**Electronic Supplementary Information**

# Lithium calix[4]arenes: structural studies and use in the ring opening polymerization of cyclic esters.

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*Crystallography*

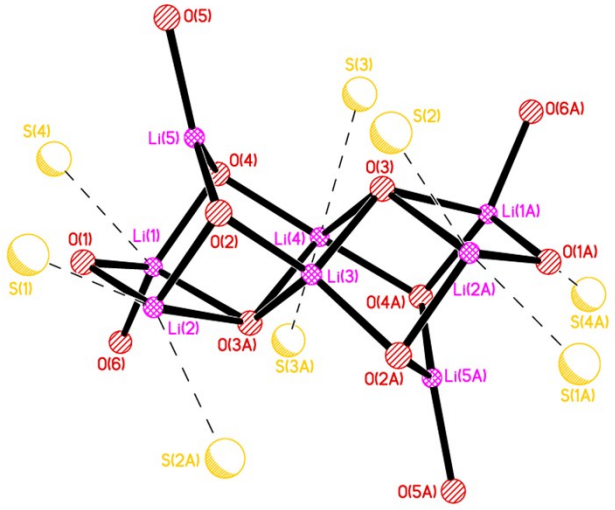


**Figure S1**. An alternative view of the core of **1**·5THF

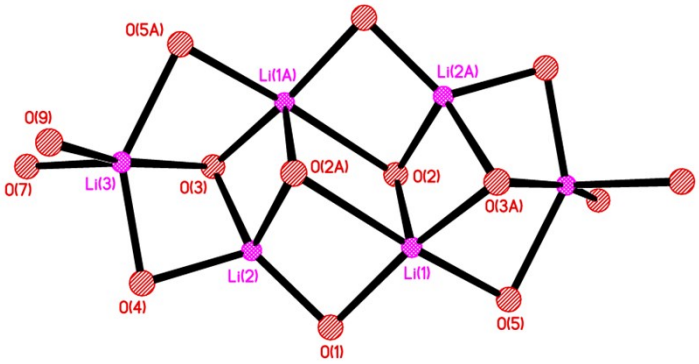


**Figure S2**. Core of **2**·5THF

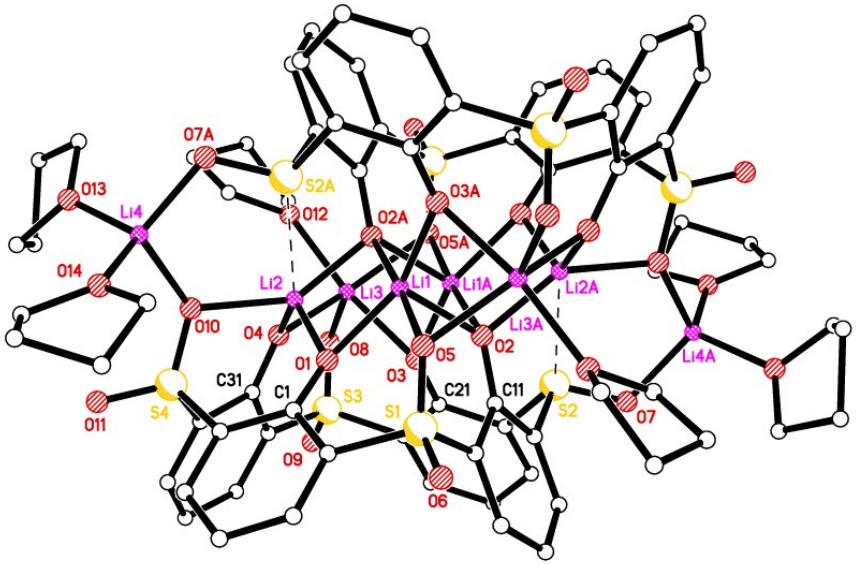


**Figure S3**. An alternative view of **3**·8THF

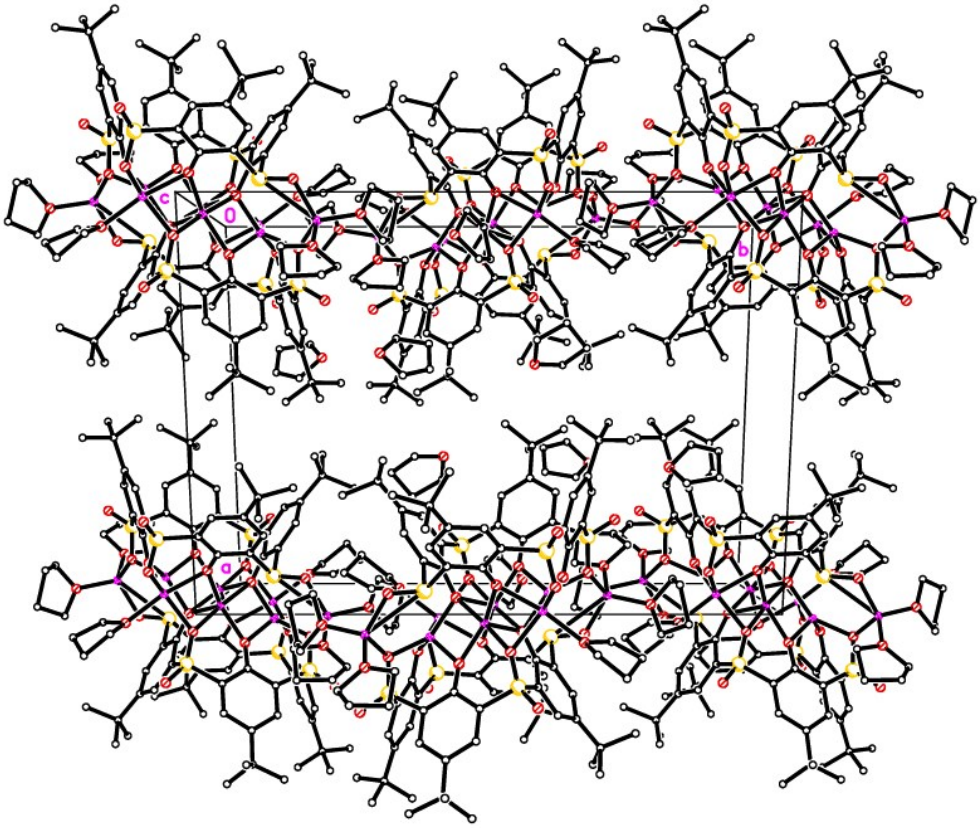


**Figure S4**. Layers in the *b*/*c* plane for **3**·8THF

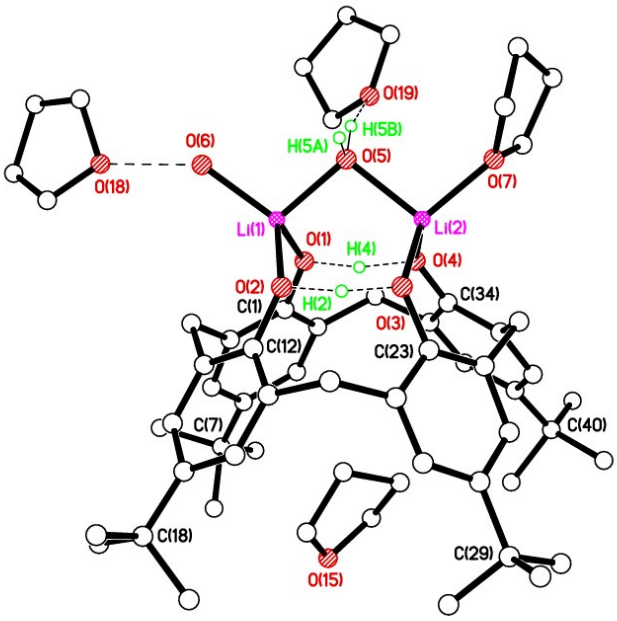


