Supporting Information

Cooperative rare earth metal-zinc based heterometallic catalysts for copolymerization of CO_2 and cyclohexene oxide

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General considerations. Complexes **1-4** were synthesized under a dry argon atmosphere using standard Schlenk techniques and were kept in the glovebox once produced. Solvents (hexane, toluene and tetrahydrofuran) were freshly distilled by refluxing over sodium/benzophenone ketyl prior to use. $NdCp_3(THF)$[1] and LH_3[2] were prepared according to published procedures. Cyclohexene oxide (CHO) was dried over CaH_2 for 2 days and distilled prior to use. Benzyl alcohol was dried over 4 Å molecular sieves for 1 week before use. $ZnEt_2$ and carbon dioxide were commercially available and used as received. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FT-IR spectrometer as KBr pellets. NMR (^1H, ^{13}C) spectra were recorde prepared in the presence of complex **1**d on a Unity Inova-400 spectrometer. Molecular weight and molecular weight distribution (PDI) were determined against a polystyrene standard by gel permeation chromatography (GPC) on a PL 50 apparatus equipped with PLgel 10μm MIXED-B columns (300×7.5 mm) and a refractive index detector, and tetrahydrofuran (HPLC grade, distilled and filtered under vacuum prior to use) was used as an eluent at a flow rate of 1.0 $mL \cdot min^{-1}$ at 40 °C. MALDI-TOF mass spectra were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). The X-ray structural determination was carried out on a Rigaku Mercury diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using *SHELEXL-97* programs.

Complex 1. To a THF solution of $(C_5H_5)_3Nd(THF)$ (1.23 g, 3.00 mmol) was added a THF solution of LH_3 (2.29 g, 3.00 mmol). The resulting mixture was stirred for 10 h at room temperature and then concentrated under vacuum. Toluene (10 mL) and DME (0.5 mL) were added to extract the residue. Blue crystals were obtained at room temperature after several days from the extract (2.70 g, 2.49 mmol, 83%). Mp: 276-278 °C. Anal. Calcd for $C_{62}H_{89}N_2O_5Nd$: C, 66.03; H, 8.20; N, 2.79; Nd, 14.74. Found: C, 66.45; H, 8.16; N, 2.82; Nd, 14.52. IR (KBr pellet, cm^{-1}): 3419(s), 3249(s), 2955(s), 2909(s), 2871(s), 2570(s), 1775(s), 1605(s), 1474(s), 1412(s), 1358(s), 1296(s), 1234(s), 1165(s), 1128(s), 1049(s), 910(s), 872(s), 833(s), 740(s), 640(s).

Complex 2. Complex **2** was synthesized in analogy to complex **1** from $(C_5H_5)_3Y(THF)$ (1.07 g, 3.00 mmol). The title compound was crystalized from THF solution (10 mL), and colorless crystals were obtained after several days (2.21 g, 2.40 mmol, 80%). Mp: 329-331 °C. ^1H NMR (*d8*-THF, 400 MHz): δ 7.66 (d, 1H, Ar-H), 7.20-7.10 (m, 3H, Ar-H), 6.88-6.83 (m, 4H, Ar-H), 6.67 (s, 1H, Ar-H), 6.42 (s, 1H, Ar-H), 4.57-4.40 (m, 2H, CH_2), 3.98 (d, J = 12 Hz, 1H, CH_2), 3.83 (br-s, 1H, CH_2), 3.72 (br-s, 1H, CH_2), 3.54 (s, α-CH_2 THF, correct integration is not possible due to ligand exchange with the solvent), 3.43 (br-s, 1H, CH_2), 1.68 (s, β-CH_2 THF, correct integration is not possible due to ligand exchange with the solvent), 1.48 (s, 9H, CH_3), 1.24 (s, 9H, CH_3), 1.19 (s, 9H, CH_3), 1.18 (s, 9H, CH_3), 1.07 (s, 9H, CH_3), 0.99 (s, 9H, CH_3). ^{13}C NMR (*d8*-THF, 100 MHz): δ 162.0, 161.96, 145.6, 135.9, 135.8, 135.6, 135.4, 127.6, 127.3, 127.0, 126.7, 125.6, 124.9, 124.2, 123.8, 123.6, 123.4 (Ar-C), 35.5, 35.3, 35.25, 34.3, 34.2, 34.0, 32.1, 32.0, 31.9, 30.3, 30.2, 30.1, 26.2 ($C(CH_3)_3$). Anal.Calcd for $C_{55}H_{79}N_2O_4Y$: C, 71.71; H, 8.64; N, 3.04; Y, 9.65. Found: C, 70.80; H, 8.47; N, 2.93; Y, 9.23. IR (KBr pellet, cm^{-1}): 3232(s), 2995(w), 2923(w), 2858(s), 2577(s), 2374(s), 2330(s),1780(s), 1600(s), 1497(w), 1467(w), 1401(s), 1354(s), 1317(s), 1236(s), 1201(s), 1168(s), 1122(s), 1020(s), 970(s), 918(s), 877(s), 831(s), 813(s), 775(s), 740(s), 673 (s), 646(s), 530(s), 441(s).

Complex 3. Benzyl alcohol (4.00 mmol) was added dropwise to a THF solution of $ZnEt_2$ (2.00 mmol) at 0 °C. The resulting mixture was stirred for 0.5 h at room temperature to form a suspension. A THF solution of complex **1** (4.00 mmol based on Nd) was added to the suspension. The resulting mixture was stirred for 10 h at room temperature and concentrated under vacuum to give solid powder. 20 mL toluene was added to extract the residue. Blue crystals were obtained at room temperature after several days from the extract (2.71 g, 1.30 mmol, 65%). Anal. Calcd for $C_{116}H_{156}N_4Nd_2O_8Zn$: C, 66.71; H, 7.53; N, 2.68; Nd and Zn, 16.94. Found: C, 66.41; H, 7.65; N, 2.78; Nd and Zn, 17.26.

Complex 4. Complex **4** was synthesized in analogy to complex **3** from $(C_5H_5)_3Y(THF)$ (1.43 g, 4.00 mmol). Yellow crystallines were obtained after several days (2.57 g, 1.30 mmol, 65%). Mp: 250-252 °C. ^1H NMR (*d8*-THF, 400 MHz): δ 7.70 (d, 2H, Ar-H), 7.32-7.13 (m, 16H, Ar-H), 7.01-6.85 (m, 8H, Ar-H), 6.70 (s, 2H, Ar-H), 6.43 (s, 2H, Ar-H), 4.55 (s, 6H, CH_2), 4.07-3.99 (m, 4H, CH_2), 3.82-3.76 (m, 4H, CH_2), 3.42 (br-s, 2H, CH_2), 1.52 (s, 18H, CH_3), 1.28 (s, 18H, CH_3), 1.22 (s, 36H, CH_3), 1.10 (s, 18H, CH_3), 1.03 (s, 18H, CH_3). ^{13}C NMR (C_4D_8O, 100 MHz): δ 162.0, 161.9, 161.3, 145.5, 136.0, 135.9, 135.8, 135.6, 135.4, 129.4, 128.7, 128.6, 127.6, 127.2, 127.0, 126.7, 125.8, 125.5, 124.9, 124.1, 123.8, 123.6, 123.4 (Ar-C), 65.0, 61.4, 57.0 ($PhCH_2$), 35.5, 35.3, 35.2, 34.3, 34.1, 34.0, 32.1, 32.0, 31.9, 30.3, 30.2, 30.1 ($C(CH_3)_3$). Anal.Calcd for $C_{116}H_{156}N_4Y_2O_8Zn$: C, 70.45; H, 7.95; N, 2.83; Y and Zn, 12.30. Found: C, 71.31; H, 8.22; N, 2.72; Y and Zn, 12.54. IR (KBr pellet, cm^{-1}): 3282(s), 3248(s), 3062(s), 2956(s), 2904(s), 2866(s), 2573(s), 2372(s), 1773(s), 1604(s), 1475(s), 1446(s), 1413(s), 1384(s), 1359(s), 1301(s), 1238(s), 1203(s), 1166(s), 1132(s), 1024(s), 964(s), 906 (s), 877 (s), 835(s), 738(s), 698 (s), 644 (s), 615 (s), 530 (s), 447(s).

