

Supplementary data

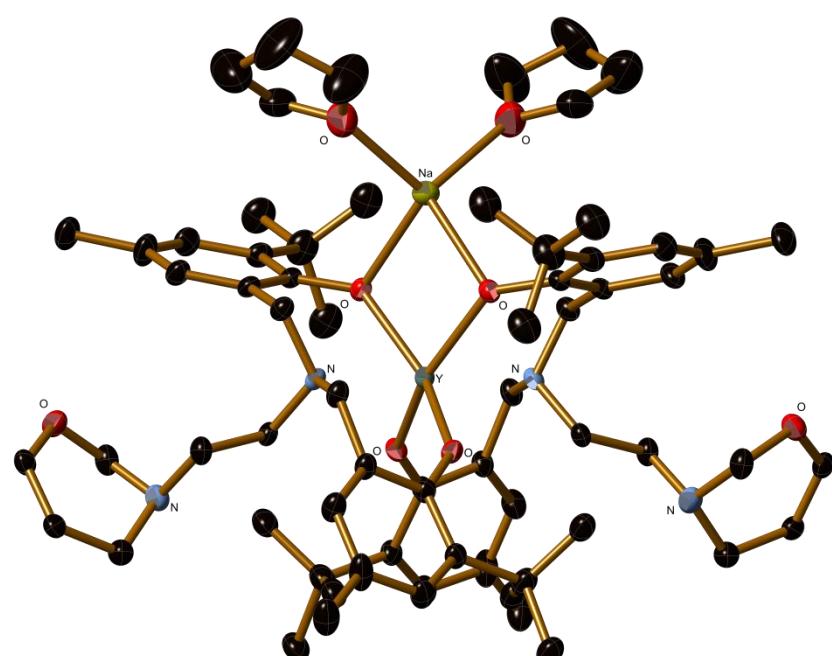


Fig. 1 X-ray structure of **1** with thermal ellipsoids at the 30% probability level.
Hydrogen atoms are omitted for clarity.

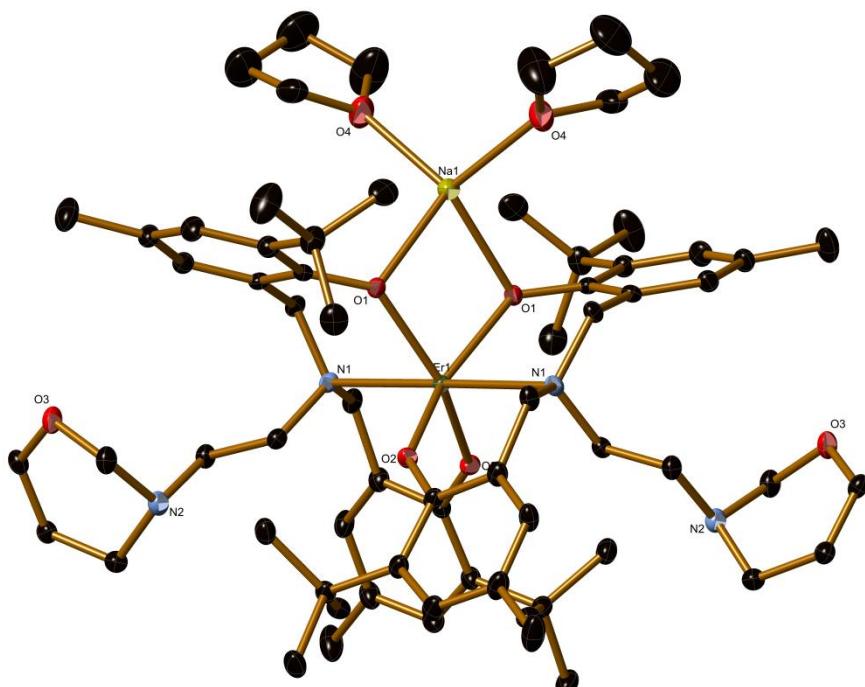


Fig. 2 X-ray structure of **3** with thermal ellipsoids at the 50% probability level.
Hydrogen atoms are omitted for clarity.

