Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Structures of Potassium Calix[4]arene Crown Ether Inclusion Complexes and Application in Polymerization of *rac*-Lactide

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Table S1. Details of the X-ray structure Determinations of Complexes **1-4**.

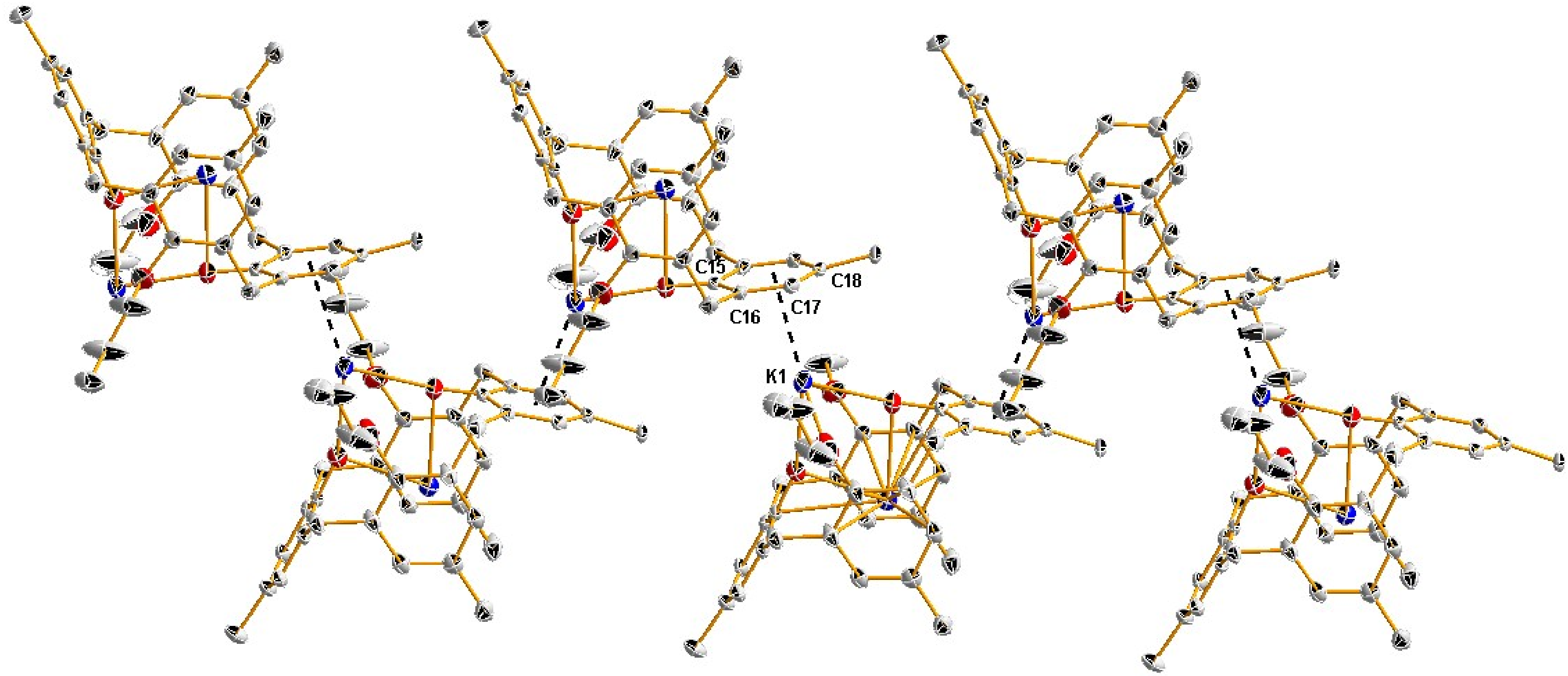

Figure S1. Molecular structure of complex **1** (**1D** zigzag polymeric chain).

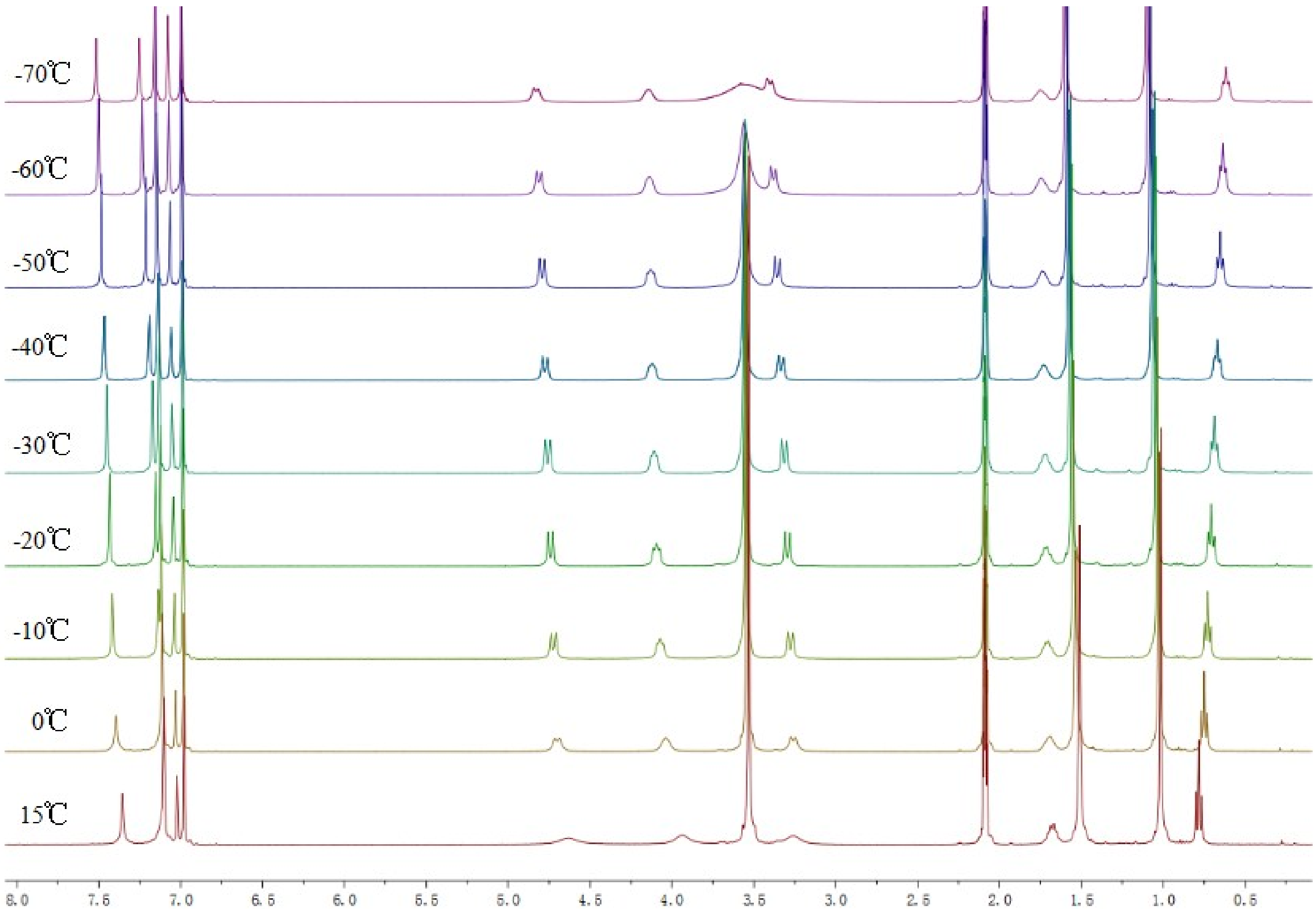

Figure S2. ^{1}H NMR spectra (Toluene-d8) recorded at different temperatures of complex **2**.

