Supporting Information

New homoleptic bis(pyrrolylpyridiylimino) Mg(II) and Zn(II) complexes as catalysts for the ring opening polymerization of cyclic esters via an "activated monomer" mechanism.

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Table of contents

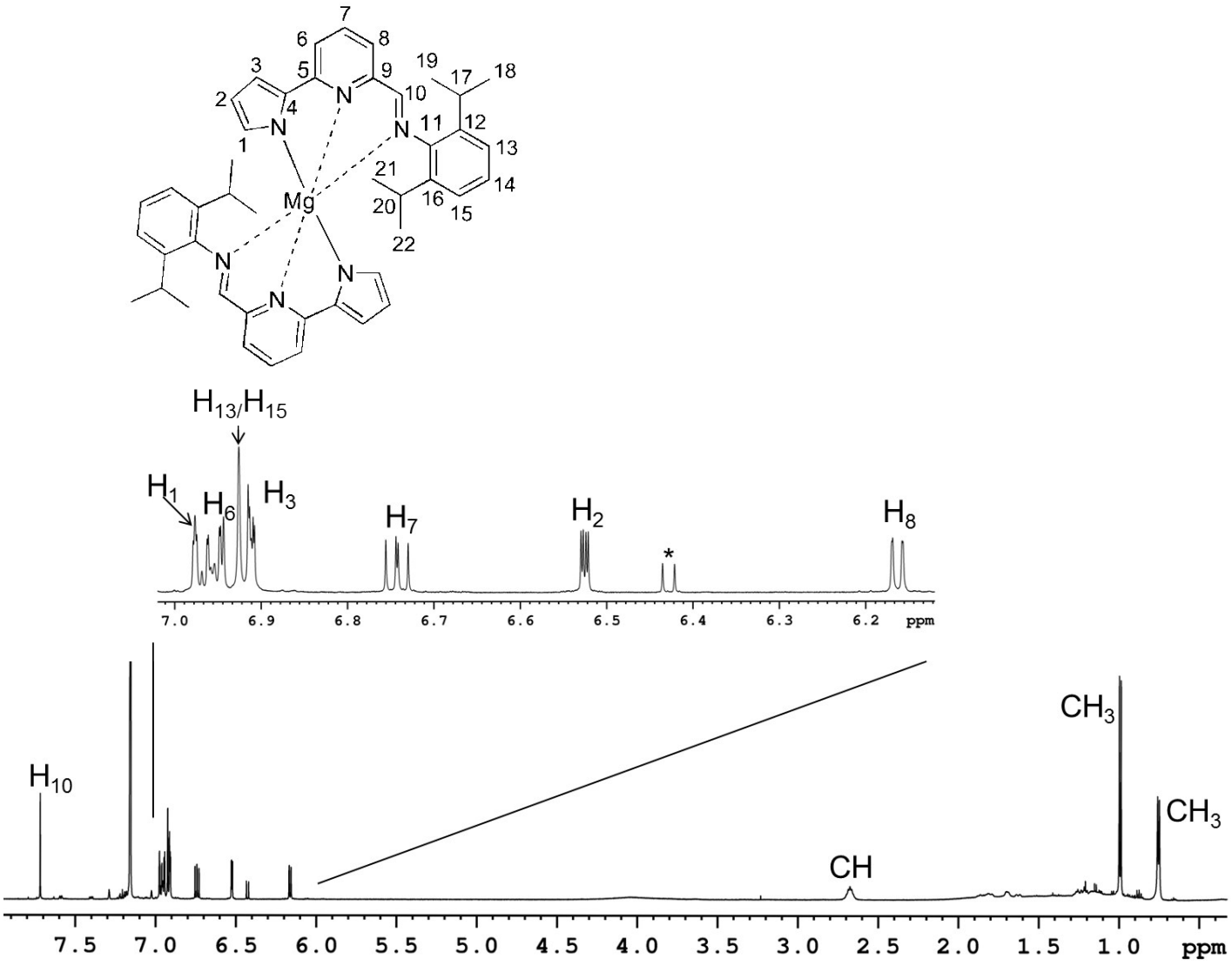


Figure S1. ^{1}H NMR spectrum (C_6D_6, 298 K, 600 MHz) of complex **1.**

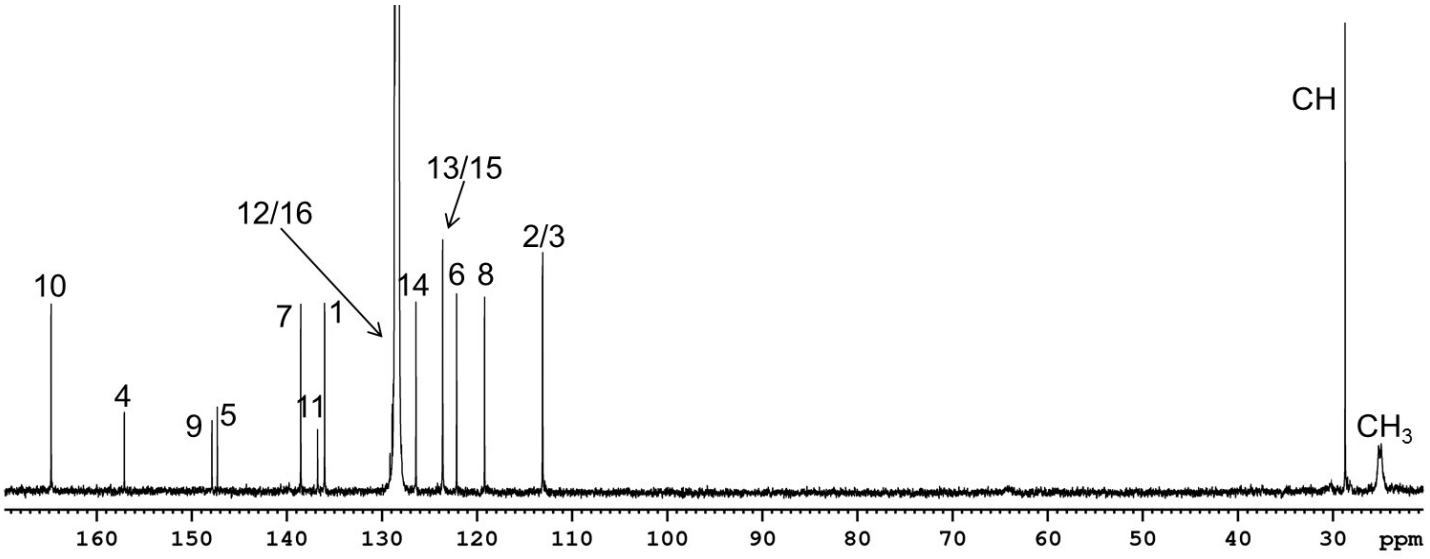


Figure S2. ^{13}C NMR spectrum (C_6D_6, 298 K, 600 MHz) of complex **1.**

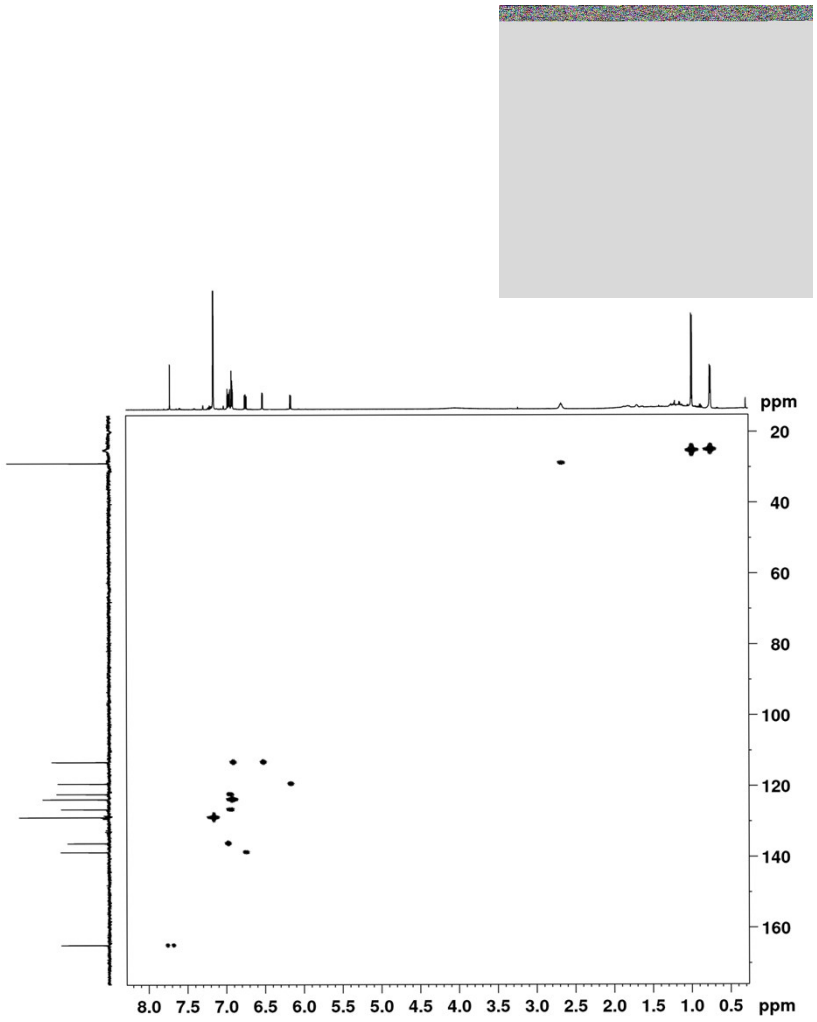


Figure S3. ^{1}H $^{13}C\{^{1}H\}$ HMQC spectrum (C_6D_6, 298 K, 600 MHz) of complex **1**