Catalytic procedure for the copolymerization of CO_2 to CHO under 0.7 Mpa CO_2. Reactions were carried out in a 100 mL stainless steel Parr reactor equipped with a stirring bar and a needle valve for injection. In a typical reaction, complex **3** (73.6 mg, 0.0295 mmol) was dissolved in 3 mL toluene, and 3 mL CHO (29.5 mmol) was added under a dry argon atmosphere. The mixture was introduced into the reactor which was dried before use. The reactor was pressurized to 0.7 MPa with carbon dioxide, and heated to 70 °C for 3 h with vigorous stirring. CH_2Cl_2 (10 mL) was added to the crude reaction mixture, which was transferred into methanol to precipitate the copolymer. The copolymer was filtered and dried in vacuum to constant weight before being analyzed by NMR spectroscopy and GPC to determine the carbonate content, molecular weight and molecular weight distribution (PDI).

General procedure for the homopolymerization of CHO. Reactions were carried out in Schlenk flasks charged with a magnetic stirrer, using standard Schlenk techniques. In a typical reaction, complex **3** (24.5 mg, 0.0098 mmol) was dissolved in 1 mL toluene, and 1 mL CHO (9.8 mmol) was added. The resulting mixture was left stirring at 70 °C for 3 h. CH_2Cl_2 (10 mL) was added to the crude reaction mixture, which was transferred into methanol to precipitate the polymer. The polymer was filtered and dried in vacuum to constant weight before being analyzed by GPC to determine molecular weight and molecular weight distribution (PDI).

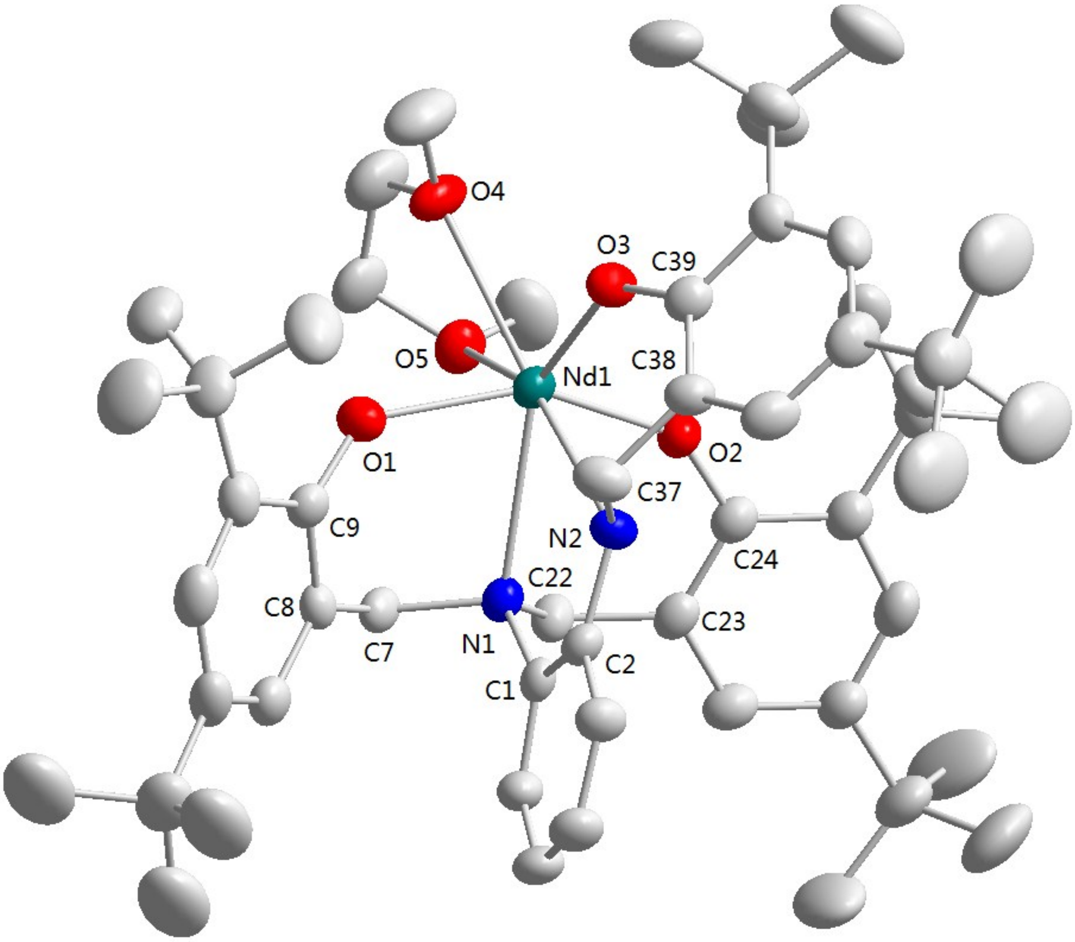

Fig. S1 ORTEP diagram of complex **1**·DME showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Nd(1)-O(1) 2.231(6), Nd(1)-O(2) 2.242(7), Nd(1)-O(3) 2.254(7), Nd(1)-O(4) 2.572(8), Nd(1)-O(5) 2.615(8), Nd(1)-N(1) 2.702(7), Nd(1)-N(2) 2.614(7); C(1)-O(1)-Nd(1) 143.8(6), C(7)-O(2)-Nd(1) 136.6(6), O(2)-Nd(1)-O(1) 149.9(2), O(2)-Nd(1)-O(3) 106.5(3), O(1)-Nd(1)-O(3) 100.5(2), O(3)-Nd(1)-O(4) 132.1(3), O(1)-Nd(1)-O(4) 79.4(3), O(2)-Nd(1)-O(4) 91.8(3), O(1)-Nd(1)-N(1) 74.5(2), O(2)-Nd(1)-N(1) 76.3(2), O(4)-Nd(1)-N(1) 110.90(13), O(2)-Nd(1)-N(2) 92.2(2), O(1)-Nd(1)-N(2) 81.8(2), O(3)-Nd(1)-N(2) 75.6(2), O(4)-Nd(1)-N(2) 148.9(3), O(3)-Nd(1)-N(1) 139.7(2), C(21)-O(3)-Nd(1) 136.6(6), O(1)-Nd(1)-O(5) 121.1(3), O(2)-Nd(1)-O(5) 77.5(3), O(3)-Nd(1)-O(5) 79.2(2), N(2)-Nd(1)-O(5) 148.8(3), O(5)-Nd(1)-N(1) 138.2(2).

