

# Supporting Information

## Highly Diastereoselective Synthesis of Chiral Aminophenolate Zinc Complexes and Isoselective Polymerization of *rac*-Lactide

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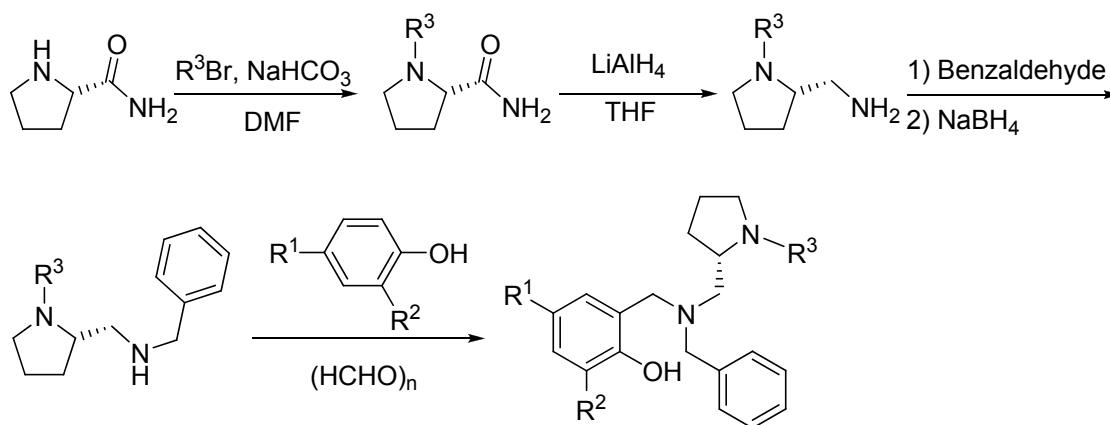
## 1. Experimental

### 1.1 Synthesis

#### 1.1.1 General considerations

All manipulations were carried out under a dry argon atmosphere using standard Schlenk-line or glove-box techniques. Toluene and *n*-hexane were refluxed over sodium benzophenone ketyl prior to use. Benzene-*d*<sub>6</sub> and other reagents were properly dried and stored in a glove-box. Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> was synthesized according to the literature method.<sup>[S1]</sup> (*S*)-(1-Ethylpyrrolidin-2-yl)methanamine and (*S*)-(1-*n*-butylpyrrolidin-2-yl)methanamine were synthesized according to the reported procedure.<sup>[S2]</sup> All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded on a Bruker AVANCE-400 spectrometer at 25 °C (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz) unless otherwise stated. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane (TMS). Elemental analyses were performed on an EA-1106 instrument.

#### 1.1.2 Synthesis of proligands



**Scheme S1.** Synthesis of chiral aminophenol proligands **L<sup>1</sup>H** – **L<sup>5</sup>H**.

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### 1.1.2.1 Synthesis of (*S*)-*N*-benzyl-1-(1-ethylpyrrolidin-2-yl)methanamine

(*S*)-(1-Ethylpyrrolidin-2-yl)methanamine (1.92 g, 0.015 mol) was added to a solution of benzaldehyde (1.75 g, 0.017 mol) in ethanol (20 mL) and the mixture was heated to reflux for 24 h. After cooling to r.t., sodium borohydride (1.33 g, 0.035 mmol) was sequentially added to the above light yellow solution in three times and the mixture was stirred for 3 h at 60 °C. The mixture was poured into water and extracted with methylene dichloride. The organic phase was dried over anhydrous MgSO<sub>4</sub>. Evaporation of the solvent gave the target product as viscous oil (2.96 g), which was used directly for the next step without further purification.

### 1.1.2.2 Synthesis of (*S*)-*N*-benzyl-1-(1-"butylpyrrolidin-2-yl)methanamine

(*S*)-(1-"Butylpyrrolidin-2-yl)methanamine (2.34 g, 0.015 mol) was added to a solution of benzaldehyde (1.75 g, 0.017 mol) in ethanol (20 mL) and the mixture was heated to reflux for 24 h. After cooling to r.t., sodium borohydride (1.33 g, 0.035 mmol) was sequentially added to the above light yellow solution in three times and the mixture was stirred for 3 h at 60 °C. The mixture was poured into water and extracted with methylene dichloride. The organic phase was dried over anhydrous MgSO<sub>4</sub>. Evaporation of the solvent gave the target product as viscous oil (3.40 g), which was used directly for the next step without further purification.

### 1.1.2.3 Synthesis of (*S*)-2-{*N*-benzyl-*N*-[(1-ethylpyrrolidin-2-yl)methyl]aminomethyl}-4, 6-dichlorophenol (**L<sup>1</sup>H**)

Paraformaldehyde (0.600 g, 20.0 mmol) and 2, 4-dichlorophenol (1.63 g, 10.0 mmol) was added to a solution of (*S*)-*N*-benzyl-1-(1-ethylpyrrolidin-2-yl)methanamine (2.18 g, 10.0 mmol) in ethanol (30 mL) at 90 °C during 12 h with magnetic stirring. The mixture was cooled to ambient temperature and concentrated under vacuum to give red oil, which was purified by column chromatography (silica gel 100 Merck, petroleum ether/ethyl acetate = 5 : 1) to provide dark red oil (2.32 g, 59.0%) after removal of all the volatiles. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.38-7.27 (m, 4H, ArH), 7.27-7.23 (m, 2H, ArH), 6.83 (d,

$^4J_{\text{HH}} = 2.4$  Hz, 1H, ArH), 3.84 (d,  $^2J_{\text{HH}} = 14.0$  Hz, 1H, ArCH<sub>2</sub>N), 3.65 (d,  $^2J_{\text{HH}} = 13.0$  Hz, 1H, ArCH<sub>2</sub>N), 3.53 (d,  $^2J_{\text{HH}} = 14.0$  Hz, 1H, ArCH<sub>2</sub>N), 3.39 (d,  $^2J_{\text{HH}} = 13.0$  Hz, 1H, ArCH<sub>2</sub>N), 3.06 (m, 1H, NCH- of pyrrolidinyl), 2.80-2.70 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 2.60-2.50 (m, 2H, NCH<sub>2</sub>CH), 2.60-2.50 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 2.21-2.08 (m, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 2.01-1.94 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 1.71-1.63 (m, 2H, -CH<sub>2</sub>- of pyrrolidinyl), 1.45-1.38 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 1.00 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 136.2, 130.2, 130.1, 129.0, 128.9, 128.1, 127.4, 125.0, 123.6, 121.9 (All ArC), 62.6 (ArCH<sub>2</sub>N), 59.3 (ArCH<sub>2</sub>N), 58.3 (NCH- of pyrrolidinyl), 57.9 (NCH<sub>2</sub>- of pyrrolidinyl), 53.7 (NCH<sub>2</sub>CH), 49.2 (NCH<sub>2</sub>CH<sub>3</sub>), 30.2 (-CH<sub>2</sub>- of pyrrolidinyl), 22.6 (-CH<sub>2</sub>- of pyrrolidinyl), 13.8 (CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd. for C<sub>21</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>2</sub>O: C, 64.12; H, 6.66; N, 7.12. Found: C, 63.64; H, 6.65; N, 6.69%.

#### 1.1.2.4 Synthesis of (S)-2-{N-benzyl-N-[(1-ethylpyrrolidin-2-yl)methyl]aminomethyl}-4, 6-dimethylphenol (L<sup>2</sup>H)

Paraformaldehyde (0.600 g, 20.0 mmol) and 2, 4-di-methylphenol (1.22 g, 10.0 mmol) was added to a solution of (S)-N-benzyl-1-(1-ethylpyrrolidin-2-yl)methanamine (2.18 g, 10.0 mmol) in ethanol (20 mL) at 90 °C during 12 h with magnetic stirring. The mixture was cooled to ambient temperature and concentrated under vacuum to give brown oil, which was purified by column chromatography (silica gel 100 Merck, petroleum/ethyl acetate = 5 : 1) to provide light brown oil (1.59 g, 45.1%) after removal of all the volatiles. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.50 (s, 1H, ArOH), 7.36-7.23 (m, 5H, ArH), 6.86 (s, 1H, ArH), 6.66 (s, 1H, ArH), 3.95 (d,  $^2J_{\text{HH}} = 13.7$  Hz, 1H, ArCH<sub>2</sub>N), 3.74 (d,  $^2J_{\text{HH}} = 13.0$  Hz, 1H, ArCH<sub>2</sub>N), 3.49 (d,  $^2J_{\text{HH}} = 13.7$  Hz, 1H, ArCH<sub>2</sub>N), 3.39 (d,  $^2J_{\text{HH}} = 13.0$  Hz, 1H, ArCH<sub>2</sub>N), 3.06 (ddd,  $^2J_{\text{HH}} = 9.5$ ,  $^3J_{\text{HH}} = 6.9$ ,  $^3J_{\text{HH}} = 2.9$  Hz, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 2.74 (dq,  $^2J_{\text{HH}} = 11.9$ ,  $^3J_{\text{HH}} = 7.2$  Hz, 1H, NCH<sub>2</sub>CH<sub>3</sub>), 2.60-2.50 (m, 2H, NCH- & NCH<sub>2</sub>- of pyrrolidinyl), 2.46 (dd,  $^2J_{\text{HH}} = 12.6$ ,  $^3J_{\text{HH}} = 9.5$  Hz, 1H, NCH<sub>2</sub>CH), 2.23 (s, 3H, ArCH<sub>3</sub>), 2.21 (s, 3H, ArCH<sub>3</sub>), 2.14 (dq,  $^2J_{\text{HH}} = 11.9$ ,  $^3J_{\text{HH}} = 7.2$  Hz, 1H, NCH<sub>2</sub>CH<sub>3</sub>), 2.10-1.95 (m, 2H, NCH<sub>2</sub>CH & -CH<sub>2</sub>- of pyrrolidinyl), 1.73-1.52 (m, 2H, -CH<sub>2</sub>- of pyrrolidinyl), 1.46-1.31 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 1.04 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 3H, NCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):

153.3, 137.1, 130.8, 130.1, 128.6, 127.9, 127.7, 127.2, 124.8, 121.4 (All Ar-C), 62.4 (ArCH<sub>2</sub>N), 59.3 (ArCH<sub>2</sub>N), 59.0 (NCH- of pyrrolidiny), 58.6 (NCH<sub>2</sub>- of pyrrolidiny), 53.8 (NCH<sub>2</sub>CH), 49.1 (NCH<sub>2</sub>CH<sub>3</sub>), 30.5 (-CH<sub>2</sub>- of pyrrolidiny), 22.6 (-CH<sub>2</sub>- of pyrrolidiny), 21.6 (ArCH<sub>3</sub>), 16.0 (ArCH<sub>3</sub>), 14.0 (CH<sub>2</sub>CH<sub>3</sub>).  
Anal. Calcd. for C<sub>23</sub>H<sub>32</sub>N<sub>2</sub>O: C, 78.36; H, 9.15; N, 7.95. Found: C, 77.67; H, 9.08; N, 7.61%.

#### 1.1.2.5 Synthesis of (*S*)-2-{*N*-benzyl-*N*-[(1-ethylpyrrolidin-2-yl)methyl]aminomethyl}-4, 6-di-*tert*-butylphenol (L<sup>3</sup>H)

Paraformaldehyde (0.600 g, 20.0 mmol) and 2, 4-di-*tert*-butylphenol (2.06 g, 10.0 mmol) was added to a solution of (*S*)-*N*-benzyl-1-(1-ethylpyrrolidin-2-yl)methanamine (2.18 g, 10.0 mmol) in ethanol (30 mL) at 90 °C during 12 h with magnetic stirring. The mixture was cooled to ambient temperature and concentrated under vacuum to give brown oil, which was purified by column chromatography (silica gel 100 Merck, petroleum ether/ethyl acetate = 20 : 1) to provide light brown oil (1.95 g, 44.7%) after removal of all the volatiles. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.55 (s, 1H, ArOH), 7.35-7.23 (m, 5H, ArH), 7.18 (s, 1H, ArH), 6.85 (s, 1H, ArH), 3.97 (d, <sup>2</sup>J<sub>HH</sub> = 13.4 Hz, 1H, ArCH<sub>2</sub>N), 3.75 (d, <sup>2</sup>J<sub>HH</sub> = 13.0 Hz, 1H, ArCH<sub>2</sub>N), 3.51 (d, <sup>2</sup>J<sub>HH</sub> = 13.4 Hz, 1H, ArCH<sub>2</sub>N), 3.37 (d, <sup>2</sup>J<sub>HH</sub> = 13.0 Hz, 1H, ArCH<sub>2</sub>N), 3.09-3.02 (m, 1H, NCH- of pyrrolidiny), 2.71-2.63 (m, 1H, NCH<sub>2</sub>- of pyrrolidiny), 2.50-2.38 (m, 3H, NCH<sub>2</sub>CH & NCH<sub>2</sub>- of pyrrolidiny), 2.11-2.01 (m, 1H, NCH<sub>2</sub>- of pyrrolidiny), 2.03-1.88 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.67-1.55 (m, 2H, -CH<sub>2</sub>- of pyrrolidiny), 1.39 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.37-1.28 (m, 1H, -CH<sub>2</sub>- of pyrrolidiny), 1.22 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.03 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): 154.0, 140.8, 137.3, 135.8, 130.1, 128.5, 127.6, 124.0, 123.1, 121.8 (All Ar-C), 62.3 (ArCH<sub>2</sub>N), 60.0 (ArCH<sub>2</sub>N), 59.4 (NCH- of pyrrolidiny), 58.6 (NCH<sub>2</sub>- of pyrrolidiny), 53.9 (NCH<sub>2</sub>CH), 49.2 (NCH<sub>2</sub>CH<sub>3</sub>), 35.1 (C(CH<sub>3</sub>)<sub>3</sub>), 34.1 (C(CH<sub>3</sub>)<sub>3</sub>), 31.9 (C(CH<sub>3</sub>)<sub>3</sub>), 30.4 (-CH<sub>2</sub>- of pyrrolidiny), 29.8 (C(CH<sub>3</sub>)<sub>3</sub>), 22.6 (-CH<sub>2</sub>- of pyrrolidiny), 14.0 (CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd. for C<sub>29</sub>H<sub>44</sub>N<sub>2</sub>O·(0.26 CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>3</sub>): C, 78.51; H, 10.11; N, 6.10. Found: C, 78.88; H, 10.03; N, 6.46%.

