Supporting Information

for

Construction of Polyphosphoesters with main chain of rigid backbone and stereostructure via Organocatalyzed Ring-Opening Polymerization

Yu-Jia Zheng,[§,†] Guan-Wen Yang,[§,‡] Bo Li,[*,†] and Guang-Peng Wu[*,‡]

[†]College of Material, Chemistry and Chemical Engineering, Hangzh ou Normal University, Hangzhou 310036, China

[‡]MOE Key Laboratory of Macromolecular Synthesis and Functionalization, and Key Laboratory of Adsorption and Separation Materials & Technologies of Zhejiang Province, Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China

Corresponding Authors

*E-mail: gpwu@zju.edu.cn (G.-P.W.).

*E-mail: boli@hznu.edu.cn. (B.L.).

Author Contributions

[§]Y.J.Z. and G.W.Y. contributed equally to this work.

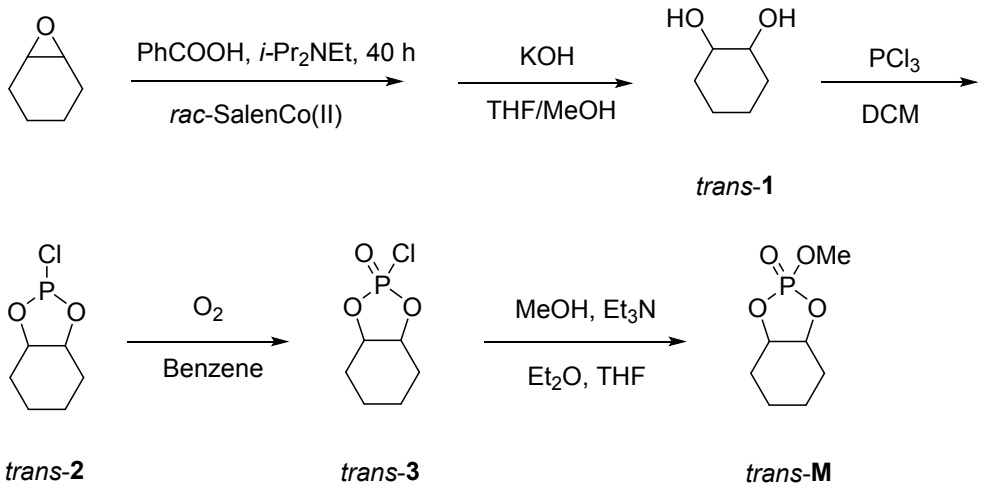
1. Materials and methods.

All manipulations involving air- and/or water-sensitive compounds were carried out in a glovebox under a nitrogen atmosphere. All reagents were commercially available and used directly unless otherwise stated. Toluene, ether, pyridine, and tetrahydrofuran (THF) were distilled under nitrogen from sodium/benzophenone. Triethylamine was distilled from calcium hydride under nitrogen. Methanol was distilled under nitrogen from Magnesium and iodine. *Rac*- or *(S,S)*-Co(II) was prepared as described in the literature[S1]. NMR spectra were recorded on Bruker Avance 400 MHz, 500 MHz or 600 MHz pectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals. DSC measurements were performed on a NETZSCH DSC 214 Polyma instrument (NETZSCH, Germany) equipped with an IC70 intra cooler and the temperatures range from -60 to 60 ^{o}C at heating/cooling rates of 10 K/min under nitrogen. Temperature and heat flow were calibrated by an indium standard. The glass transition temperature (T_g) was taken as the midpoint of the inflection tangent, upon the third heating scan. Thermogravimetric Analysis (TGA) measurements were performed on a TA-Q500 analyzer. Samples of about 5 mg were heated from room temperature to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. MALDI-TOF-MS analyses were performed on a Bruker Daltonics UltrafleXtreme system. Crude polymer samples

were dissolved in dichloromethane at 10 mg/mL. The matrix was chosen as α-cyano-4-hydroxycinnamic acid (HCCA). The resulting spectra were analyzed using the Bruker Daltonics flexAnalysis 3.4 software package.

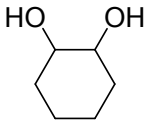
2. Synthetic procedures and characterization data

2.1 Synthesis of *trans*-**M**



Scheme S1. Synthetic routes of *trans*-**M** and chemical structures of compounds used in this work.

2.1.1 Trans-1,2-Cyclohexanediol (*trans*-**1**)



Trans-**1** was synthesized according to literature procedure[S2]. A solution of *rac*-SalenCo(II) (10.3 g, 10.2 mmol) and benzoic acid (136.9 g, 1.12 mmol) in TBME (100 mL) was stirred under O_2 for 1h. Volatile materials were removed in vacuo. The flask was recharged with nitrogen, *i*-Pr_2NEt (72.4 g, 0.56 mol) was added, and the stirred mixture was cooled to 4°C. Cyclohexene oxide (100 g, 1.02 mol) was added and the resulting dark brown solution was stirred at 4°C for 40 h. Then, the product mixture was diluted with ether (250 mL), washed with 1M HCI aq. (5 x 100 mL) and saturated $NaHCO_3$ aq. (2 x 100 mL), dried over $MgSO_4$, and filtered. The solution was concentrated in vacuo and the resulting solids were recrystallized 3 times from CH_2Cl_2/heptane to afford the product as colorless crystals (172 g, 76.6% yield).

To a solution of the previous products (152 g, 0.69 mol) in methanol (100 mL), potassium hydroxide (85 g, 1.52 mmol, 2.2 equiv) in THF (300 mL) was added at room temperature and stirred for 1.5 h. To the mixture, 1 M HCI aq. (100 mL) was added and extracted with diethyl ether (3 × 300 mL). The combined organic extract was washed with brine and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure, and purified by silica-gel column chromatography (*n*-hexane/EtOAc) to give *trans*-**1** (70 g, 87.4% yield). ^{1}H NMR (400 MHz, DMSO-d_6, 293K): 4.56 (s, 2H), 3.19 – 3.01 (m, 2H), 1.74 (dt, J = 9.9, 3.4 Hz, 2H), 1.55 (dd, J = 4.4, 2.4 Hz, 2H), 1.25 – 1.01 (m, 4H).

