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Catalytic Asymmetric Cycloaddition of Carbon Dioxide and Propylene Oxide Using Novel Chiral Polymers of BINOL-Salen-Cobalt(III) Salts

Peng Yan[a] and Huanwang Jing[a,*]

[a] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China
Fax: (+86)-931-891-2582; phone: (+86)-931-392-7959; e-mail: hw-jing@163.com

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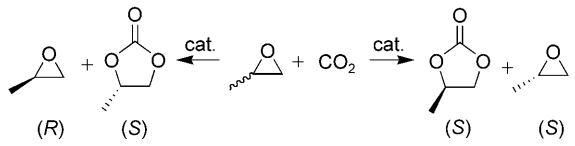
Abstract: Four new chiral polymers of BINOL-Salen-cobalt(III) salt complexes have been designed, synthesized and applied to the direct fabrication of chiral propylene carbonate from racemic propylene oxide. The (*R*/*S*)-polymer catalyst **2** and (*S*/*R*)-polymer catalyst **4** exhibit better enantioselectivity than the (*R*/*R*)-polymer catalyst **1** and the (*S*/*S*)-polymer catalyst **3** and have been recovered and reused more than ten times without loss of activity and enantioselectivity.

Keywords: chiral cobalt(salen) catalysts; chiral polymers; chiral resolution; cycloaddition; epoxides; homogenous catalysts

Introduction

Chemical fixation of carbon dioxide, which is considered as an efficient way to develop a truly environmentally benign process, has attracted a lot of attention in recent years.[1] One of the most successful examples is the synthesis of cyclic carbonates from CO_2 and epoxides.[2] Cyclic carbonates are important building blocks of chiral intermediates and precursors for polymeric materials such as polycarbonates, masked 1,2-diols, pharmaceutical/fine chemical intermediates,[3] and a lot of effective methods such as the cyclization of chiral diols with triphosgene,[4] enzyme-mediated enantioselective hydrolysis of racemic cyclic carbonates[5] or the insertion of CO_2 into chiral epoxides catalyzed by zinc(II)[6] or palladium(0) complexes[7] have been used for their preparation. Recently, Lu et al.[8] applied the simple and highly efficient chiral Salen-Co(III)/quarternary ammonium halide catalyst systems to the asymmetric cycloaddition reaction of CO_2 and propylene oxide (PO). This promising method provides not only an optically pure cyclic carbonate, but also an enantiopure epoxide, and it is convenient with perfect atom economy under solvent-free and extremely mild conditions (Scheme 1). Berkessel and Brandenburg[9] found that the combination of Co(III)-(salen)-trifluoroacetyl complex and bis(triphenylphosphoranylidene)ammonium fluoride (PPN^+F^-) is a very active and enantioselective catalyst system for the addition of carbon dioxide to propylene oxide under the conditions of atmospheric pressure and no solvent. It has been demonstrated that, in the presence of alkali metal salts, quaternary ammonium halides or ionic liquids, the chiral Co-(salen) complexes systems for the cycloaddition of CO_2 to epoxides are very efficient.[10] Our studies showed that the chiral BINAD-Co(III)X complexes in the presence of phenyltrimethylammonium tribromide (PTAT) or tetrabutylammonium bromide (TBAB) are highly efficient catalysts for the coupling of epoxides and carbon dioxide, and they afford chiral cyclic carbonates in moderate yield with high enantioselectivities under very mild conditions.[11] These studies have provided important insights on the cycloaddition of CO_2 to epoxides.



Scheme 1.

Up to now, with respect to the cycloaddition of CO_2 to epoxides, one of the existing problems needed to be solved is how to raise the *ee* value, or how to synthesize a catalyst with perfectly catalytic activity and high enantioselectivity. The other one is how to separate the catalyst from the product in the homogenous reaction without decomposition of the catalyst or formation of by-products. One solution is to develop a catalyst which possesses perfect catalytic activity and high enantioselectivity and, at the same time, to recover and reuse it with no appreciable loss of cata-

