Supporting Information

Configurationally Flexible Zinc Complexes as Catalysts for rac-Lactide Polymerisation

Pargol Daneshmand, Ina Michalsky, Frank Schaper*

Centre in Green Chemistry and Catalysis, Department of chemistry, Université de Montréal, C. P. 6128 Succ. Centre-Ville, Montréal, QC, H3T 3J7, Canada.

* Frank.Schaper@umontreal.ca

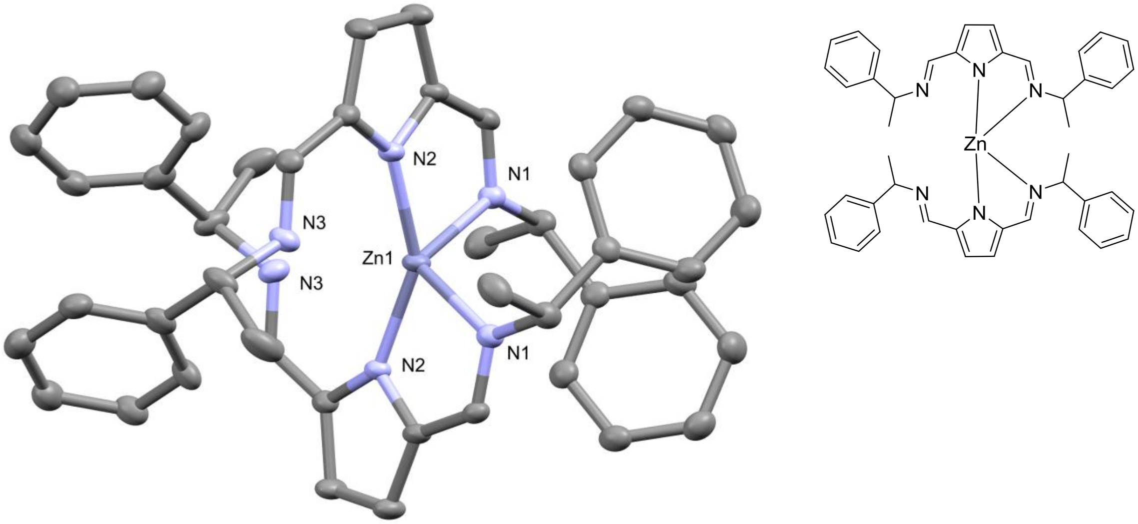

Figure S1. Crystal structure of (**L1**)$_2$Zn.
Thermal ellipsoids displayed at the 50% probability level. Hydrogen atoms omitted for clarity.

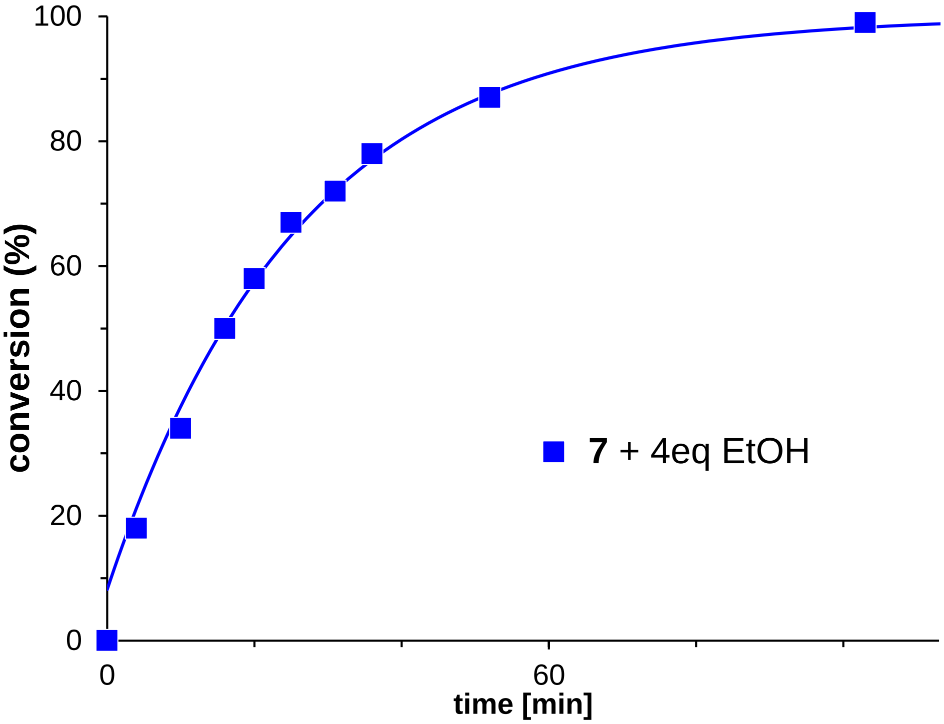

Figure S2. Conversion-time plots for *rac*-lactide polymerizations with **7** + 4eq EtOH.

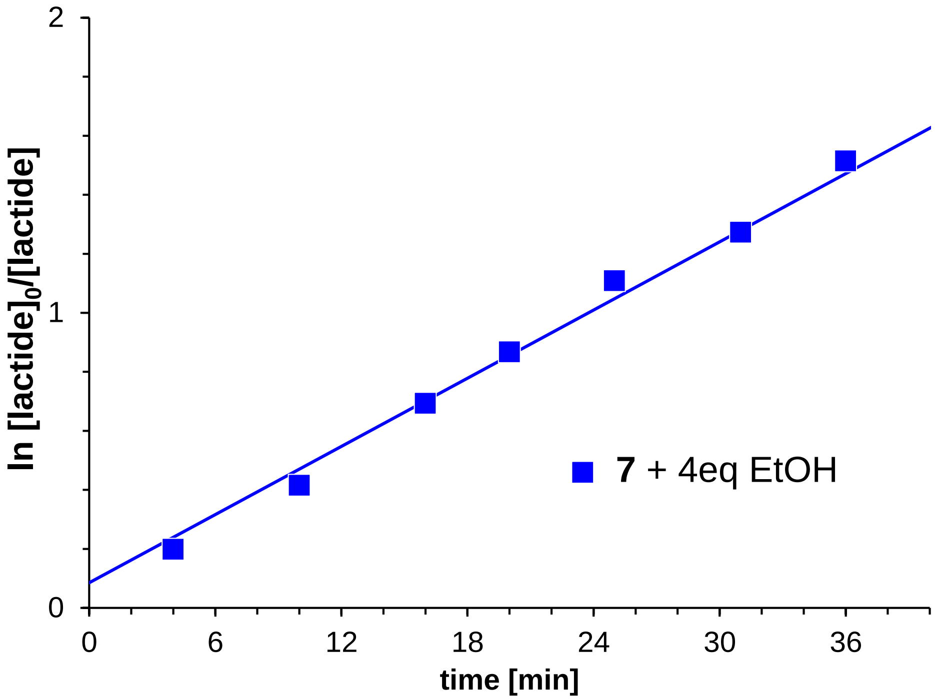

Figure S3. Linearized conversion-time plots for *rac*-lactide polymerizations with **7** + 4eq EtOH.

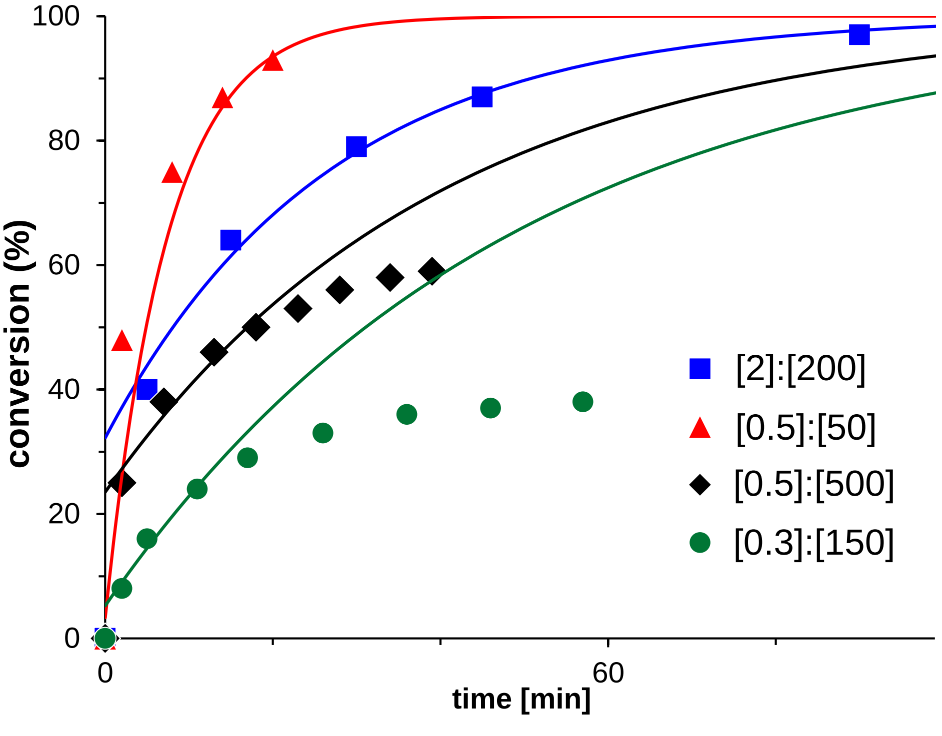

Figure S4. Conversion-time plots for *rac*-lactide polymerizations with **10** at different catalyst and lactide concentrations at RT in C_6D_6 ([**10**] = 2, 0.5, 0.3 mM).

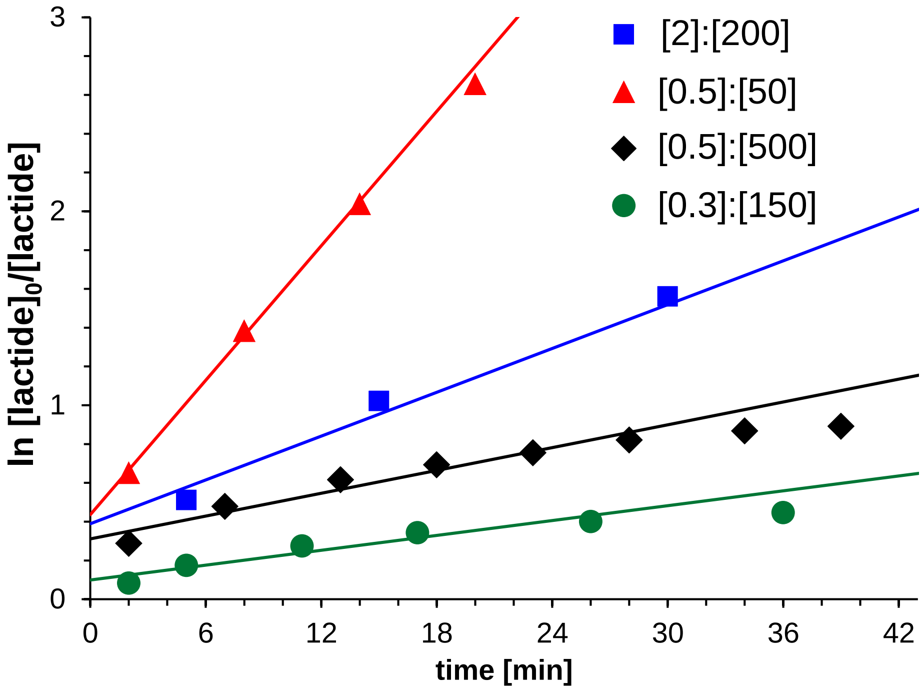

Figure S5. Linearized conversion-time plots for *rac*-lactide polymerizations with **10** at different catalyst or lactide concentrations at RT in C_6D_6 ([**10**] = 2, 0.5, 0.3 mM).

