

Supporting Information

for

Asymmetric Alternating Copolymerization of Meso-epoxides and Cyclic Anhydrides: Efficient Access to Enantiopure Polyesters

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Contents

1. General information
2. Salicylaldehyde derivatives synthesis
3. Synthetic procedures for complexes **1-5**
4. Representative procedures for copolymerizing cyclic anhydrides with *meso*-epoxides
5. Representative GPC plots for cyclic anhydride/*meso*-epoxide copolymers
6. ¹H and ¹³C NMR spectra of polyesters
7. DSC thermograms of various polyesters
8. Determination of enantiomeric purity of polyesters
9. Structure of dinuclear Al(III) complexes (*R,R,R,R,R*)-**3b** and (*R,R,S,R,R*)-**3b**
10. References

1. General information

All manipulations involving air- and/or water-sensitive compounds were carried out in a glove box or with the standard Schlenk techniques under dry nitrogen. Cyclohexene oxide (CHO) and cyclopentene oxide (CPO) were purchased from Acros and distilled over calcium hydride. Cis-2,3-epoxybutane (CBO) was purchased from Alfa Aesar and distilled over calcium hydride. 1,2-Epoxy-4-cyclohexene was according to a published method.¹ Methanol was distilled from magnesium under nitrogen. Methylene chloride and dimethylformamide were distilled from calcium hydride under nitrogen. Tetrahydrofuran and toluene were distilled from sodium/benzophenone under nitrogen. PPnCl (Bis(triphenylphosphine)iminium chloride, 97%, Energy Chemical) was recrystallized by layering a saturated methylene chloride solution with diethyl ether. Succinic anhydride, phthalic anhydride and glutaric anhydride were purchased from J&K, and 1,4-dioxane-2,6-dione was purchased from damas-bata. All anhydrides were purified by sublimation before used. All other chemicals and reagents were purchased from commercial sources (J&K, TCI, Energy Chemical and Alfa Aesar) and used as received.

NMR Experiments. ¹H and ¹³C NMR spectra were recorded on Varian INOVA-400 MHz type (¹H, 400 MHz), and a Bruker 500 MHz type (¹³C, 125 MHz) spectrometer, respectively. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ¹H NMR and against the solvent, chloroform-*d* at 77.0 ppm for ¹³C NMR, respectively.

Gel Permeation Chromatography. Molecular weights and molecular weight distributions of polymers were determined with a PL-GPC 220 high temperature chromatograph (Polymer Laboratories Ltd.) equipped with the HP 1100 series pump from Agilent Technologies. The GPC columns were eluted with tetrahydrofuran at 35 °C at 1.00 mL/min. The sample concentration was about 0.1%, and the injection volume was 100 μL. The curve was calibrated using monodisperse polystyrene standards covering the molecular weight range from 580 to 460000 Da.

Differential scanning calorimetry (DSC) was carried out with a NETZSCH DSC 206 thermal analyzer.

Mass Spectrometry. A Micromass Q-ToF (Micromass, Wythenshawe, UK) mass spectrometer equipped with an orthogonal electrospray source (Z-spray) used for the cobalt complexes in positive ion mode (Capillary = 2000 V, Sample cone = 20 V).

Wide angle X-ray diffraction (WAXD). Powder X-ray diffraction data were collected on a EMPYREAN diffractometer with Cu KR radiation ($\lambda = 1.54056 \text{ \AA}$) over the 2θ range of 5-80° with a scan speed of 0.128548/s and a step size of 0.0083556° at room temperature.

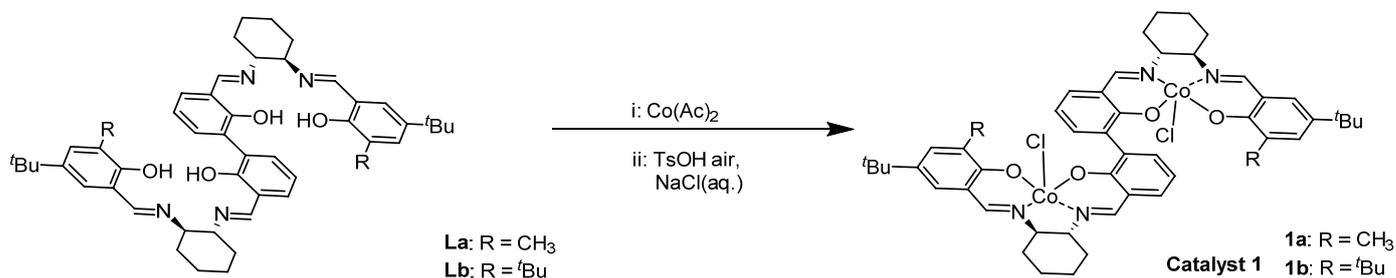
2. Salicylaldehyde derivatives synthesis

2.1. 5-*tert*-butyl-3-trimethylsilyl-2-hydroxybenzaldehyde was synthesized according to the literatures method.²

2.2. 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 5-*tert*-butyl-3-methyl-2-hydroxybenzaldehyde were all purchased or synthesized in our laboratory.

3. Synthetic procedures for complexes 1–3

3.1. Preparation of the catalyst 1a and 1b



Ligands **L-1a** and **L-1b** were synthesized according to literature method.^{3a}

Complexes **1a** and **1b** were synthesized according to literature method.^{3b}

1a: ^1H NMR($\text{DMSO}-d_6$, 400 MHz) δ 8.78-8.59 (m, 4H), 8.05-7.79 (m, 6H), 7.48-7.32 (m, 4H), 6.93-6.88 (m, 2H), 6.33-6.20 (m, 2H), 3.73-3.60 (m, 4H), 3.07-3.00 (m, 4H), 2.73-2.02 (m, 18H), 1.29 (s, 18H); HRMS (m/z): Calcd for $[\text{C}_{50}\text{H}_{58}\text{Co}_2\text{N}_4\text{O}_4]^{2+}$ ($[\mathbf{1a}-2\text{Cl}]^{2+}$): 448.1561; found: 448.1567.

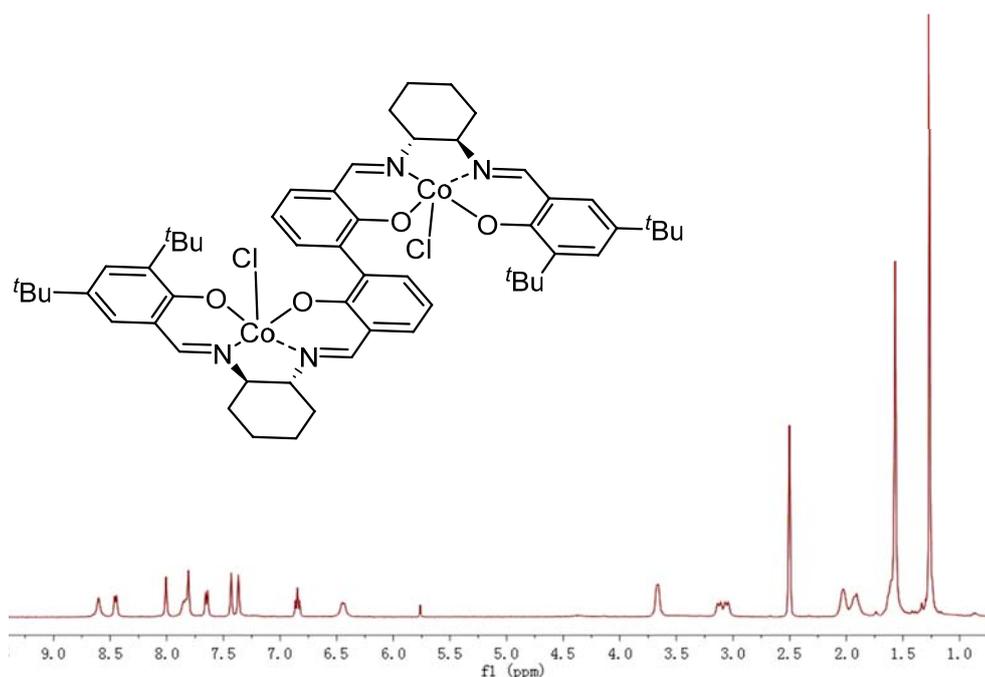
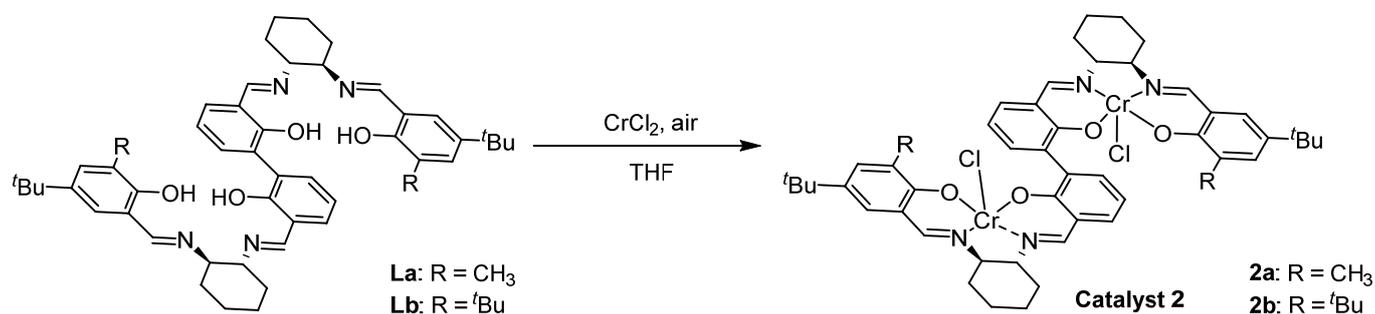


Figure S1. ^1H NMR spectrum of complex (*R,R,R,R*)-**1b**

1b: ^1H NMR (DMSO- d_6 , 400 MHz) δ 8.60-8.44 (m, 4H), 8.01 (s, 2H), 7.83-7.80 (m, 4H), 7.66-7.64 (m, 4H), 7.43-7.33 (m, 4H), 6.88-6.70 (m, 2H), 6.50-6.44 (m, 2H), 3.75-3.60 (m, 4H), 3.25-3.30 (m, 4H), 2.12-1.80 (m, 4H), 1.63(s, 18H), 1.18 (s, 18H); HRMS (m/z): Calcd for $[\text{C}_{56}\text{H}_{70}\text{Co}_2\text{N}_4\text{O}_4\text{Cl}]^+$ (**1b-Cl**) $^+$: 1015.3744; found: 1015.3745, Calcd for $[\text{C}_{58}\text{H}_{62}\text{Co}_2\text{N}_4\text{O}_4]^{2+}$ (**1b-2Cl**) $^{2+}$: 490.2025; found: 490.2029.

3.2. Preparation of complex 2



Each ligand **L** (0.5 mmol) and CrCl₂ (0.15 g, 1.2 mmol) were dissolved in THF (5 mL) and stirred under nitrogen at ambient temperature for 8 h. Then the mixture was exposed to the air stirred for 5 h. After the mixture was diluted with diethyl ether (10 mL), the organic layer was washed with aqueous

saturated NH_4Cl (3×50 mL) and the brine (3×50 mL) followed by drying with anhydrous Na_2SO_4 . After filtration to remove solids, the organic layer was removed in vacuo, obtaining a dark brown powder. The total yield was 90%. Because of the paramagnetic nature of the Cr(III) complexes, we could not obtain their ^1H NMR spectra.

2a HRMS (m/z): Calcd for $[\text{C}_{50}\text{H}_{58}\text{Cr}_2\text{N}_4\text{O}_4]^{2+}$ ($[\mathbf{2a}-2\text{Cl}]^{2+}$): 441.1634; found: 441.1630.

2b HRMS (m/z): Calcd for $[\text{C}_{56}\text{H}_{70}\text{Cr}_2\text{N}_4\text{O}_4]^{2+}$ ($[\mathbf{2b}-2\text{Cl}]^{2+}$): 483.2104; found: 483.2092.

