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Supporting Information

Towards New Robust Zn(II) Complexes for the Ring-Opening Polymerization of Lactide Under Industrially Relevant Conditions

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Table S1. Crystallographic data of **1** and **5**.

	1	**5**
CCDC	1901404	1901405
formula	$C_{30}H_{36}N_4O_{10}Zn_2$	$C_{40}H_{40}N_4O_{10}Zn_2$
sum formula	$C_{30}H_{36}N_4O_{10}Zn_2$	$C_{40}H_{40}N_4O_{10}Zn_2$
M/ g mol^{-1}	743.41	867.50
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
crystal description	colourless plate	colourless plate
a/ Å	9.4692(4)	16.9724(5)
b/ Å	13.2391(6)	14.5261(5)
c/ Å	13.1893(6)	17.2695(6)
α/ °	96.547(4)	90
β/ °	93.463(3)	115.352(2)
γ/ °	106.449(4)	90
V/ Å^3	1567.97(13)	3847.6(2)
Z	2	4
ρ_{calcd}/ g cm^{-3}	1.575	1.498
μ/ mm^{-1}	1.593	1.311
crystal size/ mm	0.136×0.050×0.046	0.120×0.106×0.075
F(000)	768	1792
T/ K	133(2)	133(2)
λ/ Å	Mo-K_α 0.71073	Mo-K_α 0.71073
Θ range/ °	2.09–28.47	1.9–28.1
Reflns. collected	8917	22994
Indep. reflns.(R_{int})	7320 (0.071)	8714 (0.033)
Parameters	415	505
$R1$ (all data)	0.0464	0.0295
$wR2$	0.1134	0.0662
GooF	0.89	0.94

Table S2. Selected bond lengths/ Å of **1** and **5**.

	Zn–N_{py}	Zn–N_{ax}	Zn–O_{ax}	Zn–O53	Zn2–O51	Zn1–O52	O51–C51	O52–C51	O53–C53	O54–C53
1	2.134(3) 2.159(3)	2.031(3) 2.021(3)	2.059(3) 2.054(3)	2.024(3) 2.035(3)	2.031(3)	1.978(3)	1.257(5)	1.270(5)	1.311(5)	1.222(5)
5	2.1189(11) 2.1662(19)	2.0330(15) 2.0424(16)	2.0435(15) 2.0500(16)	2.0396(13) 2.0499(13)	2.0086(16)	1.9708(15)	1.250(2)	1.263(2)	1.307(2)	1.221(2)

Table S3. Hydrogen bonds and angles of **1** and **5**.

		D–H/Å	H···A/Å	D···A/Å	D–H···A/°
1	C14–H14···O54[a]	0.95	2.34	3.140(5)	142
5	C13–H13···O33[b]	0.95	2.43	3.287(3)	150
	C14–H14···O54[b]	0.95	2.43	3.309(3)	154
	C27–H27A···O32[c]	0.99	2.57	3.205(3)	122
	C33–H33···O54[d]	0.95	2.46	3.175(3)	132
	C44–H44···O51[e]	0.95	2.50	3.393(3)	157
	C52–H52B···O12[f]	0.98	2.52	3.454(3)	160

a: −1+x, y, z; b: x, 1/2−y, 1/2+z; c: 1+x, y, 1+z; d: 2−x, −y, 1−z; e: 1−x, −y, 1−z; f: 2−x, −y, 2−z.

Table S4. Summary of the C–H···π interactions of **1** and **5**.

		C_g	H···C_g/Å	X–H···C_g/°	X···C_g/Å
1	C6–H6B	Zn2–N31–C35–C36–N32[a]	2.769	147	3.626(4)
	C36–H36A	Zn1–N11_C15–C16–N12[b]	2.95	135	3.718(4)
	C42–H42B	Zn2–O31–C39–C38–C37–N32[c]	2.68	138	3.479(5)
5	C32–H32	C20–C21–C22–C23–C24–C25[d]	2.67	142	3.467(2)
	C16–H16B	Zn1–O11–C19–C18–C17–N12[e]	2.48	153	3.388(2)
	C44–H44	Zn2–O31–C39–C38–C37–N32[f]	2.85	126	3.493(2)

a: −1+x, y, z; b: 1+x, y, z; c: 2−x, −y, 1−z; d : x, y, z; e: 2−x, −y, 2−z; f: 1−x, −y, 1−z.

Table S5. Selected distances and angles of the π– π and M– π interactions of **1** and **5**. C_g(I) is the centroid of the ring number I, α is the dihedral angle between the rings, β is the angle between the vector C_g(I) → C_g(J) and the normal to ring I, γ is the angle between the vector C_g(I) → C_g(J) and the normal to ring J.

	C_g(I)	C_g(J)	C_g–C_g/Å	α/°	β/°	γ/°
1	N31–C31–C32–C33–C34–C35	N31–C31–C32–C33–C34–C35[a]	3.721(2)	0.00(19)	22.1	22.1
5	N31–C31–C32–C33–C34–C35	N31–C31–C32–C33–C34–C35[b]	3.4814(12)	0.00(10)	18.0	18.0

a: 2−x, −y, 2−z; b: 2−x, −y, 1−z.

