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SUPPORTING INFORMATION

Phenoxy-imine based Mononuclear Zn(II) Compounds: Applications as Polymerization Catalysts

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Table S1. Polymerization data for *rac*-LA using **1–8** as catalysts in the ratio 200:1 at 70 °C in THF.

Entry	Catalyst	Time (h)^{a}	Conversion (%)^{b}	$M_n^{(Theo)c}$ (kg/mol)	$M_n^{(Expt)d}$ (kg/mol)	[$Đ$]^{e}	P_m/P_r^{f}
1	**1**	14	98	28.58	25.34	1.28	0.64 (P_r)
2	**2**	14	98	28.53	31.21	1.22	0.63 (P_r)
3	**3**	10	99	28.79	30.89	1.20	0.67 (P_r)
4	**4**	12	97	28.25	32.41	1.22	0.66 (P_r)
5	**5**	22	99	28.86	30.44	1.20	0.74 (P_m)
6	**6**	22	98	28.53	30.19	1.21	0.72 (P_m)
7	**7**	18	99	28.79	29.98	1.18	0.78 (P_m)
8	**8**	20	98	28.54	31.12	1.24	0.77 (P_m)

[a] Time of polymerization measured by quenching the polymerization reaction at maximum conversion. [b] Calculated from ^{1}H NMR spectrum. [c]M_n^{Theo} at maximum conversion = (200 × 144.14) × conversion + Mol $Wt_{end\ groups}$. [d] Measured by GPC at 40 °C in THF relative to polystyrene standards with Mark–Houwink corrections; $M_n^{Expt} = 0.58\ M_n^{GPC}$ for *rac*-LA.[80] [e] Measured by GPC at 40 °C. [f] Calculated from the homonuclear decoupled ^{1}H NMR spectrum.

Table S2. Polymerization data for *ε*-CL using **1–8** as catalysts in the ratio 200:1 at 100 °C.

Entry	Catalyst	Time(min)^{a}	Conversion (%)^{b}	$M_n^{(Theo)c}$ (kg/mol)	$M_n^{(Expt)d}$ (kg/mol)	[$Đ$]^{e}
1	**1**	28	99	22.93	25.32	1.21
2	**2**	30	99	22.89	25.44	1.23
3	**3**	13	99	22.85	24.12	1.18
4	**4**	15	99	22.89	25.68	1.25
5	**5**	40	99	22.93	24.13	1.17
6	**6**	37	99	22.89	24.44	1.19
7	**7**	23	99	22.85	23.57	1.15
8	**8**	26	99	22.89	24.28	1.17

[a] Time of polymerization measured by quenching the polymerization reaction at maximum conversion. [b] Calculated from ^{1}H NMR spectrum. [c] M_n^{Theo} at maximum conversion = (200 × 114.14) × conversion + Mol $Wt_{end\ groups}$. [d] Measured by GPC

at 40 °C in THF relative to polystyrene standards with Mark–Houwink corrections; M_n^{Expt} = 0.56 M_n^{GPC} for ε-CL.[80] [e] Measured by GPC at 40 °C.

Table S3. ROCOP of CO_2 with CHO using **1-8** with [CHO]/[Cat]/[CoCat] = 1000:1:1[a]

Entry	Cat (C)	Cocat (Cocat)	Time (h)	Conversion (%)[b]	CO_2 (%)[c]	Polym (%)[d]	TON[e]	TOF[f] (h^{-1})	M_n[g] (kg mol^{-1})	[Đ][g]	Isolated PCHC(g)[h], (%)	*m*- centered tetrads[i] (%)
1	**5**	PPNCl	16	60	54	56	600	37	17.58	1.17	0.95 (24)	71
2	**5**	TPPCl	16	66	61	70	660	41	19.13	1.08	1.28 (32)	72
3	**5**	TBAB	16	62	56	62	620	39	15.11	1.28	0.96 (24)	71
4	**1**	TPPCl	48	20	30	10	200	04	16.89	1.21	0.26 (6)	69
5	**2**	TPPCl	48	22	28	12	220	05	12.09	1.09	0.24 (6)	70
6	**3**	TPPCl	48	25	32	15	250	05	17.00	1.20	0.29 (7)	68
7	**4**	TPPCl	48	21	25	20	210	04	11.64	1.09	0.19 (5)	69
8	**6**	TPPCl	16	68	62	72	680	42	11.90	1.10	1.32 (33)	75
9	**7**	TPPCl	14	70	56	68	700	50	19.79	1.11	1.13 (28)	74
10	**8**	TPPCl	14	69	52	62	690	49	13.91	1.19	0.99 (25)	74

