Supporting Information for *H-bonding Organocatalysts for Ring-Opening Polymerization at Elevated Temperatures*

Danielle N. Coderre, Kurt V. Fastnacht, Thomas J. Wright, Nayanthara U. Dharmaratne and Matthew K. Kiesewetter*

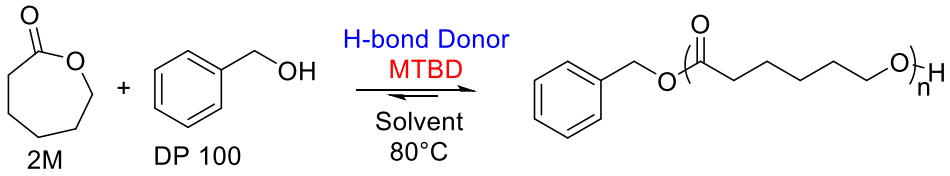
Department of Chemistry, University of Rhode Island, Kingston, RI 02881 USA

Table S1. Thermal Decomposition of H-bond Donors With and Without MTBD.

catalyst	decomposition temperature onset (°C)	decomposition temperature onset w/ MTBD (°C)
1-S	166	168
1-O	212	151
TCC	247	162
2-S	172	NA
2-O	256	162
3-S	187	196

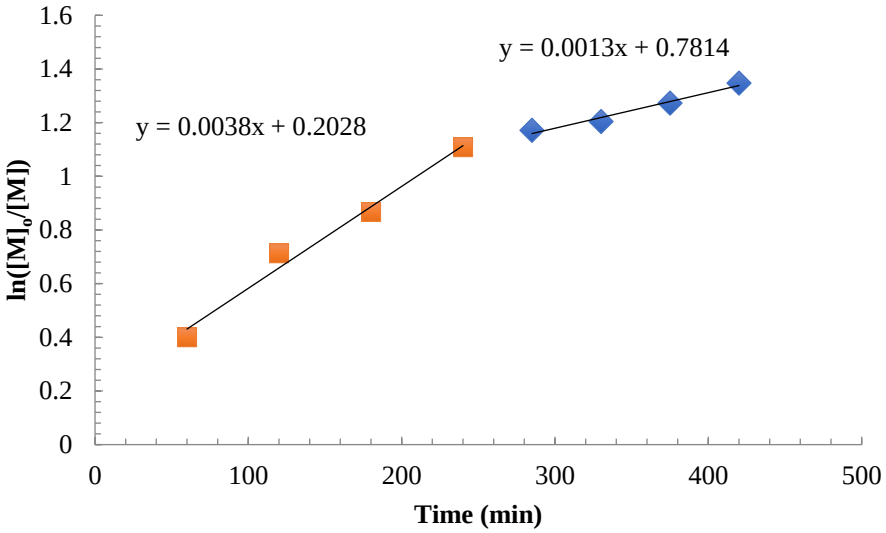
TGA conditions: Sample size ~7 mg were placed in aluminum pans. Start at 25°C, ramp to 500°C at 10°C/min, held for 5 minutes. N_2 gas flow rate of 10 mL/min. Catalyst samples were weighed from bulk samples. H-bond donor/base 1:1 mixtures were first dissolved in dichloromethane and solvent removed under vacuum. Remaining thick oil was used for samples.

Table S2. M_n and M_w/M_n for polymerizations conducted at 80°C.[a]



	Toluene				MIBK			
	Time (min)	Conv.[b]	M_n [c]	M_w/M_n [c]	Time (min)	Conv.[b]	M_n [c]	M_w/M_n [c]
1-S	360	90	19,200	1.07	950	91	13,500	1.24
1-O	335	89	18,000	1.14	880	98	10,700	1.40
2-S[d]	170	91	14,000	1.17	1600	83	9,600	1.17
2-O	120	89	11,500	1.19	260	91	8,800	1.24
3-S	960	89	12,600	1.08	4,900	41	4,200	1.13
3-O	40	90	19,000	1.04	15	91	14,300	1.10
TCC	61	90	16,800	1.17	65	94	11,100	1.28

a. Reaction conditions: CL (2M, 0.876 mmol), benzyl alcohol (0.00876 mmol), 1-X, 2-X, 3X and TCC (0.0438 mmol, 0.0219 mmol, 0.0146 mmol and 0.0438 mmol) MTBD (matched to H-bond donor mmol). b. Conversion determined by ^{1}H NMR. c. M_n and M_w/M_n determined by GPC. d. **2-S** in MIBK at 60°C.



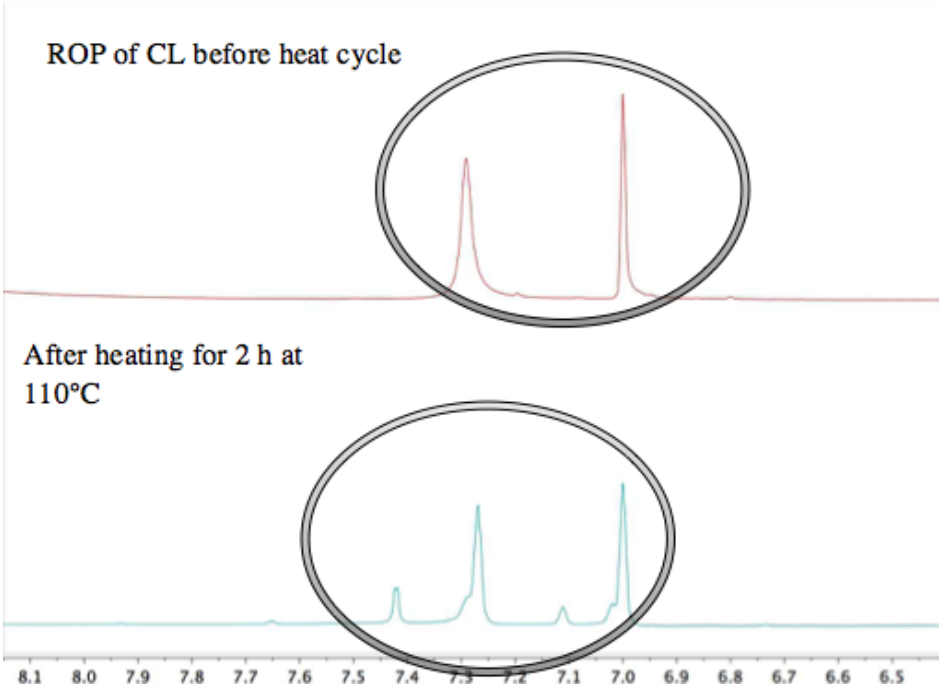


Figure S1. (upper) Temperature drop ROP of CL (2M, 0.876 mmol) in toluene, **1-S**/MTBD (0.0438 mmol each) cocatalyzed from benzyl alcohol (0.00876 mmol)**.** A decrease in k_{obs} from 0.0038 min^{-1} to 0.0013 min^{-1} is observed after the temperature change from 110°C (red) to 80°C (blue). Reaction progression tracked by aliquot, and conversion was determined by ^{1}H NMR. (lower) ^{1}H NMR (400 MHz, benzene-d_6) of the ROP of CL (0.876 mmol, 2M), benzyl alcohol (0.00876 mmol), **1-S**/MTBD (0.0438 mmol each). Top image shows the aromatic region of the ^{1}H NMR of **1-S**. Bottom image shows a second set of aromatic resonances after 2 h of heating at 110°C.

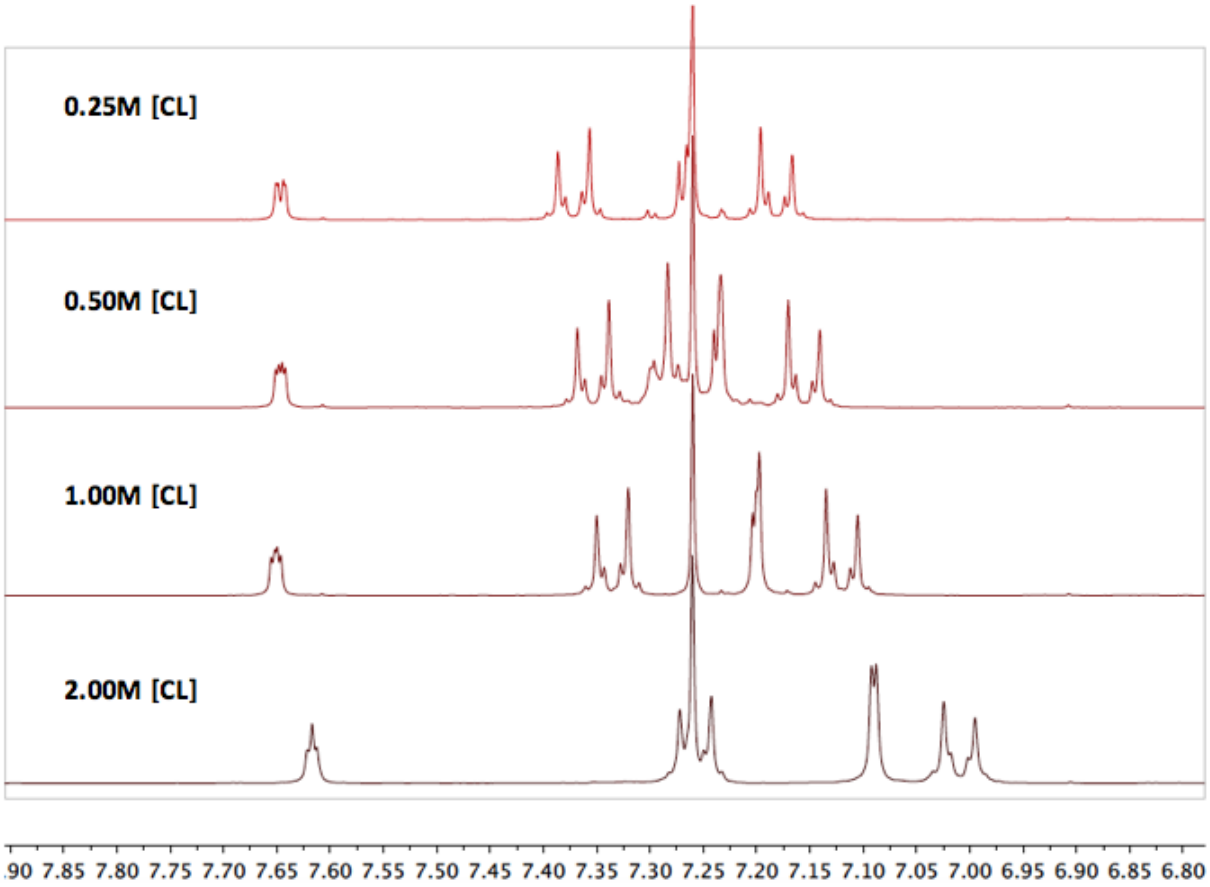


Figure S2. ^{1}H NMR spectra of TCC/MTBD (0.00438 mmol each) cocatalyst in the presence of varying [CL] (0.25-2M) in $CDCl_3$.

