Electronic Supplementary Information for:

Ring-Opening Polymerization of ε-Caprolactone with a Macrocyclic Tetracarbene Indium Complex

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Experimental Section:

General Considerations for Synthesis:

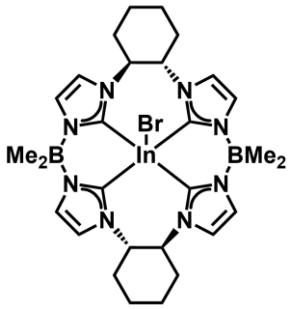
All reactions, workups and manipulations involving the NHC indium complexes were performed in an MBraun Unilab glovebox under N_2. All glassware for glovebox reactions were dried at 170 °C overnight before use. Indium(III) bromide and thallium(I) ethoxide were purchased from Thermo-Fisher at the highest available purities and used as received. ^{n}BuLi and ε-caprolactone were purchased from Sigma Aldrich at the highest available purities and ^{n}BuLi was used as received. Purification of ε-caprolactone was accomplished by first degassing with three freeze-pump-thaw cycles before stirring over CaH_2 for 48 hours under N_2 at ambient temperature followed by vacuum distillation onto freshly activated 4 Å molecular sieves. Tetrahydrofuran (THF), *n*-pentane, and benzene were dried on an Innovative Technologies Pure Solv MD-7 Solvent Purification System, degassed by three freeze-pump-thaw cycles on a Schlenk line, and subsequently stored over activated 4 Å molecular sieves prior to use. $CDCl_3$ and THF-d_8 used for NMR experiments were degassed by three freeze-pump-thaw cycles and stored over activated 4 Å molecular sieves under N_2. [($^{(S,S)\text{-Cy,BMe}}_2$TC^{H})](Br)$_2$ (**1**) was synthesized according to the previously reported literature procedure.[2]

General Considerations for Molecule Characterization:

^{1}H, ^{13}C, and 2D (HSQC, COSY) NMR spectra were recorded at 25 °C on a Bruker AVANCE NEO 500 MHz system. Chemical shifts were referenced to the residual solvent peak for ^{1}H and ^{13}C NMR experiments. High resolution mass spectrometry (HRMS) was analyzed at the Biological and Small Molecule Mass Spectrometry Core Facility located in the Department of Chemistry at the University of Tennessee. LDI-TOF MS was analyzed by Waters Synapt G2-Si MALDI mass spectrometer with a quadrupole time-of-flight mass analyzer. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance (ATR) using the neat complexes.

General Considerations for Crystallography:

Single crystal structures were determined using a Rigaku Oxford Diffraction Supernova with Cu K-alpha radiation (λ = 1.54184 Å) at 120 K (**2**) or a Bruker D8 Venture diffractometer with PHOTON II CPAD detector (**3**) and employing the use of Mo K-alpha radiation (λ = 0.71073 Å) at 100 K. All crystals were mounted on loops (MitiGen®) with Paratone-N (Hampton Research).



Synthesis of [($^{(S,S)\text{-Cy,BMe}_2}$TC^{H})InBr] (**2**):

1 (200 mg, 0.297 mmol) was suspended in 20 mL THF, stirred rapidly for 30 minutes, then cooled for 1 hour at -35°C. $InBr_3$ (116 mg, 0.326 mmol) was dissolved in 1 mL THF and cooled for 1 hour at -35°C. ^{n}BuLi (2.5 M in hexanes, 0.540 mL,1.34 mmol) was then added to the cold ligand slurry and stirred rapidly for 2 minutes at 25°C before returning to -35°C for 5 minutes. This sequence was repeated three more times for a total of 4 cycles before stirring at 25°C for 30 minutes. The clear solution was then cooled at -35°C for 30 minutes. After 30 minutes, the carbene solution was added to the $InBr_3$ solution in 2 mL portions within 1 minute. The reaction mixture was then stirred at 25°C for 18 hours, cooled for 1 hour at -35°C, filtered, then concentrated under vacuum at 25°C. The solids were extracted with 20 mL benzene before filtering and concentrating under vacuum at 25°C. This sequence was repeated two more times. After the third extraction, the solids were again extracted with 20 mL benzene, filtered and the solution was concentrated to 5 mL under vacuum at 25°C before allowing to stand overnight. The next morning the solution was filtered, diluted with 15 mL *n*-pentane, agitated, then allowed to stand for 1 hour at 25°C. The crystalline solids were filtered and washed with 2x5 mL *n*-pentane before drying under vacuum at 25°C for 18 hours to yield **2** as colorless needles (90 mg, 43%).

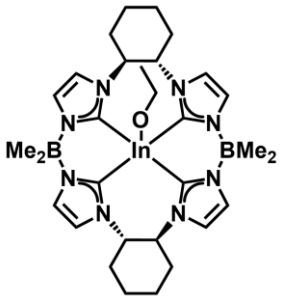
^{1}H NMR: (500 MHz, THF-d_8) δ 7.24 (s, 2H), 7.09 (s, 2H), 7.05 (s, 2H), 7.00 (s, 2H), 6.39 (s, 2H), 4.31 (s, 2H), 2.23 (s, 4H), 2.17 (s, 2H), 1.94 (s, 2H), 1.86 (s, 2H), 1.69 (s, 4H), 1.60 (s, 2H), 0.17 (s, 6H), -0.28 (s, 6H).

^{13}C NMR: (126 MHz, THF-d_8) δ 179.36, 178.15, 124.96, 124.06, 121.40, 116.24, 66.04, 58.90, 38.75, 33.05, 26.16.

