Electronic Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

Imino Phenoxide Complexes of Group 4 metals: Synthesis, Structural Characterization and Polymerization Studies

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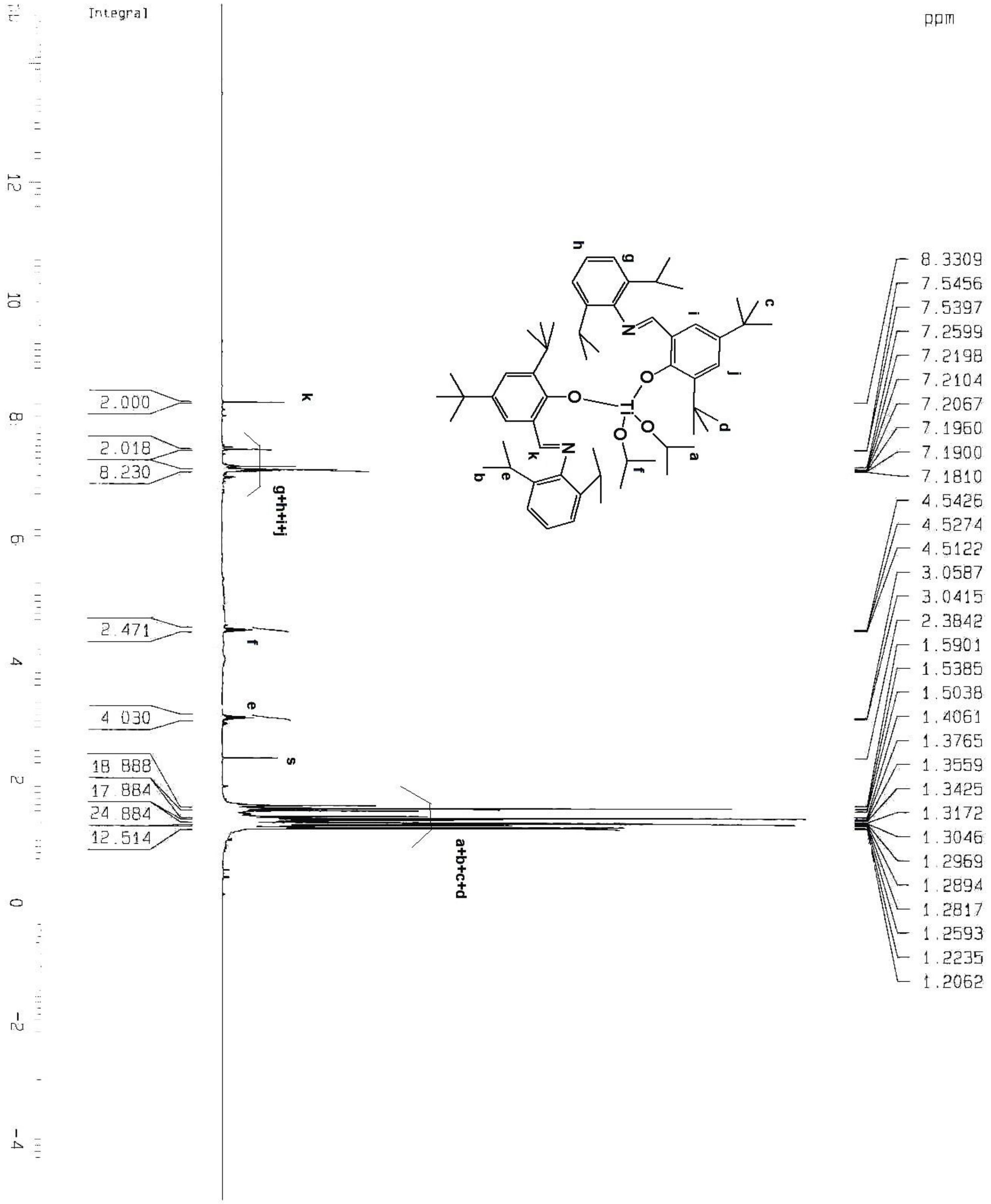


Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **1**

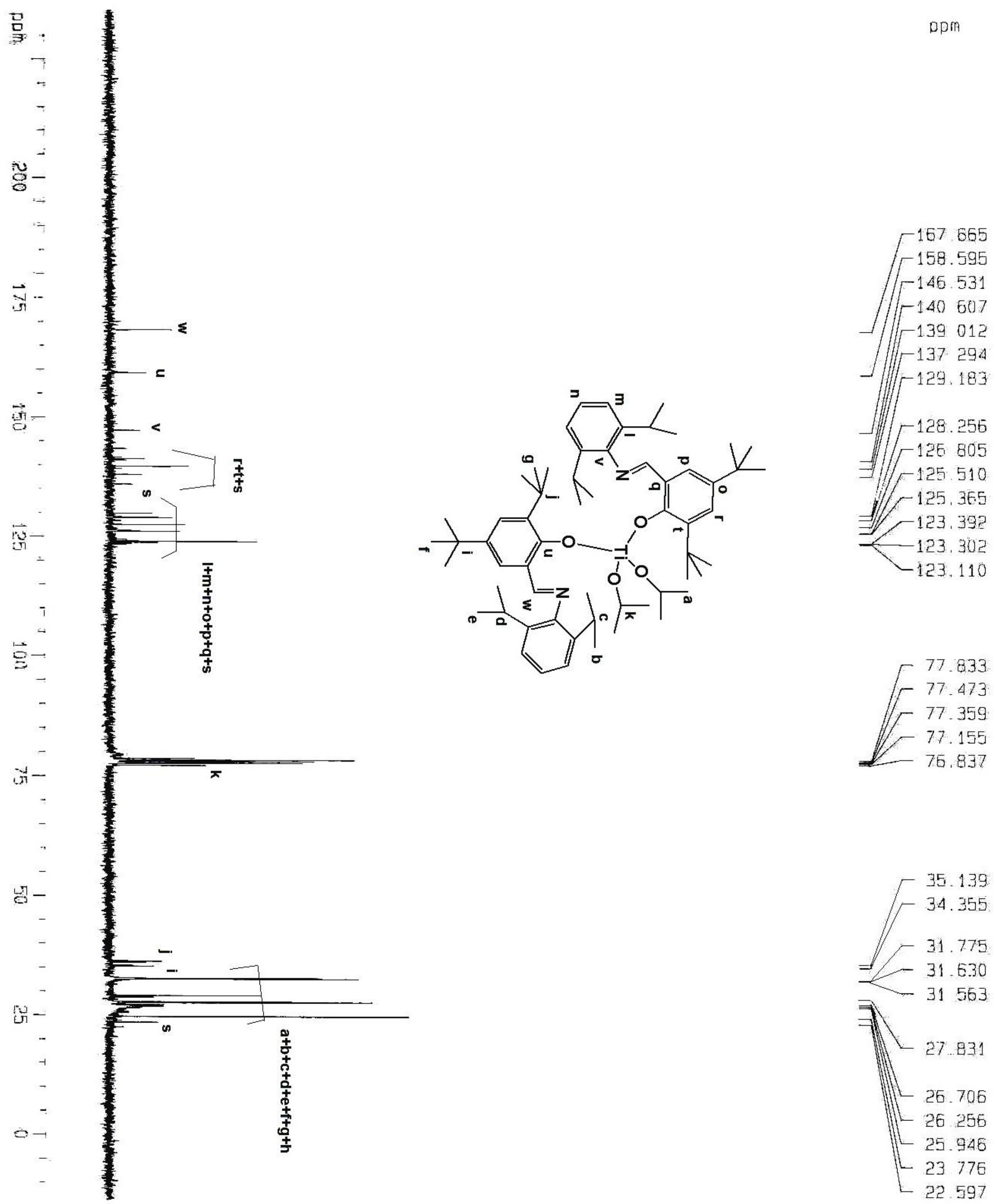


Fig. S2. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **1**

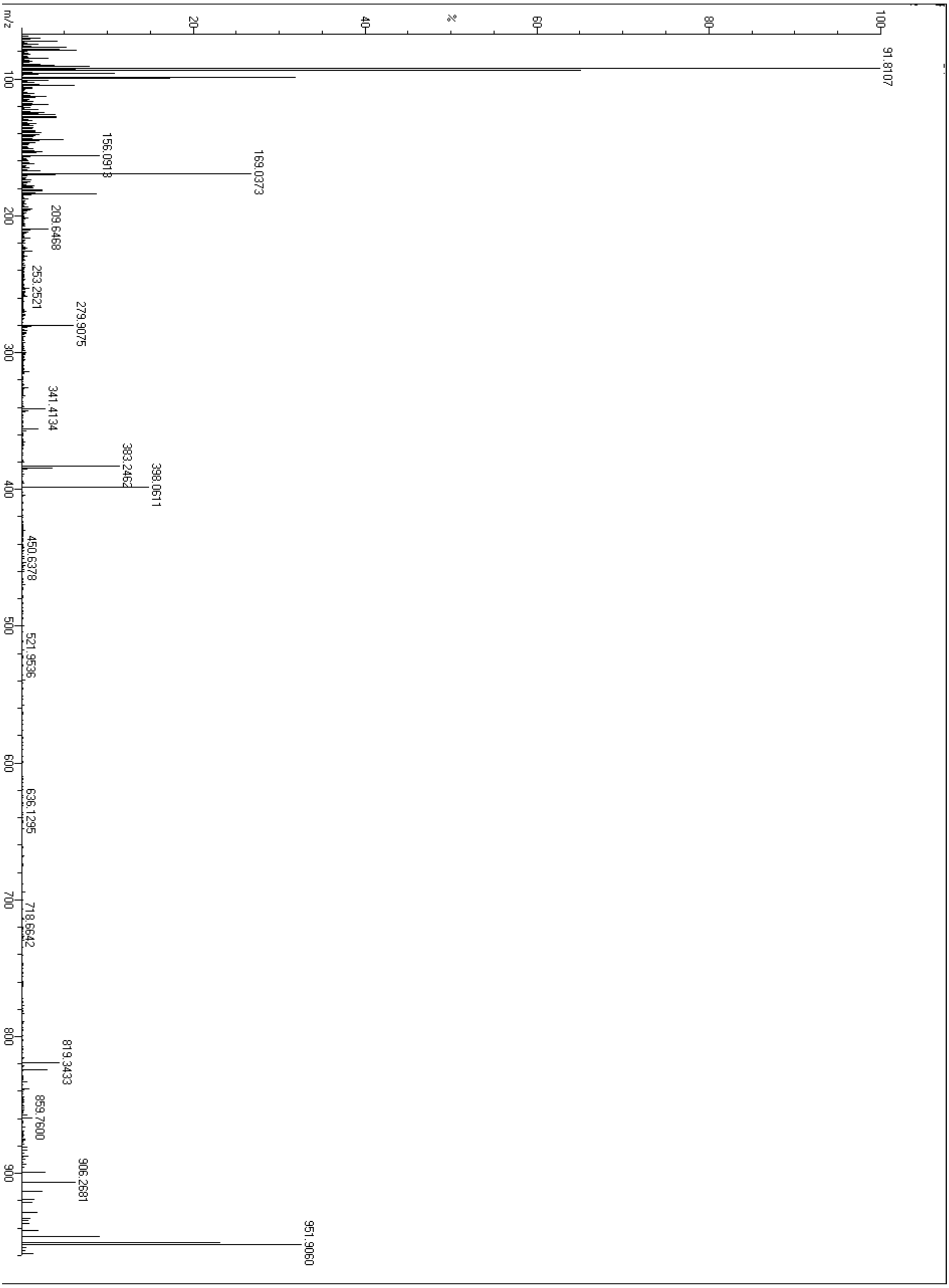


Fig. S3. ESI-Mass Spectrum of Compound **1**

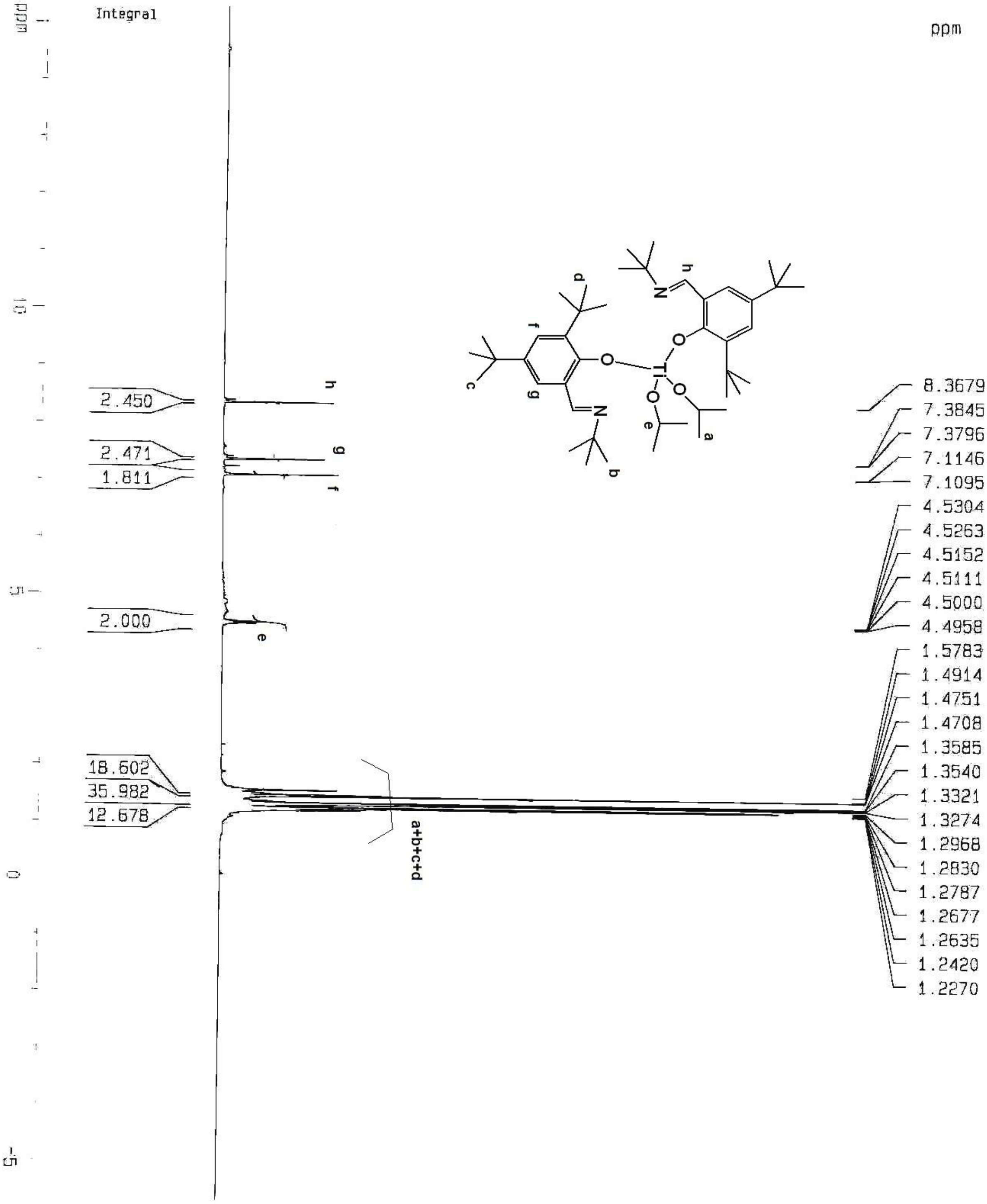


Fig. S4. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **2**

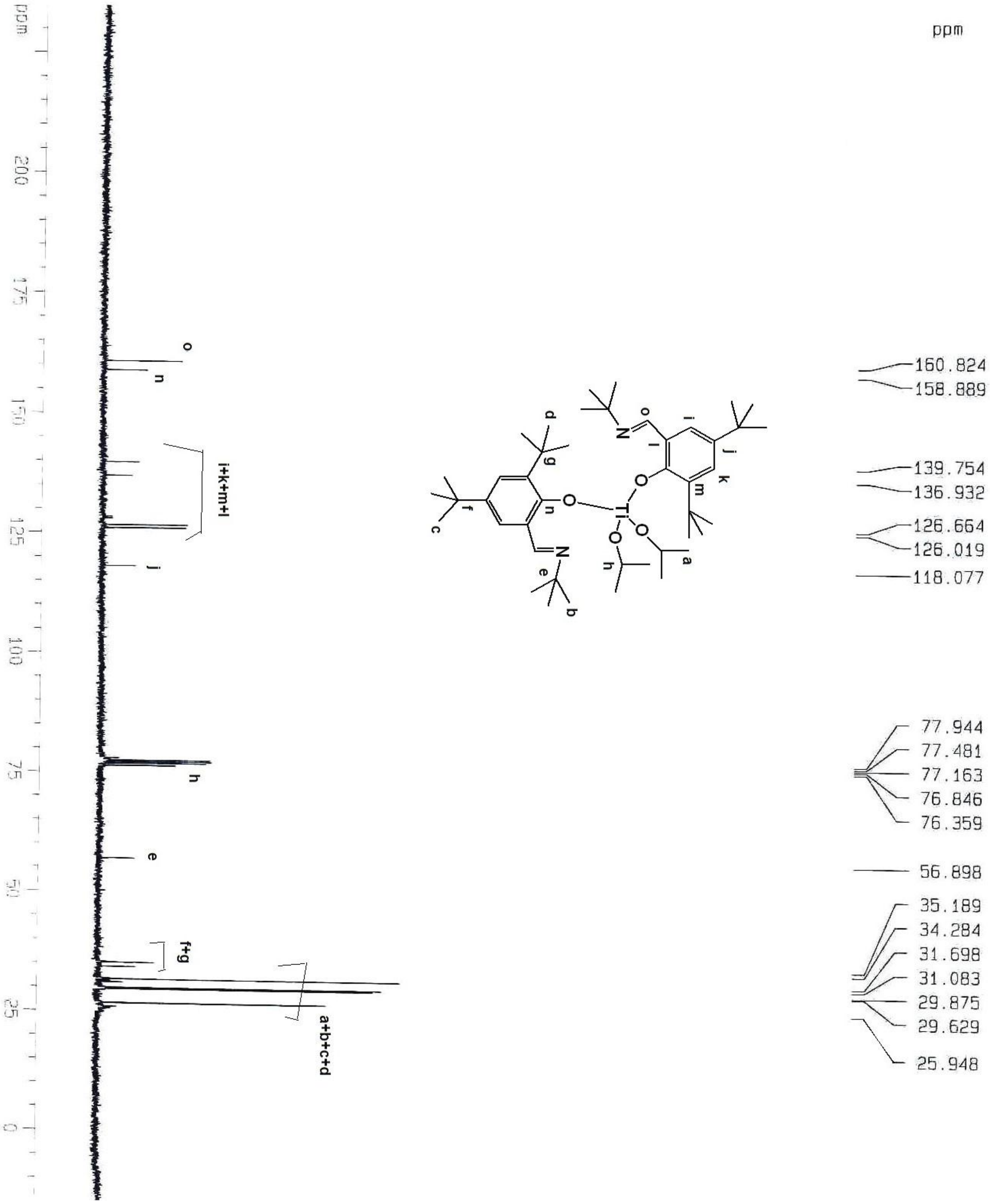


Fig. S5. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **2**

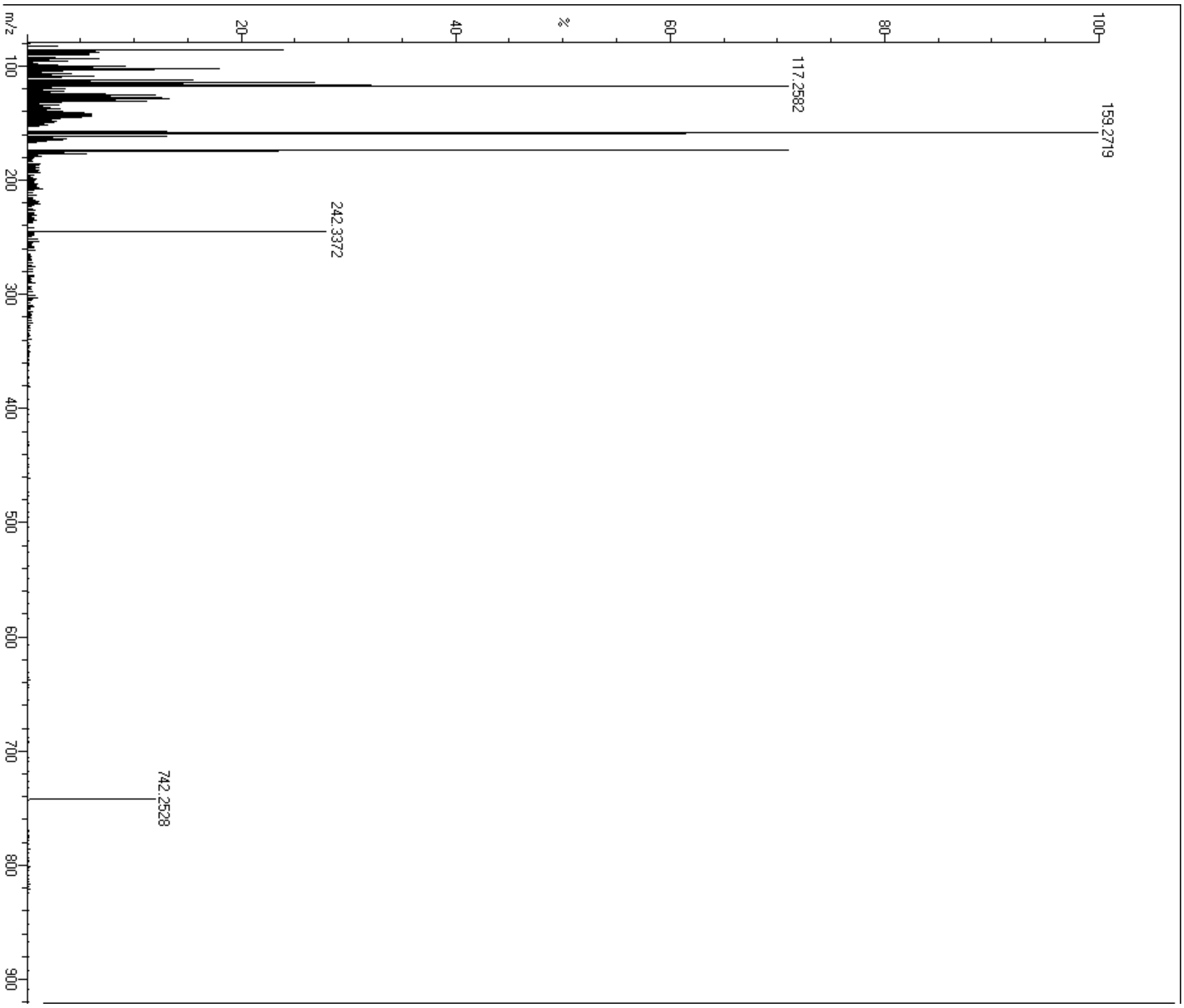


Fig. S6. ESI-Mass spectrum of Compound **2**

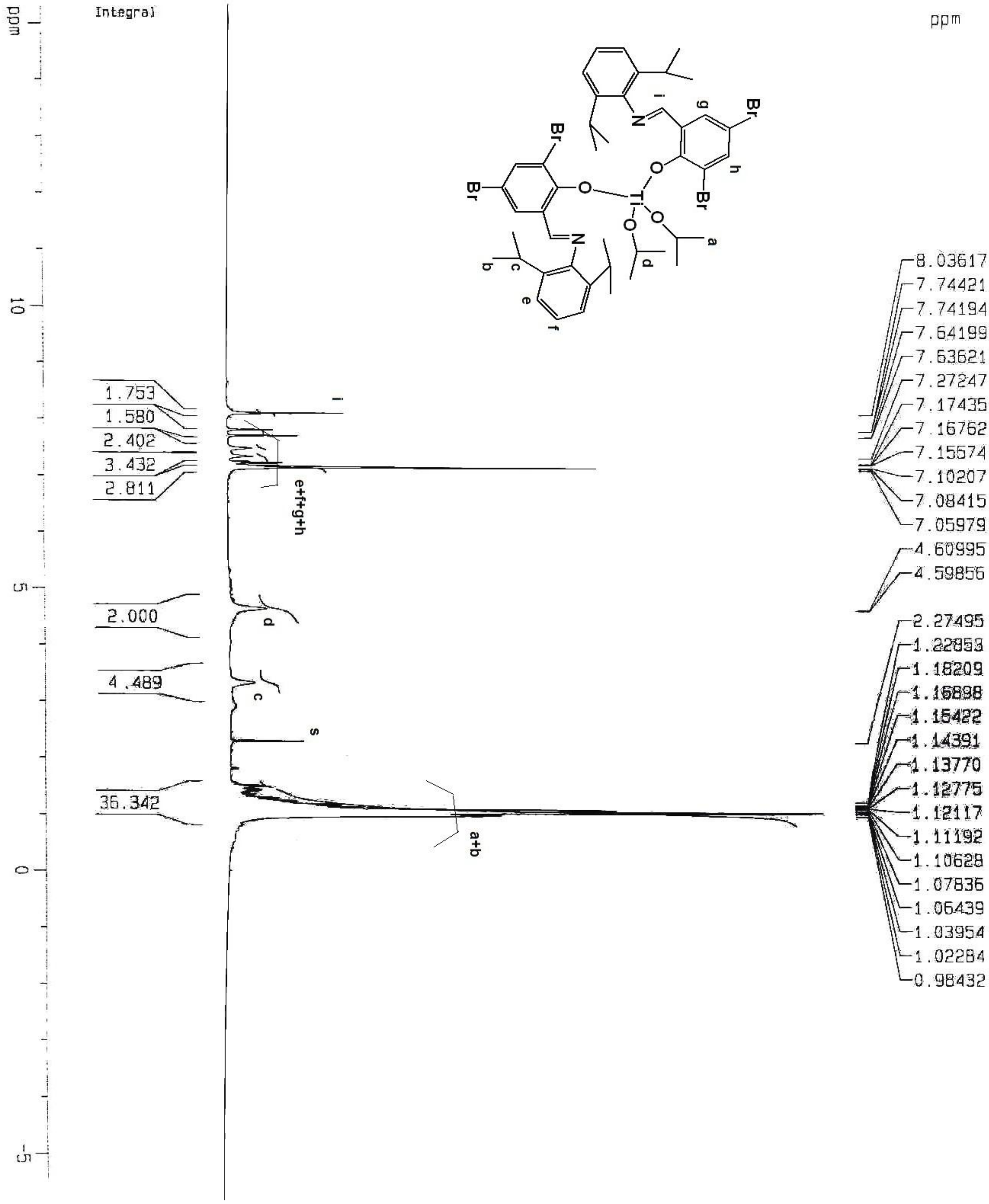


Fig. S7. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3**

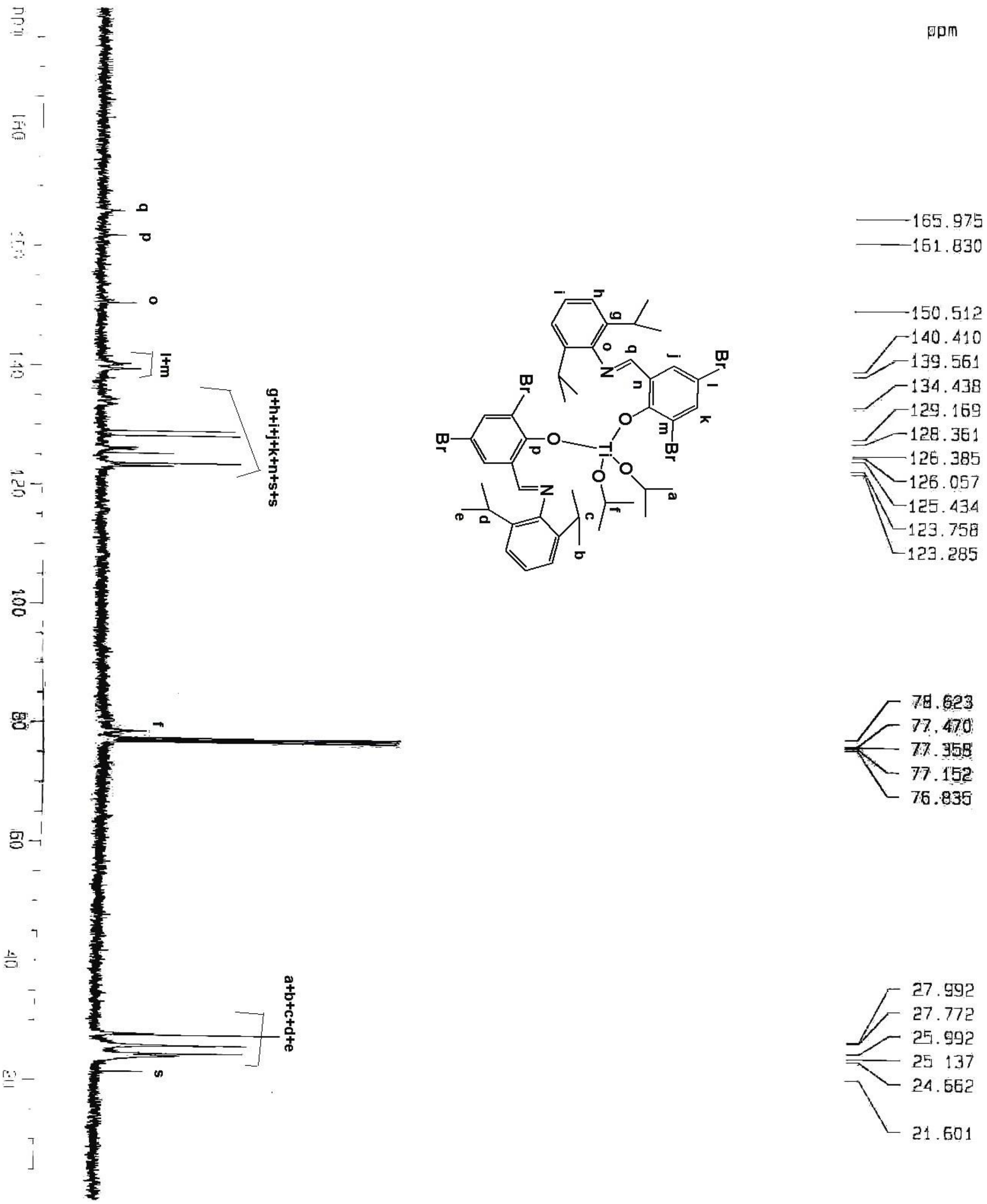


Fig. S8. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3**

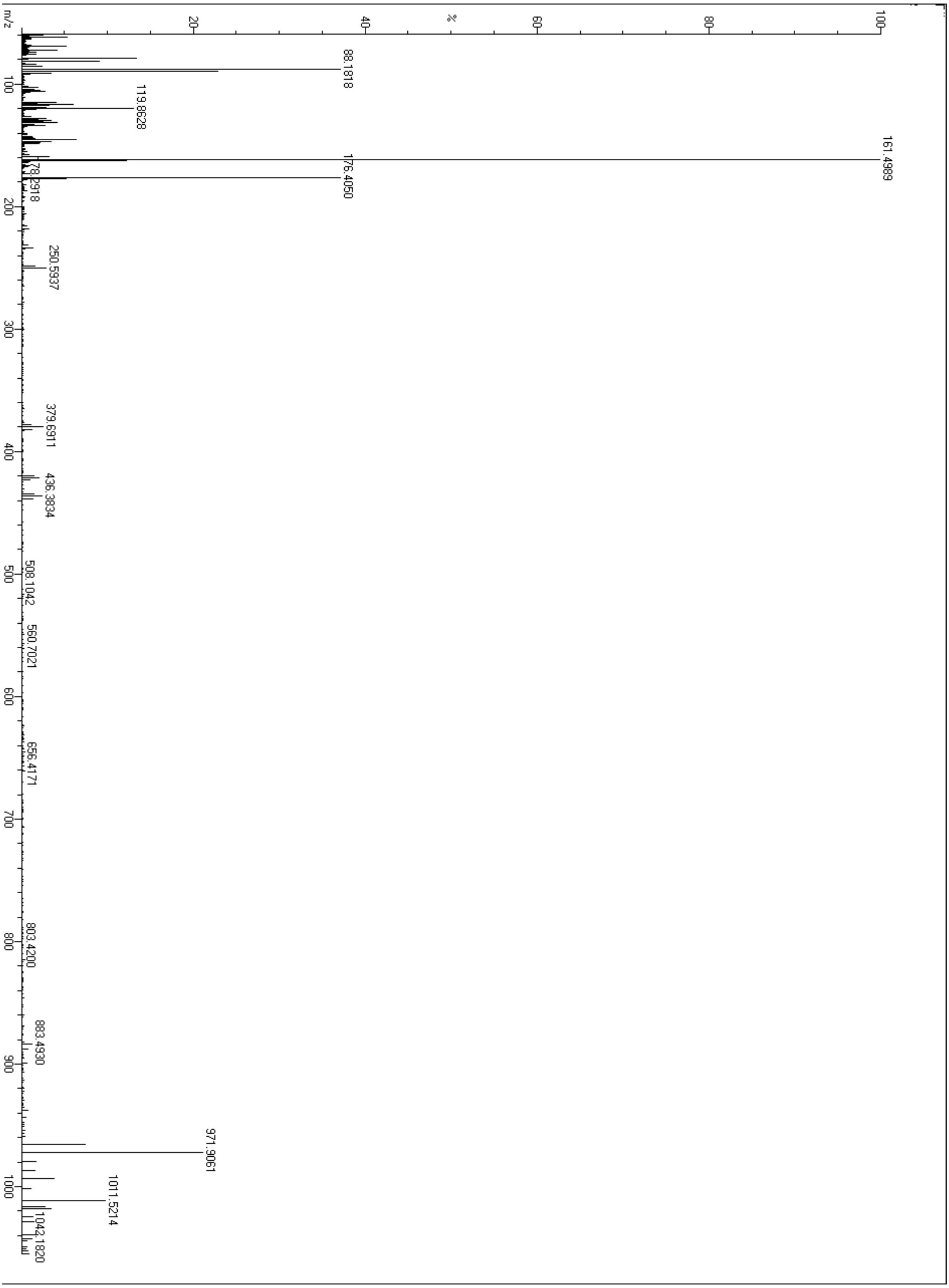


Fig. S9. ESI-Mass Spectrum of Compound **3**

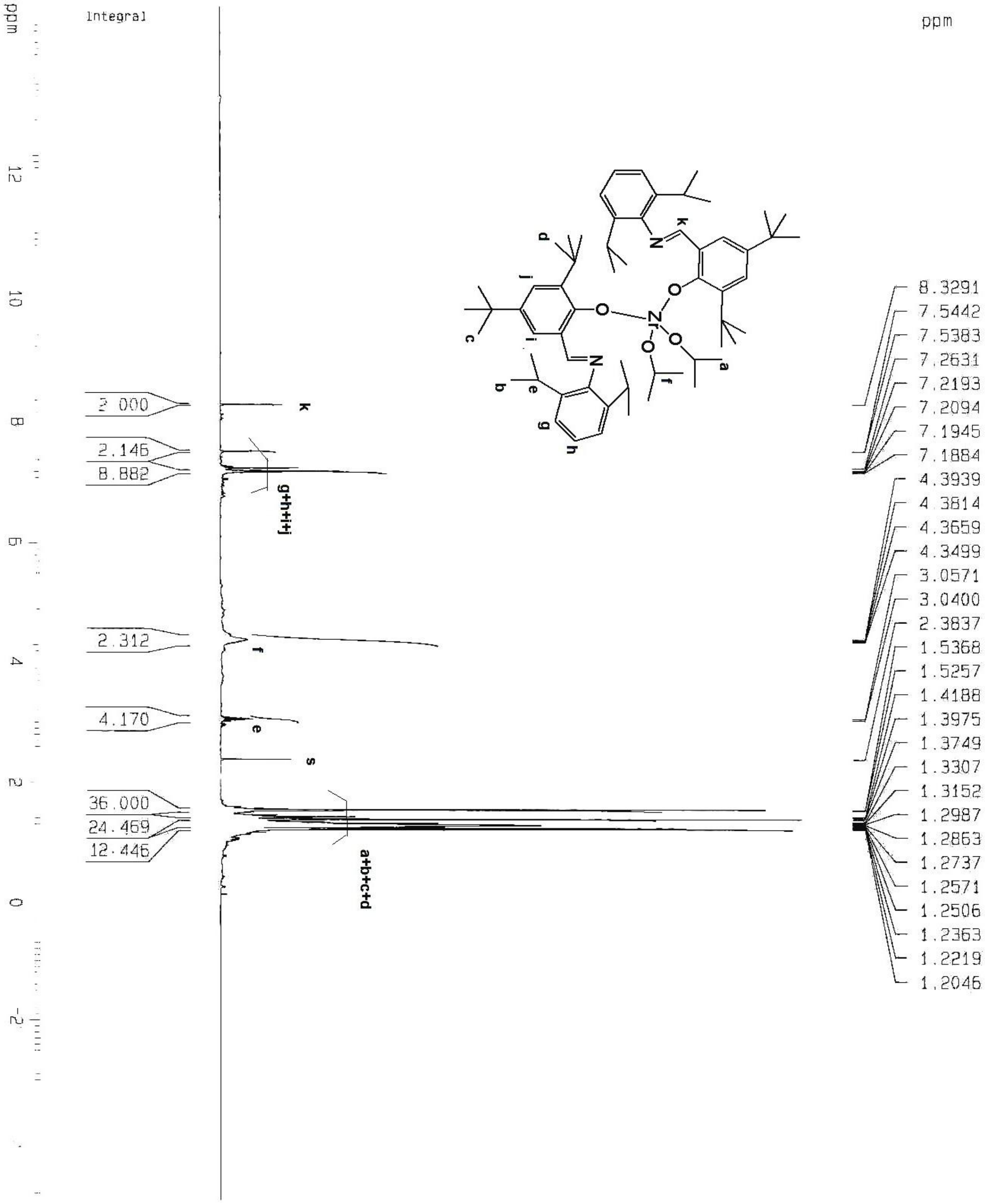


Fig. S10. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **4**