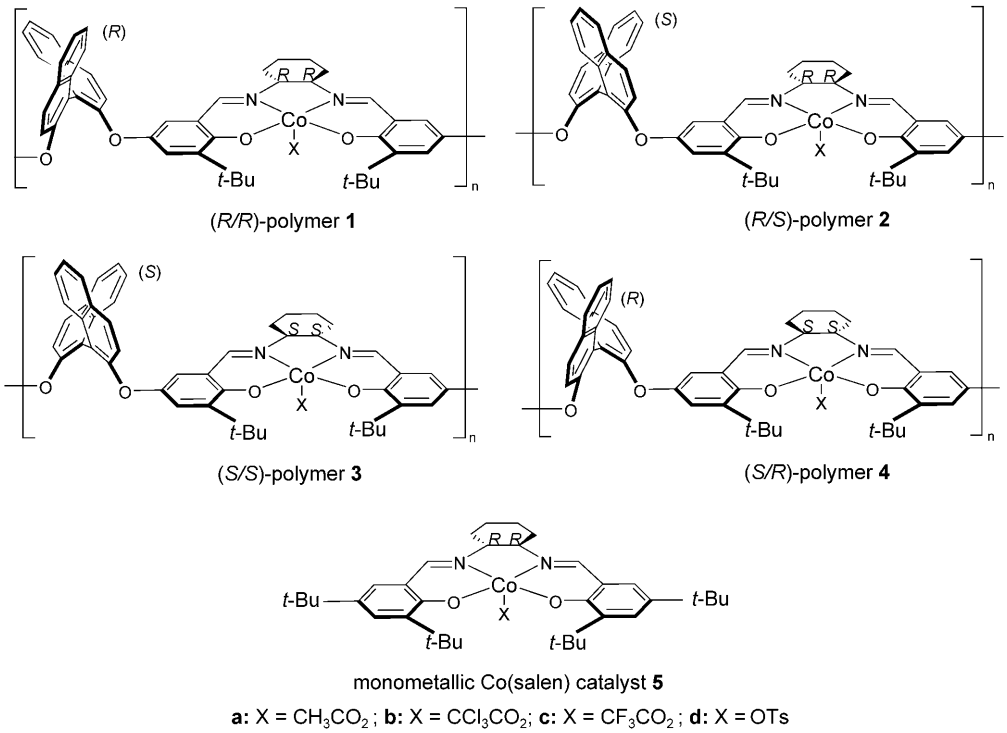


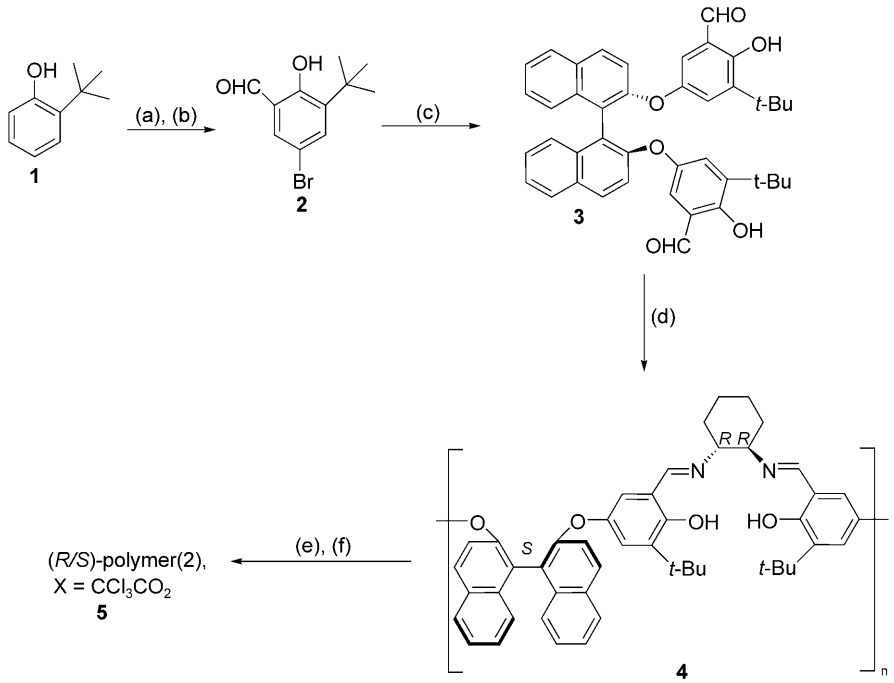
Figure 1. Configurations of polymer catalysts BINOL-salen-Co(III)X and standard monometallic Co(salen) catalyst.

lytic activity and selectivity. The previous studies have shown that an X-(salen) complex [X = Mn(III), Zn(II) or Co(III)] bearing a chiral binaphthyl unit has the higher enantioselectivity.[11,12] On the other hand, it is known that the polymer catalysts have the advantages of being easily amenable to separation from reactants and products, as well as to recovery and reusage. More importantly, they are highly efficient in homogenous catalysis.[12b,13] Based on these strategies, in the present work, we developed four new polymer BINOL-salen-Co(III)X catalysts: (*R*/*R*)-polymer **1**, (*R*/*S*)-polymer **2**, (*S*/*S*)-polymer **3** and (*S*/*R*)-polymer **4** (Figure 1) with an auxiliary chiral site, and a higher enantioselectivity was obtained as compared with the traditional salen-Co(III)X catalysts (Figure 1). Meanwhile, we examined their catalytic activities and enantioselectivities in the asymmetric cycloaddition of CO_2 and propylene oxide (PO), and found that the (*R*/*S*)-polymer catalyst **2** and (*S*/*R*)-polymer catalyst **4** have better enantioselectivity than the (*R*/*R*)-polymer catalyst **1** and the (*S*/*S*)-polymer catalyst **3** and that they can be recovered and be reused more than ten times without loss of activity and enantioselectivity.

Results and Discussion

The preparation of the catalyst (*R*/*S*)-polymer **2** is shown in Scheme 2. 3-*tert*-Butyl-2-hydroxybenzaldehyde was prepared using a modification of a procedure reported in the literature.[14] 5-Bromo-3-*tert*-butyl-2-hydroxybenzaldehyde was synthesized from 3-*tert*-butyl-2-hydroxybenzaldehyde by bromination.[15] Interestingly, during the preparation of the diaryl ether **3**, we discovered that a catalytic amount (1 mol%) of Br_2 was particularly effective as a promoter in the (*S*)-BINOL and unactivated aryl bromide **2** C–O cross-coupling procedure with 32% yield. However, no product **3** was obtained under the traditional catalytic system with K_2CO_3 and Cu/CuO or CuI even when the reaction time was extended to 48 h at an elevated temperature (130 °C). To the best of our knowledge, use of a catalytic amount of Br_2 as a promoter for the C–O cross-coupling reaction has never been reported. The addition of Br_2 made the reaction proceed efficiently, and such a process may be extended to other unactivated aryl bromide substrates. The salen ligand **4** was obtained by the condensation of the diaryl ether **3** with (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate, and then it was characterized by GPC with an average molecular weight (M_n) of 14,966, and the polymer molecular weight distribution (PDI) was 1.05. Metalation of the salen ligand **4** with $Co(OAc)_2 \cdot 4H_2O$ resulted in the corresponding diastereomeric isomer of the polymer BINOL-salenCo(II) complex. The metal-polymer of BINOL-salen-Co(II) was subsequently oxidized with trichloroacetic acid and oxygen to obtain the corresponding BINOL-salen-Co(III)X polymer.

