

## Supplementary Information

### Divergent [{ONNN}Mg-Cl] complexes in the highly active and living lactide polymerization

Tomer Rosen,<sup>†</sup> Israel Goldberg,<sup>†</sup> Wanda Navarra<sup>‡</sup>, Vincenzo Venditto<sup>‡,\*</sup> and Moshe Kol<sup>†,\*</sup>

<sup>†</sup> The School of Chemistry, Tel Aviv University, Ramat Aviv, Tel Aviv 69987, Israel

<sup>‡</sup> Department of Chemistry and Biology A. Zambelli and INSTM Research Unit, University of Salerno, Via Giovanni Paolo II 132, I-84084 Fisciano, SA, Italy.

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## General Information

All reactions with air- and/or water sensitive compounds were carried out using standard Schlenk or glovebox techniques under dry N<sub>2</sub> atmosphere. Pentane was washed with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> prior to distillation from Na/benzophenone/tetraglyme. Toluene was refluxed over Na and distilled. Dichloromethane was refluxed over CaH<sub>2</sub> and distilled. Benzyl magnesium chloride solution (1M in ether), anhydrous benzyl alcohol and salicylaldehyde were purchased from Aldrich and used as received. Bis(2-pyridylmethyl)amine was purchased from TCI and used as received. Sodium triacetoxyborohydride was purchased from Strem and used as received. L-lactide and D-lactide were given as gift from Purac (Corbion), and were purified by crystallization from dry toluene and sublimation. 3-Adamantyl-5-methylsalicylaldehyde, 3,5-bis(dimethylbenzyl)salicylaldehyde and the ligand precursors Lig<sup>2,3</sup>H were synthesized following previously published procedures.<sup>S1</sup> Deuterated chloroform was purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 4A molecular sieves prior to use.

The NMR spectra were recorded on a Bruker Avance 500 spectrometer at 25 °C, unless otherwise stated. Chemical shifts ( $\delta$ ) are listed as parts per million and coupling constants ( $J$ ) in Hertz. <sup>1</sup>H NMR spectra are referenced using the residual solvent peak at  $\delta = 7.26$  for CDCl<sub>3</sub>. <sup>13</sup>C NMR spectra are referenced using the residual solvent peak at  $\delta = 77.16$  for CDCl<sub>3</sub>. The <sup>13</sup>C NMR spectra of PLA samples (10% CDCl<sub>3</sub> solution) were acquired using recycle delay of 10s. At least 2000 scans were averaged.

The molecular weights ( $M_n$  and  $M_w$ ) and the molecular mass distributions ( $M_w/M_n$ ) of the PLA samples were measured by gel permeation chromatography (GPC) at 30 °C, using THF as solvent, a flow rate of eluent of 1 mL/min, and narrow MW polystyrene standards as reference. The measurements were performed on a Jasco system equipped with an RI 1530 detector. A correction factor of 0.58 was employed for the molecular weight of PLA relative to polystyrene. THF-insoluble PLA samples were measured using chloroform as solvent at 30 °C with a flow rate of eluent of 0.8 mL/min.

High resolution MS was obtained on SYNAPT (Waters) spectrometer. Ionization methods: APPI (positive or negative) and ESI (positive or negative). Air-sensitive compounds were injected under N<sub>2</sub> stream.

Wide-angle X-ray diffraction (WAXD) measurements of single crystal were performed on an ApexDuo (Bruker-AXS) diffractometer system, using MoK $\alpha$ ( $\lambda = 0.7107 \text{ \AA}$ ) radiation. The analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to ca. 110 K.

WAXD patterns of powder samples were obtained by an automatic Bruker D8 Advance diffractometer, in reflection, by using the nickel filtered CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ).

Differential scanning calorimetry analysis was performed on a TA Q2000 (TA Instruments) according to the following program: Equilibrate at -40°C; Ramp 10.00 °C/min to 240.00 °C; Isothermal for 3 min; Ramp 10.00 °C/min to -40.00 °C; Ramp 10.00 °C/min to 240.00 °C. Melting transitions were determined both on the first and second heating runs, with a nitrogen purge at a flow rate of 40 mL s<sup>-1</sup>. The instrument was calibrated for temperature and enthalpy by a high purity indium (156.60 °C, 28.45 J g<sup>-1</sup>) standard. DSC analyses were carried out on films obtained by casting from 1 wt % solutions, at room temperature, from dichloromethane ( $\geq 99\%$ , Aldrich code 24233-2.5L-R). Thermogravimetric analysis (TGA) was carried out in N<sub>2</sub> flow (100 cm<sup>3</sup>/min STP) with a TGA Q500, TA Instruments, in the range 20-1000 °C at 10 °C min<sup>-1</sup> heating rate.

## Synthesis of Ligands

### *Synthesis of Lig<sup>1</sup>H*

This compound was synthesized by modification of a literature procedure.<sup>S2</sup> To a solution of bis(2-pyridylmethyl)amine (720 mg, 3.61 mmol) in dichloromethane (40 mL), sodium triacetoxyborohydride (990 mg, 4.67 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 1 h, after which salicylaldehyde (440 mg, 3.61 mmol) was added. After additional 4 h stirring at room temperature, the reaction was quenched by adding NaHCO<sub>3</sub> 10% solution (20 mL). The organic phase was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and the crude product was purified by passing through a plug of silica with ethyl acetate as eluent. A yellow oil was obtained. The overall yield was 82%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 11.09 (brs, 1H, OH), 8.57 (d, 2H, *J*=4.6 Hz, ArH), 7.62 (td, 2H, *J*=1.7Hz, *J*=7.7Hz, ArH), 7.34 (d, 2H, *J*=7.8Hz, ArH), 7.19-7.14 (m, 3H, ArH), 7.06 (dd, 1H, *J*=1.3Hz, *J*=7.6Hz, ArH), 6.91 (dd, 1H, *J*=0.7Hz, *J*=8.0Hz, ArH), 6.77 (td, 1H, *J*=1.0Hz, *J*=7.4Hz, ArH), 3.88 (s, 4H, CH<sub>2</sub>), 3.80 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 158.43 (C), 157.73 (C), 149.07 (CH), 136.91 (CH), 130.30 (CH), 129.20 (CH), 123.37 (CH), 122.95 (C), 122.36 (CH), 119.00 (CH), 116.68 (CH), 59.25 (CH<sub>2</sub>), 57.10 (CH<sub>2</sub>). HRMS (ESI): Calc for C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>O: 305.1528, found: 328.1428 (M-Na<sup>+</sup>).

### *Synthesis of Lig<sup>4</sup>H*

This compound was synthesized according to the procedure described above employing 3-adamantyl-5-methylsalicylaldehyde. A yellow solid was obtained in an overall yield of 90%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 10.45 (brs, 1H, OH), 8.56 (d, 2H, *J*=4.6Hz), 7.63 (td, 2H, *J*=1.7Hz, *J*=7.7Hz, ArH), 7.33 (d, 2H, *J*=7.8Hz, ArH), 7.15 (dd, 2H, *J*=4.8Hz, *J*=7.6Hz, ArH), 6.94 (d, 1H, *J*=1.6Hz, ArH), 6.71 (d, 1H, *J*=1.4Hz, ArH), 3.85 (s, 4H, CH<sub>2</sub>), 3.76 (s, 2H, CH<sub>2</sub>), 2.23 (s, 3H, CH<sub>3</sub>), 2.20 (brs, 6H, Ad), 2.08 (brs, 6H, Ad), 1.83 (d, 3H, *J*=12.0Hz, Ad), 1.78 (d, 3H, *J*=12.0Hz, Ad). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 158.23 (C), 154.40 (C), 149.14 (CH), 136.84 (C), 136.76 (CH), 128.45 (CH), 127.21 (C), 126.93 (CH), 123.76 (CH), 122.83 (C), 122.33 (CH), 59.45 (CH<sub>2</sub>),

58.03 (CH<sub>2</sub>), 40.68 (C), 40.54 (CH<sub>2</sub>), 37.41 (CH<sub>2</sub>), 36.98 (CH), 29.40 (CH<sub>2</sub>), 20.92 (CH<sub>3</sub>). HRMS (ESI): Calc for C<sub>30</sub>H<sub>35</sub>N<sub>3</sub>O: 453.2780, found: 454.2854 (MH<sup>+</sup>).

### *Synthesis of Lig<sup>5</sup>H*

This compound was synthesized according to the procedure described above employing 3,5-bis(dimethylbenzyl)salicylaldehyde. A yellow solid was obtained in an overall yield of 94%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 10.34 (brs, 1H, OH), 8.45 (d, 2H, *J*=4.5Hz, ArH), 7.47 (td, 2H, *J*=1.8Hz, *J*=7.7Hz, ArH), 7.26-7.21 (m, 6H, ArH), 7.18-7.14 (m, 3H, ArH), 7.14-7.08 (m, 3H, ArH), 6.92 (d, 2H, *J*=7.8Hz, ArH), 6.76 (d, 1H, *J*=2.3Hz, ArH), 3.68 (s, 2H, CH<sub>2</sub>), 3.67 (s, 2H, CH<sub>2</sub>), 1.68 (s, 6H, CH<sub>3</sub>), 1.67 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 157.88 (C), 153.54 (C), 151.94 (C), 151.54 (C), 148.95 (CH), 140.02 (C), 136.81 (CH), 135.39 (C), 128.01 (CH), 127.74 (CH), 126.90 (CH), 126.67 (CH), 125.93 (CH), 125.53 (CH), 125.17 (CH), 124.71 (CH), 124.02 (CH), 122.25 (CH), 121.83 (C), 59.15 (CH<sub>2</sub>), 58.24 (CH<sub>2</sub>), 42.60 (C), 42.25 (C), 31.25 (CH<sub>3</sub>), 29.63 (CH<sub>3</sub>). HRMS (ESI): Calc for C<sub>37</sub>H<sub>39</sub>N<sub>3</sub>O: 541.3093, found: 542.3177 (MH<sup>+</sup>).

## Synthesis of Chloro-Magnesium Complexes

### *Synthesis of $[(\mu\text{-Lig}^1)\text{Mg-Cl}]_2$*

To a stirred solution of Lig<sup>1</sup>H (80 mg, 0.26 mmol) in toluene (2 mL), was added a solution of BnMgCl (0.26 mL, 1M diethyl ether solution) drop-wise. The resulting mixture was stirred at room temperature for 30 min until a precipitate appeared. The solvent was removed under vacuum and the residue was washed with pentane to give a yellow solid in 61% yield. Crystals suitable for X-ray diffraction were grown from dichloromethane solution at -30 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.95 (d, 2H,  $J=14.3\text{Hz}$ , ArH), 7.73 (t, 1H,  $J=7.2\text{Hz}$ , ArH), 7.35 (d, 1H,  $J=7.3\text{Hz}$ , ArH), 7.23 (t, 1H,  $J=7.0\text{Hz}$ , ArH), 7.04 (t, 1H,  $J=5.8\text{Hz}$ , ArH), 6.77 (t, 1H,  $J=5.8\text{Hz}$ , ArH), 6.62 (t, 2H,  $J=8.3\text{Hz}$ , ArH), 6.42 (d, 1H,  $J=12.3\text{Hz}$ , CH<sub>2</sub>), 6.19 (t, 1H,  $J=7.0\text{Hz}$ , ArH), 6.05 (t, 1H,  $J=7.0\text{Hz}$ , ArH), 5.23 (d, 1H,  $J=15.0\text{Hz}$ , CH<sub>2</sub>), 4.85 (d, 1H,  $J=7.6\text{Hz}$ , ArH), 4.10 (d, 1H,  $J=15.1\text{Hz}$ , CH<sub>2</sub>), 3.82 (d, 1H,  $J=15.0\text{Hz}$ , CH<sub>2</sub>), 3.49 (d, 1H,  $J=15.1\text{Hz}$ , CH<sub>2</sub>), 3.38 (d, 1H,  $J=12.2\text{Hz}$ , CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  163.61 (C), 156.45 (C), 156.33 (C), 151.69 (CH), 150.92 (CH), 138.40(CH), 137.14 (CH), 129.97 (CH), 128.25 (CH), 127.65 (C), 122.99 (CH), 122.72 (CH), 122.17 (CH), 120.68 (CH), 119.08 (CH), 115.40 (CH), 64.50 (CH<sub>2</sub>), 61.57 (CH<sub>2</sub>), 61.49 (CH<sub>2</sub>). HRMS (APPI): Calc for C<sub>38</sub>H<sub>36</sub>Cl<sub>2</sub>Mg<sub>2</sub>N<sub>6</sub>O<sub>2</sub>: 726.1978, found: 691.2275 ([M-Cl]<sup>+</sup>).

*Crystal Data for Complex  $[(\mu\text{-Lig}^1)\text{Mg-Cl}]_2 \cdot 2\text{CH}_2\text{Cl}_2$ .* C<sub>19</sub>H<sub>18</sub>ClN<sub>3</sub>OMg, 2CH<sub>2</sub>Cl<sub>2</sub>; M = 533.97; monoclinic; space group C2/c; a = 24.0022(18) Å, b = 8.6136(6) Å, c = 25.556(3) Å,  $\beta=116.047(3)^\circ$ , V = 4746.9(7) Å<sup>3</sup>; T = 110(2) K; Z = 8; Dc = 1.494 g cm<sup>-3</sup>;  $\mu$  (MoK $\alpha$ ) = 0.658 mm<sup>-1</sup>; R1 = 0.0516 and wR2 = 0.0972 for 4733 reflections with I > 2 $\sigma$ (I); R1 = 0.0391 and wR2 = 0.0912 for all 3904 unique reflections. CCDC No. 1537631.

### Synthesis of $[(\mu\text{-Lig}^2)\text{Mg-Cl}]_2$

To a stirred solution of Lig<sup>2</sup>H (76 mg, 0.23 mmol) in toluene (2 mL), was added a solution of BnMgCl (0.23 mL, 1M diethyl ether solution) drop-wise. The resulting mixture was stirred at room temperature for 1 h until a precipitate appeared. The solvent was removed under vacuum and the residue was washed with pentane to give a yellow solid in 74% yield.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  9.25 (d, 1H,  $J=5.7$ Hz, ArH), 9.12 (d, 1H,  $J=5.7$ Hz, ArH), 7.69 (td, 1H,  $J=1.7$ Hz,  $J=7.6$ Hz, ArH), 7.28 (d, 1H,  $J=7.7$ Hz, ArH), 7.16 (td, 1H,  $J=1.7$ Hz,  $J=7.6$ Hz, ArH), 7.07 (t, 1H,  $J=6.4$ Hz, ArH), 6.76 (t, 1H,  $J=6.4$ Hz, ArH), 6.56 (d, 1H,  $J=11.9$ Hz, CH<sub>2</sub>), 6.54 (d, 1H,  $J=2.0$ Hz, ArH), 6.37 (d, 1H,  $J=7.7$ Hz, ArH), 5.96 (d, 1H,  $J=1.6$ Hz, ArH), 4.92 (d, 1H,  $J=14.9$ Hz, CH<sub>2</sub>), 3.95 (d, 1H,  $J=14.9$ Hz, CH<sub>2</sub>), 3.61 (d, 1H,  $J=14.9$ Hz, CH<sub>2</sub>), 3.40 (d, 1H,  $J=15.1$ Hz, CH<sub>2</sub>), 3.37 (d, 1H,  $J=13.9$ Hz, CH<sub>2</sub>), 1.94 (s, 3H, CH<sub>3</sub>), 0.95 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  158.63 (C), 156.75 (C), 155.91 (C), 152.25 (CH), 149.70 (CH), 138.49 (CH), 136.62 (CH), 130.97 (CH), 129.13 (CH), 126.85 (C), 126.79 (C), 124.08 (C), 123.41 (CH), 122.75 (CH), 121.65 (CH), 120.06 (CH), 65.24 (CH<sub>2</sub>), 62.29 (CH<sub>2</sub>), 61.47 (CH<sub>2</sub>), 20.33 (CH<sub>3</sub>), 14.21 (CH<sub>3</sub>). HRMS (APPI): Calc for C<sub>42</sub>H<sub>44</sub>Cl<sub>2</sub>Mg<sub>2</sub>N<sub>6</sub>O<sub>2</sub>: 782.2604, found: 747.2916 ([M-Cl]<sup>+</sup>).

