Asymmetric Cycloaddition of CO$_2$ and Epoxide using Recyclable Bi-functional Polymeric Co(III) Salen Complexes under Mild Condition
4.1 Introduction

Due to high abundance, inexpensive, renewable, non-toxic and non-flammable nature, CO$_2$ is ideally placed as starting material for valuable chemicals.$^{1-4}$ However, the thermodynamic stability of CO$_2$ is a singular challenge in employing it as a reagent.$^5$ On the other hand racemic epoxides though available in plenty at affordable costs are highly reactive and amenable to ring opening reactions under even mild reaction conditions.$^6-^8$ Individually, enantiopure epoxides and cyclic carbonates are required in the preparation of valuable pharmaceutically and biologically important compounds.$^9-^{12}$ Classically enantiopure cyclic carbonates are prepared by the cyclization of chiral diols with highly toxic triphosgine or by enzyme mediated hydrolysis of racemic epoxides.$^{13,14}$ Therefore, utilisation of carbon dioxide for kinetic resolution (KR) of racemic epoxides is 100 % atom economical and environment friendly reaction to produce highly valuable enantiopure epoxides and cyclic carbonates in one go (Scheme 4.1).$^{15-22}$ But, unlike path-breaking findings of Jacobsen et al. in asymmetric hydrolytic kinetic resolution of racemic terminal epoxide using chiral Co(III) salen complex,$^{23,24}$ the epoxide ring opening with CO$_2$ requires harsh conditions, such as high CO$_2$ pressure and temperature which in turn adversely affect the enantiomeric purity of the products chiral cyclic carbonates and epoxides. Lu et al. were among the first to report coupling of racemic propene oxide (PO) with CO$_2$ under mild reaction conditions (15 bar, 0 °C), providing a conversion of 40 % with 70 % ee which corresponds to a selectivity factor $s$ of 9.0.$^{25}$ Lu et al. in a subsequent study demonstrated that the addition of CO$_2$ to PO can also be conducted at atmospheric pressure, with the binary system Co(III)-DACH-salen-tosylate /nBu$_4$NCl.$^{26}$ Berkessel and Brandenburg further improved the performance of Co(III) salen-trifluoroacetyl complex by using bis-(triphenylphosphoranylidene)ammonium fluoride as co-catalyst to afford propylene carbonate (PC) in 40 % yield and 83 % ee with selectivity factor of 19 at -40 °C in 120 h.$^{27}$ Chang et al. used bi-functional chiral Co(III) salen complexes as catalyst in the kinetic resolution of PO where the best results (conversion: 22.8 %; ee: 78.5 %; $K_{rel}$: 10.4) were achieved in the absence of a co-catalyst under the CO$_2$ pressure of 6 bar at 0 °C.$^{28}$
Further in this direction, Thomas et al. and Park et al. have made a strategy where carbon nitrides because of high nitrogen contents play dual role of (1) CO$_2$-phillic surface; and (2) as an organocatalyst, for activation of CO$_2$ in the preparation of cyclic carbonates.$^{29,30}$ With this background, in a quest to avoid the use of co-catalyst, near ambient reaction condition and our obsession of making the catalyst recyclable, we have designed a series of triazine-piperazine core based bi-functional chiral polymeric Co(III) salen complexes with in-built Lewis acid-base centres (Figure 4.1) and used them in asymmetric cyclo-addition of CO$_2$ to epoxide in the absence of external co-catalyst at 20 °C to 0 °C. Among these polymeric Co(III) salen catalyst 6e with CCl$_3$COO$^-$ counter ion was found to be most promising although it showed 74 % ee of PC with moderate $K_{rel}$ value of 11.2 which is comparable or better to the most of earlier reports albeit in the absence of a co-catalyst and 10 times catalyst recyclability without any significant loss of reactivity.

