Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Tuning a robust system: N,O Zinc Guanidine Catalysts for the ROP of Lactide

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1. Ligand synthesis

Methyl 2-((bis(dimethylamino)methylene)amino)-4-(dimethylamino)benzoate (TMG4NMe$_2$asme, L1):

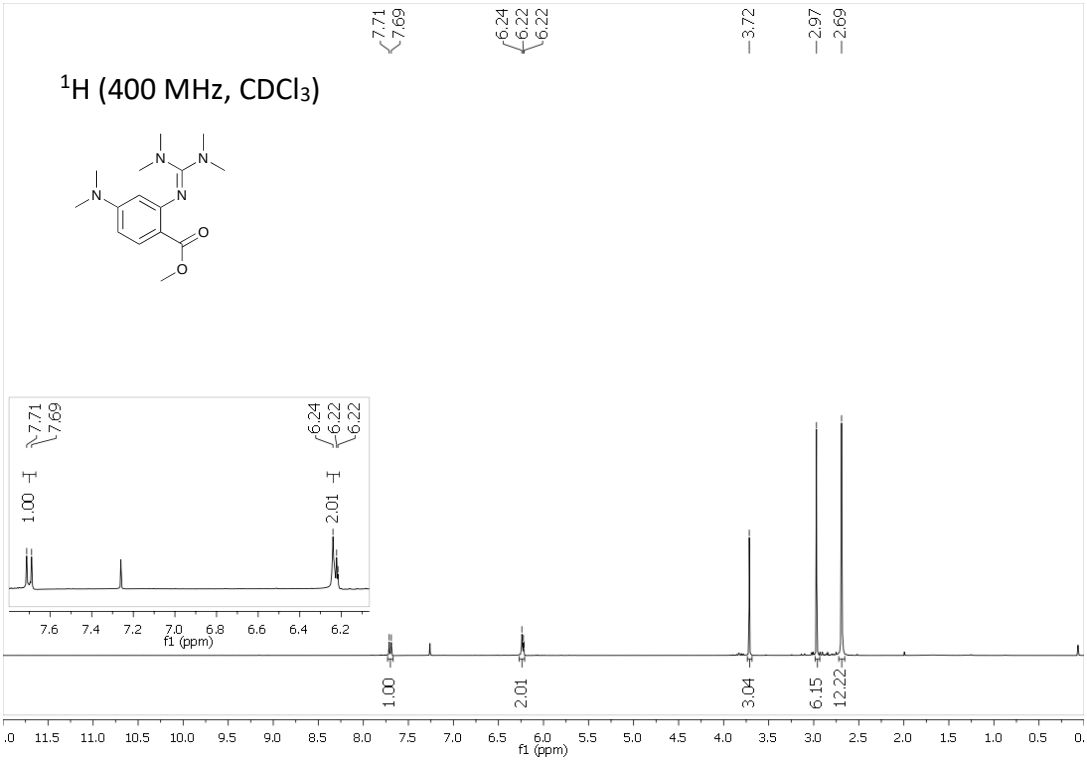


Fig SI 1. ^{1}H NMR spectrum of the ligand **L1** TMG4NMe$_2$asme (methyl 2-((bis(dimethylamino)methylene)amino)-4-(dimethylamino)benzoate).

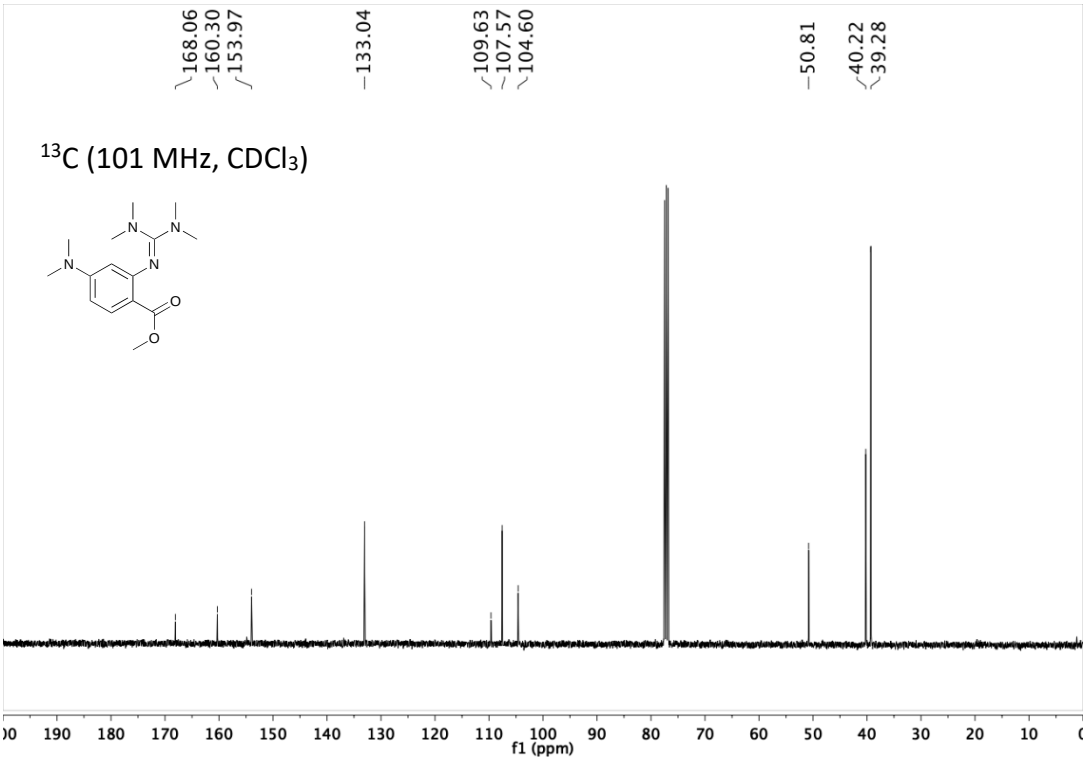


Fig SI 2. ^{13}C NMR spectrum of the ligand **L1** TMG4NMe$_2$asme (methyl 2-((bis(dimethylamino)methylene)amino)-4-(dimethylamino)benzoate).

Methyl 2-((bis(dimethylamino)methylene)amino)-5-chlorobenzoate (TMG5Clasme, L2):

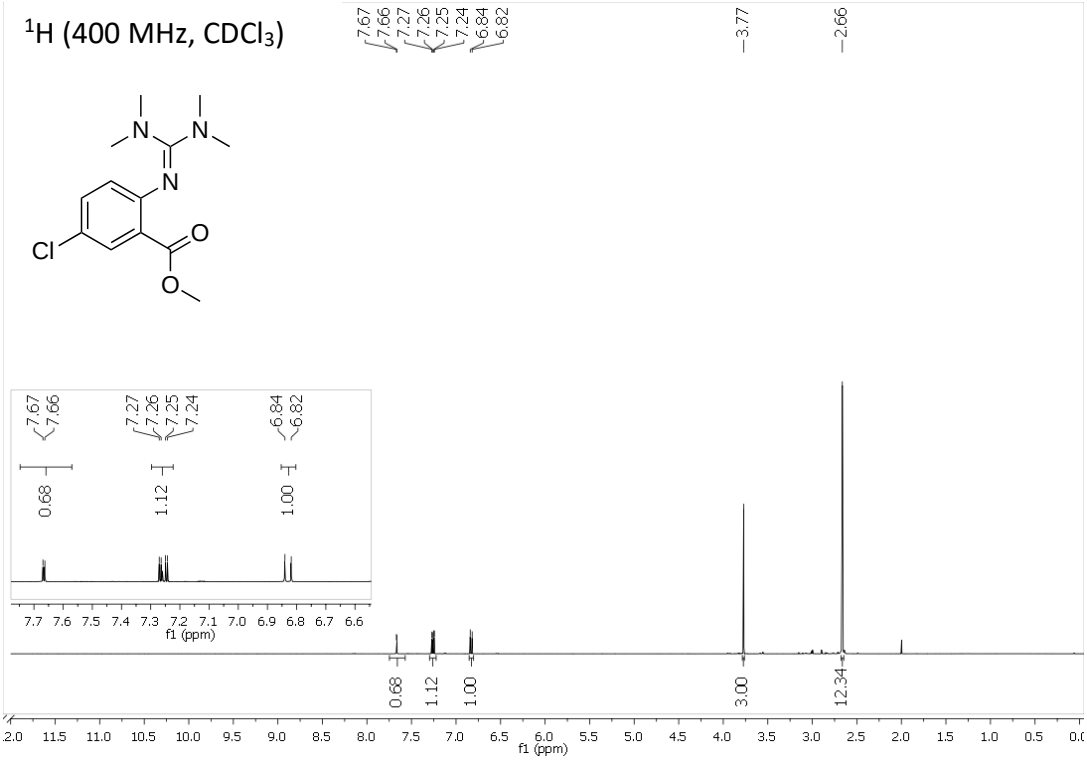


Fig SI 3. ^{1}H NMR spectrum of the ligand **L2** TMG5Clasme (methyl 2-((bis(dimethylamino)methylene)amino)-5-chlorobenzoate).

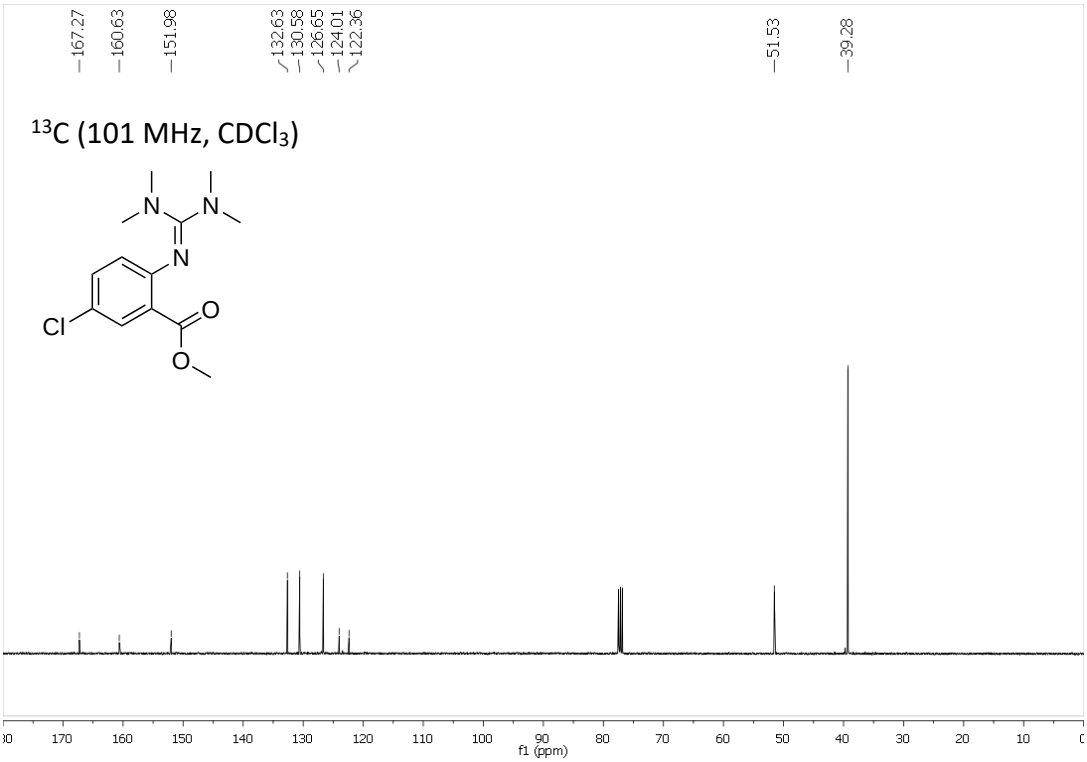


Fig SI 4. ^{13}C NMR spectrum of the ligand **L2** TMG5Clasme (methyl 2-((bis(dimethylamino)methylene)amino)-5-chlorobenzoate).

Methyl 2-((bis(dimethylamino)methylene)amino)-5-methylbenzoate (TMG5Measme, L3):

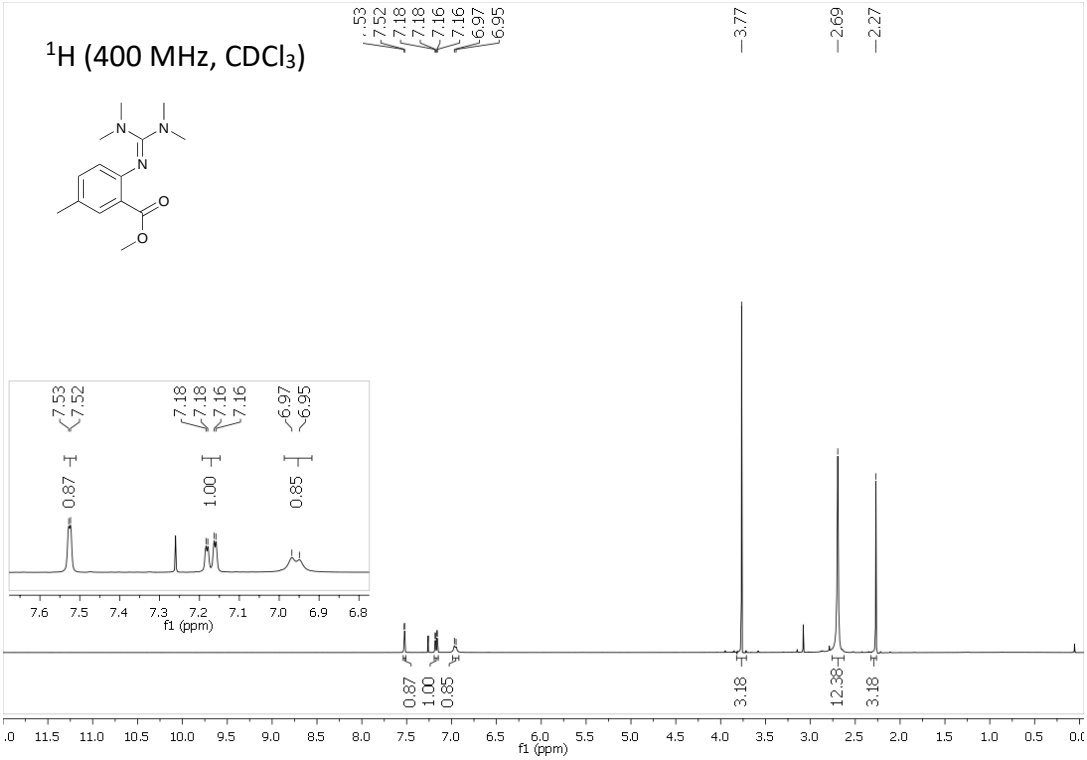


Fig SI 5. ^{1}H NMR spectrum of the ligand **L3** TMG5Measme (methyl 2-((bis(dimethylamino)methylene)amino)-5-methylbenzoate).