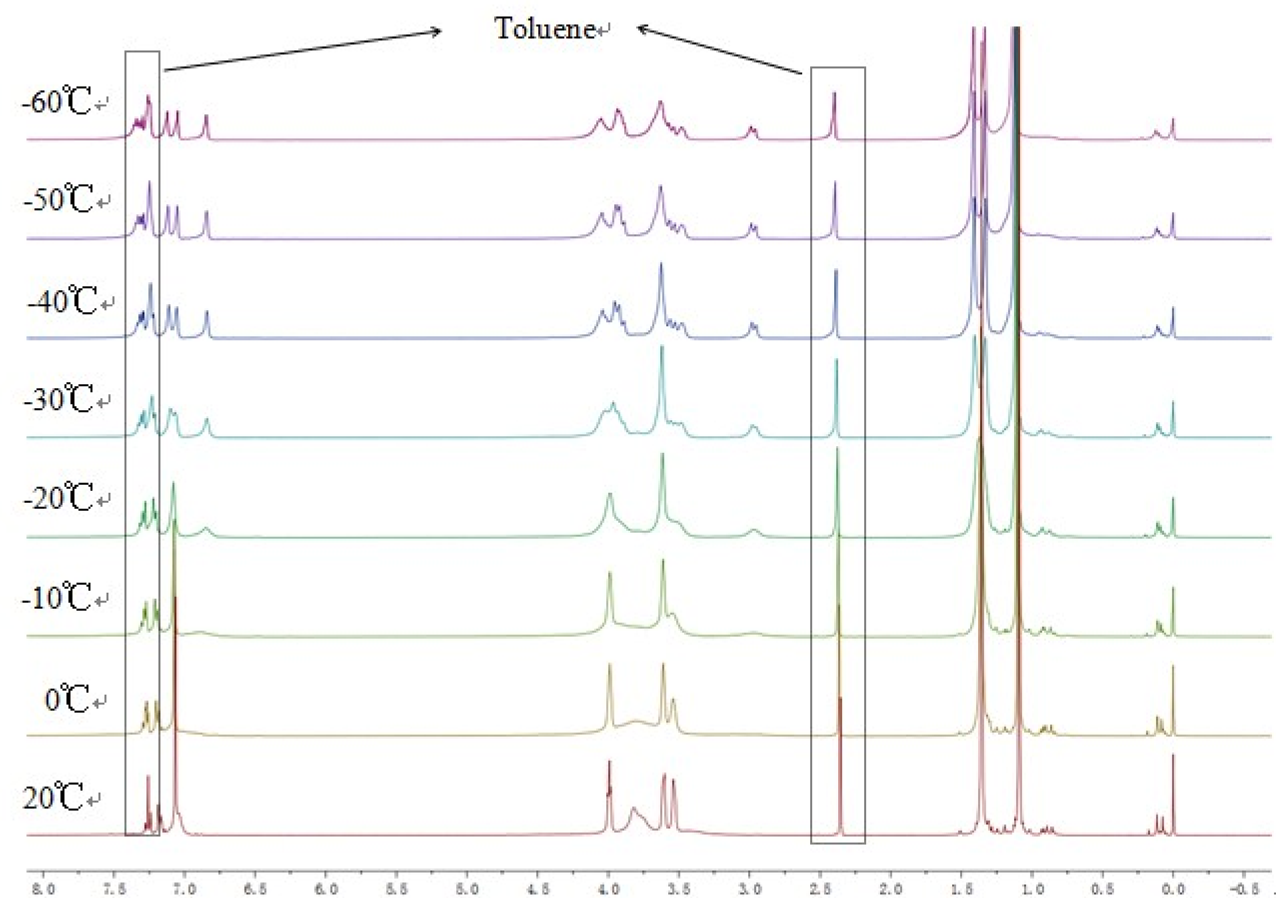

Figure S3. ^1H NMR spectra ($CDCl_3$) recorded at different temperatures of complex **3**.

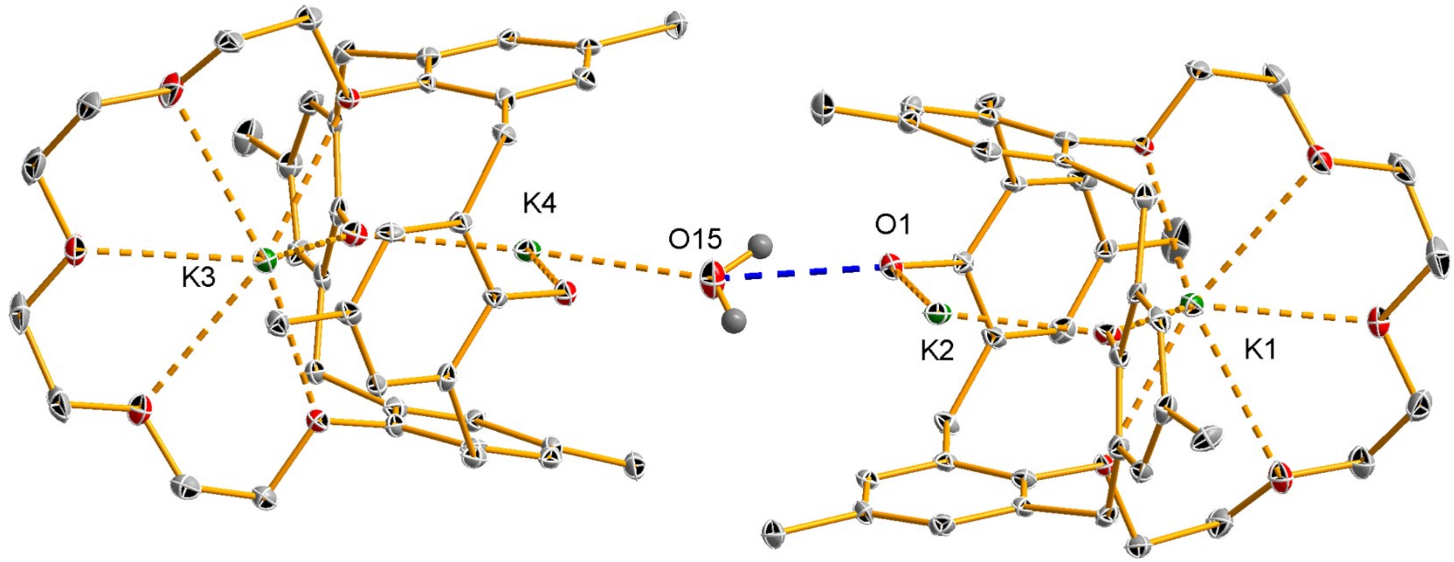

Figure S4. Molecular structure of complex **3** (two different molecular structures in one asymmetric unit).

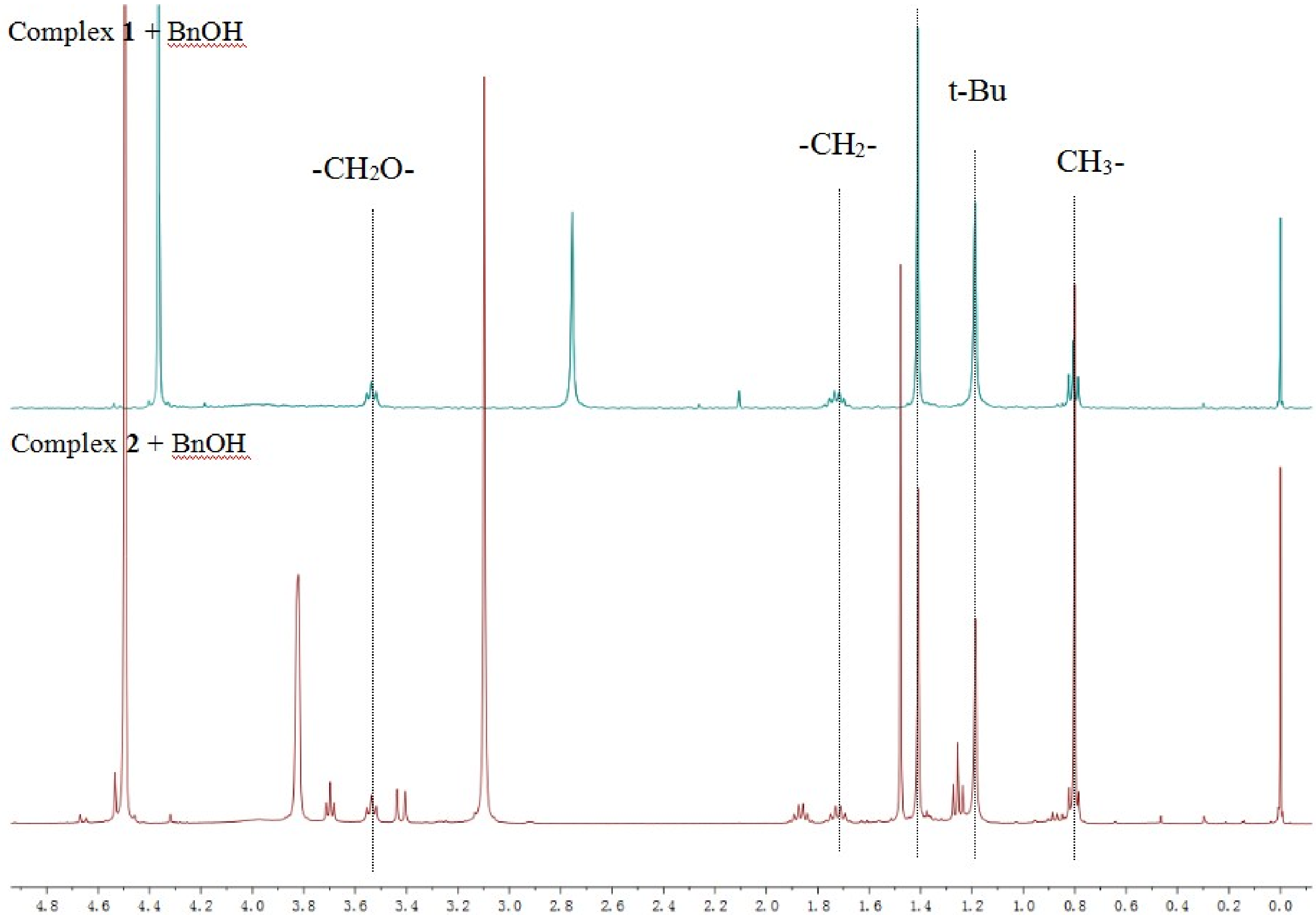

Figure S5. Comparison of complex **1** + **BnOH** (excess) and complex **2** + **BnOH** (excess) on ^1H NMR spectrum (C_6D_6, 25°C).

