## Synthesis of poly(L-lactide)-b-poly(amino acid)s block copolymers

## by noncovalent protection of hetero-initiator

Siheng Zhang,<sup>a</sup> Jianda Niu,<sup>a</sup> Enchi Hu,<sup>a</sup> Liguo Xu,<sup>b</sup> Zhixian Dong,<sup>a</sup> Jinbao Xu,<sup>\*a</sup> and Caihong Lei<sup>\*a</sup>

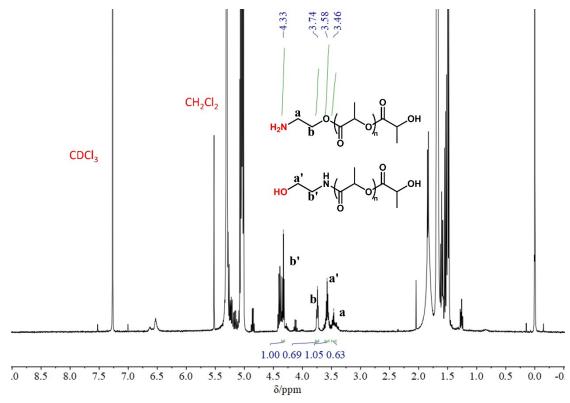
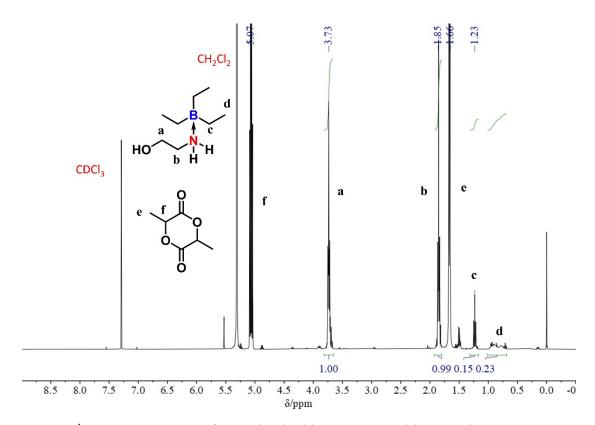


Fig. S1. <sup>1</sup>H NMR spectrum of LA mixed with AE in DCM at room temperature to observe the possible reaction (CDCl<sub>3</sub>).



**Fig. S2.** <sup>1</sup>H NMR spectrum of LA mixed with AE protected by Et<sub>3</sub>B in DCM at room temperature (CDCl<sub>3</sub>).

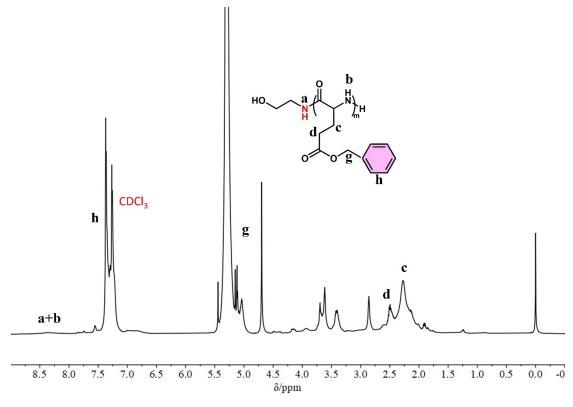
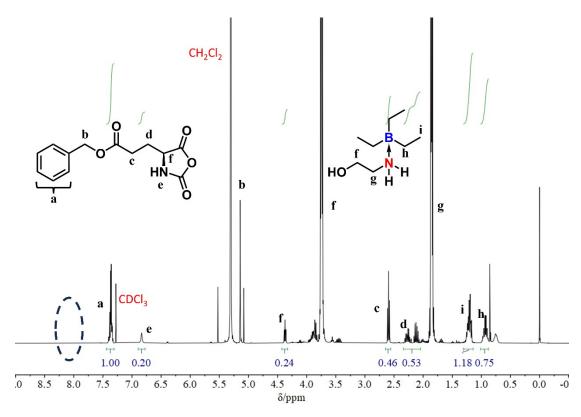
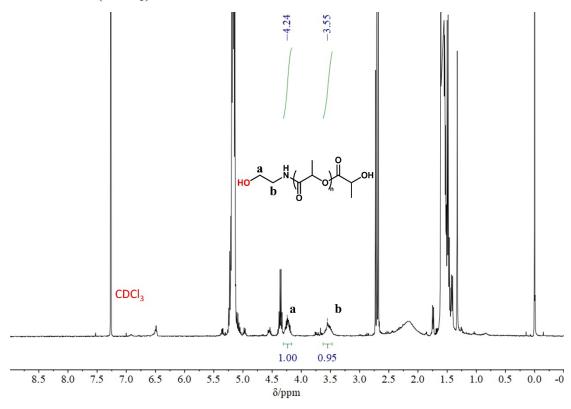