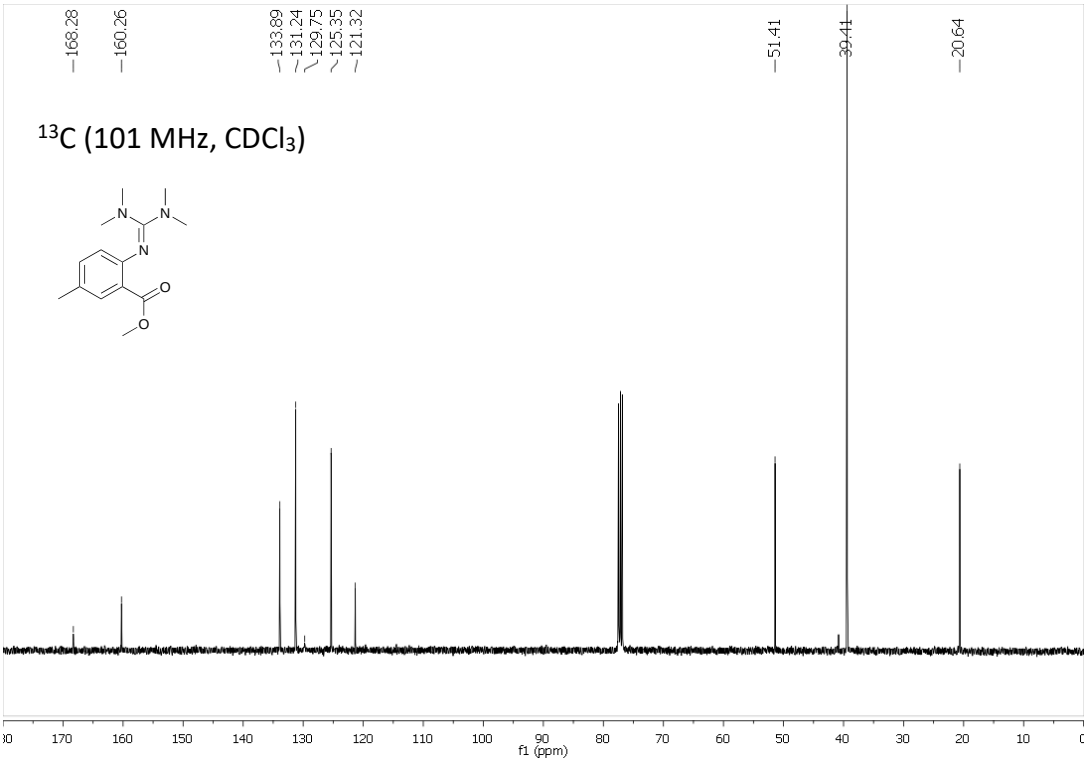


Fig SI 6. ^{13}C NMR spectrum of the ligand **L3** TMG5Measme (methyl 2-((bis(dimethylamino)methylene)amino)-5-methylbenzoate).

Methyl 2-((bis(dimethylamino)methylene)amino)-5-(dimethylamino)benzoate (TMG5NMe$_2$asme, L4):

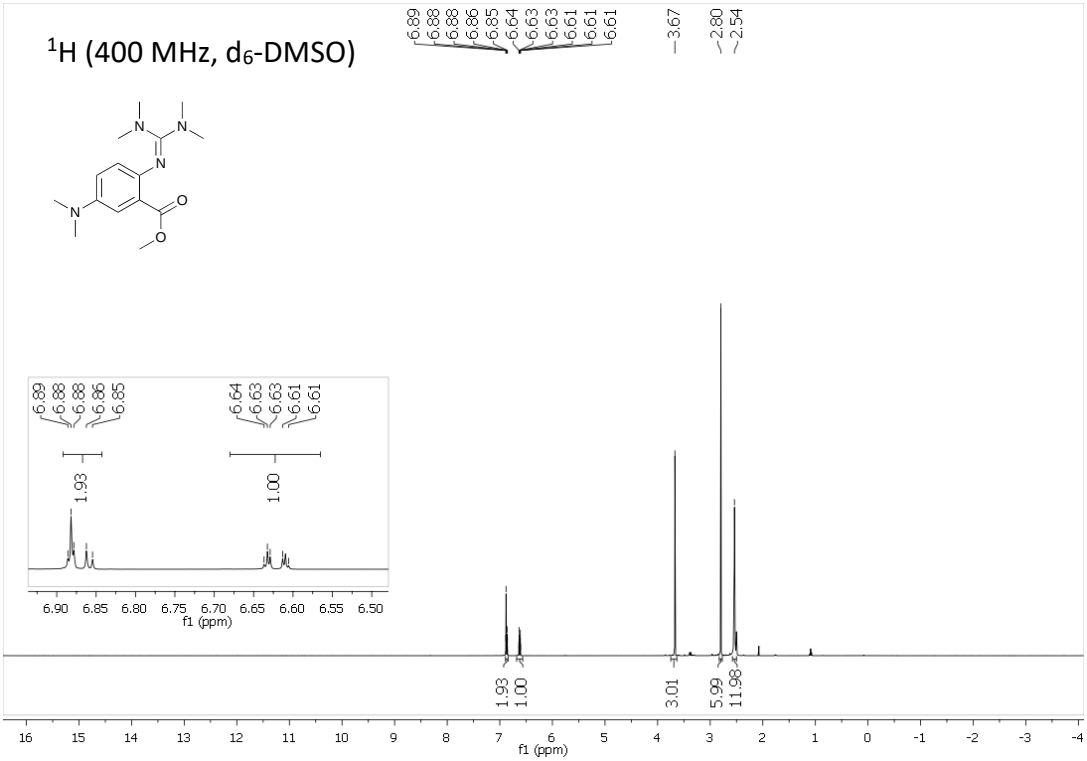


Fig SI 7. ^{1}H NMR spectrum of the ligand **L4** TMG5NMe$_2$asme (methyl 2-((bis(dimethylamino)methylene)amino)-5-(dimethylamino)benzoate).

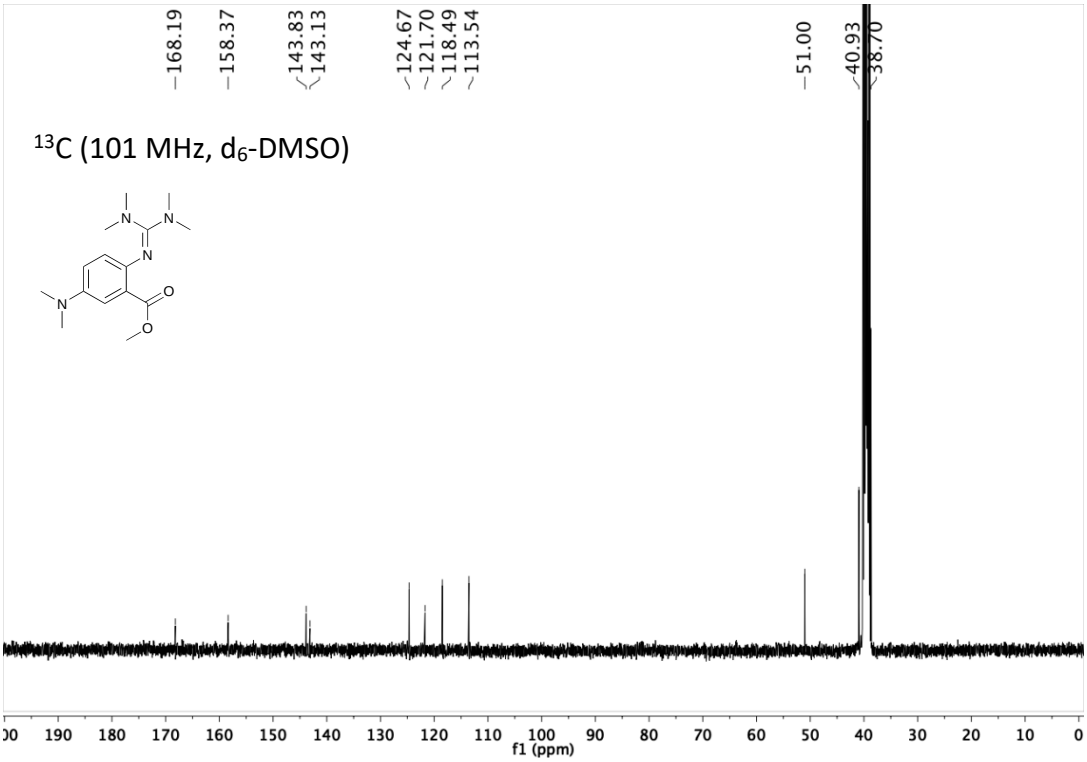


Fig SI 8. ^{13}C NMR spectrum of the ligand **L4** TMG5NMe$_2$asme (methyl 2-((bis(dimethylamino)methylene)amino)-5-(dimethylamino)benzoate).

2. Complex synthesis

[$ZnCl_2$(TMG4NMe$_2$asme)] (C1):

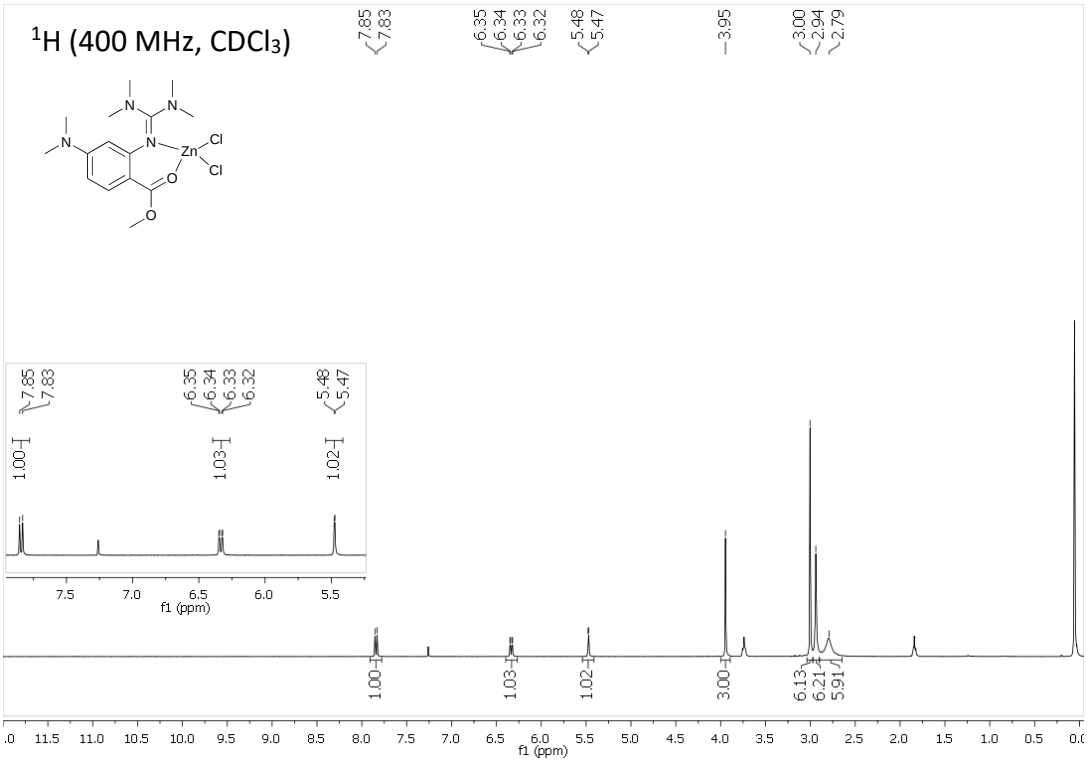


Fig SI 9. ^{1}H NMR spectrum of the complex **C1** [$ZnCl_2$(TMG4NMe$_2$asme)].

