Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

Group 4 metal initiators for the controlled stereoselective polymerization lactide monomers

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1. General Considerations

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Toluene (Fisher Scientific), *n*-hexane (Fisher Scientific) and THF (Fisher Scientific) were distilled under argon from sodium/benzophenone ketyl prior to use. *n*-Pentane was purified by distillation from sodium/triglyme benzophenone ketyl. Dichloromethane (Fisher Scientific) was distilled from calcium hydride. Benzene-d_6 (Sigma-Aldrich), chloroform-*d* (Sigma-Aldrich) were carefully dried and stored in a glovebox. *meso*-Lactide (Uhde Inventa-Fischer) was recrystallized from 2-propanol at –30 °C, washed with diethyl ether, and dried under vacuum. *Rac*-lactide and *L*-lactide were purchased from Sigma-Aldrich and purified identically as *meso*-lactide. $Zr(O^tBu)_4$ (ABCR) and $Ti(OiPr)_3Cl$ (Sigma-Aldrich) were used without any purification. 1,4-Dithiabutanediyl-2,2'-bis{4,6-di(2-phenyl-2-propyl)phenol} and 1,4-Dithiapentanediyl-2,2'-bis{4,6-di-*tert*-butyl)phenol} were synthesized according to the literature.[S1-S2] Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed to vacuum-argon cycle three times.

NMR spectra were recorded on Varian 200 and 500 spectrometers at 25 °C (^{1}H: 200, 500 MHz; ^{13}C{^{1}H}: 50, 125 MHz). Chemical shifts for ^{1}H and ^{13}C{^{1}H}: NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. Molecular weights and polydispersities were determined by size exclusion chromatography (SEC) in THF at 35 °C, at a flow rate of 1 mL/min utilizing an Agilent 1100 Series HPLC, G1310A isocratic pump, an Agilent 1100 Series refractive index detector and 8 × 600 mm, 8 × 300 mm, 8 × 50 mm PSS SDV linear M columns. Calibration standards were commercially available narrowly distributed linear polystyrene samples that cover a broad range of molar masses ($103 < M_n < 2\times10^6$ g/mol).

Polymerization example: A solution of a certain ampount of the initiator **5** in 0.5 mL of toluene (according to table entry) was added to a solution of 150 mg of *meso*-lactide which was dissolved in 1.5 mL of toluene. After the desired time the polymerization mixture was quenched with drops of moist hexanes and was added slowly to a cooled, quickly stirred hexanes solution. The polymer was filtered over a Büchner funnel, washed with diethyl ether, and dried *in vacuo*. The polymer was dissolved in minimum quantity of CH_2Cl_2 and ran through a flash silica gel column (in a Pasteur pipette) to afford a colorless solution, which was added slowly to a cooled, quickly stirred hexanes solution. The colorless polymer was filtered and dried *in vacuo*.

2. Synthesis

2.1 Complexes 1-2 and 4-5

Complexes **1-2** and **4-5** were synthesized according to the literature.[S1-S2]

2.2 Di(*tert*-butoxy){1,4-dithiabutanediyl-2,2'-bis[(2-phenyl-propyl)phenoxy]}zirconium (3)

To a solution of 1 equivalent of Zr(O^{t}Bu)$_4$ in pentane (100 mg, 0.261 mmole, 2 mL) was added 1 equivalent of a solution of 1,4-dithiabutanediyl-2,2'-bis{4,6-di(2-phenyl-2-propyl)phenol} in pentane (195.6 mg, 0.261 mmole, 2 mL) and the mixture stirred for 18 h at 25 °C. The yellow color of the solution changed to orange. The solvent was removed *in vacuo* to give a yellow powder that was dissolved in 5 mL of *n*-pentane, filtered, and stored at –30 °C for 1 d. The orange powder in was dried *in vacuo* to give **3** in quantitative yield.

^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.18 (s, 18 H, OC(CH_3)$_3$), 1.56 (s, 12 H, C(CH_3)$_2$), 1.73 (s, 6 H, C(CH_3)$_2$), 1.82 (s, 6 H, C(CH_3)$_2$), 1.90 (d, 2 H, $^2J_{HH}$ = 9.8 Hz, SCH_2), 2.26 (d, 2 H, $^2J_{HH}$ = 10.7 Hz, SCH_2), 7.01-7.13 (m, 8 H, Ph), 7.17-7.27 (m, 10 H, Ph), 7.31-7.36 (m, 4 H, Ph) and 7.44 (d, 2 H, $^3J_{HH}$ = 7.1 Hz, Ph)

^{13}C{^{1}H} NMR (400 MHz, C$_6$D$_6$): δ 28.65 (C(CH$_3$)$_2$), 29.86 (C(CH$_3$)$_2$), 30.94 (C(CH$_3$)$_2$), 32.64 (OC(CH$_3$)$_3$), 36.97 (SCH$_2$), 42.79 (C(CH$_3$)$_2$), 42.81 (C(CH$_3$)$_2$), 76.95 (OC(CH$_3$)$_3$), 117.57 (C-2), 125.28, 125.98, 126.27, 127.01, 127.94 , 128.18, 128.60, 129.72, 138.04 (*o*-, *m*-, *p*-C of Ph), 139.03 (C-6), 140.28 (C-4), 151,17 (*ipso*-C, C(CH$_3$)$_2$Ph),, 151.40 (*ipso*-C, C(CH$_3$)$_2$Ph), 165.72 (C-1).

Elemental Analysis: Calculated for C$_{58}$H$_{70}$O$_4$S$_2$Zr; C: 70.61, H: 7.15; Found C: 70.78, H: 7.82.

2.3 Chloro(isopropoxy){1,4-dithiabutanediyl-2,2'-bis[(4,6-di(2-phenylpropyl)phenoxy]} titanium (2a)

To a solution of 1 equivalent of Ti(O^{i}Pr)$_3$Cl in pentane (100 mg, 0.38 mmole, 2 mL) was added 1 equivalent of a solution of 1,4-dithiabutanediyl-2,2'-bis{4,6-di(2-phenylpropyl)phenol} in pentane (294 mg, 0.38 mmole, 2 mL) and the mixture stirred for 18 h at 25 °C. The yellow color of the solution changed to orange. The solvent was removed *in vacuo* to give an orange powder that was dissolved in 2 mL of *n*-pentane/thf (9/1), filtered, and stored at –30 °C for 2 d. The orange powder was dried *in vacuo* to give **2a** in 91 % yield (312 mg).

^{1}H NMR (400 MHz, C_6D_6): δ 0.95 (d, $^2J_{HH}$ = 6.1 Hz, 3 H, OCH(CH_3)$_2$), 0.99 (d, $^2J_{HH}$ = 6.1 Hz, 3 H, OCH(CH_3)$_2$), 1.50 (s, 3 H, C(CH_3)$_2$Ph), 1.50 (s, 3 H, C(CH_3)$_2$Ph), 1.51 (s, 3 H, C(CH_3)$_2$Ph), 1.53 (s, 3 H, C(CH_3)$_2$Ph), 1.54 (s, 3 H, C(CH_3)$_2$Ph), 1.71-1.85 (m, 2 H, SCH_2), 1.77 (s, 3 H, C(CH_3)$_2$Ph), 1.78 (s, 3 H, C(CH_3)$_2$Ph), 1.88 (s, 3 H, C(CH_3)$_2$Ph), 2.09-2.22 (m, 2 H, SCH_2), 4.40 (septet, 1 H, OCH(CH$_3$)$_2$), 6.87-7.15 (m, 12 H, Ph), 7.16-7.47 (m, 12 H, Ph).