EYRING DATA IN TOLUENE

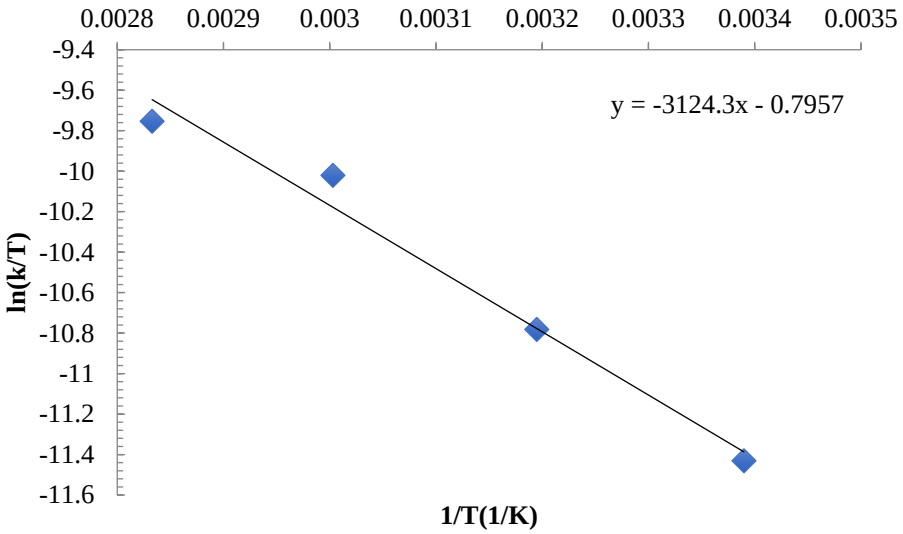


Figure S3. Eyring plot constructed from the linear portion of the observed first order rate constants for the **2-S**/MTBD (0.0219 mmol each) cocatalyzed ROP of CL (0.876 mmol, 2M) from benzyl alcohol (0.00876 mmol) in toluene.

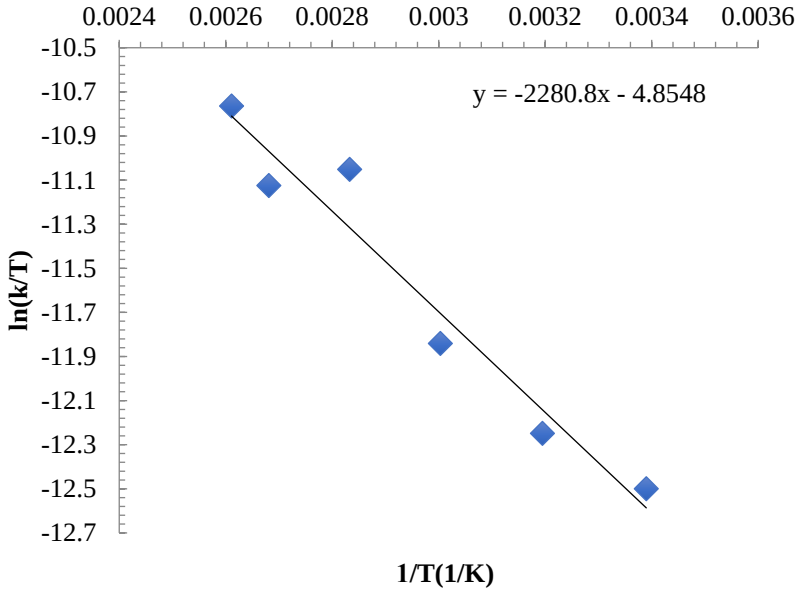


Figure S4. Eyring plot constructed from the observed first order rate constants for the **1-O**/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (0.876 mmol, 2M) from benzyl alcohol (0.00876 mmol) in toluene.

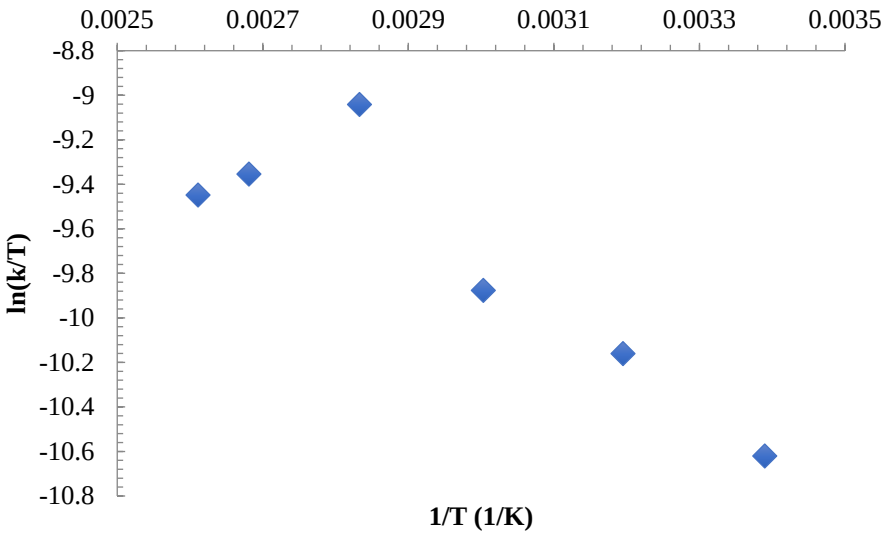


Figure S5. Eyring plot constructed from the observed first order rate constants for the TCC/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (0.876 mmol, 2M) from benzyl alcohol (0.00876 mmol) in toluene.

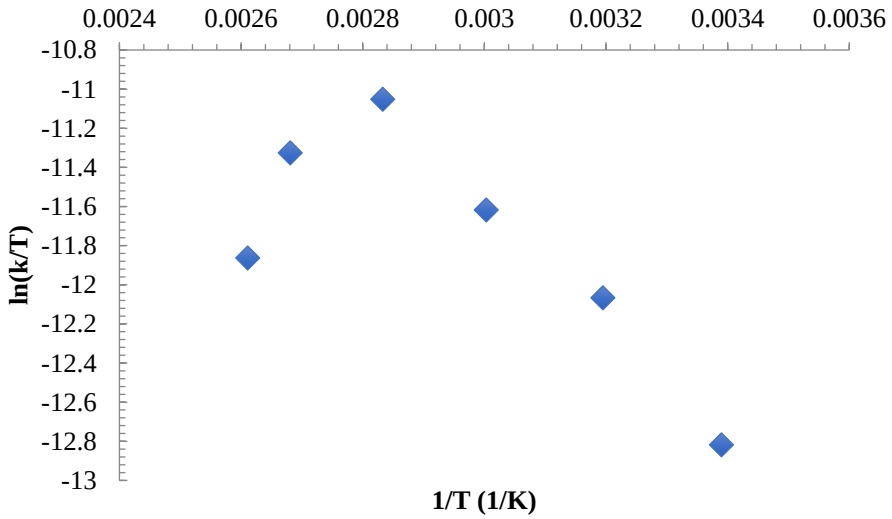


Figure S6. Eyring plot constructed from the observed first order rate constants for the **1-S**/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (0.876 mmol, 2M) from benzyl alcohol (0.00876 mmol) in toluene.

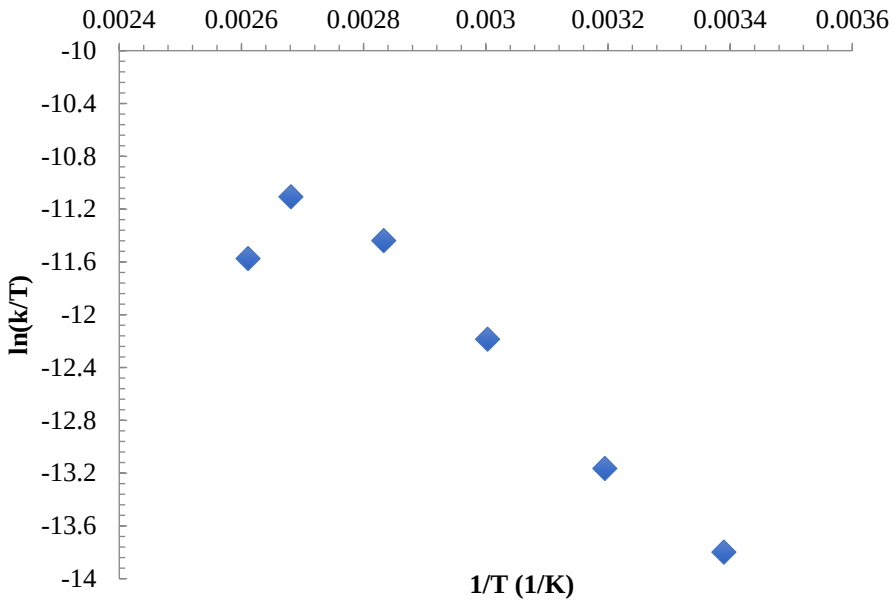


Figure S7. Eyring plot constructed from the observed first order rate constants for the **3-S**/MTBD (0.0146 mmol each) cocatalyzed ROP of CL (0.876 mmol, 2M) from benzyl alcohol (0.00876 mmol) in toluene.

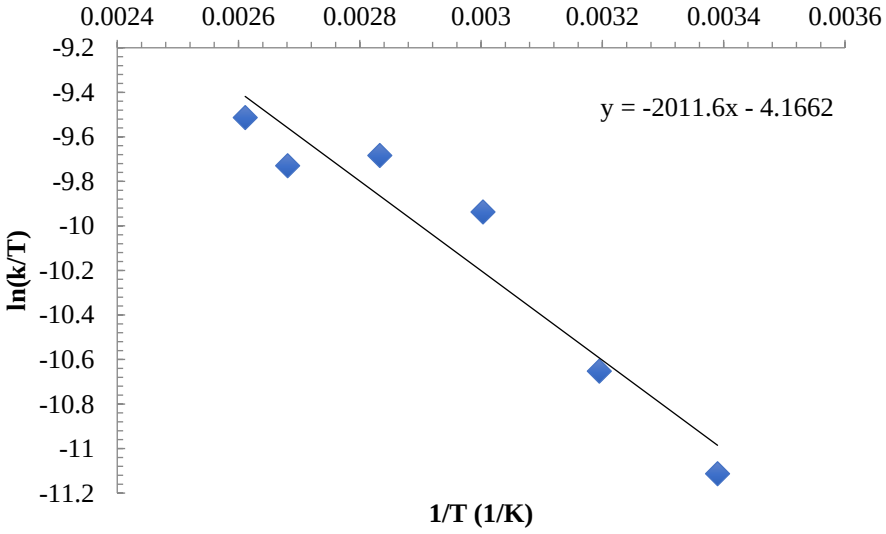


Figure S8. Eyring plot constructed from the observed first order rate constants for the **2-O**/MTBD (0.0219 mmol each) cocatalyzed ROP of CL (0.876 mmol, 2M) from benzyl alcohol (0.00876 mmol) in toluene.