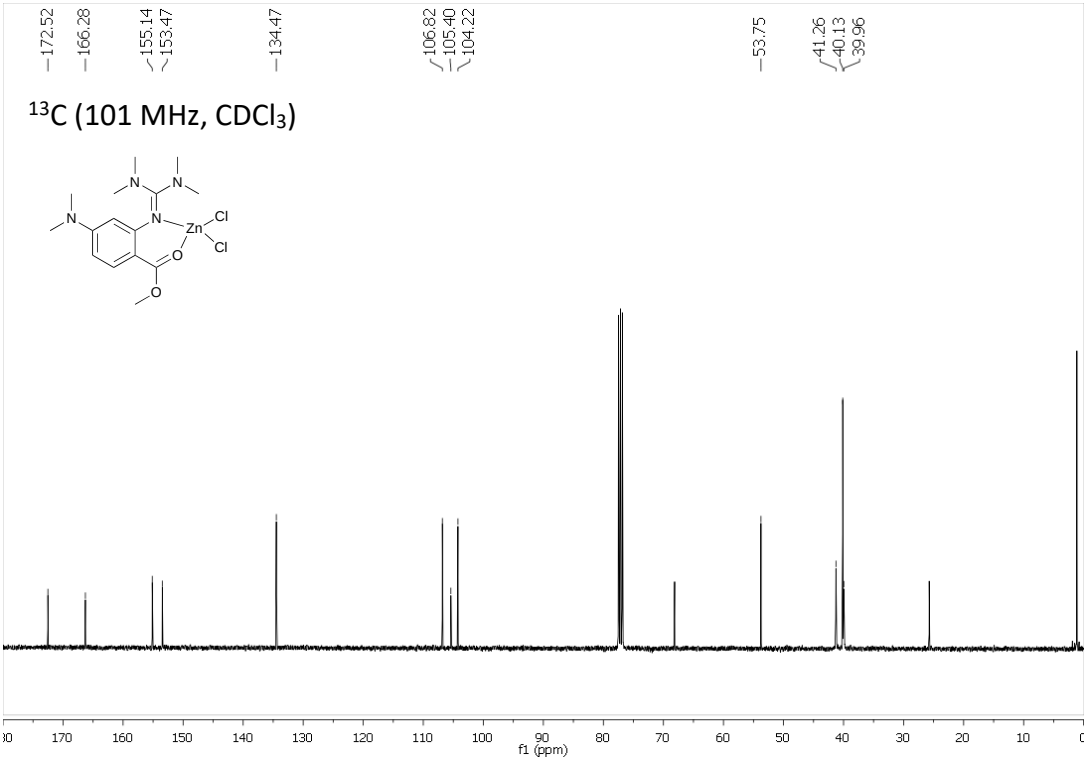


Fig SI 10. ^{13}C NMR spectrum of the complex **C1** [$ZnCl_2$(TMG4NMe$_2$asme)].

[$ZnCl_2$(TMG5Clasme)] (C2):

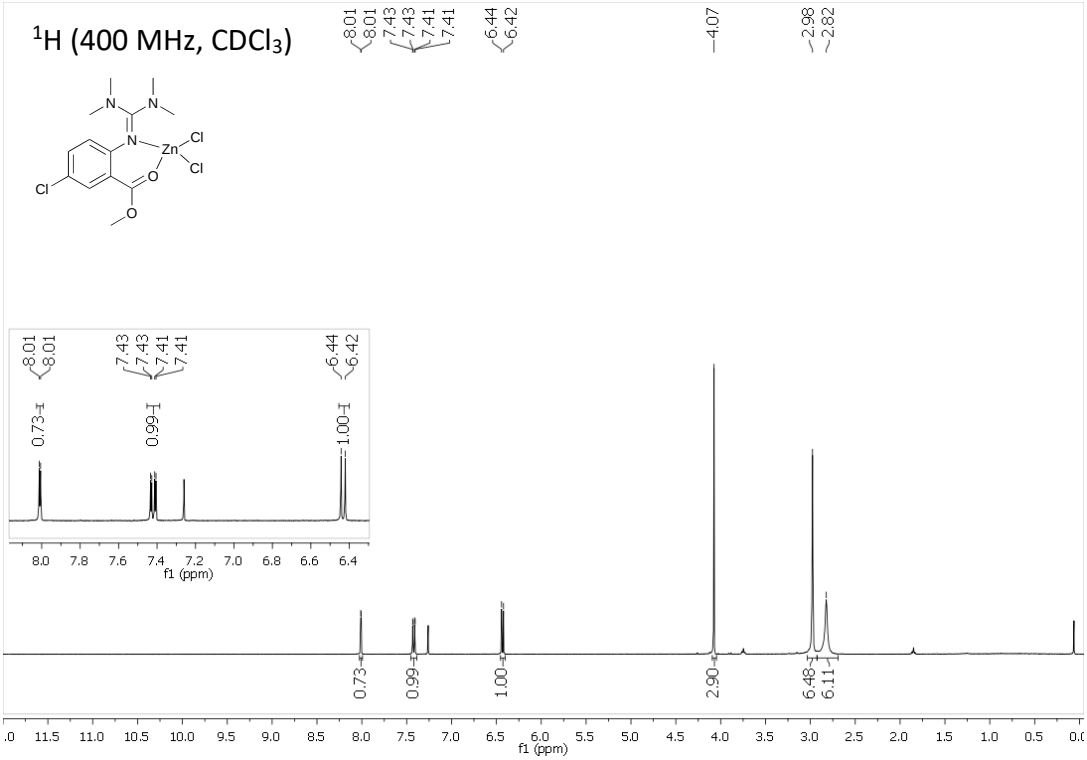


Fig SI 11. ^{1}H NMR spectrum of the complex **C2** [$ZnCl_2$(TMG5Clasme)].

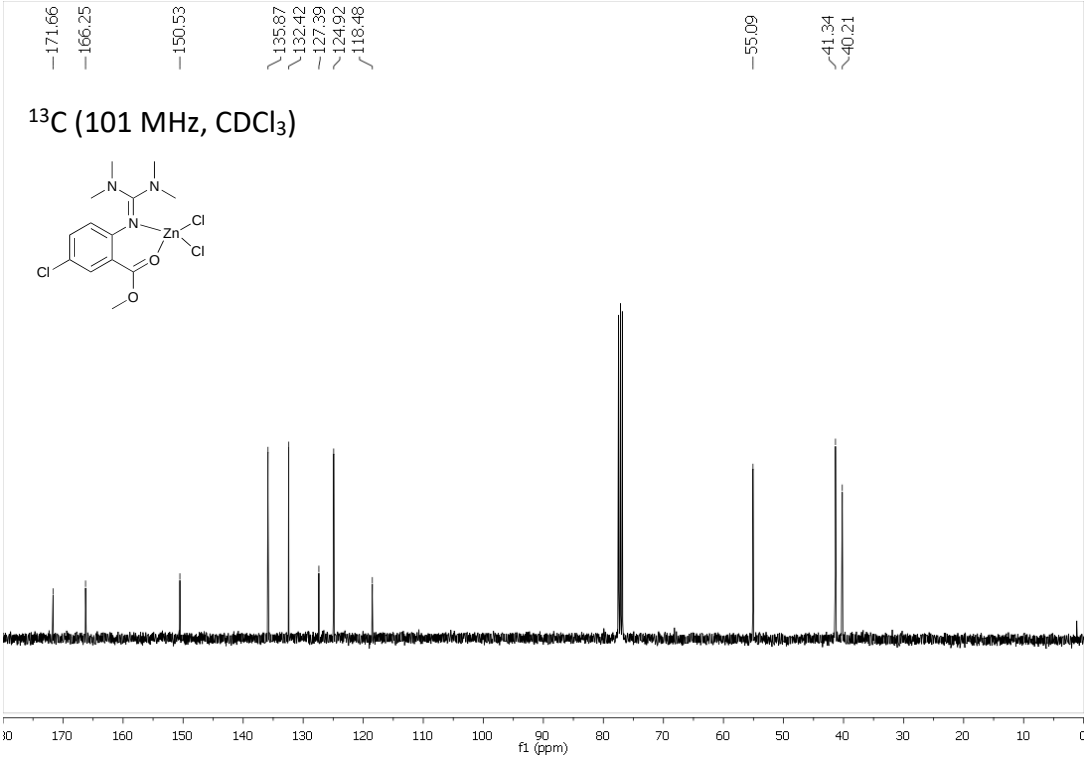


Fig SI 12. ^{13}C NMR spectrum of the complex **C2** [$ZnCl_2$(TMG5Clasme)].

[$ZnCl_2$(TMG5Measme)] (C3):

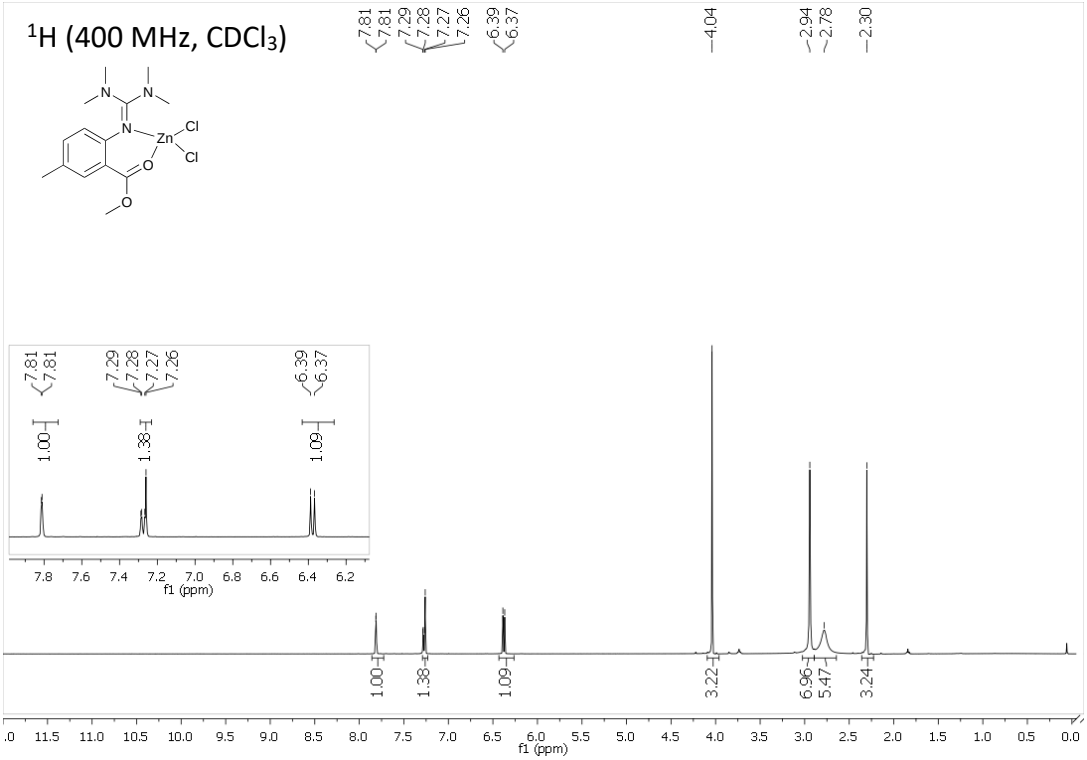


Fig SI 13. ^{1}H NMR spectrum of the complex **C3** [$ZnCl_2$(TMG5Measme)].

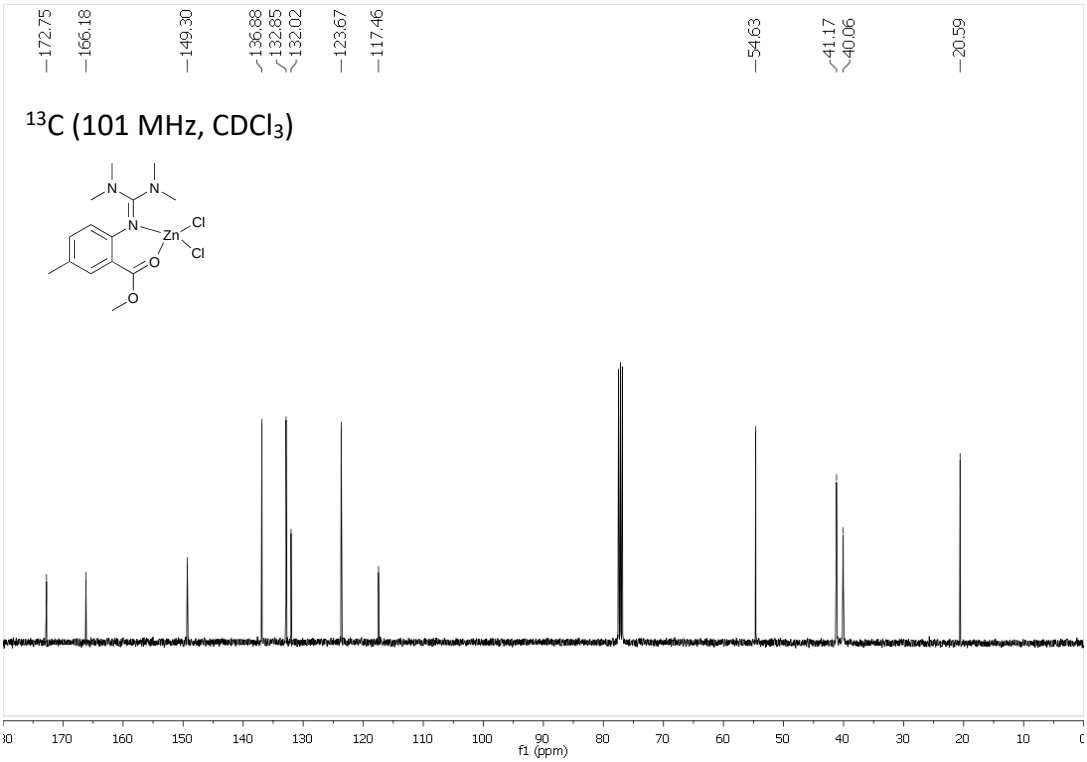


Fig SI 14. ^{13}C NMR spectrum of the complex **C3** [$ZnCl_2$(TMG5Measme)].

