Supporting Information

Zwitterionic group 4 aminophenolate catalysts for the polymerization of lactides and ethylene

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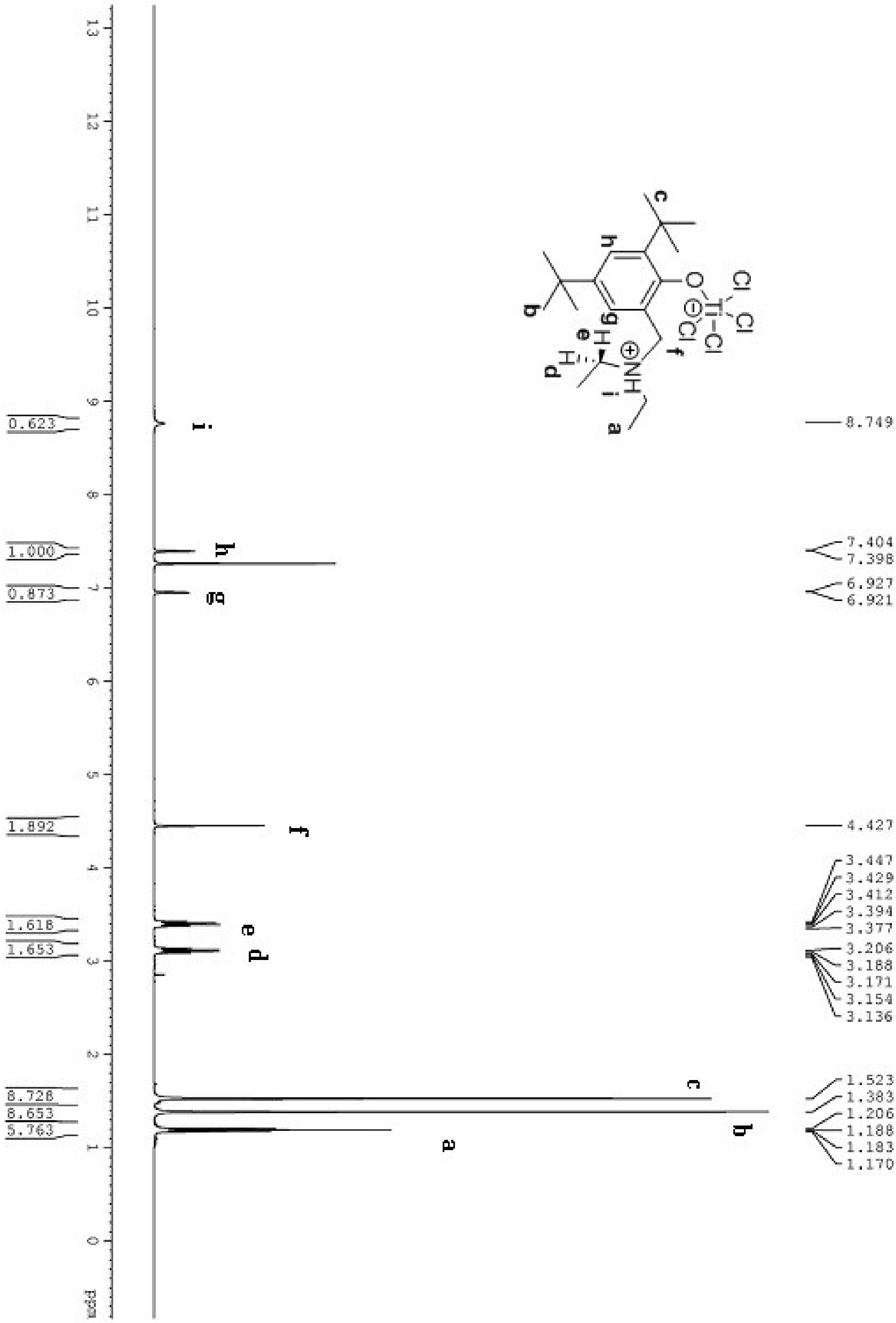