^{13}C{^{1}H} NMR (400 MHz, C_6D_6): δ 24.76 (OCH(CH$_3$)$_2$), 24.79 (OCH(CH$_3$)$_2$), 26.75 (C(CH$_3$)$_2$Ph), 28.45 (C(CH$_3$)$_2$Ph), 28.49 (C(CH$_3$)$_2$Ph), 30.92 (C(CH$_3$)$_2$Ph), 90.94 (C(CH$_3$)$_2$Ph), 90.97 (C(CH$_3$)$_2$Ph), 31.37 (C(CH$_3$)$_2$Ph), 38.03 (SCH$_2$), 38.46, (SCH$_2$), 42.31 (C(CH$_3$)$_2$Ph), 42.63 (C(CH$_3$)$_2$Ph), 42.73 (C(CH$_3$)$_2$Ph), 42.78 (C(CH$_3$)$_2$Ph), 84.79 (OCH(CH$_3$)$_2$), 117.14 (C-2), 119.58 (C-2), 125.17, 125.41, 128.94, 125.98, 126.03, 126.66, 126.76, 126.84, 127.95, 128.25, 128.30, 129.20 (*o*, *m*, *p*-C of Ph), 136.31 (C-6), 137.74 (C-6), 142.23 (C-4), 142.96 (C-4), 149.69 (*ipso*-C, C(CH$_3$)$_2$Ph), 150.58 (*ipso*-C, C(CH$_3$)$_2$Ph), 150.82 (*ipso*-C, C(CH$_3$)$_2$Ph), 151.10 (*ipso*-C, C(CH$_3$)$_2$Ph), 166.41 (C-1), 167.31 (C-1).

Elemental Analysis: Calculated for $C_{53}H_{59}ClO_3S_2Ti$; C: 71.41, H: 6.67; Found C: 69.90, H: 6,18.

2.4 Chloro(isopropoxy){1,5-dithiapentanediyl-2,2'-bis[4,6-di-*tert*-butylphenoxy]}-titanium (5a)

To a solution of 1 equivalent of Ti(O^{i}Pr)$_3$Cl in pentane (200 mg, 0.77 mmole, 2 mL) was added 1 equivalent of a solution of 1,4-dithiapentanediyl-2,2'-bis{4,6-di-*tert*-butyl)phenol} in pentane (397 mg, 0.77 mmole, 2 mL) and the mixture stirred for 18 h at 25 °C. From an instant yellow color, the solution became orange. The solvent was removed *in vacuo* to give a orange powder that was dissolved in 3 mL of *n*-pentane/thf (9/1), filtered, and stored at –30 °C for 1 d. The orange powder was dried *in vacuo* to give **5a** in 72 % yield (372 mg).

^{1}H NMR (400 MHz, C_6D_6): δ 1.24 (s, 18 H, C(CH_3)$_3$), 1.37-1.46 (m, 2 H, (CH_2)), 1.45 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, OCH(CH_3)$_2$), 1.50-1.69 (br m, 18 H, C(CH_3)$_3$), 2.72 (higher order d, 2 H, $^2J_{HH}$ = 9.2 H, SCH_2), 3.16 (higher order t, 2 H, $^2J_{HH}$ = 8.7 Hz, SCH_2), 5.16 (septet, $^3J_{HH}$ = 6.5 Hz, 1 H, OCH(CH$_3$)$_3$), 7.00 (d, 2 H, $^4J_{HH}$ = 6.3 Hz, 3-CH$_{Ar}$), and 7.40 (d, 2 H, $^4J_{HH}$ = 7.4 Hz, 5-CH$_{Ar}$)

^{13}C{^{1}H} NMR (400 MHz, C_6D_6): δ 21.90 (CH$_2$), 25.52 (OCH(CH$_3$)$_2$), 29.81 (C(CH$_3$)$_2$), 31.72 (C(CH$_3$)$_3$), 34.48 (SCH$_2$), 34.65 (SCH$_2$), 35.67 (C(CH$_3$)$_3$), 84.63 (OCH(CH$_3$)$_2$), 124.54 (C-3 and C-5), 136.83 (C-2), 143.79 (C-4 and C-6) and 164.12 (C-1).

3. Polymerization

3.1 Solution polymerization

3.1.1 Polymerization of *meso*-lactide using complex 5 at 75°C

Table S1 Polymerization of *meso*-lactide using complex **5** at 75°C

Entry	Time (h)	% Conv.[a]	$M_{n,exp}$ (g/mol)[b]	$M_{n,theo}$ (g/mol)[c]	M_w/M_n[b]
1	8	12	700	858	1.17
2	16	21	2000	1478	1.07
3	24	40	2750	2897	1.13
4	63	92	5000	6580	1.12
5	72	97	5250	6998	1.07

[a] conversion of monomer (($[mon]_0 - [mon]_t)/[mon]_0$); [b] measured by GPC; [c] $M_{n,theo}$ calculated via $M_{n,theo} = [Mon]_0/2[Init.]_0 \times M_{Mon} \times$ Conv.

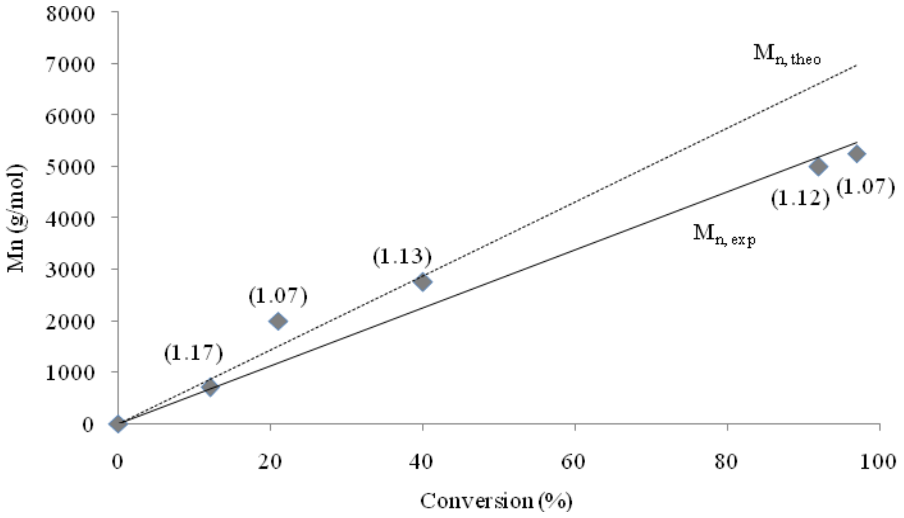

Figure S1 Polymerization of *meso*-lactide by **5** in toluene, [monomer]/[initiator] = 100, *T* =75 °C.

3.1.2 Polymerization of *meso*-lactide using complex 5 with variation of initial ratio

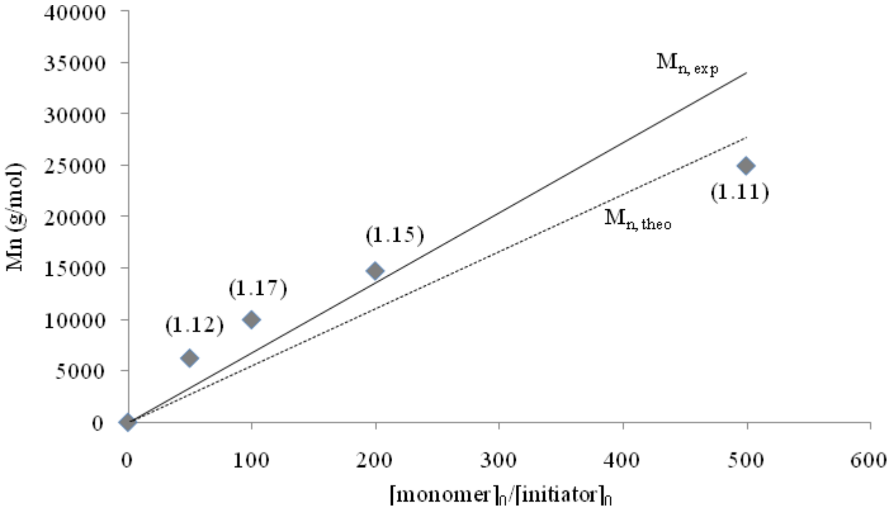

Figure S2 Polymerization of *meso*-lactide by **5** in toluene, Initial ratio variation, T =100 °C.

3.1.3 Polymerization of *meso*-lactide using complex 4

Table S2 Polymerization of *meso*-lactide using complex **4**

Entry	Time (h)	% Conv.[a]
1	16	4
2	23	8
3	48	11
4	63	13
5	72	15
6	96	20

[a] Conversion of monomer $(([mon]_0 - [mon]_t)/[mon]_0)$

3.1.4 Polymerization of *rac*-lactide using complex 5 at 100°C

Table S3 Polymerization of *rac*-lactide using complex **5** at 100°C

Entry	Time (h)	% Conv.[a]	$M_{n,exp}$ (g/mol)[b]	$M_{n,theo}$ (g/mol)[c]	M_w/M_n[b]
1	8	17	2250	2393	1.17
2	24	46	6750	6601	1.11
3	48	92	9250	13202	1.25
4	72	96	14000	13793	1.16

[a] conversion of monomer (($[mon]_0 - [mon]_t)/[mon]_0$); [b] measured by GPC; [c] $M_{n,theo}$ calculated via $M_{n,theo} = [Mon]_0/[Init.]_0 \times M_{Mon} \times$ Conv.