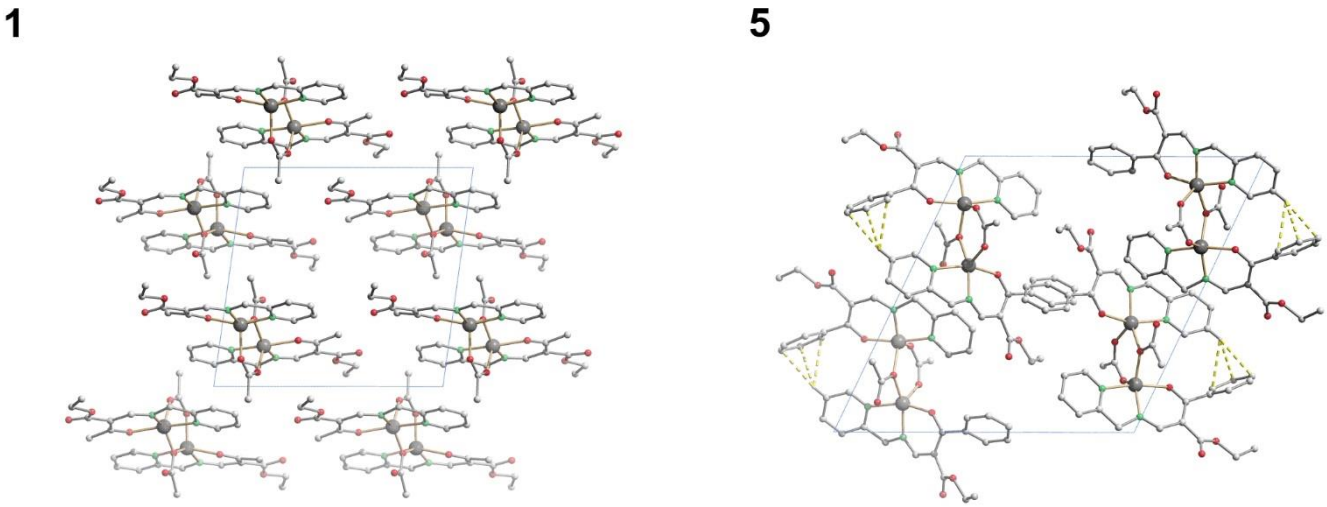


Figure S1. Molecular packing of **1** (left, along [100]) and **5** (right, along [010]). Discussed C–H···π interactions of **5** are drawn as yellow, dashed lines. Hydrogen atoms not involved in intermolecular interactions were omitted for clarity.

