

Two colorimetric fluorescent turn-on chemosensors for detection Al^{3+} and N_3^- : Synthesis, photophysical and computational studies

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Association Constant

The Benesi-Hildebrand equation was used to calculate the association constants.

$$1/A - A_0 = 1/K(A_{\max} - A_0)[M^{x+}]^n + (A_{\max} - A_0)$$

Where A_0 is the absorbance of sensors L_1 without analyte, A is the absorbance of L_1 with the analyte and A_{\max} is the absorbance with $[M^{x+}]_{\max}$.

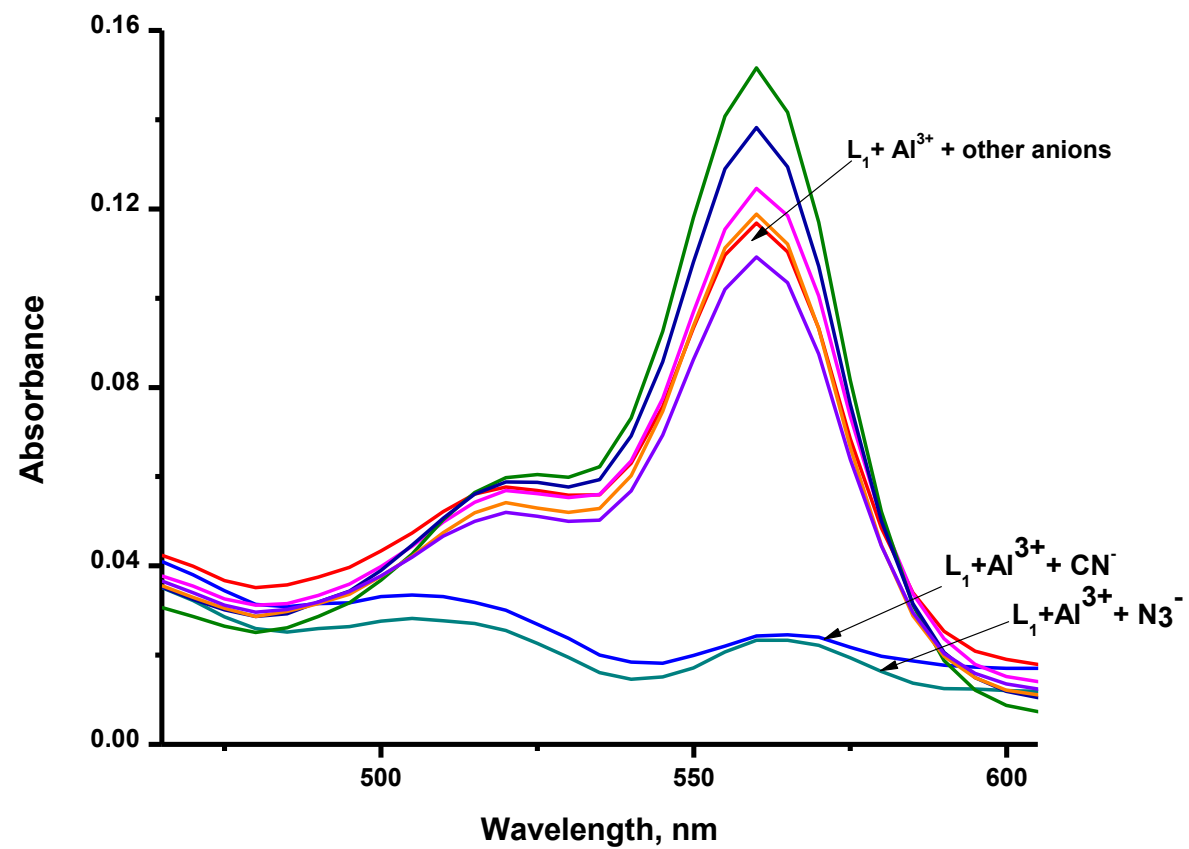


Figure S1: UV-Vis spectra of L_1 - Al^{3+} (20 μ M) upon addition of respective anions (20 μ M) in CH_3CN -water (7:3, v/v at P^H 7.0).