The asymmetric cycloaddition of *rac*-PO and CO_2 using these chiral polymer catalysts was examined and results are listed in Table 1. When the catalyst **1a**



Scheme 2. For (*R/S*)-polymer **2**, X = CCl_3CO_2: (a) CH_3CH_2Br, Mg, ether, Et_3N , Polyformaldehyde, reflux, 90%; (b) Br_2, CH_3CH_2COOH, room temperature, 98%; (c) (*S*)-(−)-BINOL, Cu, CuO, K_2CO_3, pyridine, Br_2, 115 °C, 32 %; (d) (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate, K_2CO_3, ethanol/water, THF, 90 %; (e) $Co(OAc)_2{\cdot}4H_2O$, CH_3OH, toluene, 80 °C, 100%; (f) CCl_3COOH, CH_2CCl_2, O_2, room temprature, 100%.

Table 1. Racemic propylene oxide/CO_2 coupling results.[a]

Entry	Catalyst	Co-catalayt	Time [h]	Conversion [%]	*ee* [%]	k_{rel}
1	**1a**	TBAF	4	41.2	49.2 (*S*)	4.1
2	**1a**	TBAC	4	44.5	45.2 (*S*)	3.7
3	**1a**	TBAB	2	42.3	21.1 (*S*)	1.8
4	**1a**	TBAI	2	47.1	18.3 (*S*)	1.7
5	**1a**	PTAT	2	48.9	15.4 (*S*)	1.6
6	**2a**	TBAF	4	38.2	58.4 (*S*)	5.4
7	**2a**	TBAC	4	38.7	55.3 (*S*)	4.8
8	**2a**	TBAB	4	48.4	27.5 (*S*)	2.2
9	**2a**	TBAI	4	49.5	20.4 (*S*)	1.8
10	**2b**	TBAF	4	40.2	61.2 (*S*)	6.2
11[b]	**2b**	TBAF	12	39.4	73.0 (*S*)	10.2
12	**2c**	TBAF	4	40.7	59.5 (*S*)	5.8
13[b]	**2c**	TBAF	12	36.5	72.4 (*S*)	9.3
14	**2d**	TBAF	4	32.6	59.1 (*S*)	5.1
15	**3a**	TBAF	4	48.3	48.2 (*R*)	4.4
16	**3b**	TBAF	4	52.0	49.5 (*R*)	4.9
17	**4a**	TBAF	4	40.1	58.3 (*R*)	5.5
18	**4b**	TBAF	4	40.2	60.2 (*R*)	5.9
19[b]	**4b**	TBAF	12	42.1	71.7 (*R*)	10.1
20	**5b**	TBAF	4	47.2	55.8 (*S*)	5.7
21[b]	**5b**	TBAF	12	38.6	66.4 (*S*)	7.4

[a] *Reaction conditions:* PO (100 mmol), catalyst (0.1 mmol), co-catalyst (0.2 mmol), initiate pressure of CO_2 (1.2 MPa), temperature 25 °C.
[b] 0 °C.

with the same chirality of (*R*)-BINOL and (*R*,*R*)-salen was used in this reaction at room temperature, (*S*)-propylene carbonate was obtained with a moderate 49.2% *ee* value (Table 1, entry 1). The co-catalyst effects were also investigated (Table 1, entries 1–5), and the activity order was: PTAT > TBAI[16] >

TBAB > TBAC[16] > TBAF[16], while the enantioselectivity order was: TBAF > TBAC > TBAB > TBAI > PTAT. These results were consistent with the previous results.[8–11] When the catalyst **3a** with the same chirality of (*S*)-BINOL and (*S*,*S*)-salen was used in this reaction, (*R*)-propylene carbonate was obtained with a moderate 48.2% *ee* value (Table 1, entry 15). Comparatively, when the catalysts **2a** and **4a** with the opposite chirality of BINOL and salen were used in this reaction, chiral propylene carbonate was also formed with a higher *ee* value and its chirality was controlled by the salen skeleton (Table 1, entries 6–9 and 17). When these reactions were carried out at lower temperature, the enantioselectivities of the chiral propylene carbonate products were enhanced as predicted (Table 1, entries 11, 13 and 19).[8–11] The counterion effects of BINOL-salen-Co(III)X catalysts were also considered (Table 1, entries 6, 10, 12, 14 and 15–18), and the enantioselectivity order was X = CCl_3CO_2 > CF_3CO_2 > OTs > OAc, while the activity order was X = CF_3CO_2 > CCl_3CO_2 > OAc > OTs (Table 1, entries 6, 10, 12 and 14).

