Supporting information for

[(Salen*)Co(OAc)] as robust initiator for the immortal bulk ring-opening (co)polymerization of L-lactide and ε-caprolactone

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Content

Table S1. Results of the bulk ring-opening polymerization (ROP) of ε-caprolactone (CL) at 120 °C initiated by complex **1**.

Entry	$[CL]_0/[\mathbf{1}]$	[MeOH]/[**1**]	Time (h)	Conv.[a] (%)	$M_{n,theo}$ [b] (g/mol)	$M_{n,corr}$ [c] (g/mol)	$Đ$ [d]
1	500	0	24	2.5	1400	1600	1.04
2	500	0	48	3	1700	1700	1.04
3	500	0	96	4	2300	2500	1.03
4	500	0	120	9	5100	4600	1.04
5	500	0	168	60	34200	9300	1.20
6	500	2	21.5	6	1150	1700	1.02
7	500	2	48	11	2100	2200	1.10
8	500	2	72	17	3200	3100	1.07
9	500	2	96	27	5300	5200	1.09
10	500	5	21.5	8	800	800	1.20
11	500	5	48	17	1600	1900	1.10
12	500	5	72	23	2200	2300	1.08
13	500	5	96	43	4200	4500	1.09

[a] Determined by gravimetry and/or from ^{1}H NMR analysis. [b] Calculated according to $M_{n,theo} = ([CL]_0/[\mathbf{1}]) \times (1/([\mathbf{1}]+[MeOH])) \times M_{CL} \times$ conversion, where M_{CL} = 114.14 g/mol. The molecular weights of both the α- (initiating group(s)) and ω-chain (H) end were not taking into account due to their negligible masses. [c] Determined by gel permeation chromatography (GPC), using polystyrene (PS) standards and applying the correction factor of 0.56. [d] Determined by GPC.

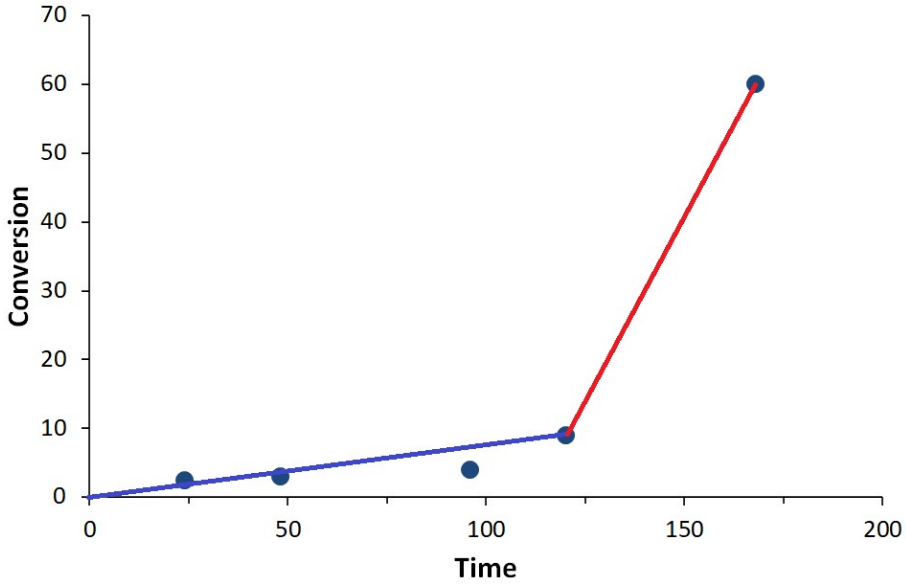

Figure S1. Plot of the conversion as a function of time for the bulk ring-opening polymerization (ROP) of ε-caprolactone (CL) at 120 °C initiated by complex **1** (initial ratio: [CL]/[**1**] = 500). Two ROP regimes can be observed, an initially slow ROP until 120 h (blue line).

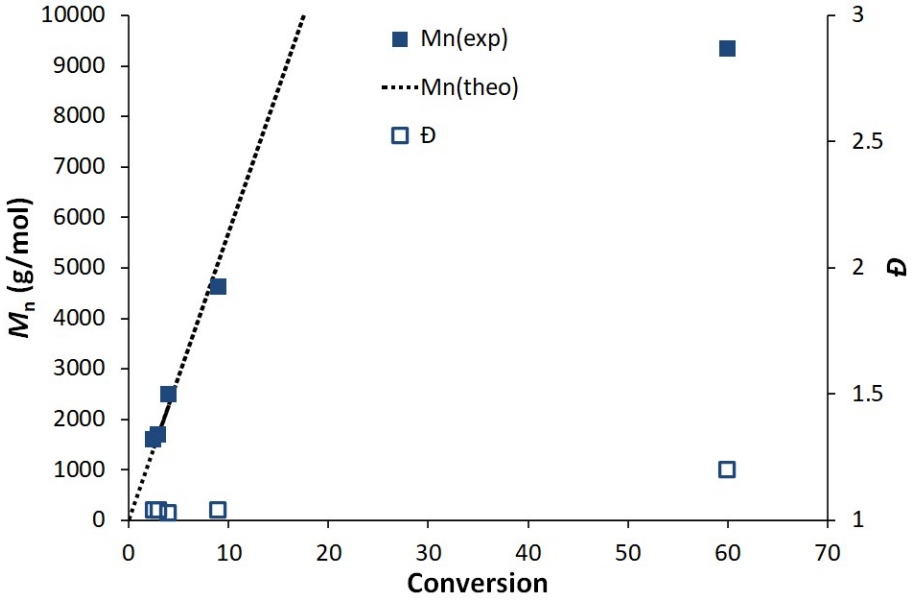

Figure S2. Dependence of the PCL molar masses ($M_{n,corr}$, solid symbols) and dispersity indexes ($Đ$, empty symbols) on the CL conversion for the bulk ROP of CL at 120 °C initiated by complex **1** (initial ratio: [CL]/[**1**] = 500). The dotted black line represents the theoretical M_n values.

