Supporting Information

Table S1. Crystal data for **3a**, **3b** and **3c**

Complex	**3a**	**3b**	**3c**
CCDC No.	1438097	1438098	1438099
Empirical formula	$C_{44}H_{60}N_8O_6Ti_2$	$C_{48}H_{68}N_8O_6Cl_4Zr_2$	$C_{46}H_{62}N_8O_6$ Cl_6Hf_2
Molecular weight	892.74	1177.34	1392.7
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P-1	P 1
Temp/K	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
a (Å)	11.1634(4)	9.9338(13)	9.6702(3)
b (Å)	24.5170(9)	11.1209(15)	10.9556(3)
c (Å)	17.6569(6)	14.560(2)	14.5845(4)
α (°)	90	106.403(6)	108.4480(10)
β (°)	94.8010(10)	91.013(7)	90.6828(11)
γ (°)	90	108.188(6)	101.2321(10)
V (Å^3)	4815.6(3)	1456.0(4)	1433.15(7)
Z	4	1	1
D_{calc} (g/cm^3)	1.231	1.343	1.614
Reflns collected	17890	15810	21435
GOF	1.022	1.111	1.054
F(000)	1888	608	688
Final R indices (I>2σ(I))^a	R_1 = 0.0384, wR_2 = 0.1006	R_1 = 0.0483, wR_2 = 0.1281	R_1 = 0.0201, wR_2 = 0.0474
R indices (all data)	R_1 = 0.0538, wR_2 = 0.1113	R_1 = 0.0640, wR_2 = 0.1496	R_1 = 0.0228, wR_2 = 0.0490

$^aR_1 = \sum|F_0| - |F_c|/\sum|F_0|$, $wR_2 = [\sum (F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

