Electronic Supplementary Information (ESI)

Dinuclear Zirconium Complex Bearing 1,5-Bridged-Calix[8]arene Ligand as Effective Catalyst for the Synthesis of Macrolactones

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1. NMR CHARACTERIZATION

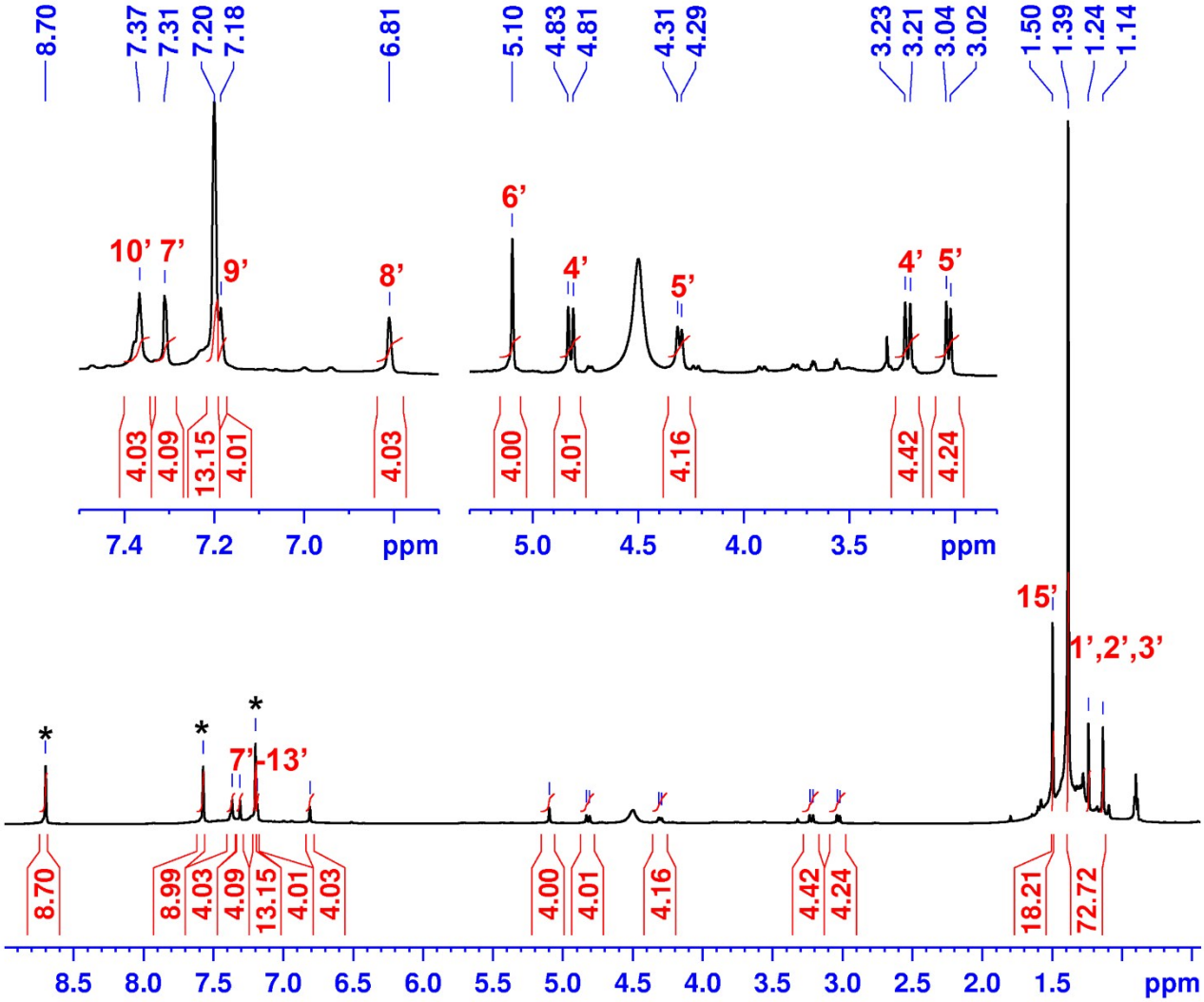


Figure S1. ^{1}H NMR spectrum of **C** (600 MHz, pyridine-d_5, 25 °C).

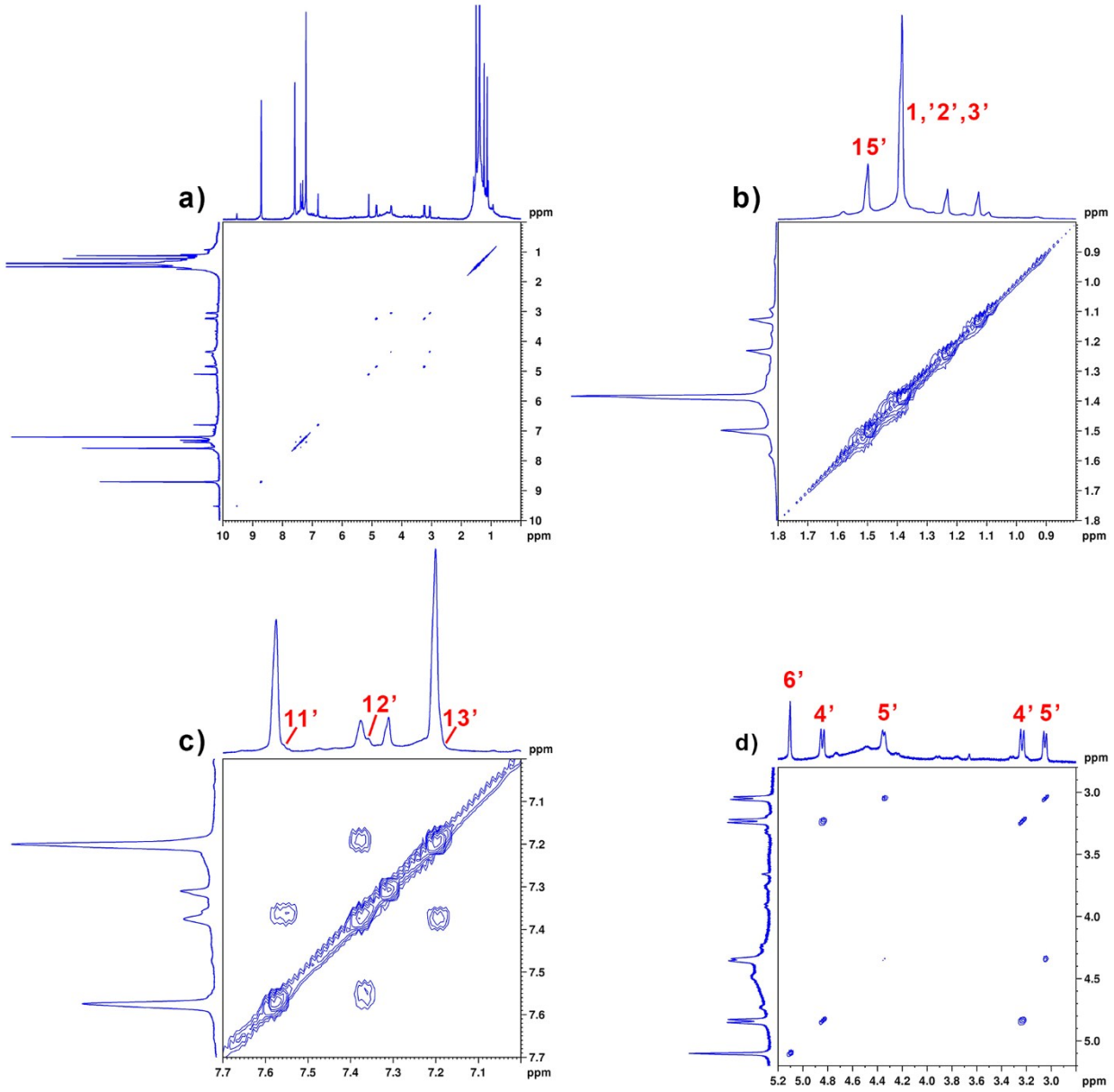


Figure S2. ^{1}H-^{1}H COSY spectrum (600 MHz, pyridine-d_5, 90°C) of **C** (a) with magnifications of the diagnostic regions (b-d).

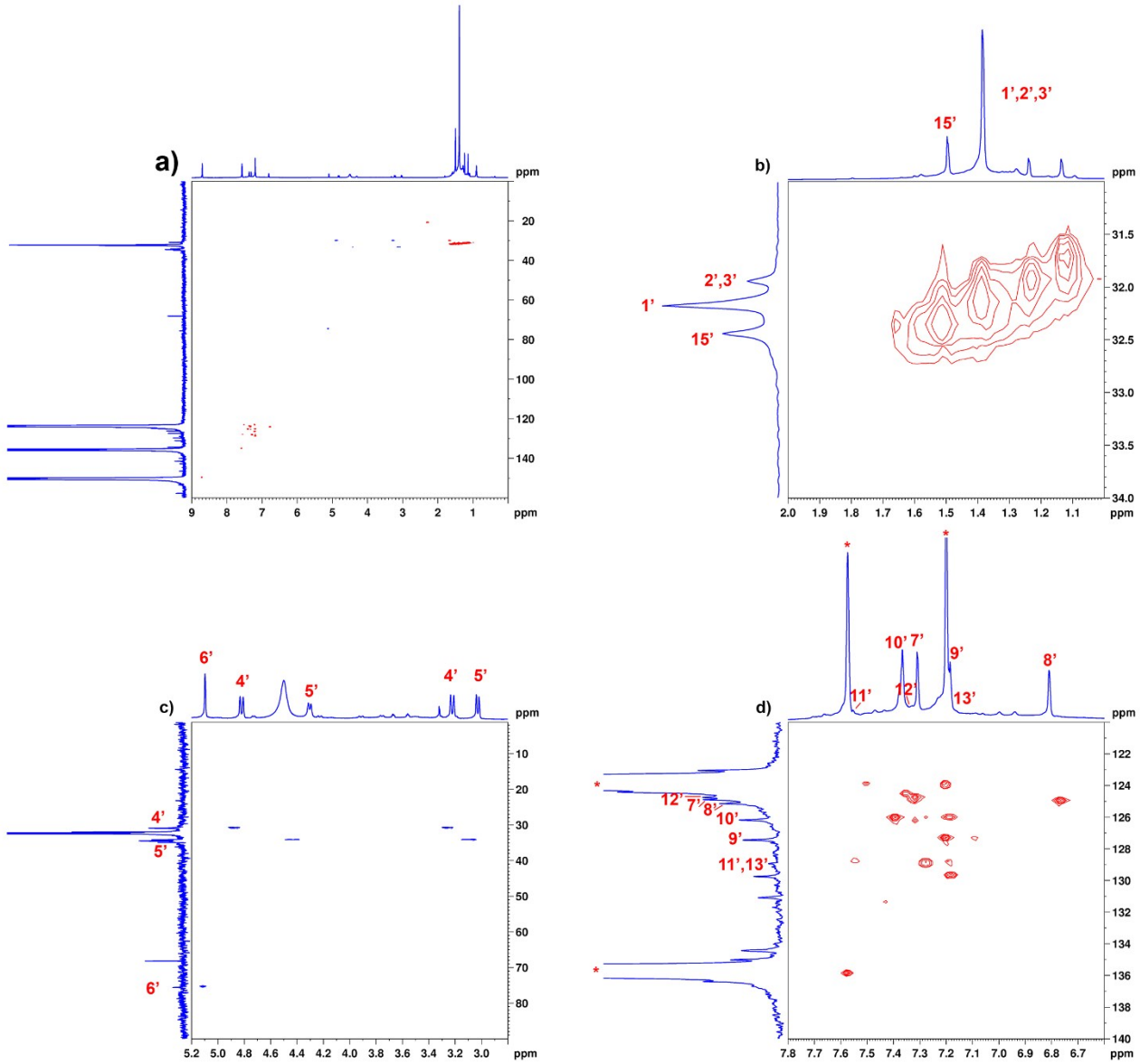


Figure S3. ^{1}H-^{13}C HSQC spectrum (600 MHz, pyridine-d_5, 25°C) of the complex **C** (a) with magnifications of the diagnostic regions (b-d).

