

Supporting information

Alkali-metal Monophenolates with a Sandwich-type Center as Catalysts for Highly Isolelective Polymerization of *rac*-Lactide

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Experiment

Materials and Methods. All the syntheses were performed under a dry nitrogen 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; CH₂Cl₂ and CHCl₃ was distilled from P₂O₅; BnOH were distilled from CaH₂; *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. ¹H NMR and ¹³C NMR were recorded on a Varian Mercury Plus 300 MHz spectrometer, JNM_ECS 400 MHz, and Varian INOVA 600 MHz. ¹H 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-d₆, δ 2.08 ppm for toluene-d₈, δ 5.32 ppm for dichloromethane-d₂. ¹³C{¹H} NMR chemical shifts are reported in ppm versus residual ¹³C in the solvent: δ 77.0 ppm for chloroform-d, δ 128.06 ppm for benzene-d₆, δ 137.48 ppm for toluene-d₈. 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 (10^2 - 10^6 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 (5.0 mg) were placed in aluminum pans and heated/cooled at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere. The previous thermal history of the samples was erased by heating them to $200\text{ }^{\circ}\text{C}$ before cooling them to $0\text{ }^{\circ}\text{C}$. Measurements were performed between $30\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$. The melting temperatures were evaluated as the maxima of the melting endotherms. The MALDI TOF mass spectroscopic data were obtained using α -cyano-4-hydroxycinnamic acid as the matrix in a Bruker Daltonics, Inc. BIFLEX III MALDI TOF mass spectrometer. The ESI mass spectroscopic data were obtained using a Thermo Scientific Orbitrap Elite MS (LTQ Orbitrap Elit).

Synthesis of HL: Under an inert atmosphere, 4-*tert*-butylphenol (0.3 g, 2.0 mmol) and xanthidrol (0.8 g, 4.0 mmol) were mixed in a 100 mL Schlenk flask. The mixture was heated to $128\text{ }^{\circ}\text{C}$ slowly to produce a melt, then the temperature was maintained for 2 h to ensure a reaction completed. After cooling to room temperature, the crude solid was recrystallized from methanol, and a white solid was achieved (0.74 g, 73 % yield). $^1\text{H NMR}$ (300 MHz, chloroform-*d*, $25\text{ }^{\circ}\text{C}$): δ 7.20-7.24 (m, 4H, Ar-*H*), 7.12 (d, 4H, Ar-*H*), 7.03 (s, 2H, Ar-*H*), 6.97 (d, 8H, Ar-*H*), 5.51 (s, 2H, Ar-*CH*-Ar), 4.53 (s, 1H, Ar-*OH*), 1.20 (s, 9H, Ar- $\text{C}(\text{CH}_3)_3$), $^{13}\text{CNMR}$ (75 MHz, chloroform-*d*, $25\text{ }^{\circ}\text{C}$): δ 151.45, 148.41, 143.77, 130.69, 128.91, 128.14, 127.43, 123.51, 123.31, 116.44

(Ar-C), 39.40 (Ar-CH-Ar), 34.04 (Ar-C(CH₃)₃), 31.46 (Ar-C(CH₃)₃). Anal. Calcd for C₃₆H₃₀O₃: C, 84.68; H, 5.92. Found: C, 84.21; H, 5.68.

General Preparation Procedures for **1a-1c**: Under an inert atmosphere, a KHMDS/NaHMDS solution (1.2 mmol, 1 mol/L in THF) was added dropwise into a THF solution (10 mL) of HL (1.0 mmol) and 18-Crown-6/15-Crown-5 (1.0 mmol). The reaction mixture was stirred overnight. The solution was filtered. Volatile materials were removed from the filtrate under vacuum and the residue was recrystallized from a THF solution affording a white crystalline powder.

Synthesis of **1a**: yield 0.52 g (61 %). ¹H NMR (400 MHz, benzene-d₆, 25 °C): δ 7.82 (d, *J* = 8 Hz, 4H, Ar-*H*), 7.24 (d, *J* = 8 Hz, 4H, Ar-*H*), 7.23 (s, 2H, Ar-*H*), 7.02 (m, 6H, Ar-*H* and Ar-CH-Ar), 6.90 (t, *J* = 8 Hz, 4H, Ar-*H*), 2.99 (s, 24H, crown ether-*H*), 1.15 (s, 9H, Ar-C(CH₃)₃), ¹³CNMR (100 MHz, benzene-d₆, 25 °C): δ 152.97, 131.13, 130.03, 126.53, 122.97, 115.79 (Ar-*C* and Ar-CH-Ar), 70.07 (crown ether-*C*), 32.42 (Ar-C(CH₃)₃). Anal. Calcd for C₄₈H₅₃O₉K·0.5 THF: C, 70.73; H, 6.77. Found: C, 70.39; H, 6.53.

Synthesis of **1b**: yield 0.45 g (57 %). ¹H NMR (400 MHz, toluene-d₈, 25 °C): δ 7.57 (br, 4H, Ar-*H*), 7.14 (m, 6H, Ar-*H*), 7.01 (m, 6H, Ar-CH-Ar and Ar-*H*), 6.83 (t, 4H, *J* = 8 Hz, Ar-*H*), 2.94 (s, 20H, crown ether-*H*), 1.13 (s, 9H, Ar-C(CH₃)₃), ¹³CNMR (150 MHz, toluene-d₈, 25 °C): δ = 152.85, 130.77, 129.18, 126.62, 122.91, 115.86 (Ar-*C* and Ar-CH-Ar), 68.91 (crown ether-*C*), 33.99 (Ar-C(CH₃)₃), 32.24 (Ar-C(CH₃)₃). Anal. Calcd for C₄₆H₄₉O₈Na·0.5 THF: C, 73.08; H, 6.77. Found: C, 72.82; H, 6.63.

Synthese of **1c**: yield 0.43 g (52 %). ^1H NMR (400 MHz, benzene- d_6 , 25 $^\circ\text{C}$): δ 7.76 (d, J = 8 Hz, 4H, Ar- H), 7.28 (s, 2H, Ar- H), 7.25 (d, J = 8 Hz, 4H, Ar- H), 7.04 (t, 4H, J = 8 Hz, Ar- H), 6.93 (t, 6H, J = 8 Hz, Ar- H and Ar-CH-Ar), 3.03 (s, 24H, crown ether- H), 1.15 (s, 9H, Ar-C(CH_3) $_3$), ^{13}C NMR (100 MHz, benzene- d_6 , 25 $^\circ\text{C}$): δ 153.06, 130.83, 130.04, 126.65, 122.92, 115.84 (Ar-C and Ar-CH-Ar), 69.30 (crown ether-C), 34.03 (Ar-C(CH_3) $_3$), 32.35 (Ar-C(CH_3) $_3$). Anal. Calcd for $\text{C}_{48}\text{H}_{53}\text{O}_9\text{Na}\cdot 0.5\text{THF}$: C, 72.10; H, 6.90. Found: C, 72.31; H, 6.50.

Typical polymerization of *rac*-lactide.

A typical polymerization procedure is exemplified by the synthesis of poly(*rac*-LA) at room temperature (Table1, entry 5). *Rac*-Lactide (0.288 g, 2.0 mmol) was added to a solution of **1a** (0.016 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 10 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 $\text{K}\alpha$ radiation (λ = 0.71073 Å). The structure was solved by direct methods of Siemens SHELXTL PLUS program.^[2] 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.

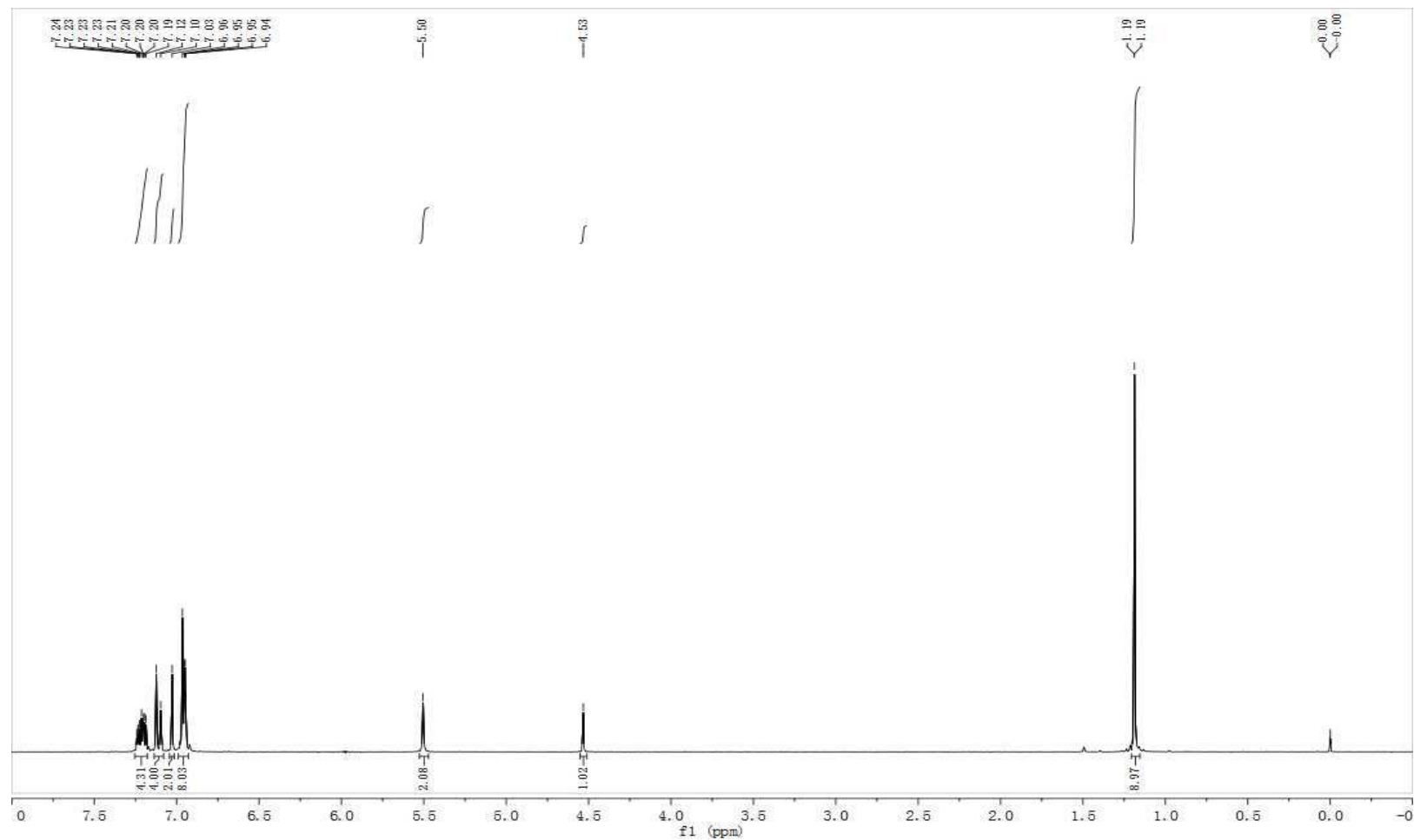


Fig. S1 ¹H NMR spectrum (300 MHz, chloroform-d, 25 °C) of HL.

