

## Supporting Information

### **Tunable hydantoin and base binary organocatalysts in ring-opening polymerizations**

Lei Zhang, Zikun Luo, Zhenjiang Li, Chan Zhang, Rui Yan, Jie Li, Bo Liu, Yongzhu Hu, Fangyuan Zhou, Kai Guo\*

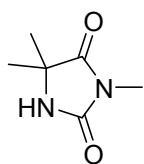
State Key Laboratory Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, 30 Puzhu Road South, Nanjing 211816, China.

Email: guok@njtech.edu.cn; zjli@njtech.edu.cn.

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### Preparation of 3,5,5-trimethylhydantoin (HHyd3)



3,5,5-Trimethylhydantoin<sup>1</sup> was prepared by literature procedures. 5,5-dimethylhydantoin (1.00 g, 7.80 mmol) and equimolar of  $K_2CO_3$  (1.10 g, 7.80 mmol) was added in 6 mL EtOH, the mixture was stirred for 0.5 h at room temperature.  $CH_3I$  (1.11 g, 7.80 mmol) was added dropwise and the mixture stirred for additional 2 h at room temperature. Then the temperature was increased to 60 °C and the mixture was stirred for 3 h. The solvent was evaporated under reduced pressure and the residue dissolved in 4 mL  $H_2O$ . Extraction with ethyl acetate (3 x 4 mL), drying over  $Na_2SO_4$  overnight and evaporation of the solvent at reduced pressure afforded the product as a white solid. Yield 86%.

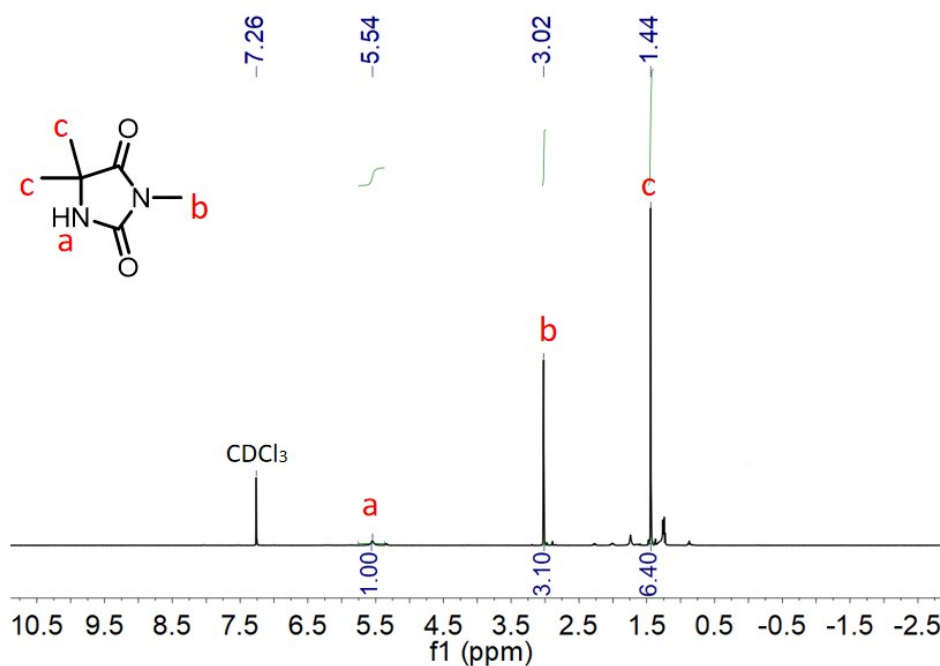


Figure S1. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of 3,5,5-trimethylhydantoin (HHyd3)

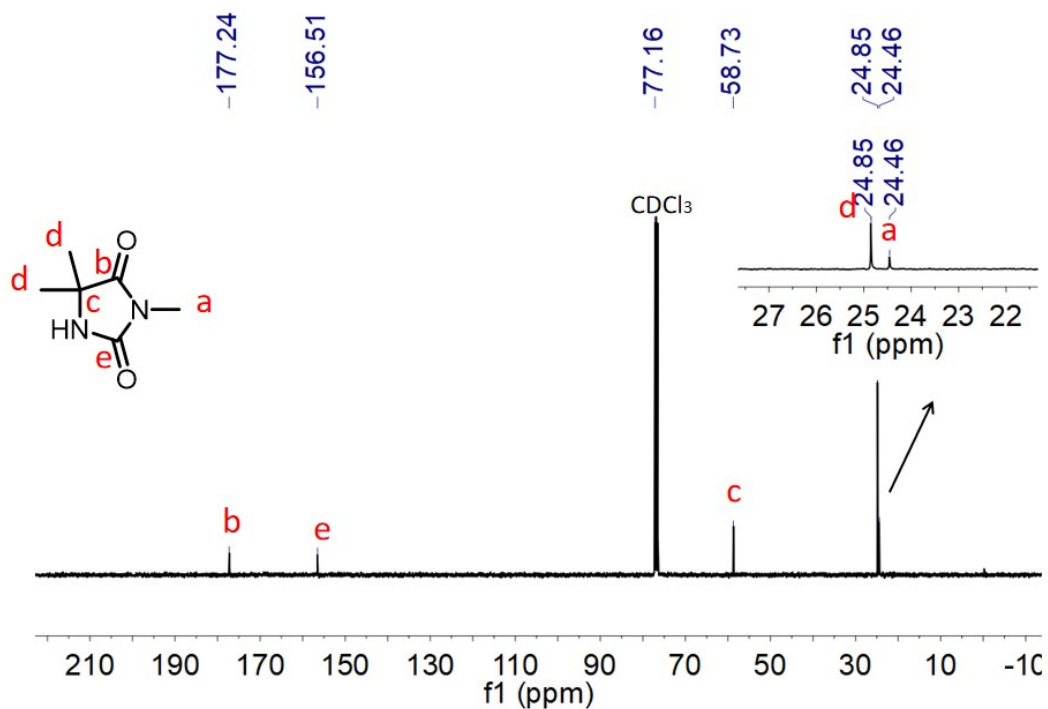
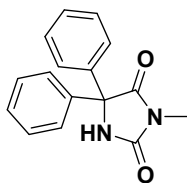


Figure S2.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 100 MHz) of 3,5,5-trimethylhydantoin (HHyd3)

#### Preparation of 3-methyl-5,5-diphenylhydantoin (HHyd4)



3-Methyl-5,5-diphenylhydantoin<sup>2</sup> was prepared by literature procedures. 5,5-diphenylhydantoin (6.30 g, 25.0 mmol) and equimolar of KOH (1.40 g, 25.0 mmol) was added in 25 mL EtOH, the mixture was stirred for 0.5 h at 95°C.  $\text{CH}_3\text{I}$  (1.56 ml, 25.0 mmol) was added dropwise and the mixture stirred for additional 5 h at room temperature. The solvent was extracted with ethyl acetate and  $\text{H}_2\text{O}$ , drying over  $\text{Na}_2\text{SO}_4$  overnight and evaporation of the solvent at reduced pressure afforded the product as a white solid. Yield 54%.

