Supporting Information

Synthesis and structural characterization of titanium and zirconium complexes containing half-salen ligands as catalysts for polymerization reactions

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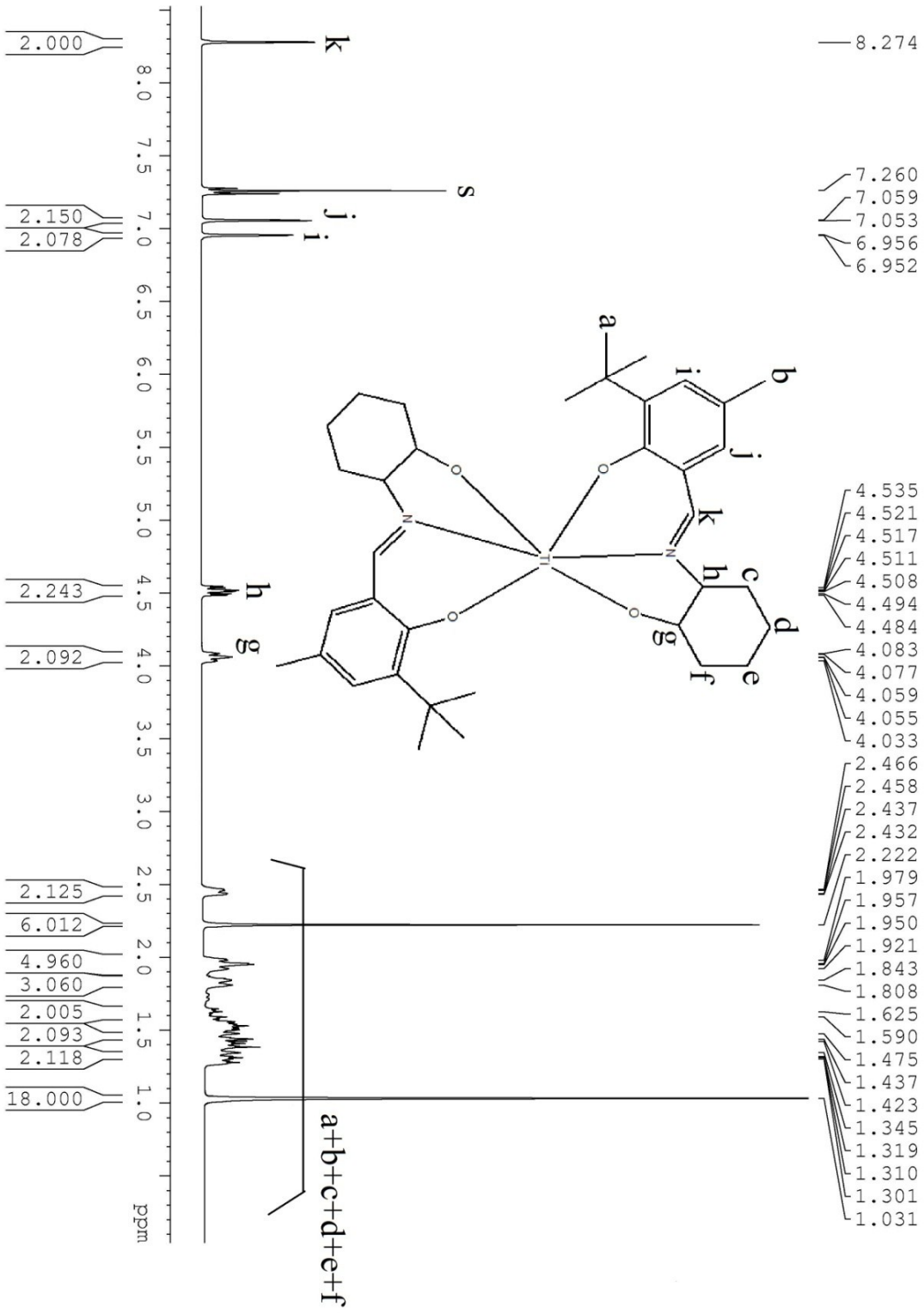