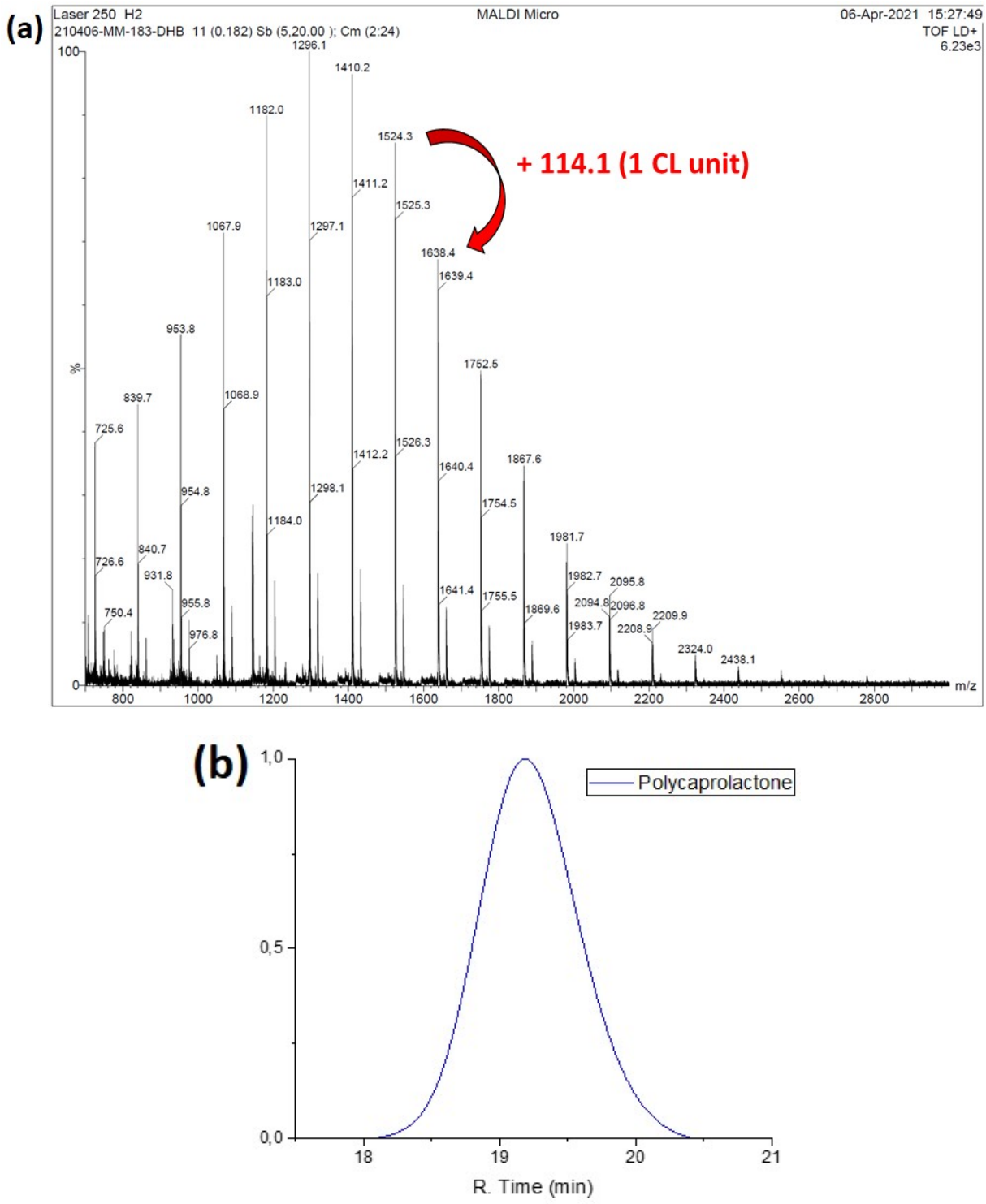

Figure S3. Analyses of the low molar-mass PCL prepared by ROP of CL mediated by **1**. Conditions: CL/**1** = 200/1, bulk, 100 °C, 70 h, 18% conversion. (a) MALDI-ToF mass spectrum (matrix: polymer/DHB/NaI 1:3:1); (b) GPC trace ($M_{n,corr}$ = 1600 g/mol, $Đ$ = 1.07).

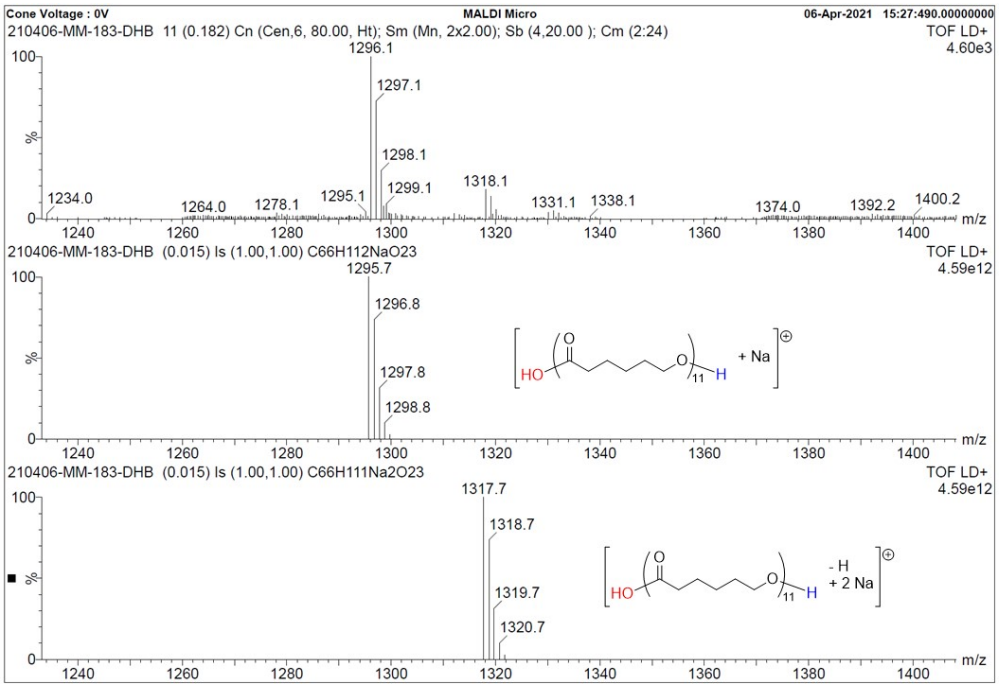

Figure S4. Expanded region of the MALDI-ToF spectrum in Figure S3 highlighting the isotopic envelopes with main peaks at 1296.1 and 1317.7 a.u. (top) and simulated isotopic distributions for two proposed formulas for 11 CL units (middle and bottom).

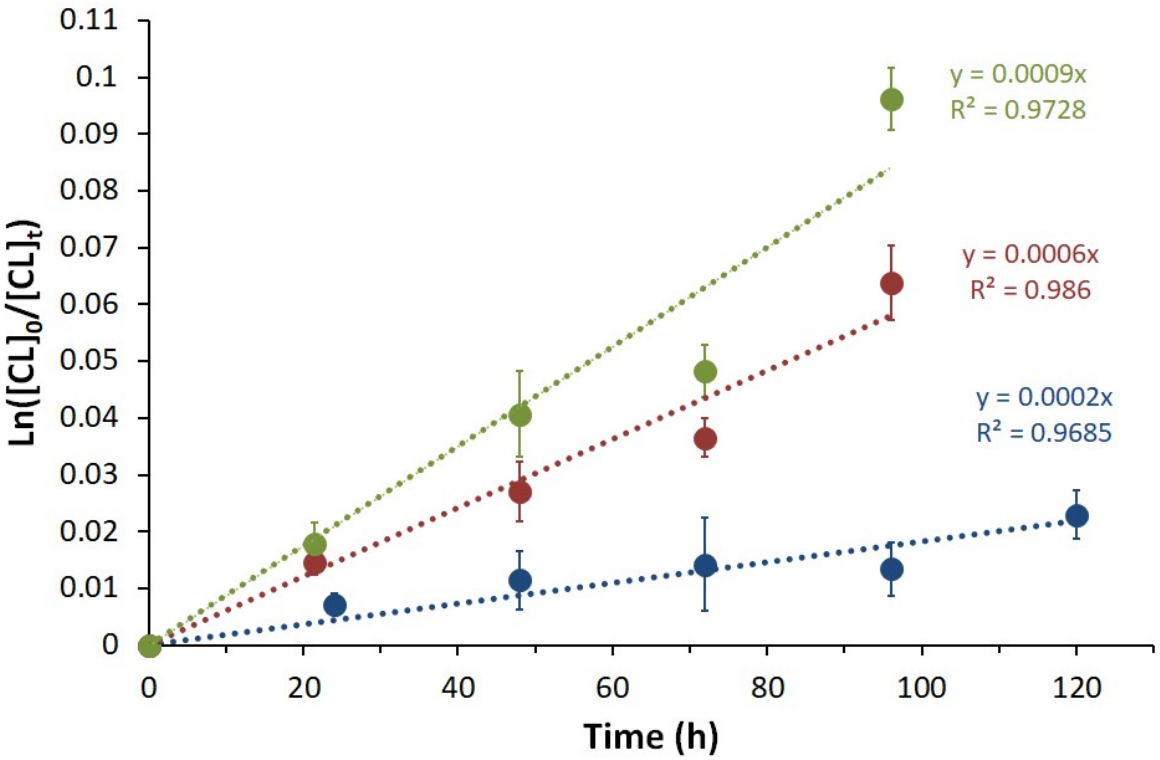

Figure S5. Pseudo-first-order kinetic data for the bulk ROP of CL at 120 °C initiated by complex **1** in the absence or presence of MeOH (initial ratio [CL]/[**1**]/[MeOH] = 500:1:0 (blue), 2 (red), 5 (green)). Each data point represents the average of three independent experiments and error bars correspond to the standard deviation. The linear fits are shown as visual guides.

