SUPPLEMENTARY INFORMATION

The Bigger, the Better: Ring-size Effects of Macrocyclic Oligomeric Co(III)-salen Catalysts

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General

Cyclooct-4-en-1-yl salen ligand monomer and the original mixture of macrocyclic salen ligands were synthesized following our previous report.[1] All reagents were obtained from commercial suppliers and, unless specified below, used without further purification. Dichloromethane was dried by passing through columns of activated copper and alumina successively. Chlorobenzene was distilled under argon prior to use. Flash column chromatography was performed using silica gel 60 Å (230-400 mesh) from Sorbent Technologies. Size-exclusive chromatography was performed using Toyopearl HW-40 SEC resin purchased from Sigma-Aldrich. ^{1}H NMR spectra were recorded at 25 °C on a Bruker AC 400 (400 MHz) spectrometer. ^{13}C NMR spectra were obtained at 100.0 MHz on a Bruker AC 400 spectrometer. All chemical shifts are reported in parts per million (ppm) with reference to solvent residual peaks. MALDI-TOF mass spectra were recorded on a Bruker OmniFLEX Maldi-TOF spectrometer using dithranol as the matrix. Gel-permeation chromatography (GPC) analyses were performed on a Shimadzu LC-10AD pump coupled to a UV detector. American Polymer Standards columns were used with THF as the mobile phase (flow rate at 1.0 mL/min) and poly(styrene)s were employed as standards for calibration. The chiral GC analyses were carried on a Shimadzu GC 14-A instrument equipped with an FID detector. Either a Chiraldex γ-TA column (Advanced Separation Technologies, Inc.) or a β-Dex 120 column (Supelco) was used with helium as the carrier gas. The chiral HPLC analyses were performed on a Shimadzu-10A

system. A Chiracel OD column (Chiral Technologies, Inc.) and HPLC grade n-hexane and isopropanol (flow rate at 1 mL/min) were used. Elemental analyses were performed by Quantitative Technologies Inc.

Macrocyclic oligomeric salen ligand separation based on ring size

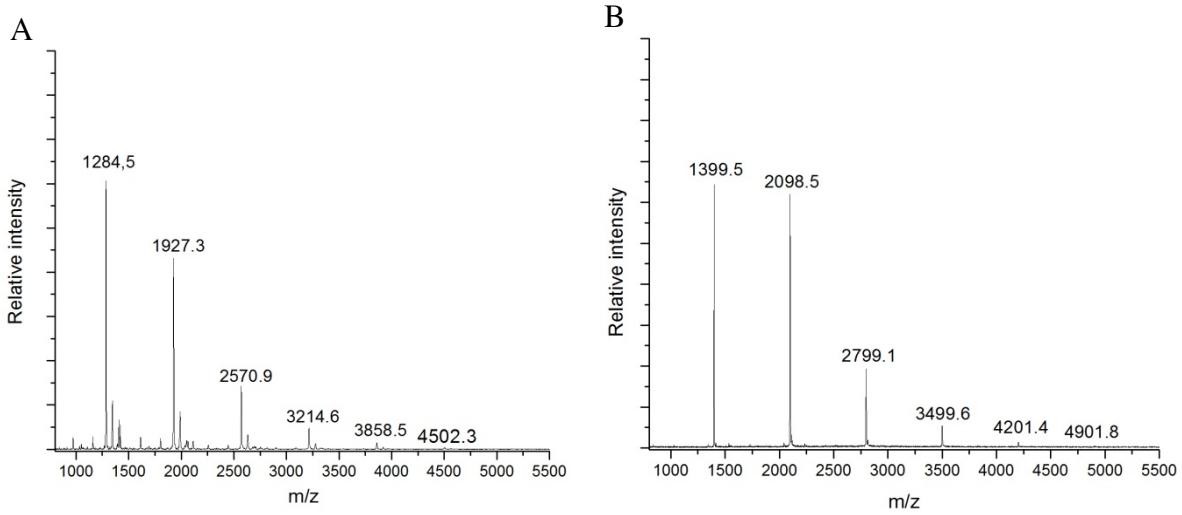


Figure S1. MALDI-TOF mass spectra of the original macrocyclic oligomer mixture; (A) non-metalated, and (B) metalated cyclic oligomers.

The crude salen oligomers were subjected to flash column chromatography with 60 Å silica gel. The elution solvent was a hexane/ethyl acetate mixture containing 0.2 % triethyl amine with a solvent gradient changing from 100/0 to 100/5 hexanes to ethyl acetate ratios. Individual fractions were analyzed with MALDI-TOF mass spectrometry. Pure dimeric ligand was obtained from the first fractions. The following fractions contain mixtures enriched with different range of ring-size oligomers. Fractions were combined resulting in four to six final fractions containing mixtures of different ring-size oligomers. After removal of the solvents, the residual solids of each fraction were re-dissolved in $CHCl_3$/methanol (1:1) and further purified by SEC column chromatography. The SEC column had a 2 cm inside diameter and was 500 cm long and filled with Toyopearl HW-40 resin. The commercial resin was stored in ethanol and it was necessary to fully exchange the solvent to $CHCl_3$/methanol. A 1:1 mixture of $CHCl_3$/methanol was used as the elution solvent. The collected fractions were analyzed with MALDI-TOF mass spectrometry. Pure trimers and higher mass mixtures (tetramer to hexamer and pentamer to decamer) were obtained. To obtain pure tetramers, three to four further SEC purification steps were necessary. In the end, the following oligomers were obtained (yields compared to the starting mixture are in parentheses): dimer (25%), trimer (16%), tetramer (2%), tetramer-hexamer (7%) and pentamer-decamer (3%).

