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Chiral catalysts for the asymmetric cycloaddition of carbon dioxide with epoxides

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ABSTRACT

Several chiral BINADCo(III)X (BINAD = Bis(1,1′-2-hydroxy-2′-alkoxy-3-naphthylidene)-1,2-cyclohexanediamine, X = OAc, CF_3CO_2, CCl_3CO_2, OTs, *p*-NO_2PhCO_2) complexes were synthesized and used to catalyze the asymmetric cycloaddition of carbon dioxide with epoxides under mild condition to afford chiral cyclic carbonates. The best catalyst of (*S*,*S*,*S*,*S*)-BINADCo(III)(OAc) **9b** and phenyltrimethylammonium tribromide (PTAT) can provide propylene carbonate with the highest ee being 95% at −20 °C.

1. Introduction

Transformation of carbon dioxide into useful organic compounds has attracted much interest during the last two decades due to the economic and environmental benefits arising from the utilization of renewable sources and the growing concern on the greenhouse effect.[1–4] The preparation of cyclic carbonates via cycloaddition of CO_2 with epoxides is one of the methodologies for CO_2 fixation.[5–11] The cyclic carbonates are widely used as organic synthetic intermediates, monomers, aprotic polar solvents, pharmaceutical/fine chemical intermediates, and in the biomedical applications.[12–21] The enantiomerically pure cyclic carbonates have rarely been reported except for the insertion of carbon dioxide into enantiomerically pure chiral epoxides or the coupling reaction of carbon dioxide with racemic epoxides catalyzed by chiral salenCo(III) catalysts.[22–26] The kinetic resolution of racemic epoxides with water is known as an efficient method for obtaining enantiopure epoxide,[27,28] the kinetic resolution of racemic epoxides with CO_2 using a chiral salenCo(III) complex as catalyst and a co-catalyst of quaternary onium salt cannot lead to the enantiopure epoxide and cyclic carbonate.[22–26] Therefore, new methodologies for the asymmetric cycloaddition of CO_2 with epoxides are still well desired in terms of their atom economic characteristic. Herein, we report our recent efforts for the synthesis of optically active cyclic carbonates with the enantiomeric excess ranging from moderate to excellent catalyzed by the novel multi-chiral catalysts of BINADCo(III)X.

2. Results and discussion

Some multi-chiral free ligands of BINAD (Fig. 1, compounds **1** and **3**) have already been reported for asymmetric catalytic reactions.[29–32] These multi-chiral free ligands can be good chiral ligands for the asymmetric cycloaddition of epoxides and CO_2. As a result, we decided to synthesize these novel multi-chiral ligands **1**-**11** (Fig. 1). The ligands were easy to convert to the multi-chiral complexes of BINADCo(II) **1a**–**11a** (Fig. 2) which were oxidized to BINADCo(III)OAc **1b**–**11b** using glacial acetic acid. The (*R*,*R*,*R*,*R*)-BINADCo(III)OAc complexes **1b**–**5b** were first obtained by tuning of the 2′-substituted group of BINOL in catalyst **1b** supplying various steric effect. These catalysts might combine the two kinds of chirality of salen-backbone and of BINOL-frame and affect their enantioselectivity in the asymmetric cycloaddition reaction. The investigation results using these new catalysts with phenyltrimethylammonium tribromide as co-catalyst are summarized in Table 1. It was found that catalyst **1b** with the smallest 2′-hydroxy group had lower enantioselectivity (entry 1) than other analogues and has lower K_{rel} values for the kinetic resolution reaction of PO and CO_2. For the catalysts **2b**–**5b**, the more bulky substituted group gave better ee values and higher K_{rel} values (entries 4–7). Catalyst **4b** with a 2′-benzyloxy group had more activity than the other analogues yielding (*S*)-propylene carbonate within 77 TOF. Modified catalysts **1b**-Cs and **1b**-Mg have more steric effect thus giving higher relative rate constants K_{rel} values (entries 2 and 3) than their precursors **1b**. On the other hand, when the chirality of 1,1′-2-binaphthol and 1,2-cyclohexanediamine were mixed to prepare the catalysts of (*S*,*R*,*R*,*S*)-BINADCo(III)OAc **6b** and (*R*,*S*,*S*,*R*)-BINADCo(III)OAc **7b**, their activity and enantioselectivity decreased (entries 8 and 9 vs entries 1 and 7). As predicted, when the configuration of both 1,1′-2-binaphthol and 1,2-cyclohexanediamine was switched from (*R*) to (*S*) in order to prepare the catalysts of (*S*,*S*,*S*,*S*)-BINADCo(III)OAc **8b**, **9b**, the chirality of the product was

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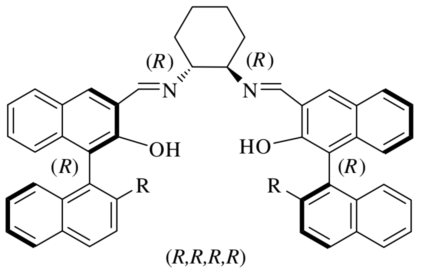
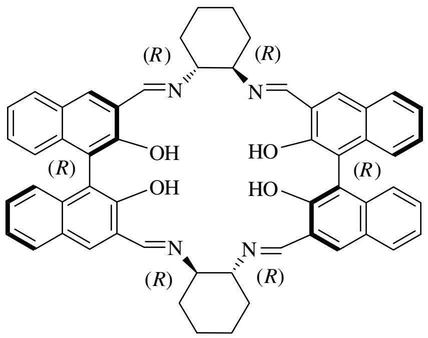


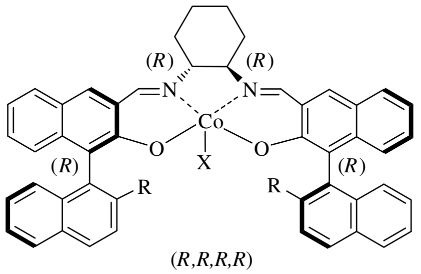
1 R=OH
2 R=OBu
3 R=OCH_3
4 R=OCH_2Ph
5 R=Ph

6 (S,R,R,S) R=OH
7 (R,S,S,R) R=Ph
8 (S,S,S,S) R=OH
9 (S,S,S,S) R=OBu



10-(R,R,R,R,R,R)
11-(S,R,R,S,R,R)

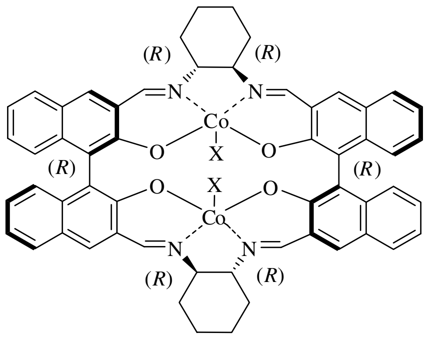
Figure 1. BINAD compounds.