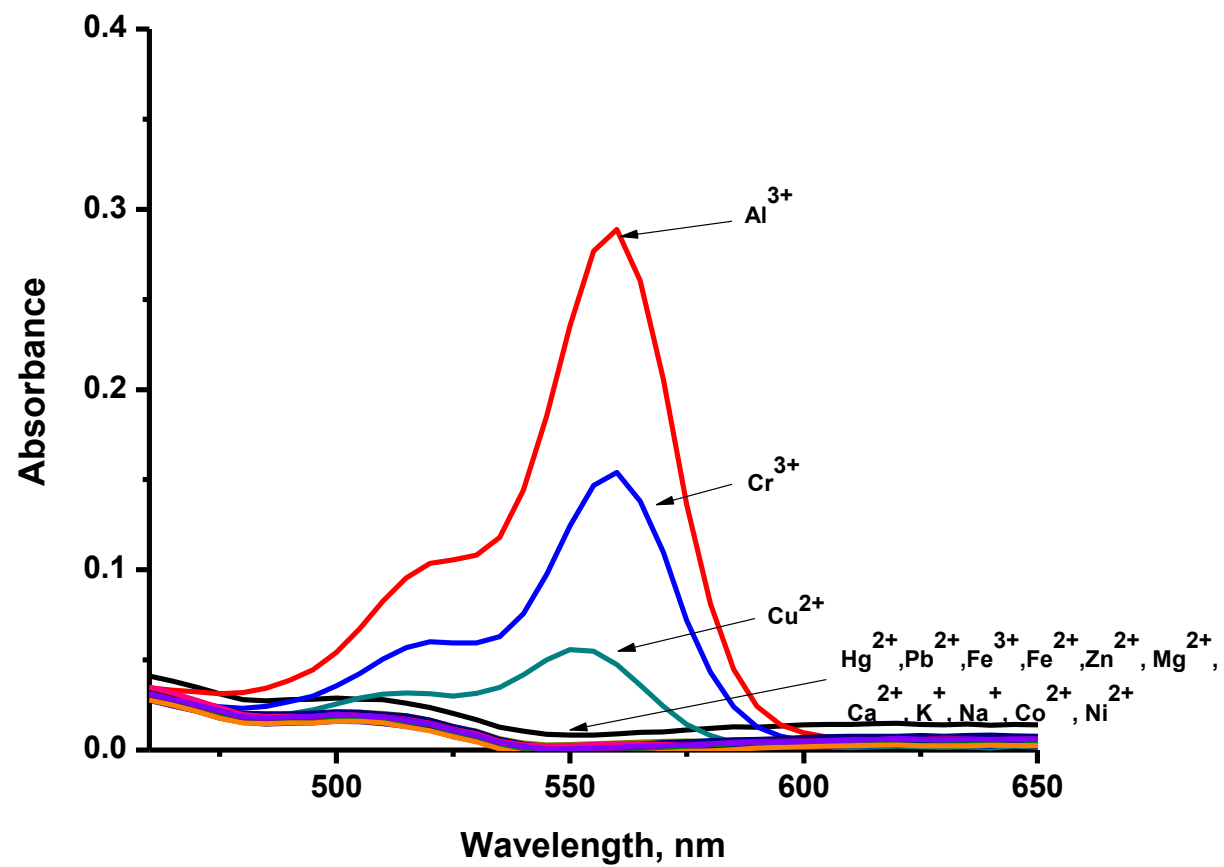


Figure S2 UV-Vis spectra of L₂ (10 μM) with metal ions

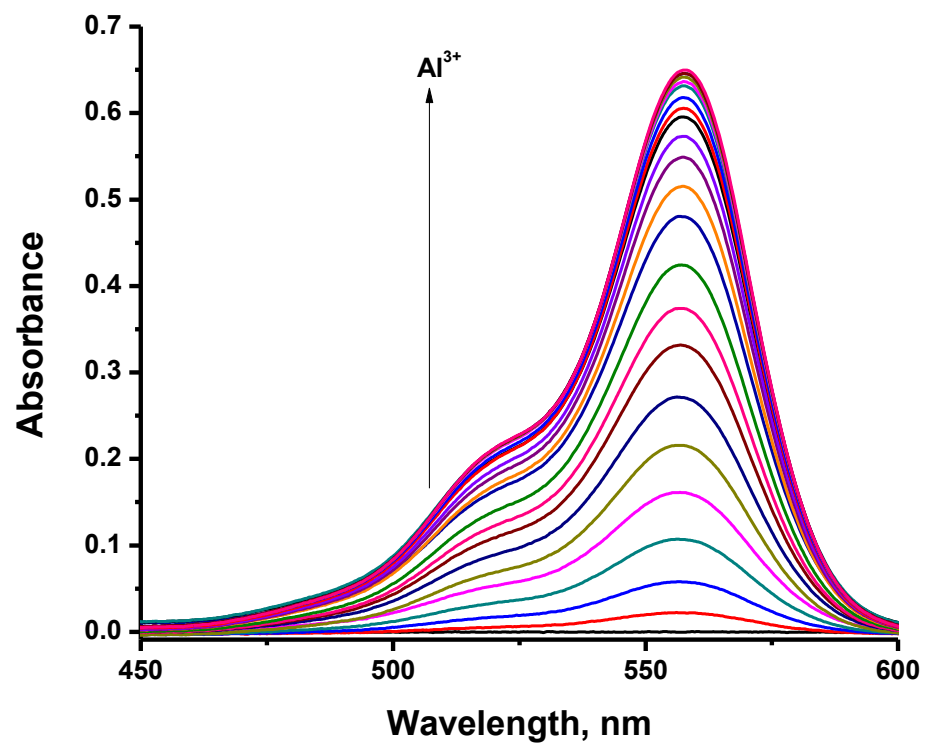


Figure S3. UV- vis absorption spectra of L2 (10μM) upon addition of Al³⁺ (0-24 μM)

