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Supporting Information

Zirconium and hafnium complexes bearing pyrrolidine derived salalen-type {ONNO} ligands and their application for ring-opening polymerization of lactides

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Table S1. Crystallographic data for complexes **1**, **3**, **4** and **5**.

Complex	**1**	**3**	**4**	**5**
Empirical formula	$C_{46}H_{58}N_4O_4Zr$	$C_{39}H_{58}N_4O_4Hf$	$C_{40}H_{60}N_4O_4Zr$	$C_{40}H_{60}N_4O_4Hf$
Formula weight	822.18	825.38	752.14	839.41
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\ 2_1\ 2_1\ 2_1$	$P\ 2_1$	$P\ 2_1$	$P\ 2_1$
Unit cell dimensions				
a (Å)	11.329(2)	10.9194(2)	11.0439(3)	11.01520(14)
b (Å)	17.763(4)	10.6543(2)	10.3438(3)	10.33345(14)
c (Å)	22.61(4)	16.9439(4)	17.7240(5)	17.7349(2)
α (°)	90	90	90	90
β (°)	90	99.216(2)	99.103(3)	99.2001(13)
γ (°)	90	90	90	90
V (Å^3)	4550.4(15)	1945.77(7)	1999.21(9)	1992.70(5)
Z	4	2	2	2
Calculated density (g/cm^3)	1.200	1.409	1.249	1.399
Absorption coefficient (mm^{-1})	0.285	2.723	0.318	
F(000)	1736	848	800	864
Crystal size (mm)	0.22 x 0.18 x 0.15	0.23 x 0.18 x 0.12	0.25 x 0.22 x 0.18	0.22 x 0.18 x 0.16
θ range for data collection (°)	3.43 to 24.99	3.31 to 25.00	3.49 to 25.00	3.38 to 24.99
Index ranges	-6<=h<=13 -20<=k<=21 -24<=l<=26	-7<=h<=12 -7<=k<=12 -19<=l<=20	-13<=h<=11 -6<=k<=12 -21<=l<=21	-13<=h<=7 -12<=k<=12 -21<=l<=20
Reflections collected	17693	7114	7417	7021
Independent reflections	7987	5153	5073	5655
R_{int}	0.0401	0.0258	0.0343	0.0233
Completeness to θ (%)	99.7	99.7	99.7	99.7
Data / restraints / parameters	7987/12/514	5153/49/433	5073/2/442	5655/25/442
Goodness-of-fit on F^2	1.005	1.001	1.002	1.006
Final R indices [I>2sigma(I)]	R_1 = 0.0509 wR_2 = 0.1090	R_1 = 0.0270 wR_2 = 0.0581	R_1 = 0.0400 wR_2 = 0.0712	R_1 = 0.0245 wR_2 = 0.0511
R indices (all data)	R_1 = 0.0623 wR_2 = 0.1146	R_1 = 0.0301 wR_2 = 0.0602	R_1 = 0.0466 wR_2 = 0.0757	R_1 = 0.0266 wR_2 = 0.0523

Largest diff. peak and hole (e. Å^{-3})	0.572 and -0.417	0.730 and -0.681	0.390 and -0.337	0.500 and -0.391

Table S2. Selected bond lengths (Å) and angles (°) for complexes **1**, **3, 4** and **5**.

Complex	**1** (M = Zr)	**3** (M = Hf)	**4** (M = Zr)	**5** (M = Hf)
M(1)-O(1)	2.163(3)	2.138(5)	2.158(3)	2.139(5)
M(1)-O(2)	2.030(3)	2.017(4)	2.021(3)	2.010(3)
M(1)-O(3)	1.939(3)	1.915(6)	1.927(3)	1.917(5)
M(1)-O(4)	1.915(3)	1.920(3)	1.926(3)	1.919(3)
M(1)-N(3)	2.352(4)	2.304(5)	2.345(4)	2.308(4)
M(1)-N(4)	2.451(4)	2.416(4)	2.451(3)	2.420(3)
O(1)-M(1)-N(3)	76.85(13)	78.2(2)	76.82(13)	77.29(16)
O(1)-M(1)-N(4)	95.86(12)	100.0(2)	98.55(13)	98.37(19)
O(2)-M(1)-O(1)	165.83(13)	166.97(19)	165.86(13)	166.31(16)
O(2)-M(1)-N(3)	89.10(14)	88.82(19)	89.04(13)	89.03(15)
O(2)-M(1)-N(4)	77.33(13)	76.65(18)	76.46(11)	77.30(15)
O(3)-M(1)-O(1)	91.09(14)	89.78(15)	90.21(11)	90.37(13)
O(3)-M(1)-O(2)	101.01(15)	102.4(2)	102.32(14)	102.06(19)
O(3)-M(1)-N(3)	153.94(15)	151.4(2)	150.30(14)	151.15(19)
O(3)-M(1)-N(4)	88.35(15)	85.2(2)	84.54(14)	85.0(2)
O(4)-M(1)-O(1)	89.92(14)	89.7(2)	89.96(14)	89.76(18)
O(4)-M(1)-O(2)	93.73(15)	90.91(19)	92.40(12)	91.91(15)
O(4)-M(1)-O(3)	106.06(16)	108.2(3)	107.65(15)	107.5(2)
O(4)-M(1)-N(3)	97.05(14)	97.7(2)	99.06(15)	98.58(18)
O(4)-M(1)-N(4)	164.40(14)	163.57(15)	165.20(10)	165.15(14)
N(3)-M(1)-N(4)	70.36(13)	71.8(2)	71.42(14)	71.4(2)

