Supporting information

Homoleptic phenoxy-imine pyridine zinc complexes: efficient and recyclable catalysts for synthesis and depolymerization of polyesters.

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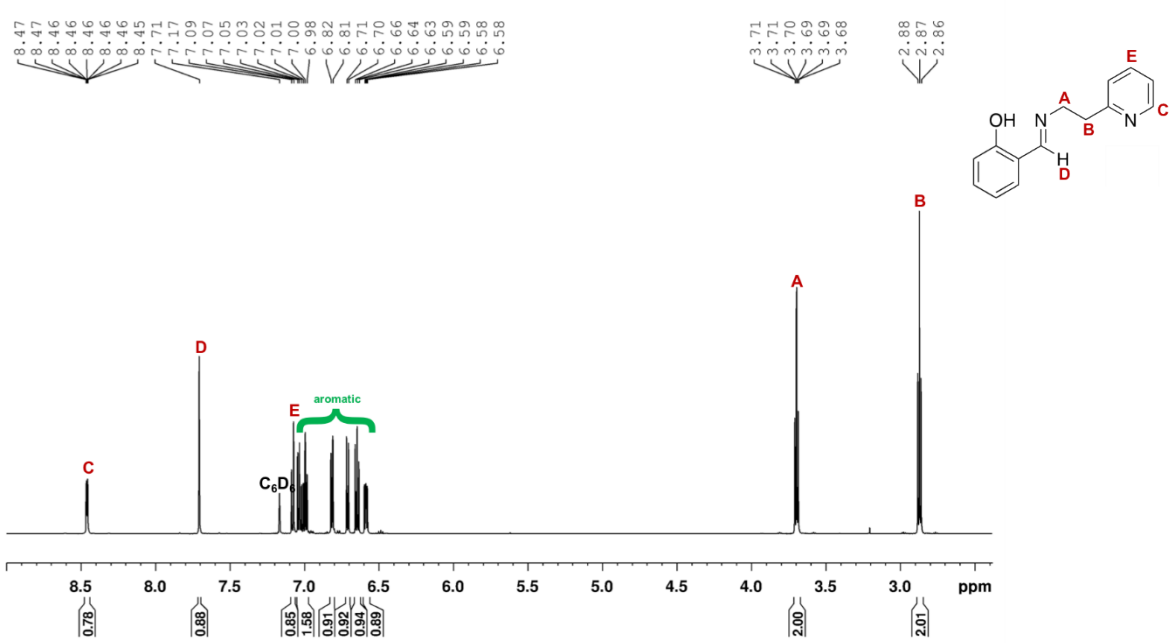


Figure S1. ^{1}H NMR spectrum (600 MHz, C_6D_6, 298 K) ligand L1H.

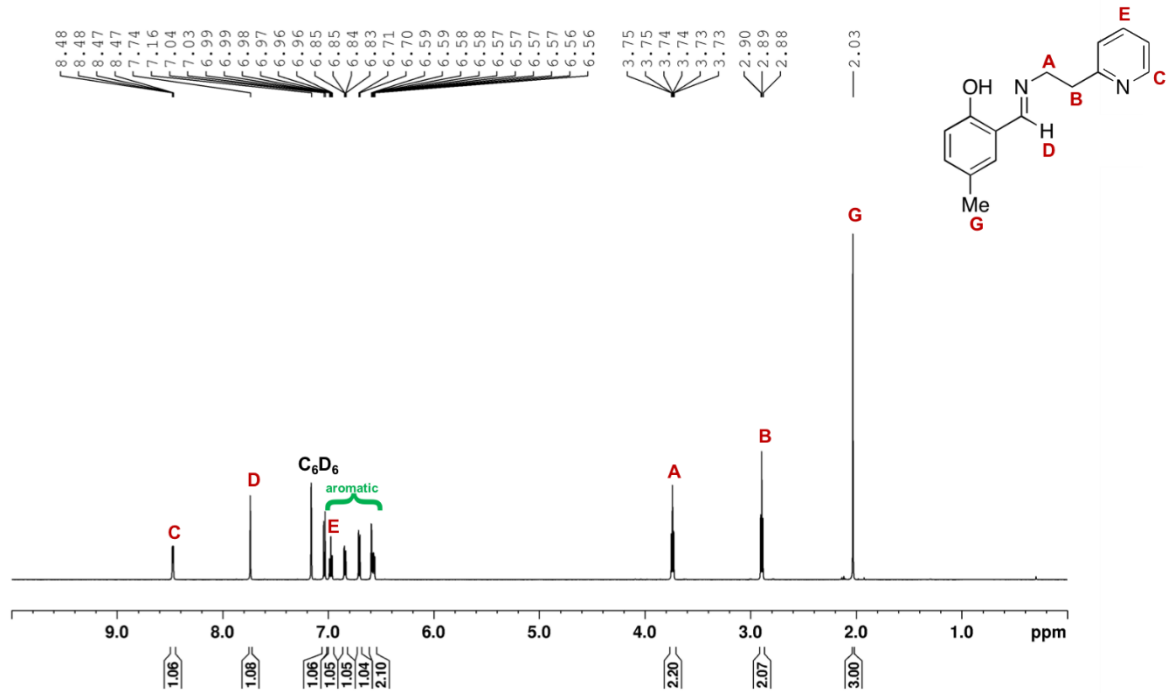


Figure S2. ^{1}H NMR spectrum (600 MHz, C_6D_6, 298 K)ligand L2H.

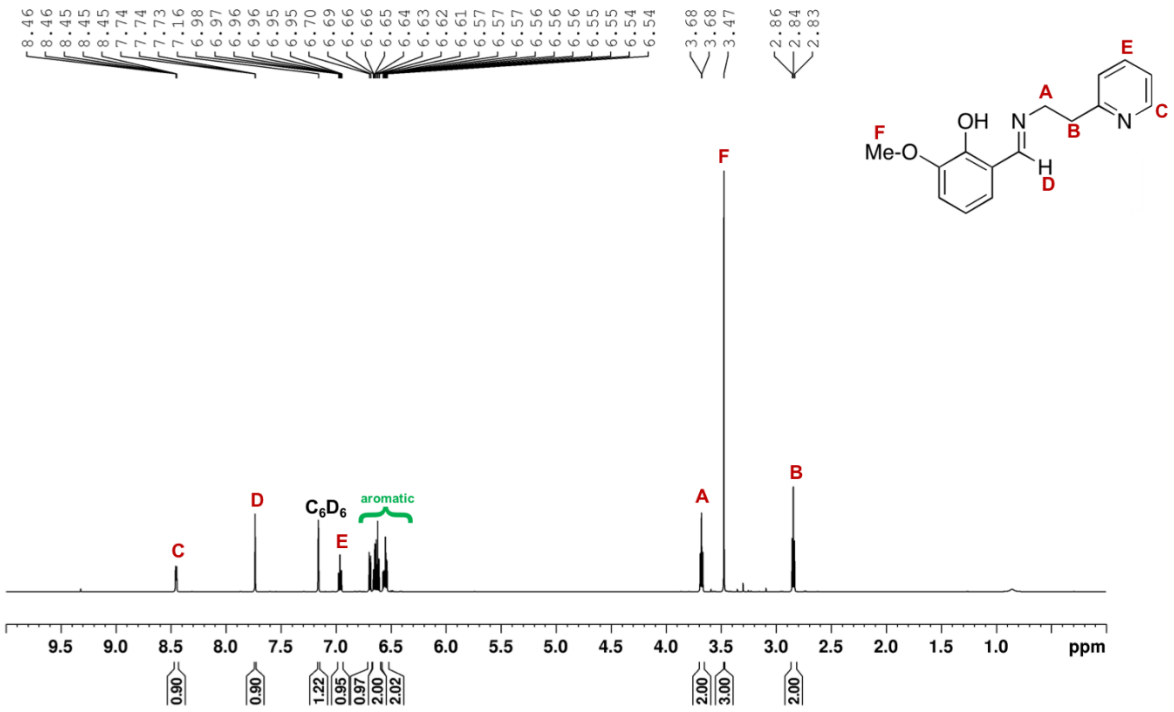


Figure S3. ^{1}H NMR spectrum (600 MHz, C_6D_6, 298 K)ligand L3H.

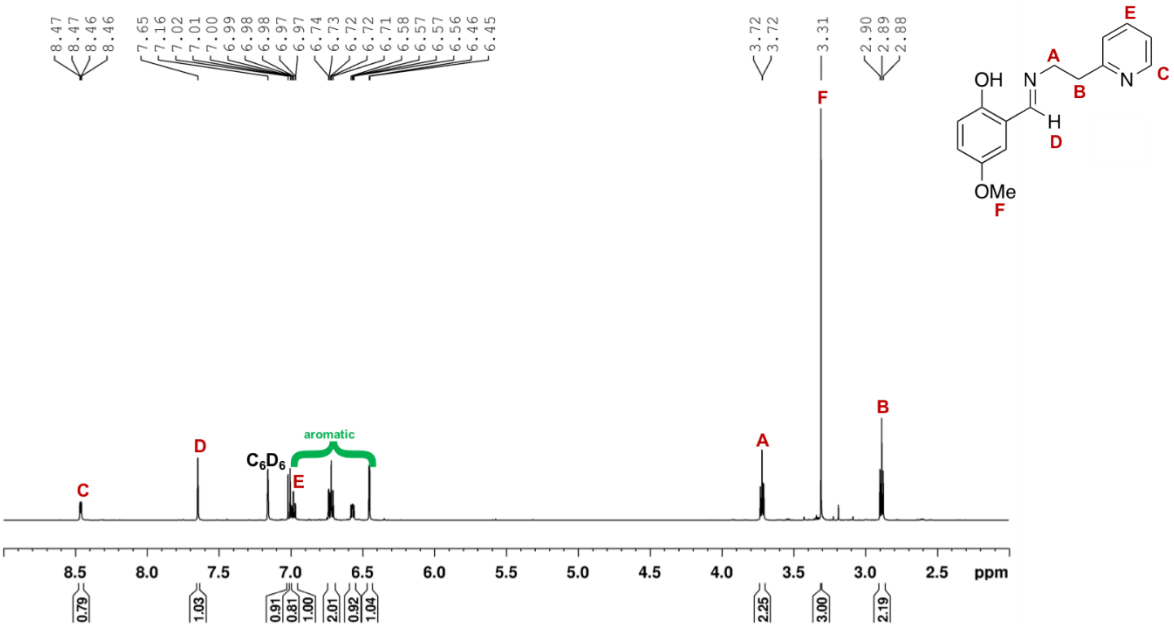


Figure S4. ^{1}H NMR spectrum (600 MHz, C_6D_6, 298 K)ligand L4H.

