

Supplementary data

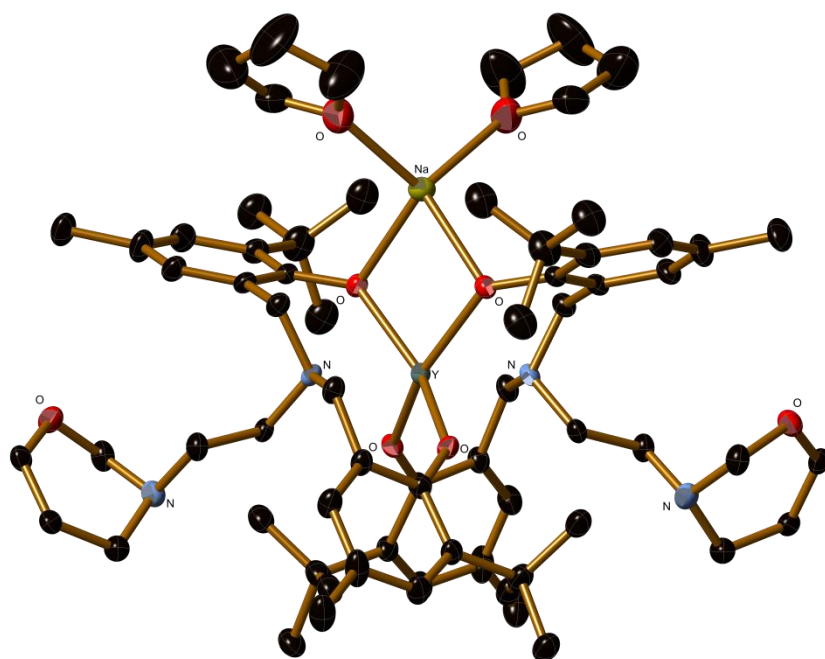


Fig. 1 X-ray structure of **1** with thermal ellipsoids at the 30% probability level.
Hydrogen atoms are omitted for clarity.

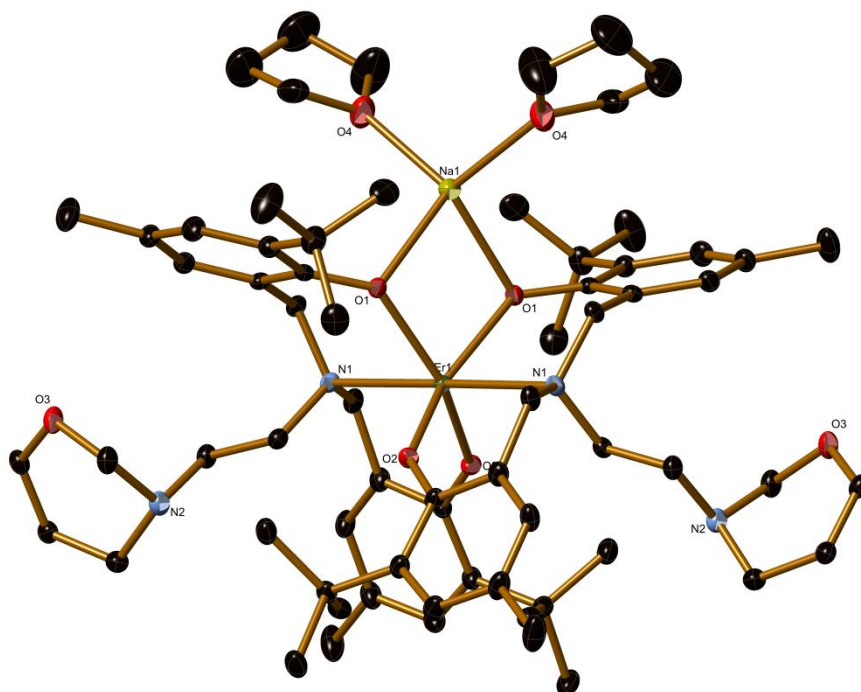


Fig. 2 X-ray structure of **3** with thermal ellipsoids at the 50% probability level.
Hydrogen atoms are omitted for clarity.