**Figure S5**. Single molecule of **7**·3THF·hexane.

*ROP Studies*

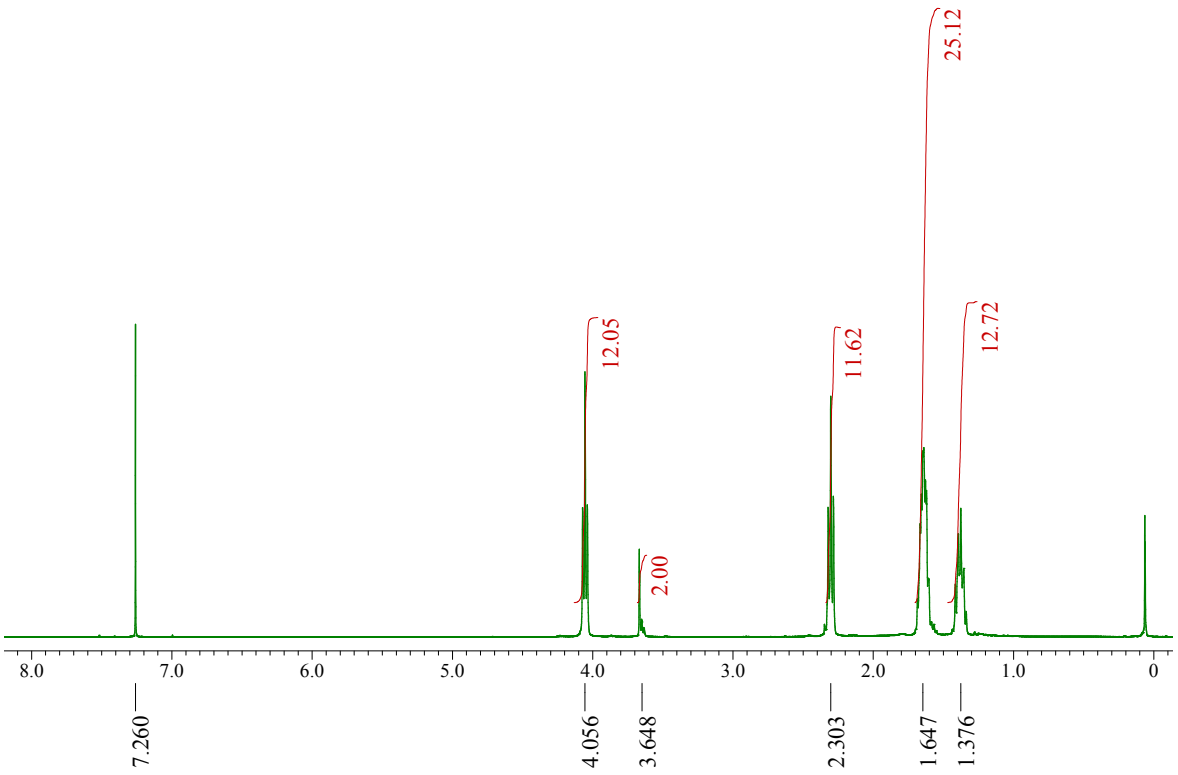


**Figure S6**. $^{1}H$ NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of the PCL synthesized in Table 2 entry 7.

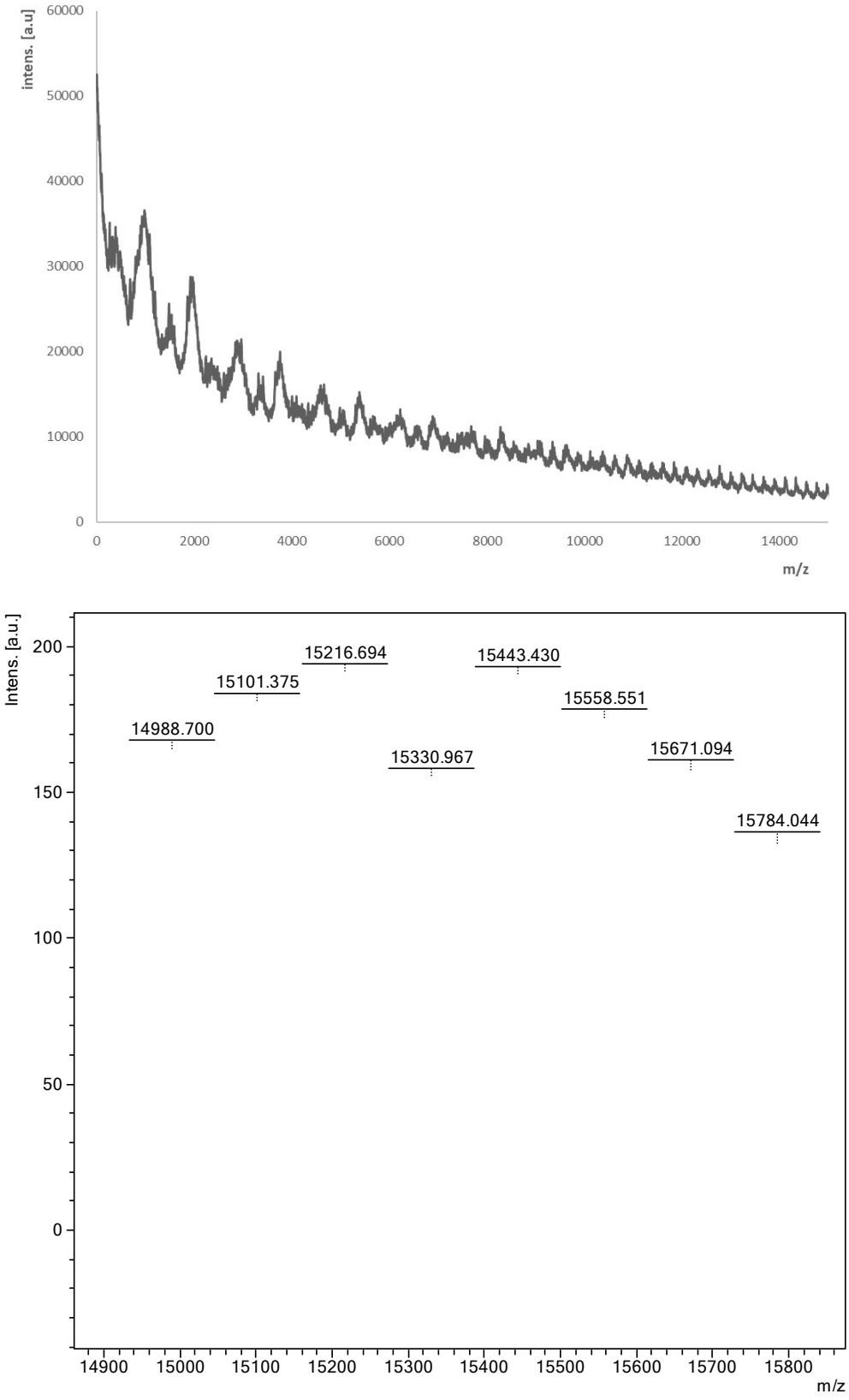


