

Supporting Information

A novel chemosensor with visible light excitability for sensing Zn²⁺ in physiological medium and in HeLa cells

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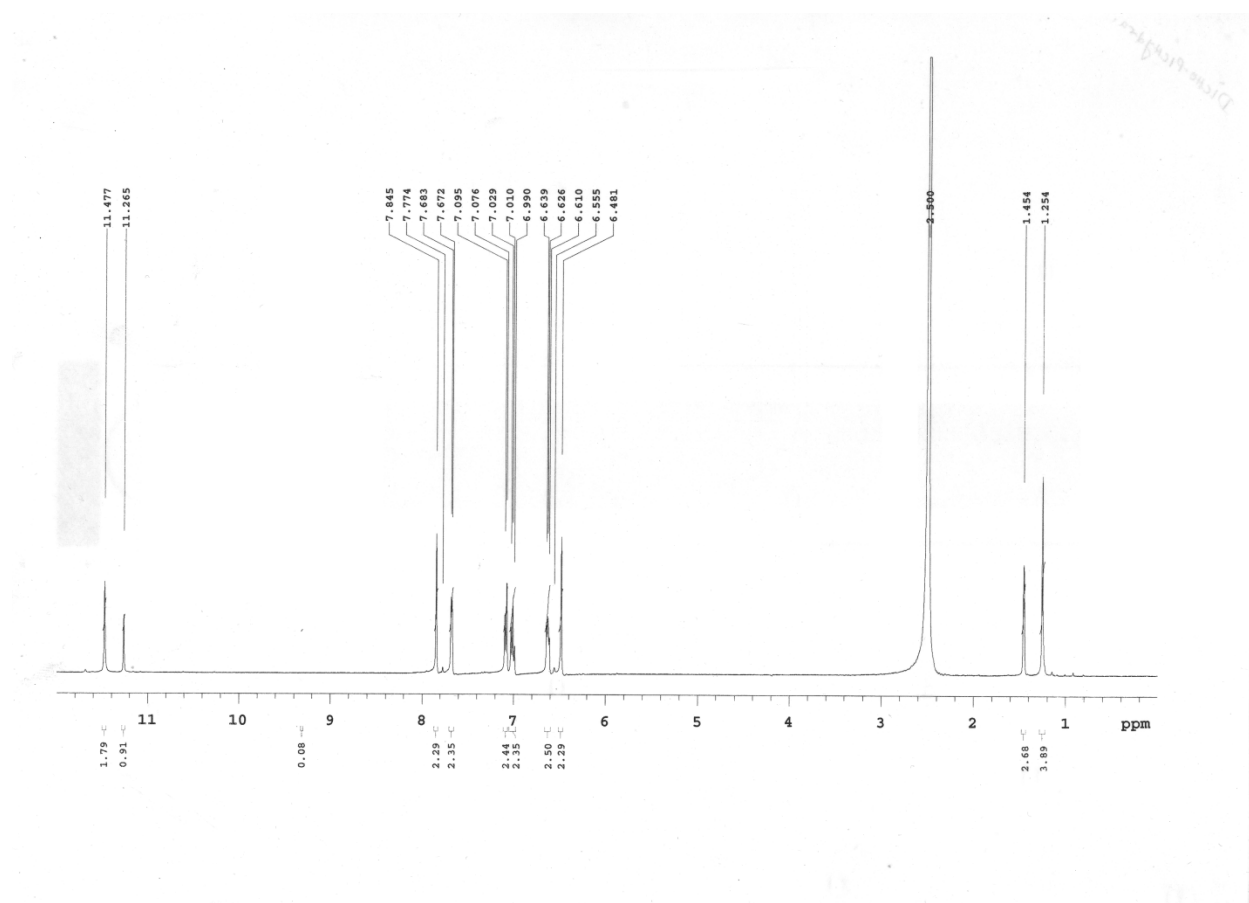


Fig. S1: ¹H- NMR spectra of **L**₁ in DMSO-d₆.