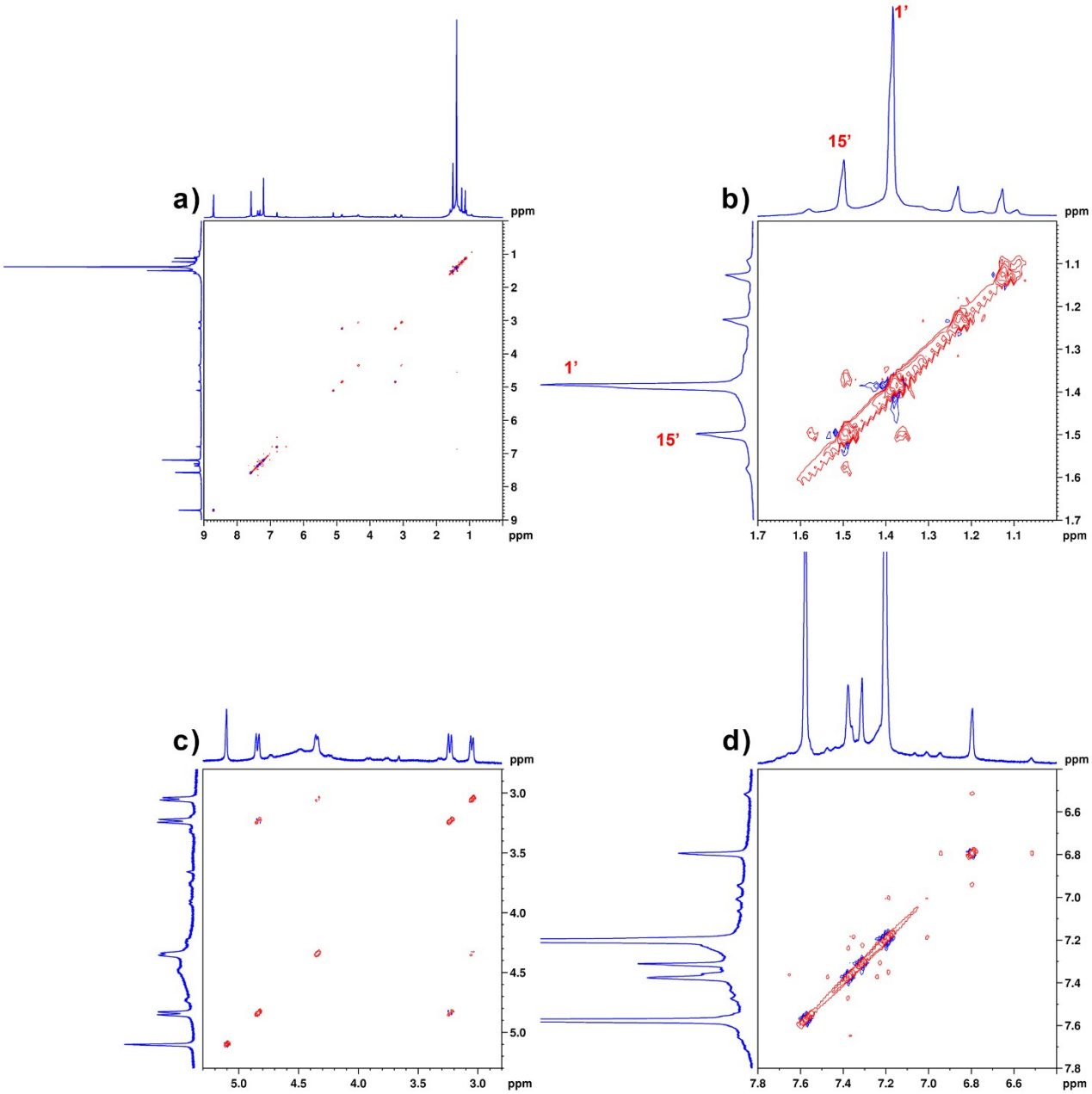


Figure S4. ^{1}H-^{1}H NOESY spectrum (600 MHz, pyridine-d_5, 90°C) of the complex **C** (a) with magnifications of the diagnostic regions (b-d).

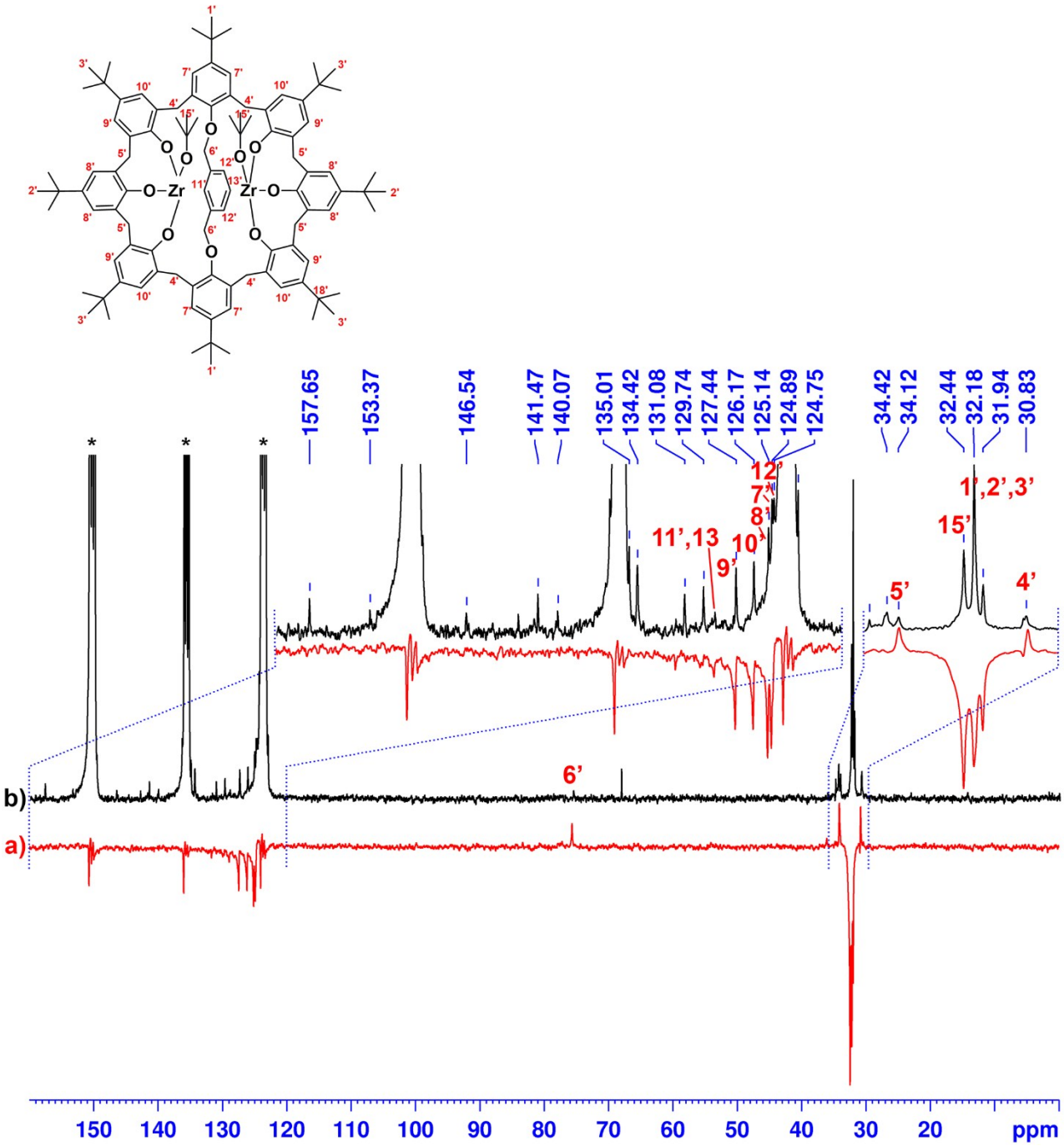


Figure S5. DEPT135 (a) and ^{13}C NMR (b) spectra (600 MHz, pyridine-d_5, 90°C) of the complex **C** (Scheme 1).

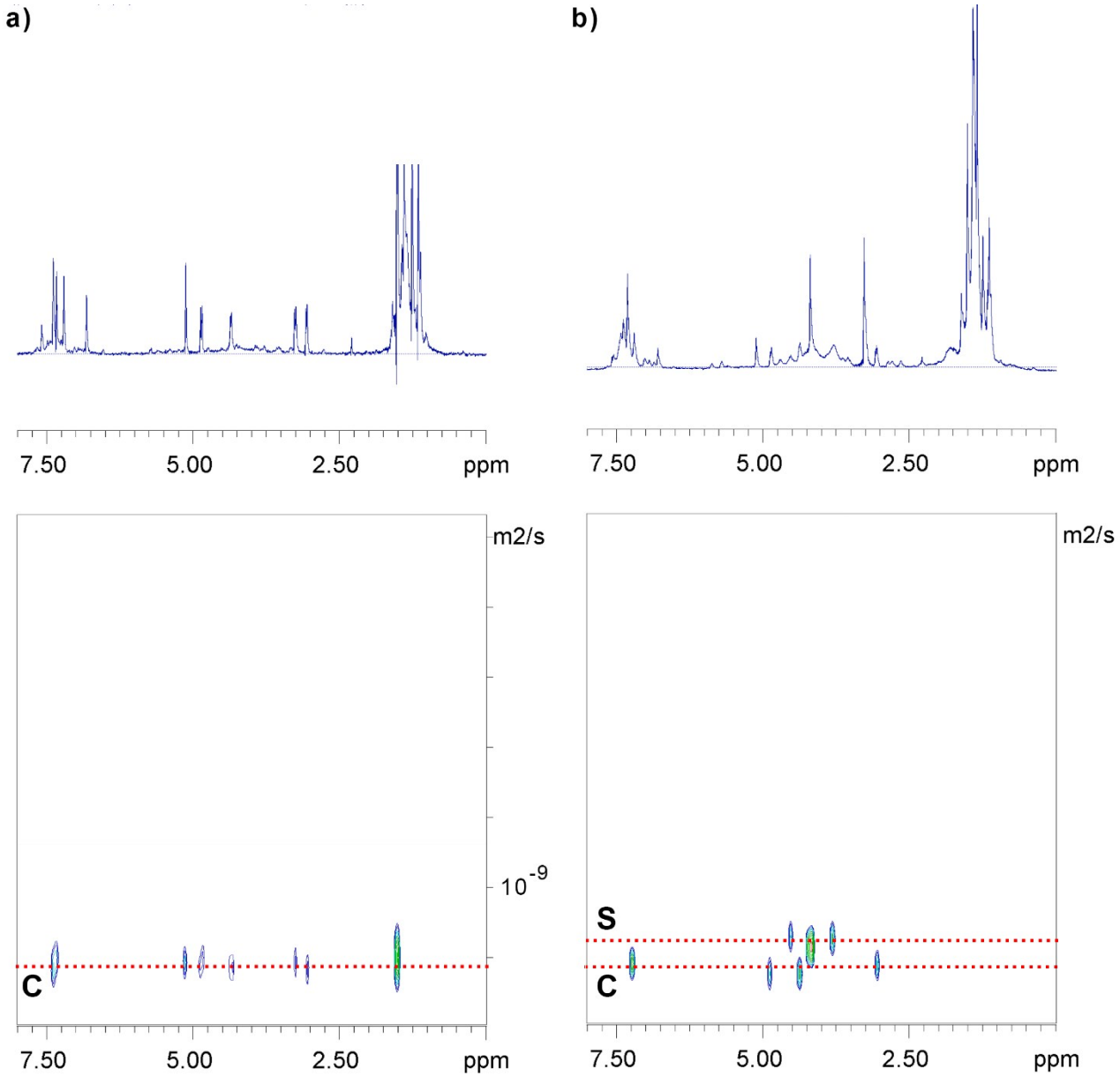


Figure S6. DOSY NMR spectra of the complex **C** (600 MHz, 25°C, benzene-d_6) (a) and of **C** (600 MHz, 25°C, benzene-d_6) in presence of the internal standard **S** as reference (b). Diffusion coefficients: C = $5.6\cdot10^{-8}\pm4.6\cdot10^{-10}$ m^2s^{-1}; S = $6.4\cdot10^{-8}\pm3.9\cdot10^{-10}$ m^2s^{-1}.