Figure S1.[1]H NMR (400 MHz, $CDCl_3$) of Compound **1**

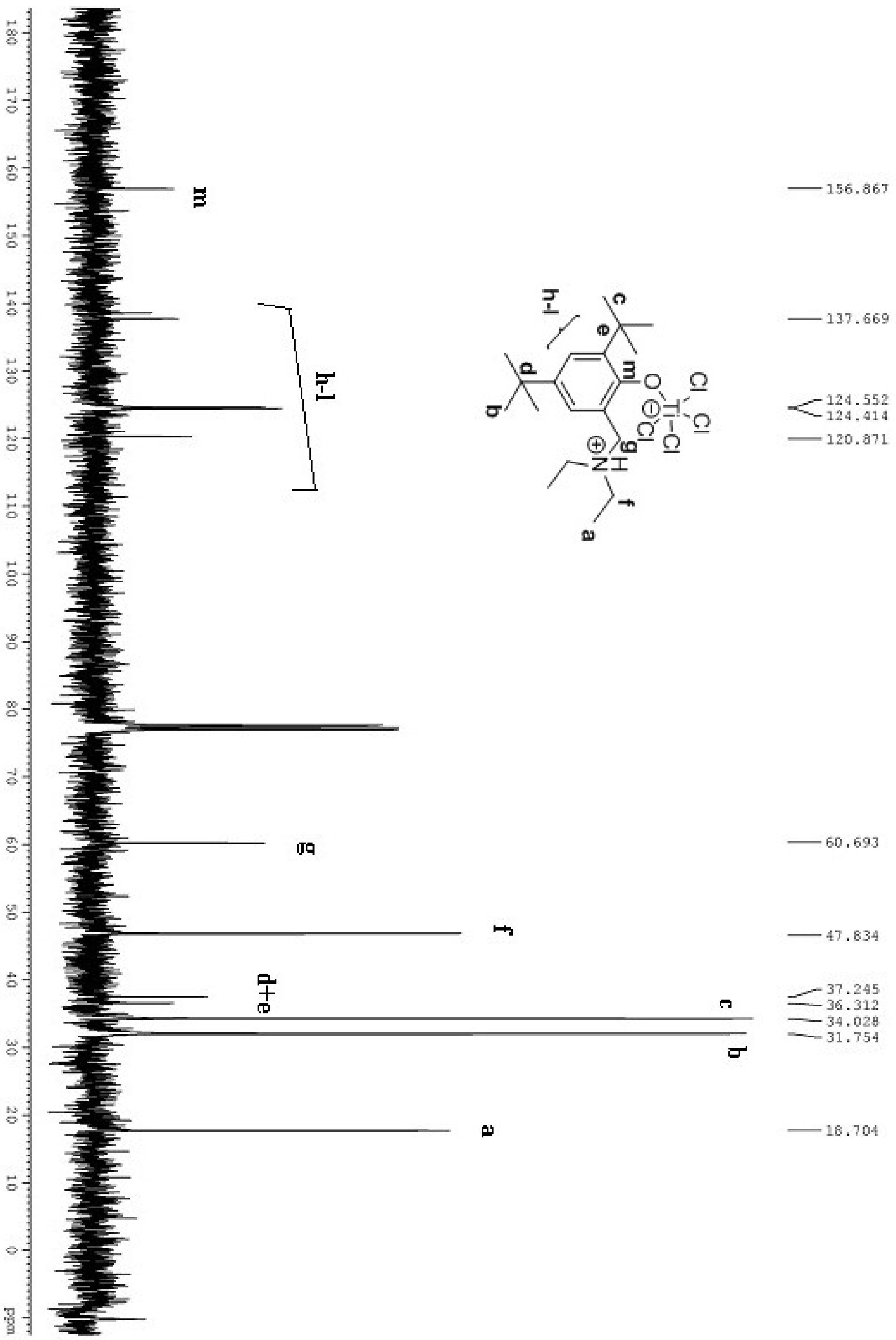

Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **1**

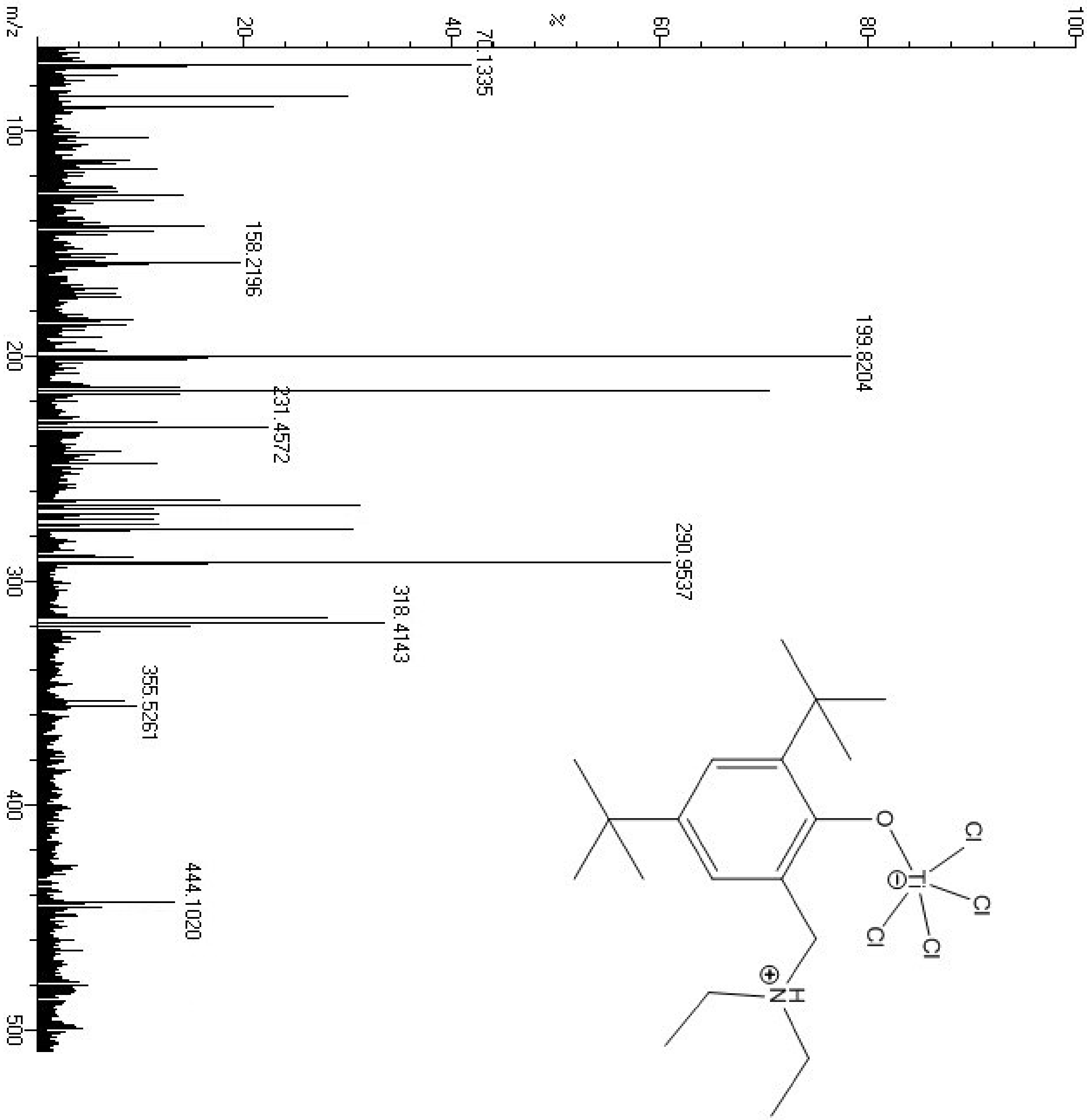

Figure S3. ESI mass spectrum of Compound **1**

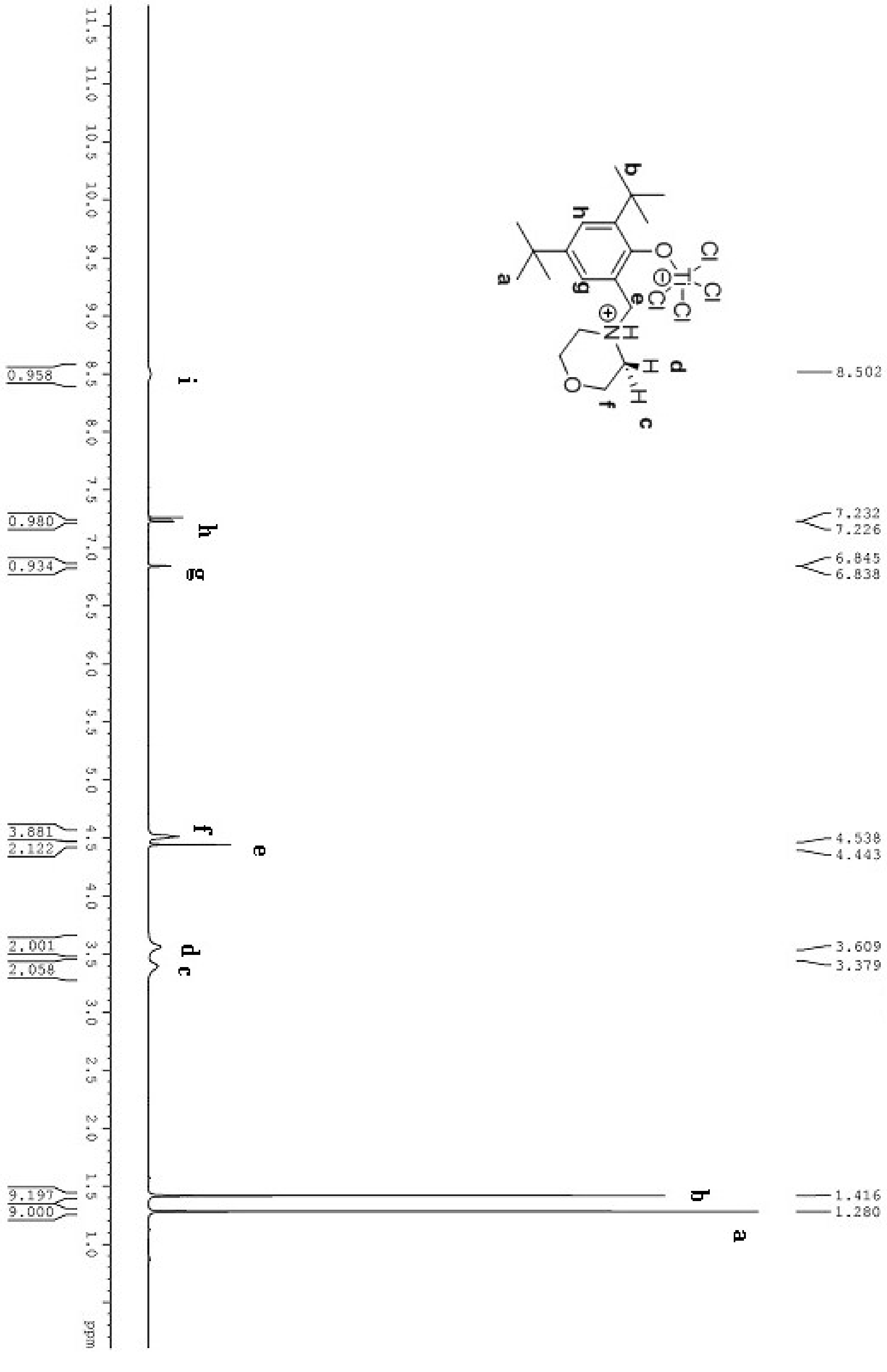

Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **2**

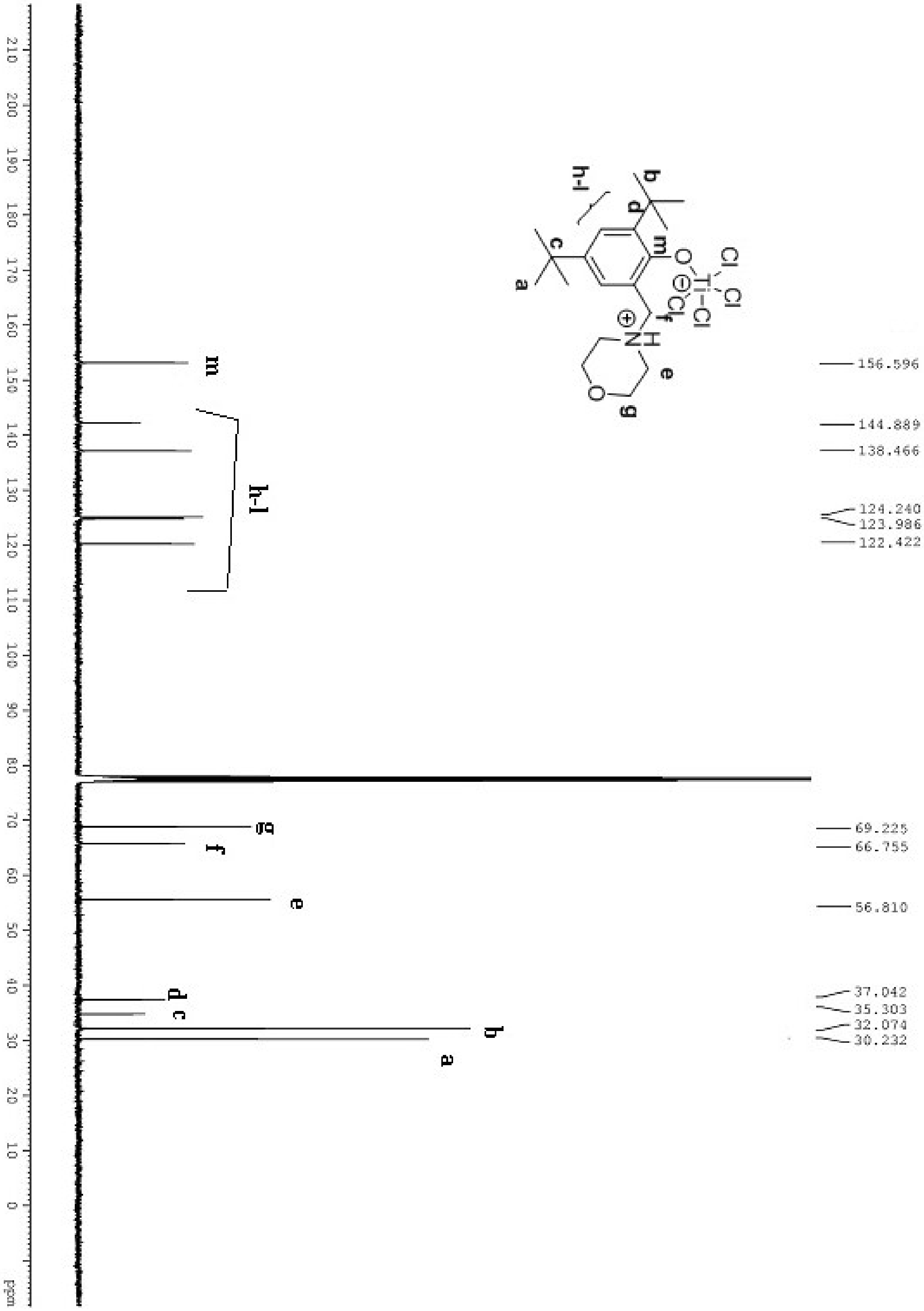

Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **2**

