Electronic Supporting Information for

Zinc and Magnesium Complexes Supported by Bulky Multidentate Amino-Ether Phenolate Ligands: Potent Pre-Catalysts for the Immortal Ring-Opening Polymerisation of Cyclic Esters

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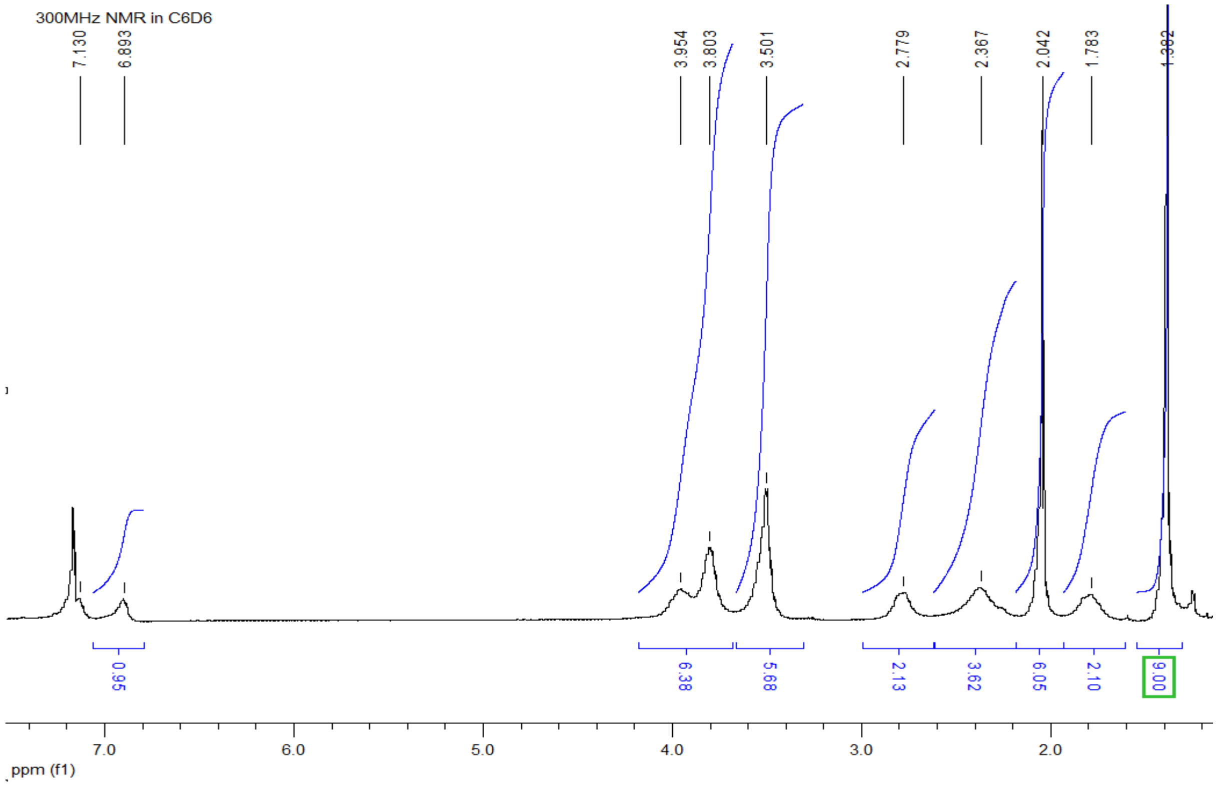


Figure S1: ^{1}H NMR spectrum of the product resulting from the reaction of {LO^{1}}Li and $Zn(OAc)_2$ (300.13 MHz, C_6D_6, 25 °C).

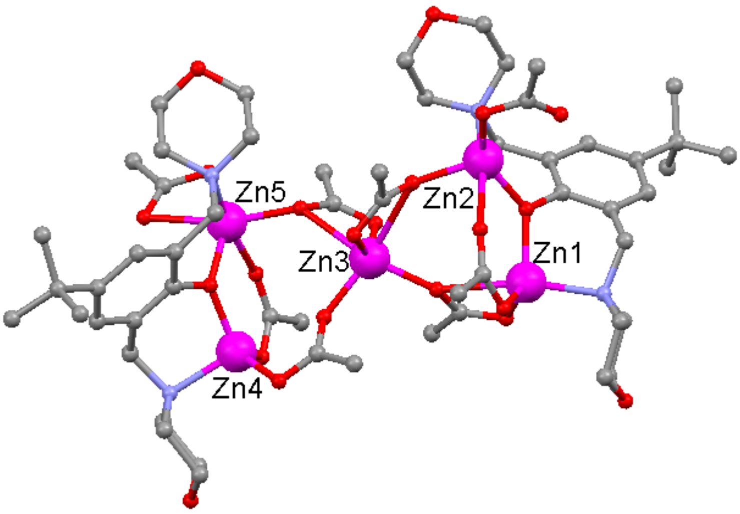


Figure S2: X-ray structure of $\{LO^1\}_2Zn_5(OAc)_8$ with atom labelling scheme. Hydrogen atoms and non-coordinated molecule of THF have been removed for the sake of clarity.

Table S1. Summary of crystal and refinement data for $\{LO^1\}_2Zn_5(OAc)_8 \cdot C_4H_8O$

Empirical formula	$C_{56}H_{88}N_4O_{22}Zn_5$, C_4H_8O
Formula weight	1568.26
Crystal system	triclinic
Space group	*P* -1
a, Å	13.7988(4)
b, Å	14.6192(4)
c, Å	18.6856(5)
α, deg	73.213(2)
β, deg	80.247(2)
γ, deg	85.375(2)
Volume, $Å^3$	3554.60(17)
Z	2
Density, $g.cm^{-3}$	1.465
Abs. coeff., mm^{-1}	1.737
F(000)	1636
Crystal size, mm	0.25 x 0.11 x 0.08
θ range, deg	2.94 to 27.71
Limiting indices	$-18 \leq h \leq 17$
	$-19 \leq k \leq 19$
	$-24 \leq l \leq 24$
*R*int	0
Reflec. collected	28712
Reflec. Unique [I>2σ(I)]	28712
Data/restraints/param.	28712 / 0 / 816
Goodness-of-fit on F^2	1.021
R_1 [I>2σ(I)] (all data)	0.0732 (0.1263)
wR_2 [I>2σ(I)] (all data)	0.186 (0.2211)
Largest diff. e A^{-3}	1.298 and −0.865