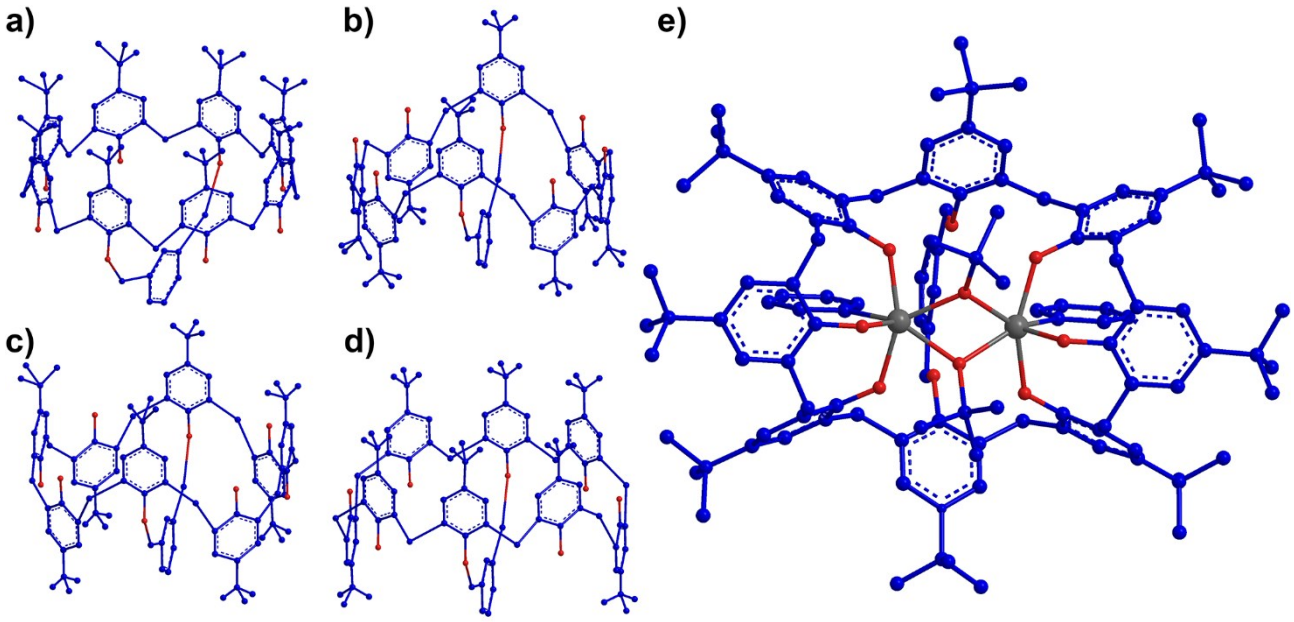


Figure S7. Possible configurations of the ligand **L** with C_{2v} symmetry (a-d) and the structure of the complex **C**, compatible with NMR information, resulting from the configuration in b.

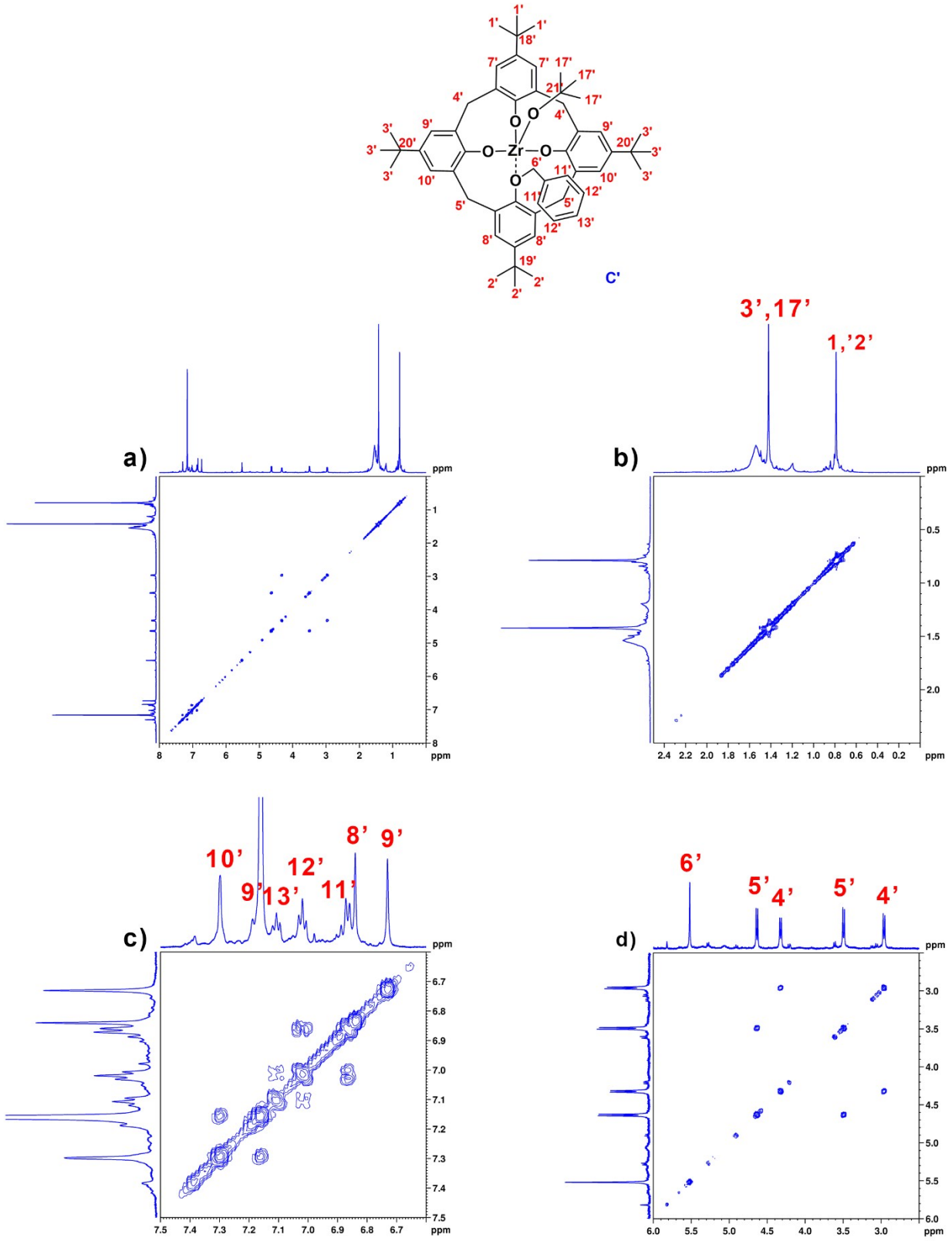


Figure S8. ^{1}H-^{1}H COSY spectrum (600 MHz, benzene-d_6, 25°C) of **C'** (a) with magnifications of the diagnostic regions (b-d).

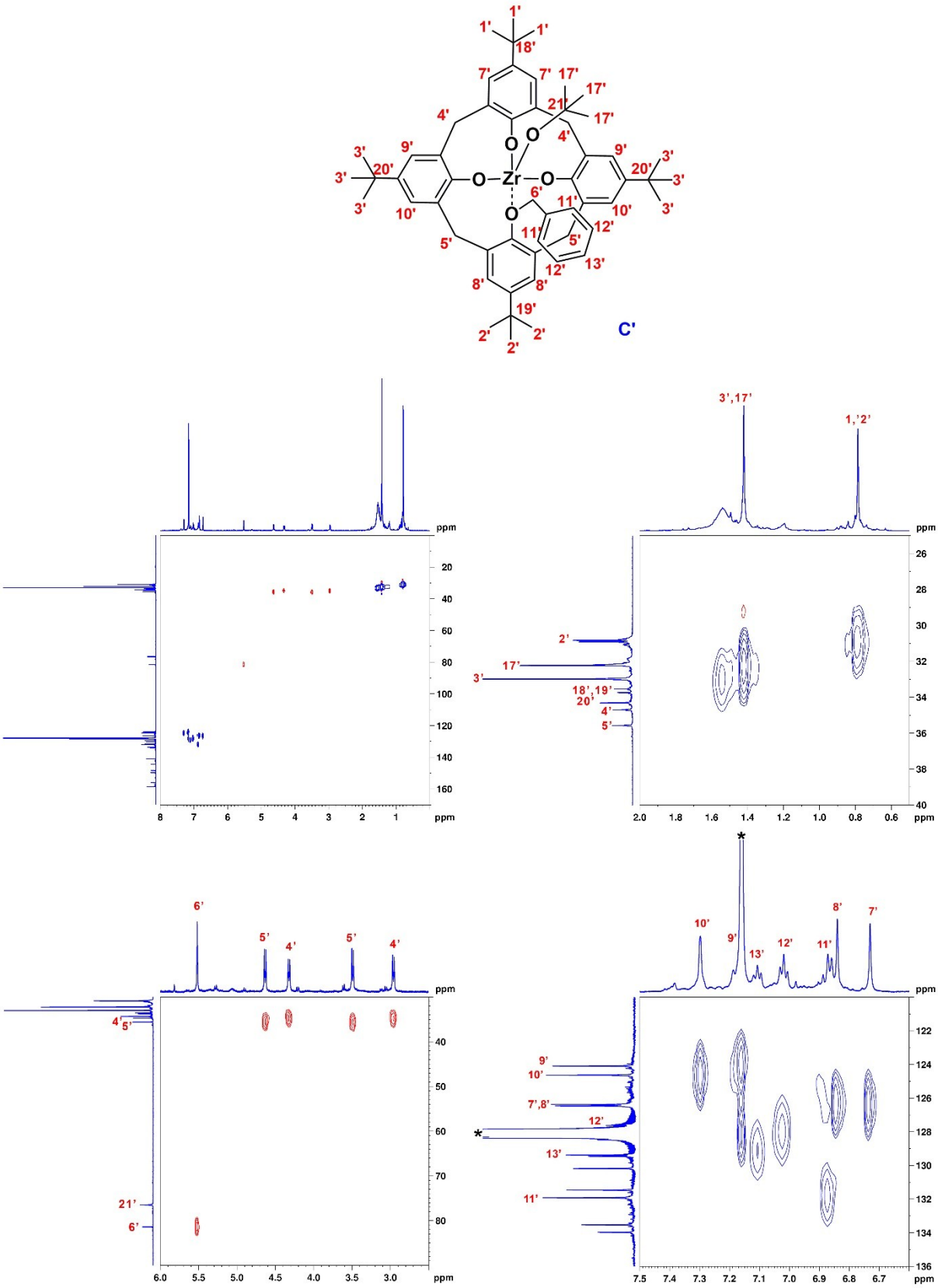


Figure S9. ^{1}H-^{13}C HSQC spectrum (600 MHz, benzene-d_6, 25°C) of the complex **C'** (a) with magnifications of the diagnostic regions (b-d).

