

## ELECTRONIC SUPPORTING INFORMATION

### **Imidodiphosphorimidate (IDPi) as efficient organocatalyst for controlled/living ring-opening polymerization of lactones**

Xun Zhang,<sup>a</sup> Yu Jiang,<sup>a</sup> Qiang Ma,<sup>a</sup> Siping Hu,<sup>a</sup> Qinggang Wang<sup>b</sup> and Saihu Liao<sup>\*a,c</sup>

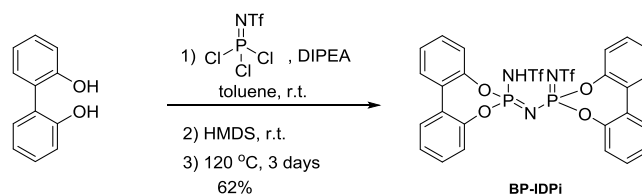
<sup>a</sup>Key Laboratory of Molecule Synthesis and Function Discovery, College of Chemistry, Fuzhou University, Fuzhou 350116, P. R. China; E-mail: shliao@fzu.edu.cn

<sup>b</sup>Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, R. R. China.

<sup>c</sup>Beijing National Laboratory for Molecular Sciences, Chinese Academy of Sciences, Beijing 100190, P. R. China

## Preparation of Imidodiphosphorimidate catalyst (BP-IDPi).

The 2,2'-biphenol derived catalyst (BP-IDPi) was prepared according to literature procedure (*Science*, 2018, **359**, 1501). In a flame dried three times Schleck flask, a suspension of 2,2'-biphenol (0.74 g, 4.00 mmol) in toluene (10 mL, 0.40 M) under argon was treated with *N*-triflylphosphorimidoyl trichloride (1.13 g, 4.00 mmol), then DIPEA (4.13 g, 32.0 mmol) was added, and stirred at RT for 15 minutes, until neat hexamethyldisilazane (HMDS, 208  $\mu$ L, 2.0 mmol) was added dropwise. The Schlenk flask was subsequently sealed and heated to 120 °C for 3 days. After cooling, aq. HCl (1 M) was added and the mixture was extracted with DCM. The combined organic layers were washed with water and brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (PE/EtOAc) afforded the desired product as a salt. The free acid was obtained after acidification in DCM stirred with aq. HCl (6 M) for 30 minutes, followed by drying under reduced pressure, affording the IDPi acid as slightly yellow solids (916mg, 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 (d, *J* = 7.5 Hz, 4H), 7.36 (m, 8H), 7.11 (d, *J* = 7.9 Hz, 4H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  146.8, 130.4, 130.2, 127.7, 127.4, 121.4, 119.4 (q, *J* = 317.9 Hz), 77.3, 77.0, 76.8; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -77.9; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  -4.9 ppm; HRMS (ESI+): ([M-H]): calculated for C<sub>26</sub>H<sub>17</sub>F<sub>6</sub>N<sub>3</sub>O<sub>8</sub>P<sub>2</sub>S<sub>2</sub>: 739.9909; found: 739.9909.



## Procedure for kinetic studies

Polymerization was carried out in toluene at 26 °C in a glovebox with a  $\delta$ -valerolactone ( $\delta$ -VL) concentration of 3M (600 mg, 6.0 mmol), and a  $\delta$ -VL/PPA/BP-IDPi molar ratio of 100/1/0.1 (8.17mg, 0.060 mmol of 3-Phenyl-1-propanol and 4.44 mg, 0.006 mmol of BP-IDPi). Aliquots were taken at given times during the polymerization, the monomer conversion and molecules weight of poly( $\delta$ -valerolactone) (PVL) was determined by <sup>1</sup>H NMR measurements (400 MHz) of the polymerization mixtures after the addition of a small amount of triethylamine. At the same time, taken two drop of the reaction solution in glass vial and 1 ml THF was added for prepare the GPC samples. The poly( $\delta$ -valerolactone) (PVL) samples were analyzed by SEC in THF solution.