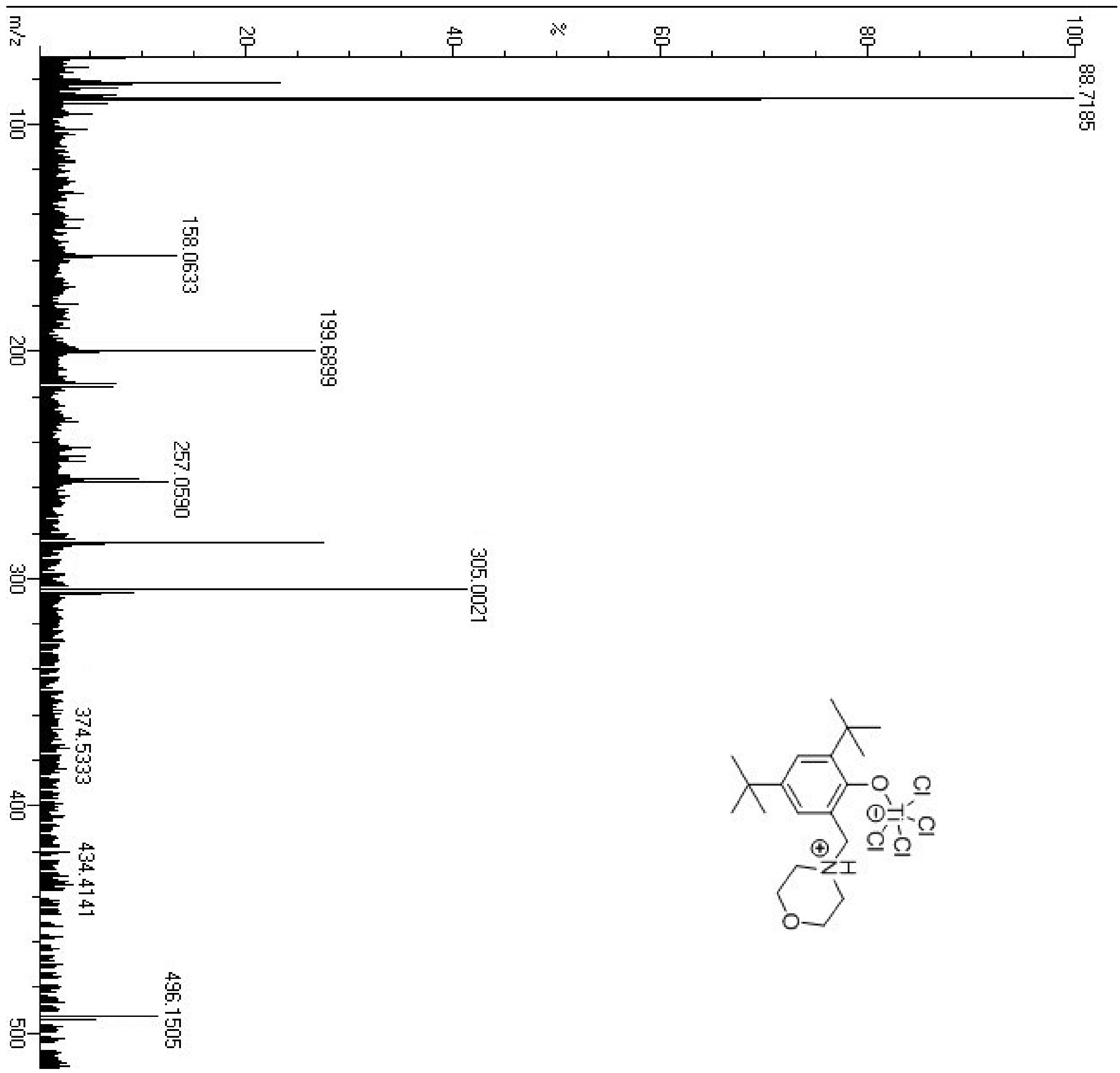

Figure S6. ESI mass spectrum of Compound **2**

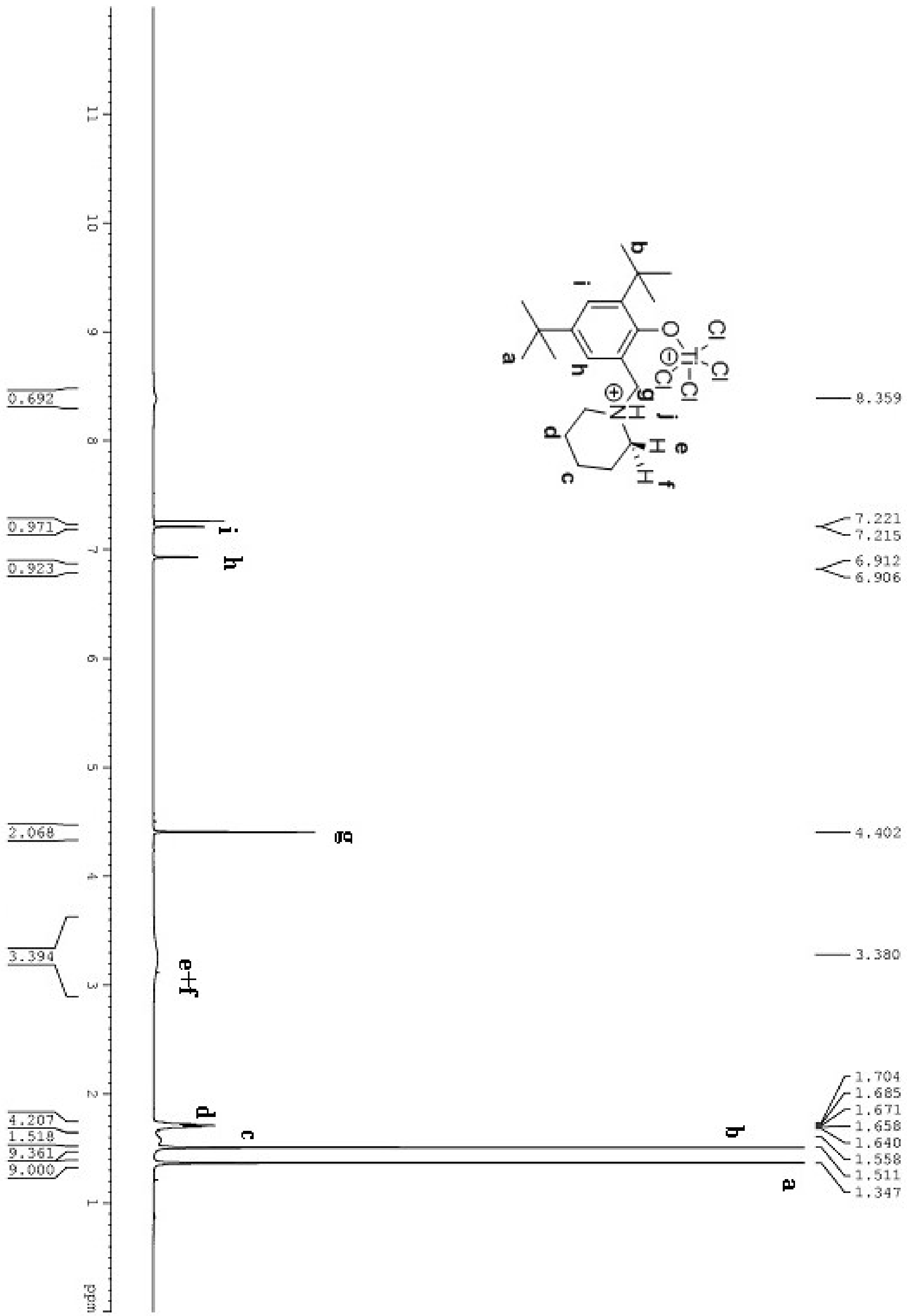

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3**

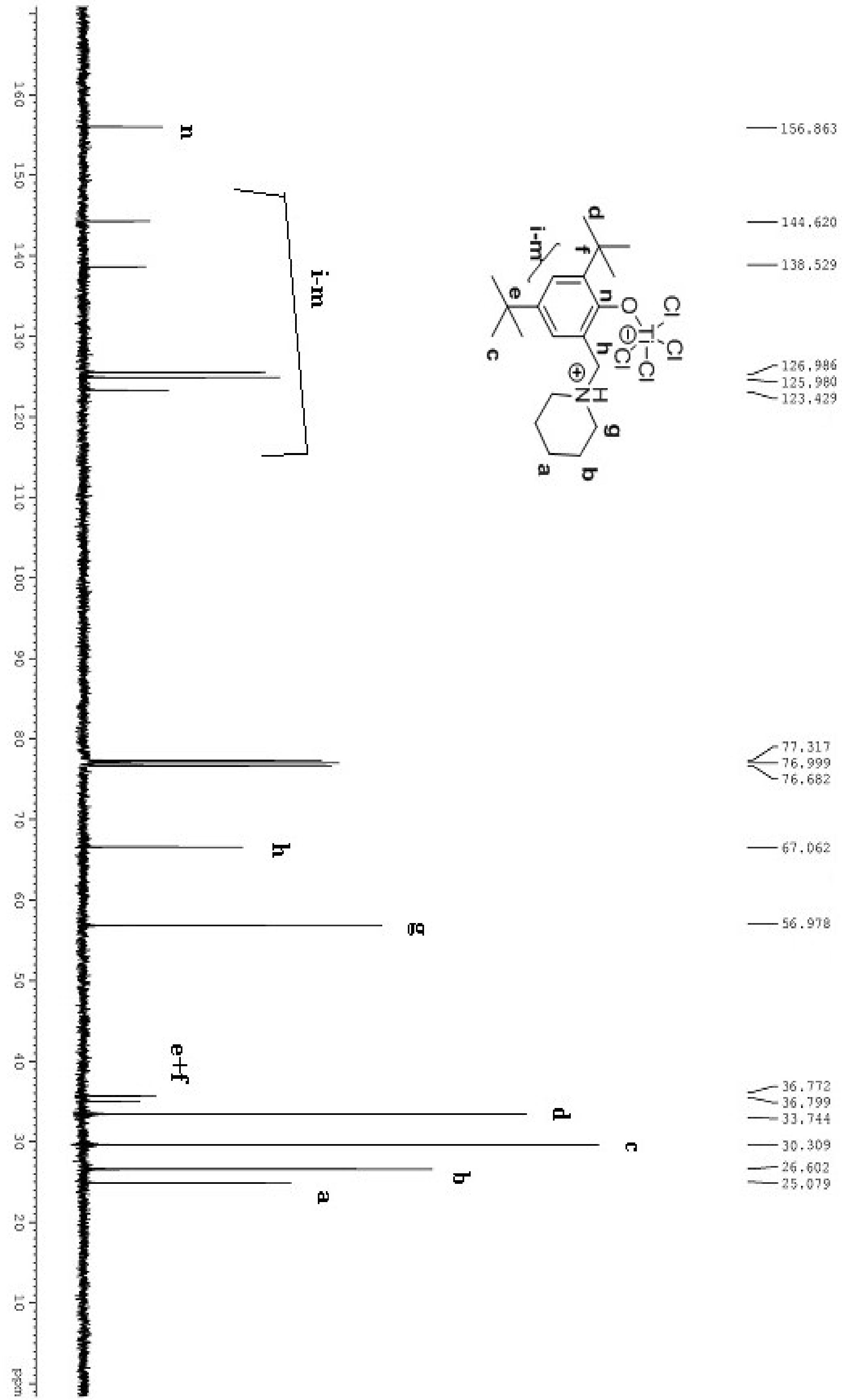

Figure S8.^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3**

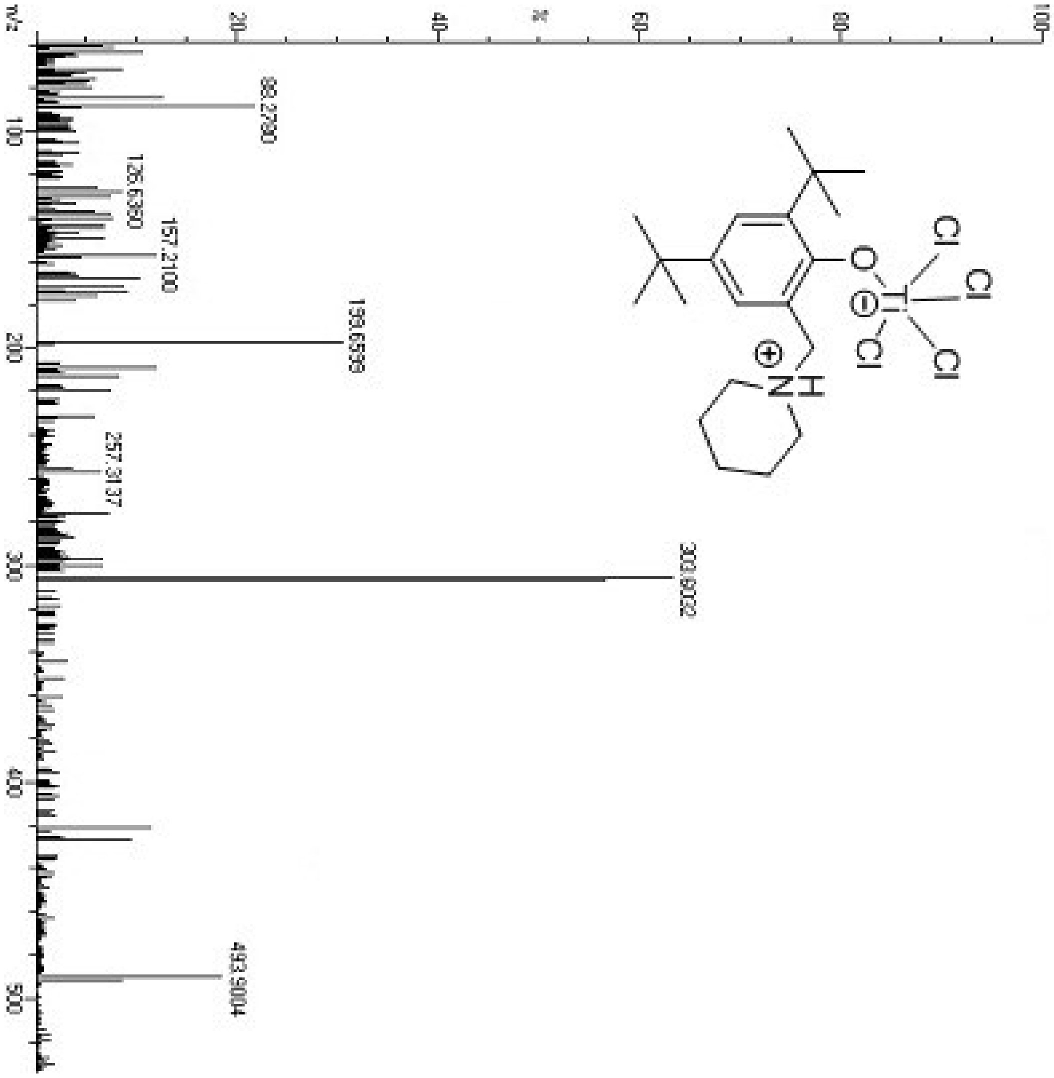

Figure S9. ESI mass spectrum of Compound **3**

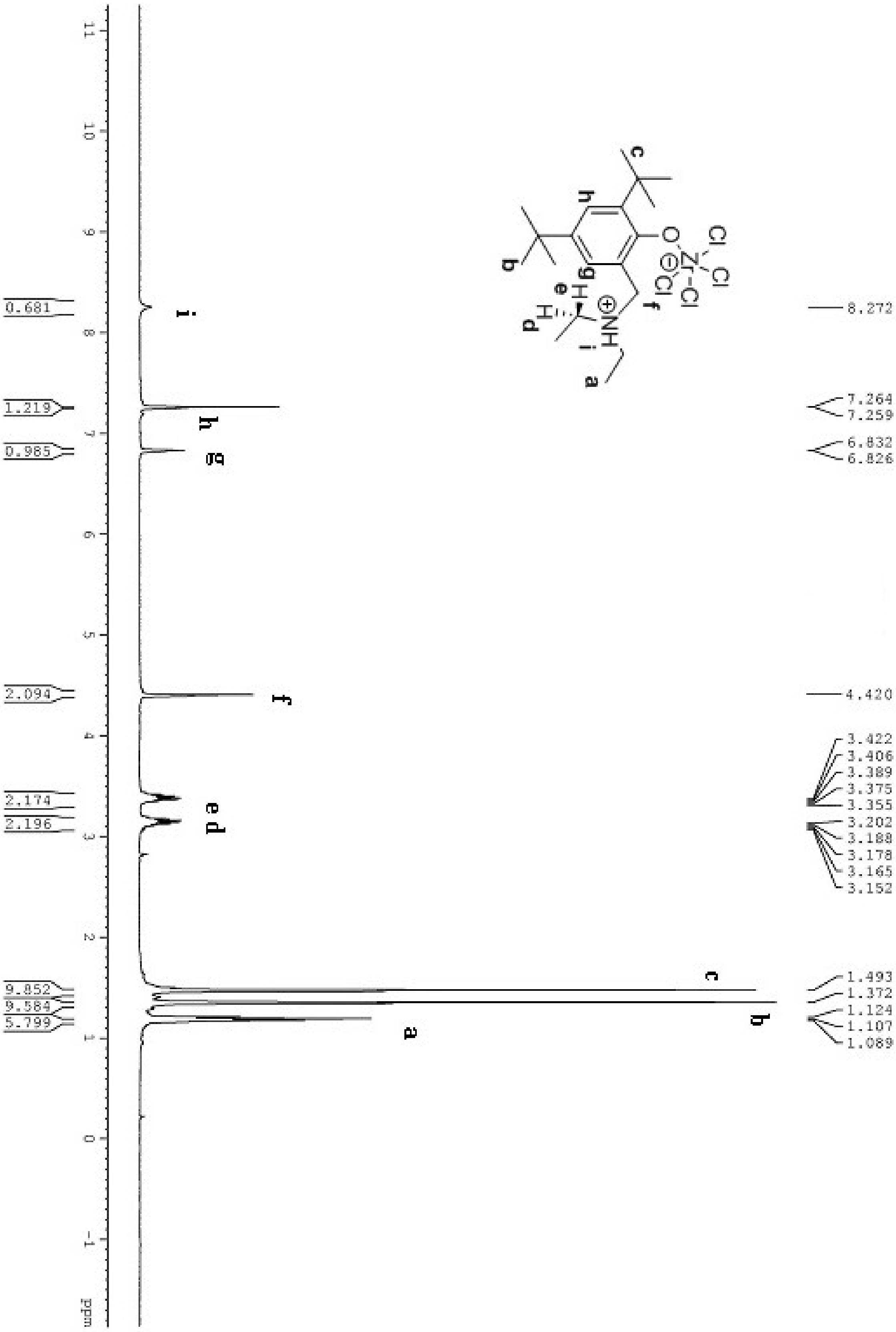

