Supporting Information

Sustainable Approach for Synthesis and Completely Recycle of Cyclic CO_2-based Polycarbonates

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Experimental Procedures

Unless otherwise stated all synthesis and manipulations discussed were carried out in flamed Schlenk-type glassware on a double-manifold Schlenk vacuum line under nitrogen atmosphere or in an argon filled glove box. Toluene were freshly refluxed over sodium/potassium alloy and distilled under nitrogen atmosphere, then stored over molecular sieves 4 Å. *meso*-CHO was purchased from sigma-aldrich and freshly distilled from CaH_2 under nitrogen atmosphere. 4,4'-diaminodiphenylmethane, 2,4-pentanedione, dimethyl zinc (1.0 M solution in toluene), benzyl amine were purchased from J&K without further purification. CO_2 (>99.999%) was dehydrated and deoxygenated before being charged into autoclave. Literature procedures were employed for the preparation of β-diiminate (BDI) ligand. NMR spectra were recorded on a Bruker Avance II 500 (500 MHz, ^1H; 126 MHz, ^{13}C) instrument at room temperature. Chemical shifts for ^1H and ^{13}C spectra were referenced to internal solvent resonances (δ 7.16 for C_6D_6, δ 7.26 for $CDCl_3$, and δ 7.09, 7.01, 6.97, 2.08 for toluene-d_8 in ^1H NMR and δ128.06 for C_6D_6 in ^{13}C NMR). Solid state magic angle rotation nuclear magnetic resonance (SS MAS NMR) was collected on Bruker Avance NEO system. Adamantane was used as the standard sample of ^1H, and the calibration was 1.91 ppm. Isolated low-MW polymers were charaterized by matrix-assissted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) on a Bruker Autoflex speed TOF/TOF mass spectrometer in positive ion, reflector mode using a Nd:YAG laser at 355 nm and 25 KV accelerating voltage. Matrix (trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propylidene] malonitrile (DCTB) and ionized reagents CF_3COONa and CF_3COOK were used. The raw data were processed in the FlexAnalysis software. FTIR experiments were conducted in stainless steel Parr autoclave reactor, modified with a ZnSeW AR window to allow for the use of an ASI ReactIR 45 system equipped with a MCT detector and 30 bounce DiCOMP in situ probe. Air sensitive NMR samples were conducted in Teflon-valve sealed J. Young-type NMR tubes.

X-ray crystallography. X-ray crystallography. Single crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120°C/10^{-6} Torr for 24 h) after decanting the crude liquor. A crystal was then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker APEX-II CCD diffractometer. The structures were solved by direct methods and refined using the Bruker SHELXTL program library by full-matrix least squares on F2 for all reflections (SHELXTL, Version 6.12; Bruker Analytical X-ray Solutions: Madison, WI, 2001). The structure was refined by full-matrix least-squares on F2 for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions. (Sheldrick, G. M. Acta Crystallogr., Sect. A. 1990, 46, 467–473 & 2008, 64, 112–122.).

General procedures for copolymerization of *meso*-CHO/CO_2. A 20 mL stainless steel reactor was dried overnight in 80°C and removed into glove box in Argon atmosphere. First, 4 mmol *meso*-CHO and 0.005 mmol (3.4 mg) catalyst **1** were dissolved in 2 mL toluene in glove box and moved into the stainless steel reactor. Then the reactor was moved outside and charged with 30 bar CO_2 (or other required pressure) and set to the desired temperature (90°C or 110°C) for 1 h or planned time. After cooling and venting the reactor, the crude liquor was extracted for ^1H NMR spectroscopy analysis. The remaining crude liquor was precipitated from n-hexane and the resultant copolymers was isolated and dried at 50°C under vacuum overnight for analysis by GPC or further application in depolymerization. It is noted that the low-MW cyclic PCHC sample for MALDI-TOF analysis was prepared when CO_2 is released at relatively low monomer conversion.

General procedures for depolymerization of PCHC. PCHC sample for depolymerization was dried in vacuum at 50°C with 48h. Generally, 43 mg(0.3 mmol) PCHC (25 equiv.) and 8.2 mg(0.012 mmol) catalyst **2** (which MW was regarded as the same with that of catalyst **1**) was dissolved in 6 mL toluene and removed into Schlenk tube in glove box and then set to desired temperature (150°C). 0.1 mL cooled crude liquor was extracted in glove box for ^1H NMR spectroscopy analysis at desired intervals.

Synthesis of catalyst 1(BDI-ZnMe)$_2$. In an argon-filled glovebox, a 250 mL Schlenk flask equipped with a stir bar was charged with 200 mL toluene, 1 mmol (524 mg) β-diketiminato (BDI) ligand[1] and 2 mL dimethyl zinc (1.0M solution in toluene). The sealed flask was removed outside and set to desired temperature (90 °C) for 24 h. The resulting mixture was filtered in glove box and the filtrate then subjected to vacuum to afford product as yellow powder. Yield: 532 mg (78%) ^1H NMR (C_6D_6, 500 MHz) *δ* 6.87-6.85 (d, *J*=10.0Hz, 8H, C-H), *δ* 6.62-6.60 (d, *J*=10.0Hz, 8H, C-H), *δ* 4.84 (s, 2H, C-H), *δ* 3.53 (s, 4H, CH_2), δ 1.95 (s,12H, CH_3), -1.37(s, 6H, Zn-CH_3).

Synthesis of catalyst 2 (BDI-($ZnMe_2$·*x*H_2O))$_n$. Take (BDI-($ZnMe_2$·0.1H_2O))$_n$ for example, 10 mL $ZnMe_2$ (1.0 M in toluene) was added 18 µL distilled water (0.1 equiv. dropwise) under N_2 atmosphere at room temperature and reacted for 2 h to give a white suspension. 2 mL suspension was extracted to react with 520 mg BDI ligand in 200 mL toluene at 90°C for 24 h in a sealed flask. The resulting mixture was filtered and the filtrate cake was washed twice by toluene, dried in vacuum under argon atmosphere. ~70 mg dark yellow powder was obtained.

Results and Discussion

1. ^{1}H NMR spectrum of catalyst 1

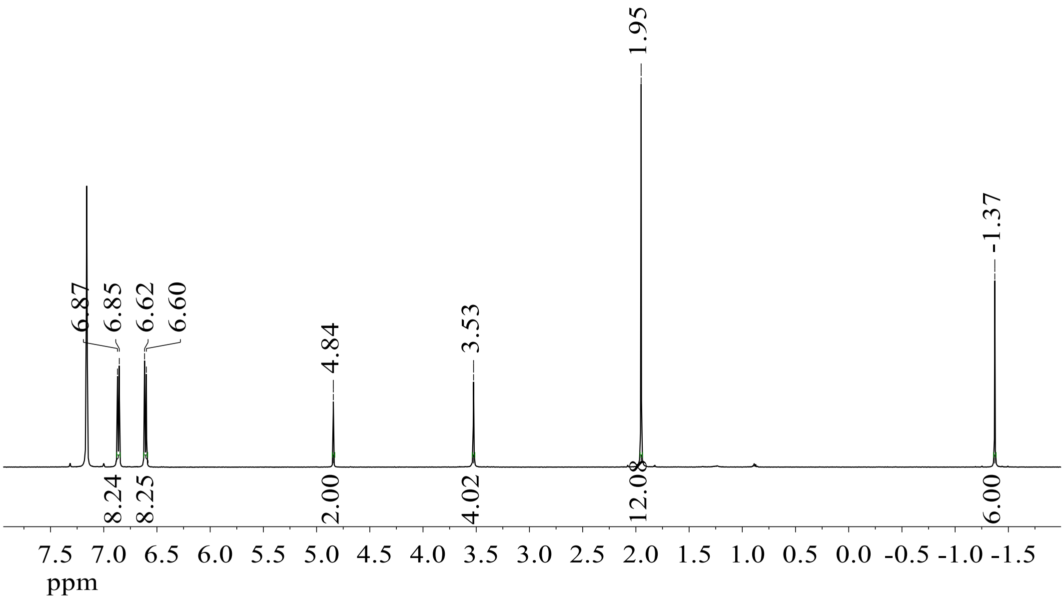

Figure S1. ^{1}H NMR (C_6D_6, 500MHz, 25°C) spectrum of catalyst **1** (BDI-ZnMe)$_2$.