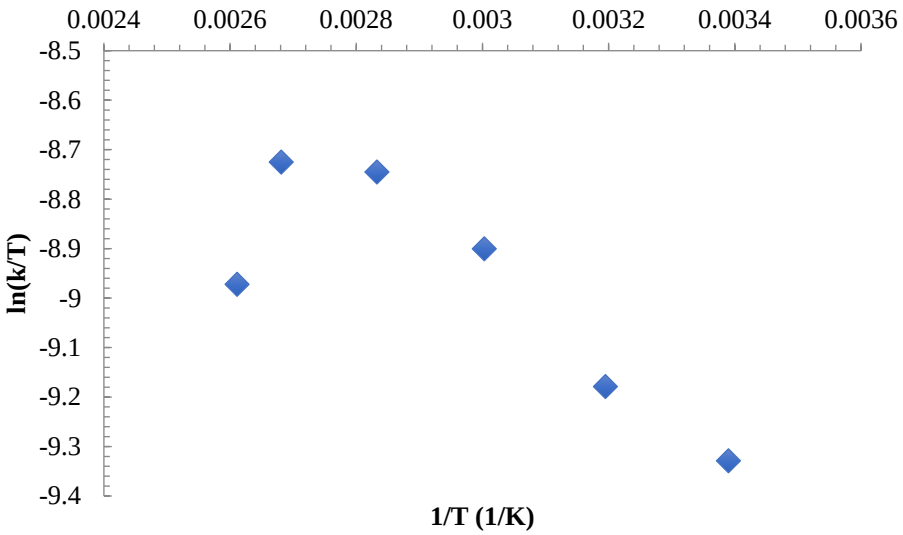


Figure S9. Eyring plot constructed from the observed first order rate constants for the **3-O**/MTBD (0.0146 mmol each) cocatalyzed ROP of CL (0.876 mmol, 2M) from benzyl alcohol (0.00876 mmol) in toluene.

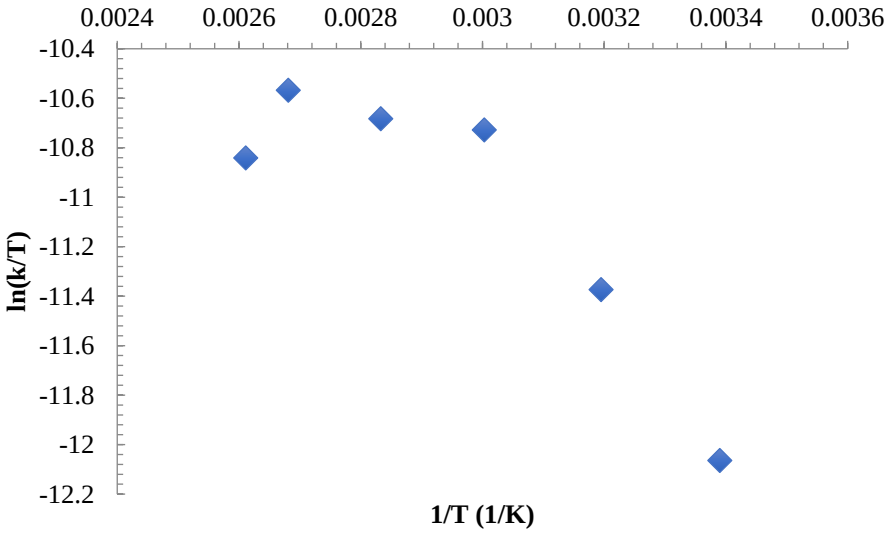


Figure S10. Eyring plot constructed from the observed first order rate constants for the TCC/DBU (0.0438 mmol each) cocatalyzed ROP of CL (0.876 mmol, 2M) from benzyl alcohol (0.00876 mmol) in toluene.

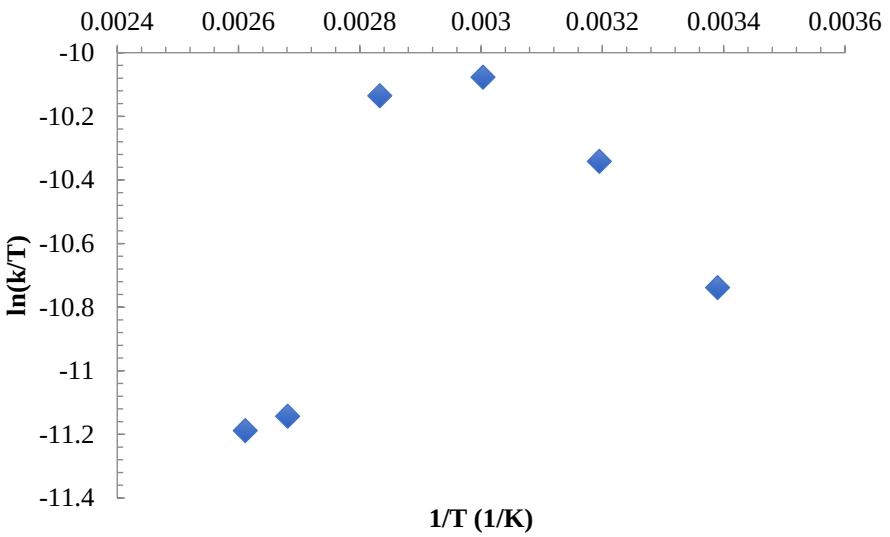


Figure S11. Eyring plot constructed from the observed first order rate constants for the TCC/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (0.876 mmol, 1M) from benzyl alcohol (0.00876 mmol) in toluene.

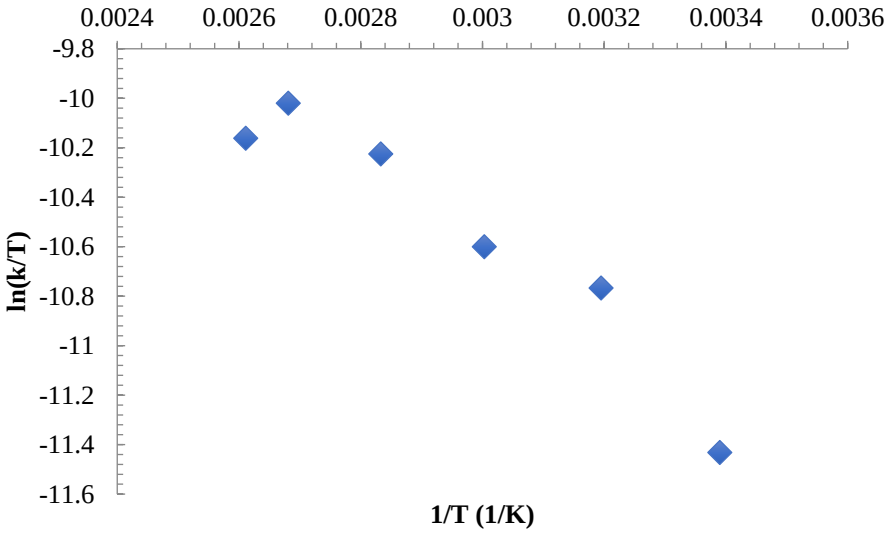


Figure S12. Eyring plot constructed from the observed first order rate constants for the **2-O**/MTBD (0.0219 mmol each) cocatalyzed ROP of CL (0.876 mmol, 1M) from benzyl alcohol (0.00876 mmol) in toluene.

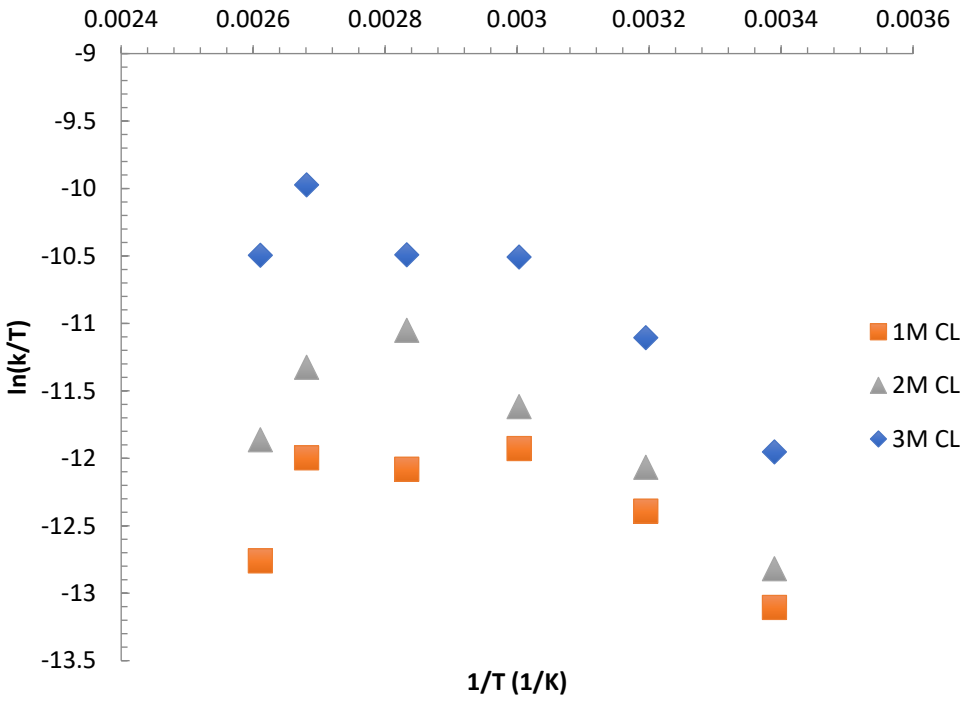


Figure S13. Eyring plot constructed from the observed first order rate constants for the **1-S**/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (0.876 mmol) from benzyl alcohol (0.00876 mmol) at 1M, 2M and 3M concentrations in toluene.

EYRING DATA IN METHYL ISOBUTYL KETONE - *LACTIDE*

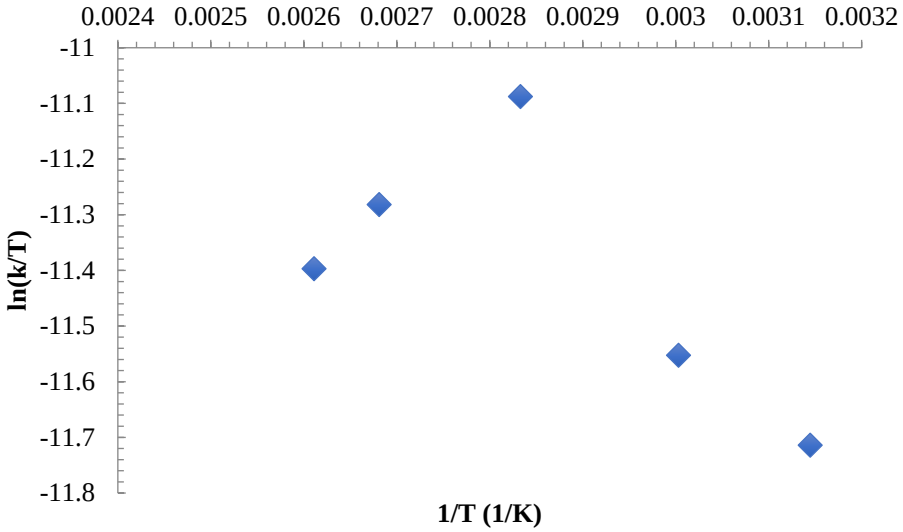


Figure S14. Eyring plot constructed from the observed first order rate constants for the **2-S**/PMDETA (0.0219 mmol each) cocatalyzed ROP of L-LA (0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone.

