

Supporting Information

Stereoselective Polymerization of *meso*-Lactide: Syndiotactic Polylactide by Heteroselective Initiators Based on Trivalent Metals

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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. [Ln{N(SiHMe₂)₂}₃(THF)_x] (Ln = Sc, Y, Lu; x = 1, 2) were synthesized according to the literature methods.^[S1,S2] *trans*-1,2-Dithiocyclohexanediyl-2,2'-bis{4,6-di(2-phenyl-2-propyl)phenol} was synthesized according to the literature.^[S3] *meso*-Lactide (Uhde Inventafischer) was recrystallized from 2-propanol at -30 °C, washed with diethyl ether, and dried under vacuum. All other chemicals were commercially available and used after appropriate purification. 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 (¹H: 200, 500 MHz; ¹³C{¹H}: 50, 125 MHz). Chemical shifts for ¹H and ¹³C{¹H}: 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 × 10⁶ g/mol).

2. Synthesis

2.1. Complex 1-3, 6, and 7. Complex 1-3, 6, and 7 were synthesized following a procedure published in the literature.^[S4]

2.2 {Bis(dimethylsilyl)amido}[*trans*-1,2-dithiocyclohexanediyl-2,2'-bis{4,6-di(2-phenyl-2-propyl)}]scandium (4). *trans*-1,2-Dithiocyclohexanediyl-2,2'-bis{4,6-di(2-phenyl-2-propyl)phenol} (313.3 mg, 0.39 mmol.) was slowly added to a solution of 200 mg (0.39 mmol.) of [Sc{N(SiMe₂H)₂(THF)}] in 5 mL of benzene at room temperature. The orange solution was stirred at 70 °C for 5 d. The solvent was removed *in vacuo* to give a white

powder that was solved in 5 mL of *n*-pentane, filtered, and stored at $-30\text{ }^{\circ}\text{C}$ for 3 d. The white powder in was dried *in vacuo* to give **4** in quantitative yield. ^1H NMR (400 MHz, C_6D_6): δ 0.33 (d, 6 H, $^3J_{\text{HH}} = 3.4\text{ Hz}$, SiCH_3), 0.34 (d, 6 H, $^3J_{\text{HH}} = 3.4\text{ Hz}$, SiCH_3), 0.60 (m, 1 H, Cy-*H*), 0.77 (m, 1 H, Cy-*H*), 1.02 (m, 4 H, THF), 1.27 (m, 2 H, Cy-*H*), 1.36 (m, 2 H, Cy-*H*), 1.58 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 1.64 (s, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3), 1.74 (m, 2 H, Cy-*H*), 1.83 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.23 (m, 1 H, SCH), 2.41 (m, 1 H, SCH), 3.10 (m, 4 H, THF), 5.13 (sept, 2 H, $^3J_{\text{HH}} = 3.4\text{ Hz}$, Si*H*), 6.99 (d, 2 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, Ph-*H*), 7.03 (d, 2 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, Ph-*H*), 7.09 (d, 2 H, $^3J_{\text{HH}} = 9.2\text{ Hz}$, Ph-*H*), 7.14 (d, 4 H, $^3J_{\text{HH}} = 6.6\text{ Hz}$, Ph-*H*), 7.18 (m, 4 H, Ph-*H*), 7.25 (m, 6 H, Ph-*H*), 7.47 (d, 2 H, $^3J_{\text{HH}} = 9.2\text{ Hz}$), 7.62 (m, 2 H, Ph-*H*). $^{13}\text{C}\{^1\text{H}\}$ -NMR (128.4 MHz, C_6D_6): δ 3.8 [$\text{Si}(\text{CH}_3)$], 24.9 (THF), 25.8 (cyclohexyl-*C*), 26.2 (cyclohexyl-*C*), 27.5 (CH_3), 28.2 (CH_3), 30.8 (CH_3), 30.9 (CH_3), 31.2 (CH_3), 31.5 (CH_3), 33.3 (cyclohexyl-*C*), 33.5 (CH_3), 33.9 (CH_3), 34.4 (cyclohexyl-*C*), 42.5 [$\text{C}(\text{CH}_3)$], 42.6 [$\text{C}(\text{CH}_3)$], 42.9 (SCH), 43.1 (SCH), 51.2 [$\text{C}(\text{CH}_3)$], 53.7 [$\text{C}(\text{CH}_3)$], 71.3 (THF), 115.8 (*C*2), 116.2 (*C*2'), 125.0 (aryl-*C*), 125.6 (aryl-*C*), 125.7 (aryl-*C*), 126.1 (aryl-*C*), 127.01 (aryl-*C*), 127.06 (aryl-*C*), 127.09 (aryl-*C*), 123.9 (aryl-*C*), 128.2 (aryl-*C*), 134.38 (*C*3), 134.41 (*C*3'), 135.7 (*C*4), 136.9 (*C*4'), 137.1 (*C*6), 137.3 (*C*6'), 151.8 (aryl-*C*), 152.1 (aryl-*C*), 152.3 (aryl-*C*), 166.4 (*C*1), 166.9 (*C*1'). Anal. Calcd. for $\text{C}_{62}\text{H}_{80}\text{NO}_3\text{S}_2\text{ScSi}_2$ (1051.47 g/mol): C, 70.75; H, 7.66; N, 1.33. Found: C, 69.85; H, 7.62; N, 1.05.

2.3 {Bis(dimethylsilyl)amido}[*trans*-1,2-dithiocyclohexanediyl-2,2'-bis{4,6-di(2-phenyl-2-propyl)}]yttrium (5). *trans*-1,2-Dithiocyclohexanediyl-2,2'-bis{4,6-di(2-phenyl-2-propyl)phenol} (256 mg, 0.32 mmol.) was slowly added to a solution of $[\text{Y}\{\text{N}(\text{SiMe}_2\text{H})_2(\text{THF})_2\}]$ (200 mg, 0.32 mmol.) in 10 mL of benzene at room temperature. The orange solution was stirred at $70\text{ }^{\circ}\text{C}$ for 1 d. The solvent was removed *in vacuo* to give a white powder that was solved in 5 mL of *n*-pentane, filtered, and stored at $-30\text{ }^{\circ}\text{C}$ for 3 d to give colorless crystals of **5** (196 mg, 0.178 mmol, 56%). ^1H NMR (400 MHz, C_6D_6): δ 0.36 (d, 12 H, $^3J_{\text{HH}} = 3.0\text{ Hz}$, SiCH_3), 0.69 (br, 2 H, Cy-*H*), 1.05 (m, 4 H, THF), 1.43 (br, 2 H, Cy-*H*), 1.62 (s, 6 H, CH_3), 1.67 (s, 6 H, CH_3), 1.70 (br, 2 H, Cy-*H*), 1.81 (br, 2 H, Cy-*H*), 1.84 (s, 6 H, CH_3), 1.91 (s, 6 H, CH_3), 2.39 (br, 2 H, SCH), 3.06 (m, 4 H, THF), 4.99 (sept, 2 H, $^3J_{\text{HH}} = 3.0\text{ Hz}$, Si*H*), 6.97 (tr., 2 H, $^3J_{\text{HH}} = 7.2\text{ Hz}$, Ph-*H*), 7.05 (m 2 H, $^3J_{\text{HH}} = 6.8\text{ Hz}$, Ph-*H*), 7.13 (m, 6 H, Ph-*H*), 7.17 (m, 4 H, Ph-*H*), 7.28 (m, 4 H, Ph-*H*), 7.37 (d, 2 H, $^3J_{\text{HH}} = 7.2\text{ Hz}$), 7.62 (br., 2 H, Ph-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (128.4 MHz, C_6D_6): δ 3.7 [$\text{Si}(\text{CH}_3)$], 3.8 [$\text{Si}(\text{CH}_3)$], 25.0 (THF), 26.0 (cyclohexyl-*C*), 30.9 (CH_3), 31.2 (CH_3), 31.5 (CH_3), 33.9 (CH_3), 34.1