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **1**

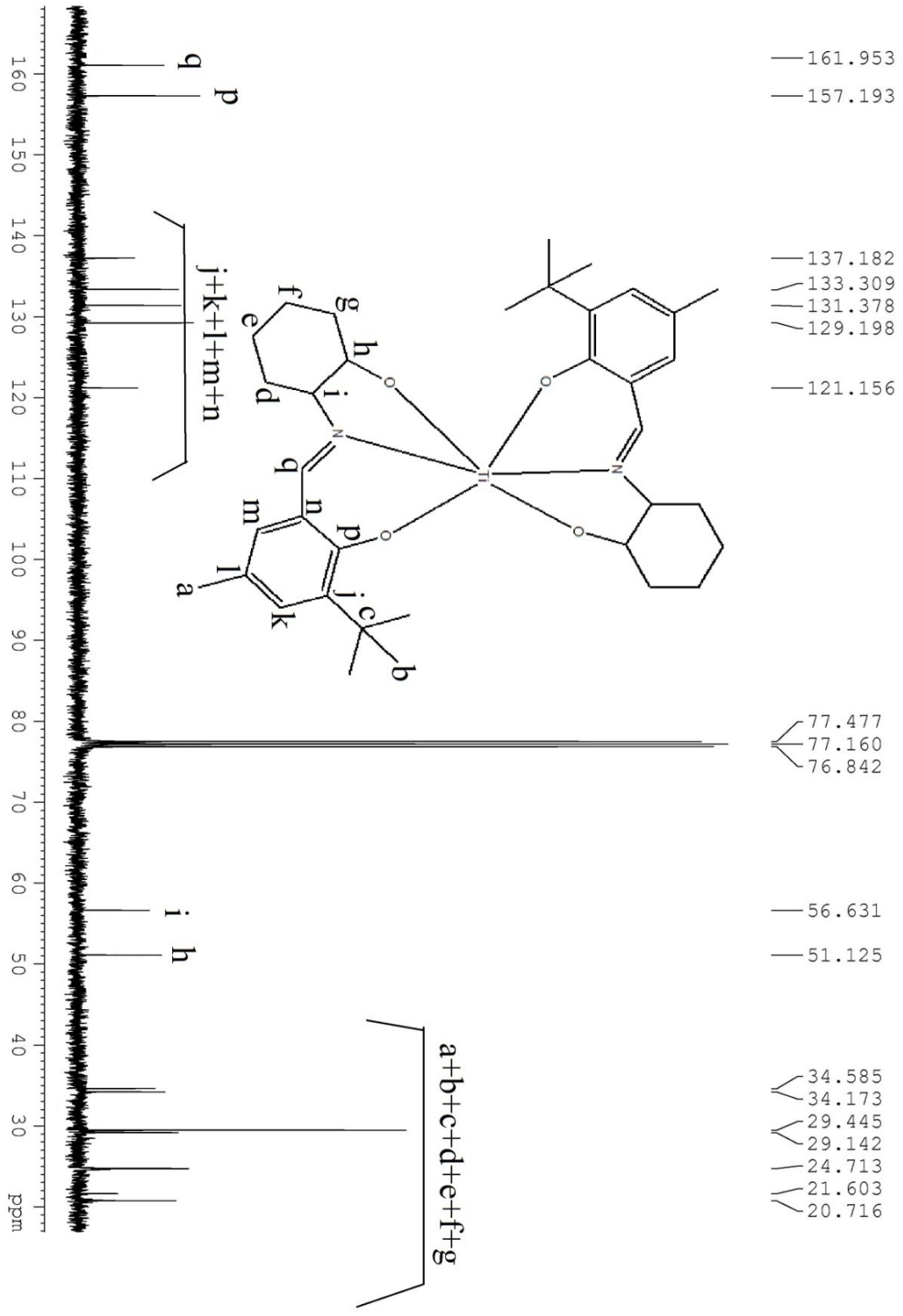


Fig. S2 ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **1**

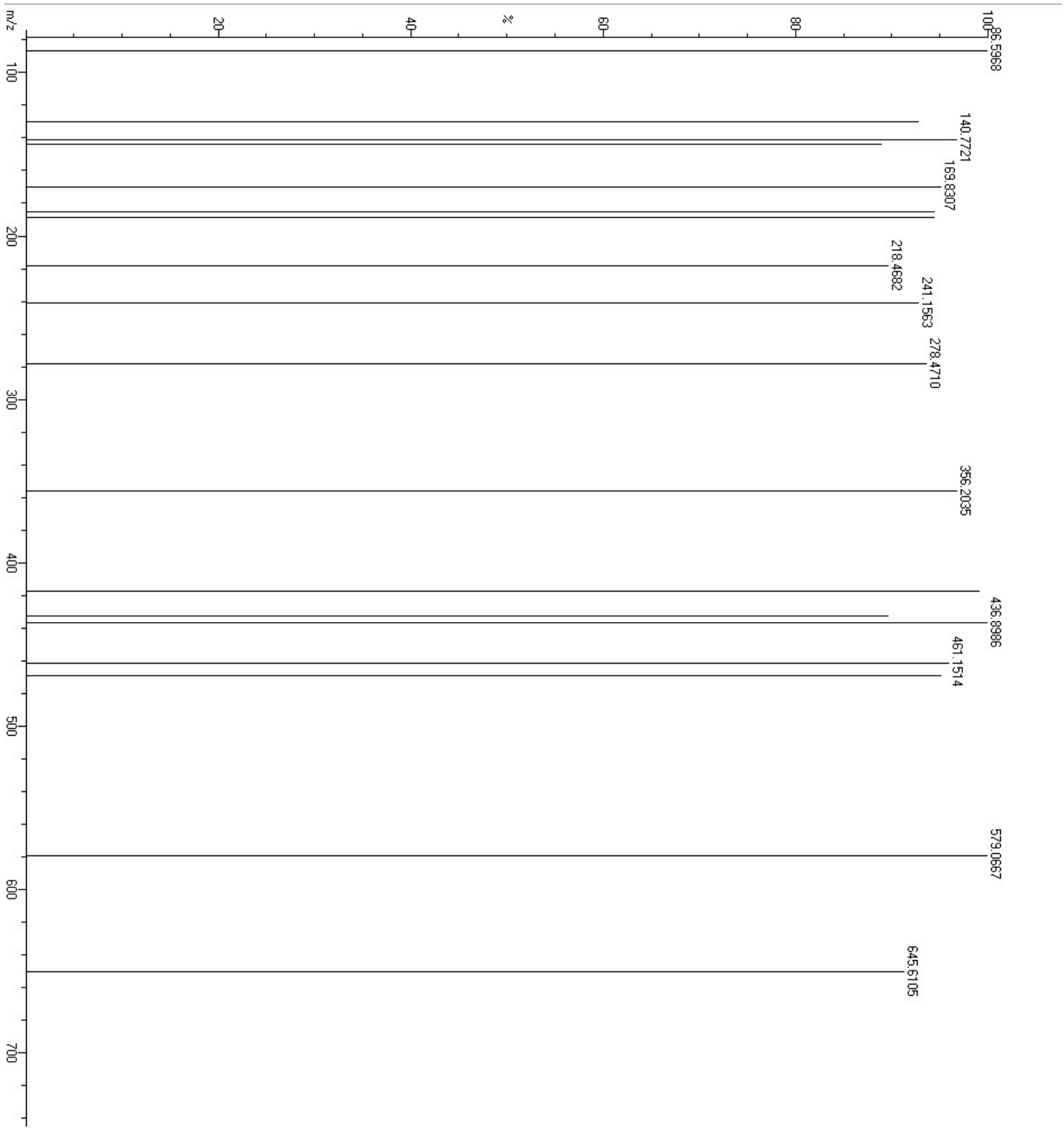


Fig. S3 ESI-Mass Spectrum of Compound **1**

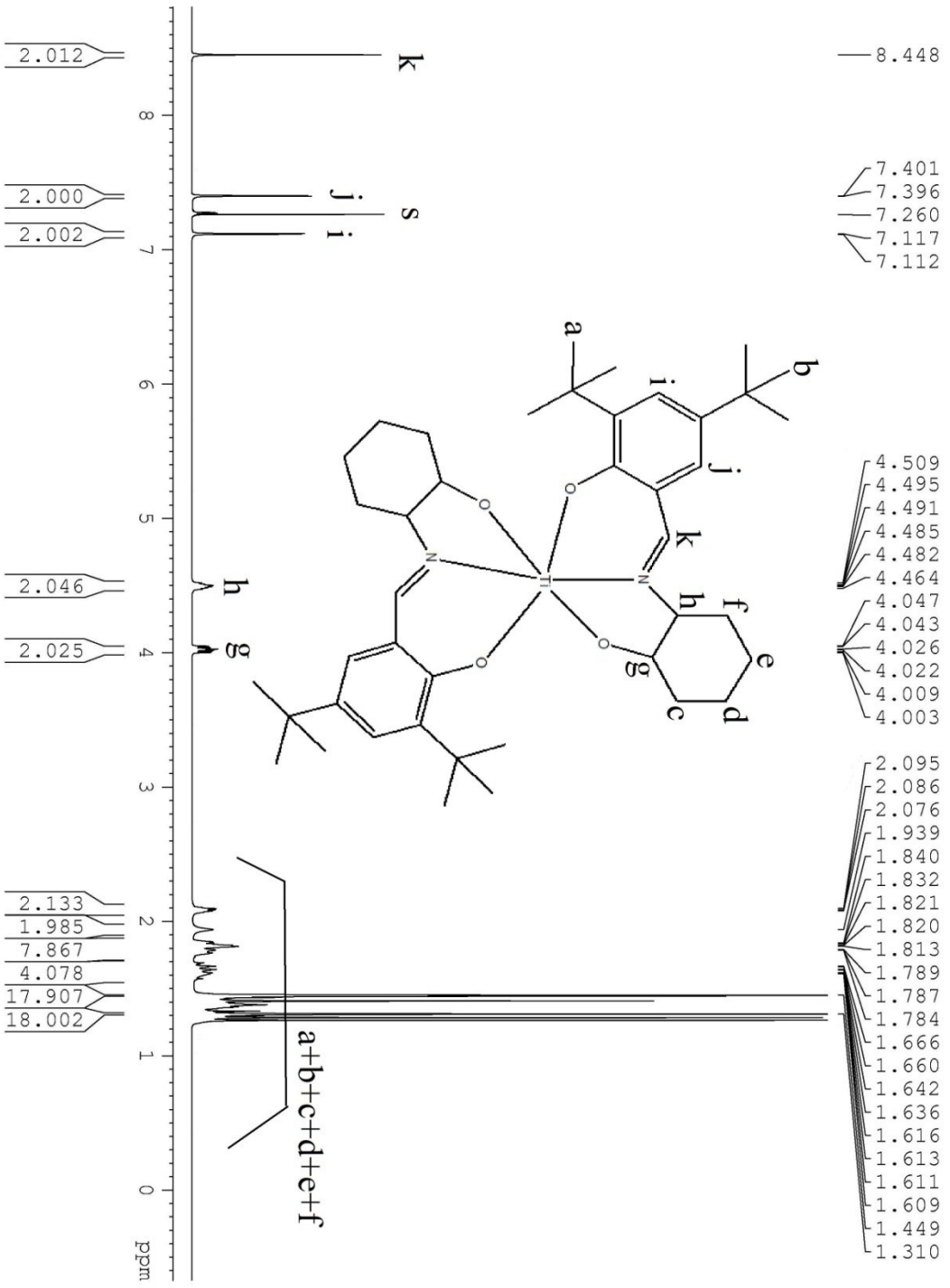


Fig. S4 ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **2**

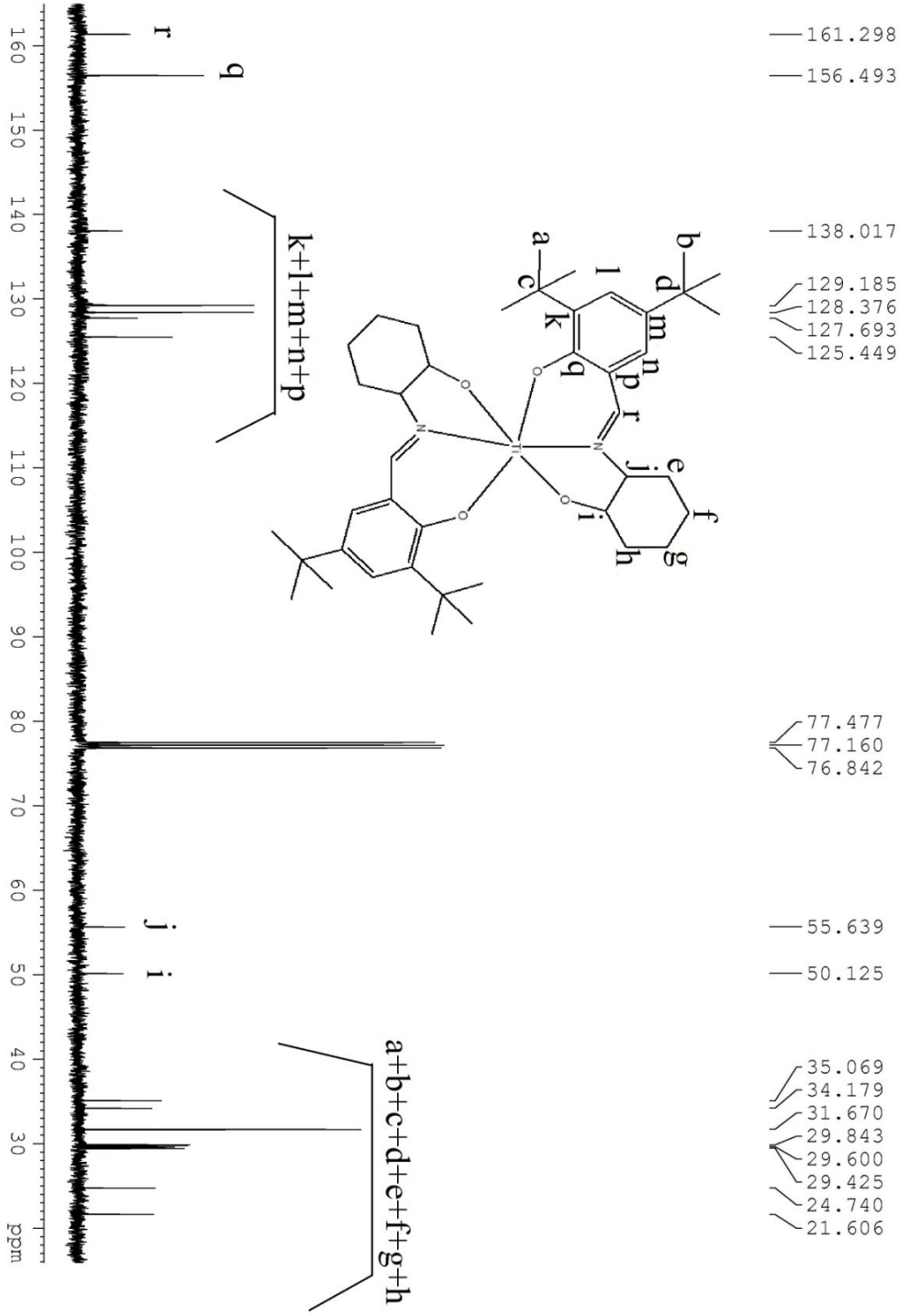


Fig. S5 ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **2**

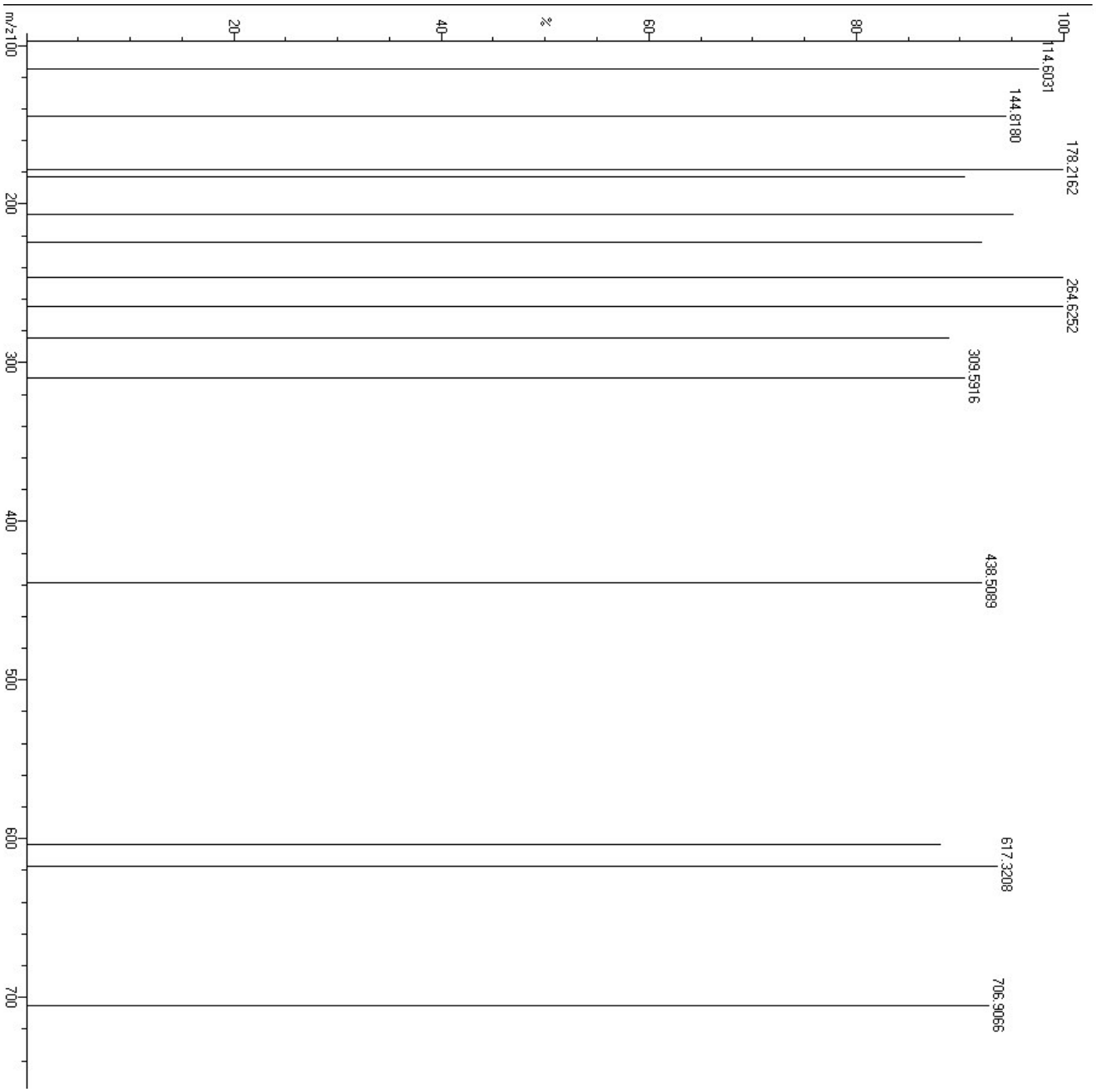


Fig. S6 ESI-Mass Spectrum of Compound **2**

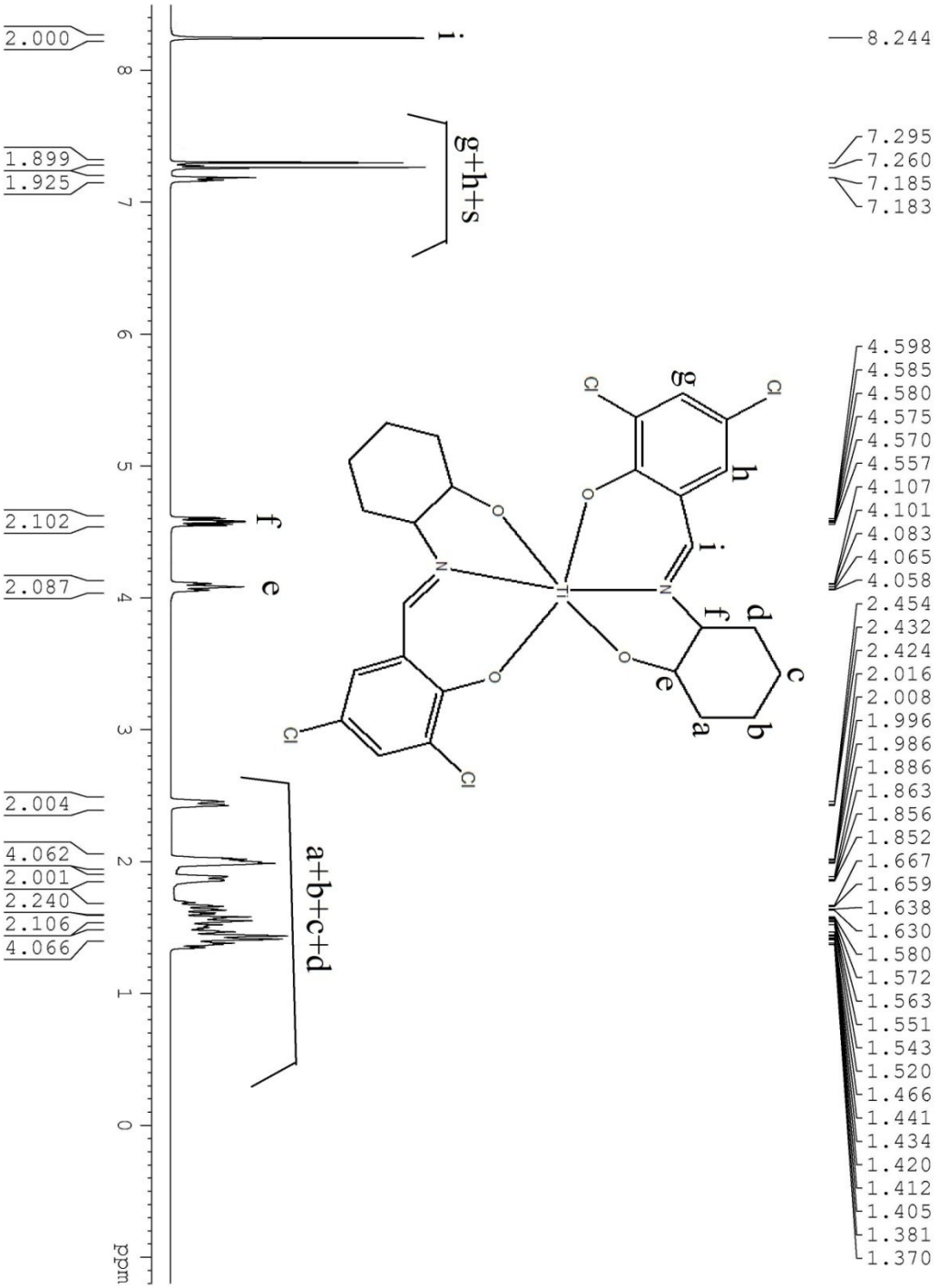


Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3**

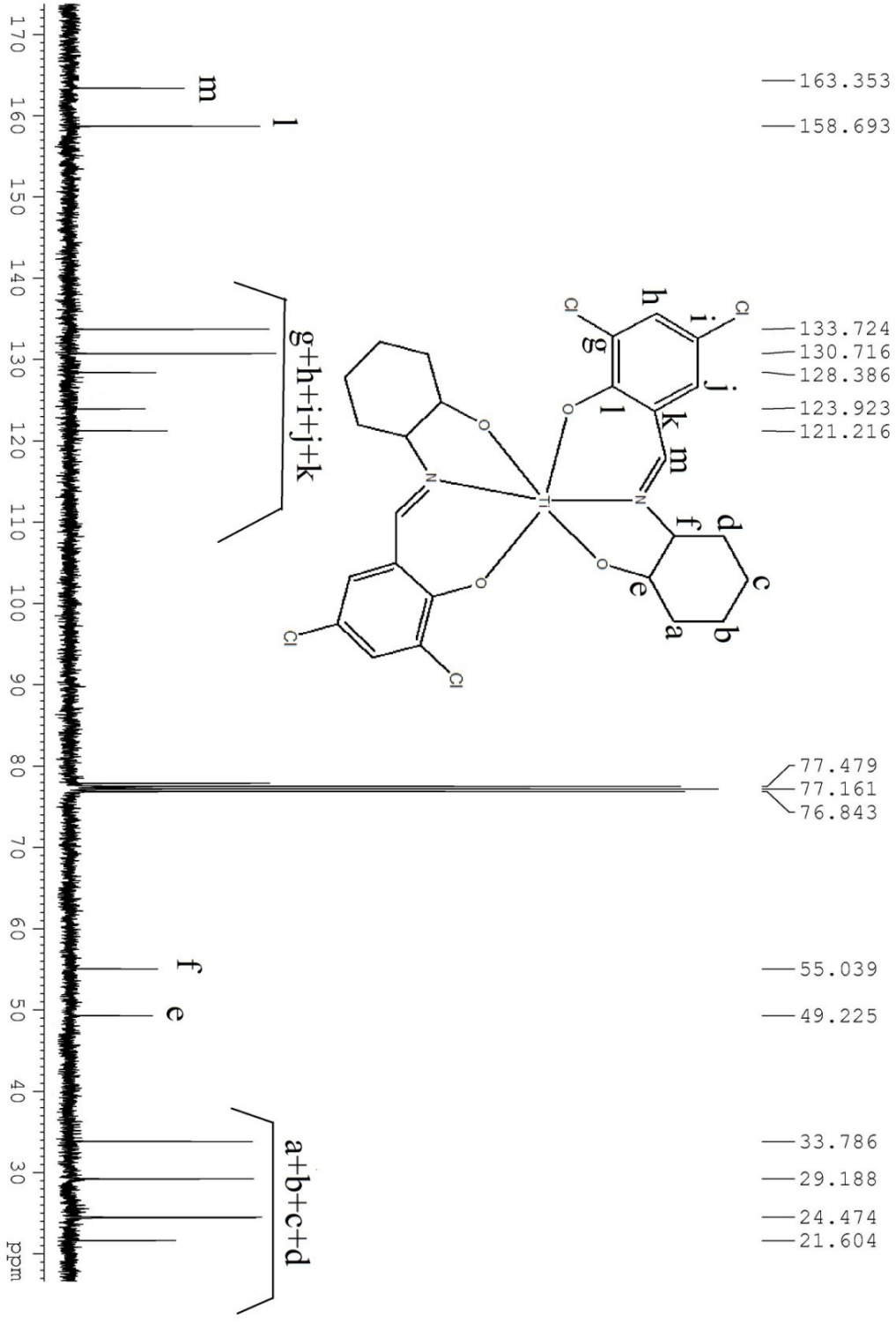


Fig. S8 ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3**

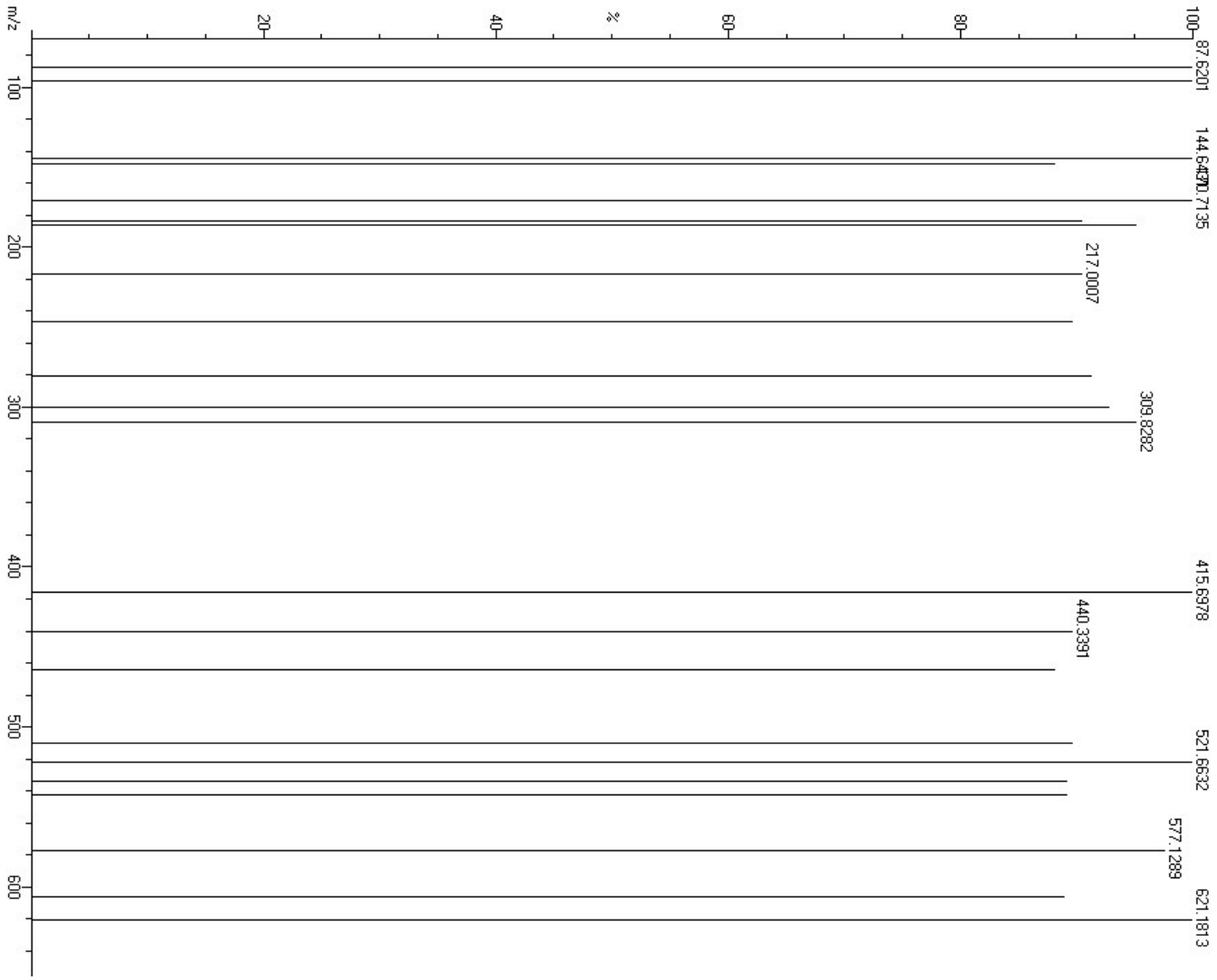


Fig. S9 ESI-Mass Spectrum of Compound **3**

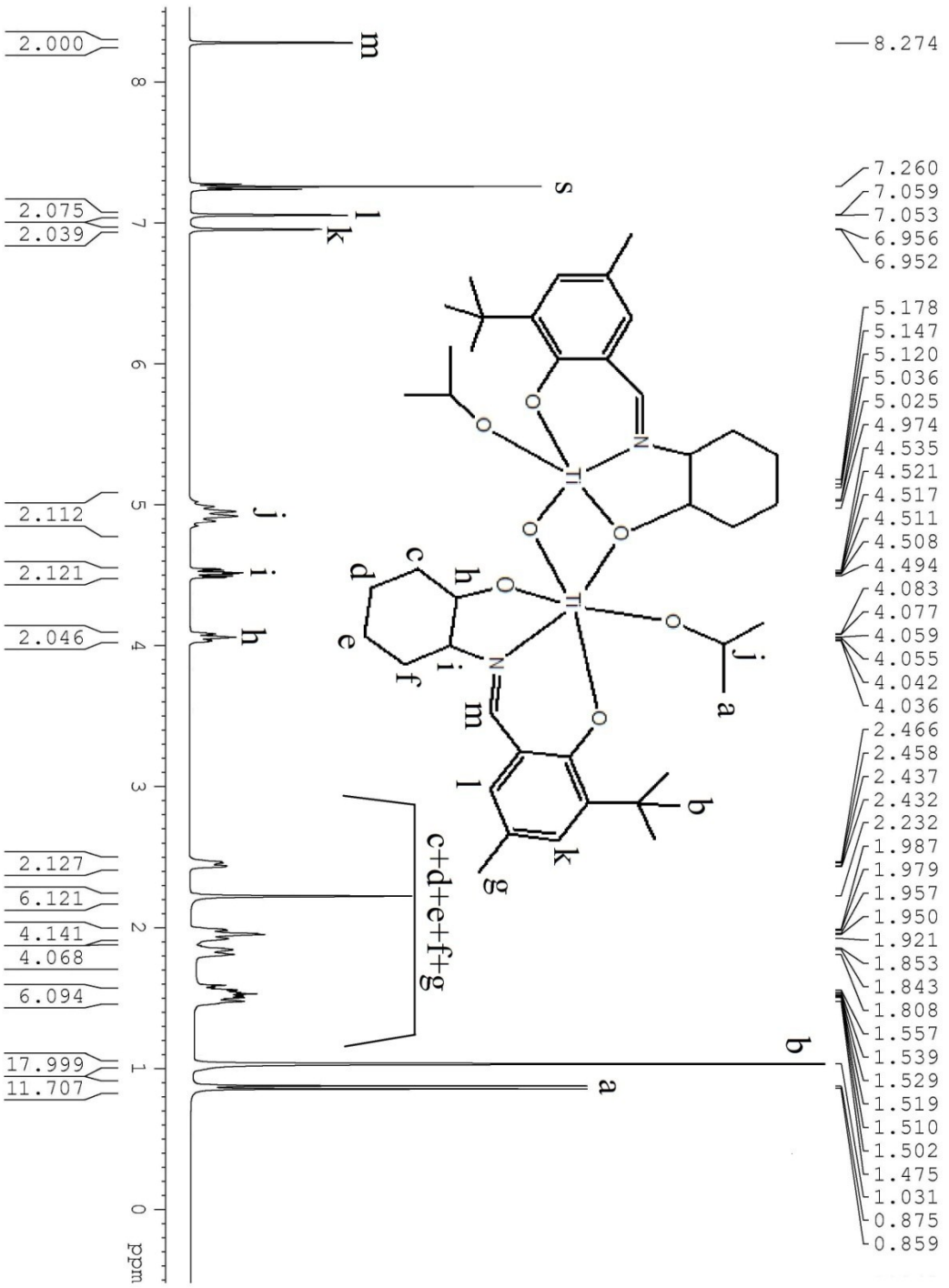


Fig. S10 ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **4**

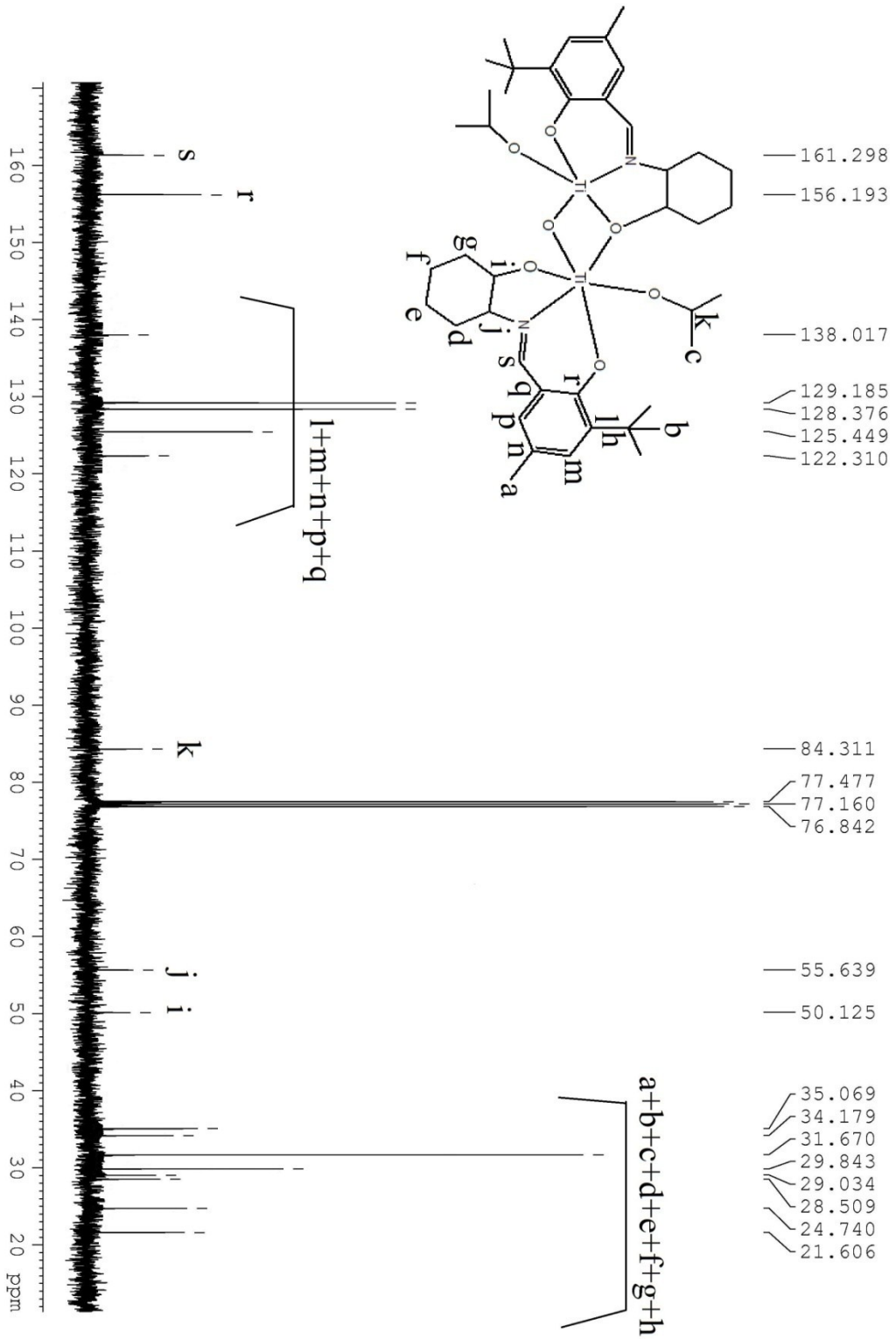


Fig. S11 ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **4**

