Electronic Supplementary Material (ESI) for Polymer Chemistry

Electronic Supporting Information

Controlled stereoselective polymerization of lactide monomers by group 4 metal initiators that contain a (OSSO)-type tetradentate bis(phenolate) ligand

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1 NMR characterisation of complexes

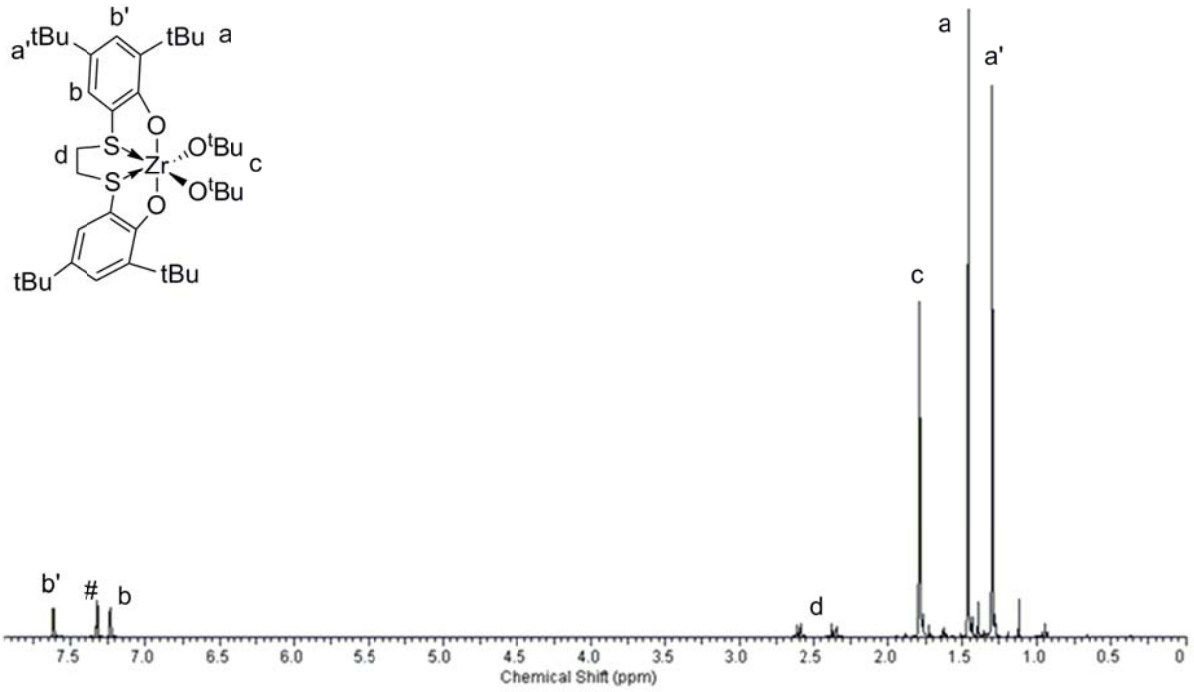

Fig. S1 ^{1}H-NMR spectrum of complex **Zr-1** (400 MHz, C_6D_6 [#], 25 °C)

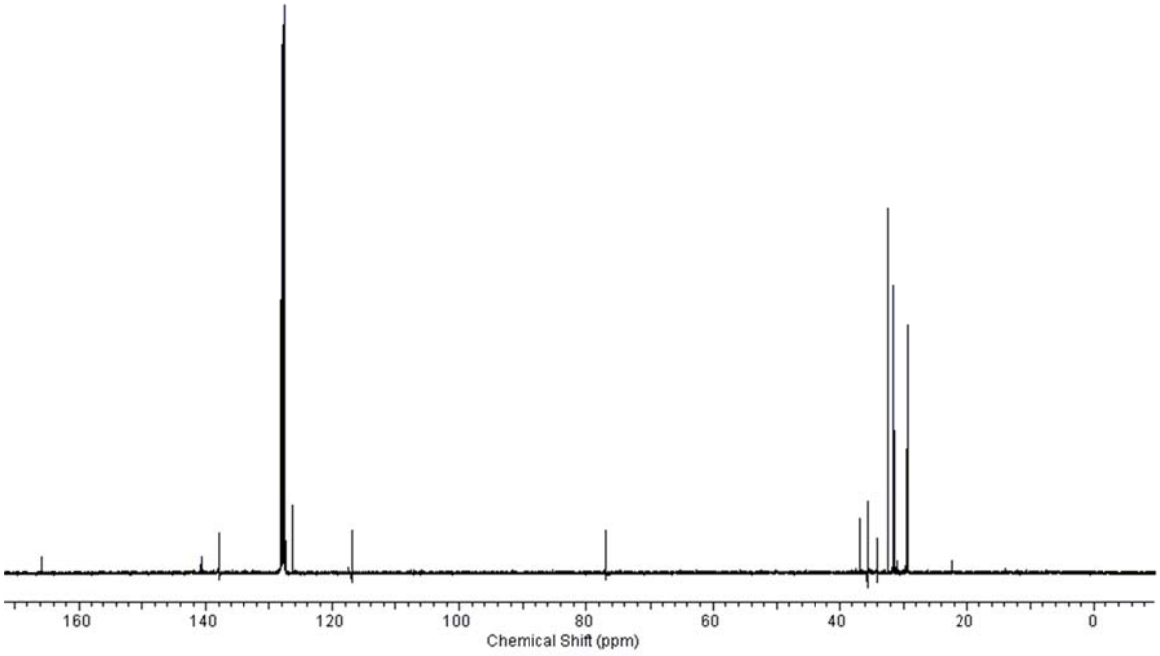

Fig. S2 ^{13}C{^{1}H}-NMR spectrum of complex **Zr-1** (100.1 MHz, C_6D_6 [#], 25 °C).