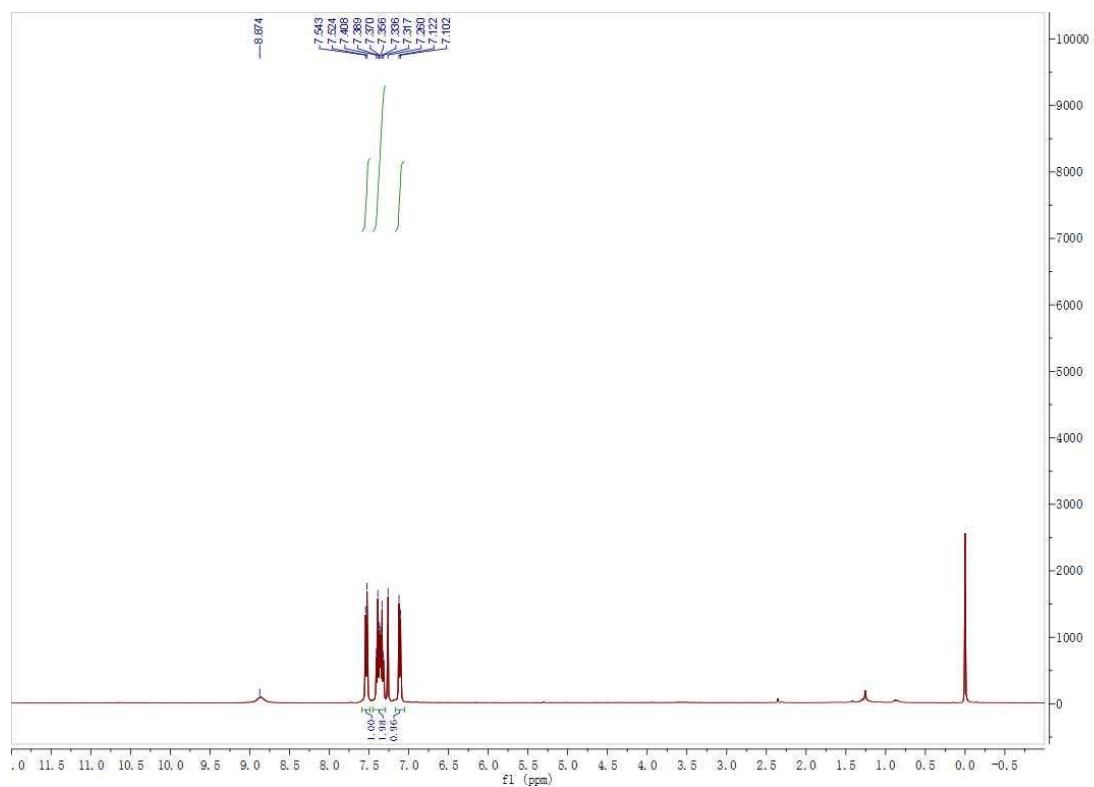


Fig. S1 <sup>1</sup>H NMR