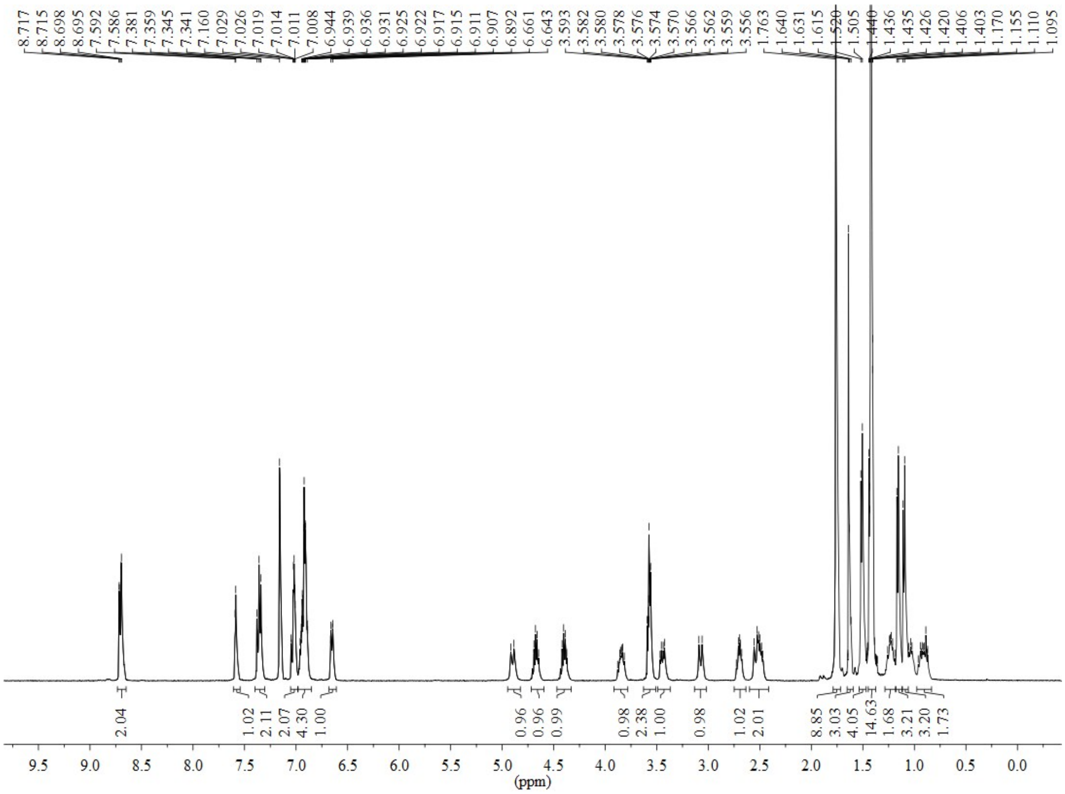

Fig. S1. ^{1}H NMR spectrum of complex **1** in C_6D_6 at 298 K.

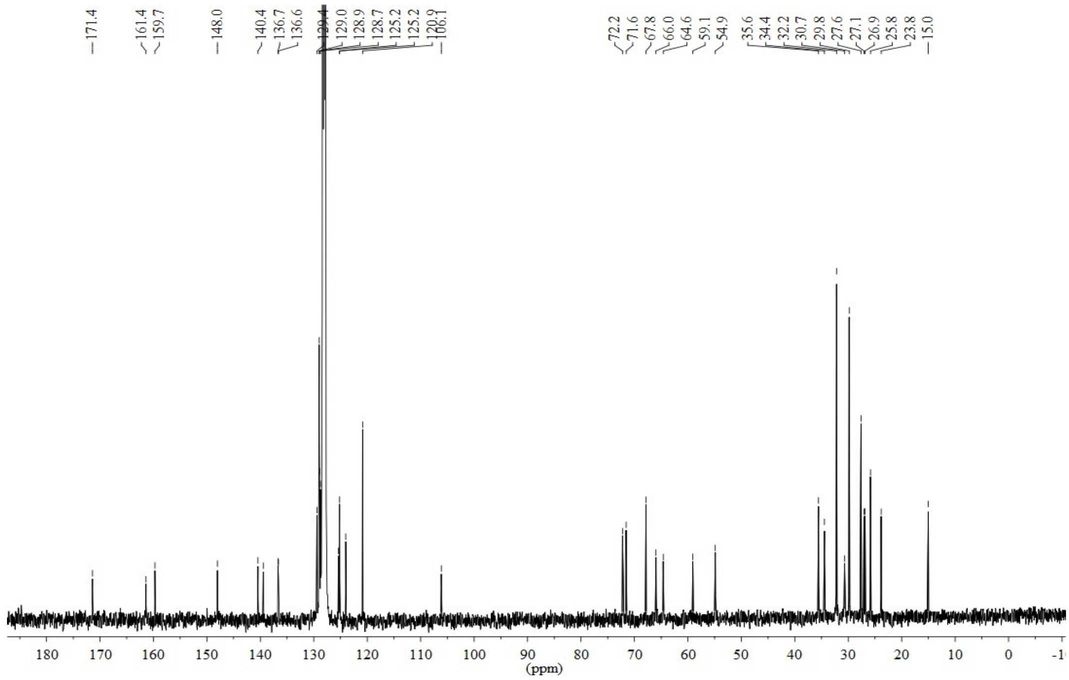

Fig. S2. ^{13}C NMR spectrum of complex **1** in C_6D_6 at 298 K.