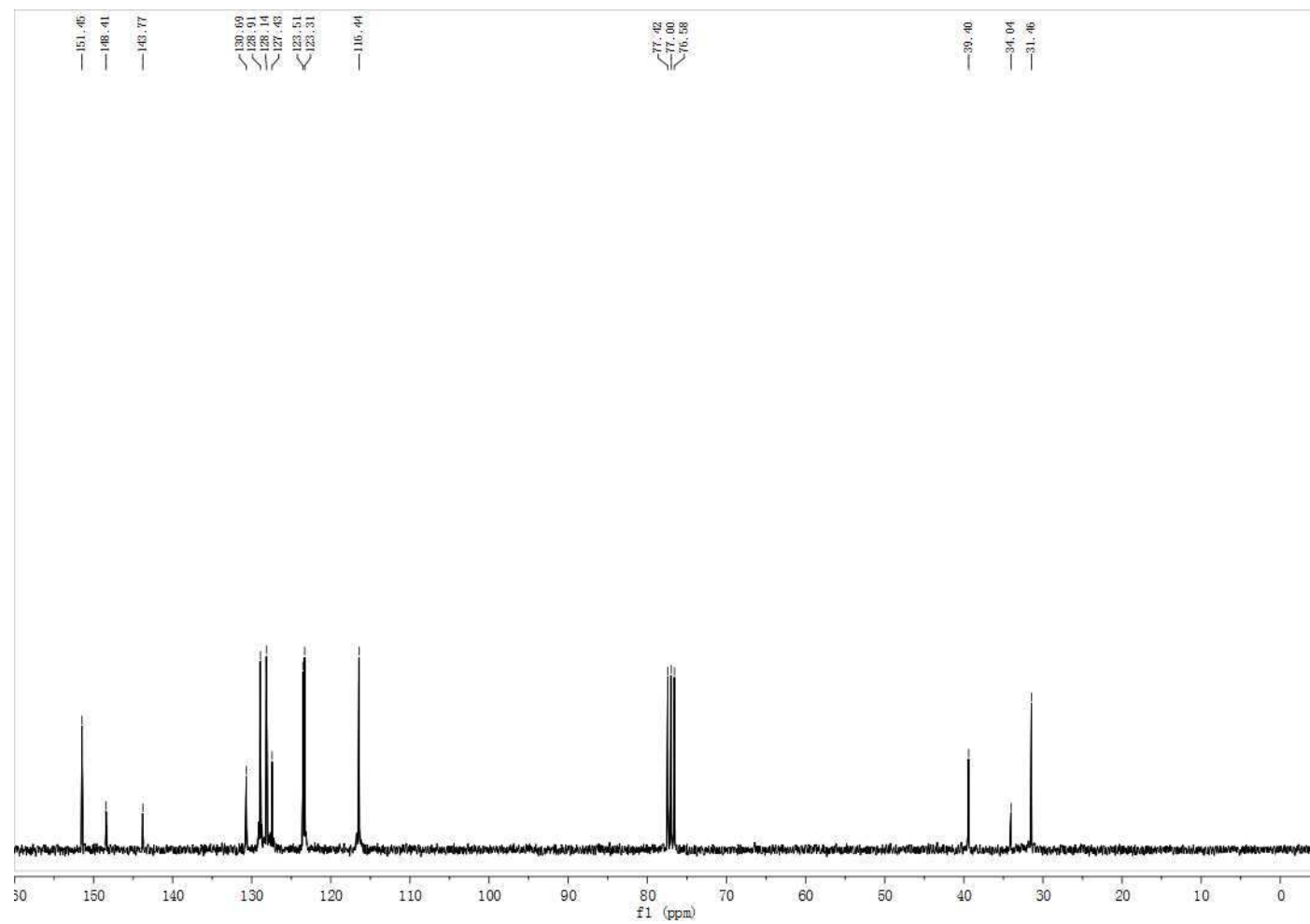


Fig. S2 ^{13}C NMR spectrum (75 MHz, chloroform-d, 25 $^{\circ}\text{C}$) of HL.

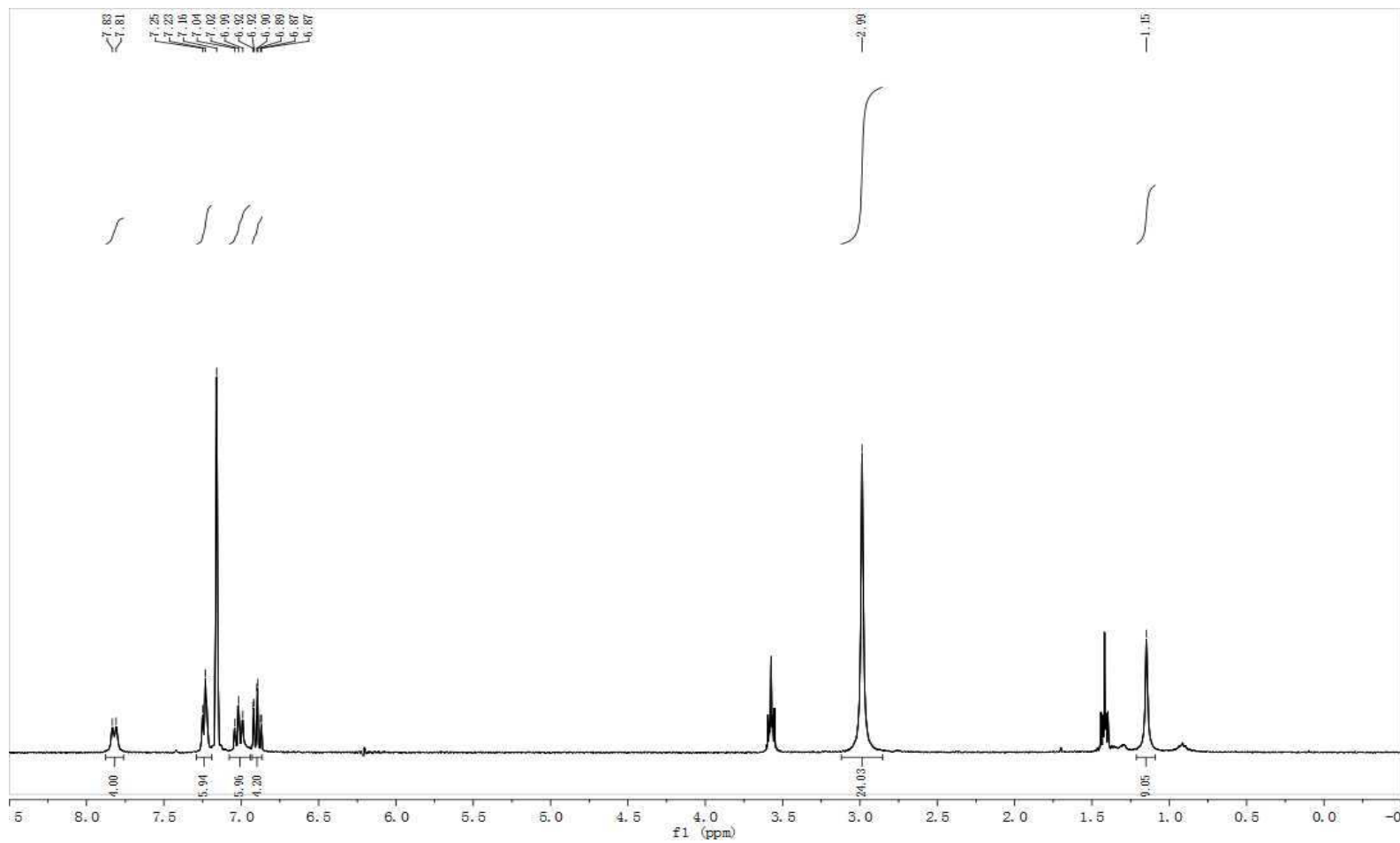


Fig. S3 ^1H NMR spectrum (400 MHz, benzene- d_6 , 25 $^\circ\text{C}$) of **1a**.

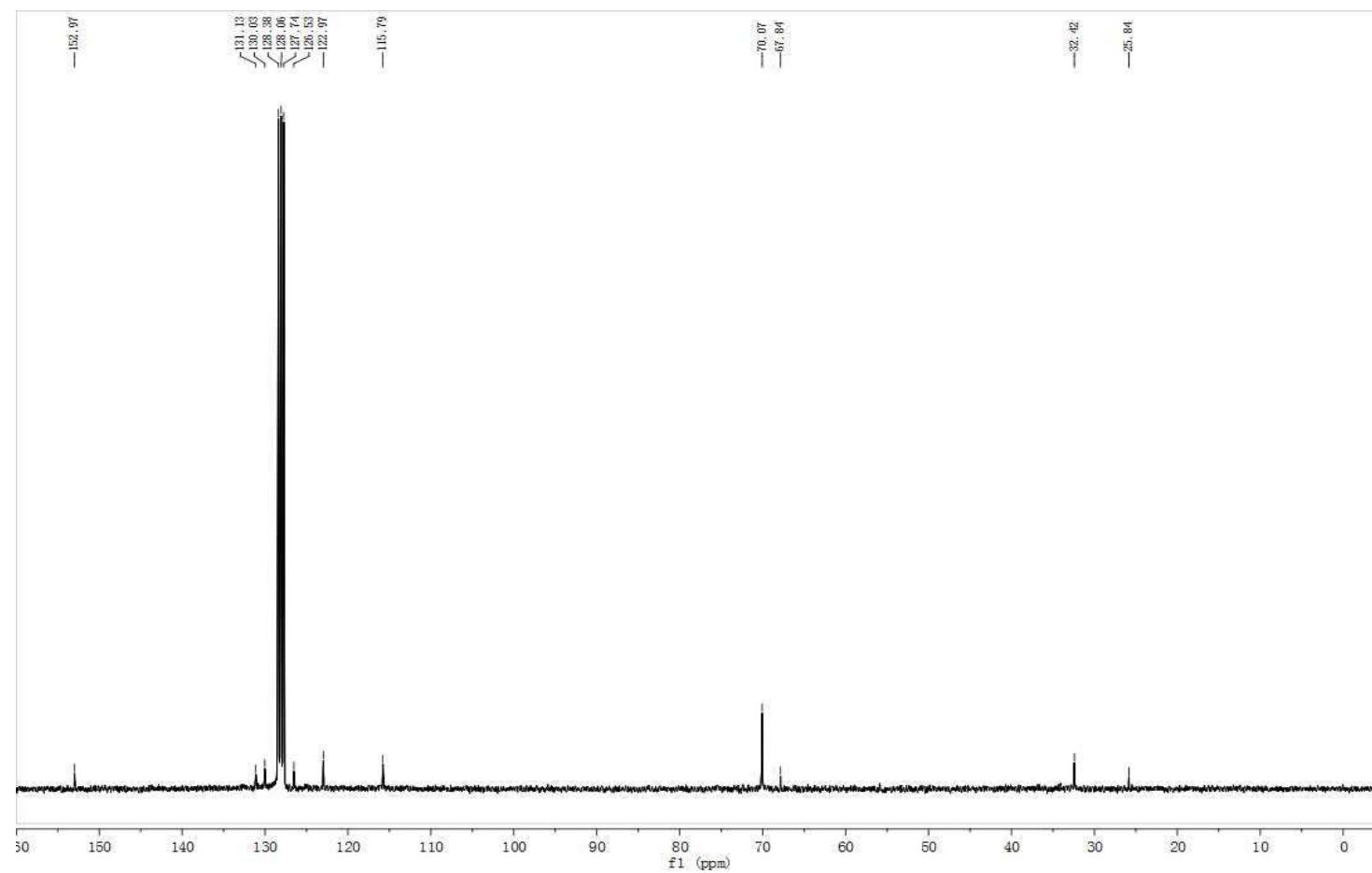


Fig. S4 ^{13}C NMR spectrum (100 MHz, benzene- d_6 , 25 $^\circ\text{C}$) of **1a**.