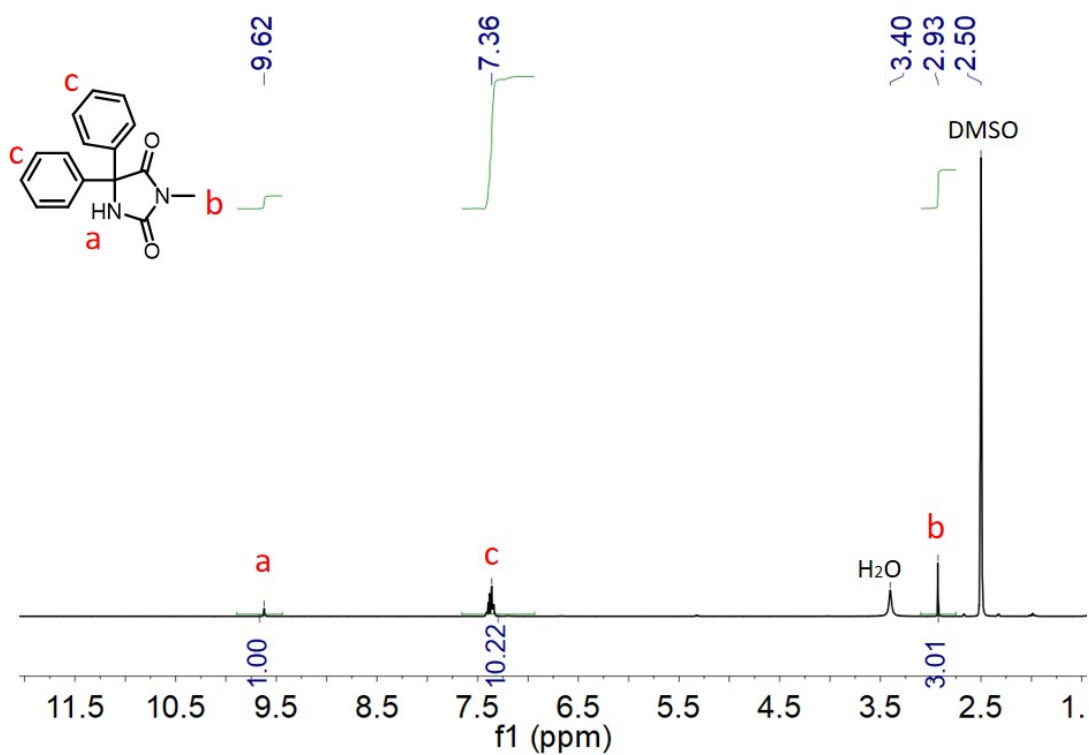


Figure S3.  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ , 400 MHz) of 3-methyl-5,5-diphenylhydantoin (HHyd4)

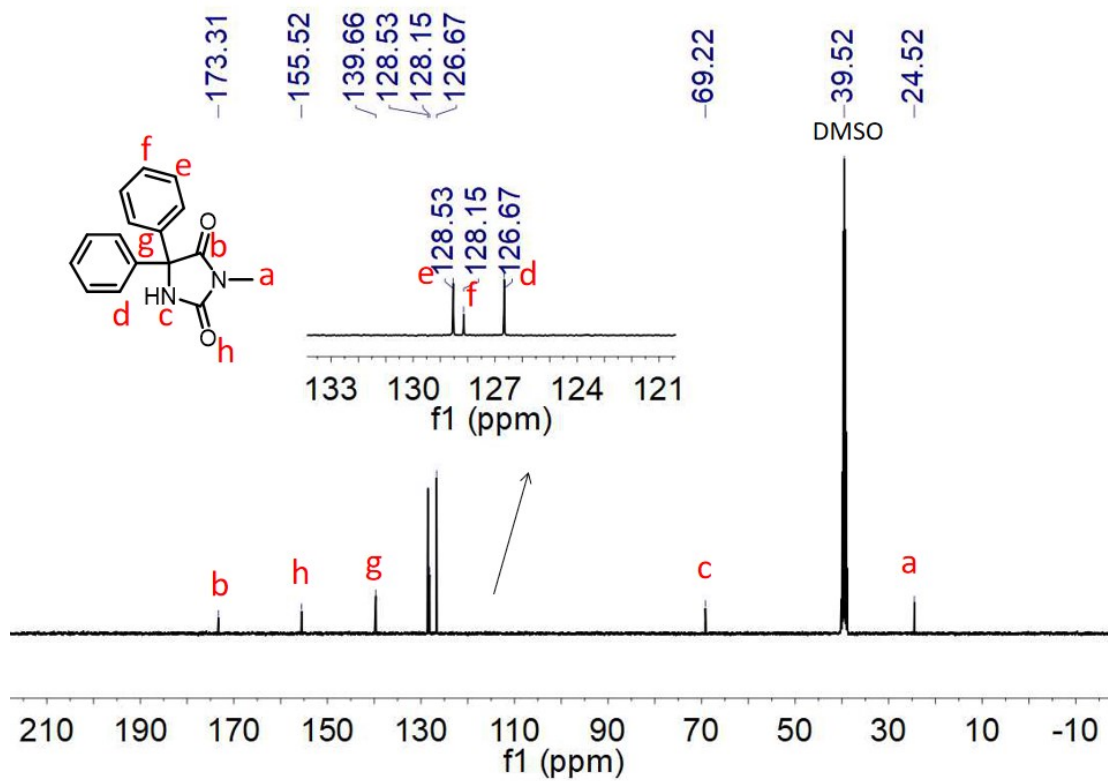
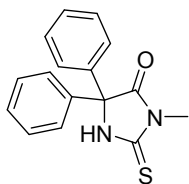


Figure S4.  $^{13}\text{C}$  NMR spectrum (DMSO- $d_6$ , 100 MHz) of 3-methyl-5,5-diphenylhydantoin (HHyd4)

### Preparation of 3-methyl-5,5-diphenyl-2-thioxoimidazolidin-4-one (HHyd5)



3-Methyl-5,5-diphenyl-2-thioxoimidazolidin-4-one<sup>3</sup> was prepared by literature procedures. 5,5-diphenyl-2-thioxoimidazolidin-4-one (6.71 g, 25.0 mmol) and equimolar of KOH (1.40 g, 25.0 mmol) was added in 25 mL EtOH, the mixture was stirred for 0.5 h at 95°C. CH<sub>3</sub>I (1.56 ml, 25.0 mmol) was added dropwise and the mixture stirred for additional 5 h at room temperature. The solvent was extracted with ethyl acetate and H<sub>2</sub>O, drying over Na<sub>2</sub>SO<sub>4</sub> overnight and evaporation of the solvent at reduced pressure. The product as a yellow solid was afforded by chromatographic column chromatography (PE: EA=5:1). Yield 38%.