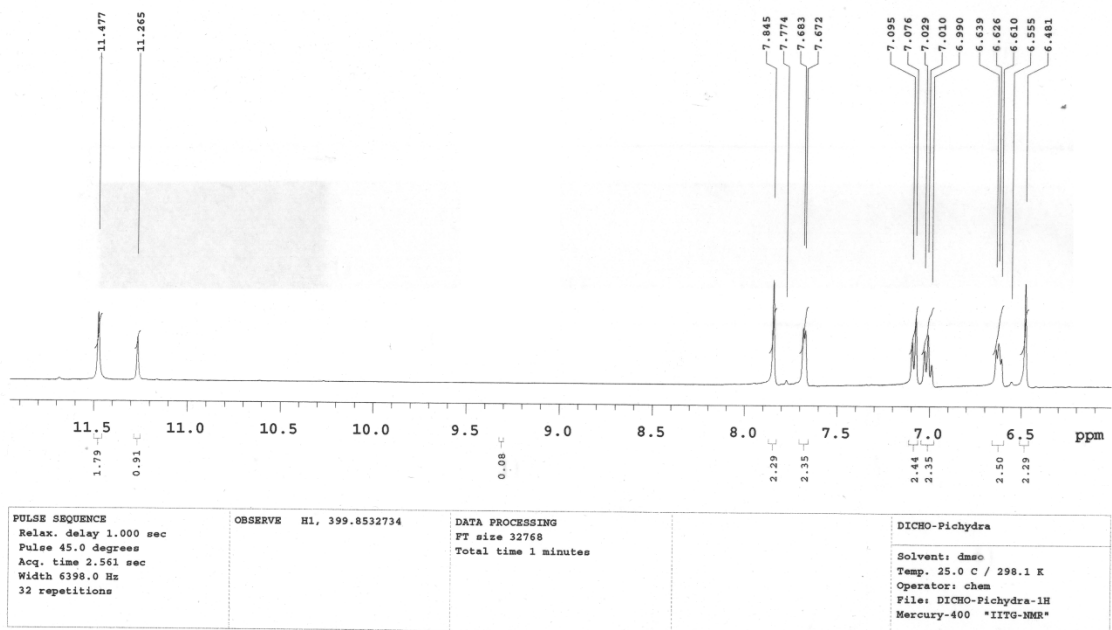


Fig. S2: Expanded ^1H - NMR spectra of L_1 in DMSO-d_6 .

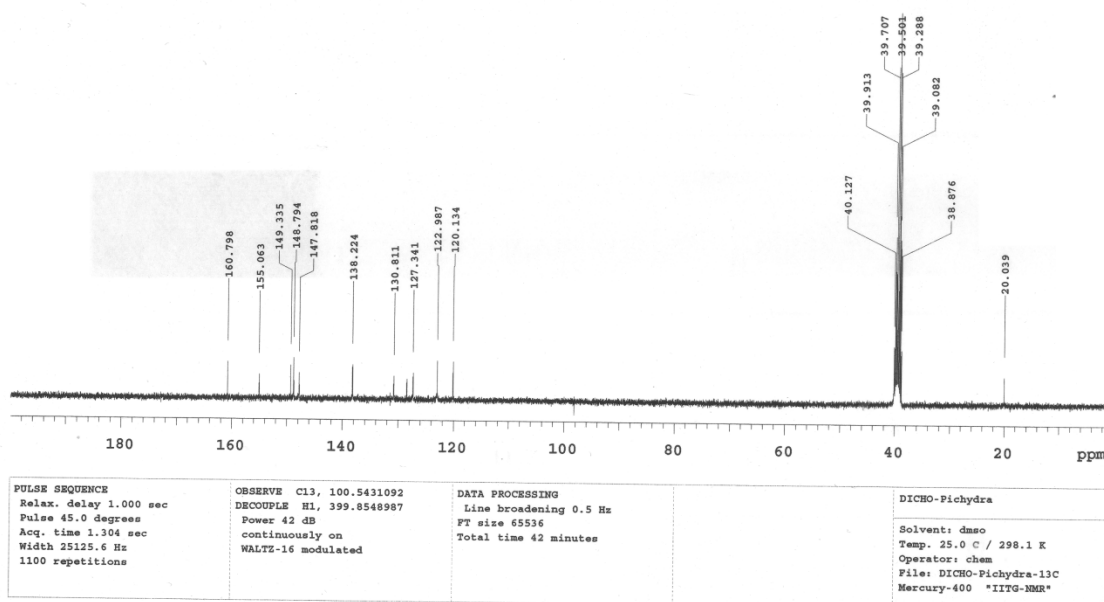


Fig. S3: ^{13}C - NMR spectra of L_1 in DMSO-d_6 .

DICHO-Pichydra
 Sample Name:
 DICHO-Pichydra
 Data Collected on:
 IITG-NMR-mercury400
 Archive directory:
 Sample directory:
 FidFile: CARBON
 Pulse Sequence: CARBON (a2pul)
 Solvent: dmsc
 Data collected on: Dec 7 2013

Temp. 25.0 C / 298.1 K
 Operator: chem
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.304 sec
 Width 25125.6 Hz
 1100 repetitions
 OBSERVE C13, 100.5431092 MHz
 DECOUPLE H1, 399.8548987 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 7 hr, 37 min

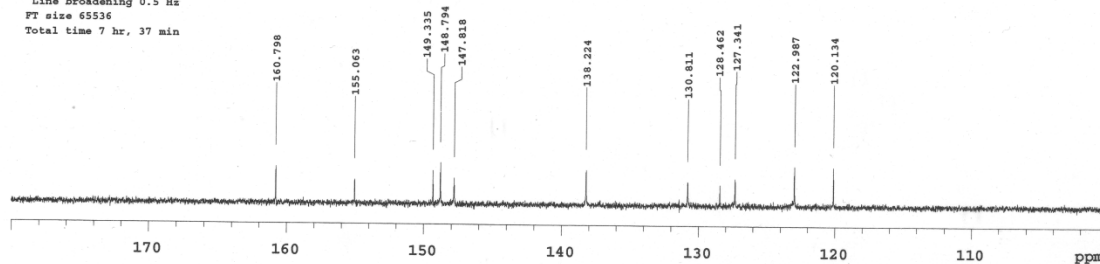


Fig. S4: Expanded ^{13}C - NMR spectra of L_1 in DMSO-d_6 .

