Supporting Information for

Efficient Production of Poly(Cyclohexene Carbonate) via ROCOP of Cyclohexene Oxide and CO_2 Mediated by NNO-Scorpionate Zinc Complexes

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1. Spectroscopic Details

Figures S1–S3. ^{1}H NMR spectrum of complexes **2**, **4** and **6**.

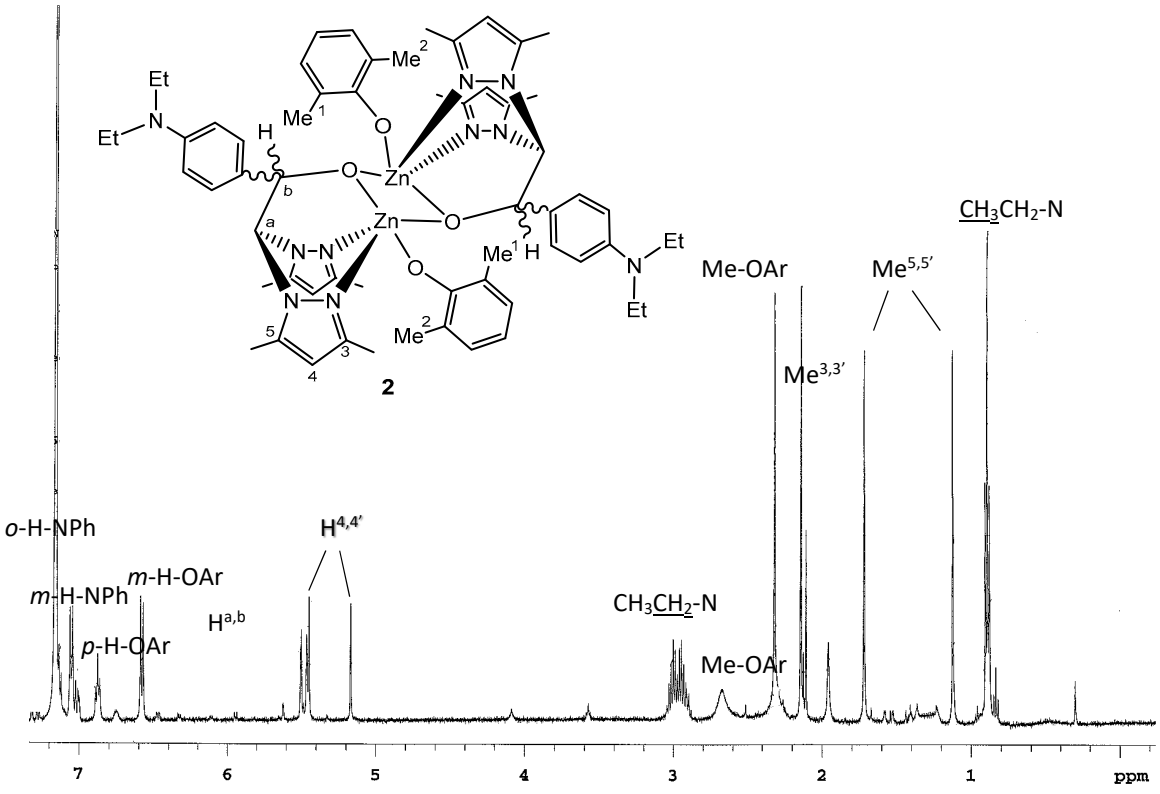

Figure S1. ^{1}H-NMR spectrum (500 MHz, 297 K, C_6D_6) for complex [Zn(2,6-$Me_2C_6H_3O$)(bpzaepe)]$_2$ **2**.