IR: 3127, 2934, 2859, 1537, 1446, 1427, 1399, 1349, 1309, 1269, 1232, 1204, 1145, 1112, 1083, 1042, 1031, 1016, 976, 946, 873, 854, 821, 786, 727, 677, 612, 555 cm^{-1}

LDI HRMS *(m/z)*: $[M\text{-}Br]^+$: $(C_{28}H_{40}B_2InN_8)^+$: 625.2632 (found), $[M\text{-}Br]^+$: $(C_{28}H_{40}B_2InN_8)^+$: 625.2610 (calculated).

Synthesis of [($^{(S,S)\text{-Cy,BMe}_2}$TC^{H})InOEt] (**3**):



2 (71 mg, 0.10 mmol) was dissolved in 10 mL benzene. Tl(OEt) (29 mg, 0.11 mmol) was dissolved in 1 mL benzene and added to the solution of **2** in one portion. Pale yellow solids precipitated immediately. The suspension was stirred for 30 minutes at 25°C, then the reaction mixture was filtered and concentrated under vacuum at 25°C. The solids were suspended in 20 mL *n*-pentane, stirred rapidly for 1 hour, filtered, washed with 2x5 mL *n*-pentane, and dried under vacuum at 25°C for 1 hour. The solids were then extracted with 20 mL benzene, filtered and the solution was concentrated to 2 mL under vacuum at 25°C before allowing to stand overnight. The next morning the solution was filtered, diluted with 18 mL *n*-pentane, agitated, then allowed to stand for 1 hour at 25°C. The crystalline solids were filtered and washed with 2x5 mL *n*-pentane before drying under vacuum at 25°C for 18 hours to yield **3** as colorless needles (44 mg, 67%).

^{1}H NMR: (500 MHz, THF-d_8) δ 7.19 (s, 2H), 7.07 (s, 2H), 7.03 (s, 2H), 7.00 (s, 2H), 6.00 (s, 2H), 4.21 (s, 2H), 4.01 (d, *J* = 25.9 Hz, 2H), 2.22 (s, 4H), 2.15 (s, 2H), 1.93 (s, 2H), 1.81 (s, 2H), 1.59 (d, *J* = 25.9 Hz, 7H), 1.23 (s, 3H), 0.16 (s, 6H), -0.28 (s, 6H).

^{13}C NMR: (126 MHz, THF-d_8) δ 181.77, 180.39, 124.91, 124.13, 121.06, 115.78, 63.14, 58.91, 38.98, 33.23, 23.65.

IR: 3374, 3123, 2940, 2866, 1629, 1536, 1452, 1387, 1348, 1311, 1261, 1122, 1083, 1035, 968, 946, 837, 794, 756, 680, 657, 576, 563, 557 cm^{-1}

LDI HRMS *(m/z)*: $[M+H]^+$: $(C_{30}H_{47}B_2InN_8O)^+$: 671.3059 (found), $[M+H]^+$: $(C_{30}H_{47}B_2InN_8O)^+$: 671.3030 (calculated).

Synthesis of polycaprolactone:

Inside a N_2 filled glovebox, initiator (0.01 mmol) was dissolved in 1 mL benzene and stirred at 25°C in an airtight vial. ε-Caprolactone (114 mg, 1 mmol) was dissolved in 0.2 mL benzene. The solution of ε-caprolactone was then added to the solution of initiator in one portion and the vial was sealed. 50 µL aliquots were removed at the specified time intervals and quenched with chloroform prior to NMR analysis. The final polycaprolactone solution was also quenched with chloroform at the last time interval. Prior to SEC analysis, all aliquot solutions and the final polycaprolactone solution were filtered before concentrating under N_2 flow then drying the solids under high vacuum at 25°C for 18 hours. No polycaprolactone was present in parallel control reactions.