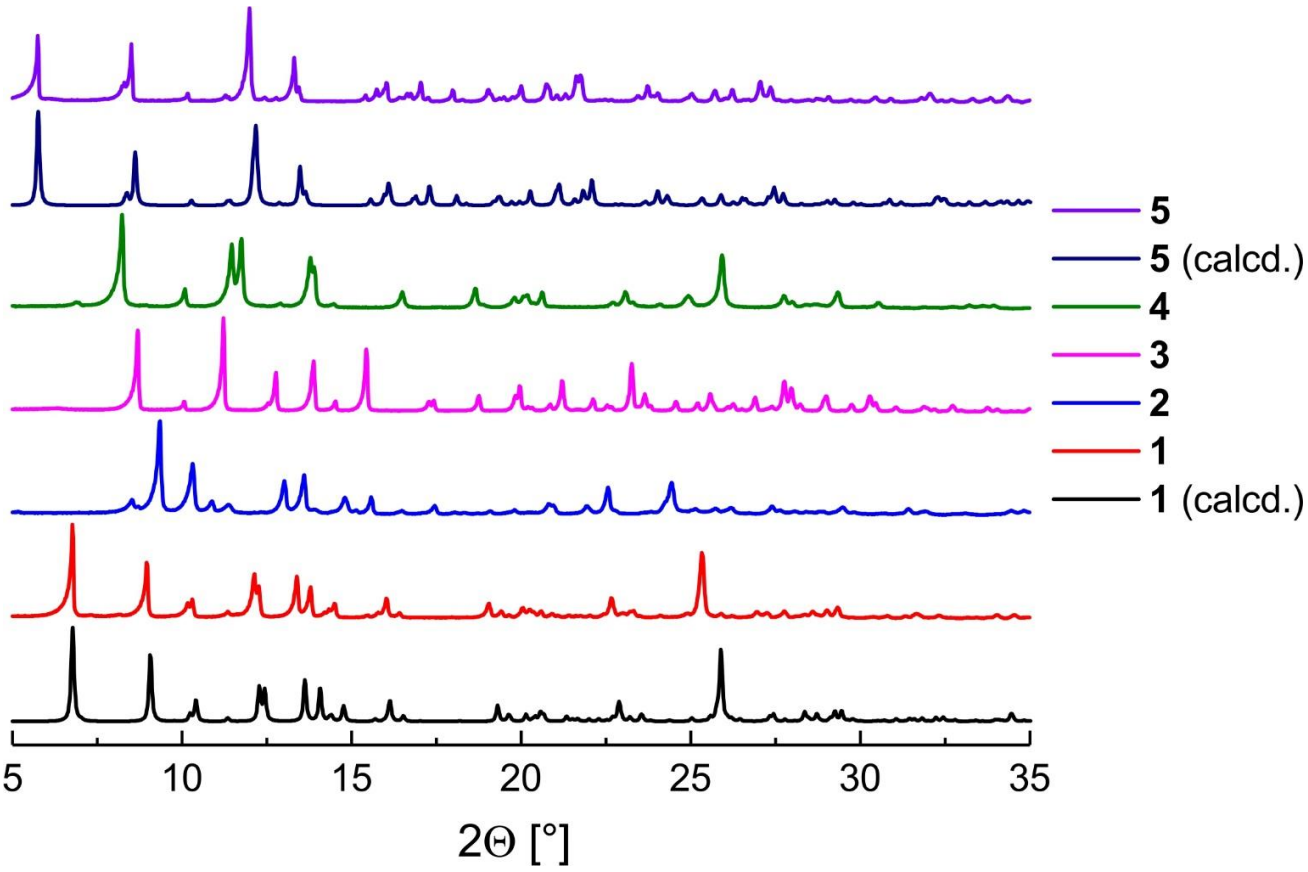


Figure S2. Powder X-ray diffraction patterns of **1**–**5**, measured and calculated. The calculated patterns were obtained at 133 K, the measured ones at room temperature.

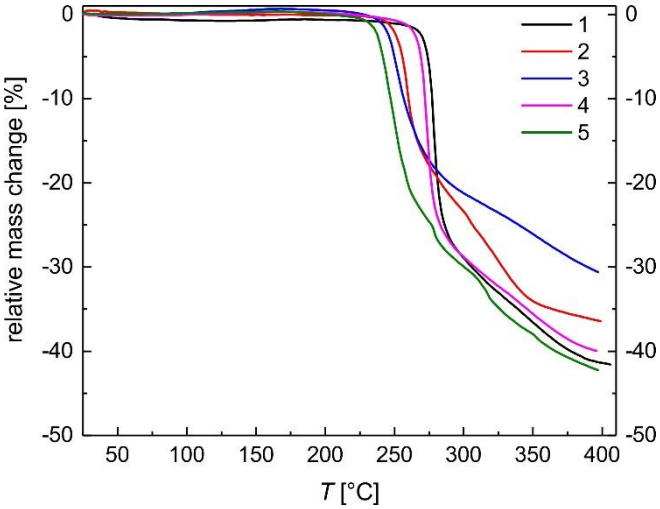


Figure S4. TGA measurements of complexes **1**–**5**.

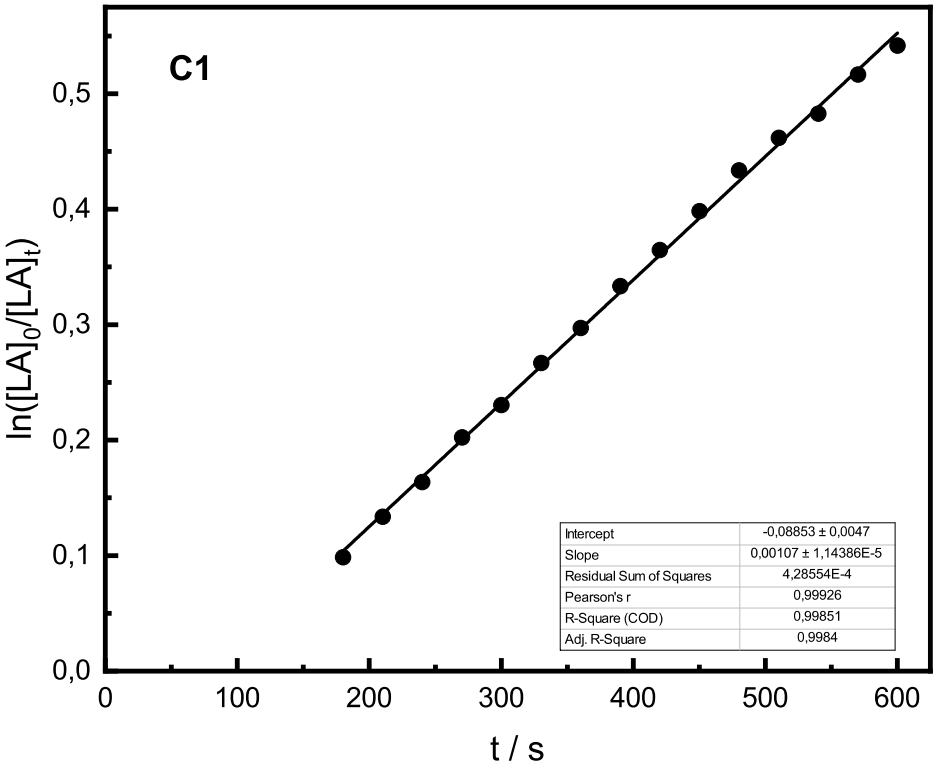


Figure S5. Semi-logarithmic plot of the polymerization of non-purified *rac*-LA with **1** [M]/[I] = 500:1, 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