From the above results, it was found that the chiral-mix catalysts of **2** and **4** led to the chiral PC with a higher *ee* as compared to the chiral-matching catalysts of **1** and **3**, and a bulky X group in the polymeric chiral BINOL-salen-Co(III)X complexes such as X = CCl_3CO_2 was essential in obtaining a high enatioselectivity in this reaction. On the other hand, it must be emphasized that the co-catalyst anion in the binary catalyst system has a great effect on the enantioselectivity of reaction (Table 1, entries 1–5 and 6–9). The co-catalyst such as *n*-Bu_4NF with a small anion was beneficial to improve the enantiomeric purity of the chiral propylene carbonate without loss of reaction rate. In contrast, the co-catalyst such as *n*-Bu_4NI with a large anion was beneficial for improving the reaction rate and decreasing the enantiomeric purity of the chiral propylene carbonate (Table 1, entries 4 and 9). The same situation was also observed for phenyltrimethylammonium tribromide (PTAT) with the largest anion. It has enormously improved the activity of chiral PC formation, but with the lowest enantiomeric purity (Table 1, entry 5).[2h] Compared to the results using standard monometallic Co(salen) catalyst (Figure 1, catalyst **5b**), the *ee* values by using the chiral-mix catalyst of **2b** were higher (Table 1, entries 10 and 11 and 20 and 21), whereas they were lower when the chiral-matching catalyst of **3b** were used (Table 1, entries 16 and 20). Therefore, it can be concluded that the chirality of the BINOL fragment has an important influence on the optical selectivity of salen-Co(III)X complexes. With regard to the four polymer catalysts: (*R*/*R*)-polymer **1**, (*R*/*S*)-polymer **2**, (*S*/*S*)-polymer **3** and (*S*/*R*)-polymer **4** (Figure 1), the BINOL fragment with the *R* configuration has the character of enhancing the optical selectivity of the (*S*,*S*)-salen-Co(III)X complex but of reducing the optical selectivity of the (*R*,*R*)-salen-Co(III)X complex. On the contrary, when the BINOL fragment had the *S* configuration, it enhanced the optical selectivity of the (*R*,*R*)-salen-Co(III)X complex but reduced the optical selectivity of the (*S*,*S*)-salen-Co(III)X complex.

Under the optimized conditions, we also examined this cycloaddtion reaction with other epoxides with carbon oxide using **2b**/TBAF as catalyst (Table 2). We found that, using 0.1 mol% **2b**, 0.2 mol% TBAF as catalyst, some monosubstituted terminal epoxides with different substitued groups could be transferred to the corresponding optically active cyclic carbonates with valuable *ee* values. Unfortunately, CO_2 was effectively incorporated into styrene oxide and phenylglcidyl ether to afford the cyclic carbonates in good yield, but these carbonates were obtained as racemates. The observation suggests that the obvious steric hindrance affects the enantiodiscrimination of the epoxide to incorporate CO_2.[17]

Table 2. Reactions of epoxides with CO_2 in the presence of **2b**/TBAF.[a]

Entry	R	Time [h]	Conversion [%]	*ee* [%]
1	CH_2CH_3	8	45	56
2	$ClCH_2$	12	41	52
3[b]	$PhOCH_2$	12	46	0
4[b]	Ph	18	37	0

[a] *Reaction conditions:* Epoxide (100 mmol), catalyst (0.1 mmol), co-catalyst (0.2 mmol), initial pressure of CO_2 (1.2 MPa), temperature 25 °C.

[b] The *ee* value was determined by HPLC (Daicel Chiralcel OD, *n*-hexane/2-propanol (9:1 v/v), 1.0 mL/min, 254 nm).

Furthermore, the more important investigations about the recycle and reuse of the metal-containing polymeric catalysts were also performed in our laboratory. The attractive results are displayed in Figure 2. The polymeric chiral BINOL-salen-Co(III)X complex could be readily recovered from the products by adding methanol after terminating the reaction. The recycle could be carried out up to 10 times without loss of activity and enantioselectivity when the reaction proceeded under mild reaction conditions.

To further extend the reaction scope for the application of our catalysts, propylene oxide was utilized as substrate in the hydrolytic kinetic resolution (HKR) using **2a** as catalyst. The results are summarized in Table 3. It can be seen that the HKR of propylene oxide catalyzed by complex **2a** affords both recovered unreacted epoxide (> 99% *ee*) and 1,2-diol (99% *ee*) in highly enantioenriched form. Meanwhile, catalytic performances of the catalyst by filtration and

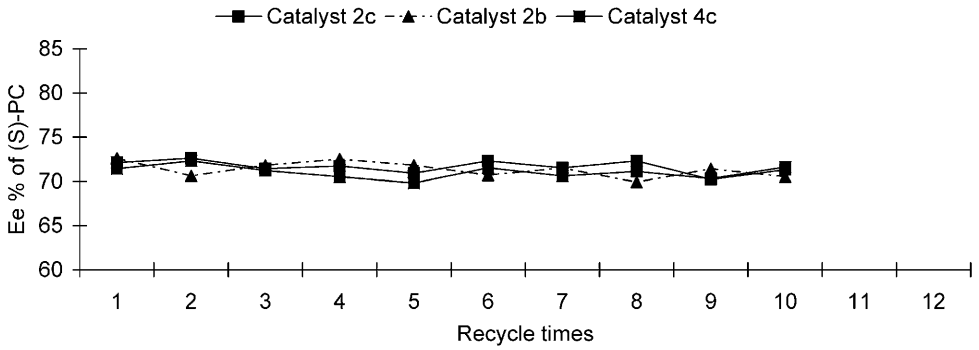


Figure 2. Recycle results using catalyst **2b**, **2c** and **4c.** *Reaction conditions:* PO (100 mmol), catalyst (0.1 mmol), TBAF (0.2 mmol), initiate pressure of CO_2 (1.2 MPa), reaction time 12 hours, temperature 0 °C.