2. NMR spectrum of polymerization mixture and purified polymer

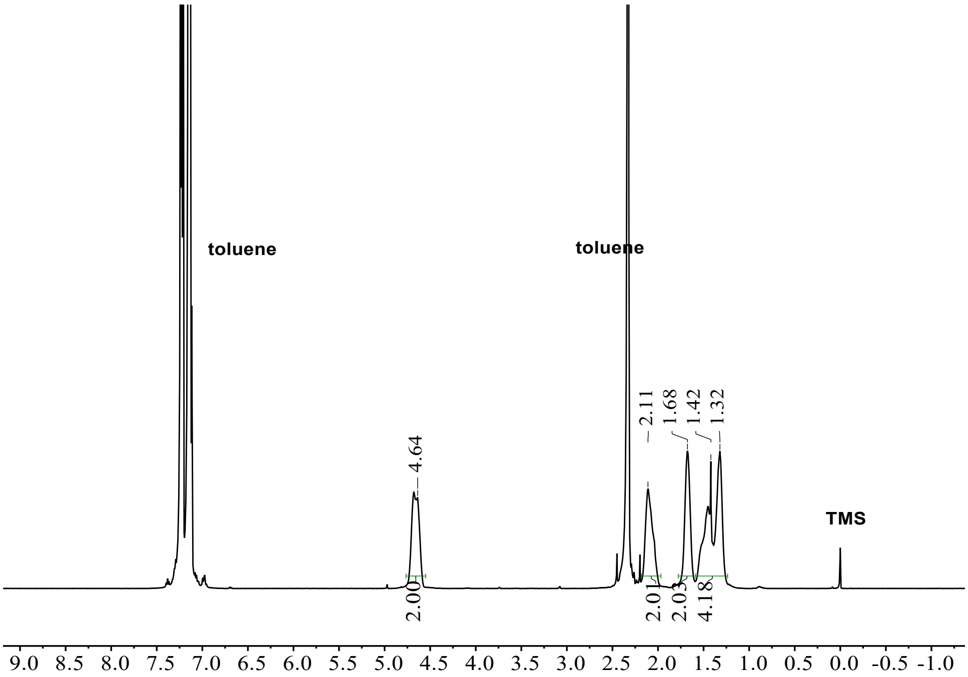

Figure S2. ^{1}H NMR ($CDCl_3$, 500MHz, 25°C) spectrum of the polymerization mixture produced from copolymerization *meso*-CHO and CO_2 performed with an 800/1 CHO/**1** ratio in toluene at 90°C for 1 h with 30 bar CO_2 pressure (Entry 2, Table 1).

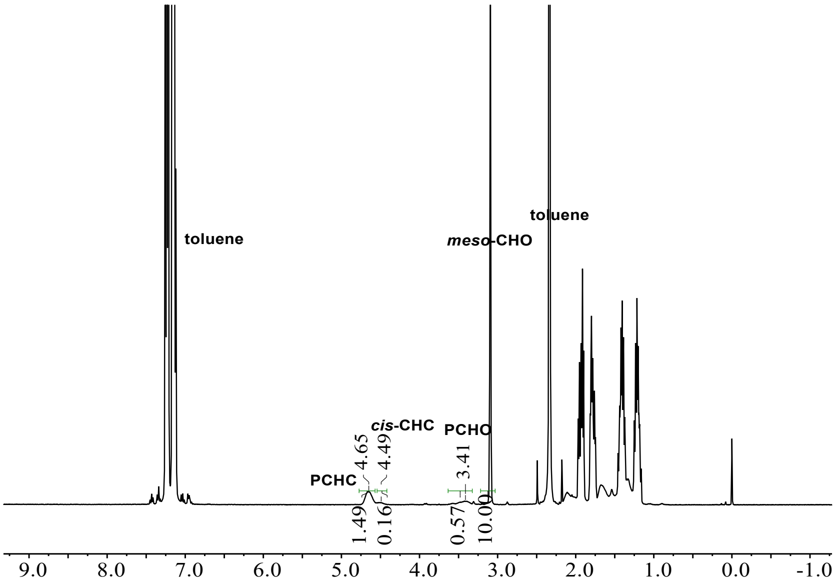

Figure S3. ^1H NMR ($CDCl_3$, 500MHz, 25°C) spectrum of the polymerization mixture produced from the copolymerization of *meso*-CHO and CO_2 performed with an 800/1 CHO/**1** ratio in toluene at 90°C for 1h with 1 bar CO_2 pressure (Entry 5, Table 1).

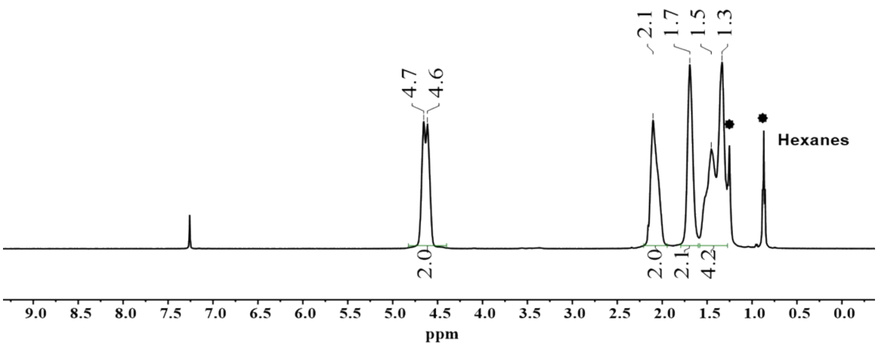

Figure S4. ^1H NMR ($CDCl_3$, 500MHz, 25°C) spectrum of purified PCHC. Asterisks are noted for hexanes.

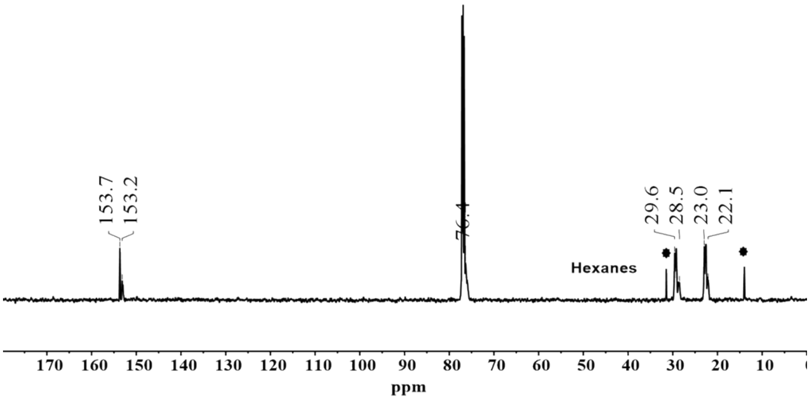

Figure S5. ^{13}C NMR ($CDCl_3$, 126MHz, 25°C) spectrum of purified PCHC. Asterisks are noted for hexanes.

