

## Supporting Information for:

### **Synthesis and characterization of lanthanide complexes supported by a new pentadentate schiff base and their application in the heteroselective polymerization of *rac*-lactide**

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#### **Table S1. Crystallographic Data for Complexes 1-3 and 5-7**

**Fig. S1** Homonuclear decoupled <sup>1</sup>H NMR spectrum of the methine region of polylactide produced from *rac*-LA using complex 3 as initiator in THF.

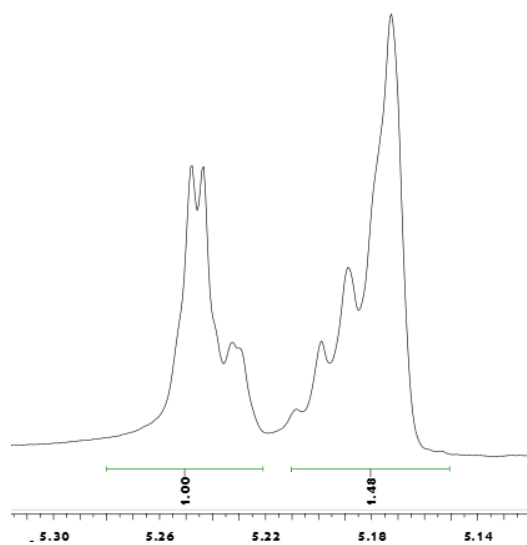
**Fig. S2** Homonuclear decoupled <sup>1</sup>H NMR spectra of the methine region of polylactides produced from *rac*-LA using complex 2 as initiator at 25 and 0 °C

**Fig. S3** MALDI-TOF mass spectrum of *rac*-LA oligomer initiated by complex 7

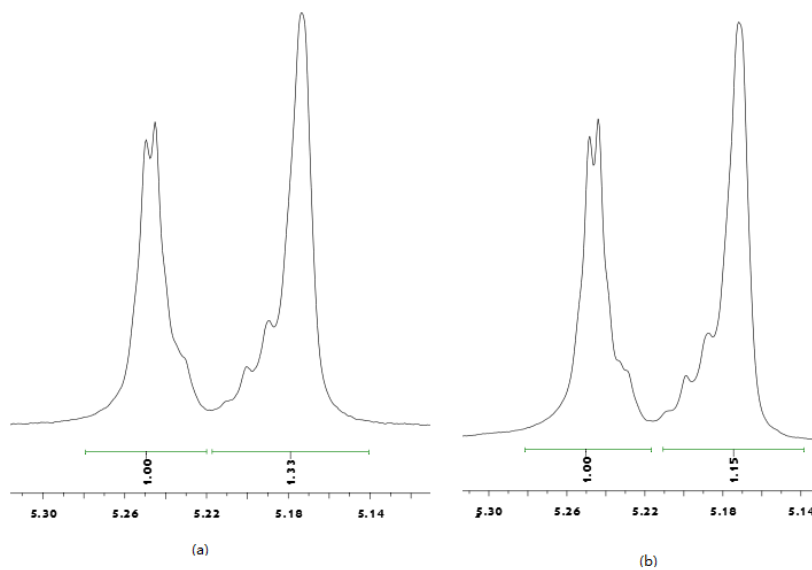
**Fig. S4** <sup>1</sup>H NMR spectrum of *rac*-LA oligomer initiated by complex 2 in CDCl<sub>3</sub>