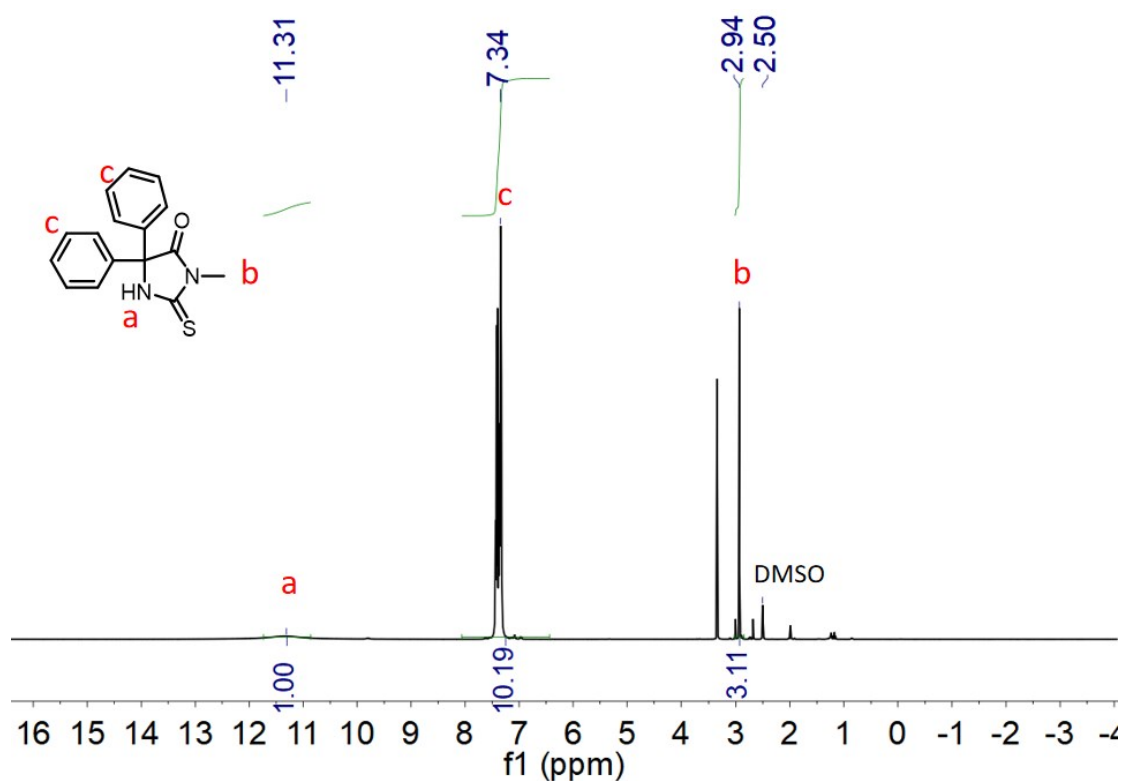


Figure S5. <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>, 400 MHz) of 3-methyl-5,5-diphenyl-2-thioxoimidazolidin-4-one (HHyd5)

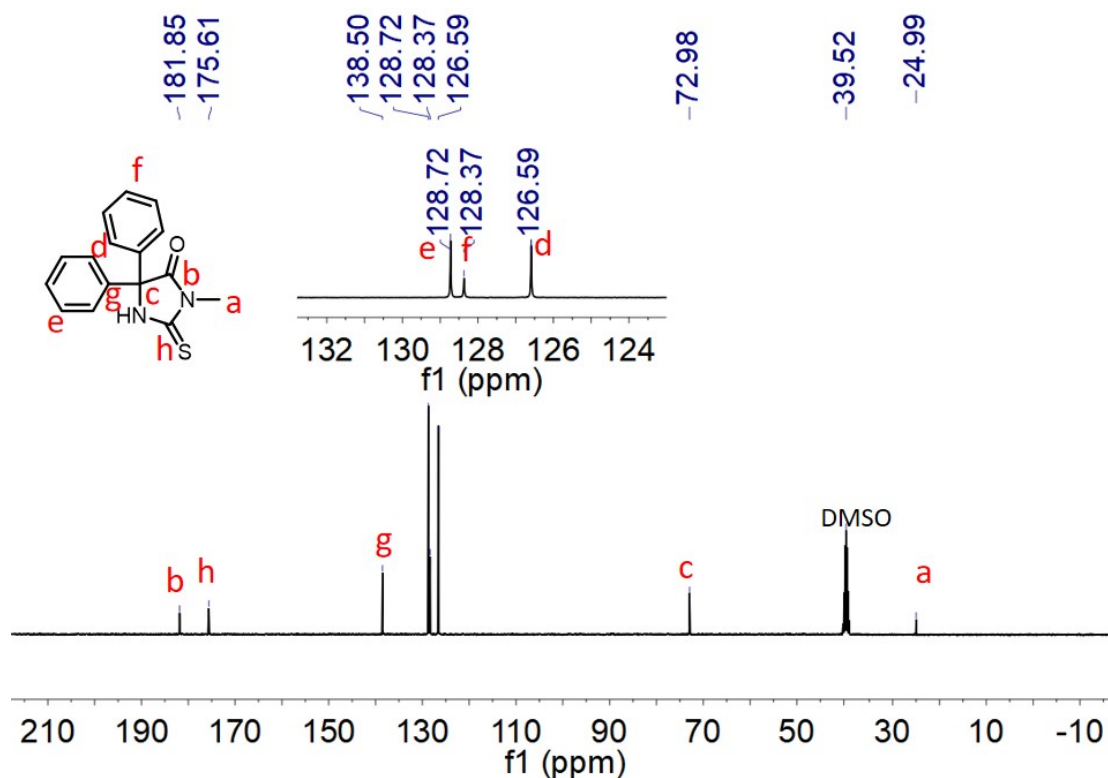
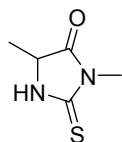


Figure S6.  $^{13}\text{C}$  NMR spectrum (DMSO- $d_6$ , 100 MHz) of 3-methyl-5,5-diphenyl-2-thioxoimidazolidin-4-one (HHyD5)

### Preparation of 3,5-dimethyl-2-thioxoimidazolidin-4-one (HHyD6)



3,5-Dimethyl-2-thioxoimidazolidin-4-one<sup>4</sup> was prepared by literature procedures. A mixture of 20 mmol of alanine, 1.8 g of ammonium thiocyanate (23 mmol), 20 mL of acetic anhydride, and 3 mL of acetic acid was stirred for 1 h at 100 °C. The solution was poured into water, and the precipitate was filtered off. The crude l-acetyl-2-thiohydantoin was suspended in 30 mL of 10% hydrochloric acid (m/m) and refluxed for 1 h. The solution was cooled and allowed to stand at 4 °C overnight. The precipitated crystalline material was filtered off and washed with water. 5-methyl-2-thioxoimidazolidin-4-one (3.25 g, 25.0 mmol) and equimolar of KOH (1.40 g, 25.0 mmol) was added in 25 mL EtOH, the mixture was stirred for 0.5 h at 95°C.  $\text{CH}_3\text{I}$  (1.56 ml, 25.0 mmol) was added dropwise and the mixture stirred for additional 5 h at room temperature. The solvent was extracted with ethyl acetate and  $\text{H}_2\text{O}$ , drying over  $\text{Na}_2\text{SO}_4$  overnight and evaporation of the solvent at reduced pressure. The product as a yellow solid was

afforded by chromatographic column chromatography (PE: EA=5:1). Yield 15%.