[a] Reaction conditions: 80 °C, 40 bar of CO_2, neat CHO (4 g, 4.12ml). [b] % CHO conversion versus the theoretical maximum (100%), determined from the ^1H NMR spectrum by comparison of the relative integrals of the resonances which are assigned as the carbonate (4.65 ppm for PCHC and 4.00 ppm for *trans*-cyclic carbonate) and ether linkages (3.45 ppm) against CHO (3.00 ppm). [c] % CO_2 uptake versus the theoretical maximum (100%), determined from the ^1H NMR spectrum by comparison of the relative integrals of the resonances assigned to the carbonate (4.65 ppm for PCHC and 4.00 ppm for *trans*-cyclic carbonate) and ether (3.45 ppm) linkages. [d] % PCHC formation versus the theoretical maximum (100%), determined from the ^1H NMR spectrum by comparison of the relative integrals due to the PCHC (4.65 ppm) and *trans*-cyclic carbonate (4.00 ppm). [e] Turnover number (TON) = number of moles of CHO consumed/number of moles of catalyst. [f] Turnover frequency (TOF) = TON/time (h). [g] Determined by GPC, in THF with calibration using narrow-M_n polystyrene standards. [h] Amount of PCHC collected (% PCHC relative to CHO used = wt. PCHC (g)/4 x 100). [i] determined by ^{13}C NMR spectroscopy ($CDCl_3$, 125 MHz).

Table S4. ROCOP of CO_2 with PO using **1-8** with [PO]/[C]/[TPPCl] = 1000:1:1[a]

Entry	Cat (C)	Time (h)	Conversion(%)[b]	CO_2 (%)[c]	Polym (%)[d]	TON[e]	TOF[f] (h^{-1})	M_n[g](kg/mol)	[Đ][g]	Isolated PPC(g)[h], (%)
1	5	14	82	63	51	820	59	11.18	1.15	0.20 (7)
2	5	14	87	68	44	870	62	11.59	1.09	0.21 (7)
3	1	18	68	70	48	680	38	12.13	1.08	0.18 (6)
4	2	18	70	72	49	700	39	15.61	1.12	0.20 (7)
5	3	18	76	77	44	760	42	13.19	1.31	0.21 (7)
6	4	18	75	72	45	750	42	12.87	1.28	0.21 (7)
7	6	14	78	70	61	780	43	16.28	1.20	0.28 (9)
8	7	14	80	72	54	800	45	13.55	1.22	0.22 (7)
9	8	14	80	70	55	800	45	12.97	1.25	0.23 (8)

[a] Reaction conditions: 40 °C, 60 bar of CO_2, neat PO (3 g, 2.20ml). . [b] % of PO conversion determined from the relative integrals in the ^1H NMR spectrum of PPC (poly(propylenecarbonate)) (4.92 ppm, 1H), PC (propylene carbonate) (4.77 ppm, 1H), and PPO (3.46−3.64 ppm, 3H). [c] % of CO_2 selectivity determined by the relative integrals in the ^1H NMR spectrum of PPC (4.92 ppm, 1H) and PC (4.77 ppm, 1H) compared with PPO (3.46−3.64 ppm, 3H). [d] Polymer selectivity determined by the relative integrals in the ^1H NMR spectra of PPC (4.92 ppm, 1H) against PC (4.77 ppm, 1H). [e] Turnover number (TON) = number of moles of PO consumed/ number of moles catalyst. [f] Turnover frequency (TOF) = TON/time(h).

[g] Determined by GPC, in THF with calibration using narrow-M_n polystyrene standards. [h] Amount of PPC collected (% PPC relative to PO used = wt. PPC (g)/3 x 100).

