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Catalytic Asymmetric Cycloaddition of CO_2 to Epoxides via Chiral Bifunctional Ionic Liquids

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Graphic Abstract

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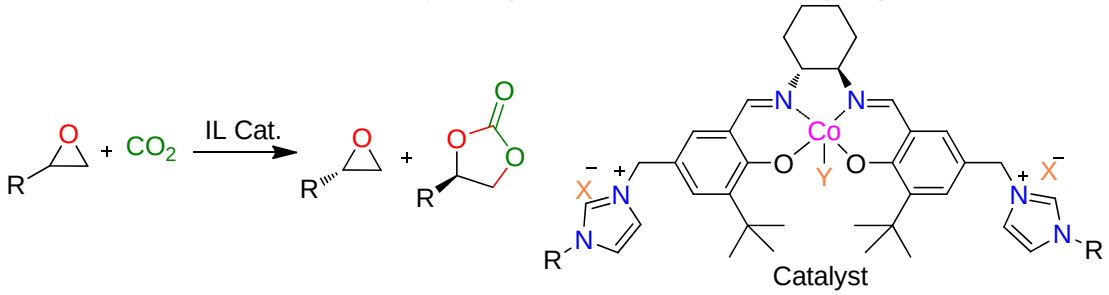

ABSTRACT

A series of new chiral ionic liquid catalysts composed of the *N*,*N*'-bis(salicyclidene)cyclohexene diaminatocobalt and an imidazolium salt were designed, prepared and applied for the chiral cyclic carbonate synthesis from racemic epoxides and carbon dioxide. All reactions exhibit good enantioselectivity for the chiral cyclic carbonate without polycarbonate and other by-products. The order of The order of catalytic activity toward the axial anions is OAc^-> $CF_3CO_2^-$ > $CCl_3CO_2^-$ > OTs^- and the order of enantioselectivity is OTs^-> OAc^- >$CCl_3CO_2^-$>$CF_3CO_2^-$.

Keywords: Asymmetric cycloaddition, Chiral ionic liquid, Carbon dioxide, Epoxide, Kinetic resolution

1. Introduction

Transformation of carbon dioxide into useful organic compounds, as an environmentally benign process, has attracted much attention during the last two decades [1-7]. The preparation of cyclic carbonates via coupling reaction of CO_2 and epoxides is one of means for CO_2 fixation [8-15]. Chiral cyclic carbonates are important building blocks of chiral intermediates and precursors of pharmaceuticals and fine chemicals [16]. A variety of methodologies such as the cyclization of chiral diol with triphogene [17], enzyme mediated enatioselective hydrolysis of racemic cyclic carbonates [18] or the insertion of CO_2 into chiral epoxides catalysed by zinc(II) [19] or palladium(0) complexes [20] have been applied to their fabrication. As far as we know, the kinetic resolution of racemic epoxides with CO_2 in the presence of a chiral SalenCo(Ⅲ) complex leading to chiral cyclic carbonates is rare reported (Scheme 1) [21-26] in spite of the kinetic resolution of racemic epoxides with water obtaining only enantiopure epoxides [27,28].

A plenty of catalyst systems have been developed for the synthesis of cyclic carbonates including inorganic and organic salts, metal oxides, organometallic compounds, ionic liquids, transition-metal and main group complexes etc. [29-35]. In which, the ionic liquids (ILs), well-known as green solvents and catalysts in organic synthesis [36-41], are few used in the asymmetric reactions, such as coupling reaction of CO_2 and epoxides to generate chiral cyclic carbonates till now [42].

In this regard, modifying chiral ligand with imidazolium cation in metal complex catalysts has been recognized as a useful methodology to improve their catalytic efficiency [39]. According to our own efforts toward the development of highly efficient catalysts for the coupling of

CO_2 and epoxides including bifunctional catalysts [43] that have been used on the asymmetric coupling reaction of CO_2 and epoxides, we devised a new series of chiral SalenCo(III)Y catalysts supported on the alkyl imidazole ionic liquids (Figure 1).

2. **Experimental**

2.1 General

Propylene oxide was distilled from CaH_2. 1,2-Diaminocyclohexane, *L*-(+)-tartaric acid (2*R*,3*R*) and other epoxides were purchased from Aldrich. Imidazole, 1-bromobutane, 1-bromooctane, 1-bromododecane were analytical reagents and used without further purification.

NMR spectra of compounds and ILs were determined with a Varian AM-400 or Am-300 spectrometer using TMS as an internal standard. IR spectra of catalysts were recorded on a Nicolet NEXUS 670 FT-IR spectrometer. Elemental analyses of catalysts were carried out on Carioel elemental analyzer. GC analyses of chiral cyclic carbonates were carried out on a Varian CP-3800 gas chromatograph equipped with FID detectors utilizing a Supelco-DEX series (225) chiral column to determine the enantiomeric excess value. HPLC analyses of chiral cyclic carbonates were carried out on a Waters 600 controller with a 2996 photodiode array detector using a chiral OD column. The mass spectra/ HRMS (ESI) were obtained by utilizing an Applied Biosystems Mariner Biospectrometry Workstation/ Bruker APEX II mass spectrometer. Melting Points were carried out on Digital Display Microscopic Melting Point Locator X-4 purchased from Beijing Tech Instrument Co., Ltd.

2.2 General procedure for coupling of epoxide and CO_2

A solution of freshly prepared SalenCo(Ⅲ)Y (0.1 mmol) and epoxide (100 mmol) was

introduced into a 100 mL stainless-steel autoclave, which was purged three times and charged with CO_2 to 1.2 MPa. The reaction mixture was stirred at room temperature. When the pressure of reactor was fall down to a presetting value, it was then vented carefully. After removing the excess epoxide, the residue was weighed to measure the conversion of epoxide, chiral cyclic carbonate (R = Me, Et, CH_2Cl) was distilled under vacuum as a colourless liquid or it (R = Ph, $PhOCH_2$) was obtained by column chromatography through a short silica-gel column to yield white solid product (ethyl acetate/ petroleum ether = 5:1).

