Electronic Supplementary Material (ESI) for RSC Advances.

Pyridine-Pyrazole Based Al(III) 'Turn on' Sensor for MCF7 Cancer Cell Imaging And Detection of Picric Acid

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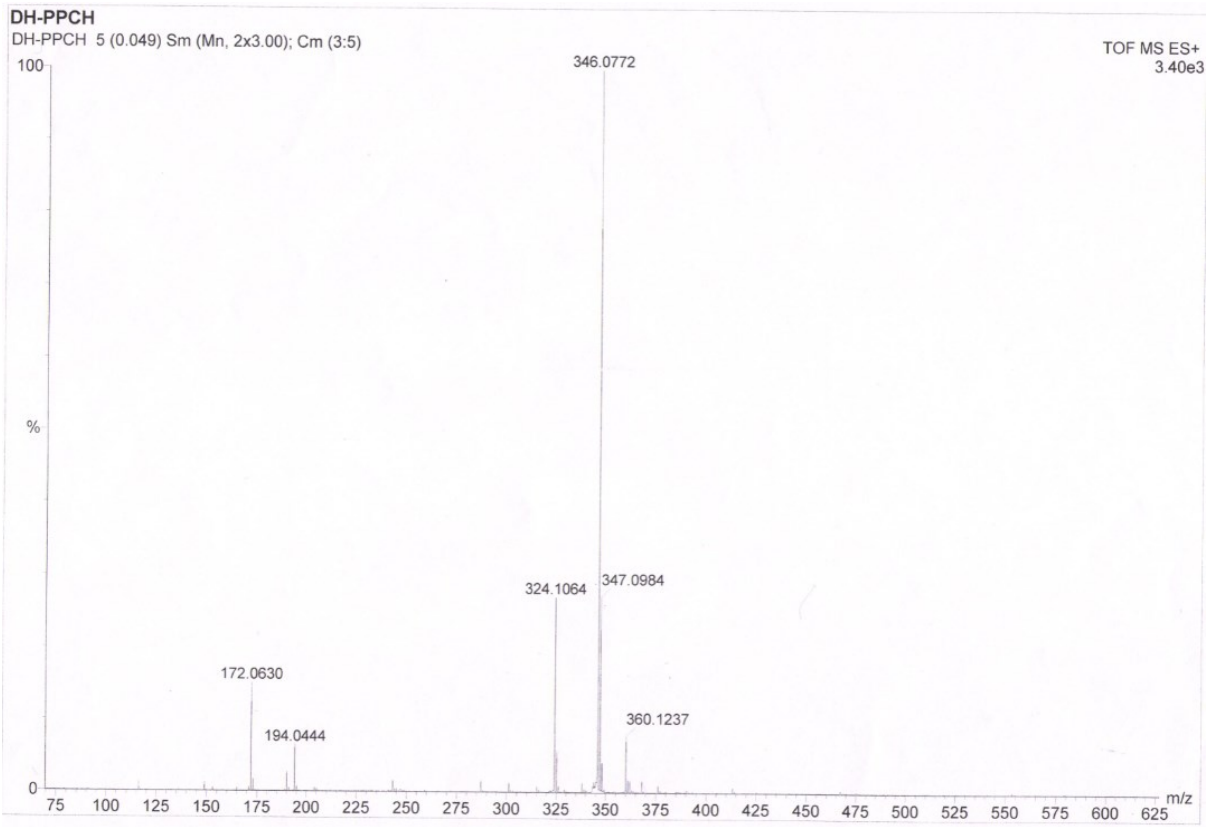


Fig. S1: Mass spectrum of free ligand.

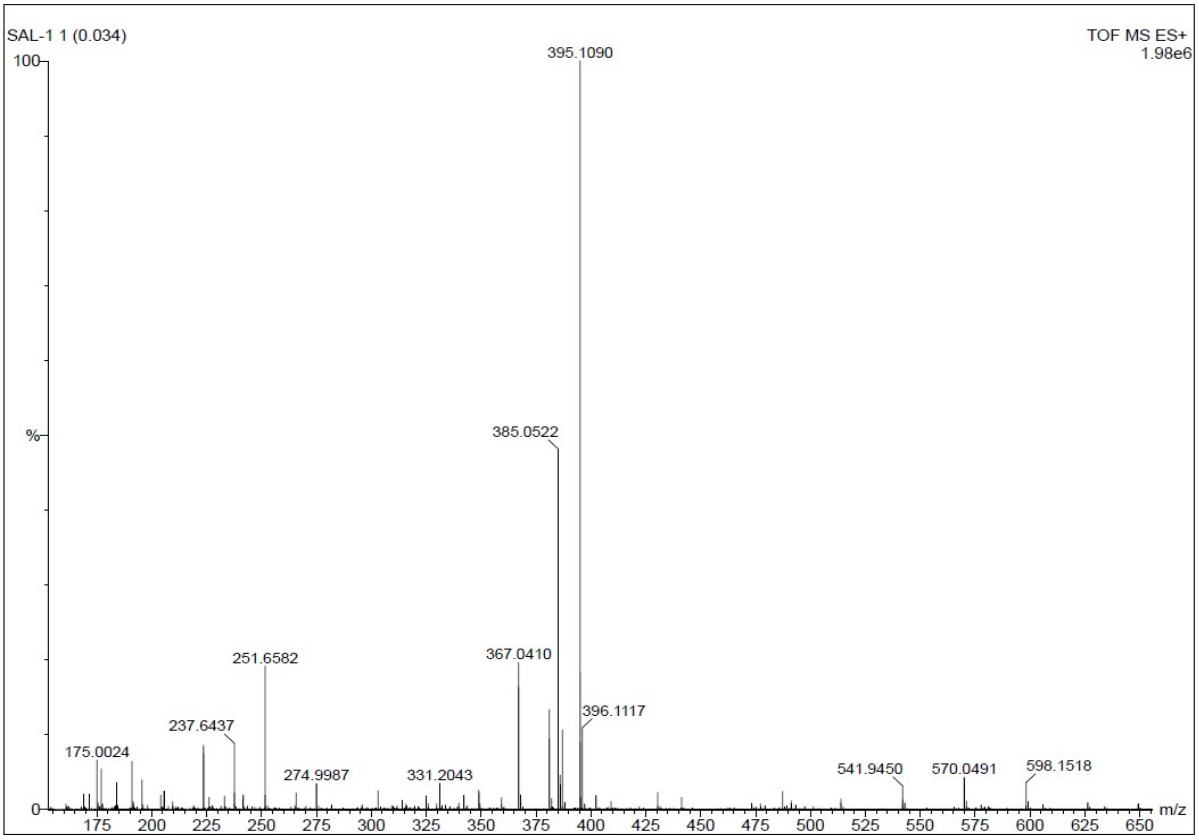


Fig. S2: Mass spectrum of metal complex.

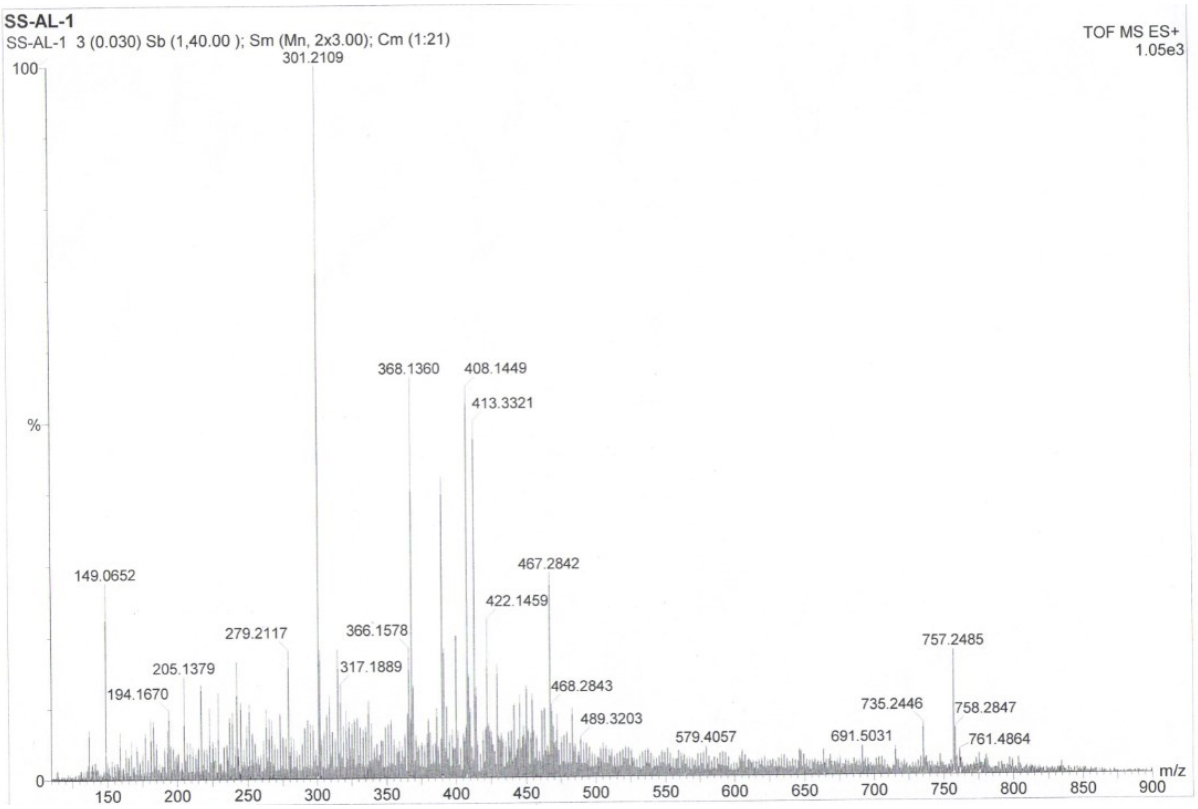


Fig. S3: Mass spectrum of complex.