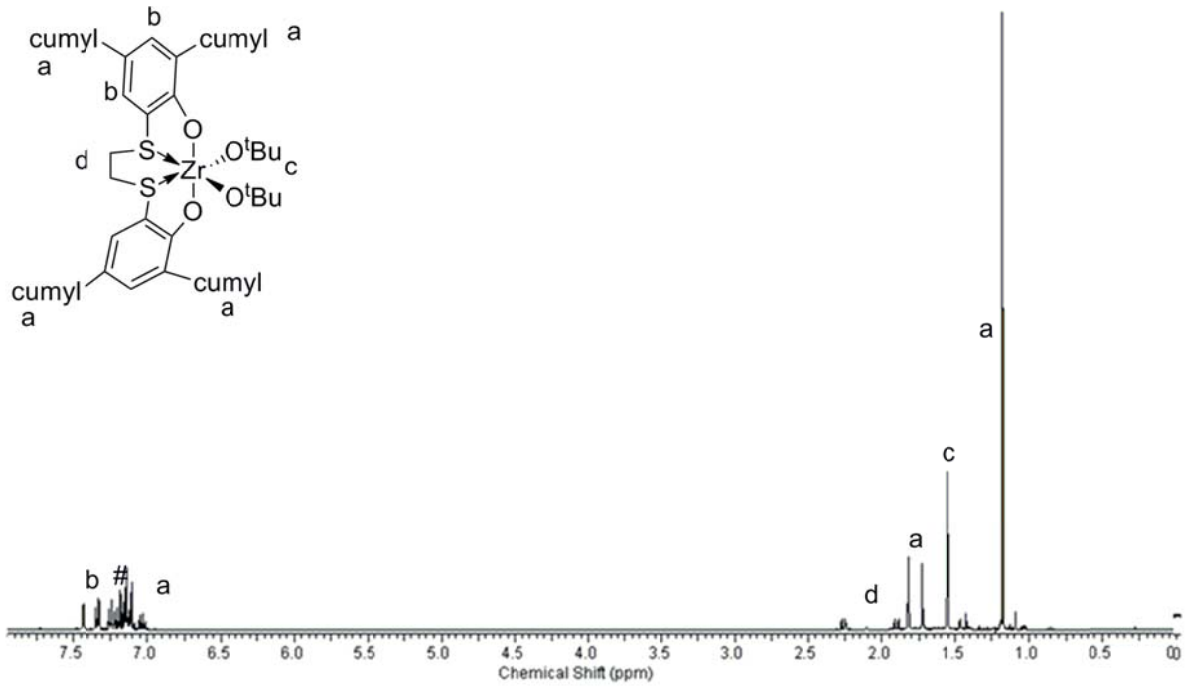

Fig. S3 ^{1}H-NMR spectrum of complex **Zr-2** (400 MHz, C_6D_6 [#], 25 °C)

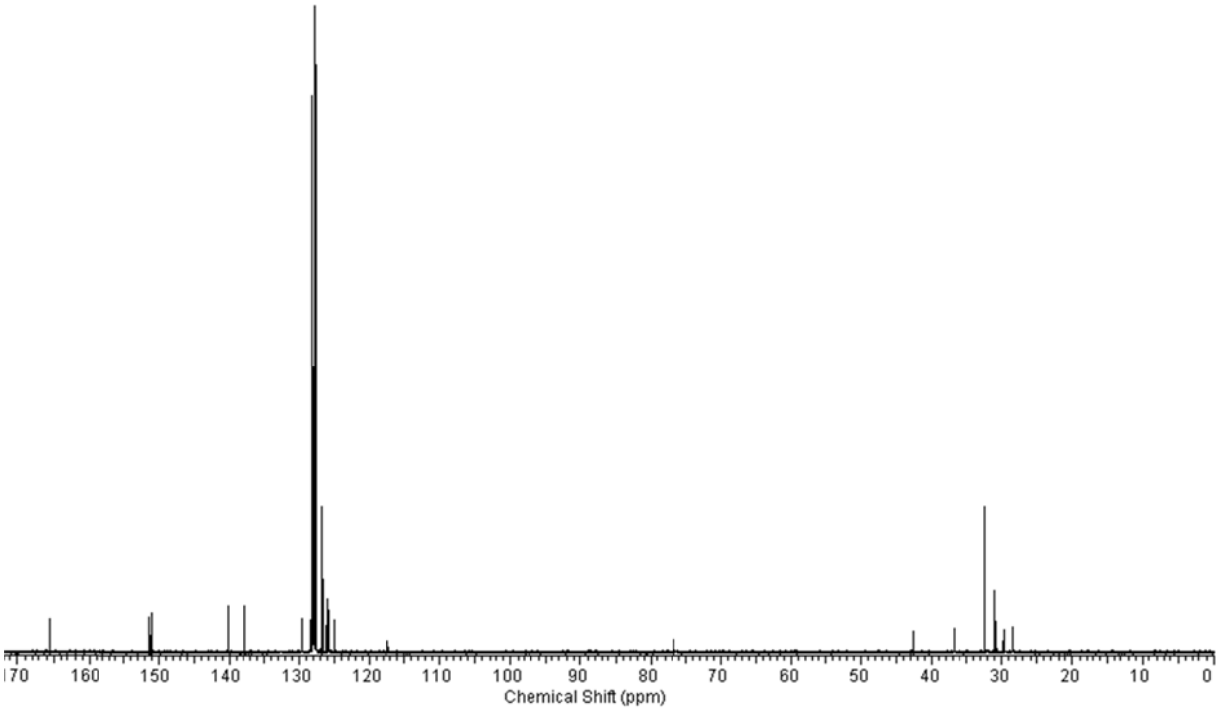

Fig. S4 ^{13}C{^{1}H}-NMR spectrum of complex **Zr-2** (100.1 MHz, C_6D_6 [#], 25 °C).