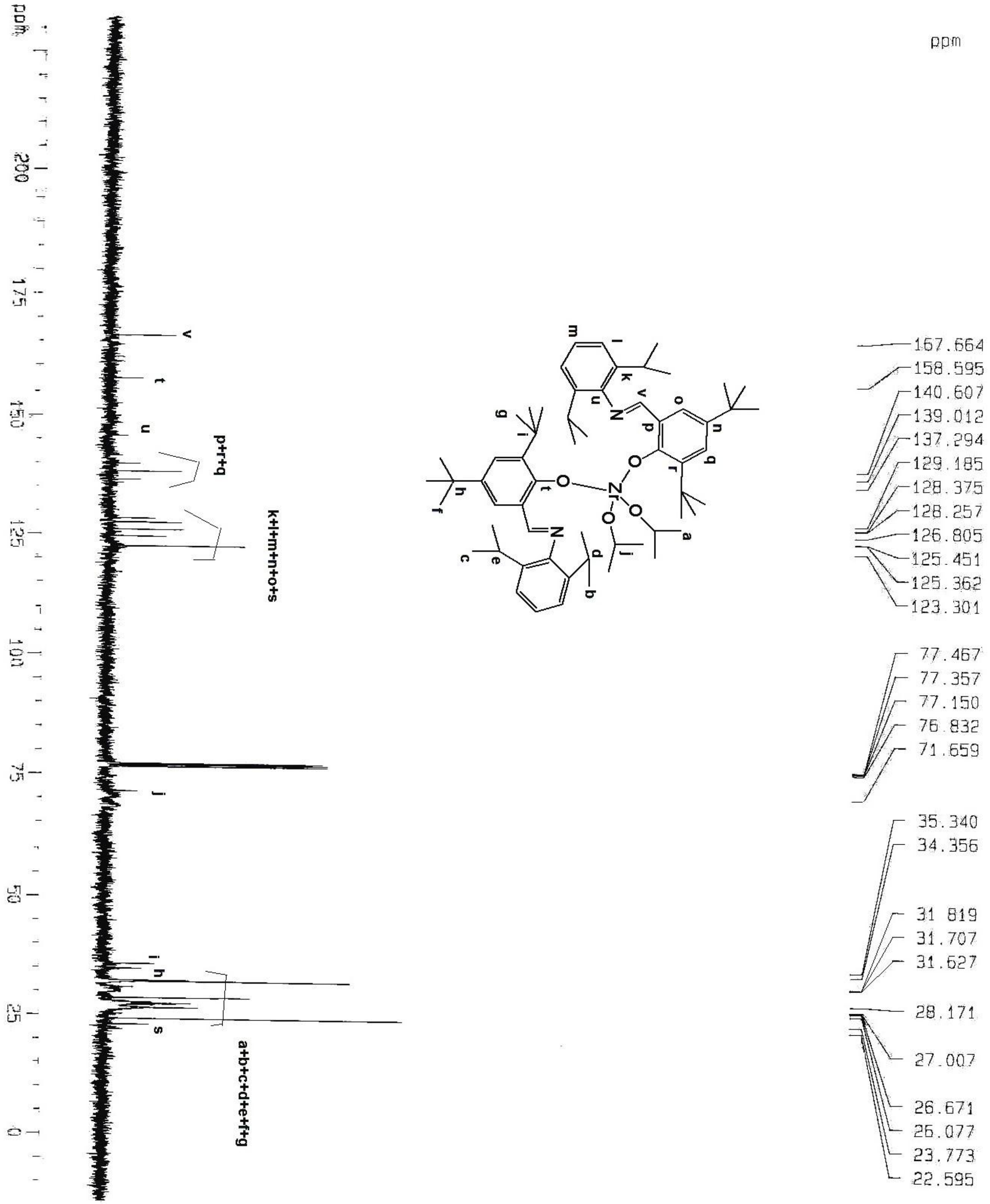


Fig. S11. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **4**

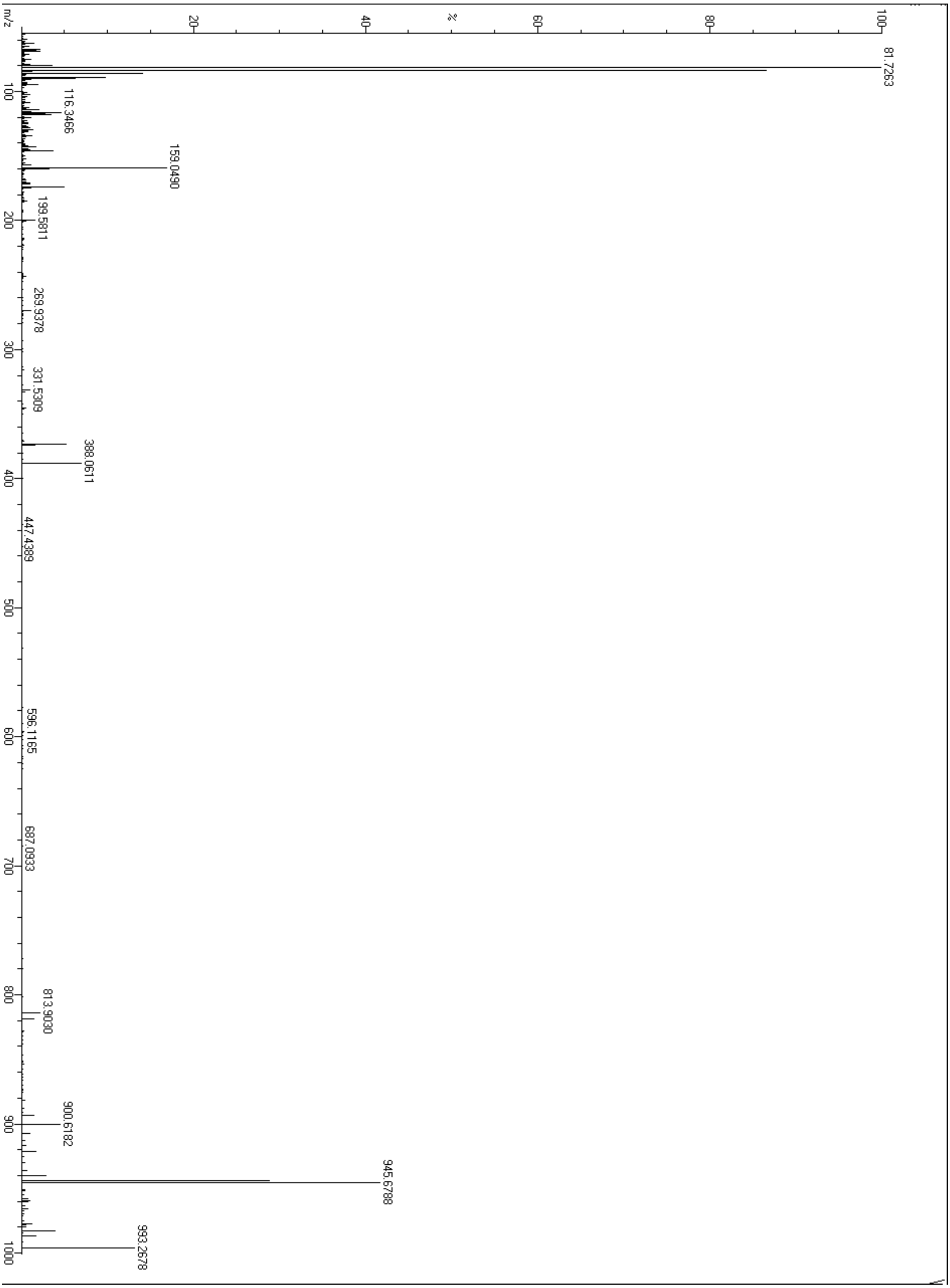


Fig. S12. ESI-Mass Spectrum of Compound **4**

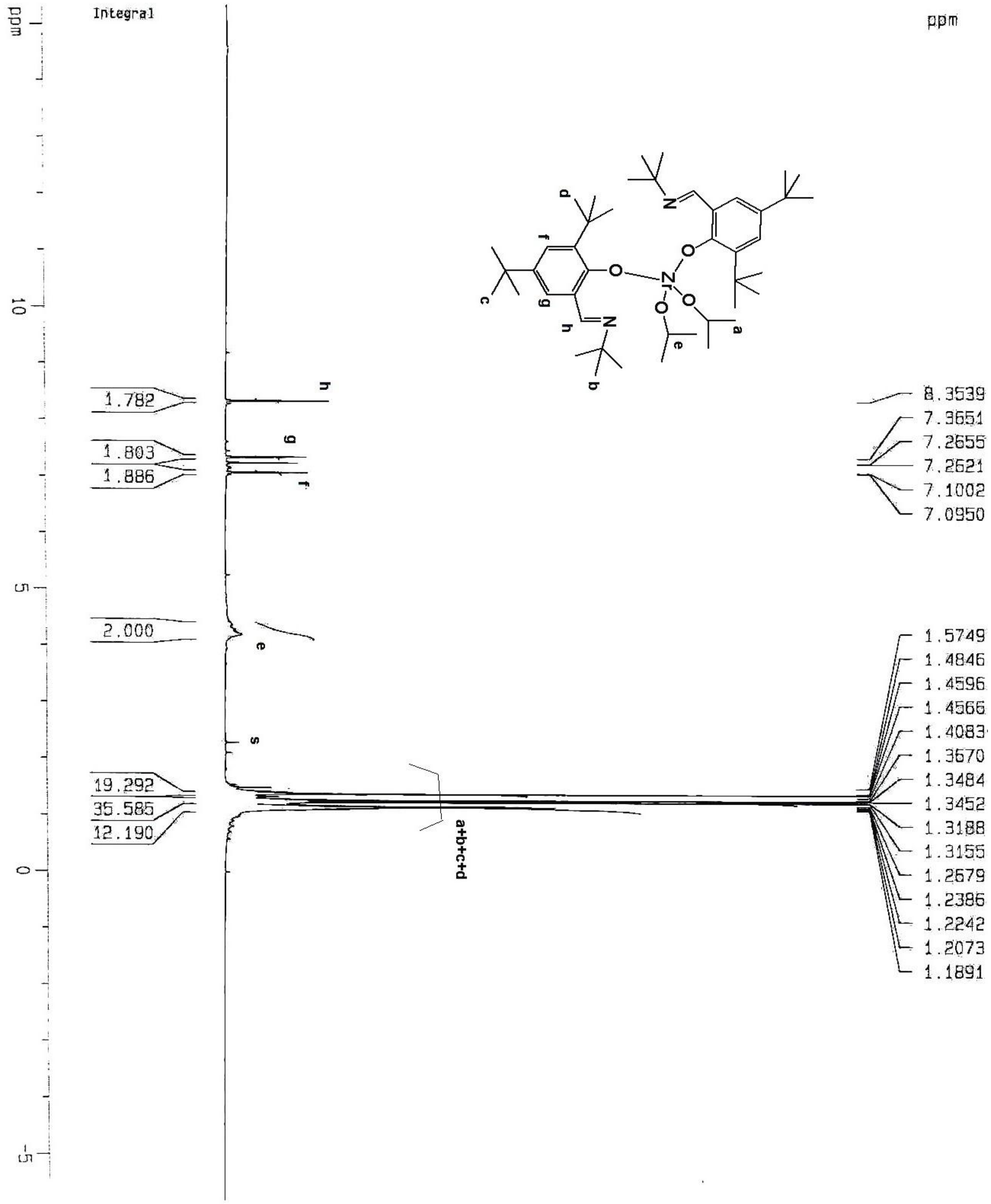


Fig. S13. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **5**

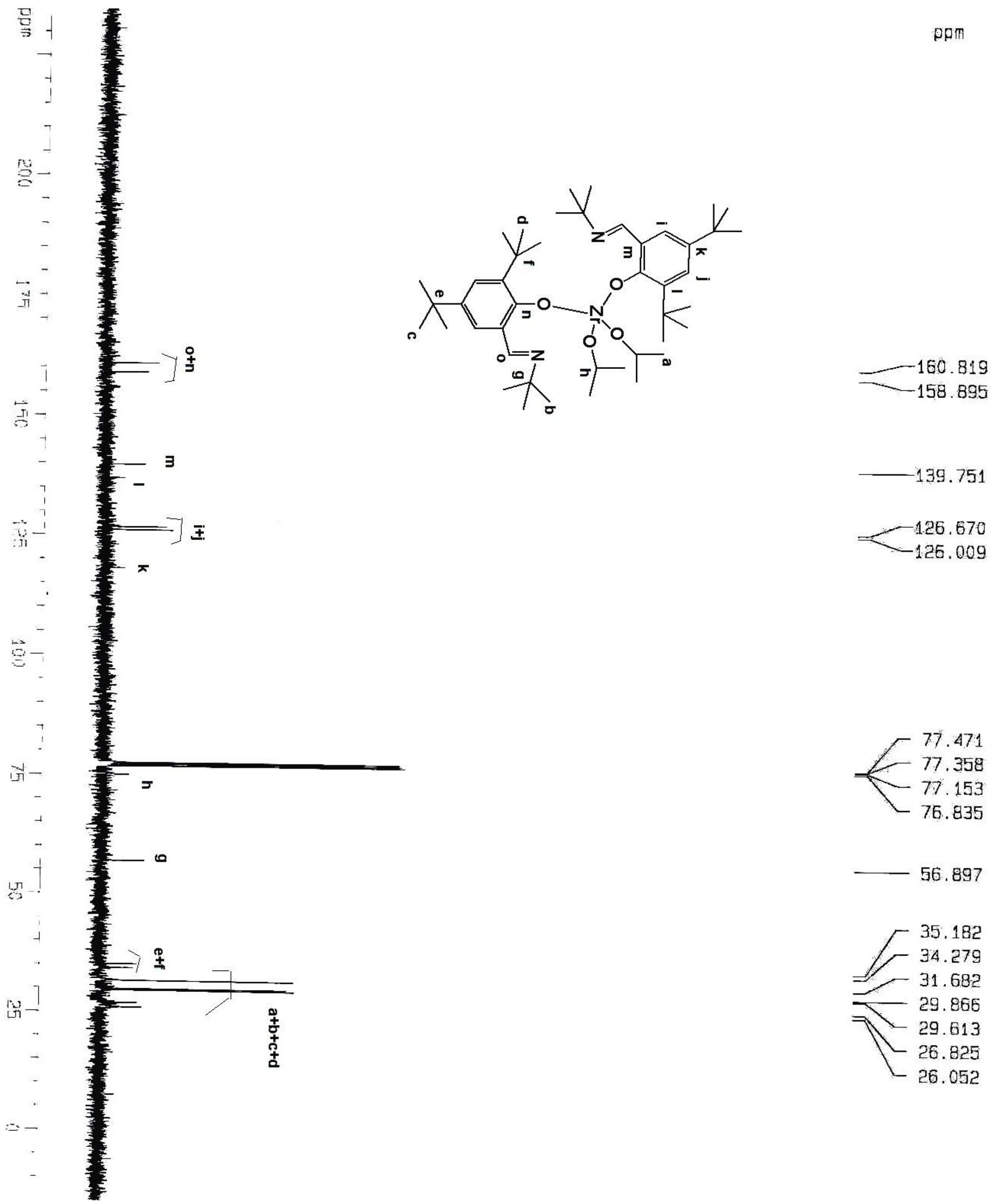


Fig. S14. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **5**

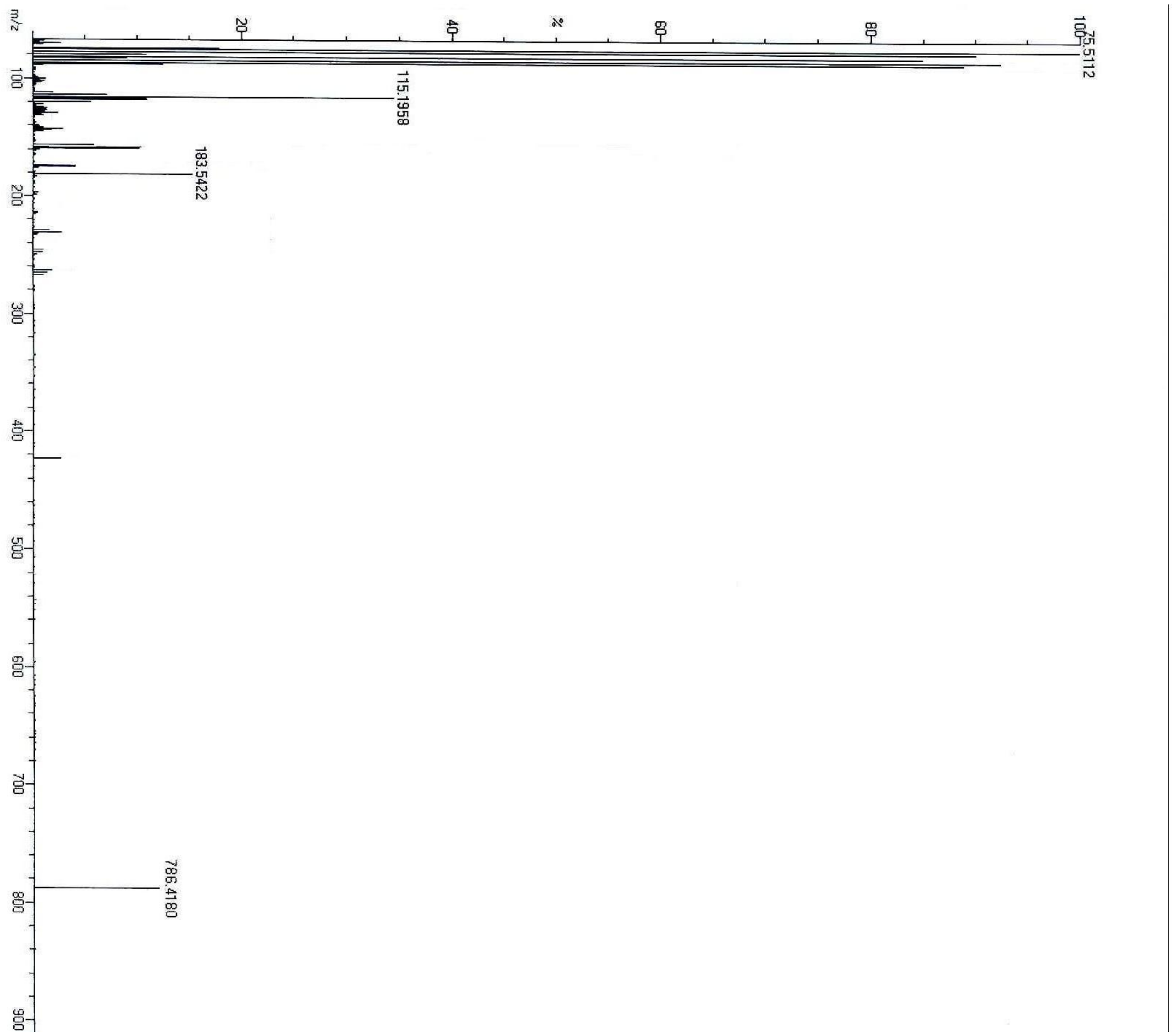


Fig. S15. ESI-Mass Spectrum of Compound **5**

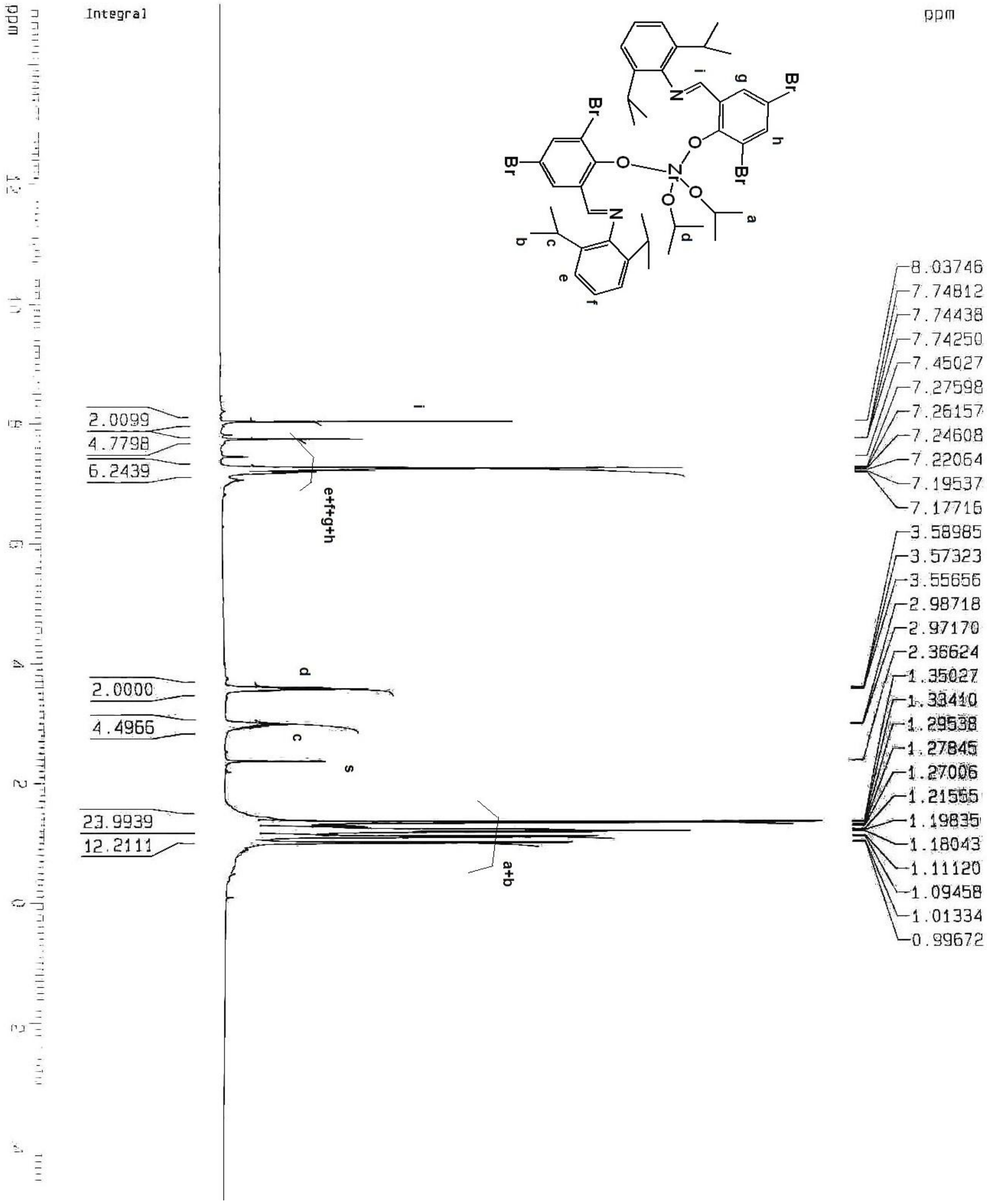


Fig. S16. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **6**

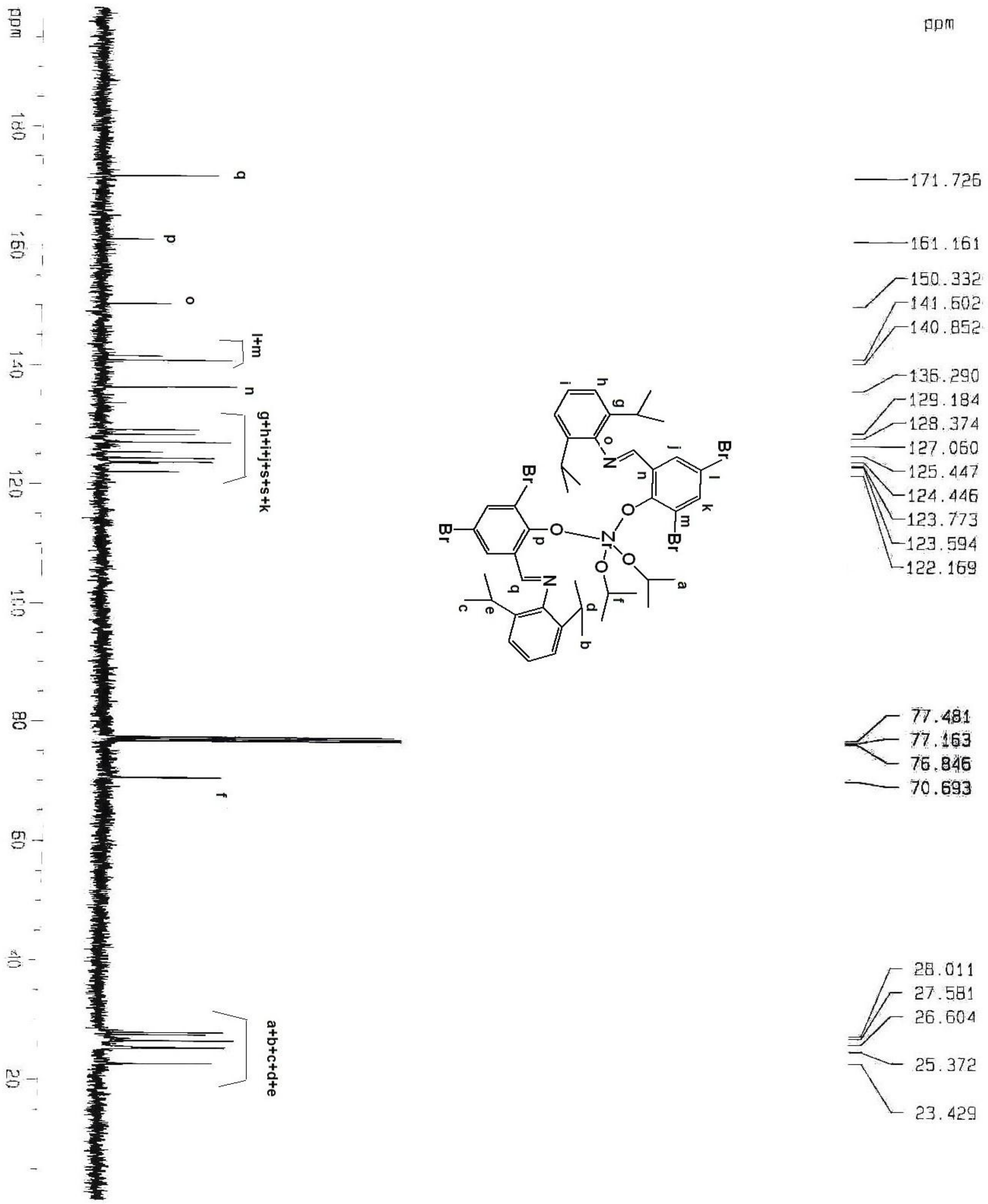


Fig. S17. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **6**

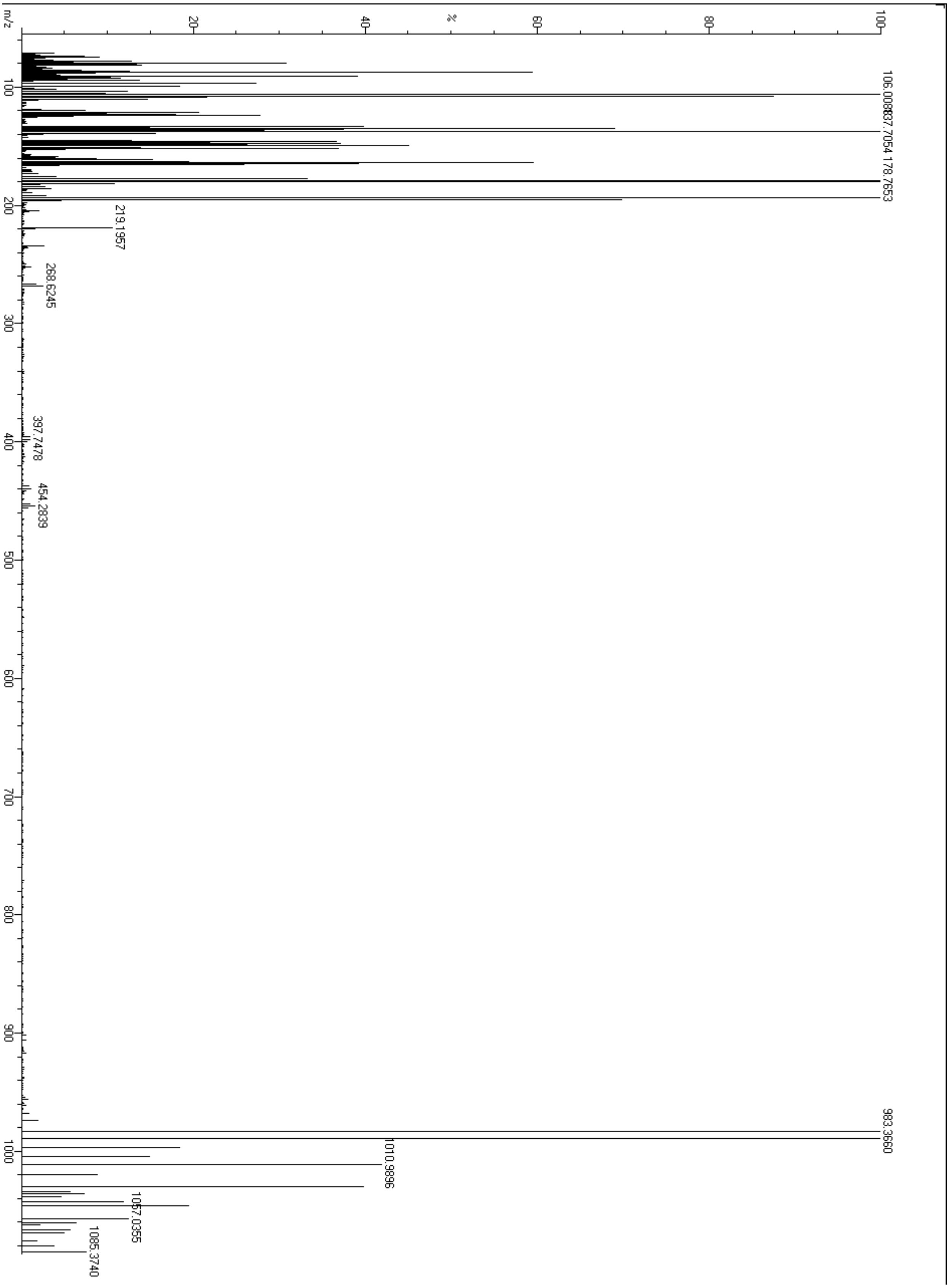


Fig. S18. ESI-Mass Spectrum of Compound **6**

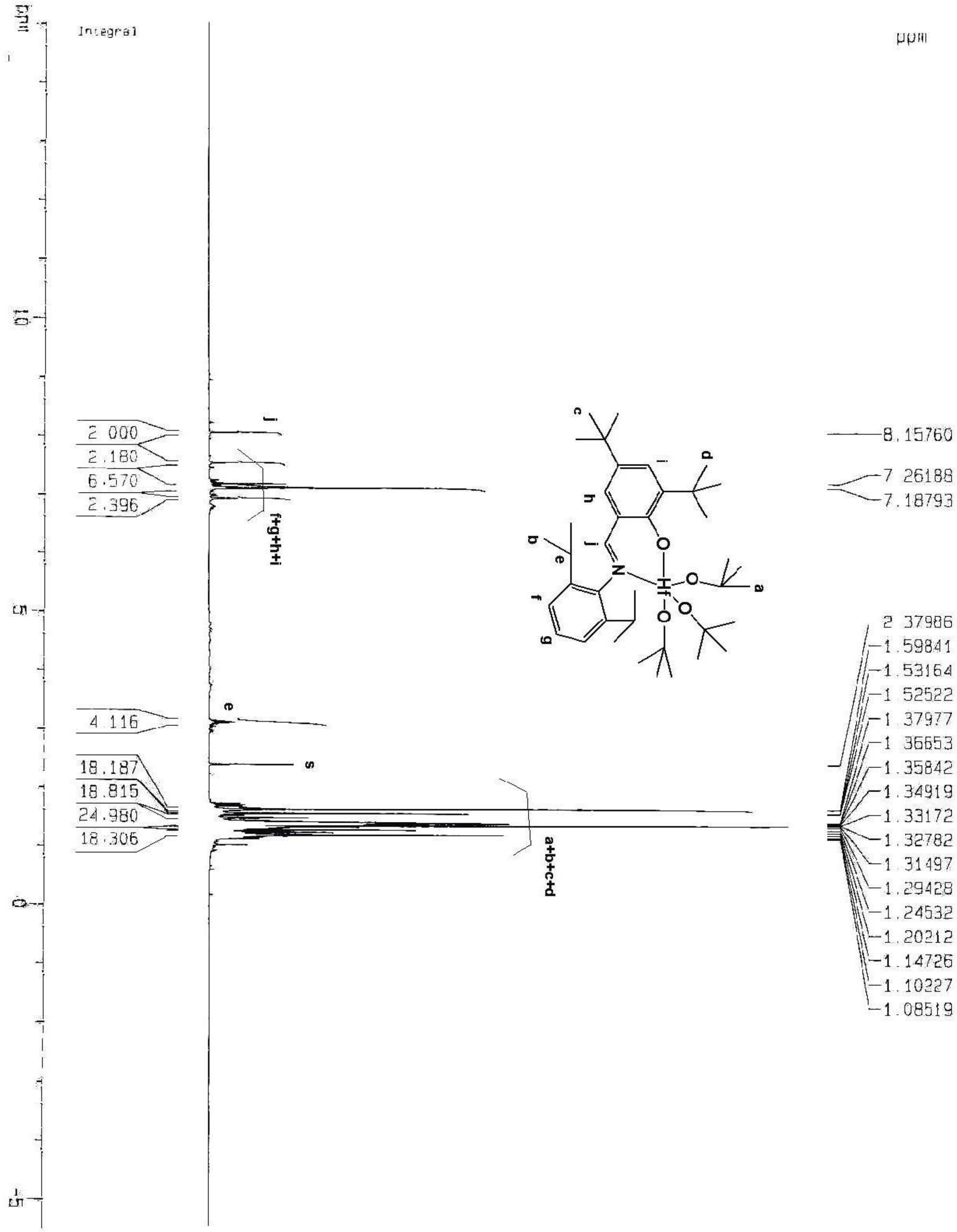


Fig. S19. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **7**