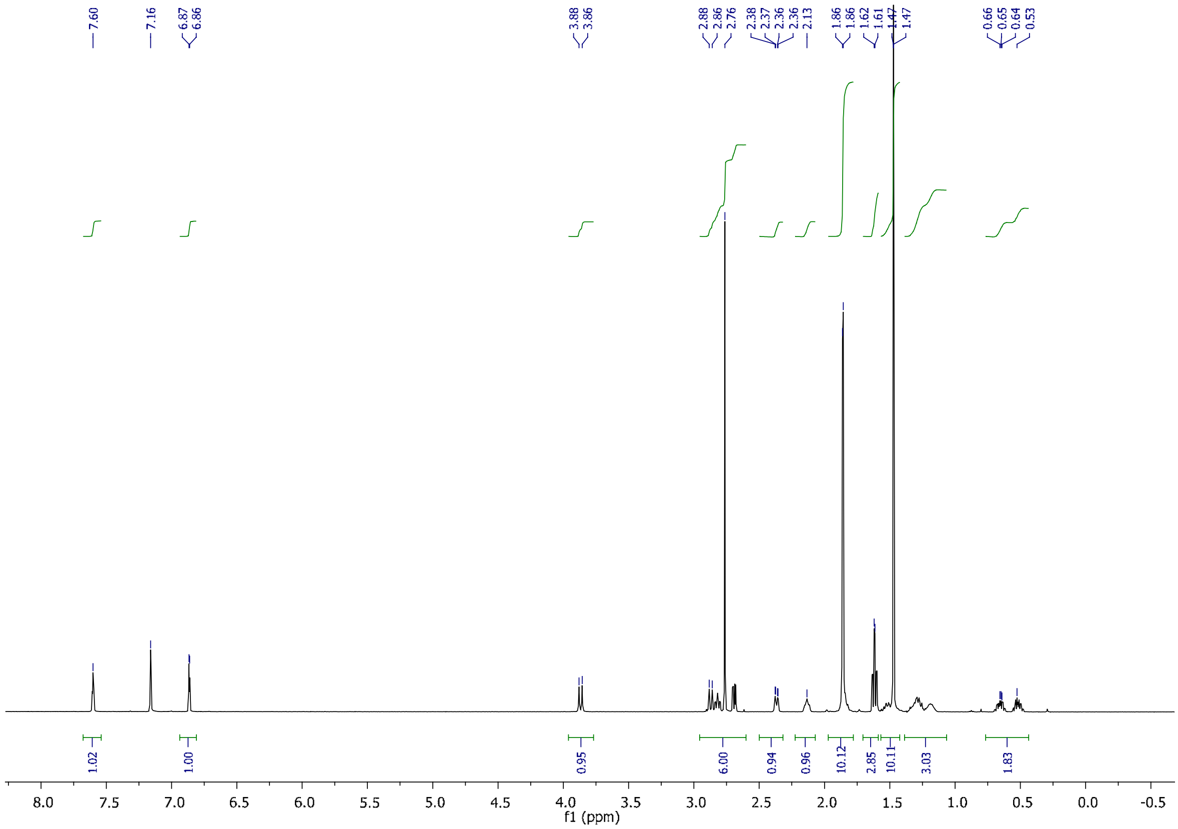


Figure S3: ^{1}H NMR spectrum of {LO^4}ZnEt (**6**) (500.13 MHz, C_6D_6, 25 °C).

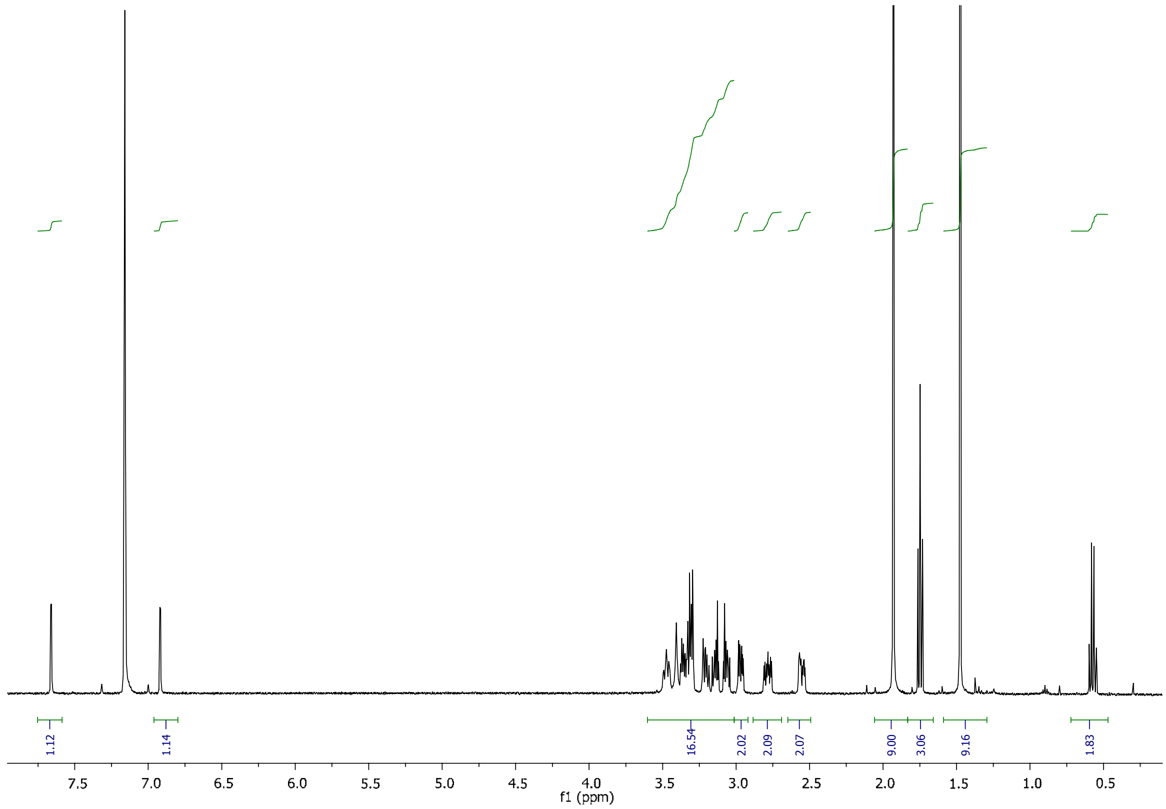


Figure S4: ^{1}H NMR spectrum of {LO^{3}}ZnEt (**7**) (500.13 MHz, C_6D_6, 25 °C).

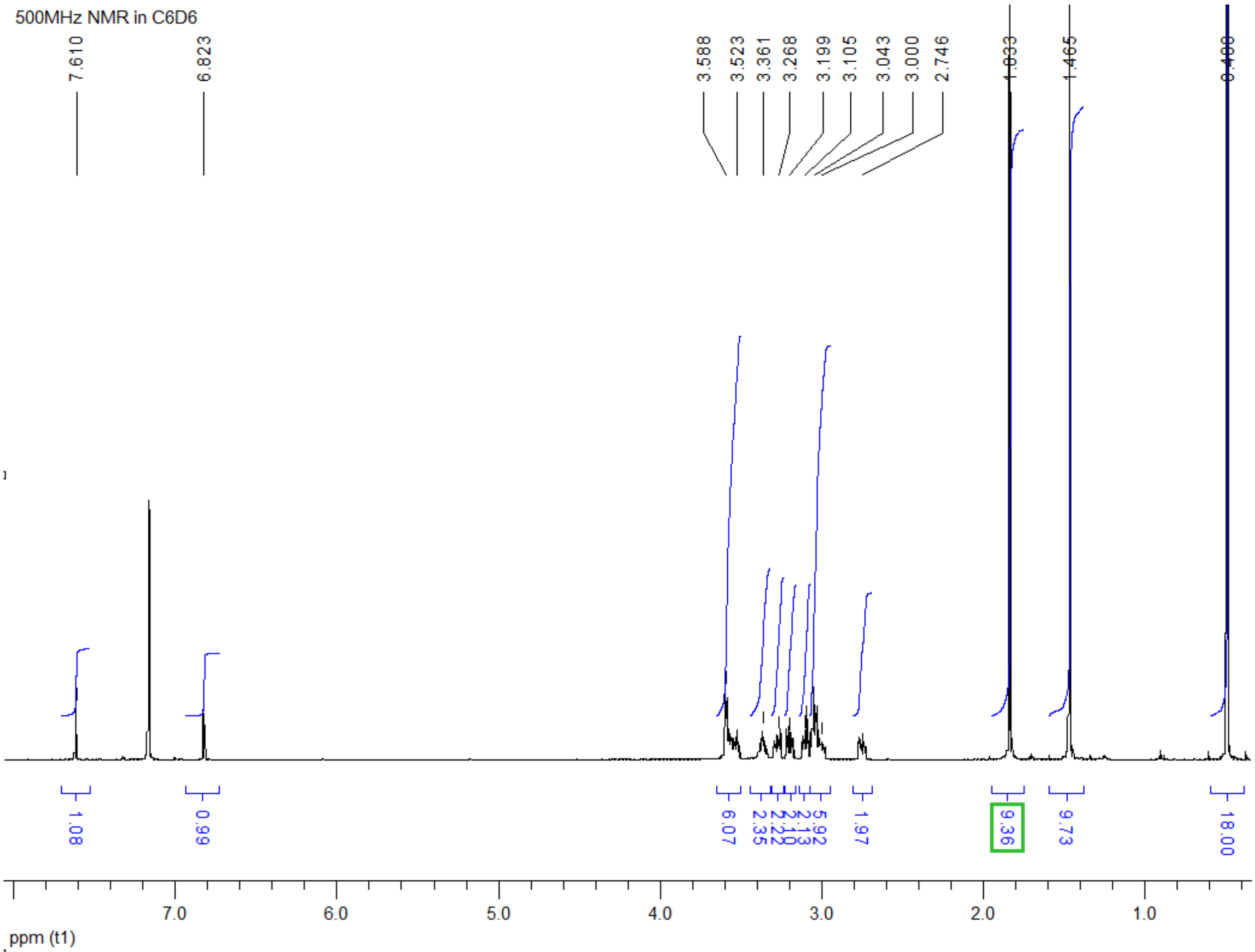


Figure S5: ^{1}H NMR spectrum of $\{LO^{3}\}ZnN(SiMe_3)_2$ (**8**) (500.13 MHz, C_6D_6, 25 °C).

