Supporting Information

2,4-Dinitrobenzenesulfonic Acid as an Efficient Brønsted Acid-
Catalyzed Controlled/Living Ring-Opening Polymerization of \( \varepsilon \)-
caprolactone

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Syntheses of End-Functionalized and \( a,ω \)-Dihydroxy Telechelic Poly(\( \varepsilon \)-caprolactone)

![Chemical structure of End-functionalized and \( a,ω \)-Dihydroxy Telechelic Poly(\( \varepsilon \)-caprolactone)](image)

**FIGURE S1** \(^1\)H NMR spectrum of End-functionalized PCL initiated from propargyl
alcohol in CDCl\(_3\).
FIGURE S2 $^1$H NMR spectrum of End-functionalized PCL initiated from 5-hexen-1-ol in CDCl$_3$.

FIGURE S3 $^1$H NMR spectrum of End-functionalized PCL initiated from 2-hydroxyethyl methacrylate in CDCl$_3$. 
**FIGURE S4** $^1$H NMR spectrum of PCL initiated from Pentaerythritol in CDCl$_3$.

**FIGURE S5** $^1$H NMR spectrum of $a,ω$-Dihydroxy Telechelic PCL initiated from 1,3-Propanediol in CDCl$_3$. 
Diblock Copolymers of $\varepsilon$-Caprolactone and $\delta$-Valerolactone, Trimethylene Carbonate.

**FIGURE S6** $^1$H NMR spectrum of PCL-$b$-PVL initiated from BnOH in CDCl$_3$.

**FIGURE S7** $^1$H NMR spectrum of PCL-$b$-PTMC initiated from BnOH in CDCl$_3$. 
The calculation details of ε-CL conversion

The calculated conversions of ε-CL were obtained from 1H NMR spectra of reaction mixtures, and the details were as follows: the integral area of the signal of methylene protons at 4.25 ppm of ε-CL monomer was appointed to 1, and then the integral area of the signal at 4.06 ppm (–CH₂CH₂O–)ₙ was appointed to n. based on the formula, conv. = n/(n+1) * 100%.