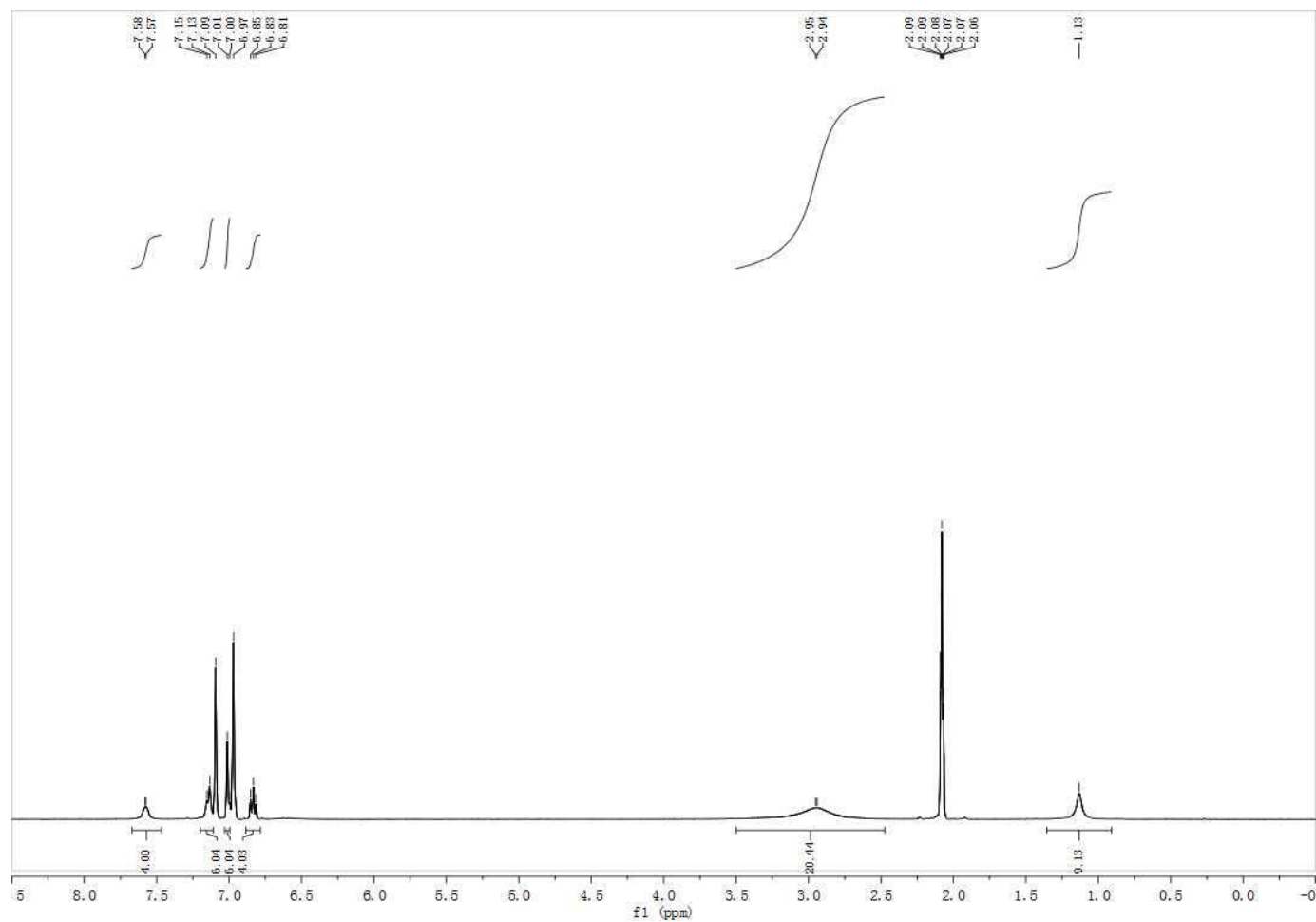


Fig. S5 ¹H NMR spectrum (400 MHz, toluene-d₈, 25 °C) of **1b**.

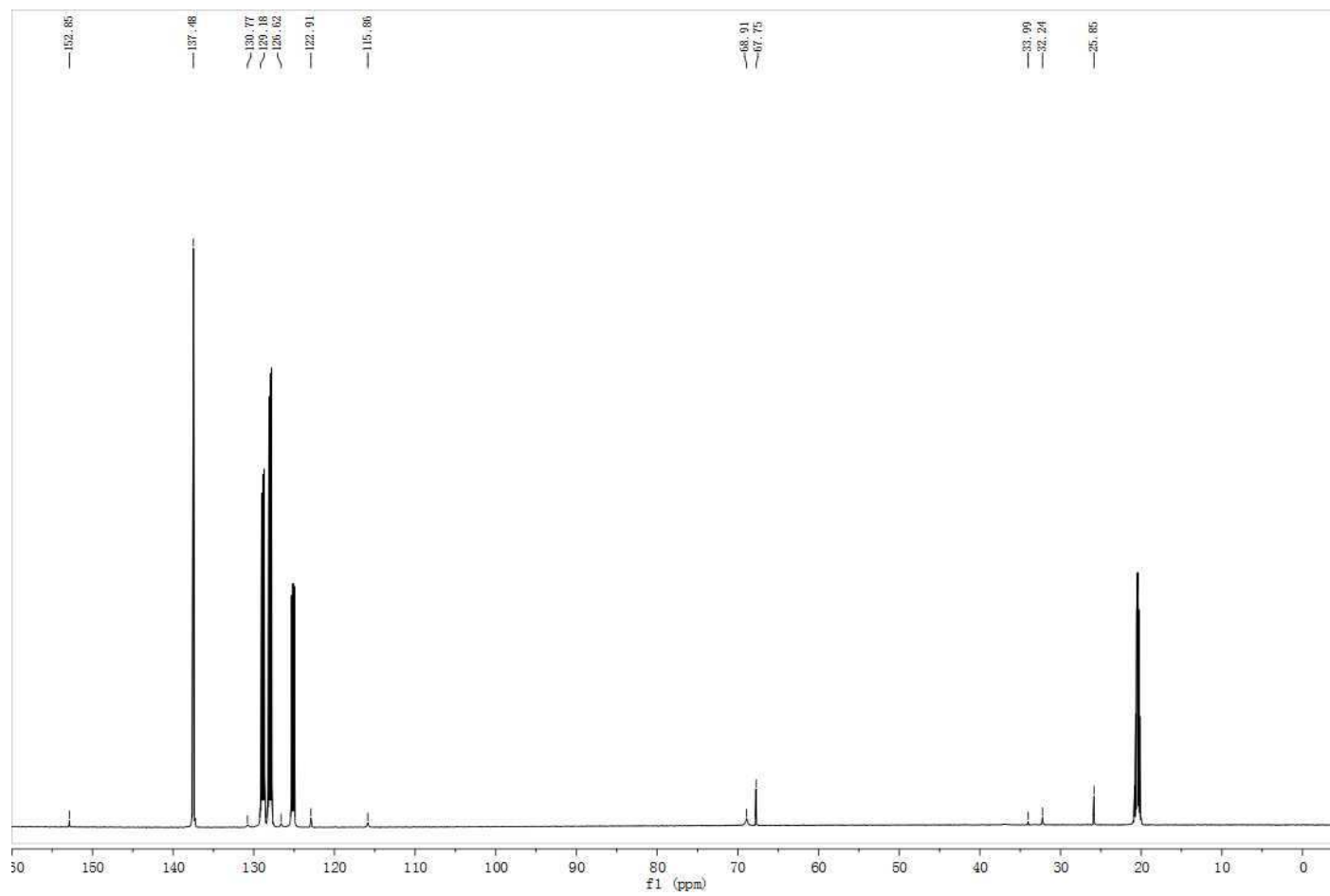


Fig. S6 ^{13}C NMR spectrum (150 MHz, toluene- d_8 , 25 $^{\circ}\text{C}$) of **1b**.

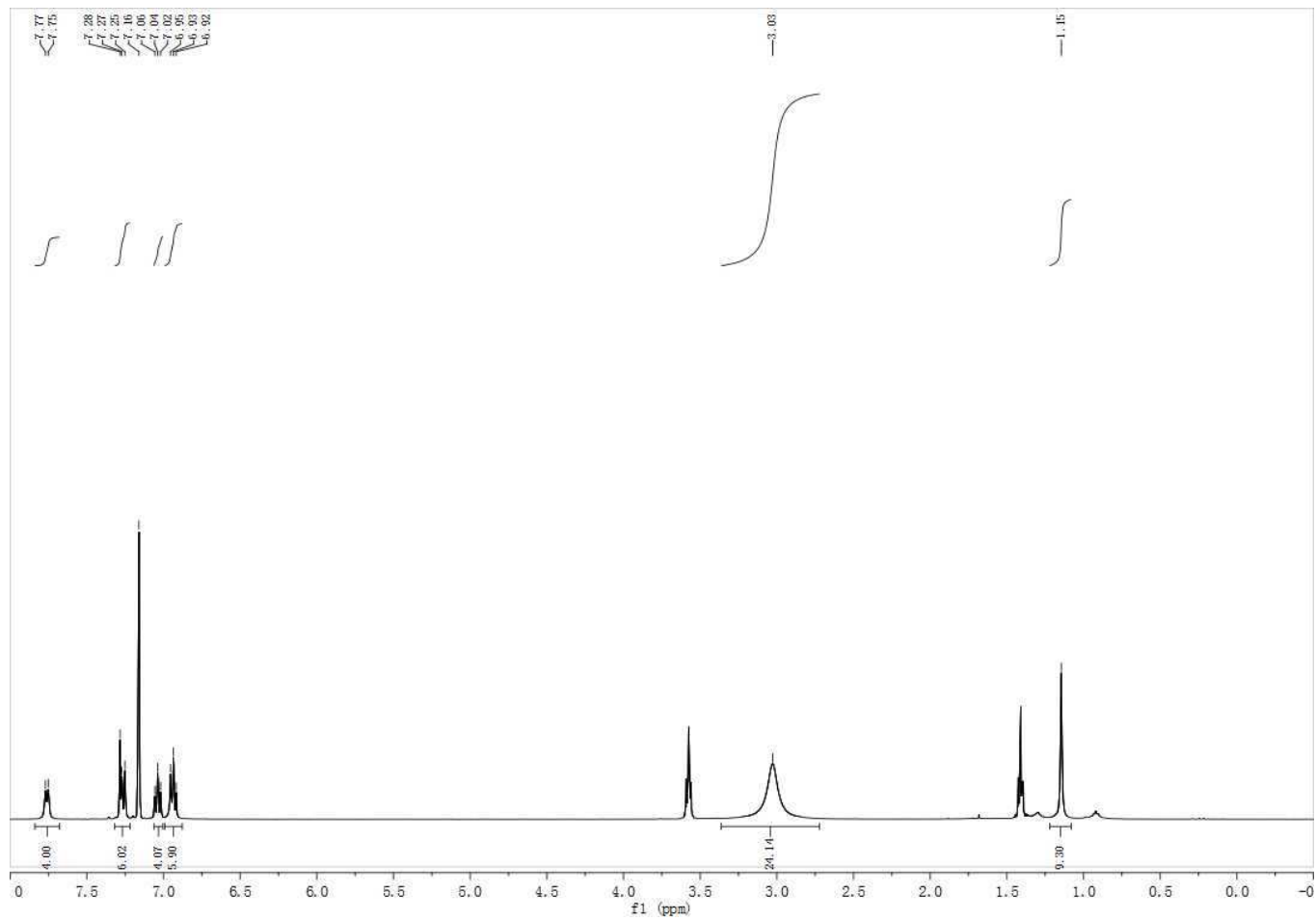


Fig. S7 ^1H NMR spectrum (400 MHz, benzene- d_6 , 25 $^\circ\text{C}$) of **1c**.

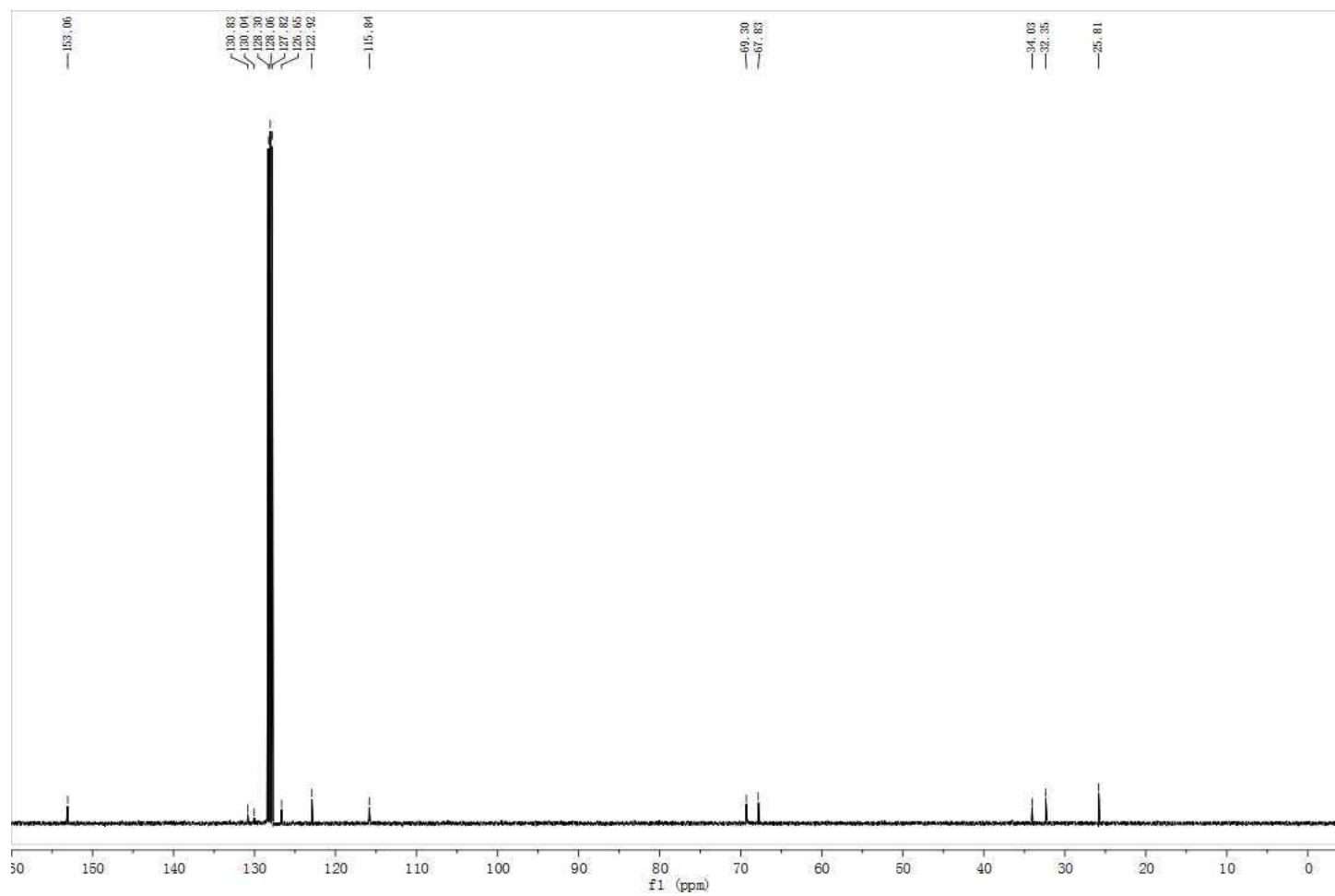


Fig. S8 ^{13}C NMR spectrum (100 MHz, benzene- d_6 , 25 $^{\circ}\text{C}$) of **1c**.

