Supporting information

Simple Sodium and Potassium Phenolates as Catalysts for Highly Iso-selective Polymerization of *rac*-Lactide

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Experimental

Materials and Methods

All the syntheses were performed under a dry argon atmosphere using standard Schlenk techniques. Reagents were purified by standard methods: toluene, n-hexane, THF were distilled under nitrogen from sodium/benzophenone ketyl prior to use; CH_2Cl_2 was distilled from P_2O_5; BnOH were distilled from CaH_2; *rac*-lactide was purchased from Daigang BIO Engineer Limited Co. of China and recrystallized from toluene; NaHMDS and KHMDS were purchased from Acros Company. Crown ethers were purchased from J&K Scientific. ^{1}H NMR and ^{13}C NMR were recorded on a Varian Mercury Plus 300 MHz spectrometer and JNM_ECS 400 MHz, ^{1}H NMR chemical shifts are reported in ppm versus residual protons in deuterated solvents as follows: δ 7.26 ppm for chloroform-d, δ 7.16 ppm for benzene-d_6. ^{13}C{1H} NMR chemical shifts are reported in ppm versus residual ^{13}C in the solvent: δ 77.0 ppm for chloroform-d, δ 128.06 ppm for benzene-d_6. The elemental analyses of the complexes were measured using an Elemental Vario EL series CHN analyzer with the samples under a nitrogen atmosphere. The molecular weights (M_n and M_w) and the molecular mass distributions (M_w/M_n) of the polymer samples were measured by gel permeation chromatography (GPC) at 25 °C using THF as the solvent, an eluent flow rate of 1 mL/min, and narrow polystyrene standards as reference samples. The measurements were performed using a Waters 1525 binary system that was equipped with a Waters 2414 RI detector using two Styragel columns (102-106 kg/mol). Each reported value is the average of two independent measurements and was corrected using a factor of 0.58 for polylactide according to the literature.[1] Calorimetric measurements were conducted using a Sapphire DSC apparatus manufactured by PerkinElmer Instruments. Polymer samples (3.0 mg) were placed in aluminum pans and heated/cooled at a rate of 10 °C min^{-1} under a nitrogen atmosphere. The previous thermal history of the samples was erased by heating them to 200 °C before cooling them to 0 °C. Measurements were performed between 30 °C and 200 °C. The melting temperatures were evaluated as the maxima of the melting endotherms.

General Preparation Procedures for **L**^{1}H-**L**^{3}H according to the literature.[2]

Sodium metal (0.11 g, 5.0 mmol) was added to different phenol (36.0 mmol) at 100 ^{o}C with vigorous stirring. triphenylchloromethane (3.6 mmol) was added to a formed melt of cresolate and this was heated for 3 h at 135-145 ^{o}C with vigorous stirring. After cooling down to ~20 ^{o}C, the reaction mixture was treated with 7 % aq. NaOH (20 mL) and ether (20 mL). The ether layer was separated and washed with 7 % aq. NaOH (5×20 mL), water (50 mL), and brine (20 mL). The organic layer was separated, dried with anhydrous Na_2SO_4, the solvent was evaporated, and the residue was recrystallized from ethanol. and a white solid was achieved.

L^{1}H was obtained by the reaction of p-cresol with triphenylchloromethane. The yield was 0.52 g (41.3 %). ^{1}H NMR (300 MHz, chloroform-d, 25 ^{o}C): δ 7.32-7.18 (m, 15 H, Ph-*H*), 7.04 (d, *J* = 9 Hz, 1H, Ar-*H*), 6.86 (s, 1H, Ar-*H*), 6.74 (d, *J* = 9 Hz, 1H, Ar-*H*), 4.33 (s, 1H, Ar-O*H*), 2.19 (s, 3H, Ar-CH_3). ^{13}CNMR (75 MHz, chloroform-d, 25 ^{o}C): δ 152.22, 144.22, 132.82, 130.97, 130.76, 129.41, 129.24, 127.89, 126.72, 117.87, 62.63, 20.96. Anal. Calcd for $C_{26}H_{22}O$: C, 89.11; H, 6.33. Found: C, 88.86; H, 6.27.

L^{2}H was obtained by the reaction of 4-methoxyphenol with triphenylchloromethane. The yield was 0.65 g (49.3 %). ^{1}H NMR (300 MHz, chloroform-d, 25 ^{o}C): δ 7.31-7.18(m, 15H, Ph-*H*), 6.79(s, 2H, Ar-*H*), 6.68(s, 1H, Ar-*H*), 4.13(s, 1H, Ar-O*H*), 3.64 (s, 3H, Ar-OCH_3). ^{13}CNMR (75 MHz, chloroform-d, 25 ^{o}C): δ 153.12, 148.36, 143.97, 134.43, 130.93, 127.93, 126.82, 118.56, 117.29, 112.92, 62.78, 55.43. Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.05; H, 6.11.