### 1.1.2.6 Synthesis of (*S*)-2-{*N*-benzyl-*N*-[(1-ethylpyrrolidin-2-yl)methyl]aminomethyl}- 4-methyl-6-(triphenylmethyl)phenol (**L<sup>4</sup>H**)

Paraformaldehyde (0.600 g, 20.0 mmol) and 2-trityl-4-methylphenol (3.50 g, 10.0 mmol) was added to a solution of (*S*)-*N*-benzyl-1-(1-ethylpyrrolidin-2-yl)methanamine (2.18 g, 10.0 mmol) in ethanol (30 mL) at 90 °C during 12 h with magnetic stirring. The mixture was cooled to ambient temperature and concentrated under vacuum to give a white solid, which was purified by column chromatography (silica gel 100 Merck, petroleum ether/ethyl acetate = 20 : 1) to provide a white powder (3.96 g, 68.2%) after removal of all the volatiles. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.3 (s, 1H ArOH), 7.28-7.20 (m, 15H, ArH), 7.18-7.14 (m, 3H, ArH), 6.95 (s, 1H ArH), 6.93-6.87 (m, 2H, ArH), 6.82 (s, 1H, ArH), 3.89 (d, <sup>2</sup>J<sub>HH</sub> = 13.5 Hz, 1H, ArCH<sub>2</sub>N), 3.54 (d, <sup>2</sup>J<sub>HH</sub> = 12.8 Hz, 1H, ArCH<sub>2</sub>N), 3.50 (d, <sup>2</sup>J<sub>HH</sub> = 13.5 Hz, 1H, ArCH<sub>2</sub>N), 3.29 (d, <sup>2</sup>J<sub>HH</sub> = 12.8 Hz, 1H, ArCH<sub>2</sub>N), 3.03-2.92 (m, 1H, NCH- of pyrrolidinyl), 2.70-2.59 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 2.30-2.21 (m, 3H, NCH<sub>2</sub>CH & NCH<sub>2</sub>CH<sub>3</sub>), 2.20 (s, 3H, ArCH<sub>3</sub>), 2.08-2.00 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 1.94 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 17.3, <sup>3</sup>J<sub>HH</sub> = 9.0 Hz, NCH<sub>2</sub>CH), 1.62-1.50 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 1.48-1.38 (m, 2H, -CH<sub>2</sub>- of pyrrolidinyl), 1.06-0.99 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.95 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): 154.1, 146.3, 137.3, 133.8, 131.5, 131.0, 130.3, 129.2, 128.4, 127.4, 127.1, 126.6, 125.5, 122.8 (All ArC), 63.5 (Ar-CPh<sub>3</sub>), 62.5 (ArCH<sub>2</sub>N), 59.8 (ArCH<sub>2</sub>N), 59.1 (NCH- of pyrrolidinyl), 57.2 (NCH<sub>2</sub>- of pyrrolidinyl), 53.7 (NCH<sub>2</sub>CH), 49.1 (NCH<sub>2</sub>CH<sub>3</sub>), 29.9 (-CH<sub>2</sub>- of pyrrolidinyl), 22.6 (-CH<sub>2</sub>- of pyrrolidinyl), 21.1 (Ar-CH<sub>3</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd. for C<sub>41</sub>H<sub>44</sub>N<sub>2</sub>O: C, 84.79; H, 7.64; N, 4.82. Found: C, 84.37; H, 7.61; N, 4.77%.

### 1.1.2.7 Synthesis of (*S*)-2-{*N*-benzyl-*N*-[(1-*n*-butylpyrrolidin-2-yl)methyl]aminomethyl}- 4-methyl-6-(triphenylmethyl)phenol (**L<sup>5</sup>H**)

Paraformaldehyde (0.600 g, 20.0 mmol) and 2-trityl-4-methylphenol (3.50 g, 10.0 mmol) was added to a solution of (*S*)-*N*-benzyl-1-(1-*n*-butylpyrrolidin-2-yl)methanamine (2.18 g, 10.0 mmol) in ethanol (30 mL) at 90 °C during 12 h with magnetic stirring. The mixture was cooled to ambient temperature and concentrated under vacuum to give a white solid, which was purified by recrystallization from methanol



to provide a white powder (5.46 g, 89.8%).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  10.59 (s, 1H, ArOH), 7.56 (d,  $^3J_{\text{HH}} = 7.5$  Hz, 6H, ArH), 7.35 (d,  $^4J_{\text{HH}} = 1.6$  Hz, 1H, ArH), 7.14-7.08 (m, 9H, ArH), 7.02 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 3H, ArH), 6.93-6.88 (m, 2H, ArH), 6.74 (d,  $^4J_{\text{HH}} = 1.6$  Hz, 1H, ArH), 3.62 (d,  $^2J_{\text{HH}} = 13.4$  Hz, 1H, ArCH<sub>2</sub>N), 3.42 (d,  $^2J_{\text{HH}} = 13.4$  Hz, 1H, ArCH<sub>2</sub>N), 3.29 (d,  $^2J_{\text{HH}} = 12.8$  Hz, 1H, ArCH<sub>2</sub>N), 3.15 (d,  $^2J_{\text{HH}} = 12.8$  Hz, 1H, ArCH<sub>2</sub>N), 2.82-2.75 (m, 1H, NCH- of pyrrolidinyl), 2.49-2.39 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 2.24 (d,  $^3J_{\text{HH}} = 5.3$  Hz, 2H, NCH<sub>2</sub>CH), 2.15 (s, 3H, ArCH<sub>3</sub>), 2.11-2.03 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 1.83-1.75 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 1.68 (dd,  $^2J_{\text{HH}} = 16.6$ ,  $^3J_{\text{HH}} = 9.0$  Hz, 1H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.38 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 1.33-1.11 (m, 6H, -CH<sub>2</sub>- of pyrrolidinyl & NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.05 (m, 1H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.84 (t,  $^3J_{\text{HH}} = 7.0$  Hz, 3H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ): 154.9, 147.2, 138.4, 134.8, 132.3, 131.7, 130.1, 129.9, 128.9, 127.8, 127.7, 127.1, 126.1, 123.1 (All ArC), 64.3 (ArCPh<sub>3</sub>), 63.3 (ArCH<sub>2</sub>N), 60.4 (ArCH<sub>2</sub>N), 59.6 (NCH- of pyrrolidinyl), 57.4 (NCH<sub>2</sub>- of pyrrolidinyl), 55.5 (NCH<sub>2</sub>CH), 54.3 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 31.6 (-CH<sub>2</sub>- of pyrrolidinyl), 30.1 (-CH<sub>2</sub>- of pyrrolidinyl), 23.1 (ArCH<sub>3</sub>), 21.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 21.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 14.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd. for C<sub>43</sub>H<sub>48</sub>N<sub>2</sub>O: C, 84.82; H, 7.95; N, 4.60. Found: C, 84.75; H, 7.80; N, 4.62%.

### 1.1.3 Synthesis of zinc complexes

#### 1.1.3.1 Synthesis of [L<sup>1</sup>ZnN(SiMe<sub>3</sub>)<sub>2</sub>] (1)

In a glove box, the aminophenol L<sup>1</sup>H (0.590 g, 1.50 mmol) was dissolved in toluene (3 mL) and was added dropwise to a solution of Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.580 g, 1.50 mmol) in *n*-hexane (3 mL). The reaction mixture was stirred at room temperature overnight, whereas a white precipitate was formed. After filtration, the collected white precipitate was washed with cold *n*-hexane (3 × 2 mL) and dried under vacuum to afford the target complex **1** in 51% (0.473 g) as a mixture of two diastereomers in 2 : 5 ratio (isomer **1a** : isomer **1b**). NMR spectroscopic data for isomer **1a**:  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.45 (d,  $^4J_{\text{HH}} = 2.7$  Hz, 1H, ArH), 7.13-7.11 (m, 3H, ArH), 7.01 (dd,  $^3J_{\text{HH}} = 6.5$ ,  $^4J_{\text{HH}} = 3.0$  Hz, 2H, ArH), 6.44 (d,  $^4J_{\text{HH}} = 2.7$  Hz, 1H, ArH), 4.07 (d,  $^2J_{\text{HH}} = 13.8$  Hz, 1H, ArCH<sub>2</sub>N), 3.75 (d,  $^2J_{\text{HH}} = 12.7$  Hz, 1H, ArCH<sub>2</sub>N),

3.64 (d,  $^2J_{\text{HH}} = 13.8$  Hz, 1H, ArCH<sub>2</sub>N), 2.76 (d,  $^2J_{\text{HH}} = 12.7$  Hz, 1H, ArCH<sub>2</sub>N), 2.62-2.52 (m, 1H, NCH- of pyrrolidinyl), 2.51-2.44 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 2.41-2.30 (m, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 2.02 (m, 1H, NCH<sub>2</sub>CH), 1.78-1.60 (m, 2H, NCH<sub>2</sub>- of pyrrolidinyl & NCH<sub>2</sub>CH), 1.16 (t,  $^3J_{\text{HH}} = 7.1$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.02-0.92 (m, 2H, -CH<sub>2</sub>- of pyrrolidinyl), 0.88-0.78 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.53 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>). 0.38-0.32 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): 162.5, 132.7, 132.4, 131.7, 130.8, 129.2, 128.5, 125.8, 125.0, 117.1 (All Ar-C), 66.7 (ArCH<sub>2</sub>N), 64.9 (ArCH<sub>2</sub>N), 59.5 (NCH- of pyrrolidinyl), 59.1 (NCH<sub>2</sub>- of pyrrolidinyl), 50.5 (NCH<sub>2</sub>CH), 50.4 (NCH<sub>2</sub>CH<sub>3</sub>), 25.6 (-CH<sub>2</sub>- of pyrrolidinyl), 20.8 (-CH<sub>2</sub>- of pyrrolidinyl), 14.5 (CH<sub>2</sub>CH<sub>3</sub>), 7.5 (Si(CH<sub>3</sub>)<sub>3</sub>). NMR spectroscopic data for isomer **1b**: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.12 (d,  $^4J_{\text{HH}} = 2.7$  Hz, 1H, ArH), 7.13-7.11 (m, 3H, ArH), 6.81 (dd,  $^3J_{\text{HH}} = 7.2$ ,  $^4J_{\text{HH}} = 2.1$  Hz, 2H, ArH), 6.37 (d,  $^4J_{\text{HH}} = 2.7$  Hz, 1H, ArH), 4.07 (pseudo d,  $^2J_{\text{HH}} = 13.3$  Hz, 2H, ArCH<sub>2</sub>N), 3.85 (d,  $^2J_{\text{HH}} = 14.0$  Hz, 1H, ArCH<sub>2</sub>N), 2.89 (d,  $^2J_{\text{HH}} = 12.9$  Hz, 1H, ArCH<sub>2</sub>N), 2.89-2.76 (m, 1H, NCH- of pyrrolidinyl), 2.62-2.44 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 2.30-2.24 (m, 2H, NCH<sub>2</sub>CH), 1.93-1.84 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 1.78-1.60 (m, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 1.14 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 3H), 1.02-0.92 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.71-0.65 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.54 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.44-0.38 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.38-0.33 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 130.9, 130.7, 129.9, 129.4, 129.3, 129.1, 128.5, 126.3, 122.6, 116.9 (All ArC), 64.9 (ArCH<sub>2</sub>N), 63.4 (ArCH<sub>2</sub>N), 59.0 (NCH- of pyrrolidinyl), 58.6 (NCH<sub>2</sub>- of pyrrolidinyl), 49.8 (NCH<sub>2</sub>CH), 48.9 (NCH<sub>2</sub>CH<sub>3</sub>), 25.0 (-CH<sub>2</sub>- of pyrrolidinyl), 19.9 (-CH<sub>2</sub>- of pyrrolidinyl), 13.7 (CH<sub>2</sub>CH<sub>3</sub>), 7.3 (Si(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd. for C<sub>27</sub>H<sub>43</sub>Cl<sub>2</sub>N<sub>3</sub>OSi<sub>2</sub>Zn: C, 52.46; H, 7.01; N, 6.80. Found: C, 52.47; H, 7.07; N, 6.86%.