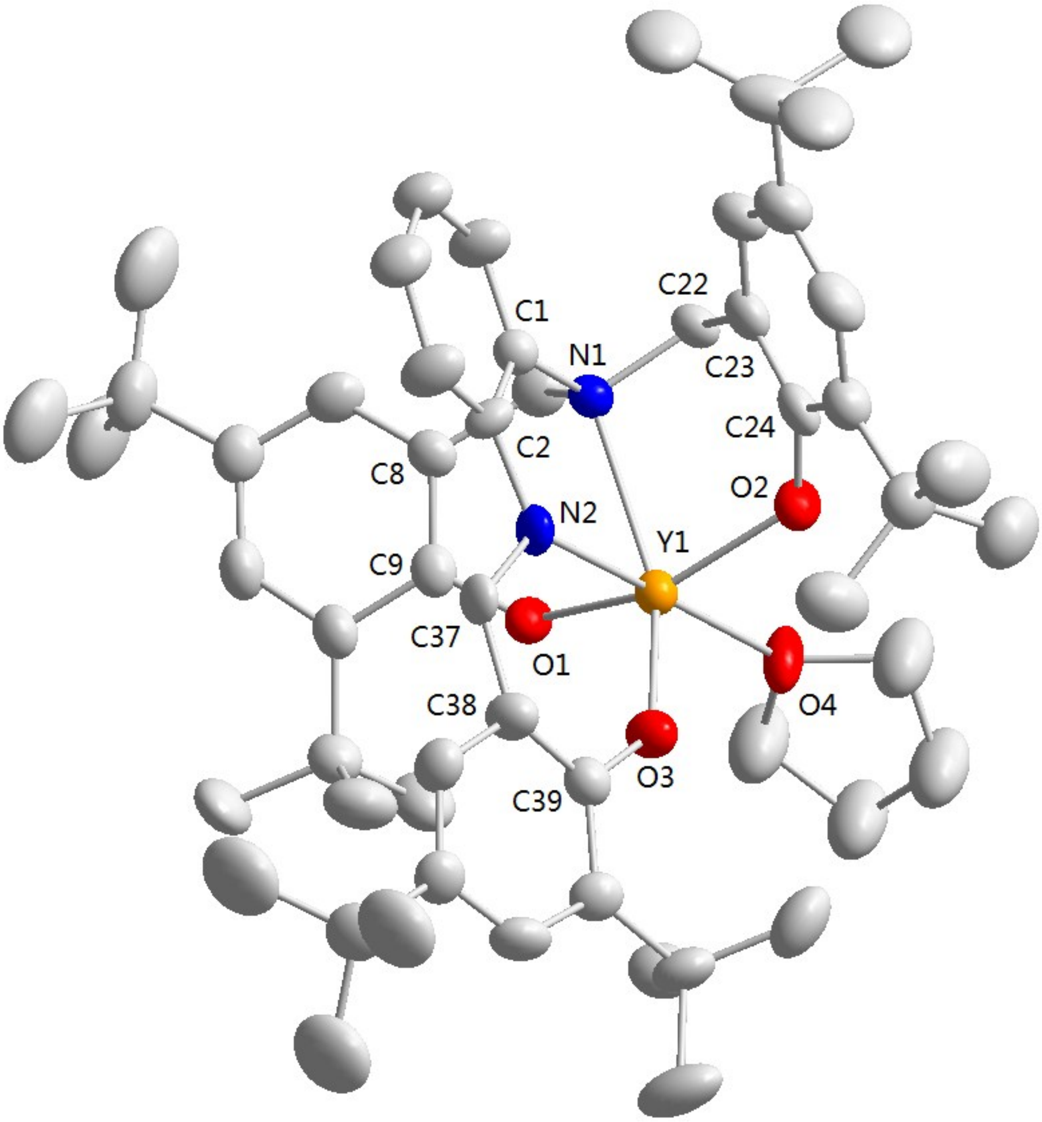

Fig. S2 ORTEP diagram of complex **2**·THF showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)-O(1) 2.155(4), Y(1)-N(1) 2.517(4), Y(1)-O(2) 2.145(4), Y(1)-N(2) 2.589(11), Y(1)-O(3) 2.113(4), O(1)-C(9) 1.347(6), Y(1)-O(4) 2.348(4), O(2)-C(24) 1.346(6), O(4)-C(55) 1.447(8), O(3)-C(39) 1.342(6); O(4)-Y(1)-N(1) 114.92(15), O(2)-Y(1)-N(1) 79.61(13), O(4)-Y(1)-N(2) 173.4(3), O(2)-Y(1)-N(2) 89.2(3), O(3)-Y(1)-O(1) 101.07(15), O(1)-Y(1)-O(4) 84.82(13), O(3)-Y(1)-O(2) 104.99(15), O(1)-Y(1)-N(1) 81.07(14), O(3)-Y(1)-O(4) 98.07(15), O(1)-Y(1)-N(2) 100.9(3), O(3)-Y(1)-N(1) 146.96(13), N(1)-Y(1)-N(2) 69.7(3), O(3)-Y(1)-N(2) 77.6(3), O(2)-Y(1)-O(4) 87.09(13), O(2)-Y(1)-O(1) 153.54(15), C(55)-O(4)-C(52) 106.7(5).

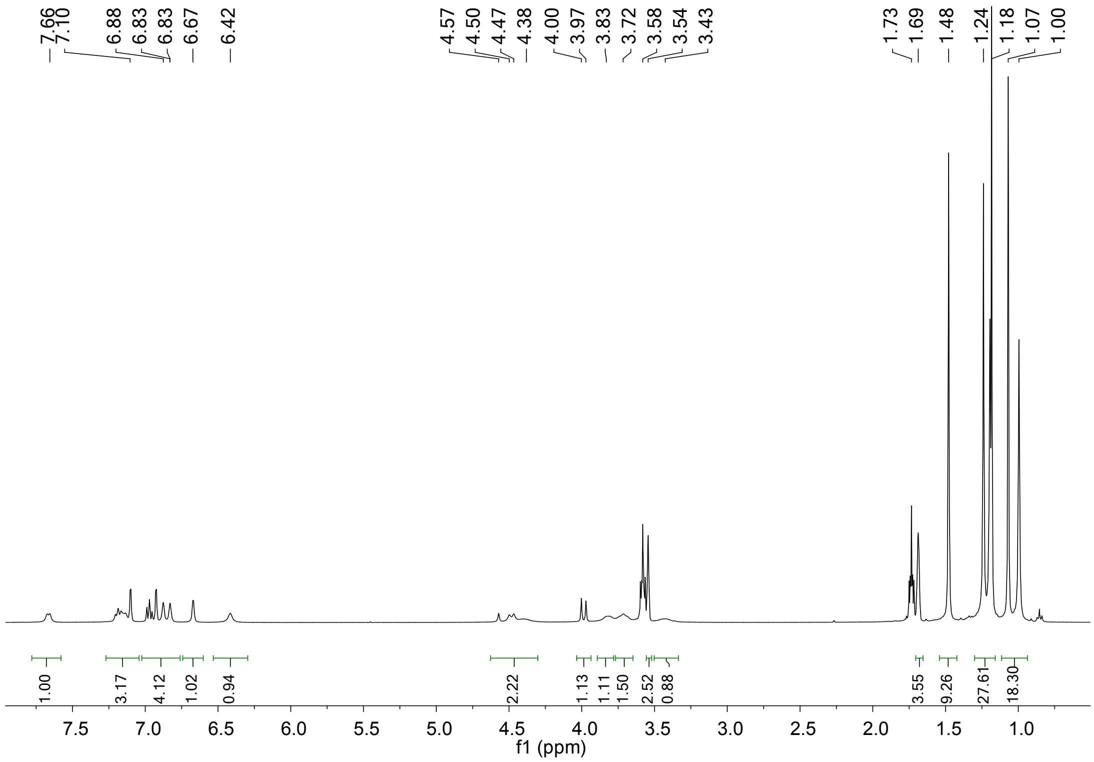

Fig. S3 ^{1}H NMR spectrum of complex **2** in *d8*-THF (298K).