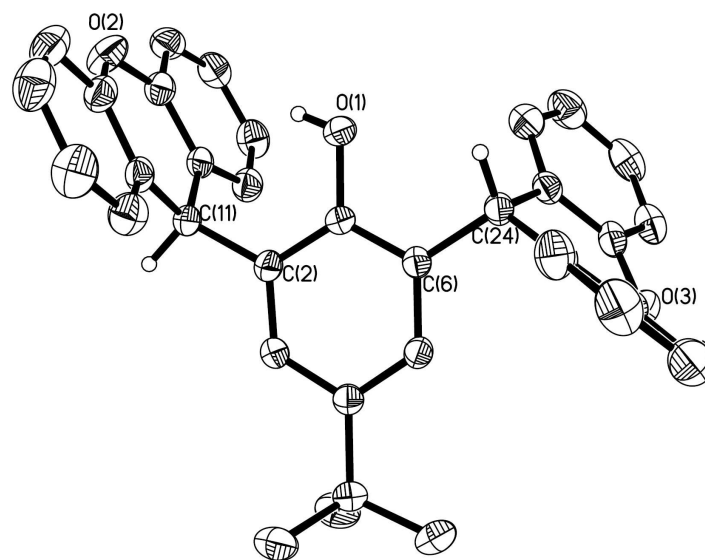


Fig. S9. ORTEP drawing of phenolic ligands (HL) with probability ellipsoids at the 30%, most of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C2-C11 1.522(3), C6-C24 1.532(3).

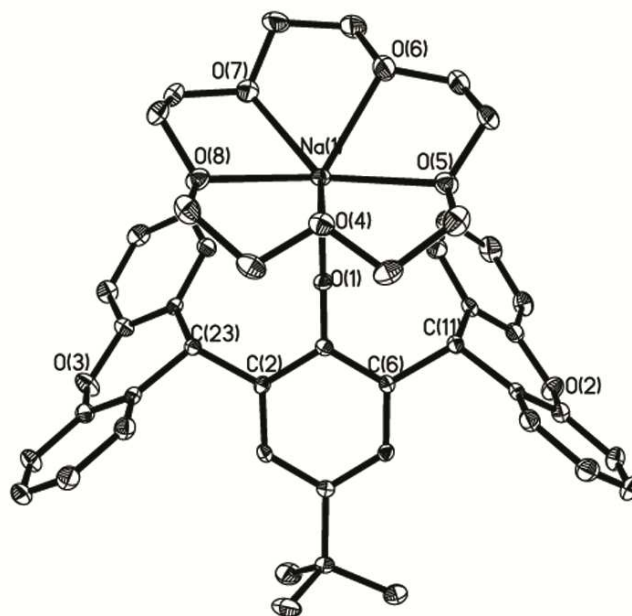


Fig. S10 ORTEP drawing of complex **1b** with probability ellipsoids at the 30%, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Na1-O1 2.1482(17), Na1-O4 2.4436(19), Na1-O5 2.4306(19), Na1-O6 2.3619(19), Na1-O7 2.457(2), Na1-O8 2.3687(18), O1-Na1-O4 93.41(7), O1-Na1-O5 94.15(6), O1-Na1-O6 136.23(8), O1-Na1-O7 115.96(7), O1-Na1-O8 98.07(6).

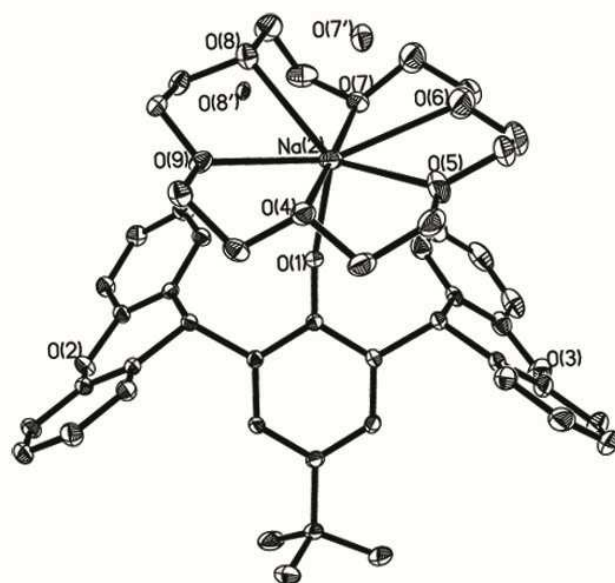


Fig. S11 ORTEP drawing of complex **1c** with probability ellipsoids at the 30%, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Na2-O1 2.1860(18), Na2-O4 2.783(2), Na2-O5 2.580(2), Na2-O6 2.865(3), Na2-O7 2.744(2), Na2-O8 2.764(4), Na2-O9 2.6329(19), O1-Na2-O4 89.81(6), O1-Na2-O5 99.35(7), O1-Na2-O6 115.06(8), O1-Na2-O7 95.61(7), O1-Na2-O8 118.66(13), O1-Na2-O9 87.57(6).

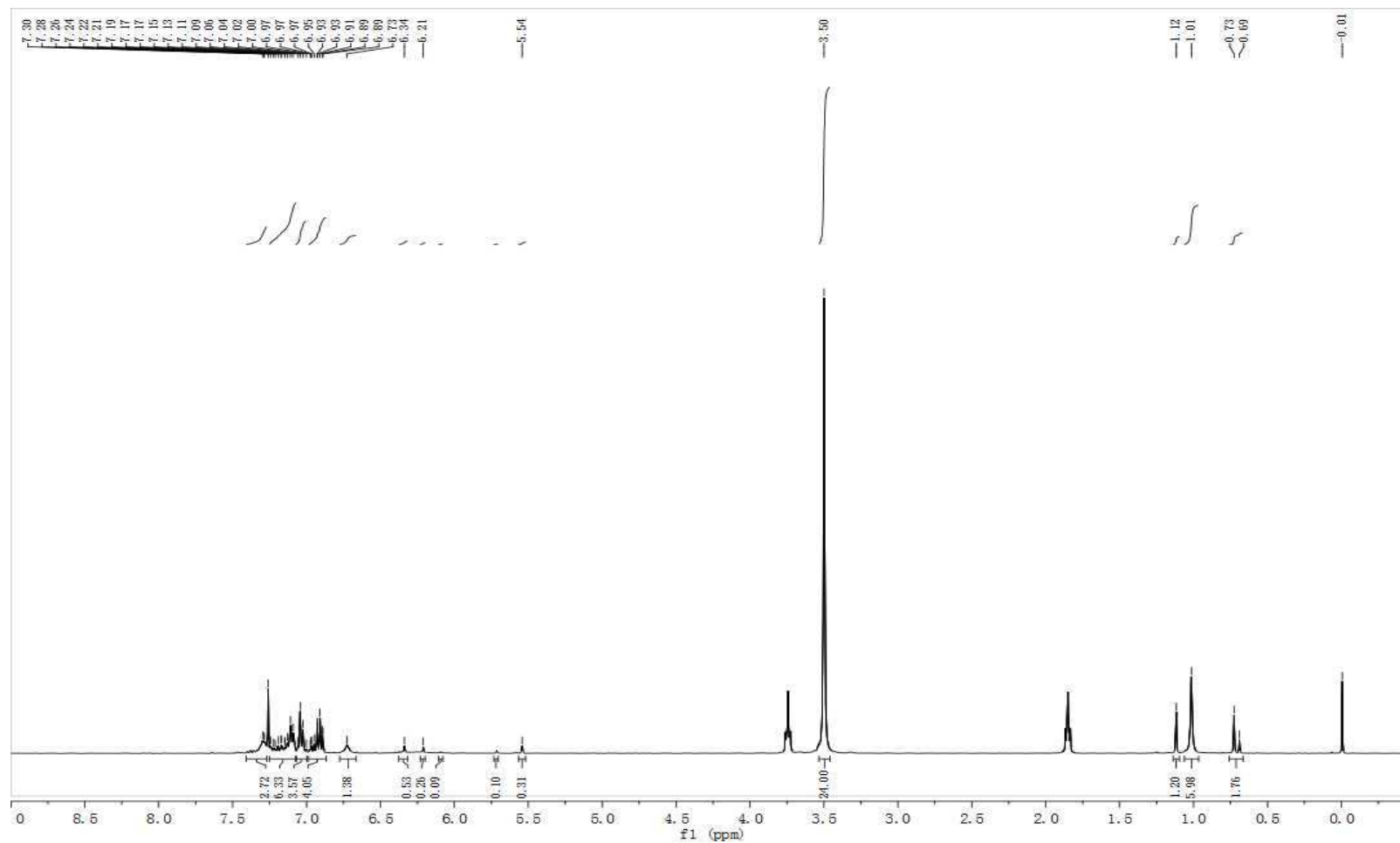


Fig. S12 ^1H NMR spectrum of **1a** in chloroform-d (400 MHz, 25 $^\circ\text{C}$).