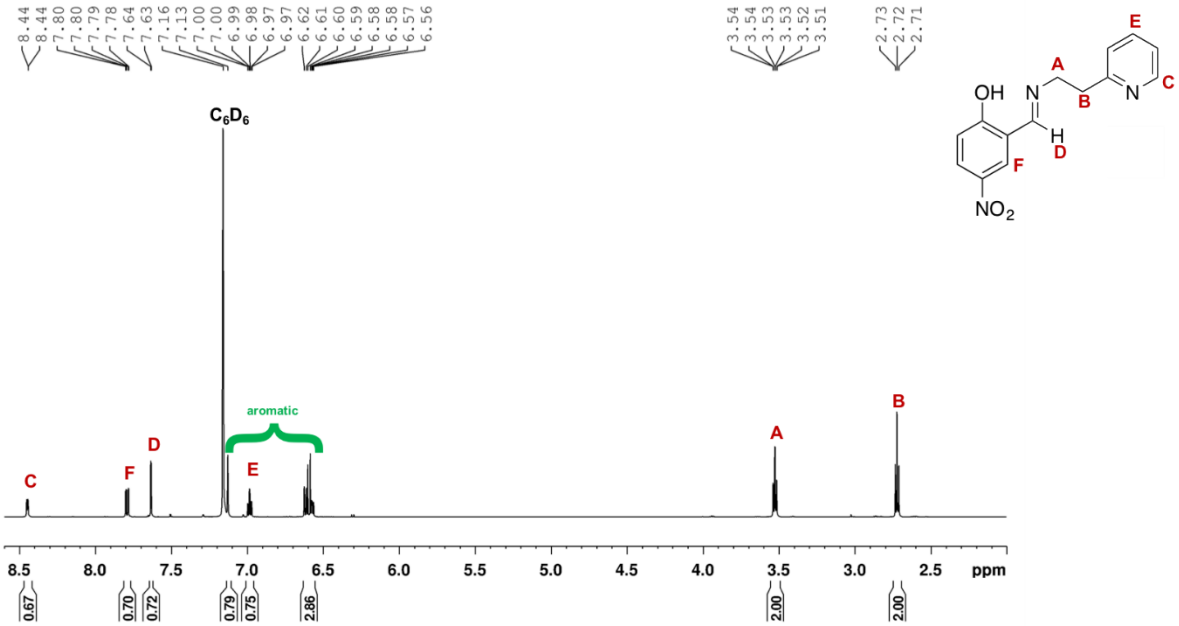


Figure S5. ^{1}H NMR spectrum (600 MHz, C_6D_6, 298 K)ligand L5H.

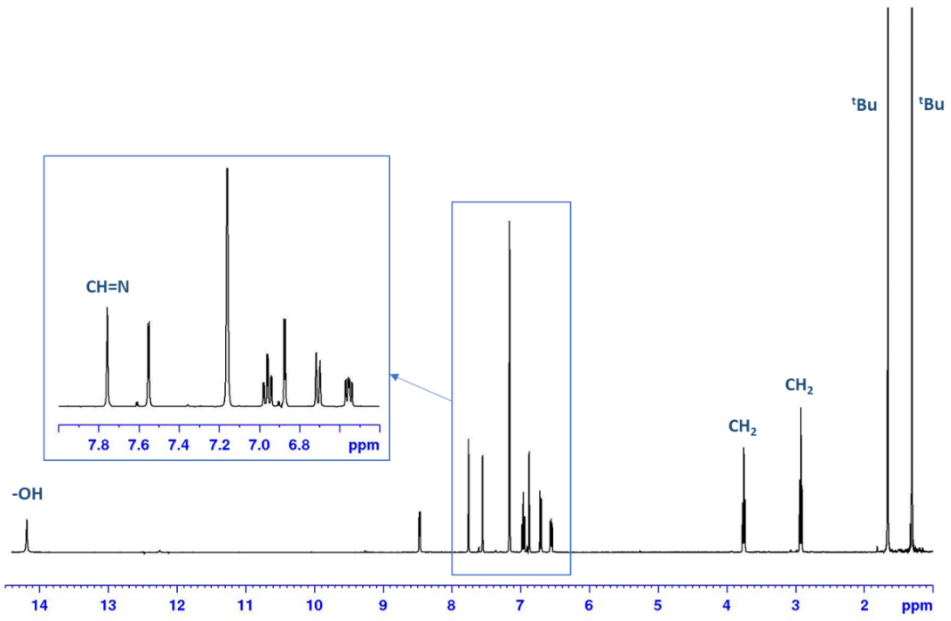


Figure S6. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) ligand L6H.

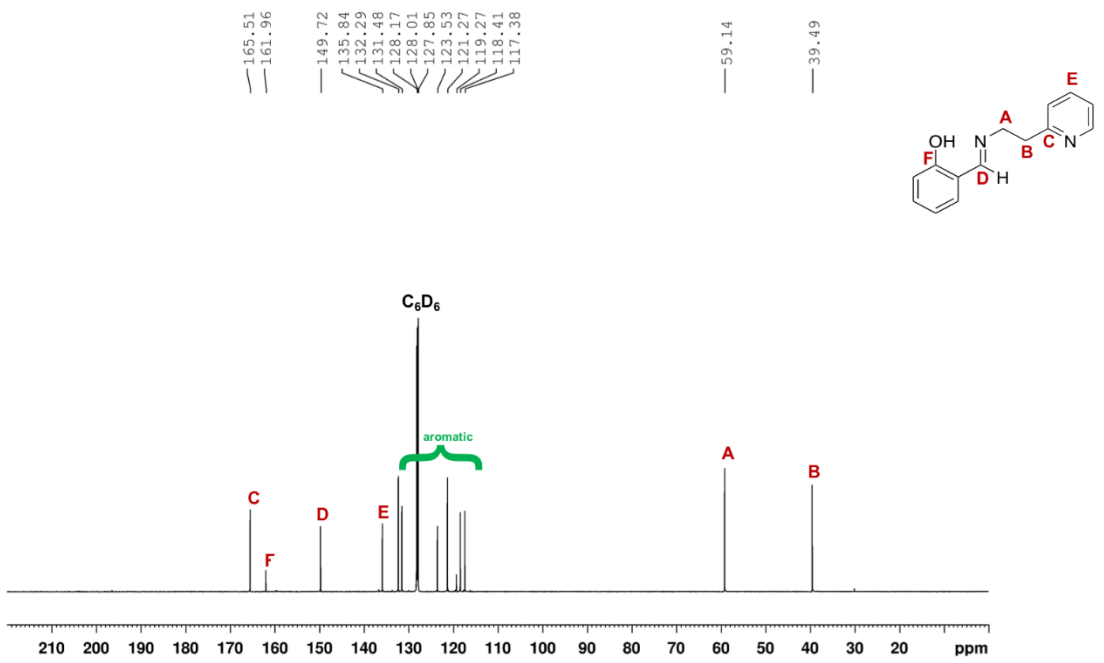


Figure S7. ^{13}C NMR spectrum (150 MHz, C_6D_6, 298 K) ligand L1H.

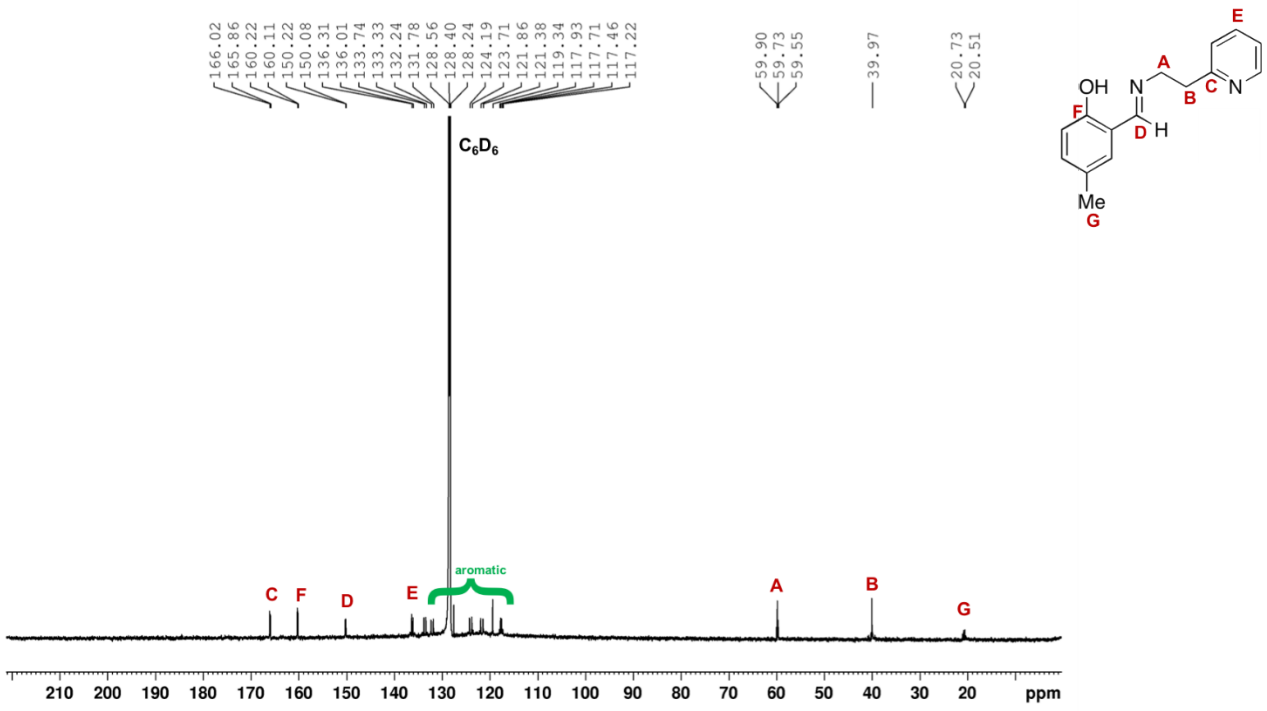


Figure S8. ^{13}C NMR spectrum (150 MHz, C_6D_6, 298 K) ligand L2H.