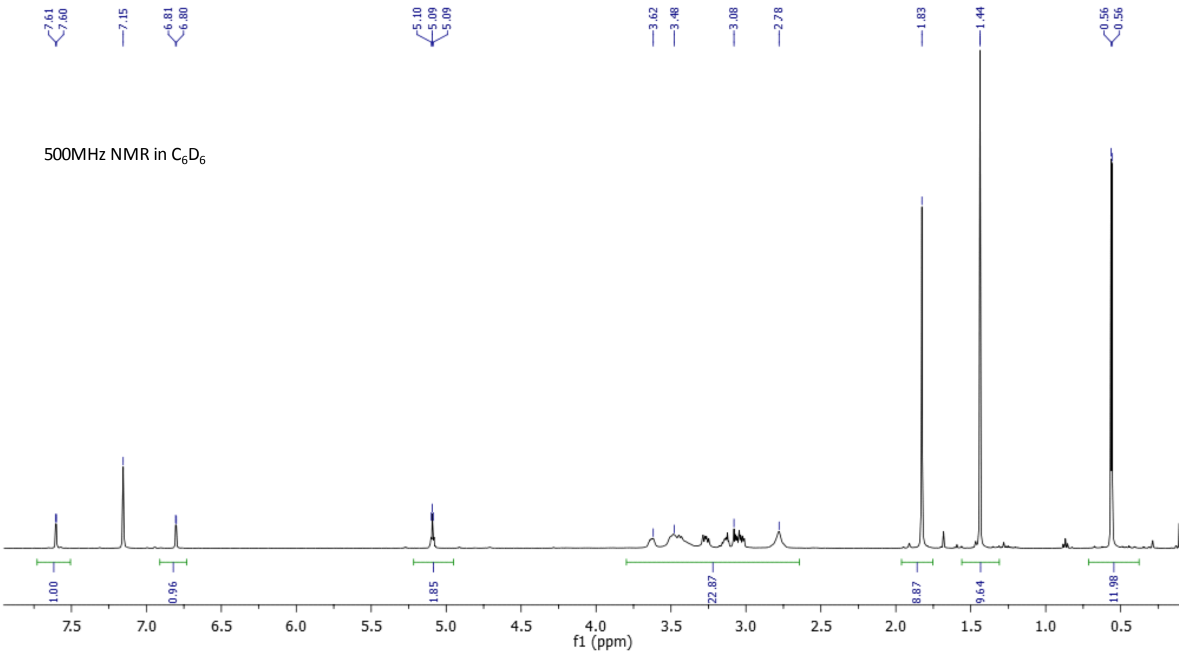


Figure S6: ^{1}H NMR spectrum of $\{LO^3\}ZnN(SiHMe_2)_2$ (**9**) (500.13 MHz, C_6D_6, 25 °C).

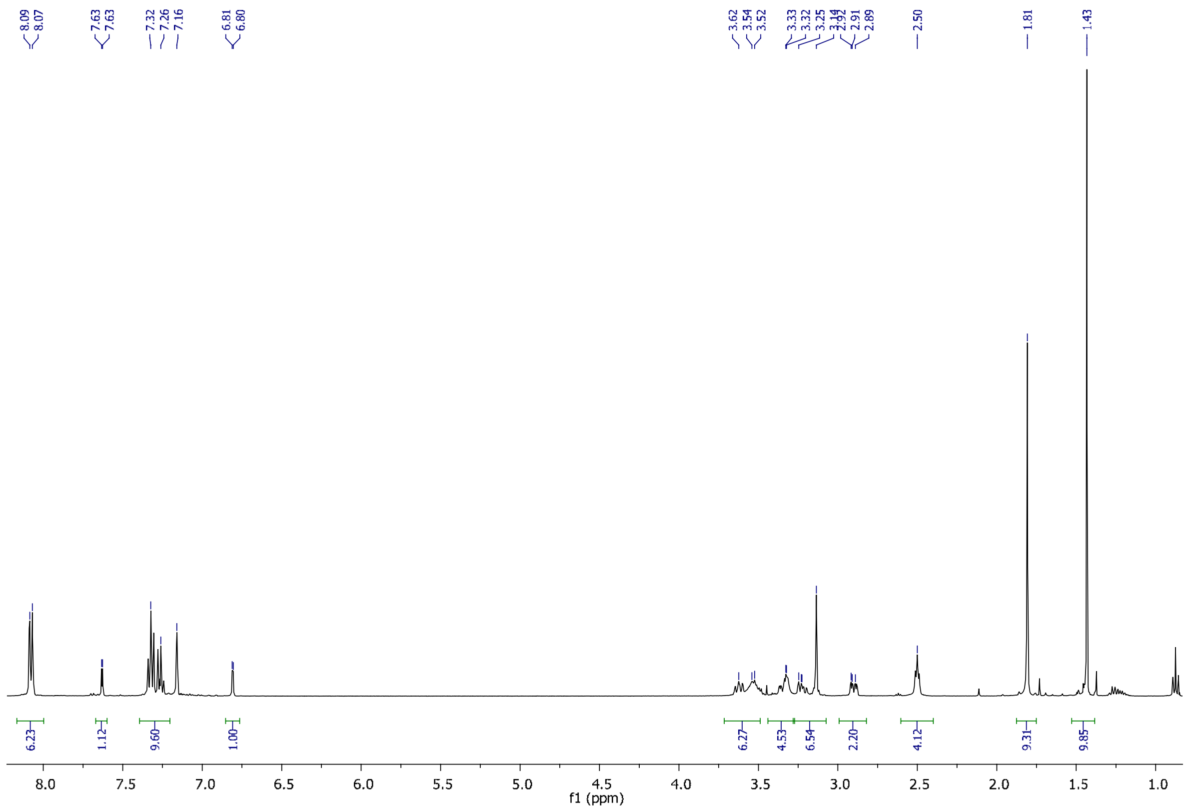


Figure S7: ^{1}H NMR spectrum of $\{LO^3\}ZnOSiPh_3$ (**10**) (400.13 MHz, C_6D_6, 25 °C).

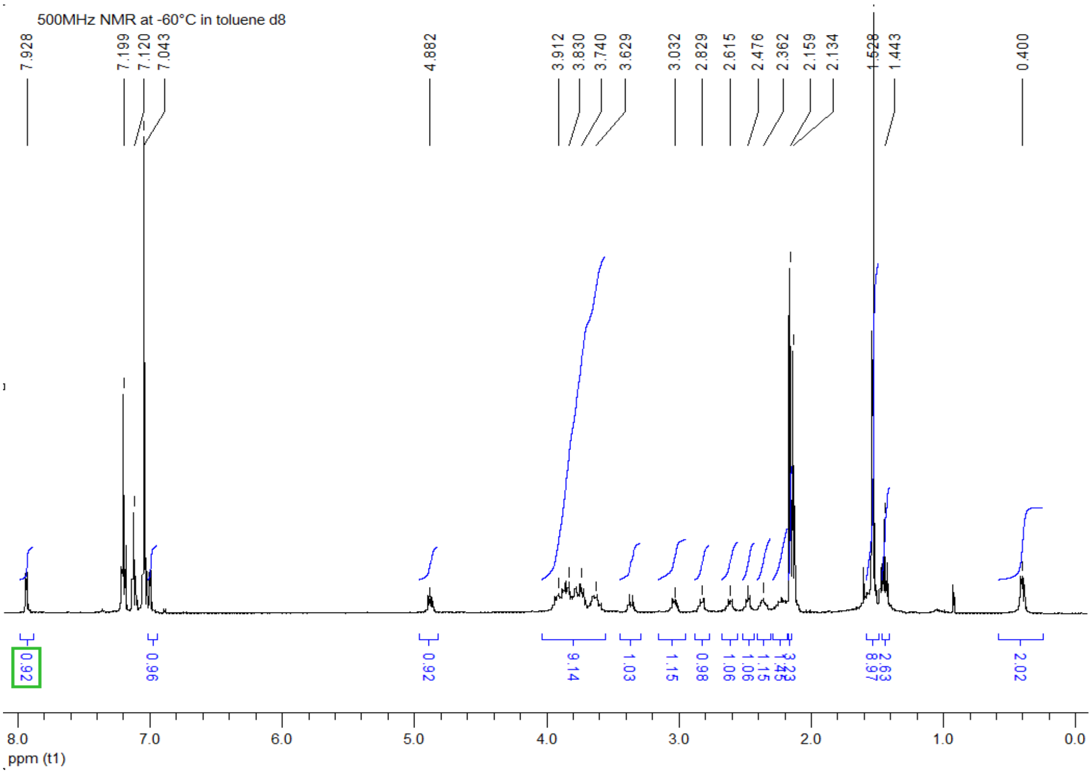


Figure S8: Low temperature ^{1}H NMR spectrum of {LO^{1}}ZnEt (**2**) (500.13 MHz, toluene-d_8, −60 °C).