Table 3. Recycle results of HKR of propylene oxide in the presence of catalyst **2a**.[a]

Recycle time	Conversion [%]	ee_{epox}[b] [%]	ee_{diol}[c] [%]
1	49.6	99	99
2	48.5	97	>99
3	49.0	99	99
4	49.3	99	99
5	49.5	99	99
6	52.5	>99	96.5
7	49.1	99	99
8	48.7	98.2	99

[a] *Reaction conditions:* PO (100 mmol), catalyst (0.1 mmol), H_2O (55 mmol) reaction time 8 hours, temperature 25 °C.
[b] Enantiomeric excess of the epoxide was determined by chiral GC.
[c] Diols were treated with 2,2-dimethoxypropane and the enantiomeric excess was determined by chiral GC.

repeated recycling demonstrated that the reactivity and enantioselectivity did not decline.[18] Relatively, the standard monometallic Co(salen) catalyst (Figure 1, catalyst **5a**) required a much higher catalyst amount (0.2–0.5%) and much longer reaction time (16 h) in order to reach the *ee* value (>99%) in this reaction.[18,19]

Conclusions

In summary, the new chiral polymer complexes of BINOL-salen-Co(III)X are effective in the asymmetric cycloaddition of carbon dioxide to propylene oxide yielding relevant chiral propylene carbonates with good enantioseletivities. The catalysts could be readily recovered and be repeatedly used without loss of either activity or enantioselectivity. Further structural optimization of these catalysts to enhance the enantioselectivity is underway in our laboratory.

Experimental Section

All reactions were carried out in oven-dried round-bottom flasks and the reactions were conducted under a positive pressure of argon, unless otherwise stated. Commercial reagents were purchased from Sigma, Aldrich, Fluka or Acros, and used as received. Solvents were distilled and dried before using the standard procedures.[20] Racemic epoxides were refluxed over a mixture of KOH and CaH_2, and fractionally distilled under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on Bruker AM-400, AM-300, AM-200 spectrometers using TMS as an internal standard. Elemental analyses were determined with a Carioel elemental analyzer. All melting points were determined on a XT-4 melting point apparatus and are uncorrected. Mass spectra were measured with a ZAB-HS spectrometer. GC analyses of cyclic carbonates were carried out on a Varian CP 3800 gas chromatograph equipped with FID detectors. For the determination of enantiomeric excesses, Supelco-DEX series (225) chiral columns were used.

General Procedure for the Synthesis of the Polymeric Chiral Salen-Co(III)X Complexes

(a) Synthesis of 3-*tert*-butyl-2-hydroxybenzaldehyde: 3-*tert*-Butyl-2-hydroxybenzaldehyde was prepared using a modification of the procedure reported in Ref.[14] About 6 mL ethyl bromide were dropwise added to ether (20 mL) containing magnesium (1.6 g) within 1 h. The mixture obtained was heated to reflux until the complete conversion of magnesium was achieved, and then cooled to ambient temperature. The 2-*tert*-butylphenol (10 g) dissolved in tetrahydrofuran (27 mL) was slowly added into the above mixture with stirring at ambient temperature and a white precipitate was formed, followed by the addition of benzene (134 mL). After removal of ether and the majority of tetrahydrofuran by distillation, another portion of benzene (34 mL) was added. Then triethylamine (10 g) and paraformaldehyde (15 g) were added into the above mixture with stirring at 100 °C for 3 h. After cooling, the mixture obtained was acidified with HCl (334 mL, 10 wt%) and separated in a separatory funnel. The aqueous phase was extracted with petroleum ether for three times (50 mL × 3) and the combined extract was washed with saturated sodium chloride solution (50 mL) then dried over anhydrous magnesium sulfate.

After the evaporation of volatile solvents, the residue was purified by silica gel column chromatography using pure petroleum ether as eluent to give 3-*tert*-butyl-2-hydroxybenzaldehyde; yield: 10.7 g (90%); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.42$ (s, 9H), 7.53 (d, $J = 7.5$ Hz, 1H), 7.40 (d, $J = 6.3$ Hz, 1H), 6.93–6.98 (m, 1H), 9.88 (s, 1H), 11.79 (s, 1H).

(b) Synthesis of 5-Bromo-3-*tert*-butyl-2-hydroxybenzaldehyde 2: 5-Bromo-3-*tert*-butyl-2-hydroxybenzaldehyde was synthesized from 3-*tert*-butyl-2-hydroxybenzaldehyde by bromination, as reported in Ref.[15] A solution of Br_2 (3.18 mL, 61.8 mmol) in acetic acid (12 mL) was added dropwise at room temperature over 15 min to a solution of 3-*tert*-butyl-2-hydroxybenzaldehyde (10.68 g, 59.9 mmol) in acetic acid (30 mL). After 1 h of the reaction, the mixture was diluted with CH_2Cl_2 (180 mL) and washed with H_2O (60 mL), saturated aqueous $Na_2S_2O_5$ (60 mL), saturated aqueous $NaHCO_3$ (60 mL), and brine (60 mL), respectively. The organic phase was dried with anhydrous magnesium sulfate and the solvents were evaporated to afford the title compound as a yellow solid; yield: 15.16 g (98%), mp 59–62 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.40$ (s, 9H), 7.45 (d, $J = 2.4$ Hz, 1H), 7.38 (d, $J = 2.1$ Hz, 1H), 9.82 (s, 1H), 11.72 (s, 1H).