L^{3}H was obtained the reaction of 2-tert-butyl-4-methylphenol with triphenylchloromethane. The yield was 0.71 g (49.9 %). ^{1}H NMR (300 MHz, chloroform-d, 25 ^{o}C): δ 7.28-7.17 (m, 15H, Ph-*H*), 7.10 (d, *J* = 3 Hz, 1H, Ar-H), 6.70(d, 1H, Ar-*H*), 4.52 (s, 1H, Ar-O*H*), 2.18 (s, 3H, Ar-CH_3), 1.29 (s, 9H, Ar-C(CH_3)$_3$). ^{13}CNMR (75 MHz, chloroform-d, 25 ^{o}C): δ 151.09, 144.31, 137.82, 133.39, 131.10, 129.05, 127.79, 126.98, 126.69, 62.97, 34.68, 29.58, 21.32. Anal. Calcd for $C_{30}H_{30}O$: C, 88.63; H, 7.44. Found: C, 88.45; H, 7.31.

General Preparation Procedures for complexes **1-6**

Under an inert atmosphere, a KHMDS/NaHMDS solution (1.2 mmol, 1 mol/L in THF) was added dropwise into a toluene solution (10 mL) of appropriate ligand (1.0 mmol) and appropriate crown ether (1.0 mmol). The reaction mixture was stirred overnight. The solution was filtered. Volatile materials were removed from the filtrate under vaccum and the residue was recrystallized from a toluene solution affording a white crystalline powder.

Synthesis of **1**: yield 0.27 g (45.6 %). ^{1}H NMR (400 MHz, benzene-d_6, 25 ^{o}C): δ 7.75 (d, *J* = 8 Hz, 6H, Ph-*H*), 7.36 (d, *J* = 4 Hz, 1H, Ar-*H*), 7.29 (s, 1H, Ar-*H*), 7.11 (t, *J* = 8 Hz, 6H, Ph-*H*), 7.00 (t, *J* = 8 Hz, 3H, Ph-*H*), 6.68 (d, *J* = 4 Hz,1H, Ar-*H*), 3.02 (br, 20H, crown ether-*H*), 2.45 (s, 3H, Ar-CH_3). ^{13}CNMR (100 MHz, benzene-d_6, 25 ^{o}C):

δ 149.65, 134.47, 132.39, 132.30, 129.38, 129.28, 126.70, 125.64, 124.31, 120.92, 68.96, 64.64, 21.71. Anal. Calcd for $C_{36}H_{41}O_6Na$: C, 72.95; H, 6.97. Found: C, 72.63; H, 6.56.

Synthesis of **2**: yield 0.34 g (55.9 %). ^{1}H NMR (400 MHz, benzene-d_6, 25 ^{o}C): δ 7.61 (d, *J* = 8 Hz, 6H, Ph-*H*), 7.24 (d, J = 8 Hz, 1H, Ar-*H*), 7.21 (s, 1H, Ar-*H*), 7.07 (t, *J* = 8 Hz, 6H, Ph-*H*), 6.98 (t, *J* = 8 Hz, 3H, Ph-*H*), 6.60 (d, *J* = 4 Hz, 1H, Ar-*H*), 3.15 (s, 20H, crown ether-*H*), 2.40 (s, 3H, Ar-CH_3). ^{13}CNMR (100 MHz, benzene-d_6, 25 ^{o}C): δ 149.34, 132.21, 132.09, 129.66, 129.28, 128.51, 126.97, 125.64, 124.91, 121.06, 69.83, 64.36, 21.61. Anal. Calcd for $C_{36}H_{41}O_6K$: C, 71.02; H, 6.79. Found: C, 70.71; H, 6.51.

Synthesis of **3**: yield 0.31 g (47.5 %). ^{1}H NMR (400 MHz, benzene-d_6, 25 ^{o}C): δ 7.77 (d, *J* = 4 Hz, 6H, Ph-*H*), 7.36 (d, *J* = 8 Hz, 1H, Ar-*H*), 7.30 (d, 1H, Ar-*H*), 7.11 (t, *J* = 8 Hz, 6H, Ph-*H*), 6.99 (t, *J* = 8 Hz, 3H, Ph-*H*), 6.70 (d, *J* = 8 Hz, 1H, Ar-*H*), 3.07 (br, 24H, crown ether-*H*), 2.47 (s, 3H, Ar-CH_3). ^{13}CNMR (100 MHz, benzene-d_6, 25 ^{o}C): δ 149.76, 134.44, 132.46, 132.27, 129.40, 126.68, 124.27, 120.65, 69.96, 64.67, 21.75. Anal. Calcd for $C_{38}H_{45}O_7K$: C, 69.91; H, 6.95. Found: C, 69.71; H, 6.62.

Synthesis of **4**: yield 0.39 g (52.1 %). ^{1}H NMR (400 MHz, benzene-d_6, 25 ^{o}C): δ 7.77 (d, *J* = 8 Hz, 6H, Ph-*H*), 7.34 (d, *J* = 4 Hz, 1H, Ar-*H*), 7.25 (d, *J* = 8 Hz, 1H, Ar-*H*), 7.04 (t, *J* = 8 Hz, 6H, Ph-*H*), 6.88 (t, *J* = 8 Hz, 3H, Ph-*H*), 6.83-6.80 (m, 4H, crown ether-*H*), 6.71 (d, *J* = 8 Hz, 1H, Ar-*H*), 6.41 (br, 4H, crown ether-*H*), 3.38 (br, 16H, crown ether-*H*), 2.43 (s, 3H, Ar-CH_3). ^{13}CNMR (100 MHz, benzene-d_6, 25 ^{o}C): δ 149.71, 134.45, 132.45, 132.27, 129.40, 129.27, 126.58, 124.08, 121.14, 120.70, 68.52, 67.26, 64.68, 21.73 Anal. Calcd for $C_{46}H_{45}O_7K$: C, 73.77; H, 6.06. Found: C, 73.33; H, 6.20.