### 1.1.3.2 Synthesis of [L<sup>2</sup>ZnN(SiMe<sub>3</sub>)<sub>2</sub>] (**2**).

In a glove box, the aminophenol **L<sup>2</sup>H** (0.529 g, 1.50 mmol) was dissolved in toluene (3 mL) and was added dropwise to a solution of Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.580 g, 1.50 mmol) in hexane (3 mL). The reaction mixture was stirred at room temperature overnight, whereas white solids was formed. After filtration, the collected white precipitate was washed with cold hexane (3 × 2 mL) and dried under vacuum to obtain the

target complex **2** in 54% (0.465 g) as a mixture of two diastereoisomers in 1 : 2 ratio (isomer **2a** : isomer **2b**). NMR spectroscopic data for isomer **2a**:  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.15-7.03 (m, 4H, ArH), 6.92-6.88 (m, 2H, ArH), 6.30 (s, 1H, ArH), 4.32 (d,  $^2J_{\text{HH}} = 12.4$  Hz, 1H), 4.17 (d,  $^2J_{\text{HH}} = 13.8$  Hz, 1H), 3.99 (d,  $^2J_{\text{HH}} = 13.8$  Hz, 1H), 3.16 (d,  $^2J_{\text{HH}} = 12.4$  Hz, 1H), 3.00-2.91 (m, 1H, -CH- of pyrrolidiny), 2.65-2.55 (m, 2H,  $\text{NCH}_2\text{CH}$ ), 2.54-2.44 (m, 1H,  $\text{NCH}_2\text{CH}_3$ ), 2.51 (s, 3H, Ar- $\text{CH}_3$ ), 2.16 (s, 3H, Ar- $\text{CH}_3$ ), 2.19-2.07 (m, 2H, - $\text{CH}_2$ - of pyrrolidiny &  $\text{NCH}_2\text{CH}_3$ ), 1.19 (t,  $^3J_{\text{HH}} = 6.4$  Hz, 3H), 1.06-0.96 (m, 2H, - $\text{CH}_2$ - of pyrrolidiny), 0.92-0.82 (m, 1H, - $\text{CH}_2$ - of pyrrolidiny), 0.72-0.62 (m, 1H, - $\text{CH}_2$ - of pyrrolidiny), 0.58 (s, 18H), 0.49-0.35 (m, 1H, - $\text{CH}_2$ - of pyrrolidiny).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  163.8, 132.7, 131.6, 130.1, 129.1, 129.1, 128.9, 128.5, 128.3, 118.9 (All ArC), 63.5 (Ar $\text{CH}_2\text{N}$ ), 59.6 (Ar $\text{CH}_2\text{N}$ ), 59.0 (NCH- of pyrrolidiny), 50.2 (NCH $_2$ - of pyrrolidiny), 49.6 (NCH $_2\text{CH}$ ), 48.4 (NCH $_2\text{CH}_3$ ), 25.1 (- $\text{CH}_2$ - of pyrrolidiny), 21.0 (Ar $\text{CH}_3$ ), 19.9 (Ar $\text{CH}_3$ ), 18.5 (- $\text{CH}_2$ - of pyrrolidiny), 13.7 (NCH $_2\text{CH}_3$ ), 7.4 ( $\text{Si}(\text{CH}_3)_3$ ). NMR spectroscopic data for isomer **2b**:  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.15-7.03 (m, 6H, ArH), 6.39 (s, 1H, ArH), 4.22 (d,  $^2J_{\text{HH}} = 13.9$  Hz, 1H), 4.05 (d,  $^2J_{\text{HH}} = 12.4$  Hz, 1H), 3.80 (d,  $^2J_{\text{HH}} = 13.9$  Hz, 1H), 3.07 (d,  $^2J_{\text{HH}} = 12.4$  Hz, 1H), 2.75-2.65 (m, 1H, -CH- of pyrrolidiny), 2.65-2.55 (m, 1H, NCH $_2\text{CH}$ ), 2.48 (s, 3H, Ar- $\text{CH}_3$ ), 2.41-2.31 (m, 2H, - $\text{CH}_2$ - of pyrrolidiny & , NCH $_2\text{CH}$ ), 2.22 (s, 3H, Ar- $\text{CH}_3$ ), 1.98-1.79 (m, 2H, - $\text{CH}_2$ - of pyrrolidiny & NCH $_2\text{CH}_3$ ), 1.75-1.65 (m, 1H, - $\text{CH}_2$ - of pyrrolidiny), 1.15 (t,  $^3J_{\text{HH}} = 6.9$  Hz, 3H), 1.06-0.96 (m, 2H, - $\text{CH}_2$ - of pyrrolidyl), 0.92-0.82 (m, 1H, - $\text{CH}_2$ - of pyrrolidiny), 0.57 (s, 18H), 0.49-0.35 (m, 1H, - $\text{CH}_2$ - of pyrrolidiny).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  164.7, 133.3, 132.9, 132.6, 131.9, 129.1, 129.1, 127.9, 121.6, 121.4 (All ArC), 66.7 (Ar $\text{CH}_2\text{N}$ ), 64.6 (Ar $\text{CH}_2\text{N}$ ), 60.4 (NCH- of pyrrolidiny), 59.2 (NCH $_2$ - of pyrrolidiny), 50.4 (NCH $_2\text{CH}$ ), 50.1 (NCH $_2\text{CH}_3$ ), 25.8 (- $\text{CH}_2$ - of pyrrolidiny), 21.1 (Ar $\text{CH}_3$ ), 20.9 (Ar $\text{CH}_3$ ), 18.0 (- $\text{CH}_2$ - of pyrrolidiny), 14.6 (NCH $_2\text{CH}_3$ ), 7.6 ( $\text{Si}(\text{CH}_3)_3$ ). Anal. Calcd. For  $\text{C}_{29}\text{H}_{49}\text{N}_3\text{OSi}_2\text{Zn}$ : C, 60.33; H, 8.56; N, 7.28. Found: C, 60.31; H, 8.50; N, 7.19%.

### 1.1.3.3 Synthesis of $[\text{L}^3\text{ZnN}(\text{SiMe}_3)_2]$ (**3**)

In a glove box, the aminophenol **L<sup>3</sup>H** (0.654 mg, 1.50 mmol) was dissolved in toluene (2 mL) and was cannulated to a solution of  $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$  (0.655 g, 1.50 mmol) in *n*-hexane. The reaction mixture was

allowed to be stirred at room temperature overnight. The solvent and volatile components were removed under reduced pressure to afford a white vesicular solid which was then recrystallized with *n*-hexane. The resulting colorless crystals were washed with cold *n*-hexane three times and dried under vacuum to give the target complex **3** in 59% (0.585 g) as a mixture of two diastereomers in 1 : 1 ratio. Due to the same percentage in the mixture, the NMR signals could be assigned properly to an exact isomer, thus all the signals were listed together. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.65-7.60 (m, 1H, ArH), 7.59-7.55 (m, 1H, ArH), 7.30-7.20 (m, 2H, ArH), 7.17-7.12 (m, 3H, ArH), 7.10-7.04 (m, 3H, ArH), 6.97 (d, <sup>4</sup>J<sub>HH</sub> = 2.3 Hz, 1H, ArH), 6.92-6.87 (m, 2H), 6.66 (d, <sup>4</sup>J<sub>HH</sub> = 2.4 Hz, 1H), 4.33 (d, <sup>2</sup>J<sub>HH</sub> = 12.4 Hz, 1H, ArCH<sub>2</sub>N), 4.31 (d, <sup>2</sup>J<sub>HH</sub> = 13.9 Hz, 1H, ArCH<sub>2</sub>N), 4.25 (d, <sup>2</sup>J<sub>HH</sub> = 14.0 Hz, 1H, ArCH<sub>2</sub>N), 4.08 (d, <sup>2</sup>J<sub>HH</sub> = 14.0 Hz, 1H, ArCH<sub>2</sub>N), 3.95 (d, <sup>2</sup>J<sub>HH</sub> = 13.9 Hz, 1H, ArCH<sub>2</sub>N), 3.64 (d, <sup>2</sup>J<sub>HH</sub> = 12.3 Hz, 1H, ArCH<sub>2</sub>N), 3.29 (d, <sup>2</sup>J<sub>HH</sub> = 12.3 Hz, 2H, ArCH<sub>2</sub>N), 3.13 (d, <sup>2</sup>J<sub>HH</sub> = 12.4 Hz, 1H, ArCH<sub>2</sub>N), 3.11-3.02 (m, 1H), 2.86 – 2.74 (m, 1H), 2.52-2.44 (m, 3H), 2.39 (m, 2H), 2.32 (m, 2H), 2.23 (m, 1H), 2.02 (dd, <sup>2</sup>J<sub>HH</sub> = 14.3, <sup>3</sup>J<sub>HH</sub> = 4.1 Hz, 1H), 1.96-1.91 (m, 1H), 1.87 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.81 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.76-1.73 (m, 1H), 1.61-1.55 (m, 2H), 1.53-1.50 (m, 1H), 1.46 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.39 – 1.33 (m, 2H), 1.27 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.23-1.20 (m, 2H), 1.20 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 1.16-1.12 (m, 1H), 0.94 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 0.71-0.65 (m, 1H), 0.59 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.48 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 165.1, 164.7, 138.9, 138.5, 135.1, 134.9, 132.6, 132.4, 131.7, 129.2, 129.1, 128.9, 128.5, 128.3, 127.1, 126.8, 125.3, 124.9, 120.7, 120.2 (All ArC), 64.2 (ArCH<sub>2</sub>N), 61.7 (ArCH<sub>2</sub>N), 60.7 (ArCH<sub>2</sub>N), 59.7 (ArCH<sub>2</sub>N), 59.1 (NCH- of pyrrolidinyl), 57.9 (NCH- of pyrrolidinyl), 54.0 (NCH<sub>2</sub>- of pyrrolidinyl), 51.2 (NCH<sub>2</sub>- of pyrrolidinyl), 49.6 (NCH<sub>2</sub>CH<sub>3</sub>), 49.4 (NCH<sub>2</sub>CH<sub>3</sub>), 36.3 (C(CH<sub>3</sub>)<sub>3</sub>), 36.3 (C(CH<sub>3</sub>)<sub>3</sub>), 34.5 (C(CH<sub>3</sub>)<sub>3</sub>), 34.3 (C(CH<sub>3</sub>)<sub>3</sub>), 32.7 (C(CH<sub>3</sub>)<sub>3</sub>), 32.5 (C(CH<sub>3</sub>)<sub>3</sub>), 30.9 (C(CH<sub>3</sub>)<sub>3</sub>), 30.6 (C(CH<sub>3</sub>)<sub>3</sub>), 26.6 (-CH<sub>2</sub>- of pyrrolidinyl), 24.9 (-CH<sub>2</sub>- of pyrrolidinyl), 21.8 (-CH<sub>2</sub>- of pyrrolidinyl), 19.6 (-CH<sub>2</sub>- of pyrrolidinyl), 14.1 (CH<sub>2</sub>CH<sub>3</sub>), 13.2 (CH<sub>2</sub>CH<sub>3</sub>), 7.7 (Si(CH<sub>3</sub>)<sub>3</sub>), 7.4 (Si(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd. for C<sub>35</sub>H<sub>61</sub>N<sub>3</sub>OSi<sub>2</sub>Zn: C, 63.55; H, 9.30; N, 6.35. Found: C, 63.84; H, 9.07; N, 5.87%.

#### 1.1.3.4 Synthesis of [L<sup>4</sup>ZnN(SiMe<sub>3</sub>)<sub>2</sub>] (**4**).

In a glove box, the aminophenol **L<sup>4</sup>H** (0.871 g, 1.50 mmol) was dissolved in toluene (2 mL) and was cannulated to a solution of Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.580 g, 1.50 mmol) in *n*-hexane. The reaction mixture was allowed to be stirred at room temperature overnight. The solvent and volatile components were removed under reduced pressure to afford a white vesicular solid which was then recrystallized with a mixture of *n*-hexane and toluene. The resulting colorless crystals were washed with cold *n*-hexane three times and dried under vacuum to give a white solid **4** in 52.3% (0.631 g) as a mixture of two diastereomers in 7 : 1 (isomer **4a** : isomer **4b**). Due to a relatively small percentage in the mixture, the NMR signals of isomer **4b** could not be identified completely, thus only the NMR spectroscopic data of isomer **4a** was listed: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.67-7.55 (m, 6H, ArH), 7.39 (d, <sup>4</sup>J<sub>HH</sub> = 2.2 Hz, 1H, ArH), 7.14-7.09 (m, 7H, ArH), 7.07-6.87 (m, 7H, ArH), 6.40 (d, <sup>4</sup>J<sub>HH</sub> = 2.2 Hz, 1H, ArH), 4.38 (d, <sup>2</sup>J<sub>HH</sub> = 12.3 Hz, 1H, ArCH<sub>2</sub>N), 4.21 (d, <sup>2</sup>J<sub>HH</sub> = 14.2 Hz, 1H, ArCH<sub>2</sub>N), 4.07 (d, <sup>2</sup>J<sub>HH</sub> = 14.2 Hz, 1H, ArCH<sub>2</sub>N), 3.27 (d, <sup>2</sup>J<sub>HH</sub> = 12.3 Hz, 1H, ArCH<sub>2</sub>N), 3.02-2.93 (m, 1H, NCH- of pyrrolidinyl), 2.26-2.15 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 2.05 (s, 3H, ArCH<sub>3</sub>), 1.98-1.89 (m, 2H, NCH<sub>2</sub>CH), 1.86-1.75 (m, 1H, NCH<sub>2</sub>CH<sub>3</sub>), 1.39-1.29 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 1.18-1.05 (m, 2H, NCH<sub>2</sub>CH<sub>3</sub> & -CH<sub>2</sub>- of pyrrolidinyl), 1.02 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 0.97-0.83 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.60-0.52 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.50-0.40 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.35 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 165.0, 135.8, 134.9, 132.8, 132.7, 132.4, 131.6, 129.7, 129.2, 128.9, 127.8, 127.5, 126.0, 125.4, 120.8, 120.7 (All ArC), 64.7 (ArCPh<sub>3</sub>), 62.9 (ArCH<sub>2</sub>N), 59.7 (ArCH<sub>2</sub>N), 58.3 (NCH- of pyrrolidinyl), 49.8 (NCH<sub>2</sub>- of pyrrolidinyl), 48.7 (NCH<sub>2</sub>CH), 48.4 (NCH<sub>2</sub>CH<sub>3</sub>), 24.9 (-CH<sub>2</sub>- of pyrrolidinyl), 21.1 (ArCH<sub>3</sub>), 20.0 (-CH<sub>2</sub>- of pyrrolidinyl), 14.2 (CH<sub>2</sub>CH<sub>3</sub>), 7.6 (Si(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd. for C<sub>47</sub>H<sub>61</sub>N<sub>3</sub>OSi<sub>2</sub>Zn: C, 70.07; H, 7.63; N, 5.22. Found: C, 69.95; H, 7.46; N, 4.56%.