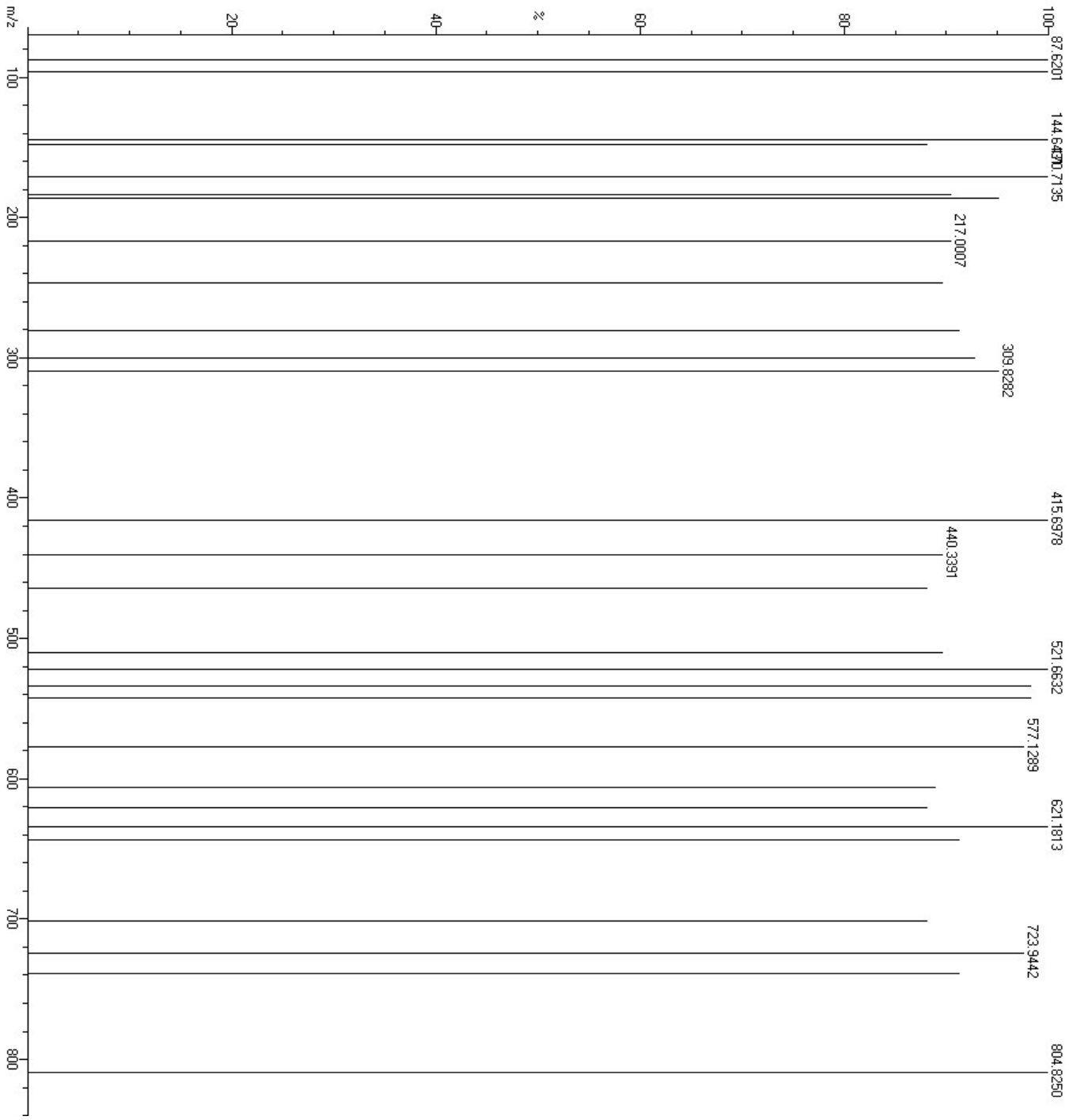


Fig. S12 ESI-Mass Spectrum of Compound **4**

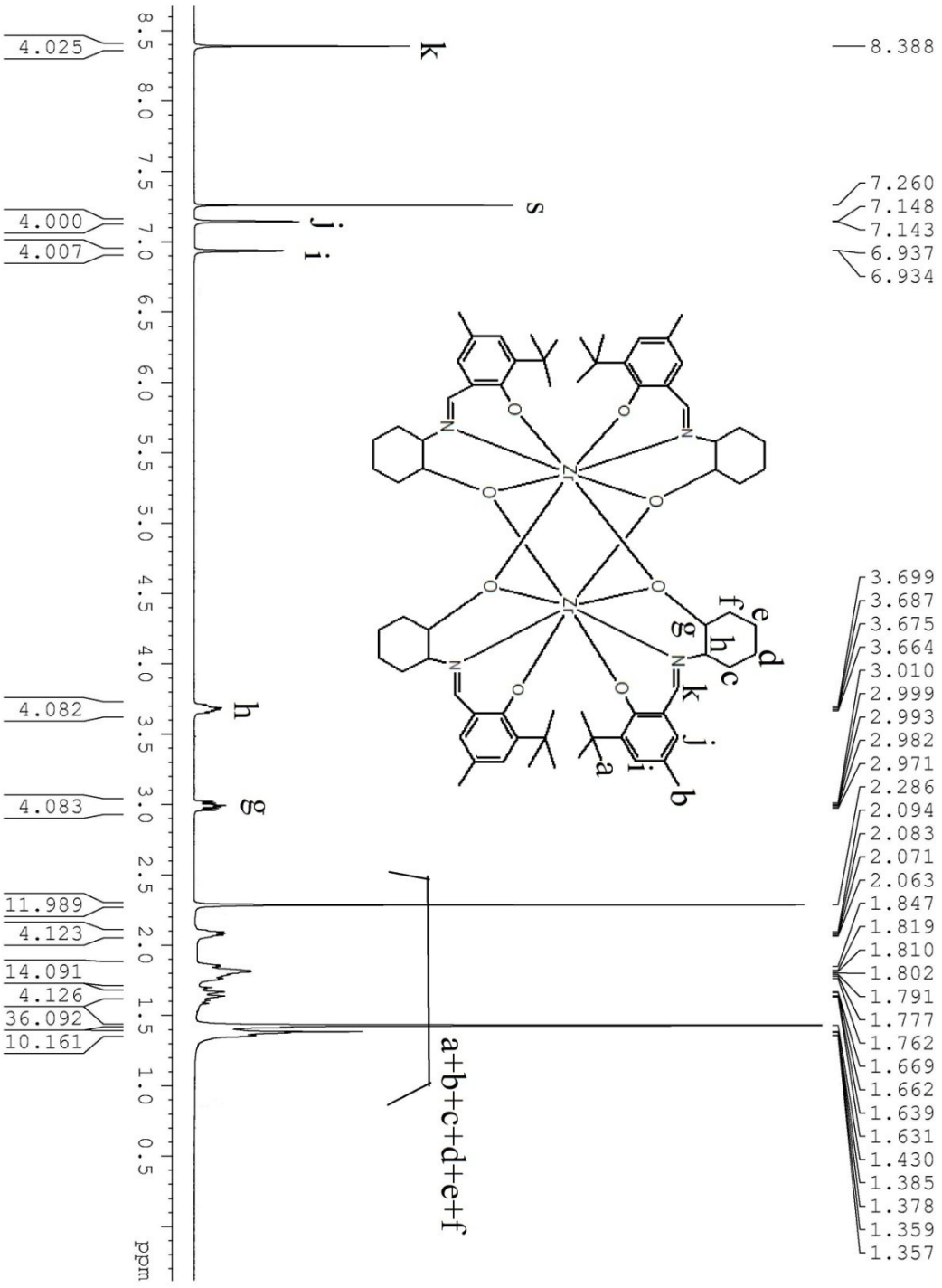


Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **5**

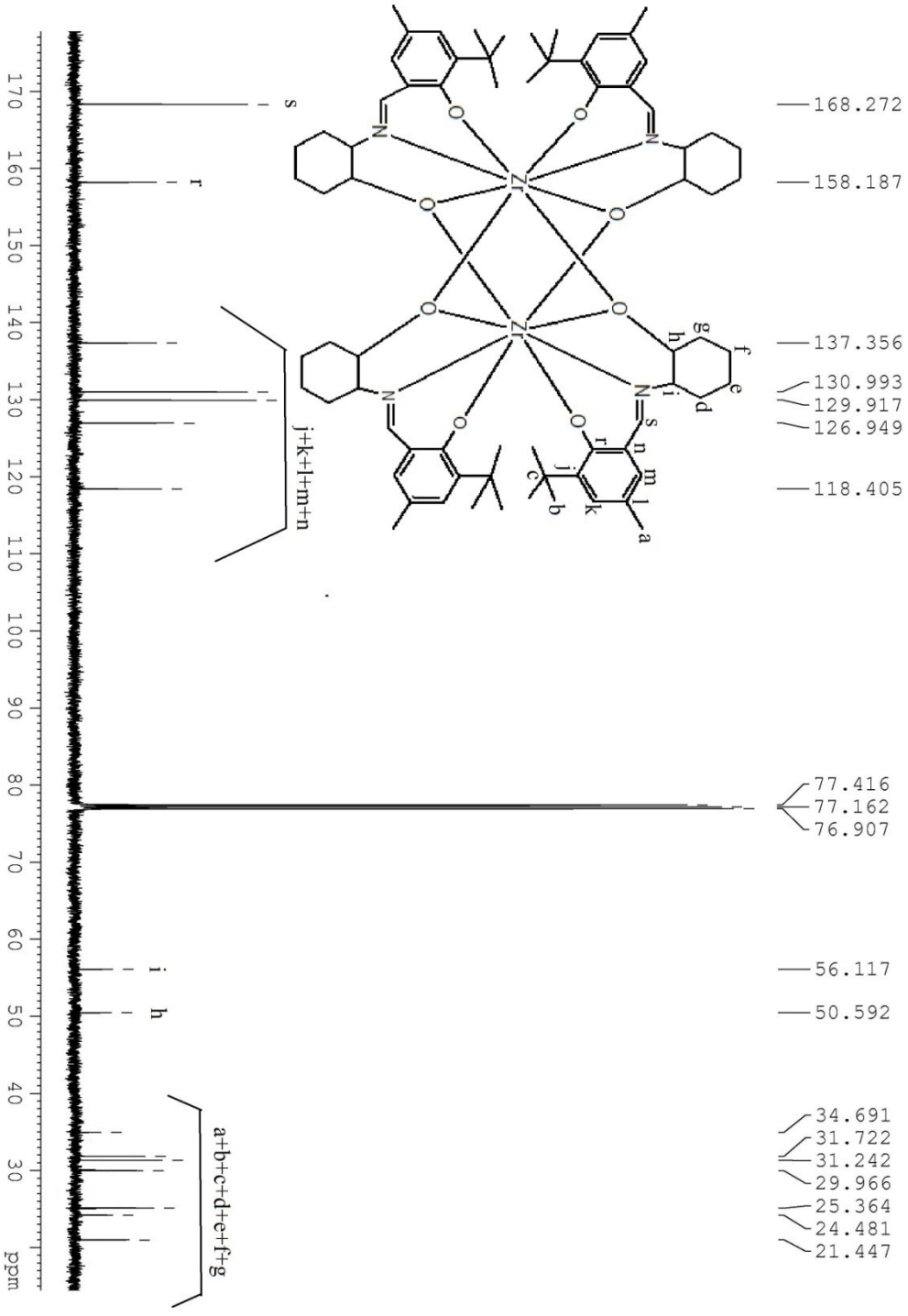


Fig. S14 ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **5**

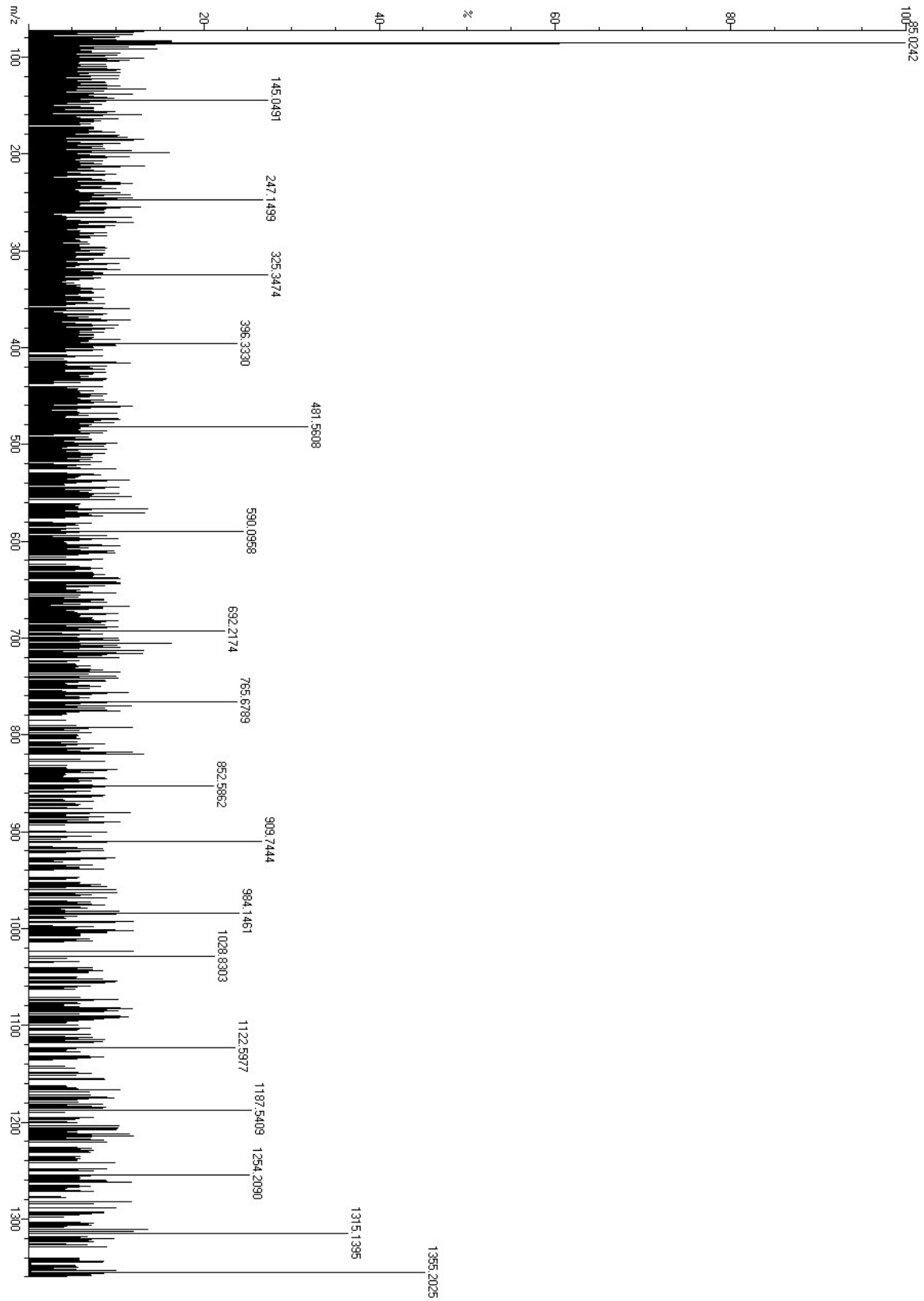


Fig. S15 ESI-Mass Spectrum of Compound **5**

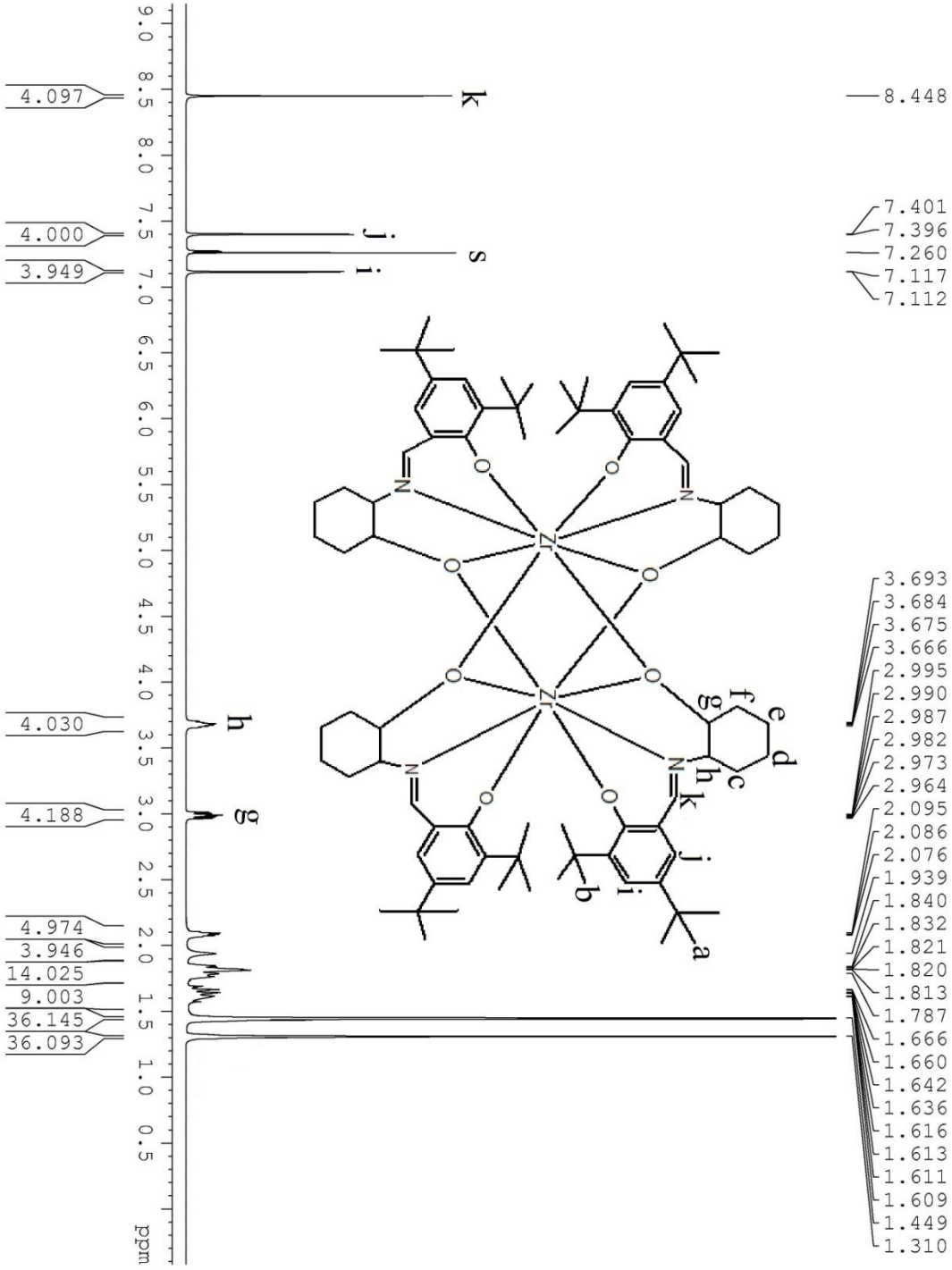


Fig. S16 ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **6**

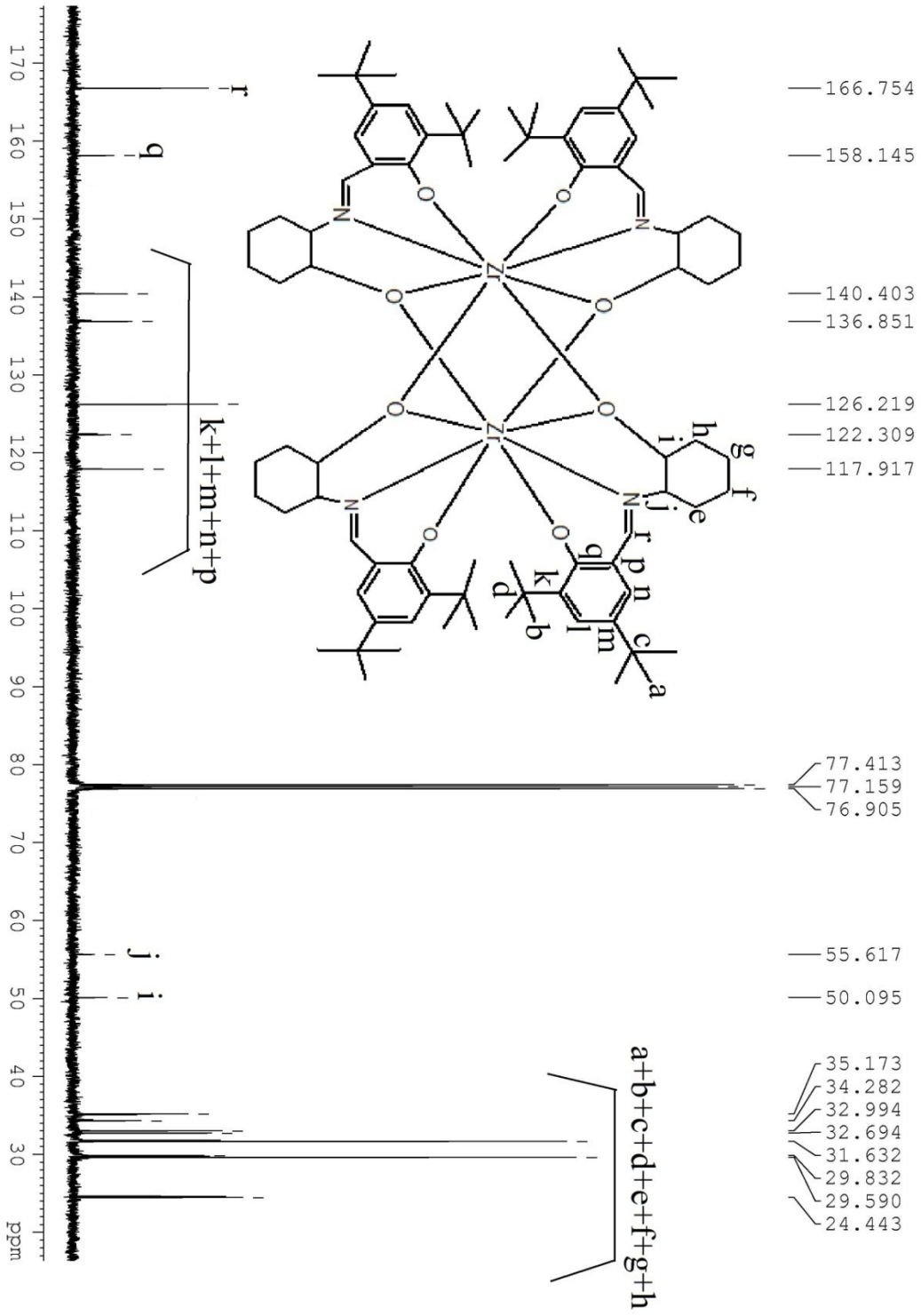


Fig. S17 ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **6**

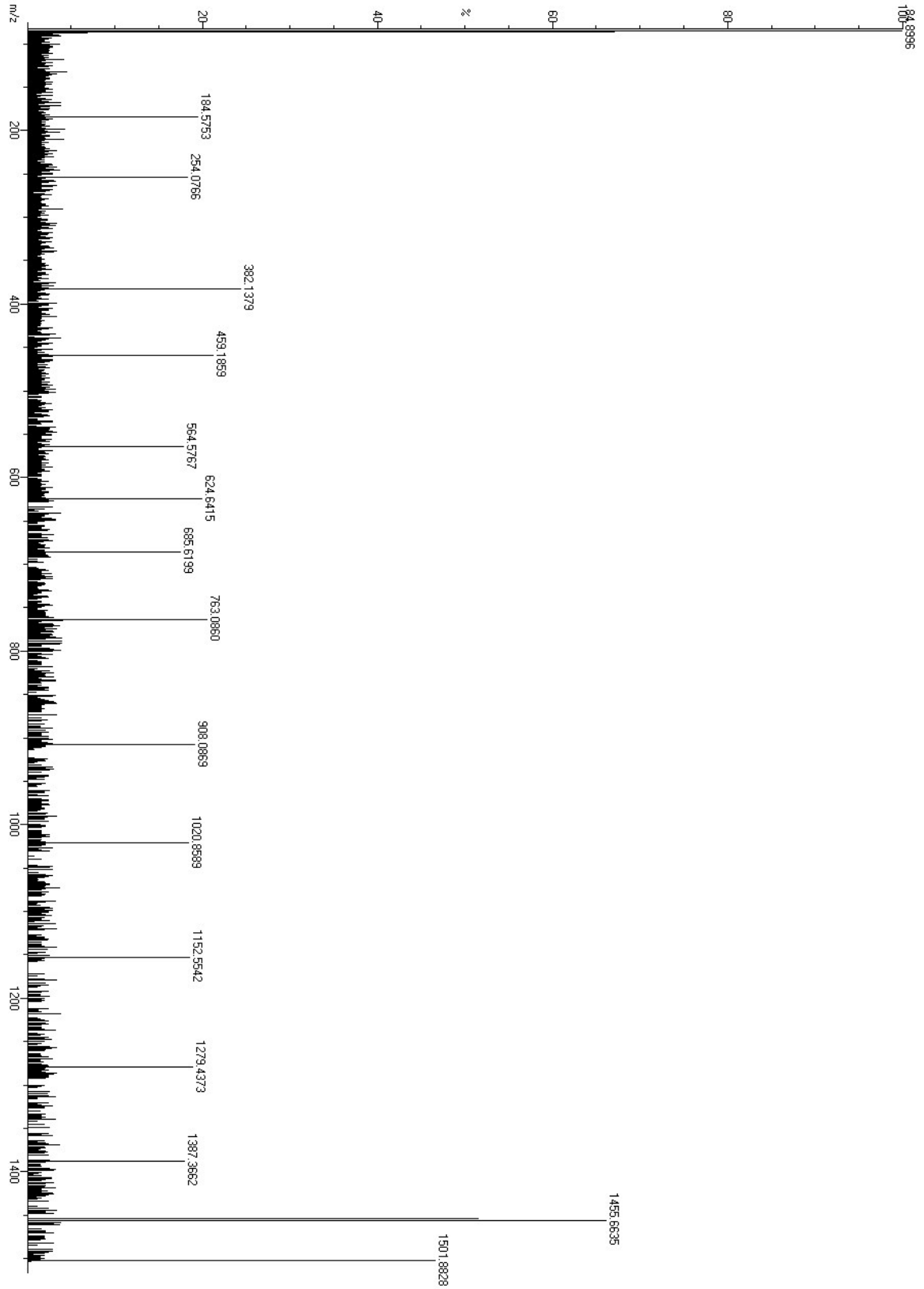


Fig. S18 ESI-Mass Spectrum of Compound **6**

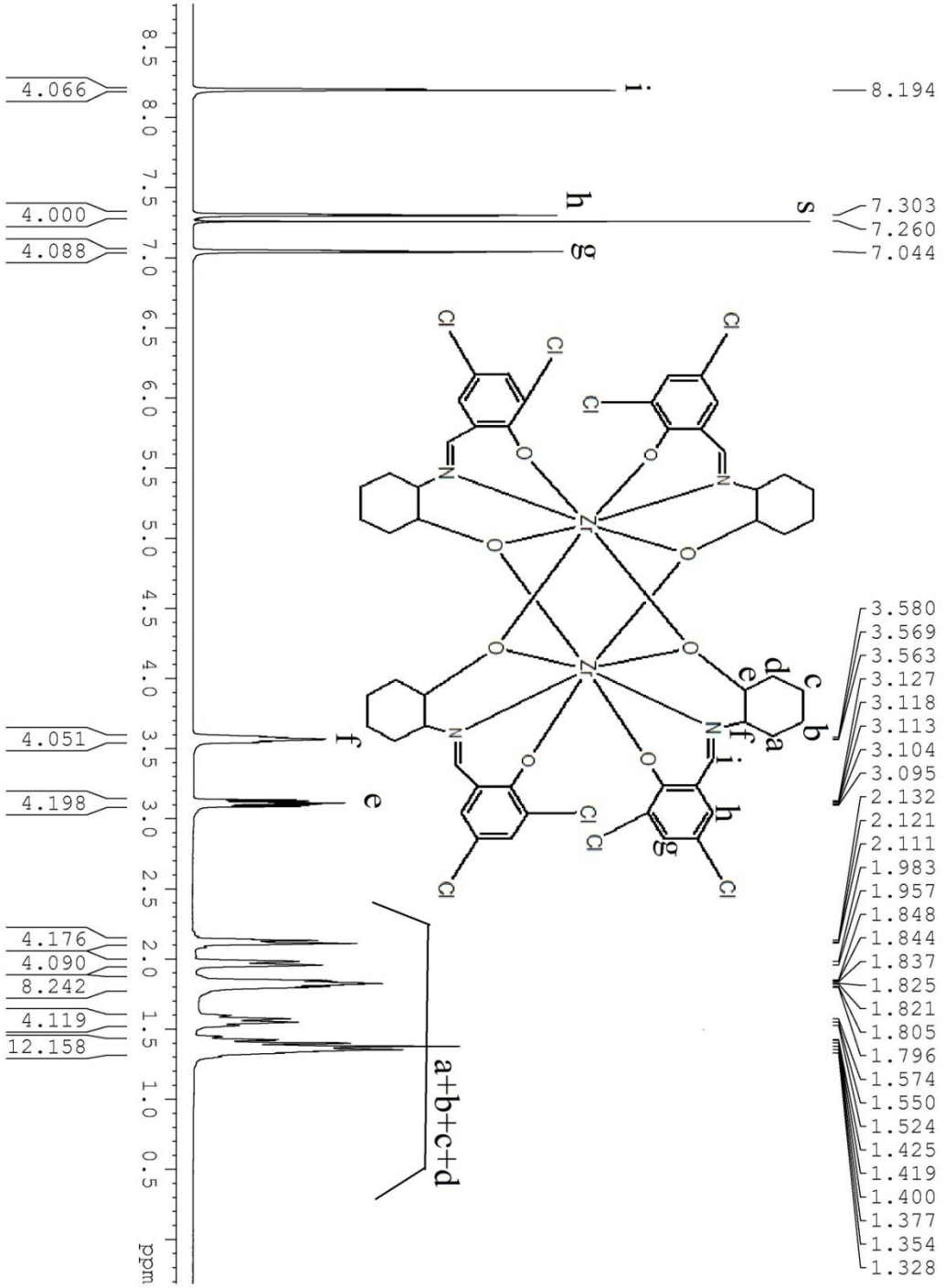


Fig. S19 ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **7**

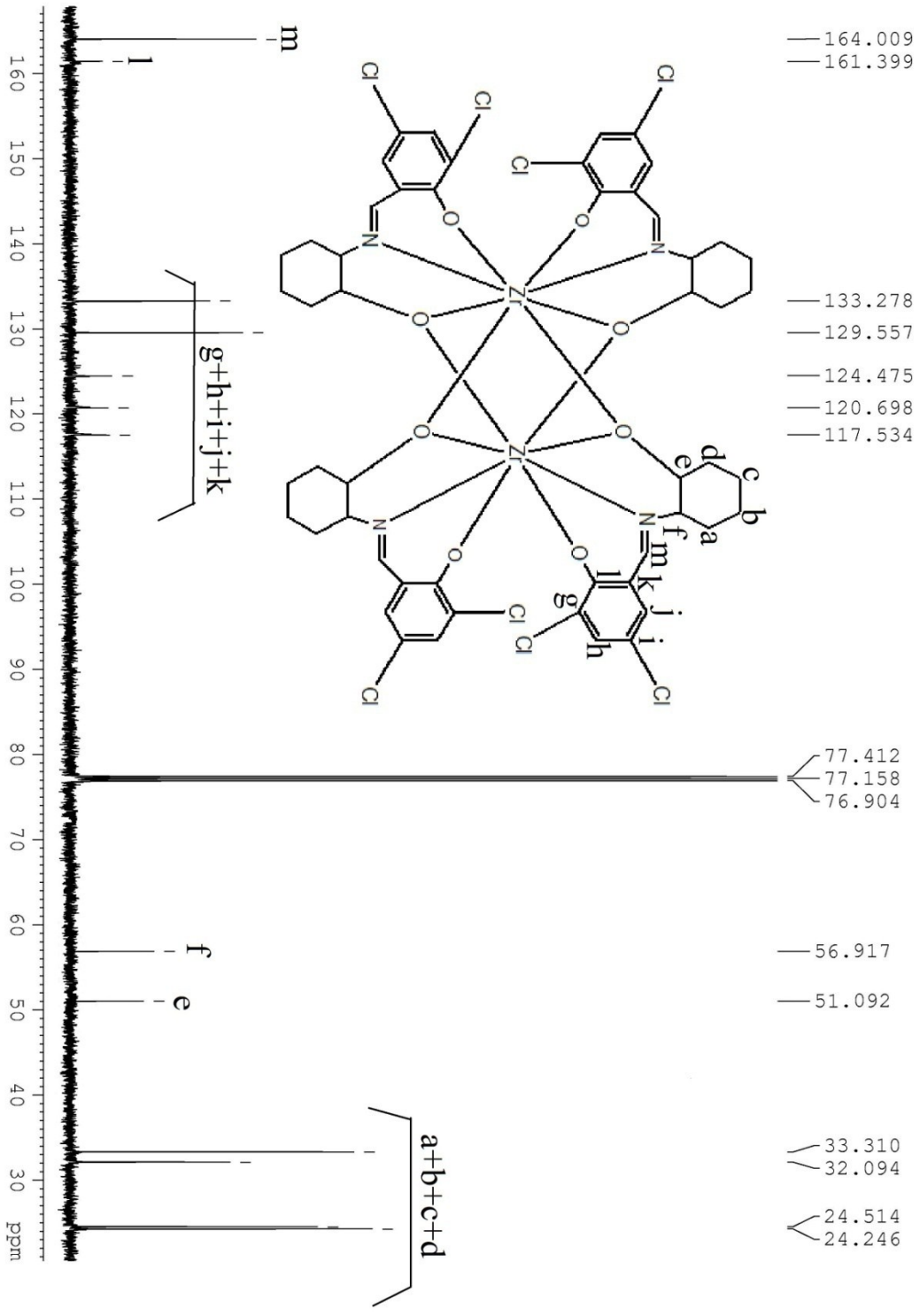


Fig. S20 ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **7**

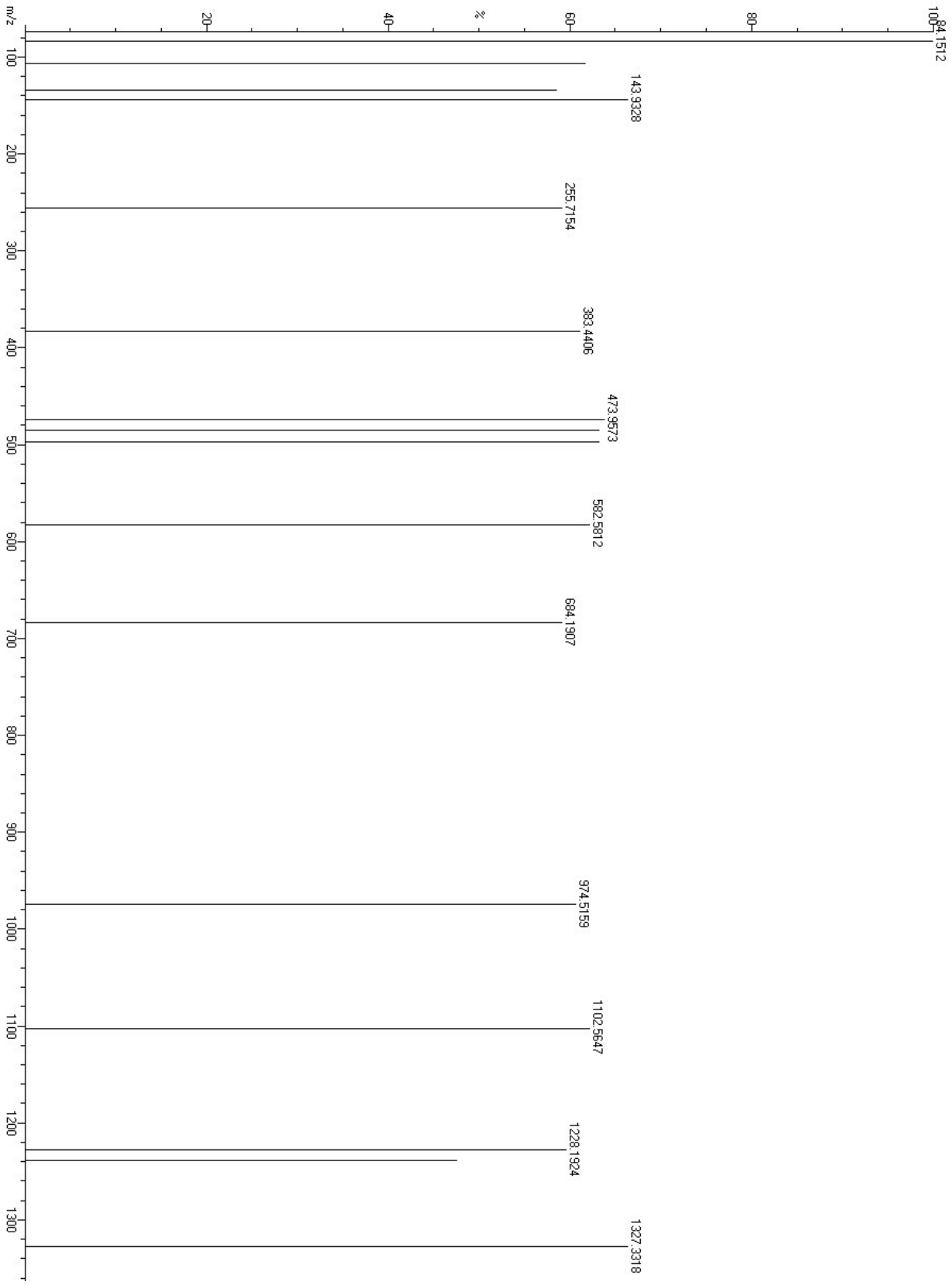


Fig. S21 ESI-Mass Spectrum of Compound **7**

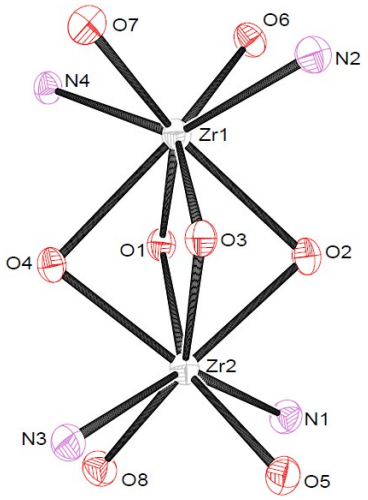