Figure S10.[1]H NMR (400 MHz, $CDCl_3$) of Compound **4**

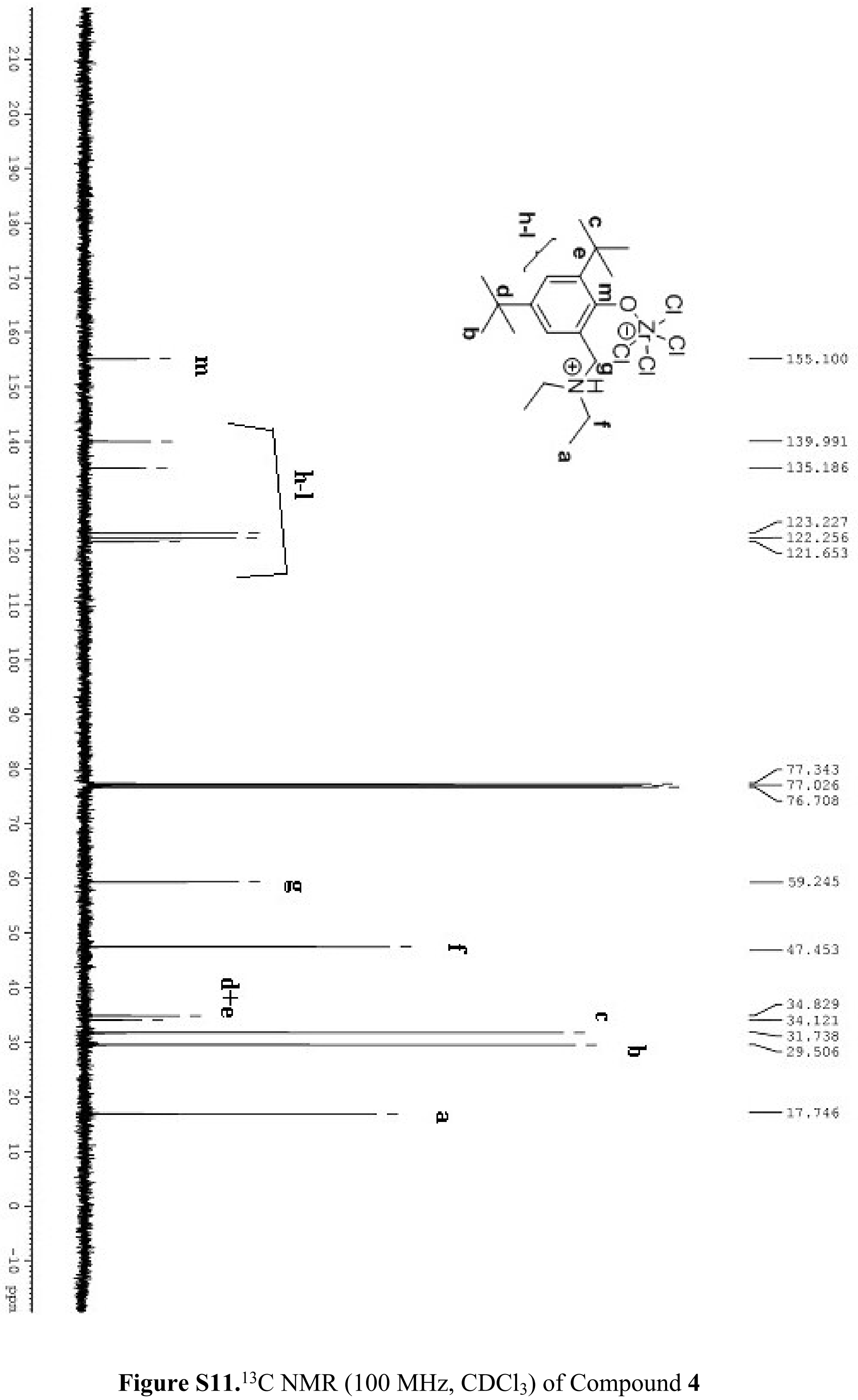

Figure S11.^{13}C NMR (100 MHz, $CDCl_3$) of Compound **4**

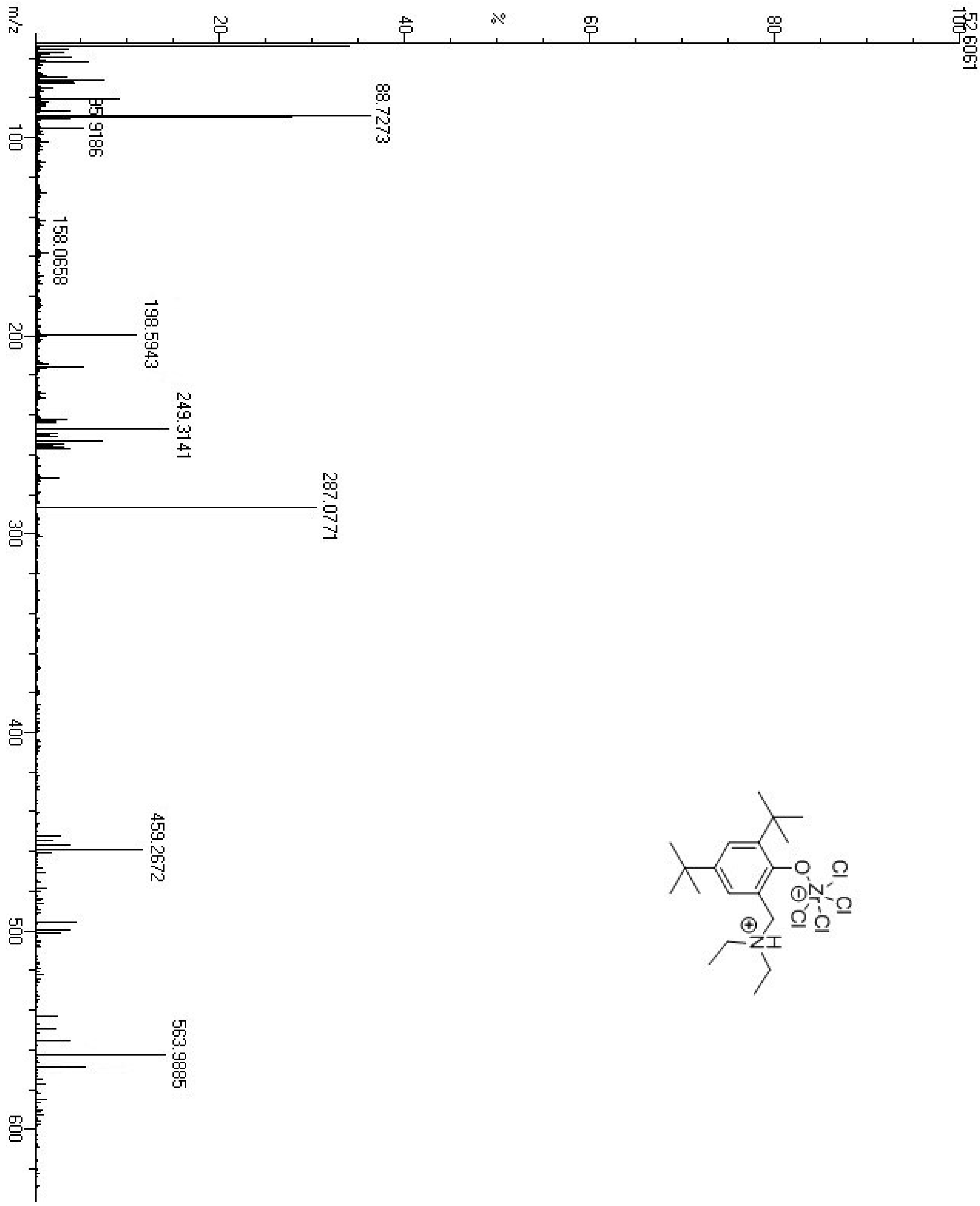

Figure S12. ESI mass spectrum of Compound **4**

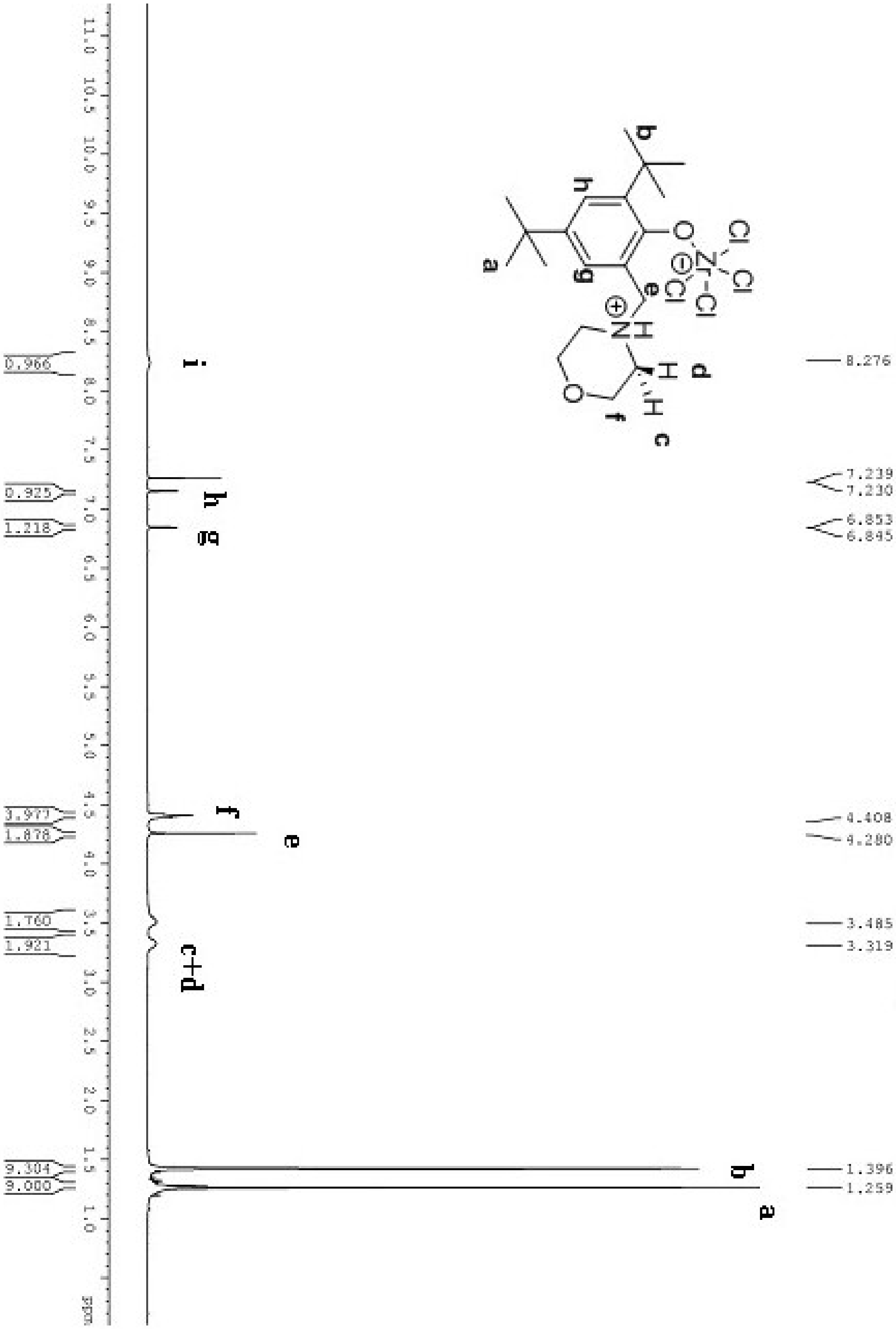

Figure S13.[1]H NMR (400 MHz, $CDCl_3$) of Compound **5**

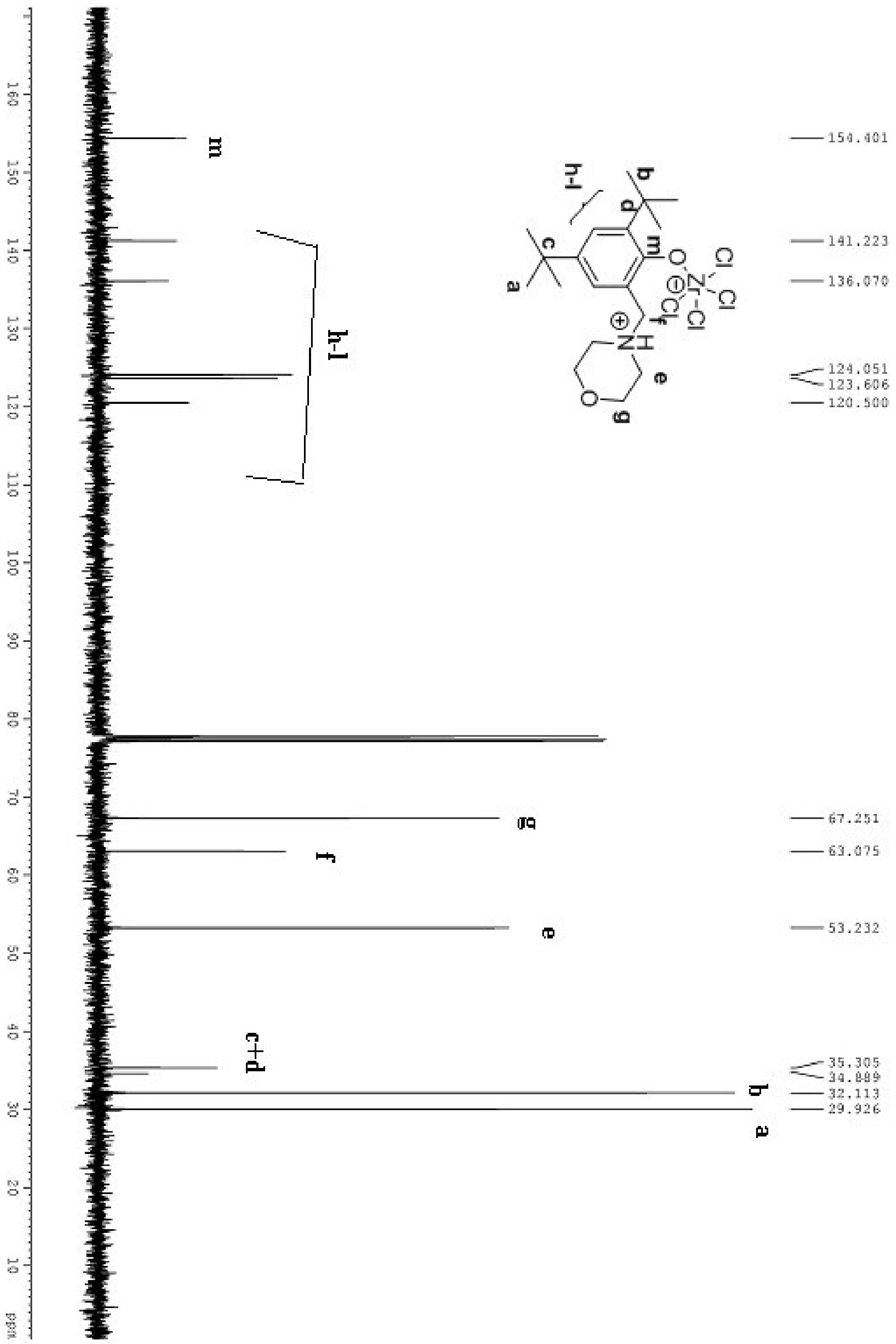

Figure S14.[13]C NMR (100 MHz, $CDCl_3$) of Compound **5**

