Electronic Supplementary Material (ESI) for Chemical Science.
This journal is © The Royal Society of Chemistry 2020

Supporting Information for

The crucial roles of guest water in a biocompatible coordination network on catalytic ring-opening polymerization of cyclic esters: a new mechanism perspective

Sheng-Chun Chen[a], Fei-Hang Zhang,[a] Kun-Lin Huang,[b] Feng Tian,[a] Zhi-Hui Zhang,[a] Renxian Zhou,[c] Xue-Jun Feng,[a] Xiaoying Zhou,[a] Ming-Yang He,[a] Jiande Gu,*[d] Qun Chen,*[a] and Chuan-De Wu*[c]

[a] *Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, P. R. China*

[b] *College of Chemistry, Chongqing Normal University, Chongqing 401331, P. R. China*

[c] *Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China*

[d] *Drug Design & Discovery Center, State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, CAS, Shanghai 201203, P. R. China*

Contents

1. General information

Glycolide (GA; >98%, Tokyo Kasei Kogyo Co., Ltd. (TCI)), L-Lactide (L-LA; >98%, TCI), 15-pentadecalactone (PDL; >98%, Sigma-Aldrich), trimethylene carbonate (TMC; >98%, TCI), and 5,5-dimethyl-1,3-dioxan-2-one (DMTMC; >99%, Energy Chemical) were purified by recrystallization from dry petroleum ether/ethyl acetate. ε-Caprolactone (CL; >99%, TCI) and δ-valerolactone (VL; >99%, Energy Chemical) were distilled over CaH_2 under reduced pressure. HPLC-grade tetrahydrofuran (THF) was purchased from TEDIA (USA). HPLC-grade hexafluoroisopropanol (HFIP) was purchased from Sigma-Aldrich. Polystyrene (PS) standards were purchased from Sigma-Aldrich (M_n = 1770, 17300, 135000, 305000, 502000 and 970800 Da). Poly(methyl methacrylate) (PMMA) standards were purchased from Sigma-Aldrich (M_n = 2000, 8000, 20000, 50000 and 100000 Da). Monomers, including 4-methyl-ε-caprolactone (4-MeCL), 4,4-dimethyl-ε-caprolactone (4,4-MeCL), 6-methyl-ε-caprolactone (6-MeCL) and 7-heptalactone (HL), were prepared according to the literature procedures.[S1] Other reagents and solvents for the synthesis and analysis were commercially available and used as received without further purification.

Primary fibroblasts (FBs) and smooth muscle cells (SMCs) were freshly isolated from rats (six-week wistar rats, male, 250 – 300 g) purchased from Changzhou Cavens Lab Animal Company (China) and cultured with Dulbecco's Modified Eagle Medium (DMEM, GIBCO Invitrogen Corporation, Carlsbad, CA, USA) containing 10% fetal bovine serum (FBS, GIBCO) and 4% Penicillin-Streptomycin (GIBCO). Fresh isolated FBs and SMCs from passages 2 – 4 were used for cytotoxicity experiments using 96 well Nunclon TC plates.

2. Characterization techniques

Thin layer chromatography (TLC) was conducted with TLC plates (Silica gel 60 F254, Qingdao Haiyang) and visualized with UV lamps and potassium permanganate stain.

Column chromatography was performed on silica gel 300 – 400 mesh with freshly distilled solvents.

Fourier transform infra-red (FTIR) spectra (KBr pellets) were taken on a Nicolet ESP 460 FT-IR spectrometer in the range of 4000–400 cm^{-1}.

Elemental analyses were performed on a PE–2400II (Perkin-Elmer) analyzer.

High resolution mass spectra (HRMS) were carried out using the electron impact (EI) mode at 70 eV or by QTOF using electrospray ionization (ESI) mode.

Nuclear magnetic resonance spectroscopy. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300 MHz NMR spectrometer (Bruker AVANCE). Chemical shifts for protons were reported in parts per million (ppm) downfield and were referenced to residual protium in the NMR solvent ($CDCl_3$, δ 7.26; DMSO-d_6, δ 2.50). Chemical shifts for carbons were reported in ppm downfield and were referenced to the carbon resonances of solvent ($CDCl_3$, δ 77.16; DMSO-d_6, δ 39.52). Data are represented as follows: chemical shift, multiplicity (br, broad; s, singlet; d, double; t, triplet; q, quartet; m, multiplet), coupling constants in Hertz (Hz), integration.

Powder X-ray diffraction (PXRD). Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/ max-2000 diffractometer at 40 kV and 100 mA for a Cu-target tube (λ = 1.5418 Å), and the calculated PXRD pattern was obtained from the single-crystal diffraction data using the PLATON software.[S2]

Thermogravimetric analysis (TGA) was carried out in the temperature range of 25–800 °C on a Dupont thermal analyzer under N_2 atmosphere at a heating rate of 15 °C/min.

Brunauer–Emmett–Teller (BET) surface area analysis was performed on a Micromeritics ASAP 2460 surface area analyzer at 77 K.

X-Ray photoelectron spectroscopy (XPS) was conducted on a PHI 5000 Versa Probe X-ray photoelectron spectrometer equipped with Al Kα radiation (1486.6 eV).

Inductively coupled plasma-mass spectrometry (ICP-MS) was used to determine the metal contents in the samples. Mass spectrometric analyses were conducted using positive-ion electrospray ionization on a PerkinElmer NexION 350X mass spectrometer.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were operated on a Nicolet 6700 apparatus outfitted with a HgCdTe (MCT) detector. The DRIFTS

cell was equipped with CaF_2 windows and a heated reaction chamber. DRIFTS spectra were recorded at a resolution of 4 cm^{-1} and an accumulation of 32 scans.

Gel permeation chromatography (GPC). GPC spectra were measured on a Gel permeation chromatography (GPC, Shimadzu) equipped with a LC-20AD HPLC pump, a refractive index detector (RID-10A, 120 V) and a Waters Styragel guard column (20 μm, 4.6 × 30 mm) followed by two Waters Styragel columns (HR 4E, 5 μm, mixed bed, 7.8 × 300 mm, and HR 5E, 5 μm, mixed bed, 7.8 × 300 mm), and calibrated with polystyrene standards.

Matrix-assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF MS). MALDI-TOF MS measurements were performed on a 4800 plus MALDI-TOF/TOF mass spectrometer (AB Sciex, U.S.A) equipped with a 355 nm NdYAG laser, a repetition rate of 200 Hz, and an acceleration voltage of 20 KV. Spectra were acquired in the positive-ion reflection mode. The polymer samples were dissolved in THF (Adamas) at a concentration of 10 mg mL^{-1}, and trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB; TCI) matrix was dissolved in THF at a concentration of 20 mg mL^{-1}. The sample solution and the matrix solution were mixed in 1:1 v/v ratio. Approximately, 1 uL of the obtained mixture was hand-spotted onto the stainless-steel target plate.

X-Ray structure determination. The crystal data of CZU-1 was collected on a Bruker Apex II CCD diffractometer at 293 K with Mo Kα radiation (λ = 0.71073 Å). A semiempirical absorption correction was applied using SADABS,[S3] and the program SAINT was used for integration of the diffraction profiles.[S4] The structure was solved by the direct methods using SHELXS program of SHELXTL packages and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on F^2 with SHELXL.[S5] C-bond hydrogen atoms were placed in geometrically calculated positions by using a riding model. O-bond hydrogen atoms were firstly localized by difference Fourier maps and then fixed geometrically with isotropic temperature factors. Further crystal data and structural refinement parameters are summarized in **Table S1**. CCDC-1842876 (CZU-1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223–336033; or

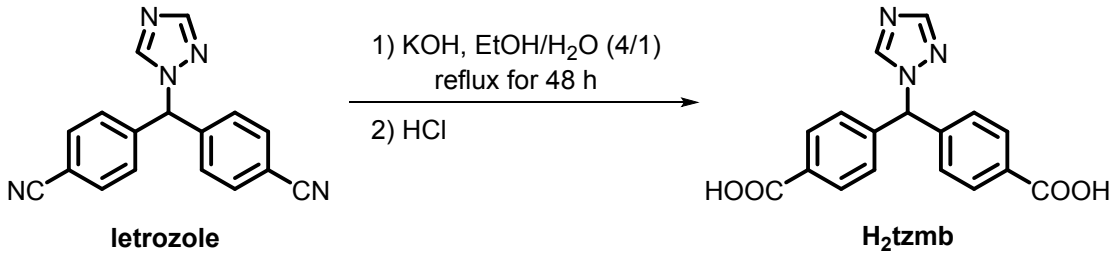
deposit@ccdc.cam.ac.uk).

Table S1. Crystallographic data and structure refinement for CZU-1.

Complex	**CZU-1**
Empirical formula	$C_{102}H_{68}N_{18}O_{27}Zn_8$
Formula weight	2500.70
Temperature (K)	296(2)
Crystal system	trigonal
Space group	*R*-3
a (Å)	22.979(5)
b (Å)	22.979(5)
c (Å)	15.496(4)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	7086(4)
Z	3
D_{calc} (g cm^{-3})	1.758
Absorption coefficient (mm^{-1})	2.088
F(000)	3786
Reflections collected/unique	13592/2921
R_{int}	0.0755
Data/restraints/parameters	2921/6/234
Goodness-of-fit on F^2	1.192
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0627$, $wR_2 = 0.1507$
R indices (all data)	$R_1 = 0.0825$, $wR_2 = 0.1594$
Largest diff. peak and hole (e Å^{-3})	0.869 and –0.736

3. Methods

3.1 Procedures for H_2tzmb ligand synthesis



letrozole **H_2tzmb**

Scheme S1. Hydrolysis of Letrozole

A mixture of letrozole (17.1 g, 0.06 mol), KOH (67.2 g, 1.2 mol) and EtOH (400 mL) in water (100 mL) was charged in a four-necked round bottom flask and refluxed for 48 h. Then, the solution was concentrated under reduced pressure to yield brown solid, which was dissolved in water (200 mL) and acidified to pH = 2 with 0.5 M HCl. Precipitate was collected by filtration, washed with water and dried in air to afford white solid (16.7 g; 86.1% yield). M.p.: 227.1 – 227.5 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 13.06 (s, 2H), 8.69 (s, 1H), 8.12 (s, 1H), 7.96 (d, J = 8.4 Hz, 4H), 7.35 (d, J = 8.3 Hz, 4H), 7.33 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 167.06, 152.31, 144.90, 143.10, 130.96, 129.80, 128.40, 64.77. m.p.: 227.5 °C; FT-IR (cm^{-1}, KBr pellet): 3435 m, 3128 m, 3058 m, 2923 m, 2629 m, 2508 m, 1934 w, 1695 s, 1607 m, 1573 w, 1508 m, 1415 m, 1314 m, 1284 s, 1108 m, 1135 s, 1013 m, 975 w, 867 w, 783 m, 754 s, 677 w, 519 w; HRMS calcd for $C_{17}H_{13}N_3O_4$ $[M–H]^+$: m/z 322.0828; found: 322.0613.

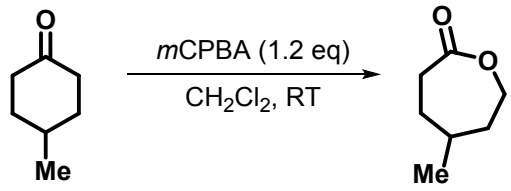
3.2 Procedures for CZU-1 synthesis

Hydrothermal synthesis of CZU-1. A mixture of $Zn(OAc)_2{\cdot}2H_2O$ (22.0 mg, 0.1 mmol), H_2tzmb (32.3 mg, 0.1 mmol) and NaOH (8 mg, 0.2 mmol) in water (6 mL) was stirred for 30 min at room temperature, which was subsequently sealed in a 15-mL Teflon-lined stainless steel autoclave, and heated at 180 °C for 72 h. After cooling down to room temperature at a rate of 5 °C/h, colorless block-shaped crystals were collected, washed with water (2 × 20 mL), methanol (2 × 20 mL), and dried. Yield: 34.6 mg (83% based on H_2tzmb). Anal. calcd for $C_{102}H_{68}N_{18}O_{27}Zn_8$: C, 48.99; H, 2.74; N, 10.08%; found: 48.26; H, 2.75; N, 10.12%. FTIR (cm^{-1}, KBr pellet): 3433 br, 3124 m, 3118 m, 2976 m, 1587 s, 1536 m, 1491 s, 1414 m, 1382

s, 1336 m, 1285 s, 1208 w, 1124 s, 1034 s, 898 m, 854 w, 784 m, 661 s, 610 m.

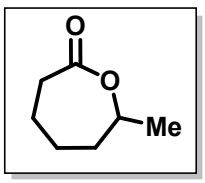
Bulky synthesis of CZU-1. A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (1.09 g, 5.0 mmol), H_2tzmb (1.62 g, 5.0 mmol) and NaOH (0.4 g, 10.0 mmol) in purified water (150 mL) was placed in a three-neck flask (250 mL), and refluxed for 48 h. After cooling down to room temperature, white precipitate was collected by filtration, washed with water (2 × 20 mL), methanol (2 × 20 mL), and dried in air (yield: 1.51 g, 72%).

3.3 Procedures for monomer synthesis

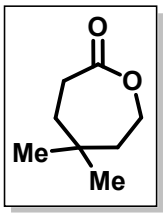


Scheme S2. Direct room-temperature lactonisation of 4-methylcyclohexanone

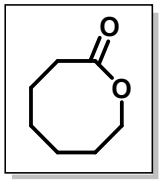
Cyclic esters were synthesized via the Baeyer-Villiger reaction. In a typical procedure, meta-chloroperbenzoic acid (*m*CPBA) (2.07 g, 12 mmol) was added into a 30 mL CH_2Cl_2 solution of 4-methylcyclohexanone (1.12 g, 10 mmol) at 0 ºC. The reaction mixture was stirred at room temperature. After completion of the reaction (as determined by TLC analysis), the reaction solution was washed three times with 10% K_2CO_3 aqueous solution and saturated $Na_2S_2O_3$ aqueous solution. The organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:3) to afford 4-methyl-*ε*-caprolactone (4-MeCL) as colorless liquid (0.92 g, 72% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.12 – 4.29 (m, 2H), 2.64 – 2.59 (m, 2H), 1.94 – 1.25 (m, 5H), 1.33 (d, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.2, 68.2, 37.3, 35.4, 33.3, 30.8, 22.2.



6-Methyl-*ε*-caprolactone (6-MeCL): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.48 – 4.38 (m, 1H), 2.69 – 2.54 (m, 2H), 1.93 – 1.85 (m, 3H), 1.60 – 1.56 (m, 3H), 1.33 (d, J = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.8, 77.0, 36.3, 35.1, 28.4, 23.0, 22.7.



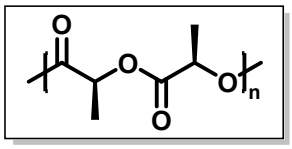
4,4-Dimethyl-ε-caprolactone (4,4'-MeCL): white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.22 – 4.19 (m, 2H), 2.62 – 2.58 (m, 2H), 1.67 – 1.54 (m, 4H), 1.02 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.4, 64.9, 42.0, 35.8, 32.1, 30.2, 28.6.



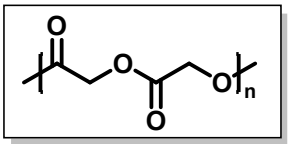
7-Heptalactone (HL): colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.33 – 4.30 (m, 2H), 2.54 – 2.49 (m, 2H), 1.87 – 1.73 (m, 4H), 1.62 – 1.49 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.8, 68.0, 31.3 30.9, 28.4, 25.8, 23.9.

3.4 Procedures for solvent-free ROP of cyclic esters and carbonates catalyzed by CZU-1

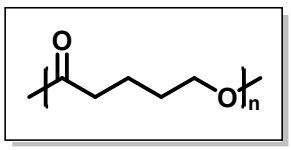
In a typical procedure, L-LA (1.15 g, 8 mmol) and CZU-1 catalyst (5.0 mg, 0.025 mol%) were added into a 10-mL Schlenk flask. The mixture was stirred at 160 °C under N_2 atmosphere. After the required polymerization time, polymer was obtained by dissolving the reaction mixture in a small amount of dichloromethane, and the catalyst was separated by centrifugation. Excess cold methanol or *n*-hexane was added to the supernate, producing white precipitate. The product was dried under vacuum to a constant weight.



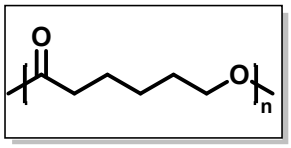
PLLA (M_n 32.60 kDa, PDI 1.52). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.15 (q, J = 7.1 Hz, 1H), 1.57 (d, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.74, 69.12, 16.76.



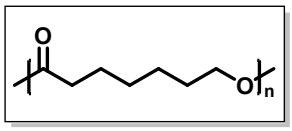
PGA (M_n 45.41 kDa, PDI 1.39). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.90 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.21, 61.69.



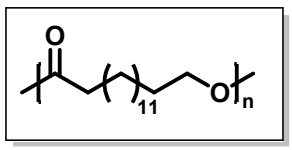
PVL (M_n 16.72 kDa, PDI 1.51). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.07 (t, J = 6.0 Hz, 2H), 2.33 (t, J = 7.0 Hz, 2H), 1.74 – 1.58 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.42, 64.05, 33.80, 28.18, 21.53.



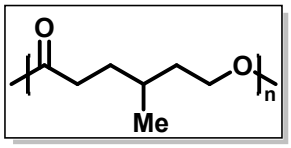
PCL (M_n 22.25 kDa, PDI 1.36). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.05 (t, J = 6.7 Hz, 2H), 2.30 (t, J = 7.5 Hz, 2H), 1.69 – 1.59 (m, 4H), 1.42 – 1.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.70, 64.29, 34.24, 28.47, 25.65, 24.70.



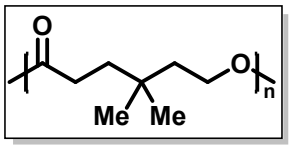
PHL (M_n 17.57 kDa, PDI 1.48). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.04 (t, J = 6.7 Hz, 2H), 2.28 (t, J = 7.5 Hz, 2H), 1.67 – 1.53 (m, 4H), 1.41 – 1.27 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.91, 64.40, 34.32, 28.89, 28.59, 25.75, 24.94.



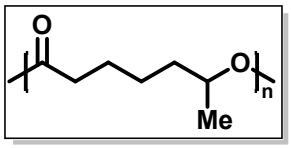
PPDL (M_n 27.83 kDa, PDI 1.03). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.04 (t, J = 6.7 Hz, 2H), 2.28 (t, J = 7.5 Hz, 2H), 1.63 – 1.56 (m, 4H), 1.36 – 1.18 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.20, 64.55, 34.54, 29.79, 29.76, 29.74, 29.69, 29.63, 29.44, 29.41, 29.31, 28.77, 26.07, 25.16.



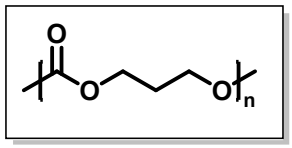
P(4-MeCL) (M_n 17.23 kDa, PDI 1.43). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.14 – 4.01 (m, 2H), 2.37 – 2.19 (m, 2H), 1.72 – 1.37 (m, 5H), 0.89 (d, J = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.87, 62.70, 35.28, 31.98, 31.83, 29.62, 19.11.



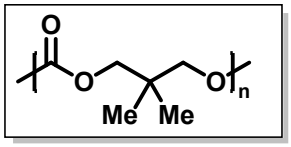
P(4,4-MeCL) (M_n 23.80 kDa, PDI 1.59). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.10 (t, J = 7.6 Hz, 2H), 2.31 – 2.21 (m, 2H), 1.56 (dd, J = 15.2, 7.6 Hz, 4H), 0.91 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.21, 61.69, 39.61, 36.95, 32.00, 29.68, 26.94.



P(6-MeCL) (M_n 11.36 kDa, PDI 1.60). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.91 – 4.81 (m, 1H), 2.24 (t, J = 7.5 Hz, 2H), 1.66 – 1.47 (m, 4H), 1.36 – 1.24 (m, 2H), 1.17 (d, J = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.27, 70.67, 35.64, 34.57, 25.05, 24.92, 20.04.



PTMC (M_n 12.74 kDa, PDI 1.62). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.23 (t, J = 6.2 Hz, 4H), 2.04 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.03, 64.40, 28.14.



PDMTMC (M_n 8.45 kDa, PDI 1.59). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.95 (s, 4H), 0.99 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.06, 155.41, 72.91, 72.52, 68.06, 36.65, 35.23, 21.37.

3.5 Cytotoxicity assay

Fresh primary fibroblasts and smooth muscle cells were isolated and seeded in 96 well plate (5 × 10^3 cells/well) till 75% confluence, then treated with CZU-1, PLLA-CZU-1, PGA-

CZU-1, PCL-CZU-1, $Sn(Oct)_2$, PLLA-$Sn(Oct)_2$, PGA-$Sn(Oct)_2$ and PCL-$Sn(Oct)_2$ at different Zn or Sn concentrations (0, 0.01, 0.1, 1.0 and 10 μmol L^{-1}), respectively, in serum free condition for 24 h (n = 6). Thiazolyl blue tetrazolium bromide (Sigma-Aldrich, USA) at a final concentration of 0.5 mg/mL was added to each well and incubated at 37 °C for 4 h. DMSO was added to dissolve the formazan crystals. The absorbance was examined by Bio-Rad micro-plate reader at 570 nm. Relative growth rate (RGR, %) = (A material – A blank control) / (A untreated control – A blank control) × 100%. According to the relative growth rate (RGR), the cytotoxicity was evaluated according to the toxicity grading method of American Pharmacopoeia. The evaluation criteria are as follows: (1) RGR value was more than 75%, and cytotoxicity grade was 0 or 1, qualified; (2) RGR value was 50 – 74%, and cytotoxicity grade was 2, which should be combined with cell morphology comprehensive evaluation; RGR value was less than 49%, and cytotoxicity grade was 3 – 5, unqualified.

3.6 Computational details

All calculations were carried out by using density functional theory (DFT). The functional by Truhlar and Zhao (M06-L)[S6] along with the split valence basis set cc-pVDZ[S7] have been used. Geometries of all the reactants, intermediates, transition states, and products were fully optimized. Analytical frequency analyses were performed to ensure the local minima for stable intermediates and stationary point (with only one negative frequency) for transition states. Vibrational mode analyses and the IRC calculations were also performed to ensure the correct connections between the transition states and the corresponding intermediates. The Gaussian-09 package of programs[S8] was used for all computations.

4. Characterizations of H_2tzmb ligand and CZU-1

4.1 Characterizations of H_2tzmb ligand

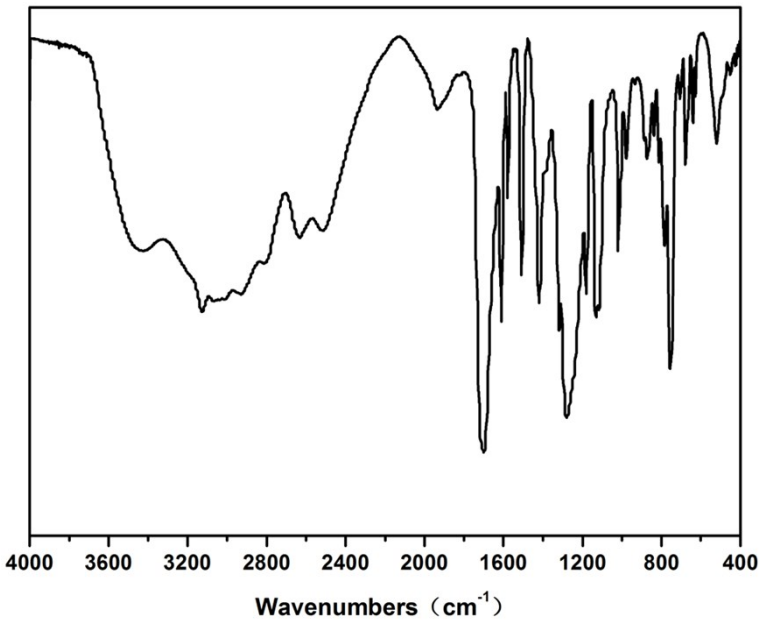


Fig. S1 FT-IR spectrum of H_2tzmb ligand.