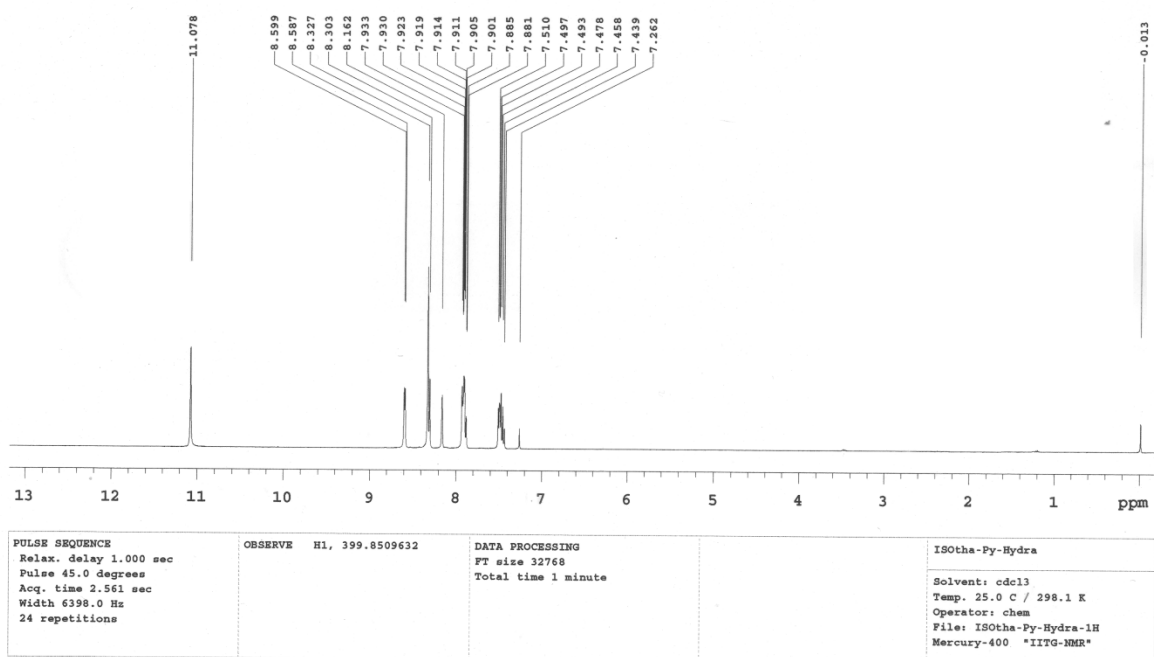


Fig. S5: ^1H - NMR spectra of L_2 in CDCl_3 .

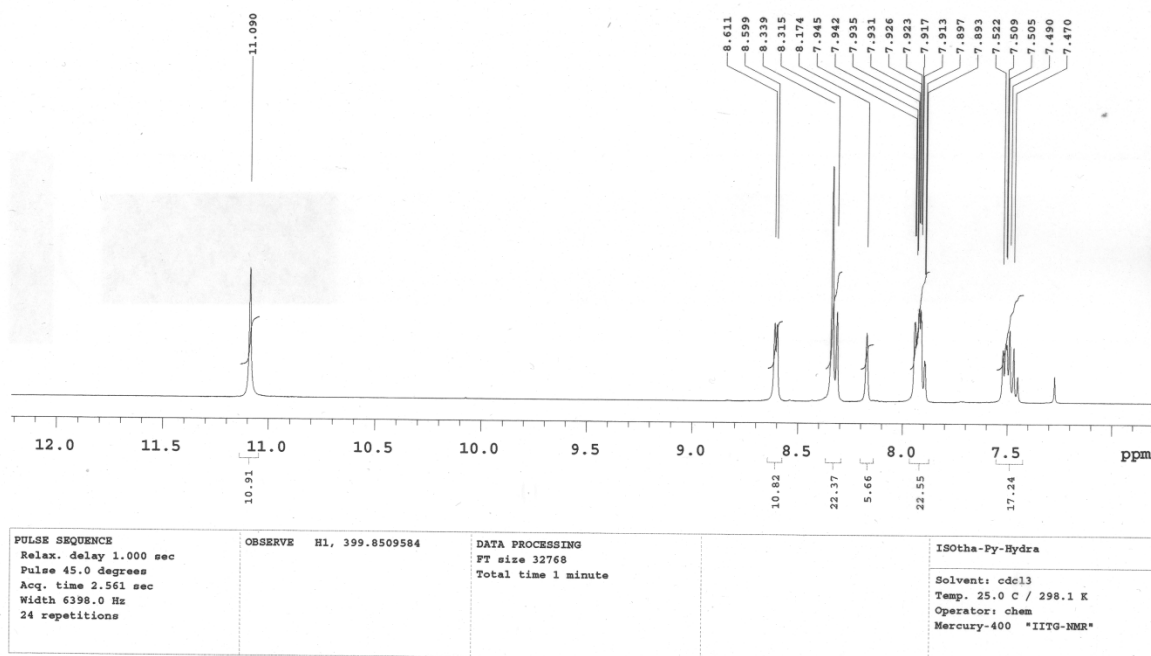


Fig. S6: Expanded ^1H - NMR spectra of L_2 in CDCl_3 .