spectrum of BP-IDPi

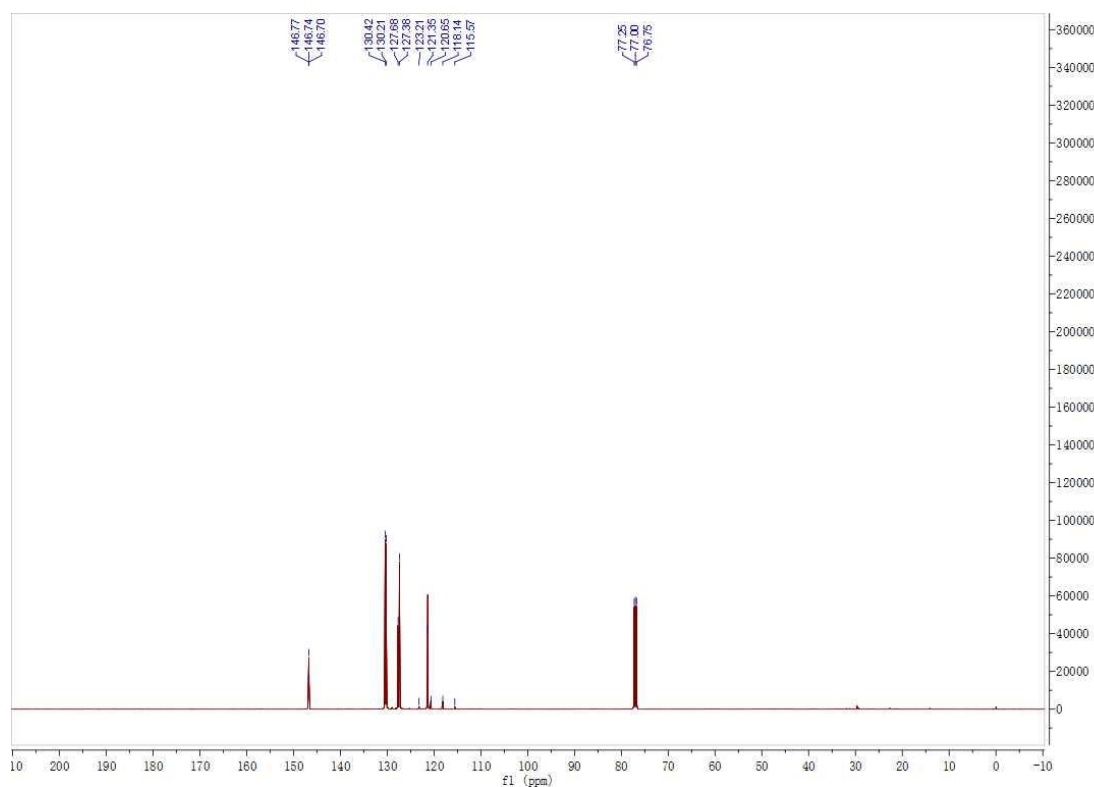