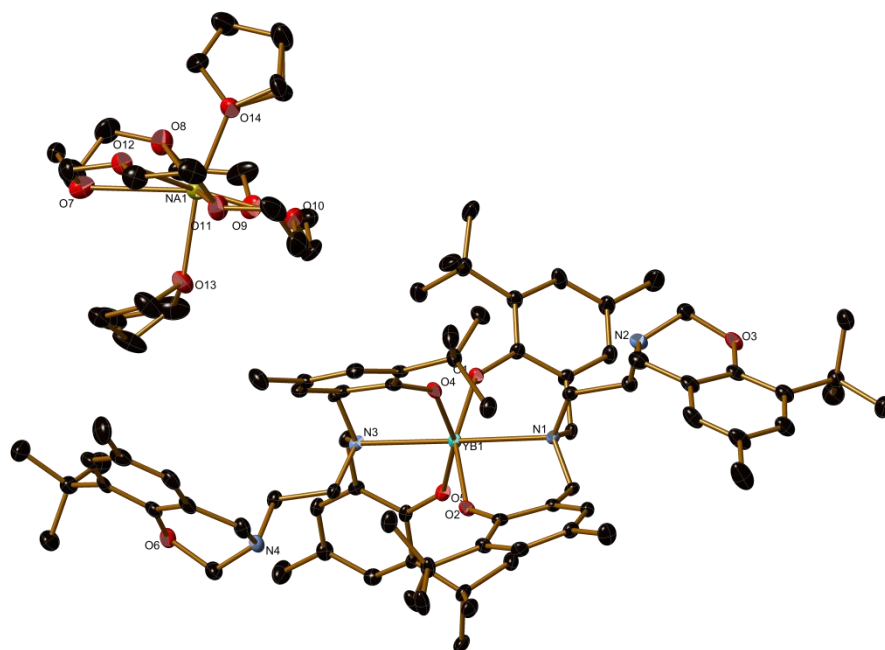


Table 1 Polymerization of CL initiated by complexes **1** and **2**^a

entry	initiator	Temp. (°C)	solvent	[CL]/[I] ^b	Conversion (%)
1	1	25	toluene	100	0
2	1	25	THF	100	0
3	2	25	toluene	100	45
4	2	25	toluene	200	33
5	2	25	THF	100	0
6	2	25	THF	200	0

^a Conditions: [CL]₀=1 mol/L, reaction for 24 h.

^b CL/initiator molar ratio

¹H-NMR study of obtained PCLs and PLAs

PCL and PLLA obtained by these complexes were studied by ¹H-NMR analysis to find the end group of the polymers. As shown in Figure 4, the PCL contains a methoxy end group which appeared as a singlet at δ3.67 and hydroxy group appeared as a triplet at δ3.65 in the ¹H-NMR spectrum.

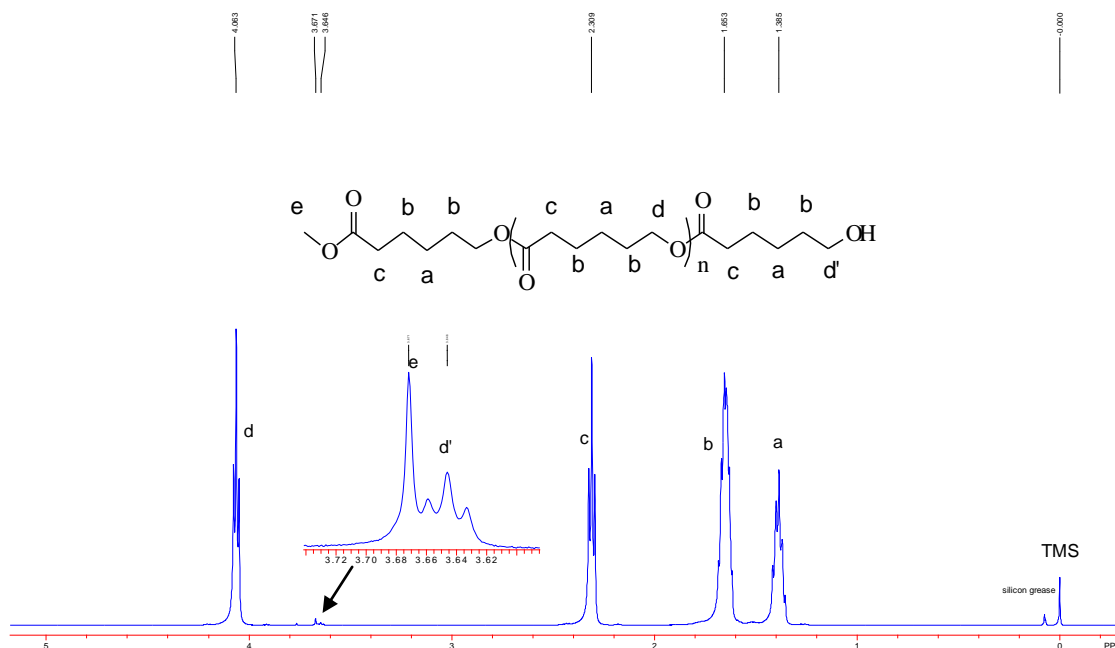


Figure 4 Full assignment of ¹H-NMR spectrum of PCL initiated by complex **1** from entry 1 of **Table 3** in the main text