[$ZnCl_2$(TMG5NM$e_2$asme)] (C4):

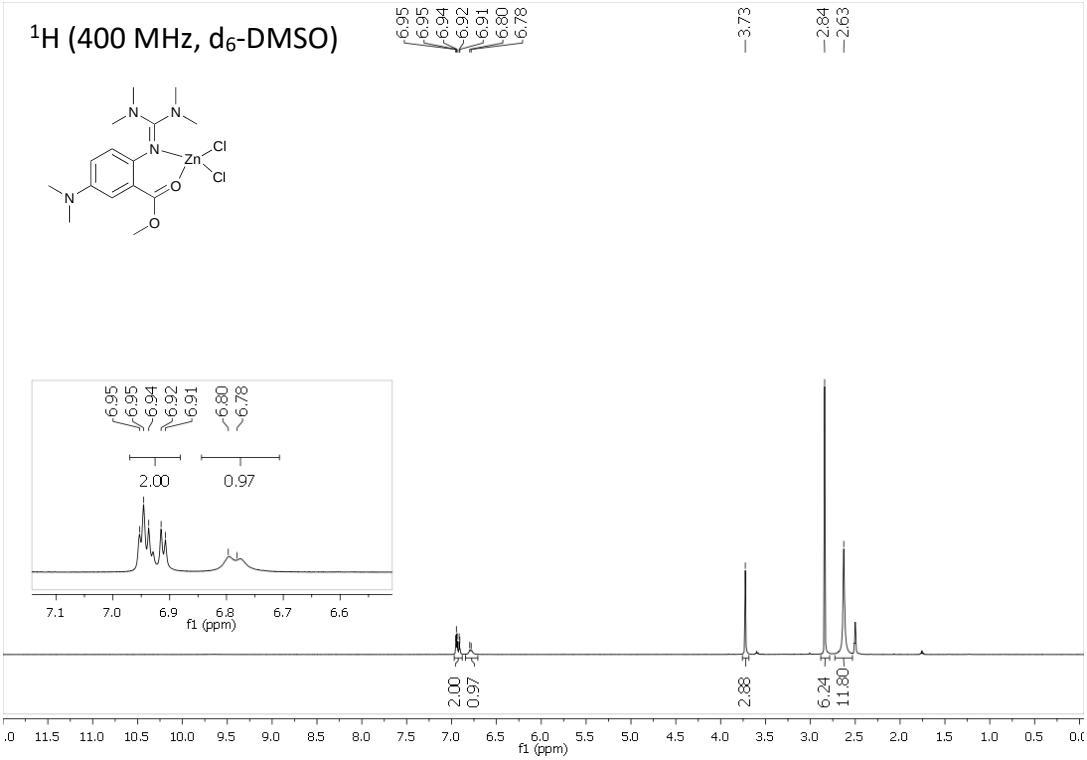


Fig SI 15. ^{1}H NMR spectrum of the complex **C4** [$ZnCl_2$(TMG5NM$e_2$asme)].

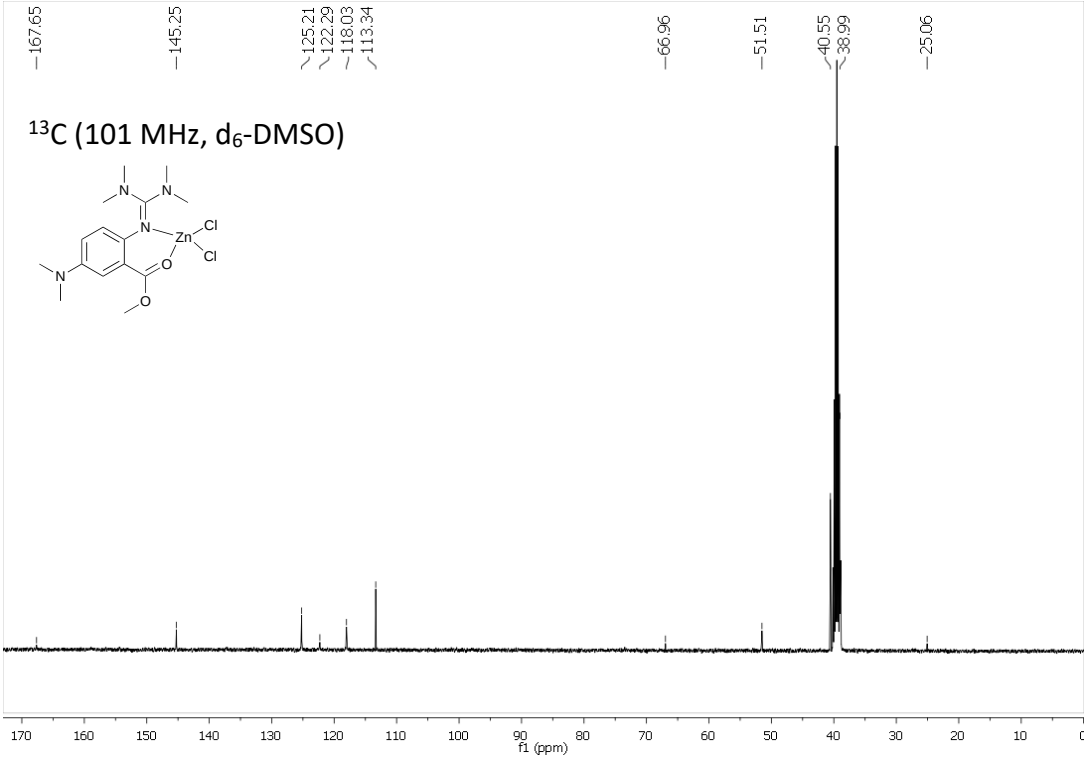


Fig SI 16. ^{13}C NMR spectrum of the complex **C4** [$ZnCl_2$(TMG5NM$e_2$asme)].

3. Kinetics

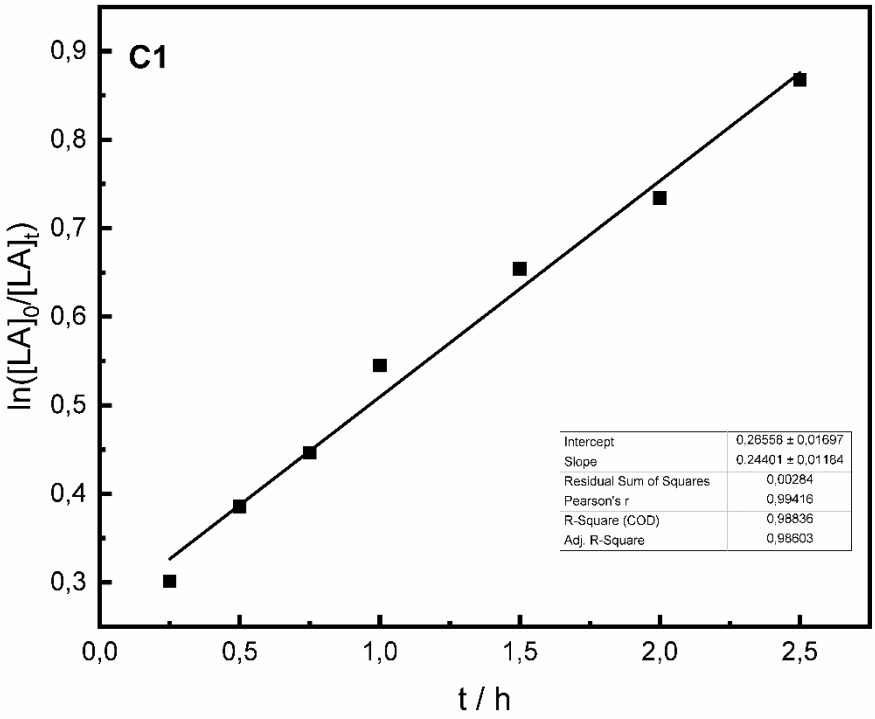


Fig SI 17. Semi-logarithmic plot of the polymerisation of non-purified *rac*-LA with **C1** [$ZnCl_2$(TMG4NMe$_2$asme)] [M]/[I] = 500:1, 150 °C, 260 rpm, Schlenk tube-technic, conversion determined by ^{1}H NMR spectroscopy.

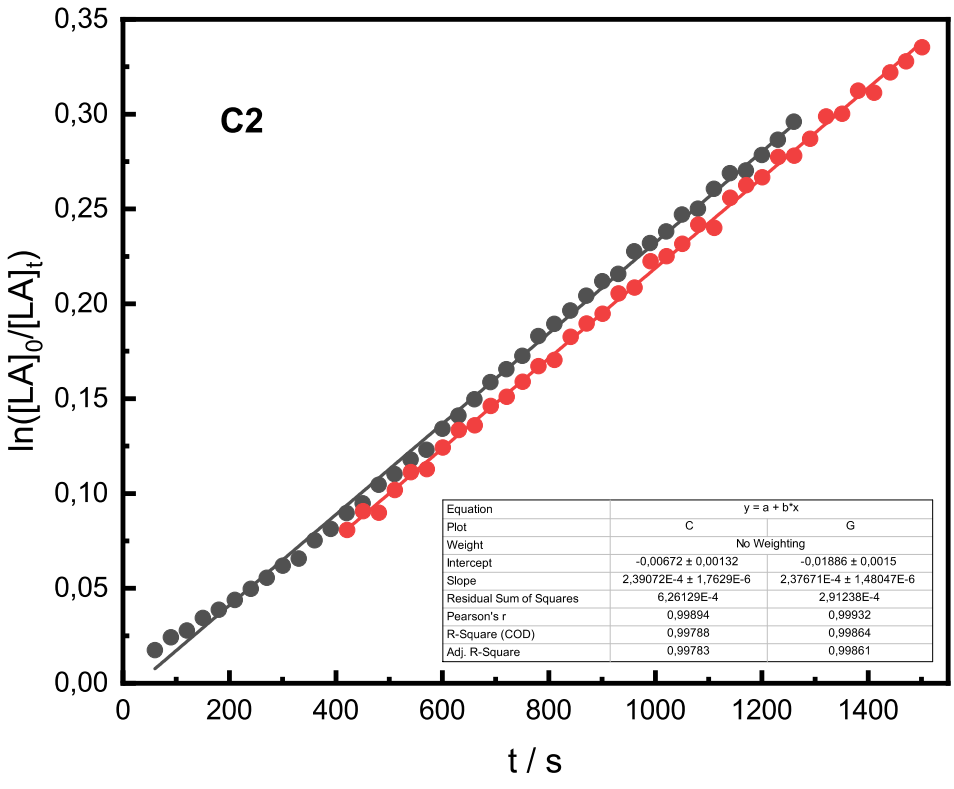


Fig SI 18. Semi-logarithmic plot of the polymerisations of non-purified *rac*-LA (determined twice) with **C2** [$ZnCl_2$(TMG5Clasme)] [M]/[I] = 500:1, 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

Table S1. Polymerisation data for *rac*-LA with catalyst **C2**.[a]

init.	k_{app} [s^{-1}][b]	time	conv. [%][c]	$M_{n,theo}$ [g mol^{-1}]	M_n [g mol^{-1}][d]	*PD*
C2	2.39 x 10^{-4}	53 min	25	18 000	43 900	1.4
C2	2.38 x 10^{-4}	60 min	28	20 000	43 000	1.3

[a] Conditions: 150 °C, solvent free, non-purified technical grade *rac*-LA, [M]/[I] = 500:1. [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.

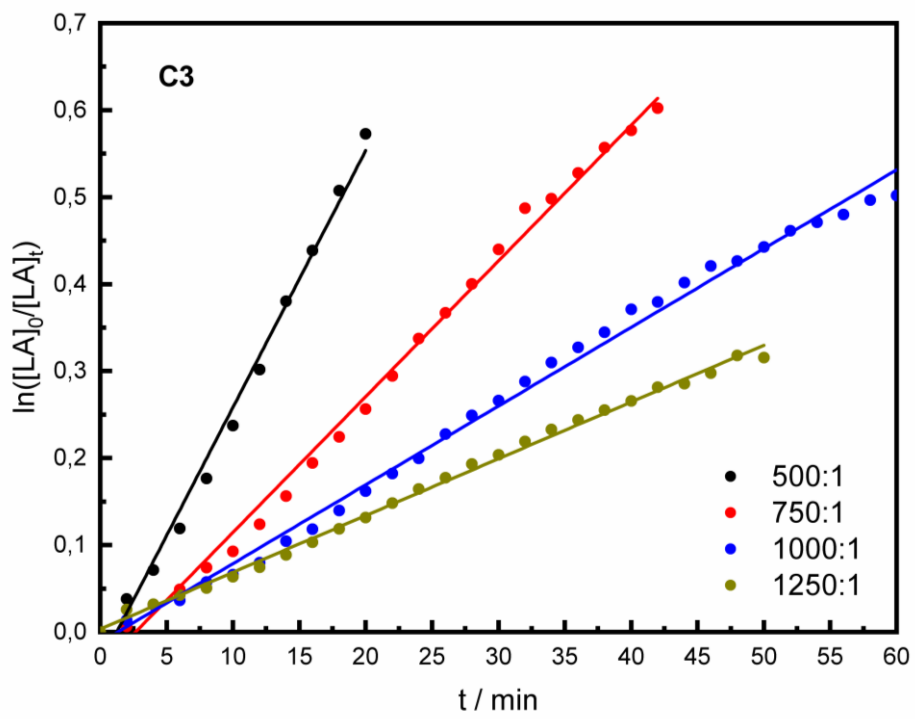


Fig SI 19. Semi-logarithmic plot of the polymerisation of non-purified *rac*-LA with **C3** [$ZnCl_2$(TMG5Measme)] [M]/[I] = 500:1 (k_{app} = 2.95 x 10^{-2} min^{-1}), 750:1 (k_{app} = 1.56 x 10^{-2} min^{-1}), 1000:1 (k_{app} = 0.91 x 10^{-2} min^{-1}) and 1250:1 (k_{app} = 0.65 x 10^{-2} min^{-1}) at 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

Table S2. Polymerisation data for *rac*-LA with catalyst **C3**.[a]

[M]/[I]	k_{app} [min^{-1}][b]	time	conv. [%][c]	$M_{n,theo}$ [g mol^{-1}]	M_n [g mol^{-1}][d]	*PD*
500	2.95 x 10^{-2}	36 min	68	49 000	85 500	1.5
750	1.56 x 10^{-2}	78 min	63	68 000	74 700	1.5
1000	0.91 x 10^{-2}	170 min	58	83 500	56 300	1.4
1250	0.65 x 10^{-2}	322 min	54	97 200	46 400	1.3

[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.