*Crystal Data for Complex  $[(\mu\text{-Lig}^2)\text{MgCl}]_2 \cdot 5\text{CH}_2\text{Cl}_2$ .* C<sub>42</sub>H<sub>44</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>2</sub>Mg<sub>2</sub>, 5CH<sub>2</sub>Cl<sub>2</sub>; M = 1208.98; monoclinic; space group C2/c; a = 27.2980(18) Å, b = 14.9001(12) Å, c = 16.8775(10) Å,  $\beta=124.630(2)^\circ$ , V = 5648.6(7) Å<sup>3</sup>; T = 110(2) K; Z = 4; Dc = 1.422 g cm<sup>-3</sup>;  $\mu$  (Mo K $\alpha$ ) = 0.653 mm<sup>-1</sup>; R1 = 0.0702 and wR2 = 0.0567 for 5026 reflections with I > 2 $\sigma$ (I); R1 = 0.1604 and wR2 = 0.1488 for all 4116 unique reflections. CCDC No. 1537632.

### *Synthesis of Lig<sup>3</sup>Mg-Cl*

To a stirred solution of Lig<sup>3</sup>H (92 mg, 0.22 mmol) in toluene (2 mL), was added a solution of BnMgCl (0.22 mL, 1M diethyl ether solution) drop-wise. The resulting mixture was stirred at room temperature for 1 h until a precipitate appeared. The solvent was removed under vacuum and the residue was washed with pentane to give a yellow solid in 90% yield.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 9.35 (d, 2H, *J*=5.1Hz, ArH), 7.84 (td, 2H, *J*=1.4Hz, *J*=7.5Hz, ArH), 7.41 (t, 2H, *J*=6.5Hz, ArH), 7.29 (d, 2H, *J*=7.7Hz, ArH), 7.17 (d, 1H, *J*=2.5Hz, ArH), 6.80 (d, 1H, *J*=2.5Hz, ArH), 4.09 (d, 2H, *J*=15.7Hz, CH<sub>2</sub>), 3.82 (d, 2H, *J*=15.7Hz, CH<sub>2</sub>), 3.75 (brs, 2H, CH<sub>2</sub>), 1.43 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.24 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 163.35 (C), 157.00 (C), 151.75 (CH), 139.99 (CH), 138.58 (C), 134.07 (C), 129.19 (CH), 128.38 (CH), 125.45 (CH), 125.33 (CH), 124.30 (CH), 124.16 (CH), 123.18 (CH), 120.99 (C), 60.92 (CH<sub>2</sub>), 58.45 (CH<sub>2</sub>), 35.36 (C), 33.95 (C), 32.06 (CH<sub>3</sub>), 29.78 (CH<sub>3</sub>). HRMS (APPI): Calc for C<sub>27</sub>H<sub>34</sub>N<sub>3</sub>OCIMg: 475.2241, found: 476.2302 (MH<sup>+</sup>).

### *Synthesis of Lig<sup>4</sup>Mg-Cl*

To a stirred solution of Lig<sup>3</sup>H (104 mg, 0.23 mmol) in toluene (2 mL), was added a solution of BnMgCl (0.23 mL, 1M diethyl ether solution) drop-wise. The resulting mixture was stirred at room temperature for 1 h until a precipitate appeared. The solvent was removed under vacuum and the residue was washed with pentane to give a yellow solid in 91% yield.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 9.38 (d, 2H, *J*=4.9Hz, ArH), 7.84 (td, 2H, *J*=1.7Hz, *J*=7.7Hz, ArH), 7.42 (t, 2H, *J*=6.5Hz, ArH), 7.28 (d, 2H, *J*=7.8Hz, ArH), 6.88 (d, 1H, *J*=2.1Hz, ArH), 6.64 (d, 1H, *J*=2.0Hz, ArH), 4.07 (d, 2H, *J*=15.8Hz, CH<sub>2</sub>), 3.79 (d, 2H, *J*=15.7Hz, CH<sub>2</sub>), 3.73 (brs, 1H, CH<sub>2</sub>), 2.21 (d, 6H, *J*=2.0Hz, Ad), 2.18 (s, 3H, CH<sub>3</sub>), 2.04 (brs, 3H, Ad), 1.87 (d, 3H, *J*=11.3Hz, Ad), 1.72 (d, 3H, *J*=11.7Hz, Ad). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 163.43 (C), 156.99 (C), 151.85 (CH), 140.03 (CH), 139.74 (C), 129.19 (CH), 129.11 (CH), 128.38 (CH), 127.80 (CH), 125.45 (CH), 124.20 (CH), 123.16 (CH), 122.13 (C), 120.63 (C), 60.35 (CH<sub>2</sub>), 58.29 (CH<sub>2</sub>), 40.21 (CH<sub>2</sub>), 37.61



(CH<sub>2</sub>), 37.21 (C), 29.59 (CH<sub>3</sub>), 20.89 (CH). HRMS (APPI): Calc for C<sub>30</sub>H<sub>34</sub>N<sub>3</sub>OCIMg: 511.2241, found: 512.2300 (MH<sup>+</sup>).

### *Synthesis of Lig<sup>5</sup>Mg-Cl*

To a stirred solution of Lig<sup>5</sup>H (110 mg, 0.20 mmol) in toluene (2 mL), was added a solution of BnMgCl (0.20 mL, 1M diethyl ether solution) drop-wise. The resulting mixture was stirred at room temperature for 1 h until a precipitate appeared. The solvent was removed under vacuum and the residue was washed with pentane to give a yellow solid in 88% yield.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 9.11 (d, 2H, *J*=4.5Hz, ArH), 7.79 (td, 2H, *J*=1.7Hz, *J*=7.7Hz, ArH), 7.36 (t, 2H, *J*=6.2Hz, ArH), 7.25-7.18 (m, 7H, ArH), 7.13-7.11 (m, 3H, ArH), 6.77 (t, 2H, *J*=7.3Hz, ArH), 6.63 (d, 1H, *J*=2.5Hz, ArH), 6.58 (t, 1H, *J*=7.2Hz, ArH), 3.75 (d, 2H, *J*=15.5Hz, CH<sub>2</sub>), 3.58 (d, 4H, *J*=15.5Hz, CH<sub>2</sub>), 1.69 (brs, 6H, CH<sub>3</sub>), 1.65 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 162.23 (C), 156.68 (C), 152.91 (C), 152.76 (C), 151.96 (CH), 139.73 (CH), 138.77 (C), 133.24 (C), 127.74 (CH), 127.22 (CH), 126.99 (CH), 126.74 (CH), 126.08 (CH), 126.04 (CH), 125.13 (CH), 123.87 (CH), 123.83 (CH), 122.88 (CH), 121.07 (C), 60.00 (CH<sub>2</sub>), 42.37 (C), 42.30 (C), 31.38 (CH<sub>3</sub>). HRMS (APPI): Calc for C<sub>37</sub>H<sub>38</sub>N<sub>3</sub>OCIMg: 599.2554, found: 600.2634 (MH<sup>+</sup>).

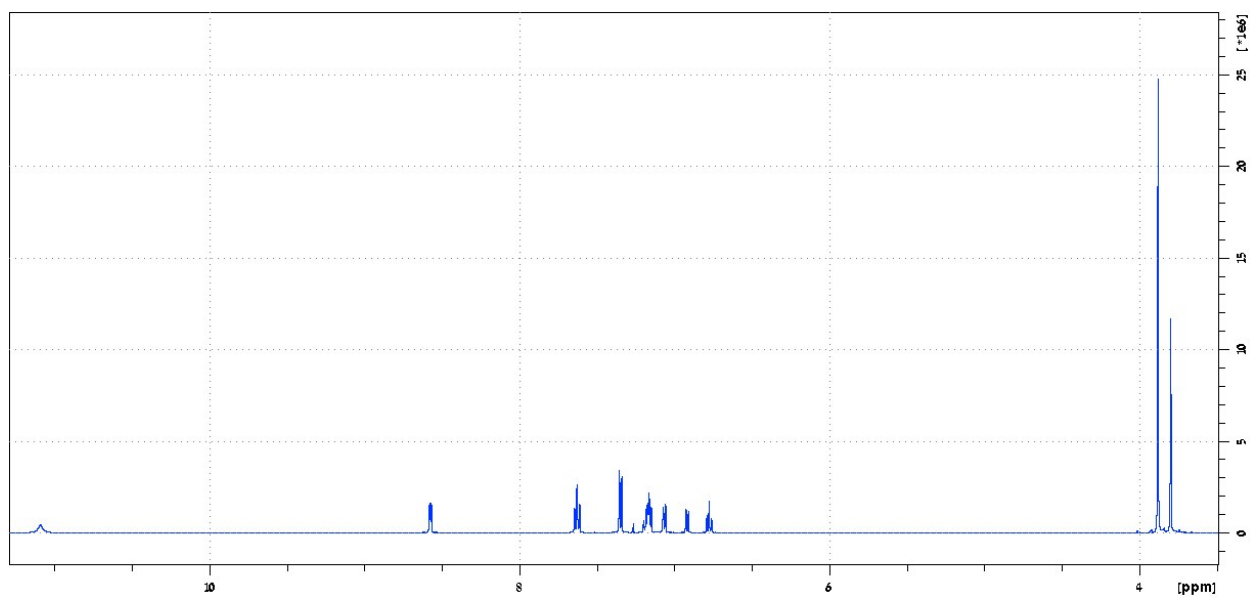
### **General Homo-Polymerization Procedure**

To a solution of the catalyst (0.01 mmol) in dichloromethane (5 mL), benzyl alcohol (either none or 0.01-0.04 mmol) was added, and the reaction mixture was stirred at room temperature for 2 min. Then, L-lactide (432 mg, 3 mmol) was added, and the reaction was stirred at room temperature. After the desired time, the reaction was terminated by exposing to air and the volatiles were removed under vacuum.

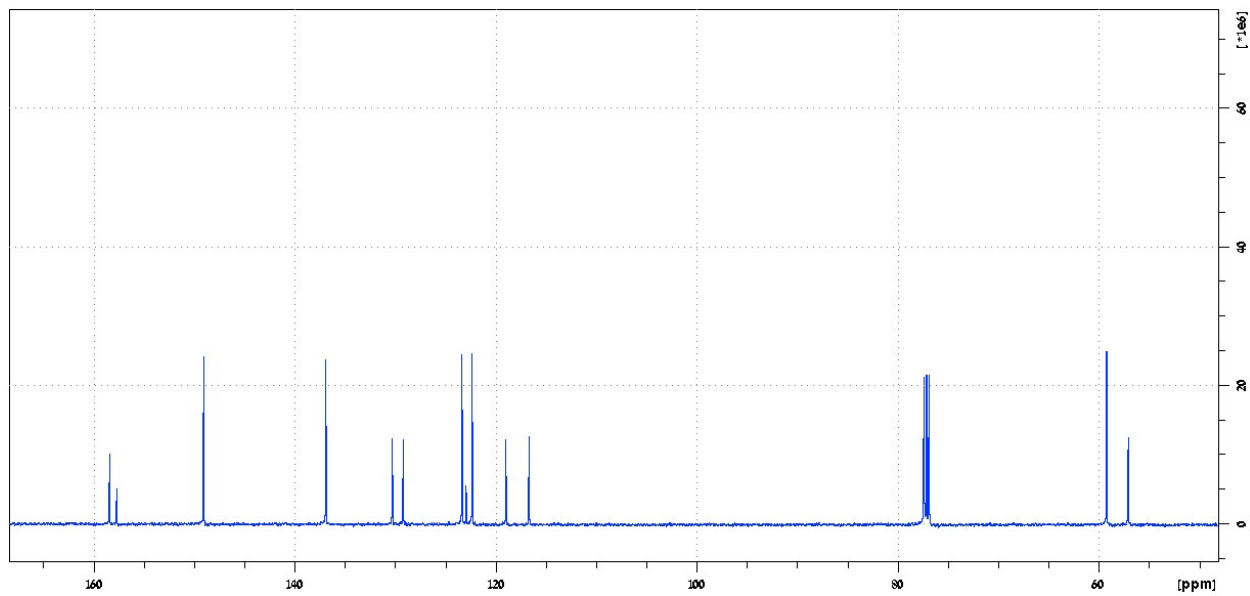
### **General Block-Copolymerization Procedure**

To a solution of the catalyst (0.01 mmol) in dichloromethane (5 mL), benzyl alcohol was added and the reaction mixture was stirred at room temperature for 2 min. Then, either D- or L-Lactide were sequentially added, maintaining the necessary delay (5-10 min) between each addition. The reaction was terminated by exposing to air and the volatiles were removed under vacuum. The tacticity of the PLA samples was determined by the homonuclear-decoupled  $^1\text{H}$  NMR spectrometry ( $\text{CDCl}_3$ , 500 MHz) and by  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) as previously described.<sup>S3</sup>

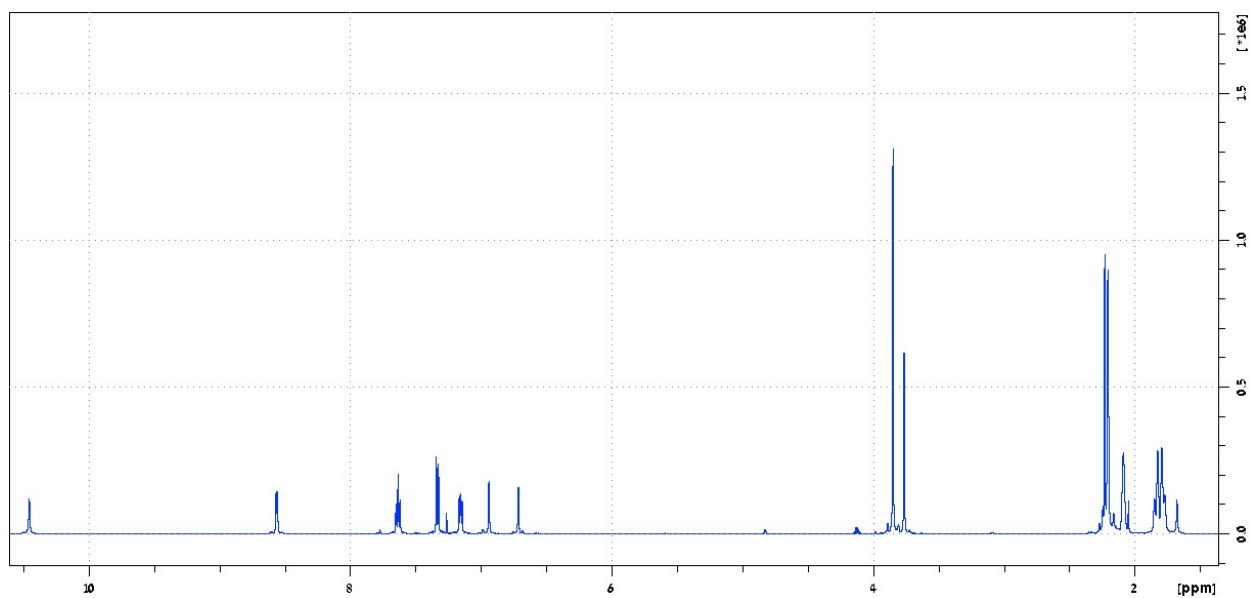
## NMR Spectra of the Ligands Precursors