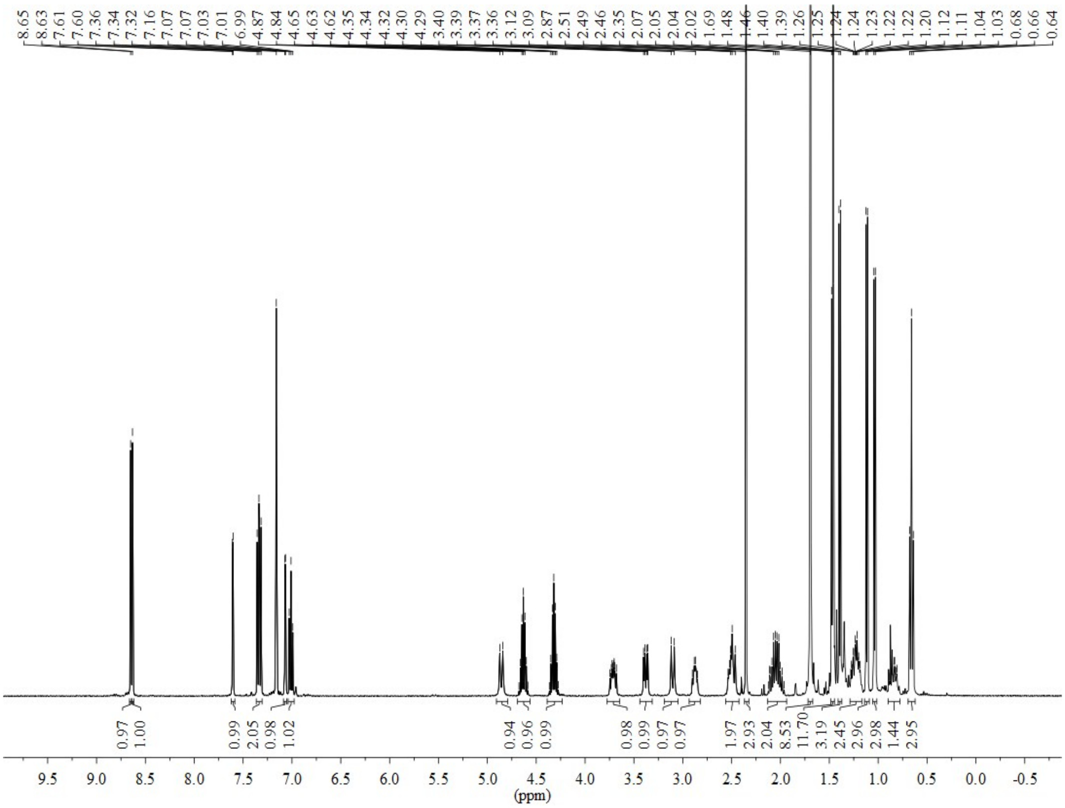

Fig. S3. ^{1}H NMR spectrum of complex **2** in C_6D_6 at 298 K.

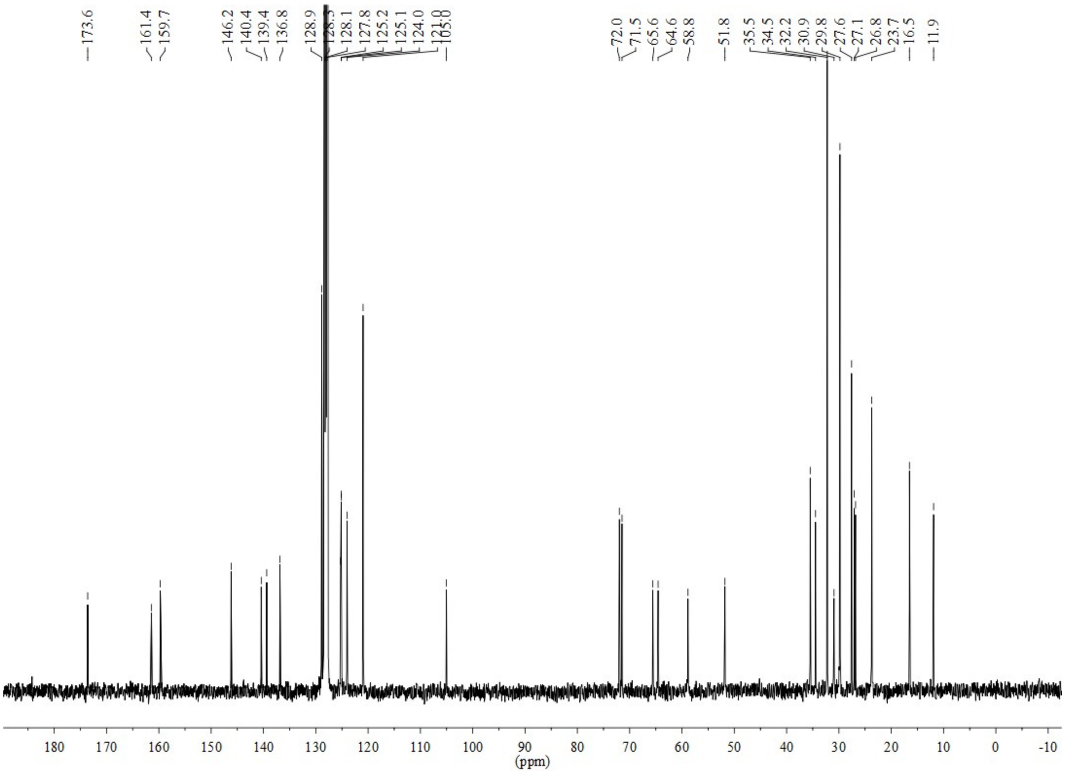

Fig. S4. ^{13}C NMR spectrum of complex **2** in C_6D_6 at 298 K.