For complex **1**, full resonance assignment (see Figures 1-3 and S1-S3) was obtained by following the scalar and/or dipolar connectivity in 1D and 2D homo- and hetero-nuclear NMR experiments (^{1}H COSY , ^{1}H NOESY and $^{13}C\{^{1}H\}$ HMBC). The H10 resonance (δH = 8.08 ppm, see Figure 1 for numbering), easily recognized since it is the only singlet integrating for one proton in the ^{1}H NMR spectrum, was considered as the starting point. NOE experiments allowed to discriminate between protons H8 and H6 because of the NOE interaction of proton H8 with imine proton H10. Similarly, H3 was discriminated from H1 because of the NOE contact with proton H6 (see Figure 2 B).

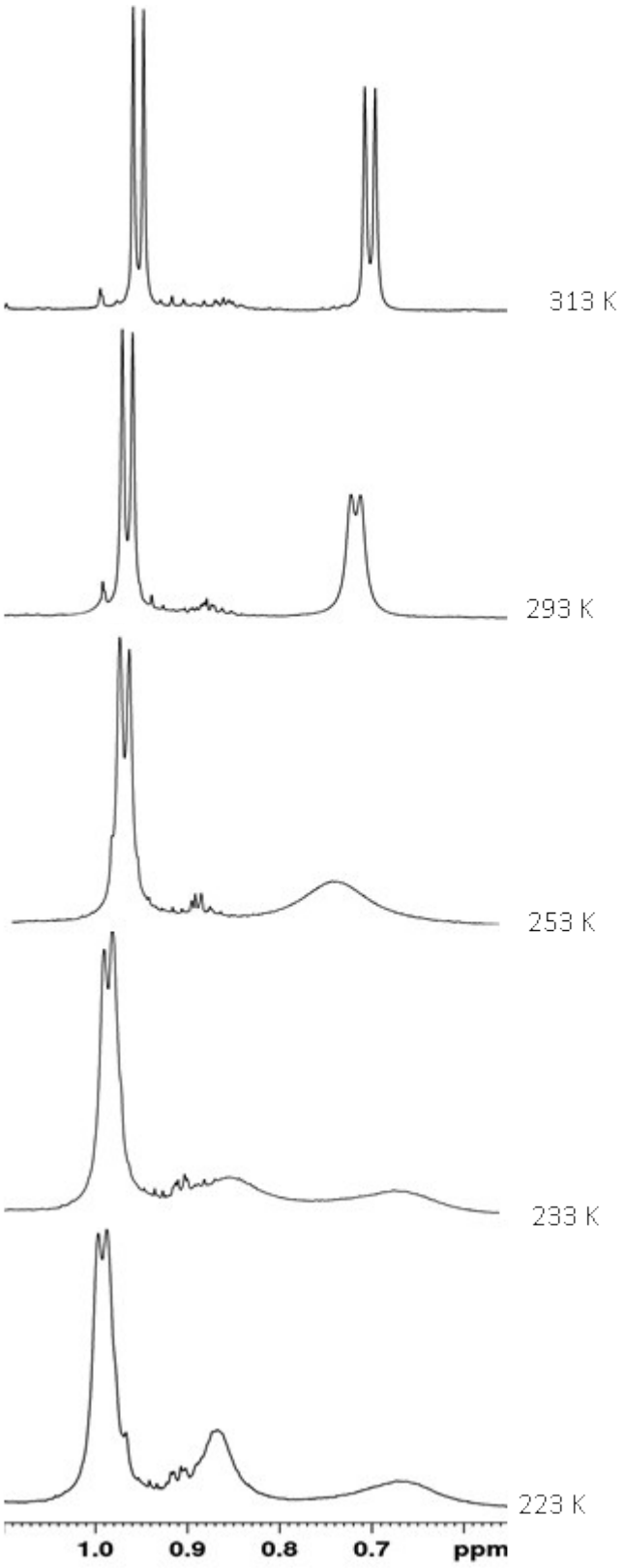
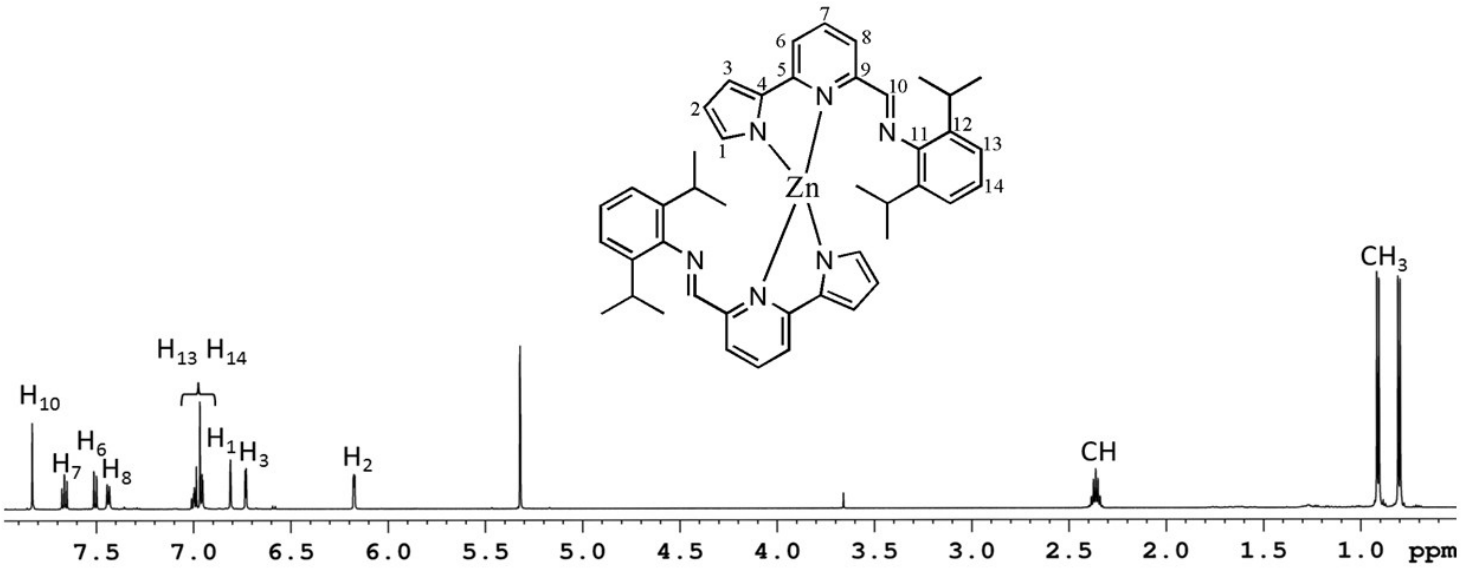