#### 1.1.3.5 Synthesis of [L<sup>5</sup>ZnN(SiMe<sub>3</sub>)<sub>2</sub>] (**5**).

In a glove box, the aminophenol **L<sup>5</sup>H** (0.912 g, 1.50 mmol) was dissolved in toluene (3 mL) and added dropwise to a solution of Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.580 g, 1.50 mmol) in hexane (2 mL). The reaction mixture was allowed to be stirred at room temperature overnight. All the volatiles were removed under vacuum to

afford a white solid which was then recrystallized with a mixture of hexane and toluene. Colorless crystals were obtained in 60% (0.749 g) as enantiomerically pure complex **5**.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.67-7.50 (m, 6H), 7.40 (d,  $^4J_{\text{HH}} = 2.2$  Hz, 1H, ArH), 7.14-7.07 (m, 9H, ArH), 7.02-6.89 (m, 5H, ArH), 6.39 (d,  $^4J_{\text{HH}} = 2.2$  Hz, 1H, ArH), 4.38 (d,  $^2J_{\text{HH}} = 12.3$  Hz, 1H, ArCH<sub>2</sub>N), 4.25 (d,  $^2J_{\text{HH}} = 14.2$  Hz, 1H, ArCH<sub>2</sub>N), 4.12 (d,  $^2J_{\text{HH}} = 14.2$  Hz, 1H, ArCH<sub>2</sub>N), 3.27 (d,  $^2J_{\text{HH}} = 12.3$  Hz, 1H, ArCH<sub>2</sub>N), 3.06-2.98 (m, 1H, NCH- of pyrrolidinyl), 2.28-2.18 (m, 1H, NCH<sub>2</sub>- of pyrrolidinyl), 2.05 (s, 3H, ArCH<sub>3</sub>), 1.98-1.91 (m, 2H, NCH<sub>2</sub>CH), 1.86-1.76 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.49-1.31 (m, 2H, -CH<sub>2</sub>- of pyrrolidinyl & NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.23-1.06 (m, 3H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.02-0.95 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.98 (t,  $^3J_{\text{HH}} = 7.1$  Hz, 3H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.88-0.79 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.67-0.54 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.52-0.43 (m, 1H, -CH<sub>2</sub>- of pyrrolidinyl), 0.35 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  165.2, 135.6, 134.9, 132.9, 132.7, 131.7, 129.2, 128.7, 128.5, 128.3, 127.9, 125.4, 120.9, 120.7 (All ArC), 64.8 (ArCPh<sub>3</sub>), 63.6 (ArCH<sub>2</sub>N), 59.7 (ArCH<sub>2</sub>N), 58.4 (NCH<sub>2</sub>- of pyrrolidinyl), 56.3 (NCH- of pyrrolidinyl), 49.1 (NCH<sub>2</sub>CH), 48.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 30.9 (-CH<sub>2</sub>- of pyrrolidinyl), 25.1 (-CH<sub>2</sub>- of pyrrolidinyl), 21.2 (Ar-CH<sub>3</sub>), 21.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 14.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.6 (Si(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd. for C<sub>49</sub>H<sub>65</sub>N<sub>3</sub>OSi<sub>2</sub>Zn·C<sub>7</sub>H<sub>8</sub>: C, 72.65; H, 7.95; N, 4.54. Found: C, 72.32; H, 8.02; N, 4.41%.

## 1.2 X-Ray diffraction measurements

Single crystals of complexes **1** and **5** were obtained from benzene-*d*<sub>6</sub> by slow evaporation at room temperature, and single crystals of complex **3** were isolated from a saturated *n*-hexane solution at -38 °C. The X-ray diffraction measurements were performed at room temperature on a Bruker SMART APEX II diffractometer with graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. All data were collected at 20 °C using the  $\omega$ -scan techniques. All structures were solved by direct methods and refined using Fourier techniques. An absorption correction based on SADABS was applied.<sup>[S3]</sup> All non-hydrogen atoms were refined by full-matrix least-squares on  $F^2$  using the SHELXTL program package.<sup>[S4]</sup> Hydrogen atoms were located and refined by the geometry method. The cell refinement, data collection, and

reduction were done by Bruker SAINT.<sup>[S5]</sup> The structure solution and refinement were performed by SHELXS-97<sup>[S6]</sup> and SHELXL-97<sup>[S7]</sup> respectively. For further crystal data and details of measurements see Table S1. Molecular structures were generated using ORTEP program.<sup>[S8]</sup> CCDC numbers 936902 (**1a/1b**), 936900 (**3a**), and 936901 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### 1.3 Ring-opening polymerization of *rac*-lactide

#### 1.3.1 General considerations

*rac*-Lactide was recrystallized with dry toluene and then sublimed twice under vacuum at 90 °C. 2-Propanol was dried over calcium hydride prior to distillation. Glassware and vials used in the polymerization were dried in an oven at 120°C overnight and exposed to vacuum-argon cycle three times. Gel permeation chromatography (GPC) analyses were carried out on a Agilent 1260 infinity instrument in THF at 25 °C, at a flow rate of 1 mL·min<sup>-1</sup>, with two PLgel 5µm Mixed-C columns (7.5×300 mm). Calibration standards were commercially available narrowly distributed linear polystyrene samples that cover a broad range of molar masses ( $10^3 < M_n < 4.4 \times 10^4$  g·mol<sup>-1</sup>).

Monomer conversion determination was monitored by integration of monomer vs. polymer methine resonances in <sup>1</sup>H NMR spectra. All spectroscopic analyses of polymers and homonuclear decoupled <sup>1</sup>H NMR spectra were performed in CDCl<sub>3</sub> on a Bruker Avance 400 MHz spectrometer with acryoprobe.

#### 1.3.2 Typical polymerization procedure

In a glove box, an initiator solution (0.5 mL, 10 mmol/mL) from a stock solution in toluene or THF was injected sequentially to a series of 10 mL vials loaded with *rac*-lactide (0.144 g, 1.0 mmol) and suitable amounts (0.5 mL) of the same dry solvent. The mixture was stirred at room temperature and quenched at the specific time intervals by adding an excess amount of normal light petroleum ether. After being dissolved with dichloromethane, a small amount of aliquot of the bulk solution was withdrawn and



dried under reduced pressure for monomer conversion characterization via  $^1\text{H}$  NMR spectroscopy. The bulk solution was slightly concentrated and the polymer was precipitated from dichloromethane via the addition of excess methanol. The collected polymer sample was further dried in a vacuum oven at 60 °C for 16 h to constant weight for gel permeation chromatography (GPC),  $^1\text{H}$  and homonuclear decoupled  $^1\text{H}$  NMR analyses.

In the cases where 2-propanol was used, the monomer solution was treated first with the solution of 2-propanol for 5 min, and then the solution of initiator was injected to the mixture. Otherwise the procedures were the same.

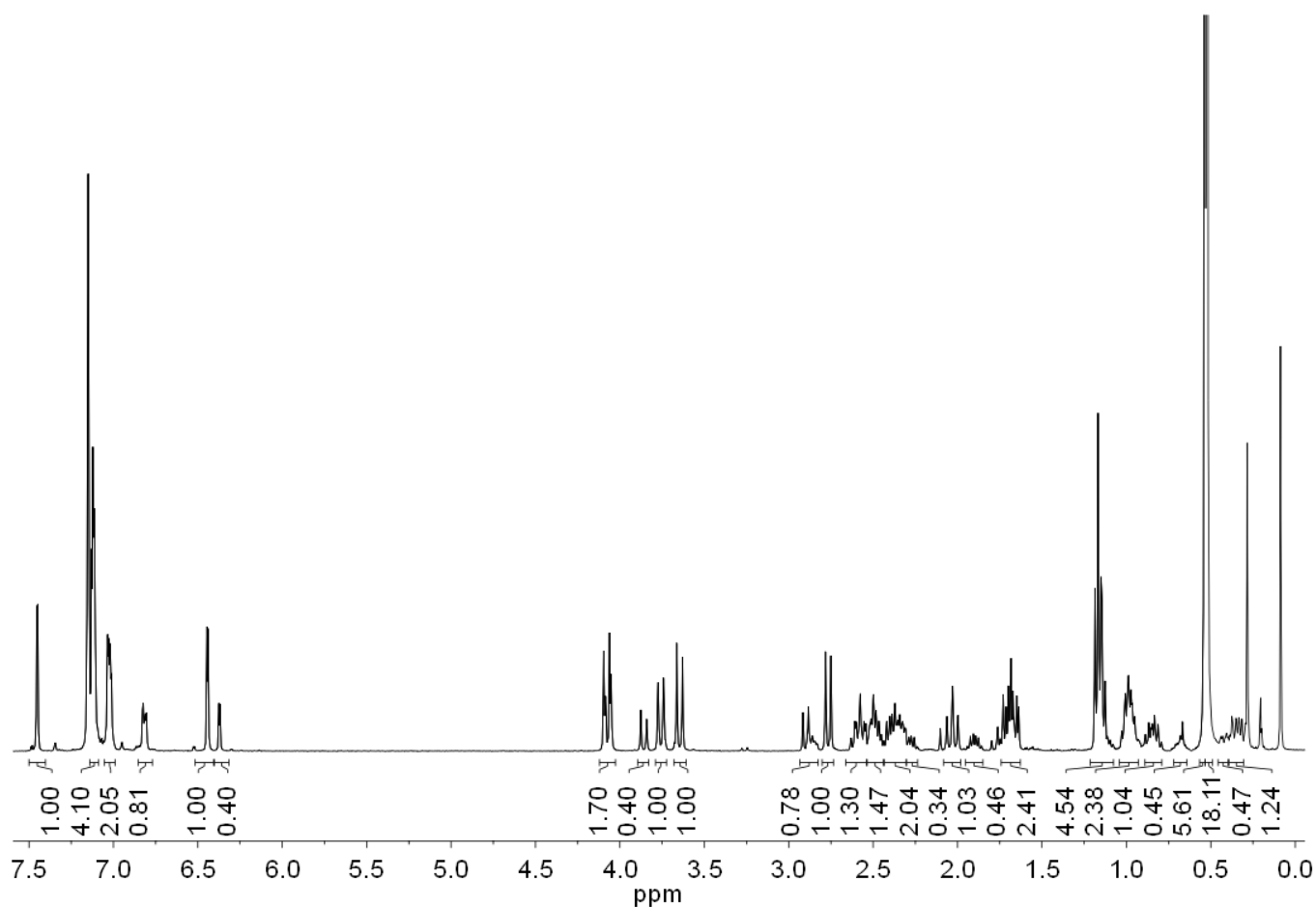
### 1.3.3 Kinetic studies

In a teflon sealed NMR tube, *D*- or *L*-lactide (36 mg, 0.25 mmol) was added to a solution of **5** in 0.50 mL of  $\text{C}_6\text{D}_6$  (0.01 M, 0.005 mmol). This mixture was immediately cooled with ice/water mixture. The NMR tube was warmed to room temperature before being inserted into the NMR spectrometer. The reaction mixture was determined in the specific time intervals (Bruker Avance 400 MHz spectrometer). Rate constants  $k_{\text{obsd}}$  for the ROP of *D*- or *L*-lactide with **5** as the initiator were determined by the slope of the plots of  $\ln([\text{LA}]_0/[\text{LA}]_t)$  vs. polymerization time.