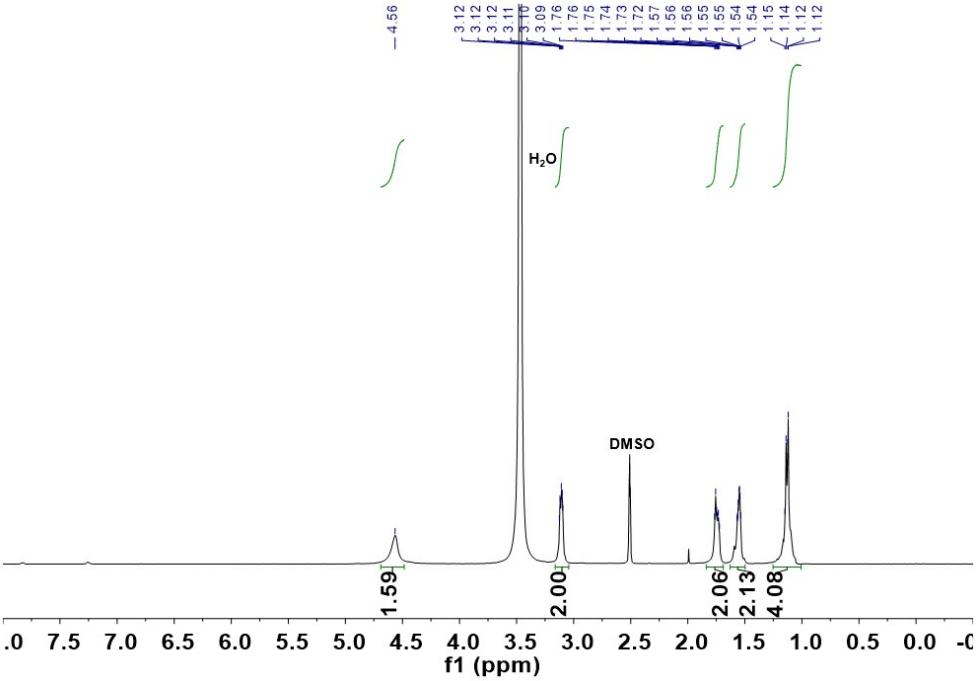
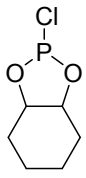


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293K) recorded for *trans*-**1**.

2.1.2 Trans-2-chlorohexahydrobenzo[d][1,3,2]dioxaphosphole (*trans*-**2**)



Into a solution of phosphorus trichloride (9.2 g, 66.8 mmol) in dichloromethane (100 mL), *trans*-**1** (0.67 M in dichloromethane, 100 mL) was added dropwise under nitrogen atmosphere. The mixture solution was then stirred for 1h. The solution was concentrated under reduced pressure, then fractionated distillation yielded the desired product as colorless oil (6.6 g, yield 55%, bp 76 °C, oil pump vacuum). ^{1}H NMR (600 MHz, $CDCl_3$, 293K):

4.13 – 3.90 (m, 1H), 3.48 (s, 1H), 2.35 (d, *J* = 11.9 Hz, 2H), 1.89 (d, *J* = 12.4 Hz, 2H), 1.68 – 1.50 (m, 2H), 1.44 – 1.17 (m, 2H).

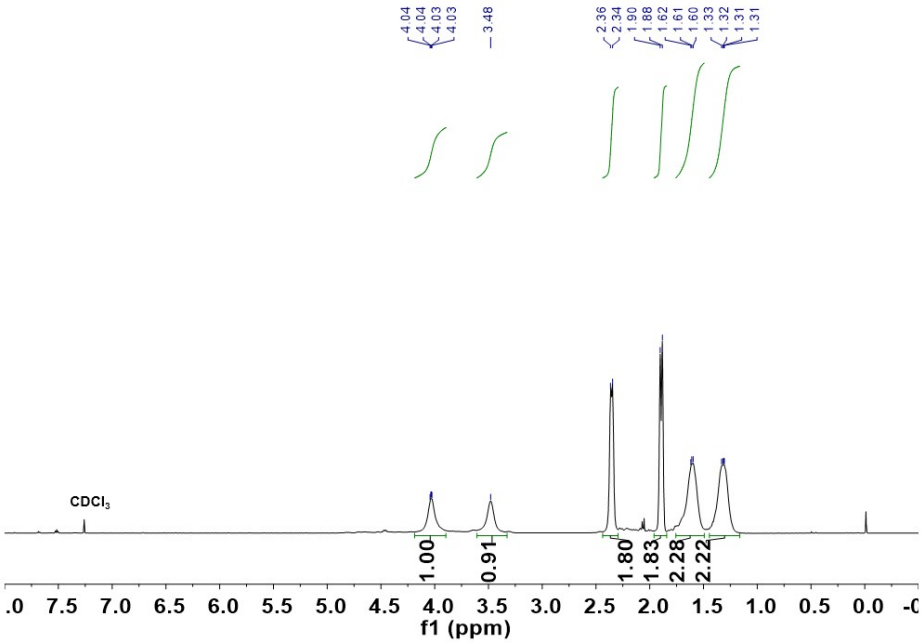
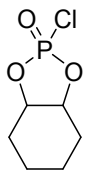


Figure S2. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 293K) recorded for *trans*-**2**.

2.1.3 Trans-2-chlorohexahydrobenzo[d][1,3,2]dioxaphosphole 2-oxide (*trans*-**3**)



A solution of *trans*-**2** (5 g, 27.7 mmol) in anhydrous toluene (50 mL) was stirred at 50 ^{o}C under O_2 atmosphere for 24 h. The solution was concentrated under reduced pressure, then fractionated distillation yielded the desired product as colorless oil (3.1g, yield 57%, bp 130 °C, oil pump vacuum). ^{1}H NMR (500 MHz, $CDCl_3$, 293K): 4.33 – 4.14 (m, 2H), 2.34 – 2.21 (m, 2H), 1.98 – 1.85 (m, 2H), 1.70 (ddd, *J* = 35.9, 11.8, 3.9 Hz, 2H), 1.45 – 1.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 293K): 86.0, 84.7, 29.8, 29.5, 29.1, 23.5.