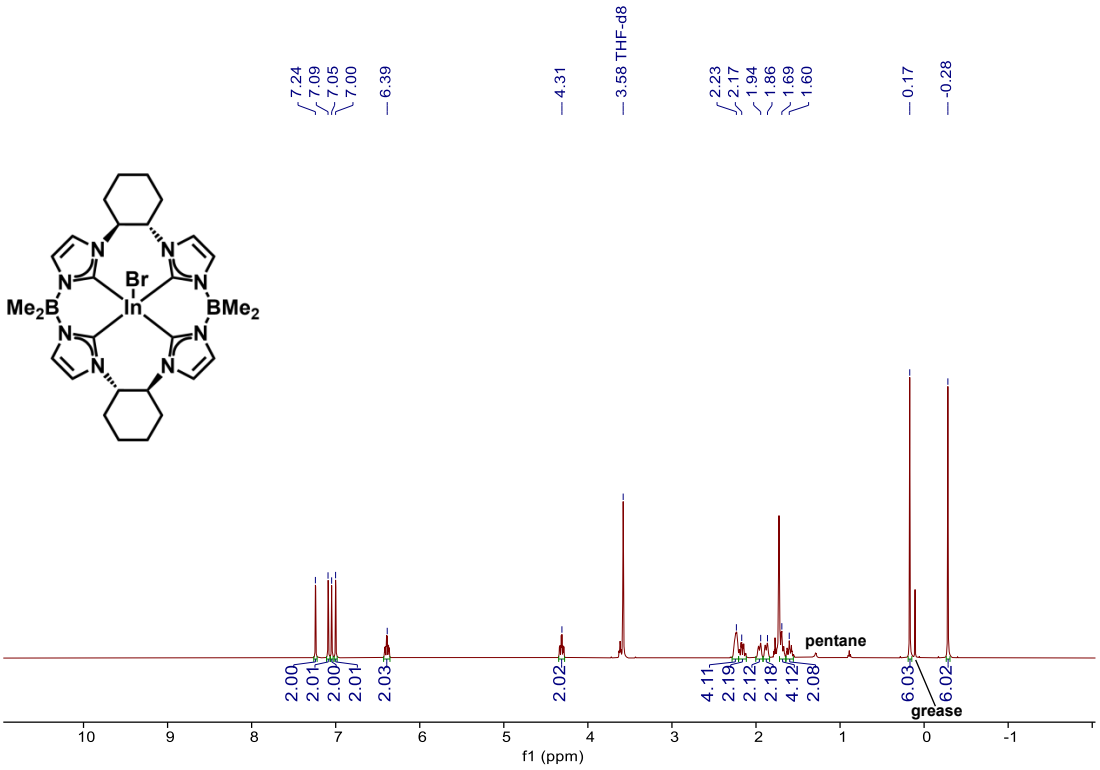


Figure S1. ^{1}H NMR of **2** in THF-d_8.

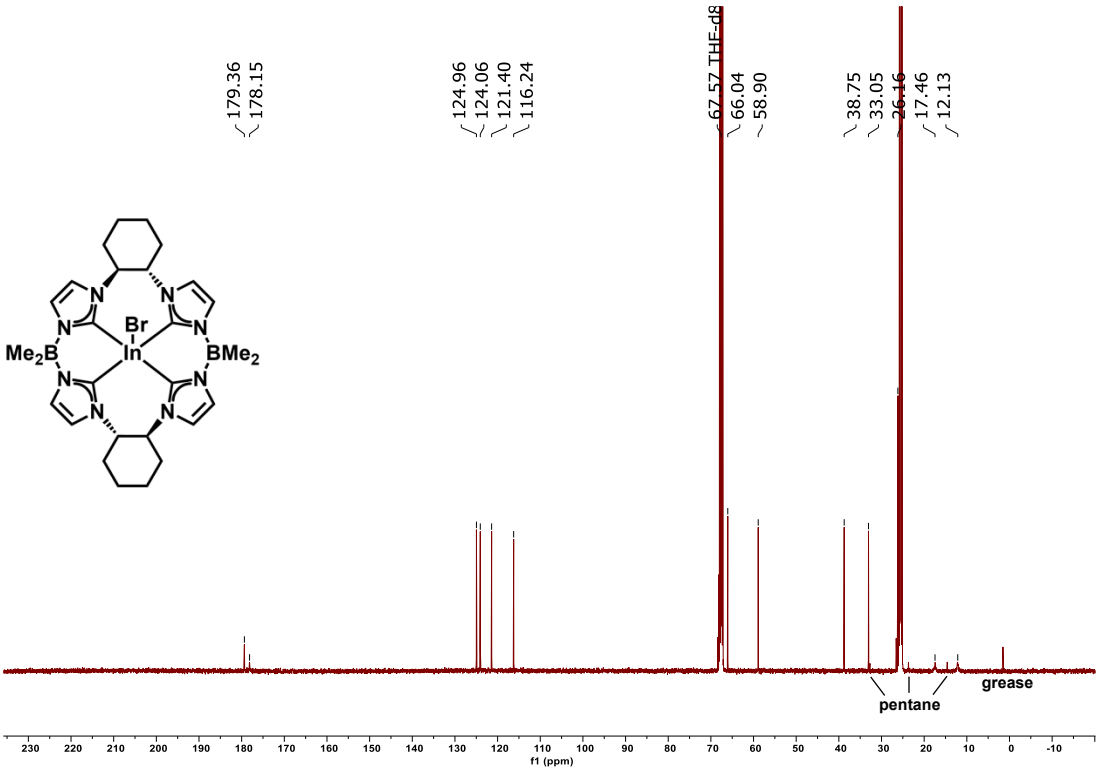


Figure S2. ^{13}C NMR of **2** in THF-d_8.