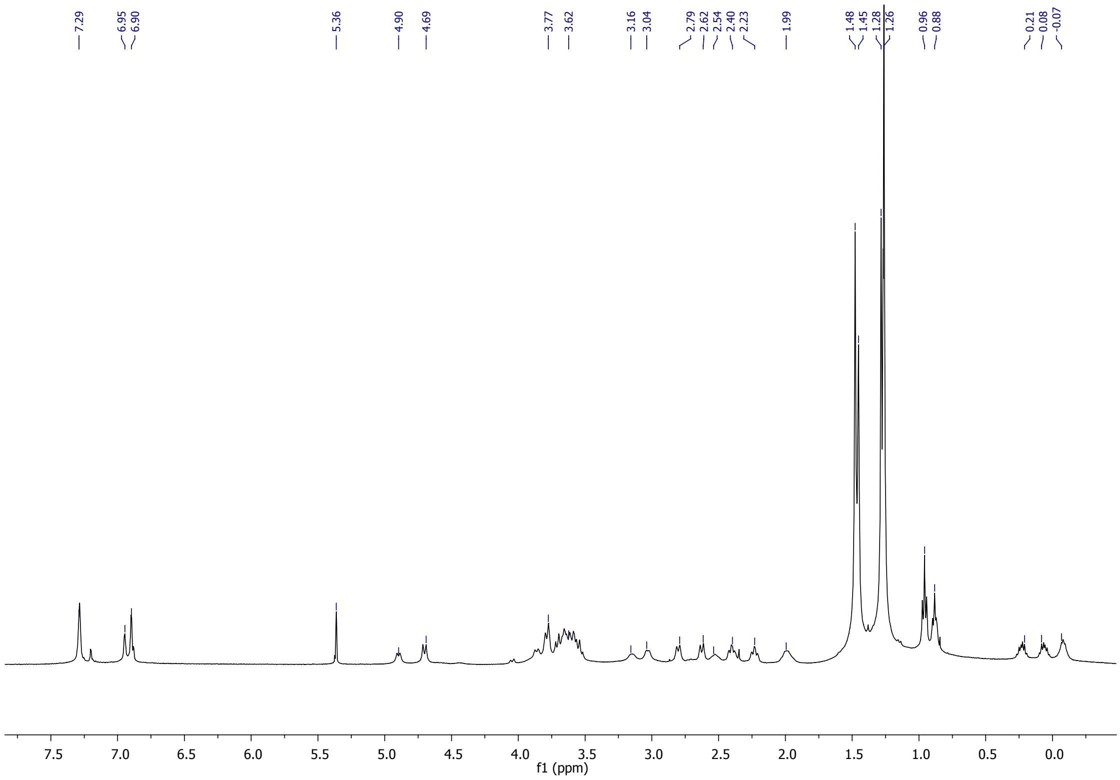


Figure S9: Low temperature ^{1}H NMR spectrum of {LO^{2}}ZnEt (**5**) (500.13 MHz, toluene-d_8, −60 °C).

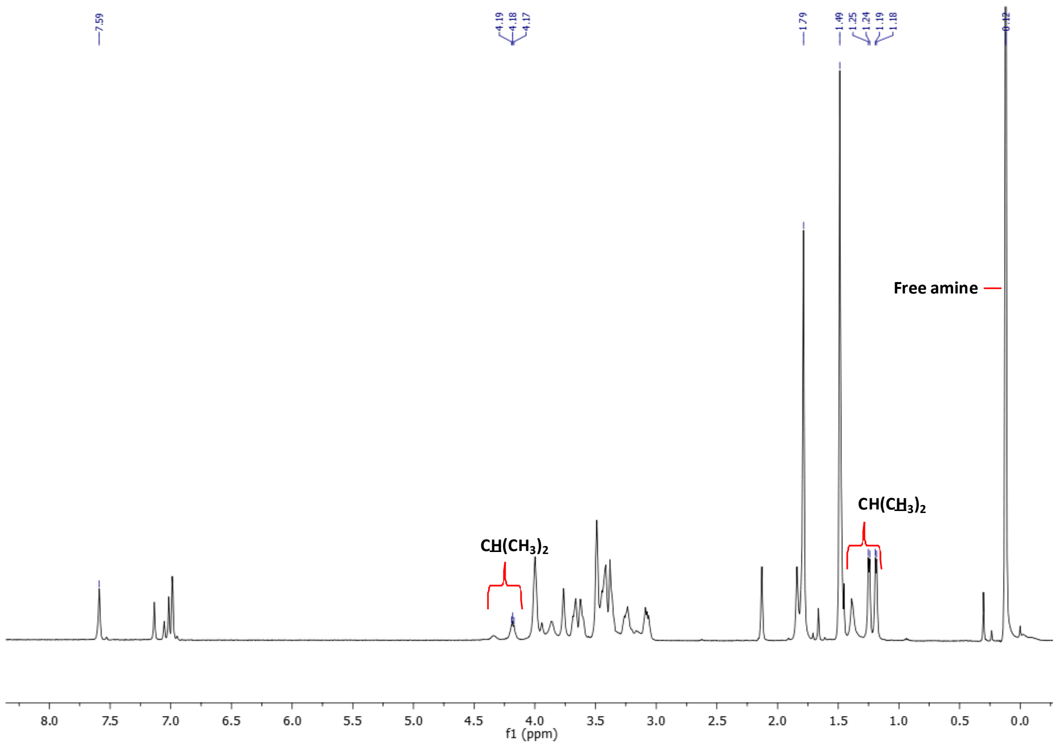


Figure S10: ^{1}H NMR spectrum of "{LO^3}ZnO^{i}Pr" generated *in-situ* by reaction of **8** and 1 equiv. of ^{i}PrOH