EYRING DATA IN METHYL ISOBUTYL KETONE - *CAPROLACTONE*

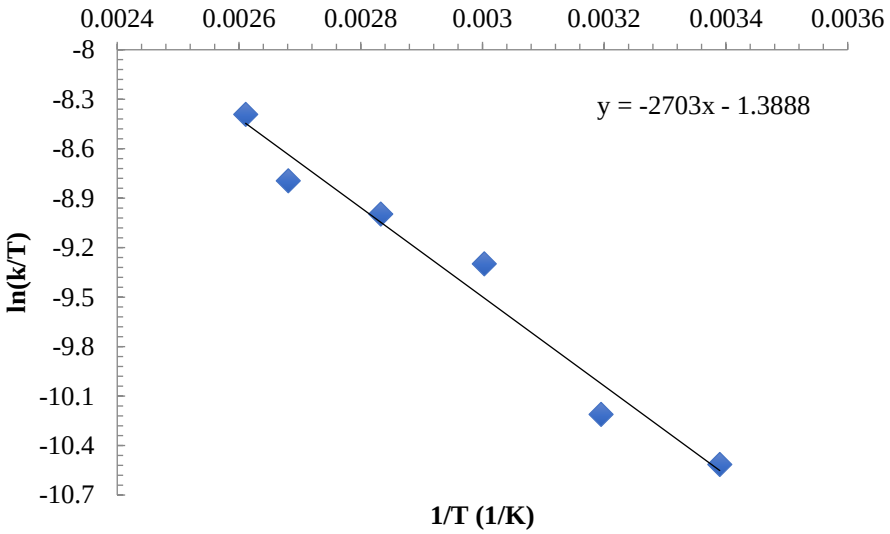


Figure S15. Eyring plot constructed from the observed first order rate constants for the TCC/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone.

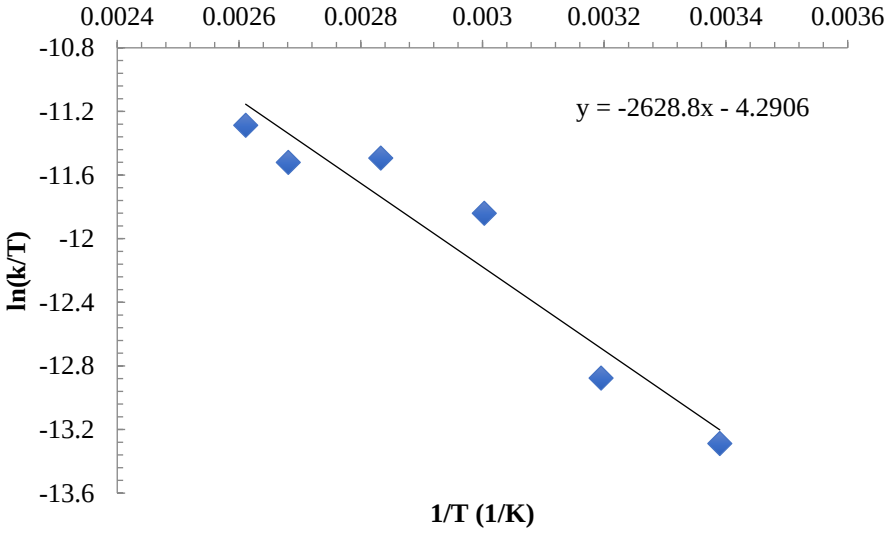


Figure S16. Eyring plot constructed from the observed first order rate constants for the **1-S**/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone.

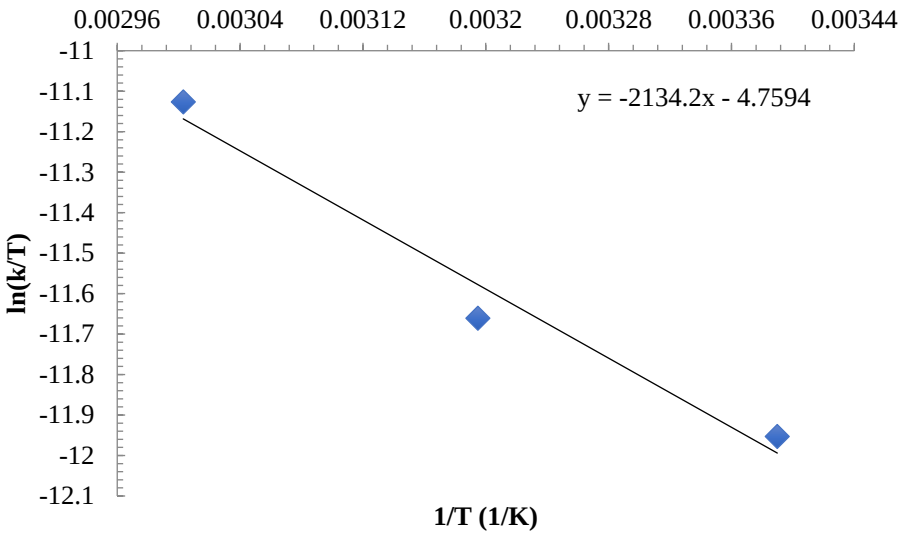


Figure S17. Eyring plot constructed from the observed first order rate constants for the **2-S**/MTBD (0.0219 mmol each) cocatalyzed ROP of CL (0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone.

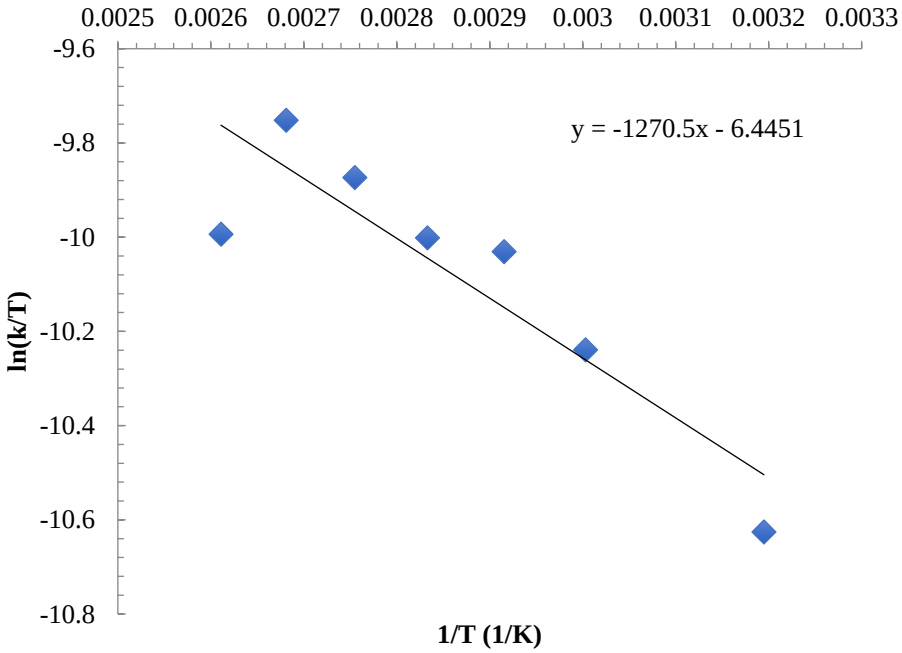


Figure S18. Eyring plot constructed from the observed first order rate constants for the **2-O**/MTBD (0.0219 mmol each) cocatalyzed ROP of CL (0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone.

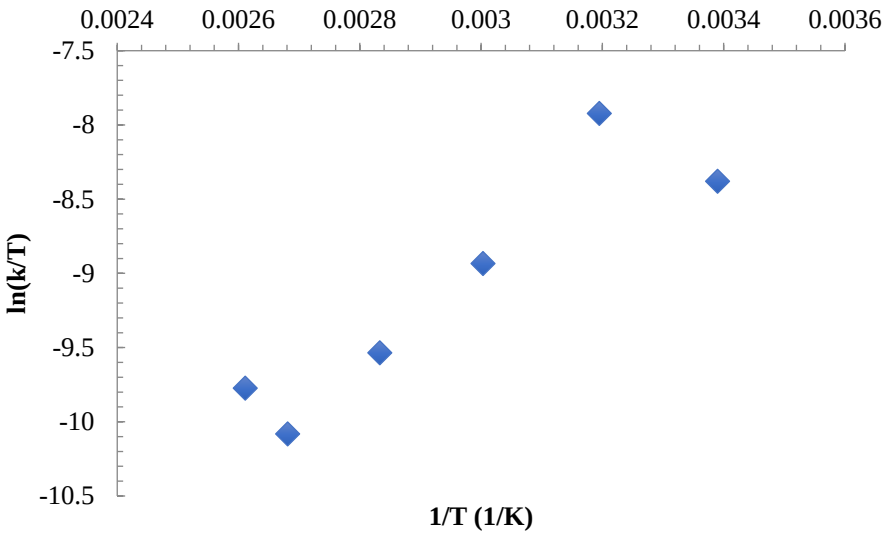


Figure S19. Eyring plot constructed from the observed first order rate constants for the **3-O**/MTBD (0.0146 mmol each) cocatalyzed ROP of CL (0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone.

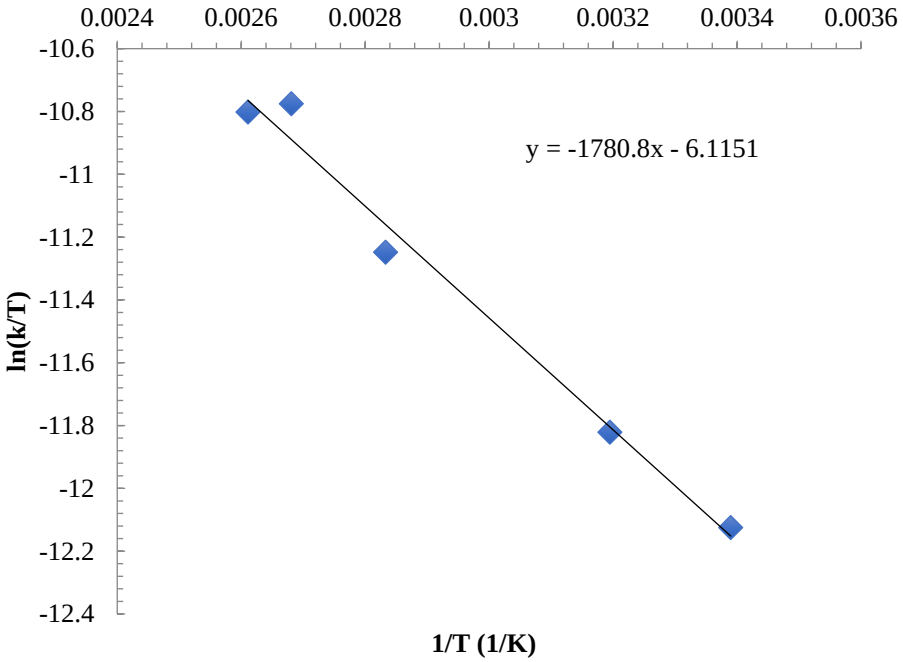


Figure S20. Eyring plot constructed from the observed first order rate constants for the **1-O**/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone.