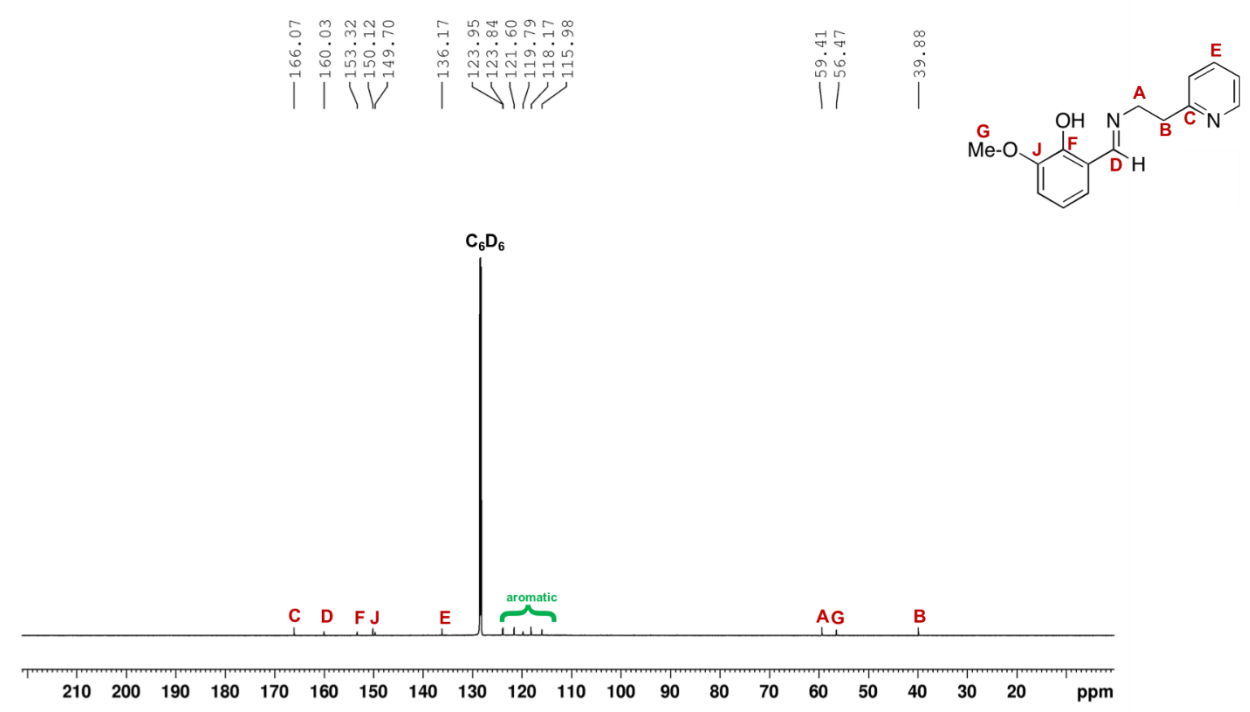


Figure S9. ^{13}C NMR spectrum (150 MHz, C_6D_6, 298 K) ligand L3H.

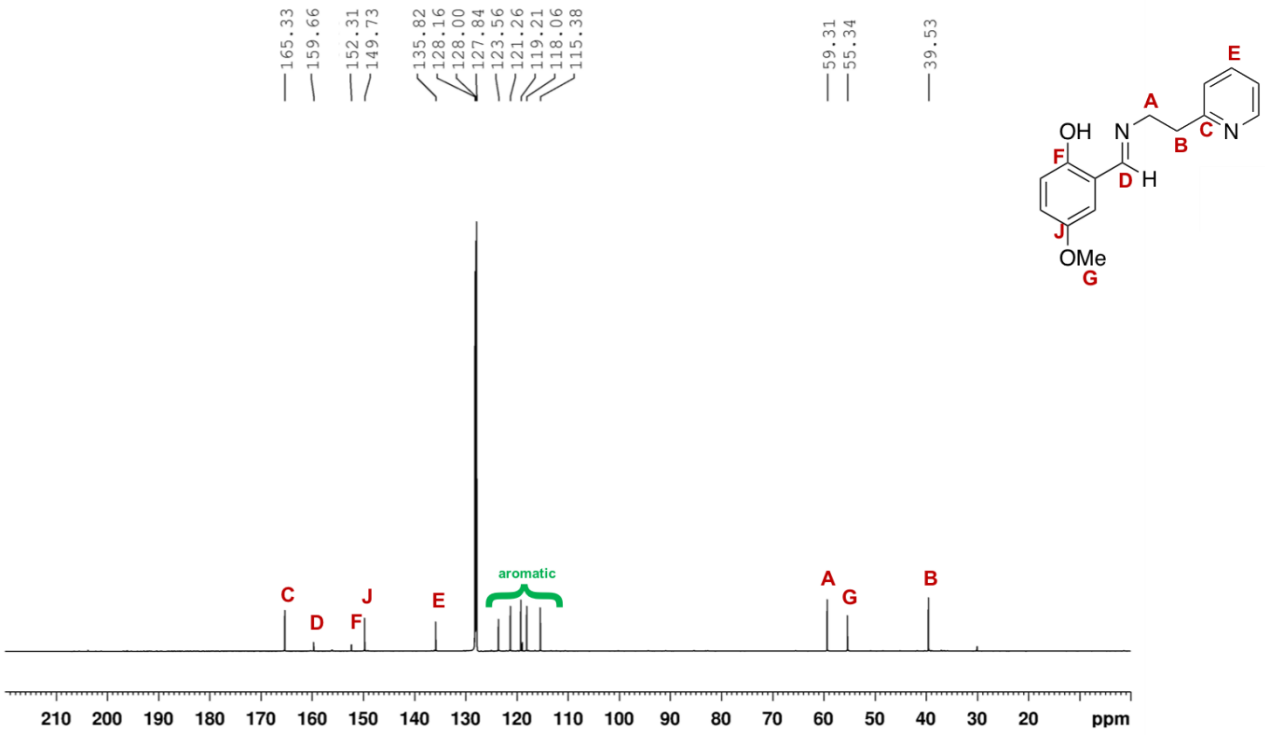


Figure S10. ^{13}C NMR spectrum (150 MHz, C_6D_6, 298 K) ligand L4H.

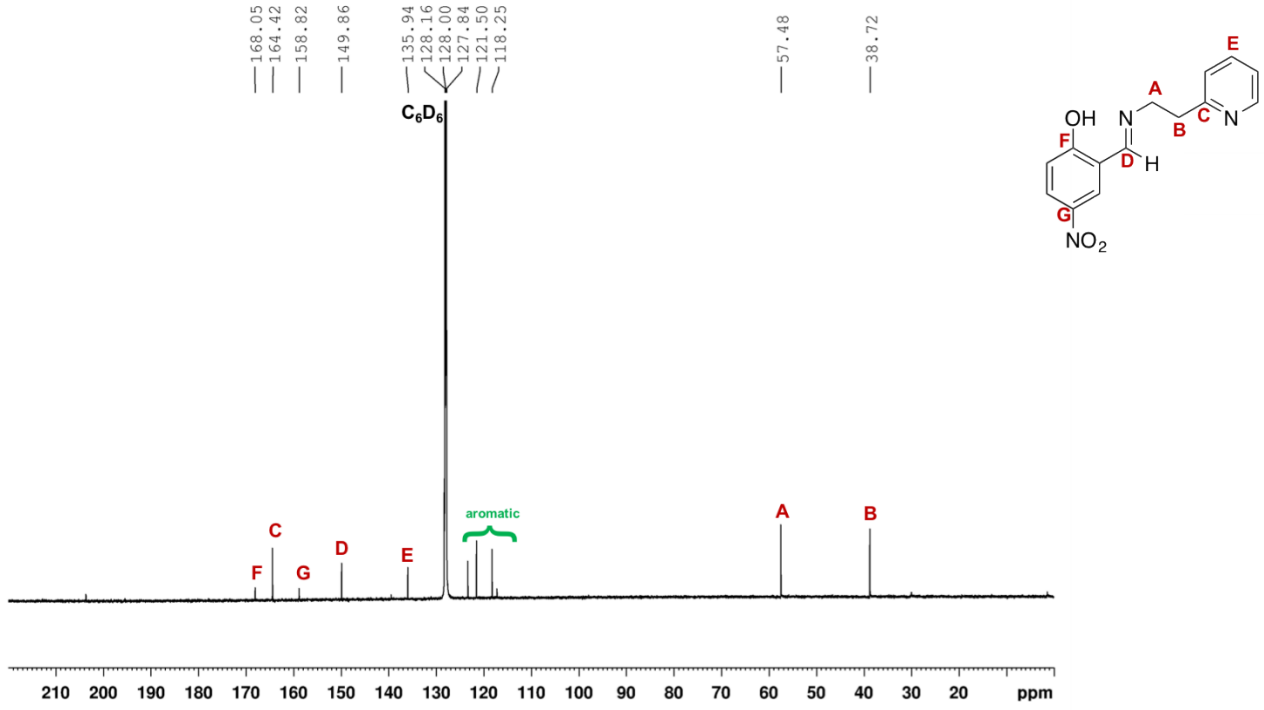


Figure S11. ^{13}C NMR spectrum (150 MHz, C_6D_6, 298 K) ligand L5H.

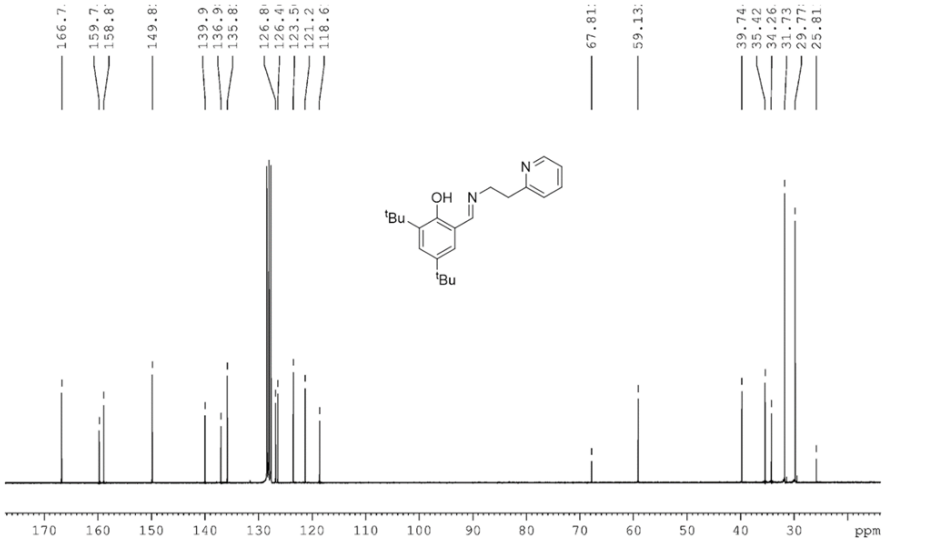


Figure S12. ^{13}C NMR spectrum (75 MHz, C_6D_6, 298 K) ligand L6H.