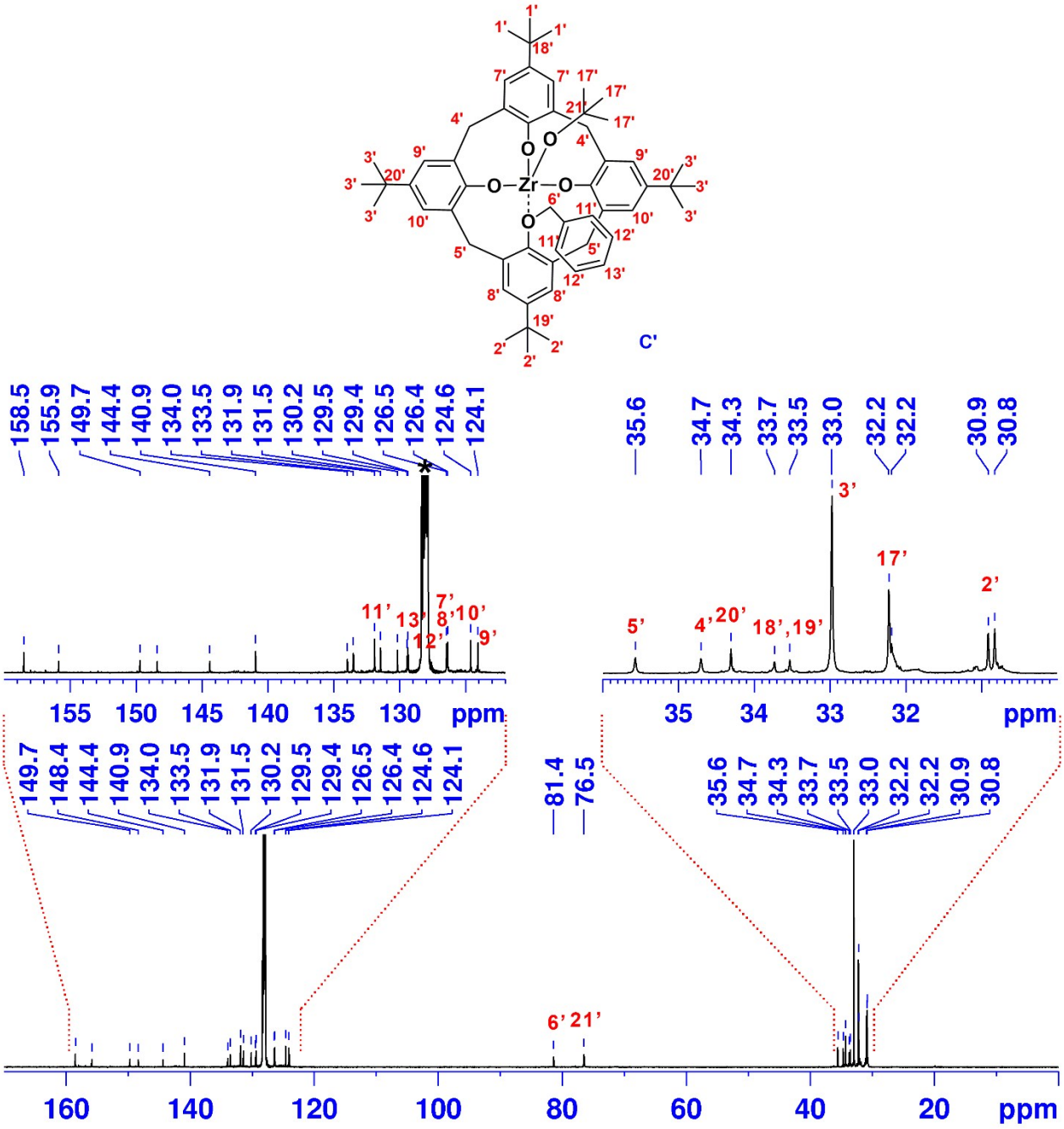


Figure S10. ^{13}C NMR spectrum of the complex **C**' with diagnostic signal labelled (600 MHz, benzene-d_6, 25°C).

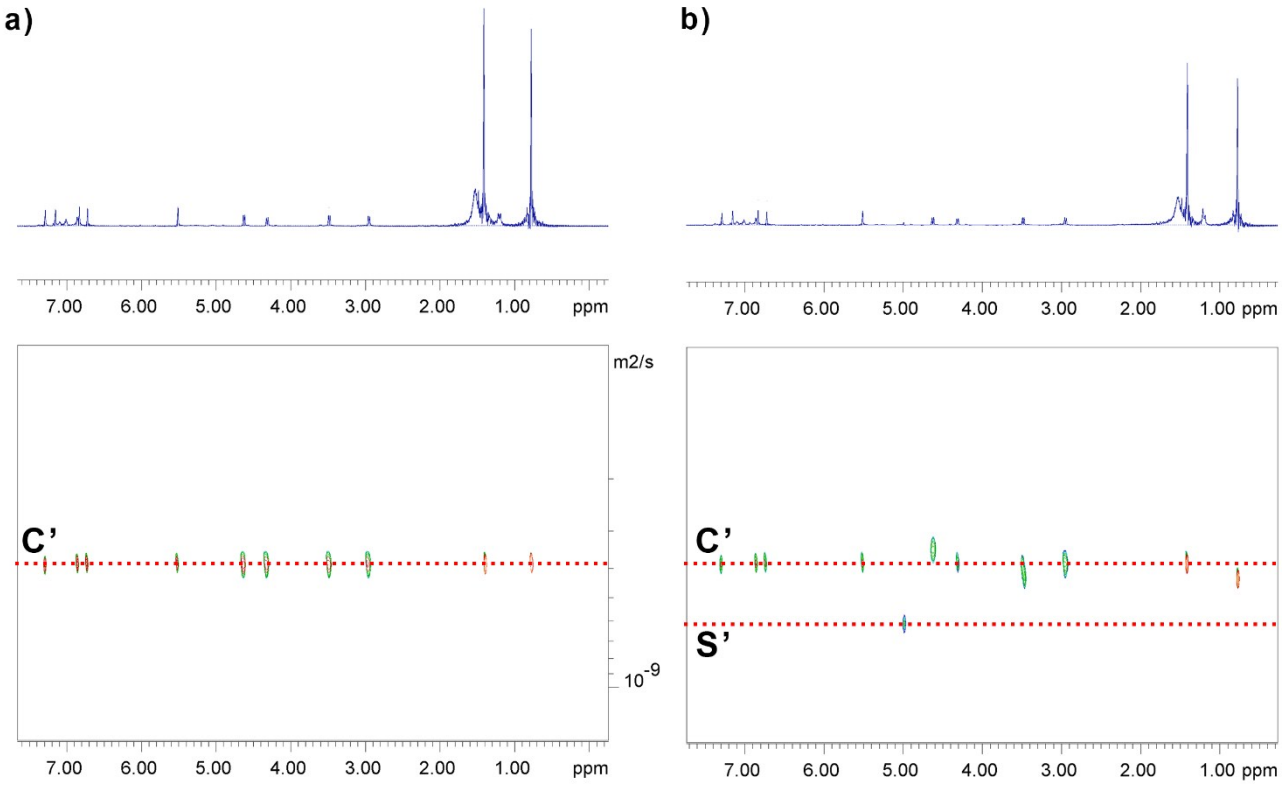


Figure S11. DOSY NMR spectra of the complex **C'** (a) and of **C'** in presence of the internal standard **S'** as reference (b). Diffusion coefficients: C = $4.30 \cdot 10^{-10} \pm 8.56 \cdot 10^{-13}$ m^2s^{-1}; S = $4.35 \cdot 10^{-10} \pm 5.68 \cdot 10^{-13}$ m^2s^{-1}.

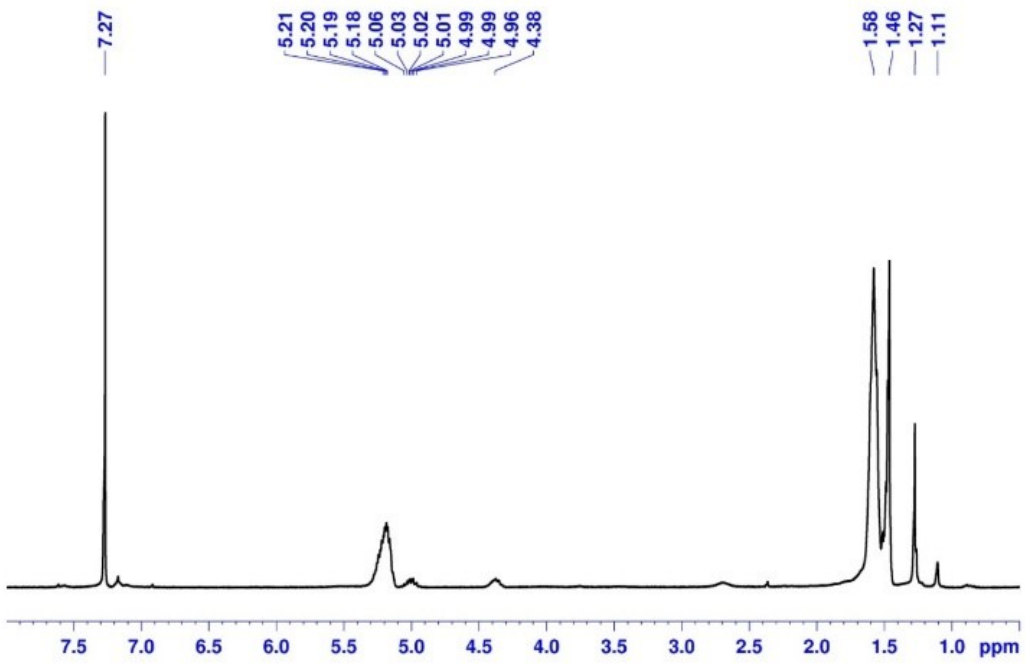


Figure S12. ^{1}H NMR spectrum of cyclic PLA synthesized by **C** (entry **4** of Table 1; $CDCl_3$, 300 MHz, 25°C).

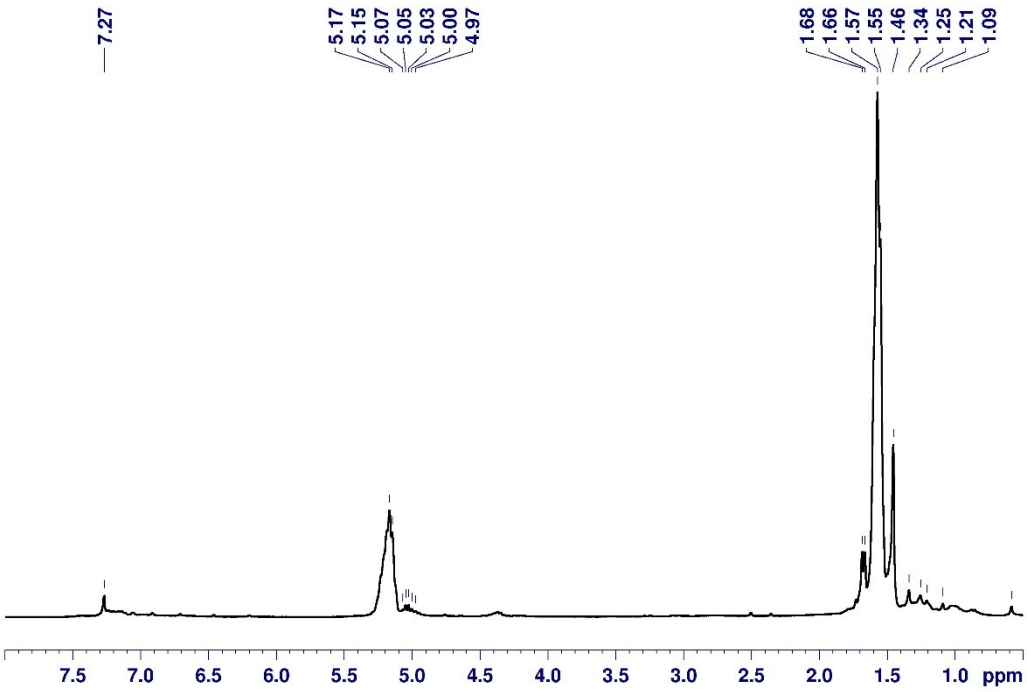


Figure S13. ^{1}H NMR spectrum of linear PLA synthesized by **C'** (entry **9** of Table 1; $CDCl_3$, 300 MHz, 25°C).