Salen ligand dimer (n = 2): ^{1}H NMR (400 MH$_Z$, CDCl$_3$) δ (ppm) 13.87 (m, 1H, O*H*), 13.64 (br, 13.60 side peak, 1H, O*H*), 8.32 (m, 1H, N=C*H*), 8.26 (m, 8.12 side peak, 1H, N=C*H*), 7.35 (d, *J* = 1.4 Hz, 1H, Ar-*H*), 7.01 (d, *J* = 1.2 Hz, 1H, Ar-*H*), 6.91 (m, 1H, Ar-*H*), 6.77 (m, 6.67 side peak, 1H, Ar-*H*), 5.48 (m, br, 2H, C*H*=C*H*), 3.32 (m, br, 2H, 2 NC*H*CH$_2$), 2.49-2.94 (m, br, 1H, C*H*CO), 2.33-1.35 (m, 18H), 1.42 (s, 9H, C(C*H*$_3$)$_3$), 1.40 (s, 9H, C(C*H*$_3$)$_3$), 1.24 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 174.9-175.3 (m, 1C, *C*O$_2$, multiple chemical environments), 165.9, 164.5, 158.1, 158.0, 141.5, 140.0, 138.3, 136.2, 129.1-132.1 (m, 2C, *C*H=*C*H, multiple chemical environments),126.9, 126.0,122.5, 121.2, 118.1, 117.7,72.5, 72.3, 41.2-44.1 (m, 1C, *C*HCO$_2$, multiple chemical environments), 35.0, 34.9, 34.0, 33.1 (br, overlapping signals), 31.4 (overlapping signals), 29.5 (overlapping signals), 29.2 (overlapping signals), 29.1, 24.3 (br, overlapping signals); MALDI-TOF MS (*m/z*) calcd. for $C_{82}H_{116}N_4O_8$, 1285.8, found, 1286.5 (M+H); GPC: M_n = 1650, M_w = 1774, PDI = 1.06. Anal. Calcd for $(C_{41}H_{58}N_2O_4)_2$: C, 76.60; H, 9.09; N, 4.36. Found: C, 76.83; H, 9.28; N, 4.21.