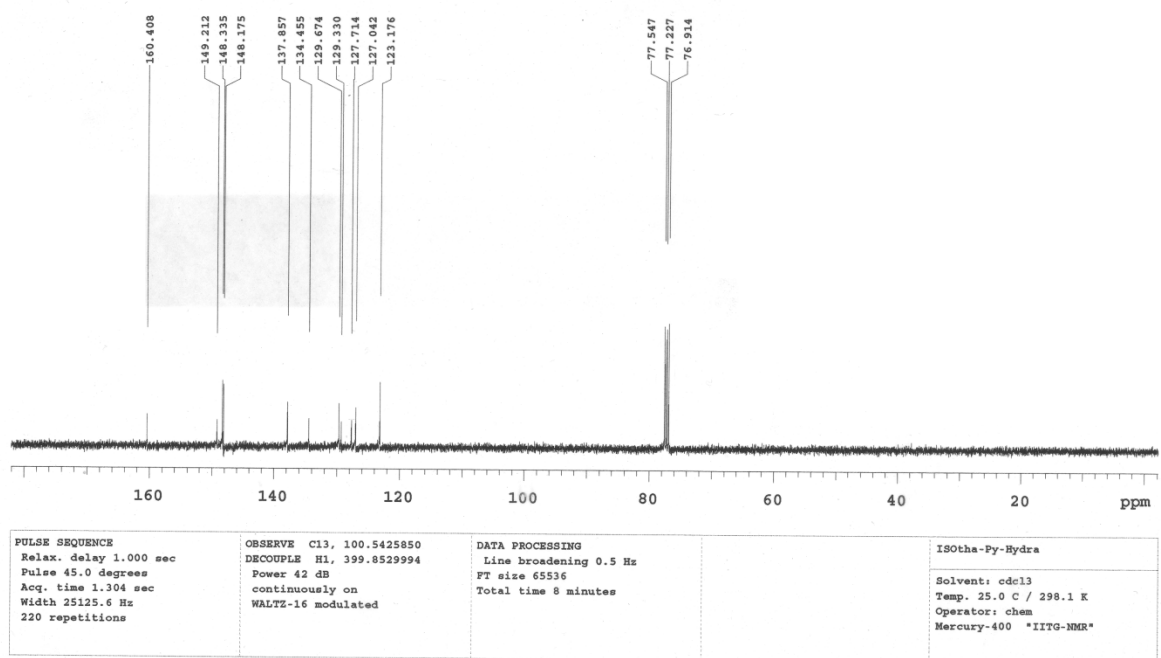


Fig. S7: ^{13}C - NMR spectra of L_2 in CDCl_3 .

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Inj Vol	Unavailable	InjPosition	Unavailable	SampleType	Unavailable	IRM Calibration Status	Success
Data Filename	PICH.d	ACQ Method		Comment	Sample information is unavailable	Acquired Time	Unavailable

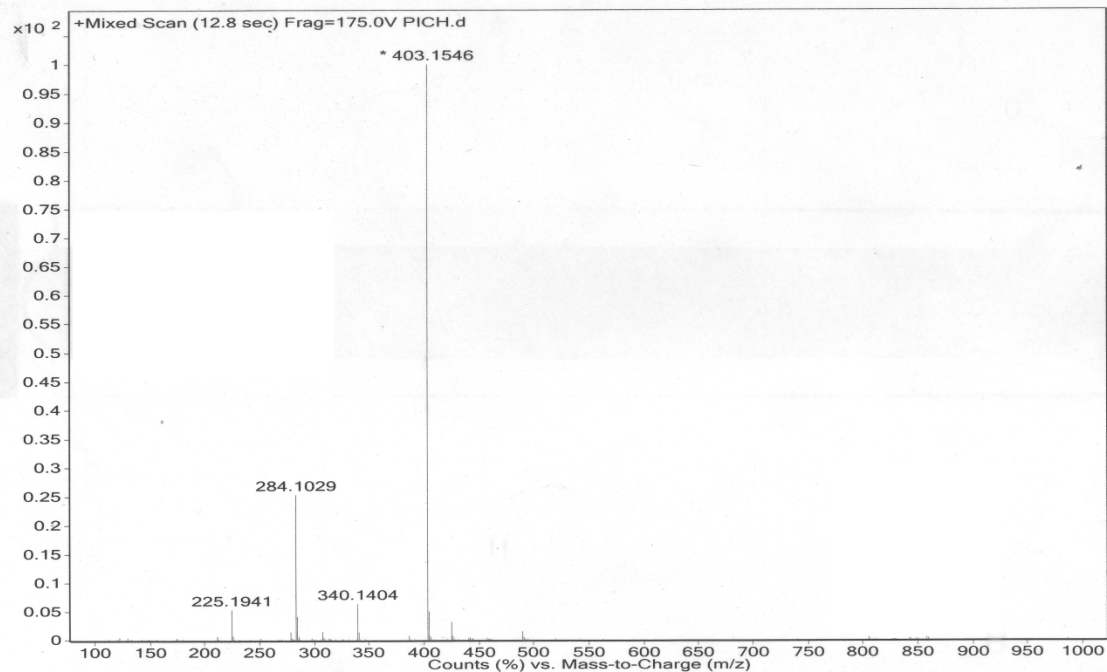


Fig. S8: Mass spectrum of L_1 (positive mode), Expected m/z for $C_{21}H_{19}N_6O_3 (L_1+H)^+$ = 403.1519, Found 403.1546.