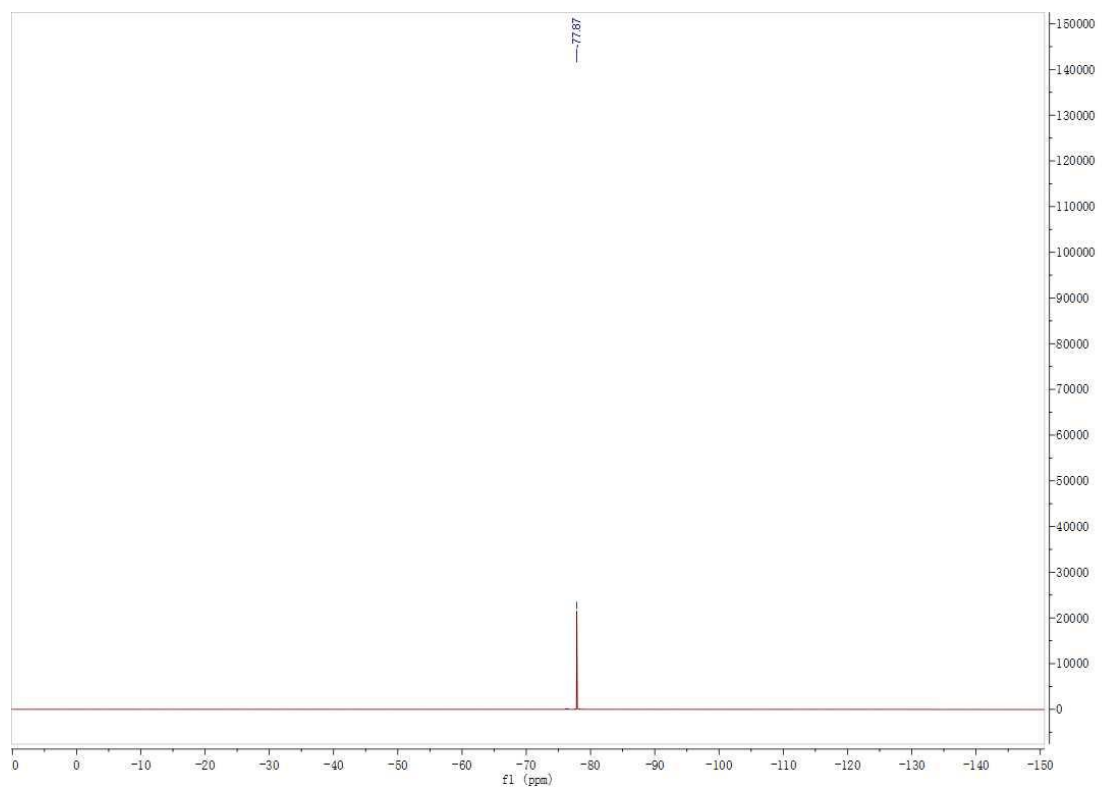
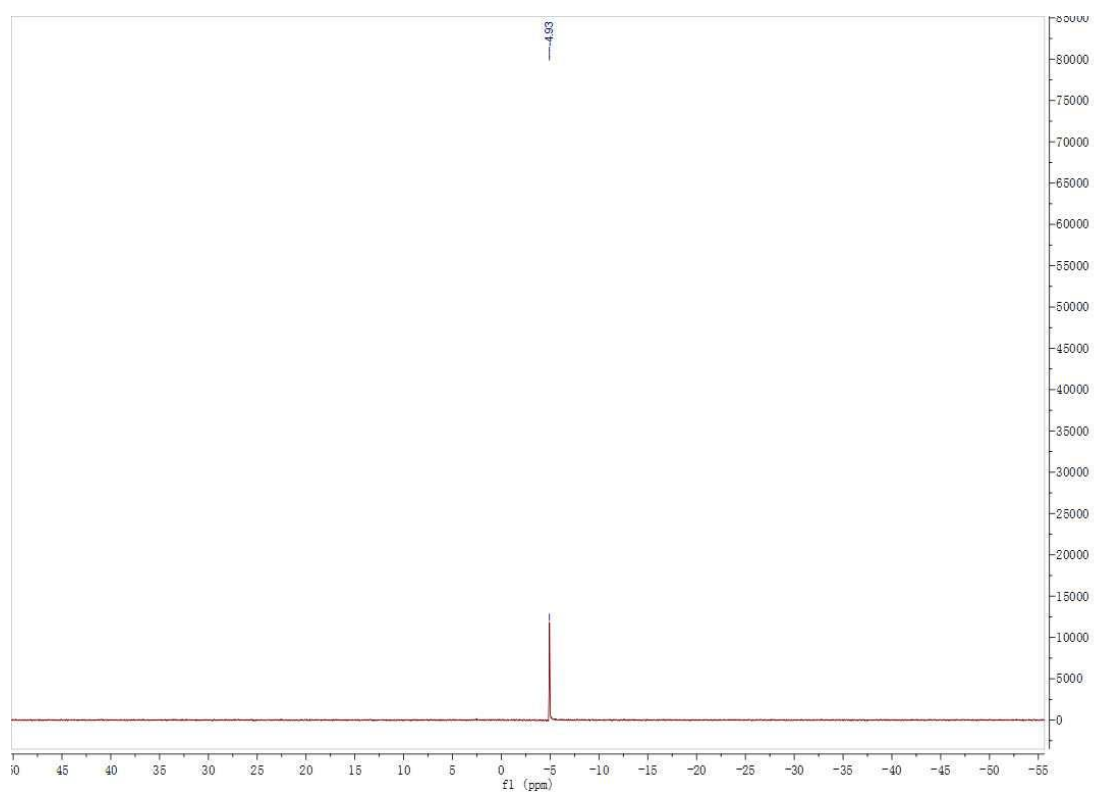