2.3 Synthesis of catalysts

2.3.1 Synthesis of N-alkylimidazoles (Scheme 3):

N-Butylimidazole and *N*-octylimidazole were synthesized following the procedure of literature [44]: To a round-bottomed flask, imidazole (6.0 g, 88 mmol), 1-bromobutane/1-bromooctane (90 mmol), acetonitrile (50 mL) and potassium hydroxide (9.9 g, 177 mmol), were added in sequence. The reaction mixture was refluxed for 4 h and then cooled down to room temperature. After evaporating the solvent, the residue was purified by a flash column chromatography utilizing ethyl acetate/methanol (v/v = 25:1) as eluent. The pure product of 1-butylimidazole/1-octylimidazole was isolated as a pale yellow oil (~83%).

N-Butylimidazole: ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.85 (t, J = 7.3 Hz, 3H, CH_3), 1.20-1.27 (m, 2H, CH_2), 1.62-1.72 (m, 2H, CH_2), 3.85 (t, J = 7.3 Hz, 2H, CH_2), 6.83 (s, 1H, ImH), 6.94 (s, 1H, ImH), 7.37(s, 1H, ImH). ^{13}C NMR ($CDCl_3$): δ (ppm) = 13.3, 19.5, 32.8, 46.5, 118.7, 128.9, 136.8.

N-Octylimidazole: ^{1}H NMR: ($CDCl_3$): δ (ppm) = 0.87 (t, J = 6.5 Hz, 3H, CH_3), 1.28 (br, 10H,

CH_2), 1.77 (br, 2H, CH_2), 3.92 (t, J = 7.2 Hz, 2H, CH_2), 6.90 (s, 1 H, ImH), 7.04 (s, 1H, ImH), 7.45 (s, 1H, ImH). ^{13}C NMR ($CDCl_3$): δ (ppm) = 13.9, 22.5, 26.4, 28.9, 29.0, 31.0, 31.6, 46.9, 118.7, 129.2, 136.9.

N-Dodecylimidazole was obtained following the procedure of literature [45]. To a solution of imidazole (0.7 g, 10 mmol) in NaOH (50%) solution (1.0 g, 11 mmol), a solution of 1-bromododecane (2.5 g, 10 mmol) in THF (10 mL) was added dropwise. The obtained mixture was refluxed for three days. After cooling, THF was removed by a rotary evaporator. The residue was extracted with dichloromethane three times. The combined organic layer was washed with water and then dried over anhydrous Na_2SO_4. The filtrate was concentrated and purified by a column chromatography to produce clear yellow oil (2.0 g, 81%).

^{1}H NMR ($CDCl_3$): δ (ppm) = 0.83 (t, J = 5.1 Hz, 3H, CH_3), 1.10-1.21 (m, 18H, CH_2), 1.69 (br, J = 7.0 Hz, 2H, CH_2), 3.84 (t, J = 6.2 Hz, 2H, CH2), 6.89 (s, 1H, ImH), 7.04 (s, 1H, ImH), 7.44 (s, 1H, ImH). ^{13}C NMR ($CDCl_3$): δ (ppm) = 13.7, 22.3, 26.1, 28.7, 28.9, 29.0, 29.2, 20.7, 31.5, 46.5, 118.3, 128.2, 136.6

2.3.2 Synthesis of ligands

Synthesis of N-alkylimidazolium salicylaldehydes, ***Aa-Ca*** *and* ***Ab-Cb*** (Scheme 4): A solution of 3-*tert*-Butyl-5-bromomethyl-2-hydroxybenzaldehyde [46, 47] in toluene (5.0 mL) was added dropwise to a solution of *N*-alkylimidazole (10.0 mmol) in toluene (20.0 mL) over 10 min at room temperature. The mixture was then heated to reflux for 5 h. After cooling to room temperature, the precipitate product was filtered, washed with toluene (3×5 mL) and dried under reduced pressure.

Aa: yield 97%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.95 (t, J = 6.9 Hz, 3H, CH_3), 1.39 (m, 11H, CH_2+^{t}Bu), 1.91 (t, J = 7.2 Hz, 2H, CH_2), 4.31 (t, J = 7.2 Hz, 2H, Im-CH_2), 5.65 (s, 2H, ph-CH_2-Im), 7.42 (s, 1H, ImH), 7.58 (s, 1H, ArH), 7.64 (s, 1H, ArH), 7.95 (s, 1H, ImH), 9.96 (s, 1H, ImH), 10.51 (s, 1H, CHO), 11.91 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ *(ppm)* = 13.3, 19.4, 29.0, 31.9, 35.0, 50.0, 52.6, 120.5, 122.0, 123.8, 133.2, 134.4, 139.7, 161.7, 197.2. MS (ESI-MS): *m/z* [*M*-Br]$^+$ calcd. for $C_{19}H_{27}N_2O_2Br$: 315.2; found: 315.3.

Ba: yield 98%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.86 (t, J = 6.2 Hz, 3H, CH_3), 1.24-1.40 (m, 19H, CH_2+^{t}Bu), 1.93-1.98 (m, 2H, CH_2), 4.29 (t, J = 7.7 Hz, 2H, ImCH_2), 5.66 (s, 2H, ph-CH_2-Im), 7.28 (s, 1H, ImH), 7.44 (s, 1H, ArH), 7.61 (s, 1H, ArH), 7.94 (s, 1H, ImH), 9.96 (s, 1H, ImH), 10.74 (s, 1H, CHO), 11.94 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ (ppm) = 14.0, 22.5, 26.2, 28.85, 28.98, 29.1, 30.1, 31.6, 35.0, 50.3, 52.7, 120.6, 121.6, 123.7, 133.2, 134.3, 137.2, 139.8, 161.8, 197.2. MS (ESI): *m/z* [M-Br]$^+$ calcd. for $C_{23}H_{35}N_2O_2Br$: 371.3; found: 371.4.

Ca: yield 98%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.88 (t, J = 6.2 Hz, 3H, CH_3), 1.24-1.40 (m, 27H, CH_2+^{t}Bu), 1.92 (br, 2H, CH_2), 4.28 (t, J = 7.5 Hz, 2H, CH_2), 5.67 (s, 2H, CH_2), 7.28 (s, 1H, ImH), 7.43 (s, 1H, ArH), 7.61 (s, 1H, ArH), 7.94 (s, 1H, ImH), 9.96 (s, 1H, ImH), 10.79 (s,

1H, CHO), 11.94 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ (ppm) = 14.1, 22.6, 26.2, 28.9, 29.1, 29.25, 29.31, 29.4, 29.5, 30.1, 31.8, 35.0, 50.3, 52.6, 120.6, 121.9, 123.9, 133.3, 134.4, 137.0, 139.8, 161.8, 197.2. MS (ESI): *m/z* [*M*-Br]$^+$ calcd. for $C_{27}H_{43}N_2O_2Br$: 427.3; found 427.4.