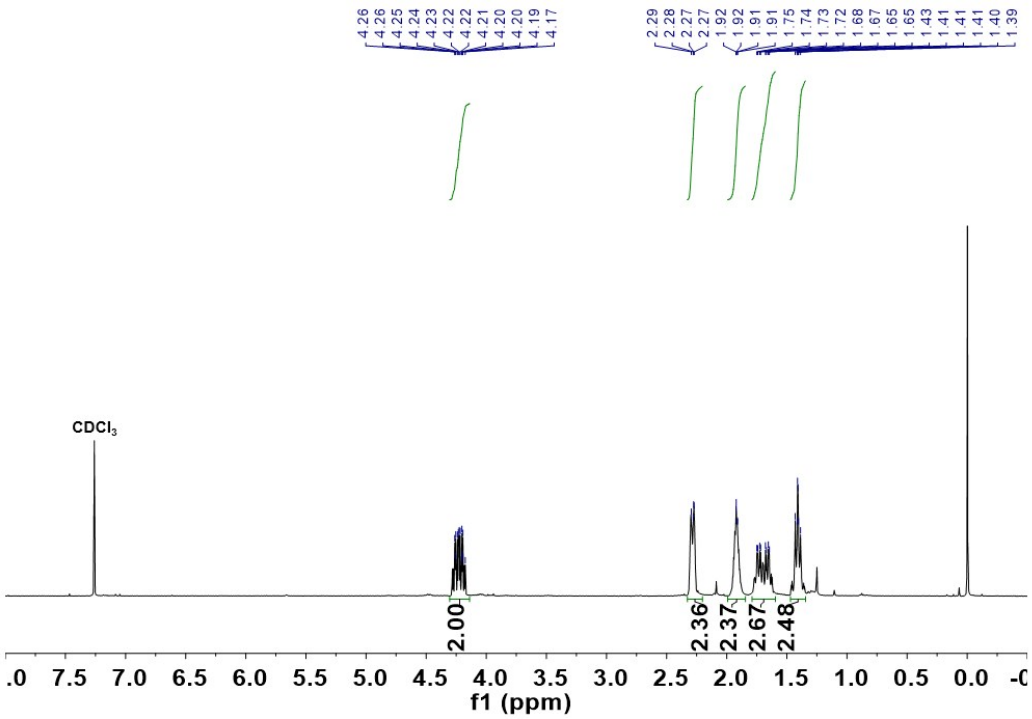


Figure S3. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 293K) recorded for *trans*-**3**.

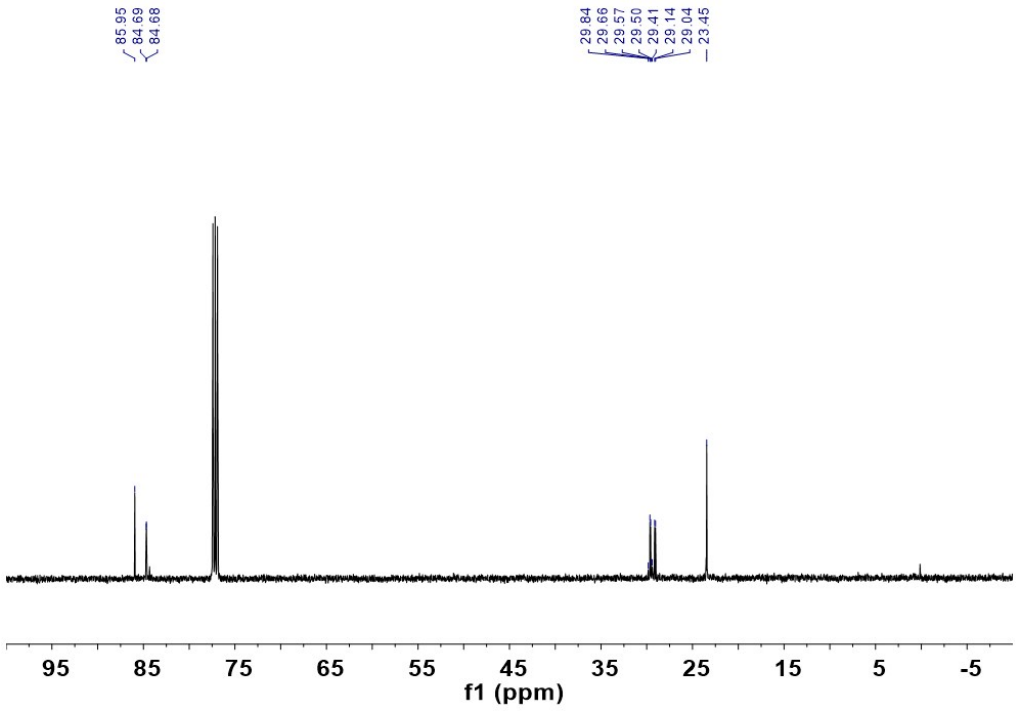
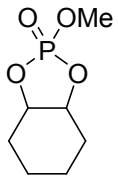


Figure S4. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 293K) recorded for *trans*-**3**.

2.1.4 Trans-2-methoxyhexahydrobenzo[d][1,3,2]dioxaphosphole 2-oxide (*trans*-**M**)



A solution of dry methanol (0.49 g, 15.3 mmol) and dry triethylamine (1.5 g, 15.3 mmol) in dry ether (20 mL) was added dropwise to a stirred solution of *trans*-**3** (3 g, 15.3 mmol) in dry ether (100 mL) at -5 °C within 1 h. Triethylamine hydrochloride is removed by filtration. The solution was concentrated under reduced pressure, then fractionated distillation yielded the desired product as colorless oil (2.2g, yield 73%, bp 145 °C, oil pump vacuum). $[\alpha]_D^{20}$ = - 0.8 (*c* = 1 g/mL, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 293K): 4.18 – 4.07 (m, 1H), 4.06 – 3.95 (m, 1H), 3.86 (d, *J* = 11.7 Hz, 3H), 2.20 (d, *J* = 11.9 Hz, 2H), 1.87 (d, *J* = 6.5 Hz, 2H), 1.73 – 1.51 (m, 2H), 1.46 – 1.32 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 293K): 84.2, 55.3, 29.6, 29.5, 29.4, 23.6, 1.2.

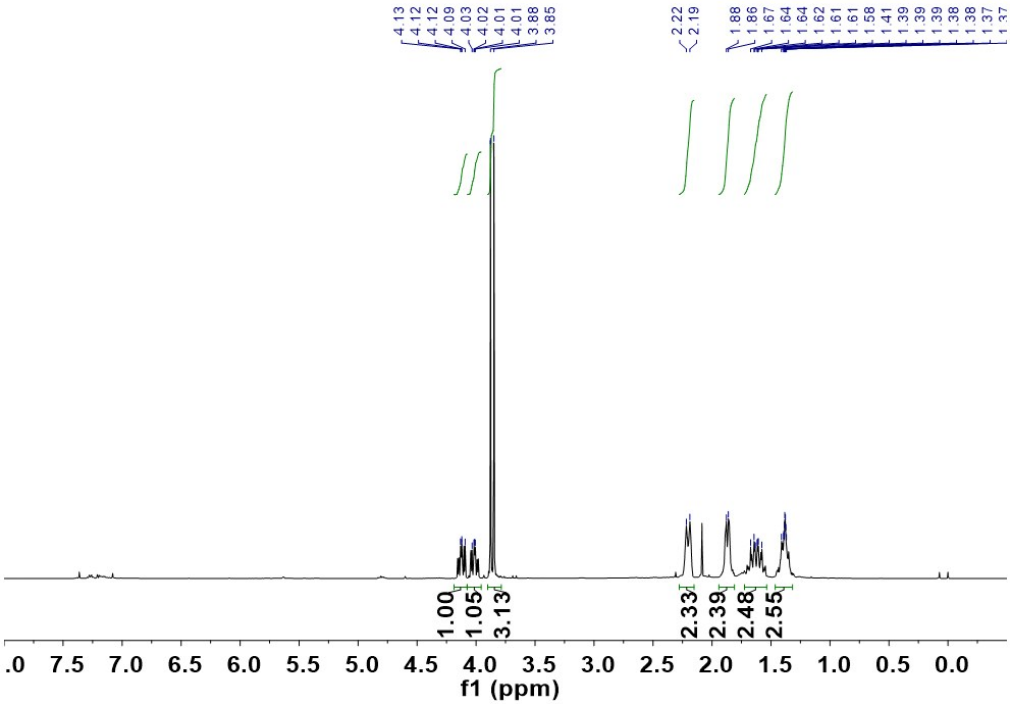


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293K) recorded for *trans*-**M**.