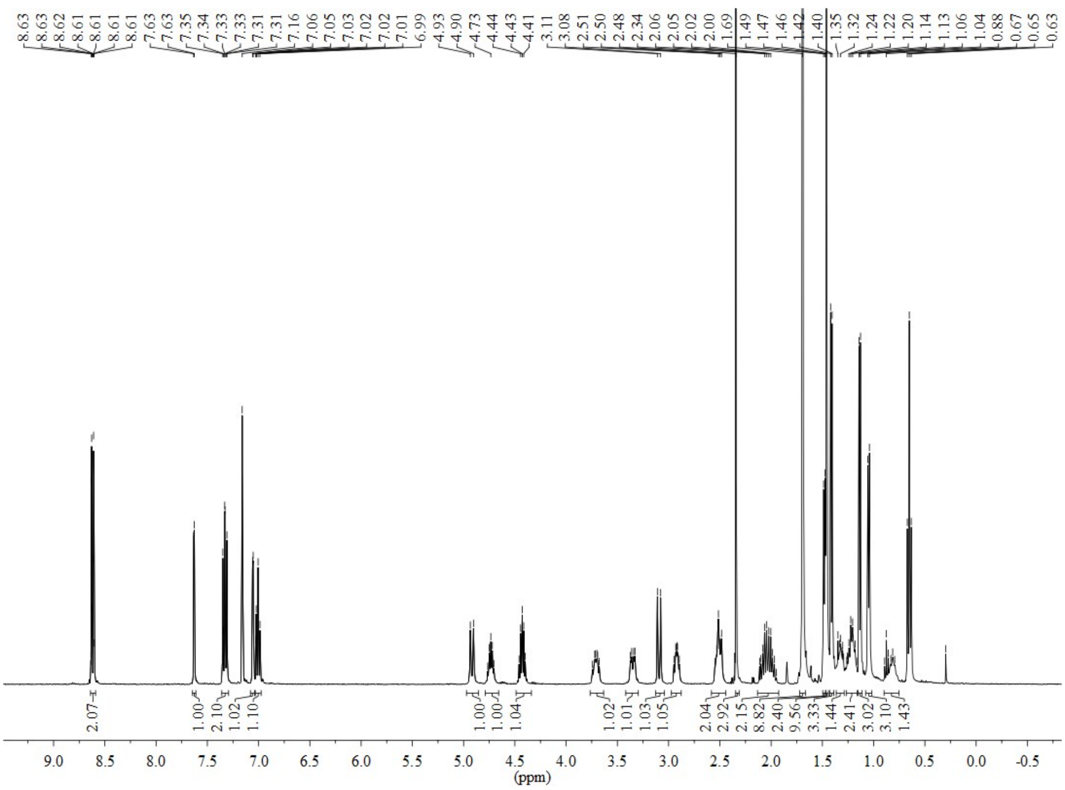

Fig. S5. ^{1}H NMR spectrum of complex **3** in C_6D_6 at 298 K.

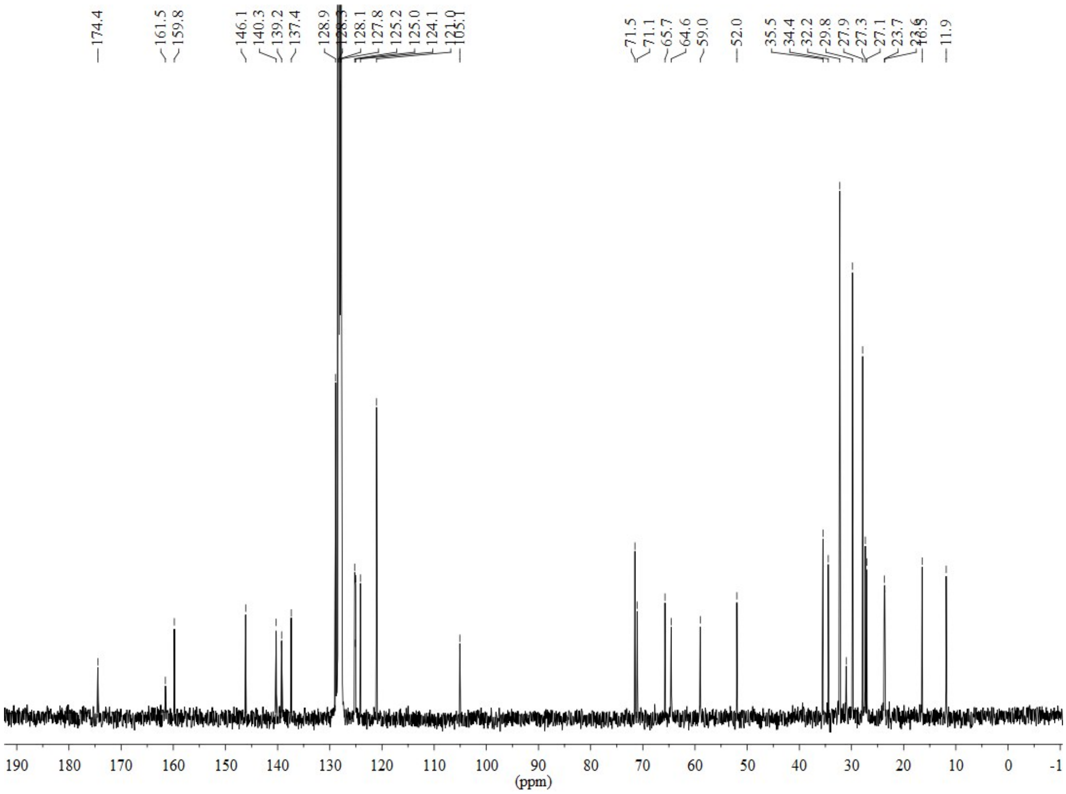

Fig. S6. ^{13}C NMR spectrum of complex **3** in C_6D_6 at 298 K.