EYRING DATA IN BENZENE

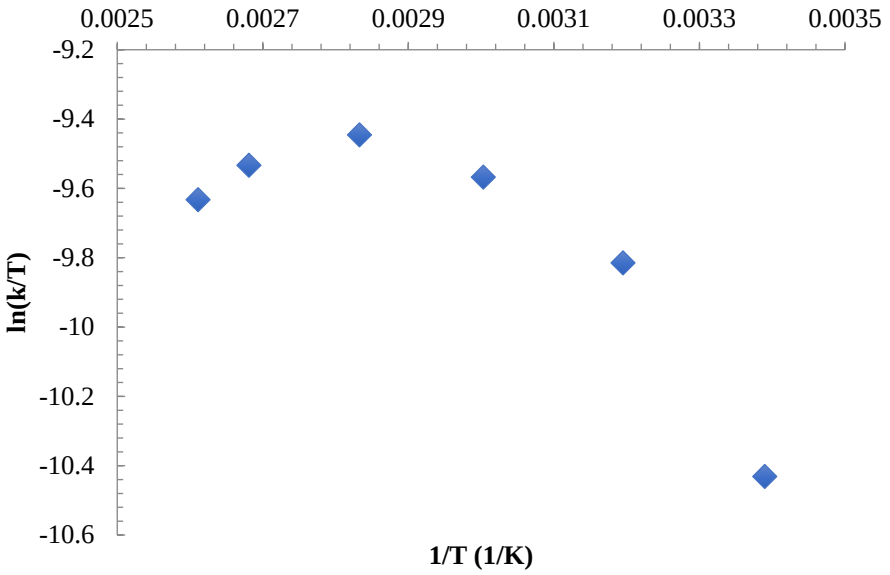


Figure S21. Eyring plot constructed from the observed first order rate constants for the TCC/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (0.876 mmol) from benzyl alcohol (0.00876 mmol) in benzene.

FIRST ORDER PLOTS - TOLUENE

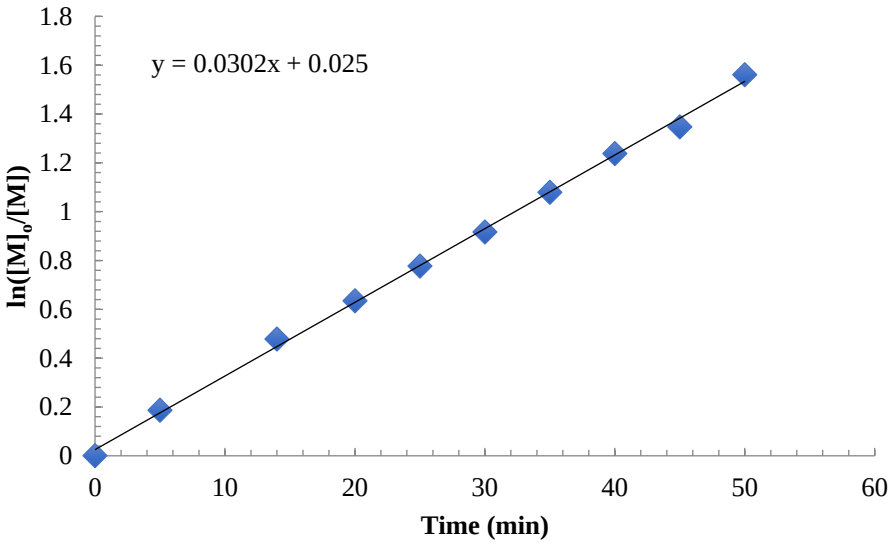


Figure S22. First order evolution of [CL] versus time for the TCC/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 110°C.

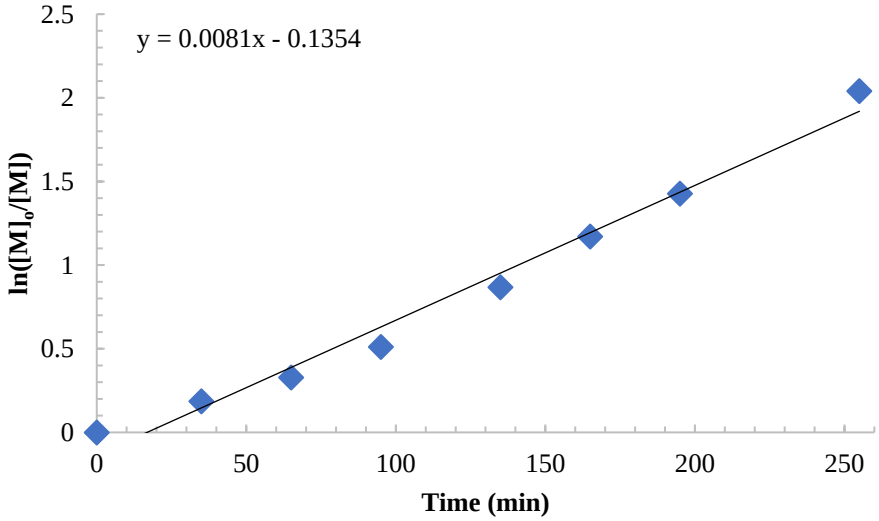


Figure S23. First order evolution of [CL] versus time for the **1-O**/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 110°C.

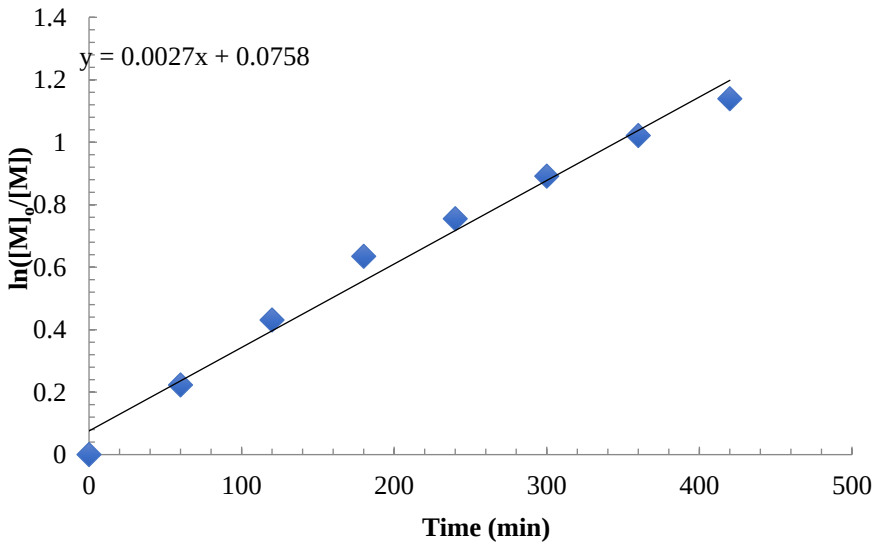


Figure S24. First order evolution of [CL] versus time for the **1-S**/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 110°C.

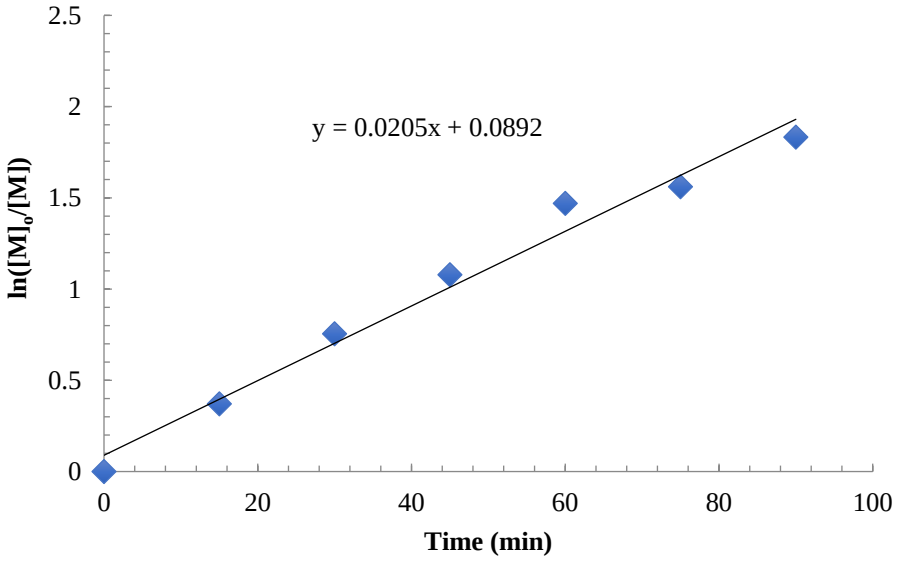


Figure S25. First order evolution of [CL] versus time for the **2-S**/MTBD (0.0219 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 80°C.

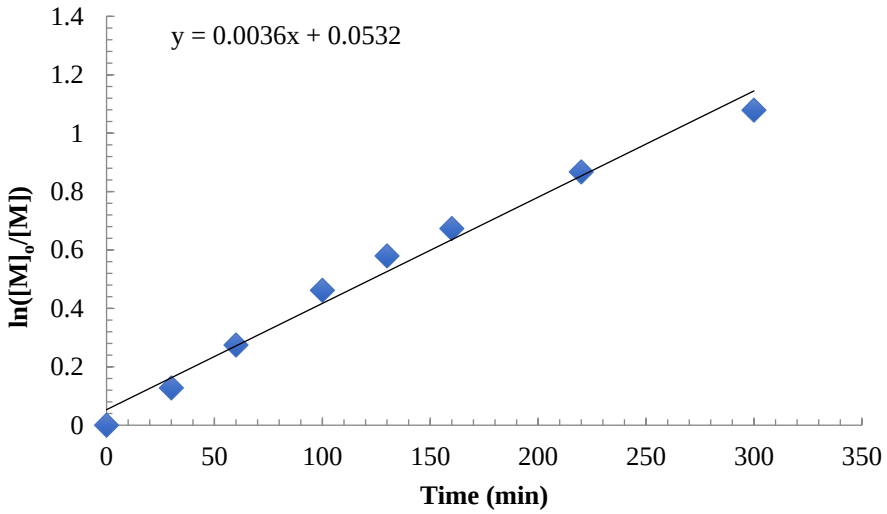


Figure S26. First order evolution of [CL] versus time for the **3-S**/MTBD (0.0146 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 110°C.

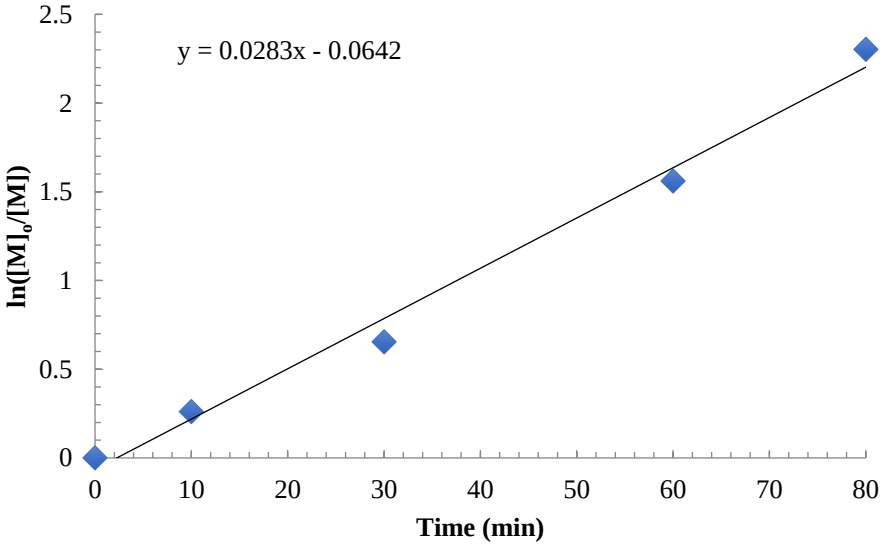


Figure S27. First order evolution of [CL] versus time for the **2-O**/MTBD (0.0219 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 110°C.

