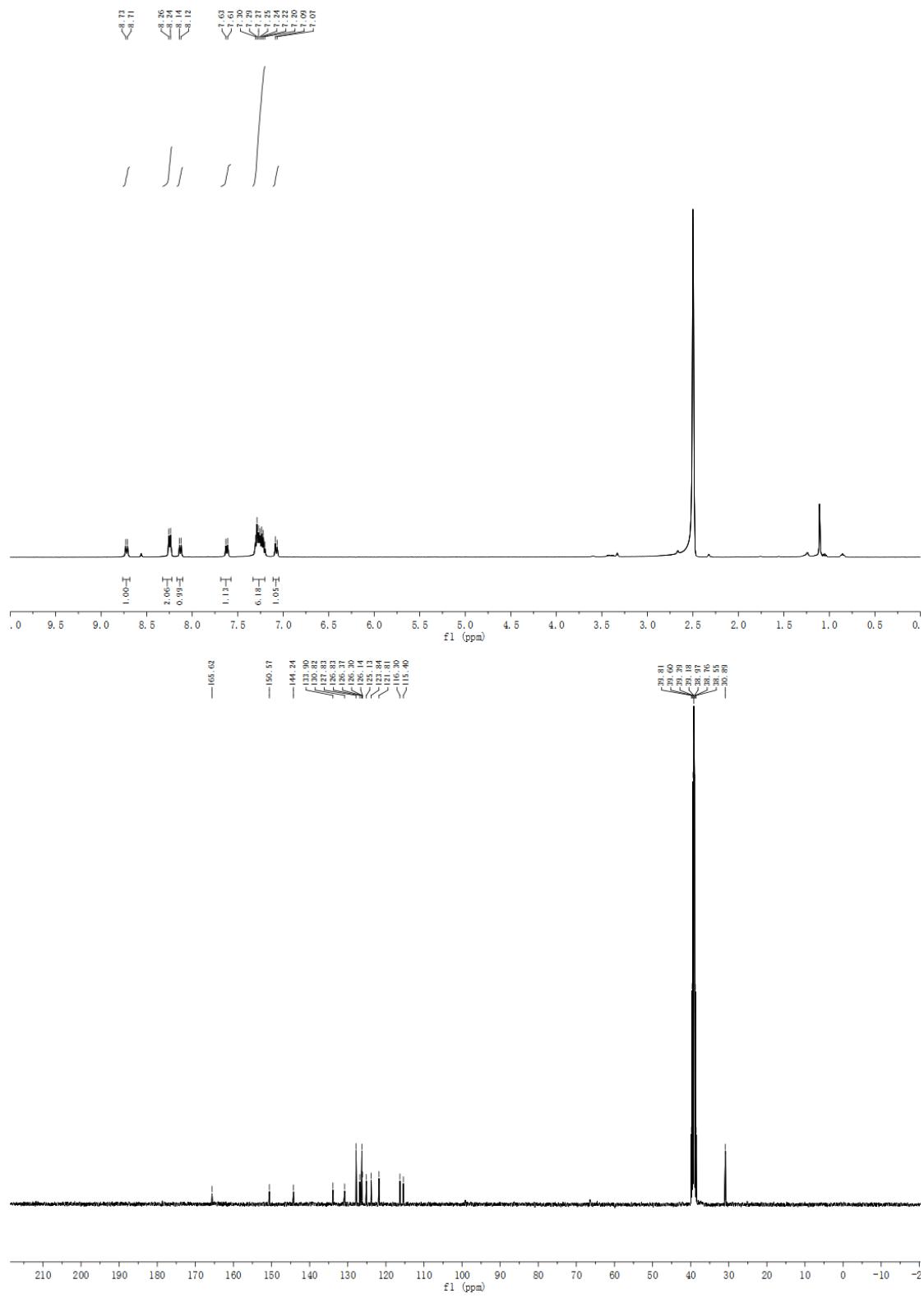


Supplementary Information  
for

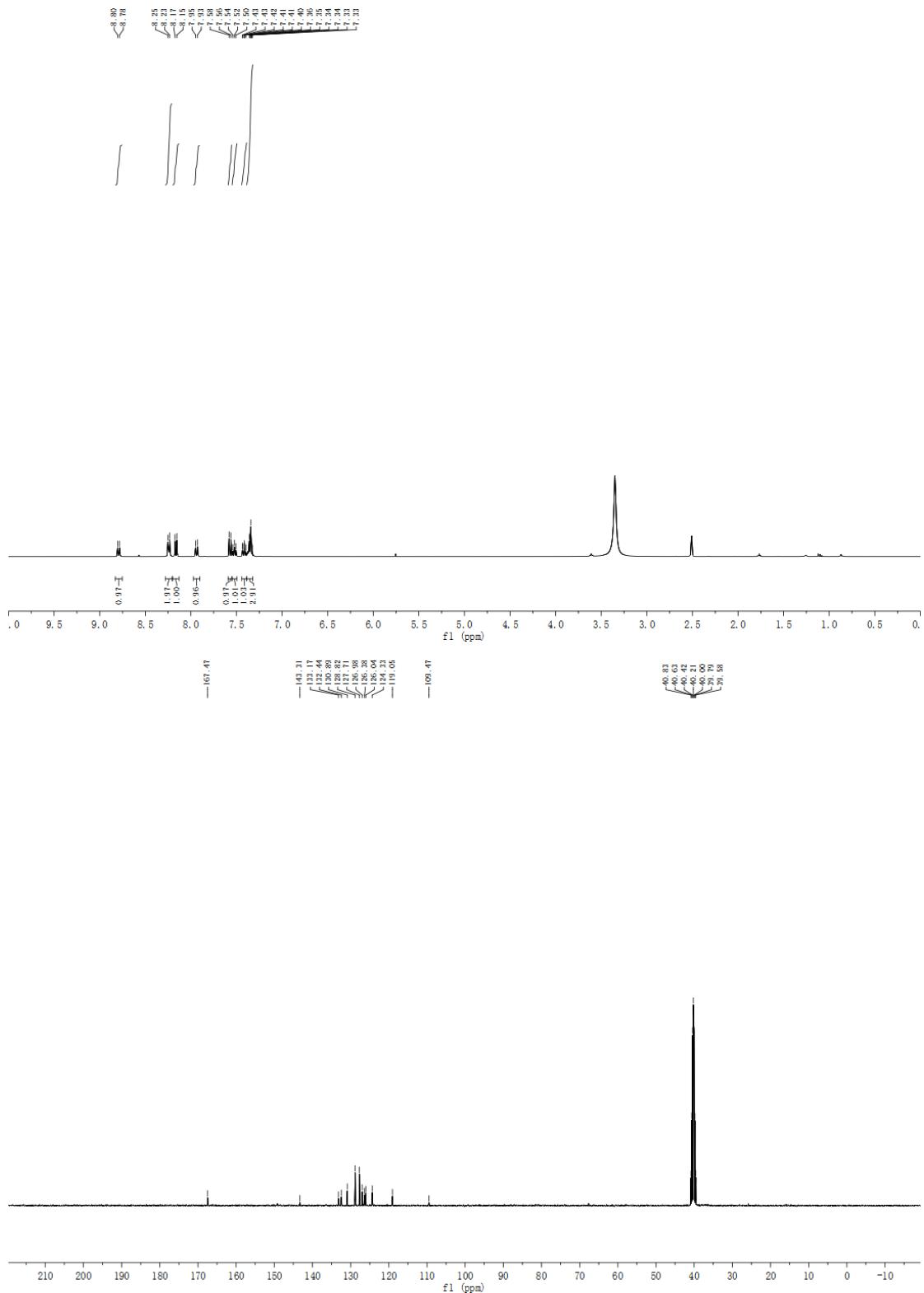
**Isoselective Ring-Opening Polymerization of *rac*-Lactide Catalyzed by Simple  
Potassium Amides Complexes Containing Polycyclic Aryl Group**