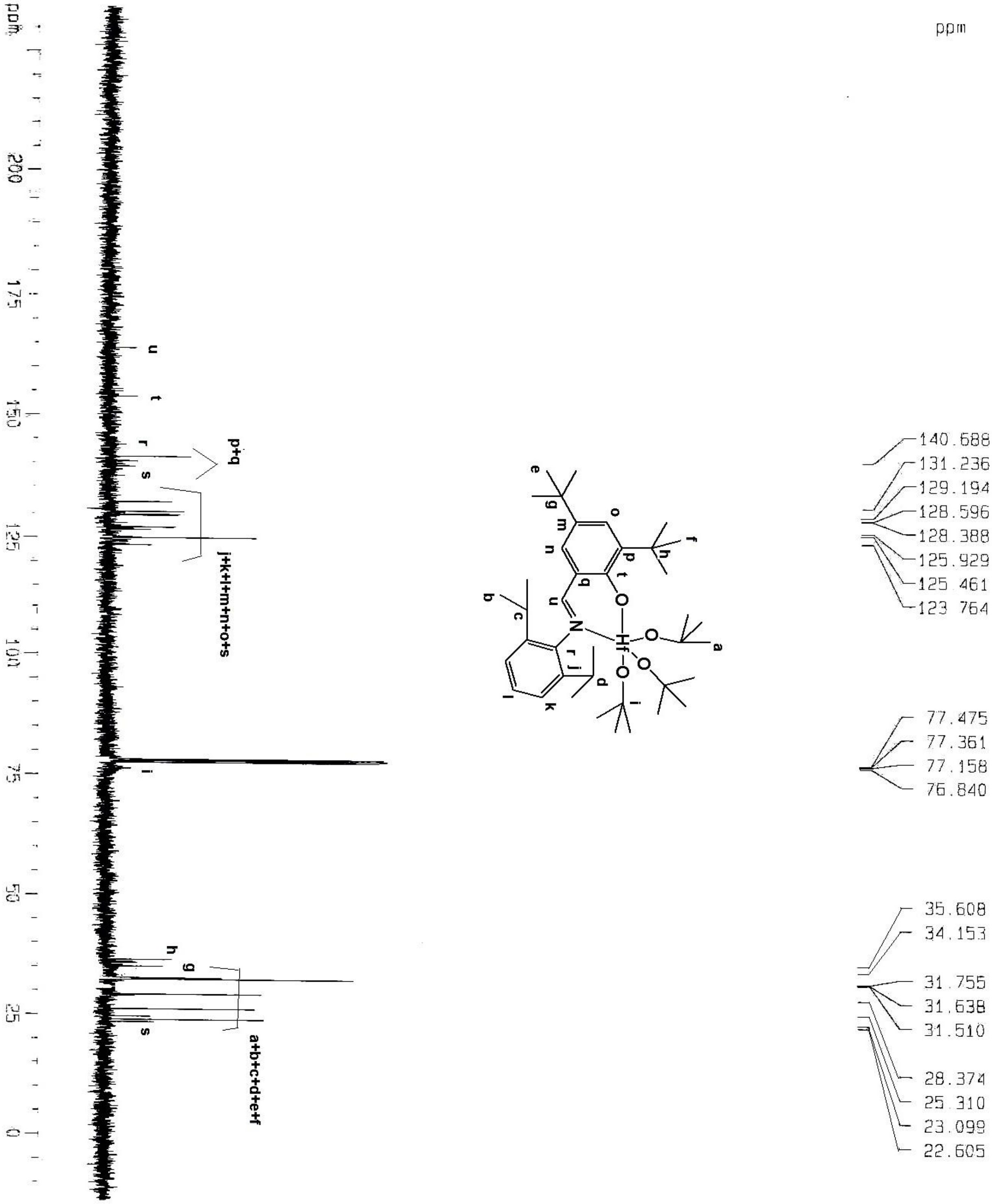


Fig. S20. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **7**

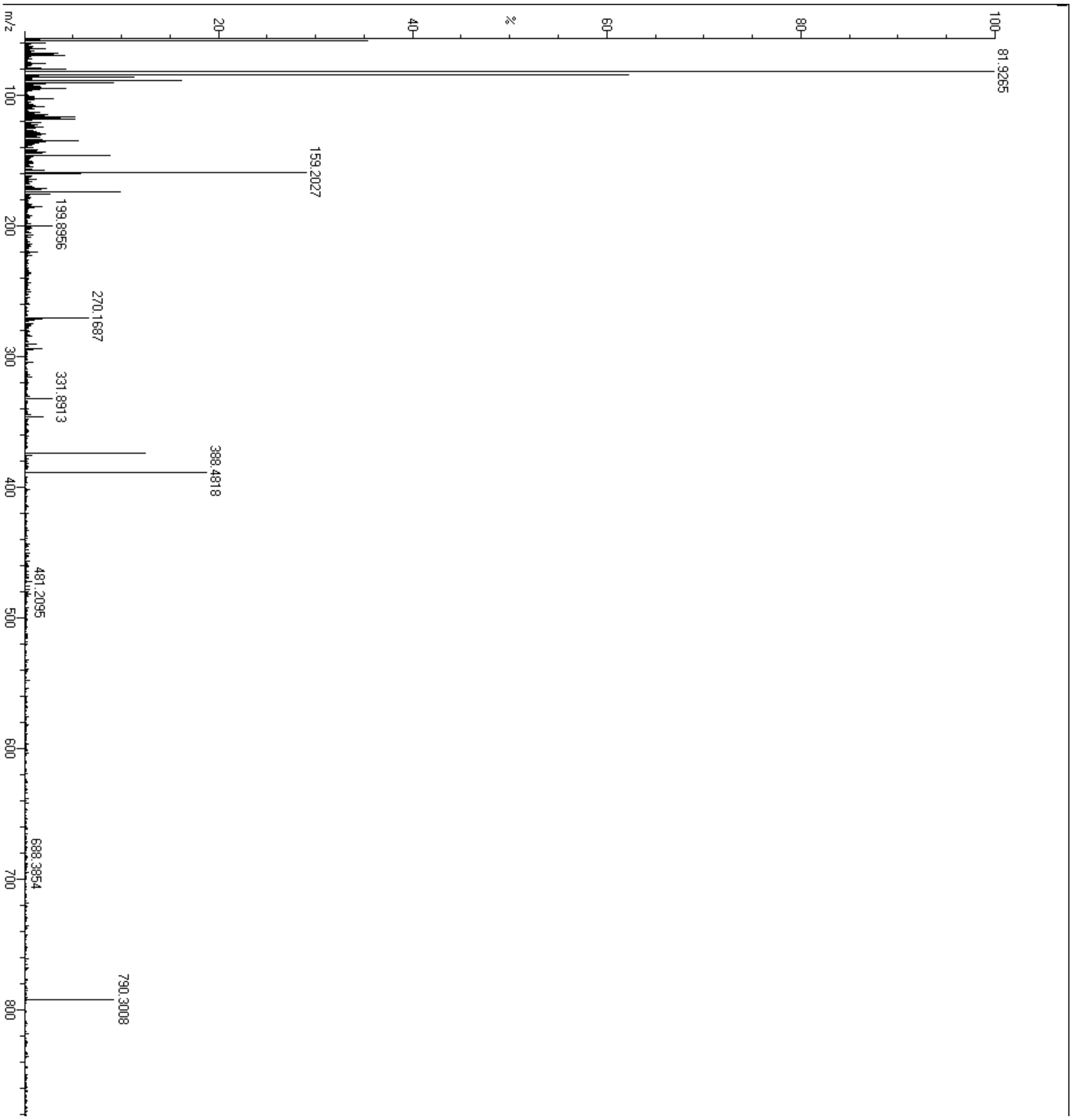


Fig. S21. ESI-Mass Spectrum of Compound **7**

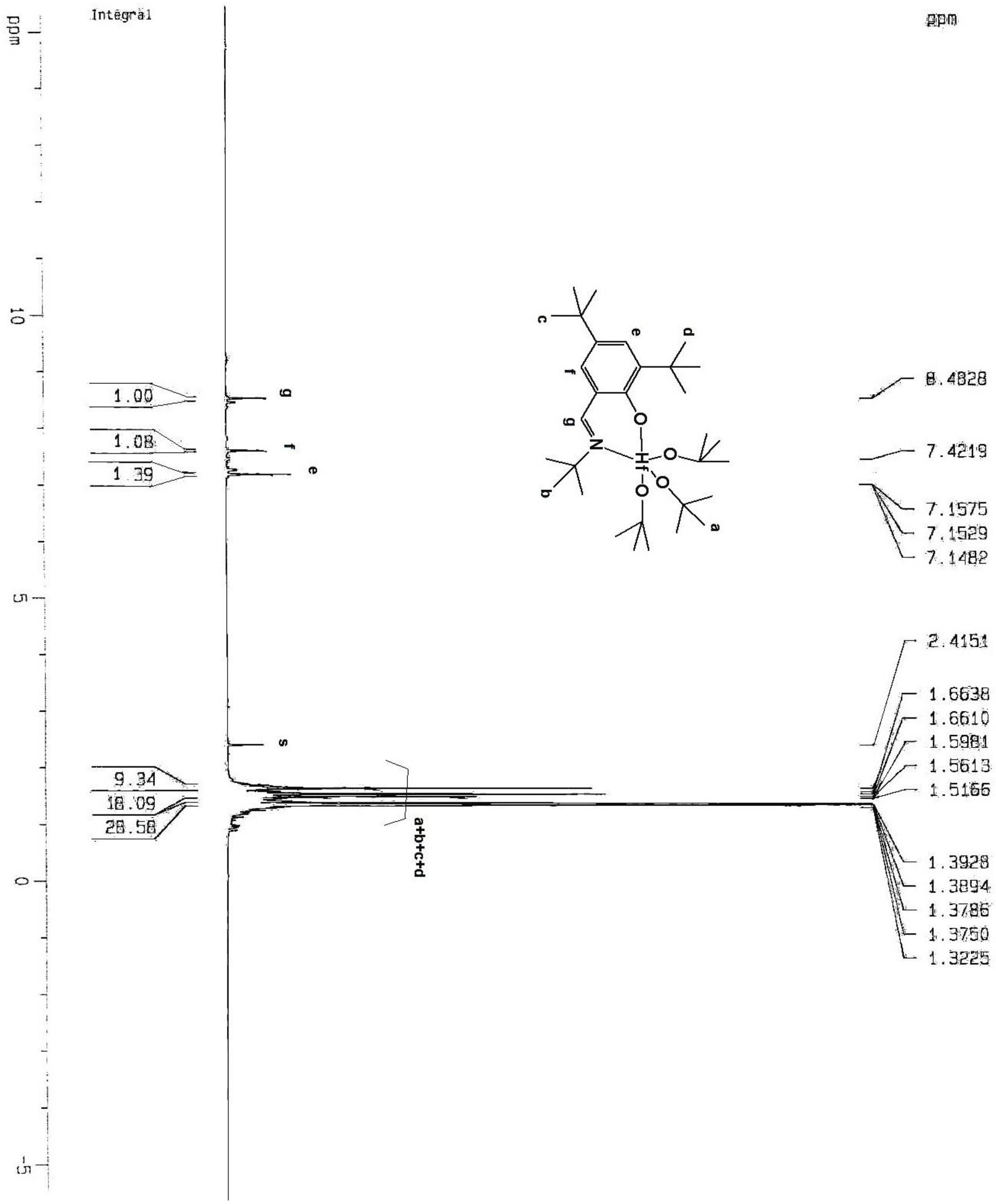


Fig. S22. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **8**

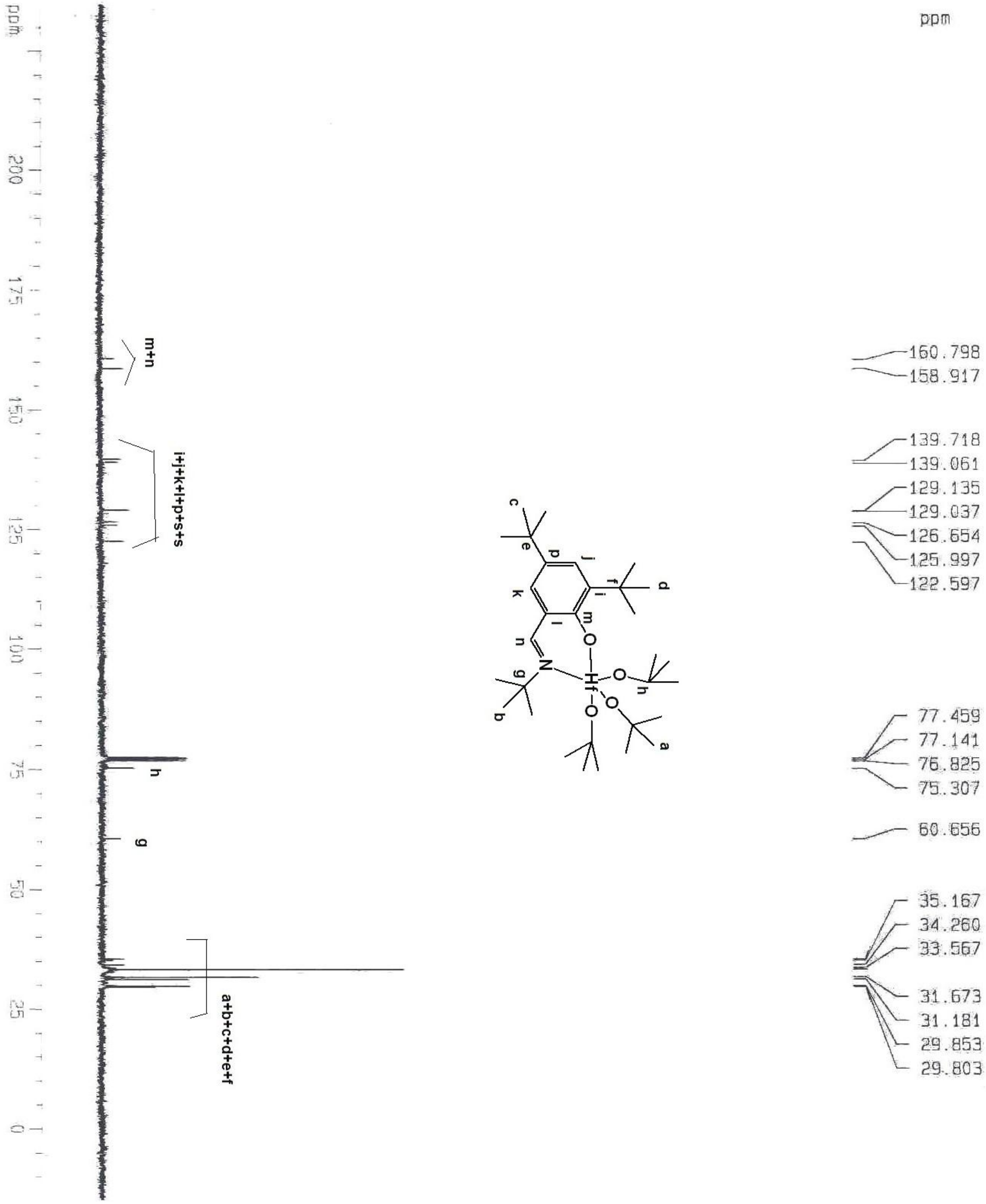


Fig. S23. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **8**

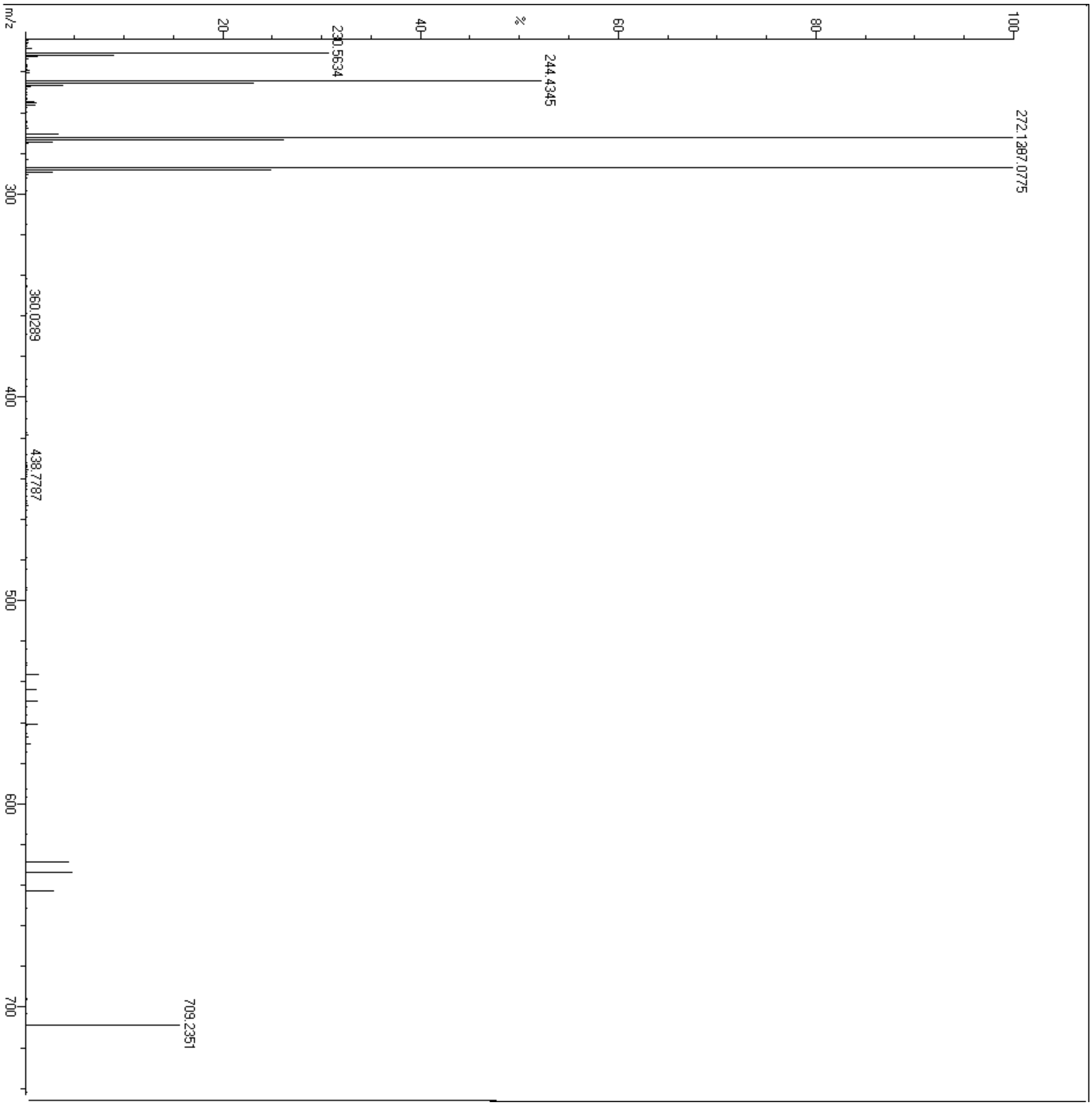


Fig. S24. ESI-Mass Spectrum of Compound **8**

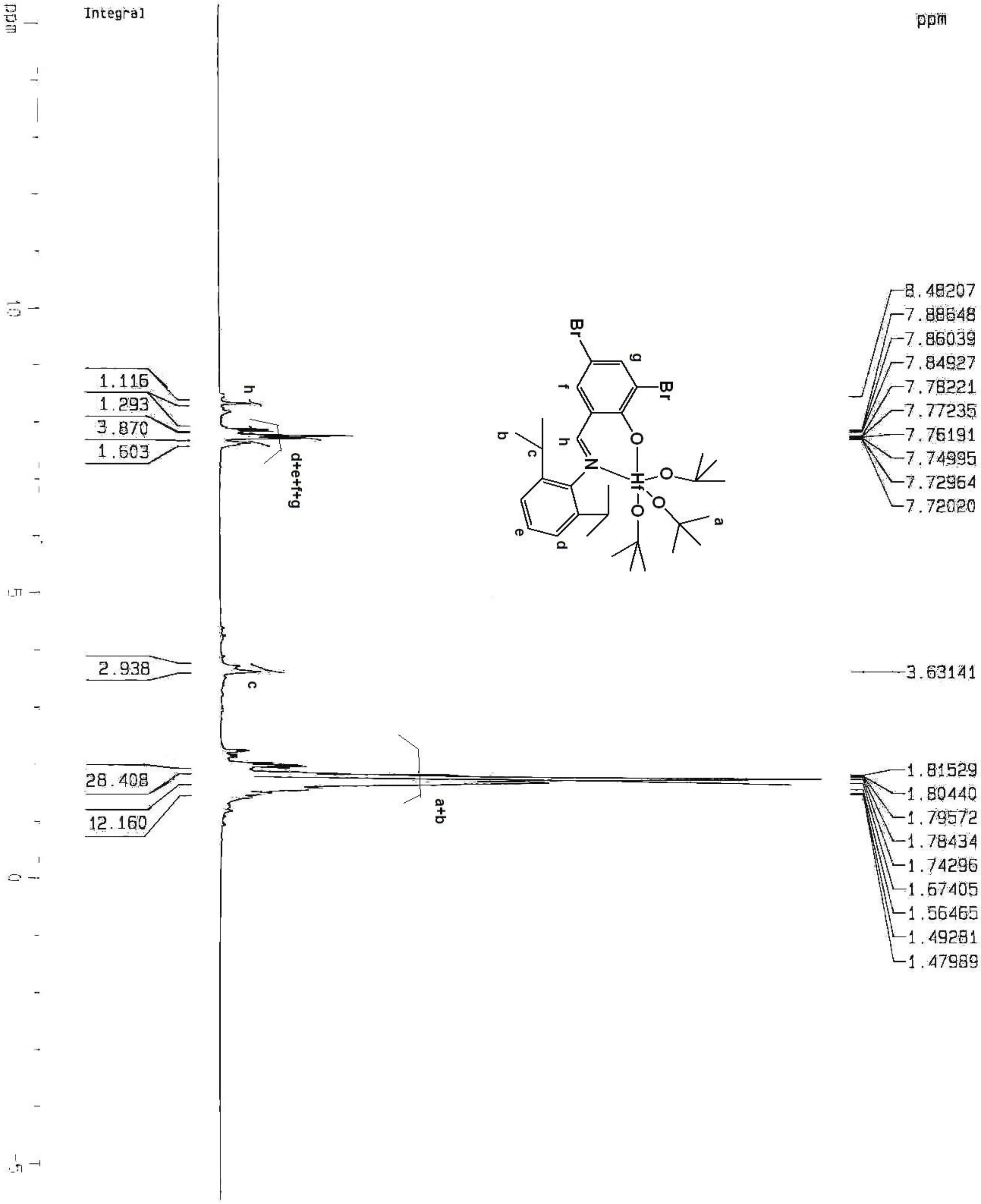


Fig. S25. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **9**

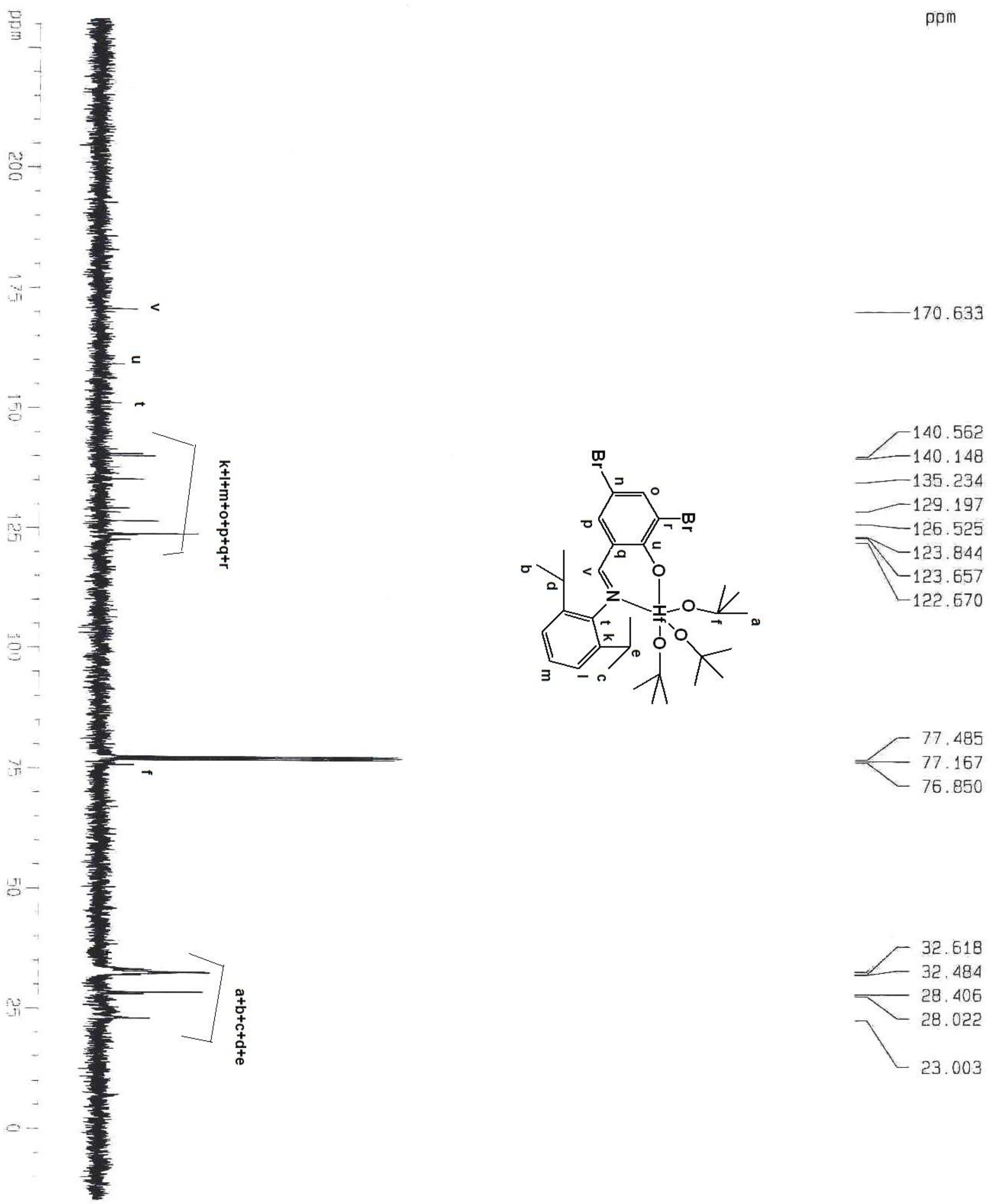


Fig. S26. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **9**

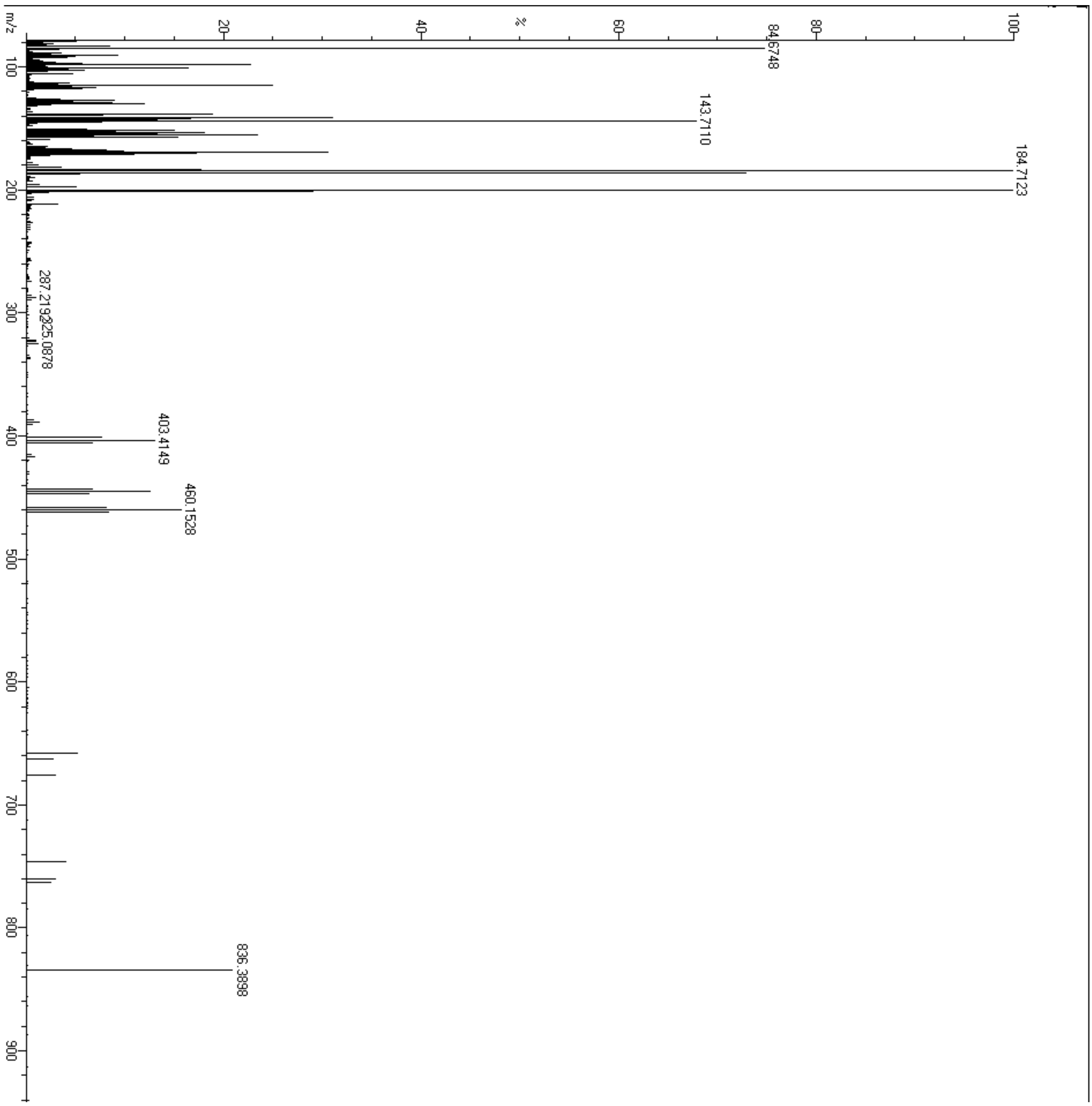


Fig. S27. ESI-Mass Spectrum of Compound **9**

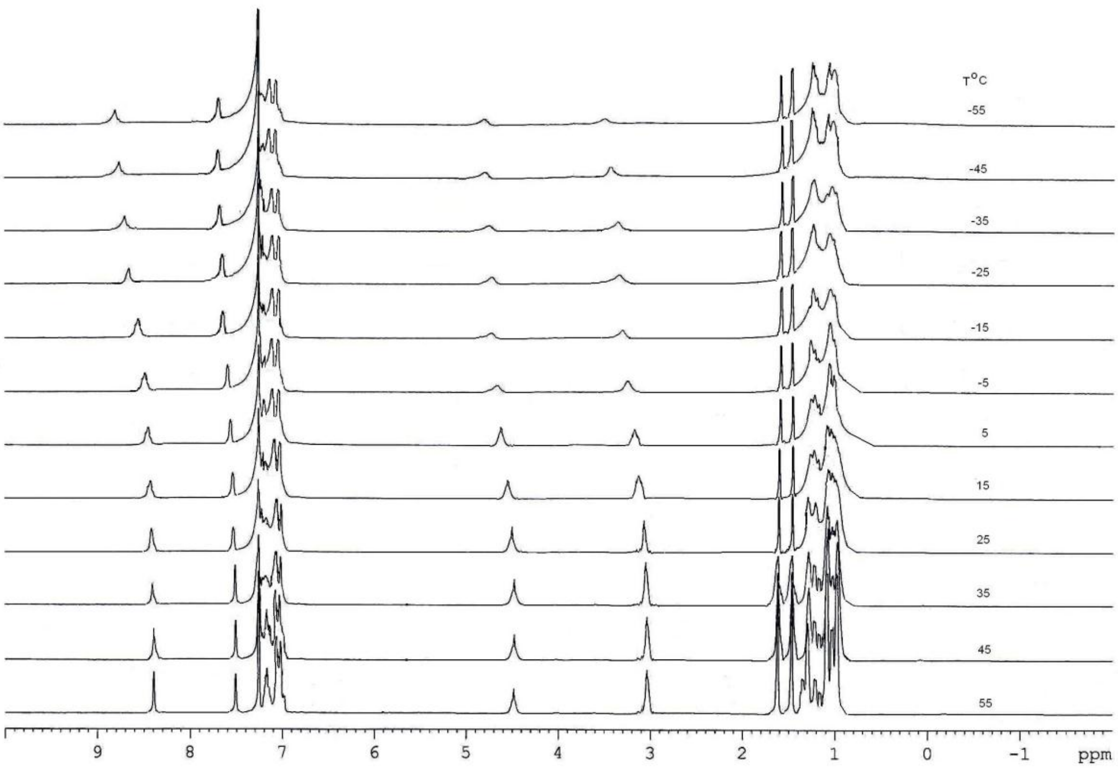


Fig. S28. Variable temperature [1]H NMR (400 MHz, $CDCl_3$) of Compound **1**

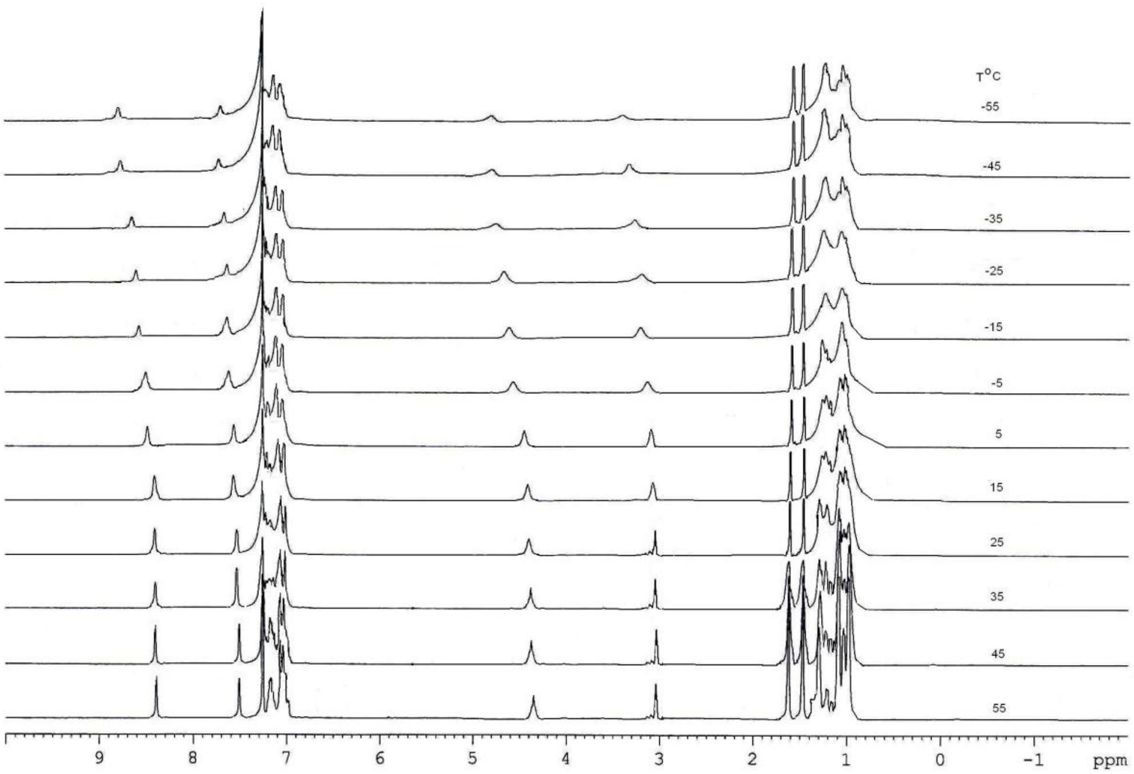