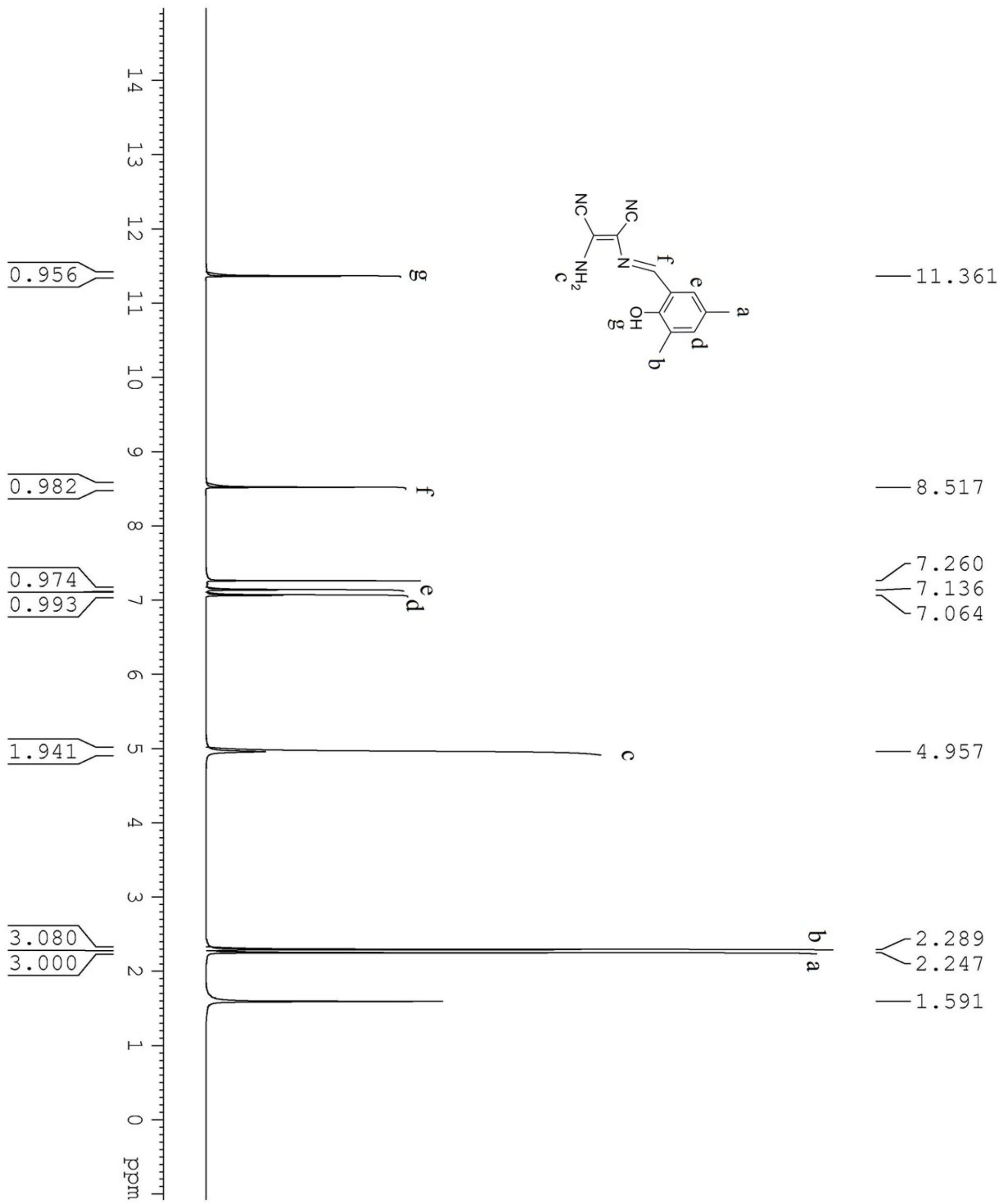


Fig. S1. ^{1}H NMR (500 MHz, $CDCl_3$) of **L2(H)$_2$**

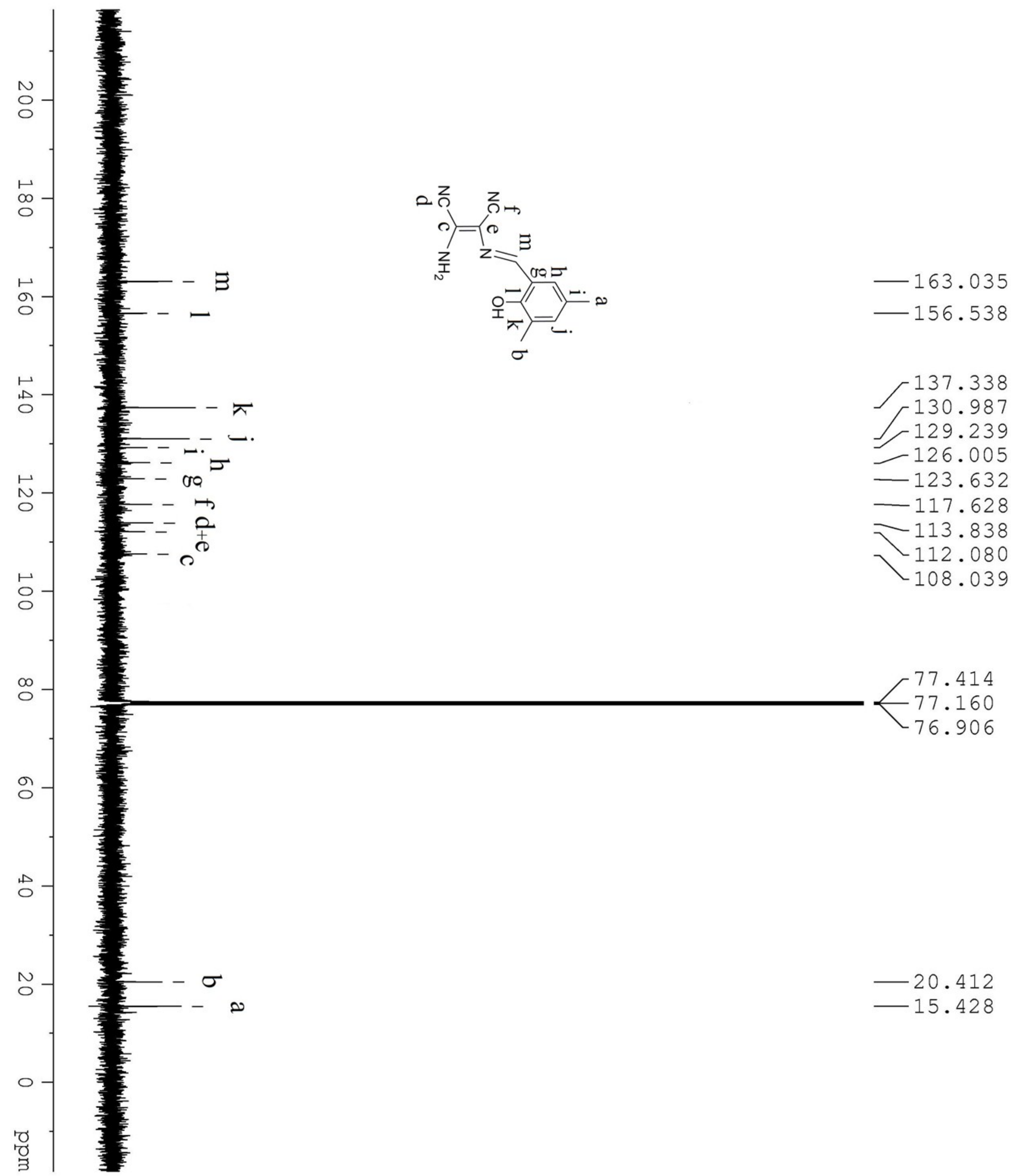


Fig. S2. ^{13}C NMR (125 MHz, $CDCl_3$) of **L2(H)$_2$**

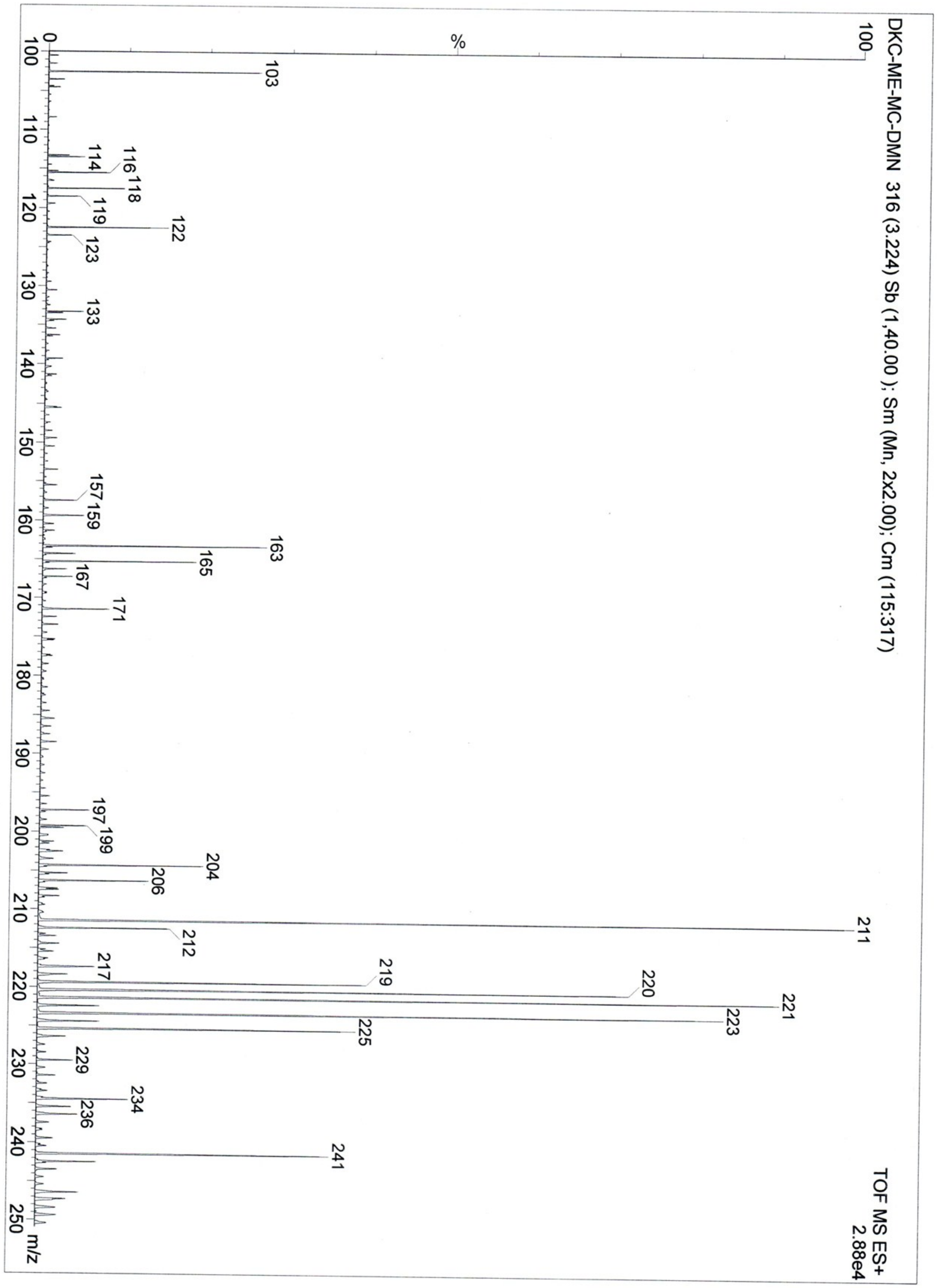


Fig. S3. ESI-MS spectrum of **L2(H)$_2$**

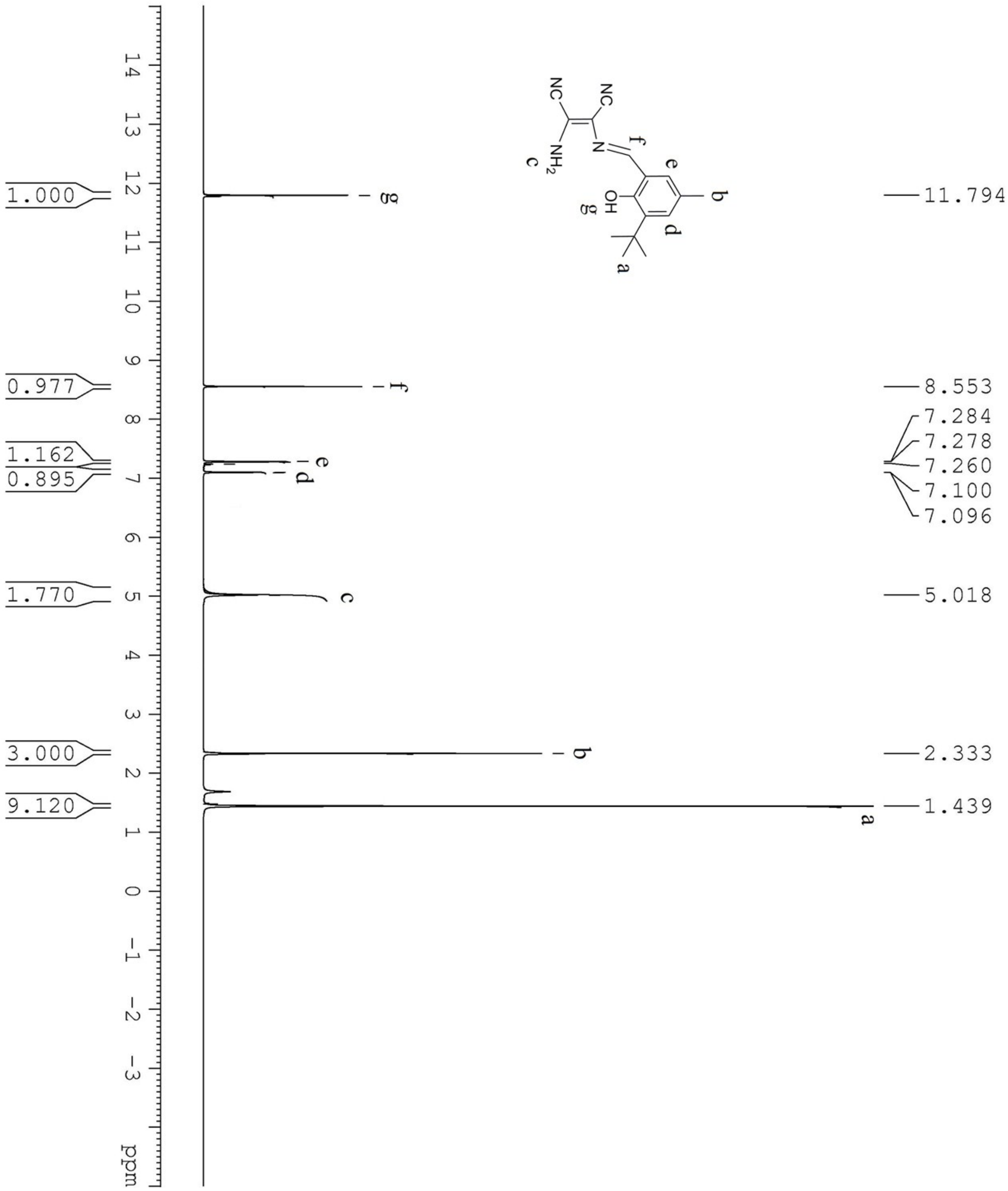


Fig. S4. ^{1}H NMR (400 MHz, $CDCl_3$) of **L3(H)$_2$**

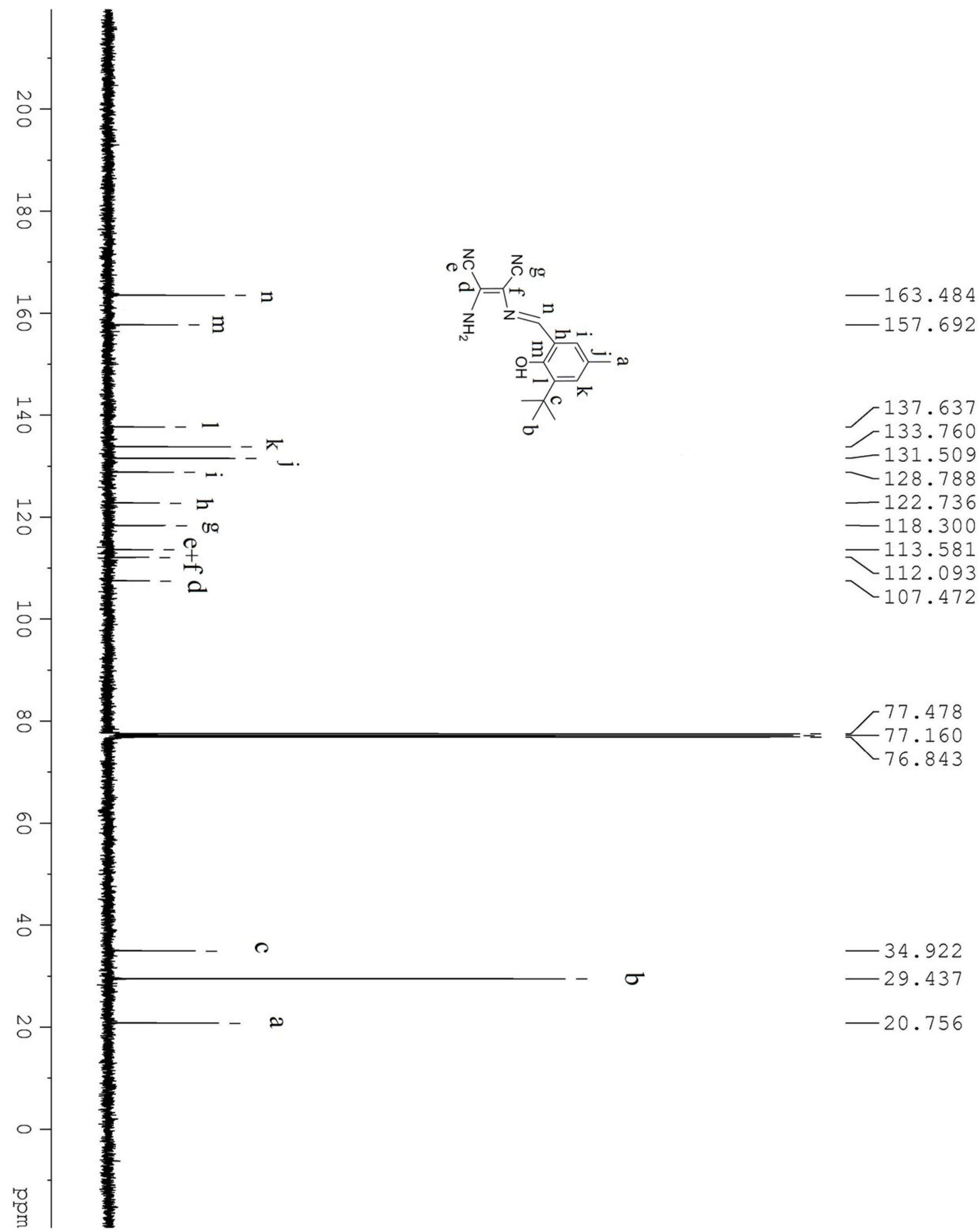


Fig. S5. ^{13}C NMR (100 MHz, $CDCl_3$) of **L3(H)$_2$**

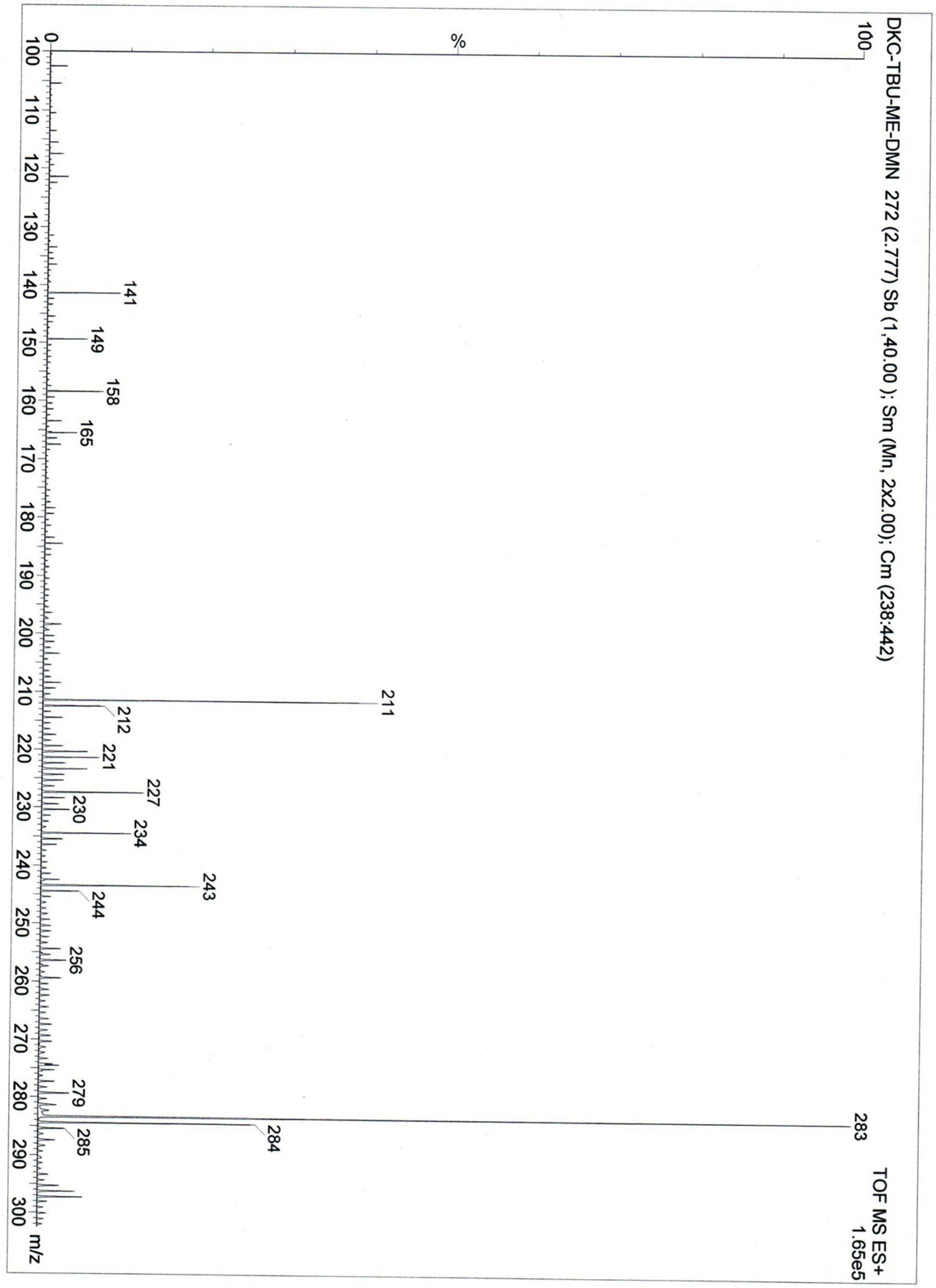


Fig. S6. ESI-MS spectrum of **L3(H)$_2$**