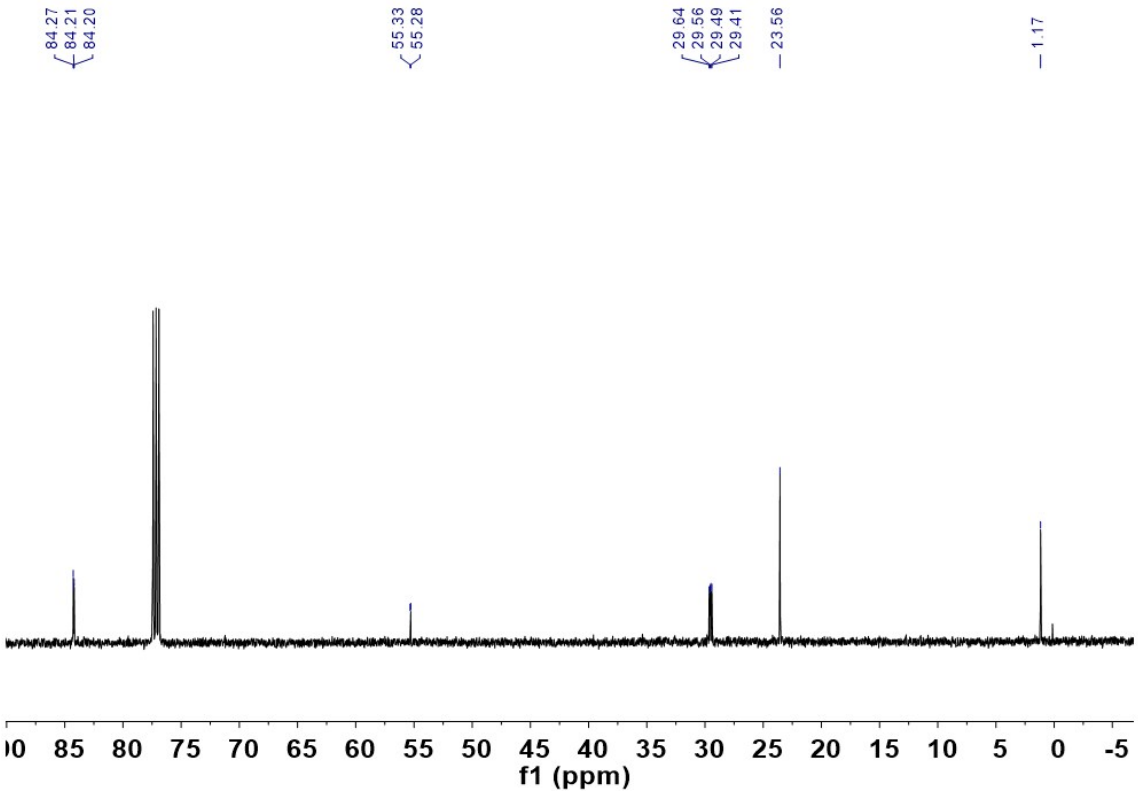
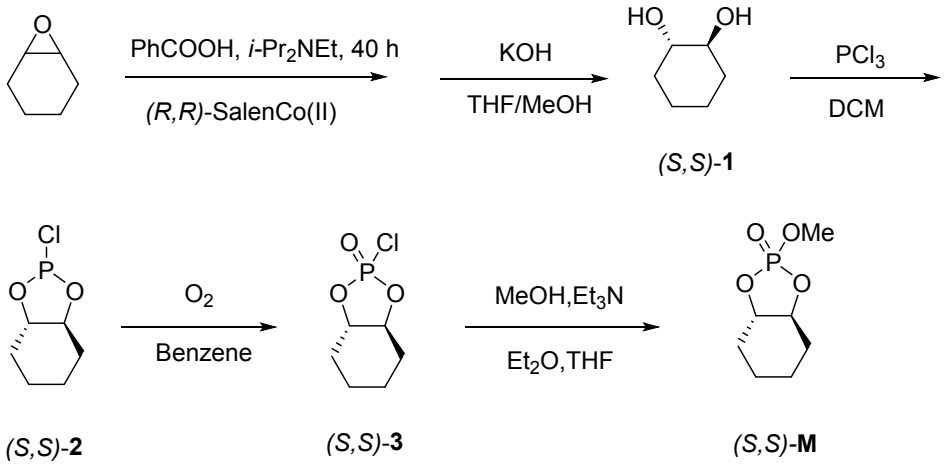


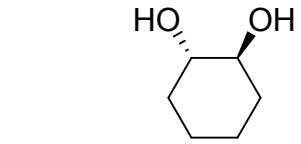
Figure S6. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 293K) recorded for *trans*-**M**.

2.2 Synthesis of *(S,S)*-**M**



Scheme S2. Synthetic routes of *(S,S)*-**M** and chemical structures of compounds used in this work.

2.2.1 (S,S)-1,2-Cyclohexanediol (*(S,S)*-**1**)



(1*S*,2*S*)-cyclohexane-1,2-diol

Compound *(S,S)*-**1** was synthesized using the same procedure as that of *trans*-**1**. Yield: 85%. ^{1}H NMR (400 MHz, DMSO-d_6, 293K): 4.72 (s, 2H), 3.10 (dd, J = 6.3, 3.5 Hz, 2H), 1.83 – 1.66 (m, 2H), 1.62 – 1.49 (m, 2H), 1.20 – 1.04 (m, 4H).