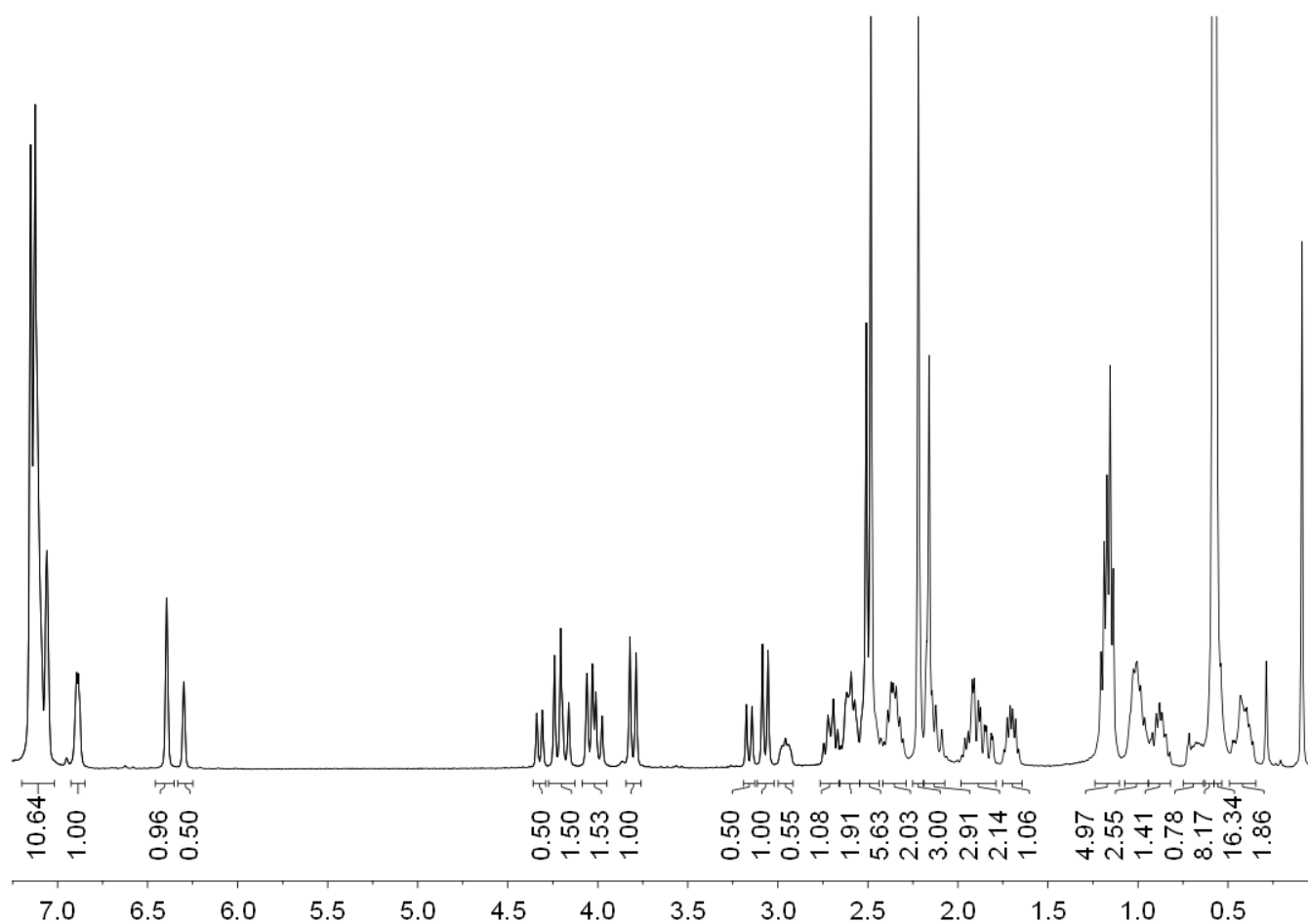


## 2. Results

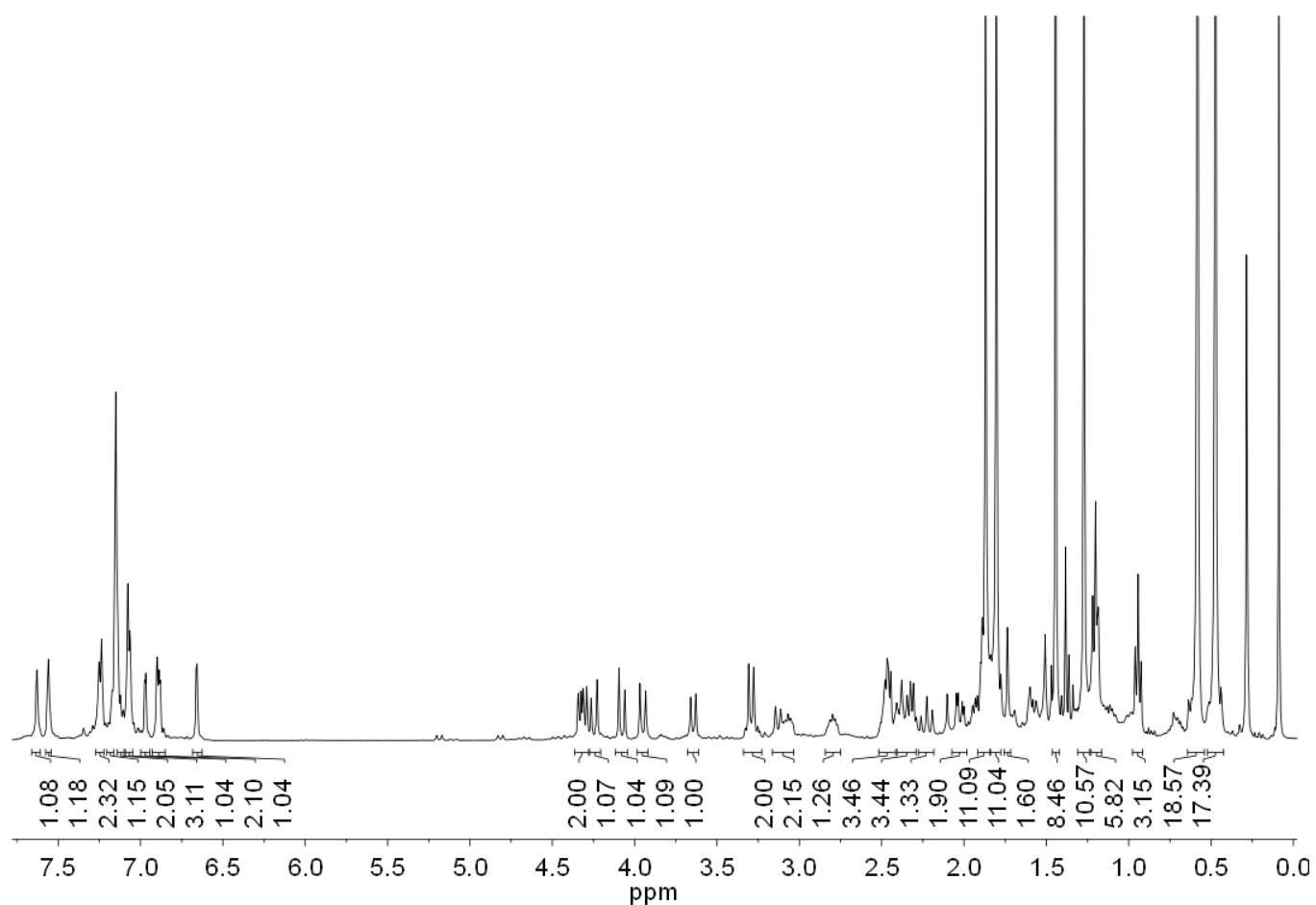
### 2.1 $^1\text{H}$ NMR spectra of zinc complexes



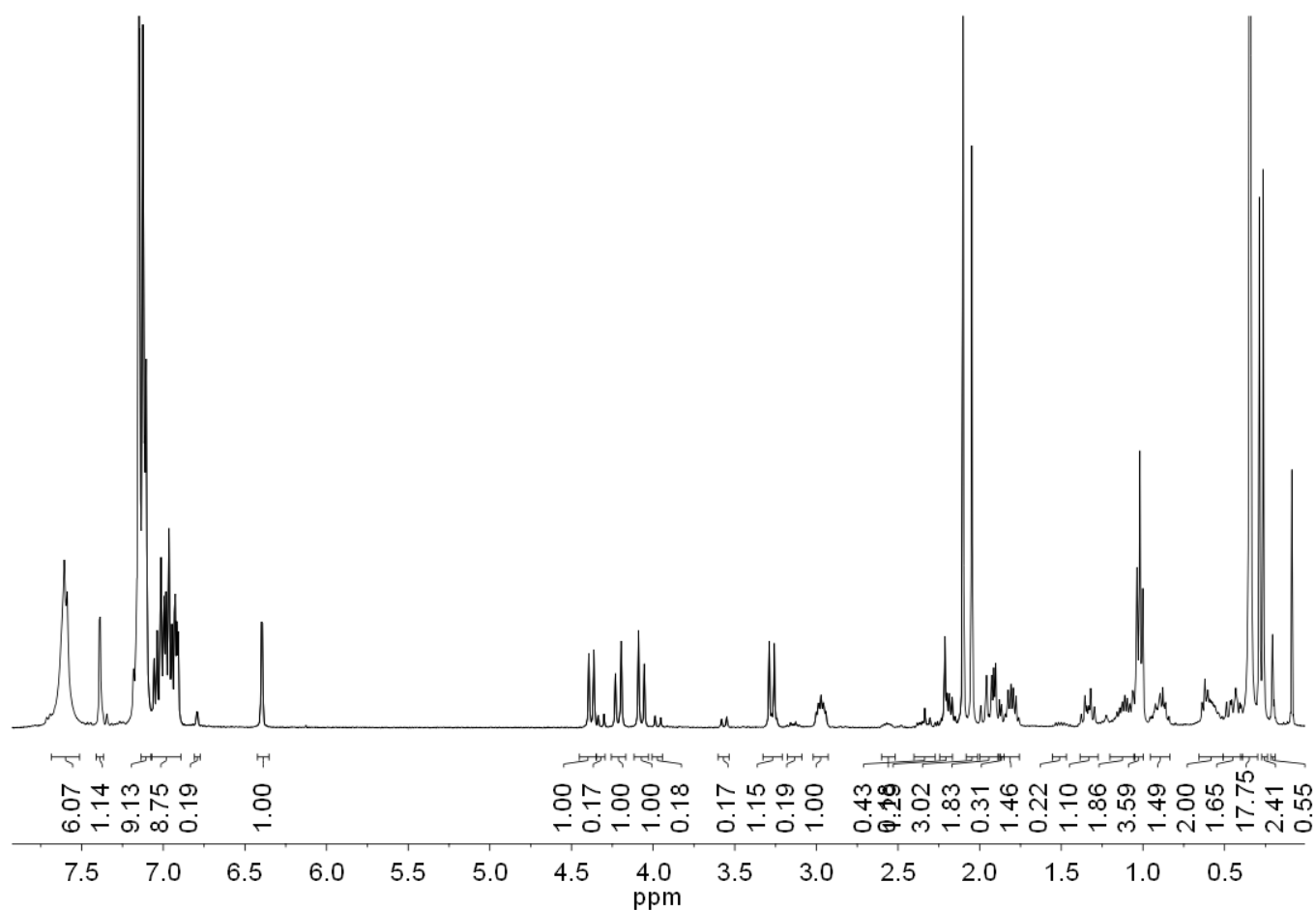
**Figure S1.**  $^1\text{H}$  NMR spectrum of **1a** and **1b** ( $\text{C}_6\text{D}_6$ , 400 MHz).



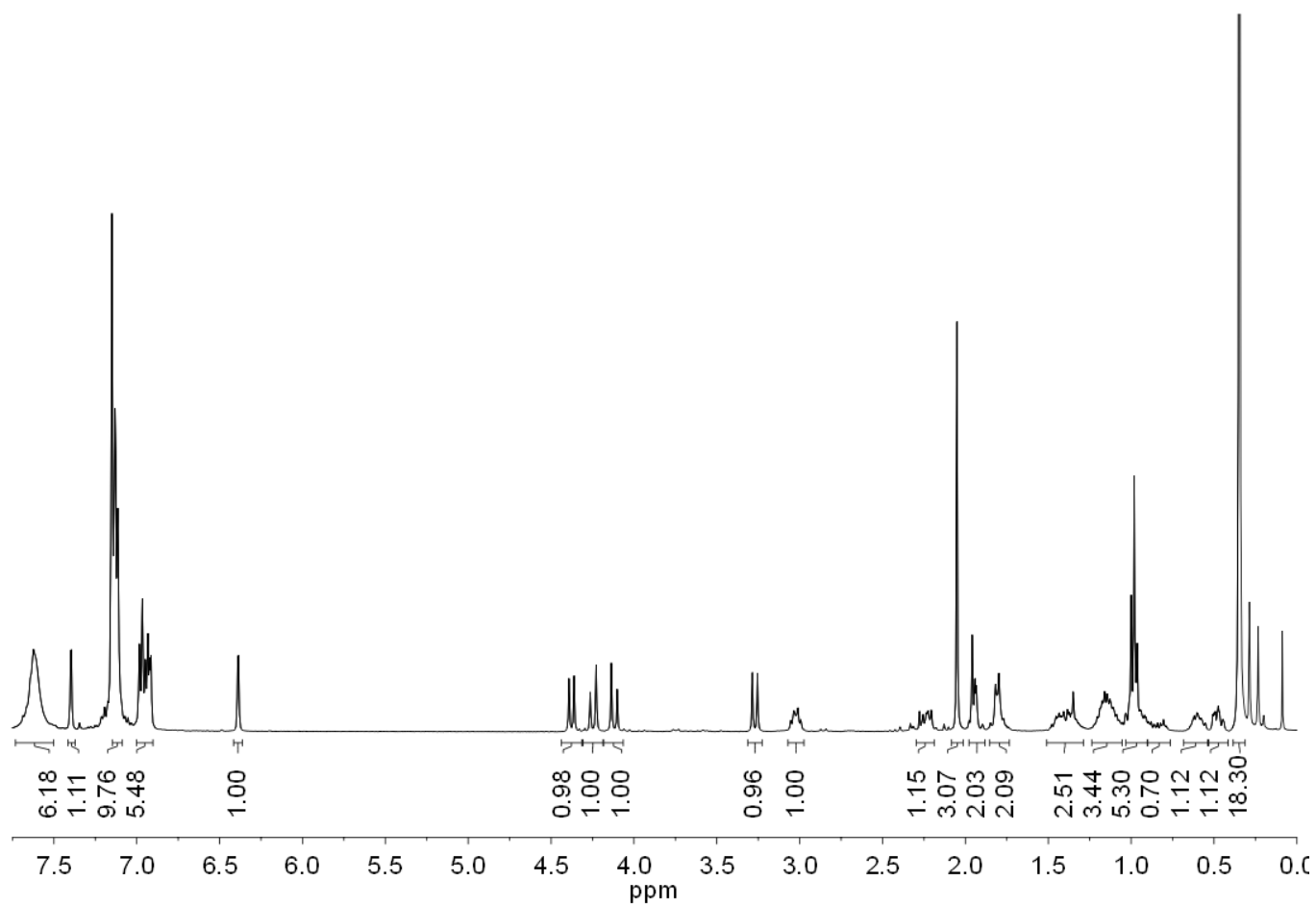
**Figure S2.**  $^1\text{H}$  NMR spectrum of **2a** and **2b** ( $\text{C}_6\text{D}_6$ , 400 MHz).