Figure S4. A representative section of the variable-temperature ^{1}H-NMR spectra of **1** in toluene-d_8.



FigureS5. ^{1}H NMR spectrum (CD_2Cl_2, 298 k, 600 MHz) of complex **2.**

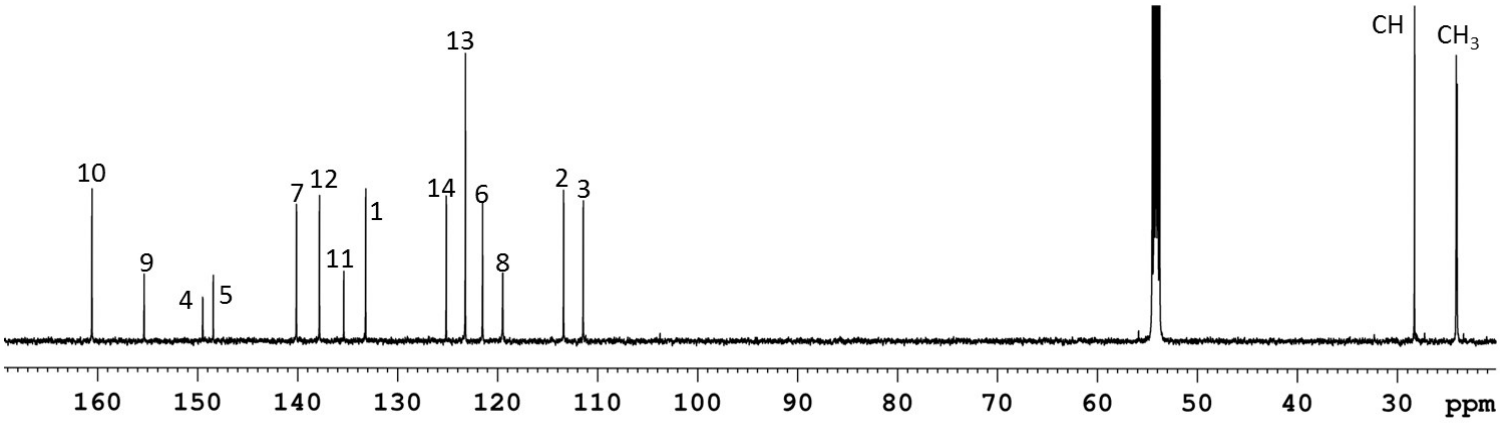


Figure S6. ^{13}C NMR spectrum (CD_2Cl_2, 298 k, 600 MHz) of complex **2**

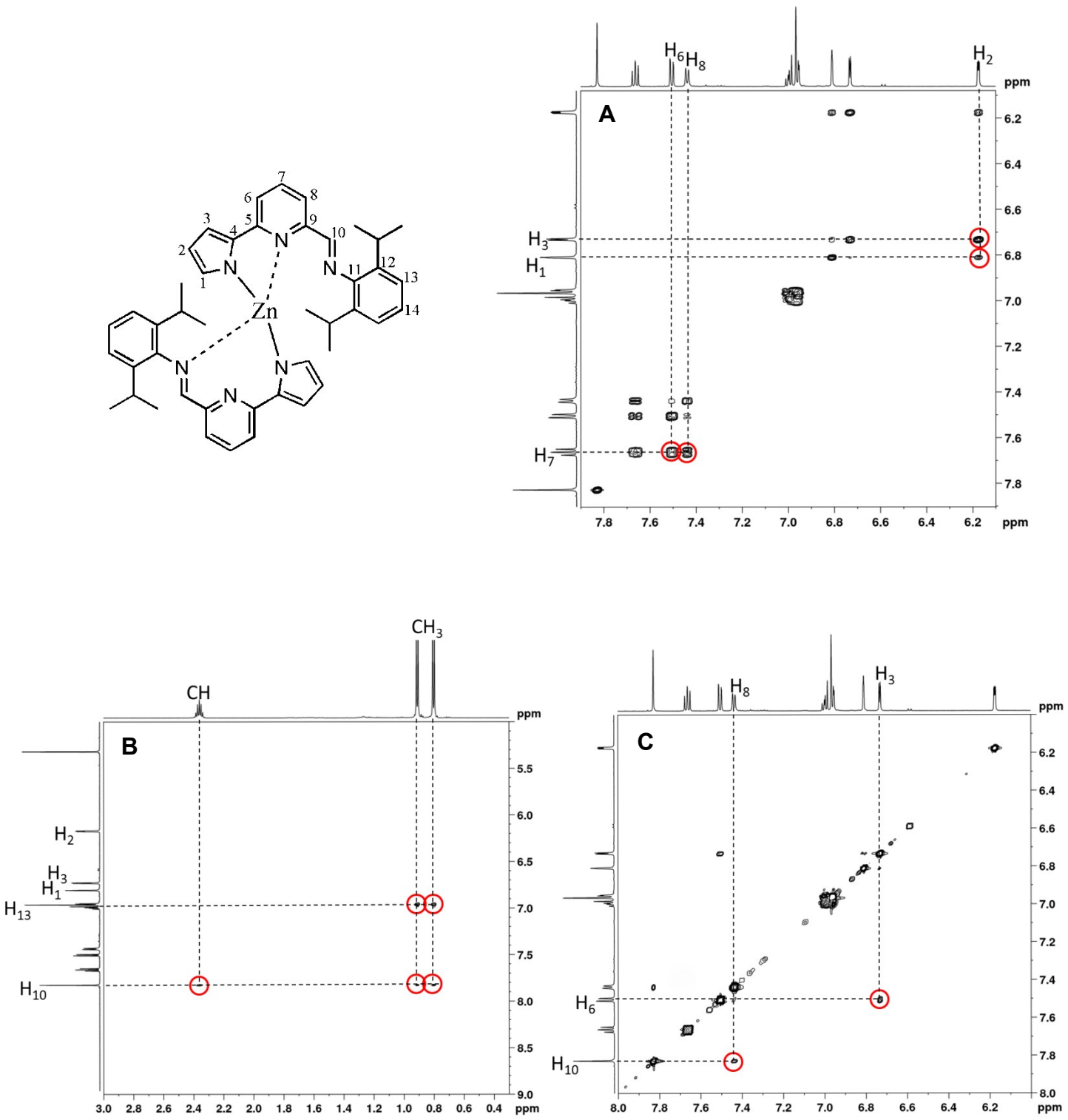
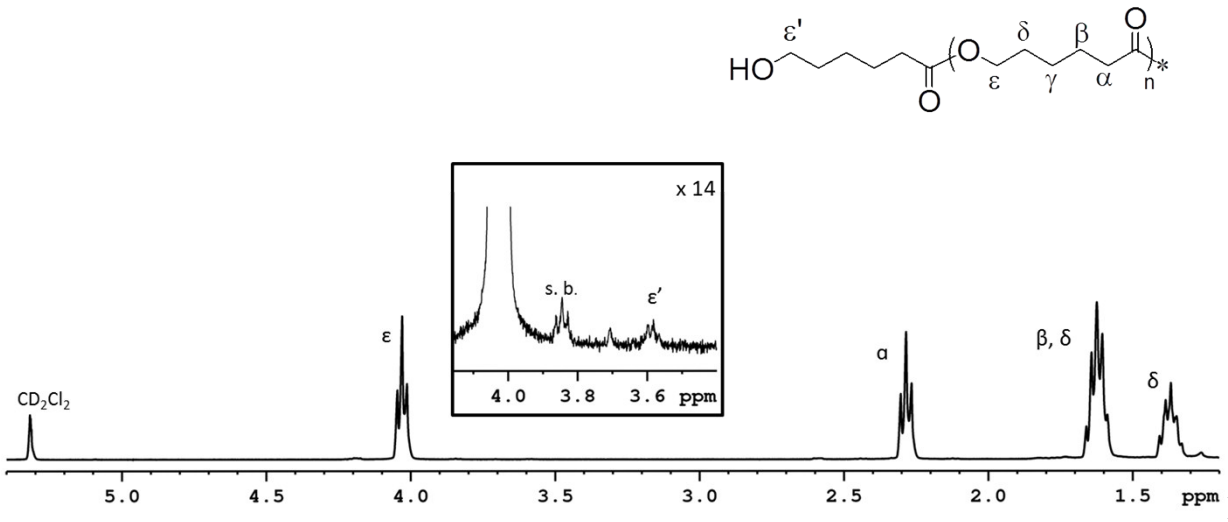


Figure S7. A: A section of the ^{1}H COSY NMR spectrum of **2** (CD_2Cl_2, 298 K, 600 MHz);
B and C: two sections of ^{1}H ^{1}H NOESY NMR spectrum of **2** (CD_2Cl_2, 298 K, 600 MHz).