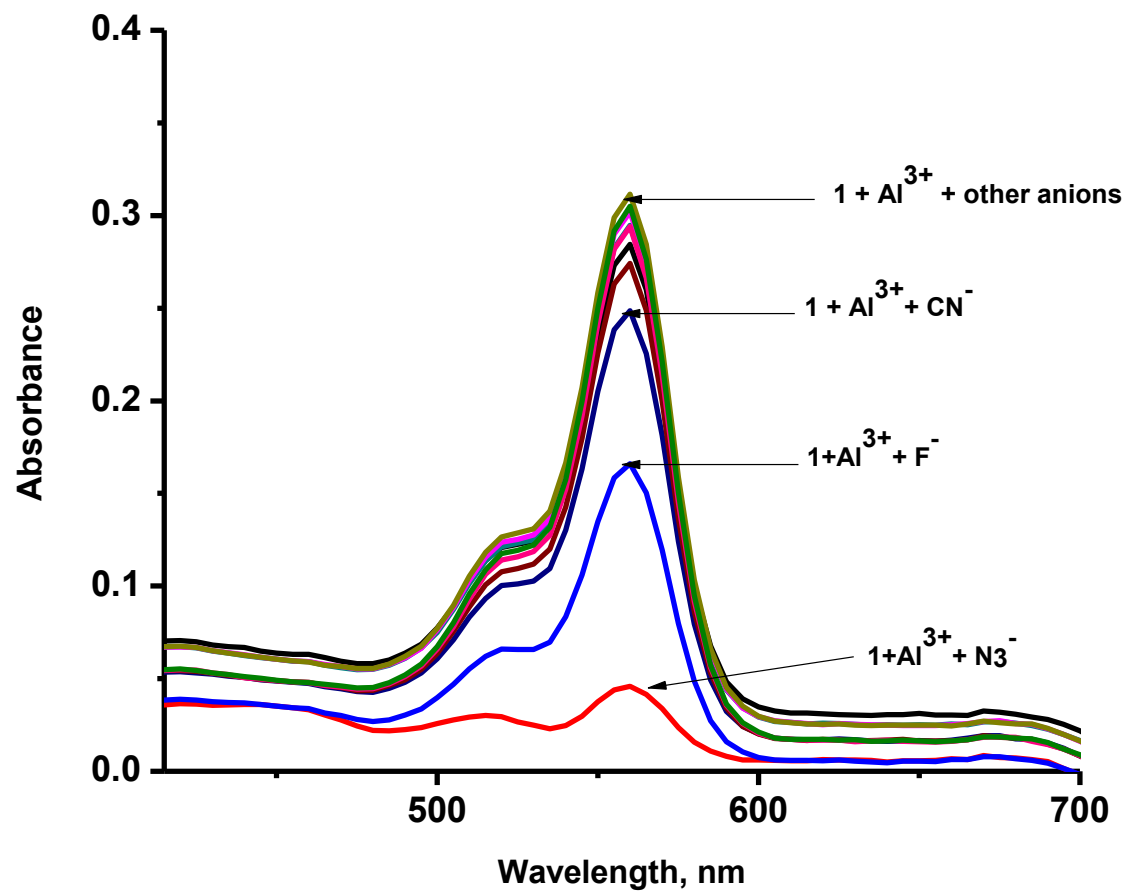


Figure S4: UV-Vis spectra of L_2-Al^{3+} (20 μM) upon addition of respective anions (20 μM) in CH_3CN -water (7:3, v/v at P^H 7.0).

