Supporting Information

Tunable Benzamidinate Zinc Complexes: Coordination Modes and Catalytic Activity in the Ring-Opening Polymerization of L-lactide

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Crystal structure data

Table S1. Crystallographic data and refinement details for complexes **1**-**4** and **7**

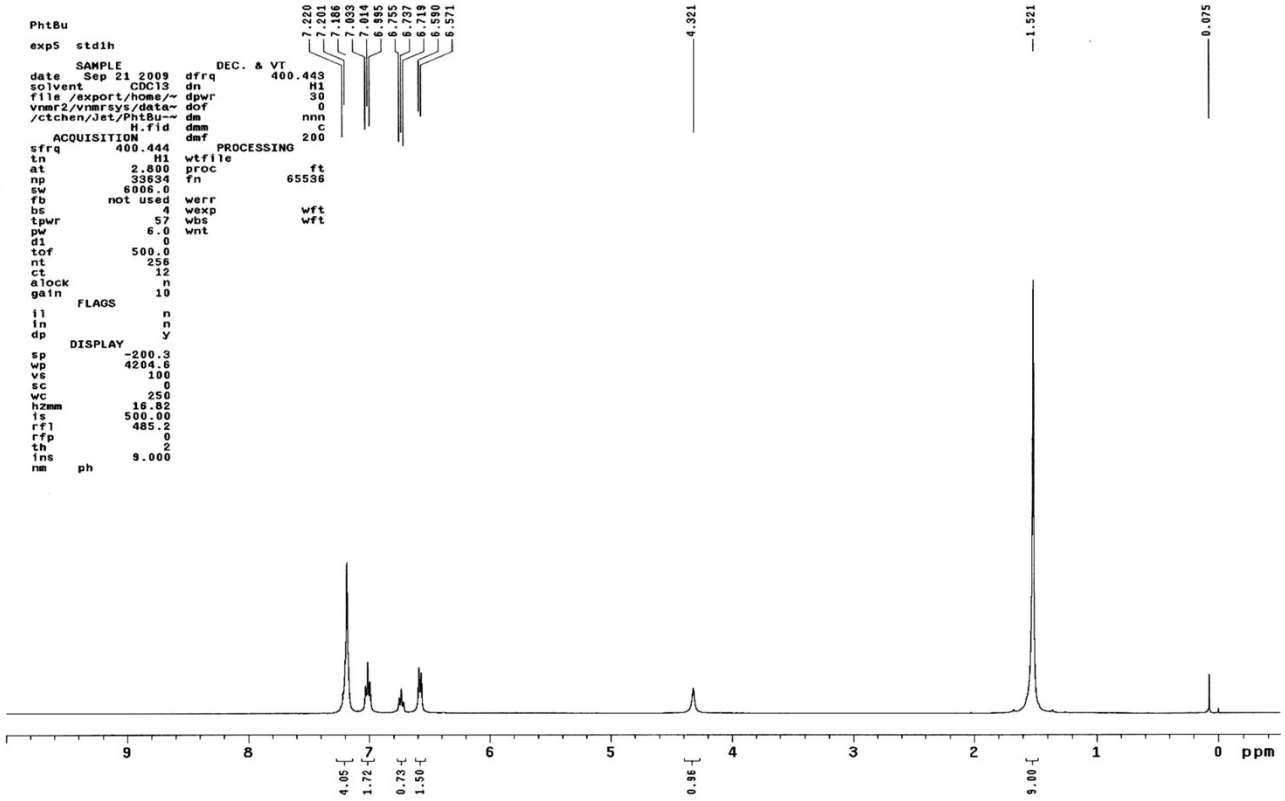
	1	**2**	**3**	**4**	**7**
Formula	$C_{38}H_{48}N_4Zn_2$	$C_{36}H_{44}N_4O_2Zn_2$	$C_{38}H_{50}N_6Zn_2$	$C_{68}H_{76}N_8Zn_2$	$C_{38}H_{32}N_6Zn$
Fw	691.54	695.49	721.58	1136.11	638.07
T, K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	*P-1*	C_2/c	*P*2(1)/n	C_2/c	P_{bca}
a, Å	9.4824(4)	12.7899(4)	8.4604(2)	14.8451(4)	13.3353(3)
b, Å	10.0818(5)	12.0267(3)	9.6640(2)	20.7782(5)	18.1750(4)
c, Å	10.7058(4)	22.7927(6)	22.0213(5)	20.2976(5)	26.2092(6)
a °	103.486(4)	90	90	90	90
β °	104.402(4)	92.379(2)	98.548(2)	103.280(3)	90
γ °	109.408(4)	90	90	90	90
V, Å^3	877.31(7)	3502.96(17)	1780.49(7)	6093.5(3)	6352.3(2)
Z	1	4	2	4	8
ρ_{calc}, Mg/m^3	1.309	1.319	1.346	1.238	1.334
μ(Mo Kα), mm^{-1}	1.398	1.405	1.382	0.834	0.810
Reflections collected	7035	15350	13549	15464	36959
No. of parameters	199	199	221	352	406
Indep. reflns (R_{int})	3973 (0.0146)	4300 (0.0237)	4231 (0.0171)	7071 (0.0391)	7946 (0.0235)
Final R indices R_1[a], wR_2[a]	0.0241, 0.0738	0.0274, 0.0698	0.0338, 0.1230	0.0455, 0.0699	0.0276, 0.0738
R indices (all data)	0.0264, 0.0748	0.0379, 0.0716	0.0414, 0.1267	0.0854, 0.0731	0.0433, 0.0779
GoF [b]	1.040	1.017	1.024	1.030	1.034

[a] $P_1 = [\ \Sigma(|\Phi_0| - |\Phi_\chi|]/\ \Sigma\ |\Phi_0|]$; $\omega P_2 = [\Sigma\ \omega(\Phi_0^2 - \Phi_\chi^2)^2/\ \Sigma\ \omega(\Phi_0^2)^2]^{1/2}$, ω = 0.10.

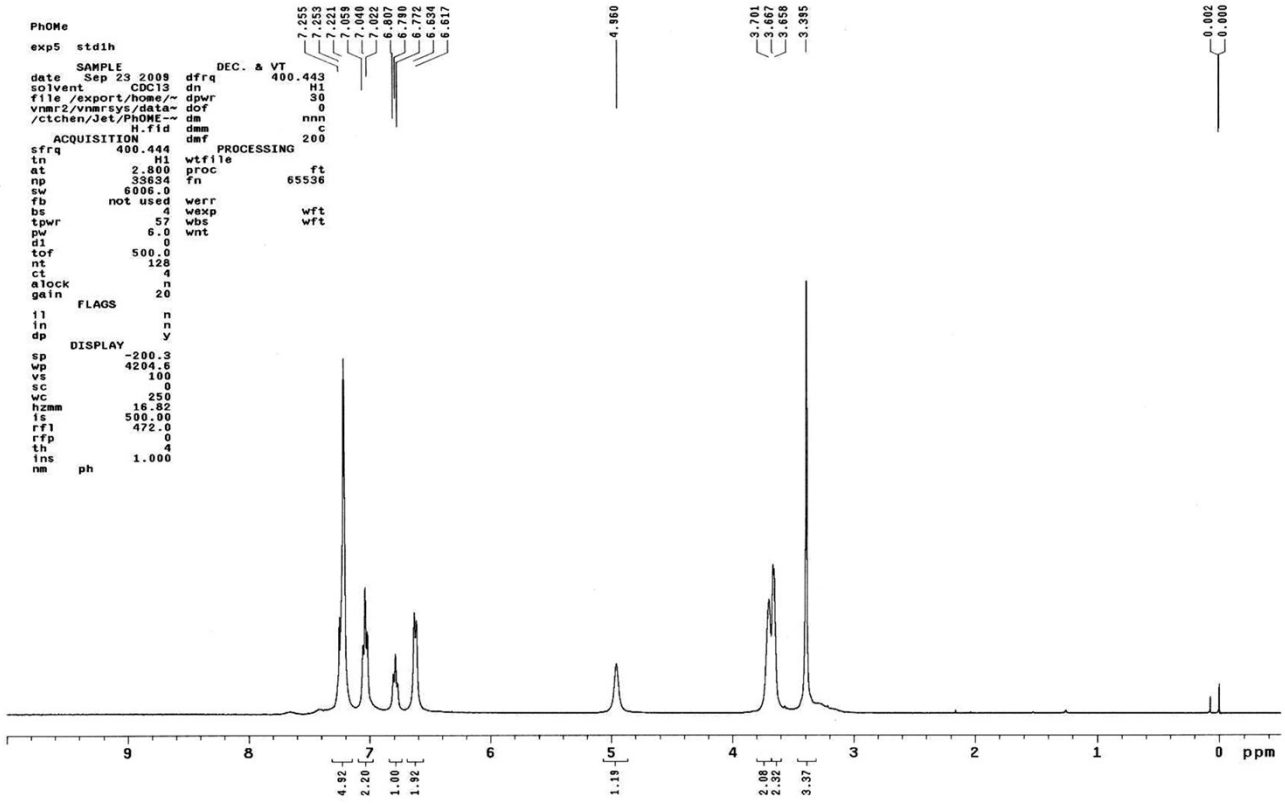
[b] GoF = $[\Sigma w(F_0^2\text{-}F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$