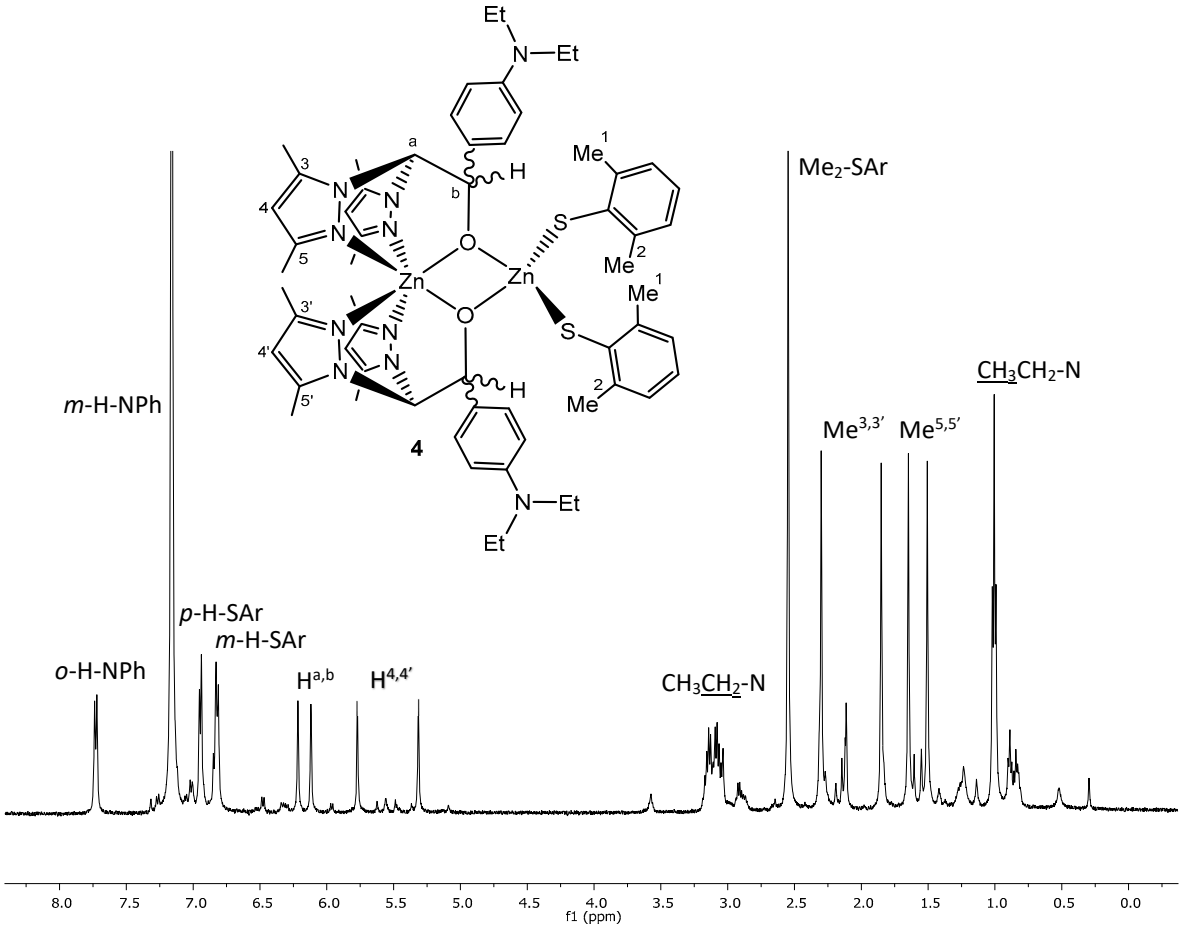

Figure S2. ^{1}H-NMR spectrum (500 MHz, 297 K, C_6D_6) for complex [Zn(bpzaepe)$_2${Zn(2,6-$Me_2C_6H_3S)_2$}] **4**.