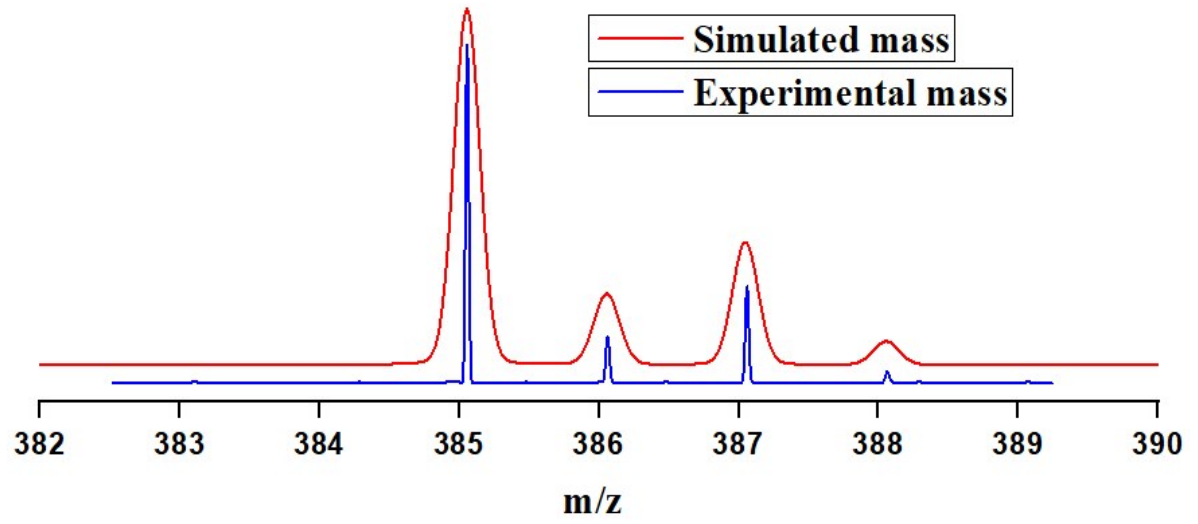


Fig. S4: The isotopic distribution of the complex.

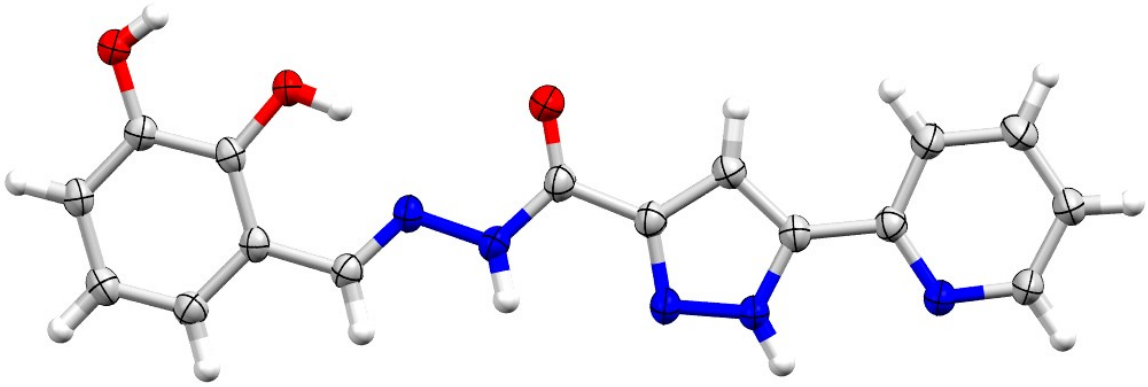
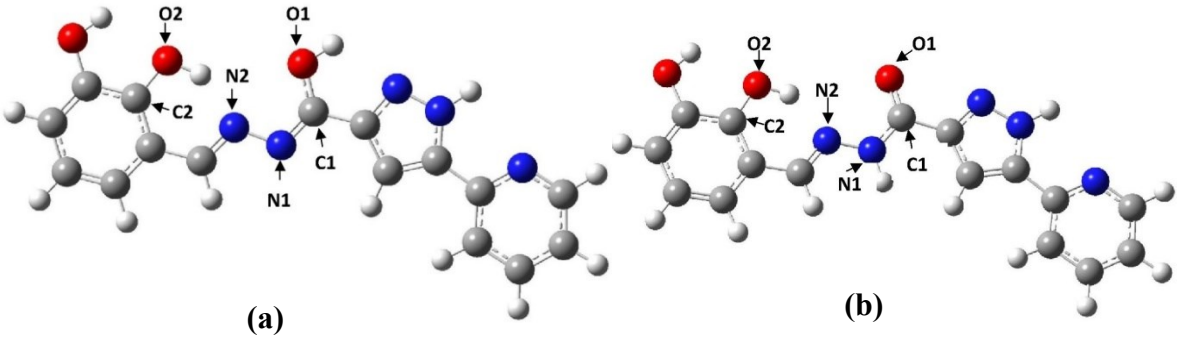
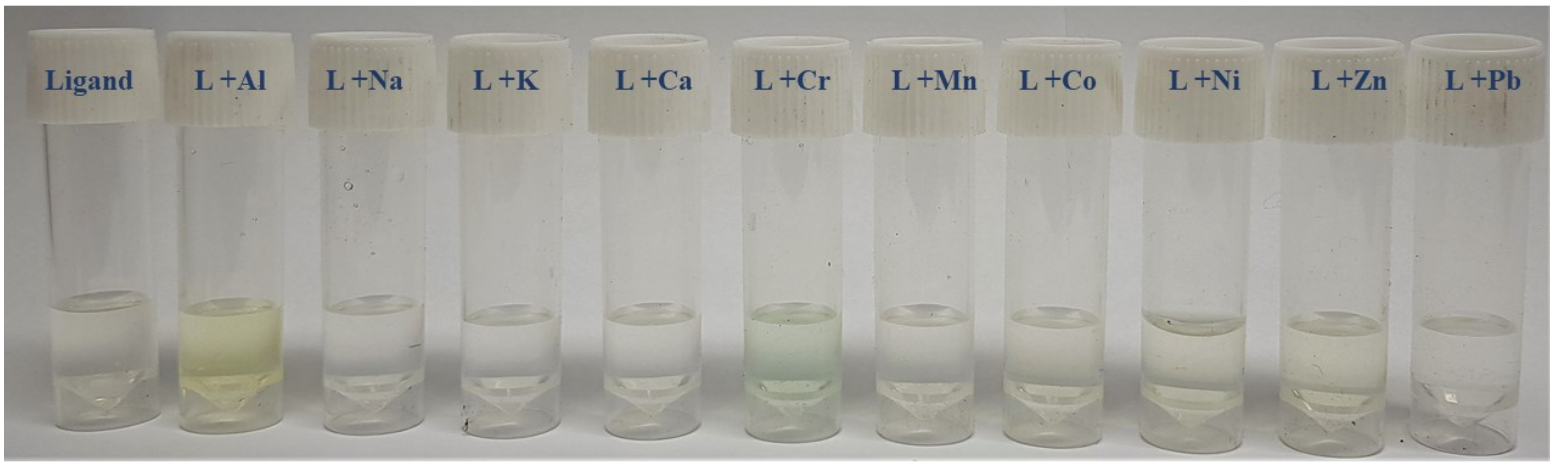


Fig. S5: Molecular structures of H_2DPC with probability thermal ellipsoids.

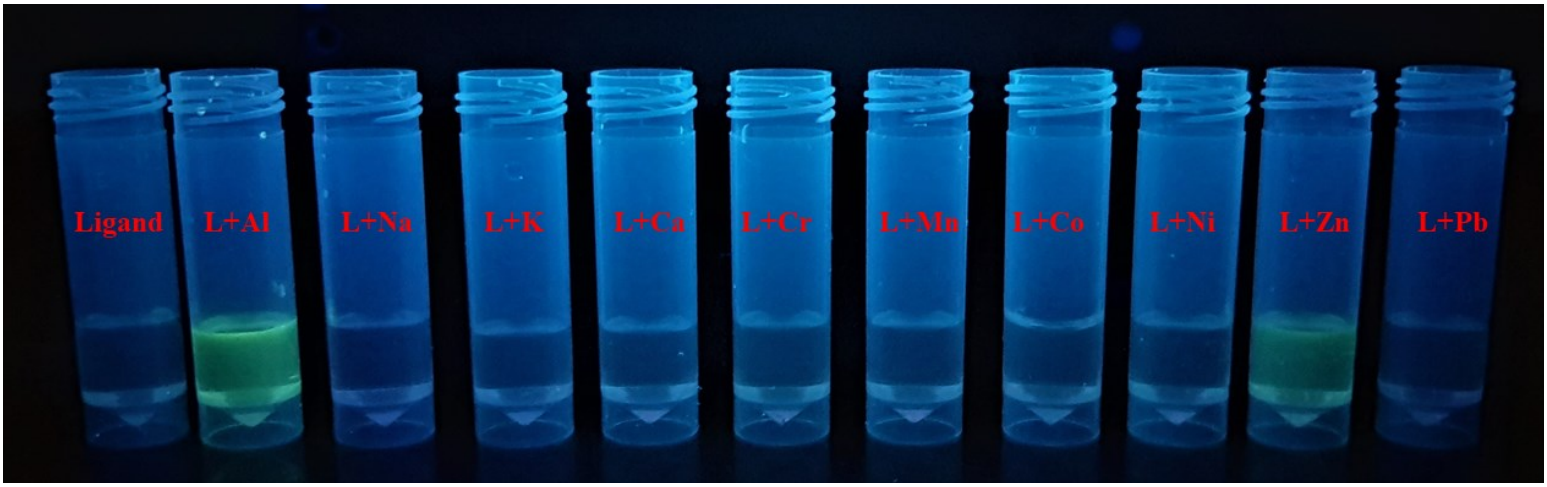


(a) **(b)**

Fig. S6: Optimized geometry of (a) enol-H_2DPC and (b) keto-H_2DPC.



(a)



(b)

Fig. S7: Images of ligand solution and mixture of different ligand-metal solutions under (a) visible light and (b) UV light (365 nm).