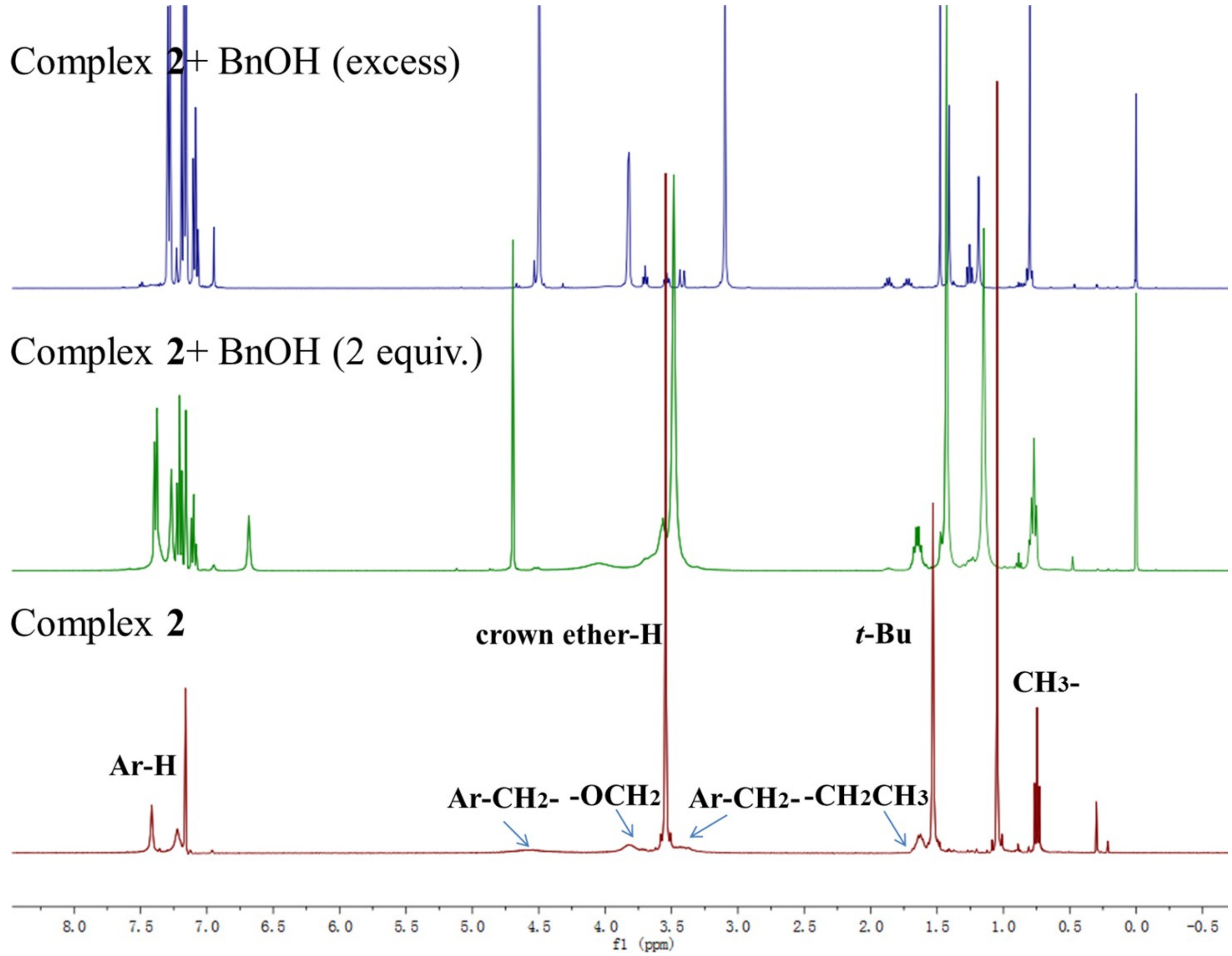

Figure S6. Comparison of complex **2**, complex **2** + **BnOH** (2 equiv.) and complex **2** + **BnOH** (excess) on ^{1}H NMR spectrum (C_6D_6, 25°C).

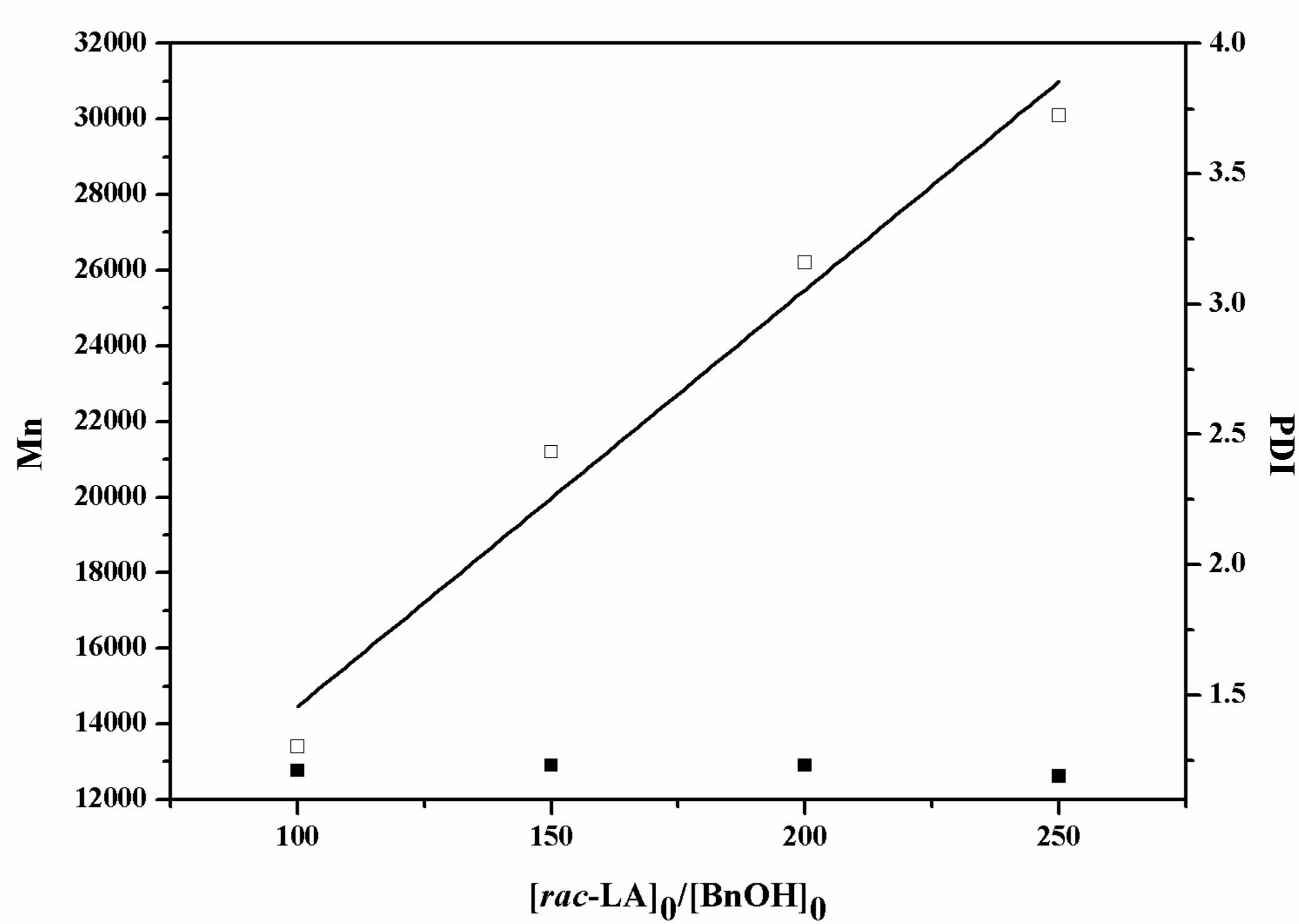

Figure S7. Polymerization of *rac*-LA catalyzed by complex **2** in toluene at room temperature. The relationships between PDI(■), Mn (□) of the polymer and the initial mole ratios $[LA]_0/[BnOH]_0$ (Table 1, entries 1, 7, 8, 9) is shown.