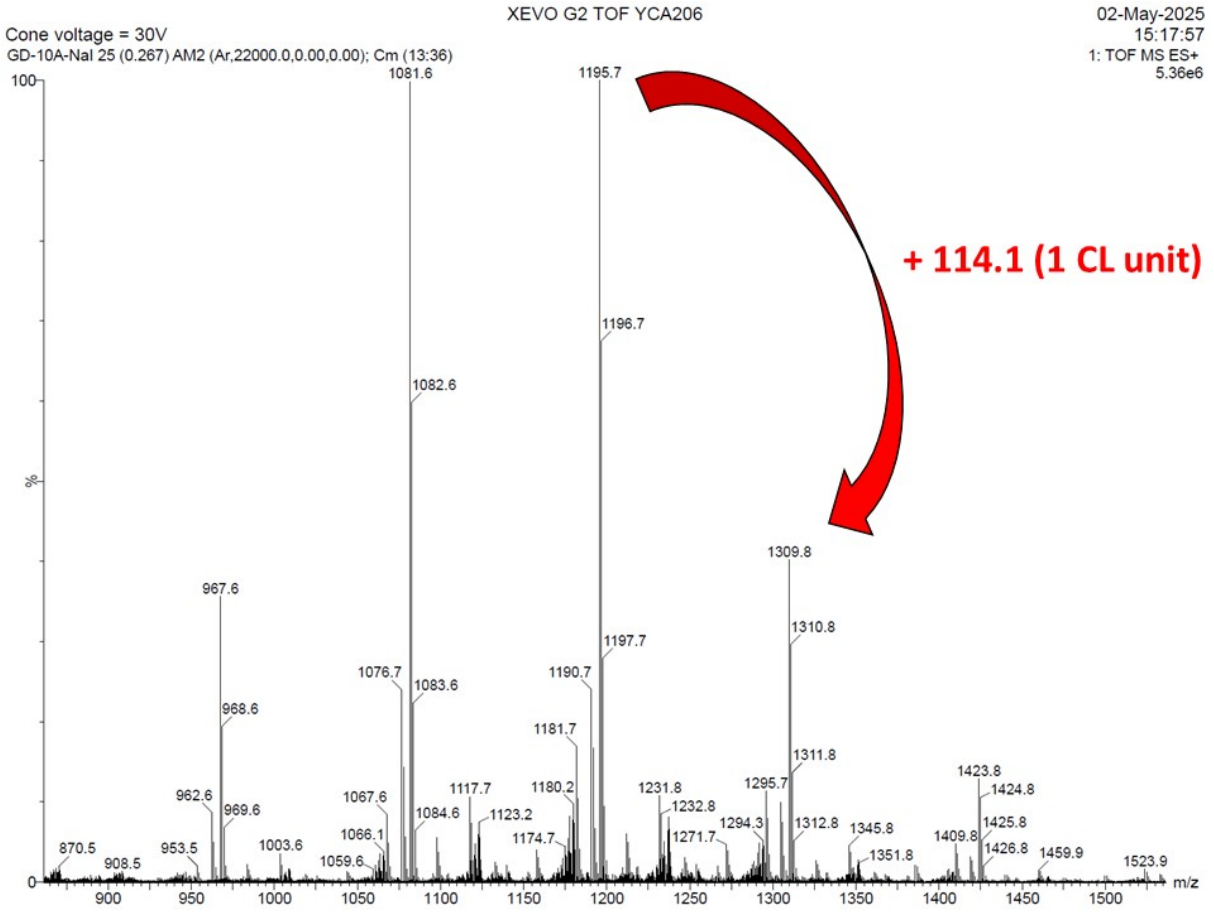

Figure S6. ESI-MS spectrum (with addition of NaI) of the low molar-mass PCL prepared by immortal ROP of CL mediated by **1**. Conditions: CL/**1**/MeOH = 500/1/2, bulk, 120 °C, 21.5 h, 6% conversion, $M_{n,corr}$ = 1700 g/mol, $Đ$ = 1.02 (Table S1, Entry 6).

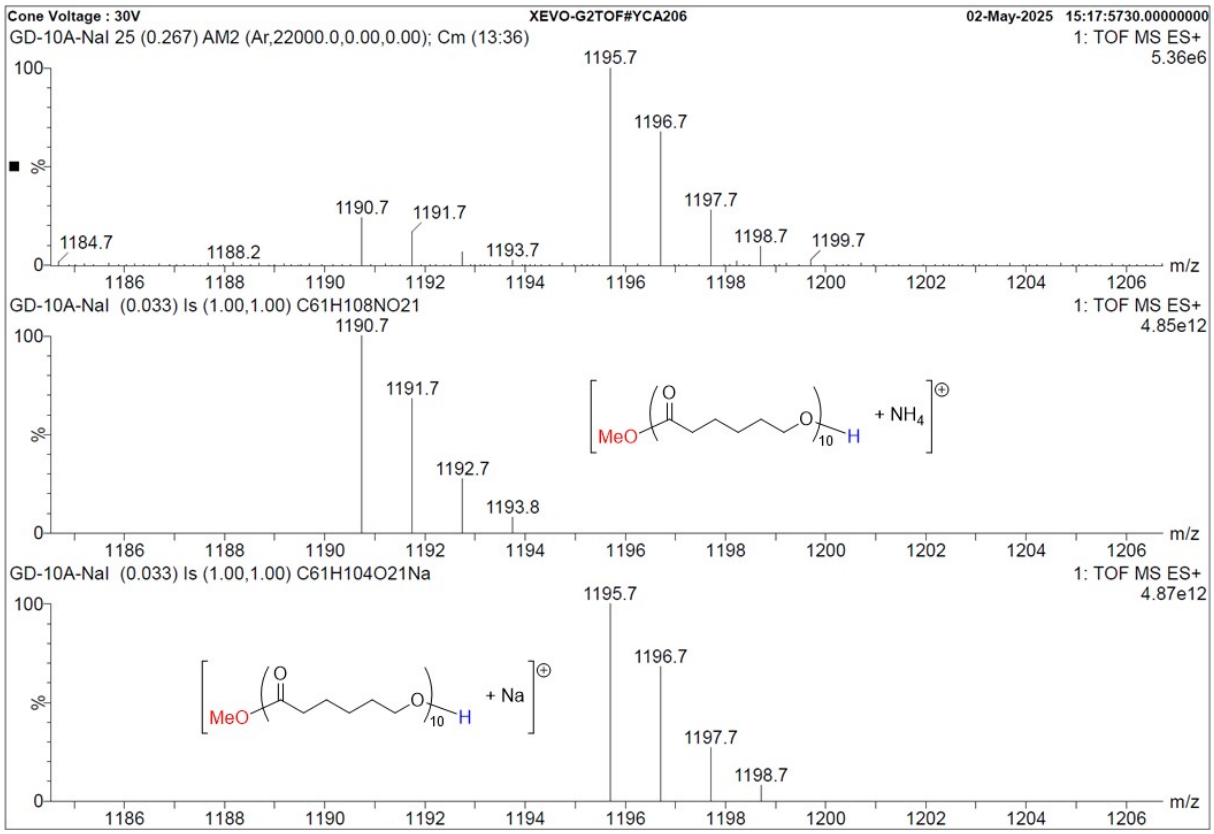

Figure S7. Expanded region of the ESI-MS spectrum in Figure S5 highlighting the isotopic envelopes with peaks at 1190.7 and 1195.7 a.u. (top) and simulated isotopic distributions for two proposed formulas for 10 CL units (middle and bottom).

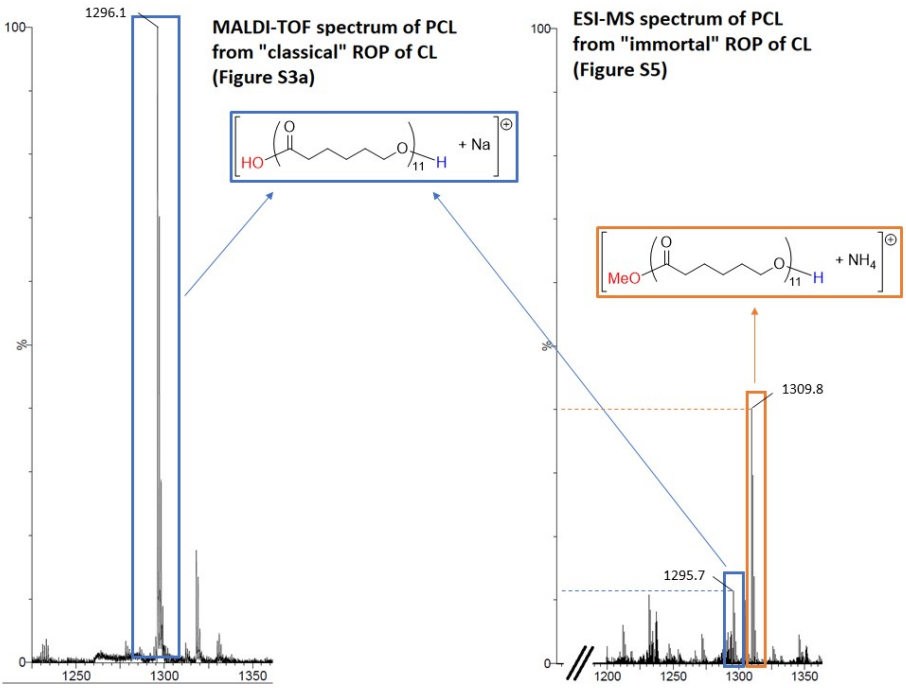

Figure S8. Expanded regions of the MALDI-ToF spectra in Figure S3a and ESI-MS spectrum in Figure S5 highlighting the presence of the isotopic envelope corresponding to PCL initiated by the OAc group (blue boxes) in both spectra.