3.3. Preparation of complexes **3a**, **3b** and **3c**

The ligand **L-3c** was synthesized according to literature method.^{3a}

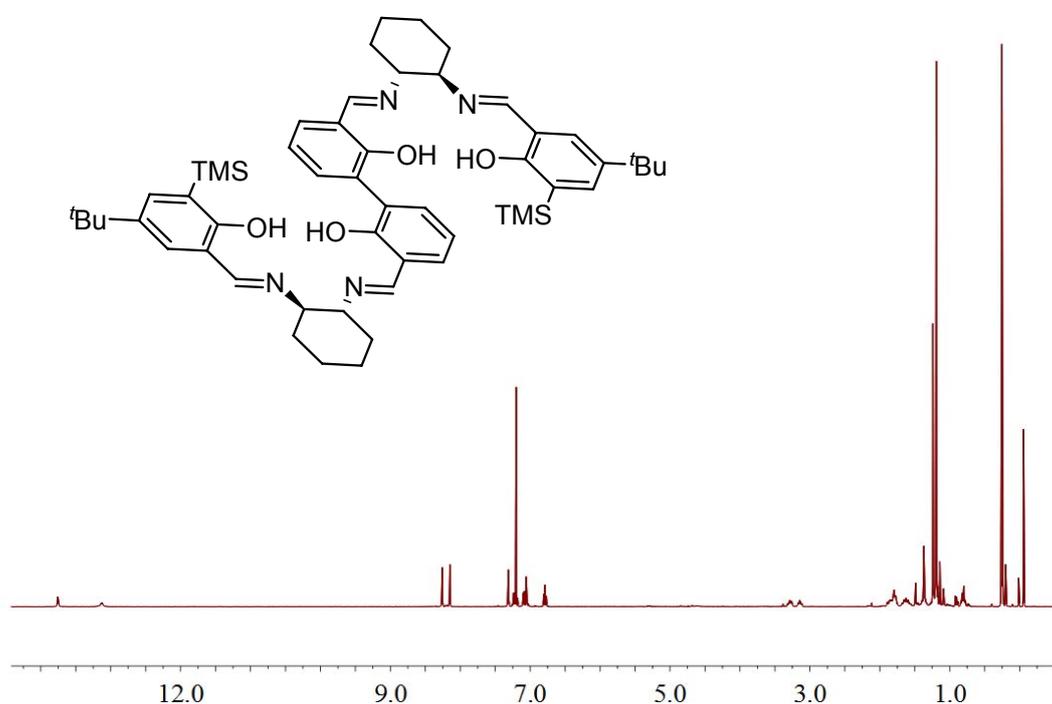
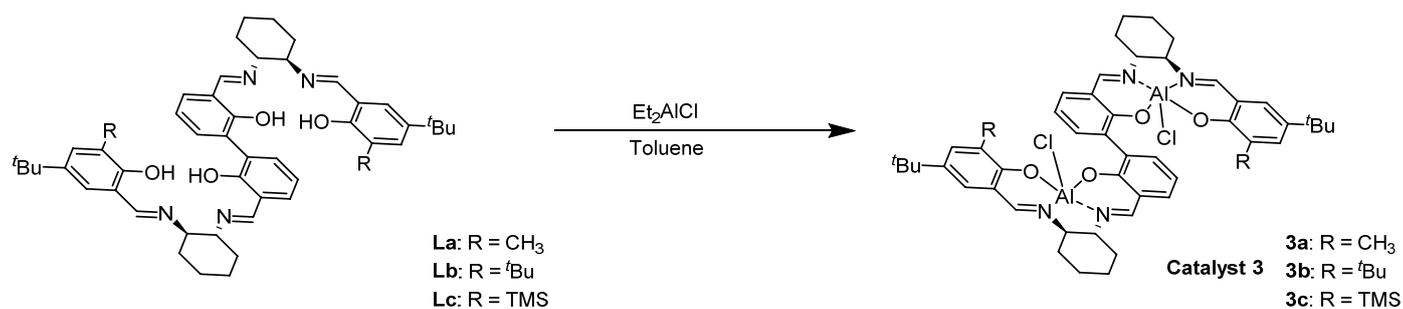


Figure S2. ^1H NMR spectrum of ligand **L-3c**

Ligand L-3c: ^1H NMR (CDCl_3 , 400 MHz) δ 13.81 (s, 2H), 13.19 (s, 2H), 8.42 (s, 2H), 8.12 (s, 2H), 7.32 (d, $J = 2.5$ Hz, 2H), 7.30-7.27 (m, 2H), 7.18-7.13 (m, 2H), 7.05 (d, $J = 2.5$ Hz, 2H), 6.90-6.81 (m, 2H), 3.35-3.07 (m, 4H), 1.96-1.22 (m, 16H), 1.22-1.16 (m, 18H), 0.30-0.22 (m, 18H).



Each ligand (0.5 mmol) was dissolved in toluene (5 mL). Then a solution of Et₂AlCl (2.0 M, 0.5 mL, 1 mmol) in toluene (1 mL) was added dropwise *via* cannula in glovebox until ethane no longer formed. The mixture was allowed to stir for 24 h at 75 °C to give a yellow suspension. After removal of toluene in vacuo, the suspension were dissolved in CH₂Cl₂ (0.5 mL) and excess cold hexane was added. After filtration, the suspension was rinsed with cold hexane (3 × 5 mL). The yellow solid was collected and dried in vacuo to yield the aluminum(III) complex. The total yield was about 60%.

3a: ¹H NMR (DMSO-*d*₆, 400 MHz): δ 8.48 (s, 2H), 8.26 (s, 2H), 7.98-7.89 (m, 2H), 7.45-7.42(m, 2H), 7.38-7.20 (m, 4H), 6.78-6.70 (m, 2H), 3.33-3.28 (m, 4H), 2.65-2.40(m, 8H), 2.30-1.65 (m, 14H), 1.23 (s, 18H).

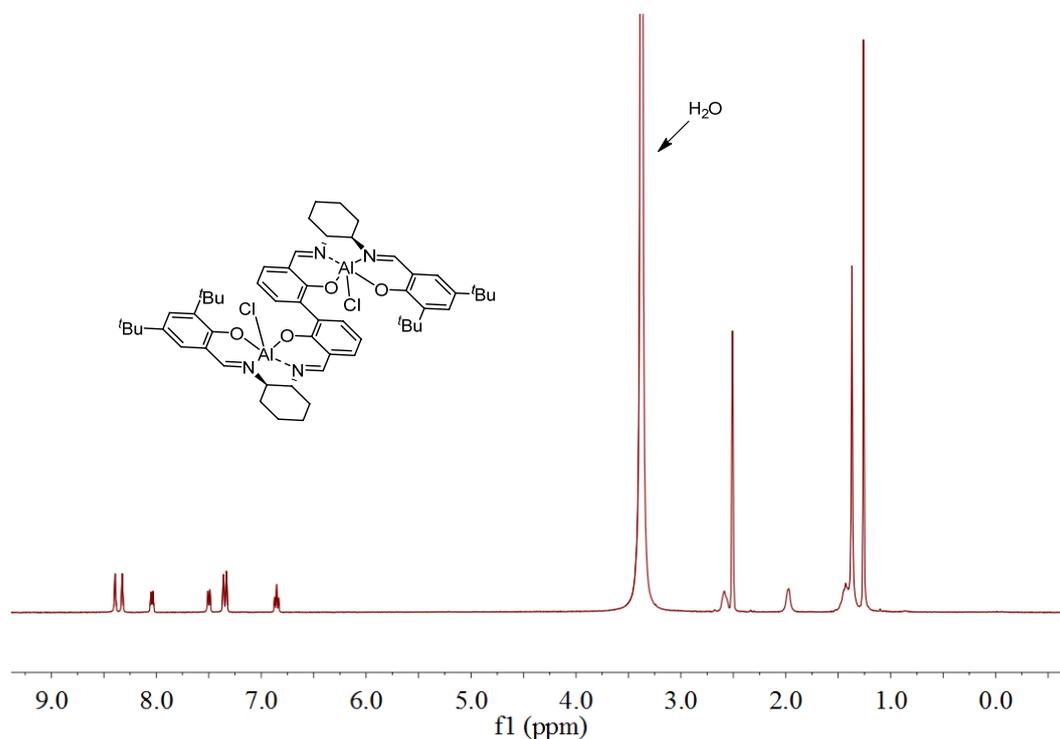


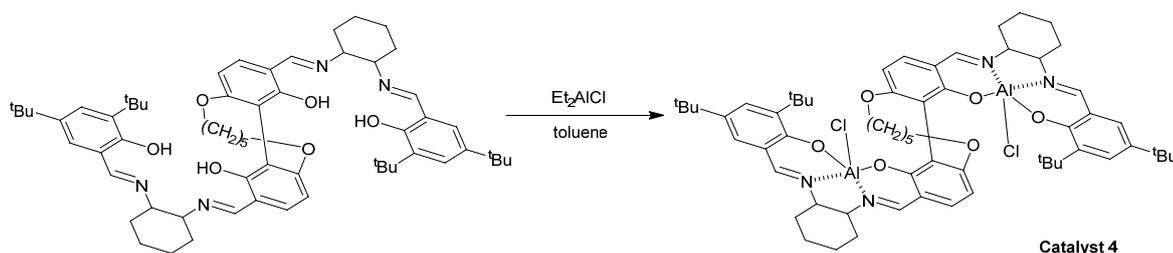
Figure S3. ¹H NMR spectrum of complex (*R,R,R,R*)-**3b**

3b: ¹H NMR (DMSO-*d*₆, 400 MHz): δ 8.39 (s, 2H), 8.32 (s, 2H), 8.09-8.02 (m, 2H), 7.55-7.44 (m, 2H),

7.40-7.33 (m, 4H), 6.88-6.82 (m, 2H), 2.65-2.40 (m, 4H), 2.00-1.92 (m, 4H), 1.50-1.20 (m, 28H), 1.26 (s, 18H). ^{13}C NMR (DMSO- d_6 , 400 MHz): δ 164.45, 164.07, 162.01, 161.94, 149.68, 138.44, 136.80, 133.77, 129.40, 129.04, 128.77, 120.54, 119.32, 116.25, 63.79, 35.42, 34.14, 31.83, 30.28, 27.48, 24.02.

3c: ^1H NMR (DMSO- d_6 , 400 MHz): δ 8.38 (s, 2H), 8.27 (s, 2H), 7.77-7.71 (m, 2H), 7.50-7.46 (m, 2H), 7.44-7.26 (m, 4H), 6.72-6.68 (m, 2H), 3.38-3.33 (m, 4H), 2.54-2.13 (m, 16H), 1.78-1.19 (m, 18H), 0.26 (s, 18H).

3.4. Preparation of complex 4



The ligand of complex 4 was prepared according to the literature method.^{3c} The synthesis of the catalyst 4 was similar to catalyst 3.

