SUPPORTING INFORMATION

A BINARY NEODYMIUM CATALYST FOR THE POLYMERIZATION OF LACTONES

Ruvanthi N. Kularatne, Somayeh Taslimy, Abhi Bhadran, John Michael O. Cue, Chandima Bulumulla, Erika L. Calubaquib, Ruwan Gunawardhana, Michael C. Biewer, and Mihaela C. Stefan*

Ruvanthi N. Kularatne and Somayeh Taslimy contributed equally to this paper.

The Department of Chemistry and Biochemistry, The University of Texas at Dallas, 800 W. Campbell Road, Richardson, Texas 75080

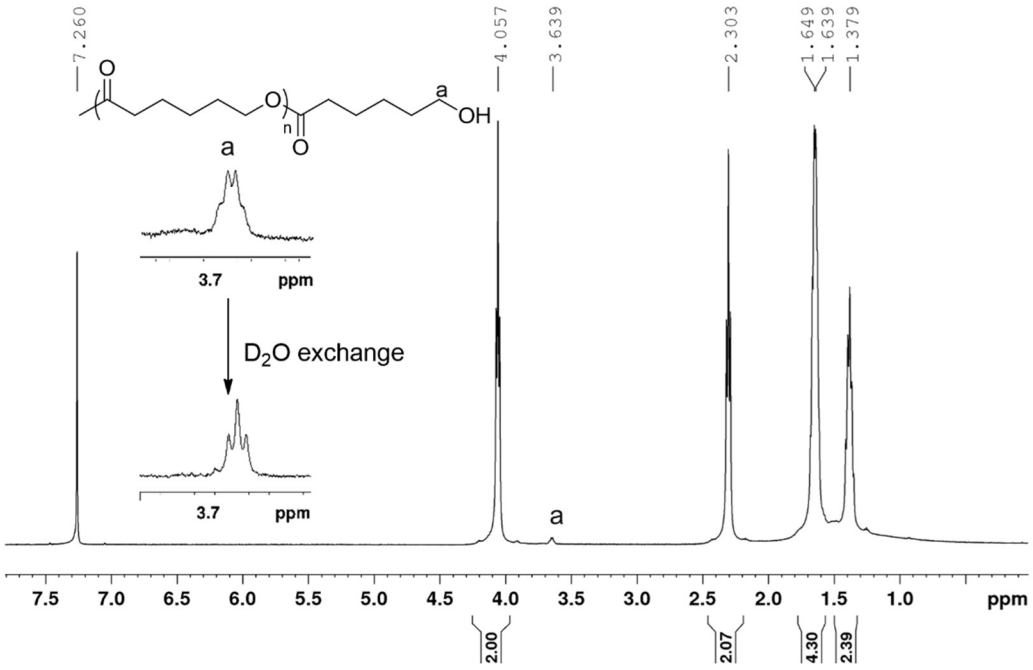


Figure S1. ^{1}H and NMR spectrum of polycaprolactone obtained with $NdCl_3$·3TEP/TIBA catalytic system

From the slopes of the plot in Figure S2 (c), k_{app} (kapp = k x [M*], where k = rate constant and [M*]=concentration of active species, which is constant for a *living* polymerization) was calculated at the three temperatures and E_a was determined from the Arrhenius plot (Figure S2 (d)) derived from the Arrhenius equation shown below,

$$\ln k = -\frac{E_a}{RT} + \ln A$$

where k = rate constant

E_a = activation energy

R= universal gas constant

T= absolute temperature

A= Arrhenius constant

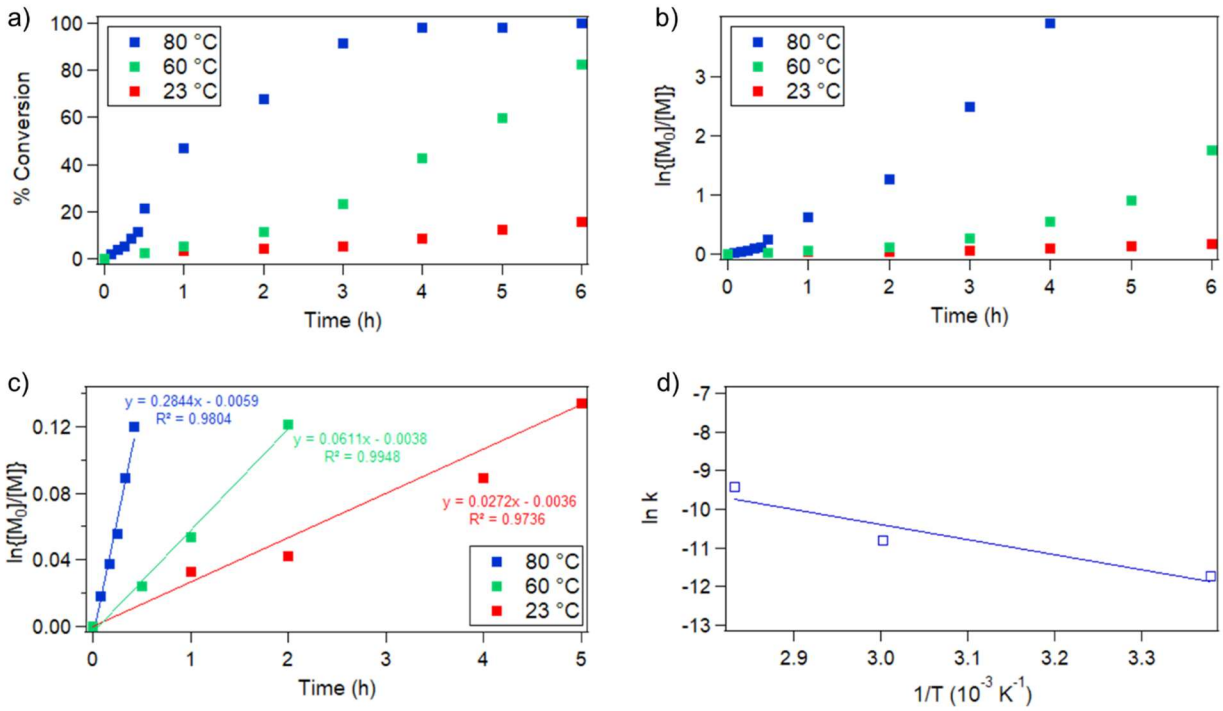


Figure S2. (a) % Conversion vs. time, (b) ln{[M]$_0$/[M]} vs. time, (c) ln{[M]$_0$/[M]} vs. time for conversions < 20%, at different temperatures and (d) Arrhenius plot for the polymerization of ε-CL with $NdCl_3$·3TEP/TIBA catalytic system at a [ε-CL]:[Nd]:[Al] ratio of 500:1:5

