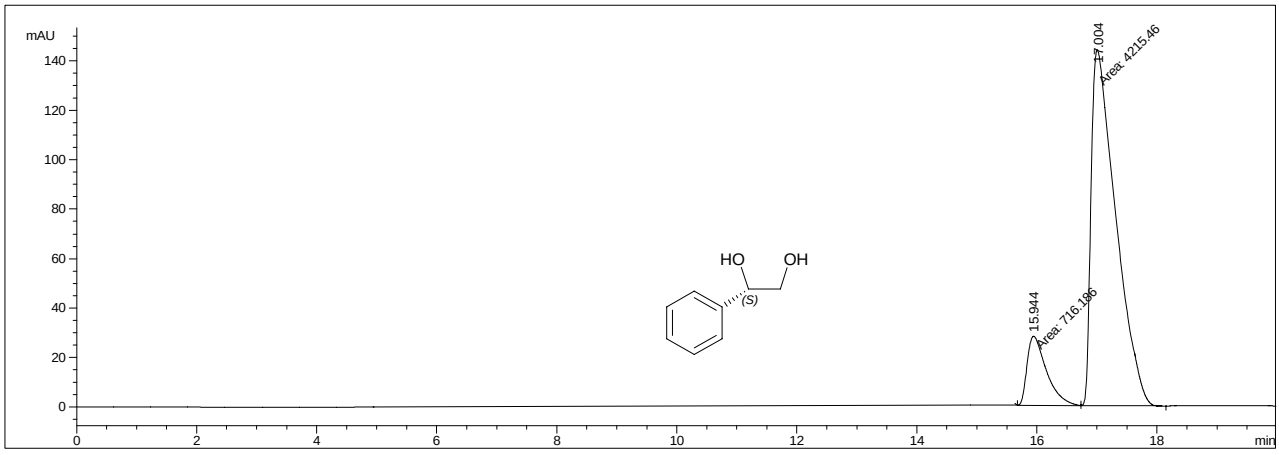
Figure S15. The chiral HPLC analysis of (*S*)-configuration-enriched 3-phenoxypropane-1,2-diol

(*S*)-4-phenyl-1,3-dioxolan-2-one: The ee of the resulting 4-phenyl-1,3-dioxolan-2-one was determined to be 71.0% by chiral HPLC analysis of the diol derivative from hydrolysis with 1 M NaOH (OD-H, 9:1 hexane:*i*-PrOH, t_R(minor) = 15.94 min, t_R(minor) = 17.00 min) .



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.690	VV	0.4161	4110.88139	145.56360	49.86585
2	17.139	VB	0.4943	4181.62895	125.34576	50.13415
Totals :				8292.51034	271.90936	

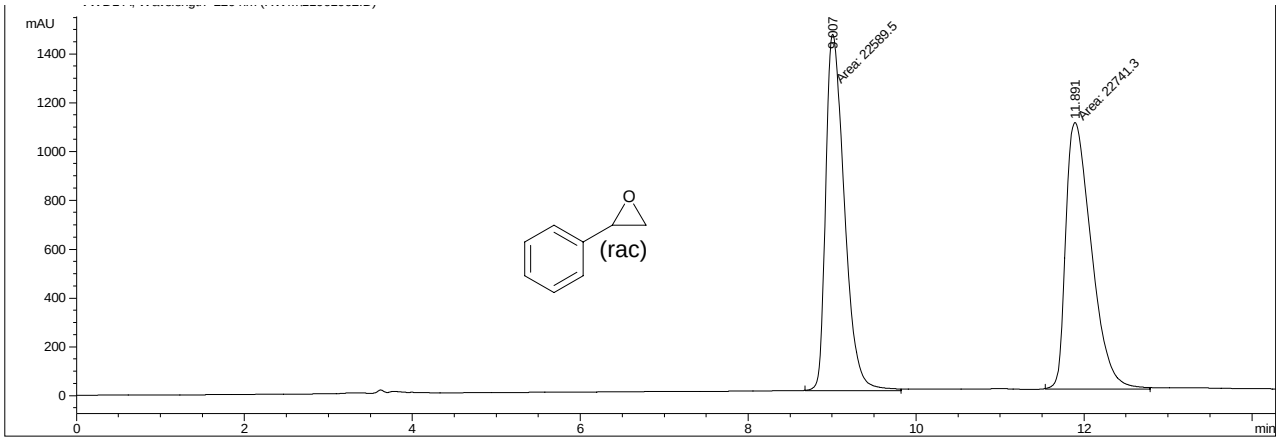
Figure S16. The chiral HPLC analysis of racemic 1-phenylethane-1,2-diol



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.944	VB	0.4883	716.18672	26.33786	15.99695
2	17.004	BB	0.5714	4215.46921	145.78908	84.00305
Totals :				4931.65593	172.12694	

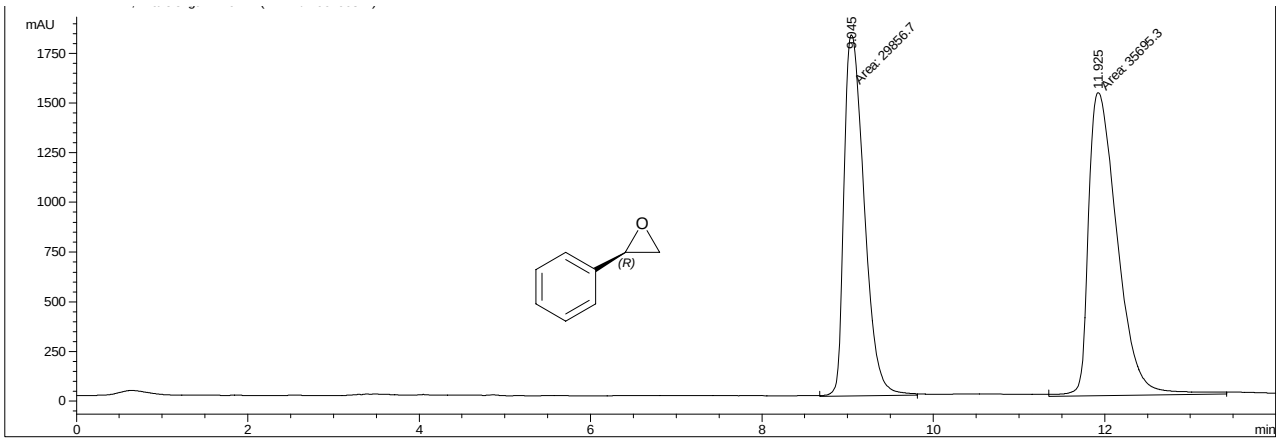
Figure S17. The chiral HPLC analysis of (*S*)-configuration-enriched 1-phenylethane-1,2-diol

(*R*)-Styrene oxide: The ee of the recovered styrene oxide was determined to be 8.8% by chiral HPLC analysis (Whelk-O 1, 99:1 hexane:*i*-PrOH, t_R(minor) = 9.05 min, t_R(major) = 11.93 min) .



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	9.007	PB	0.2391	2.25895e4	1458.71753	49.00926
2	11.891	VB	0.3307	2.27413e4	1092.92480	50.99074
Totals :				4.53308e4	2551.64233	

Figure S18. The chiral HPLC analysis of racemic styrene oxide



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	9.045	VV	0.2529	2.98567e4	1818.27551	45.45397
2	11.925	VB	0.3637	3.56953e4	1525.91260	54.54603
Totals :				6.55520e4	2551.64233	

Figure S19. The chiral HPLC analysis of (*R*)-configuration-enriched styrene oxide