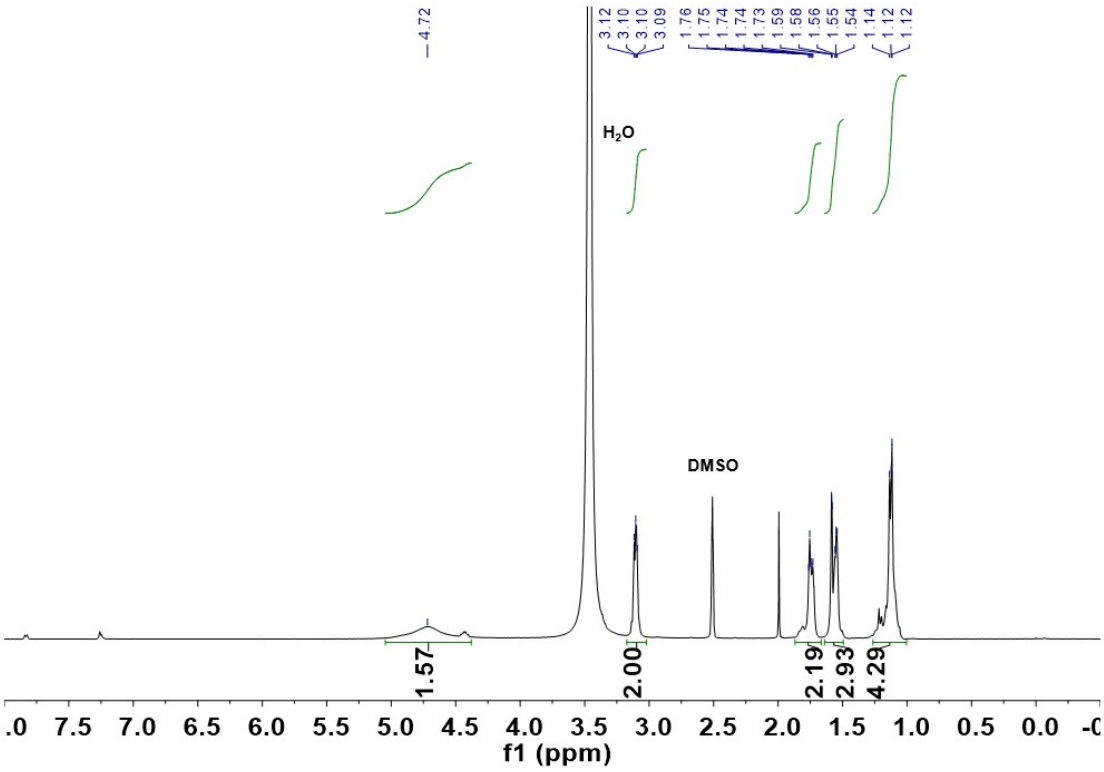
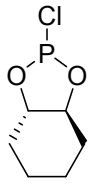


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293K) recorded for *(S,S)*-**1**.

2.2.2 (S,S)-2-chlorohexahydrobenzo[d][1,3,2]dioxaphosphole (*(S,S)*-**2**)



Compound *(S,S)*-**2** was synthesized using the same procedure as that of *trans*-**2**. Yield: 60%. bp 74 °C, oil pump vacuum. ^{1}H NMR (500 MHz, $CDCl_3$, 293K): 4.05 (s, 1H), 3.48 (d, J = 3.8 Hz, 1H), 2.37 (s, 2H), 1.95 – 1.83 (m, 2H), 1.75 – 1.52 (m, 2H), 1.46 – 1.26 (m, 2H).

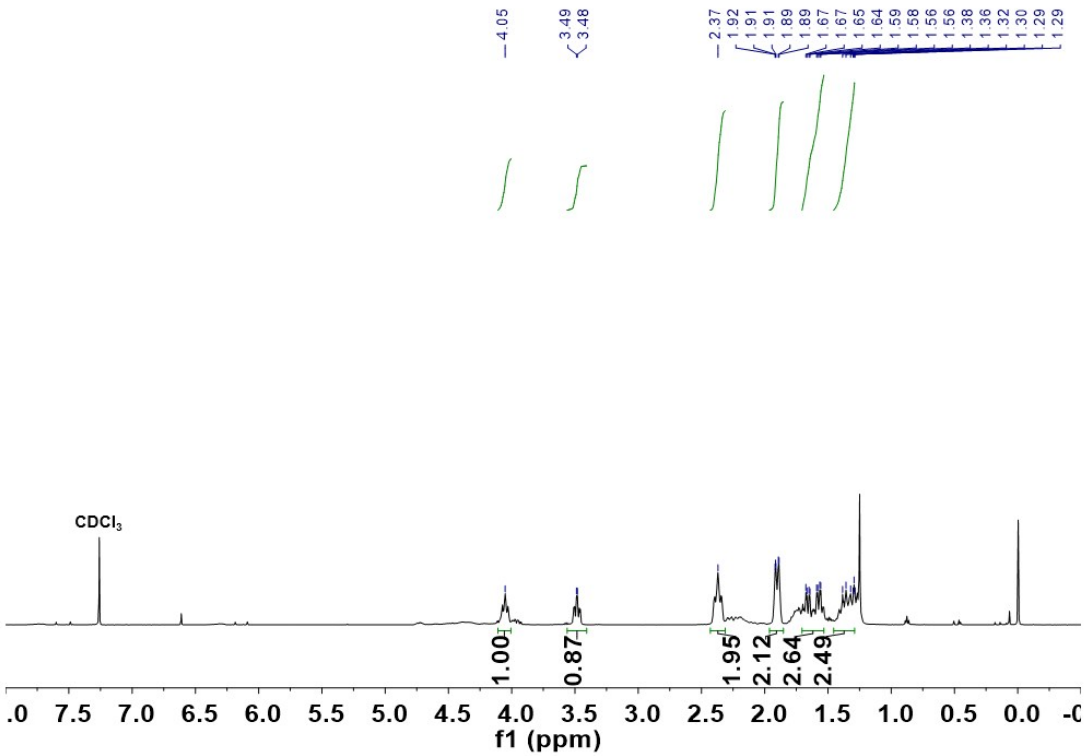
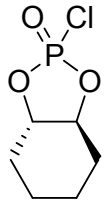


Figure S8. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 293K) recorded for *(S,S)*-**2**.

2.2.3 (S,S)-2-chlorohexahydrobenzo[d][1,3,2]dioxaphosphole 2-oxide (*(S,S)*-**3**)



Compound *(S,S)*-**3** was synthesized using the same procedure as that of *trans*-**3**. Yield: 58%. bp 130 °C, oil pump vacuum. ^{1}H NMR (500 MHz, $CDCl_3$, 293K): 4.32 – 4.15 (m, 2H), 2.28 (dd, J = 11.3, 4.0 Hz, 2H), 1.92 (d, J = 5.3 Hz, 2H), 1.80 – 1.59 (m, 2H), 1.47 – 1.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 293K): 86.0, 84.7, 29.8, 29.5, 29.1, 23.5.