Sample Name	PY-HY-ZN	Position	-1	Instrument Name	Instrument 1	User Name	
Inj Vol	-10	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	PY-HY-ZN.d	ACQ Method		Comment		Acquired Time	11/8/2013 12:06:21 PM

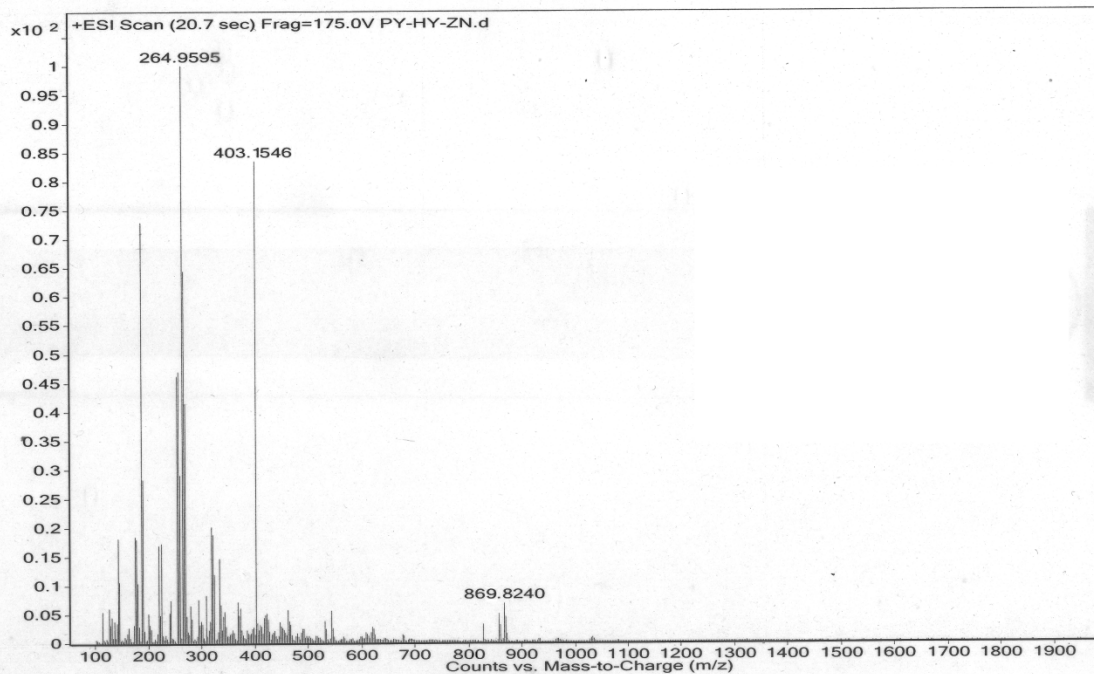


Fig. S9: Mass spectrum of zinc complex of L_1 (positive mode). Expected m/z for $C_{23}H_{21}Cl_3N_7O_{15}Zn_2$ ($L_1 + 2Zn + 3ClO_4 + CH_3CN$) = 869.8713, found 869.8240.

Sample Name	PY-HY-ZN	Position	-1	Instrument Name	Instrument 1	User Name	
Inj Vol	-10	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	PY-HY-ZN.d	ACQ Method		Comment		Acquired Time	11/8/2013 12:06:21 PM

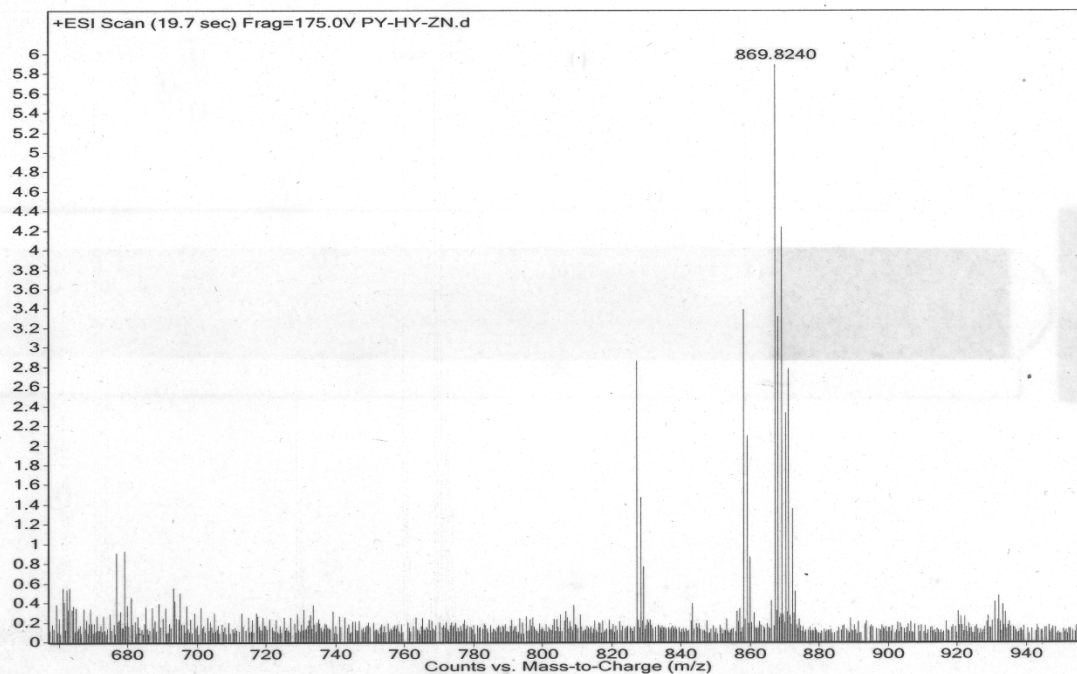


Fig. S10: Expanded mass spectrum of zinc complex of L_1 (positive mode).