Scheme 4.1 Asymmetric cycloaddition of CO$_2$ and racemic epoxioide.
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4.2 Experimental

4.2.1 Methods and Materials

Cobalt acetate was purchased from SD Fine Chemicals India and was used as received. (1R,2R)-(-)-1,2-diaminocyclohexane, cyanuric chloride, 1-Boc piperazine, N,N-Diethylisopropyl amine, quaternary ammonium salts, cinchonine derivatives, counter ion sources and epoxides were purchased from Sigma-Aldrich, Across and Alfa-Aesar and were used without any further purification. All the epoxides i.e. propylene oxide, 1,2-epoxybutane, 1,2-epoxyhexane, epichlorohydrin and phenyl glycidyl ether were distilled from CaH\(_2\). All the solvents were dried prior to use in the reaction. Microanalysis of the intermediates, ligand and catalysts was carried out on a Perkin Elmer 2400 CHNS analyzer. All the melting points reported here were determined on a Mettler Toledo-FB62 and were uncorrected. \(^1\)H & \(^{13}\)C NMR spectra were recorded on Bruker 200 MHz or 500 MHz spectrometer at ambient temperature using TMS as an internal standard. FTIR spectra were recorded on a Perkin Elmer Spectrum GX spectrophotometer as KBr pellet. Optical rotation of the chiral polymeric salen ligand was recorded on an automatic polarimeter (Digipol 78, Rudolph) instrument. High-resolution mass spectra were obtained with a LC-MS (Q-TOFF) LC (Waters), MS (Micromass), MALDI-TOF, Model make Ultra flex TOF/TOF, Burker Daltonics, Germany instruments. For product purification, flash chromatography was performed using silica gel 60-200 mesh purchased from SD Fine-Chemicals Limited, Mumbai (India). The purity of the solvents, epoxides and the analysis of the product, cyclic carbonates were carried out by gas chromatography (GC) on Shimadzu GC 14B instrument with a stainless-steel column (2 m long, 3 mm inner diameter, 4 mm outer diameter) packed with 5 % SE30 (mesh size 60–80) and equipped with an FID detector. Ultrapure nitrogen was used as carrier gas (rate 30 mL/min). Injection port and detector temperature was kept at 200 °C. For analysis of cyclic carbonate products of aliphatic terminal olefins used in the reaction the column temperature was kept at 160 °C isothermal. The ee of aliphatic cyclic carbonates was determined on GC using a chiral capillary column (Chiraldex BTA). For styrene carbonate, the ee was determined on HPLC (Shimadzu SCL-10AVP) by using a Chiralcel OD column.
4.2.2 Synthesis of tri-tert-butyl 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(piperazine-1-carboxylate) (A)