(cyclohexyl-C), 34.4 (CH₃), 42.5 [C(CH₃)], 42.6 [C(CH₃)], 43.1 (SCH), 52.5 [C(CH₃)], 70.3 (THF), 115.8 (C2), 124.8 (aryl-C), 125.6 (aryl-C), 126.5 (aryl-C), 127.1 (aryl-C), 128.2 (aryl-C), 134.9 (C3), 136.6 (C3'), 136.9 (C4), 137.1 (C6), 152.0 (aryl-C), 152.3 (aryl-C), 166.8 (C1), 166.9 (C1'). Anal. Calcd. for C₆₂H₈₀NO₃S₂YSi₂ (1096.42 g/mol): C, 67.91; H, 7.35; N, 1.28. Found: C, 67.05; H, 7.44; N, 1.16.

3. Polymerization

3.1 General Procedure

All polymerizations were performed under an inert atmosphere of argon using glove box techniques. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed to vacuum-argon cycle three times. Toluene and THF were distilled under argon from sodium/benzophenone ketyl prior to use. Benzene-*d*₆, toluene-*d*₈, THF-*d*₈ and chloroform-*d* were carefully dried.

A solution of 10 mg of the initiator **7** in 0.5 mL of toluene or THF was added to a solution of the desired amount of *meso*-lactide (according to table entry) which was dissolved in 1.5 mL of toluene or THF. 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 CH₂Cl₂ 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*.

3.2 Solution polymerization

Table S1. Polymerization of *meso*-lactide using **7** with variation of the initial ratio.

| entry | cat : mon. ratio | time [min] | conv. ^b [%] | $M_{n,exp}^c$ [g·mol ⁻¹] | M_w/M_n^c | P_s^d |
|-------|----------------------|---------------|---------------------------|---|-------------|---------|
| 1 | 1 : 50 ^a | 30 | > 99 | 10 500 | 1.68 | 0.90 |
| 2 | 1 : 100 ^a | 30 | > 99 | 19 000 | 1.80 | 0.89 |
| 3 | 1 : 200 ^a | 30 | 96 | 34 750 | 2.04 | 0.89 |

^a Toluene; ^b conversion of monomer ($([mon]_0 - [mon]_t)/[mon]_0$); ^c measured by GPC; ^d P_s is the probability of a new *s* dyad.

Table S2. Polymerization of *meso*-lactide using **7** (ratio : **7** mon. = 1: 200).

| entry | solvent | T [°C] | time [min] | conv. ^a [%] | $M_{n,exp}^b$ [g·mol ⁻¹] | M_w/M_n^b | P_s^c |
|-------|---------|-------------|---------------|---------------------------|---|-------------|---------|
| 1 | THF | 25 | 1.8 | 12 | - | - | 0.70 |
| 2 | THF | 25 | 7.2 | 27 | 6 000 | 1.40 | 0.78 |
| 3 | THF | 25 | 15 | 27 | 5 000 | 2.01 | 0.83 |
| 4 | THF | 25 | 30 | 74 | 11 000 | 1.87 | 0.86 |
| 5 | THF | 25 | 60 | 93 | 192 000 | 1.23 | 0.84 |
| 6 | toluene | 25 | 1.8 | 92 | 3 000 | 1.76 | 0.85 |
| 7 | toluene | 25 | 9 | 81 | 15 000 | 2.32 | 0.85 |
| 8 | toluene | 25 | 19.8 | 86 | 16 000 | 1.63 | 0.85 |
| 9 | toluene | 25 | 40 | 94 | - | - | 0.85 |
| 10 | toluene | 25 | 60 | 88 | - | - | 0.86 |
| 11 | toluene | 60 | 10.2 | 56 | 15 000 | 1.63 | 0.86 |

^a Conversion of monomer ($([mon]_0 - [mon]_t)/[mon]_0$); ^b measured by GPC; ^c P_s is the probability of a new *s* dyad.

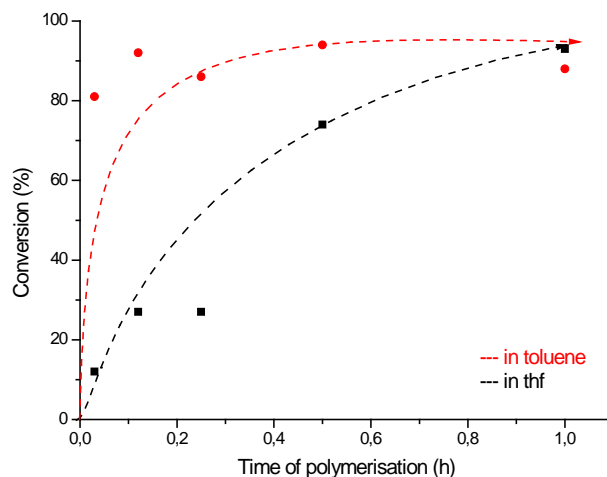


Figure S 1 Polymerization of *meso*-lactide by **7** in toluene (red) and THF (black).