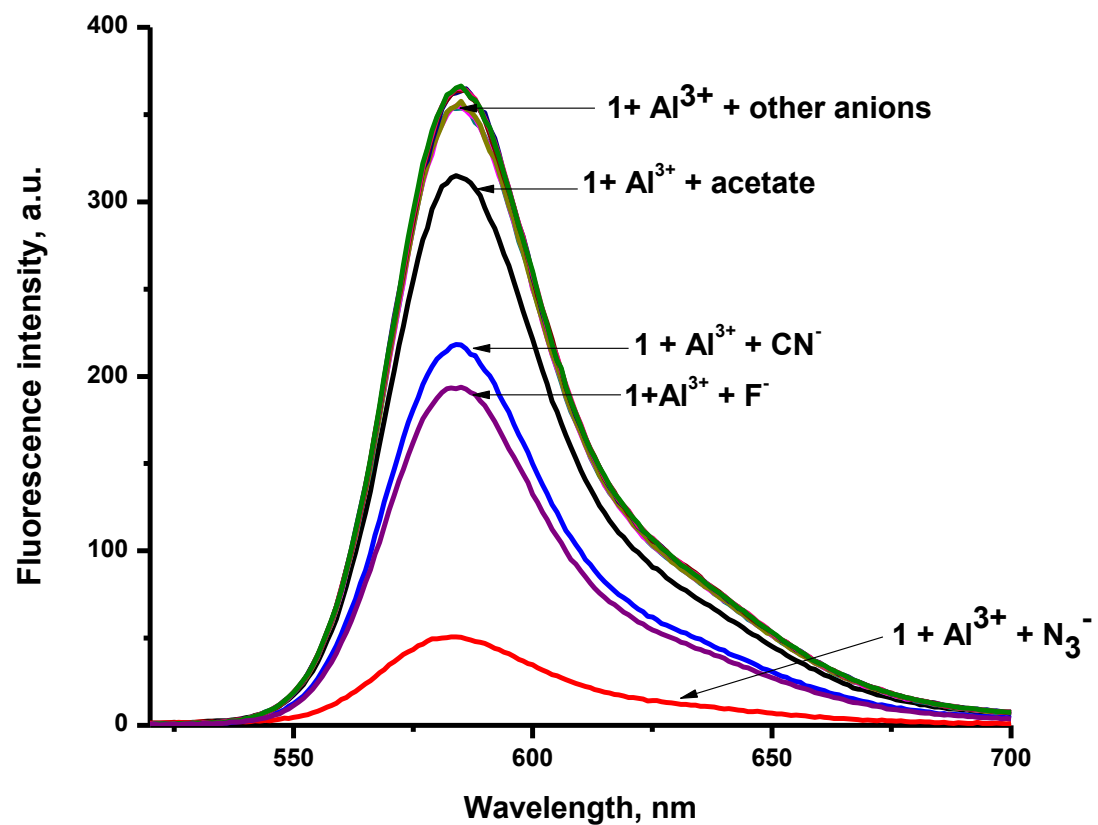


Figure S5. Fluorescence emission changes of L_2-Al^{3+} (10 μM) upon addition of different anions (1 equiv.) in CH_3CN -Water (7:3, v/v), (excitation at 510nm).



Figure S5-1. Photographs of L₁ and L₂ (20uM) upon addition of 2 equivalent of Al³⁺ in aqueous acetonitrile solution taken under UV light.

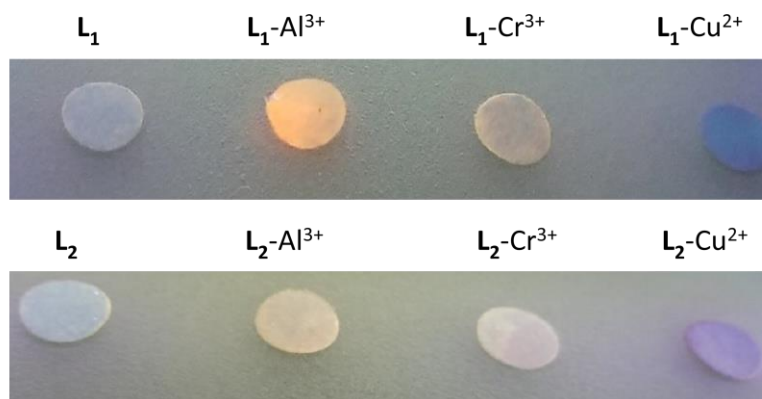


Figure S5-2 Real-color photographs of fluorescence emission from L₁ and L₂ dried on to solid surface before and after addition of Al³⁺, Cr³⁺ and Cu²⁺.

