Facilely synthesized benzotriazole phenolate zirconium complexes as versatile catalysts for copolymerization of carbon dioxide with cyclohexene oxide and lactide polymerization

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Fig. S1 ORTEP drawing of complex **2** with probability ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity.

Fig. S2 Polymerization of L-LA initiated by Zr complex **1** in toluene at 80 °C. The relationship between the Mn (□) or the PDI value (●) of the polymer and the initial molar ratio $[\text{L-LA}]_0/[\mathbf{1}]_0$ is shown.

Fig. S3 ^{1}H NMR spectrum of poly(L-lactide) (Table 3, entry 3) in $CDCl_3$.

Fig. S4 ^{1}H NMR spectrum of poly(L-lactide) (Table 3, entry 10) in $CDCl_3$.

Table S1 Copolymerization of CHO and CO_2 catalysed by Zr complex **1**[a]

Table S2 Crystallographic data of complexes **1**, **2**, **3** and **6**

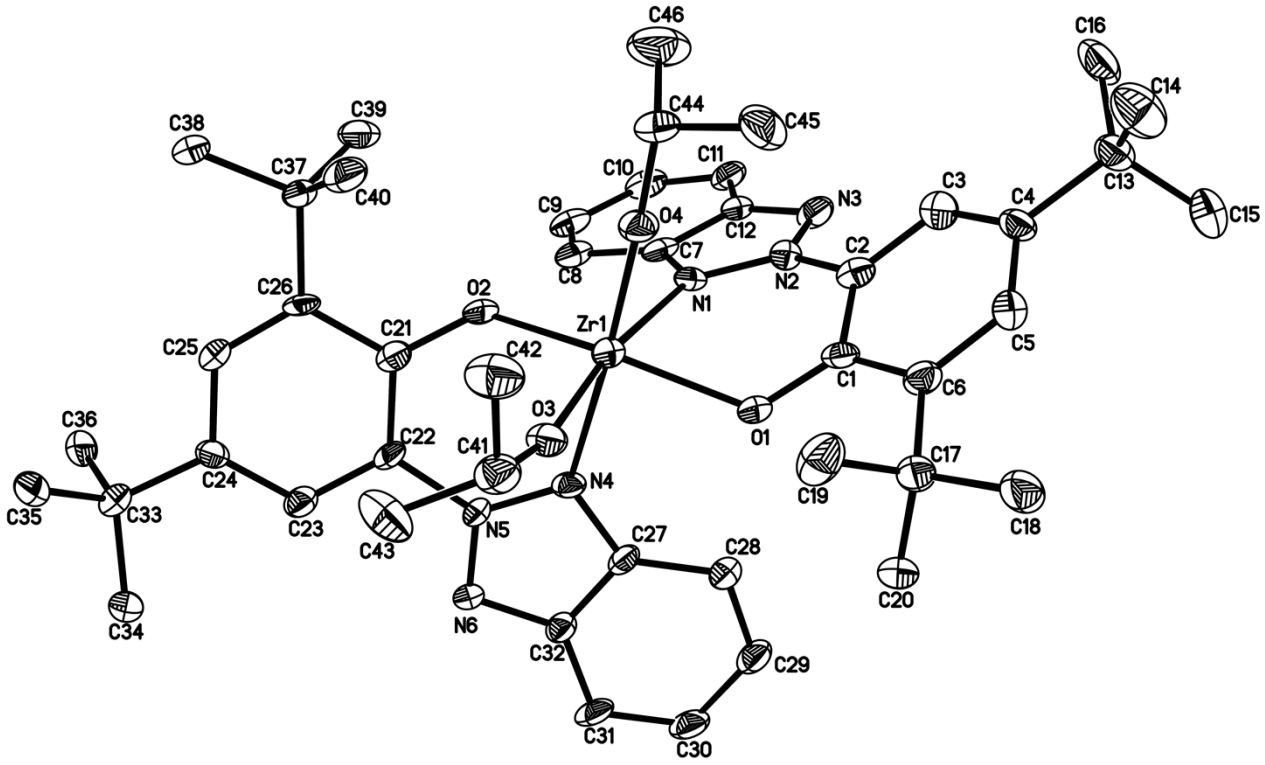

Fig. S1 ORTEP drawing of complex **2** with probability ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr(1)-O(1) 2.062(4), Zr(1)-O(2) 2.042(4), Zr(1)-O(3) 1.932(4), Zr(1)-O(4) 1.910(4), Zr(1)-N(1) 2.437(5), Zr(1)-N(4) 2.419(5), O(1)-Zr(1)-O(2) 152.24(18), O(1)-Zr(1)-O(4) 96.73(18), O(1)-Zr(1)-O(3) 99.39(18), O(1)-Zr(1)-N(1) 74.07(17), O(1)-Zr(1)-N(4) 86.64(17), O(4)-Zr(1)-O(2) 99.71(18), O(3)-Zr(1)-O(2) 98.57(18), O(2)-Zr(1)-N(1) 84.84(17), O(2)-Zr(1)-N(4) 73.73(17), O(3)-Zr(1)-O(4) 102.82(19), O(4)-Zr(1)-N(1) 86.18(18), O(4)-Zr(1)-N(4) 169.96(18), O(3)-Zr(1)-N(1) 169.59(17), O(3)-Zr(1)-N(4) 85.87(18), N(4)-Zr(1)-N(1) 85.67(17).