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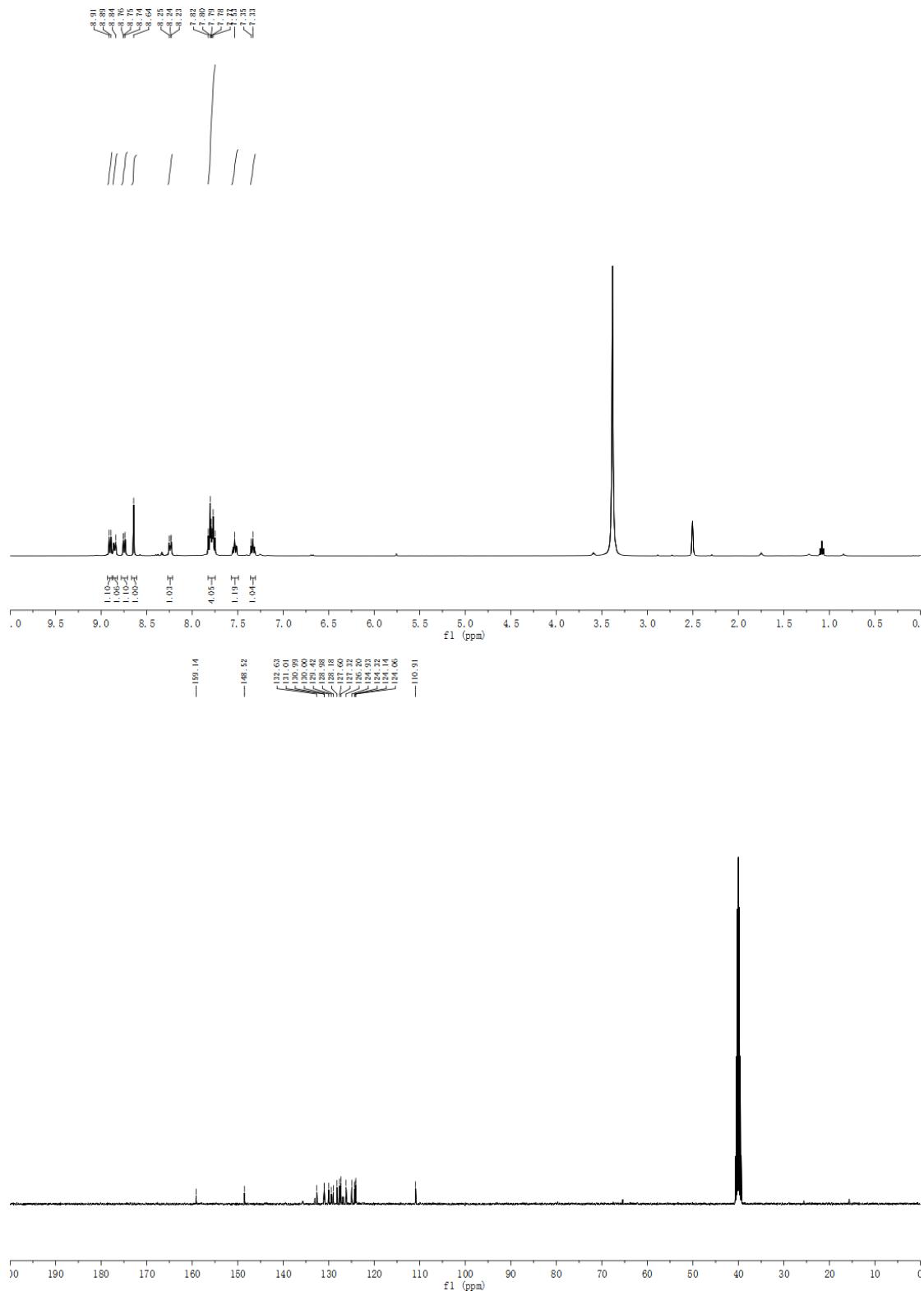
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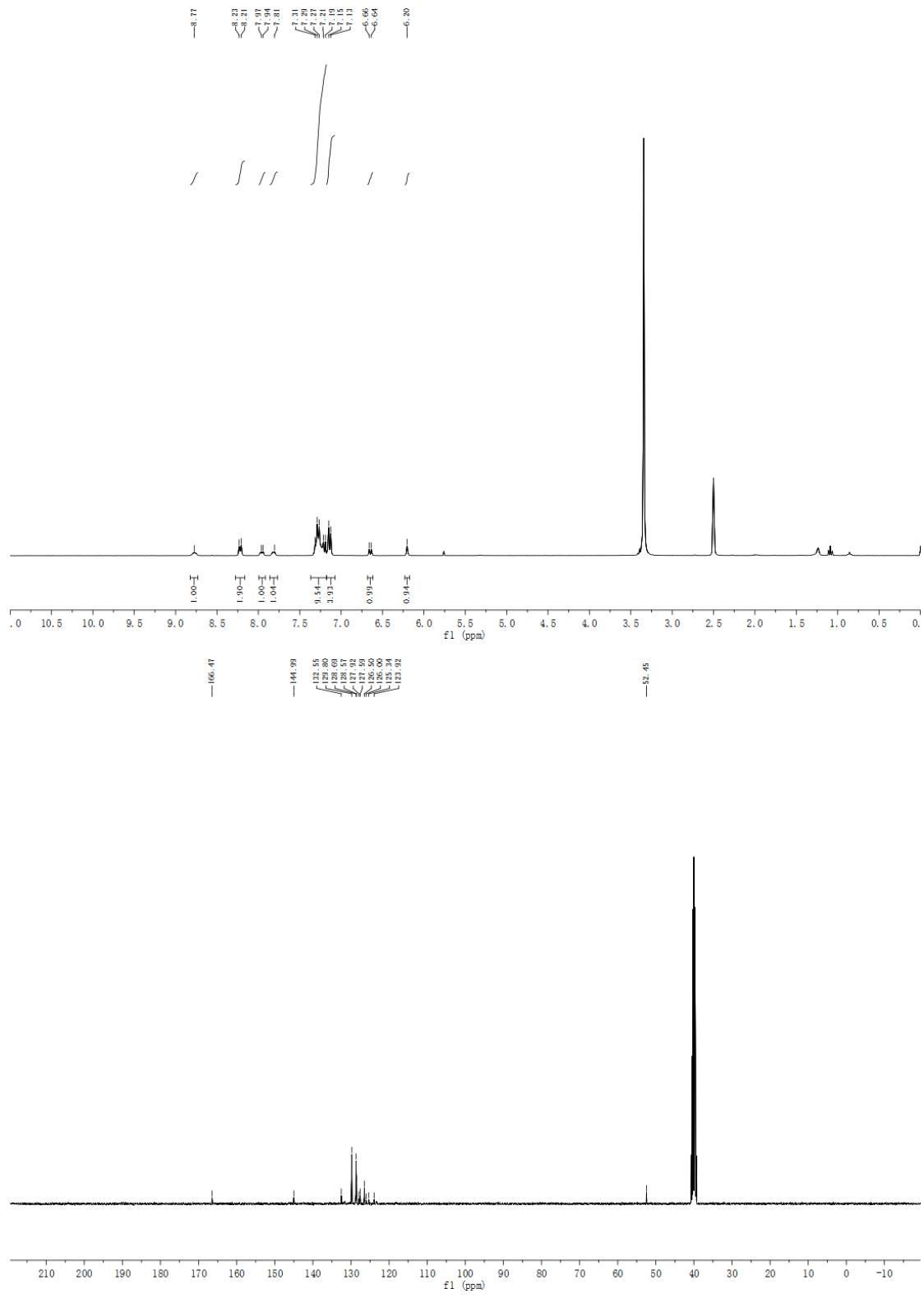
**Figure S1**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **K1** (recorded in  $d_6$ -DMSO).