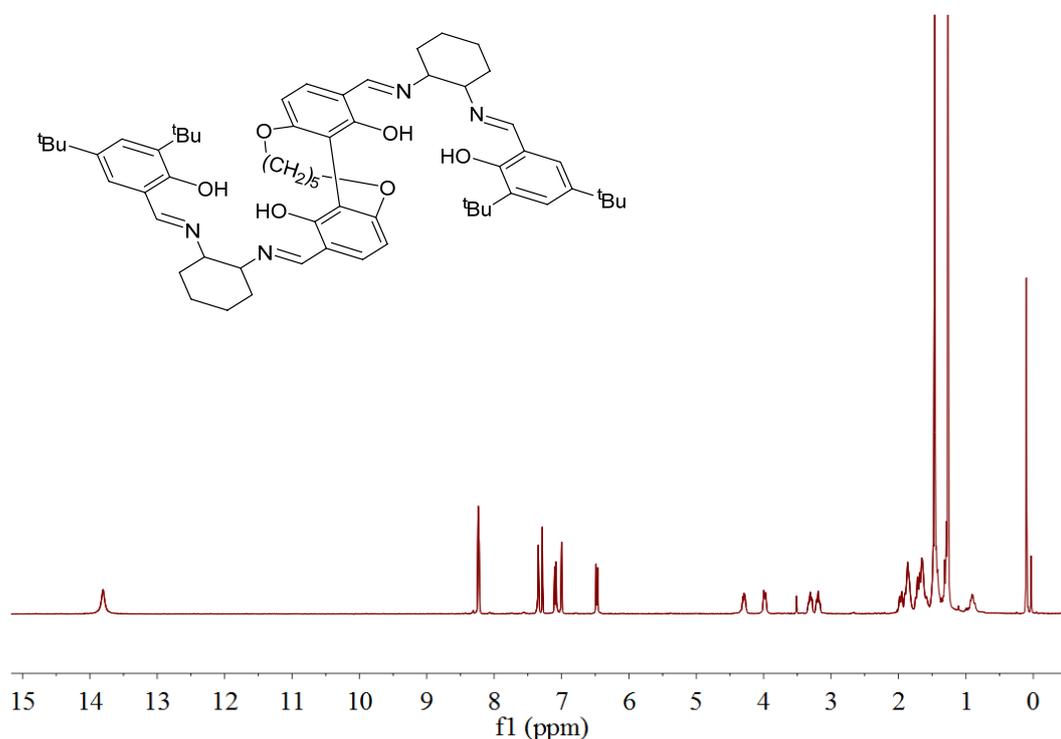


Figure S4. ^1H NMR spectrum of the ligand (R,R,R,R)-L4

(R,R,R,R)-**L4** ^1H NMR (CDCl_3 , 400 MHz) δ 13.80-13.60 (m, 4H), 8.26-8.21 (m, 4H), 7.36-7.33 (m, 2H), 7.09 (d, $J = 8.6$ Hz, 2H), 7.02-6.98 (m, 2H), 6.48 (d, $J = 8.6$ Hz, 2H), 4.41-4.11 (m, 2H), 4.11-3.83 (m, 2H), 3.43-2.98 (m, 4H), 2.19-1.56 (m, 16H), 1.56-1.38 (m, 18H), 1.38-1.16 (m, 24H).

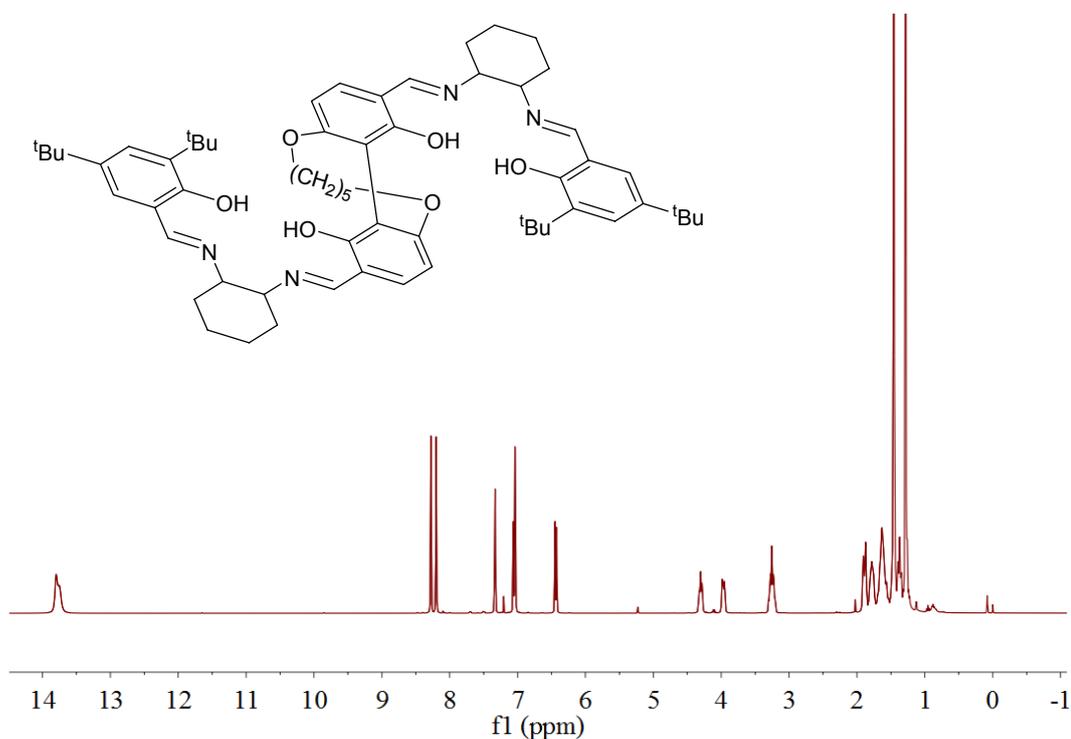


Figure S5. ^1H NMR spectrum of the ligand *(R,R,S,R,R)*-**L4**

(R,R,S,R,R)-**L4**: ^1H NMR (CDCl_3 , 400 MHz) δ 13.88-13.78 (m, 4H), 8.28 (s, 2H), 8.20 (s, 2H), 7.35-7.30 (m, 2H), 7.07-7.01 (m, 4H), 6.45-6.41 (m, 2H), 4.35-4.25 (m, 2H), 4.00-3.90 (m, 2H), 3.34 - 3.18 (m, 4H), 1.96-1.54 (m, 16H), 1.51-1.42 (m, 18H), 1.31-1.23 (m, 24H).

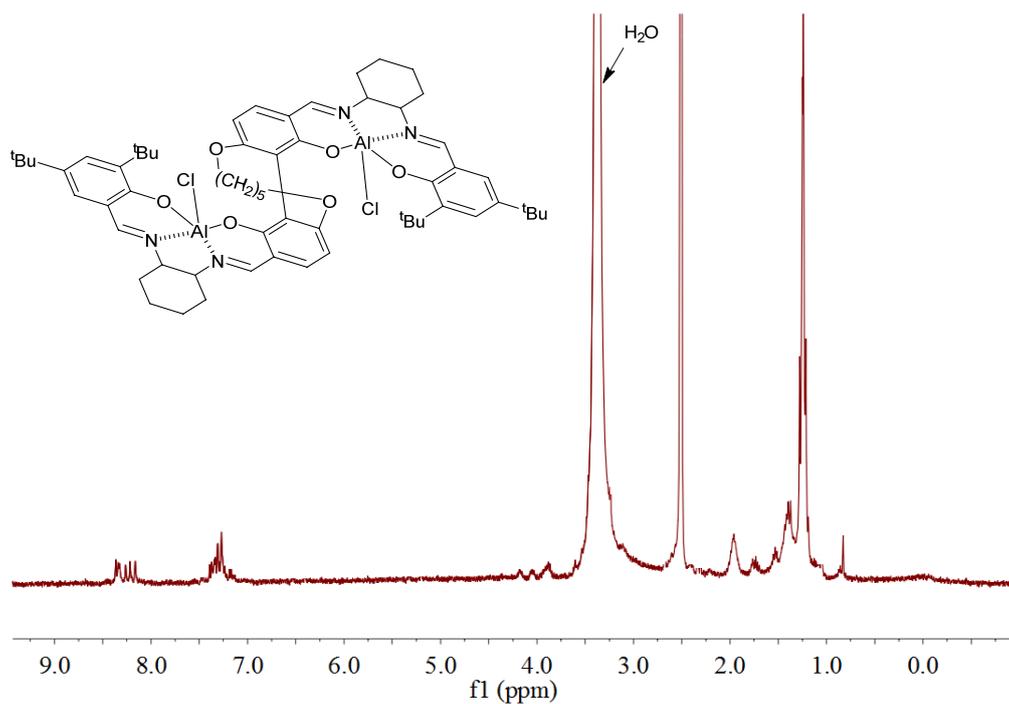
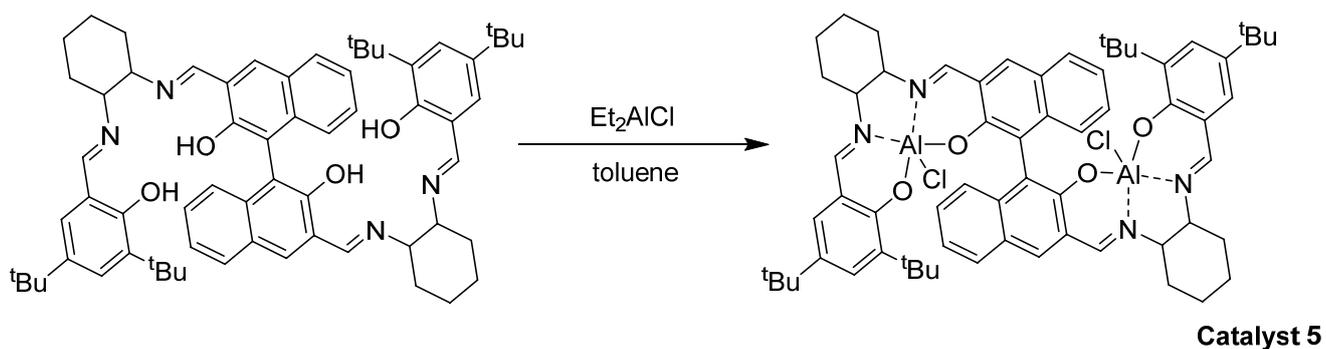


Figure S6. ^1H NMR of complex (R,R,R,R,R) -**4**

(R,R,R,R,R) -**4** ^1H NMR ($\text{DMSO-}d_6$, 400 MHz): δ 8.28-8.13 (m, 4H), 7.38-6.38 (m, 8H), 4.50-3.61 (m, 8H), 2.08-1.91(m, 8H), 1.58-1.12 (m, 52H).

3.5. Preparation of complex **5**



The synthesis of the ligand of complex **5** was prepared according to the literature method.^{3d} The synthesis of complex **5** was similar to complex **3**.

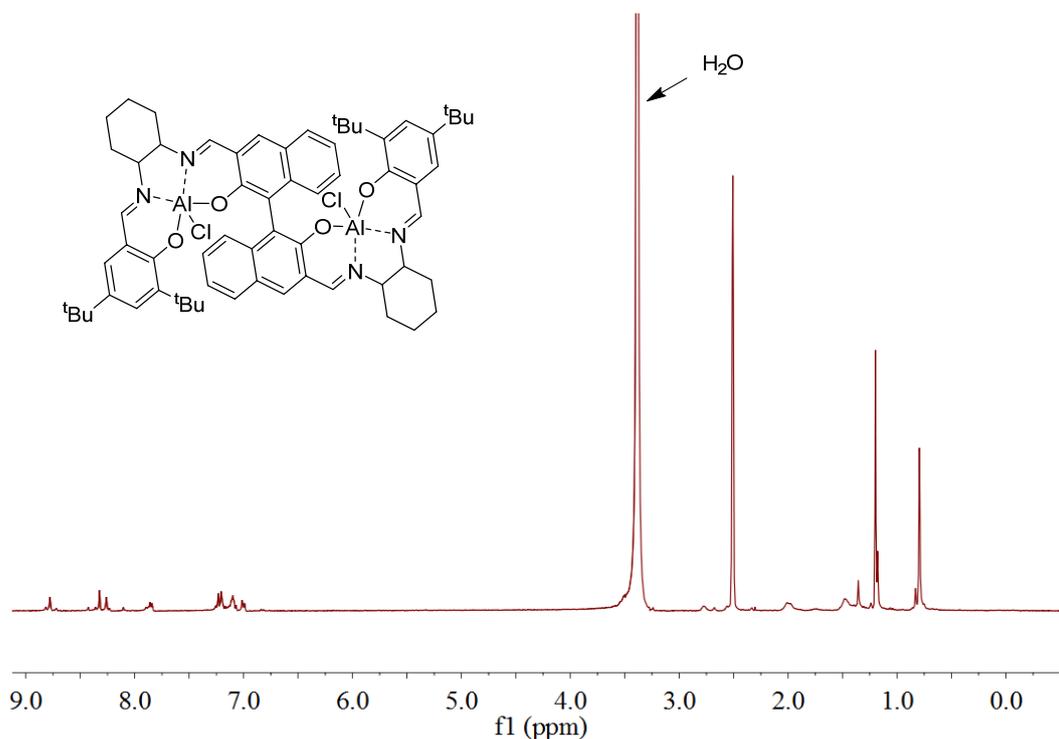


Figure S7. ^1H NMR spectrum of complex (R,R,R,R) -5

(R,R,R,R) -5 ^1H NMR ($\text{DMSO-}d_6$, 400 MHz) δ 8.74-8.70 (m, 2H), 8.43-8.12 (m, 4H), 7.86-7.82 (m, 2H), 7.41-6.78 (m, 10H), 2.83-2.72 (m, 4H), 2.08-1.92 (m, 6H), 1.55-1.40 (m, 8H), 1.25-1.10 (m, 18H), 0.88-0.77(s, 18H).

