Supporting Information

Homoleptic titanium and zirconium complexes exhibiting unusual O_{iminol}-metal coordination: Application in stereoselective ring-opening polymerization of lactide

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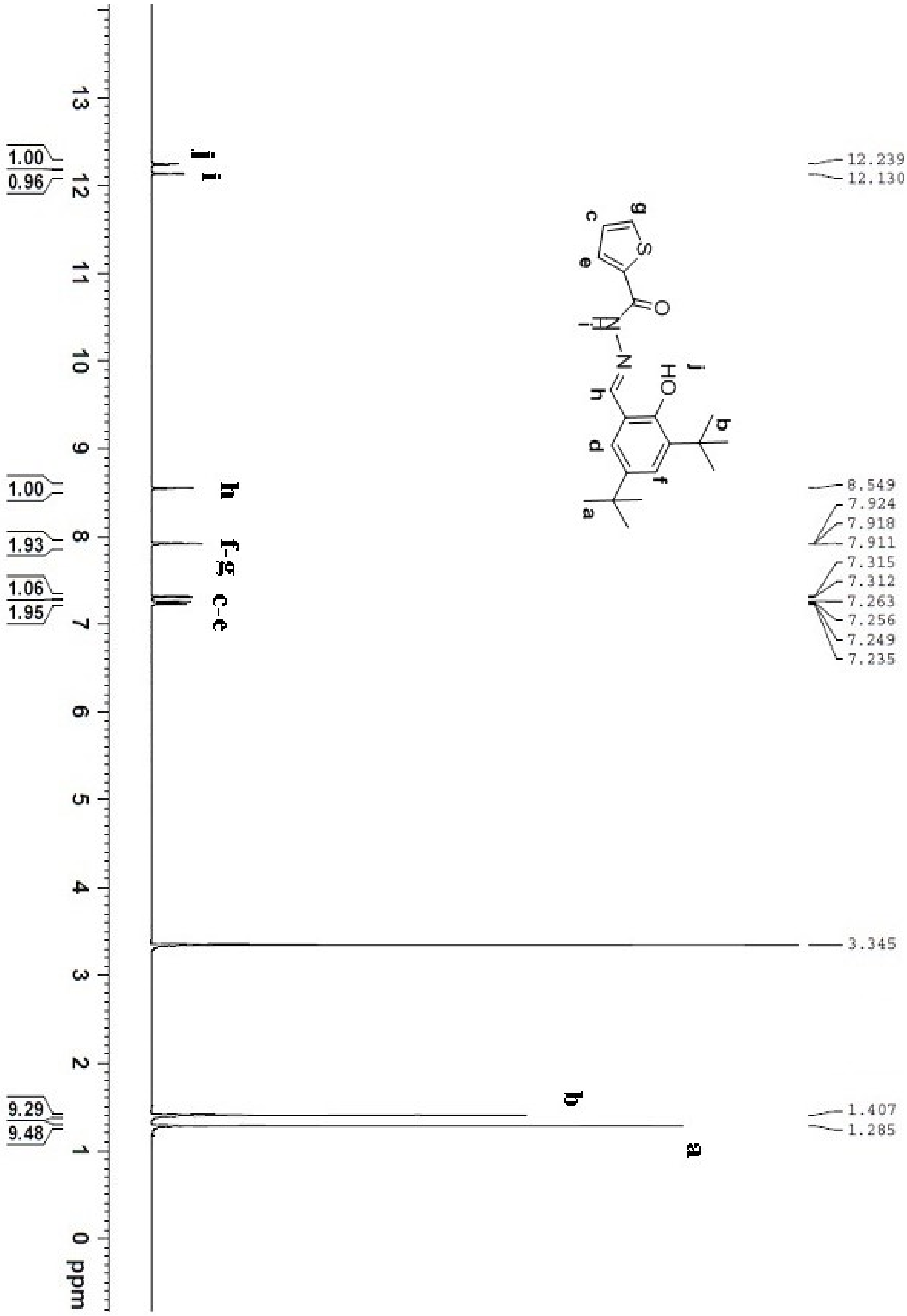


Fig. S1.[1]H NMR (400 MHz, DMSO-d$_6$) of Compound **L1H$_2$**

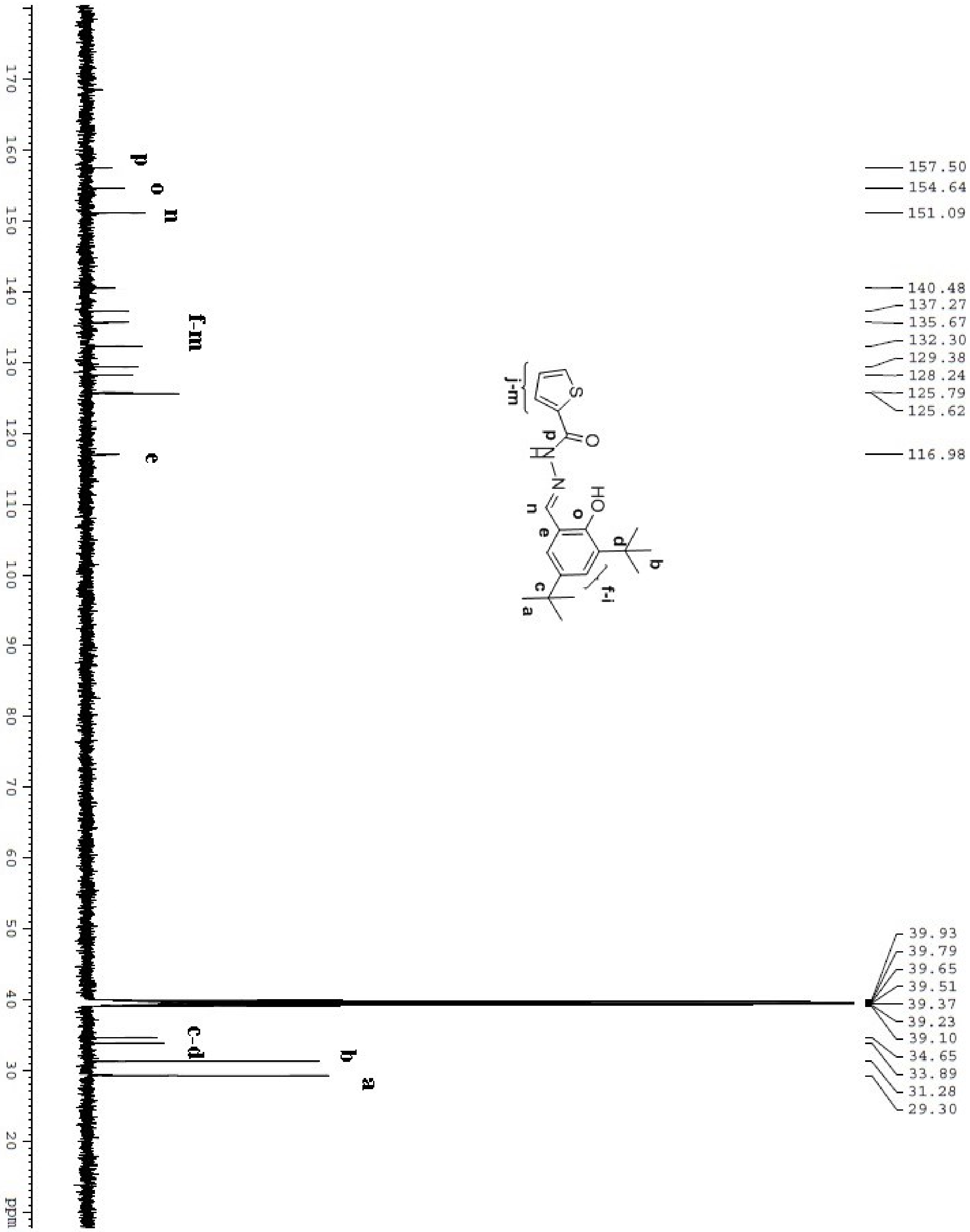
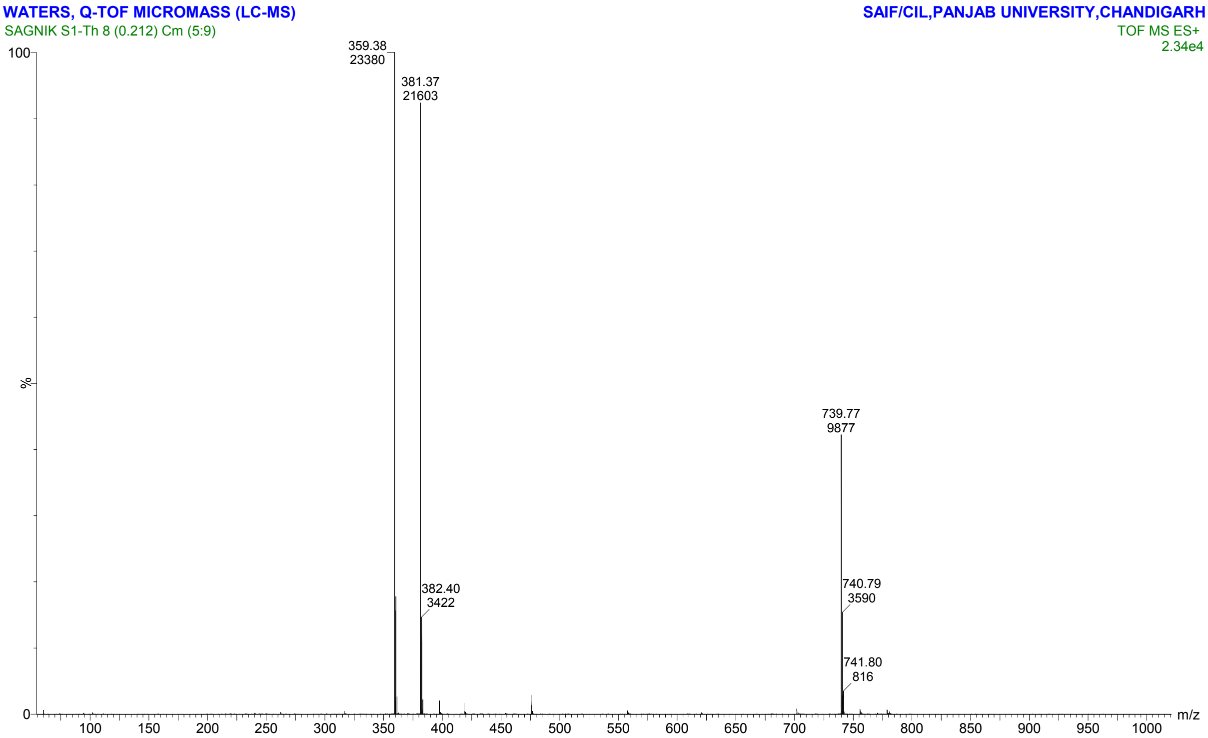