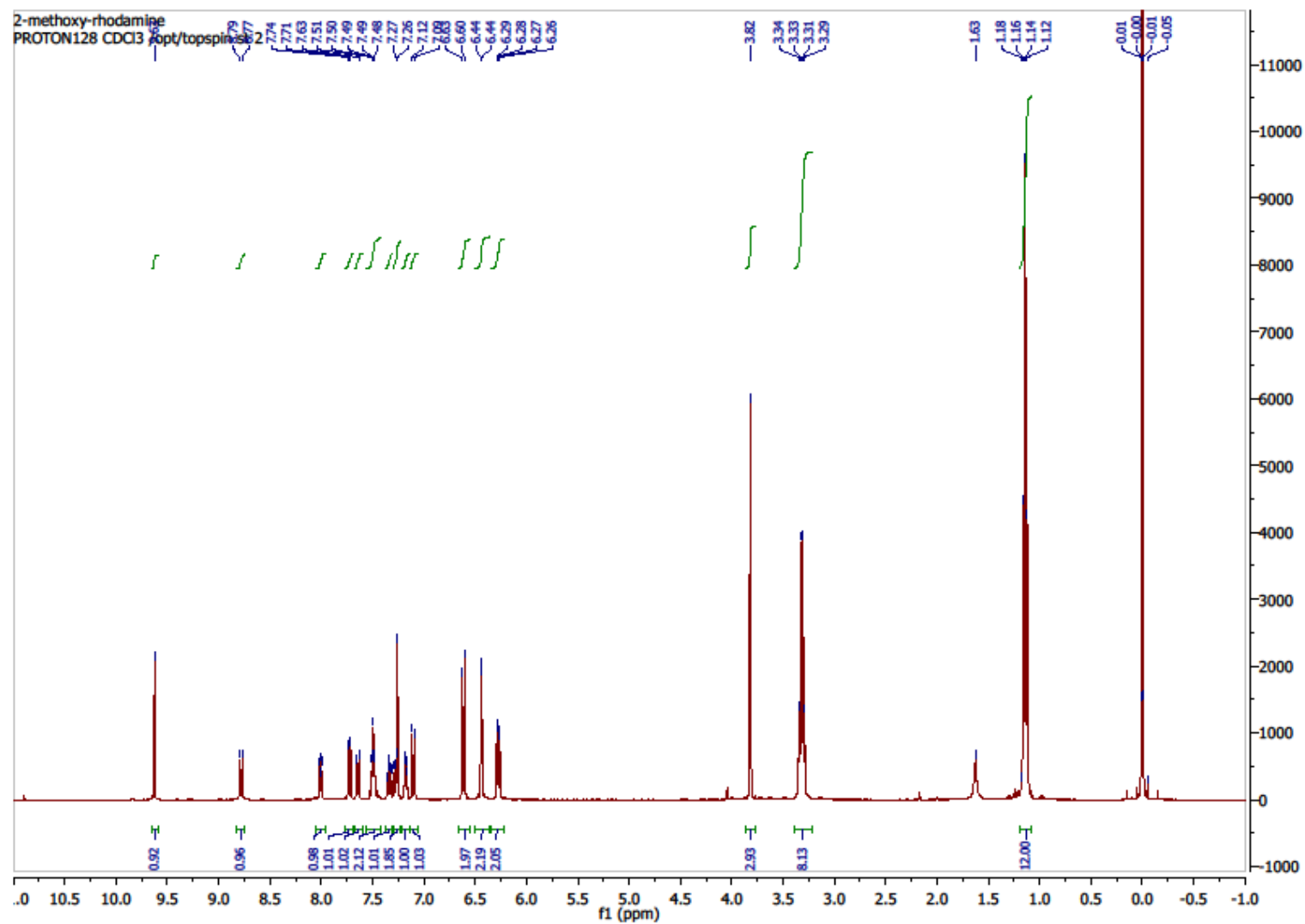


Figure S6: ^1H -NMR spectrum of compound **L1** (CDCl_3 , 400MHz)