4. Representative procedures for copolymerizing cyclic anhydrides with meso-epoxides

In a 20 mL autoclave equipped with a magnetic stirrer, catalyst (0.05 mmol, 1 equiv), PPNCl (0.10 mmol, 2 equiv) and phthalic anhydride (12.5 mmol, 250 equiv) were dissolved in meso-epoxide (50 mmol, 1000 equiv) in a argon atmosphere. After an appropriate time at a certain reaction condition, a small amount of the resultant mixture was removed from the flask for ^1H NMR analysis to quantitatively to give the selectivity of polyester to polyether, as well as polyester linkages. The hydrogen chloride-diethylether solution (2 M, 0.1mL) was added dropwise before the crude polymer was dissolved in 10 mL CH_2Cl_2 . The solution was precipitated with excess methanol. This process was repeated 3-5 times to completely remove the catalyst, and white polymer was obtained by vacuum-drying. As for other employed anhydrides, the hexane was used instead of methanol.

5. Representative GPC plots of polyesters

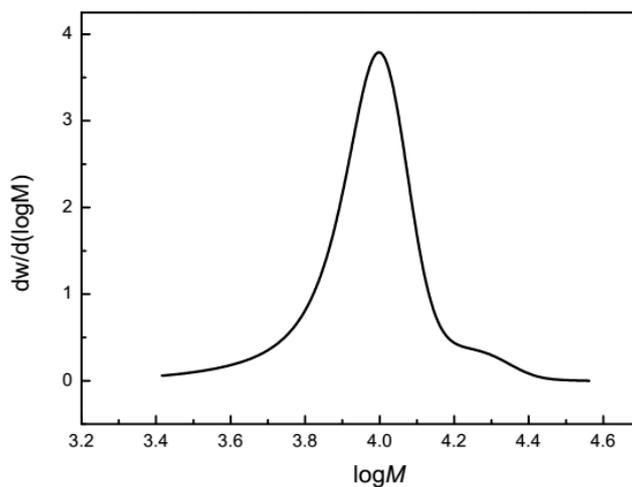


Figure S8. GPC plot of a representative sample of poly(CHO-*alt*-PA) ($M_n = 8.8$ Kg/mol, PDI = 1.14).

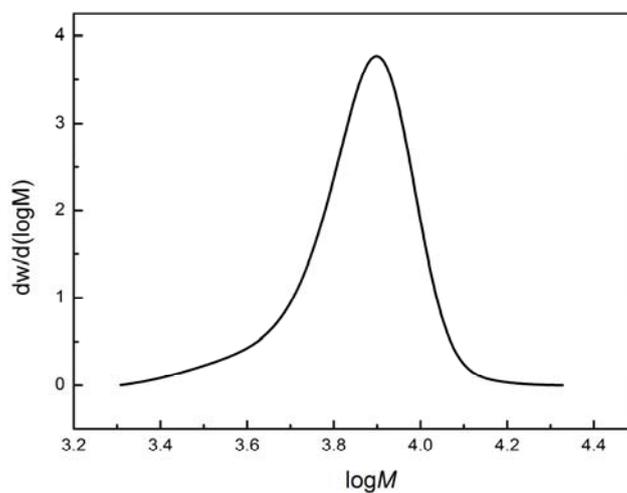


Figure S9. GPC plot of a representative sample of poly(CPO-*alt*-PA) ($M_n = 6.1$ Kg/mol, PDI = 1.24).

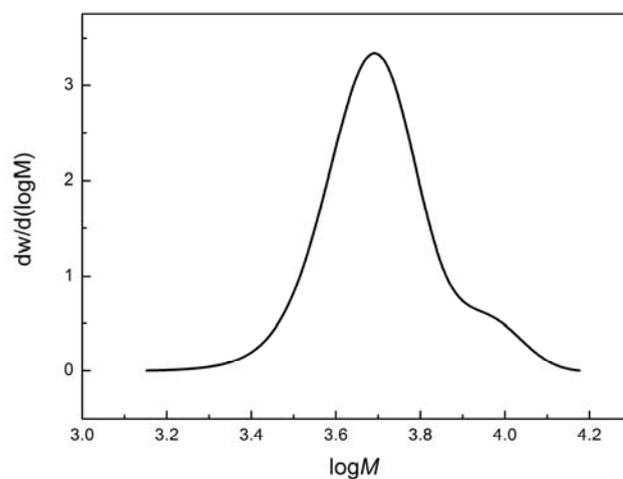


Figure S10. GPC plot of a representative sample of poly(CBO-*alt*-PA) ($M_n = 4.8$ Kg/mol, PDI = 1.10).

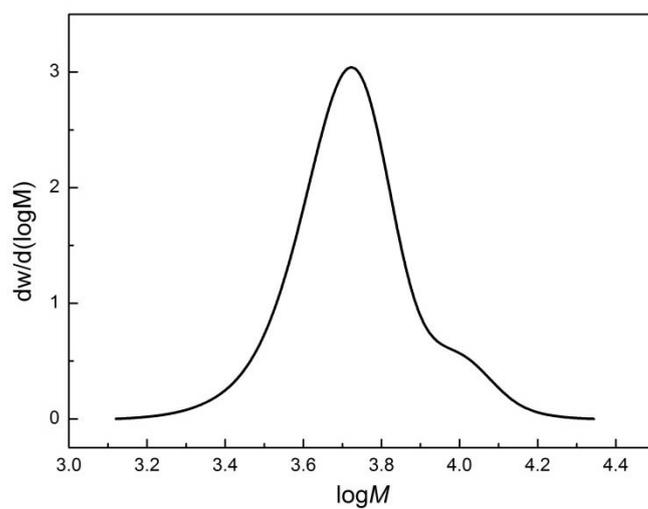


Figure S11. GPC plot of a representative sample of poly(CEO-*alt*-PA) ($M_n = 5.0$ Kg/mol, PDI = 1.13).

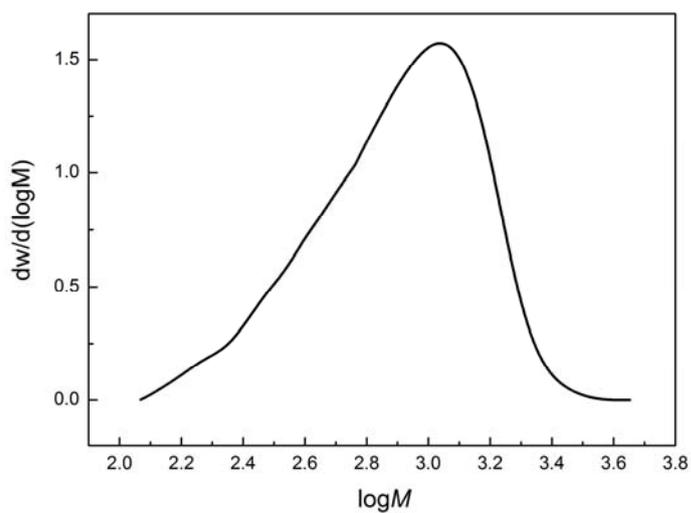


Figure S12. GPC plot of a representative sample of poly(CHO-*alt*-DGA) ($M_n = 0.5$ Kg/mol, PDI = 1.45).

6. ^1H and ^{13}C NMR spectra of polyesters.

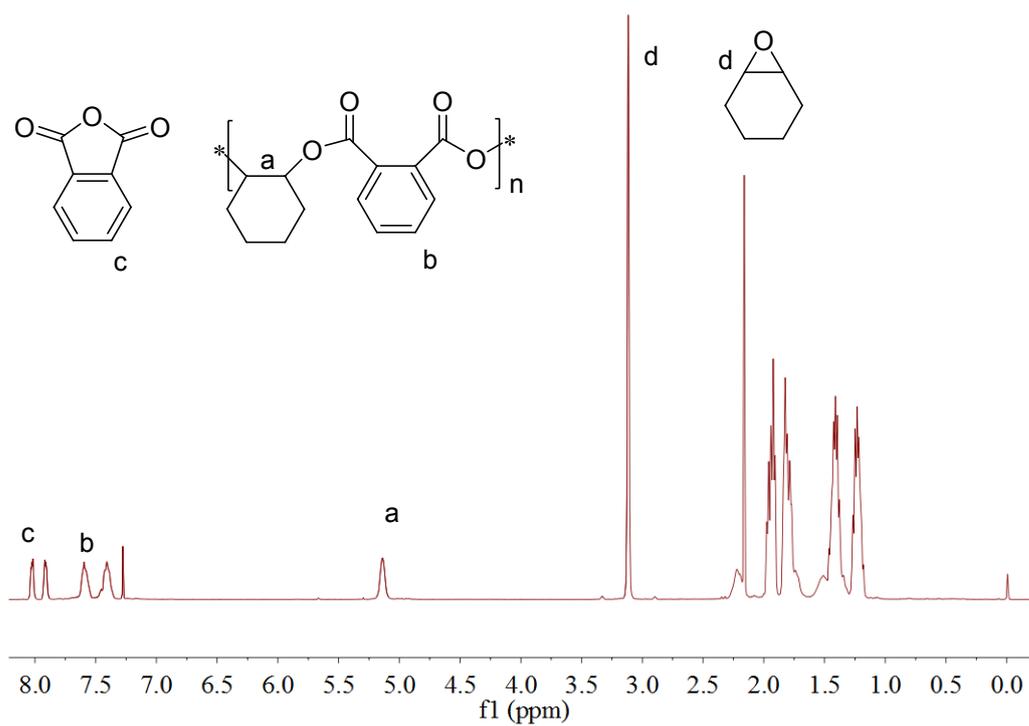


Figure S13. ^1H NMR spectrum of the sample from the reaction mixture of CHO/PA copolymerization in neat epoxide catalyzed by **3b**/PPNCl with 64% conversion of PA in CDCl_3 .

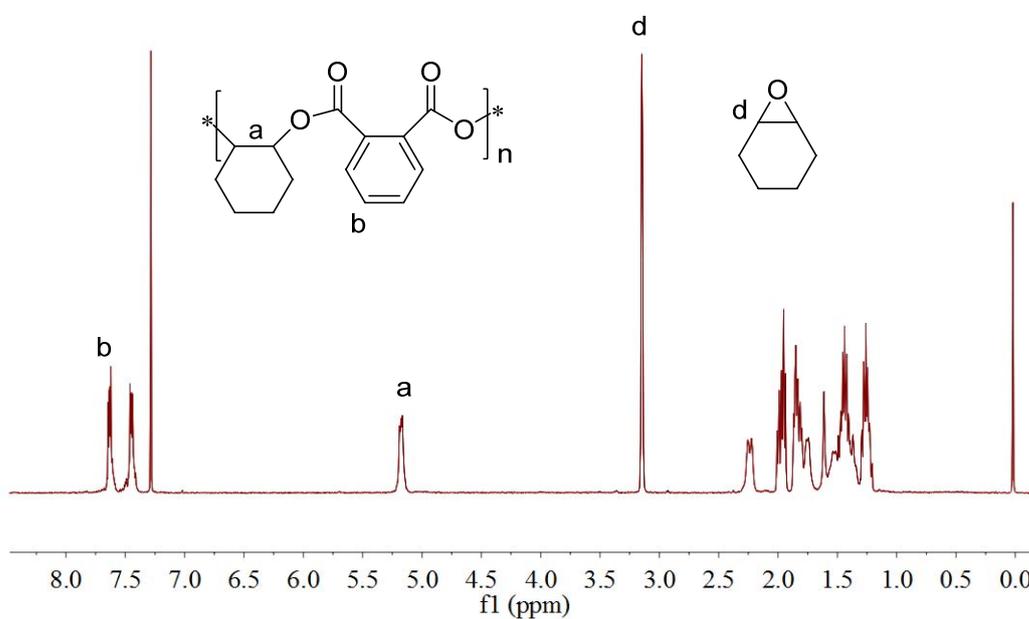


Figure S14. ^1H NMR spectrum of the sample from the reaction mixture of CHO/PA copolymerization in neat epoxide catalyzed by **3b**/PPNCl with 100% conversion of PA in CDCl_3 .