2. UV-VIS ANALYSIS

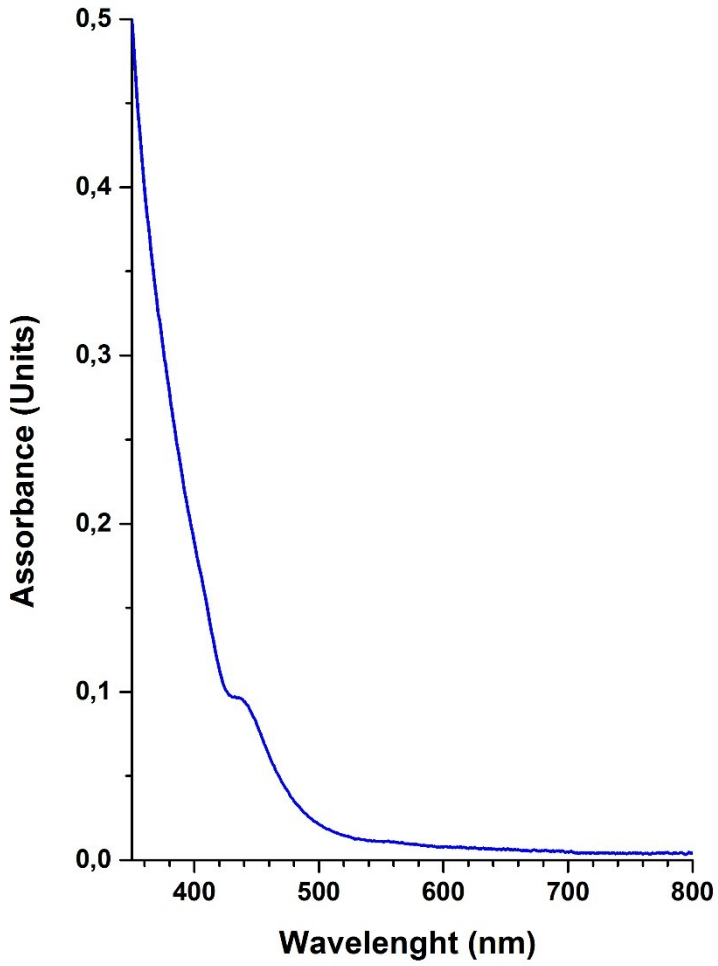


Figure S14. UV-Vis spectrum of **C** ($5.8 \cdot 10^{-3}$ M; pyridine; 25 °C; ε_{436} = 166 $Lmol^{-1}cm^{-1}$).

3. ESI-MS AND MALDI-MS ANALYSES

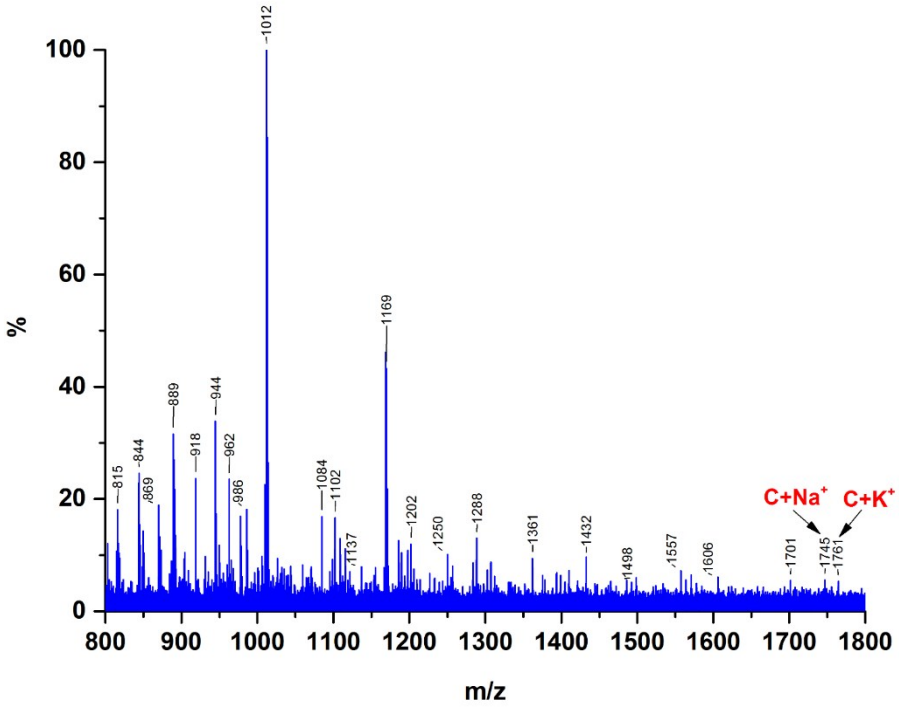


Figure S15. ESI-MS spectrum of the complex **C** (toluene/methanol solvents mixture).

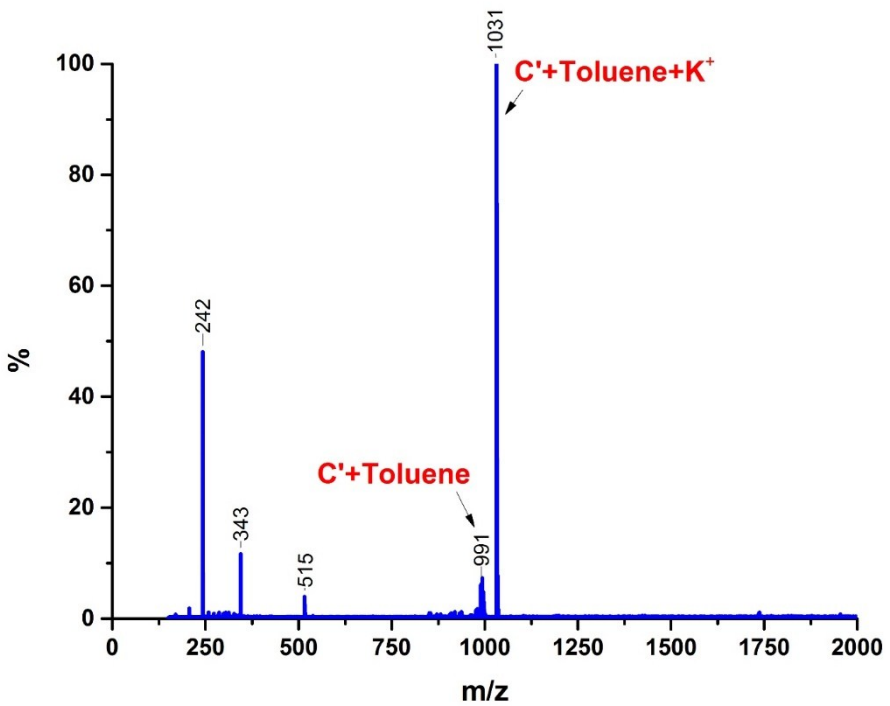


Figure S16. ESI-MS spectrum of the complex **C'** (toluene/methanol solvents mixture).

4. Kinetic Investigations

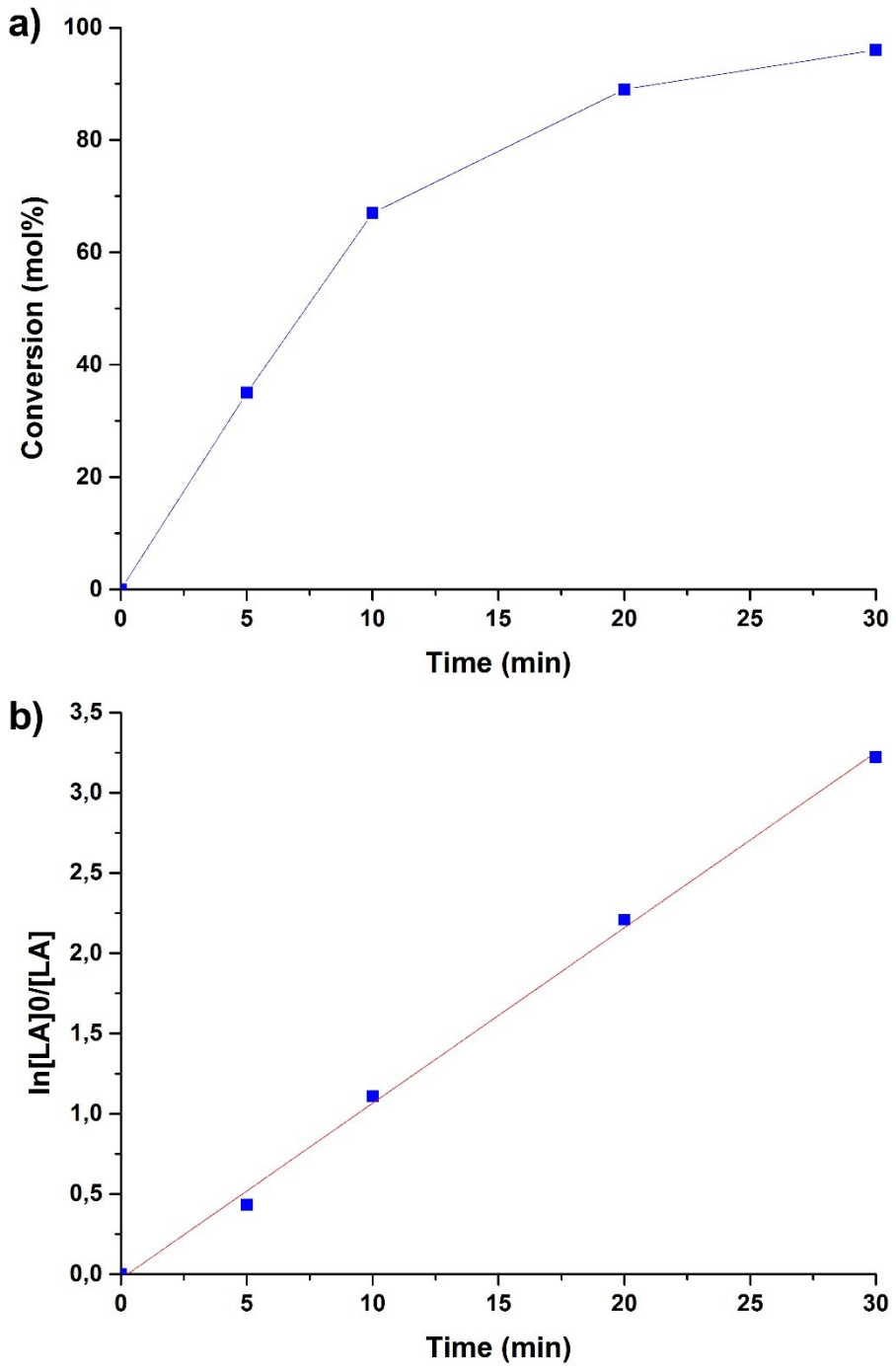


Figure S17. Polymerization of *rac*-LA catalyzed by **C** (a) with the corresponding plot of $\ln([LA]_0/[LA])$ versus time.

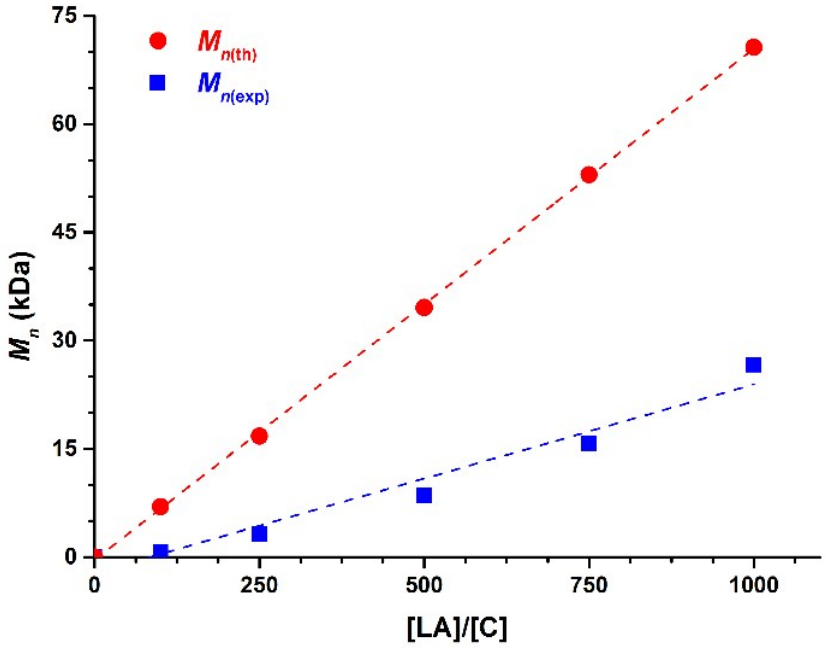


Figure S18. Plot of number-averaged molecular weights $M_{n(exp)}$ (square) *vs* monomer to initiator ratio with theoretical molecular weights $M_{n(th)}$ (dots) for LA polymerization catalyzed by **C** (reaction conditions in Table 1).