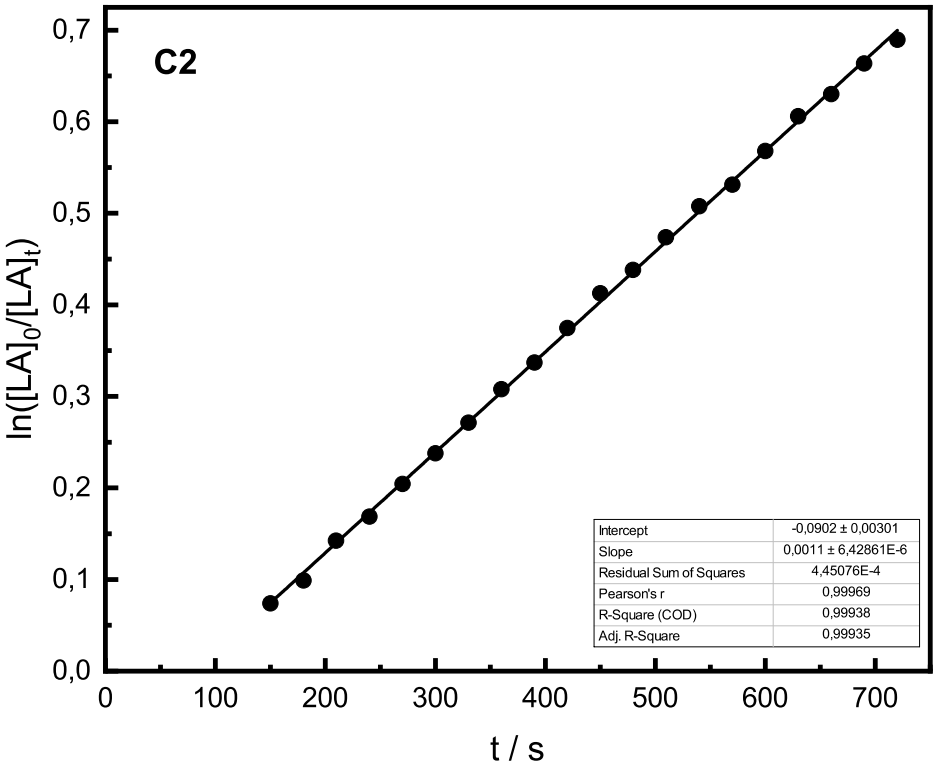


Figure S6. Semi-logarithmic plot of the polymerization of non-purified *rac*-LA with **2** [M]/[I] = 500:1, 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

Table S7. Polymerization data for *rac*-LA with catalyst **2**.

[M]/[I]	k_{app} (s^{-1})[b]	time (min)	conv. (%)[c]	$M_{n,theo}$ (g mol^{-1})	M_n (g mol^{-1})[d]	*PD*
500	1.14 x 10^{-3}	25	62	45 000	65 000	1.5
625	8.60 x 10^{-4}	30	78	70 000	54 000	1.8
1000	4.22 x 10^{-4}	27	65	94 000	81 000	1.4
1500	2.23 x 10^{-4}	61	57	123 000	43 000	1.8
2000	1.28 x 10^{-4}	112	56	161 000	21 000	2.2

[a] Conditions: 150 °C, solvent free, non-purified technical grade *rac*-LA. [b] Determined from the slope of the plots of $\ln([LA]_0/[LA]_t)$ versus time. [c] As determined by ^{1}H NMR spectroscopy. [d] Determined by GPC (in THF), $M_{n,theo}$: 72 000 g mol^{-1} for 100% conversion.

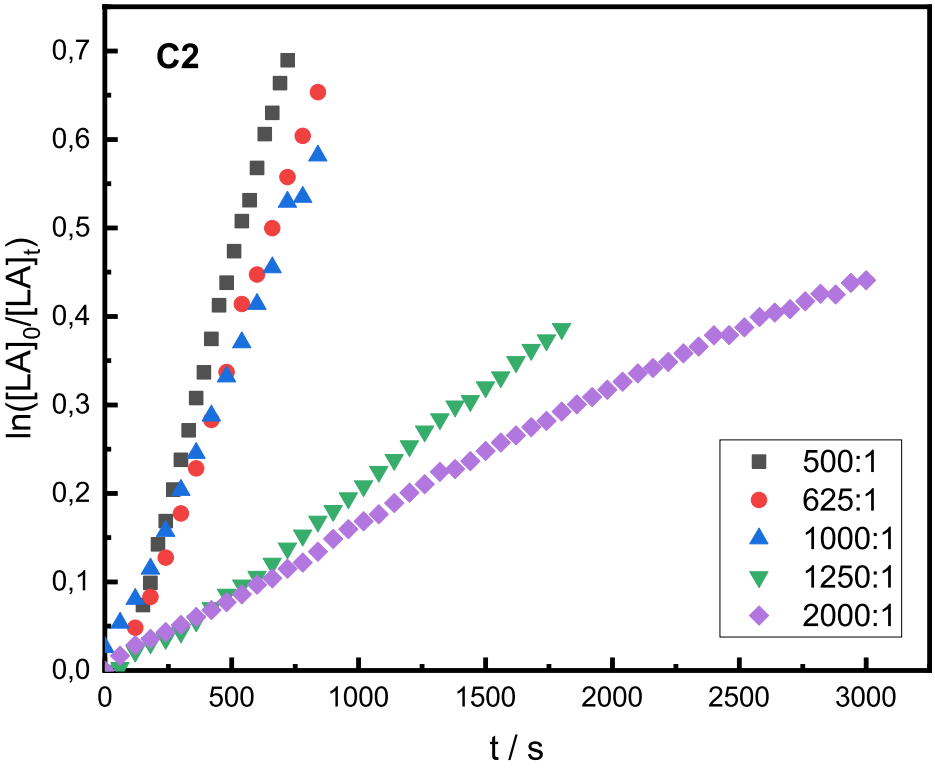


Figure S7. Semi-logarithmic plot of the polymerization of non-purified *rac*-LA with **2** [M]/[I] = 500:1 (k_{app} =), [M]/[I] = 625:1 (k_{app} =), [M]/[I] = 1000:1 (k_{app} =), [M]/[I] = 1250:1 (k_{app} =), [M]/[I] = 2000:1 (k_{app} =), 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