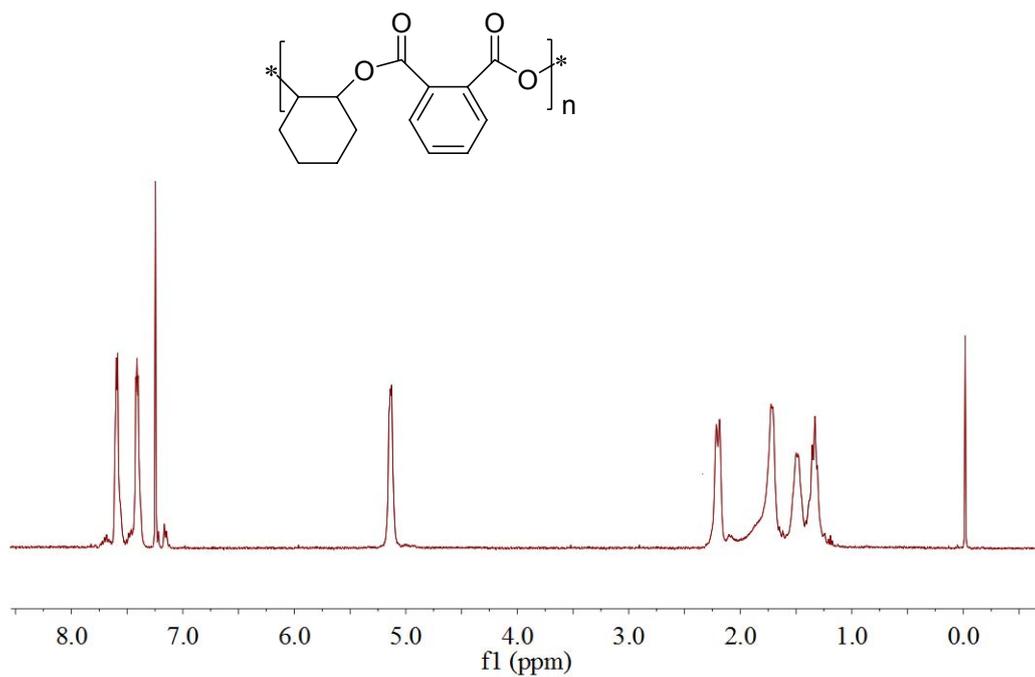


Figure S15. ¹H NMR spectrum of poly(CHO-*alt*-PA).

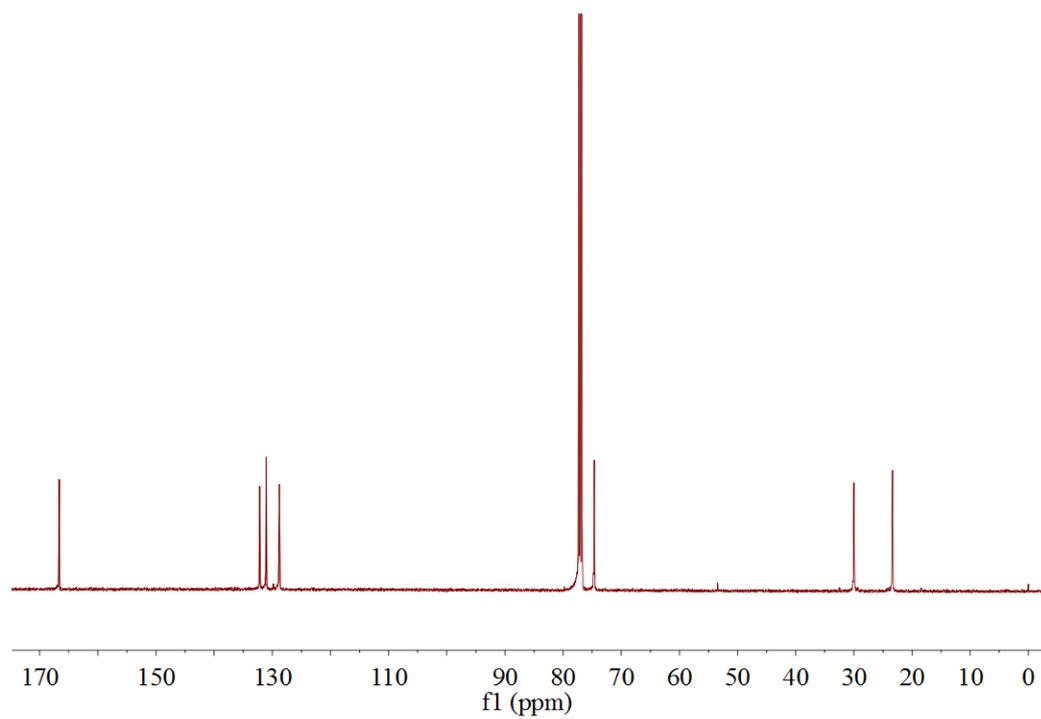


Figure S16. ¹³C NMR spectrum of poly(CHO-*alt*-PA).

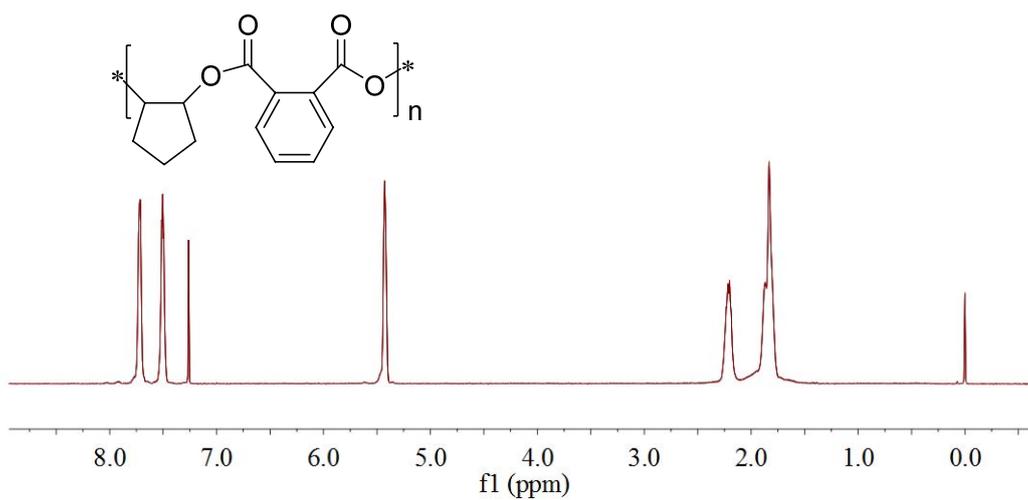


Figure S17. ¹H NMR spectrum of poly(CPO-*alt*-PA).

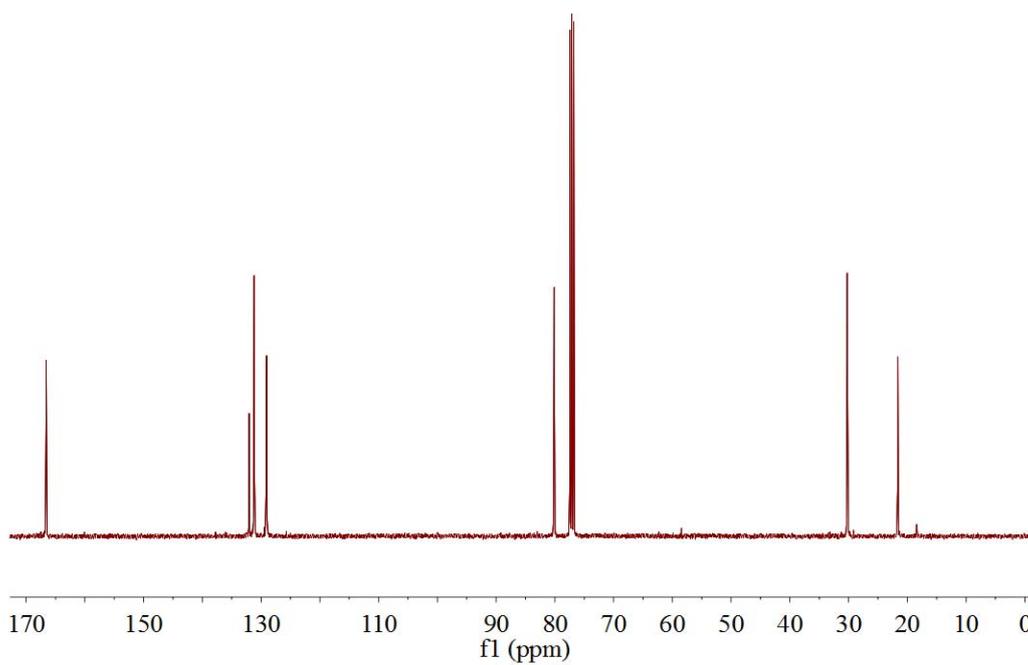


Figure S18. ¹³C NMR spectrum of poly(CPO-*alt*-PA).

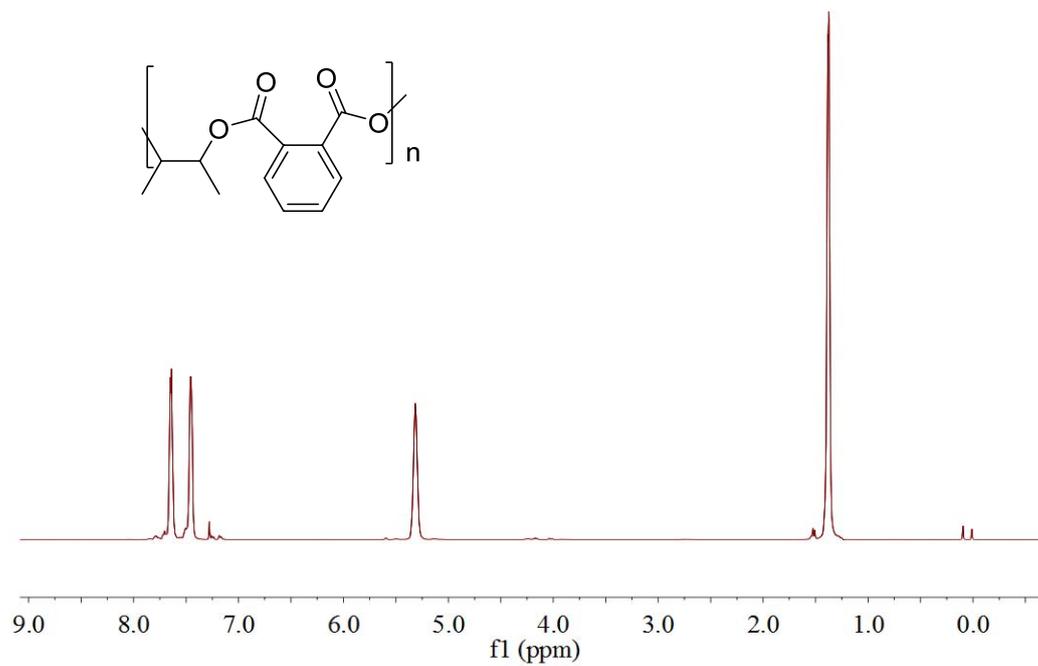


Figure S19. ¹H NMR spectrum of poly(CBO-*alt*-PA).