X = none, **1a** ~ **11a**
X = OAc, **1b** ~ **11b**

1b R=OH
1b-Cs R=OCs
1b-Mg R=O1/2Mg
2b R=OBu
3b R=OCH_3
4b R=OCH_2Ph

5b (R,R,R,R) R=Ph
6b (S,R,R,S) R=OH
7b (R,S,S,R) R=Ph
8b (S,S,S,S) R=OH
9b (S,S,S,S) R=OBu

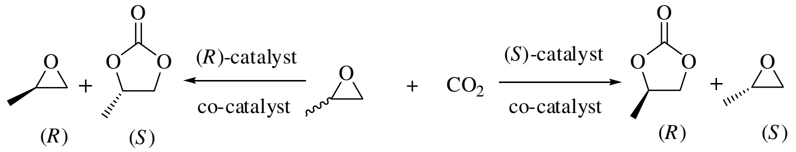


10b-(R,R,R,R,R,R)
11b-(S,R,R,S,R,R)

Figure 2. BINADCo(III) complexes.

Table 1

BINADCo (III) complexes in asymmetric cycloaddition of CO_2 and PO[a]



Entry	Catalyst	Conv (%)	PC[b] (ee%/yield)	t (h)	TOF[c] (h^{-1})	K_{rel}[d]
1	**1b**	39	33 (S)/38.5	24	32	2
2	**1b-Cs**	24	45 (S)/23.5	12	40	3
3	**1b-Mg**	27	55 (S)/27	24	22	4
4	**2b**	25	60 (S)/24.8	20	23	4
5	**3b**	36	55 (S)/35.6	20	36	5
6[e]	**4b**	46	44 (S)/45.8	12	77	4
7	**5b**	33	49 (S)/32.6	17	38	4
8	**6b**	41	24 (S)/40.7	48	17	2
9	**7b**	30	30 (R)/29.5	98	6	2
10	**10b**	43	54 (S)/42.8	42	36	5
11	**11b**	34	45 (S)/33.7	24	29	3

[a] Reaction condition: catalyst (0.05 mmol), PTAT (0.1 mmol), PO (100 mmol, 7 mL), temperature: 25 °C, CO_2: 0.5 MPa.

[b] ee value was determined by Varian CP-3800 GC on a Supelco-DEX series (225) chiral column.

[c] TOF: Turnover frequence, moles of product/per mole catalyst per hour.

[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 resulting propylene carbonate.

[e] The 36.8% ee of remaining PO was determined by converting to related PC using unchiral catalyst.

also switched from (*S*)-PC to (*R*)-PC (Table 2, entries 5 and 6). These results reveal that the chirality of PC is affiliated with chirality of salen-backbone and of BINOL-frame: the same chiralities of binaphthol and diamine are consistent to enhance the enantioselectivity, whereas the contrary chiralities of them are inconsistent to decrease the ee value of PC.

Furthermore, the effect of temperature was also investigated (Table 2). When the reaction temperature decreased from room temperature to 0 °C, the K_{rel} value was augmented from 4 to 18 along with the ee value of (*S*)-PC improved obviously to 87% (Table 2, entry 1) using (*R*,*R*,*R*,*R*)-BINADCo(III)OAc **2b** as catalyst and PTAT as co-catalyst; otherwise, the K_{rel} value was augmented to 21 along with the ee value of (*R*)-PC which increased to 90% (Table 2, entry 7 at 0 °C) using (*S*,*S*,*S*,*S*)-BINADCo(III)OAc (**9b**) as catalyst and PTAT as co-catalyst. When the reaction temperature was cooled down to −20 °C, the enantiomeric excess and the relative rate constant K_{rel} values of (*R*)-PC approached to 95% and 41, respectively (Table 2, entry 8). These results demonstrated that catalysts **2b** and **9b** have excellent catalytic abilities and enantioselectivities with regard to the synthesis of chiral PC.

Table 2
The effect of temperature on asymmetric cycloaddition of CO_2 and PO[a]

Entry	Catalyst	*T* (°C)	Conv (%)	PC (ee%/yield)	*t* (h)	K_{rel}
1	**2b**	0	20	87 (*S*)/20	72	18
2	**6b**	0	20	41 (*S*)/20.1	48	3
3	**3b**	0	20	71 (*S*)/20	96	7
4	**4b**	0	11	64 (*S*)/11.1	120	5
5	**8b**	10	28	50 (*R*)/27.7	17	4
6	**9b**	10	13	81 (*R*)/12.9	20	11
7	**9b**	0	10	90 (*R*)/10	54	21
8	**9b**	−20	5	95 (*R*)/4.9	100	41

[a] Reaction condition: catalyst (0.05 mmol), PTAT (0.1 mmol), PO (100 mmol, 7 mL), CO_2: 0.5 MPa.

Meanwhile, the co-catalysts of quaternary ammonium halogenide were screened in order to enhance the activity and enantioselectivity of catalyst for asymmetric cycloaddition of CO_2 with propylene oxide (PO). The results are listed in Table 3. It can be seen that the PTAT and TBAB were the good co-catalysts (entries 1 and 4), while the TBAC showed less activity (entry 5) and TBAF showed no activity (entry 6) under the reaction conditions.

Table 3
The effect of co-catalyst on asymmetric cycloaddition of CO_2 and PO[a]

Entry	Catalyst	Co-catalyst	*T* (°C)	Conv. (%)	PC (ee%/yield)	*t* (h)	K_{rel}
1	**9b**	Bu_4NBr	0	17	84 (*R*)/16.8	24	14
2	**2b**	PTAT	0	20	87 (*S*)/19.7	72	18
3	**2b**	Bu_4NBr	10	25	63 (*S*)/24.6	20	5
4	**2b**	Bu_4NBr	0	14	78 (*S*)/13.9	36	9
5	**2b**	Bu_4NCl	10	3	80 (*S*)/3	196	9
6	**2b**	Bu_4NF	10	—	—	5 days	—

[a] Reaction condition: catalyst (0.05 mmol), co-catalyst (0.1 mmol), PO (100 mmol, 7 mL), CO_2: 0.5 MPa.