Fig. S2.[13]C NMR (100 MHz, DMSO-d$_6$) of Compound **L1H$_2$**



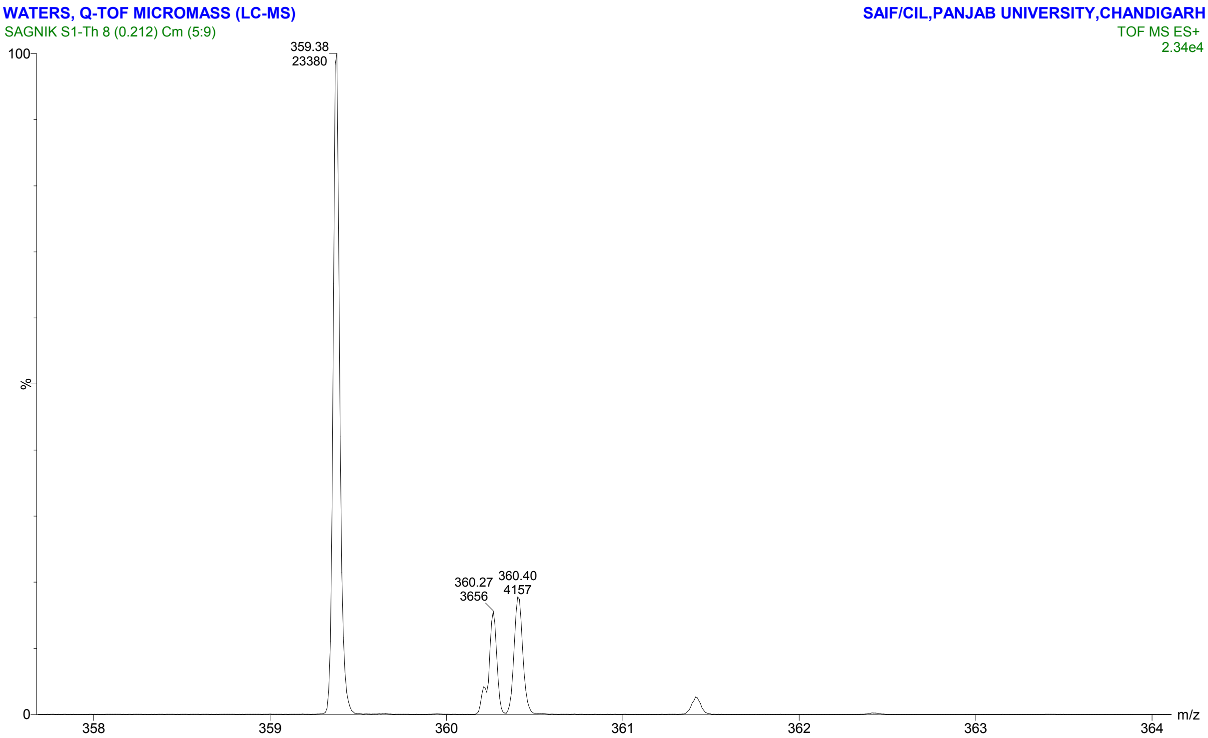


Fig. S3. ESI mass spectrum of Compound $\mathbf{L1H_2}$

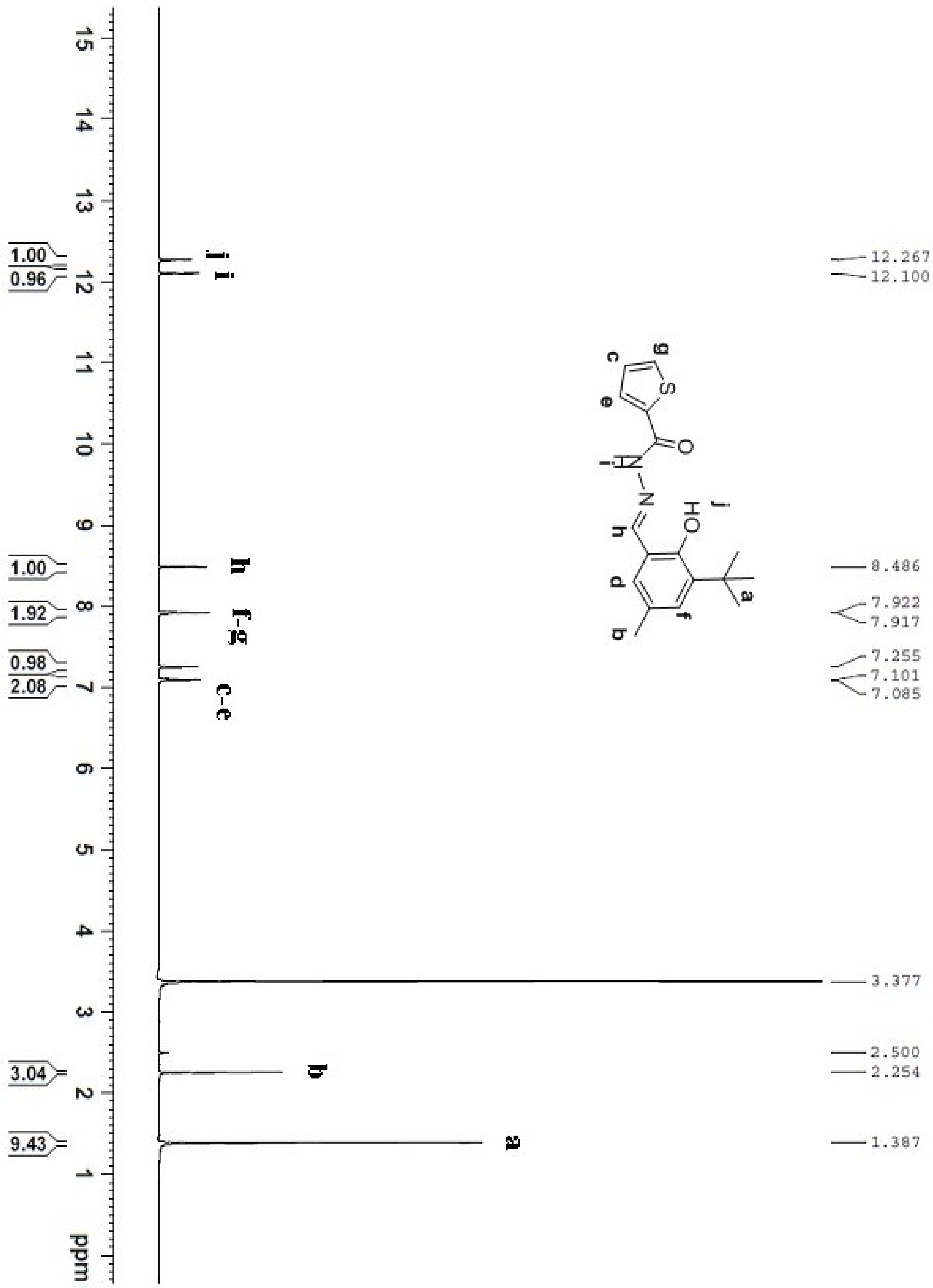


Fig. S4.[1]H NMR (400 MHz, DMSO-d_6) of Compound **L2H$_2$**

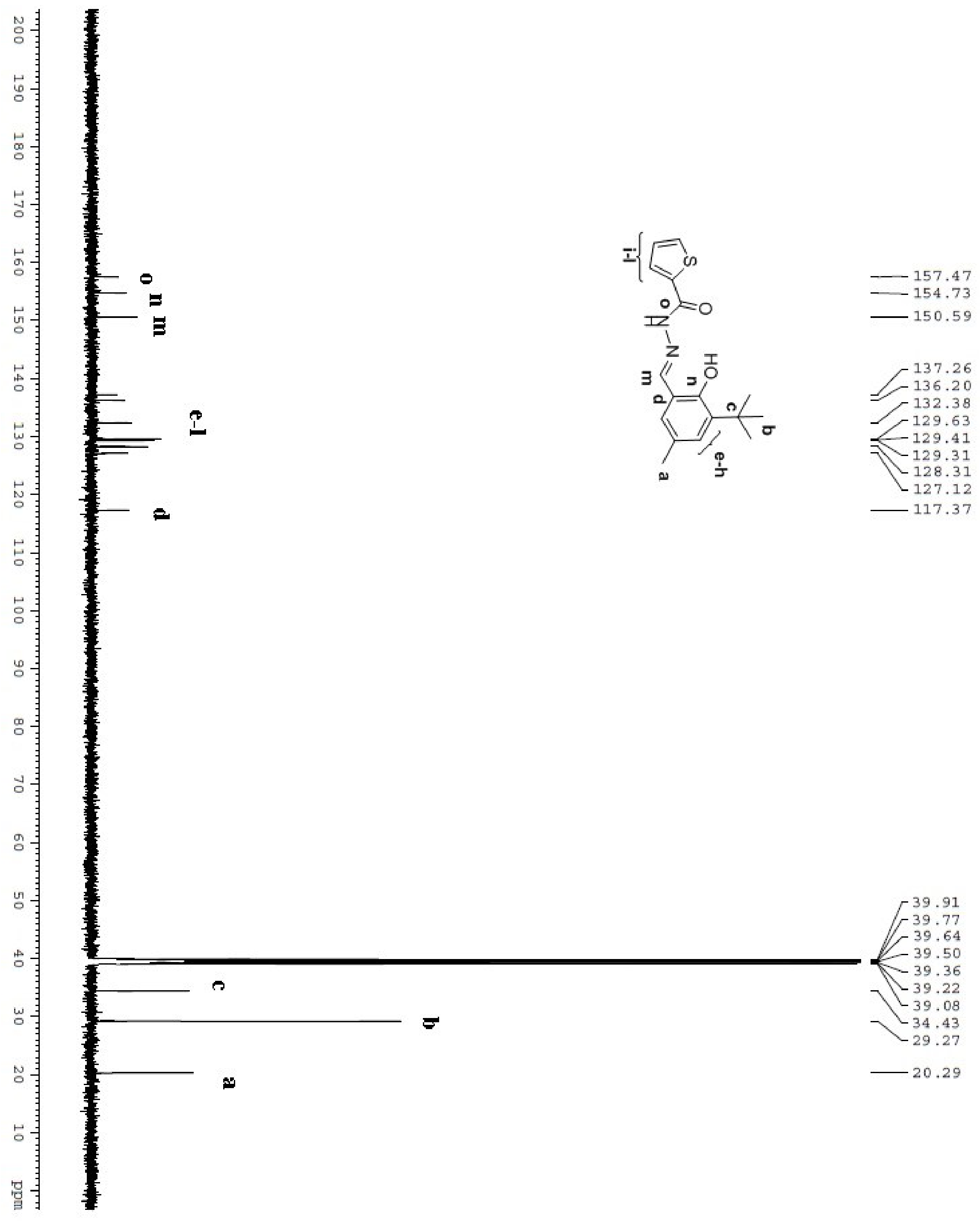
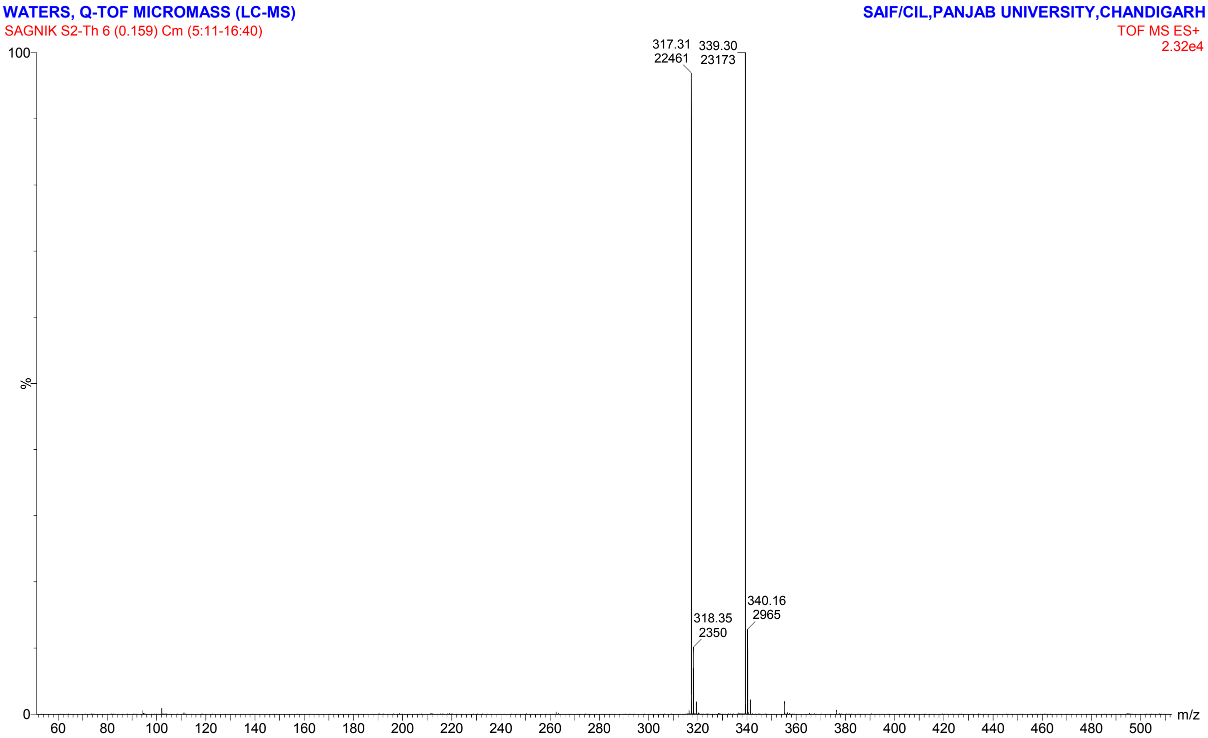