In a 3 neck round-bottom flask cynauric chloride (1.84 g, 10 mmol) and 1-Boc piperazine (5.59 g, 30 mmol) were added together in 50 ml of dry THF and stirred at room temperature for 1 h under nitrogen atmosphere. N,N-Diethylisopropyl amine (17.4 mL, 100 mmol) was added to the reaction mass and the resultant solution was allowed to stir for 1 h at room temperature followed by heating to reflux at 85 °C for 16 h (checked on TLC). After completion of reaction, the reaction mixture was allowed to cool to room temperature and then the solvent was evaporated under reduced pressure. The solid obtained was dissolved in 100 mL of DCM and washed successively with water (3x 100 mL) and brine (2x 100 mL). The organic layer was dried over anhydrous Na₂SO₄. After filtration, the solvent was evaporated under reduced pressure to give light yellow solid which on recrystallization from DCM-hexane gave white crystalline solid A: Yield 94%; Melting Point 240 °C; Elemental analysis found: C 56.92, H 8.16, N 19.85; C₃₀H₅₁N₉O₆ calcd. C 56.85, H 8.11, N 19.89 %; Rₜ (DCM/MeOH 95:5) 0.60; FT-IR (KBr, ν cm⁻¹): 3376, 2978, 2926, 2860, 1697, 1542, 1483, 1421, 1236, 1172, 1115, 1069, 999, 865, 765, 537; ¹H NMR (500 MHz, CDCl₃) δ in ppm: 1.48 (s, 27H), 3.44 (m, 12H), 3.73 (m, 12H); ¹³C NMR (125 MHz, CDCl₃) δ in ppm: 30.3, 44.9, 81.7, 156.7, 167.2 ; MS (HRMS) m/z: 634.4069 [M+H]+.
5 g of white crystalline solid (compound A) obtained in earlier step was taken in 50 mL of MeOH in a RBF. The temperature of the reaction mass was lowered to 0 °C followed by addition of 30 mL of 6 N HCl to it. The resulting solution was allowed to stir at the same temperature for 3 h and then at room temperature for another 12 h. After completion of the reaction (checked on TLC) the volatile organic solvent was removed from the reaction mixture under reduced pressure and 10 % NaOH solution was added to it to make alkaline (pH 14). The milky white solution thus obtained was extracted with DCM (3x 50 mL) and the combined organic layer was dried over anhydrous Na₂SO₄. After filtration evaporation of the organic solvent under reduced pressure led to the desired product as a white solid which was further crystallized out from CHCl₃-hexane to obtain a white crystalline material B: Yield 92 %; Melting Point 224 °C; Elemental analysis found: C 54.08, H 8.12, N 37.88; C₁₃H₂₇N₉ calcd. C 54.03, H 8.16, N 37.81 %; FT-IR (KBr, ν cm⁻¹): 3412, 3299, 2933, 2849, 1536, 1482, 1439, 1366, 1246, 1174, 1056, 1005, 806, 542; ¹H NMR (500 MHz, CDCl₃) δ in ppm: 1.86 (s, 3H), 2.87 (m, 12H), 3.73 (m, 12H); ¹³C NMR (125 MHz, CDCl₃) δ in ppm: 46.2, 47.9, 167.2; HR-MS m/z: 334.2279 [M+H]^+.
White crystalline solid B (2 g, 6 mmol) was taken in 50 mL of dry toluene and a solution of 5-chloromethyl-3-tert-butylsalicylaldehyde (4.2 g, 18.4 mmol in 10 mL of dry toluene) was added to it. The resulting solution was refluxed for 8 h under nitrogen atmosphere. The solid thus precipitated out was filtered and washed successively with toluene and diethyl ether. Afterwards the solid was taken in DCM and neutralized with aqueous NaHCO$_3$ solution. The organic phase was collected, dried over anhydrous Na$_2$SO$_4$ followed by evaporation of the solvent leads to white solid which on recrystallization from a mixture of DCM and hexane gave compound C: Yield 95 %; Melting Point 126 °C; Elemental analysis found: C 67.80, H 7.71, N 13.82; C$_{51}$H$_{69}$N$_9$O$_6$ calcd. C 67.75, H 7.69, N 13.84 %; R$_f$ (DCM/MeOH 95:5) 0.42; FT-IR (KBr, $\nu$ cm$^{-1}$): 3422, 3291, 2952, 2854, 2808, 1653, 1539, 1481, 1438, 1369, 1312, 1252, 1151, 1002, 802, 710; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ in ppm: 1.42 (s, 27H), 2.43 (m, 12H), 3.49 (s, 6H), 3.76 (s, 12H), 7.37 (s, 3H), 7.46 (s, 3H), 9.87 (s, 3H), 11.72 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ in ppm: 29.3, 34.8, 43.1, 53.0, 62.4, 120.4, 128.6, 132.0, 135.2, 138.1, 160.3, 166.3, 197.1; HR-MS m/z: 904.1027 [M+H]$^+$. 

4.2.5 Synthesis of polymeric salen ligand (6’)

A solution of (1R,2R)-(-)-1,2-diaminocyclohexane (366 mg, 3.2 mmol in 10 mL of THF) was added drop wise to another solution of compound C (2 mmol, 1.8 g in 10 mL of THF) and the resulting mixture was allowed to reflux for 2 h (checked on TLC). The resulting dark yellow solution was cooled to room temperature followed by evaporation of solvent under reduced pressure. The yellow solid thus obtained was taken in DCM and washed successively with water and brine. The organic layer was dried over anhydrous Na$_2$SO$_4$ and afterwards evaporation of DCM gave salen ligand
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6’ as yellow solid: Yield 98 %; Elemental analysis found: C 68.26, H 8.12, N 19.39; C₄₅H₆₄N₁₁O₂ calcd. C 68.32, H 8.15, N 19.48 %; [α]D²⁴ = -180 (c=0.5 in THF); FT-IR (KBr, ν cm⁻¹): ν 3403, 2930, 2859, 2805, 1630, 1540, 1480, 1438, 1367, 1308, 1249, 1199, 1154, 1002, 802, 702, 551; ¹H NMR (500 MHz, CDCl₃) δ in ppm: 1.24-1.43 (m, 23H), 1.78-1.88 (m, 9H), 2.27-2.40 (m, 8H), 2.79-2.87 (m, 1H), 3.33-3.73 (m, 13H), 6.83-7.26 (m, 4H), 8.16-8.41 (m, 2H), 13.78-13.90 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ in ppm: 24.3, 24.7, 29.4, 33.1, 33.4, 33.6, 34.7, 43.0, 52.9, 54.7, 62.6, 62.8, 72.5, 118.3, 126.8, 130.3, 130.4, 130.6, 136.8, 159.4, 159.5, 164.3, 165.4, 165.8.