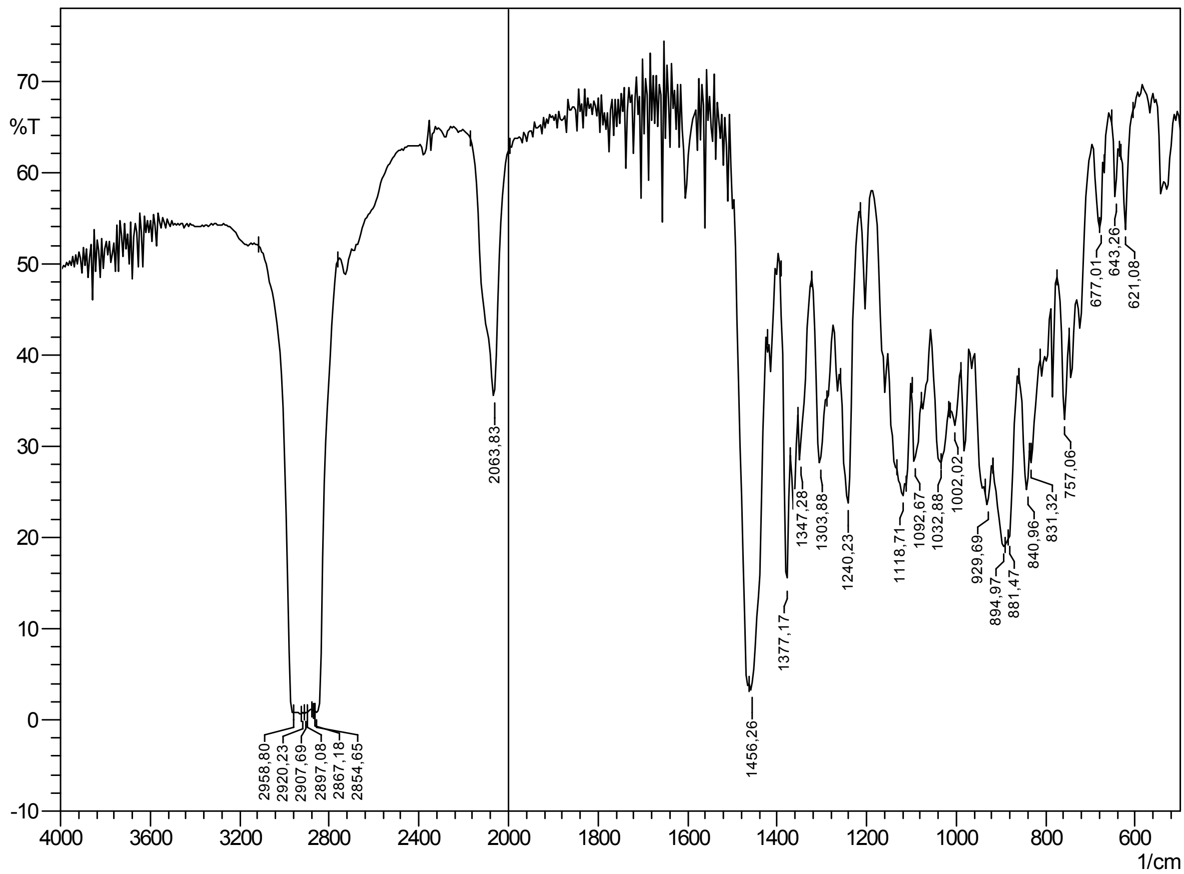


Figure S11: FT-IR spectrum of $\{LO^3\}ZnN(SiHMe_2)_2$ **9** (recorded in KBr plates as a nujol mull).

Table S2. L-LA polymerisation data using **2-10** / ^{i}PrOH binary catalytic systems.[a]

Entry	Initiator	$[L\text{-}LA]_0/[Met]_0/[^{i}PrOH]_0$	$[L\text{-}LA]_0$ (mol·L^{-1})	Time (min)	Yield[b] (%)	TOF[c] (h^{-1})	$M_{n,calc}$[d] (g·mol^{-1})	$M_{n,SEC}$[e] (g·mol^{-1})	M_w/M_n[e]
1	**2**	1 000/1/-	2.0	60	18	180	26 000	10 300	2.24
2	**2**	1000/1/10	2.0	15	20	800	2900	4700	1.09
3	**2**	1 000/1/10	2.0	60	97	970	14 000	15 100	1.10
4	**2**	5 000/1/25	4.0	60	71	3550	20 500	20 600	1.09
5	**2**	5 000/1/25	4.0	90	94	3130	27 100	26 200	1.16
6	**2**	20 000/1/500	6.0	180	97	6470	5700	5400	1.32
7	**2**	50 000/1/500	6.0	16×60	100	3125	14 500	13 500	1.60
8	**3**	200/1/-	2.0	10	92	1100	26 600	14 000	1.63
9	**3**	1000/1/10	2.0	3	83	16 600	12 000	11 500	1.11
10	**3**	1 000/1/10	2.0	6	96	9600	13 900	13 100	1.14
11	**3**	5000/1/10	4.0	90	82	2730	59 100	31 200	1.32
12	**3**	5000/1/25	4.0	90	97	3230	28 000	24 000	1.27
13	**3**	5000/1/50	4.0	90	96	3200	13 900	12 900	1.26
14	**3**	5 000/1/100	4.0	90	91	3030	6600	5500	1.18
15	**4**	1000/1/10	2.0	15	98	3920	14 200	12 900	1.12
16	**5**	1000/1/10	2.0	15	0				
17	**5**	1000/1/10	2.0	60	98	980	14 200	15 100	1.09
18	**5**	5000/1/25	2.0	60	45	2250	13 000	13 000	1.09
19	**5**	5000/1/25	2.0	90	92	3070	26 600	26 300	1.12
20	**6**	1000/1/10	2.0	60	97	970	14 000	15 300	1.09
21	**6**	5000/1/25	4.0	90	98	3270	28 300	26 100	1.14
22	**6**	5000/1/100	4.0	90	97	3230	7100	8400	1.12
23	**7**	1000/1/10	2.0	15	0				
24	**7**	1000/1/10	2.0	60	96	960	13 900	15 500	1.07
25	**7**	5000/1/25	4.0	60	43	2150	12 400	13 000	1.06
26	**8**	200/1/0	0.5	15	49	390	14 200	67 400	1.39
27	**8**	1000/1/-	2.0	15	43	1720	62 000	244 000	1.59
28	**8**	1000/1/10	2.0	5	87	10 440	12 600	15 100	1.07
29	**8**	1000/1/10	2.0	10	94	5640	13 600	16 600	1.07
30	**8**	5000/1/25	4.0	60	95	4750	27 400	24 700	1.18
31	**8**	5000/1/50	4.0	60	99	4950	14 300	14 100	1.16
32	**8**	5000/1/100	4.0	60	98	4900	7100	8200	1.12
33	**8**	5000/1/175	4.0	60	99	4950	4100	4700	1.11
34	**8**	5000/1/250	4.0	60	96	4800	2800	2900	1.16
35	**9**	200/1/0	0.5	15	56	450	16 200	69 300	1.73
36	**9**	1000/1/10	2.0	10	96	5760	13 900	13 800	1.08
37	**10**	200/1/0	0.5	60	37	74	10 700	47 400	1.28
38	**10**	1000/1/10	2.0	60	52	520	7550	8700	1.07

[a] Polymerisations performed in toluene at 60 °C. [b] Isolated yield of PLLA. [c] Non-optimized turnover frequency (mol(L-LA)·mol(Met)$^{-1}$·h^{-1}) calculated over the whole reaction time. [d] Calculated from $[L\text{-}LA]_0/[^{i}PrOH]_0$ × monomer conversion × $M_{L\text{-}LA}$ + M_{iPrOH}, with $M_{L\text{-}LA}$ = 144 g·mol^{-1} and M_{iPrOH} = 60 g·mol^{-1}. [e] Determined by size exclusion chromatography *vs.* polystyrene standards and corrected by a factor of 0.58.

Table S3. *rac*-LA polymerisation data using **2,3,5,6** and **8** / ^{i}PrOH binary catalytic systems.[a]

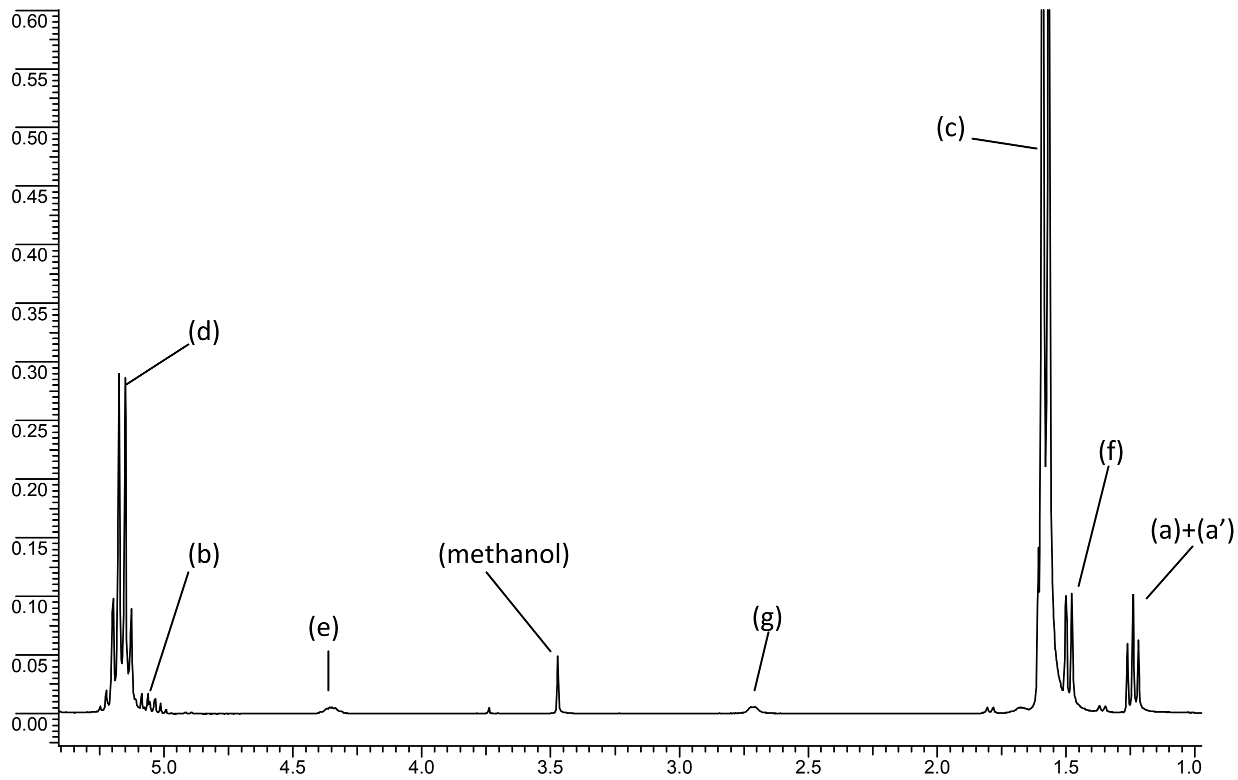
Entry	Initiator	solvent	Time (min)	Yield[b] (%)	TOF[c] (h^{-1})	$M_{n,calc}$[d] ($g \cdot mol^{-1}$)	$M_{n,SEC}$[e] ($g \cdot mol^{-1}$)	M_w/M_n[e]	Pr[f]
1	**2**	Toluene	60	99	990	14 300	12 200	1.20	0.50
2	**2**	THF	60	68	680	9 900	9600	1.12	0.55
3	**3**	Toluene	15	99	3960	14 300	15 200	1.21	0.46
4	**3**	THF	15	90	3600	13 000	12 700	1.19	0.59
5	**5**	Toluene	60	99	990	14 300	12 200	1.20	0.55
6	**5**	THF	60	92	920	13 300	9100	1.32	0.60
7	**6**	Toluene	60	99	990	14 300	13 700	1.23	0.61
8	**6**	THF	60	95	950	13 800	11 100	1.20	0.61
9	**8**	Toluene	15	97	3880	14 000	13 000	1.08	0.51
10	**8**	THF	15	88	3520	12 700	9900	1.09	0.63