Synthesis of **5**: yield 0.33 g (43.2 %). ^{1}H NMR (400 MHz, benzene-d_6, 25 ^{o}C): δ 7.72 (d, *J* = 4 Hz, 6H, Ph-*H*), 7.23 (d, 1H, Ar-*H*), 7.02 (t, *J* = 8 Hz, 6H, Ph-*H*), 6.88 (t, *J* = 8 Hz, 3H, Ph-*H*), 6.84-6.80 (m, 4H, crown ether-*H*), 6.67 (d, *J* = 8 Hz,1H, Ar-*H*), 6.43-6.41 (m, 4H, crown ether-*H*), 3.61 (s, 3H, Ar-OCH_3), 3.41 (br, 8H, crown ether-*H*), 3.35 (br, 8H, crown ether-*H*). ^{13}CNMR (100 MHz, benzene-d_6, 25 ^{o}C): δ 149.29, 147.79, 145.39, 134.08, 132.42, 129.34, 126.72, 124.34, 121.19, 119.85, 119.04, 115.74, 111.24, 68.33, 67.70, 64.74, 56.83. Anal. Calcd for $C_{46}H_{45}O_8K$: C, 72.23; H, 5.93. Found: C, 71.82; H, 5.98.

Synthesis of **6**: yield 0.40 g (49.8 %). ^{1}H NMR (300 MHz, benzene-d_6, 25 ^{o}C): δ 7.68 (br, 6H, Ph-*H*), 7.48 (s, 1H, Ar-*H*), 7.01 (t, *J* = 9 Hz, 6H, Ph-*H*), 6.92 (t, *J* = 9 Hz, 3H, Ph-*H*), 6.84 (m, 4H, crown ether-*H*), 6.47 (br, 4H, crown ether-*H*), 3.41 (br, 8H, crown ether-*H*), 3.12 (br, 8H, crown ether-*H*), 2.46 (s, 3H, Ar-CH_3), 1.57 (s, 9H, Ar-C(CH_3)$_3$). ^{13}CNMR (100 MHz, benzene-d_6, 25 ^{o}C): δ 147.84, 133.08, 132.52, 126.64, 124.58, 121.31, 111.61, 67.47, 66.17, 35.56, 32.76, 30.41. Anal. Calcd for $C_{50}H_{53}O_7K$: C, 74.60; H, 6.64. Found: C, 74.86; H, 6.67.

Typical polymerization of *rac*-lactide

A typical polymerization procedure is exemplified by the synthesis of poly(*rac*-LA) at room temperature (Table 1, entry 4). *Rac*-Lactide (0.288 g, 2.0 mmol) was added to a solution of **4** (0.015 g, 0.02 mmol) and BnOH (2.0 μl, 0.02 mmol) in toluene (5 mL). After the solution was stirred at room temperature for 1 min, the reaction was then quenched by the addition of a drop of water. Then the solution was concentrated under vacuum, and the polymer was recrystallized from dichloromethane and hexane. The final polymer was then dried under vacuum to constant weight.

Crystallographic Studies

The data were collected on SuperNova (Dual) X-ray diffraction diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods of Siemens SHELXTL PLUS program.[3] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms were placed by geometrical considerations and were added to the structure-factor calculation.

Figure S1 ^{1}H NMR spectrum (300 MHz, chloroform-d, 25 ^{o}C) of **L**^{1}H.

Figure S2 ^{13}C NMR spectrum (75 MHz, chloroform-d, 25 ^{o}C) of **L**^{1}H.

Figure S3 ^{1}H NMR spectrum (300 MHz, chloroform-d, 25 ^{o}C) of **L**^{2}H.

Figure S4 ^{13}C NMR spectrum (75 MHz, chloroform-d, 25 ^{o}C) of **L**^{2}H.

Figure S5 ^{1}H NMR spectrum (300 MHz, chloroform-d, 25 ^{o}C) of $\mathbf{L^{3}H}$.

Figure S6 ^{13}C NMR spectrum (75 MHz, chloroform-d, 25 ^{o}C) of $\mathbf{L^{3}H}$.

Figure S7 ^{1}H NMR spectrum (400 MHz, benzene-d_6, 25 ^{o}C) of **1**.