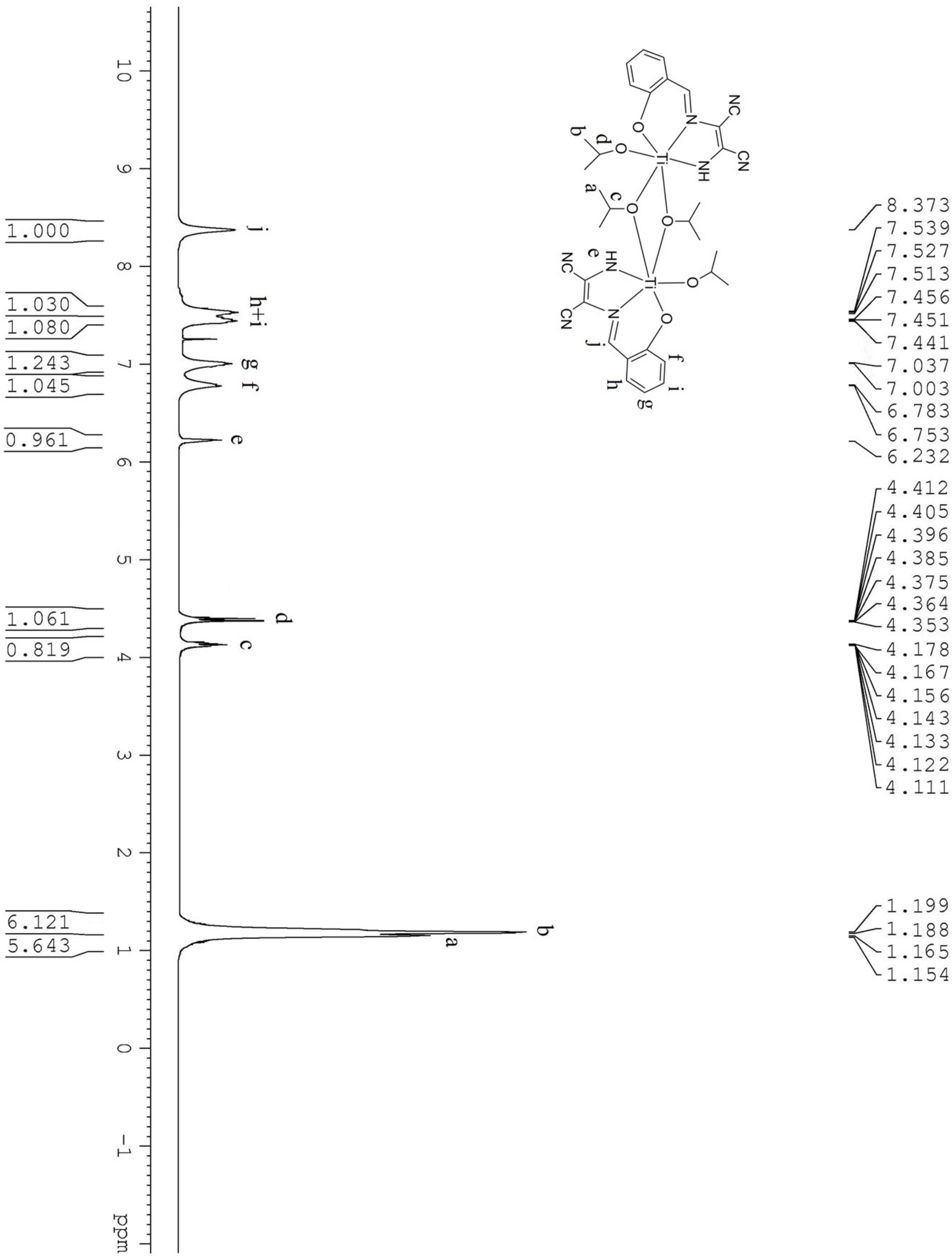


Fig. S7. ^{1}H NMR (500 MHz, $CDCl_3$) of **1a**

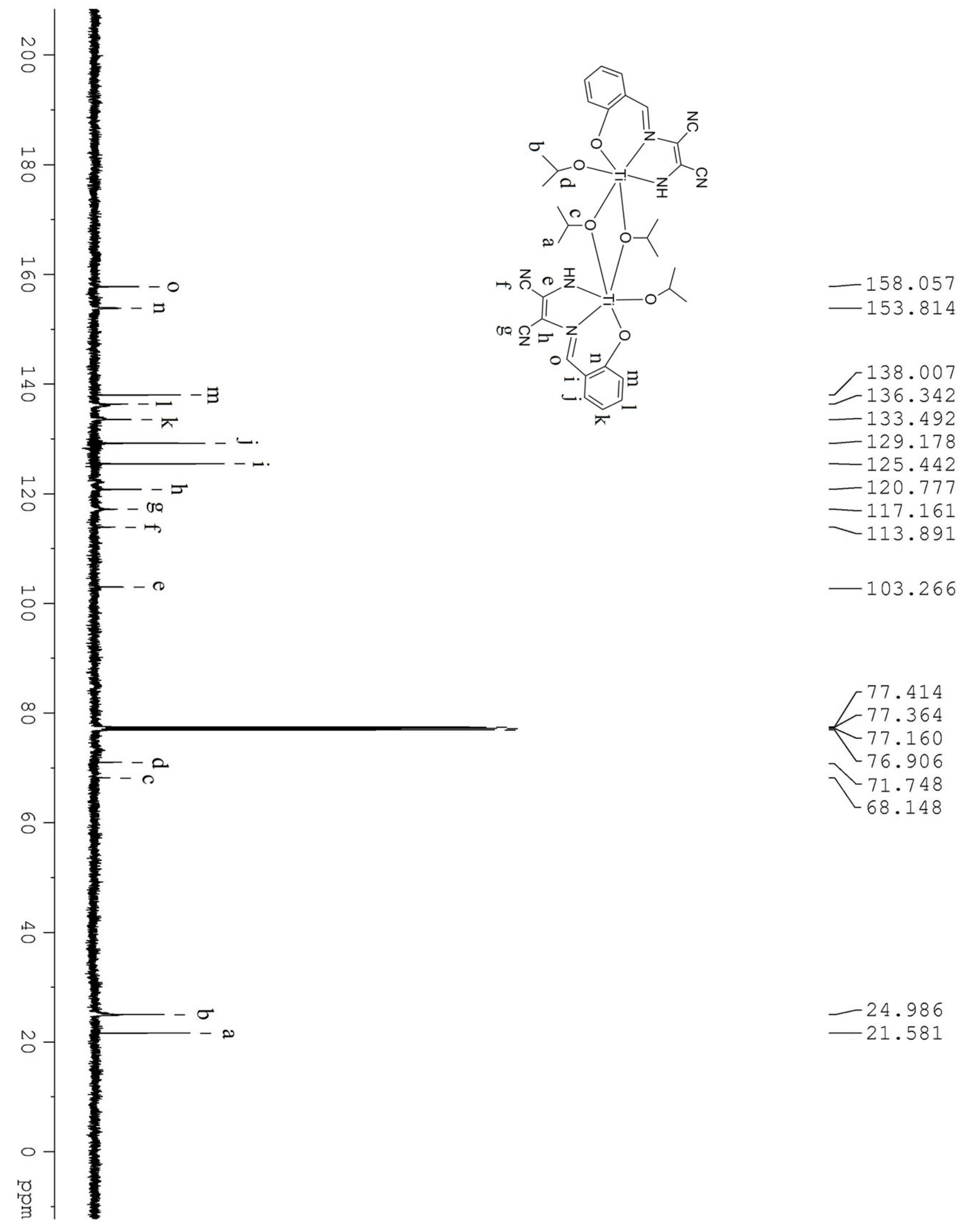


Fig. S8. ^{13}C NMR (125 MHz, $CDCl_3$) of **1a**

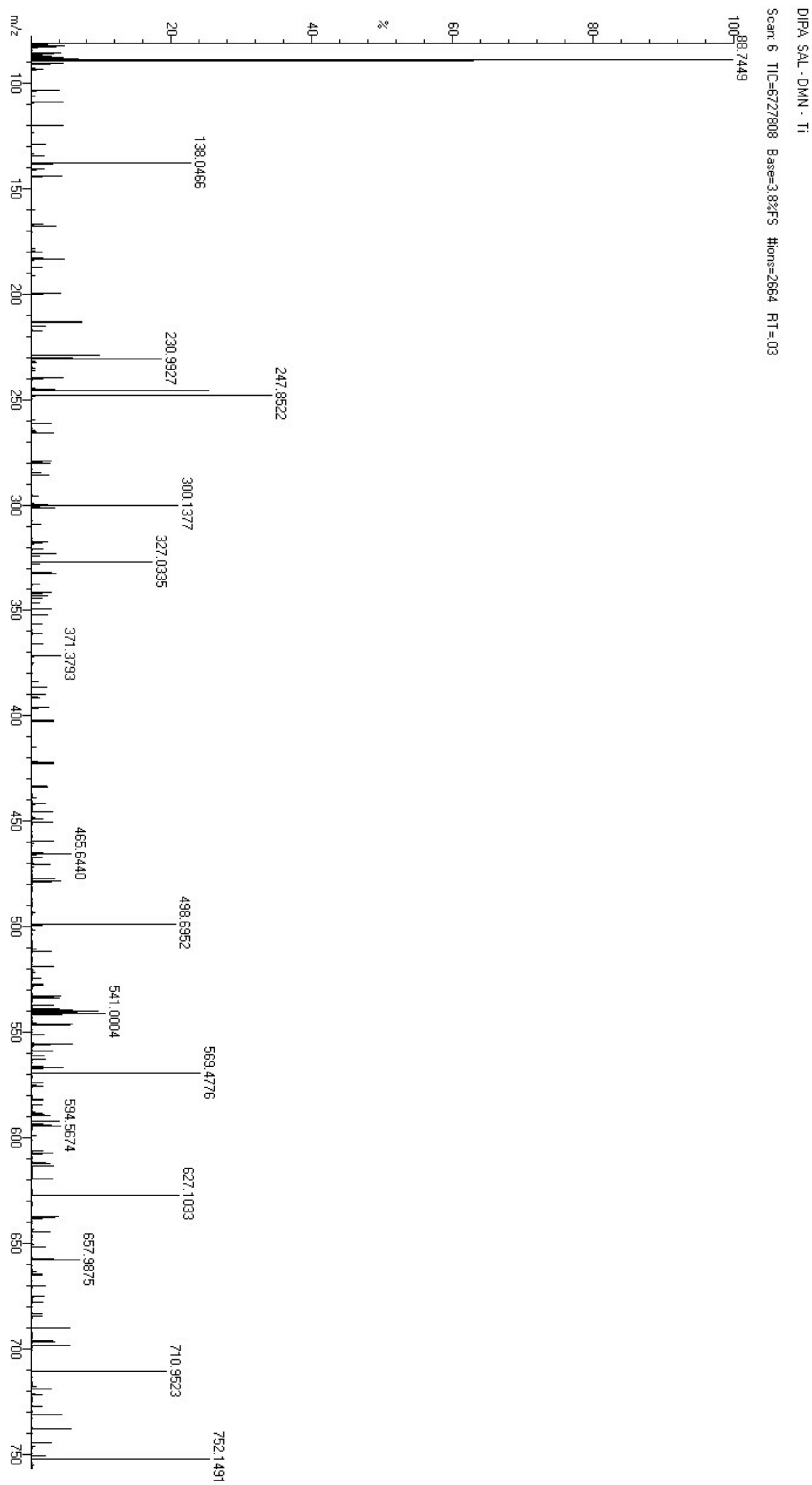


Fig. S9. EI-MS spectrum of **1a**

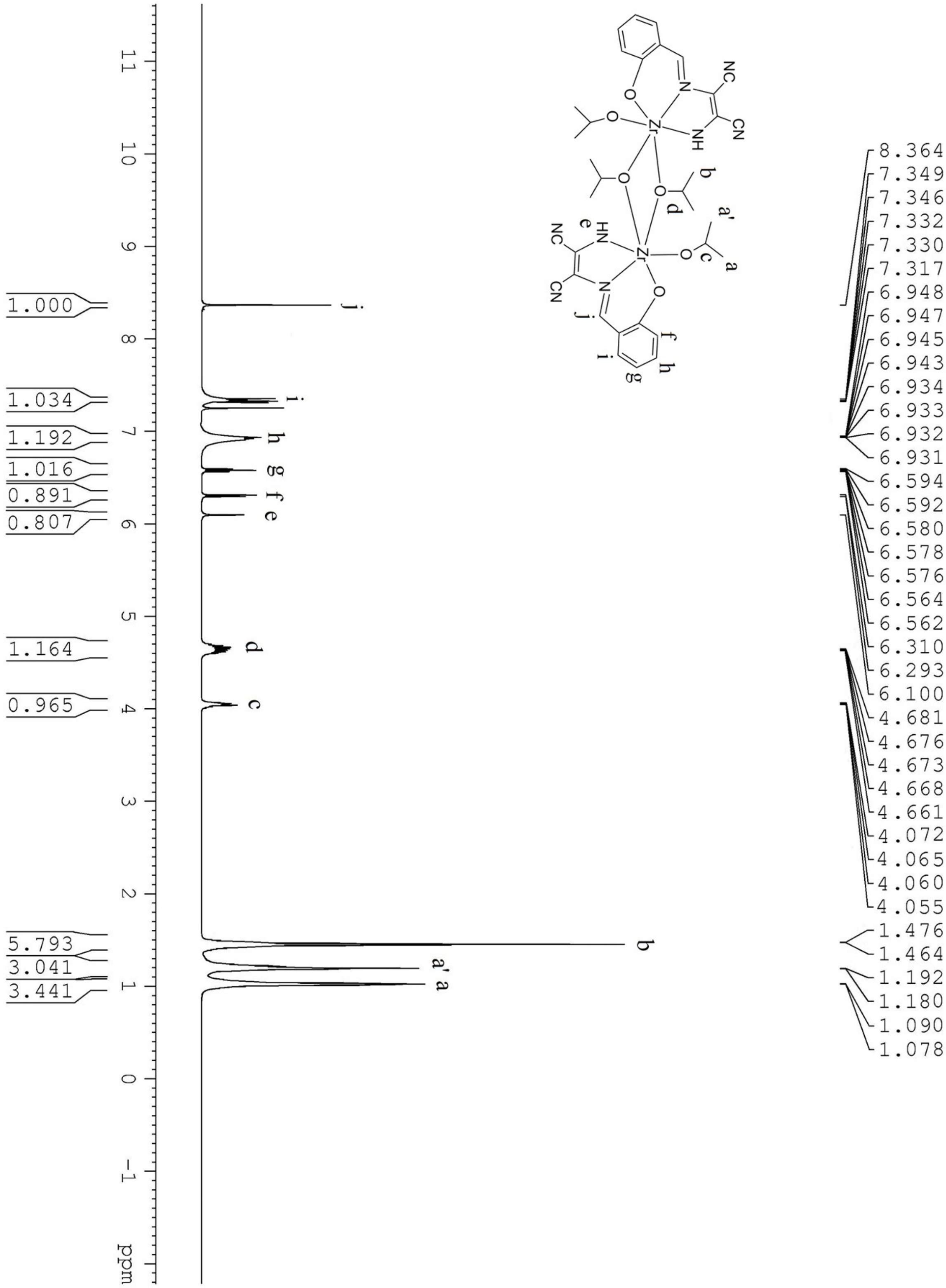


Fig. S10. ^{1}H NMR (500 MHz, $CDCl_3$) of **1b**

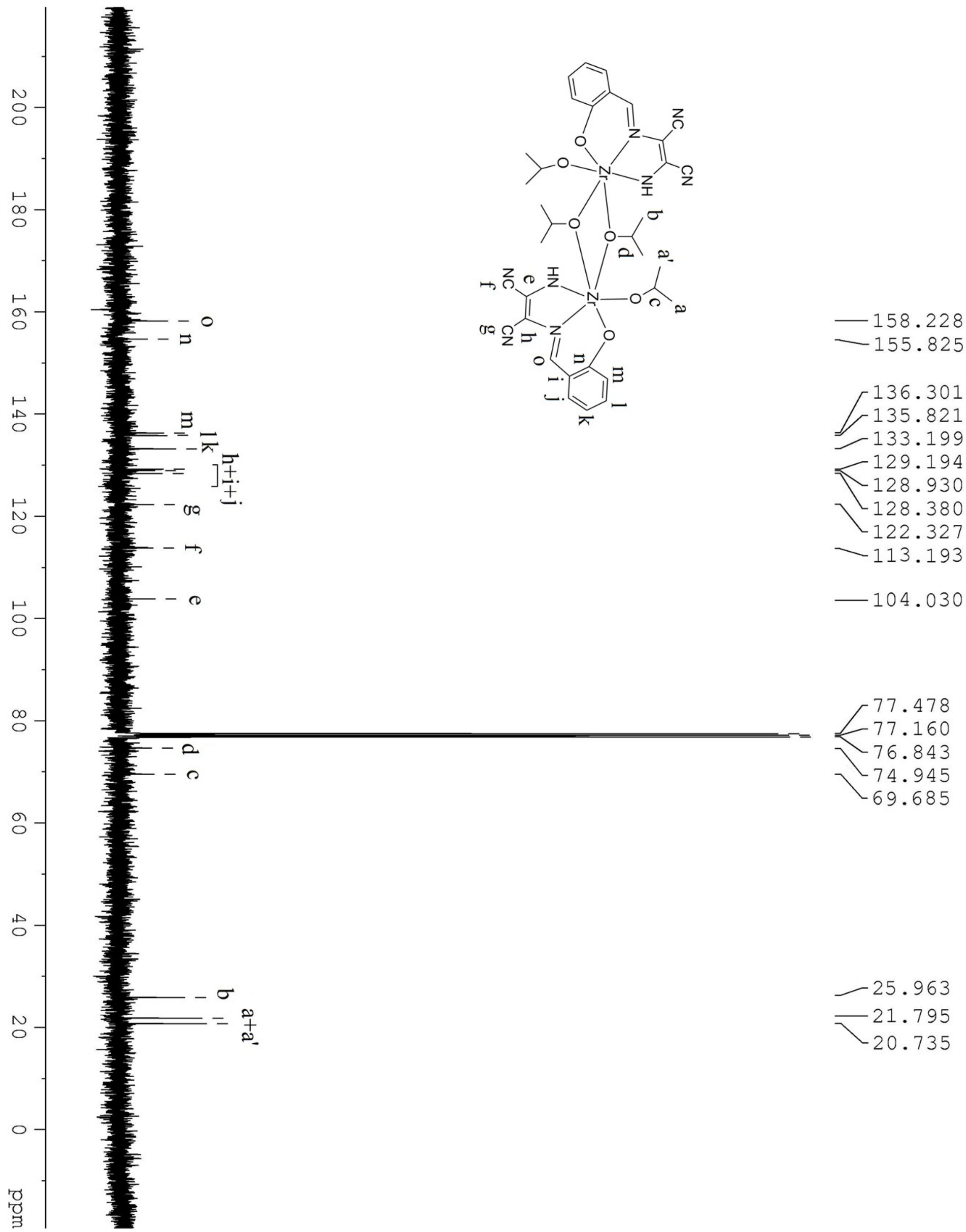


Fig. S11. ^{13}C NMR (125 MHz, $CDCl_3$) of **1b**

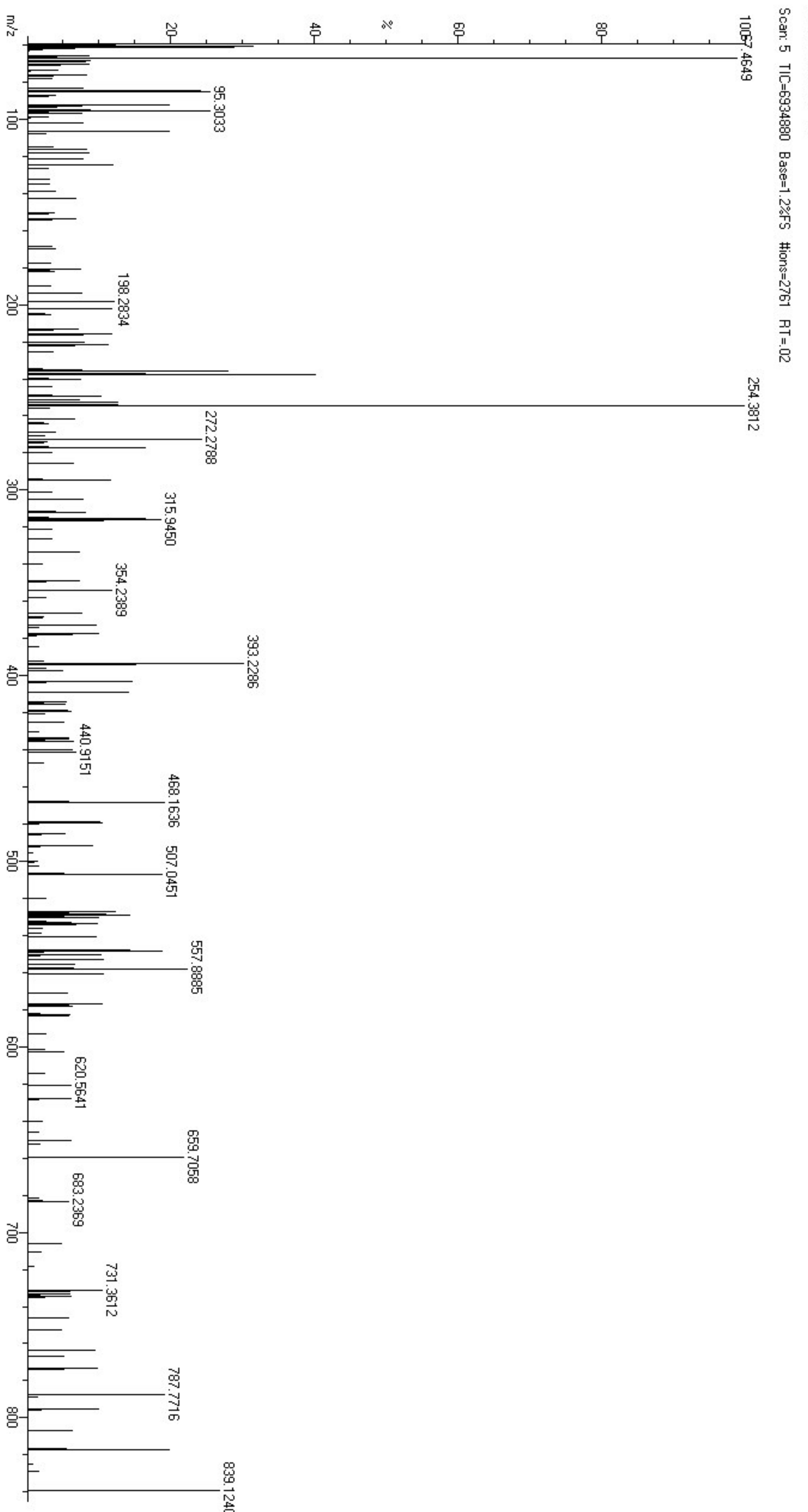


Fig. S12. EI-MS spectrum of **1b**

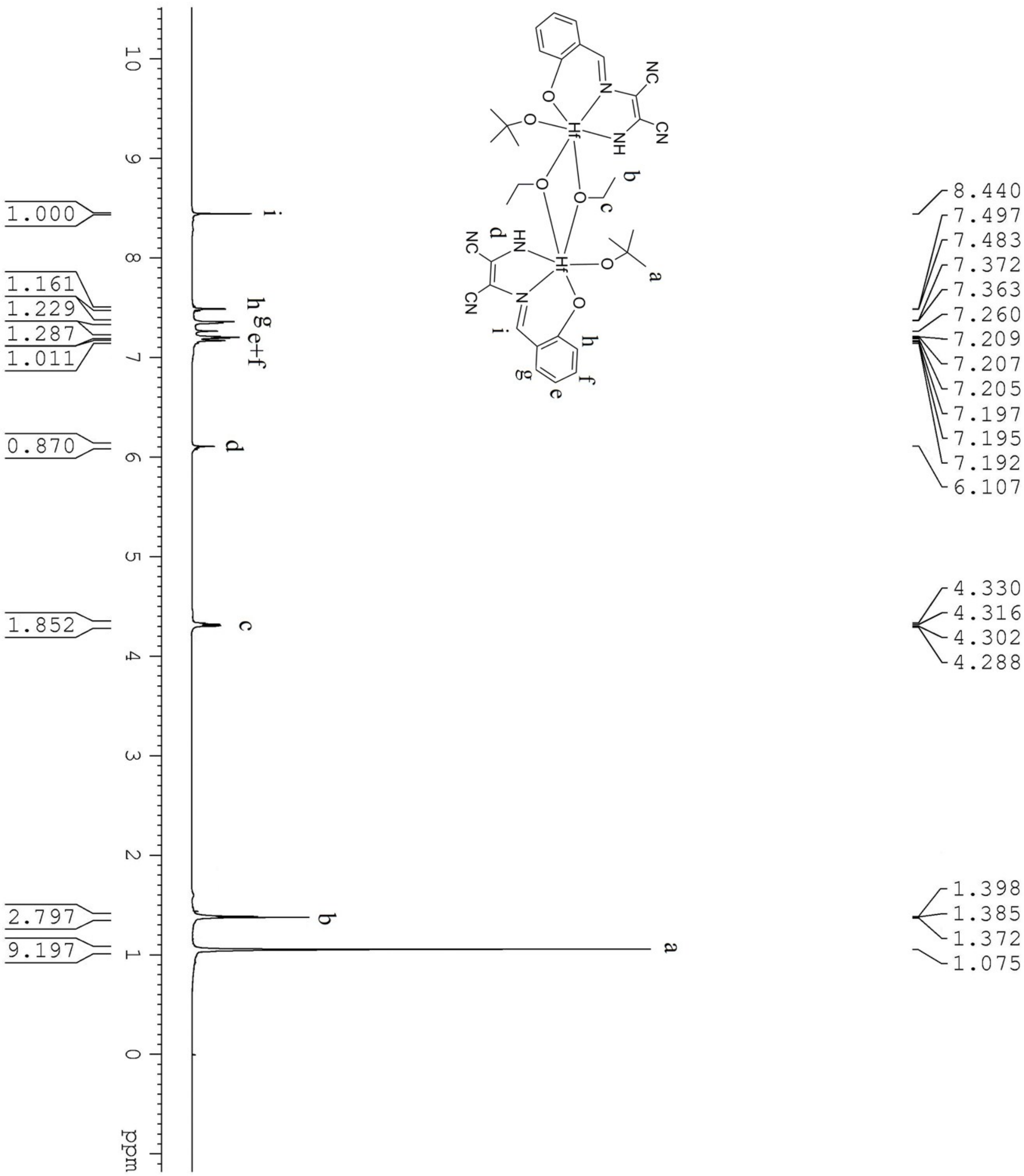