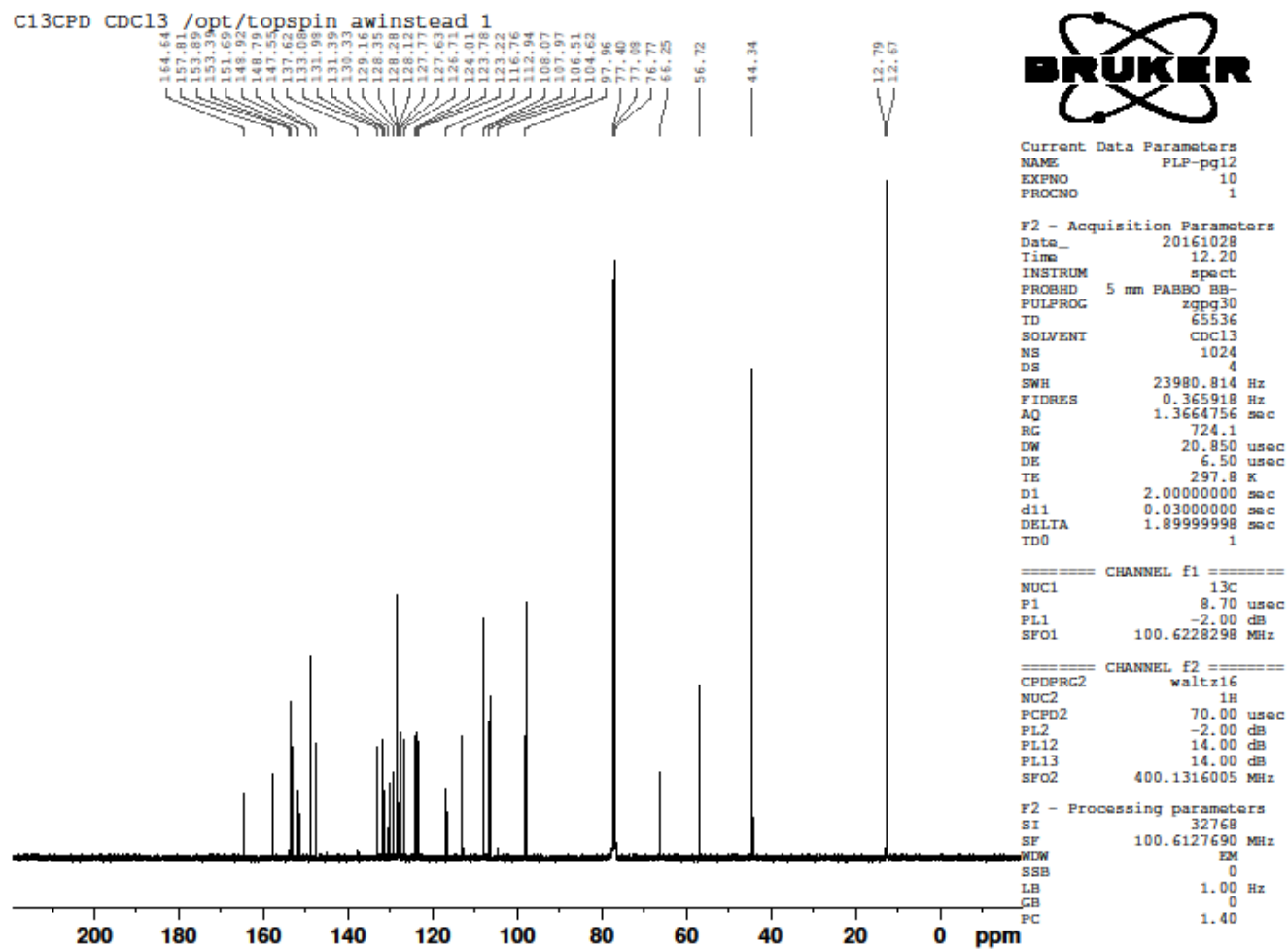


Figure S7: ^{13}C -NMR spectrum of compound **L**₁ (CDCl_3 , 400MHz)