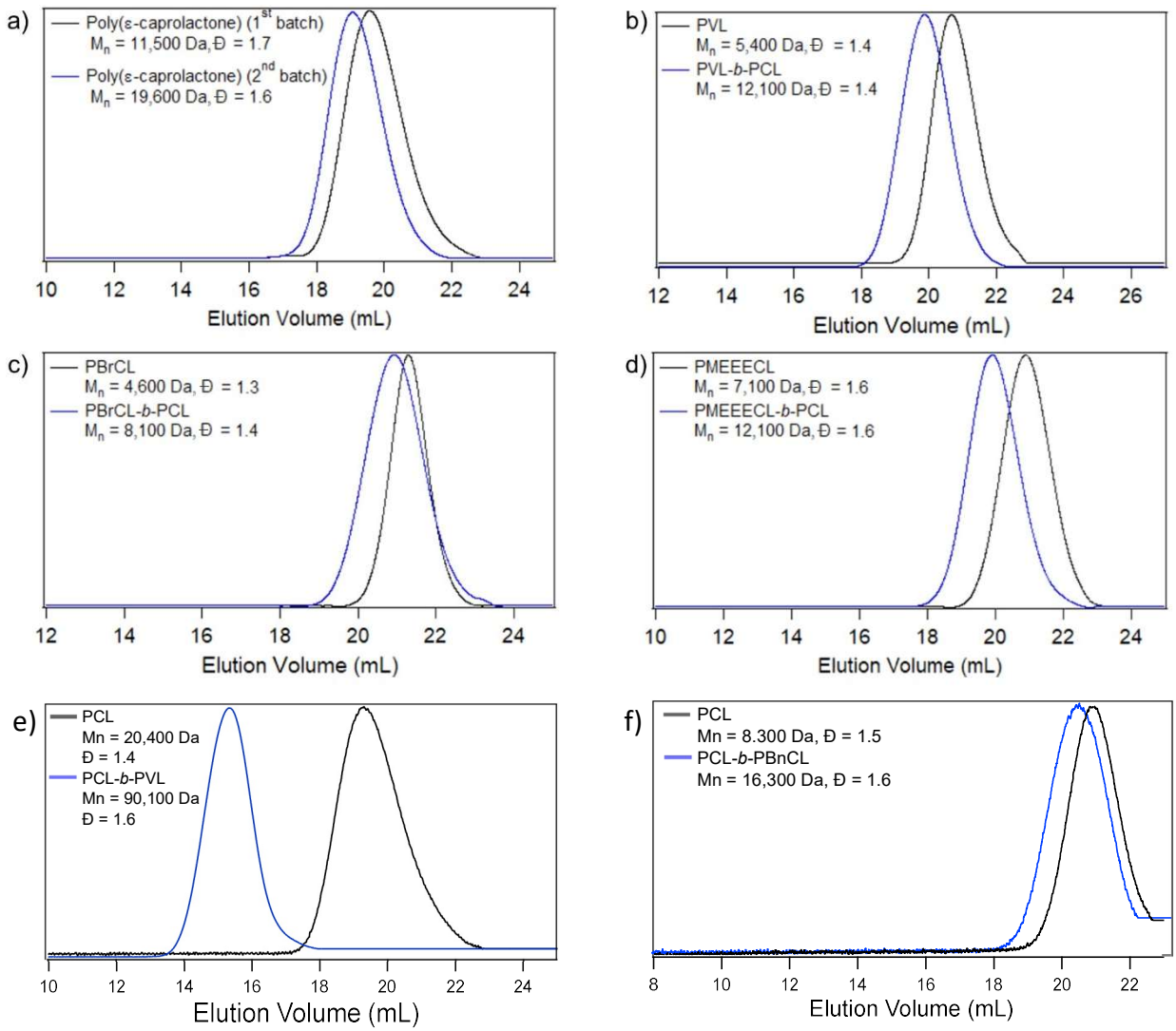
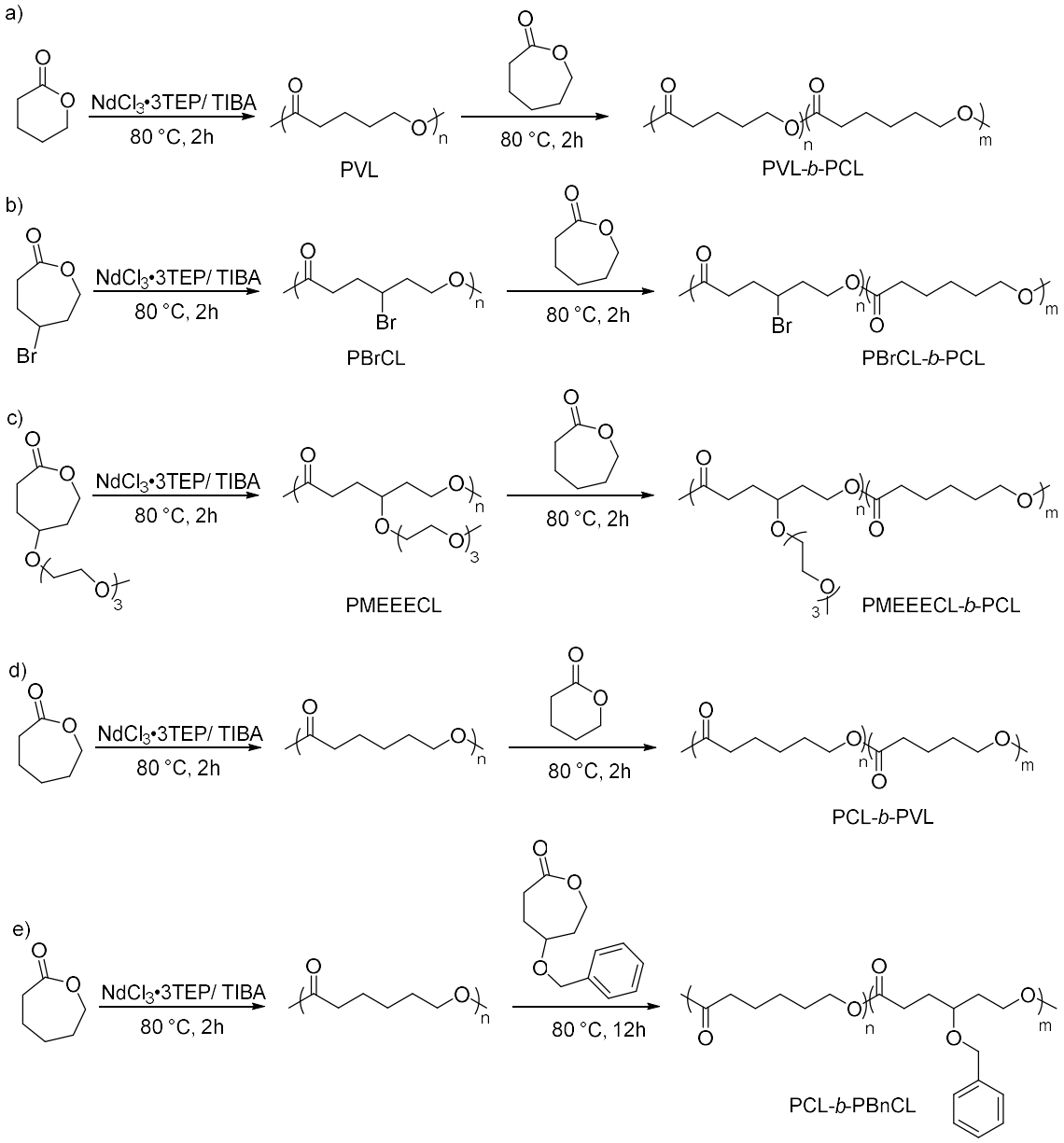