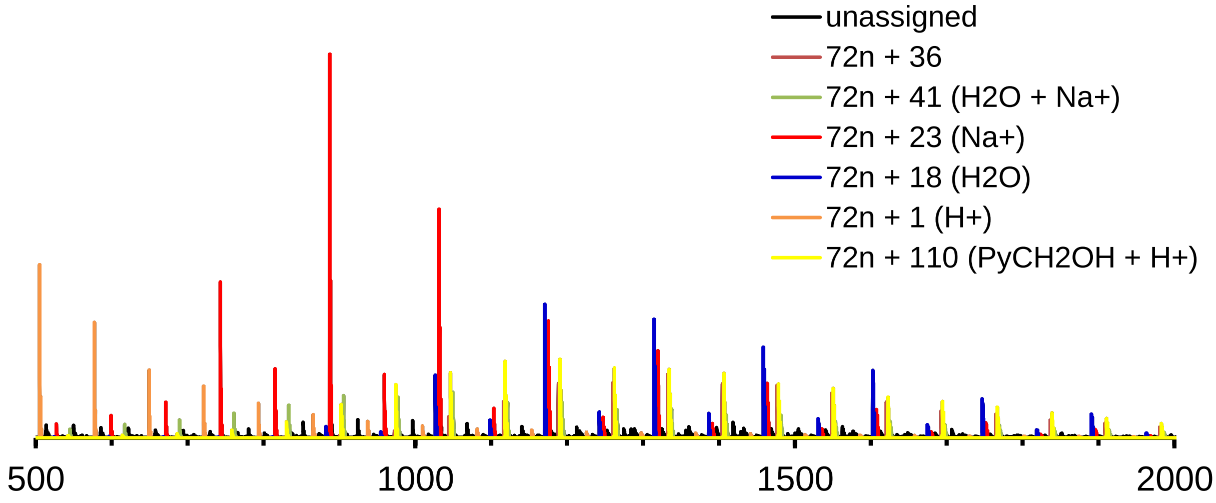

Figure S6. MALDI spectrum of PLA produced with **2** (sodium added to the matrix).

Most series agree with the formation of cyclic oligomers. Hydroxide-terminated chains are most likely obtained by opening of cyclic oligomers with water under MS conditions, since initiation by zinc hydroxide seems unlikely. The main cyclic oligomer series, m/z = $72n+M(\mathrm{Na}^+)$, shows a suppression of peaks with m/z = $72(2n+1)+M(\mathrm{Na}^+)$, which is unexpected in typical transesterifications and reminiscent of ROP with neutral nucleophiles.

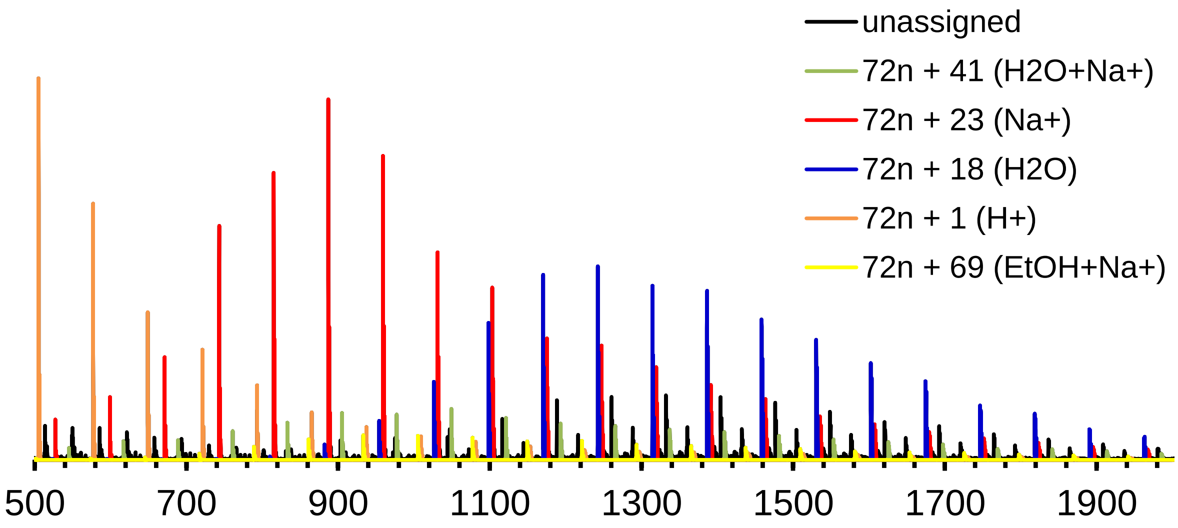

Figure S7. MALDI spectrum of PLA produced with **7** (2 mM, [lactide] = 200 mM).

Sodium salts were added to the matrix. Most series agree with the formation of cyclic oligomers. Hydroxide-terminated chains are most likely obtained by opening of cyclic oligomers with water under MS conditions, since initiation by zinc hydroxide seems unlikely.

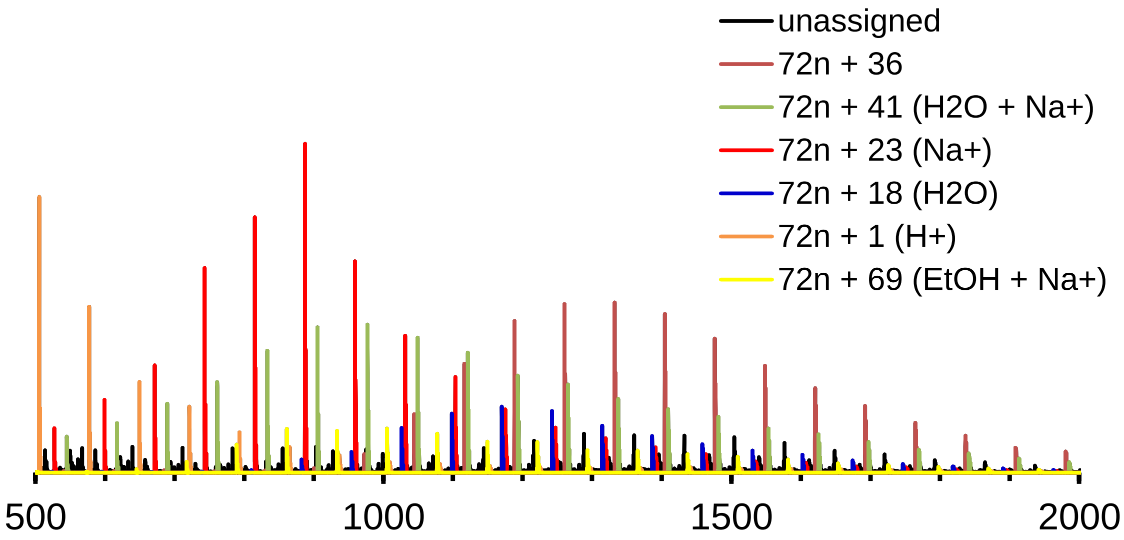

Figure S8. MALDI spectrum of PLA produced with **7** (0.5 mM, [lactide] = 50 mM).

Sodium salts were added to the matrix. Most series agree with the formation of cyclic oligomers. Hydroxide-terminated chains are most likely obtained by opening of cyclic oligomers with water under MS conditions.

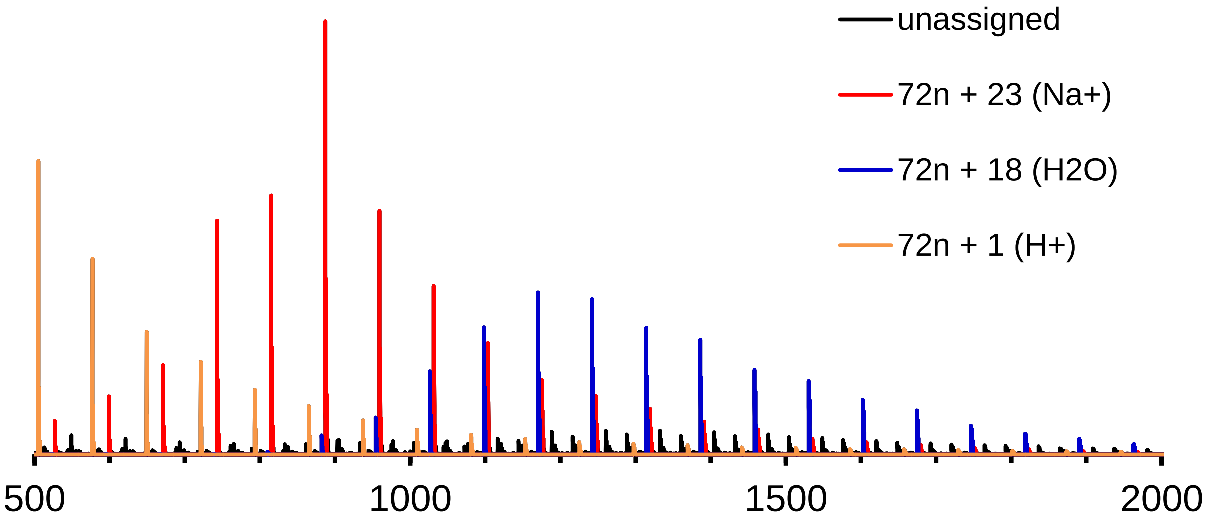

Figure S9. MALDI spectrum of PLA produced with **7** (0.5 mM, [lactide] = 50 mM).

Sodium salts were added to the matrix. Most series agree with the formation of cyclic oligomers. Hydroxide-terminated chains are most likely obtained by opening of cyclic oligomers with water under MS conditions, since initiation by zinc hydroxide seems unlikely.

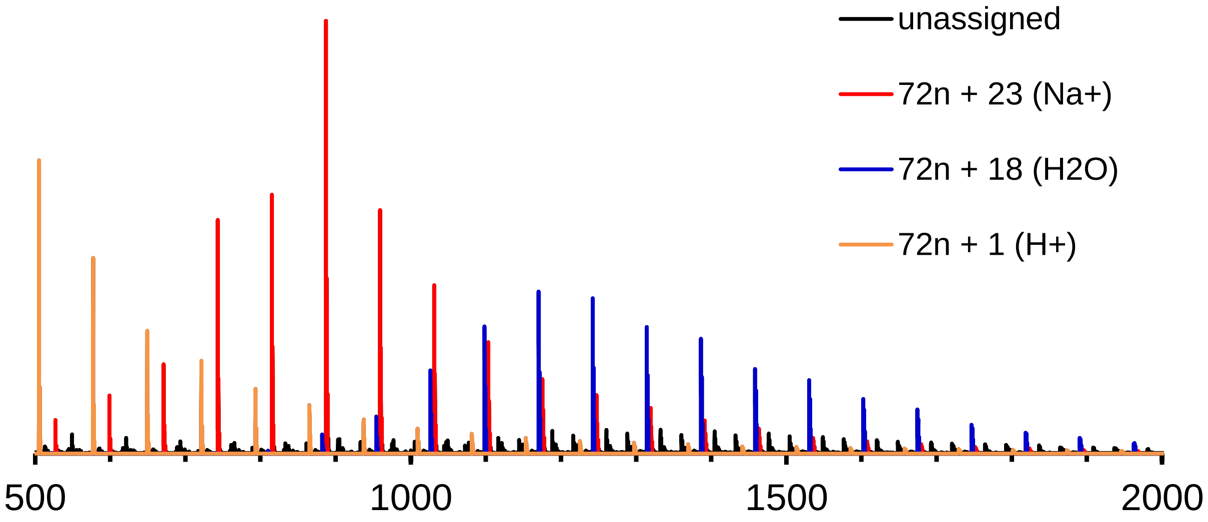

Figure S10. MALDI spectrum of PLA produced with **10** (2 mM, [lactide] = 200 mM, Table 3, entry 4).