Fig. S5.[13]C NMR (100 MHz, DMSO-d_6) of Compound **L2H$_2$**



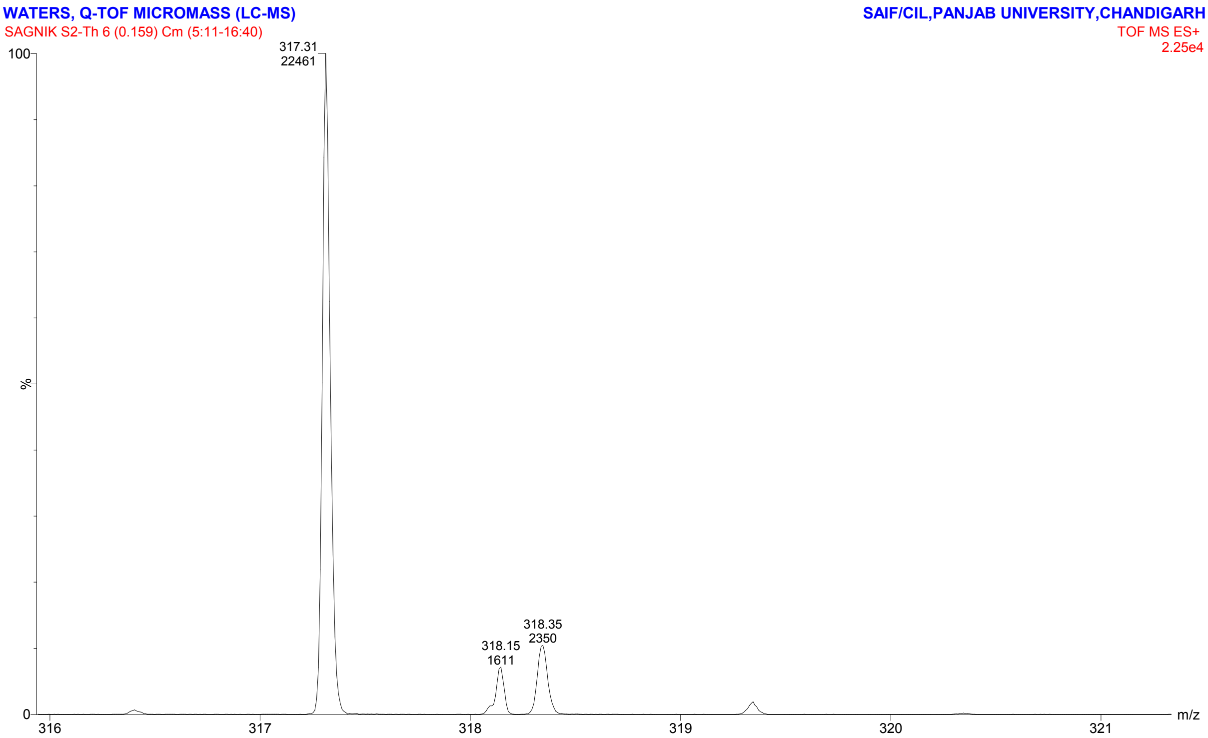


Fig. S6. ESI mass spectrum of Compound **L2H$_2$**

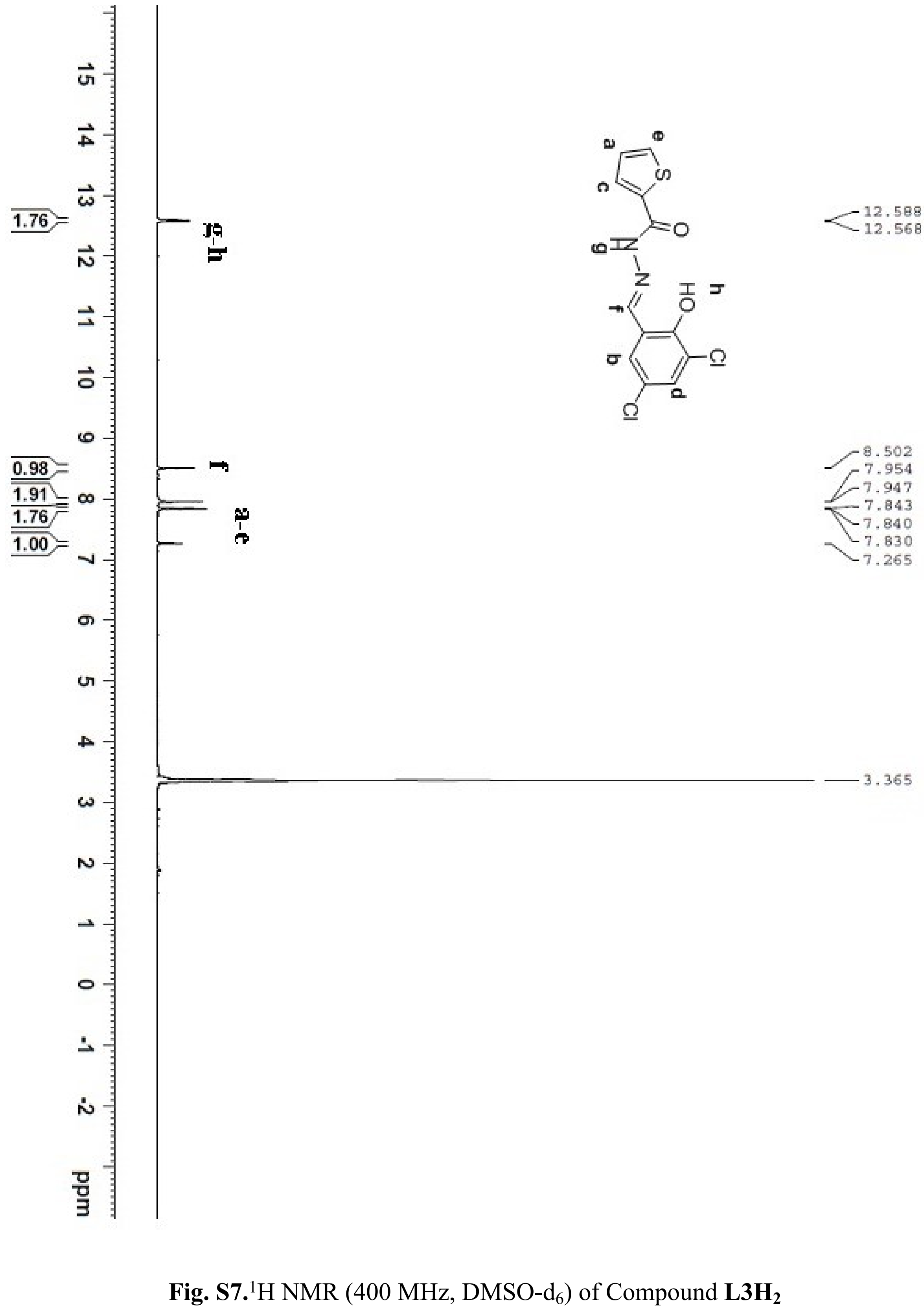


Fig. S7. [1]H NMR (400 MHz, DMSO-d_6) of Compound **L3H$_2$**

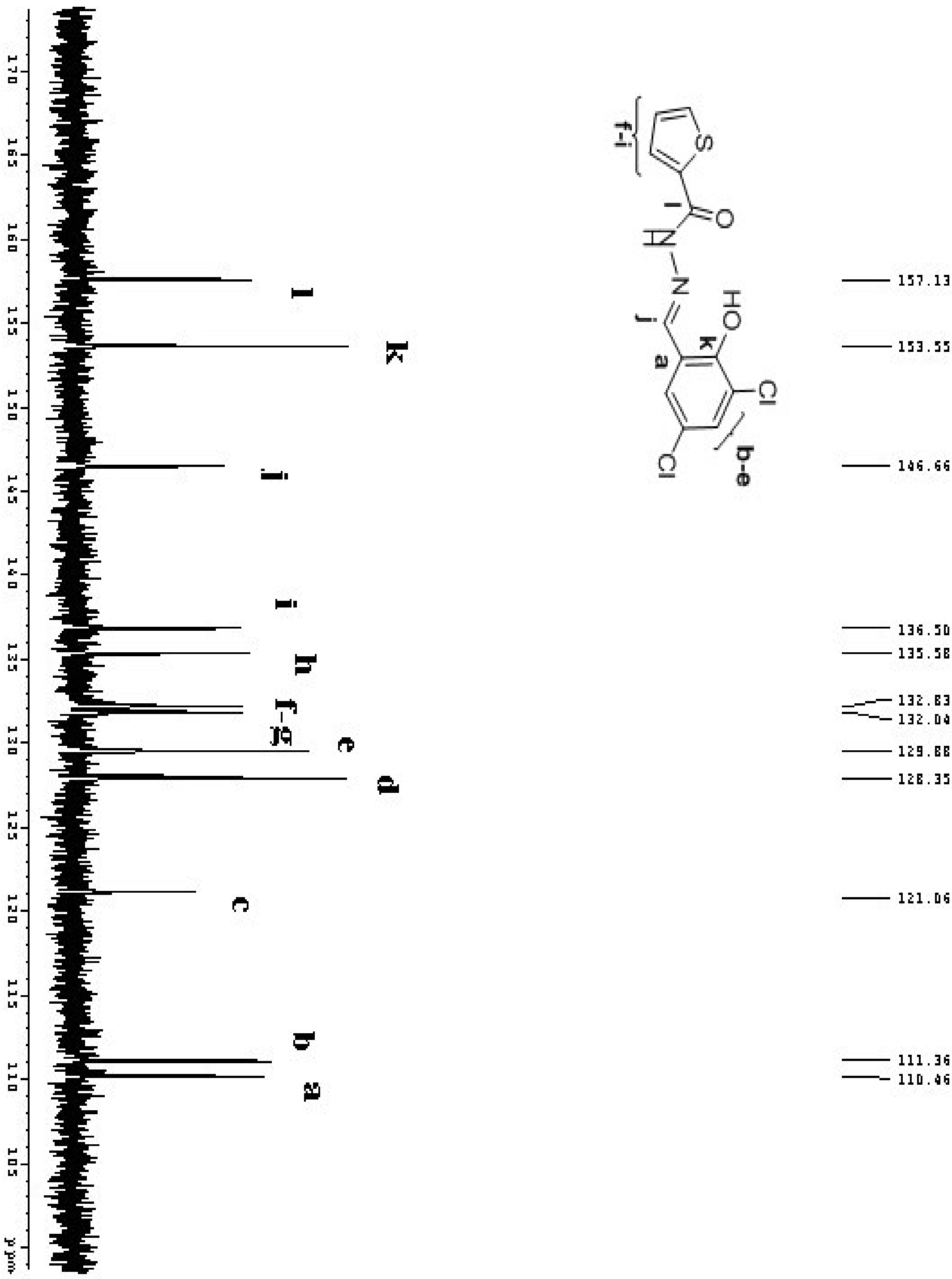
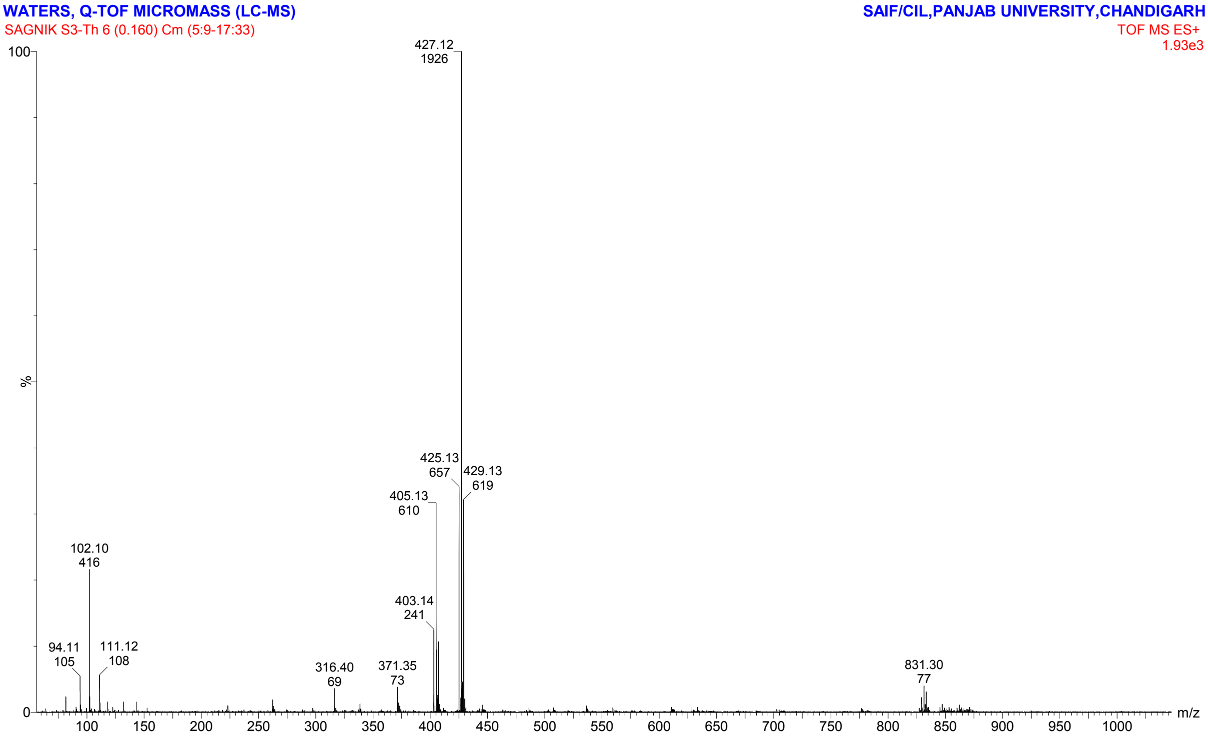