3. GPC traces of PCHCs obtained from a variety of feed ratios

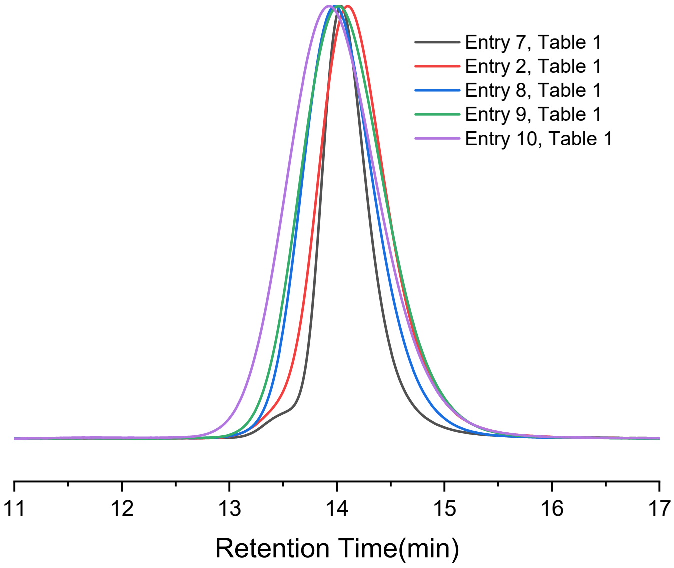

Figure S6. GPC traces of PCHCs obtained from copolymerization performed with *meso*-CHO/**1** with different feed ratio (Table 1).

4. MALDI-TOF MS spectra of PCHC

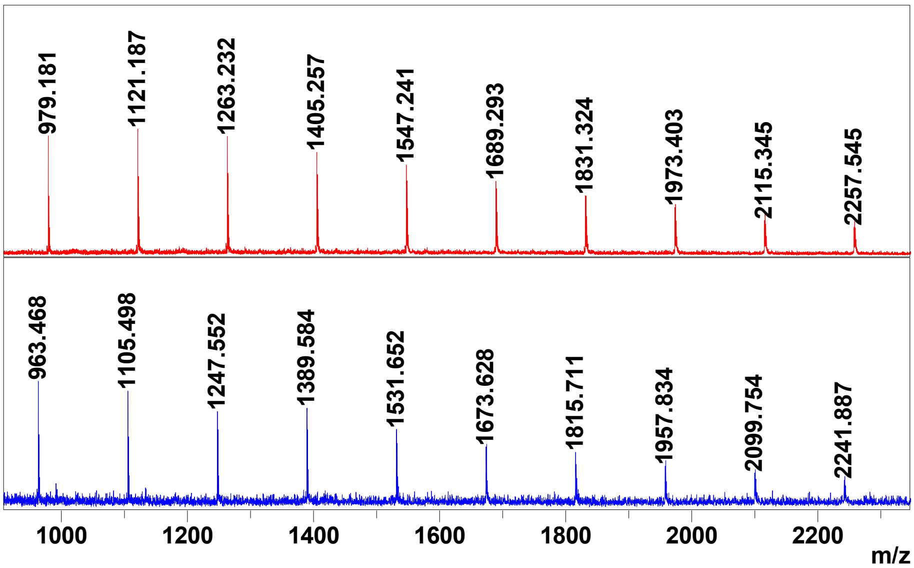

Figure S7. MALDI-TOF mass spectra of PCHC produced by **1** at a 4000/1 CHO/**1** ratio, [CHO]=2.0M, room temperature and 20 bar CO_2 for 10 min. CF_3COOK (red) and CF_3COONa (blue) were used as ionizing agent.

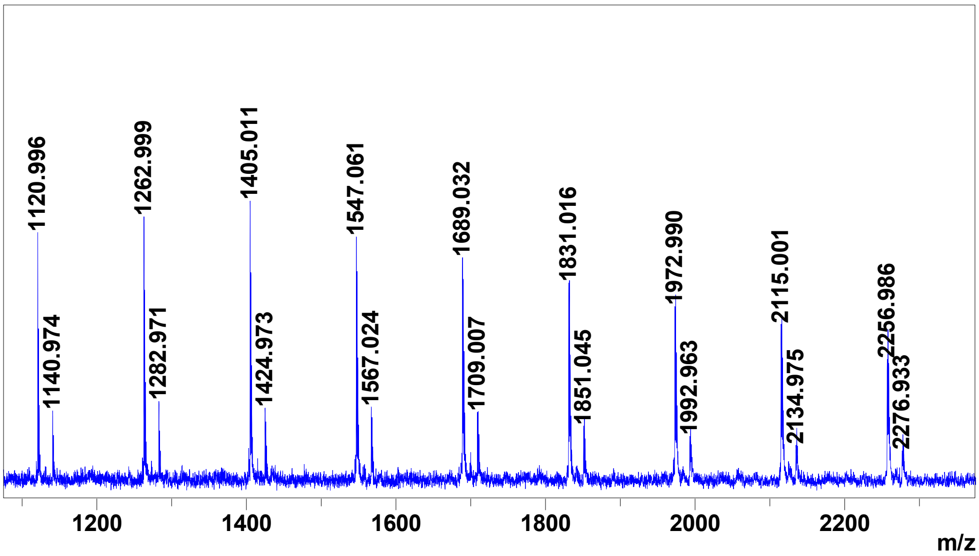

Figure S8. MALDI-TOF mass spectra of PCHC produced by **1** at a 4000/1/2 CHO/**1**/BnOH ratio in 2 M toluene solution, at 30 bar CO_2 for 10 min. CF_3COOK was used as ionizing agent.

5. ^{13}C NMR spectrum of $^{13}CO_2$-labeled PCHC

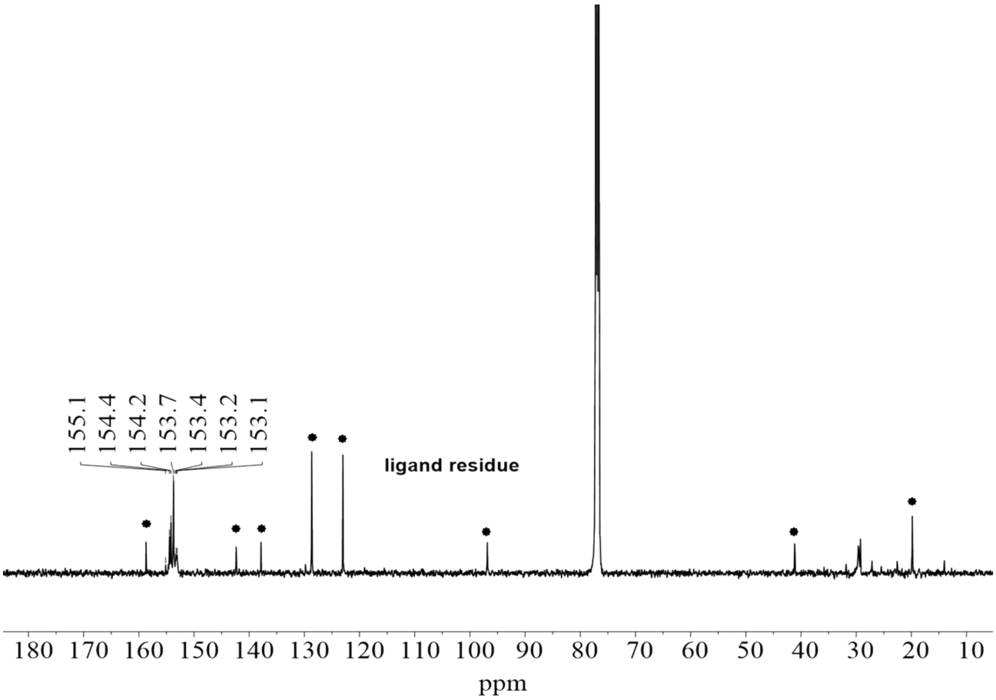

Figure S9. ^{13}C NMR ($CDCl_3$, 126MHz, 25°C) spectrum of the $^{13}CO_2$-labeled low MW of PCHC. Asterisks are noted for the catalyst ligand residues.)