Ab: yield 97%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.94 (t, *J* = 6.8 Hz, 3H, CH_3), 1.23-1.39 (m, 11H, CH_2+^{t}Bu), 1.90-2.00 (m, 2H, CH_2), 4.38 (t, *J* = 8.4 Hz, 2H, CH_2), 5.65 (s, 2H, CH_2), 7.42 (s, 1H, ImH), 7.57 (s, 1H, ArH), 7.64 (s, 1H, ArH), 7.94 (s, 1H, ImH), 9.88 (s, 1H, ImH), 10.86 (s, 1H, CHO), 11.90 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ (ppm) = 13.2, 19.3, 28.9, 31.8, 34.8, 49.7, 52.3, 120.4, 122.0, 124.1, 133.1, 134.3, 137.0, 139.5, 161.5, 197.1. MS (ESI): *m/z* [*M*-Cl]$^+$ calcd. for $C_{19}H_{27}N_2O_2Cl$: 315.2; found 315.3.

Bb: yield 98%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.86 (t, *J* = 3.3 Hz, 3H, CH_3), 1.25-1.36 (m, 19H, CH_2+^{t}Bu), 1.91-1.98 (m, 2H, CH_2), 4.28 (t, *J* = 7.2 Hz, 2H, CH_2), 5.65 (s, 2H, CH_2), 7.23 (s, 1H, ImH), 7.40 (s, 1H, ArH), 7.60 (s, 1H, ArH), 7.90 (s, 1H, ImH), 9.94 (s, 1H, ImH), 10.96 (s, 1H, CHO), 11.93 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ (ppm) = 13.2, 19.3, 28.9, 29.5, 31.8, 34.5, 34.8, 49.7, 52.3, 120.4, 122.0, 124.1, 133.1, 134.3, 137.0, 139.5, 161.5, 197.1. MS (ESI): *m/z* [*M*-Cl]$^+$ calcd. for $C_{23}H_{35}N_2O_2Cl$: 371.3; found 371.4.

Cb: yield 97%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.84 (t, *J* = 5.9 Hz 3H, CH_3), 1.21-1.35 (m, 27H, CH_2+^{t}Bu), 1.88 (br, 2H, CH_2), 4.24 (t, *J* = 7.5 Hz, 2H, CH_2), 5.63 (s, 2H, CH_2), 7.29 (s, 1H, ImH), 7.46 (s, 1H, ArH), 7.58 (s, 1H, ArH), 7.89 (s, 1H, ImH), 9.92 (s, 1H, ImH), 10.97 (s, 1H, CHO), 11.89 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ (ppm) = 14.0, 22.6, 26.2, 28.9, 29.0, 29.2, 29.3, 29.4, 29.5, 30.1, 31.8, 34.9, 50.1, 52.4, 120.5, 121.7, 133.2, 134.4, 139.7, 161.6, 197.2. MS (ESI): *m/z* [*M*-Cl]$^+$ calcd. for $C_{27}H_{43}N_2O_2Cl$: 427.3; found 427.4.

General procedure for the preparation of Salen ligands (**1Aa**-**1Ca**, **1Ab**-**1Cb** (Scheme 3): (1*R*,

2*R*)-1,2-diaminocyclohexane (0.5 mmol) and *N*-alkylimidazolium salicylaldehyde (**Aa-Ca**, **Ab-Cb**, 1.0 mmol) were dissolved in ethanol (10.0 mL) in a two-necked round-bottomed flask equipped with a condenser and gas-protector. The mixed solution was refluxed for 5 h under argon. The solvent was evaporated near to dry, and diluted by hexane (15 mL) to precipitate the crude product that was filtered, washed with hexane and dried in vacuum [48].

1Aa: m.p. 74 - 75 °C, $[\alpha]_{589}^{18}$ = -199º(c = 1.0, acetone). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.81 (t, J = 7.8 Hz, 6H, CH_3), 1.18-1.28 (m, 26H, CH_2+^{t}Bu), 1.63-1.82 (m, 8H, CH_2), 1.86-1.94 (m, 2H, CH), 4.14-4.28 (m, 4H, CH_2), 5.27-5.46 (m, 4H, CH_2), 7.17 (s, 2H, ArH), 7.25 (s, 2H, ImH), 7.30 (s, 2H, ImH), 7.52 (s, 2H, ArH), 8.67 (s, 2H, CH=N), 10.29 (s, 2H, ImH), 14.15 (s, 2H, OH); ^{13}C NMR ($CDCl_3$): δ (ppm) = 13.3, 19.3, 19.6, 22.4, 24.0, 29.1, 29.6, 31.9, 32.9, 34.9, 46.7, 49.8, 52.9, 71.6, 118.3, 118.8, 121.6, 122.4, 128.8, 129.9, 130.6, 136.3, 138.8, 161.4, 165.0. MS (ESI): *m/z* [*M*-2Br]$^{2+}$/2 calcd. for $C_{44}H_{64}Br_2N_6O_2$: 354.3; found 354.5; IR (KBr) (cm^{-1}): 3363.0, 2958.5, 2918.5, 2850.0, 1740.9, 1629.1, 1561.3, 1462.2, 1379.5, 1270.5, 1210.6, 1158.0, 1089.3, 1047.1, 879.6, 723.4.

1Ba: m.p. 83 - 84 °C, $[\alpha]_{589}^{18}$ = -206º (*c* = 1.0, acetone). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.86 (t, J = 6.9 Hz, 6H, CH_3), 1.25-1.48 (m, 42H, CH_2+^{t}Bu), 1.77-1.97 (m, 8H, CH_2), 1.99-2.02 (m, 2H, CH), 4.28 (t, J = 7.8 Hz, 4H, CH_2), 5.34-5.54 (m, 4H, CH_2), 6.91 (s, 2H, ArH), 7.18 (d, J = 1.8 Hz, 2H, ImH), 7.33 (d, 2H, J = 1.8 Hz, ImH), 7.51 (s, 2H, ArH), 8.26 (s, 2H, CH=N), 10.48 (s, 2H, ImH), 14.23 (s, 2H, OH); ^{13}C NMR ($CDCl_3$): δ (ppm) = 14.0, 22.5, 22.6, 24.1, 26.2, 28.9, 29.0, 29.3, 30.2, 31.6, 31.9, 35.0, 37.0, 50.2, 52.9, 71.7, 118.4, 121.1, 121.6, 130.0, 138.9, 165.1; MS (ESI): *m/z*: [*M*-2Br]$^{2+}$/2 calcd. for $C_{52}H_{80}Br_2N_6O_4$: 410.3; found 410.4; IR (KBr) (cm^{-1}): 3383.9, 3130.7, 3062.9, 2926.1, 2857.1, 2193.7, 1731.9, 1664.4, 1629.4, 1559.6,

1444.2, 1377.9, 1318.1, 1211.7, 1158.6, 1096.2, 918.7, 732.2, 643.2, 511.8.