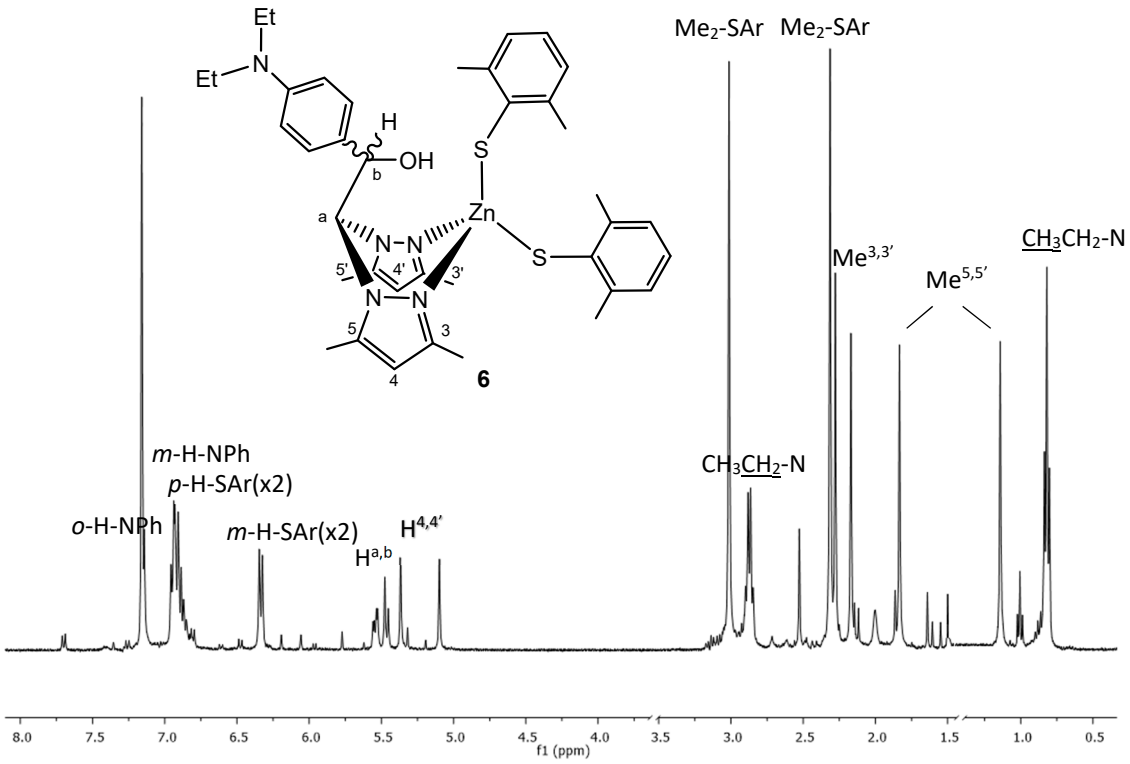

Figure S3. ^{1}HNMR spectrum (500 MHz, 297 K, C_6D_6) for complex [Zn(2,6-$Me_2C_6H_3S)_2$(Hbpzaepe)] **6**.

2. **X-Ray Diffraction Studies:** Crystallographic structure determination for the complexes **4**, **5** and **6**.

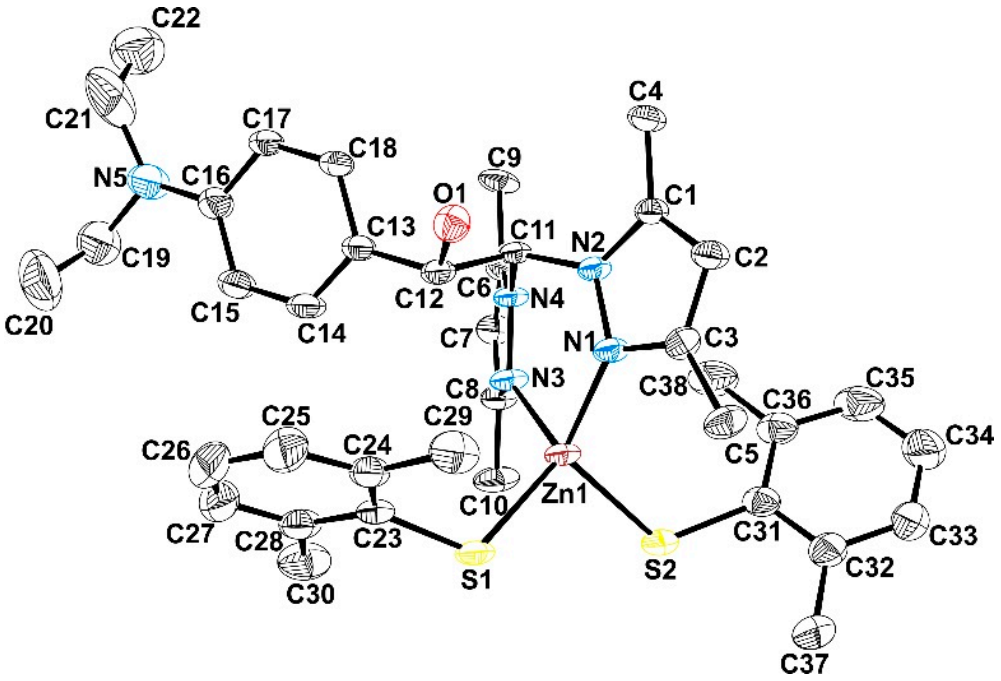

Figure S4. ORTEP view of the complex [Zn(2,6-$Me_2C_6H_3S)_2$(bpzaepeH)] **6** Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table S1. Crystal data and structure refinement for **4**, **5** and **6**.