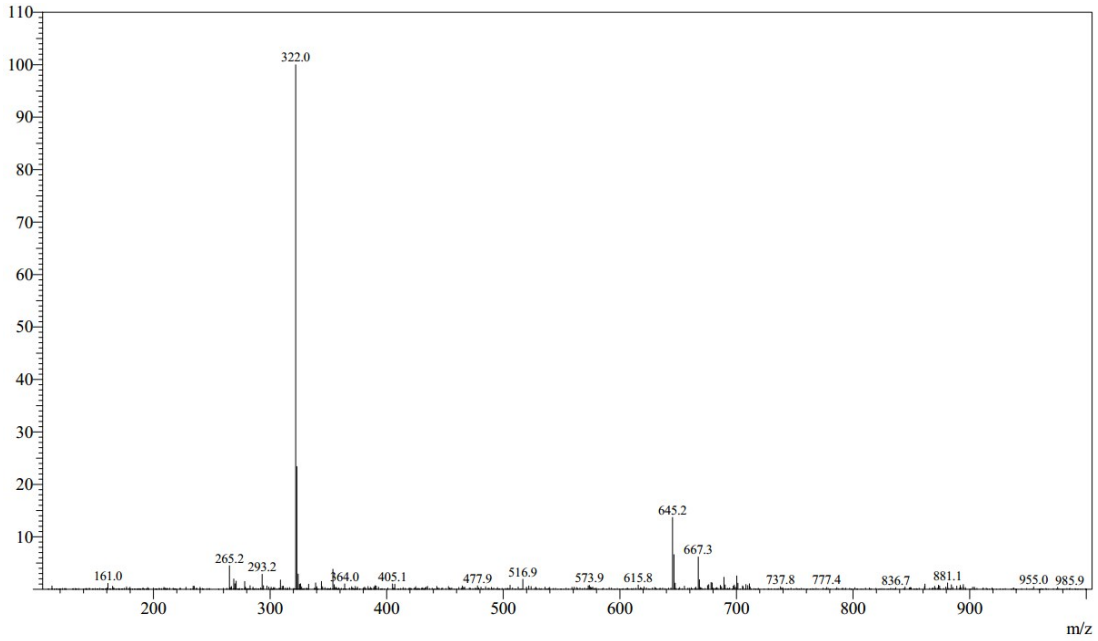


Fig. S2 HMRS spectrum of H_2tzmb ligand.

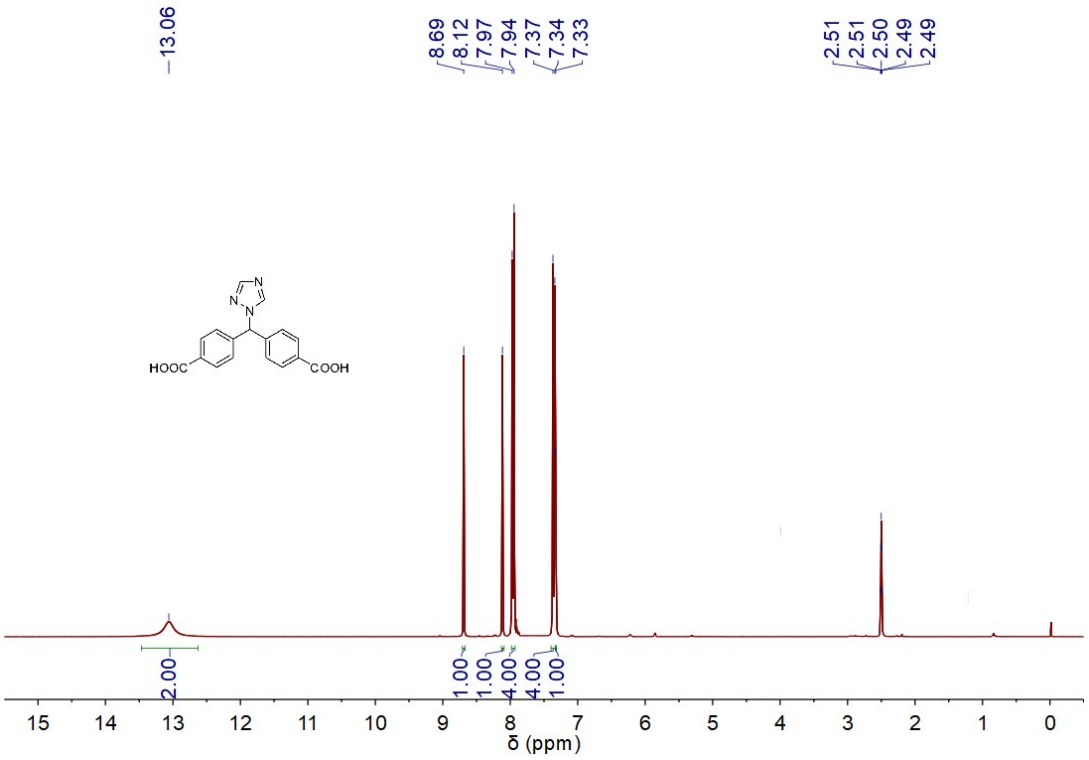


Fig. S3 ^{1}H NMR spectrum of H_2tzmb ligand.

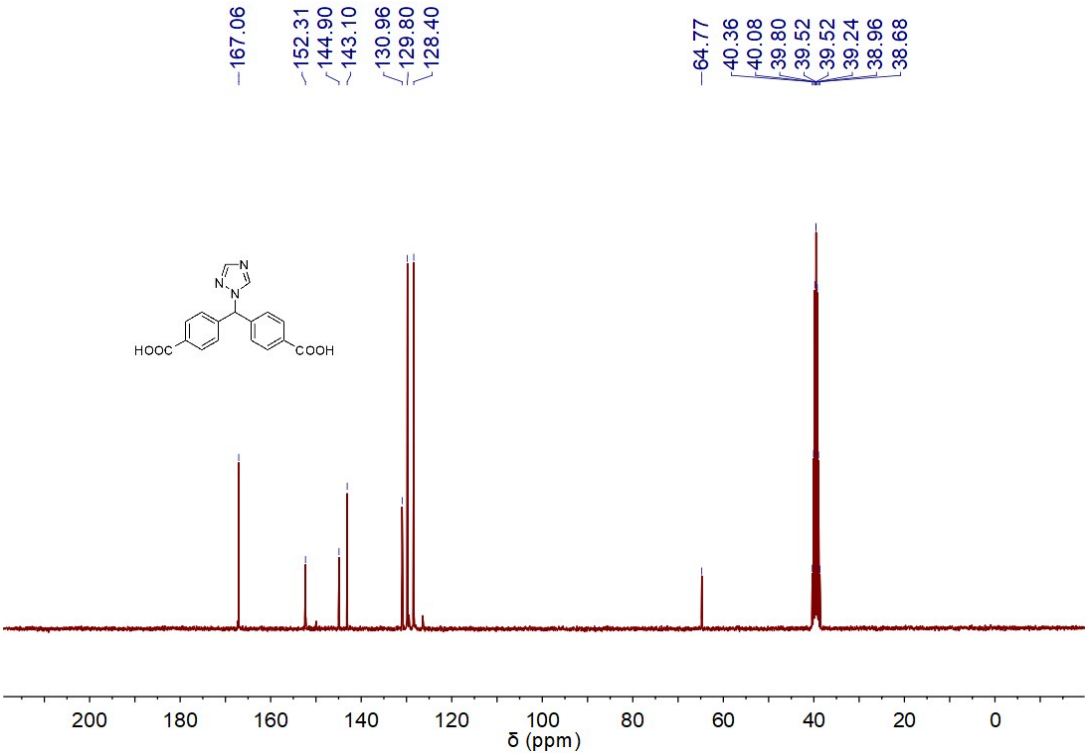


Fig. S4 ^{13}C NMR spectrum of H_2tzmb ligand.

4.2 Characterizations of CZU-1

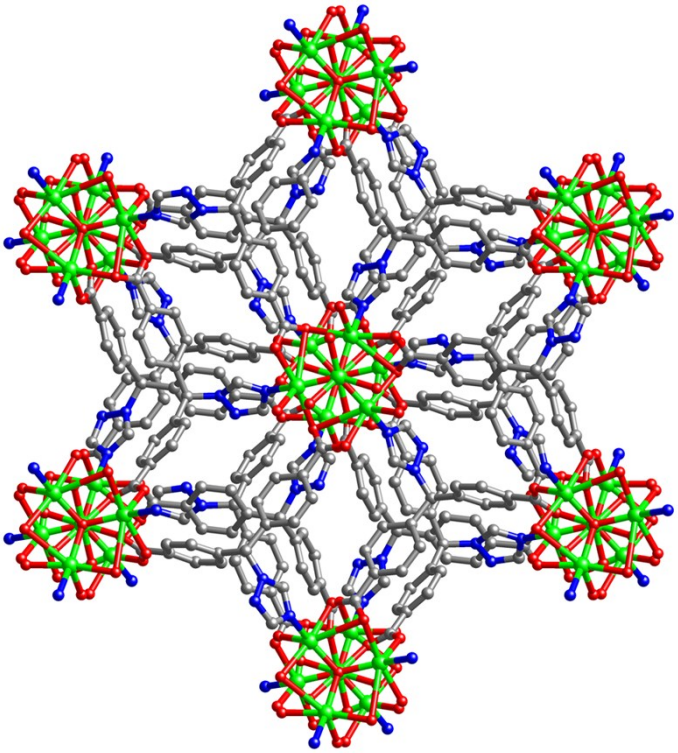


Fig. S5 The **xmz** net of CZU-1 in ball and stick model, viewed along the [001] direction.

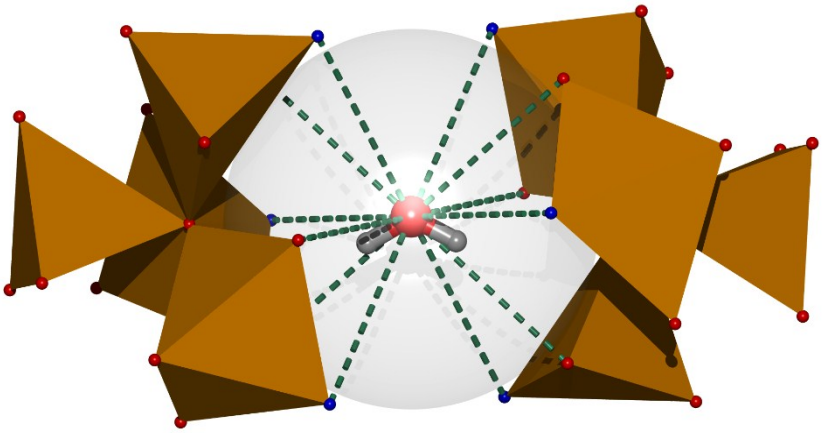


Fig. S6 The intermolecular hydrogen bonding interactions (turquoise dashed lines) between guest water and neighboring $Zn_4(\mu_4\text{-}O)(COO)_6$ SBUs in CZU-1.

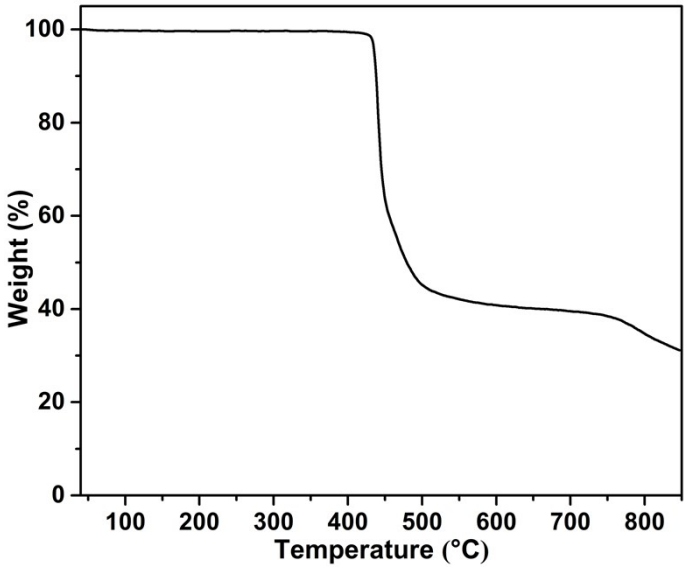


Fig. S7 The TGA profile of CZU-1.

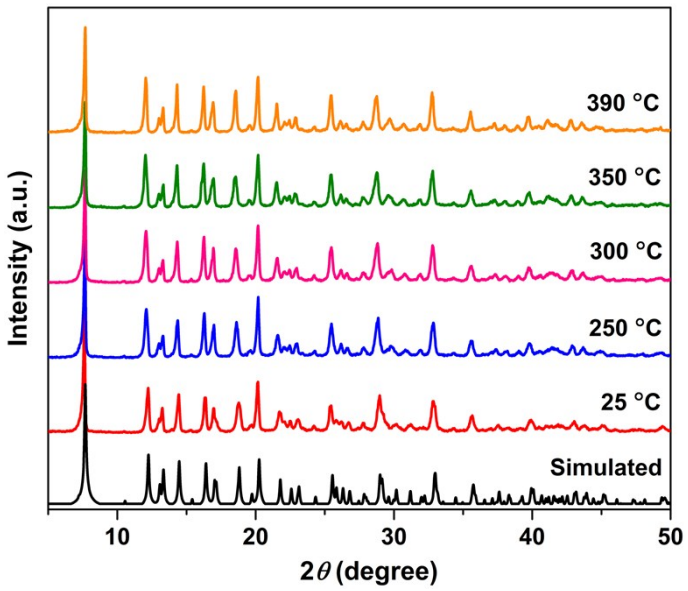


Fig. S8 Thermal stability tests for CZU-1 monitored by PXRD analysis after the crystalline samples of CZU-1 were heated at 250, 300, 350, and 390 °C in air for 6 h.

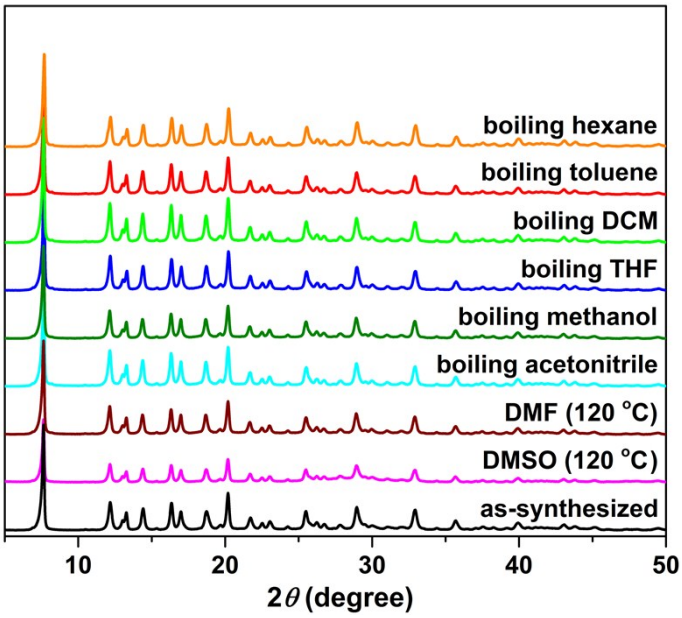


Fig. S9 PXRD patterns of as-synthesized CZU-1 and treated CZU-1 by immersing in boiling organic solvents, including hexane, toluene, dichloromethane (DCM) and THF, for 24 h, and in hot organic solvents, including DMF and DMSO, for 72 h.

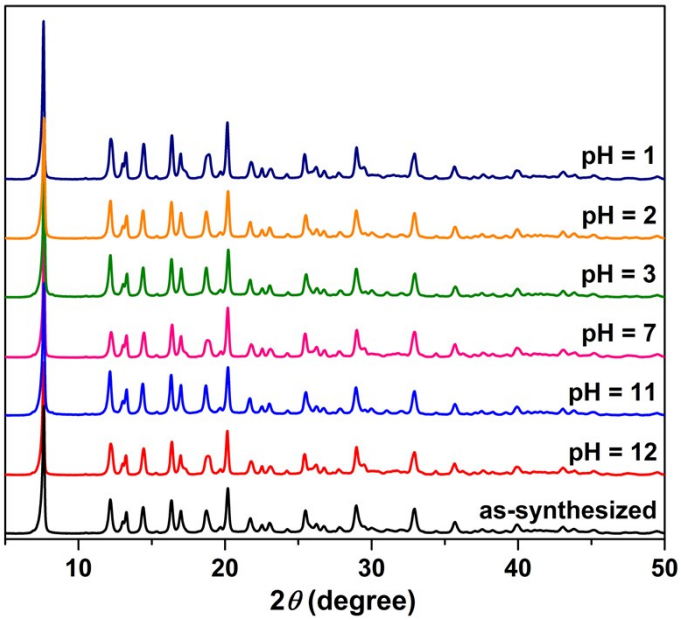


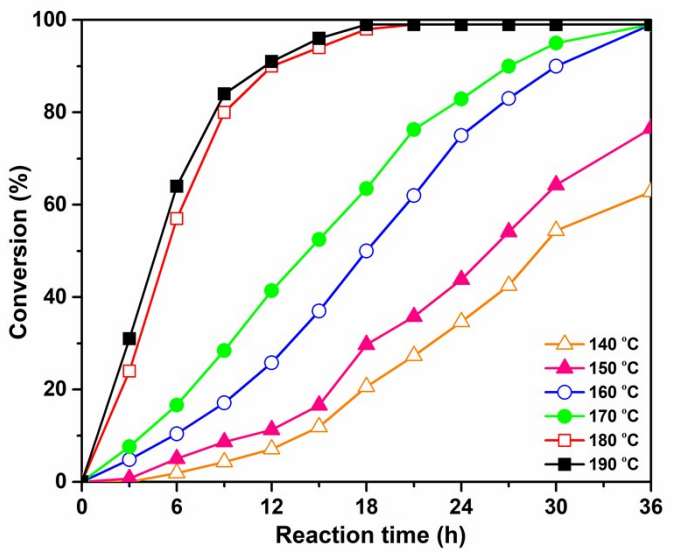
Fig. S10 PXRD patterns for CZU-1 after immersing in aqueous solutions with different pH values at room temperature for 24 h.

5. CZU-1-catalyzed ROP reaction

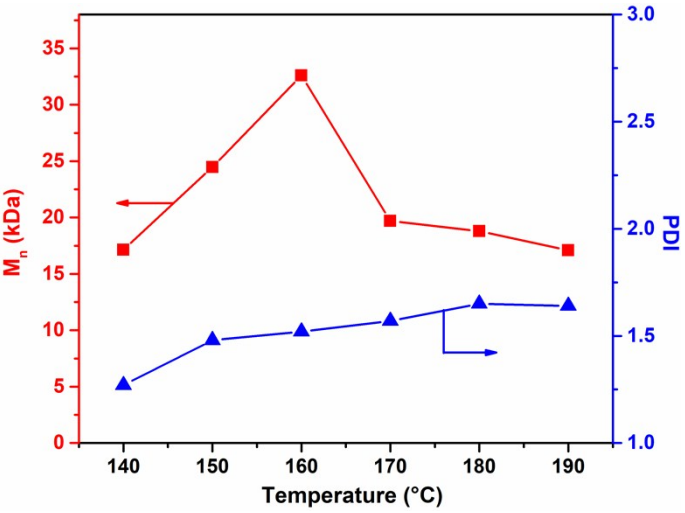
Table S2. Comparison of the catalytic properties of Zn(II)-based catalysts in ROP of cyclic esters

Entry	catalyst	monomer	Solvent	T (°C)	t (h)	conv. (%)	M_n (kDa)	PDI	Reference
1	CZU-1	L-LA	–	160	36 h	>99	32.6	1.52	This work
2	CZU-1	CL	–	160	36 h	>99	22.2	1.36	This work
3	[Zn(TMEGpy)Cl_2]	D,L-LA	–	150	48 h	88	46.0	2.09	[S9]
4	[Zn(TMGqu)Cl_2]	D,L-LA	–	150	48 h	0	–	–	[S9]
5	silica + $ZnMe_2$	*rac*-LA	–	130	24 h	40	18.5	1.47	[S10]
6	[L^1Zn_2(μ-OEt)Cl_2]	*rac*-LA	CH_2Cl_2	25	3	90	18.5	1.15	[S11]
7	[L^1Zn_2(μ-OEt)Br_2]	*rac*-LA	CH_2Cl_2	25	0.3	90	18.5	1.15	[S11]
8	[L^1Zn_2(μ-OEt)I_2]	*rac*-LA	CH_2Cl_2	25	24	98	18.2	1.15	[S11]
9	[L^2Zn_2(μ-OEt)Br_2]	*rac*-LA	CH_2Cl_2	25	71.5	91	14.2	1.06	[S11]
10	Zn-carbene	D,L-LA	CH_2Cl_2	25	0.5	96	17.2	1.25	[S12]
11	Zn-carbene[a]	D,L-LA	CH_2Cl_2	25	0.5	98	16.9	1.23	[S12]
12	[LO^1]ZnEt	LA	toluene	60	1	18	26.0	2.24	[S12]
13	[LO^1]ZnEt[b]	LA	toluene	60	1	97	14.0	1.10	[S13]
14	[{Zn(C_6F_5)}$_2L^1$]	CL	toluene	100	2	95	4.7	2.68	[S14]
15	[{Zn(C_6F_5)}$_2L^1$][a]	CL	toluene	100	4	90	7.6	1.48	[S14]
16	Zn(C_6F_5)$_2$	CL	MeTHF	65	5	95	24.3	1.3	[S15]
17	[L^1Zn(*μ*-OBn)]$_2$	L-LA	toluene	25	0.5	91	17.4	1.04	[S16]
18	[(BpyPh)Zn(μ-OBn)]$_2$	CL	toulene	70	2	97.0	9.1	1.11	[S17]
19	($NN_{Me}O_{tBu}$)Zn(OCH_2Ph)	*rac*-LA	CH_2Cl_2	25	4.5	99	17.4	1.40	[S18]
20	Zn-3*t*Bu MeCN	CL	toulene	130	24	0	–	–	[S19]
21	Zn/Co-5*t*Bu MeCN	CL	toulene	130	24	96.2	7.1	1.79	[S19]
22	(Ph-PPP)ZnEt	CL	toulene	25	8	46.0	19.7	1.20	[S20]
23	(Ph-PPP)ZnEt	CL	toulene	50	1.5	70.0	47.1	1.20	[S20]
24	*trans*-Zn-NO_2	CL	THF	25	2	22	2.4	1.10	[S21]
25	*cis*-Zn-NO_2	CL	THF	25	2	60	6.4	1.07	[S21]
26	*trans*-Zn-NO_2	LA	THF	25	2	76	5.6	1.27	[S21]
27	*cis*-Zn-NO_2	LA	THF	25	2	64	3.9	1.27	[S21]
28	[NNN]$_2$Zn	CL	toluene	25	2	0	–	–	[S22]
29	[NNN]$_2$Zn	LA	xylene	100	6	90	19.5	1.22	[S22]

[a]Benzyl alcohol added. [b]Isopropanol added.