**Figure S7.** MALDI-ToF spectrum of the PCL synthesized in Table 2, entry 7.

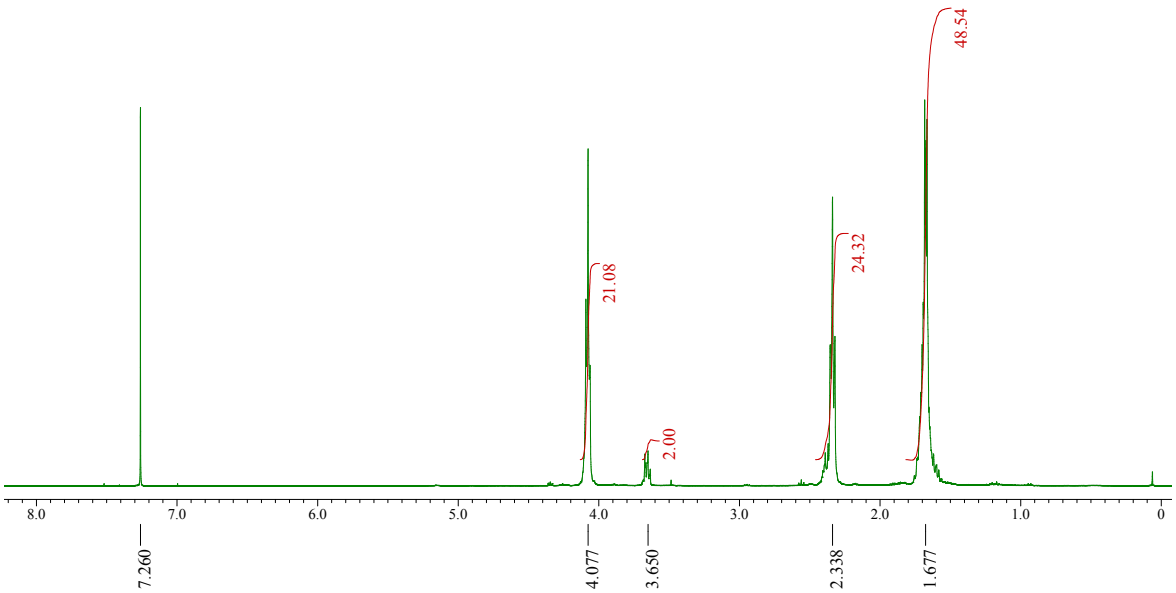


**Figure S8**. $^{1}H$ NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of the PVL synthesized in Table 3 entry 4.

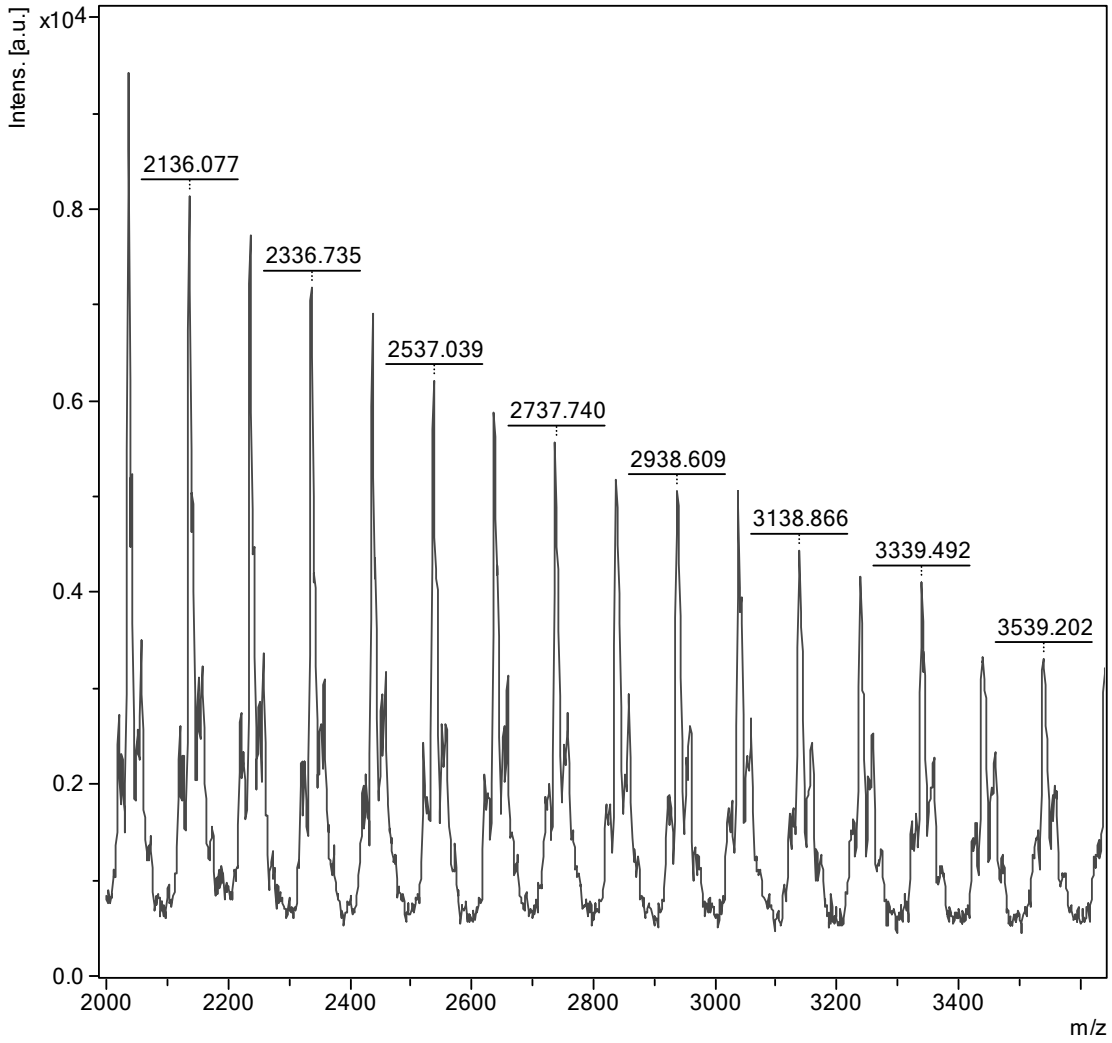