4.2.6 General procedure for synthesis of polymeric Co(III)X salen complex 6a-g

To a solution of polymeric salen ligand 6’ (1 mmol) in toluene (10 mL) heated at 50 °C under N₂ atmosphere was added the Co(OAc)₂·4H₂O (2 mmol) in dry MeOH (10 mL). The resulting reddish colored solution thus obtained was stirred for another 30 min. Then suitable source of counter ion (1.2 mmol) dissolved in dichloromethane was added to the above solution and kept it under air. After 3 h the solvent was evaporated under reduced pressure. The brown colored residue was again dissolved in dichloromethane and filtered through celite pad followed by evaporation to dryness and washed with methanol.

6a: FT-IR (KBr, ν cm⁻¹): 3403, 2930, 2859, 2805, 1630, 1540, 1480, 1438, 1367, 1308, 1249, 1199, 1154, 1002, 802, 702, 551; Elemental analysis found: C 62.09, H 7.28, N 16.92; C₄₇H₆₅N₁₁O₄Co calcd. C 62.24, H 7.22, N 16.99 %.
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6b: FT-IR (KBr, v cm$^{-1}$): 2944, 2864, 1615, 1542, 1436, 1374, 1308, 1255, 1192, 1155, 991, 787, 701, 548; Elemental analysis found: C 61.42, H 6.91, N 15.02, S 3.14; C$_{52}$H$_{69}$N$_{11}$O$_5$SCo calcd. C 61.28, H 6.82, N 15.12, S 3.15 %.

6c: FT-IR (KBr, v cm$^{-1}$): 2942, 2860, 1614, 1542, 1520, 1435, 1378, 1362, 1305, 1254, 1189, 1155, 790, 700, 550; Elemental analysis found: C 61.72, H 6.65, N 16.52; C$_{52}$H$_{66}$N$_{12}$O$_6$Co calcd. C 61.59, H 6.56, N 16.57 %.

6d: FT-IR (KBr, v cm$^{-1}$): 2943, 2865, 1614, 1540, 1441, 1381, 1310, 1256, 1189, 1157, 792, 704, 552; Elemental analysis found: C 58.88, H 6.60, N 15.92; C$_{47}$H$_{62}$N$_{11}$O$_5$F$_3$Co calcd. C 58.74, H 6.50, N 16.03 %.

6e: FT-IR (KBr, v cm$^{-1}$): 2941, 2865, 1616, 1539, 1440, 1377, 1312, 1255, 1191, 1159, 790, 700, 548; Elemental analysis found: C 55.93, H 6.22, N 15.22; C$_{47}$H$_{62}$N$_{11}$O$_4$Cl$_3$Co calcd. C 55.87, H 6.19, N 15.25 %.

6f: FT-IR (KBr, v cm$^{-1}$): 2944, 2868, 1614, 1540, 1443, 1380, 1312, 1258, 1190, 1158, 791, 6990, 550; Elemental analysis found: C 57.93, H 6.77, N 16.42; C$_{45}$H$_{62}$N$_{11}$O$_5$F$_4$BCo calcd. C 57.82, H 6.69, N 16.48 %.

6g: FT-IR (KBr, v cm$^{-1}$): 2943, 2872, 1616, 1541, 1442, 1381, 1310, 1256, 1192, 1156, 788, 703, 548; Elemental analysis found: C 54.61, H 6.42, N 15.35; C$_{45}$H$_{62}$N$_{11}$O$_2$F$_6$PCo calcd. C 54.43, H 6.29, N 15.52 %.

4.2.7 General Procedure for synthesis of chiral cyclic carbonates

A solution of freshly prepared bifunctional Co(III) polymeric salen complex 6a-g (0.1 mmol w.r.t monomeric unit) in epoxide (100 mmol) was taken in an reaction vial which was purged three times with carbon dioxide. CO$_2$ was introduced into the reaction vial at atmospheric pressure and the reaction mixture was allowed to stir at desired temperature. After completion of the reaction the reaction vial was vented and the catalyst was separated from the reaction mixture by precipitating out in methanol. The product carbonates were distilled under reduced pressure or recrystallized from ethanol. The catalyst which was precipitated out earlier was washed several times with methanol, dried overnight in a desiccator and used as such for next cycle.
4.2.8 Characterization data of the products

Colorless liquid; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ in ppm: 1.48-1.51 (d, 3H, $J = 6$Hz), 4.01-4.09 (t, 1H, $J = 8$Hz), 4.55-4.63 (t, 1H, $J = 8$Hz), 4.81-4.98 (m, 1H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ in ppm: 19.2, 70.7, 73.7, 155.2; The enantiomeric excess was determined by GC with Astec CHIRALDEX BTA column, 160 °C isothermal $t_R = 9.2$ min (minor), $t_R = 9.9$ min (major).

