

# Supporting Information for

## Bio-based Polyesters with High Glass Transition Temperatures and Gas Barrier Properties

### Derived from Renewable Rigid Tricyclic Diacid or Tetracyclic Anhydride

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## 1. Materials

Furan (99%) was purchased from Beijing InnoChem Science & Technology Co., Ltd.. Maleic anhydride (99%), tert-butyl alcohol (99%), potassium permanganate (99%), and paraformaldehyde (96%) were purchased from Tianjin Guangfu Fine Chemical Research Institute. Ethylene glycol (99%), 1,3-propanediol (99%), 1,4-butanediol (99%), and 1,5-pentanediol (98%) were purchased from Alfa Aesar (China) Chemical Co., Ltd.. 1, 6-Hexanediol (97%), 1,8-octanediol (98%), and 1,10-decanediol (98%) were purchased from Adama reagent Co., Ltd.. Titanium butoxide (TBT, 99%) was purchased from Acros Organics. Propylene oxide (99%), 1,2-butylenoxide (99%) and cyclohexene oxide (98%) was purchased from TCI and stirred over freshly ground  $\text{CaH}_2$  for 3 days, then vacuum transferred to the dry straus flasks and stored in the glovebox. 4-Fluorophenol (99%) and diethylaluminium chloride (0.9 M solution in toluene) were purchased from Acros Organics and used directly. Tin (IV) chloride (99.995%) was purchased from sigma-aldrich. and stored in the glovebox. Bis(triphenylphosphine)iminium chloride [(PPN)Cl, 97%] was purchased from Alfa Aesar (China) Chemical Co., Ltd., and recrystallized using dry acetonitrile and diethyl ether, the resulting crystals were dried at 60 °C under vacuum then stored in a glovebox. Toluene and hexanes were dried over reflux with sodium, and transferred to the dry straus flask by distillation under  $\text{N}_2$  atmosphere. N,N-Dimethylformamide (DMF) (99.9%), extra dry with molecular sieves, water  $\leq 50$  ppm in resealable bottle was purchased from Innochem. Other reagents and solvents were analytical grade and used as received.

## 2. General methods

**The  $^1\text{H}$  NMR spectra,  $^{13}\text{C}$  NMR spectra,  $^1\text{H} / ^{13}\text{C}$  - HMBC and -HSQC NMR** were recorded on a Bruker spectrometer ( $^1\text{H}$  600 MHz,  $^{13}\text{C}$  150 MHz or  $^1\text{H}$  400 MHz,  $^{13}\text{C}$  100 MHz) at 25 °C with tetramethylsilane (TMS) as an internal reference with the samples (10 mg for  $^1\text{H}$  NMR and 30 mg for  $^{13}\text{C}$  NMR, respectively) were dissolved in 0.5 mL of dimethylsulfoxide-*d* (DMSO-*d*<sub>6</sub>), chloroform-*d* ( $\text{CDCl}_3$ ), or trifluoroacetic acid-*d* (TFA-*d*). **High Resolution Mass Spectrum (HRMS)** was conducted on LTQ Orbitrap Velos Pro (Thermo Fisher scientific, USA) with HESI in the negative ion mode, and the mass resolution was 60000 with the scan ranges (*m/z*) from 150-1000 Da. **MALDI-TOF-MS** spectrometer was recorded on autoflex III smartbeam (Bruker, Germany), equipped with smartbeam laser at 355 nm. 2-[(2E)-3-(4-tert-buthyl-phenyl)-2-Methylprop-2-enylidene] malononitrile (DCTB) and sodium trifluoroacetate ( $\text{CH}_3\text{COONa}$ ) were used as matrix and Ionized reagent, respectively. Spectra were recorded in reflector mode at positive polarity.  $\text{CH}_3\text{COONa}$  (5 mg/mL), polyester (5 mg/mL) and salt (0.1 N solution) in DCM were premixed in a ratio of 3: 1:

1. The mixture was deposited on the target and left to dry at room temperature before testing. **Gas Chromatography-Mass Spectrometer (GC-MS)** was conducted on Agilent 5975 in the mode of splitless at the flow rate of 1.0 mL/min, equipped with Agilent 19091J-433 of capillary column (30.0 m  $\times$  0.25 mm  $1\text{dc} \times 0.25 \mu\text{m}$   $1\text{df}$ , phenyl arylene polymer virtually equivalent to a (5%-phenyl)-methylpolysiloxane), used to analyze the purity of anhydride. The column operation conditions of the GC-MS were as follows: helium carrier gas at 1.0 mL/min; splitless inlet at 260 °C; GC oven temperature program of 80 °C for 3min and then +15 °C/min to 280 °C, holding for 26 min; a transfer line temperature of 325 °C. The corresponding parameters of mass spectrometry for the GC-MS were as follows: ion source temperature of 230 °C; electron energy of -70 eV; acquisition delay of 2.5 min.

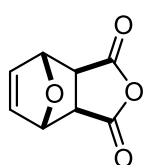
**Wide-Angle X-ray** scattering measurement was conducted to denote the structure of the bio-based

monomer by Smart Apex X-ray Diffractometer (Bruker, Germany) using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), equipped with CCD detector. The data was collected at room temperature, operating at 50 kV and 30 mA with the  $2\theta$  ranging from 0 to 60°. **The DFT calculations** were carried out with B3LYP functional and 6-31G (d, p) basis sets using the Gaussian 09 package. The TCDA structures with *exo-exo*, *exo-endo* and *endo-endo* configurations were optimized without any symmetry constrains. **Gel Permeation Chromatography (GPC)**, was recorded on a Waters 1515 HPLC apparatus to test number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and its distribution (PDI). Hexafluoroisopropanol (HFIP) with sodium trifluoroacetate ( $\text{CF}_3\text{COONa}$ , 5mmol/L) or tetrahydrofuran (THF) were used as eluents (1.0 mL/min, 30 °C) to evaluate relative molecular weight of different polyesters, and polymethyl methacrylate (PMMA) was used to establish a calibration curve. **Thermogravimetric Analysis (TGA)** was performed on a Mettler TGA/DSC Instrument to determine the thermal stability of polyesters. About 5-10 mg of each sample was heated from 30 to 600 °C at 10 °C/min under a nitrogen flow of 20 mL / min. The weight loss of 5% ( $T_{d,5\%}$ ) is a criterion to estimate that thermal stability of polymer and the maximum decomposition rate ( $T_{dmax}$ ) is evaluated as well from TGA curves. **Differential Scanning Calorimetry (DSC)** measurement was conducted by a Mettler Instrument. Measurements were carried out under N<sub>2</sub> atmosphere with a flow rate of 200 mL / min and about 5 to 10 mg of each sample was used for testing the thermal performance. The specific testing parameters were as follows: first heating scan was recorded from 25 °C to 200 °C at 10 °C/min and holded at 200 °C for 5 min to eliminate the thermal history, then cooled to -40 °C at 10 °C/min, second heating scan was recorded from -40 °C to 200 °C at 10 °C/min. The relevant results were obtained from TA Universal Analysis. **Wide-angle X-ray Diffraction (WAXD)** measurement was carried out by a Bruker D8 Advance using amorphous films from the melt-press/quench procedures. The results were collected in the range from 5° to 60° using

the Cu-K $\alpha$  radiation of wavelength 0.154 nm. **Gas Barrier Properties** were examined by Labthink VAC-V2 gas permeability tester using amorphous films from the melt-press/quench procedures and they were conducted at 23.0 °C with the relative humidity (RH) of 0%. The purity of the oxygen and carbon dioxide reached over 99.99%. The samples were cut into circular discs with a diameter around 1.0 cm, and were measured at three times to ensure the accuracy of the results. **Positron Annihilation Lifetime Spectroscopy (PALS)** measurement was employs a fast-slow coincidence scheme. A 13  $\mu$ Ci  $^{22}\text{Na}$  positron source was sandwiched between two 1 mm thick polymer disks to ensure that the positrons were not penetrated. The sample-source assembly was placed between two photomultiplier tubes (PMT) each equipped with BaF<sub>2</sub> gamma radiation sensitive scintillators. The total life spectrum count is 2 million to ensure statistical with the time resolution of spectrometer is about 195 ps. Finally, LT9.0 software was used to analyze the annihilation spectra assuming three components.

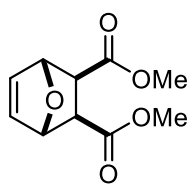
### 3. Synthesis of bio-based monomers diacid and anhydride.

#### *exo*-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**I**)



Maleic anhydride (98.1 g, 1.0 mol) was dispersed into furan (362.10 mL, 5.0 mol) in a 1 L two-necked round-flask with a magnetic stirring, and stirred at room temperature (about 25 °C) under N<sub>2</sub> atmosphere for 24 h. The desired product was crystallized from the solvent, filtered, washed with cool Et<sub>2</sub>O and dried under dry nitrogen atmosphere to afford **I** (143.9 g, yield 86%) as a white crystal. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  6.58 (s, 2 H), 5.34 (s, 2 H), 3.31 (s, 2 H).

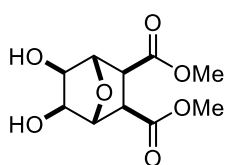
#### *exo*-5,6-Dimethyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**II**)



In a 1 L round-flask with a magnetic stirrer was added anhydride **I** (83.07 g, 0.5 mol) and MOH (800 mL) at ambient temperature, and then concentrated sulfuric acid (25.0 mL) was added dropwise slowly. After stirred for 16 h, the precipitate was

filtered, washed with ice MOH and dried in the vacuum oven at 45 °C to afford **II** (88.2 g, yield 83%) as a white crystal. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.46 (s, 2 H), 5.27 (s, 2 H), 3.71 (s, 6 H), 2.83 (s, 2 H).

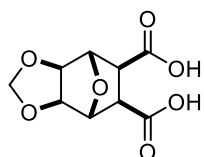
***exo,exo*-5,6-Dihydroxyl-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylate (**III**)**



A solution of potassium permanganate (18.9 g, 76.0 mmol) in deionized water (300 mL) was added slowly to a mixture solution of dimethyl ester **II** (20.56 g, 120.0 mmol) and 0.4 M NaOH in tertbutyl alcohol (200 mL) at 0 °C. After the

addition was complete, the mixture was stirred for 10 min and then quenched with a saturated aqueous solution of sodium metabisulfite until the solution turned colorless. The mixture was filtered, and the tert-butyl alcohol was removed from the filtrate in vacuo. The solution was extracted with boiling ethyl acetate repeatedly, and the combined organic layers dried over anhydrous sodium sulphate, filtered, and concentrated in vacuo to afford **III** (7.7 g, yield 26%) as a white crystal. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 4.81 (s, 2 H), 4.32 (s, 2 H), 3.77 (s, 2 H), 3.53 (s, 6 H), 3.02 (s, 2 H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>): δ 173.59, 85.69, 74.69, 54.16, 48.91.

***exo,exo*-5,6-Methylenedioxy-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid (TCDA).**

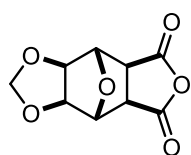


Dihydroxyl dimethyl ester **III** (12.30 g, 0.05 mol) and paraformaldehyde (12.30 g) were dissolved in concentrated hydrochloric acid (90 mL) and refluxed at 105 °C

for 3 h. The precipitate was filtered, washed with ice water and dried in vacuum oven at 55 °C to

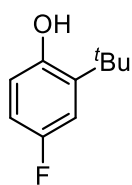
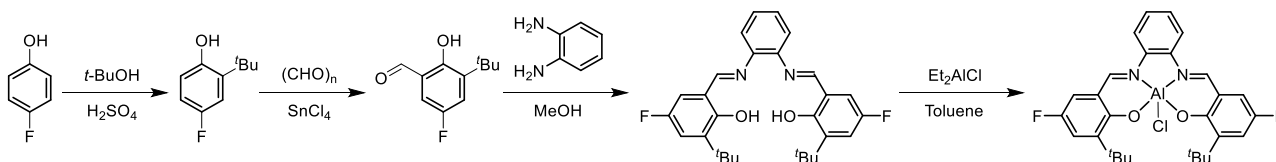
afford **TCDA** (8.98 g, yield 78%) as a white solid powder.  $^1\text{H}$  NMR (600 MHz, DMSO- $d_6$ ):  $\delta$  12.26 (s, 2 H), 4.94 (s, 1 H), 4.74 (s, 1 H), 4.56 (s, 2 H), 4.28 (s, 2 H), 2.86 (s, 2 H).  $^{13}\text{C}$  NMR (150 MHz, DMSO- $d_6$ ):  $\delta$  172.19, 96.86, 81.86, 81.02, 46.09. HRMS  $m/z$  calculated for  $\text{C}_9\text{H}_9\text{O}_7^-$  ( $[\text{M}-\text{H}]^-$ ), 229.03483, found 229.03493.

***exo,exo*-5,6-Methylenedioxy-7-oxabicyclo[2.2.1]hept-2,3-dicarboxylic anhydride (TCAH)**



TCDA (3.00 g, 0.013 mol) and dry acetic anhydride (60 mL) were placed into a 100 mL round-bottomed flask with magnetic stirring, and then was reacted at 90 °C for 2 h. The most of excess acetic anhydride was removed in vacuum, following 5 mL of anhydrous toluene was added to remove water and residual acetic anhydride. After dried in vacuum oven to afford **TCAH** (2.52 g, yield 91%) as a white solid.  $^1\text{H}$  NMR (600 MHz, DMSO- $d_6$ ):  $\delta$  4.94 (s, 1 H), 4.81 (s, 2 H), 4.78 (s, 1 H), 4.48 (s, 2 H), 3.43 (s, 2 H).  $^{13}\text{C}$  NMR (150 MHz, DMSO- $d_6$ ):  $\delta$  172.30, 97.17, 82.97, 80.18, 46.76. GC-MS  $m/z$  calculated for  $\text{C}_9\text{H}_9\text{O}_6^-$  ( $[\text{M}-\text{H}]^-$ ), 211.0, found 221.0.

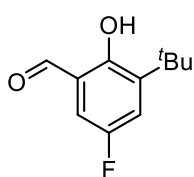
**4. Synthesis of metallation of salph ligands  $\text{Et}_2\text{AlCl}$  [ $^{\text{F}}$  (salph)AlCl].**



**2-*tert*-Butyl-4-fluorophenol.** 4-Fluorophenol (5.0 g, 44.6 mmol) was mixed with *tert*-butyl alcohol (8.53 mL, 89.2 mol) in a flask. After adding 4 mL of  $\text{H}_2\text{SO}_4$  slowly, the solution was stirred for 23 h. Then dichloromethane was used for diluting the solution

and the acid layer was removed using a separatory funnel and organic layer was neutralized by

saturated Na<sub>2</sub>CO<sub>3</sub> solution, washed with saturated NaCl. Then aqueous layer was extracted with EtOAc repeatedly and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The resulting residue was purified by column chromatography (ethyl acetate : petroleum ether = 1 : 10) to afford 2-*tert*-butyl-4-fluorophenol (4.16 g, yield 55%) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.96 (m, 1H), 6.74 (m, 1H), 6.58 (m, 1H), 4.78 (s, 1H), 1.39 (s, 9H).



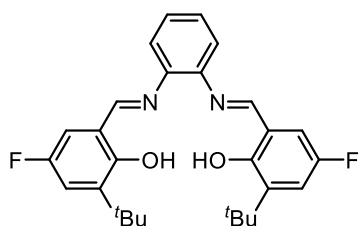
**2-*tert*-Butyl-4-fluorosalicylaldehyde.** 2-*tert*-Butyl-4-fluorophenol (3.50 g, 20.8

mmol) and 2,6-lutidine (3.71 mL, 31.2 mmol) were added into a side-arm round-

bottom flask with paraformaldehyde (4.68 g, 104 mmol) and evacuated. Dry toluene

(32 mL) was added and the mixture was stirred under N<sub>2</sub> atmosphere. After cooling to 0 °C for 0.5 h, anhydrous SnCl<sub>4</sub> (1.21 mL, 10.4 mmol) was added using syringe. The reaction was allowed to warm to room temperature gradually and subsequently raised to 90 °C for 18 h. Then the reaction was cooled to room temperature naturally and 45 mL of HCl (2 M) was added and to break apart the solid on the wall of flask under vigorous stirring. The suspension was filtered, and the solution was extracted with Et<sub>2</sub>O, washed with saturated NaCl, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After distilling and recrystallization with methanol to afford 2-*tert*-butyl-4-fluorosalicylaldehyde (1.05 g, yield 26%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 11.58 (s, 1H), 9.82 (s, 1H), 7.29-7.26 (dd, *J* = 3.08 Hz, *J* = 10.56 Hz, 1H), 7.08-7.06 (dd, *J* = 3.12 Hz, *J* = 7.00 Hz, 1H), 1.41 (s, 9H).

**N,N'-Bis(3-*tert*-butyl-5-fluorosalicylidene)-1,2-diaminobenz-ene ((salph-F)-H<sub>2</sub>).** 2-*tert*-Butyl-4-



fluorosalicylaldehyde (1.05 g, 5.3 mmol) and 1,2-diaminobenzene

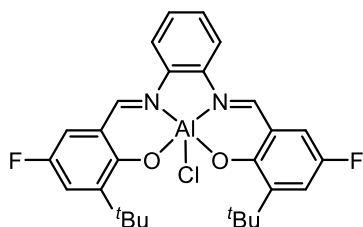
(0.30 g, 2.7 mmol) were dissolved in the methanol (13 mL), and

refluxed for 21 h. The solid was filtrated and washed with small

amount of cold methanol repeatedly to afford (salph-F)-H<sub>2</sub>. (1.11 g, yield 45%) as a yellow solid. <sup>1</sup>H



**NMR** (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  13.81 (s, 2H), 8.94 (s, 2H), 7.53-7.51 (m, 2H), 7.45-7.43 (m, 2H), 7.36-7.34 (dd,  $J = 1.92$  Hz,  $J = 8.12$  Hz, 2H), 7.17-7.14 (dd,  $J = 1.92$  Hz,  $J = 10.68$  Hz, 2H), 1.35 (s, 18H).