**Figure S9.** MALDI-TOF spectrum of the PVL synthesized in table 3, entry 4. Main population corresponding to α,ω-OH-terminated linear polymers;

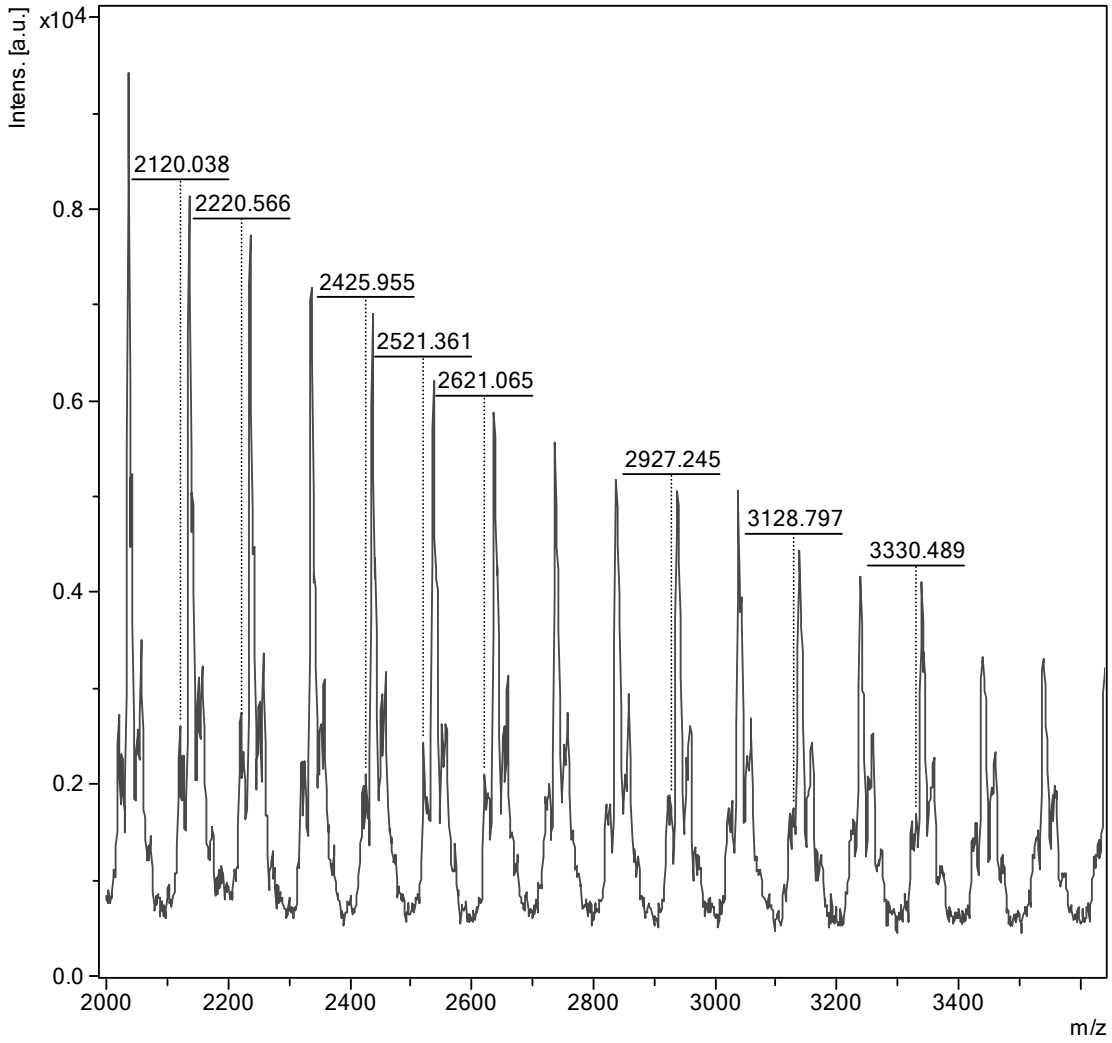


**Figure S10.** MALDI-TOF spectrum of the PVL synthesized in table 3, entry 4. Minor population accountable to cyclic species