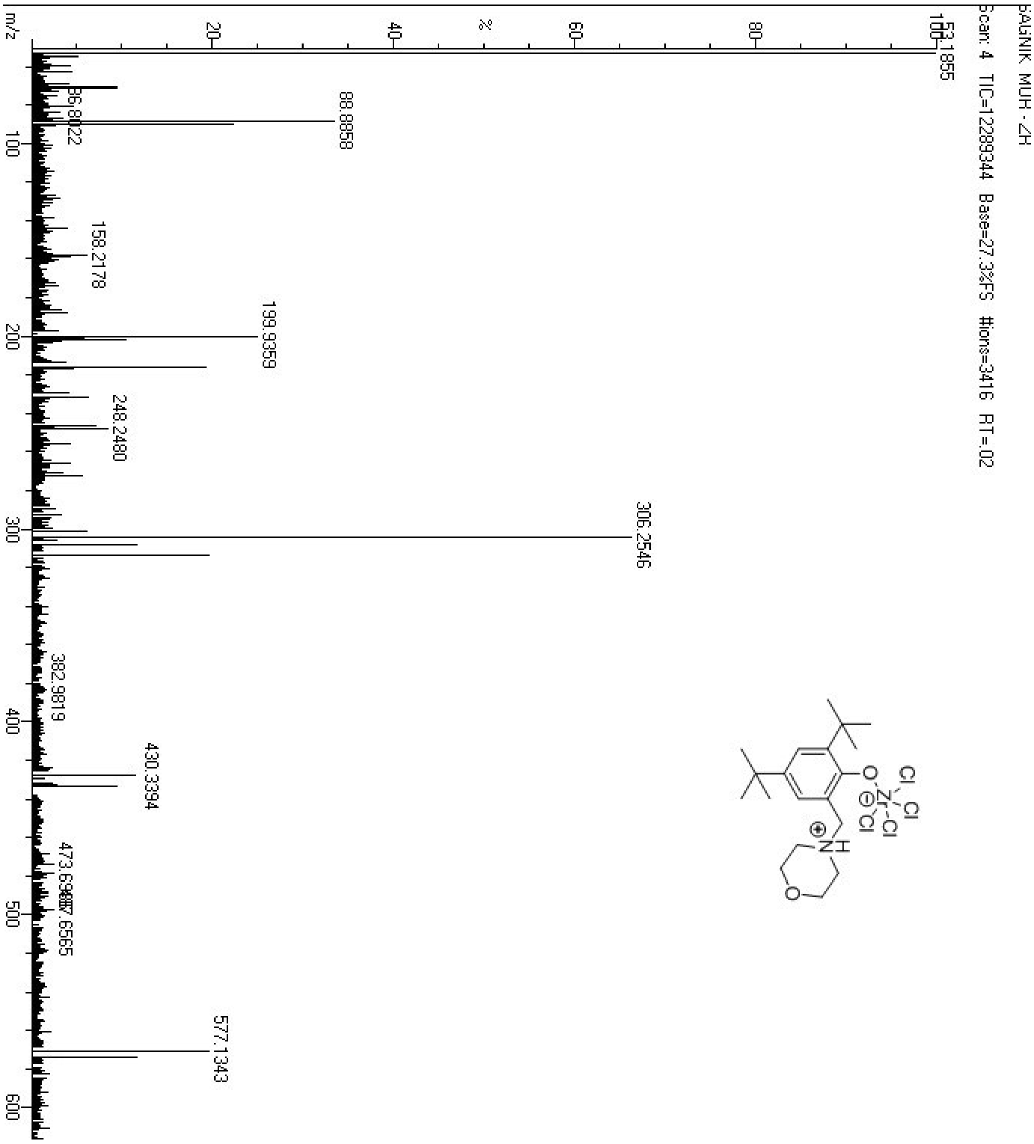

Figure S15. ESI mass spectrum of Compound **5**

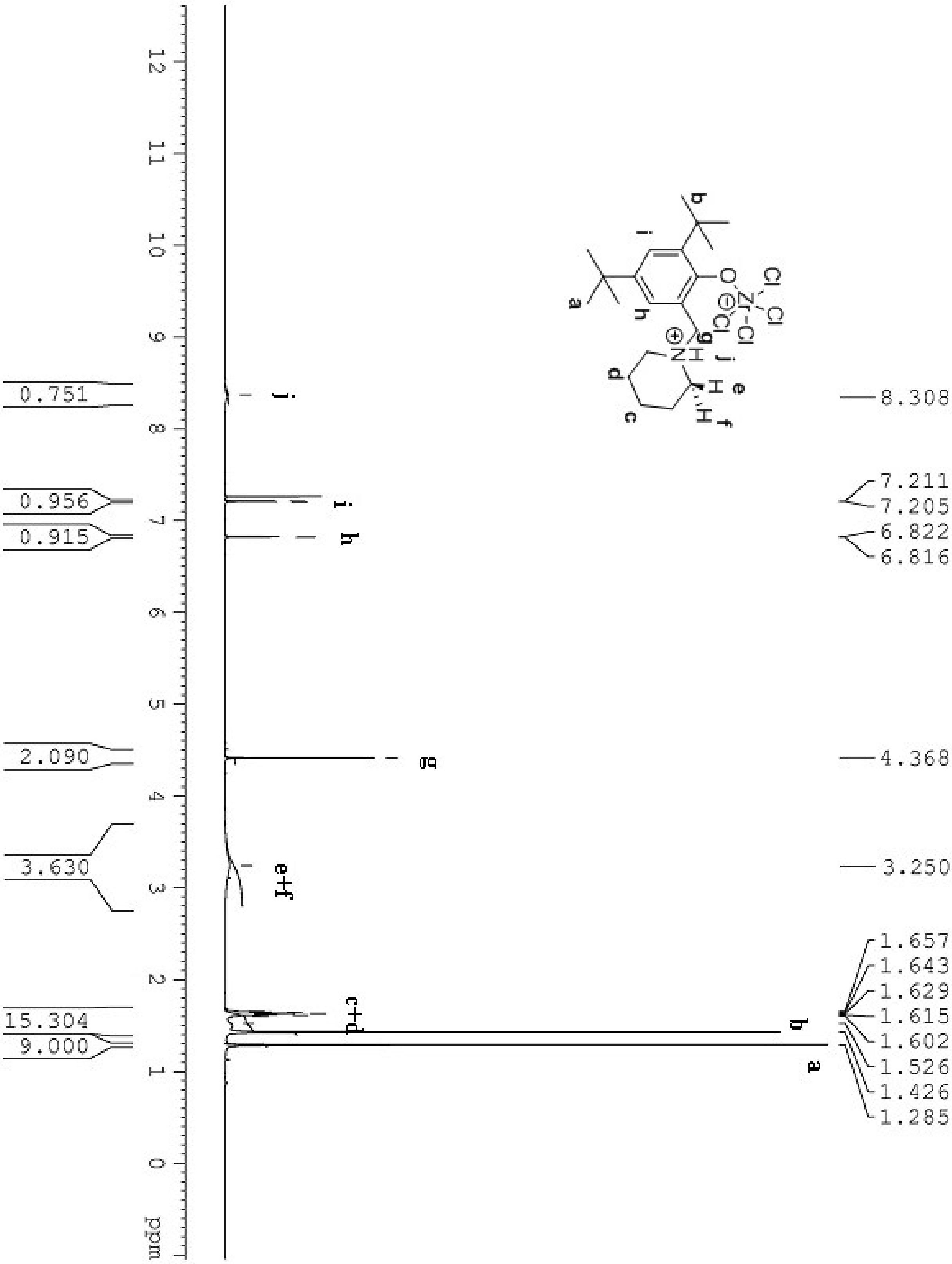

Figure S16.^{1}H NMR (400 MHz, $CDCl_3$) of Compound **6**

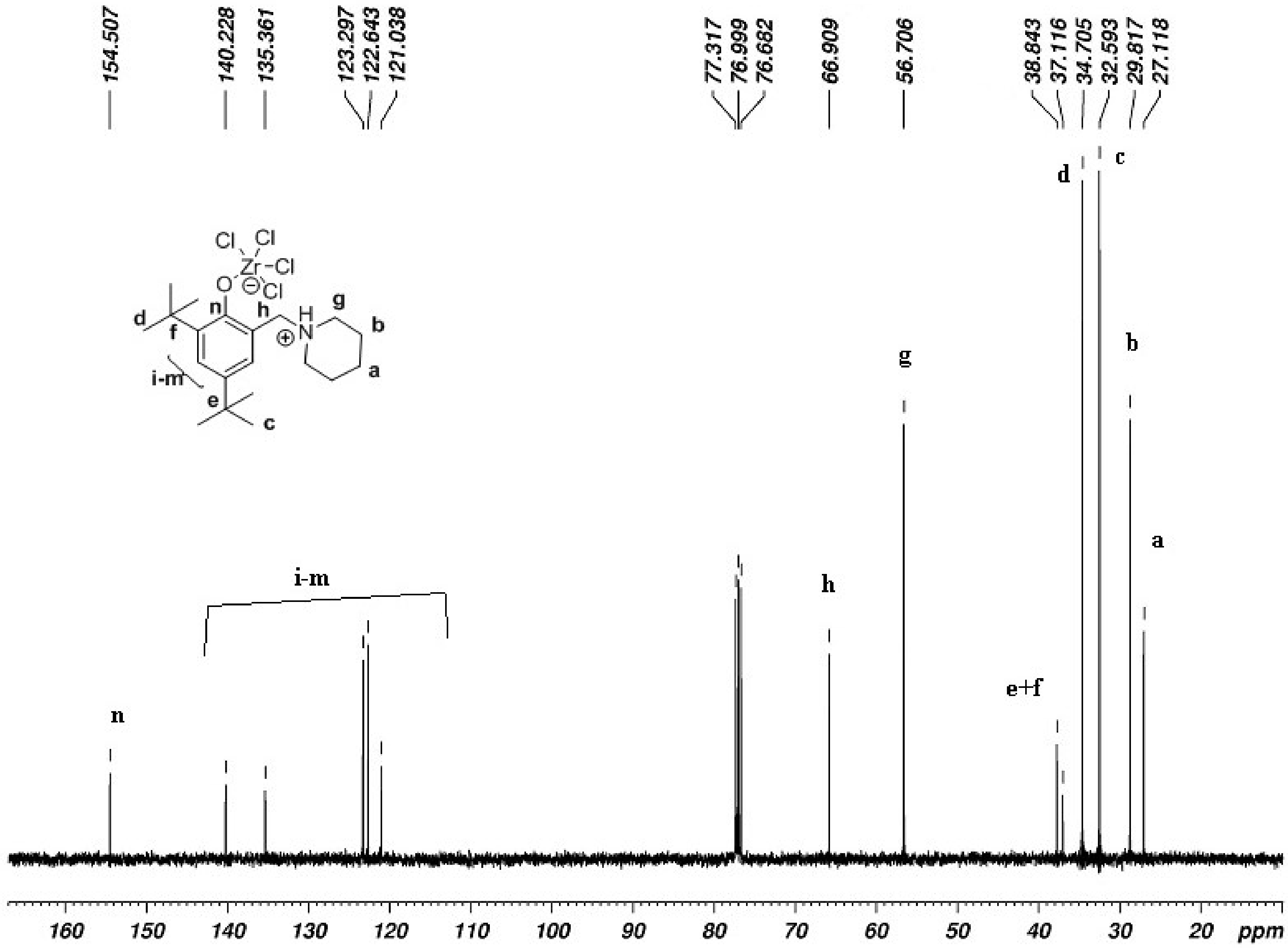
154.507
140.228
135.361
123.297
122.643
121.038
77.317
76.999
76.682
66.909
56.706
38.843
37.116
34.705
32.593
29.817
27.118
n
i-m
h
g
e+f
d
c
b
a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