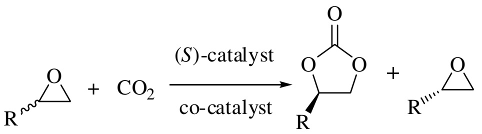
To screen for the best catalyst system, the various acids were used in the oxidation of BINADCo(II) leading to catalyst BINADCo(III)X($X = CH_3CO_2^-$ **2b**, $CF_3CO_2^-$ **2c**, $CCl_3CO_2^-$ **2d**, TsO^- **2e**, and $p - NO_2PhCO_2^-$ **2f**). The catalytic properties of these catalysts were then investigated at 0 °C. The results (Table 4) show that catalyst **2b** with OAc as the counterion has better enantioselectivity (entry 1, 87% ee) than the other analogues, and that catalyst **2c** with $CF_3CO_2^-$ as counterion has better activity than others (entry 2).

Table 4
The anoin effect of catalyst on asymmetric cycloaddition of CO_2 and PO[a]

Entry	BINADCo(III)X	Conv (%)	PC (ee%/yield)	*t* (h)	K_{rel}
1	**2b** ($X = CH_3CO_2^-$)	20	87 (*S*)/20.2	72	18
2	**2c** ($X = CF_3CO_2^-$)	30	65 (*S*)/29.6	70	6
3	**2d** ($X = CCl_3CO_2^-$)	20	53 (*S*)/20.1	90	4
4	**2e** ($X = TsO^-$)	26	43 (*S*)/25.9	55	3
5	**2f** ($X = p\text{-}NO_2PhCO_2^-$)	27	83 (*S*)/26.8	150	15

[a] Reaction condition: catalyst (0.05 mmol), PTAT (0.1 mmol), PO (100 mmol, 7 mL), CO_2: 0.5 MPa, 0 °C.

Table 5
Asymmetric cycloaddition of CO_2 with various epoxides[a]



Entry	R=	Conv (%)	CC (ee%/yield)	*t* (h)	K_{rel}
1[b]	CH_3	33	89 (*R*)/33.2	120	26
2	$ClCH_2$	15	68 (*S*)/14.8	72	6
3[c]	$PhOCH_2$	10	10 (*R*)/9.7	48	1
4[c]	Ph	5	6 (*R*)/4.6	48	1
5	Et	5	86 (*R*)/4.8	120	14

[a] Reaction condition: catalyst **9b** (0.05 mmol), PTAT (0.1 mmol), epoxide (100 mmol, 7 mL), CO_2: 0.5 MPa, 0 °C.

[b] The 42.4% ee of remaining PO was determined.

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

With the optimized conditions, we examined this asymmetric cycloaddition reaction of other epoxides with carbon dioxide using **9b** as catalyst (Table 5). We found that, using 0.05% catalyst, 0.1% PTAT as catalyst, various mono-substituted terminal epoxides with different substituted groups can be transferred to the corresponding optically active cyclic carbonates (CC) with considerable to good ee value. It is worth noting that when the conversion was augmented from 10% (Table 2, entry 7) to 33% (Table 5, entry 1), the ee and K_{rel} values sustained the same level.

3. Conclusion

In conclusion, we have demonstrated that a series of multichiral BINADCo(III)X complexes in the presence of PTAT or TBAB are highly efficient catalysts for the coupling of epoxides and carbon dioxide affording chiral cyclic carbonates in moderate yield with high enantioselectivities under very mild condition. Comparing with the results using chiral Schiff base catalyst contained only one chiral center,[22–24] our investigation results with regard to the ee value of cyclic carbonates achieved much progress. The chiralities of BINOL-frame and backbone of Schiff base might have some synergic effects: the same absolute configuration of it has a positive effect giving a higher ee value of propylene carbonate; on the other hand, the opposite absolute configuration of it had a negative effect giving a lower ee value of propylene carbonate that phenomena are consistent with literature reports.[33,34] The substituted groups on the frame of these catalysts play very important roles. Therefore, decorating of these new catalysts will be a further improvement.

4. Experimental

Epoxides were purchased from Aldrich and Alfa Aesar company and distilled from CaH_2, (*S*)-1,1′-bi-2-naphthol and (*R*)-1,1′-bi-2-naphthol were purchased from Lianyungang Chiral Chemicals Co. Ltd (China) and used without further purification. (1*R*,2*R*)-(−)-*N*,*N*′-Bis((*R*)-2,2′-dihydroxy-3-naphthylidene)-1,2-cyclohexanediamine **1**, (1*R*,2*R*)-(−)-*N*,*N*′-bis((*S*)-2,2′-dihydroxy-3-naphthyli-dene)-

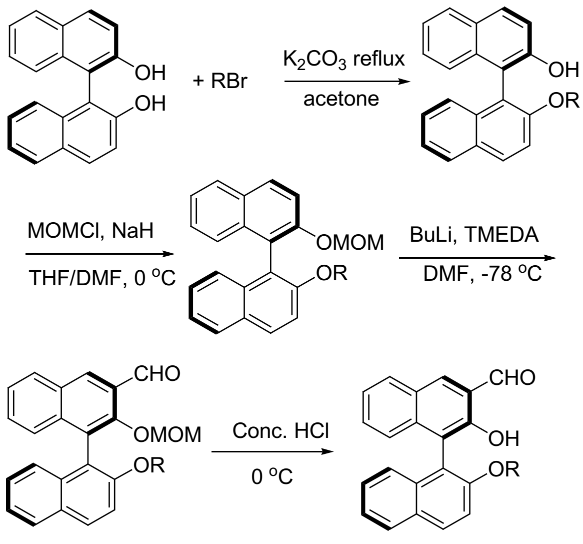
1,2-cyclohexanediamine **6**, (1*S*,2*S*)-(−)-*N*,*N*′-bis((*S*)-2,2′-dihydroxy-3-naphthylidene)-1,2-cyclohexanediamine **8**, and (1*R*,2*R*)-(−)-*N*,*N*′-bis((*R*)-1,1′-2-hydroxy-2′-methoxy-3-naphthyli-dene)-1,2-cyclohexanediamine **3** were prepared according to the literature methods.[35–38] ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 300 and Varian 400 spectrometers, with TMS as internal reference (δ_H = 7.26 ppm for $CDCl_3$, δ_C = 77 ppm for $CDCl_3$). Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (*J*) are given in Hertz (Hz). HRESIMS were carried out on a Bruker APEX II mass spectrometer with glycerol as the matrix. Elemental analyses were carried out on Carioel elemental analyzer. The enantiomeric excesses of the resulting cyclic carbonate without fluorescence were determined by chiral GC analysis (Supelco-DEX series (225) chiral column; injection temperature = 250 °C; detection temperature = 250 °C; 180 °C isothermal.) using a Varian CP-3800 gas chromatograph or Shimadzu GC-9AM equipped with a flame-ionization detector (FID), and N_2 as a carry gas. The enantiomeric excesses of the resulting cyclic carbonate with fluorescence were determined by chiral HPLC analysis (Daicel Chiralcel OD chiral column, *n*-hexane/2-propanol (9:1 v/v), 1.0 mL/min, 254 nm) using a Water 600 controller with 2996 pholodiode Array detector.