Figure S3. SEC traces for (a) PCL before and after chain extension obtained at a [ε-CL1]: [ε-CL2]:[Nd]:[Al] ratio of 50:100:1:5 and (b) PVL and PVL-*b*-PCL (c) PBrCL and PBrCL-*b*-PCL (d) PMEEECL and PMEEECL-*b*-PCL obtained at a [M]: [ε-CL]:[Nd]:[Al] ratio of 50:100:1:5 (e) PCL and PCL-*b*-PVL at a [ε-CL]: [δ-VL]:[Nd]:[Al] ratio of 200:1000:1:5 (f) PCL and PCL-*b*-PBnCL at a [ε-CL]: [δ-BnCL]:[Nd]:[Al] ratio of 75:25:1:5 at 80 °C (M = δ-VL or MEEECL)



Scheme S1. Schematic representation of the synthesis of (a) PVL-*b*-PCL, (b) PBrCL-*b*-PCL, (c) PMEEECL-*b*-PCL, d) PCL-*b*-PVL, and e) PCL-*b*-PBnCL

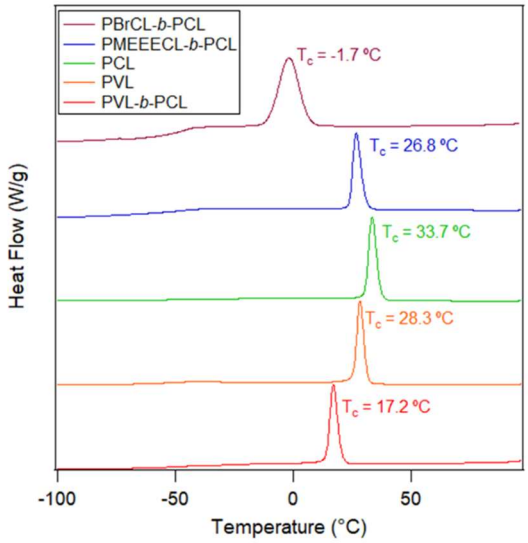


Figure S4. DSC traces for PBrCL-*b*-PCL, PMEEECL-*b*-PCL, PCL, PVL and PVL-*b*-PCL for the temperature range of -100 °C to 100 °C

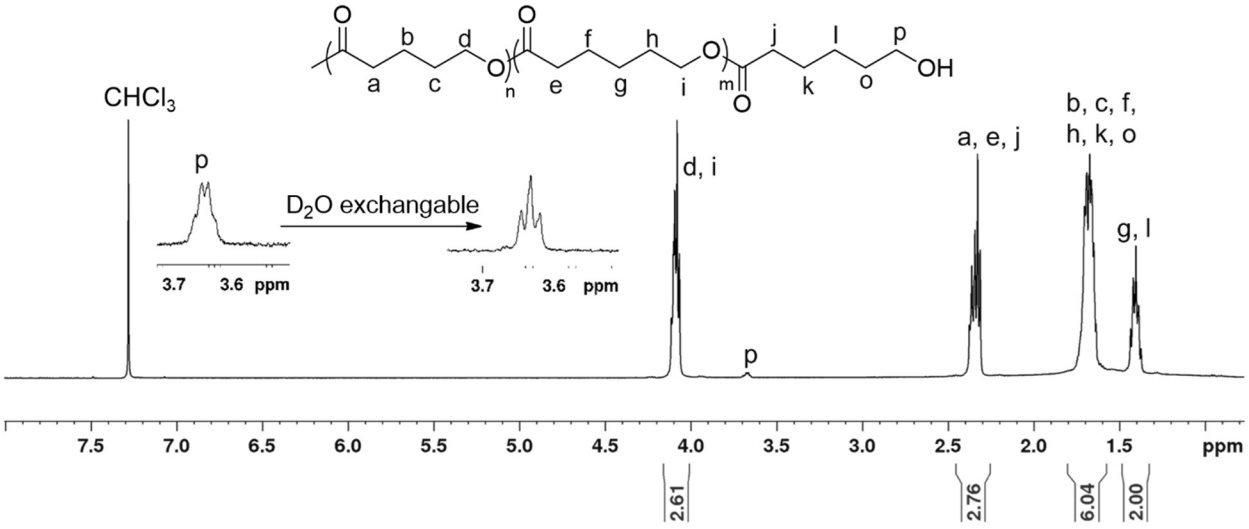


Figure S5. ^{1}H NMR spectrum of PVL-*b*-PCL. (M_n = 12,100 Da, Đ = 1.4, composition for δ-VL and ε-CL is 29 and 71 mol% respectively)

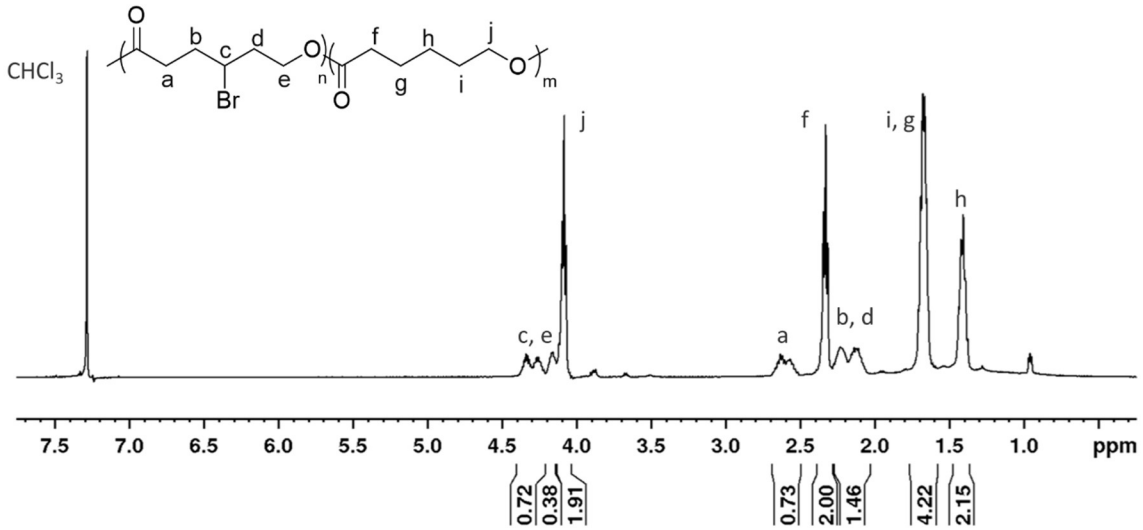


Figure S6. [1]H NMR spectrum of PBrCL-*b*-PCL. (M_n = 8,100 Da, Đ = 1.4, composition for BrCL and ε-CL is 27 and 73 mol% respectively)

