Supporting Information

**Structural and Catalytic Studies of Lithium Complexes Bearing Pendant Amino-Phenolate Ligands**

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Fig.S1 Molecular structure of HONMePhSMe. Only hydrogen atom on the oxygen atom of phenol is exhibited.

Fig.S2 Homonuclear-decoupled methine $^1$H NMR spectrum (400 MHz, CDCl$_3$) of poly(L-Lactide) synthesized at 26.5°C for 5 min in CH$_2$Cl$_2$ using 6 as initiator at ([M]:[Li]:[BnOH] = 50:1 (Table 1 entry 10).