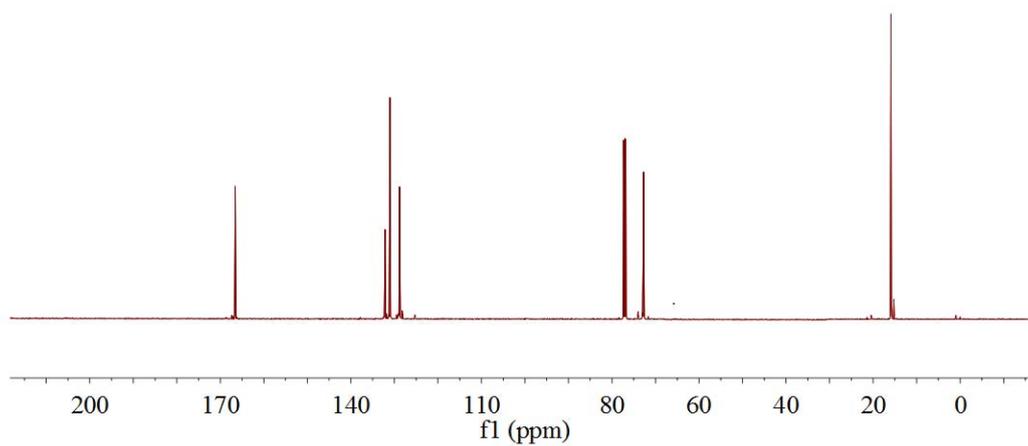


Figure S20. ¹³C NMR spectrum of poly(CBO-*alt*-PA).

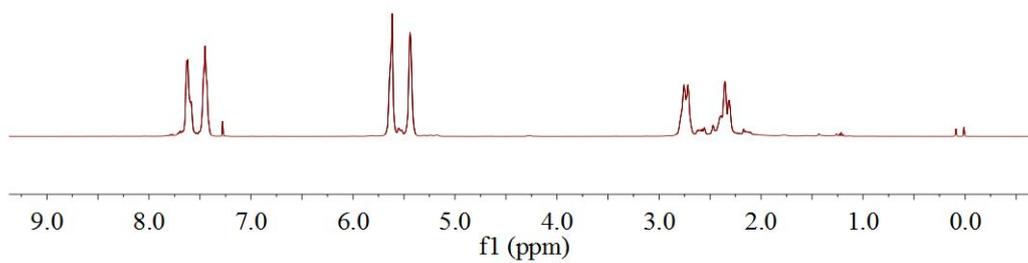
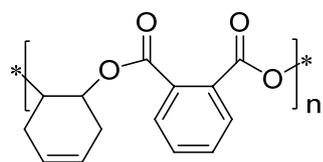


Figure S21. ¹H NMR spectrum of poly(CEO-*alt*-PA).

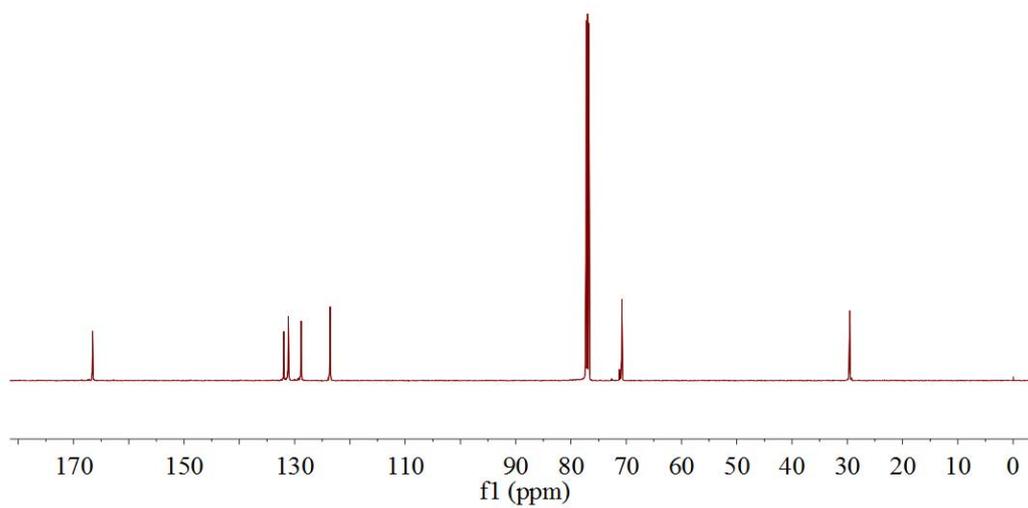


Figure S22. ¹³C NMR spectrum of poly(CEO-*alt*-PA).

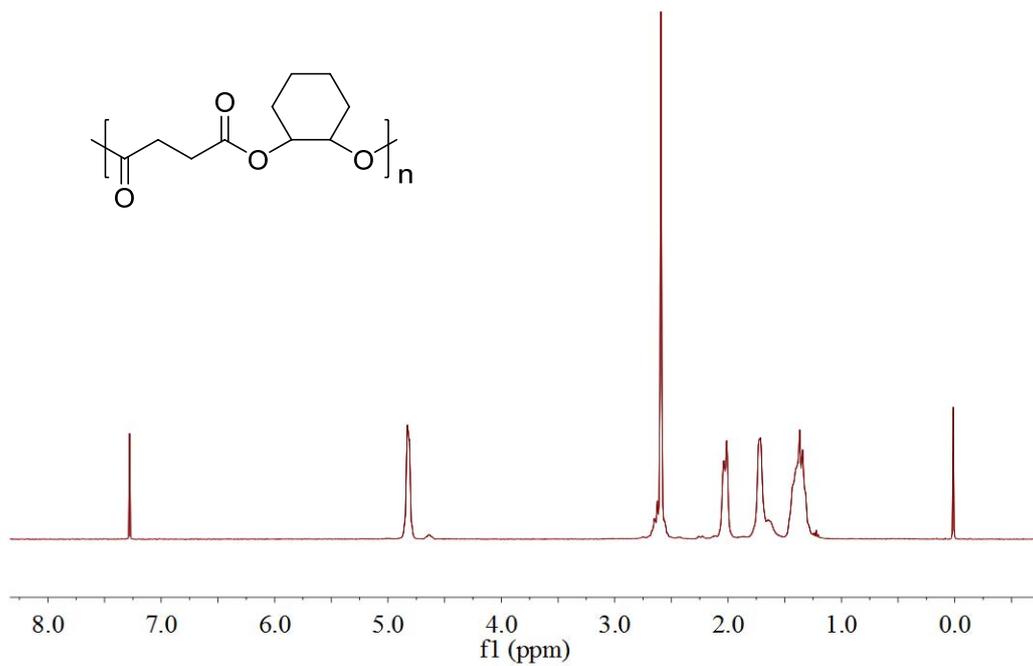


Figure S23. ¹H NMR spectrum of poly(CHO-*alt*-SA).

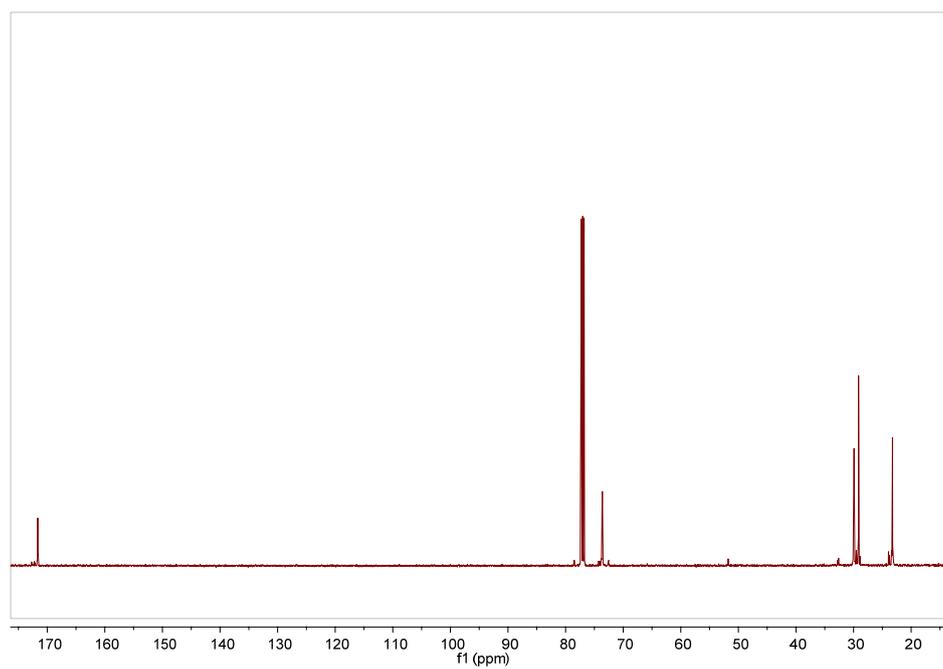


Figure S24. ¹³C NMR spectrum of poly(CHO-*alt*-SA).

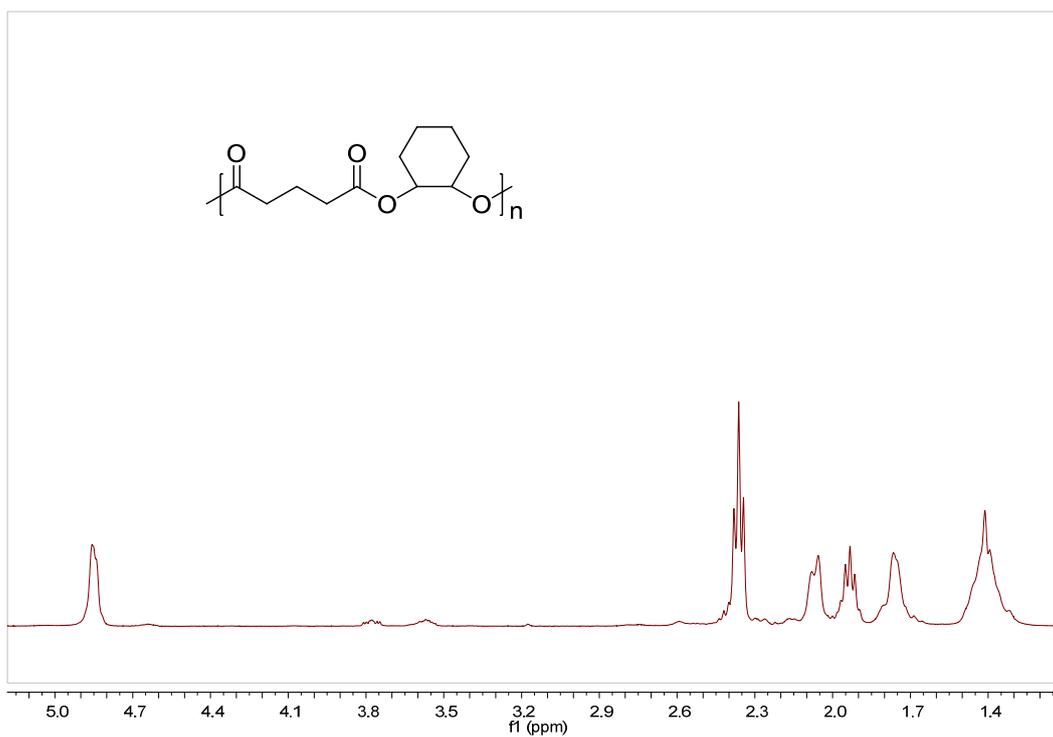


Figure S25. ¹H NMR spectrum of poly(CHO-*alt*-GA).