Table S2. Results of the bulk ROP of *L*-lactide (LLA) at 120 °C initiated by complex **1**.

Entry	$[LLA]_0/[\mathbf{1}]$	[BnOH]/[**1**]	Time (h)	Conv.[a] (%)	$M_{n,theo}$ [b] (g/mol)	$M_{n,corr}$ [c] (g/mol)	$Đ$ [d]
1	500	0	9	3	2200	700	1.03
2	500	0	24	6	4300	1900	1.34
3	500	0	35	11	7900	7600	1.13
4	500	0	48	16	11500	10800	1.34
5	500	0	96	33	23800	14100	1.30
6	500	2	21.5	11.5	2900	1700	1.20
7	500	2	48	28.5	7000	3800	1.33
8	500	2	72	36	8800	4800	1.31
9	500	2	96	45	10900	5700	1.36
10	500	5	21.5	23	2900	2000	1.25
11	500	5	46	36	4400	5300	1.19
12	500	5	72	45	5500	6200	1.29

[a] Determined by gravimetry and/or from ^{1}H NMR analysis. [b] Calculated according to $M_{n,theo}$ = ($[LLA]_0/[\mathbf{1}]$) × (1/([**1**]+[MeOH])) × M_{LLA} × conversion, where [init] = 1, 3 or 6 for [BnOH]/[**1**] = 0, 2, 5, respectively, and M_{LLA} = 144.13 g/mol. The molecular weights of both the α- (initiating group(s)) and ω-chain (H) end were not taking into account due to their negligible masses. [c] Determined by GPC using polystyrene standards and applying the correction factor of 0.58. [d] Determined by GPC.

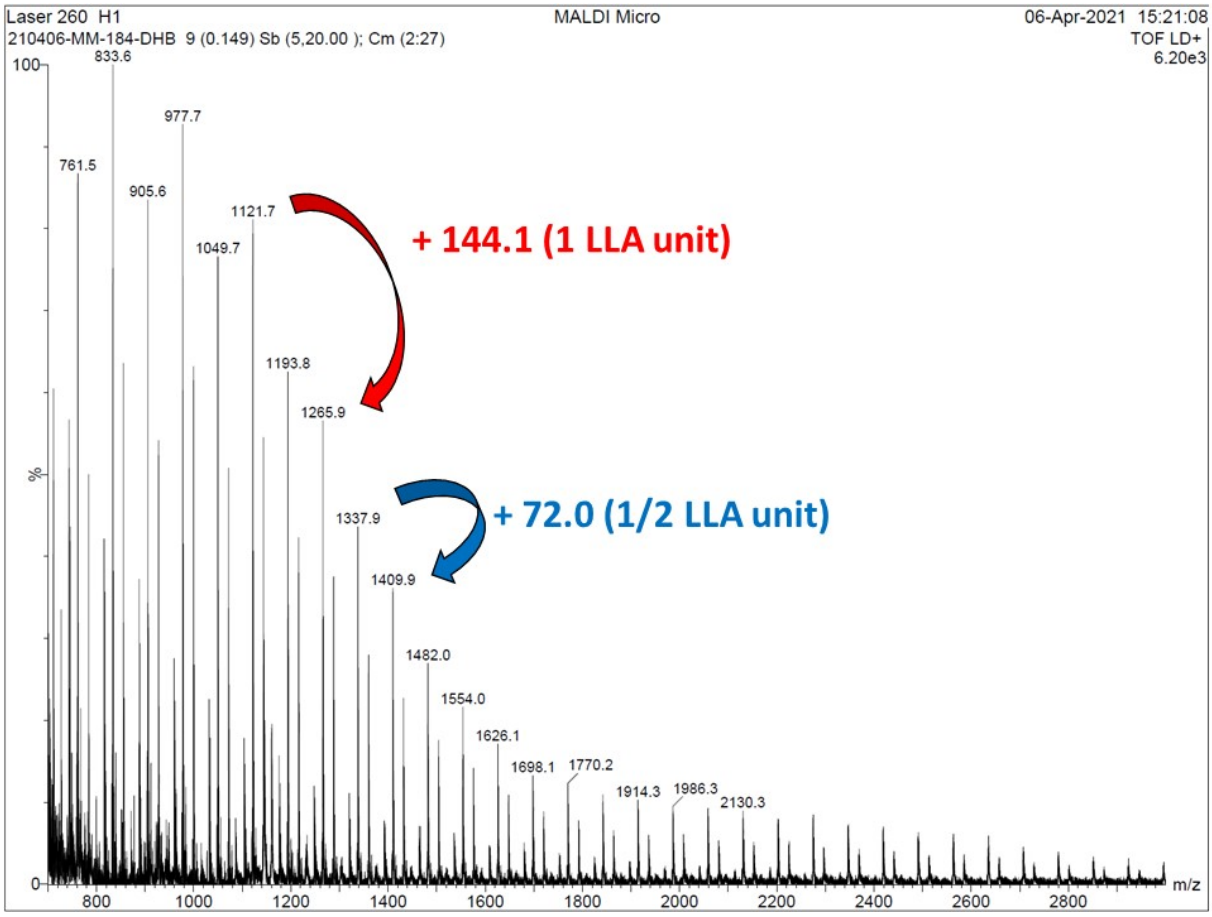

Figure S9. MALDI-ToF mass spectrum (matrix: polymer/DHB/NaI 1:3:1) of the low molar-mass PLLA prepared by ROP of LLA mediated by **1**. Conditions: LLA/**1** = 500/1, bulk, 120 °C, 24 h, 6% conversion, $M_{n,corr}$ = 1900 g/mol, $Đ$ = 1.14 (Table S2 – Entry 2).