Fig. S2 <sup>13</sup>C NMR spectrum of BP-IDPi



**Fig. S3**  $^{19}\text{F}$  NMR spectrum of BP-IDPi



**Fig. S4**  $^{31}\text{P}$  NMR spectrum of BP-IDPi

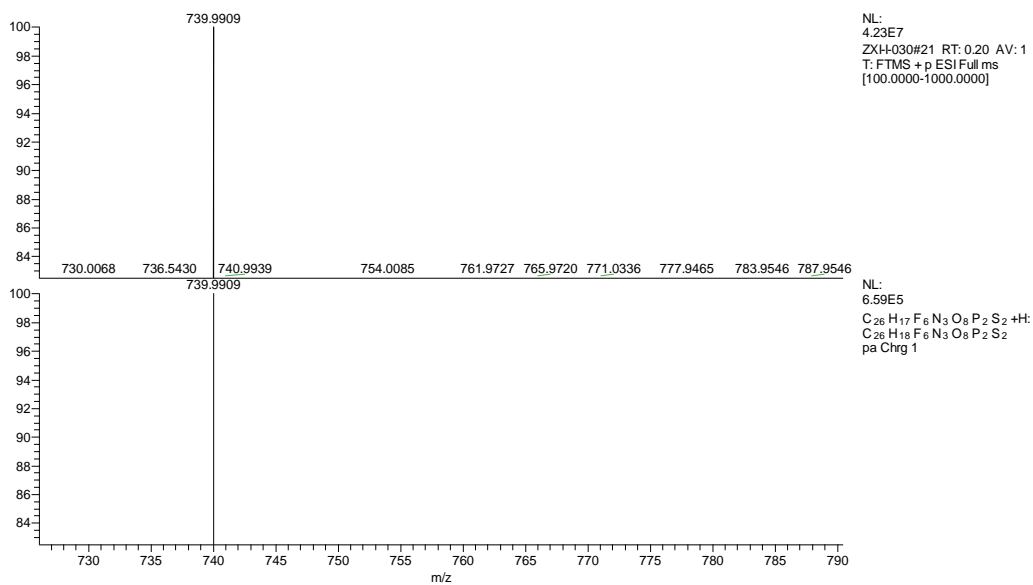


Fig. S5 HRMS spectrum of IDPi-P

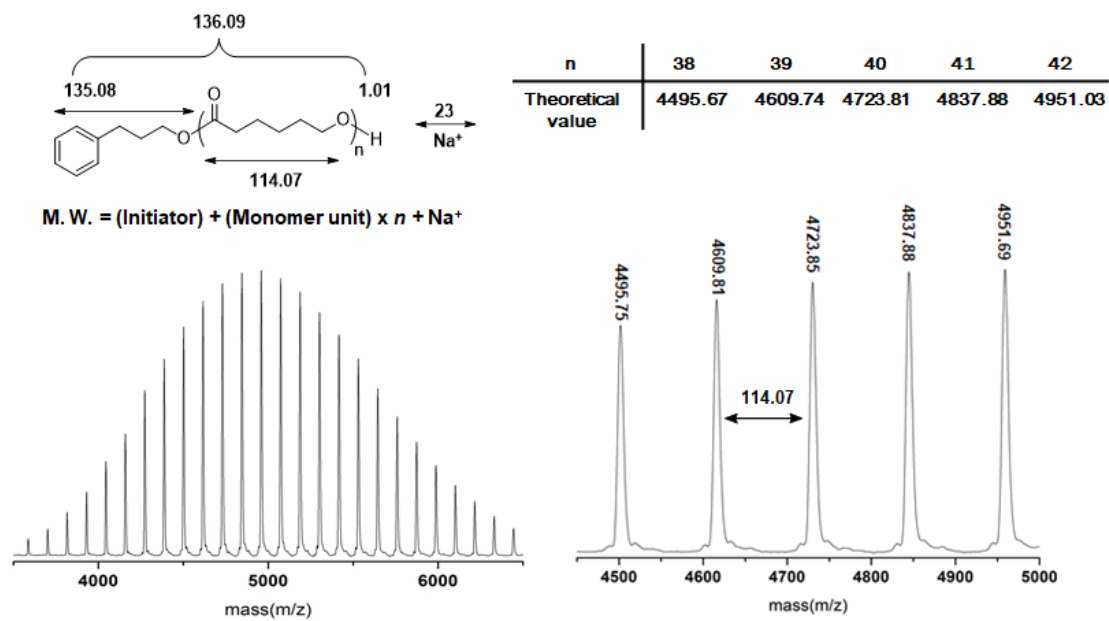


Fig. S6 MALDI-TOF MS spectrum of the obtained PCL ([ $\epsilon$ -CL]<sub>0</sub>/[PPA]<sub>0</sub>/[IDPi-P] = 50/1/0.1)