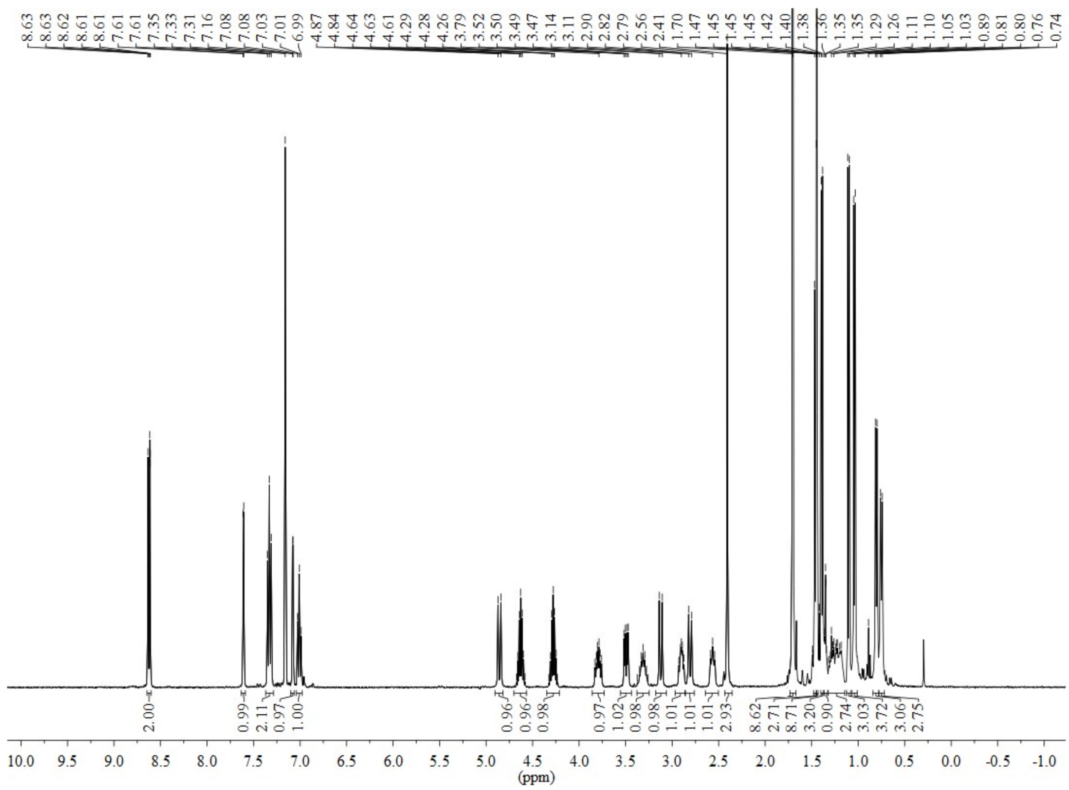

Fig. S7. ${}^{1}H$ NMR spectrum of complex **4** in C_6D_6 at 298 K.

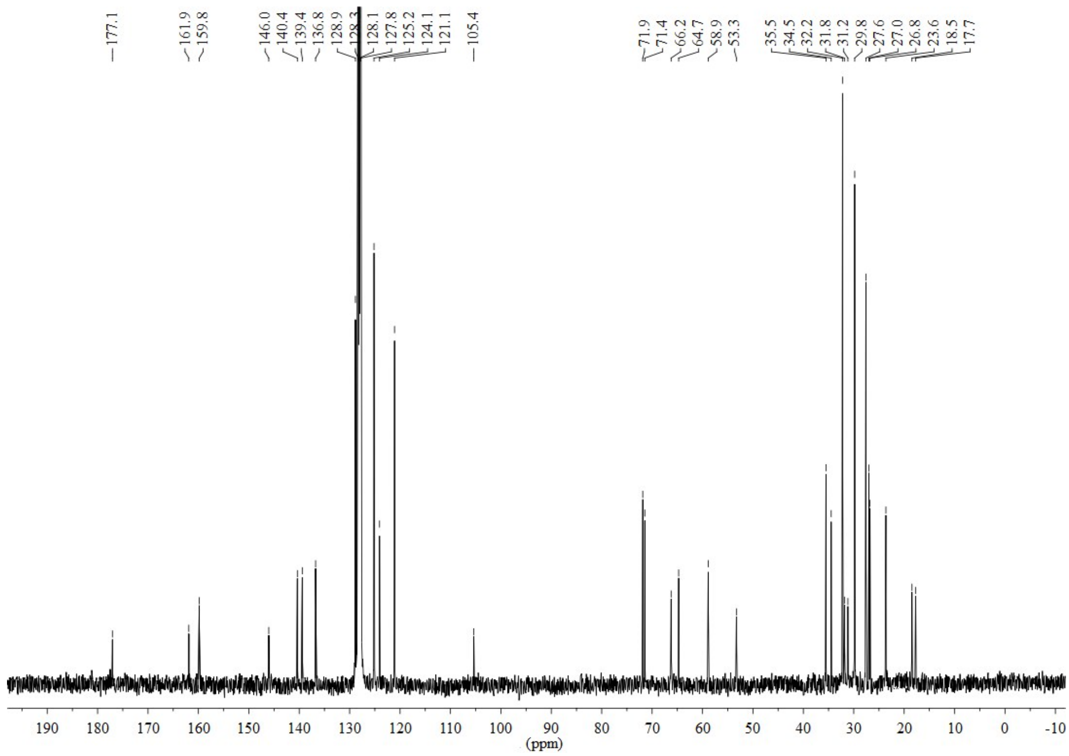

Fig. S8. ${}^{13}C$ NMR spectrum of complex **4** in C_6D_6 at 298 K.