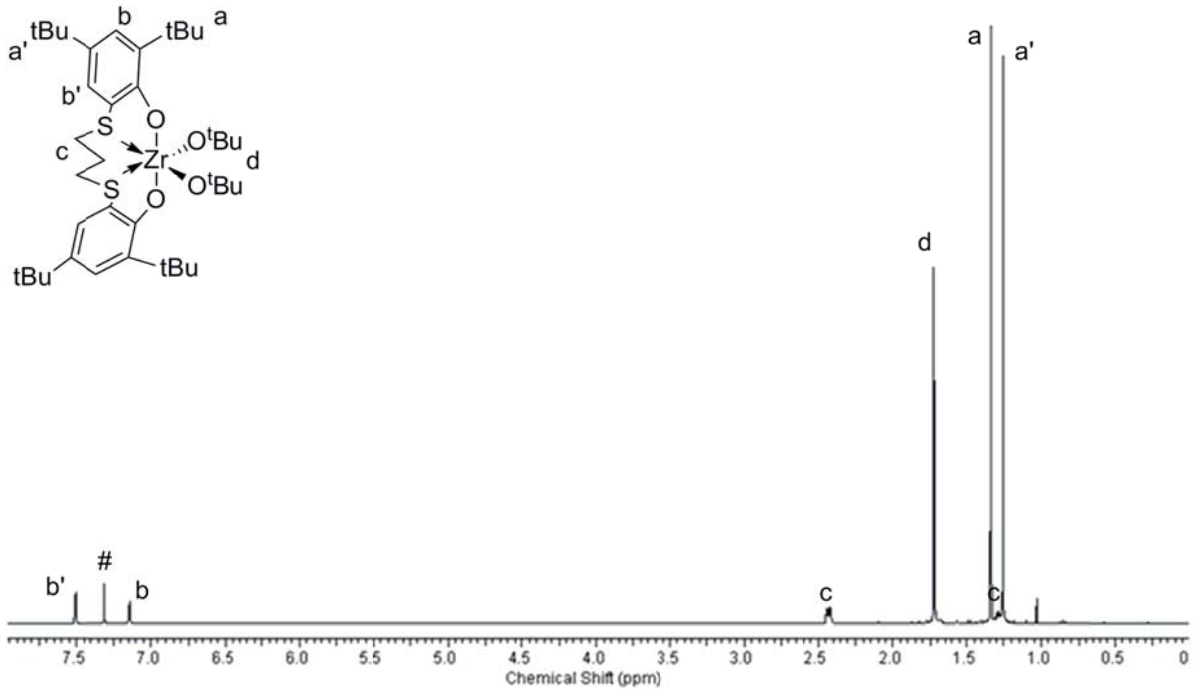

Fig. S5 ^{1}H-NMR spectrum of complex **Zr-3** (400 MHz, C_6D_6 [#], 25 °C)

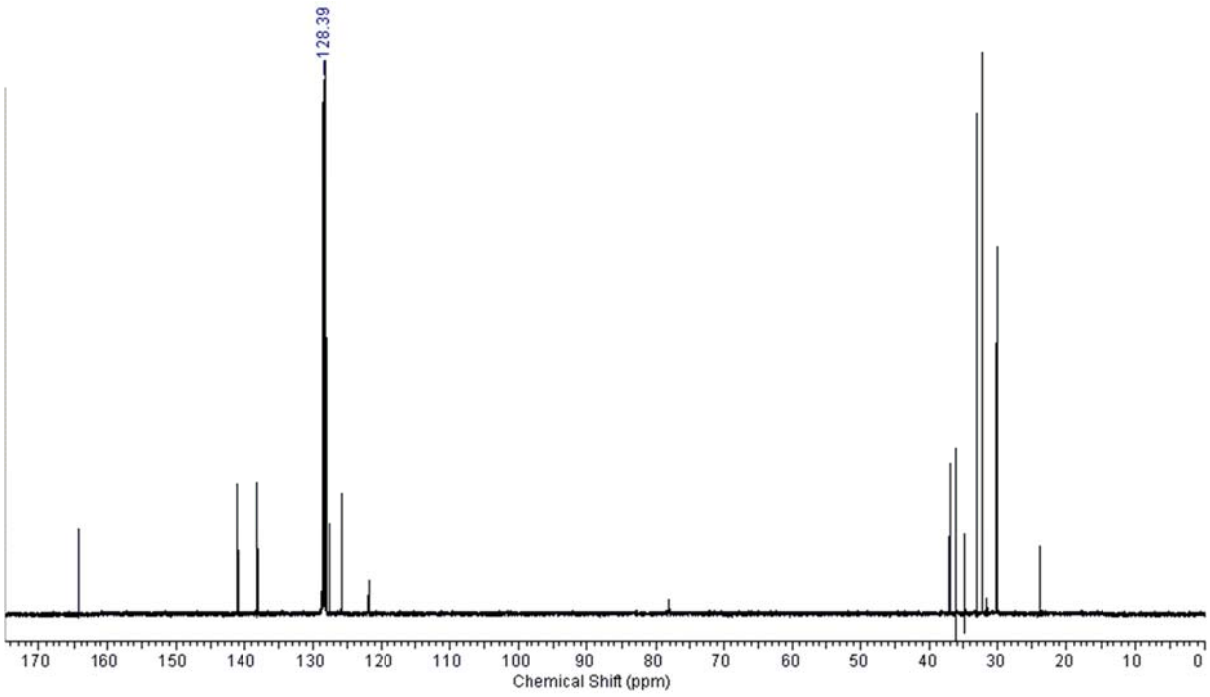

Fig. S6 ^{13}C{^{1}H}-NMR spectrum of complex **Zr-3** (100.1 MHz, C_6D_6 [#], 25 °C).

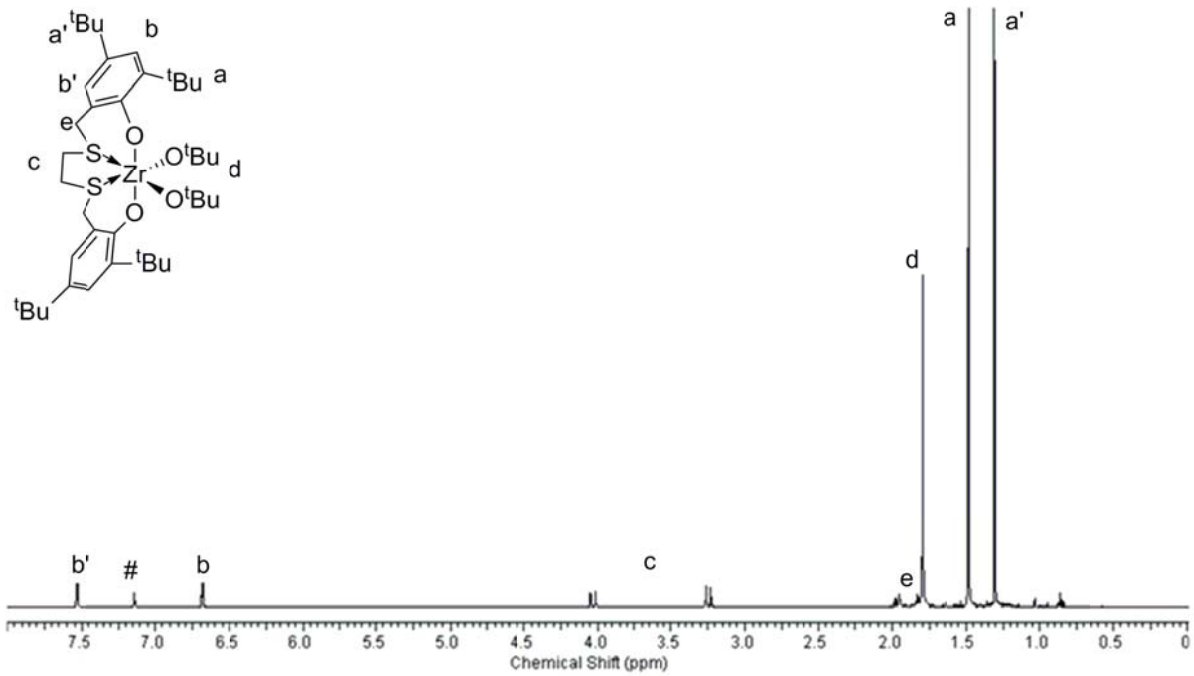

Fig. S7 ^{1}H-NMR spectrum of complex **Zr-4** (400 MHz, C_6D_6 [#], 25 °C)