(c) Synthesis of the target compound 3: Under an argon gas atmosphere, a 50-mL three-necked flask equipped with a magnetic stirring bar connected to a ball condenser was charged with (*S*)-1,1′-bi-2-naphthol (1.8 g, 6.29 mmol), 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde (6.5 g, 25 mmol), Cu (1.2 g, 18.75 mmol), CuO (1.25 g, 15.75 mmol), K_2CO_3 (2.15 g, 15.75 mmol), Br_2 (10 mg, 0.06 mmol), and pyridine (5 mL). The mixture was heated for 36 h at 115 °C, then cooled to room temperature. Then, the resulted mixture was washed with HCl (25 mL, 10 wt%), and subsequently was extracted using CH_2Cl_2 (20 mL). The organic phase was dried with anhydrous magnesium sulfate. After the evaporation of volatile solvents, the residue was purified by silica gel column chromatography using a mixed solvent of petroleum ether and ethyl acetate (10:1, v/v) as eluent to give the target compound **3**; yield: 1.27 g (32%). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.24$ (s, 18H), 6.72 (d, $J = 2.7$ Hz, 2H), 7.00 (d, $J = 2.4$ Hz, 2H), 7.20–7.44 (m, 8H), 7.88–7.92 (m, 4H), 9.43 (s, 2H), 11.43 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta =$ 28.9, 34.9, 117.0, 118.8, 119.8, 119.9, 124.9, 125.6, 126.5, 126.8, 128.2, 130.0, 130.4, 132.2, 140.0, 149.4, 152.8, 157.0, 196.1; FAB-MS: $m/z = 638.8$, calcd.: 638.8; anal. calcd. for $C_{42}H_{38}O_6$: C 78.97, H 6.00; found: C 78.86, H 5.94; $[\alpha]_{589}^{20}$: −45 (*c* 1.0, THF).

(d) Synthesis of chiral ploymer ligand 4: Under an argon gas atmosphere, a solution of (1*R*,2*R*)-(+)-1,2-diaminocyclohexane L-tartrate (0.3383 g, 1.28 mmol) and K_2CO_3 (0.3612 g, 2.6 mmol) in ethanol-water (1:1, 9 mL) was heated to reflux at 80 °C. Then a solution of the compound **3** (0.84 g, 1.32 mmol) in tetrahydrofuran (5 mL) was added dropwise to the above solution for 30 min. The reaction mixture was heated for 4 h at 80 °C. The yellow reaction mixture was cooled, and then water (5 mL) was added. The product was extracted with CH_2Cl_2 (50 mL × 3), the combined organic fractions were washed with water (30 mL), brine (20 mL × 2), and dried ($MgSO_4$). Removal of solvents afforded a yellow solid, and then the solid was purified by the addition of a mixed solvent of CH_2Cl_2 and *n*-hexane (1:50 v/v) to give the target compound **4** as a yellow powder; yield: 0.85 g (90%). ^{1}H NMR (300 MHz): $\delta = 13.43$ (s, 2H), 8.00–8.25 (m, 2H), 7.64-7.97 (m, 4H), 7.24–7.51 (m, 4H), 6.91–7.45 (m, 3H), 6.80 (s, 3H), 6.55 (s, 1H), 6.10 (s, 1H), 3.24 (s, 2H), 1.36–1.83 (m, 8H), 1.27 (s, 18H); ^{13}C NMR (50 MHz): $\delta = 164.6$, 156.2, 155.7, 153.8, 152.9, 148.4, 138.3, 134.2, 130.2, 129.5, 128.1, 126.4, 125.7, 124.2, 121.8, 119.7, 118.9, 72.2, 34.8, 33.0, 29.2, 24.2; average molecular weight: Mn = 14966 (GPC); FT-IR (KBr): $\tilde{\nu} = 3429$ (s), 2952 (s), 2862 (m), 1628 (s), 1589 (s), 1464 (m), 1434 (s), 1390 (m), 1314 (m), 1262 (m), 1233 (s), 1146 (m), 1034 (m), 1001 (m), 813 (m), 748 cm^{-1} (m); anal. calcd. for $C_{40}H_{32}N_2O_4$: C 79.45, H 5.33, N 4.63; found: C 79.34, H 5.27, N 4.58; $[\alpha]_{589}^{20}$: −45° (*c* 1.0, THF).

(e) Procedure for the metalation of salen ligand 4: To a solution of the compound **4** (0.77 g, 1.03 mmol) in toluene (10 mL) under argon was added a solution of $Co(OAc)_2 \cdot 4H_2O$ (0.266 g, 1.5 mmol) in MeOH (10 mL) via a cannula, affording a dark red precipitate. The mixture was stirred at 80 °C for 2 h. After the reaction mixture had been cooled down to room temperature and concentrated under vacuum, the residue was dissolved in CH_2Cl_2 (50 mL) and passed through a celite pad to remove the excess $Co(OAc)_2$. Removal of the solvent from the filtrate afforded a dark red powder; yield: 0.83 g (100%). FT-IR (KBr): $\tilde{\nu} = 2942$ (s), 2862 (m), 1623 (s), 1594 (s), 1531 (s), 1433(s), 1409 (s), 1386 (s), 1354 (s), 1356 (s), 1230 (s), 1149 (m), 1031 (s), 1002 (m), 975 (m), 813 (m), 730 (m), 691 cm^{-1} (m); anal. calcd. for $C_{40}H_{30}N_2O_4Co$: C 72.61, H 4.57, N 4.23; found: C 72.54, H 4.47, N 4.08.