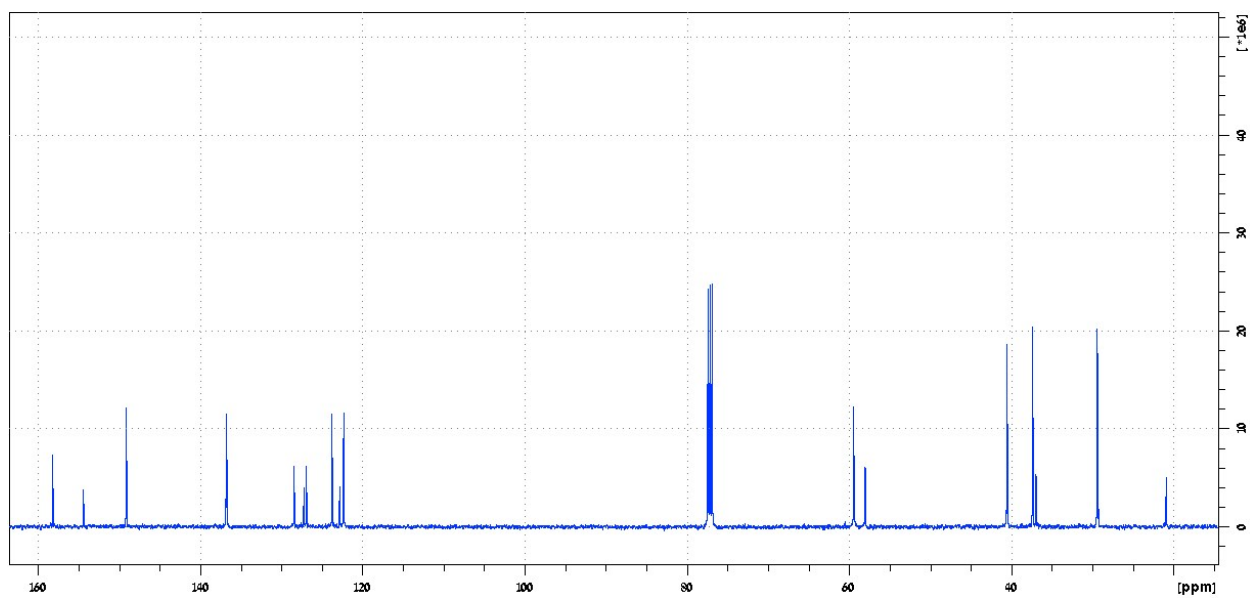
**Figure S1.** <sup>1</sup>H-NMR of Lig<sup>1</sup>H (CDCl<sub>3</sub>, 500MHz).



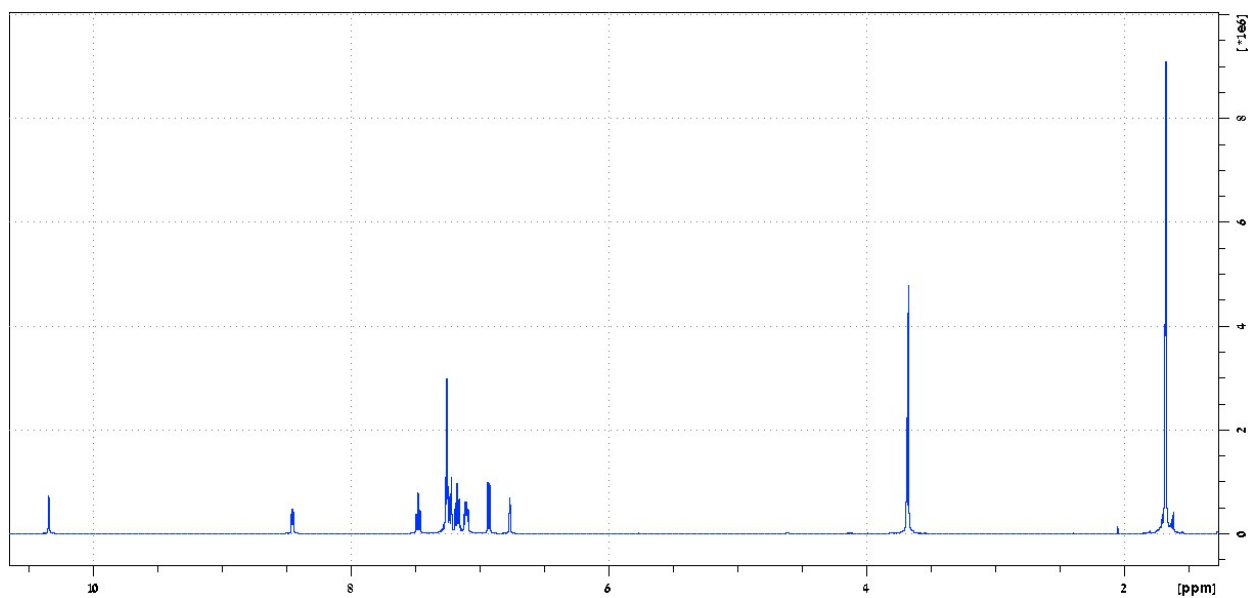
**Figure S2.** <sup>13</sup>C-NMR of Lig<sup>1</sup>H (CDCl<sub>3</sub>, 125MHz).



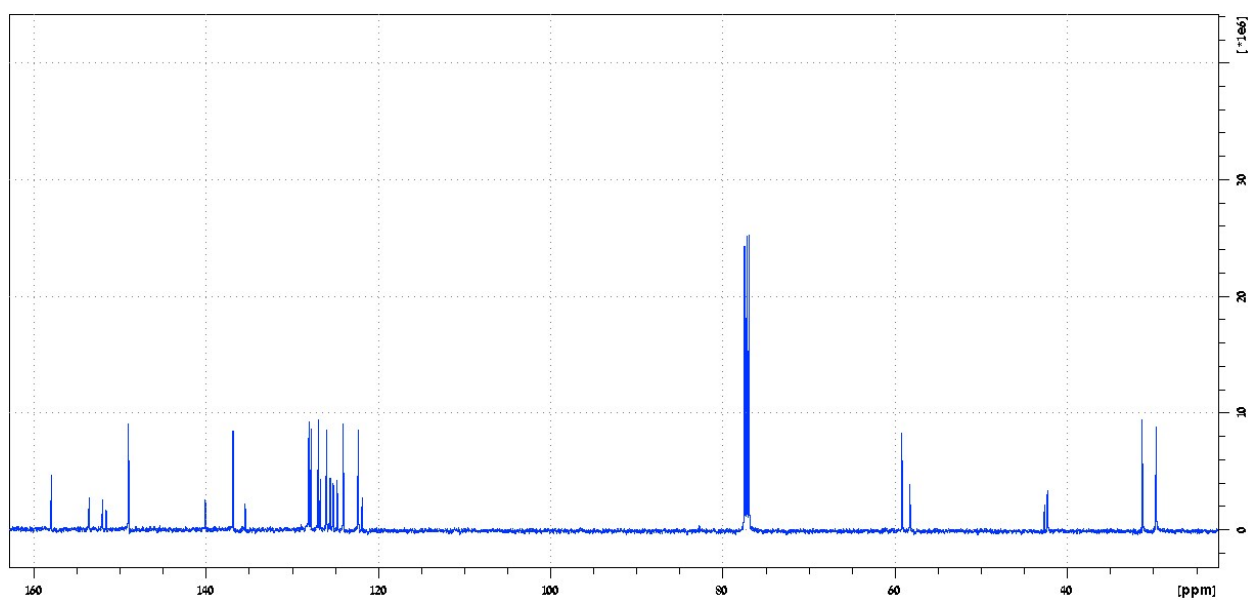
**Figure S3.**  $^1\text{H}$ -NMR of  $\text{Lig}^4\text{H}$  ( $\text{CDCl}_3$ , 500MHz).



**Figure S4.**  $^{13}\text{C}$ -NMR of  $\text{Lig}^4\text{H}$  ( $\text{CDCl}_3$ , 500MHz).

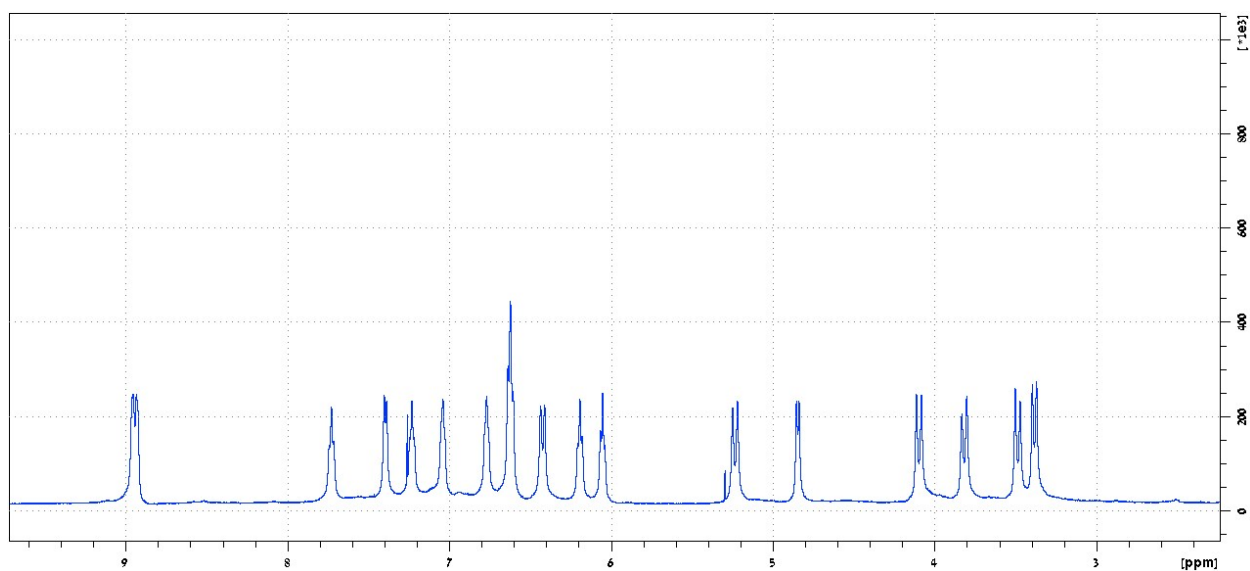


**Figure S5.**  $^1\text{H}$ -NMR of Lig $^5\text{H}$  ( $\text{CDCl}_3$ , 500MHz).

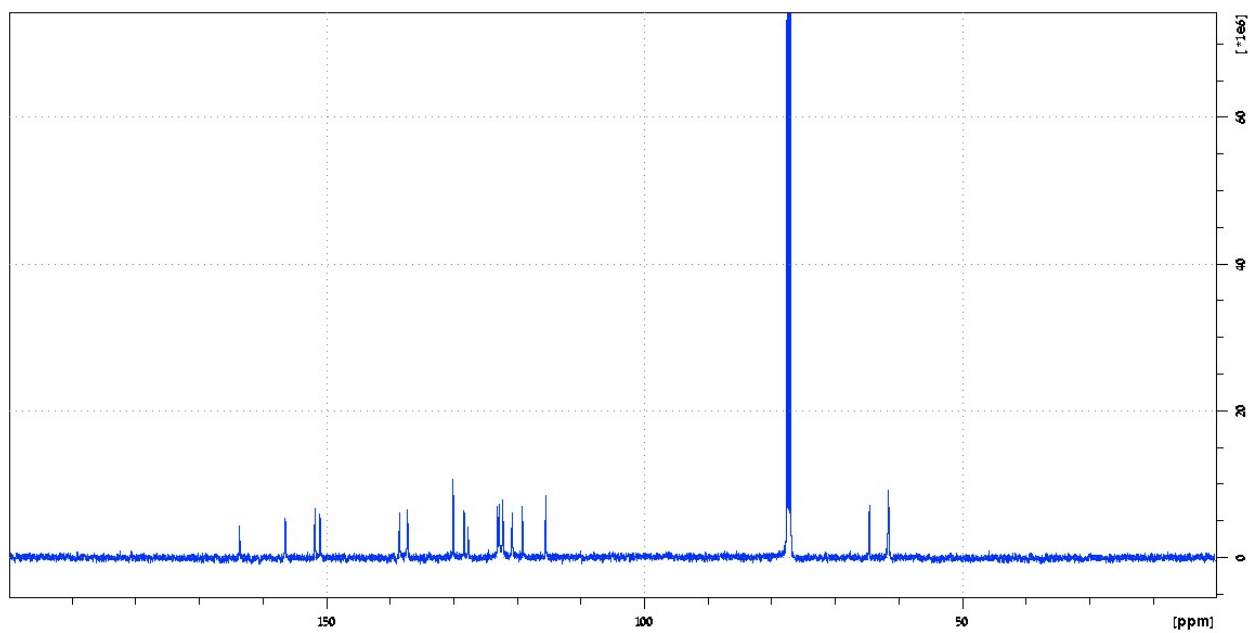


**Figure S6.**  $^{13}\text{C}$ -NMR of Lig $^5\text{H}$  ( $\text{CDCl}_3$ , 500MHz).

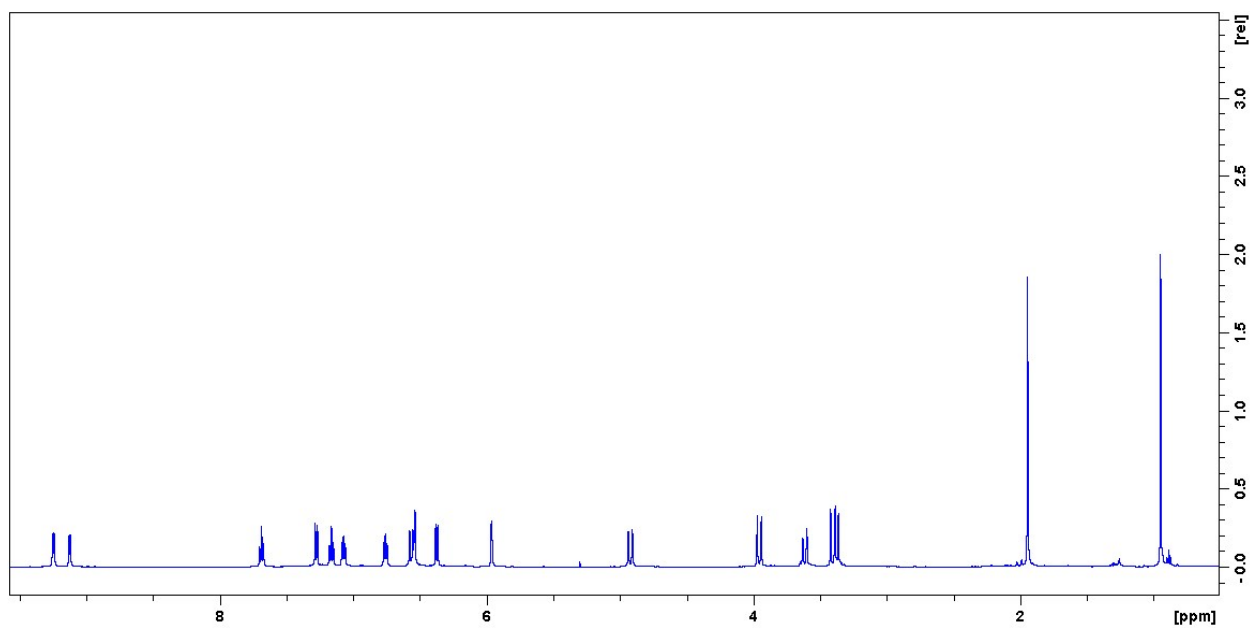
## NMR Spectra of the Magnesium Complexes