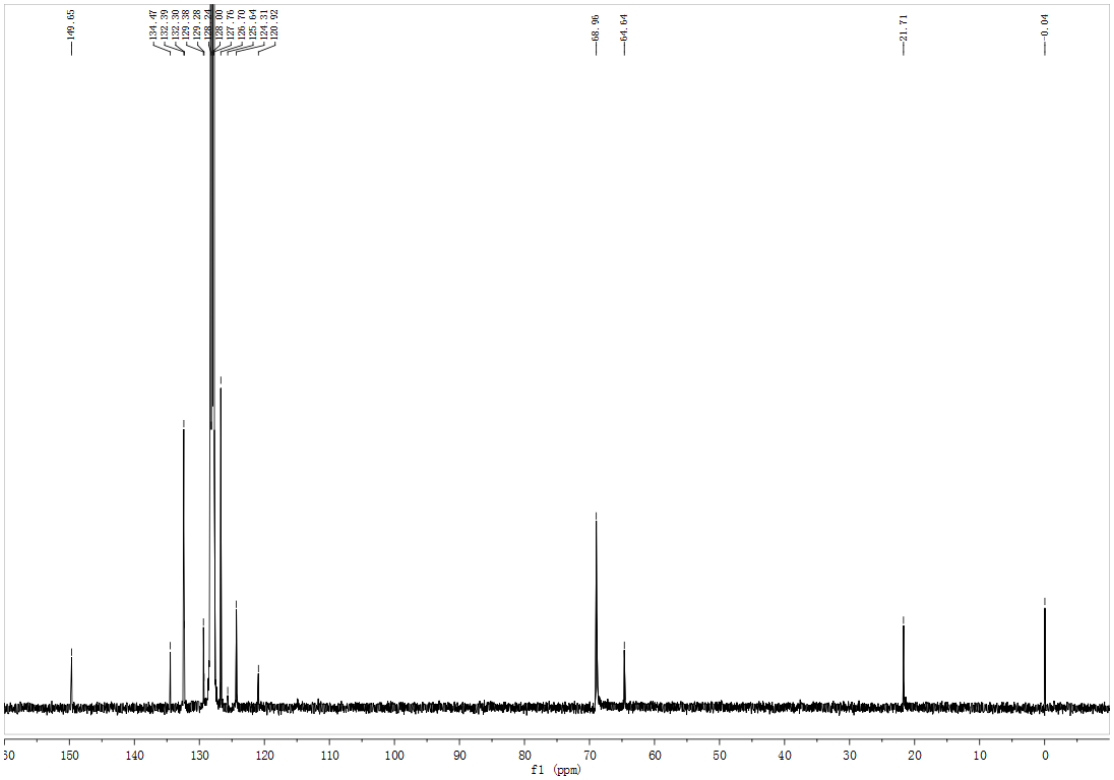

Figure S8 ^{13}C NMR spectrum (100 MHz, benzene-d_6, 25 ^{o}C) of **1**.

Figure S9 ^{1}H NMR spectrum (400 MHz, benzene-d_6, 25 ^{o}C) of **2**.

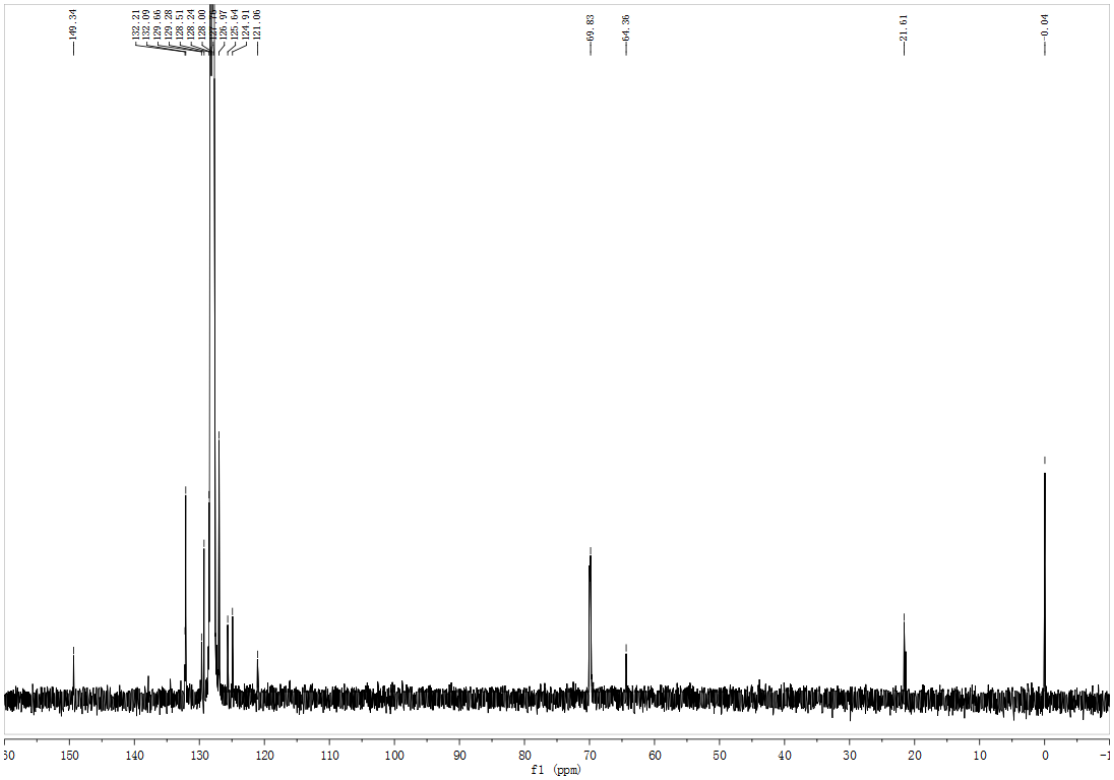

Figure S10 ^{13}C NMR spectrum (100 MHz, benzene-d_6, 25 ^{o}C) of **2**.

Figure S11 ^{1}H NMR spectrum (400 MHz, benzene-d_6, 25 ^{o}C) of **3**.