Spectra of ligand precursors L1a-L1b

^{1}H NMR of **L1a** in $CDCl_3$

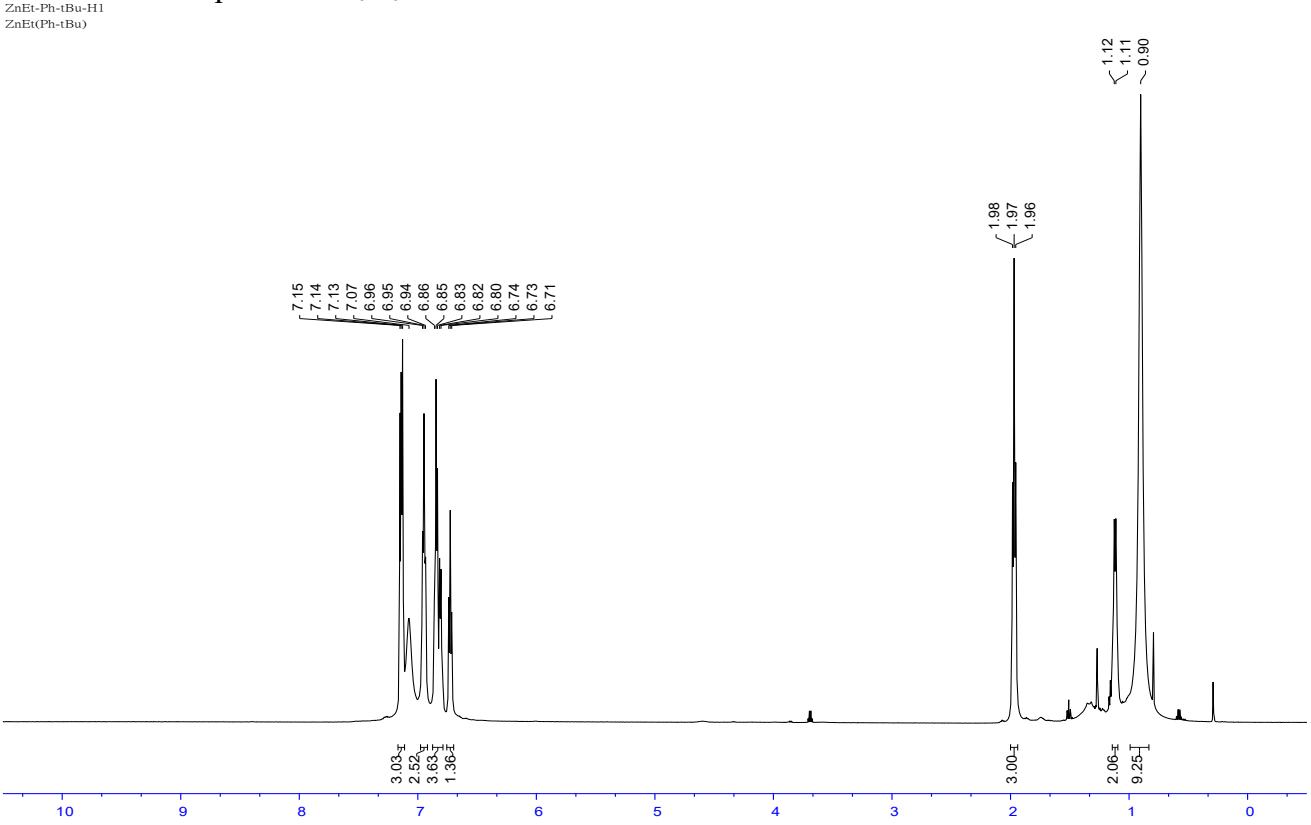


^{1}H NMR of **L1b** in $CDCl_3$

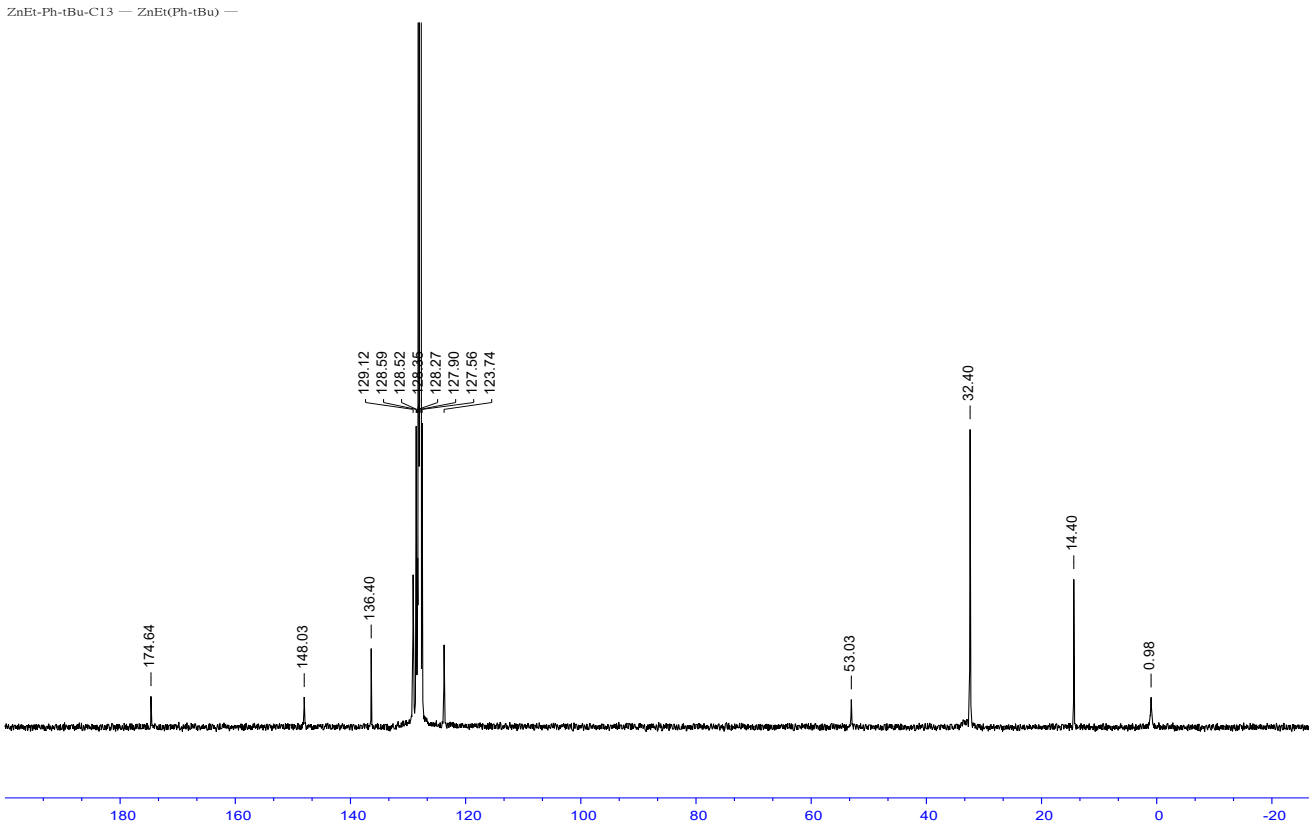


Spectra of complexes 1-7

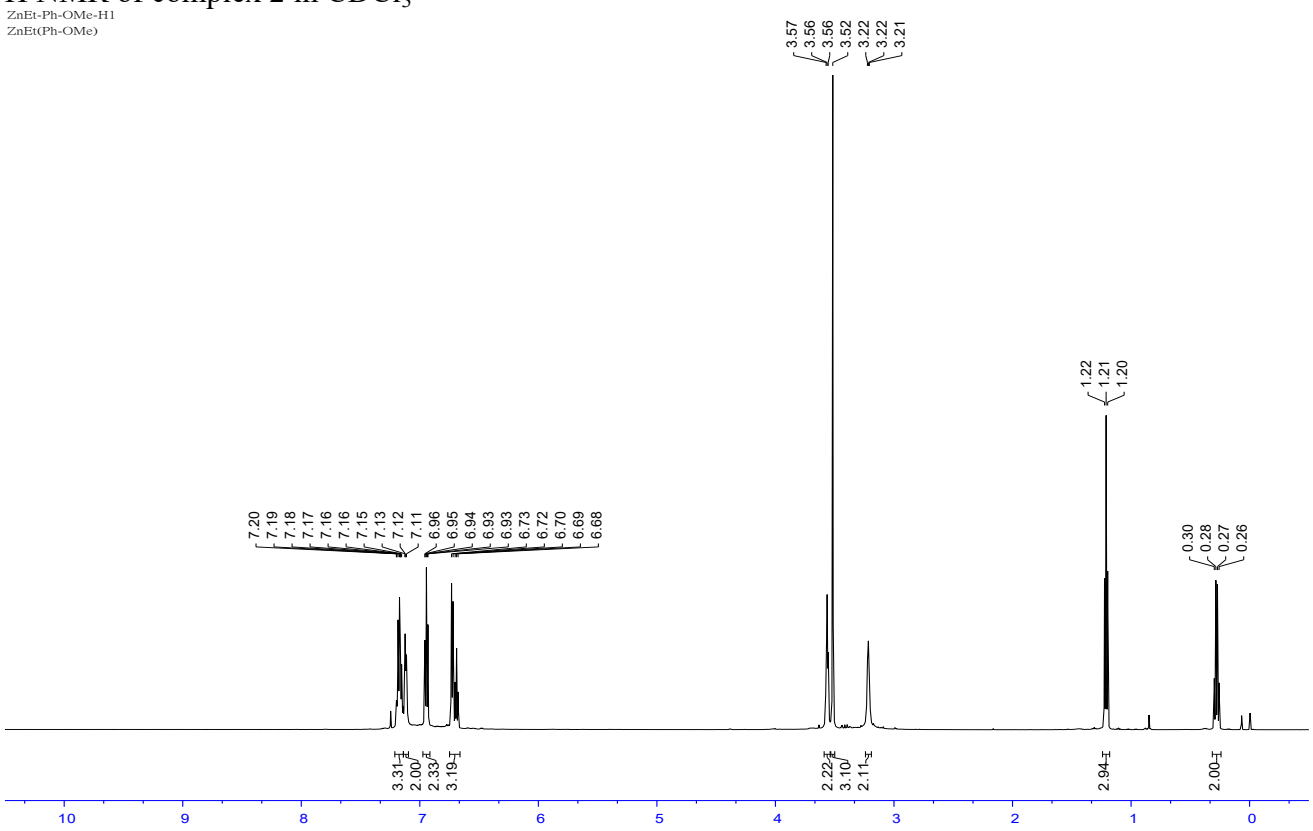
^{1}H NMR of complex **1** in C_6D_6



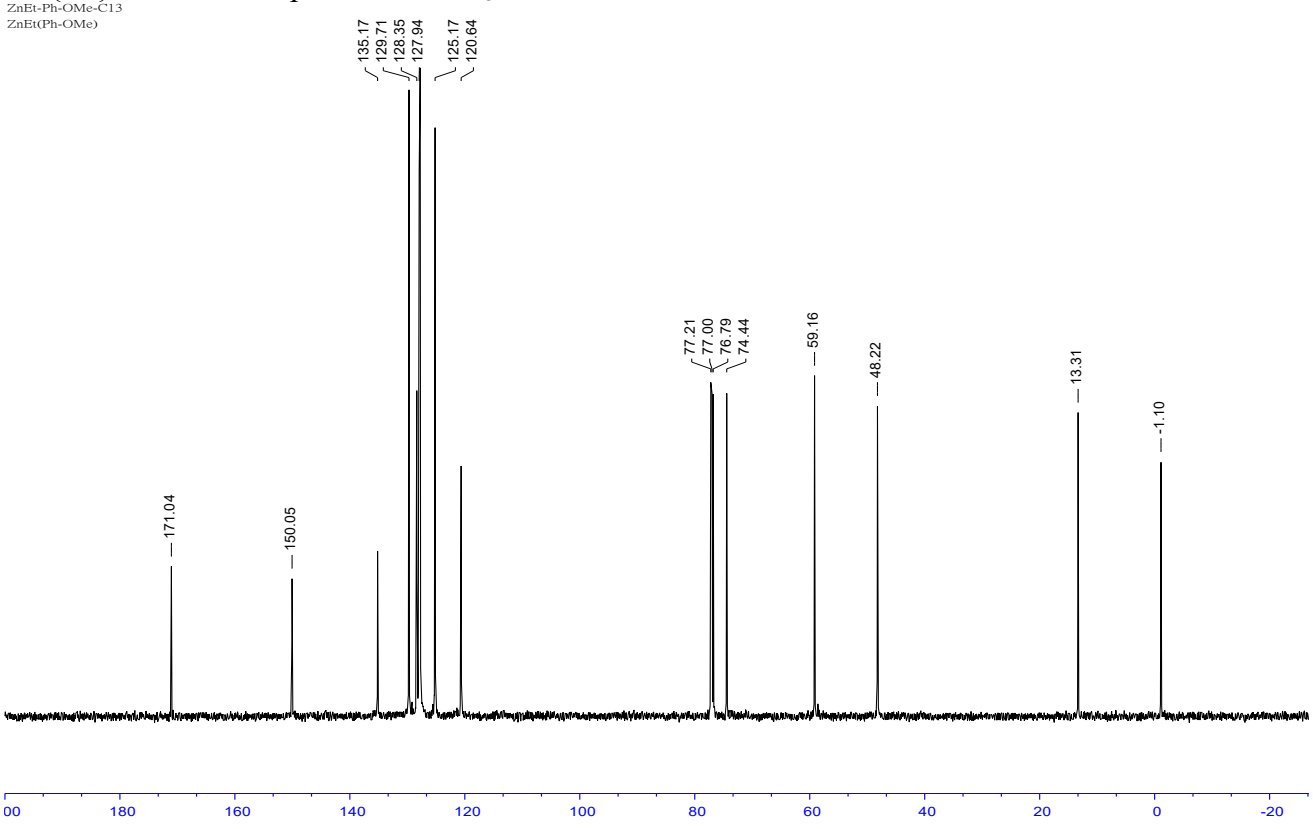
$^{13}C\{^{1}H\}$ NMR of complex **1** in C_6D_6