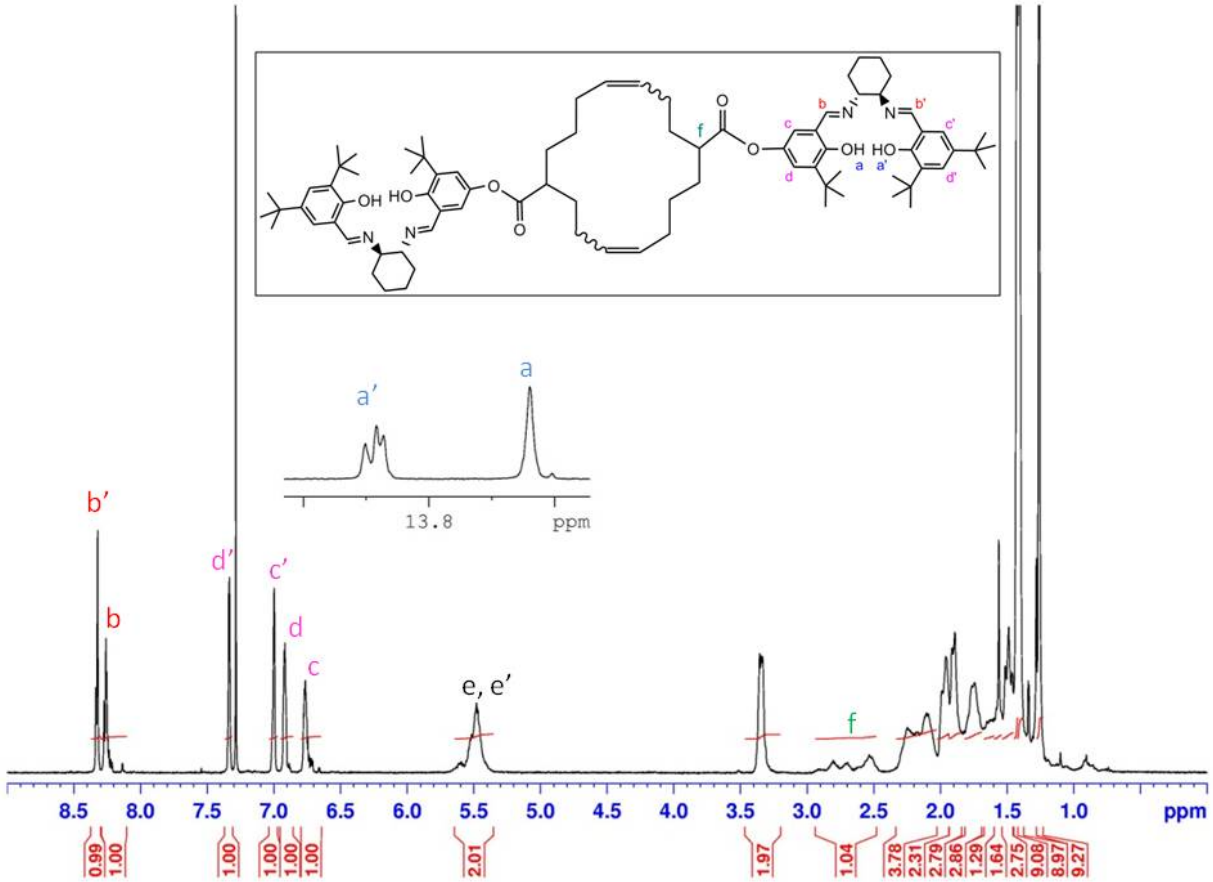


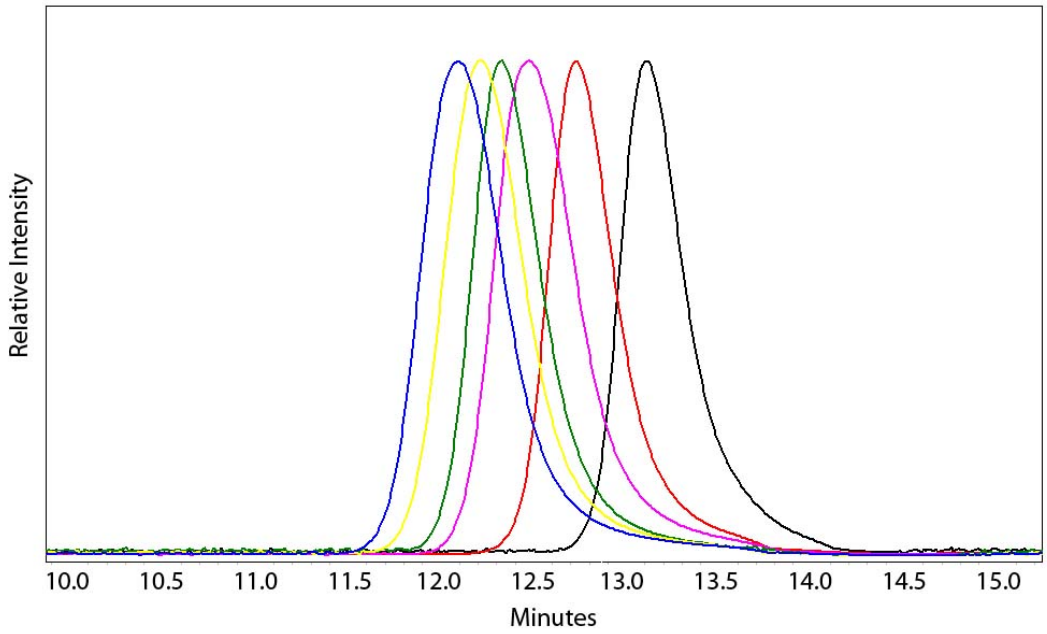
Figure S2. ^{1}H NMR spectrum (400 MH$_Z$, CDCl$_3$, room temperature) of the dimer ligand.
Although proton signals a', b', b, c and f are highly split, careful integration shows that all split peaks (the side peaks were integrated together with the main signals) integrate as one proton.

Salen ligand trimer (n = 3): ^{1}H NMR (400 MH_Z, $CDCl_3$) δ (ppm) 13.89 (s, br, 1H, O*H*), 13.62 (s, br, 1H, O*H*), 8.32 (s, 1H, N=C*H*), 8.25 (s, 1H, N=C*H*), 7.33 (d, *J* = 1.3 Hz, 1H, Ar-*H*), 7.00 (d, *J* = 1.2 Hz, 1H, Ar-*H*), 6.90 (s, 1H, Ar-*H*), 6.76 (s, 1H, Ar-*H*), 5.40 (m, br, 2H, C*H*=C*H*), 3.31 (m, br, 2H, 2 NC*H*CH_2), 2.58 (s, br, 1H, C*H*CO), 2.38-1.38 (m, 18H), 1.41 (s, 9H, C(CH_3)$_3$), 1.39 (s, 9H, C(CH_3)$_3$), 1.24 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.1, 165.9, 164.7, 158.1, 158.0, 141.6, 140.0, 138.5, 136.4, 129.7-131.3 (m, 2C, *C*H=*C*H, multiple chemical environments),126.9, 126.0,122.7, 121.3, 118.2, 117.8,72.5, 72.2, 42.2(m, br), 35.0, 34.9, 34.0, 33.2, 33.1, 31.4 (overlapping signals), 29.5 (overlapping signals), 29.2 (overlapping signals), 24.3 (br, overlapping signals); MALDI-TOF MS calcd. for $C_{123}H_{174}N_6O_{12}$ (*m/z*), 1928.7, found, 1928.3 (M+H); GPC: M_n = 2164, M_w = 2397, PDI = 1.08. Anal. Calcd for $(C_{41}H_{58}N_2O_4)_3$: C, 76.60; H, 9.09; N, 4.36. Found: C, 76.48; H, 9.47; N, 4.18.