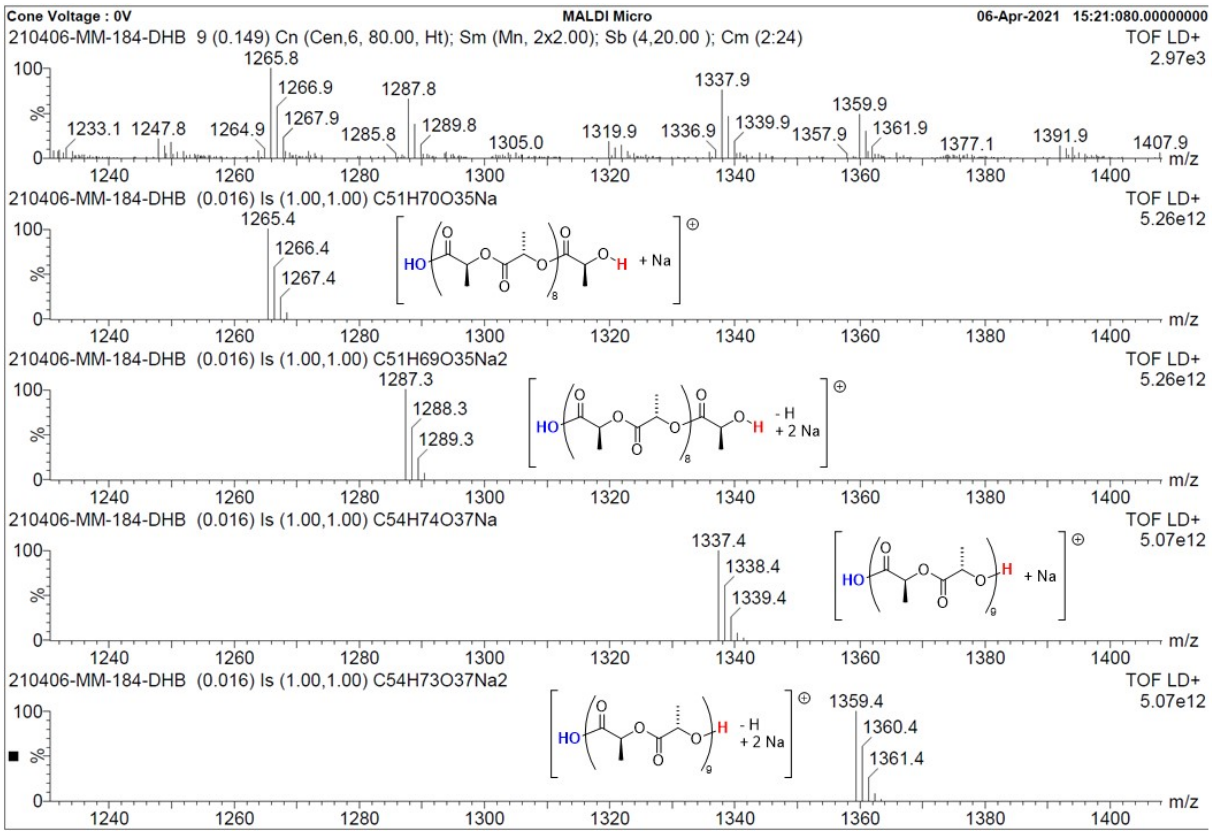

Figure S10. Expanded region of the ESI-MS spectrum in Figure S7 highlighting different isotopic envelopes in the region 1265.8-1359.4 a.u. (1st line) and simulated isotopic distributions for four proposed formulas for 8 LLA units (2nd and 3rd lines) and 9 LLA units (4th and 5th lines).

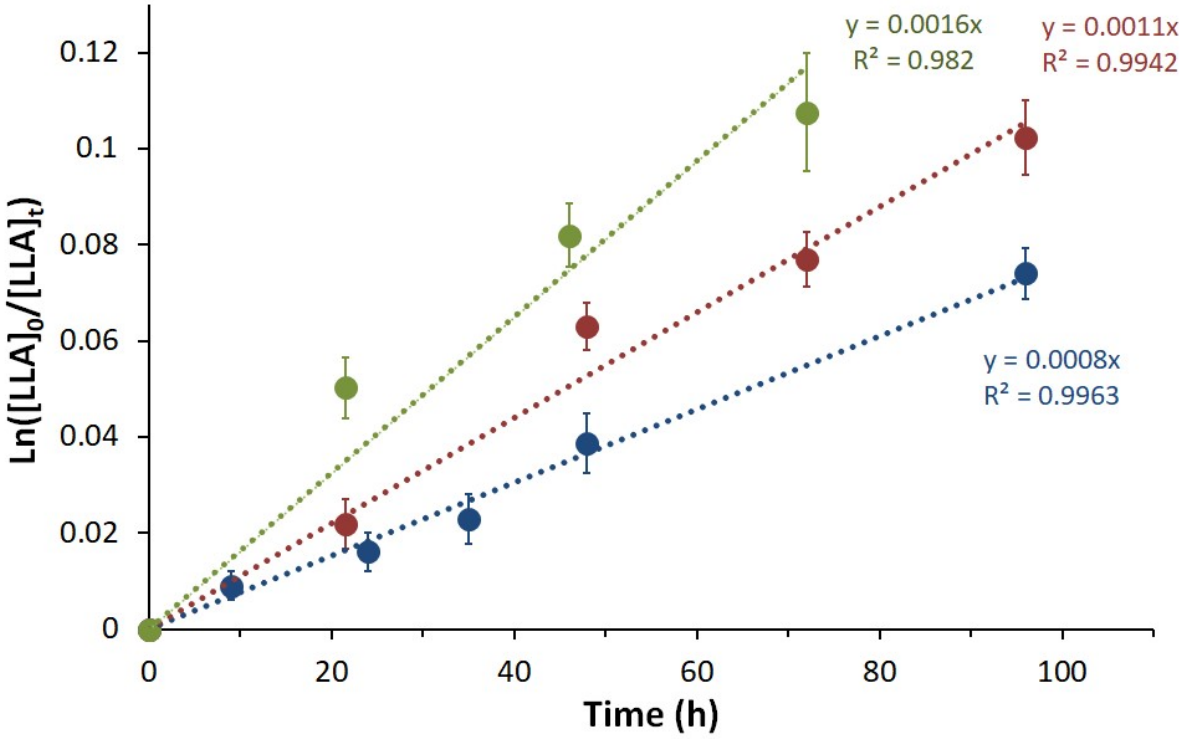

Figure S11. Pseudo-first-order kinetic data for the bulk ROP of LLA at 120 °C initiated by complex **1** in the absence or presence of MeOH (initial ratio [LLA]/[**1**]/[MeOH] = 500:1:0 (blue), 2 (red), 5 (green)). Each data point represents the average of three independent experiments and error bars correspond to the standard deviation. The linear fits are shown as visual guides.

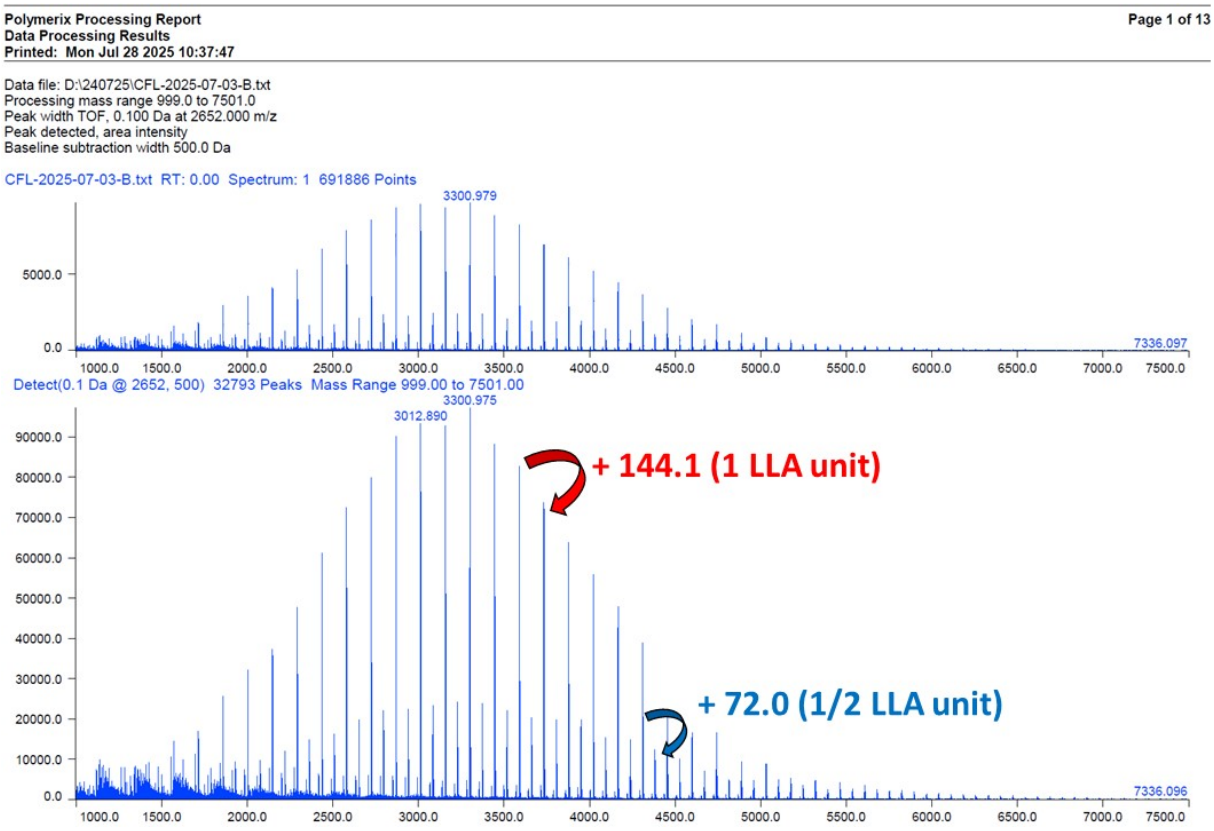

Figure S12. MALDI-ToF mass spectrum (matrix: polymer/DHB/NaI 1:3:1) of the low molar-mass PLLA prepared by immortal ROP of LLA mediated by **1**. Conditions: LLA/**1** = 500/5, bulk, 120 °C, 24 h, 29% conversion, $M_{n,corr}$ = 3300 g/mol, $Đ$ = 1.16.