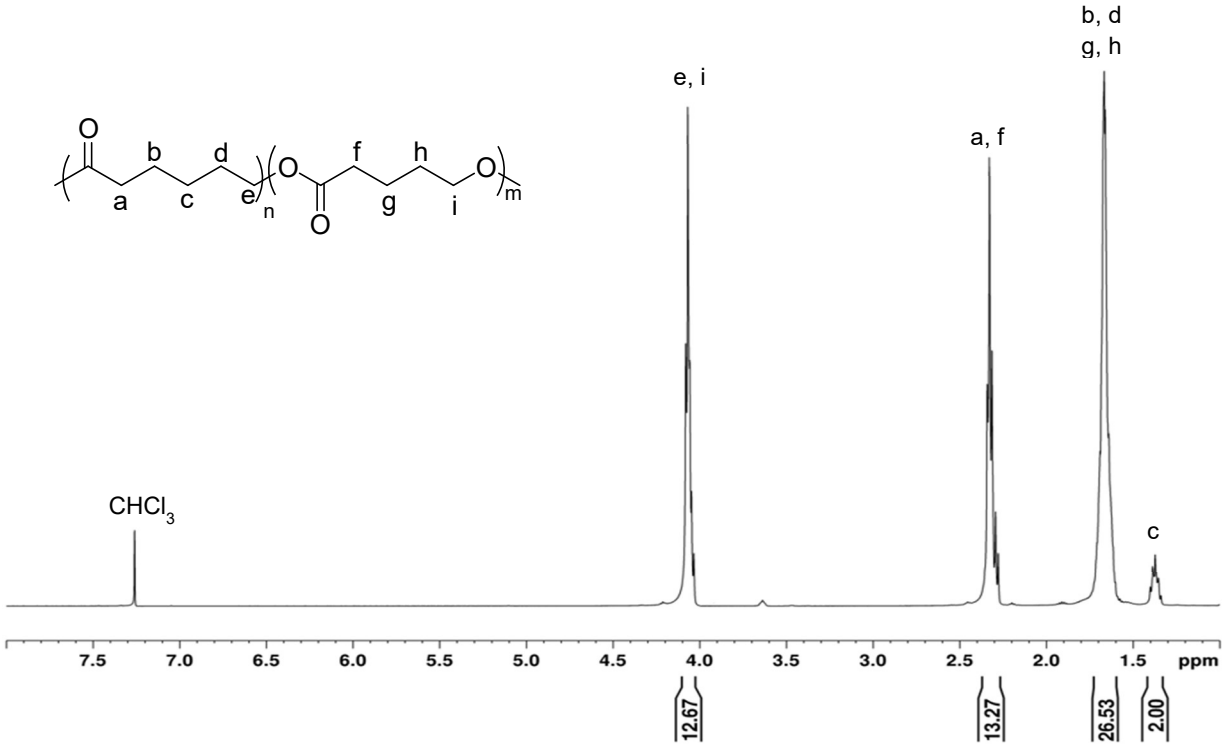


Figure S7. [1]H NMR spectrum of PCL-*b*-PVL. (M_n = 90,100 Da, Đ = 1.6, composition for ε-CL and δ-VL is 15 and 85 mol% respectively)

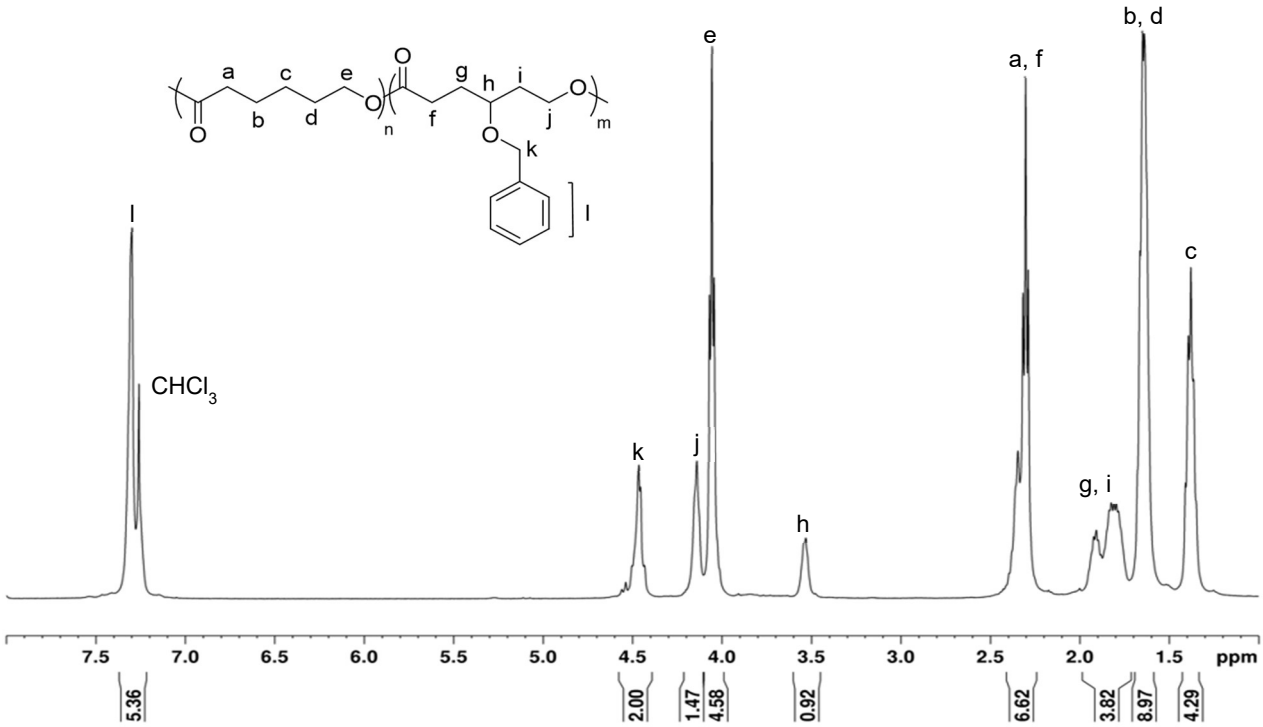


Figure S8. ^{1}H NMR spectrum of PCL-*b*-PBnCL. (M_n = Da, Đ = 1, composition for ε-CL and δ-BnCL is 70 and 30 mol% respectively)