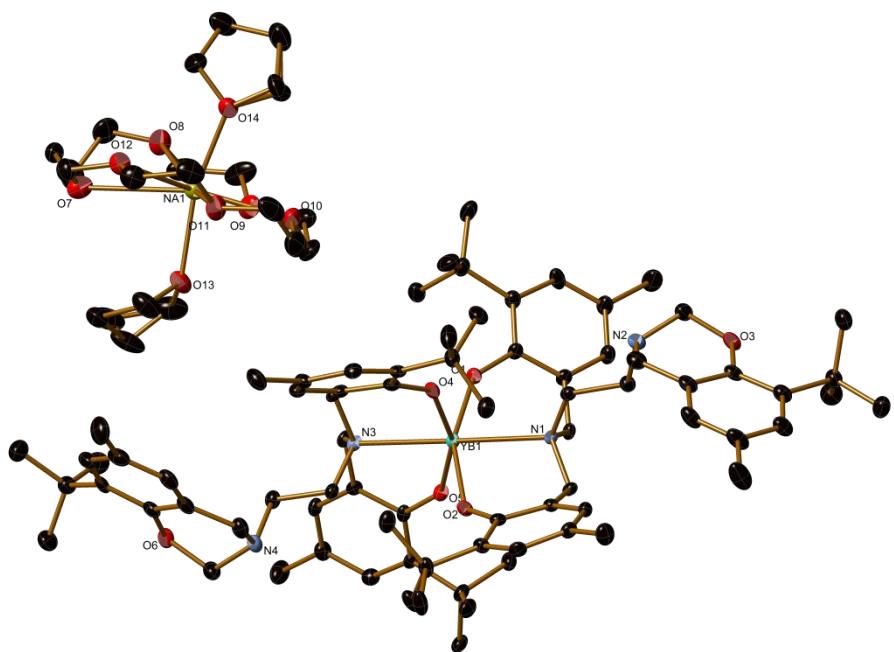


Fig.3 X-ray structure of **6** with thermal ellipsoids at the 50% probability level.
Hydrogen atoms are omitted for clarity.

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 $^1\text{H-NMR}$ 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 δ 3.67 and hydroxy group appeared as a triplet at δ 3.65 in the $^1\text{H-NMR}$ spectrum.

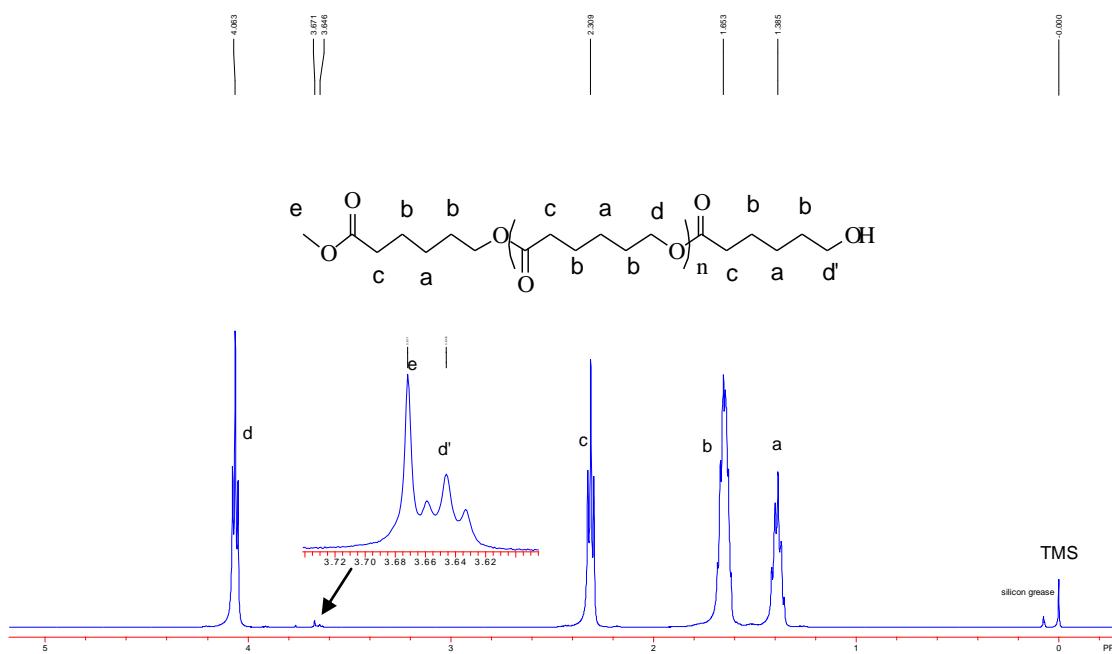


Figure 4 Full assignment of ^1H -NMR spectrum of PCL initiated by complex **1** from entry 1 of **Table 3** in the main text