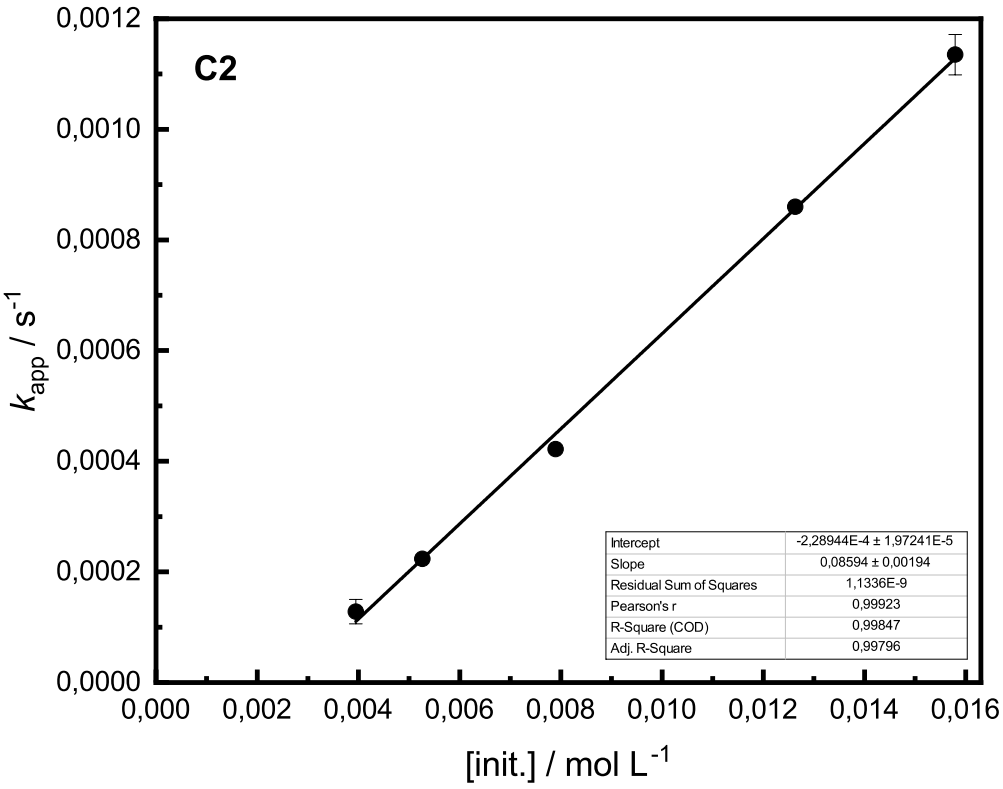


Figure S8. Plot of k_{app} versus [init.] for **2**. Conditions: rac-LA, 150 °C, 260 rpm, non-purified; [M]/[I] = 500:1, 625:1, 1000:1, 1500:1, 2000:1.

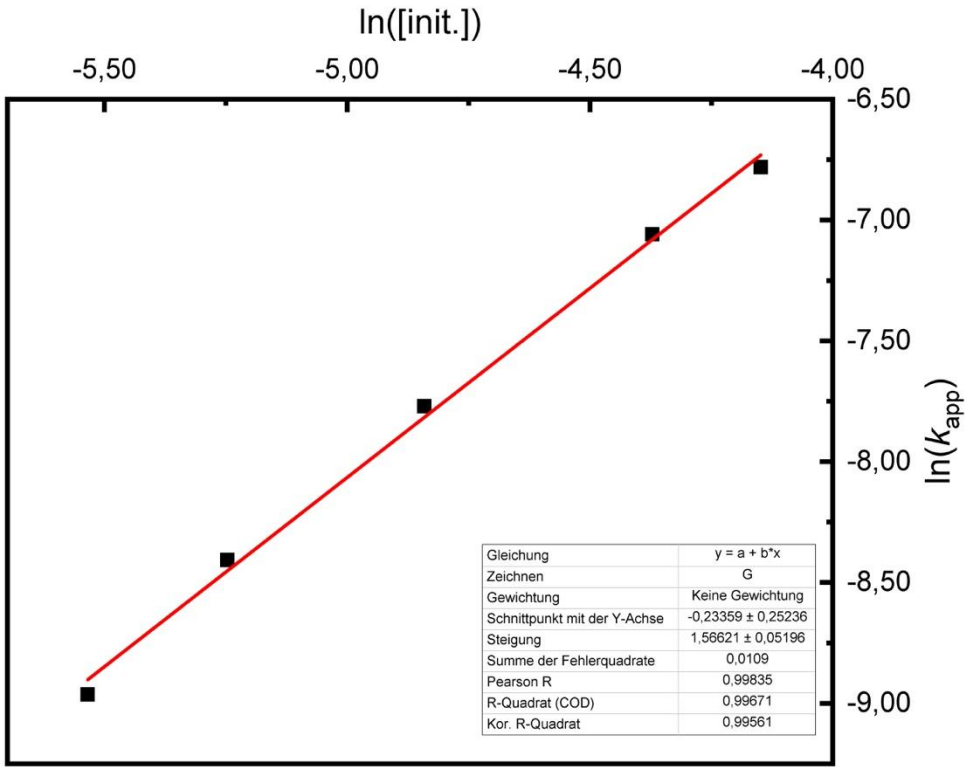


Figure S9. Logarithmic plot of ln(k_{app}) versus ln([init.]) for the polymerization of non-purified *rac*-LA with **4** [M]/[I] = 500:1, 150 °C, 260 rpm.