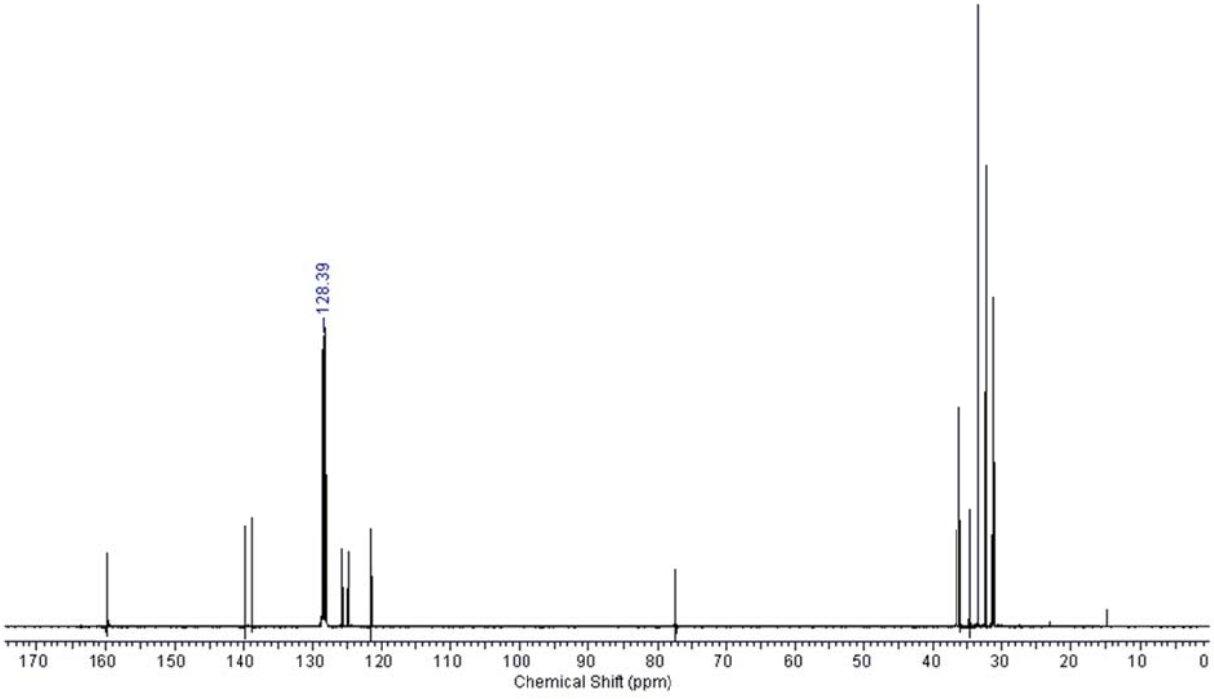

Fig. S8 ^{13}C{^{1}H}-NMR spectrum of complex **Zr-4** (100.1 MHz, C_6D_6 [#], 25 °C).

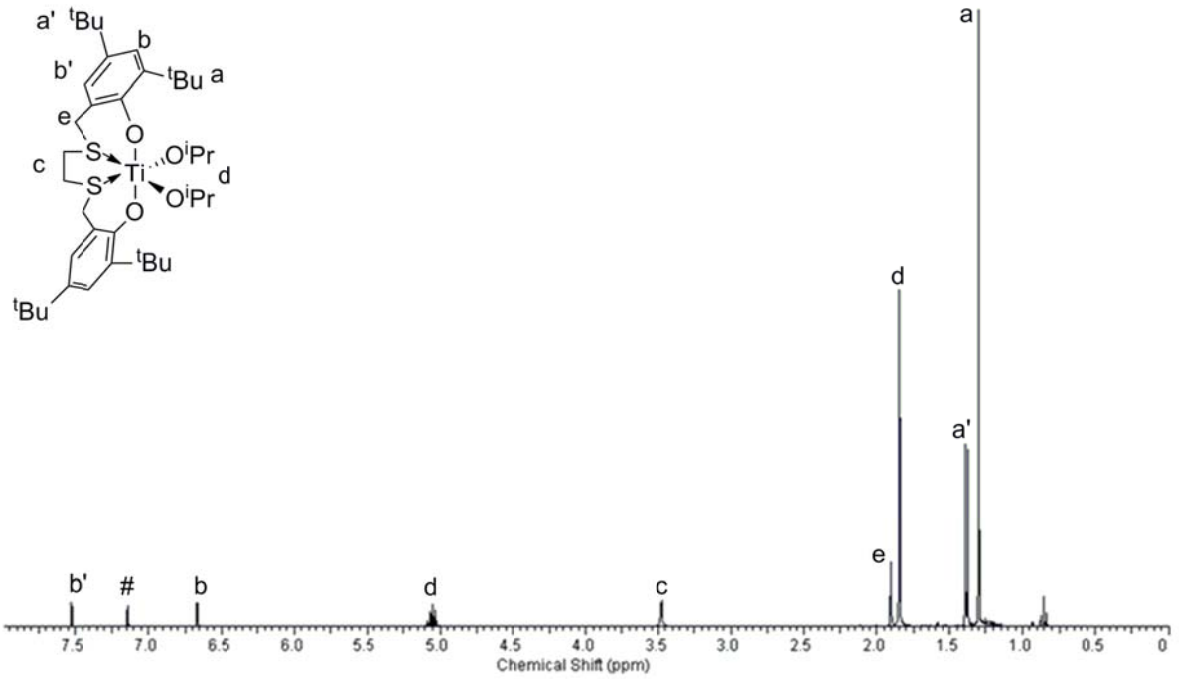

Fig. S9 1H-NMR spectrum of complex **Ti-4** (400 MHz, C_6D_6 [#], 25 °C)