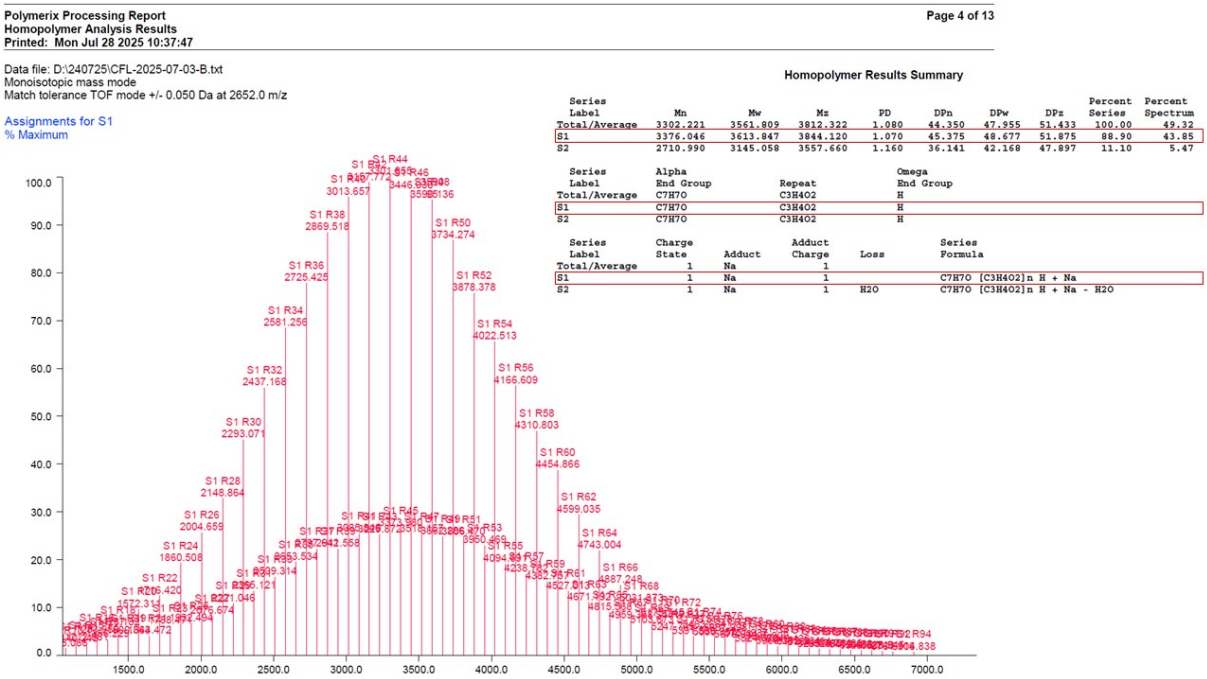

Figure S13a. Most abundant homopolymer identified using the Polymerix software, from the MALDI-ToF mass spectrum in Figure S9.

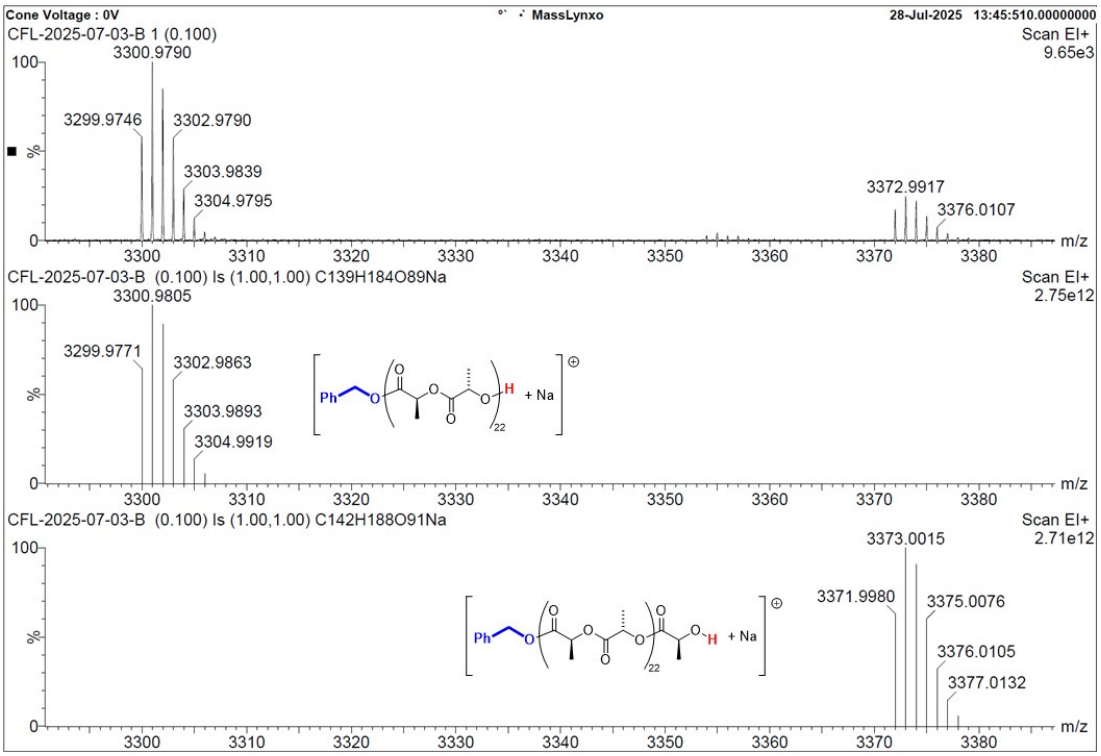

Figure S13b. Expanded region of the MALDI-ToF spectrum in Figure S9 highlighting the isotopic envelopes with main peaks at 3300.9 and 3372.9 a.u. (top) and simulated isotopic distributions for two proposed formulas for 22 LLA units (middle and bottom).

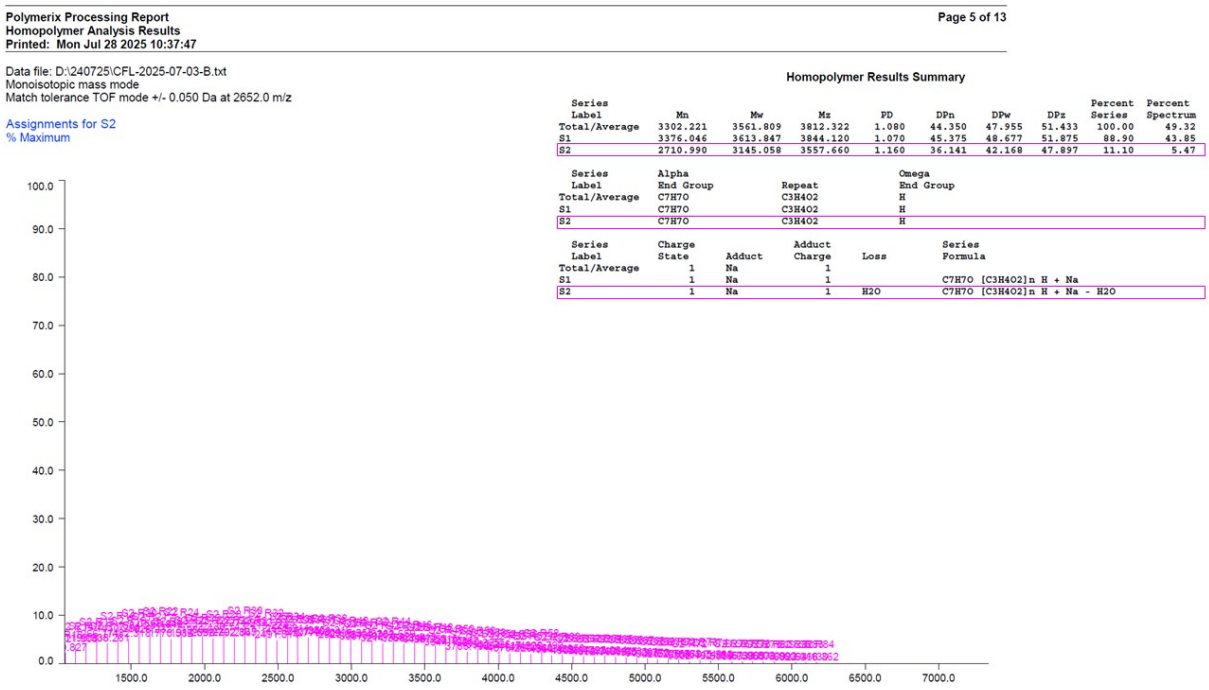

Figure S14a. Lowest abundant homopolymer identified using the Polymerix software, from the MALDI-ToF mass spectrum in Figure S9.