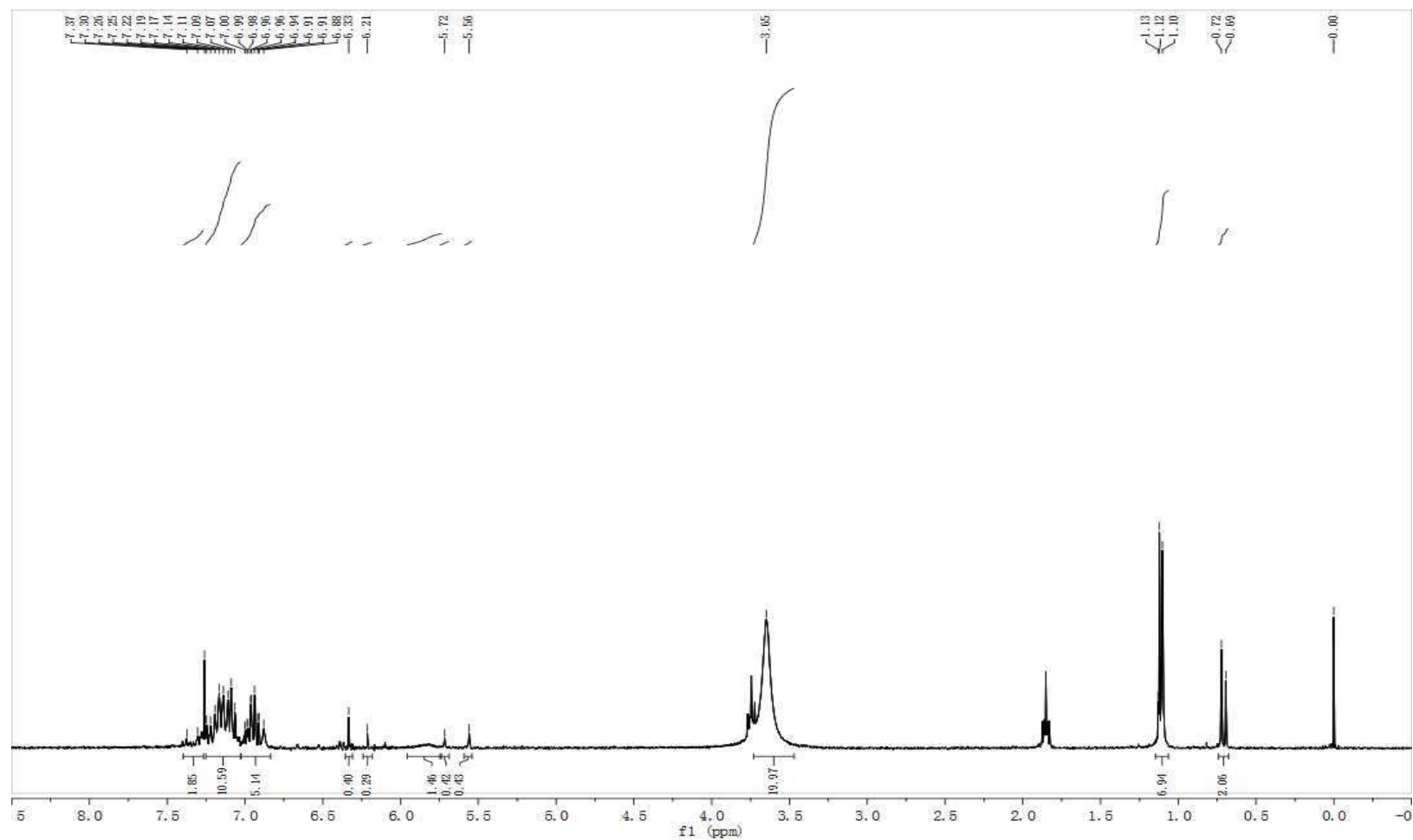


Fig. S13 ¹H NMR spectrum of **1b** in chloroform-d (400 MHz, 25 °C).

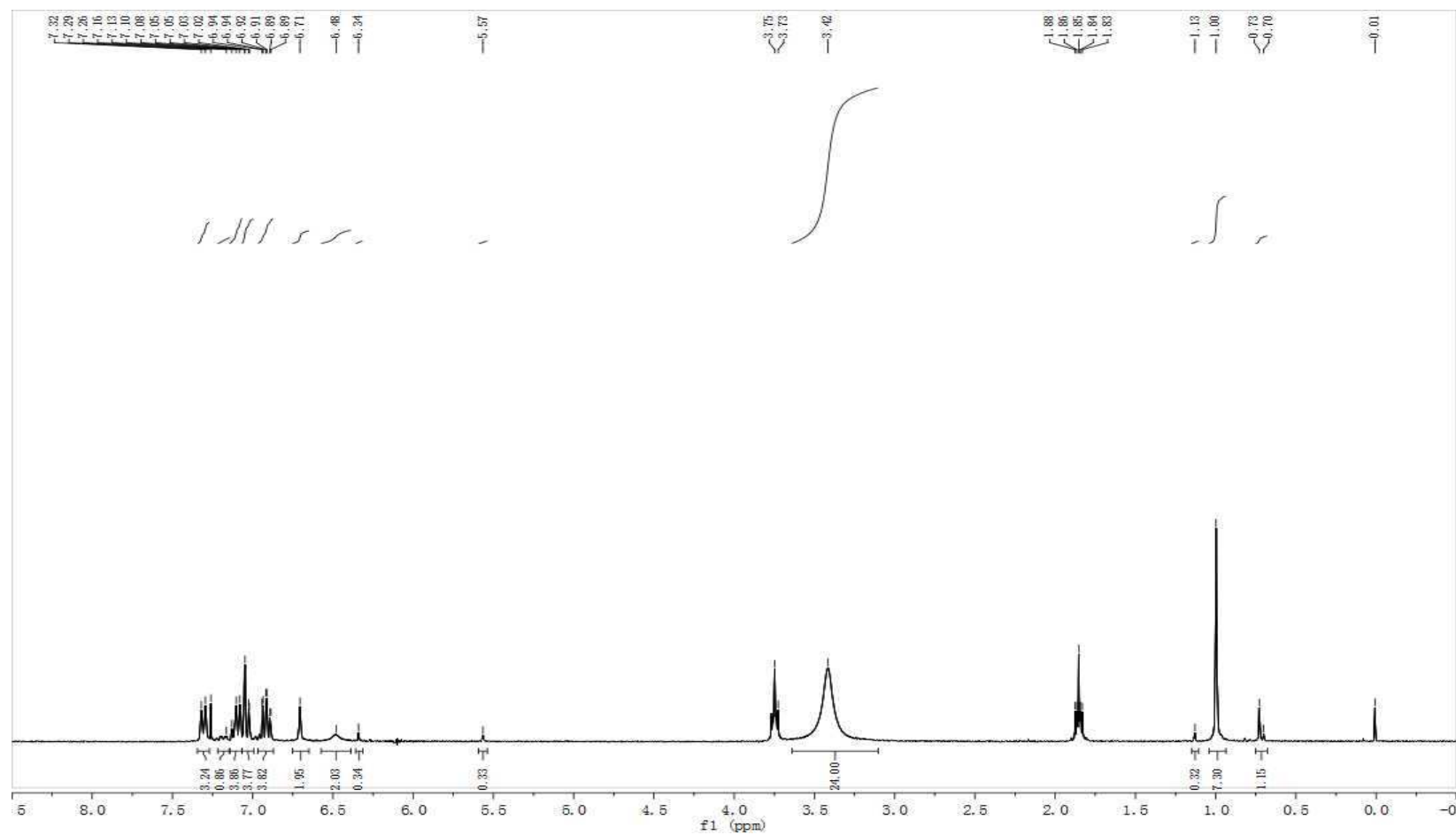


Fig. S14 ^1H NMR spectrum of **1c** in chloroform- d (400 MHz, 25 $^{\circ}\text{C}$).

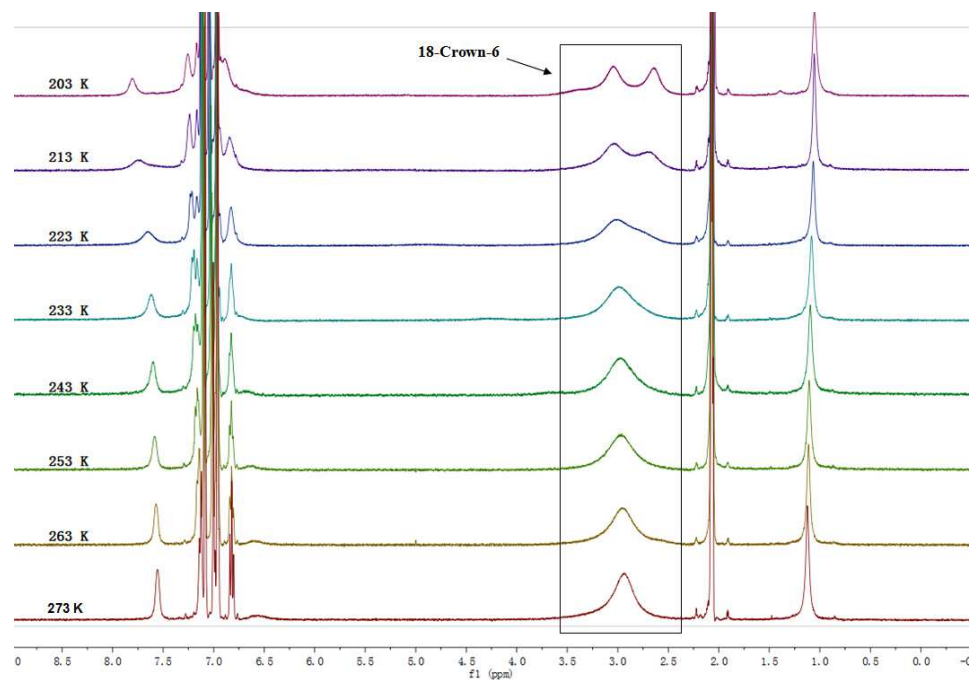


Figure. S15 Variable temperature dependent ^1H NMR spectra of **1a**. (toluene- d_8 , 273K-203K, 400 MHz). (18-crown-6 is firmly coordinated to K^+ , because almost no NMR peaks of free 18-crown-6 exists in solution which also can be proved in our previous work (J. Zhang, J. Xiong, Y. Sun, N. Tang and J. Wu, *Macromolecules* 2014, **47**, 7789-7796.). The split NMR peaks may results from the restriction of the rotation of 18-crown-6 around K^+ .)

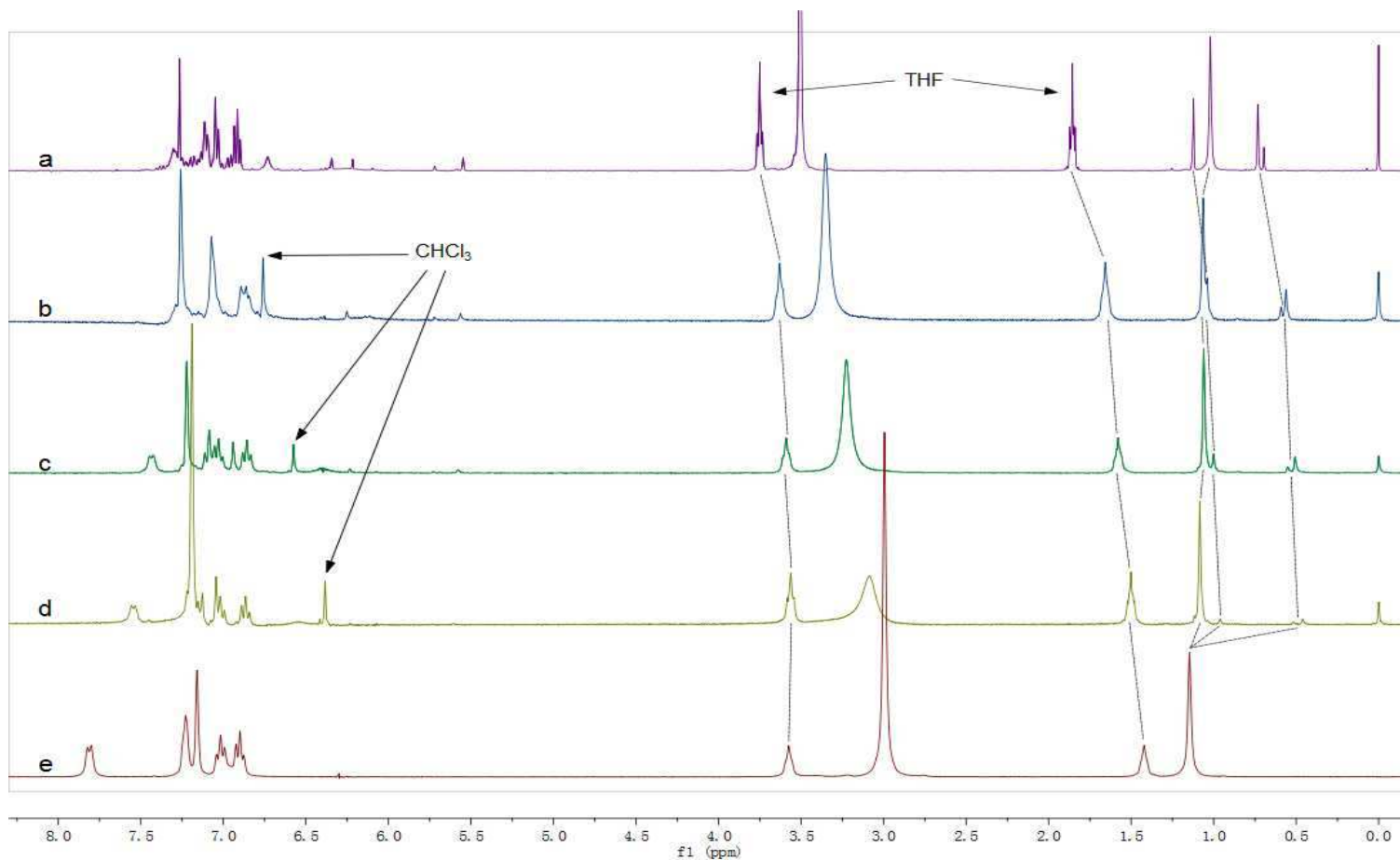


Fig. S16 ¹H NMR spectra of **1a** in different polarity of solvents: (a) chloroform-d; (b) chloroform-d : benzene-d₆ = 2:1; (c) chloroform-d : benzene-d₆ = 1:1; (d) chloroform-d : benzene-d₆ = 1:2; (e) benzene-d₆.