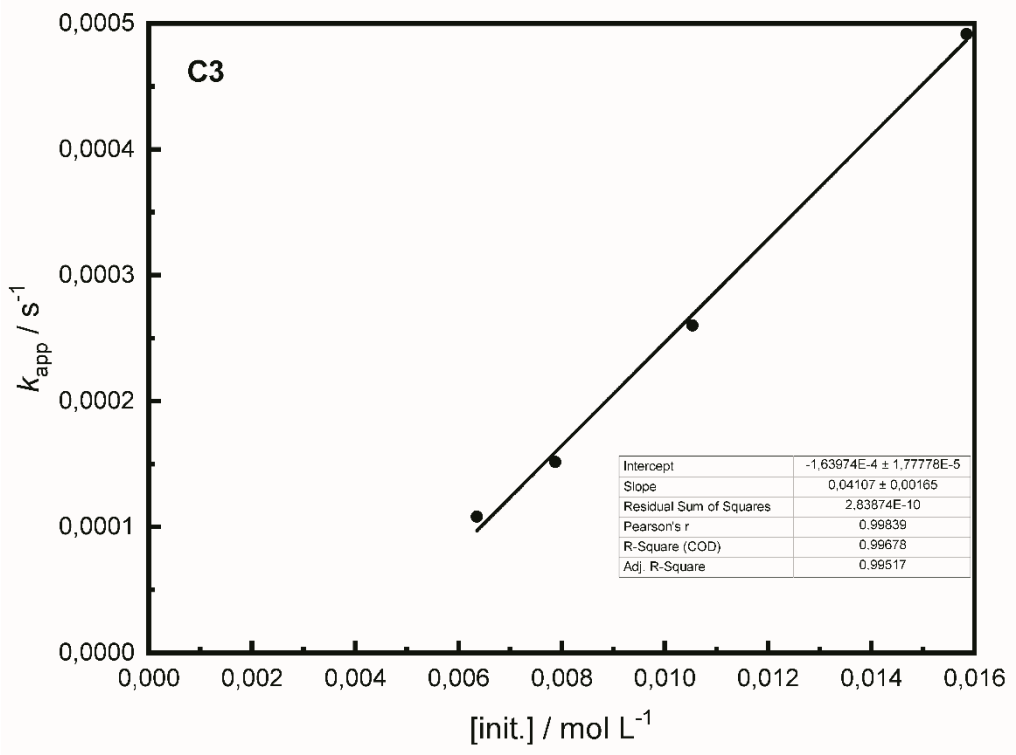


Fig SI 20. Plot of k_{app} versus [init.] for **C3**. Conditions: *rac*-LA, 150 °C, 260 rpm, non-purified lactide; [M]/[I] = 500:1, 750:1, 1000:1, 1250:1. No conversion is detected below a catalyst concentration of 0.004 mol L^{-1}, this is presumably due to deactivation by impurities in the monomer feed. Above 0.004 mol L^{-1} conversion is observed.

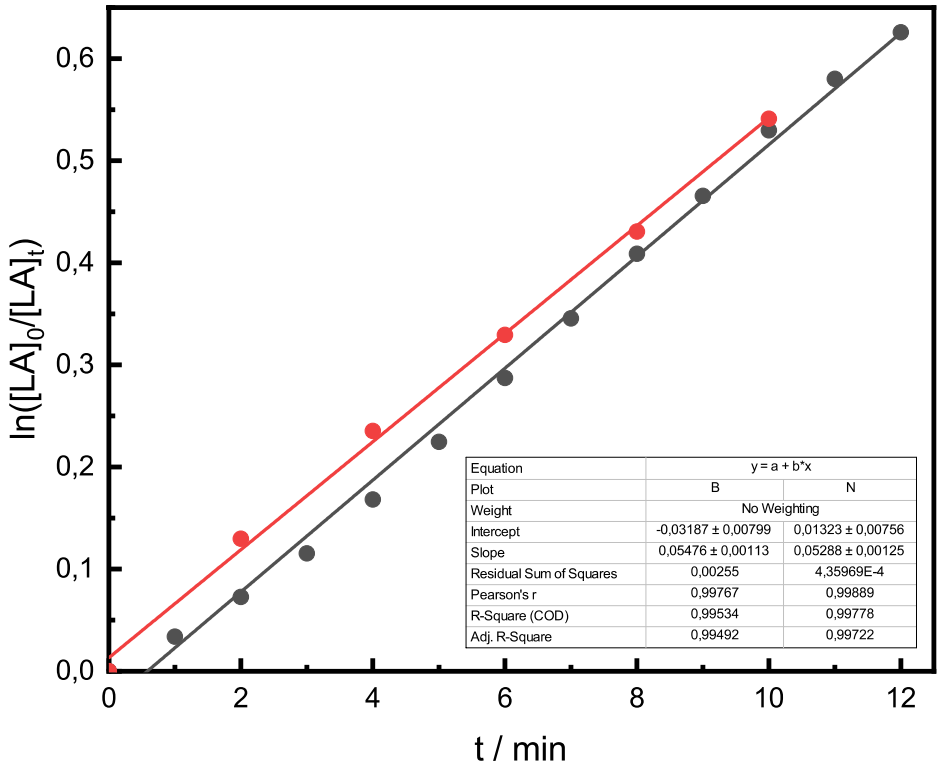


Fig SI 21. Semi-logarithmic plot of the polymerisations of non-purified *rac*-LA (determined twice) with **C4** [$ZnCl_2$(TMG5Clasme)] [M]/[I] = 500:1, 150 °C, 260 rpm, conversion determined by *in situ* Raman and IR spectroscopy.

Table S3. Polymerisation data for *rac*-LA with catalyst **C4**.[a]

init.	k_{app} [min^{-1}][b]	time	conv. [%][c]	$M_{n,theo}$ [g mol^{-1}]	M_n [g mol^{-1}][d]	*PD*
C4	5.48 x 10^{-2}	30 min	69	50 000	55 000	1.3
C4	5.29 x 10^{-2}	120 min	81	58 000	71 000	1.4

[a] Conditions: 150 °C, solvent free, non-purified technical grade *rac*-LA, [M]/[I] = 500:1. [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.

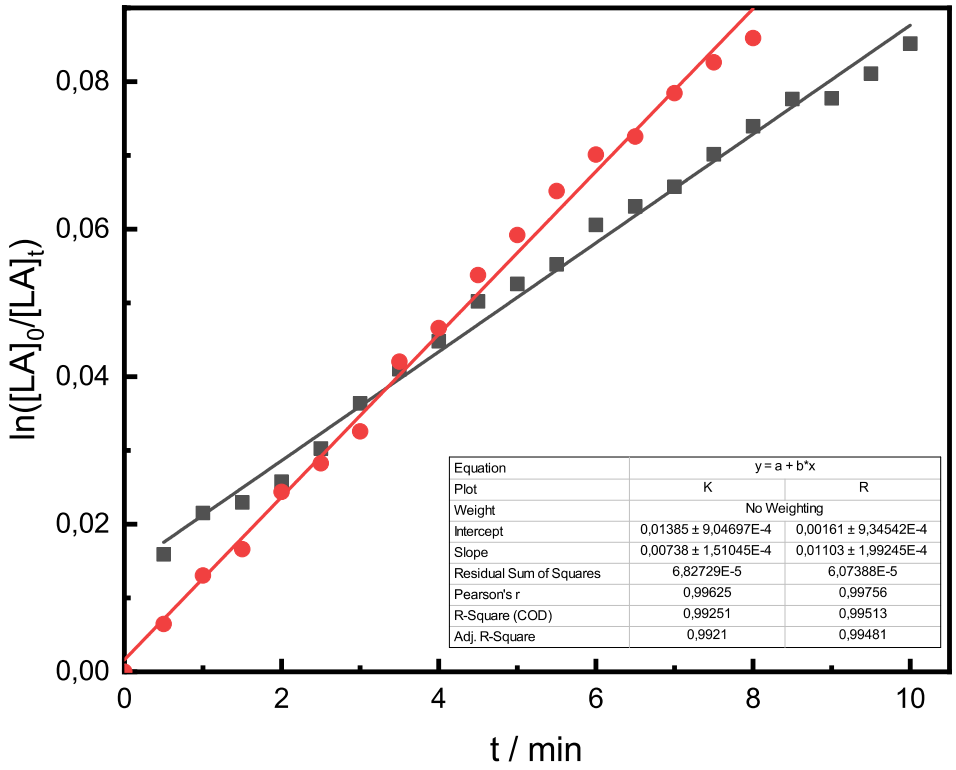


Fig SI 22. Semi-logarithmic plot of the polymerisations of non-purified *rac*-LA (determined twice) with **C4** [$ZnCl_2$(TMG5Clasme)] [M]/[I] = 2000:1, 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

Table S4. Polymerisation data for *rac*-LA with catalyst **C4**.[a]

init.	k_{app} [min^{-1}][b]	time	conv. [%][c]	$M_{n,theo}$ [g mol^{-1}]	M_n [g mol^{-1}][d]	*PD*
C4	7.38 x 10^{-3}	40 min	27	50 000	-	-
C4	11.03 x 10^{-3}	46 min	29	58 000	-	-

[a] Conditions: 150 °C, solvent free, non-purified technical grade *rac*-LA, [M]/[I] = 2000:1. [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.

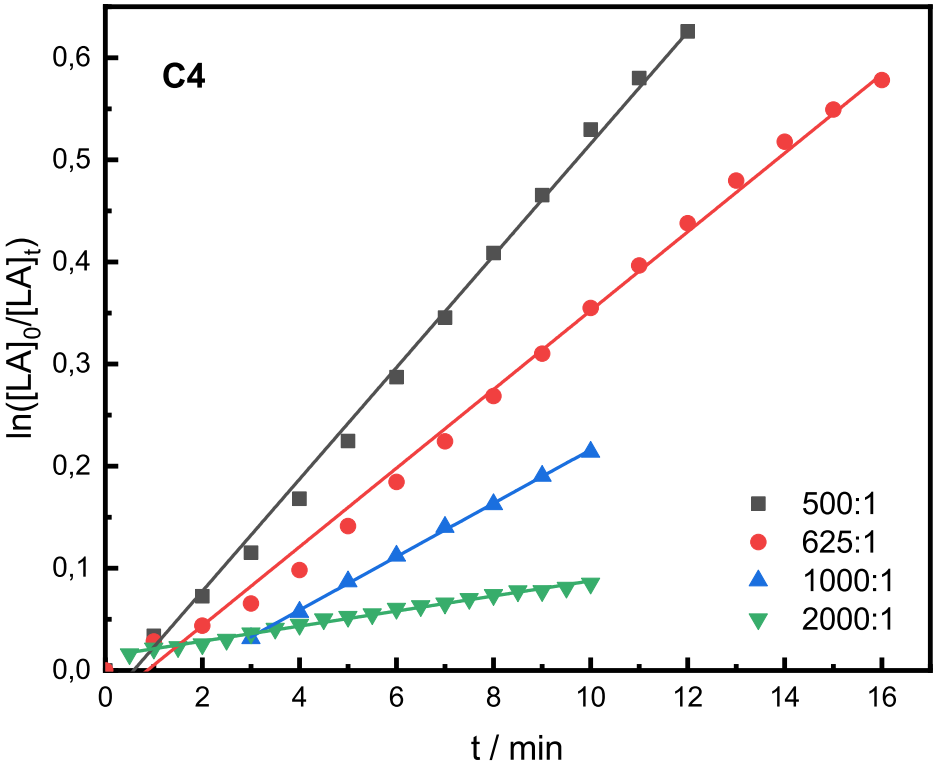


Fig SI 23. Semi-logarithmic plot of the polymerisation of non-purified *rac*-LA with **C4** [$ZnCl_2$(TMG5NMe$_2$asme)] [M]/[I] = 500:1 (k_{app} = 5.48 x 10^{-2} min^{-1}), 625:1 (k_{app} = 3.86 x 10^{-2} min^{-1}), 1000:1 (k_{app} = 0.97 x 10^{-2} min^{-1}) and 2000:1 (k_{app} = 0.20 x 10^{-2} min^{-1}) at 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

Table S5. Polymerisation data for *rac*-LA with catalyst **C4**.[a]

[M]/[I]	k_{app} [min^{-1}][b]	time	conv. [%][c]	$M_{n,theo}$ [g mol^{-1}]	M_n [g mol^{-1}][d]	*PD*
500	5.48 x 10^{-2}	30 min	69	49 000	55 500	1.3
625	3.86 x 10^{-2}	38 min	73	68 000	70 000	1.4
1000	0.97 x 10^{-2}	90 min	49	83 500	45 000	1.2
2000	0.20 x 10^{-2}	46 min	29	97 200	-	-

[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.