4.1. General procedure for the preparation of new BINAD ligands

The chiral 1,2-cyclohexanediammonium mono-L-tartrate (0.5 mmol) and K_2CO_3 (1 mmol) were dissolved in 1.2 mL 50% ethanol. The obtained solution was then added dropwise to a solution of 3-formyl-2-hydroxy-2′-substituted-1,1′-binaphthyl (1 mmol) in ethanol (5 mL) and stirred at room temperature for 24 h. The precipitate was collected by filtration, washed with cold ethanol, and dried in vacuum oven to obtain the product with high yield (85–90%). The configurations of the ligands are shown in Figure 1.

4.1.1. Syntheses of 3-formyl-2-hydroxy-2′-substituted-1,1′-binaphthyl

The synthetic route to fabricate 3-formyl-2-hydroxy-2′-alkoxy-1,1′-binaphthyl was depicted in Scheme 1.



Scheme 1. Synthetic route to 3-formyl-2-hydroxy-2′-alkoxy-1,1′-binaphthyl.

4.1.1.1. General procedure for the synthesis of 2-hydroxy-2′-alkoxy-1,1′-binaphthyl. To a 50 mL three-necked flask equipped with a argon gas protector, a pressure-funnel and a magnetic stir bar, BINOL (2.86 g, 10 mmol), K_2CO_3 (4 g) and acetone (20 mL) were added. The mixture was stirred and heated to reflux for 3.5 h. Then, the bromide was added in one portion from a pressure-funnel and the reaction mixture was continued for 3 h under reflux conditions. After evaporating the acetone using a rotary evaporator, the residue was treated with a flash chromatograph using the petroleum ether and ethyl acetate as eluent (10:1, v/v). The colorless liquid was obtained with the yield from 30% to 66% (For OR = Ph, this procedure was alternated to treat BINOL firstly with the triflic anhydride and then following a standard Grignard reaction using Ni(DPPE)Cl_2 as catalyst).

4.1.1.2. General procedure for synthesis of 2-methoxymethyl-2′-alkoxy-1,1′-binaphthyl. To a 250 mL three-necked flask equipped with a pressure-funnel, a rubber-stopper and a magnetic stir bar, 2′-alkoxy-BINOL (10 mmol), THF/DMF (60 mL, 2:1v/v) and NaH (0.46 g, 60%) were added. When the mixture was cooled down to 0 °C, a solution of 2-hydroxy-2′-alkoxy-1,1′-binaphthyl (10 mmol) in 12 mL THF was added dropwise. After 1 h additional stirring, 1.2 mL methoxymethyl chloride (MOMCl) was added by a syringe. The reaction was then continued for another 4 h at room temperature and then quenched with 100 mL water. This mixture was extracted three times with 50 mL ethyl acetate. The combined organic phase was washed with water and brine, and dried over $MgSO_4$. After removing the organic solvent using a rotary evaporator, the residue was treated with a flash chromatography using the petroleum ether and ethyl acetate as eluent (10:1, v/v). The colorless liquid was obtained in 50–60% yield.

4.1.1.3. General procedure for synthesis of 3-formyl-2-methoxymethyl-2′-alkoxy-1,1′-binaphthyl. To a solution of 2-methoxymethyl-2′-alkoxy-1,1′-binaphthyl and TMEDA (18 mL) in THF (400 mL), 1 M BuLi (140 mL in ethyl ether) was added within 15 min at −78 °C under argon. The mixture was warmed up to 0 °C and stirred for 30 min and then cooled down to −78 °C. A solution of DMF (9 mL) in THF (50 mL) was added dropwise. This reaction was carried out at −78 °C for 30 min and then at 0 °C for 40 min. The obtained yellow solution was quenched with 50 mL saturated NH_4Cl solution and then with 50 mL 1 M HCl solution. After separating the organic layer, the water layer was extracted with ethyl ether. The combined organic layer was washed with saturated $NaHCO_3$ and brine, and dried over $MgSO_4$. After removing the organic solvent using a rotary evaporator, the residue was treated with a flash chromatography using the petroleum ether and ethyl acetate as eluent (10:1, v/v). The product was obtained in 60–76% yield.

4.1.1.4. General procedure for the synthesis of 3-formyl-2-hydroxy-2′-alkoxy-1,1′-binaphthyl. To a solution of 3-formyl-2-methoxymethyl-2′-alkoxy-1,1′-binaphthyl (10 mmol) in 10 mL THF, 50 mL concentrated HCl was added dropwise at 0 °C. This mixture was then stirred 3 h at room temperature and then extracted with ethyl acetate. The obtained solution was washed with water, saturated $NaHCO_3$ and brine, and dried with Na_2SO_4. After evaporating the solvent, the product was obtained with nearly quantitative yield and characterized by ^{1}H NMR and MS that was consistent with literature.

4.1.2. (1*R*,2*R*)-(−)-*N*,*N*′-Bis((*R*)-1,1′-2-hydroxy-2′-butoxy-3-naphthylidene)-1,2-cyclohexanediamine 2

Pale yellow solid. 85% yield, $[\alpha]_D^{20} = -88$ (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.70 (t, *J* = 7.5 Hz, 6H), 1.00–1.07 (m, 4H), 1.42–1.56 (m, 8H), 1.69–1.95 (m, 4H), 3.30 (d, *J* = 9.6 Hz, 2H), 3.97–4.05 (m, 4H), 7.02–7.13 (m, 6H), 7.18–7.47 (m, 6H), 7.72 (dd, *J* = 6.3 Hz, *J* = 8.4 Hz, 4H), 7.89–7.96 (m, 6H), 8.45 (s, 2H), 13.1 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 18.6, 24.0, 31.2, 32.7, 69.5, 72.8, 116.0, 117.2, 119.8, 120.3, 122.9, 123.5, 123.6, 124.8, 125.1, 126.3, 127.2, 127.9, 128.0, 128.6, 129.4, 133.0, 133.8, 135.3, 154.3, 154.6, 165.1; HRMS (ESI): calcd for [M+H]$^+$ ($C_{56}H_{55}N_2O_4$) requires *m*/*z* = 819.4162, found: 819.4153; Anal. Calcd for $C_{56}H_{54}N_2O_4$: C, 81.90; H, 6.51; N, 3.14. Found: C, 82.12; H, 6.65; N, 3.42.