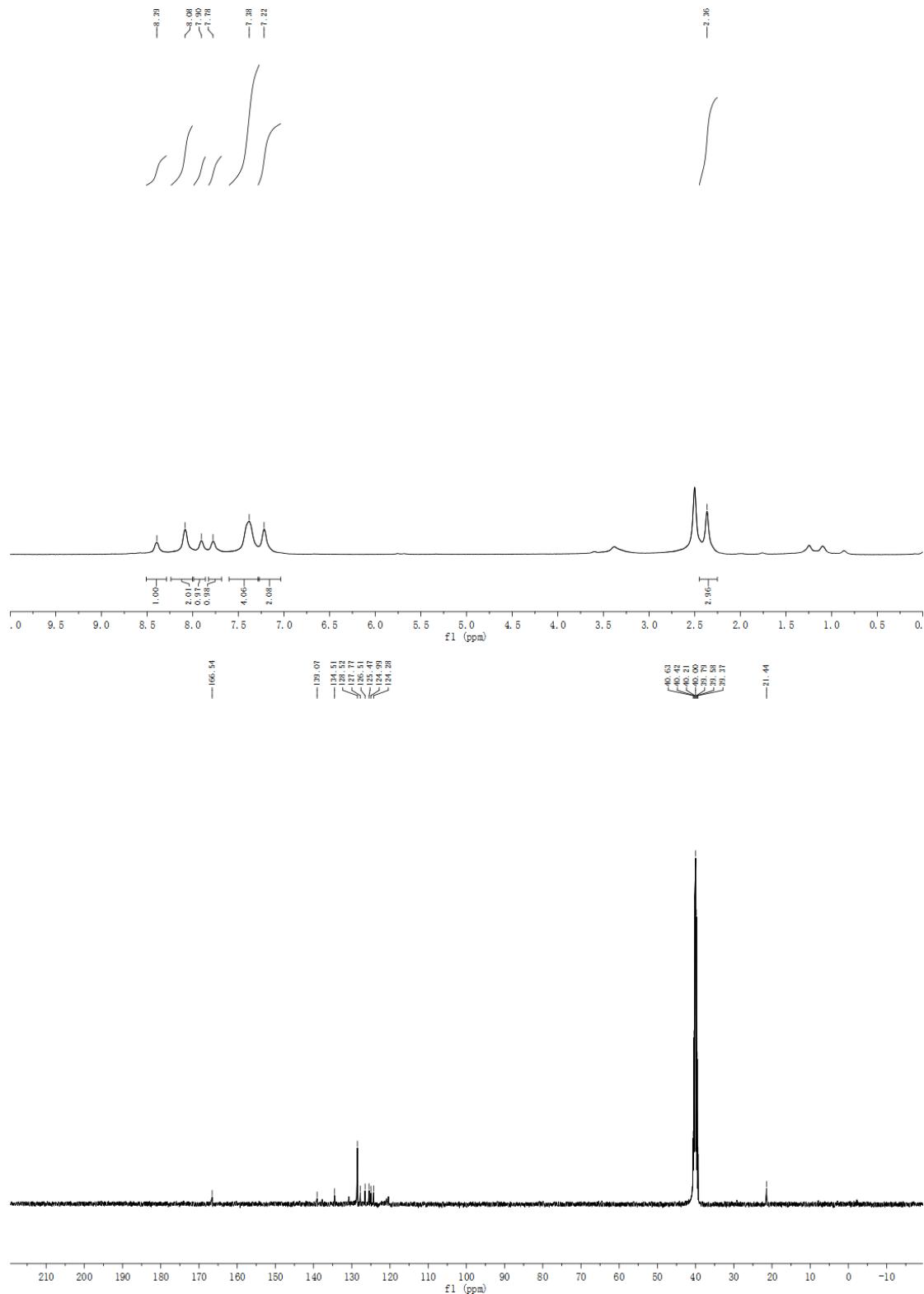
**Figure S2**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **K2** (recorded in  $d_6$ -DMSO)



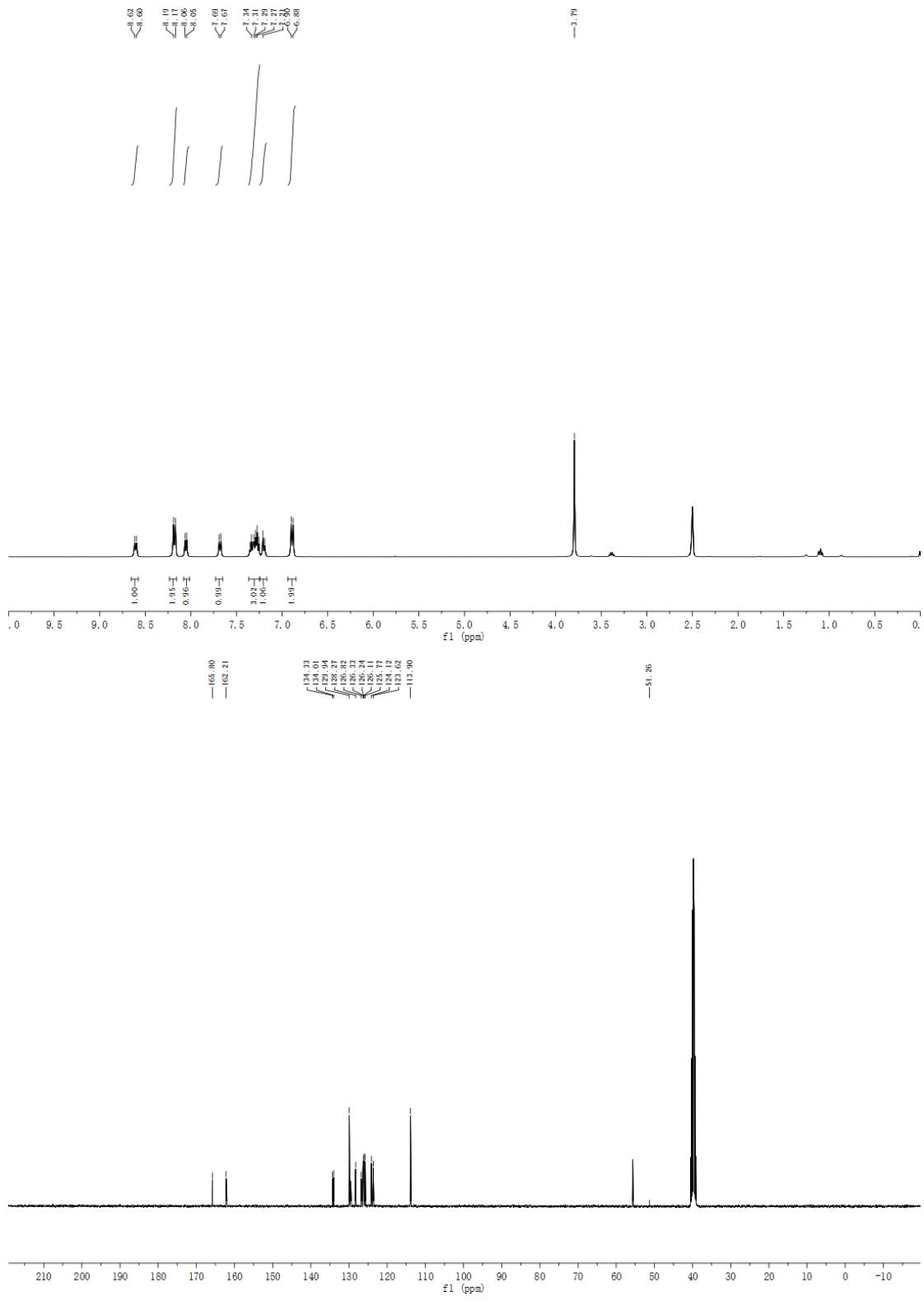
**Figure S3**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **K3** (recorded in  $d_6$ -DMSO)