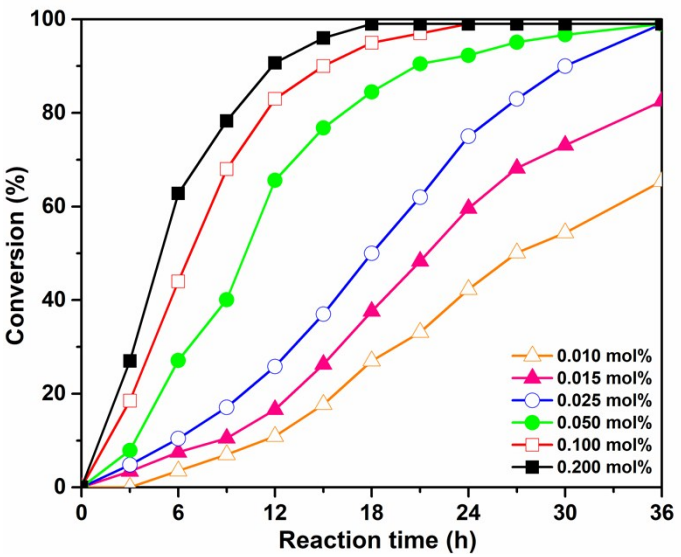


(a)

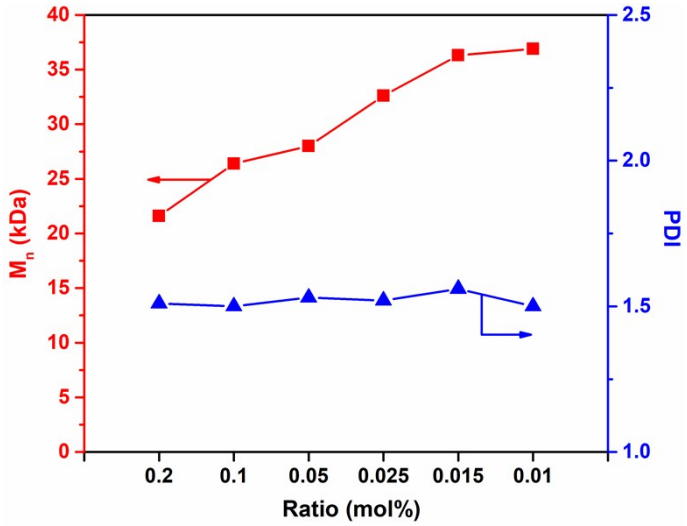


(b)

Fig. S11 Effect of reaction temperature on the conversion of L-LA (a), and the molecular weight and PDI of PLLA (b).



(a)



(b)

Fig. S12 Effect of catalyst concentration on the conversion of L-LA (a), and the molecular weight and PDI of PLLA (b).

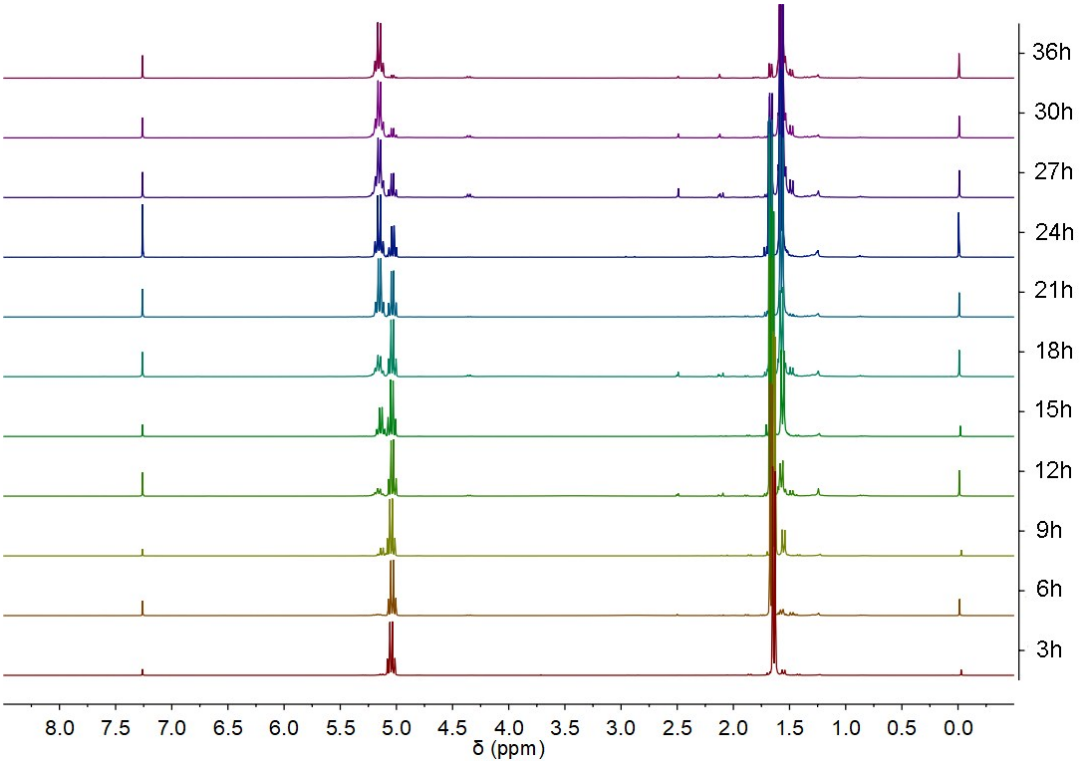


Fig. S13 ^{1}H NMR analysis ($CDCl_3$, 300 MHz) results, showing the effect of reaction time on the bulk ROP of L-LA (0.025 mol% CZU-1, 160 °C).

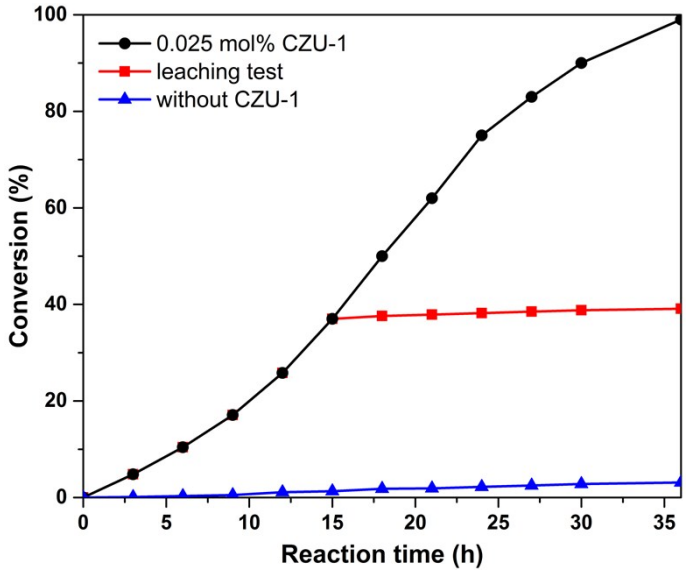


Fig. S14 Control experiments on solvent-free ROP of L-LA carried out with and without CZU-1 catalyst, as well as leaching test.

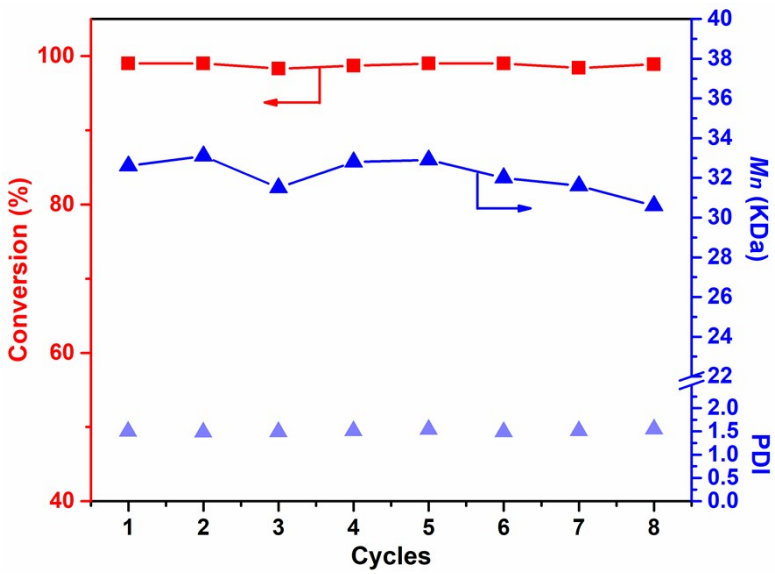


Fig. S15 Recycling tests on CZU-1-catalyzed solvent-free ROP of L-LA.

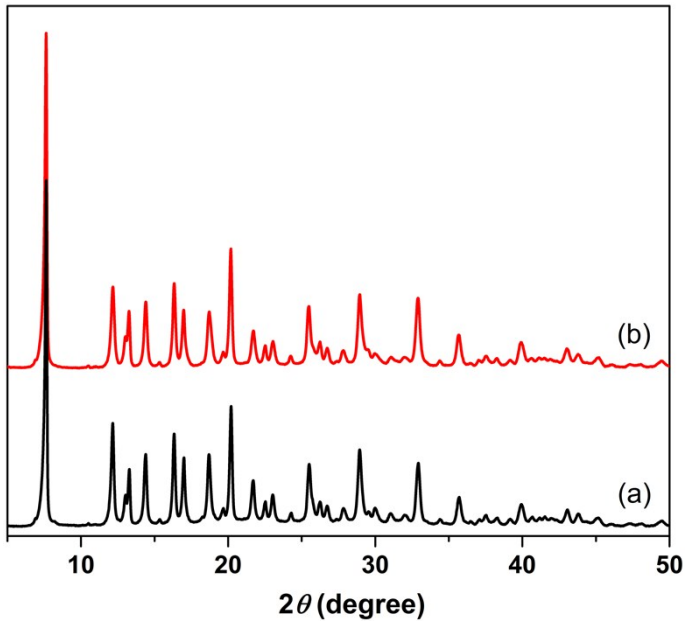


Fig. S16 PXRD patterns of CZU-1: (a) as-synthesized and (b) after the eighth run catalysis.

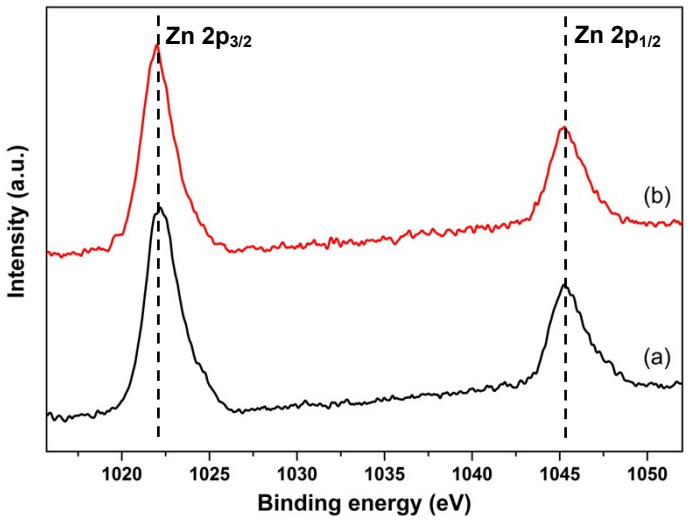


Fig. S17 XPS spectra of CZU-1: (a) as-synthesized and (b) after the eighth run catalysis.

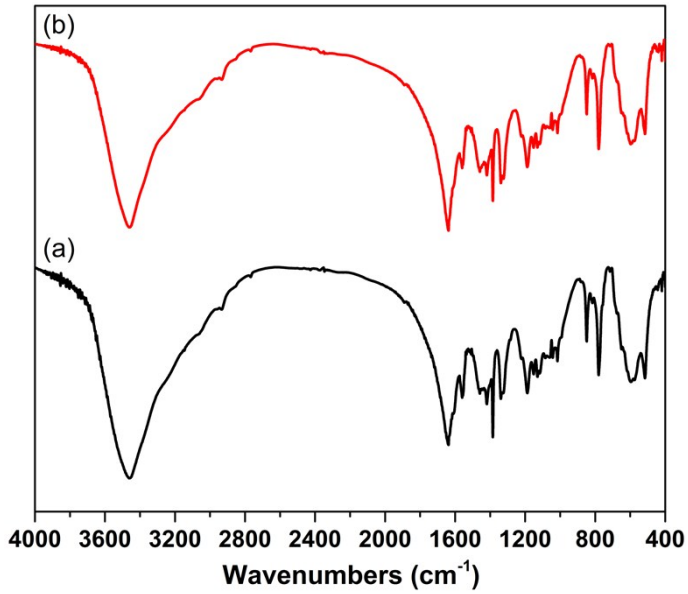


Fig. S18 FT-IR spectra of CZU-1: (a) as-synthesized and (b) after the eighth run catalysis.

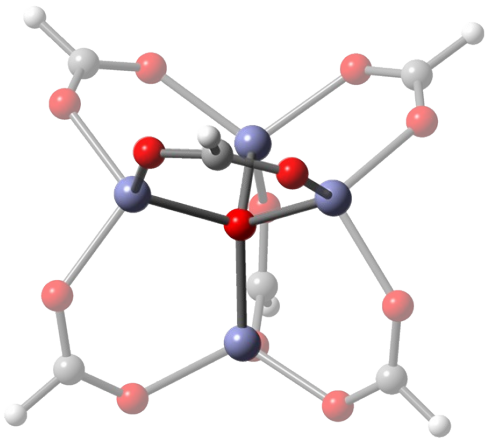


Fig. S19 Optimized structure of the $Zn_4(\mu_4\text{-}O)(COO)_6$ core in CZU-1. Color scheme: O, red; H, light grey; C, gray; Zn, blue.

6. XYZ coordinates of the optimized structures of the models.

Table S3. XYZ coordinates of **1a** in Fig. 3.

Zn	2.12710100	0.10189600	-0.11492800
C	2.09956300	-1.67024700	-2.47837000
O	0.85279800	-1.83980000	-2.55400800
O	2.75573500	-0.97993400	-1.65559700
O	0.17172100	0.00817400	-0.01596100
Zn	-0.60856900	-1.08756600	-1.44261700
Zn	-0.46703500	-0.76904400	1.68257300
Zn	-0.68486300	1.76973400	-0.15642700
C	2.40043600	-1.09622200	2.52840800
C	1.98176100	3.03166700	-0.44191200
C	-2.14841700	1.13087900	-2.62115700
C	-1.77907600	-3.05355800	0.41636300
C	-1.81585800	1.67840600	2.55674500
O	1.17176800	-1.25085900	2.73692100
O	0.73165900	3.15651700	-0.35507300
O	2.97635800	-0.59306900	1.52351900
O	2.67798500	1.98347500	-0.38875000
O	-1.80963900	-0.08183700	-2.67092800
O	-1.33742700	-2.53878200	1.47377600
O	-1.75391400	2.27928000	1.44726700
O	-1.84305400	1.99933500	-1.76211200
O	-1.69461300	-2.61843300	-0.76713700
O	-1.35540600	0.55093000	2.86640200
H	-2.35248900	2.21809000	3.36379300
H	-2.31871900	-4.01499600	0.53550700
H	-2.80919200	1.47779300	-3.44198100
H	2.54816500	3.97426200	-0.58478300
H	3.07742900	-1.44782500	3.33341700
H	2.70004900	-2.20369300	-3.24278600
O	-2.76212700	-0.13840300	0.27813300
H	-3.31487000	0.65474900	0.30859400
H	-3.21460400	-0.72727200	-0.34184700

Table S4. XYZ coordinates of **1aTs** in Fig. 3.

Zn	0.59297500	-1.17209400	0.91594100
C	-0.78248100	0.65175800	3.06235600
O	-1.24956400	1.63965200	2.42058000
O	-0.09997900	-0.30560700	2.63504000
O	-0.22166700	0.26946600	-0.34426700
Zn	-0.93149100	1.88864600	0.50588100
Zn	2.08511100	0.41654200	-0.97480900
Zn	-1.75246800	-0.96977200	-0.81427800
C	3.57395000	-0.98132600	0.85070600
C	-1.67593600	-2.92298700	1.21351100
C	-3.32517300	1.44793300	-1.21648500
C	1.54853000	3.32270600	-0.05665000
C	0.53303000	-2.27746500	-1.97304500
O	3.70359700	-0.33447800	-0.23007100
O	-2.46241500	-2.12310700	0.62727200
O	2.51415800	-1.22264500	1.47530400
O	-0.42156200	-2.86470100	1.25350200
O	-2.63482600	2.20863400	-0.49300100
O	2.25595700	2.30645300	-0.27992100
O	-0.72320000	-2.17701100	-2.01868300
O	-3.15343600	0.22284100	-1.47904500
O	0.30799500	3.39180300	0.15664000
O	1.31810500	-1.82829800	-1.08788300
H	0.99634600	-2.84178300	-2.80825600
H	2.08608800	4.29359200	-0.04027500
H	-4.21161900	1.90897900	-1.69651900
H	-2.15322200	-3.76852200	1.74644000
H	4.51408800	-1.36007500	1.29381700
H	-1.01444900	0.65076700	4.14728700
O	0.84690100	0.65442600	-2.46805700
H	0.10398300	0.50436900	-1.47421100
H	0.78294600	1.56989300	-2.77197100

Table S5. XYZ coordinates of **1b** in Fig. 3.

Zn	0.76230100	-0.22253800	1.16308900
C	-1.02986000	1.81246300	2.60558100
O	-1.90522500	2.08937500	1.73119400
O	0.02584900	1.15557600	2.46090100
O	-0.50891200	0.05395200	-0.42580900
Zn	-1.51538800	1.74137200	-0.15935500
Zn	2.38136400	0.09295900	-1.25287900
Zn	-1.62848000	-1.59579800	-0.42998200
C	3.79645300	-0.07019400	1.03622600
C	-1.09331300	-2.34390000	2.23663800
C	-3.66030900	0.23168100	-1.53797900
C	1.04900400	2.86943200	-0.70630400
C	0.95187400	-2.60633300	-1.18773900
O	3.99975700	0.02329000	-0.21495900
O	-2.01571000	-2.28265800	1.36946400
O	2.70227400	-0.14139600	1.63741300
O	0.02820200	-1.78641700	2.21011000
O	-3.16498900	1.33189400	-1.17453400
O	1.63324700	1.84866500	-0.25568600
O	-0.28688500	-2.82120900	-1.24667100
O	-3.24377900	-0.94377400	-1.34361400
O	-0.19514700	3.07903100	-0.79250400
O	1.55843100	-1.74125000	-0.48689500
H	1.57920300	-3.27326900	-1.81545100
H	1.68377600	3.70623500	-1.07179300
H	-4.60515900	0.30410100	-2.11329200
H	-1.31700100	-2.97163800	3.12272200
H	4.71095400	-0.08850200	1.65901800
H	-1.23436500	2.21151000	3.61976800
O	1.12563100	0.05293600	-2.62053300
H	-0.02682200	0.09448600	-1.30208300
H	1.11047600	0.83417000	-3.18662500

Table S6. XYZ coordinates of **2a** in Fig. 4.

Zn	-1.70862300	1.26376100	0.20261000
C	-3.89555400	0.22173400	-1.76762700
O	-3.50438200	-0.94067700	-2.10385800
O	-3.28037600	1.08352200	-1.10367300
O	-1.02966100	-0.63585200	-0.00177000
Zn	-1.64748600	-1.40361400	-1.71595200
Zn	1.32574800	2.25864900	-0.18836100
Zn	-1.10687100	-1.61780100	1.70973500
C	-0.75631300	4.12947500	0.29729100
C	-3.17479900	-0.03816500	2.65379400
C	-0.89776100	-3.86561200	-0.23686200
C	0.12046500	0.74985900	-2.55738400
C	0.89889200	0.42944000	2.25510900
O	0.48477800	4.01250500	0.08694200
O	-2.72502900	-1.22649500	2.72491300
O	-1.62774300	3.23123700	0.36492400
O	-2.77845500	0.89648100	1.92561700
O	-1.19775900	-3.28662700	-1.31752700
O	-0.07572300	1.41930700	-1.49383100
O	0.41308000	-0.66462900	2.62946000
O	-0.85074600	-3.42090900	0.94327500
O	-0.49668700	-0.27635600	-2.92888900
O	0.44556000	1.19049000	1.34366500
H	1.80762400	0.76827800	2.79476200
H	0.91472900	1.11761900	-3.24196400
H	-0.64105800	-4.93960500	-0.34048100
H	-4.02183000	0.17635700	3.33681600
H	-1.11728800	5.16740100	0.44037600
H	-4.91229600	0.48862200	-2.12062400
O	3.10452700	1.85114100	-0.56143900
H	-0.06311600	-0.55852500	-0.14330000
C	5.53716500	-1.04300700	0.22963300
C	4.51783500	-0.26919000	1.01850600
C	2.79468300	-0.87846900	-0.46382100
C	3.89273000	-0.92298300	-1.48332500
H	4.53684000	0.79714000	0.73489900
H	4.02690600	0.11051500	-1.84103100
O	5.12398000	-1.46090200	-0.99394400
O	3.16493700	-0.72901800	0.80910400
O	1.61930300	-0.99635100	-0.75532800
O	6.64462000	-1.28931700	0.62337300
H	3.58387000	-1.55640400	-2.31999400

H	4.71850200	-0.38324500	2.08658800
H	3.58624600	2.64309800	-0.82701000

Table S7. XYZ coordinates of **2aTs** in Fig. 4.

Zn	-1.56415200	1.38050000	0.37263100
C	-3.95167300	0.80079100	-1.48929600
O	-3.69804500	-0.36633200	-1.92068400
O	-3.21456500	1.55075700	-0.81207200
O	-0.98327800	-0.52549800	-0.08198200
Zn	-1.87033500	-1.04113700	-1.77708100
Zn	1.44553400	1.72823000	-0.14858300
Zn	-1.26065800	-1.67045200	1.51301800
C	-0.05424200	3.97111800	0.62272100
C	-3.17173800	0.00607400	2.63164800
C	-1.53636500	-3.74104000	-0.59446200
C	0.02361000	0.93760000	-2.64302900
C	0.91025500	0.02396700	2.38387800
O	1.11558400	3.61695900	0.30315000
O	-2.89508400	-1.22574600	2.49242000
O	-1.09217000	3.26867000	0.69240900
O	-2.62414000	0.98429100	2.07736600
O	-1.76139800	-3.00584400	-1.59448300
O	-0.08558400	1.58851800	-1.55724900
O	0.31548700	-1.06731300	2.58274600
O	-1.33905100	-3.43040900	0.61214400
O	-0.68152600	-0.02929400	-3.02556900
O	0.57575100	0.94874000	1.58455500
H	1.81431500	0.19074400	3.00481100
H	0.81167700	1.26691100	-3.35239700
H	-1.51113300	-4.82888000	-0.80847600
H	-3.99794900	0.22346700	3.33852300
H	-0.17698100	5.04285900	0.87379500
H	-4.95404500	1.19073800	-1.75804500
O	3.33357100	1.21776400	-0.40557300
H	-0.01333900	-0.52138800	-0.25070000
C	5.58153700	-1.08133100	0.11955600
C	4.43420900	-1.62648300	0.93889800
C	2.91865500	-0.48656000	-0.51647200
C	3.91665100	-0.94573400	-1.54865700
H	4.69082100	-1.55091300	2.00011800

H	3.76576500	-0.39397800	-2.47960200
O	5.27003700	-0.71497800	-1.14634100
O	3.17935200	-0.96873800	0.75472400
O	1.69359700	-0.39878600	-0.83381100
O	6.70904600	-0.99311800	0.52786200
H	3.75445800	-2.01940400	-1.74551400
H	4.32697500	-2.70119500	0.70221800
H	4.01170700	1.43922100	0.25015200

Table S8. XYZ coordinates of **2b** in Fig. 4.