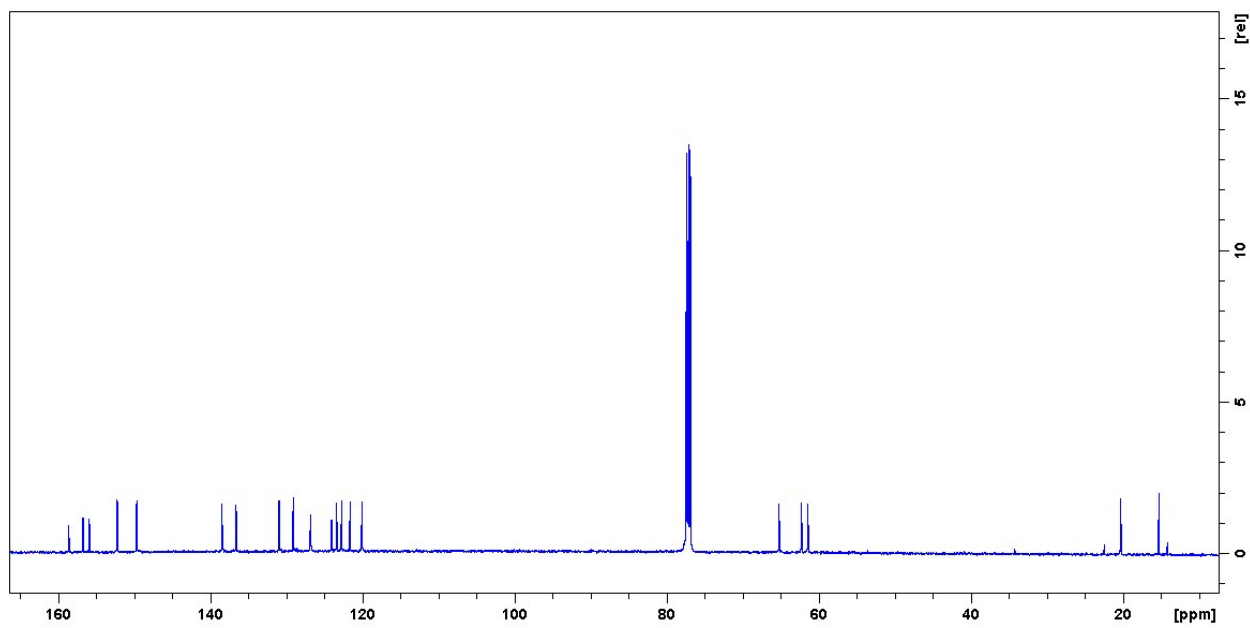
**Figure S7.**  $^1\text{H-NMR}$  of  $[(\mu\text{-Lig}^1)\text{Mg-Cl}]_2$  ( $\text{CDCl}_3$ , 500MHz).



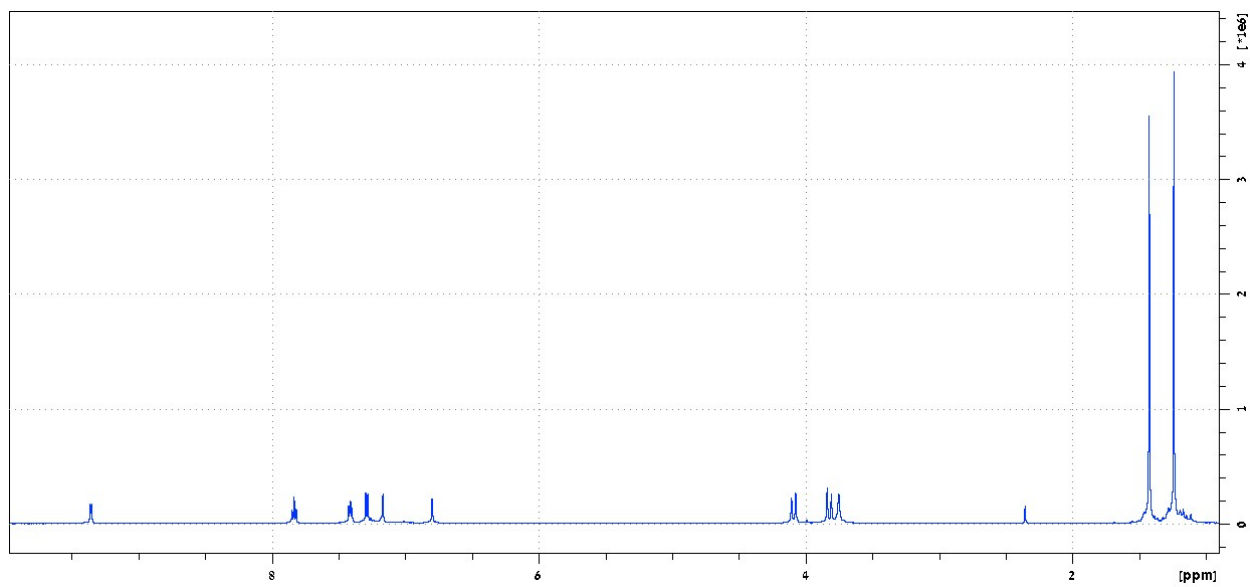
**Figure S8.**  $^{13}\text{C-NMR}$  of  $[(\mu\text{-Lig}^1)\text{Mg-Cl}]_2$  ( $\text{CDCl}_3$ , 500MHz).



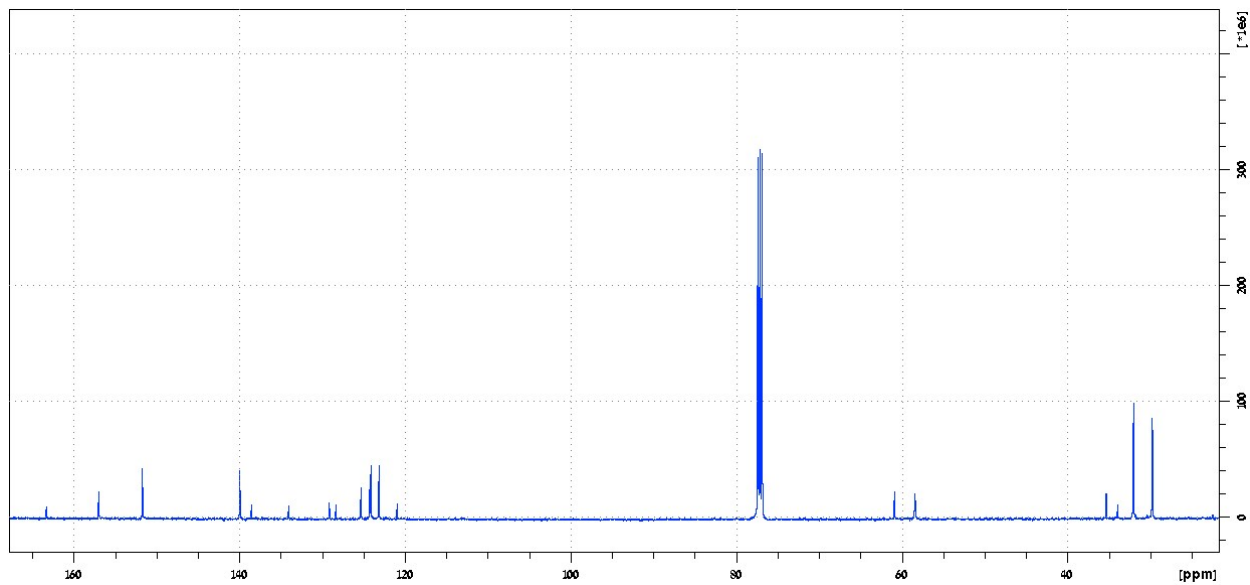
**Figure S9.**  $^1\text{H}$ -NMR of  $[(\mu\text{-Lig}^2)\text{Mg-Cl}]_2$  ( $\text{CDCl}_3$ , 500MHz).