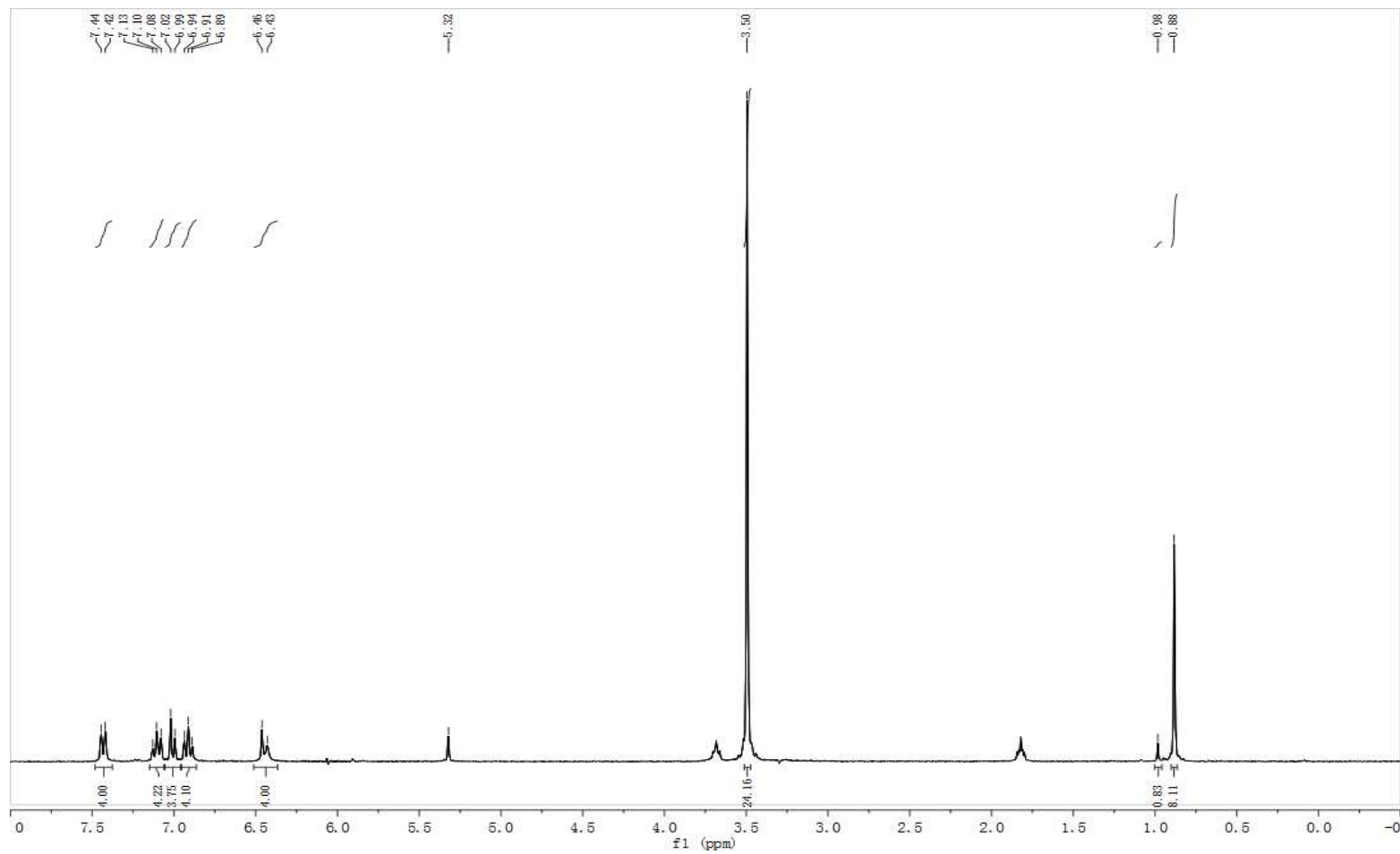


Fig. S17 ¹H NMR spectrum of **1a** in Dichloromethane-d₂ (300 MHz, 25 °C).

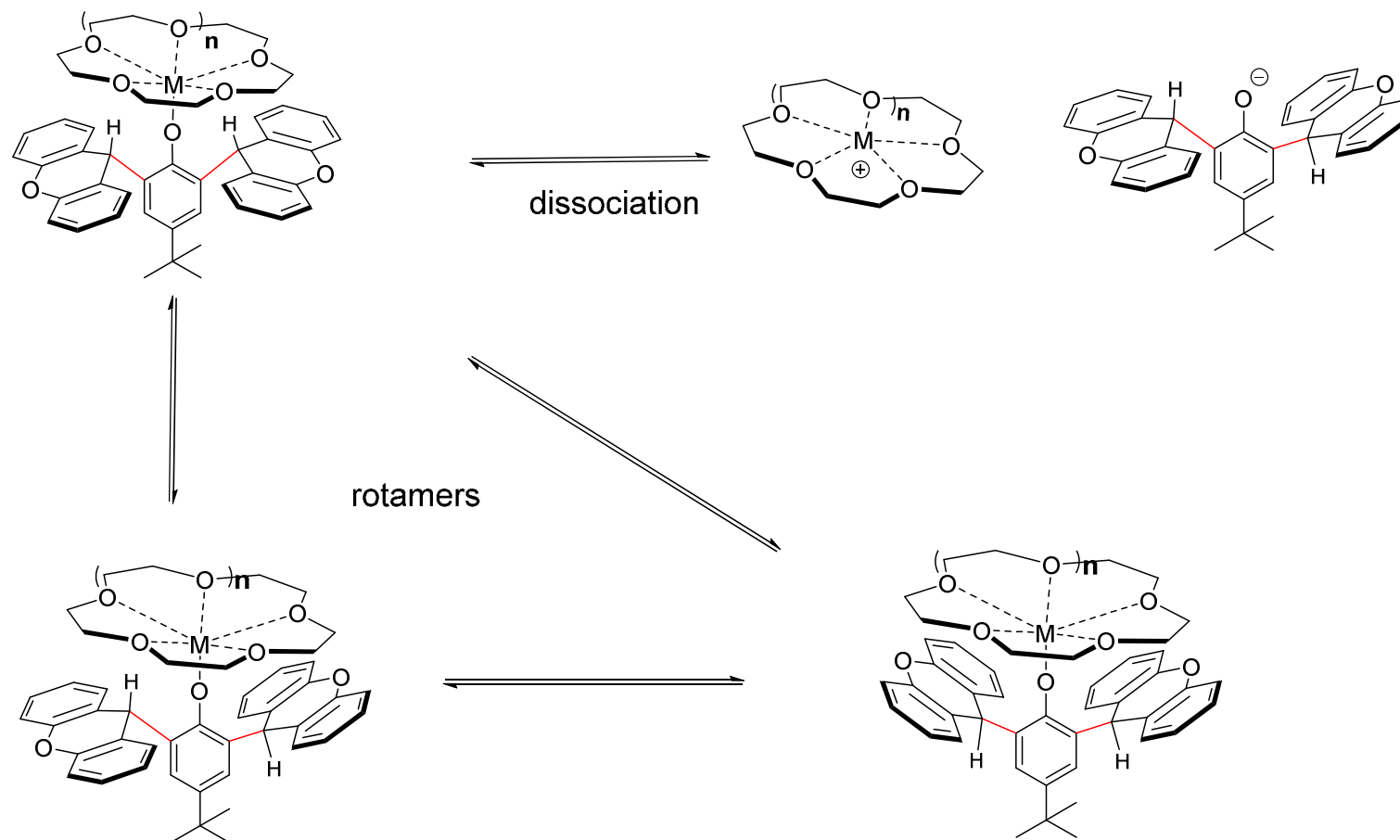


Fig. S18 Some possible rotational isomers.

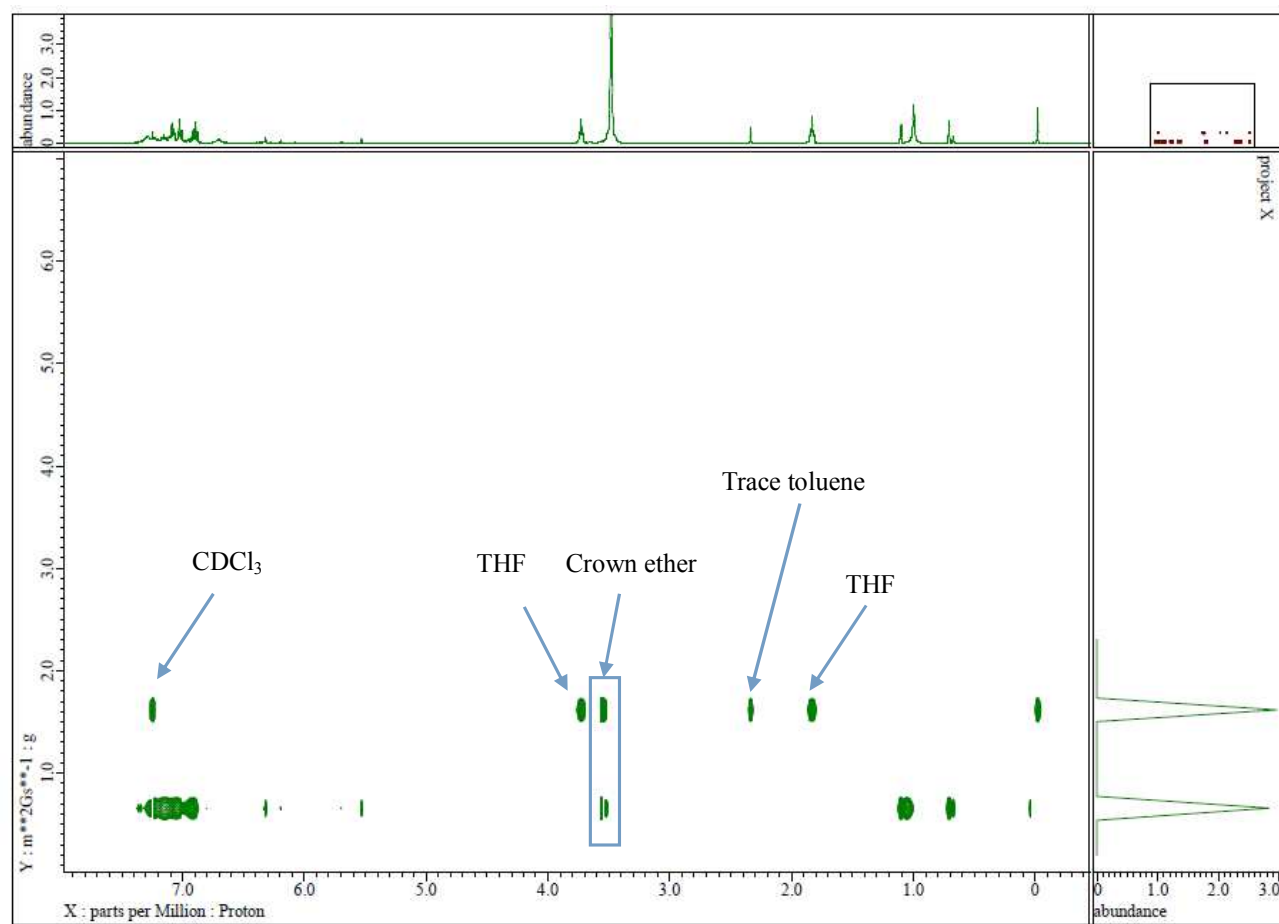


Fig. 19 DOSY spectra (CDCl₃, 25 °C) of complex **1a**.