1Ca: m.p. 75 - 76 °C, $[\alpha]_{589}^{18}$ = -203.5º(*c* = 1.0, acetone). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.88 (t, 6H, *J* = 6.6 Hz, CH_3), 1.18-1.37 (m, 58H, CH_2+^{t}Bu), 1.76-1.91 (m, 8H, CH_2), 2.02-2.06 (m, 2H, CH), 4.28 (t, *J* = 7.4 Hz, 4H, CH_2), 5.35-5.67 (m, 4H, CH_2), 7.06 (s, 2H, ArH), 7.18 (s, *J* = 2.1 Hz, 2H, ImH), 7.33 (d, *J* = 2.1 Hz, 2H, ImH), 7.56 (s, 2H, ArH), 8.29 (s, 2H, CH=N), 10.52 (s, 2H, ImH), 14.23 (s, 2H, OH); ^{13}C NMR ($CDCl_3$): δ (ppm) = 14.1, 22.6, 26.2, 28.9, 29.2, 29.3, 29.4, 29.5, 29.6, 30.2, 31.8, 34.9, 50.1, 52.9, 71.7, 118.3, 121.1, 121.6, 122.2, 123.0, 130.7, 136.4, 136.9, 161.5, 165.1; MS (ESI): *m/z* $[M\text{-}2Br]^{2+}/2$ calcd. for $C_{60}H_{96}Br_2N_6O_4$: 466.3; found 466.6; IR (KBr) (cm^{-1}): 3388.8, 3124.0, 3058.4, 2925.1, 2854.6, 2191.6, 1731.8, 1629.1, 1596.3, 1559.2, 1444.1, 1359.3, 1273.9, 1212.0, 1160.2, 1096.4, 1026.2, 921.2, 861.2, 777.2, 732.4, 643.1.

1Ab: m.p. 86 - 87 °C, $[\alpha]_{589}^{18}$= -223º (*c* = 1.0, acetone). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.96 (t, *J* = 4.8 Hz, 6H, CH_3), 1.28-1.36 (m, 26H, CH_2+^{t}Bu), 1.71-1.88 (m, 8H, CH_2), 1.97-1.99 (m, 2H, CH), 4.28 (t, *J* = 7.2 Hz, 4H, CH_2), 5.33-5.54 (m, 4H, CH_2), 6.94 (s, 2H, ArH), 7.04 (s, 1H, 2mH), 7.47 (s, 2H, ImH), 7.55 (s, 2H, ArH), 8.28 (s, 2H, CH=N), 10.74 (s, 2H, ImH), 14.24 (s, 2H, OH); ^{13}C NMR ($CDCl_3$): δ (ppm) = 13.4, 19.5, 24.1, 24.6, 29.2, 29.6, 32.0, 32.5, 34.9, 49.9, 53.3, 60.5, 72.6, 87.3, 121.8, 129.8, 147.7, 161.5, 165.3; HRMS (ESI): *m/z* $[M\text{-}2Cl]^{2+}/2$ calcd. for $C_{44}H_{64}Cl_2N_6O_4$: 354.2540; found 354.2536; IR (KBr) (cm^{-1}): 3417.0, 3131.0, 2956.2, 2930.2, 2862.5, 2609.7, 2193.6, 1729.5, 1663.6, 1629.7, 1560.5, 1443.0, 1362.1, 1272.5, 1211.3, 1159.7, 1096.8, 1028.5, 995.1, 924.1, 804.3, 731.1, 642.4.

1Bb: m.p. 81 - 82 °C, $[\alpha]_{589}^{18}$ = -211º (*c* = 1.0, acetone). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.87 (t, 3H, *J* = 2.7 Hz, CH_3), 1.25-1.49 (m, 19H, CH_2+^{t}Bu), 1.77-1.90 (m, 6H, CH_2), 1.97-2.00 (m,

1H, CH), 4.27 (br, 2H, CH_2), 5.33-5.49 (m, 2H, CH_2), 6.97 (s, 1H, ArH), 7.05 (s, 1H, ImH), 7.12 (s, 1H, ImH), 7.44 (s, 1H, ArH), 8.25 (s, 1H, CH=N), 10.88 (s, 1H, ImH), 14.22 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ (ppm) = 13.9, 22.4, 23.1, 24.0, 26.1, 28.8, 28.9, 29.1, 29.6, 30.1, 31.5, 32.4, 34.8, 50.0, 52.8, 118.3, 121.1, 121.7, 129.8, 130.5, 138.8, 165.0, 175.1; HRMS (ESI): *m/z* $[M\text{-}2Cl]^{2+}/2$ calcd. for $C_{52}H_{80}Cl_2N_6O_4$: 410.3166; found 410.3170; IR (KBr) (cm^{-1}): 3421.3, 3133.1, 3060.6, 2954.2, 2927.9, 2857.7, 2398.0, 1727.1, 1660.7, 1629.9, 1560.0, 1443.1, 1363.3, 1272.7, 1211.5, 1159.3, 1029.3, 863.1, 776.1, 730.5, 643.3, 535.7.