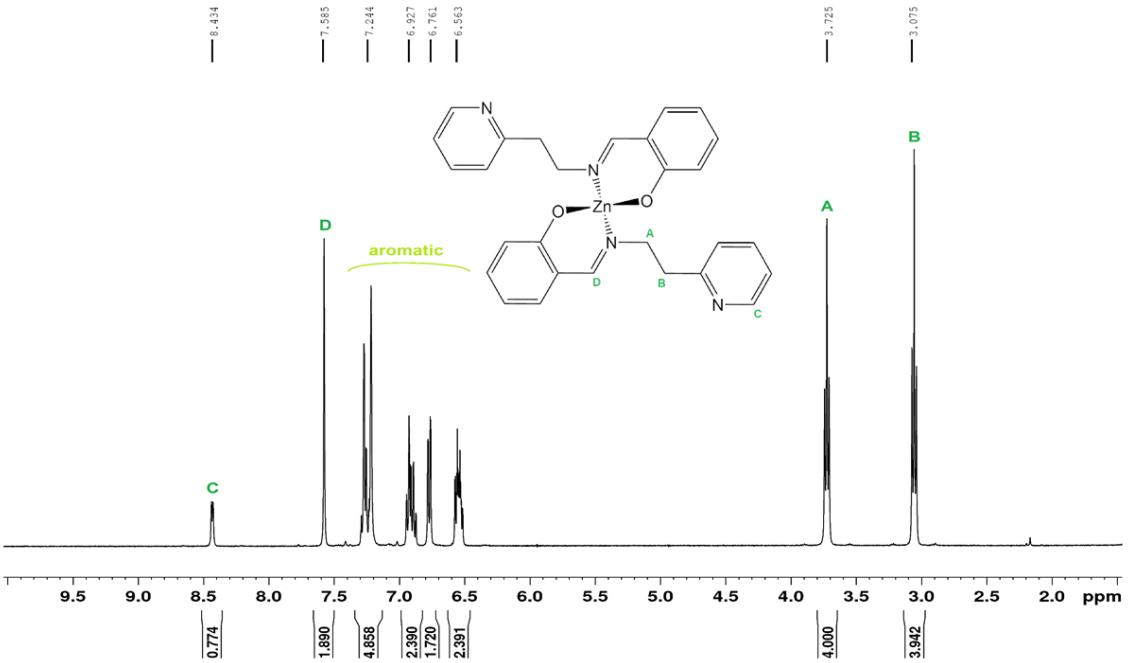


Figure S13. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) complex **1**.

^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 171.5, 158.5, 135.9, 134.8, 127.8, 124.0, 123.6, 121.2, 118.3, 113.9, 60.5, 38.3.

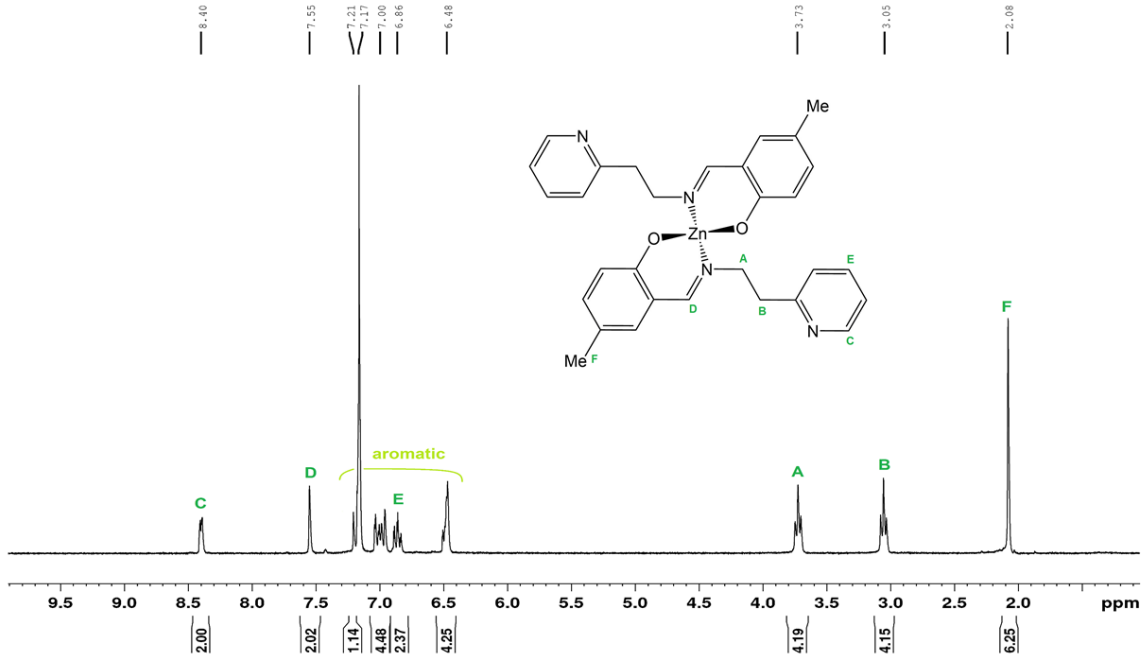


Figure S14. ^{1}H NMR spectrum (300 MHz, C_6D_6, 298 K) complex **2**.

^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 171.4, 158.3, 149.2, 136.1, 135.8, 135.0, 123.4, 122.0, 121.0, 117.5, 99.46, 60.2, 38.2, 19.8.

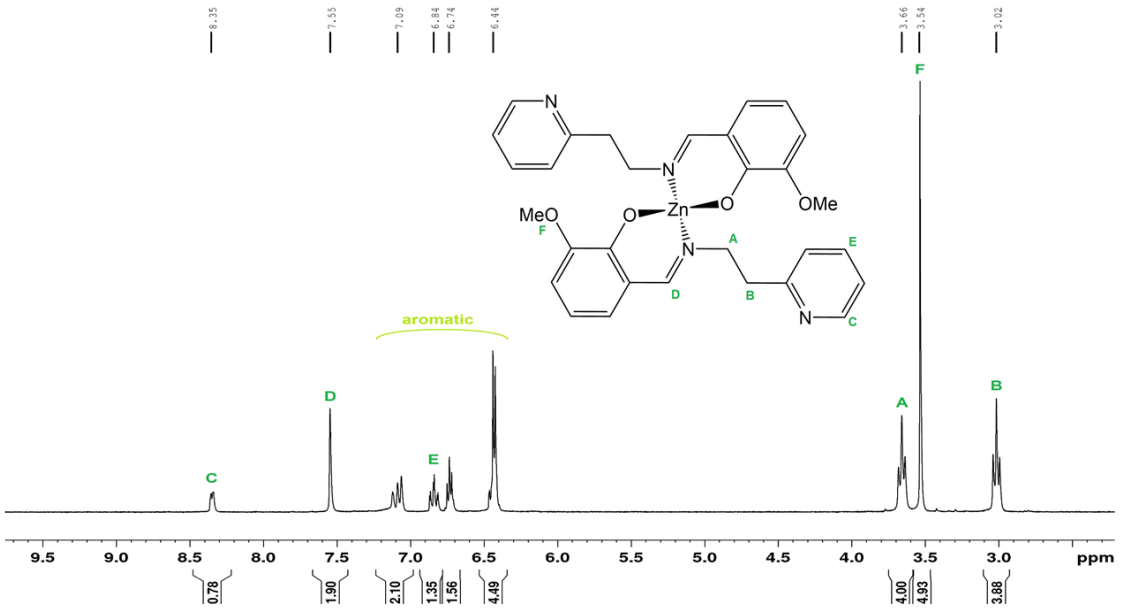


Figure S15. ^{1}H NMR spectrum (300 MHz, C_6D_6, 298 K) complex **3**.

^{13}C NMR (100 MHz, C_6D_6, 298 K): δ 171.3, 159.8, 159.2, 149.5, 136.8, 136.2, 135.4, 123.8, 121.4, 117.2, 113.1, 60.2, 55.5, 39.1.

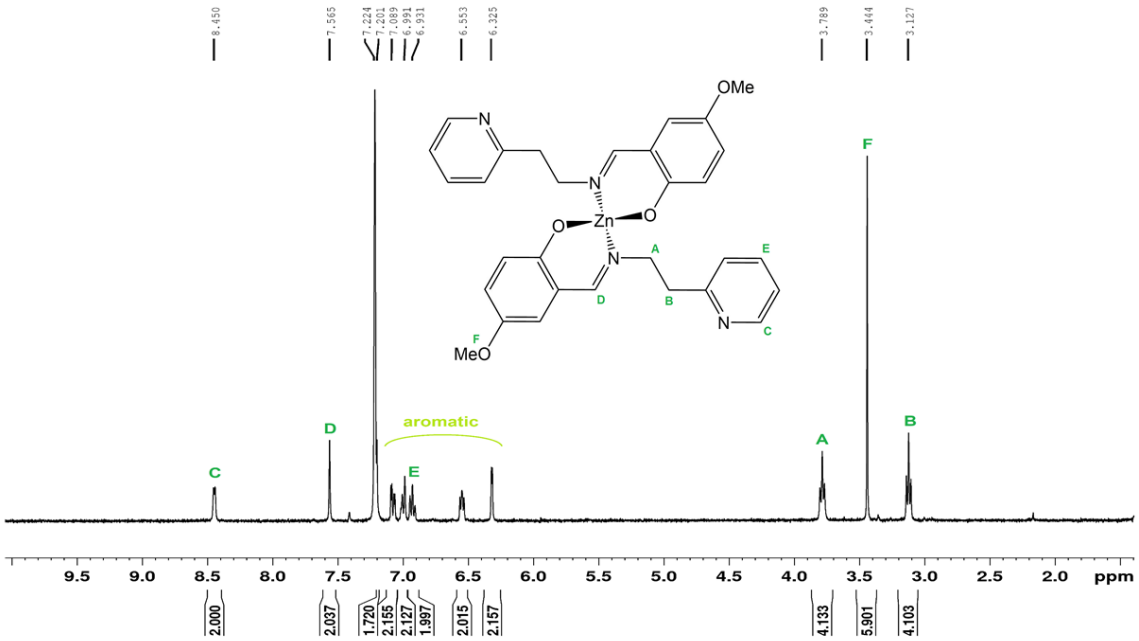


Figure S16. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) complex **4**.

^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 171.4, 163.4, 158.6, 153.2, 149.0, 135.8, 124.3, 120.9, 118.9, 116.3, 112.7, 60.1, 55.9, 38.0.