**Figure S10.**  $^{13}\text{C}$ -NMR of  $[(\mu\text{-Lig}^2)\text{Mg-Cl}]_2$  ( $\text{CDCl}_3$ , 500MHz).

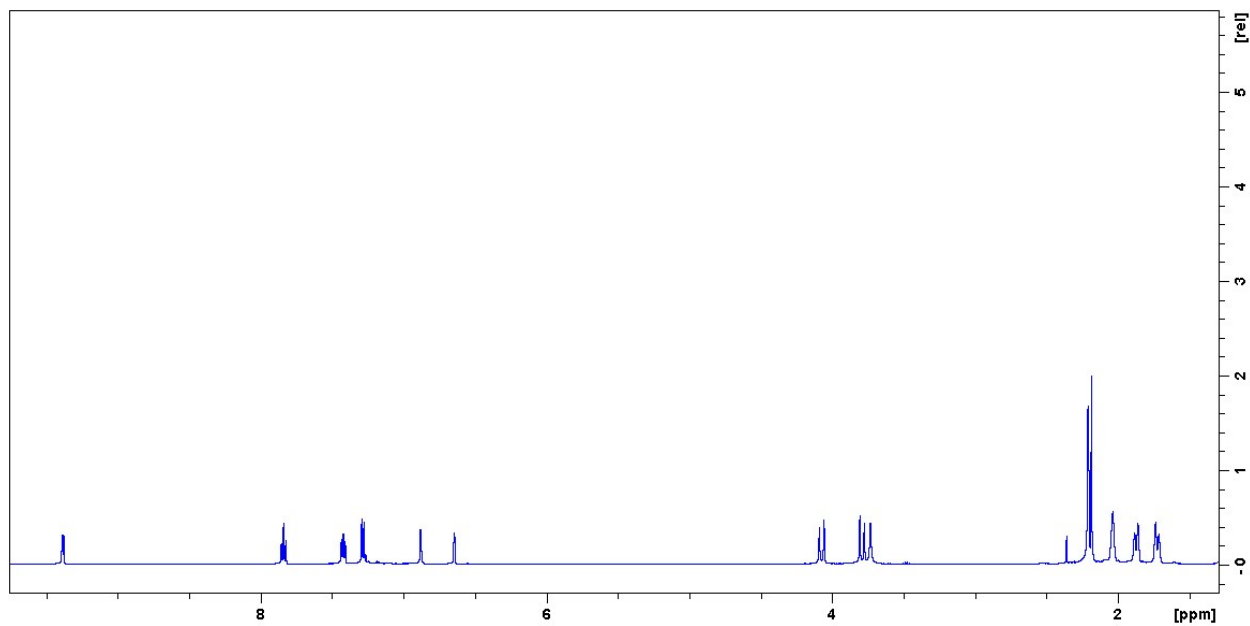


**Figure S11.**  $^1\text{H-NMR}$  of  $\text{Lig}^3\text{Mg-Cl}$  ( $\text{CDCl}_3$ , 500MHz).

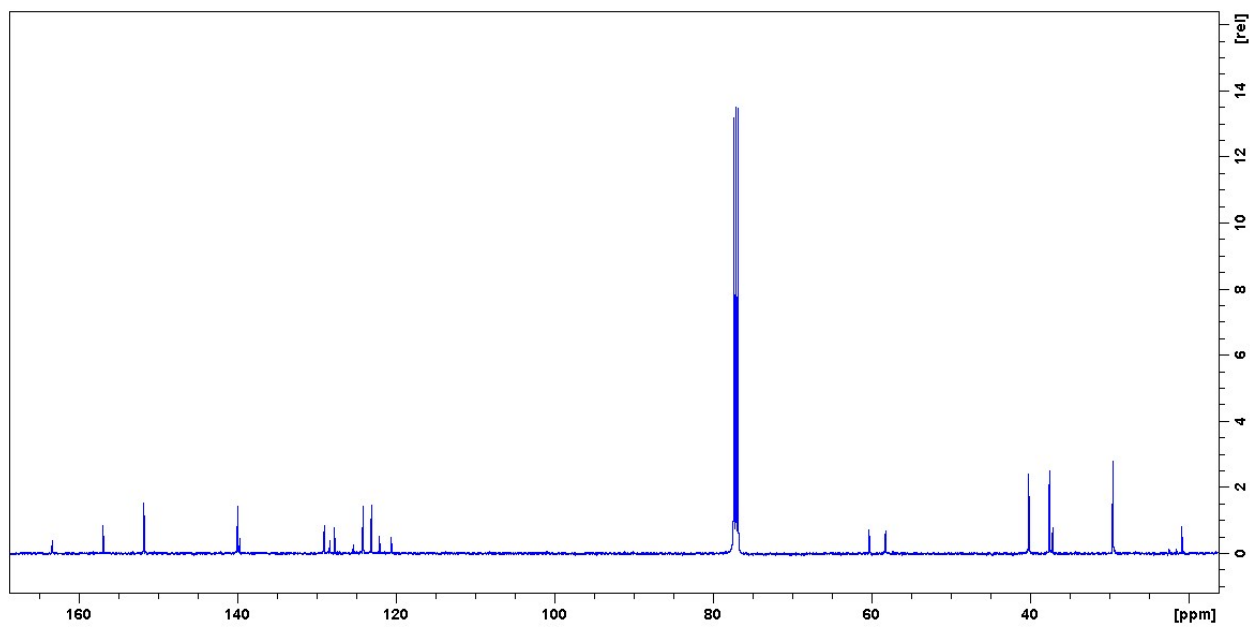


**Figure S12.**  $^{13}\text{C-NMR}$  of  $\text{Lig}^3\text{Mg-Cl}$  ( $\text{CDCl}_3$ , 500MHz).

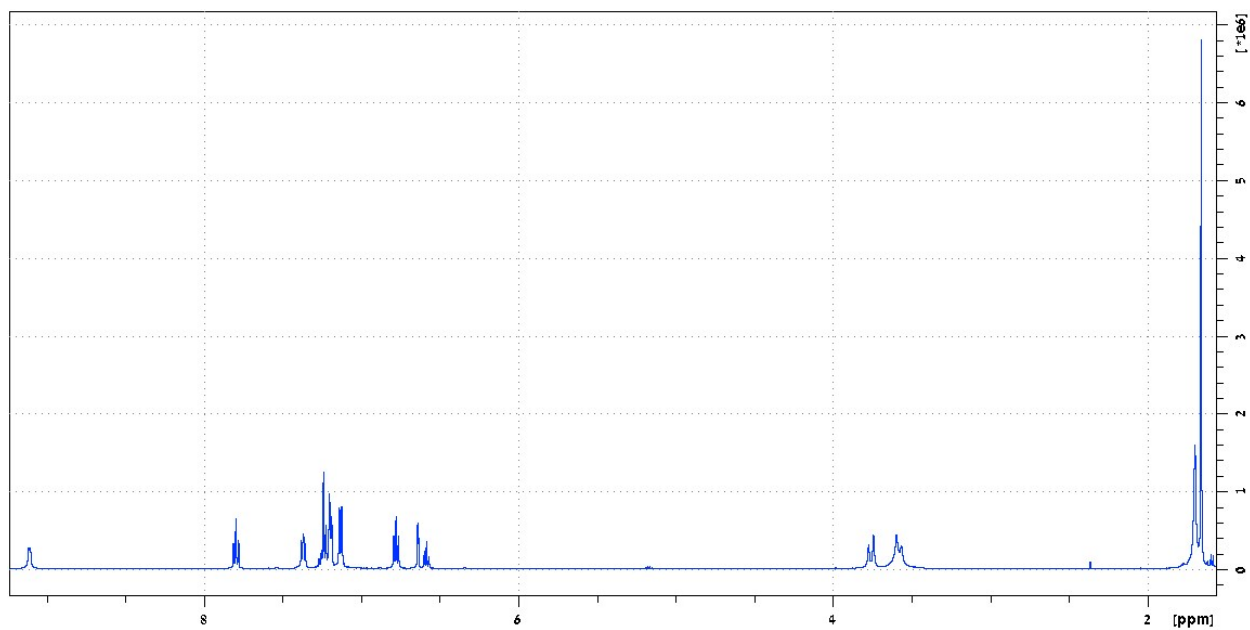




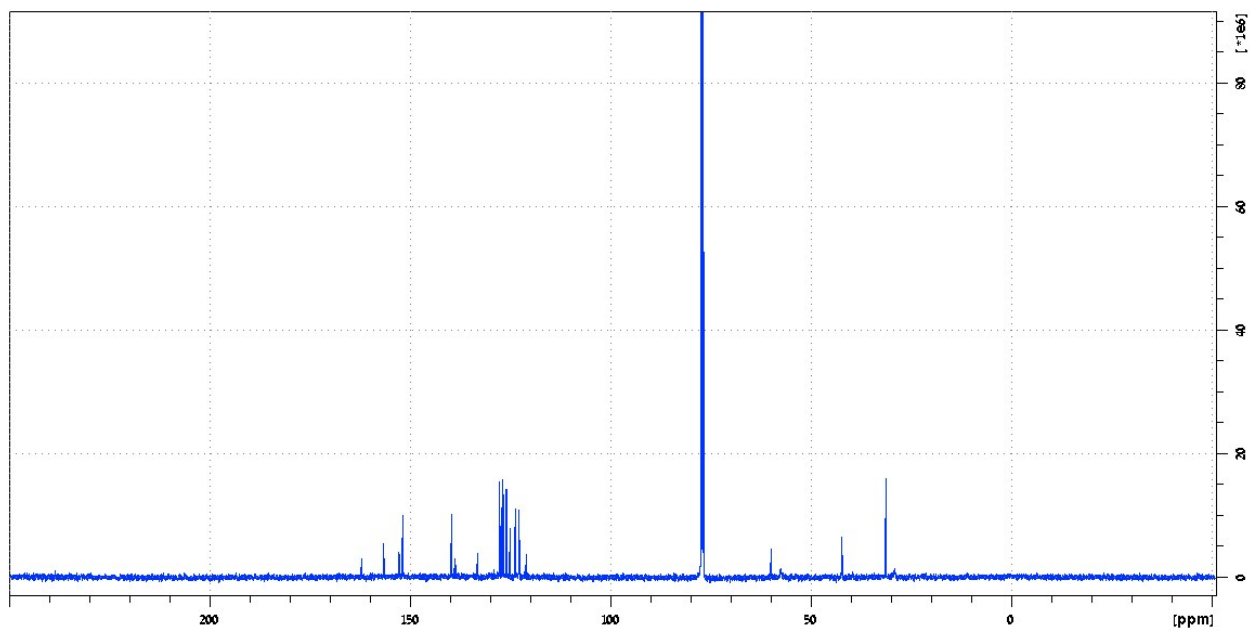
**Figure S13.**  $^1\text{H}$ -NMR of  $\text{Lig}^4\text{Mg-Cl}$  ( $\text{CDCl}_3$ , 500MHz).



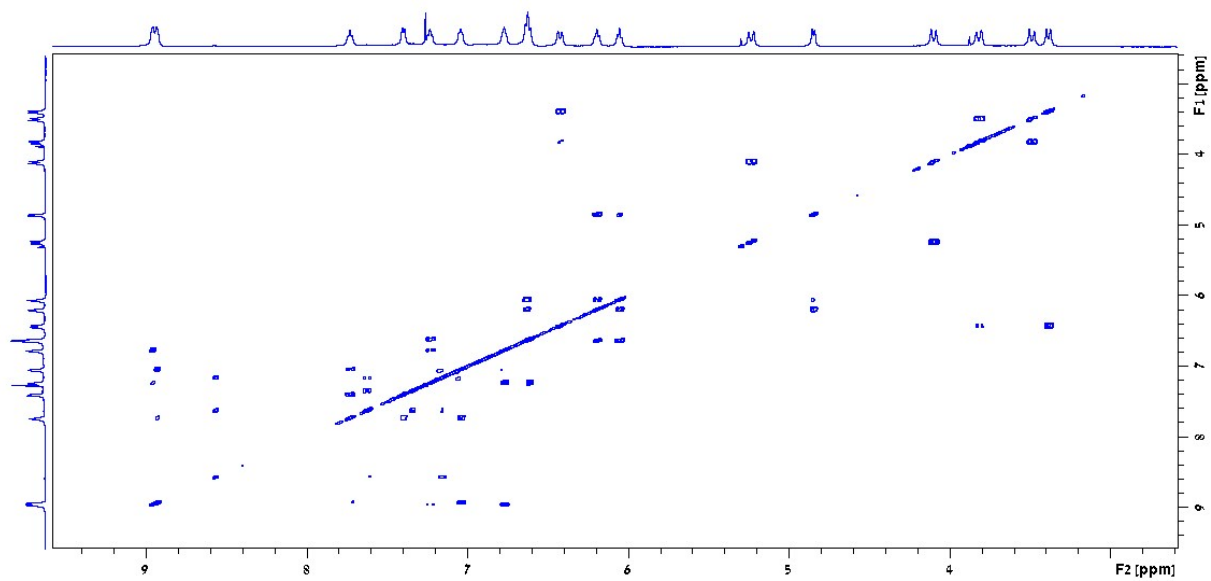
**Figure S14.**  $^{13}\text{C}$ -NMR of  $\text{Lig}^4\text{Mg-Cl}$  ( $\text{CDCl}_3$ , 500MHz).



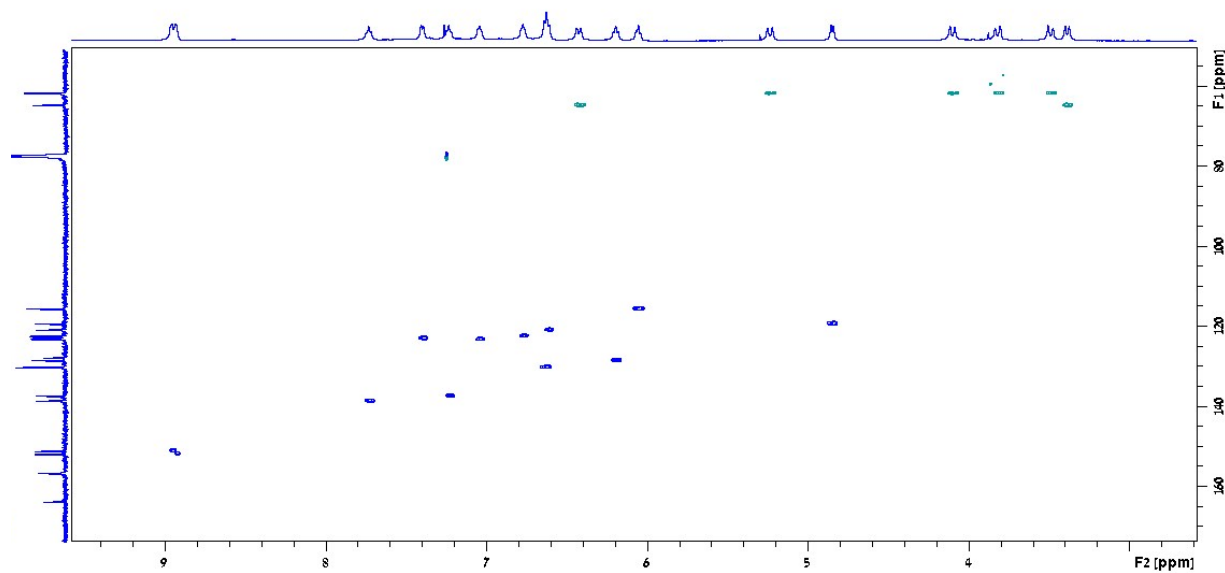
**Figure S15.**  $^1\text{H-NMR}$  of  $\text{Lig}^5\text{Mg-Cl}$  ( $\text{CDCl}_3$ , 500MHz).



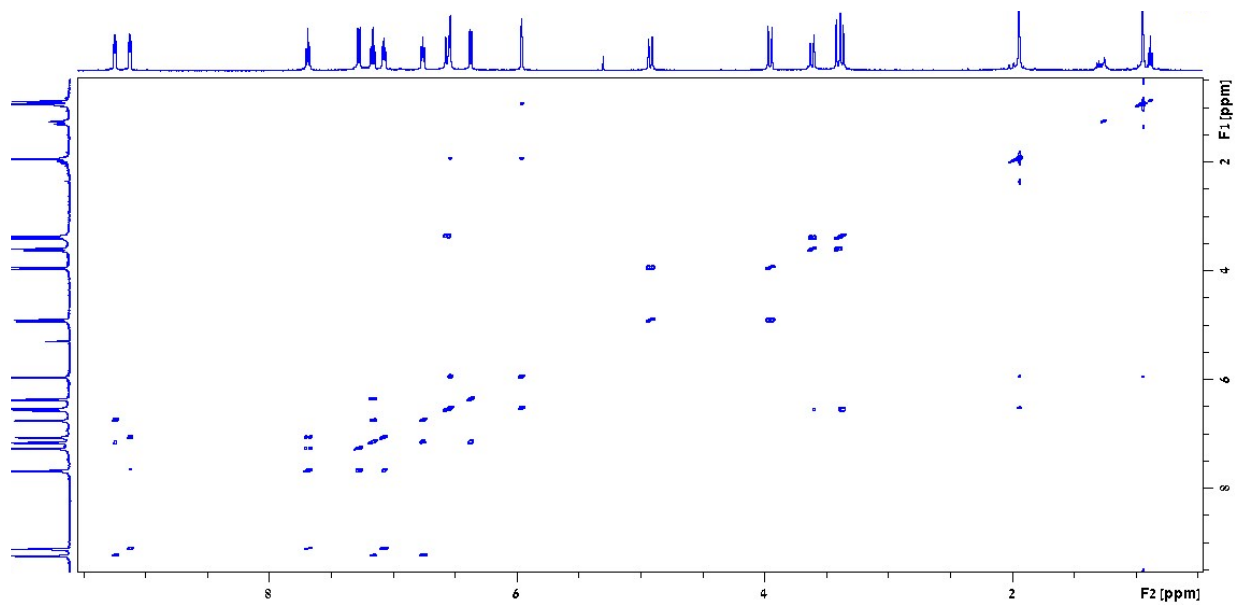
**Figure S16.**  $^{13}\text{C-NMR}$  of  $\text{Lig}^5\text{Mg-Cl}$  ( $\text{CDCl}_3$ , 500MHz).



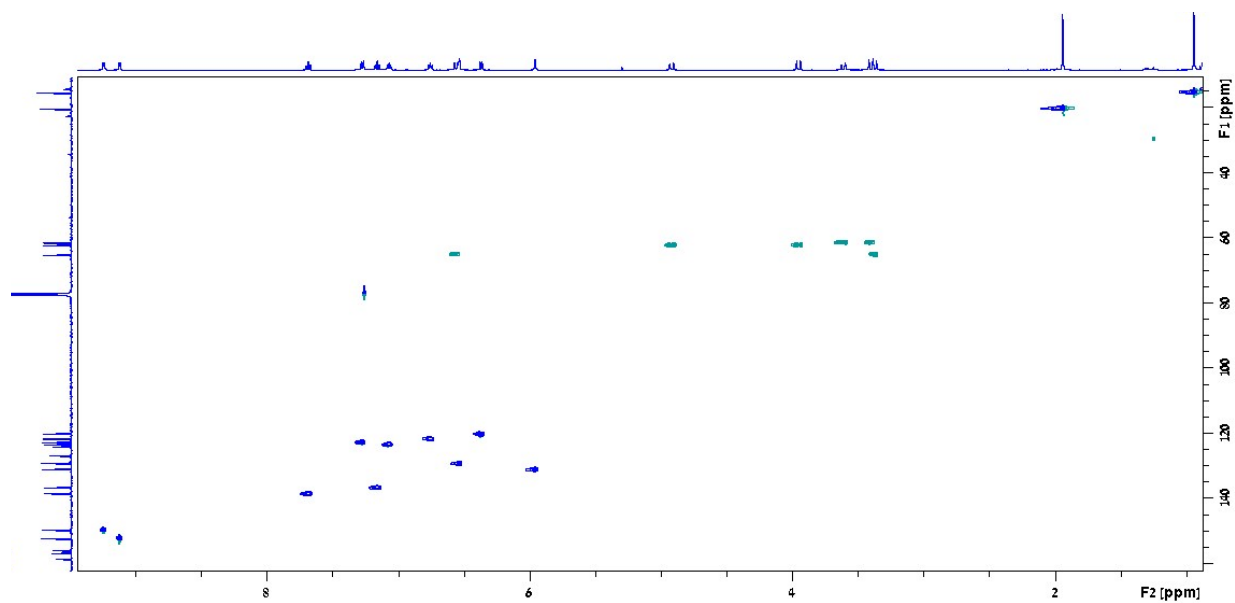
**Figure S17.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR of  $[(\mu\text{-Lig}^1)\text{Mg-Cl}]_2$  ( $\text{CDCl}_3$ , 500MHz).



**Figure S18.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR of  $[(\mu\text{-Lig}^1)\text{Mg-Cl}]_2$  ( $\text{CDCl}_3$ , 500MHz).

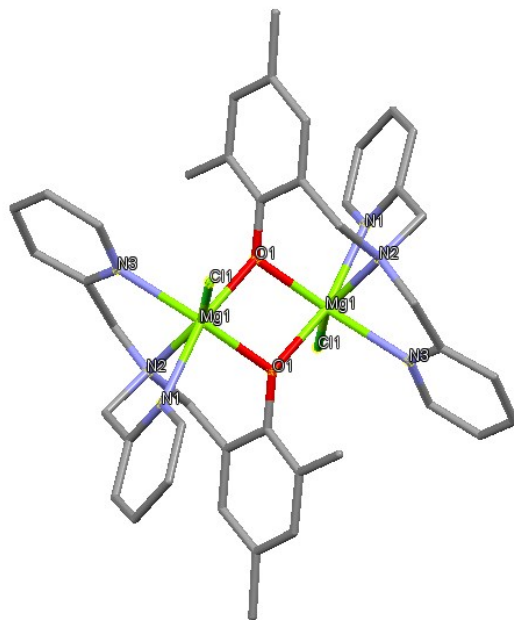


**Figure S19.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR of  $[(\mu\text{-Lig}^2)\text{Mg-Cl}]_2$  ( $\text{CDCl}_3$ , 500MHz).



**Figure S20.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR of  $[(\mu\text{-Lig}^2)\text{Mg-Cl}]_2$  ( $\text{CDCl}_3$ , 500MHz).

## Crystallographic Structure of $[(\mu\text{-Lig}^2)\text{Mg-Cl}]_2$



**Figure S21.** Molecular representation of the crystallographic structure of  $[(\mu\text{-Lig}^2)\text{Mg-Cl}]_2$ . Selected Bond lengths (Å) and angles (°): Mg(1)-O(1) 2.026(2), Mg(1)-O(1) 2.062 (3), Mg(1)-Cl(1) 2.443(2), Mg(1)-N(1) 2.287(3), Mg(1)-N(2) 2.325(1), Mg(1)-N(3) 2.223(2), O(1)-Mg(1)-Cl(1) 113.43(8), O(1)-Mg(1)-Cl(1) 96.54(8), O(1)-Mg(1)-N(1) 88.9(1), O(1)-Mg(1)-N(2) 86.5(1), O(1)-Mg(1)-N(3) 154.1(1), N(1)-Mg(1)-N(2) 74.1(1), N(1)-Mg(1)-N(3) 100.5(1), N(2)-Mg(1)-N(3) 73.2(1).