Fig. S22 Central part of the molecular structure of **5**.

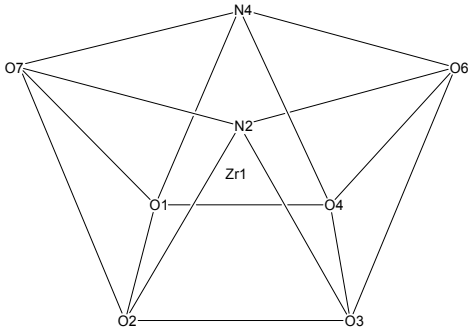
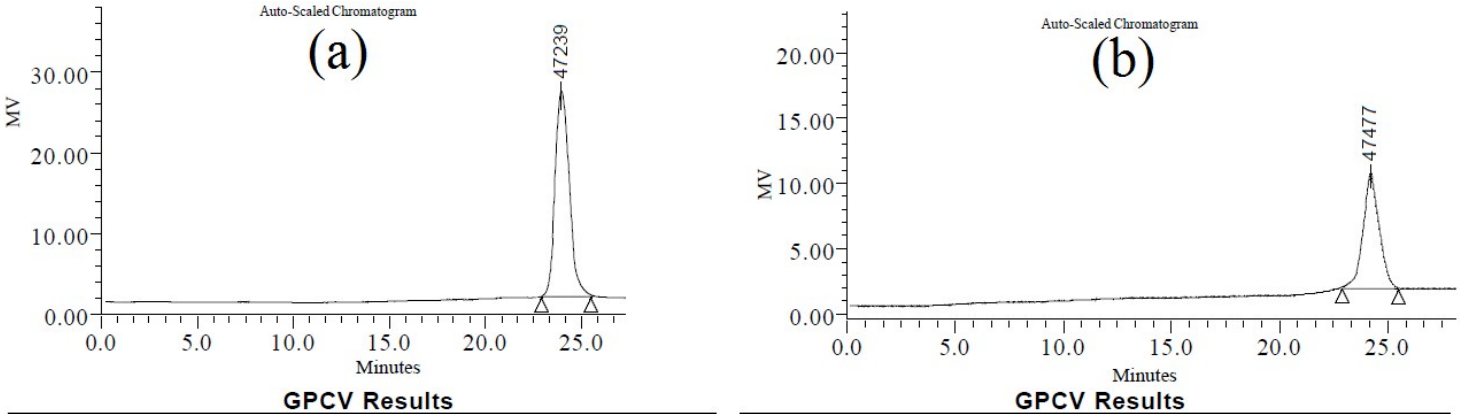


Fig. S23 Coordination polyhedron of a distorted square antiprism geometry.



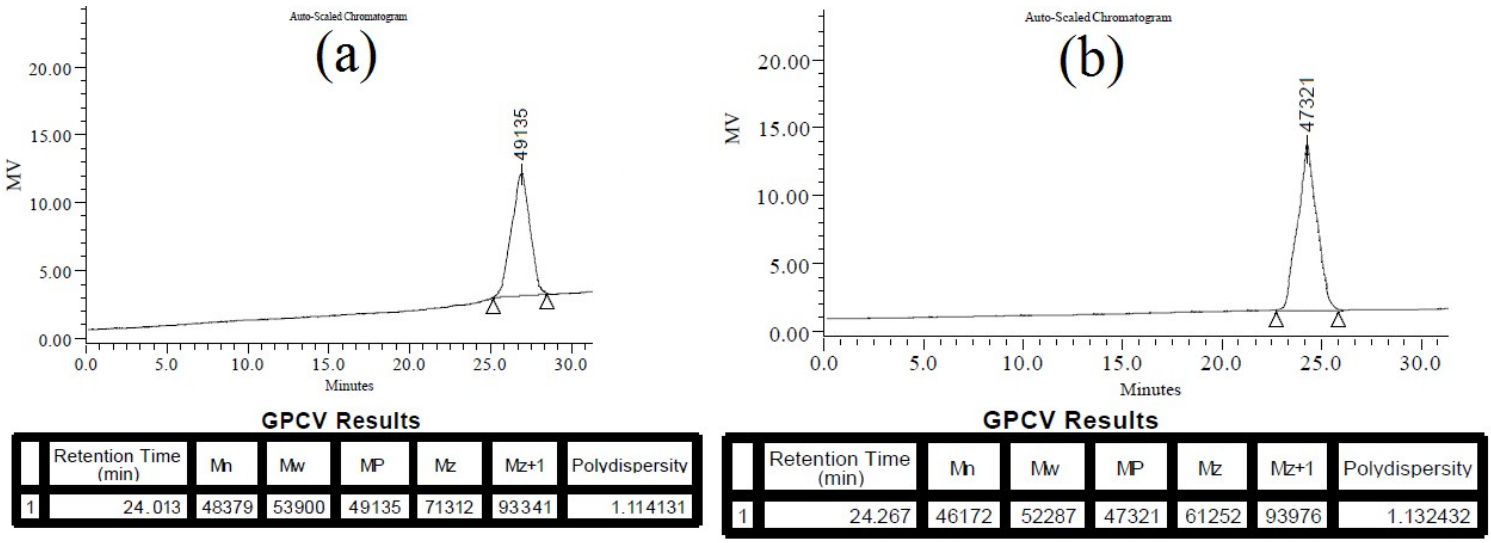
GPCV Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	23.881	49810	54944	47239	70979	92813	1.103087

GPCV Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	24.202	46621	52776	47477	77515	97007	1.132021

Fig. S24 Representative GPC traces for the polymerization of *rac*-LA: (a) entry 6, Table 1; (b) entry 1, Table 1.



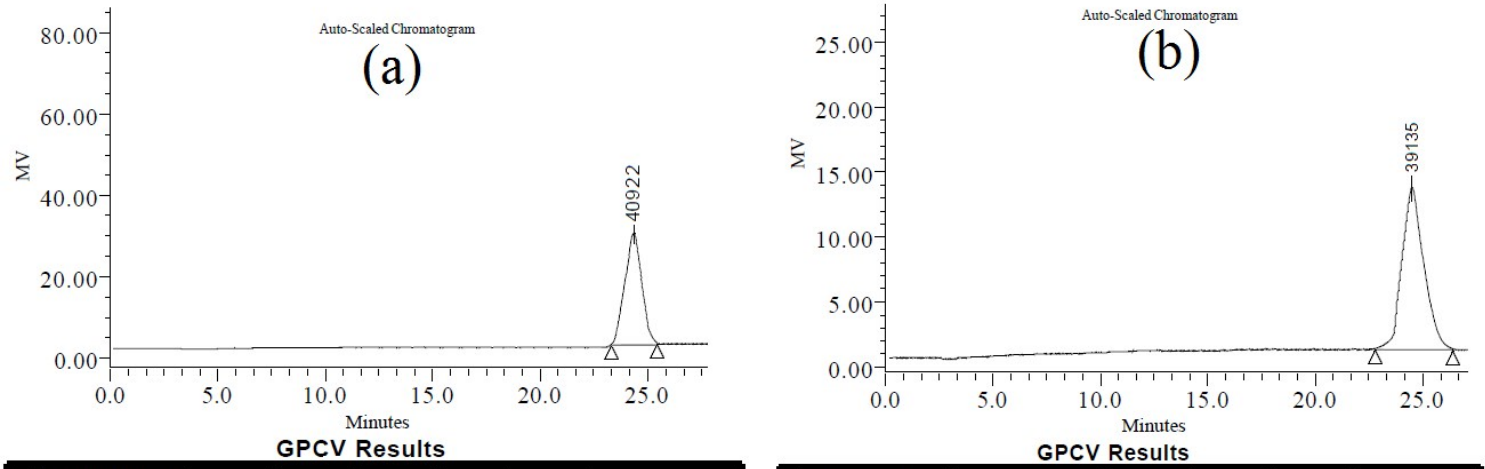
GPCV Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	24.013	48379	53900	49135	71312	93341	1.114131

GPCV Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	24.267	46172	52287	47321	61252	93976	1.132432

Fig. S25 Representative GPC traces for the polymerization of *L*-LA: (a) entry 13, Table 1; (b) entry 10, Table 1.



GPCV Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	24.423	39678	44582	40922	62153	90679	1.123591