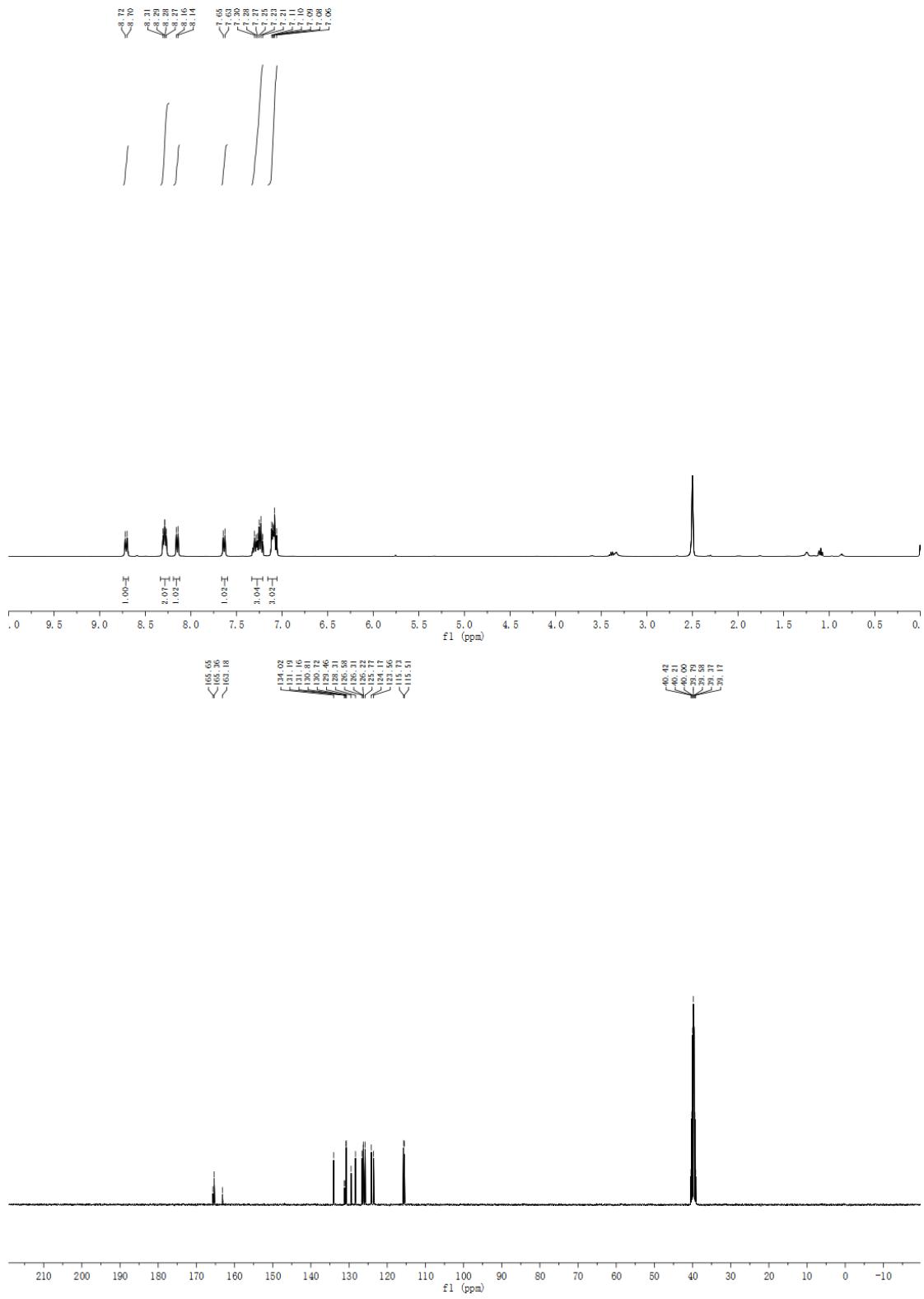
**Figure S4**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **K4** (recorded in  $d_6$ -DMSO)



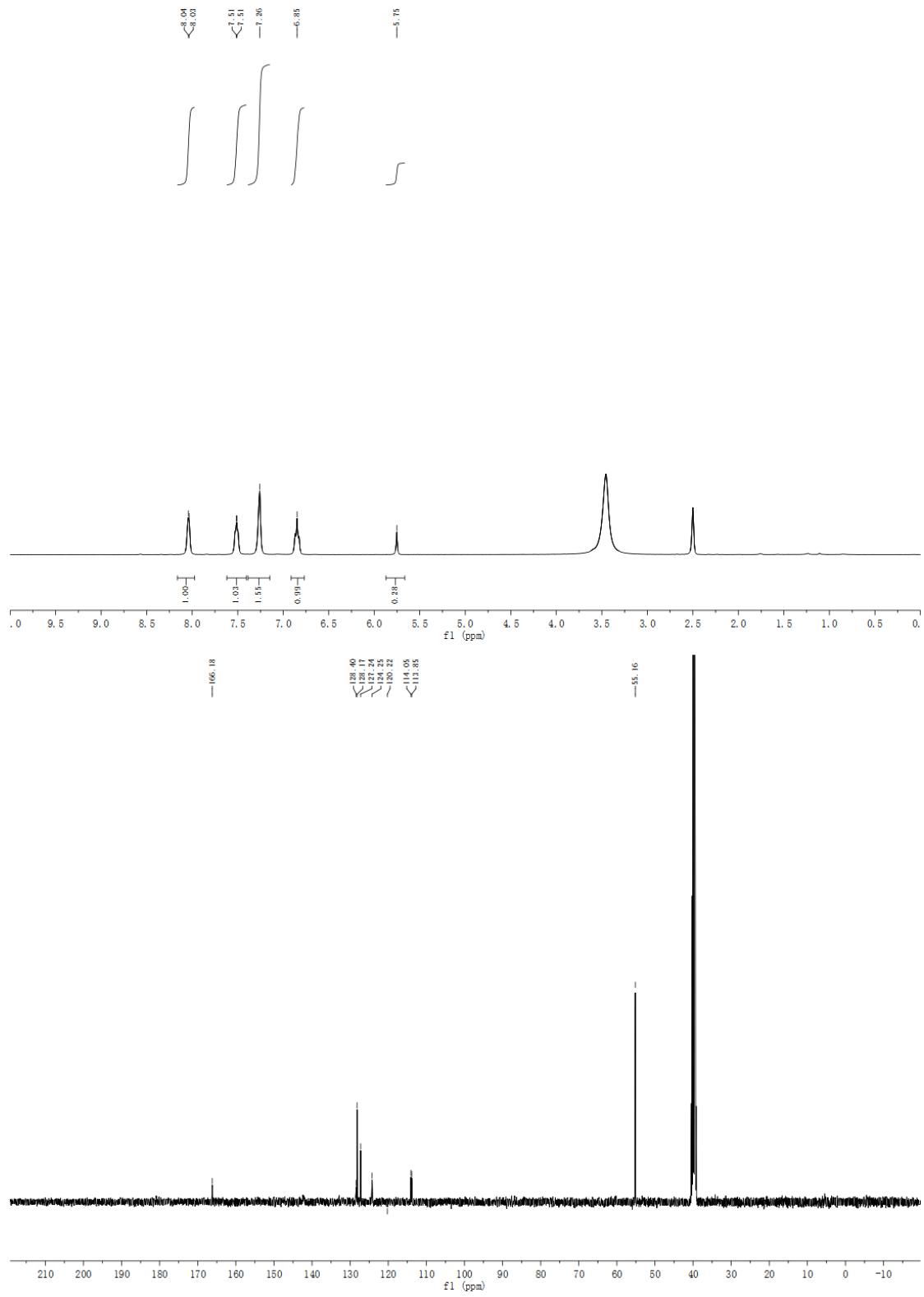
**Figure S5** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **K5** (recorded in *d*<sub>6</sub>-DMSO)