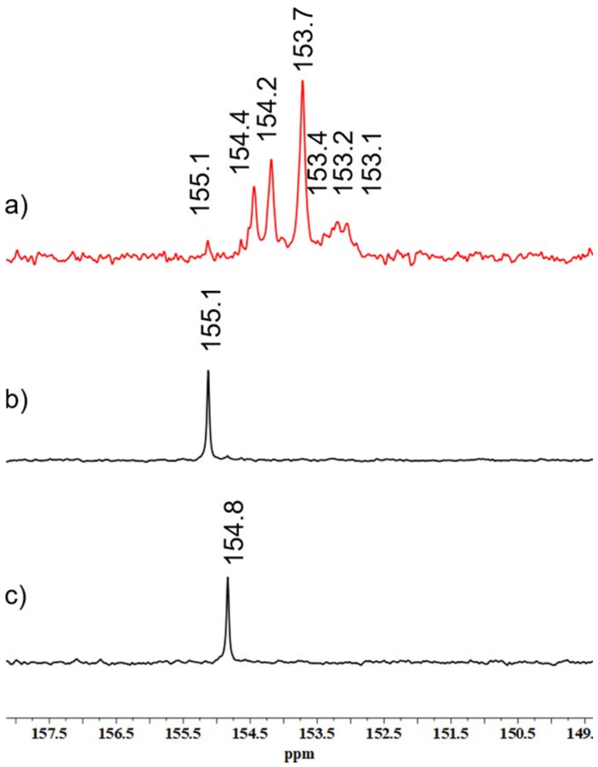

Figure S10. Overlay of the carbonyl region in the ^{13}C NMR ($CDCl_3$, 126MHz, 25°C) spectra of (a) $^{13}CO_2$ labeled low MW of PCHC, (b) *trans*-CHC and (c) *cis*-CHC.

6. MALDI-TOF mass spectra of cyclic PCHC before and after heating at 150 °C

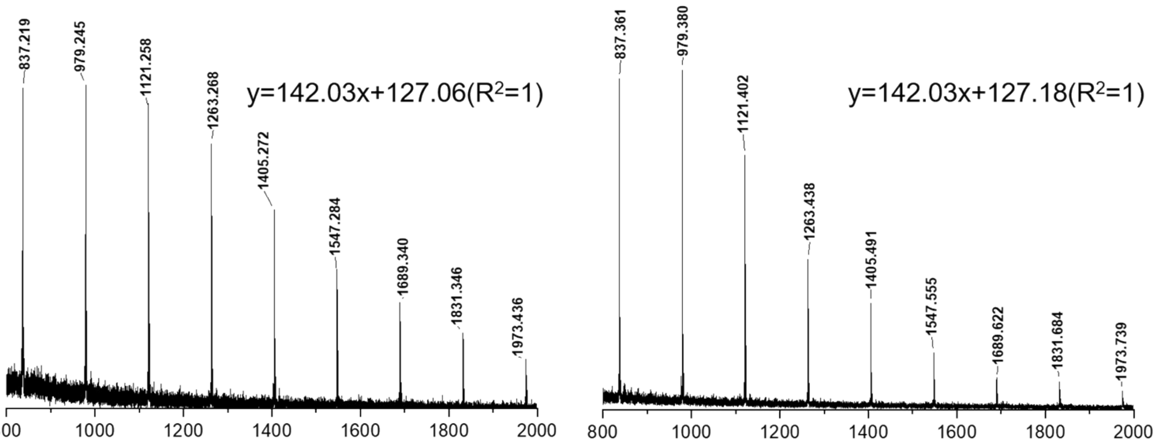

Figure S11. MALDI-TOF mass spectra of cyclic PCHC before (left) and after (right) heating at 150 °C in toluene for 30min in the absence of catalyst.

7. MALDI-TOF mass spectra of cyclic PCHC before and after reacting with benzyl amine

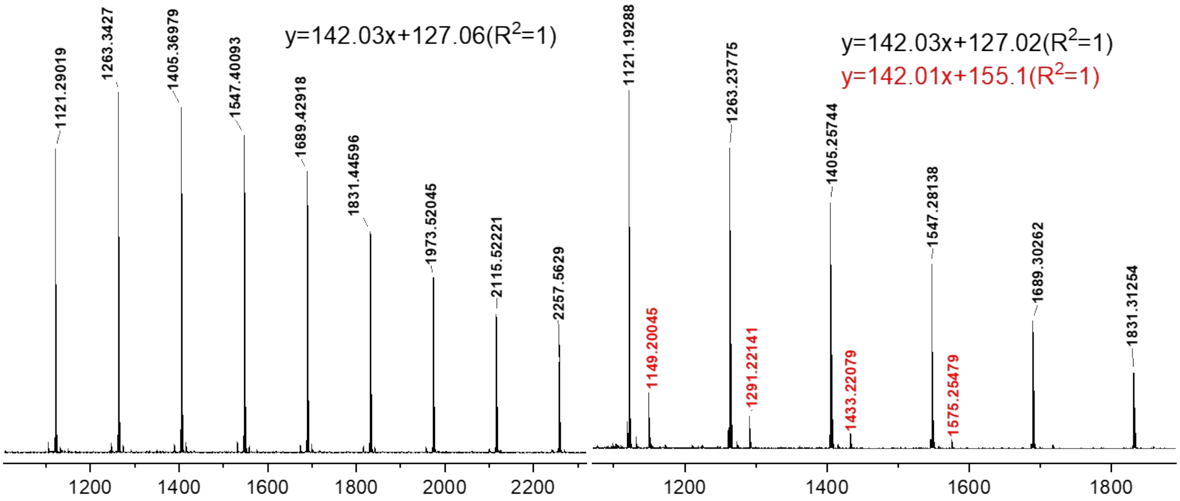

Figure S12. MALDI-TOF mass spectra of cyclic PCHC (left) before and (right) after reacting with benzyl amine.