1Cb: m.p. 54 - 55 °C, $[\alpha]_{589}^{18}$ = -229° (*c* = 1.0, acetone). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.87 (t, *J* = 6.9 Hz, 3H, CH_3), 1.17-1.35 (m, 27H, CH_2+^{t}Bu), 1.82-1.88 (m, 6H, CH_2), 1.96-2.06 (m, 1H, CH), 4.27 (t, *J* = 7.5 Hz, 2H, CH_2), 5.33-5.53 (m, 2H, CH_2), 6.86 (s, 1H, ArH), 7.03 (s, 1H, ImH), 7.29 (s, 1H, ImH), 7.44 (s, 1H, ArH), 8.27 (s, 1H, CH=N), 10.94 (s, 1H, ImH), 14.21 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ (ppm) = 14.0, 22.6, 24.0, 26.2, 28.9, 29.2, 29.5, 29.6, 30.2, 31.8, 32.9, 34.8, 46.9, 50.1, 52.9, 118.3, 121.0, 122.2, 124.9, 130.7, 138.1, 138.9, 161.4, 168.6, 186.5; HRMS (ESI): *m/z* $[M\text{-}2Cl]^{2+}/2$ calcd. for $C_{60}H_{96}Br_2N_6O_4$: 466.3792; found 466.3785; IR (KBr) (cm^{-1}): 3389.1, 3130.5, 3061.3, 2925.6, 2854.9, 2190.7, 1919.3, 1629.5, 1597.5, 1560.7, 1463.2, 1444.2, 1379.1, 1361.2, 1273.2, 1211.0, 1161.0, 1096.8, 1027.0, 905.5, 863.8, 777.1, 731.8, 643.6, 622.6. (Im = imidazolium)

2.3.3 Synthesis of IL catalysts

General procedure for the synthesis of the imidazole ionic liquid bifunctional metal complex catalysts (Scheme 2): In a round-bottomed flask, $Co(OAc)_2{\cdot}4H_2O$ (1.0 mmol) dissolved in methanol (1.0 mL) was added into an ethanol solution (5.0 mL) of *N*-imidozolium Salen

ligand (**1Aa-1Ca**, **1Ab-1Cb,** 1.0 mmol) under argon. Then, the obtained solution was heated and refluxed for 2 h. After evaporating the solvent, the crude SalenCo(II) complex was gained. The desired catalysts of SalenCo(III)Y were prepared by oxidizing the SalenCo(II) complex dissolved in dichloromethane in the presence of relevant acid (0.1 mmol) under oxygen.

3Aap: m.p. 101 - 102 °C, $[\alpha]_{589}^{18}$ = -229º (c = 1.0, EtOH). MS (ESI): *m/z* [*M*-OAc+K]$^+$ calcd. for $C_{46}H_{65}Br_2CoN_6O_4$: 966.2; found 966.3; Anal. calcd. for $C_{46}H_{65}Br_2CoN_6O_4$: C, 56.10; N, 8.53; H, 6.65. Found C, 56.28; N, 8.64; H, 6.54.

3Bap: m.p. 119 -120 °C, $[\alpha]_{589}^{18}$ = -286º (c = 1.0, EtOH). MS (ESI): *m/z* [*M*-OAc-Br+2Na]$^+$ calcd. for $C_{54}H_{81}Br_2CoN_6O_4$: 1002.5; Found 1002.6; Anal. calcd. for $C_{54}H_{81}Br_2CoN_6O_4$·1/2 hexane·1/2CH_2Cl_2 (%): C, 58.40; N, 7.11; H, 7.59. Found C, 58.53; N, 6.81; H, 8.02.

3Cap: m.p. 115 - 116 °C, $[\alpha]_{589}^{18}$ = -235º (c = 1.0, EtOH). MS (ESI): *m/z* [*M*-OAc-Br+2Na]$^+$ calcd. for $C_{62}H_{97}Br_2CoN_6O_4$: 1114.6; Found 1114.7; Anal. calcd. for $C_{62}H_{97}Br_2CoN_6O_4$·1/2 CH_2Cl_2: C, 59.88; N, 6.70; H, 8.04. Found C, 60.19; N, 6.92; H, 7.69.

3Abp: m.p. 156 - 157 °C, $[\alpha]_{589}^{18}$= -274º (c = 1.0, EtOH). MS (ESI): *m/z* [*M*-OAc+NH_4]$^+$ calcd. for $C_{46}H_{65}Cl_2CoN_6O_4$: 855.4; Found 855.2; Anal. calcd for $C_{46}H_{65}Cl_2CoN_6O_4$·1/3CH_2Cl_2: C, 60.21; N, 9.09; H, 7.16. Found C, 60.07; N, 8.85; H, 7.31.

3Bbp: m.p. 130 - 131 °C, $[\alpha]_{589}^{18}$ = -239º (c = 1.0, EtOH). MS (ESI): *m/z* [*M*]$^+$ calcd. for $C_{54}H_{81}Cl_2CoN_6O_4$: 1008.1; found 1008.2; Anal. calcd. for $C_{54}H_{81}Cl_2CoN_6O_4$·1/2CH_2Cl_2: C, 62.31; N, 8.00; H, 7.87. Found C, 62.16; N, 8.24; H, 7.96.

3Cbp: m.p. 101 - 102 °C, $[\alpha]_{589}^{18}$ = -242º (c = 1.0, EtOH). MS (ESI): *m/z* [*M*-OAc+NH_4]$^+$ calcd. for $C_{54}H_{81}Cl_2CoN_6O_4$: 1079.3; found 1079.4; Anal. calcd for $C_{62}H_{97}Cl_2CoN_6O_4$ 1/4 CH_2Cl_2(%): C, 65.50; N, 7.36; H, 8.61. Found C, 65.74; N, 7.66; H, 8.46.

3Cbq: m.p. 102 - 103 °C, $[\alpha]_{589}^{18}$ = -235º (c = 1.0, EtOH). MS (ESI): *m/z* [*M*-CF_3CO_2+H]$^+$ calcd. for $C_{62}H_{97}Cl_2CoN_6O_4$:1061.6; found 1061.6; Anal. calcd for $C_{62}H_{94}Cl_2CoF_3N_6O_4$·3/2 CH_2Cl_2: C, 58.59; N, 6.46; H, 7.51. Found C, 58.20; N, 6.38; H, 7.12.

3Cbr: m.p. 97 - 98 °C, $[\alpha]_{589}^{18}$ = -245º (c = 1.0, EtOH). MS (ESI): *m/z* [*M*-CCl_3COO+NH_4]$^+$ calcd. for $C_{62}H_{94}Cl_5CoN_6O_4$: 1079.3; found 1079.5; Anal. calcd. for $C_{62}H_{94}Cl_5CoN_6O_4$·hexane: C, 62.35; N, 6.42; H, 8.31. Found C, 62.48; N, 6.60; H, 8.28.