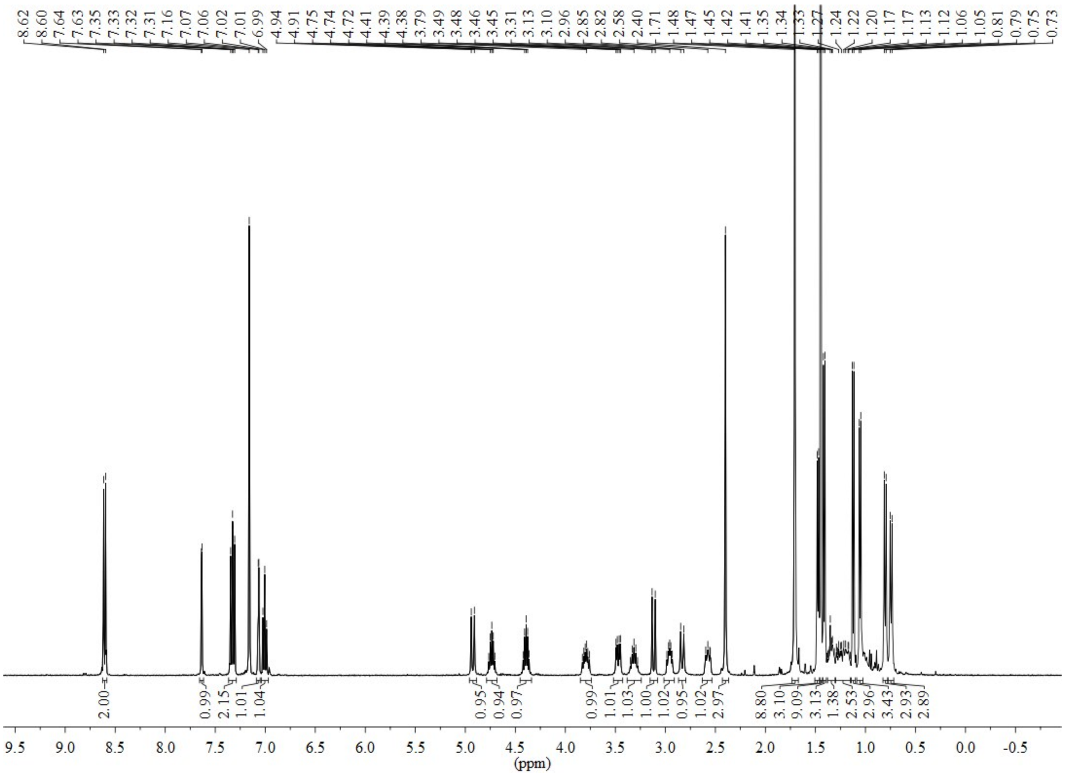

Fig. S9. ^{1}H NMR spectrum of complex **5** in C_6D_6 at 298 K.

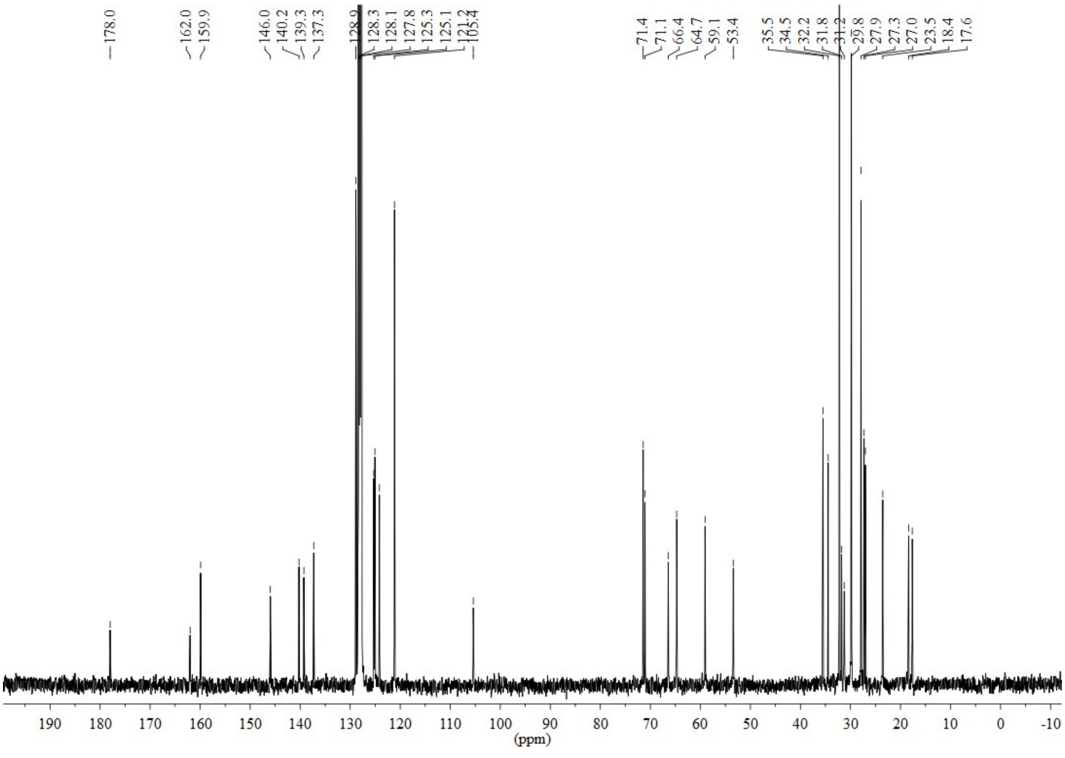

Fig. S10. ^{13}C NMR spectrum of complex **5** in C_6D_6 at 298 K.