Figure S17.[13]C NMR (100 MHz, $CDCl_3$) of Compound **6**

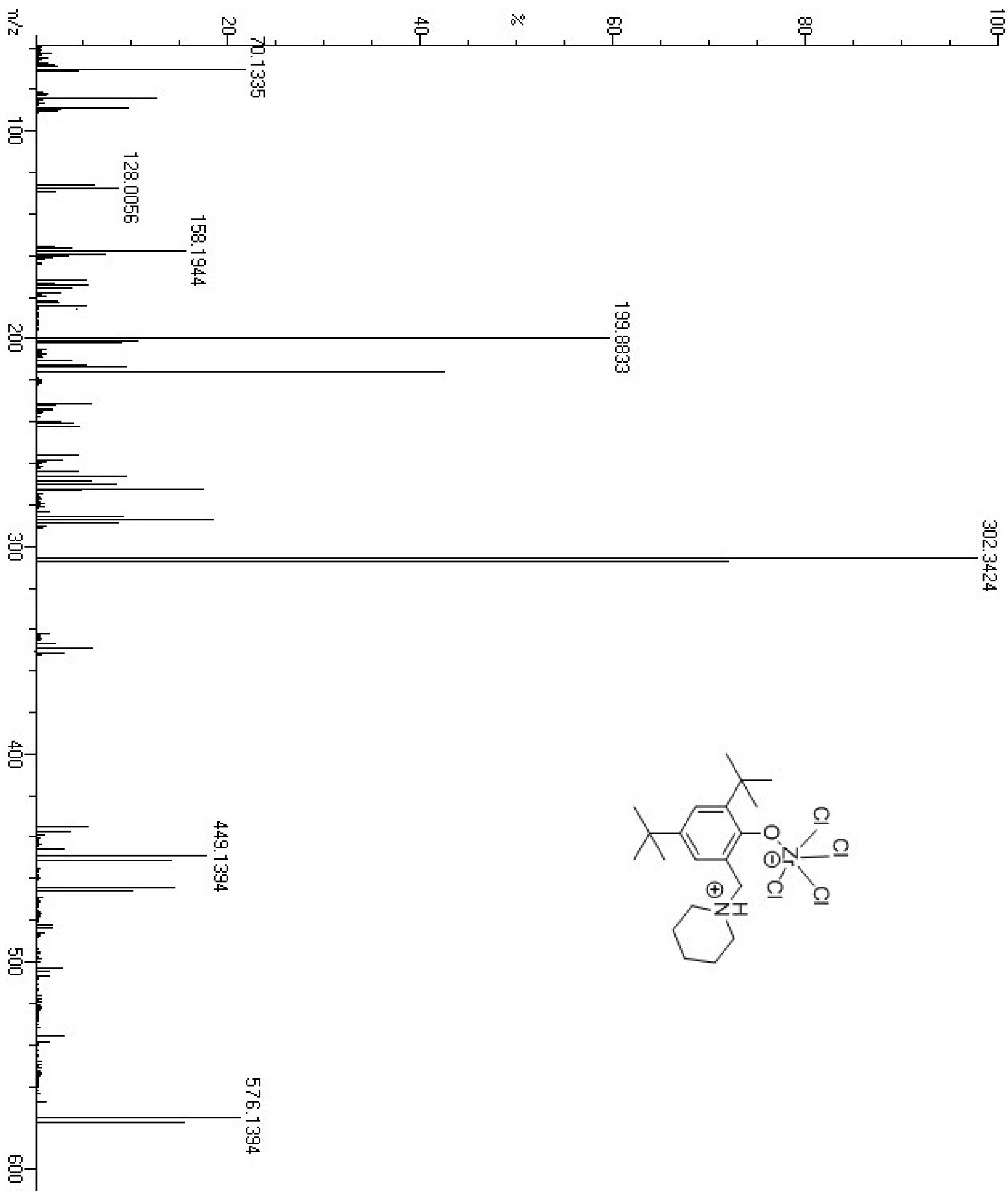

Figure S18. ESI mass spectrum of Compound **6**

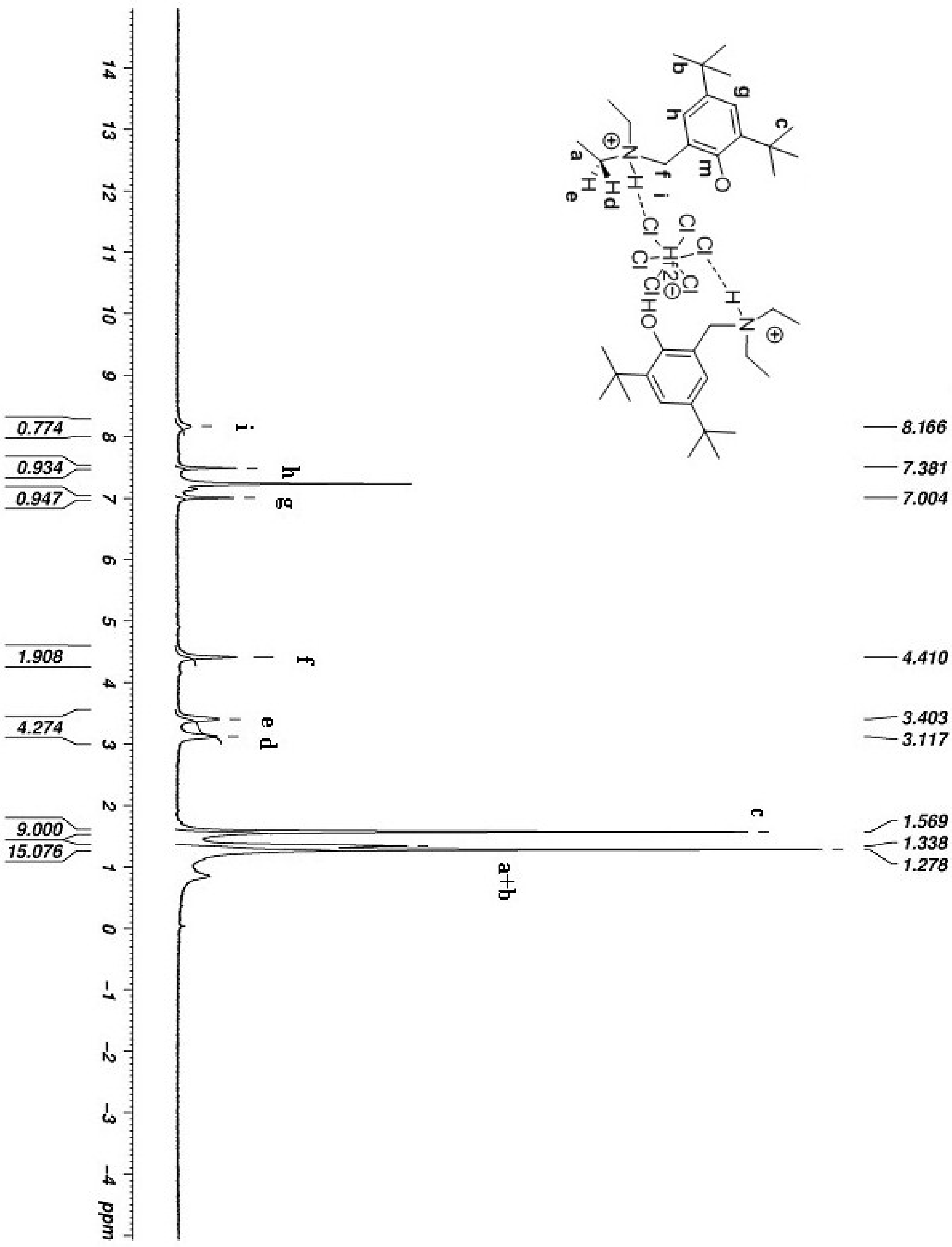

Figure S19.[1]H NMR (400 MHz, $CDCl_3$) of Compound **7**

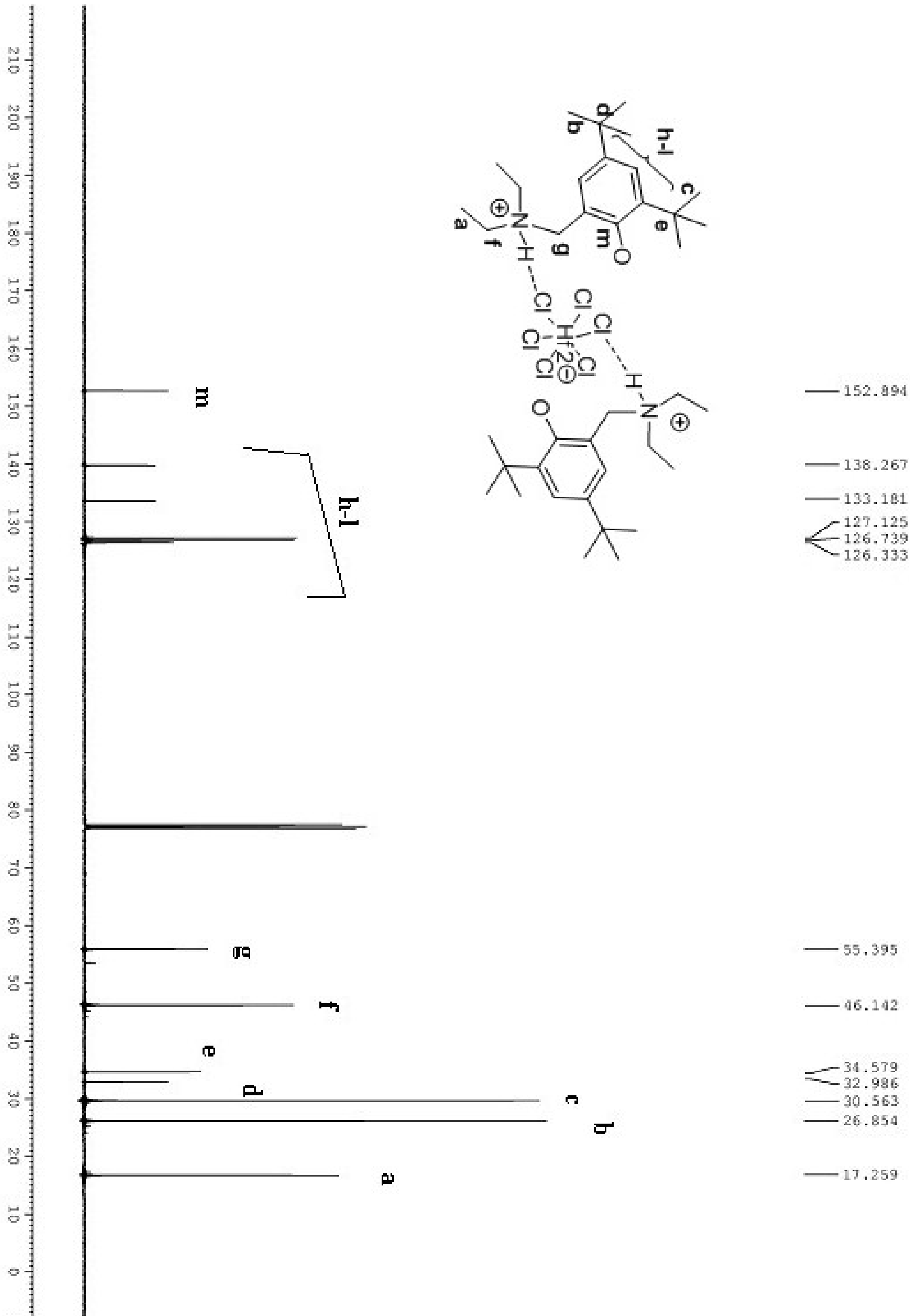

Figure S20. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **7**

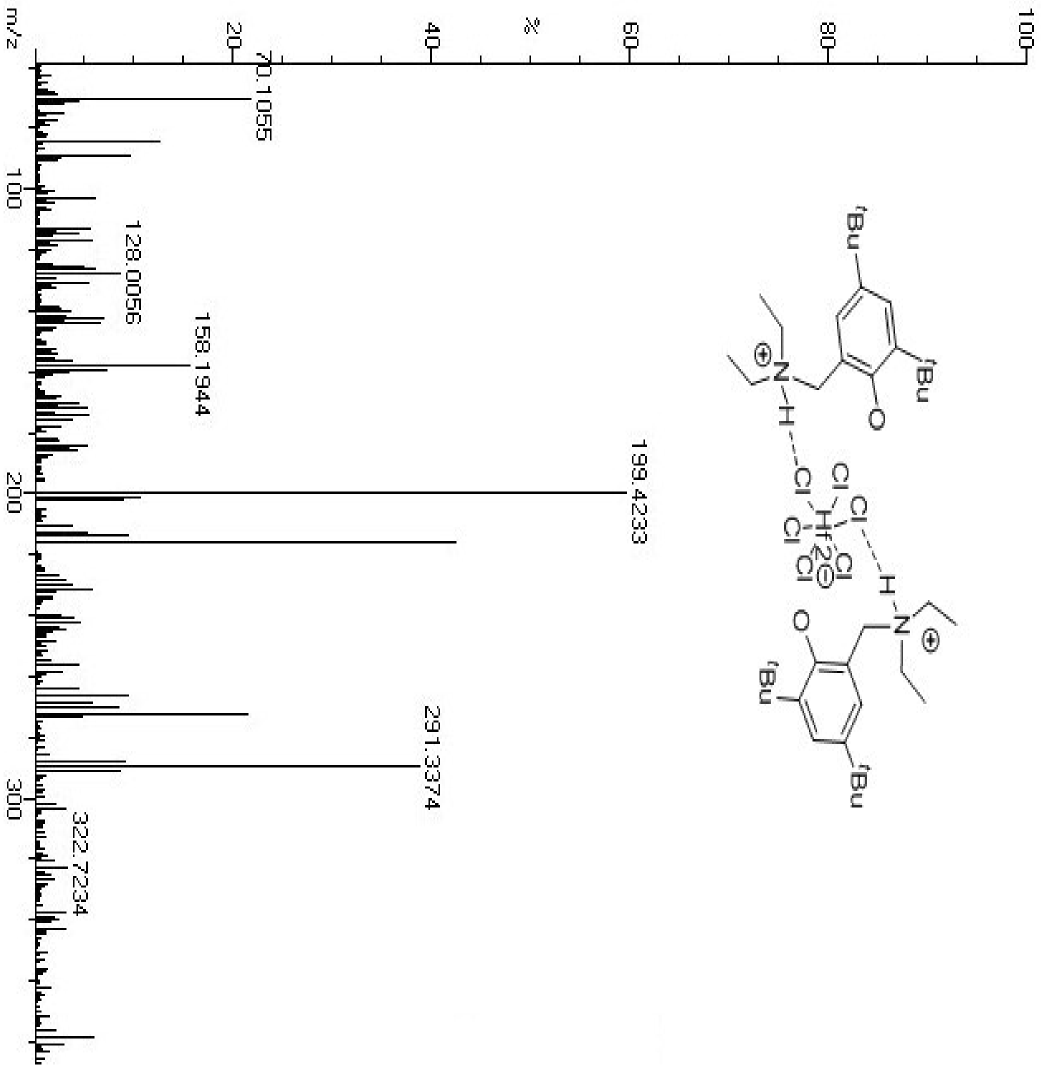

Figure S21. ESI mass spectrum of Compound **7**

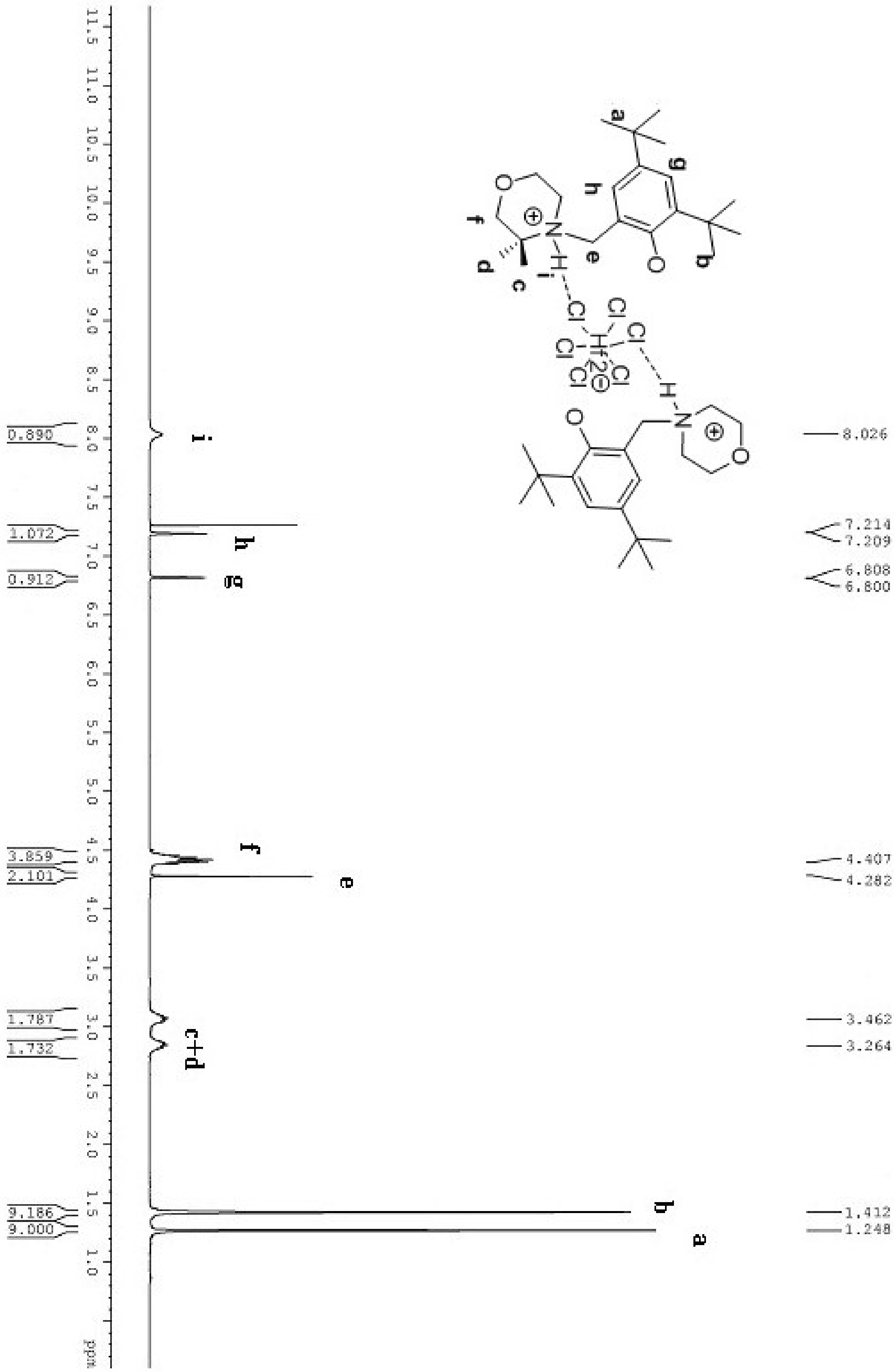

Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **8**

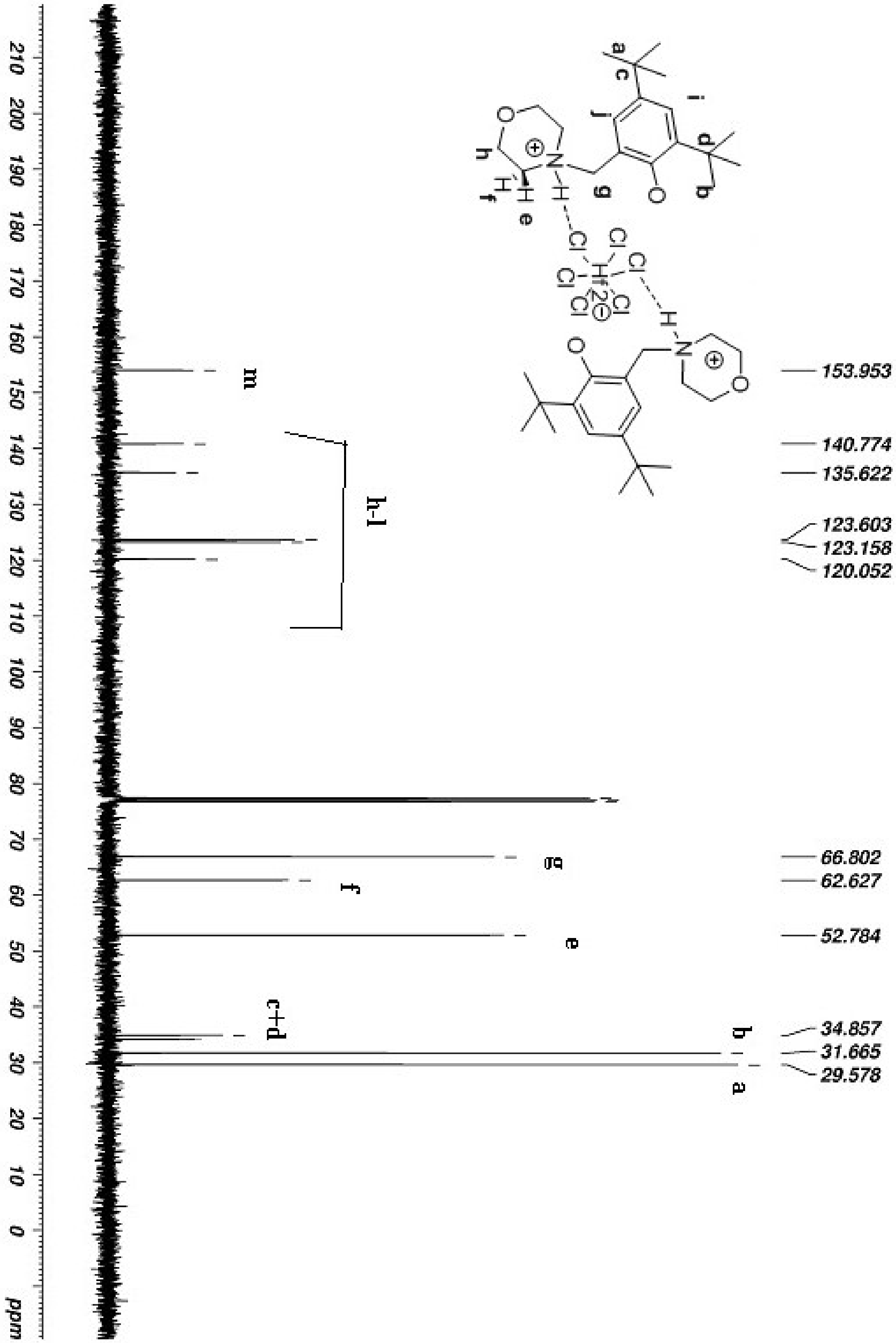

Figure S23. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **8**

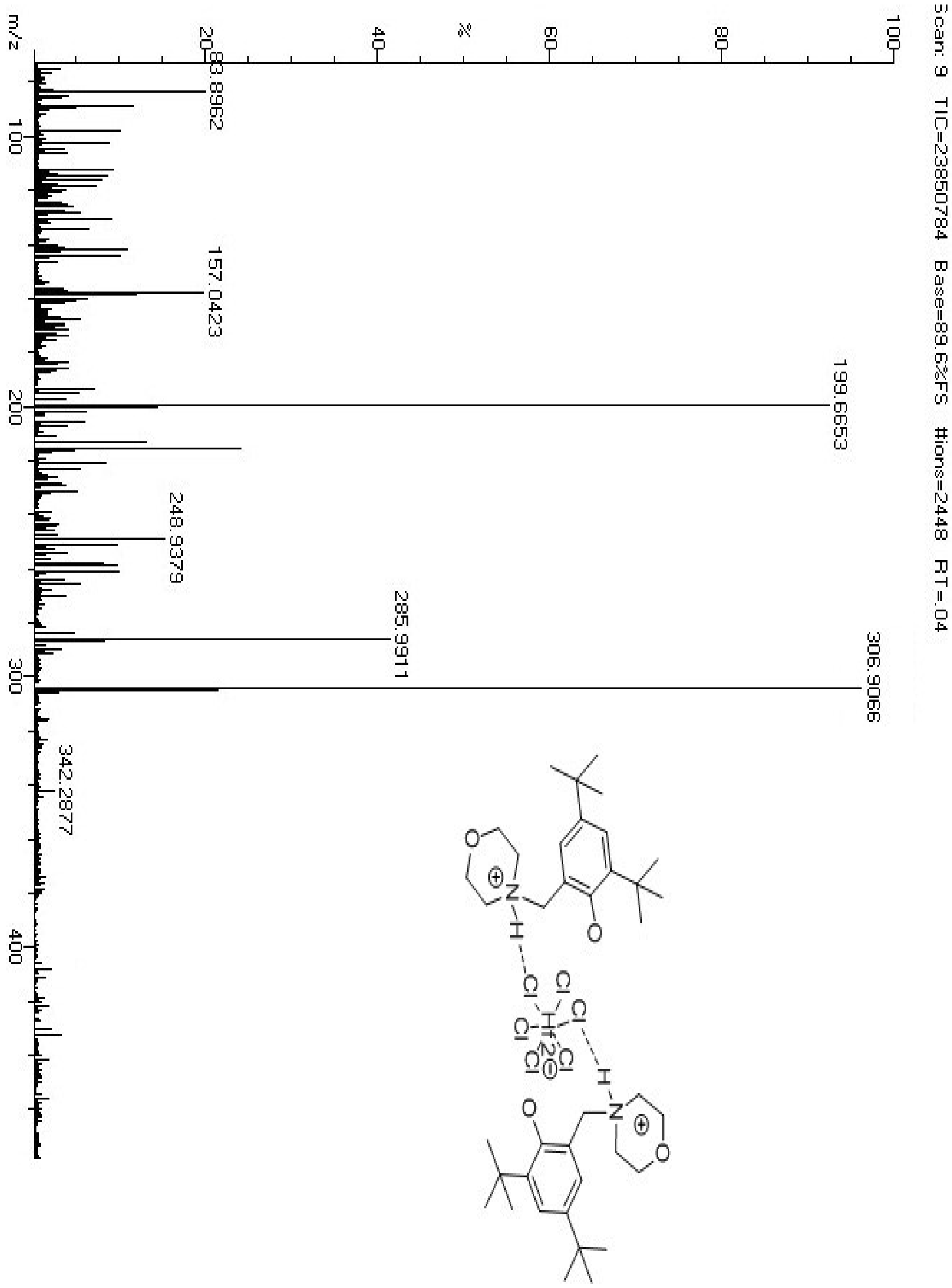

Figure S24. ESI mass spectrum of Compound **8**

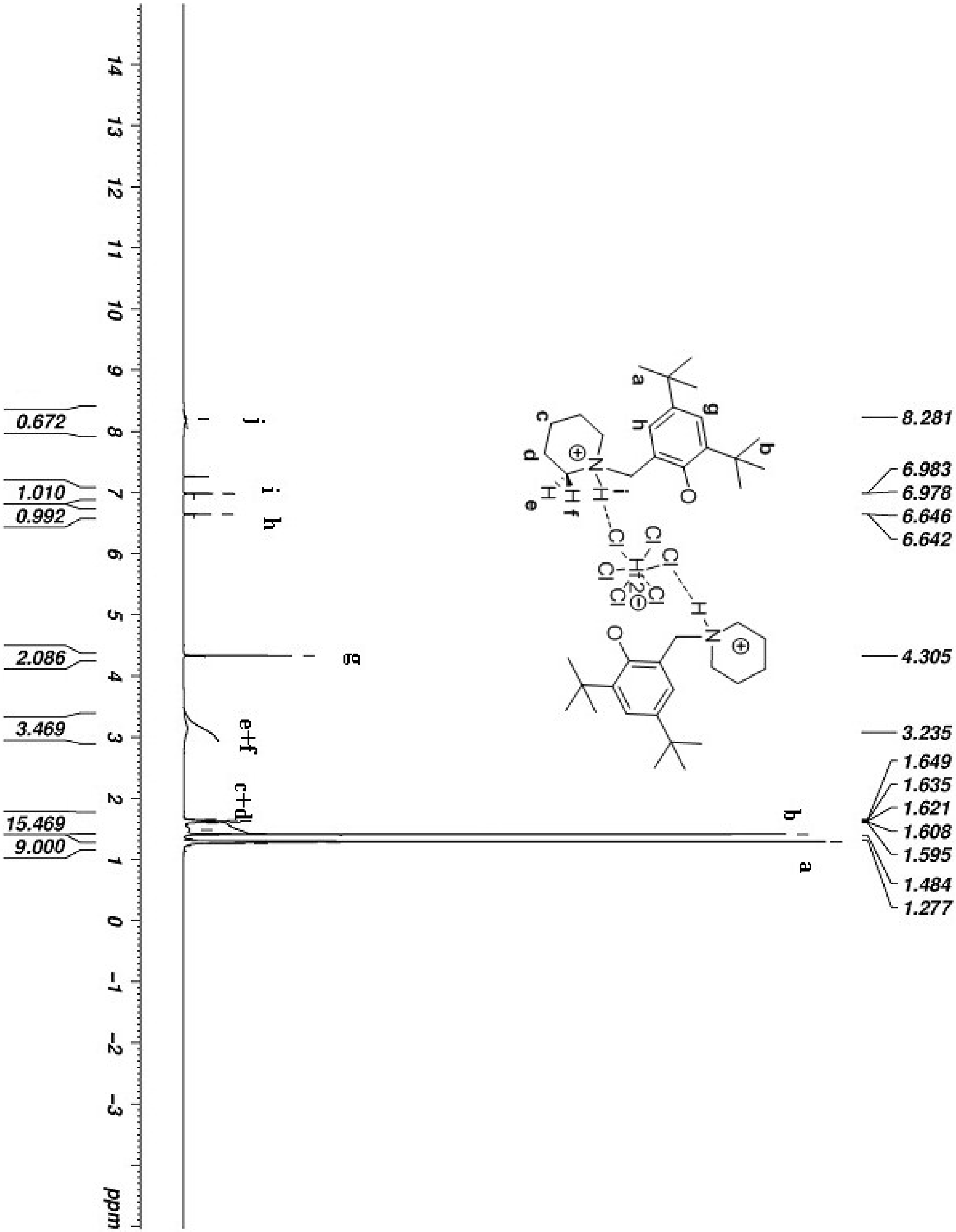

Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **9**

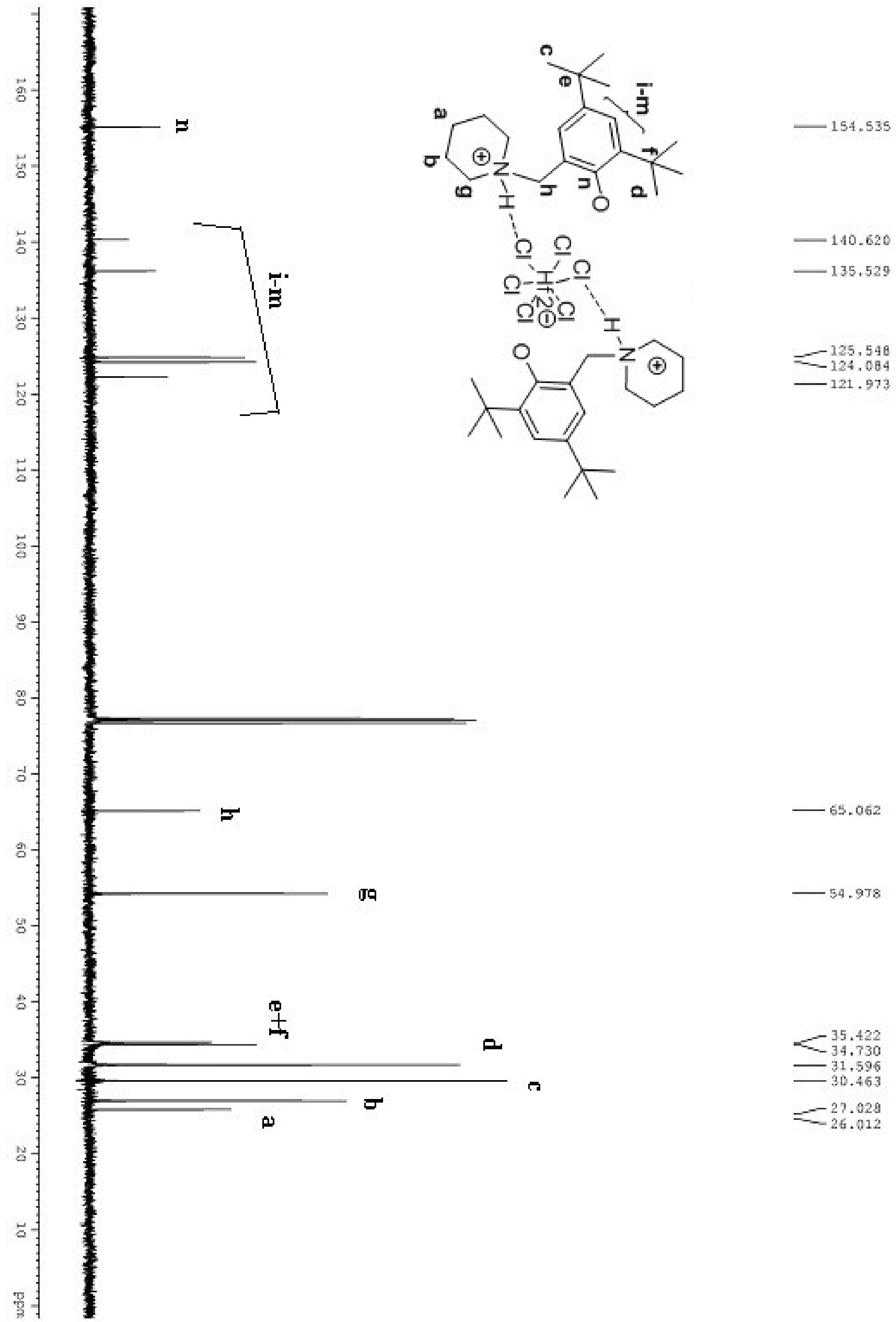

Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **9**

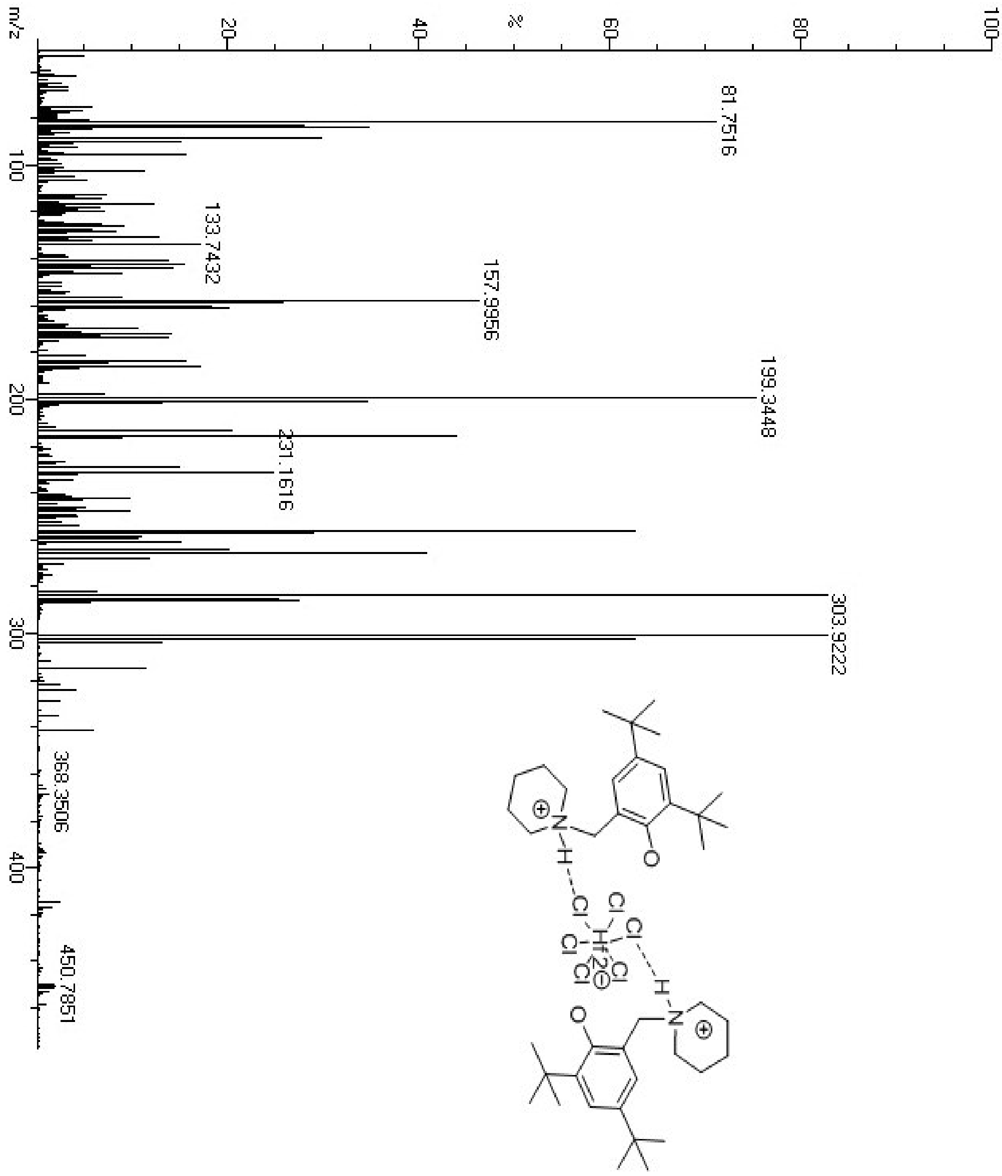

Figure S27. ESI mass spectrum of Compound **9**

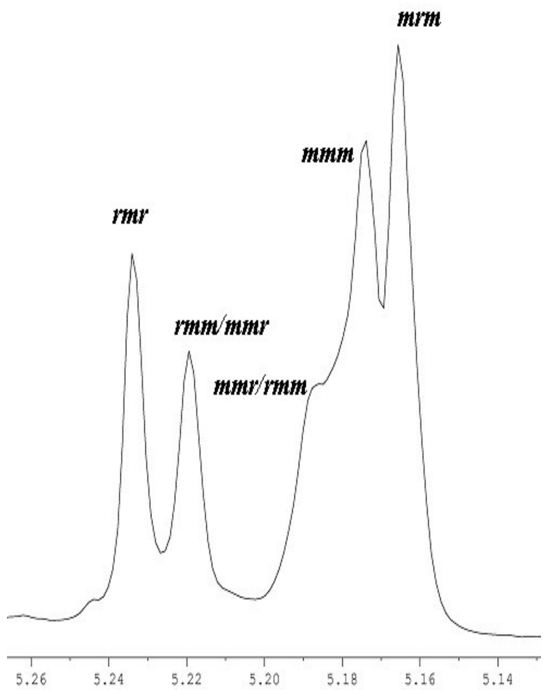

Figure S28. Homonuclear decoupled ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of the methine region of PLA obtained using **1**

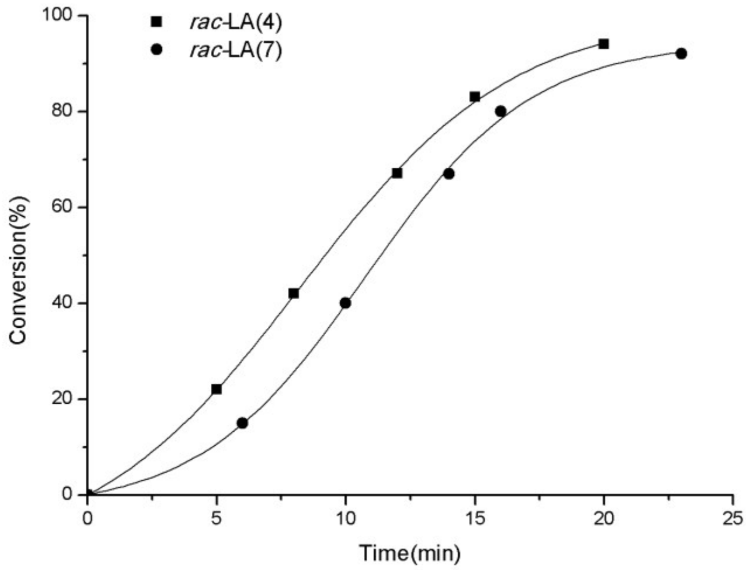