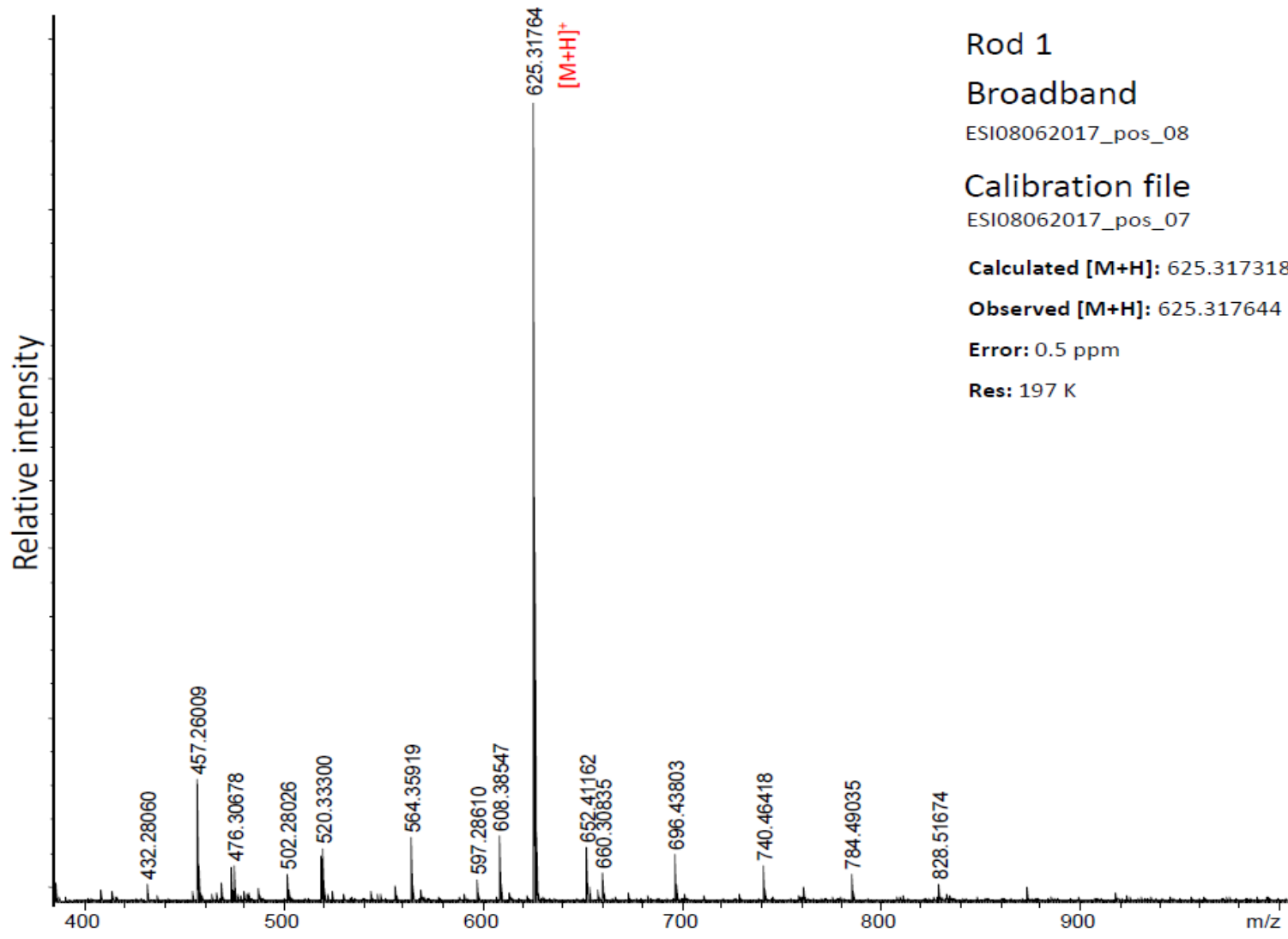
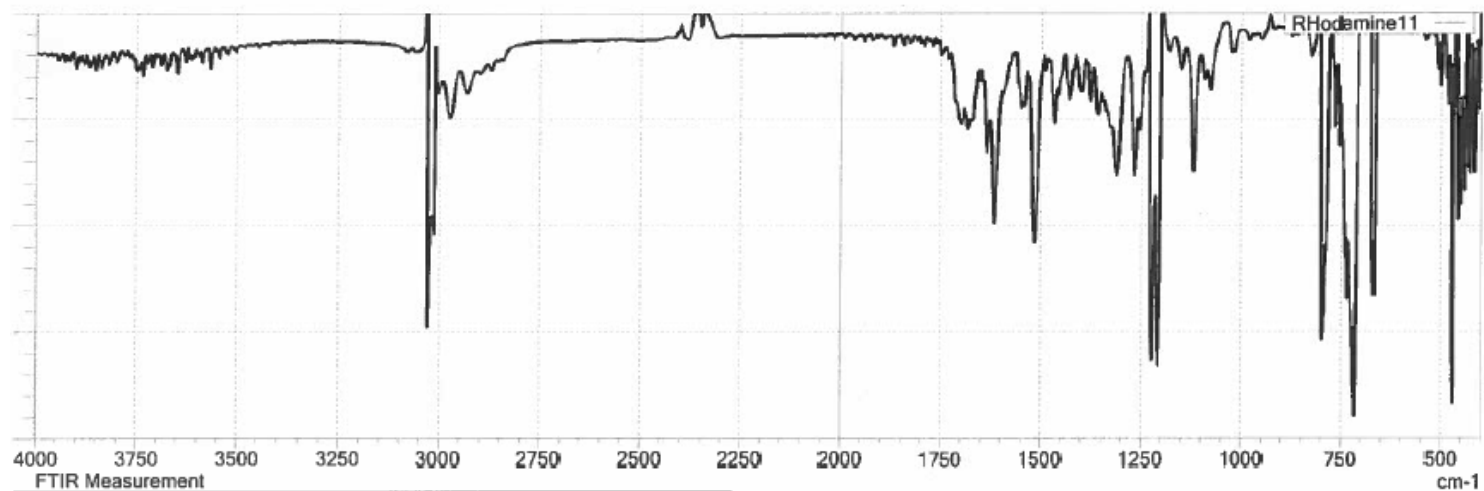