Fig. S13. ^{1}H NMR (500 MHz, $CDCl_3$) of **1c**

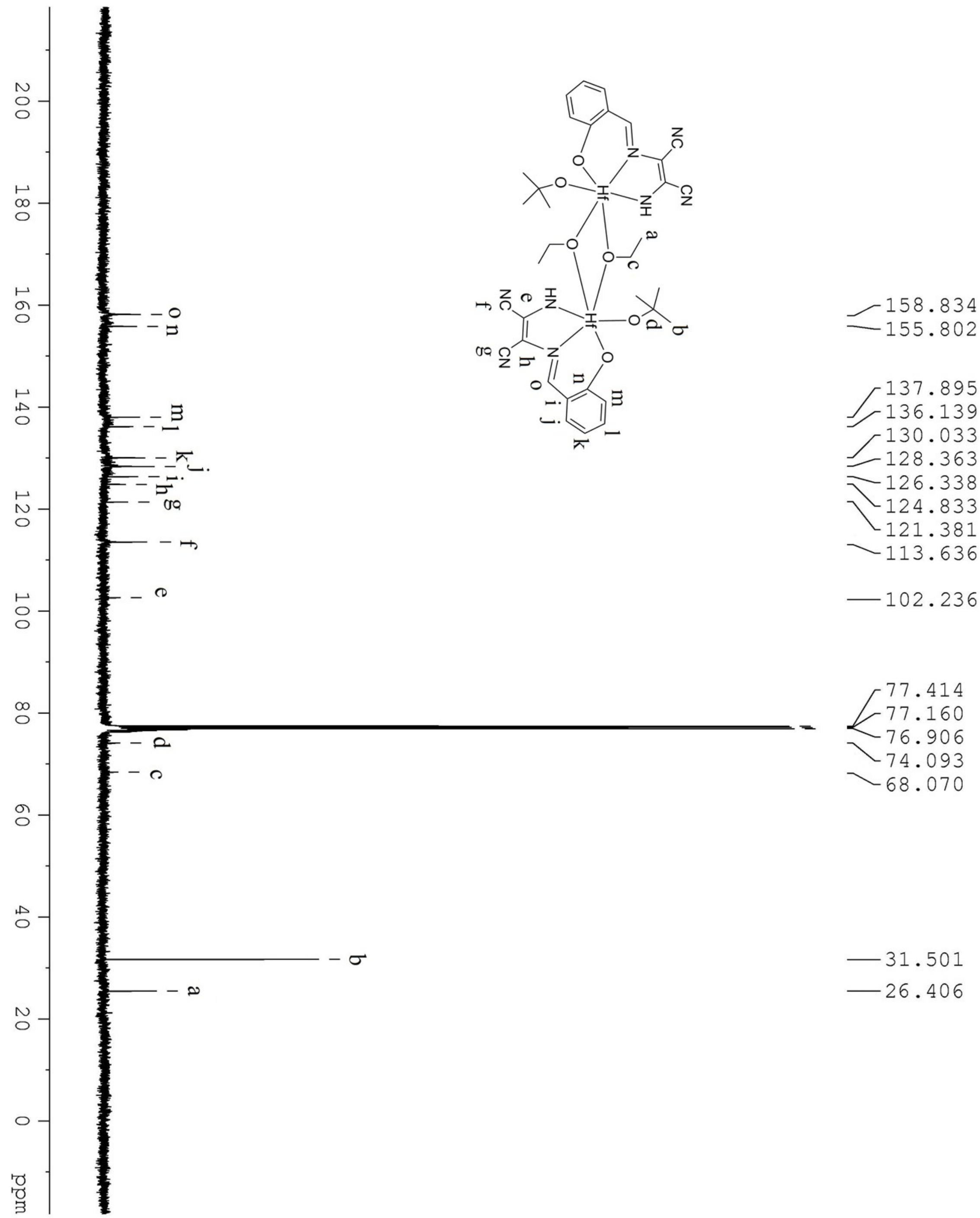


Fig. S14. ^{13}C NMR (125 MHz, $CDCl_3$) of **1c**

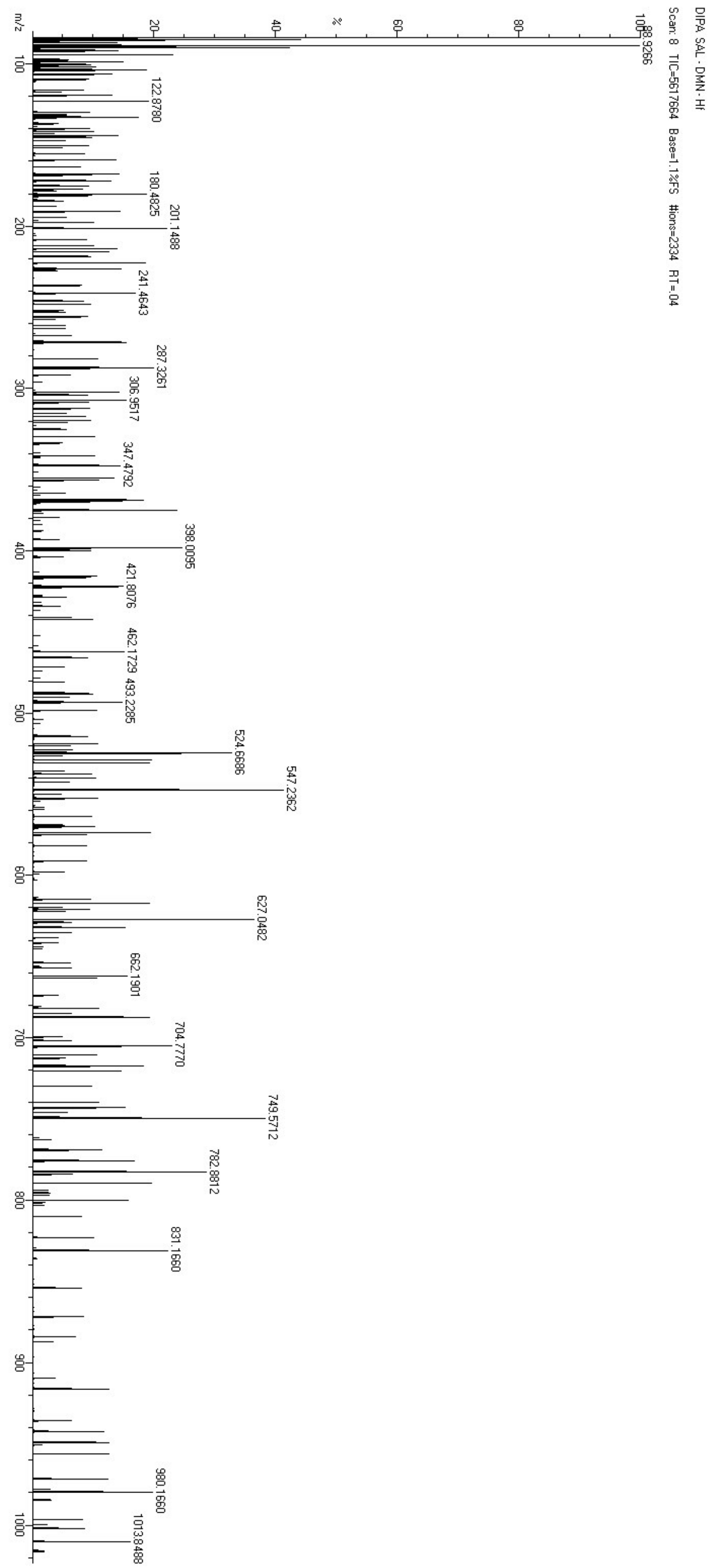


Fig. S15. EI-MS spectrum of **1c**

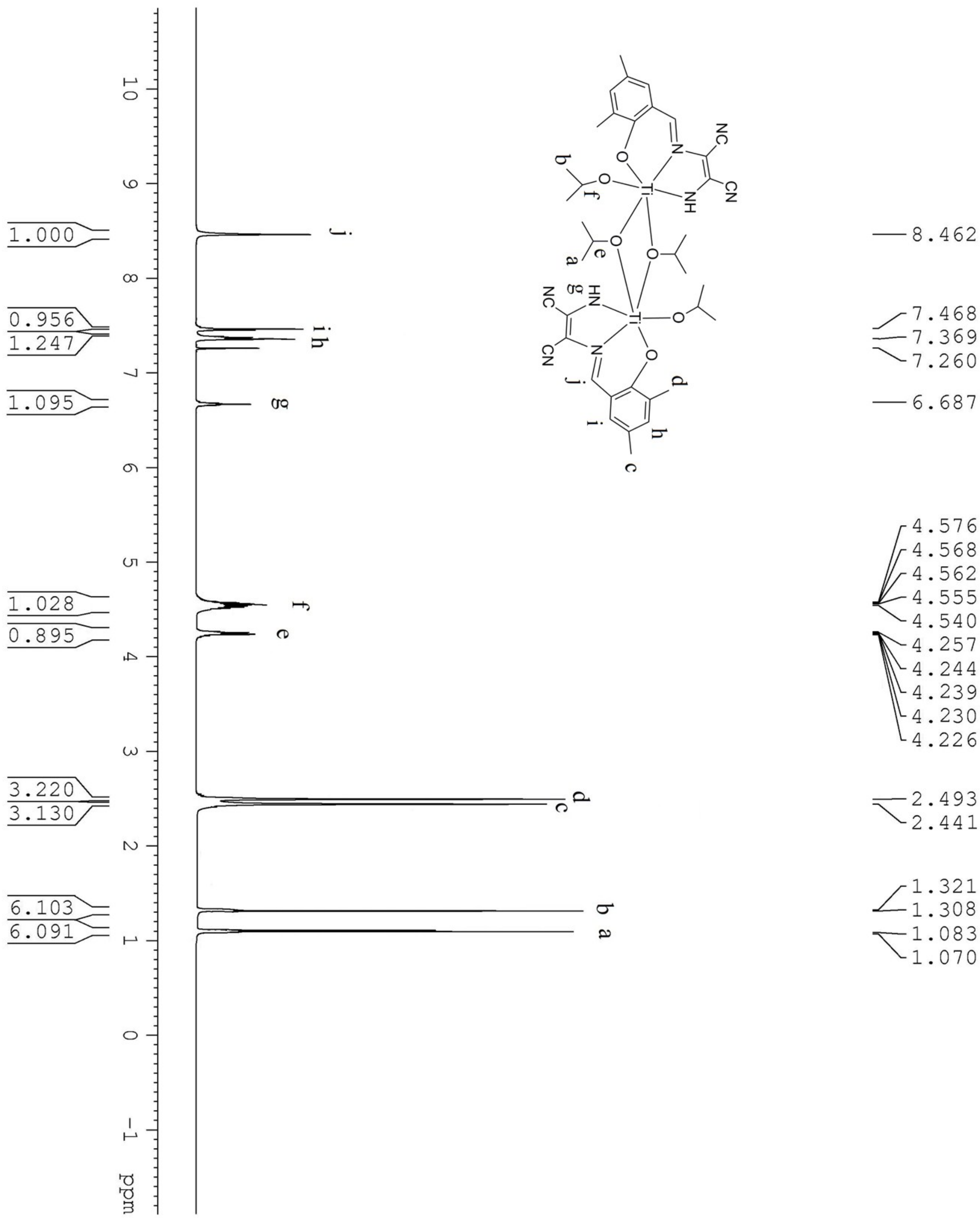


Fig. S16. ^{1}H NMR (500 MHz, $CDCl_3$) of **2a**

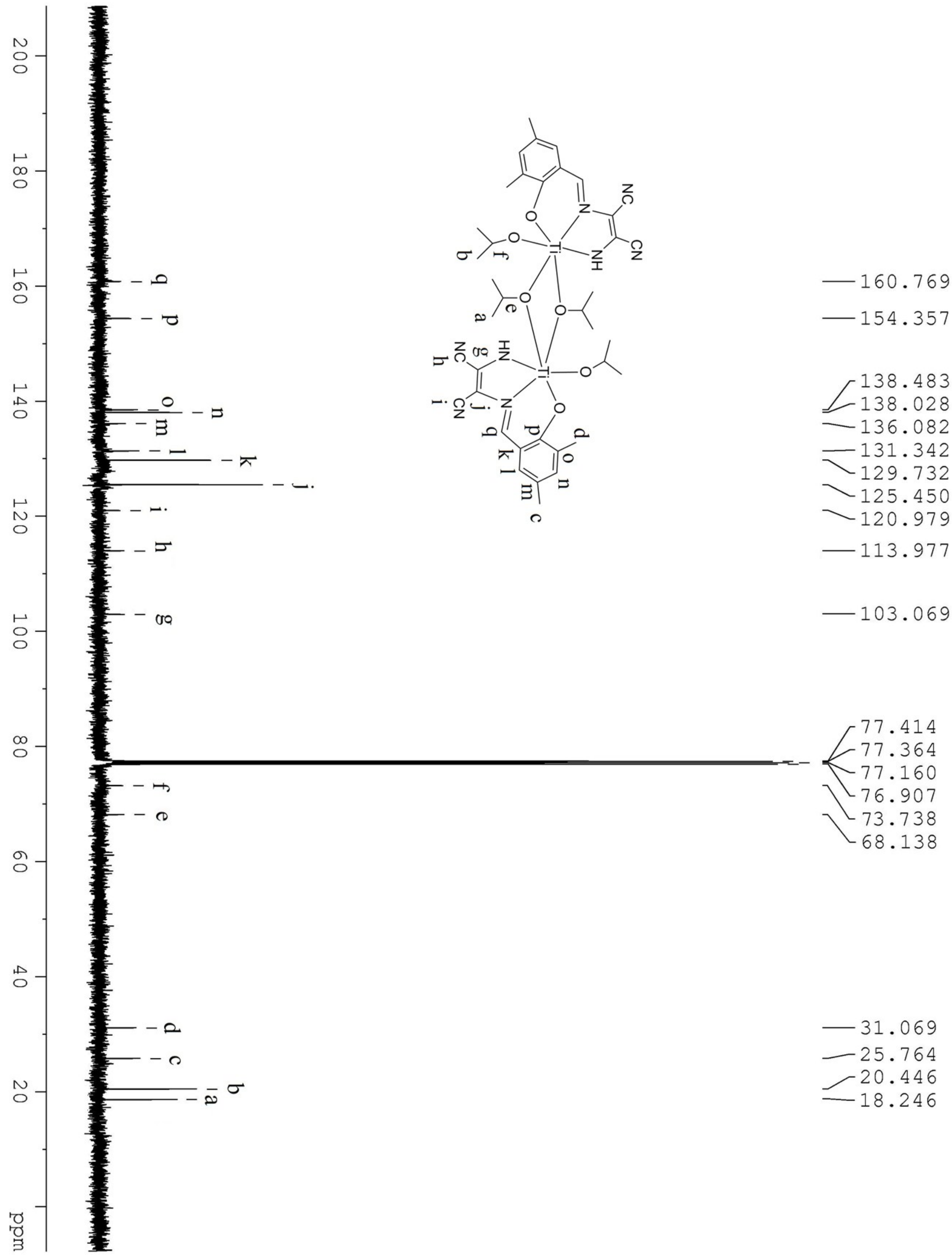


Fig. S17. ^{13}C NMR (125 MHz, $CDCl_3$) of **2a**

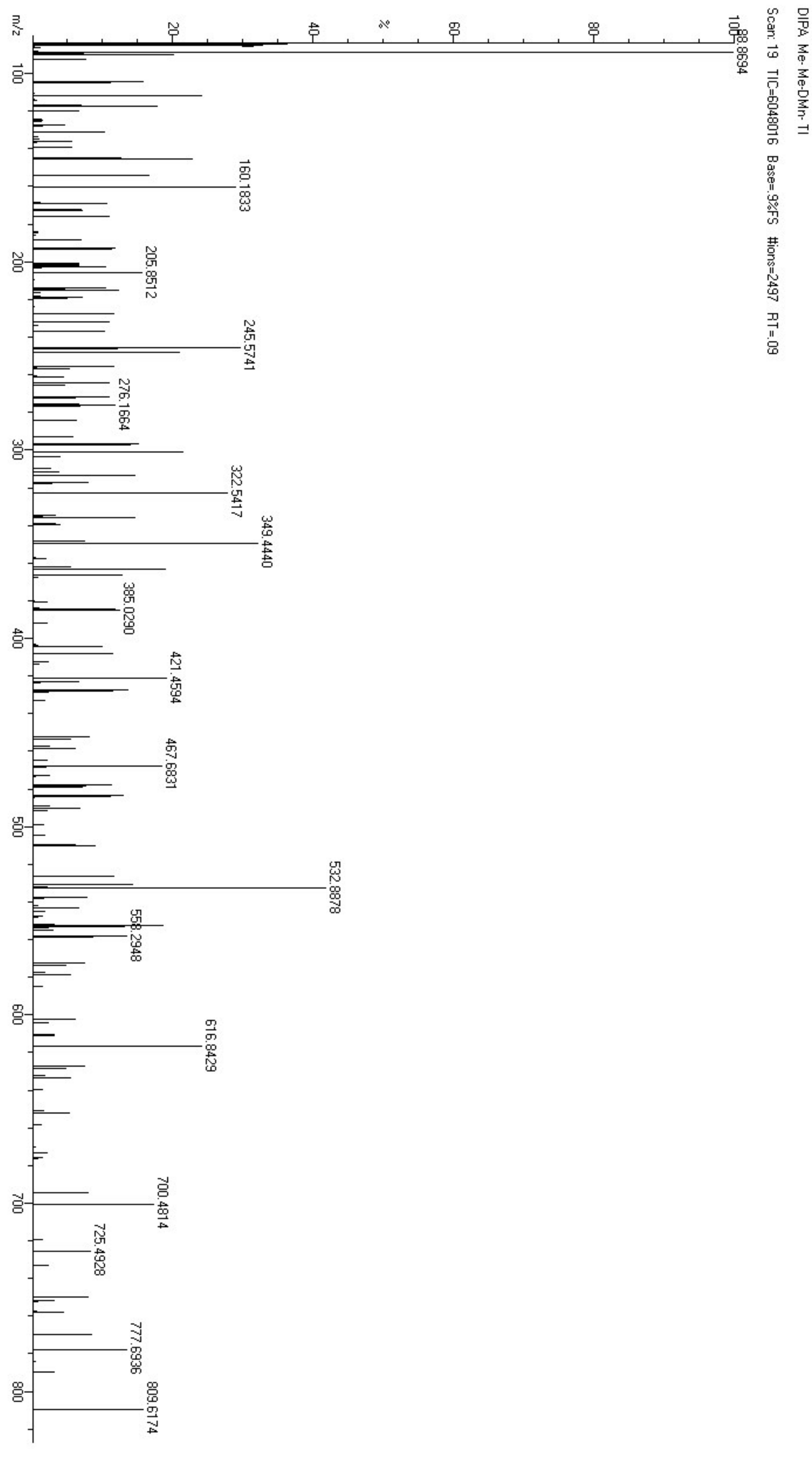


Fig. S18. EI-MS spectrum of **2a**

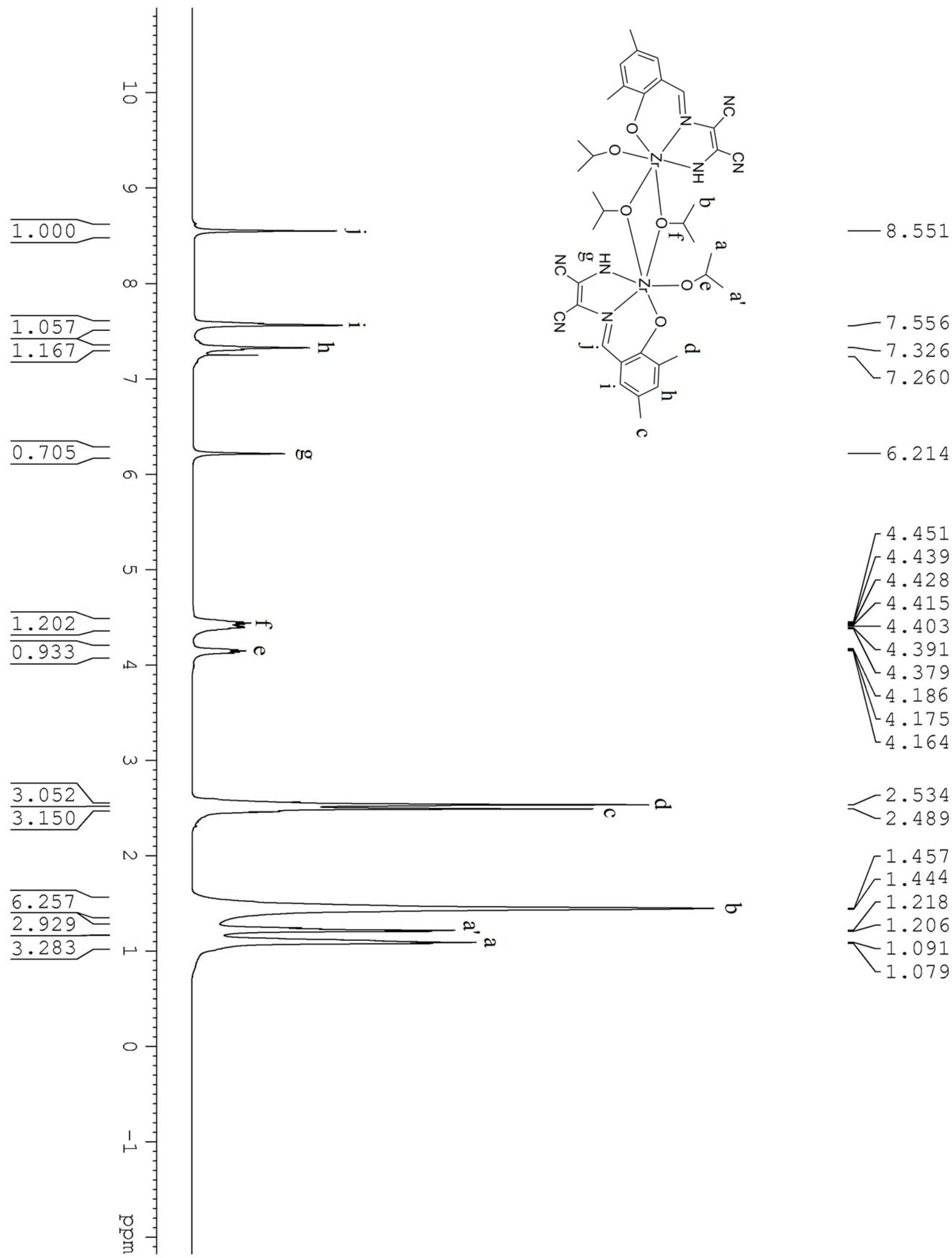