Zn	-1.93265400	0.94693500	0.40414800
C	-4.14349300	-0.62153700	-0.95735200
O	-3.50381400	-1.65731600	-1.31820400
O	-3.68260300	0.44601400	-0.49323100
O	-0.59742400	-0.53500800	-0.11374500
Zn	-1.56725200	-1.52526300	-1.55106100
Zn	0.66324800	2.21105000	-0.27246200
Zn	-0.01533100	-1.59286600	1.46070900
C	-1.22644300	3.89748400	0.68980800
C	-2.44036000	-0.94013800	2.76772800
C	0.21098100	-3.69647200	-0.62212400
C	-1.03163500	1.11521300	-2.68105400
C	1.23931100	0.71216600	2.37170600
O	-0.05932600	3.94184000	0.18664700
O	-1.62968800	-1.89116600	2.56329600
O	-1.95334300	2.89658400	0.87292100
O	-2.49591400	0.17042400	2.18828900
O	-0.56261200	-3.21305000	-1.49700200
O	-1.09429600	1.71736700	-1.56596900
O	1.20472100	-0.52690600	2.60833700
O	0.51790300	-3.25859700	0.51776200
O	-1.26999900	-0.09589000	-2.92748600
O	0.47690400	1.34536200	1.59073300
H	2.00743000	1.28591800	2.93101500
H	-0.74710000	1.73127900	-3.55979300
H	0.68716900	-4.65732800	-0.90392800
H	-3.18904800	-1.11908500	3.56689000
H	-1.63524400	4.87629100	1.00508400

H	-5.24353000	-0.68206000	-1.07625300
O	3.11450800	1.62424600	0.11778800
H	0.20300600	-0.19040900	-0.56900900
C	4.98527700	-0.81205000	-0.06987100
C	3.65613200	-1.02854200	0.61537100
C	2.71011200	0.60131000	-0.83079600
C	3.79799400	0.30924000	-1.84048400
H	3.74137500	-0.56090400	1.61091200
H	4.03239800	1.20008300	-2.43815300
O	5.02633500	-0.10164000	-1.22954500
O	2.49087900	-0.57525500	-0.06081500
O	1.55305100	0.94540900	-1.40774500
O	6.01014500	-1.21680700	0.41132700
H	3.43039500	-0.47016400	-2.52335700
H	3.53629000	-2.10724500	0.78360200
H	3.82586900	2.15300200	-0.27147500

Table S9. XYZ coordinates of **2bTs** in Fig. 4.

Zn	-1.62755500	1.26441600	0.46847100
C	-4.11507700	0.41768500	-1.09949700
O	-3.76884400	-0.71871700	-1.54673400
O	-3.40299300	1.26884800	-0.52134600
O	-0.80612800	-0.54426500	-0.11885800
Zn	-1.86708500	-1.15514600	-1.69258400
Zn	1.15091800	1.86369300	-0.27796500
Zn	-0.88803700	-1.73497600	1.47351300
C	-0.28894600	3.99734400	0.55345800
C	-2.91387900	-0.31704700	2.75809500
C	-1.08672500	-3.80542000	-0.62902000
C	-0.50302900	1.13316500	-2.74794200
C	0.99226300	0.25395100	2.36015200
O	0.88387100	3.72359400	0.14288800
O	-2.52955300	-1.50323300	2.52092000
O	-1.25698500	3.22129300	0.70769600
O	-2.50856900	0.74194100	2.22755200
O	-1.50362800	-3.09222900	-1.58232500
O	-0.51861300	1.71602800	-1.62461100
O	0.59658400	-0.92943500	2.52696700
O	-0.80623200	-3.48247200	0.55797600

O	-1.03543000	0.03353100	-3.05606600
O	0.49821700	1.13267100	1.59003600
H	1.85436000	0.55961800	2.98656800
H	0.02488600	1.64935000	-3.57804800
H	-0.94633600	-4.87815400	-0.87017800
H	-3.69952100	-0.22142900	3.53433700
H	-0.45744200	5.06267300	0.80007900
H	-5.18274600	0.67567200	-1.24891700
O	3.91367900	1.12744400	-1.06973500
H	0.13030200	-0.43749300	-0.40258300
C	5.40070400	-1.14512400	0.20940400
C	4.52213800	-0.29970600	1.10237800
C	3.07556500	0.02161100	-0.73899000
C	3.56880300	-1.27431600	-1.35179100
H	5.05514800	0.65399500	1.25104100
H	3.56215300	-1.22011500	-2.44849600
O	4.91021900	-1.59498400	-0.97173100
O	3.18681300	-0.07946800	0.67136100
O	1.78919100	0.24800900	-1.06183400
O	6.53033000	-1.41407800	0.52518300
H	2.89121800	-2.08604800	-1.04762000
H	4.46819000	-0.79945100	2.07928000
H	3.96619900	1.17308600	-2.03474500

Table S10. XYZ coordinates of **2c** in Fig. 4.

Zn	-1.38500100	1.39781800	0.57212300
C	-4.05207200	1.17934900	-0.92164000
O	-3.95601400	0.03601000	-1.46492200
O	-3.16744800	1.81902900	-0.31070800
O	-0.98652300	-0.50151100	-0.13150000
Zn	-2.18835400	-0.76385000	-1.69831500
Zn	1.48317600	1.49960800	-0.25397000
Zn	-1.20240300	-1.76628200	1.38874100
C	0.44713200	3.81052300	0.77131400
C	-2.77665700	-0.04140500	2.91827100
C	-1.96201500	-3.58870200	-0.81843200
C	-0.37352400	1.22873700	-2.66408700
C	1.17036000	-0.32234600	2.14733100

O	1.52876100	3.36057900	0.28077300
O	-2.61916300	-1.27037900	2.63815300
O	-0.63669700	3.20911000	0.94473600
O	-2.25481200	0.94765700	2.35963900
O	-2.24400600	-2.73956300	-1.70682000
O	-0.25677300	1.74102000	-1.51175300
O	0.57171400	-1.42748500	2.25293700
O	-1.57088500	-3.41734200	0.36921200
O	-1.14740100	0.29994900	-3.01932300
O	0.75434500	0.72838900	1.58020000
H	2.17526500	-0.28222400	2.62032200
H	0.26337200	1.64765400	-3.47052500
H	-2.07599900	-4.64763700	-1.12600600
H	-3.45999200	0.16133300	3.76714700
H	0.48084900	4.87155800	1.08434300
H	-5.04781800	1.65893700	-1.00954800
O	3.78565600	-0.22925200	-2.06637500
H	-0.05600200	-0.55913300	-0.44526200
C	5.42749000	-1.04835100	0.26649000
C	4.83869300	0.34490000	0.31259000
C	2.97607100	-0.52248100	-0.94708500
C	3.26328800	-1.90714500	-0.39965800
H	5.40200900	0.95959900	-0.40610600
H	3.01491000	-2.67704200	-1.14201600
O	4.64691200	-2.09892000	-0.07643700
O	3.43692300	0.41949000	0.06122200
O	1.67848500	-0.25855100	-1.11778500
O	6.58878500	-1.22549100	0.52732500
H	2.64946500	-2.08652700	0.49557200
H	5.01583500	0.75511900	1.31515500
H	3.44812500	-0.76083700	-2.79956300

Table S11. XYZ coordinates of **2cTs** in Fig. 4.

Zn	1.28352500	1.53585600	0.23446800
C	-0.69984200	3.80281200	0.31488400
O	-1.77980800	3.20239900	0.04463100
O	0.45307200	3.32188800	0.42759100
O	1.07593000	-0.48587800	-0.05579700
Zn	-1.70347300	1.25362000	-0.22413300
Zn	1.59405900	-1.40462500	1.62511500

Zn	2.09062500	-0.94709700	-1.69848500
C	3.15360700	0.70762400	2.54618100
C	3.77057700	1.27735000	-1.57448500
C	-0.11645100	0.62894800	-2.70258700
C	-0.84970400	-0.10842400	2.42640300
C	2.28215900	-3.55066700	-0.30910200
O	3.12429400	-0.56153900	2.50452000
O	3.75843200	0.05120100	-1.90565500
O	2.41545800	1.51474700	1.93960000
O	2.88880800	1.91983700	-0.96317700
O	-0.16670700	1.34967200	-1.65649500
O	-0.03838500	-1.02799000	2.70557500
O	2.35936400	-2.87442000	-1.37193000
O	0.75509900	-0.22332300	-3.00296400
O	-0.71357400	0.79161900	1.54373500
O	2.02746300	-3.18070500	0.86878500
H	2.46975000	-4.63660600	-0.43083700
H	-1.76899000	-0.07834700	3.04734700
H	-0.91891400	0.77904300	-3.45540300
H	4.68102500	1.83481300	-1.87402200
H	3.93029200	1.13636300	3.21135000
H	-0.78850300	4.89545100	0.47351700
C	-5.62780000	-0.77103200	0.02704600
C	-4.74443500	0.41180500	0.37423300
C	-2.74695200	-1.19273400	-0.36758100
C	-3.79712500	-1.79345100	-1.26574800
H	-5.29873900	1.32567900	0.10939900
H	-3.85436200	-1.21720800	-2.19739300
O	-5.07863100	-1.85567400	-0.61200700
O	-3.50228300	0.37917500	-0.25986100
O	-1.60888100	-0.84703300	-0.82295900
O	-6.77511800	-0.83397300	0.37710200
H	-3.55154500	-2.83623100	-1.50906800
H	-4.66182200	0.41239800	1.48004600
O	-2.75101700	-1.69015300	0.91128000
H	0.12753800	-0.68722400	-0.22718700
H	-3.60012300	-2.13293900	1.07203300

Table S12. XYZ coordinates of **2d** in Fig. 4.

Zn	1.28490700	1.58639100	0.01233400
C	-0.57421100	3.99330400	0.09927700
O	-1.72954100	3.47707900	0.12858900
O	0.53649400	3.41608400	0.07078000
O	1.24503600	-0.43180100	-0.03092100
Zn	-1.91273300	1.52989300	0.13921800
Zn	1.87699200	-1.20578800	1.67751800
Zn	1.77991700	-1.12611300	-1.80284400
C	3.41136100	1.05712600	2.22793100
C	3.28619600	1.15530200	-2.33877000
C	-0.73951500	0.22296100	-2.37310300
C	-0.61722000	0.06798900	2.45166100
C	2.17684300	-3.54987400	-0.13629100
O	3.38273300	-0.20126400	2.40663700
O	3.25142300	-0.09579400	-2.56420200
O	2.65028000	1.76017100	1.52806300
O	2.55861800	1.82668100	-1.57552400
O	-0.60229400	1.03573500	-1.40636600
O	0.25263500	-0.77042600	2.78424900
O	2.08147300	-3.00175200	-1.26983900
O	0.10451000	-0.59841300	-2.80142400
O	-0.52039000	0.92502500	1.51303000
O	2.16860700	-3.04484900	1.01941400
H	2.29651900	-4.65208200	-0.16219100
H	-1.55405200	0.06878300	3.04472400
H	-1.70826200	0.25046000	-2.91989200
H	4.06592200	1.70547800	-2.90385200
H	4.22039400	1.58353000	2.77462500
H	-0.55130900	5.10048900	0.10085100
C	-5.40305900	-0.74468500	-0.22574600
C	-4.55309200	0.47978800	-0.50673200
C	-2.33150500	-1.90114800	0.23261600
C	-3.44190100	-2.07979000	-0.77067700
H	-4.36185000	0.51494300	-1.60687000
H	-3.28446200	-1.38755400	-1.60737000
O	-4.73348400	-1.96788600	-0.18613000
O	-3.40811100	0.42162500	0.26984100
O	-1.17646900	-1.71231000	-0.10661100
O	-6.57603700	-0.74998500	0.01752600
H	-3.37604200	-3.10101500	-1.17725900
H	-5.20298000	1.34772300	-0.29385200
O	-2.65655600	-2.08114200	1.50959600
H	0.29990200	-0.68894600	-0.00088400
H	-3.63104600	-2.13333800	1.55052600

Table S13. XYZ coordinates of **3a** in Fig. 5.

Zn	1.71488800	1.35192000	-0.24403600
C	3.85642700	0.67934600	1.91593500
O	3.54849900	-0.48736700	2.31568100
O	3.22584400	1.42236200	1.13342800
O	1.21150900	-0.58516000	0.04204900
Zn	1.80120800	-1.20577300	1.82750200
Zn	-1.41811900	2.03906100	-0.03407600
Zn	1.45658500	-1.64272900	-1.61107700
C	0.46656200	4.09905700	-0.48550000
C	3.38223600	0.10567100	-2.57685400
C	1.48762300	-3.81128500	0.43306000
C	-0.29718400	0.69413500	2.44259700
C	-0.73022400	0.14011300	-2.34490900
O	-0.76615300	3.86888200	-0.32928000
O	3.06579600	-1.12613500	-2.58647000
O	1.41951900	3.28467500	-0.48089400
O	2.86440000	1.03204500	-1.91684500
O	1.66206300	-3.14801700	1.49239800
O	-0.04890800	1.38761500	1.40685300
O	-0.12202300	-0.91859200	-2.63158300
O	1.40738300	-3.42829100	-0.76640400
O	0.38837800	-0.25159300	2.90082400
O	-0.38821600	0.99879500	-1.47055000
H	-1.64560600	0.35212000	-2.93399100
H	-1.21307800	0.95533900	3.01666700
H	1.39728000	-4.90681500	0.57956100
H	4.22327300	0.37307900	-3.24849200
H	0.73553500	5.16126300	-0.64873000
H	4.80874400	1.07355700	2.32610100
C	-3.98018600	2.28693500	1.13004500
H	-3.62841400	2.35603000	2.18165700
H	-4.08892700	3.32711400	0.76520200
H	-5.00425900	1.86329600	1.17154200
O	-3.16494100	1.48735000	0.32084400
H	0.23715800	-0.57792700	0.12584600
C	-5.41545400	-1.52721000	-0.30559200

C	-4.47283000	-0.72425400	-1.15705400
C	-2.65719400	-1.17977200	0.27199600
C	-3.69987300	-1.34083500	1.33982600
H	-4.55806500	0.34929400	-0.91952600
H	-3.87898300	-0.34988700	1.78512600
O	-4.92665600	-1.92344900	0.89725400
O	-3.08486700	-1.08253400	-0.98759900
O	-1.46615800	-1.19872400	0.52016600
O	-6.53179300	-1.81751100	-0.63962100
H	-3.30470300	-2.00223600	2.11758700
H	-4.70563600	-0.89478800	-2.21121400

Table S14. XYZ coordinates of **3aTs** in Fig. 5.

Zn	1.50343700	1.42739100	-0.47238500
C	3.95680100	1.23766700	1.39469300
O	3.85191700	0.07657500	1.89939100
O	3.11995900	1.85029900	0.69614600
O	1.12090800	-0.49798900	0.11883200
Zn	2.09711000	-0.78136100	1.82304300
Zn	-1.50533500	1.44591100	-0.05574600
Zn	1.52167300	-1.73564300	-1.38245500
C	-0.27690800	3.81489900	-0.90255600
C	3.28914300	0.05436000	-2.58693100
C	2.00053300	-3.59154400	0.87496400
C	0.02356700	1.10211200	2.54840500
C	-0.78049500	-0.35230500	-2.42498200
O	-1.40312100	3.34811700	-0.56920000
O	3.12498400	-1.18447300	-2.36053700
O	0.83161500	3.22714300	-0.94176700
O	2.63708200	1.01477300	-2.12155100
O	2.16309300	-2.75526100	1.80568600
O	0.01498600	1.64591600	1.40122400
O	-0.07899000	-1.39049700	-2.52412100
O	1.77110100	-3.40447800	-0.35137600
O	0.82782700	0.24116300	2.98498000
O	-0.54976800	0.66009500	-1.69558700
H	-1.67892100	-0.31812900	-3.07518200
H	-0.75237500	1.43733200	3.26879500

H	2.07340200	-4.65447000	1.18177100
H	4.11180400	0.29666400	-3.28972800
H	-0.27069800	4.88162200	-1.20151000
H	4.90986500	1.75983200	1.61339700
C	-4.03983300	1.55591100	1.30369000
H	-3.43203400	1.51883400	2.22942200
H	-4.16681800	2.61325900	1.02767100
H	-5.03399900	1.13382700	1.51834200
O	-3.42117100	0.87174700	0.22717400
H	0.16206200	-0.58424900	0.31894500
C	-5.37494900	-1.35974800	-0.24225100
C	-4.23626600	-1.34611400	-1.23114400
C	-2.78113000	-0.75587600	0.54176800
C	-3.74484700	-1.35844600	1.52419800
H	-4.42230000	-0.50158600	-1.91176900
H	-3.72425800	-0.80687800	2.47093700
O	-5.10378000	-1.37885500	1.08554900
O	-2.90483600	-1.27036700	-0.72742300
O	-1.58314000	-0.54441200	0.91285000
O	-6.51693800	-1.36163600	-0.61857300
H	-3.40493700	-2.38609800	1.72893300
H	-4.30486600	-2.26731700	-1.82644600

Table S15. XYZ coordinates of **3b** in Fig. 5.

Zn	1.58575600	1.31269300	-0.54697800
C	4.17259000	0.91871500	1.03399000
O	3.97182600	-0.21319200	1.57121900
O	3.35348800	1.62777100	0.40731000
O	0.94420600	-0.52149900	0.18547500
Zn	2.12080000	-0.82720200	1.76816600
Zn	-1.28895500	1.65267300	0.01744200
Zn	1.12028400	-1.84731900	-1.28623800
C	-0.05398500	3.84042800	-1.01641000
C	3.02414500	-0.35536900	-2.68255700
C	1.64336200	-3.64543200	1.01154400
C	0.50106800	1.42876100	2.55369300
C	-1.01232300	-0.29297100	-2.33943100
O	-1.18973000	3.50519600	-0.55546800

O	2.75073000	-1.54652800	-2.34409800
O	0.97606300	3.13789600	-1.11968800
O	2.51162500	0.70277900	-2.25148100
O	1.99281900	-2.79164300	1.87311900
O	0.43151900	1.88239300	1.37269300
O	-0.43626200	-1.40799400	-2.43865700
O	1.29898900	-3.48675100	-0.19039000
O	1.18612600	0.45858600	2.97319000
O	-0.61297600	0.71808200	-1.69077900
H	-1.95290400	-0.18737400	-2.91926500
H	-0.09723500	1.95423700	3.32684800
H	1.64253700	-4.69555600	1.36711100
H	3.80903300	-0.25165600	-3.45901700
H	0.01831900	4.88564800	-1.37338700
H	5.20109500	1.31732200	1.14352100
C	-4.23722200	1.84179000	0.75965100
H	-3.71100900	2.14379700	1.68262100
H	-4.40086900	2.73312700	0.14363500
H	-5.21089800	1.40038600	1.01867800
O	-3.45386800	0.93994700	-0.02351200
H	0.01544000	-0.46824500	0.50761100
C	-5.15805000	-1.59596200	-0.10895500
C	-3.89821100	-1.59533500	-0.94291400
C	-2.87455000	-0.23689800	0.70717400
C	-3.83389800	-0.79195300	1.73437500
H	-4.11558900	-0.96018400	-1.81872900
H	-4.04444400	-0.06562100	2.52760000
O	-5.10007300	-1.16364600	1.17697700
O	-2.69094600	-1.19385800	-0.31218200
O	-1.70055100	0.12962900	1.20598000
O	-6.21186000	-1.94515900	-0.57182600
H	-3.35193100	-1.66609300	2.19587600
H	-3.74464900	-2.61584800	-1.31886100

Table S16. XYZ coordinates of **3bTs** in Fig. 5.

Zn	-1.38040900	1.54271600	0.25261000
C	-3.76250400	1.21304200	-1.69534800
O	-3.73609900	-0.01909300	-1.99960100
O	-2.91360700	1.86827500	-1.05178000
O	-1.18091300	-0.49458400	-0.02295500
Zn	-2.10162300	-1.04858300	-1.69262600
Zn	1.55528300	1.12243300	-0.19703400
Zn	-1.85350300	-1.30294500	1.67388500
C	0.70818100	3.72401800	0.02745100
C	-3.39472500	0.90015700	2.45221100
C	-2.46849600	-3.55211700	-0.14319300
C	0.08348800	0.41122500	-2.82463700
C	0.52940700	0.09919600	2.51418600
O	1.77440300	3.04972100	-0.10204300
O	-3.40175500	-0.36929800	2.42207700
O	-0.46939300	3.30783200	0.12362100
O	-2.60941900	1.67917500	1.86783800
O	-2.46287300	-2.94039600	-1.24502200
O	0.17788000	1.13660100	-1.79600500
O	-0.25781000	-0.84695600	2.78092900
O	-2.27319600	-3.11513800	1.02487300
O	-0.74081300	-0.51968100	-3.04006600
O	0.39344300	0.99460600	1.62570700
H	1.44049500	0.15250400	3.14329000
H	0.79121700	0.60979400	-3.65851900
H	-2.67201100	-4.63978100	-0.20759700
H	-4.18170000	1.35969400	3.08292400
H	0.84679700	4.82175400	0.05846900
H	-4.65334900	1.76559500	-2.05629100
C	3.50324600	-0.49447100	-2.47438200
H	2.54326400	-0.99972700	-2.67213500
H	3.62956400	0.33384300	-3.18072100
H	4.33073400	-1.20777300	-2.61870600
O	3.53301600	0.05682300	-1.16478500
H	-0.23423900	-0.73391600	-0.08952700
C	5.62395800	-0.84813800	0.60489100
C	4.68150900	0.15751800	1.22858400
C	2.97124400	-0.83334800	-0.13083900
C	3.70840100	-2.14571700	-0.05790000
H	4.97560600	1.14600200	0.84476200
H	3.51508700	-2.76031700	-0.94491700
O	5.12588700	-1.96112800	0.00904400
O	3.28255800	-0.06215600	1.04780200
O	1.66335600	-0.89832400	-0.24602600

O	6.81408500	-0.67962500	0.64798600
H	3.34936400	-2.69582600	0.82400900
H	4.87444800	0.15807300	2.31101600

Table S17. XYZ coordinates of **3c** in Fig. 5.

Zn	1.47052200	1.43828600	-0.46996800
C	-0.26794700	3.91926200	-0.58943100
O	-1.37768900	3.47370500	-0.16226100
O	0.80428200	3.29691400	-0.76213300
O	0.98766900	-0.47640600	0.13705300
Zn	-1.39893600	1.58456900	0.27340500
Zn	1.25393700	-1.64932000	-1.44501600
Zn	2.15211800	-0.85408800	1.70855900
C	3.00296500	0.08049100	-2.74784900
C	4.09852000	1.04120800	1.07703800
C	0.38640900	1.15834100	2.73337600
C	-1.00298000	-0.08805600	-2.29453600
C	1.83266500	-3.62347900	0.67698100
O	2.83543200	-1.15104000	-2.48786100
O	3.96167800	-0.12570000	1.55830300
O	2.40906800	1.05801700	-2.24072900
O	3.23804100	1.73997200	0.49720400
O	0.29677900	1.72535400	1.60485200
O	-0.37264500	-1.16323300	-2.48661900
O	2.12502800	-2.83135500	1.61308200
O	1.13138300	0.19434500	3.05538800
O	-0.65277300	0.88732200	-1.56509300
O	1.48102000	-3.37809300	-0.51079600
H	1.89305600	-4.70032600	0.93473700
H	-1.95088900	0.01429100	-2.86031200
H	-0.24755100	1.55807500	3.55186100
H	5.10847700	1.48317800	1.19621900
H	3.76496500	0.29879800	-3.52303300
H	-0.26078600	4.99735500	-0.84034400
C	-5.55462600	-0.60868800	0.01329400
C	-4.70271600	0.52363600	-0.52083100
C	-2.85362700	-0.53099100	0.61610600
C	-3.82679200	-1.09501600	1.62978700
H	-5.27104700	1.45608400	-0.40893600
H	-3.93037900	-0.37989700	2.45800600

O	-5.10889400	-1.36450000	1.04529400
O	-3.44648600	0.70588500	0.12972100
O	-1.67333900	-0.18115200	1.12418200
O	-6.62889300	-0.83886500	-0.47692600
H	-3.47118400	-2.04634800	2.04332100
H	-4.56633300	0.34194500	-1.59810000
C	-2.25467100	-2.62559800	-0.35271800
H	-2.02305300	-3.03440700	-1.34259100
H	-1.32423800	-2.58570400	0.24090300
H	-2.97581100	-3.29456800	0.14630300
O	-2.79296100	-1.33267100	-0.55885200
H	0.04877300	-0.50653400	0.43477500

Table S18. XYZ coordinates of **3cTs** in Fig. 5.