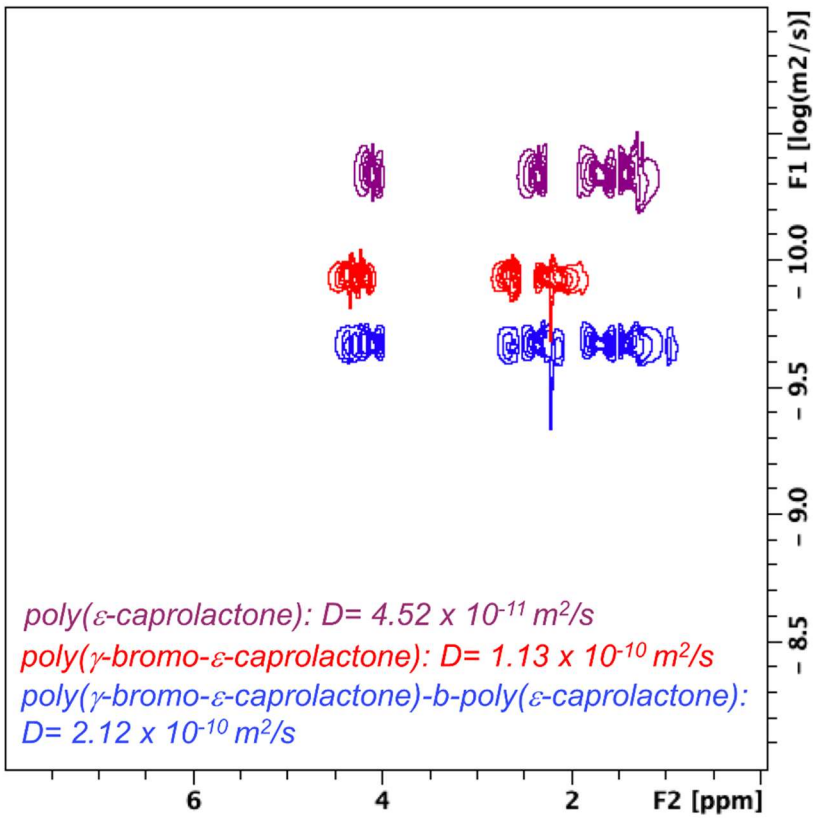


Figure S9. 2D DOSY plot for PCL (purple), PBrCL (red) and PBrCL-*b*-PCL (blue)

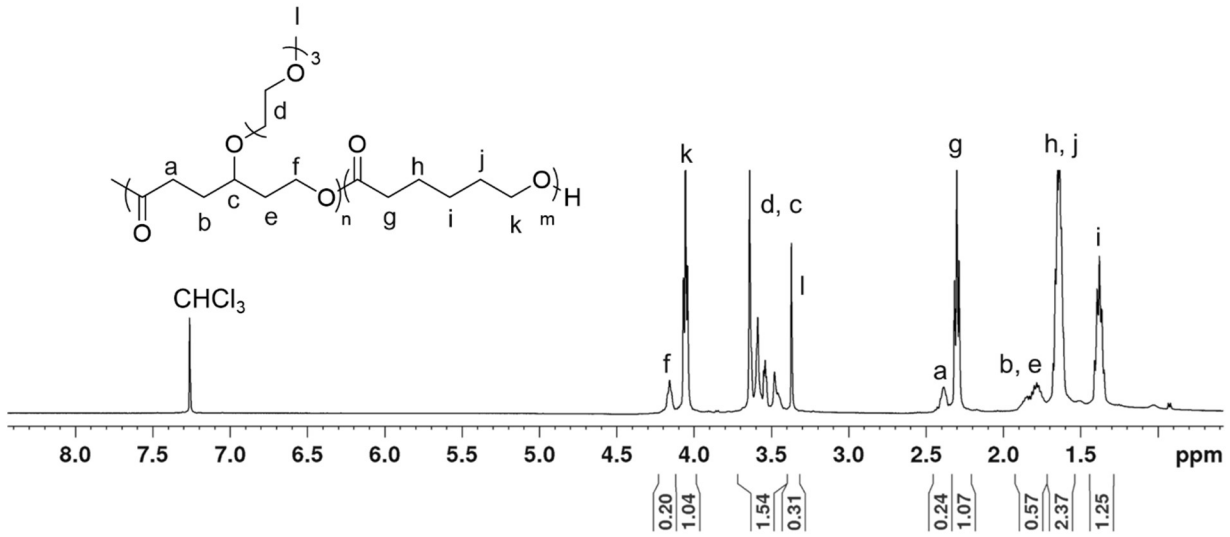
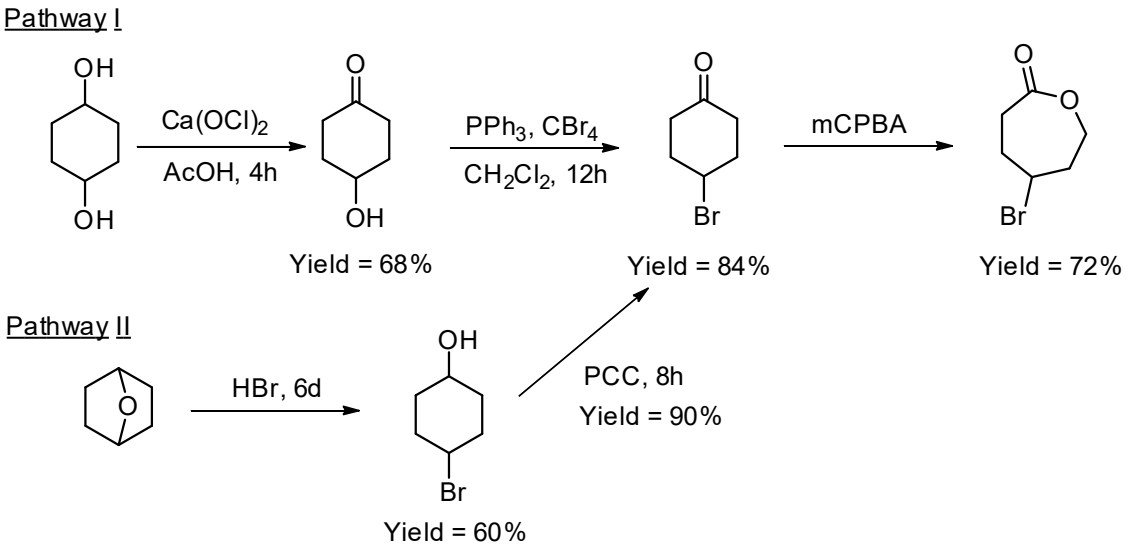