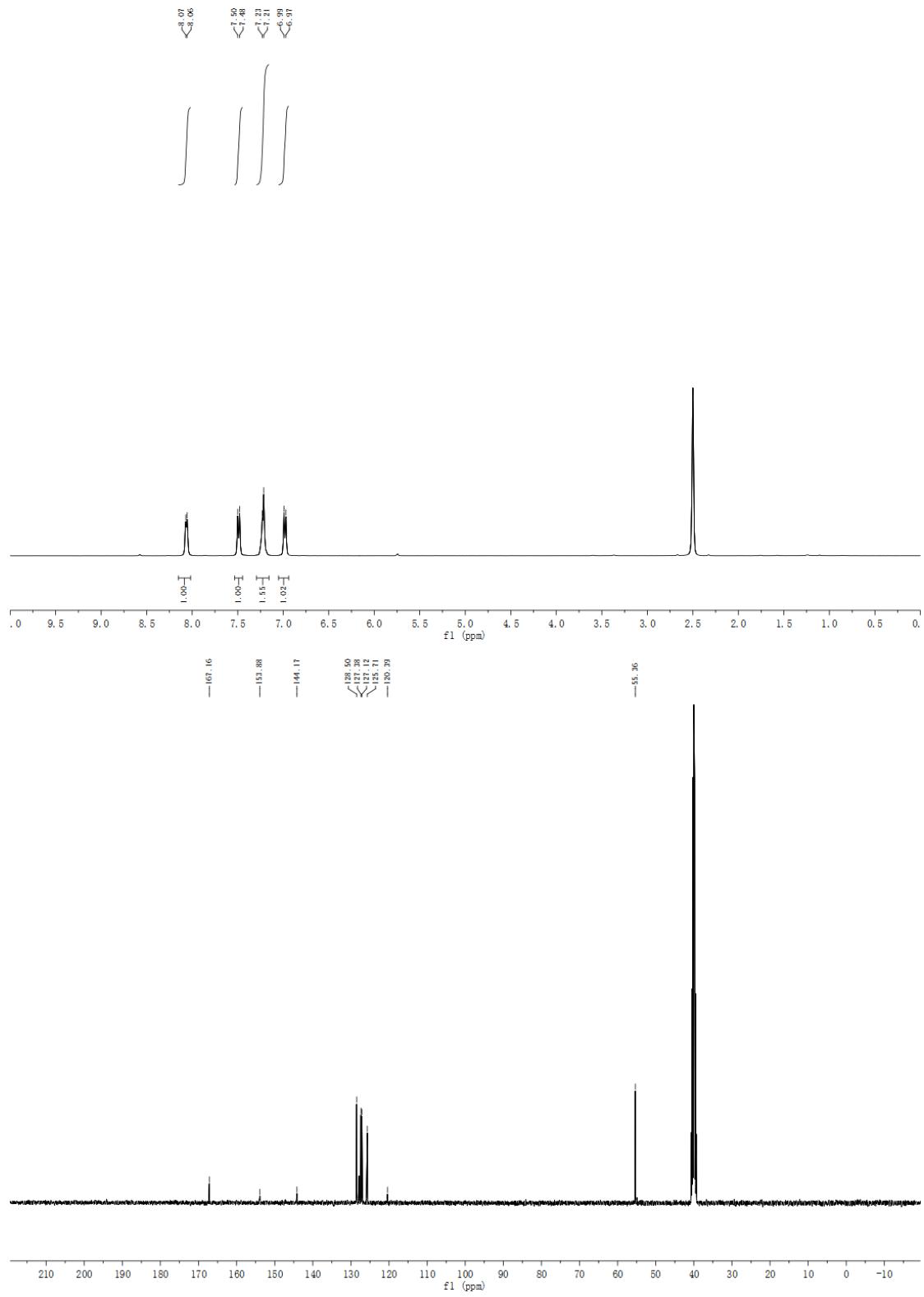
**Figure S6**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **K6** (recorded in  $d_6$ -DMSO)



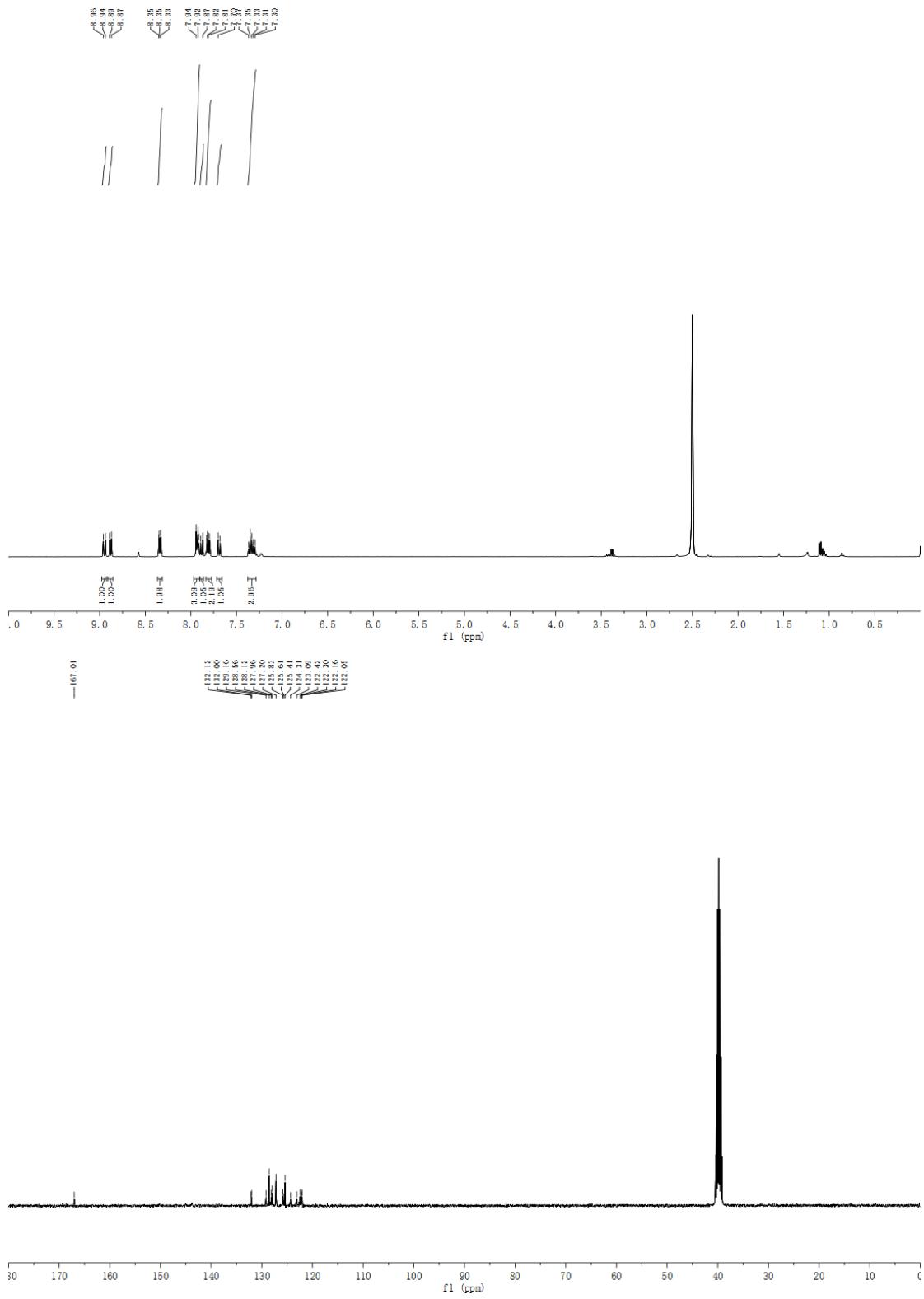
**Figure S7**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **K7** (recorded in  $d_6$ -DMSO).