Zn	-1.55333000	1.49478300	0.37501900
C	0.19902500	3.97797000	0.49175400
O	1.35700700	3.53994800	0.23170300
O	-0.87986900	3.34069700	0.54994000
O	-1.16263600	-0.42986900	-0.07882100
Zn	1.51644100	1.62159800	-0.14393700
Zn	-1.47051900	-1.55768300	1.52083700
Zn	-1.95833800	-0.91424000	-1.83016500
C	-3.19219700	0.31175400	2.68640800
C	-3.87258800	1.13327700	-1.62911300
C	0.24484400	0.70018700	-2.64591700
C	0.85572900	-0.03091400	2.33598100
C	-1.77165400	-3.61653700	-0.57939100
O	-3.01506000	-0.93807000	2.54945100
O	-3.67549600	-0.02736400	-2.10373800
O	-2.59894600	1.24576200	2.10085700
O	-3.14480900	1.79130100	-0.85240000
O	0.12503300	1.42917000	-1.60942000
O	0.17406500	-1.06144100	2.56427700
O	-1.98222500	-2.87666500	-1.57669500
O	-0.58067900	-0.14811400	-3.05957300
O	0.57076700	0.90404600	1.52199100
O	-1.57790600	-3.31388100	0.63228300
H	-1.76168500	-4.70454500	-0.79354300
H	1.77854500	0.08293400	2.93810900
H	1.14966200	0.84454000	-3.27221900

H	-4.81644800	1.61487200	-1.95495400
H	-3.96938200	0.59627000	3.42366200
H	0.13495300	5.06494000	0.69117100
C	5.37194100	-0.33629000	-0.13324700
C	4.41789200	0.81050200	0.13078300
C	2.58774900	-1.03175000	-0.44184100
C	3.65237100	-1.55300600	-1.37404100
H	4.90983600	1.72569500	-0.23747900
H	3.54231100	-1.05974400	-2.34966500
O	4.98256200	-1.40982500	-0.87108700
O	3.15910800	0.65901100	-0.47964800
O	1.39638300	-0.99054200	-0.81352700
O	6.49370100	-0.30889600	0.30263400
H	3.51402000	-2.63290100	-1.52886000
H	4.35067000	0.90320800	1.22952300
C	2.70381800	-2.61860600	1.29096400
H	2.74001200	-2.65302400	2.38480000
H	1.72540300	-3.00084300	0.95778700
H	3.51057700	-3.25221500	0.88719800
O	2.88067500	-1.25565000	0.91741800
H	-0.19108800	-0.53940300	-0.22738600

Table S19. XYZ coordinates of **3d** in Fig. 5.

Zn	-1.47680300	1.43671500	0.44856700
C	-0.01881100	4.07834600	0.61623600
O	1.13538500	3.78102300	0.19115900
O	-1.01480900	3.33198000	0.76353700
O	-1.06194300	-0.48296200	-0.04799000
Zn	1.54600300	1.93831000	-0.32860600
Zn	-1.00299300	-1.62433900	1.55780500
Zn	-2.09721800	-0.97578500	-1.66420700
C	-2.82810900	0.01047400	2.85553200
C	-4.06532700	0.90952800	-1.18924100
C	-0.23299600	1.03766200	-2.64490900
C	1.14630800	0.14169500	2.24759700
C	-1.36028300	-3.65347700	-0.57976200
O	-2.55352300	-1.21899400	2.69534800
O	-3.91842500	-0.26775800	-1.64557500
O	-2.34121300	0.99446600	2.25402800
O	-3.21958400	1.62358800	-0.60692100

O	-0.10032500	1.58473100	-1.49934500
O	0.56965500	-0.92469000	2.58615000
O	-1.81135400	-2.92559700	-1.50657500
O	-1.08918100	0.18579600	-2.97148300
O	0.77397400	0.96103300	1.35795200
O	-1.02299400	-3.36227900	0.60187200
H	-1.24825300	-4.72518900	-0.84408600
H	2.07482100	0.38233300	2.81087300
H	0.46409600	1.36900900	-3.44129400
H	-5.07456200	1.34439800	-1.33908900
H	-3.58995100	0.22177100	3.63383300
H	-0.16036800	5.14110900	0.89383800
C	5.01133200	-0.32404800	0.01258600
C	4.15783300	0.93070500	0.08965300
C	2.18425700	-1.41117500	-0.99830900
C	3.54704800	-1.47271200	-1.63885000
H	4.88729000	1.76072400	-0.01645000
H	3.56370000	-0.70484900	-2.41881000
O	4.67129700	-1.40011300	-0.77306500
O	3.09939200	1.00868700	-0.79072300
O	1.20987600	-1.02823800	-1.62310100
O	6.00495000	-0.44444800	0.68207100
H	3.64227600	-2.45594300	-2.12952700
H	3.86492000	0.96873300	1.16551500
C	2.92228200	-2.61893000	1.00585600
H	2.31251800	-3.21228000	1.69522500
H	3.50705200	-3.27889400	0.35613100
H	3.60072100	-1.97649200	1.58158800
O	1.97680500	-1.83107000	0.25963500
H	-0.15897800	-0.53109700	-0.42863500

Table S20. XYZ coordinates of **4cTs** in Fig. 6.

Zn	1.99809100	1.52178800	-0.13321800
C	0.41838500	3.83797500	0.49848000
O	-0.67765500	3.22434200	0.37895400
O	1.57955300	3.36030100	0.45226300
O	0.43374400	-0.29675800	0.09622400
Zn	-0.93330100	1.30309600	0.12919700
Zn	1.87140700	-1.24038100	-1.10421800
Zn	0.44466600	-1.41694700	1.76530300

C	4.33737200	0.12483300	-1.02265200
C	2.93971200	-0.18960400	2.33909600
C	-1.70984100	0.06946300	2.91001800
C	0.75470700	0.82156800	-2.72418400
C	0.63014300	-3.68795100	-0.07650000
O	3.79875600	-1.00455800	-0.82106600
O	2.26962400	-1.25347200	2.47547900
O	3.77315700	1.24564600	-1.01273600
O	2.65361600	0.81839400	1.65046500
O	-1.72872600	0.90779700	1.97820200
O	1.37842200	-0.27143900	-2.76037400
O	0.16124900	-3.22851200	0.99538400
O	-0.96114900	-0.94430000	3.03307800
O	0.73046700	1.65694700	-1.76826600
O	1.34041800	-3.10410200	-0.94322200
H	0.39614000	-4.74790200	-0.29609300
H	0.19056000	1.09910500	-3.63407300
H	-2.43716700	0.22002600	3.73272100
H	3.88562800	-0.15285200	2.91755200
H	5.42492200	0.11272800	-1.22616900
H	0.34159200	4.92715600	0.67526500
C	-4.73522100	0.24089200	0.49476100
C	-3.99622400	1.32171000	-0.25695900
C	-2.58475600	-0.45786300	-1.29344800
C	-3.00642000	-1.34212800	-0.12573300
H	-3.88169000	2.18314900	0.41381700
H	-2.21350900	-1.31797400	0.64218500
O	-4.25767300	-1.02467800	0.49400900
O	-2.70692700	0.97111700	-0.75413800
O	-1.34481800	-0.61549800	-1.64516300
O	-5.76801200	0.48781100	1.06265400
H	-3.09383300	-2.38285800	-0.46689600
H	-4.63703800	1.63148800	-1.09710300
C	-3.38475300	-1.49417200	-3.25107900
H	-4.19099400	-1.38475500	-3.98398800
H	-2.41161300	-1.43214100	-3.75889100
H	-3.47397300	-2.48992300	-2.78153200
O	-3.55083400	-0.44655700	-2.31373700
H	-0.28921200	-0.62010600	-0.58360700

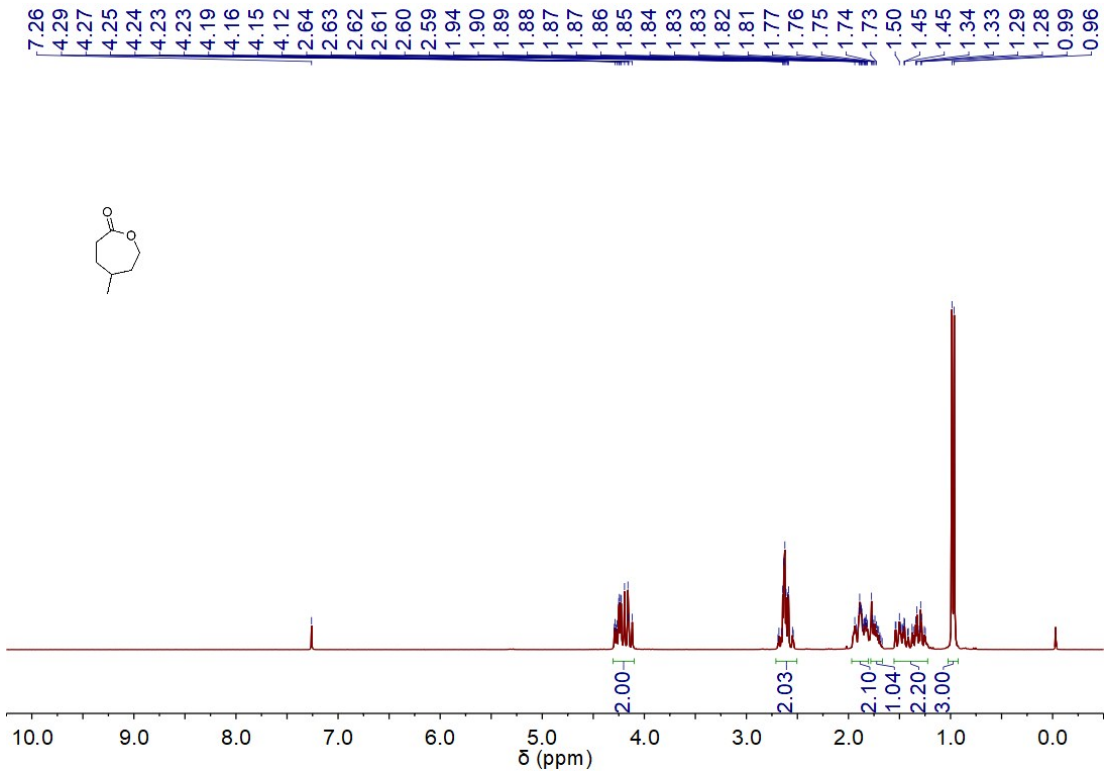
Table S21. XYZ coordinates of **4d** in Fig. 6.

Zn	2.52299200	-1.14739900	0.51062600
C	0.97933100	-3.62547200	0.56636900
O	-0.04397000	-3.18617800	-0.01124200
O	2.01996900	-2.99693800	0.91729600
O	0.99732200	-0.01500600	-0.02570400
Zn	-0.54695600	-1.24928600	-0.23474300
Zn	0.71054500	1.26616000	1.43085800
Zn	1.41038400	0.90667200	-1.70531700
C	3.34516900	0.88882900	2.49886600
C	4.10359900	-0.25832600	-1.79843900
C	-0.43090300	-0.65938400	-3.23861600
C	-1.13335600	-0.38466600	2.74843500
C	0.51519100	3.45253300	-0.51347900
O	2.43972100	1.74125900	2.27611600
O	3.32770100	0.66079200	-2.17175100
O	3.42732900	-0.29115000	2.07130400
O	3.92844300	-1.11621700	-0.89219700
O	-0.76665100	-1.37776800	-2.26993100
O	-0.56623800	0.74961500	2.82113200
O	1.16296800	2.88489800	-1.42012600
O	0.37164200	0.31929800	-3.26049200
O	-1.06731000	-1.22078400	1.82263400
O	-0.04366300	2.91468000	0.49790300
H	0.39688000	4.55151000	-0.60310100
H	-1.75522600	-0.64898400	3.63100100
H	-0.88612900	-0.90828100	-4.22025300
H	5.06946300	-0.32140300	-2.33922700
H	4.16908100	1.22649300	3.15904000
H	0.98579900	-4.70970300	0.79801900
C	-5.14661900	-0.93260100	-0.01048400
C	-3.76585400	-1.48227700	0.25852200
C	-2.91332900	0.64983600	-0.36483100
C	-4.12526700	0.87719200	-1.24140900
H	-3.71551700	-2.50497100	-0.13589600
H	-3.89443800	0.50907300	-2.25167200
O	-5.28129300	0.22263600	-0.71595100
O	-2.68844400	-0.75853300	-0.34346800
O	-1.79551300	1.20415200	-0.95705700
O	-6.12453500	-1.48946900	0.40940600
H	-4.37462600	1.94238200	-1.31461500
H	-3.62842400	-1.53625300	1.34883100
C	-3.55217900	2.34205800	1.19784500
H	-3.36190300	2.54853000	2.25565300
H	-3.00617900	3.08486700	0.59560900

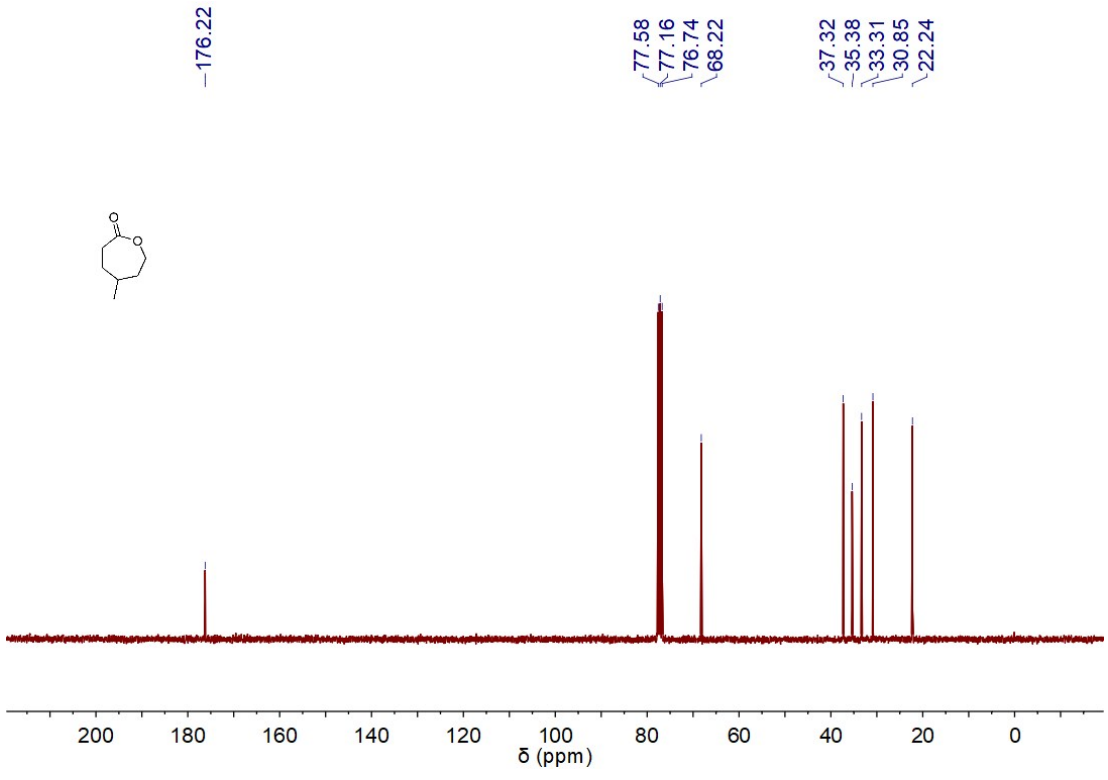
H	-4.63252900	2.41661900	0.99952300
O	-3.07347700	1.01876800	0.96588800
H	-1.32193800	1.74691900	-0.29243900