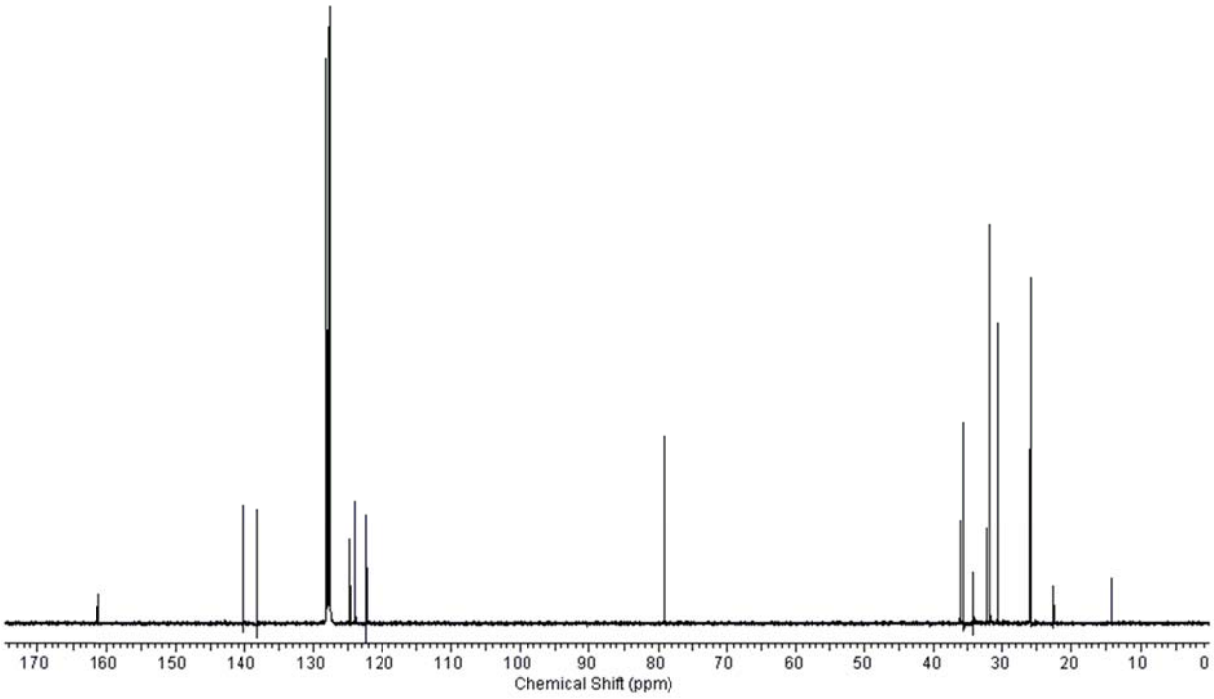

Fig. S10: $^{13}C\{1H\}$-NMR spectrum of complex **Ti-4** (100.1 MHz, C_6D_6 [#], 25 °C).

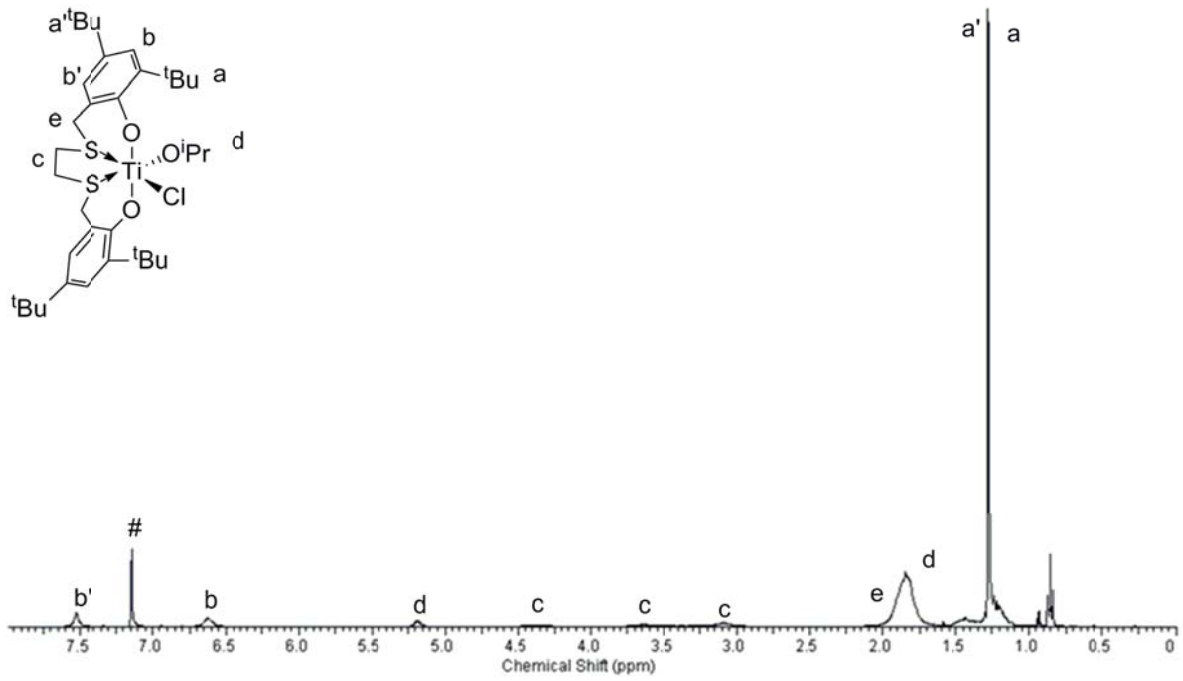

Fig. S11 1H-NMR spectrum of complex **Ti-4a** (400 MHz, C_6D_6 [#], 25 °C)