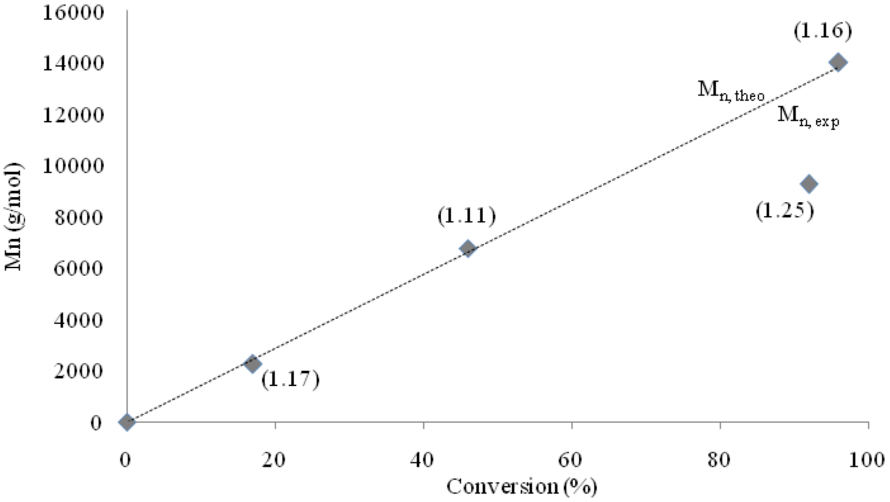

Figure S3 Polymerization of *rac*-lactide by **5** in toluene, [monomer]/[initiator] = 100, T =100 °C.

3.1.5 Polymerization of *L*-lactide using complex 5 at 100°C

Table S4 Polymerization of *L*-lactide using complex **5** at 100°C

Entry	Time (h)	% Conv.[a]	$M_{n,exp}$ (g/mol)[b]	$M_{n,theo}$ (g/mol)[c]	M_w/M_n[b]
1	8	38	6 500	5 520	1.19
2	16	78	8 500	11 228	1.18
3	24	94	11 500	13 548	1.29
4	48	92	11 000	13 318	1.50
5	72	93	11 500	13 361	1.27

[a] conversion of monomer (([mon]$_0$ – [mon]$_t$)/[mon]$_0$); [b] measured by GPC; [c] $M_{n,theo}$ calculated via $M_{n,theo} = [Mon]_0/[Init.]_0 \times M_{Mon} \times Conv.$

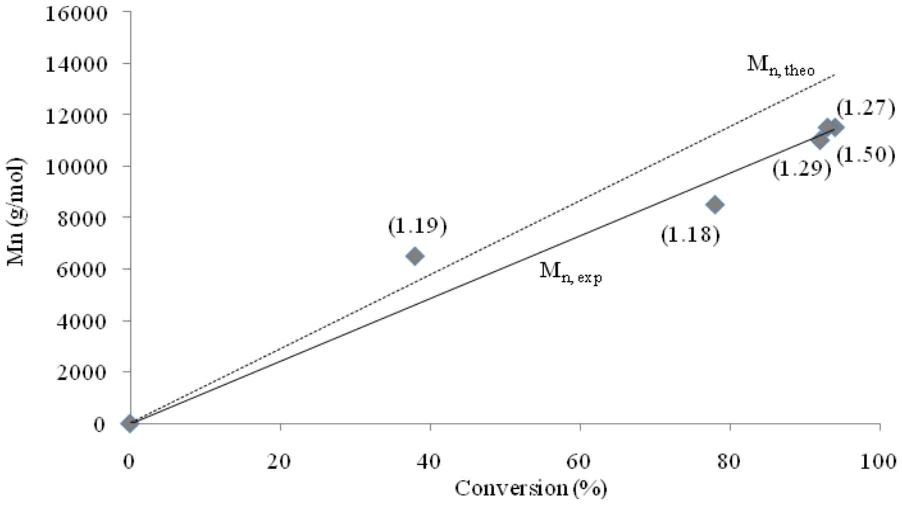

Figure S4 Polymerization of *L*-lactide by **5** in toluene, [monomer]/[initiator] = 100, T =100 °C.

3.2 Melt polymerization

Table S5 Polymerization of *meso*-lactide using complex **5** at 100°C in melt

Entry	Time (h)	% Conv.[a]	$M_{n,exp}$ (g/mol)[b]	$M_{n,theo}$ (g/mol)[c]	M_w/M_n[b]
1	1	7	800	1052	1.01
2	2	21	2000	2998	1.20
3	4	43	5250	6126	1.07
4	8	74	10000	10608	1.06

[a] conversion of monomer (([mon]$_0$ – [mon]$_t$)/[mon]$_0$); [b] measured by GPC; [c] $M_{n,theo}$ calculated via $M_{n,theo}$ = [Mon]$_0$/2[Init.]$_0$ × M_{Mon} × Conv.

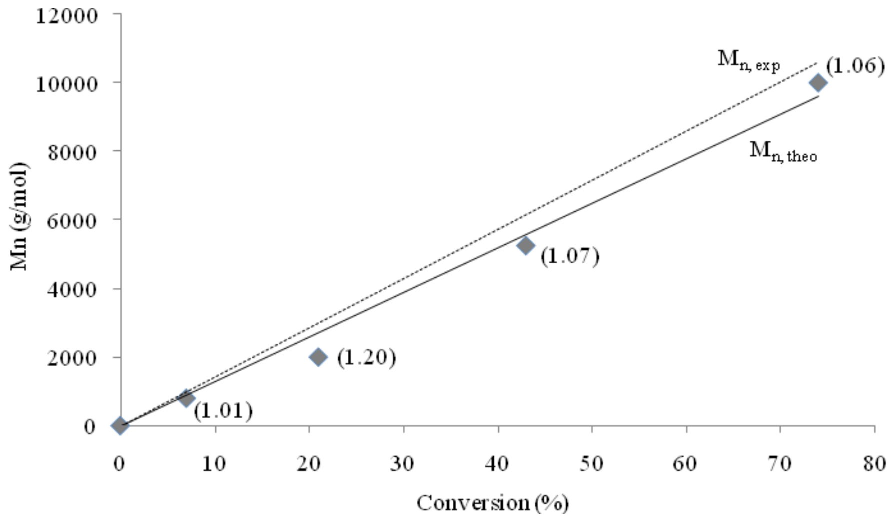

Figure S5 Polymerization of *meso*-lactide by **5** in melt, [monomer]/[initiator] = 100, T =100 °C.

3.3 Polymerization of meso-lactide using asymetric complexes

3.3.1 Polymerization of *meso*-lactide using complex 2a

Table S6: Polymerization of *meso*-lactide using complex **2a** at 100°C in C_6D_6

Entry	Time (h)	% Conv.[a]
1	4	12
2	7	23
3	10	34
4	14	42
5	16	46
6	20.5	60
7	24	71

[a] conversion of monomer $(([mon]_0 - [mon]_t)/[mon]_0)$

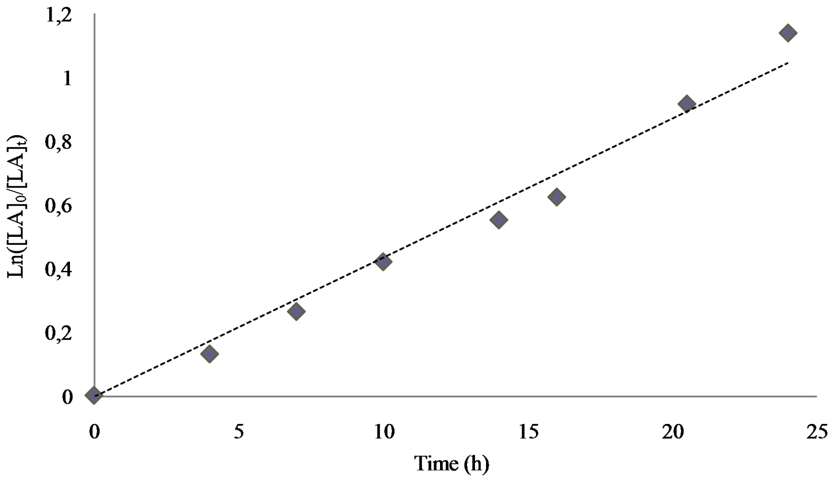

Figure S6: Polymerization of *meso*-lactide by **2a** in C_6D_6, [monomer]/[initiator] = 50, T =100 °C.

