Supporting Information

β-Pyridylenolate Zinc Catalysts for the Ring-Opening Homo- and Copolymerization of ε-Caprolactone and Lactides

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Table S2. Crystallographic Data for Complexes 1-4, 6

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Table S3. Crystallographic Data for Complexes 7-11

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<td>C₃₂H₳₄N₂O₂Zn₂</td>
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**Figure S1.** X-ray structure of complex 3 with thermal ellipsoids represented at the 20% probability level. Hydrogen atoms are omitted for clarity.

**Figure S2.** X-ray structure of complex 4 with thermal ellipsoids represented at the 20% probability level. Hydrogen atoms are omitted for clarity.
Figure S3. X-ray structure of complex 7 with thermal ellipsoids represented at the 20% probability level. Hydrogen atoms are omitted for clarity.

Figure S4. X-ray structure of complex 9 with thermal ellipsoids represented at the 20% probability level. Hydrogen atoms are omitted for clarity.
Figure S5. X-ray structure of complex 11 with thermal ellipsoids represented at the 20% probability level. Hydrogen atoms as well as solvent molecules omitted are omitted for clarity.

Figure S6. $^1$H NMR spectrum of PCL-40 initiated by 10/BnOH in the ratio of $[^\varepsilon-\text{CL}]_0 : [\text{Zn}]_0 : [\text{BnOH}]_0 = 40 : 1 : 1$ in toluene at 35 °C for 20 min (CDCl$_3$, 25 °C, 600 MHz).
**Figure S7.** Methine region spectrum of homonuclear decoupled $^1$H NMR spectrum (CDCl$_3$, 25 ºC, 600 MHz, $P_r=0.54$, Table 2, entry 1)

**Figure S8.** Methine region spectrum of homonuclear decoupled $^1$H NMR spectrum (CDCl$_3$, 25 ºC, 600 MHz, $P_r=0.51$, Table 2, entry 2)
Figure S9. Methine region spectrum of homonuclear decoupled $^1$H NMR spectrum (CDCl$_3$, 25 °C, 600 MHz, $P_r=0.52$, Table 2, entry 6)

Figure S10. Methine region spectrum of homonuclear decoupled $^1$H NMR spectrum (CDCl$_3$, 25 °C, 600 MHz, $P_r=0.51$, Table 2, entry 10)
Figure S11. $^1$H NMR spectrum of PLLA-$b$-PCL copolymer by complex 10 (CDCl$_3$, 25 °C, 600 MHz)

Figure S12. $^{13}$C HNR spectrum of PCL-$b$-PLLA copolymer by complex 10 (CDCl$_3$, 25 °C, 150 MHz)
Figure S13. DSC analysis of PLLA-b-PCL copolymer prepared by complex 10.

Figure S14. $^1$H NMR spectrum of PCL-ran-PLLA prepared by complex 10 (CDCl$_3$, 25 °C, 600MHz).
Figure S15. Spectra composition at different molar ratios in the initial feed (Table 5, CDCl₃, 25 ºC, 600 MHz).

Figure S16. ¹H NMR spectrum of PCL-ran-PDLLA by complex 10 (CDCl₃, 25 ºC, 600 MHz).
Figure S17. $^{13}$C NMR spectrum of the PCL-ran-PDLA by complex 10 (CDCl$_3$, 25 °C, 150 MHz).