Sodium salts were added to the matrix. Most series agree with the formation of cyclic oligomers. Hydroxide-terminated chains are most likely obtained by opening of cyclic oligomers with water under MS conditions, since initiation by zinc hydroxide seems unlikely.

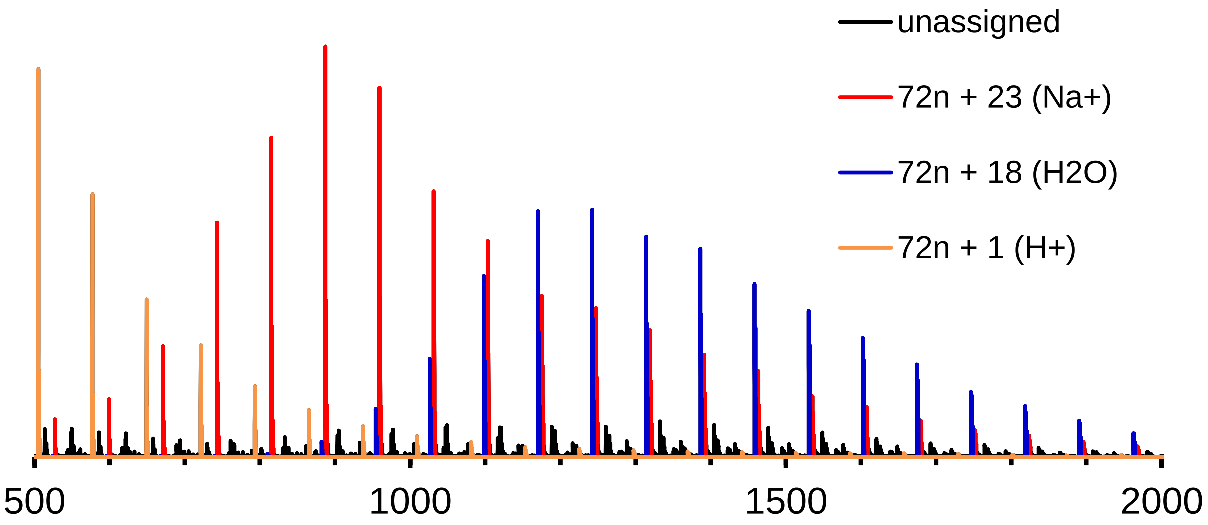

Figure S11. MALDI spectrum of PLA produced with **10** (0.5 mM, [lactide] = 50 mM, Table 3, entry 6).

Sodium salts were added to the matrix. Most series agree with the formation of cyclic oligomers. Hydroxide-terminated chains are most likely obtained by opening of cyclic oligomers with water under MS conditions, since initiation by zinc hydroxide seems unlikely.

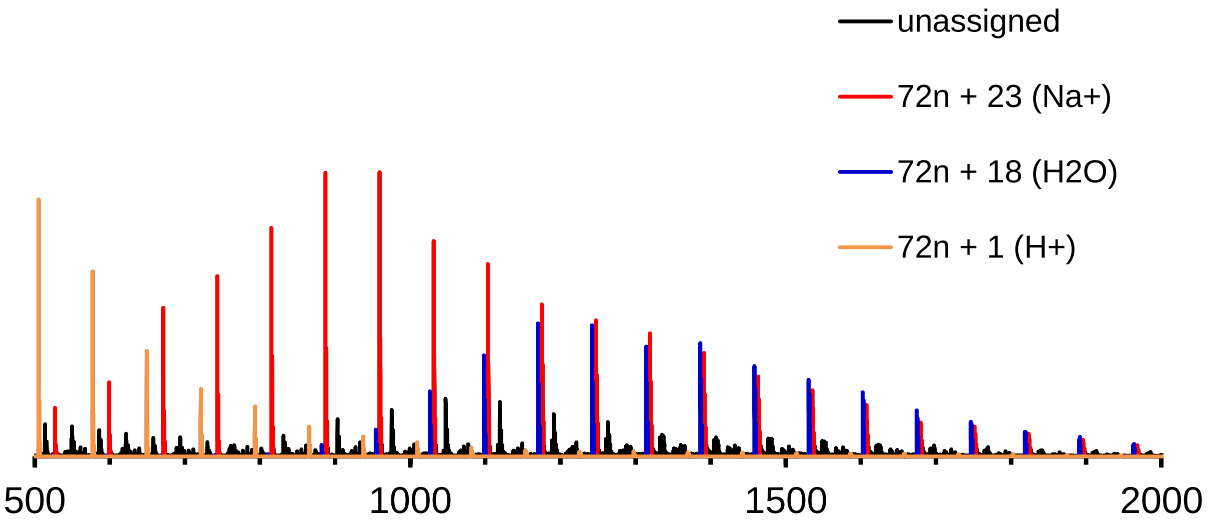

Figure S12. MALDI spectrum of PLA produced with **10** (0.5 mM, [lactide] = 200 mM, Table 3, entry 7).

Sodium salts were added to the matrix. Most series agree with the formation of cyclic oligomers. Hydroxide-terminated chains are most likely obtained by opening of cyclic oligomers with water under MS conditions, since initiation by zinc hydroxide seems unlikely.

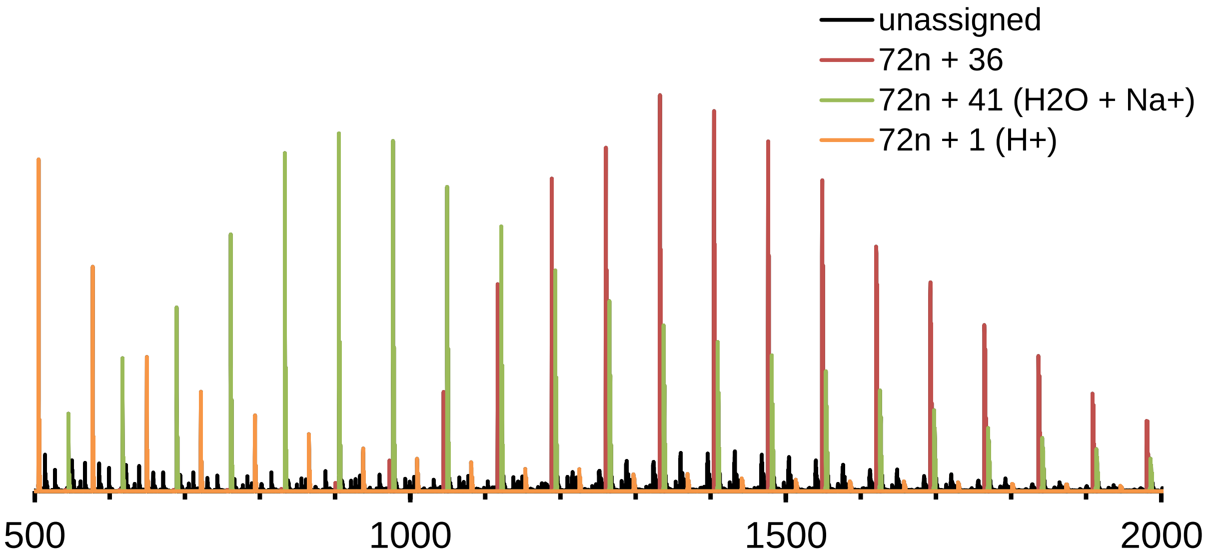

Figure S13. MALDI spectrum of PLA produced with **10** (0.5 mM, [lactide] = 1000 mM, Table 3, entry 8).

Sodium salts were added to the matrix. Most series agree with the formation of cyclic oligomers. Hydroxide-terminated chains are most likely obtained by opening of cyclic oligomers with water under MS conditions, since initiation by zinc hydroxide seems unlikely.

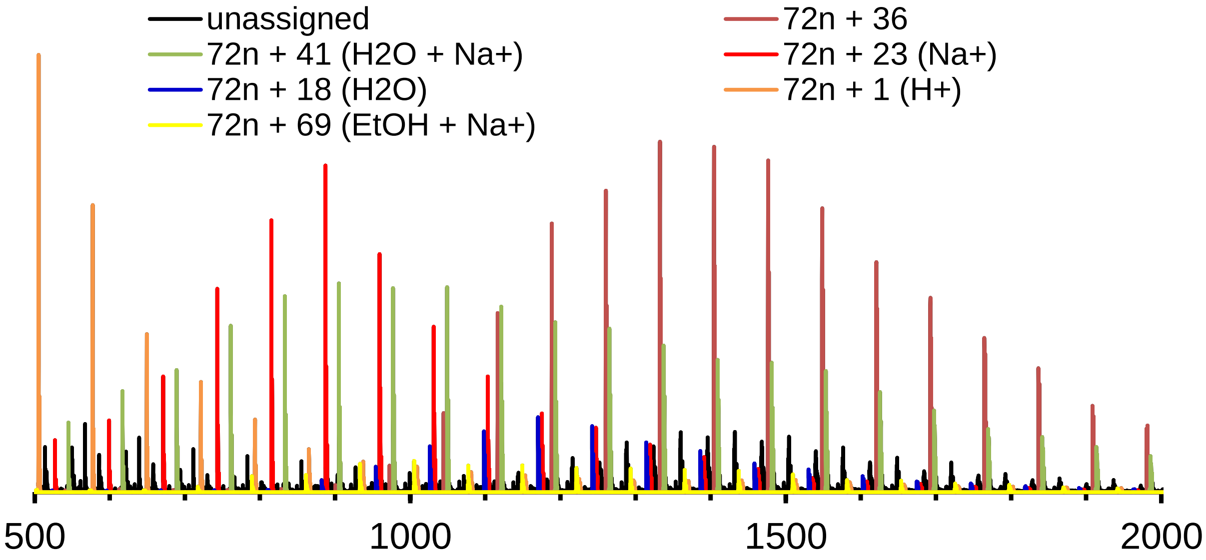

Figure S14. MALDI spectrum of PLA produced with **10** (0.3 mM, [lactide] = 150 mM, Table 3, entry 9).

Sodium salts were added to the matrix. Most series agree with the formation of cyclic oligomers. Hydroxide-terminated chains are most likely obtained by opening of cyclic oligomers with water under MS conditions, since initiation by zinc hydroxide seems unlikely.