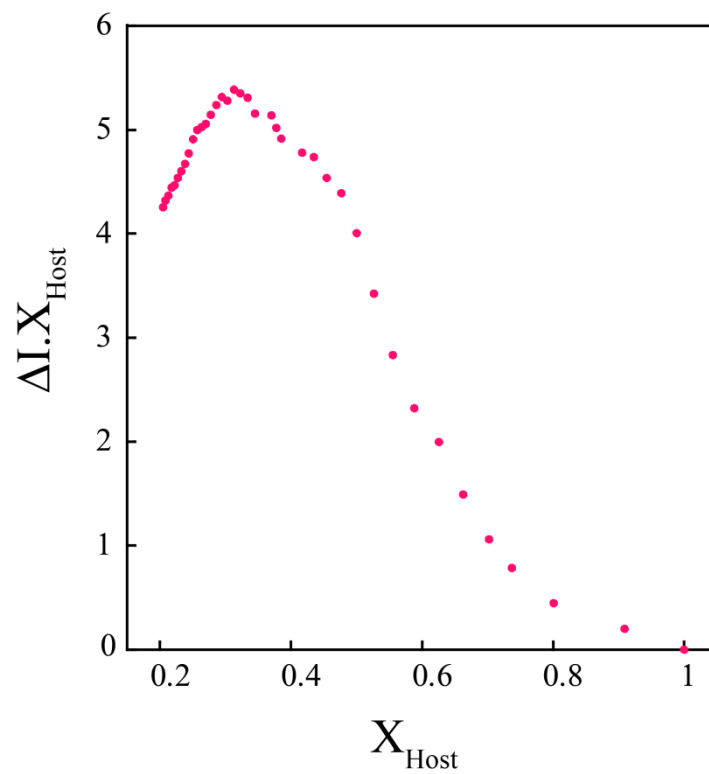


Fig. S11: Job's plot between L_1 and Zn^{2+} .

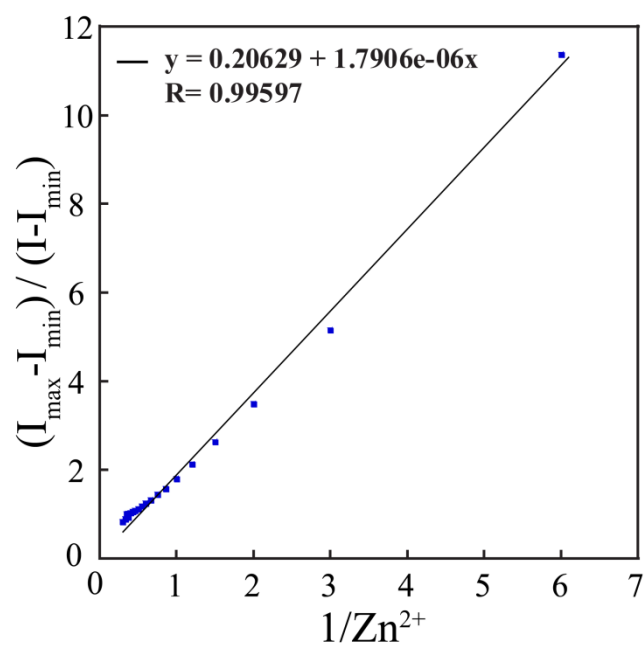


Fig. S12: Benesi-Hildebrand plot between L_1 and Zn^{2+} .



Fig. S13: Visual color change upon the addition of Zn^{2+} to L_1 solution.