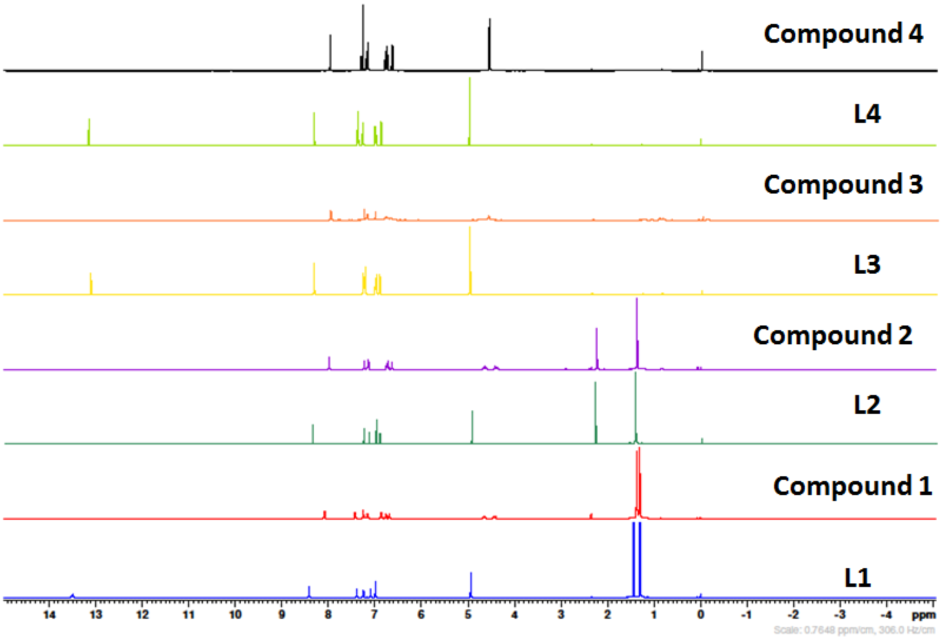


Fig. S1. Stacked ^1H NMR of ligands and compound **1-4**.

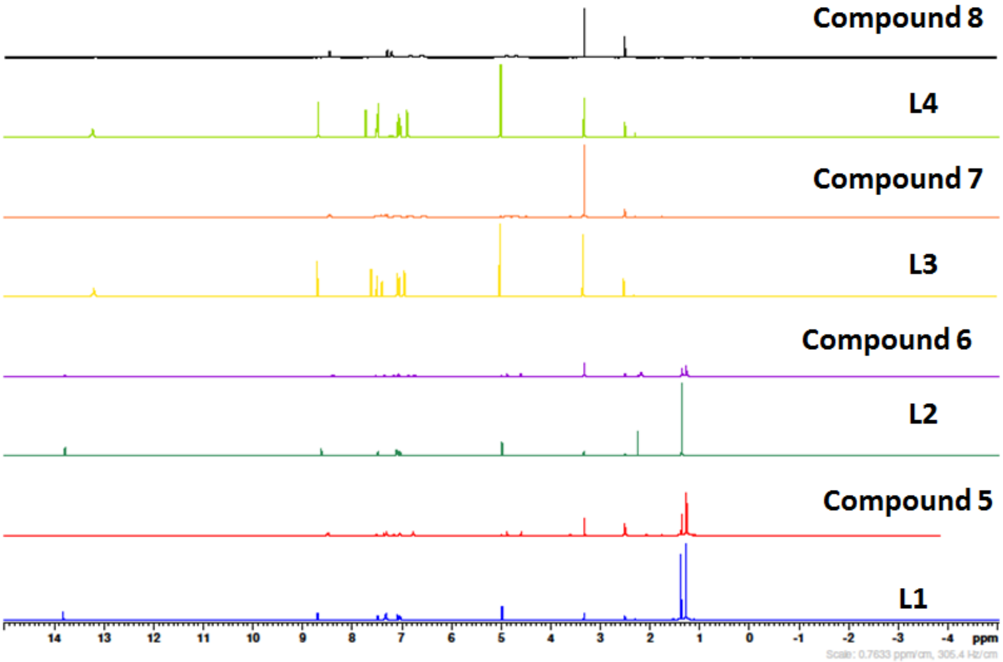


Fig. S2. Stacked ^1H NMR of ligands and compound **5-8**.