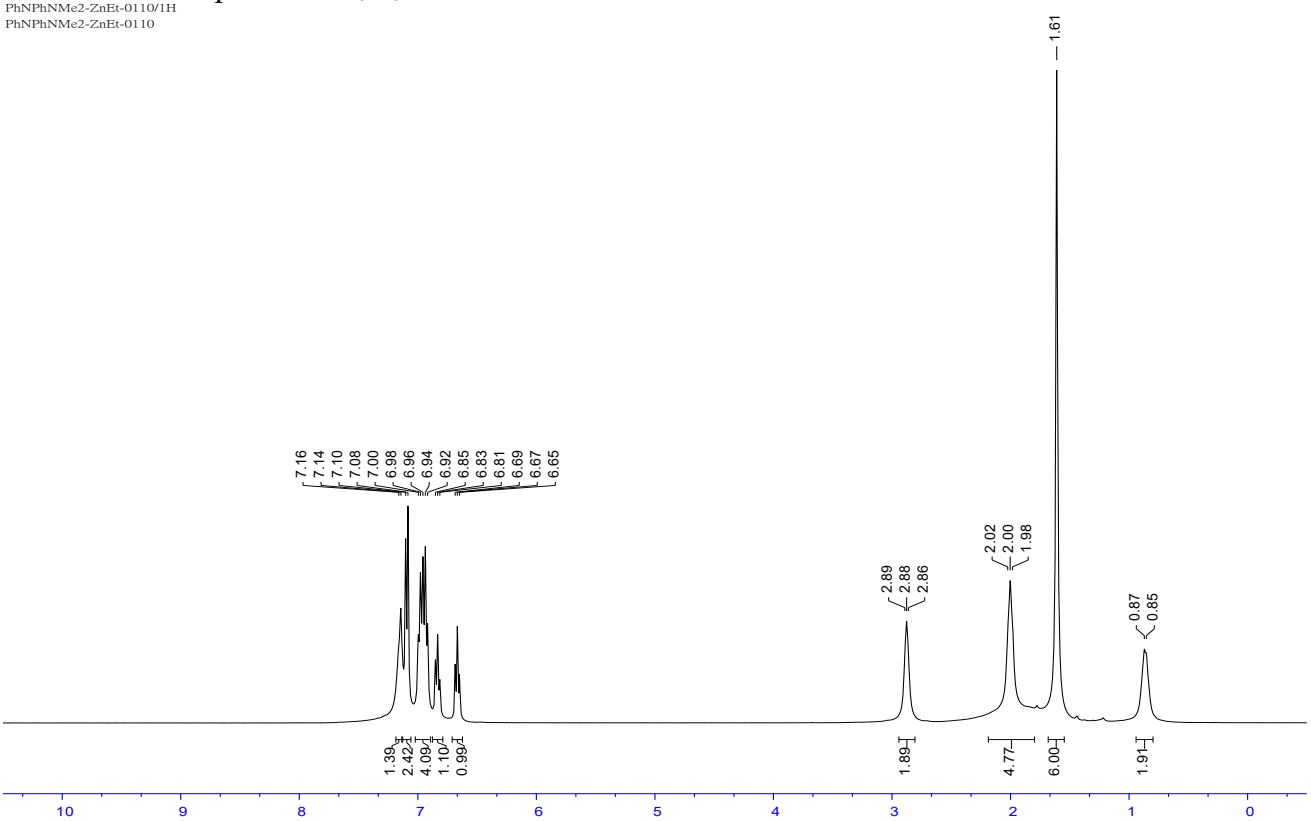
H NMR of complex **2** in $CDCl_3$



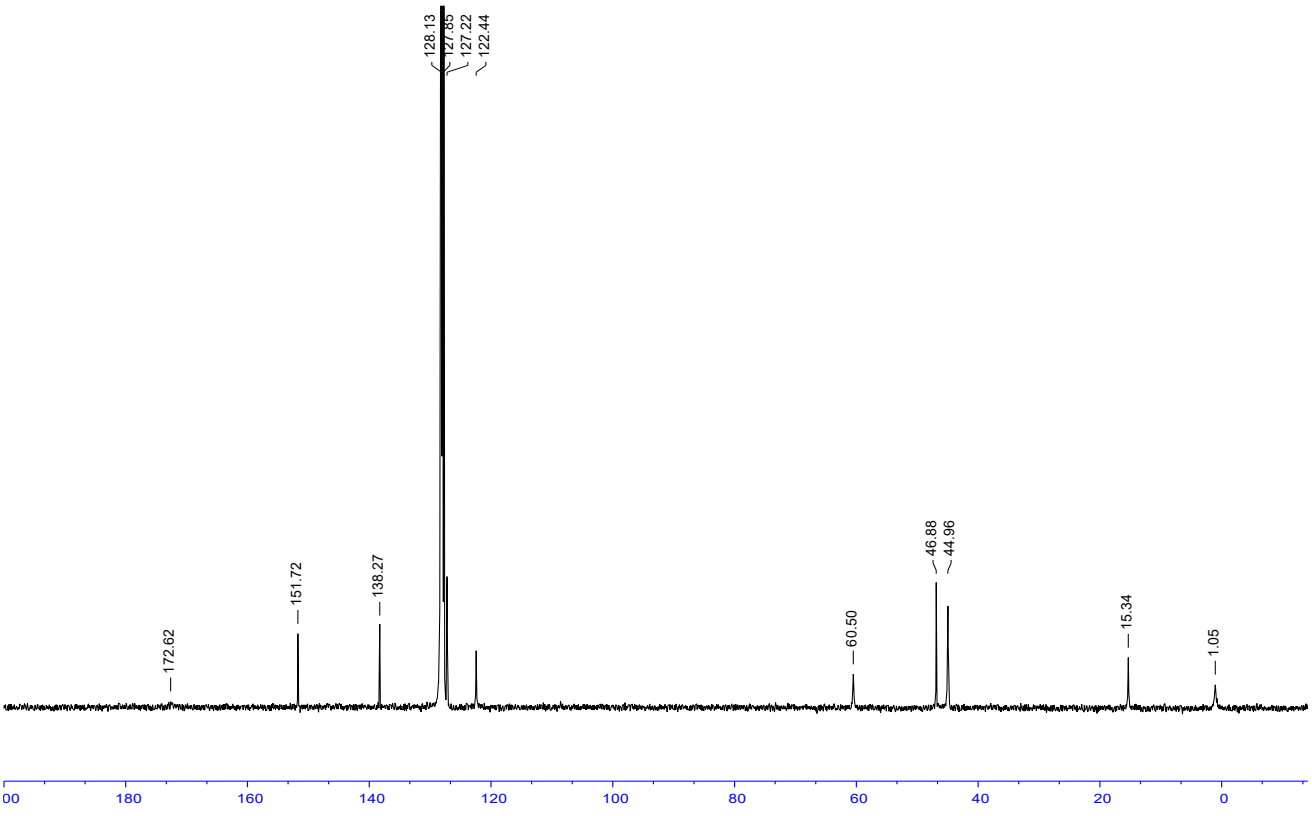
$^{13}C\{^{1}H\}$ NMR of complex **2** in $CDCl_3$