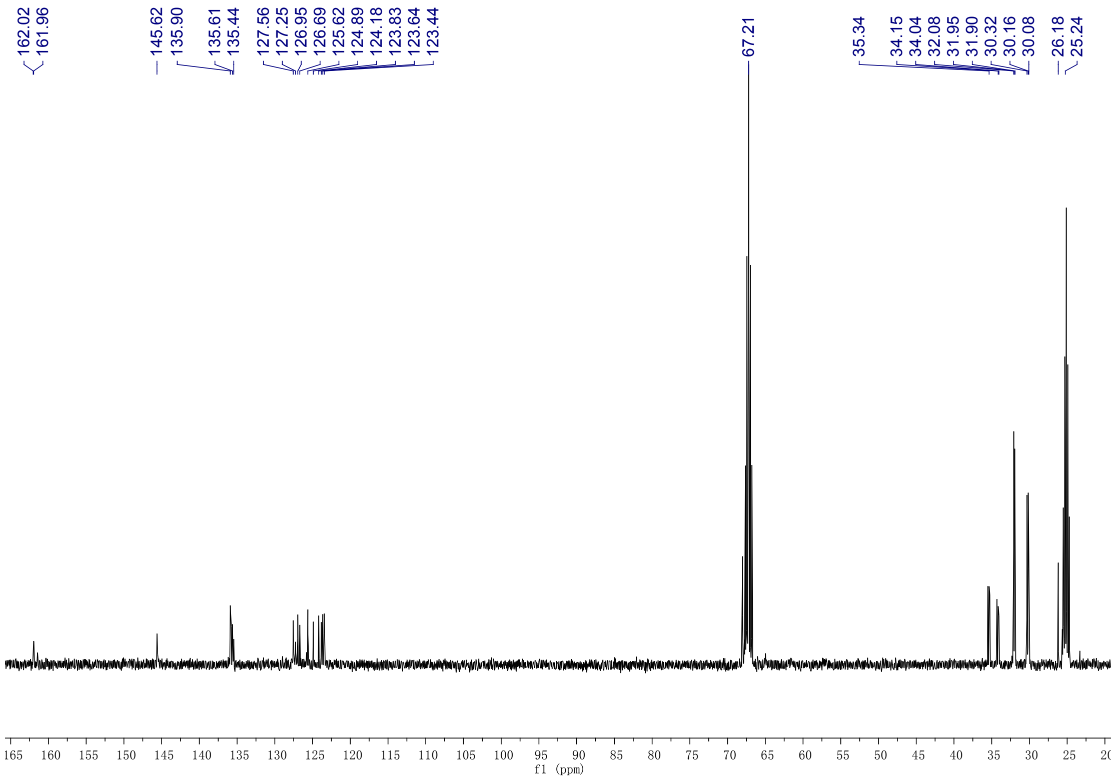

Fig. S4 ^{13}C NMR spectrum of complex **2** in *d8*-THF (298K).

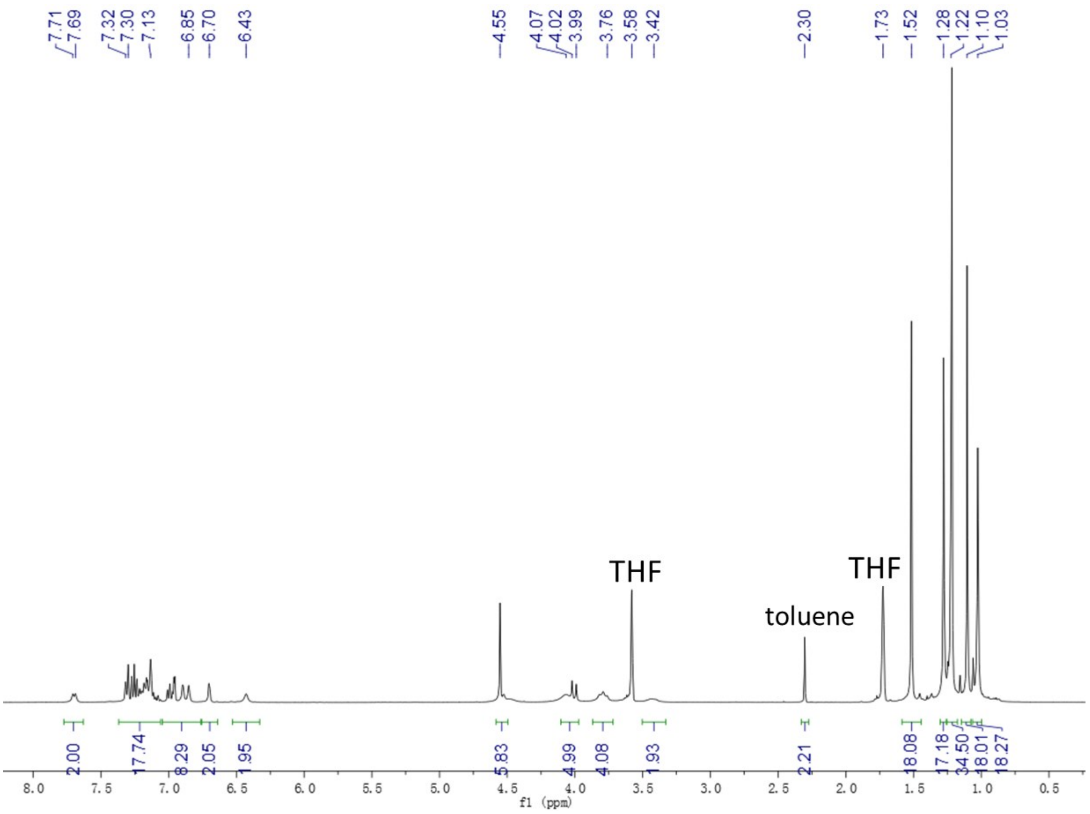

Fig. S5 ^{1}H NMR spectrum of complex **4** in *d8*-THF (298K).

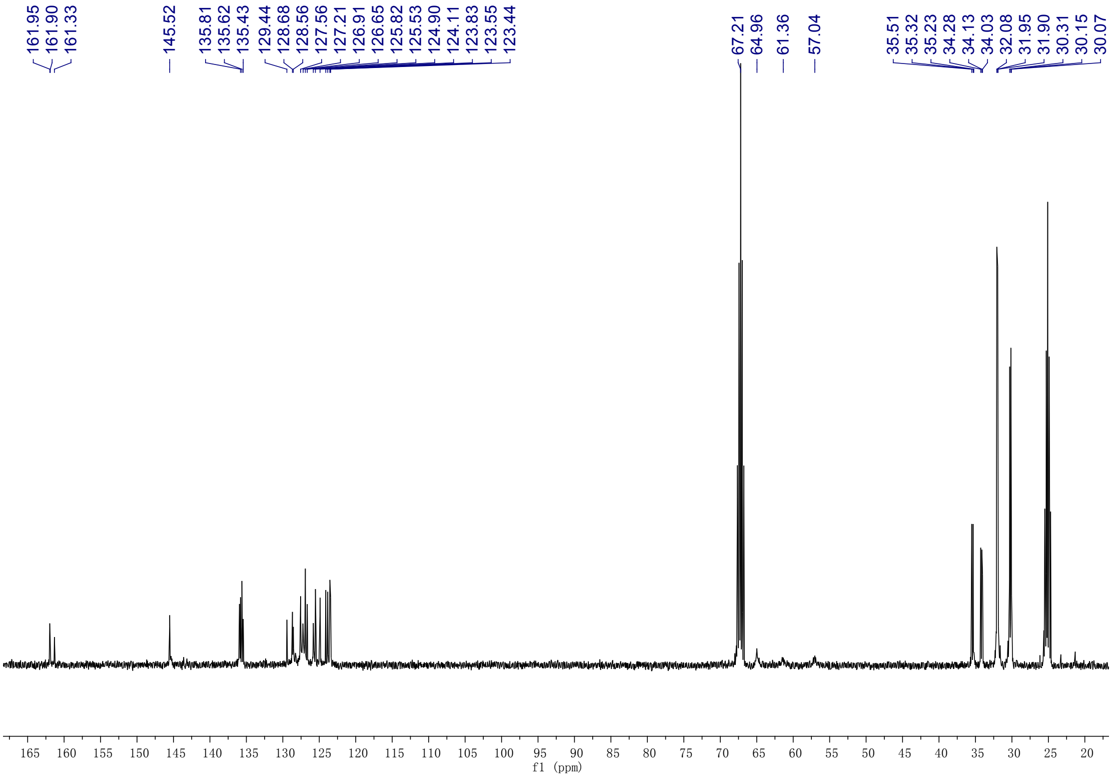

Fig. S6 ^{13}C NMR spectrum of complex **4** in *d8*-THF (298K).