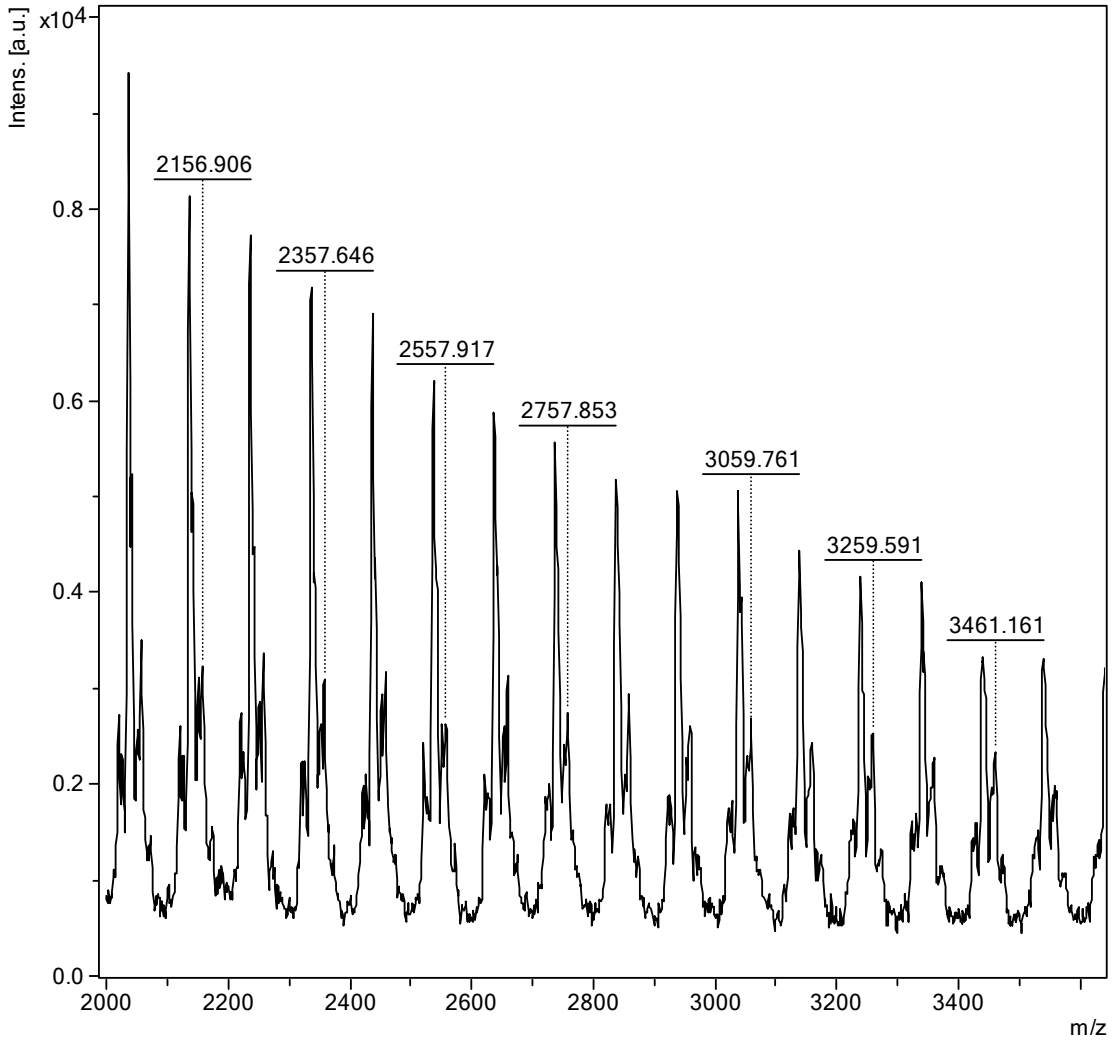


**Figure S11.** MALDI-TOF spectrum of the PVL synthesized in table 3, entry 4. Na-adducts of the linear fragments.

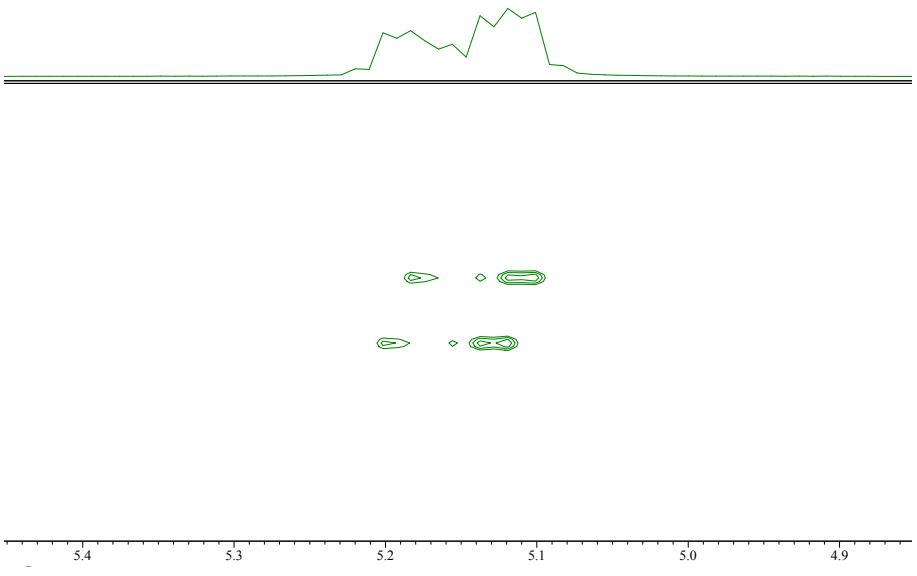

**Figure S12.** 2D *J*-resolved $^{1}H$ NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of the PLA synthesized with **1** (Table 4, run 1).