[a] Polymerisations performed in at 60 °C with a $[rac\text{-LA}]_0/[\text{Met}]_0/[^{i}\text{PrOH}]_0$ ratio of 1000:1:10 and $[rac\text{-LA}]_0 = 2.0$ mol·L^{-1} . [b] Isolated yield of PLA. [c] Non-optimized turnover frequency (mol(*rac*-LA)·mol(Met)$^{-1}$·h^{-1}) calculated over the whole reaction time. [d] Calculated from $[rac\text{-LA}]_0/[^{i}\text{PrOH}]_0$ × monomer conversion × $M_{rac\text{-LA}}$ + M_{iPrOH}, with $M_{rac\text{-LA}}$ = 144 g·mol^{-1} and M_{iPrOH} = 60 g·mol^{-1}. [e] Determined by size exclusion chromatography *vs.* polystyrene standards and corrected by a factor of 0.58. [f] Probability of a *racemic* linkage between two repetitive units as determined by examination of the methine region of the ^{1}H homonuclear decoupled NMR spectrum of the polymers

Table S4. TMC and BBL polymerisation data using **2** and **8** / ROH binary catalytic systems.

Entry	Monomer	Initiator	$[M]_0/[Met]_0/[ROH]_0$	Time (min)	Temperature (°C)	Yield[d] (%)	TOF[e] (h^{-1})	$M_{n,calc}$[f] ($g \cdot mol^{-1}$)	$M_{n,SEC}$[g] ($g \cdot mol^{-1}$)	M_w/M_n[e]
1[a]	TMC	**2**	100 000/1/100	48*60	60	93	1940	95 100	88 700	1.61
2[a]	TMC	**2**	100 000/1/100	8*60	110	96	12 000	98 100	94 400	1.51
3[b]	TMC	**8**	1000/1/10	5	60	94	11 280	9 700	13 800	1.49
4[c]	BBL	**2**	500/1/10	3*60	60	95	160	4100	4300	1.07
5[c]	BBL	**8**	500/1/10	3*60	60	63	105	2800	2 920	1.26

[a] Polymerisation performed in bulk with benzyl alcohol. [b] Polymerisation performed in toluene with $[TMC]_0$ = 2 M and using isopropanol. [c] Polymerisation performed in bulk with isopropanol. [d] Isolated yield. [e] Non-optimized turnover frequency (mol(Monomer)·mol(Met)$^{-1}$·h^{-1}) calculated over the whole reaction time. [f] Calculated from $[M]_0/[ROH]_0$ × monomer conversion × $M_{monomer}$ + M_{ROH}. [g] Determined by size exclusion chromatography *vs.* polystyrene standards, corrected by a factor of 0.88 for PTMC and not corrected for PHB.



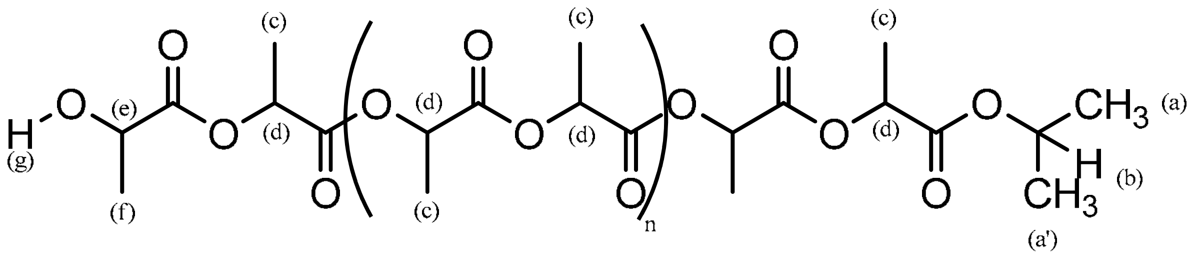


Figure S12: ^{1}H NMR spectrum of a low molecular weight PLLA prepared with L-LA/**2**/^{i}PrOH in relative amounts of 100/1/10 (500.13 MHz, $CDCl_3$, 25 °C, 16 scans, D1 = 0.50 sec).