Table S3. Polymerization of *meso*-lactide with variation of the $[\text{mon}]_0/[\text{initiator}]_0$ using complex **7**

| entry | $[\text{mon}]_0/[\text{initiator}]_0$ | T [°C] | time [min] | conv. ^a [%] | $M_{n,\text{exp}}$ ^b [g·mol ⁻¹] | $M_{n,\text{theo}}$ ^c [g·mol ⁻¹] | M_w/M_n ^b |
|-------|---------------------------------------|-------------|---------------|---------------------------|---|--|------------------------|
| 1 | 50 | 25 | 60 | > 99 | 10 500 | 7206 | 1.68 |
| 2 | 100 | 25 | 60 | > 99 | 19 000 | 14 413 | 1.80 |
| 3 | 200 | 25 | 60 | > 99 | 34 750 | 28 826 | 2.04 |
| 4 | 500 | 25 | 120 | > 99 | 56 000 | 72 065 | 2.23 |
| 5 | 1 000 | 25 | 120 | > 99 | 172 500 | 144 130 | 2.17 |

^a Conversion of monomer ($([\text{mon}]_0 - [\text{mon}]_t)/[\text{mon}]_0$); ^b measured by GPC; ^c molecular weight theoretical calculated $M_{n,\text{theo}} = 144.13 \times [\text{mon}]_0/[\text{initiator}]_0 \times \text{conv.}$

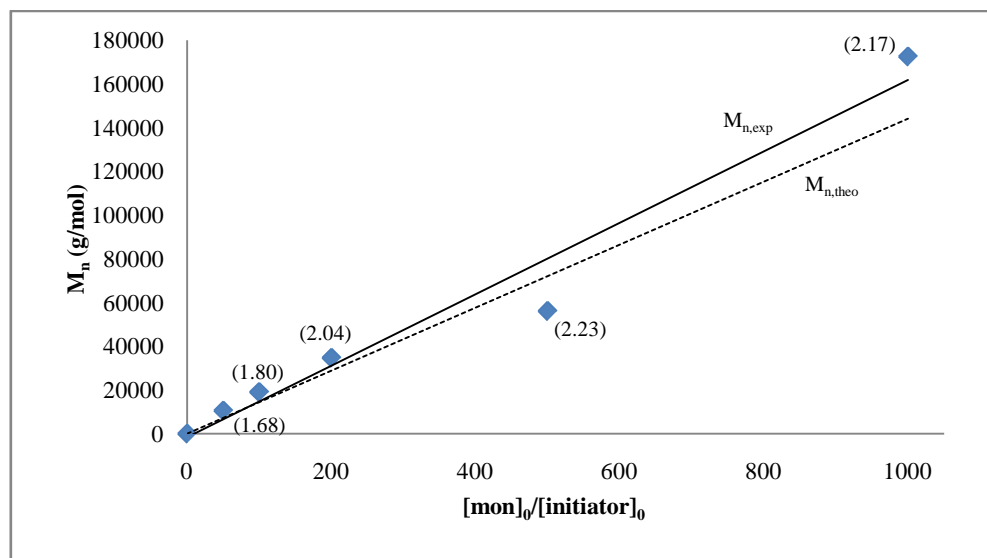


Figure S2: Polymerization of *meso*-lactide with variation of the $[\text{mon}]_0/[\text{initiator}]_0$ using **7**

3.3 Melt polymerization data

Table S 4 Melt polymerization of *meso*-lactide using **7** (ratio :7 mon. = 1: 200).

| entry | <i>T</i> (°C) | cat : monomer ratio | time [min] | conv. ^b [%] | <i>M_{n,exp}</i> ^c [g·mol ⁻¹] | <i>M_w</i> / <i>M_n</i> ^c | <i>P_s</i> ^d |
|-------|------------------|---------------------------|---------------|---------------------------|---|---|-----------------------------------|
| 1 | 60 ^a | 1 : 200 ^a | 10.2 | 56 | 15 000 | 1.63 | 0.86 |
| 2 | 100 ^a | 1 : 200 ^a | 7.2 | 54 | 14 000 | 2.80 | 0.85 |
| 3 | 130 ^a | 1 : 200 ^a | 7.2 | 88 | 45 500 | 1.59 | 0.83 |

^a Melt polymerization; ^b conversion of monomer ($([\text{mon}]_0 - [\text{mon}]_t)/[\text{mon}]_0$); ^c measured by GPC; ^d *P_s* is the probability of a new *s* dyad.

3.4 Polymerization using [1,4-dithiabutanediylbis(4,6-di-*tert*-butylphenolato)-(isopropoxy)indium]

Table S 5. Polymerization of *meso*-lactide using indium complex^[S6]

| entry | cat : mon. ratio | <i>T</i> (°C) | time [h] | conv. ^c [%] | <i>M_{n,exp}</i> ^d [g·mol ⁻¹] | <i>M_w</i> / <i>M_n</i> ^d | <i>P_s</i> ^e |
|-------|---------------------|------------------|-------------|---------------------------|---|---|-----------------------------------|
| 1 | 1: 47 ^a | 70 | 18 | > 99 | 7 500 | 1.14 | 0.93 |
| 2 | 1: 100 ^b | 25 | 16 | > 99 | 25 500 | 1.05 | 0.93 |
| 3 | 1: 200 ^b | 25 | 16 | > 99 | 36 500 | 1.09 | 0.92 |

^a C₆D₆; ^b Toluene ^c conversion of monomer ($([\text{mon}]_0 - [\text{mon}]_t)/[\text{mon}]_0$); ^d measured by GPC; ^e *P_s* is the probability of a new *s* dyad.

3.4 Polymerization using amine tris(4,6-*tert*-butylphenolato)(isopropoxy)zirconium^[S7]

Davidson et al. showed that with an initiator : monomer ratio of 1 : 100, 50% conversion of *rac*-lactide was attained after 48 h at 25 °C with high heterotacticity of 98% (*M_n* = 11 700 g/mol and *M_w*/*M_n* = 1.09).^[S7]

Table S6. Polymerization of *meso*-lactide using zirconium complex^[S6]

| entry | cat : mon. ratio | <i>T</i> (°C) | time [h] | conv. ^b [%] | <i>M_{n,exp}</i> ^c [g·mol ⁻¹] | <i>M_w</i> / <i>M_n</i> ^c | <i>P_s</i> ^d |
|-------|---------------------|------------------|-------------|---------------------------|---|---|-----------------------------------|
| 1 | 1: 100 ^a | 25 | 48 | > 99 | 12 500 | 1.18 | 0.84 |
| 2 | 1: 100 ^a | 50 | 16 | > 99 | 15 000 | 1.17 | 0.85 |

^aToluene ^bconversion of monomer ($([\text{mon}]_0 - [\text{mon}]_t)/[\text{mon}]_0$); ^cmeasured by GPC; ^d*P_s* is the probability of a new *s* dyad.