Binding Constant Evaluation

The binding constant of the ligand metal complex was calculated by using the Benesi-Hildebrand (B-H) plot (equation (1))

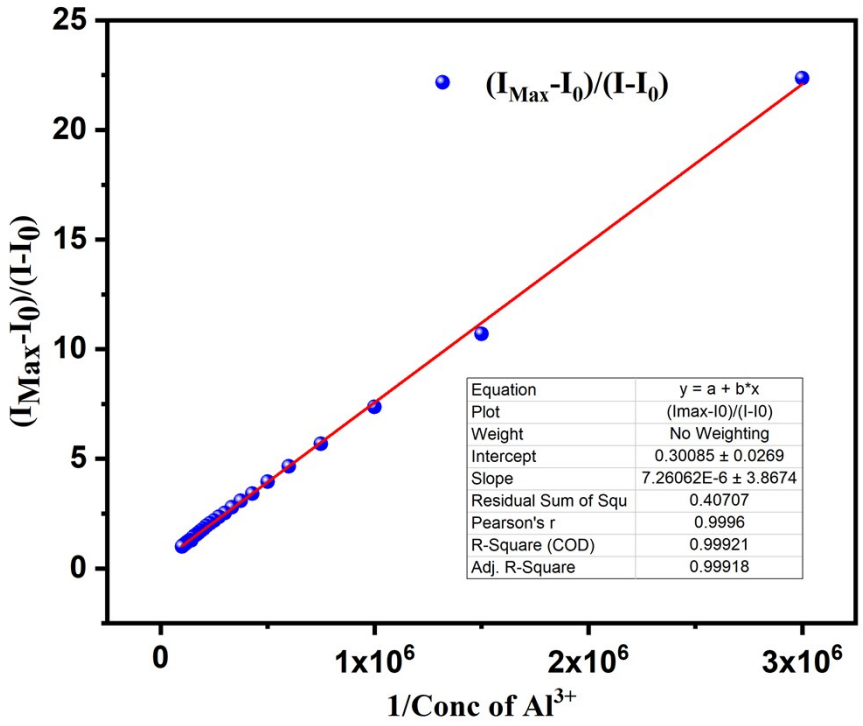
$$1/(I-I_0) = 1/\{K(I_{max}-I_0)[Al^{3+}]\} + 1/(I_{max}-I_0) \quad (1)$$

I_0 is the emission intensity of ligand individually observed at 504 nm, I is the observed emission intensity at 504 nm in thepresence of aluminium ions, $[Al^{3+}]$, I_{max} is the maximum value of emission intensity that was obtained at 504 nm during titration with changing Al^{3+} ionconcentration, K is the binding constant (M^{-1}) andcalculated from the slope of the linear plot.The binding constant was also calculated from the absorptiontitration experiment using the Benesi-Hildebrand (B-H) plot(equation (2))

$$1/(A-A_0) = 1/\{K_a(A_{max}-A_0)[Al^{3+}]\} + 1/(A_{max}-A_0) \quad (2)$$

where, A_0 and A are the absorbances of L in the absence andpresence of Al^{3+} ionsrespectively and A_{max} is the saturatedabsorbance of L in the presence of Al^{3+} ions and K_a is the binding

constant and the values come for K_a from PL study is 1.37×10^5 and from the UV study the



value is 3.50×10^5

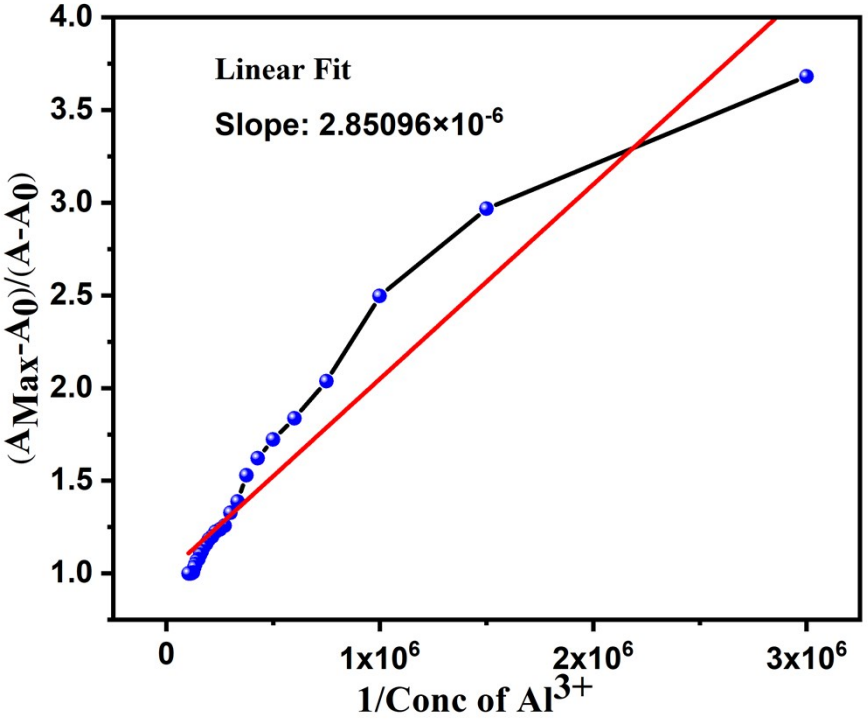


Fig. S8: Plots for determination of binding constant from (a) PL data (b) UV-Vis data.

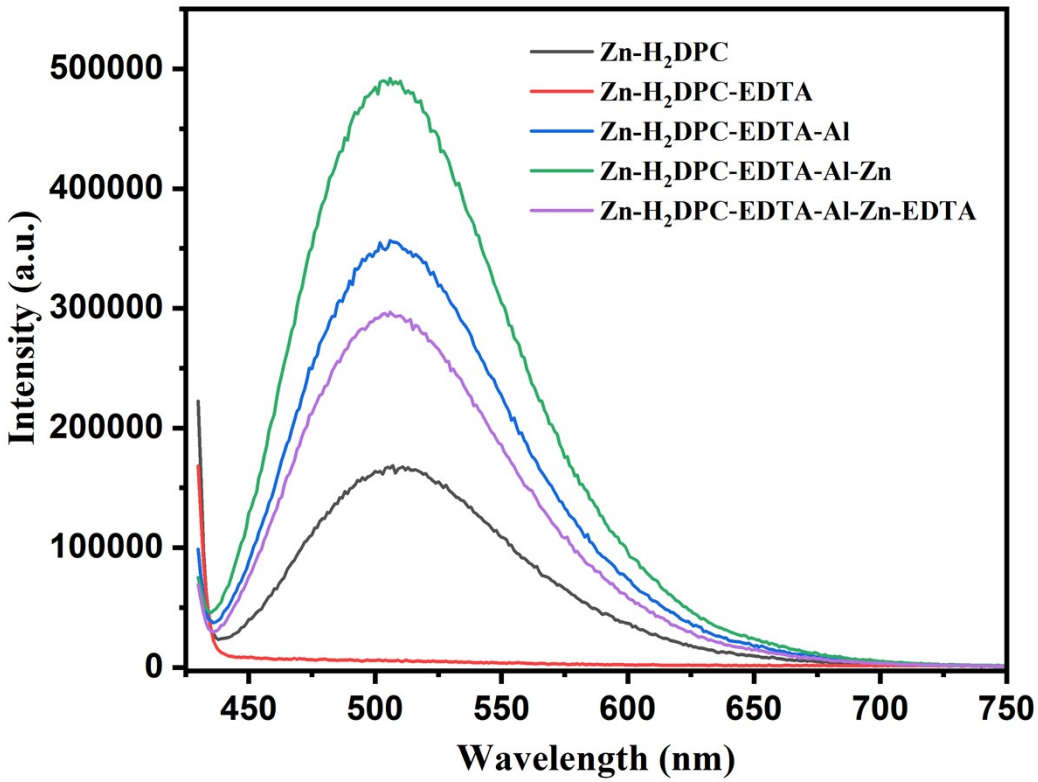


Fig. S9: Step by step addition of EDTA to Zn-H_2DPC complex to eliminate the participation of Zn^{2+} ion in presence of Al^{3+}.

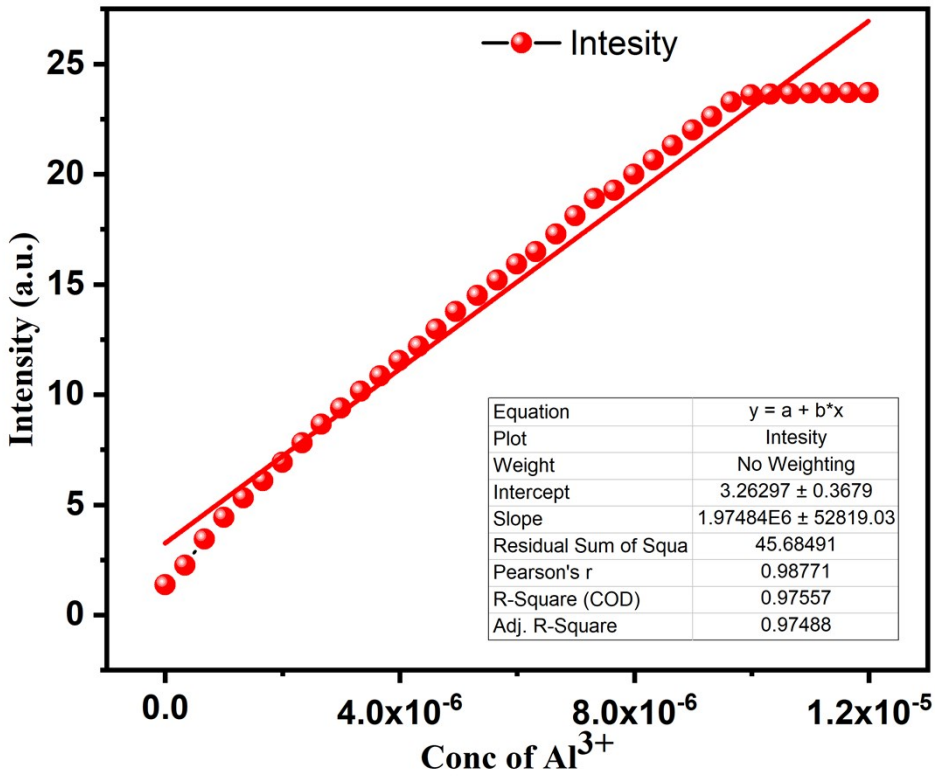
Limit of Detection

On the basis of fluorescence titration experiment the limit of detection was calculated at 503 nm. The fluorescence spectrum of L-Metal complex at the saturation point was measured 8 times to calculate the standard deviation. And to gain the slope the intensity was measured by adding 0.5µL of 1.5 molar aqueous aluminium solution into the DMSO solution of ligand repeatedly and plotted the corresponding intensity with respect to the conc. of aluminium salt.

The detection limit was then calculated by making use of the following equation

$$\textbf{Detection limit} = 3\sigma/k$$

where, σ is the standard deviation of blank measurement, and k is the slope in the plot of



fluorescence emission intensity versus respective analyte concentration for our ligand metal system the standard deviation is 0.141902 and the value of K is 1.97484×10^{6} for our system the value of LOD is 2.1565×10^{-7}(M)

Fig. S10: Plot for the determination of limit of detection (LOD).