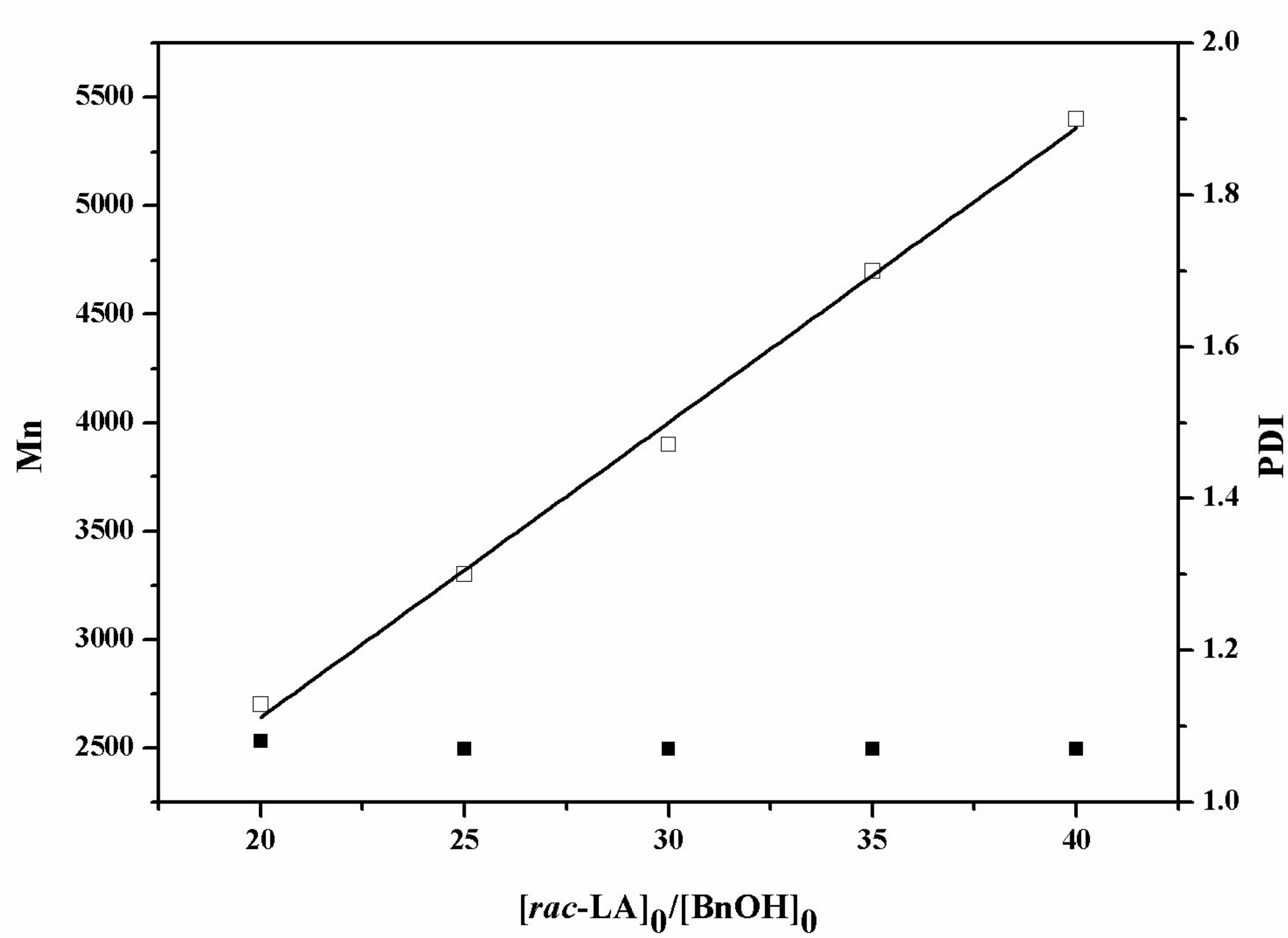

Figure S8. Polymerization of *rac*-LA catalyzed by complex **3** in toluene at room temperature. The relationships between PDI(■) , Mn (□) of the polymer and the initial mole ratios [LA]$_0$/[BnOH]$_0$ (Table 1, entries 17, 20-23) is shown.

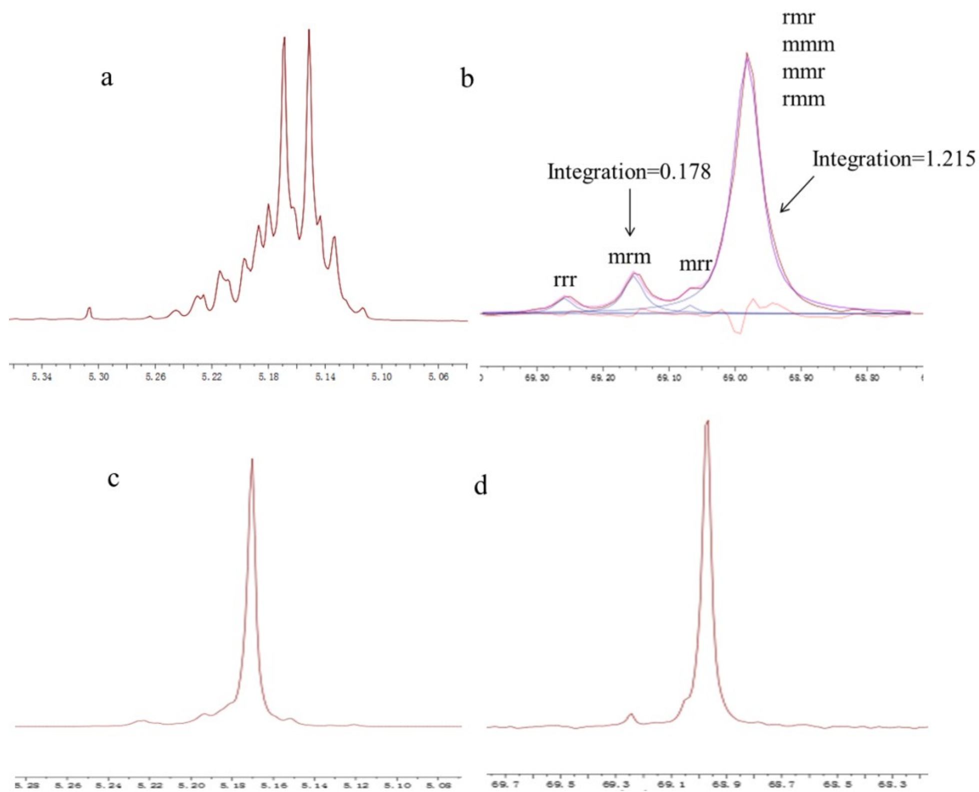

Figure S9. Methine region of the (a) ^1H NMR spectrum (b) ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of the poly(*rac*-lactide) produced from *rac*-LA using complex **3** (Table 1, entry 25). Methine region of the (c) homonuclear decoupled ^1H NMR spectrum($CDCl_3$, 400 MHz) (d) ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of the poly(*L*-lactide) produced from *L*-LA using complex **3** (Table 1, entry 26). The P_m values determined by homonuclear decoupled ^1H NMR and ^{13}C NMR of the methine region.[1]

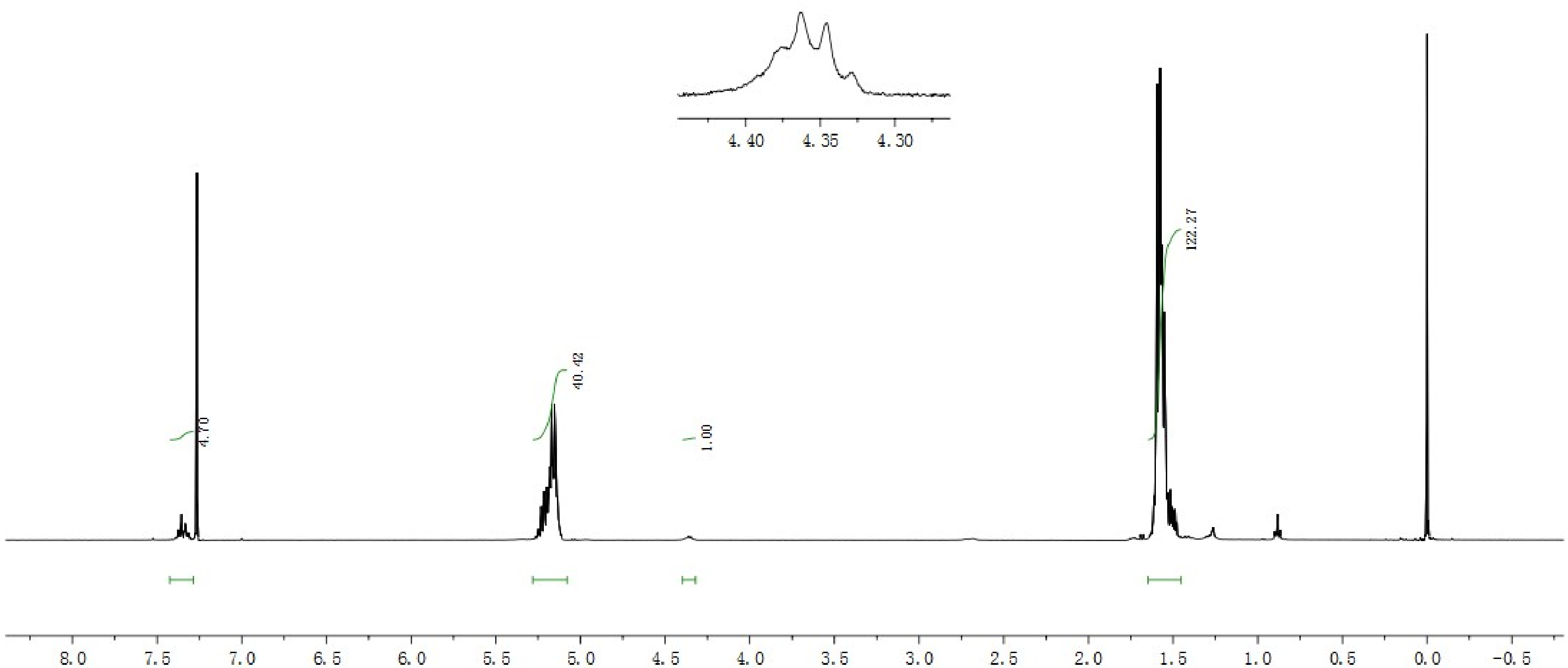

Figure S10. [1]H NMR analysis of the small molecular weight poly (*rac*-LA) obtained from polymerization of *rac*-LA initiated by complex **3** (Table 1, entry 17, $[LA]_0/[cat.]_0/[BnOH]_0 = 200:1:10$)