Fig. S8.[13]C NMR (100 MHz, DMSO-d_6) of Compound **L3H$_2$**



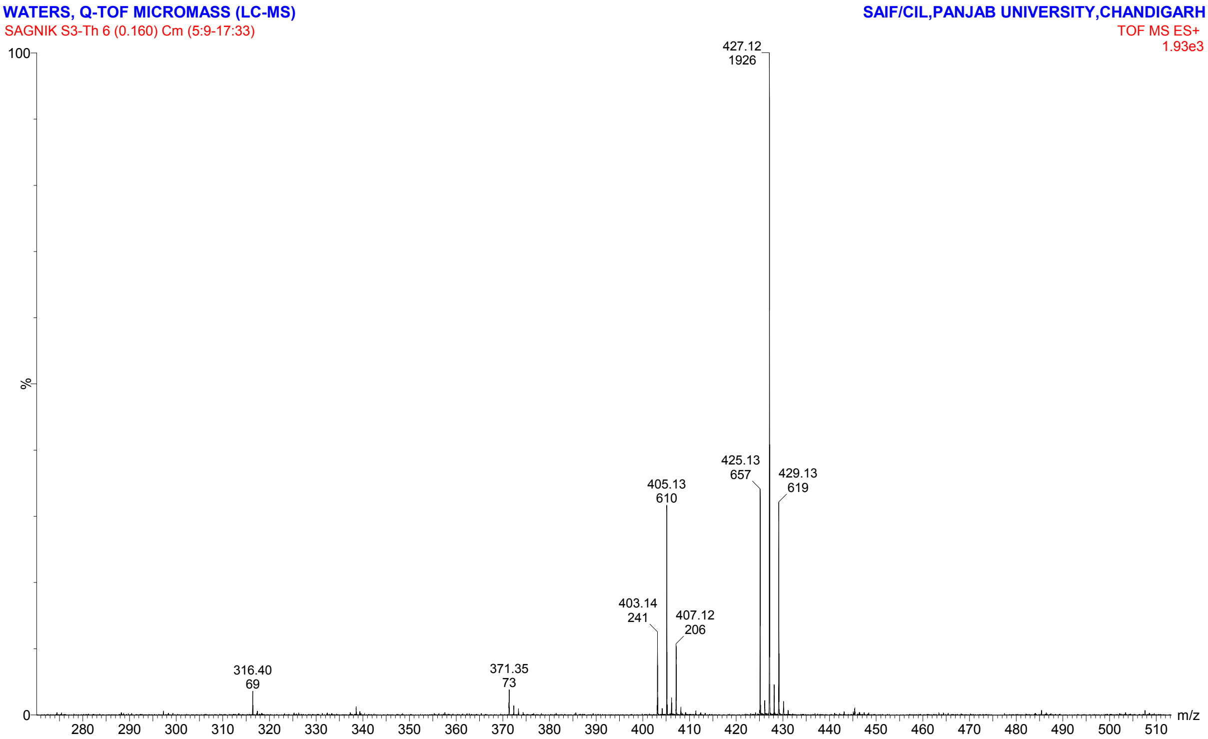


Fig. S9. ESI mass spectrum of Compound $\mathbf{L3H_2}$

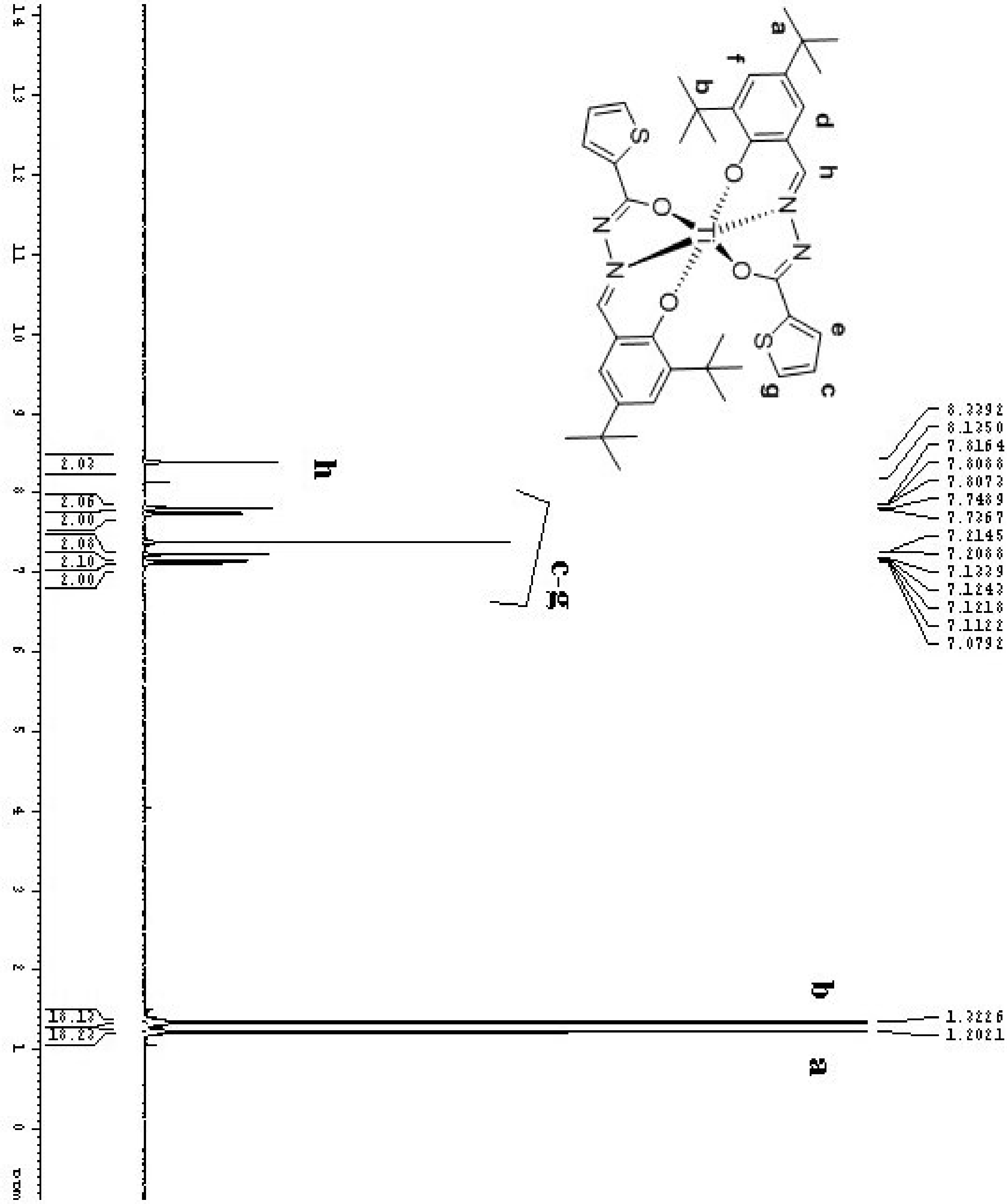


Fig. S10. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **1**

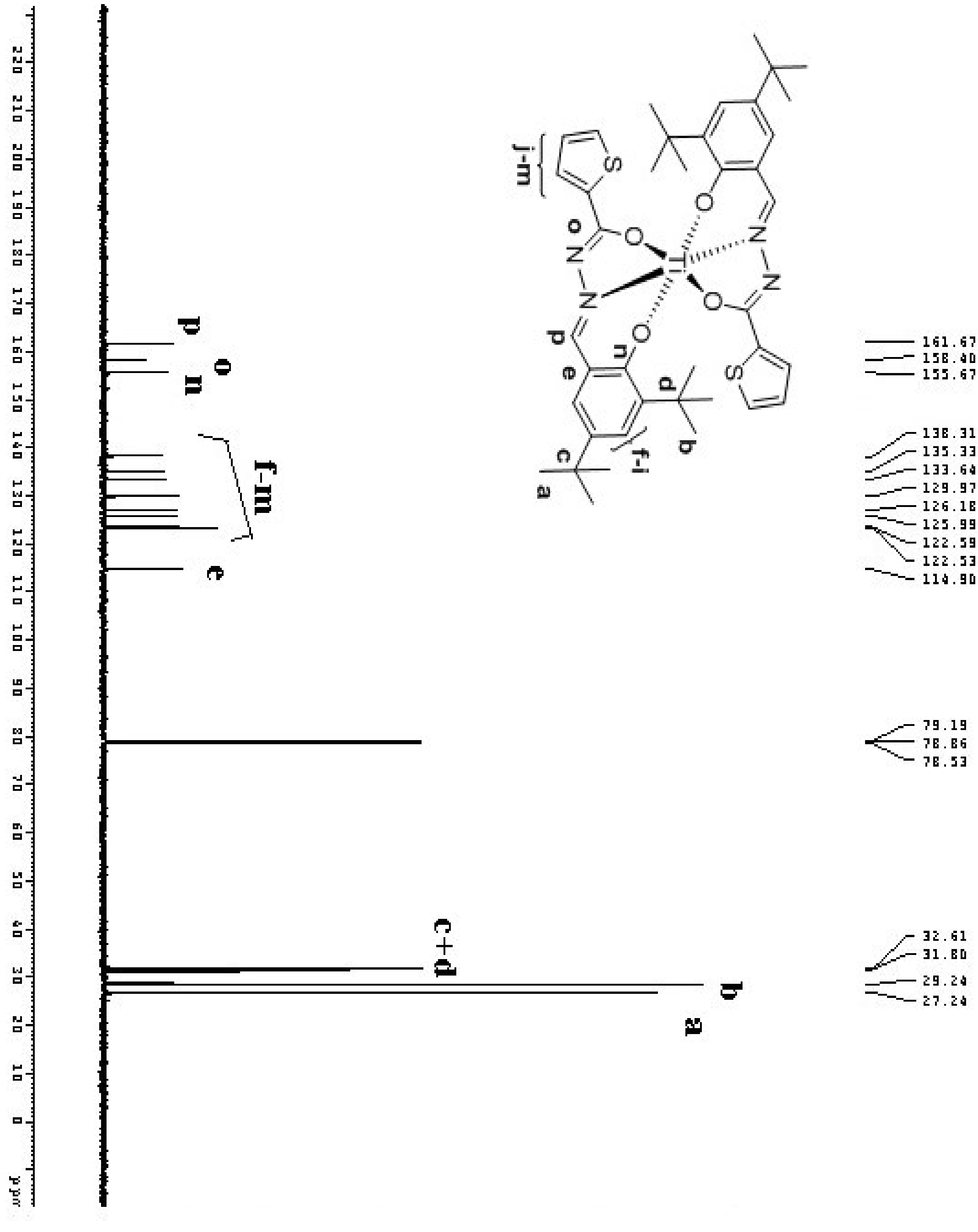


Fig. S11. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **1**

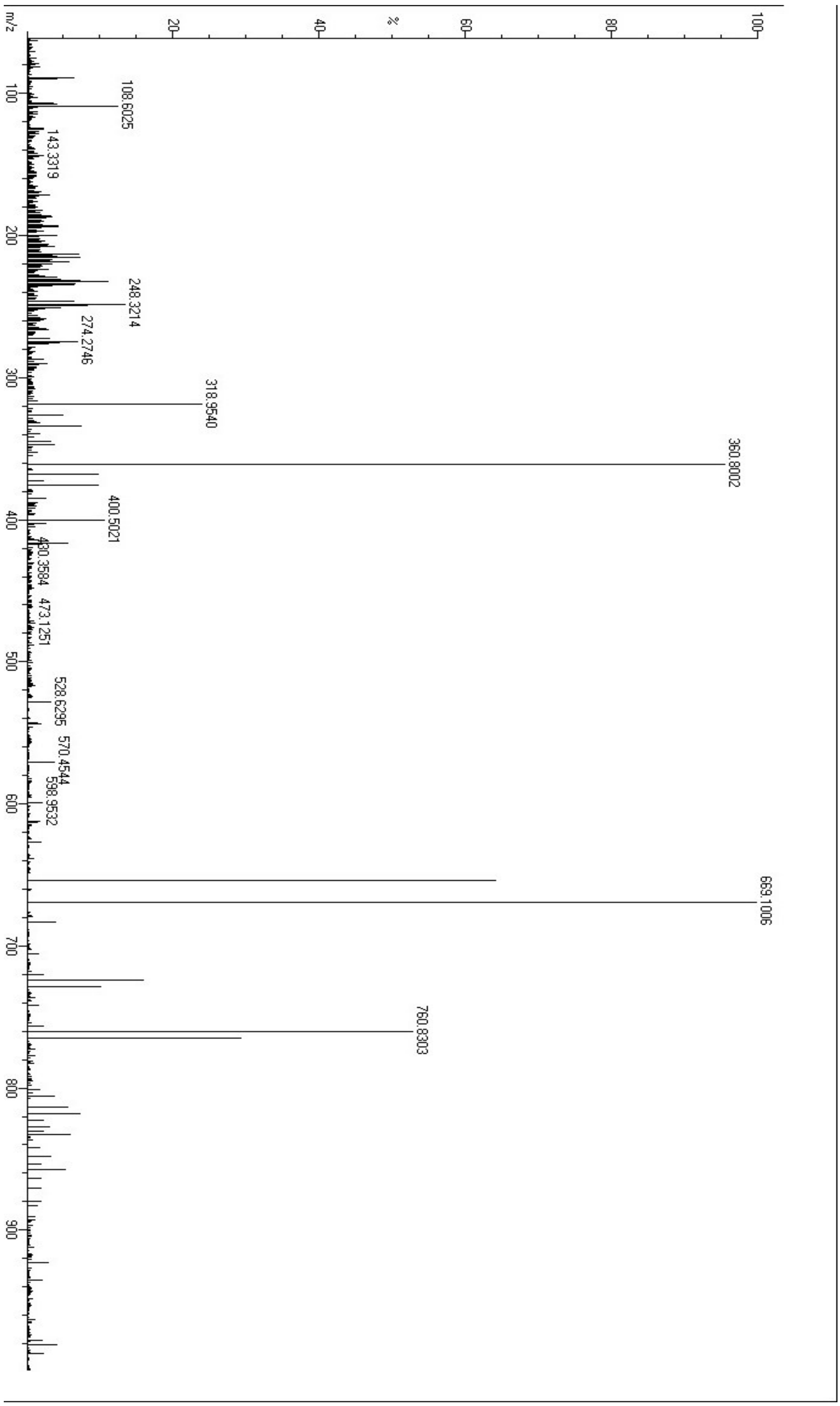


Fig. S12. ESI mass spectrum of Compound **1**

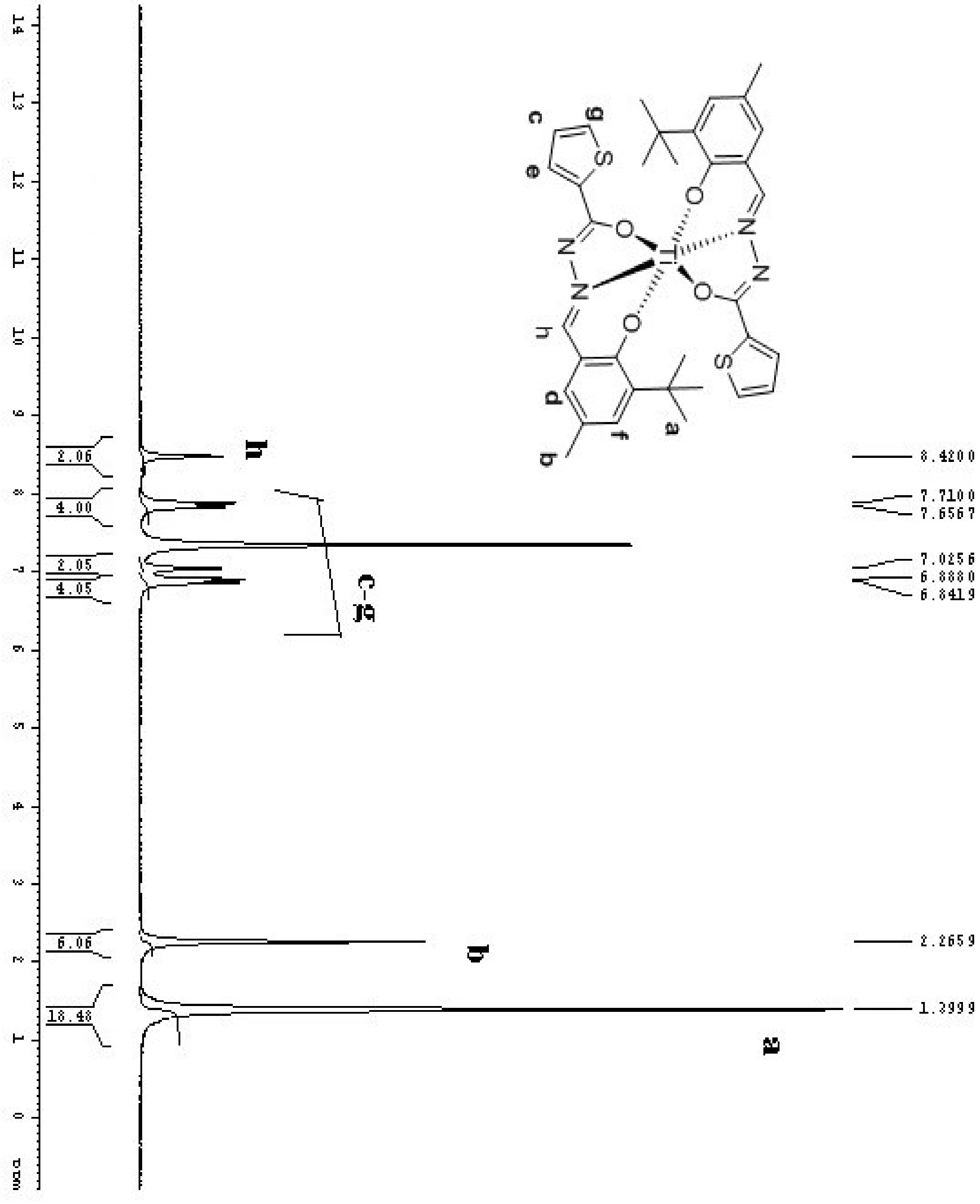


Fig. S13.[1]H NMR (400 MHz, $CDCl_3$) of Compound **2**

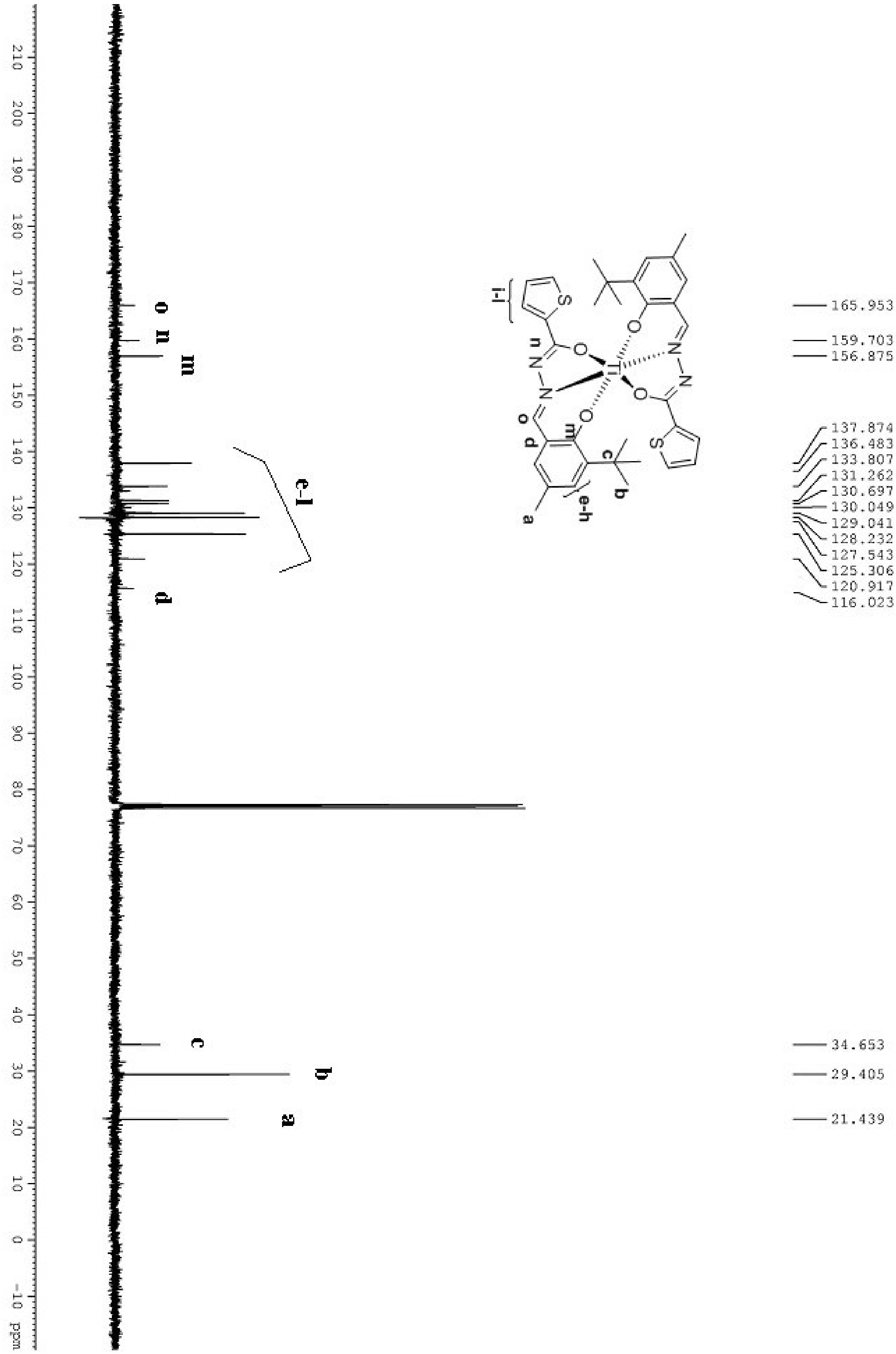


Fig. S14. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **2**

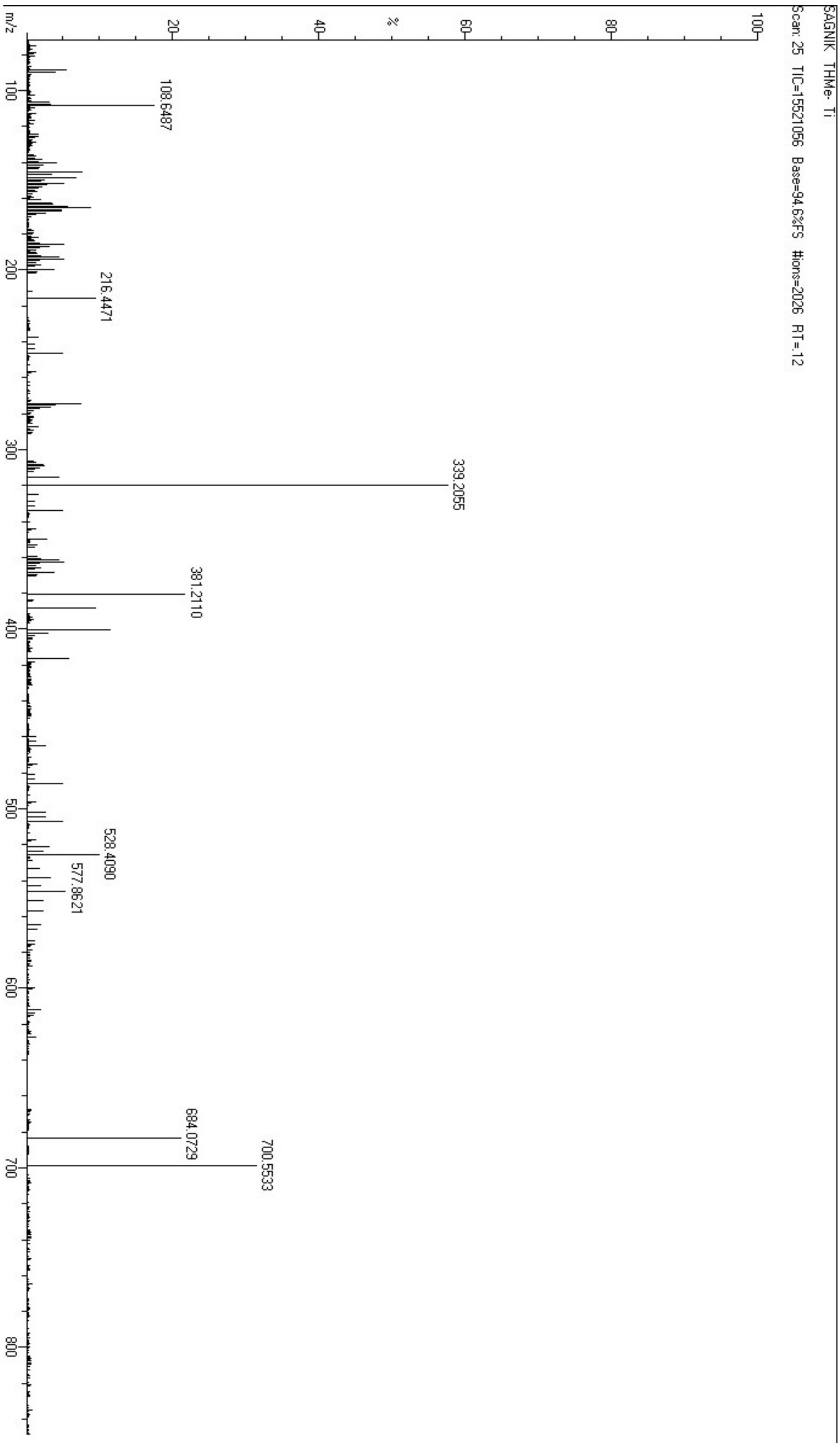


Fig. S15. ESI mass spectrum of Compound **2**

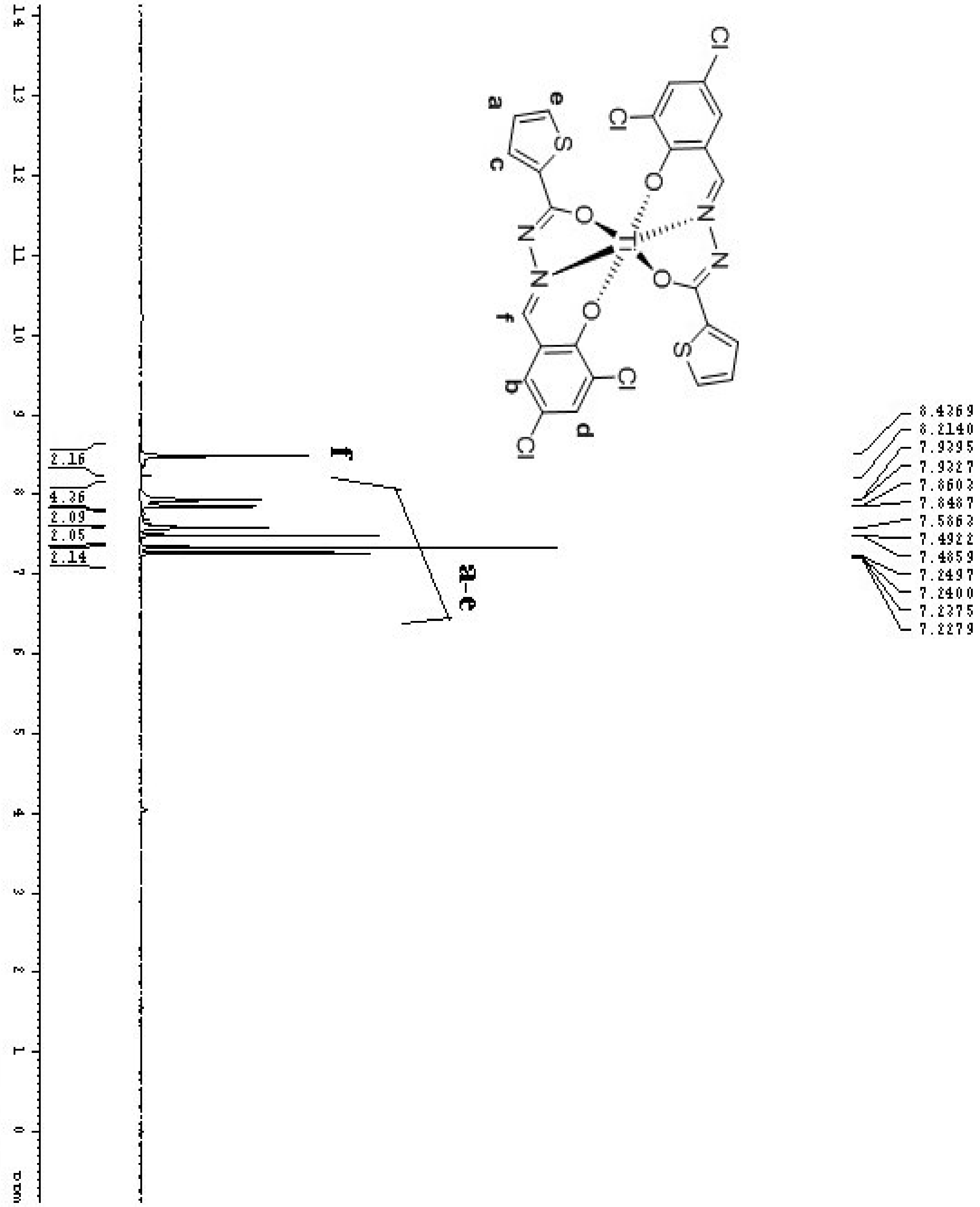