Fig. S29. Variable temperature [1]H NMR (400 MHz, $CDCl_3$) of Compound **4**

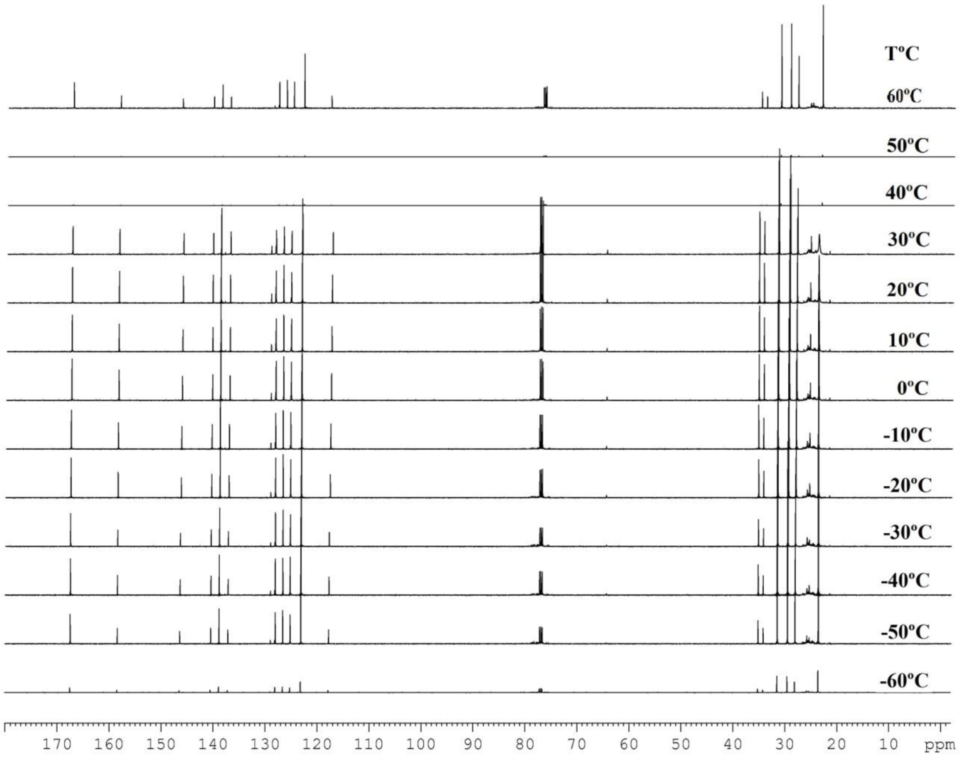


Fig. S30. Variable temperature ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **1**

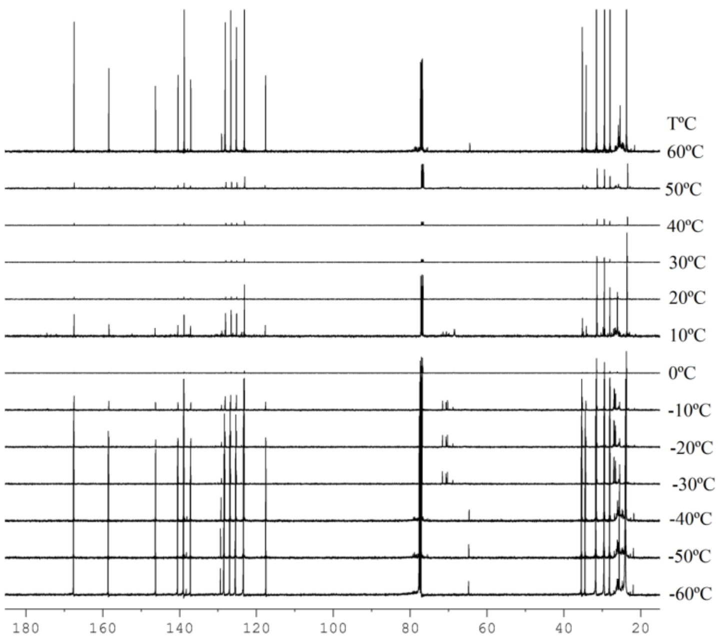


Fig. S31. Variable temperature ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **4**

Table Solution polymerization data for *rac*-LA, *L*-LA and CL using **1–9** in 200:1 ratio at 80 °C

Entry	Initiator	Monomer	Yield (%)	Time[a]/ min	[b]M_n^{obs}/ kgmol^{-1}	[c]M_n^{theo}/ kgmol^{-1}	M_w/M_n	P_r[d]
1	**1**	*rac*-LA	99	55	30.22	28.89	1.03	0.68
2	**2**	*rac*-LA	99	80	29.94	28.89	1.02	0.69
3	**3**	*rac*-LA	98	71	30.12	28.89	1.04	0.70
4	**4**	*rac*-LA	99	68	31.25	28.89	1.02	0.72
5	**5**	*rac*-LA	97	88	30.46	28.89	1.04	0.71
6	**6**	*rac*-LA	98	92	30.64	28.89	1.05	0.74
7	**7**	*rac*-LA	98	70	31.39	28.89	1.02	0.68
8	**8**	*rac*-LA	99	100	30.05	28.89	1.03	0.70
9	**9**	*rac*-LA	98	140	31.56	28.89	1.06	0.66