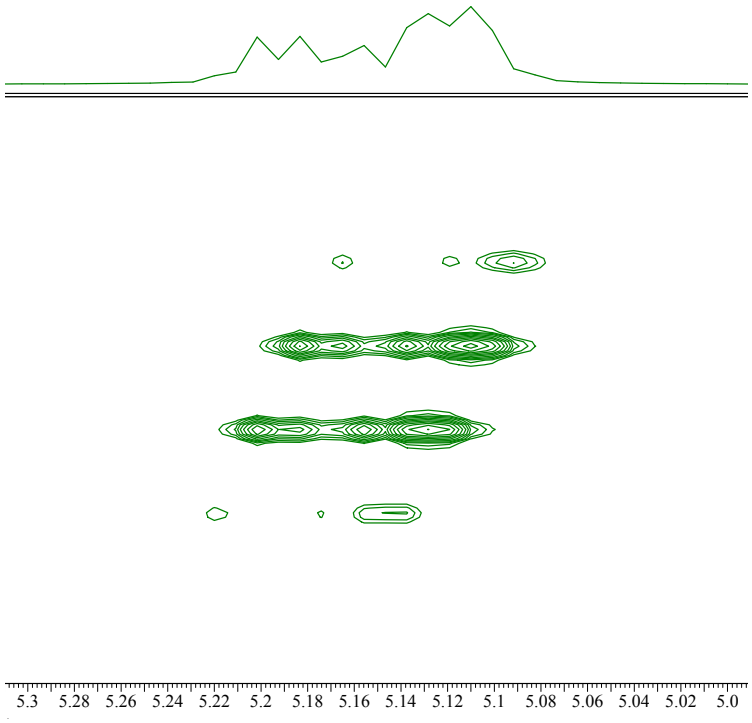


**Figure S13.** 2D *J*-resolved $^{1}H$ NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of the PLA synthesized with **6** (Table 4, run 5).

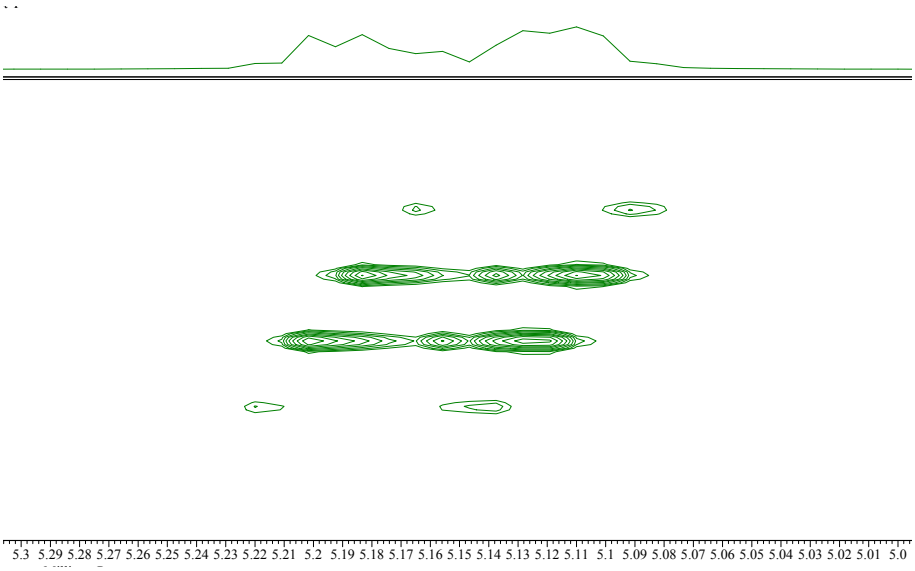


**Figure S14.** 2D *J*-resolved $^{1}H$ NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of the PLA synthesized with **8** (Table 4, run 7).