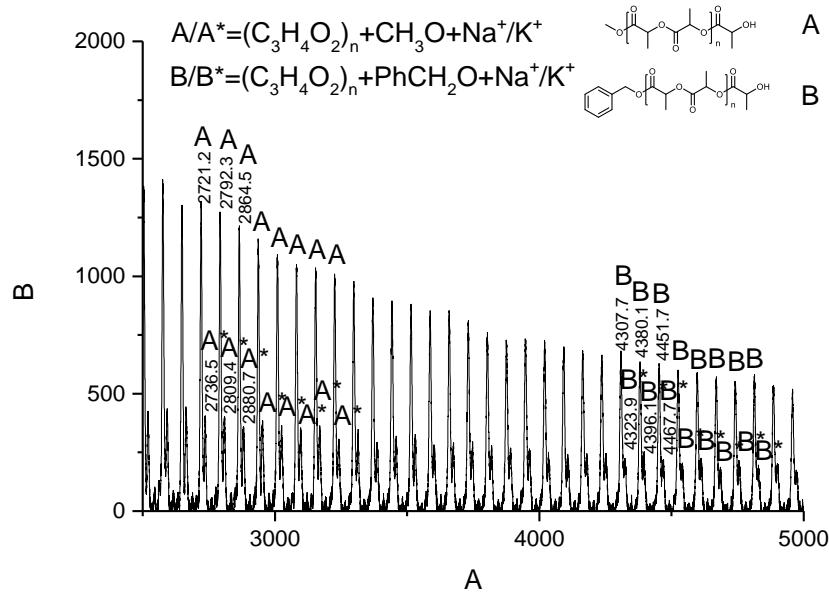
**Figure S8** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **K8** (recorded in *d*<sub>6</sub>-DMSO).



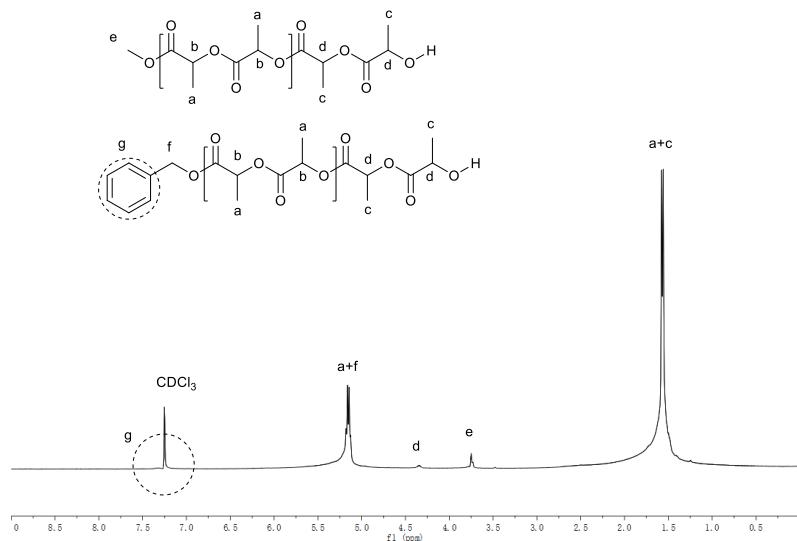
**Figure S9**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **K9** (recorded in  $d_6$ -DMSO).



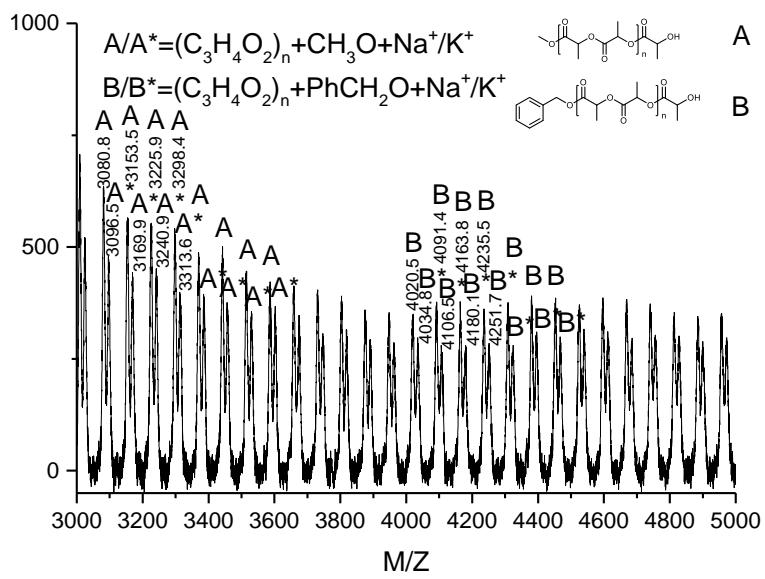
**Figure S10**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **K10** (recorded in  $d_6$ -DMSO).



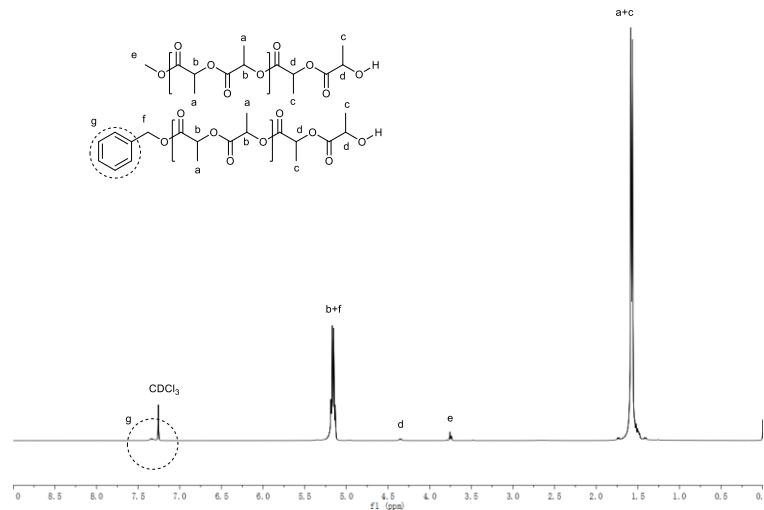
**Figure S11.** MOLDI-TOF spectrum of PLA obtained by **K2** and 1 equiv. of BnOH



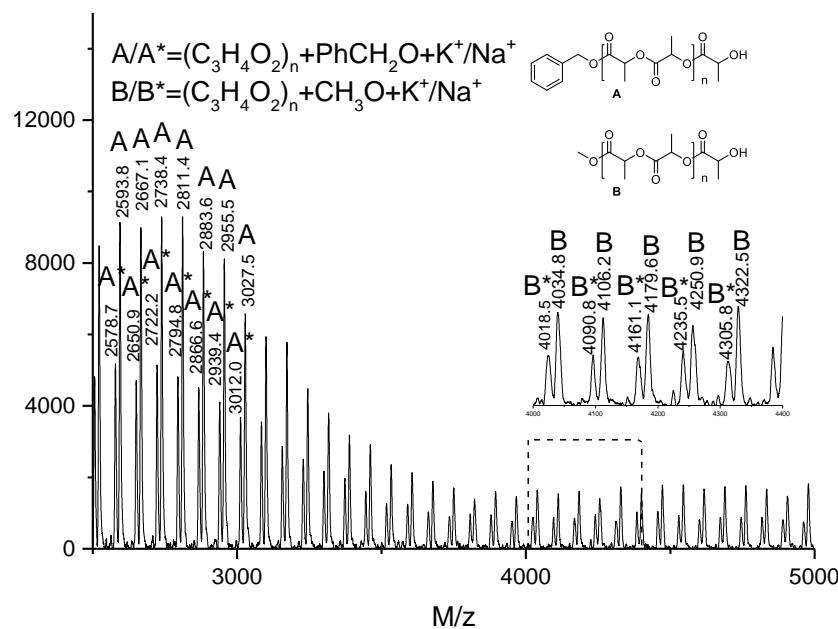
**Figure S12**  $^1\text{H}$  NMR spectra of obtained PLA by K2 and 1 equiv. of BnOH