4.1.3. (1*R*,2*R*)-(−)-*N*,*N*′-Bis((*R*)-1,1′-2-hydroxy-2′-ben-zyloxy-3-naphthylidene)-1,2-cyclohexanediamine 4

Yellow solid. 87% yield, $[\alpha]_D^{20} = -108$ (*c* 1.0, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$): δ 1.40–1.54 (m, 4H), 1.69–1.95 (m, 4H), 3.30 (d, *J* = 9.3 Hz, 2H), 5.04 (s, 4H), 6.93–7.06 (m, 12H), 7.20–7.31 (m, 10H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 9.9 Hz, 4H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 8.47 (s, 2H), 13.2 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.0, 32.7, 71.3, 72.9, 116.1, 117.1, 120.1, 120.5, 123.1, 123.8, 124.9, 125.2, 125.6, 125.8, 126.2 126.4, 126.8, 126.9, 127.3, 127.3, 128.0, 128.7, 129.5 129.6, 133.2, 133.9, 135.3, 137.5, 154.1, 154.4, 165.1. HRMS (ESI): Calcd. for [M+H]$^+$ ($C_{62}H_{51}N_2O_4$) requires *m*/*z* = 887.3849, found: 887.3831. Anal. Calcd for $C_{62}H_{50}N_2O_4/CHCl_3$: C, 75.18; H, 5.11; N, 2.78. Found: C, 75.42; H, 5.09; N, 2.38.

4.1.4. (1*R*,2*R*)-(−)-*N*,*N*′-Bis((*R*)-1,1′-2-hydroxy-2′phenyl-3-naphthylidene)-1,2-cyclohexanediamine 5

Yellow solid. 87% yield, $[\alpha]_D^{20} = -85$ (*c* 1.0, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$): δ 1.40–1.54 (m, 4H), 1.69–1.95 (m, 4H), 3.28 (d, *J* = 9.3 Hz, 2H), 6.77 (t, *J* = 7.8 Hz, 2H), 7.00–7.08 (m, 12H), 7.15–7.34 (m, 6H), 7.57–7.66 (m, 6H), 7.92 (d, *J* = 7.8 Hz, 2H), 8.00 (d, *J* = 8.7 Hz, 4H), 8.36 (s, 2H), 13.0 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.0, 32.7, 73.0, 119.7, 119.8, 122.9, 124.7, 125.6, 126.0, 126.2, 126.9, 127.2, 127.5, 127.7, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 131.2, 132.5, 132.8, 132.9, 133.1, 135.1, 140.2, 142.1, 154.6, 164.9. HRMS (ESI): calcd for [M+H]$^+$ ($C_{60}H_{47}N_2O_2$) requires *m*/*z* = 827.3638, found: 827.3640. Anal. Calcd for $C_{60}H_{46}N_2O_2\cdot CH_2Cl_2$: C, 80.34; H, 5.31; N, 3.07. Found: C, 80.65; H, 5.32; N, 2.78.

4.1.5. (1*S*,2*S*-(−)-*N*,*N*′-Bis((*R*)-1,1′-2-hydroxy-2′-phenyl-3-naphthylidene)-1,2-cyclohexanediamine 7

Yellow solid. 87% yield. $[\alpha]_D^{20} = +197$ (*c* 0.2, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 1.41–1.54 (m, 4H), 1.70–1.96 (m, 4H), 3.28 (d, *J* = 9.3 Hz, 2H), 6.78 (t, *J* = 7.8 Hz, 2H), 7.02–7.09 (m, 12H), 7.16–7.35 (m, 6H), 7.56–7.66 (m, 6H), 7.93 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 4H), 8.37 (s, 2H), 13.0 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.0, 32.7, 73.0, 119.7, 119.8, 122.9, 124.7, 125.6, 126.0, 126.2, 126.9, 127.2, 127.5, 127.7, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 131.2, 132.5, 132.8, 132.9, 133.1, 135.1, 140.1, 142.1, 154.6, 164.9. HRMS (ESI): calcd for [M+H]$^+$ ($C_{60}H_{47}N_2O_2$) requires *m*/*z* = 827.3638, found: 827.3640. Anal. Calcd for $C_{60}H_{46}N_2O_2\cdot CH_2Cl_2$: C, 80.34; H, 5.31; N, 3.07. Found: C, 80.69; H, 5.29; N, 3.08.

4.1.6. (1*S*,2*S*)-(−)-*N*,*N*′-Bis((*S*)-1,1′-2-hydroxy-2′-butoxy-3-naphthylidene)-1,2-cyclohexanediamine 9

Pale yellow solid. 86% yield. $[\alpha]_D^{20} = +88$ (*c* 1.0, CH_2Cl_2); ^{1}HNMR (300 MHz, $CDCl_3$) δ 0.71 (t, *J* = 7.5 Hz, 6H), 1.0–1.1 (m, 4H), 1.47–1.60 (m, 8H), 1.72–1.98 (m, 4H), 3.32 (d, *J* = 9.6 Hz, 2H), 3.98–4.2 (m, 4H), 7.05–7.16 (m, 6H), 7.20–7.49 (m, 6H), 7.75 (dd, *J* = 6.3 Hz, *J* = 8.4 Hz 4H), 7.92–7.99 (m, 6H), 8.47 (s, 2H), 13.12 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.5, 18.6, 24.0, 31.2, 32.7, 69.5, 72.8, 116.0, 117.2, 119.8, 120.3, 122.9, 123.5, 123.6, 124.8, 125.1, 126.3, 127.2, 127.9, 128.0, 128.6, 129.4, 133.0, 133.8, 135.3, 154.3, 154.6, 165.0; HRMS (ESI): calcd for [M+H]$^+$ ($C_{56}H_{55}N_2O_4$) requires *m*/*z* = 819.4162, found: 819.4161. Anal. Calcd for $C_{56}H_{54}N_2O_4$: C, 81.90; H, 6.51; N, 3.14. Found: C, 82.00; H, 6.45; N, 3.34.