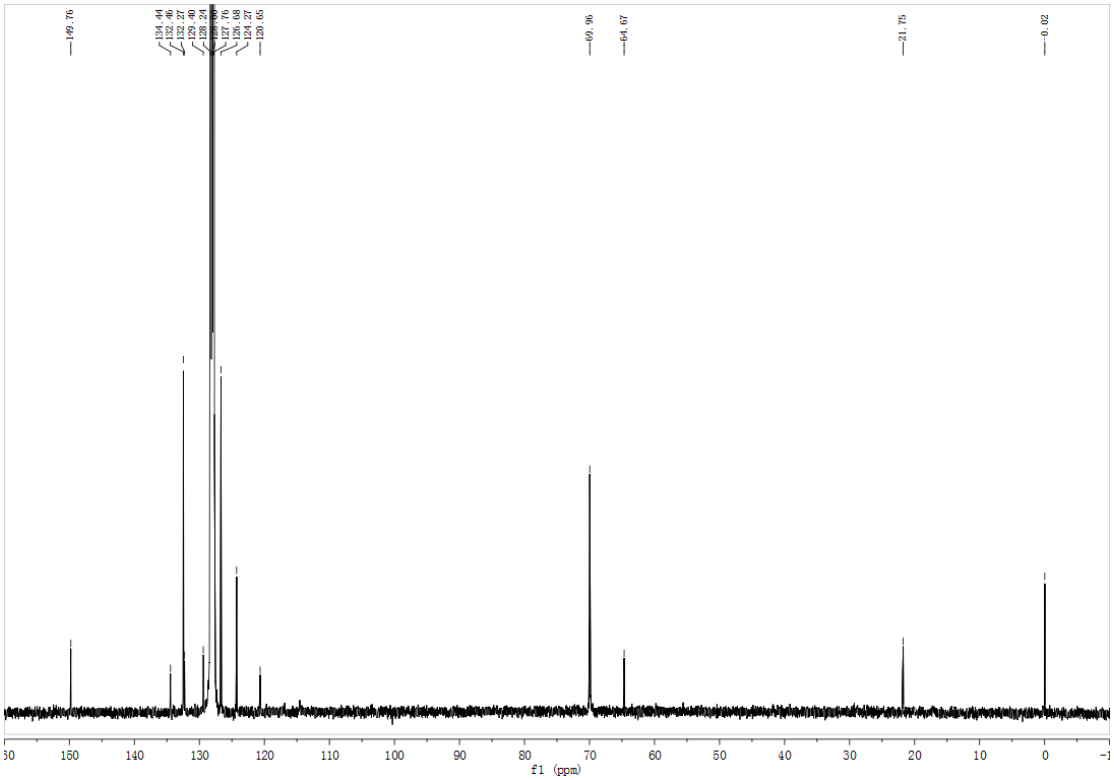

Figure S12 ^{13}C NMR spectrum (100 MHz, benzene-d_6, 25 ^{o}C) of **3**.

Figure S13 ^{1}H NMR spectrum (400 MHz, benzene-d_6, 25 ^{o}C) of **4**.

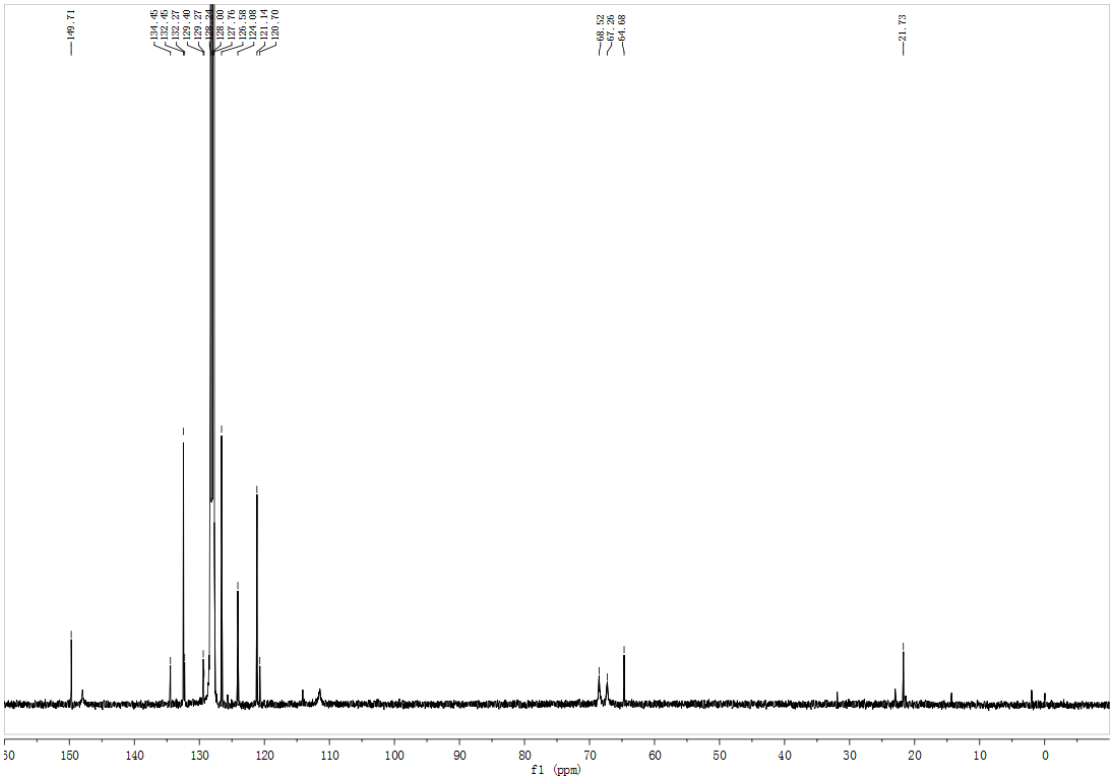

Figure S14 ^{13}C NMR spectrum (100 MHz, benzene-d_6, 25 ^{o}C) of **4**.