8. Mark–Houwink plots of PCHC

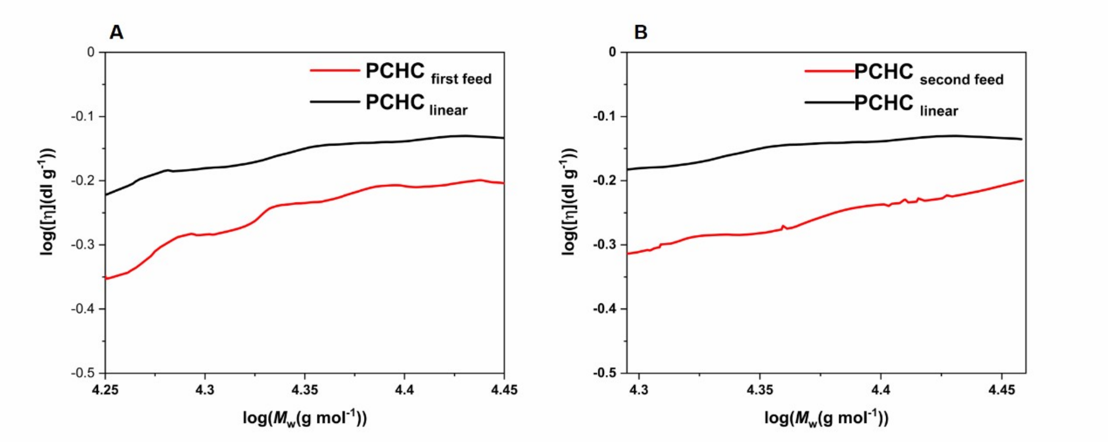

Figure S13. Double logarithm (Mark–Houwink) plots of intrinsic viscosity [η] versus weight-average MW (Mw) of the PCHC produced by catalyst **1** (black line: (A) the first 800 equiv. of *meso*-CHO; (B) the second 800 equiv. of *meso*-CHO) and linear samples prepared by Lu's group (red line).

9. DCS and TGA curves of the cyclic PCHC

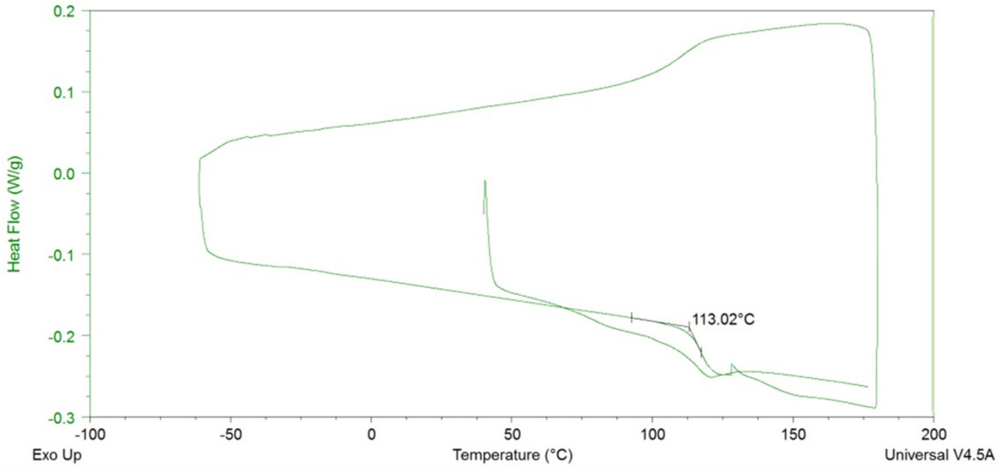

Figure S14. DSC curve of the cyclic PCHC.

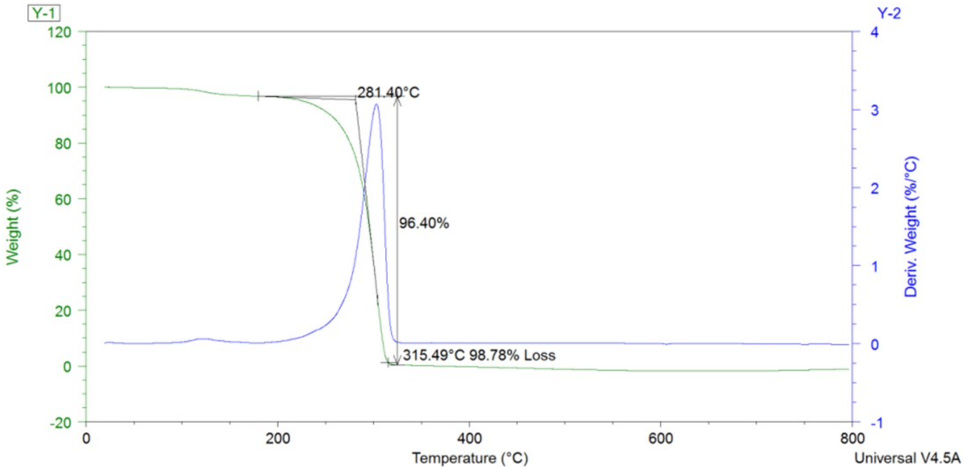

Figure S15. TGA curve of the cyclic PCHC.

10. Stoichiometric NMR reactions and in-situ IR study.

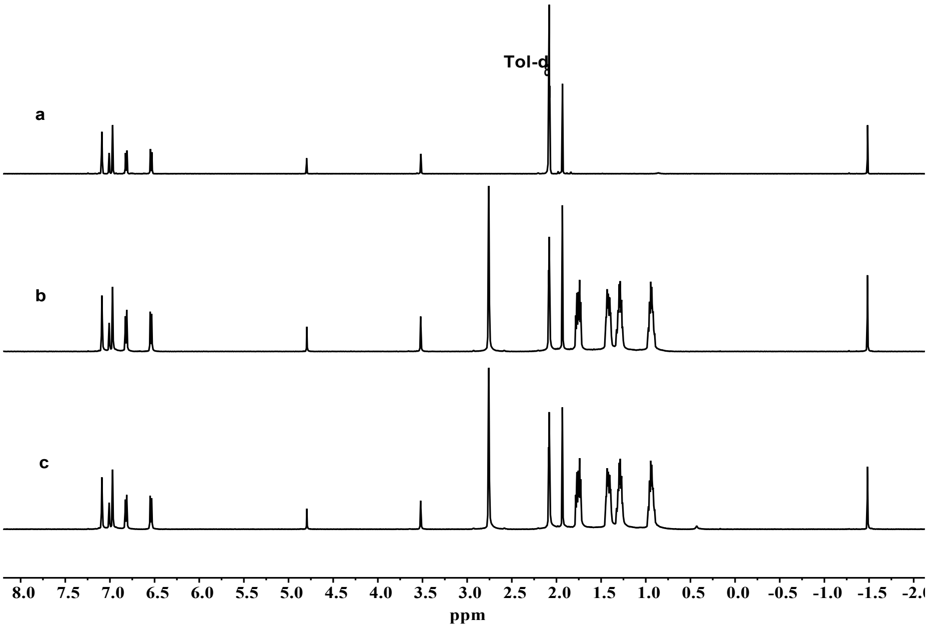

Figure S16. Overlay of the ^{1}H NMR spectra (toluene-d8, 500MHz) obtained for (a) catalyst **1** (25°C), (b) reaction of 1 equiv. of **1** and 15 equiv. of *meso*-CHO (25°C) and (c) reaction of 1 equiv. of **1** and 15 equiv. of *meso*-CHO were heated in J Young tube at 120°C for 40 min.