4.1.7. Bis((1*R*,2*R*)-(−)-*N*,*N*′-(*R*)-1,1′-bi-2-hydroxy-3-naphthylidene)-1,2-cyclohexanediamine 10

(1*R*,2*R*)-(−)-Cyclohexanediammonium mono-L-tartrate (1 mmol) and K_2CO_3 (2 mmol) were dissolved in 2.4 mL 50% ethanol and then added dropwise to a solution of (*R*)-(+)-3,3′-diformyl-2,2′-dihydroxy-1,1′-binaphthyl in ethanol (5 mL). The slurry was then stirred at room temperature for at least 24 h. The precipitate was then collected by filtration, washed with cold ethanol, and dried in vacuum oven to obtain the pale yellow solid with 80% yield, $[\alpha]_D^{20} = -184$ (*c* 0.5, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$): δ 1.42–1.56 (m, 8H), 1.69–1.95 (m, 8H), 3.29 (br, 4H), 6.98 (m, 12H), 7.74–7.76 (m, 8H), 8.46 (s, 4H), 13.2 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.1, 32.7, 73.0, 116.3, 120.5, 123.2, 124.4, 127.5, 128.2, 128.9, 133.4, 135.1, 154.4, 165.1. HRMS (ESI): calcd for [M+H]$^+$ ($C_{56}H_{49}N_4O_4$) requires *m*/*z* = 841.3754, found: 841.3741. Anal. Calcd for $C_{56}H_{48}N_4O_4$: C, 79.75; H, 5.70; N, 6.25. Found: C, 79.98; H, 5.75; N, 6.66.

4.1.8. Bis((*1R*,*2R*)-(−)-*N*,*N*′-(*S*)-1,1′-bi-2-hydroxy-3-naphthylidene)-1,2-cyclohexanediamine) 11

Pale yellow solid. 80% yield. $[\alpha]_D^{20} = -558$ (*c* 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 1.42–1.56 (m, 2H), 1.70–1.96 (m, 2H), 3.27 (br, 1H), 6.96 (m, 3H), 7.75 (m, 2H), 8.45 (s, 1H), 13.2 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 32.7, 73.0, 116.3, 120.5, 123.2, 124.4, 127.5, 128.2, 128.9, 133.4, 135.1, 154.4, 165.1. HRMS (ESI): calcd for [M+H]$^+$ ($C_{56}H_{49}N_4O_4$) requires *m*/*z* = 841.3754, found: 841.3741. Anal. Calcd for $C_{56}H_{48}N_4O_4$: C, 79.75; H, 5.70; N, 6.25. Found: C, 79.78; H, 5.70; N, 6.26.

4.2. General procedure for the preparation of new BINADCo(II) complexes

New ligand BINAD **1**–**11** (1 mmol), $Co(OAc)_2\cdot 4H_2O$ (0.249 g, 1 mmol) and 10 mL methanol were added in a three-necked flask. The mixture was heated at reflux for 2.5 h under Ar. The resulting precipitate was collected by filtration, washed with cold methanol, and dried in vacuum oven to give BINADCo(II) complexes in 80–85% yield. The complexes were characterized by elemental analysis and HRMS.

Compound **1a**: HRMS (ESI): calcd for *m*/*z* 763.2007 ($C_{48}H_{36}N_2O_4Co$), found *m*/*z* 763.2018. Anal. Calcd for $C_{48}H_{36}N_2O_4Co$: C, 75.49; H, 4.75; N, 3.67. Found: C, 75.23; H, 4.66; N, 3.55.

Compound **2a**: HRMS (ESI): calcd for *m*/*z* 875.3259 ($C_{56}H_{52}N_2O_4Co$), found *m*/*z* 875.3265. Anal. Calcd for $C_{56}H_{52}N_2O_4Co$: C, 76.78; H, 5.98; N, 3.20. Found: C, 77.01; H, 5.98; N, 2.78.

Compound **3a**: HRMS (ESI): calcd for *m*/*z* 791.2320 ($C_{50}H_{40}N_2O_4Co$), found *m*/*z* 791.2332. Anal. Calcd for $C_{50}H_{40}N_2O_4Co\cdot CH_2Cl_2$: C, 69.87; H, 4.83; N, 3.20. Found: C, 69.54; H, 4.68; N, 3.22.

Compound **4a**: HRMS (ESI): calcd for *m*/*z* 943.2946 ($C_{62}H_{48}N_2O_4Co$), found *m*/*z* 943.2937. Anal. Calcd for $C_{62}H_{48}N_2O_4Co$: C, 78.88; H, 5.13; N, 2.97. Found: C, 79.05; H, 4.94; N, 2.83.

Compound **5a**: HRMS (ESI): calcd for *m*/*z* 883.2735 ($C_{60}H_{44}N_2O_2Co$), found *m*/*z* 883.2728. Anal. Calcd for $C_{60}H_{44}N_2O_2Co\cdot CH_3OH$: C, 79.99; H, 5.28; N, 3.06. Found: C, 79.63; H, 5.04; N, 2.83.

Compound **6a**: HRMS (ESI): calcd for *m*/*z* 763.7436 ($C_{48}H_{36}N_2O_4Co$), found *m*/*z* 763.7441. Anal. Calcd for $C_{48}H_{36}N_2O_4Co$: C, 75.49; H, 4.75; N, 3.67. Found: C, 75.11; H, 4.71; N, 3.42.

Compound **7a**: HRMS (ESI): calcd for *m*/*z* 883.2735 ($C_{60}H_{44}N_2O_2Co$), found *m*/*z* 883.2721. Anal. Calcd for $C_{60}H_{44}N_2O_2Co$: C, 81.53; H, 5.02; N, 3.17. Found: C, 81.21; H, 4.94; N, 2.89.

Compound **8a**: HRMS (ESI): calcd for *m*/*z* 763.2007 ($C_{48}H_{36}N_2O_4Co$), found *m*/*z* 763.2019. Anal. Calcd for $C_{48}H_{36}N_2O_4Co$: C, 75.49; H, 4.75; N, 3.67. Found: C, 75.22; H, 4.66; N, 3.35.

Compound **9a**: HRMS (ESI): calcd for *m*/*z* 875.3259 ($C_{56}H_{52}N_2O_4Co$), found *m*/*z* 875.3271. Anal. Calcd for $C_{56}H_{52}N_2O_4Co$: C, 76.78; H, 5.98; N, 3.20. Found: C, 77.01; H, 6.02; N, 2.81.