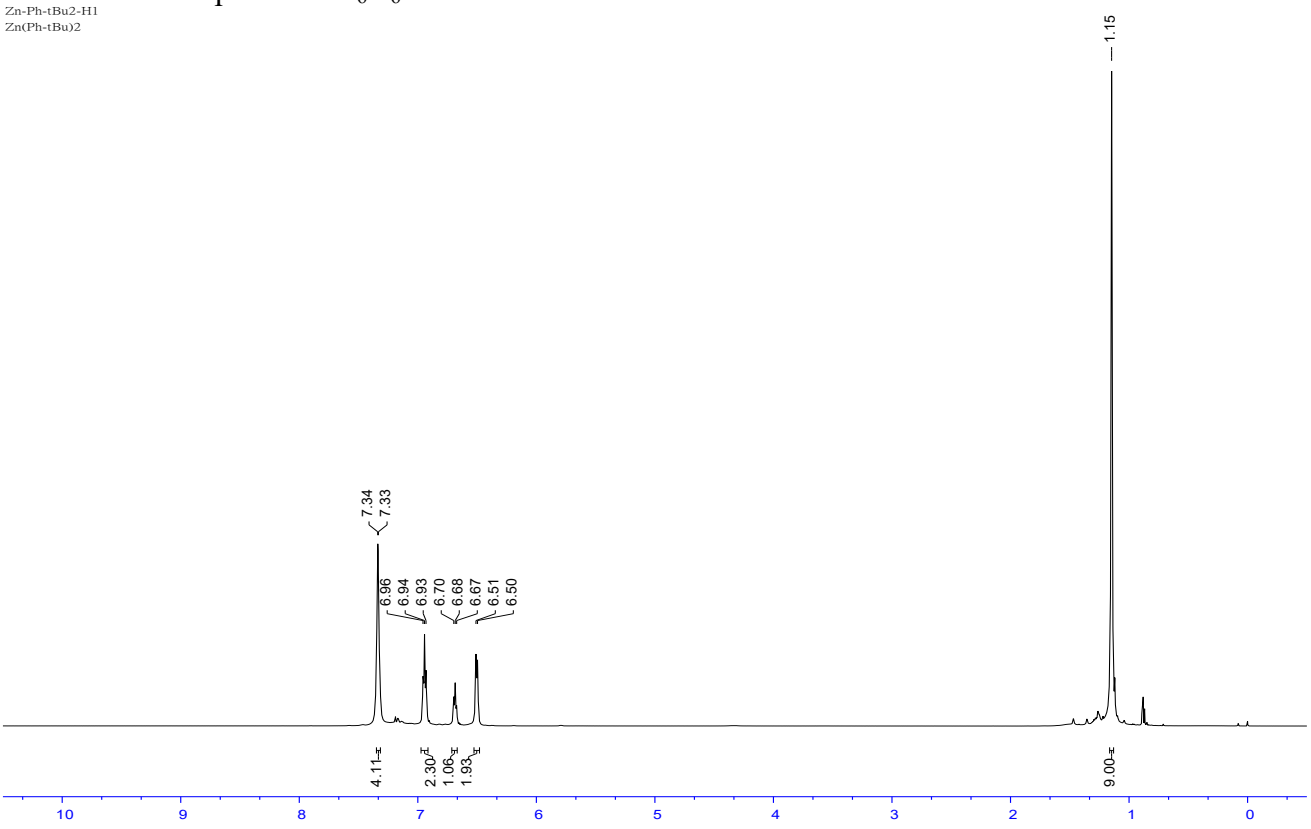
^{1}H NMR of complex **3** in C_6D_6



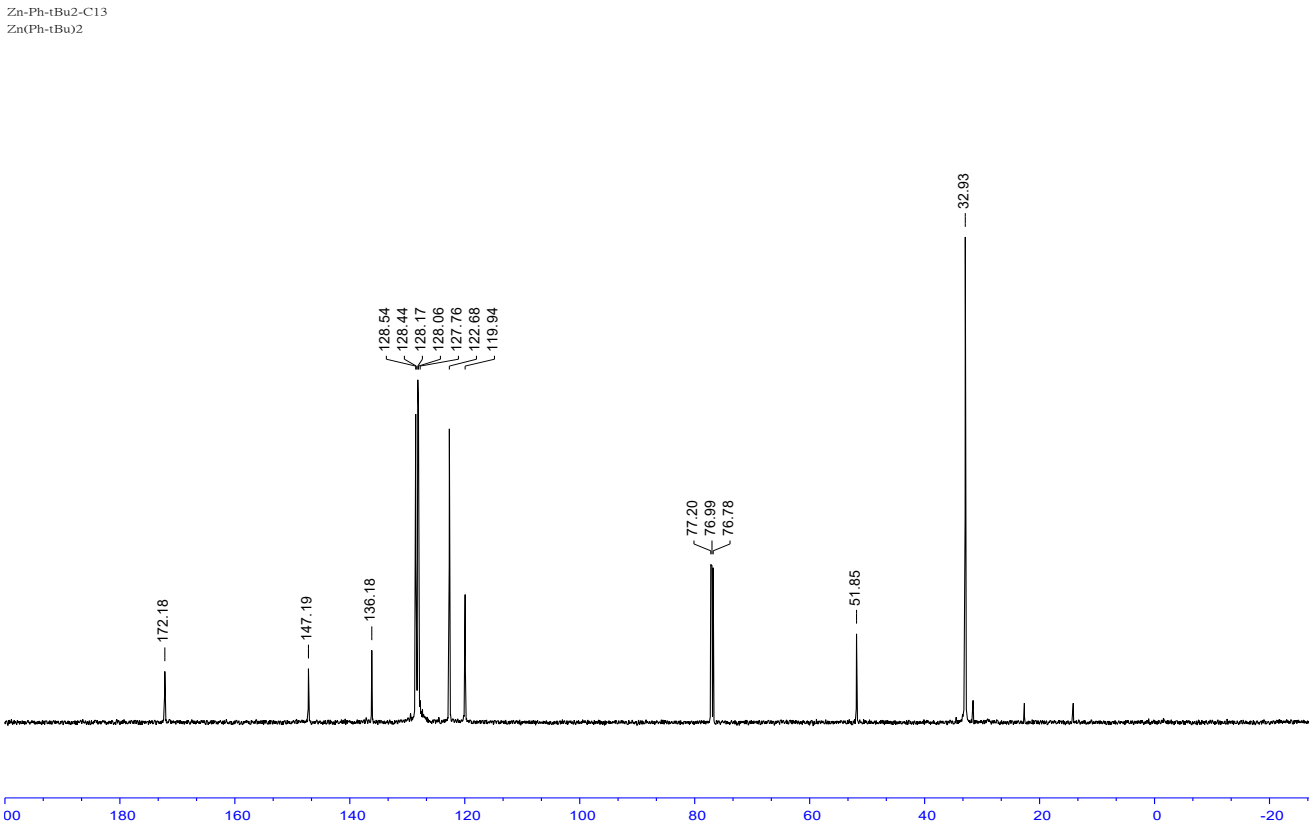
$^{13}C\{^{1}H\}$ NMR of complex **3** in C_6D_6



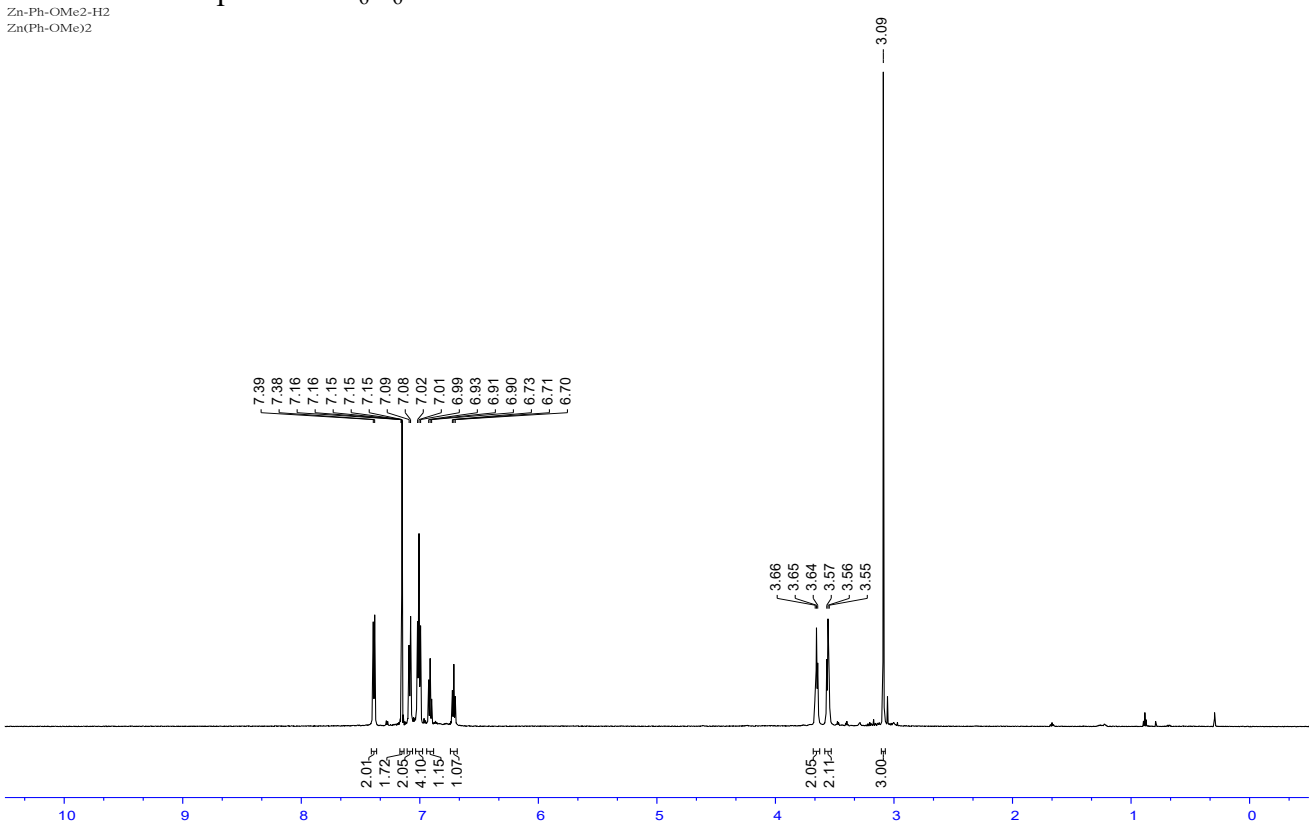
^{1}H NMR of complex **4** in C_6D_6



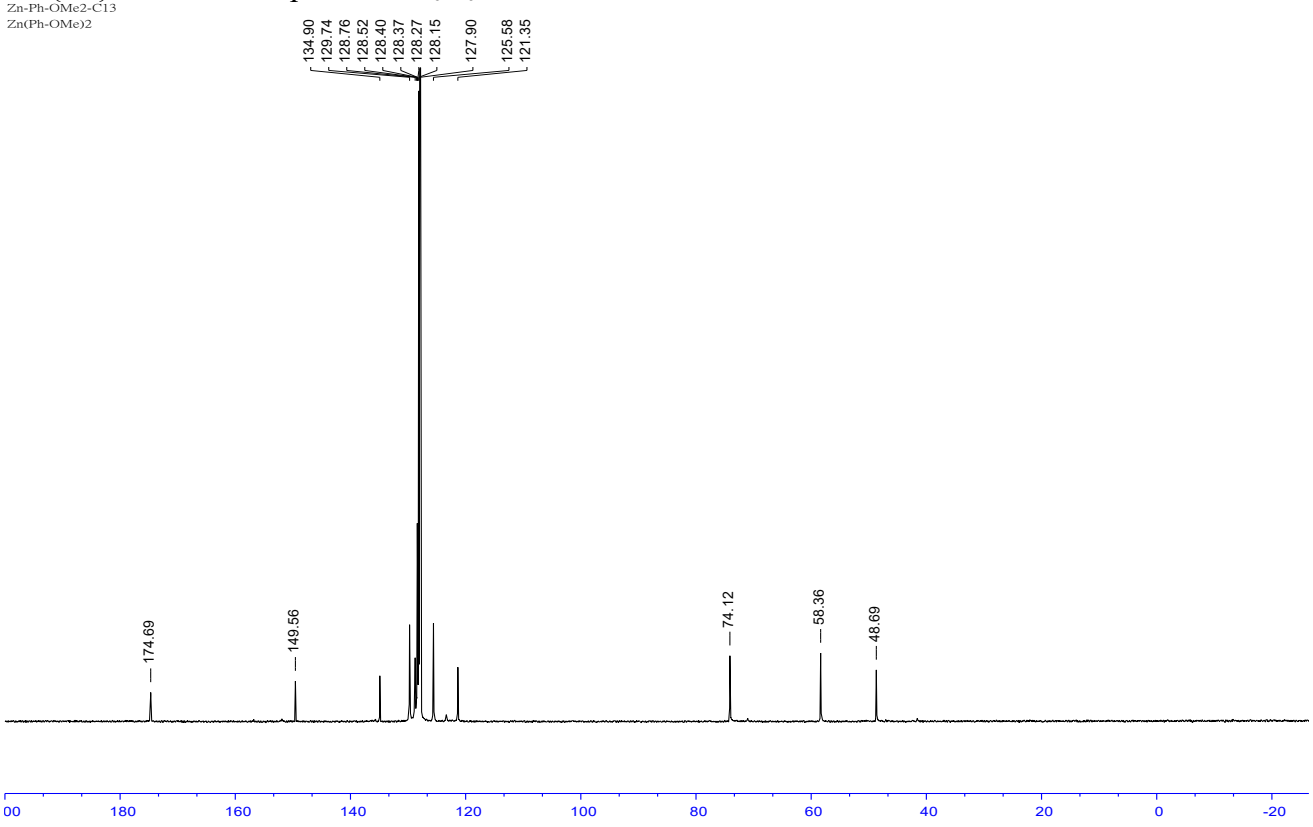
$^{13}C\{^{1}H\}$ NMR of complex **4** in C_6D_6