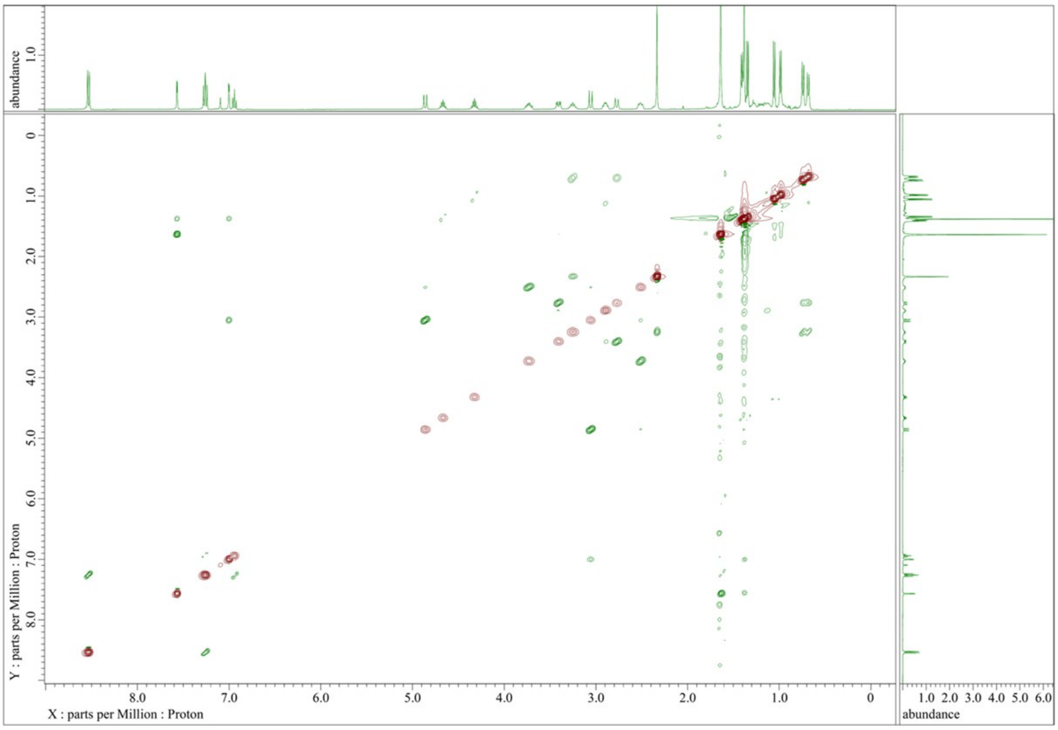

Fig. S11. NOESY spectrum of complex **5** [$L^3Hf(O^iPr)_2$] in C_6D_6 at 298 K.

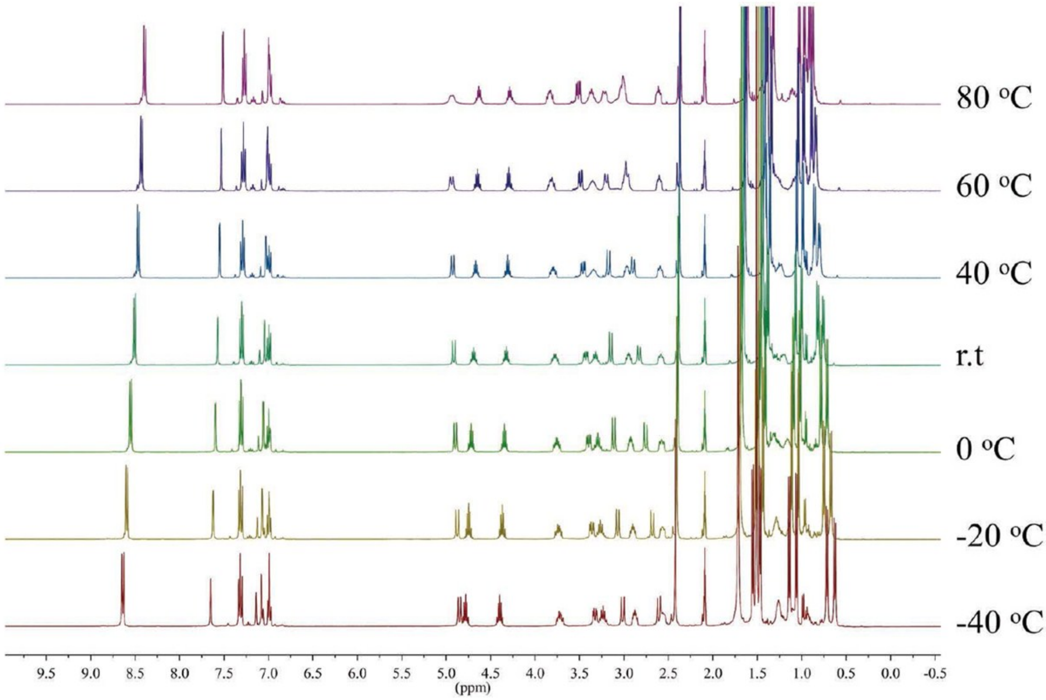

Fig. S12. Variable temperature ^1H NMR spectra for complex **5** in C_7D_8.

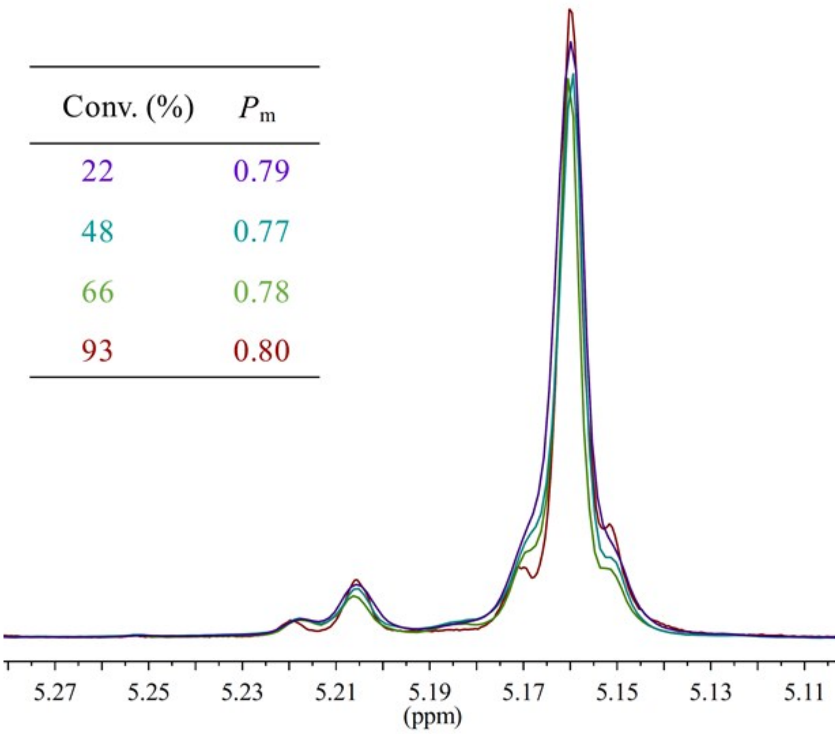

Fig. S13. Methine region of the homonuclear-decoupled [1]H NMR spectra of isotactic PLAs at different conversions produced using initiator **5**.