GPCV Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	24.513	38482	44413	39135	59312	73341	1.154131

Fig. S26 Representative GPC traces for the polymerization of ε-CL: (a) entry 20, Table 1; (b) entry 17, Table 1.

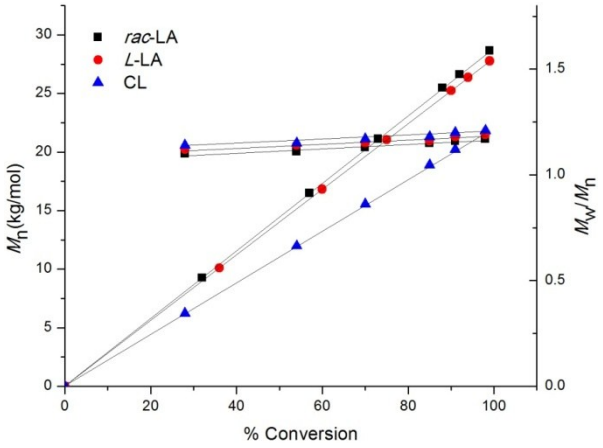


Fig. S27 Plot of M_n and M_w/M_n *vs.* % conversion for *L*-LA, *rac*-LA and *ε*-CL polymerization using **4** at 140 °C.

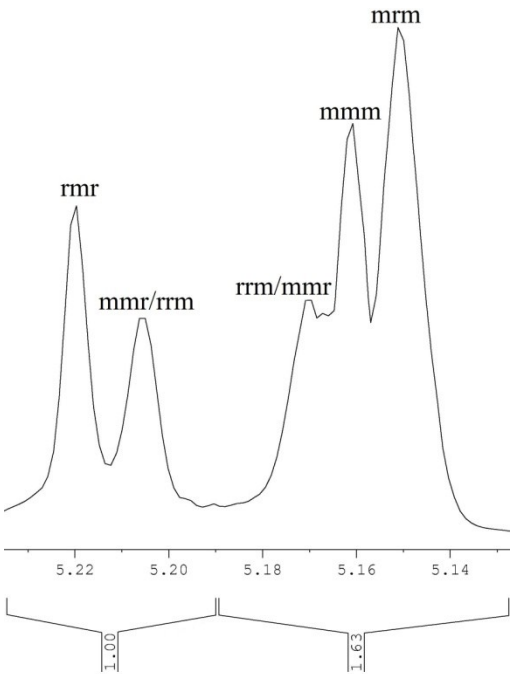


Fig. S28 Homonuclear decoupled ^{1}H NMR spectra of PLA from *rac*-LA using **4** in $CDCl_3$. $P_r = 2 \cdot I_1/(I_1+I_2)$, with I_1 = 5.19–5.23 ppm (*rmr*, *mmr*/*rrm*), I_2 = 5.13–5.19 ppm (*rrm*/*mmr*, *mmm*, *mrm*). $P_r = 2*1/(1+1.63) = 2/2.63 = 0.76$.

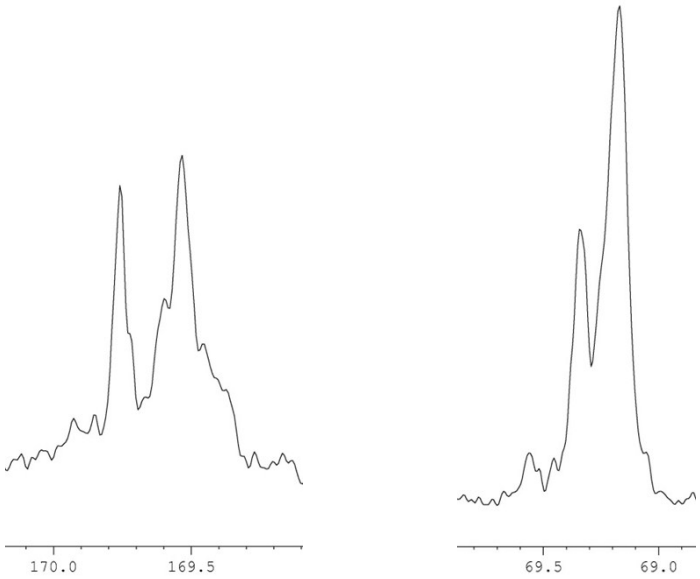


Fig. S29 ^{13}C NMR spectrum of heterotactic PLA synthesized using complex **4**, (1) carbonyl region (left), (2) methine region (right).

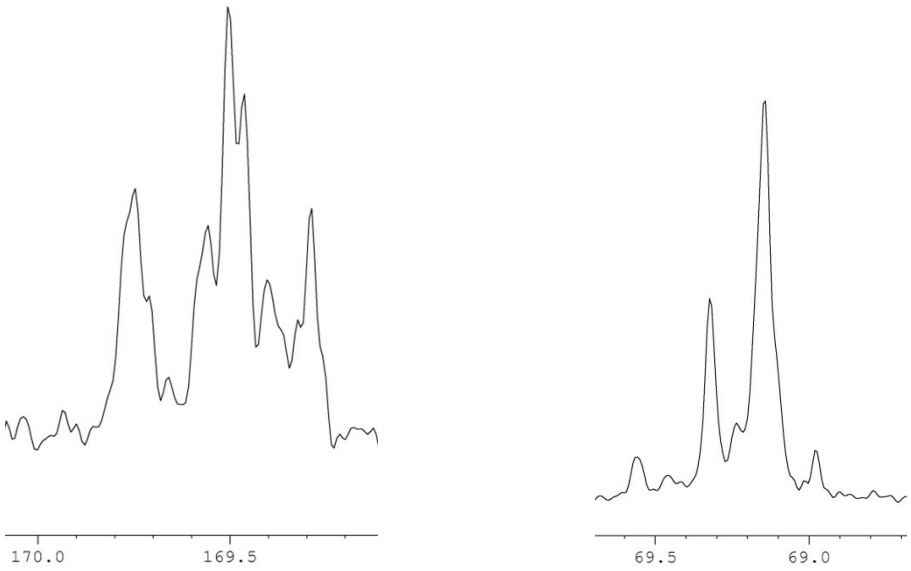


Fig. S30 ^{13}C NMR spectrum of heterotactic PLA synthesized using complex **1**, (1) carbonyl region (left), (2) methine region (right).