Table S1: Comparison with few reported chemosensors of Al^{3+}

Sample Name.	Excitation(nm)/ Emission(nm)	LOD	Binding Constant (K_a) (M^{-1})	Nitro Aromatic Sensing	Cell Imaging	Ref.
N′1,N′3-bis((E)-4 −(diethylamino)-2-hydroxybenzylidene)-isophthalohydrazide (NDHIPH)	(λ_{ex} 383 nm)/ (λ_{em}485 nm)	2.53 nM	4.25×10^{12} M^{-1}	YES	NO	1
2-Quinolinecarboxylic acid, 2-[[4 (diethylamino)-2-hydroxyphenyl] methylene] hydrazide	(λ_{ex}390 nm)/ (λ_{em}480nm), (λ_{ex} 440 nm)/ (λ_{em} 590 nm)	0.104µM at 480nm, 4.17µM at 590 nm	$1.67 \times 10^5 M^{-1}$ for the 590 nm emission	NO	YES	2
5-(diethylamino)-2-(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)-Phenol	(λ_{ex}375 nm)/ (λ_{em}412nm)	0.5 nM	3.36×10^5 M^{-1}	NO	NO	3
(E)-4-(((2-hydroxynaphthalen-1-yl)methylene) amino)-N-(5-methylisoxazol-3-yl)benzenesulfonamide	(λ_{ex}360 nm)/ (λ_{em}450 nm)	33.2 nM	$1.04 + 0.01) \times10^4$ M^{-1}	NO	YES	4
1-[(8-quinolinylimino) methyl]- 2-Naphthalenol,	(λ_{ex}320 nm.)/ (λ_{em}520 nm)	1.0 µM	5.01×10^8 M^{-1}	NO	NO	5

4-(8′-hydroxyquino-lin-5′-yl)methyleneimino-1-phenyl-2,3-dimethyl-5-pyzole	**(λ_{ex}378nm.)/ (λ_{em}470 nm)**	**0.1 µM**	**log β = 6.8**	**NO**	**NO**	**6**
2-[1-(2-pyrazinyl) ethylidene] hydrazide Benzoic acid,	**(λ_{ex}390nm.)/ (λ_{em}506 nm)**	**0.1 µM**	**1.24×10^7 M^{-1}**	**NO**	**NO**	**7**
1-[[(2-pyridinylmethyl) imino]methyl]- 2-Naphthalenol,	**(λ_{ex}355nm,)/ (λ_{em}432 nm,370 nm)**	**0.648 mM**	**1×10^5 M^{-1}**	**NO**	**NO**	**8**
[4-amino-3-[[(2-hydroxyphenyl) methylene]amino] phenyl]phenyl-Methanone	**(λ_{ex}334nm.)/ (λ_{em}502 nm)**	**8.12 µM**	**1×10^4 M^{-1}**	**NO**	**NO**	**9**
NPRB.	**(λ_{ex}490nm.)/ (λ_{em}578 nm)**	**0.3 µM**		**NO**	**YES**	**10**
(E)-N'-(2,3-dihydroxybenzylidene)-3-(pyridin-2-yl)-1H-pyrazole-5-carbohydrazide (H_2DPC)	**(λ_{ex}417 nm)/ (λ_{em}504 nm)**	**0.215µM**	**1.37×10^5 M^{-1}**	**YES**	**YES**	**Our result**

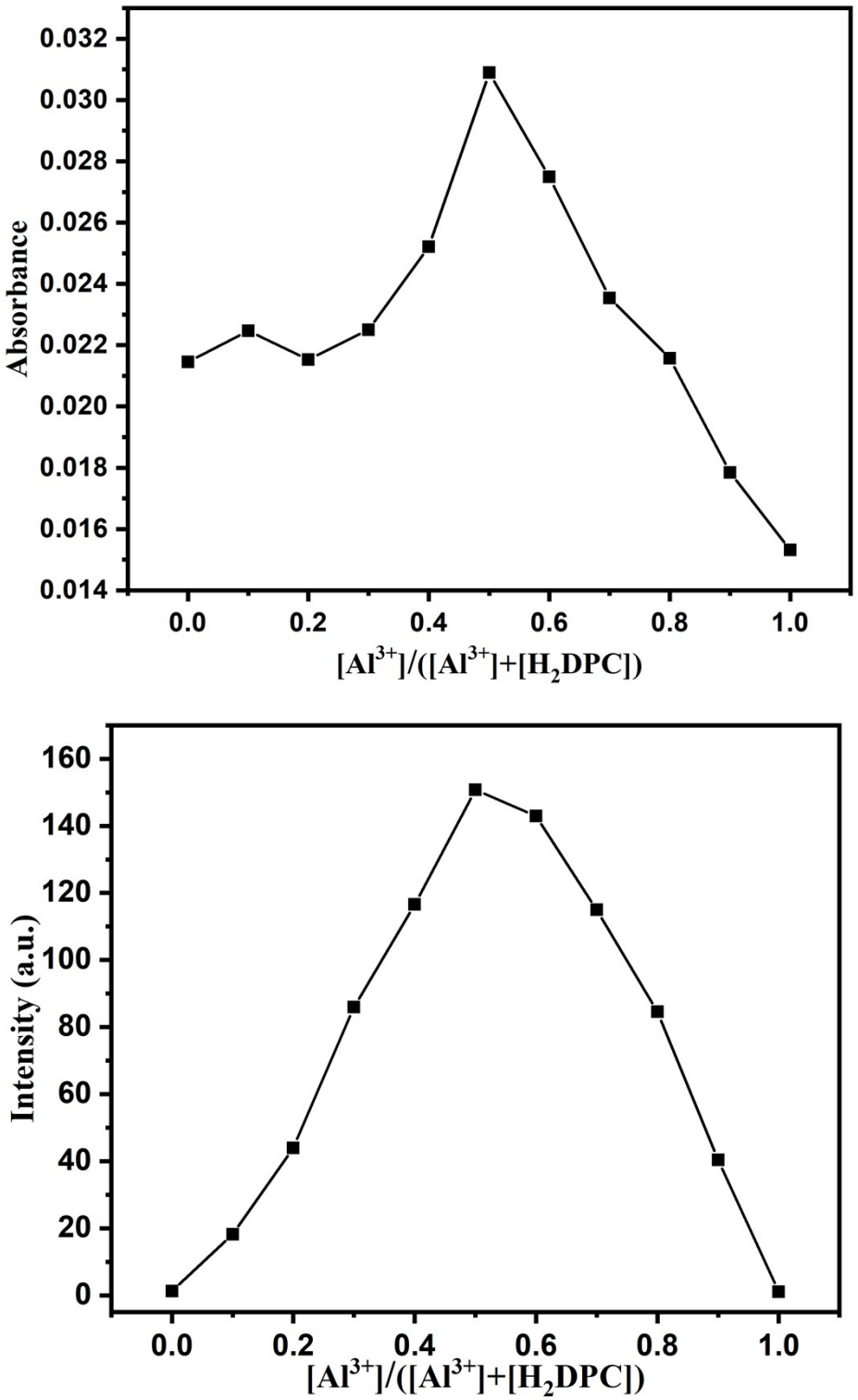
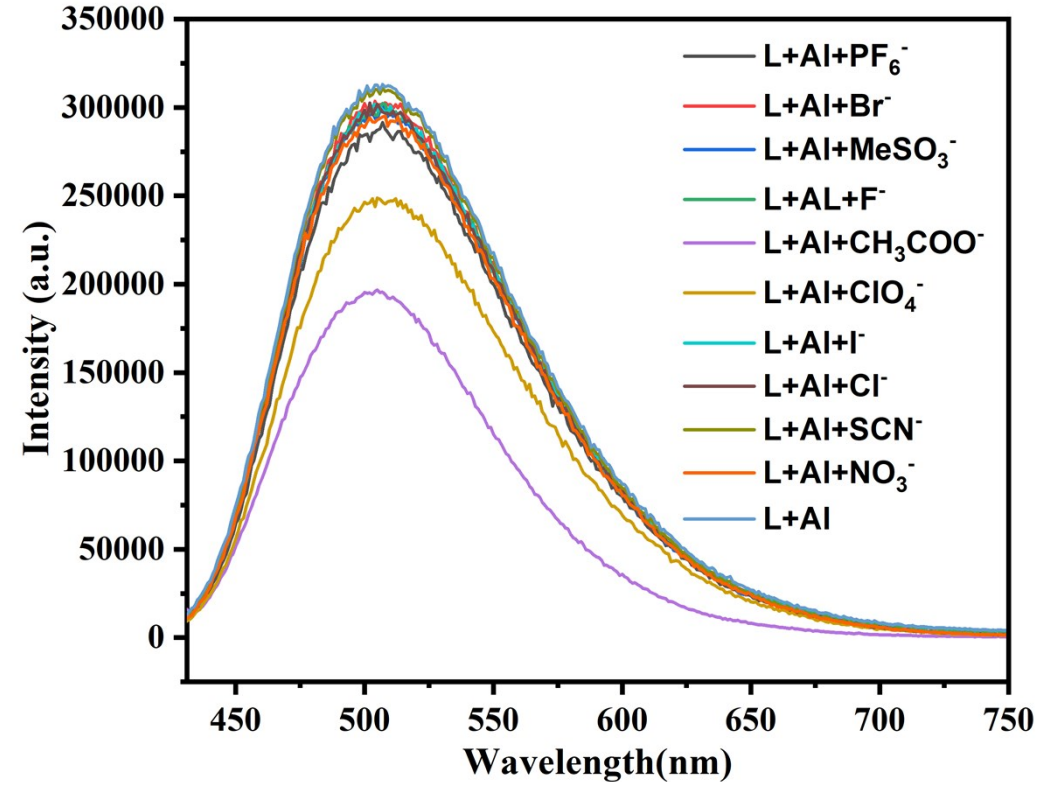


Fig. S11: Jobs plot from (a) UV-Vis data and (b) PL data.