3Cbs: m.p. 101 - 102 °C, $[\alpha]_{589}^{18}$ = -254º (c = 1.0, EtOH). MS (ESI): *m/z* [*M*-2Cl]$^{2+}$/2 calcd. for $C_{67}H_{101}Cl_2CoN_6O_5S$: 580.8; found 580.8; Anal. calcd. for $C_{67}H_{101}Cl_2CoN_6O_5S$·1/2$CH_2Cl_2$: C, 63.59; N, 6.59; H, 8.06. Found C, 63.80; N, 6.50; H, 8.07.

3. **Results and discussion**

Understanding the mechanism of catalytic coupling reaction between epoxide and CO_2 concerning two catalytic sites: Lewis acid and Lewis base, new catalysts should include metal as Lewis acid and halogen anion as nucleophile (Lewis base). Following our own efforts to develop highly efficient catalysts for the asymmetric cycloaddition of carbon dioxide to epoxides, new bifunctional catalysts of imidazole ionic liquid combined a chiral metal-salen complex with a quaternary ammonium salt in one molecule were devised and prepared successfully.

The asymmetric cycloaddition of racemic propylene oxide (PO) and CO_2 catalysed by these chiral bifunctional IL was carefully investigated (Table 1). The results demonstrated that the axial anions (Y^-) had both effects on the catalytic activity and enantioselectivity. The order of catalytic activity toward the axial anions is OAc^-> $CF_3CO_2^-$ > $CCl_3CO_2^-$ > OTs^- and the

order of enantioselectivity is OTs^-> OAc^- >$CCl_3CO_2^-$>$CF_3CO_2^-$ (Table 1, entries 3-6 and 12-15). Taking one with another, the chiral IL bifunctional catalyst with OAc^- as axial anion gave better enantioselectivity and activity than other IL complexes in 47.9% yield and 23.2% ee value at room temperature (Table 1, entry 7). Furthermore, when the reaction temperature was decreased from 25 ^oC to 0 ^oC, the enantioselectivity of PC was increased from 37.1% up to 57.2% ee for catalyst **3Abp** (Table 1, entries 10 *vs* 19). Thus, the temperature was indispensable factor in this kinetic resolution reaction.

To optimize and select the best catalyst system, screening of the coordinated counterions (X^-) of the catalyst system was also proceeded (Table 2). The bifunctional ionic liquid catalysts with various counterion X^- and axial anion (OAc^-) influenced both the catalytic activity and enantioselectivity of the reaction (Table 2, entries 1,4,7 and 2,5,8 and 3,6,9). The order of activity for counterion is Br^->Cl^->F^-; and the order of enantioselectivity is Cl^->Br^->F^-. This can be explained to the dissociation of a halide ion from the imidazolium moiety, which attacks onto the terminal carbon atom of epoxide with more nucleophilic bromide ions based on the understanding of the mechanism (Scheme 1) [25,49,50].

We must point out the more nucleophilicity of counterions of catalyst, the more catalytic activity and enantioselectivity in a certain degree. However, what is the effect of imidazolium cation? In order to answer this question, the investigations were carried out using catalysts with various imidazolium moities (Table 2, Figure 1). The catalytic results revealed that the

alkyl chain length of imidazolium moities can also affect the activity of catalysts for asymmetric coupling reaction of CO_2 and epoxides in spite of their enantioselectivity. The reaction rates are dramatically enhanced almost 4 times when increasing the alkyl chain length from 4 (*n*-butyl) to 12 (*n*-dodecyl) (TOF 5.1 *vs* 19.5 h^{-1}) (Table 2, entries 4-6). This is attributed to the better CO_2 solubility with longer alkyl chain length. Therefore, the best catalyst **3Cbp** was choosen in the next investigations considering all factors.

To further extend the scope of this reaction, various substituted terminal epoxides were investigated using **3Cbp** as catalyst under optimized conditions (Table 3). Epichlorohydrin and 1,2-epoxydodecane were converted to corresponding chiral cyclic carbonates in moderate yield and considerable enantioexcess values (Table 3, entries 2, 3). However, styrene oxide and phenyl glycidyl ether were transformed into their cyclic carbonates in valuable yield and lower enantioselectivies (3 and 2 % ee, respectively).

Considering the mechanism of coupling reaction of epoxide and CO_2 reported in literatures [51-53], a proposed mechanism is illustrated in Scheme 2. The epoxide is firstly activated by a Lewis acidic center of SalenCo(Ⅲ)Y to form a complex **1** that is attacked by a nucleophile X^- to produce a requisite metal alkoxide intermediate **2**. CO_2 inserts into the intermediate **2** leading to an intermediate **3**. After an intramolecular cyclization of **3** releasing a halogen anion to stabilize the imidazolium of the ionic liquid, complex **4** is generated and releases a chiral propylene carbonate when an epoxide approaches to it. The complex **1** is recycled thereof and supplies the next catalytic cycle. According to this mechanism, it insists that both Lewis acidic and Lewis basic center have the same importance in the coupling reaction. Noteworthy, our chiral bifunctional IL catalysts can synchronously provide Lewis acid and

Lewis base that satisfy the asymmetric catalytic cycloaddition of CO_2 to epoxide without additional co-catalyst.

4. Conclusion

In summary, new bifunctional catalysts based on imidazolium ionic liquid were successfully synthesized. The most melting points of these new ionic liquid are around 100 ^oC. A kinetic resolution of racemic epoxides with CO_2 via these new chiral bifunctional ionic liquids yielding chiral cyclic carbonates in reasonable to high yield under very mild reaction conditions were carefully investigated. Furthermore, the effects of axial anion, counterions and the chain length of alkyl group in the imidazolium cations were fully studied and discussed, respectively. The counterion acts as nucleophile and gives deep infection to the activity and selectivity of catalyst. The imidazolium moiety with longer alkyl chain length can dramatically enhance the catalytic activity and the reaction rate except their enantioselectivity.