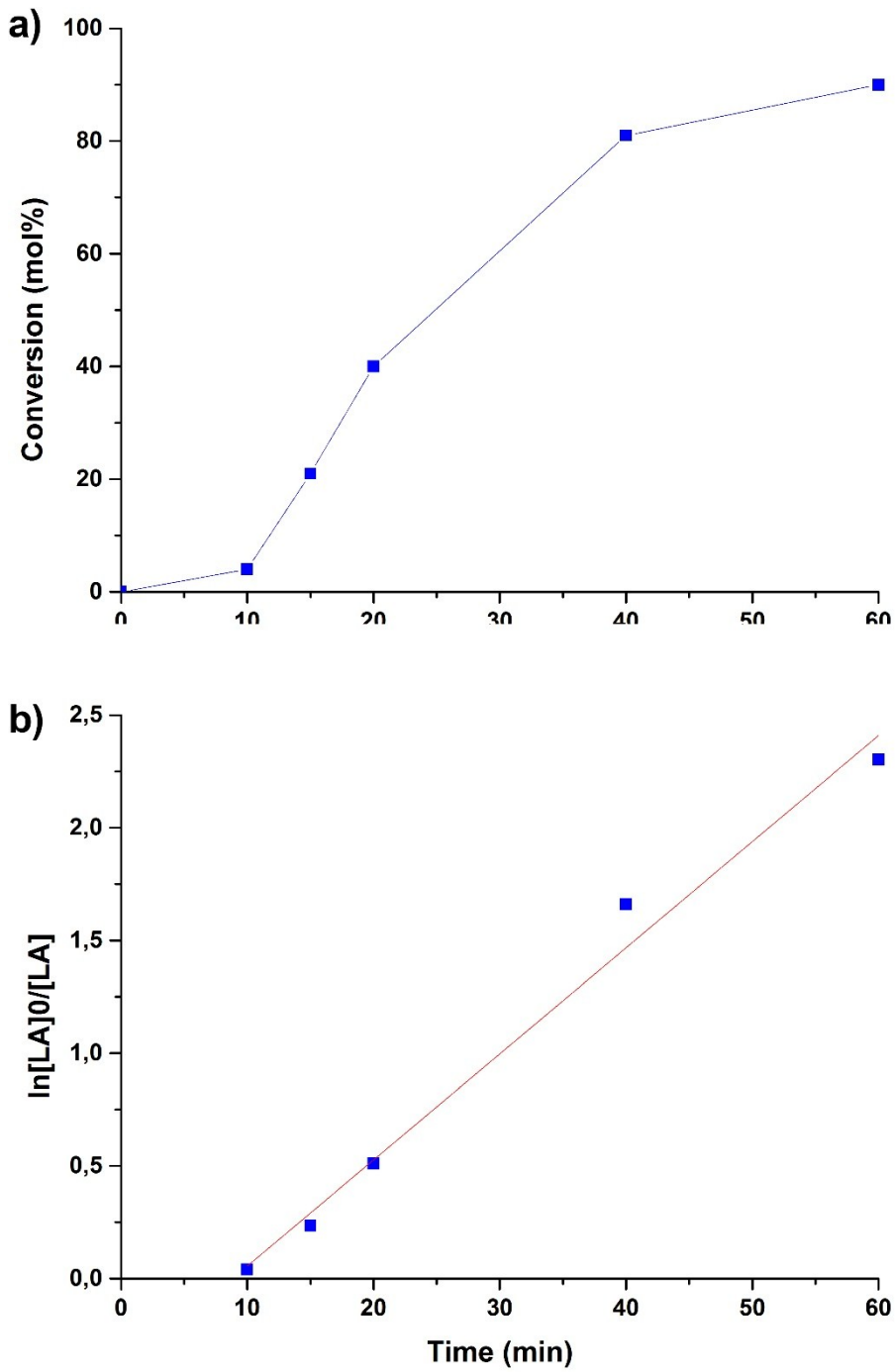


Figure S19. Polymerization of *rac*-LA catalyzed by **C'** (a) with the corresponding plot of $\ln([LA]_0/[LA])$ versus time.

Table S1. Reaction rate as a function of catalyst concentration for ROP of LA with C.

Entry	**[C] (M)**	**[*rac*-LA]/[C] (molar ratio)**	**r ($M\ s^{-1}$)**
S1	$1.42\cdot10^{-2}$	50	$2.7\cdot10^{-3}\pm1.5\cdot10^{-4}$
S2	$7.07\cdot10^{-3}$	100	$1.7\cdot10^{-3}\pm1.3\cdot10^{-4}$
S3	$4.72\cdot10^{-3}$	150	$1.2\cdot10^{-3}\pm6.3\cdot10^{-}$
S4	$3.53\cdot10^{-3}$	200	$7.3\cdot10^{-4}\pm3.7\cdot10^{-5}$

Reaction conditions: [*rac*-LA] = 0.706 M, TCE-d_2 = 0.6 mL, T = 80 °C; reactions carried out inside NMR tubes and monitored with interval of one minute.

5. Gel Permeation Chromatography.

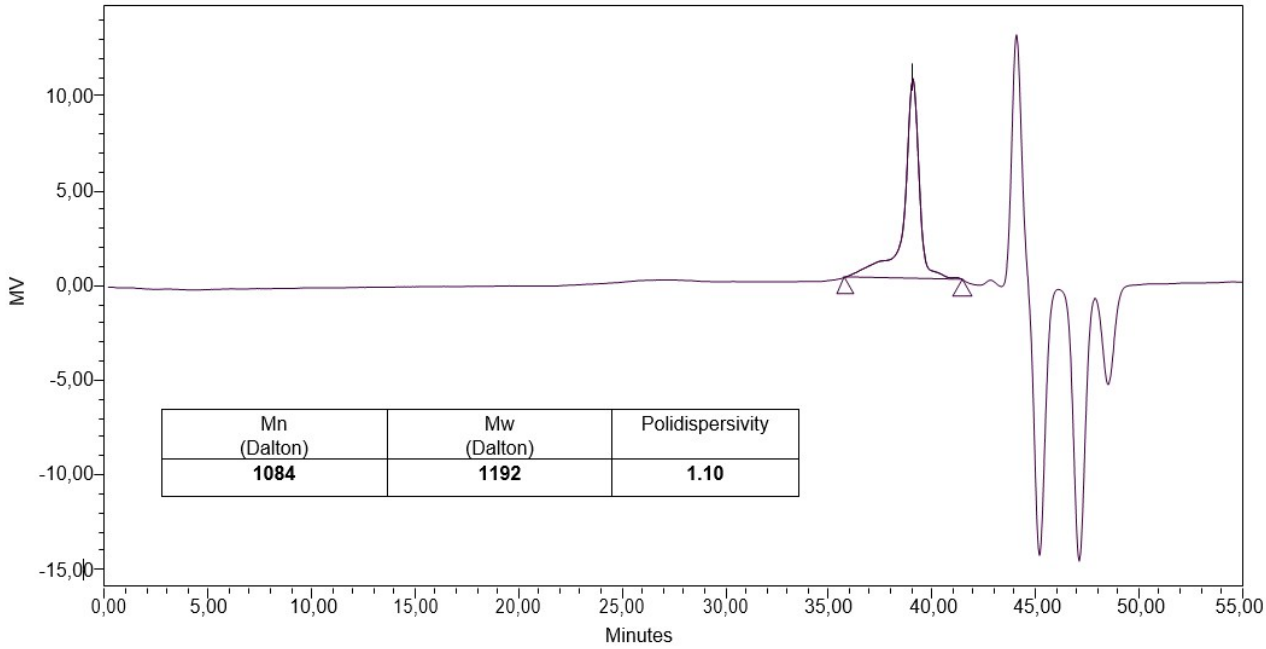


Figure S20. Gel permeation chromatogram of the polymer sample from entry **1** of Table 1.

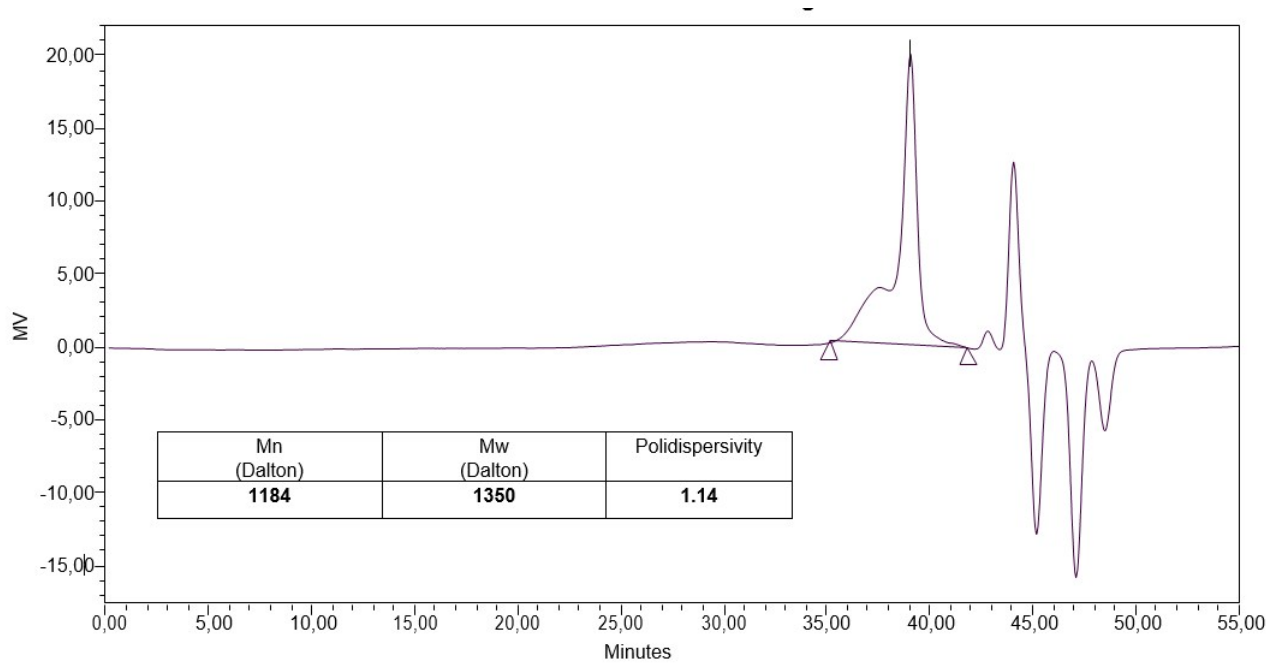


Figure S21. Gel permeation chromatogram of the polymer sample from entry **2** of Table 1.