Fig. S3. <sup>1</sup>H NMR spectrum of Bn-GLuNCA mixed with AE in DCM for 16 h (CDCl<sub>3</sub>).



**Fig. S4.** <sup>1</sup>H NMR spectrum of Bn-GLuNCA mixed with AE protected by Et<sub>3</sub>B in DCM for 4 h (CDCl<sub>3</sub>).



**Fig. S5.** <sup>1</sup>H NMR spectrum of the isolated product of LA mixed with AE and DBU in DCM (CDCl<sub>3</sub>).

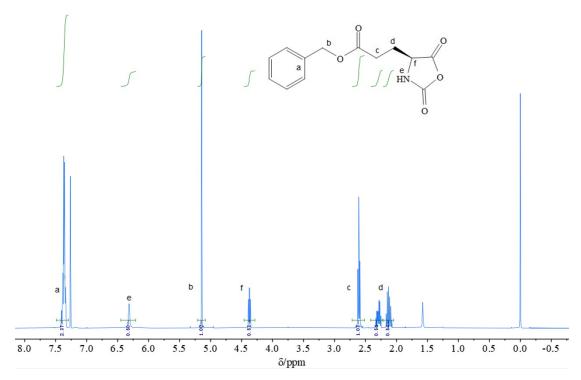


Fig. S6. <sup>1</sup>H NMR spectrum of the isolated product of Bn-GLuNCA (CDCl<sub>3</sub>).

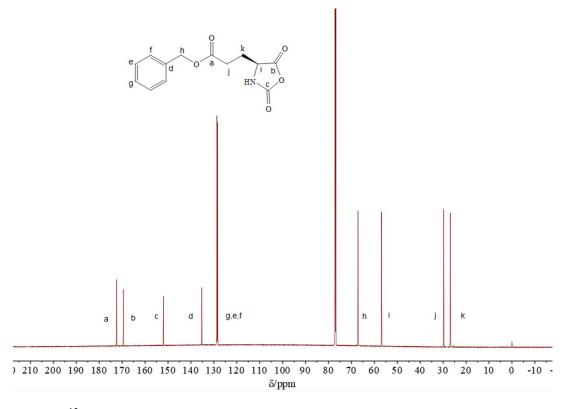
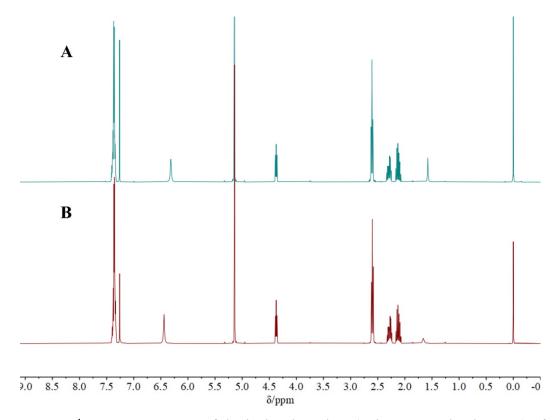


Fig. S7. <sup>13</sup>C NMR spectrum of the isolated product of BLG-NCA (CDCl<sub>3</sub>).



**Fig. S8.** <sup>1</sup>H NMR spectrum of the isolated product (A in 2023 and B in 2024) of Bn-GLuNCA (CDCl<sub>3</sub>).