Compound **10a**: HRMS (ESI): calcd for *m*/*z* 954.2027 ($C_{56}H_{44}N_4O_4Co_2$), found *m*/*z* 954.2034. Anal. Calcd for $C_{56}H_{44}N_4O_4Co_2$: C, 70.44; H, 4.64; N, 5.87. Found: C, 70.65; H, 4.49; N, 5.76.

Compound **11a**: HRMS (ESI): calcd for *m*/*z* 954.2027 ($C_{56}H_{44}N_4O_4Co_2$), found *m*/*z* 954.2021. Anal. Calcd for $C_{56}H_{44}N_4O_4Co_2$: C, 70.44; H, 4.64; N, 5.87. Found: C, 70.79; H, 4.45; N, 5.84.

4.3. General procedure for the preparation of new BINADCo(III)X catalysts

The relevant acid (0.05 mmol) was added to a solution of complex BINADCo(II) (0.05 mmol) in 5 mL CH_2Cl_2, and stirred at room temperature for 4 h. After removing the solvent under reduced pressure, a solid of catalyst, BINADCo(III)X was obtained with quantity yield. When the complex **1b** was treated with $CsCO_3$ or $MgEt_2$ in THF, it yielded **1b**-Cs or **1b**-Mg catalyst, respectively.[29] The characterization results of catalysts **1b**–**11b**, **2c**–**2f** using HRMS are the same of **1a**–**11a**.

Compound **1b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40–1.54 (m, 4H), 1.69–1.95 (m, 4H), 3.29 (d, *J* = 9.6 Hz, 2H), 3.58 (q, *J* = 7.2 Hz, 3H), 5.09 (s, 2H), 6.97–7.95 (m, 22H), 8.47 (s, 2H).

Compound **2b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.59 (t, *J* = 7.2 Hz, 6H), 0.81–1.00 (m, 4H), 1.18–1.23 (m, 4H), 1.37–1.91 (m, 8H), 3.27 (d, *J* = 9.3 Hz, 2H), 3.48 (q, *J* = 7.2 Hz, 3H), 3.95–4.01 (m, 4H), 7.04–7.31 (m, 12H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.72 (s, 2H), 7.74 (d, *J* = 9.0 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 8.45 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.4, 18.6, 21.2, 23.9, 31.2, 32.6, 69.4, 72.7, 115.9, 117.2, 119.7, 120.3, 122.9, 123.5, 123.6, 124.8, 125.1, 126.3, 127.2, 127.8, 127.9, 128.6, 129.4, 132.9, 133.8, 135.3, 154.3, 154.5, 165.1, 196.8.

Compound **3b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33–1.84 (m, 8H), 3.25 (d, *J* = 9.3 Hz, 2H), 3.41 (q, *J* = 7.2 Hz, 3H), 3.71 (s, 6H), 6.93–7.06 (m, 6H), 7.20–7.31 (m, 4H), 7.48 (d, *J* = 9.9 Hz, 2H), 7.74 (d, *J* = 11.7 Hz, 4H), 7.81 (d, *J* = 1.2 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 2H), 8.00 (d, *J* = 7.8 Hz, 2H), 8.45 (s, 2H).

Compound **4b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42–1.92 (m, 8H), 3.30 (d, *J* = 9.3 Hz, 2H), 3.48 (q, *J* = 7.2 Hz, 3H), 5.09 (s, 4H), 6.93–7.06 (m, 12H), 7.20–7.31 (m, 10H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.75 (s, 2H), 7.76 (d, *J* = 9.3 Hz, 2H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.94 (d, *J* = 9.3 Hz, 2H), 8.47 (s, 2H).

Compound **5b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42–2.13 (m, 8H), 3.25 (d, *J* = 9.3 Hz, 2H), 3.45 (q, *J* = 7.2 Hz, 3H), 6.74–7.30 (m, 22H), 7.54 (s, 2H), 7.61 (d, *J* = 9.0 Hz, 2H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 4H), 8.33 (s, 2H).

Compound **6b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40–1.54 (m, 4H), 1.69–1.95 (m, 4H), 3.29 (d, *J* = 9.6 Hz, 2H), 3.58 (q, *J* = 7.2 Hz, 3H), 5.09 (s, 2H), 6.97–7.95 (m, 22H), 8.47 (s, 2H).

Compound **7b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42–2.13 (m, 8H), 3.25 (d, *J* = 9.3 Hz, 2H), 3.45 (q, *J* = 7.2 Hz, 3H), 6.74–7.30 (m, 22H), 7.54 (s, 2H), 7.61 (d, *J* = 9.0 Hz, 2H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 4H), 8.33 (s, 2H).

Compound **8b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40–1.54 (m, 4H), 1.69–1.95 (m, 4H), 3.29 (d, *J* = 9.6 Hz, 2H), 3.58 (q, *J* = 7.2 Hz, 3H), 5.09 (s, 2H), 6.97–7.95 (m, 22H), 8.47 (s, 2H).

Compound **9b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.59 (t, *J* = 7.2 Hz, 6H), 0.81–1.00 (m, 4H), 1.18–1.23 (m, 4H), 1.37–1.91 (m, 8H), 3.27 (d, *J* = 9.3 Hz, 2H), 3.48 (q, *J* = 7.2 Hz, 3H), 3.95–4.01 (m, 4H), 7.04–7.31 (m, 12H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.72 (s, 2H), 7.74 (d, *J* = 9.0 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 8.45 (s, 2H).

Compound **10b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42–1.95 (m, 8H), 3.25 (br, 2H), 3.48 (m, 3H), 6.98–8.46 (m, 12H).

Compound **11b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42–1.95 (m, 8H), 3.23 (br, 2H), 3.45 (m, 3H), 6.93–8.44 (m, 12H).

Compound **2e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.52–1.84 (m, 22H), 3.22 (br, 2H), 3.42 (br, 3H), 3.93 (br, 4H), 6.99–7.37 (m, 18H), 7.65 (br, 4H), 7.80 (br, 2H), 7.88 (br, 2H), 8.38 (s, 2H).

Compound **2f**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.57–2.18 (m, 22H), 3.49 (br, 2H), 5.25 (br, 4H), 7.26–7.66 (m, 28H).