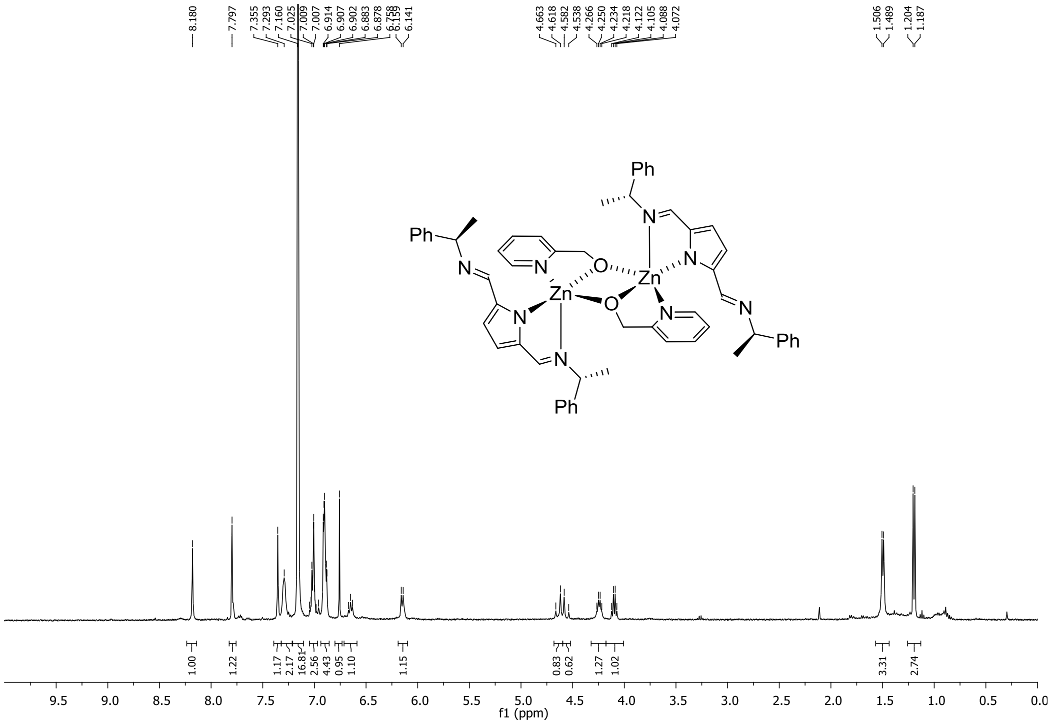

Figure S15. ^{1}H-NMR (400 MHz) spectra of **2** in C_6D_6.

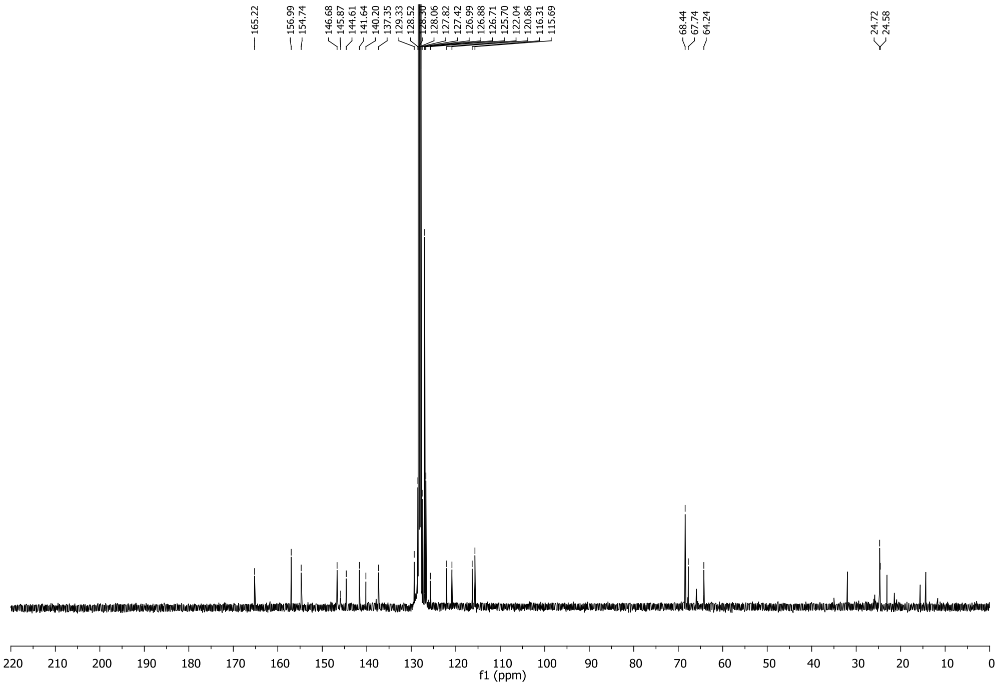

Figure S16. ^{13}C-NMR (101 MHz) spectra of **2** in C_6D_6.

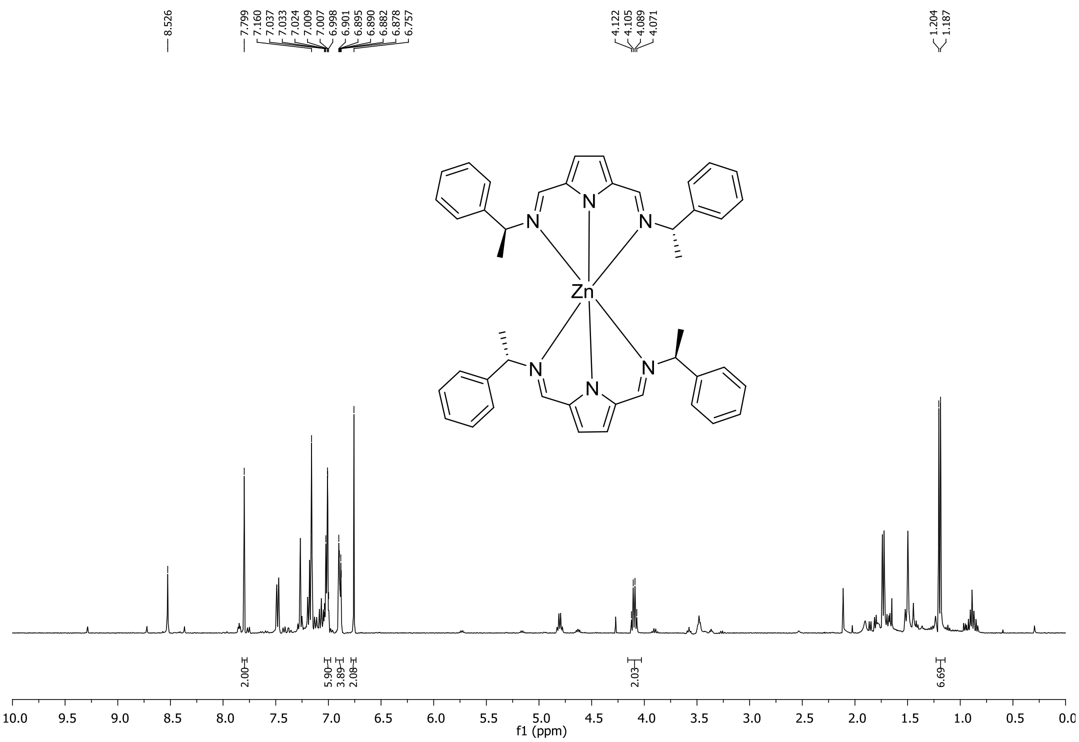

Figure S17. ^{1}H-NMR (400 MHz) spectra of **(L1)$_2$Zn** in C_6D_6.

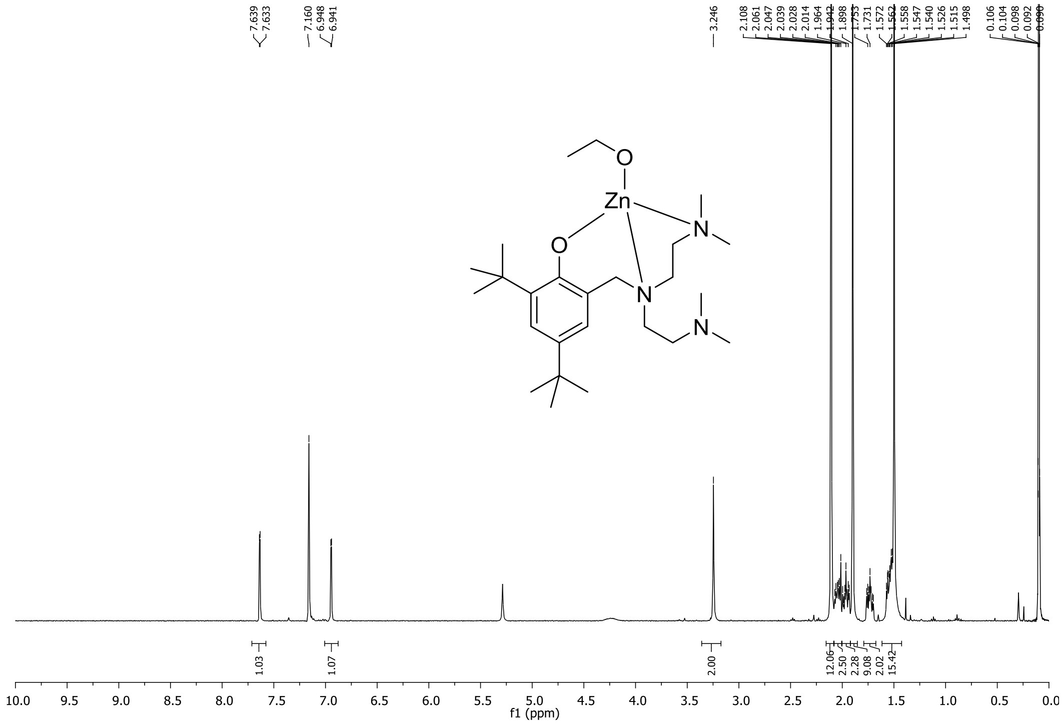

Figure S18. ^{1}H-NMR (400 MHz) spectra of **7** in C_6D_6.

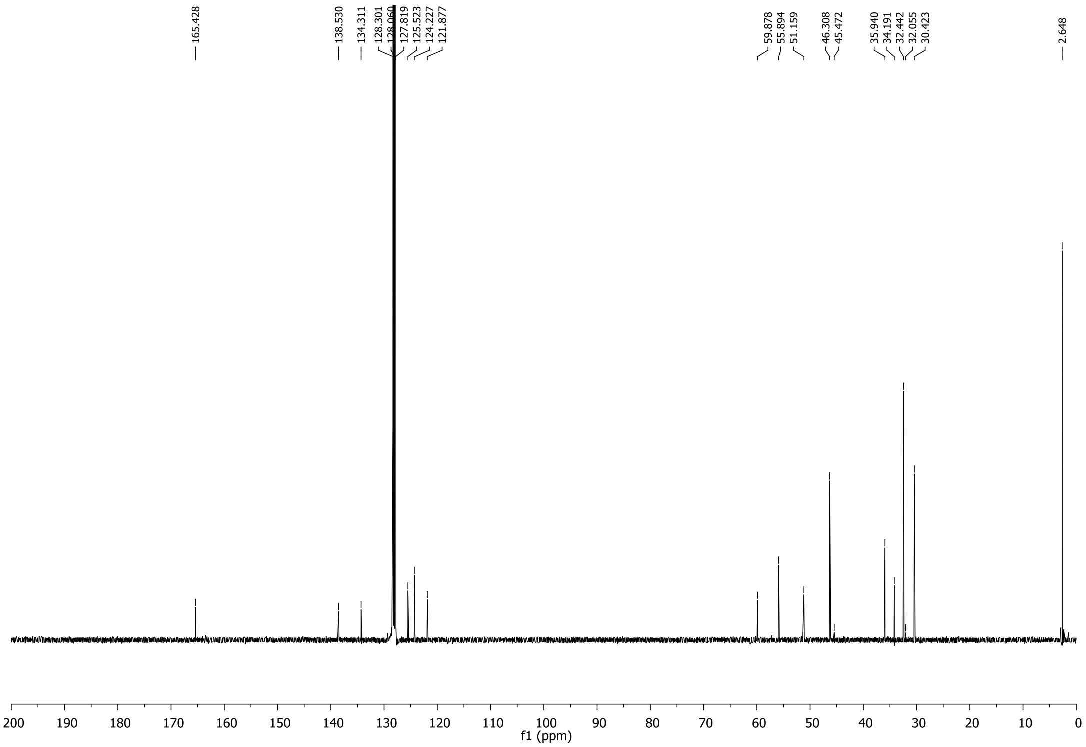

Figure S19. ^{13}C-NMR (101 MHz) spectra of **7** in C_6D_6.