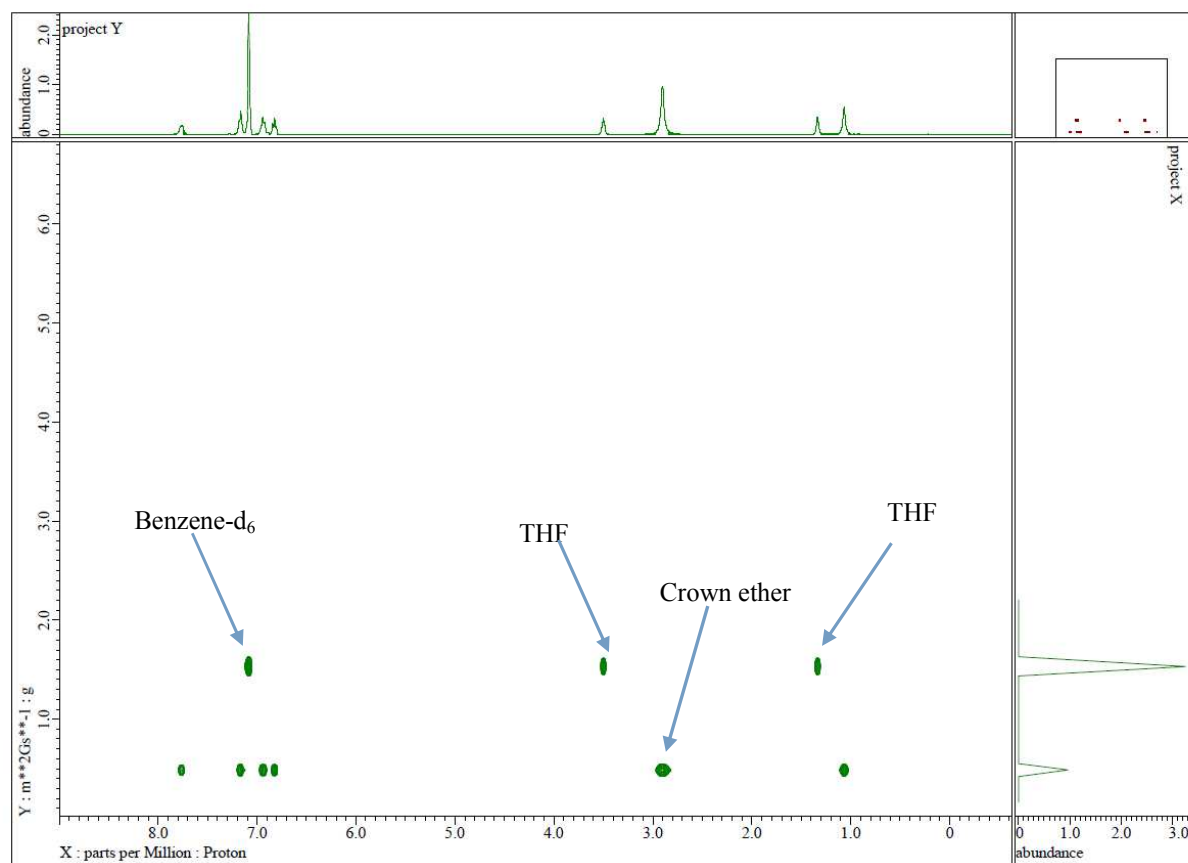


Fig. S20 DOSY spectra (benzene- d_6 , 25 °C) of complex **1a**.

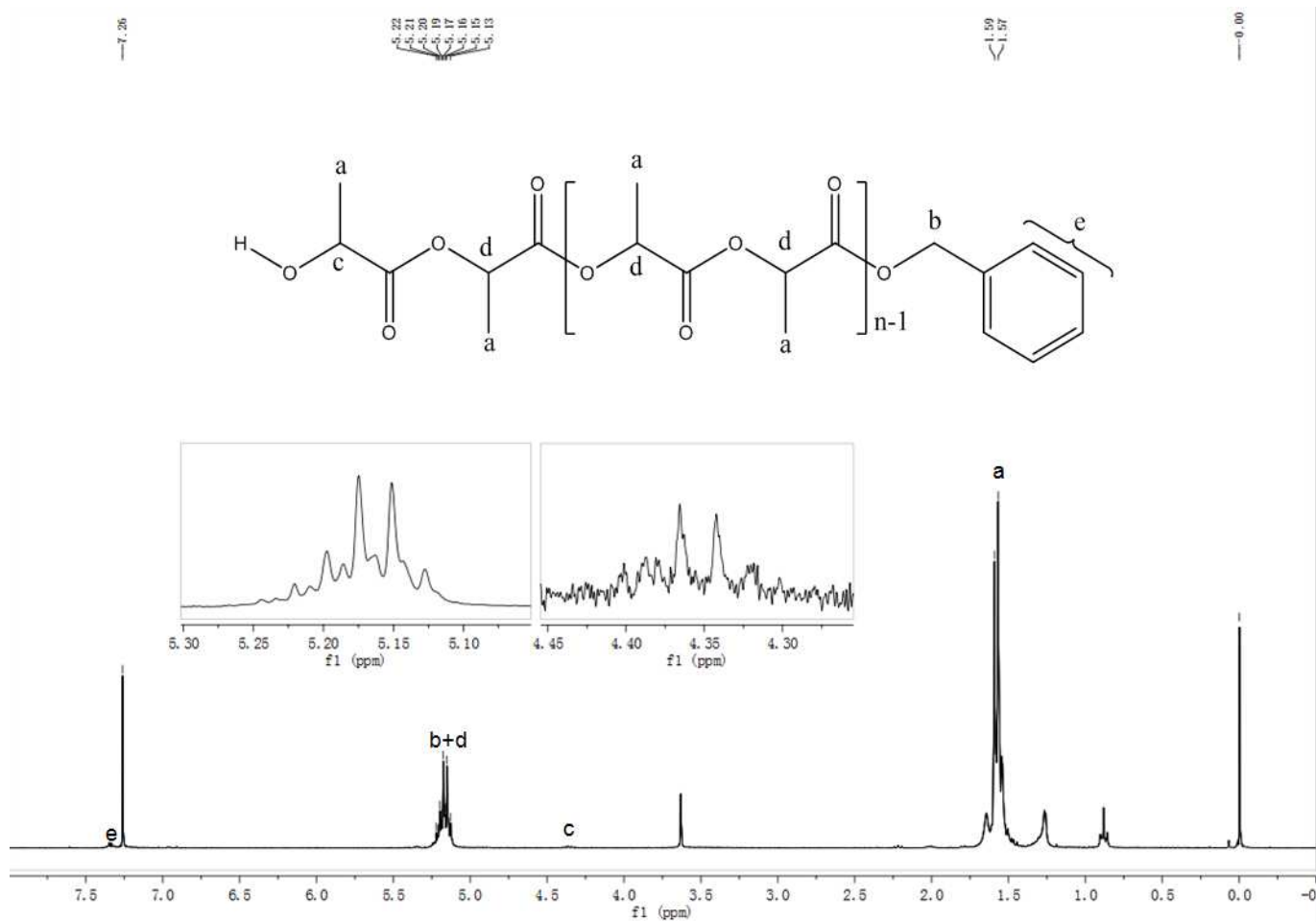


Fig. S21 ¹H NMR spectrum of PLA prepared by catalyst **1a** ([LA]₀/[M]₀/[BnOH]₀ = 25:1:1).

daizhongran-1 141103095844#1 RT: 0.01 AV: 1 NL: 4.29E4
T: FTMS+cESI Full ms [200.00-4000.00]

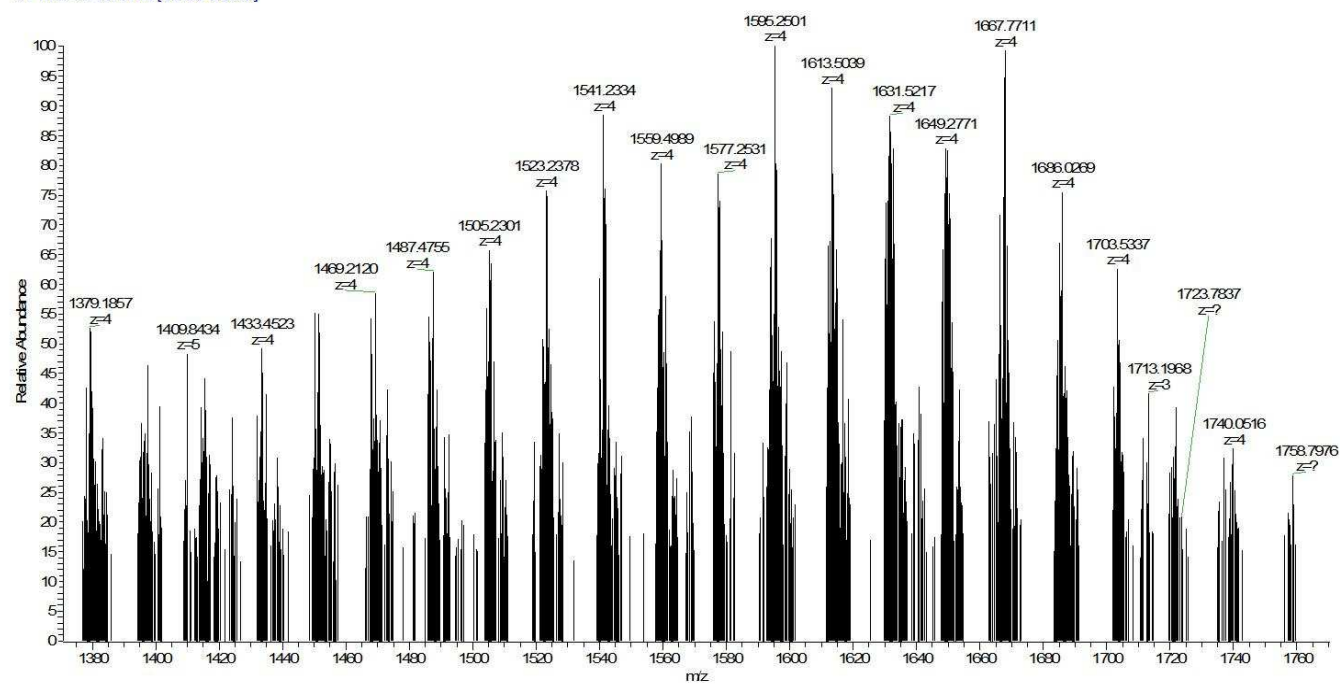


Fig. S22 ESI-MS spectrum of PLA prepared by catalyst **1a** ($[LA]_0:[M]_0:[BnOH]_0 = 50 : 1 : 1$, Mass = $(72.0211m + 108.0575 (\text{PhCH}_2\text{OH}) + 4.0313 (4\text{H}^+))/4$).

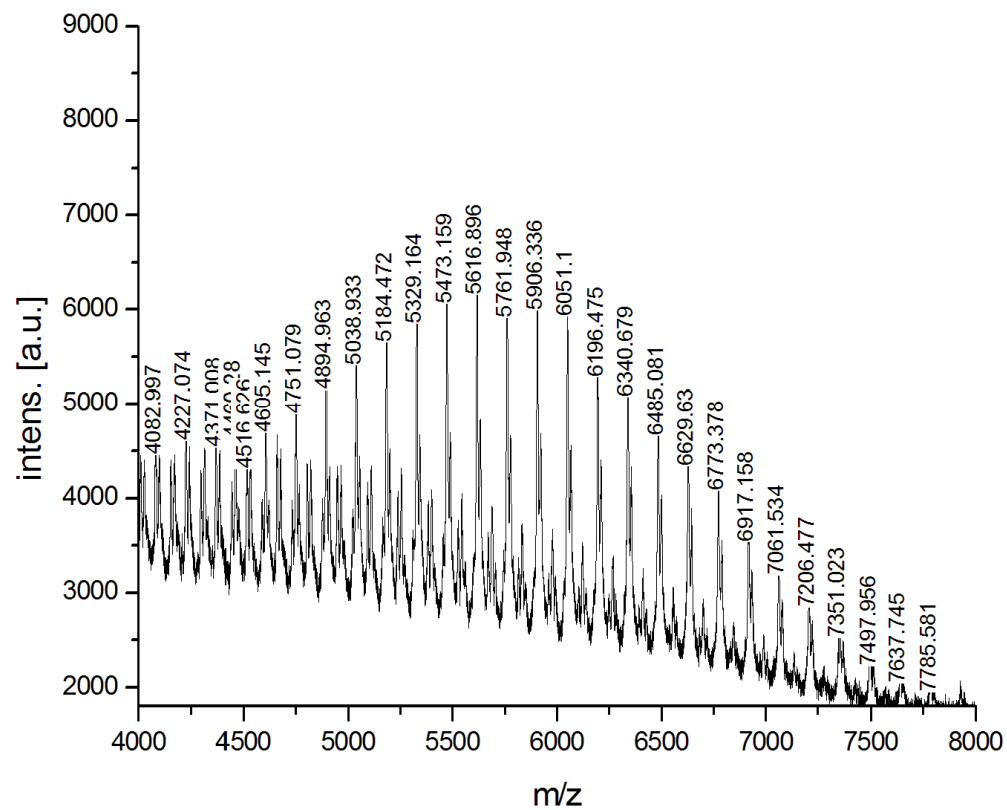


Fig. S23 MALDI-TOF-MS spectrum of PLA prepared by catalyst **1a** ([LA]₀: [M]₀: [BnOH]₀ = 50 : 1 : 1).