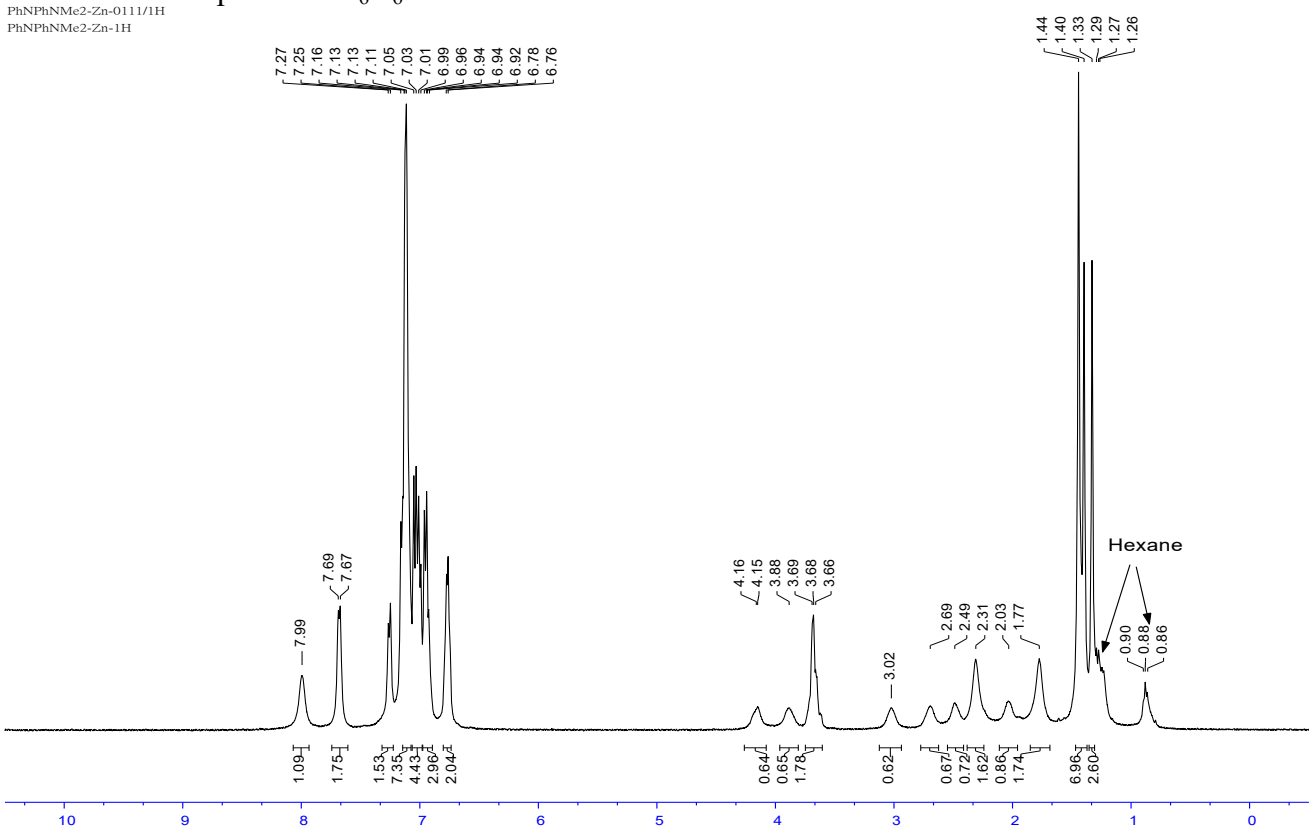
^{1}H NMR of complex **5** in C_6D_6



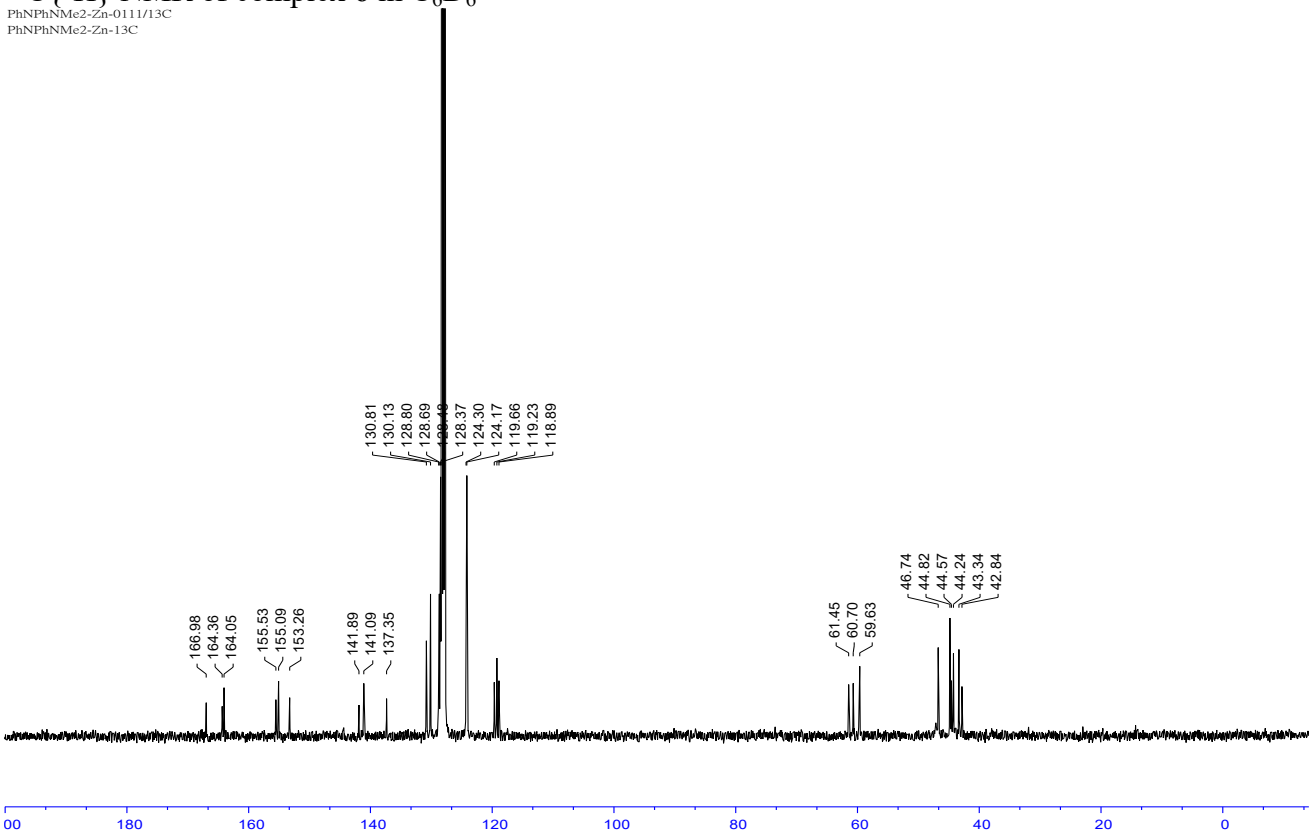
$^{13}C\{^{1}H\}$ NMR of complex **5** in C_6D_6