10	**1**	*L*-LA	99	50	31.23	28.89	1.02	
11	**2**	*L*-LA	99	74	30.45	28.89	1.03	
12	**3**	*L*-LA	99	60	29.22	28.89	1.02	
13	**4**	*L*-LA	97	78	29.62	28.89	1.04	
14	**5**	*L*-LA	98	88	31.98	28.89	1.05	
15	**6**	*L*-LA	97	76	30.21	28.89	1.07	
16	**7**	*L*-LA	98	105	29.34	28.89	1.08	
17	**8**	*L*-LA	98	134	30.66	28.89	1.06	
18	**9**	*L*-LA	98	138	29.11	28.89	1.05	
19	**1**	CL	99	44	24.59	22.83	1.03	
20	**2**	CL	99	64	23.98	22.83	1.05	
21	**3**	CL	99	48	25.17	22.83	1.06	
22	**4**	CL	99	49	25.02	22.83	1.02	
23	**5**	CL	98	82	24.64	22.83	1.04	
24	**6**	CL	98	60	21.32	22.83	1.03	
25	**7**	CL	97	77	24.79	22.83	1.03	
26	**8**	CL	99	97	25.11	22.83	1.02	
27	**9**	CL	98	87	25.78	22.83	1.05	

[a]Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b]Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n for LA polymerization. [c]M_n (theoretical) at 100 % conversion = $[M]_o/[C]_o$ × mol wt (monomer) + $M_{end\ groups}$ [d]Calculated from homonuclear decoupled ^{1}H NMR spectrum.