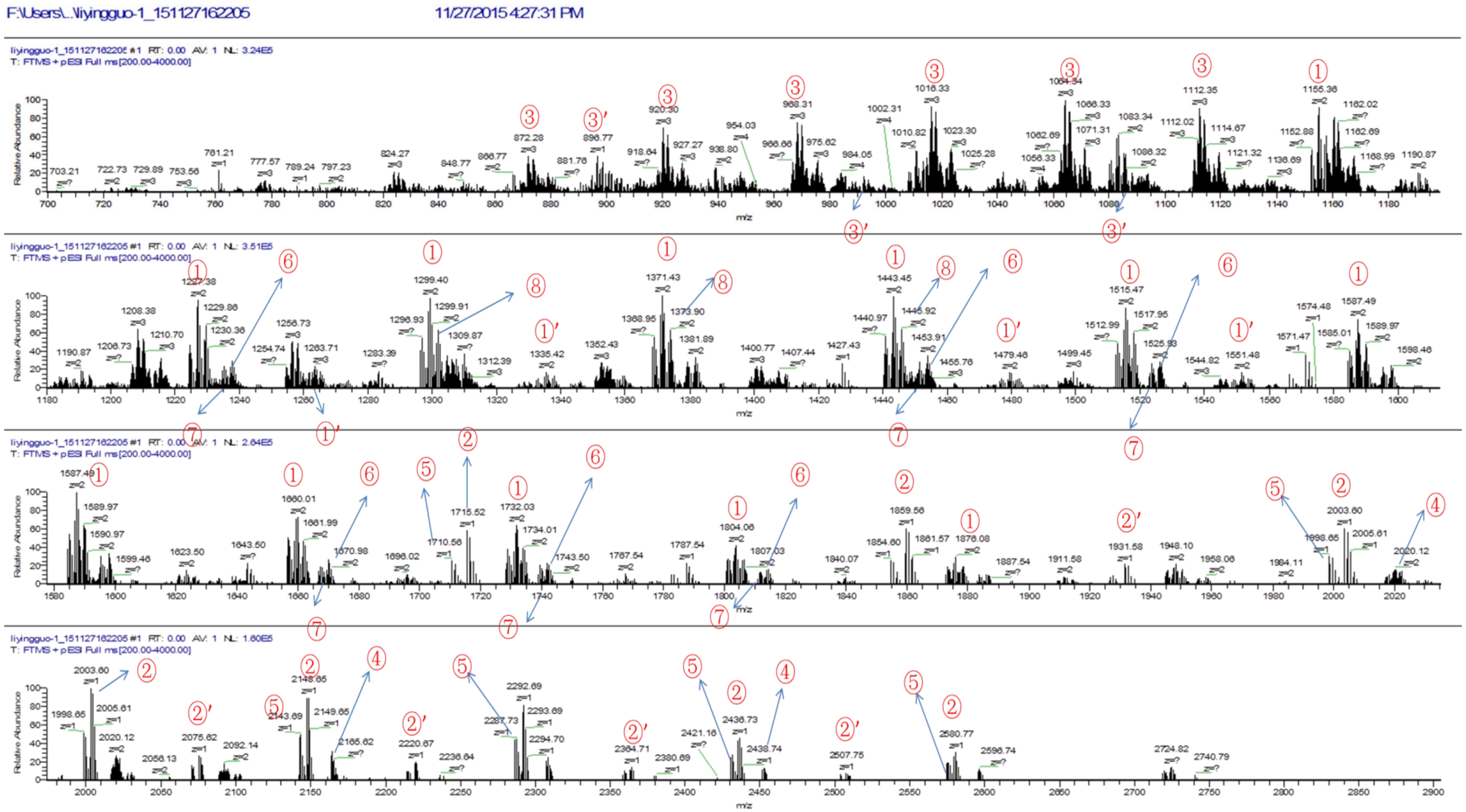

Figure S11. Enlarged ESI-MS spectrum of poly(*rac*-LA) prepared by ROP of *rac*-LA (Table 1, entry 17)

In EMS-MS spectrum:

①: 144.04n+BnOH+Na^++H_3O^+ ①’: 144.04n+BnOH+Na^++H_3O^++72.02

②: 144.04n+BnOH+Na^+ ②’: 144.04n+BnOH+Na^++72

③: 144.04n+BnOH+Na^++2H_3O^+ ③’: 144.04n+BnOH+Na^++2H_3O^++72

④: 144.04n+BnOH+K^+ ⑤: 144.04n+BnOH+NH_4^+

⑥: 144.04n+BnOH+Na^++ K^+ ⑦: 144.04n+BnOH+K^+

⑧: 144.04n+BnOH+2Na^+

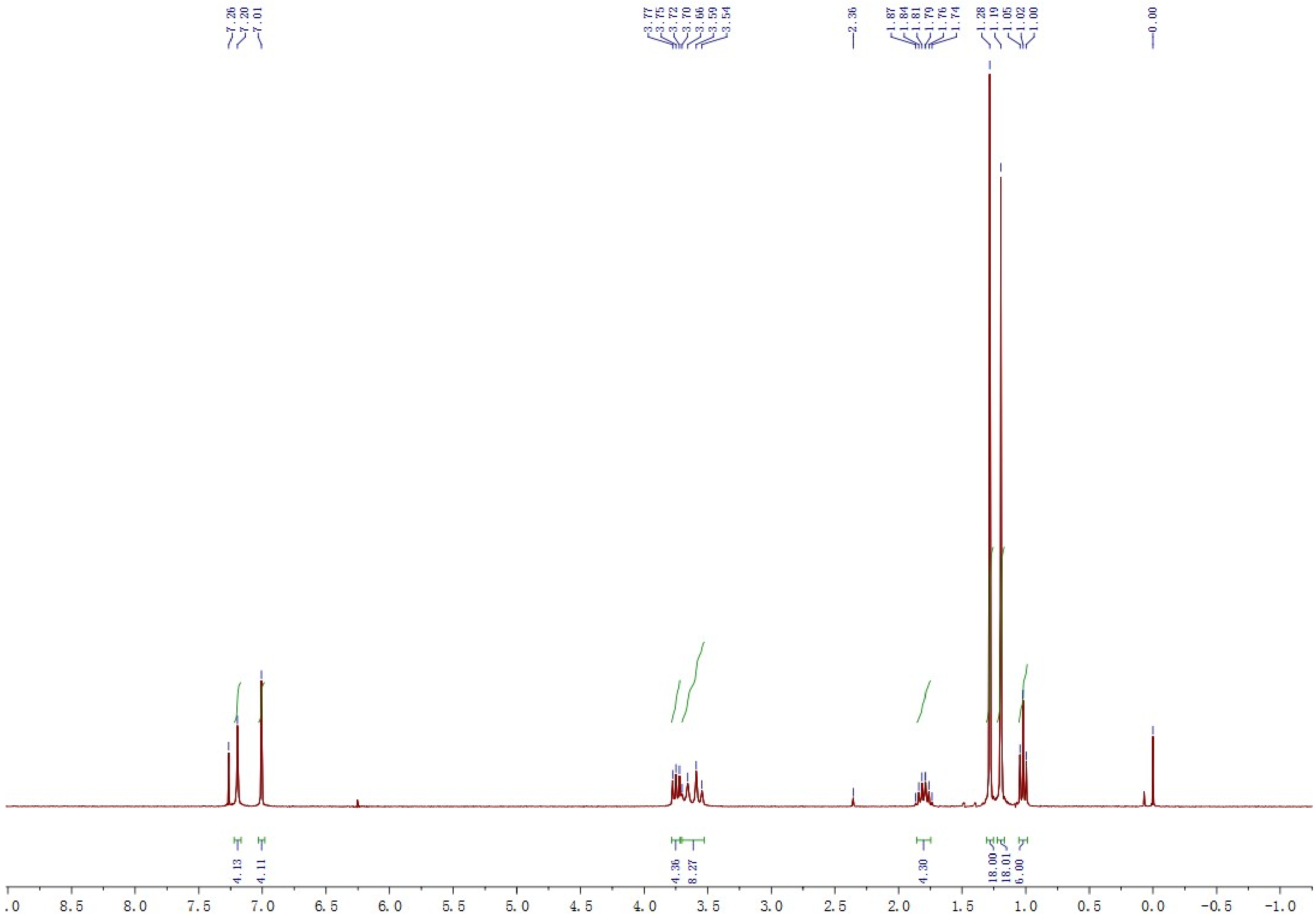

Figure S12. [1]H NMR spectrum ($CDCl_3$, 25°C) of complex **1**.