Salen ligand tetramer (n = 4, contaminated with trimer and pentamer combined ca. 5%): ^{1}H NMR and ^{13}C NMR spectra are equivalent to those of the trimer ligand. MALDI-TOF MS (*m/z*) calcd. for $C_{164}H_{232}N_8O_{16}$, 2571.6, found, 2571.9 (M+H); GPC: M_n = 2604, M_w = 2786, PDI = 1.11. Anal. Calcd for $(C_{41}H_{58}N_2O_4)_4$: C, 76.60; H, 9.09; N, 4.36. Found: C, 76.66; H, 9.42; N, 4.24.

Salen ligands tetramer-hexamer (n = 4 - 6): ^{1}H NMR and ^{13}C NMR are equivalent to those of the trimer ligand. MALDI-TOF MS (*m/z*) calcd. for $C_{164}H_{232}N_8O_{16}$ (n = 4), 2571.6, found, 2572.1 (M+H, 98%); calcd. for $C_{205}H_{290}N_{10}O_{20}$ (n = 5), 3214.6, found 3214.1 (M+H, 100%); calcd. for $C_{246}H_{348}N_{12}O_{24}$ (n = 6), 3857.5, found 3856.8 (M+H, 27%); GPC: M_n = 2978, M_w = 3309, PDI = 1.11. Anal. Calcd for $(C_{41}H_{58}N_2O_4)_{4\sim6}$: C, 76.60; H, 9.09; N, 4.36. Found: C, 76.62; H, 8.94; N, 4.39.

Salen ligands pentamer-decamer (n = 5 - 10): ^{1}H NMR and ^{13}C NMR are equivalent to those of the trimer ligand. MALDI-TOF MS (*m/z*) calcd. for $C_{205}H_{290}N_{10}O_{20}$ (n = 5), 3214.6, found 3215.5 (M+H, 58%); calcd. for $C_{246}H_{348}N_{12}O_{24}$ (n = 6), 3857.5, found 3856.6 (M+H, 100%); calcd. for $C_{287}H_{406}N_{14}O_{28}$ (n = 7), 4500.4, found 4497.9 (M+H, 83%); calcd. for $C_{328}H_{464}N_{16}O_{32}$ (n = 8), 5143.3, found 5138.4 (M+H, 39%); calcd. for $C_{369}H_{522}N_{18}O_{36}$ (n = 9), 5786.2, found 5777.8 (M+H, 12%); calcd. for $C_{410}H_{580}N_{20}O_{40}$ (n = 10), 6429.1, found 6420.0 (M+H, 3%); GPC: M_n = 3342, M_w = 3759, PDI = 1.12. Anal. Calcd for $(C_{41}H_{58}N_2O_4)_2$: C, 76.60; H, 9.09; N, 4.36. Found: C, 76.50; H, 9.19; N, 4.21.



ck: monomer ligand; red: dimer ligand; magenta: trimer ligand; green: tetramer ligand; yellow: tetramer-hexamer ligands; blue: pentamer-decamer ligands.

Table S4. Characterization of monomer and macrocyclic salen oligomers by GPC.

Macrocyclic Salen Oligomer	*Calculated Molecular Weight*	M_n	M_w	*PDI*
Monomer	642.4	1100	1200	1.06
Dimer	1285.8	1700	1800	1.08
Trimer	1928.7	2200	2400	1.11
Tetramer	2571.6	2600	2800	1.07
Tetramer-Hexamer	2571.6, 3214.6, 3857.5	3000	3300	1.11
Pentamer-Decamer	3214.6, 3857.5, 4500.4, 5143.3, 5786.2, 6428.1	3300	3800	1.12

General procedure for the metalation of the macrocyclic oligomeric salen ligand

The metalation was carried out in a glove box. The salen oligomer of interest (1 equiv.) was dissolved in degassed dichloromethane (40 mM) in a reaction vial equipped with a micro stirbar. A cobalt(II) acetate

tetrahydrate methanol solution (1.5 equiv. 60 mM) was added to the salen solution. The mixture turned red immediately and some dark red precipitate formed gradually. After the reaction mixture was stirred at room temperature overnight, most of the dichloromethane was removed by vacuum. A small amount of methanol was added. The reaction vial was shaken by a vortex followed by centrifugation for 2 minutes. The supernate was decanted. This procedure was repeated two more times. The final product was dried under high vacuum overnight to afford a brick red solid.