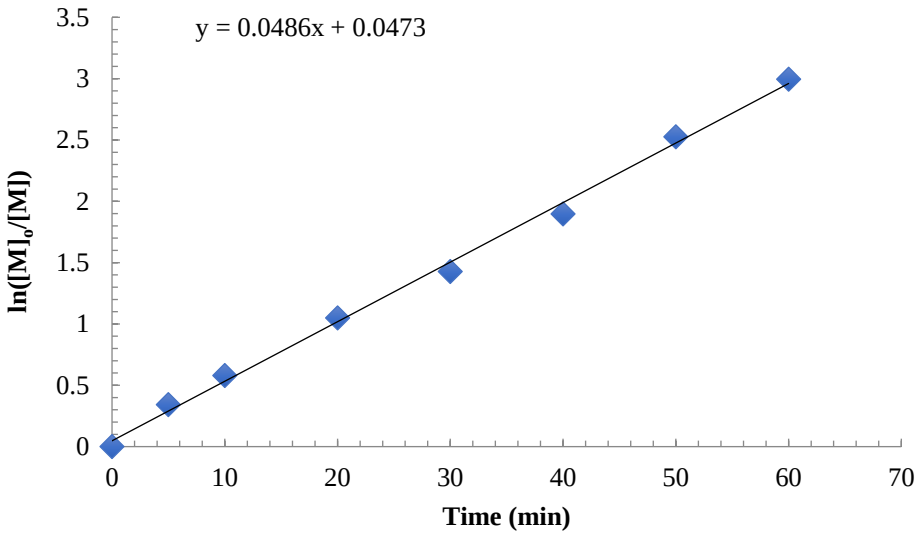


Figure S28. First order evolution of [CL] versus time for the **3-O**/MTBD (0.0146 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 110°C.

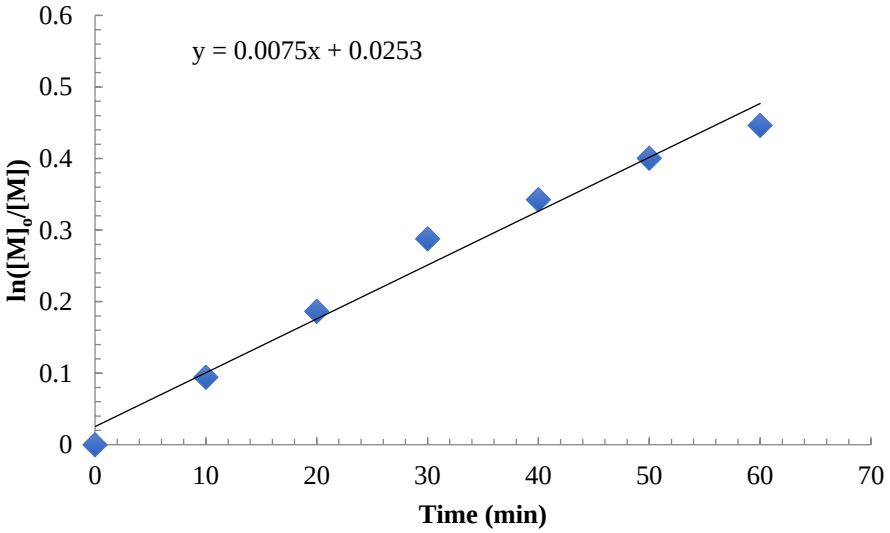


Figure S29. First order evolution of [CL] versus time for the TCC/DBU (0.0438 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 110°C.

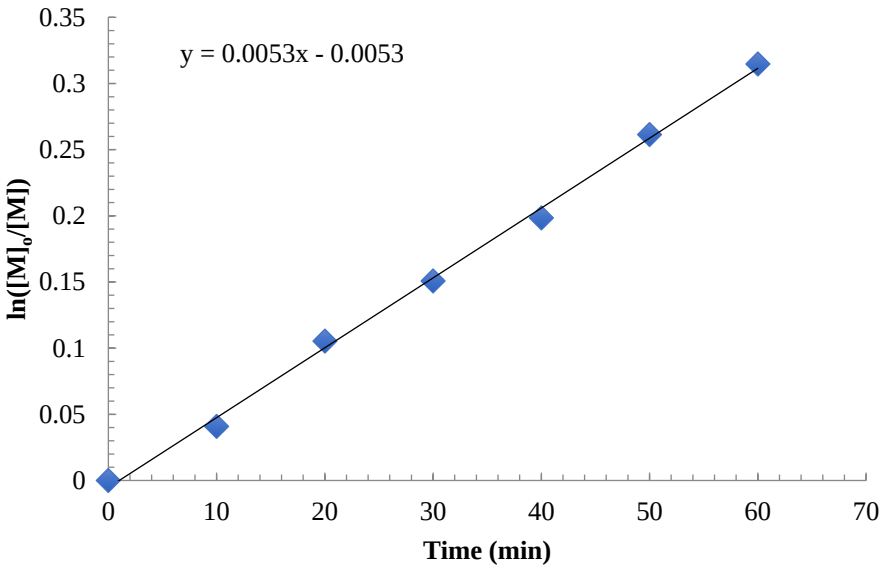


Figure S30. First order evolution of [CL] versus time for the TCC/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (1M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 110°C.

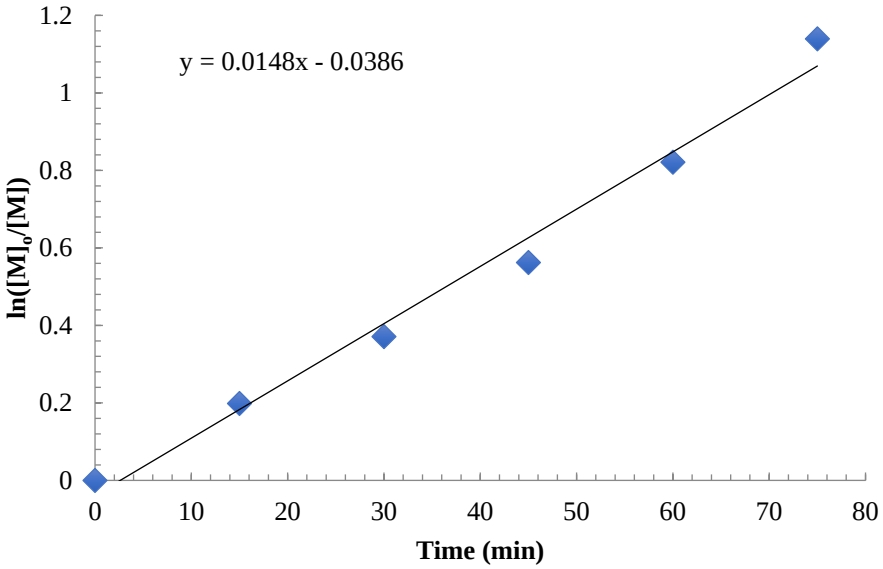


Figure S31. First order evolution of [CL] versus time for the **2-O**/MTBD (0.0219 mmol each) cocatalyzed ROP of CL (1M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 110°C.

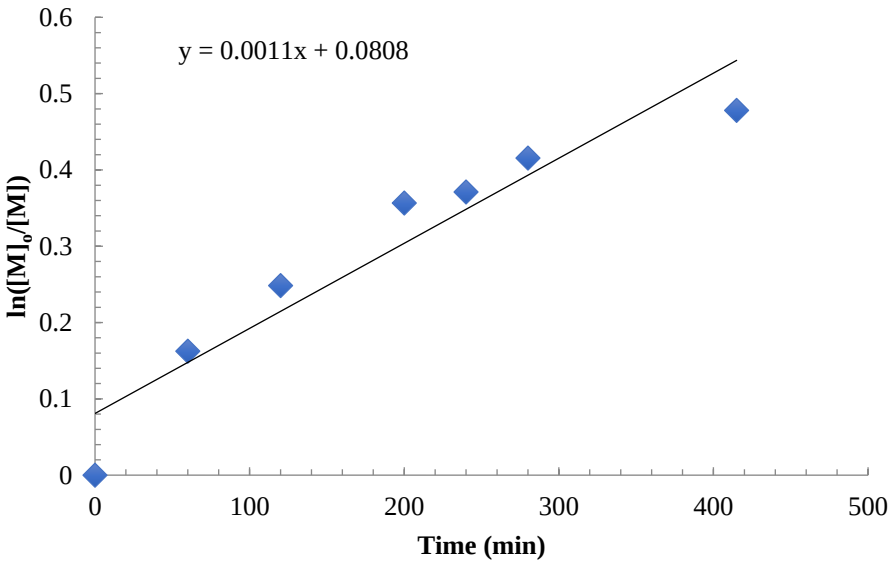


Figure S32. First order evolution of [CL] versus time for the **1-S**/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (1M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 110°C.

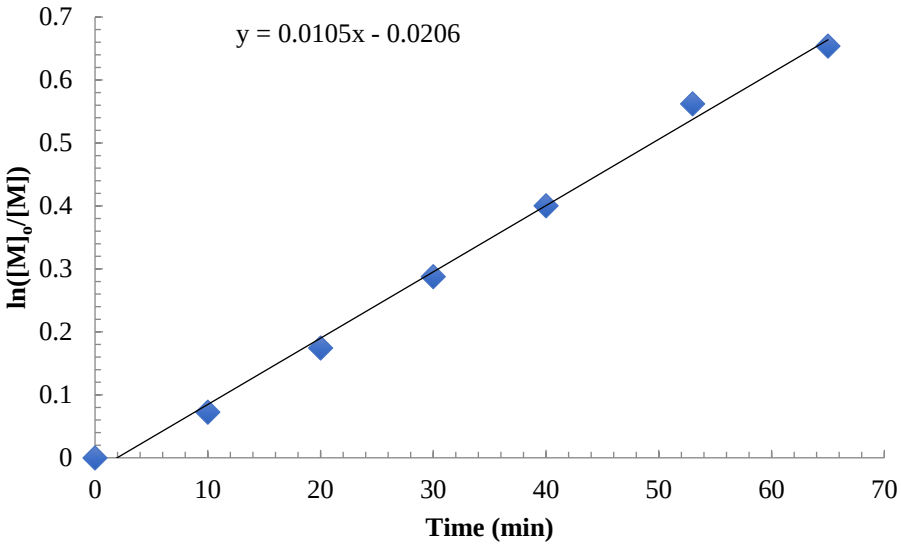


Figure S33. First order evolution of [CL] versus time for the **1-S**/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (3M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in toluene at 110°C.

FIRST ORDER PLOTS – METHYL ISOBUTYL KETONE

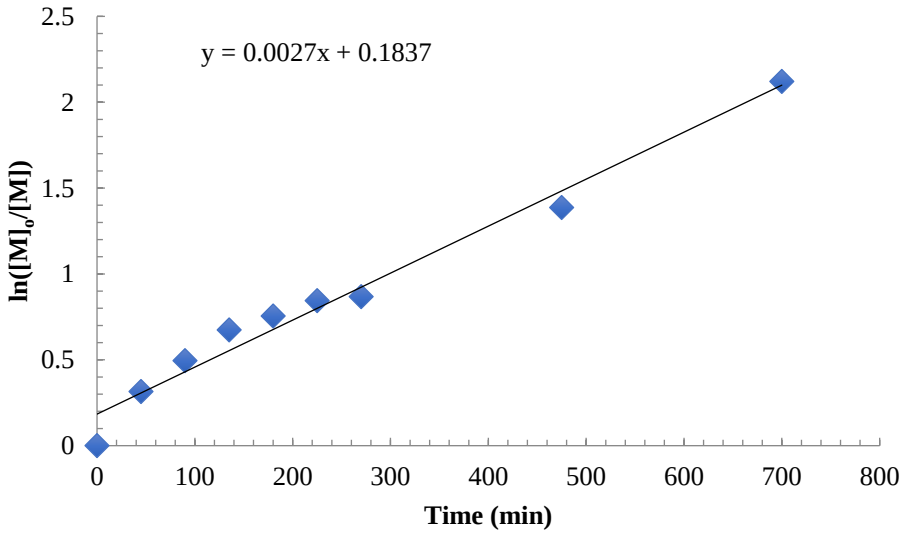


Figure S34. First order evolution of [CL] versus time for the **1-S**/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone at 110°C.