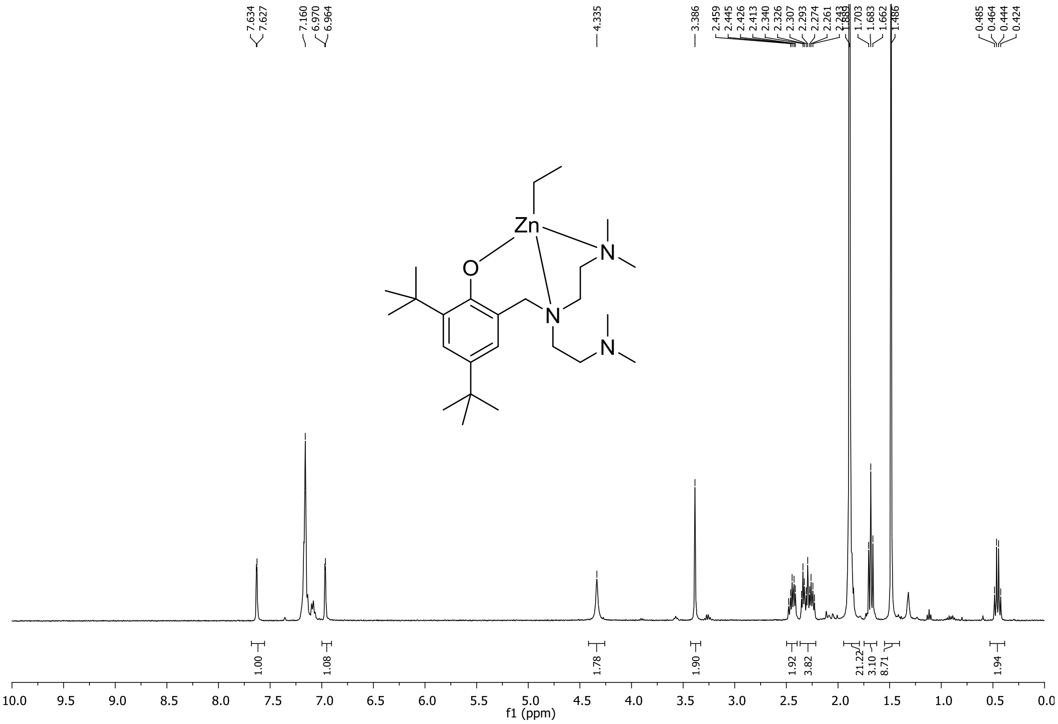

Figure S20. ^{1}H-NMR (400 MHz) spectra of **8** in C_6D_6.

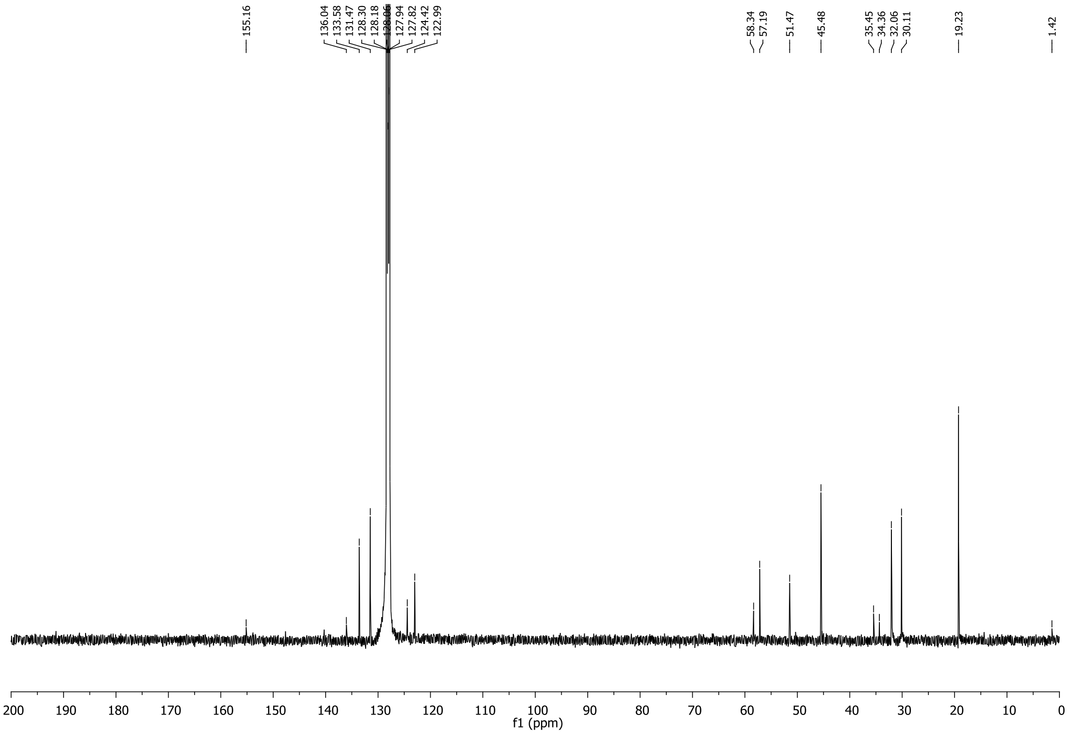

Figure S21. ^{13}C-NMR (101 MHz) spectra of **8** in C_6D_6.

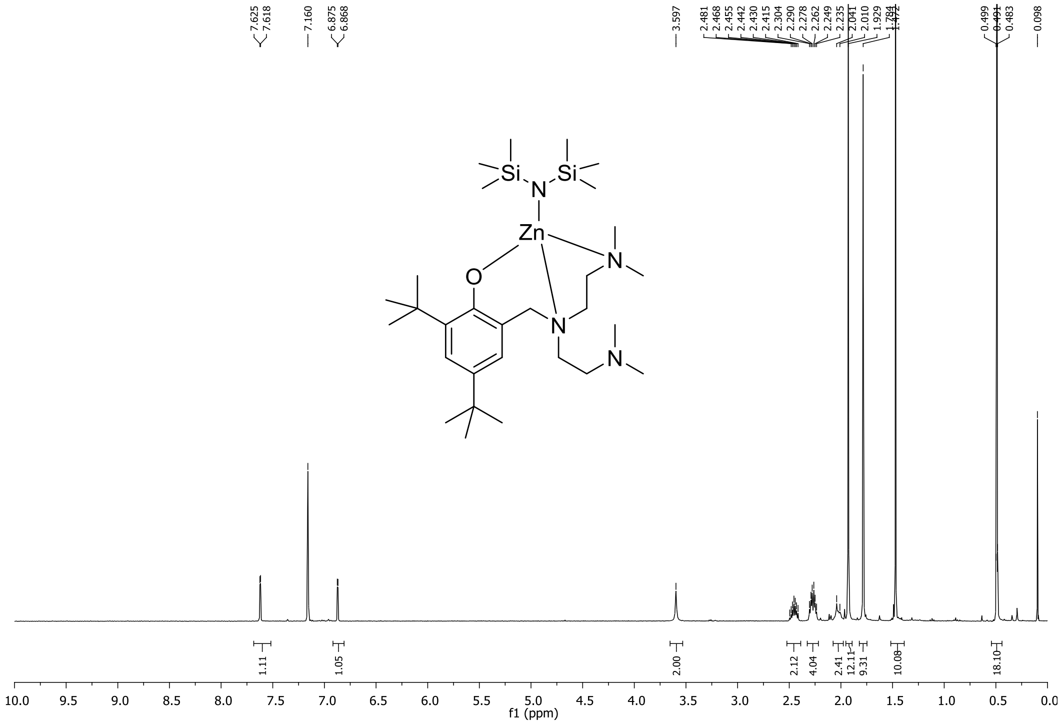

Figure S22. ^{1}H-NMR (400 MHz) spectra of **9** in C_6D_6.

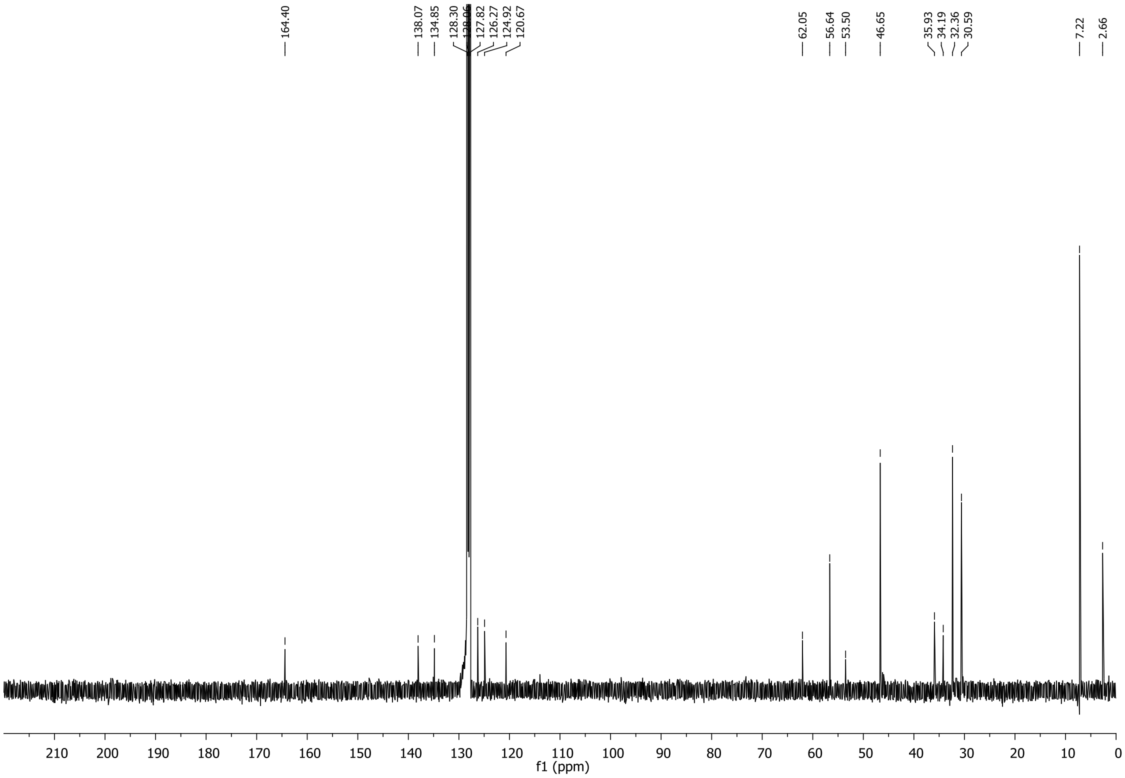

Figure S23. ^{13}C-NMR (101 MHz) spectra of **9** in C_6D_6.