Fig. S19. ^{1}H NMR (500 MHz, $CDCl_3$) of **2b**

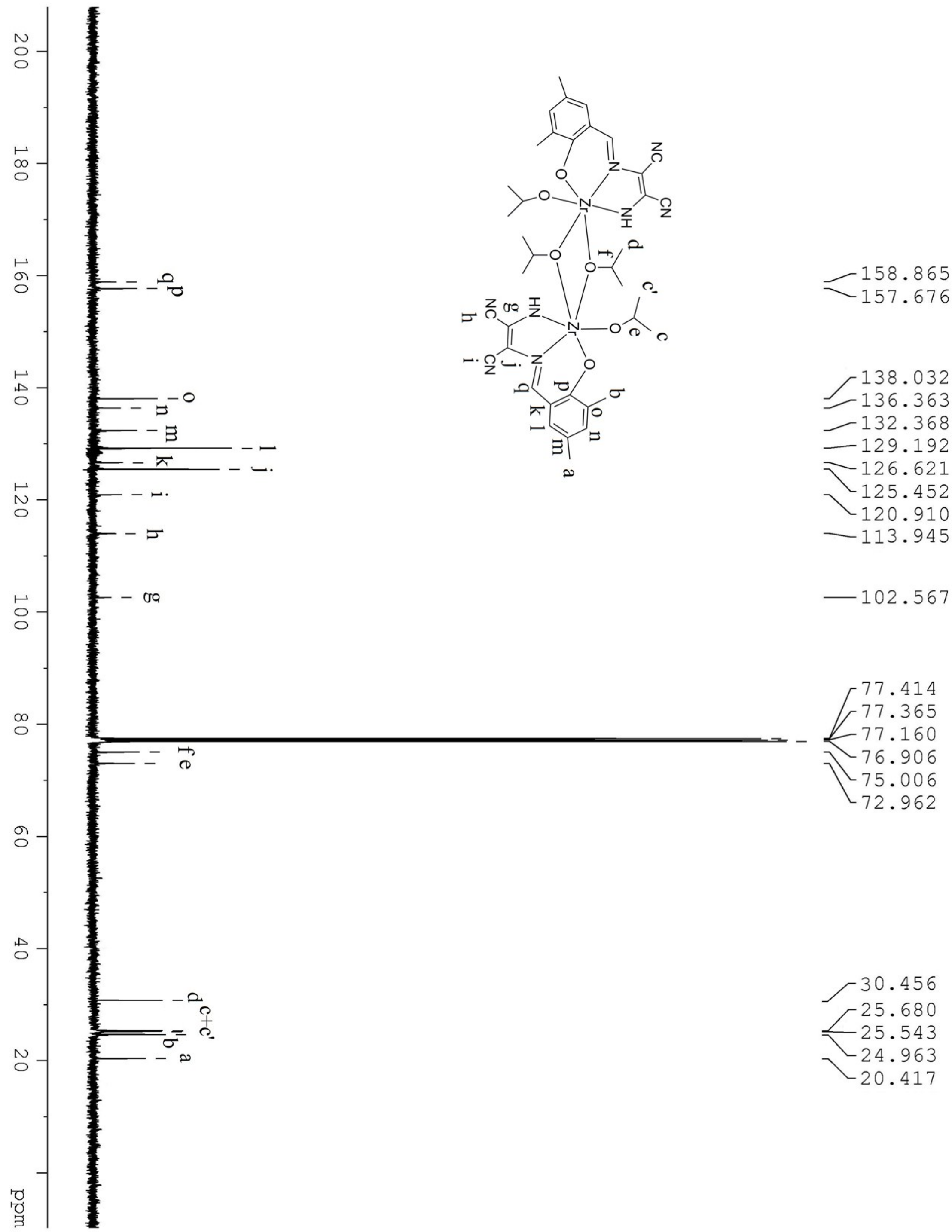


Fig. S20. ^{13}C NMR (125 MHz, $CDCl_3$) of **2b**

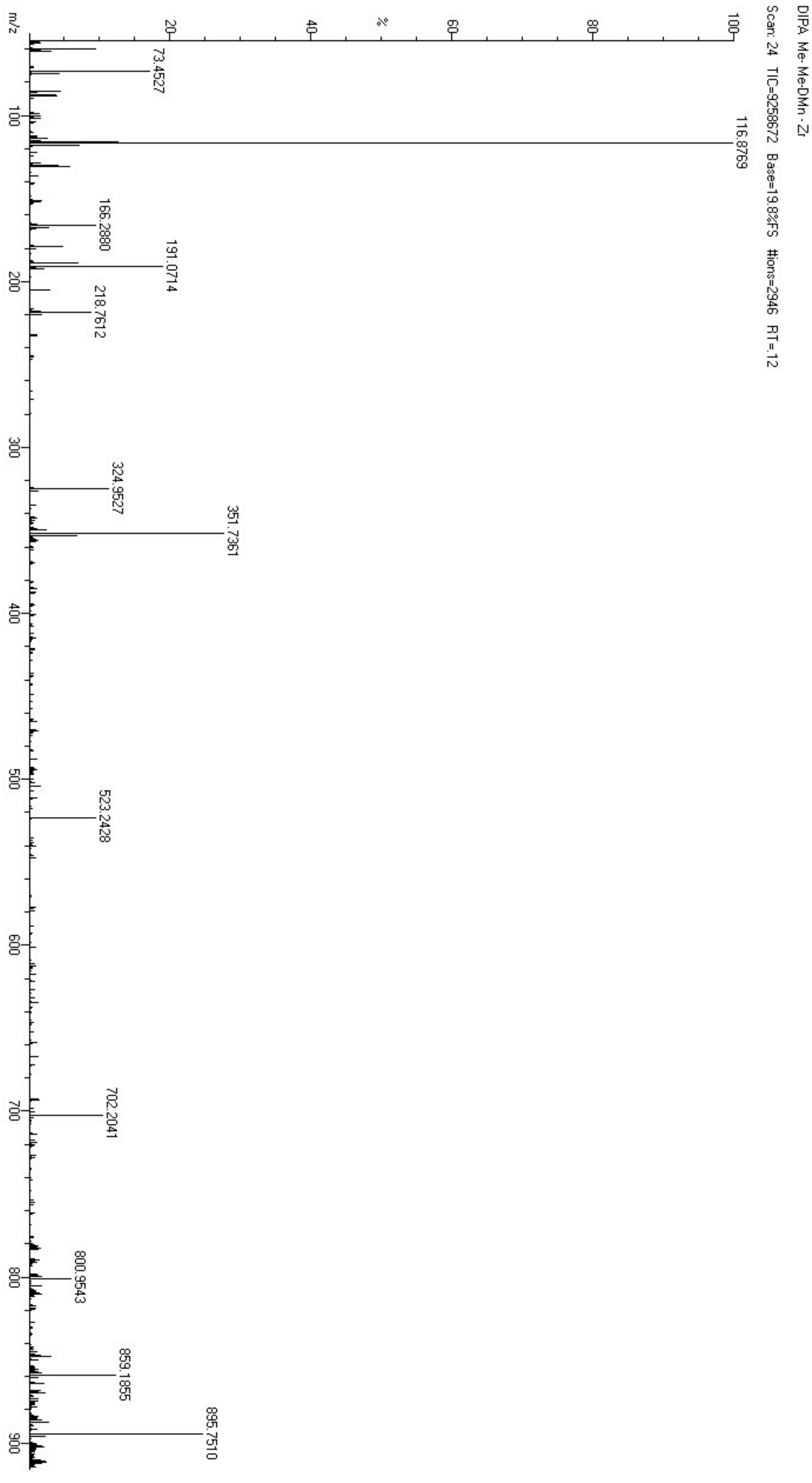


Fig. S21. EI-MS spectrum of **2b**

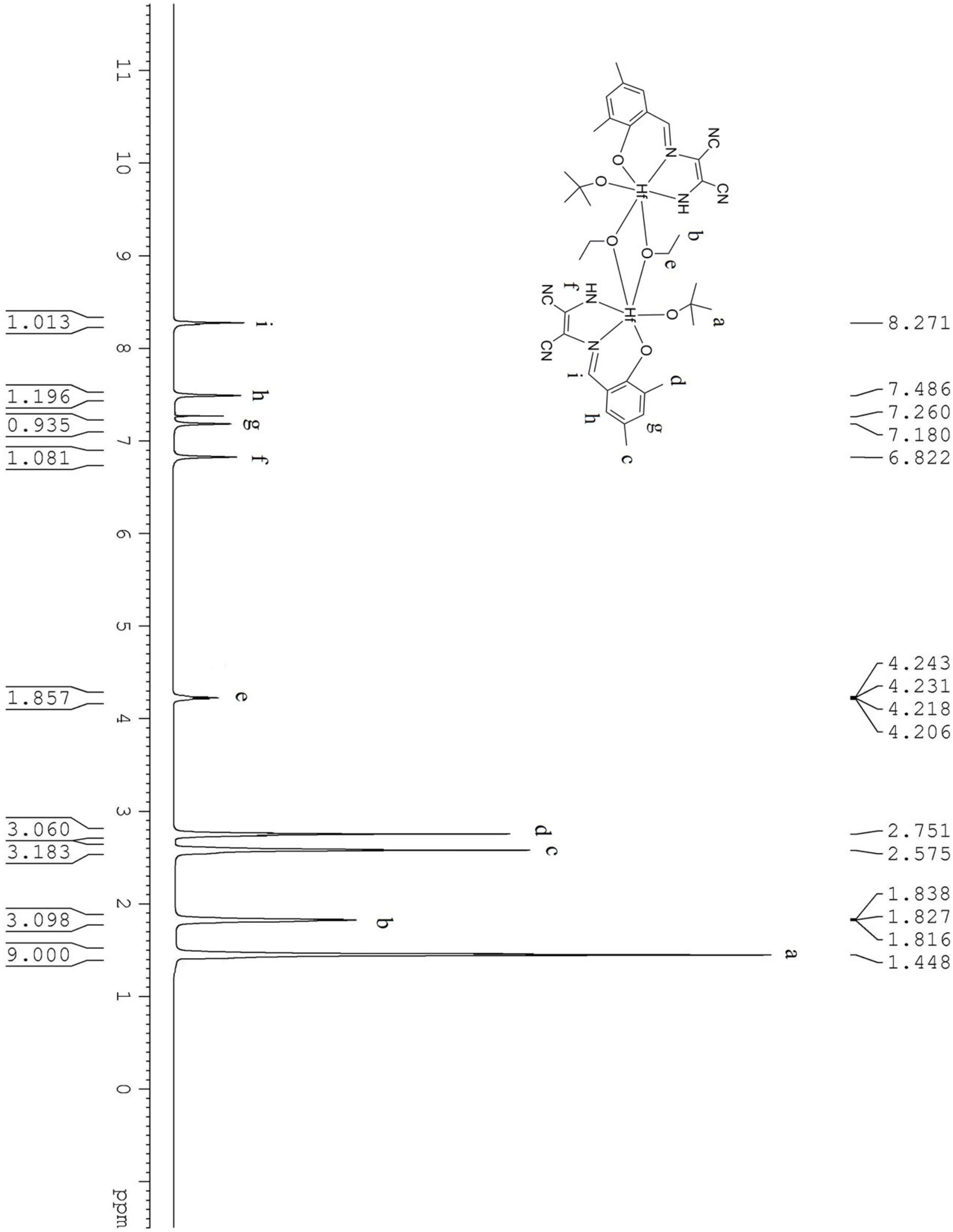


Fig. S22. ^{1}H NMR (500 MHz, $CDCl_3$) of **2c**

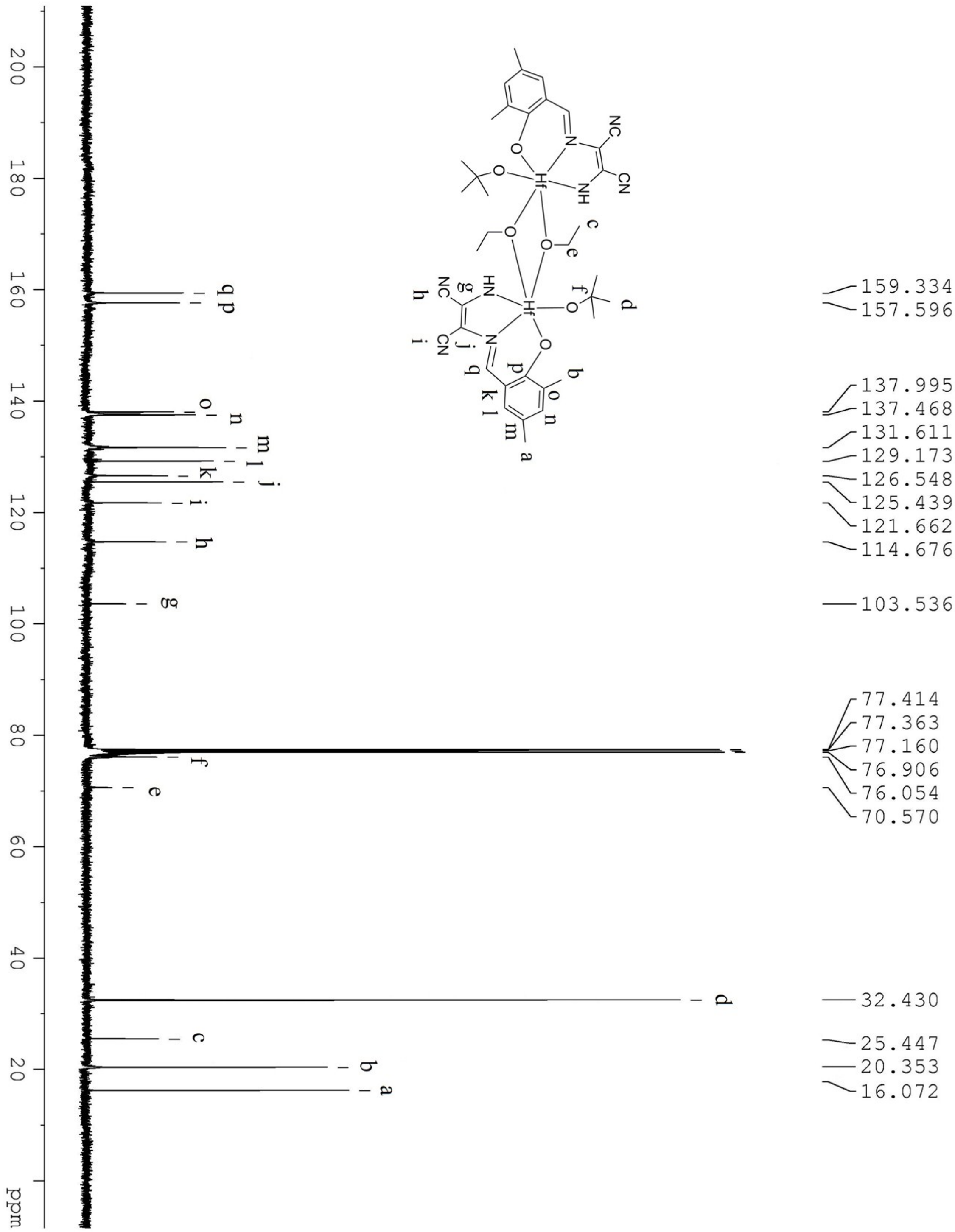


Fig. S23. ^{13}C NMR (125 MHz, $CDCl_3$) of **2c**

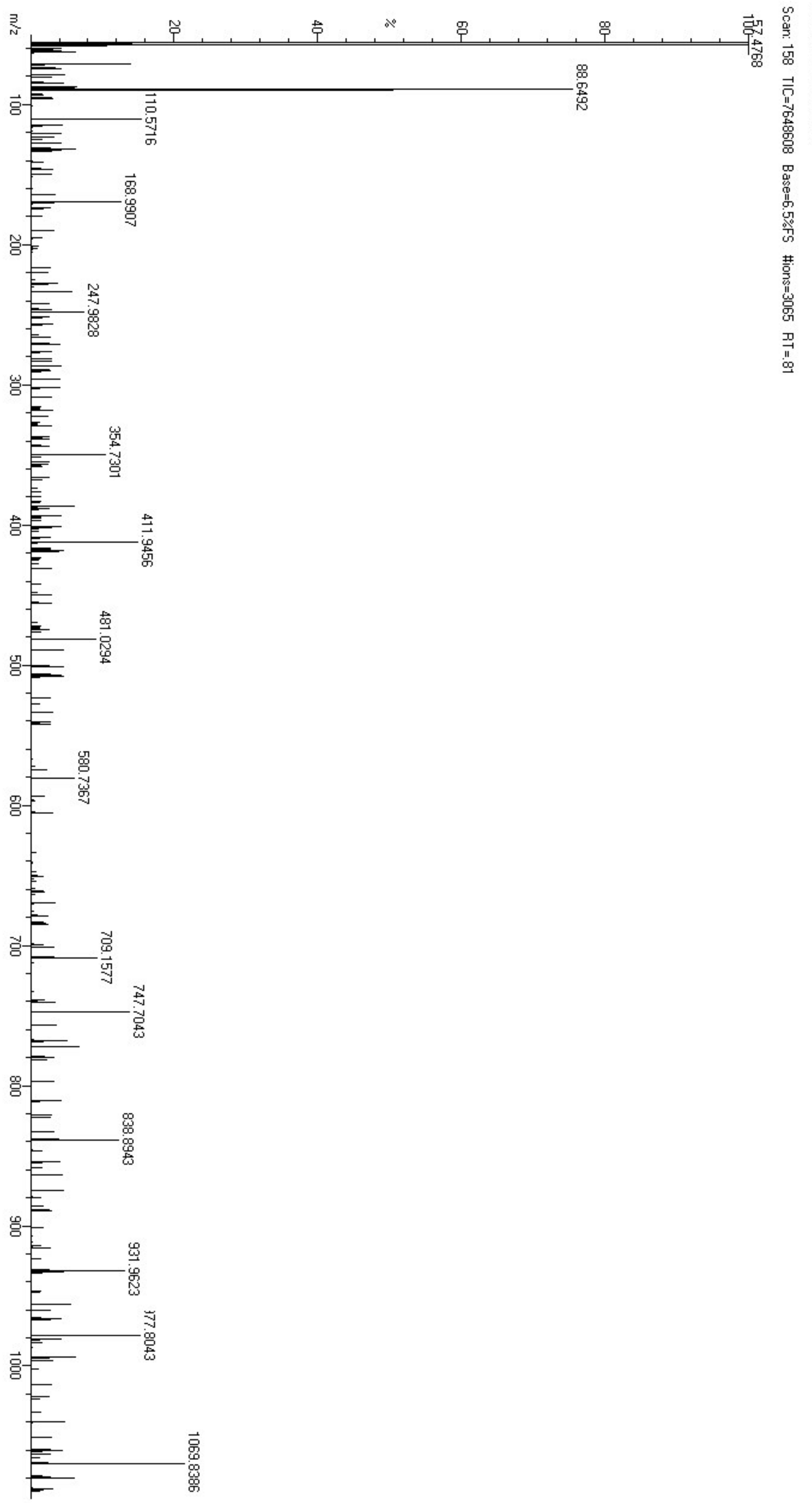


Fig. S24. EI-MS spectrum of **2c**

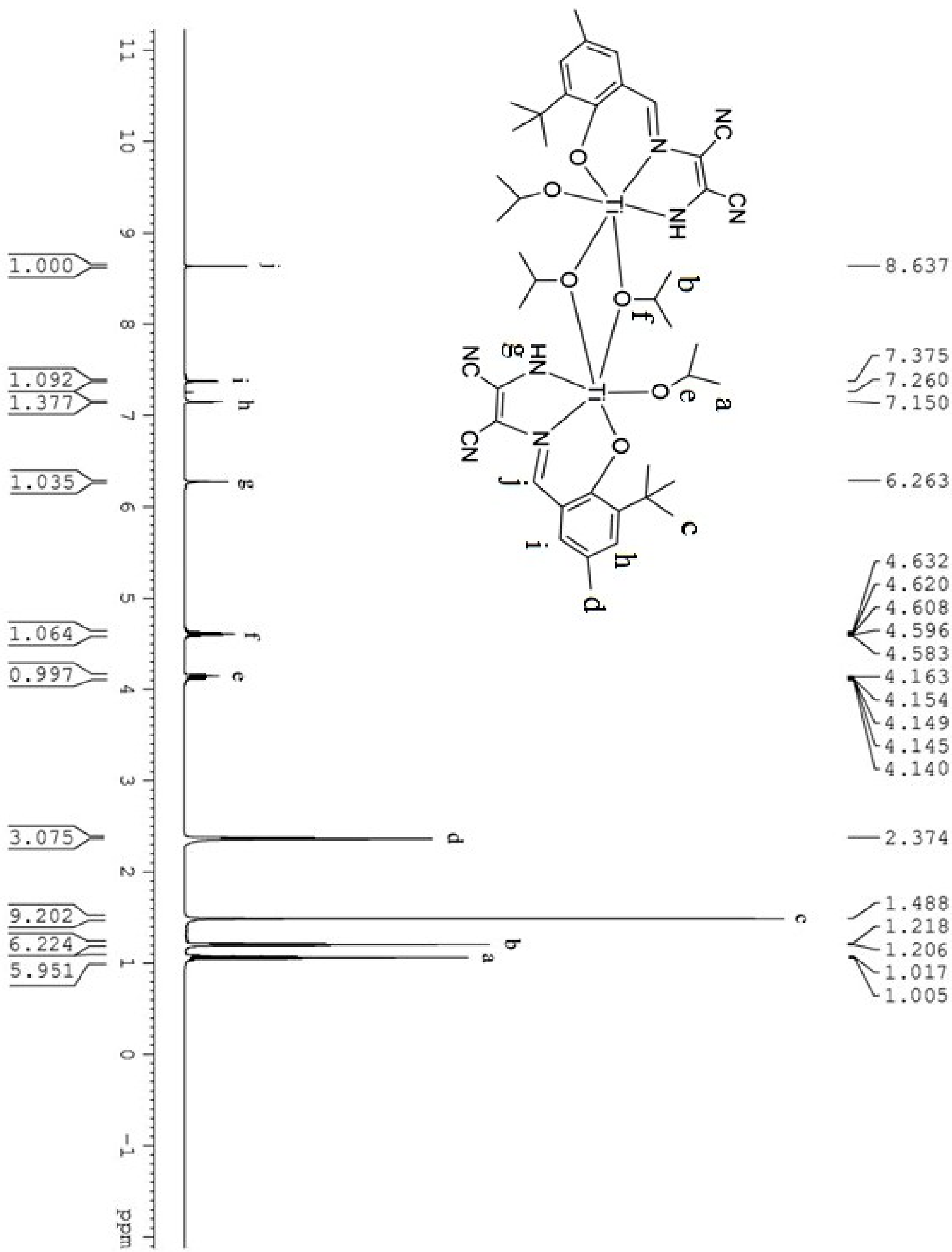


Fig. S25. ^{1}H NMR (500 MHz, $CDCl_3$) of **3a**