^{1}H NMR of complex **6** in C_6D_6

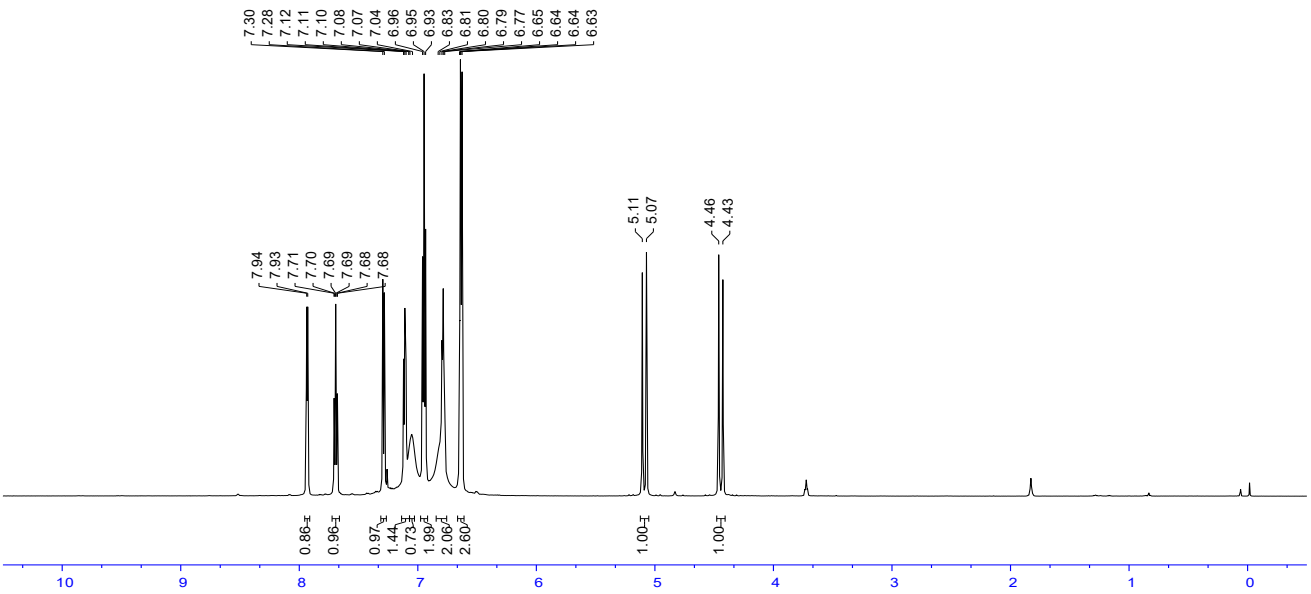


$^{13}C\{^{1}H\}$ NMR of complex **6** in C_6D_6



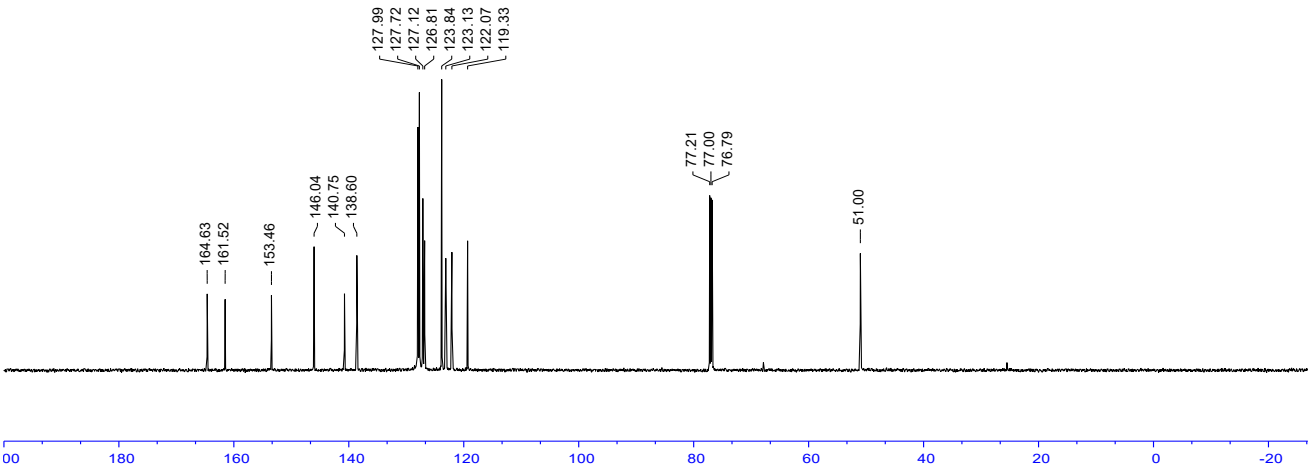
^{1}H NMR of complex **7** in $CDCl_3$

Zn-Ph-Py2-H1
Zn(Ph-Py)2



$^{13}C\{^{1}H\}$ NMR of complex **7** in $CDCl_3$

Zn-Ph-Py2-C13
Zn(Ph-Py)2



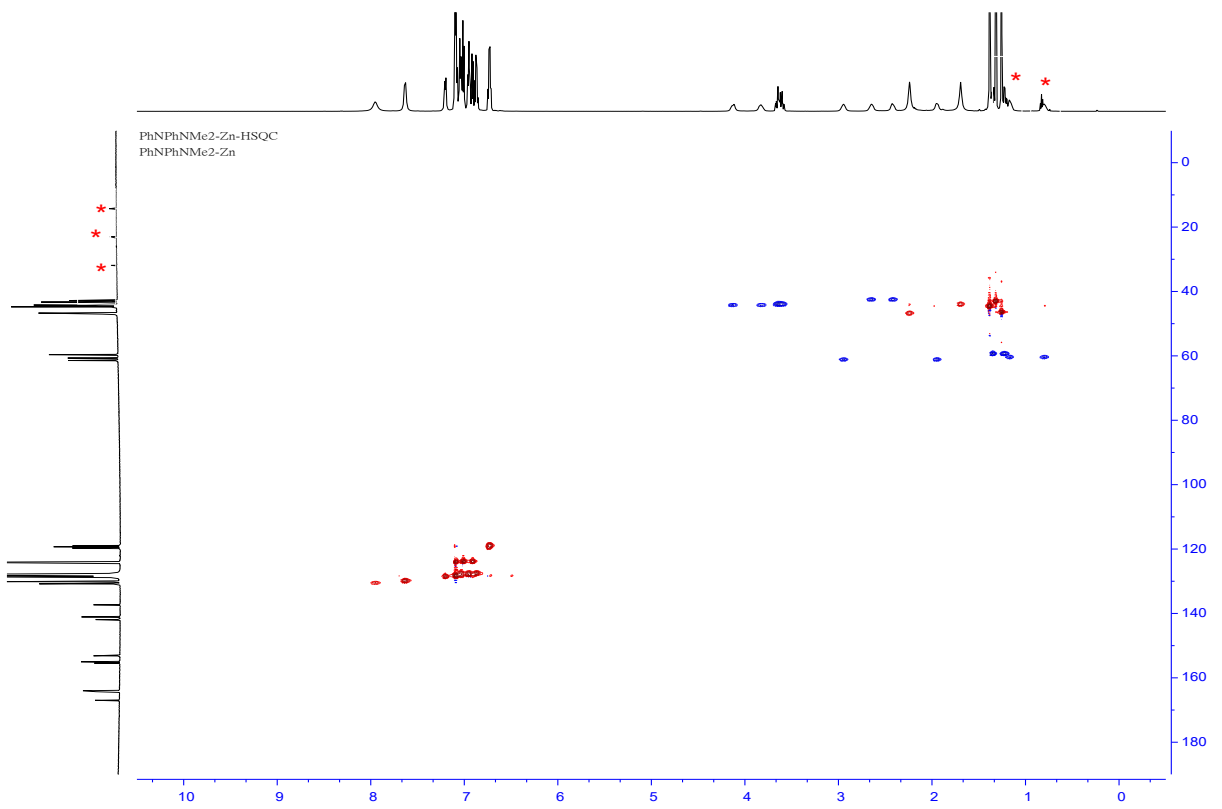


Figure S1. The HSQC NMR spectrum of complex **6** at 25°C in C_6D_6 (*: hexane).

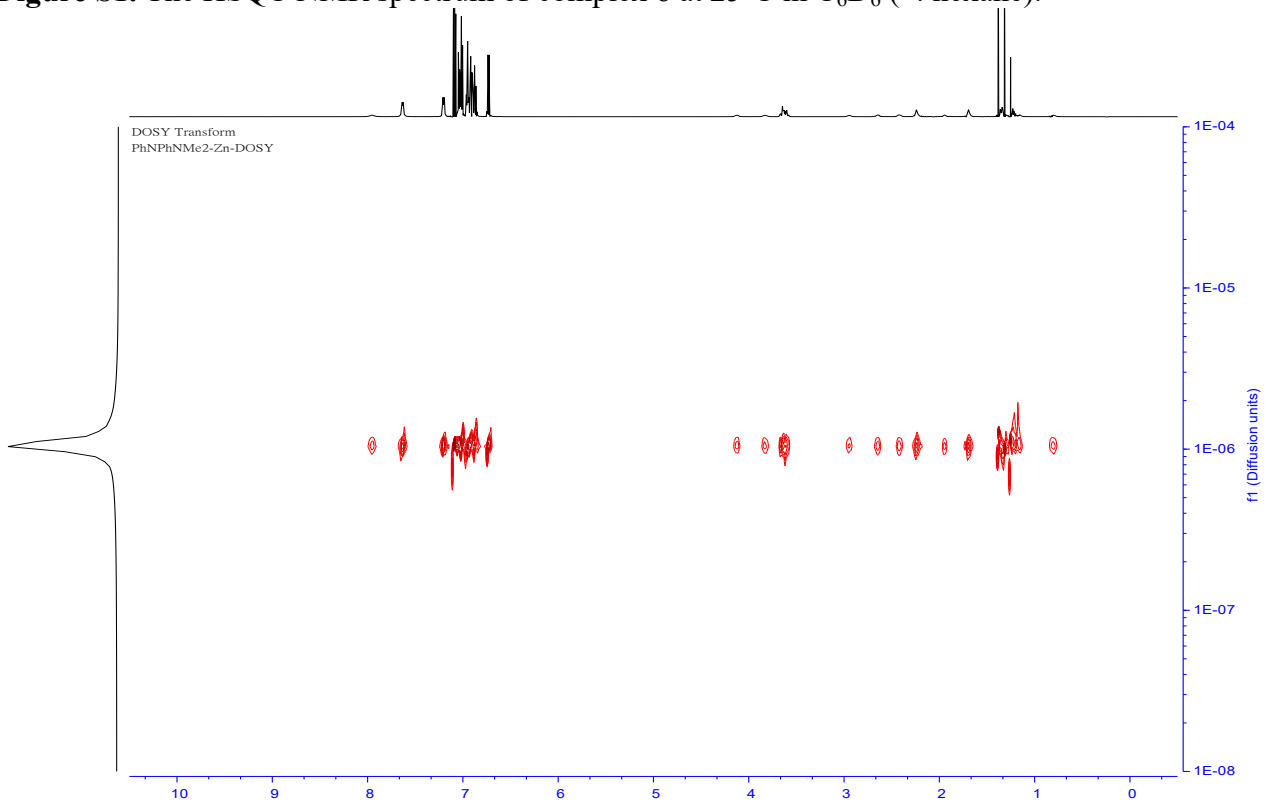


Figure S2. The ^{1}H DOSY NMR spectrum of complex **6** obtained at 25°C in C_6D_6.

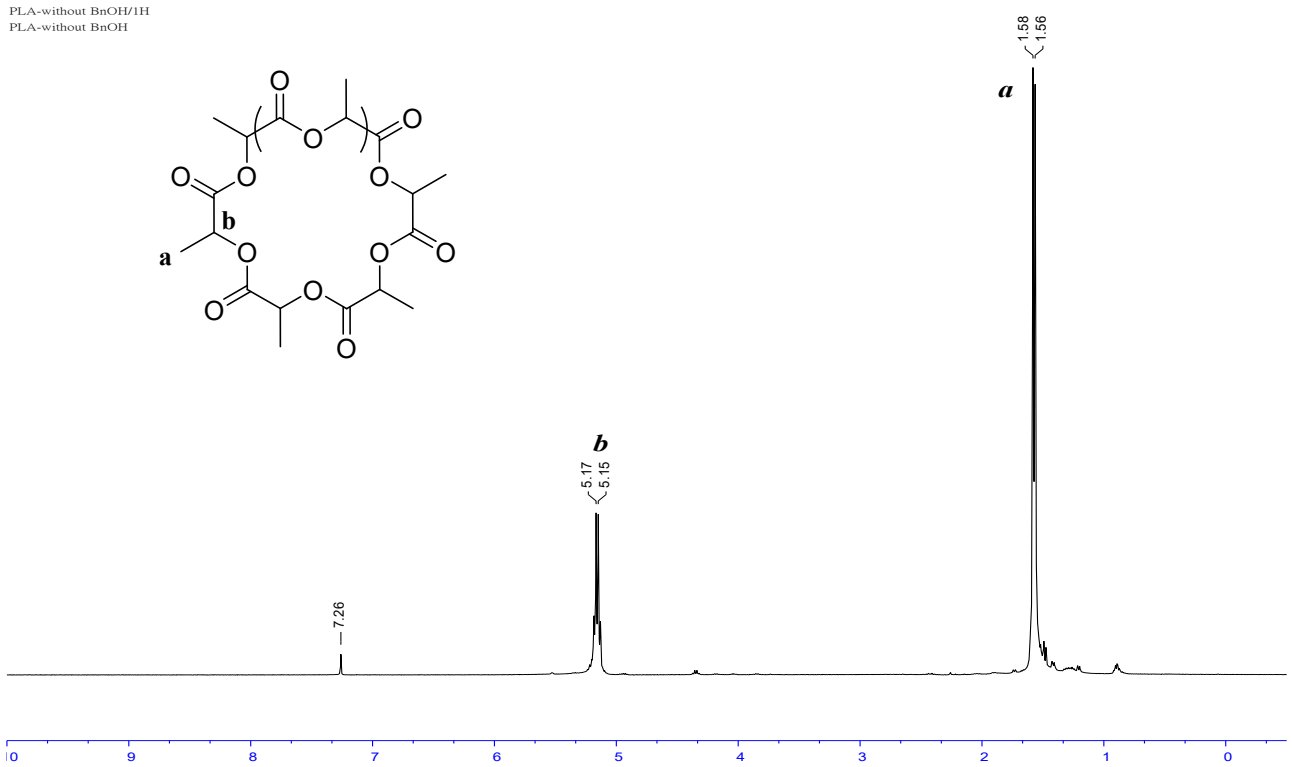


Figure S3. The ^{1}H NMR spectrum ($CDCl_3$) of PLA-50 catalyzed by **7** in toluene at 25°C.