3.3.2 Polymerization of *meso*-lactide using complex 5a

Table S7: Polymerization of *meso*-lactide using complex **5a** at 100°C in C_6D_6

Entry	Time (h)	% Conv.[a]
1	2	4
2	4	11
3	6	23
4	7	30
5	10	49
6	14	67
7	16	74
8	20.5	84
9	24	89

[a] conversion of monomer $(([mon]_0 - [mon]_t)/[mon]_0)$

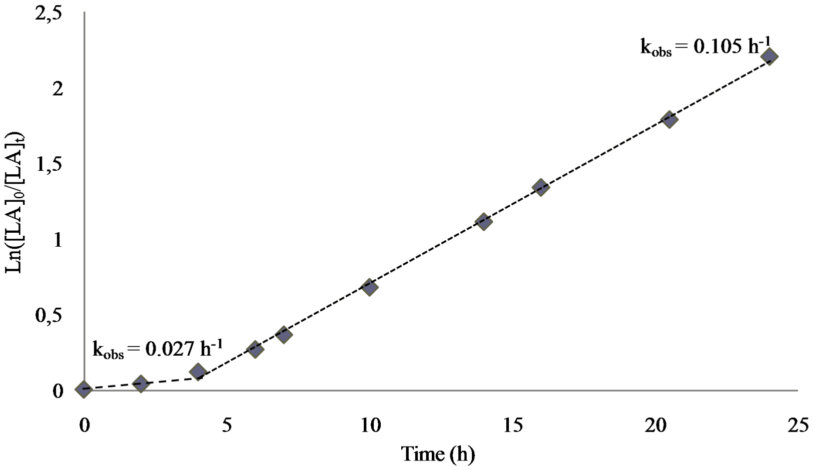

Figure S7: Polymerization of *meso*-lactide by **5a** in C_6D_6, [monomer]/[initiator] = 100, T =100 °C.

4. Microstructure Analysis

4.1 Solution Polymerization of *meso*-lactide using complex 5

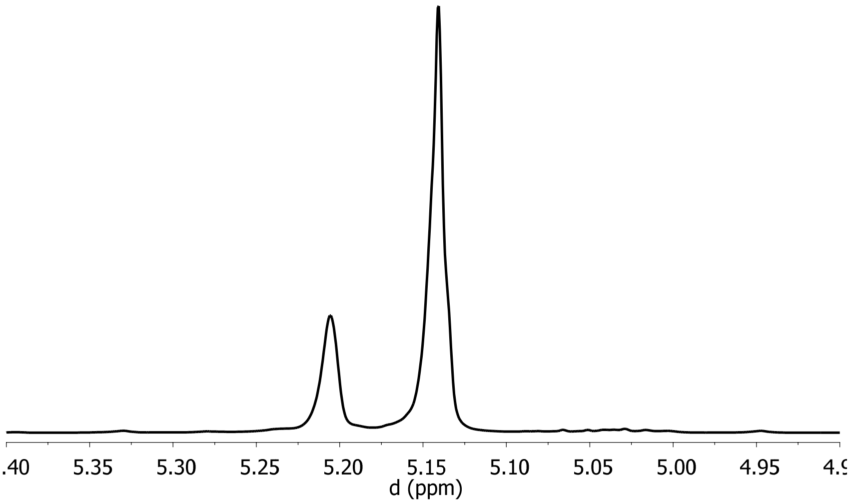

Figure S8: $^1H\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, Toluene (in $CDCl_3$, 400 Mhz).

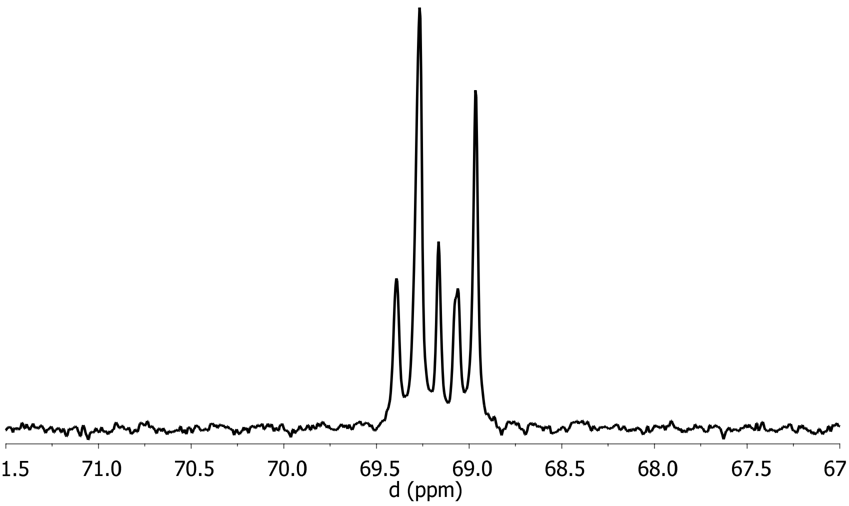

Figure S9: $^{13}C\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, Toluene (in $CDCl_3$, 400 Mhz).

4.2 Melt Polymerization of *meso*-lactide using complex 1

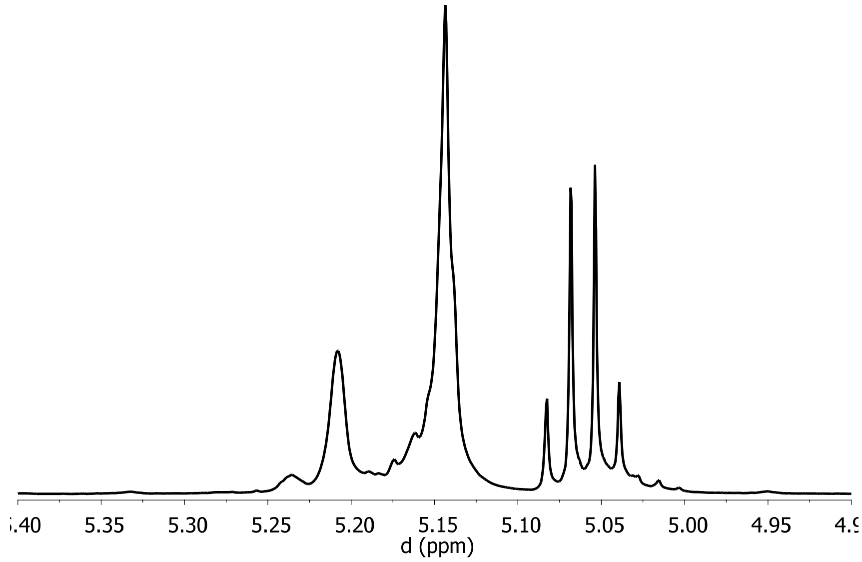

Figure S10: $^1H\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **1**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

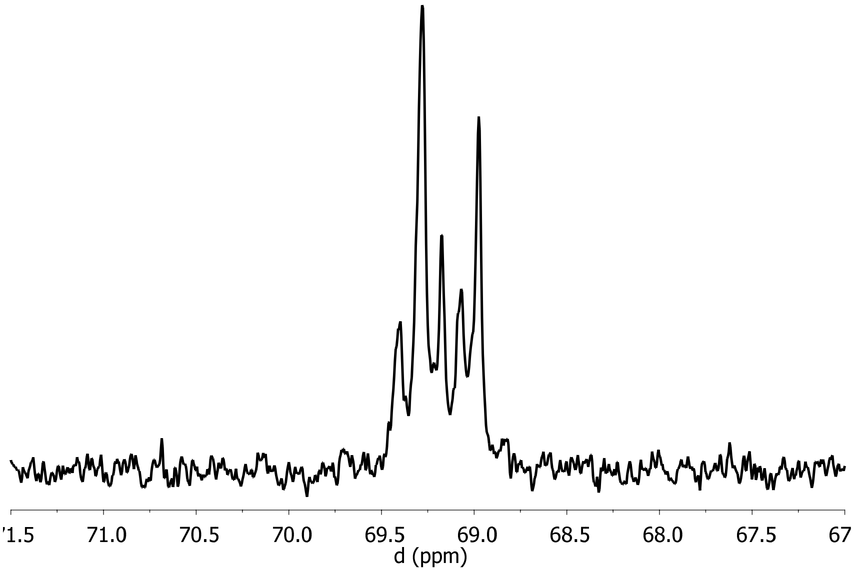

Figure S11: $^{13}C\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **1**, [monomer]/[initiator] = 100, T = 100°C, Melt (in $CDCl_3$, 400 Mhz).