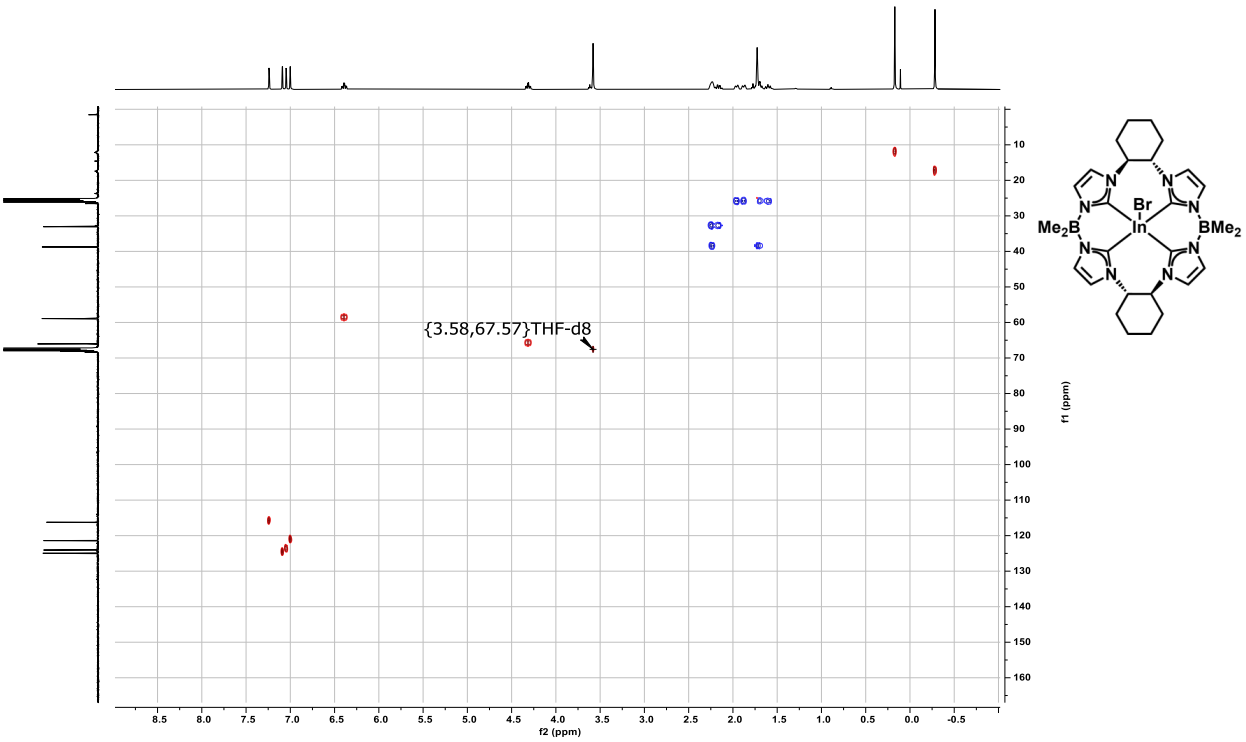


Figure S3. HSQC NMR of **2** in THF-d_8.

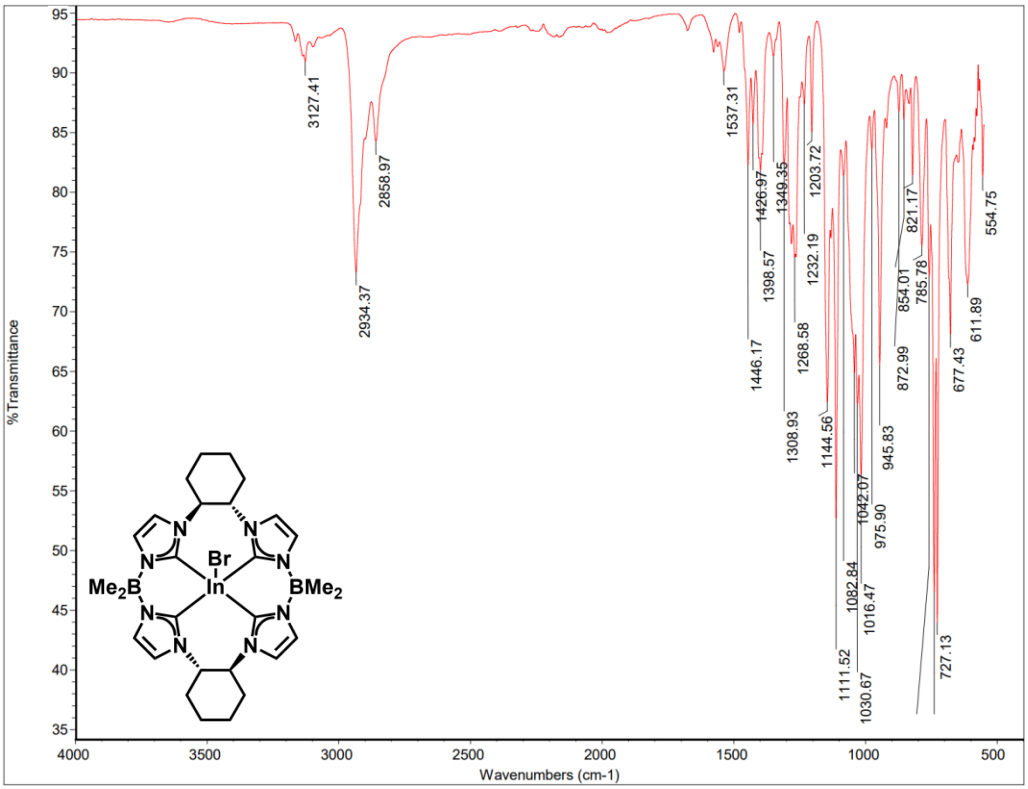


Figure S4. IR of **2**.