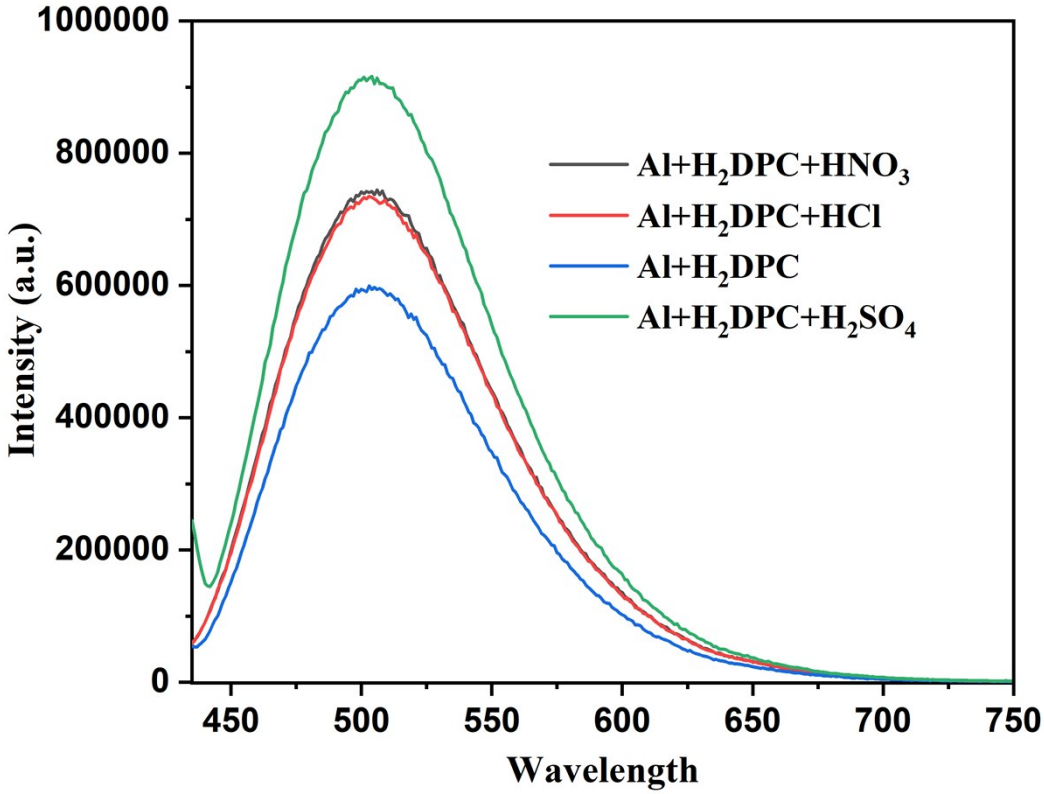


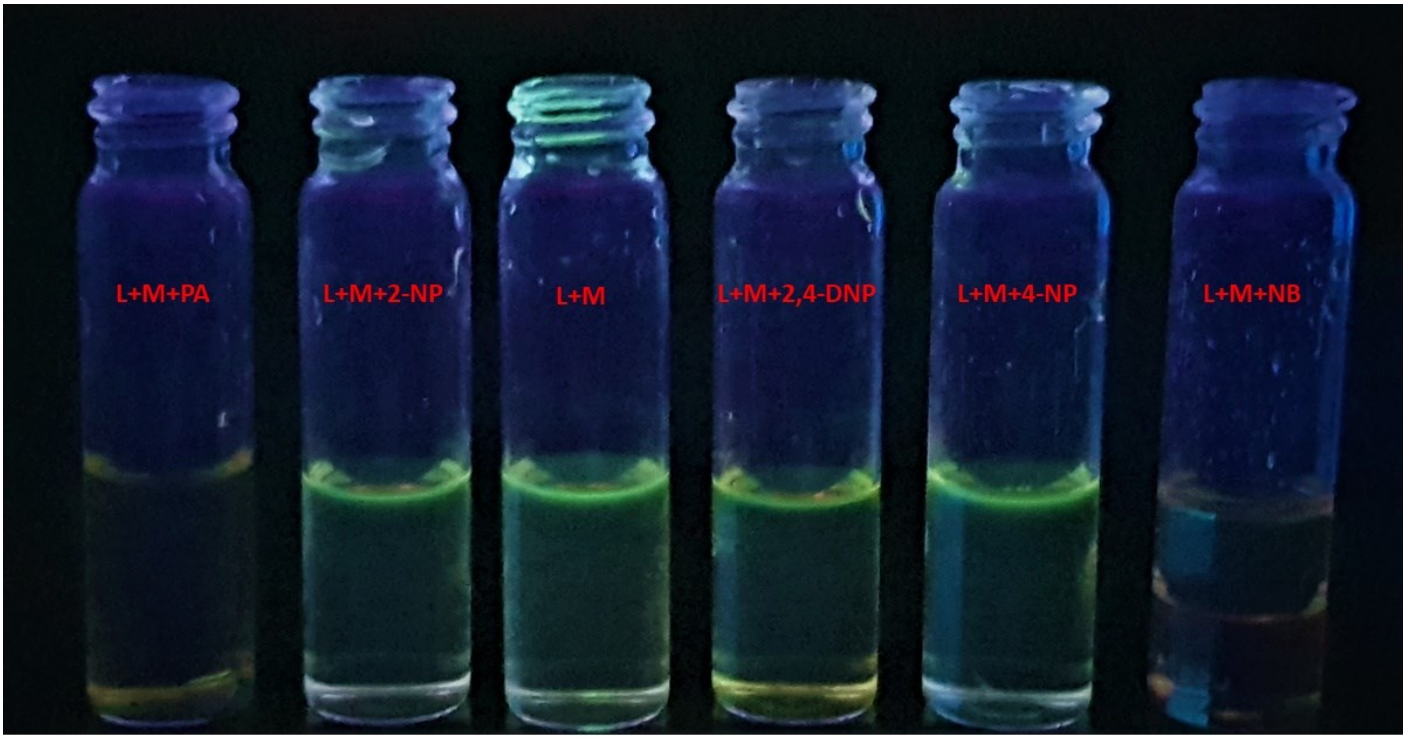
Fig. S12: PL spectra of Al-H_2DPC complex in presence of various counter anion.

Fig. S13: PL spectra of Al-H_2DPC complex in presence of inorganic acids.

Table S2: Selected bond lengths from theoretical calculations

Molecule	O1-C1	C1-N1	N1-N2	O2-C2	Al-O2	Al-O1	Al-Cl
keto-DHPCH	1.23	1.37	1.36	1.35	-	-	-
enol-DHPCH	1.34	1.28	1.38	1.35	-	-	-
Al-DHPCH	1.31	1.31	1.39	1.34	1.80	1.85	2.22

(a)



(b)

Fig. S14: Images of ligand-Al^{3+} solution and mixture of ligand-Al^{3+}-nitroaromatics solutions under (a) visible light and (b) UV light.

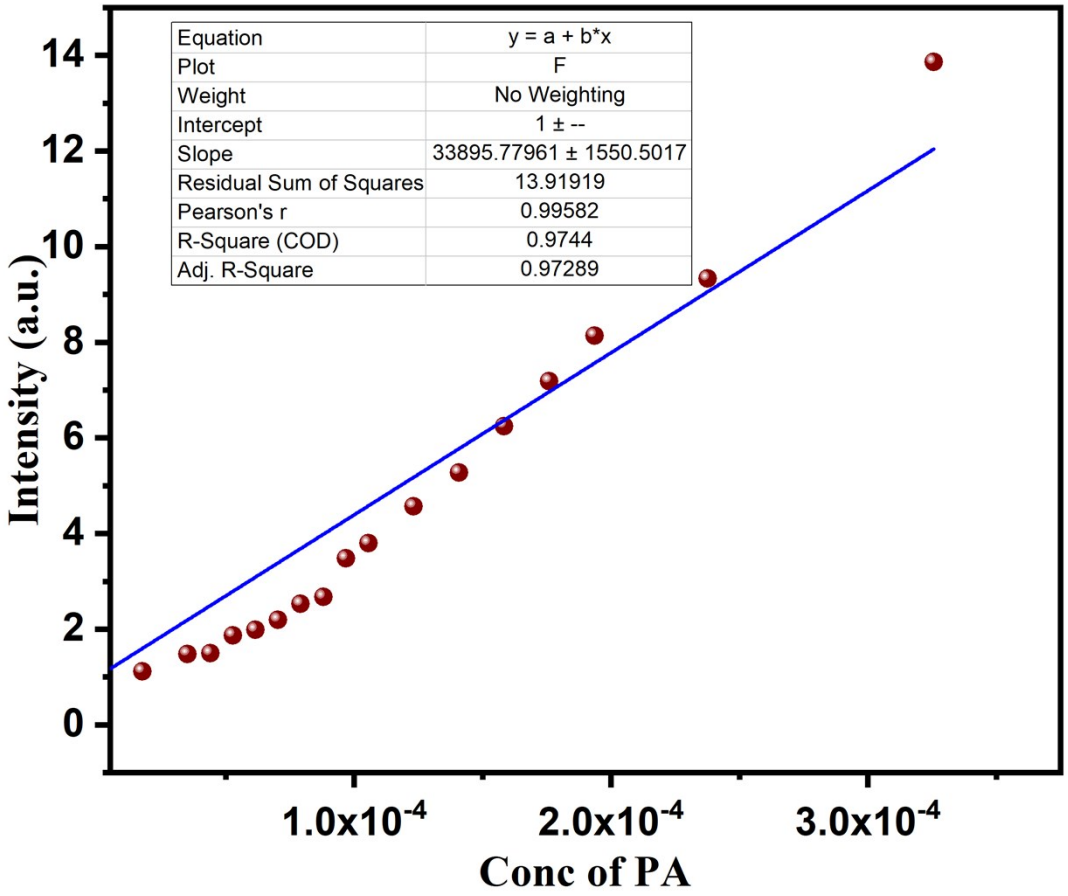


Fig. S15: Limit of detection (LOD) for picric acid.

Detection limit = 3σ/k Standard deviation=1.384999, Slope =33895.77

LOD =1.2257×10^{-4}(M)