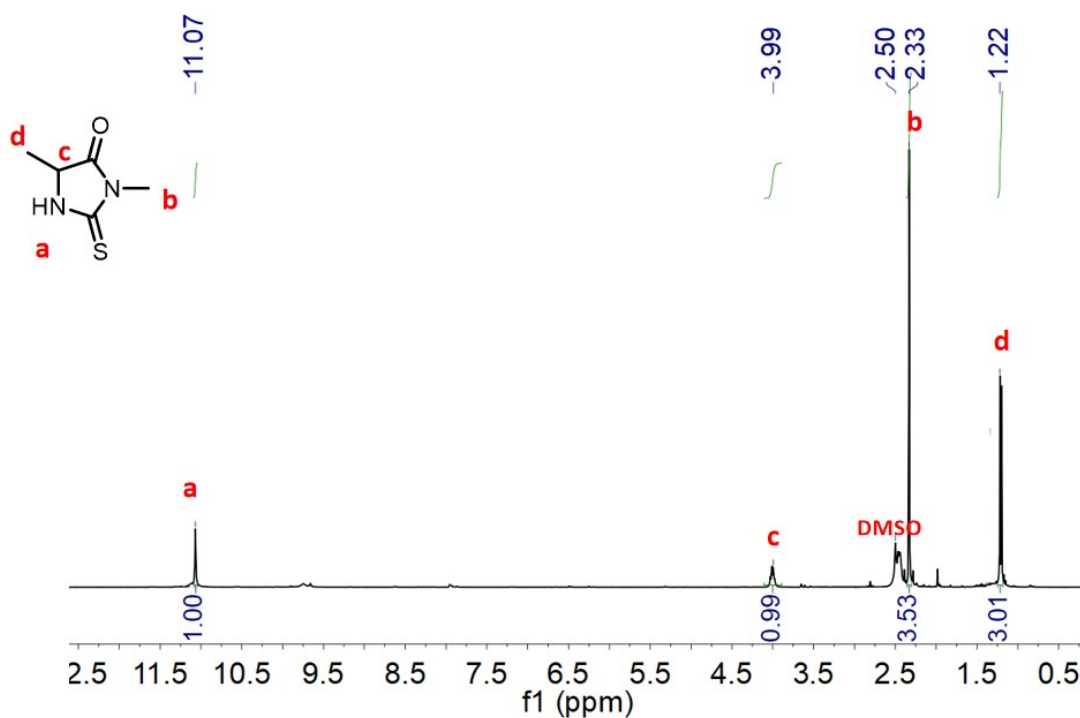


Figure S7.  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ , 400 MHz) of 3,5-dimethyl-2-thioxoimidazolidin-4-one (HHyd6)

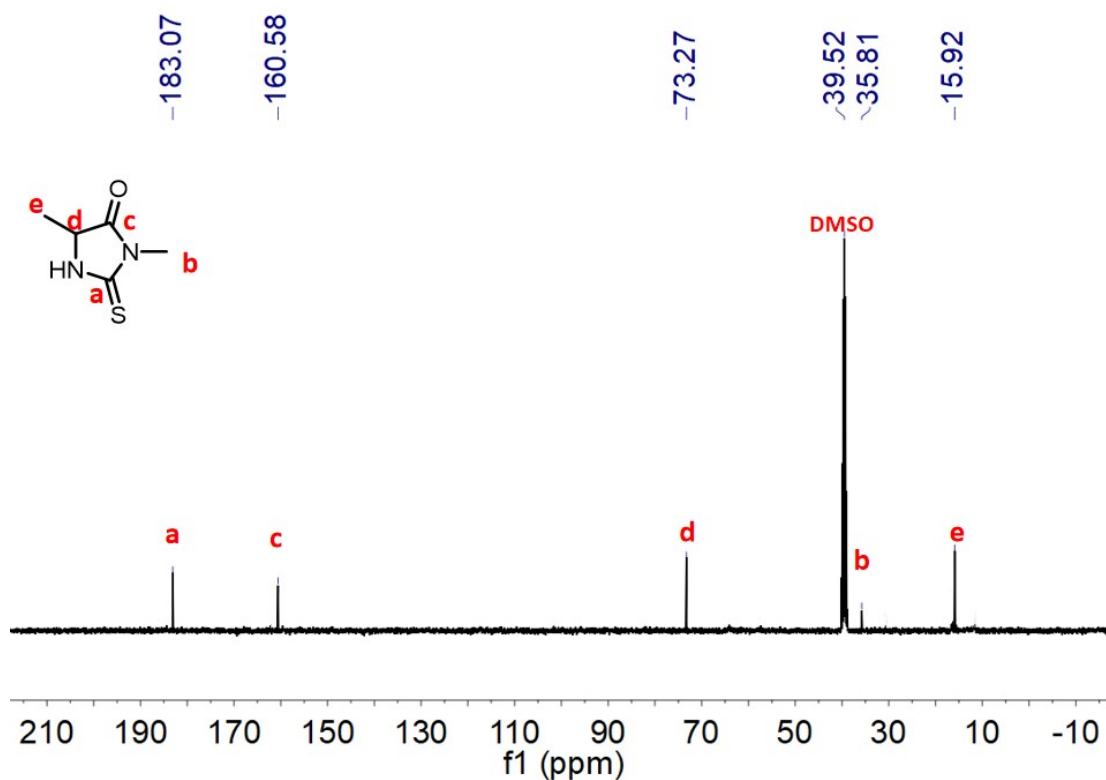


Figure S8.  $^{13}\text{C}$  NMR spectrum (DMSO- $d_6$ , 100 MHz) of 3,5-dimethyl-2-thioxoimidazolidin-4-one (HHyd6)



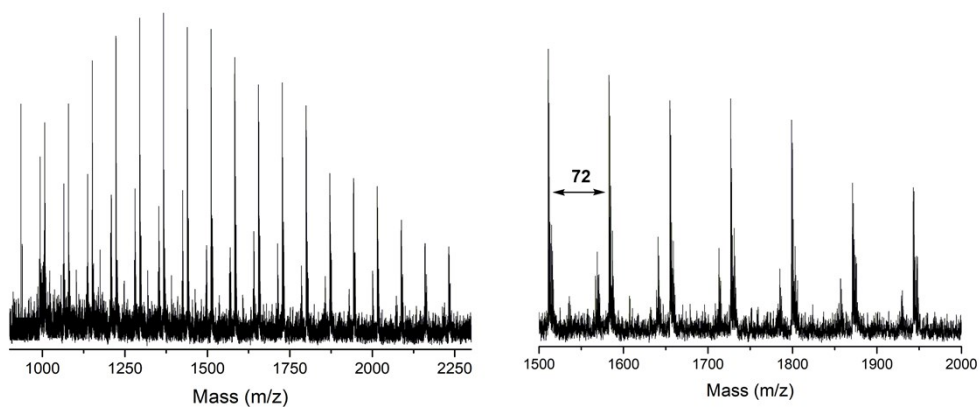
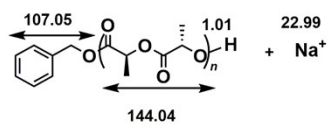
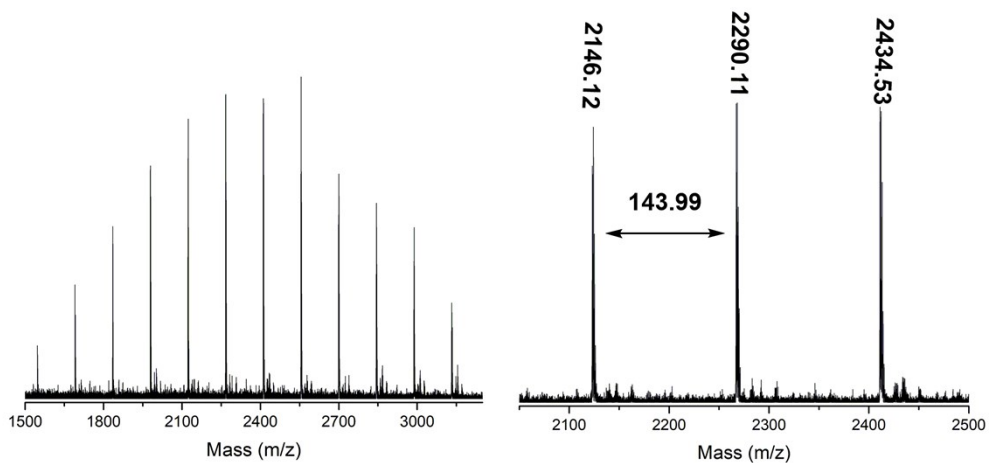