Figure

Figure S8. ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of the oligomer of ε-caprolactone using **1** as initiator. Conditions: $[\varepsilon\text{-CL}]_0/[I]_0 = 15$, toluene, 298 K

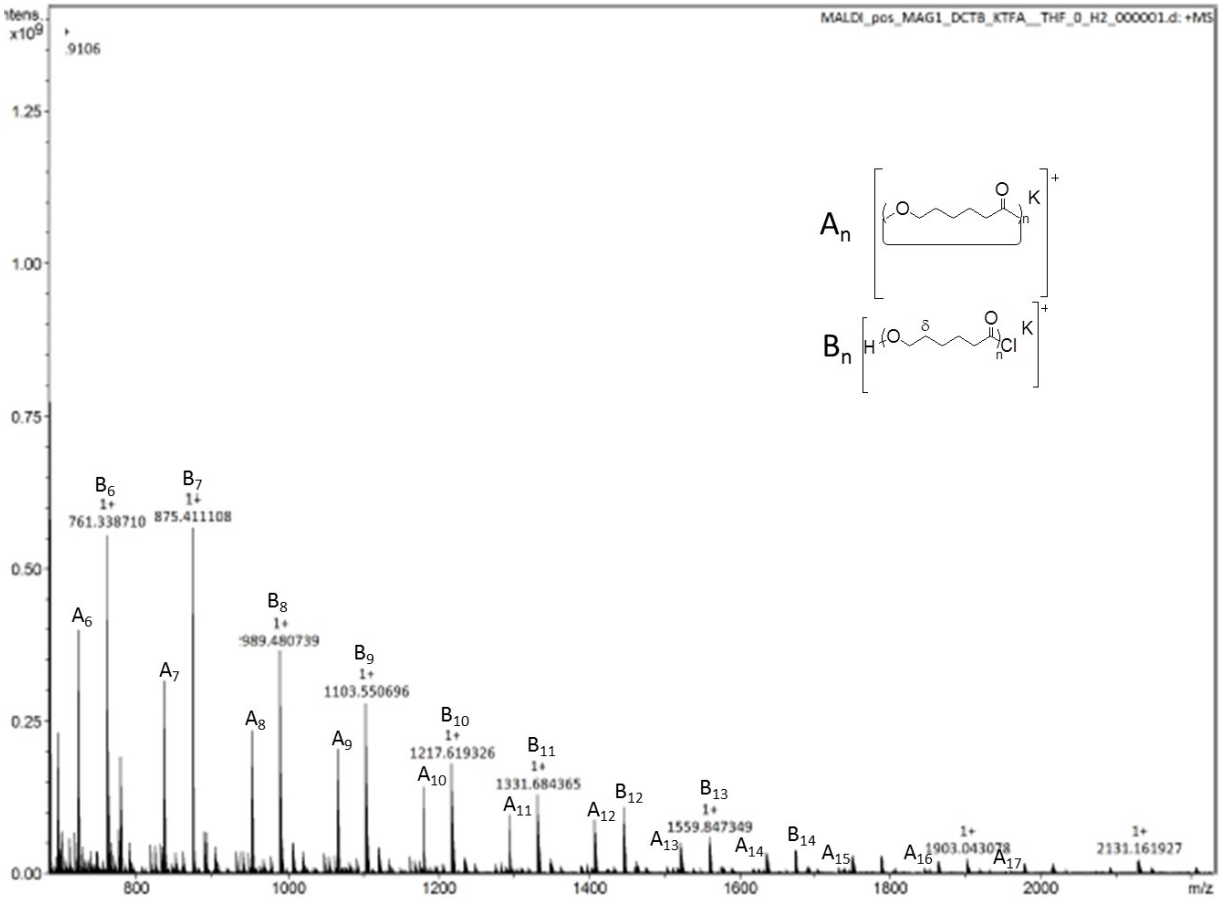


Figure S9. MALDI-TOF mass spectrum of the oligomer of ε-caprolactone using **1** as initiator (doped with K^+). B_n fragments are reasonably produced by chlorination of carboxyl end groups by the methylene chloride solvent used to dissolve the sample for the MS analysis.