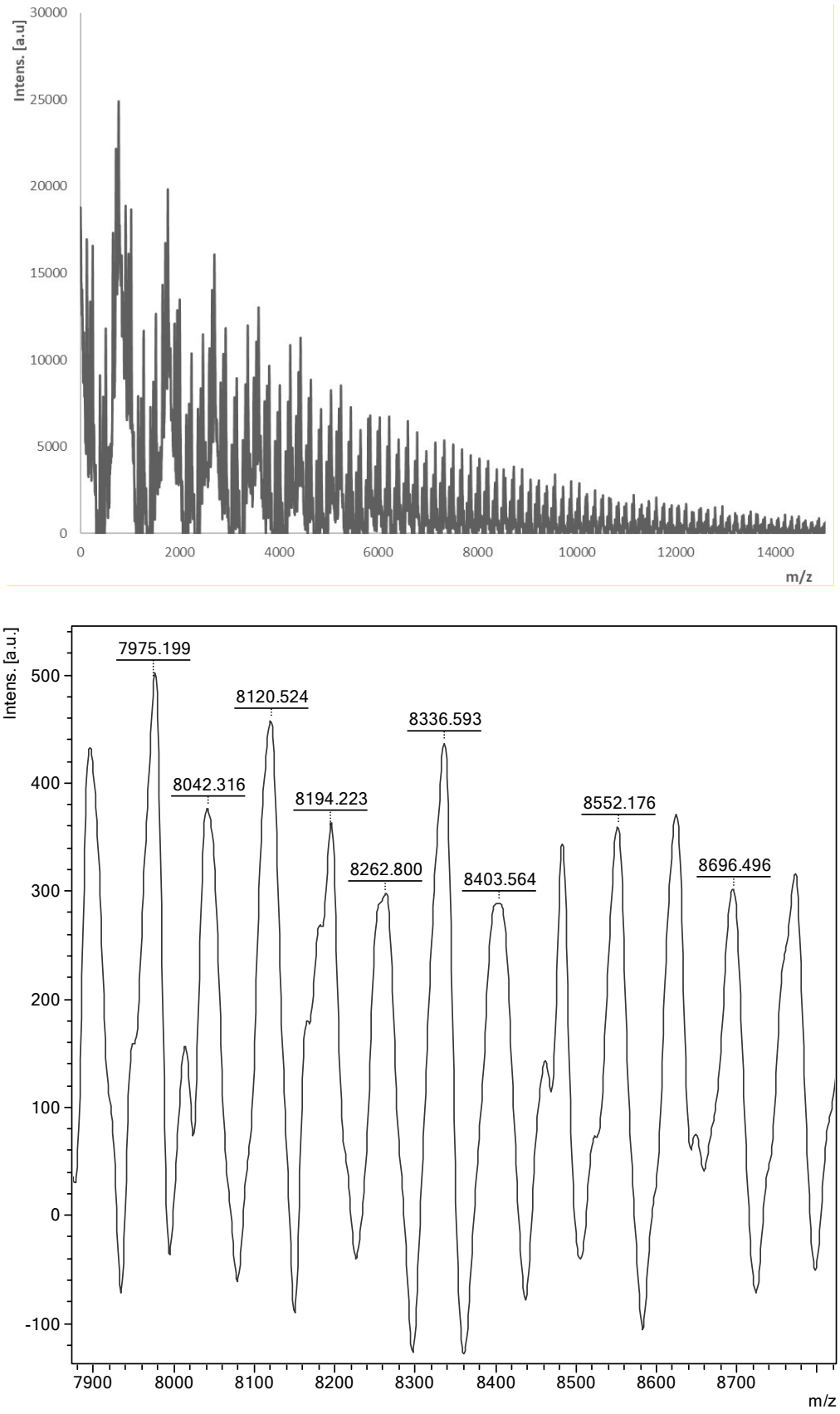


**Figure S15.** MALDI-ToF spectrum of the PLA synthesized in Table 4, entry 5.

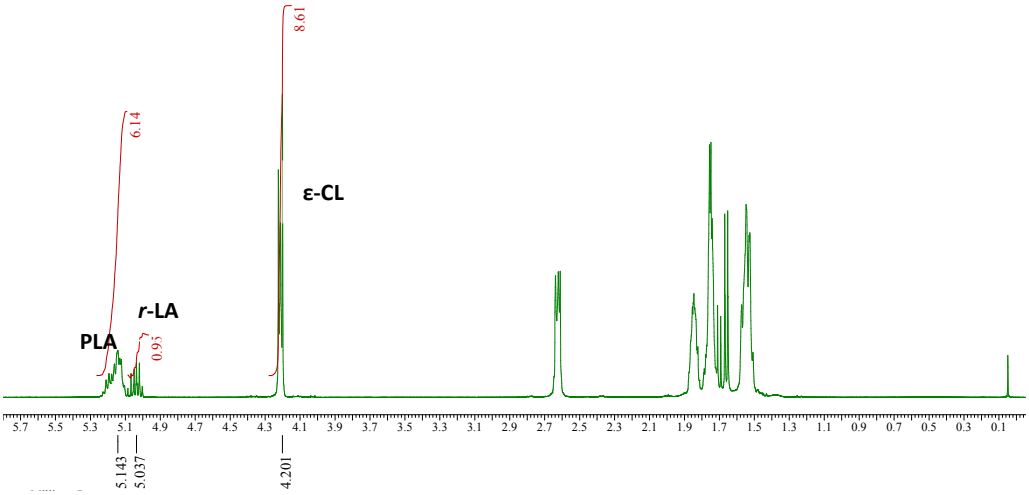


**Figure S16.** $^{1}H$ NMR ($CDCl_3$, 400 MHz, 298 K)

spectrum of the crude reaction mixture of the attempted CL/LA copolymerization with **8** (Table 5, run 6) showing unreacted ε-CL, 83% *r*-LA conversion.