Figure S9. MALDI-ToF MS spectrum of the PLA catalyzed by HHyd3/DBU.



$$\text{Mass} = [\text{BnOH}] + [\text{LA unit}] \times n + \text{Na}^+$$

OR

$$\text{Mass} = [\text{H}_2\text{O}] + [\text{LA unit}] \times n + \text{Na}^+$$

Cation agent	[Initiator]=BnOH					
	n					
Na <sup>+</sup>	14	15	16	17	18	
	Calc.	2147.61	2291.65	2435.65	2579.69	2723.73
	Exp.	2146.12	2290.11	2434.53	2578.51	2722.67

Figure S10. MALDI-ToF MS spectrum of the PLA catalyzed by HHyd2/DBU.

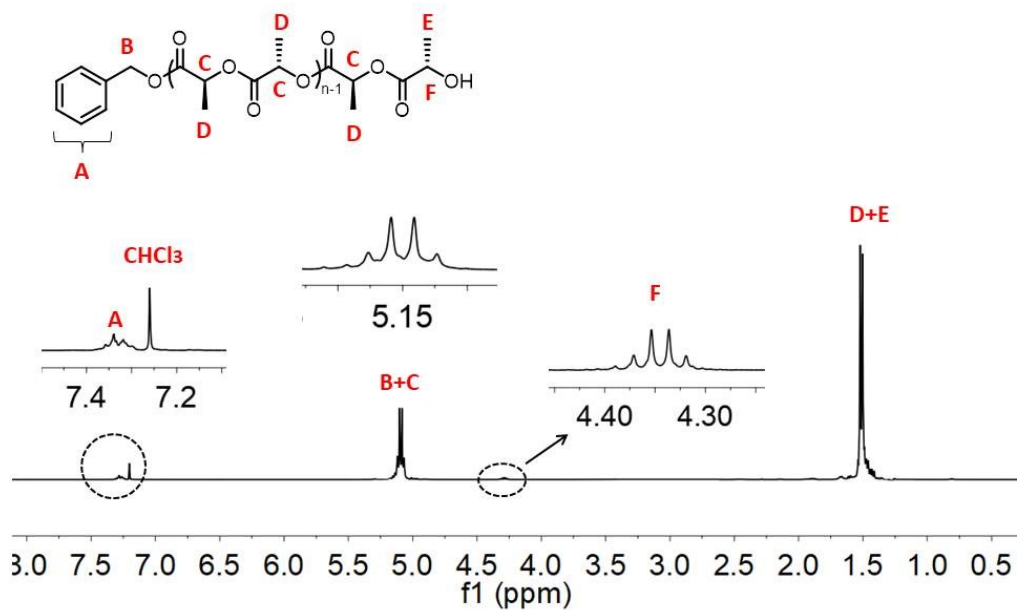


Figure S11.  $^1\text{H}$  NMR spectrum of PLLA initiated from BnOH in  $\text{CDCl}_3$ (HHyd2/DBU)

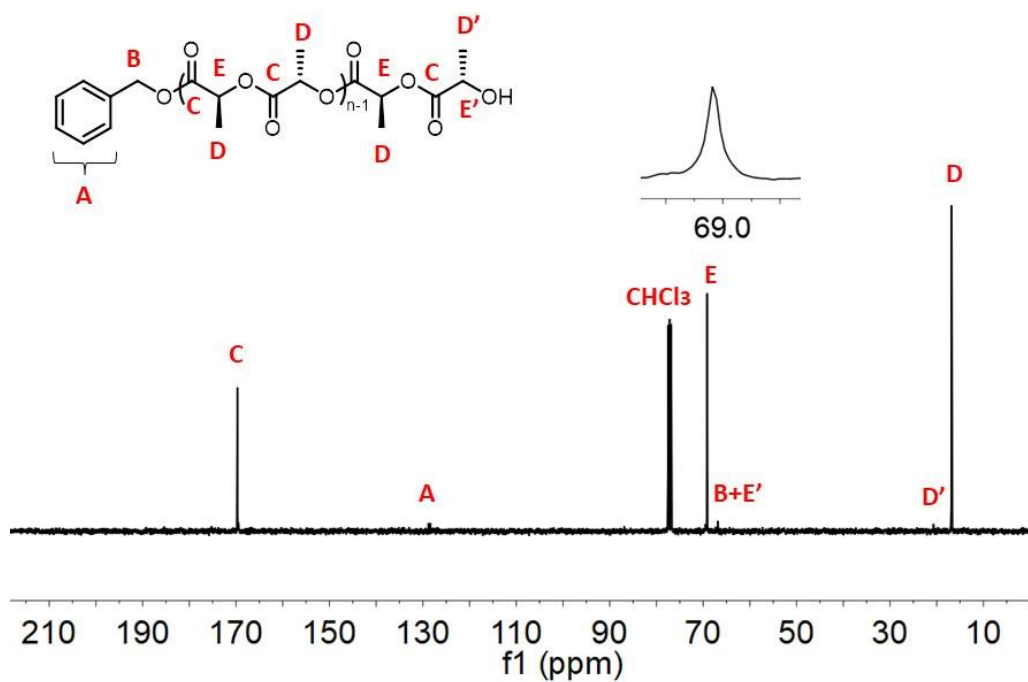


Figure S12.  $^{13}\text{C}$  NMR spectrum of PLLA initiated from BnOH in  $\text{CDCl}_3$ (HHyd2/DBU)