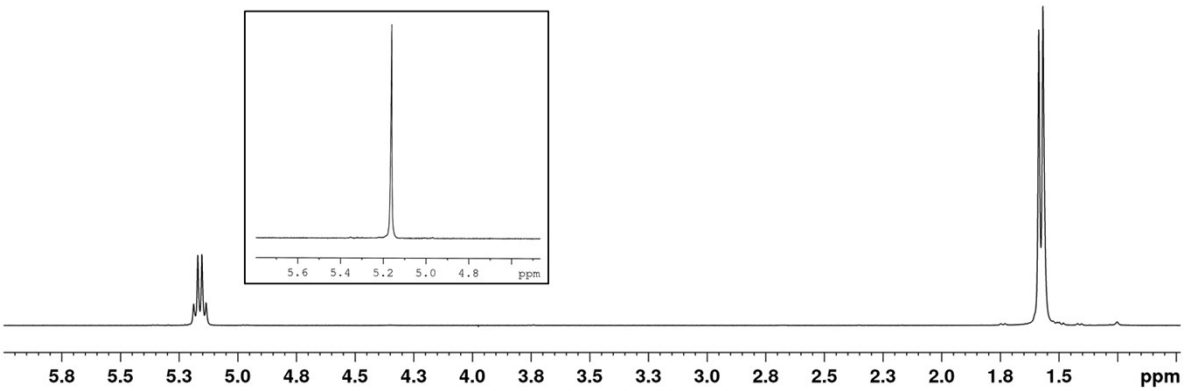


Figure S10. ^{1}H NMR and ^{1}H HD NMR ($CDCl_3$, 400MHz, 298K) of a sample of PLA (entry 10, table 3).

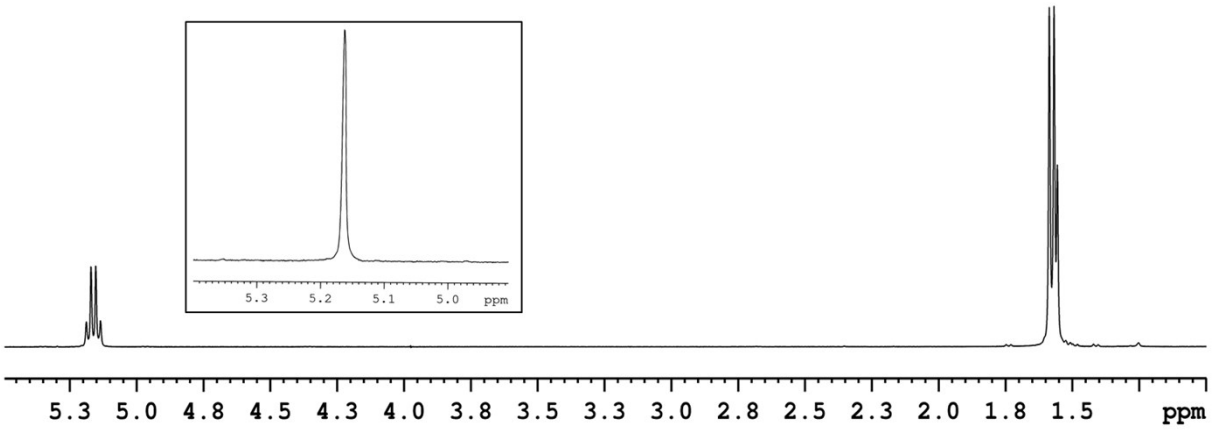


Figure S11. ^{1}H NMR and ^{1}H HD NMR ($CDCl_3$, 400MHz, 298K) of a sample of PLA (entry 12, table 3).

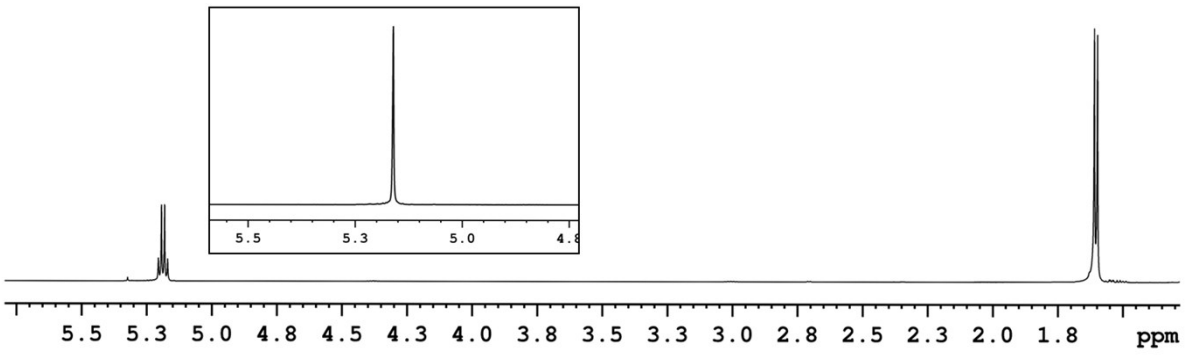
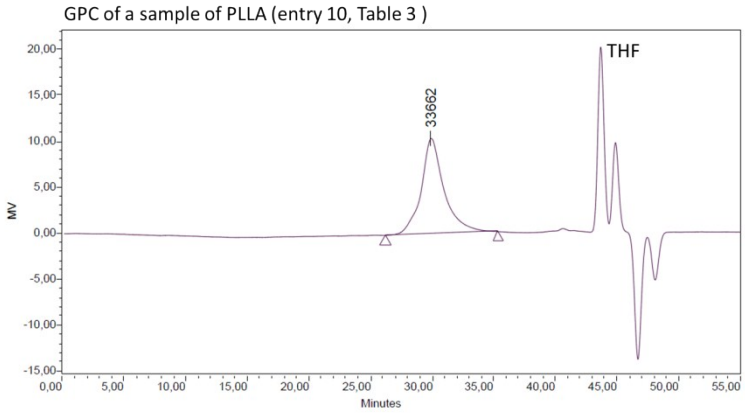
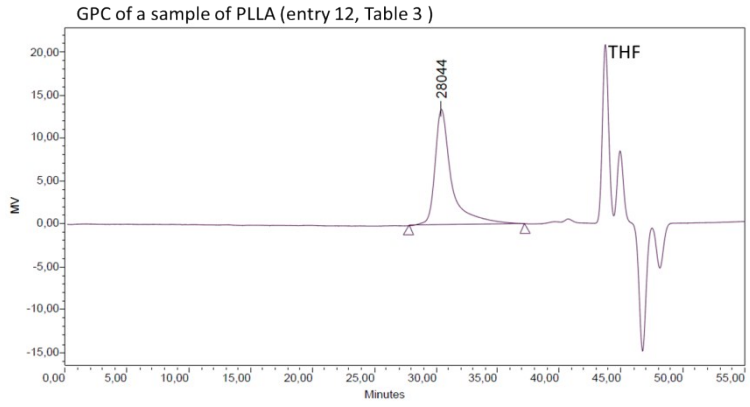


Figure S12. ^{1}H NMR and ^{1}H HD NMR ($CDCl_3$, 400MHz, 298K) of a sample of PLA (entry 13, table 3).