4. ^1H and ^{13}C NMR Spectra

4.1 Table 1, Entry 1

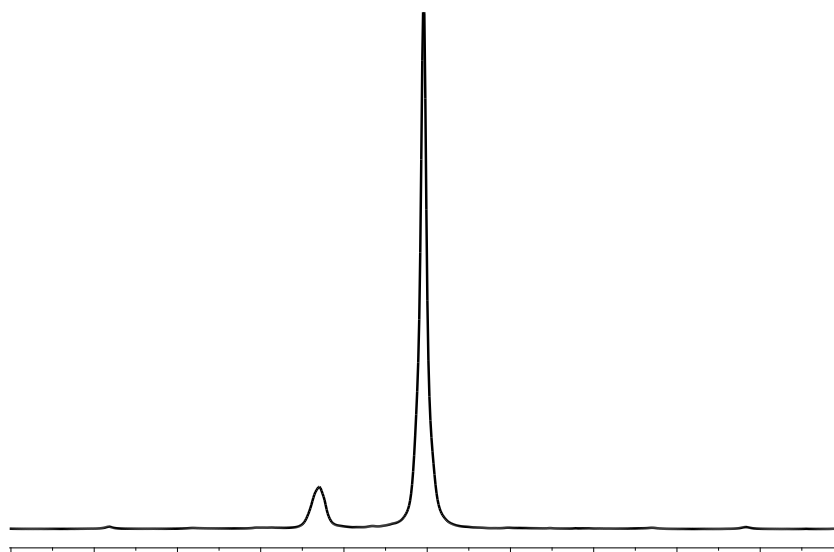


Figure S3: $^1\text{H}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **1**, Table 1 Entry 1.

4.2 Table 1, Entry 2

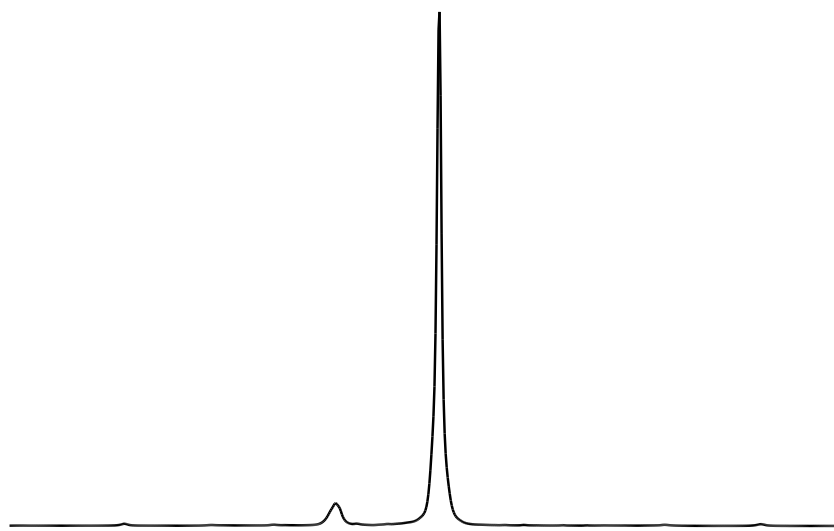


Figure S4: $^1\text{H}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **2**, Table 1 Entry 2.

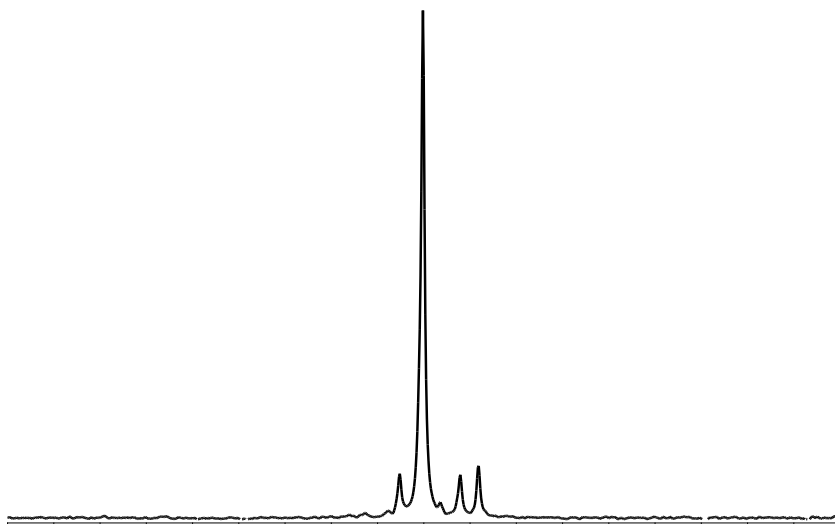


Figure S5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **2**, Table 1 Entry 2.

4.3 Table 1, Entry 3

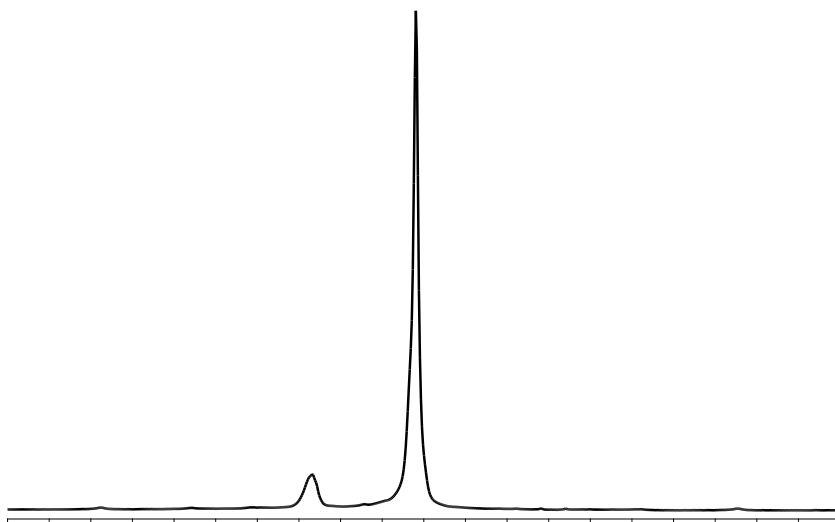


Figure S6: $^1\text{H}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **3**, Table 1 Entry 3.

4.4 Table 1, Entry 4

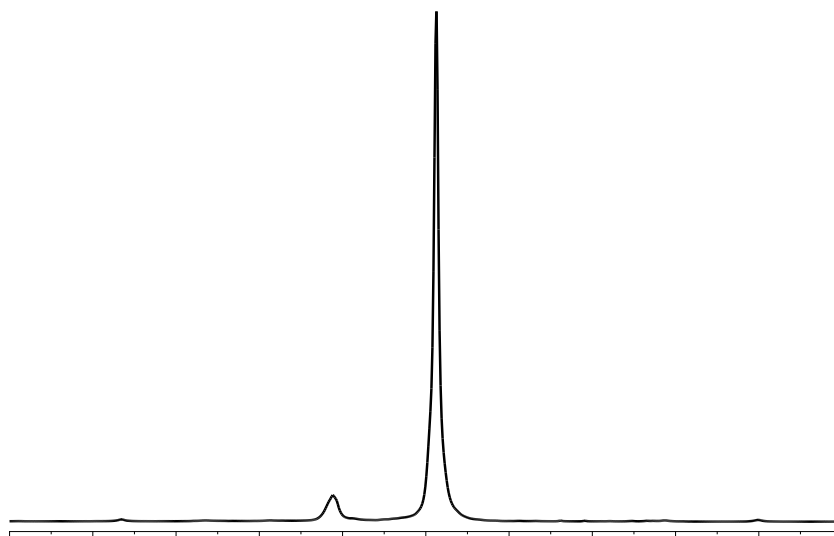


Figure S7: ¹H{¹H} NMR spectrum of polylactide synthesized using complex **4**, Table 1 Entry 4.