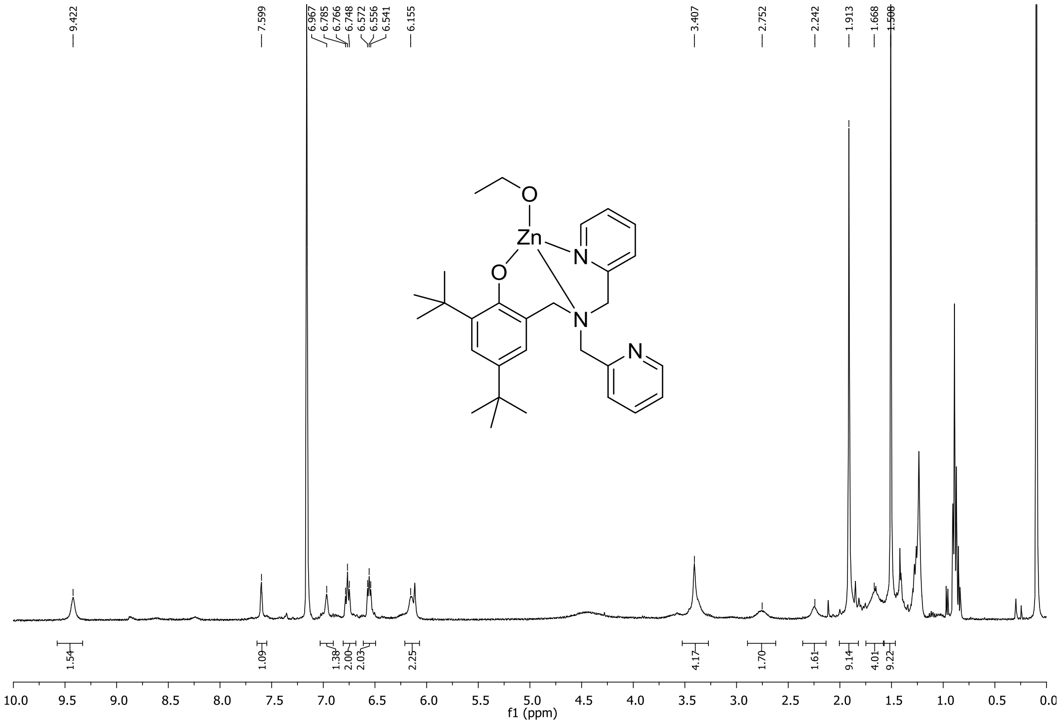

Figure S24. ^{1}H-NMR (400 MHz) spectra of **10** in C_6D_6.

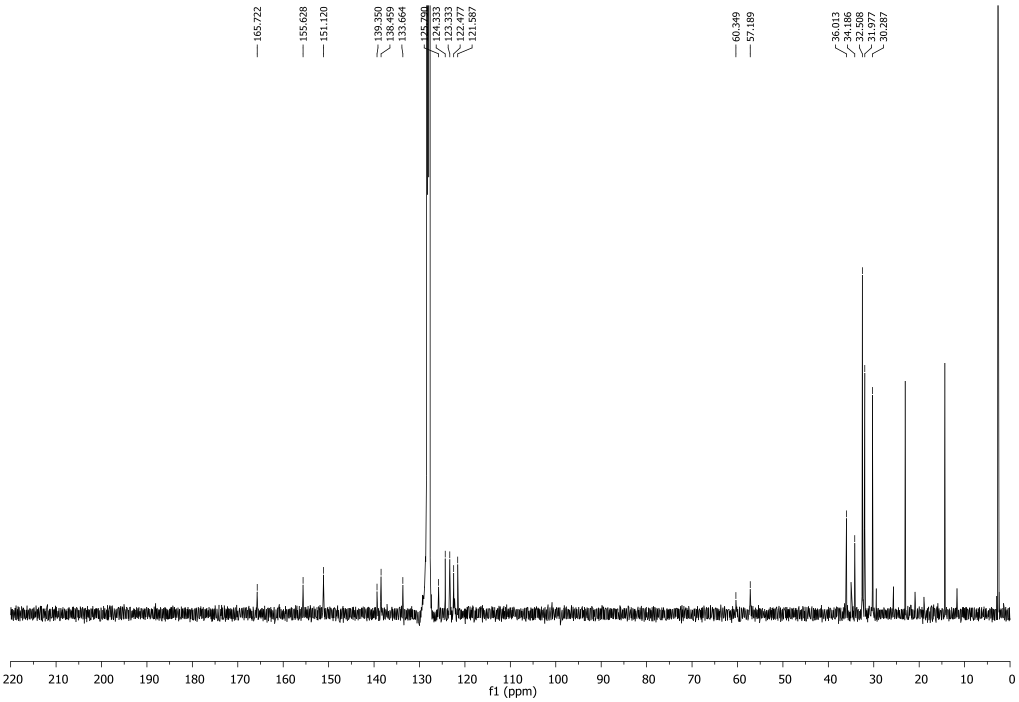

Figure S25. ^{13}C-NMR (101 MHz) spectra of **10** in C_6D_6.

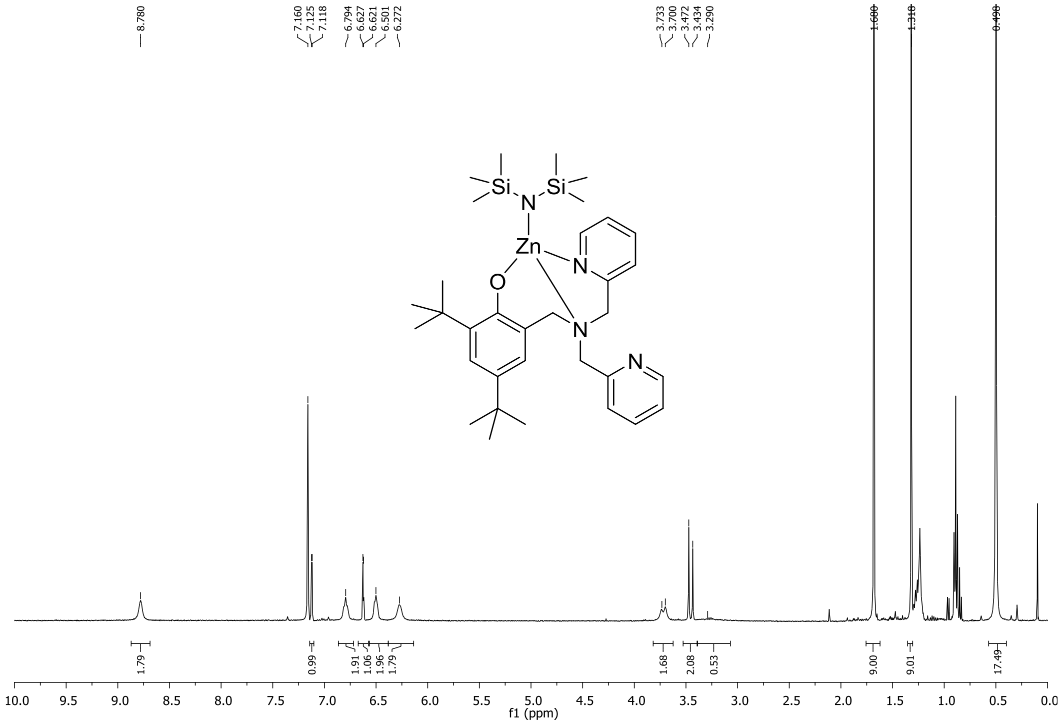

Figure S26. ^{1}H-NMR (400 MHz) spectra of **11** in C_6D_6.

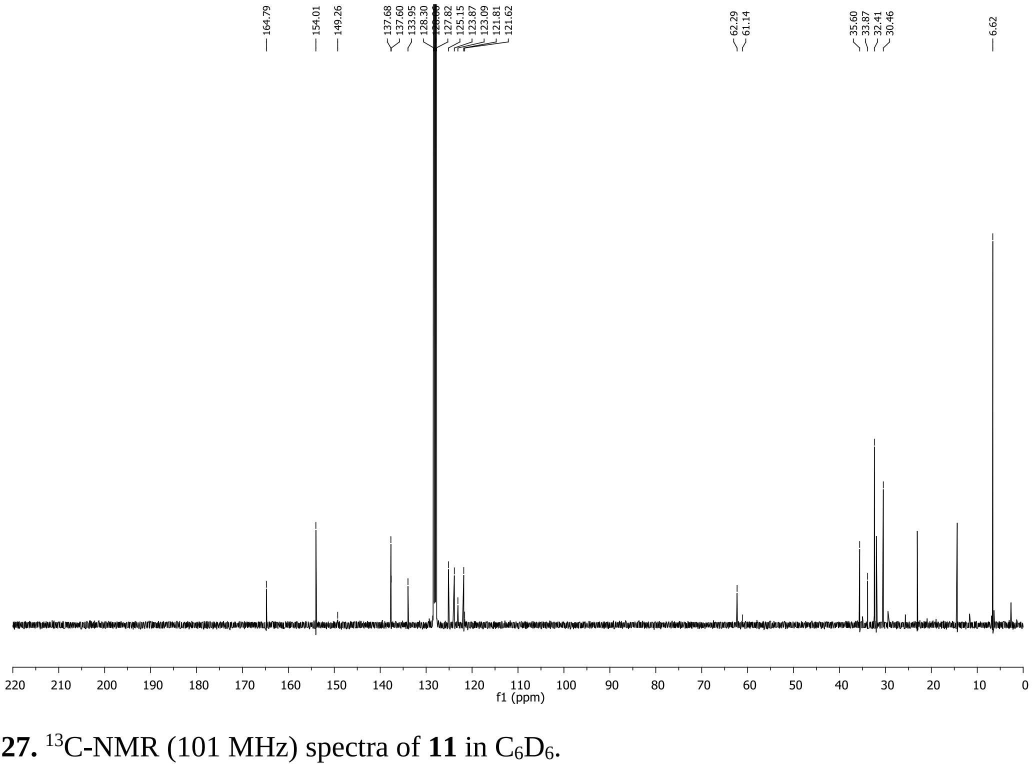

Figure S27. ^{13}C-NMR (101 MHz) spectra of **11** in C_6D_6.

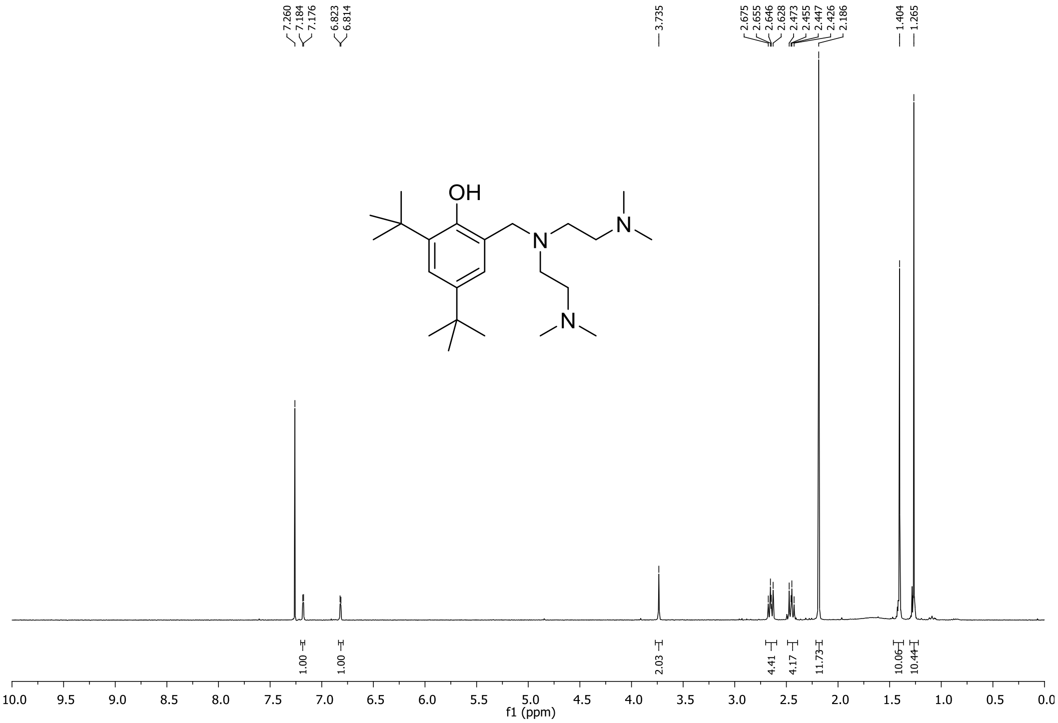

Figure S28. ^{1}H-NMR (300 MHz) spectra of **L2** in CDCl$_3$.