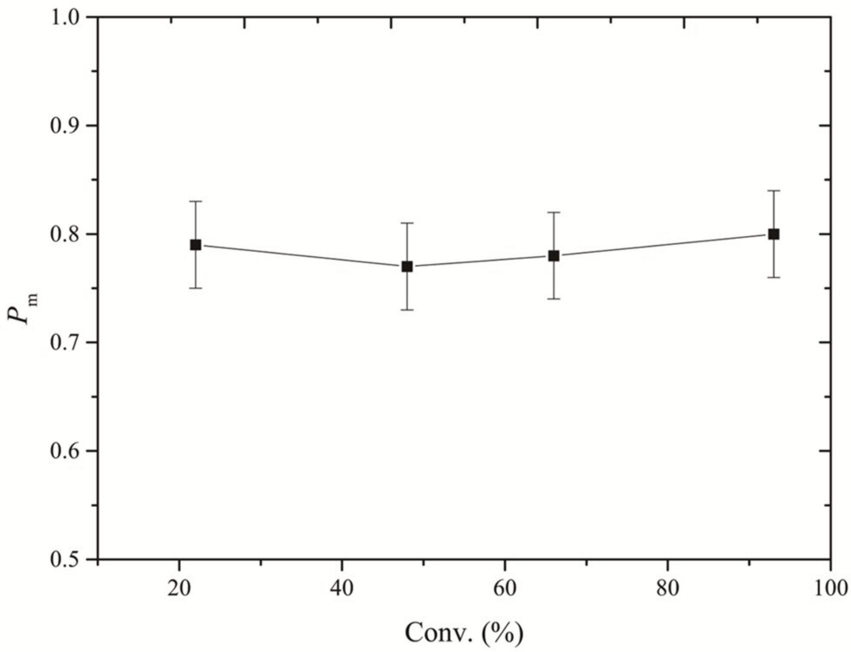

Fig. S14. Plot of P_m *vs*. conversion for polymerization of *rac*-LA with **5**.

Table S3. Tetrad probabilities based on Bernoullian Statistics (Th) and experimental values (Exp) as obtained by NMR analysis.

Tetrad	Formula	Th	Exp	Th	Exp
		22% conversion $P_m = 0.79$		93% converson $P_m = 0.80$	
[mmm]	$P_m^2+P_rP_m/2$	0.710	0.710	0.720	0.720
[mmr]	$P_rP_m/2$	0.083	0.078	0.080	0.076
[rmm]	$P_rP_m/2$	0.083	0.076	0.080	0.077
[rmr]	$P_r^2/2$	0.022	0.021	0.020	0.020
[mrm]	$(P_r^2+P_rP_m)/2$	0.105	0.116	0.100	0.111

Table S4. Tetrad probabilities based on Enantiomorphic Site Control Statistics (Th) and experimental values (Exp) as obtained by NMR analysis.

Tetrad	Formula	Th	Exp	Th	Exp
		22% conversion $\alpha = 0.87$		93% converson $\alpha = 0.87$	
[mmm]	$[\alpha^2+(1-\alpha)^2+\alpha^3+(1-\alpha)^3]/2$	0.710	0.710	0.710	0.720
[mmr]	$[\alpha^2(1-\alpha)+\alpha(1-\alpha)^2]/2$	0.057	0.079	0.057	0.076
[rmm]	$[\alpha^2(1-\alpha)+\alpha(1-\alpha)^2]/2$	0.057	0.078	0.057	0.077
[rmr]	$[\alpha^2(1-\alpha)+\alpha(1-\alpha)^2]/2$	0.057	0.021	0.057	0.020
[mrm]	$[\alpha(1-\alpha)+\alpha(1-\alpha)]/2$	0.113	0.116	0.113	0.111

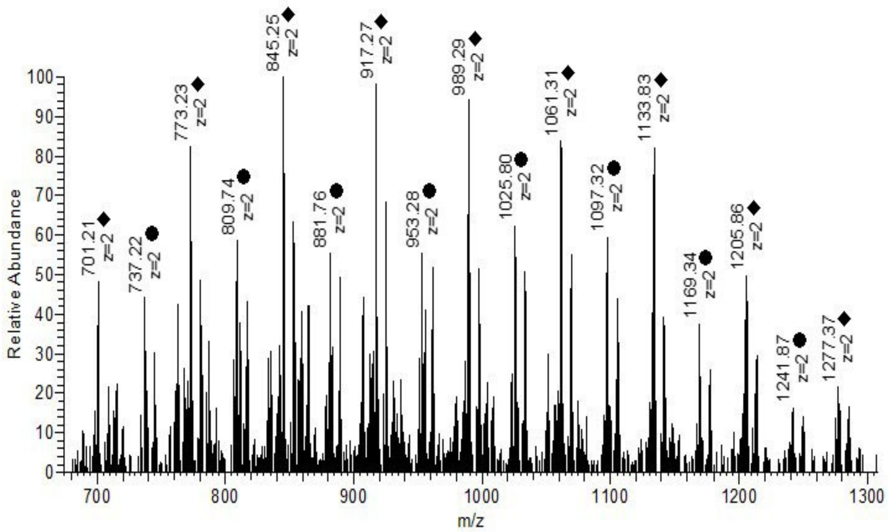

Fig. S15. ESI-MS spectrum of oligomer of *rac*-lactide prepared by complex **5**.