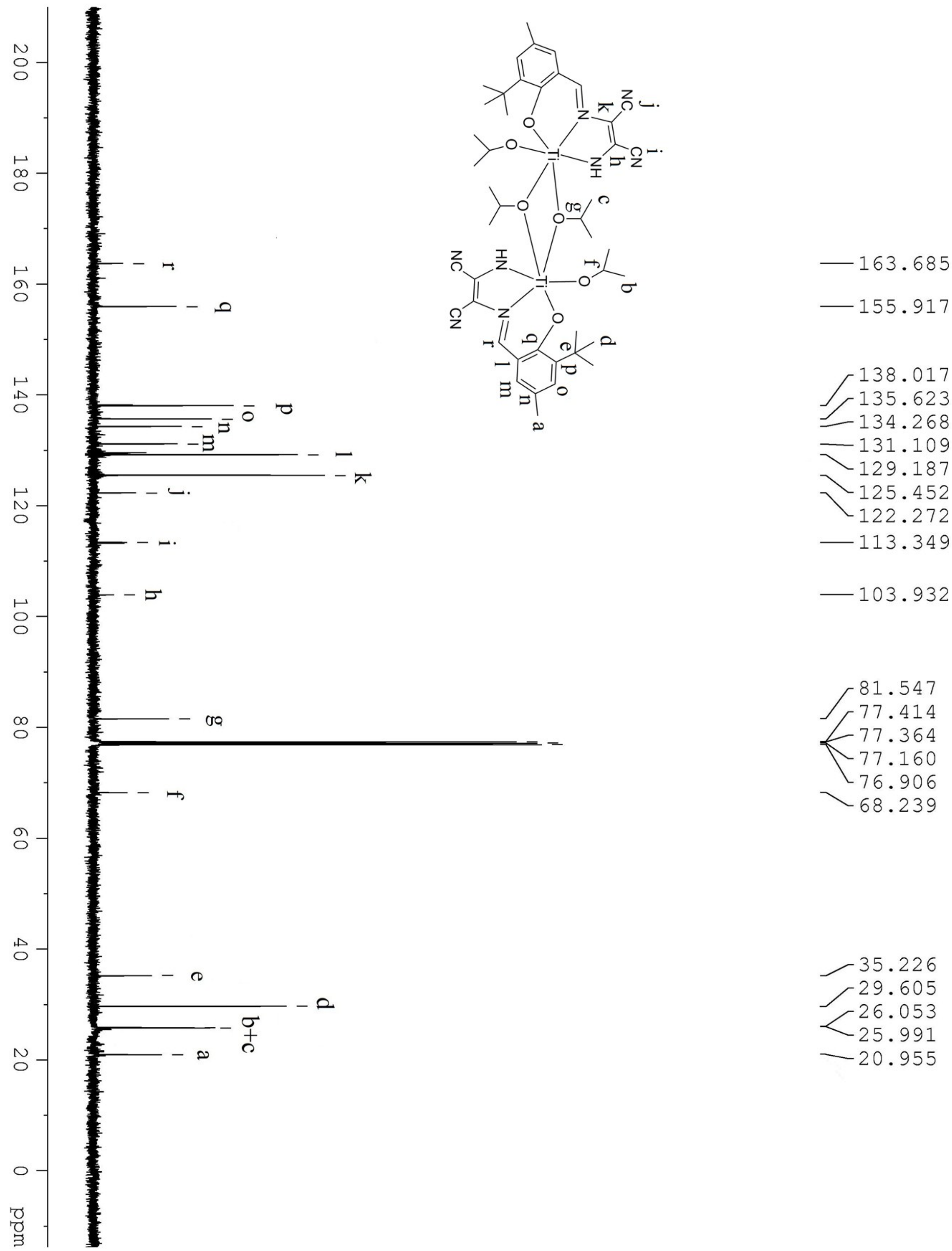


Fig. S26. ^{13}C NMR (125 MHz, $CDCl_3$) of **3a**

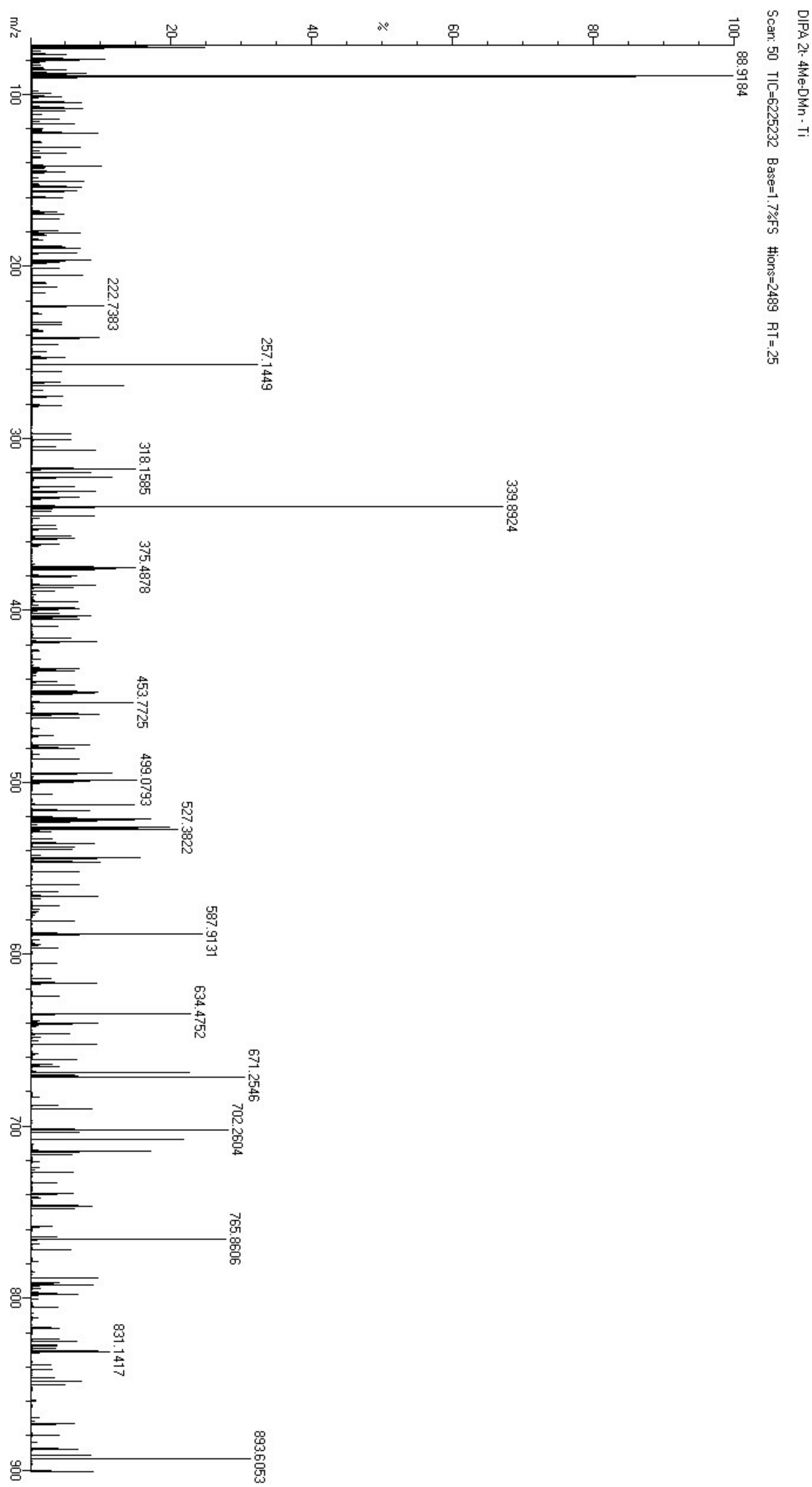


Fig. S27. EI-MS spectrum of **3a**

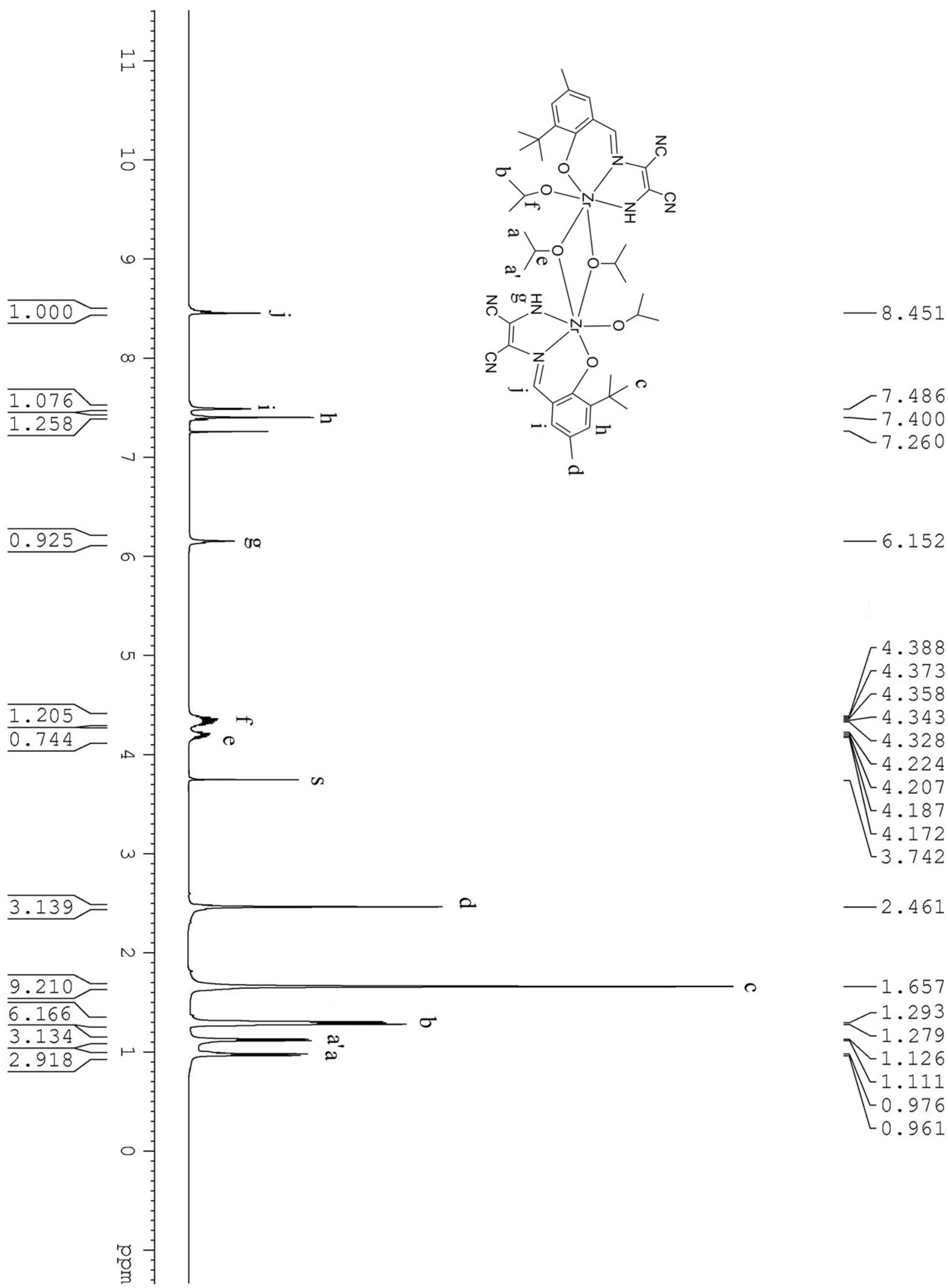


Fig. S28. [1]H NMR (500 MHz, $CDCl_3$) of **3b**

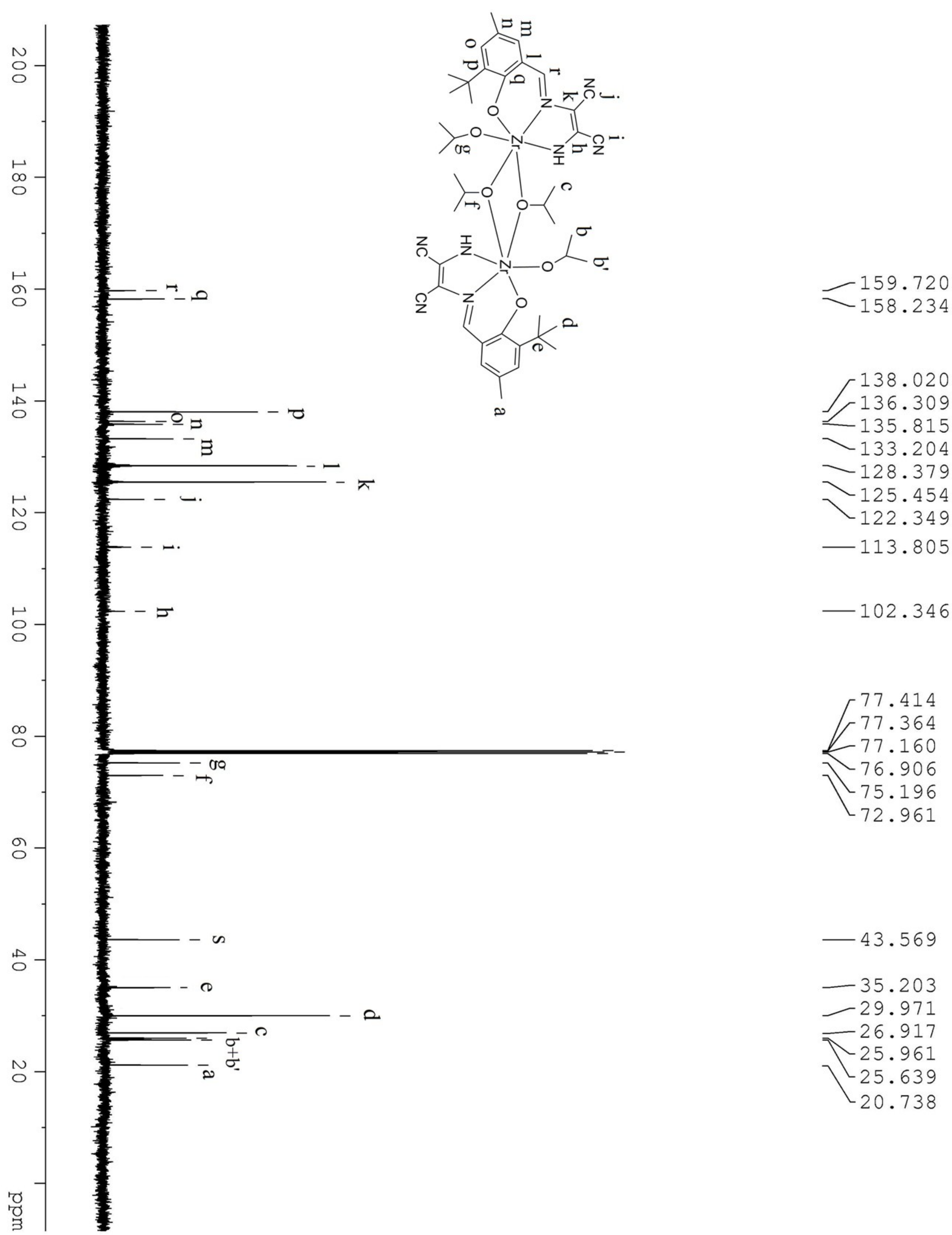


Fig. S29. ^{13}C NMR (125 MHz, $CDCl_3$) of **3b**

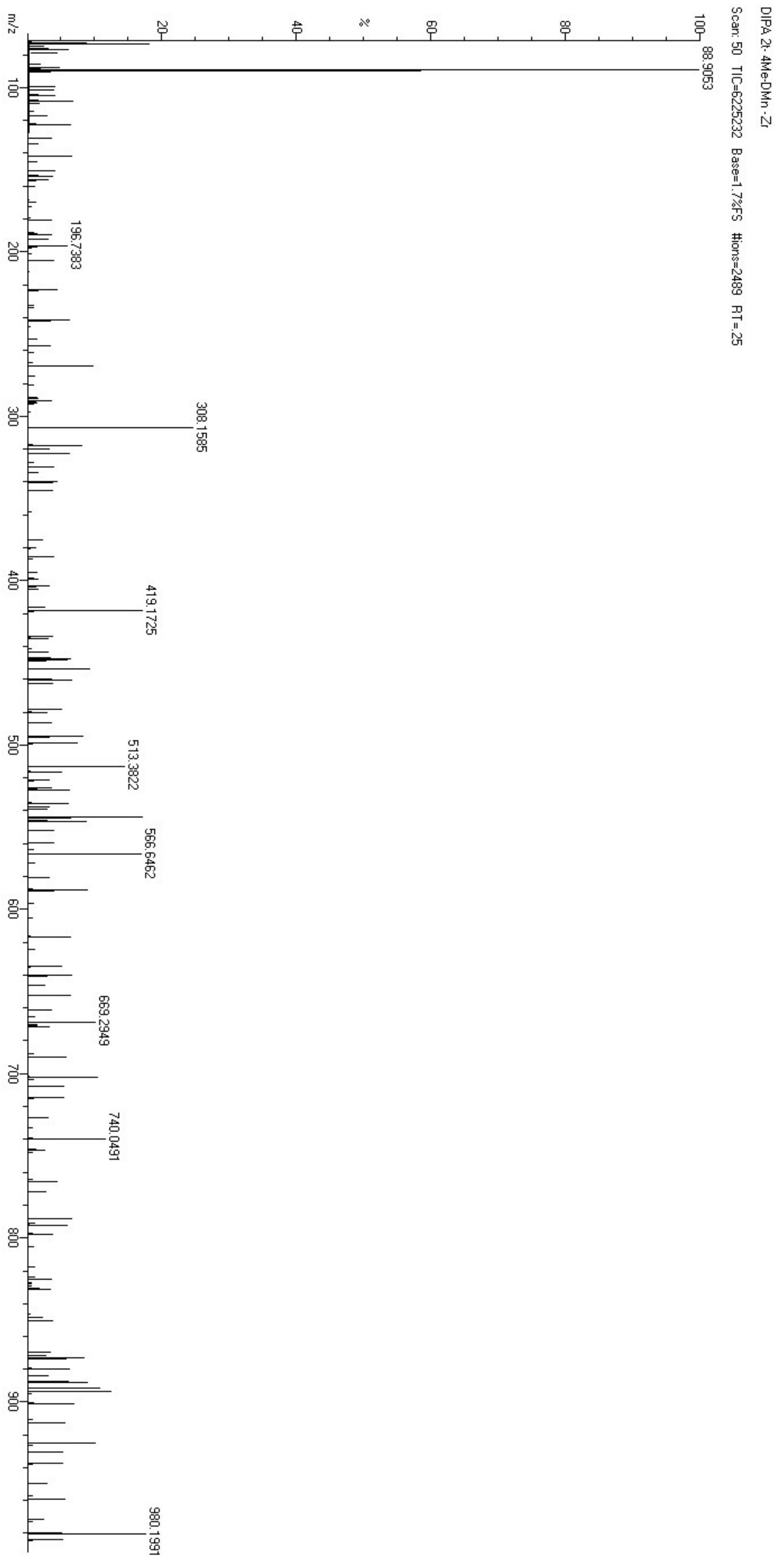


Fig. S30. EI-MS spectrum of **3b**

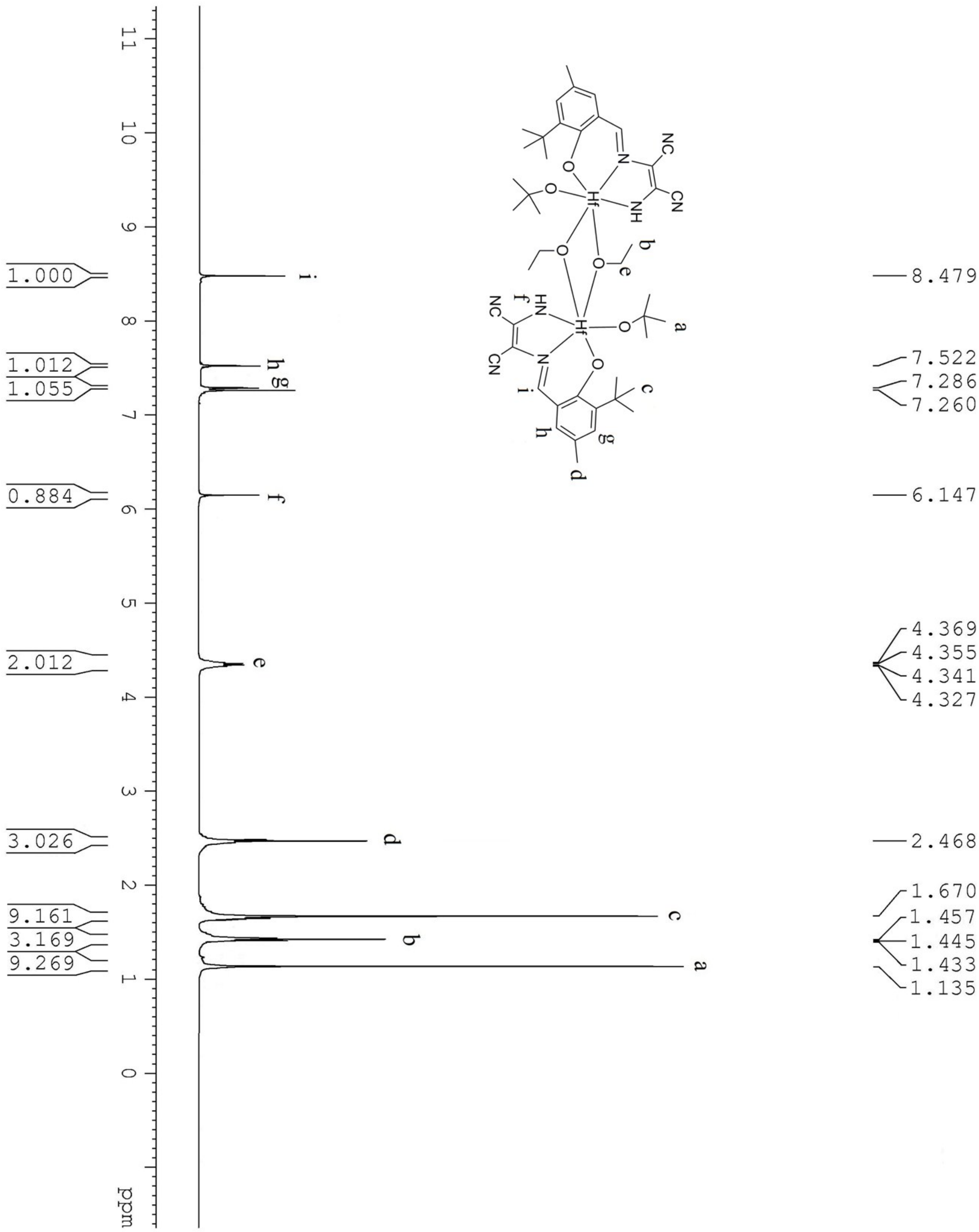


Fig. S31. ^{1}H NMR (500 MHz, $CDCl_3$) of **3c**

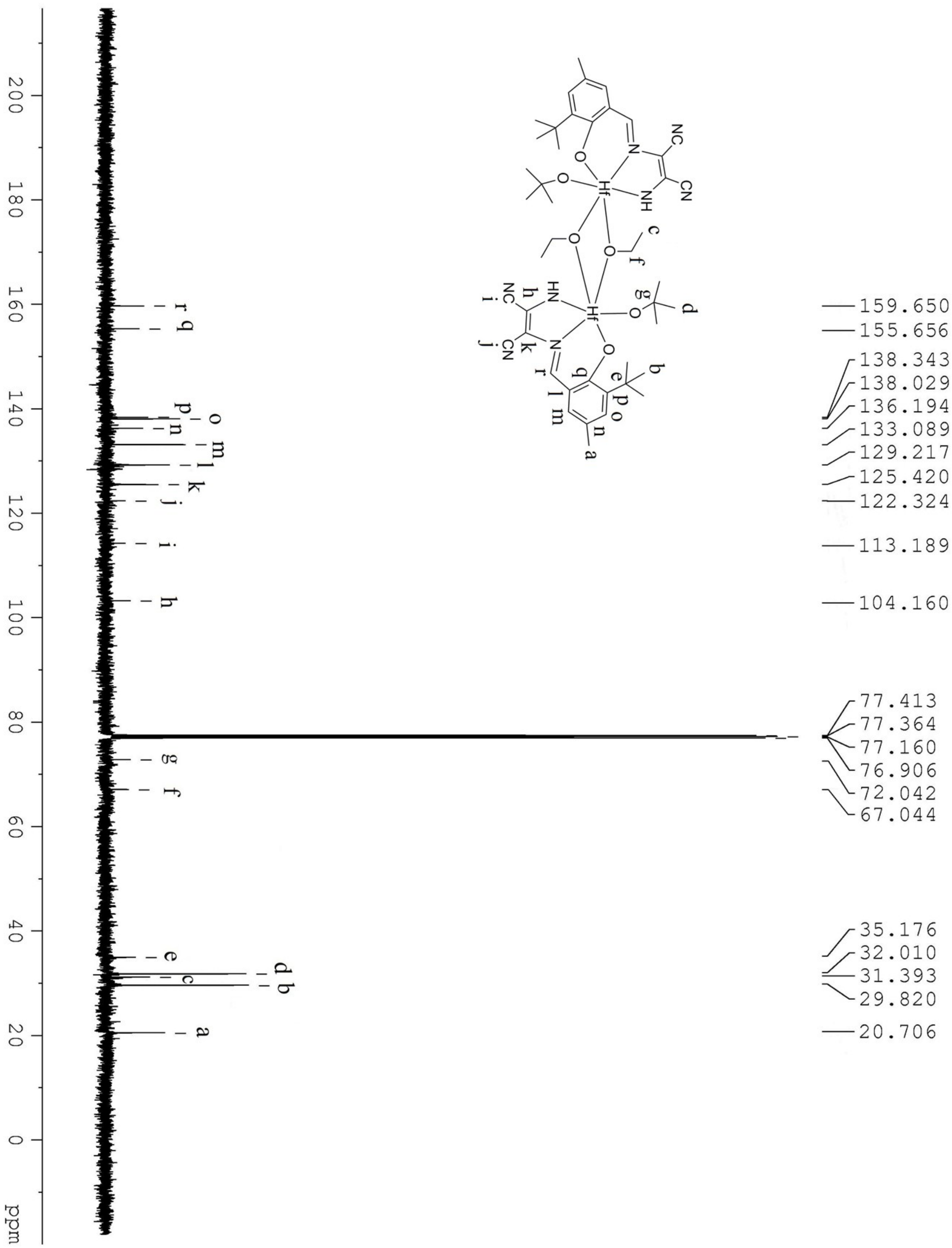