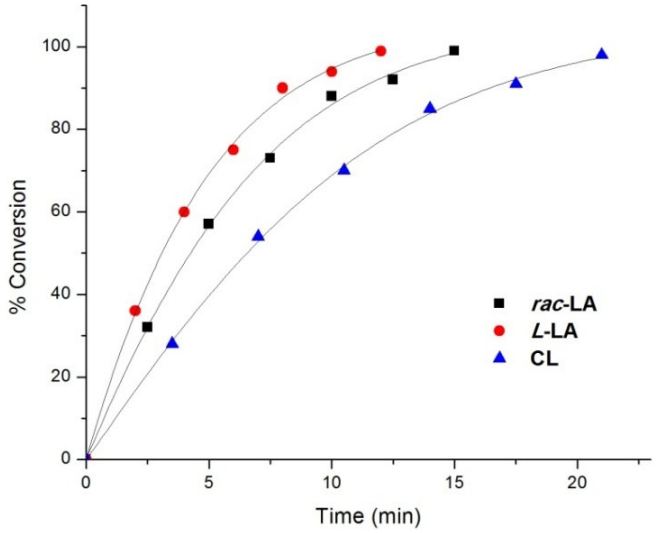


Fig. S31 Plot of % conversion *vs.* time for *L*-LA, *rac*-LA and ε-CL polymerization using **4** at 140 °C.

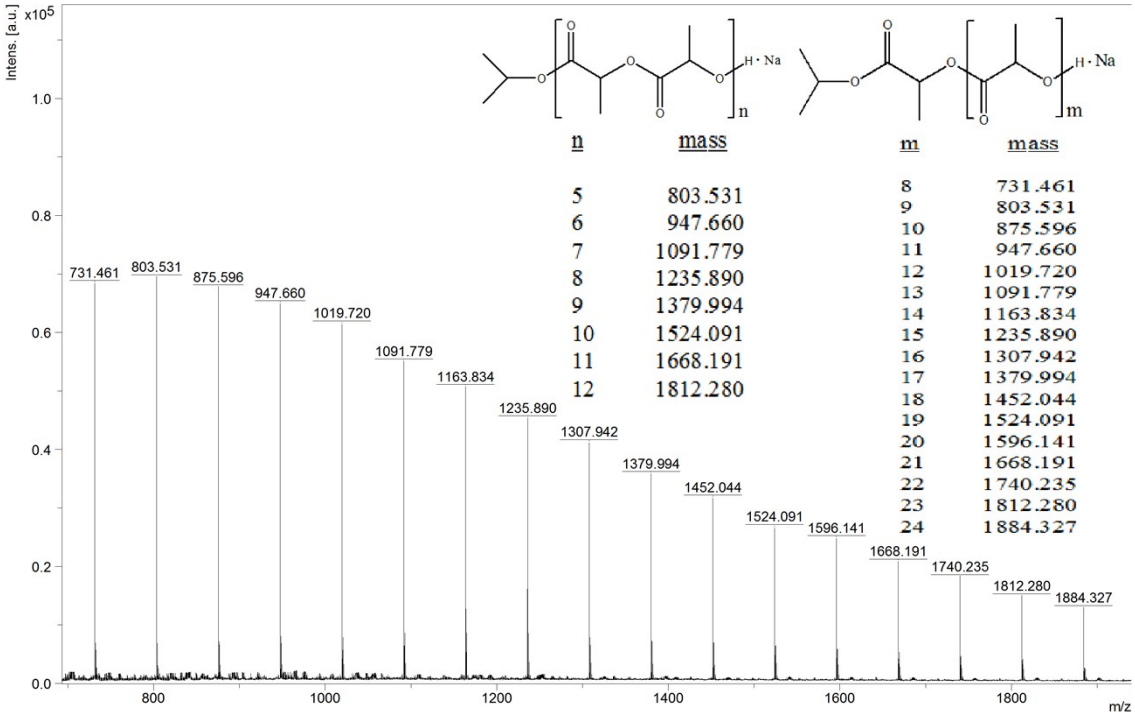


Fig. S32 MALDI-TOF of the crude product obtained from a reaction between *rac*-LA and **4** in 15: 1 ratio.

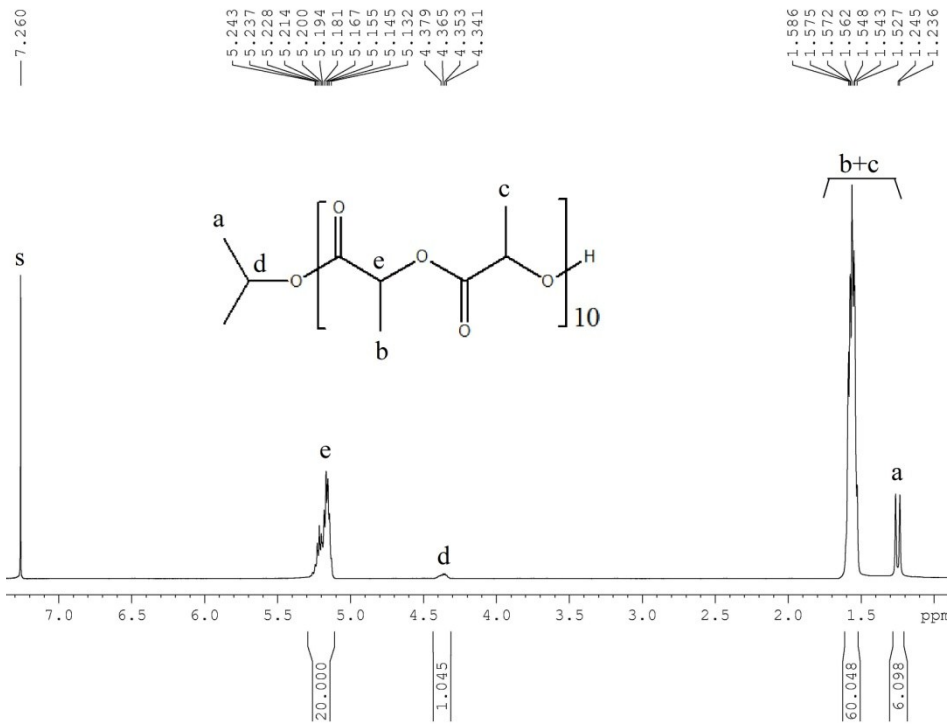
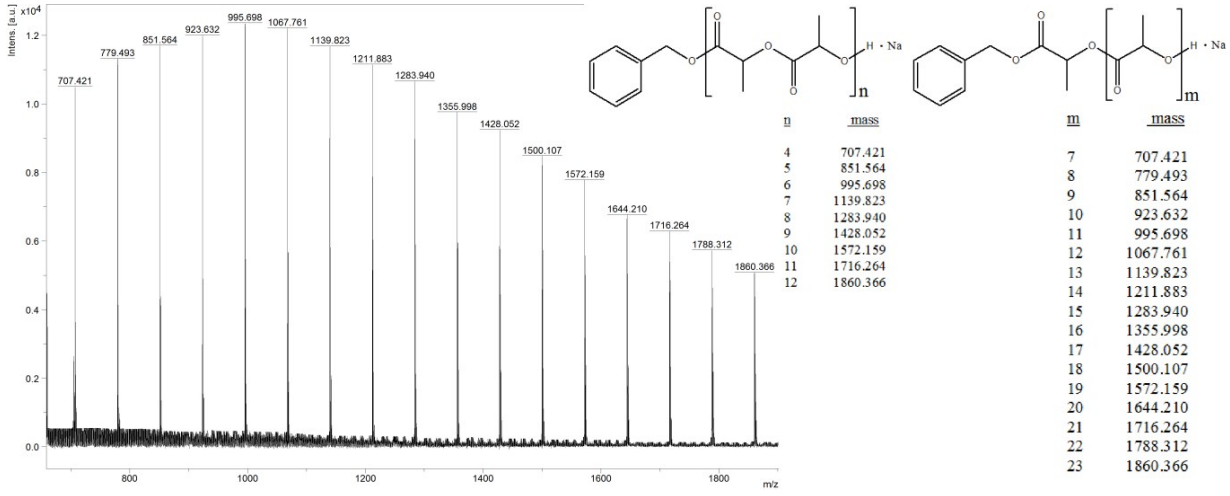


Fig. S33 ^{1}H NMR spectrum of the crude product obtained from a reaction between *rac*-LA and **4** in 10: 1 ratio.



n	mass
4	707.421
5	851.564
6	995.698
7	1139.823
8	1283.940
9	1428.052
10	1572.159
11	1716.264
12	1860.366

m	mass
7	707.421
8	779.493
9	851.564
10	923.632
11	995.698
12	1067.761
13	1139.823
14	1211.883
15	1283.940
16	1355.998
17	1428.052
18	1500.107
19	1572.159
20	1644.210
21	1716.264
22	1788.312
23	1860.366

Fig. S34 MALDI-TOF of the crude product obtained from a reaction between *rac*-LA and **1** in the presence of BnOH in 15: 1: 2 ratio.

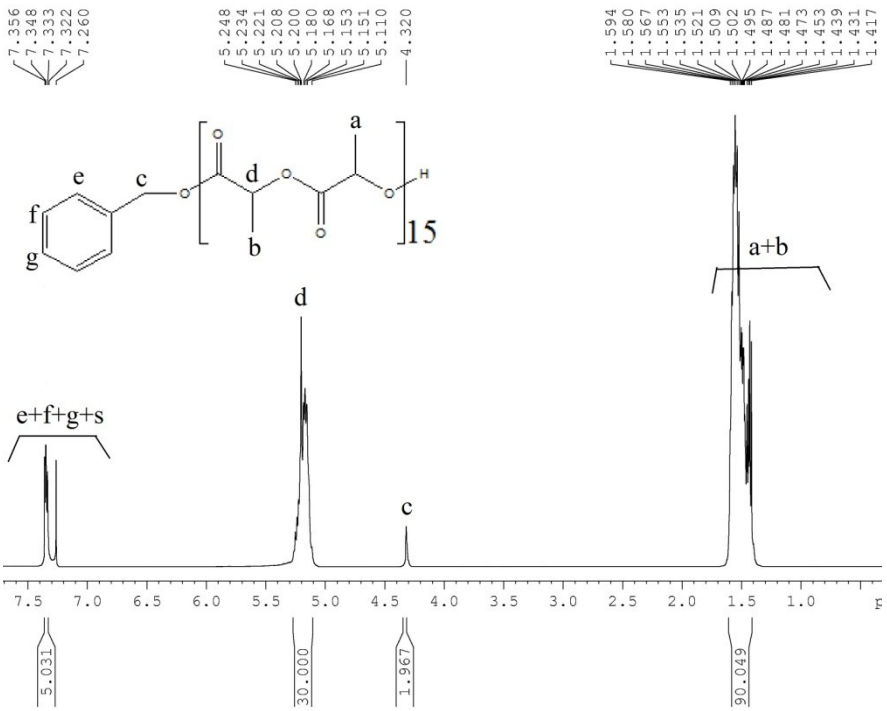


Fig. S35 ^{1}H NMR spectrum of the crude product obtained from a reaction between *rac*-LA and **1** in the presence of BnOH in 15: 1: 2 ratio.

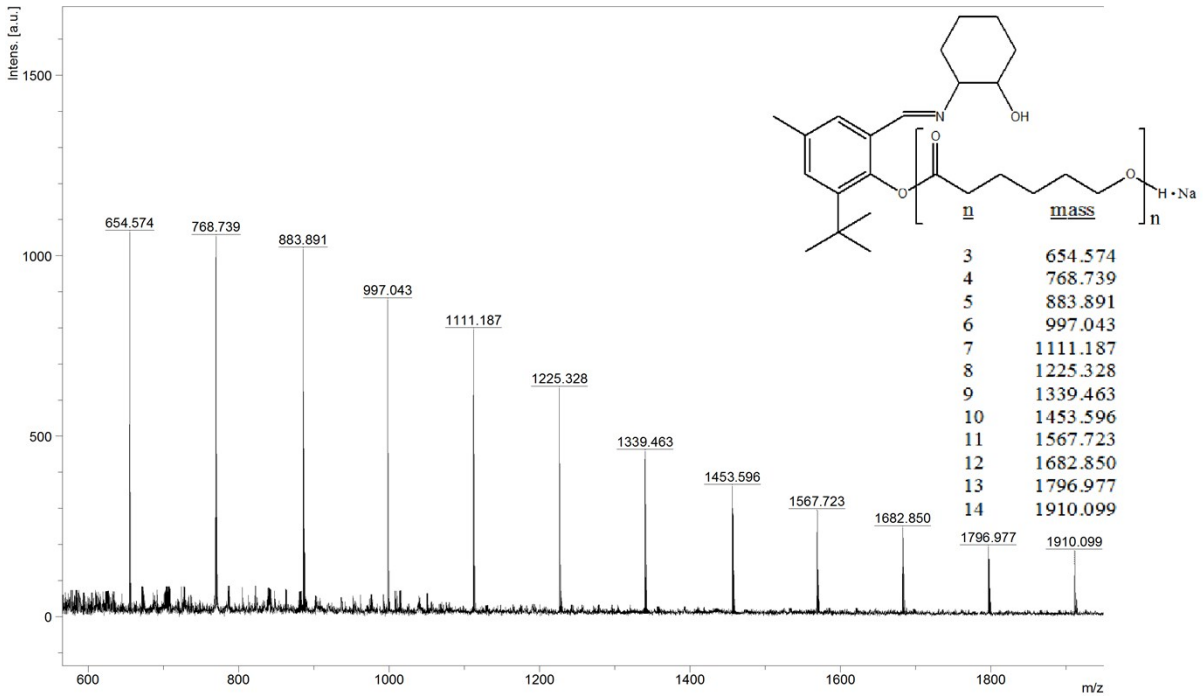


Fig. S36 MALDI-TOF of the crude product obtained from a reaction between ε-CL and **1** in 15: 1 ratio.

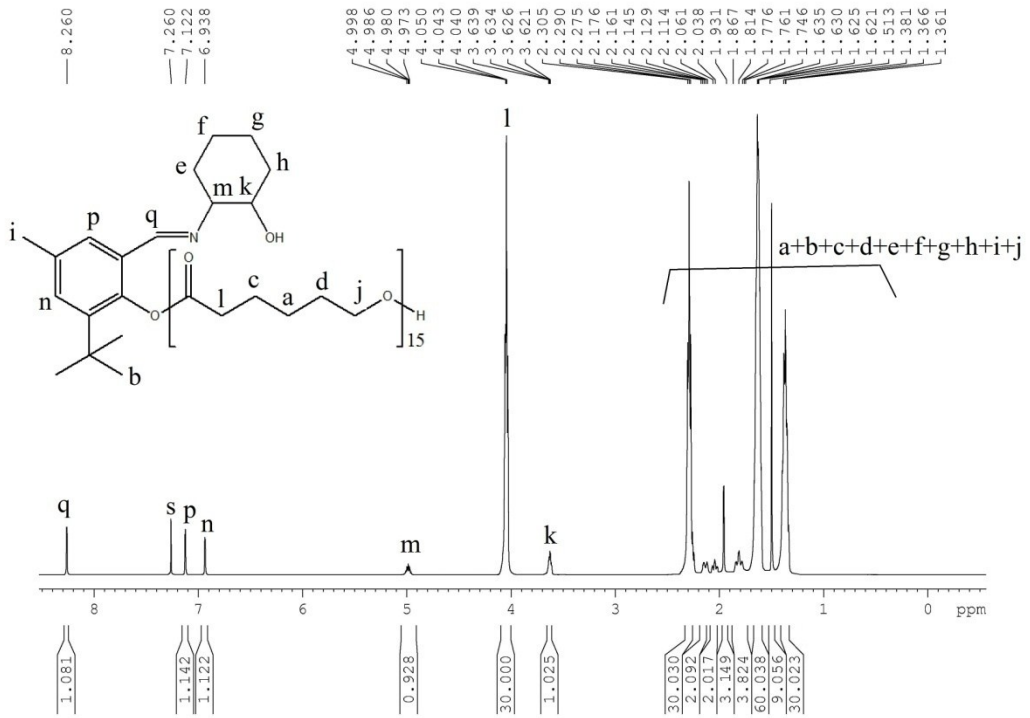


Fig. S37 ^{1}H NMR spectrum of the crude product obtained from a reaction between *ε*-CL and **1** in 15: 1 ratio.

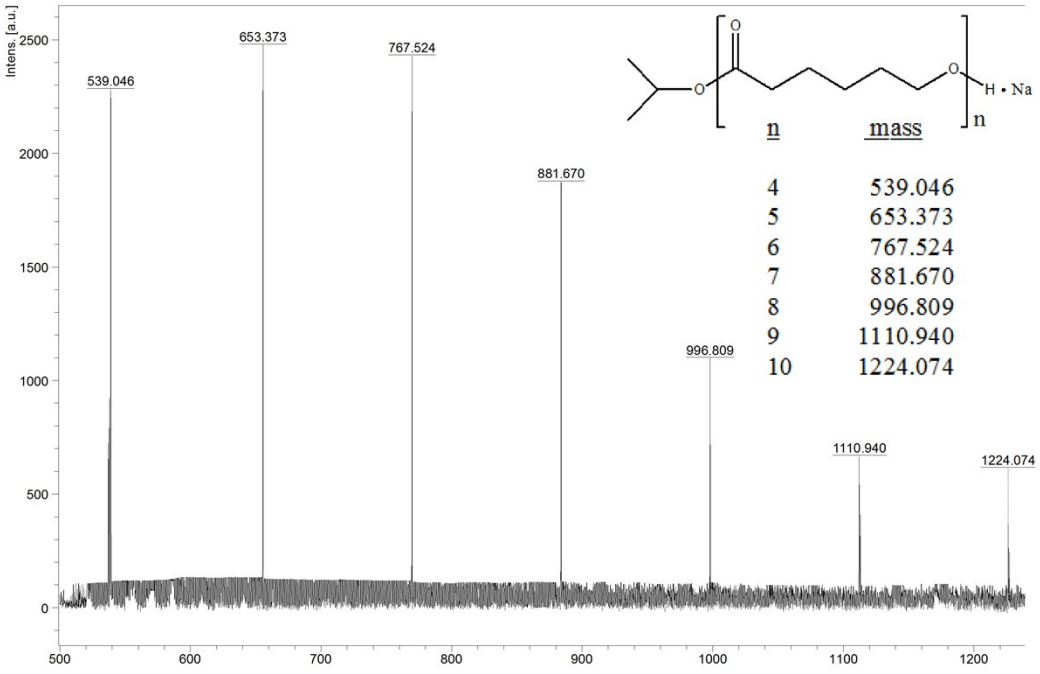


Fig. S38 MALDI-TOF of the crude product obtained from a reaction between *ε*-CL and **4** in 15: 1 ratio.