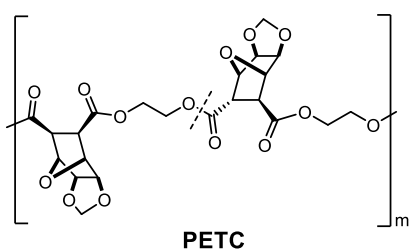


**Catalyst of [(<sup>F</sup>Salph)AlCl].** The charging process was conducted in a glovebox. (salph-F)-H<sub>2</sub> (0.23 g, 0.5 mmol) was dissolved in dry, degassed toluene. Subsequently, a solution of diethylaluminium chloride (0.6 mL, 0.55 mol) was added dropwise with stirring. The

flask was sealed and sent out from glovebox, then raised to 90 °C for 18 h. The precipitation was filtered, washed with dry hexanes, dried under vacuum to afford [(<sup>F</sup>salph)AlCl] (207 mg, yield 80%) as an orange crystal which was stored in glovebox. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.29 (s, 2H), 8.14-8.12 (m, 2H), 7.41-7.38 (dd,  $J = 3.24$  Hz,  $J = 8.44$  Hz, 2H), 7.33-7.30 (dd,  $J = 3.28$  Hz,  $J = 10.64$  Hz, 2H), 1.55 (s, 18H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  161.92, 161.39, 153.65, 152.12, 142.99, 137.60, 129.40, 122.00, 121.84, 118.97, 118.92, 117.31, 117.20, 35.74, 29.68.

## 5. Synthesis of bio-based polyesters by melt polycondensation.

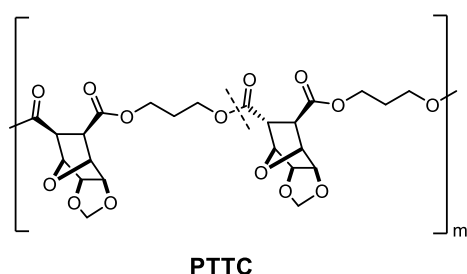
*This series of polyesters were synthesized via the conventional two-steps polycondensation procedure as follows:*



**Synthesis of PETC.** TCDA (3.45 g, 0.015 mol), ethylene glycol (1.49 g, 0.024 mol) and TBT (0.025 g, 0.5 mol% of TCDA) were loaded into a 25 mL three-neck flask equipped with a mechanical agitator. The air in the reactor was evacuated and replaced by

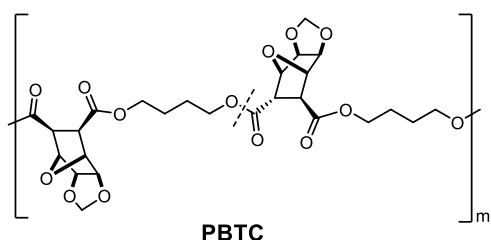
nitrogen. The esterification reaction was carried out under stirring at 160 °C for 1 h, 180 °C for 1h,

and 190 °C for 3 h. Then, the pressure in the reactor was decreased below 70 Pa and the temperature was raised to 190 °C and then polycondensation reaction was performed at 190 °C for 1 h and 220 °C for 4 h under the above conditions. After cooling to room temperature, the resultant polymer PETC (2.30 g, yield 60%) was appeared as a light brown solid material. **<sup>1</sup>H NMR** (600 MHz, TFA-*d*): δ 5.17 - 5.09 (m, 3 H), 4.91 (s, 1 H), 4.61 -4.57 (m, 2 H), 4.53 – 4.45 (m, 4H), 3.71 (s, 0.72 H), 3.24 (s, 1.28 H). **<sup>13</sup>C NMR** (150 MHz, TFA-*d*): δ 173.67, 172.64, 171.58, 97.36, 97.21, 84.40, 82.79, 81.42, 79.73, 64.66, 64.54, 64.47, 47.65, 46.95, 46.16.



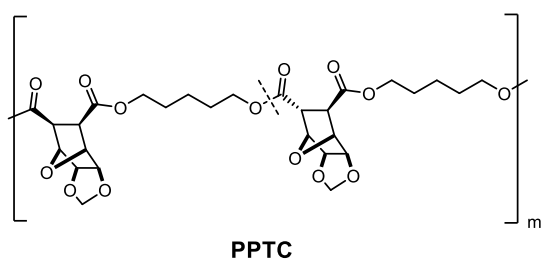
**Synthesis of PTTC.** TCDA (3.45 g, 0.015 mol), ethylene glycol (1.82 g, 0.024 mol) and TBT (0.025 g, 0.5 mol% of TCDA) were loaded into a 25 mL three-neck flask equipped with a mechanical agitator. The air in the reactor was

evacuated and replaced by nitrogen. The esterification reaction was carried out under stirring at 160 °C for 1 h, 180 °C for 1h, and 190 °C for 3 h. Then, the pressure in the reactor was decreased below 70 Pa and the temperature was raised to 190 °C and then polycondensation reaction was performed at 190 °C for 1 h and 220 °C for 4 h under the above conditions. After cooling to room temperature, the resultant polymer PTTC (2.67 g, yield 66%) was appeared as a light brown solid material. **<sup>1</sup>H NMR** (600 MHz, TFA-*d*): δ 5.14 – 5.05 (m, 3 H), 4.89 – 4.88 (m, 1 H), 4.57 -4.51 (m, 2 H), 4.31 - 4.28 (m, 4H), 3.65 (s, 0.50 H), 3.20 (s, 1.50 H), 2.07 (s, 2 H) **<sup>13</sup>C NMR** (150 MHz, TFA-*d*): δ 174.12, 173.45, 172.10, 97.36, 97.12, 84.41, 82.60, 81.38, 79.66, 64.35, 64.13, 47.78, 47.03, 46.20, 27.33.



**Synthesis of PBTC.** TCDA (3.45 g, 0.015 mol), 1,4-butanediol (3.38 g, 0.0375 mol) and TBT (0.025 g, 0.5 mol% of TCDA) were loaded into a 25 mL three-neck flask equipped with a mechanical agitator. The air in the reactor was

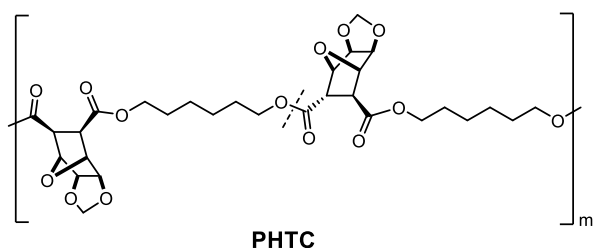
evacuated and replaced by nitrogen. The esterification reaction was carried out under stirring at 160 °C for 1 h, 180 °C for 1h, and 190 °C for 3 h. Then, the pressure in the reactor was decreased below 70 Pa and the temperature was raised to 190 °C and then polycondensation reaction was performed at 190 °C for 1 h and 220 °C for 4 h under the above conditions. After cooling to room temperature, the resultant polymer PTTC (2.76 g, yield 64%) was appeared as a light brown solid material. <sup>1</sup>H NMR (600 MHz, TFA-*d*): δ 5.16 – 5.03 (m, 3 H), 4.87 – 4.86 (m, 1 H), 4.56 –4.50 (m, 2 H), 4.23 – 4.18 (m, 4H), 3.63 (s, 0.48 H), 3.19 (s, 1.50 H), 1.74 (s, 4 H). <sup>13</sup>C NMR (150 MHz, TFA-*d*): δ 174.40, 173.76, 172.41, 97.39, 97.17, 84.49, 82.57, 81.44, 79.71, 67.63, 64.53, 47.91, 47.20, 46.30, 24.94, 24.87, 24.77.



**Synthesis of PPTC.** TCDA (3.45 g, 0.015 mol), 1,5-pentanediol (3.14 g, 0.03 mol) and TBT (0.025 g, 0.5 mol% of TCDA) were loaded into a 25 mL three-neck flask equipped with a mechanical agitator. The air in the

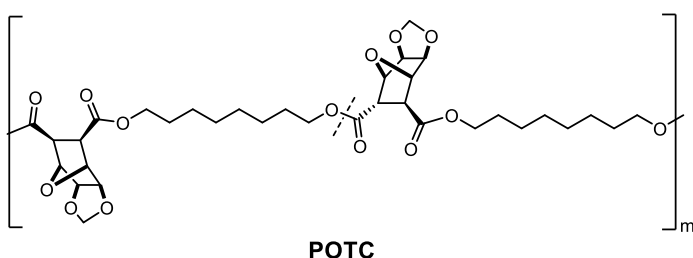
reactor was evacuated and replaced by nitrogen. The esterification reaction was carried out under stirring at 160 °C for 1 h, 180 °C for 1h, and 190 °C for 3 h. Then, the pressure in the reactor was decreased below 70 Pa and the temperature was raised to 190 °C and then polycondensation reaction was performed at 190 °C for 1 h and 220 °C for 4 h under the above conditions. After cooling to room temperature, the resultant polymer PPTC (3.67 g, yield 82%) was appeared as a light brown solid

material. **<sup>1</sup>H NMR** (600 MHz, TFA-*d*): δ 5.12 – 5.01 (m, 3 H), 4.86 – 4.83 (m, 1 H), 4.54 -4.49 (m, 2 H), 4.19 – 4.11 (m, 4H), 3.61 (s, 0.37 H), 3.18 (s, 1.62 H), 1.65 (s, 4 H), 1.38 (s, 2 H). **<sup>13</sup>C NMR** (150 MHz, TFA-*d*): δ 174.42, 173.80, 172.47, 97.32, 97.07, 84.40, 82.49, 81.36, 79.65, 68.06, 67.97, 47.89, 47.20, 46.23, 27.90, 22.22, 22.17, 22.13.



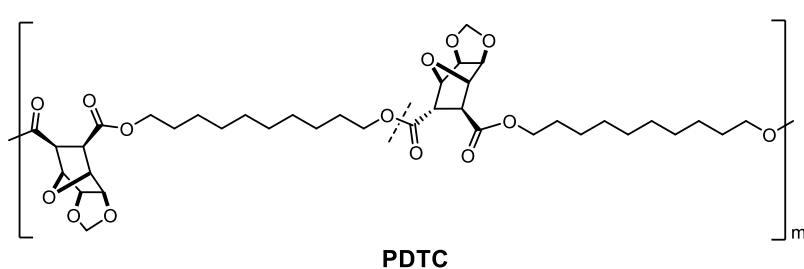
**Synthesis of PHTC.** TCDA (3.45 g, 0.015 mol), 1, 6-Hexanediol (2.13 g, 0.018 mol) and TBT (0.025 g, 0.5 mol% of TCDA) were loaded into a 25 mL three-neck flask equipped with a mechanical

agitator. The air in the reactor was evacuated and replaced by nitrogen. The esterification reaction was carried out under stirring at 160 °C for 1 h, 180 °C for 1h, and 190 °C for 3 h. Then, the pressure in the reactor was decreased below 70 Pa and the temperature was raised to 190 °C and then polycondensation reaction was performed at 190 °C for 1 h and 220 °C for 4 h under the above conditions. After cooling to room temperature, the resultant polymer PHTC (4.23 g, yield 90%) was appeared as a light yellow solid material. **<sup>1</sup>H NMR** (600 MHz, TFA-*d*): δ 5.22 -5.08 (m, 3 H), 4.93 - 4.90 (m, 1 H), 4.61 – 4.56 (m, 2 H), 4.24 – 4.17 (m, 4H), 3.67 (s, 0.33 H), 3.24 (s, 1.67 H), 1.68 (s, 4 H), 1.39 (s, 4 H). **<sup>13</sup>C NMR** (150 MHz, TFA-*d*): δ 174.52, 173.89, 172.58, 97.36, 97.11, 84.44, 82.52, 81.38, 79.68, 68.36, 47.96, 47.25, 46.28, 28.17, 25.56, 25.50, 25.45.



**Synthesis of POTC.** TCDA (3.45 g, 0.015 mol), 1,8-octanediol (2.63 g, 0.018 mol) and TBT (0.025 g, 0.5 mol% of TCDA) were loaded into a 25 mL three-neck flask

equipped with a mechanical agitator. The air in the reactor was evacuated and replaced by nitrogen. The esterification reaction was carried out under stirring at 160 °C for 1 h, 180 °C for 1h, and 190 °C for 3 h. Then, the pressure in the reactor was decreased below 70 Pa and the temperature was raised to 190 °C and then polycondensation reaction was performed at 190 °C for 1 h and 220 °C for 4 h under the above conditions. After cooling to room temperature, the resultant polymer POTC (4.77 g, yield 94%) was appeared as a light yellow solid material. **<sup>1</sup>H NMR** (600 MHz, TFA-*d*): δ 5.22 -5.08 (m, 3 H), 4.93 – 4.90 (m, 1 H), 4.61 - 4.56 (m, 2 H), 4.25 – 4.17 (m, 4H), 3.66 (s, 0.31 H), 3.25 – 3.20 (m, 1.67 H), 1.66 (s, 4 H), 1.33 (s, 8 H) **<sup>13</sup>C NMR** (150 MHz, TFA-*d*): δ 174.72, 174.07, 172.79, 97.50, 97.22, 84.56, 82.65, 81.52, 79.82, 68.81, 48.20, 47.41, 46.44, 29.36, 29.31, 28.43, 26.00, 25.93, 25.89.



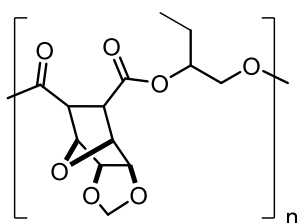
**Synthesis of PDTC.** TCDA (3.45 g, 0.015 mol), 1,10-decanediol (3.14 g, 0.018 mol) and TBT (0.025 g, 0.5 mol% of TCDA) were

loaded into a 25 mL three-neck flask equipped with a mechanical agitator. The air in the reactor was evacuated and replaced by nitrogen. The esterification reaction was carried out under stirring at 160 °C for 1 h, 180 °C for 1h, and 190 °C for 3 h. Then, the pressure in the reactor was decreased below 70 Pa and the temperature was raised to 190 °C and then polycondensation reaction was performed at 190 °C for 1 h and 220 °C for 4 h under the above conditions. After cooling to room temperature, the resultant polymer PDTC (4.91 g, yield 89%) was appeared as a light yellow solid material. **<sup>1</sup>H NMR** (600 MHz, TFA-*d*): δ 5.18 – 5.05 (m, 3 H), 4.90 – 4.86 (m, 1 H), 4.58 – 4.52 (m, 2 H), 4.19 - 4.12 (m, 4H), 3.63 (s, 0.28 H), 3.21 -3.17 (m, 1.70 H), 1.62 (s, 4 H), 1.25 (s, 12 H). **<sup>13</sup>C NMR** (150

MHz, TFA-*d*):  $\delta$  174.28, 174.11, 172.86, 97.55, 97.26, 84.57, 82.71, 81.57, 79.87, 68.96, 48.30, 47.45, 46.51, 30.00, 29.54, 29.47, 28.52, 26.08.

## 6. Synthesis of bio-based polyesters by ring opening polymerization.

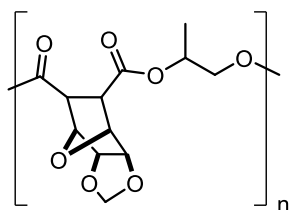
*Representative of PBOTC, PPOTC, and PCHOTC were synthesized via the ring opening polymerization as follows:*



### Synthesis of PBOTC with 42% *exo-endo* diester groups.

In a glovebox, TCAH (220.6 mg, 1.0 mmol) the [ $^F$ Salph)AlCl] (2.73 mg, 5.0  $\mu$ mol) and [PPN]Cl (2.89 mg, 4.5  $\mu$ mol) were placed into an oven-dried 3-mL vial equipped with a magnetic stir bar. Then, BO (0.44 mL, 5.0 mmol) was added,

afterwards, the appropriate amount of dry DMF (0.1 mL). The vial was sealed, removed from the glovebox, and set in an oil bath preheated to 90 °C. After 2.5 h, the reaction mixture was then diluted with approximately 0.5 mL of chloroform and precipitated into 10 mL of ethyl ether with vigorous stirring, and this process was done for three times. After dried under vacuum at 60 °C, the resultant polymer PBOTC was appeared as a bright yellow solid powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.11 (s, 1H), 5.00 – 4.84 (m, 4 H), 4.45 – 3.99 (m, 4 H), 3.49 (q,  $J$  = 8.0 Hz, 0.42 H), 2.88 (s, 1.66 H), 1.62 (s, 2H), 0.93 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.99, 169.88, 169.77, 97.83, 97.58, 82.19, 82.05, 81.15, 77.36, 77.04, 76.72, 73.58, 65.21, 46.66, 46.04, 23.71, 23.55, 15.27, 9.50.

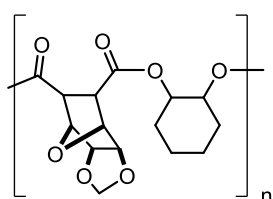


### Synthesis of PPOTC with 40% *exo-endo* diester groups.

In a glovebox, TCAH (220.6 mg, 1.0 mmol) the [ $^F$ Salph)AlCl] (2.73 mg, 5.0  $\mu$ mol) and [PPN]Cl (2.89 mg, 4.5  $\mu$ mol) were placed into an oven-dried 3-mL vial

equipped with a magnetic stir bar. Then, PO (0.36 mL, 6.5 mmol) was added, afterwards, the appropriate amount of dry DMF (0.1 mL). The vial was sealed, removed from the glovebox, and set

in an oil bath preheated to the 90 °C for 1.5 h. After treating by the methods mentioned earlier, and dried under vacuum at 60 °C, the resultant polymer PPOTC was appeared as a bright yellow solid powder. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 5.15 - 5.11 (m, 2 H), 4.95 - 4.85 (m, 3 H), 4.37 – 3.89 (m, 4 H), 3.48 (q, *J* = 8.0 Hz, 0.40 H), 2.89 (s, 1.61 H), 1.25 - 1.19 (m, 3 H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 171.25, 170.47, 170.15, 100.04, 98.45, 98.17, 82.70, 81.76, 81.29, 79.70, 78.01, 77.69, 77.38, 67.11, 46.71, 44.11, 16.96, 15.90.