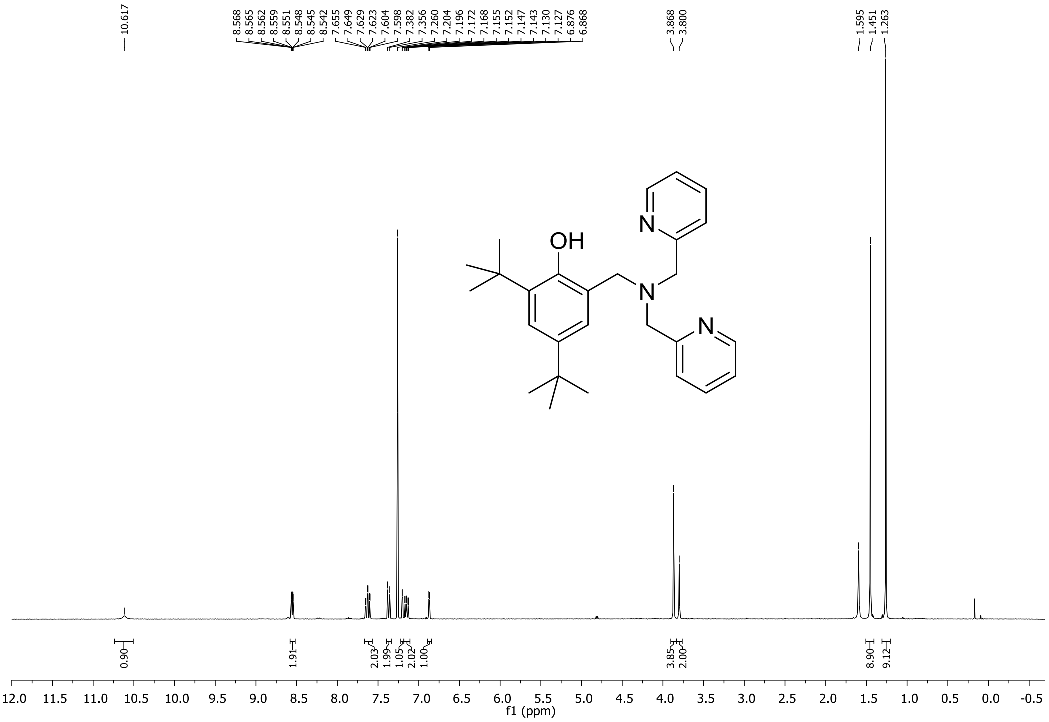

Figure S29. ^{1}H-NMR (300 MHz) spectra of **L3** in CDCl$_3$.

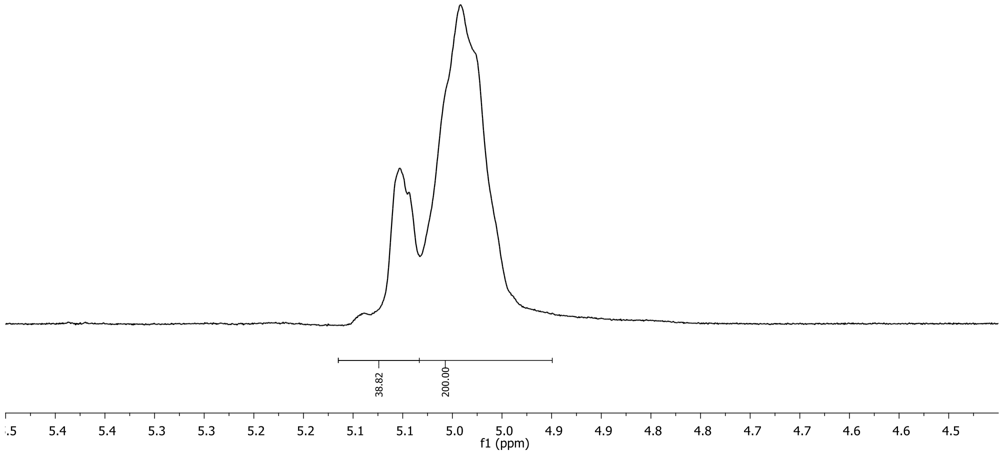

Figure S30. Selectively decoupled ^{1}H-NMR (40 MHz) spectrum of the methine region for PLA produced with **10** at 0.3 mM concentration.

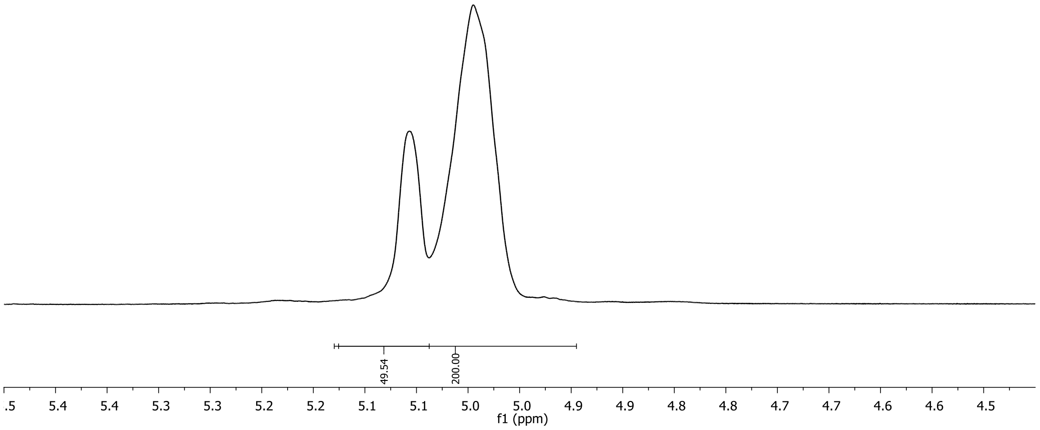

Figure S31. Selectively decoupled ^{1}H-NMR (40 MHz) spectrum of the methine region for PLA produced with **10** at 2 mM concentration.

Variable-temperature NMR studies on compound 11

^{1}H NMR studies were conducted on d_8-toluene solutions of **11** in a temperature range of 188 – 343 K on a Bruker AV500 instrument. Peak assignment are based on COSY and selected 1D-NOESY spectra. Activation barriers have been estimated from the temperature closest to the coalescence temperature according to $\Delta G^{\ddagger} = RT_C ln\frac{\pi(\nu_A-\nu_B)h}{\sqrt{2}k_BT_C}$.

Signals	**estimated T_C**	**estimated $\Delta G^{\ddagger}$**
ortho pyridine (9.1/8.8 ppm)	278 K	54 kJ/mol
meta pyridine (6.3/6.0 ppm)	278 K	54 kJ/mol
meta pyridine (6.5/6.3 ppm)	268 K	54 kJ/mol
para pyridine (6.8/6.6 ppm)	268 K	53 kJ/mol
ArCH$_2$ (3.7/2.2 ppm)	313 K	57 kJ/mol
PyCH$_2$ (3.3/3.0 ppm)	278 K	53 kJ/mol
N(SiMe$_3$)$_2$ (1.1/0.1 ppm)	248 K	46 kJ/mol

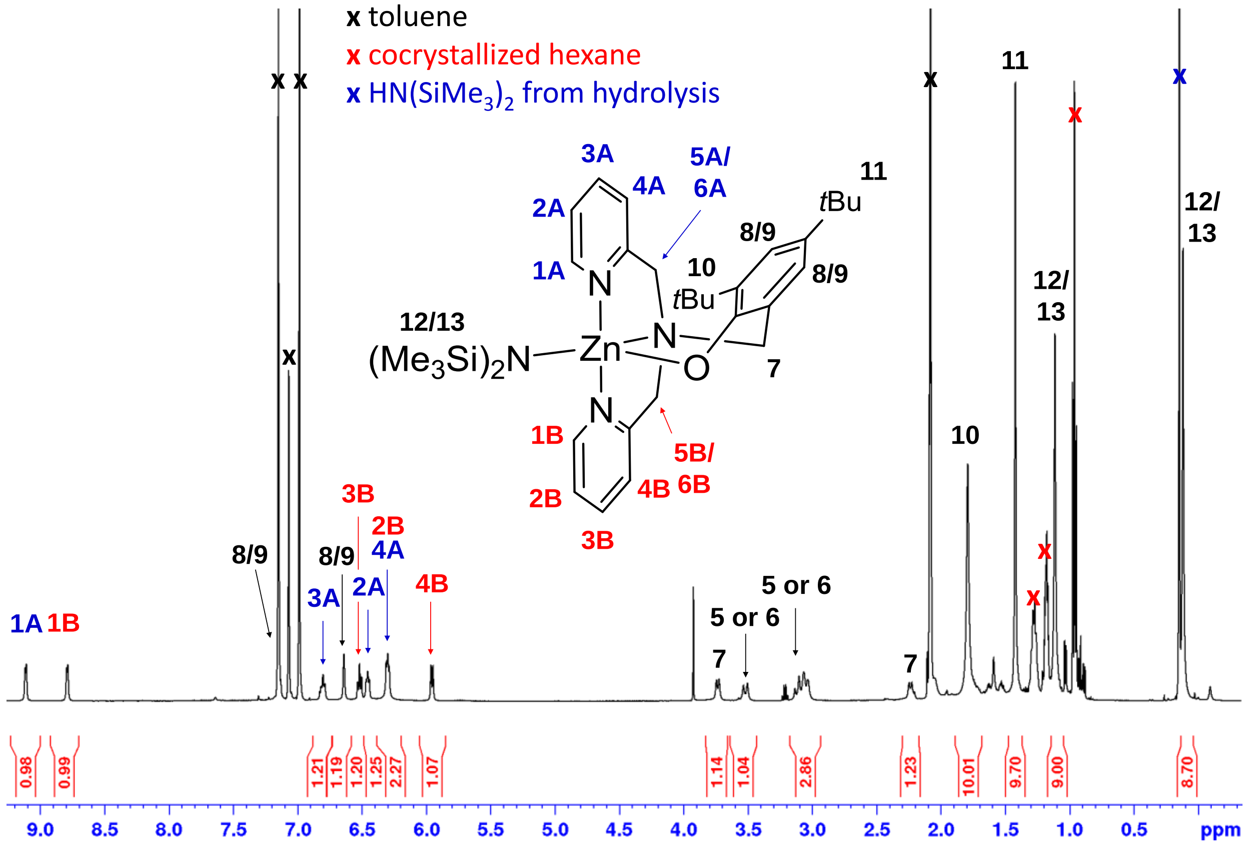

Figure S32. ^{1}H-NMR (500 MHz) spectrum of **11** in d_8-toluene at 188 K.