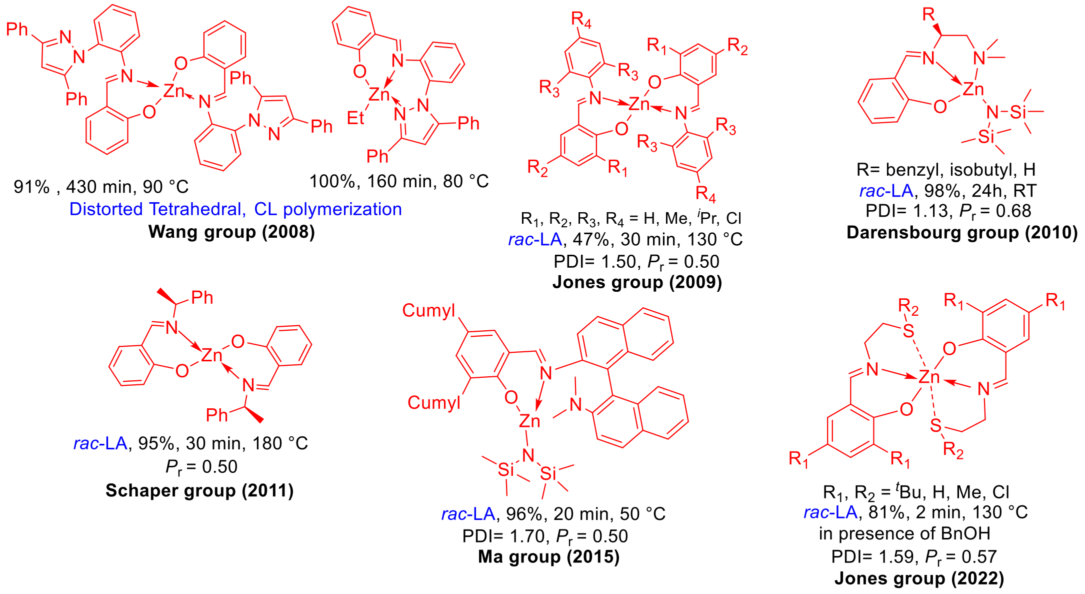


Fig. S3. Bidentate and tridentate imino-phenolate zinc compounds reported by different research groups.