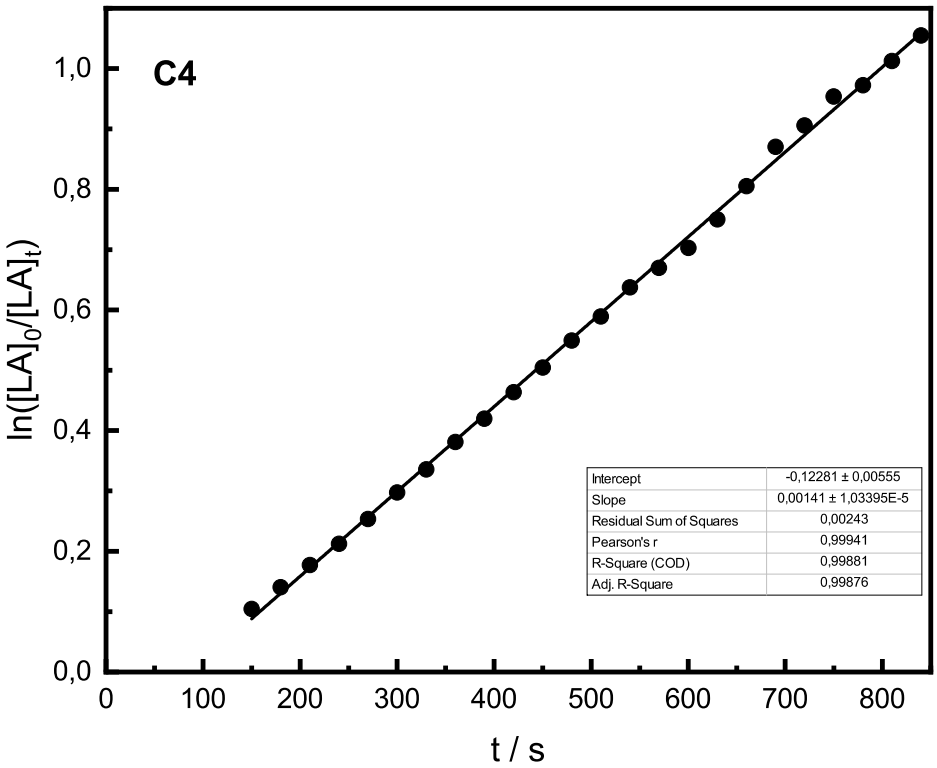


Figure S10. Semi-logarithmic plot of the polymerization of non-purified *rac*-LA with **4** [M]/[I] = 500:1, 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

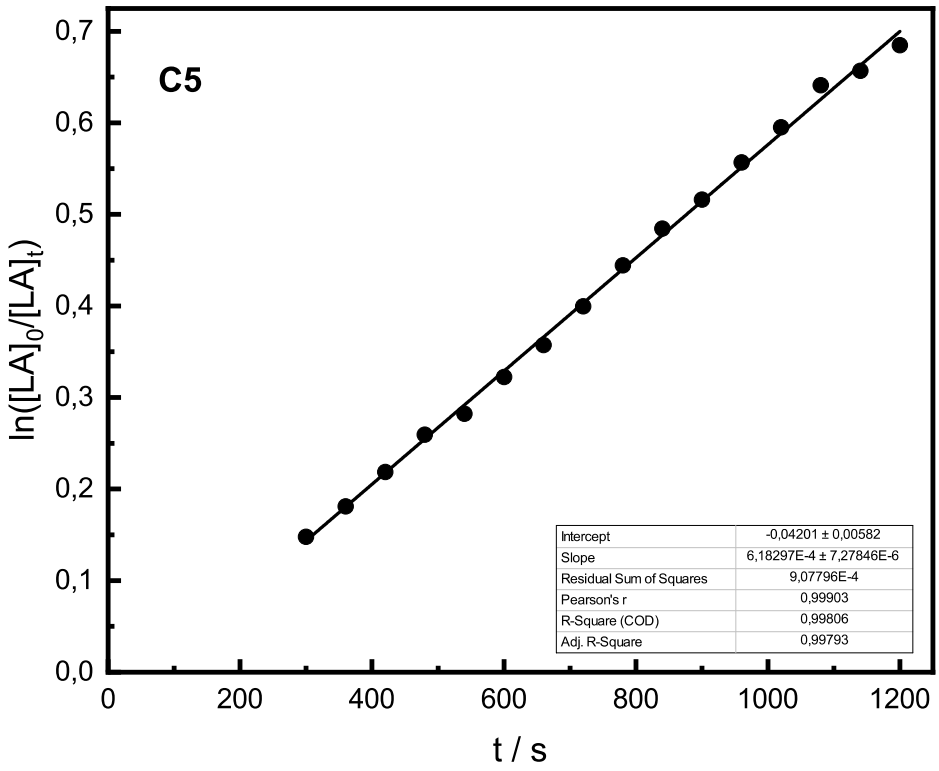


Figure S11. Semi-logarithmic plot of the polymerization of non-purified *rac*-LA with **5** [M]/[I] = 500:1, 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