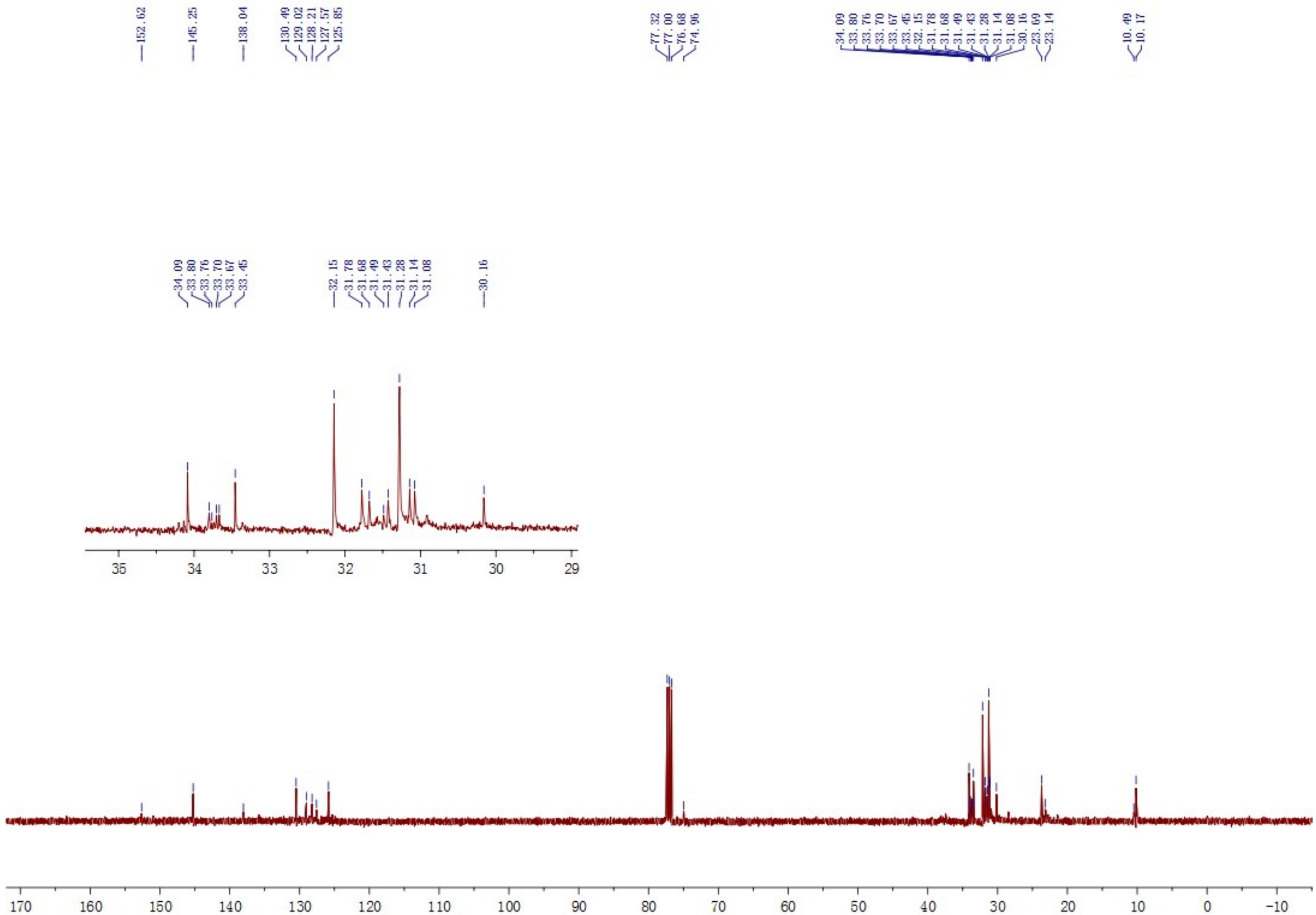

Figure S13. ^{13}C NMR spectrum ($CDCl_3$, 25^{o}C) of complex **1**.

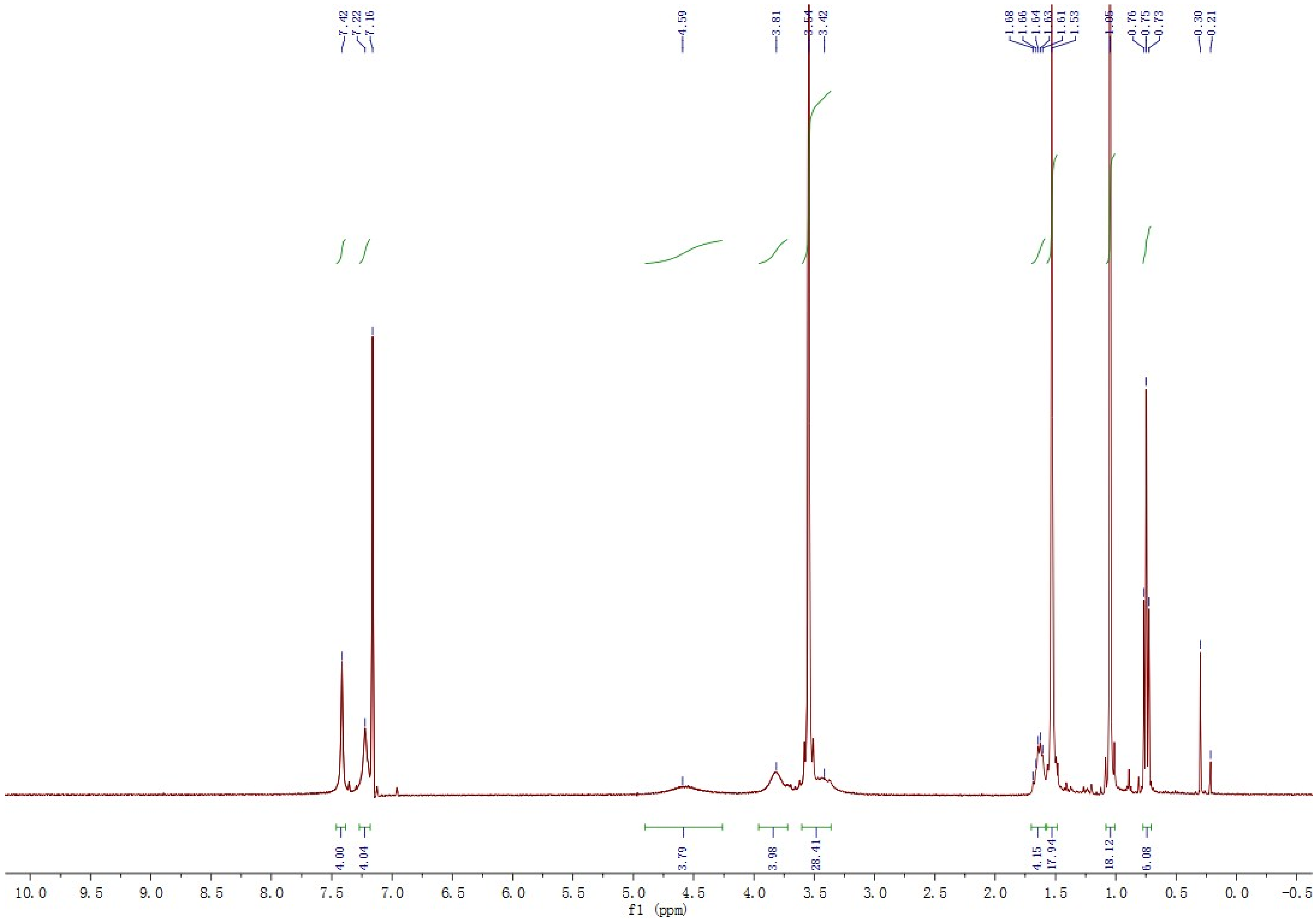

Figure S14. ^{1}H NMR spectrum (C_6D_6, 25°C) of complex **2**.

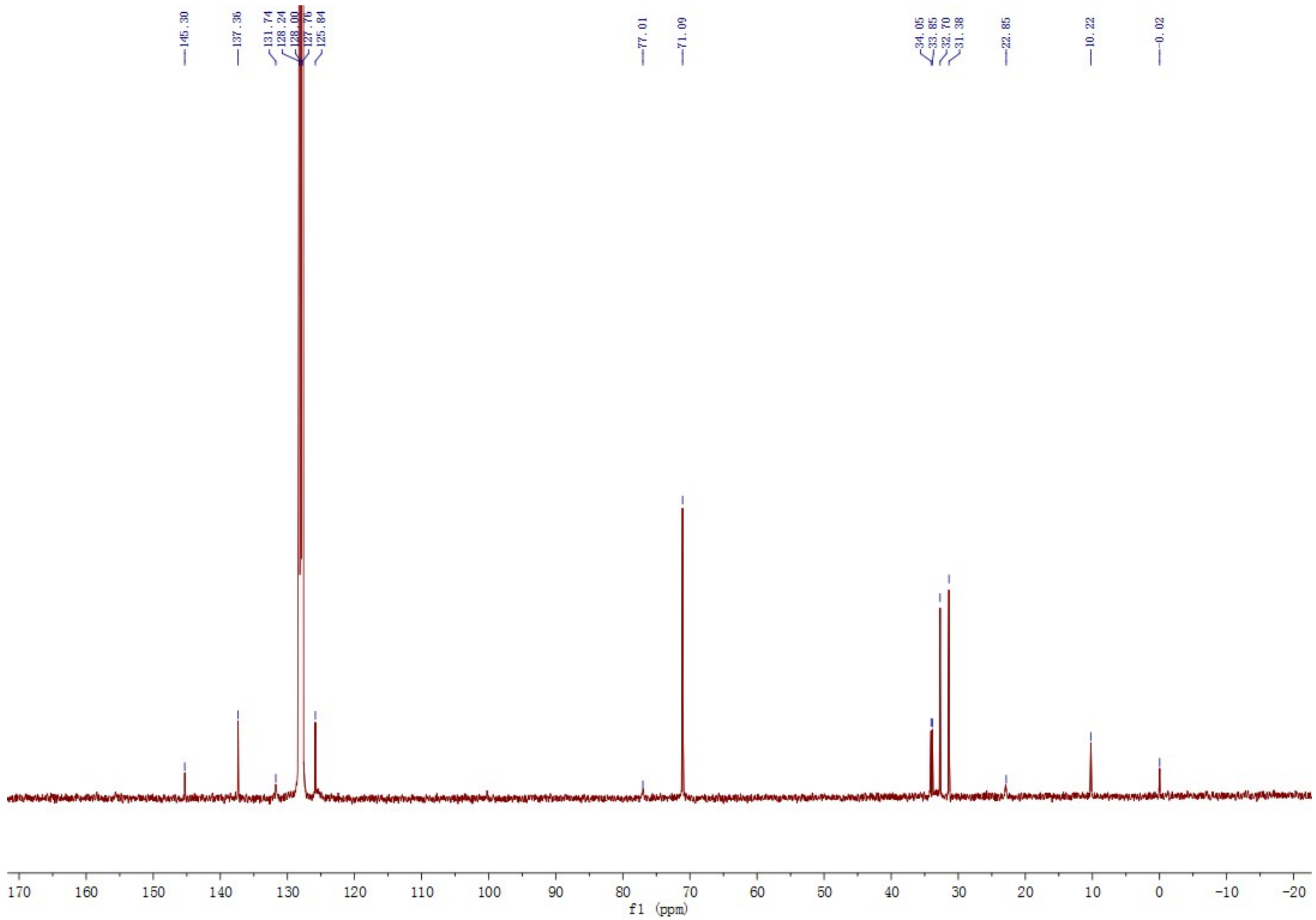

Figure S15. ^{13}C NMR spectrum (C_6D_6, 25°C) of complex **2**.