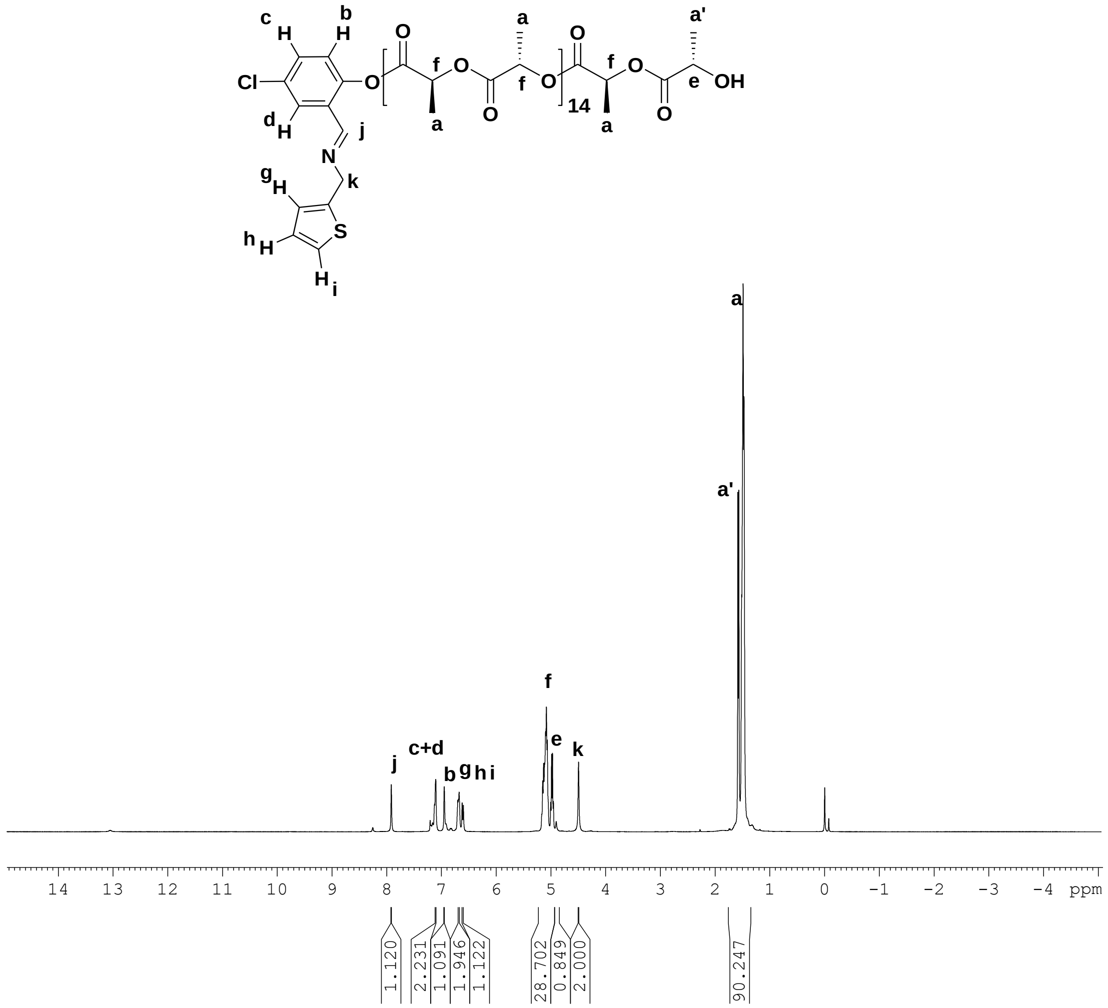
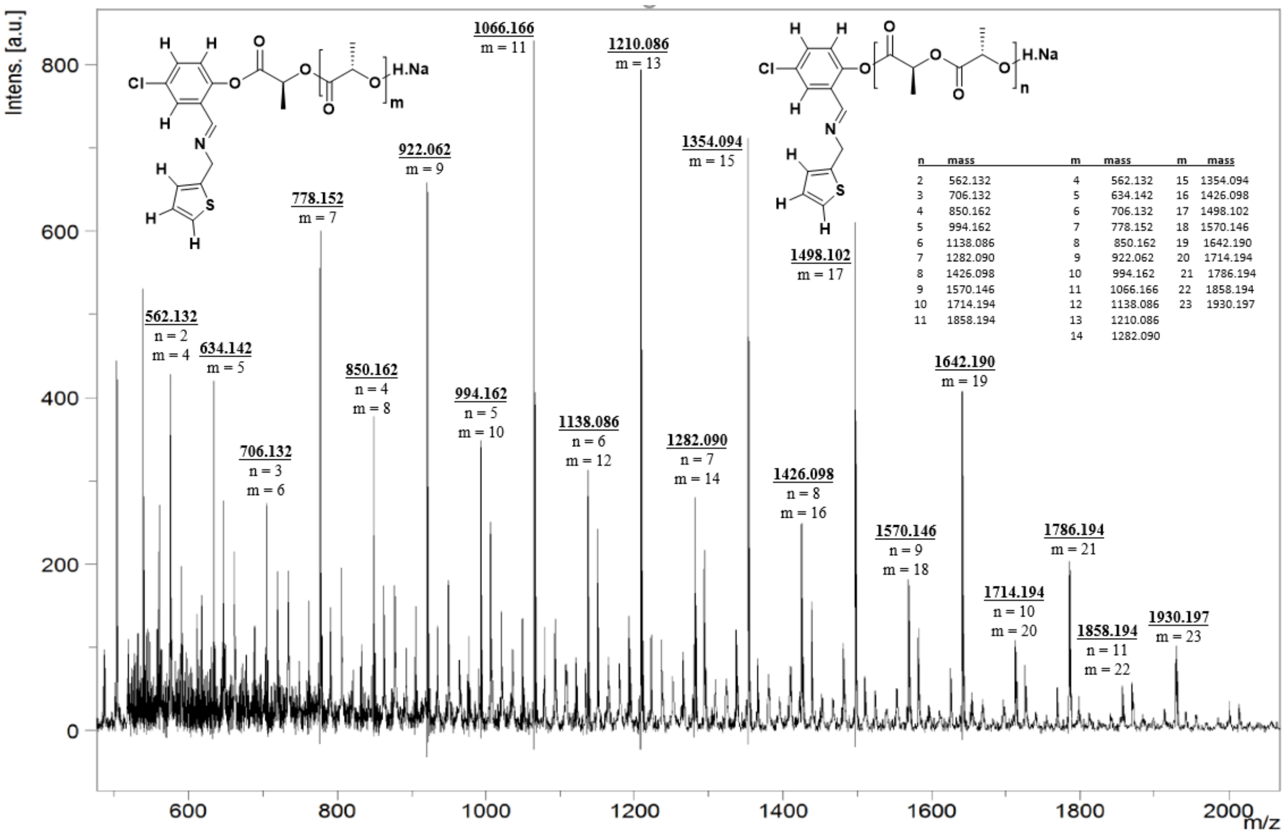


Fig. S4. ^{1}H NMR spectrum of the crude product of *rac*-LA and **7** in the ratio of 15:1.



n	mass	m	mass	m	mass
2	562.132	4	562.132	15	1354.094
3	706.132	5	634.142	16	1426.098
4	850.162	6	706.132	17	1498.102
5	994.162	7	778.152	18	1570.146
6	1138.086	8	850.162	19	1642.190
7	1282.090	9	922.062	20	1714.194
8	1426.098	10	994.162	21	1786.194
9	1570.146	11	1066.166	22	1858.194
10	1714.194	12	1138.086	23	1930.197
11	1858.194	13	1210.086		
		14	1282.090		

Fig. S5. MALDI-TOF spectrum of the oligomer of *rac*-LA and **7** in the ratio of 15:1.