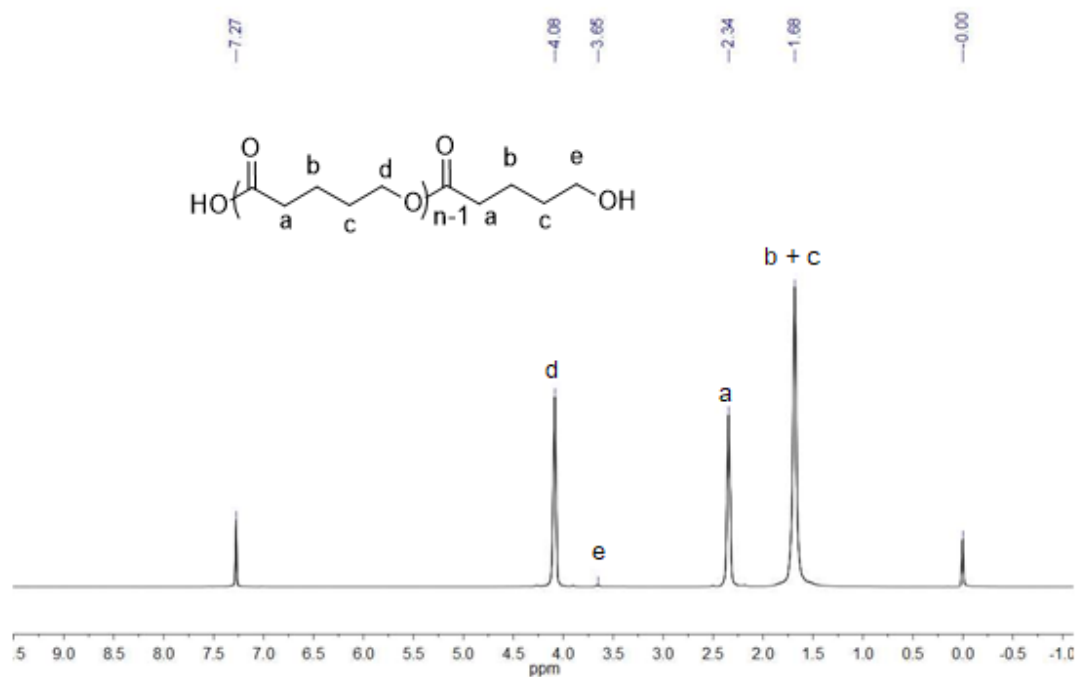


Fig. S7 <sup>1</sup>H NMR spectrum of PVL Initiated by H<sub>2</sub>O

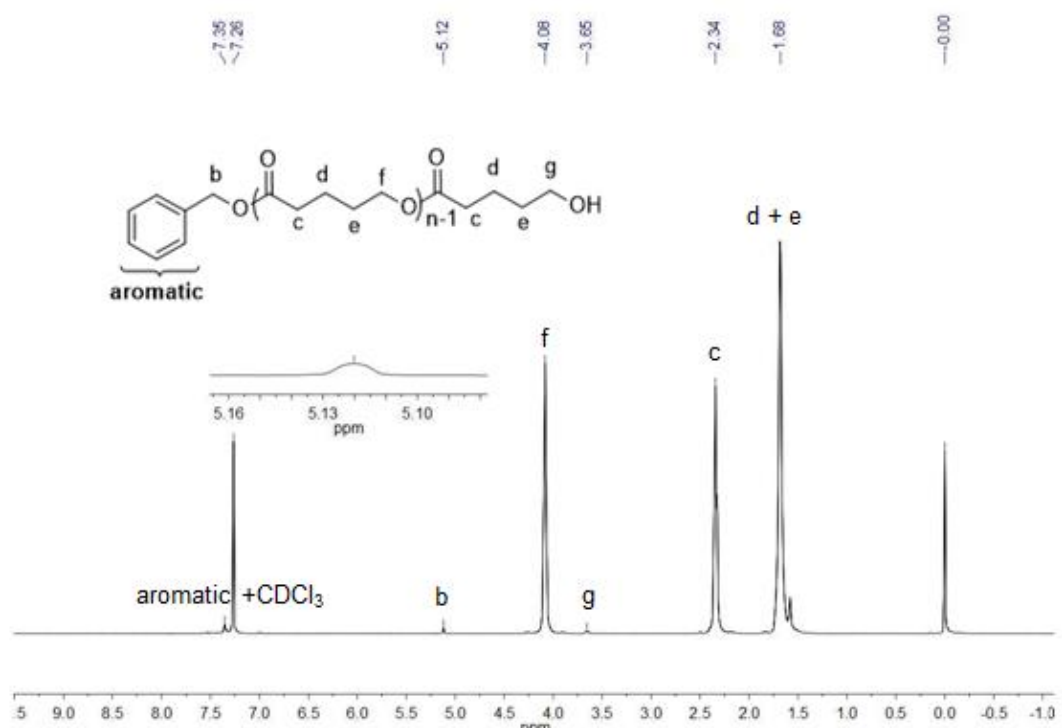