4.5 Table 2, Entry 5

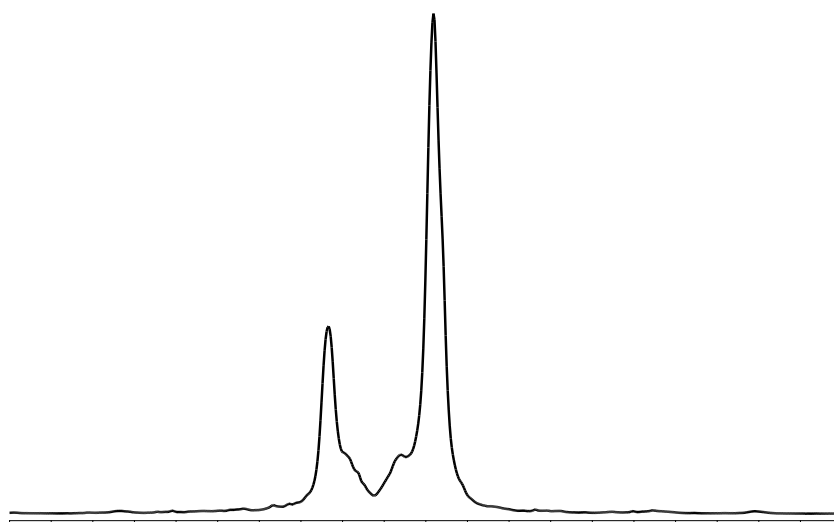


Figure S8: ¹H{¹H} NMR spectrum of polylactide synthesized using complex **5**, Table 1 Entry 5.

4.6 Table 1, Entry 6

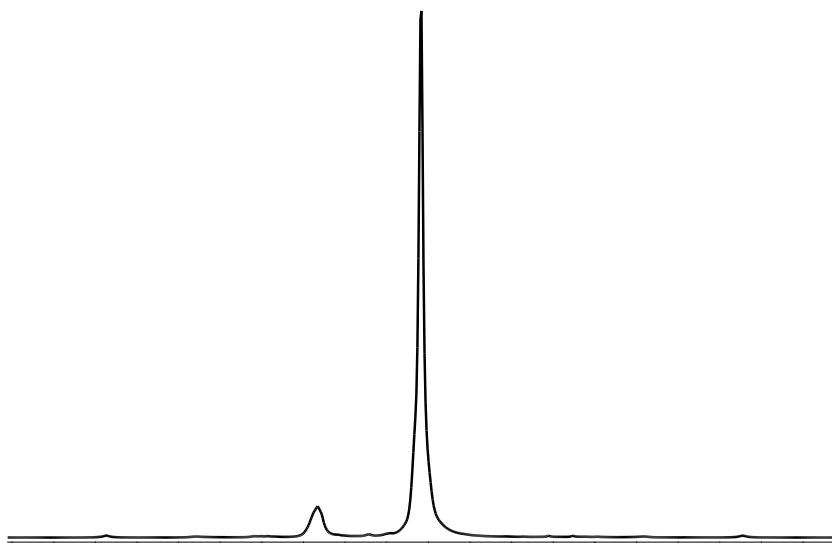


Figure S9: $^1\text{H}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **6**, Table 1 Entry 6.

4.7 Table 1, Entry 7

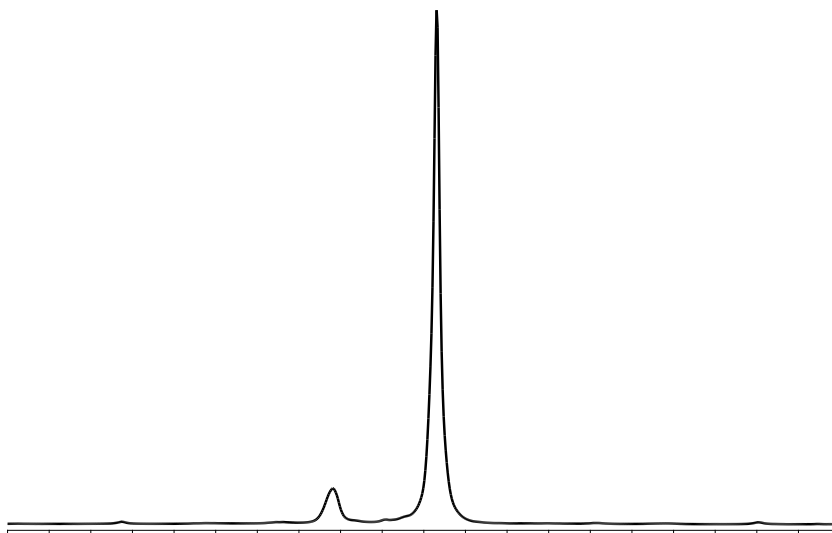


Figure S10: $^1\text{H}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **7**, Table 1 Entry 7.

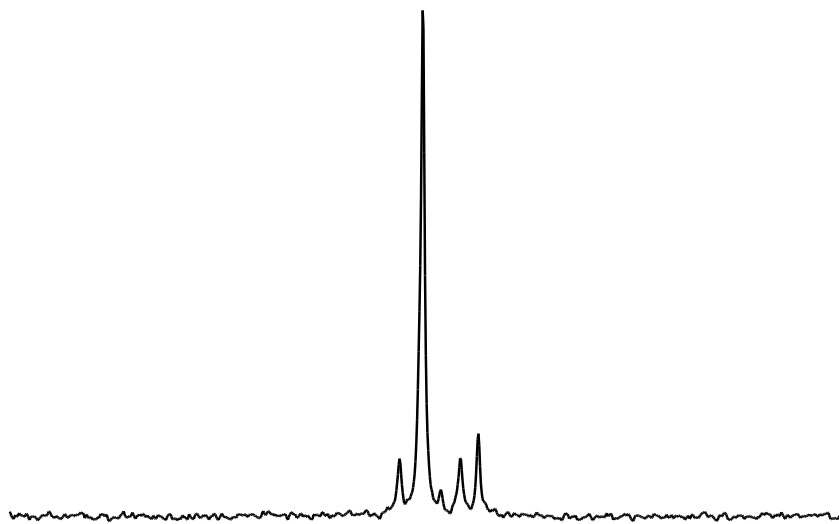


Figure S11: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **7**, Table 1 Entry 7.