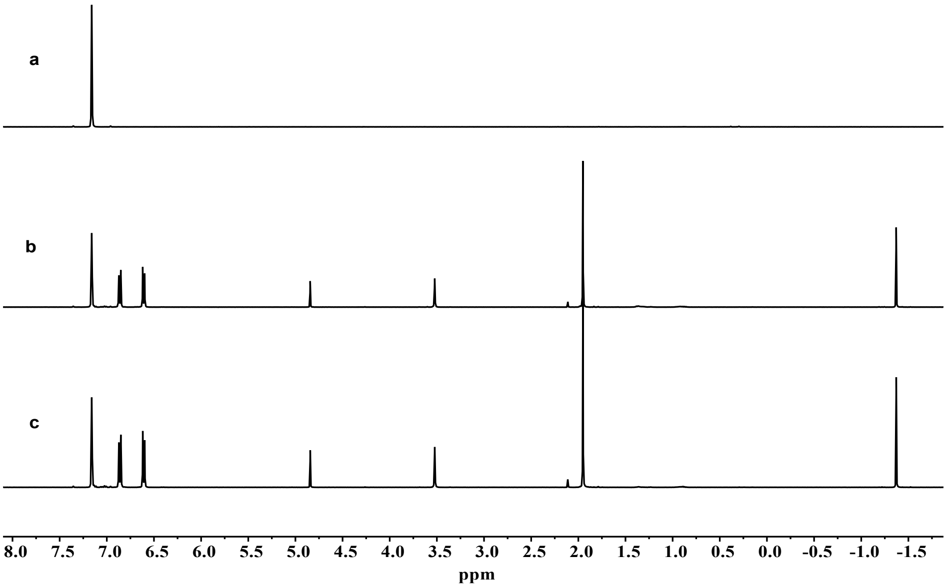

Figure S17. Overlay of ^{1}H NMR spectra (500MHz) obtained for (a) 1 bar CO_2 in C_6D_6 (25 °C) and (b) catalyst **1** in C_6D_6 (25°C) in J Young tube, as well as (c) reaction of **1** and 20 bar CO_2 performed in autoclave at 90°C for 24 h.

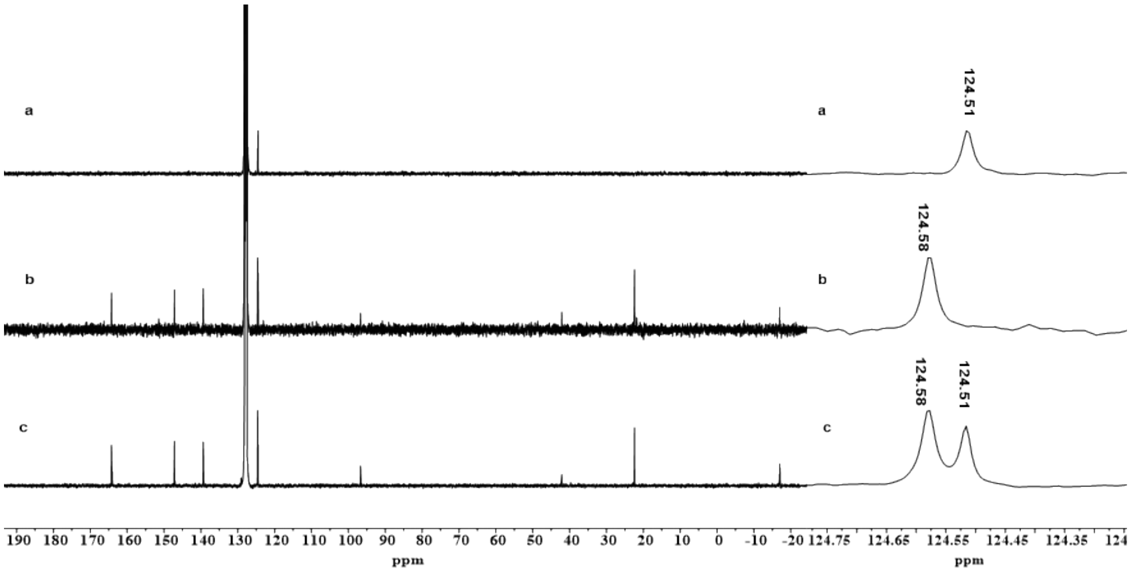

Figure S18. Overlay of ^{13}C NMR spectra (C_6D_6, 126MHz) obtained for (a) 1 bar CO_2 in C_6D_6 (25°C) and (b) catalyst **1** in C_6D_6 (25°C) in J Young tube, as well as (c) reaction of **1** and 20 bar CO_2 performed in autoclave at 90°C for 24 h.

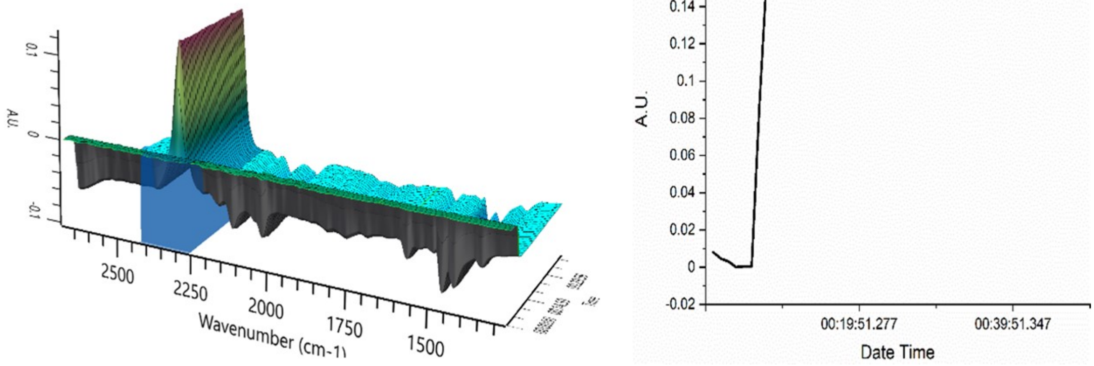

Figure S19. 3D stack plot of the IR spectra of CO_2 dissovled in toluene (90°C, 40bar CO_2 pressure).