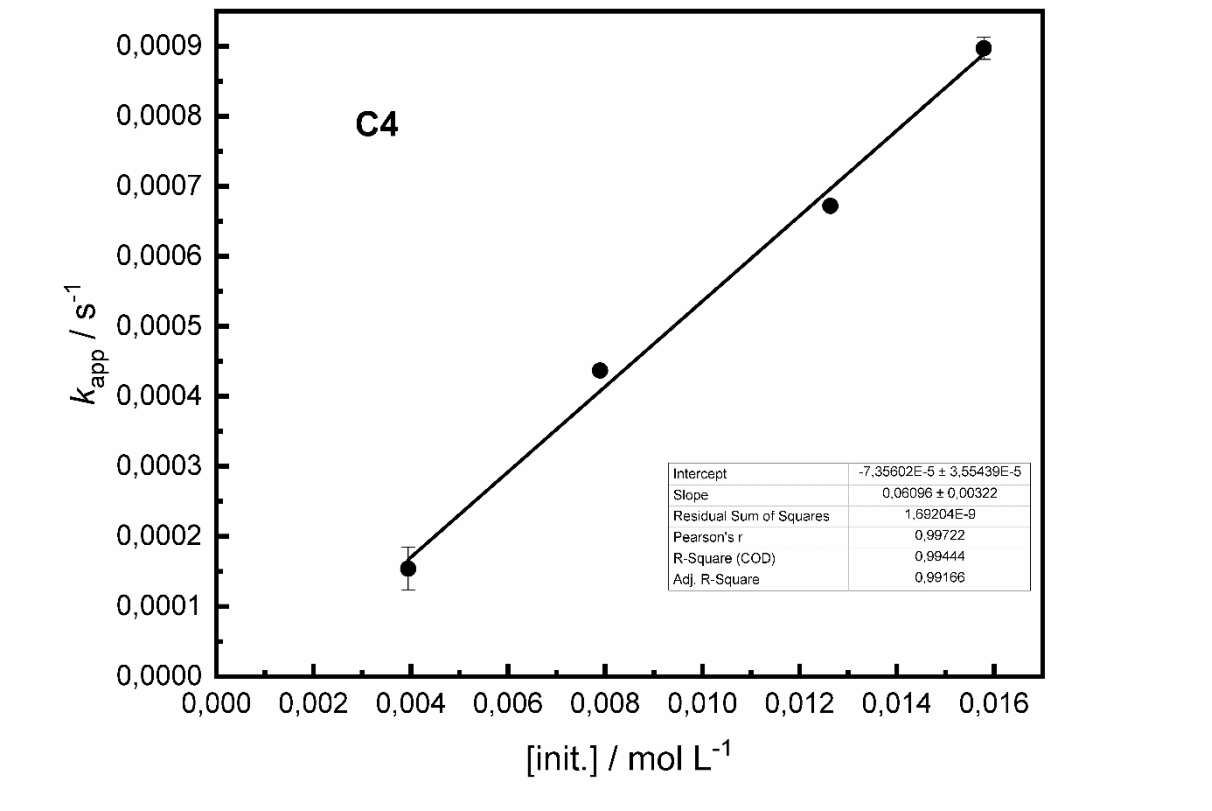


Fig SI 24. Plot of k_{app} versus [init.] for **C4**. Conditions: *rac*-LA, 150 °C, 260 rpm, non-purified lactide; [M]/[I] = 500:1, 625:1, 1000:1, 2000:1.

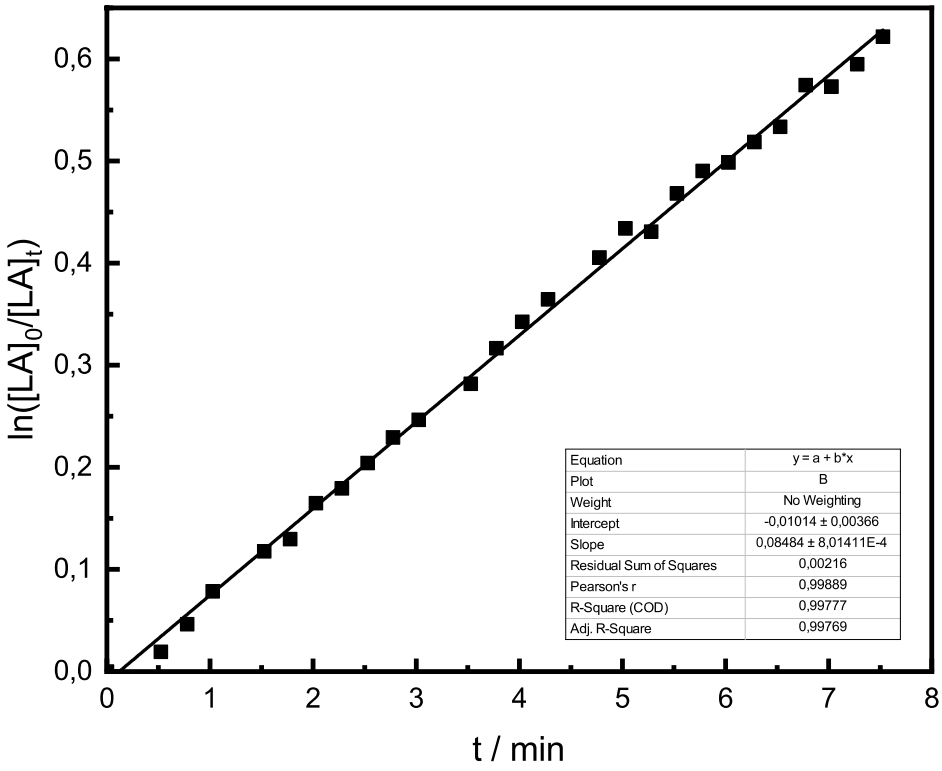


Fig SI 25. Semi-logarithmic plot of the polymerisation of non-purified *rac*-LA with **C4** [$ZnCl_2$(TMG5NM$e_2$asme)] and (3,5-bis(trifluoromethyl)benzyl alcohol) (co-init.), [M]/[I] = 625:1:1, 150 °C, 260 rpm, Schlenk tube-technic, conversion determined by ^{1}H NMR spectroscopy. k_{app} = 14.14 x 10^{-4} s^{-1}.

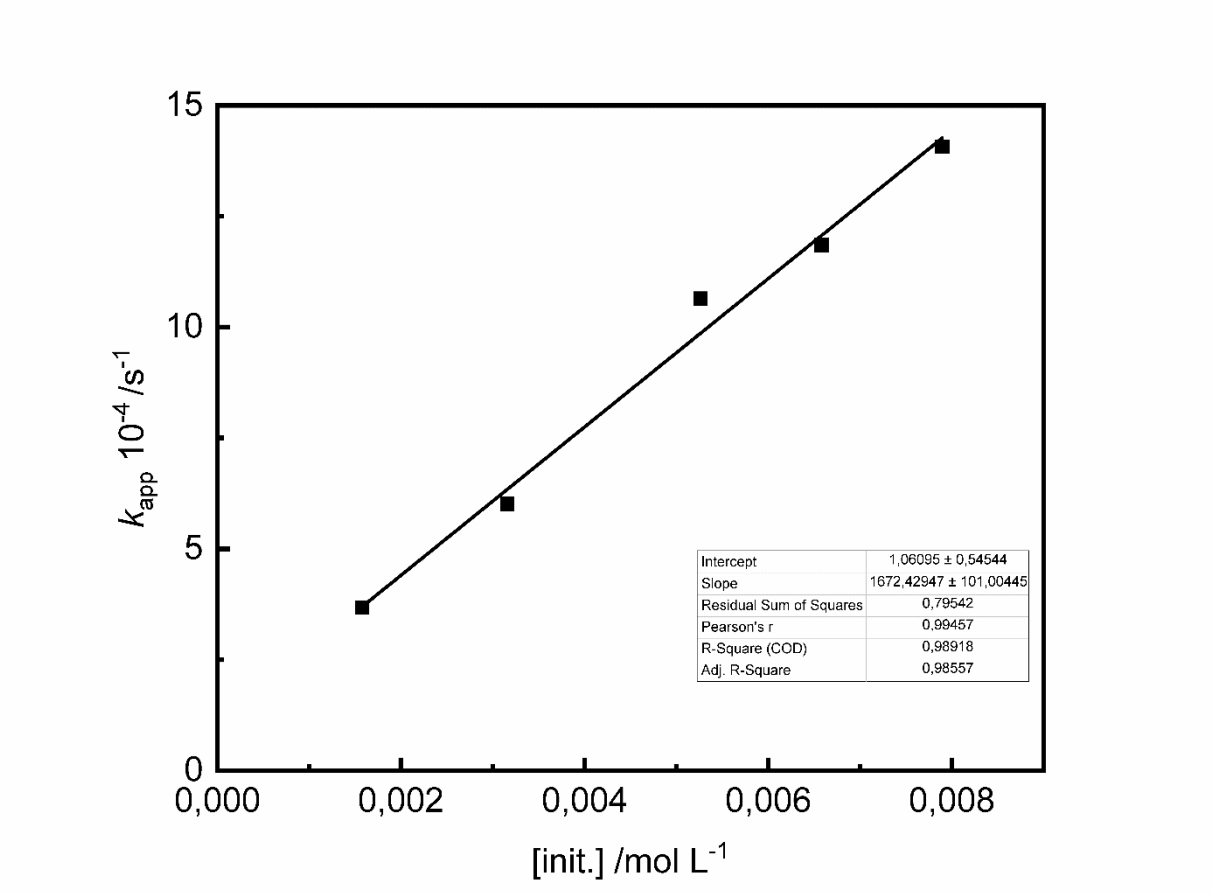


Fig SI 26. Plot of k_{app} versus [init.] for $Sn(Oct)_2$. Conditions: *rac*-LA, 150 °C, 260 rpm, non-purified lactide; [M]/[I] = 1000:1, 1250:1, 1500:1, 2500:1, 5000:1.

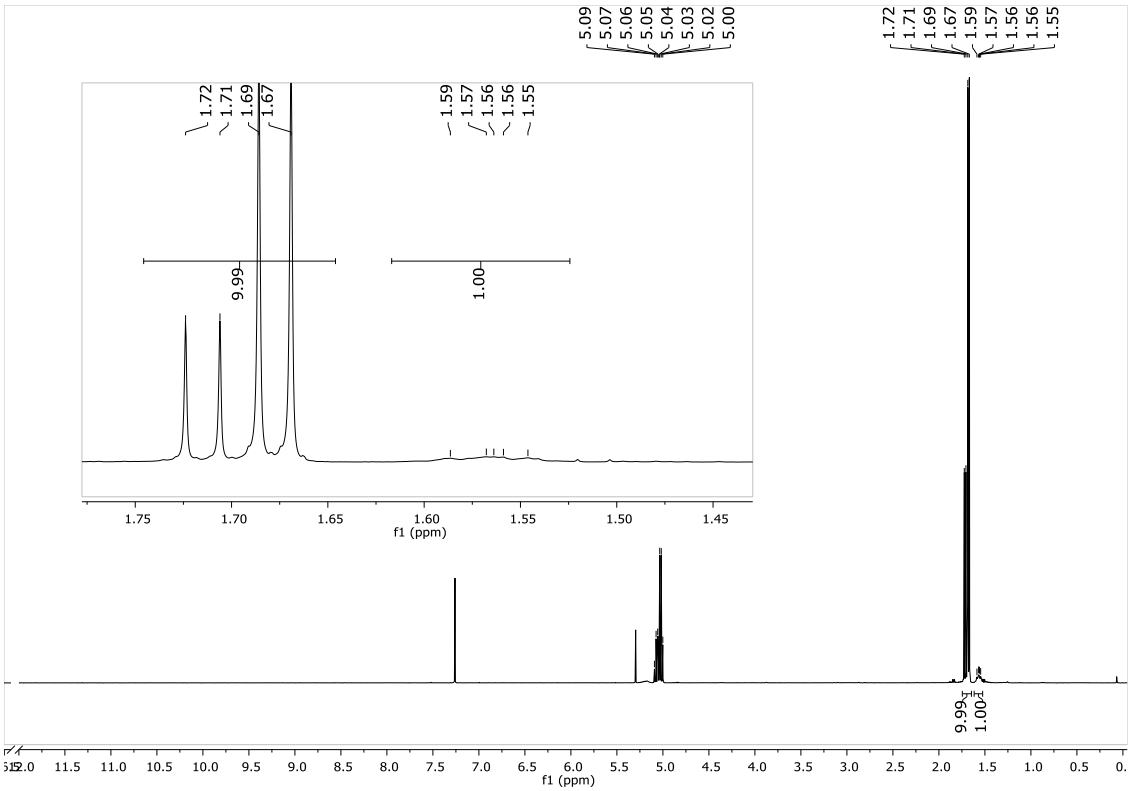


Fig SI 27. ^{1}H NMR spectrum of the polymerisation of non-purified *rac*-lactide ([M]/init.] = 500:1) using TMG5NMe$_2$asme at 150 °C, 260 rpm. Conversion of 9% after 90 min, no polymer has been obtained for further characterisations. Formation of *meso*-lactide (1.72 ppm, d) during the reaction.