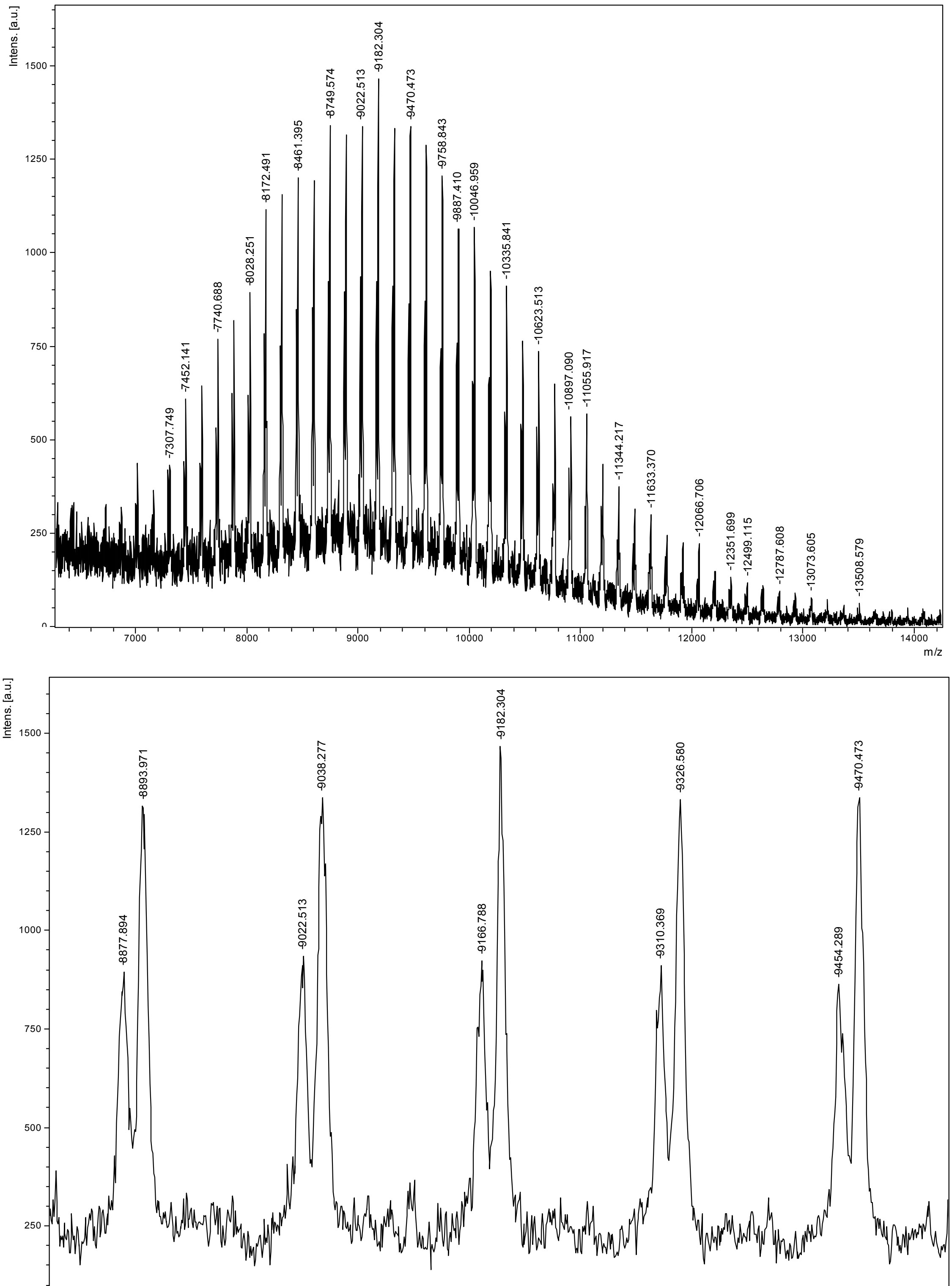


Figure S13: MALDI-TOF mass spectrum (main population: K^+; minor population: Na^+) of a PLLA having a number average molecular weight $\overline{Mn}_{SEC}$ of 13 500 g·mol^{-1}, prepared with L-LA/**2**/^{i}PrOH in relative amounts of 50 000/1/1000 (100 % conversion).

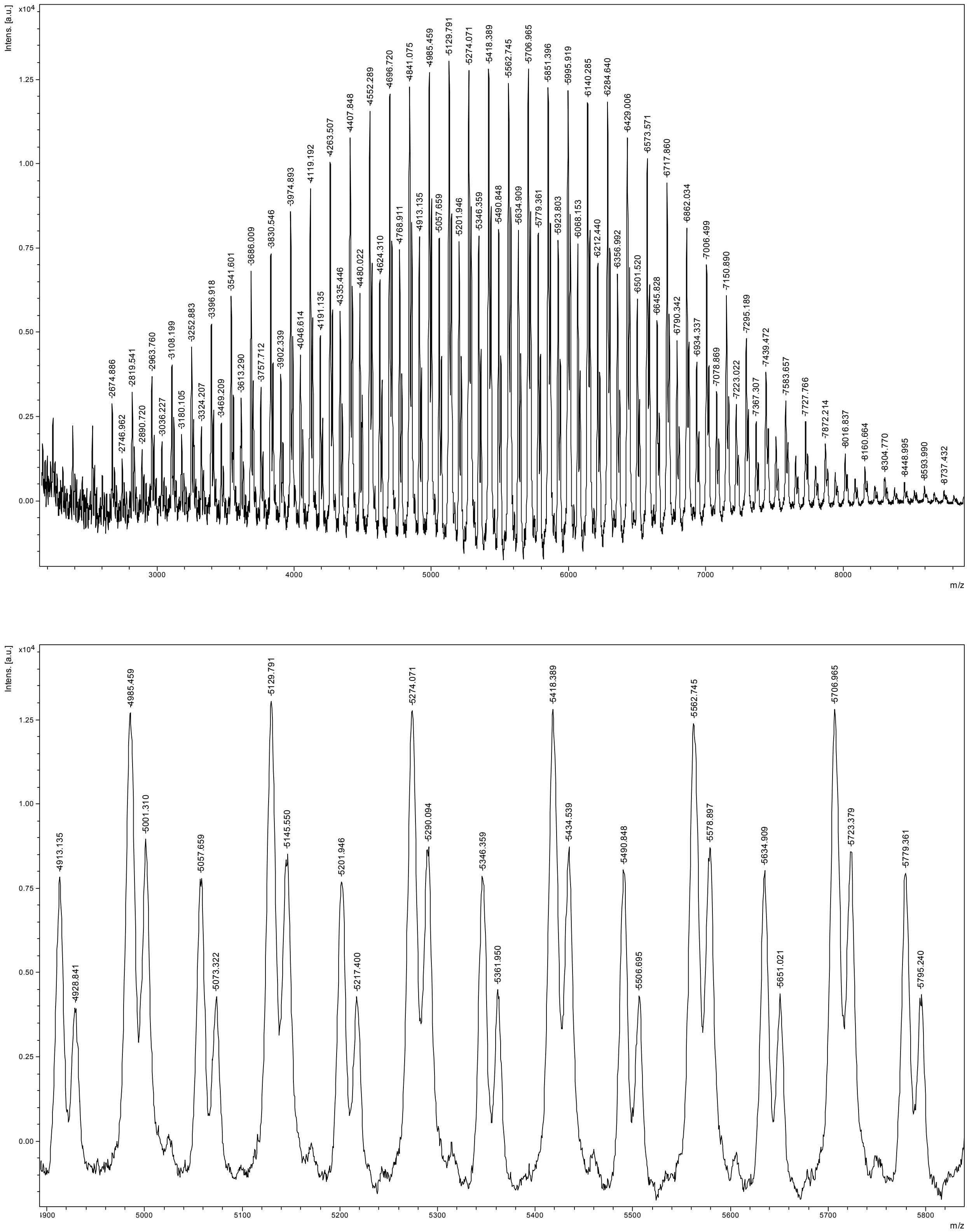


Figure S14: MALDI-TOF mass spectrum (main population: Na^+; minor population: K^+) of a low molecular weight PLLA having a number average molecular weight $\overline{Mn}_{\text{SEC}}$ of 4600 g·mol^{-1}, prepared with L-LA/**3** /^{i}PrOH in relative amounts of 5000/1/100 (71% conversion).