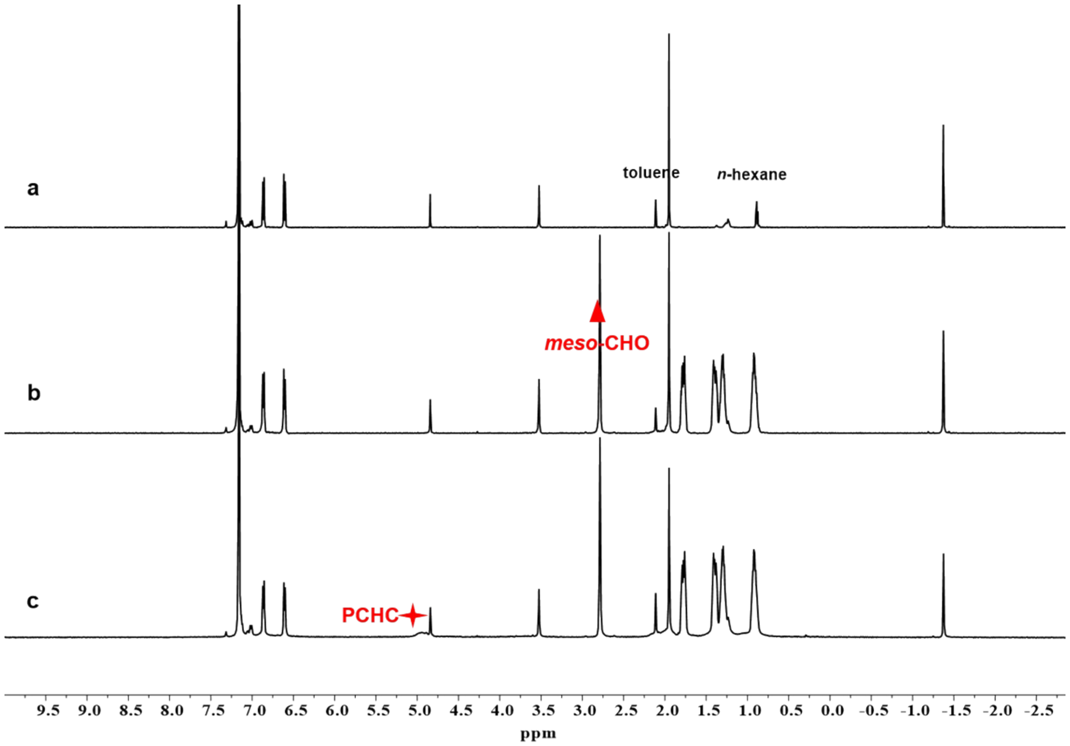

Figure S20. Overlay of ^1H NMR spectra (C_6D_6, 500MHz, 25 °C) obtained for copolymerization performed in stainless steel reactor: (a) catalyst **1** (b) 1 equiv. of **1** and 10 equiv. of *meso*-CHO were dissolved in C_6D_6 and (c) charged with 20 bar CO_2 then heated in stainless steel reactor at 40°C for 24 h.

11. ^{1}H NMR spectrum of mononuclear zinc catalyst

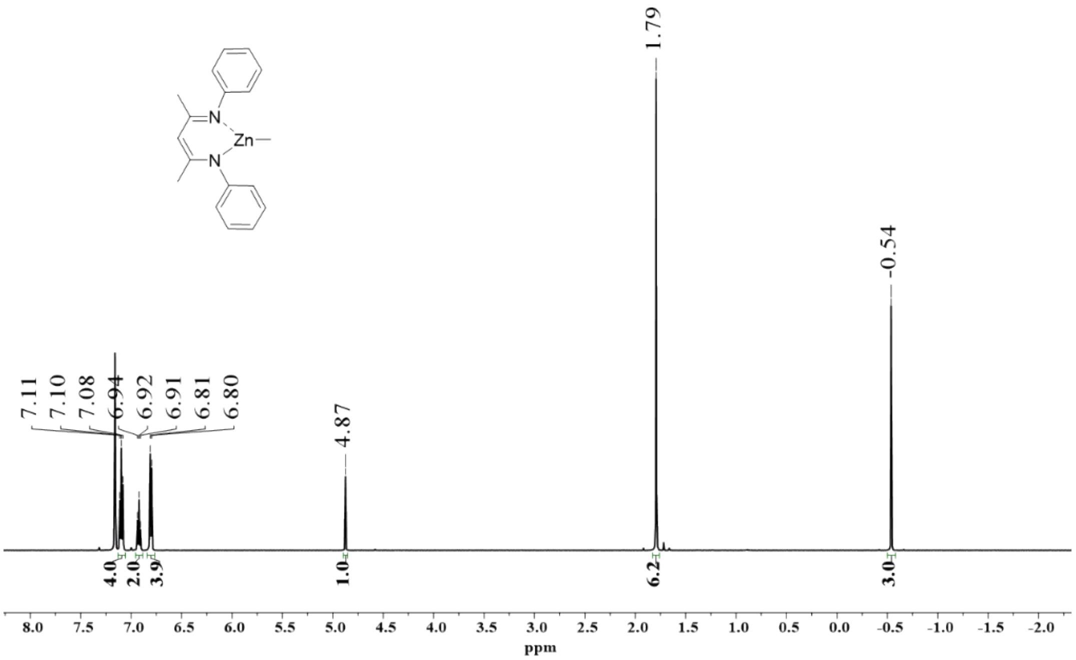

Figure S21. ^{1}H NMR spectrum (C_6D_6, 500MHz, 25°C) of mononuclear zinc catalyst BDI-ZnMe.

12. Solid state NMR spectrum of catalyst 2

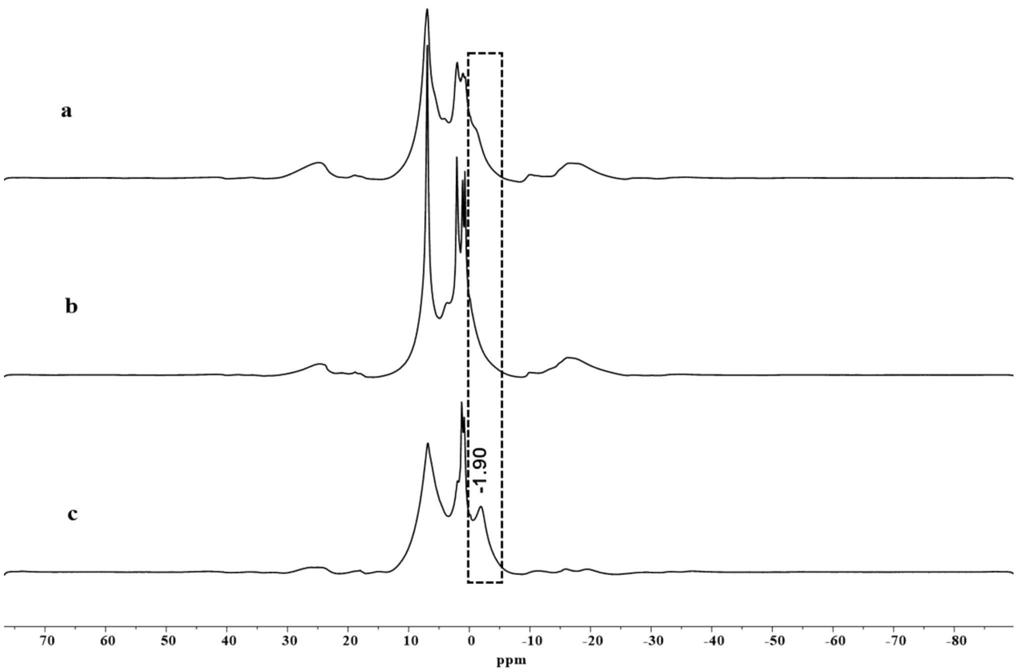

Figure S22. Solid state NMR spectra of heterogeneous complexes, [a] (BDI-($ZnMe_2\cdot0.1H_2O$))$_n$, [b] (BDI-($ZnMe_2\cdot0.5H_2O$))$_n$, [c] (BDI-ZnMe)$_2$

13. ^{1}H NMR spectrum of the depolymerization mixture.

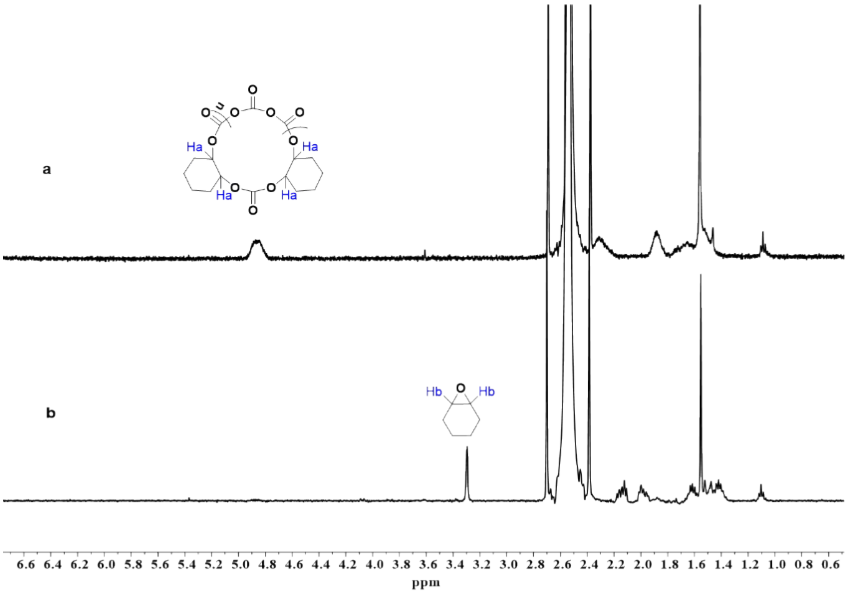

Figure S23. Overlay of the ^{1}H NMR ($CDCl_3$, 500MHz, 25 °C) spectra of the mixture obtained (a) before degradation; (b) after degradation by $(BDI-(ZnMe_2{\cdot}0.1H_2O))_n$ at ratio of 25/1, 150°C, 9 h.