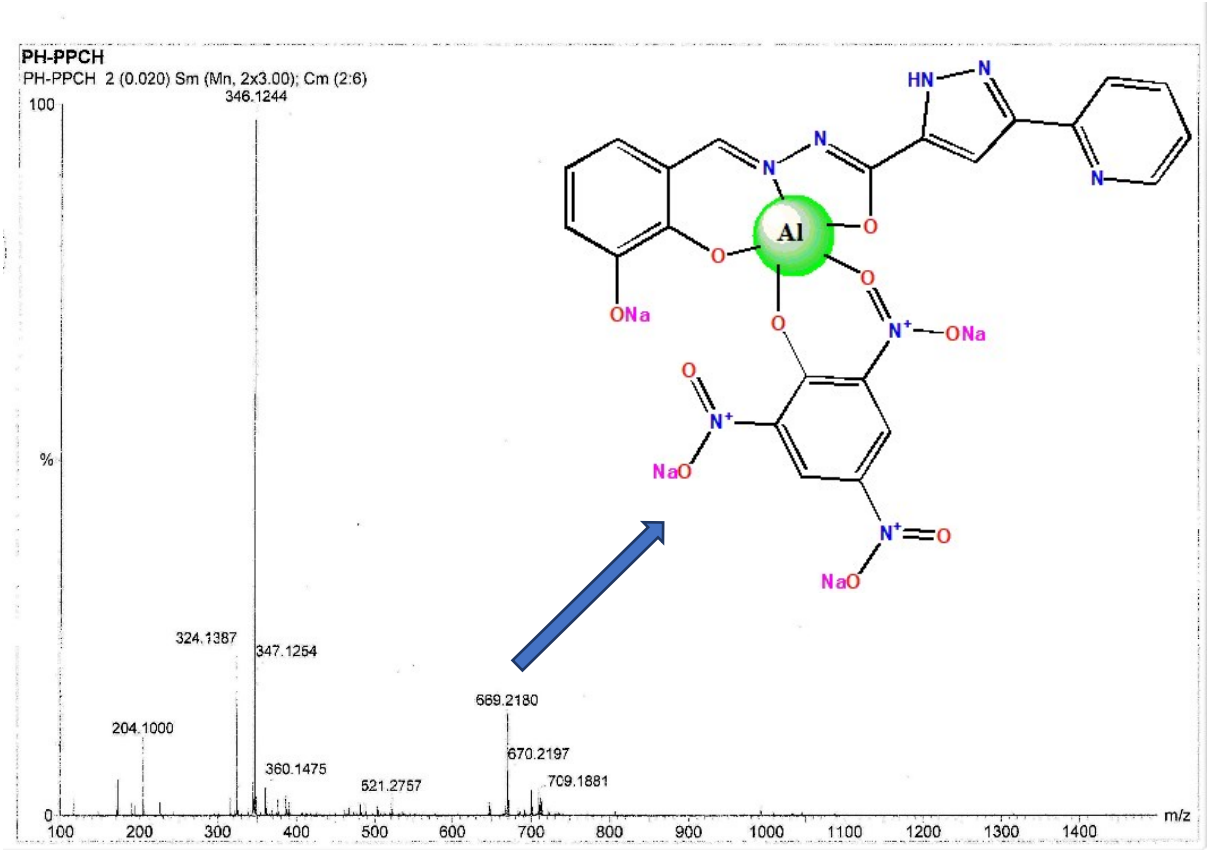


Fig. S16: Mass spectrum of metal complex with picric acid.

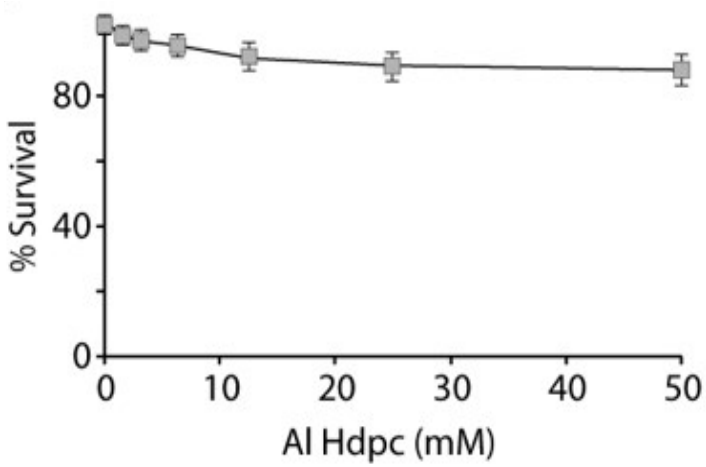
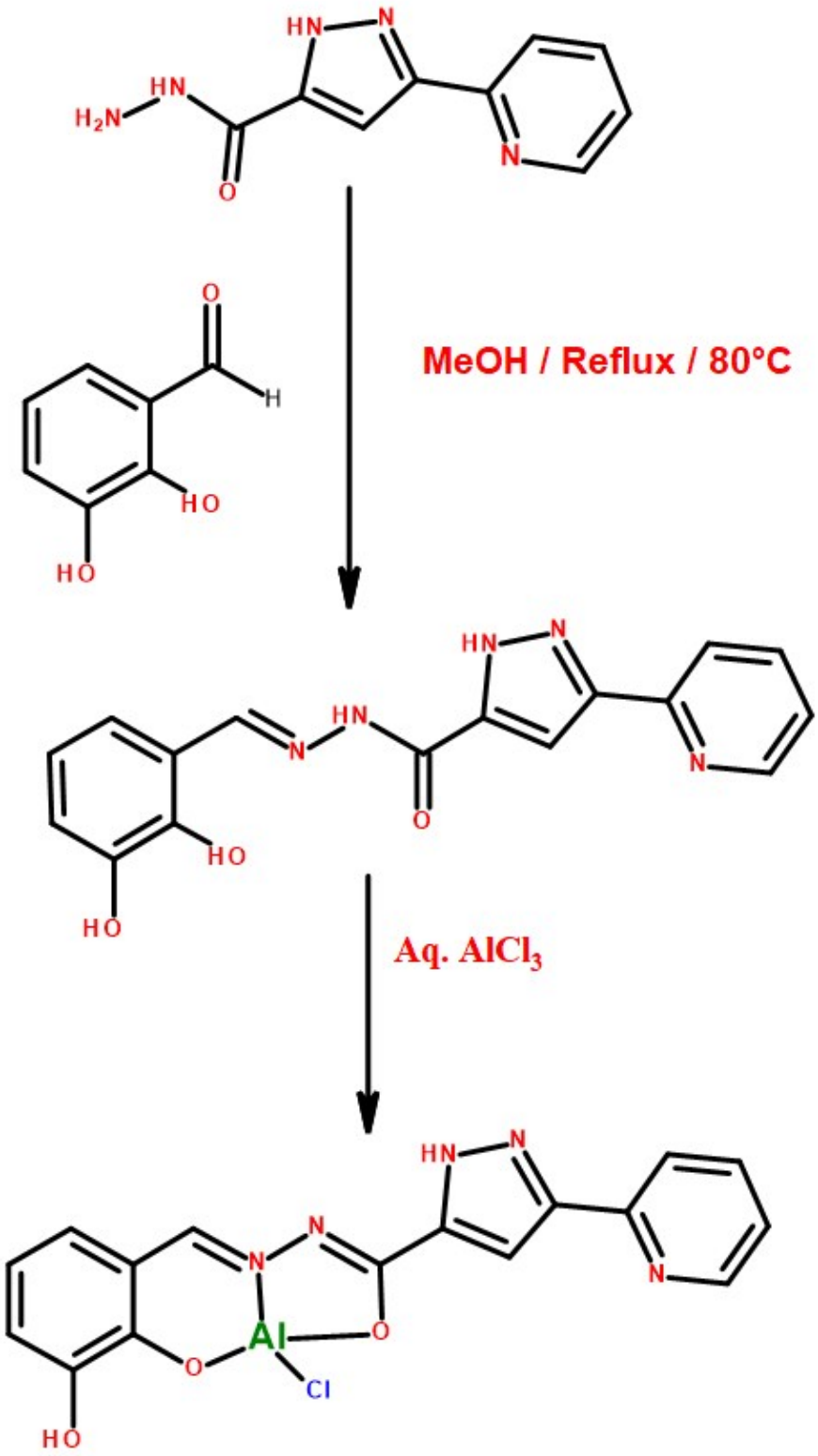


Fig. S17: Cell survival assay with compounds H_2DPC-Al reveals no apparent cytotoxicity. Survival curves of MCF7 cells treated with H_2DPC-Al for 72 hrs. Cell viability was determined by MTT assays. Errors bars represent standard deviation (n≥3).



Scheme S1: Schematic diagram of synthetic procedure.

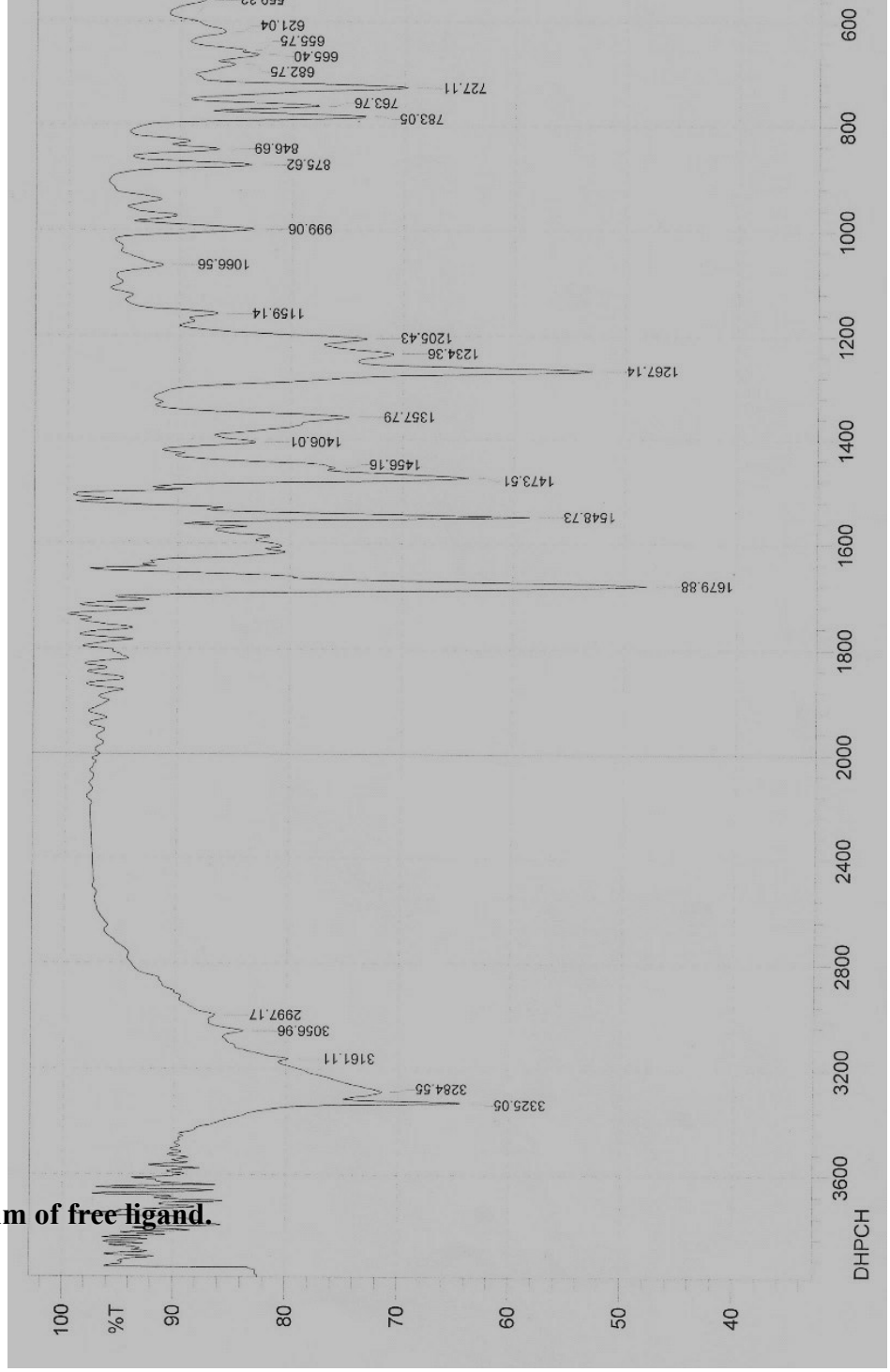


Fig. S18: FT-IR spectrum of free ligand.