	4	**5**	**6**
Empirical formula	$C_{62}H_{82}N_{10}O_{2.5}S_2Zn_2$	$C_{40}H_{53}N_5O_2S_2Zn$	$C_{42}H_{57}N_5O_2S_2Zn$
Formula weight	1202.23	765.36	793.41
Temperature (K)	240(2)	290(2)	200(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P ī	P 2_1/n	C 2/c
a(Å)	14.9313(12)	16.608(5)	30.2612(7)
b(Å)	14.9352(13)	17.144(6)	16.7513(3)
c(Å)	20.0887(17)	17.136(6)	18.4092(3)
α(°)	85.716(4)	90	90
β(°)	69.721(4)	113.998(5)	92.921(2)
γ(°)	76.817(4)	90	90
Volume($Å^3$)	4091.4(6)	4458(3)	9319.8(3)
Z	2	4	8
Density (calculated) (g/cm^3)	0.976	1.140	1.131
Absorption coefficient (mm^{-1})	0.676	0.680	0.653
F(000)	1272	1624	3376
Crystal size (mm^3)	0.37 x 0.08 x 0.04	0.22 x 0.14 x 0.04	0.24 x 0.09 x 0.04
Index ranges	-18 ≤ h ≤ 17 -18 ≤ k ≤ 18 -24 ≤ l ≤ 24	-19 ≤ h ≤ 17 -20 ≤ k ≤ 20 -20 ≤ l ≤ 20	-35 ≤ h ≤ 35 -19 ≤ k ≤ 19 0 ≤ l ≤ 21
Reflections collected	86477	29051	16073
Independent reflections	14449 [R(int) = 0.1416]	7761 [R(int) = 0.1666]	8203 [R(int) = 0.0287]
Data / restraints / parameters	14449 / 5 / 720	7761 / 0 / 463	8203 / 101 / 588
Goodness-of-fit on F^2	1.070	0.930	1.076
Final R indices [$I>2\sigma(I)$]	R1 = 0.1007 wR2 = 0.2765	R1 = 0.0794 wR2 = 0.1561	R1 = 0.0667 wR2 = 0.1939
Largest diff. peak / hole, e.$Å^{-3}$	0.972 and -1.387	0.441 and -0.318	0.890 d -0.276

3. Experimental details for the synthesis of poly(cyclohexene carbonate)

Table S2. Effect of catalyst loading on the synthesis of poly(cyclohexene carbonate) catalysed by complex **4**[a].

Entry	4 (%)	Conv. PCHC (%)[a]	Selectivity PCHC (%)[a]
1	0.5	15	63
2	0.8	50	90
3	1.0	85	93
4	1.25	91	94

[a] Reaction condition: 80 ºC, 40 bar CO_2, substrate: cyclohexene oxide, 16 h.