Fig. S8 <sup>1</sup>H NMR spectrum of PVL Initiated by Benzyl alcohol

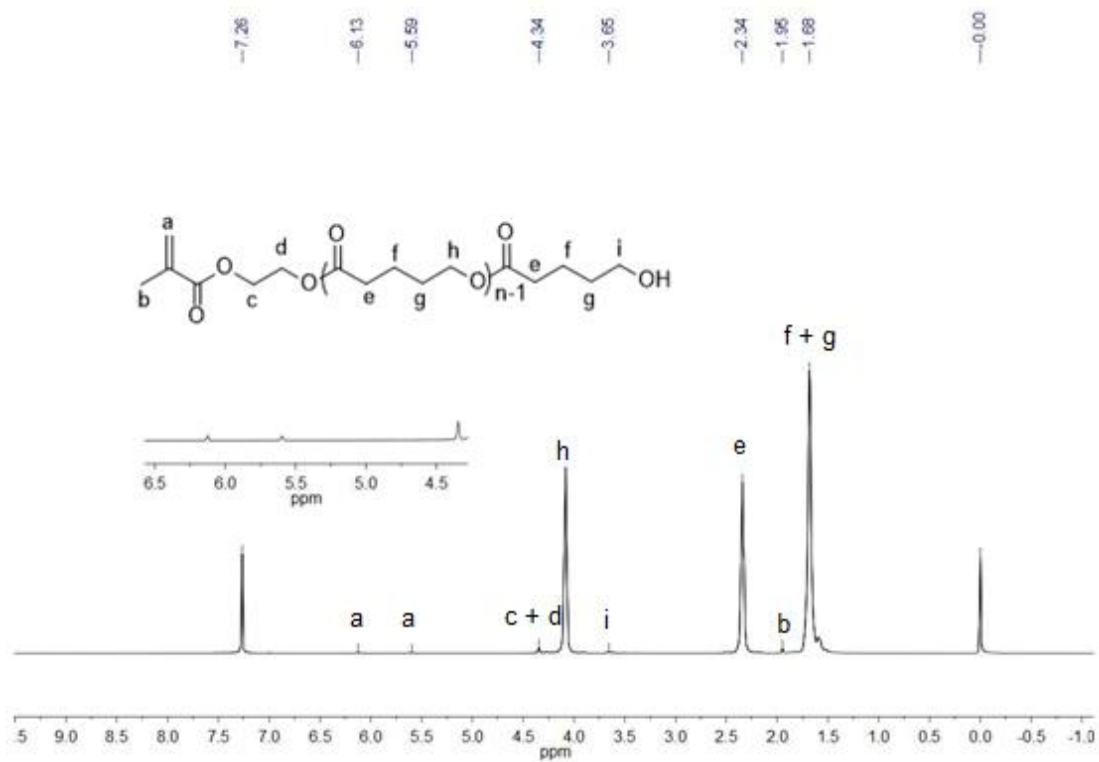


Fig. S9  $^1\text{H}$  NMR spectrum of PVL Initiated by Hydroxyethyl methacrylate