(f) Synthesis of the target compound 5: The target compound was prepared using a modification of the procedure reported in Ref.[9] To a stirred mixture of the CoII(salen) complex (0.116 g, 0.144 mmol) in CH_2Cl_2 (5 mL) was added trichloroacetic acid (0.0245 g, 0.151 mmol, 1.05 equiv.). The solution was stirred under a dry oxygen atmosphere at room temperature for 10 h. The solvent was removed under vacuum to leave a crude dark green solid; yield: 0.131 g (*ca.* 100%). Anal. calcd. for $C_{42}H_{30}Cl_3N_2O_6Co$: C 61.22, H 3.67, N 3.40; found: C 61.52, H 3.84, N 3.56.

For oxidation of the other polymeric chiral Co(II)-salen complexs, refer to the procedure in Ref.[9]

Representative Procedure for the Asymmetric Cycloaddition of CO_2 with Racemic Terminal Epoxides

A stirred mixture of complex **2b** (0.0967 g, 0.1 mmol) was dissolved in racemic propylene oxide (7 mL, 100 mmol) to form a red-brown solution, then TBAF (0.0522 g, 0.2 mmol) was added under a nitrogen atmosphere. The mixtrue was stirred about 15 minutes and then charged into a pre-dried 100-mL autoclave equipped with a magnetic stirrer under a CO_2 atmosphere (1.2 MPa). After the allotted reaction time, the unreacted propylene oxide was isolated at ambient temperature under vacuum. Propylene carbonate was obtained by reduced pressure distillation (1 mbar/80 °C). The *ee* value of propylene carbonate was determined by chiral GC analysis (Chiraldex-B, 180 °C): tR (minor) = 7.44 min, tR (major) = 8.23 min.

Catalyst Recycling Experiment for the Asymmetric Cycloaddition of CO_2 with Racemic Propylene Oxide

All polymeric Co complexs were seperated from the reaction mixtures by precipitation into methanol and by subsequent centrifugation. The residue obtained after centrifugation was dissolved in CH_2Cl_2, trichloroacetic acid (0.024 g, 0.10 mmol) was added, and the mixture was stirred under an atmosphere of air for 10 h. The solvent was removed under vacuum to leave a dark green solid. And then the obtained catalyst was utilized in the next cycle. The propylene carbonate was obtained by reduced pressure distillation from the mixture of methanol and propylene carbonate.

Representative Procedure for the Hydrolytic Kinetic Resolution of Racemic Propylene Oxide

A 100-mL flask equipped with a stir bar was charged with the mixture of complex **2a** (0.0862 g, 0.1 mmol) and propylene oxide (7 mL, 100 mmol) at room temperature. The solution was cooled to 0 °C, and H_2O (0.99 mL, 55 mmol, 0.55 equiv.) was added dropwise over 5 min. The reaction mixture was allowed to warm to room temperature and stirred for 8 h at which time (*R*)-propylene oxide (yield: 2.75 g, 47 mmol, 47%) was isolated by distillation from the reaction mixture at 36 °C. The recovered epoxide was determined to be >99% *ee* by chiral GC analysis of the propylene carbonate derivative (obtained by cycloaddition with CO_2 using the racemic Jacobsen catalyst, Chiraldex-B, 180 °C): tR (major) = 7.14 min, tR (minor) = 8.40 min.

The propylene diol was removed by vacuum distrillation (75°C). The *ee* of the propylene diol was determined to be 99% by chiral GC analysis of the acetonide derivative (obtained by using 1% w/v camphorsulfonic acid in dimethoxypropane, Chiraldex-B, 50 °C): tR (major) = 5.38 min, tR (minor) = 6.31 min).

The polymeric Co complex was separated from the reaction mixtures by precipitation into Et_2O and by subsequent centrifugation. The residue obtained after centrifugation was dissolved in CH_2Cl_2; acetic acid (0.006 g, 0.10 mmol) was added, and the mixture was stirred under an atmosphere of air for 2 h. The solvent was removed under vacuum to leave a crude dark green solid. And then the obtained catalyst was utilized in the next cycle.

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References

[1] a) A. Behr, *Angew. Chem.* **1988**, *100*, 681–698; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 661–678; b) X.-L. Yin, J. R. Moss, *Coord. Chem. Rev.* **1999**, *181*, 27–59; c) D. Walther, M. Ruben, S. Rau, *Coord. Chem. Rev.* **1999**, *182*, 67–100; d) D. H. Gibson, *Chem. Rev.* **1996**, *96*, 2063–2095; e) K. Nakano, T. Kamada, K. Nozaki, *Angew. Chem.* **2006**, *118*, 7432–7435; *Angew. Chem. Int. Ed.* **2006**, *45*, 7274–7277.