Colorless liquid; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ in ppm: 1.00-1.07 (t, 3H, $J = 6$Hz), 1.75-1.84 (m, 2H), 4.06-4.14 (t, 1H, $J = 8$Hz), 4.51-4.59 (t, 1H, $J = 8$Hz), 4.63-4.76 (m, 1H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ in ppm: 8.4, 26.9, 69.0, 78.0, 155.2; The enantiomeric excess was determined by GC with Astec CHIRALDEX BTA column, 160 °C isothermal $t_R = 10.3$ min (major); $t_R = 11.2$ min (minor).

Colorless liquid; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ in ppm: 0.89-0.96 (t, 3H, $J = 6$Hz), 1.37-1.42 (m, 4H), 1.68-1.83 (m, 2H), 4.04-4.12 (t, 1H, $J = 8$Hz), 4.51-4.59 (t, 1H, $J = 8$Hz), 4.66-4.76 (m, 1H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ in ppm: 13.8, 22.2, 26.4, 33.5, 69.4, 77.1, 155.2; The enantiomeric excess was determined by GC with Astec CHIRALDEX BTA column, 160 °C isothermal $t_R = 10.5$ min (minor), $t_R = 10.9$ min (major).

Colorless liquid; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ in ppm: 3.71-3.91 (qd, 2H, $J = 12$Hz, 4Hz), 4.37-4.45 (t, 1H, $J = 8$Hz), 4.58-4.66 (t, 1H, $J = 8$Hz), 4.99-5.10 (m, 1H); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ in ppm: 44.2, 67.0, 74.5, 154.6; The enantiomeric excess was determined by GC with Astec CHIRALDEX BTA column, 160 °C isothermal $t_R = 14.1$ min (minor), $t_R = 14.8$ min (major).
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Colorless Solid; ¹H NMR (200 MHz, CDCl₃) δ in ppm: 4.29-4.37 (t, 1H, J = 8Hz), 4.76-4.84 (t, 1H, J = 8Hz), 5.63-5.71 (t, 1H, J = 8Hz), 7.38-7.44 (m, 5H); ¹³C NMR (50 MHz, CDCl₃) δ in ppm: 71.2, 125.9, 129.2, 129.7, 135.8, 154.9; The enantiomeric excess was determined by Chiralcel OD column, flowrate 1.0 ml/min, Hexane:IPA 90:10, tᵣ = 14.45 min (minor), tᵣ = 16.52 min (major).

4.3. Results and Discussion

As we have stated above that the prior art in the asymmetric cycloaddition of epoxide with CO₂, requires a chiral Co(III)-salen complex as a catalyst and a base for the efficiency of this catalytic system. This motivated us for synthesizing the present ligand system where salen moiety was integrated with a triazine-piperazine core (Scheme 4.2). Accordingly, in the first step N-Boc-piperazine was condensed with 2,4,6-trichloro-1,3,5-triazine (cynauric chloride) using THF as a solvent under refluxing condition where all the chlorines of cynauric chloride were substituted with secondary amine group of N-Boc-piperazine. In the subsequent step tert-butyl carbamate (Boc) group from the compound A, was removed by its treatment with hydrochloric acid (6 N) in methanol to get compound B, which on condensation with 5-chloromethyl-3-tert-butyalsalicylaldehyde provided trialdehyde C. The desired polymeric salen ligand 6' was obtained by the condensation of the trialdehyde C with (1R,2R)-(−)-1,2-diamino cyclohexane. The average molecular weight (Mn) of the polymeric salen ligand 6' was found to be 6727, which correspond to eight salen units (n=8) with 1.2 polymer distribution index (PDI) showing good homogeneity of the polymer.
The $^1$H NMR of the ligand 6’ gave multiple azomethine (3 major signals at $\delta$ value of 8.16-8.41) which is not unusual for cross-linked nature of a polymer synthesized by the condensation of trialdehyde with diamine. The absence of any resonance originating from aldehyde group ($\delta = 9.87$ at $^1$H NMR and $\delta = 197.1$ at $^{13}$C NMR) confirms that the residual aldehyde C used in the synthesis is not present in polymer salen ligand 6’. Further absence of any free $-\text{NH}_2$ in the polymer was established by D$_2$O exchange-$^1$H NMR which doesn’t show disappearance of any peak (Figure 4.2).