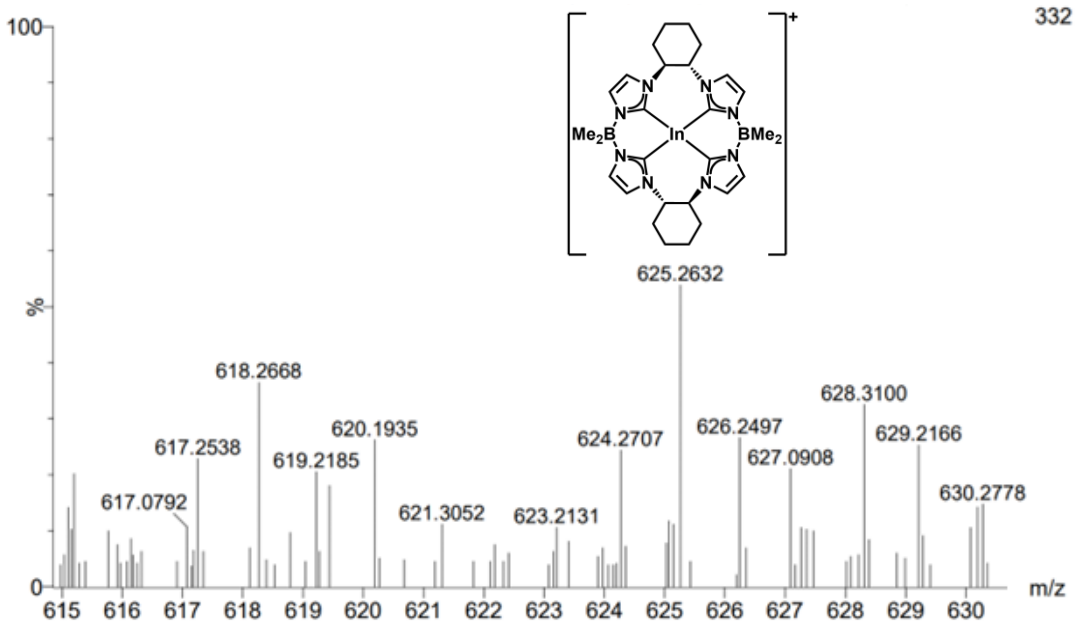


Figure S5. LDI HRMS of **[2-Br]⁺**.

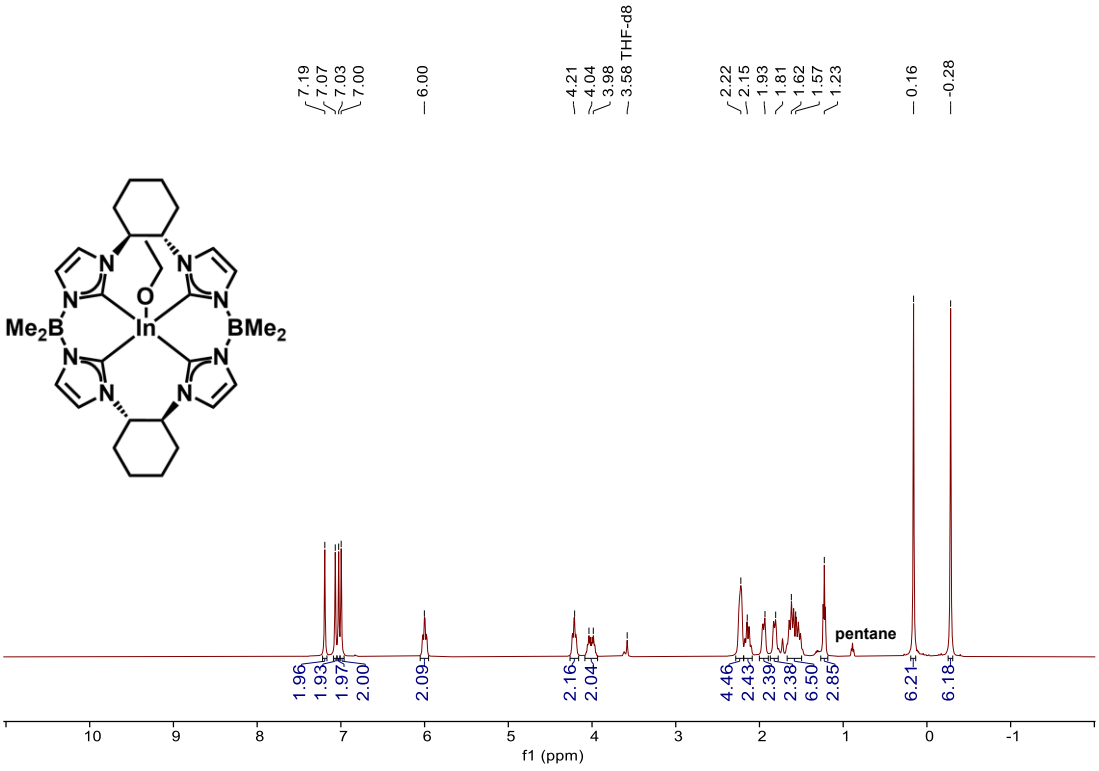


Figure S6. ^{1}H NMR of **3** in THF-d_8.