Figure S10. ^{1}H NMR of PMEEECL-*b*-PCL. (M_n = 12,100 Da, Đ = 1.6, composition for MEEECL and ε-CL is 17 and 83 mol% respectively)



Scheme S2. Synthesis of γ-bromo-ε-caprolactone using different synthetic routes

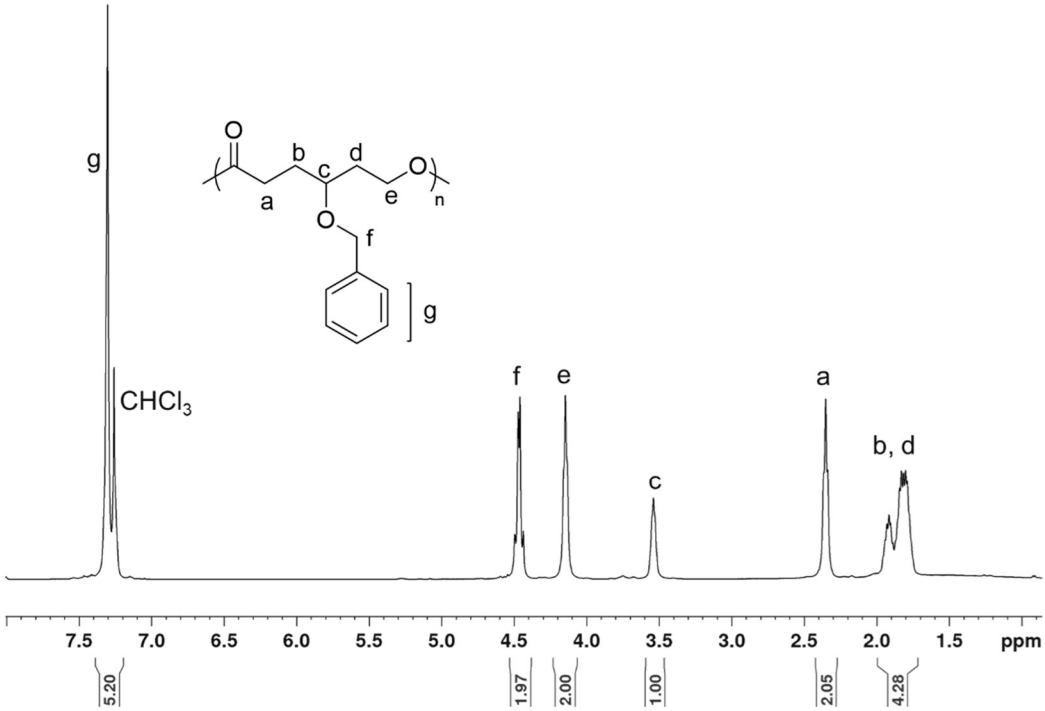


Figure S11. ^{1}H NMR spectrum of poly(γ-benzyl-ε-caprolactone). (M_n = 17,600 Da, Đ = 1.6)

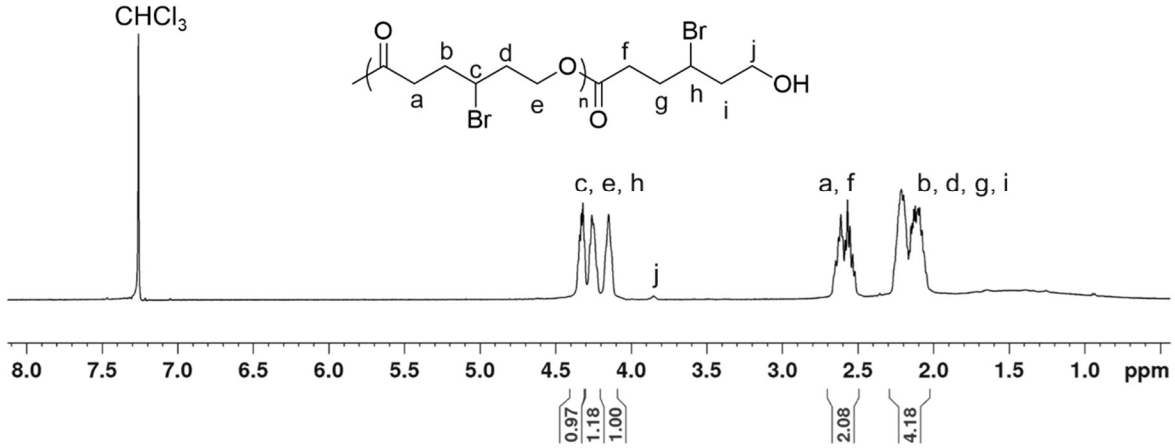


Figure S12. ^{1}H NMR spectrum of poly(γ-bromo-ε-caprolactone). (M_n = 23,400 Da, Đ = 1.8)

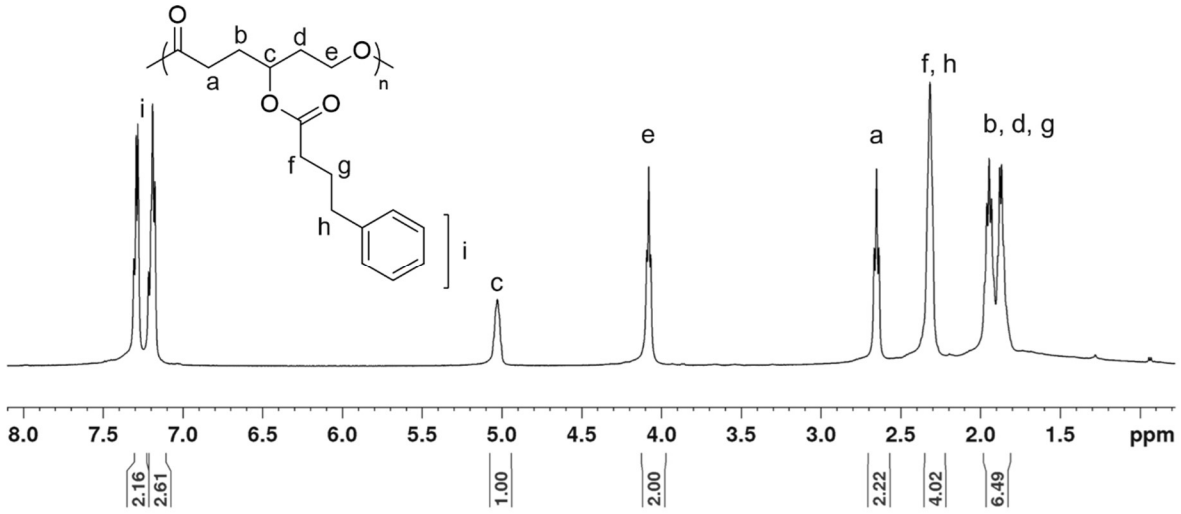


Figure S13. ^{1}H NMR spectrum of poly(γ-phenylbutyrate-ε-caprolactone). (M_n = 22,000 Da, Đ = 1.5)