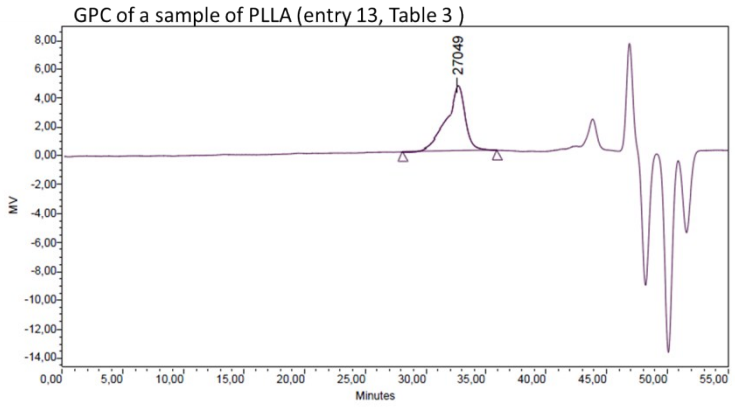
GPC Results

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1		*28131*	*33359*	*33662*	*38596*	*44501*	*1,185825*



GPC Results

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1		*20863*	*25087*	*28044*	*27682*	*29643*	*1,202455*



GPC Results

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1		33650	41094	27049	51613	64432	1,221226

Figure S13. GPC traces of PLA samples (entry 10,12 and 13, table 3)

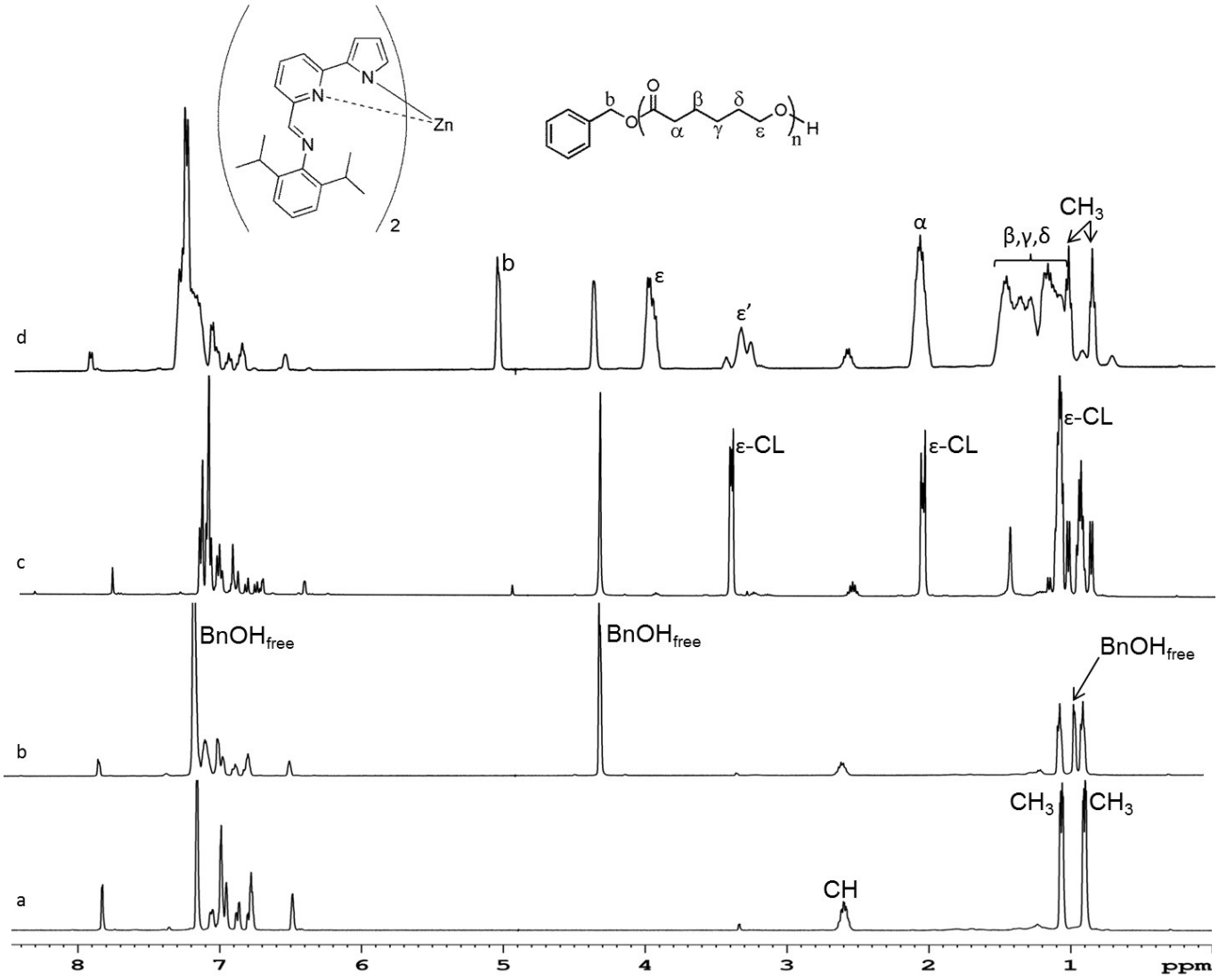


Figure S14. Monitoring of reaction by ^{1}H NMR spectra (C_6D_6, 373K, 400 MHz) : a) Complex **2**; b) Complex **2** with BnOH; c) Complex with BnOH and ε-CL at first time and d) Complex **2** with BnOH and olycaprolactone at end of reaction.