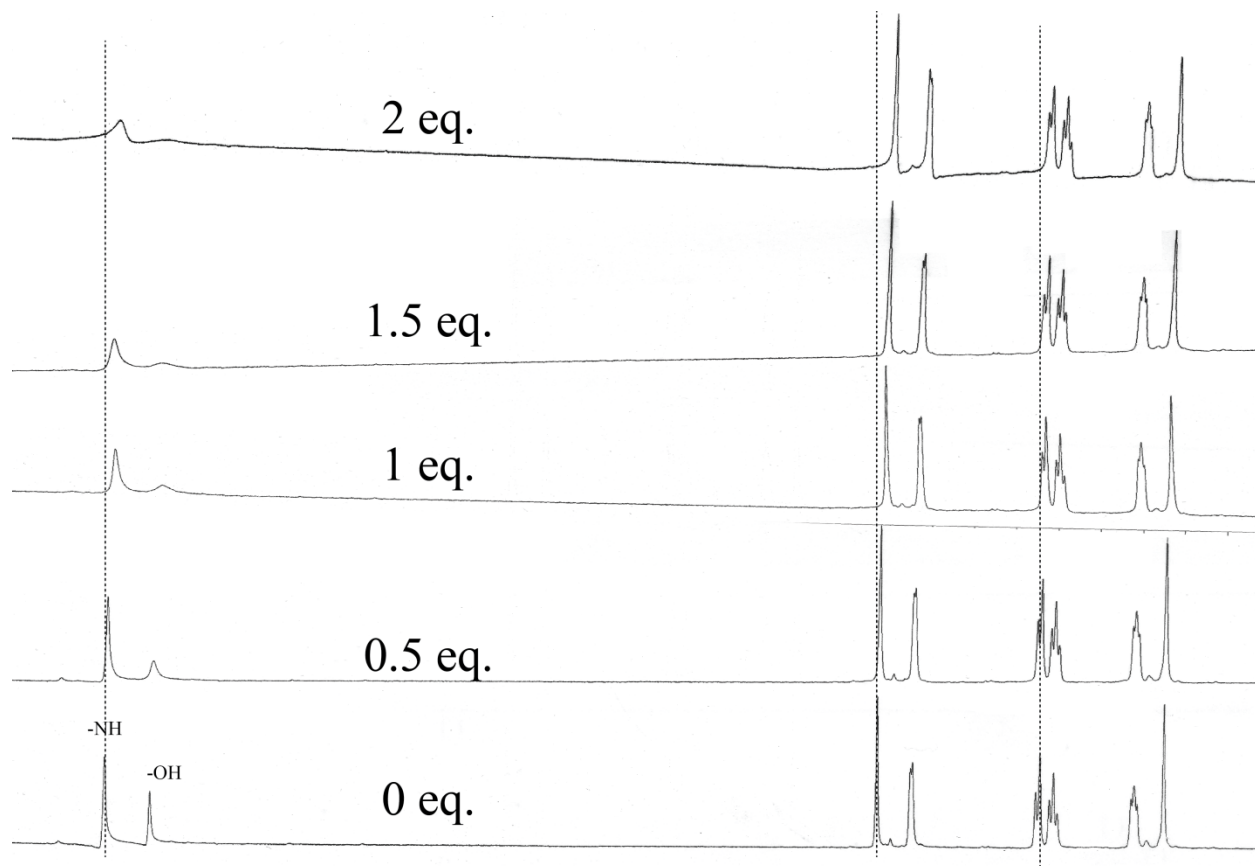


Fig. S14: ^1H -NMR titration of L_1 with Zn^{2+} in DMSO-d_6 .

Cytotoxicity assay for L_1 and L_1 -Zn complex

A standard MTT assay was performed to determine the cytotoxic effect of L_1 and L_1 -Zn complex on HeLa cells. MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) solution was procured from Sigma-Aldrich, USA. Initially HeLa cells were grown in 25 cm² tissue culture flask in Dulbecco's modified Eagle medium (DMEM) supplemented with 10% (v/v) fetal bovine serum (FBS), penicillin (100g/mL) and streptomycin (100μg/mL) at 37°C in a CO₂ incubator. Prior to MTT assay, cells were seeded onto 96-well tissue culture plates (approximately 10⁴ cells per well) and incubated with various concentrations of compound L_1 and L_1 -Zn complex (5.0μM, 12.5μM, 15μM, 25μM and 50μM) made in DMEM for a period of 24h. HeLa cells treated with DMSO or Zn(ClO₄)₂ alone were also included in parallel sets. Following 24 h incubation, the growth media was carefully aspirated and fresh DMEM containing MTT solution was added to the cells and incubated for 3–4 h at 37°C. Subsequently, the MTT solution was removed and the insoluble colored formazan product was solubilized in DMSO and its absorbance was measured in a microtitre plate reader (Infinite M200, TECAN, Switzerland) at 550 nm. MTT assay for every sample was performed in six sets. Data analysis and calculation of standard deviation was performed with Microsoft Excel 2010 (Microsoft Corporation, USA).

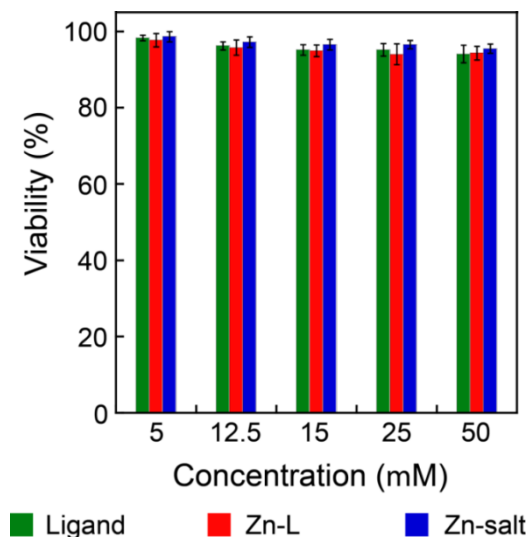


Fig. S15: MTT assay to determine the cytotoxic effect of compound L_1 and L_1 -Zn complex on HeLa cells.

