**Supporting Information**

**Microstructurally Controlled Polymers of *rac*-Lactide by Lithium Complexes**

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**Supporting information**

Figure S1. 1H NMR spectrum of **3**

Figure S2. 13C{1H} NMR spectrum of **3**

Figure S3. 1H NMR spectrum of **4**

Figure S4. 13C{1H} NMR spectrum of **4**

Figure S5. 1H NMR spectrum of **5**

Figure S6. 13C{1H} NMR spectrum of **5**

Figure S7. 1H NMR spectrum of **5a**

Figure S8. 13C{1H} NMR spectrum of **5a**

Figure S9.1H NMR spectra of **3** and **3-Li2**

Figure S10.Homonuclear decoupled 1H NMR spectrum of PLA



Figure S1. 1H NMR spectrum of **3** in CDCl3 (300 MHz)



Figure S2. 13C{1H} NMR spectrum of **3** in CDCl3 (75 MHz)



Figure S3. 1H NMR spectrum of **4** in CDCl3 (300 MHz)



Figure S4. 13C{1H} NMR spectrum of **4** in CDCl3 (75 MHz)

Figure S5. 1H NMR spectrum of **5** in CDCl3 (300 MHz)

Figure S6. 13C{1H} NMR spectrum of **5** CDCl3 (75 MHz)

Figure S7. 1H NMR spectrum of **5a** in CDCl3(300 MHz)

Figure S8. 13C{1H} NMR spectrum of **5a** in CDCl3(75 MHz)

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**Figure S9.** 1H NMR spectrum of **3** in THF-d8 (bottom); 1H NMR spectrum of **3-Li2** in THF-d8 (top) (400 MHz)



**Figure S10.** Homonuclear decoupled 1H NMR spectrum of PLA produced from *rac*-lactide using **3-Li2/**NpOHas initiator (entry 5, Table 1) in CDCl3 (400 MHz).