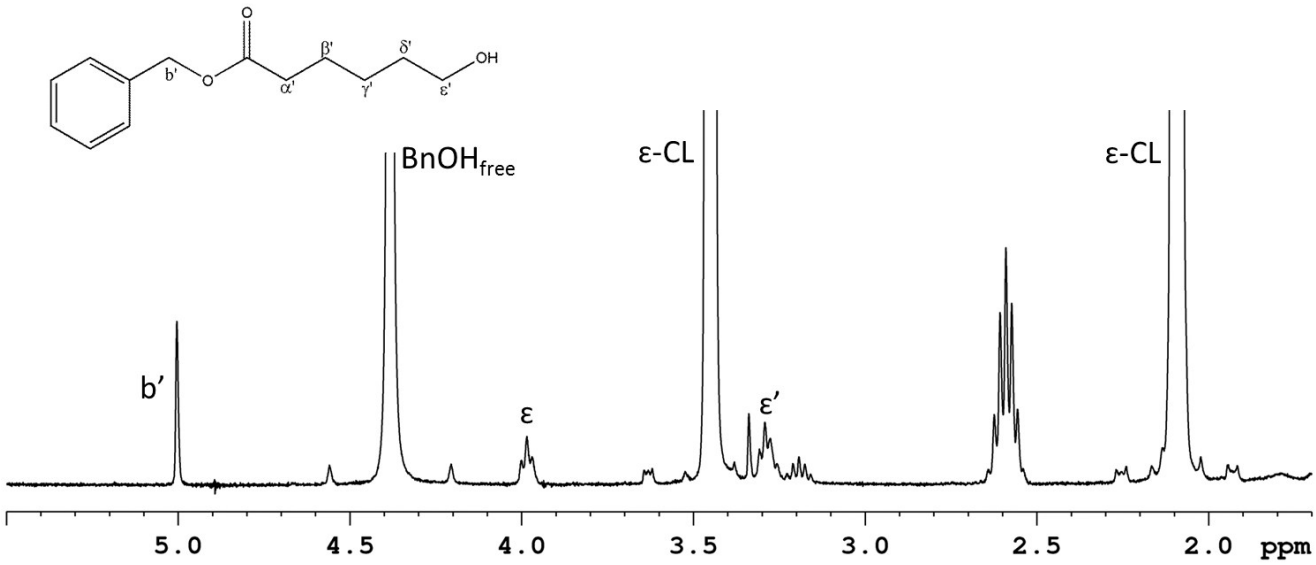


Figure S15. An enlargement of ^{1}H NMR spectrum ***c*** (figure 4) (C_6D_6, 373K, 400 MHz) in which signals of benzyl-6-hydroxyhexanoate are showed.

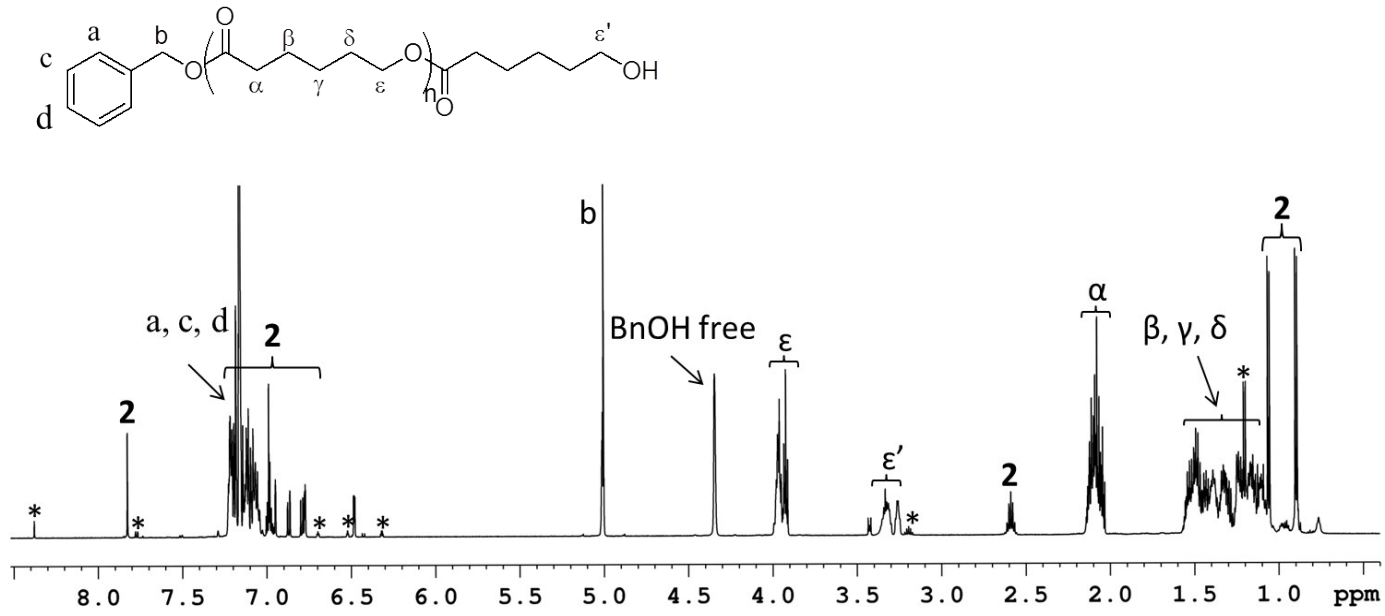


Figure S16. ^{1}H NMR spectrum (C_6D_6, 298K, 400 MHz) of the mixture of complex **2**, BnOH and polycaprolactone at the end of reaction; signals with <*> belong to traces of ligand.

