Electronic supporting information for

## Alkali aminoether-phenolate complexes: Synthesis, structural characterization and evidences for an activated monomer ROP mechanism<sup>†</sup>

Sorin C. Roșca,<sup>a</sup> Dragoș A. Roșca,<sup>a,b</sup> Vincent Dorcet,<sup>a</sup> Christopher M. Kozak,<sup>c</sup>

Francesca M. Kerton,<sup>c</sup> Jean-François Carpentier<sup>\*a</sup> and Yann Sarazin<sup>\*a</sup>

## Contents

- S1 <sup>1</sup>H NMR spectrum (0-12 ppm) of BnOH in  $CD_2Cl_2$  (500.13 MHz, 298 K)
- S2 <sup>1</sup>H NMR spectrum (0-12 ppm) of L-LA in  $CD_2Cl_2$  (500.13 MHz, 298 K)
- S3  ${}^{1}$ H NMR spectrum (0-12 ppm) of {LO}{}^{3}H in CD<sub>2</sub>Cl<sub>2</sub> (500.13 MHz, 298 K)
- S4 <sup>1</sup>H NMR spectrum (0-12 ppm) of BnOLi in  $CD_2Cl_2$  (500.13 MHz, 298 K)
- S5 <sup>1</sup>H NMR spectrum (0-12 ppm) of  $\{LO^3\}Li$  (**3**) in CD<sub>2</sub>Cl<sub>2</sub> (500.13 MHz, 298 K)
- S6 <sup>1</sup>H NMR spectrum (0-12 ppm) of a 1:1 mixture of BnOH and **3** in  $CD_2Cl_2$  (500.13 MHz, 298 K)
- S7 <sup>1</sup>H NMR spectrum (0-12 ppm) of a 5:1 mixture of BnOH and **3** in  $CD_2Cl_2$  (500.13 MHz, 298 K)
- S8 <sup>1</sup>H NMR spectrum (0-12 ppm) of a 1:1:1 mixture of BnOH, L-LA and **3** in  $CD_2Cl_2$  (500.13 MHz, 298 K) leading to the formation of **P**<sub>1</sub>
- S9 <sup>1</sup>H NMR spectrum (0-12 ppm) of a 5:5:1 mixture of BnOH, L-LA and **3** in  $CD_2Cl_2$  (500.13 MHz, 298 K) leading to the formation of **P**<sub>1</sub>
- S10 <sup>1</sup>H NMR spectrum (0-12 ppm) of a 1:2:1 mixture of BnOH, L-LA and **3** in CD<sub>2</sub>Cl<sub>2</sub> (500.13 MHz, 298 K) leading to the formation of **P**<sub>2</sub>
- S11 <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 500.13 MHz, 298 K) of a PLLA sample prepared with **3**/BnOH (from Table 2, entry 8)
- S12 VT <sup>7</sup>Li NMR for  $\{LO^3\}Li \cdot LiN(SiMe_2H)_2$  (5) in toluene- $d_8$  (258–353 K)

S1. <sup>1</sup>H NMR spectrum (0-12 ppm) of BnOH in CD<sub>2</sub>Cl<sub>2</sub> (500.13 MHz, 298 K)



S2. <sup>1</sup>H NMR spectrum (0-12 ppm) of L-LA in CD<sub>2</sub>Cl<sub>2</sub> (500.13 MHz, 298 K)



S3. <sup>1</sup>H NMR spectrum (0-12 ppm) of {LO<sup>3</sup>}H in CD<sub>2</sub>Cl<sub>2</sub> (500.13 MHz, 298 K)



S4. <sup>1</sup>H NMR spectrum (0-12 ppm) of BnOLi in CD<sub>2</sub>Cl<sub>2</sub> (500.13 MHz, 298 K)



S5. <sup>1</sup>H NMR spectrum (0-12 ppm) of {LO<sup>3</sup>}Li (**3**) in CD<sub>2</sub>Cl<sub>2</sub> (500.13 MHz, 298 K)



S6. <sup>1</sup>H NMR spectrum (0-12 ppm) of a 1:1 mixture of BnOH and **3** in CD<sub>2</sub>Cl<sub>2</sub> (500.13 MHz, 298 K)







S8. <sup>1</sup>H NMR spectrum (0-12 ppm) of a 1:1:1 mixture of BnOH, L-LA and **3** in  $CD_2Cl_2$  (500.13 MHz, 298 K) leading to the formation of **P**<sub>1</sub>



S9. <sup>1</sup>H NMR spectrum (0-12 ppm) of a 5:5:1 mixture of BnOH, L-LA and **3** in  $CD_2Cl_2$  (500.13 MHz, 298 K) leading to the formation of **P**<sub>1</sub>



S10. <sup>1</sup>H NMR spectrum (0-12 ppm) of a 1:2:1 mixture of BnOH, L-LA and **3** in  $CD_2Cl_2$  (500.13 MHz, 298 K) leading to the formation of  $P_2$ 



S11. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 500.13 MHz, 298 K) of a PLLA sample prepared with **3**/BnOH (from Table 2, entry 8)



## S12 VT <sup>7</sup>Li NMR for $\{LO^3\}Li \cdot LiN(SiMe_2H)_2$ (5) in toluene- $d_8$ (258–353 K)