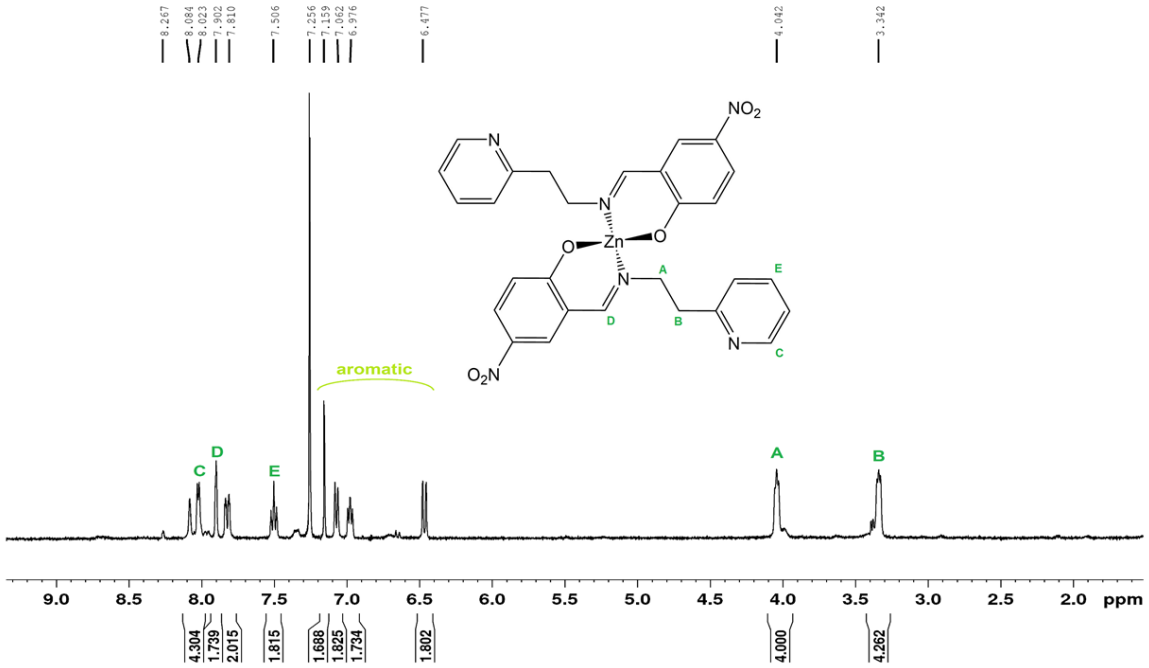


Figure S17. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) complex **5**.

^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 172.1, 163.4, 158.6, 153.2, 149.0, 135.8, 124.3, 120.9, 118.9, 116.3, 112.7, 55.9, 38.0.

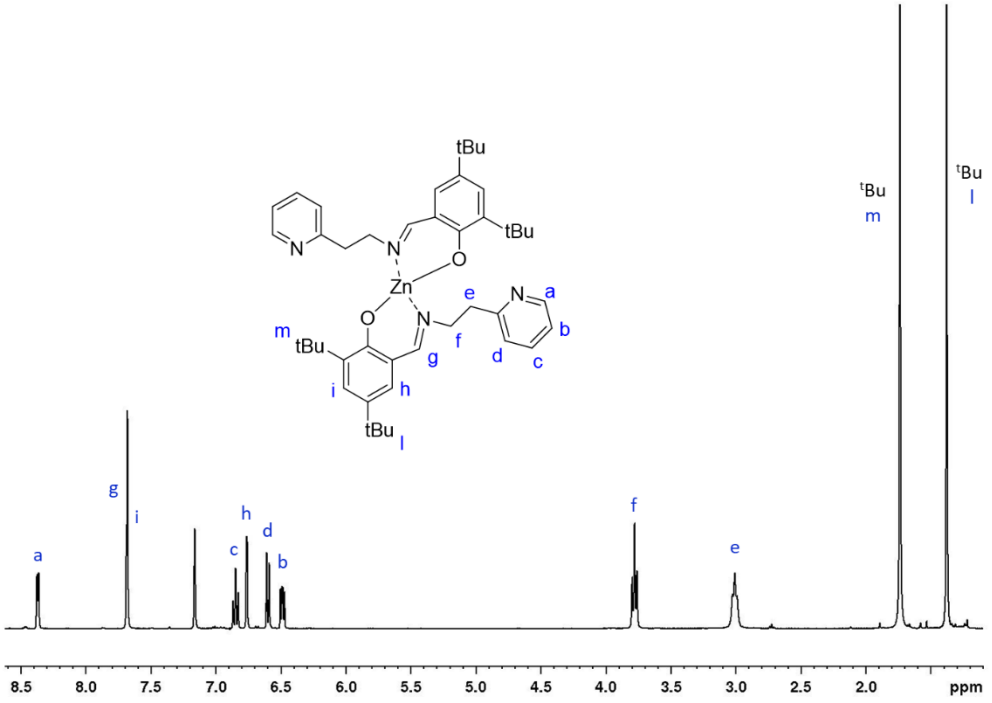


Figure S18. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) complex **6**.

^{13}C NMR (100 MHz, C_6D_6, 298 K): δ 172.6, 169.4, 158.9, 149.6, 141.7, 136.0, 135.2, 130.2, 129.8, 123.7, 121.4, 117.9, 60.3, 39.2, 36.0, 34.1, 31.9, 30.0.

Table S1. Crystal data and refinement details for complexes **1**, **2** and **4**

Compound	1	2	4
Formula	$C_{28}H_{26}N_4O_2Zn$	$C_{30}H_{30}N_4O_2Zn \cdot C_6H_6$	$C_{30}H_{30}N_4O_4Zn$
Formula weight	515.92	622.01	575.97
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P2/c*	*P2/n*	*C2/c*
***a* (Å)**	9.7337(10)	9.911(3)	28.036(13)
***b* (Å)**	6.0539(6)	6.0729(9)	5.992(3)
***c* (Å)**	21.730(2)	27.229(4)	19.822(9)
***β*(°)**	101.532(3)	93.877(16)	123.660(18)
***V* (Å³)**	1254.6(2)	1635.1(7)	2772(2)
Z	2	2	4
D_c (g cm^{-3})	1.366	1.327	1.388
μ (mm^{-1})	1.614	1.544	1.584
F(000)	536.0	652	1200.0
Indep. refl. measured	2358	2767	2235
Param./restraints	211	187/2	178
R1 [F_o> 4 σF_o)]	0.0388 (2191)	0.0564 (2236)	0.0360 (2067)
$_w$R2 (all refl)	0.1071	0.1665	0.1004
GooF	1.089	1.039	1.054
ρ min (eÅ^{-3})	-0.501	-0.33	-0.19
ρ max (e Å^{-3})	0.212	0.46	0.23

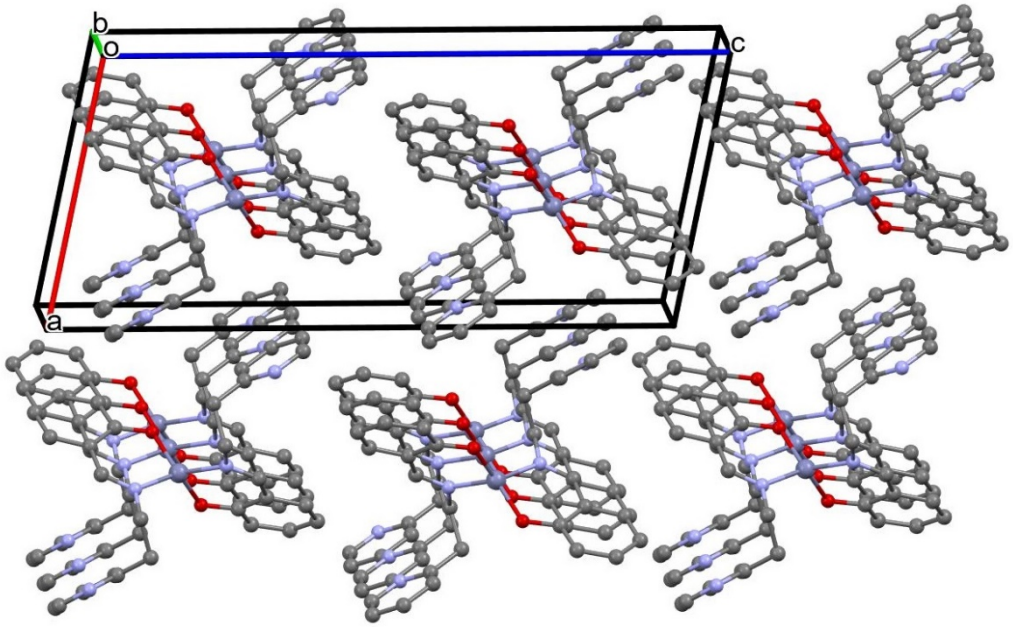


Figure S19. Crystal packing of compound **1**.

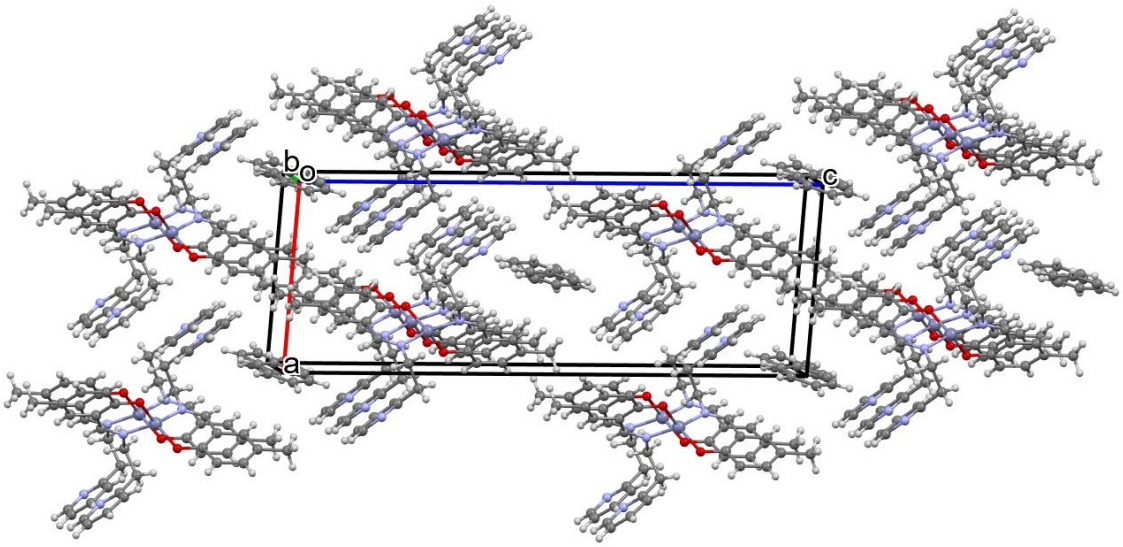


Figure S20. Crystal packing of compound **2**.