Fig. S16.^{1}H NMR (400 MHz, $CDCl_3$) of Compound **3**

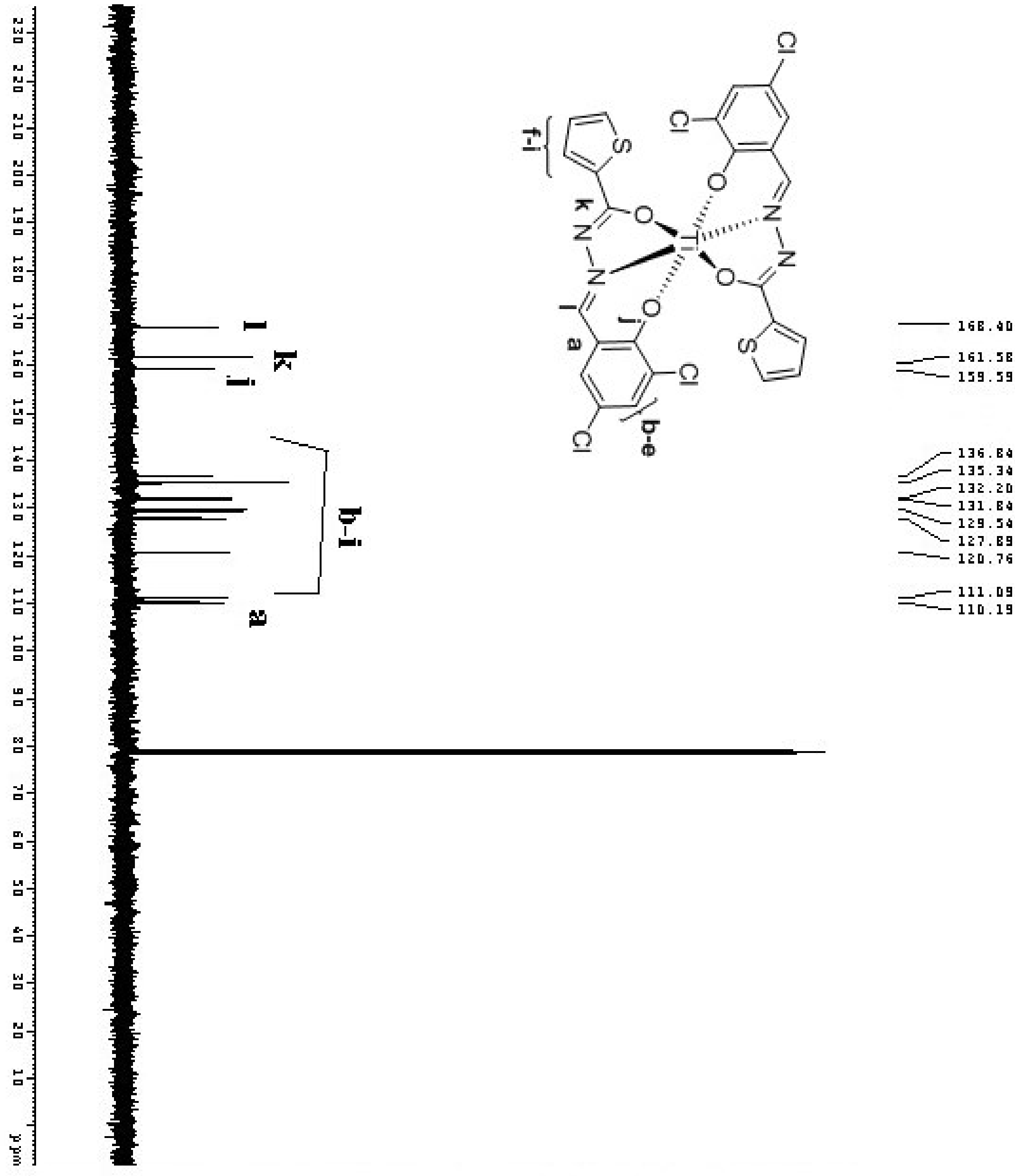


Fig. S17. ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **3**

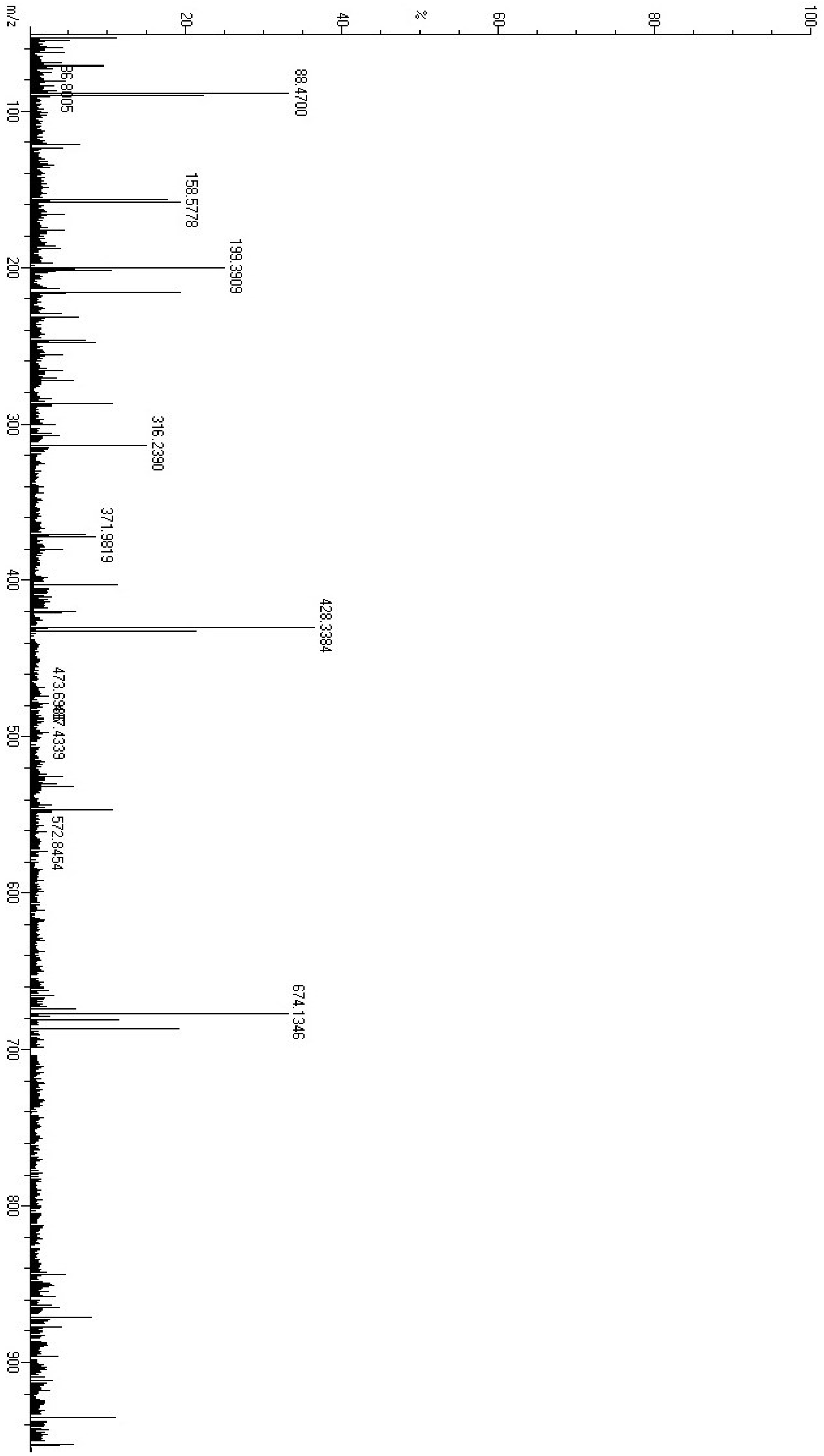


Fig. S18. ESI mass spectrum of Compound **3**

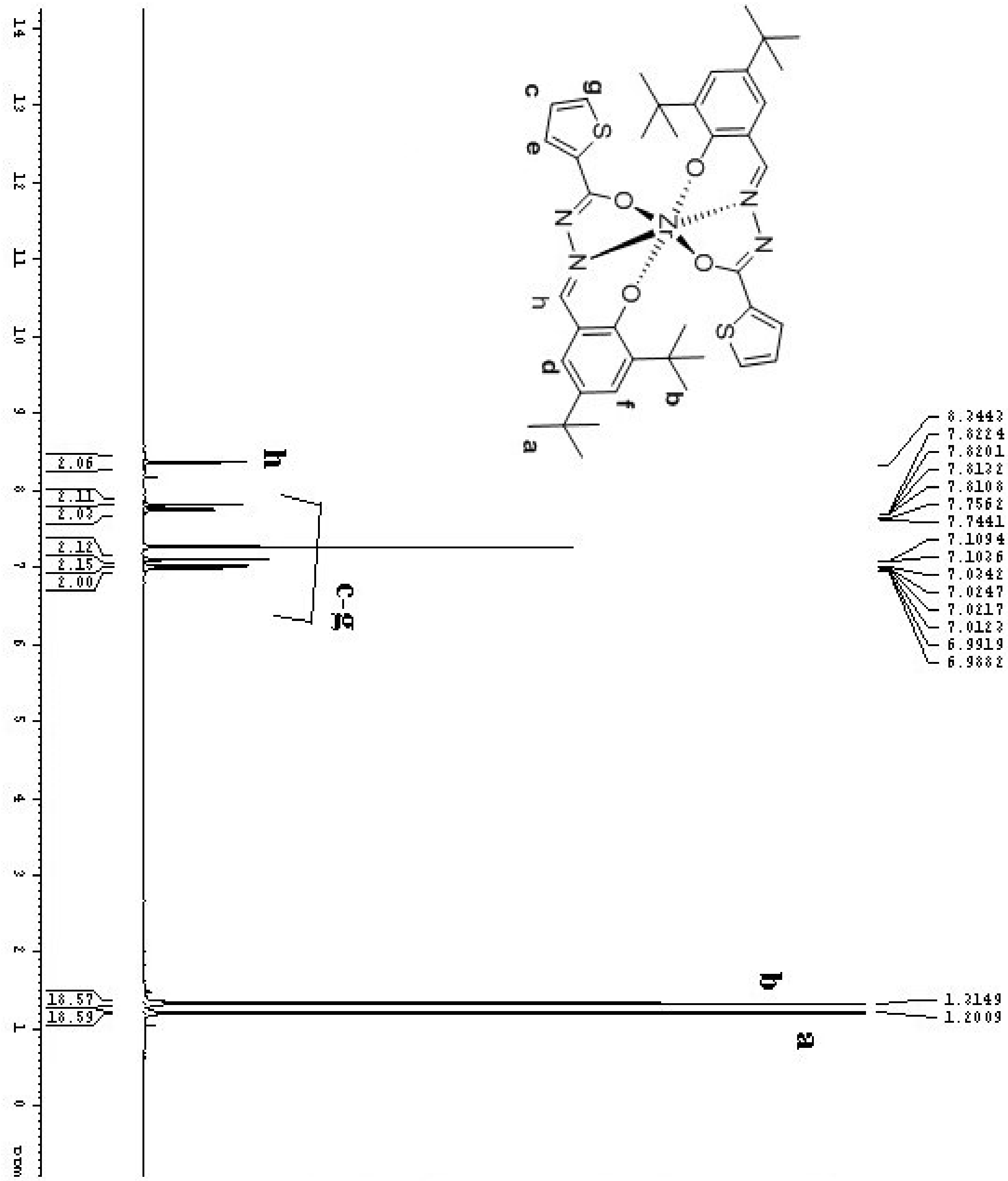


Fig. S19.^{1}H NMR (400 MHz, $CDCl_3$) of Compound **4**

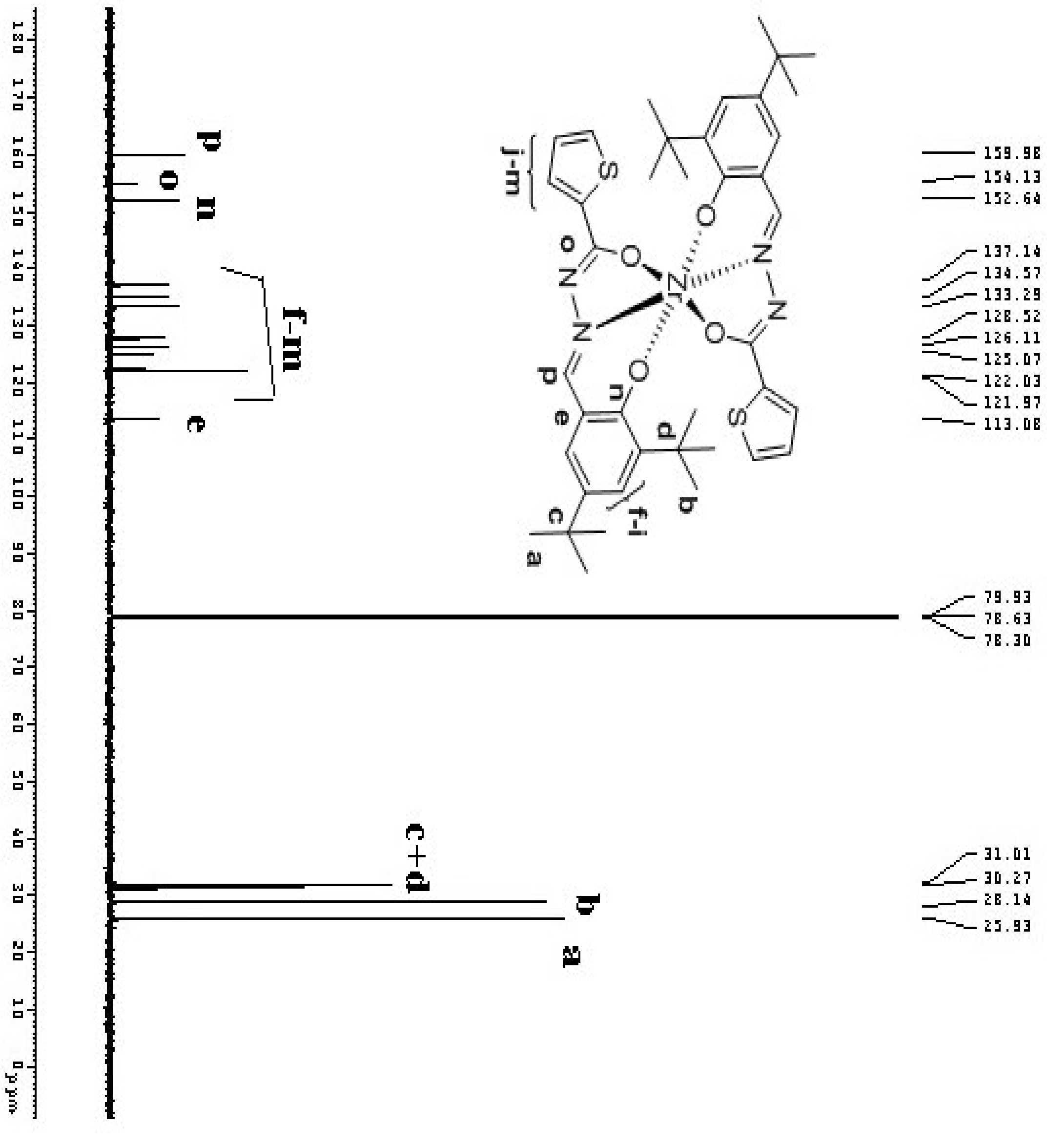


Fig. S20.^{13}C NMR (100 MHz, $CDCl_3$) of Compound **4**

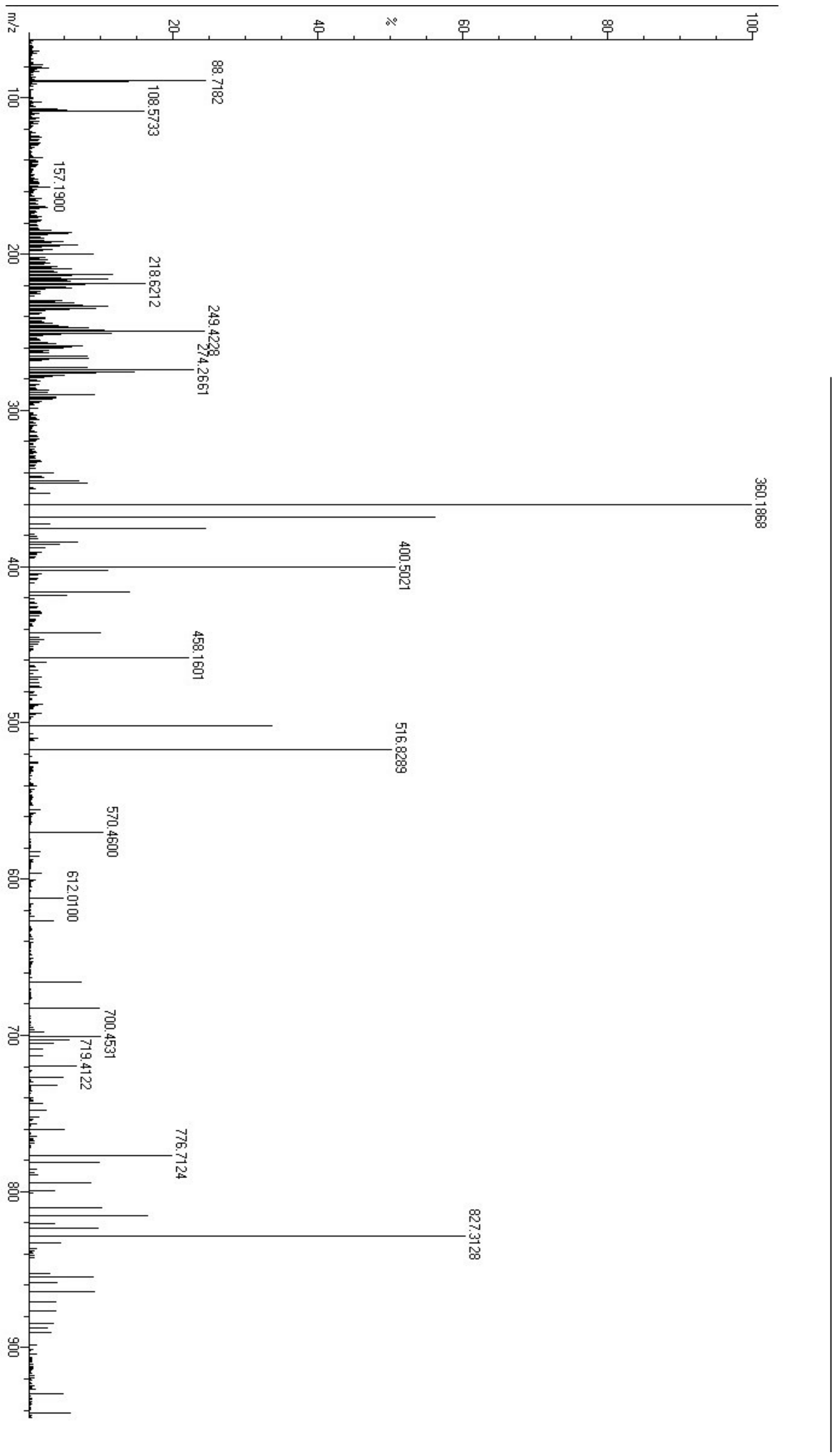


Fig. S21. ESI mass spectrum of Compound **4**

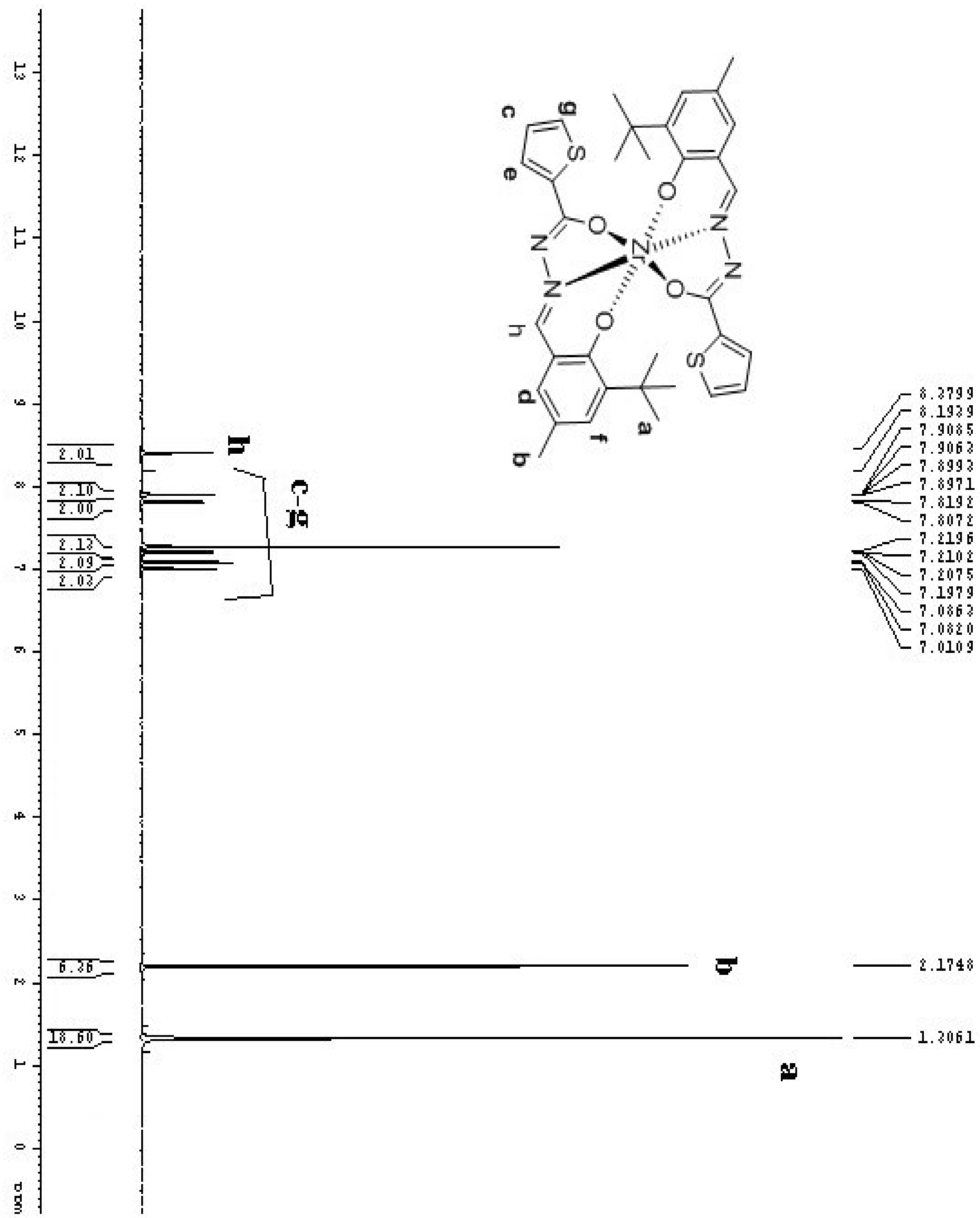


Fig. S22. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **5**

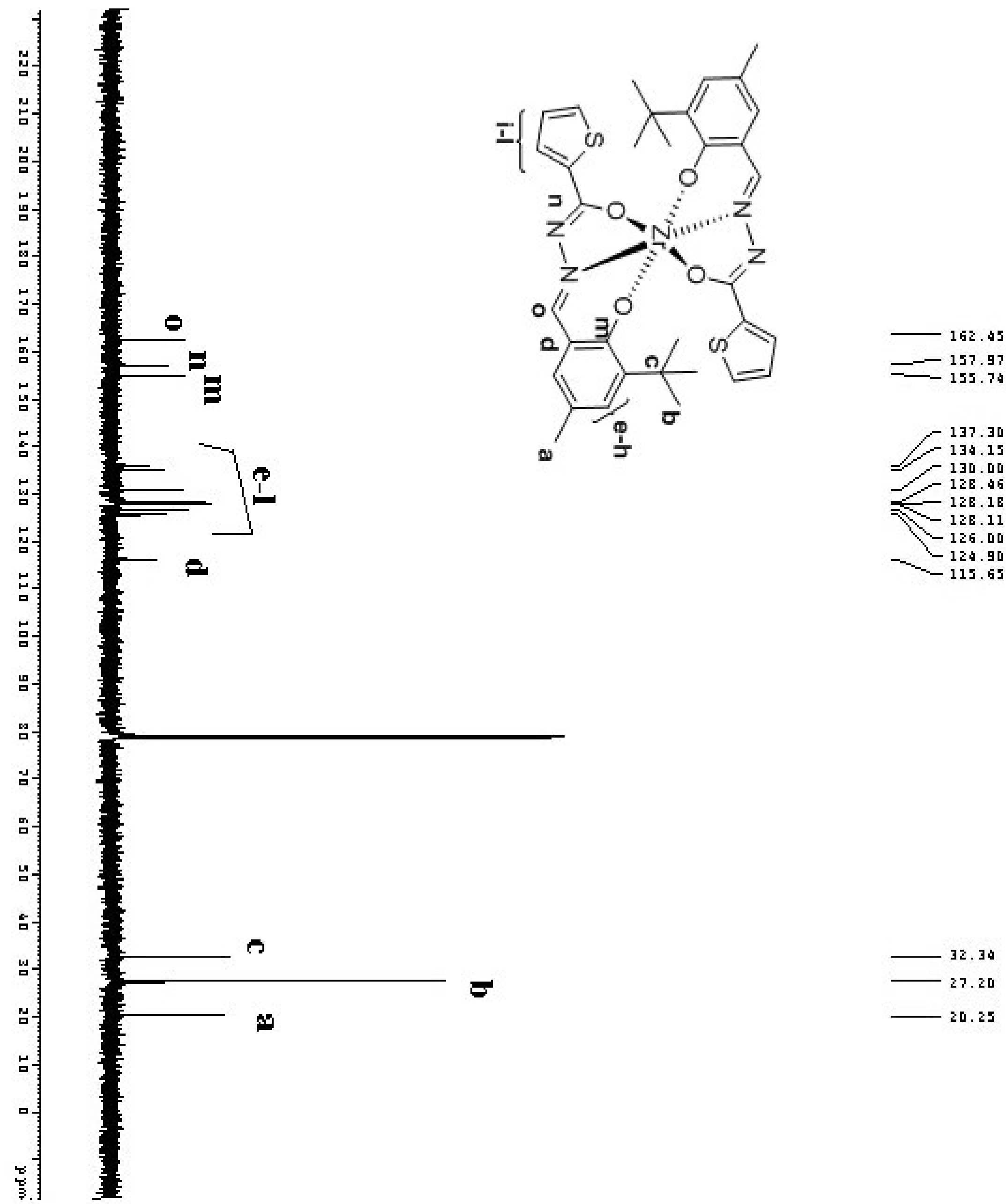


Fig. S23.^{13}C NMR (100 MHz, $CDCl_3$) of Compound **5**

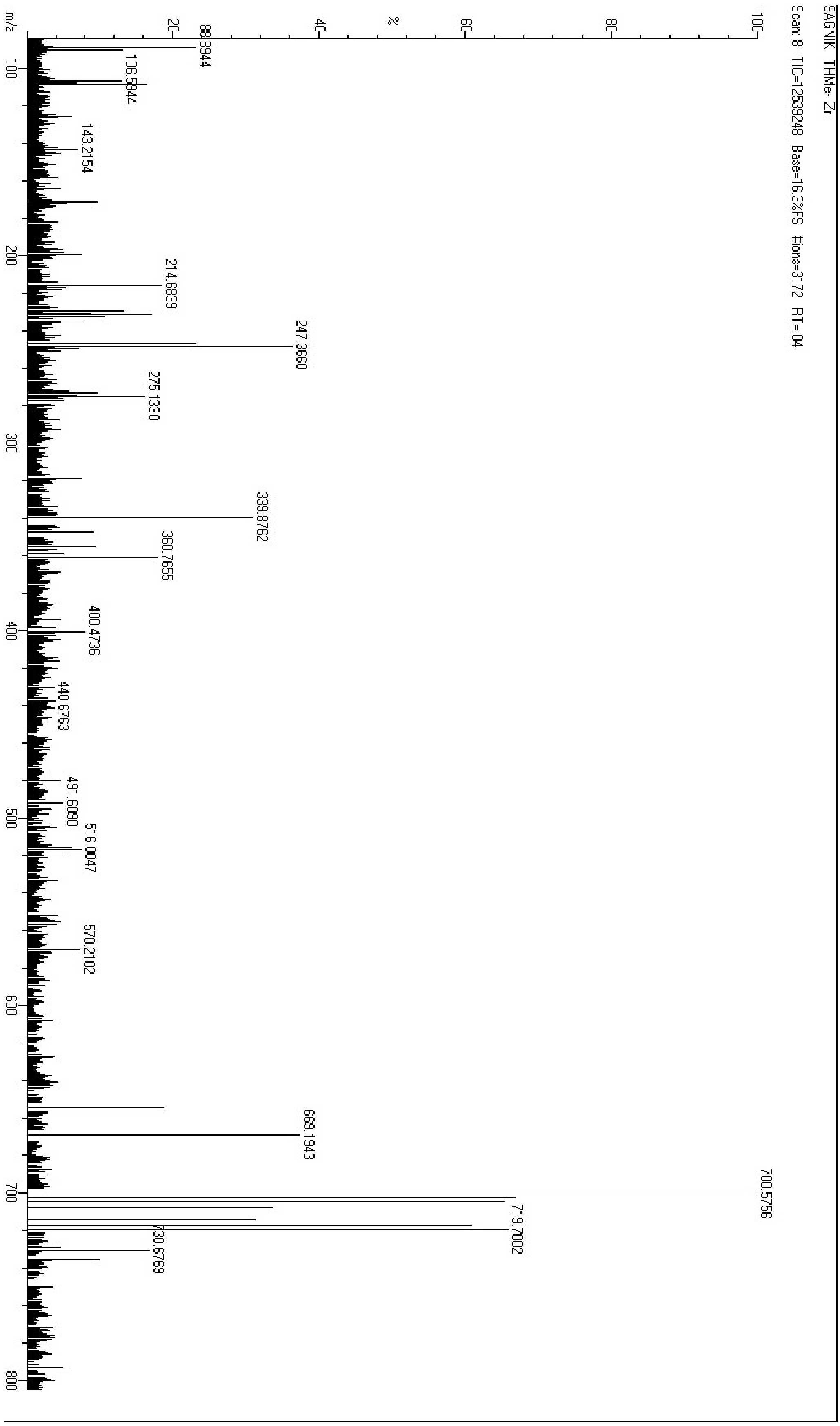


Fig. S24. ESI mass spectrum of Compound **5**