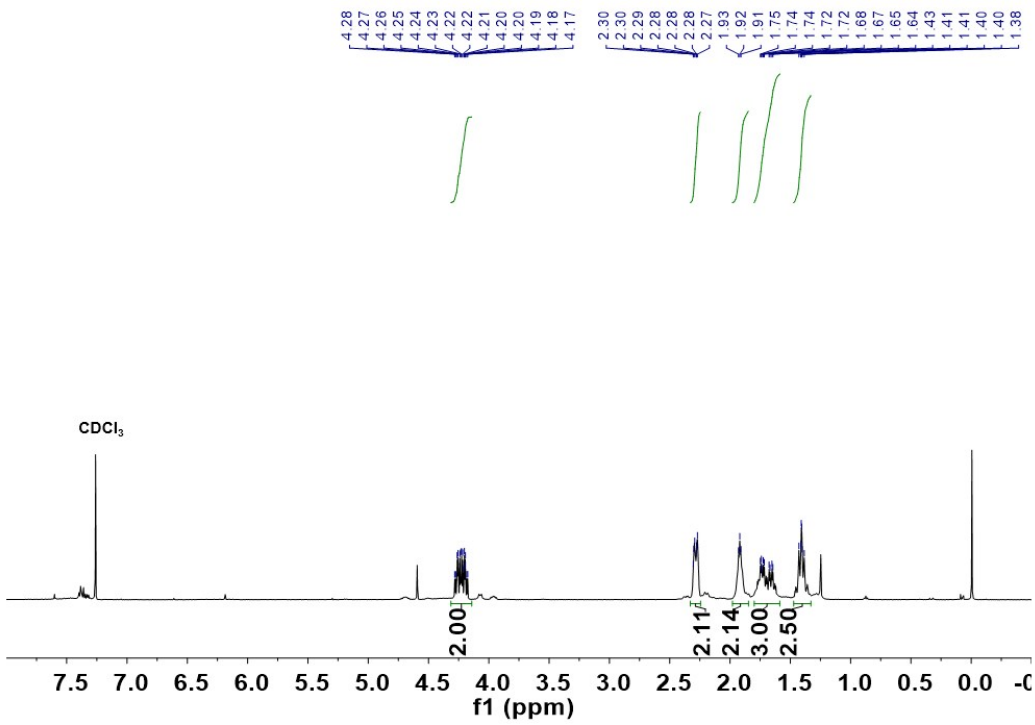


Figure S9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 293K) recorded for *(S,S)*-**3**.

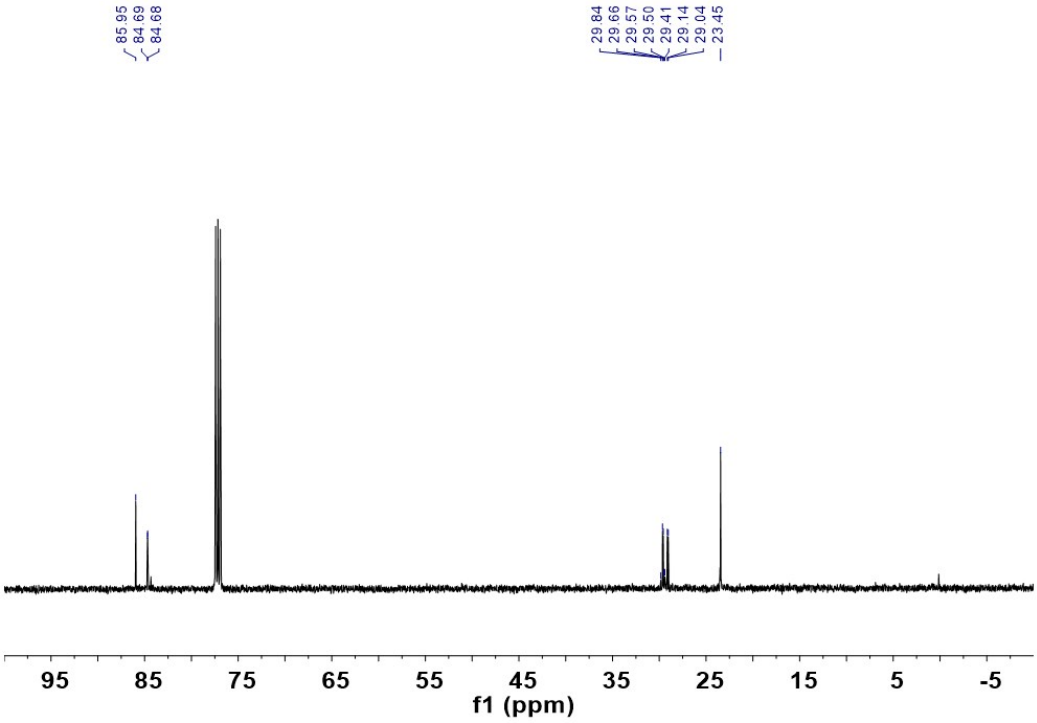
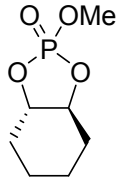


Figure S10. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 293K) recorded for *(S,S)*-**3**.

2.2.4 (S,S)-2-methoxyhexahydrobenzo[d][1,3,2]dioxaphosphole 2-oxide (*(S,S)*-**M**)



Compound *(S,S)*-**M** was synthesized using the same procedure as that of *trans*-**M**. Yield: 77%. bp 143 °C, oil pump vacuum. $[\alpha]_D^{20}$ = + 6.6 (*c* = 1 g/mL, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 293K): 4.18 – 4.07 (m, 1H), 4.05 – 3.94 (m, 1H), 3.87 (d, *J* = 11.7 Hz, 3H), 2.24 – 2.16 (m, 2H), 1.86 (d, *J* = 9.1 Hz, 2H), 1.62 (dd, *J* = 37.6, 11.9 Hz, 2H), 1.41 – 1.30 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 293K): 84.3, 55.3, 29.6, 29.5, 29.4, 23.5, 1.1.