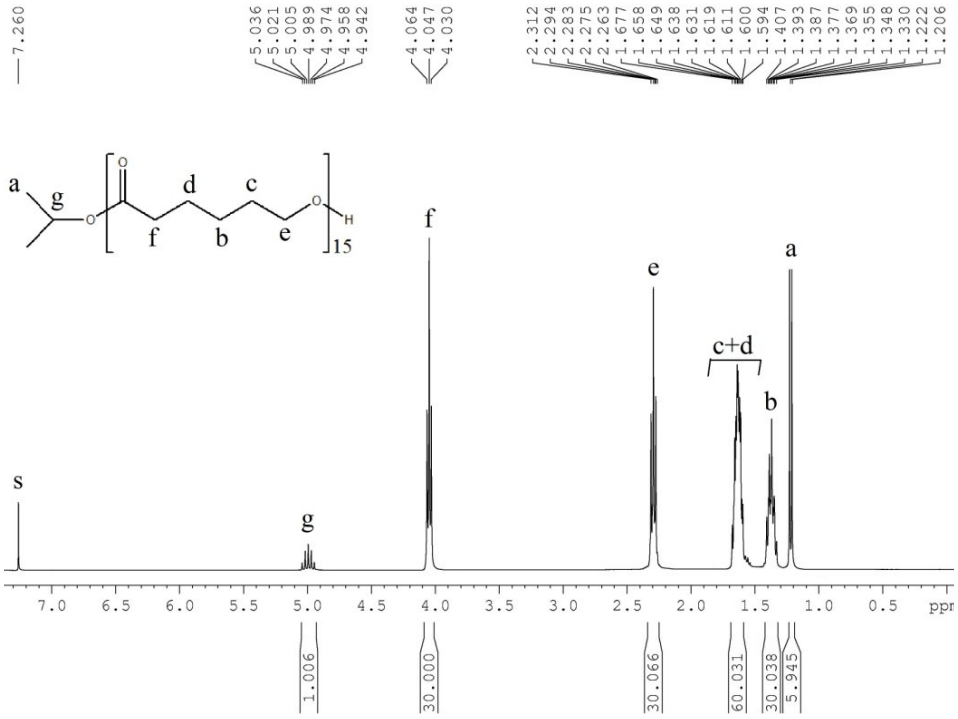


Fig. S39 ^{1}H NMR spectrum of the crude product obtained from a reaction between ε-CL and **4** in 15: 1 ratio.

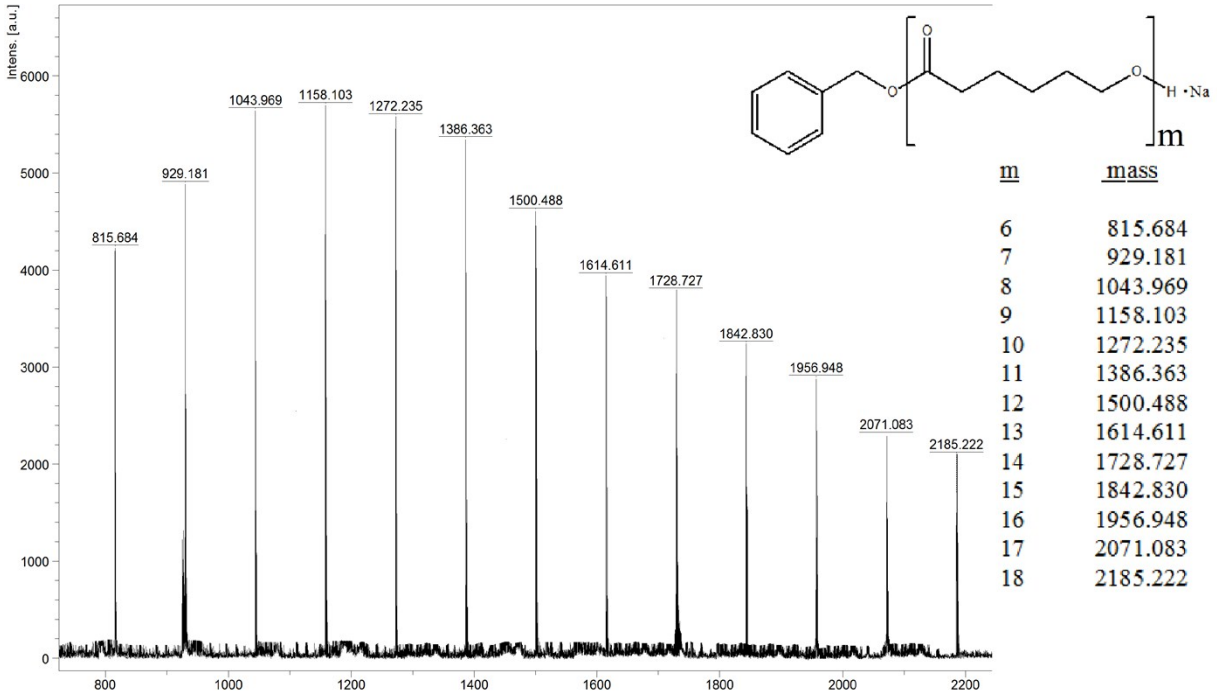


Fig. S40 MALDI-TOF of the crude product obtained from a reaction between ε-CL and **1** in the presence of BnOH in 15: 1: 2 ratio.

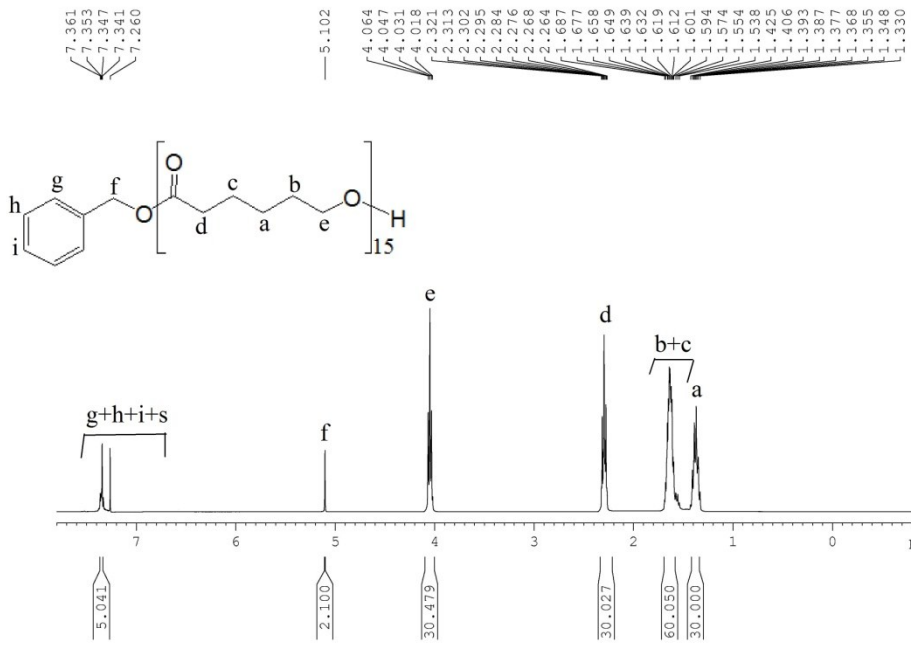
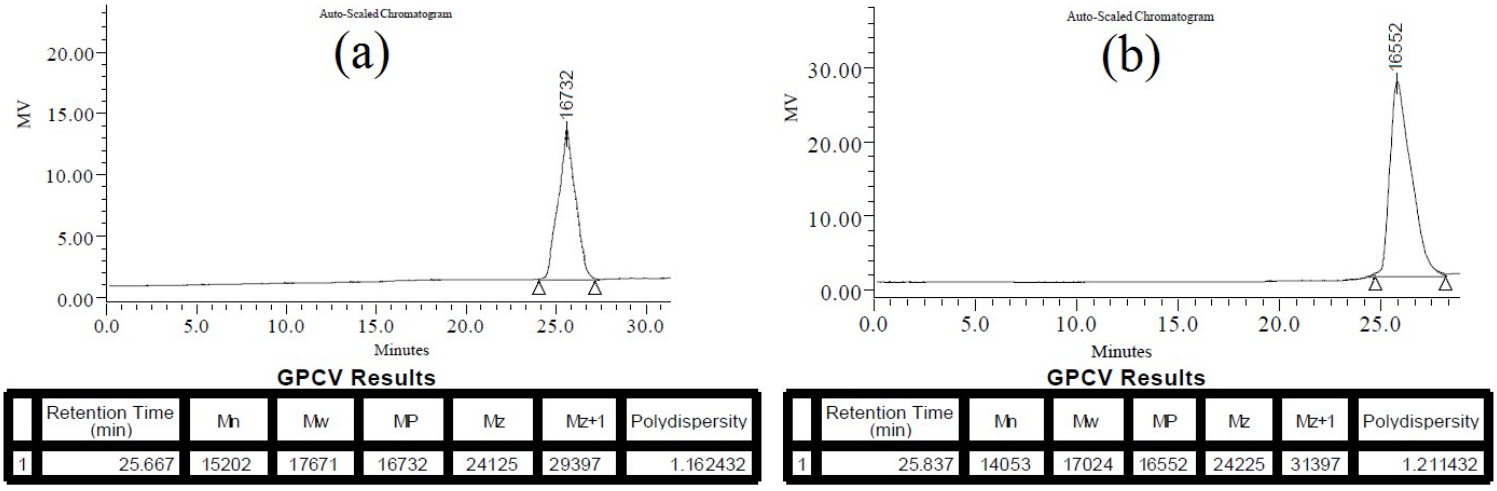


Fig. S41 ^{1}H NMR spectrum of the crude product obtained from a reaction between *ε*-CL and **1** in the presence of BnOH in 15: 1: 2 ratio.



GPCV Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	25.667	15202	17671	16732	24125	29397	1.162432

GPCV Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	25.837	14053	17024	16552	24225	31397	1.211432

Fig. 42 Representative GPC traces for the copolymerization of CHO with CO_2: (a) entry 4, Table 3; (b) entry 1, Table 3.

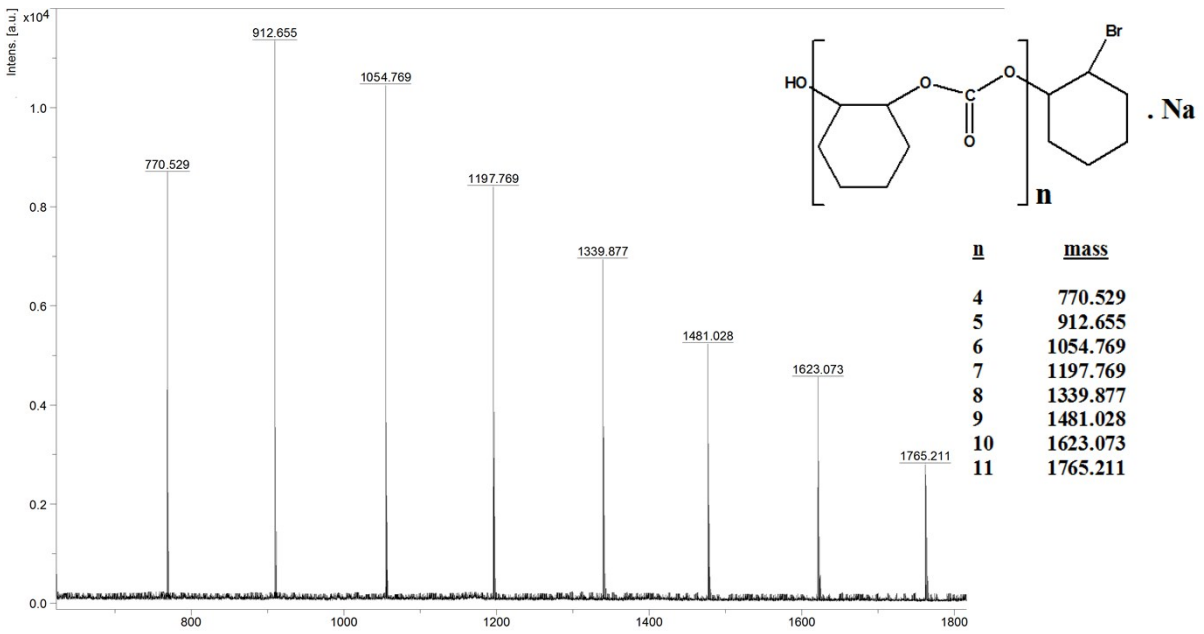


Fig. S43 MALDI-TOF mass spectrum of PCHC sample produced by **4** at 50 °C and 35 bar CO_2 pressure from CHO and CO_2 using TBAB as cocatalyst.

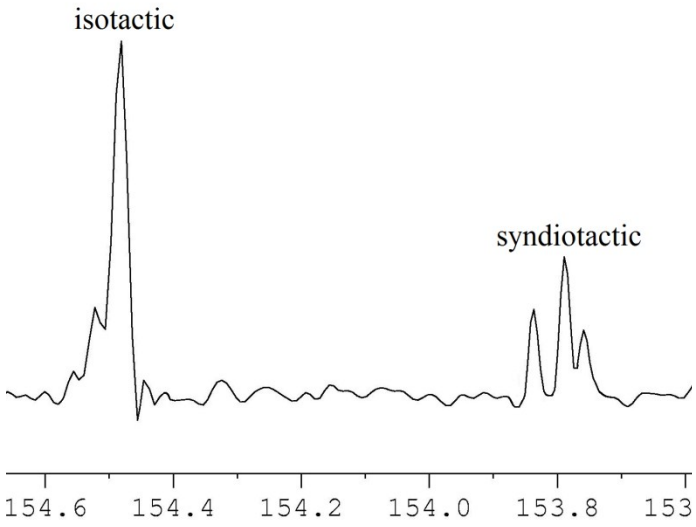


Fig. S44 ^{13}C NMR spectrum of poly(cyclohexene carbonate) in the carbonate region produced from cyclohexene oxide and CO_2.

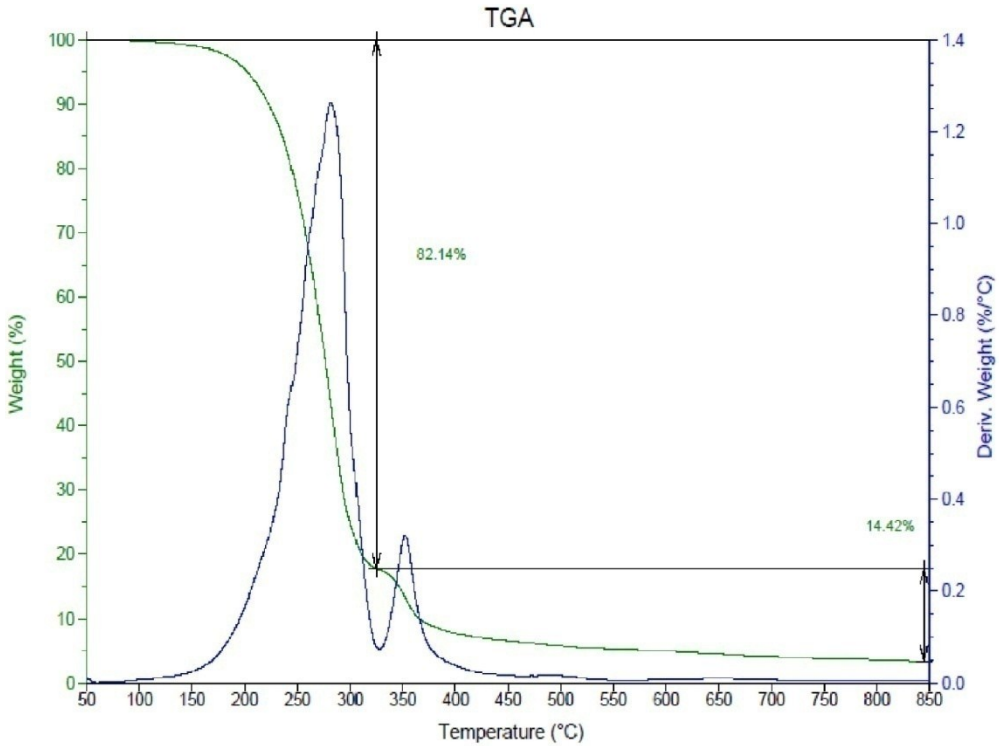


Fig. S45 Representative TGA trace and derivative plot of PCHC produced by **4** (Table 3, entry 4).

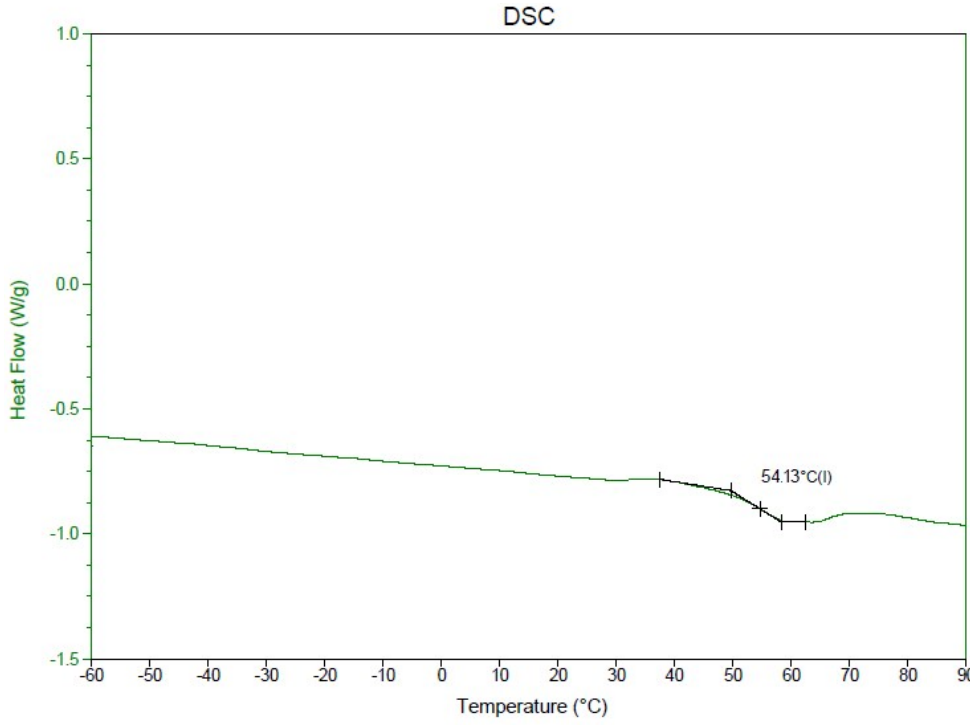


Fig. S46 Representative DSC trace of PCHC produced by **2**, 2nd heat cycle (Table 3, entry 4).