4.8 NMR scale polymerization

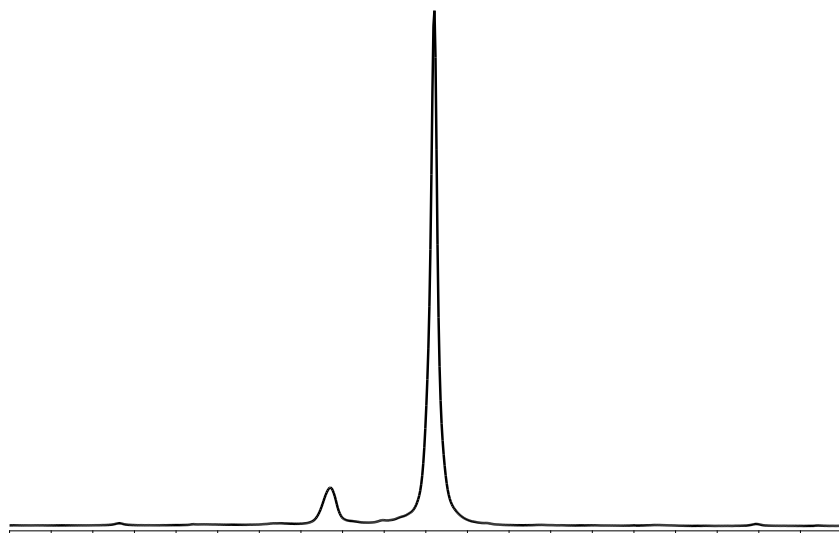


Figure S12: $^1\text{H}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **7**, [monomer]/[initiator] = 52, C_6D_6 , 25 °C, 30 min.

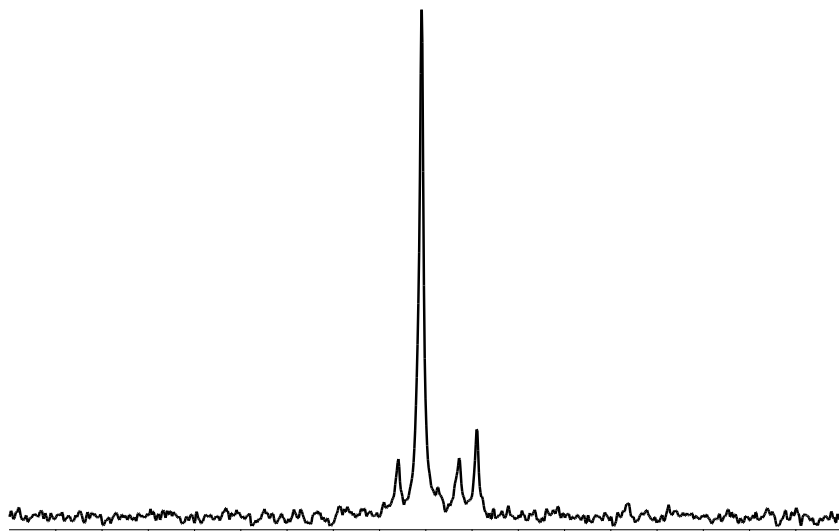


Figure S13: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **7**, [monomer]/[initiator] = 52, C_6D_6 , 25 °C, 30 min.

4.9 Table S1, Entry 1

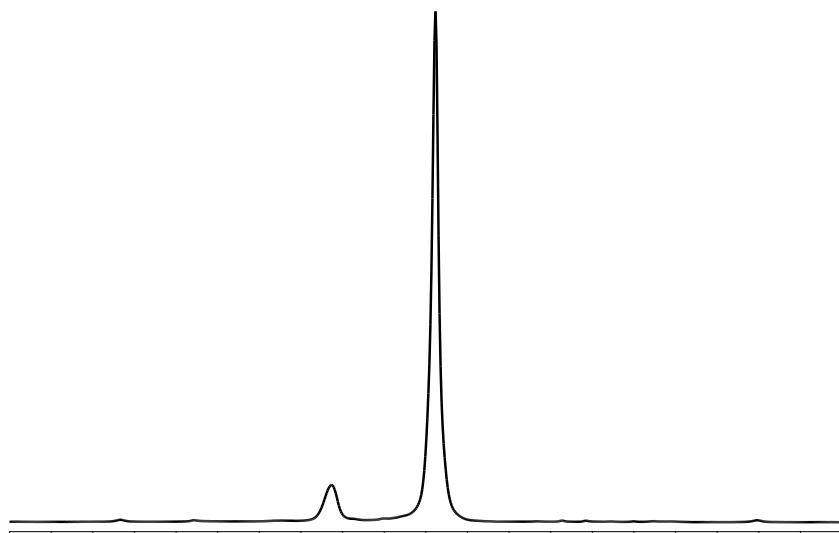


Figure S14: $^1\text{H}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **7**, Table S1, Entry 1.

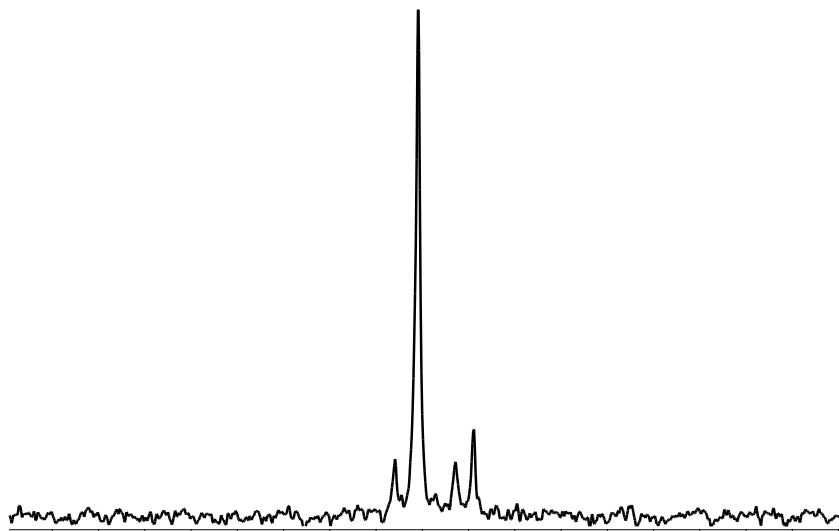


Figure S15: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **7**, Table S1 Entry 1.