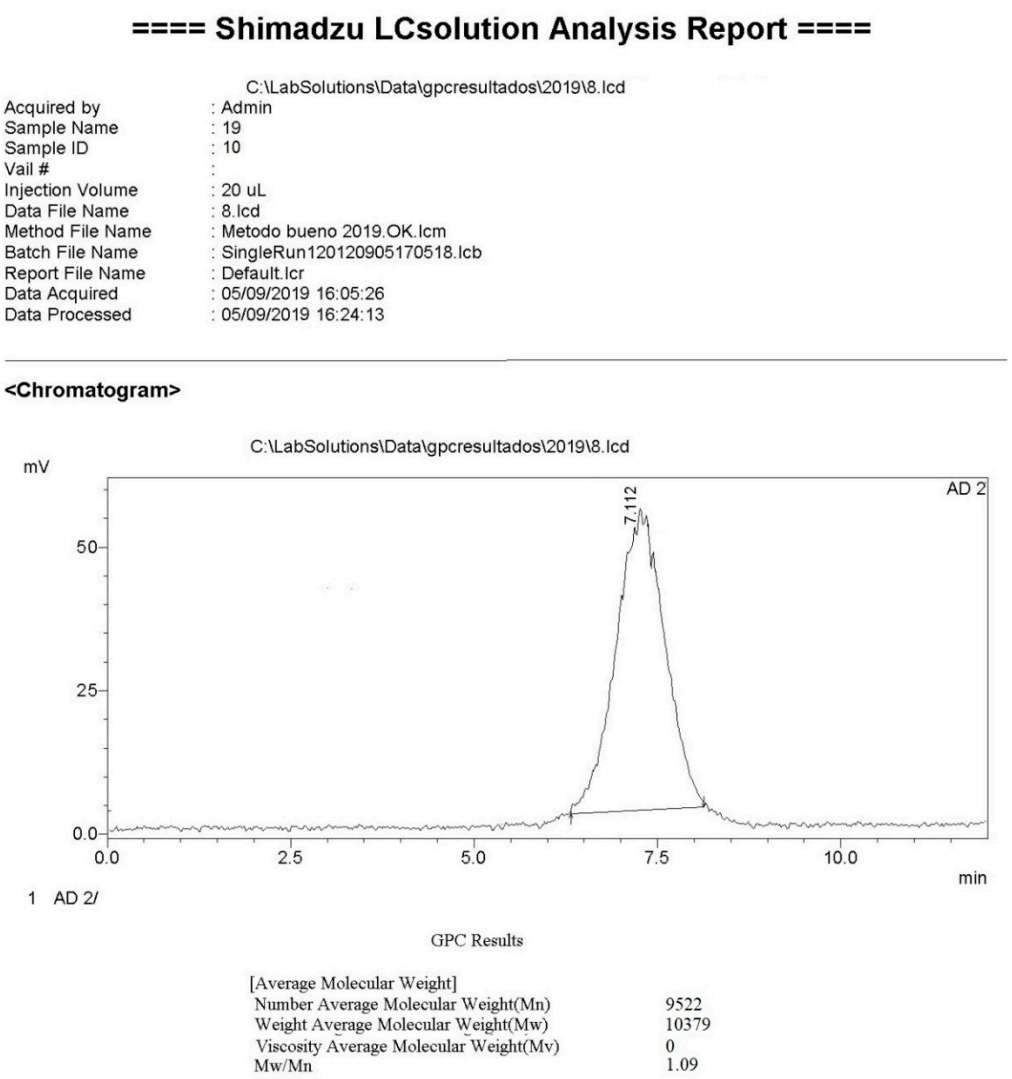

Figure S5. GPC trace of poly(cyclohexene carbonate) produced by complex **4** at 70 °C and 10 bar CO_2 (Table 5, entry 6).

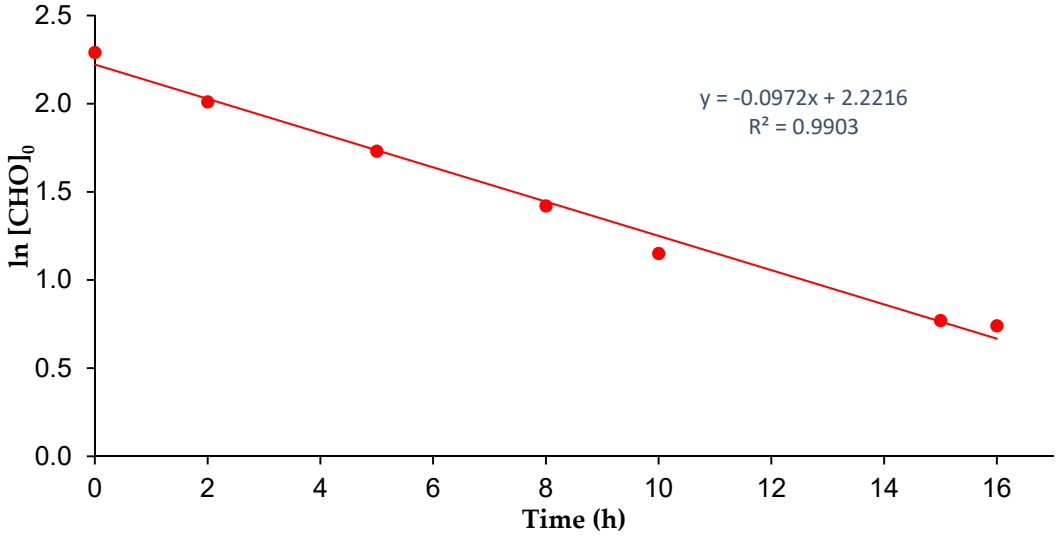

Figure S6. Pseudo first-order kinetic plot for the ring-opening copolymerisation of cyclohexene oxide and carbon dioxide catalysed by complex **4** at 70 °C and 10 bar CO_2.