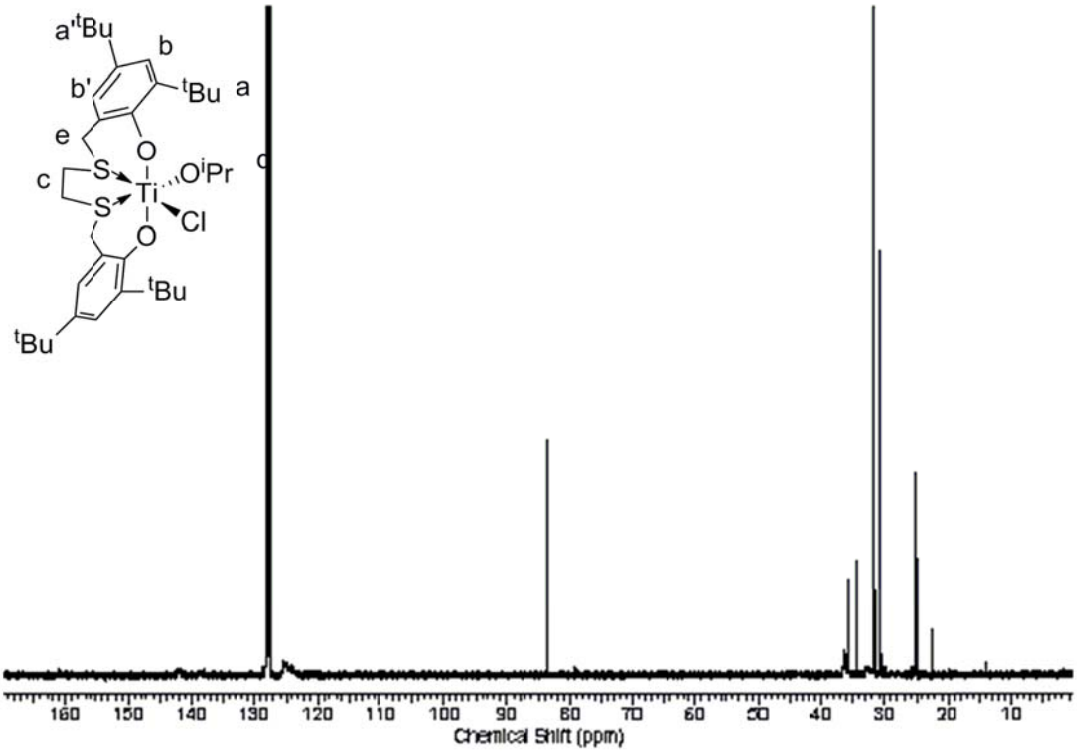

Fig. S12: $^{13}C\{^1H\}$-NMR spectrum of complex **Ti-4a** (100.1 MHz, C_6D_6 [#], 25 °C).

2 Polymerization of lactide monomers

2.1 Polymerization of *meso*-lactide

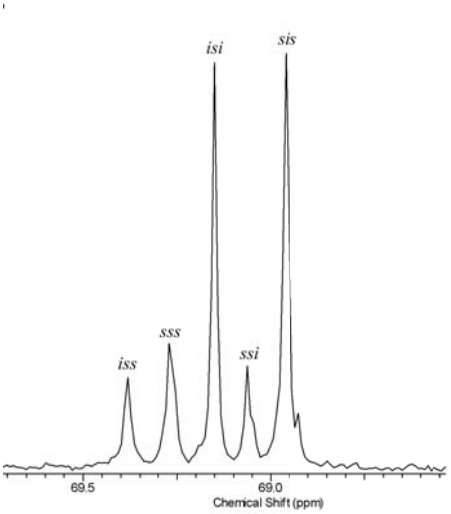

Fig. S13 $^{13}C\{^{1}H\}$-NMR spectrum of the polymerization of *meso*-lactide using **Zr-2**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6.

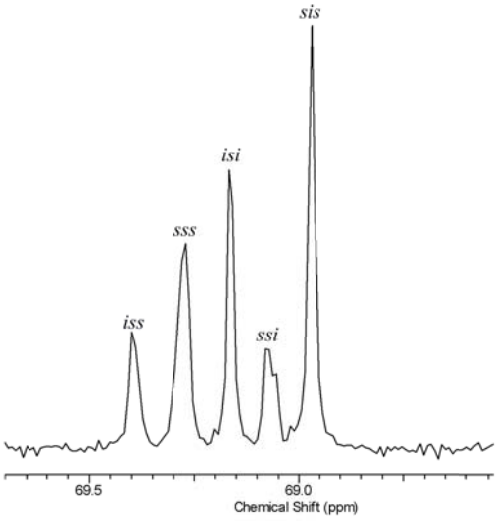

Fig. S14 $^{13}C\{^{1}H\}$-NMR spectrum of the polymerization of *meso*-lactide using **Zr-3**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6.

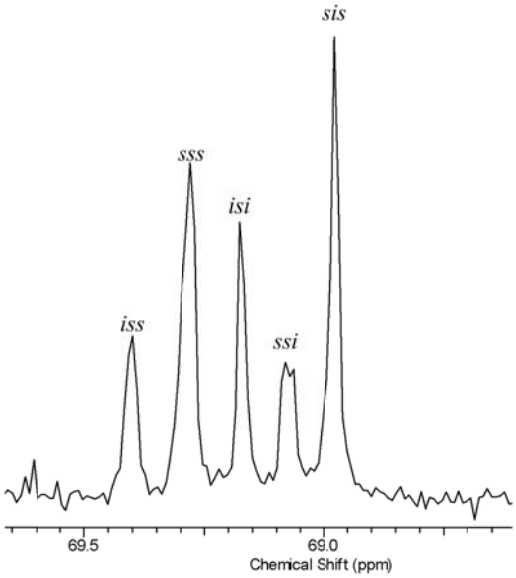

Fig. S15 $^{13}C\{^{1}H\}$-NMR spectrum of the polymerization of *meso*-lactide using **Ti-4**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6.

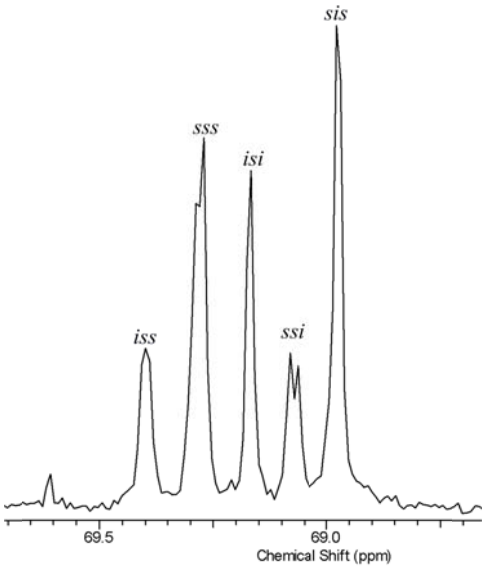

Fig. S16 $^{13}C\{^{1}H\}$-NMR spectrum of the polymerization of *meso*-lactide using **Ti-4a**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6.

2.2 Polymerization of *rac*-lactide

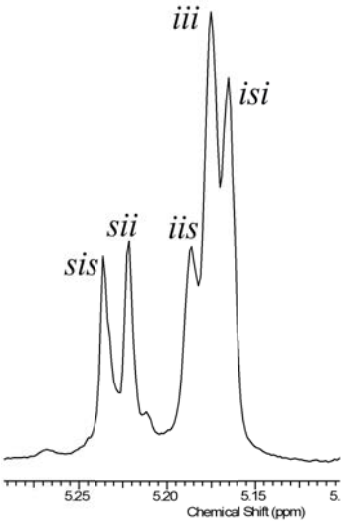

Fig. S17 $^{1}H\{^{1}H\}$-NMR spectrum of the polymerization of *rac*-lactide using **Zr-1**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6.