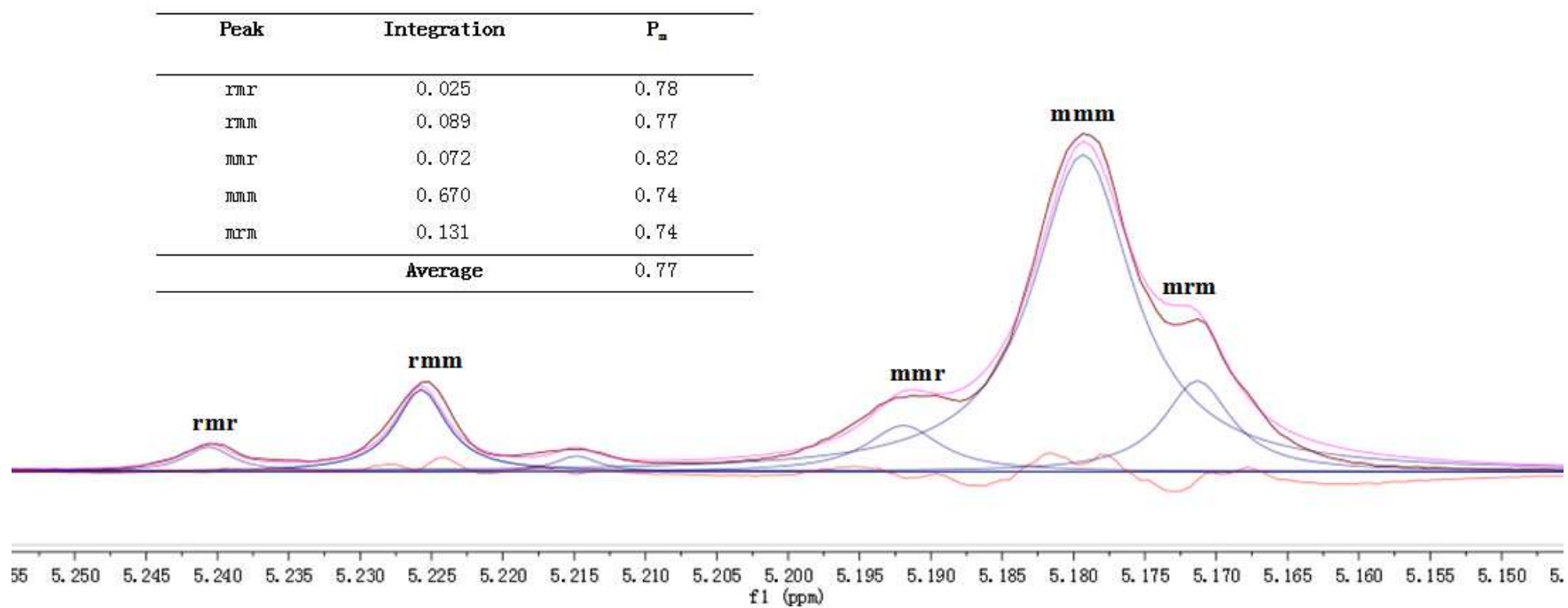


Fig. S24 The homonuclear-decoupled ¹H NMR spectrum of PLA ([LA]₀/[M]₀/[BnOH]₀ = 100:1:1, 25 °C, entry 5, P_n = 0.77)

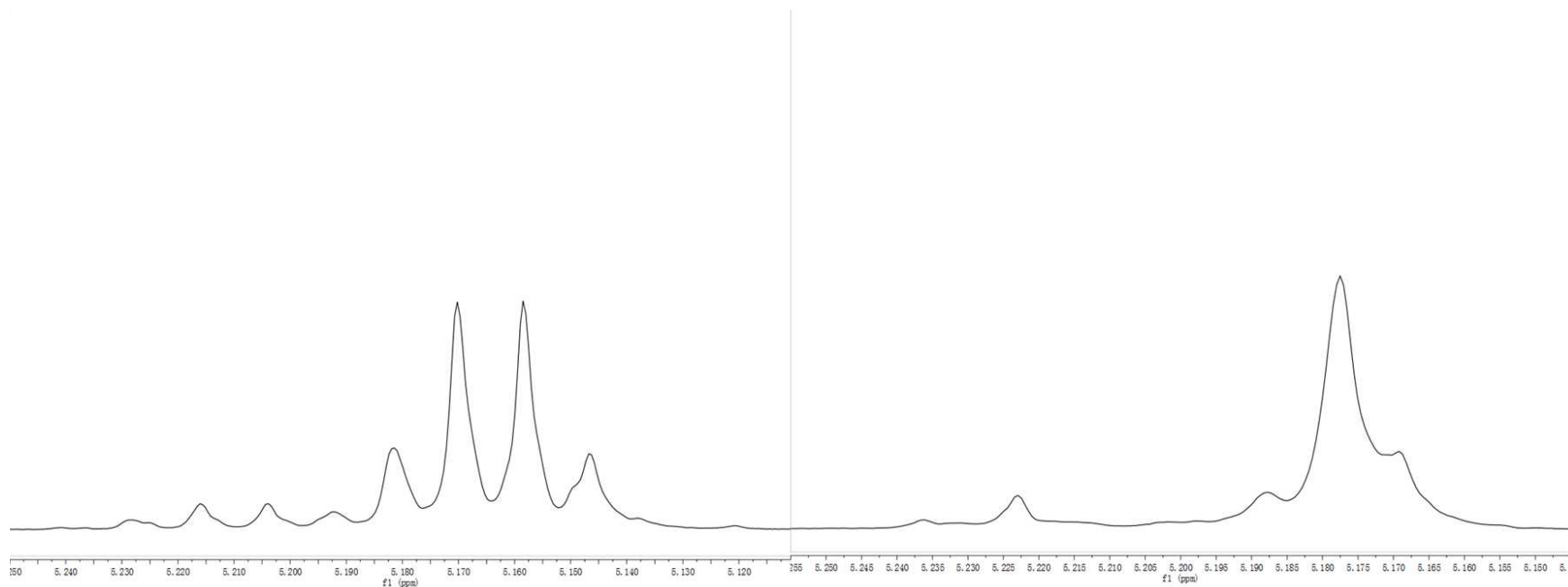


Fig. S25 The ^1H NMR spectrum (left) of PLA vs the homonuclear-decoupled ^1H NMR spectrum (right) of PLA ($[\text{LA}]_0/[\text{M}]_0/[\text{BnOH}]_0 = 100:1:1$, 0 \square , entry 12).

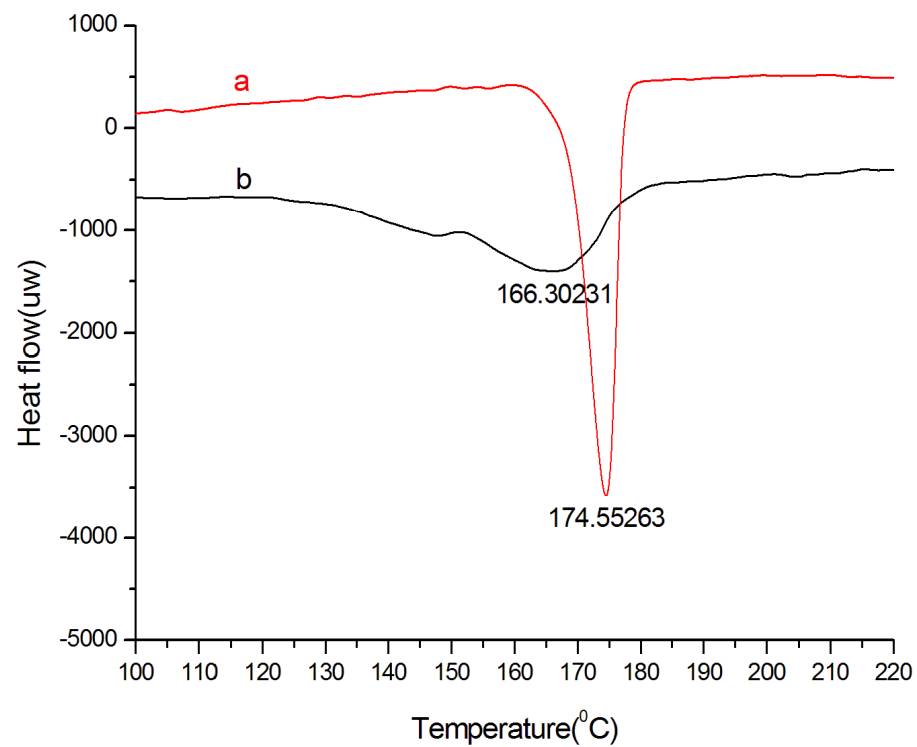


Fig. S26 DSC thermograms of the second heating cycles of the poly(*rac*-LA) obtained from ROP of *rac*-lactide by using **1a** as a catalyst ($[LA]_0/[M]_0/[BnOH]_0 = 100:1:1$, 0 °C, $P_m = 0.82$, entry 12, Table 1, the curve shows a melting point (T_m) of 166 °C.) (b) and the PLA sample prepared from poly(L-LA) (a).

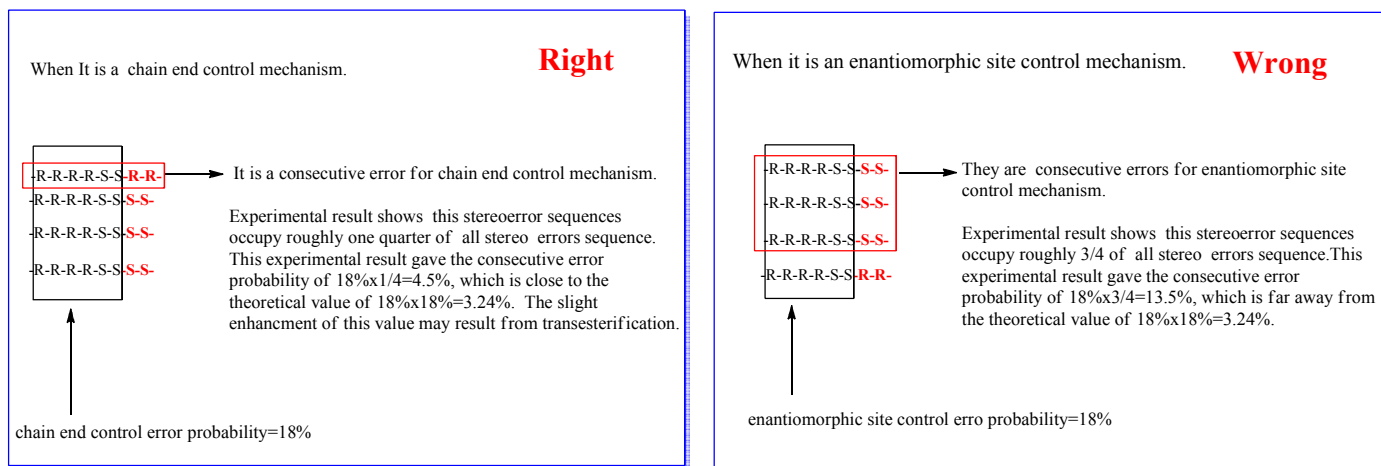


Fig.S27 the consecutive errors analysis of the homonuclear-decoupled ^1H NMR spectrum of PLA ($[\text{LA}]_0/[\text{M}]_0/[\text{BnOH}]_0 = 100:1:1$, 0 □, entry 12, Table 1)

[1] A. Kowalski, A. Duda, S. Penczek, *Macromolecules* **1998**, *31*, 2114-2122.

[2] G. M. Sheldrick, SHELXL-97 Program; University of Göttingen: Göttingen, Germany, **1996**.