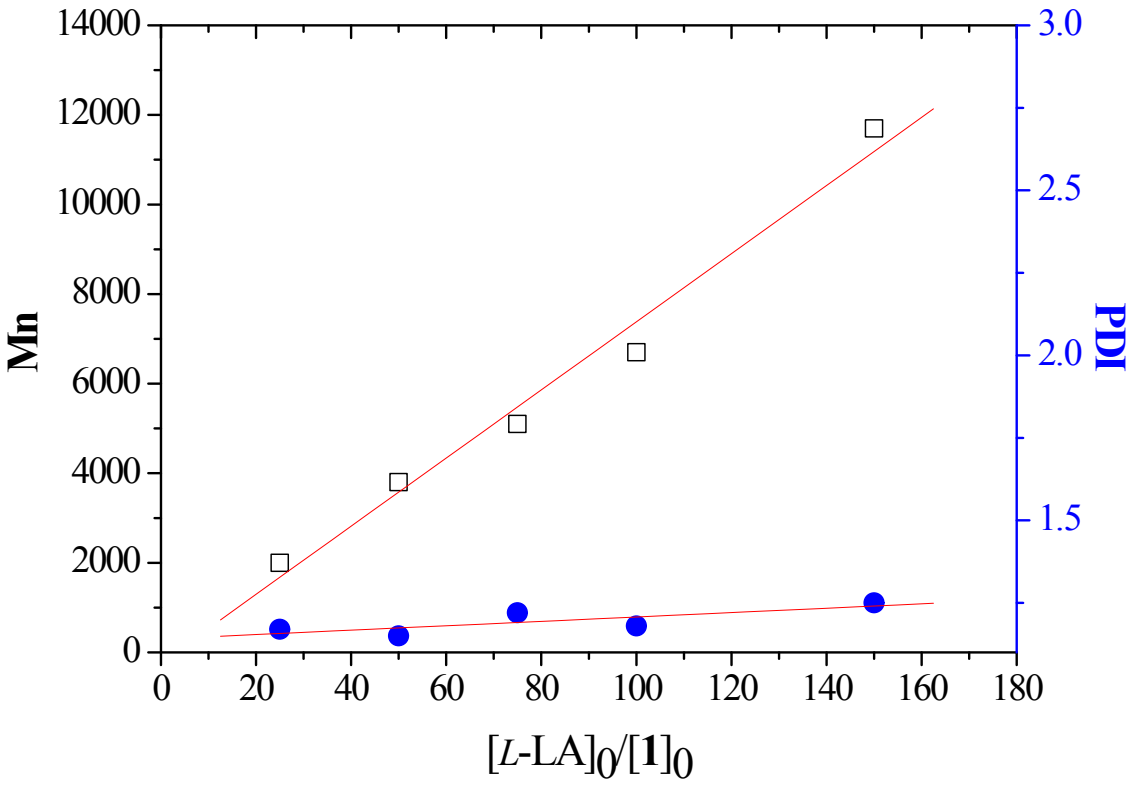

Fig. S2 Polymerization of L-LA initiated by Zr complex **1** in toluene at 80 °C. The relationship between the Mn (□) or the PDI value (●) of the polymer and the initial molar ratio $[\text{L-LA}]_0/[\mathbf{1}]_0$ is shown.