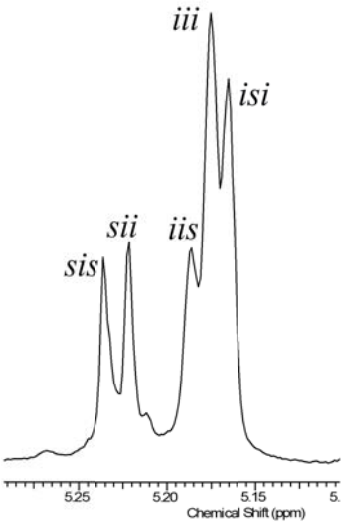

Fig. S18 $^{1}H\{^{1}H\}$-NMR spectrum of the polymerization of *rac*-lactide using **Zr-4**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6.

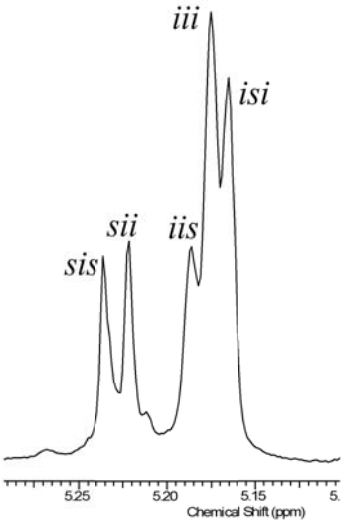

Fig. S19 $^{1}H\{^{1}H\}$-NMR spectrum of the polymerization of *rac*-lactide using **Ti-4**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6.

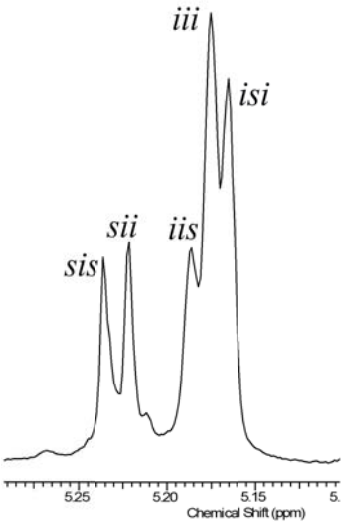

Fig. S20 $^{1}H\{^{1}H\}$-NMR spectrum of the polymerization of *rac*-lactide using **Ti-4a**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6.

2.3 Polymerization of L-lactide

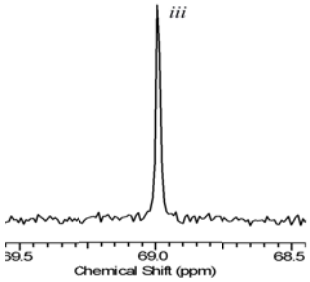

Fig. S21 $^{13}C\{^{1}H\}$-NMR spectrum of the polymerization of L-lactide using **Zr-1**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6.

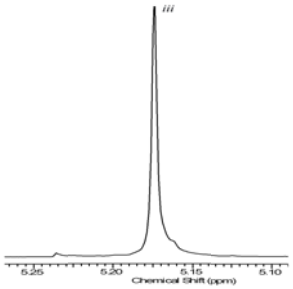

Fig. S22 $^{1}H\{^{1}H\}$-NMR spectrum of the polymerization of L-lactide using **Zr-4**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6.

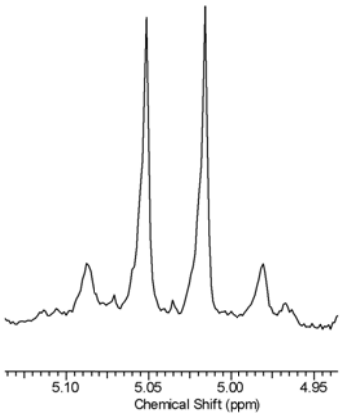

Fig. S23 ^{1}H NMR spectrum of the polymerization of L-lactide using **Ti-4**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6

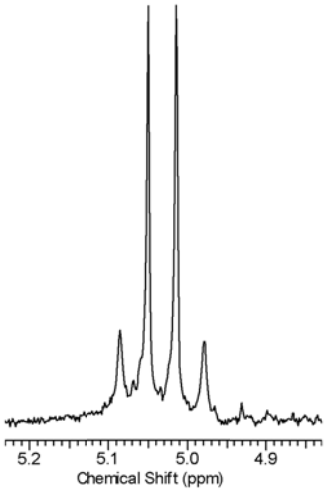

Fig. S24 ^{1}H NMR spectrum of the polymerization of L-lactide using **Ti-4a**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, C_6D_6.

3 Kinetic of polymerization

3.1 Kinetic of polymerization of *rac*-lactide

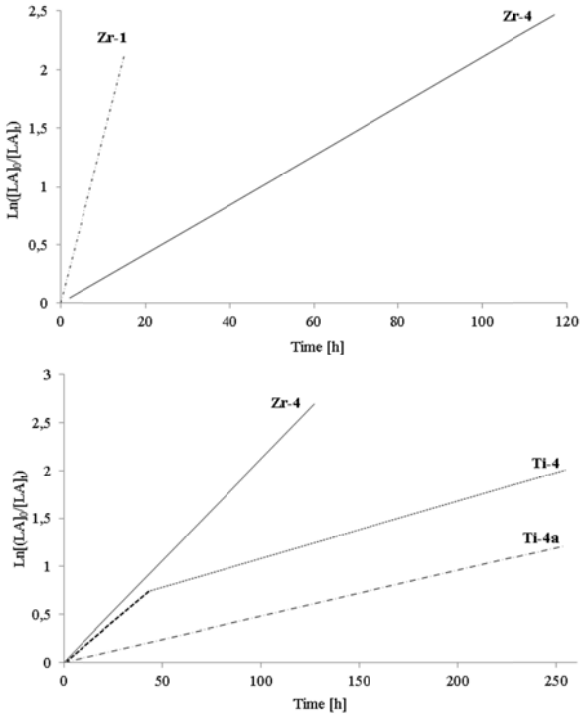

Fig. S25 Semilogarithmic plots of *rac*-lactide conversion vs. time, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL): a) using zirconium complexes: **Zr-1** ($k_{obs} = 142 \times 10^{-3}$ h^{-1}), and **Zr-4** ($k_{obs} = 21 \times 10^{-3}$ h^{-1}), and b) using the flexible ligand **4**: **Ti-4** ($k_{obs} = 14 \times 10^{-3}$ h^{-1}) and ($k_{obs} = 5 \times 10^{-3}$ h^{-1}), and **Ti-4a** ($k_{obs} = 5 \times 10^{-3}$ h^{-1}).