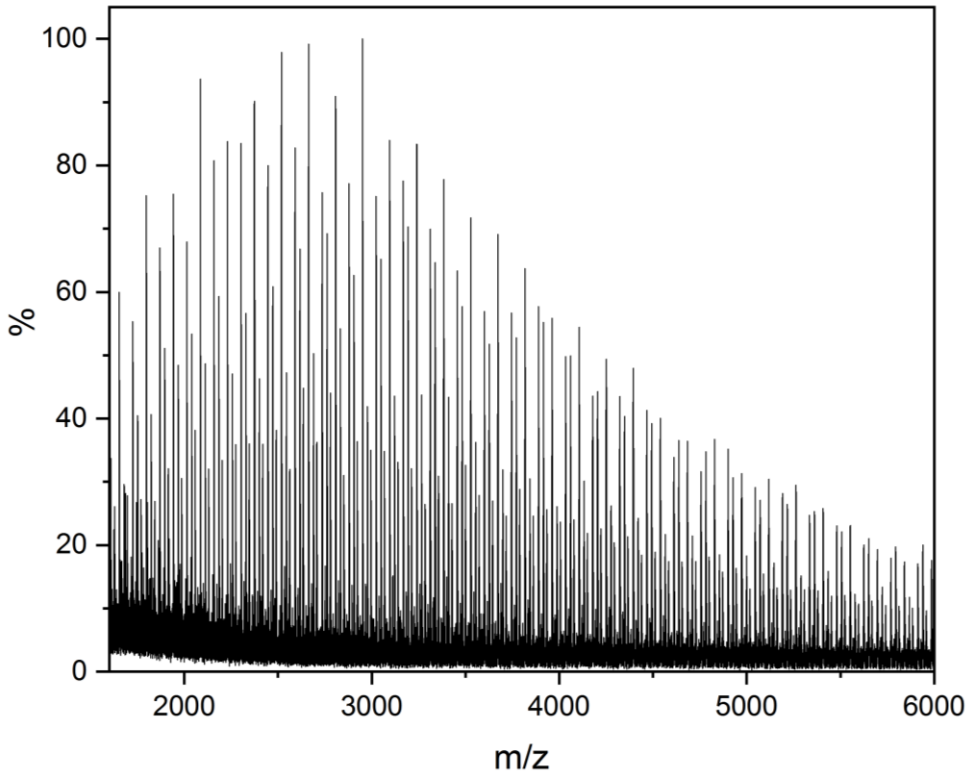


Figure S12. Stack of MALDI-ToF spectra obtained for a polymerisation with **4** [M]/[I] = 70:1, 150 °C, 260 rpm, *rac*-LA.

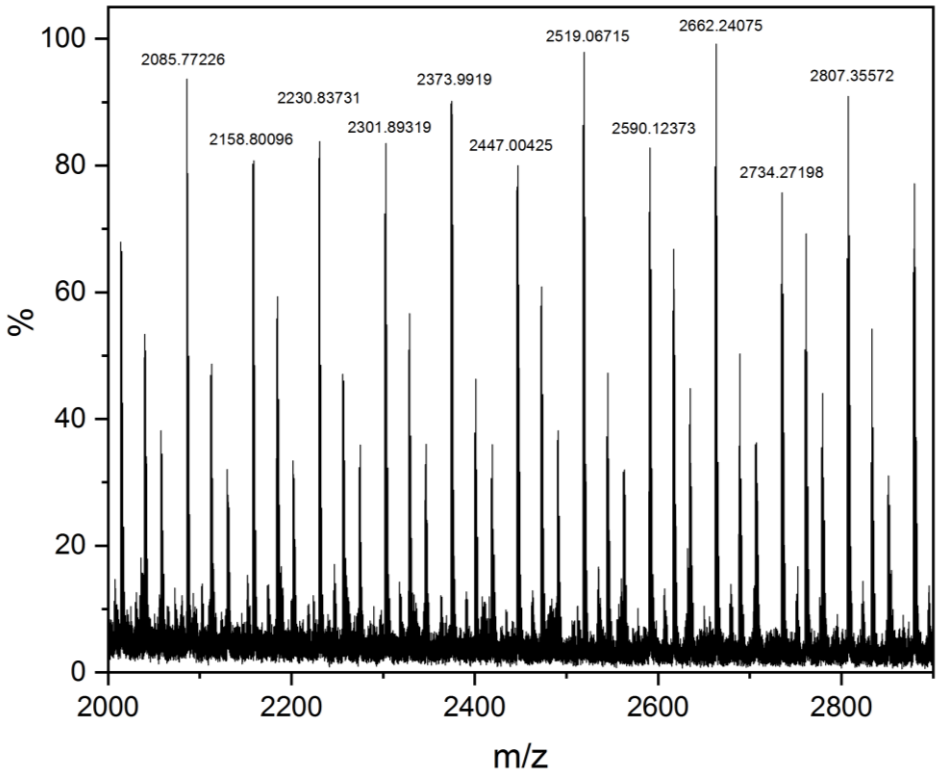


Figure S13. Stack of MALDI-ToF spectra obtained for a polymerisation with **4** [M]/[I] = 70:1, 150 °C, 260 rpm, *rac*-LA. For m/z 2807.35572:

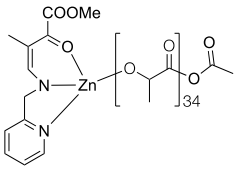
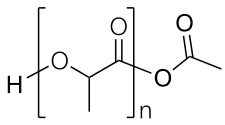
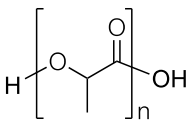
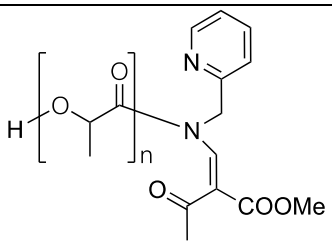
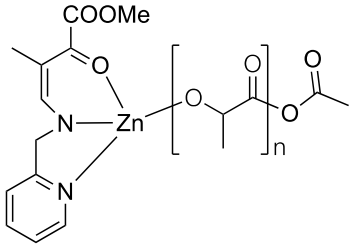
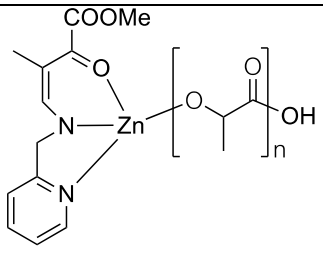
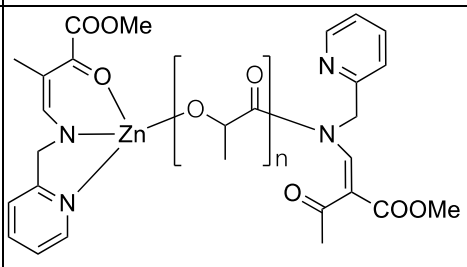


Table S8. Possible end-groups for the obtained polymer initiated by **4** [M]/[I] = 70:1, 150 °C, 260 rpm, *rac*-LA.

Results of the MALDI-ToF analysis for all series of the spectrum:

Ligand-Zn-PLA:	26.77%
Ligand-PLA:	10.59%
Acetate-PLA:	22.94%
OH:	10.53%
H:	17.29%

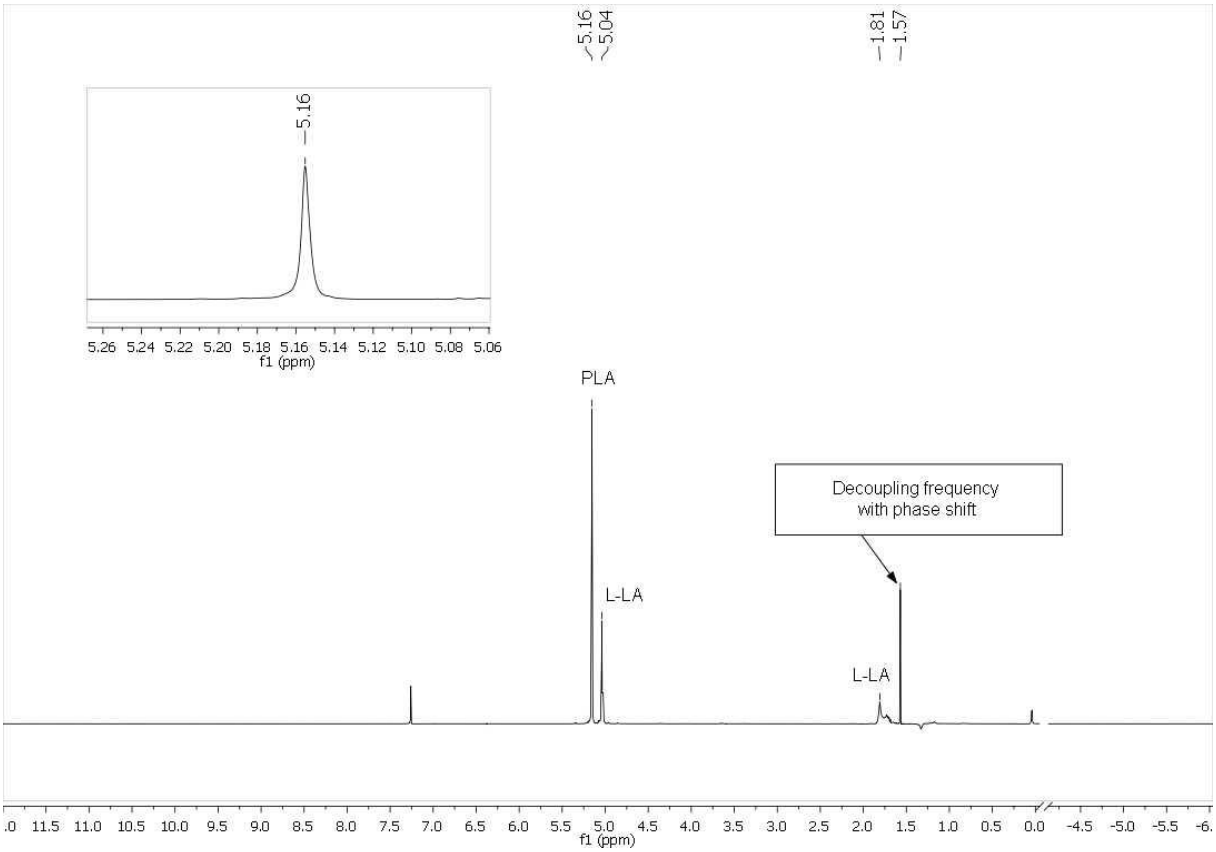


Figure S14. Homonuclear decoupled ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of PLA prepared by polymerization of L-lactide with **2** at 150 °C.