14. Crystal data of catalyst 1

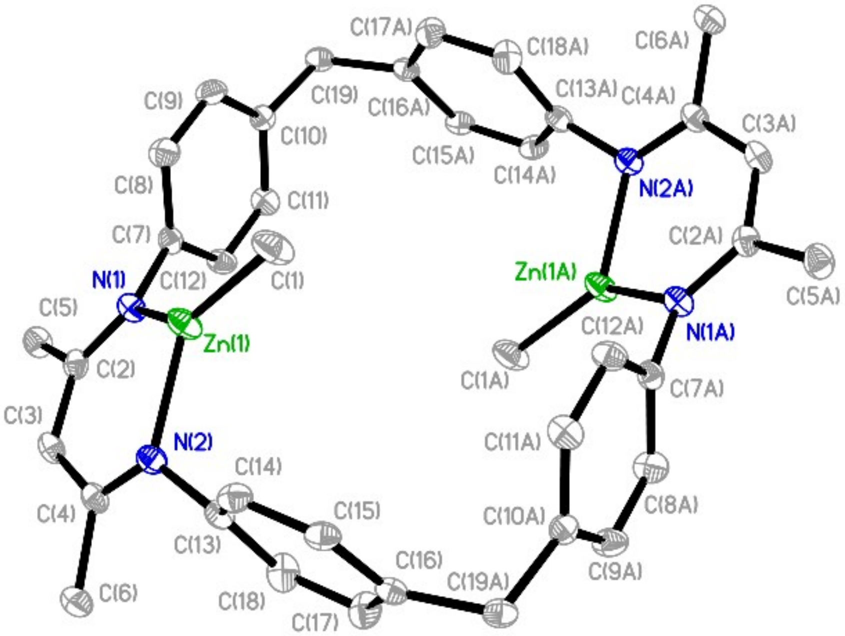

Figure S24. X-ray single-crystal structure of catalyst **1** $(BDI-ZnMe)_2$

Table 1. Crystal data and structure refinement for catalyst 1.

Identification code	**1**	
Empirical formula	$C_{38}H_{40}N_4Zn_2$	
Formula weight	683.48	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P2(1)/c	
Unit cell dimensions	a = 10.9337(4) Å	alpha = 90 deg.
	b = 16.6716(7) Å	beta = 98.9760(10) deg.
	c = 9.6093(4) Å	gamma = 90 deg.
Volume	1730.15(12) $Å^3$	
Z, Calculated density	2, 1.312 Mg/m^3	
Absorption coefficient	1.417 mm^{-1}	
F(000)	712	
Crystal size	0.12 x 0.11 x 0.10 mm	
Theta range for data collection	3.087 to 28.312 deg.	
Limiting indices	-14<=h<=14, -22<=k<=22, -12<=l<=10	
Reflections collected / unique	24441 / 4301 [R(int) = 0.0281]	
Completeness to theta = 25.242	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4301 / 0 / 199	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.1072	
R indices (all data)	R1 = 0.0482, wR2 = 0.1095	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.670 and -0.561 $eÅ^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for catalyst 1.

Zn(1)-C(1)	1.957(3)	C(10)-C(19)	1.519(3)
Zn(1)-N(1)	1.959(2)	C(16)-C(17)	1.395(3)
Zn(1)-N(2)	1.990(2)	C(16)-C(15)	1.394(3)
N(2)-C(4)	1.327(3)	C(16)-C(19)#1	1.517(3)
N(2)-C(13)	1.424(3)	C(19)-C(16)#1	1.517(3)
N(1)-C(2)	1.333(3)	C(14)-C(15)	1.393(4)
N(1)-C(7)	1.430(3)	C(14)-C(13)	1.397(3)
C(3)-C(2)	1.411(3)	C(11)-C(12)	1.386(3)
C(3)-C(4)	1.414(3)	C(8)-C(9)	1.394(4)
C(4)-C(6)	1.519(3)	C(8)-C(7)	1.395(3)
C(2)-C(5)	1.510(3)	C(13)-C(18)	1.398(3)
C(10)-C(9)	1.391(3)	C(7)-C(12)	1.397(3)
C(10)-C(11)	1.397(3)	C(17)-C(18)	1.385(4)
C(1)-Zn(1)-N(1)	134.22(11)	C(17)-C(16)-C(15)	117.8(2)
C(1)-Zn(1)-N(2)	129.07(11)	C(17)-C(16)-C(19)#1	120.1(2)
N(1)-Zn(1)-N(2)	95.05(9)	C(15)-C(16)-C(19)#1	121.3(2)
C(4)-N(2)-C(13)	122.1(2)	C(16)#1-C(19)-C(10)	107.66(19)
C(4)-N(2)-Zn(1)	123.15(17)	C(15)-C(14)-C(13)	120.4(2)
C(13)-N(2)-Zn(1)	111.94(15)	C(12)-C(11)-C(10)	121.4(2)
C(2)-N(1)-C(7)	121.0(2)	C(9)-C(8)-C(7)	120.2(2)
C(2)-N(1)-Zn(1)	123.19(17)	C(10)-C(9)-C(8)	121.3(2)
C(7)-N(1)-Zn(1)	114.99(15)	C(14)-C(13)-C(18)	118.3(2)
C(2)-C(3)-C(4)	127.4(2)	C(14)-C(13)-N(2)	119.5(2)
N(2)-C(4)-C(3)	123.2(2)	C(18)-C(13)-N(2)	121.4(2)
N(2)-C(4)-C(6)	120.8(2)	C(14)-C(15)-C(16)	121.1(2)
C(3)-C(4)-C(6)	115.9(2)	C(12)-C(7)-C(8)	118.7(2)
N(1)-C(2)-C(3)	123.7(2)	C(12)-C(7)-N(1)	120.7(2)
N(1)-C(2)-C(5)	119.6(2)	C(8)-C(7)-N(1)	120.1(2)
C(3)-C(2)-C(5)	116.6(2)	C(11)-C(12)-C(7)	120.4(2)
C(9)-C(10)-C(11)	117.8(2)	C(18)-C(17)-C(16)	121.3(2)
C(9)-C(10)-C(19)	122.0(2)	C(17)-C(18)-C(13)	120.6(2)
C(11)-C(10)-C(19)	119.8(2)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+2,-z+1

Reference

1. M. W. Lehenmeier, S. Kissling, P. T. Altenbuchner, C. Bruckmeier, P. Deglmann, A. K. Brym and B. Rieger, *Angew Chem Int Ed* 2013, **52**, 9821-9826.