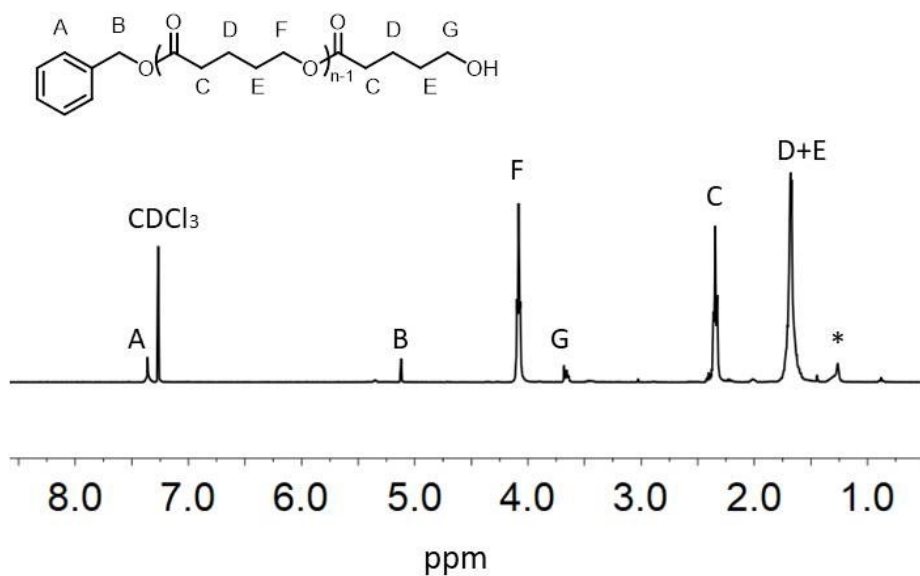
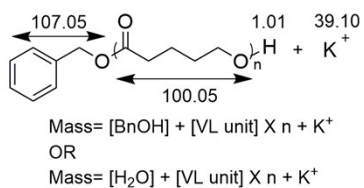
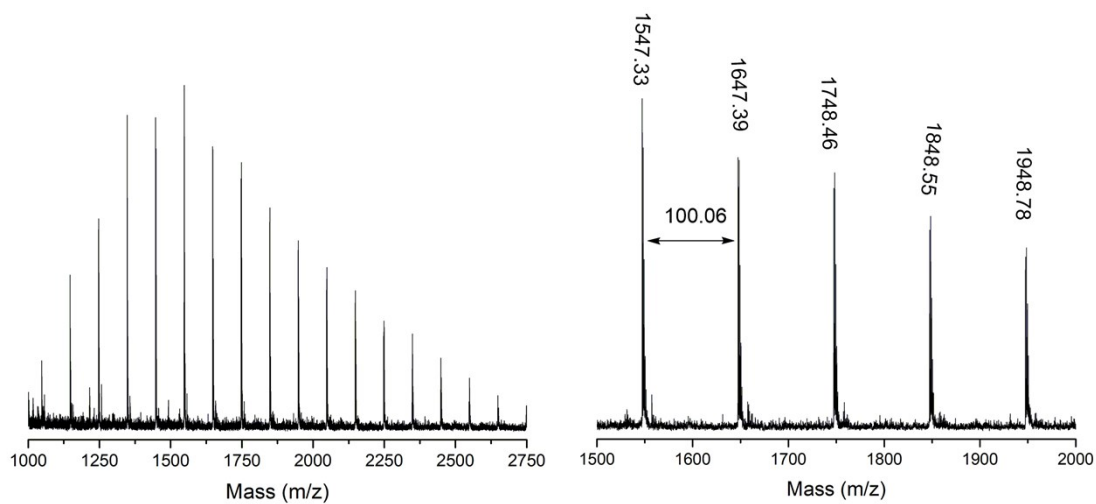


Figure S13. <sup>1</sup>H NMR spectrum of PVL initiated from BnOH in CDCl<sub>3</sub>, asterisk refers to the residual grease in polymers.



Cation agent	[Initiator]=BnOH n					
	17	18	19	20	21	
Na <sup>+</sup>	Calc.	1547.93	1647.98	1748.03	1848.08	1948.13
	Exp.	1547.33	1647.39	1748.46	1848.55	1948.78

Figure S14. MALDI-ToF MS spectrum of the PVL catalyzed by HHyd2/DBU.

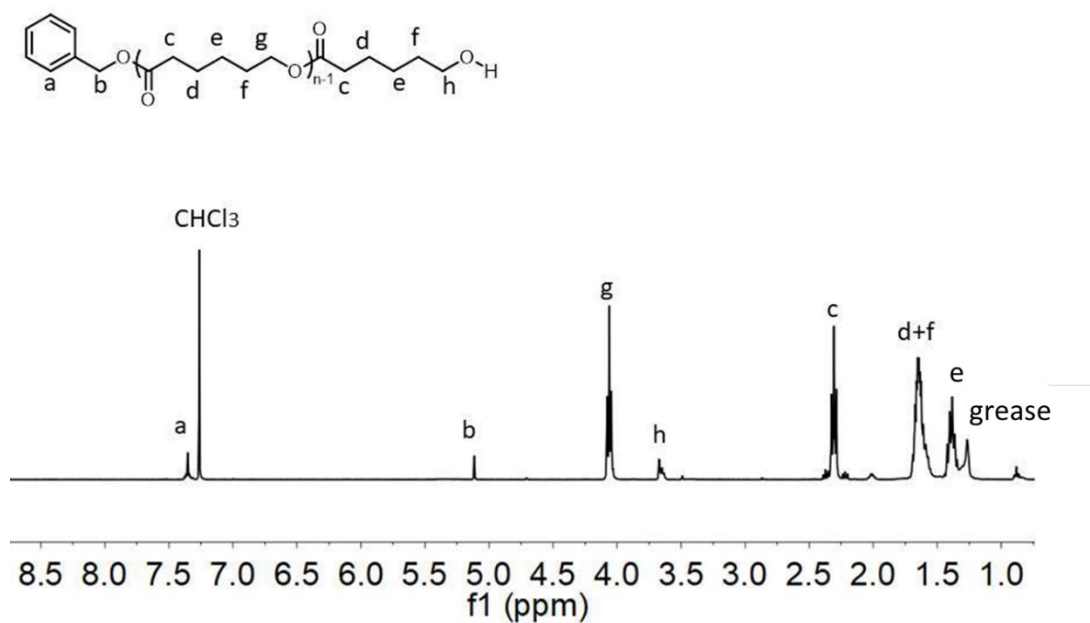
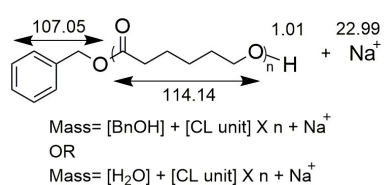
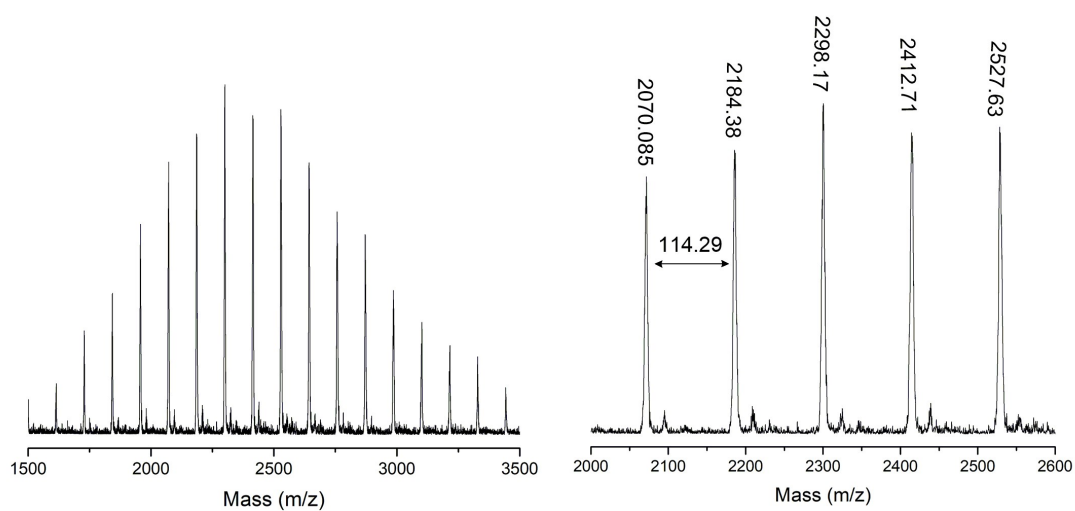


Figure S15.  $^1\text{H}$  NMR spectrum of PCL initiated from BnOH in  $\text{CDCl}_3$ , asterisk refers to the residual grease in polymers.