Figure S15 ^{1}H NMR spectrum (400 MHz, benzene-d_6, 25 ^{o}C) of **5**.

Figure S16 ^{13}C NMR spectrum (100 MHz, benzene-d_6, 25 ^{o}C) of **5**.

Figure S17 ^{1}H NMR spectrum (300 MHz, benzene-d_6, 25 ^{o}C) of **6**.

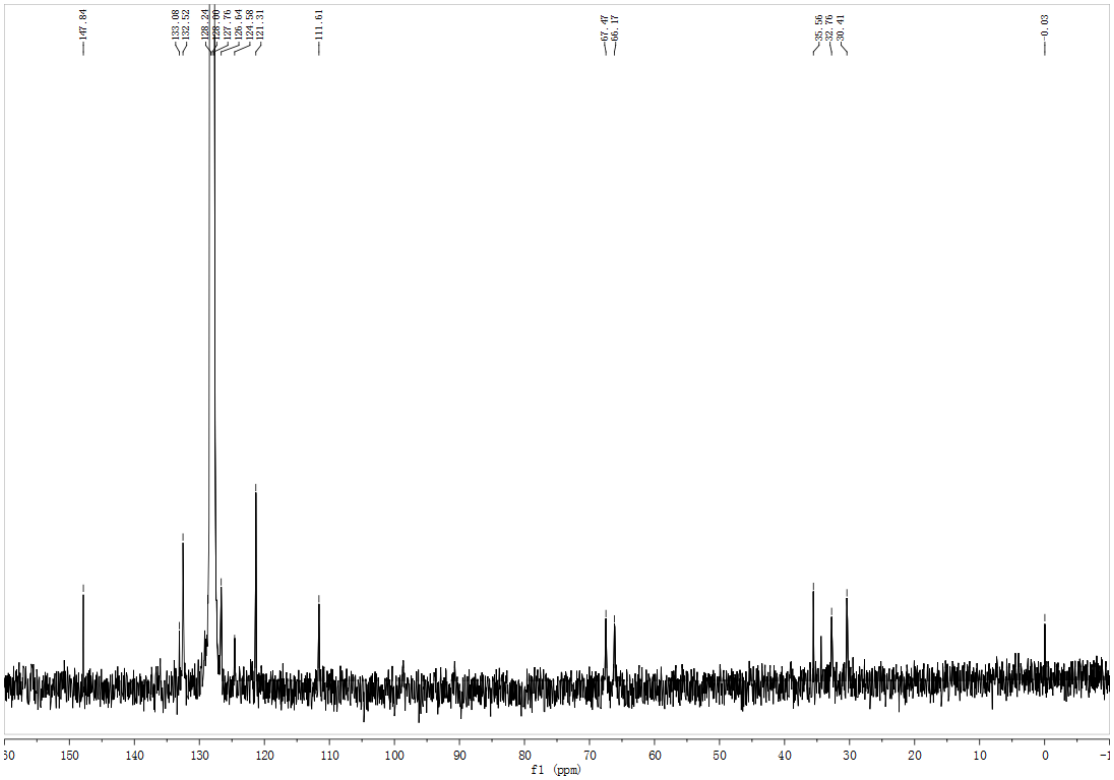

Figure S18 ^{13}C NMR spectrum (100 MHz, benzene-d_6, 25 ^{o}C) of **6**.

Peak	Integration	P_m
rmr	0.030	0.75
rmm	0.082	0.79
mmr	0.079	0.80
mmm	0.659	0.75
mrm	0.132	0.74
	Average	0.77