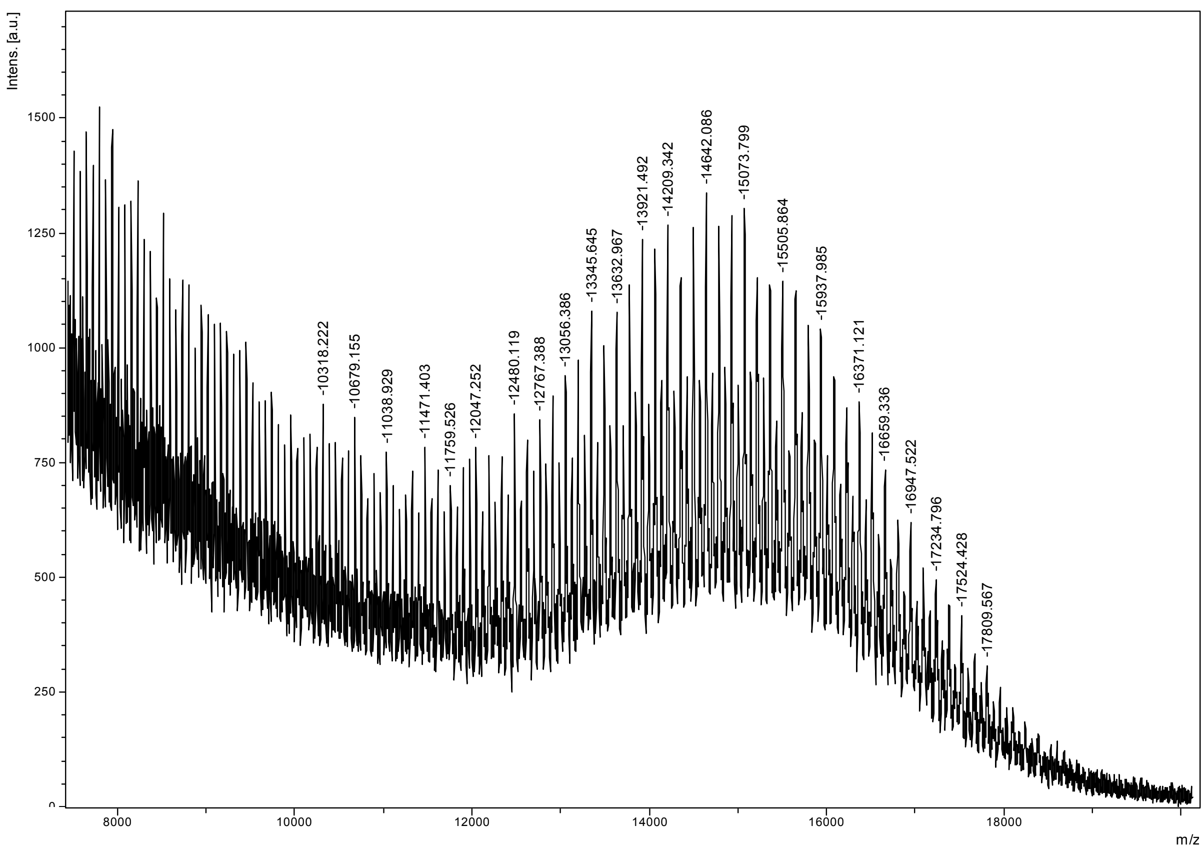


Figure S15: MALDI-TOF mass spectrum (main population: Na^+) of a PLA having a number average molecular weight $\overline{Mn}_{\mathrm{SEC}}$ of 12 200 g·mol^{-1}, prepared with *rac*-LA/**5**/^{i}PrOH in relative amounts of 1000/1/10 (100% conversion).

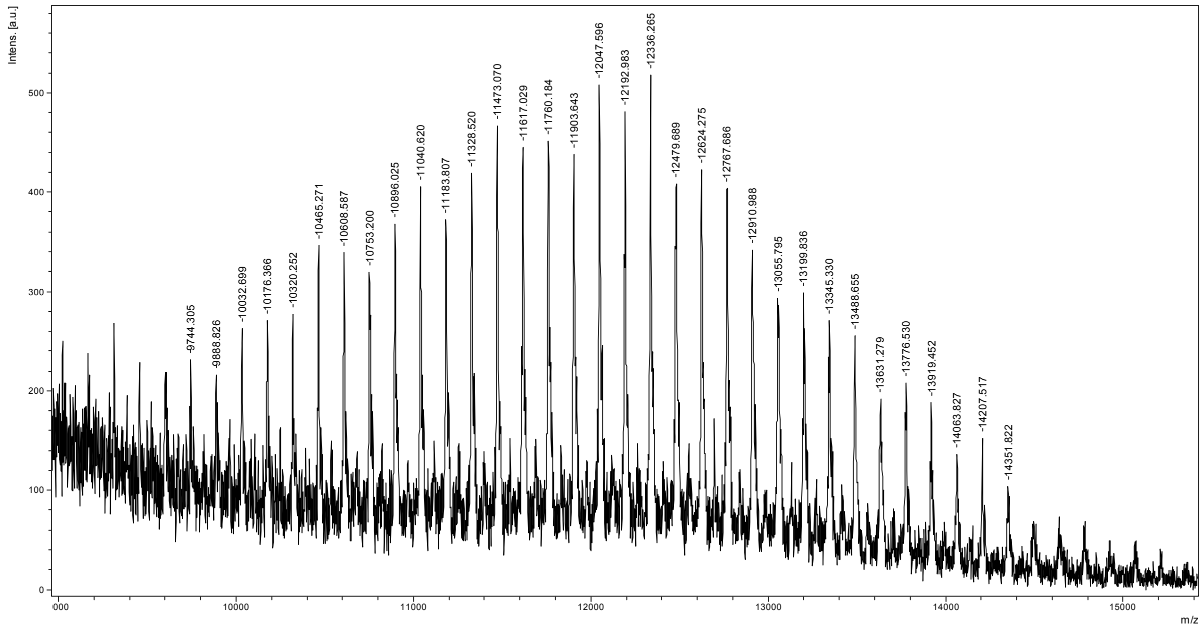


Figure S16: MALDI-TOF mass spectrum (main population: Na^+) of a PLLA having a number average molecular weight $\overline{Mn}_{\mathrm{SEC}}$ of 14 100 g·mol^{-1}, prepared with L-LA/**8**/^{i}PrOH in relative amounts of 5000/1/50 (99% conversion).

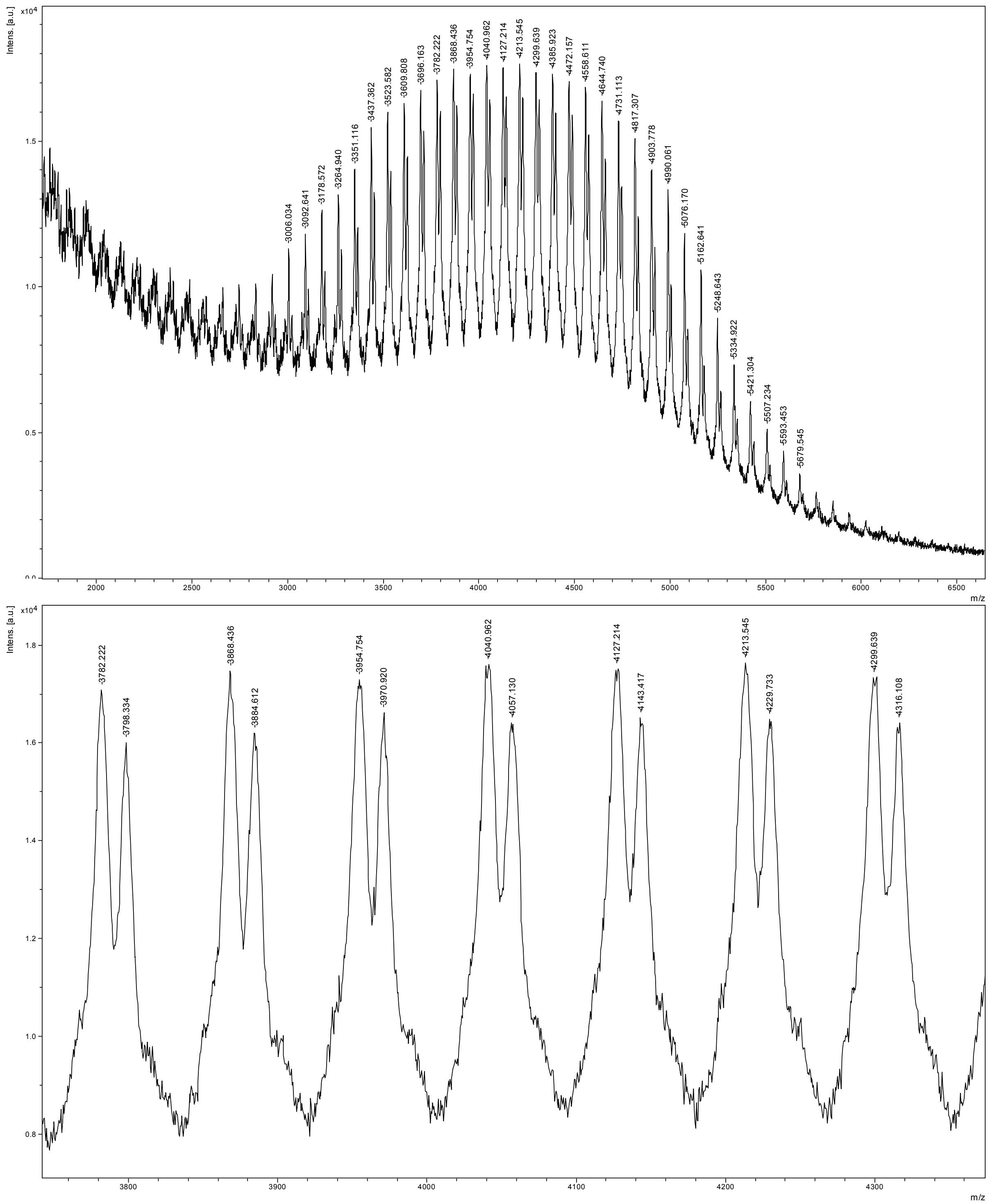


Figure S17: MALDI-TOF mass spectrum (main populations: Na^+ and K^+) of a PHB having a number average molecular weight $\overline{Mn}_{\mathrm{SEC}}$ of 4300 g·mol^{-1}, prepared with *rac*-BBL/**2**/^{i}PrOH in relative amounts of 200/1/10 (95 % conversion).