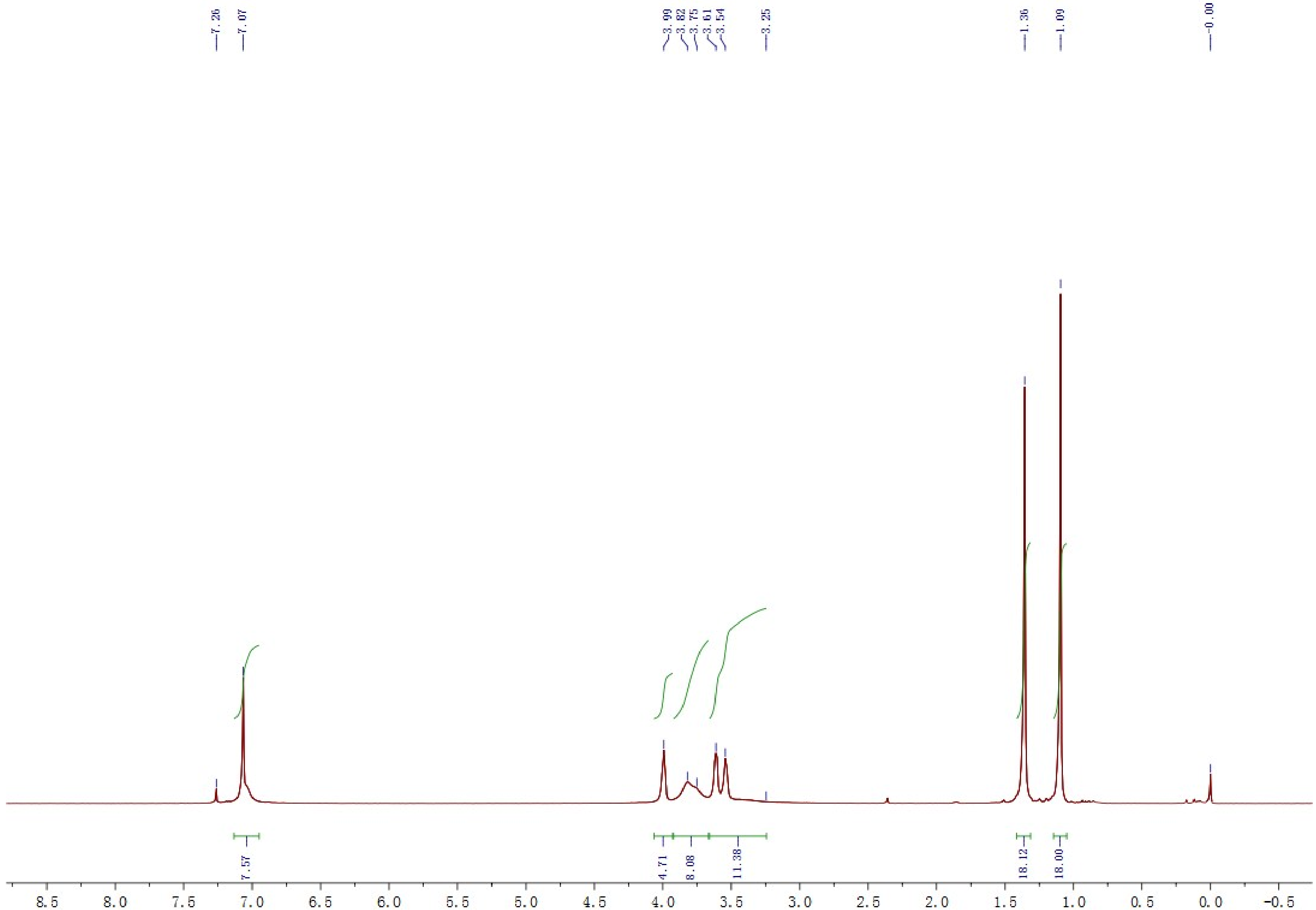

Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 25^{o}C) of complex **3**.

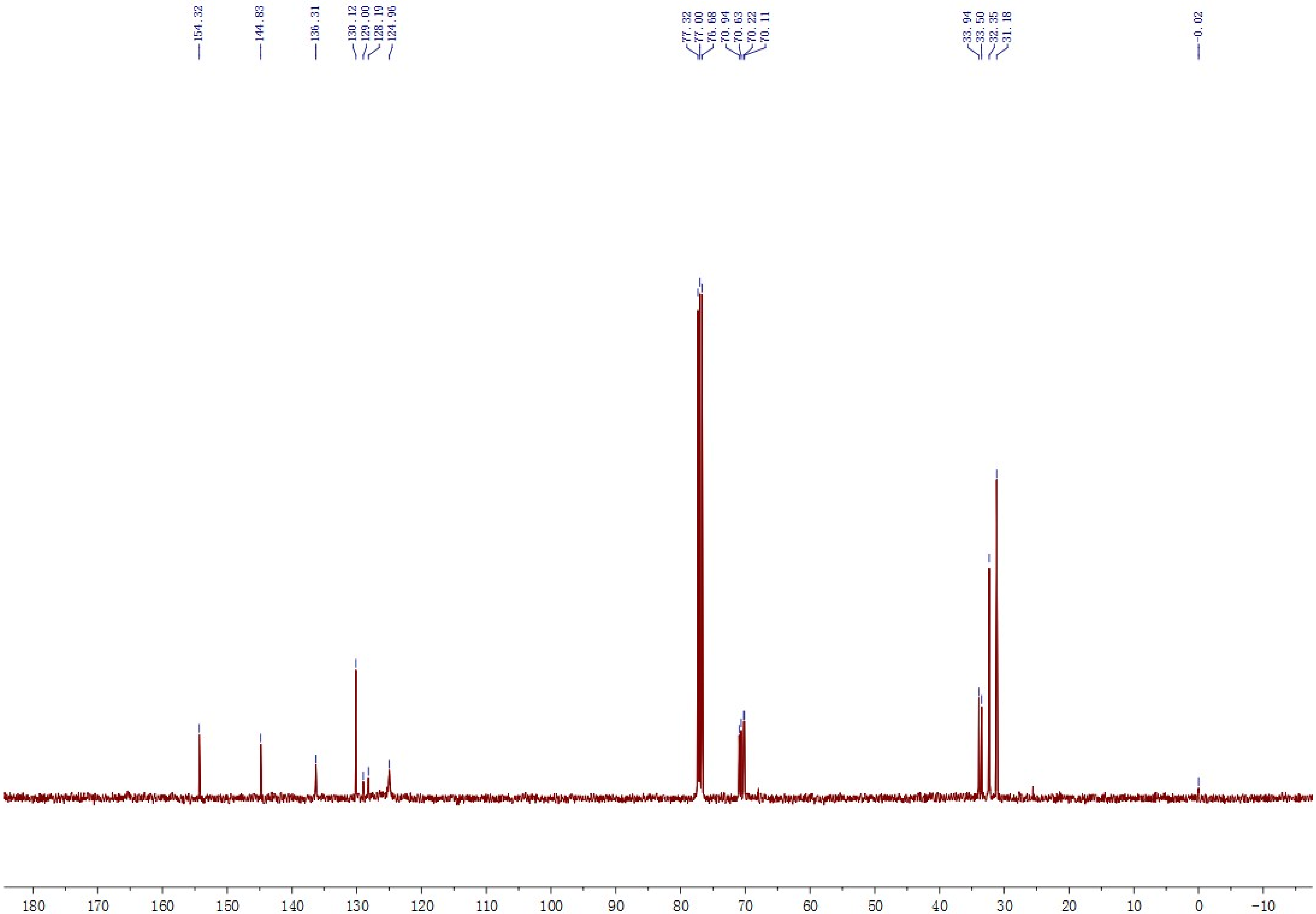

Figure S17. ^{13}C NMR spectrum ($CDCl_3$, 25°C) of complex **3**.