**Synthesis of PCHOTC with 50% *exo-endo* diester groups..** In a glovebox,

TCAH (220.6 mg, 1.0 mmol) the [<sup>F</sup>Salph)AlCl] (2.73 mg, 5.0 μmol) and

[PPN]Cl (2.89 mg, 4.5 μmol) were placed into an oven-dried 3-mL vial

equipped with a magnetic stir bar. Then, CHO (0.50 mL, 5.0 mmol) was added, afterwards, the appropriate amount of dry DMF (0.1 mL). The vial was sealed, removed from the glovebox, and set in an oil bath preheated to the 90 °C for 1.5 h. After treating by the methods mentioned earlier, and dried under vacuum at 60 °C, the resultant polymer PCHOTC was appeared as a bright yellow solid powder. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 5.07 (s, 1 H), 4.87 - 4.73 (m, 5 H), 4.33 - 4.22 (m, 2 H), 3.50 - 3.43 (s, 0.53 H), 3.03 - 2.76 (m, 1.53 H), 2.08 - 2.04 (m, 2 H), 1.73 (s, 2H), 1.41 - 1.35 (m, 4H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 171.28, 170.54, 170.02, 98.48, 98.28, 84.68, 82.87, 81.78, 79.63, 75.11, 47.25, 46.56, 30.58, 23.93.

## 7. Characterization of X-ray diffraction

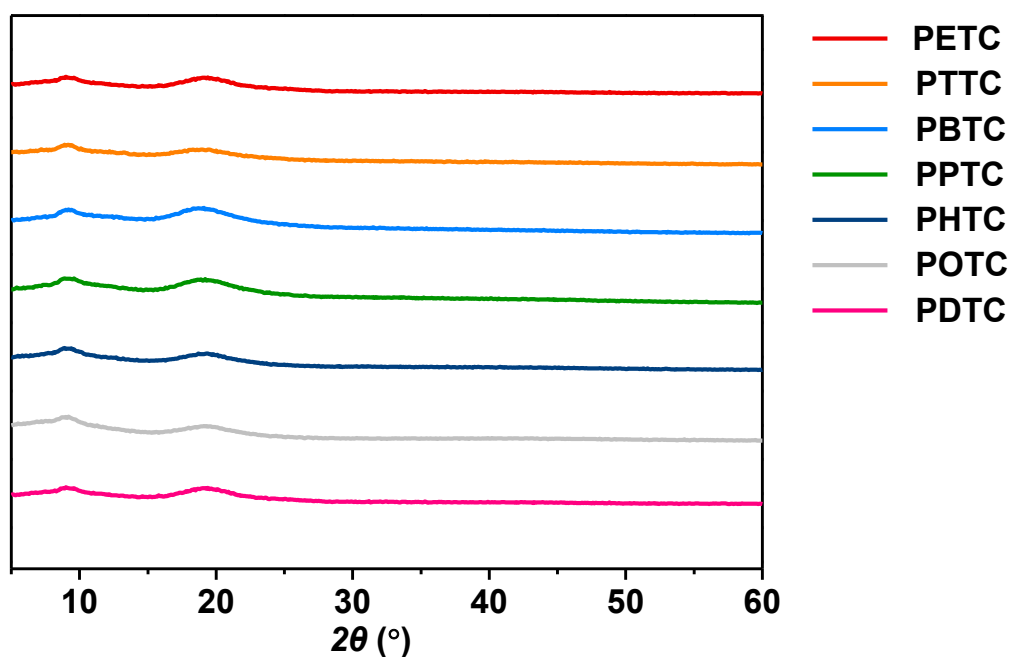


Figure S1. X-ray diffraction profiles of polyesters synthesis *via* melt polycondensation.

## 8. Energetics Calculation by Gauss

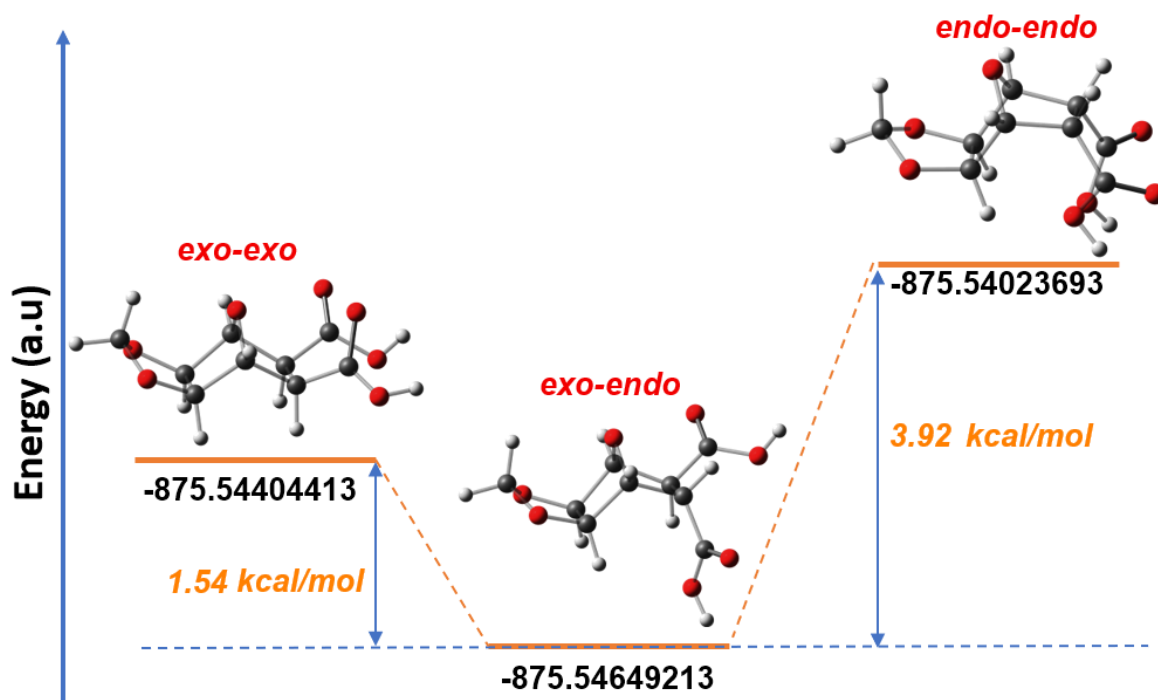
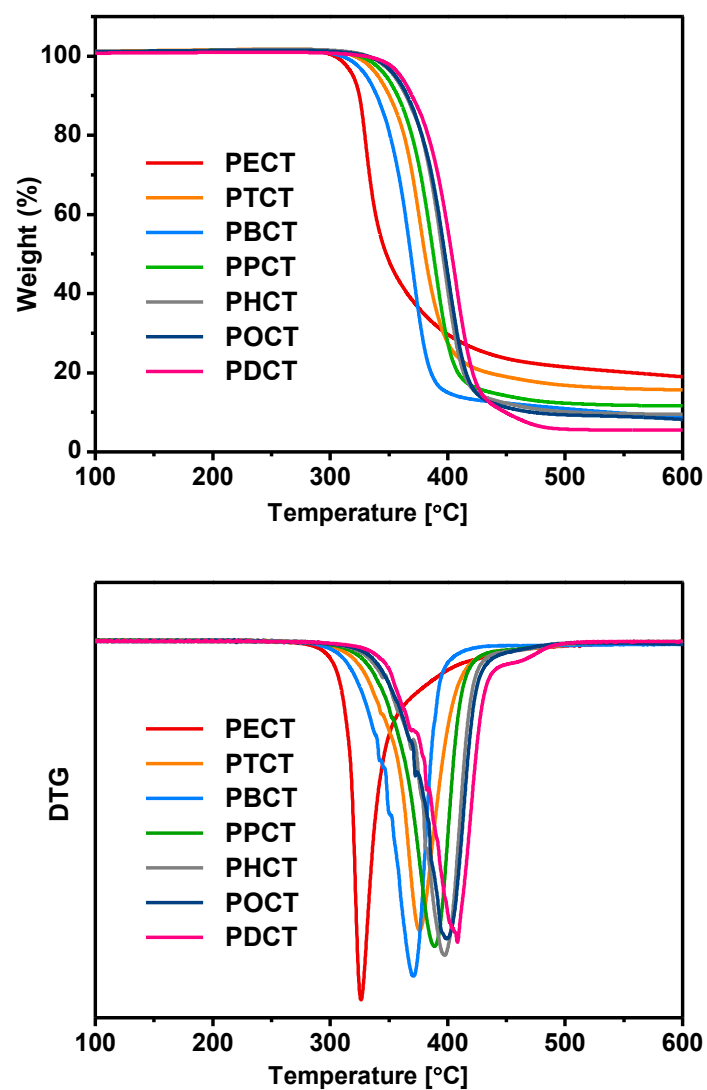


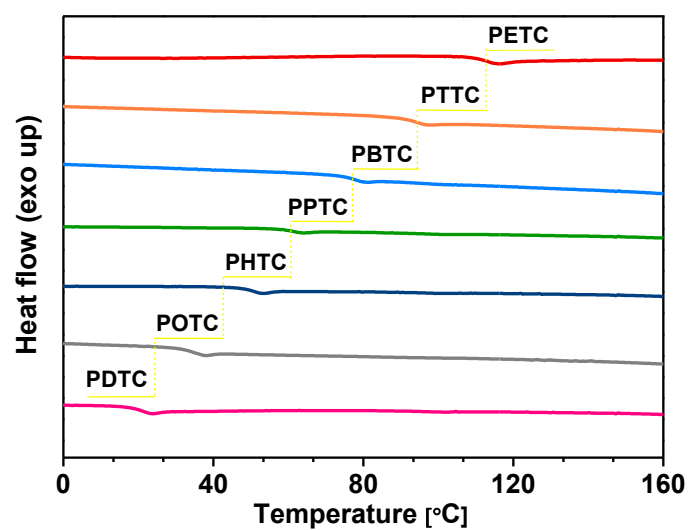
Figure S2. Structures and relative energetics of the TCDA with various configurations.



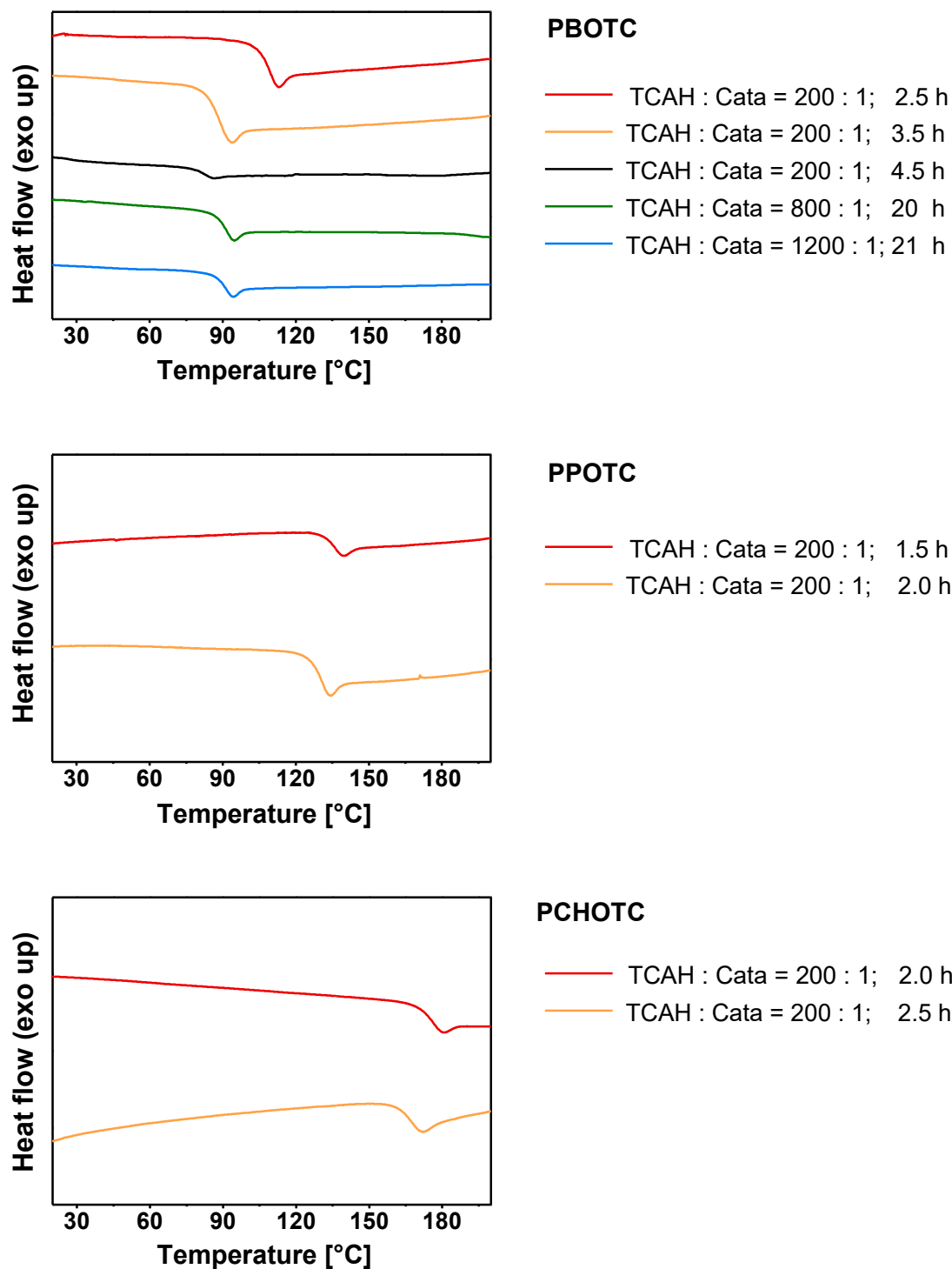
## 9. Characterization of Thermal Properties



**Figure S3.** TGA traces of melt polycondensation series of polyesters.



**Figure S4.** Second heating DSC curves of melt polycondensation series of polyesters.



**Figure S5.** Second heating DSC curves of ring opening polymerization series of polyesters. Reactions were performed in 0.1 mL dry DMF with TCAH (220.6 g, 1.0 mmol), epoxide (5.0 mmol) and [PPN]Cl was 0.9 eq of  $[\text{F}(\text{salph})\text{AlCl}]$  at 90 °C. Up curves were PBOTC synthesized from TCAH and BO; Middle curves were PPOTC synthesized from TCAH and PO; Down curves were PCHOTC synthesized from TCAH and CHO.

## 10. Crystal data of bio-based monomers.

**Table S1.** Crystal data and structure refinement for the TCDA.

Identification code	Monomer
Empirical formula	C <sub>9</sub> H <sub>10</sub> O <sub>7</sub>
Formula weight	230.17
Temperature/K	298(2)
Crystal system	Monoclinic
space group	P2 <sub>1</sub> /n
a/Å	4.7265(6)
b/Å	9.5602(12)
c/Å	21.230(3)
$\alpha$ /°	90
$\beta$ /°	96.210(2)
$\gamma$ /°	90
Volume/ Å <sup>3</sup>	953.7(2)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.603
$\mu/\text{mm}^{-1}$	0.141
F(000)	480.0
Crystal size/mm <sup>3</sup>	0.21 x 0.19 x 0.11
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	1.93 to 26.39
Index ranges	-5 $\leq$ h $\leq$ 5, -11 $\leq$ k $\leq$ 10, -26 $\leq$ l $\leq$ 26
Reflections collected	5218
Independent reflections	1940 [ $R_{\text{int}}$ = 0.0155]
Data/restraints/parameters	1940 / 0 / 147
Goodness-of-fit on F <sup>2</sup>	1.022
Final R indexes [ $I \geq 2\sigma(I)$ ]	R <sub>1</sub> = 0.0471, wR <sub>2</sub> = 0.1366
Final R indexes [all data]	R <sub>1</sub> = 0.0544, wR <sub>2</sub> = 0.1456
Largest diff. peak/hole / e Å <sup>-3</sup>	0.388 / -0.250

**Table S2.** Crystal data and structure refinement for the TCAH.

Identification code	Monomer
Empirical formula	C <sub>9</sub> H <sub>8</sub> O <sub>6</sub>
Formula weight	212.15
Temperature/K	298(2)
Crystal system	Monoclinic
space group	P2 <sub>1</sub> /n
a/Å	7.484(2)
b/Å	6.1093(17)
c/Å	18.715(5)
$\alpha$ /°	90
$\beta$ /°	91.886(4)
$\gamma$ /°	90
Volume/ Å <sup>3</sup>	855.2(4)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.648
$\mu/\text{mm}^{-1}$	0.142
F(000)	440
Crystal size/mm <sup>3</sup>	0.21 x 0.19 x 0.12
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	2.18 to 26.47
Index ranges	-9 $\leq$ h $\leq$ 8, -6 $\leq$ k $\leq$ 7, -23 $\leq$ l $\leq$ 23
Reflections collected	4385
Independent reflections	1732 [ $R_{\text{int}}$ = 0.0284]
Data/restraints/parameters	1732 / 0 / 136
Goodness-of-fit on F <sup>2</sup>	1.102
Final R indexes [ $I \geq 2\sigma(I)$ ]	R <sub>1</sub> = 0.0858, wR <sub>2</sub> = 0.2587
Final R indexes [all data]	R <sub>1</sub> = 0.0892, wR <sub>2</sub> = 0.2601
Largest diff. peak/hole / e Å <sup>-3</sup>	0.435 / -0.418

## 11. NMR Spectroscopic Characterization.

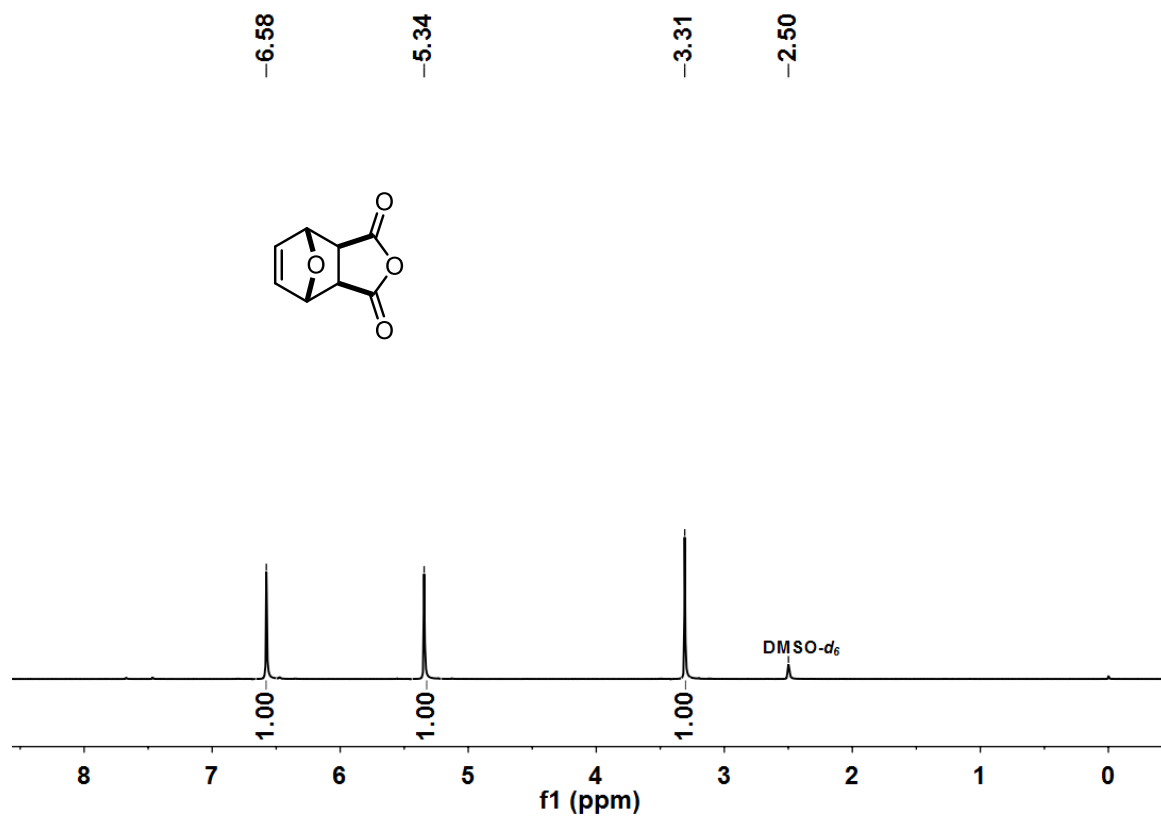


Figure S6.  $^1\text{H}$  NMR spectrum of **I**.