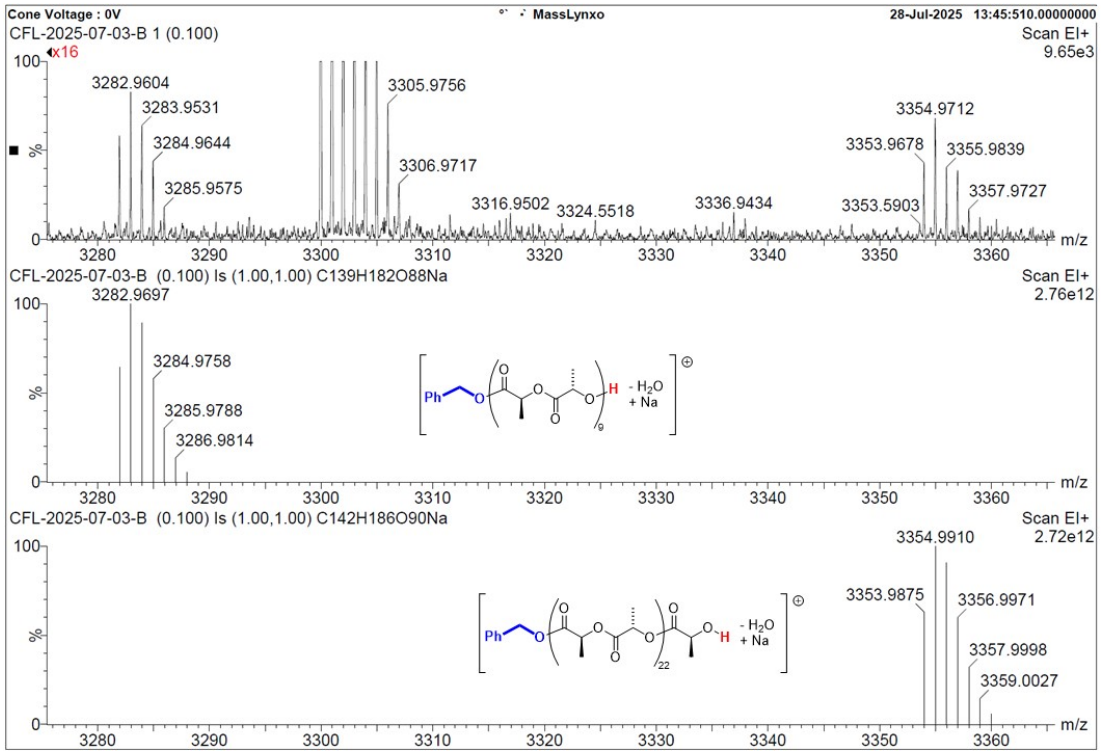

Figure S14b. Expanded region of the MALDI-ToF spectrum in Figure S9 (zoom x16) highlighting the isotopic envelopes with main peaks at 3282.9 and 3354.9 a.u. (top) and simulated isotopic distributions for two proposed formulas for 22 LLA units (middle and bottom).

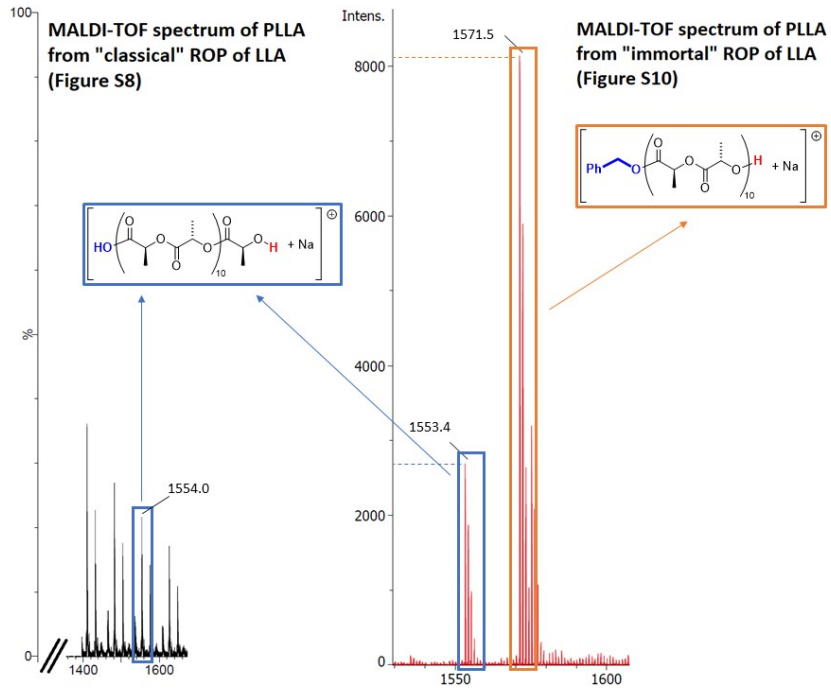

Figure S15. Expanded regions of the MALDI-ToF spectra in Figure S8 and Figure S10 highlighting the presence of the isotopic envelope corresponding to PLLA initiated by the OAc group (blue boxes) in both spectra.

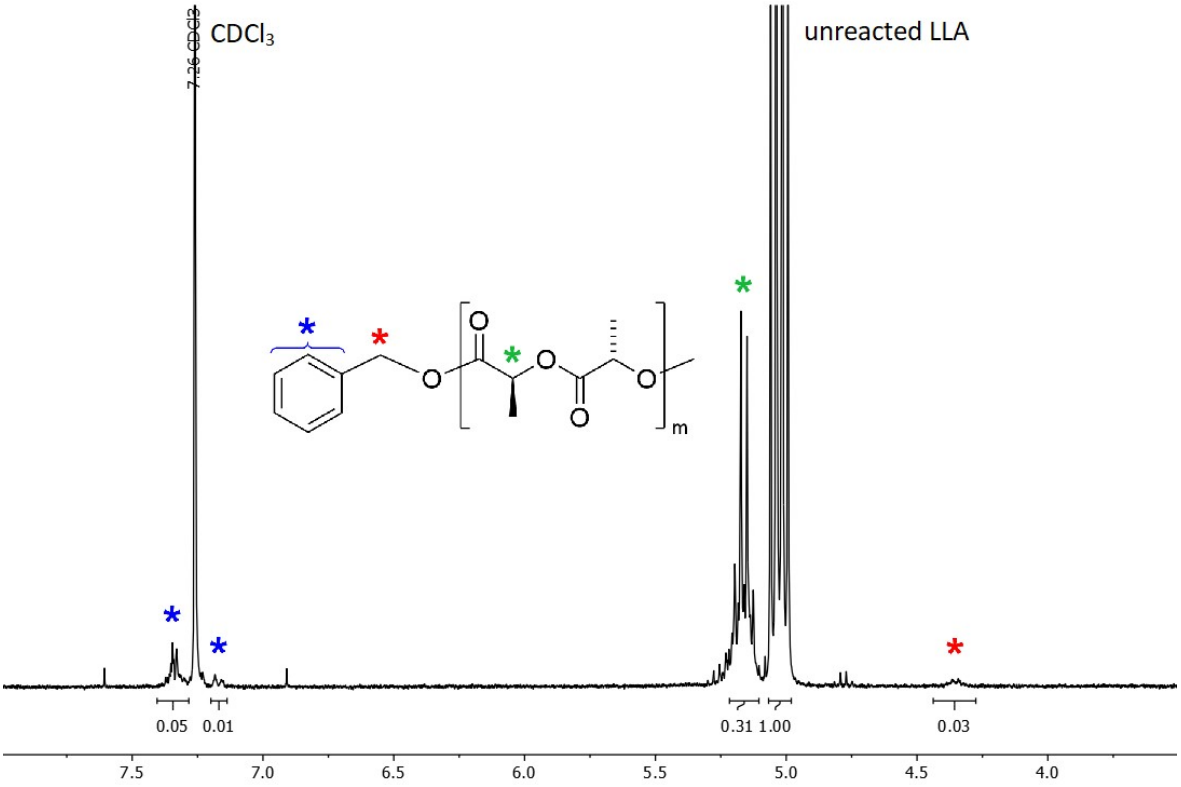

Figure S16. ^{1}H NMR spectrum (expansion of the 3.5-8 ppm region, $CDCl_3$) of the PLLA prepared by immortal ROP of LLA mediated by **1**, showing the signals of the terminal PLLA-OCH_2Ph group. Conditions: LLA/**1**/BnOH = 500/1/5, bulk, 120 °C, 21.5 h, 23% conversion, $M_{n,corr}$ = 1700 g/mol, $Đ$ = 1.02 (Table S1- Entry 10).