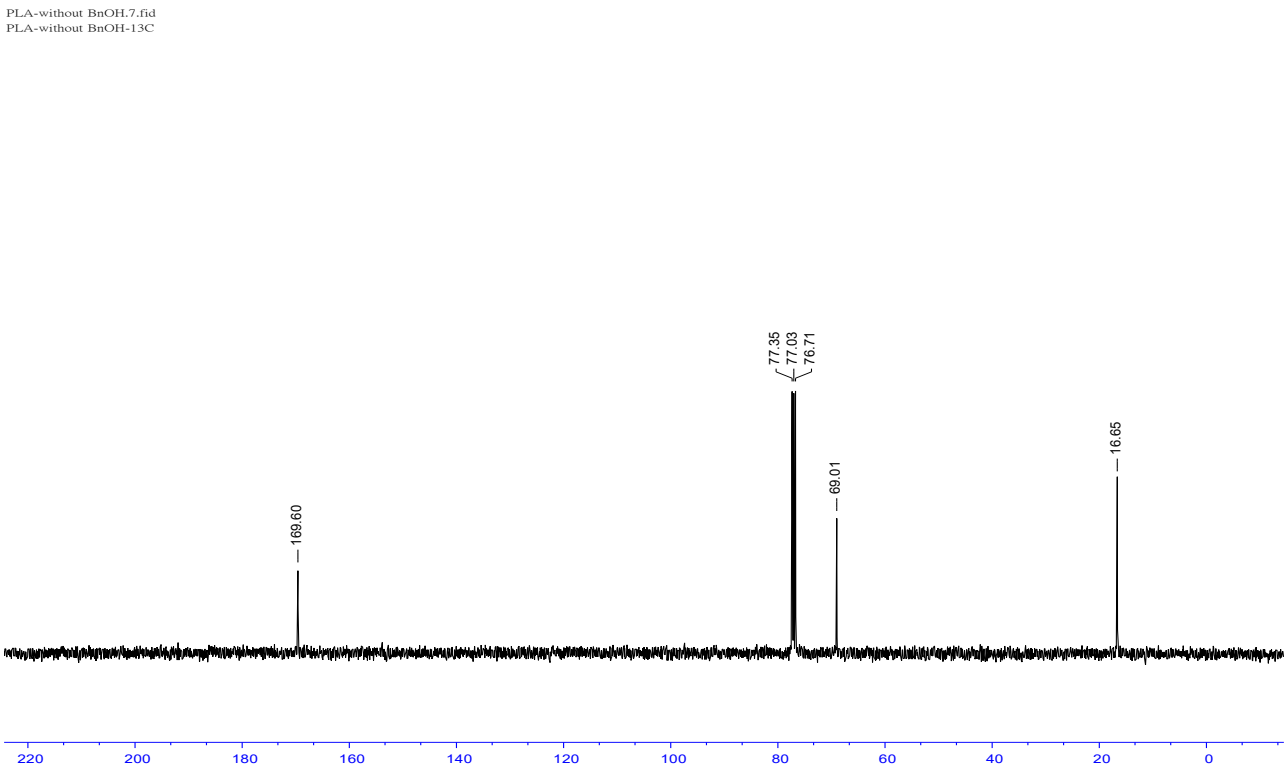


Figure S4. The $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of PLA-50 catalyzed by **7** in toluene at 25°C.

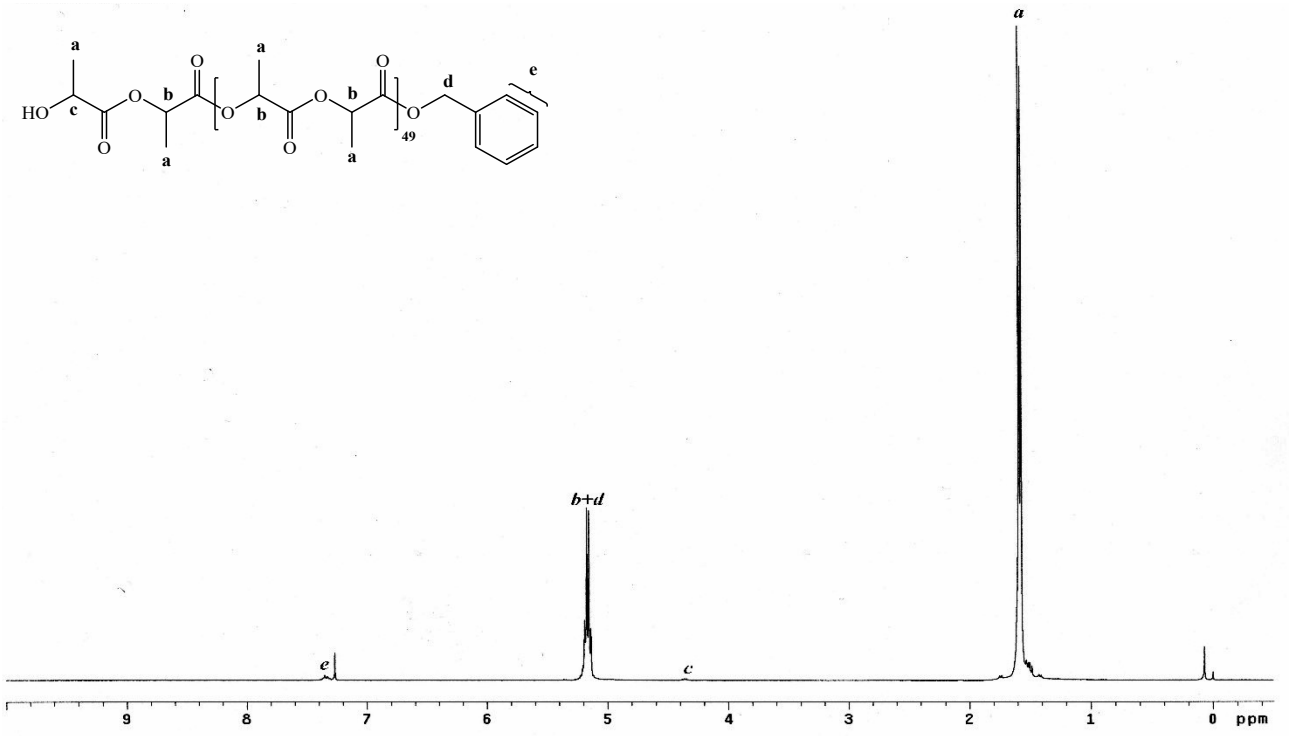


Figure S5. The ^{1}H NMR spectrum ($CDCl_3$) of PLA-50 catalyzed by **2**/BnOH in toluene at 50°C.

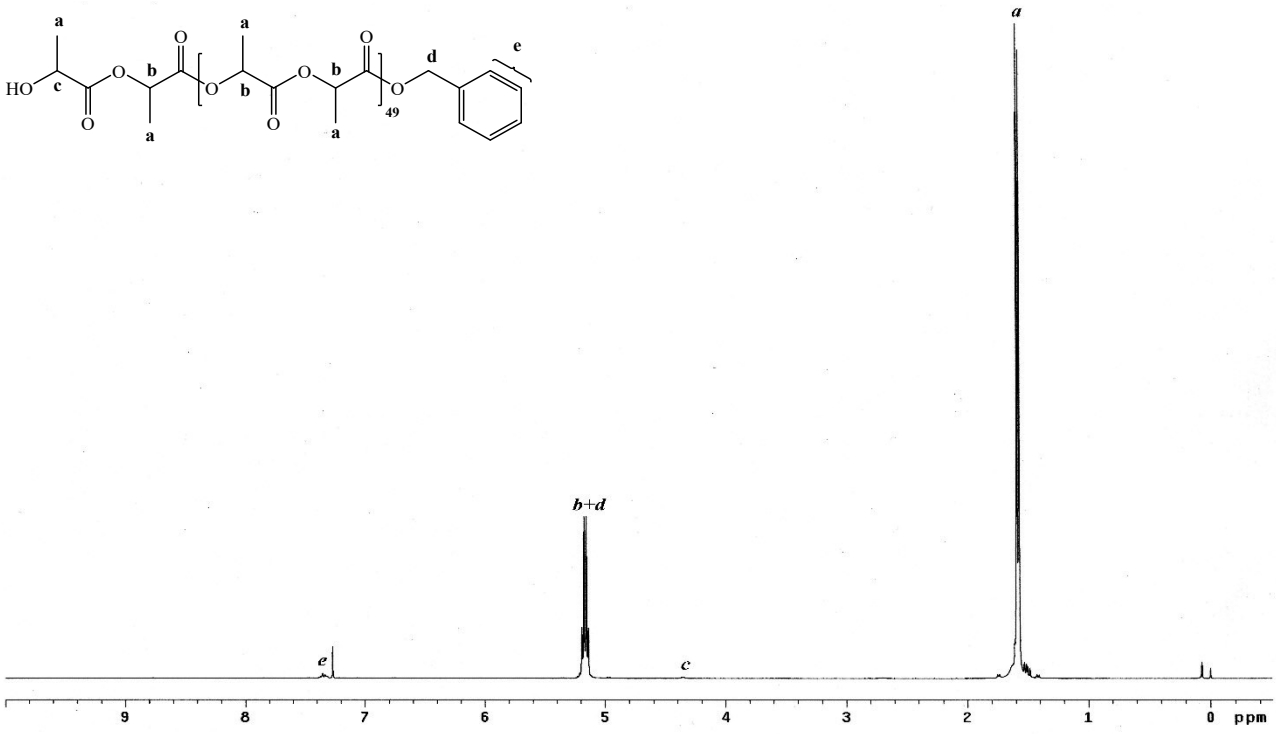


Figure S6. The ^{1}H NMR spectrum ($CDCl_3$) of PLA-50 catalyzed by **7**/BnOH in toluene at 25°C.

^{1}H NMR study of the Mechanism in the ROP of L-lactide

*** In a typical experiment, a J. Young NMR tube was charged with a solution of complex (0.0125 mmol for **1**; 0.025 mmol for **7**), benzyl alcohol (0.025 mmol, 2.6 μL), and L-lactide (1.25 mmol, 0.18 g) in 0.8 mL of d_8-toluene. The tube was then transferred to the spectrometer, and ^{1}H NMR spectra were recorded at the reaction temperature at different time. The internal standard was referenced to d_8-toluene (2.35 ppm).