4.4. General procedure for the asymmetric cycloaddition of epoxides with carbon dioxide

All reactions were carried out in a 100 mL stainless-steel pressure reactor was charged with catalyst (0.05 mmol), epoxide (100 mmol), and co-catalyst (0.1 mmol). The reaction vessel was purged three times with carbon dioxide, and filled carbon dioxide to 0.5 MPa, stirred. When the pressure of reactor declined after appropriate time, it was released to terminate the reaction. After removing the unreacted epoxide weighed to measure its conversion, chiral cyclic carbonate (R = Me, Et, CH_2Cl), weighed to calculate the yield of cyclic carbonate, was distilled under vacuum as a colorless liquid or it (R = Ph, $PhOCH_2$) was recrystallized with ethanol. The ^{1}H NMR and TOFMS of product mixture were also carried out showing no side products of copolymer of epoxide and carbon dioxide.

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References

1. Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155–174.
2. Darensbourg, D. J.; Mackiewicz, R. M.; Phelps, A. L.; Billodeaux, D. R. *Acc. Chem. Res.* **2004**, *37*, 836–844.
3. Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618.
4. Sugimoto, H.; Inoue, S. *J. Polym. Sci. Part A* **2004**, *42*, 5561.
5. Jin, L.-L.; Jing, H.-W.; Chang, T.; Bu, X.-L.; Wang, L.; Liu, Z.-L. *J. Mol. Catal. A: Chem.* **2007**, *261*, 262–266.
6. Kim, H. S.; Kim, J. J.; Lee, S. D.; Lah, M. S.; Moon, D.; Jang, H. G. *Chem. Eur. J.* **2003**, *9*, 678–686.
7. Shen, Y.; Duan, W.-L.; Shi, M. *Adv. Synth. Catal.* **2003**, *345*, 337–340.
8. Jing, H.-W.; Nguyen, S. T. *J. Mol. Catal. A: Chem.* **2007**, *261*, 12–15.
9. Kim, Y. J.; Varma, R. S. *J. Org. Chem.* **2005**, *70*, 7882–7891.
10. Shen, Y.-M.; Duan, W.-L.; Shi, M. *J. Org. Chem.* **2003**, *68*, 1559–1562.
11. Jiang, J.-L.; Gao, F.-X.; Hua, R.-M.; Qiu, X.-Q. *J. Org. Chem.* **2005**, *70*, 381–383.
12. Huang, J.-W.; Shi, M. *J. Org. Chem.* **2003**, *68*, 6705–6709.
13. Sit, W. N.; Ng, S. M.; Kwong, K. Y.; Lau, C. P. *J. Org. Chem.* **2005**, *70*, 8583–8586.
14. Alvaro, M.; Baleizao, C.; Das, D.; Carbonell, E.; Garcia, H. *J. Catal.* **2004**, *228*, 254–258.
15. Shaikh, A.-A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951–976.
16. Biggadike, K.; Angell, R. M.; Burgess, C. M.; Farrell, R. M.; Hancock, A. P.; Harker, A. J.; Irving, A. J.; Irving, W. R.; Ioannou, C. P.; Procopiou, A.; Shaw, R. E.; Solanke, Y. E.; Singh, O. M. P.; Snowden, M. A.; Stubbs, R.; Walton, S.; Weston, H. E. *J. Med. Chem.* **2000**, *43*, 19–21.
17. Paddock, R. L.; Nguyen, S. T. *J. Am. Chem. Soc.* **2001**, *123*, 11498–11499.
18. Caló, V.; Nacci, A.; Monopoli, A.; Fanizzi, A. *Org. Lett.* **2002**, *4*, 2561–2563.
19. Yang, H.; Gu, Y.; Deng, Y.; Shi, F. *Chem. Commun.* **2002**, 274–275.
20. Yano, T.; Matsui, H.; Koike, T.; Ishiguro, H.; Fujihara, H.; Yoshihara, M.; Maeshima, T. *Chem. Commun.* **1997**, 1129–1130.
21. Paddock, R. L.; Nguyen, S. T. *Chem. Commun.* **2004**, 1622–1623.
22. Albrecht, B.; Marc, B. *Org. Lett.* **2006**, *8*, 4401–4404.
23. Chen, S.; Kawthekar, R. B.; Kim, G. J. *Tetrahedron Lett.* **2007**, *48*, 297–300.
24. Lu, X.-B.; Liang, B.; Zhang, Y.-J.; Tian, Y.-Z.; Wang, Y.-M.; Bai, C.-X.; Wang, H.; Zhang, R. *J. Am. Chem. Soc.* **2004**, *126*, 3732–3733.
25. Chang, T.; Jing, H.-W.; Jin, L.-L.; Qiu, W.-Y. *J. Mol. Catal. A: Chem.* **2007**, *264*, 241–247.
26. Yamada, W.; Kitaichi, Y.; Tanaka, h.; Kojima, T.; Sato, M.; Ikeno, T.; Yamada, T. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1391–1401.
27. Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936–938.
28. Gansauer, A.; Baechuk, A.; Keller, F.; Schmitt, M.; Grimme, S.; Gerenkmp, M.; Muck-Lichtenfeld, C.; Daasbjerg, K.; Svith, H. . *J. Am. Chem. Soc.* **2007**, *129*, 1359–1371.
29. DiMauro, E. F.; Kozlowski, M. C. *Organometallics* **2002**, *21*, 1454–1461.

30. Li, Z.-B.; Rajaram, A. R.; Decharin, N.; Qin, Y.-C.; Pu, L. *Tetrahedron Lett.* **2005**, *46*, 2223–2226.
31. Sasaki, H.; Irie, R.; Hamada, T.; Suzuki, K.; Katsuki, T. *Tetrahedron* **1994**, *50*, 11827–11838.
32. Hamada, T.; Fukuda, T.; Imanishi, H.; Katsuki, T. *Tetrahedron* **1996**, *52*, 515–530.
33. Punniyamurthy, T.; Irie, R.; Katsuki, T.; Moro-oka, Y. *Synlett* **1999**, 1049–1052.
34. Punniyamurthy, T.; Miyafuji, A.; Katsuki, T. *Tetrahedron Lett.* **1998**, *39*, 8295–8298.
35. Matsunaga, S.; Das, J.; Roels, J.; Vogl, E. M.; Yamamoto, N.; Iida, T.; Yamaguchi, K.; Shibasaki, M. *J. Am. Chem. Soc.* **2000**, *122*, 2252–2260.
36. Frantz, D. E.; Weaver, D. G.; Carey, J. P.; Kress, M. H.; Dolling, U. H. *Org. Lett.* **2002**, *4*, 4717–4718.
37. Brunner, H.; Schiessling, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 125–126.
38. Zhang, H.-C.; Huang, W.-S.; Pu, L. *J. Org. Chem.* **2001**, *66*, 481–487.