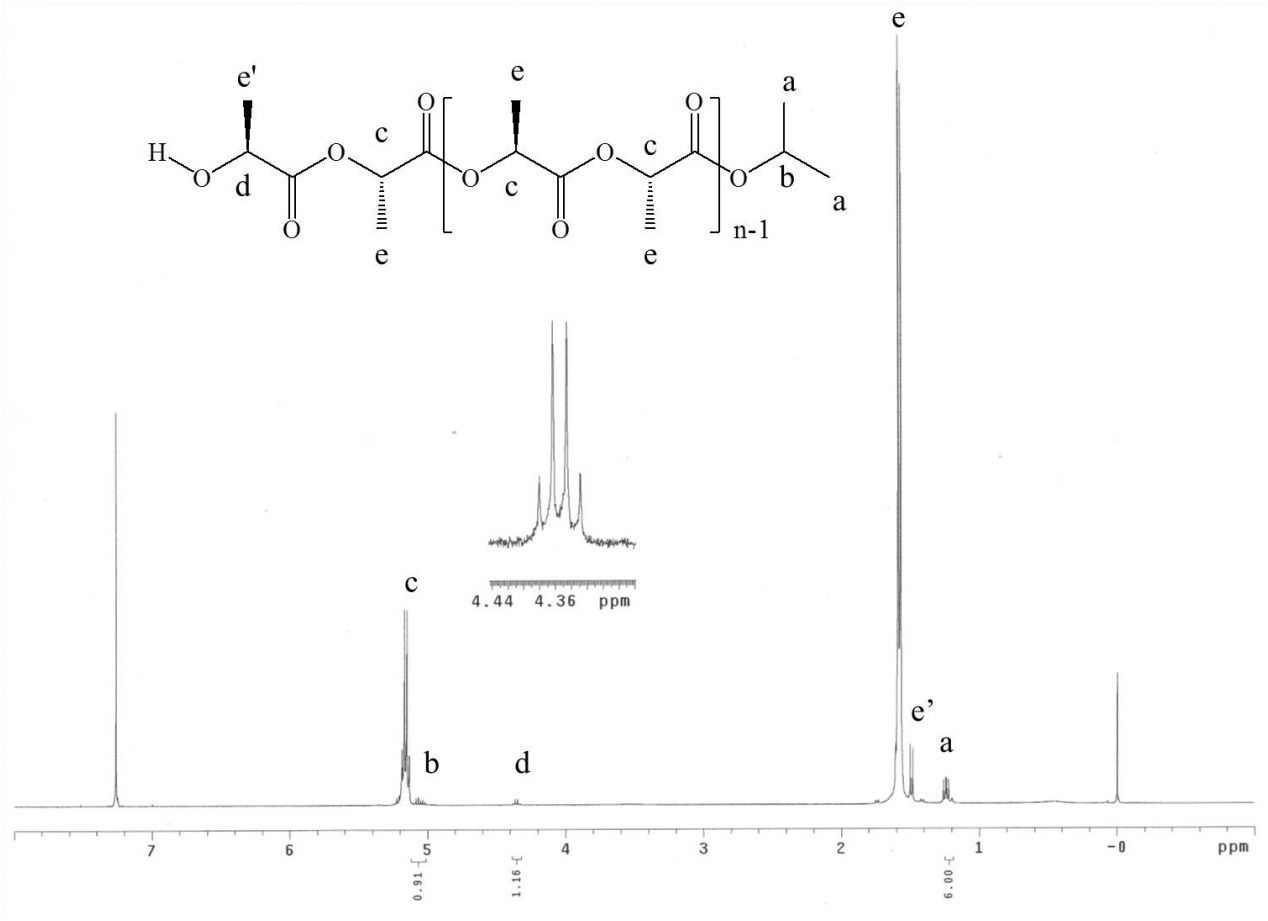

Fig. S3 ^{1}H NMR spectrum of poly(L-lactide) (Table 3, entry 3) in $CDCl_3$.