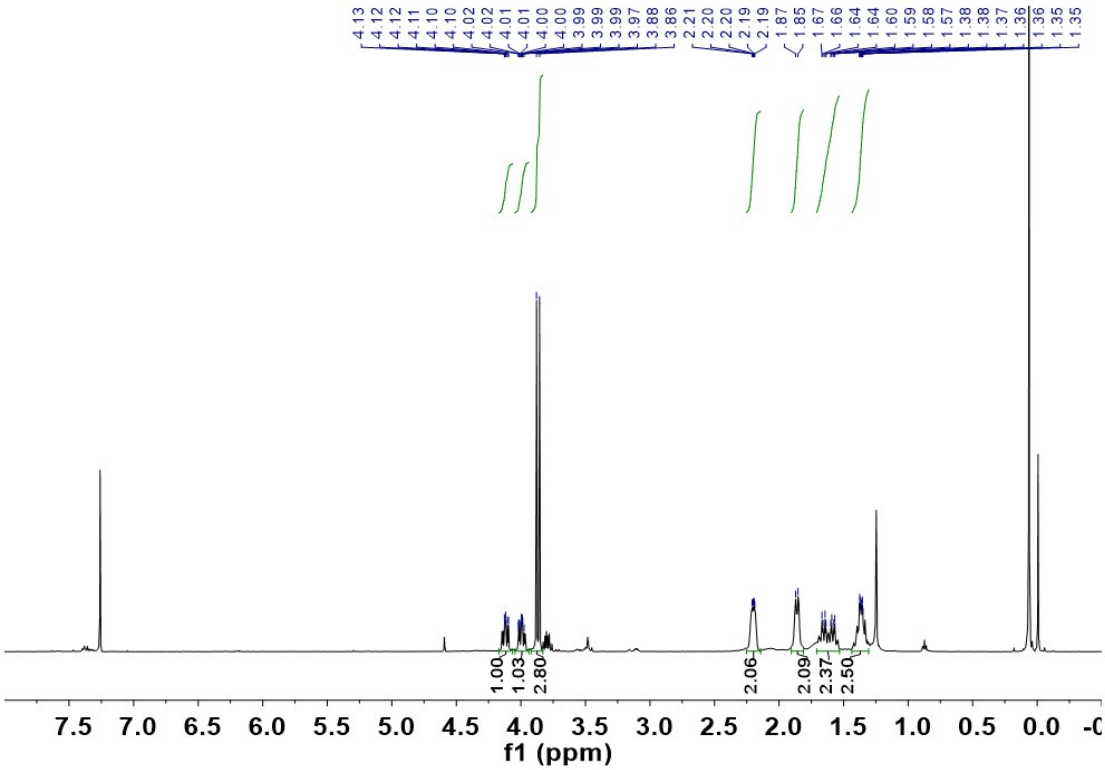


Figure S11. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 293K) recorded for *(S,S)*-**M**.

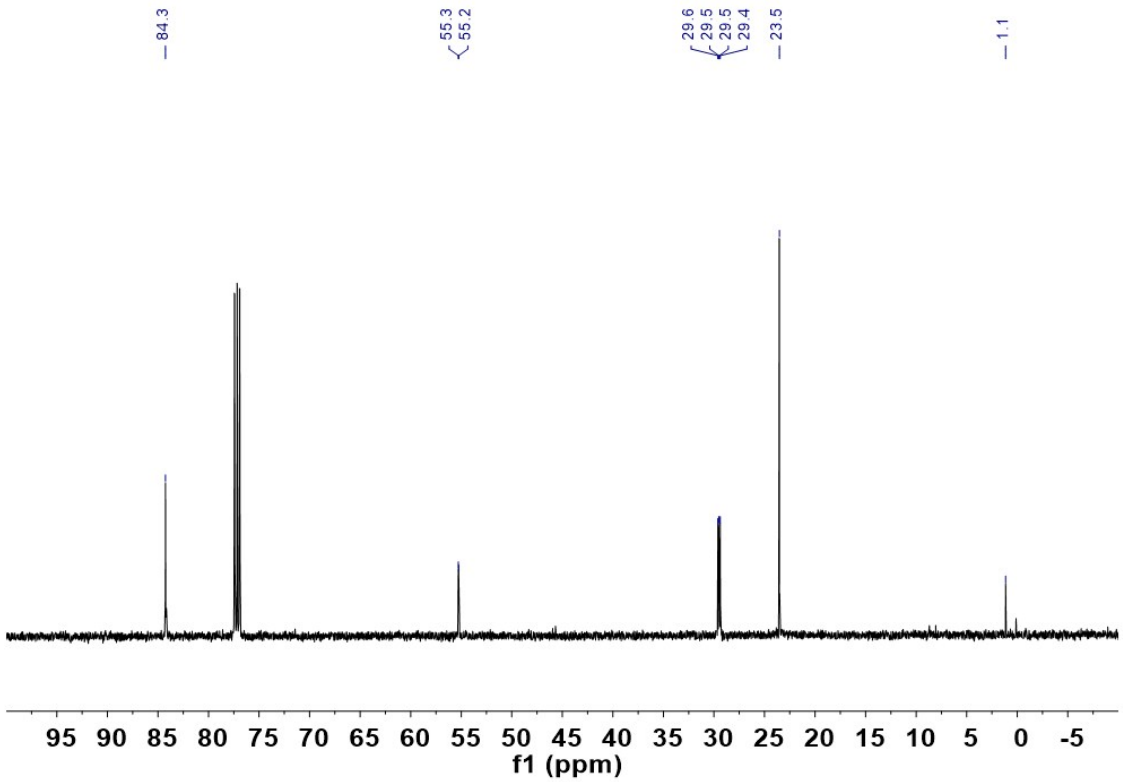


Figure S12. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 293K) recorded for *(S,S)*-**M**.

2.3 *Preparation of polyphosphoesters*

Representative procedure for ring-opening polymerization of *trans*-**M** in the presence of DBU/TU: The monomer *trans*-**M** (0.24 g, 1.25 mmol) in chloroform (0.5 mL) was added into a dry Schlenk-tube which recharged with nitrogen and stirred at setting temperature. Then benzylalcohol (1.4 mg, 0.0125 mmol) was transferred to the Schlenk-tube. The polymerization was started by the rapid addition of 0.5 mL chloroform solution of DBU (3.8 mg，0.025 mmol) and TU (5.8 mg，0.025 mmol) .The polymerization was terminated by an excess of benzoic acid dissolved in dichloromethane (10 mg, 1 mL). The polymer was purified by ether precipitation for three times and dried *in vacuo*. ^{1}H NMR (400 MHz, $CDCl_3$, 293K): δ 7.55 – 7.20 (m, 5H), 5.02 – 4.90 (m, 2H), 3.86-3.62 (m 2H), 3.47 (d, J = 11.7 Hz, 3H), 2.10 (s, 2H), 1.67 (d, J = 6.5 Hz, 4H), 1.46 – 1.32 (m, 2H).