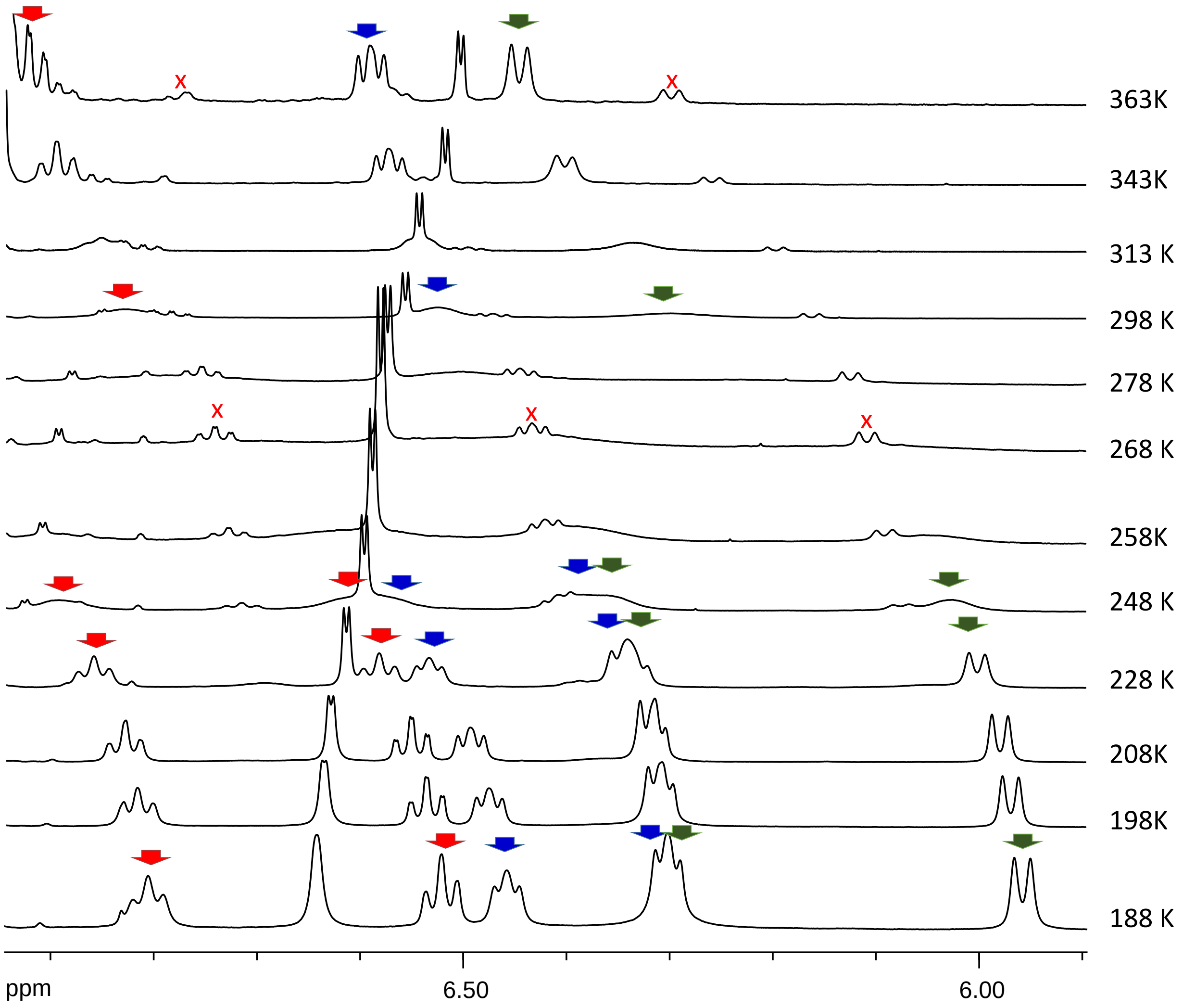

Figure S33. VT-^{1}H-NMR (500 MHz) spectra of the aromatic region of **11** in d_8-toluene at 188-363 K.

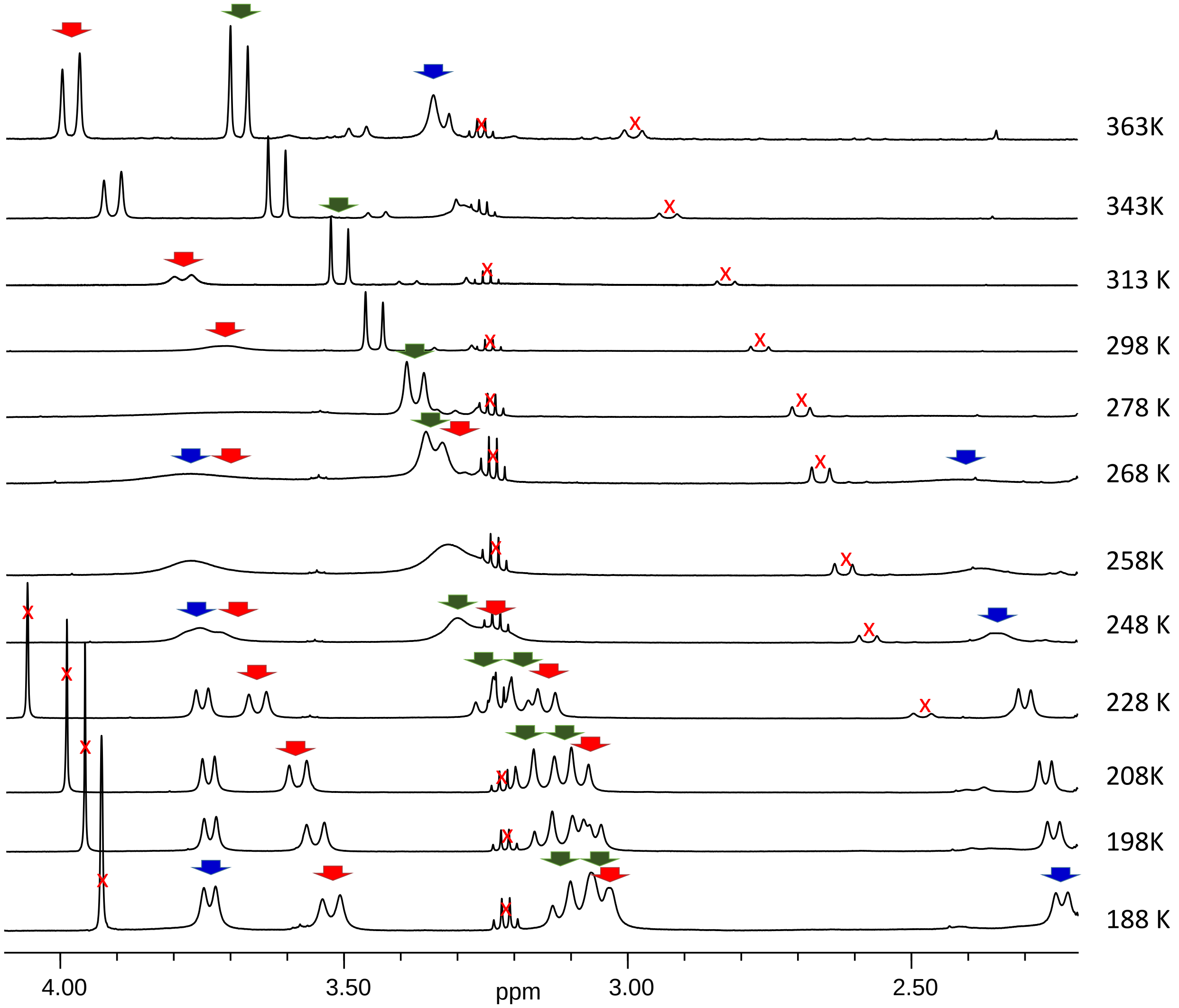

Figure S34. VT-^{1}H-NMR (500 MHz) spectra of the methylene region of **11** in d_8-toluene at 188-363 K.

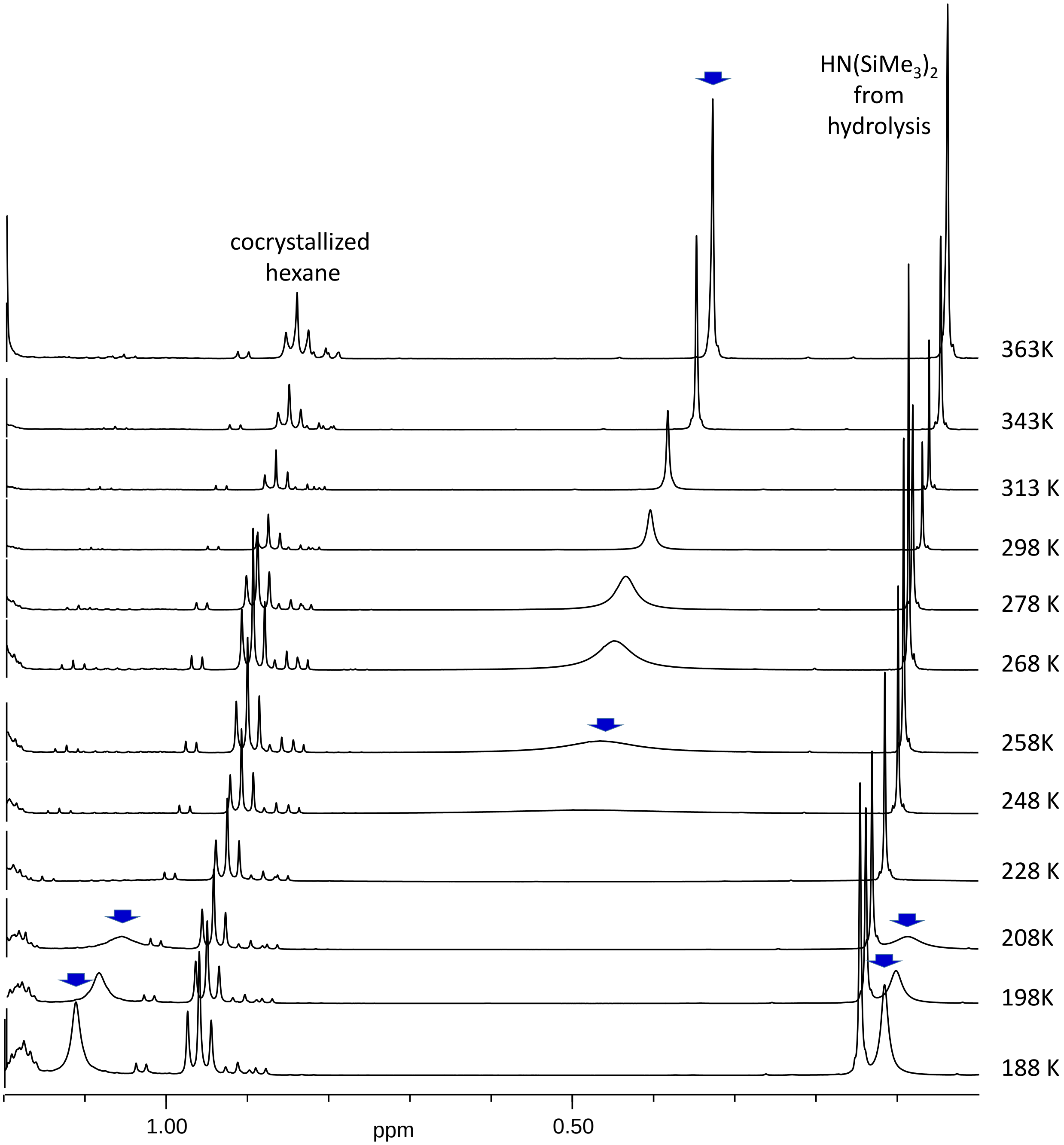

Figure S35. VT-^{1}H-NMR (500 MHz) spectra of the aliphatic region of **11** in d_8-toluene at 188-363 K.