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Notes and references

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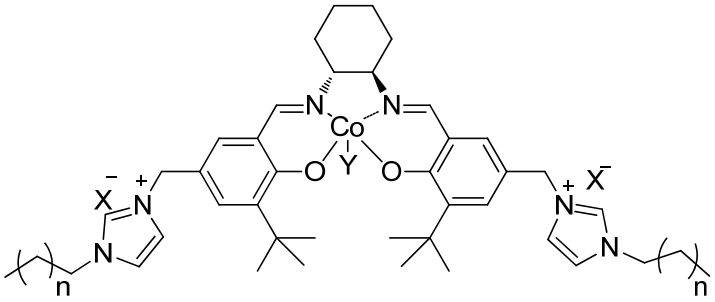
Figure caption



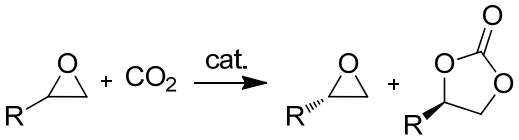
n = 2, **3A**; n = 6, **3B**; n = 10, **3C**

X = Br(**a**); Cl(**b**); Y = OAc(**p**), CF_3COO(**q**), CCl_3COO(**r**), OTs(**s**)

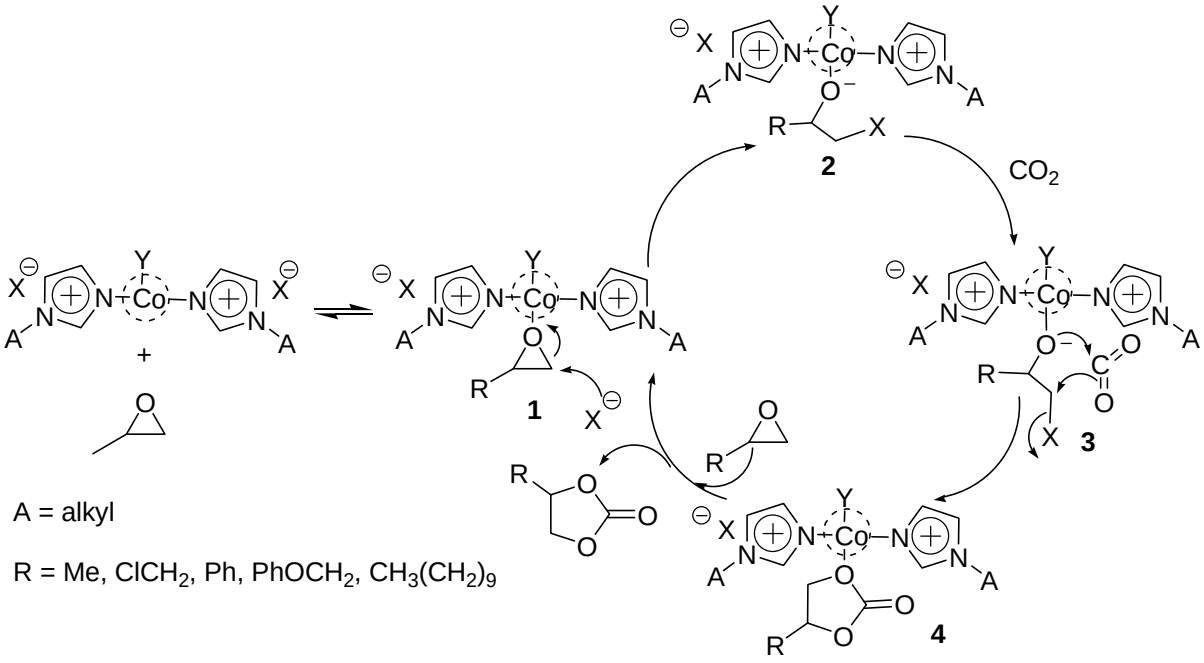
3Aap: X = Br, Y = OAc
3Abp: X = Cl, Y = OAc
3Bap: X = Br, Y = OAc
3Bbp: X = Cl, Y = OAc

3Cap: X = Br, Y = OAc
3Cbp: X = Cl, Y = OAc
3Cbq: X = Cl, Y = CF_3CO_2
3Cbr: X = Cl, Y = CCl_3CO_2
3Cbs: X = Cl, Y = OTs

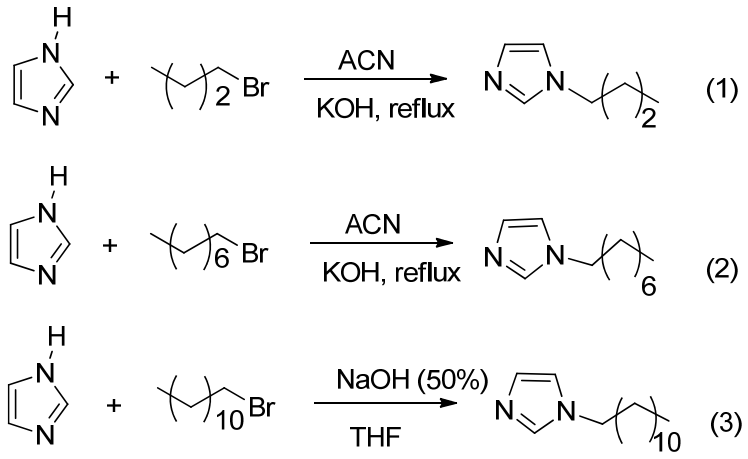
Figure 1. Structures of chiral bifunctional ILs