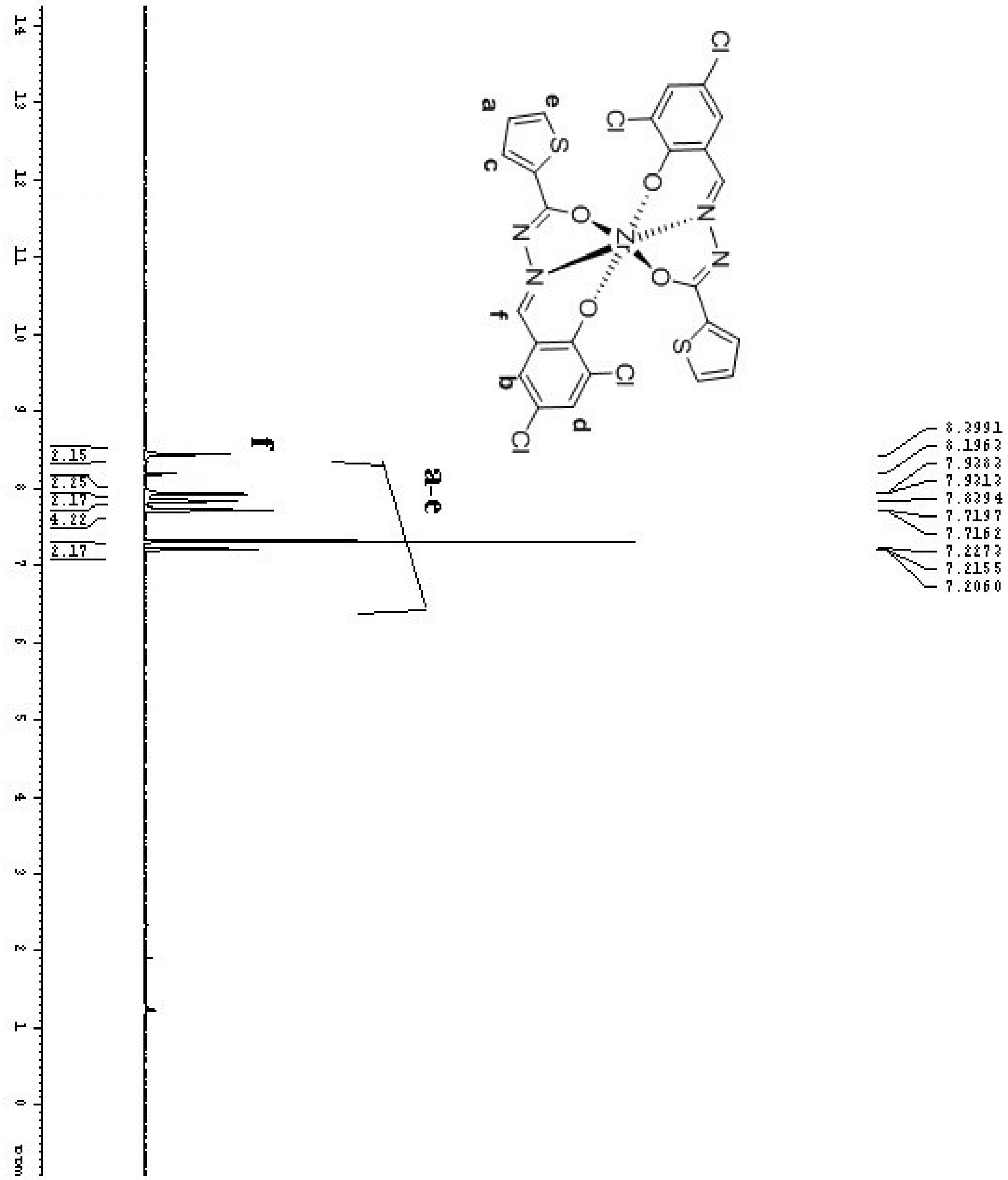


Fig. S25.[1]H NMR (400 MHz, $CDCl_3$) of Compound **6**

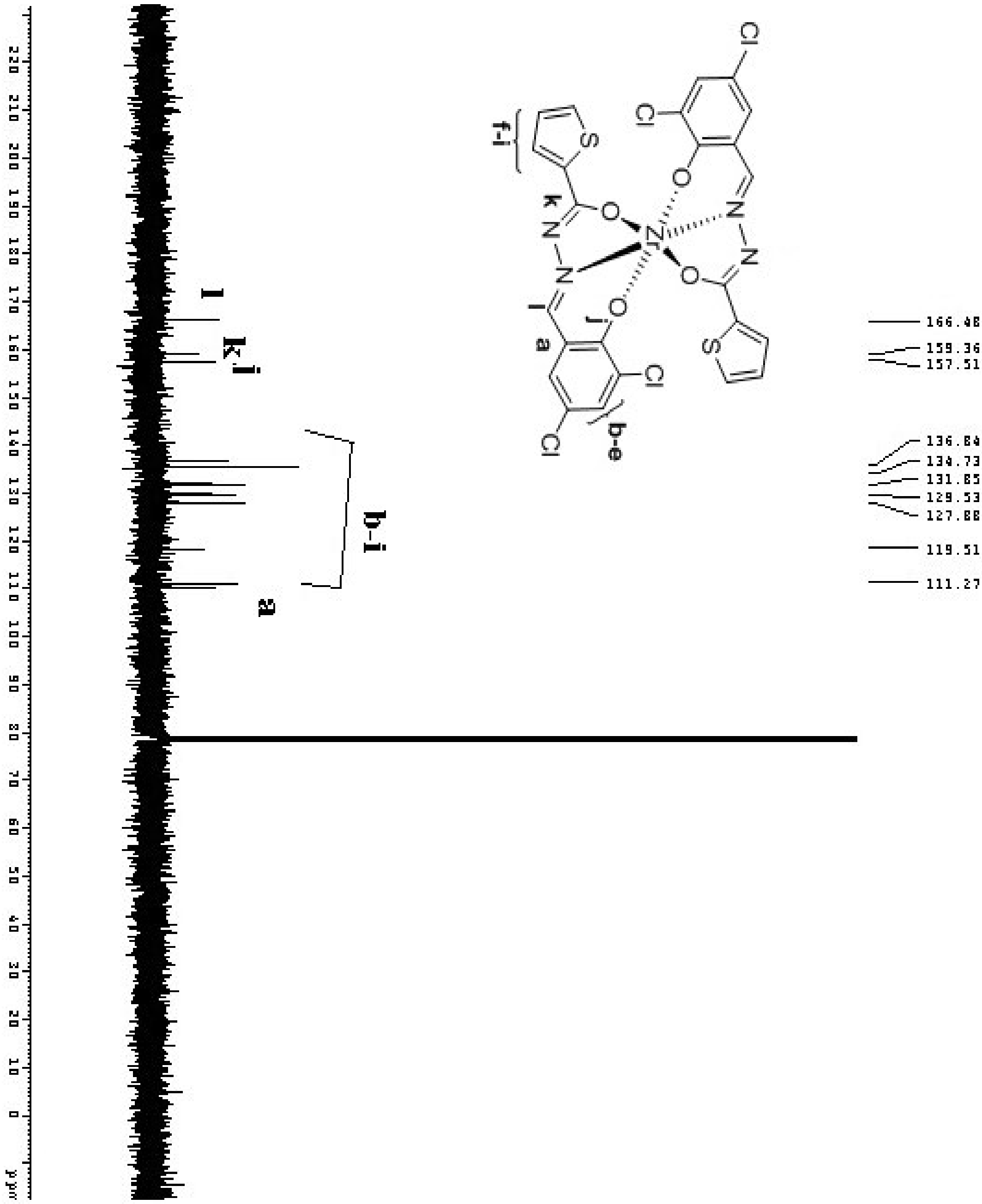


Fig. S26.^{13}C NMR (100 MHz, $CDCl_3$) of Compound **6**

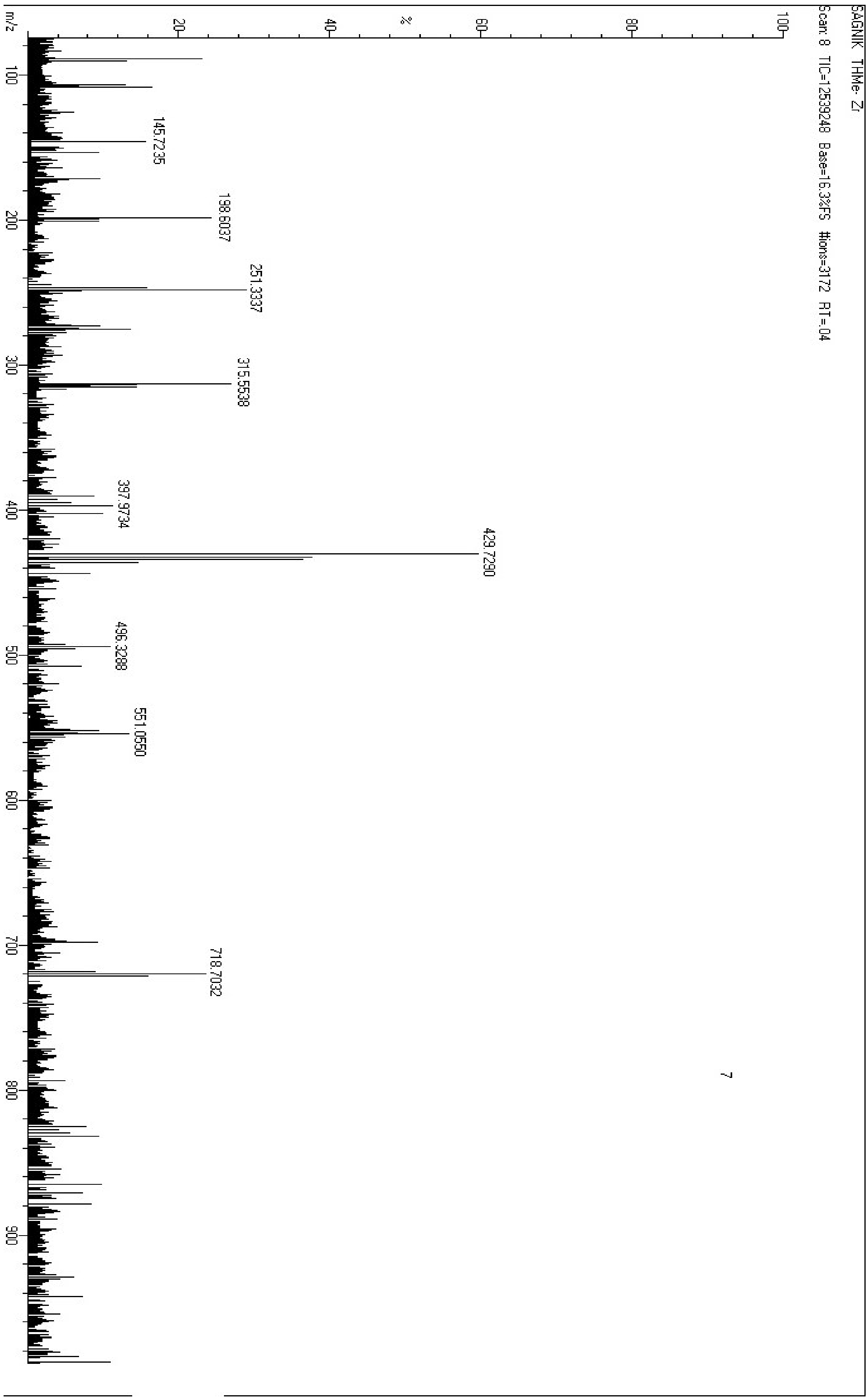


Fig. S27. ESI mass spectrum of Compound **6**

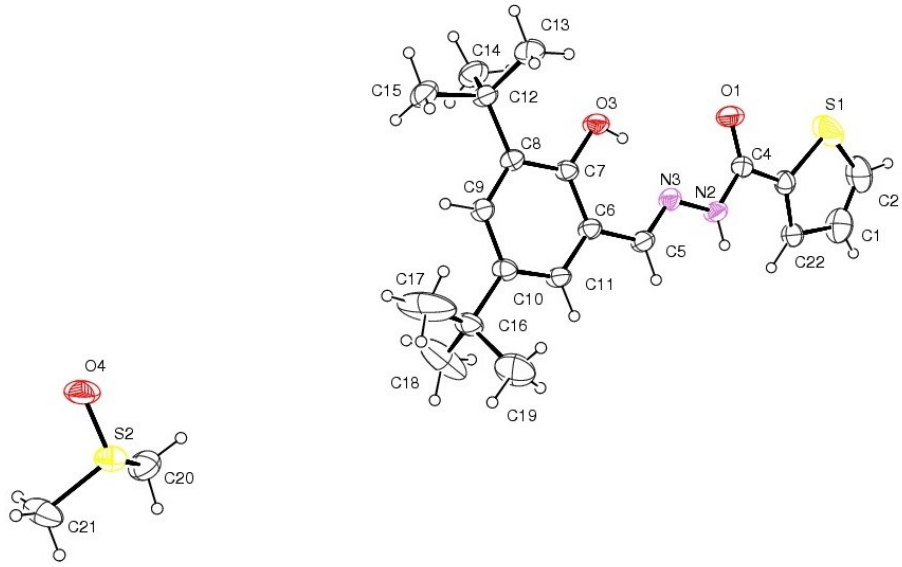


Fig. S28. Molecular structure of L**1H$_2$**

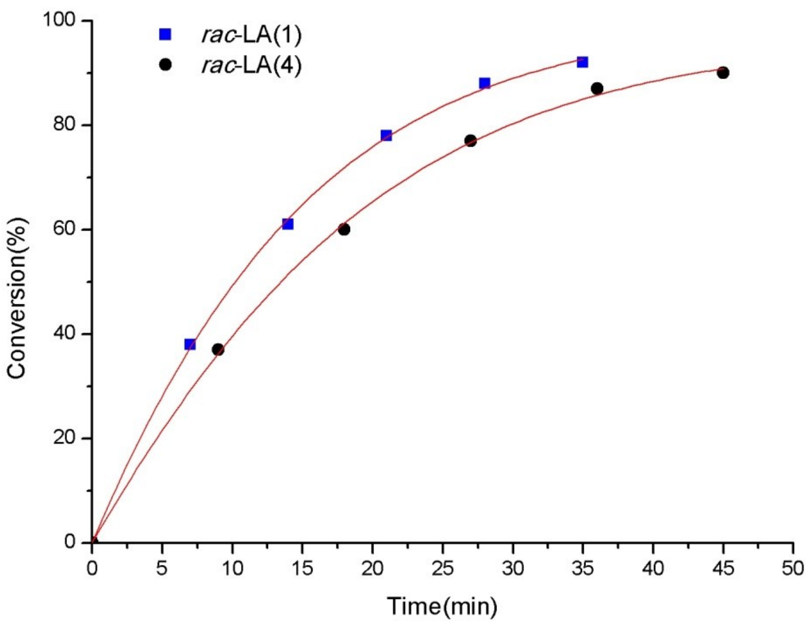


Fig. S29. *rac*-LA conversion *vs.* time plot using **1** and **4**: $[M]_o/[Cat]_o$= 200 at 140 °C

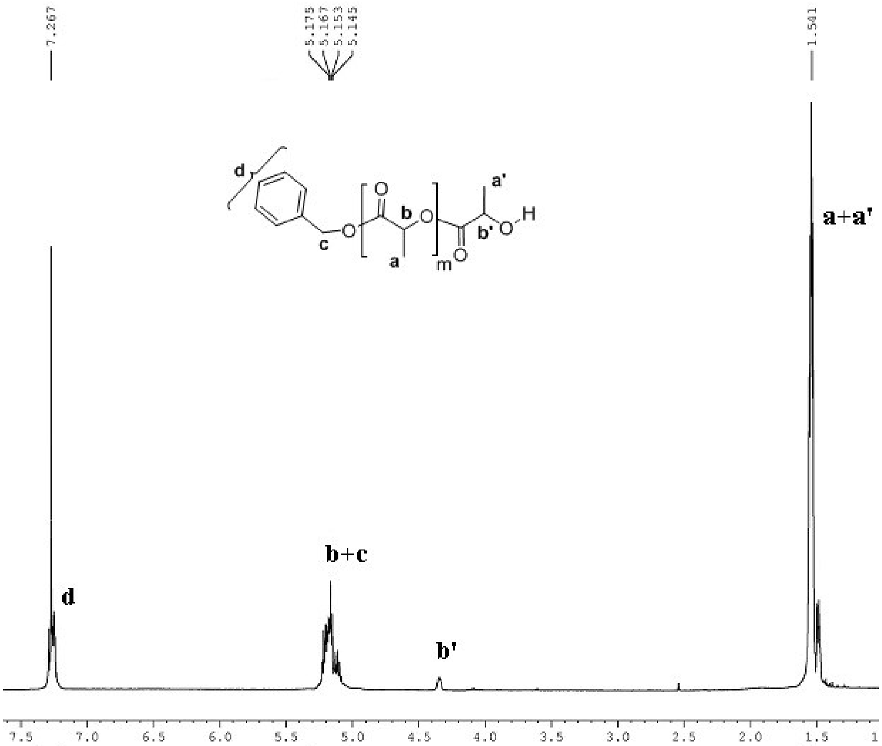


Fig. S30. [1]H NMR spectrum (400 MHz, $CDCl_3$) of the crude product obtained from a reaction between *rac*-LA and **1** and BnOH in 15: 1: 5 ratios at 140 °C.

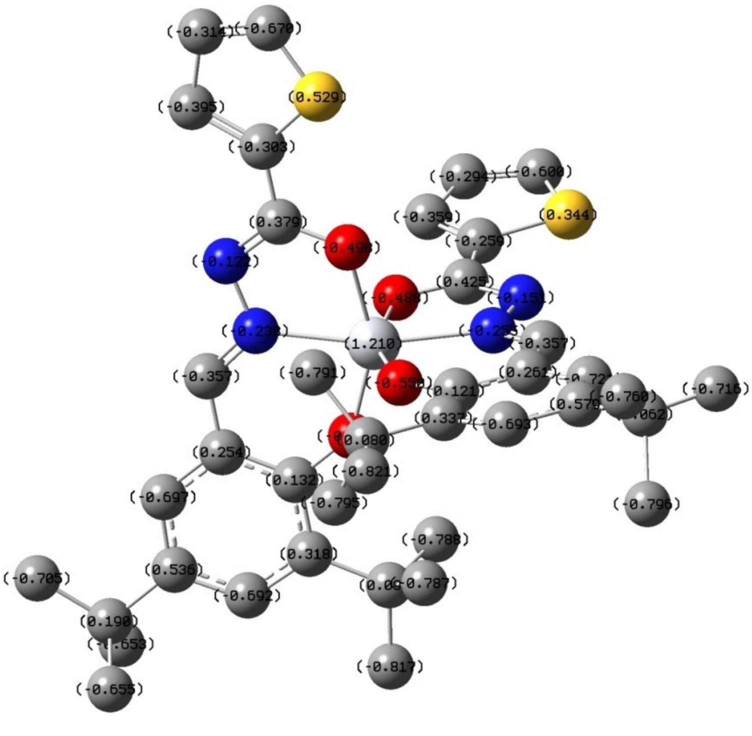


Fig. S31. Net Mulliken charge analysis of the optimized geometry of **1**.