As shown in figure 5, the PLLA contains a methoxy end group which appeared as a singlet at $\delta 3.76$ and hydroxy group appeared as a quartet at $\delta 4.36$ in the ^1H -NMR spectrum.

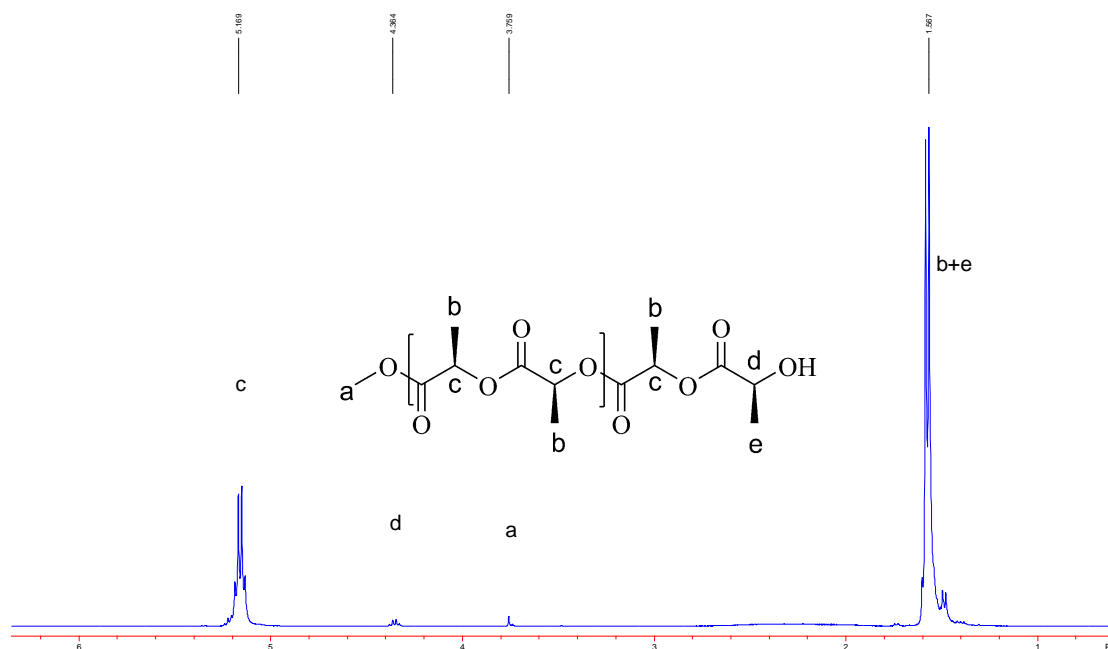


Figure 5 Full assignment of ^1H -NMR spectrum of PLA initiated by complex **1** from entry 2 of **Table 4** in the main text

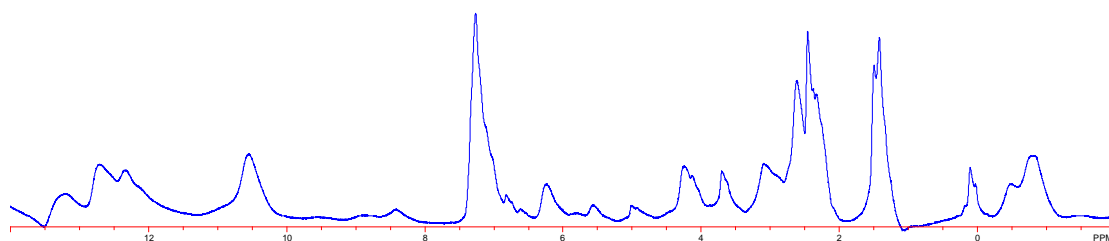


Figure 6 ^1H -NMR spectrum of $[\text{Nd}(\text{L})_2\text{Na}(\text{THF})_2]$ (**2**)

The spectrum is unresolvable due to the strong paramagnetism of the neodymium ion.