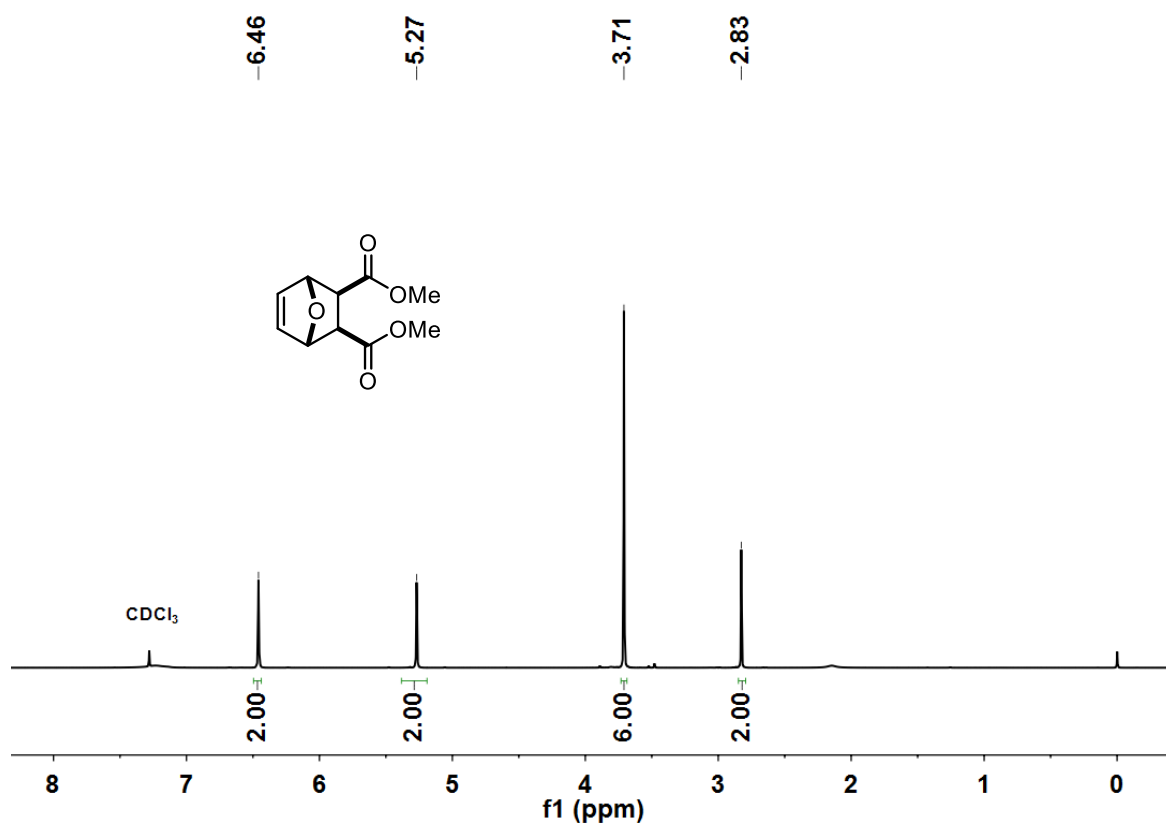


Figure S7.  $^1\text{H}$  NMR spectrum of **II**.

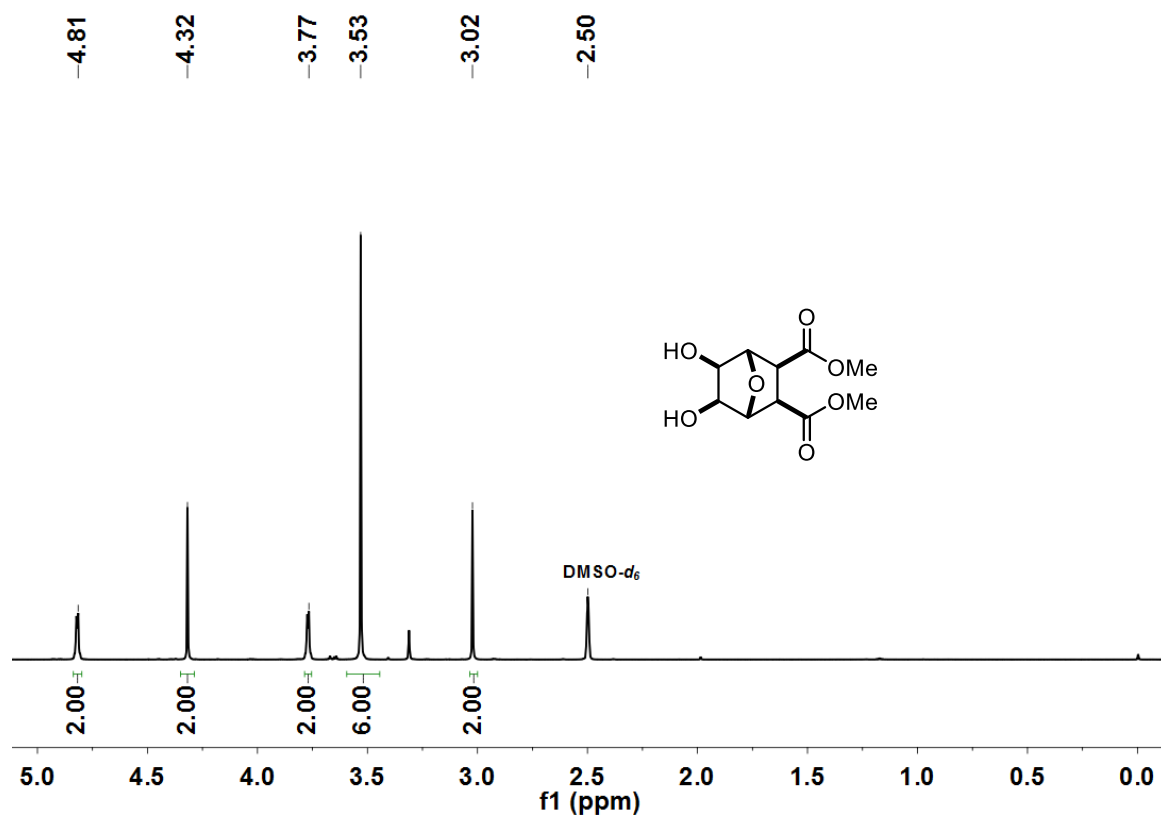


Figure S8. <sup>1</sup>H NMR spectrum of **III**.

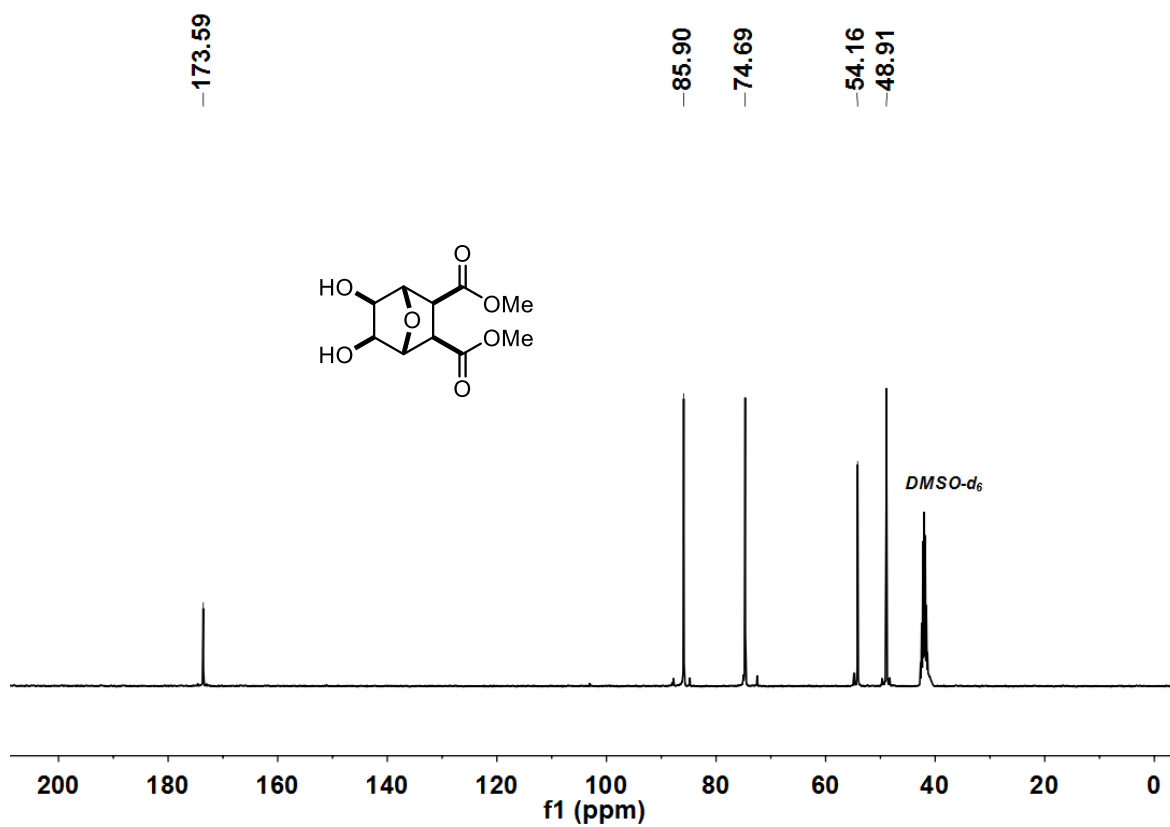


Figure S9. <sup>13</sup>C NMR spectrum of **III**.

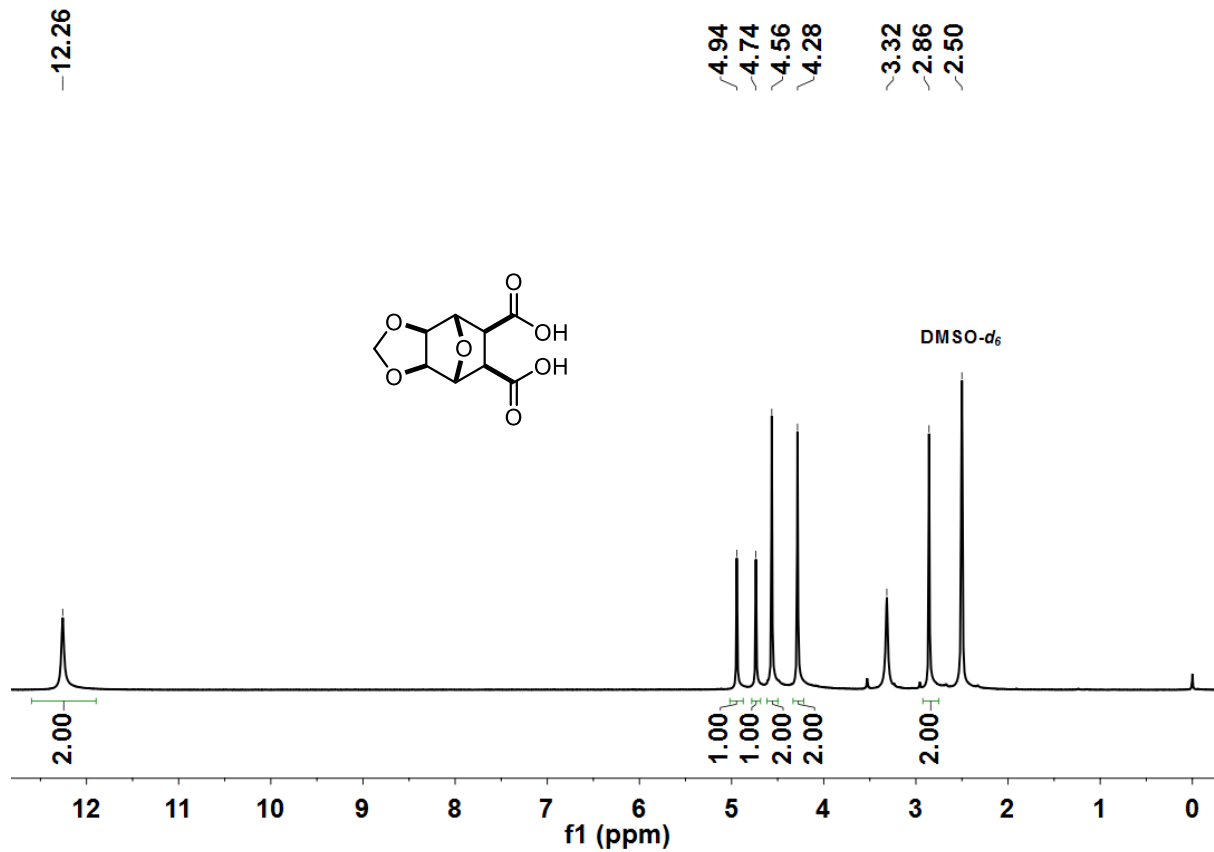


Figure S10. <sup>1</sup>H NMR spectrum of TCDA.

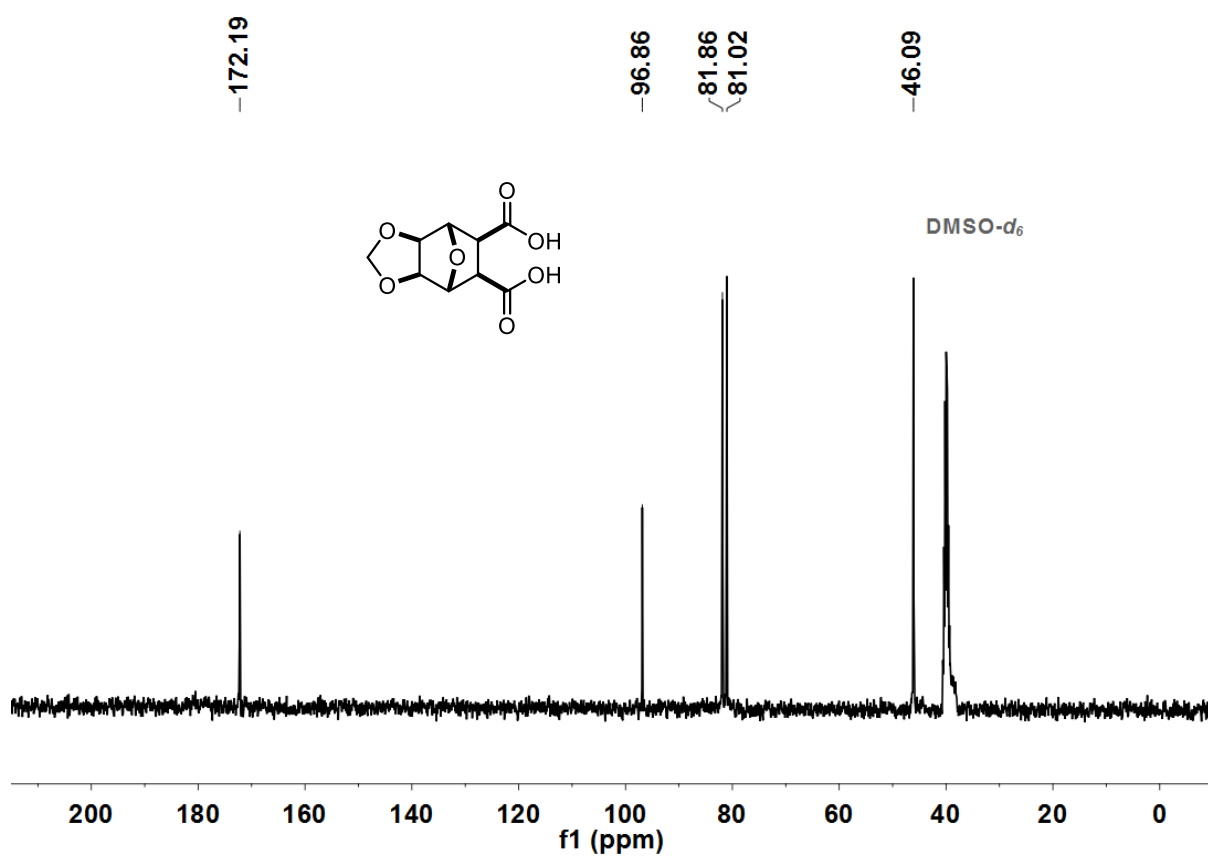


Figure S11. <sup>13</sup>C NMR spectrum of TCDA.