Figure S29. *rac*-LA conversion vs time plot using **4** and **7**: $[M]_0/[Cat]_0$= 200 at 140 °C

Table S1. Polymerization data for *rac*-LA catalyzed by complexes **2**, **3**, **4**, **5**, **8** and **9** in different $[rac\text{-LA}]_0/[\text{Cat}]_0$ ratio at 140 °C

Entry	Cat.	$[rac\text{-LA}]_0/[\text{Cat}]_0$	time[a] (min)	Yield (%)	M_n(GPC)[b] (kg/mol)	$M_n^{(\text{theoretical})c}$ (kg/mol)	TOF[d] (min^{-1})	M_w/M_n
1	**2**	400/1	50	98	59.24	57.95	7.84	1.08
2	**2**	800/1	80	97	117.05	115.62	9.70	1.10
3	**3**	400/1	50	98	55.70	57.95	7.84	1.09
4	**3**	800/1	85	98	115.04	115.62	9.22	1.12
5	**5**	400/1	55	98	60.03	57.95	7.13	1.10
6	**5**	800/1	90	97	118.65	115.62	8.62	1.11
7	**6**	400/1	60	99	59.20	57.95	6.60	1.08
8	**6**	800/1	92	97	116.42	115.62	8.43	1.09
9	**8**	400/1	70	97	56.30	57.95	5.54	1.14
10	**8**	800/1	98	97	117.28	115.62	7.92	1.15
11	**9**	400/1	75	98	55.83	57.95	5.23	1.11
12	**9**	800/1	105	97	116.77	115.62	7.39	1.12

[a]Time of polymerization was measured by quenching the polymerization reaction when all the monomer were found to be consumed. [b]Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n. [c]$M_n^{(\text{theoretical})}$ at 100% = $[M]_0/[C]_0$ × molecular weight of monomer + molecular weight of end group. [d]TOFs were calculated as (mol of LA consumed) / (mol of catalyst × time of polymerization).