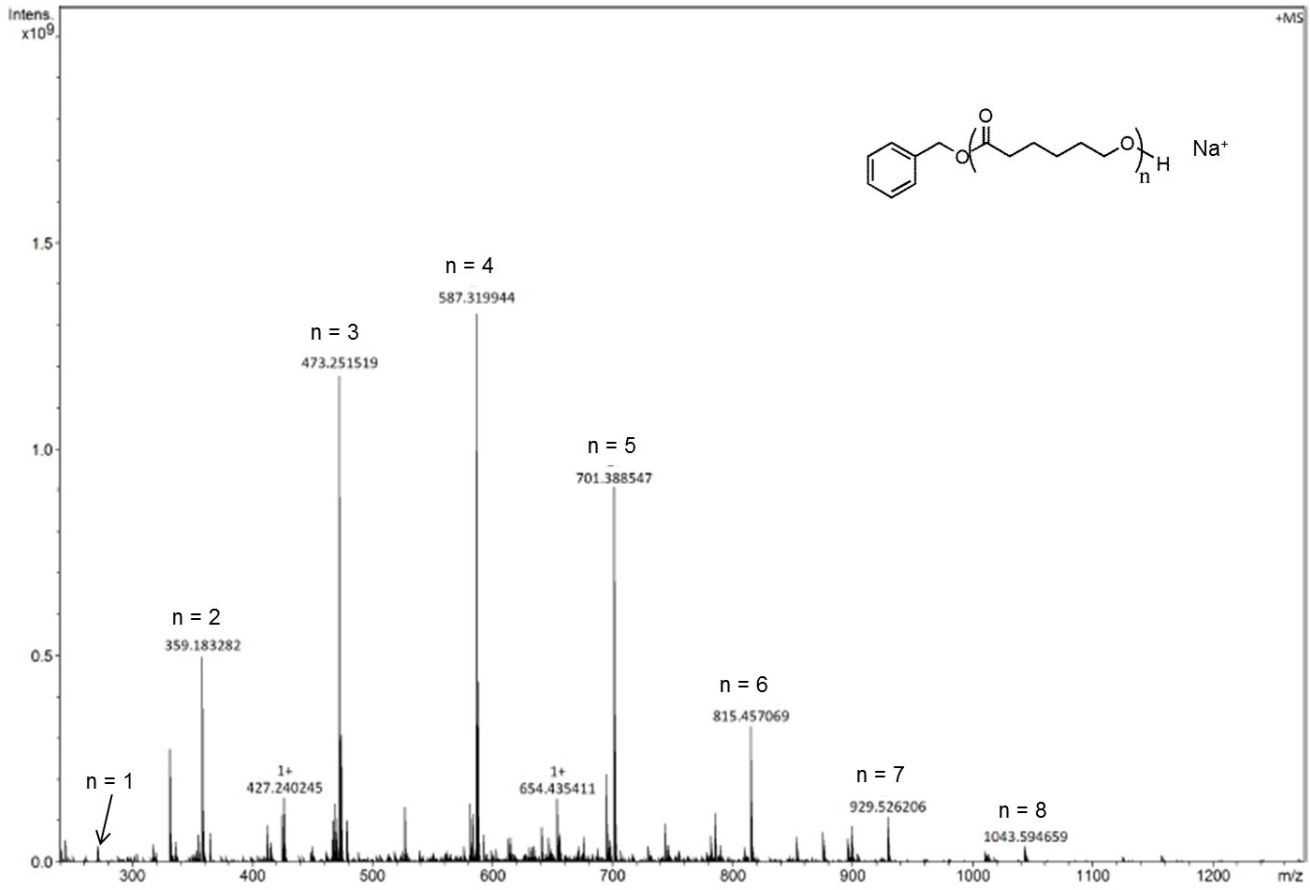


Figure S17. MALDI-TOF mass spectrum of the mixture of complex **2**, BnOH and polycaprolactone.

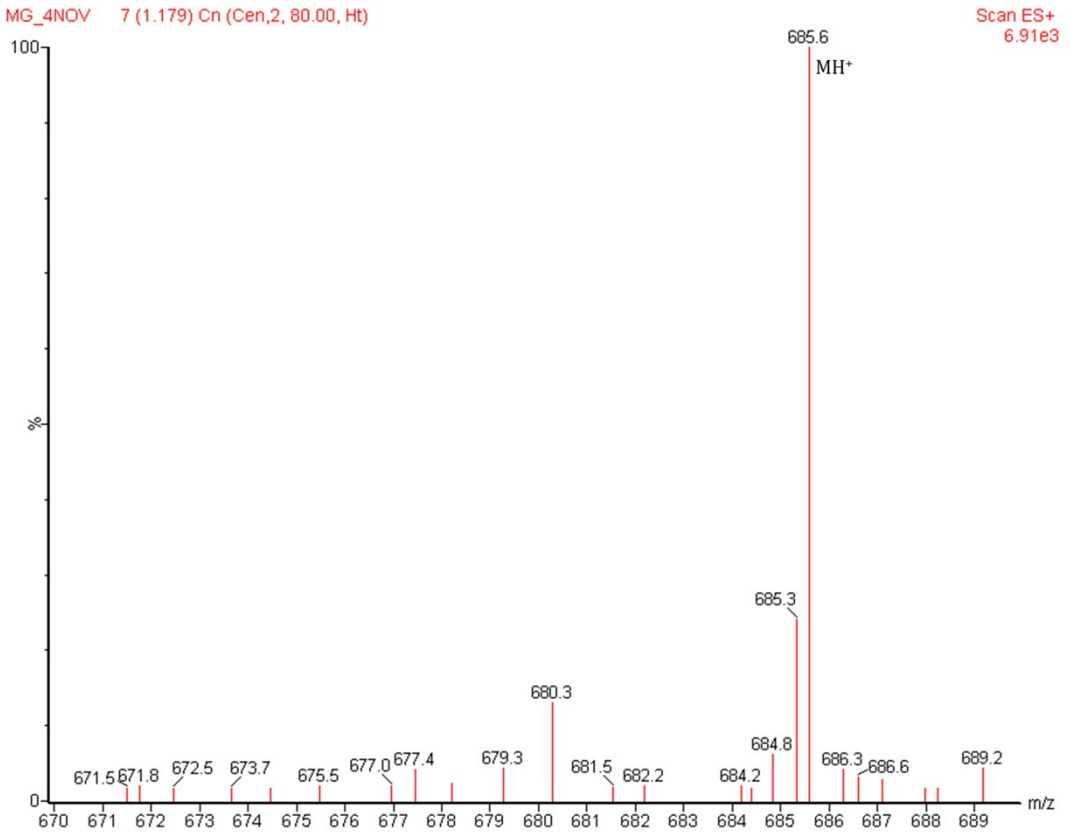


Figure S18. ESI Mass spectrum of complex **1**

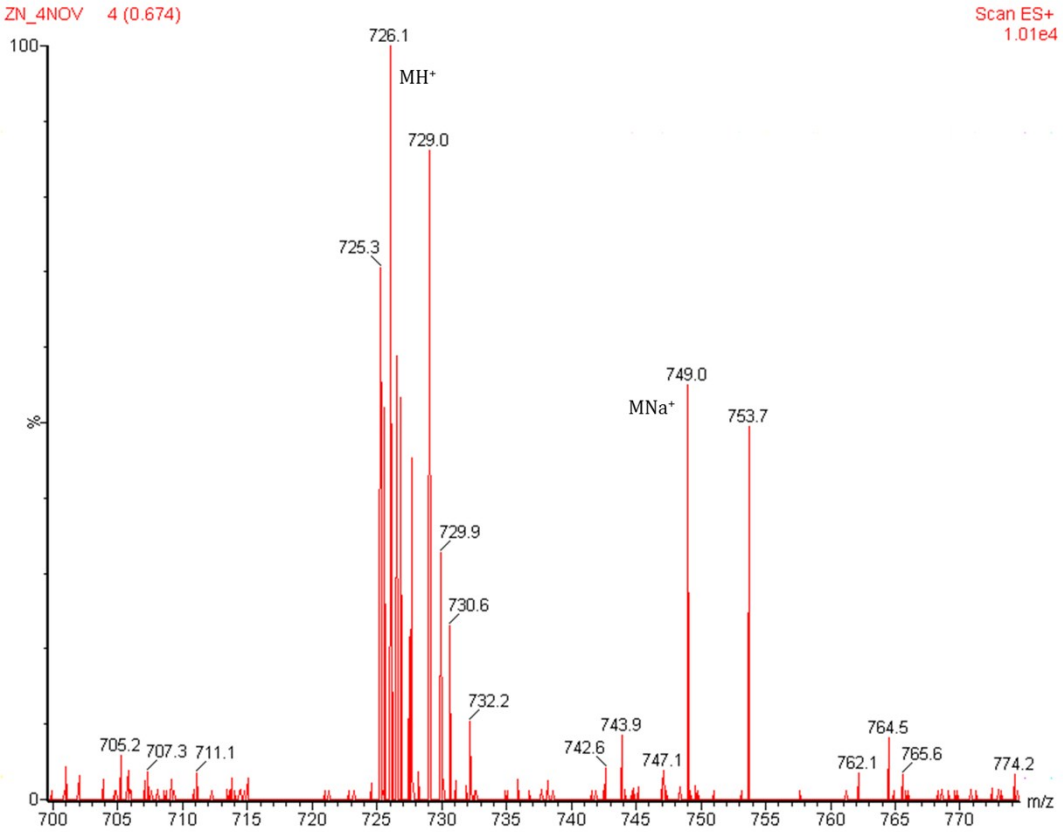


Figure S19. ESI Mass spectrum of complex **2**