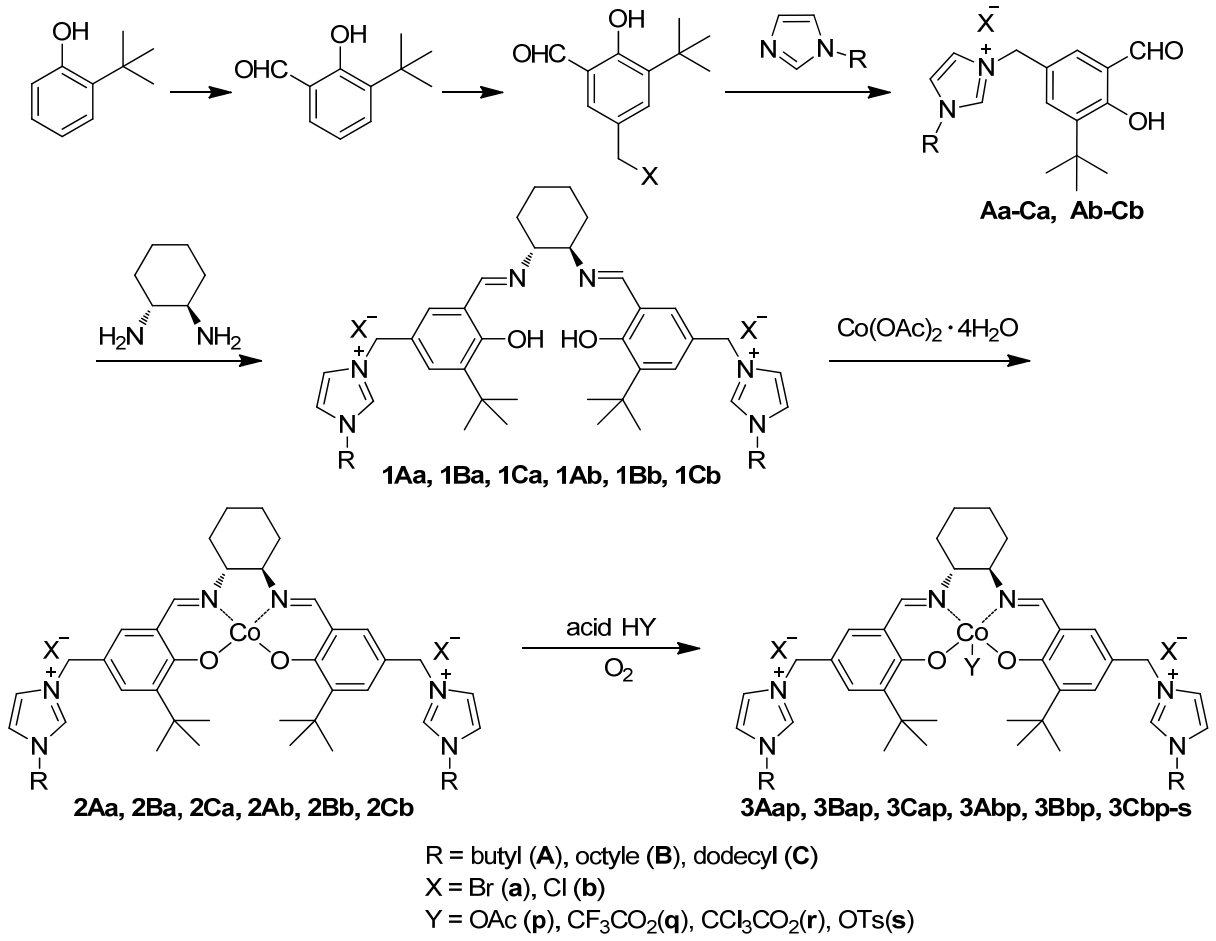
Scheme 1 Kinetic resolution of epoxide by CO_2



Scheme 2**. Proposed mechanism for the coupling of CO_2 and epoxide**



Scheme 3 Synthesis of *N*-alkylimidazoles



Scheme 4. Synthesis of ligands and IL catalysts

Table caption

Table 1 The effect of axial anion on the synthesis of chiral PO [a]

Entry	Catalyst	Axial anion	Time(h)	Yield(%)	ee%	TON[b]	TOF[c]
1	**3Aap**	OAc	10	34.0	19.8	340	34
2	**3Aaq**	CF_3CO_2	10	42.5	12.6	425	42.5
3	**3Bap**	OAc	8	39.1	22.6	391	48.8
4	**3Baq**	CF_3CO_2	7.5	28.1	15.4	281	37.4
5	**3Bar**	CCl_3CO_2	11	34.1	19.4	341	31
6	**3Bas**	OTs	4(d)	29.1	33.1	291	3.0
7	**3Cap**	OAc	7.5	47.9	23.2	479	63.8
8	**3Caq**	CF_3CO_2	23	34.0	13.7	340	14.7
9	**3Car**	CCl_3CO_2	9.5	40.9	14.6	409	43.0
10	**3Abp**	OAc	3(d)	37.3	37.1	373	5.1
11	**3Bbp**	OAc	46	24.0	32.1	240	5.2
12	**3Cbp**	OAc	25	48.9	38.8	489	19.5
13	**3Cbq**	CF_3CO_2	24	38.1	37.7	381	15.8
14	**3Cbr**	CCl_3CO_2	34	39.8	38.6	398	16.5
15	**3Cbs**	OTs	48	41.2	39.9	412	8.5
16[d]	**3Aap**	OAc	62	25.3	35.4	253	4.0
17[d]	**3Baq**	OAc	15	7.2	38.6	72	4.8
18[d]	**3Cap**	OAc	90	37.7	28.2	377	4.1
19[d]	**3Abp**	OAc	9(d)	6.2	57.2	62	0.2

20[d]	**3Bbp**	OAc	6(d)	3.8	43.5	38	0.2
21[d]	**3Cbp**	OAc	5(d)	10.1	50.5	101	0.8

[a] Reaction conditions: PO 100 mmol; P_{CO2} = 1.2 MPa; catalyst 0.1 mmol; T = 25 °C.

[b] Turnover number.

[c] Moles of PC produced by per mole of catalyst per hour.

Table 2 The effect of counterions on the synthesis of chiral PO [a]

Entry	Catalyst	Counterions	Time(h)	Yield(%)	ee%	TON[b]	TOF[c]
1	**3Aap**	Br	10	34.0	19.8	340	34
2	**3Bap**	Br	8	39.1	22.6	391	48.8
3	**3Cap**	Br	7.5	47.9	23.2	479	63.8
4	**3Abp**	Cl	3 (d)	37.3	37.1	373	5.1
5	**3Bbp**	Cl	46	24.0	32.1	240	5.2
6	**3Cbp**	Cl	25	48.9	38.8	489	19.5
7	**3Acp**	F	6(d)	2.4	18.9	24	0.2
8	**3Bcp**	F	2 (d)	49.7	33.8	497	10.3
9	**3Ccp**	F	30.5	38.8	32.2	388	12.7

[a] Reaction conditions: PO 100 mmol; P_{CO2} = 1.2 MPa; catalyst 0.1 mmol; T = 25 °C.

[b] Turnover number.

[c] Moles of PC produced by per mole of catalyst per hour.

Table 3 The effect of counterions on the synthesis of chiral PO [a]

Entry	Catalyst	Substrate (R =)	Time(h)	Yield(%)	ee%	TON[b]	TOF[c]
1	**3Cbp**	CH_3	48.9	25	38.8	489	19.5
2	**3Cbp**	$ClCH_2$	36.1	20.5	29.7	361	17.6
3	**3Cbp**	$CH_3(CH_2)_9$	34.1	22.5	27.8	341	15.1
4	**3Cbp**	Ph	39.1	2(d)	3	391	8.1
5	**3Cbp**	$PhOCH_2$	28.6	1.3(d)	2	286	9.1

[a] Reaction conditions: PO 100 mmol; P_{CO2} = 1.2 MPa; catalyst 0.1 mmol; T = 25 °C.

[b] Turnover number.

[c] Moles of PC produced by per mole of catalyst per hour.