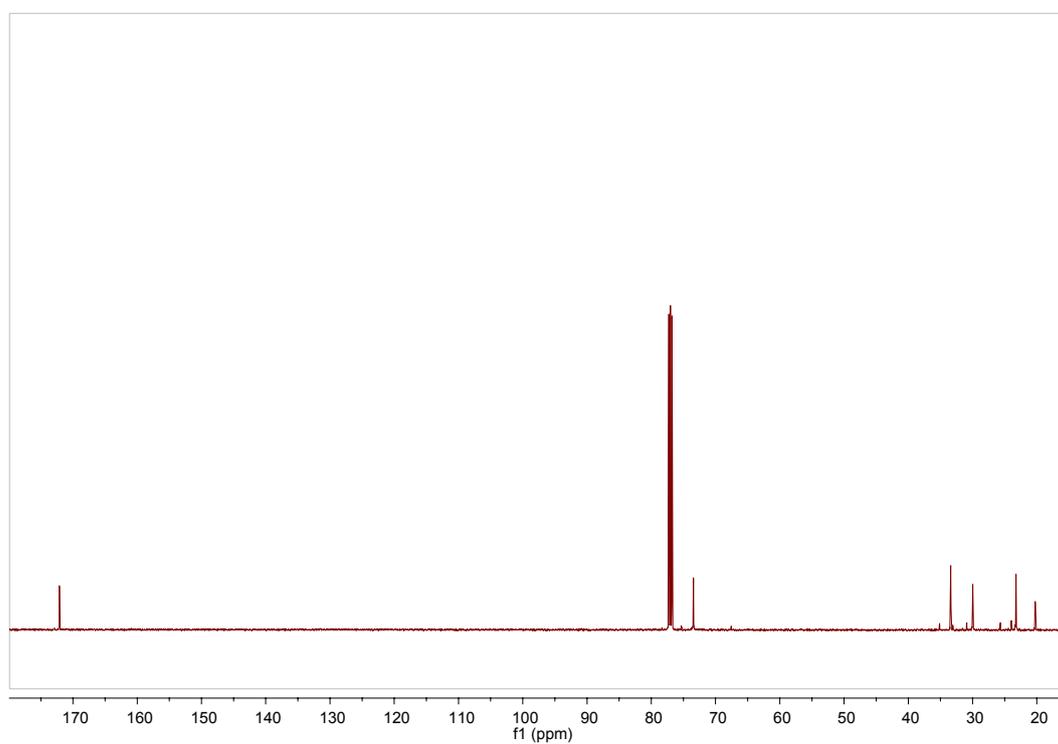


Figure S26. ¹³C NMR spectrum of poly(CHO-*alt*-GA).

7. DSC thermgrams of various polyesters.

For all DSC analysis, the result was given based on second cycle.

Poly(CHO-*alt*-PA): First cycle: from 20 °C to 100 °C at a heating rate of 10 K/min and holding at 100 °C for 2 h, and from 100 °C to 20 °C at a cooling rate of 10 K/min. Second cycle: from 20 to 260 °C at a heating rate of 10 K/min.

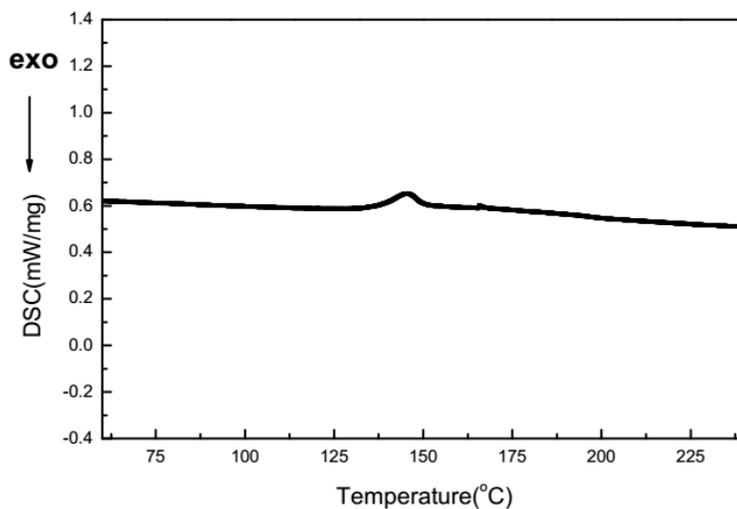


Figure S27. DSC thermgrams of poly(CEO-*alt*-PA).

Poly(CPO-*alt*-PA): First cycle: from 20 °C to 180 °C at a heating rate of 10 K/min and holding at 180 °C for 2 h, and from 180 °C to 20 °C at a cooling rate of 10 K/min. Second cycle: from 20 to 260 °C at a heating rate of 10 K/min.

Poly(CBO-*alt*-PA): First cycle: from 20 °C to 60 °C at a heating rate of 10 K/min and holding at 60 °C for 2 h, and from 60 °C to 20 °C at a cooling rate of 10 K/min. Second cycle: from 20 to 260 °C at a heating rate of 10 K/min.

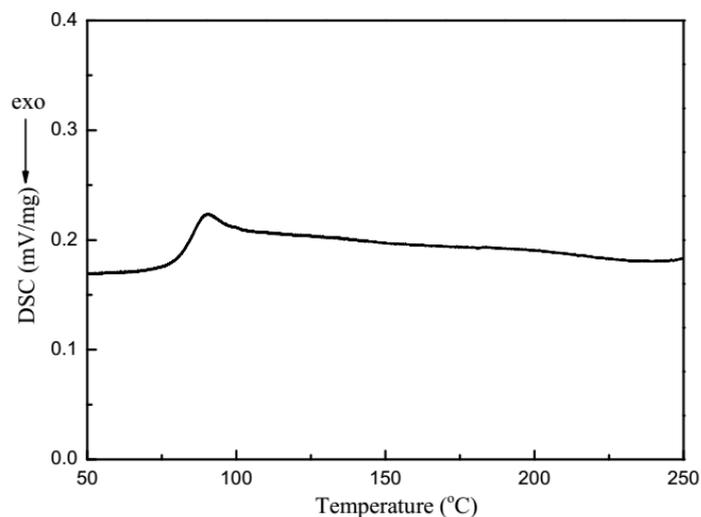


Figure S28. DSC thermgrams of poly(CBO-*alt*-PA).

Poly(CEO-*alt*-PA): First cycle: from 20 °C to 60 °C at a heating rate of 10 K/min and holding at 60 °C for 2 h, and from 60 °C to 20 °C at a cooling rate of 10 K/min. Second cycle: from 20 to 260 °C at a heating rate of 10 K/min.

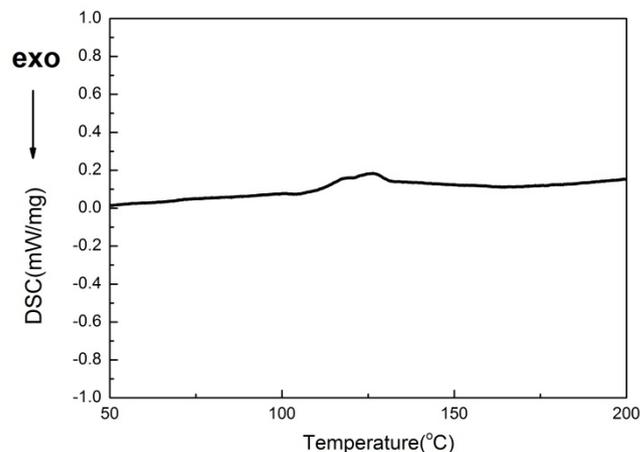


Figure S29. DSC thermgrams of poly(CEO-*alt*-PA).

Poly(CHO-*alt*-SA): First cycle: from 20 °C to 50 °C at a heating rate of 10 K/min and holding at 60 °C for 2 h, and from 60 °C to 20 °C at a cooling rate of 10 K/min. Second cycle: from 20 to 180 °C at a heating rate of 10 K/min.

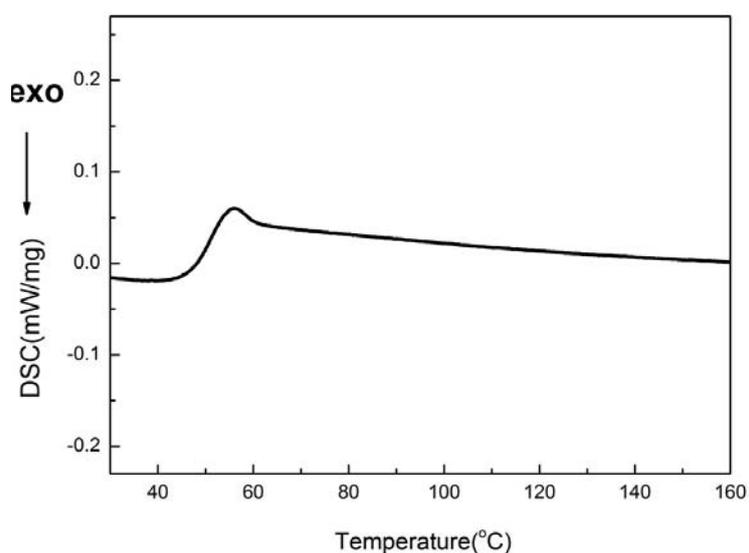


Figure S30. DSC thermgrams of poly(CHO-*alt*-SA).

Poly(CHO-*alt*-GA): First cycle: from 20 °C to 50 °C at a heating rate of 10 K/min and holding at 50 °C for 2 h, and from 60 °C to 20 °C at a cooling rate of 10 K/min. Second cycle: from 20 to 180 °C at a heating rate of 10 K/min.

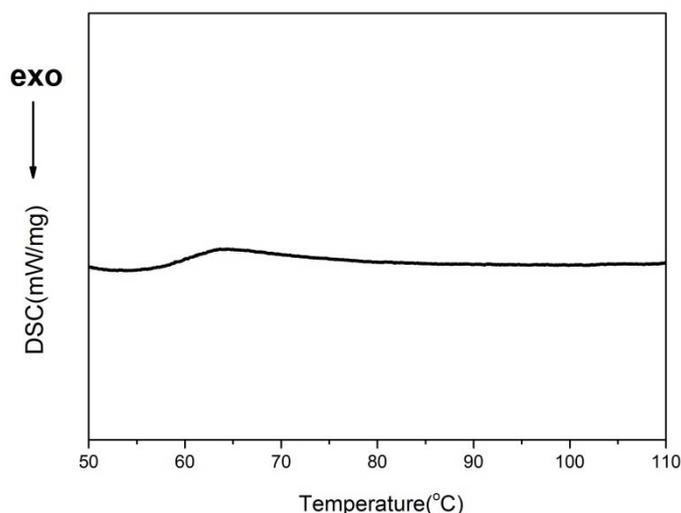


Figure S31. DSC thermograms of poly(CHO-*alt*-GA).

8. Determination of enantiomeric purity of polyesters

A round-bottomed flask was charged with polyesters (50 mg), THF (5 mL), MeOH (1 mL) and NaOH (4 M, 1 mL). The resultant mixture was stirred at room temperature for 24 h. Then, it was concentrated to 4 mL by evaporation. The solution was extracted with ethyl acetate (5 mL \times 3). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated by evaporation.⁴

The enantiomeric excess of the resultant diols were determined by GC analysis with a chiral GC column (Agilent HP-Chiral 19091G-B213, 30 m \times 0.25 mm id \times 0.25 μ m film) except for the cyclopentane diol (Hydrodex- β -TBDAC, 25m L x 0.25mm ID, from MACHEREYNAGEL).

Cyclohexane diol: Injection temp. = 275 °C; detection temp. = 275 °C; Oven temperature 120 °C.
t[(*S,S*)-diol] = 14.5 min, t[(*R,R*)-diol] = 15.5 min).