Fig. S32. ^{13}C NMR (125 MHz, $CDCl_3$) of **3c**

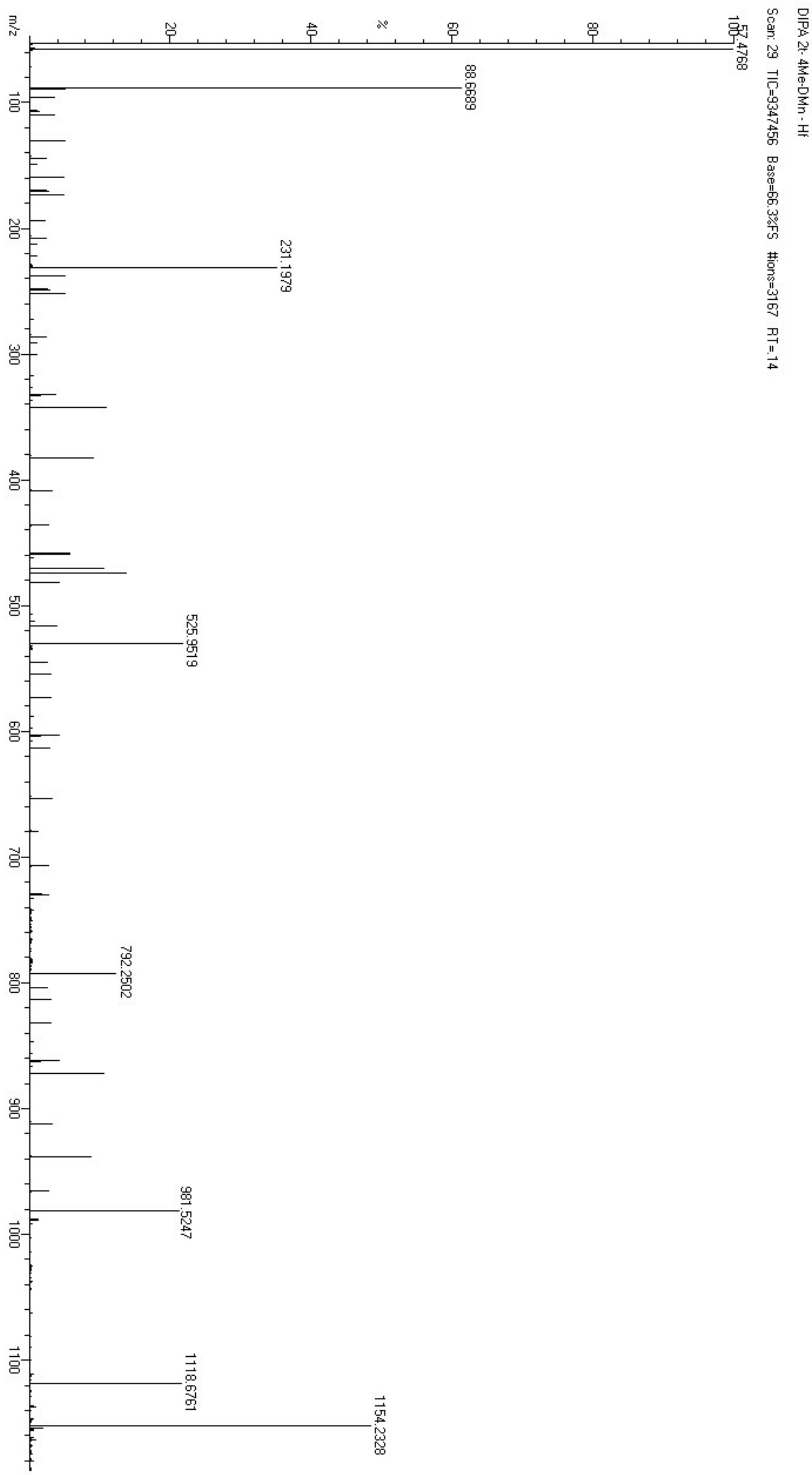


Fig. S33. EI-MS spectrum of **3c**

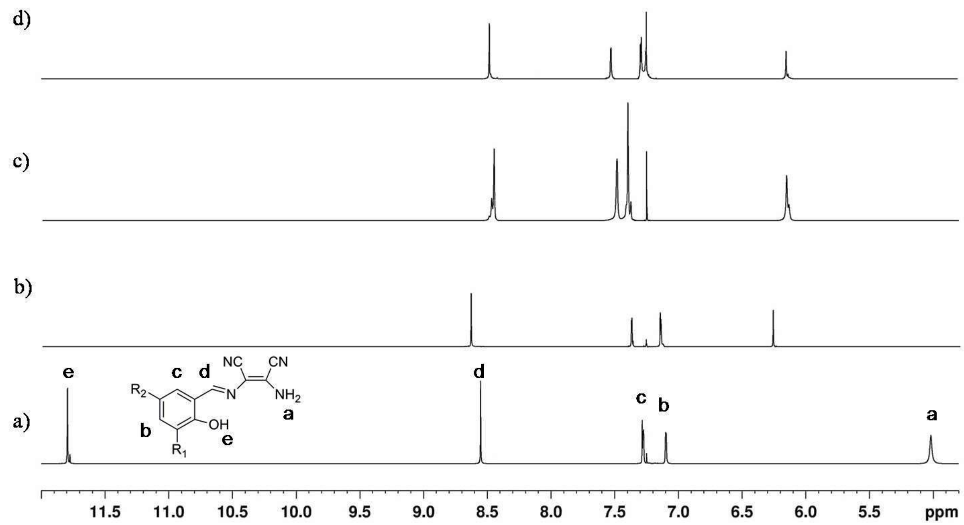


Figure S34. ^{1}H NMR spectra in $CDCl_3$ a) ligand [**L3(H$_2$)**]; b) [Ti(**L3**)(O^{i}Pr)$_2$]$_2$, **3a**; c) [Zr(**L3**)(O^{i}Pr)$_2$]$_2$, **3b**; d) [Hf(**L3**)(O^{i}Pr)(OEt)]$_2$, **3c**.

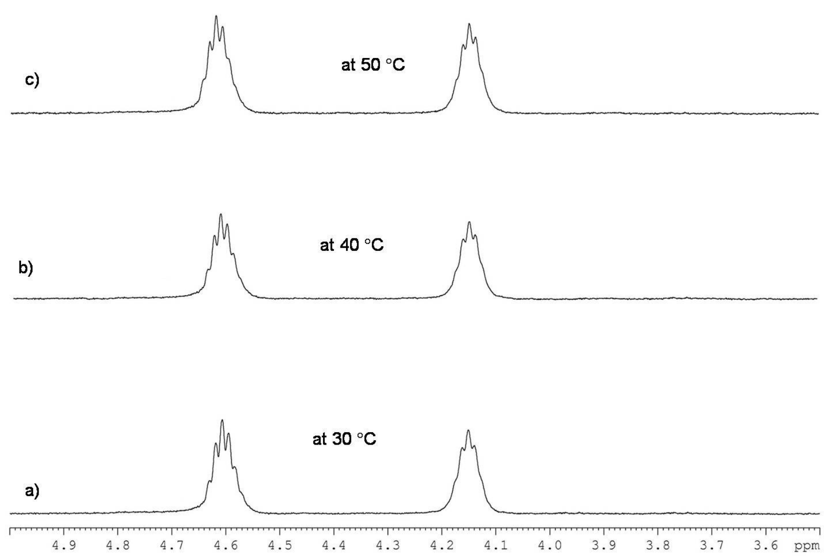


Figure S35. ^{1}H NMR spectra of the methine region of **3a** in $CDCl_3$ at variable temperature a) 30 °C; b) 40 °C and c) 50 °C.