For complex **1**

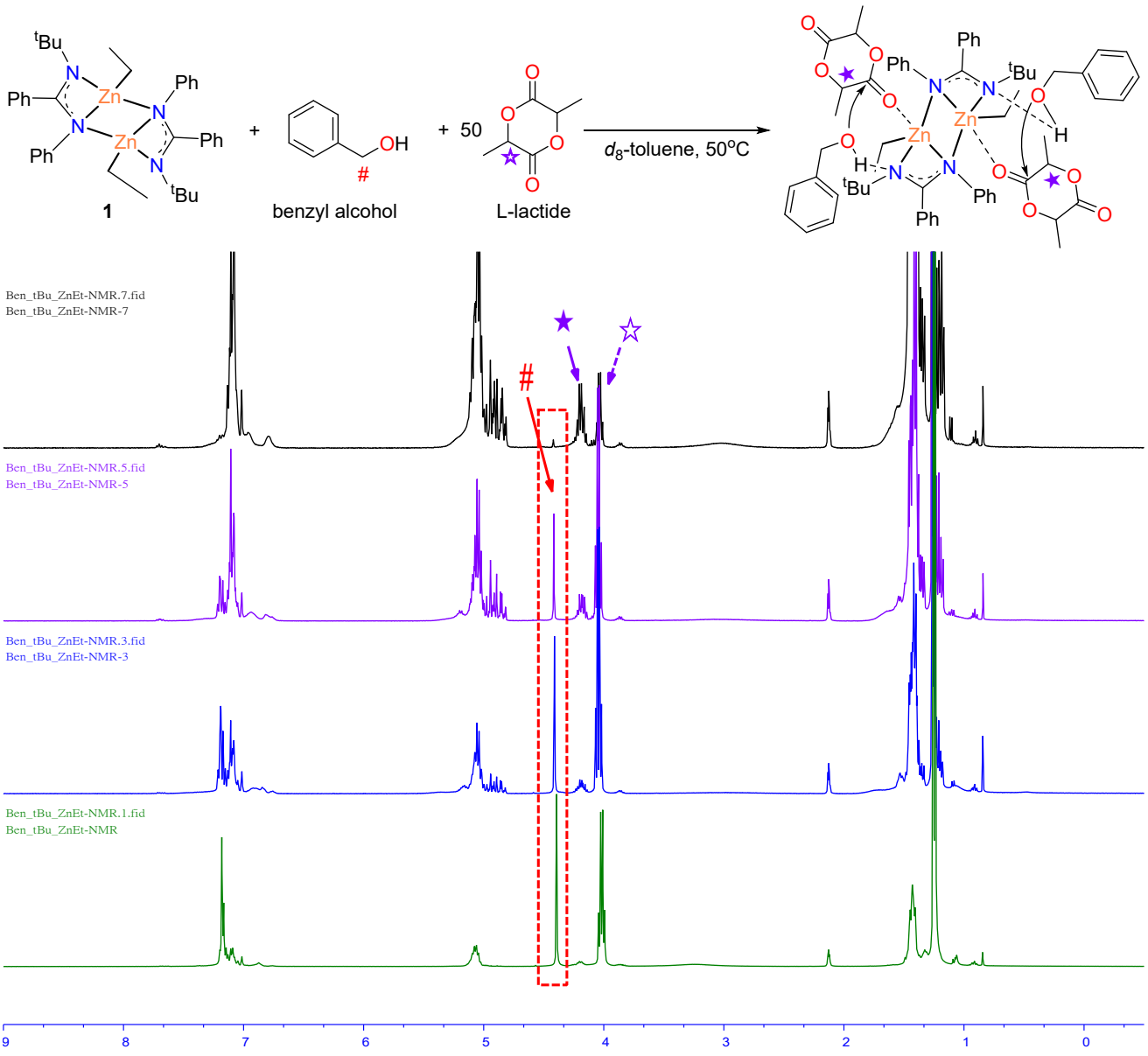


Figure S7. ^{1}H NMR spectra of complex **1**/BnOH/L-LA at different time at 50°C in d_8-toluene (#benzyl alcohol; ★activated L-lactide).

For complex **7**

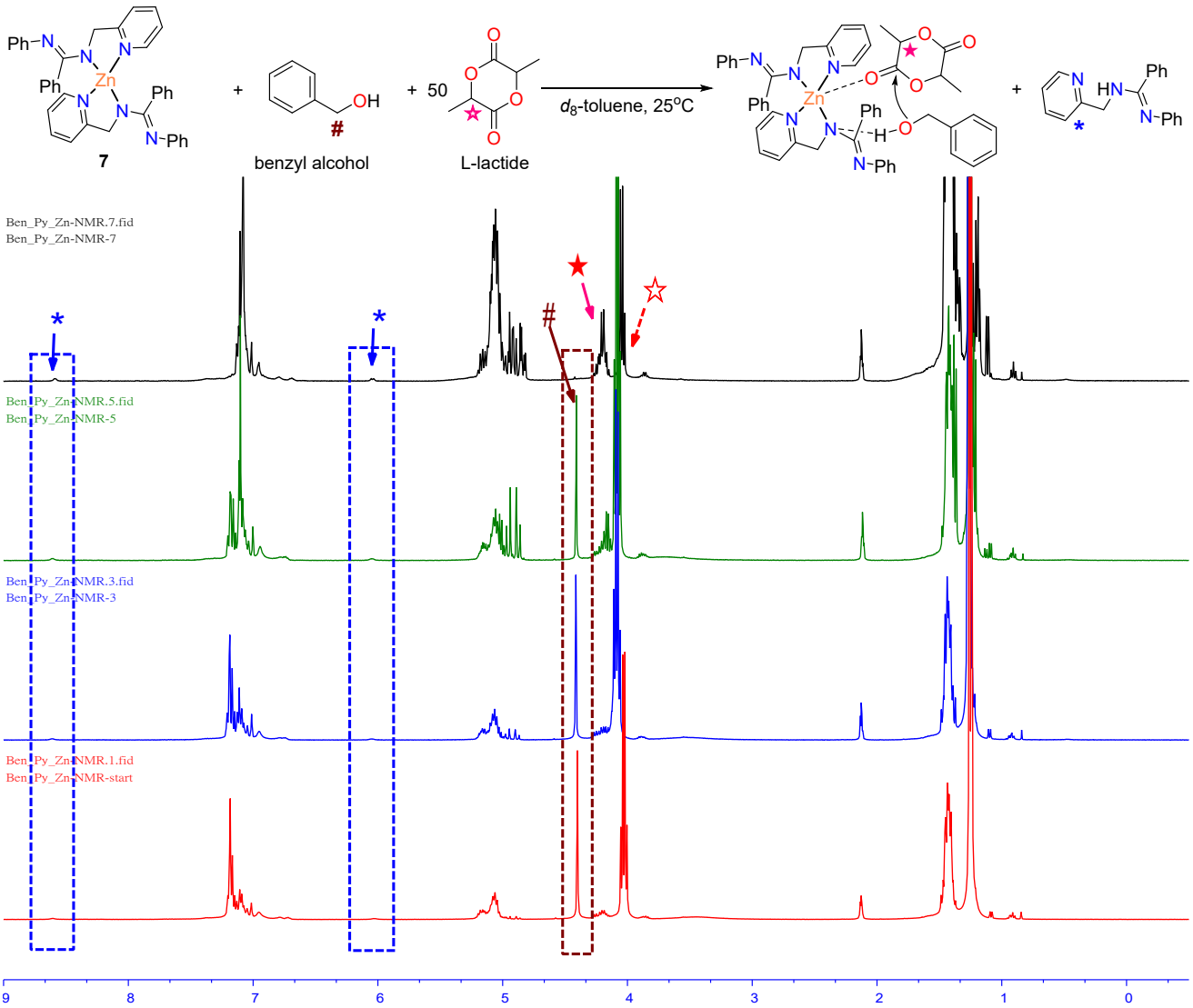


Figure S8. ^{1}H NMR spectra of complex **7**/BnOH/L-LA at different time at 25°C in d_8-toluene (*ligand precursor **L1d**; #benzyl alcohol; ★activated L-lactide).

MALDI-TOF mass analysis of prepared PLAs

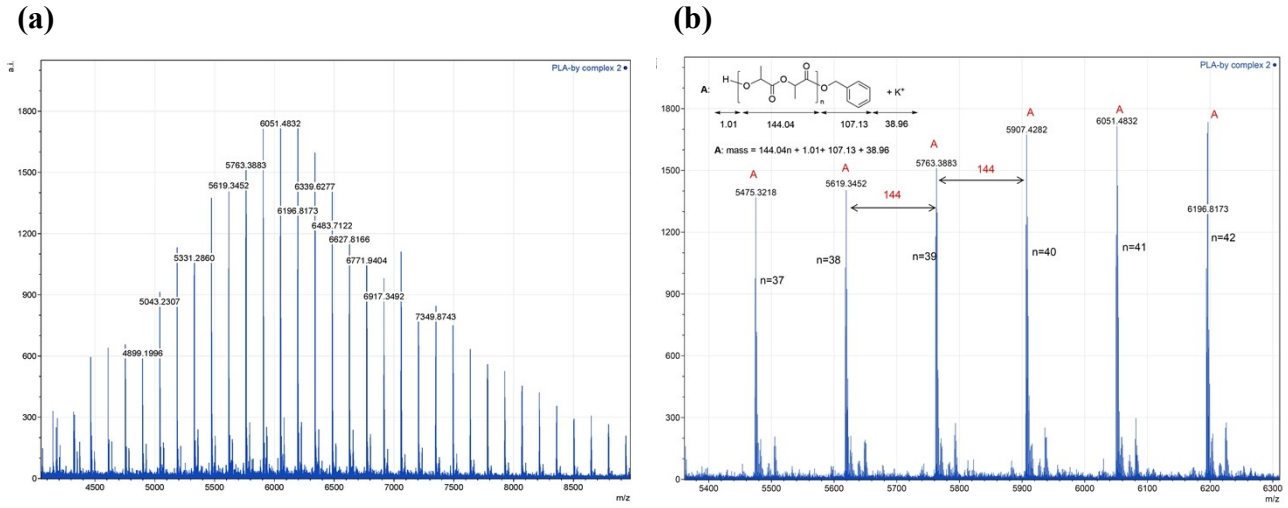


Figure S9. (a)-(b) MALDI-TOF spectrum of PLA initiated by L-LA/complex **2**/BnOH (Table 2, entry 11).

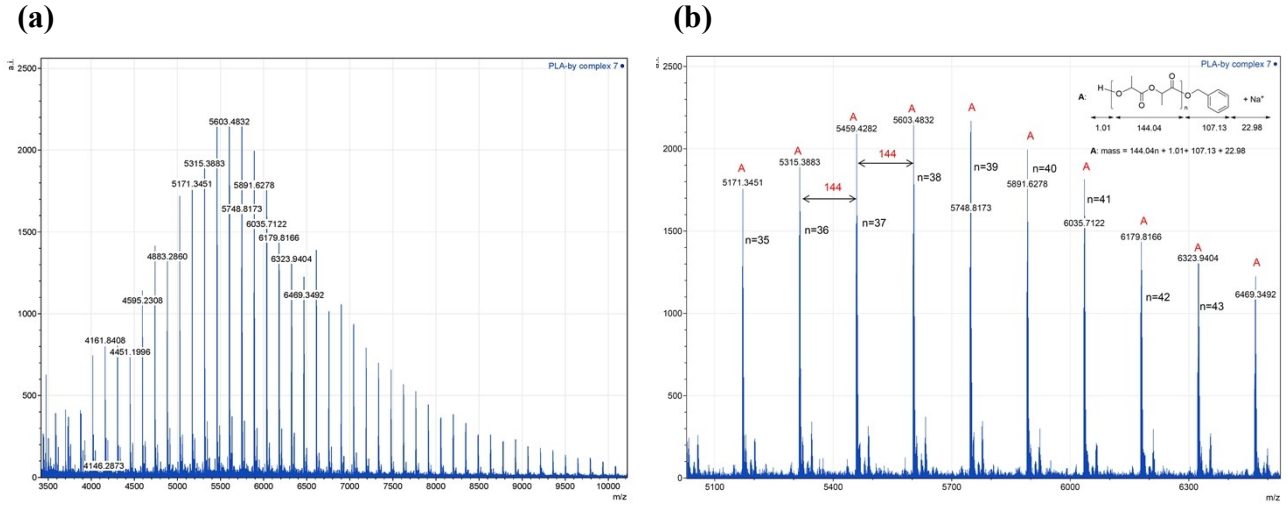


Figure S10. (a)-(b) MALDI-TOF spectrum of PLA initiated by L-LA/complex **7**/BnOH (Table 2, entry 1).