4.3 Melt Polymerization of *meso*-lactide using complex 2

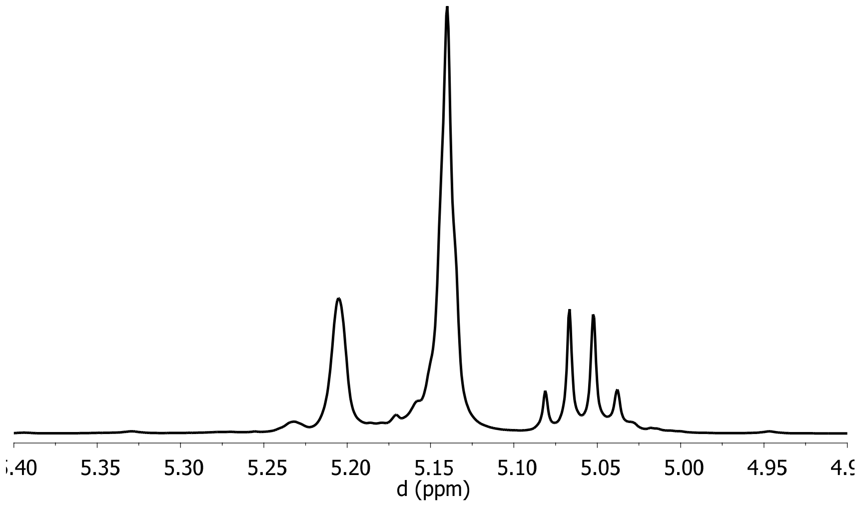

Figure S12: $^1H\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **2**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

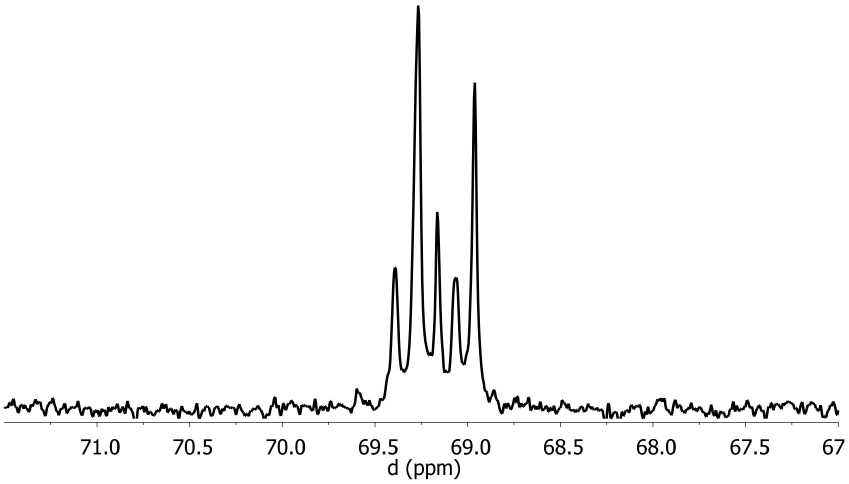

Figure S13: $^{13}C\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **2**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

4.4 Melt Polymerization of *meso*-lactide using complex 4

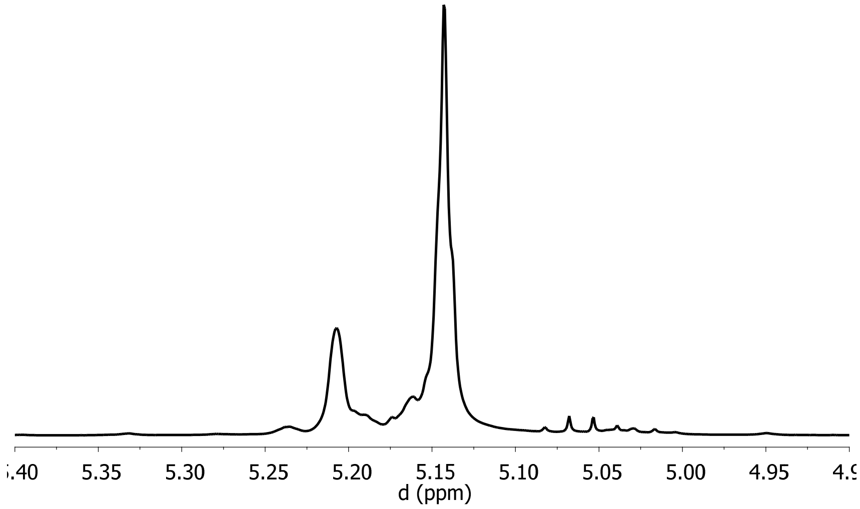

Figure S14: $^{1}H\{^{1}H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **4**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

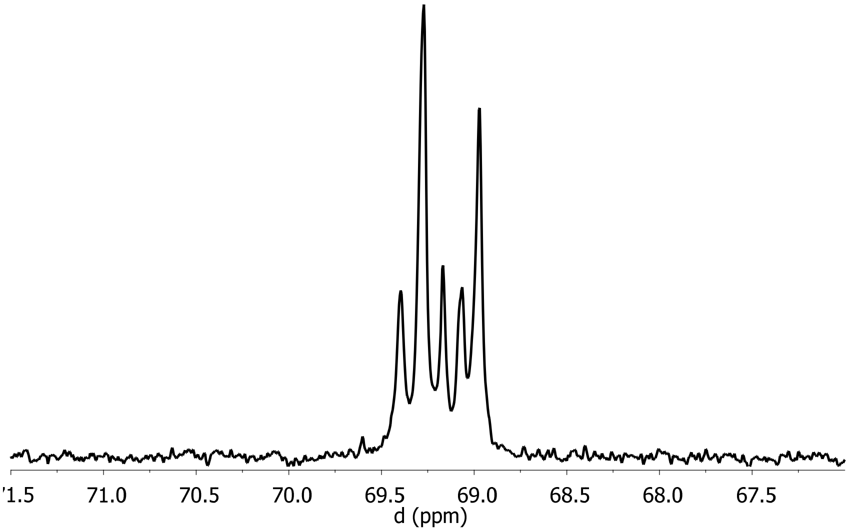

Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **4**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