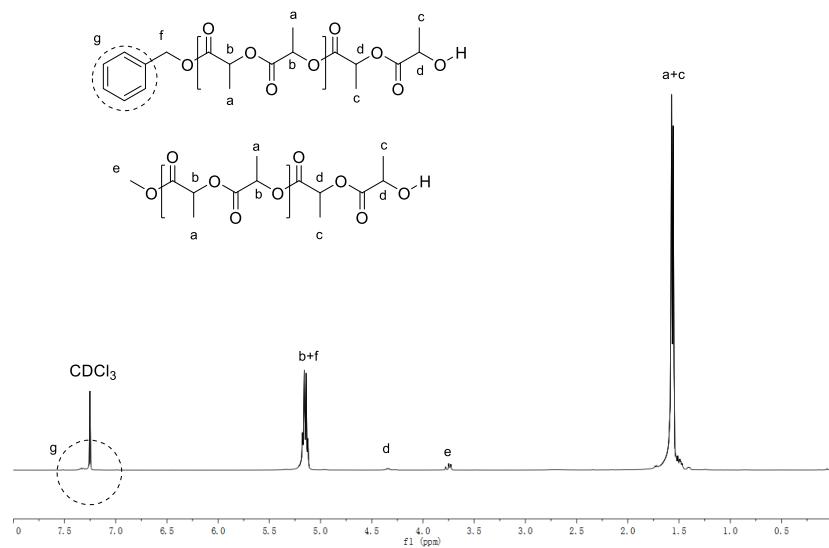
**Figure S13** MALDI-TOF spectrum of PLLA obtained by **K2** and 2 equiv. of BnOH



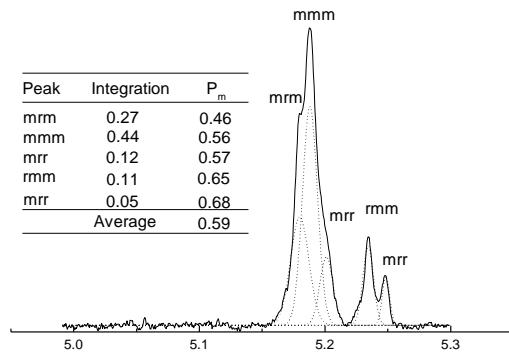
**Figure S14**  $^1\text{H}$  NMR spectra of obtained PLA by **K2** and 2 equiv. of BnOH



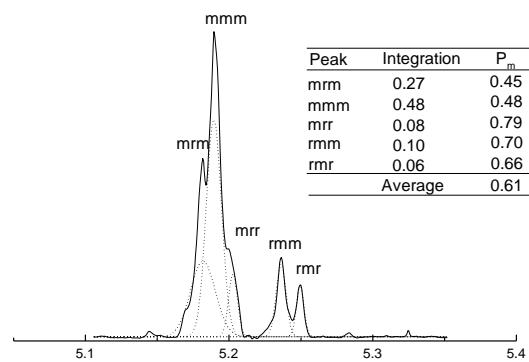
**Figure S15** MALDI-TOF spectrum of PLLA obtained by **K2** and 5 equiv. of BnOH



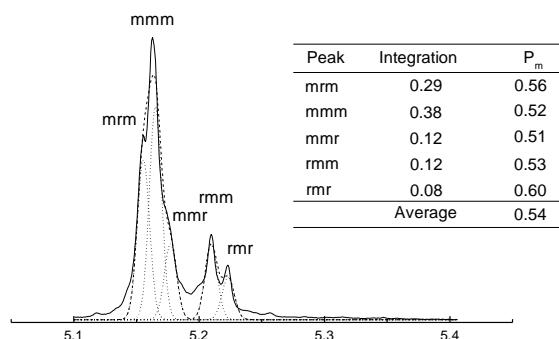
**Figure S16.** MOLDI-TOF spectrum of PLLA prepared by **K2** and 5equiv BnOH



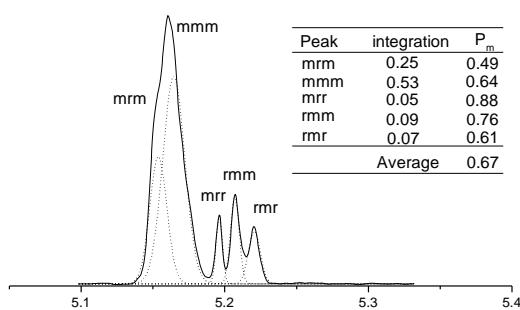
**Figure S17** Homonuclear-decoupled <sup>1</sup>H NMR spectroscopy of *rac*-LA obtained by **K1** in 60 min



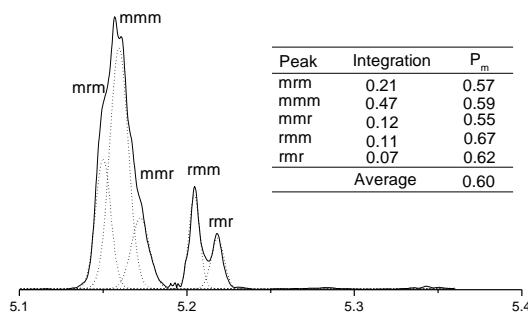
**Figure S18** Homonuclear-decoupled <sup>1</sup>H NMR spectroscopy of *rac*-LA obtained by **K2** in 60 min



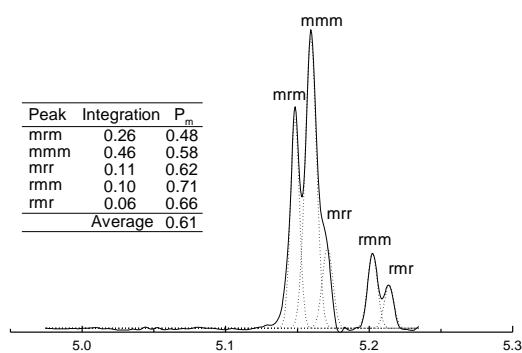
**Figure S19** Homonuclear-decoupled <sup>1</sup>H NMR spectroscopy of *rac*-LA obtained by **K3** in 60 min



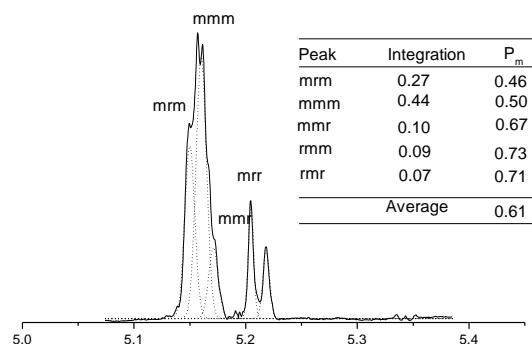
**Figure S20** Homonuclear-decoupled  $^1\text{H}$  NMR spectroscopy of *rac*-LA obtained by **K4** in 60 min



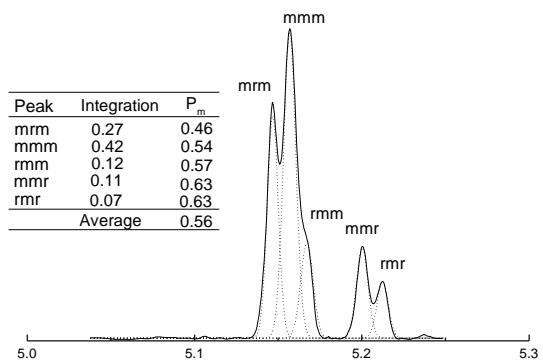
**Figure S21** Homonuclear-decoupled  $^1\text{H}$  NMR spectroscopy of *rac*-LA obtained by **K5** in 60 min