## Polymerization Results

**Table S1.** Polymerization of L-LA in dichloromethane at room temperature.<sup>a</sup>

Entry	Initiator	[I]/[BnOH]/[LA]	Time (min)	Conv. <sup>b</sup>	$M_n$ calc <sup>c</sup>	$M_n$ <sup>d</sup>	PDI <sup>e</sup>
1.	$[(\mu\text{-Lig}^1)\text{Mg-Cl}]_2$	1/1/300	15	0.90	38,880	30,397	1.08
2.	$[(\mu\text{-Lig}^1)\text{Mg-Cl}]_2$	1/2/600	20	0.91	39,312	32,478	1.08
3.	$[(\mu\text{-Lig}^1)\text{Mg-Cl}]_2$	1/10/1000	20	0.97	13,968	15,023	1.05
4.	$[(\mu\text{-Lig}^2)\text{Mg-Cl}]_2$	1/1/300	15	0.88	38,016	39,150	1.07
5.	$[(\mu\text{-Lig}^2)\text{Mg-Cl}]_2$	1/10/1000	20	0.90	12,960	10,780	1.06
6.	Lig <sup>3</sup> Mg-Cl	1/1/300	5	0.98	42,336	33,940	1.04
7.	Lig <sup>3</sup> Mg-Cl	1/10/1000	5	0.99	14,256	13,860	1.04
8.	Lig <sup>3</sup> Mg-Cl	1/1/1000	10	0.98	141,120	86,597	1.06
9.	Lig <sup>4</sup> Mg-Cl	1/1/300	2	0.98	42,336	46,527	1.08
10.	Lig <sup>4</sup> Mg-Cl	1/4/600	3	0.98	21,168	20,155	1.04
11.	Lig <sup>4</sup> Mg-Cl	1/1/1000	4	0.97	139,680	111,510	1.05
12.	Lig <sup>4</sup> Mg-Cl	1/10/1000	2	0.98	14,112	13,540	1.04
13.	Lig <sup>4</sup> Mg-Cl	1/1/2000	5	0.96	276,480	271,452	1.06
14.	Lig <sup>5</sup> Mg-Cl	1/1/300	5	0.95	41,040	35,860	1.08
15.	Lig <sup>5</sup> Mg-Cl	1/10/1000	10	0.95	13,680	12,950	1.04
16.	Lig <sup>5</sup> Mg-Cl	1/1/1000	10	0.91	131,140	123,450	1.07
17.	$[(\mu\text{-Lig}^1)\text{Mg-Cl}]_2$	1/0/300	15	0.42	18,144	27,369	1.20
18.	$[(\mu\text{-Lig}^2)\text{Mg-Cl}]_2$	1/0/300	15	0.87	37,584	103,378	1.27
19.	Lig <sup>3</sup> Mg-Cl	1/0/300	5	0.93	40,176	309,139	1.26
20.	Lig <sup>4</sup> Mg-Cl	1/0/300	10	0.93	40,176	297,372	1.20
21.	Lig <sup>5</sup> Mg-Cl	1/0/300	5	0.88	38,016	211,172	1.35

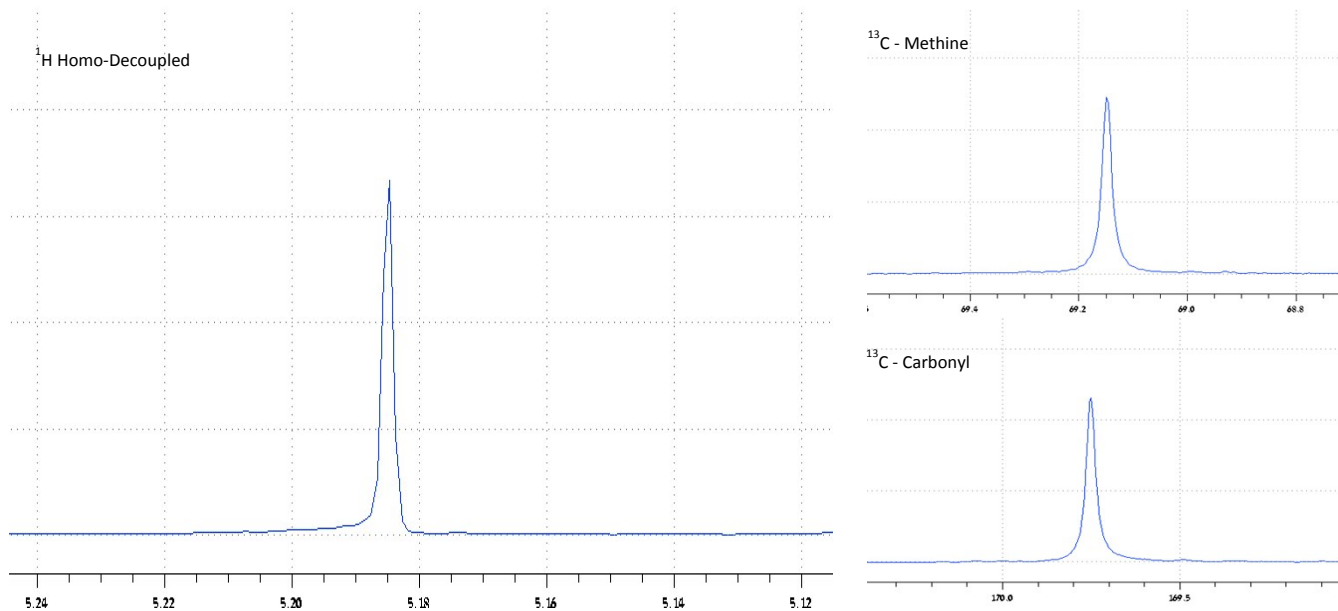
[a] The polymerizations were performed in CH<sub>2</sub>Cl<sub>2</sub> (5mL) employing 10 μmol of catalyst. [b] Determined by <sup>1</sup>H NMR spectroscopy (500 MHz). [c] Calculated from monomer conversion assuming full benzyl alcohol participation or full catalyst activation. Values are given in g mol<sup>-1</sup> [d]  $M_n$  was determined by GPC analysis with THF as eluent calibrated with polystyrene standards and multiplied by a correction factor of 0.58. [e] PDI: polydispersity index ( $M_w/M_n$ ). Determined by GPC analysis.

**Table S2.** Preparation of stereoblock PLA copolymers by sequential addition of L-LA and D-LA.<sup>a</sup>

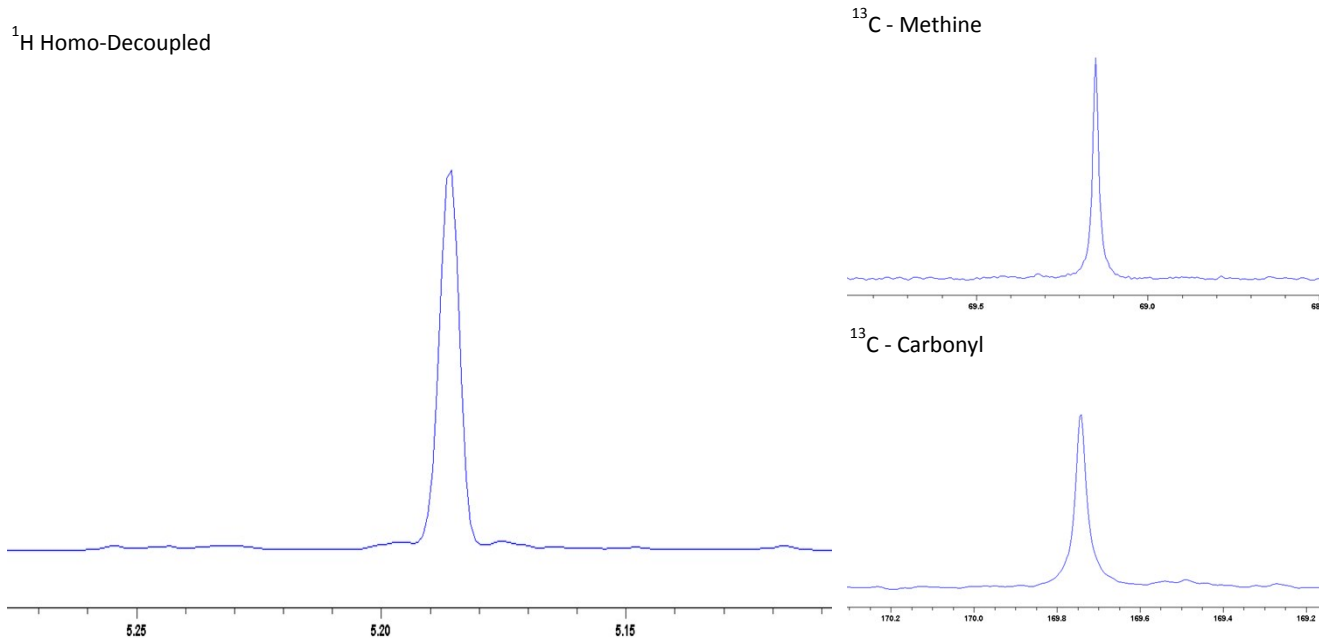
Entry	Initiator	Type	Composition	Time (min) <sup>b</sup>	Conv. <sup>c</sup>	P <sub>m</sub> <sup>d</sup>	M <sub>n calc</sub> <sup>e</sup>	M <sub>n</sub> <sup>f</sup>	PDI <sup>g</sup>
1.	Lig <sup>3</sup> Mg-Cl	Di Block	L(100)- <i>b</i> -D(100)	10	>0.98	>0.99	28800	26700	1.11
2.	Lig <sup>3</sup> Mg-Cl	Di Block	L(200)- <i>b</i> -D(200)	10	>0.98	>0.99	57600	62670	1.20
3.	Lig <sup>3</sup> Mg-Cl	Di Block	L(300)- <i>b</i> -D(300)	20	>0.98	>0.99	86400	66480	1.34
4.	Lig <sup>4</sup> Mg-Cl	Di Block	L(100)- <i>b</i> -D(100)	10	>0.98	>0.99	28800	22900	1.06
5.	Lig <sup>4</sup> Mg-Cl	Di Block	L(200)- <i>b</i> -D(200)	10	>0.98	>0.99	57600	62900	1.04
6.	Lig <sup>4</sup> Mg-Cl	Di Block	L(300)- <i>b</i> -D(300)	11	>0.98	>0.99	86400	85800	1.04
7.	Lig <sup>4</sup> Mg-Cl	Di Block	L(400)- <i>b</i> -D(400)	12	>0.98	>0.99	115200	113670	1.06
8.	Lig <sup>4</sup> Mg-Cl	Di Block	L(500)- <i>b</i> -D(500)	13	>0.98	>0.99	144000	149110	1.07
9.	Lig <sup>4</sup> Mg-Cl	Di Block	L(800)- <i>b</i> -D(800)	20	>0.98	>0.99	228100	202300	1.09
10.	Lig <sup>4</sup> Mg-Cl	Tri Block	L(100)- <i>b</i> -D(100)- <i>b</i> -L(100)	15	>0.98	0.98	43200	45860	1.08
11.	Lig <sup>4</sup> Mg-Cl	Tri Block	L(200)- <i>b</i> -D(200)- <i>b</i> -L(200)	16	>0.98	0.98	86400	88940	1.13
12.	Lig <sup>4</sup> Mg-Cl	Tri Block	L(300)- <i>b</i> -D(300)- <i>b</i> -L(300)	18	>0.98	0.98	129600	120590	1.12
13.	Lig <sup>4</sup> Mg-Cl	Tetra Block	L(100)- <i>b</i> -D(100)- <i>b</i> -L(100)- <i>b</i> -L(100)	22	>0.98	0.97	57600	64690	1.10
14.	Lig <sup>4</sup> Mg-Cl	Tetra Block	L(200)- <i>b</i> -D(200)- <i>b</i> -L(200)- <i>b</i> -L(200)	24	>0.98	0.96	115200	104230	1.13
15.	Lig <sup>4</sup> Mg-Cl	Tetra Block	L(300)- <i>b</i> -D(300)- <i>b</i> -L(300)- <i>b</i> -L(300)	24	>0.98	0.96	172800	166100	1.10

[a] The polymerizations were performed in CH<sub>2</sub>Cl<sub>2</sub> (5mL) employing 10 μmol of catalyst and 2 equiv of BnOH. [b] Total polymerization time given in minutes. 5-15 min were maintained between each monomer addition, depending on the monomer amount and length of polymer chain. [c] Determined by <sup>1</sup>H NMR spectroscopy (500 MHz). [d] P<sub>meso</sub>: the probability of a *meso* linkage between lactide units. Determined by the <sup>1</sup>H homonuclear-decoupled NMR spectrometry (CDCl<sub>3</sub>, 500 MHz) and by <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125MHz). [e] Calculated from monomer conversion assuming full benzyl alcohol participation. Values are given in g mol<sup>-1</sup> [f] M<sub>n</sub> was determined by GPC analysis with CHCl<sub>3</sub> as eluent calibrated with polystyrene standards and multiplied by a correction factor of 0.58. [g] PDI: polydispersity index (M<sub>w</sub>/M<sub>n</sub>). Determined by GPC analysis.

## $^1\text{H}$ Homonuclear Decoupled NMR and $^{13}\text{C}$ NMR of PLA Samples



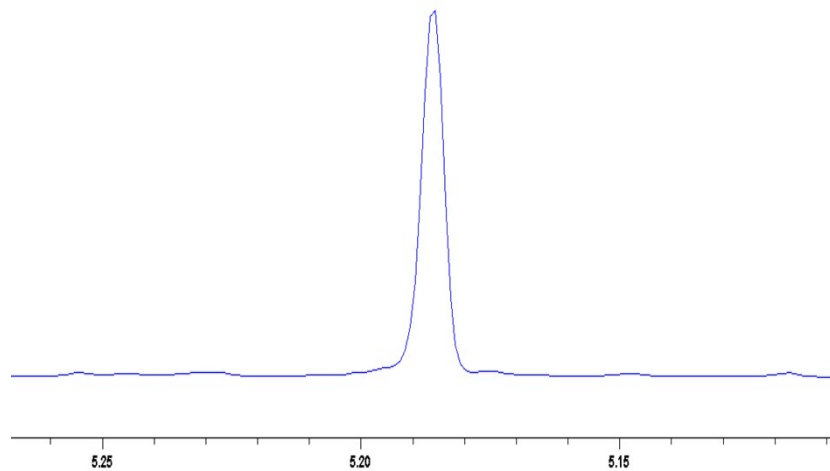
**Figure S22.**  $^1\text{H}$  HD NMR ( $\text{CDCl}_3$ , 500 MHz) and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) of a homopolymer PLLA sample ( $M_n=46500 \text{ g mol}^{-1}$ ) obtained with  $\text{Lig}^4\text{Mg-Cl}$ .



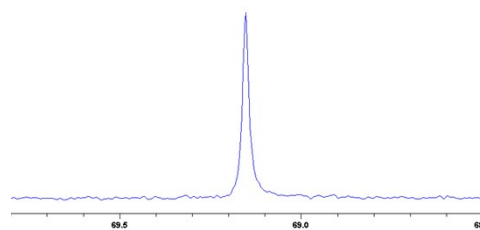
**Figure S23.**  $^1\text{H}$  HD NMR ( $\text{CDCl}_3$ , 500 MHz) and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) of L100-*b*-D100 di-block PLA copolymer sample obtained with  $\text{Lig}^4\text{Mg-Cl}$ .