**Figure S3.**  $^1\text{H}$  NMR spectrum of **3a** and **3b** ( $\text{C}_6\text{D}_6$ , 400 MHz).

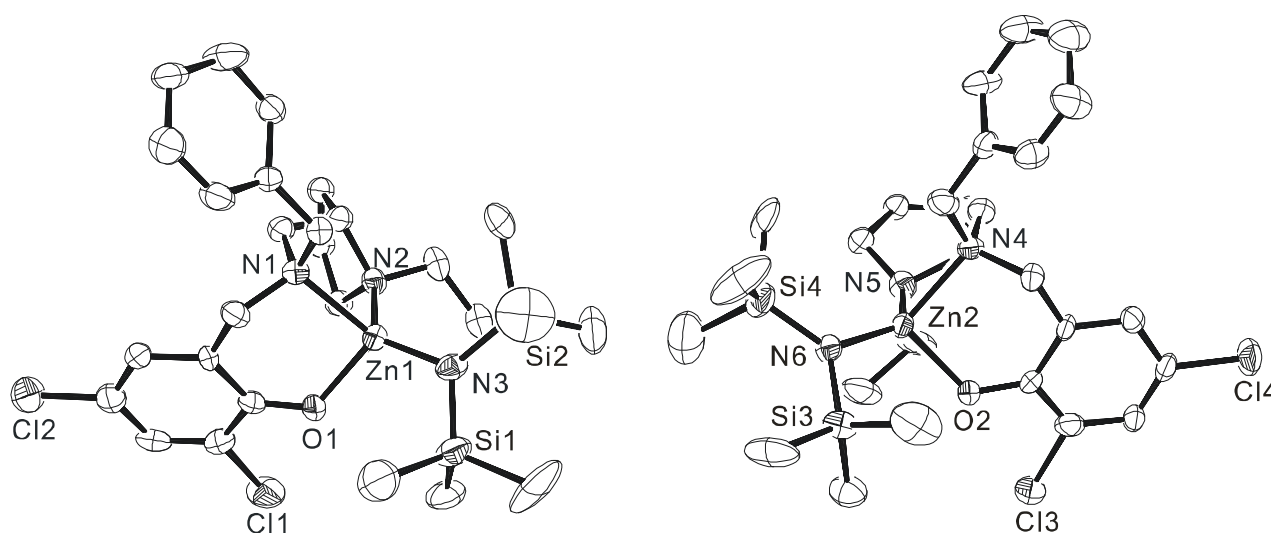


**Figure S4.**  $^1\text{H}$  NMR spectrum of **4a** and **4b** ( $\text{C}_6\text{D}_6$ , 400 MHz).

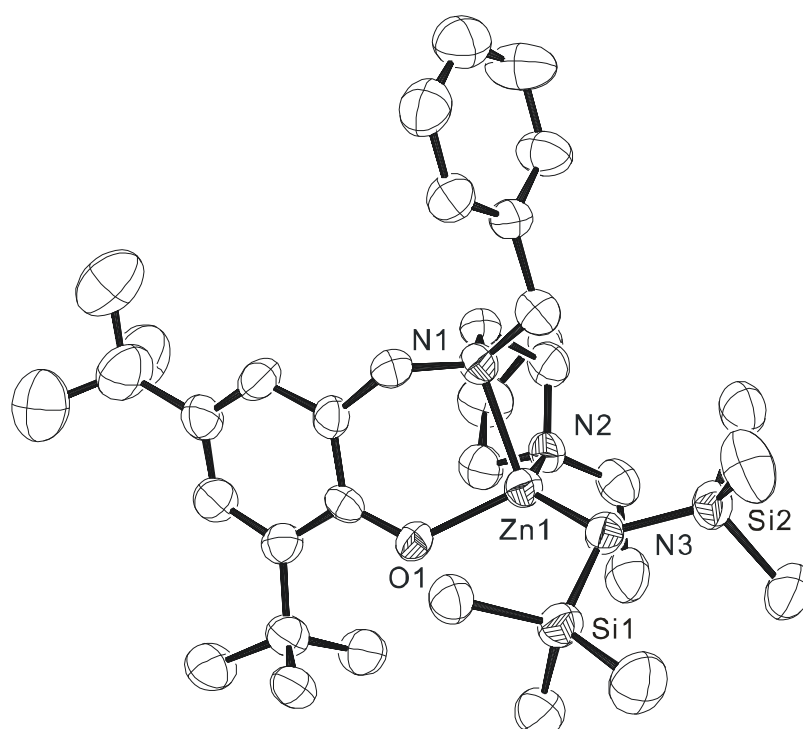


**Figure S5.**  $^1\text{H}$  NMR spectrum of **5** ( $\text{CDCl}_3$ , 400 MHz).

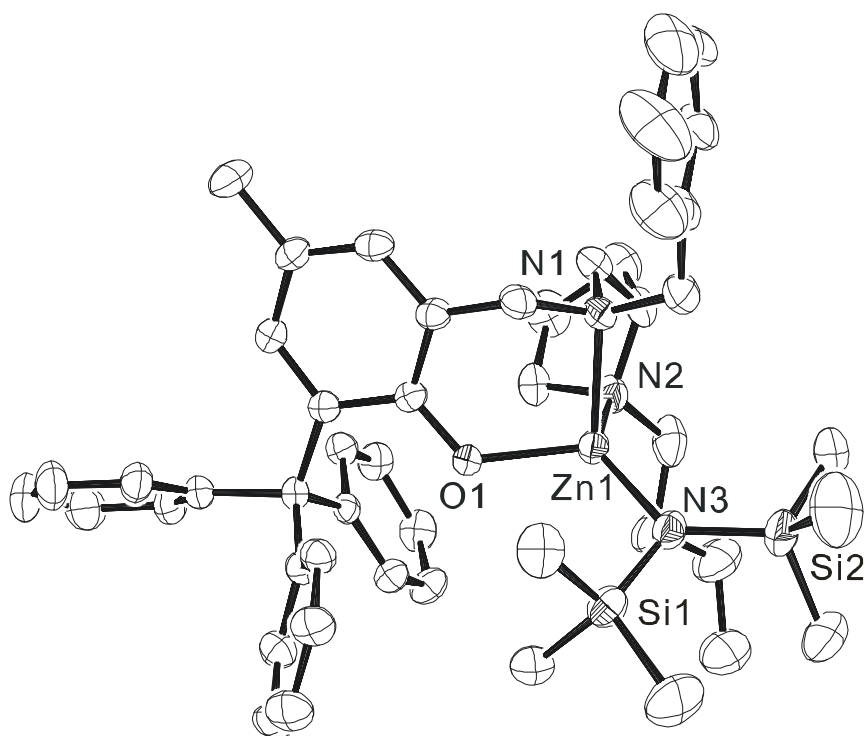
## 2.2 X-Ray molecular structures



**Figure S6.** X-Ray molecular structure of **1a** (left) and **1b** (right). Thermal ellipsoids represent the 30% probability surfaces. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and angles (°), for **1a**: Zn1–O1 1.934(10), Zn1–N3 1.935(11), Zn1–N2 2.108(12), Zn1–N1 2.138(11), O1–Zn1–N3 115.2(5), O1–Zn1–N2 100.4(5), N3–Zn1–N2 130.2(5), O1–Zn1–N1 95.3(4), N3–Zn1–N1 121.6(5), N2–Zn1–N1 86.1(4); for **1b**: Zn2–N6 1.902(12), Zn2–O2 1.947(10), Zn2–N5 2.105(11), Zn2–N4 2.142(11), N6–Zn2–O2 114.3(5), N6–Zn2–N5 127.7(5), O2–Zn2–N5 101.0(5), N6–Zn2–N4 126.6(5), O2–Zn2–N4 93.4(4), N5–Zn2–N4 86.0(4).



**Figure S7.** X-Ray molecular structure of **3a**. Thermal ellipsoids represent the 30% probability surfaces. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and angles (°): Zn1–N3 1.913(5), Zn1–O1 1.932(4), Zn1–N1 2.093(5), Zn1–N2, 2.120(6), N3–Zn1–O1 116.80(19), N3–Zn1–N1 118.43(19), O1–Zn1–N1 96.62(18), N3–Zn1–N2 127.7(2), O1–Zn1–N2 104.4(2), N1–Zn1–N2 85.1(2).



**Figure S8.** X-Ray molecular structure of **5**. Thermal ellipsoids represent the 30% probability surfaces. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and angles (°): Zn1–N3 1.941(3), Zn1–O1 1.962(2), Zn1–N2 2.137(3), Zn1–N1 2.145(3), N3–Zn1–O1 119.37(12), N3–Zn1–N2 127.10(13), O1–Zn1–N2 103.70(11), N3–Zn1–N1 116.68(12), O1–Zn1–N1 97.41(11), N2–Zn1–N1 83.89(12).



**Table S1.** Crystallographic data for **1a/1b**, **3a** and **5**.

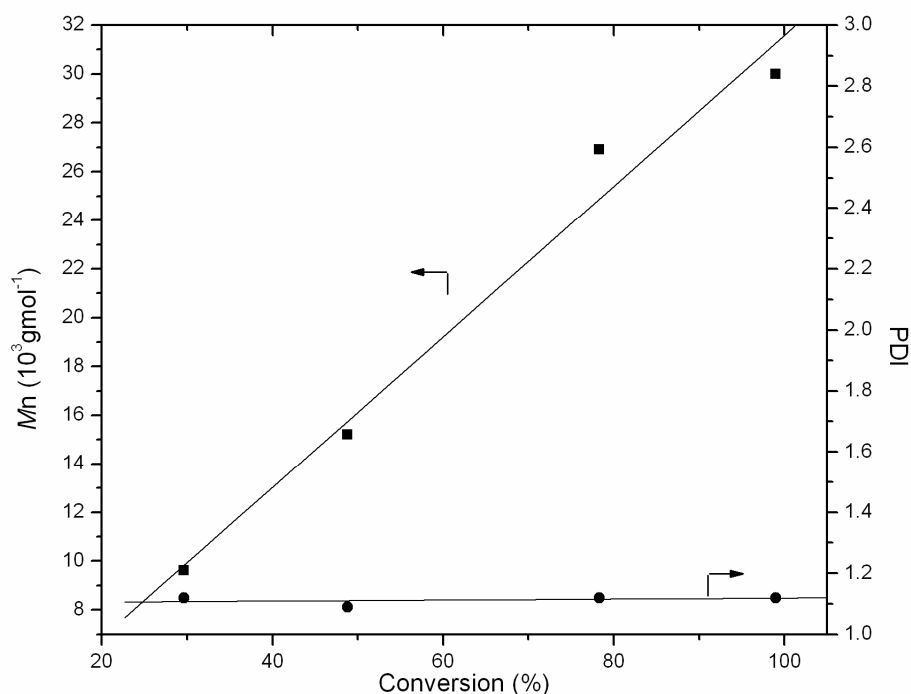
| Compound reference  | <b>1a / 1b</b>   | <b>3a</b>  | <b>5</b>   |
|---|--|--|--|
| Chemical formula  | C <sub>27</sub> H <sub>43</sub> Cl <sub>2</sub> N <sub>3</sub> OSi <sub>2</sub> Zn | C <sub>35</sub> H <sub>61</sub> N <sub>3</sub> OSi <sub>2</sub> Zn | C <sub>49</sub> H <sub>65</sub> N <sub>3</sub> OSi <sub>2</sub> Zn |
| Formula Mass  | 618.09   | 661.42   | 833.59   |
| Crystal system  | Monoclinic   | Orthorhombic   | Tetragonal   |
| <i>a</i> /Å   | 26.943(3)  | 17.997(2)  | 19.5766(7)   |
| <i>b</i> /Å   | 13.5555(12)  | 18.266(2)  | 19.5766(7)   |
| <i>c</i> /Å   | 17.9722(16)  | 14.8576(16)  | 13.6033(7)   |
| <i>α</i> /°   | 90.00  | 90.00  | 90.00  |
| <i>β</i> /°   | 100.167(2)   | 90.00  | 90.00  |
| <i>γ</i> /°   | 90.00  | 90.00  | 90.00  |
| Unit cell volume/ <sup>3</sup>  | 6460.8(10)   | 4884.2(9)  | 5213.4(4)  |
| Temperature/K   | 293(2)   | 293(2)   | 293(2)   |
| Space group   | <i>P</i> 2(1)/ <i>c</i>  | <i>P</i> 2(1)2(1)2   | <i>P</i> 4(1)  |
| No. of formula units per unit cell, <i>Z</i>                                  | 8  | 4  | 4  |
| Radiation type  | Mo-Kα  | Mo-Kα  | Mo-Kα  |
| Absorption coefficient, μ/mm <sup>-1</sup>                                    | 1.023  | 0.574  | 0.551  |
| No. of reflections measured   | 36037  | 9603   | 10207  |
| No. of independent reflections  | 11995  | 9603   | 10207  |
| <i>R</i> <sub>int</sub>   | 0.0739   | 0.0000   | 0.0000   |
| Final <i>R</i> <sub>I</sub> values ( <i>I</i> > 2σ( <i>I</i> ))               | 0.1523   | 0.0653   | 0.0506   |
| Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> )) | 0.3275   | 0.1456   | 0.1118   |
| Final <i>R</i> <sub>I</sub> values (all data)                                 | 0.1882   | 0.1528   | 0.0757   |
| Goodness of fit on <i>F</i> <sup>2</sup>                                      | 1.140  | 0.808  | 0.940  |
| Flack parameter   | 0.03(2)  | 0.024(11)  |  |