Co(II)-salen complex dimer (n = 2): MALDI-TOF MS (*m/z*) calcd. for $C_{82}H_{112}N_4O_8Co_2$, 1399.7, found, 1399.5 (M+H); ICP-MS calcd. for Co (%) 8.42, found 7.38 (87.6% Co loading).

Co(II)-salen complex trimer (n = 3): MALDI-TOF MS (*m/z*) calcd. for $C_{123}H_{168}N_6O_{12}Co_3$, 2099.5, found, 2100.1 (M+H); ICP-MS calcd. for Co (%) 8.42, found 7.78 (92.4% Co loading).

Co(II)-salen complex tetramer (n = 4): MALDI-TOF MS (*m/z*) calcd. for $C_{164}H_{224}N_8O_{16}Co_4$, 2799.3, found, 2799.7 (M+H); ICP-MS calcd. for Co (%) 8.42, found 8.03 (95.4% Co loading).

Co(II)-salen complex tetramer-hexamer (n = 4 - 6): MALDI-TOF MS (*m/z*) calcd. for $C_{164}H_{224}N_8O_{16}Co_4$ (n = 4), 2799.3, found, 2799.1 (M+H, 100%); calcd. for $C_{205}H_{280}N_{10}O_{20}Co_5$ (n = 5), 3499.1, found, 3500.6 (M+H, 85%); calcd. for $C_{246}H_{336}N_{12}O_{24}Co_6$ (n = 6), 4199.0, found, 4198.9 (M+H, 21%); ICP-MS calcd. for Co (%) 8.42, found 7.84 (93.1% Co loading).

Co(II)-salen complex tetramer-hexamer (n = 5 - 10): MALDI-TOF MS (*m/z*) calcd. for $C_{205}H_{280}N_{10}O_{20}Co_5$ (n = 5), 3499.1, found, 3501.9 (M+H, 45%); calcd. for $C_{246}H_{336}N_{12}O_{24}Co_6$ (n = 6), 4199.0, found, 4201.7 (M+H, 100%); calcd. for $C_{287}H_{392}N_{14}O_{28}Co_6$ (n = 7), 4898.8, found, 4901.3 (M+H, 87%); calcd. for $C_{328}H_{448}N_{16}O_{32}Co_8$ (n = 8), 5598.6, found, 5601.3 (M+H, 51%); calcd. for $C_{369}H_{504}N_{18}O_{36}Co_9$ (n = 9), 6298.5, found, 6299.8 (M+H, 18%); calcd. for $C_{410}H_{560}N_{20}O_{40}Co_{10}$ (n = 10), 6988.3, found, 6999.0 (M+H, 5%); ICP-MS calcd. for Co (%) 8.42, found 7.62 (90.5% Co loading).

General procedures for Hydrolytic Kinetic Resolution (HKR)

The Co(II)-salen oligomers of interest (0.005 mmol based on cobalt) were dissolved in dichloromethane (1 mL) in a 20 mL reaction vial. Glacial acetic acid (10 μL) was added to the solution and the mixture was stirred in the open air for 40 min during which time the color changed from red to dark brown. The solvent and the excess acetic acid were removed by rotary evaporation. Residual solvent was further removed azeotropically with toluene (2×100 μL) and the remaining solid was dried overnight under high vacuum. The racemic epoxide of interest (2 ~ 50 mmol depending on catalyst ratios) was added to the activated catalyst followed by chlorobenzene (about 500 μL) as an internal standard. The reaction vial

was immersed into a water bath at 25˚C and an aliquot of the solution (4 μL) was taken and analyzed. Deionized water (0.54 mL, 30 mmol, 0.6 equiv) was added to the reaction mixture to start the reaction. The resolution reaction was monitored by chiral GC. For kinetic studies, aliquots (4 μL) were taken at certain times and diluted with 3 mL diethyl ether. The diethyl ether solutions were then passed through plugs of silica gel packed in a Pasteur pipet. The filtrates were concentrated to about 100 μL and subject to chiral GC analyses. The absolute configurations were assigned by comparison with authentic samples.[1]

(R)-1,2-Epoxyhexane (Table 1, Entry 1)

Tetramer-hexamer catalyst (0.01 mol%), reaction time: 80 minutes. (R)-1,2-epoxyhexane was obtained in > 99% ee (Chiraldex γ-TA, 60 ^{o}C, isothermal, t_R(R, major) = 11.30 min, t_R(S, minor) = 10.83 min).

(S)-Epichlorohydrin (Table 1, Entry 2)

Tetramer-hexamer catalyst (0.01 mol%), reaction time: 100 minutes. (S)-epichlorohydrin was obtained in > 99% ee (Chiraldex γ-TA, 90 ^{o}C, isothermal, t_R(R, minor) = 6.16 min, t_R(S, major) = 5.96 min).

(S)-Allyl glycidyl ether (Table 1, Entry 3)

Tetramer-hexamer catalyst (0.01 mol%), reaction time: 5 hours. (S)-allyl glycidyl ether was obtained in > 99% ee (Chiraldex γ-TA, 90 ^{o}C, isothermal, t_R(S, major) = 9.86 min, t_R(R, minor) = 9.24 min).