7. NMR spectra

4-MeCL

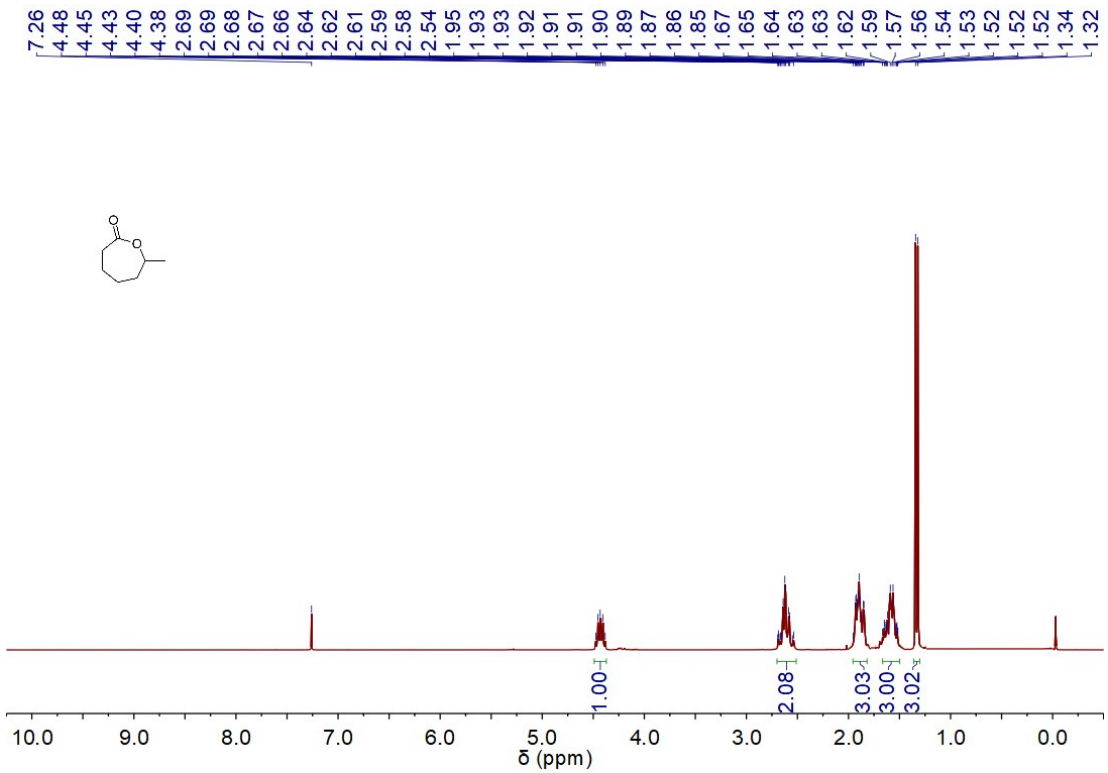


^{1}H NMR of 4-MeCL

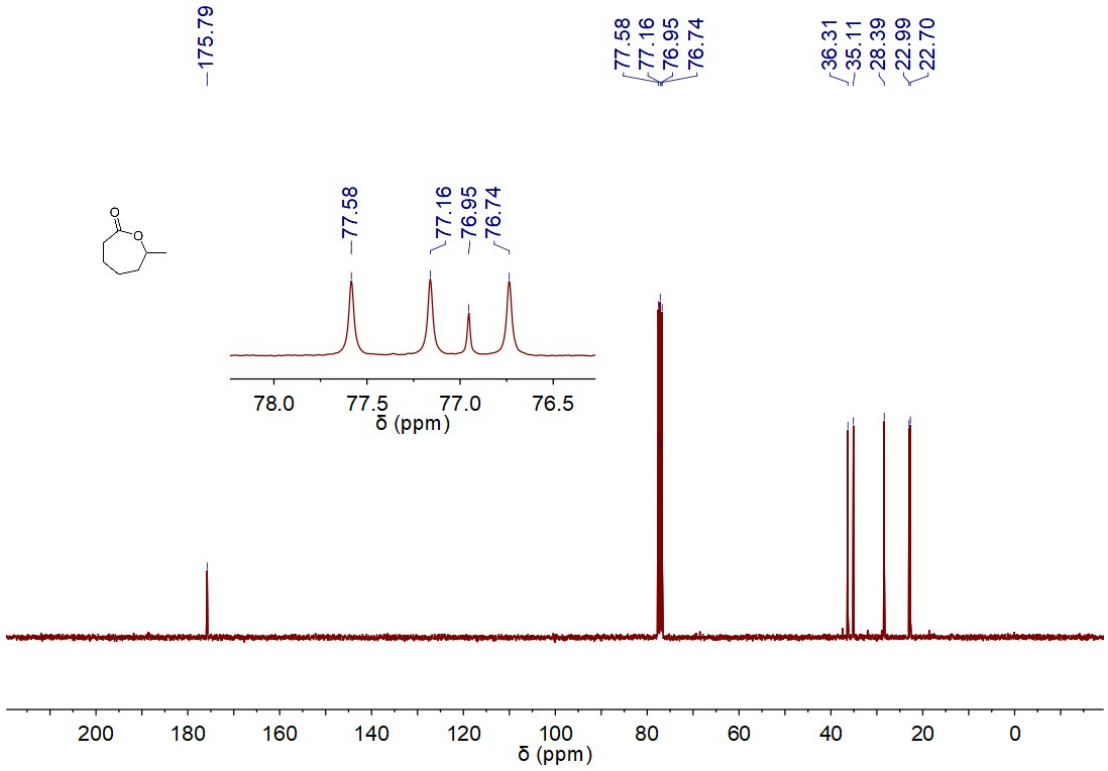


^{13}C NMR of 4-MeCL

6-MeCL

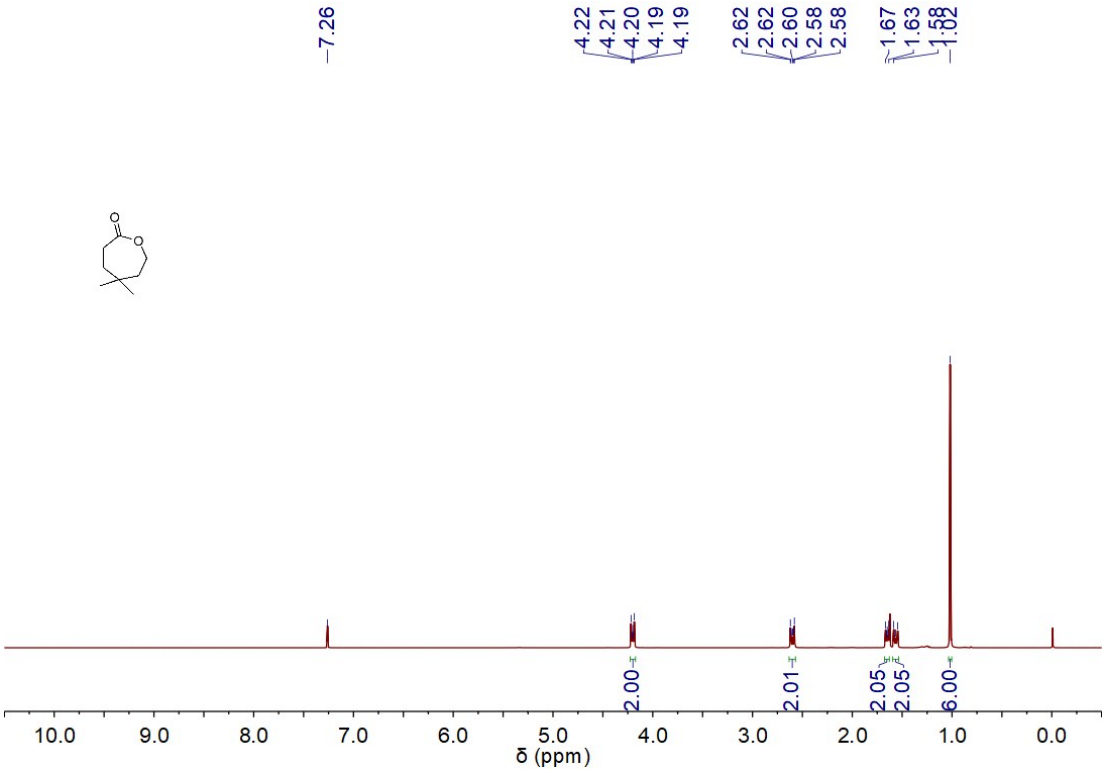


^{1}H NMR of 6-MeCL

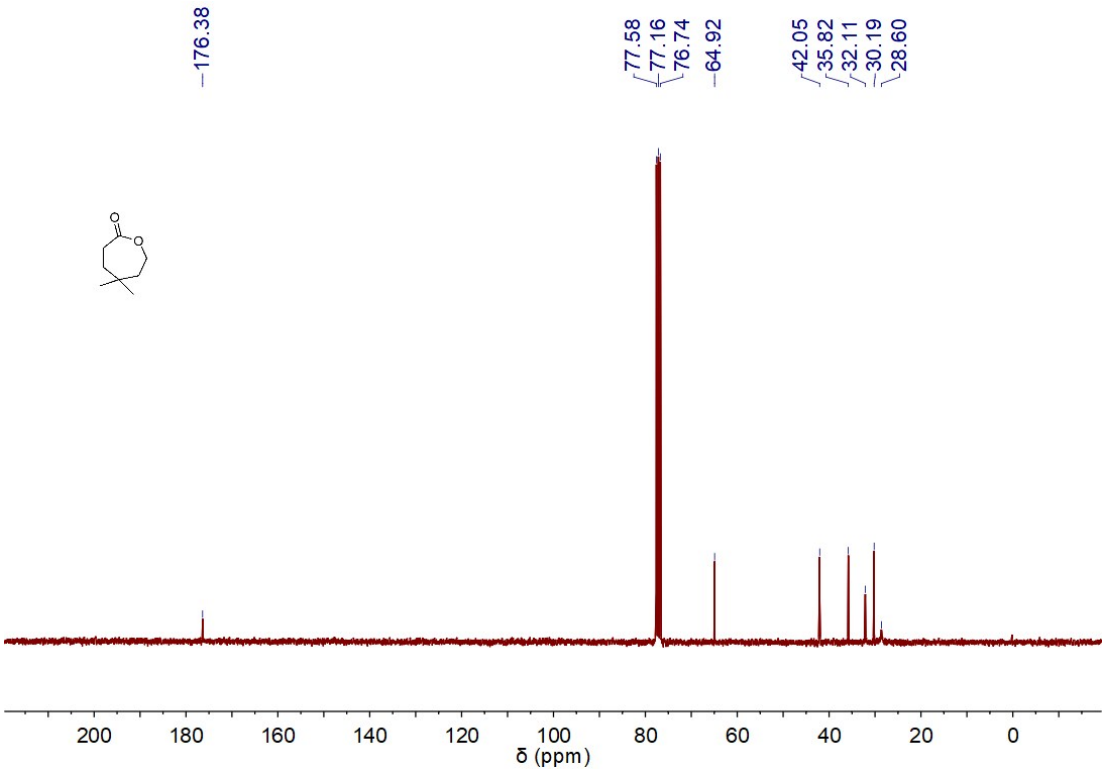


^{13}C NMR of 6-MeCL

4,4’-MeCL

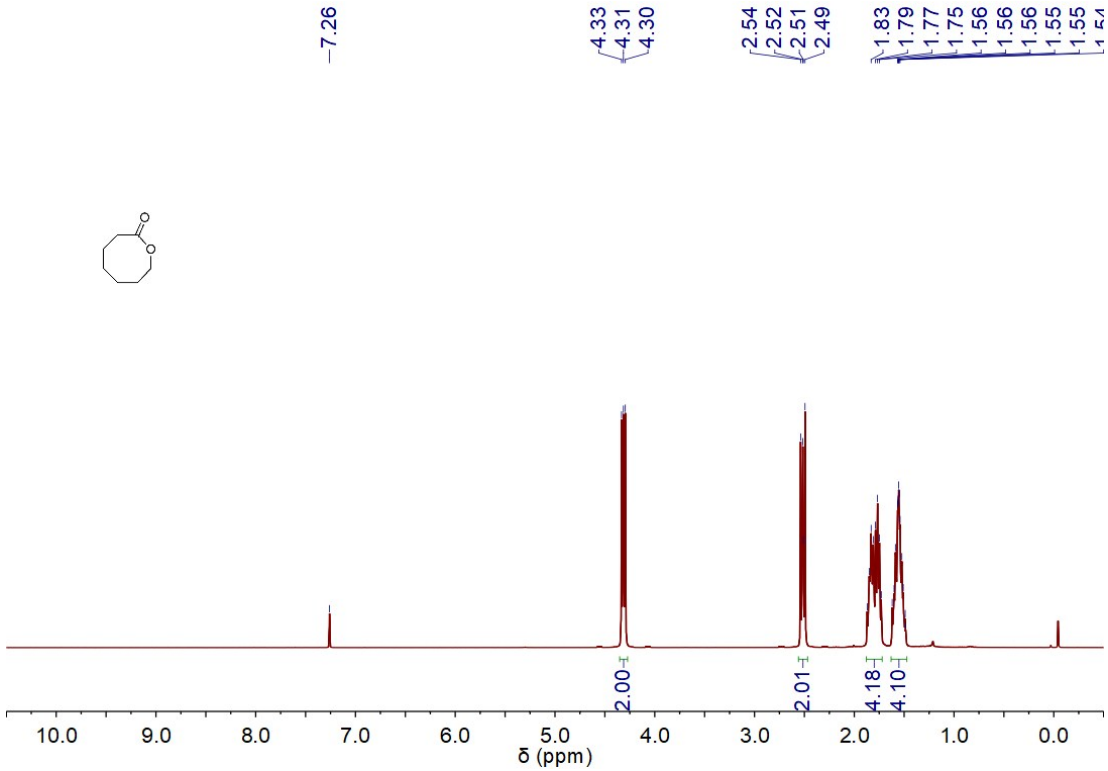


^{1}H NMR of 4,4’-MeCL

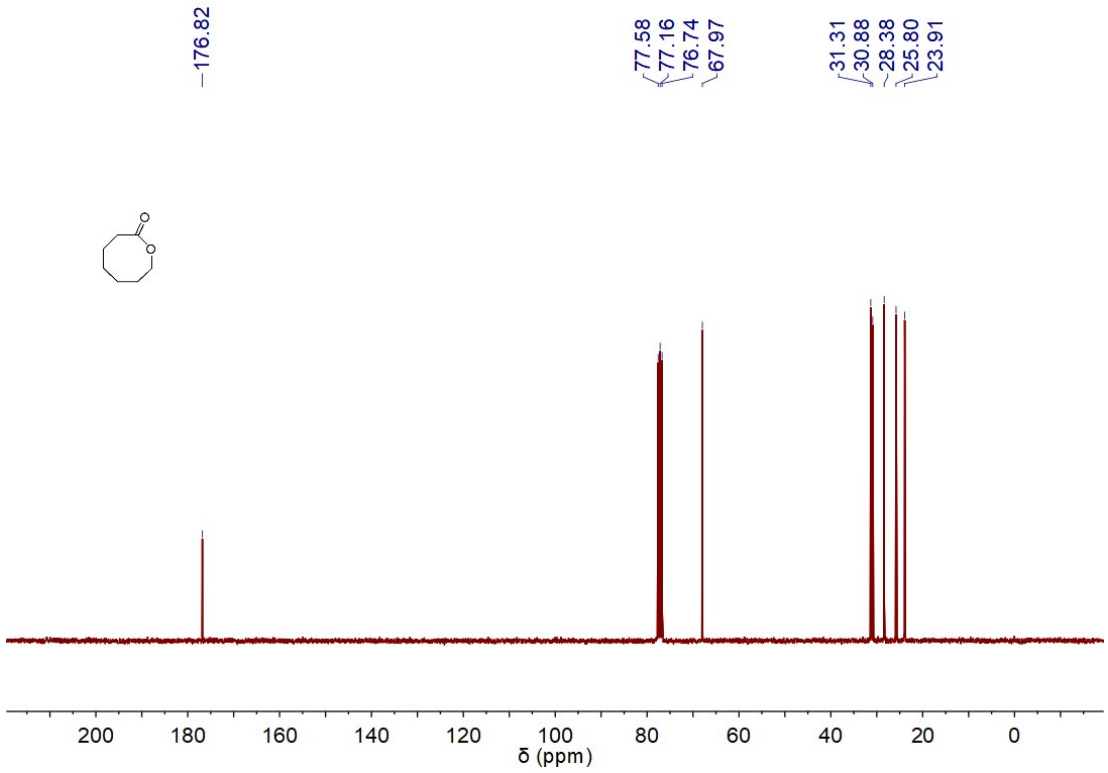


^{13}C NMR of 4,4’-MeCL

HL

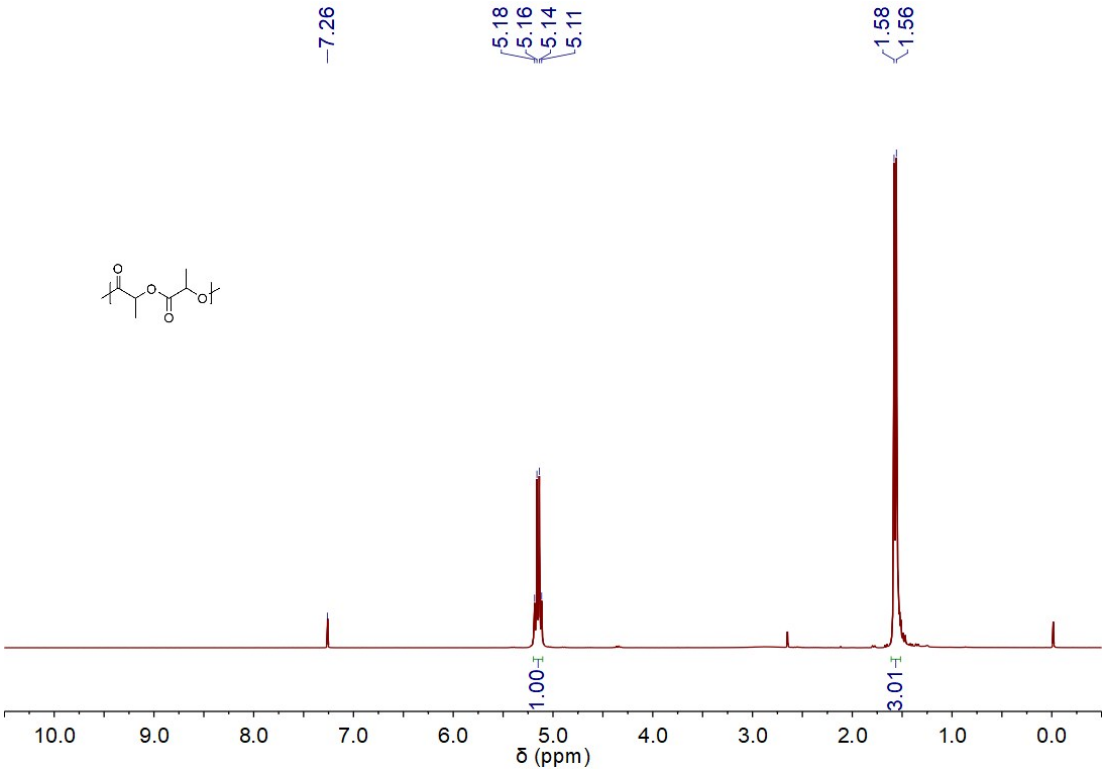


^{1}H NMR of HL

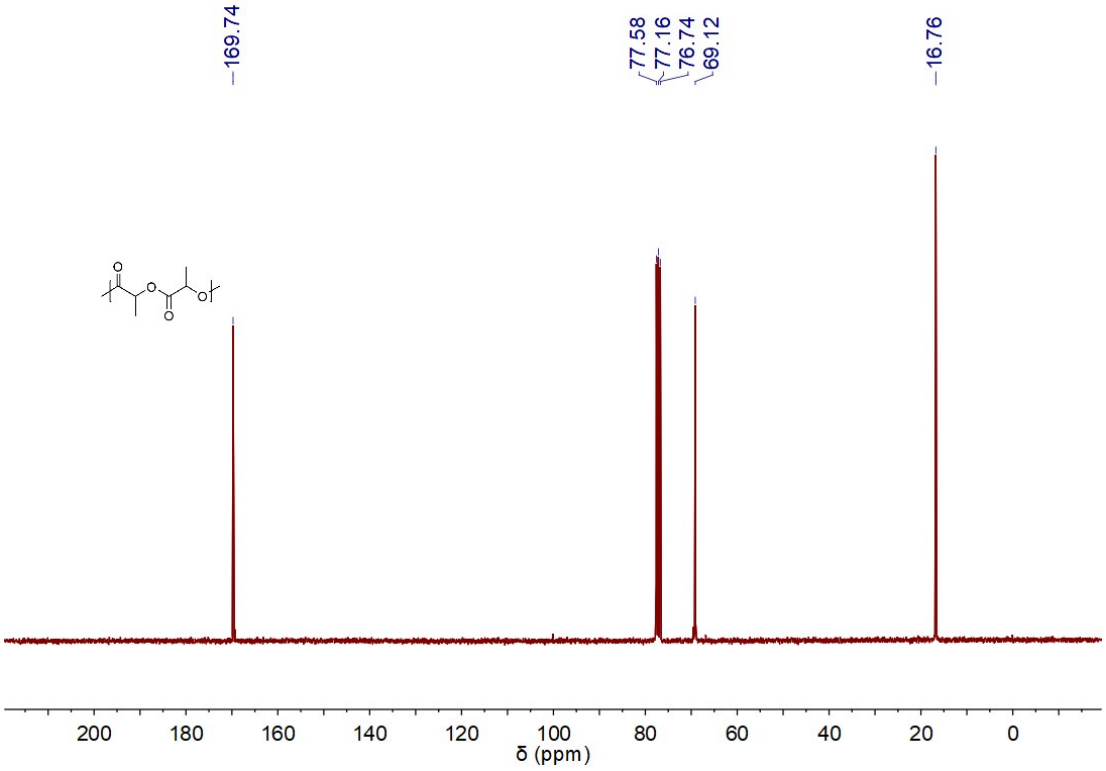


^{13}C NMR of HL

PLLA

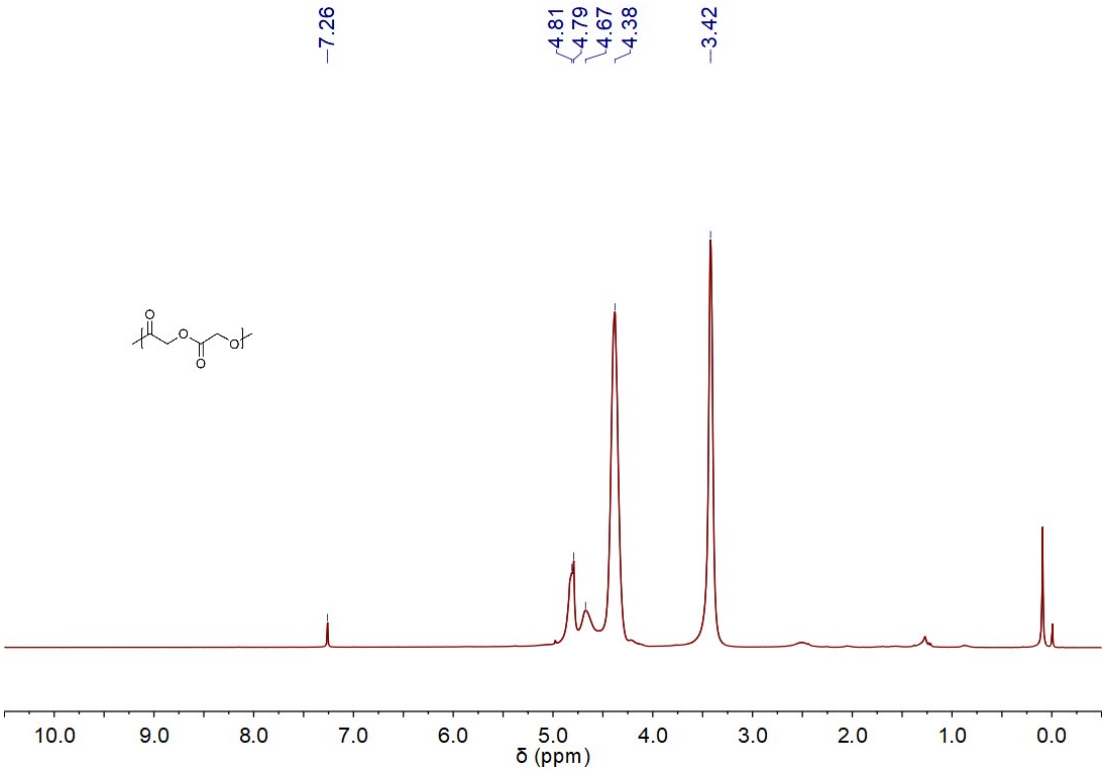


^{1}H NMR of PLLA

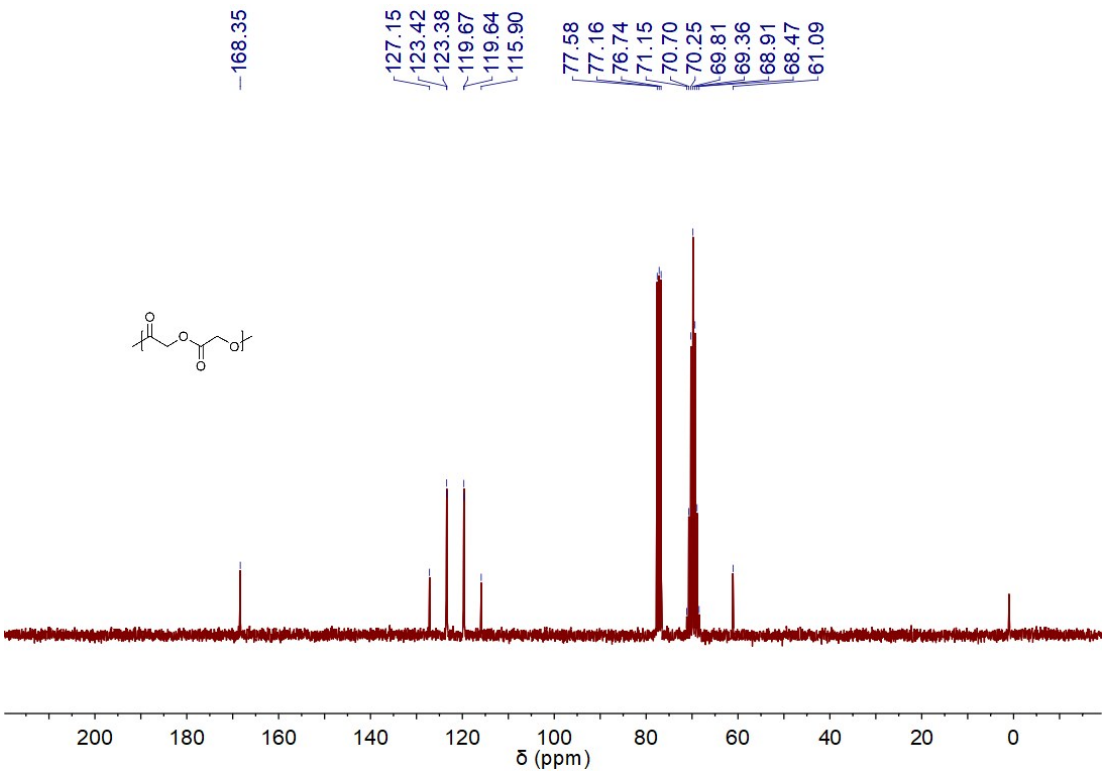