Table S1. Crystal data for the structure **L1H$_2$**, **L2H$_2$**, **1**, **2** and **4**

Compound	**L1H$_2$.DMSO**	**L2H$_2$.DMSO**	**1**	**2**	**4**
Molecular formula	$C_{22}H_{32}N_2O_3S_2$	$C_{19}H_{26}N_2O_3S_2$	$C_{40.03}H_{46.03}$ N4 O_4S_2 Ti	$C_{34}H_{36}N_4O_4S_2$ Ti	$C_{40}H_{48}N_4O_4S_2$ Zr
Formula weight	436.61	394.54	758.83	676.69	804.16
T/K	296(2)	296(2)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P1$	$P1$	$P2_1$/c	$P2_1$/n	$P2_1$/c
a/Å	9.2586(2)	9.8710(3)	17.7190(9)	13.081(4)	17.8233(9)
b/Å	9.6167(2)	9.8841(3)	10.8186(5)	23.840(8)	10.9084(6)
c/Å	15.5862(4)	10.9592(3)	21.7958(11)	15.426(5)	21.6049(11)
α (°)	89.2238(12)	98.4485(11)	90	90	90
β (°)	75.0508(11)	94.8760(11)	93.293(2)	101.148(12)	94.0606(18)
γ (°)	65.7927(10)	94.1161(12)	90	90	90
V/Å^3	1216.17(5)	1049.95(5)	4171.2(4)	4720(3)	4190.0(4)