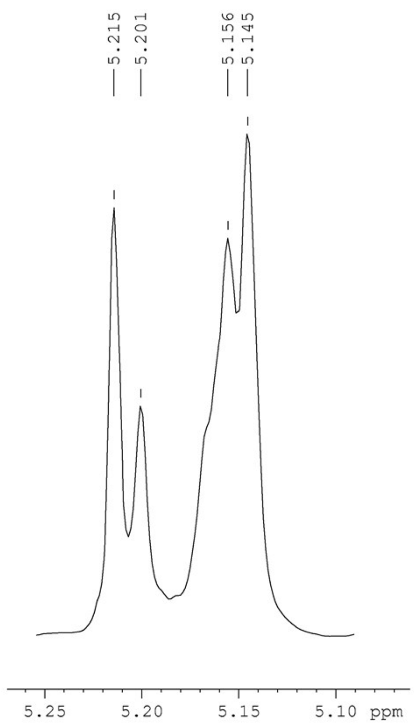


Fig. S36. Homonuclear decoupled ¹H NMR of the methine region of PLA prepared with *rac*-LA and **3c.** [Heterotactic-rich, P_r= 0.80]

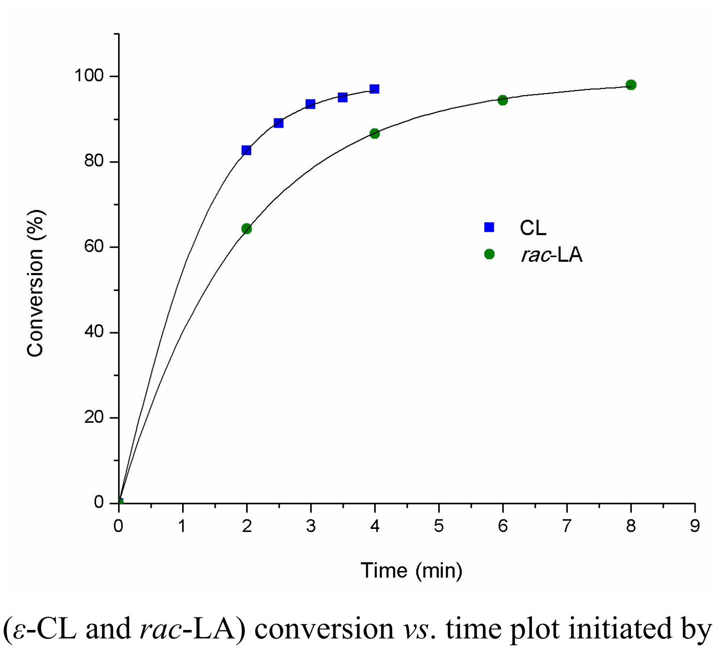


Fig. S37. Monomer (*ε*-CL and *rac*-LA) conversion *vs*. time plot initiated by **1**at $[M]_o/[C]_o$= 200:1

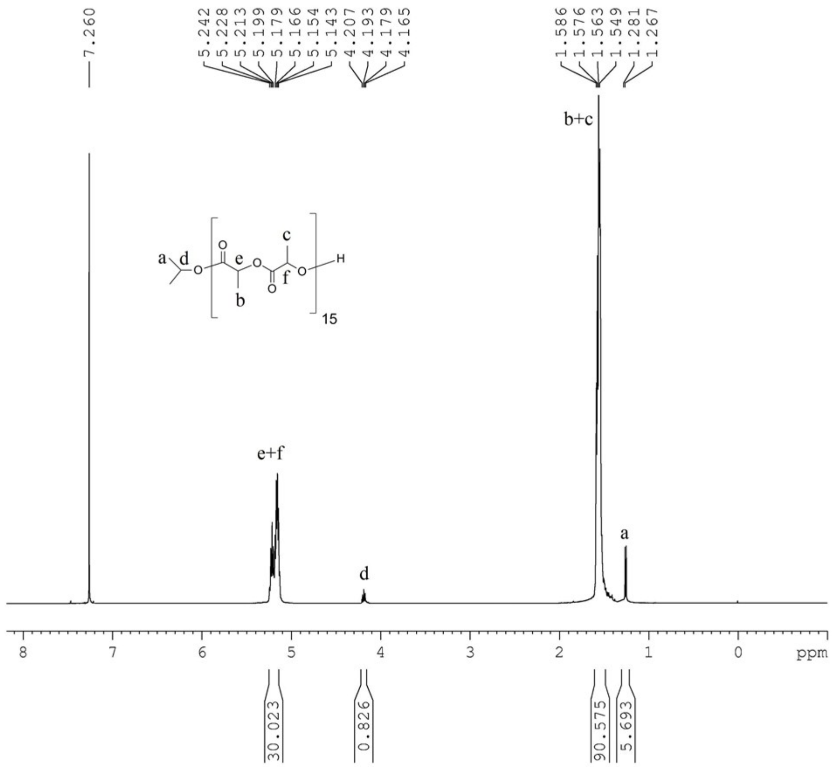


Figure S38. [1]H NMR spectrum (in $CDCl_3$, 500 MHz) of the low molecular weight PLA obtained from *rac*-LA and **3a** at $[M]_o/[Cat]_o$=15:1 at 140 °C.

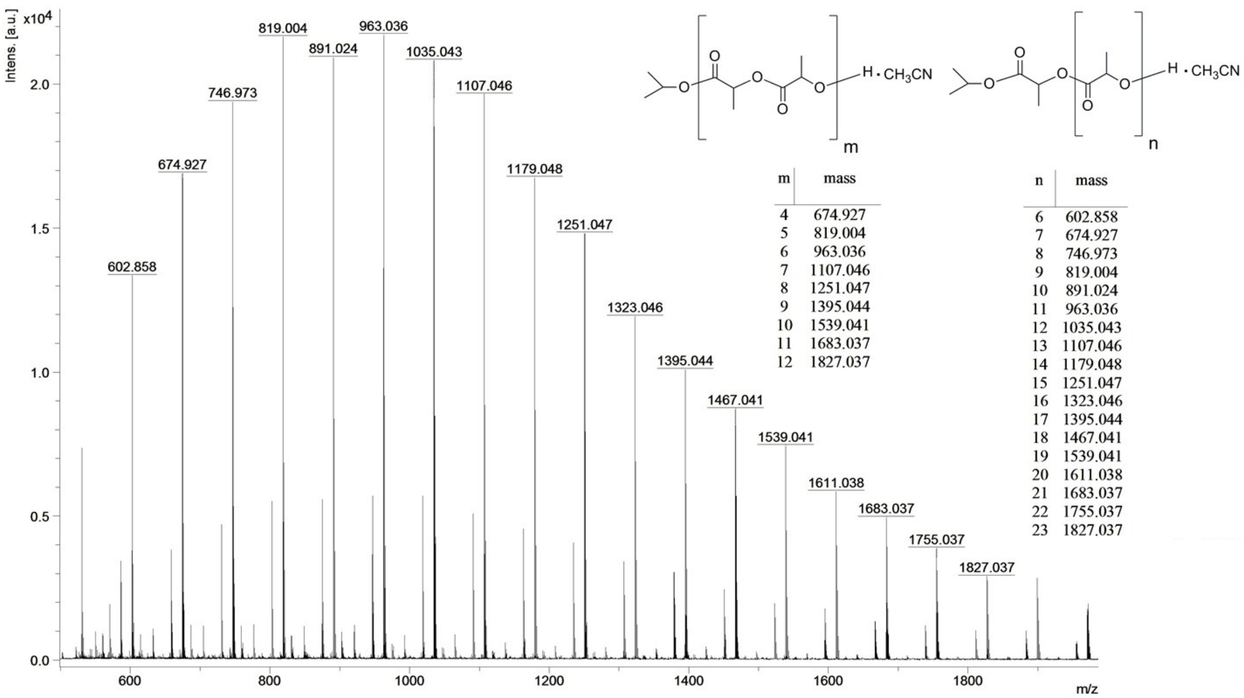
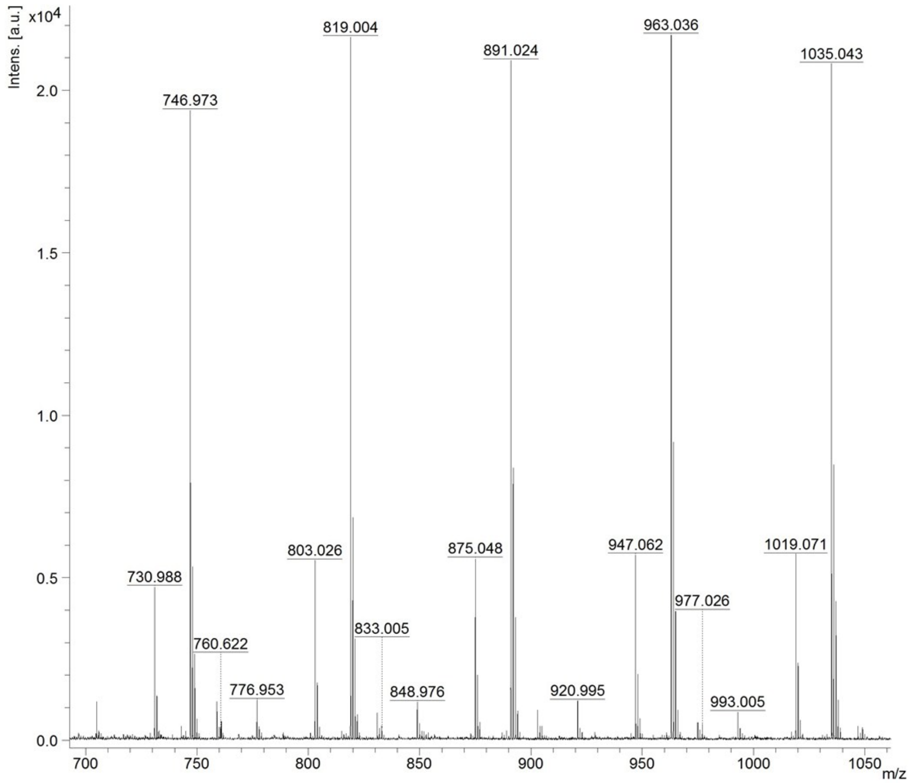
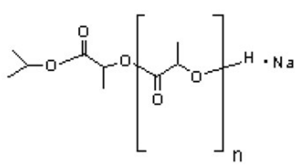
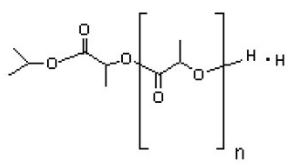
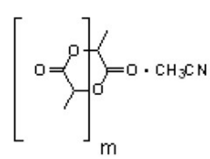


Figure S39. MALDI-TOF mass spectrum of the low molecular weight PLA obtained from *rac*-LA and **3a** at $[M]_o/[Cat]_o$=15:1 at 140 °C.









m	Mass
9	760.622
10	833.005
11	905.027
12	977.026

n	Mass
9	803.026
10	875.048
11	947.062
12	1019.071

n	Mass
9	776.953
10	848.976
11	920.995
12	993.005

Fig. S40. Intramolecular transesterification products present in MALDI-TOF spectrum

Table S2. Homopolymerization of *rac*-CHO, *rac*-PO and *rac*-SO catalyzed by **1a-1c** and **2a-2c**[a].

Entry	Catalyst	Epoxide monomer	Time [h]	Conv. [b] [%]	Yield[c] [%]	TOF[d] [h^{-1}]	M_n^e(obs) [kg mol^{-1}]	M_w/M_n^e
1	**2a**	CHO	8	80	76	100.00	28.25	1.28
2	**2b**	CHO	8	76	72	95.00	27.11	1.32
3	**2c**	CHO	8	75	74	93.75	26.67	1.33
4	**1a**	CHO	8	72	70	90.00	29.77	1.30
5	**1b**	CHO	8	69	66	86.25	25.54	1.36
6	**1c**	CHO	8	68	65	85.00	25.99	1.35
7	**2a**	PO	16	66	62	41.25	20.98	1.29
8	**2b**	PO	16	61	57	38.12	19.90	1.34
9	**2c**	PO	16	62	60	38.75	21.91	1.36
10	**1a**	PO	16	65	63	40.62	22.54	1.32
11	**1b**	PO	16	60	57	37.50	18.31	1.34
12	**1c**	PO	16	61	58	38.12	19.14	1.36
13	**2a**	SO	12	65	64	54.17	37.65	1.39
14	**2b**	SO	12	63	62	52.50	39.22	1.42
15	**2c**	SO	12	60	56	50.00	40.24	1.43
16	**1a**	SO	12	61	58	50.83	38.86	1.38
17	**1b**	SO	12	62	61	47.50	35.59	1.42
18	**1c**	SO	12	60	58	50.00	37.92	1.43

[a]Polymerization conditions: $[M]_o/[C]_o$ = 1000, under sovent-free. [b]Determined from ^1H NMR in $CDCl_3$ at 25 °C. [c]Based on gm of polymer obtained. [d]Turnover frequency (TOF) =Mol of epoxide×(mol of catalyst) $^{-1}$ h^{-1}. [e]Measured by GPC at 27 ℃ in THF relative to polystyrene standards.

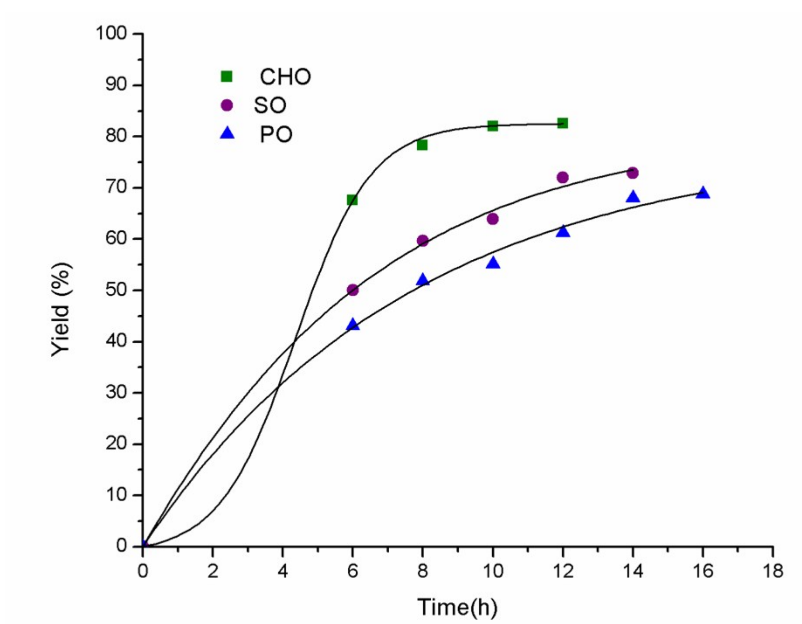


Fig. S41. Epoxide polymer yield (%) *vs*. time plot initiated by **3a** at $[M]_o/[C]_o$ = 1000:1

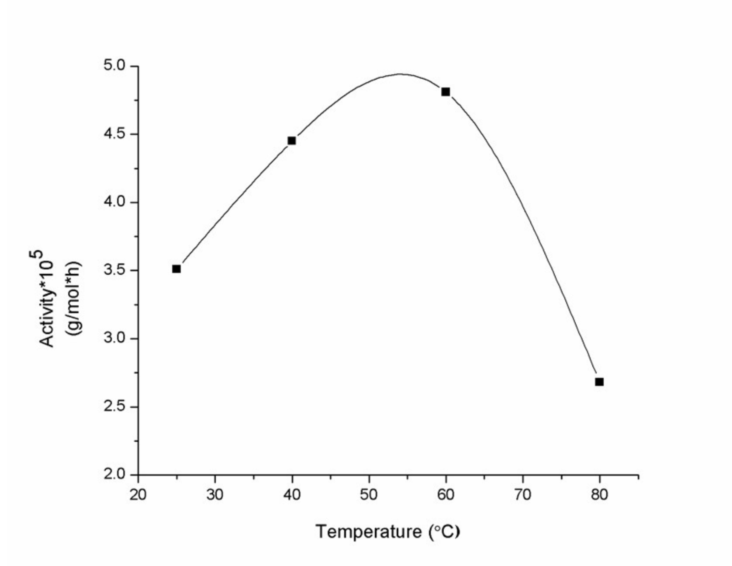


Fig. S42. Plot for Activity versus temp using **3a** for ethylene polymerization

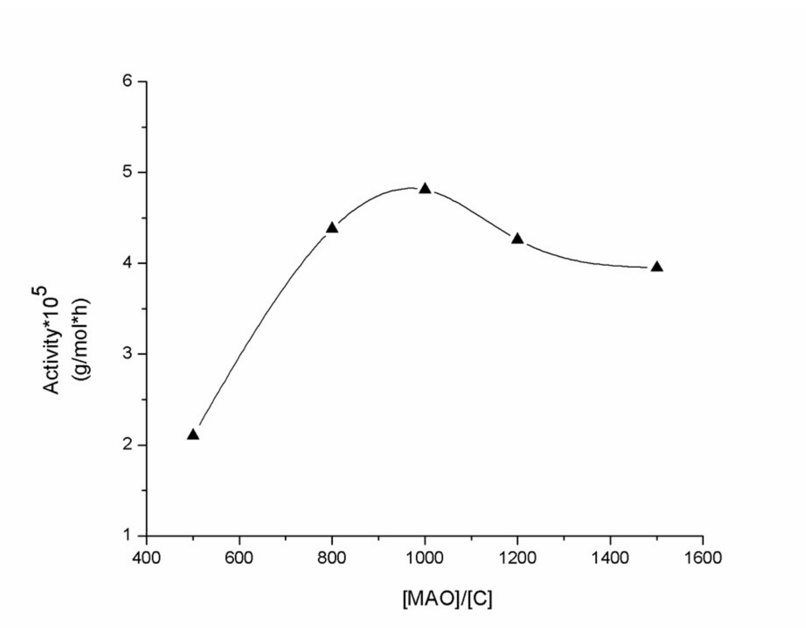


Fig. S43. Plot for Activity versus [MAO]/[**3a**] ratio for ethylene polymerization

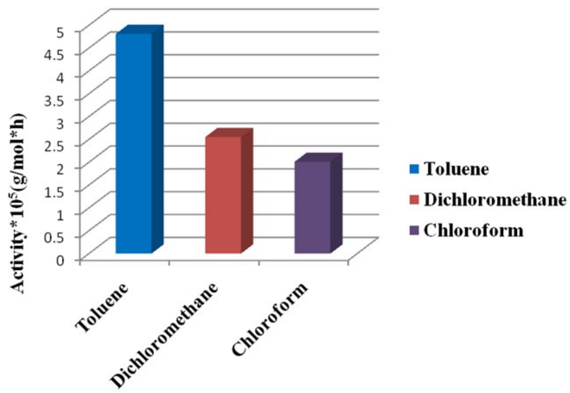


Fig. S44. Plot for effect of the solvent on the activity using **3a**