Cyclohex-1-ene-1,2-diol: Injection temp. = 275 °C; detection temp. = 275 °C; Oven temperature 120 °C.
t[(*S,S*)-diol] = 14.1 min, t [(*R,R*)-diol] = 15.5 min)

Butane-2,3-diol: Injection temp. = 275 °C; detection temp. = 275 °C; Oven temperature 120 °C.
t[(*S,S*)-diol] = 6.9 min, t[(*R,R*)-diol] = 7.5 min)

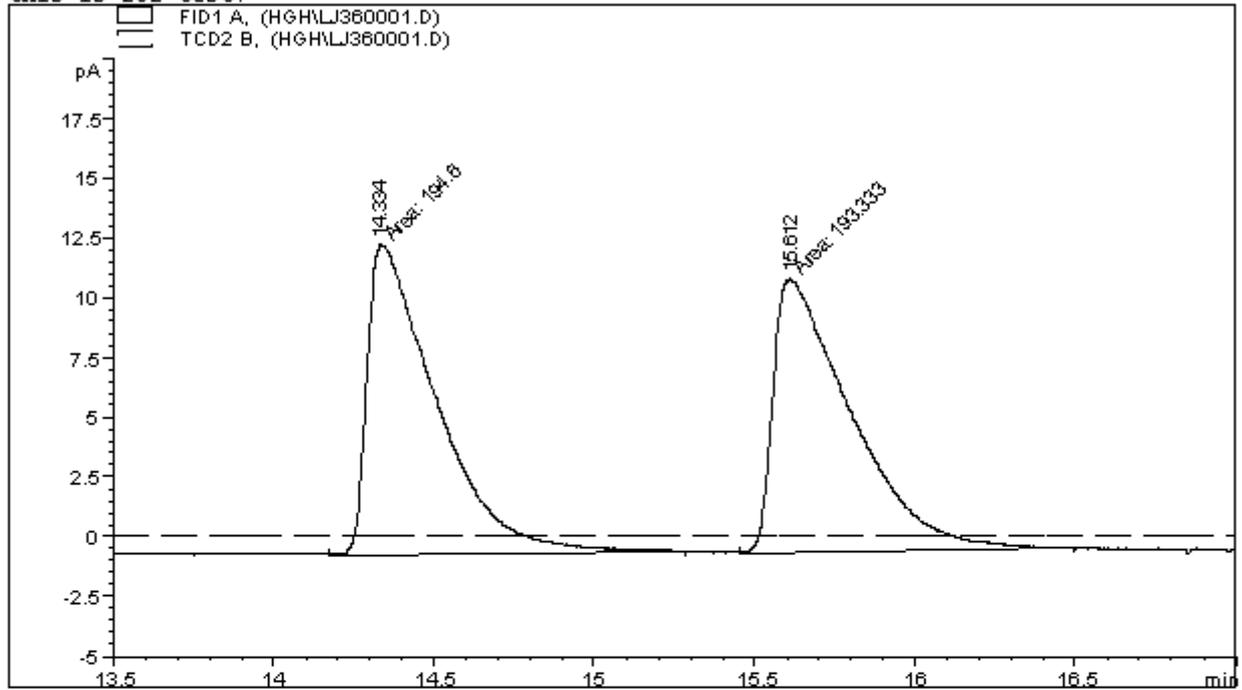
cyclopentane diol: Injection temp. = 200 °C; detection temp. = 200 °C; Oven temperature 150 °C.
t[(*S,S*)-diol] = 10.5 min, t[(*R,R*)-diol] = 11 min)

```

=====
Injection Date : 6/28/2016 3:32:52 PM
Sample Name    : LJ36                      Location : Vial 2
Acq. Operator  : HGH                      Inj     : 1
Acq. Instrument: Instrument 1             Inj Volume : Manually
Acq. Method    : C:\HPCHEM\1\METHODS\OAC-1.M
Last changed   : 6/28/2016 2:51:57 PM by LYN
                (modified after loading)
Analysis Method: C:\HPCHEM\1\METHODS\OAC-1.M
Last changed   : 7/7/2016 9:36:31 AM by LYN
                (modified after loading)

```

this is for test!



```

=====
                          Area Percent Report
=====

```

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
Use Multiplier & Dilution Factor with ISTDs

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.334	MM	0.2498	194.59953	12.98197	50.16324
2	15.612	MM	0.2797	193.33299	11.52042	49.83676

```
Totals :                      387.93253  24.50239
```

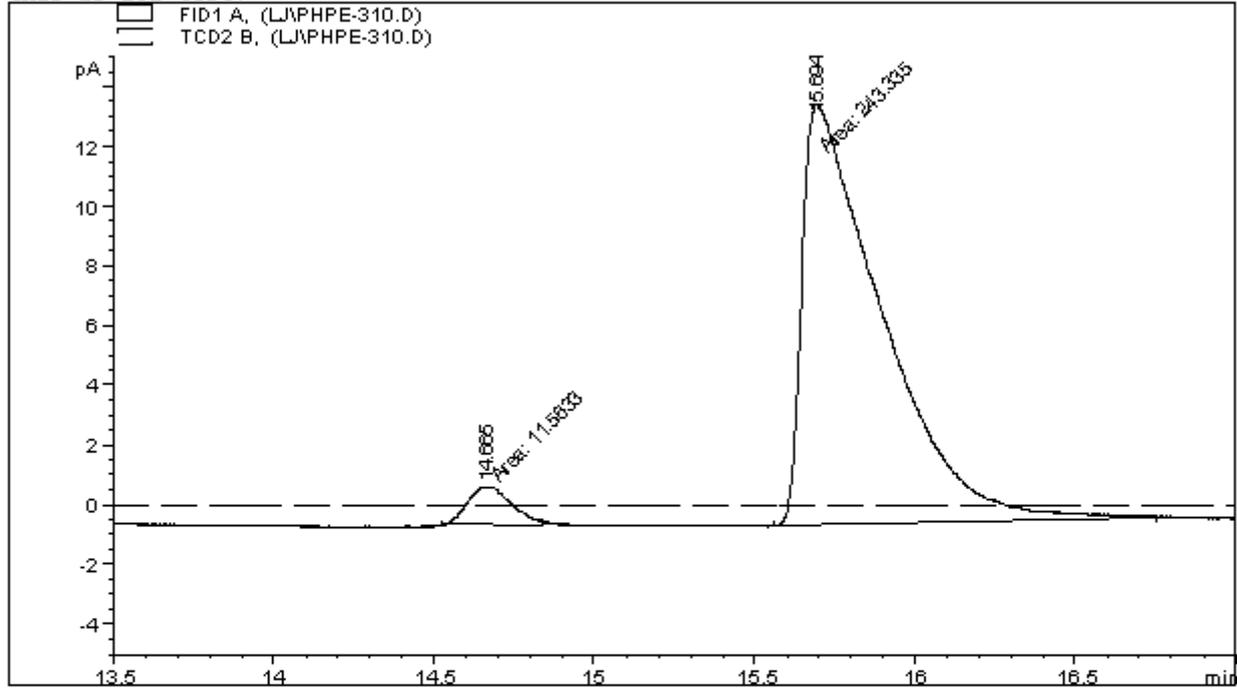
Results obtained with enhanced integrator!

PHPE-31

```

=====
Injection Date : 6/6/2016 6:51:27 PM
Sample Name    : PHPE-31                      Location : Vial 2
Acq. Operator  : LJ                          Inj      : 1
Acq. Instrument: Instrument 1                 Inj Volume: Manually
Acq. Method    : C:\HPCHEM\1\METHODS\OAC-1.M
Last changed   : 6/6/2016 6:51:16 PM by LJ   (modified after loading)
Analysis Method: C:\HPCHEM\1\METHODS\OFF3.M
Last changed   : 6/29/2016 2:29:29 PM by LYN (modified after loading)
    
```

this is for test!



Area Percent Report

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Use Multiplier & Dilution Factor with ISTDs
    
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.665	MM	0.1526	11.56328	1.26286	4.53643
2	15.694	MM	0.2874	243.33484	14.11126	95.46357

Totals : 254.89812 15.37411

Results obtained with enhanced integrator!

Figure S33. (R,R)-enriched cyclohexane-1,2-diol

9. Structure of dinuclear Al(III) complexes (*R,R,R,R,R*)-**3b** and (*R,R,S,R,R*)-**3b**^{3d}

The single crystal of dinuclear Al(III) complex (*R,R,R,R,R*)-**3b** (CCDC 943314) data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

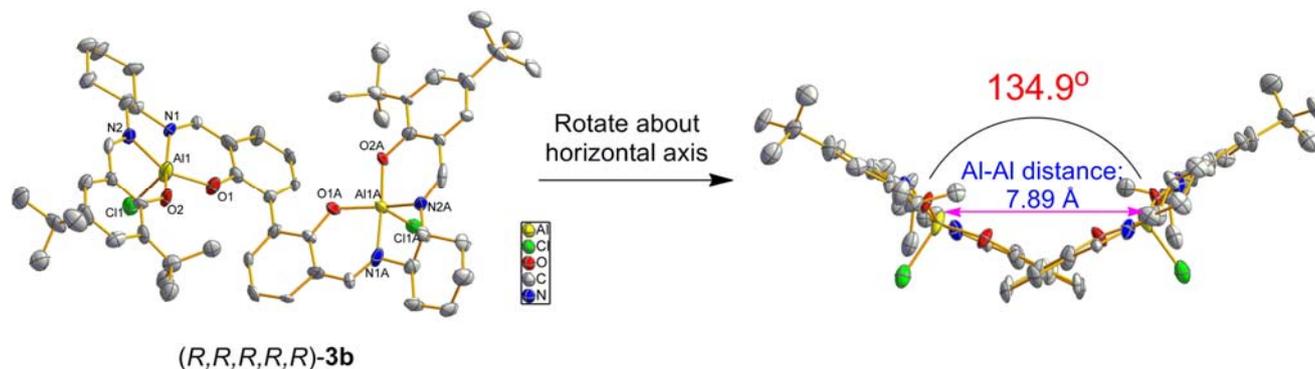


Figure S34. Molecular structure of (*R,R,R,R,R*)-**3b** (hydrogen atoms and uncoordinated solvent omitted for clarity; carbon atoms are unlabeled). Thermal ellipsoids are at the 30% probability level. It shows a Al–Al distance of 7.89 Å and endo phenol–phenol dihedral angle of 134.9°.

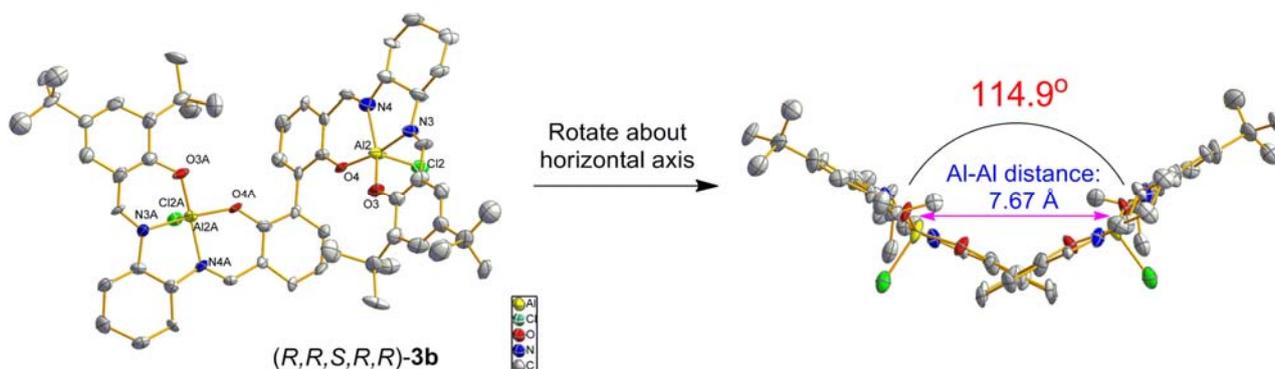


Figure S35. Molecular structure of (*R,R,S,R,R*)-**3b** (hydrogen atoms and uncoordinated solvent omitted for clarity; carbon atoms are unlabeled). Thermal ellipsoids are at the 30% probability level. It shows a Al–Al distance of 7.67 Å and endo phenol–phenol dihedral angle of 114.9°.

10. References.

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