3.2 Kinetic of polymerization of L-lactide

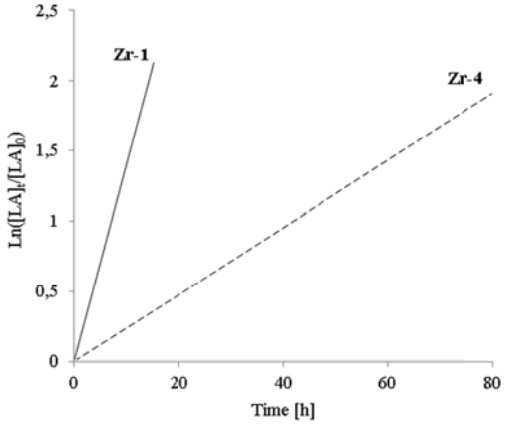

Fig. S26 Semilogarithmic plots of L-lactide conversion vs. time, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL): **Zr-1** ($k_{obs} = 164 \times 10^{-3}$ h^{-1}), and **Zr-4** ($k_{obs} = 24 \times 10^{-3}$ h^{-1}).

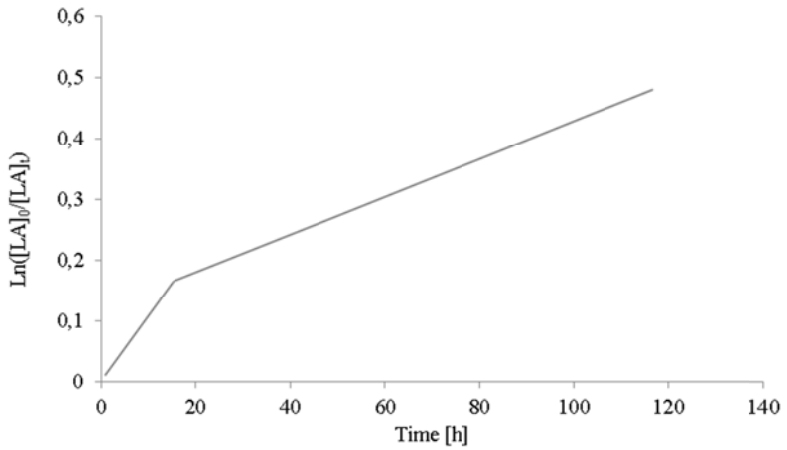

Fig. S27 Semilogarithmic plots of L-lactide conversion vs. time, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL) using **Ti-4** ($k_{obs} = 3 \times 10^{-3}$ h^{-1}).

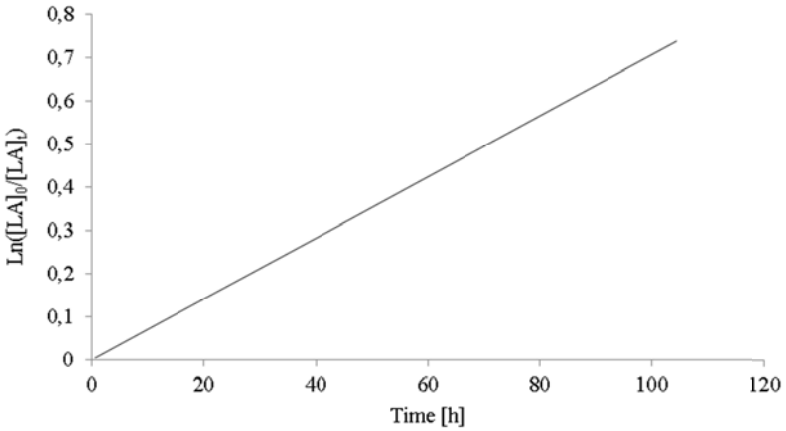

Fig. S28 Semilogarithmic plots of L-lactide conversion vs. time, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL) using **Ti-4a** ($k_{obs} = 7 \times 10^{-3}$ h^{-1}).

4 Polymerization Data

4.1 Tables of polymerization of *meso*-lactide

Table S1 Polymerization of *meso*-lactide using **Zr-1**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	1	12
2	2	22
3	4	47
4	8	77
5	13	88
6	15	91

Table S2 Polymerization of *meso*-lactide using **Zr-2**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	0.5	8
2	1	20
3	2	41
4	4	67

Table S3 Polymerization of *meso*-lactide using **Zr-3**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	0.5	10
2	1	21
3	2	53
4	4	89
5	4.5	92
6	5	93

Table S4 Polymerization of *meso*-lactide using **Zr-4**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	0.5	1
2	2.67	5
3	4	9
4	16	44
5	32	73
6	48	84

Table S5 Polymerization of *meso*-lactide using **Ti-4**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time/ hours	Conversion/ %
1	4	7
2	8	14
3	72	67
4	88	78
5	103	83
6	121	85
7	137	85

Table S6 Polymerization of *meso*-lactide using **Ti-4a**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	4	2
2	8	5
3	72	48
4	88	56
5	103	63
6	121	70
7	137	74

4.2 Tables of polymerization of *rac*-lactide

Table S7 Polymerization of *rac*-lactide using **Zr-1**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	1	10
2	2	21
3	4	48
4	8	72
5	15	87

Table S8 Polymerization of *rac*-lactide using **Zr-4**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	2	7
2	8	18
3	16	33
4	42.5	61
5	69	78
6	93	86
7	117	91
8	141	91

Table S9 Polymerization of *rac*-lactide using **Ti-4**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	2	3
2	8	14
3	16	24
4	42.5	42
5	93	67
6	117	73
7	141	75
8	209.5	82
9	233.5	85
10	254.5	86

Table S10 Polymerization of *rac*-lactide using **Ti-4a**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	2	1
2	8	6
3	16	7
4	42.5	21
5	69	30
6	93	40
7	117	47
8	141	54
9	209	63
10	233.5	65
11	254.5	69

4.3 Tables of polymerization of L-lactide

Table S11 Polymerization of L-lactide using **Zr-1**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	1	12
2	2	22
3	4	47
4	8	77
5	13	88
6	15	91

Table S12 Polymerization of L-lactide using **Zr-4**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	4	9
2	12	16
3	32	50
4	56	76
5	80	85
6	104.5	88

Table S13 Polymerization of L-lactide using **Ti-4**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	0	0
2	4	0,05
3	8	0,08
4	16	0,15
5	24	0,18
6	91	0,37

Table S14 Polymerization of L-lactide using **Ti-4a**, $[LA]_0/[init]_0 = 100$, $[LA]_0 = 0.520$ M, $T = 100$ °C, benzene-d_6 (0.5 mL)

Entry	Time [h]	Conversion [%]
1	4	3
2	12	10
3	32	21
4	56	29
5	80	44
6	104.5	53