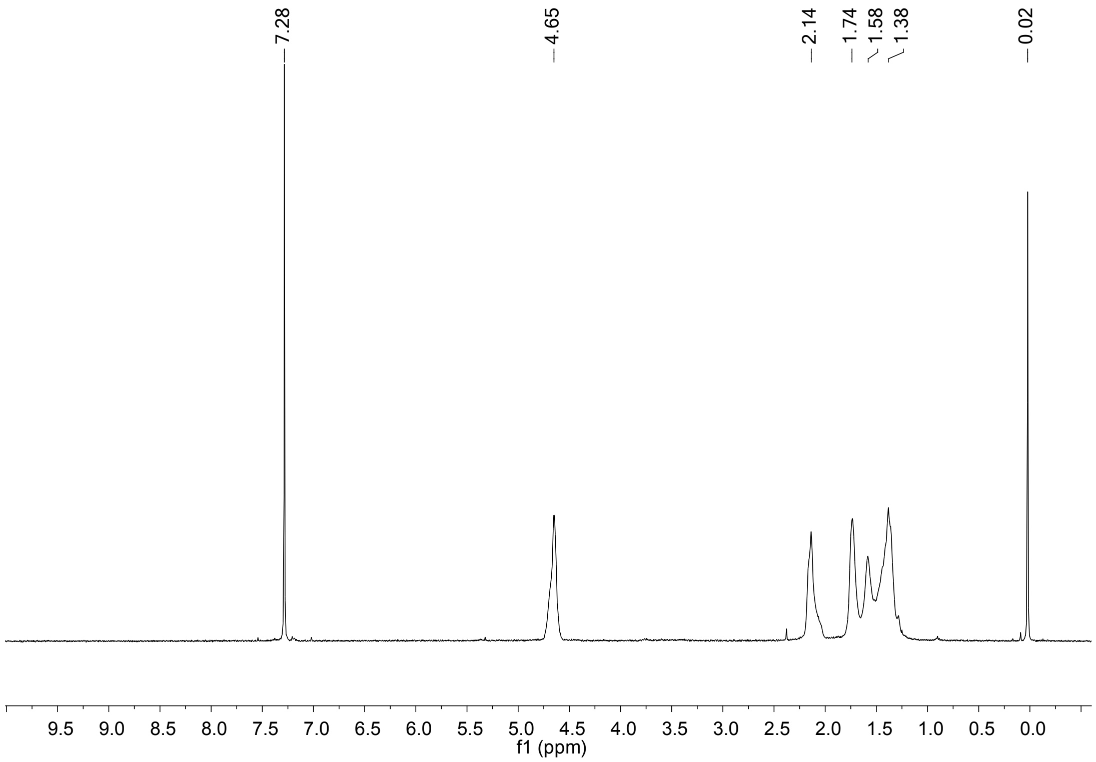

Fig. S7 Representative ^{1}H NMR spectrum of PCHC in $CDCl_3$. The signal at 4.64 ppm is assigned to the methyne groups in PCHC. No signal at 3.45 ppm is detected, which supports the absence of polyether of the copolymer.

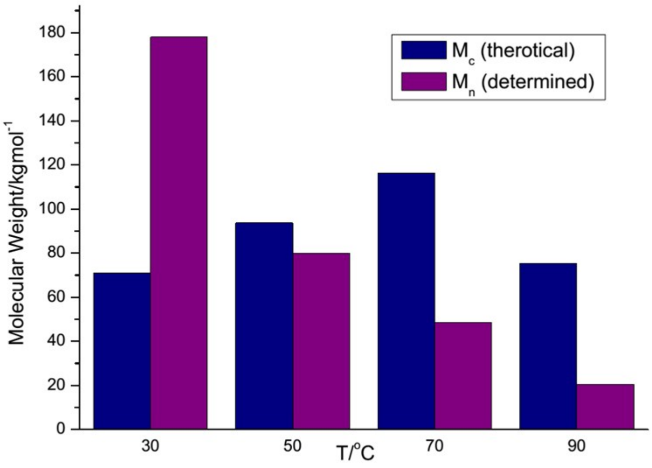

Fig. S8 Molecular weight (M_n) of polymers prepared at various reaction temperatures determined by GPC.

Table S1. Degradation of PCHC initiated by complex **3**. [a]

Entry	$M_{initiator}$/g	M_n[b,c]/g·mol^{-1}	PDI[b,c]
1	0.0130	172,800	2.08
2	0.0229	80,800	1.70
3	0	234,600	1.96

[a] Conditions: 3 h, 90 °C, 0.5 mL toluene, 0.477 g PCHC (molecular weight of the used PCHC was 295,800 g/mol). [b] Data after depolymerization. [c] Determined by GPC versus polystyrene standards.

Table S2. Copolymerization of styrene oxide or propylene oxide with CO_2. [a]

Entry	Monomer	[**3**]: [CHO]	T/°C	Pressure/MPa	Time/h	Yield*ᵇ*/%
1	styrene oxide	1:1000	70	0.7	3	trace
2	styrene oxide	1:200	70	0.7	3	trace
3	styrene oxide	1:100	70	3.0	12	trace
4	styrene oxide	1:100	50	3.0	12	trace
5	styrene oxide	1:100	90	3.0	12	trace
6	propylene oxide	1:100	70	3.0	12	trace
7	propylene oxide	1:100	50	3.0	12	trace
8	propylene oxide	1:100	90	3.0	12	trace

[a] Conditions: [CHO] = 4.92 M in toluene. [b] Isolated yield.

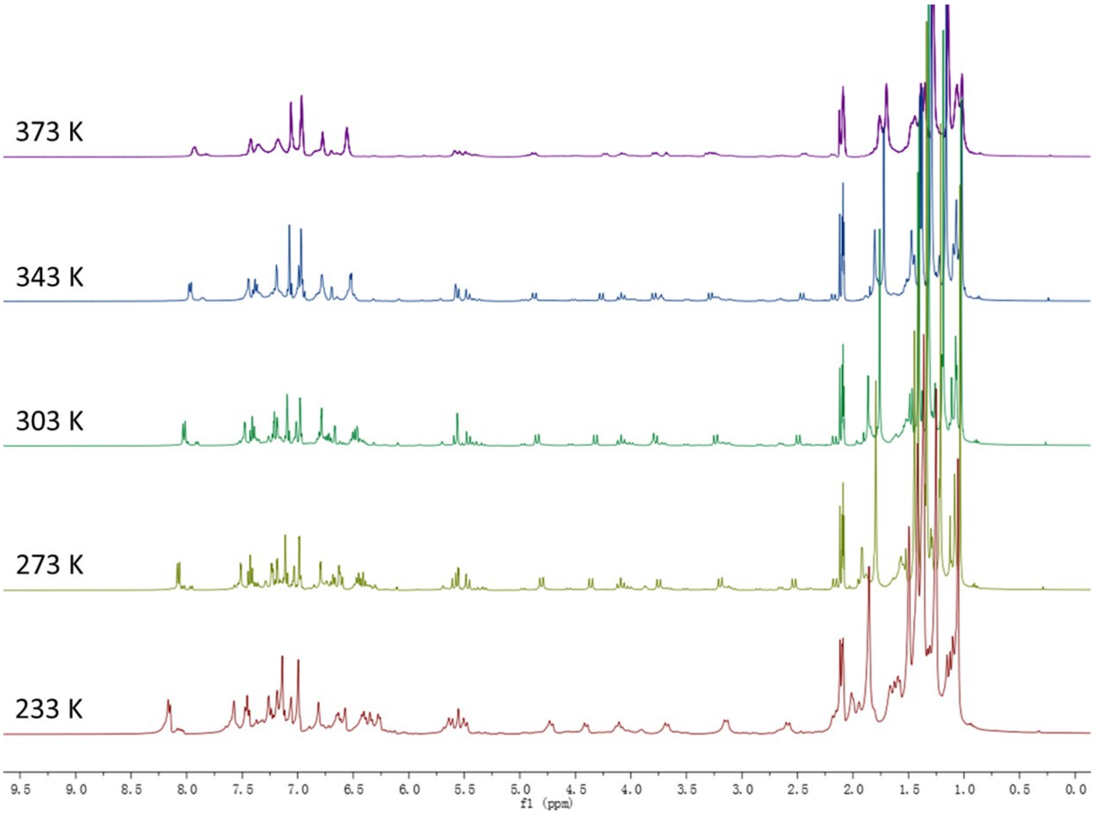

Fig. S9 Variable-temperature ^{1}H NMR spectra of complex **4** (233-373K) in C_7D_8.