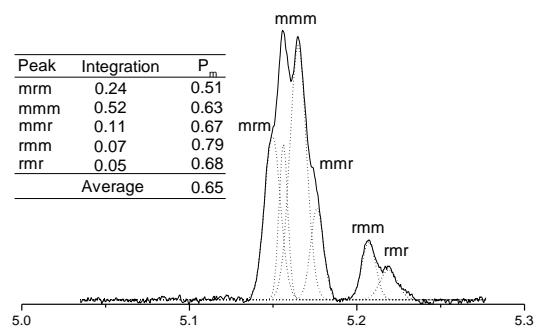
**Figure S22** Homonuclear-decoupled  $^1\text{H}$  NMR spectroscopy of *rac*-LA obtained by **K6** in 60 min



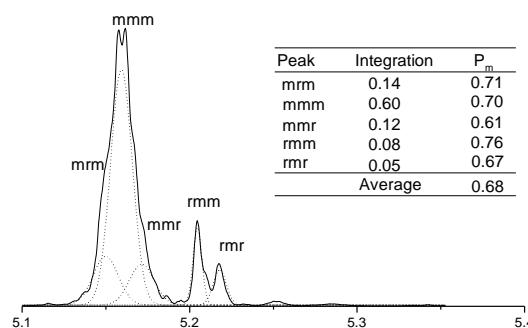
**Figure S23** Homonuclear-decoupled  $^1\text{H}$  NMR spectroscopy of *rac*-LA obtained by **K7** in 60 min



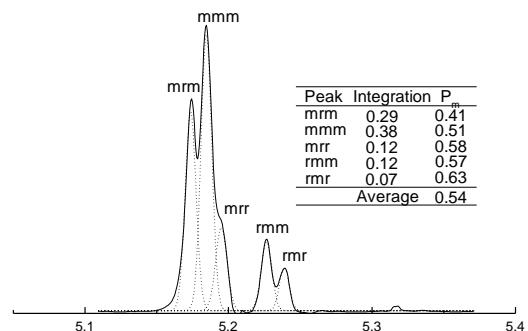
**Figure S24** Homonuclear-decoupled  $^1\text{H}$  NMR spectroscopy of *rac*-LA obtained by **K8** in 60 min



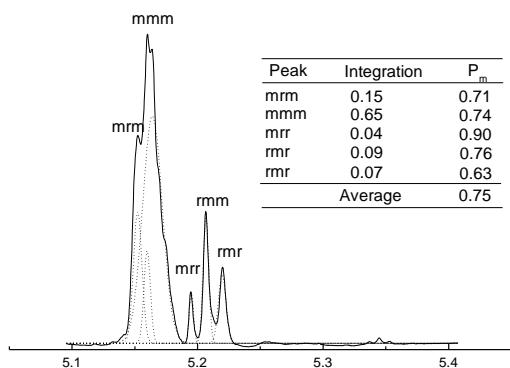
**Figure S25** Homonuclear-decoupled  $^1\text{H}$  NMR spectroscopy of *rac*-LA obtained by **K9** in 60 min



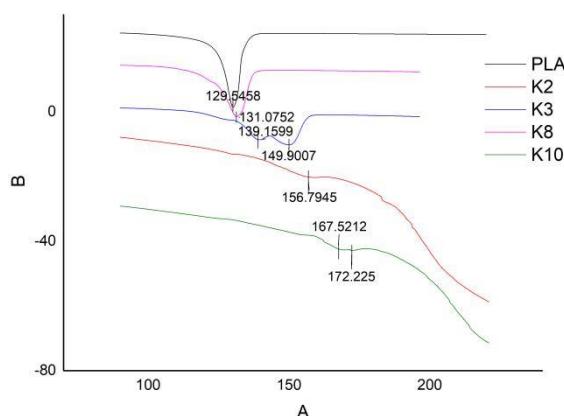
**Figure S26** Homonuclear-decoupled  $^1\text{H}$  NMR spectroscopy of *rac*-LA obtained by **K10** in 60 min



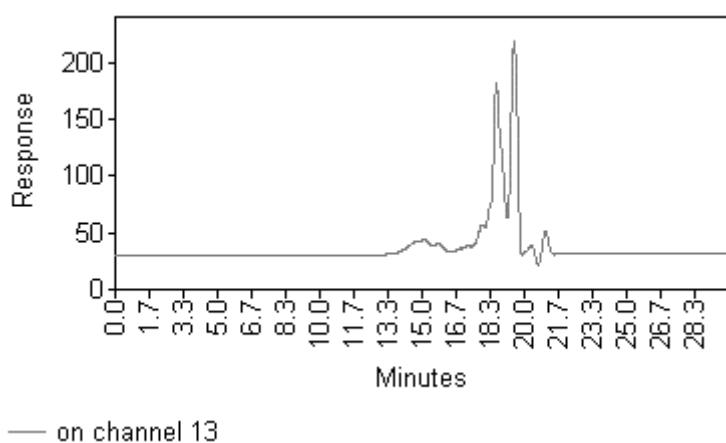
**Figure S27** Homonuclear-decoupled  $^1\text{H}$  NMR spectroscopy of *rac*-LA obtained by **K11** in 60 min



**Figure S28** Homonuclear-decoupled  $^1\text{H}$  NMR spectroscopy of *rac*-LA obtained by **K2** within 10 min



**Figure S29.** Comparing the  $T_m$  by using different catalysts (run 2, 3, 8, 10, Table 4; PLA was the polymer which catalytic with L-LA by K2, run 5, Table 2)



**Figure S30.** GPC curves of the PLLA produced using **K2** (runs 9, Table 2)

**Table S1.** Crystallographic data and refinement details for **K2** and **K10**

Identification code	<b>K2</b>	<b>K10</b>
Empirical formula	BrC <sub>17</sub> KNO	C <sub>46</sub> H <sub>28</sub> K <sub>2</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	353.19	718.90
Temperature/K	170.00(10)	169.99(14)
Crystal system	orthorhombic	monoclinic
Space group	Pbca	P2 <sub>1</sub> /c
a/Å	11.80430(10)	28.2391(6)
b/Å	11.04670(10)	11.9423(3)
c/Å	22.6296(2)	10.6840(3)
α/°	90	90
β/°	90	98.068(2)
γ/°	90	90
Volume/Å <sup>3</sup>	2950.87(4)	3567.41(16)
Z	8	4
ρ <sub>calcg/cm<sup>3</sup></sub>	1.590	1.339
μ/mm <sup>-1</sup>	6.291	2.681
F(000)	1368.0	1488.0
Crystal size/mm <sup>3</sup>	0.25 × 0.15 × 0.05	0.1 × 0.08 × 0.005
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.814 to 150.308	6.322 to 151.232
Index ranges	-11 ≤ h ≤ 14, -13 ≤ k ≤ 13, -28 ≤ l ≤ 26	-26 ≤ h ≤ 34, -14 ≤ k ≤ 14, -13 ≤ l ≤ 13
Reflections collected	10706 2943	24756 6838
Independent reflections	[R <sub>int</sub> = 0.0338, R <sub>sigma</sub> = 0.0285]	[R <sub>int</sub> = 0.0511, R <sub>sigma</sub> = 0.0463]
Data/restraints/parameters	2943/0/190	6838/0/469
Goodness-of-fit on F <sup>2</sup>	1.080	1.293
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0440, wR <sub>2</sub> = 0.1348	R <sub>1</sub> = 0.1087, wR <sub>2</sub> = 0.3039
Final R indexes [all data]	R <sub>1</sub> = 0.0466, wR <sub>2</sub> = 0.1371	R <sub>1</sub> = 0.1281, wR <sub>2</sub> = 0.3224
Largest diff. peak/hole / e Å <sup>-3</sup>	0.85/-0.66	1.72/-0.61