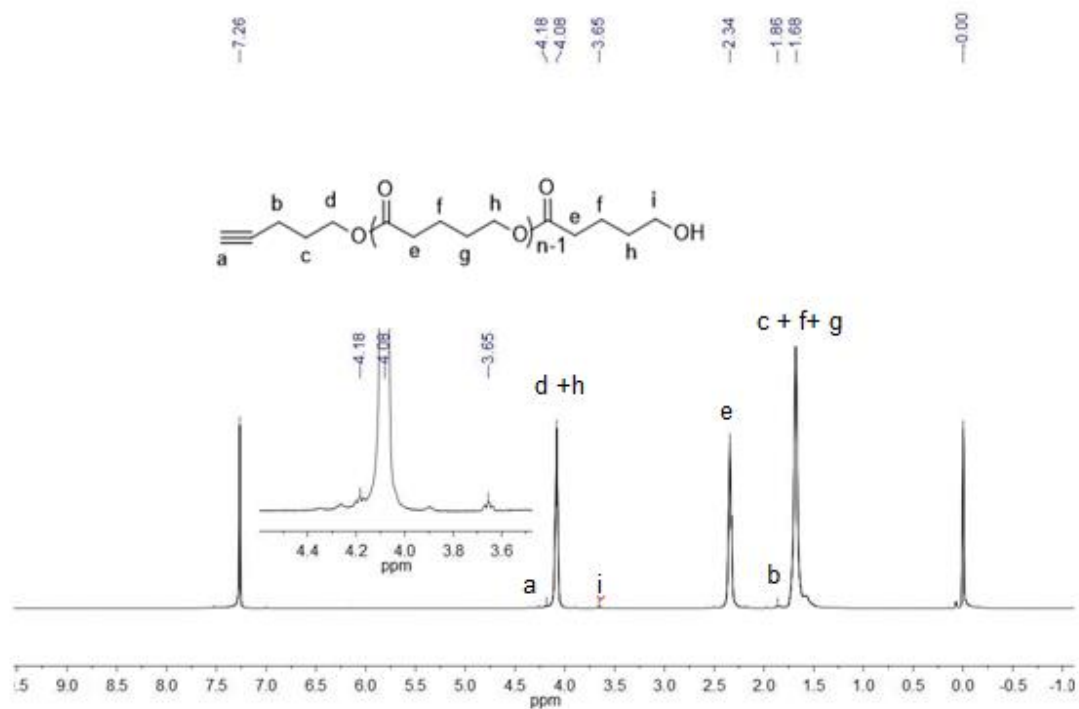


Fig. S10  $^1\text{H}$  NMR spectrum of PVL Initiated by 4-Pentyn-1-ol

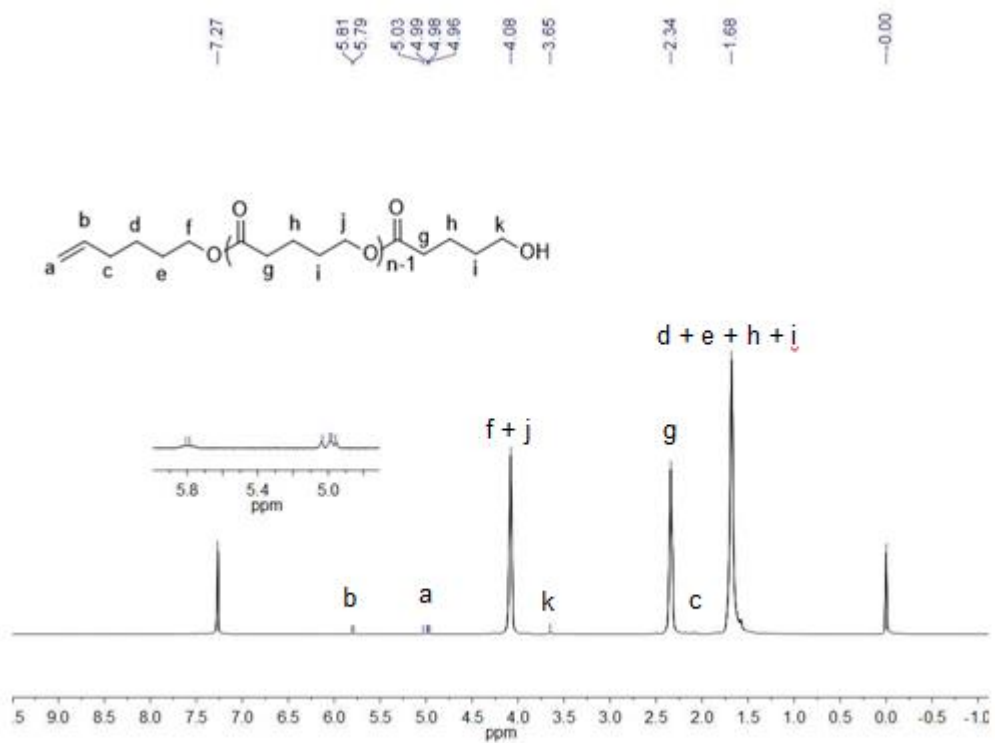


Fig. S11  $^1\text{H}$  NMR spectrum of PVL Initiated by 5-Hexen-1-ol