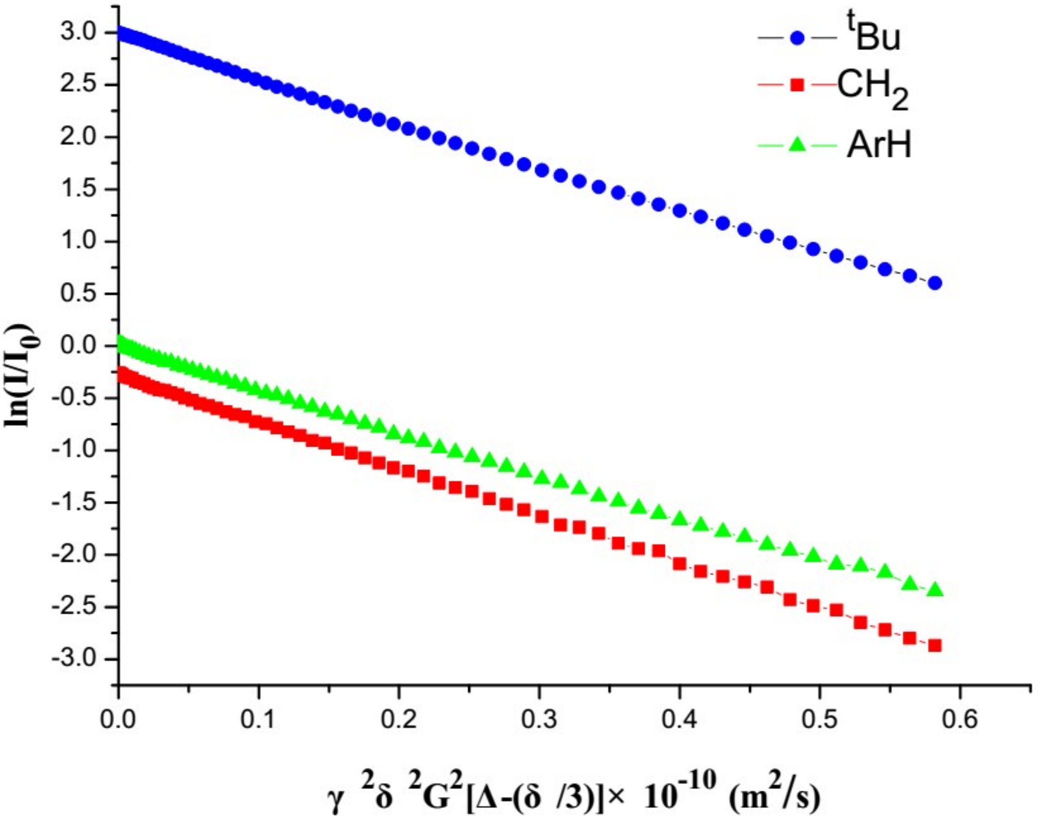

Fig. S10 Plot of $\ln(I/I_0)$ vs. $\gamma^2\delta^2G^2[\Delta-(\delta/3)]\times10^{-10}(m^2/s)$ from PGSE experiments for complex **2** (20 mM) in C_7D_8 at 25 °C. The average value of the translational diffusion coefficient (D_t), determined for three separate signals in the PGSE NMR spectrum, is 4.37×10^{-10} m^2/s. I = observed spin echo intensity, I_0 = intensity in the absence of a gradient, G = gradient strength, γ = gyromagnetic ratio, δ = length of gradient pulse, Δ = delay between gradient midpoints.

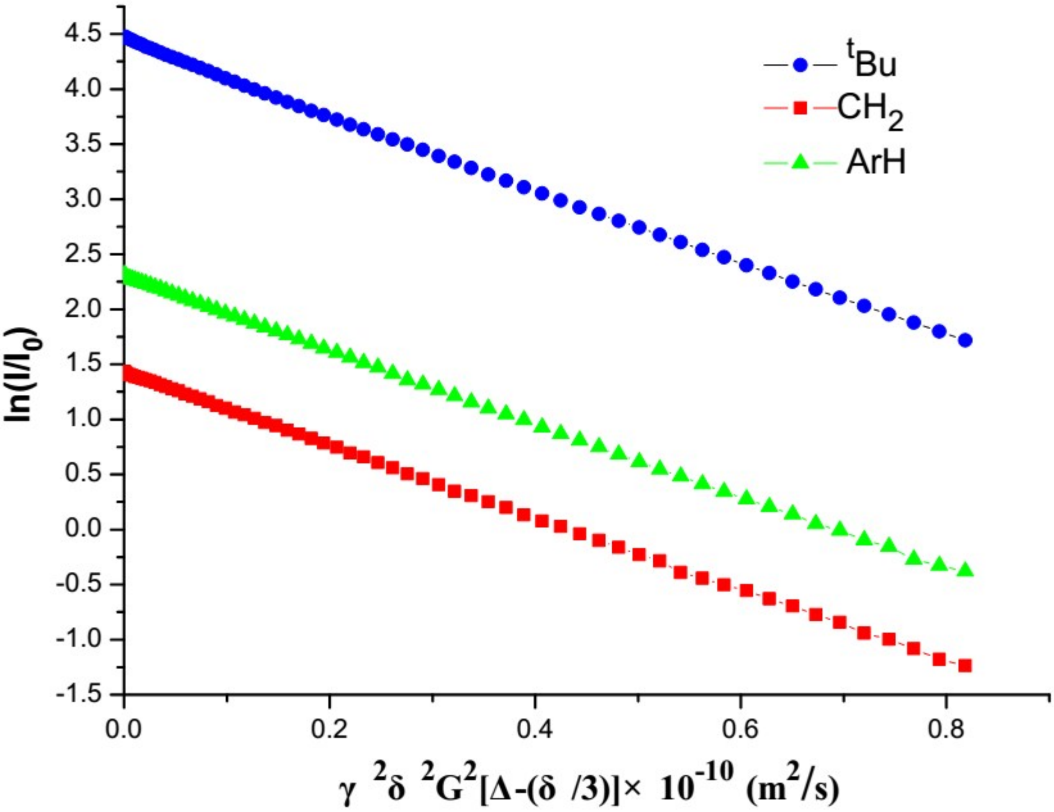

Fig. S11 Plot of ln(I/I_0) vs. $\gamma^2\delta^2G^2[\Delta-(\delta/3)]\times10^{-10}$($m^2/s$) from PGSE experiments for complex **4** (20 mM) in C_7D_8 at 25 °C. The average value of the translational diffusion coefficient (D_t), determined for three separate signals in the PGSE NMR spectrum, is 3.30×10^{-10} m^2/s. I = observed spin echo intensity, I_0 = intensity in the absence of a gradient, G = gradient strength, γ = gyromagnetic ratio, δ = length of gradient pulse, Δ = delay between gradient midpoints.