(S)-Phenyl glycidyl ether (Table 1, Entry 4)

Tetramer-hexamer catalyst (0.01 mol%), reaction time: 2 hours. (S)-phenyl glycidyl ether was obtained in > 99% ee (Chiracel OD, isopropanol : hexane = 10 : 90 (v/v), t_R(S, major) = 10.85 min, t_R(R, minor) = 7.48 min).

(R)-Styrene oxide (Table 1, Entry 5)

Tetramer-hexamer catalyst (0.1 mol%), reaction time: 3.5 hours. (R)-styrene oxide was obtained in > 99% ee (β-Dex 120, temperature programming: 89 ^{o}C 5min, 89 ^{o}C to 110 ^{o}C at 3 ^{o}C/min, 110 ^{o}C 10min; t_R(S, minor) = 18.55 min, t_R(R, major) = 18.08 min).

(R)-tert-Butyloxirane (Table 1, Entry 6)

Tetramer-hexamer catalyst (0.25 mol%), reaction time: 5 hours. (R)-tert-butyloxirane was obtained in > 99% ee (Chiraldex γ-TA, 40 ^{o}C, isothermal, t_R(S, minor) = 14.06 min, t_R(R, major) = 12.74 min).

Reaction scope test of the asymmetric ring-opening of epoxides

The catalyst activation was carried out as described above. The absolute configuration of (R)-1-chloro-3-phenoxy-2-propanol was assigned by comparing the sign of the measured optical rotation with the literature report.[2] (R)-1-(2-trimethylsilyl ethoxy)-2-hexanol was assigned by conversion to 1,2-hexane diol and compared with an authentic sample. (S,S)-Cyclohexane-1,2-diol was assigned by comparison with an authentic sample.

Asymmetric ring-opening of epichlorohydrin with phenol

Epichlorohydrin (383 μL, 4.88 mmol, 2.22 equiv) and CH_3CN (0.2 mL) were added to the activated Co(III)-salen complex (0.25 mol%). The reaction vial was immerged in a 4 ^oC water bath. Phenol (206.8 mg, 2.2 mmol, 1 equiv) was added to start the reaction. The reaction was monitored by GC-MS. After 4 hours, the reaction solution was diluted with 5 mL of diethyl ether and filtered through a pad of silica gel. The plug of silica gel was washed with 20 mL diethyl ether. The combined filtrates were concentrated under reduced pressure to provide the crude product, (R)-1-chloro-3-phenoxy-2-propanol, as a yellowish oil (399 mg, 98 % yield). The acetate derivative (prepared by 4 μL product, 400 μL dichloromethane, 44 μL pyridine, 40 μL acetyl chloride and stirring for 15 min followed by filtration through a plug of silica gel) has at least an enantiomeric excess of 99 % as determined by chiral GC analysis (Chiraldex γ-TA column, 155 ^oC, isothermal, t_R (S, minor) = 29.1 min, t_R (R, major) = 32.9 min). ^1H NMR (400 MH_Z, $CDCl_3$) δ (ppm): 7.33 (m, 2H), 7.01 (t, J = 1.1 Hz, 1H), 6.94 (d, J = 1.3 Hz, 2H), 4.22 (m, 1H), 4.11 (m, 2H), 3.76 (m, 2H), 2.90 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.2, 129.6, 121.5, 114.6, 69.9, 68.5, 46.0. $[\alpha]^{23}_D$ = -0.4 (c = 2.01, CH_2Cl_2), lit. -0.7 (c = 2.09, CH_2Cl_2).[2]

Asymmetric ring-opening of 1,2-epoxyhexane with trimethyl silyl ethanol

1,2-Epoxyhexane (794 μL, 6.6 mmol, 2.5 equiv) and CH_3CN (0.2 mL) were added to the activated Co(III)-salen complex (0.2 mol%). The reaction vial was immerged in a water bath at room temperature. Trimethylsilyl ethanol (376 μL, 2.6 mmol, 1 equiv) was added to start the reaction. The reaction was monitored by GC mass spectrometry. After 5 hours, the reaction solution was diluted with 5 mL of diethyl ether and filtered through a pad of silica gel. The plug of silica gel was washed with 20 mL of diethyl ether. The combined filtrates were concentrated under reduced pressure to provide the crude product, (R)-1-(2-trimethylsilyl ethoxy)-2-hexanol, as a yellowish oil (584 mg, 96 % yield). To measure the *ee*, the product was converted to the diol via deprotection (4 mg product in 0.4 mL dichloromethane was treated with 1 mL $LiBF_4$ (1 M) CH_3CN solution and heated at 80 ^oC for 2 hours). The bis TFA ester derivative from the diol (1 mg diol in 2 mL anhydrous dichloromethane was treated with 0.3 mL trifluoroacetic anhydride and heated at 60 ^oC for 30 min) was analyzed by chiral GC (Chiraldex γ-TA