[2] a) R. L. Paddock, S. T. Nguyen, *J. Am. Chem. Soc.* **2001**, *123*, 11498–11499; b) H. Jing, K. E. Smita, J. Gibbs, C. Stern, H. Zhou, S. T. Nguyen, *Inorg. Chem.* **2004**, *43*, 4315–4327; c) F. Shi, Q. Zhang, Y. Ma, Y. He, Y. Deng, *J. Am. Chem. Soc.* **2005**, *127*, 4182–4183; d) F. Li, C. Xia, L. Xu, W. Sun, G. Chen, *Chem. Commun.* **2003**, 2042–2043; e) W. J. Kruper, D. D. Dellar, *J. Org. Chem.* **1995**, *60*, 725–727; f) Y. Xie, Z.-F. Zhang, T. Jiang, J.-L. He, B.-X. Han, T.-B. Wu, K.-L. Ding, *Angew. Chem.* **2007**, *119*, 7393–7396; *Angew. Chem. Int. Ed.* **2007**, *46*, 7255–7258; g) Y. Shen, W.-L. Duan, M. Shi, *Adv. Synth. Catal.* **2003**, *345*, 337–340; h) T. Chang, H. Jing, L. Jin, W. Qiu, *J. Mol. Catal. A: Chem.* **2007**, *264*, 241–247.

[3] a) K. C. Nicolaou, Z. Yang, J.-J. Liu, H. Ueno, P. G. Nantermet, R. K. Guy, C. F. Claiborne, J. Renaud, E. A. Couladouros, K. Paulvannanand, E. J. Sorensen, *Nature* **1994**, *367*, 630–634; b) T. Takata, Y. Furusho, K. Murakawa, T. Endo, H. Matsuoka, T. Hirasa, J. Matsuo, M. Sisido, *J. Am. Chem. Soc.* **1998**, *120*, 4530–4531; c) J. H. Clements, *Ind. Eng. Chem. Res.* **2003**, *42*, 663-674.

[4] a) R. M. Burk, M. B. Roof, *Tetrahedron Lett.* **1993**, *34*, 395–398; b) S. K. Kang, J. H. Jeon, K. S. Nam, C. H. Park, H. W. Lee, *Synth. Commun.* **1994**, *24*, 305–312.

[5] a) K. Matsumoto, S. Fuwa, H. Kitajima, *Tetrahedron Lett.* **1995**, *36*, 6499–6502; b) M. Shimojo, K. Matsumoto, M. Hatanaka, *Tetrahedron* **2000**, *56*, 9281–9288.

[6] H. Hisch, R. Millini, I.-J. Wang, *Chem. Ber.* **1986**, *119*, 1090–1094.

[7] B. M. Trost, S. R. Angle, *J. Am. Chem. Soc.* **1985**, *107*, 6123–6124.

[8] X.-B. Lu, B. Liang, Y.-J. Zhang, Y.-Z. Tian, Y.-M. Wang, C.-X. Bai, H. Wang, R. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 3732–3733.

[9] A. Berkessel, M. Brandenburg, *Org. Lett.* **2006**, *8*, 4401–4404.

[10] S.-W. Chen, R. B. Kawthekar, G.-J. Kim, *Tetrahedron Lett.* **2007**, *48*, 297–300.

[11] L.-L. Jin, Y.Z. Huang, H. W. Jing, T. Chang, P. Yan, *Tetrahedron: Asymmetry* **2008**, *19*, 1947–1953.

[12] a) S.-I. Murahashi, S. Noji, N. Komiya, *Adv. Synth. Catal.* **2004**, *346*, 195–198; b) T. Maeda, T. Takeuchi, Y. Furusho, T. Takata, *J. Polym. Sci. Part. A: Polym. Chem.***2004**, *42*, 4693–4703.

[13] a) R. Kureshy, I. Ahmad, K. Pathak, N. Khan, S. R. Abdi, J. Prathap, R. Jasra, *Chirality* **2007**, *19*, 352–357; b) S. Jammi, L. Rout, T. Punniyamurthy, *Tetrahedron: Asymmetry* **2007**, *18*, 2016–2020.

[14] R. Tan, D.-H. Yin, N.-Y. Yu, L. Tao, Z.-H. Fu, D.-L. Yin, *J. Mol. Catal. A: Chem.* **2006**, *259*, 125–132.

[15] M. Cavazzini, A. Manfredi, F. Montanari, S. Quici, G. Pozzi, *Eur. J. Org. Chem.* **2001**, 4639–4649.

[16] TBAI: tetra-*n*-butylammonium iodide, TBAC: tetra-*n*-butylammonium chloride, TBAF: tetra-*n*-butylammonium fluoride.

[17] W. Yamada, Y. Kitaichi, H. Tanaka, T. Kojima, M. Sato, T. Ikeno, T. Yamada, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1391–1401.

[18] a) J. M. Ready, E. N. Jacobsen, *J. Am. Chem. Soc.* **2001**, *123*, 2687–2688; b) S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunaga, K. B. Hansen, A. E. Gould, M. E. Furrow, E. N. Jacobsen, *J. Am. Chem. Soc.* **2002**, *124*, 1307–1315; c) X.-L. Zheng, C. W. Jones, M. Weck, *J. Am. Chem. Soc.* **2007**, *129*, 1105–1112.

[19] a) M. Tokunaga, J. F. Larrow, F. Kakiuchi, E. N. Jacobsen, *Science* **1997**, *277*, 936–938; b) L. P. C. Nielsen, C. P. Stevenson, D. G. Blackmond, E. N. Jacobsen, *J. Am. Chem. Soc.* **2004**, *126*, 1360–1362.

[20] W. L. F. Armarego, C. L. L. Chai. *Purification of Laboratory Chemicals*, 5th edn., Butterworth-Heinemann, Oxford, **2003**.