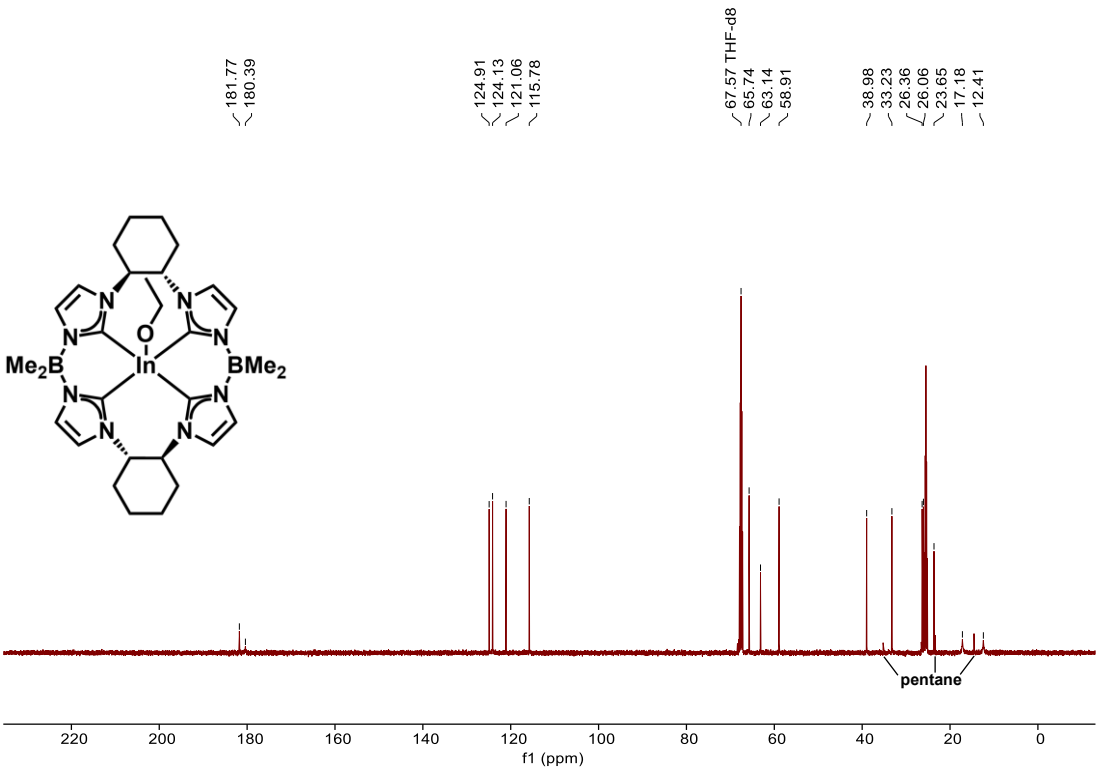


Figure S7. ^{13}C NMR of **3** in THF-d_8.

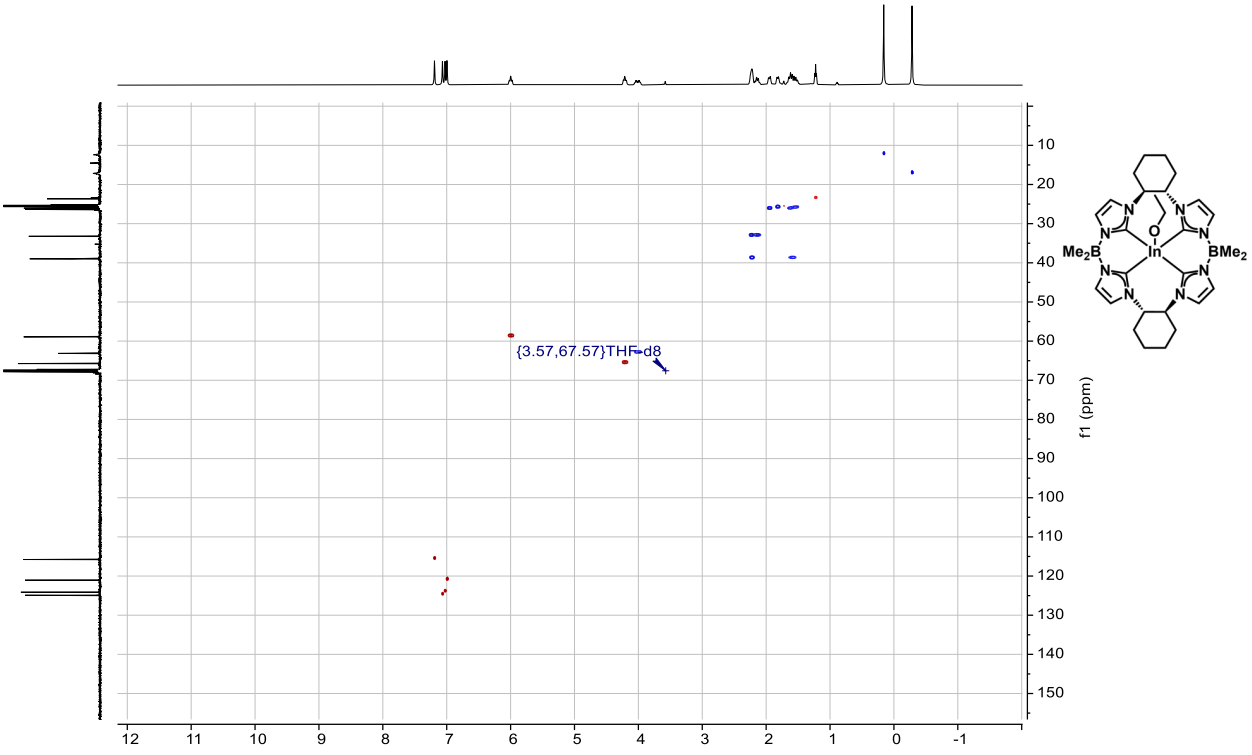


Figure S8. HSQC NMR of **3** in THF-d_8.