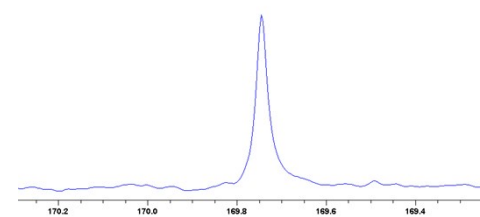
$^1\text{H}$  Homo-Decoupled



$^{13}\text{C}$  - Methine

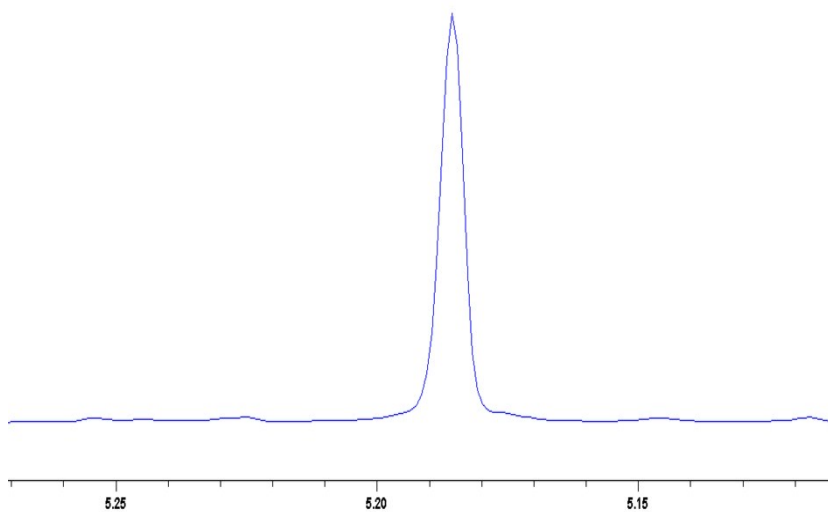


$^{13}\text{C}$  - Carbonyl

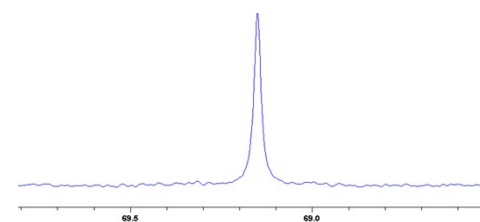


**Figure S24.**  $^1\text{H}$  HD NMR ( $\text{CDCl}_3$ , 500 MHz) and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) of L200-*b*-D200 di-block PLA copolymer sample obtained with  $\text{Lig}^4\text{Mg-Cl}$ .

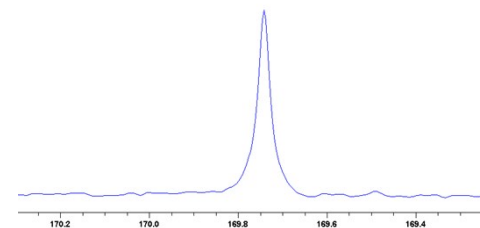
$^1\text{H}$  Homo-Decoupled



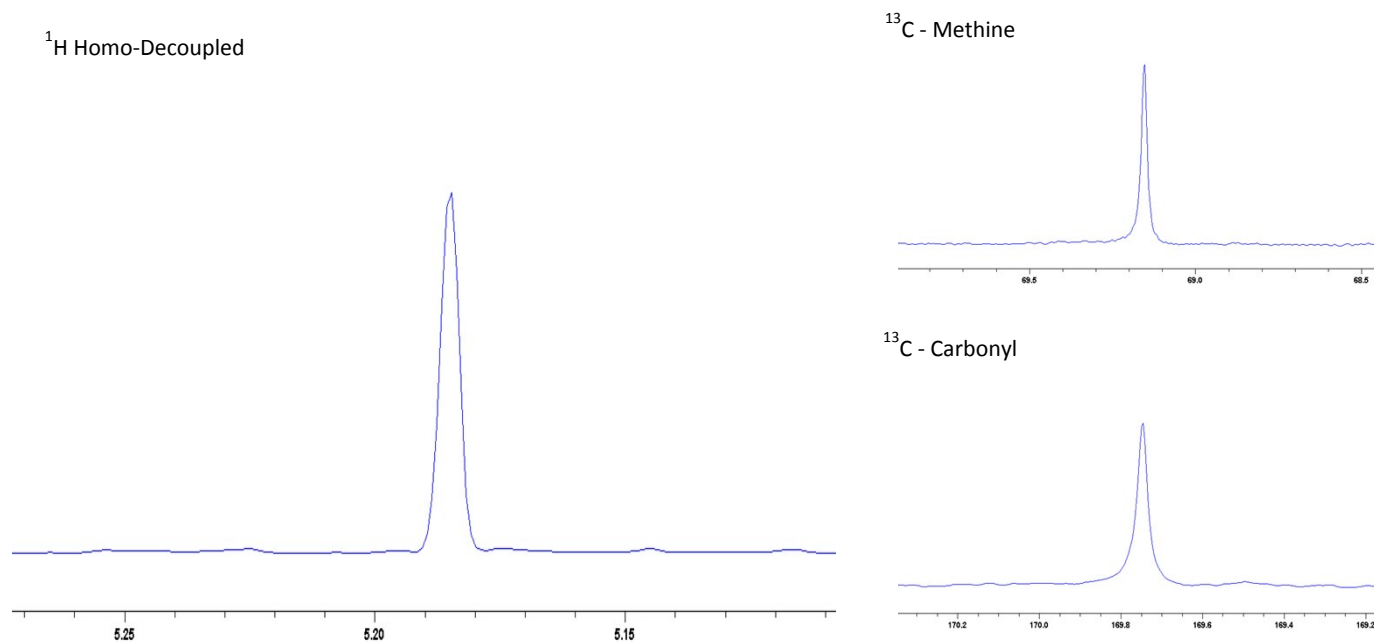
$^{13}\text{C}$  - Methine



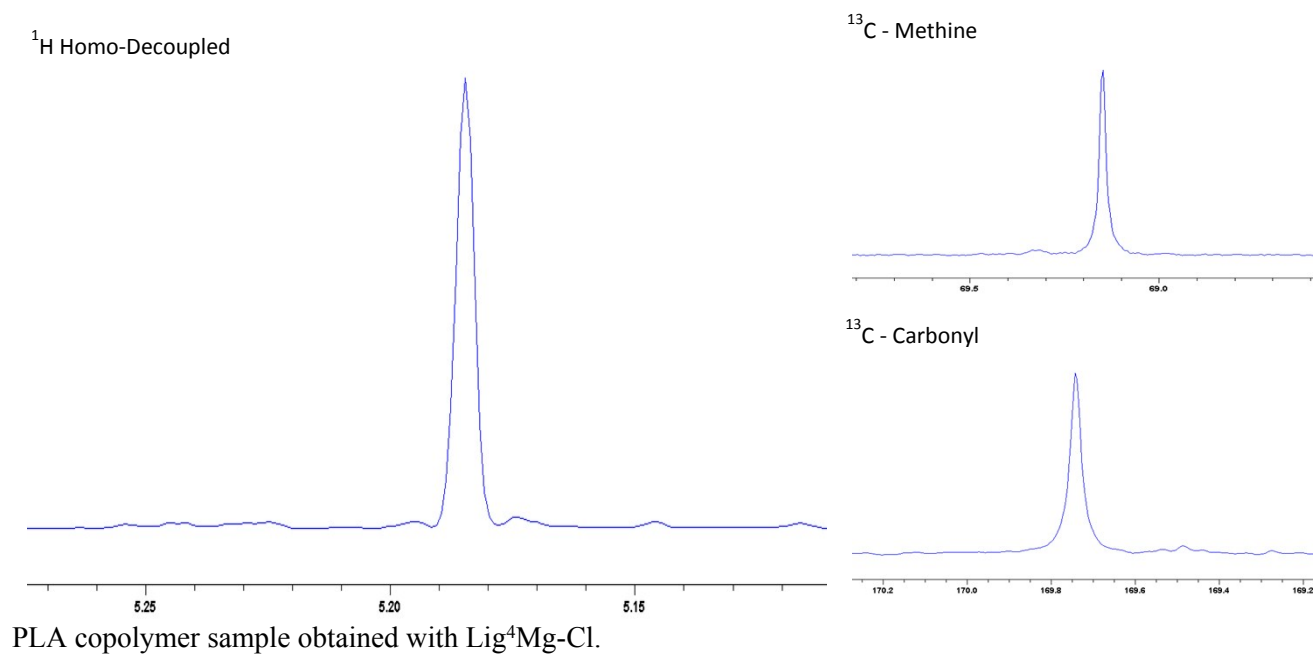
$^{13}\text{C}$  - Carbonyl



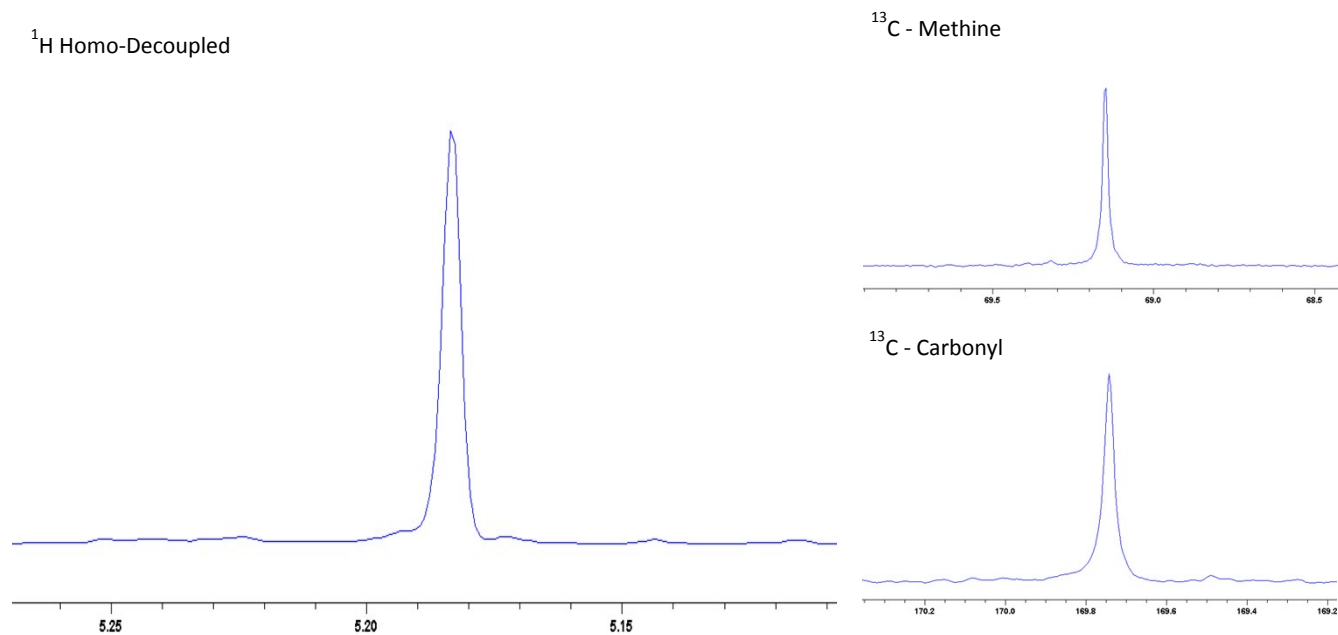
**Figure S25.**  $^1\text{H}$  HD NMR ( $\text{CDCl}_3$ , 500 MHz) and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) of L300-*b*-D300 di-block PLA copolymer sample obtained with  $\text{Lig}^4\text{Mg-Cl}$ .



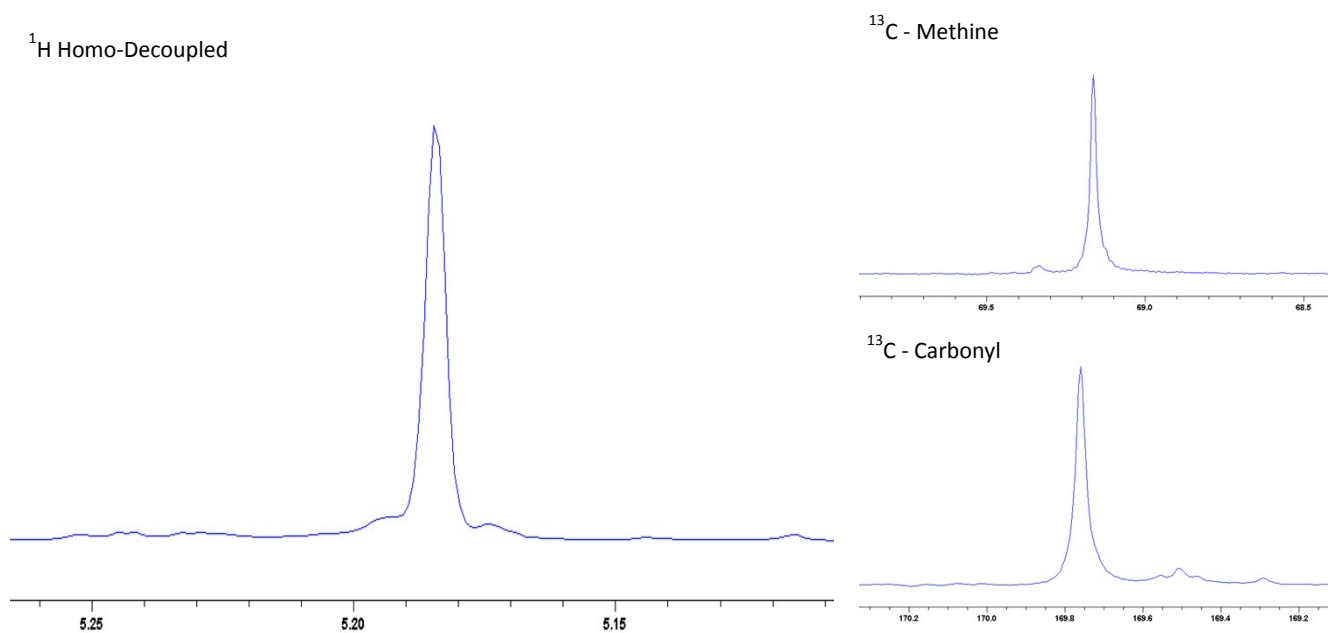
**Figure S26.**  $^1\text{H}$  HD NMR ( $\text{CDCl}_3$ , 500 MHz) and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) of L500-*b*-D500 di-block PLA copolymer sample obtained with  $\text{Lig}^4\text{Mg-Cl}$ .



**Figure S27.**  $^1\text{H}$  HD NMR ( $\text{CDCl}_3$ , 500 MHz) and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) of L100-*b*-D100-*b*-L100 tri-block PLA copolymer sample obtained with  $\text{Lig}^4\text{Mg-Cl}$ .



**Figure S28.**  $^1\text{H}$  HD NMR ( $\text{CDCl}_3$ , 500 MHz) and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) of L200-*b*-D200-*b*-L200 tri-block PLA copolymer sample obtained with  $\text{Lig}^4\text{Mg-Cl}$ .



**Figure S29.**  $^1\text{H}$  HD NMR ( $\text{CDCl}_3$ , 500 MHz) and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) of L100-*b*-D100-*b*-L100-*b*-D100 tetra-block PLA copolymer sample obtained with  $\text{Lig}^4\text{Mg-Cl}$ .