column, 85 °C, isothermal, t_R (S, minor) = 15.4 min, t_R (R, major) = 16.9 min). The *ee* was determined to be above 99%. ^{1}H NMR (400 MH_Z, $CDCl_3$) δ (ppm): 3.71 (m, 1H), 3.54 (m, 2H), 3.41 (dd, J = 2.8, 9.0, 1H), 3.22 (dd, J = 8.4, 9.3, 1H), 2.84 (br, 1H), 1.48 (m, 3H), 1.31 (m, 3H), 0.90 (m, 5H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 76.2, 71.7, 69.9, 34.4, 29.1, 24.1, 19.6, 15.4, 0.00. $[\alpha]^{23}_D$ = +1.8 (c = 1.03, CH_2Cl_2).

Asymmetric ring-opening of cyclohexene oxide with water

Cyclohexene oxide (115.5 µL, 1.14 mmol, 1 equiv) and CH_3CN/CH_2Cl_2 (1:1, 0.3 mL) were added to an activated Co(III)-salen complex (1 mol%). The reaction vial was immerged in an oil bath at 40 °C. Deionized water (51.3 µL, 2.85 mmol, 2.5 equiv) was added to start the reaction. The reaction was monitored by GC mass spectrometry. Some precipitation formed during the reaction process. After 50 hours, the solution was diluted with diethyl acetate and passed through a pad of silica gel. The pad was washed with 200 mL of ethyl acetate. The combined filtrates were concentrated under reduced pressure to provide the crude product, (S,S)-cyclohexane-1,2-diol, as a white solid (121 mg, 92 % yield). The bis-TFA derivative was prepared from 1 mg diol in 2 mL anhydrous dichloromethane treated with 0.3 mL trifluoroacetic anhydride and heated at 60 °C for 30 min. The *ee* was determined to be above 99% by chiral GC analysis (Chiraldex γ-TA column, 110 °C, isothermal, t_R (R,R, minor) = 9.01 min, t_R (S,S, major) = 9.69 min). ^{1}H NMR (400 MH_Z, $CDCl_3$) δ (ppm): 3.70 (br, 2H), 3.32 (m, 2H), 1.95 (m, 2H), 1.70 (m, 2H), 1.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 75.7, 32.9, 24.4. $[\alpha]^{23}_D$ = +30.6 (c = 1.2, CH_2Cl_2).

Appendix A

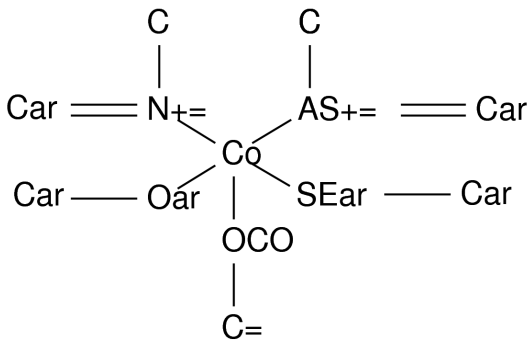


Figure S5. Reduced Co(III)salen complex with OAc counter-ion that shows the atom type that was used in the force field for the atoms directly involved in parameterization to extend the MMFF94 force field.

Table S6. Cartesian coordinates (X, Y, Z) and electrostatic point charges for the optimized geometry of the singlet state for the reduced Co-salen complex with the acetate counter-ion.

Atom	X(Å)	Y(Å)	Z(Å)	Charge
N1	-1.9680103790	-0.1242184687	0.0641556408	-0.62937
N2	-0.1630708440	1.7239565025	-0.1441722134	-0.65036
O1	0.0266303159	-1.9346544090	0.7116227391	-0.53077
O2	1.6539633444	-0.0632622838	0.8771604198	-0.51227
C1	-2.2568918387	-2.5449426969	0.1295055377	-0.18083
C2	-0.8910016489	-2.8402356126	0.5025981065	0.50648
C3	2.1157840659	2.2942729254	0.5059429235	-0.13198
C4	2.4711465418	0.9590039689	0.9216305420	0.47351
C5	-2.7187900854	-1.1954455744	-0.0065021229	0.22486
C6	0.8124336477	2.5906539387	-0.0042068365	0.17309
H1	-3.8023311520	-1.0664323773	-0.1573382197	0.07110
H2	0.6221541310	3.6384788010	-0.2844071064	0.08720
C7	-2.5224268816	1.2454955344	-0.0272647644	0.35996
H3	-2.5713233153	1.6393377875	1.0117731728	-0.01789
C8	-1.4540982433	2.0762830637	-0.7744717962	0.49821
H4	-1.3999529995	1.6770989686	-1.8093913773	-0.00819
Co	-0.0673742758	-0.1317415226	0.1839442789	1.00709
C9	-3.9096624430	1.4016715426	-0.6741148833	-0.09596
H5	-3.8898280186	0.9659799552	-1.6931716942	0.03560
H6	-4.6734313699	0.8484858606	-0.0966823787	0.04697
C10	-4.2979255826	2.8950078190	-0.7394622506	-0.12096
C11	-1.8347023626	3.5651899438	-0.8260947425	-0.26740
H7	-1.8352571628	3.9841861807	0.2007475685	0.06680
H8	-1.0903243936	4.1358676751	-1.4116502478	0.08468
C12	-3.2297994118	3.7320627246	-1.4675414733	-0.03260
H9	-3.5132968500	4.8006968999	-1.4668901279	0.05020
H10	-3.1799296478	3.4200597184	-2.5301881138	0.02177