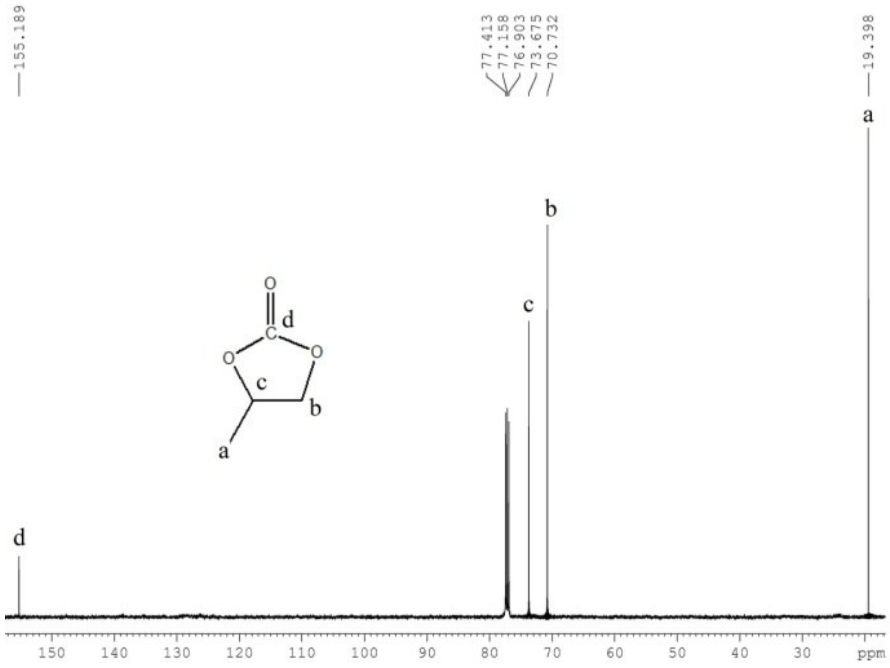


Fig. S47 ^{13}C NMR spectrum of an aliquot from the reaction mixture of PO/CO_2 in $CDCl_3$.

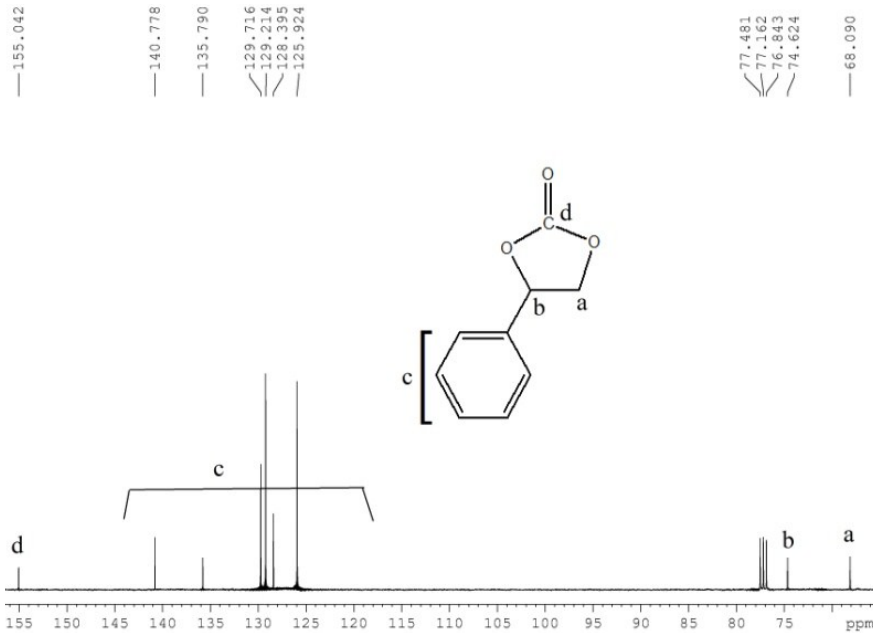
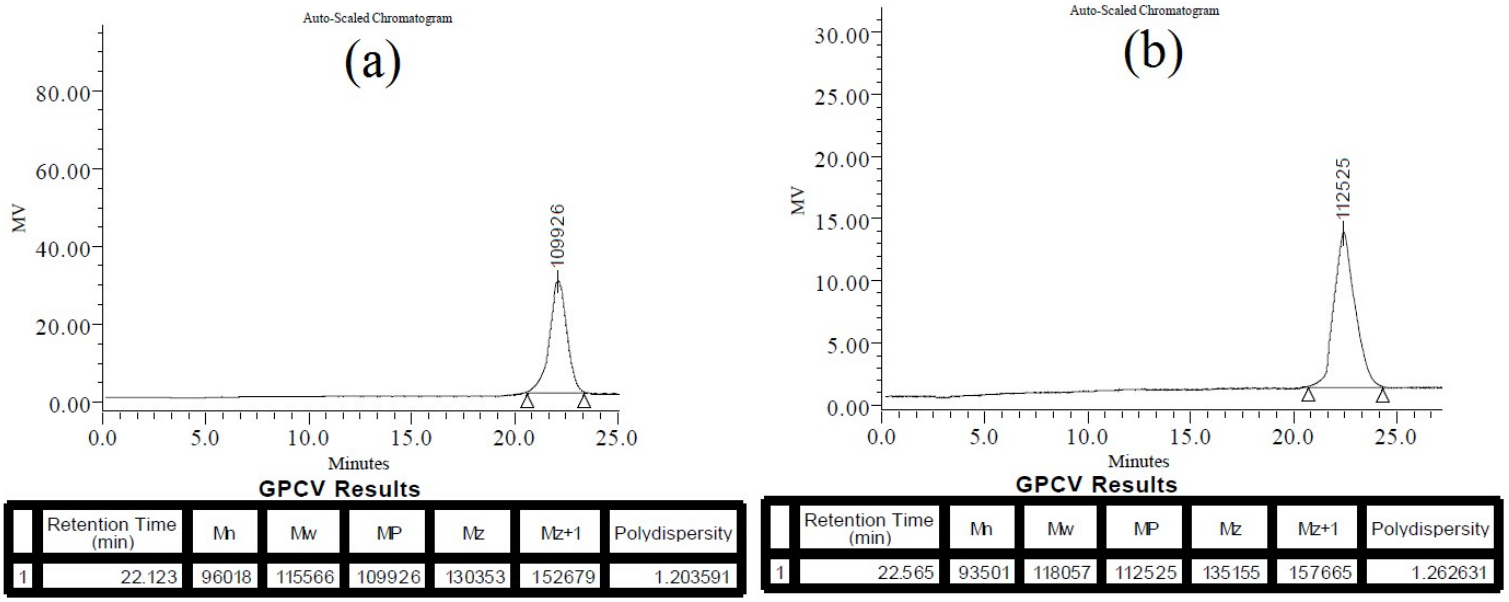


Fig. S48 ^{13}C NMR spectrum of an aliquot from the reaction mixture of SO/CO_2 in $CDCl_3$.



GPCV Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	22.123	96018	115566	109926	130353	152679	1.203591

GPCV Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	22.565	93501	118057	112525	135155	157665	1.262631

Fig. S49 Representative GPC traces for the homopolymerization of CHO: (a) entry 2, Table 5; (b) entry 4, Table 5.

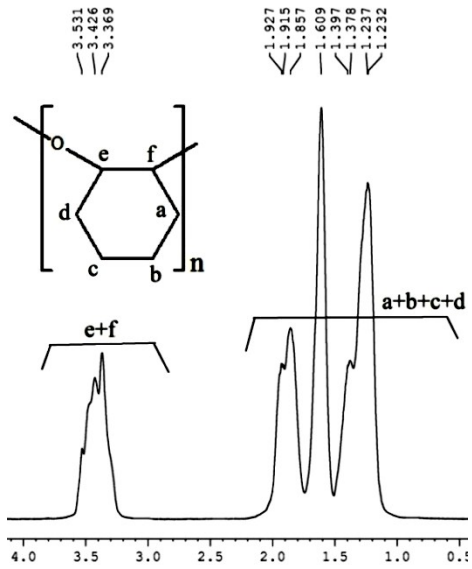


Fig. S50 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of poly(cyclohexene oxide) (PCHO) using **4** in 1000: 1 ratio.

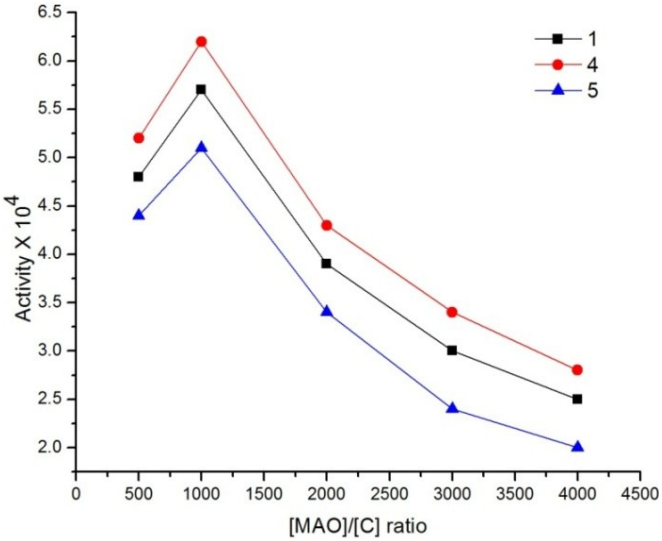


Fig. S51 Plot of activity *vs*. [MAO]/[C] ratio for **1**, **4** and **5** for ethylene polymerization.

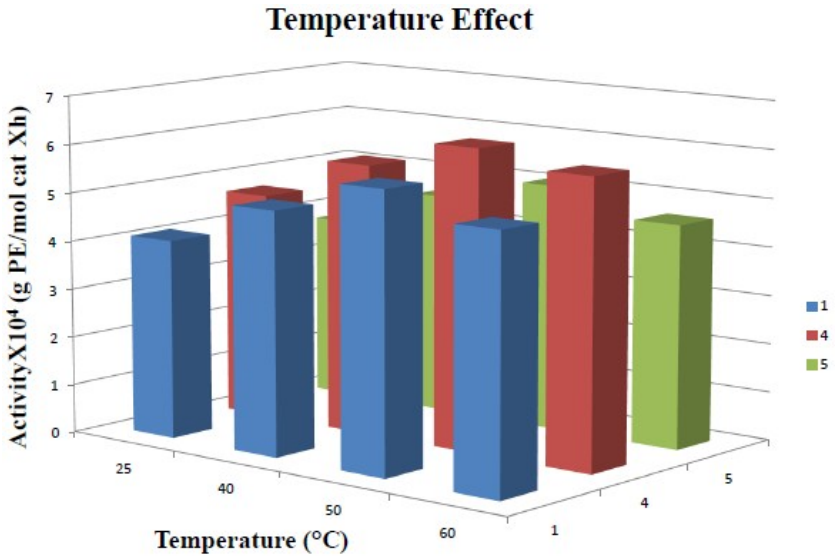


Fig. S52 Effect of temperature on the activity for the complexes **1**, **4** and **5** towards ethylene polymerization.

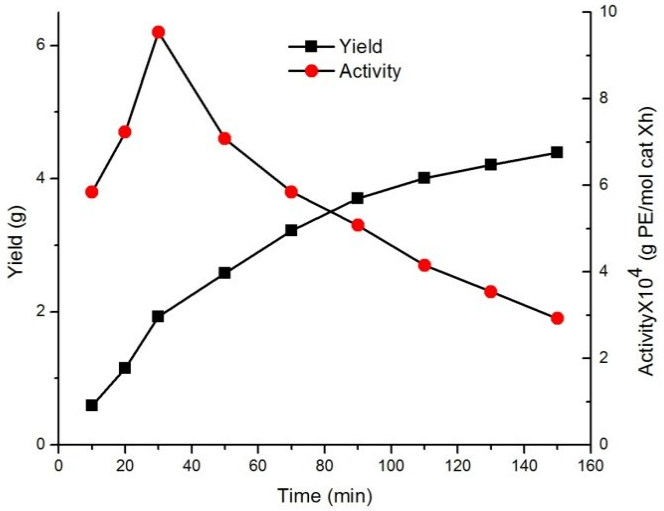


Fig. S53 Effect of time on the yield and activity for the complex **4** towards ethylene polymerization.

Table S1 Crystal data for the structures of **1, 3, 4** and **5**

Compounds	**1**	**3**	**4**	**5**
Emperical formula	$C_{36}H_{50}N_2O_4Ti$	$C_{26}H_{26}Cl_4N_2O_4Ti$	$C_{42}H_{64}N_2O_7Ti_2$	$C_{72}H_{100}N_4O_8Zr_2$
Formula weight	622.68	620.19	804.75	1332.00
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*I*2/*a*	*P*-1	*P*2(1)/*c*	*P*2(1)/*n*
Temp/K	296(2)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
a (Å)	14.4864(9)	10.3126(3)	14.9452(5)	20.5673(8)
b (Å)	17.4311(13)	12.8248(5)	18.7424(6)	13.9216(5)
c (Å)	16.5711(16)	12.9776(4)	18.6507(5)	29.0288(10)
α (°)	90	63.2283(19)	90	90
β (°)	104.720(3)	68.1217(13)	107.1600(10)	108.3780(10)
γ (°)	90	66.2981(14)	90	90
V (Å^3)	4047.1(6)	1364.07(8)	4991.7(3)	7887.9(5)
Z	4	2	4	4
D_{calc} (g/cm^3)	1.022	1.510	1.071	1.122
Reflns collected	19126	18344	32072	37053
No. of indepreflns	5037	4790	8217	9605
Absorption correction	multi-scan	none	multi-scan	multi-scan
GOF	1.103	1.032	1.029	1.016

F(000)	1336	636	1720	2816
Final *R*	R_1 = 0.0451,	R_1 = 0.0336,	R_1 = 0.0459,	R_1 = 0.0402,
indices(I>2σ(I))	wR_2 = 0.1357	wR_2 = 0.0776	wR_2 = 0.1243	wR_2 = 0.1089
R indices (all data)	R_1 = 0.0626,	R_1 = 0.0439,	R_1 = 0.0705,	R_1 = 0.0542,
	wR_2 = 0.1426	wR_2 = 0.0831	wR_2 = 0.1347	wR_2 = 0.1153
CCDC	1422871	1422870	1422869	1422873

$R_1 = \sum|F_0| - |F_c|/\sum|F_0|$, $wR_2 = [\sum (F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

Table S2 Polymerization data for *rac*-LA, *L*-LA and ε-CL using **1–7** in the presence of benzyl alcohol in 200: 1: 2 (monomer: initiator: benzyl alcohol) ratio.

Entry	Catalyst	Monomer	T / °C	Yield (%)	[a]Time/ min	[b]TOF/min	[c]M_n^{obs}/ kgmol^{-1}	[d]M_n^{theo}/ kgmol^{-1}	M_w/M_n
1	**1**	*rac*-LA	140	96	31	3.1	15.09	14.52	1.12
2	**2**	*rac*-LA	140	96	39	2.5	14.90	14.52	1.12
3	**3**	*rac*-LA	140	97	27	3.6	15.55	14.52	1.11
4	**4**	*rac*-LA	140	99	21	4.7	16.01	14.52	1.10
5	**5**	*rac*-LA	140	95	50	1.9	14.02	14.52	1.13
6	**6**	*rac*-LA	140	93	58	1.6	13.69	14.52	1.14
7	**7**	*rac*-LA	140	95	45	2.1	14.67	14.52	1.13
8	**1**	*L*-LA	140	96	26	3.7	14.31	14.52	1.15
9	**2**	*L*-LA	140	95	34	2.8	13.52	14.52	1.16
10	**3**	*L*-LA	140	96	21	4.6	14.73	14.52	1.13
11	**4**	*L*-LA	140	98	16	6.1	15.55	14.52	1.12
12	**5**	*L*-LA	140	93	45	2.1	13.02	14.52	1.17
13	**6**	*L*-LA	140	92	52	1.8	12.88	14.52	1.16
14	**7**	*L*-LA	140	94	39	2.4	13.27	14.52	1.16
15	**1**	ε-CL	80	97	39	2.5	12.08	11.52	1.20
16	**2**	ε-CL	80	96	47	2.0	11.72	11.52	1.19
17	**3**	ε-CL	80	96	32	3.0	12.62	11.52	1.18
18	**4**	ε-CL	80	98	27	3.6	12.98	11.52	1.17
19	**5**	ε-CL	80	93	61	1.5	10.68	11.52	1.21
20	**6**	ε-CL	80	93	72	1.3	10.09	11.52	1.22
21	**7**	ε-CL	80	95	53	1.8	11.11	11.52	1.21

[a]Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b]Turnover frequency (TOF) = Number of moles of monomer consumed / (mole of catalyst × time of polymerization). [c]Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n for ε-CL (0.56) and LA (0.58) polymerization. [d]M_n (theoretical) at 100 % conversion = $[M]_0/[C]_0$ × mol wt (monomer) + mol wt (BnOH).

Table S3 Polymerization data based on changing ratios in case of *rac*-LA using **1**, **4** and **5** in the presence of benzyl alcohol at 140 °C.[a]

Entry	Catalyst (C)	[M]: [C]: [BnOH] ratio	Yield (%)	[b]Time/min	[c]TOF/min	[d]M_n^{obs}/ kgmol^{-1}	[e]M_n^{theo}/ kgmol^{-1}	M_w/M_n
1	**1**	100: 1: 2	99	16	3.1	8.904	7.315	1.10
2	**1**	200: 1: 2	97	27	3.6	15.55	14.52	1.11
3	**1**	400: 1: 2	96	43	4.5	30.89	28.94	1.12
4	**1**	600: 1: 2	95	68	4.2	44.44	43.35	1.14
5	**1**	800: 1: 2	93	97	3.8	59.05	57.76	1.16
6	**4**	100: 1: 2	98	12	4.1	9.251	7.315	1.09
7	**4**	200: 1: 2	99	21	4.7	16.01	14.52	1.10
8	**4**	400: 1: 2	95	34	5.6	31.84	28.94	1.12
9	**4**	600: 1: 2	94	55	5.1	47.05	43.35	1.14
10	**4**	800: 1: 2	92	84	4.4	60.06	57.76	1.15
11	**5**	100: 1: 2	97	28	1.7	8.017	7.315	1.12
12	**5**	200: 1: 2	95	45	2.1	14.67	14.52	1.13
13	**5**	400: 1: 2	94	67	2.8	29.92	28.94	1.15
14	**5**	600: 1: 2	93	99	2.8	44.08	43.35	1.16
15	**5**	800: 1: 2	91	142	2.6	57.35	57.76	1.18

[a]M = Monomer, C = Catalyst. [b]Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [c]Turnover frequency (TOF) = Number of moles of monomer consumed / (mole of catalyst × time of polymerization). [d]Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n for *rac*-LA (0.58) polymerization. [e]M_n (theoretical) at 100 % conversion = $[M]_0/[C]_0$ × mol wt (monomer) + mol wt (BnOH).

Table S4 DSC and TGA measurements for the different copolymers obtained in **Table 3**.

Entry	Initiator	Copolymers	T_g[a] (°C)	T_{d5}[b] (°C)	T_{d50}[b] (°C)	T_{d95}[b] (°C)
1	**1**	PCHC	50	191	269	579
2	**4**	PCHC	54	202	277	597
3	**5**	PCHC	47	175	256	562

[a]T_g values represent the midpoint temperature during the second heating cycle determined by DSC. [b]T_{d5}, T_{d50}, and T_{d95} are the decomposition temperature at 5%, 50%, and 95% weight loss, respectively determined by TGA analysis.