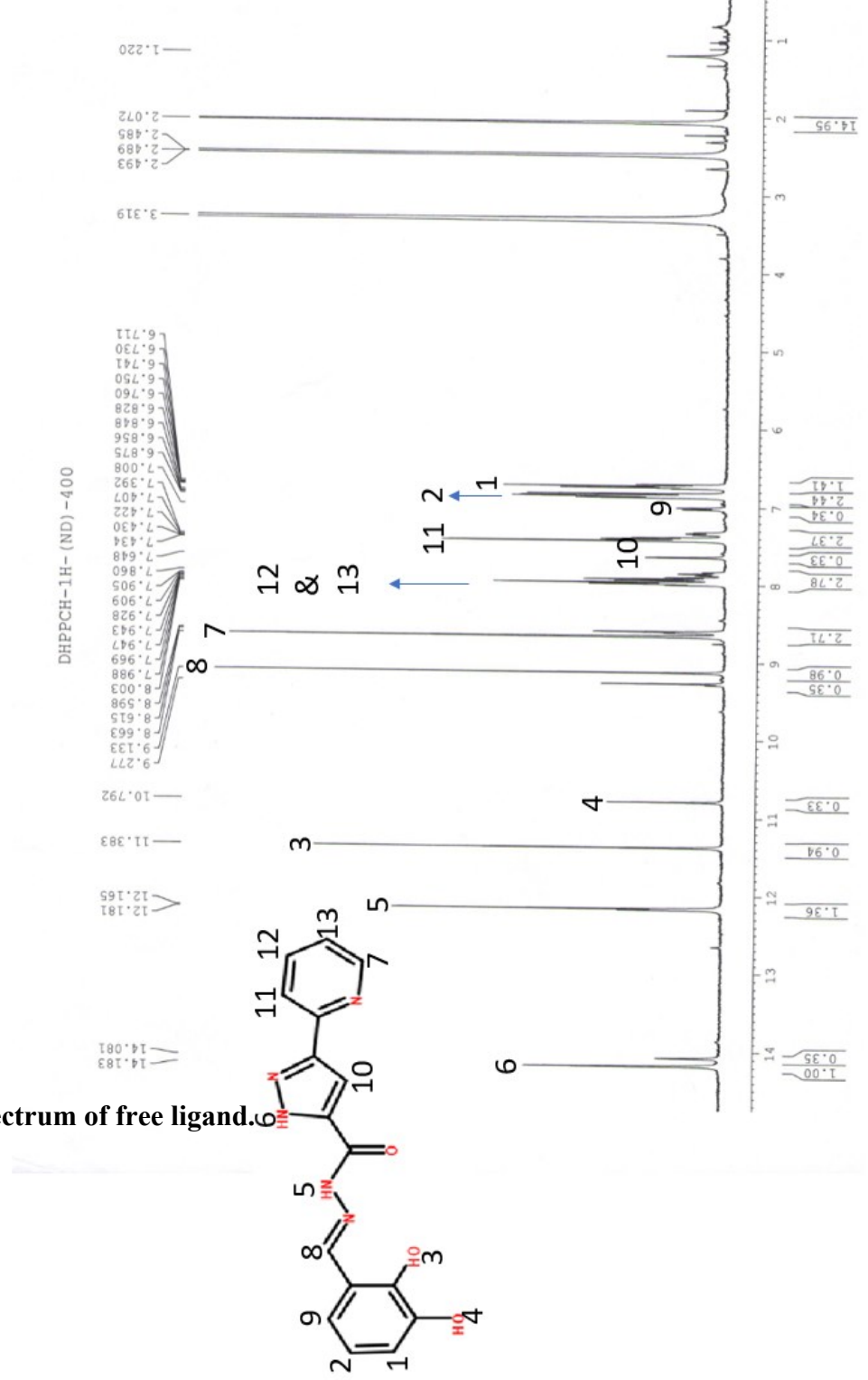


Fig. S19(a): ^{1}H NMR spectrum of free ligand.

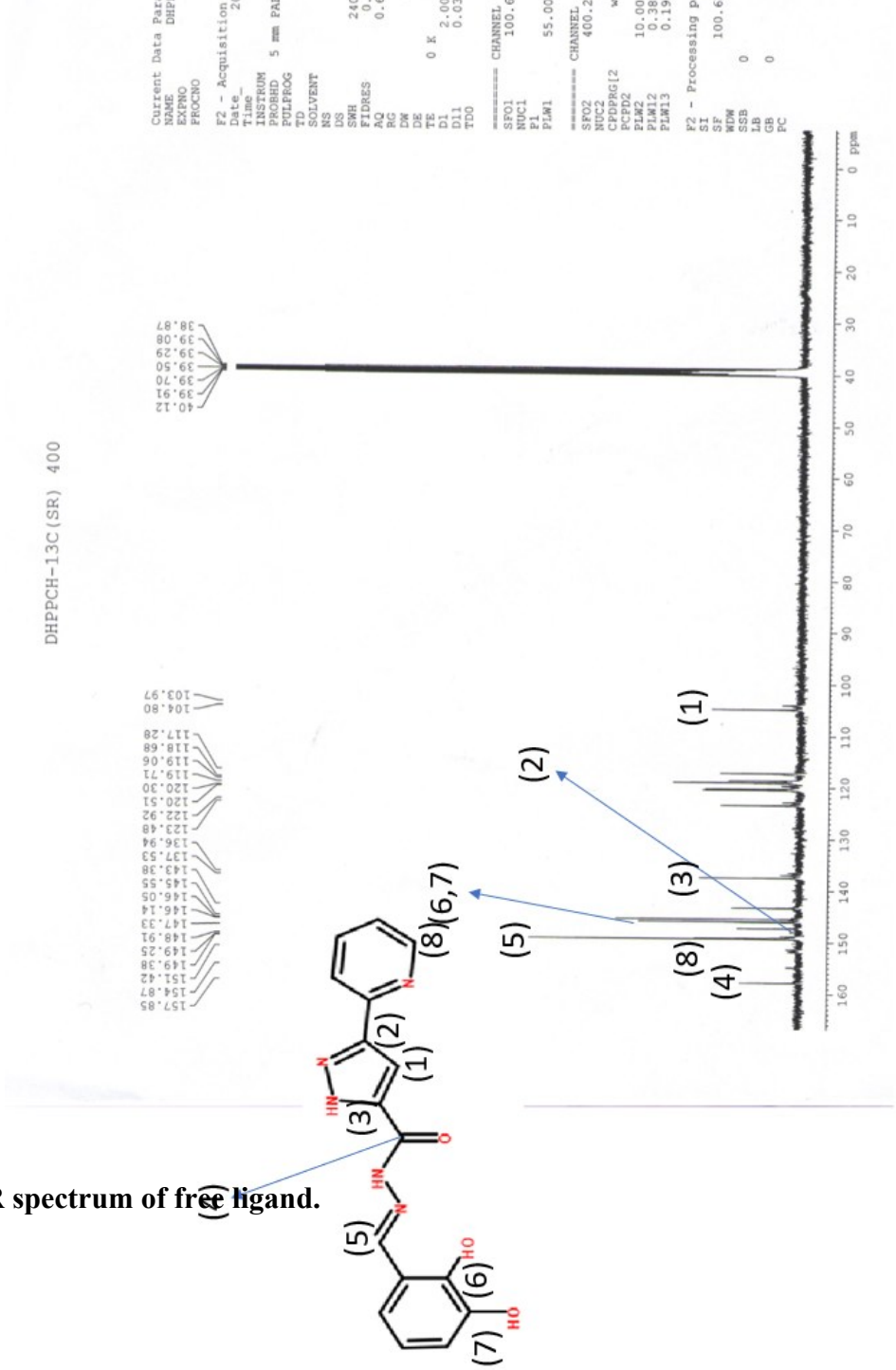


Fig. S19(b): ^{13}C NMR spectrum of free ligand.