4.10 Table S1, Entry 2

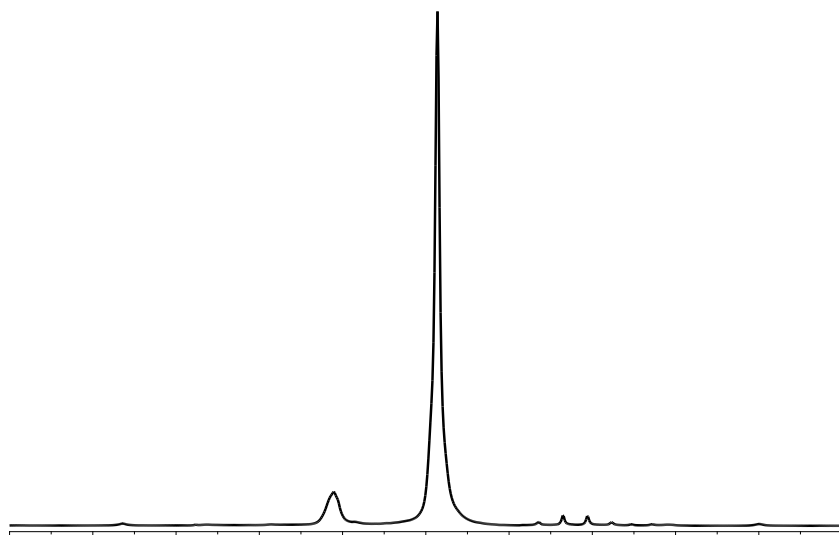


Figure S16: $^1\text{H}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **7**, Table S1, Entry 2.

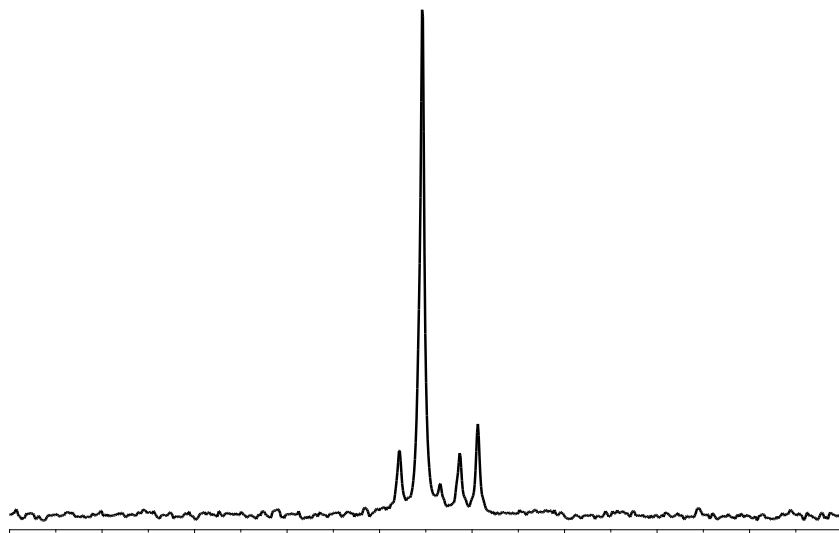


Figure S17: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **7**, Table S1, Entry 2.

4.11 Table S3, Entry 1

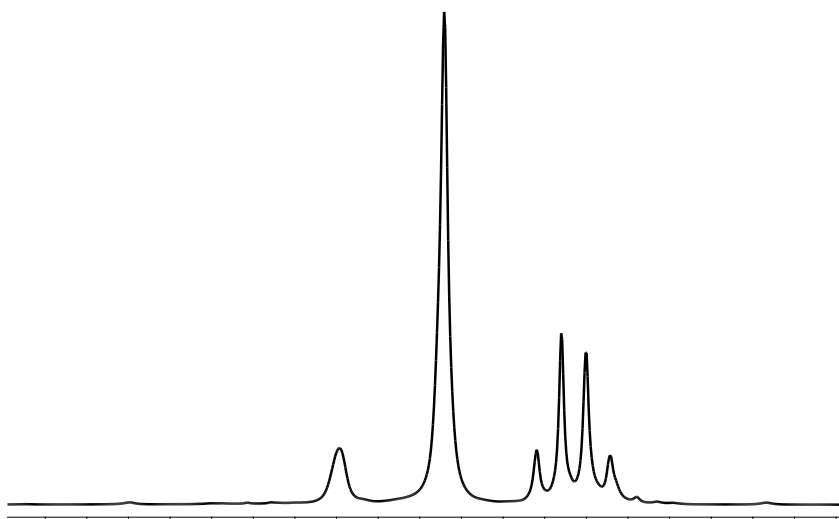


Figure S18: $^1\text{H}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **7**, Table S3, Entry 1.

4.12 Table S3, Entry 2

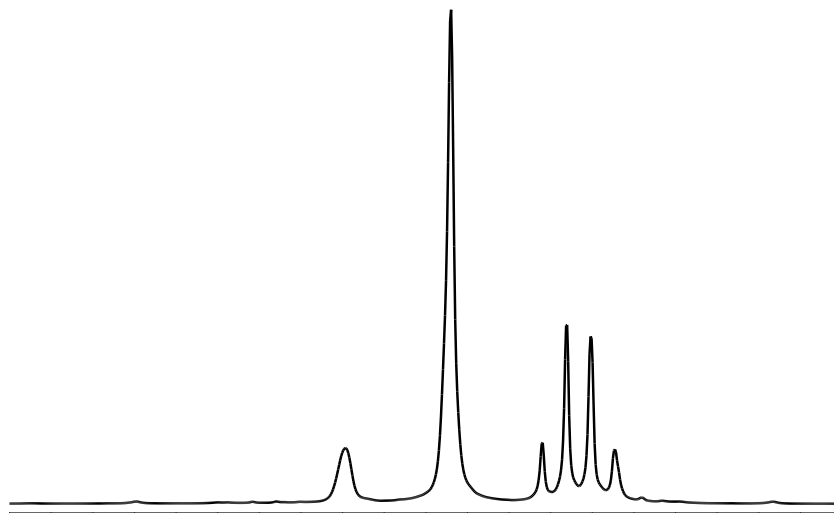


Figure S19: $^1\text{H}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **7**, Table S3, Entry 2.

4.13 Table S3, Entry 3

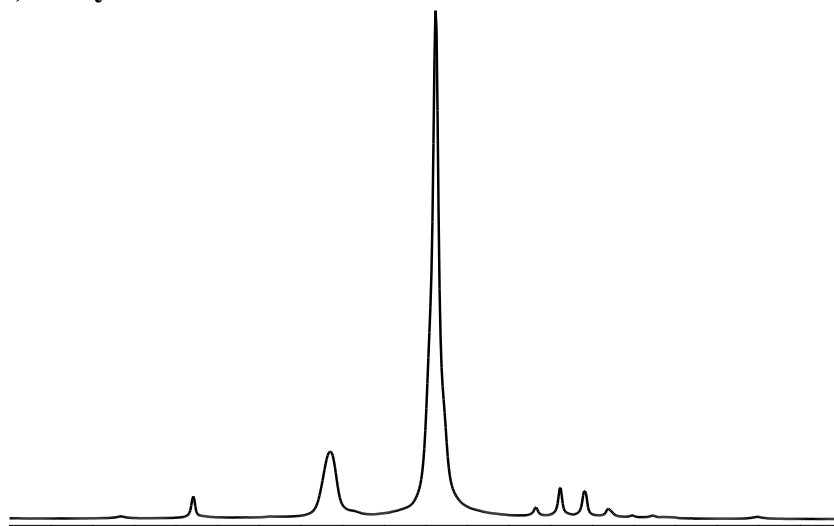


Figure S20: $^1\text{H}\{^1\text{H}\}$ NMR spectrum of polylactide synthesized using complex **7**, Table S3, Entry 3.