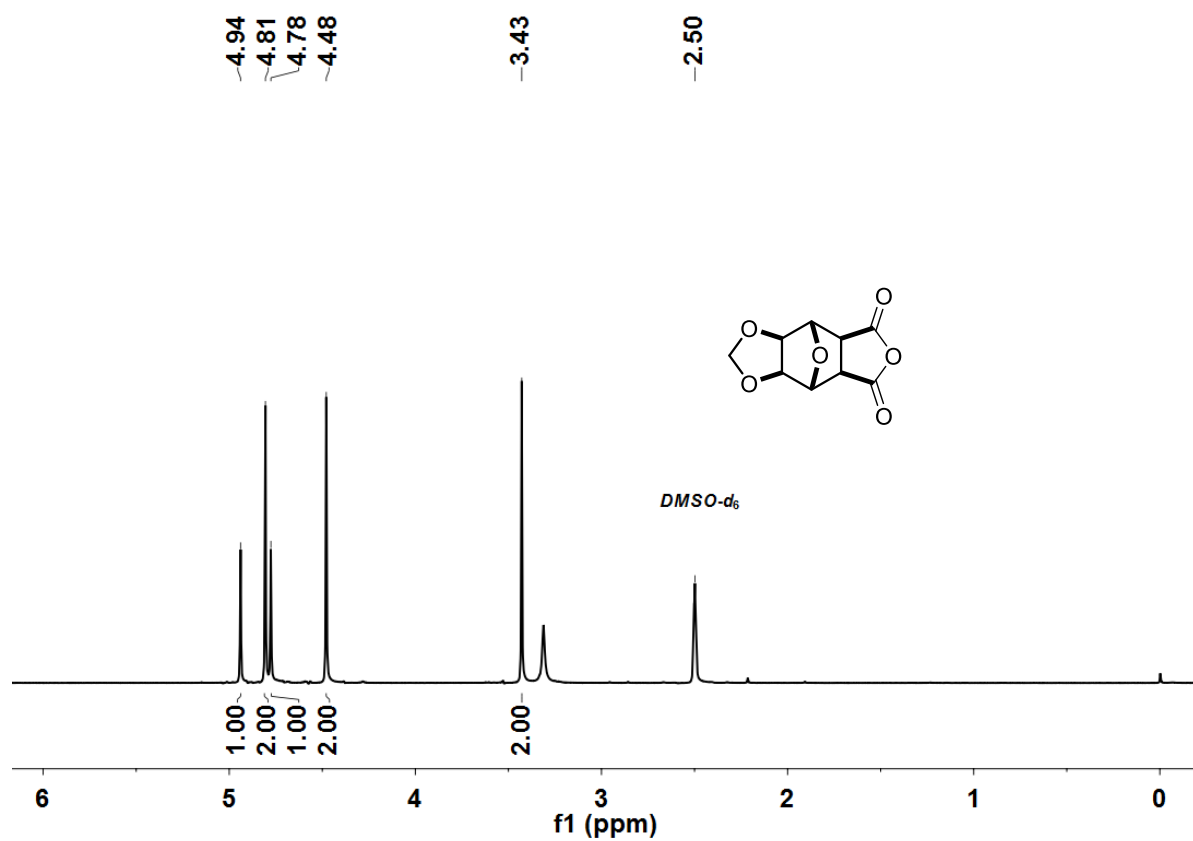


Figure S12. <sup>1</sup>H NMR spectrum of TCAH.

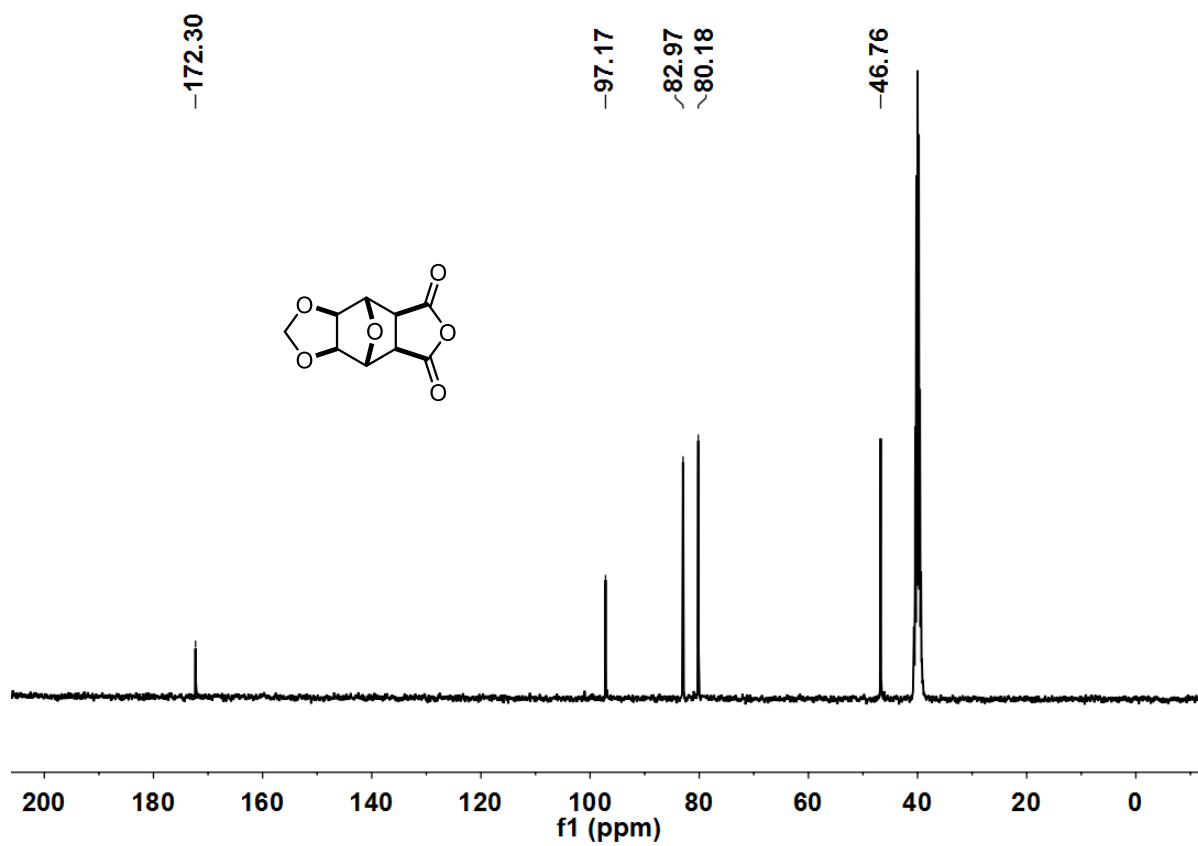


Figure S13. <sup>13</sup>C NMR spectrum of TCAH.



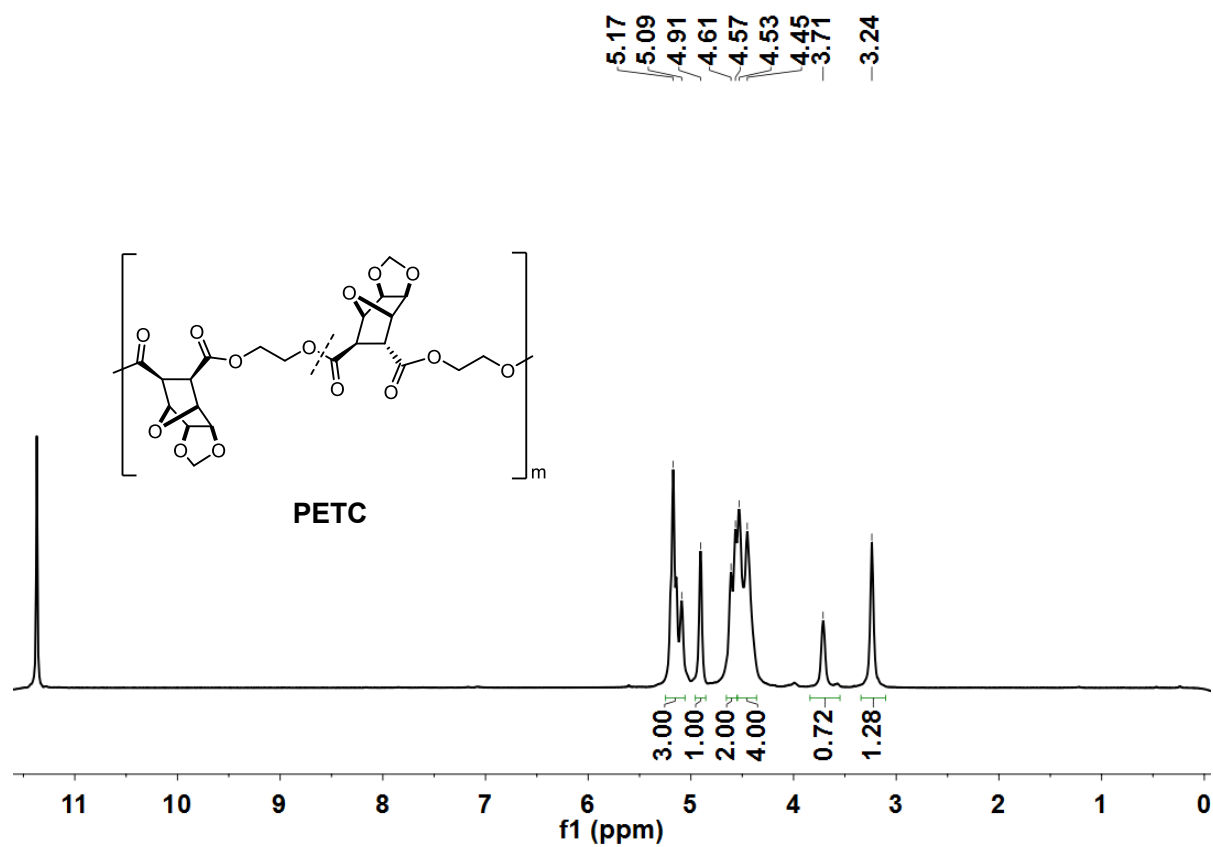


Figure S14.  $^1\text{H}$  NMR spectrum of PETC.

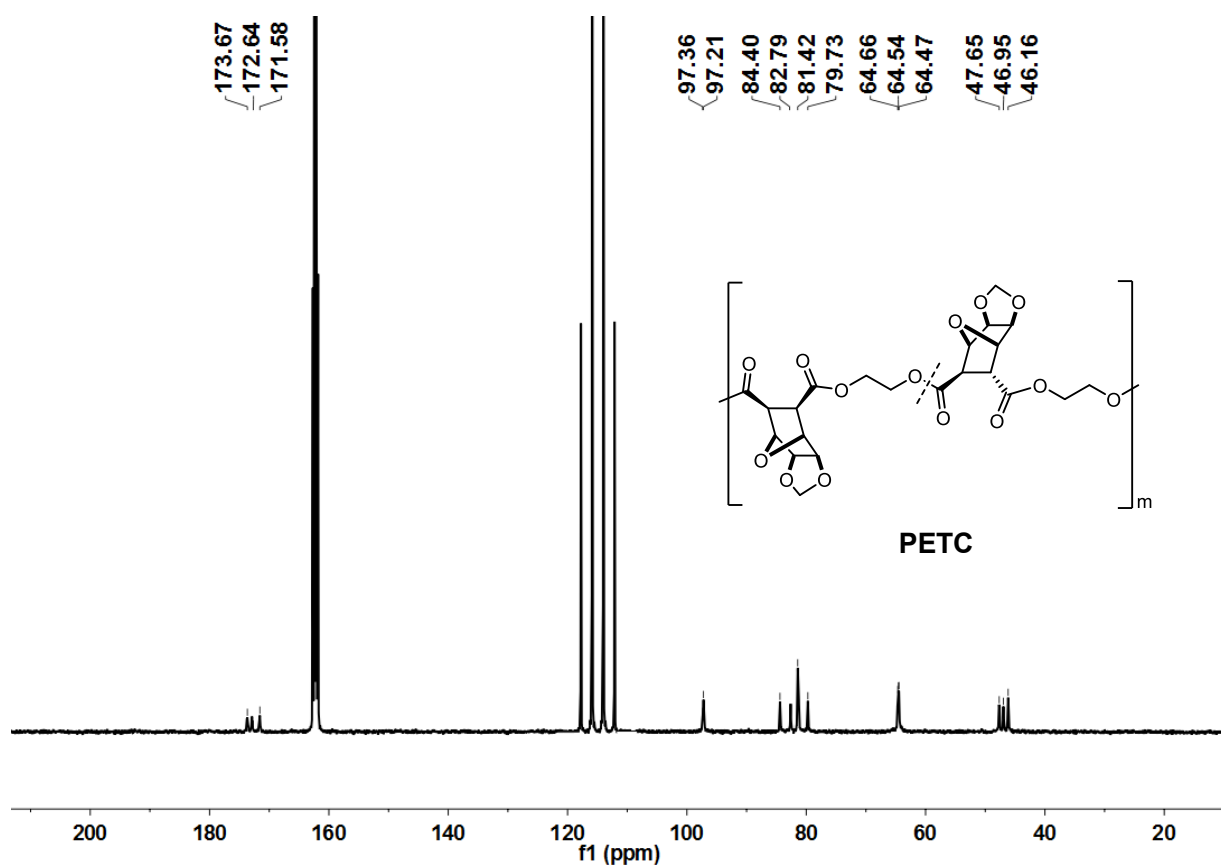


Figure S15.  $^{13}\text{C}$  NMR spectrum of PETC.

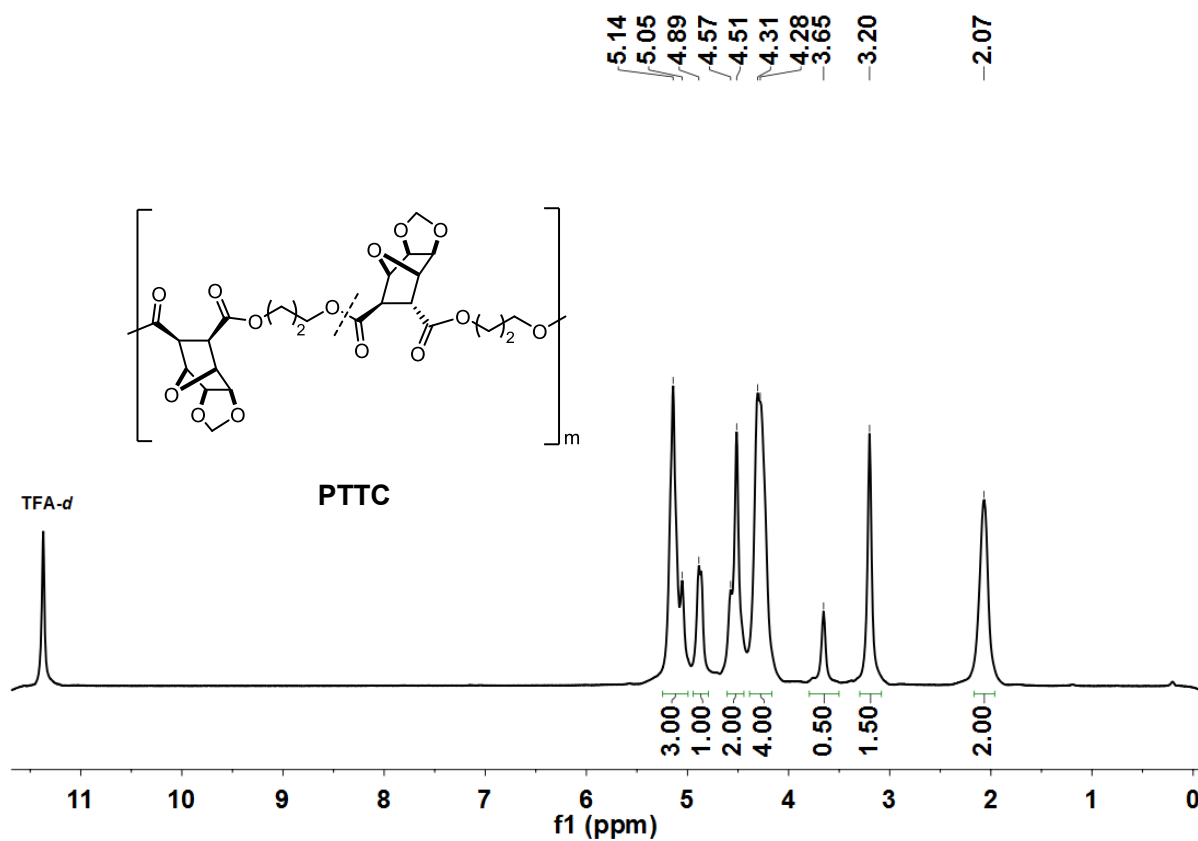


Figure S16.  $^1\text{H}$  NMR spectrum of PTTC.