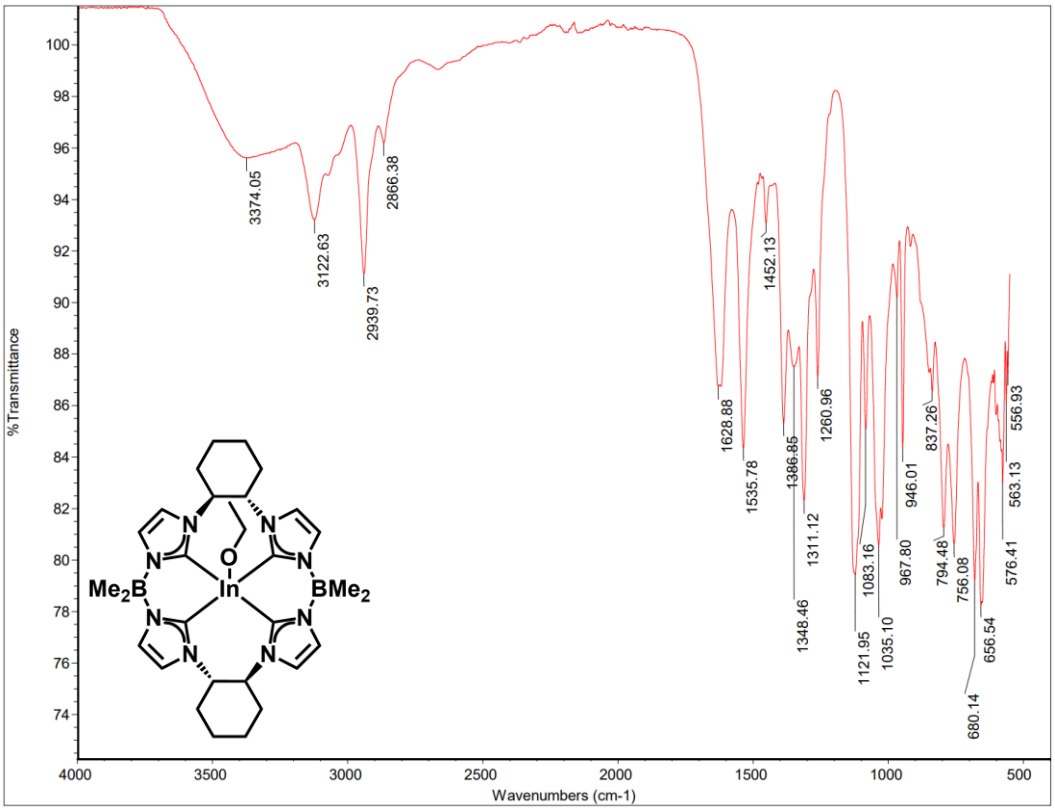


Figure S9. IR of **3.**

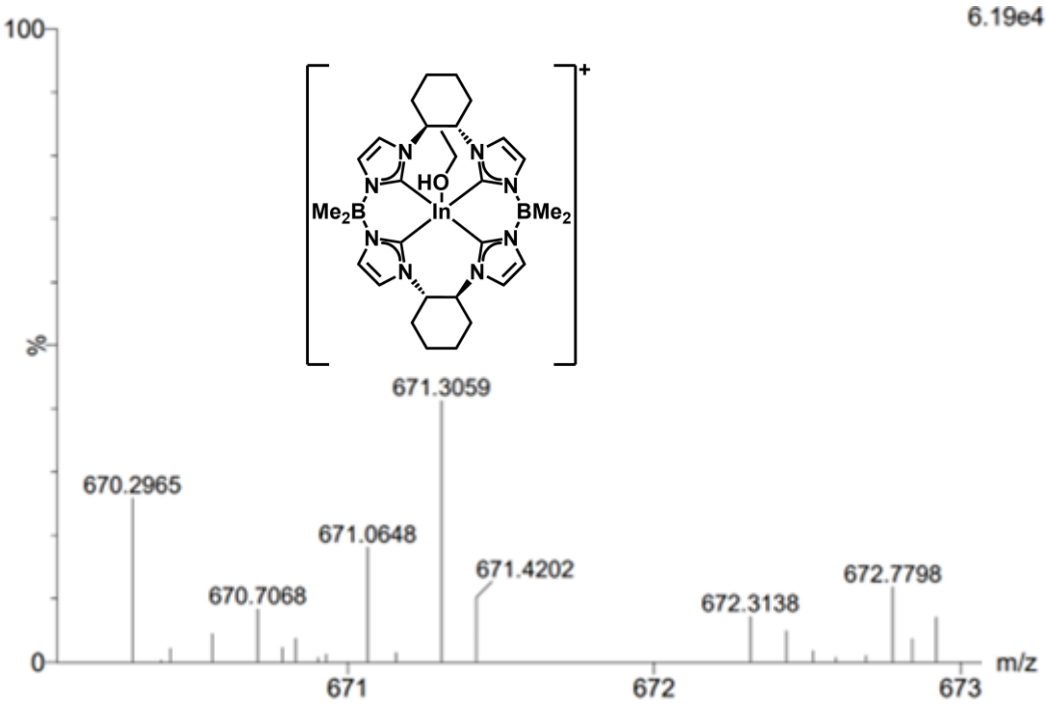


Figure S10. LDI HRMS of **[3+H]⁺**.