4.14 Study of the End Group

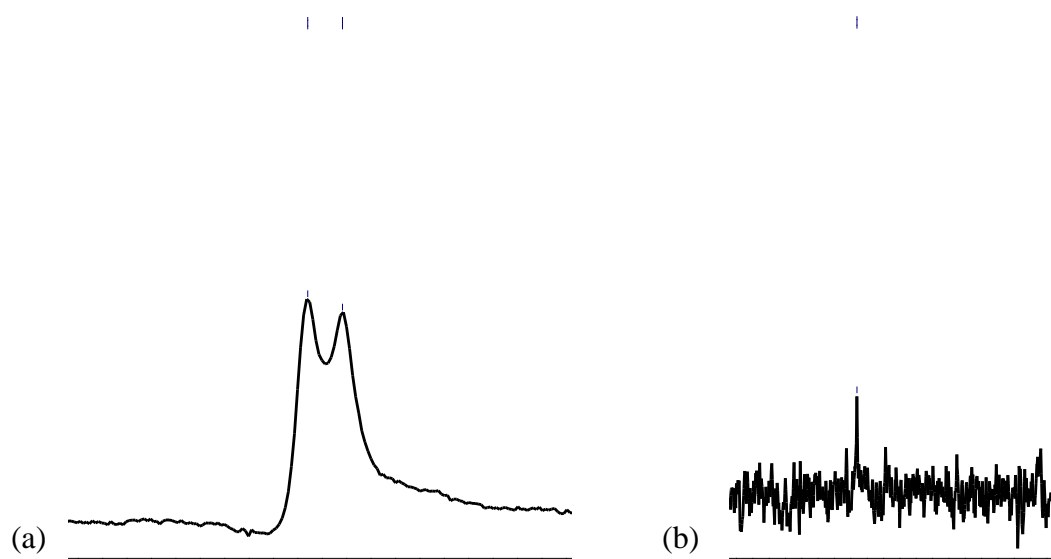


Figure S21: NMR spectra of the Polymerization of *meso*-lactide using complex **1**, 25 °C, 60 minutes, [mon]/[initiator] = 20: (a) ^1H and (b) $^{13}\text{C}\{^1\text{H}\}$

These resonances correspond to a $-\text{N}(\text{SiHMe}_3)$ group with the diagnostic doublet for the Me_3 proton

5. DSC Experiment

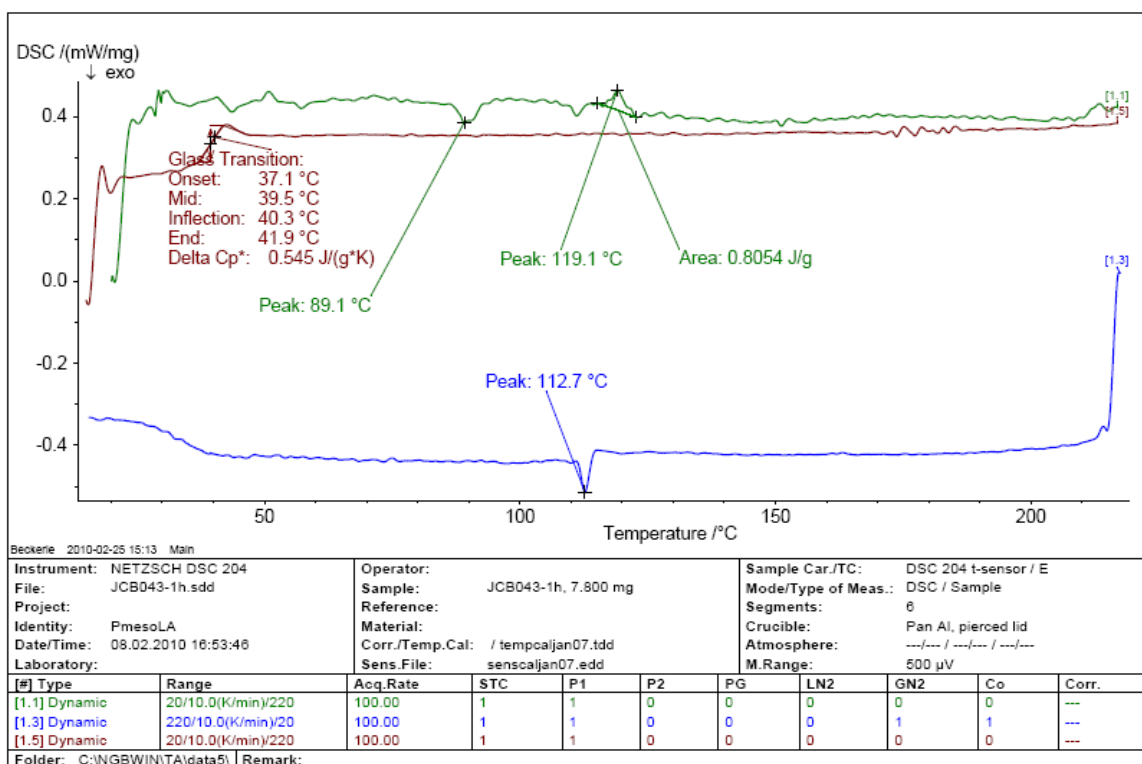


Figure S22: DSC diagram of the polylactide synthesized using complex **4**, Table 1, Entry 4.

6. References

- [S1] Anwander, R.; Runte, O.; Eppinger, J.; Gerstberger, G.; Herdtweck, E.; Spiegler, M. *J. Chem. Soc., Dalton Trans.* **1998**, 847.
- [S2] Eppinger, J.; Spiegler, M.; Hieringer, W.; Herrmann, W. A.; Anwander, R. *J. Am. Chem. Soc.* **2000**, *122*, 3080.
- [S3] Marcseková, K.; Loos, C.; Rominger, F.; Doye, S., *Synlett*, **2007**, *16*, 2564.
- [S4] Ma, H.; Spaniol, T. P.; Okuda, J. *Angew. Chem.* **2006**, *118*, 7982; *Angew. Chem. Int. Ed.* **2006**, *45*, 7818.
- [S5] Ma, H.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2008**, *47*, 3328.
- [S6] Peckermann, I.; Kapelski, A.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2009**, *48*, 5526.
- [S7] Chmura, A. J.; Davidson, M. G.; Frankis, C. J.; Jones, M. D.; Lunn, M. D. *Chem. Commun.* **2008**, 1293-1295.