H11	-5.2773553698	3.0019975886	-1.2411068588	0.05492
H12	-4.4286602474	3.2822709358	0.2913041313	0.04107
C13	4.6864829805	1.8024968629	1.5466925995	-0.08259
C14	3.7803719304	0.7529983062	1.4525174359	-0.26362
H13	5.6899308460	1.6113998439	1.9461094695	0.12233
C15	3.0694089691	3.3430222368	0.6128522484	-0.13705
C16	4.3406869946	3.1105732343	1.1229442523	-0.15224
C17	-1.4803358521	-5.2256168407	0.5210659158	-0.07453
C18	-0.5435282971	-4.2152918994	0.6966363775	-0.29241
H14	-1.1769195631	-6.2690705757	0.6713387636	0.12076
C19	-3.1891344086	-3.6077984462	-0.0367824088	-0.13286
C20	-2.8179571803	-4.9332669054	0.1480116909	-0.16470
H15	2.7833068731	4.3490194169	0.2782688737	0.11943
H16	-4.2214700709	-3.3577320900	-0.3160081981	0.11725
C21	1.0944409479	-0.4133520256	-2.3358991614	0.70934
O3	-0.0372353784	-0.5529798463	-1.6448305876	-0.49516
O4	2.1609131769	0.0650050900	-1.9555155712	-0.47585
H17	-3.5450629824	-5.7404733310	0.0131125493	0.12379
H18	0.4905432274	-4.4334681632	0.9827508436	0.16219
H19	5.0687360895	3.9253686869	1.1939359351	0.12297
H20	4.0418993660	-0.2632961534	1.7637004638	0.16175
C22	0.9007044395	-0.9752509773	-3.7571036302	-0.59829
H21	1.7682697964	-0.6942887920	-4.3730155106	0.14905
H22	0.8256342531	-2.0756973252	-3.7094735777	0.17481
H23	-0.0295634744	-0.5985687821	-4.2142095045	0.16069

Table S7. Parameters for initial charges (q_0) and van der Waals radius (R_i) and well depth (ε) for Co-salen.

Atom	R_i(Å)	e ε (kcal/mole)	q_0
N+=	-	-	-0.100
CO	2.009	0.298	3.00
Oar	1.825	-	-0.25-1.00
OCO	-	-	

Table S8. Parameters for bond stretch and bond charge increment parameters for Co-salen. The units for k_x/(mole Å).

Atom i	Atom j	r_0(Å)	k_2	k_3	k_4	w_{ij}
CO	N+=	1.885	155.726	-311.452	363.361	0.3125
CO	Oar	1.845	222.353	-444.706	518.824	0.3125
CO	OCO	1.877	279.851	-559.702	652.986	0.7500
N+=	Car	1.296	320.335	-640.670	747.448	0.3000
Car	Oar	1.306	528.606	-1057.212	1233.414	-0.3500
C	N+=	1.486	-	-	-	-

Table S9. Parameters for linear angle bend parameters for Co-salen.

Atom i	Atom j	Atom k	$q\theta_0$(°)	k_{θ_q}

				(kcal mole^{-1})
Oar	CO	AS+=	180	72.2528
SEar	CO	N+=	180	72.2528

Table S10. Parameters for normal angle bend parameters for Co-salen. The units for $k_{\theta x}$ are kcal/(mole rad^{x}).

Atom i	Atom j	Atom k	$q\theta_0$(°)	$K_{\theta 2q2}$	$K_{\theta 3q3}$
Oar	CO	OCO	90.000	32.3020	-12.9208
N+=	CO	OCO	90.000	33.0406	-13.2162
AS+=	CO	N+=	90.000	34.8000	-13.9200
N+=	CO	Oar	90.000	33.7495	-13.4998
Oar	CO	SEar	90.000	32.8852	-13.1541
HC	Car	Car	120.571	40.5167	-16.2500
C	C	N+=	106.424	84.4157	-33.8567
HC	C	N+=	106.973	62.8980	-25.2265
CO	Oar	Car	128.965	61.5483	-24.6193
CO	N+=	C	111.553	47.2114	-18.8846
CO	AS+=	C	123.395	47.2114	-18.8846
CO	N+=	Car	125.243	46.9740	-18.7896
Oar	Car	Car	121.185	52.1477	-20.8591
C	N+=	Car	122.374	50.4427	-20.1771
N+=	Car	Car	125.505	57.2041	-22.8816
N+=	Car	HC	117.202	48.3113	-19.3245
CO	OCO	C1=	119.679	48.9986	-19.5994

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