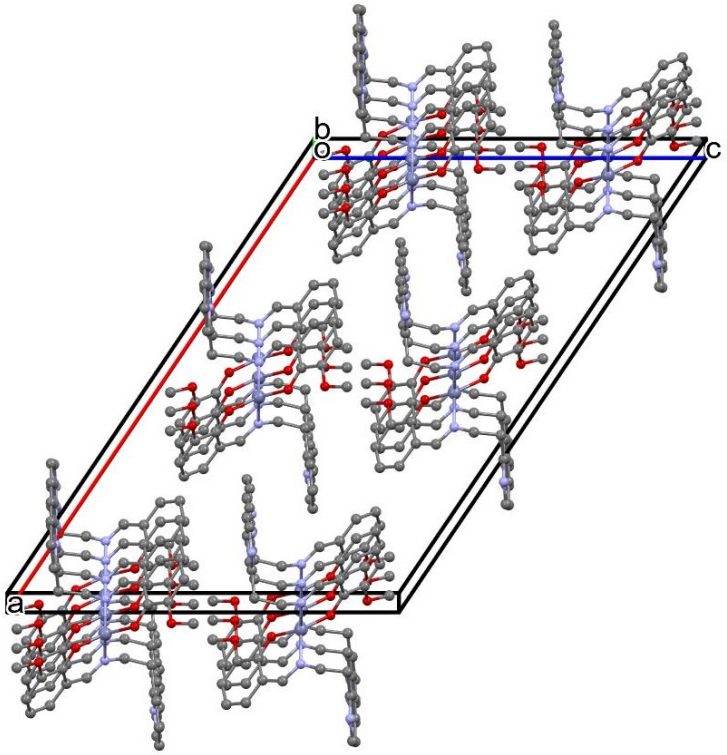
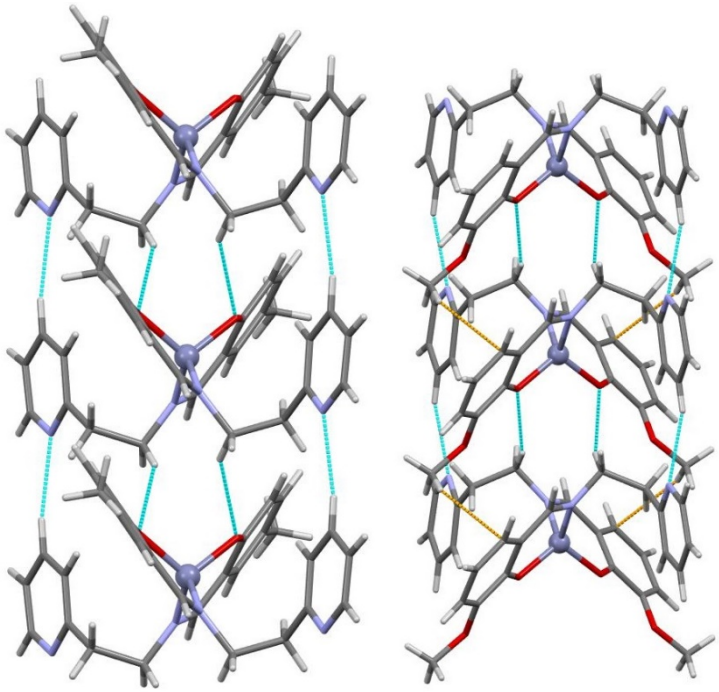


Figure S21. Crystal packing of compound **4**.



(a) **(b)**

Figure S22. Columnar assembly along the *b*-axis for (a) compound **2** and (b) compound **4**. CH···O and CH···N short distances are depicted in light blue, CH-pi short distances in orange

Table S2. Thermal analysis of complexes **1-5**

	Dynamic		Isothermal (250°C)	
Complex	**Degradation temperature (°C)**	**Loss in weight (%)**	**Degradation time (min)**	**Loss in weight (%)**
1	298	-40	48	-40
2	300	-40	47	-39
3	286	-42	38	-35
4	290	-67	44	-25
5	291	-21	46	-22

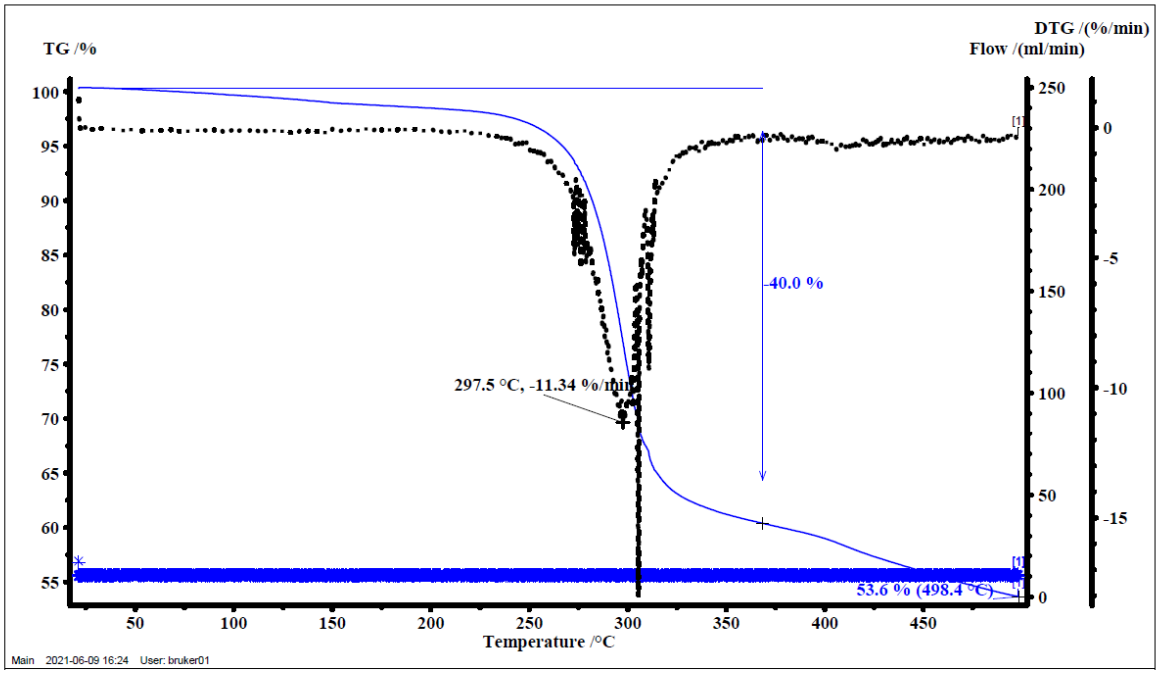


Figure S23. TGA of complex **1**.

Stability test.

In the glovebox 0.0070 g (11µmol) of **2** were weighted and then transferred to an NMR tube. The compound was stored under air atmosphere in an oil bath at 150°C for 15 hours. Then, the solid was dissolved in 0.5mL of C_6D_6 and analyzed by ^{1}H NMR spectroscopy.

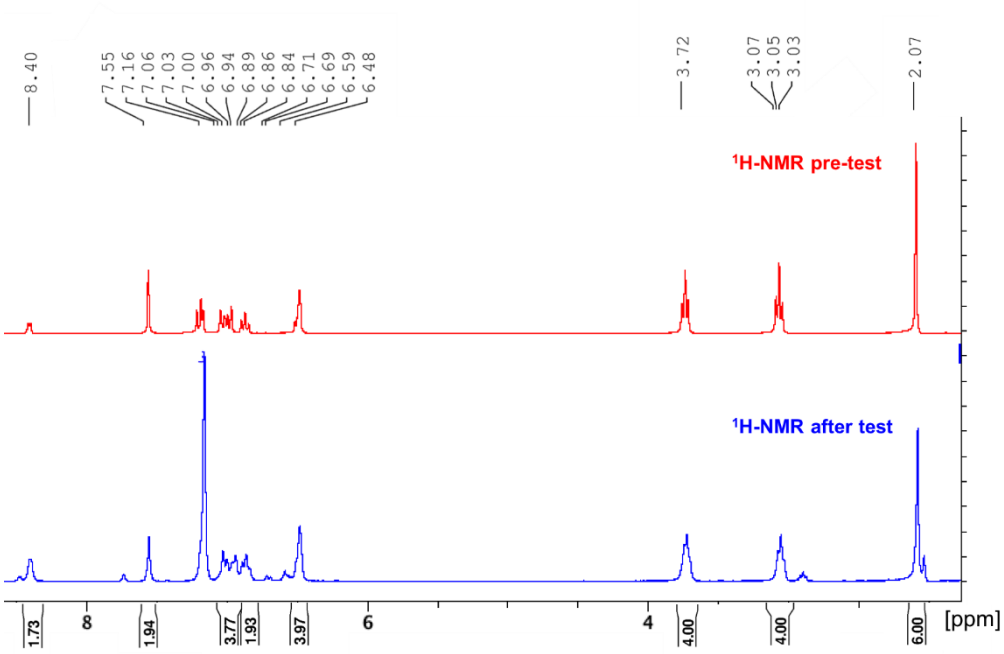


Figure S24. ^{1}H NMR spectra (400 MHz, C_6D_6, 25°C) of complex 2 before and after the stability test.

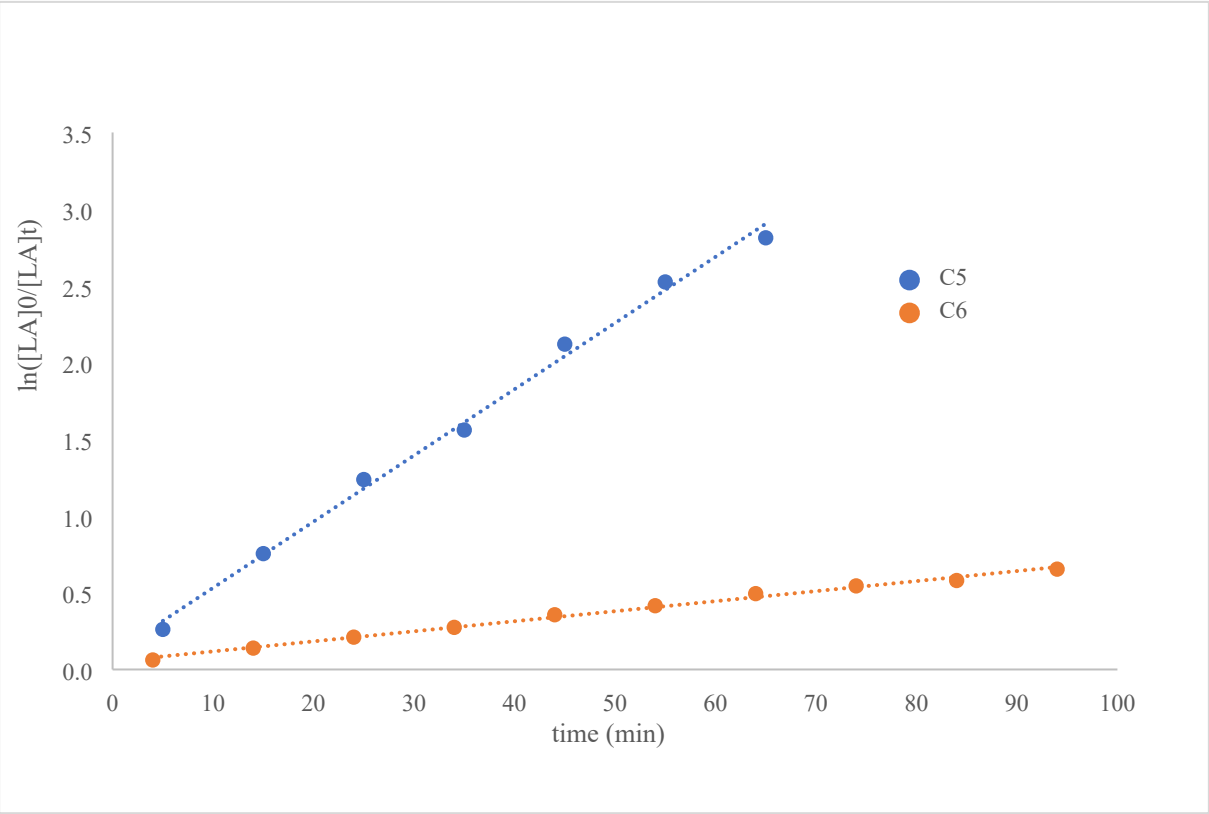


Figure S25. Kinetic plots for ROP of L-LA promoted by Zn catalysts **5** and **6** depicting reaction orders of unity with respect to the monomer concentration. Reaction conditions: Zn = 5µmol; [L-LA] : [Zn] : [BnOH] = 100:1:1; T=50 °C; 0.5 mL of $CDCl_3$.