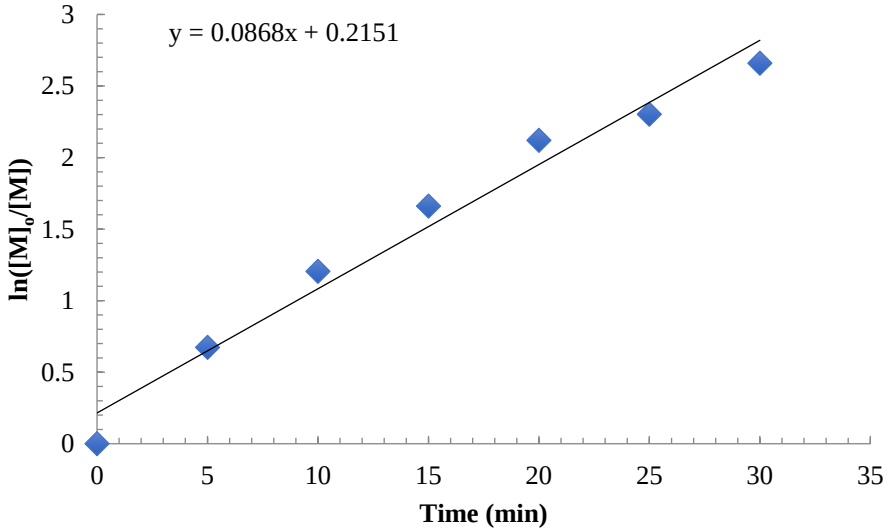


Figure S35. First order evolution of [CL] versus time for the TCC/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone at 110°C.

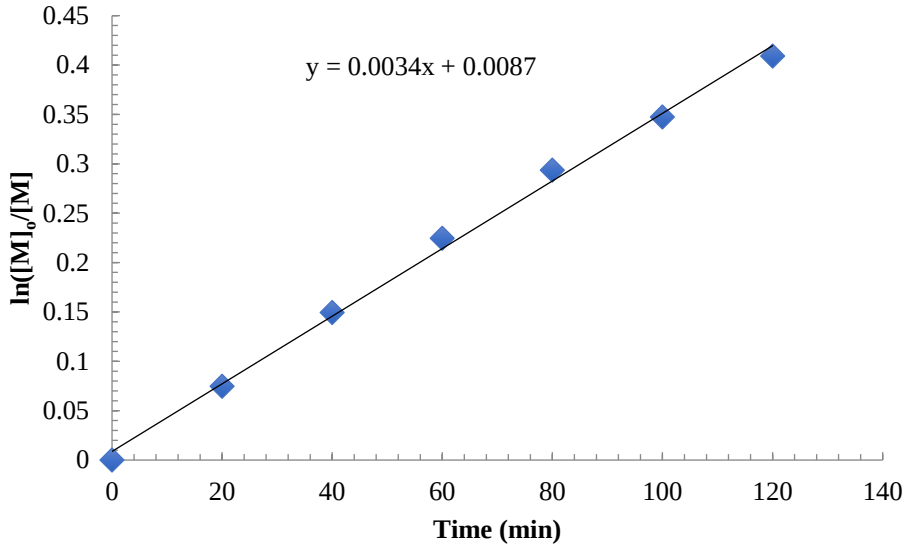


Figure S36. First order evolution of [CL] versus time for the **2-S**/MTBD (0.0219 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone at 60°C.

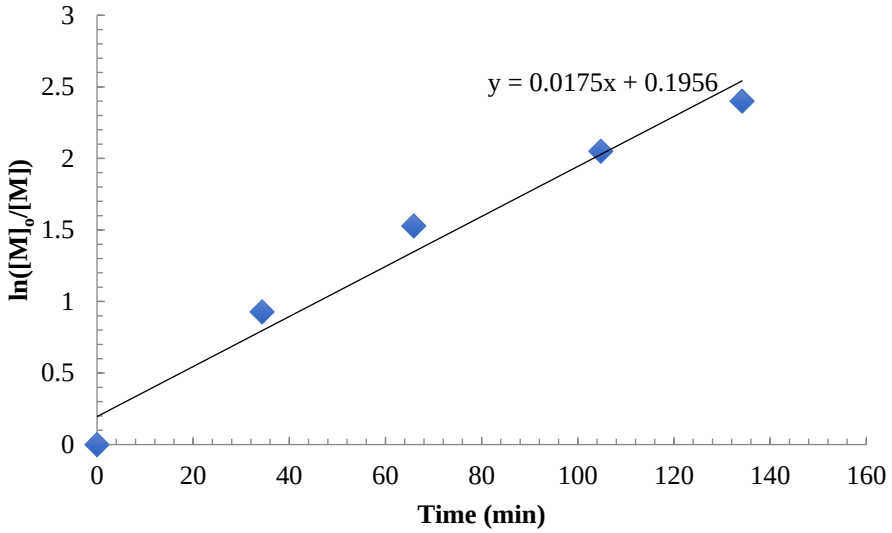


Figure S37. First order evolution of [CL] versus time for the **2-O**/MTBD (0.0219 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone at 110°C.

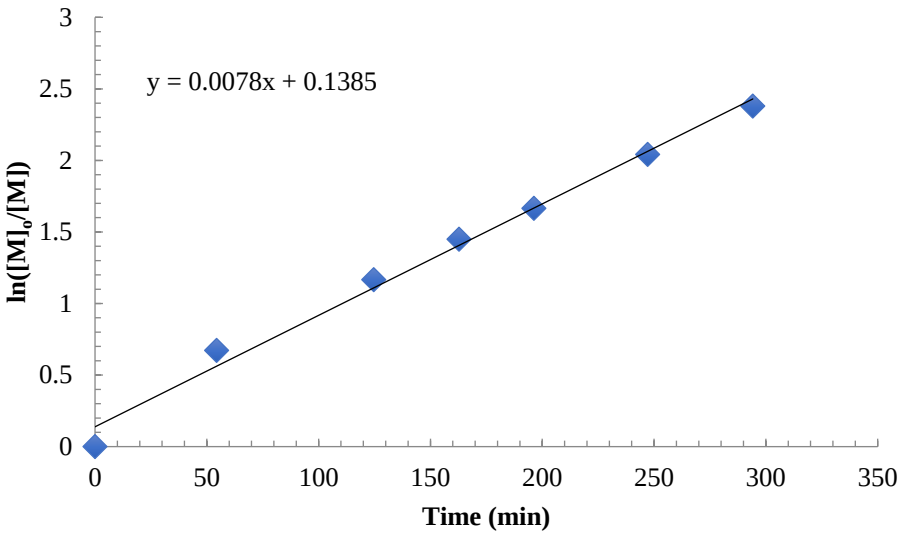


Figure S38. First order evolution of [CL] versus time for the **1-O**/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone at 110°C.

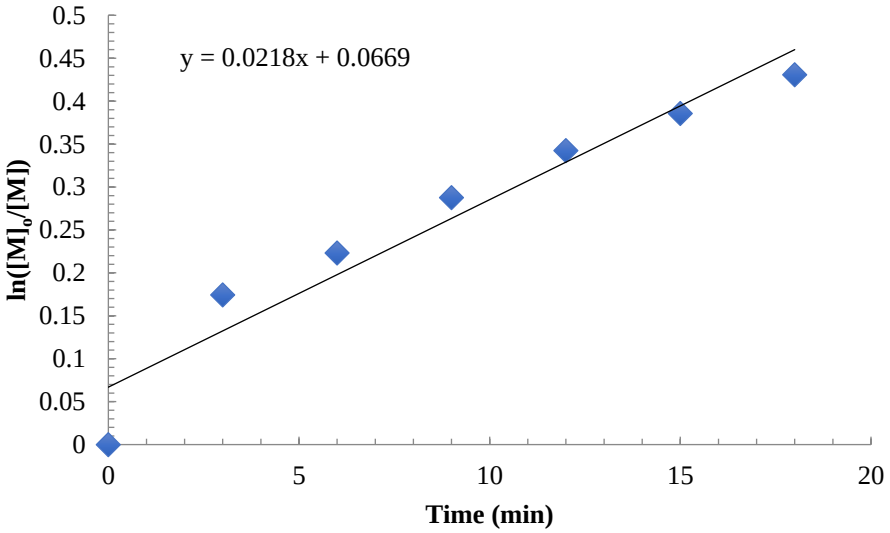


Figure S39. First order evolution of [CL] versus time for the **3-O**/MTBD (0.0146 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in methyl isobutyl ketone at 110°C.

FIRST ORDER PLOT –BENZENE

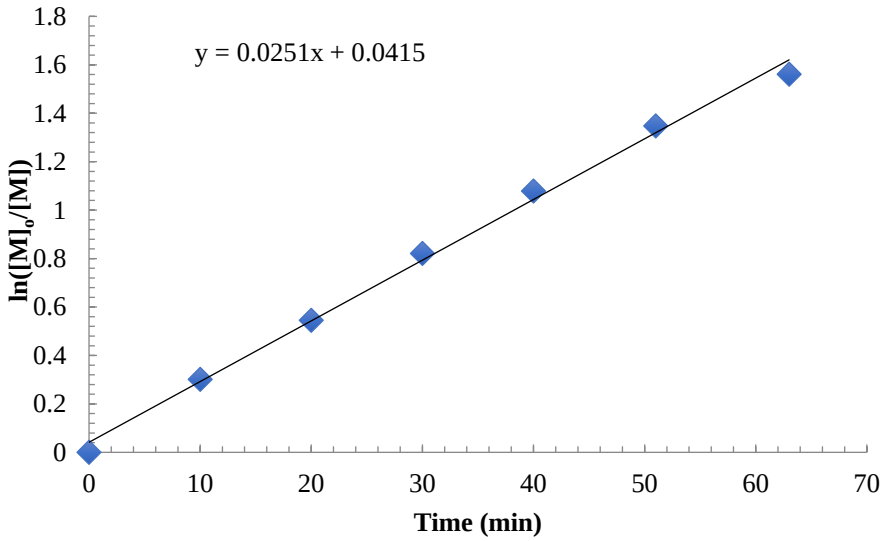


Figure S40. First order evolution of [CL] versus time for the TCC/MTBD (0.0438 mmol each) cocatalyzed ROP of CL (2M, 0.876 mmol) from benzyl alcohol (0.00876 mmol) in benzene at 110°C.