Scheme 4.2 Schematic representation for synthesis of catalyst 6a-g.
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Figure 4.2 D₂O exchange- ¹H NMR of compound 6'.

Metalation of the ligand 6' with Co(OAc)₂·4H₂O under inert atmosphere in methanol gave polymeric Co(II)-salen complex which was found to be extremely air sensitive, hence the isolation of Co(II)-salen complex was circumvented and a counter ion chosen from a-g (Figure 4.3) was added to the above solution while the reaction mixture exposed to air.

Figure 4.3 Additive tested for asymmetric cycloaddition of CO₂ to propylene oxide using catalyst 6e.
A brown coloured chiral Co(III)-polymeric salen complexes 6a-g thus obtained were used as catalyst in the KR of racemic epoxides. It is known in the literature that different counter ions impart different activity and enantioselectivity on the KR of racemic epoxides. That was precisely the reason for preparing the complexes 6a-g, and use them as catalysts in KR of racemic epoxides by taking propylene oxide as a test substrate with CO$_2$ at 20 °C (Table 4.1). It is obvious from these results that the cobalt complexes where the counter ions capable of acting as an axial ligand (Table 4.1, entries 1-5) to the metal centre are significantly more active and enantioselective than those having ionic interactions (Table 4.1, entries 6-7). Among these the catalyst 6e (0.1 mol %) with bulkier CCl$_3$COO axial ligand/counter ion gave relatively better performance (Table 4.1, entry 5) with a $K_{rel}$ value of 9.4. Hence, 6e was taken forward for further optimization of the reaction parameters in the KR of propylene oxide. At first we altered the catalyst loading by keeping other reaction parameters constant. On increasing the catalyst loading from 0.1 mol % to 0.2 mol % (Table 4.1, entry 8) there was no observable change in the catalyst performance, however, decreasing the catalyst loading to 0.05 mol % caused slight decrease in both activity and enantioselectivity (Table 4.1, entry 9).

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<th>Counter-ion</th>
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<th>ee (%)</th>
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<th>Entry</th>
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<td>6e CCl$_3$COO (e)</td>
<td>TBAB 6</td>
<td>43.0</td>
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<td>6.3</td>
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<td>6e CCl$_3$COO (e)</td>
<td>TBAI 6</td>
<td>45.2</td>
<td>55.7</td>
<td>5.4</td>
<td>20.93</td>
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<td>6e CCl$_3$COO (e)</td>
<td>Chiral Imine 16</td>
<td>35.9</td>
<td>65.1</td>
<td>6.7</td>
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<td>15$^f$</td>
<td>6e CCl$_3$COO (e)</td>
<td>Chiral Imine 16</td>
<td>35.7</td>
<td>54.5</td>
<td>4.5</td>
<td>6.20</td>
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<td>6e CCl$_3$COO (e)</td>
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<td>58.4</td>
<td>5.4</td>
<td>8.84</td>
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<td>17$^f$</td>
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<td>Cinchonine-bromide Salt 12</td>
<td>38.0</td>
<td>55.8</td>
<td>4.9</td>
<td>8.80</td>
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<tr>
<td>18$^g$</td>
<td>6e CCl$_3$COO (e)</td>
<td>-</td>
<td>48</td>
<td>40.3</td>
<td>74.0$^h$</td>
<td>11.2</td>
<td>2.33</td>
</tr>
</tbody>
</table>

$^a$Reaction Conditions: PO(100 mmol), Catalyst (0.1 mmol, w.r.t monomeric unit), 1 atm of CO$_2$ pressure, temperature 20°C, Co-Catalyst (0.2 mmol) if used.

$^b$$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 (PC).

$^c$Turn over frequency is calculated by the expression [product]/[catalyst] x time (s$^{-1}$).

$^d$Catalyst Loading 0.2 mmol, $^e$Catalyst Loading 0.05 mmol.

$^f$Catalyst with opposite absolute configuration was used.

$^g$Reaction temperature 0°C.

$^h$ee of unreacted epoxide was determined to be 70%.