Z, Calculated density(Mg/ m^3)	2, 1.192	2, 1.248	4, 1.208	4, 0.952	4, 1.275
Absorption coefficient (mm^{-1})	0.242	0.273	0.347	0.301	0.404
Reflections collected/Independent reflections	16707 / 4271	15632 / 3699	14548 / 3837	13883 / 4625	31084 / 7376
Data/restraints/parameters	4271 / 0 / 278	3699 / 0 / 249	3837 / 68 / 535	4625 / 6 / 424	7376 / 50 / 514
Goodness of fit on F^2	1.037	1.042	1.057	1.111	1.077
Final R indices [I >2σ(I)]	R_1 = 0.0737, wR_2 = 0.2182	R_1 = 0.0743, wR_2 = 0.2076	R_1 = 0.0471, wR_2 = 0.1194	R_1 = 0.0585, wR_2 = 0.1552	R_1 = 0.0374, wR_2 = 0.0951
R indices (all data)	R_1 = 0.0850, wR_2 = 0.2338	R_1 = 0.0832, wR_2 = 0.2207	R_1 = 0.0730, wR_2 = 0.1493	R_1 = 0.0769, wR_2 = 0.1676	R_1 = 0.0569, wR_2 = 0.1113
CCDC	1562812	1562816	1562817	1562818	1562819

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