Table S3. Polymerization tests of L-lactide promoted by **1-6** in toluene at 80 °C. Conversions after 2 min for the calculation of TOF.

Entry[a]	Cat	Conv1 (%)	TOF [b] (h^{-1})	Conv2 (%)	M_{nGPC}[c] (10^3)	$Đ$[c]	M_n^{th}[c] (10^3)
1	1	49	1470	94	4.4	1.6	13.5
2	2	51	1530	>99	4.6	1.8	14.4
3	3	28	815	83	3.9	1.6[e]	12.0
4	4	65	1950	>99	4.1	1.7	14.4
5	5	46	1380	84	3.9	1.7[e]	12.1
6	6	85	2550	>99	4.2	1.6	12.2

Conv 1 after reaction time of 2 min. [b] TOF values were evaluated by NMR after 2 min; Conv 2= conversion after reaction time of 20 min.

Table S4. Polymerization experiments at 180 °C.

Run	Cat	Time (min)	Conv (%)	TOF[c] (h^{-1})
1	**1**	20	40	$6.00 \cdot 10^3$
		3h (1h)	>99	
2	**2**	20	36	$5.40 \cdot 10^3$
		3h (1h)	>99	
3	**3**	20	5	$7.51 \cdot 10^2$
		18h	>99	
4	**4**	20	15	$2.25 \cdot 10^3$
		8h	>99	
5	**5**	20	60	$9.00 \cdot 10^3$
		2h	>99	
6	**6**	20	67	$1.00 \cdot 10^4$

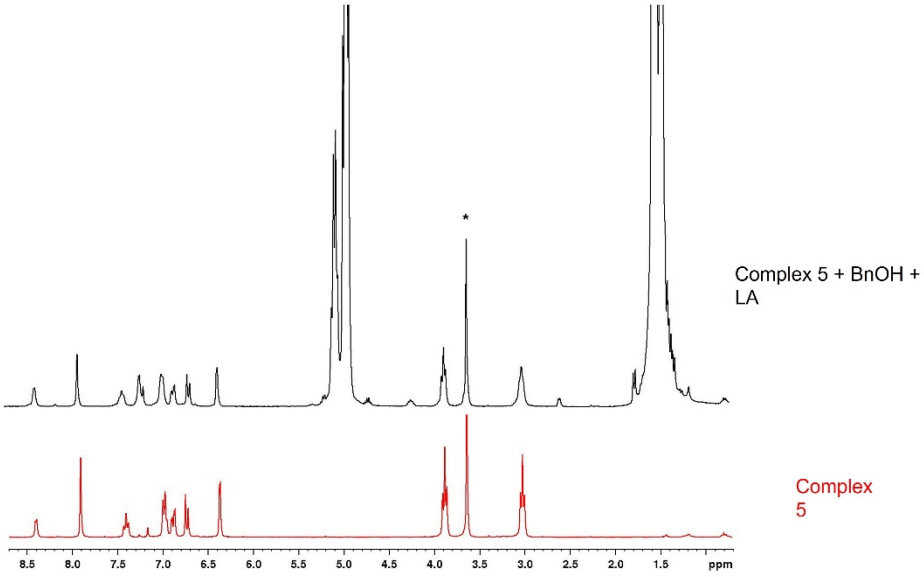


Figure S26. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 50 °C) of the kinetic experiment with complex **5**.

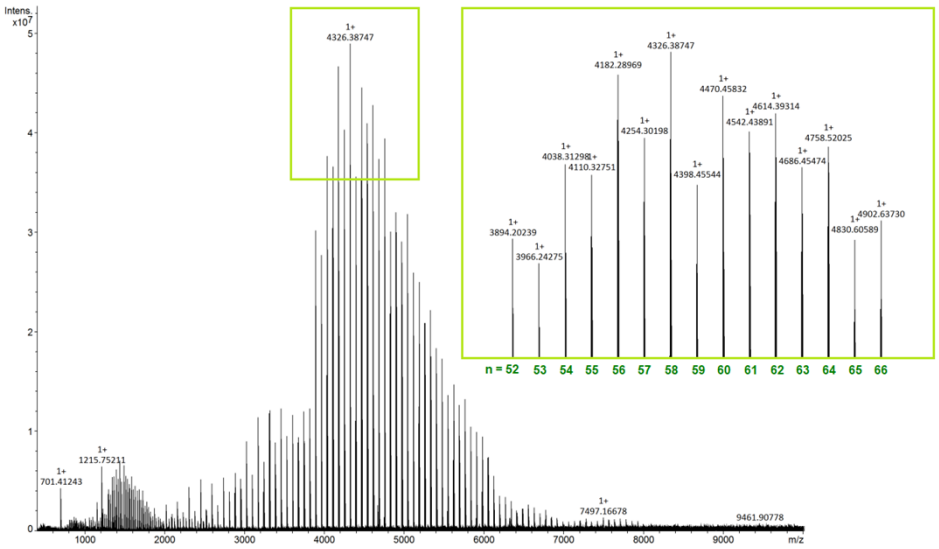
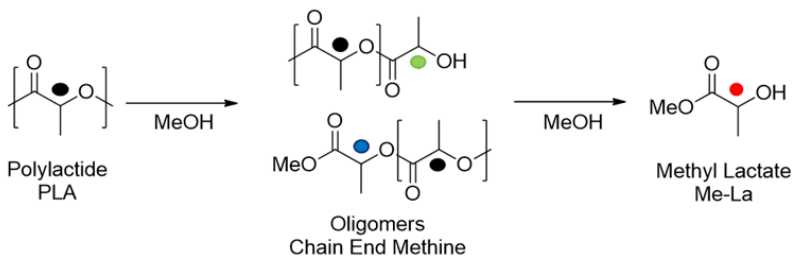


Figure S27. MALDI TOF spectrum of a PLA sample obtained by the test conditions: [L-LA]:[1][BnOH] of 20:1:1, 1 eq = 30µmol, 80°C in toluene, 1 h after the quantitative conversion of monomer.



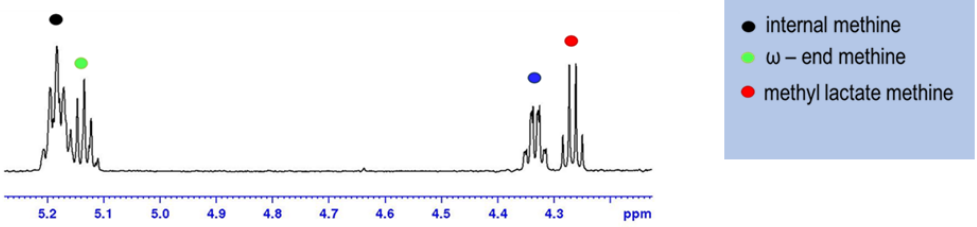


Figure S28. ^{1}H NMR spectrum of a degradation reaction of PLLA (entry 1 of Table 6).

- Test of recycling of the catalyst per the PLA degradation by methanolysis.

0.576 g (8mmol) of PLA plastic cups, 10 mL of methanol and 0.026 g of **1** (50 μmol,) were added to a 25mL Schlenk tube. Methanolysis was carried out at 65°C. After two hours, the reaction mixture was analyzed by ^{1}H NMR spectroscopy (Figure S33). The resonances of methyl lactate as single product of degradation were observed. The methanol and methyl lactate were removed under vacuum to recover the catalyst and the solid residue was analyzed by ^{1}H NMR spectroscopy (Figure S34). Then, equal amounts of methanol (10mL) and PLA plastic cups (0.5760mg, 8mmol, 800eq) were added to the Schlenk tube and refluxed for two more hours. The reaction mixture was analyzed by ^{1}H NMR spectroscopy (Figure S35).

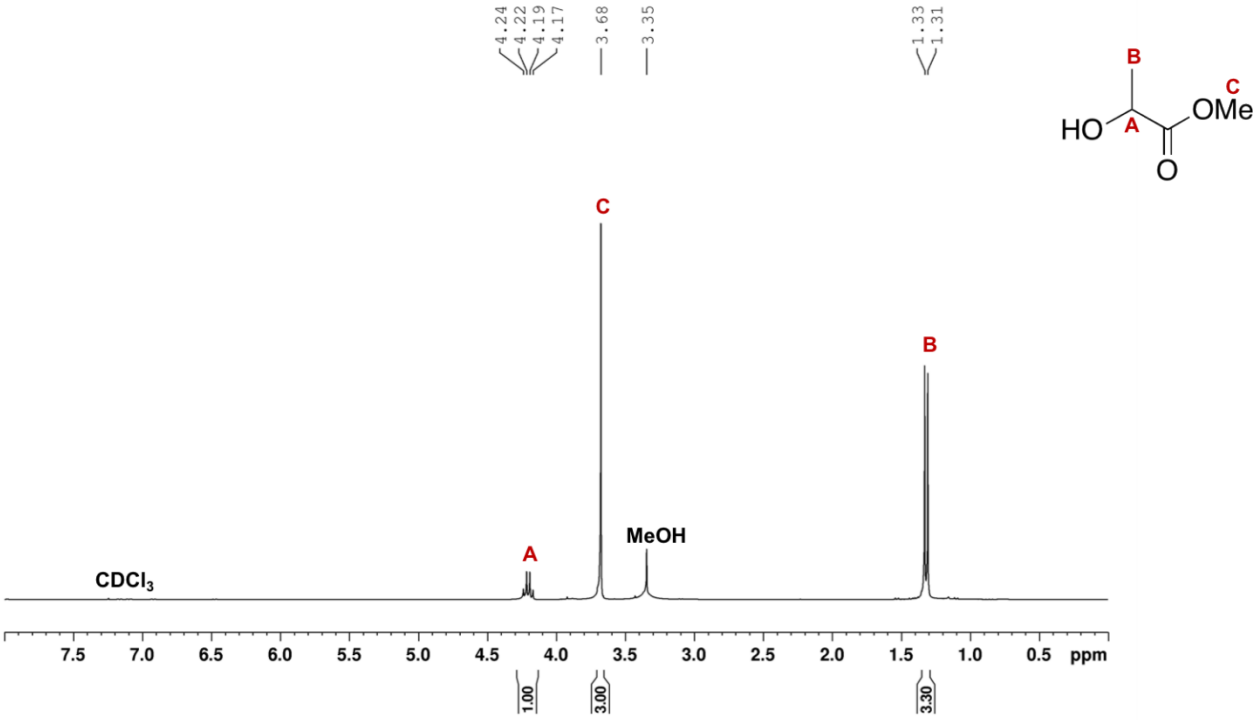


Figure S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of the PLA degradation by complex **2**. First step.