MOLECULAR WEIGHT VS CONVERSION

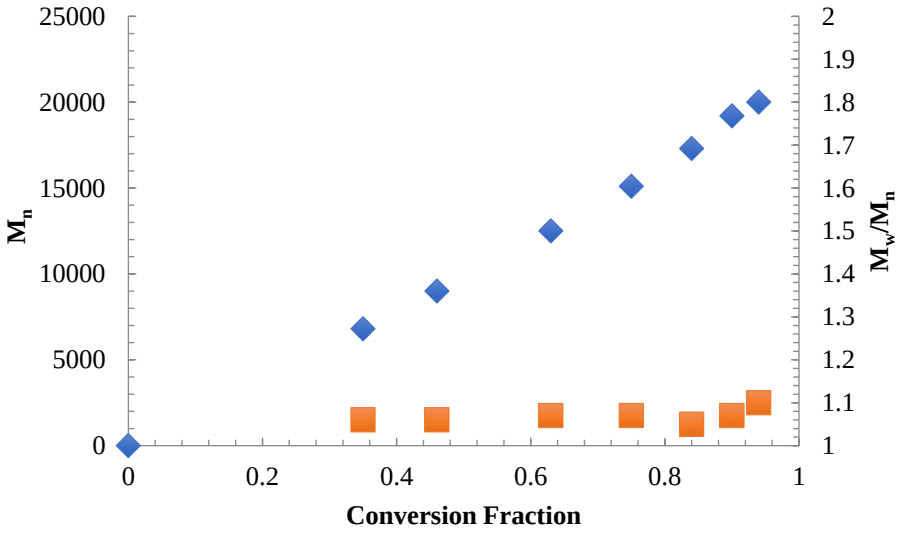


Figure S41. M_n and M_w/M_n versus conversion plot for **1-S** at 80°C. Reaction conditions: CL (0.876 mmol, 2M) in toluene, **1-S**/MTBD (0.0438 mmol each) cocatalyzed from benzyl alcohol (0.00876 mmol).

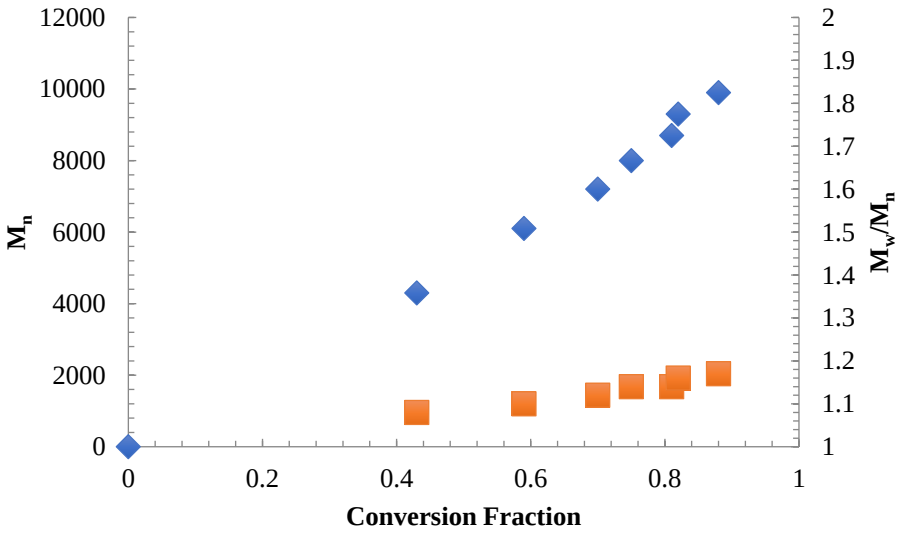


Figure S42. M_n and M_w/M_n versus conversion plot for **1-S** at 110°C. Reaction conditions: CL (0.876 mmol, 2M) in toluene, **1-S**/MTBD (0.0438 mmol each) cocatalyzed from benzyl alcohol (0.0175 mmol).

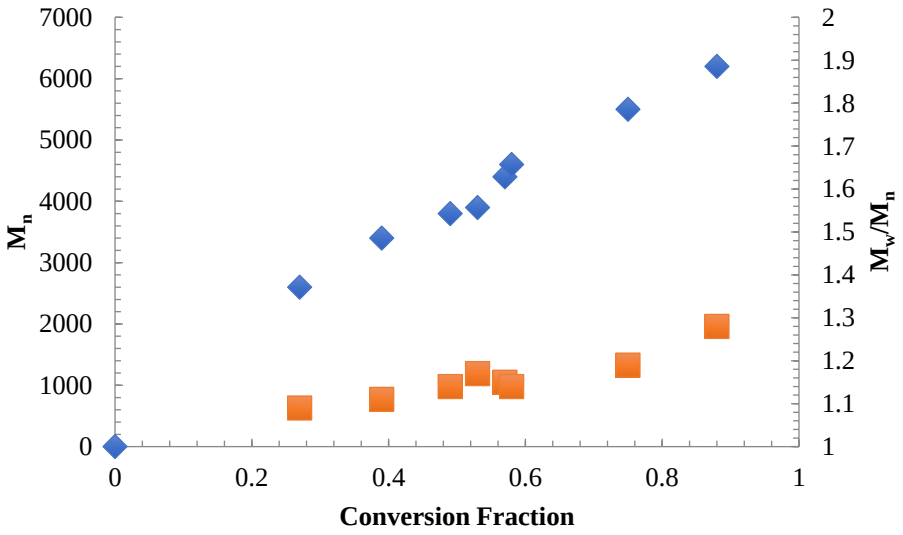


Figure S43. M_n and M_w/M_n versus conversion plot for **1-S** at 110°C. Reaction conditions: CL (0.876 mmol, 2M) in methyl isobutyl ketone, **1-S**/MTBD (0.0438 mmol each) cocatalyzed from benzyl alcohol (0.0175 mmol).

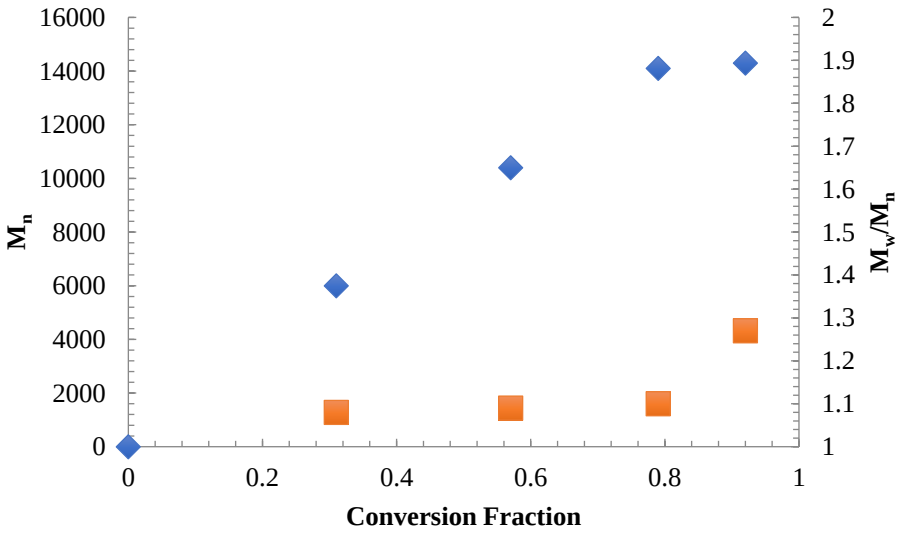


Figure S44. M_n and M_w/M_n Versus Conversion plot for **2-O** at 110°C. Reaction conditions: CL (0.876 mmol, 2M) in toluene, **2-O**/MTBD (0.0219 mmol each), benzyl alcohol (0.00876 mmol).

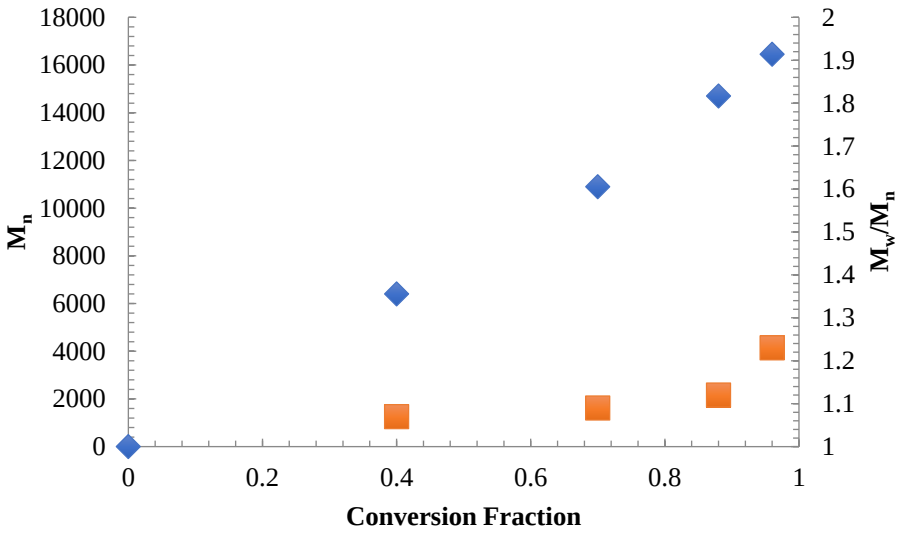


Figure S45. M_n and M_w/M_n Versus Conversion plot for **2-O** at 90°C. Reaction conditions: CL (0.876 mmol, 2M) in toluene, **2-O**/MTBD (0.0219 mmol each) cocatalyzed from benzyl alcohol (0.00876 mmol).

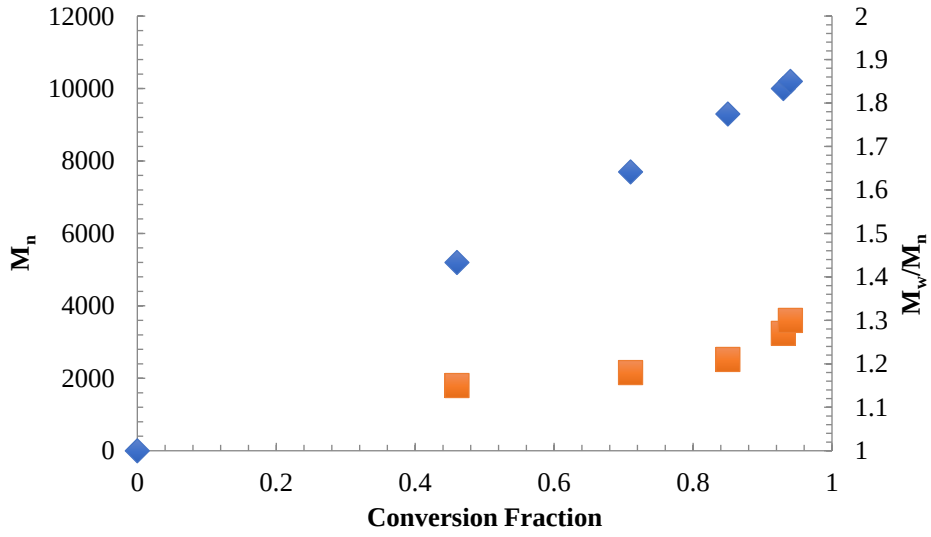


Figure S46. M_n and M_w/M_n versus conversion plot for **2-O** at 90°C. Reaction conditions: CL (0.876 mmol, 2M) in methyl isobutyl ketone, **2-O**/MTBD (0.0219 mmol each) cocatalyzed from benzyl alcohol (0.0175 mmol).