^{13}C NMR of PLLA

PGA

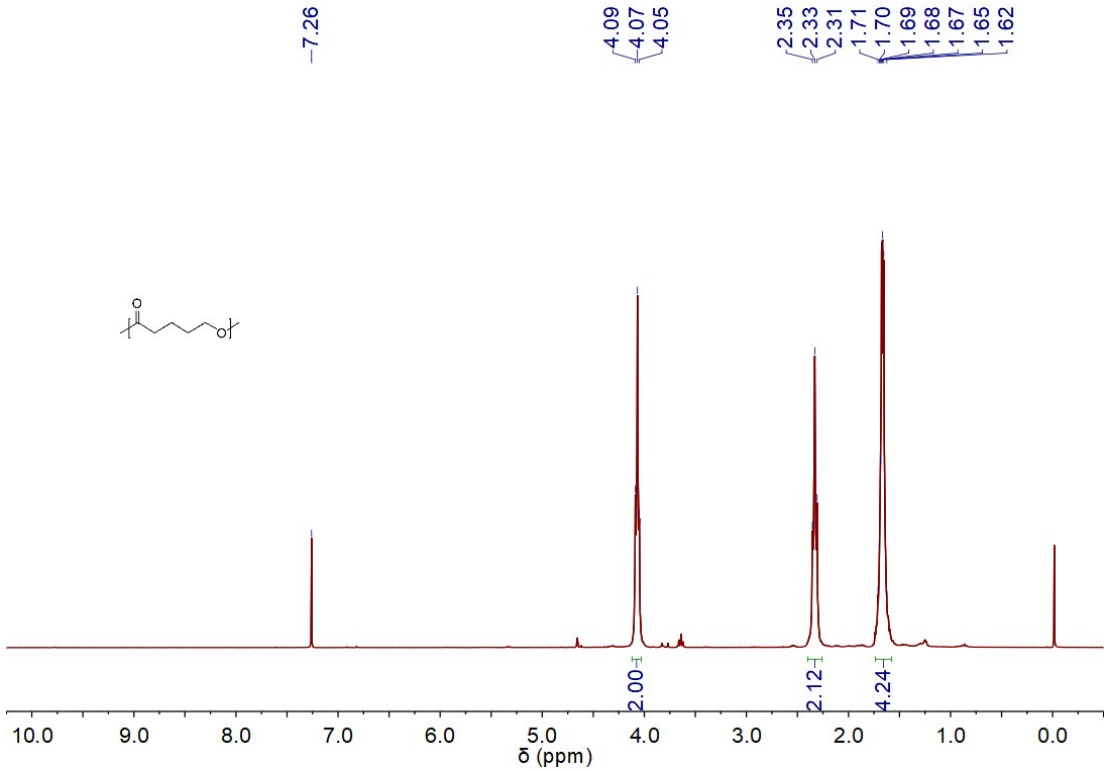


^{1}H NMR of PGA

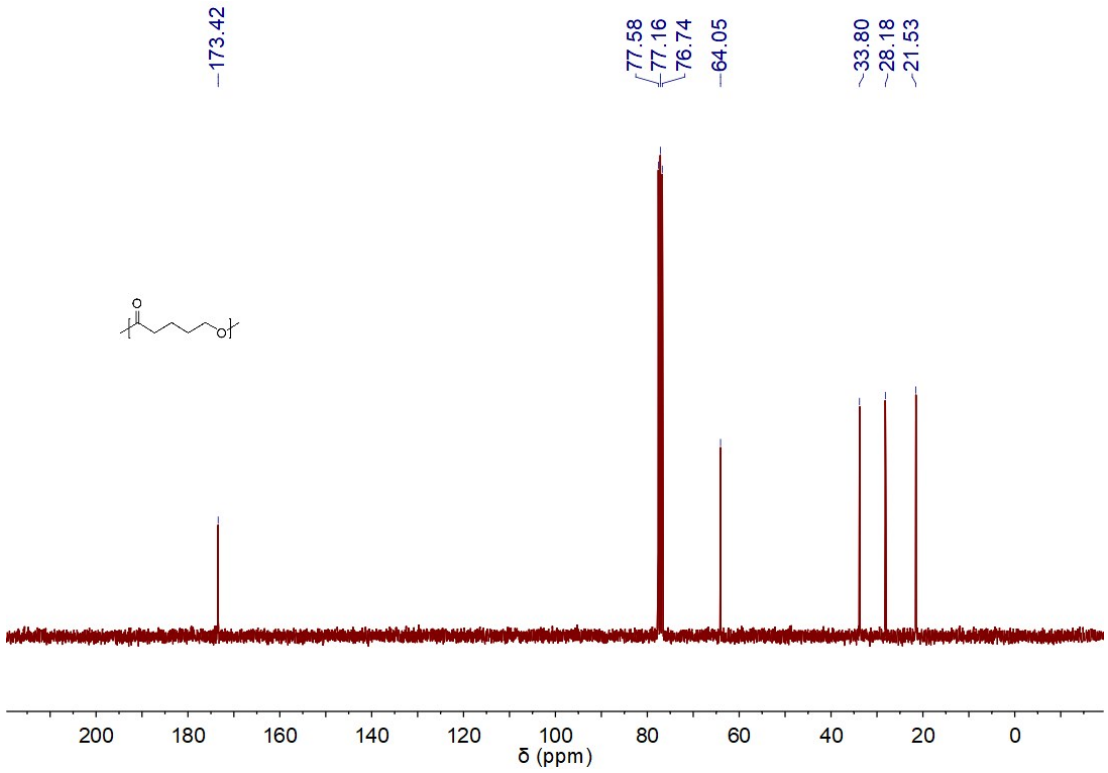


^{13}C NMR of PGA

PVL

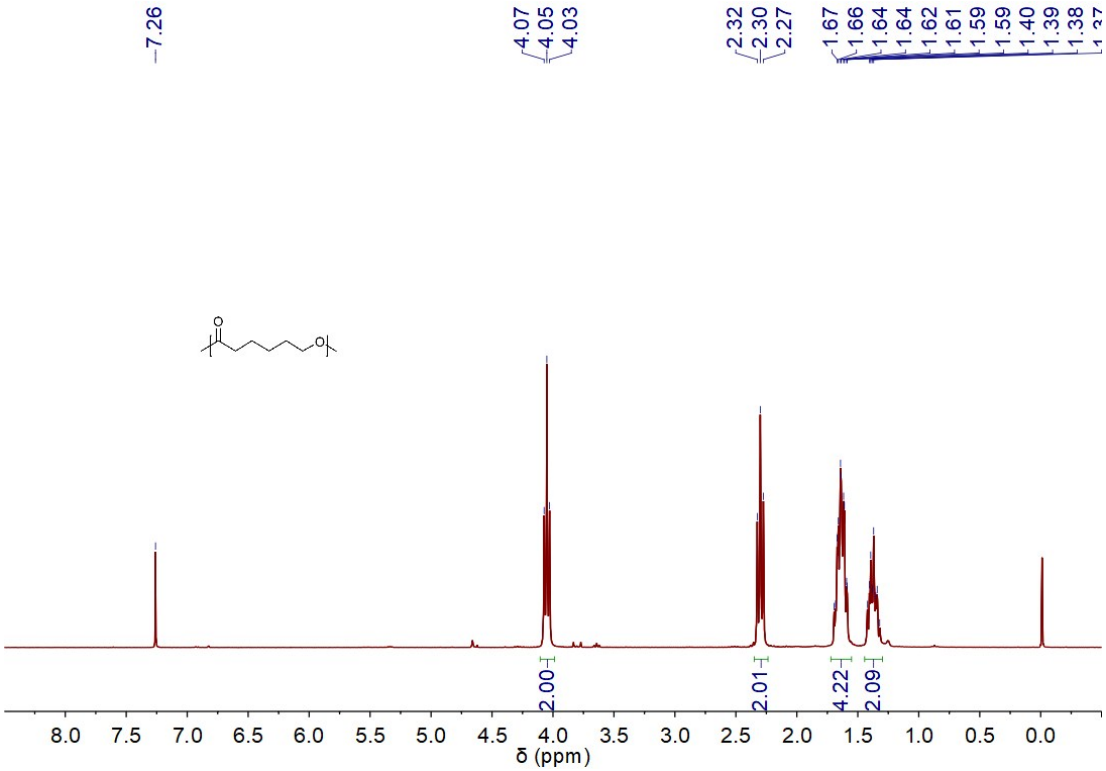


^{1}H NMR of PVL

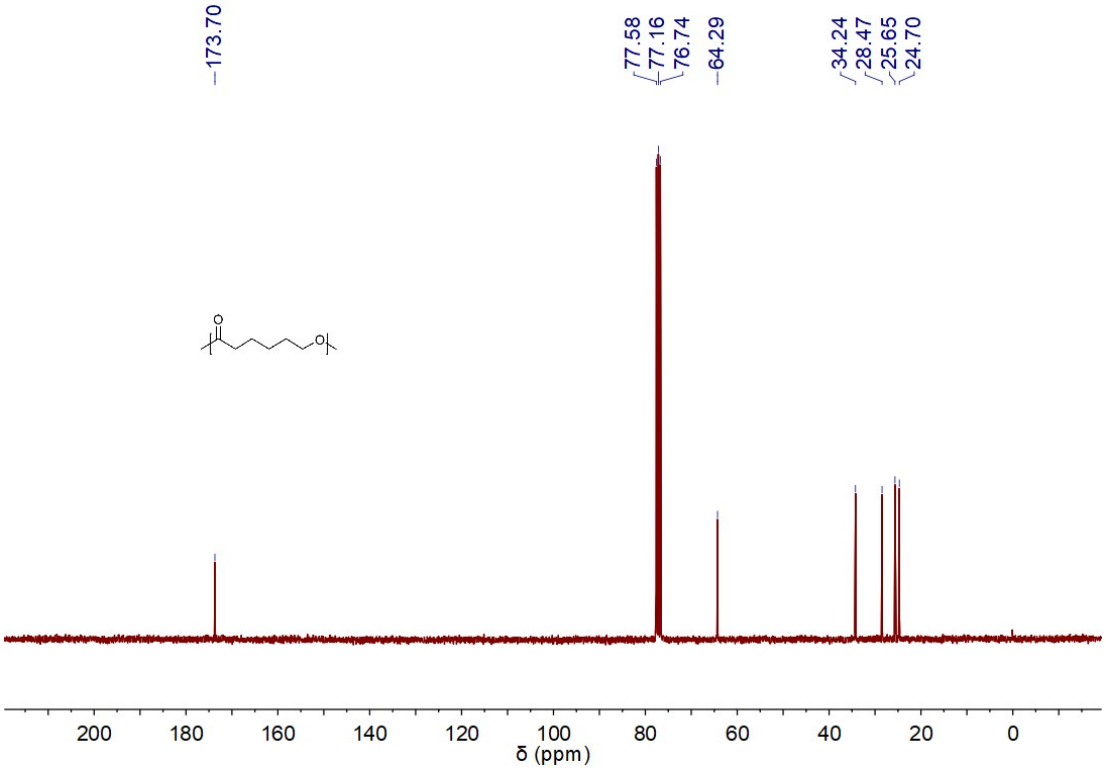


^{13}C NMR of PVL

PCL

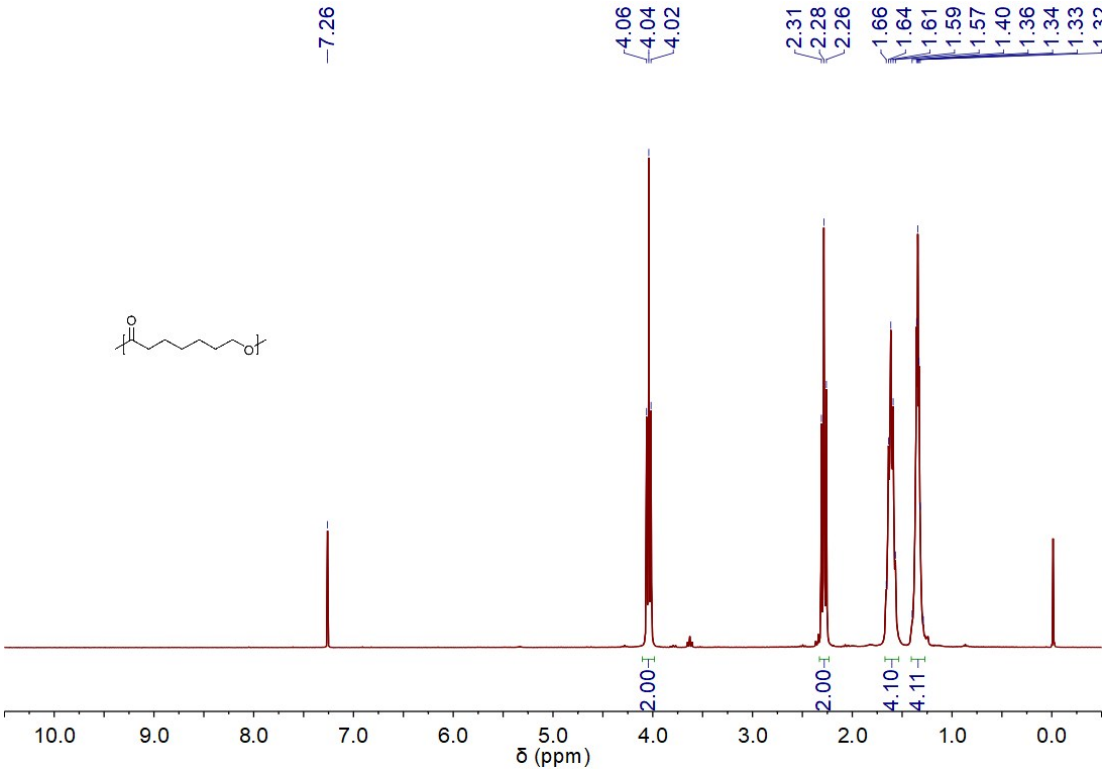


^{1}H NMR of PCL

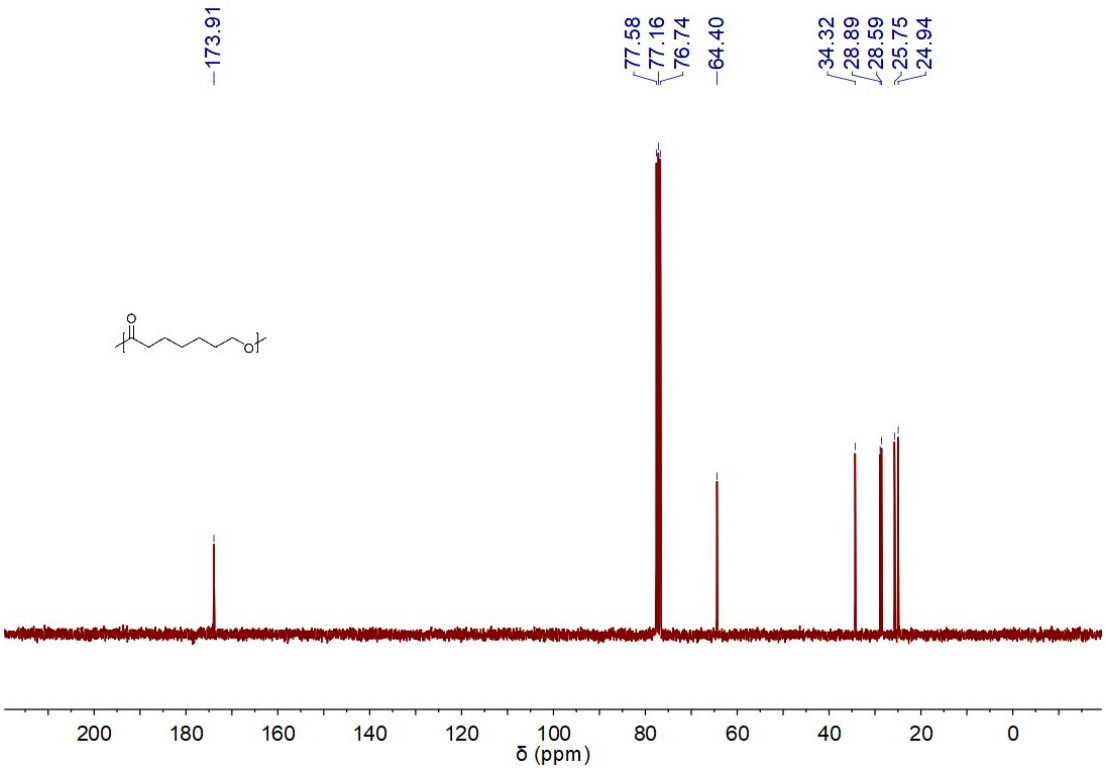


^{13}C NMR of PCL

PHL

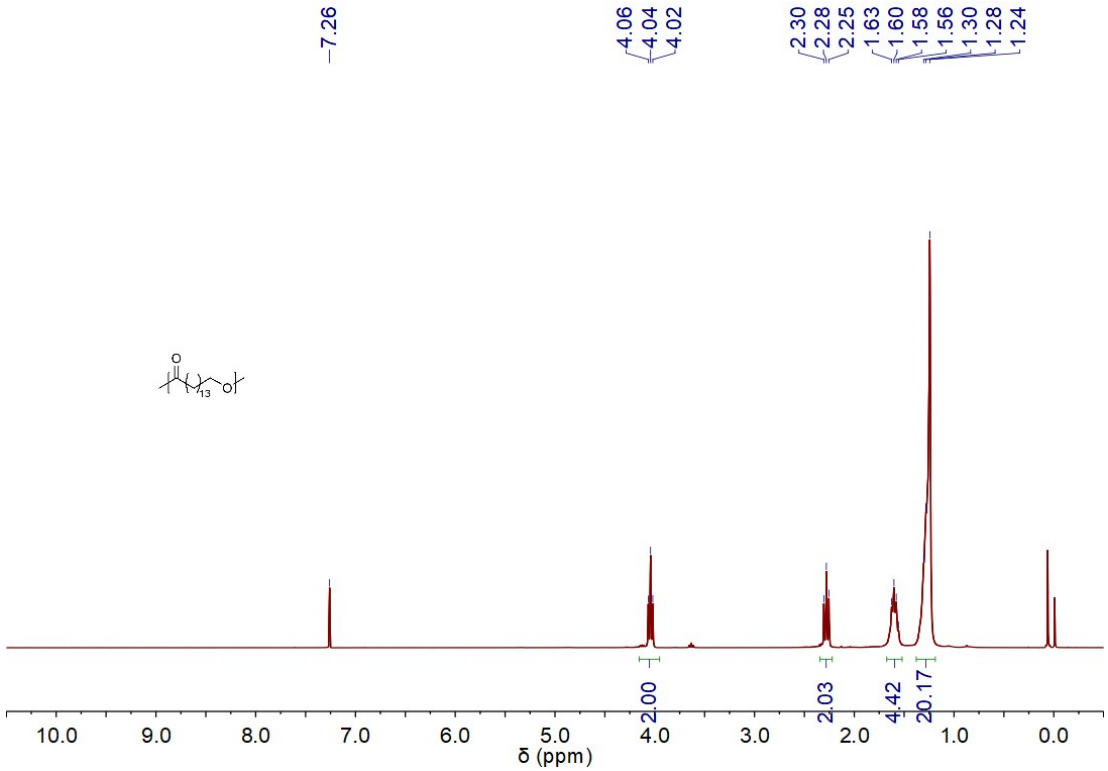


^{1}H NMR of PHL

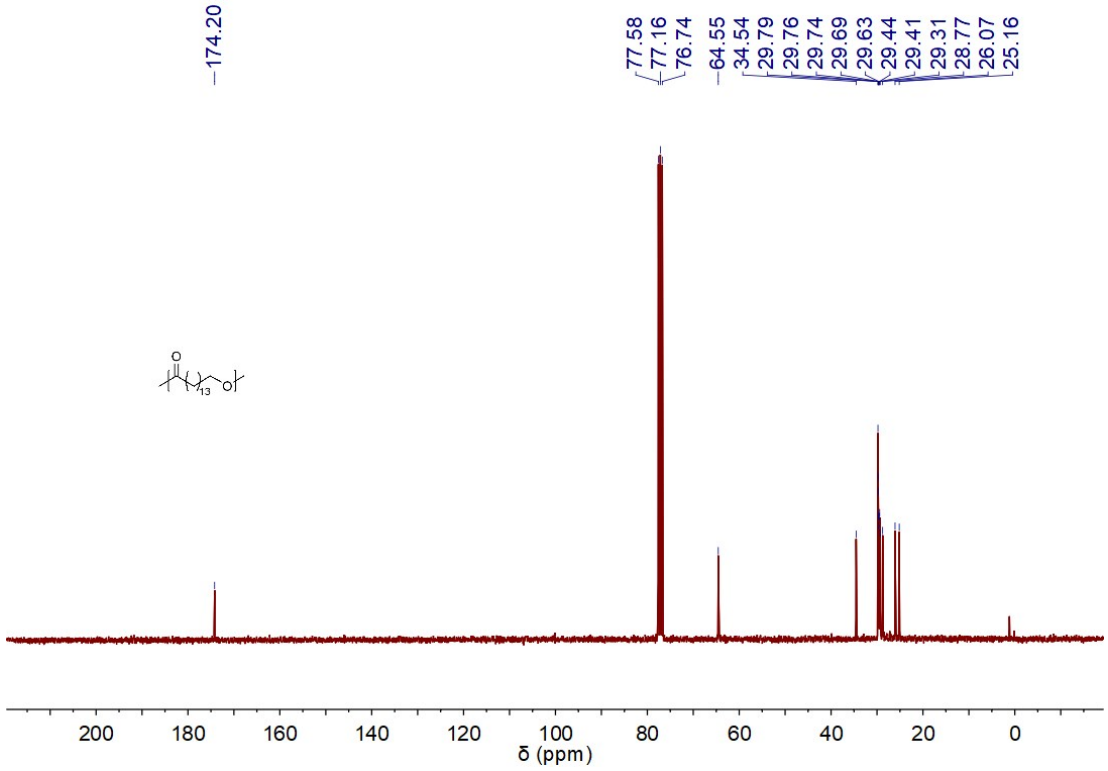


^{13}C NMR of PHL

PPDL

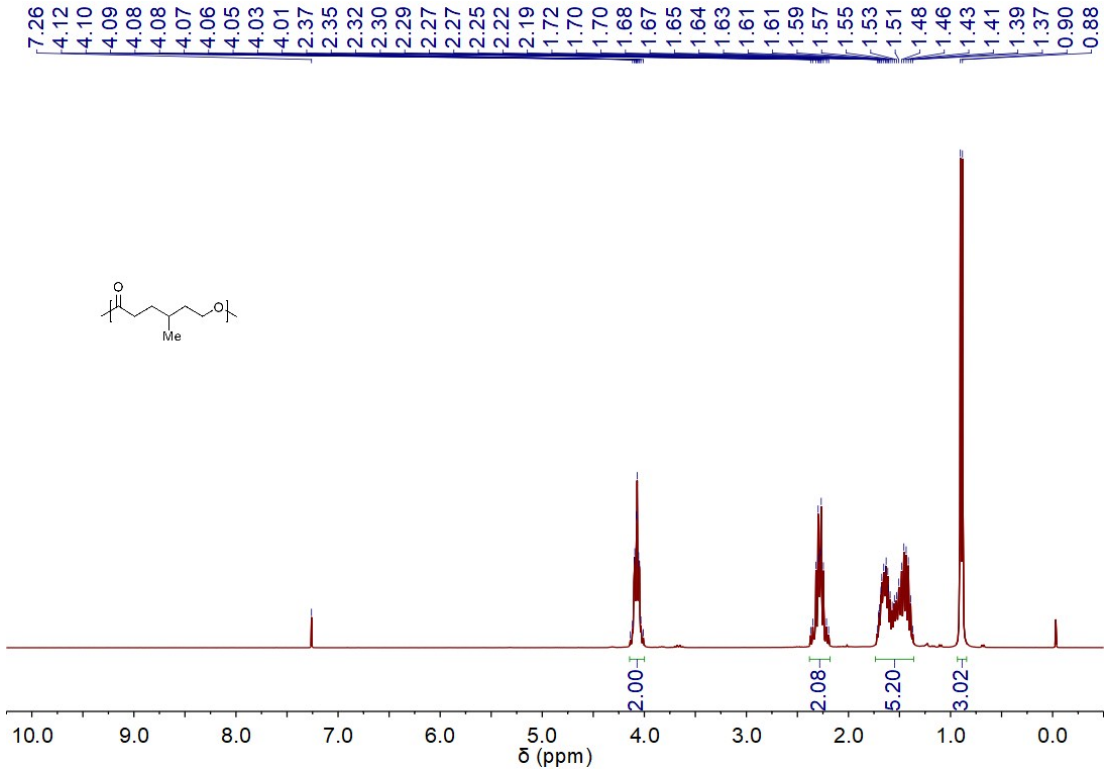


^{1}H NMR of PPDL

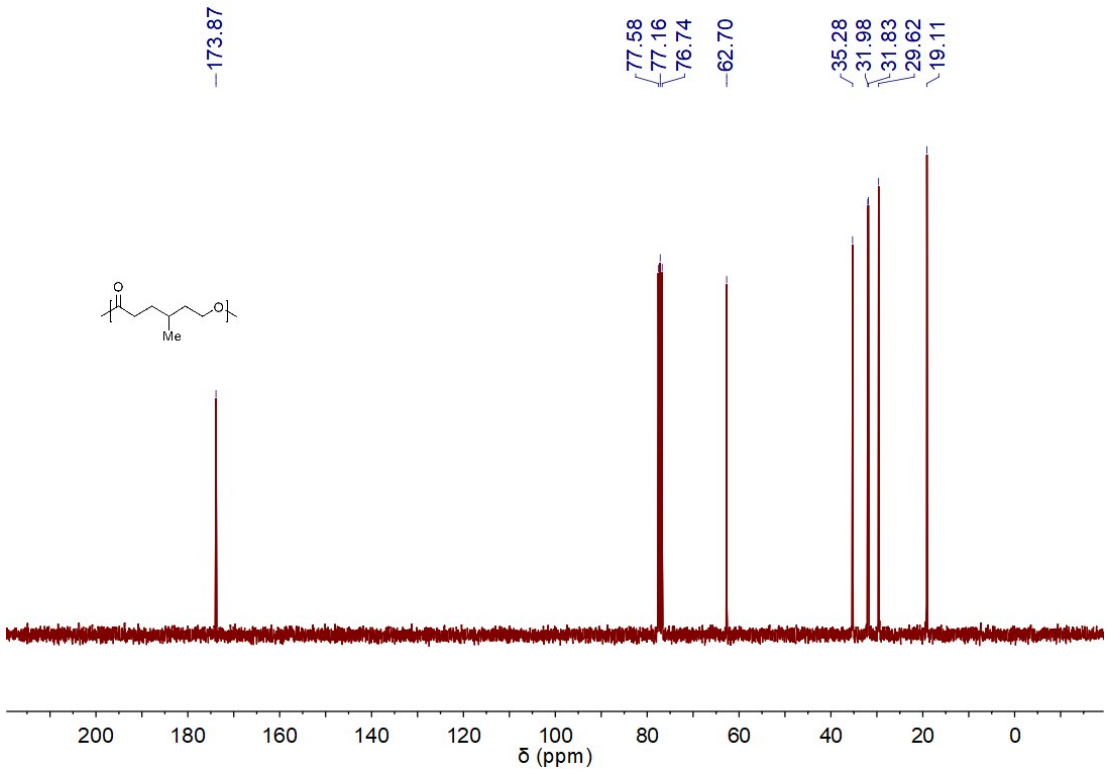


^{13}C NMR of PPDL

P(4-MeCL)