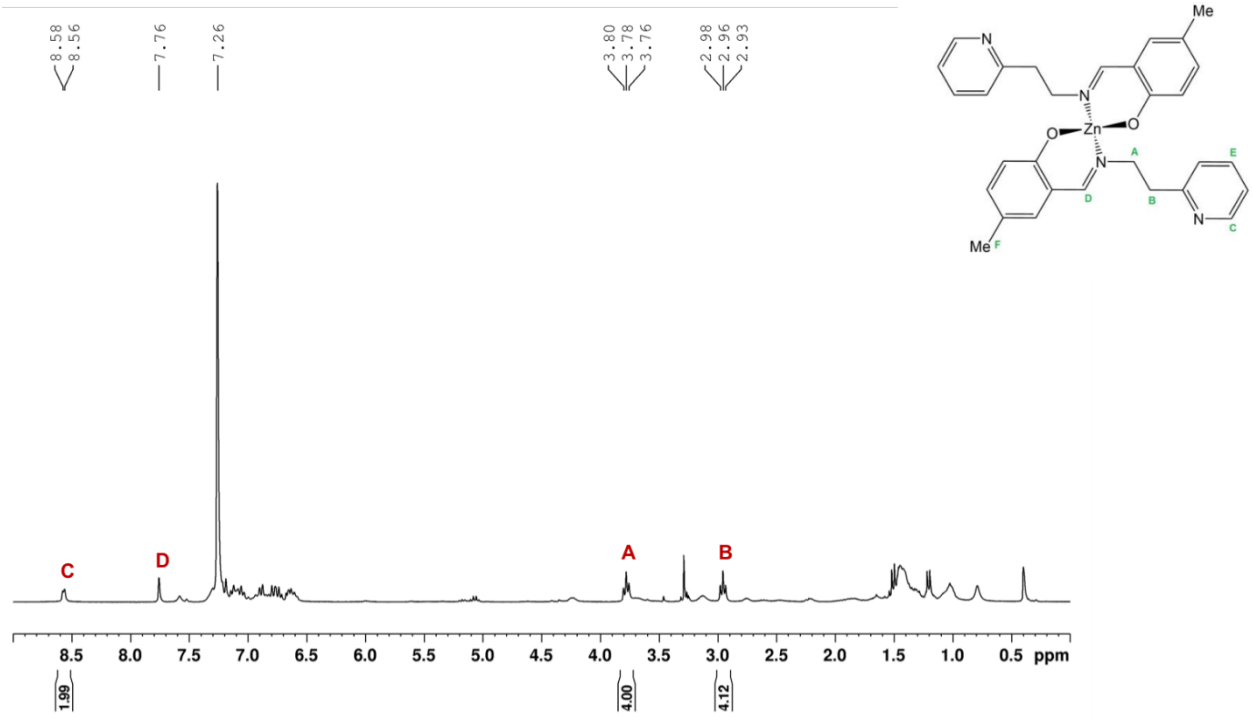


Figure S30. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of the solid residual after evaporation in vacuo of methyl lactate.

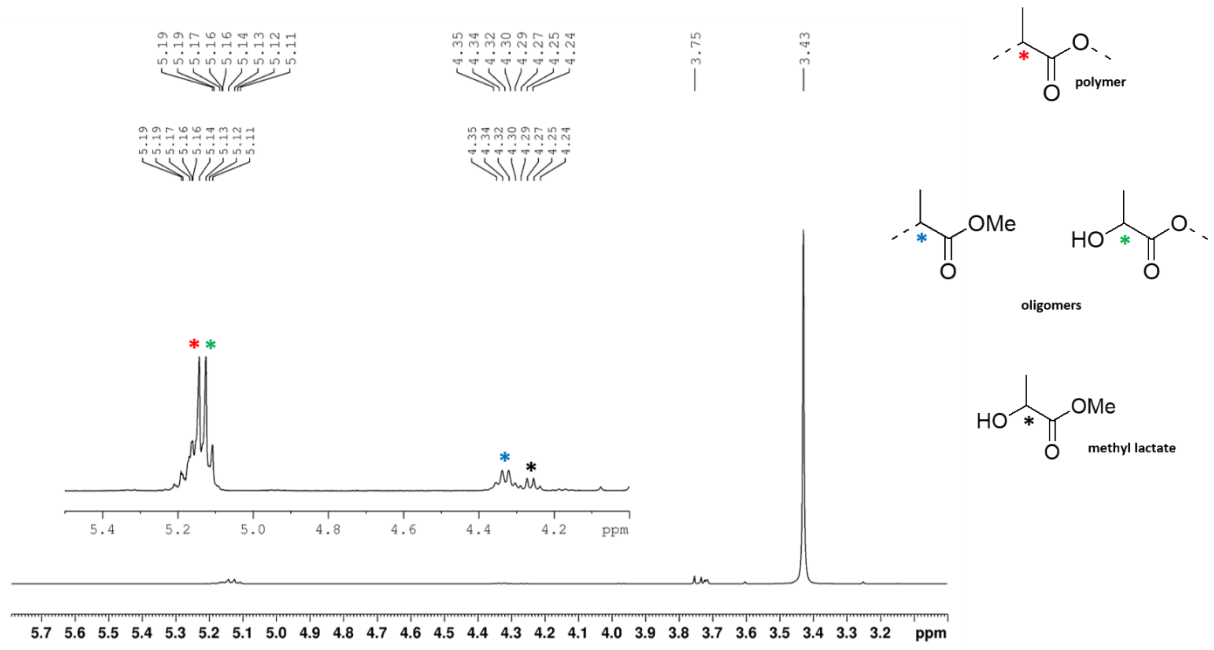


Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of the products after the second degradation step.

Stability test of complex 2 for glycolysis reaction.

In the glovebox 0.0027g (5μmol) of 2 and 0.4mL of ethylene glycol were weighted and then transferred to a 10mL tube with a magnetic stirrer. The test was conducted in the air, heating the mixture at 150°C. After one hour, the reaction mixture was dried under vacuum and then analyzed by ^{1}H NMR spectroscopy.

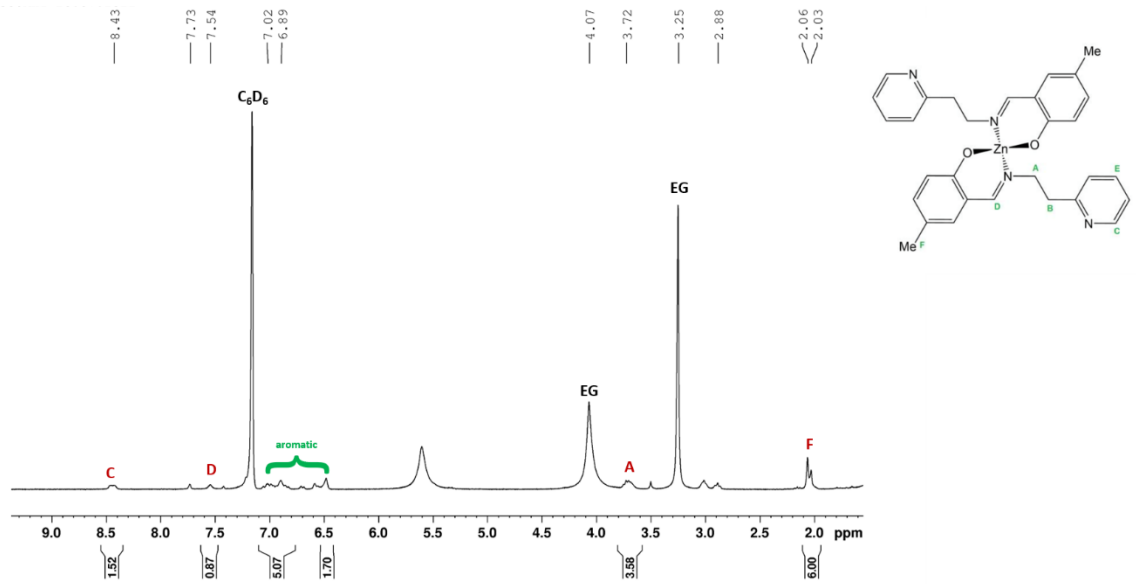


Figure S32. ^{1}H NMR spectrum (400 MHz, C_6D_6, 25 °C) of the solid residue of complex **2** after heating with ethylene glycol.

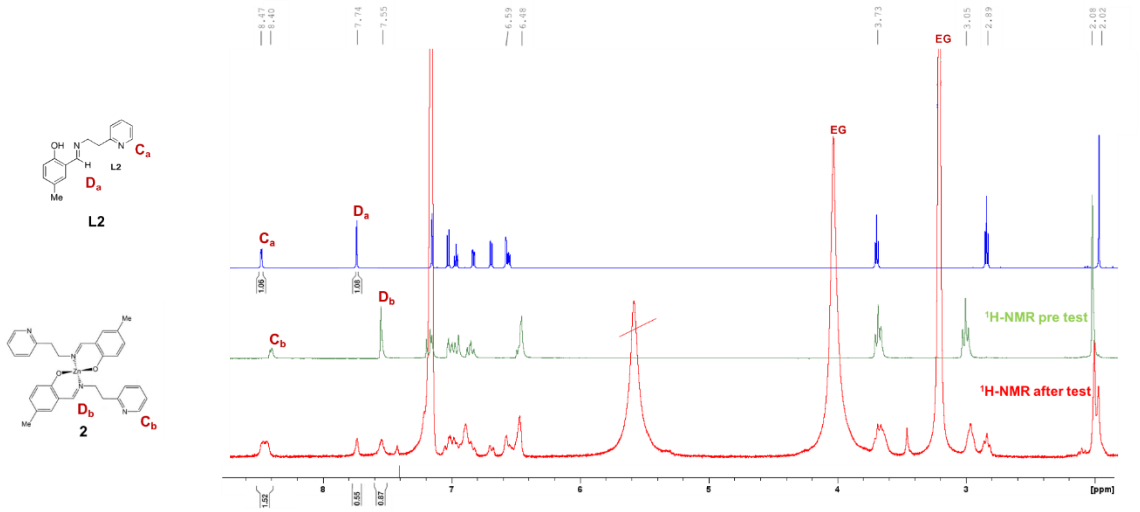


Figure S33. ^{1}H NMR spectrum (400 MHz, C_6D_6, 25 °C) of the solid residue of complex 2 after heating with ethylene glycol in comparison to the complex 2 and the related ligand.