3. Ring-opening polymerization of (S,S)-M with methanol as initiator

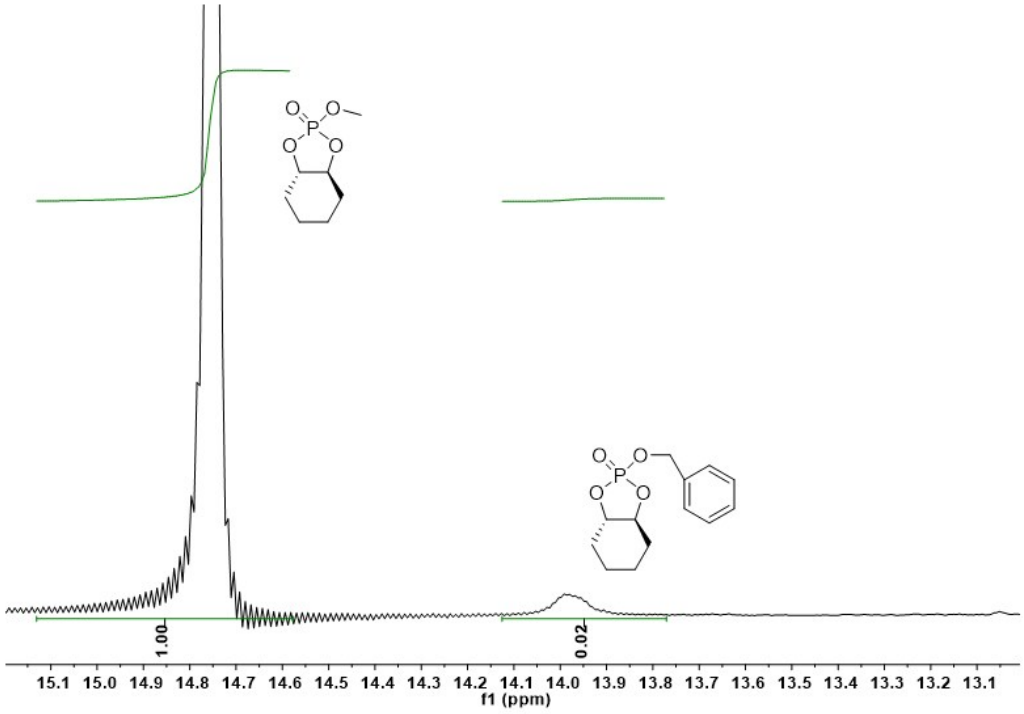
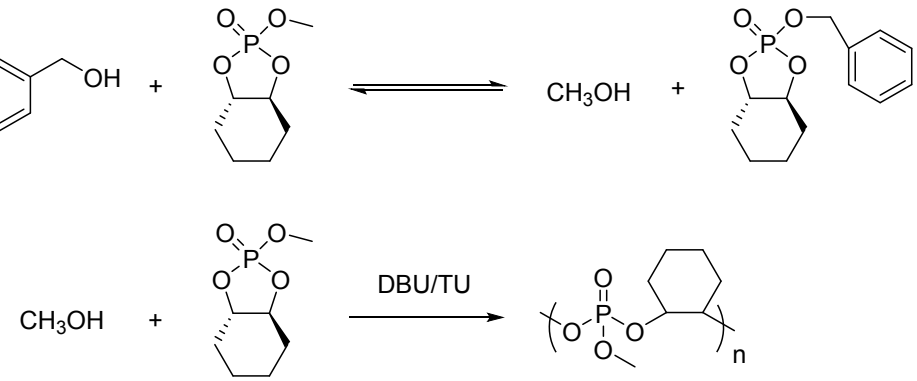


Figure S13. Phosphorus spectrum for the ring-opening polymerization of (*S,S*)-**M** with methanol as initiator**.**



Scheme S3. Possible intermolecular transesterification reactions in the ring-opening polymerization *of (S,S)*-**M.**

4. Thermogravimetric analysis of the polymers

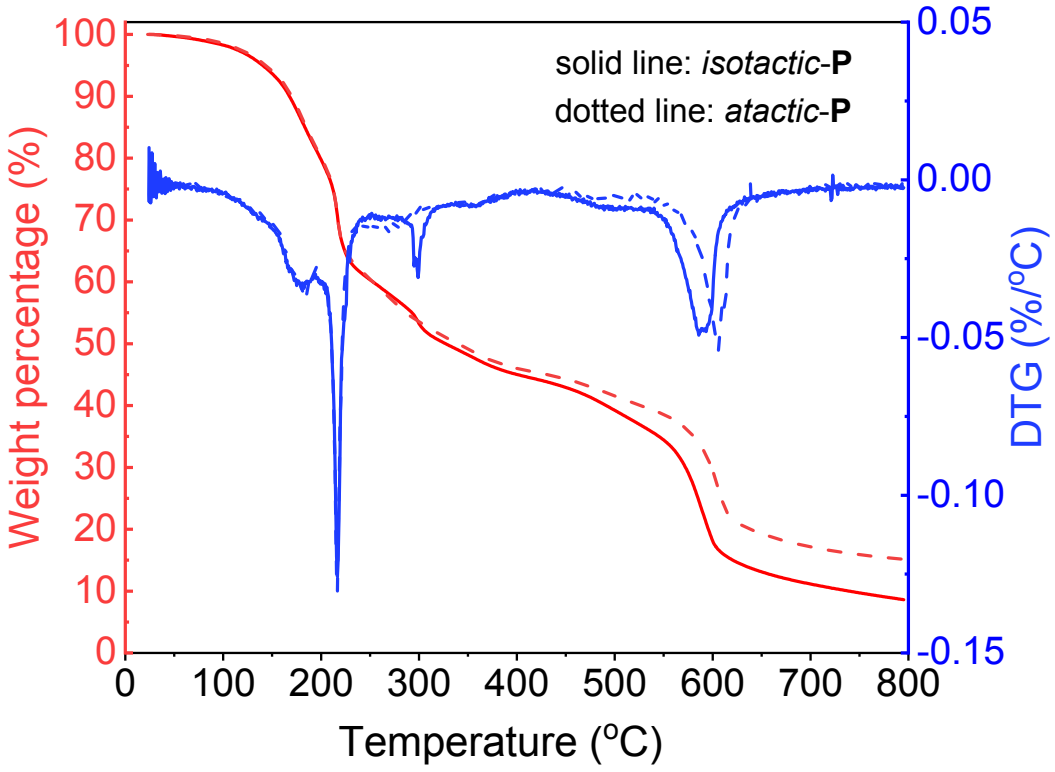


Figure S14. TGA curves for *atactic*-**P** and *isotactic*-**P** samples.

5. References

S1. W. H. Leung, E. Y. Y. Chan, E. K. F. Chow, I. D. Williams and S. M. Peng, *J Chem Soc Dalton Trans*, 1996, 1229−1236.

S2. H. Ochiai, T. Niwa and T. Hosoya, *Org Lett*, 2016, **18**, 5982−5985.