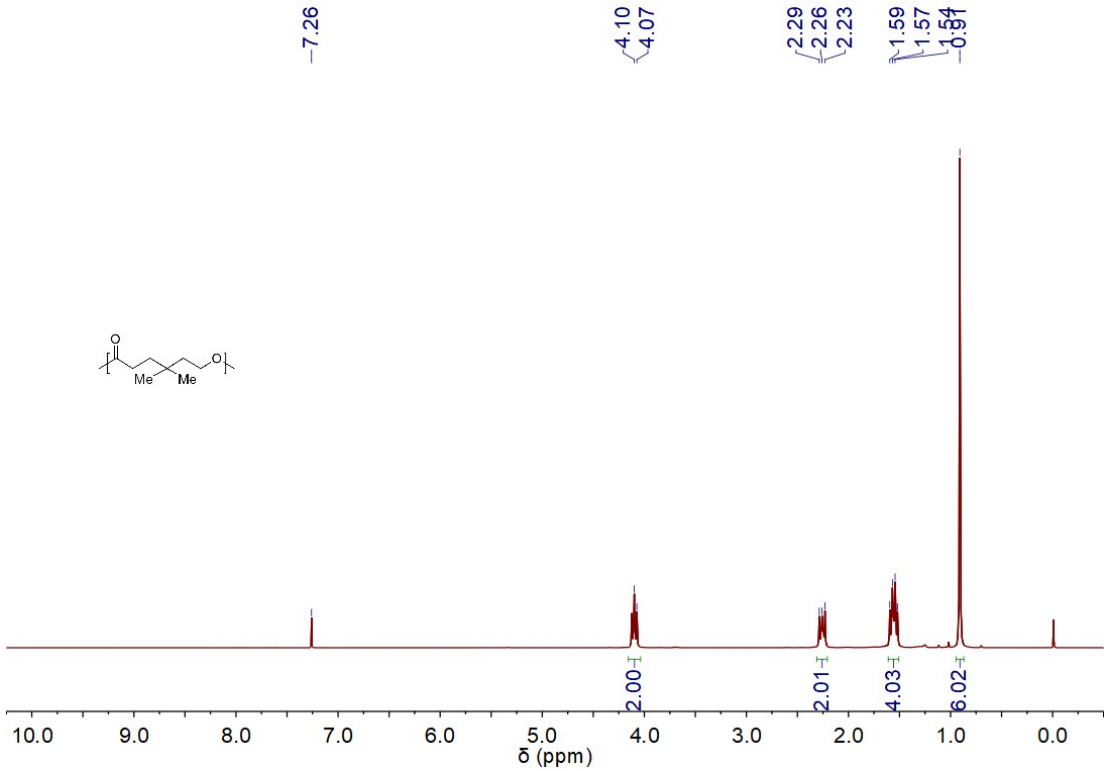


^{1}H NMR of P(4-MeCL)

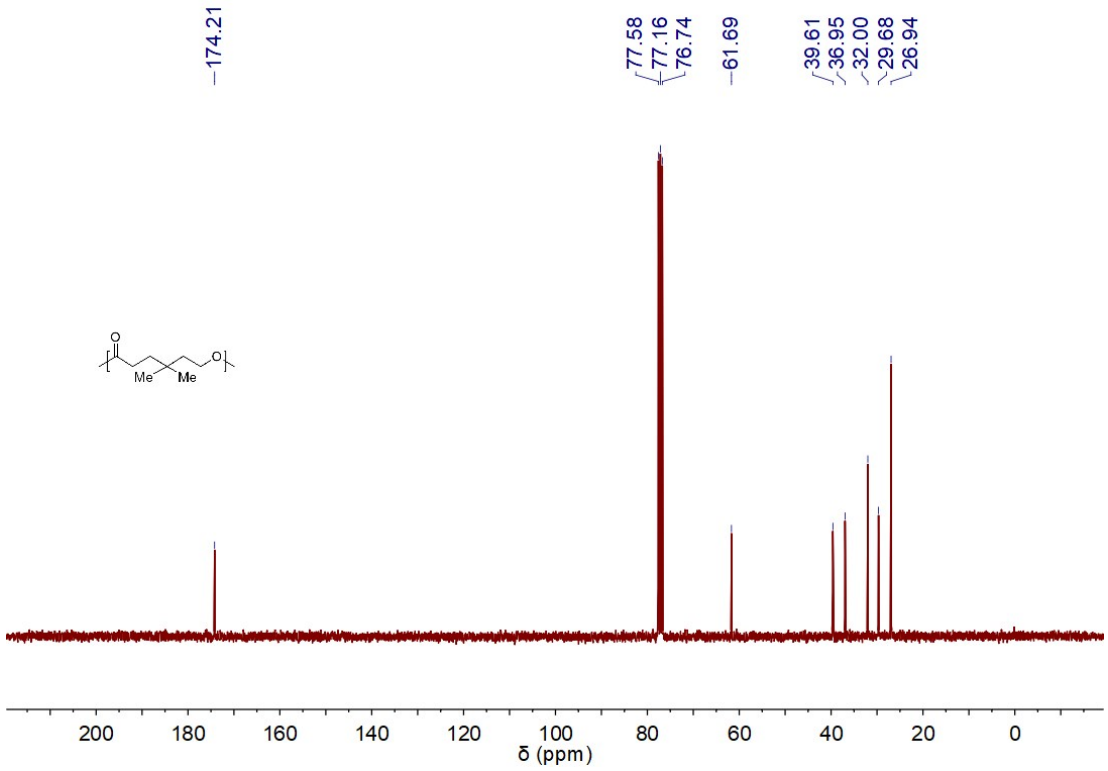


^{13}C NMR of P(4-MeCL)

P(4,4'-MeCL)

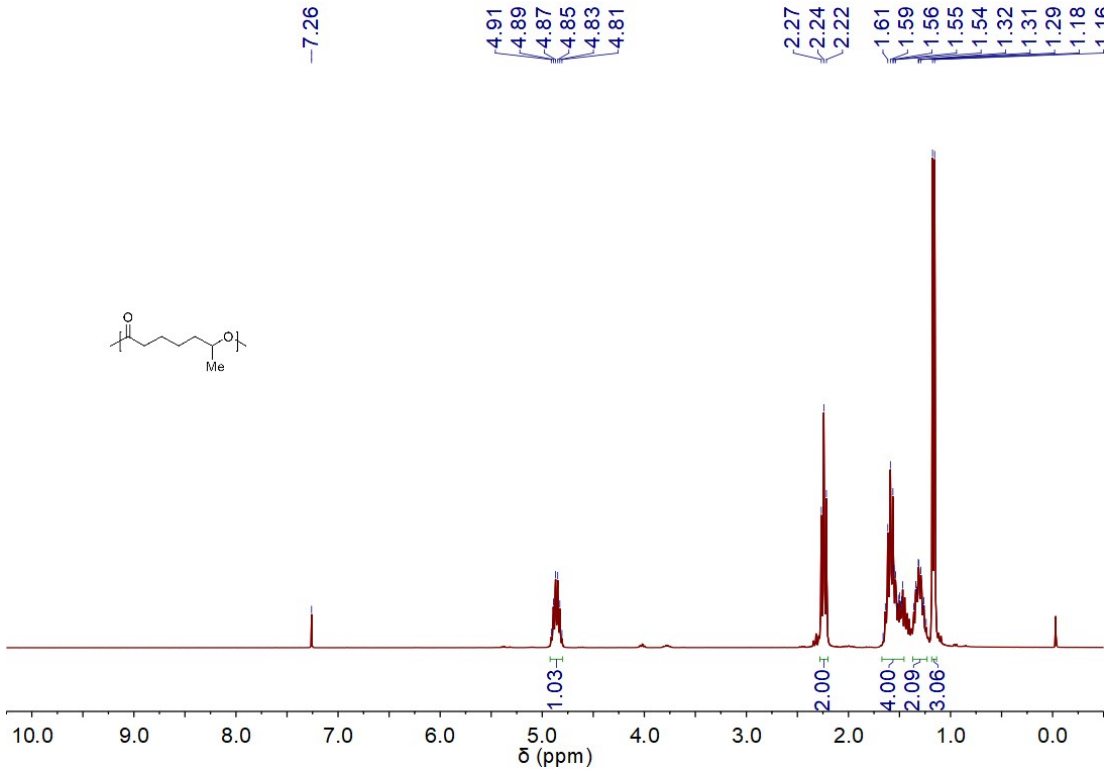


^{1}H NMR of P(4,4'-MeCL)

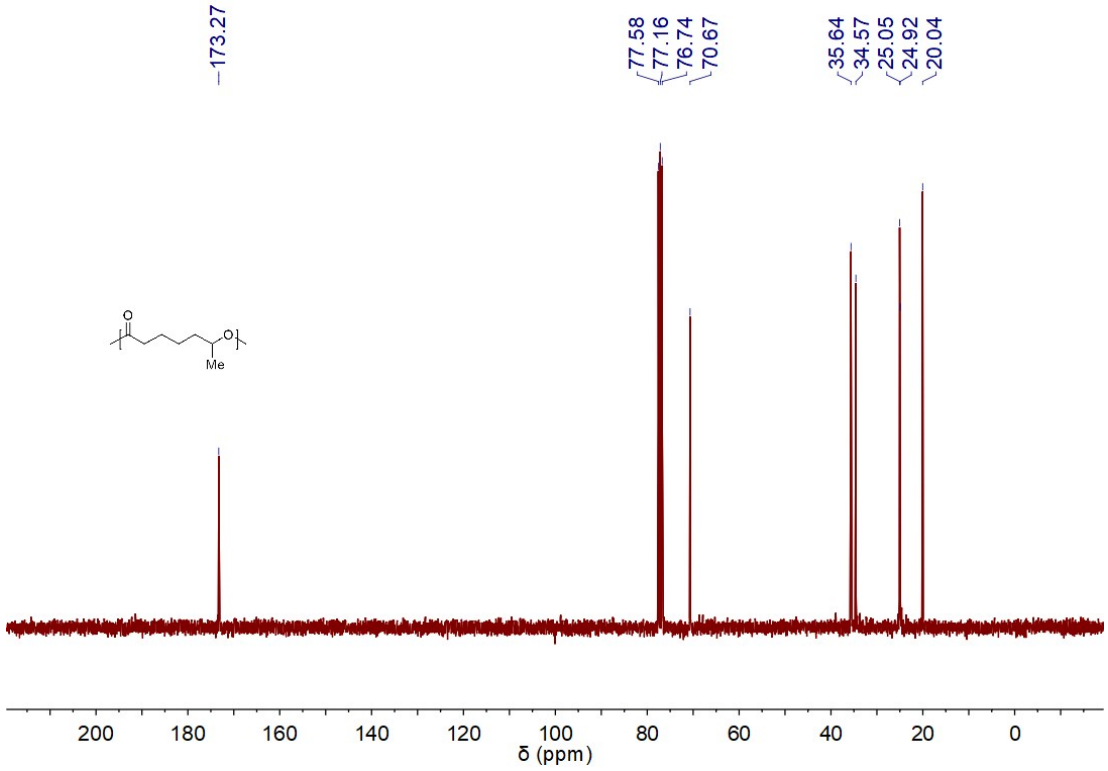


^{13}C NMR of P(4,4'-MeCL)

P(6-MeCL)

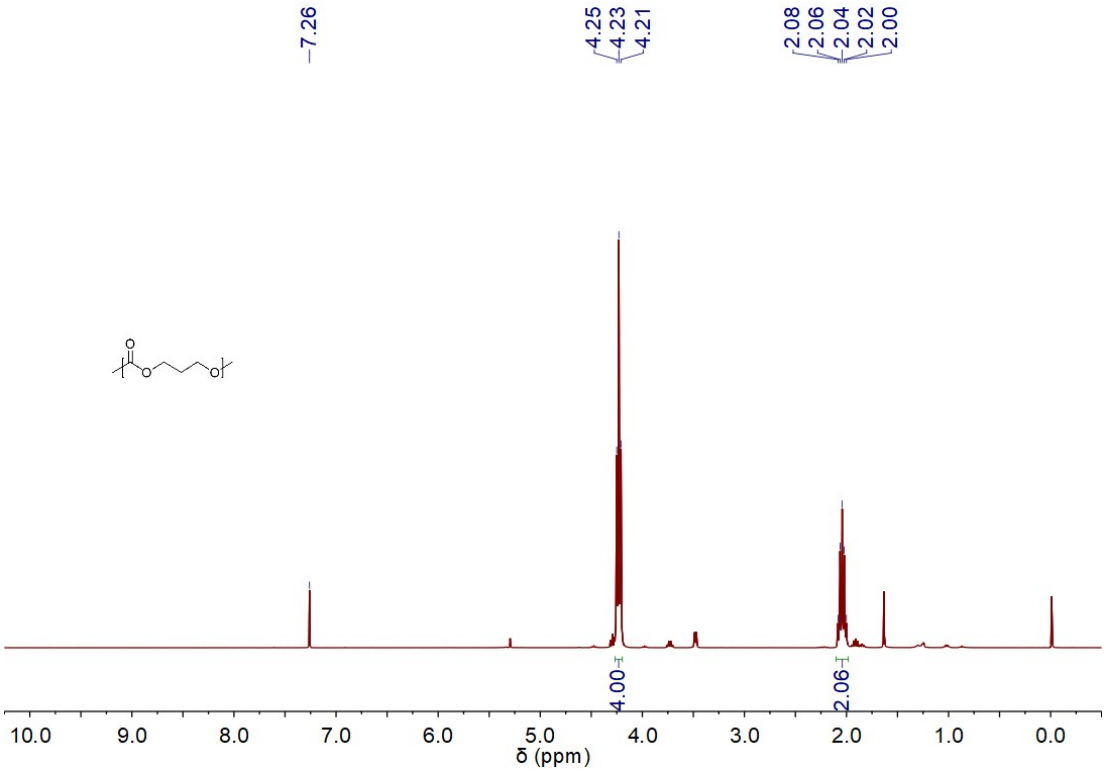


^{1}H NMR of P(6-MeCL)

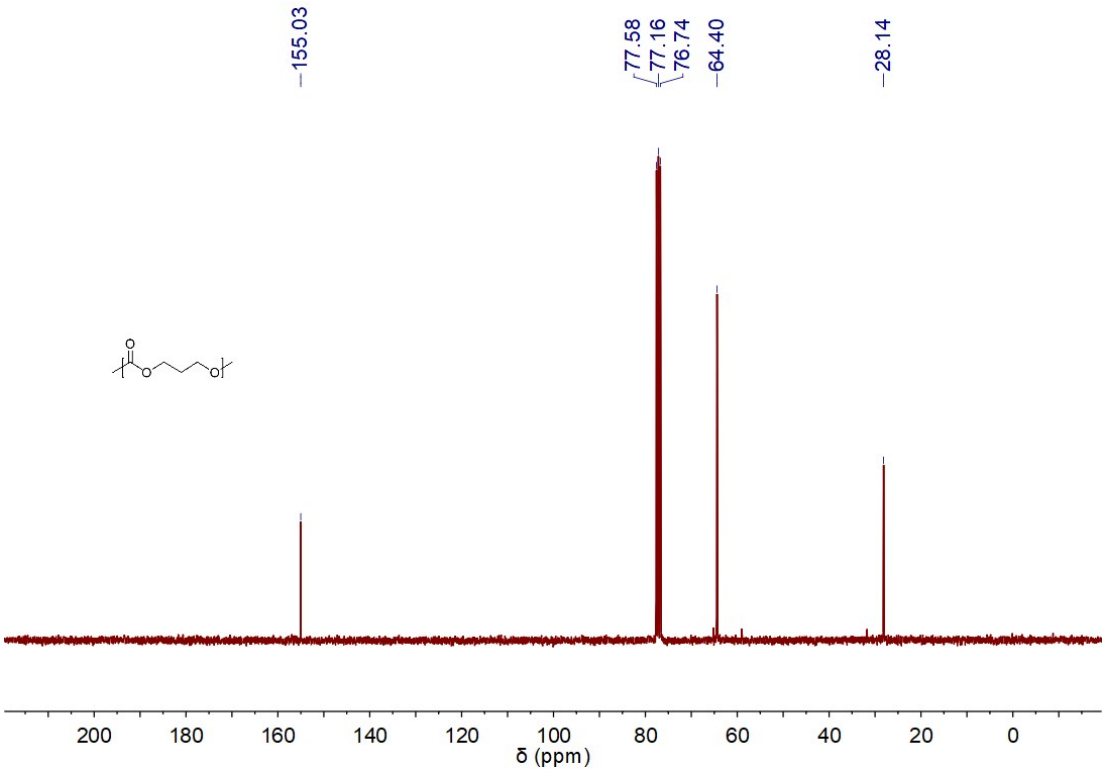


^{13}C NMR of P(6-MeCL)

PTMC

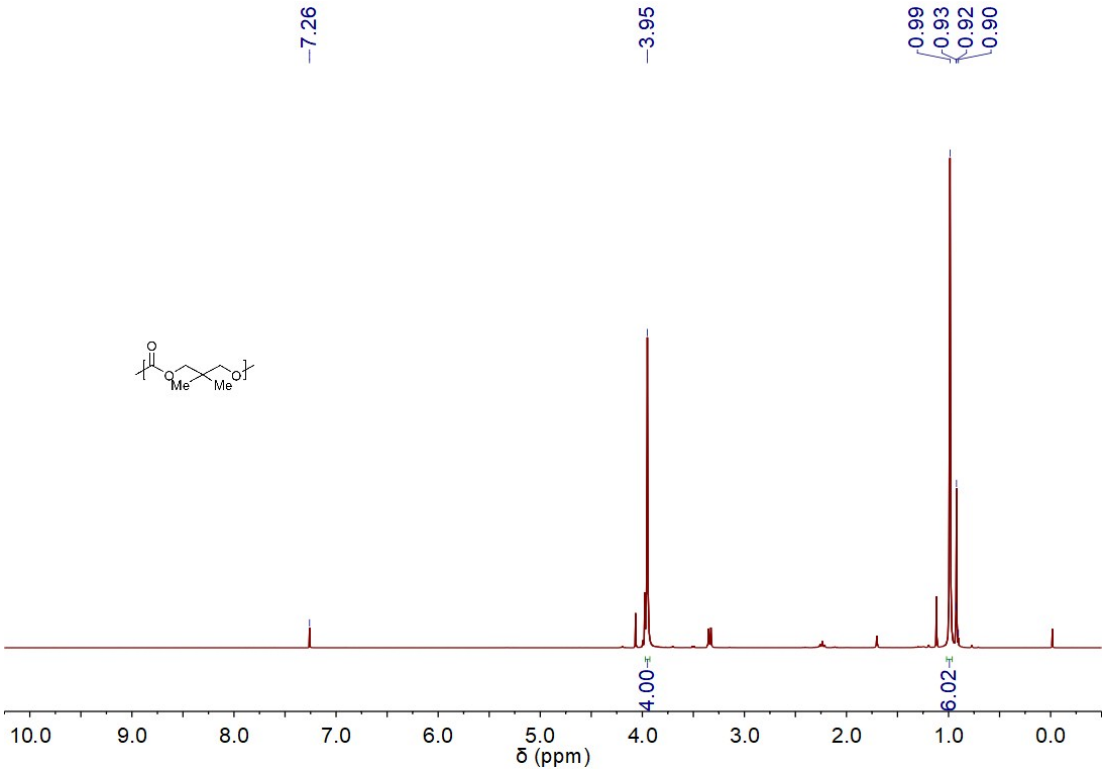


^{1}H NMR of PTMC

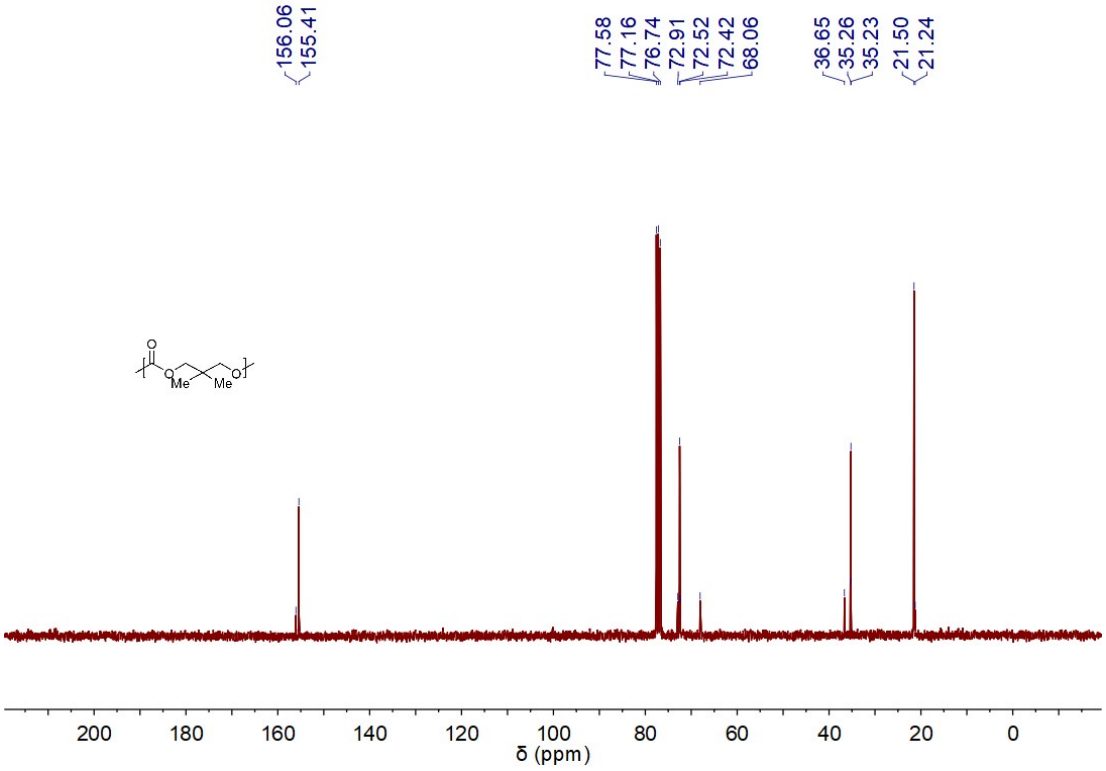


^{13}C NMR of PTMC

PDMTMC



^{1}H NMR of PDMTMC



^{13}C NMR of PDMTMC

8. Supporting references

S1 V. Valerio, D. Petkova, C. Madelaine and N. Maulide, *Chem. Eur. J.*, 2013, **19**, 2606–2610.

S2 A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13.

S3 G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 2002.

S4 Bruker AXS, SAINT Software Reference Manual V. 6.23; Madison, WI, 1998.

S5 G. M. Sheldrick, SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

S6 Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101.

S7 T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007–1023.

S8 Gaussian 09, Revision D**.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, M. A. Scuseria, J. R. Robb, G. Cheeseman, V. Scalmani, B. Barone, G. A. Mennucci, G. E. Petersson, et al. Gaussian, Inc., Wallingford CT, 2009.

S9 J. Börner, U. Flörke, K. Huber, A. Döring, D. Kuchling and S. Herres-Pawlis, *Chem. Eur. J.*, 2009, **15**, 2362–2376.

S10 C. Di Iulio, M. D. Jones, M. F. Mahon and D. C. Apperley, *Inorg. Chem.*, 2010, **49**, 10232–10234.

S11 P. D. Knight, A. J. P. White and C. K. Williams, *Inorg. Chem.*, 2008, **47**, 11711–11719.

S12 T. R. Jensen, L. E. Breyfogle, M. A. Hillmyer and W. B. Tolman, *Chem. Commun.*, 2004, **21**, 2504–2505.

S13 V. Poirier, T. Roisnel, J.-F. Carpentier and Y. Sarazin, *Dalton. Trans.*, 2009, **44**, 9820–9827.

S14 M. J. Walton, S. J. Lancaster, J. A. Wright, M. R. J. Elsegood and C. Redshaw, *Dalton. Trans.*, 2014, **43**, 18001–18009.

S15 E. Piedra-Arroni, C. Ladavière, A. Amgoune and D. Bourissou, *J. Am. Chem. Soc.*, 2013, **135**, 13306–13309.

S16 H.-Y. Chen, H.-Y. Tang and C.-C. Lin, *Macromolecules*, 2006, **39**, 3745–3752.

S17 Y.-L. Hsieh, Y.-C. Lin, G.-H. Lee and C.-H. Peng, *Polymer*, 2015, **56**, 237–244.

S18 T. Ebrahimi, E. Mamleeva, I. Yu, S. G. Hatzikiriakos and P. Mehrkhodavandi, *Inorg. Chem.*, 2016, **55**, 9445–9453.

S19 K. Wang, T. J. Prior and C. Redshaw, *Chem. Commun.*, 2019, **55**, 11279–11282.

S20 I. D'Auria, M. Lamberti, M. Mazzeo, S. Milione, G. Roviello and C. Pellecchia, *Chem. Eur. J.*, 2012, **18**, 2349–2360.

S21 M. Li, P. Zhang and C. Chen, *Macromolecules*, 2019, **52**, 5646–5651.

S22 I. D'Auria, C. Tedesco, M. Mazzeo and C. Pellecchia, *Dalton Trans.*, 2017, **46**, 12217–12225.