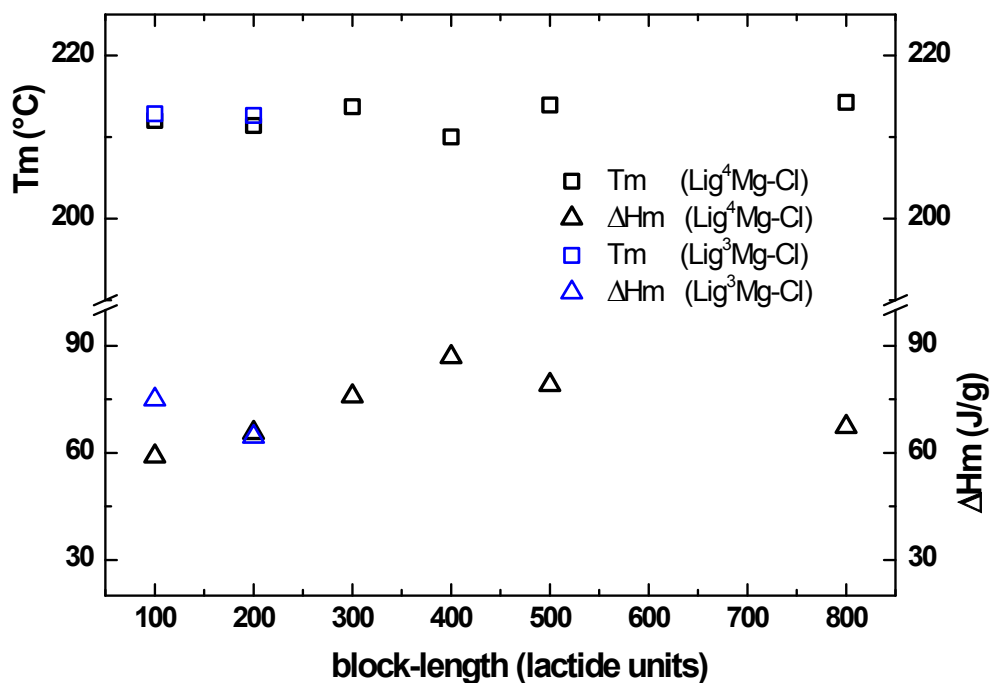
## Thermal and WAXD Analysis of Stereo-*n*-Block PLA Samples

*Thermal and WAXD analysis of stereo-diblocks*

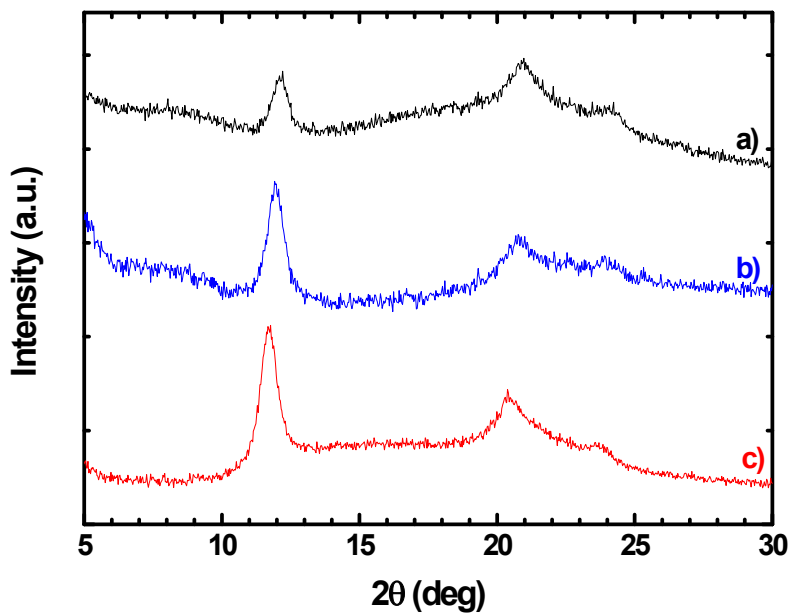
**Table S3.** DSC analysis of stereo-diblocks.

Initiator	Composition	First run		Cooling		Second run			
		$T_m$	$\Delta H_m$	$T_c$	$\Delta H_c$	$T_g$	$T_c/\Delta H_c$	$T_m$	$\Delta H_m$
$\text{Lig}^3\text{Mg-Cl}$	L(100)- <i>b</i> -D(100)	213	75	140	58	56	-	212	58
$\text{Lig}^3\text{Mg-Cl}$	L(200)- <i>b</i> -D(200)	213	64	117	47	56	-	211	48
$\text{Lig}^4\text{Mg-Cl}$	L(100)- <i>b</i> -D(100)	212	59	132	46	58	-	210	42
$\text{Lig}^4\text{Mg-Cl}$	L(200)- <i>b</i> -D(200)	211	66	135	52	62	-	213	50
$\text{Lig}^4\text{Mg-Cl}$	L(300)- <i>b</i> -D(300)	214	76	127	49	58	-	205	51
$\text{Lig}^4\text{Mg-Cl}$	L(400)- <i>b</i> -D(400)	210	87	139	60	59	106/7	213	61
$\text{Lig}^4\text{Mg-Cl}$	L(500)- <i>b</i> -D(500)	214	79	153	54	58	101/3	211	51
$\text{Lig}^4\text{Mg-Cl}$	L(800)- <i>b</i> -D(800)	214	67	154	43	57	-	216	44

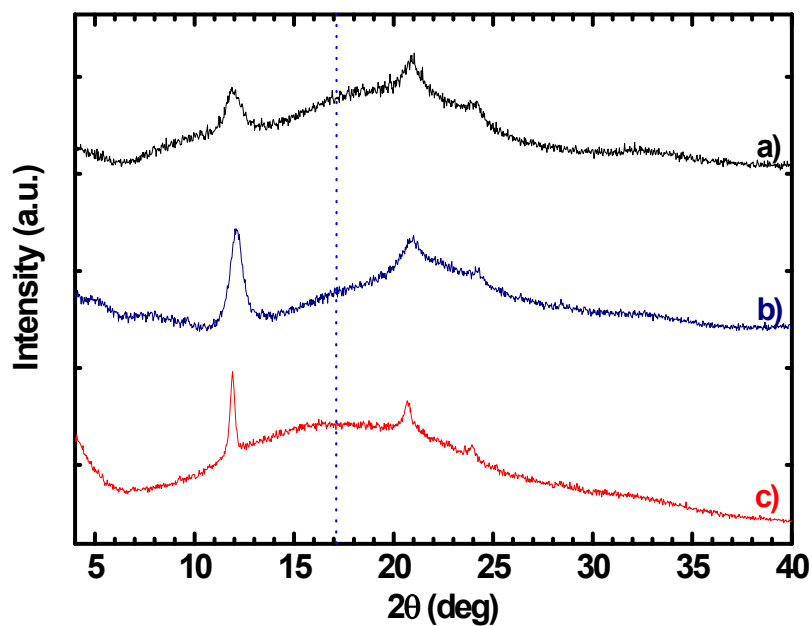
$T$  ( $^{\circ}\text{C}$ );  $\Delta H$  (J/g)



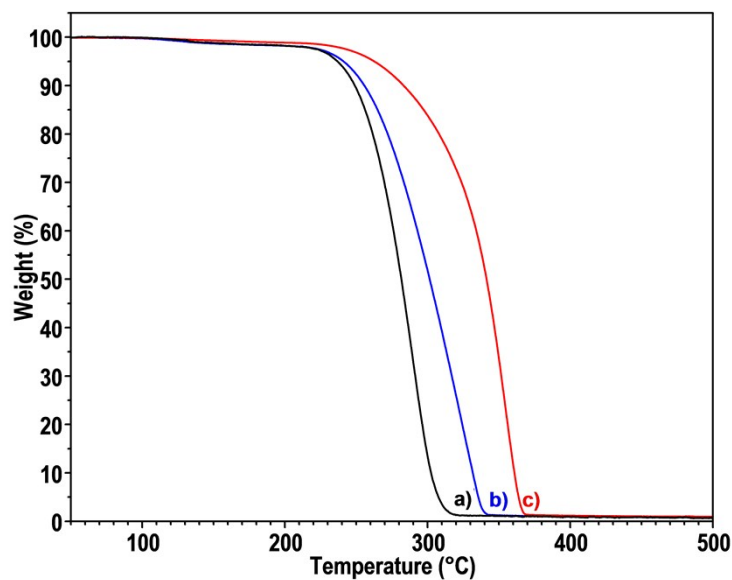
**Figure S30.**  $T_m$  and  $\Delta H_m$  vs. block length (first DSC heating run) of stereo-diblocks.



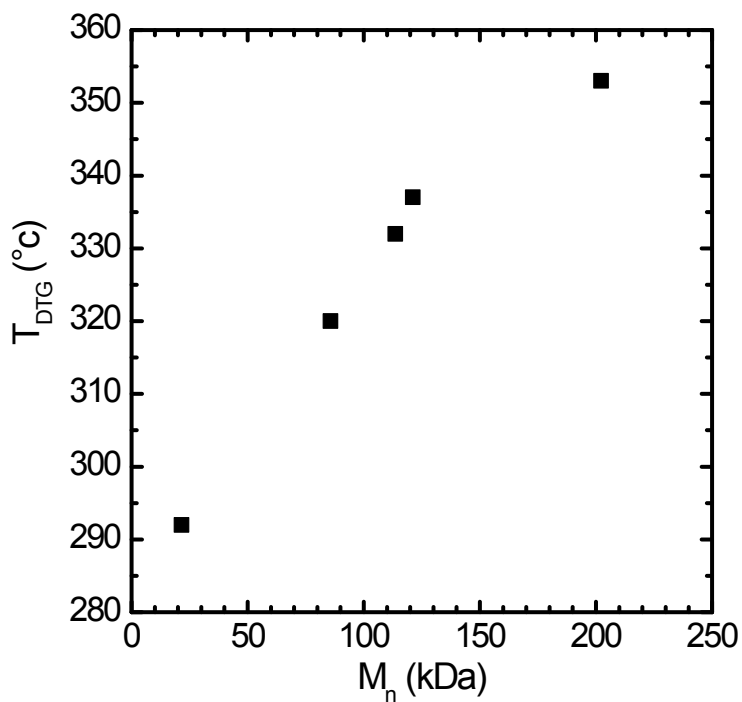
**Figure S31.** WAXD patterns of stereo-diblocks having a) 100 (black), b) 300 (blue) and c) 800 (red) *mer* block lengths. All samples were in form of DCM casting film.



**Figure S32.** WAXD patterns of stereo-diblocks L(800)-*b*-D(800) crystallized from a) polymerization solution, b) DCM solution, c) melt during DSC cooling run.



**Figure S33.** Thermogravimetric curves of stereo-diblock copolymers having a) 100 (black), b) 300 (blue) and c) 800 (red) *mer* block lengths. All samples were crystallized from polymerization solution (“as-polymerized” samples).



**Figure S34.** Degradation temperature ( $T_{DTG}$ ) vs  $M_n$  (see Table S2), for stereo-diblock copolymers having 100-800 mer block length.

**Table S4.** Degradation temperatures of stereo-diblocks and high MW PLLA and PDLA homopolymers blend.

Initiator	Composition	$M_n$ (kDa)	$T_{\text{weight loss 5\%}}$	$T_{\text{weight loss 10\%}}$	$T_{\text{onset}}$	$T_{DTG}$
Lig <sup>3</sup> Mg-Cl	L(100)- <i>b</i> -D(100)	24	236	249	256	290
Lig <sup>4</sup> Mg-Cl	L(300)- <i>b</i> -D(300)	86	240	255	267	320
Lig <sup>4</sup> Mg-Cl	L(400)- <i>b</i> -D(400)	114	237	257	267	334
Lig <sup>4</sup> Mg-Cl	L(300)- <i>b</i> -D(300)	121	242	260	279	344
Lig <sup>4</sup> Mg-Cl	L(800)- <i>b</i> -D(800)	202	262	284	319	354
Lig <sup>4</sup> Mg-Cl	L(1000)- <i>b</i> -D(1000)	321	281	300	325	357
	PLLA (185KDa) and PDLA (230 KDa) 1:1 mix	208	nd	nd	341	361

nd – not detected

Thermal and WAXD analysis of stereo-tri- and tetrablock copolymers

Table S5. DSC analysis of stereo-triblocks.

Initiator	Composition	First run		Cooling		Second run			
		$T_m$	$\Delta H_m$	$T_c$	$\Delta H_c$	$T_g$	$T_c/\Delta H_c$	$T_m$	$\Delta H_m$
Lig <sup>4</sup> Mg-Cl	L(100)- <i>b</i> -D(100)- <i>b</i> -L(100)	202	36	106	4	55	99/25	196	29
Lig <sup>4</sup> Mg-Cl	L(200)- <i>b</i> -D(200)- <i>b</i> -L(200)	205	41	115	23	58	98/12.5	200	33
Lig <sup>4</sup> Mg-Cl	L(300)- <i>b</i> -D(300)- <i>b</i> -L(300)	201	40	108	11	58	101/21.3	197	31

T (°C);  $\Delta H$  (J/g)

Table S6. DSC data of stereo-tetrablocks.

Initiator	Composition	First run		Cooling		Second run			
		$T_m$	$\Delta H_m$	$T_c$	$\Delta H_c$	$T_g$	$T_c/\Delta H_c$	$T_m$	$\Delta H_m$
Lig <sup>4</sup> Mg-Cl	L(100)- <i>b</i> -D(100)- <i>b</i> -L(100)- <i>b</i> -D(100)	202	49	115	22	59	97/21	204	43
Lig <sup>4</sup> Mg-Cl	L(200)- <i>b</i> -D(200)- <i>b</i> -L(200)- <i>b</i> -D(200)	205	56	119	37	57	97/9	201	39
Lig <sup>4</sup> Mg-Cl	L(300)- <i>b</i> -D(300)- <i>b</i> -L(300)- <i>b</i> -D(300)	179	18	-	-	57	140/5	185	6

T (°C);  $\Delta H$  (J/g)

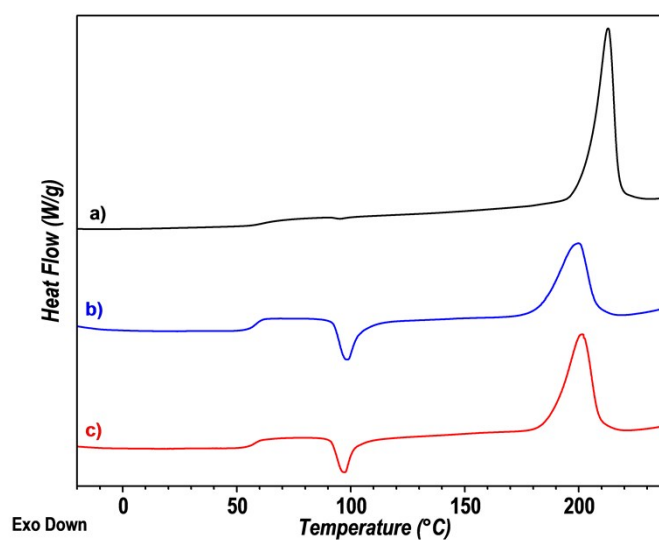
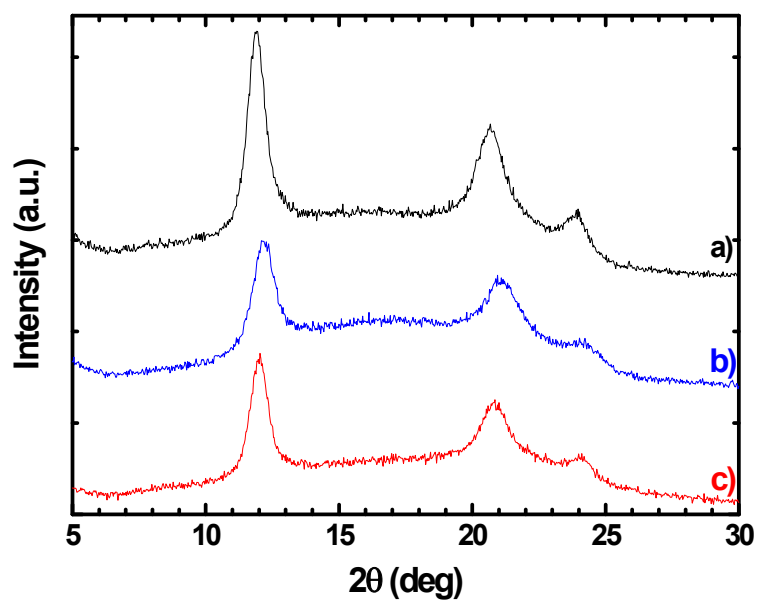


Figure S35. Thermograms of second DSC heating run of stereo- di (a), tri (b), and tetra-blocks (c) having 200 *mer* block length.





**Figure S36.** WAXD patterns of stereo a) di (black), b) tri (blue) and c) tetra blocks (red) samples having 200 *mer* block length. All samples were crystallized from polymerization solution (“as-polymerized” samples).

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