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

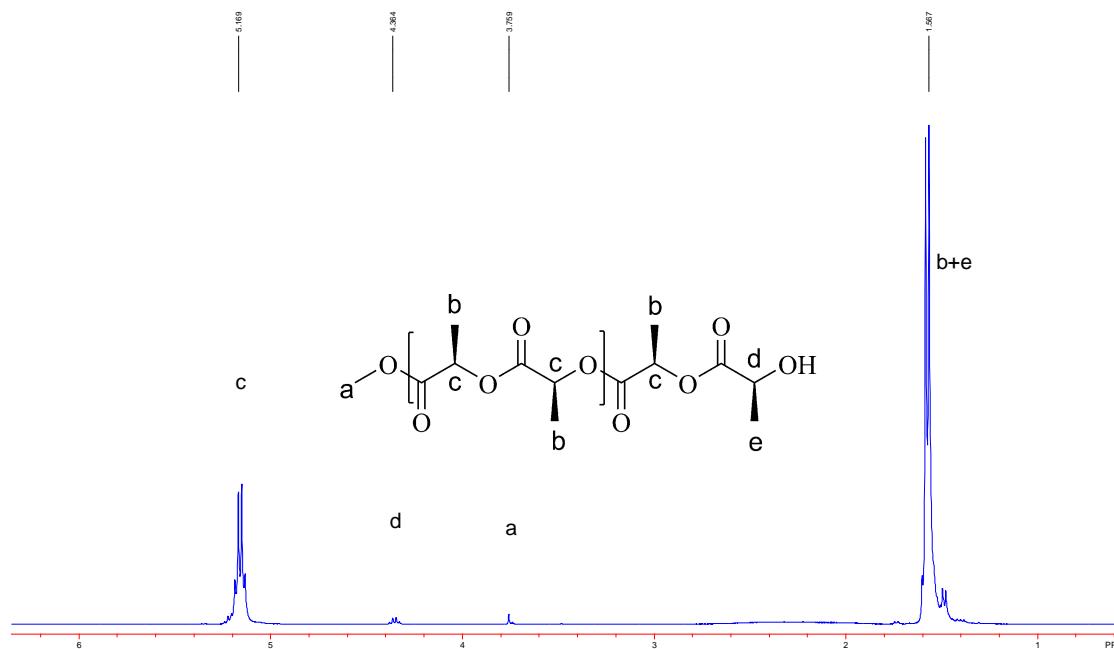


Figure 5 Full assignment of ^1H -NMR spectrum of PLA initiated by complex **1** from entry 2 of **Table 4** in the main text

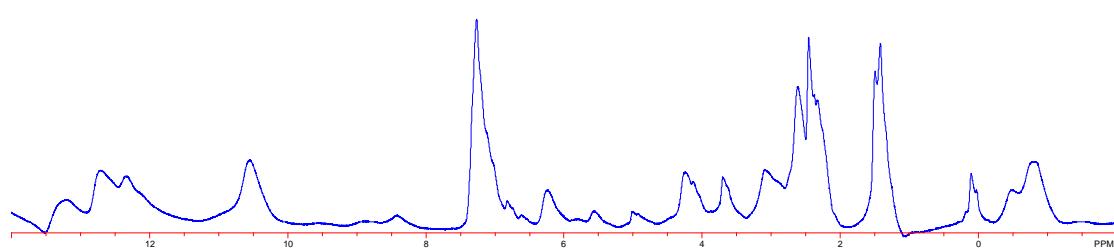


Figure 6 ^1H -NMR spectrum of $[\text{Nd}(\text{L})_2\text{Na}(\text{THF})_2]$ (2)

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