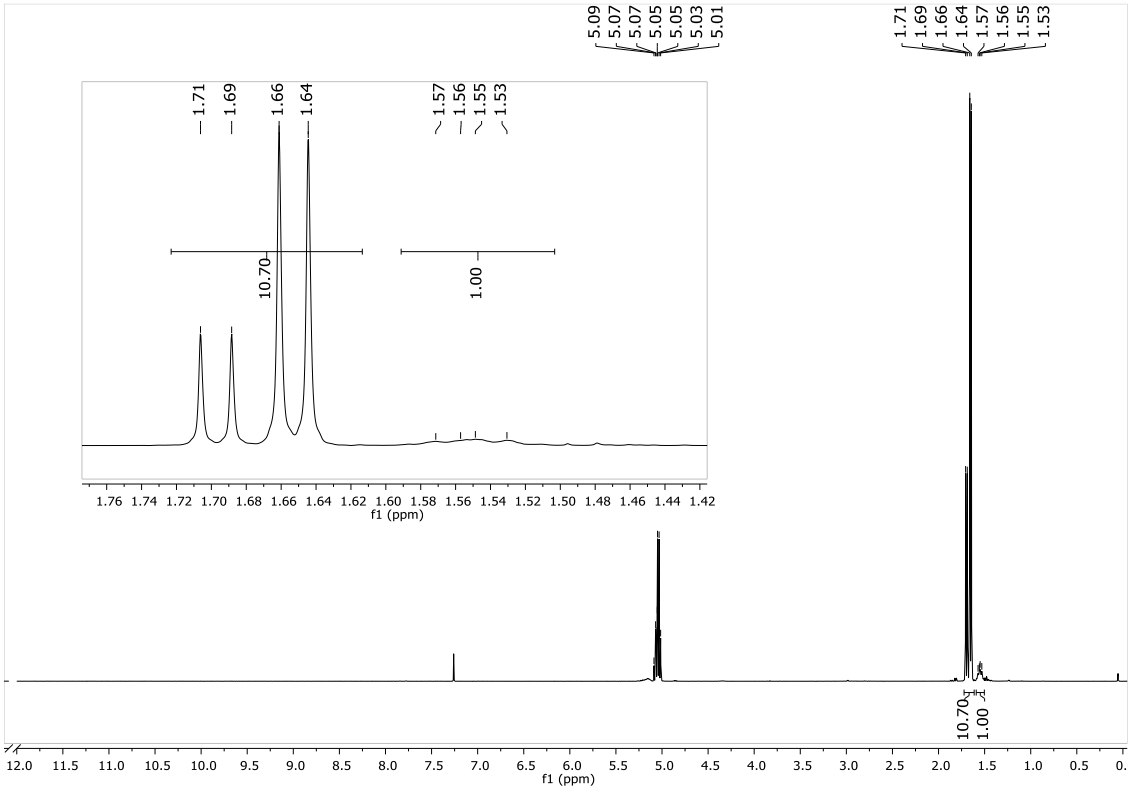


Fig SI 28. ^{1}H NMR spectrum of the polymerisation of non-purified *rac*-lactide ([M]/[init.]/[co-init.] = 500:1:1) using TMG5NMe$_2$asme (init.) and (3,5-bis(trifluoromethyl)benzyl alcohol) (co-init.) at 150 °C, 260 rpm. Conversion of 9% after 90 min, no polymer has been obtained for further characterisations. Formation of *meso*-lactide (1.72 ppm, d) during the reaction.

4. End-group analysis

4.1. MALDI-ToF

End group analysis was performed by MALDI-ToF on a Bruker ultrafleXtreme equipped with a 337 nm smartbeam laser in the reflective mode. THF solutions of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (5 µL of a 20 mg/mL solution), sodium trifluoroacetate (0.1 µL of a 10 mg/mL solution), and analyte (5 µL of a 10 mg/mL) were mixed and a droplet thereof applied on the sample target. Protein 1 calibration standard is the name of the protein mixture used for calibration. For spectra 4000 laser shots with 24% laser power were collected. The laser repetition rate was 1000 Hz. The homopolymer analysis was performed using Polymerix software (Sierra analytics).

4.2.

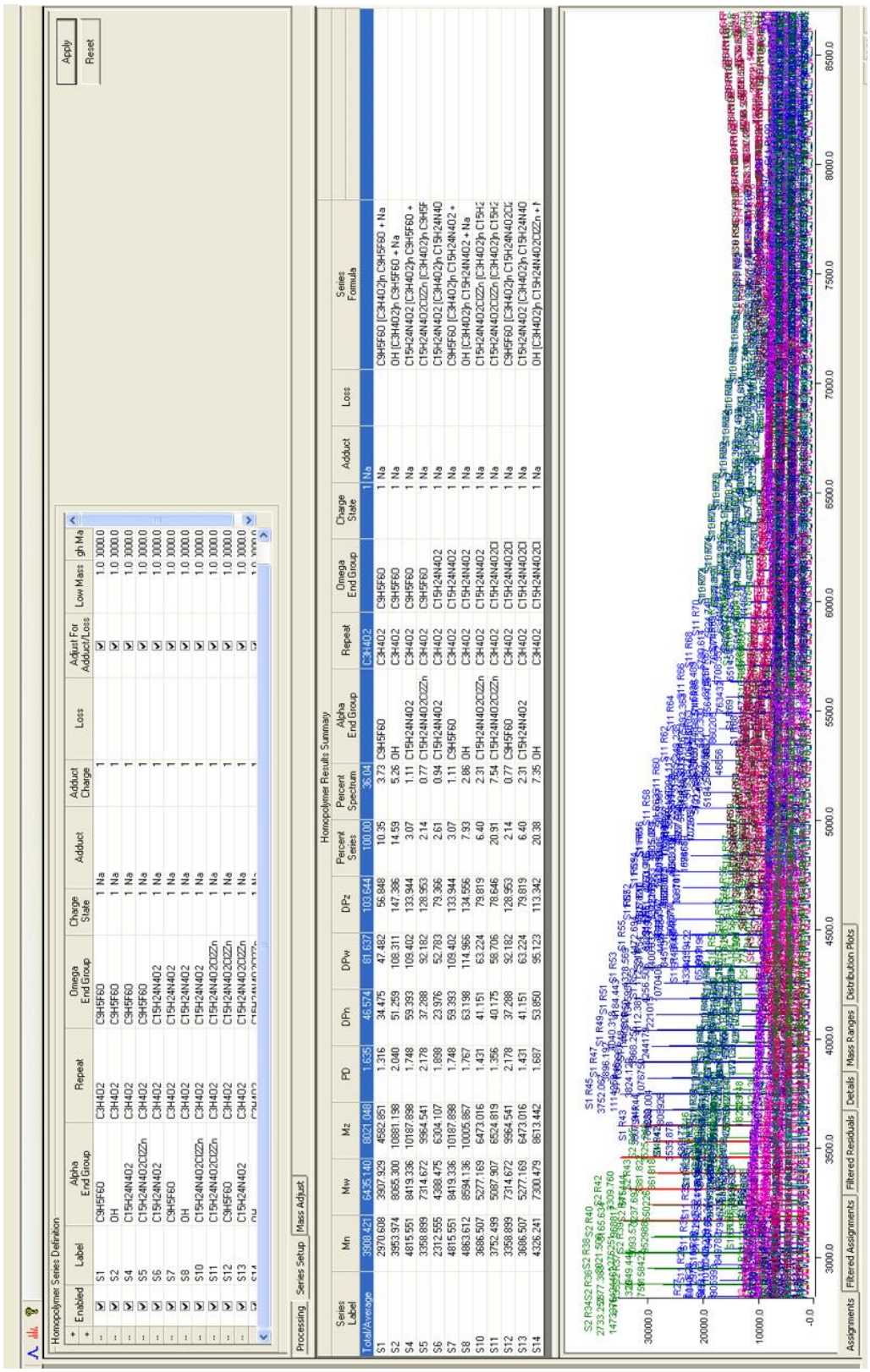


Fig SI 29. Stack of MALDI-ToF spectra obtained for a polymerisation initiated with **C4** [$ZnCl_2$(TMG5NMe$_2$asme)] and the co-initiator (3,5-bis(trifluoromethyl)benzyl alcohol) ([M]/[init.]/[co-init.] = 100:1:1) 1.5 min, 150 °C, 260 rpm, subl. *rac*-LA,. M_n: 17.000 g mol^{-1}, M_w: 20.300 g mol^{-1}, *PD*: 1.2, conversion: 79%.

4.3. NMR spectroscopy

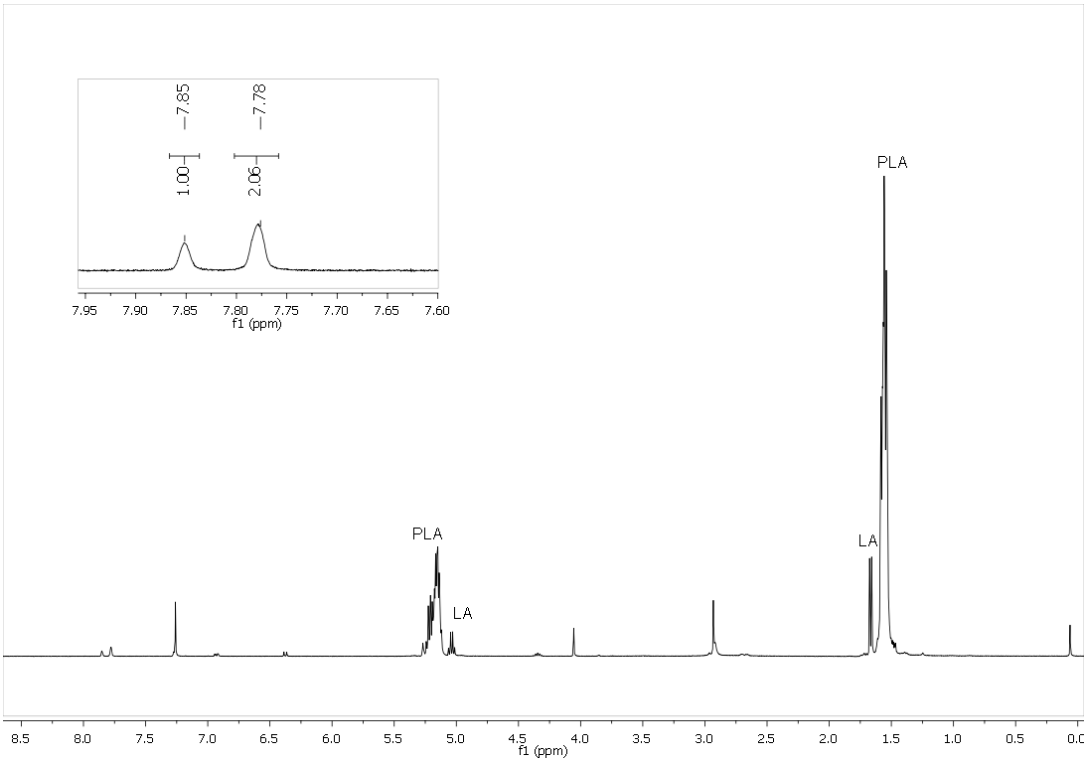


Fig SI 30. ^{1}H NMR spectrum of the polymer initiated with [$ZnCl_2$(TMG5NMe$_2$asme)] and the co-initiator (3,5-bis(trifluoromethyl)benzyl alcohol) ([M]/[init.]/[co-init.] = 50:1:1), 2 min, 150 °C, 260 rpm, non-purified *rac*-LA,. M_n: 10.000 g mol^{-1}, M_w: 14.300 g mol^{-1}, *PD*: 1.2, conversion: 94%.