4.5 Melt Polymerization of *meso*-lactide using complex 5

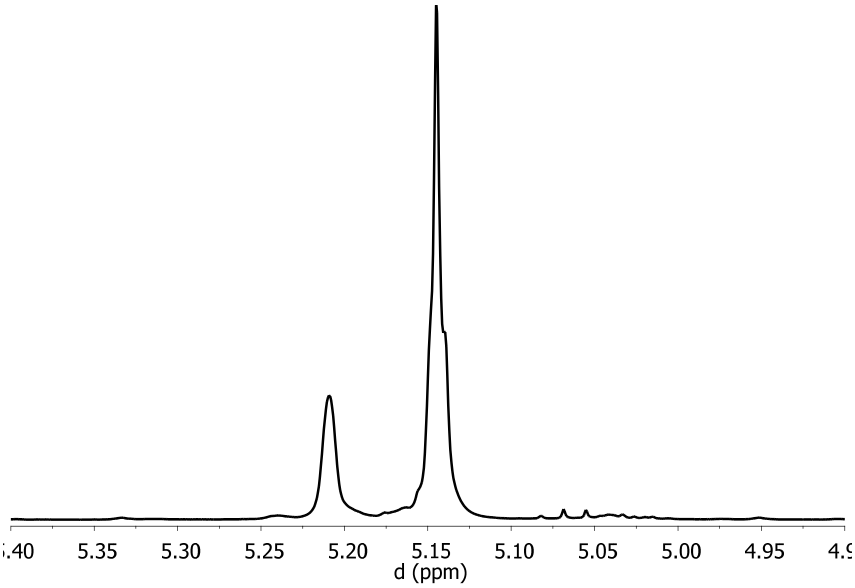

Figure S16: $^1H\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

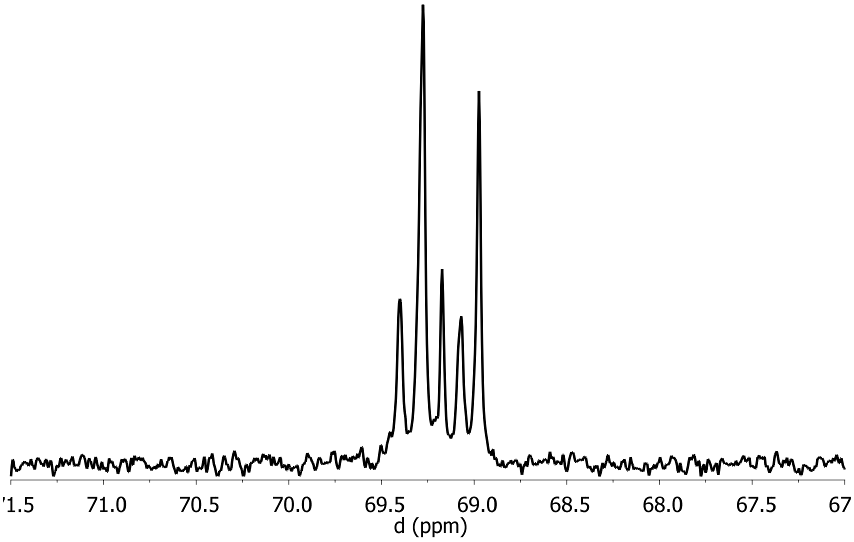

Figure S17: $^{13}C\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

4.6 Melt Polymerization of *meso*-lactide using complex 5, Time Variation

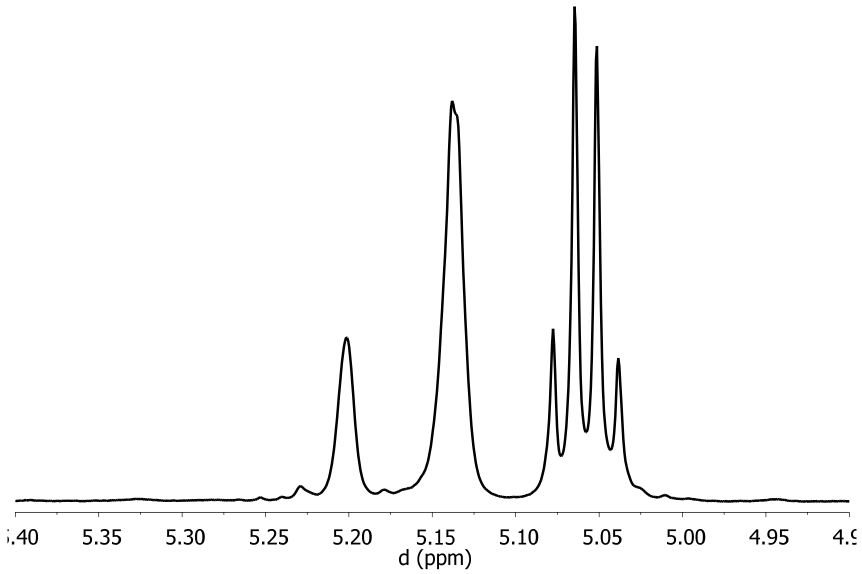

Figure S18: $^1H\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, 2h, Melt (in $CDCl_3$, 400 Mhz).

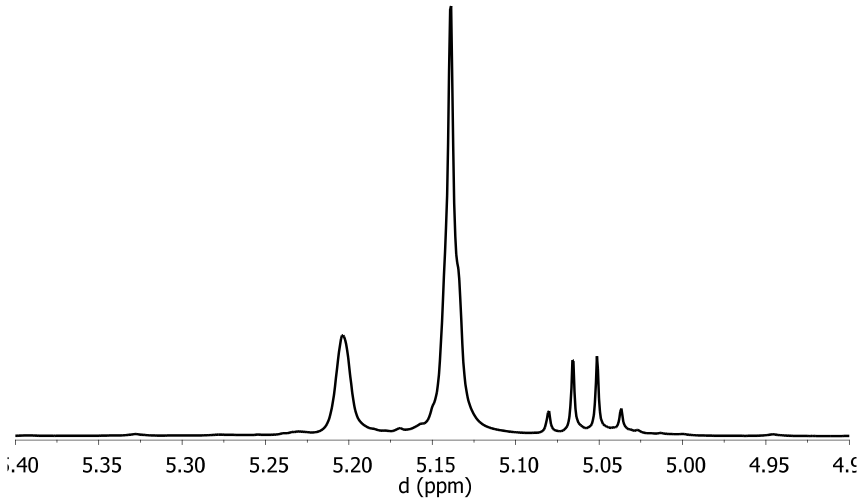

Figure S19: $^1H\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, 4h, Melt (in $CDCl_3$, 400 Mhz).

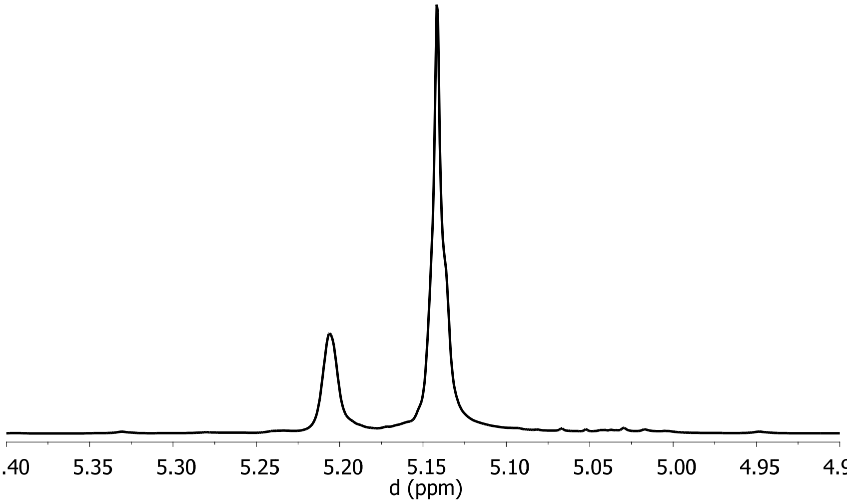

Figure S20: $^{1}H\{^{1}H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, 8h, Melt (in $CDCl_3$, 400 Mhz).

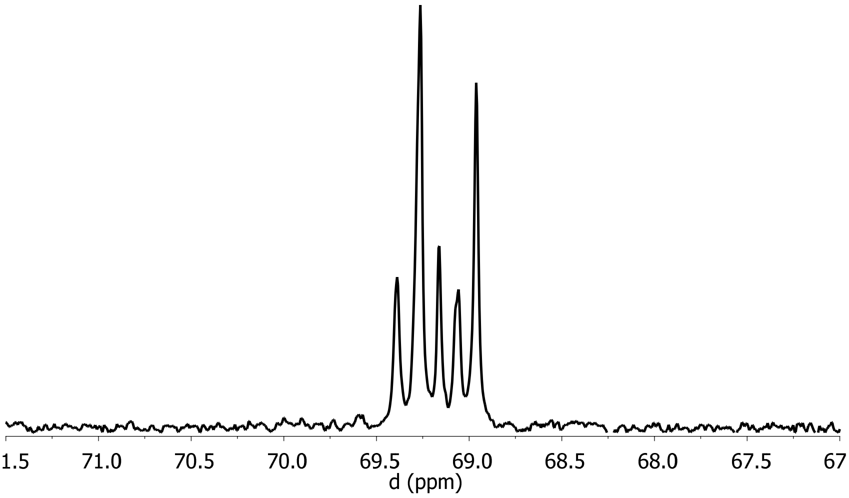

Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, 8h, Melt (in $CDCl_3$, 400 Mhz).