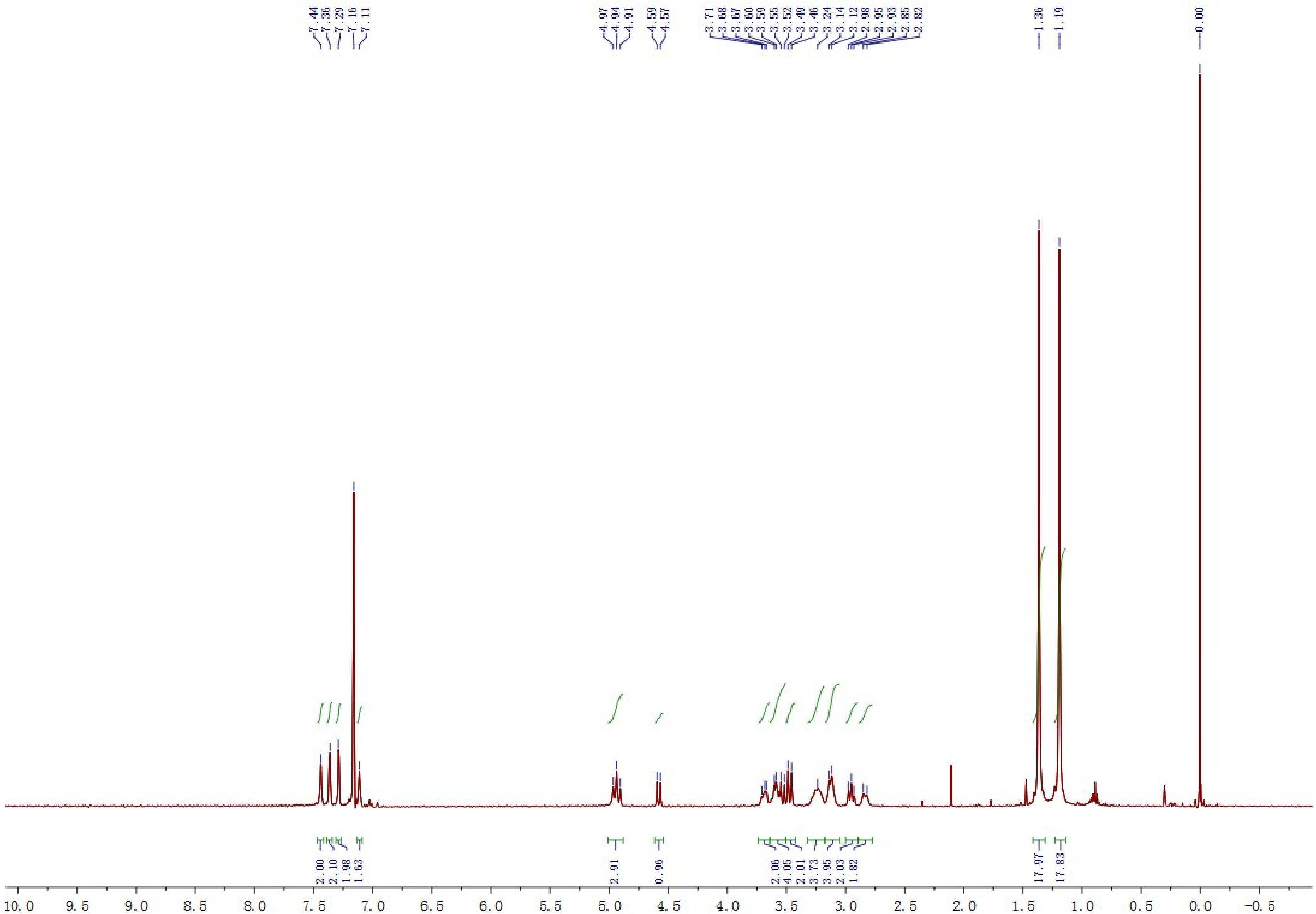

Figure S18. ^{1}H NMR spectrum (C_6D_6, 25°C) of complex **4**.

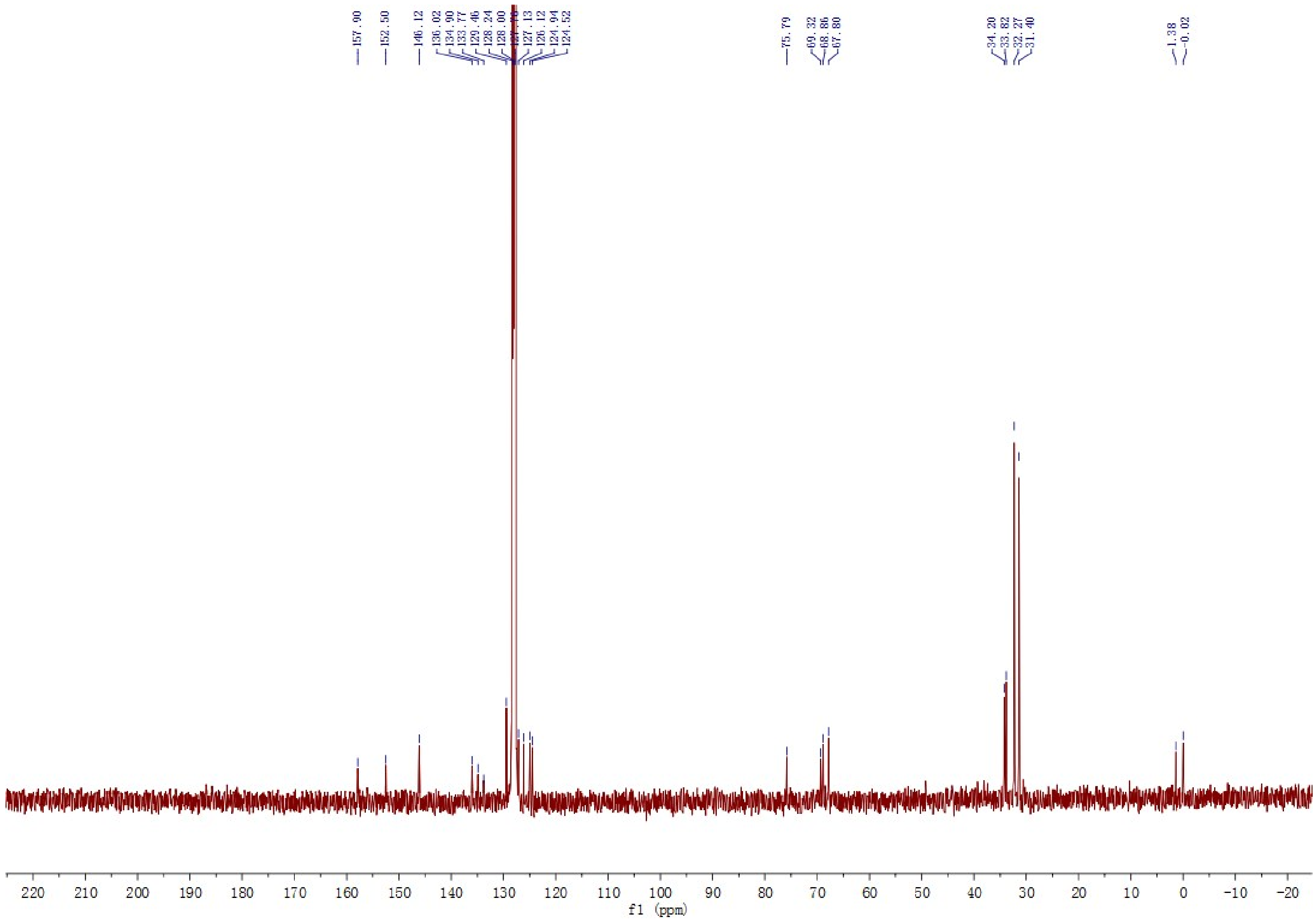

Figure S19. ^{13}C NMR spectrum (C_6D_6, 25°C) of complex **4**.

Table S1. Details of the X-ray structure Determinations of Complexes **1-4**.

	1	**2**	**3**	**4**
Formula	$C_{50}H_{66}K_2O_4$	$C_{62}H_{90}K_2O_{10}$	$C_{52}H_{68}K_2O_7$	$C_{52}H_{69}KO_7THF$
Fw	808.23	1072.68	882.42	916.53
Temp	220.60(10)	173.00(10)	296(2)	293(2)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	Pnma	C2/c	$P2_1$	$P2_1/c$
a Å	12.2579(5)	11.1093(3)	13.4859(10)	16.3022(3)
b Å	17.9504(9)	26.4085(9)	20.6897(15)	29.2158(5)
c Å	21.1486(6)	20.4600(7)	20.2255(15)	15.5007(3)
α°	90.00	90.00	90.00	90.00
β°	90.00(3)	92.614(3)	109.1440(10)	94.8725(19)
γ°	90.00	90.00	90.00	90.00
V $Å^3$	4653.4(3)	5996.3(3)	5331.2(7)	7356.0(2)
Z	4	8	2	4
Density(calcd) $g \cdot cm^{-3}$	1.155	1.189	1.214	1.154
Absorb.coeff. mm^{-1}	0.245	0.213	0.231	1.102
F(000)	1744	2320	2092	2784
Index ranges	$-8 \leq h \leq 16$ $-23 \leq k \leq 24$ $-25 \leq l \leq 27$	$-14 \leq h \leq 14$ $-32 \leq k \leq 35$ $-15 \leq l \leq 25$	$-18 \leq h \leq 18$ $-19 \leq k \leq 29$ $-26 \leq l \leq 26$	$-17 \leq h \leq 19$ $-31 \leq k \leq 35$ $-18 \leq l \leq 18$
Data/restr./param	5681/28/321	6823/84/373	15886/133/1276	13341/7/907
GOF	1.06	1.00	0.91	1.025

$[I > 2\sigma(I)]$	R_1=0.086 wR_2=0.253	R_1=0.0497 wR_2=0.1156	R_1=0.060, wR_2=0.133	R_1=0.068 wR_2=0.214
CCDC number	1456971	1456970	1456968	1456969

References

(1) (a) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229. (b) Kasperczyk, J.; Bero, M. *Polymer* **2000**, *41*, 391.