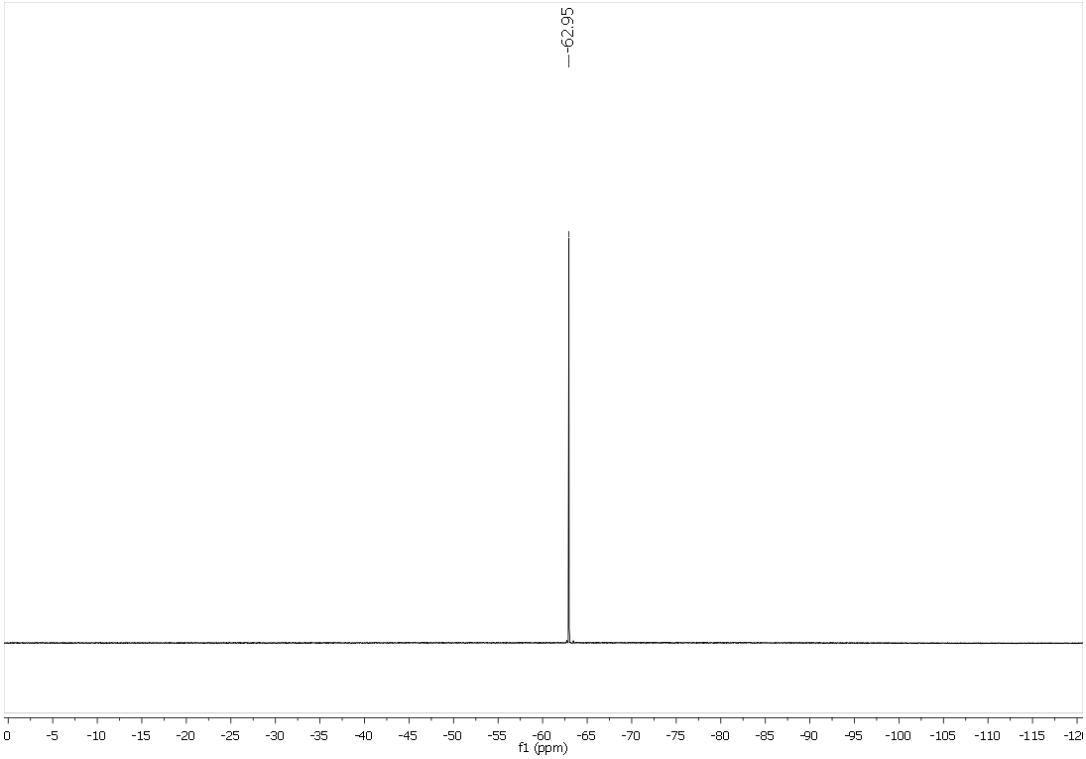
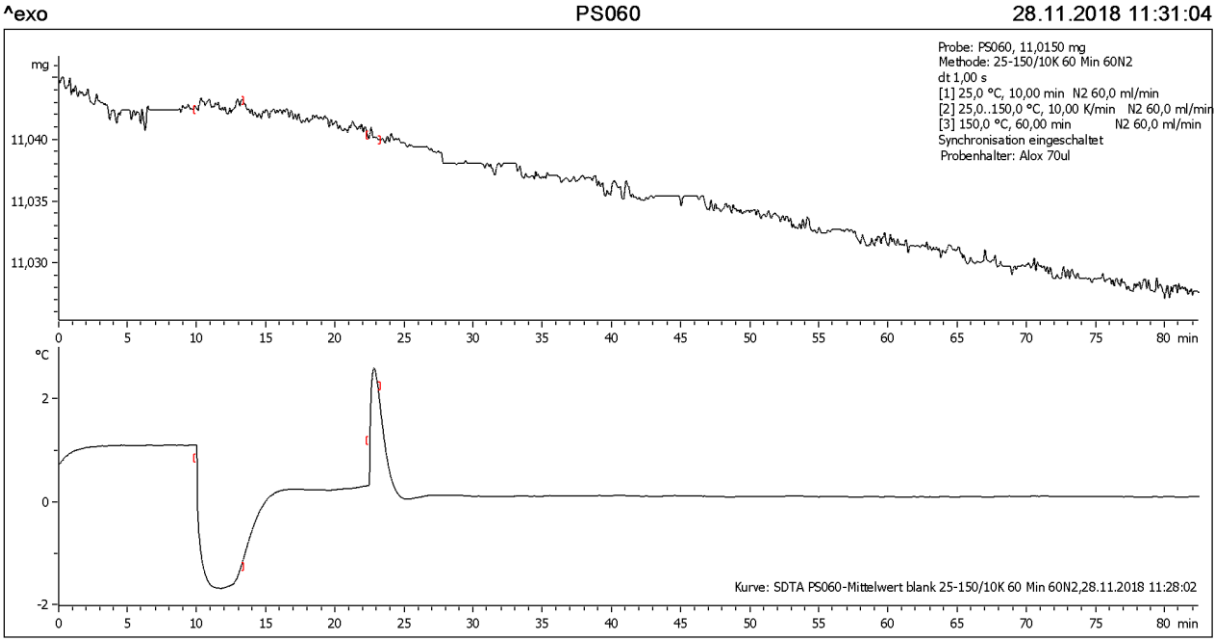


Fig SI 31. ^{19}F NMR spectrum of the polymer initiated with [$ZnCl_2$(TMG5NMe$_2$asme)] and the co-initiator (3,5-bis(trifluoromethyl)benzyl alcohol) ([M]/[init.]/[co-init.] = 50:1:1), 2 min, 150 °C, 260 rpm, non-purified *rac*-LA,. M_n: 10.000 g mol^{-1}, M_w: 14.300 g mol^{-1}, *PD*: 1.2, conversion: 94%.

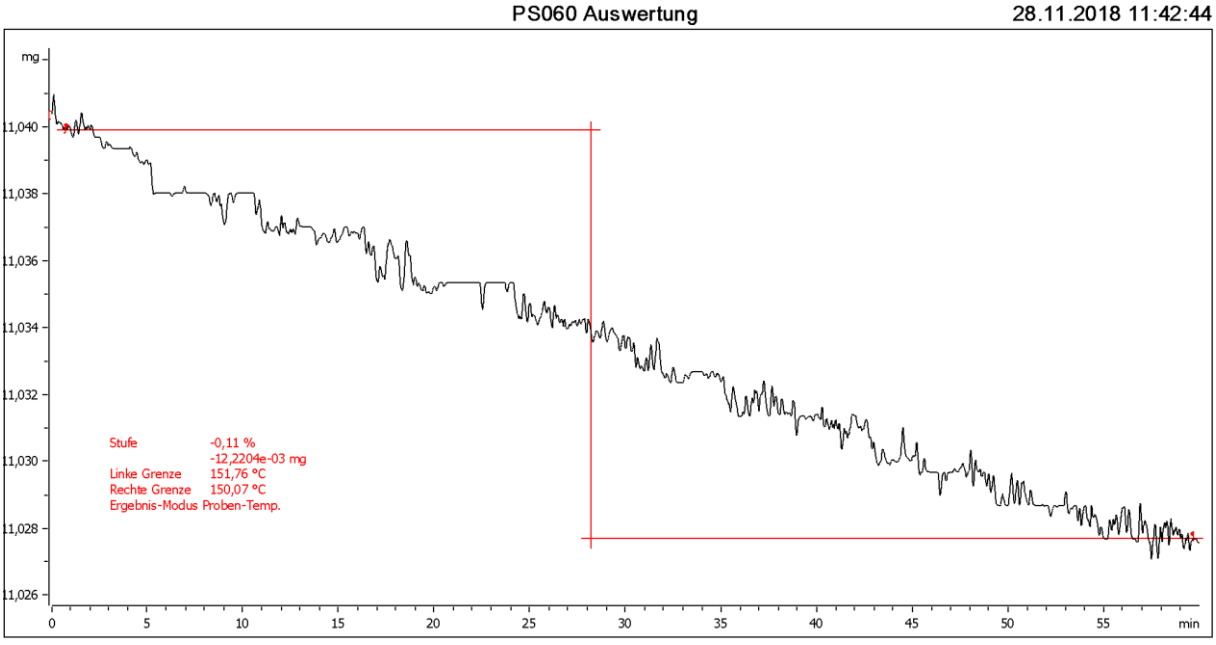
4.4. Polymerisation without co-initiator

The polymerisations with a ratio of 10:1 and 30:1 have been performed in Schlenk-tubes using sublimed *rac*-lactide (500 mg) and the catalyst **C4**.
[M]/[I] = 10:1, conversion: 94% (45 s), M_n = 32.600 g mol^{-1}, M_w = 51.000 g mol^{-1}, *PD* = 1.6;
[M]/[I] = 30:1, conversion: 41% (60 s), M_n = 44.100 g mol^{-1}, M_w = 53.700 g mol^{-1}, *PD* = 1.2;

5. Thermogravimetrical analysis (TGA)



RWTH-Aachen IAC : METTLER STAR^e SW 12.10
Fig SI 32. Results of TGA measurements. Whole measurement.



RWTH-Aachen IAC : METTLER STAR^e SW 12.10
Fig SI 33. Results of TGA measurement. No significant mass loss was detected while the temperature was constantly at 150 °C for 1 hour.

6. Tacticity

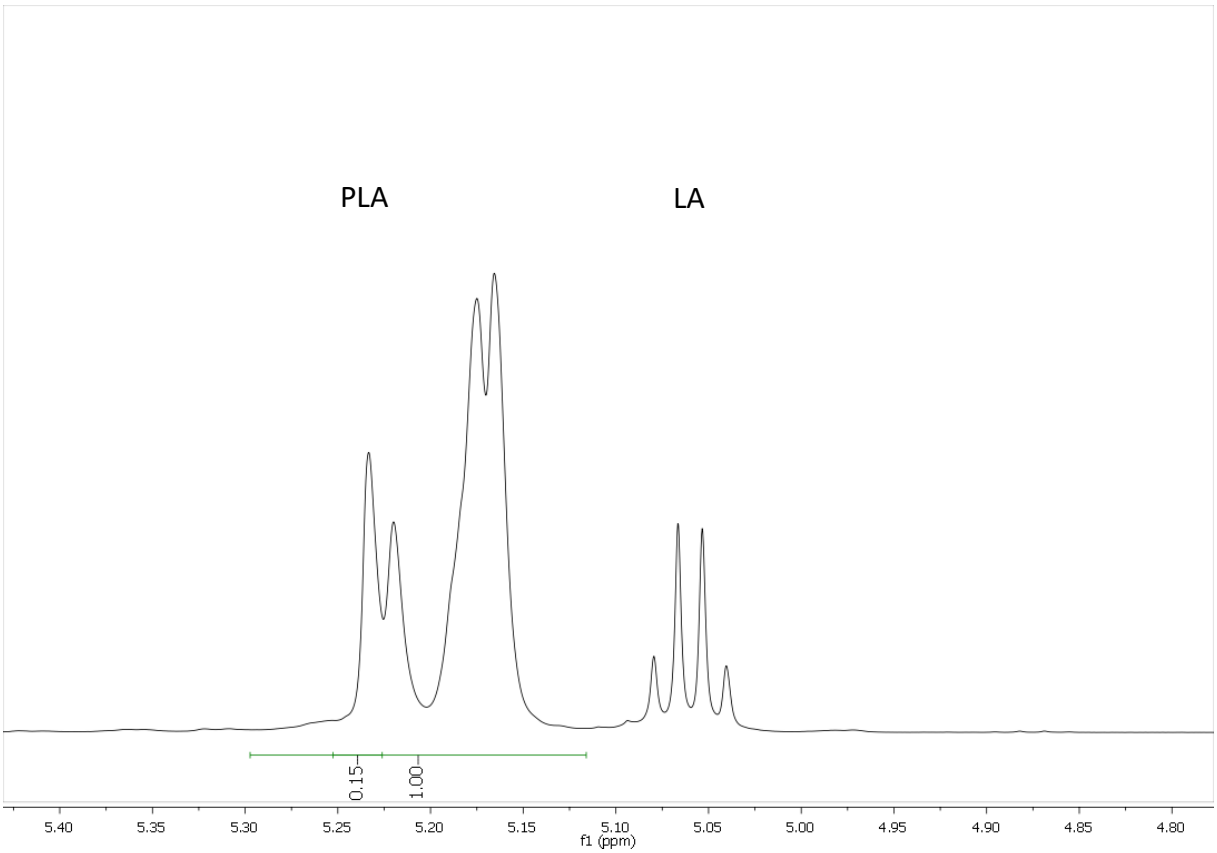


Fig SI 34. Homonuclear decoupled ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of PLA prepared by polymerisation of *rac*-lactide with **C4** [$ZnCl_2$(TMG5NM$e_2$asme)] at 150 °C, P_r = 0.55.

7. Crystallographic data

Table S6. Crystallographic data and parameters of the Zn complexes [$ZnCl_2$(TMG4NMe_2asme)] (**C1**), [$ZnCl_2$(TMG5Clasme)] (**C2**), [$ZnCl_2$(TMG5Measme)] (**C3**) and [$ZnCl_2$(TMG5NMe_2asme)] (**C4**).[a]

Parameter	[$ZnCl_2$(TMG4NMe_2asme)] (**C1**)	[$ZnCl_2$(TMG5Clasme)] (**C2**)	[$ZnCl_2$(TMG5Measme)] (**C3**)	[$ZnCl_2$(TMG5NMe_2asme)] (**C4**)
empirical formula	$C_{15}H_{24}Cl_2N_4O_2Zn$	$C_{13}H_{18}Cl_3N_3O_2Zn$	$C_{14}H_{21}Cl_2N_3O_2Zn$	$C_{15}H_{24}Cl_2N_4O_2Zn$
formula mass [g mol^{-1}]	428.65	420.02	399.61	428.65
Crystal size [mm]	0.48 x 0.25 x 0.23	0.25 x 0.14 x 0.13	0.23 x 0.22 x 0.18	0.16 x 0.14 x 0.07
T [K]	100(2)	100(2)	100(2)	100(2)
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	15.010(2)	9.4998(4)	9.5828(4)	17.377(4)
b [Å]	12.9027(19)	16.0292(7)	16.0067(7)	8.0888(16)
c [Å]	20.065(3)	11.7929(5)	11.7969(5)	13.258(3)
V [$Å^3$]	3886.0(10)	1734.20(13)	1748.53(13)	1863.5(7)
α [°]	90	90	90	90
β [°]	90	105.0450(10)	104.9170(10)	90.439(4)
γ [°]	90	90	90	90
Z	8	4	4	4
ρ_{calcd} [g cm^{-3}]	1.465	1.609	1.518	1.528
μ [mm^{-1}]	1.554	1.886	1.719	1.620
λ [Å]	0.71073	0.71073	0.71073	0.71073
F(000)	1776	856	824	888
hkl range	$-18 \le h \le 18$	$-13 \le h \le 13$	$-13 \le h \le 13$	$-21 \le h \le 21$
	$-16 \le k \le 16$	$-22 \le k \le 23$	$-23 \le k \le 22$	$-10 \le k \le 10$
	$-25 \le l \le 25$	$-16 \le l \le 16$	$-17 \le l \le 16$	$-16 \le l \le 16$
reflections collected	44 769	26 252	26 572	22 033
independent reflections	3991	5186	5265	3855
R_{int}	0.0983	0.0320	0.0307	0.0922
number of parameters	224	204	205	224
R_1 [$I>2\sigma(I)$]	0.0359	0.0274	0.0261	0.0418
wR_2 (all data)	0.0877	0.0667	0.0678	0.1039
goodness-of-fit	1.038	1.071	1.047	1.024
largest diff. peak, hole [$e^- Å^{-3}$]	0.500, –0.453	0.514, –0.308	0.468, –0.257	0.644, –0.385