4.7 Melt Polymerization of *rac*-lactide using complex 4

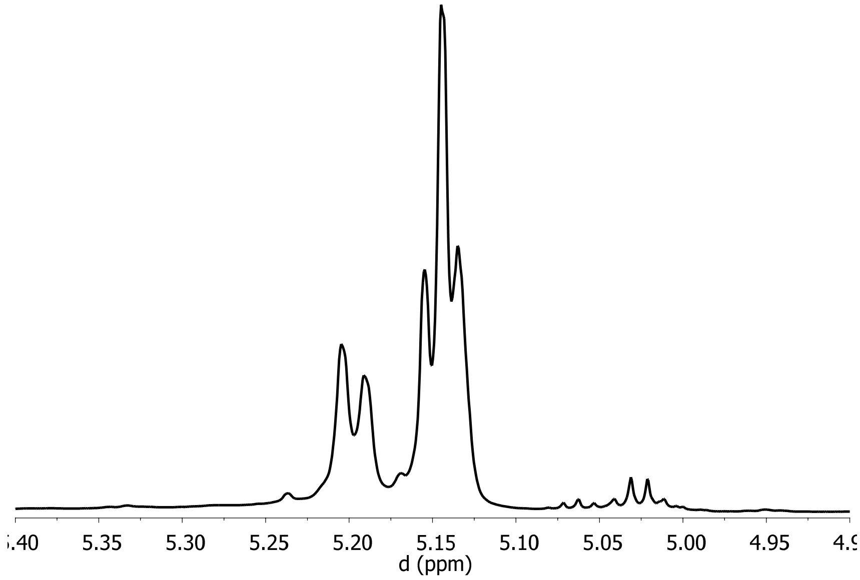

Figure S22: $^{1}H\{^{1}H\}$ NMR spectrum of *rac*-polylactide synthesized using complex **4**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

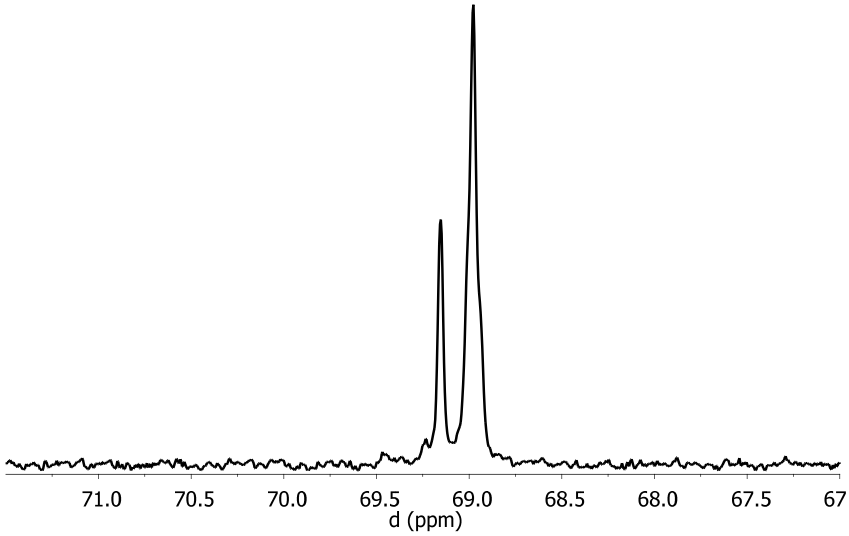

Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum of *rac*-polylactide synthesized using complex **4**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

4.8 Melt Polymerization of *rac*-lactide using complex 5

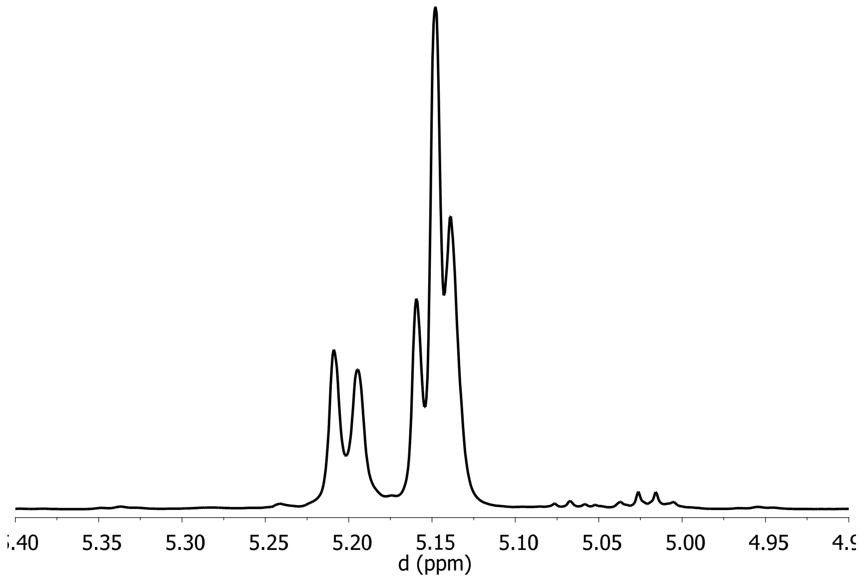

Figure S24: $^1H\{^1H\}$ NMR spectrum of *rac*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

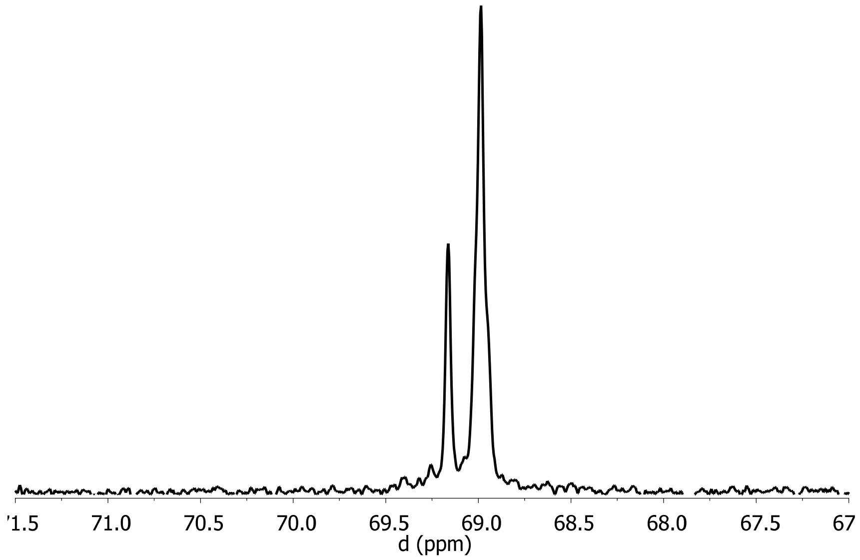

Figure S25: $^{13}C\{^1H\}$ NMR spectrum of *rac*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

4.9 Melt Polymerization of *L*-lactide using complex 5

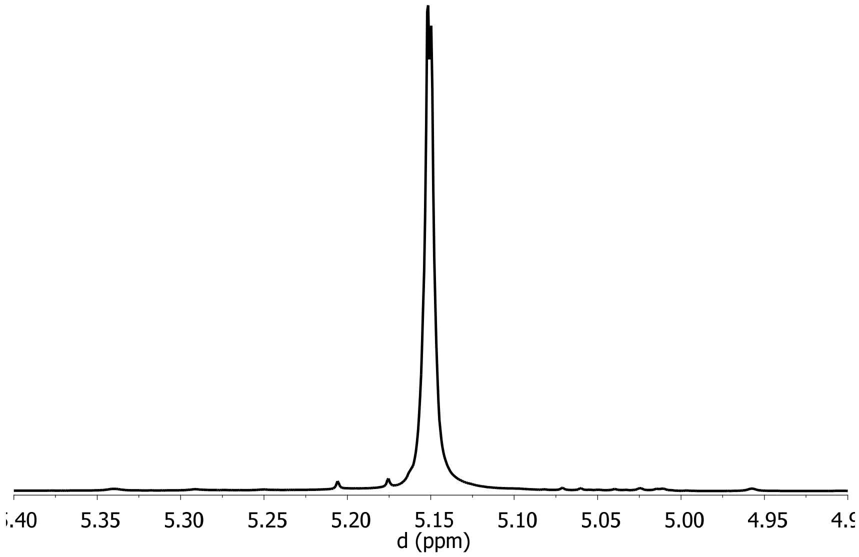

Figure S26: $^1H\{^1H\}$ NMR spectrum of *L*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