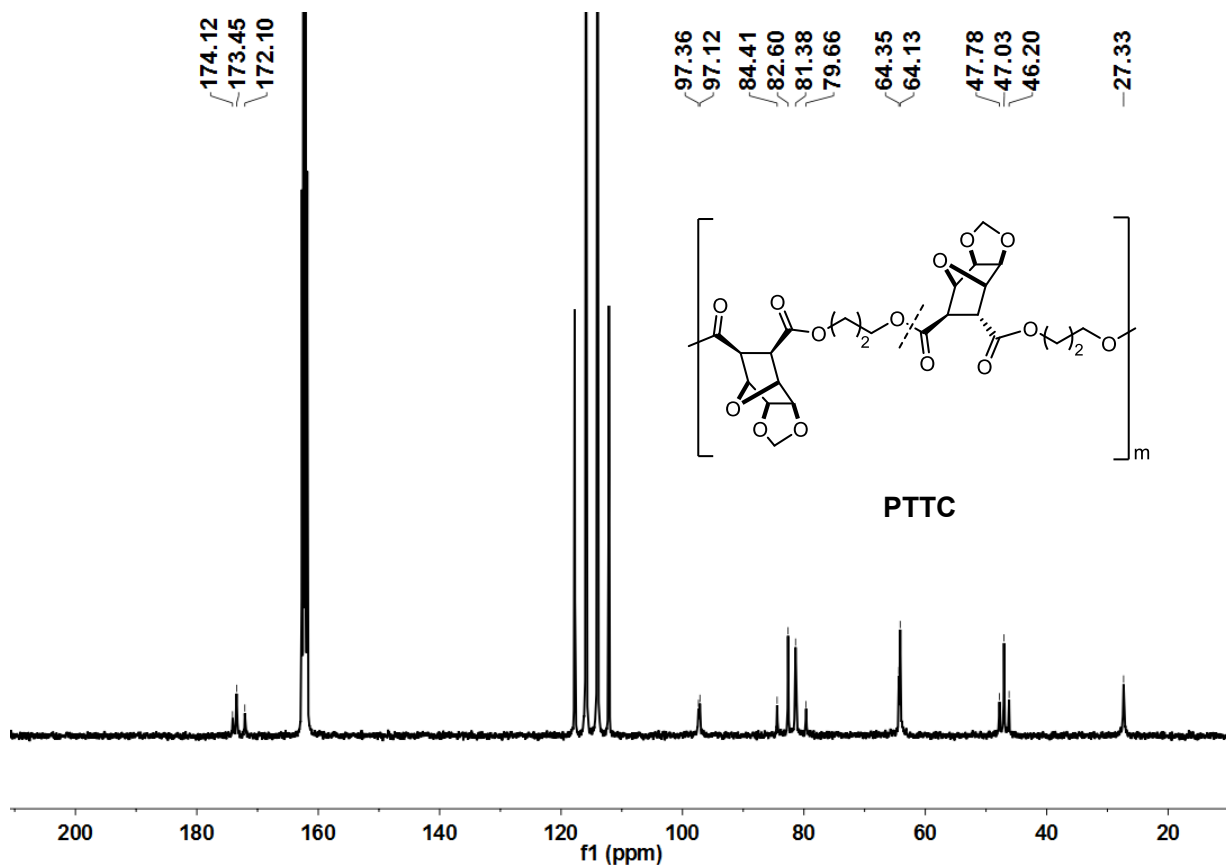


Figure S17.  $^{13}\text{C}$  NMR spectrum of PTTC.

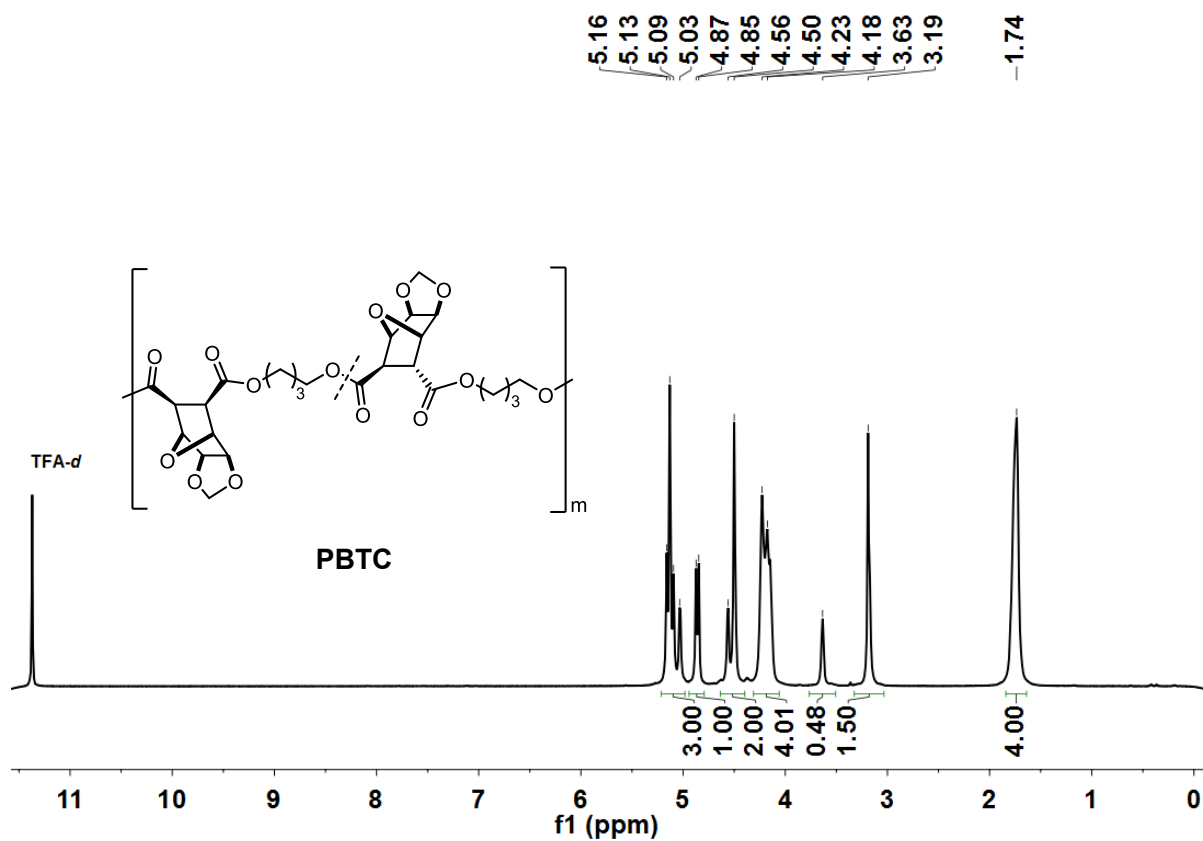


Figure S18. <sup>1</sup>H NMR spectrum of PBTC.

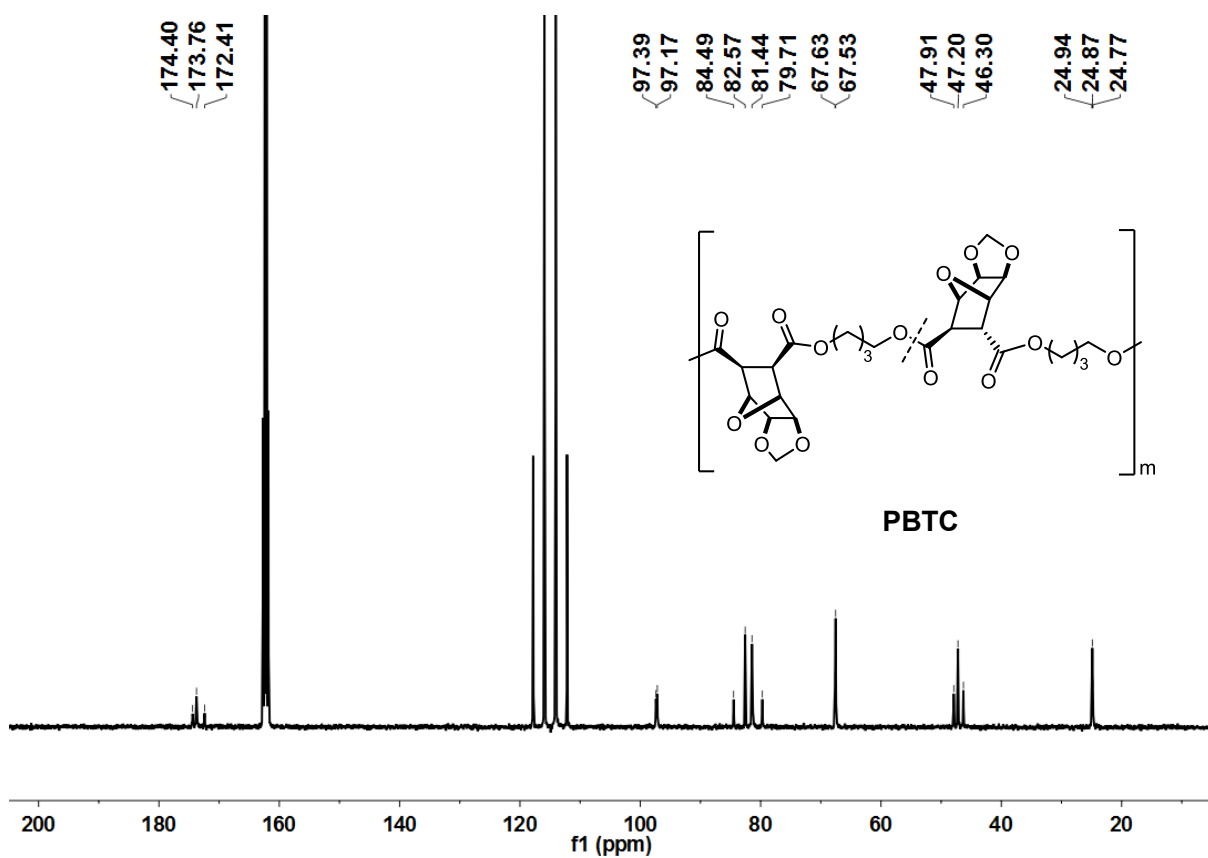


Figure S19. <sup>13</sup>C NMR spectrum of PBTC.

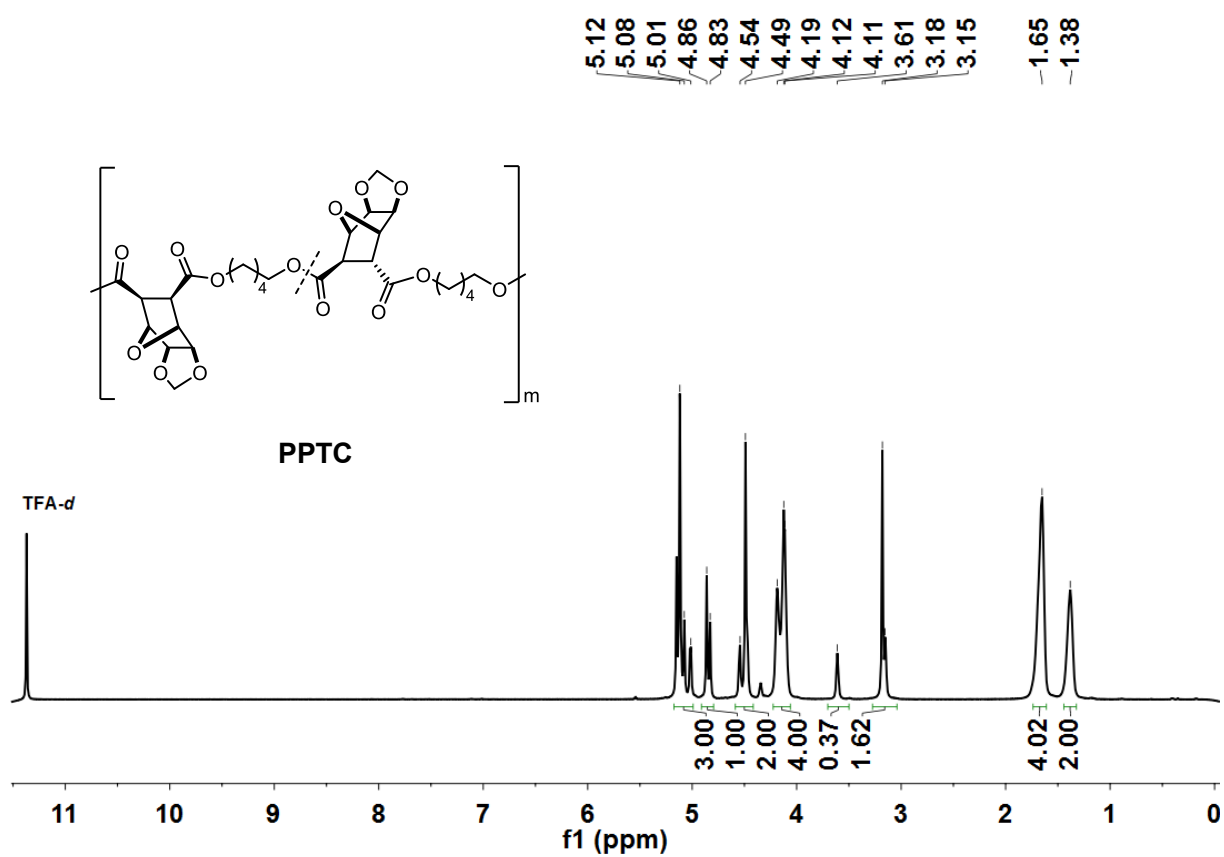


Figure S20. <sup>1</sup>H NMR spectrum of PPTC.

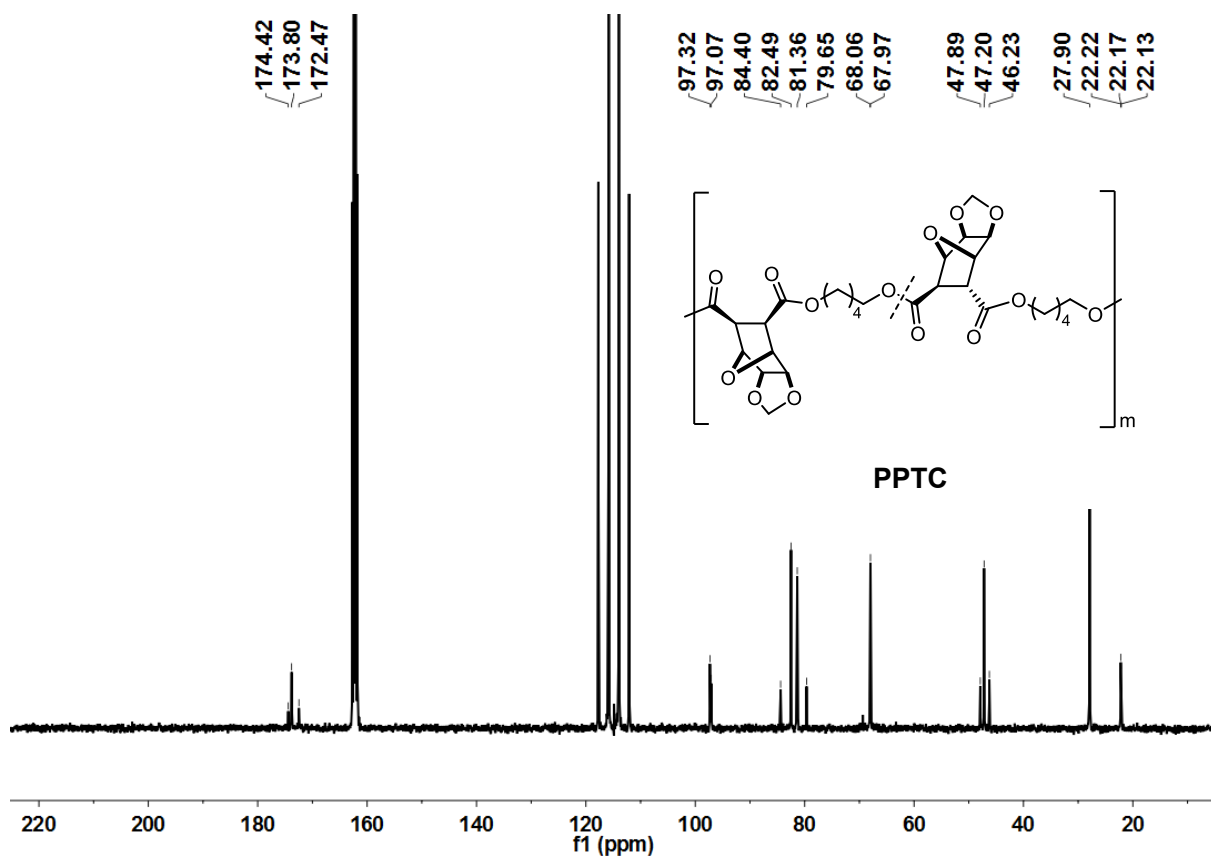


Figure S21. <sup>13</sup>C NMR spectrum of PPTC.

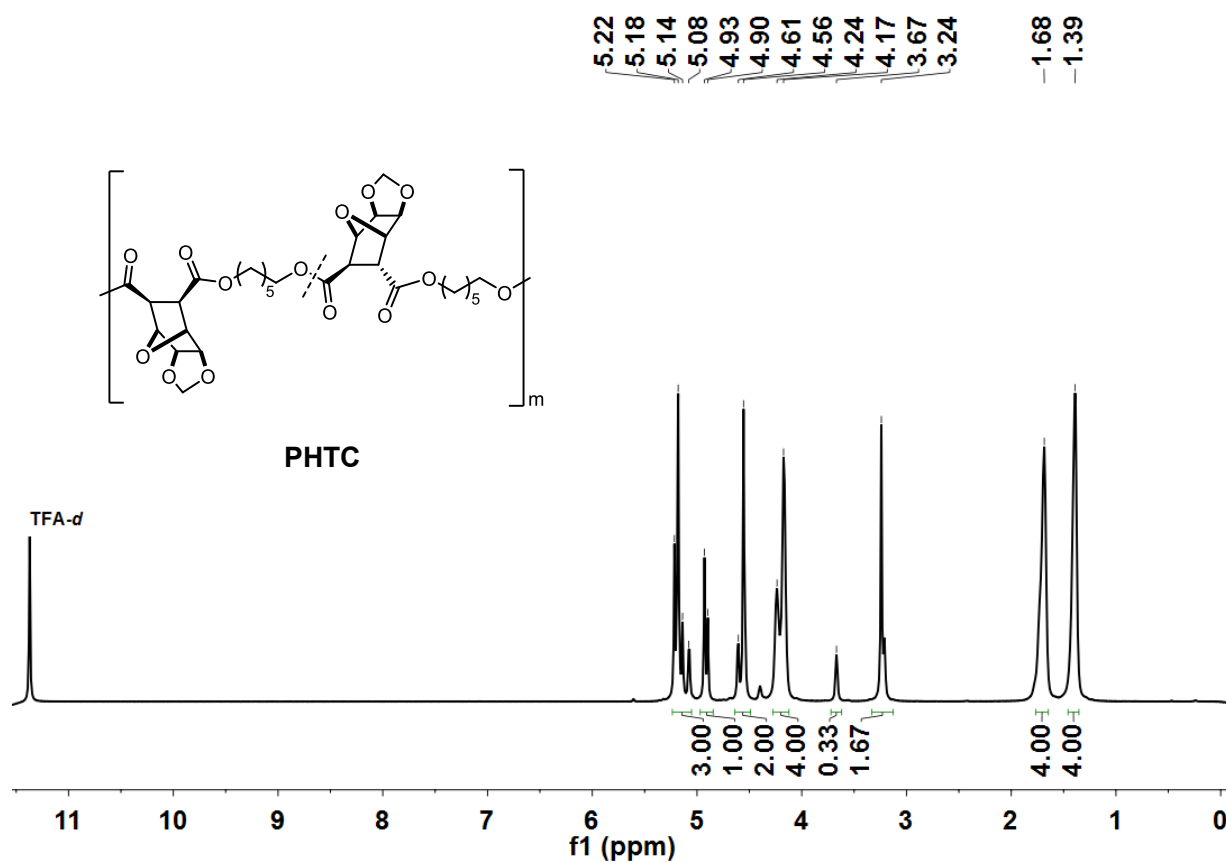


Figure S22.  $^1\text{H}$  NMR spectrum of **PHTC**.