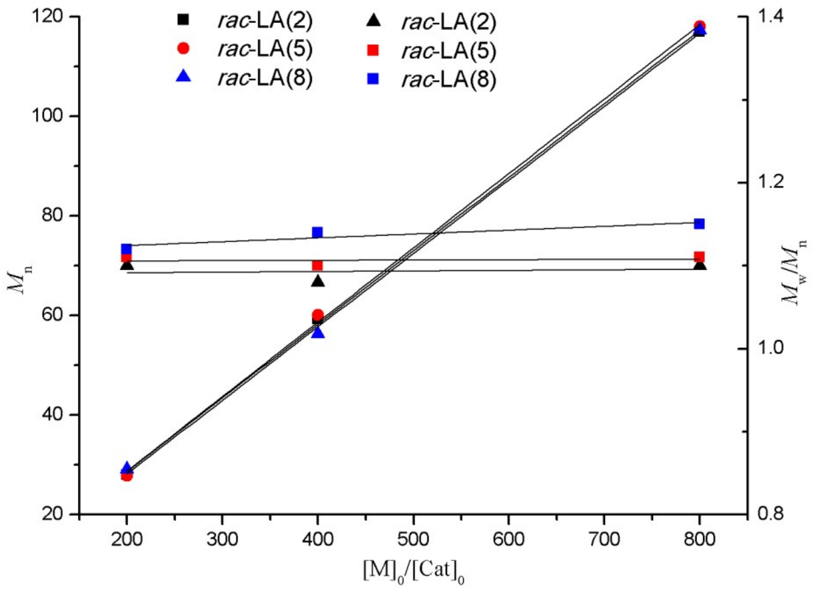

Figure S30. Plot of M_n and MWD *vs*. $[M]_0/[\text{Cat}]_0$ for *rac*-LA polymerization at 140 °C using **2**, **5** and **8**

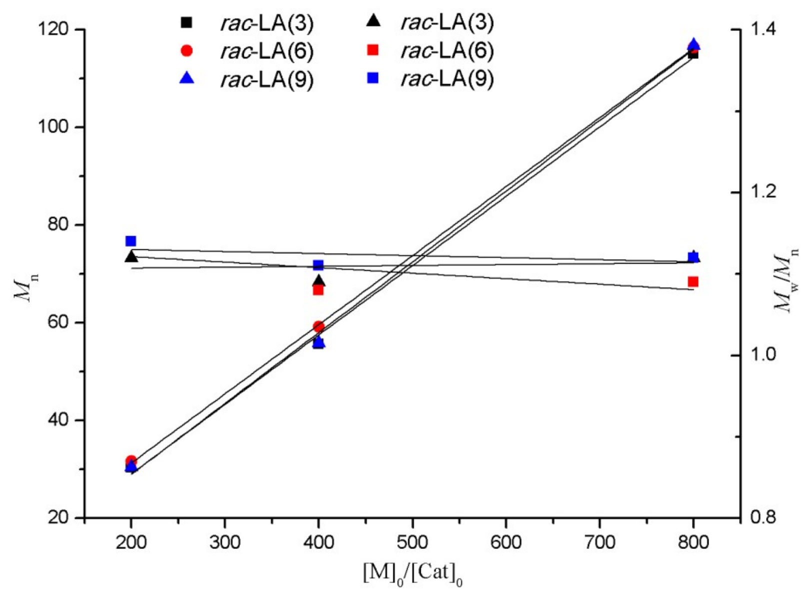

Figure S31. Plot of M_n and MWD *vs*. $[M]_0/[Cat]_0$ for *rac*-LA polymerization at 140 °C using **3**, **6** and **9**

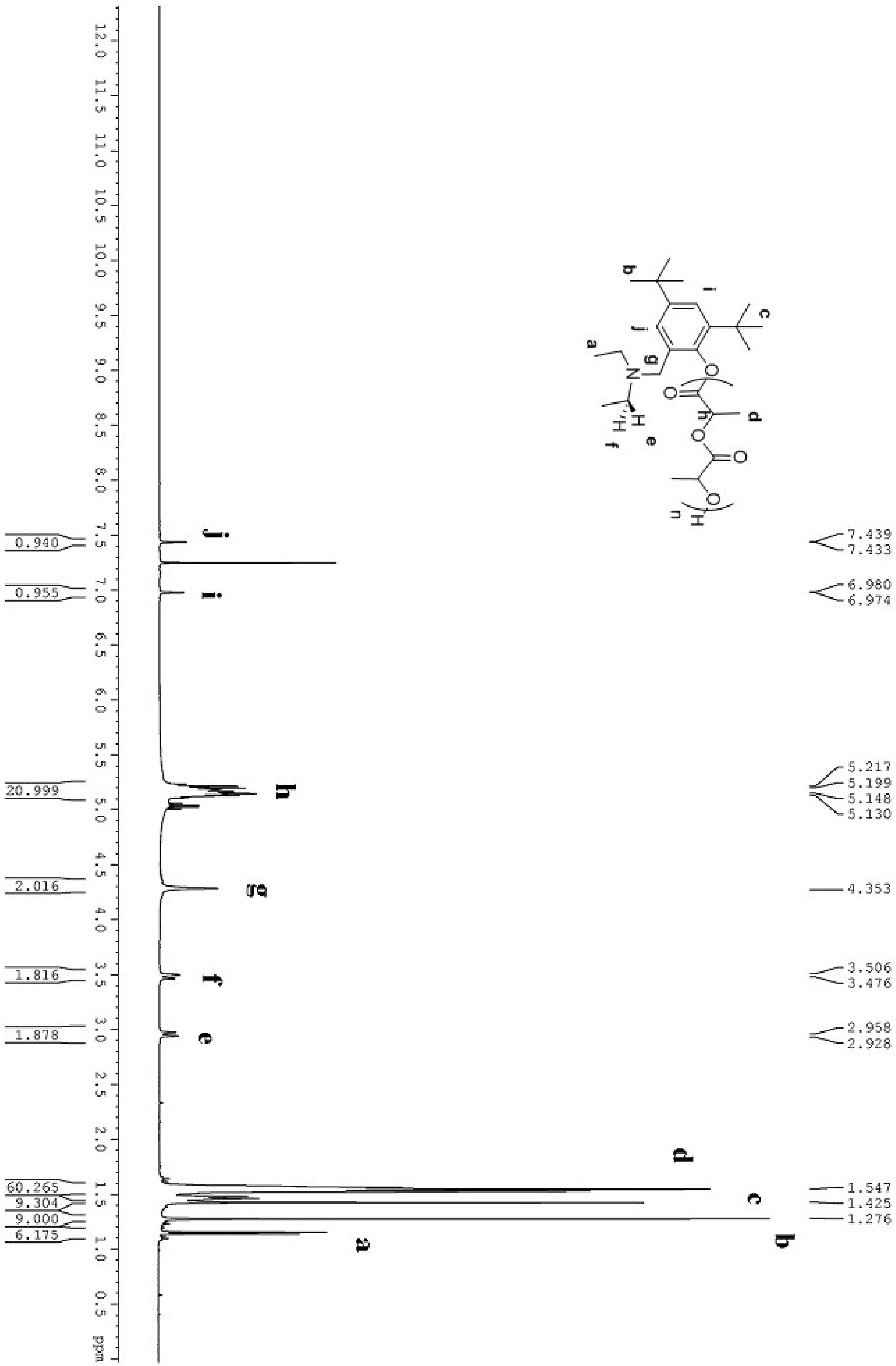

Figure S32. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the crude product obtained from a reaction between *rac*-LA and **1** in 10:1 ratio at 140 °C

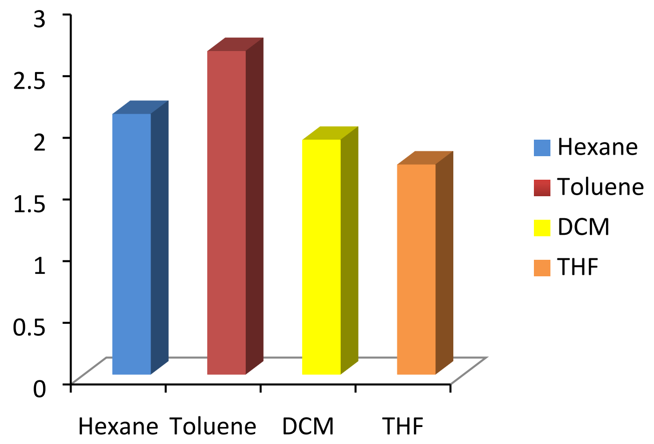

Figure S33. Activity of **1** in different solvent in ethylene polymerization

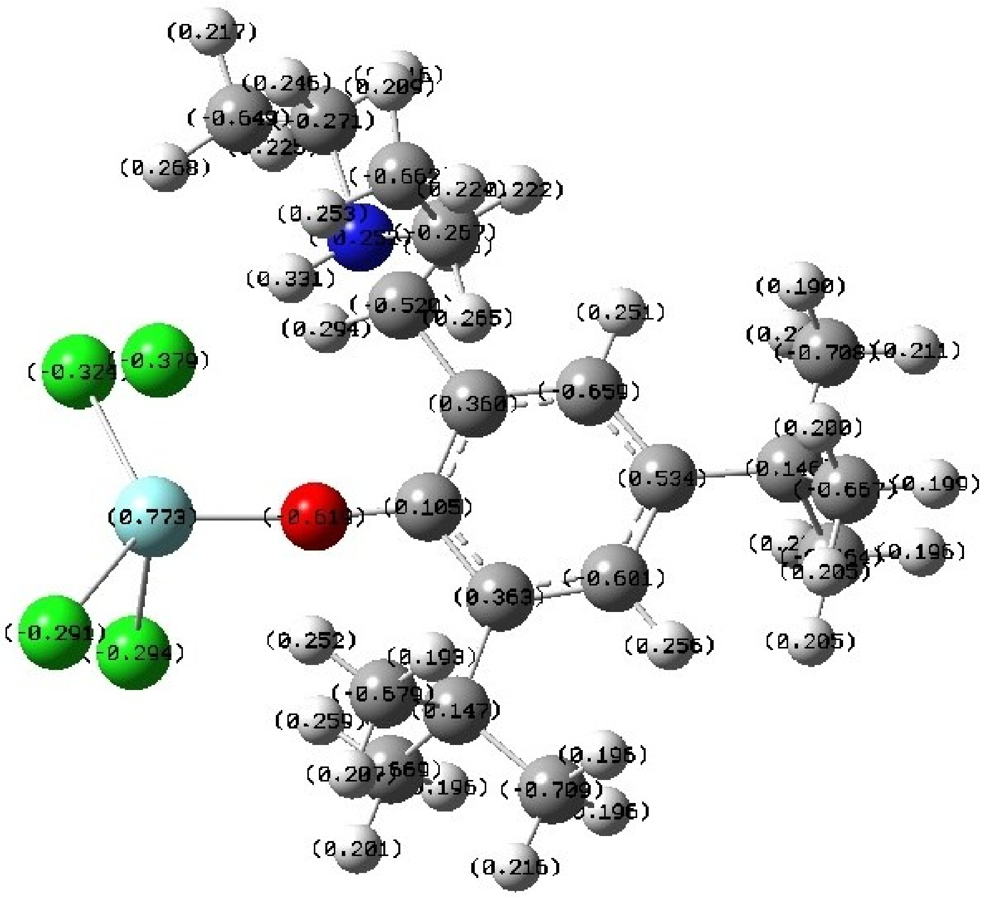

Figure S34. Mulliken partial charges of complex **4**

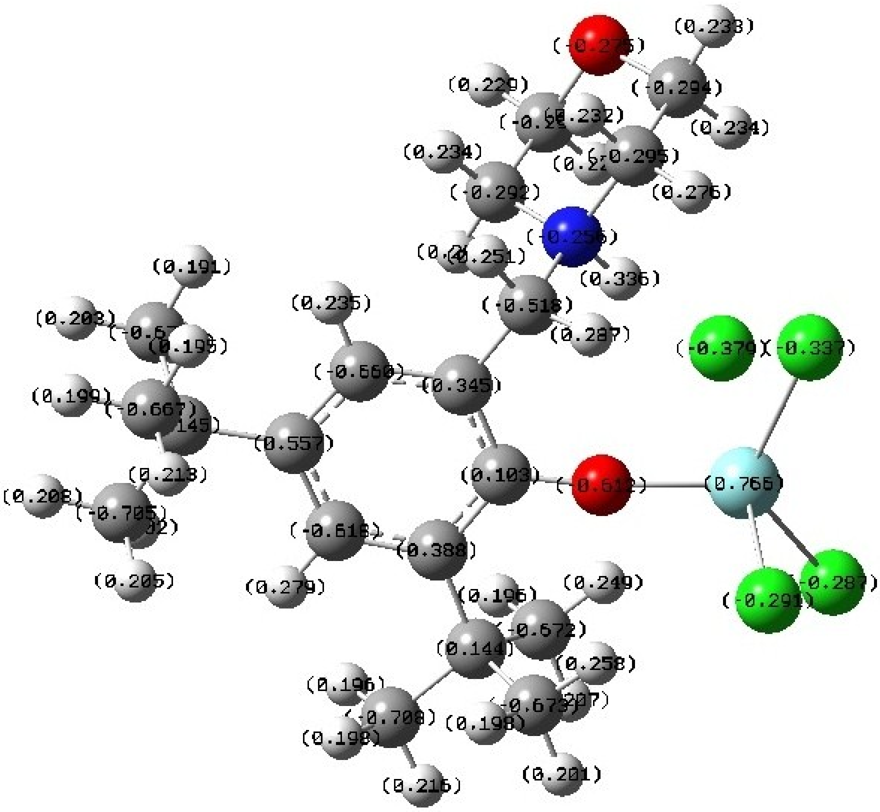

Figure S35. Mulliken partial charges of complex **5**

Table S2. Selected X-ray and calculated bond lengths and bond angles of **1, 4** and **5**

S. No.	Compound	Bond Length (Å)			Bond Angle (°)		
		Entry	X-ray	Calculated	Entry	X-ray	Calculated
1.	**1**	O1-Ti1	1.76(7)	1.75	O1-Ti1-Cl3	116.7(6)	115.0
2.		Cl1-Ti1	2.31(9)	2.32	O1-Ti1-Cl4	114.0(6)	112.8
3.		Cl2-Ti1	2.37(7)	2.36	Cl3-Ti1-Cl4	129.1(3)	128.4
4.		Cl3-Ti1	2.28(7)	2.29	Cl1-Ti1-Cl2	174.8(3)	175.1
5.		Cl4-Ti1	2.24(6)	2.25			
6.	**4**	O1-Zr1	1.95(2)	1.96	O1-Zr1-N1	176.3(1)	178.4
7.		Cl1-Zr1	2.43(1)	2.41	Cl1-Zr1-Cl2	93.3(4)	91.7
8.		Cl2- Zr1	2.45(1)	2.44	Cl1-Zr1-Cl4	89.9(3)	88.5
9.		Cl3- Zr1	2.49(1)	2.48	Cl2-Zr1-Cl4	167.3(4)	170.4
10.		Cl4- Zr1	2.50(1)	2.49			
11.		N1- Zr1	2.34(3)	2.36			
12.	**5**	O1-Zr1	1.92(2)	1.88	O1-Zr1-N1	168.9(1)	172.4
13.		Cl1-Zr1	2.51(9)	2.49	Cl2-Zr1-Cl3	87.1(3)	88.2
14.		Cl2- Zr1	2.52(1)	2.50	Cl3-Zr1-Cl5	85.9(3)	87.6
15.		Cl3- Zr1	2.43(1)	2.44	Cl5-Zr1-Cl4	89.6(3)	87.5
16.		Cl4- Zr1	2.44(1)	2.46			
17.		N1- Zr1	2.38(3)	2.36			