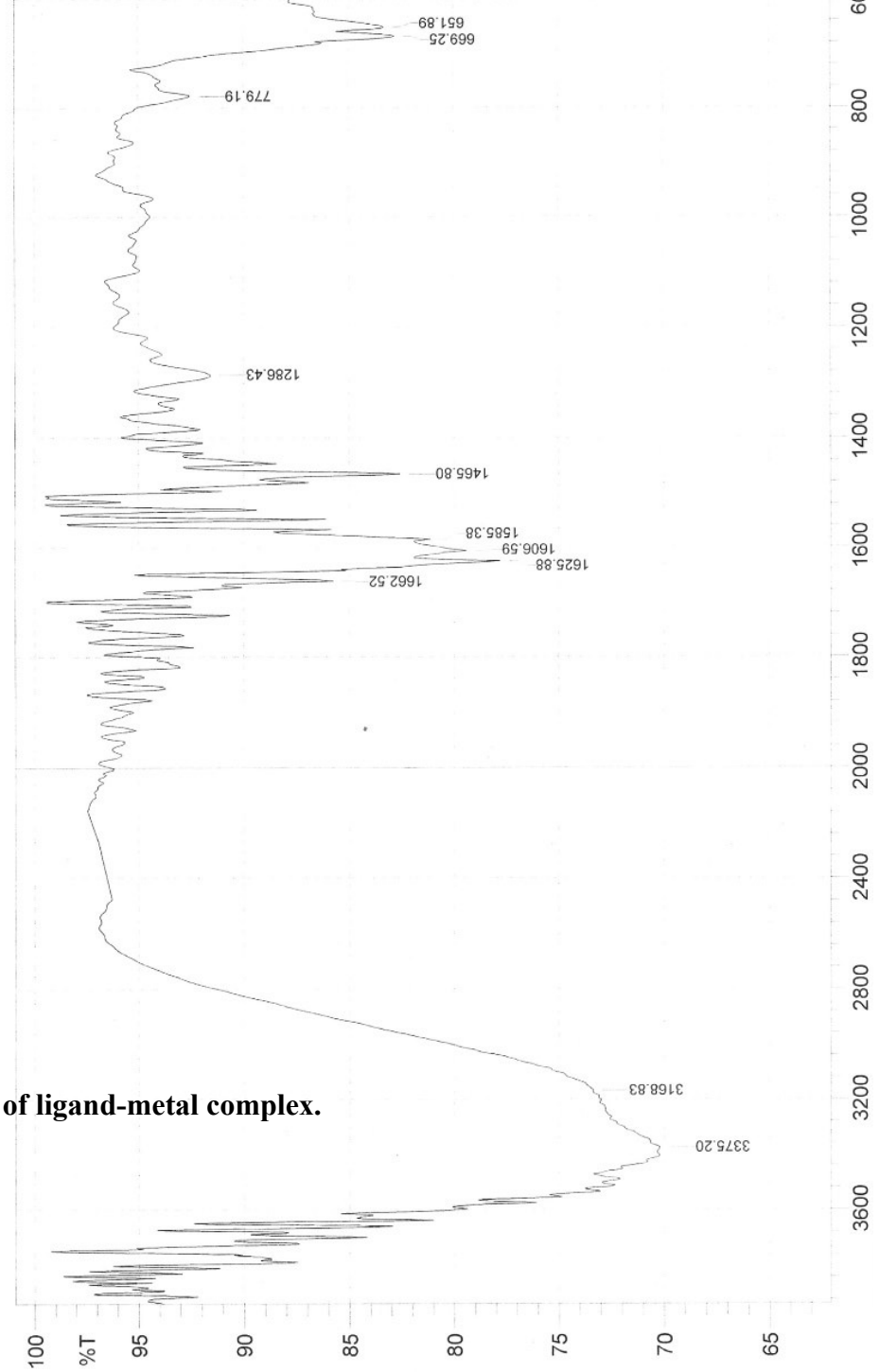


Fig. S20: FT-IR spectrum of ligand-metal complex.

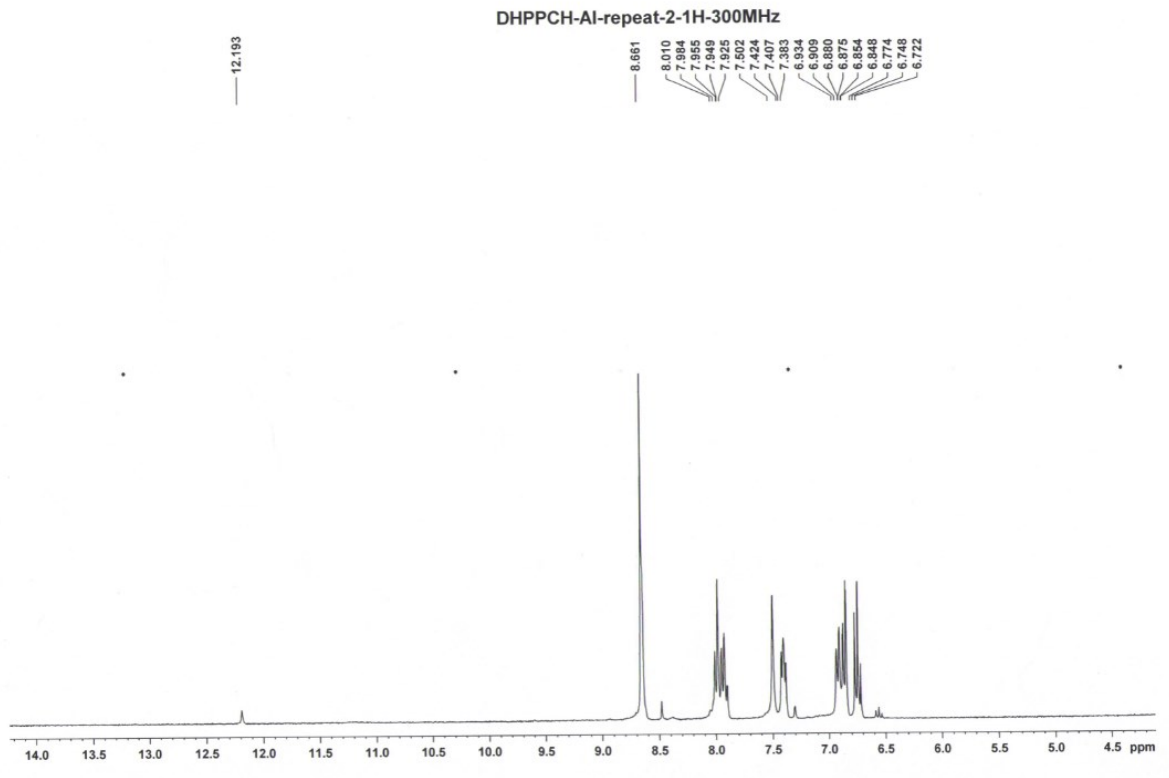


Fig. S21: ^{1}H NMR spectrum of ligand-metal complex.

Table S3: Coordinates of the molecules from theoretical studies

keto-DHPCH

C	-6.81719700	1.12258900	-0.00027600
C	-6.18043300	-0.10766700	-0.00004700
C	-4.78205000	-0.17984500	0.00015700
C	-4.02045700	0.99918900	0.00011700
C	-4.68018200	2.23927700	-0.00014900
C	-6.06389900	2.29983400	-0.00032600
H	-7.90205300	1.15154500	-0.00043200
H	-4.08762500	3.14896200	-0.00021100
H	-6.56851300	3.25981500	-0.00049700
O	-6.91874700	-1.25478900	-0.00006800
H	-6.32143100	-2.01945300	0.00036800
O	-4.24261000	-1.42328000	0.00043300
C	-2.56510000	0.96014700	0.00022800
N	-1.94101200	-0.16096000	-0.00000100
H	-2.02940400	1.91328900	0.00040900
N	-0.58029500	-0.13439300	-0.00009000
C	0.12309800	-1.30018200	0.00000900
O	-0.41826200	-2.40381100	0.00009000
H	-0.10622100	0.76377000	0.00002100
C	3.68776600	-0.40939300	-0.00000700
C	2.38193000	0.04273200	0.00006500
C	1.59812000	-1.13084500	-0.00001200
H	2.05581200	1.07195700	0.00009800
N	2.36605900	-2.22277000	-0.00009700
N	3.61180000	-1.76235300	-0.00003900
C	7.26886100	0.07333900	-0.00036700
C	7.45024700	1.45257300	-0.00003800
C	6.32206700	2.26571100	0.00033500
C	5.06513400	1.67536900	0.00036000
C	4.98364400	0.28263300	-0.00001200
N	6.06716300	-0.50706600	-0.00036400
H	6.41797200	3.34659400	0.00061000
H	8.12527900	-0.59549100	-0.00065800
H	8.45019500	1.87148000	-0.00007000
H	4.16642300	2.28164500	0.00067000
H	4.39777500	-2.40084100	-0.00013500
H	-3.25655200	-1.33822100	0.00010200

enol-DHPCH

C	-6.90517600	0.93546900	0.00066000
C	-6.18079100	-0.24472000	0.00048600
C	-4.78048800	-0.21327100	0.00012700
C	-4.10757000	1.01986000	0.00000100
C	-4.85678000	2.20891000	0.00018300
C	-6.24069700	2.16644800	0.00050100
H	-7.98933300	0.88519000	0.00093000
H	-4.33222600	3.15933700	0.00009100
H	-6.81600400	3.08585200	0.00064000
O	-6.83028700	-1.44489100	0.00063900
H	-6.17470600	-2.16042500	0.00063300

O	-4.14314200	-1.40625600	-0.00004200
C	-2.65465200	1.07270300	-0.00025300
N	-1.95922000	-0.00921700	-0.00040200
H	-2.16507300	2.04929400	-0.00027800
N	-0.58910500	0.18513800	-0.00059700
C	0.09228300	-0.90402600	-0.00058300
O	-0.46542000	-2.12147000	-0.00047300
C	3.69617300	-0.32689400	-0.00040200
C	2.43621400	0.24370400	-0.00043700
C	1.55748300	-0.85509100	-0.00069800
H	2.18324100	1.29232100	-0.00015000
N	2.22135400	-2.01209100	-0.00092200
N	3.50597800	-1.66939600	-0.00075300
C	7.30622900	-0.16076100	0.00234500
C	7.60713300	1.19757200	0.00103200
C	6.55440900	2.10620800	-0.00091100
C	5.25070900	1.62770500	-0.00145300
C	5.04844100	0.24759600	0.00004400
N	6.05854500	-0.63403700	0.00189100
H	6.74430700	3.17459100	-0.00203400
H	8.10108100	-0.90162700	0.00385000
H	8.63984100	1.52766400	0.00150700
H	4.40740500	2.30881000	-0.00307300
H	4.23211600	-2.37493500	-0.00084500
H	-3.15976500	-1.22182200	-0.00020400
H	0.23952800	-2.79455100	-0.00043000

Al-DHPCH

C	6.52193000	1.45060200	-0.19574300
C	5.80737300	0.28075500	-0.36427000
C	4.40442400	0.25625600	-0.22564400
C	3.73534100	1.45925800	0.08347200
C	4.47957800	2.64759700	0.24554900
C	5.85319500	2.64345500	0.11229000
H	7.60132500	1.42881000	-0.30797700
H	3.94909800	3.56708100	0.47270600
H	6.41939400	3.55957900	0.23916700
O	6.44807400	-0.88223600	-0.66997900
H	5.77129600	-1.57804100	-0.73808700
O	3.82236800	-0.93129300	-0.40820300
C	2.29714400	1.53779900	0.16960300

N	1.53656300	0.50125200	0.07059000
H	1.83111500	2.51596700	0.28669400
N	0.16023700	0.67682600	0.04442700
C	-0.39178200	-0.44337000	-0.34380900
O	0.29426000	-1.51491000	-0.65011600
C	-4.02313800	-0.10960900	-0.26123700
C	-2.79205300	0.46935900	-0.02080000
C	-1.85686300	-0.50858600	-0.41686600
H	-2.58881900	1.44580200	0.39008200
N	-2.46475900	-1.60714400	-0.87132400
N	-3.76496800	-1.34049300	-0.76855900
C	-7.63715800	-0.13884400	-0.19287500
C	-8.00085000	1.10527600	0.31182800
C	-6.99117100	2.00335500	0.64151100
C	-5.66745800	1.62700800	0.45744100
C	-5.40035400	0.35583700	-0.05253100
N	-6.36903100	-0.51372600	-0.37426600
H	-7.22994900	2.98503500	1.03754300
H	-8.39656000	-0.86782800	-0.46249000
H	-9.04738100	1.35745400	0.44077300
H	-4.85670400	2.30297100	0.70442000
H	-4.45629900	-2.02375800	-1.05043100
Al	2.08273500	-1.34840700	-0.19300100
Cl	1.98206300	-2.49236300	1.70173000

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