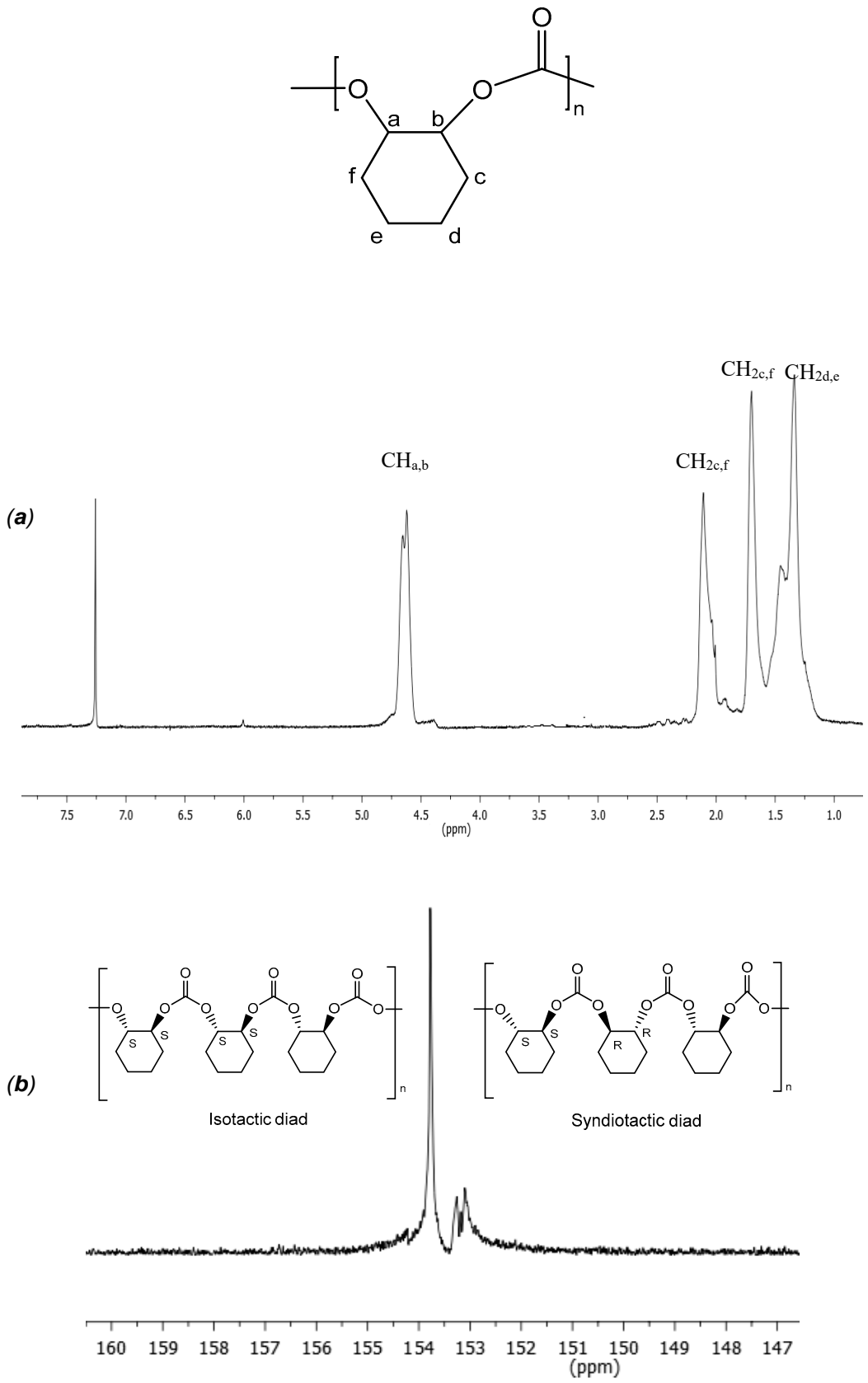

Figure S7: (*a*) ^{1}H NMR and (*b*) ^{13}C-{^{1}H} NMR spectrum of poly(cyclohexene carbonate) sample (Table 4, entry 5) using complex **4** as catalyst at 70 °C and 10 bar CO_2.