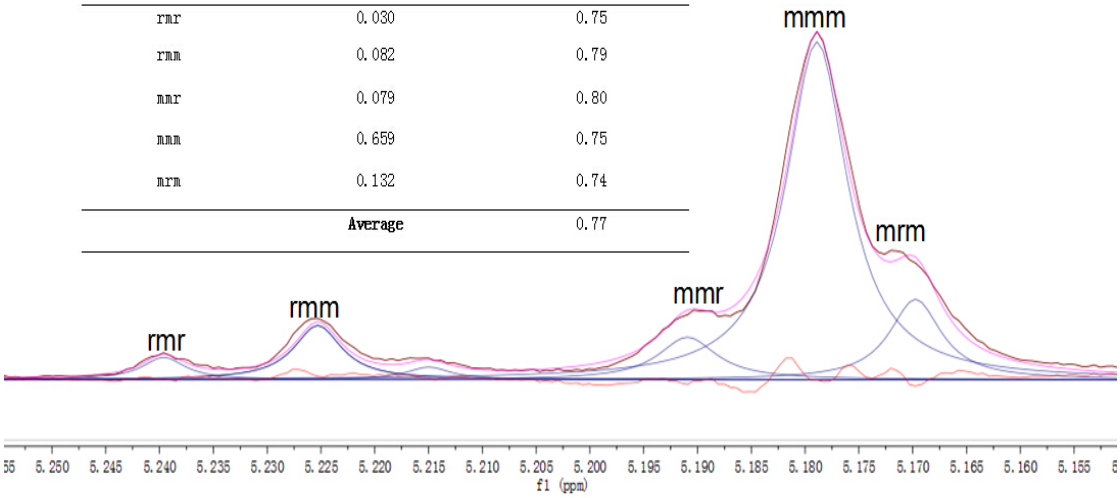

Figure S19 The homonuclear-decoupled ^{1}H NMR spectrum of PLA. ($[LA]_0/[M]_0/[BnOH]_0$ = 100:1:1, entry 4, P_m = 0.77, Table 1).

Peak	Integration	P_m
rmr	0.023	0.79
rmm	0.052	0.88
mmr	0.055	0.87
mmm	0.767	0.83
mrm	0.082	0.84
	Average	0.84

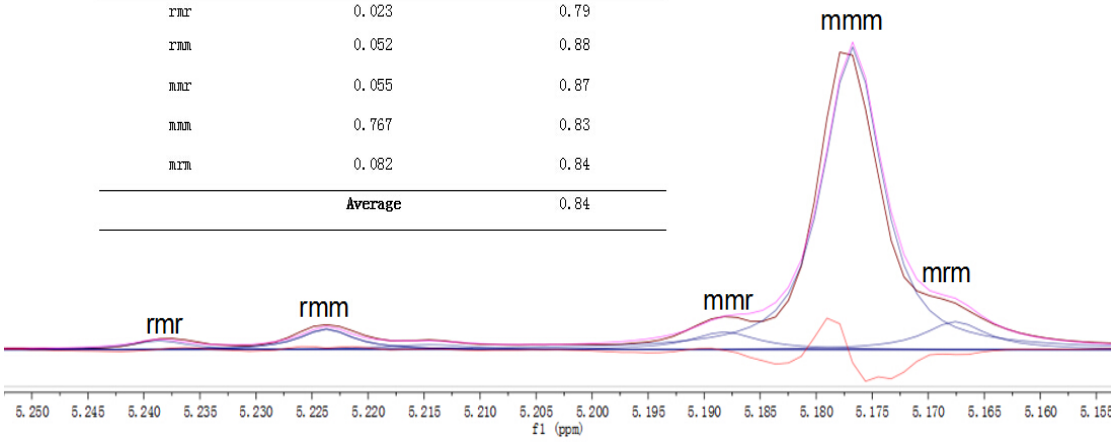

Figure S20 The homonuclear-decoupled ^{1}H NMR spectrum of PLA. ($[LA]_0/[M]_0/[BnOH]_0$ = 100:1:1, P_m = 0.84, entry 14, Table 1).

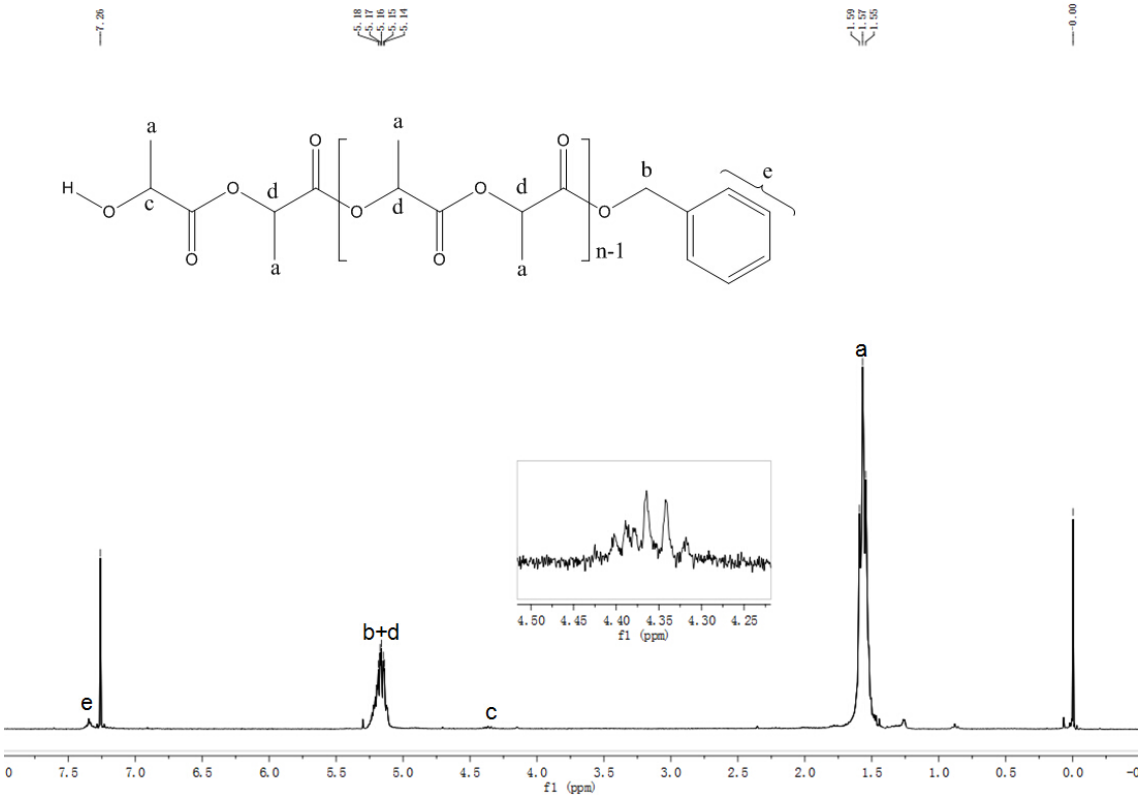

Figure S21 ^{1}H NMR spectrum of PLA prepared by catalyst **4** ($[LA]_0/[M]_0/[BnOH]_0$ = 20:1:1).