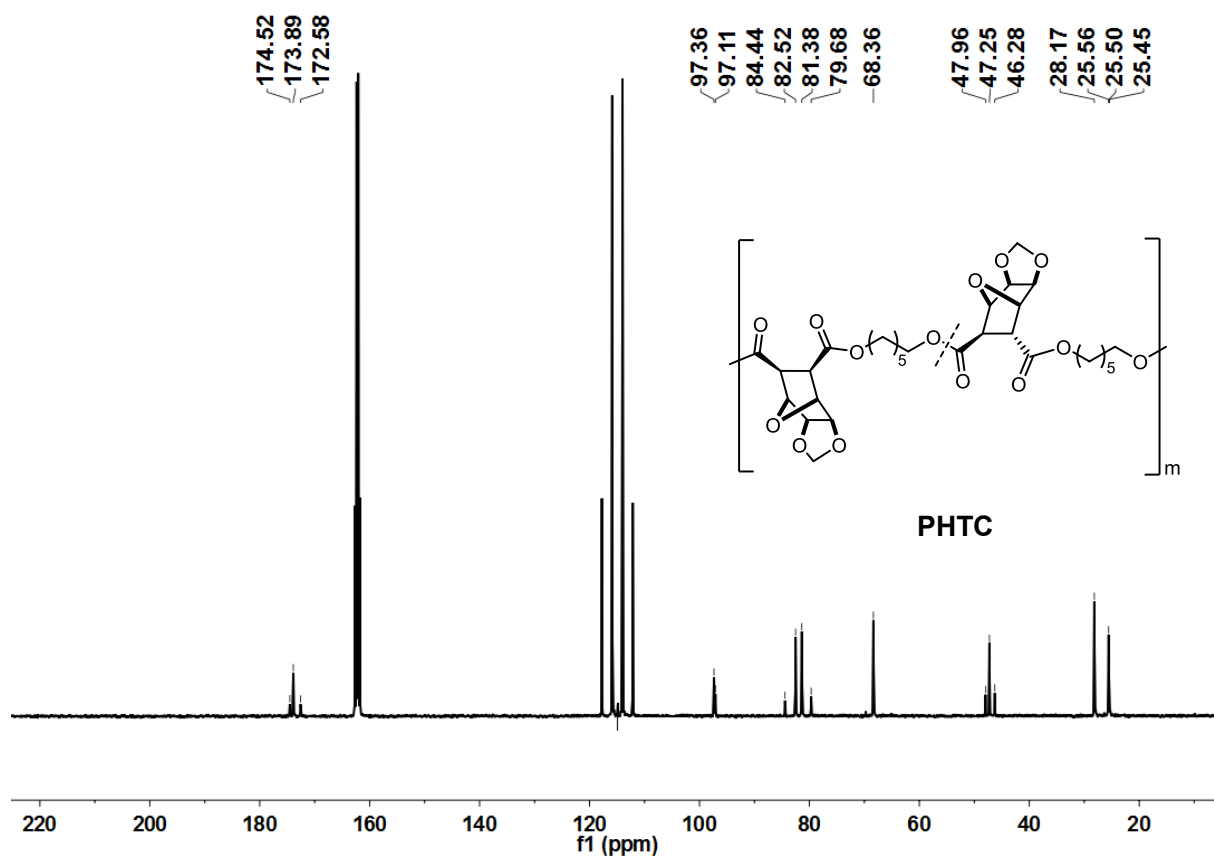


Figure S23.  $^{13}\text{C}$  NMR spectrum of **PHTC**.



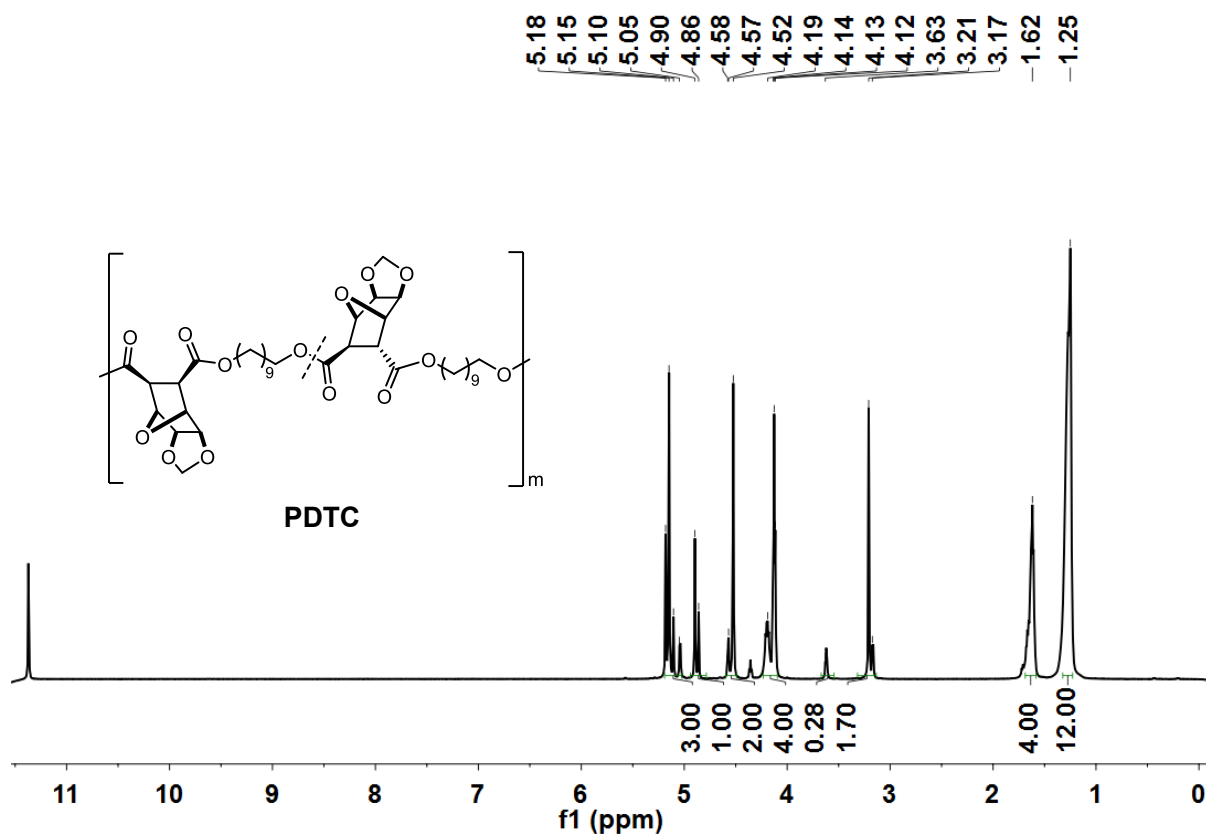


Figure S26. <sup>1</sup>H NMR spectrum of PDTC.

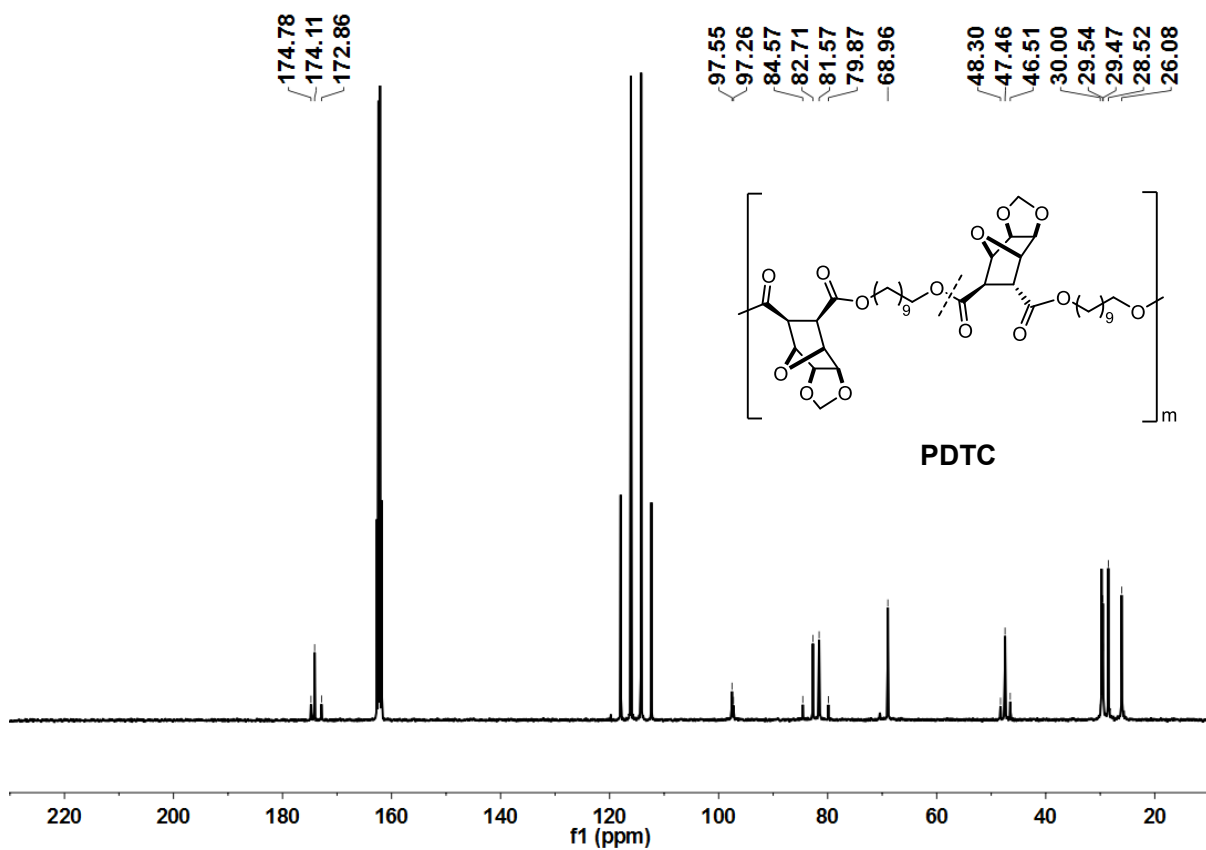


Figure S27. <sup>13</sup>C NMR spectrum of PDTC.

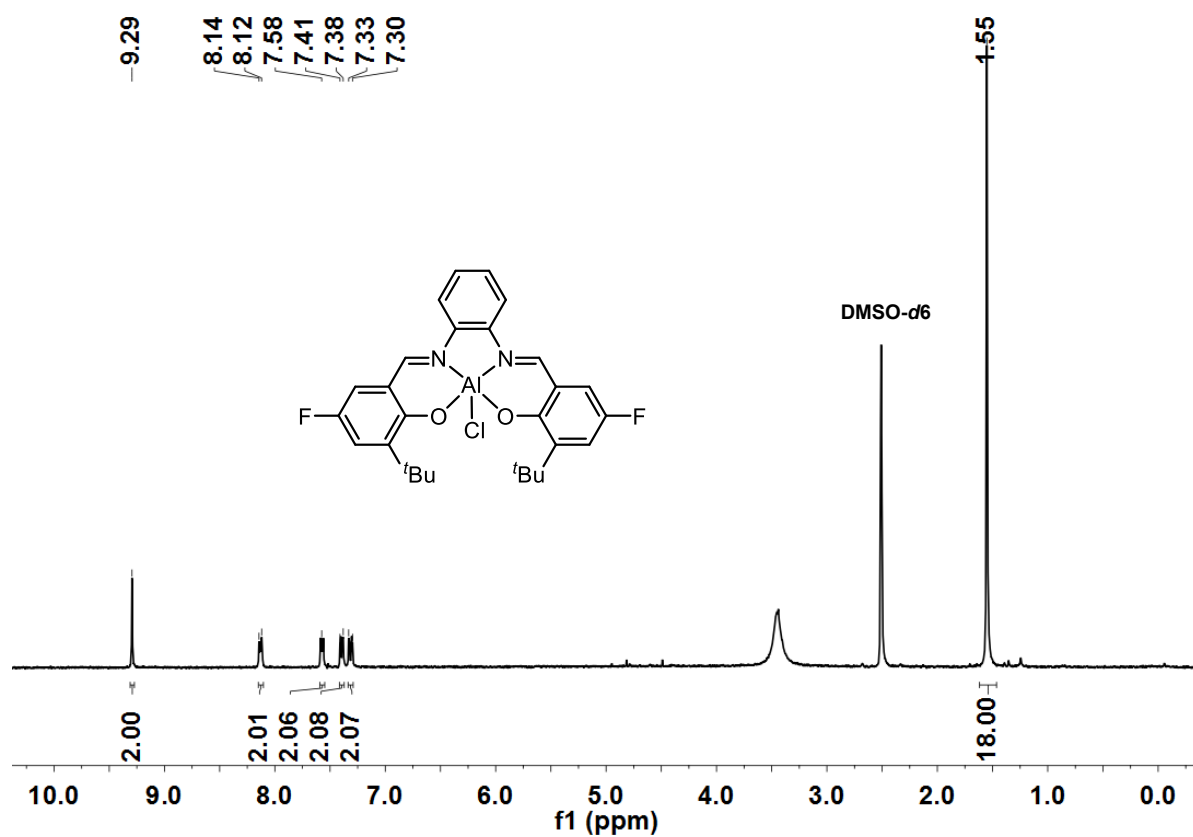


Figure S28. <sup>1</sup>H NMR spectrum of [F(salph)AlCl].