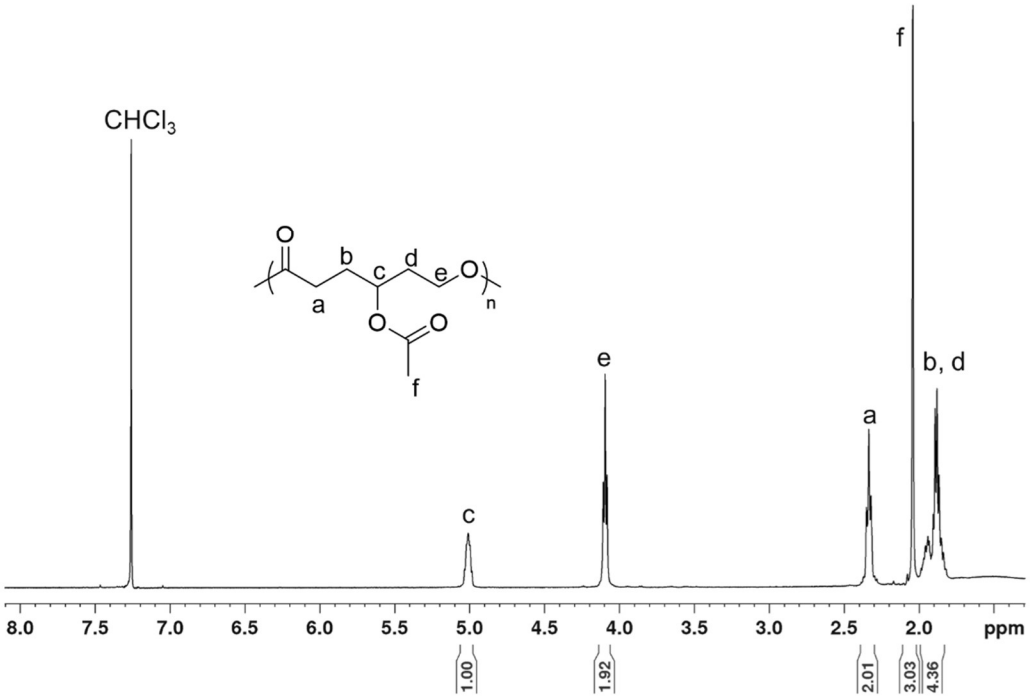


Figure S14. ^{1}H NMR spectrum of poly(γ-acetate-ε-caprolactone). (M_n = 11,300 Da, Đ = 1.3)

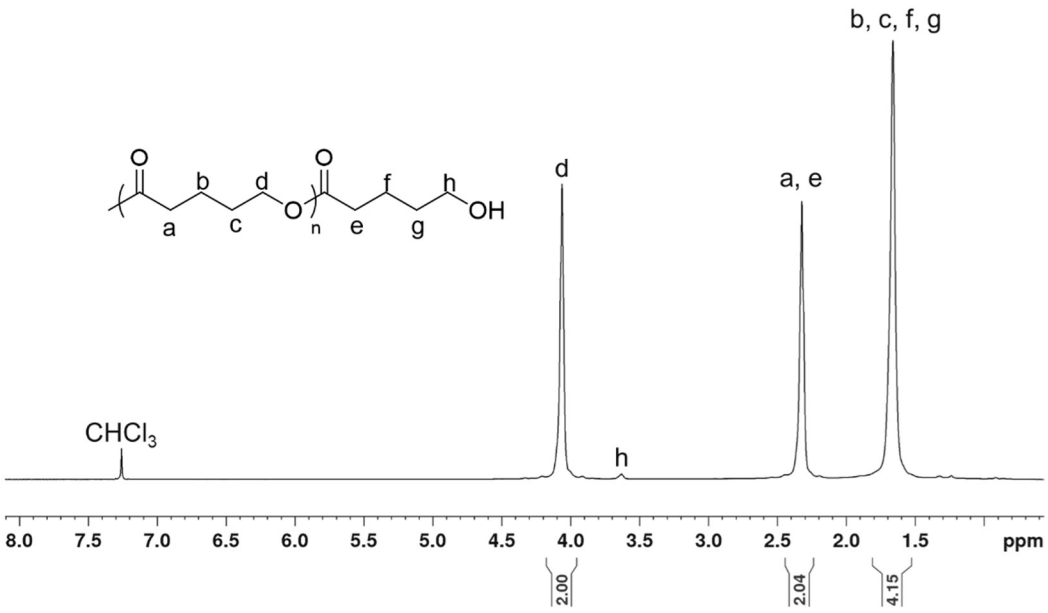


Figure S15. ^{1}H NMR spectrum of polyvalerolactone. (M_n = 18,300 Da, Đ = 1.5)

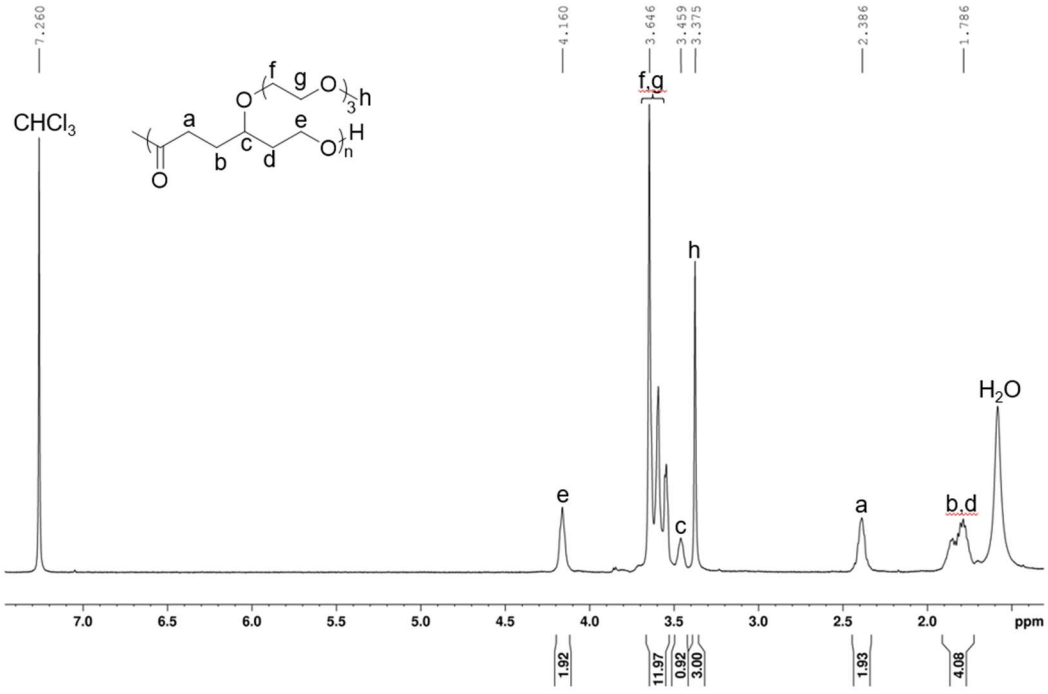


Figure S16. ^{1}H NMR spectrum of poly (γ-2-[2-(2-methoxyethoxy)ethoxy]ethoxy-ε-caprolactone). (M_n = 8,300 Da, Đ = 1.1)