Although the triazine-piperazine functionalities present in the catalyst was found to be good enough to provide the Lewis basicity required for the reaction, we still examined whether there is any added benefit of an external Lewis base as reported by He and co-workers in the case of Co(III)salen based bifunctional catalysts$^{33}$ (Table 4.1, entries 10-17). It has been observed that addition of an external cationic Lewis base though increased the TOF of the reaction significantly.
but there was a drop in enantioselectivity, possibly due to the background reaction which progress via racemic pathway. Having established incompetence of these additives in improving the enantioselectivity of cyclic carbonates, we decided to use binary Co(III)CCl$_3$COO salen complex 6e alone for further study of the asymmetric cycloaddition reaction of epoxide and CO$_2$ without using any external additive.

On varying the reaction temperature it has been found that best $K_{rel}$ value was obtained at 273 K for the synthesis of optically active propylene carbonate (Table 4.1, entry 18). Noticeably, the ee of the product remain steady throughout the reaction and no racemization of the product was observed with time (Figure 4.4). Further lowering of the temperature made the reaction too sluggish with no benefit of improved ee of the product.

To extend the scope of the reaction we have employed our best catalyst 6e for the asymmetric cycloaddition reaction of various terminal epoxides and got 48, 53 and 71 % ee respectively with 1,2-epoxy butane, epichlorohydrin and 1,2-epoxy hexane (Table 4.2).

However, the results were not very encouraging with styrene oxide (ee, 13 %). The catalyst 6e demonstrated excellent stability under reaction condition used for
the KR of PO with CO\textsubscript{2} and was recycled 10 times with no sign of diminished catalyst performance (Figure 4.5).

**Table 4.2** Asymmetric cycloaddition of terminal epoxides with CO\textsubscript{2} in the presence of 6e\textsuperscript{a}.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>ee (%)\textsuperscript{b}</th>
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<tbody>
<tr>
<td>1</td>
<td>n-Et</td>
<td>48</td>
<td>44</td>
<td>48</td>
</tr>
<tr>
<td>2</td>
<td>ClCH\textsubscript{2}</td>
<td>48</td>
<td>40</td>
<td>53</td>
</tr>
<tr>
<td>3</td>
<td>n-Bu</td>
<td>48</td>
<td>35</td>
<td>71</td>
</tr>
<tr>
<td>4</td>
<td>Ph</td>
<td>48</td>
<td>37</td>
<td>13\textsuperscript{b}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction Conditions: Epoxide (100 mmol), Catalyst (0.1 mmol), 1 atm of CO\textsubscript{2} pressure, Temperature 20 °C.

\textsuperscript{b}The ee value was determined by HPLC. (Daicel chiral OD column, n-Hexane/2-propanol (9:1 v/v), 1.0 ml/min, 220 nm).

**Figure 4.5** Recycling results using the catalyst 6e. Reaction conditions: PO (100 mmol), catalyst (0.1 mmol), 0 °C, 1 atm CO\textsubscript{2} pressure.

We also checked the efficacy of catalyst 6a in the hydrolytic kinetic resolution of racemic epichlorohydrin as representative substrate. In this case as well we got
(S)-epichlorohydrin in 49.2 % yield (out of maximum 50 % theoretical yield) and >99 % enantiomeric excess (Figure 4.6).

**Figure 4.6** The catalytic activity of catalyst 6a in HKR of racemic epichlorohydrin at Reaction Conditions: Epichlorohydrin (100 mmol), water (55 mmol), Catalyst (0.01 mmol).

### 4.4 Conclusion

In summary, we have designed and synthesized a series of recyclable bifunctional polymeric Co(III) salen complexes based on a triazine-piperazine core and utilized them in asymmetric cycloaddition of various terminal epoxide with CO\(_2\) at atmospheric pressure and at lower temperature (20 °C to 0 °C). The best catalyst Co(III)CCl\(_3\)COO gave optically active propylene carbonate with up to 74 % ee under mild condition without the use of any external Lewis base as an additive. Although, the catalyst performance in the present report was at par with previously reported catalysts, efficient catalyst recyclability (10 cycles) without any loss in activity or enantioselectivity is most striking feature of the present catalyst design. The present catalyst framework with some modifications in catalyst core reaction site is expected to enhance the ee of cyclic carbonates to the desired level for their commercial applications.
Chapter 4  
Asymmetric Cycloaddition of CO\textsubscript{2} and Epoxide....

4.5 References