Table Solution polymerization data for *rac*-LA, *L*-LA and CL using **1–9** in the presence of benzyl alcohol in 200:1:5 ratio at 80 °C

Entry	Initiator	Monomer	Yield (%)	Time[a]/ min	[b]M_n^{obs}/ kgmol^{-1}	[c]M_n^{theo}/ kgmol^{-1}	M_w/M_n	P_r[d]
1	**1**	*rac*-LA	98	25	6.89	5.76	1.10	0.69
2	**2**	*rac*-LA	99	32	6.81	5.76	1.11	0.71
3	**3**	*rac*-LA	99	27	6.02	5.76	1.13	0.70
4	**4**	*rac*-LA	99	21	6.92	5.76	1.10	0.74
5	**5**	*rac*-LA	98	29	7.05	5.76	1.11	0.72
6	**6**	*rac*-LA	99	31	6.99	5.76	1.12	0.71
7	**7**	*rac*-LA	97	24	6.11	5.76	1.13	0.69
8	**8**	*rac*-LA	97	35	7.07	5.76	1.11	0.70
9	**9**	*rac*-LA	98	48	7.04	5.76	1.14	0.69
10	**1**	*L*-LA	99	17	6.48	5.76	1.11	
11	**2**	*L*-LA	99	24	6.59	5.76	1.12	
12	**3**	*L*-LA	97	18	7.35	5.76	1.14	
13	**4**	*L*-LA	97	28	7.21	5.76	1.13	
14	**5**	*L*-LA	99	32	6.78	5.76	1.14	
15	**6**	*L*-LA	99	26	7.44	5.76	1.11	
16	**7**	*L*-LA	99	37	6.66	5.76	1.12	
17	**8**	*L*-LA	98	42	7.34	5.76	1.10	
18	**9**	*L*-LA	98	47	7.56	5.76	1.10	
19	**1**	CL	97	13	6.73	4.56	1.13	
20	**2**	CL	98	20	5.55	4.56	1.13	
21	**3**	CL	98	17	5.69	4.56	1.11	
22	**4**	CL	99	19	7.13	4.56	1.15	
23	**5**	CL	98	26	6.33	4.56	1.11	
24	**6**	CL	99	18	7.01	4.56	1.10	
25	**7**	CL	99	26	6.47	4.56	1.13	
26	**8**	CL	98	32	7.08	4.56	1.12	
27	**9**	CL	98	29	6.18	4.56	1.11	

[a]Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b]Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n for LA polymerization. [c]Mn (theoretical) at 100 % conversion = [M]o/[C]o × mol wt (monomer) + 108.14. [d]Calculated from homonuclear decoupled ^{1}H NMR spectrum.

Table Polymerization data based on changing [*rac*-LA]/[C] ratio in case of *rac*-LA using **3**, **6** and **9** at 130 °C

Entry	Initiator	[M]/[C] ratio	Time[a] /min	Yield (%)	M_n[b]/ kgmol^{-1}	M_w/M_n
1	**3**	200	14	99	41.62	1.13
2	**3**	400	32	98	82.22	1.14
3	**3**	600	55	97	119.72	1.16
4	**3**	800	70	99	155.89	1.18
5	**3**	1000	85	98	212.14	1.20
6	**3**	1200	140	99	253.67	1.21
7	**6**	200	18	97	82.52	1.12
8	**6**	400	35	98	150.79	1.14
9	**6**	600	62	99	240.25	1.15
10	**6**	800	81	99	326.74	1.17
11	**6**	1000	105	98	415.52	1.19
12	**6**	1200	162	95	499.31	1.22
13	**9**	200	29	99	41.44	1.18
14	**9**	400	62	97	83.98	1.20
15	**9**	600	95	96	128.43	1.23
16	**9**	800	130	98	160.69	1.25
17	**9**	1000	165	98	205.52	1.27
18	**9**	1200	195	97	252.76	1.30

[a]Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b]Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n for LA polymerization. [M] = number of moles of monomer, [C] = number of moles of catalyst

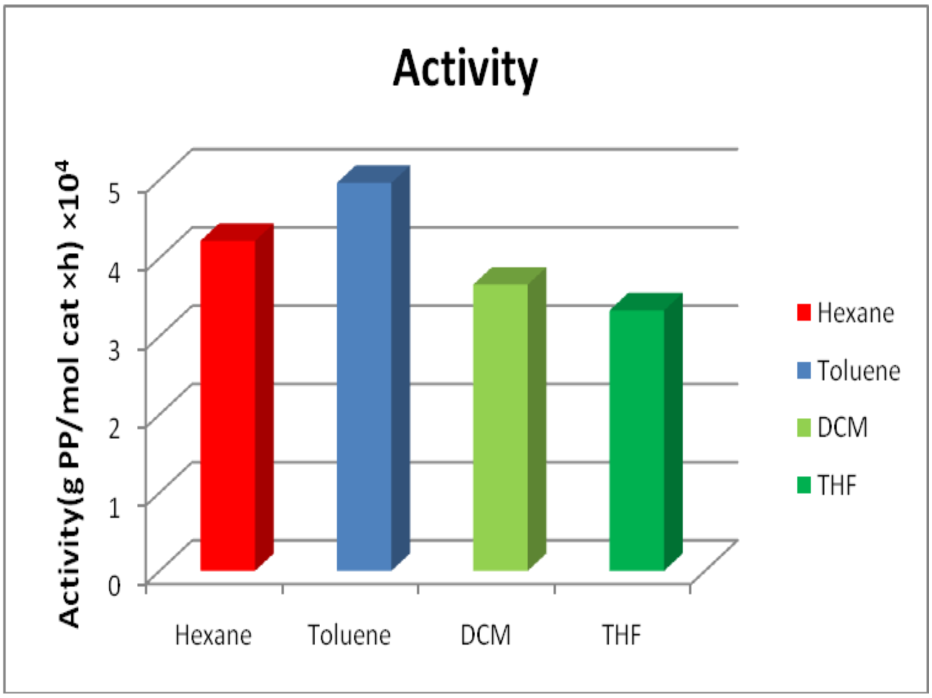


Fig. S32. Activity of **4** in different solvent in propylene polymerization

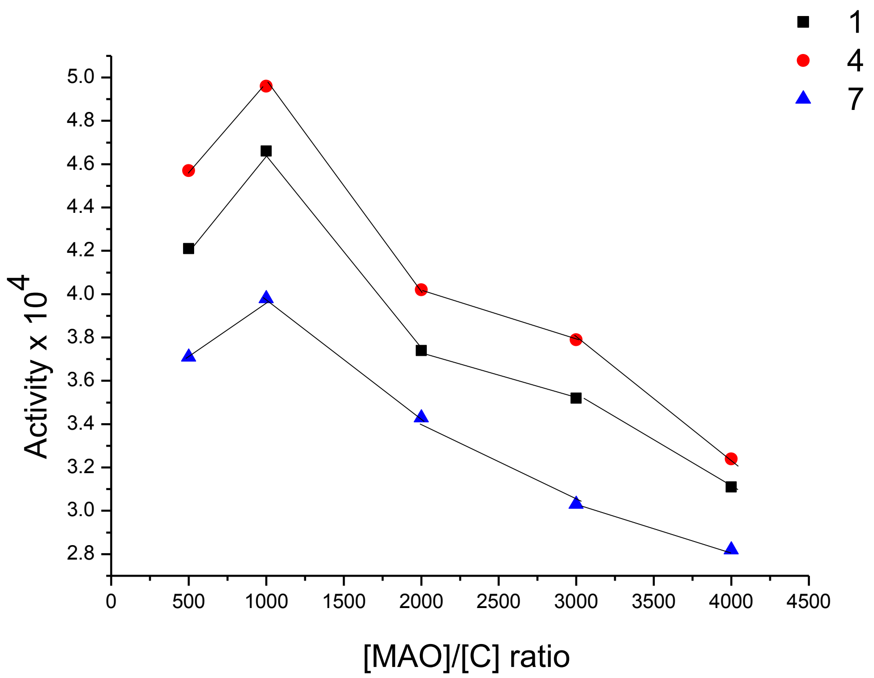


Fig. S33. Plot of activity vs [MAO]/[C] ratio for **1**, **4** and **7** for propylene polymerization

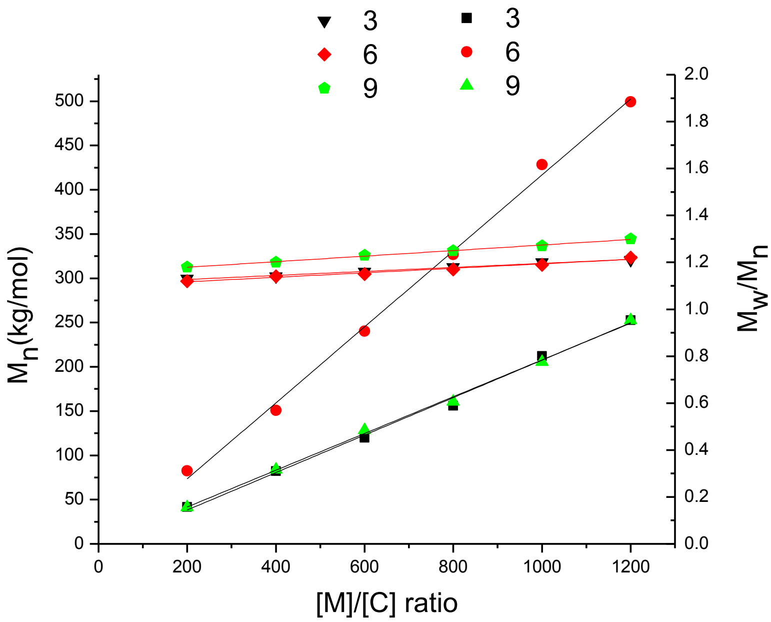


Fig. S34. Plot of M_n and M_w/M_n vs. $[M]_o/[C]_o$ for *rac*-LA polymerization at 130 °C using **3, 6** and **9**

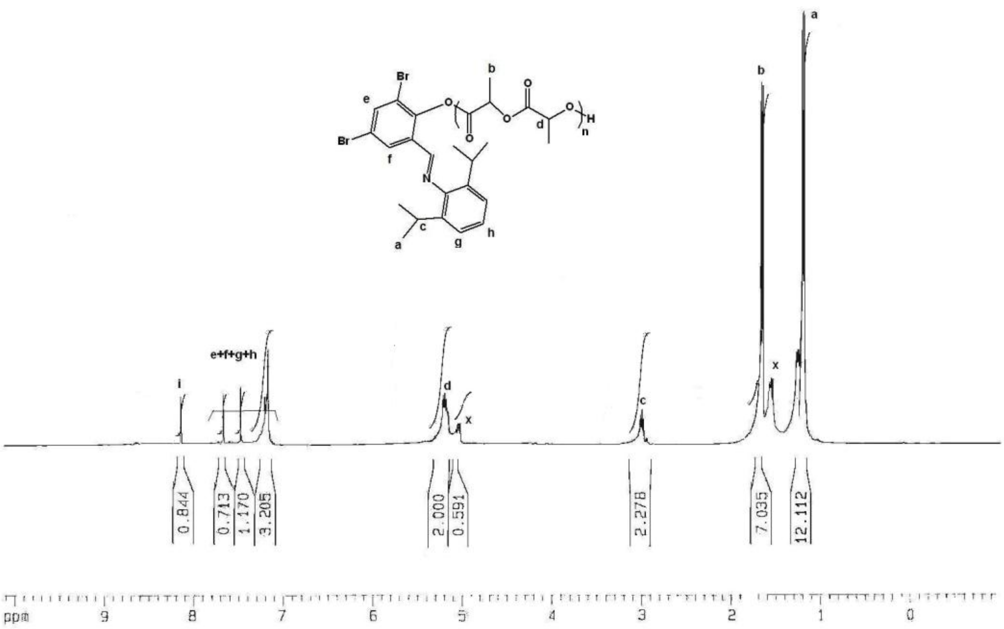


Fig. S35. [1]H NMR spectrum of the crude product obtained from a reaction between *rac*-LA and **6** in 10:1 ratio (x = peaks corresponding to *rac*-LA)

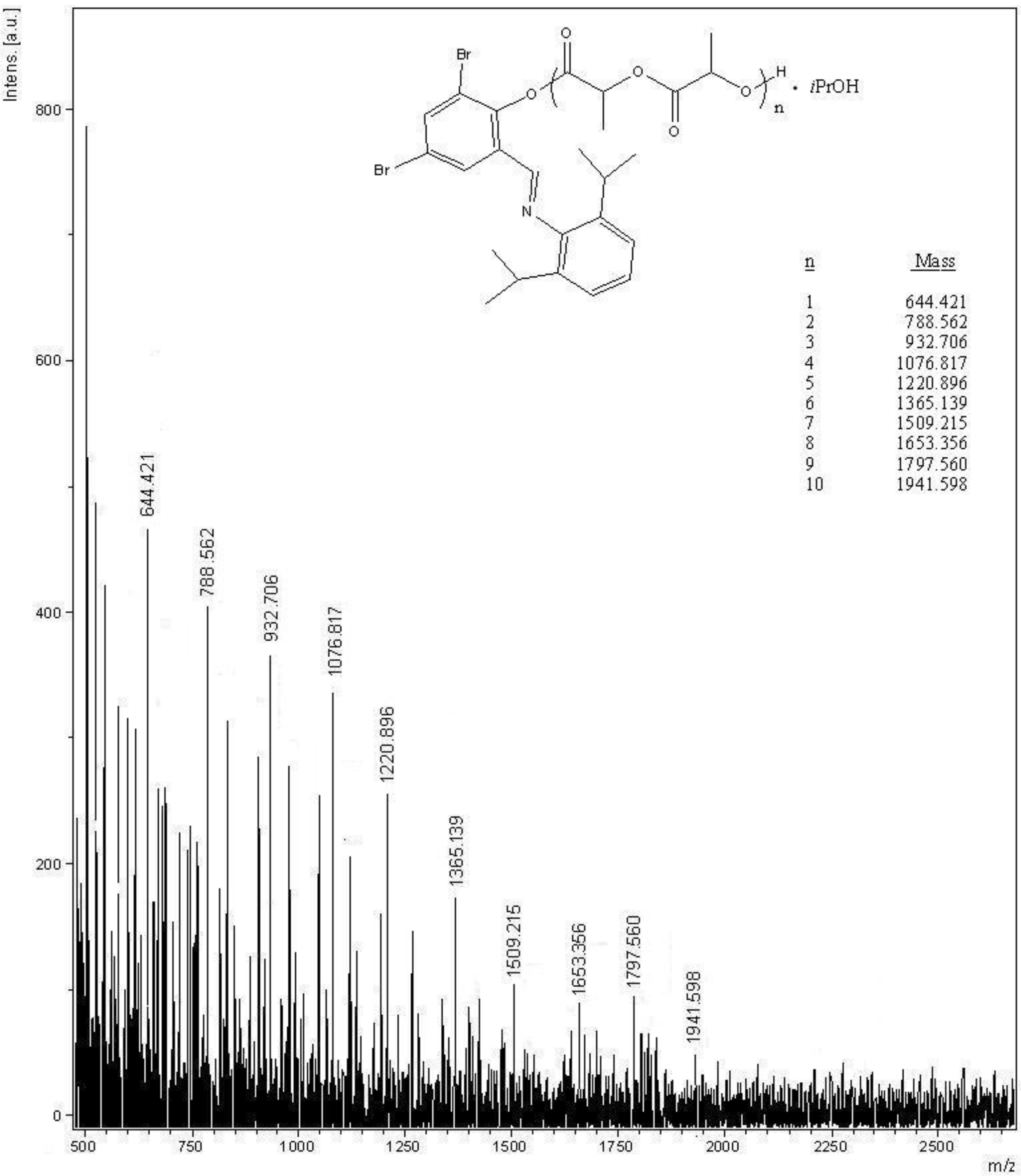


Fig.S36. MALDI-TOF of the crude product obtained from a reaction between *rac*-LA and **6** in 10:1 ratio

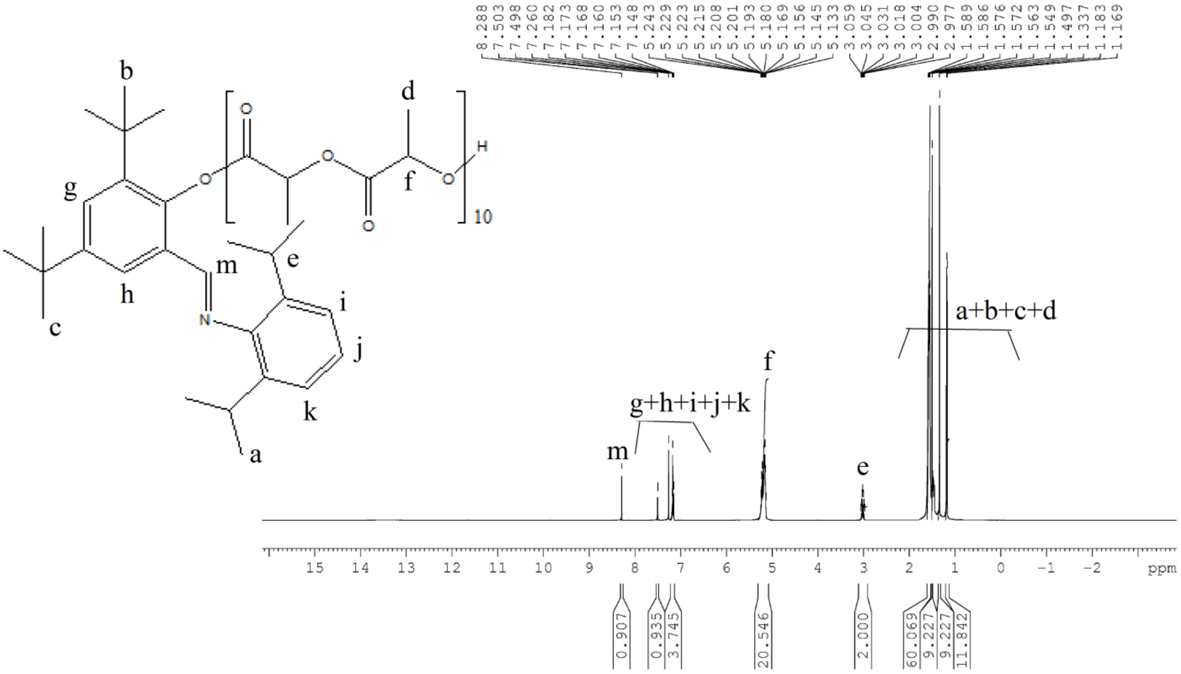
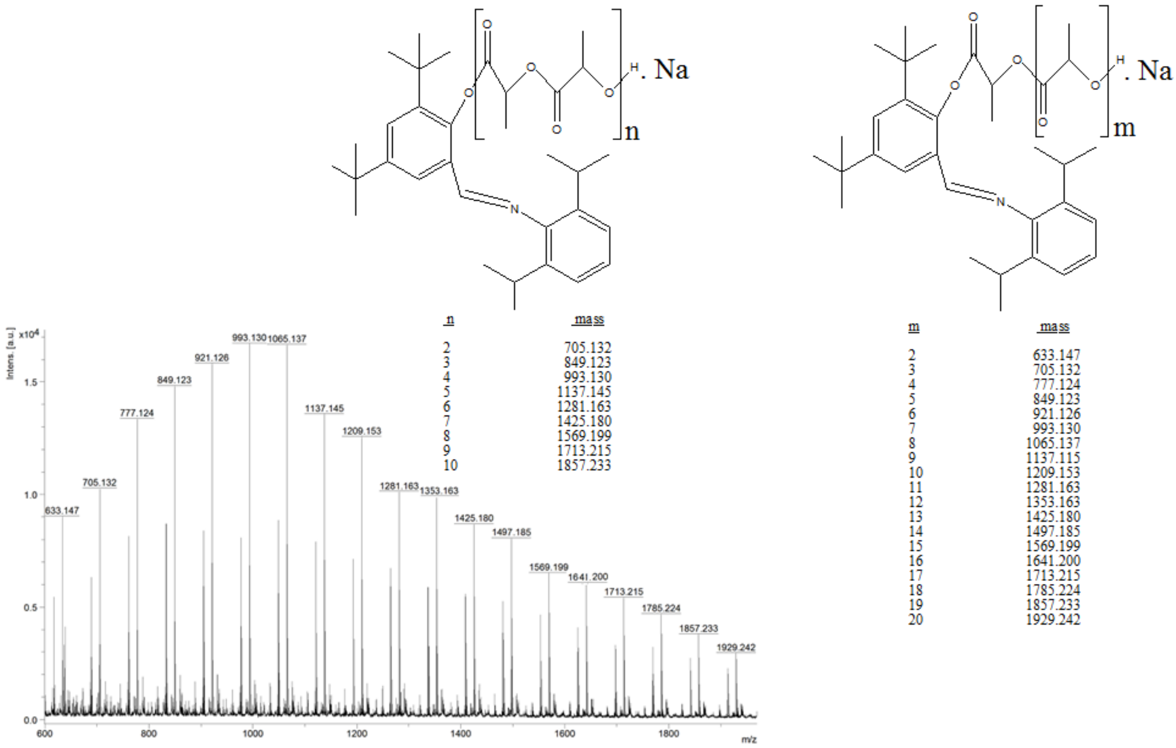