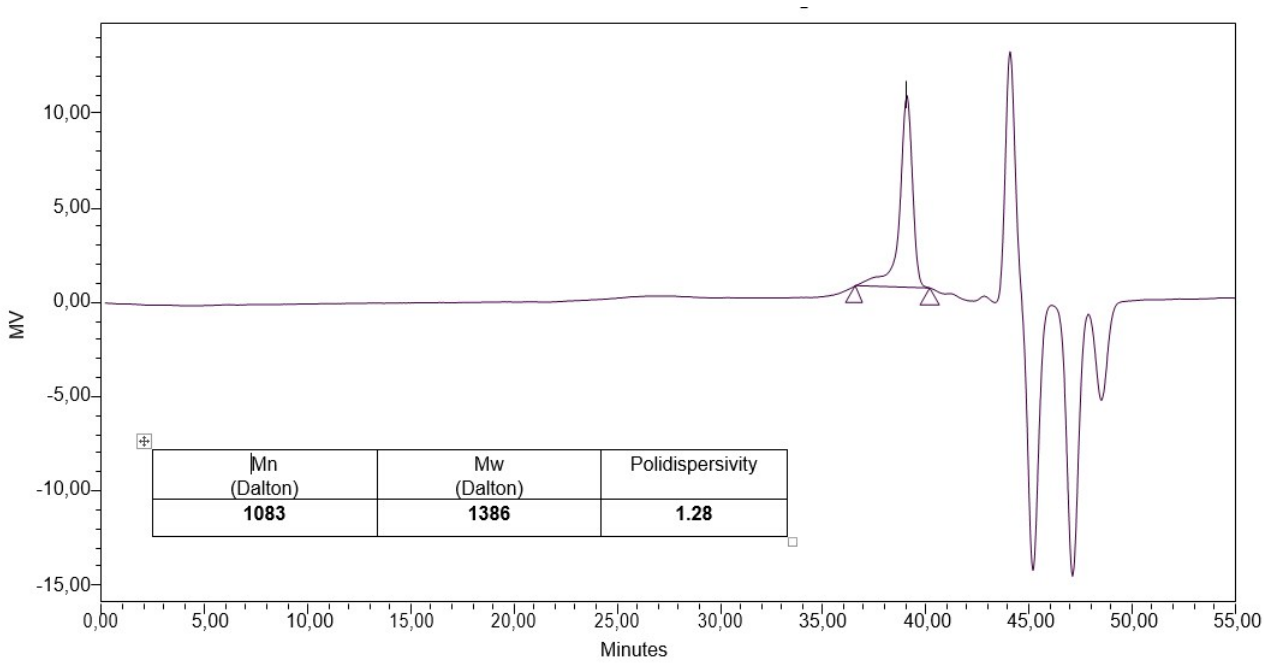


Figure S22. Gel permeation chromatogram of the polymer sample from entry **3** of Table 1.

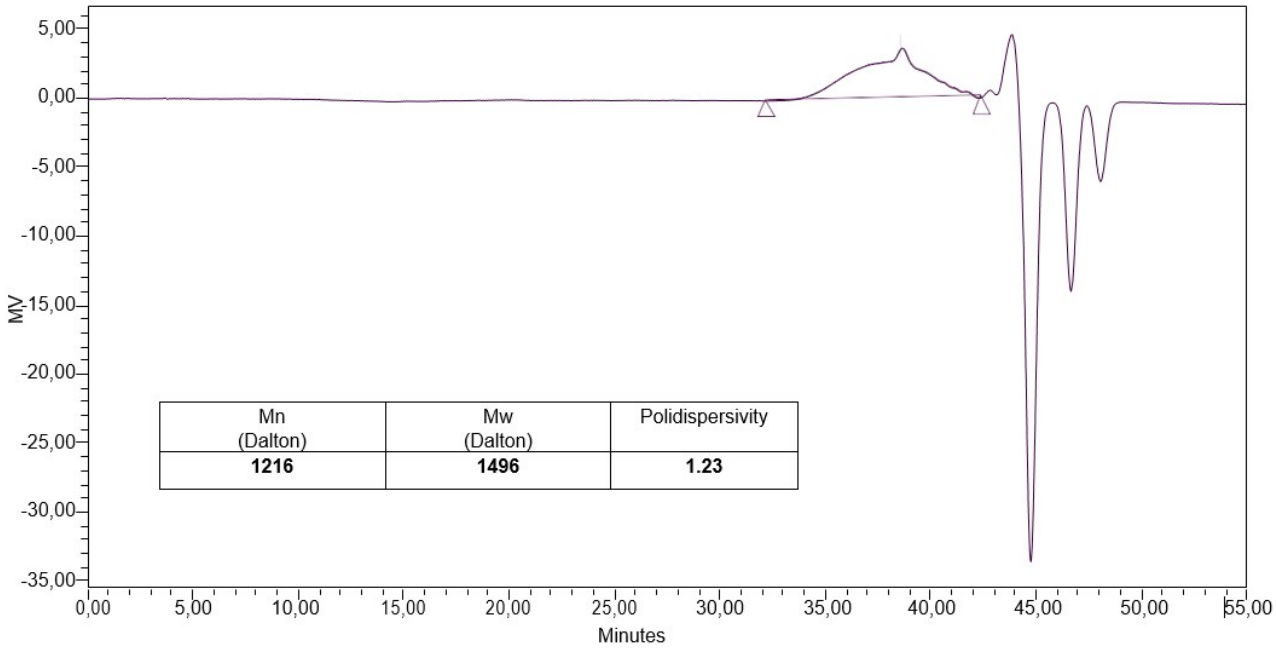


Figure S23. Gel permeation chromatogram of the polymer sample from entry **4** of Table 1.

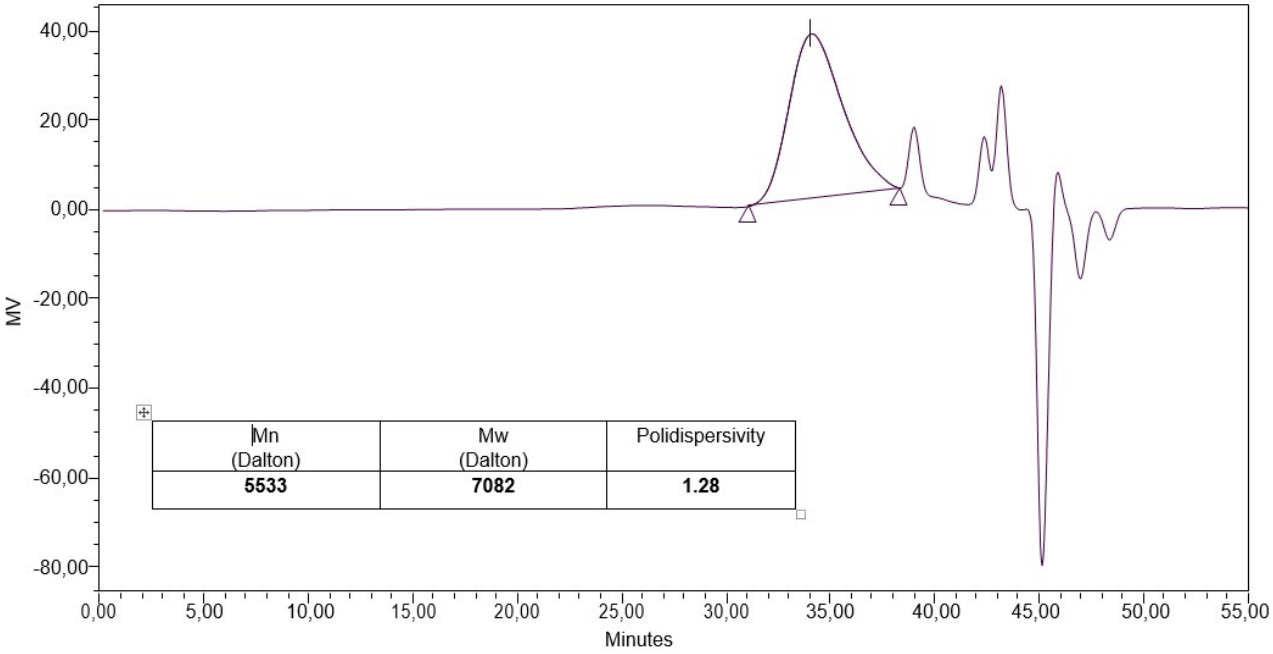


Figure S24. Gel permeation chromatogram of the polymer sample from entry **5** of Table 1.

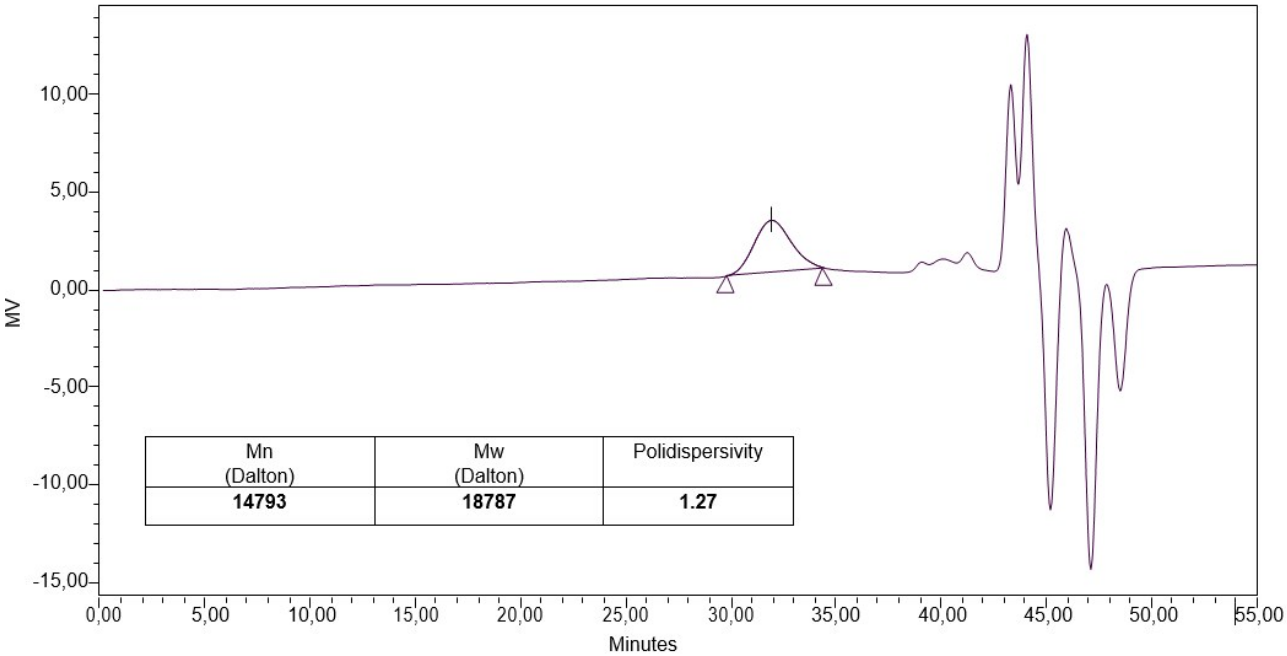


Figure S25. Gel permeation chromatogram of the polymer sample from entry **6** of Table 1.

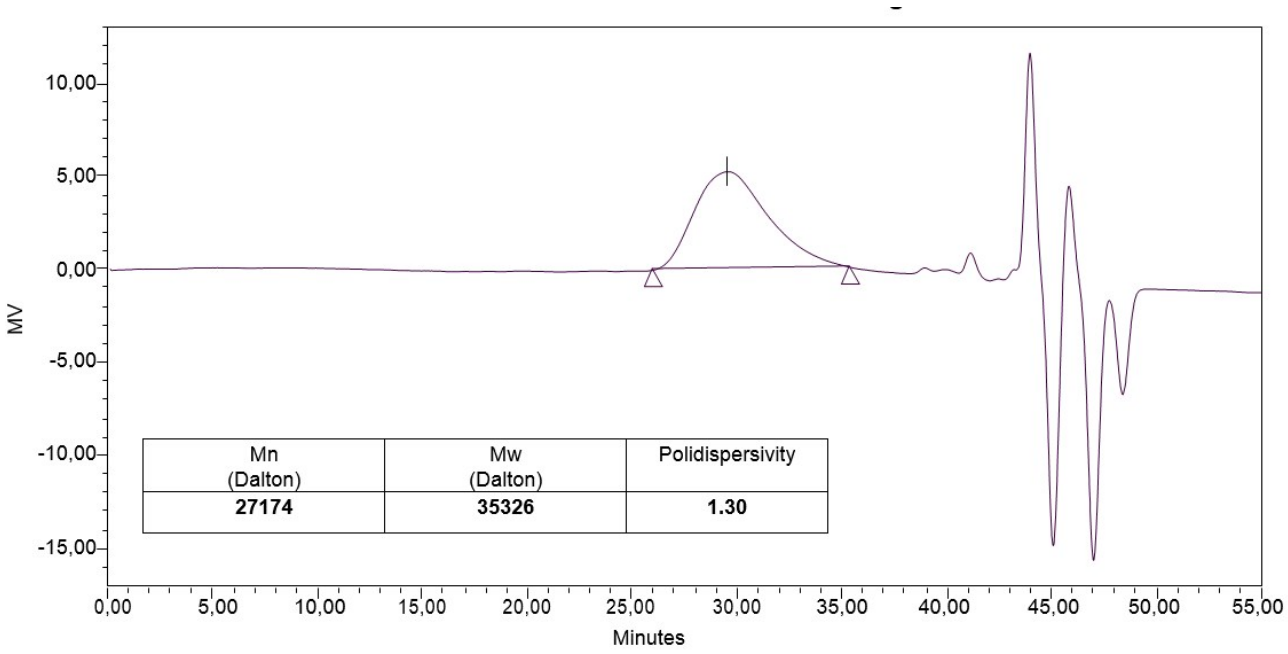


Figure S26. Gel permeation chromatogram of the polymer sample from entry **7** of Table 1.