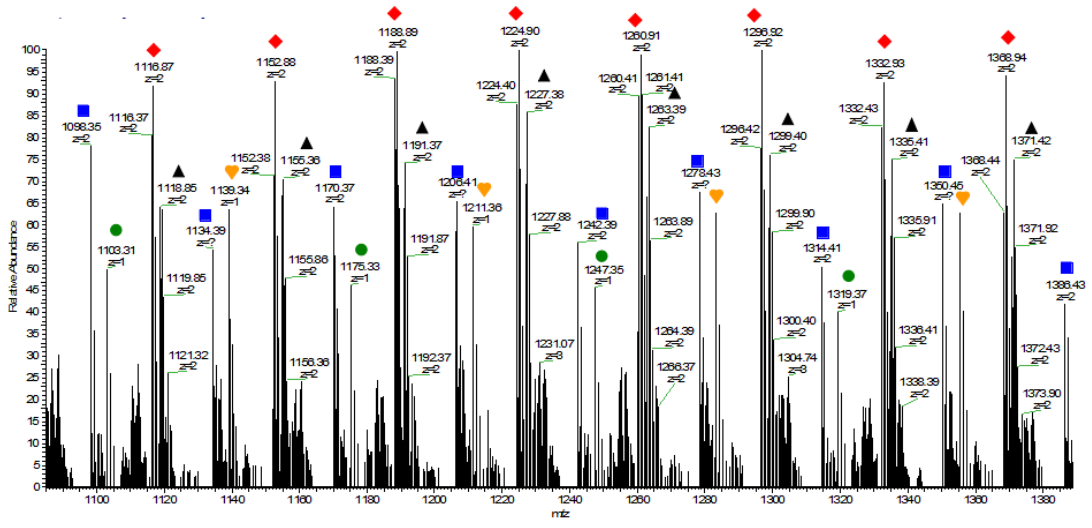

Figure S22 ESI-MS spectrum of PLA prepared by catalyst **4**. ($[LA]_0$:$[M]_0$:$[BnOH]_0$ = 20 : 1 :1, Mass (♦)= (72m + 108($PhCH_2OH$) + 38 ($2H_3O^+$))/2; Mass (▲)= (72m + 108($PhCH_2OH$) + 19 (H_3O^+) + 23 (Na^+))/2; Mass (■)= (72m +36($2NH_4^+$))/2; Mass (●)= (72m + 23 (Na^+)); Mass (♥)= 72m + 108($PhCH_2OH$) + 23 (Na^+)).

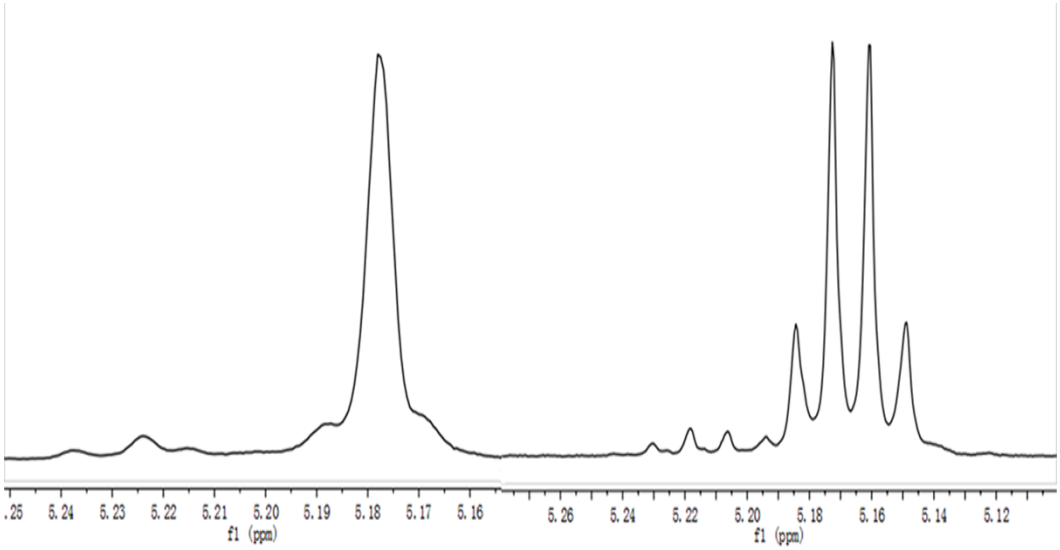

Figure S23. The homonuclear-decoupled ^{1}H NMR spectrum (left) of PLA vs the ^{1}H NMR spectrum (right) of PLA. (entry 15, Table 1).

References

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