Cation agent	[Initiator]=BnOH					
	n					
Na <sup>+</sup>	17	18	19	20	21	
	Calc.	2071.51	2185.65	2299.78	2413.93	2528.07
	Exp.	2070.08	2184.38	2298.17	2412.71	2527.63

Figure S16. MALDI-ToF MS spectrum of the PCL catalyzed by HHyd2/DBU.

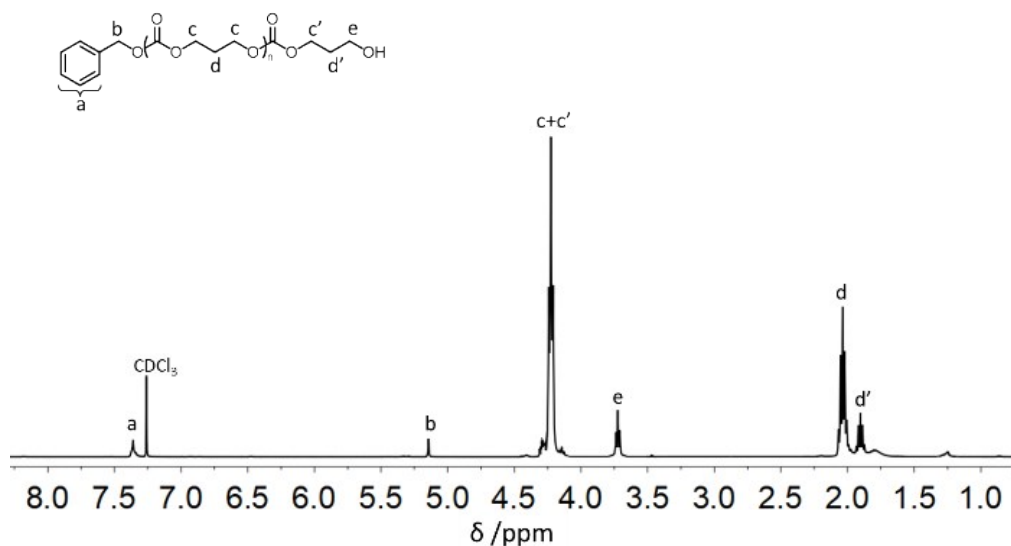


Figure S17.  $^1\text{H}$  NMR spectrum of PTMC initiated from BnOH in  $\text{CDCl}_3$ .

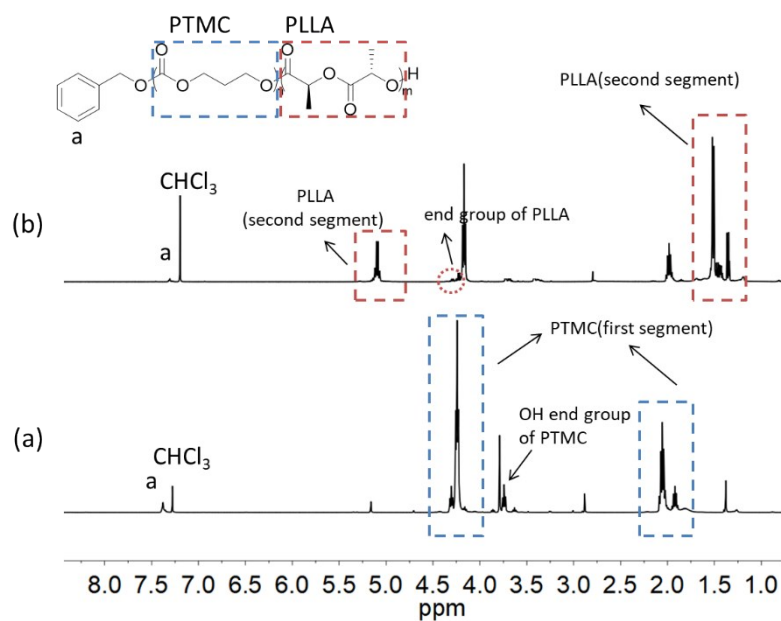


Figure S18.  $^1\text{H}$  NMR spectra of PTMC and PTMC-*b*-PLLA initiated from BnOH in  $\text{CDCl}_3$ , (a) a first ROP of TMC by HHyd2/DBU; (b) a second ROP of LLA by postpolymerization.

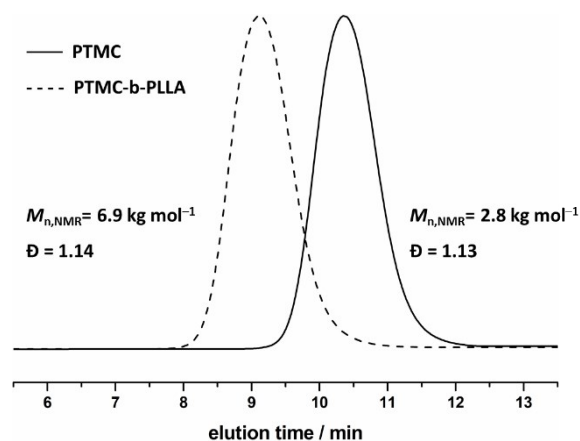


Figure S19. SEC traces of first poly(trimethylene carbonate) (PTMC) (solid line) and poly(trimethylene carbonate)-*block*-poly(L-lactide) (PTMC-*b*-PLLA) (dashed line) (eluent, THF; flow rate, 0.7 mL min<sup>-1</sup>).

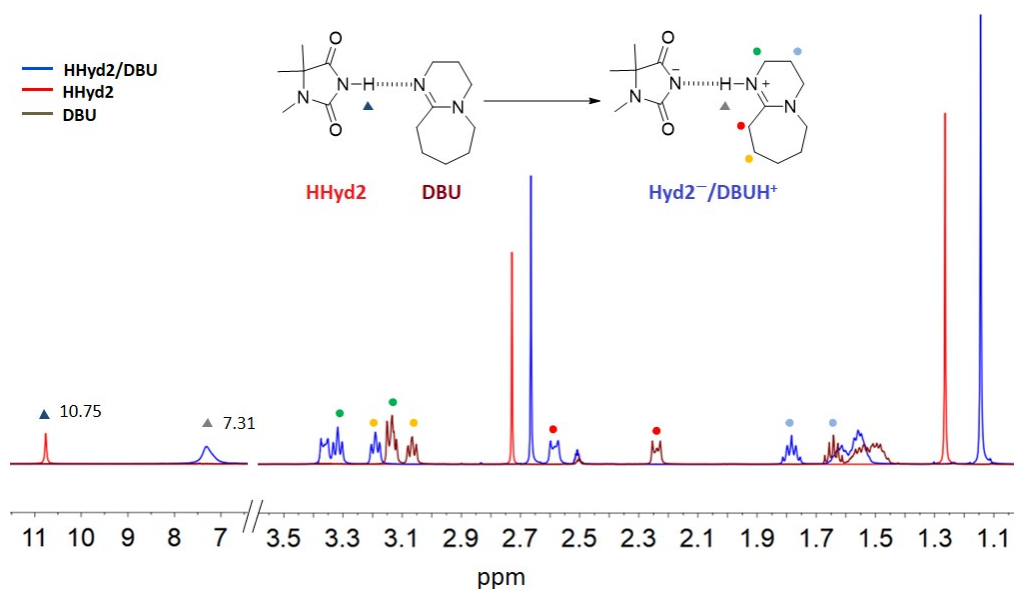


Figure S20. <sup>1</sup>H NMR spectra of hydantoin (HHyd2, in red), DBU (in brown), and a stoichiometric mixture of HHyd2/DBU (in blue). N3-H of hydantoin, originally resonances at 10.75 ppm, was abstracted by DBU, shifted to 7.31 ppm in DBUH<sup>+</sup> (all in DMSO-*d*<sub>6</sub>).