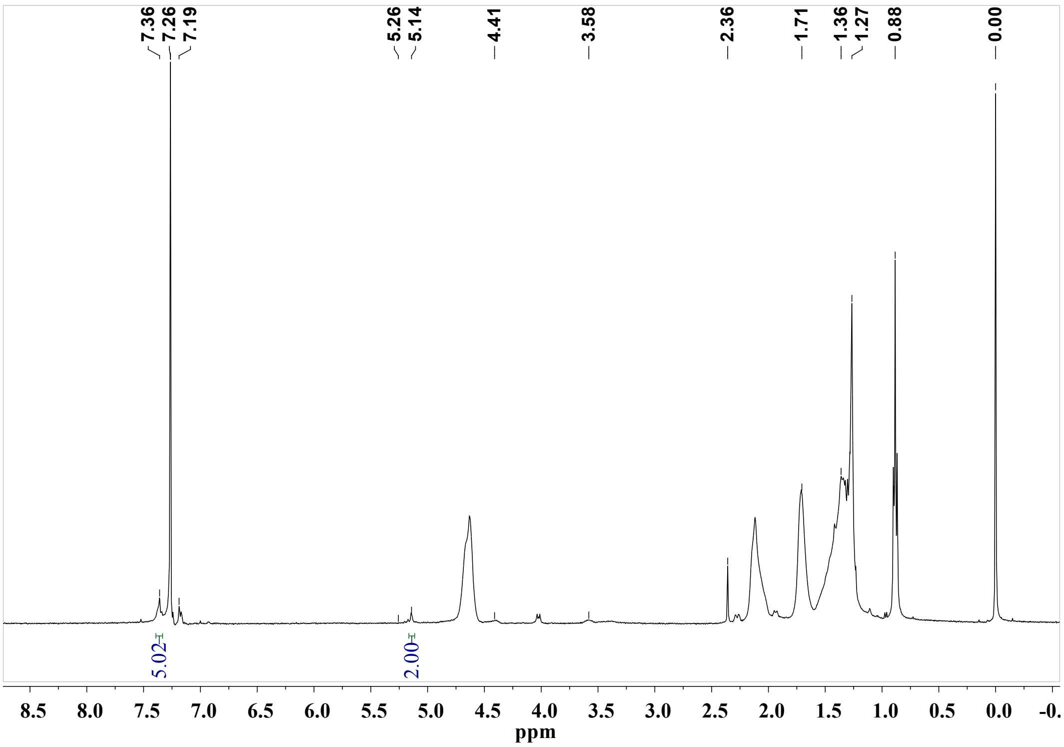

Fig. S12 ^{1}H NMR spectrum of PCHC oligomer in $CDCl_3$ (298 K, 400 MHz) prepared in the presence of complex **3**. Signals at 7.36 and 5.14 ppm are assigned to the benzyloxy end group ($PhCH_2O$).[3] Signals at 4.41 and 3.58 ppm are assigned to the methyne groups on the end group ($OCHC_4H_8CHOH$).[4] Signals at 7.19 and 2.36 ppm are assigned to the residual toluene solvent.[5] Signals at 1.27 and 0.88 ppm are assigned to the residual hexane solvent.

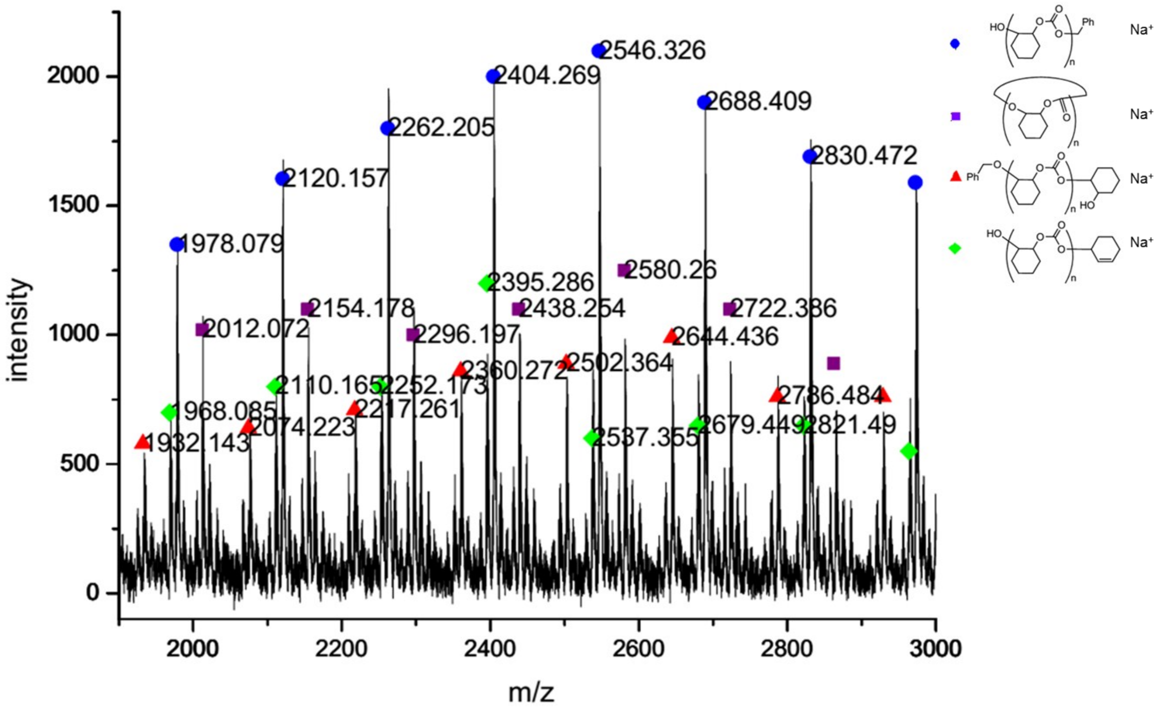

Fig. S13 MALDI-TOF mass spectrum of poly(cyclohexene carbonate) prepared in the presence of complex **3**.

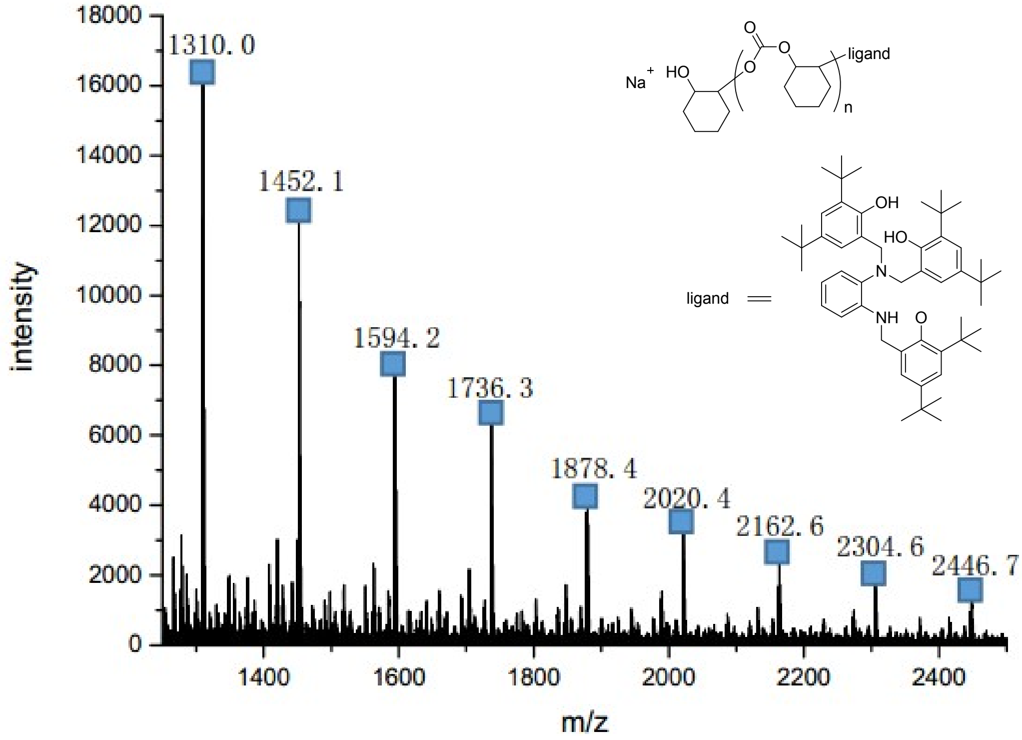

Fig. S14 MALDI-TOF mass spectrum of poly(cyclohexene carbonate) prepared in the presence of complex **1**. Polymerization conditions: 70 °C, 3 MPa of CO_2, 5 h, CHO: **1** = 40:1.

