## **Supplementary Information**

## Internal Lewis pair enhanced H-bond donor: Boronate–urea and tertiary amine co-catalysis in ring-opening polymerization

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Figure S1. <sup>1</sup>H NMR spectrum of the Boronate urea pinacol ester (400 MHz, DMSO).



Figure S2. <sup>13</sup>C NMR spectrum of the Boronate urea pinacol ester (400 MHz, DMSO).



Figure S3. <sup>1</sup>H NMR spectrum of the 1-(3,5-bis(trifluoromethyl)phenyl)-3-phenylurea (400 MHz,DMSO).



Figure S4. <sup>13</sup>C NMR spectrum of the 1-(3,5-bis(trifluoromethyl)phenyl)-3-phenylurea (400 MHz, DMSO)



Figure S5 Methine region of <sup>13</sup>C NMR spectrum of the obtained PLA prepared at room temperature (400 MHz, CDCl3).



Figure S6 MALDI-ToF MS spectrum of PLLA.



Figure S7 <sup>1</sup>H NMR spectrum (in CDCl3) of PTMC-b-PLLA initiated by BnOH.



Fig.S8 <sup>13</sup>C NMR spectrum in (CDCl<sub>3</sub>) of PTMC-*b*-PLLA initiated by BnOH