### 2.3 Ring-opening polymerization

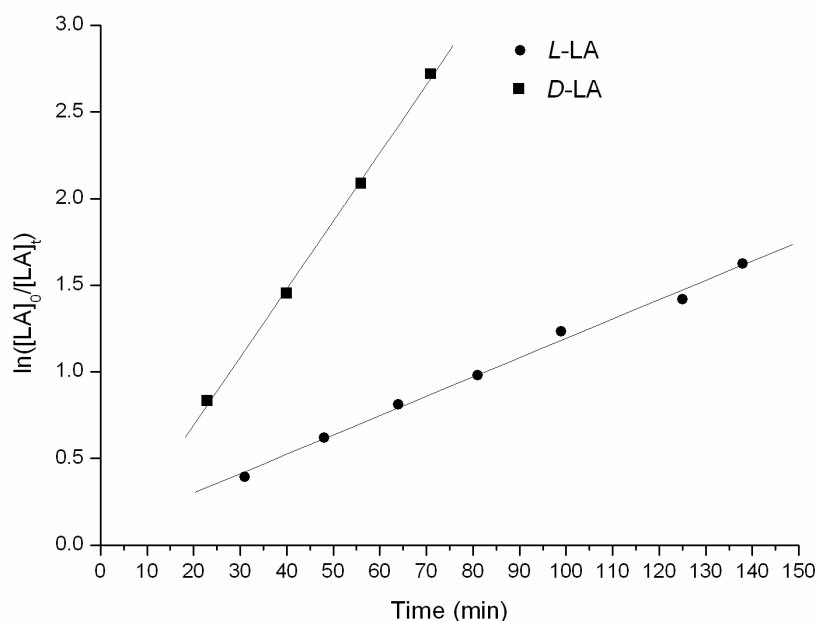
**Table S2.** ROP of *rac*-lactide initiated by zinc complexes **1**, **3-5** in THF.<sup>a</sup>

| Cat.     | [LA] <sub>0</sub> /[Zn] <sub>0</sub> /[ <sup>i</sup> PrOH] <sub>0</sub> | Time<br>(min)    | Conv. <sup>b</sup><br>(%) | <i>M</i> <sub>n,calcd</sub> <sup>c</sup><br>(×10 <sup>4</sup> ) | <i>M</i> <sub>n</sub> <sup>d</sup><br>(×10 <sup>4</sup> ) | <i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> <sup>d</sup> | <i>P</i> <sub>m</sub> <sup>e</sup> |
|----------|---|------------------|---------------------------|---|---|--|------------------------------------|
| <b>1</b> | 200:1:0   | 15               | 98                        | 2.82  | 16.7  | 1.54   | 0.39                               |
| <b>1</b> | 200:1:1   | 3                | 99                        | 2.85  | 2.69  | 1.49   | 0.40                               |
| <b>3</b> | 200:1:0   | 30               | 99                        | 2.85  | 5.72  | 1.59   | 0.74                               |
| <b>3</b> | 200:1:1   | 20               | 98                        | 2.82  | 2.62  | 1.53   | 0.74                               |
| <b>4</b> | 200:1:0   | 300              | 94                        | 2.70  | 7.36  | 1.47   | 0.77                               |
| <b>4</b> | 200:1:1   | 60               | 84                        | 2.42  | 2.25  | 1.15   | 0.78                               |
| <b>5</b> | 200:1:0   | 300              | 75                        | 2.16  | 9.07  | 1.25   | 0.80                               |
| <b>5</b> | 200:1:1   | 180              | 86                        | 2.48  | 3.34  | 1.09   | 0.80                               |
| <b>5</b> | 200:1:1   | 4 d <sup>f</sup> | 96                        | 2.76  | 4.11  | 1.40   | 0.84                               |

<sup>a</sup> [LA]<sub>0</sub> = 1.0 mmol·L<sup>-1</sup>, in THF, 25 °C. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> *M*<sub>n,calcd</sub> = [LA]<sub>0</sub>/[Zn]<sub>0</sub> × Conv.% × 144.13 g·mol<sup>-1</sup>. <sup>d</sup> Determined by GPC. <sup>e</sup> Determined by analysis of all of the tetrad signals in the methine region of the homonuclear-decoupled <sup>1</sup>H NMR spectrum. <sup>f</sup> At -38°C.

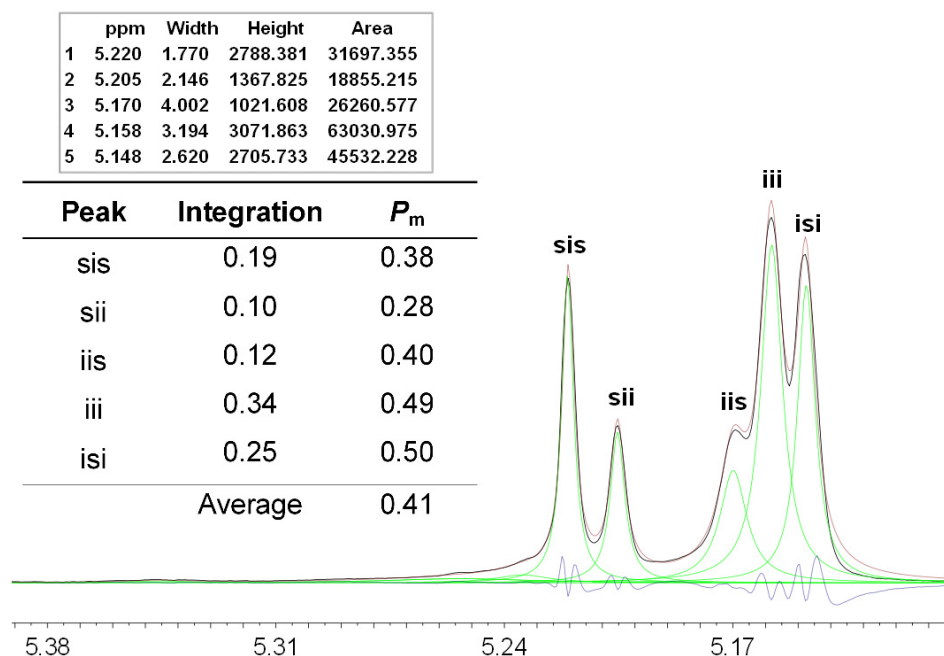


**Figure S9.** Plots of observed *M*<sub>n</sub> (■) and molecular weight distribution (●) of PLA sample vs. monomer conversion obtained by **5** ([LA]<sub>0</sub>/[Zn]<sub>0</sub>/[<sup>i</sup>PrOH]<sub>0</sub> = 200 : 1 : 1, toluene, 25 °C).

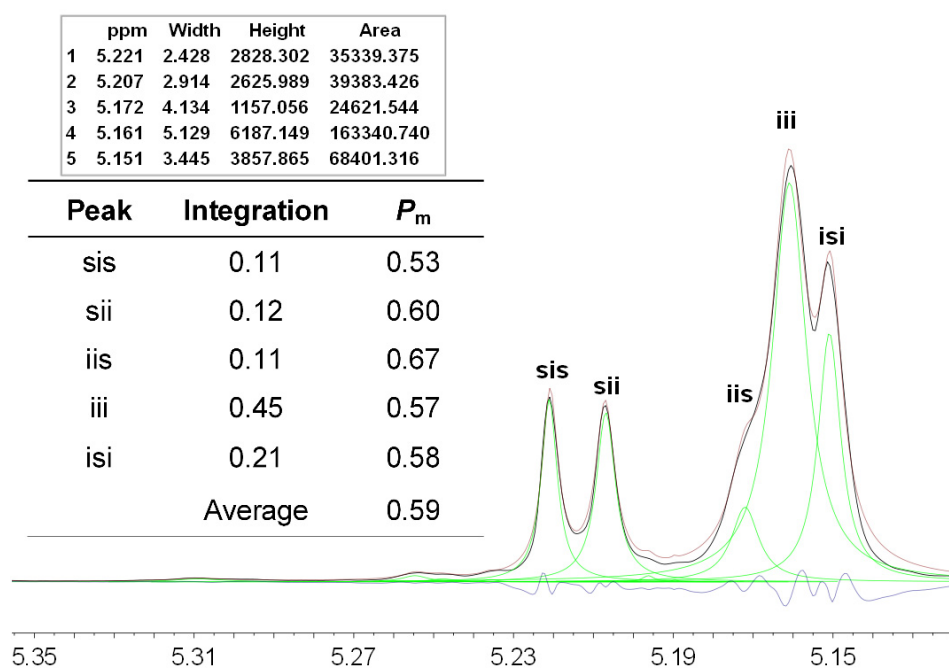


**Figure S10.**  $\ln([LA]_0/[LA]_t)$  vs time plots for the ROP of *D*- and *L*-lactide catalyzed by complex **5** at 20 °C in  $C_6D_6$ . The rate constants are  $k_{D(obsd)} = 3.93 \times 10^{-2} \text{ min}^{-1}$  and  $k_{L(obsd)} = 1.12 \times 10^{-2} \text{ min}^{-1}$  respectively.

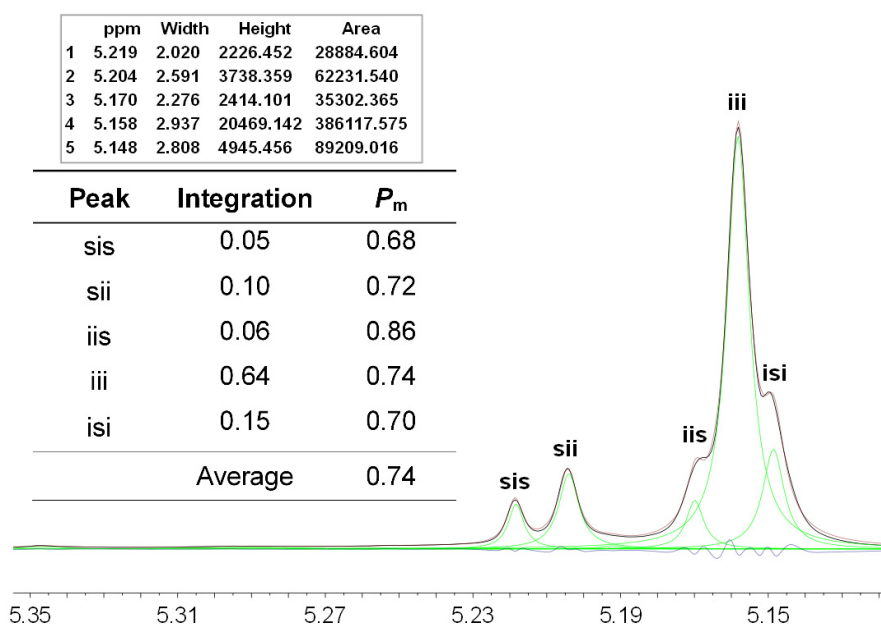
## 2.4 Microstructure analysis of poly(*rac*-lactide)



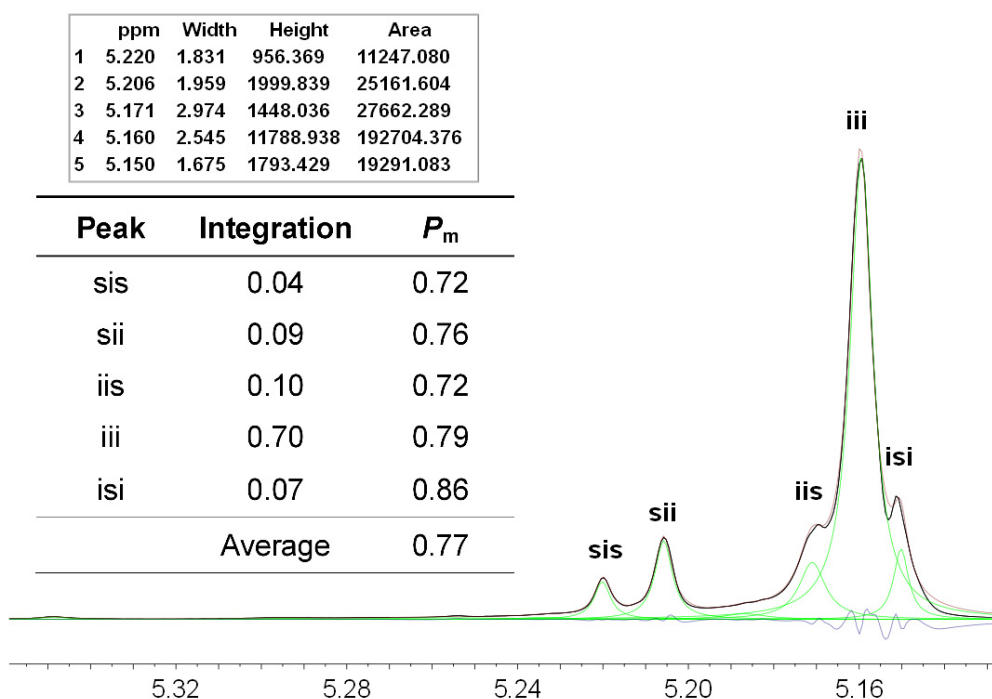
**Figure S11.** De-convoluted homonuclear decoupled  $^1H$  NMR spectrum of PLA obtained from *rac*-lactide by using **1** as initiator in toluene at 25 °C ( $CDCl_3$ , 400 MHz,  $P_m = 0.41$ ).