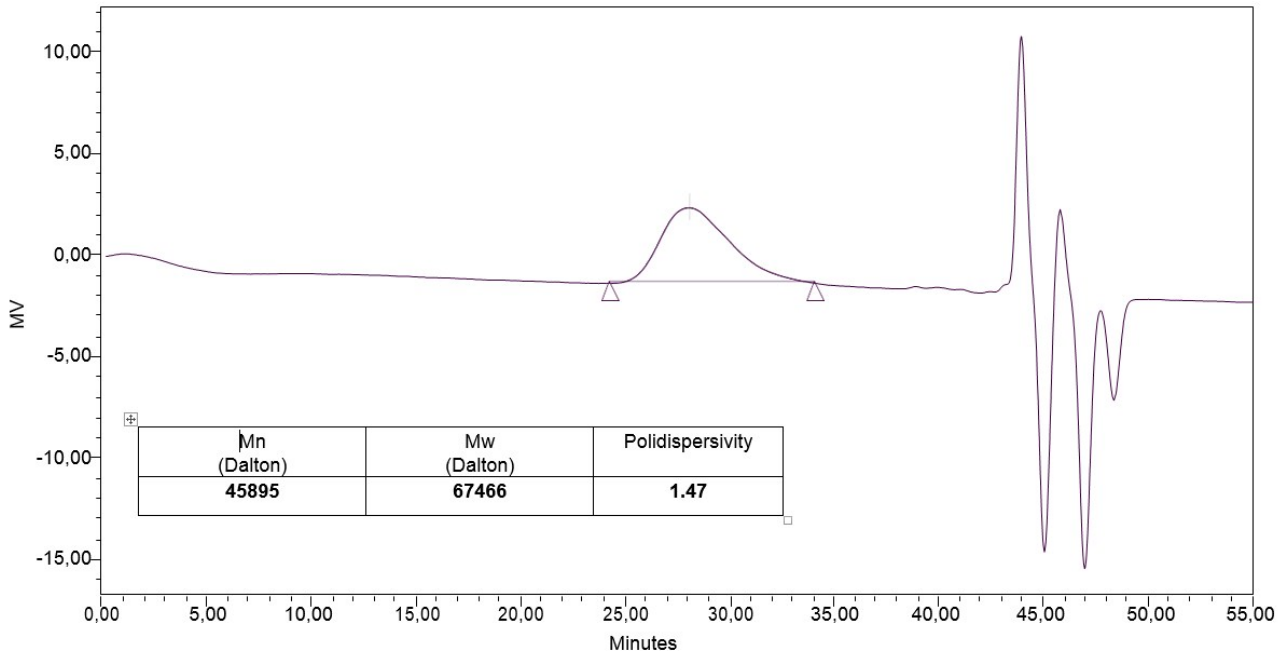


Figure S27. Gel permeation chromatogram of the polymer sample from entry **8** of Table 1.

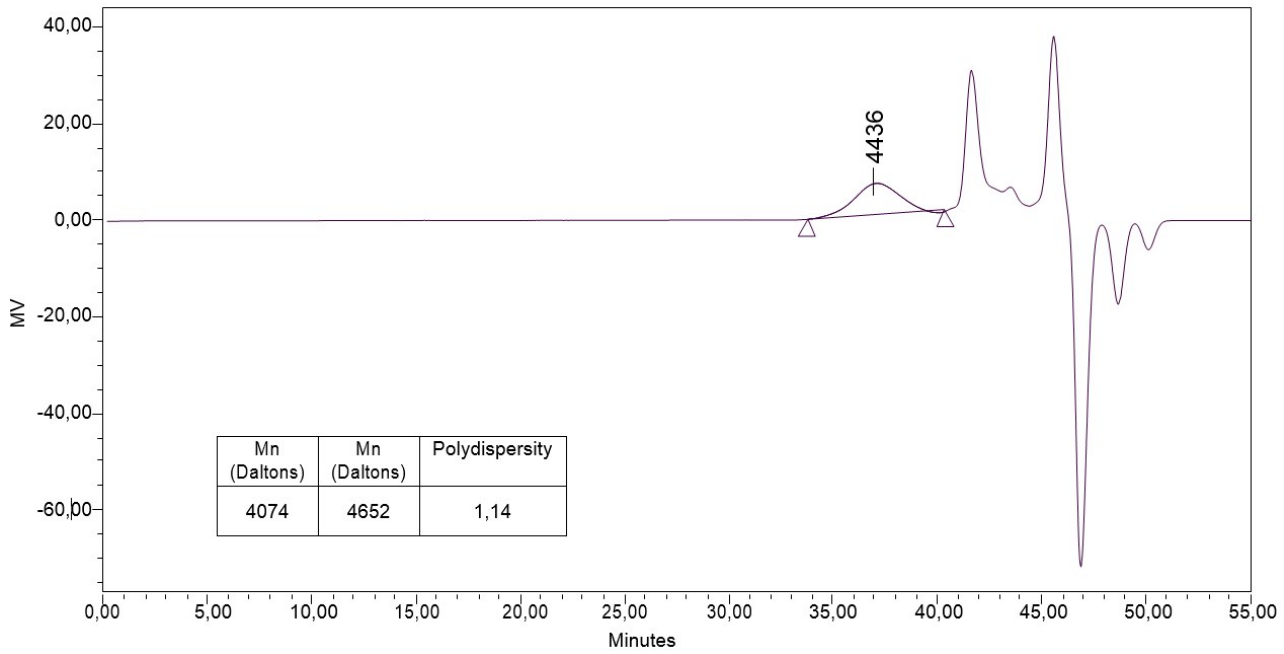


Figure S28. Gel permeation chromatogram of the polymer sample from entry **9** of Table 1.

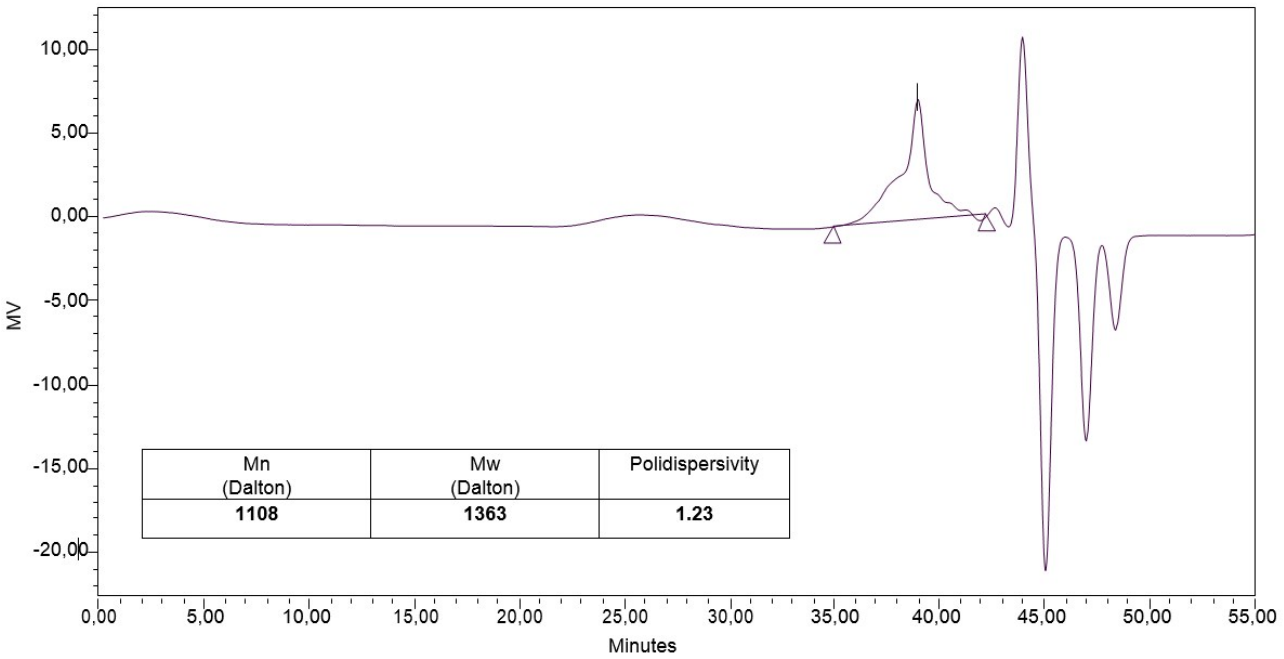
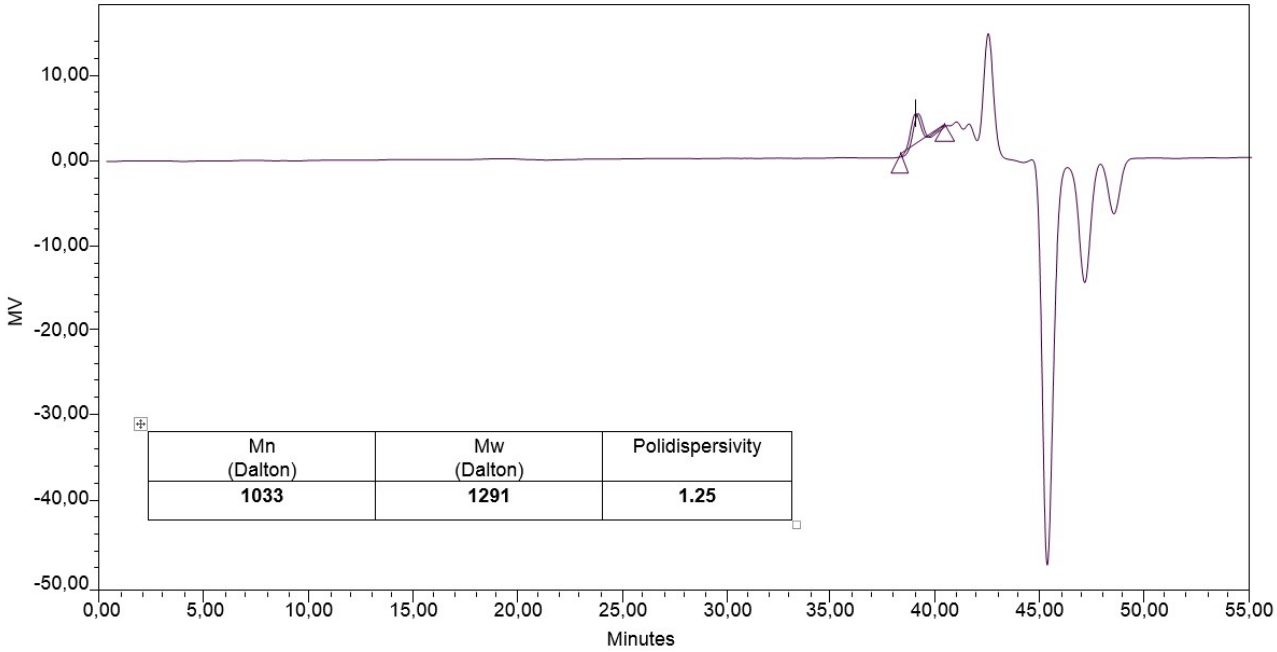


Figure S29. Gel permeation chromatogram of the polymer sample from entry **10** of Table 1.



Mn (Dalton)	Mw (Dalton)	Polidispersivity
1033	**1291**	**1.25**

Figure S30. Gel permeation chromatogram of the polymer sample from entry **11** of Table 1.