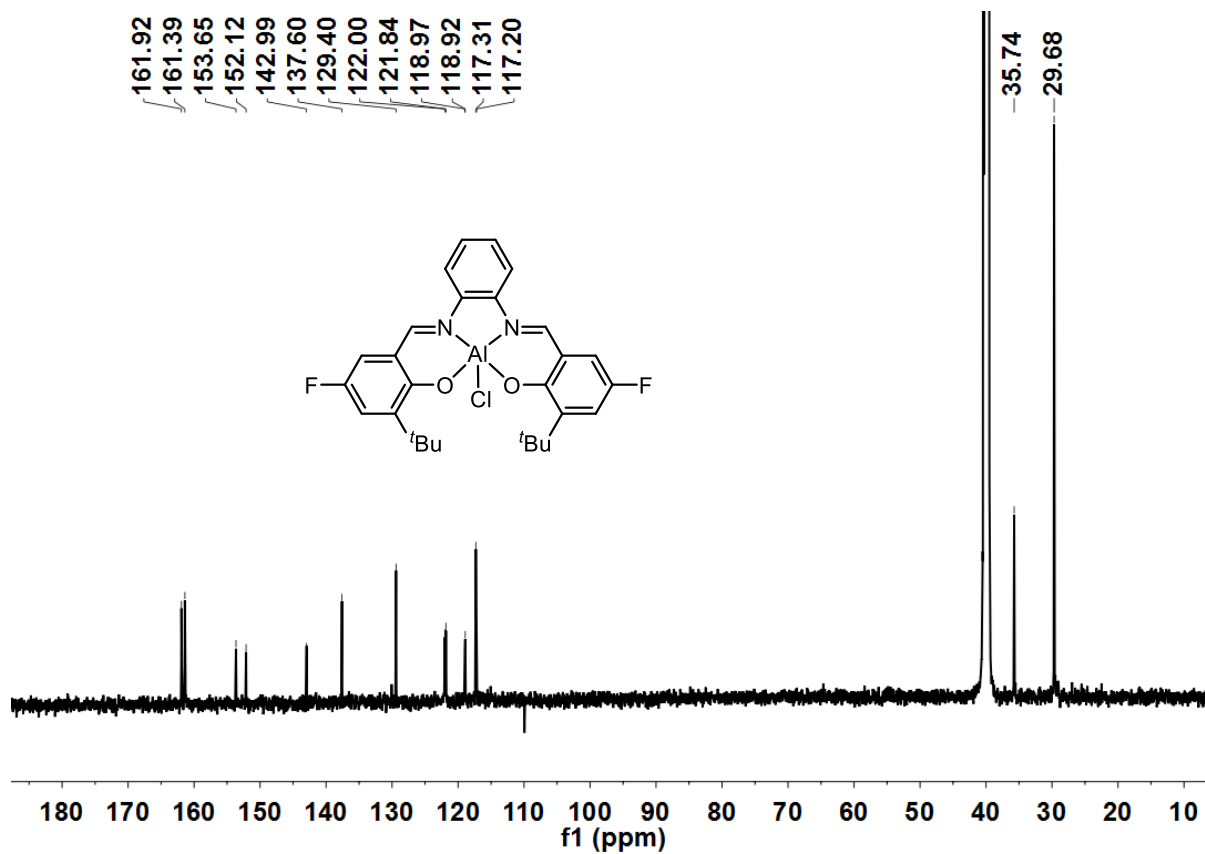
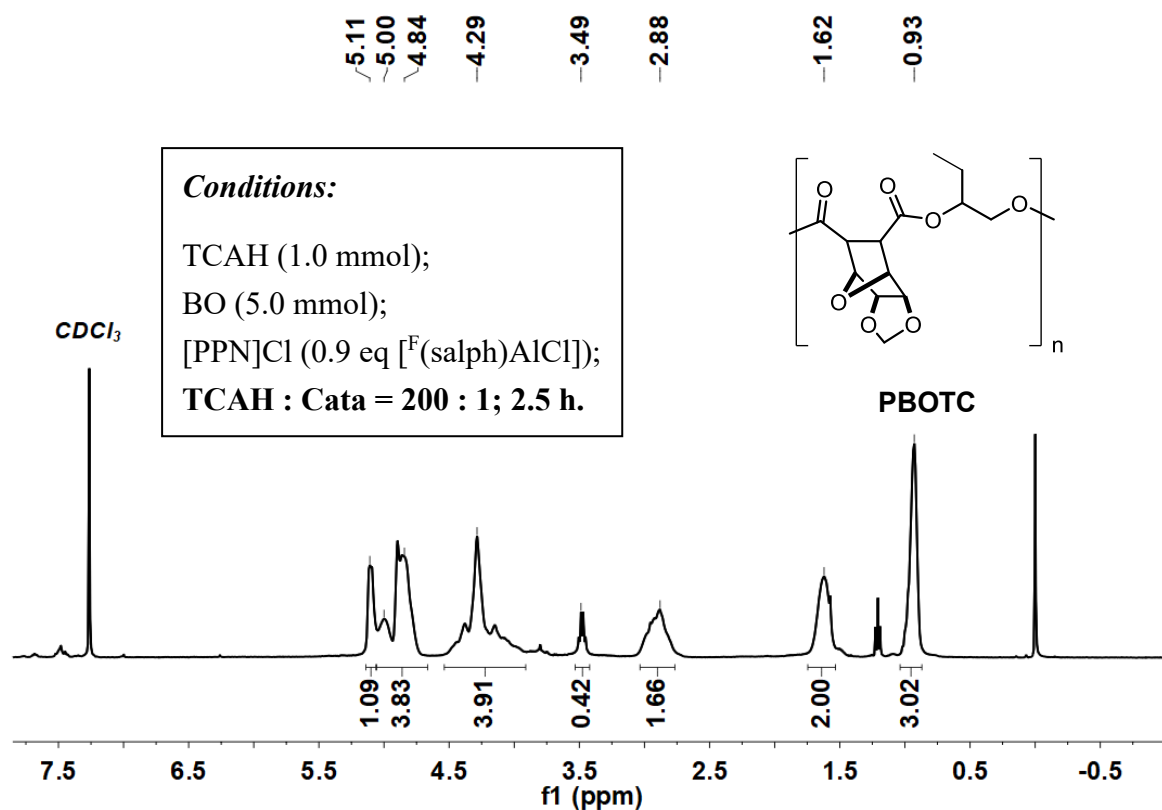
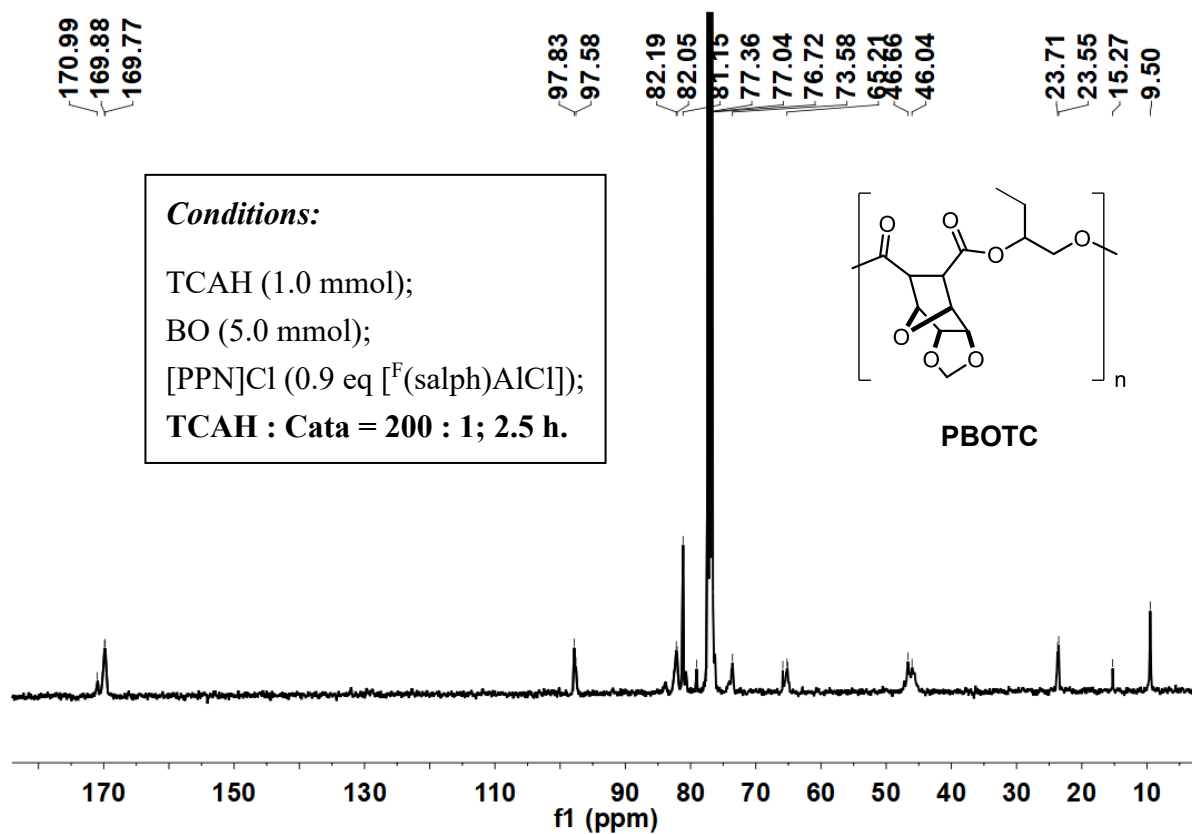


Figure S29. <sup>13</sup>C NMR spectrum of [F(salph)AlCl].

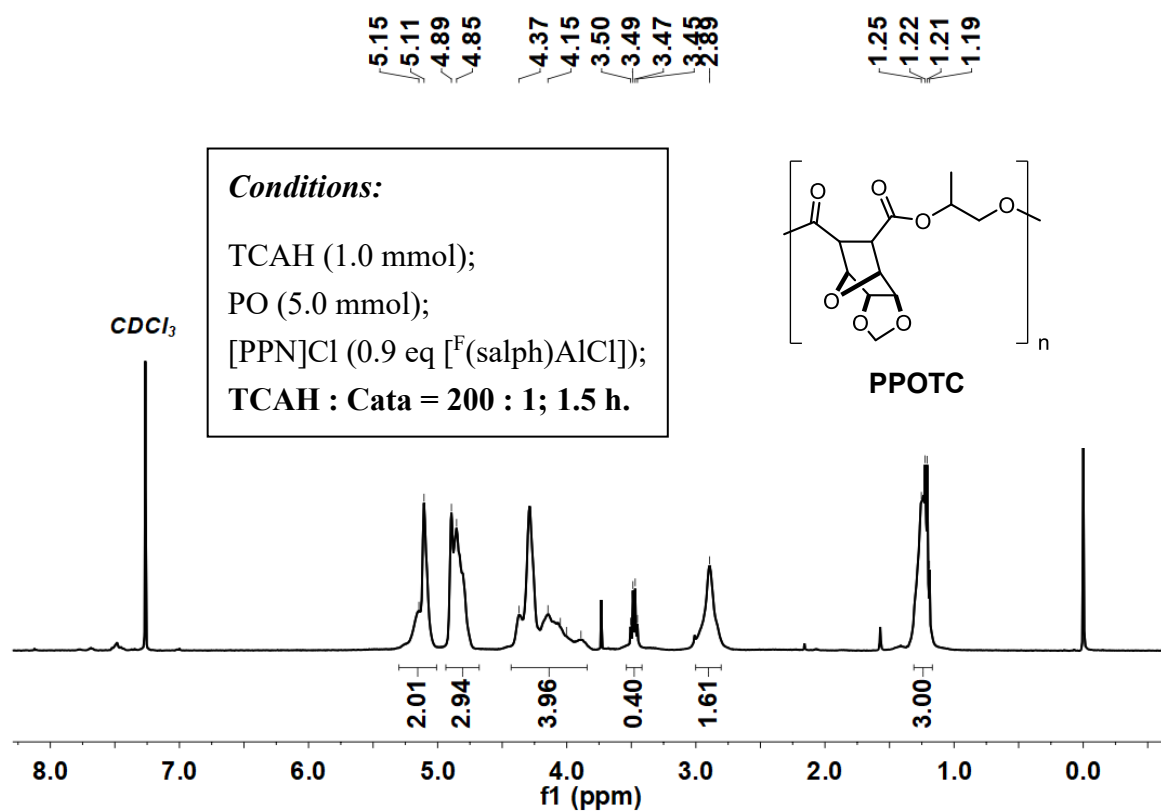




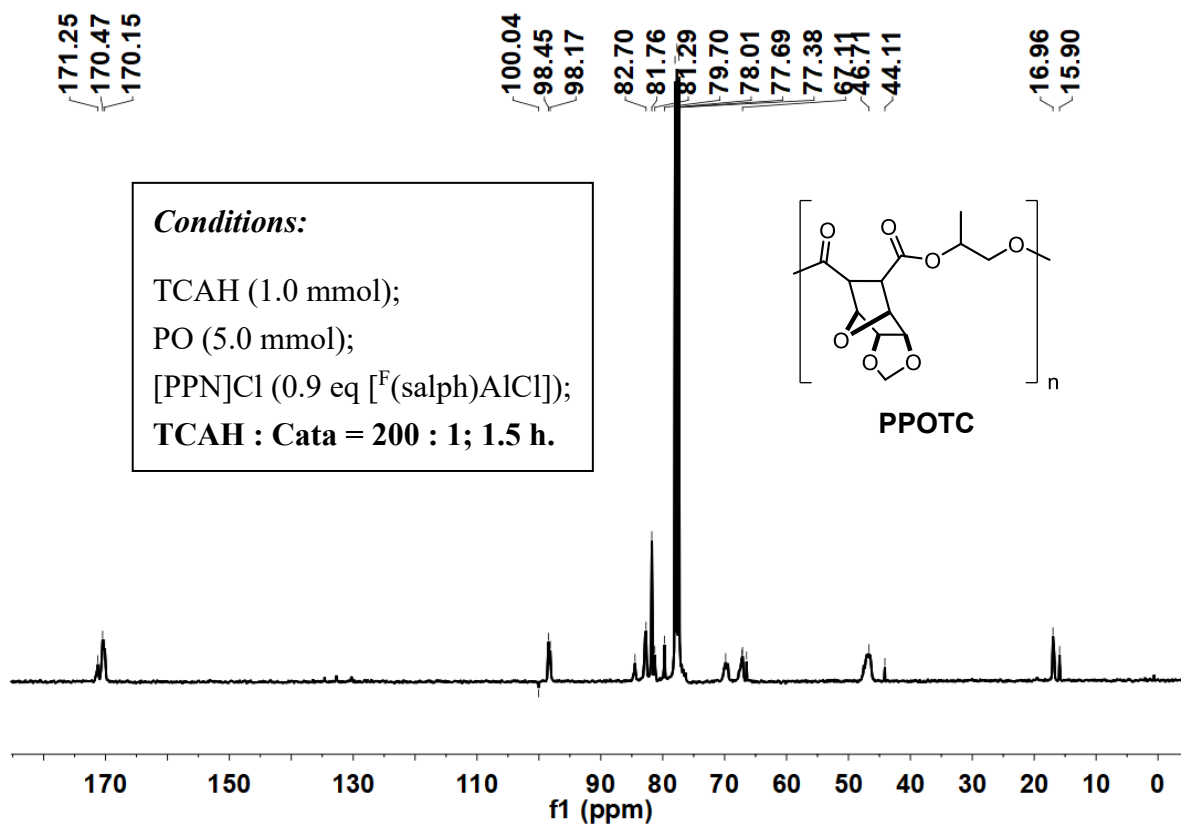
**Figure S30.** <sup>1</sup>H NMR spectrum of **PBOTC** with 42% *exo-endo* diester groups.



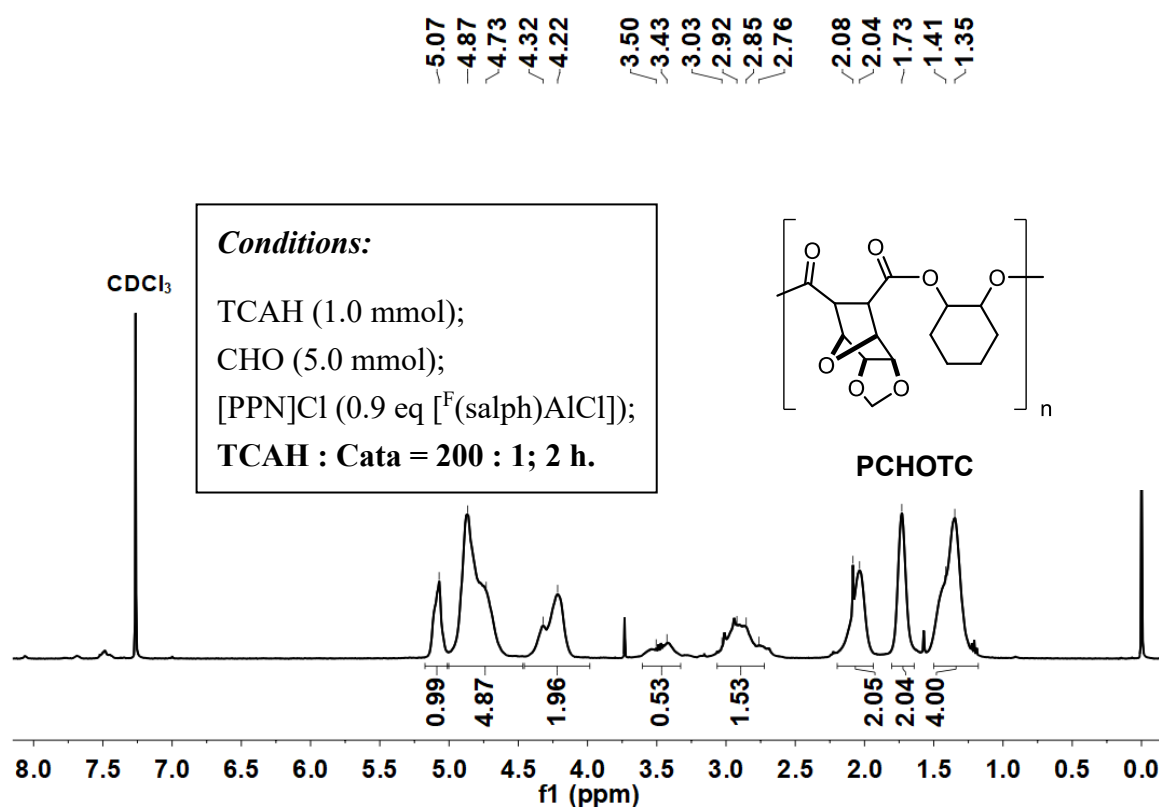
**Figure S31.** <sup>13</sup>C NMR spectrum of **PBOTC** with 42% *exo-endo* diester groups.



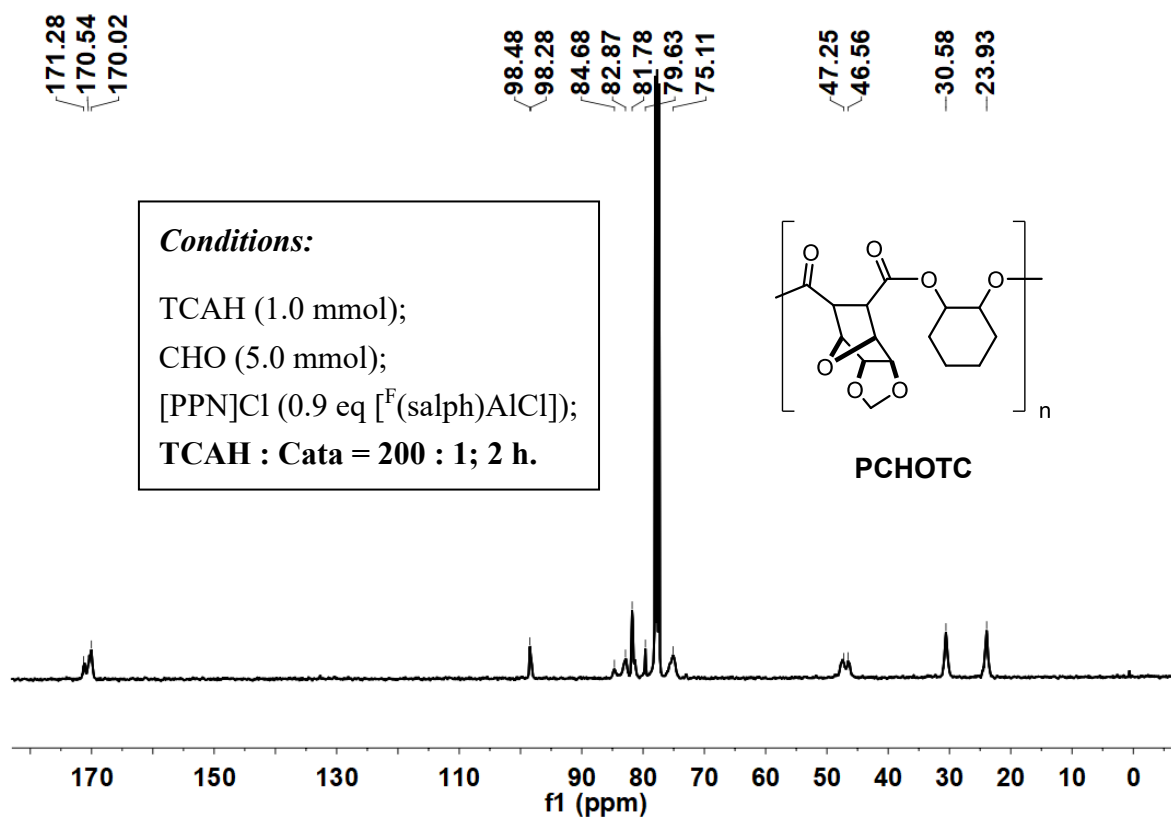
**Figure S32.** <sup>1</sup>H NMR spectrum of **PPOTC** with 40% *exo-endo* diester groups.



**Figure S33.** <sup>13</sup>C NMR spectrum of **PPOTC** with 40% *exo-endo* diester groups.



**Figure S34.** <sup>1</sup>H NMR spectrum of **PCHOTC** with 50% *exo-endo* diester groups.



**Figure S35.** <sup>13</sup>C NMR spectrum of **PCHOTC** with 50% *exo-endo* diester groups.