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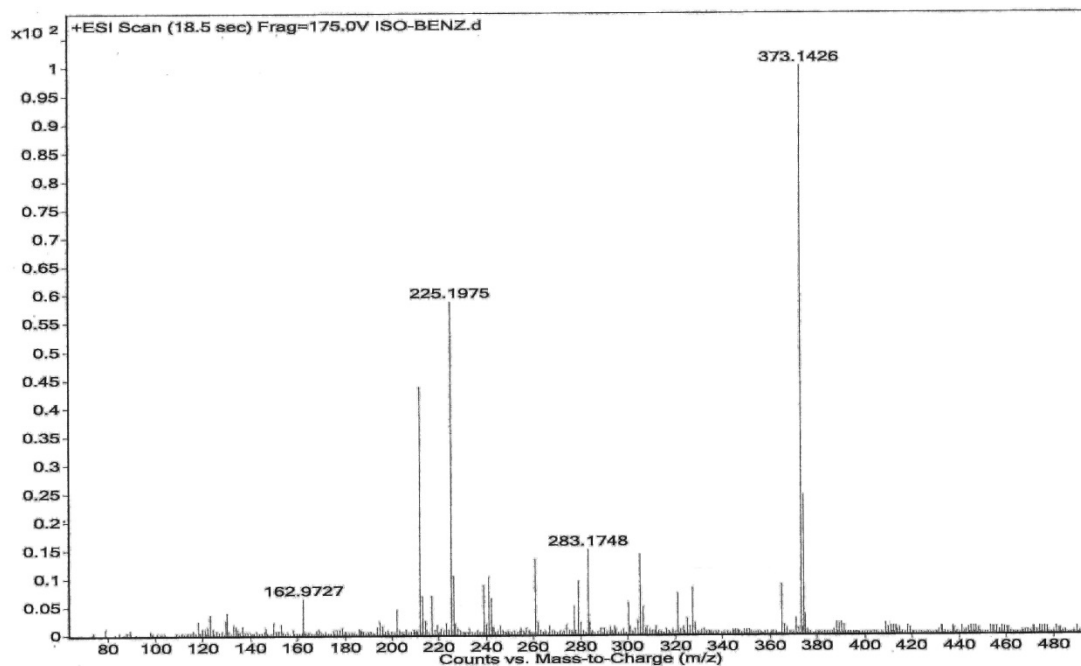


Fig. S16: Mass spectrum of L_2 (positive mode), Expected m/z for $C_{20}H_{17}N_6O_2$ (L_2+H)⁺ = 373.1413, Found 373.1426.

Table S1. Selected orbitals and their energies for **L₁** at B3LYP/6-31G(d,p).

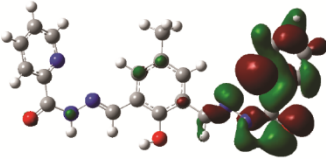
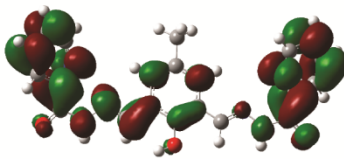
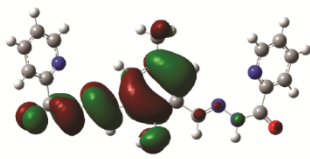
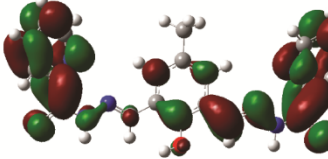
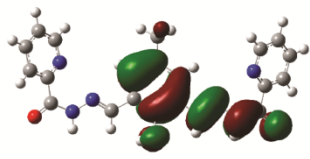
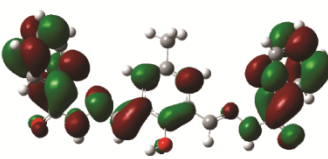
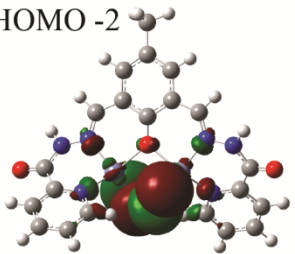
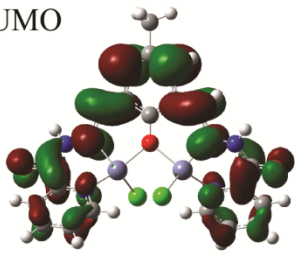
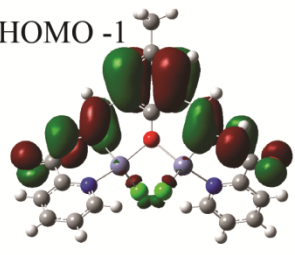
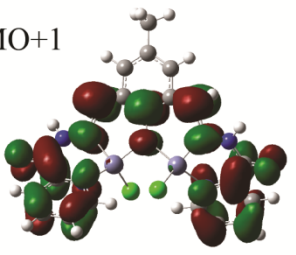
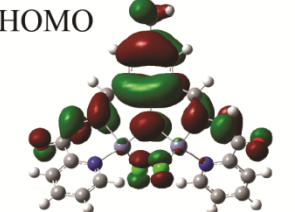
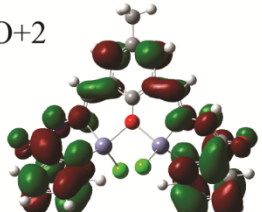
Occupied Orbitals	Energy (eV)	Vacant Orbitals	Energy (eV)
HOMO -2 	-6.6684	LUMO 	-1.7665
HOMO -1 	-5.9307	LUMO+1 	-1.4209
HOMO 	-5.7751	LUMO+2 	-1.1535

Table S2. Selected orbitals and their energies for L_1 -Zn²⁺ complex at B3LYP/6-31G(d,p).

Occupied Orbitals	Energy (eV)	Vacant Orbitals	Energy (eV)
 HOMO -2	-9.9906	 LUMO	-5.3925
 HOMO -1	-9.5457	 LUMO+1	-5.1796
 HOMO	-9.0872	 LUMO+2	-4.7617

Reference:

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, 2004.