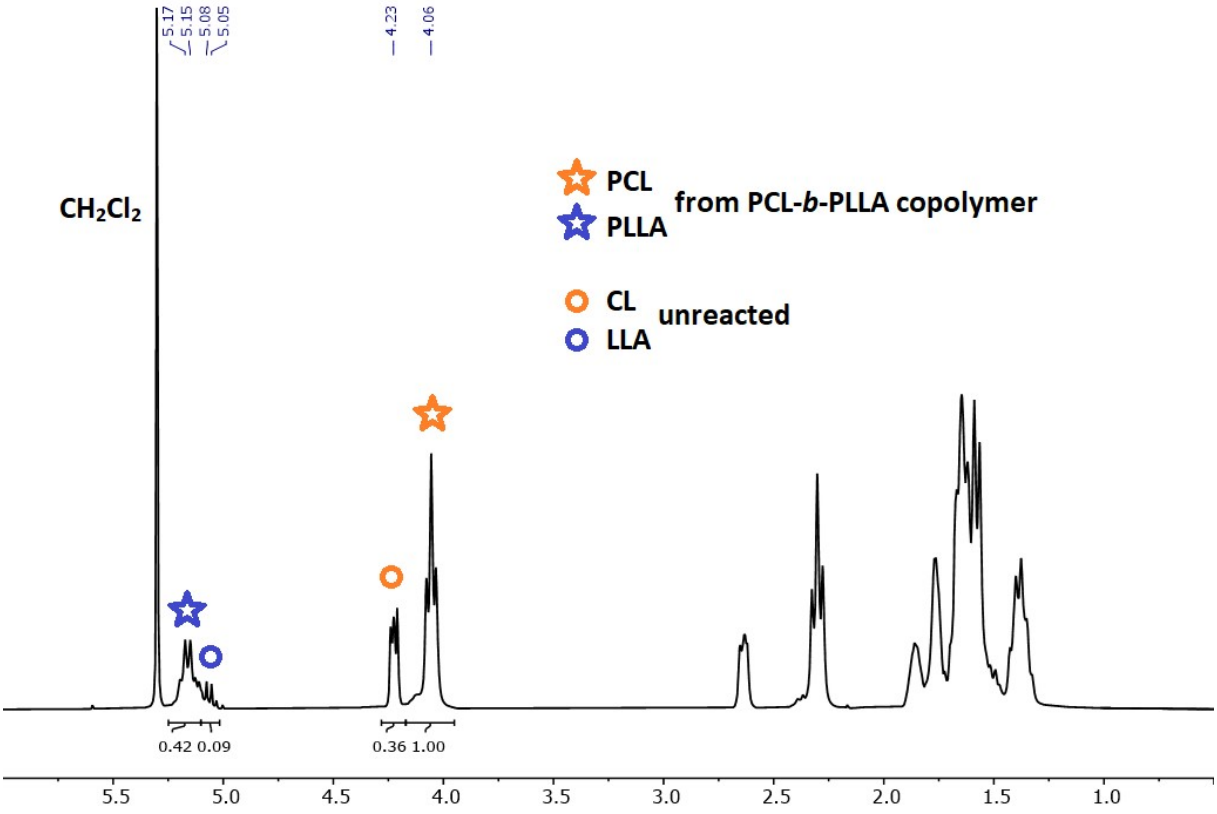

Figure S17. ^{1}H NMR spectrum (expansion of the 0.5-6 ppm region, $CDCl_3$) of the reaction medium (diluted in CH_2Cl_2) of the sequential bulk copolymerization of CL and LLA catalysed by complex **1** under immortal conditions. Conditions: Co/CL/LLA/BnOH = 1/500/500/10, bulk, 120 °C, 108 + 48 h, 73% and 82% conversion of CL and LLA, respectively.

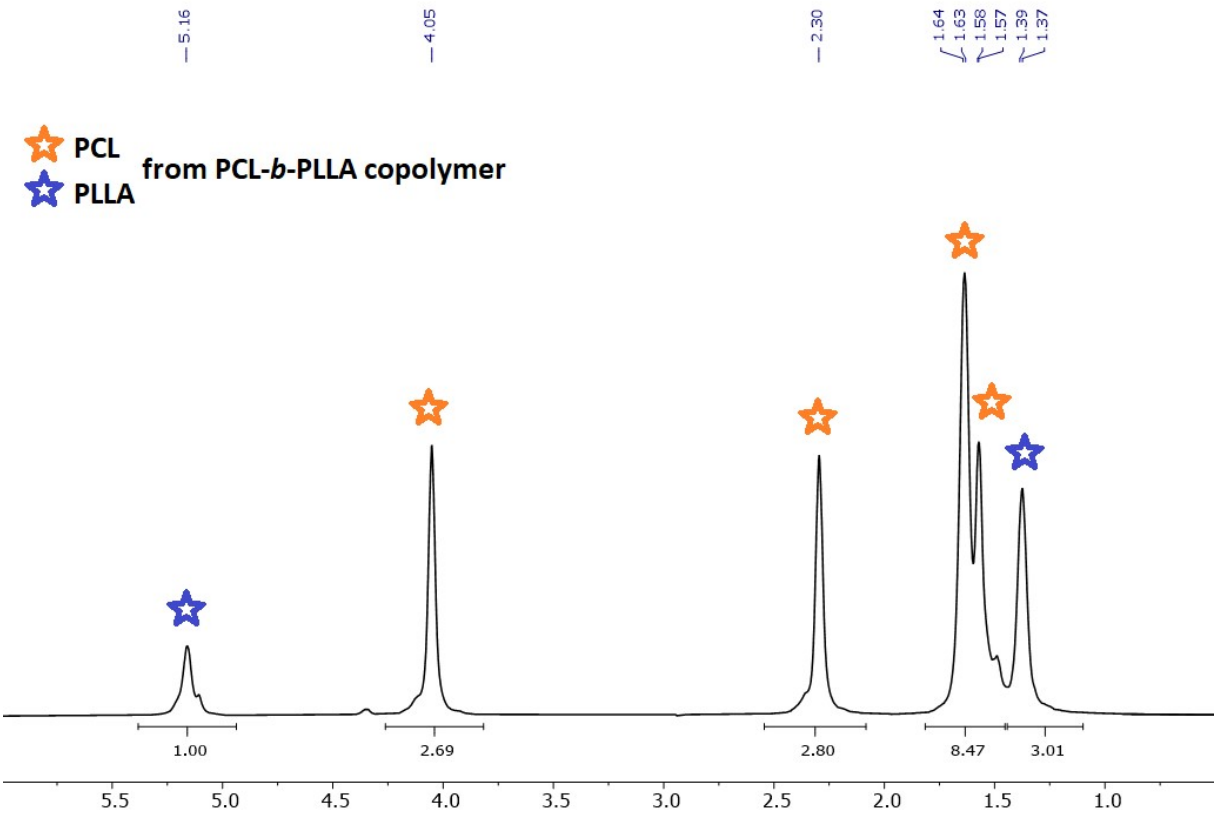

Figure S18. ^{1}H NMR spectrum (expansion of the 0.5-6 ppm region, $CDCl_3$) of the isolated PCL-*b*-PLLA block copolymer synthesized by sequential bulk copolymerization of CL and LLA catalysed by complex **1** under immortal conditions. Conditions: Co/CL/LLA/BnOH = 1/500/500/10, bulk, 120 °C, 108 + 48 h, 73% and 82% conversion of CL and LLA, respectively.