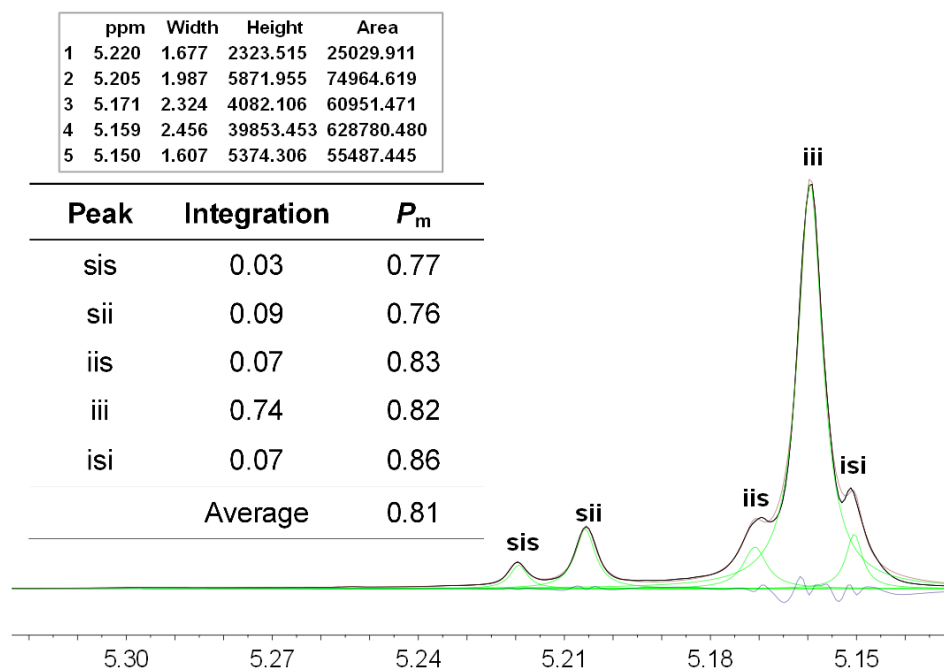
**Figure S12.** De-convoluted homonuclear decoupled  $^1\text{H}$  NMR spectrum of PLA obtained from *rac*-lactide by using **2** as initiator in toluene at 25 °C ( $\text{CDCl}_3$ , 400 MHz,  $P_m = 0.59$ ).



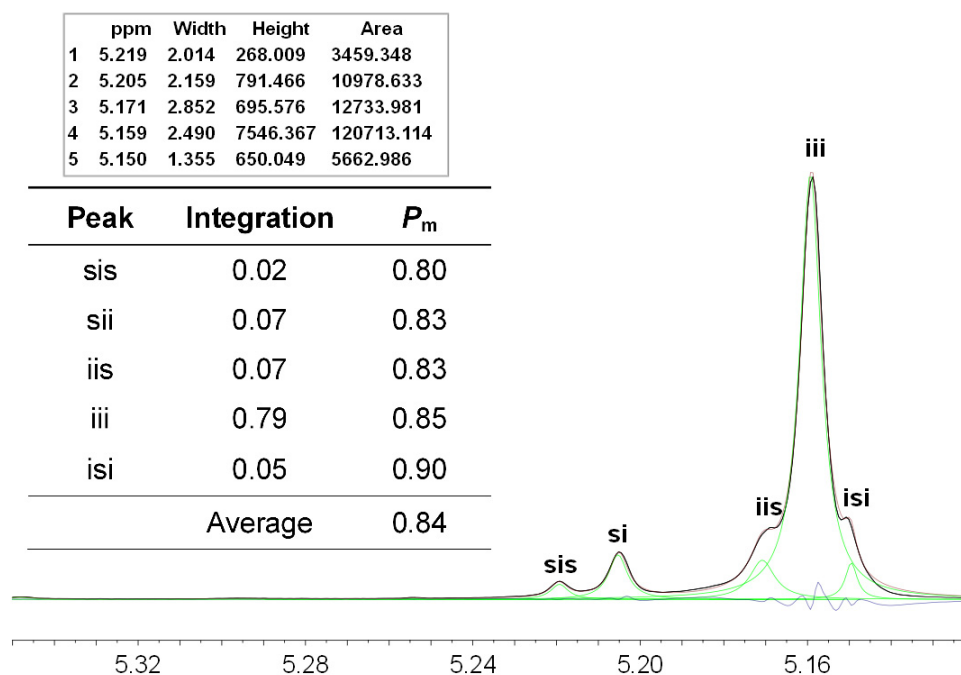
**Figure S13.** De-convoluted homonuclear decoupled  $^1\text{H}$  NMR spectrum of PLA obtained from *rac*-lactide by using **3** as initiator in toluene at 25 °C ( $\text{CDCl}_3$ , 400 MHz,  $P_m = 0.74$ ).



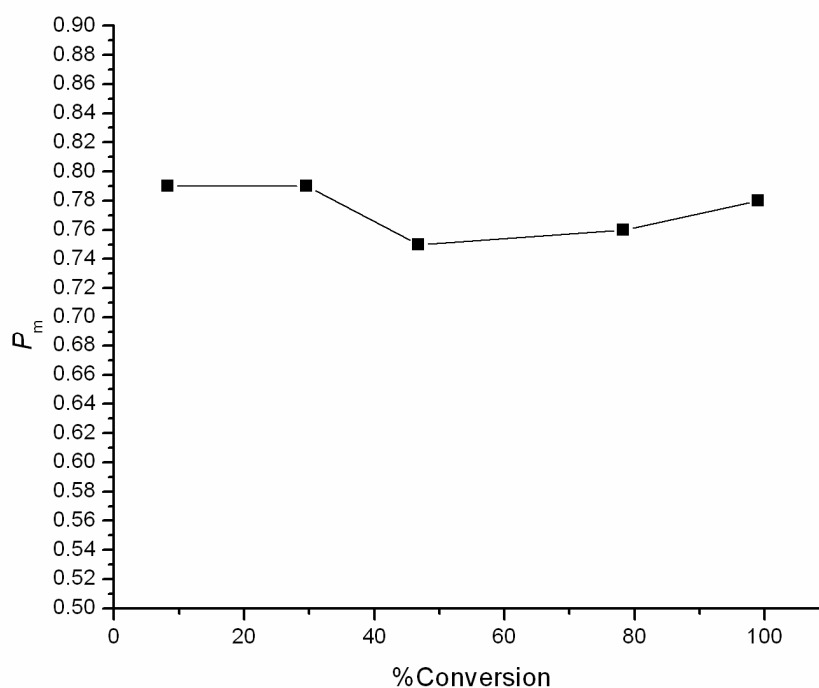
**Figure S14.** De-convoluted homonuclear decoupled  $^1\text{H}$  NMR spectrum of PLA obtained from *rac*-lactide by using **4** as initiator in toluene at 25 °C ( $\text{CDCl}_3$ , 400 MHz,  $P_m = 0.77$ ).



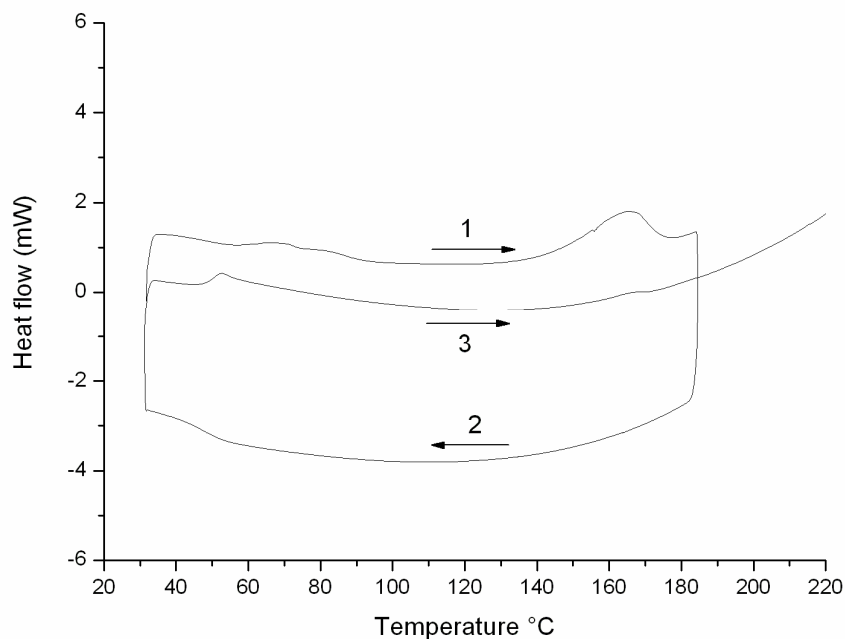
**Figure S15.** De-convoluted homonuclear decoupled  $^1\text{H}$  NMR spectrum of PLA obtained from *rac*-lactide by using **5** as initiator in toluene at 25 °C ( $\text{CDCl}_3$ , 400 MHz,  $P_m = 0.81$ ).



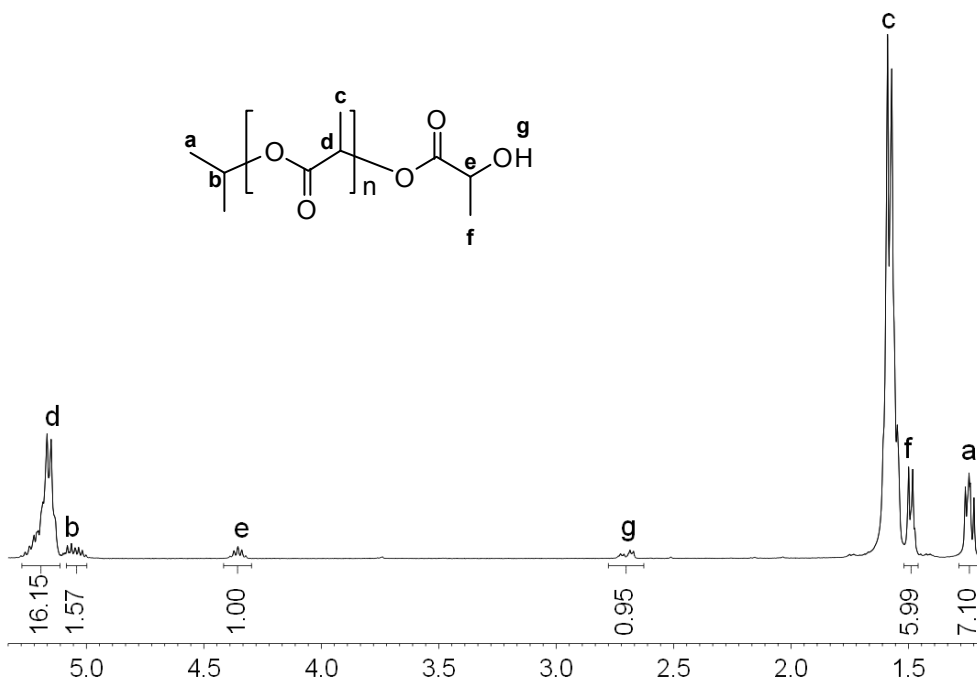
**Figure S16.** De-convoluted homonuclear decoupled  $^1\text{H}$  NMR spectrum of PLA obtained from *rac*-lactide by using **5** as initiator in toluene at  $-38\text{ }^\circ\text{C}$  ( $\text{CDCl}_3$ , 400 MHz,  $P_m = 0.84$ ).



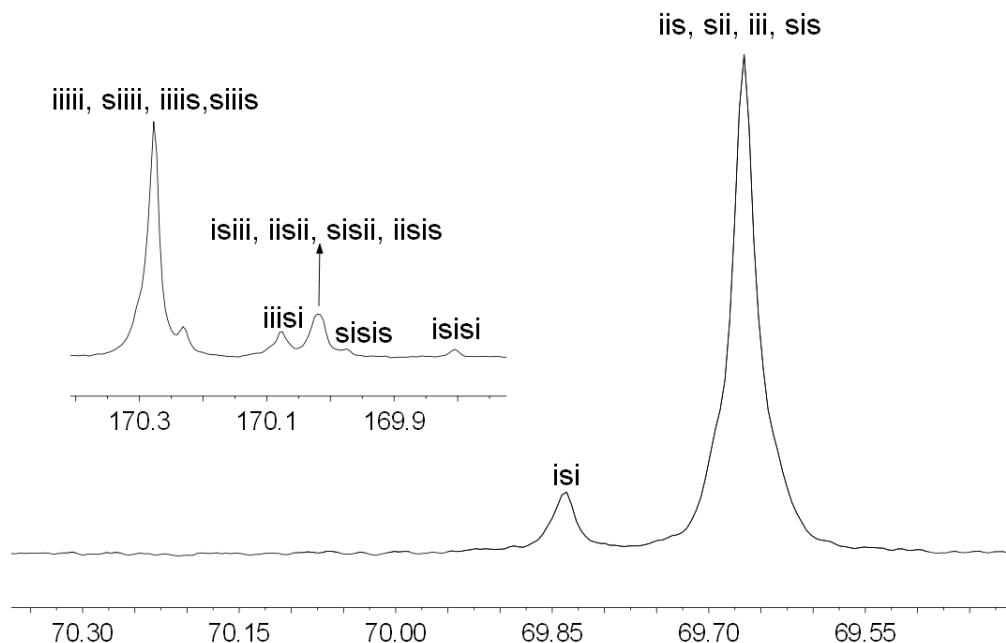
**Figure S17.** Plot of  $P_m$  vs. conversion for polymerization of *rac*-LA with **5** as the initiator ( $[\text{LA}]_0/[\textbf{5}]/[{}^i\text{PrOH}]_0 = 200 : 1 : 1$ ,  $[\text{LA}]_0 = 1.0\text{ mmol}\cdot\text{L}^{-1}$ , toluene,  $25\text{ }^\circ\text{C}$ ).



**Figure S18.** Heat flow vs. temperature curve for PLA obtained from *rac*-lactide by using **5** as initiator at  $-38\text{ }^{\circ}\text{C}$  ( $[\text{LA}]_0/[\text{Zn}]_0/[\textit{i}\text{PrOH}]_0 = 200:1:1$ , in toluene,  $P_m = 0.84$ ). The curve shows a glass transition temperature of  $53\text{ }^{\circ}\text{C}$ , a melting point of  $166\text{ }^{\circ}\text{C}$ .



**Figure S19.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 400 MHz) of *rac*-lactide oligomer obtained by complex **5/2**-propanol in toluene ( $[\text{LA}]_0/[\text{Zn}]_0/[\textit{i}\text{PrOH}]_0 = 20:1:1$ ).



**Figure S20.** The carbonyl and methine regions of  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 500 MHz) of PLA obtained from *rac*-lactide by using **5** as initiator in toluene at  $-38^\circ\text{C}$ .

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