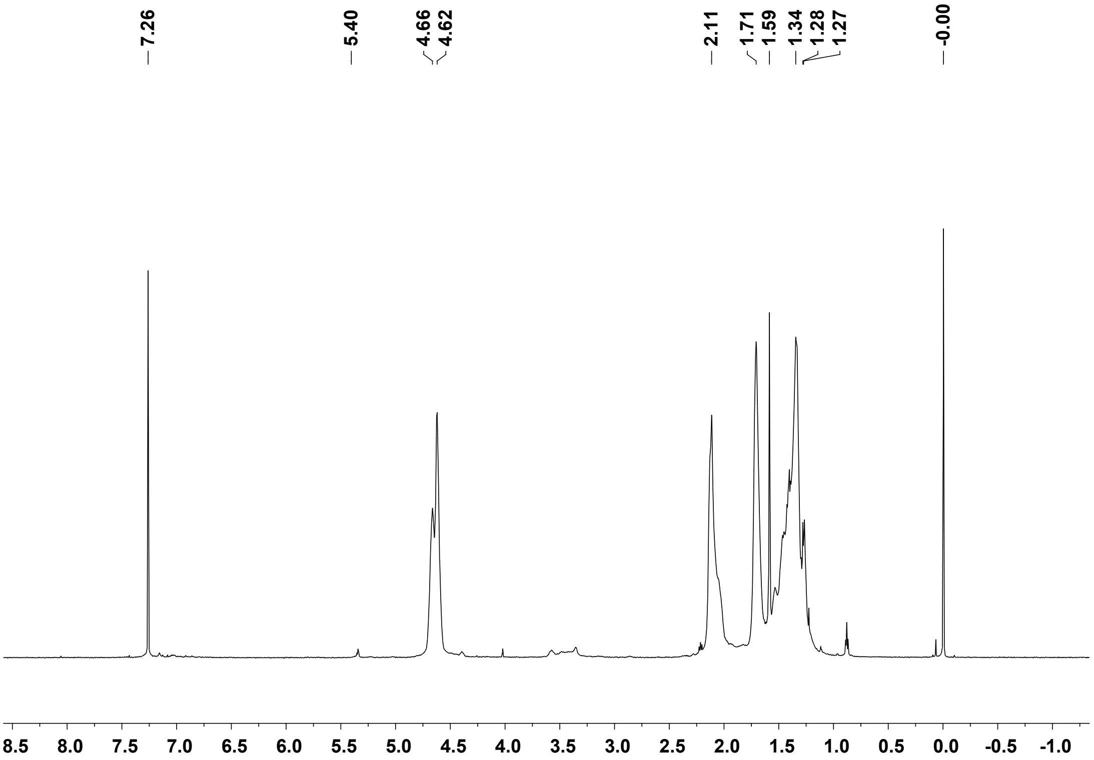

Fig. S15 ^{1}H NMR spectrum of PCHC oligomer in $CDCl_3$ (298 K, 600 MHz) prepared in the presence of complex **1**. Polymerization conditions: 70 °C, 3 MPa of CO_2, 5 h, CHO: **1** = 40:1.

Table S3 Crystallographic data for complexes **1**·DME (CCDC 1435035), **2**·THF (CCDC 1435036) and **3**·2THF·3Hex (CCDC 1435037)

Complexes	**1**·DME	**2**·THF	**3**·2THF·3Hex
formula	$C_{55}H_{81}N_2NdO_5$	$C_{55}H_{79}N_2O_4Y$	$C_{142}H_{214}N_4Nd_2O_{10}Zn$
M_r	994.46	921.11	2491.02
T(K)	223(2)	223(2)	223(2)
crystal system	Triclinic	Monoclinic	Monoclinic
space group	$P\bar{1}$	$P\ 2_1/n$	$C\ 2/c$
a (Å)	13.610(3)	15.2272(13)	25.713(3)
b (Å)	15.446(3)	14.1936(11)	25.211(3)
c (Å)	15.506(3)	24.434(2)	25.540(3)
α (deg)	98.661(3)	90	115.838(2)
β (deg)	107.060(2)	99.252(2)	90
γ (deg)	112.680(3)	90	90
V (Å^3)	2743.6(9)	5212.2(7)	14901(3)
Z	2	4	4
ρ_{calcd} (g cm^{-3})	1.204	1.174	1.110
μ (mm^{-1})	0.990	1.163	0.897
F (000)	1050	1976	5296
θ_{max} (deg)	25.50	25.50	25.50
measured reflections	22391	25557	35720
independent reflections	10154	9682	13767
no. of variables	589	548	622
GOF	1.121	1.056	1.069
wR	0.0811	0.1297	0.0990
R	0.0672	0.0851	0.0813
R_{int}	0.0577	0.0738	0.0485
Largest diff. peak and hole	1.706 and -1.148 e A^{-3}	0.832 and -0.777 e A^{-3}	2.063 and -0.982 e A^{-3}

Table S4 Selected bond lengths (Å) and angles (deg) of complex **3**·2THF·3Hex

Nd(1)-O(1)	2.195(4)	O(1)-C(9)	1.349(8)
Nd(1)-O(2)	2.446(4)	O(2)-C(24)	1.374(7)
Nd(1)-O(3)	2.180(4)	O(3)-C(39)	1.330(7)
Nd(1)-O(4)	2.372(5)	O(4)-C(52)	1.471(12)
Nd(1)-N(1)	2.628(5)	Zn(1)-O(4)	1.947(4)
Nd(1)-N(2)	2.657(5)	Zn(1)-O(4A)	1.947(4)
Nd(1)-Zn(1)	3.3934(5)	Zn(1)-O(2)	1.979(4)
O(1)-Nd(1)-O(2)	152.82(14)	N(1)-Nd(1)-N(2)	65.43(15)
O(3)-Nd(1)-O(1)	99.07(17)	O(4)-Zn(1)-O(4A)	118.0(3)
O(1)-Nd(1)-O(4)	116.18(17)	O(4)-Zn(1)-O(2A)	122.84(18)
O(1)-Nd(1)-N(1)	75.44(15)	O(4)-Zn(1)-O(2)	87.53(17)
O(1)-Nd(1)-N(2)	95.49(17)	Zn(1)-O(2)-Nd(1)	99.63(15)
O(3)-Nd(1)-O(2)	105.11(15)	Zn(1)-O(4)-Nd(1)	103.12(18)
O(4)-Nd(1)-O(2)	68.59(14)	O(2)-Zn(1)-O(2A)	122.0(2)
O(2)-Nd(1)-N(1)	78.02(14)	O(4A)-Zn(1)-O(2)	122.84(18)
O(2)-Nd(1)-N(2)	78.56(14)	O(4)-Nd(1)-N(2)	146.70(15)
O(3)-Nd(1)-O(4)	106.44(17)	O(3)-Nd(1)-N(2)	76.48(16)
O(3)-Nd(1)-N(1)	140.50(16)	O(4)-Nd(1)-N(1)	111.02(16)

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