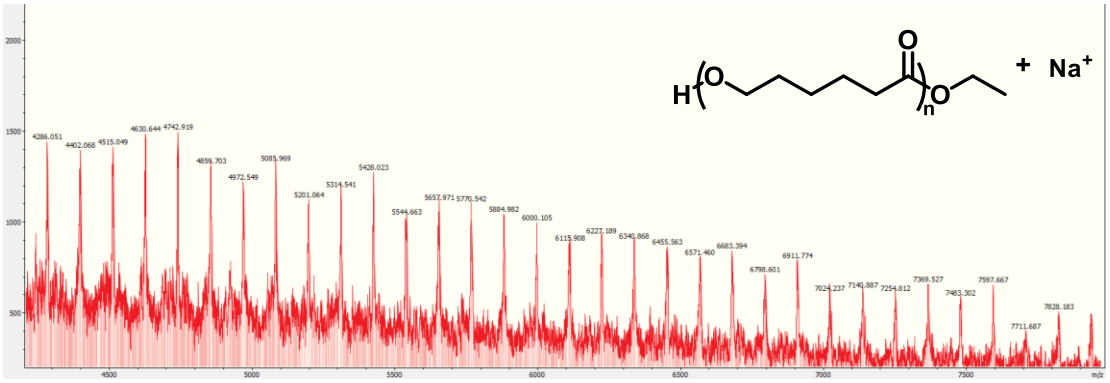


Figure S11. MALDI-TOF MS of polycaprolactone synthesized using **3.**

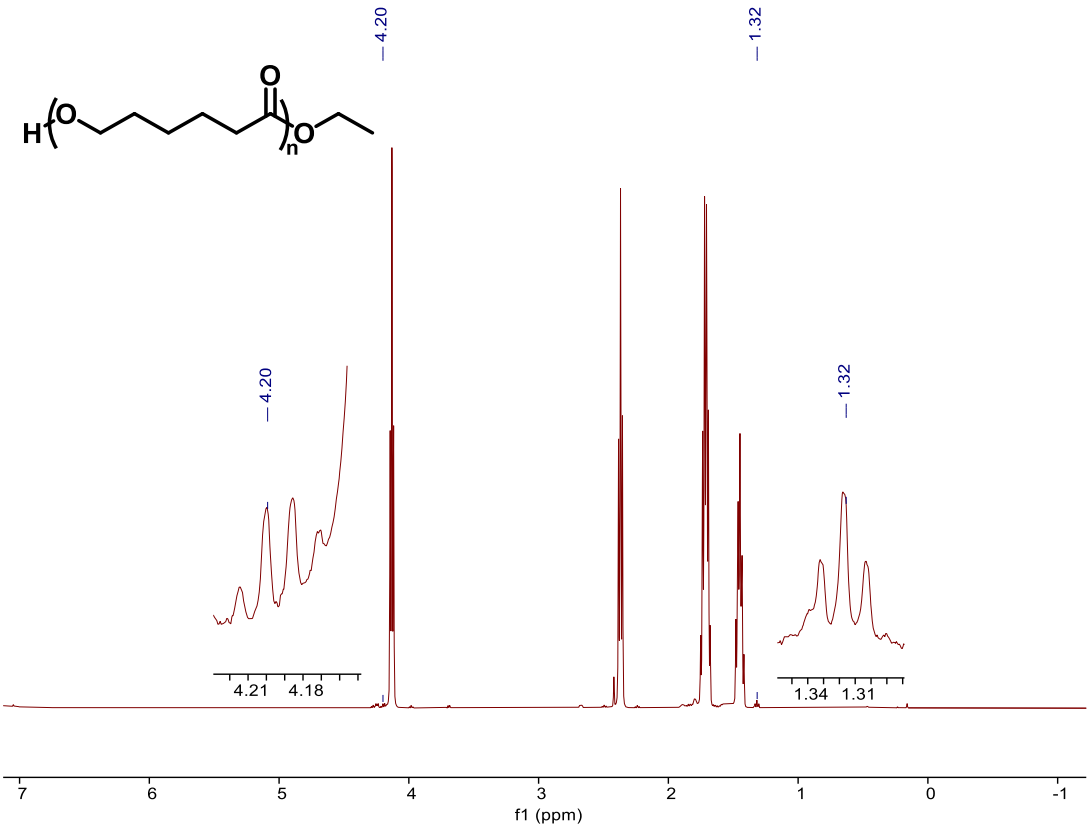
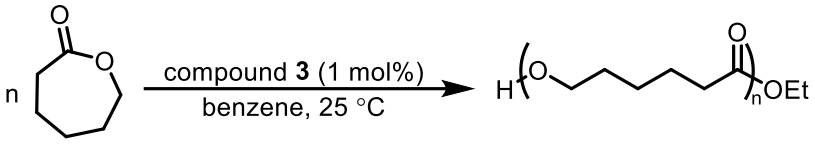


Figure S12. ^{1}H NMR of polycaprolactone in $CDCl_3$ synthesized using **3** showing ethoxy initiator peaks**.**

Table S1. Polymerization of ε-caprolactone (CL) using **3** as initiator.



Entry	Time (min)	Conversion (%)[a]	$M_{n,calc}$ (kDa)[b]	$M_{n,obs}$ (kDa)[c]	Đ[c]
1	5	15	1.7	1.7	1.31
2	10	33	3.7	4.3	1.17
3	15	50	5.7	6.9	1.11
4	20	64	7.3	8.9	1.09
5	25	77	8.8	11.5	1.08
6	30	87	9.9	12.8	1.08
7	35	93	10.6	13.6	1.08
8	40	96	10.9	14.3	1.07
9	45	98	11.2	14.6	1.07

[initiator]:[CL] = 1:100, [M] = 0.075 M in benzene. [a] Conversion calculated using ^{1}H NMR spectroscopy. [b] $M_{n,calc}$ of polymers calculated from the monomer conversion $M_{n,calc} = M_{CL} \times ([M]/[I]) \times$ conversion assuming 1 chain per catalyst. [c] Determined by SEC analysis using polystyrene standard in THF. M_n values corrected by a correction coefficient (0.56).[3]

References

1. Cramer, S.A.; Sturgill, F.L.; Chandrachud, P.P.; Jenkins, D.M. *Dalton Trans.*, **2014**, *43*, 7687-7690.
2. DeJesus, J.D.; Jenkins, D.M. *Chem. Eur. J.,* **2020**, *26*, 1429.
3. M. Save, M. Schappacher and A. Soum, *Macromol. Chem. Phys.*, **2002**, *203*, 889–899.