Fig. S37. ^{1}H NMR spectrum of the crude product obtained from a reaction between *rac*-LA and **7** in 10:1 ratio



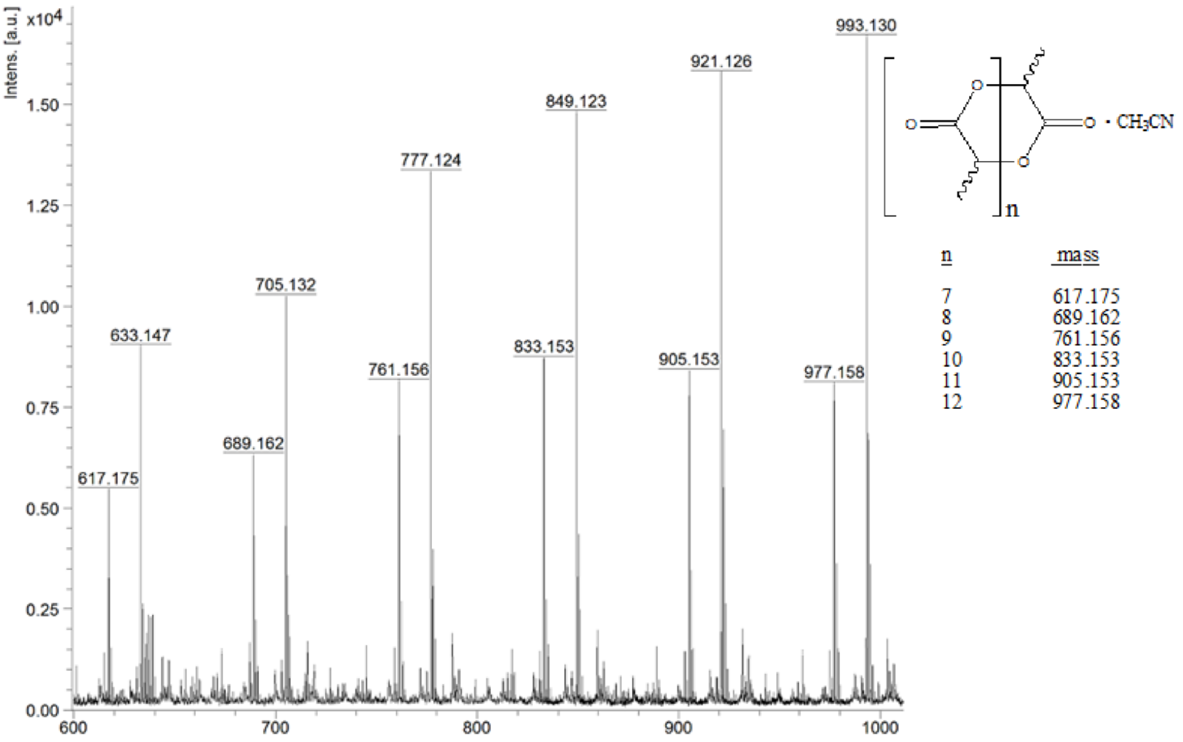


Fig.S38. MALDI-TOF of the crude product obtained from a reaction between *rac*-LA and **7** in 10:1 ratio

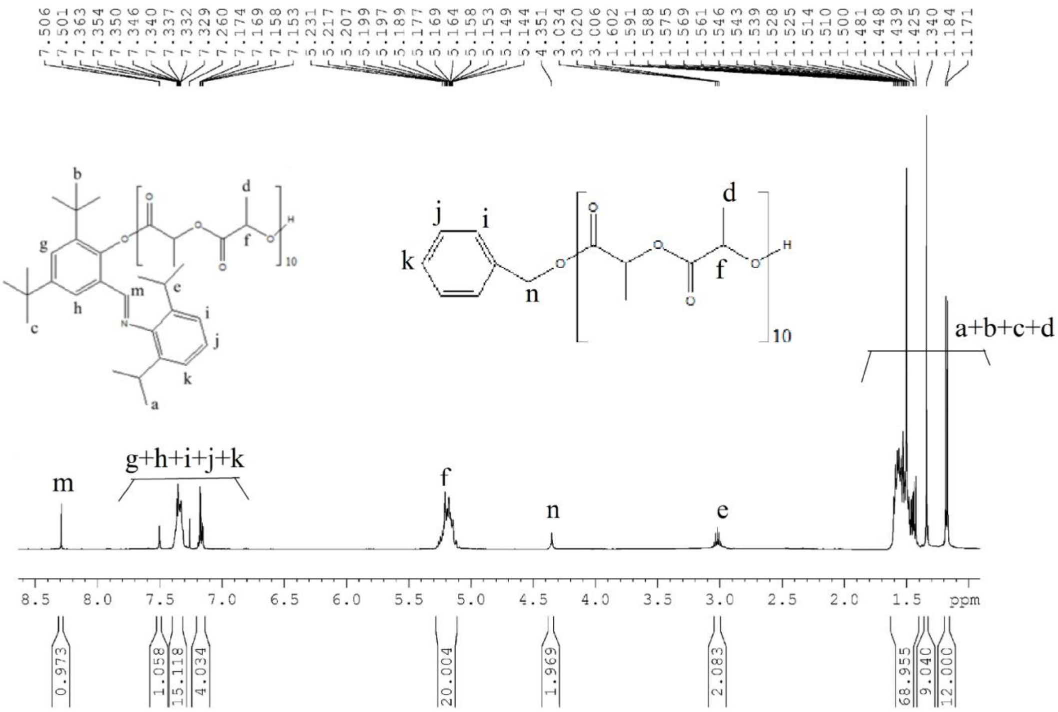


Fig. S39. [1]H NMR spectrum of the crude product obtained from a reaction between *rac*-LA, **4** and BnOH in 10:1:2 ratio

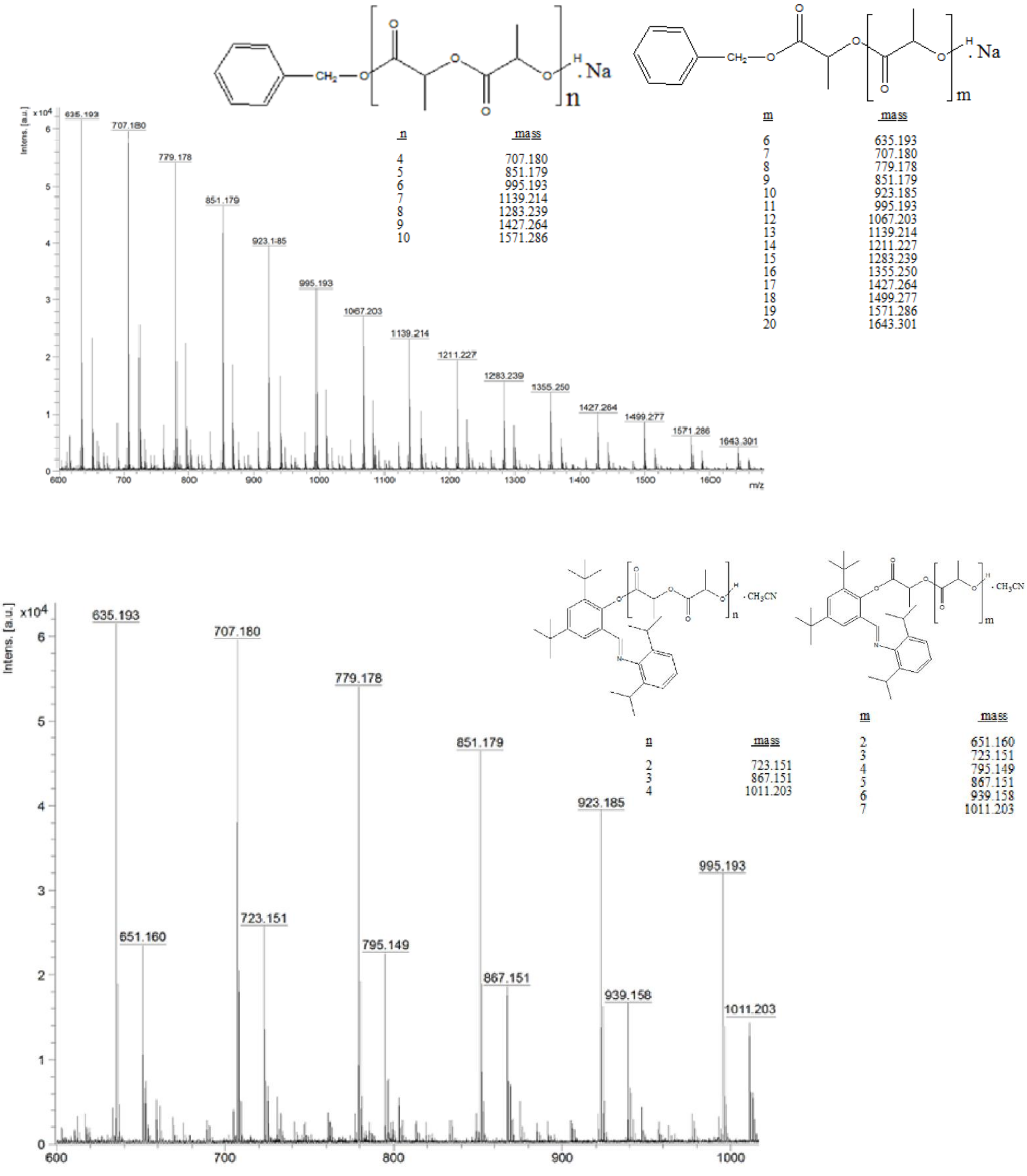


Fig. S40. MALDI-TOF spectrum of the crude product obtained from a reaction between *rac*-LA, **4** and BnOH in 10:1:2 ratio

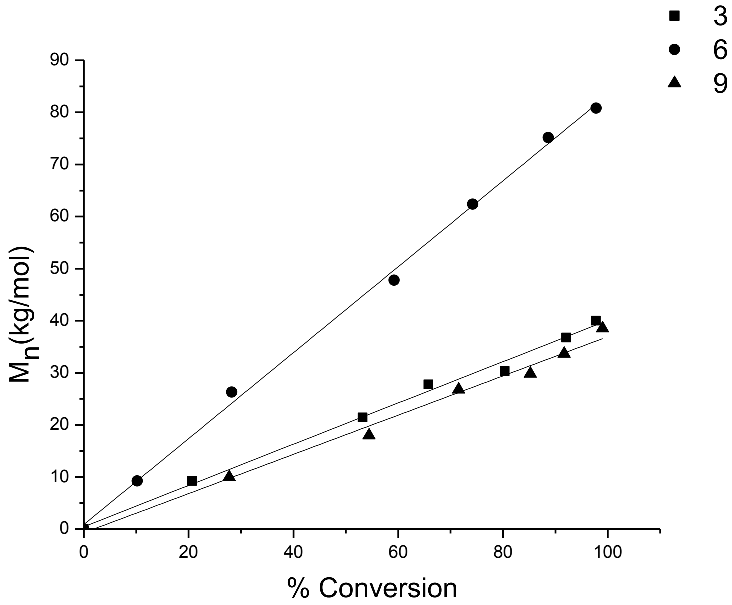


Fig. S41. Plot of M_n vs. % conversion of monomer

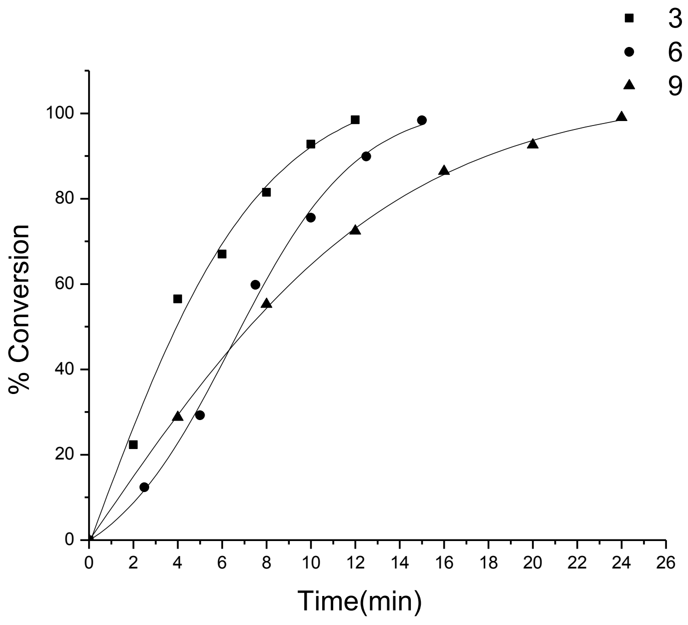


Fig. S42. *rac*-LA conversion vs. time plot using **3, 6** and **9**: [*rac*-LA]$_o$/[Cat]$_o$ = 200 at 130 °C

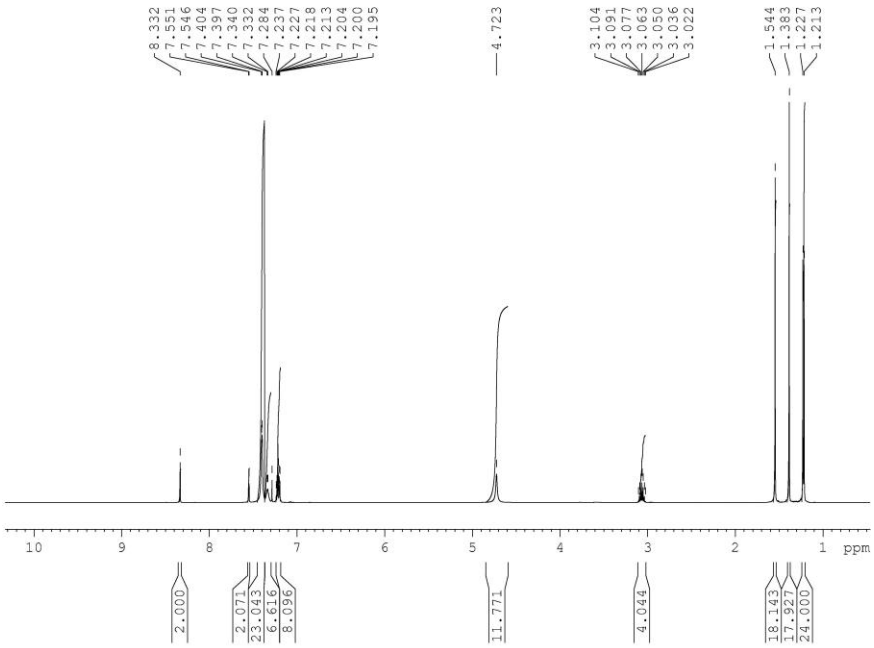


Fig. S45. ^{1}H NMR spectrum of the crude product obtained from a reaction between **4** and BnOH in 1:5 ratio

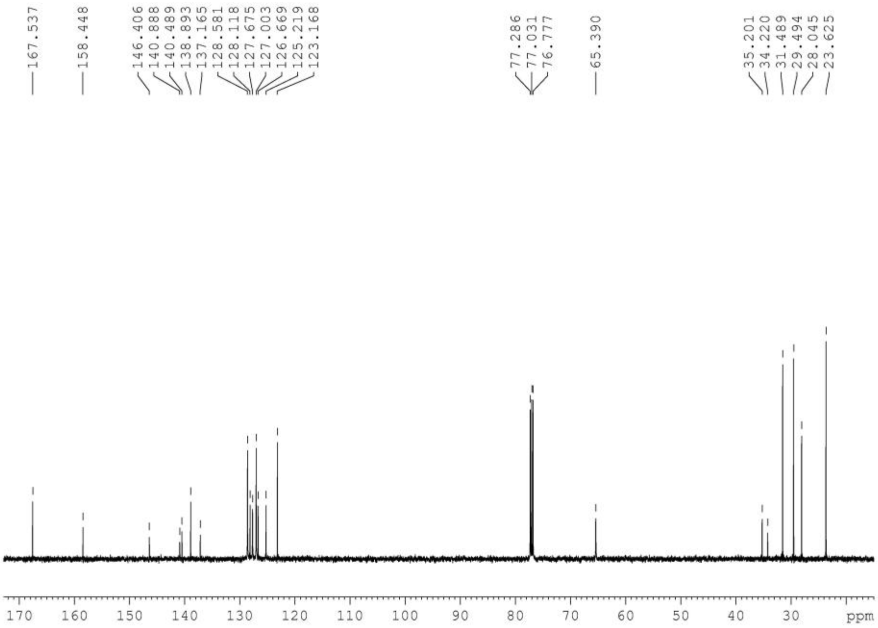


Fig. S46. ^{13}C NMR spectrum of the crude product obtained from a reaction between **4** and BnOH in 1:5 ratio