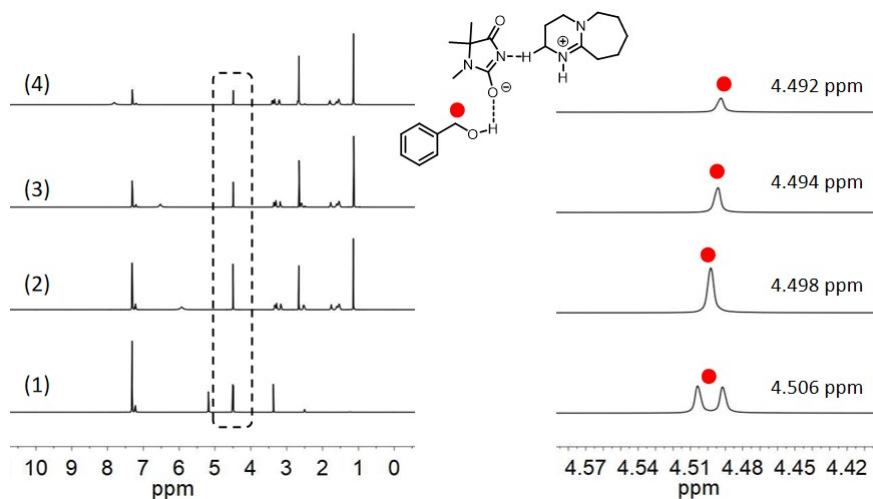


Figure S21. The chemical shifts of methylene protons of benzyl alcohol in mixtures with HHyd2/DBU in DMSO- $d_6$ . (1) BnOH (2) HHyd2/DBU/BnOH = 0.5/0.5/1 (3) HHyd2/DBU/BnOH = 1/1/1 (4) HHyd2/DBU/BnOH = 2/2/1

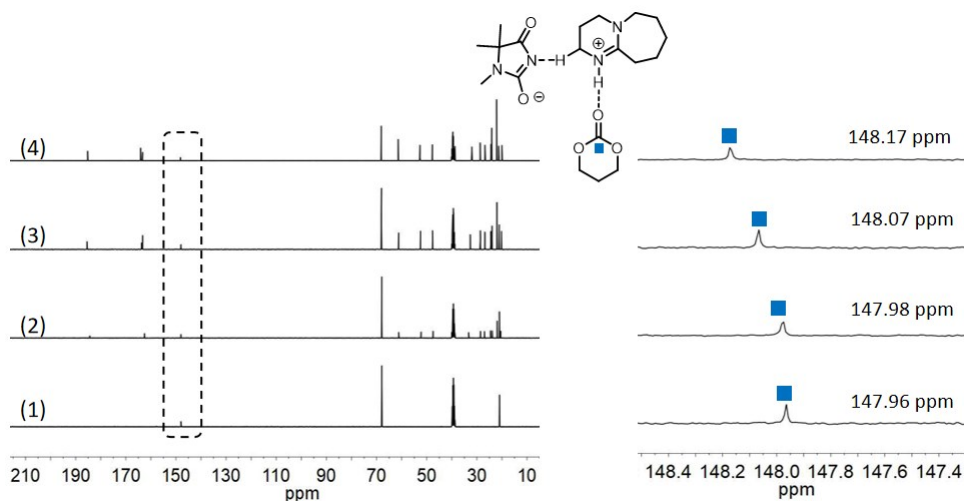


Figure S22. Chemical shifts of carbonyl carbon of TMC in  $^{13}\text{C}$  NMR spectra observed in mixtures with HHyd2/DBU in DMSO- $d_6$ . (1) TMC (2) HHyd2/DBU/TMC = 0.5/0.5/1 (3) HHyd2/DBU/TMC = 1/1/1 (4) HHyd2/DBU/TMC = 2/2/1

Table S1 Ring-opening polymerization of TMC with different catalysis<sup>a</sup>

Entry	Catalysis	time (h)	conv. <sup>b</sup> (%)	$M_{n,calc.}^c$ (kg mol <sup>-1</sup> )	$M_{n,NMR.}^b$ (kg mol <sup>-1</sup> )	$M_{n,GPC}^d$ (kg mol <sup>-1</sup> )	$\bar{D}$
1	HHyd1/DIEA	6	3	–	–	–	–
2	HHyd1/sparteine	6	20	–	–	–	–
3	HHyd1/DBU	6	93	3.0	3.2	3.5	1.20
4	HHyd3/DIPEA	6	–	–	–	–	–
5	HHyd3/pyridine	6	10	–	–	–	–
6	HHyd3/sparteine	6	23	–	–	–	–

<sup>a</sup>[M]<sub>0</sub>: [I]<sub>0</sub>: [HHyd]: [Base] = 30:1:1:1; room temperature; solvent, DCM; [M]<sub>0</sub> = 3 mol L<sup>-1</sup>. <sup>b</sup>Determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>c</sup>Calculated from  $([M]_0/[I]_0) \times \text{conv.} \times (M_w \text{ of TMC}) + (M_w \text{ of BnOH})$ . <sup>d</sup>Determined by SEC in THF using absolute method of measurement ( $dn/dc = 0.042$ ).

Table S2 Ring-opening polymerization of TMC with different solvents<sup>a</sup>

Entry	solvent	time (h)	conv. <sup>b</sup> (%)	$M_{n,calc.}^c$ (kg mol <sup>-1</sup> )	$M_{n,NMR.}^b$ (kg mol <sup>-1</sup> )	$M_{n,GPC}^d$ (kg mol <sup>-1</sup> )	$\bar{D}$
1	CH <sub>2</sub> Cl <sub>2</sub>	6	92	2.9	2.6	2.8	1.13
2	THF	6	80	2.5	2.9	2.7	1.16
3	Toluene	6	76	2.4	3.0	2.8	1.18
4 <sup>e</sup>	–	0.5	97	3.1	3.0	3.2	1.12

<sup>a</sup>[M]<sub>0</sub>: [I]<sub>0</sub>: [HHyd]: [Base] = 30:1:1:1; room temperature; solvent, DCM; [M]<sub>0</sub> = 3 mol L<sup>-1</sup>. <sup>b</sup>Determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>c</sup>Calculated from  $([M]_0/[I]_0) \times \text{conv.} \times (M_w \text{ of TMC}) + (M_w \text{ of BnOH})$ . <sup>d</sup>Determined by SEC in THF using absolute method of measurement ( $dn/dc = 0.042$ ). <sup>e</sup>Temperature, 60°C, bulk.



## References for SI.

1. B. W. McCann, H. Song, H. B. Kocer, I. Cerkez, O. Acevedo and S. D. Worley, *J. Phys. Chem. A*, 2012, **116**, 7245-7252.
2. N. Trisovic, N. Valentic and G. Uscumlic, *Chem. Cent. J.*, 2011, **5**.
3. A. O. Yuce, E. Telli, B. D. Mert, G. Kardas and B. Yazici, *J. Mol. Liq.*, 2016, **218**, 384-392.
4. J. Marton, J. Enisz, S. Hosztafi and T. Timar, *J. Agric. Food Chem.*, 1993, **41**, 148-152.