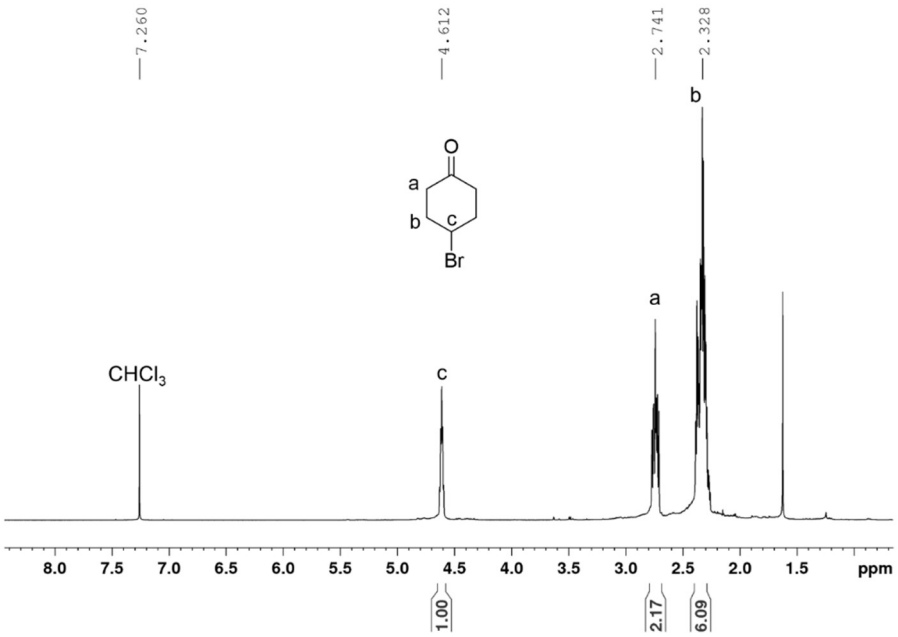


Figure S17. ^{1}H NMR spectrum of 4-bromocyclohexanone

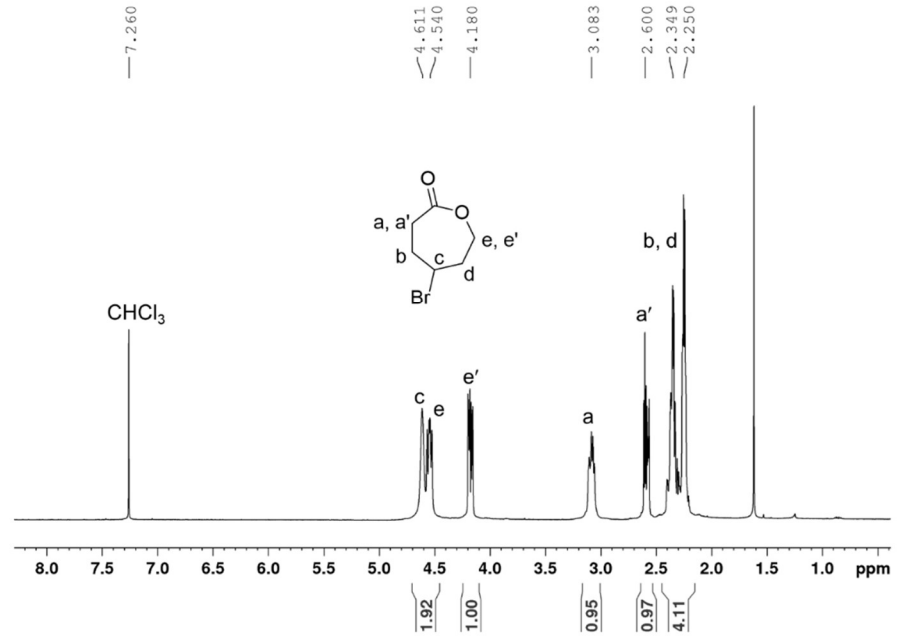


Figure S18. ^{1}H NMR spectrum of γ-bromo-ε-caprolactone

Figure S19. ^{1}H NMR spectrum of 4-oxocyclohexyl acetate

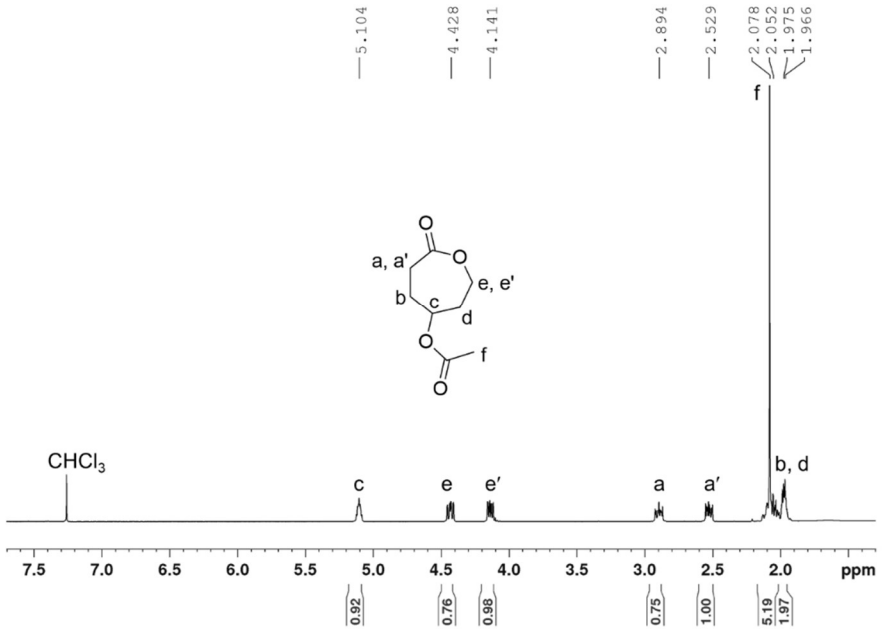


Figure S20. ^{1}H NMR spectrum of γ-acetate-ε-caprolactone