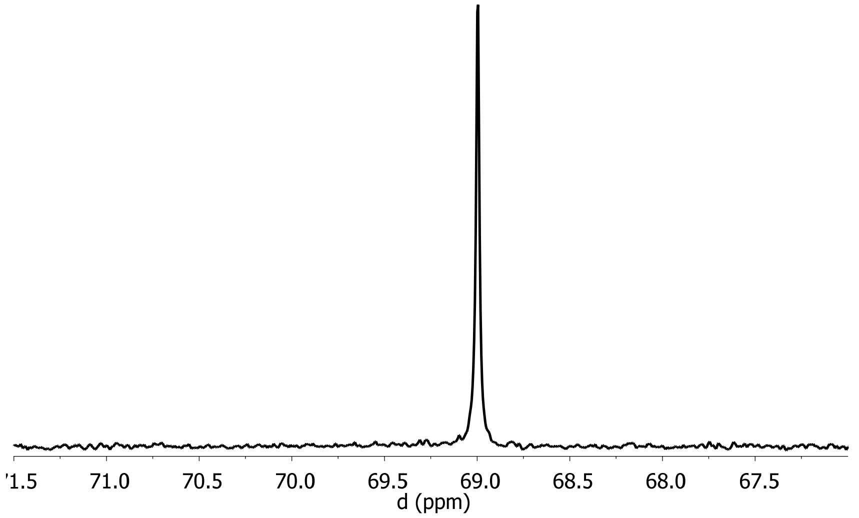

Figure S27: $^{13}C\{^1H\}$ NMR spectrum of *L*-polylactide synthesized using complex **5**, [monomer]/[initiator] = 100, T = 100 °C, Melt (in $CDCl_3$, 400 Mhz).

4.10 Polymerization of *meso*-lactide using complex 2a

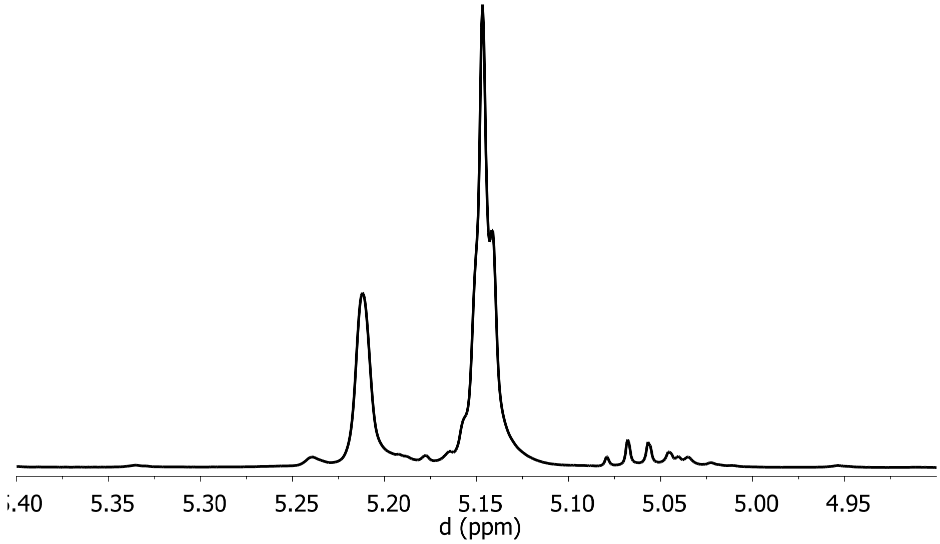

Figure S28: $^1H\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **2a**, [monomer]/[initiator] = 50, T = 100 °C, in C_6D_6 (in $CDCl_3$, 400 Mhz).

4.11 Polymerization of *meso*-lactide using complex 5a

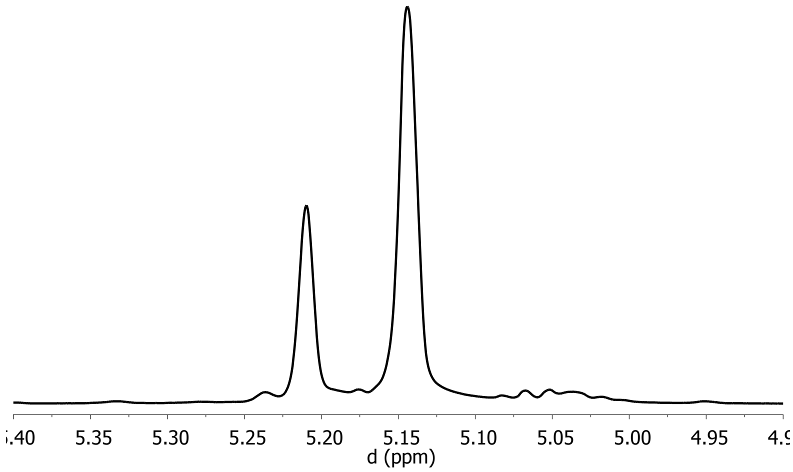

Figure S29: $^1H\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **5a**, [monomer]/[initiator] = 50, T = 100 °C, in C_6D_6 (in $CDCl_3$, 400 Mhz).

4.12 Polymerization of *meso*-lactide using complex 5a

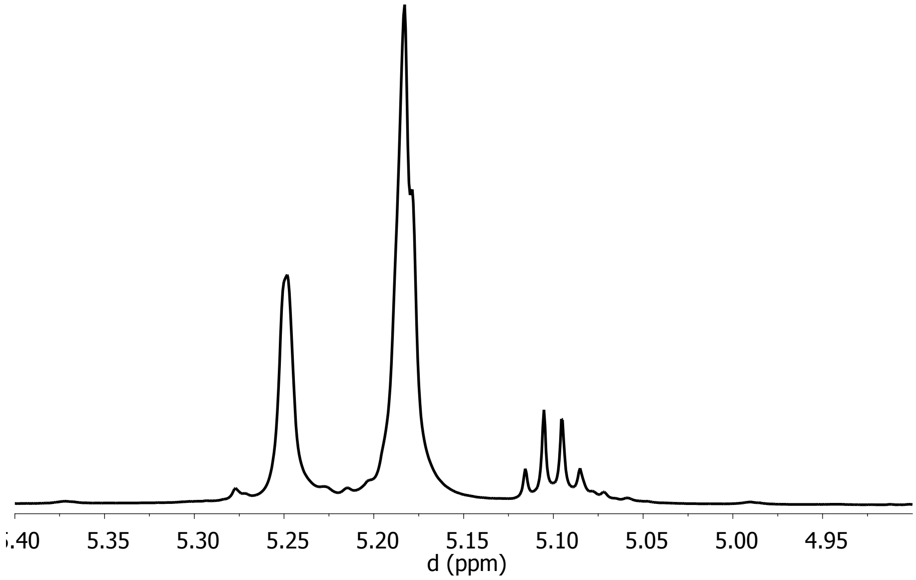

Figure S30: $^1H\{^1H\}$ NMR spectrum of *meso*-polylactide synthesized using complex **5a**, [monomer]/[initiator] = 100, T = 100 °C, in C_6D_6 (in $CDCl_3$, 400 Mhz).

Complex 3[S3]

Crystal data	
Chemical formula	$C_{63}H_{82}O_4S_2Zr$
M_r	1058.63
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	9.9818 (16), 18.392 (3), 31.754 (5)
V (Å^3)	5829.8 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.31
Crystal size (mm)	0.51 × 0.34 × 0.12
Data collection	
Diffractometer	*APEX* Area Detector diffractometer
Absorption correction	Multi-scan Bruker *SADABS*
T_{min}, T_{max}	0.611, 0.894
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	70189, 11966, 10389
R_{int}	0.169
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.117, 0.95
No. of reflections	11966
No. of parameters	647
No. of restraints	0
H-atom treatment	Riding
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.82, −1.17
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881
Flack parameter	−0.04 (3)

5. References

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[S2] Carmine Capacchione, Antonio Proto, Henner Ebeling, Rolf Mülhaupt, Klaus Möller, Thomas P. Spaniol, and Jun Okuda, *J. Am. Chem. Soc.*, 2003, **125**, 4964

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