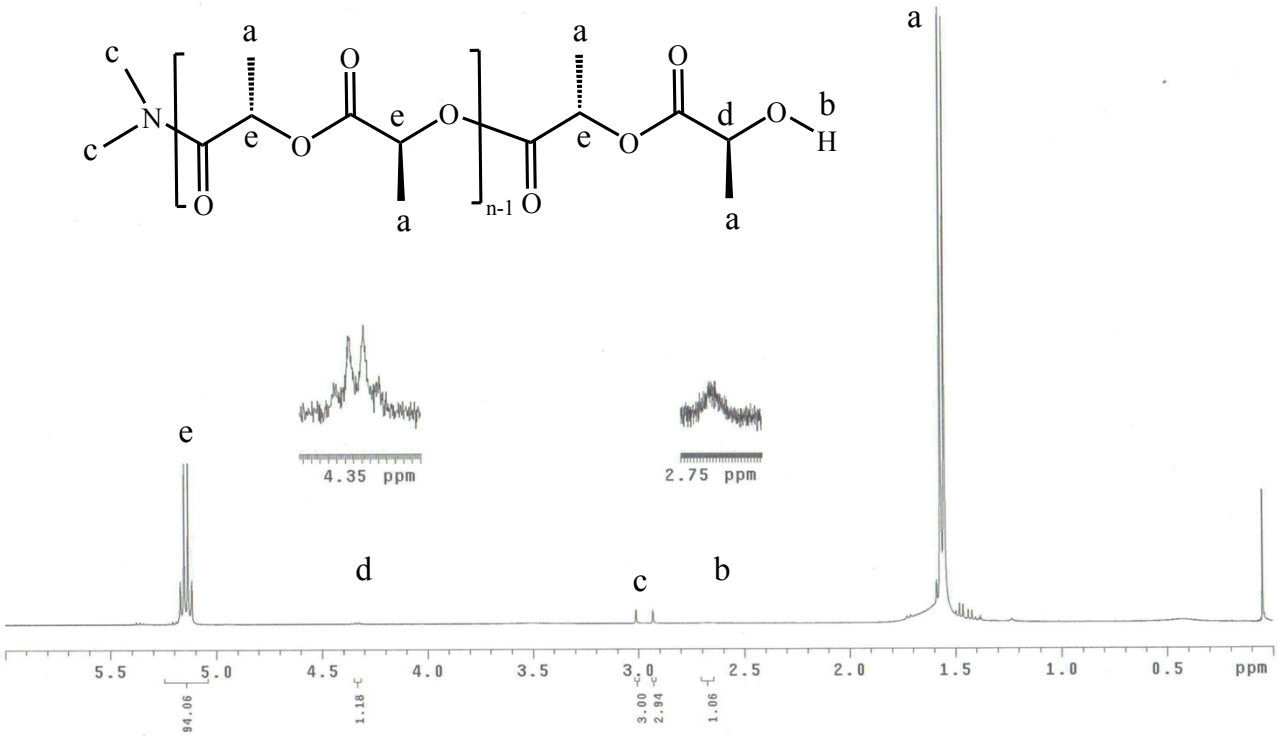

Fig. S4 ^{1}H NMR spectrum of poly(L-lactide) (Table 3, entry 10) in $CDCl_3$.

Table S1 Copolymerization of CHO and CO_2 catalysed by Zr complex **1**[a]

Entry	Cat. (mol%)	pCO_2^0 (psi)	Temp (^oC)	Time (h)	% CHO Conv.[b]	TON[c]	TOF /h^{-1}[d]	% carbonate[b]	M_n [M_w/M_n][e]
S1	**1**(0.50)	300	60	16	12	24	1.5	<2	-
S2	**1**(0.50)	300	80	16	64	128	8.0	69	5500[1.22]
S3	**1**(0.50)	300	120	16	68	136	8.5	38	6300[1.31]
S4	**1**(0.25)	500	100	16	41	164	10.3	49	4000[1.39]
S5	**1**(0.75)	600	100	4	49	65.3	16.3	90	2500[1.28]
S6	**1**(0.75)	600	100	6	69	92	15.3	90	4000[1.28]
S7	**1**(0.75)	600	100	8	83	110.7	13.8	90	4700[1.26]

[a] 50 mmol CHO. [b] Determined by comparison of the integrals of signals arising from the methylene protons in the ^1H NMR spectra. [c] TON = number of moles of CHO consumed per mole of catalyst. [d] TOF = TON per hour. [e] Obtained from GPC analysis.

Table S2 Crystallographic data of complexes **1**, **2**, **3** and **6**

	1	**2**	**3**	**6**·C_6H_{14}
Formula	$C_{46}H_{62}N_6O_4Zr$	$C_{92}H_{124}N_{12}O_8Zr_2$	$C_{44}H_{60}N_8O_2Zr$	$C_{68}H_{92}N_{10}O_3Zr$
Formula weight	854.24	1708.48	824.22	1188.74
Temp (K)	100(2) K	100(2) K	120(2) K	120(2) K
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	*P*2(1)/n	*P*-1	*P*-1	*P*-1
a (Å)	9.5189(4)	10.6166(7)	10.7550(3)	15.3623(6)
b (Å)	31.1912(12)	21.7128(13)	13.5703(5)	16.4184(7)
c (Å)	15.2281(7)	22.4253(14)	15.8579(6)	16.5697(7)
α (deg)	90	105.216(4)	105.254(3)	102.383(4)
β (deg)	106.939(2)	98.526(4)	93.273(3)	113.997(4)
γ (deg)	90	95.426(4)	99.663(3)	109.584(4)
V(Å^3)	4325.2(3)	4884.6(5)	2188.71(13)	3284.9(2)
Z	4	2	2	2
D_{calc}(Mg/m^3)	1.312	1.211	1.251	1.202
μ (Mo Kα)(mm^{-1})	0.304	0.272	0.296	0.219
F(000)	1808	1880	872	1268
Reflections collected	40616	81995	24509	29369
No. of parameters	528	1083	512	804
Indep. reflns (R_{int})	10715 (0.0665)	24142 (0.0925)	10241 (0.0343)	15090 (0.0287)
$R1[I > 2\sigma(I)]$	0.0776	0.0992	0.0393	0.0539
w$R2$ $[I > 2\sigma(I)]$	0.2122	0.2525	0.0836	0.1257
Goodness-of-fit on F^2	1.023	1.010	1.021	1.002