**Table S1. Crystallographic Data for Complexes 1-3 and 5-7**

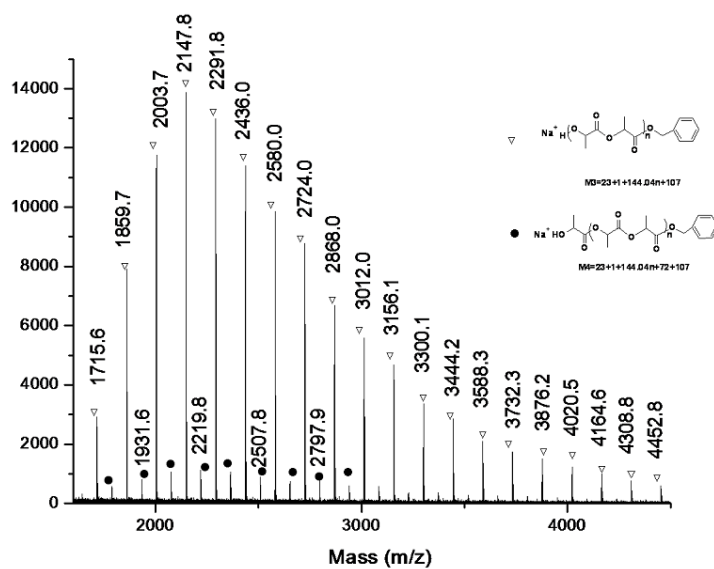
Compound	1·THF·0.5hexane	2·THF·0.5toluene	3·3THF	5·3THF	6·THF	7·THF
Formula	C <sub>64</sub> H <sub>88</sub> N <sub>2</sub> O <sub>5</sub> Sc	C <sub>64.5</sub> H <sub>85</sub> N <sub>2</sub> O <sub>5</sub> Yb	C <sub>73</sub> H <sub>105</sub> N <sub>2</sub> O <sub>8</sub> Y	C <sub>73</sub> H <sub>105</sub> N <sub>2</sub> O <sub>8</sub> Nd	C <sub>52</sub> H <sub>76</sub> N <sub>3</sub> O <sub>4</sub> Si <sub>2</sub> Yb	C <sub>52</sub> H <sub>76</sub> N <sub>3</sub> O <sub>4</sub> Si <sub>2</sub> Y
fw	1010.32	1141.39	1227.50	1282.83	1036.38	952.25
T/K	223(2)	223(2)	223(10)	223(10)	293(2)	223(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	12.8779(9)	13.1060(3)	10.8744(3)	10.8719(18)	17.715(10)	17.6572(6)
<i>b</i> /Å	19.9196(14)	19.8031(4)	29.9882(13)	30.0322(4)	14.656(8)	14.6349(5)
<i>c</i> /Å	24.2784(19)	24.2374(5)	21.5416(8)	21.6152(5)	20.41(2)	20.3043(7)
$\beta$ /deg	103.146(7)	103.0929(3)	99.001(3)	99.151(4)	98.17(2)	98.333(3)
<i>V</i> /Å <sup>3</sup>	6064.8(7)	6127.0(2)	6938.3(4)	6967.7(5)	5247(7)	5191.5(3)
<i>Z</i>	4	4	4	4	4	4
<i>D</i> <sub>calcd</sub> /g cm <sup>-3</sup>	1.107	1.237	1.175	1.223	1.312	1.218
$\mu$ /mm <sup>-1</sup>	0.168	1.573	0.894	0.798	1.872	1.214
<i>F</i> (000)	2188	2384	4026	2724	2156	2032
Crystal size/mm	0.30 x 0.20 x 0.10	0.60 x 0.40 x 0.20	0.70 x 0.20 x 0.10	0.60 x 0.40 x 0.10	1.00 x 0.40 x 0.40	0.40 x 0.30 x 0.20
$\theta$ <sub>max</sub> /deg	26.37	26.37	26.37	26.37	27.51	26.37
Collected	38195	40384	41035	53214	25045	37426
Unique reflns	12384	12514	14175	14233	9748	10607
GOF	1.044	1.075	1.021	1.050	0.995	0.976
<i>R</i>	0.0696	0.0364	0.0658	0.0418	0.0595	0.0460
w <i>R</i>	0.2074	0.0950	0.1922	0.1157	0.1364	0.0878
<i>R</i> <sub>int</sub>	0.0598	0.0340	0.0613	0.0447	0.0588	0.0714
Largest diff. peak and hole/e Å <sup>-3</sup>	0.691 and -0.421	1.401 and -0.721	0.764 and -0.809	1.078 and -0.589	0.748 and -1.164	0.334 and -0.390



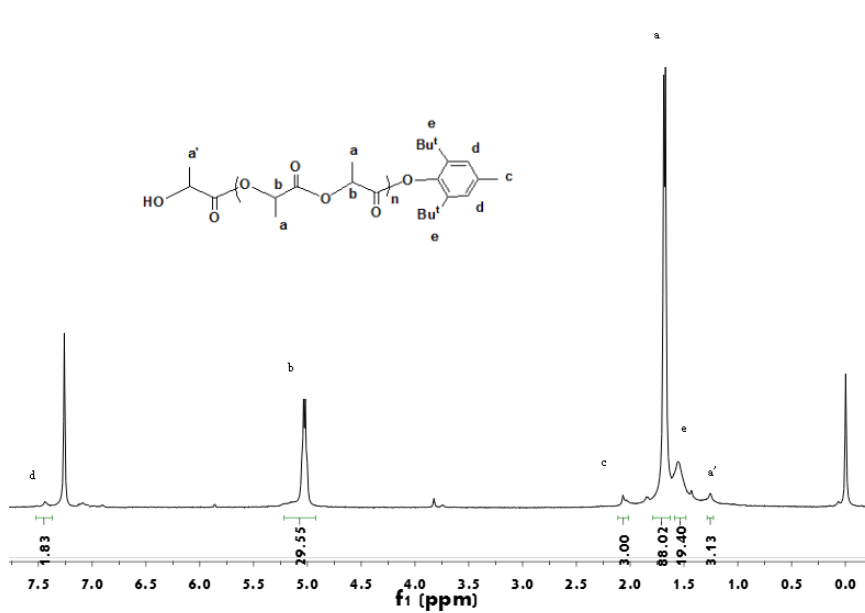
**Fig. S1** Homonuclear decoupled  $^1\text{H}$  NMR spectrum of the methine region of poly(lactide) produced from *rac*-LA using complex **3** as initiator in THF at 25 °C ( $P_r = 0.81$ , Table 3, entry 8, 400 MHz,  $\text{CDCl}_3$ .)



**Fig. S2** Homonuclear decoupled  $^1\text{H}$  NMR spectrum of the methine region of poly(lactides) produced from *rac*-LA using complex **2** as initiator ((a) at 25 °C,  $P_r = 0.85$ , Table 3, entry 3; (b) at 0 °C,  $P_r = 0.93$ , Table 3, entry 7, 400 MHz,  $\text{CDCl}_3$ .)



**Fig. S3** MALDI-TOF mass spectrum of *rac*-LA oligomer initiated by complex **7** ( $[M]_0/[I]_0 = 20:1$ , in THF, 25 °C; doped with  $CF_3CO_2Na$ ).



**Fig. S4.**  $^1H$  NMR spectrum of *rac*-LA oligomer initiated by complex **2** in  $CDCl_3$  ( $[M]/[I] = 20:1$ , in THF, 25 °C).