Figure S8: HRMS (ESI) spectrum of L₁

7/31/2017 12:34:41 AM



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Sample Name	Benzoin
Sample ID	Cortez S-A
Measurement	FTIR Measurement
Number of Scans	5
Resolution	4 [cm-1]
Apodization	Happ-Genzel

Figure S9: FTIR spectrum of compound L₁

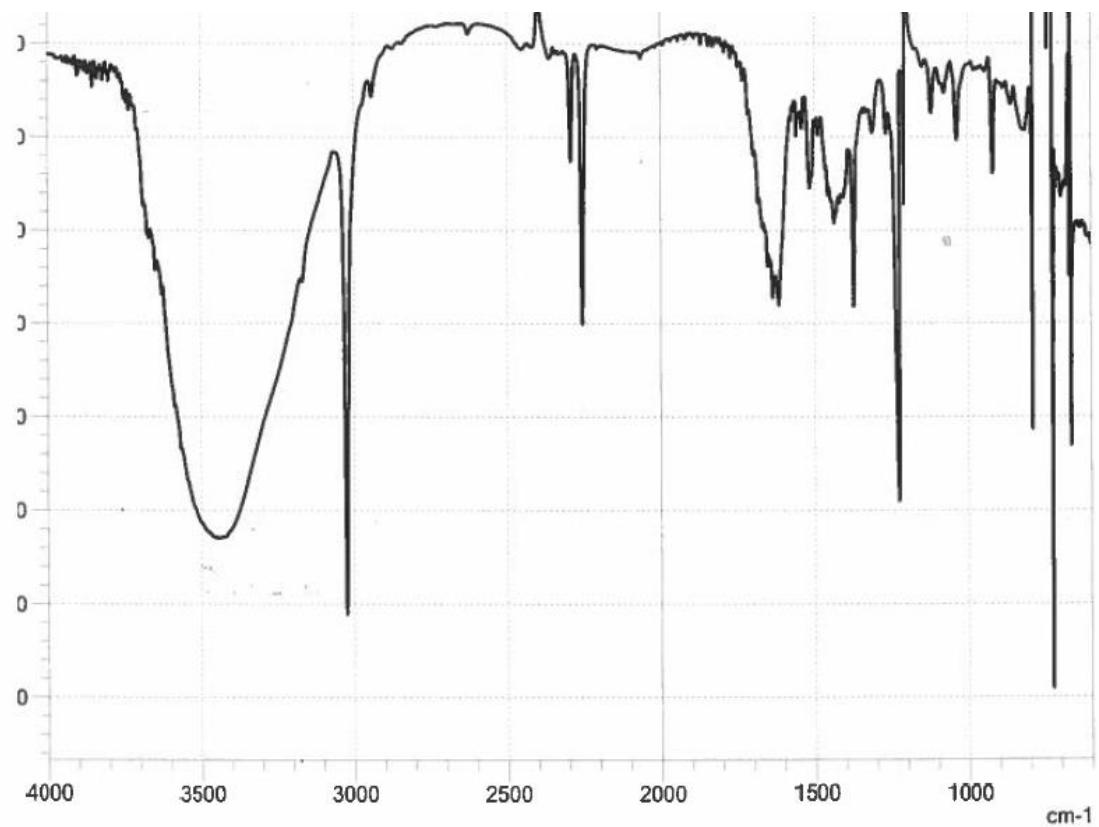


Figure S9-1: FTIR spectrum of compound $L_1 + Al^{3+}$

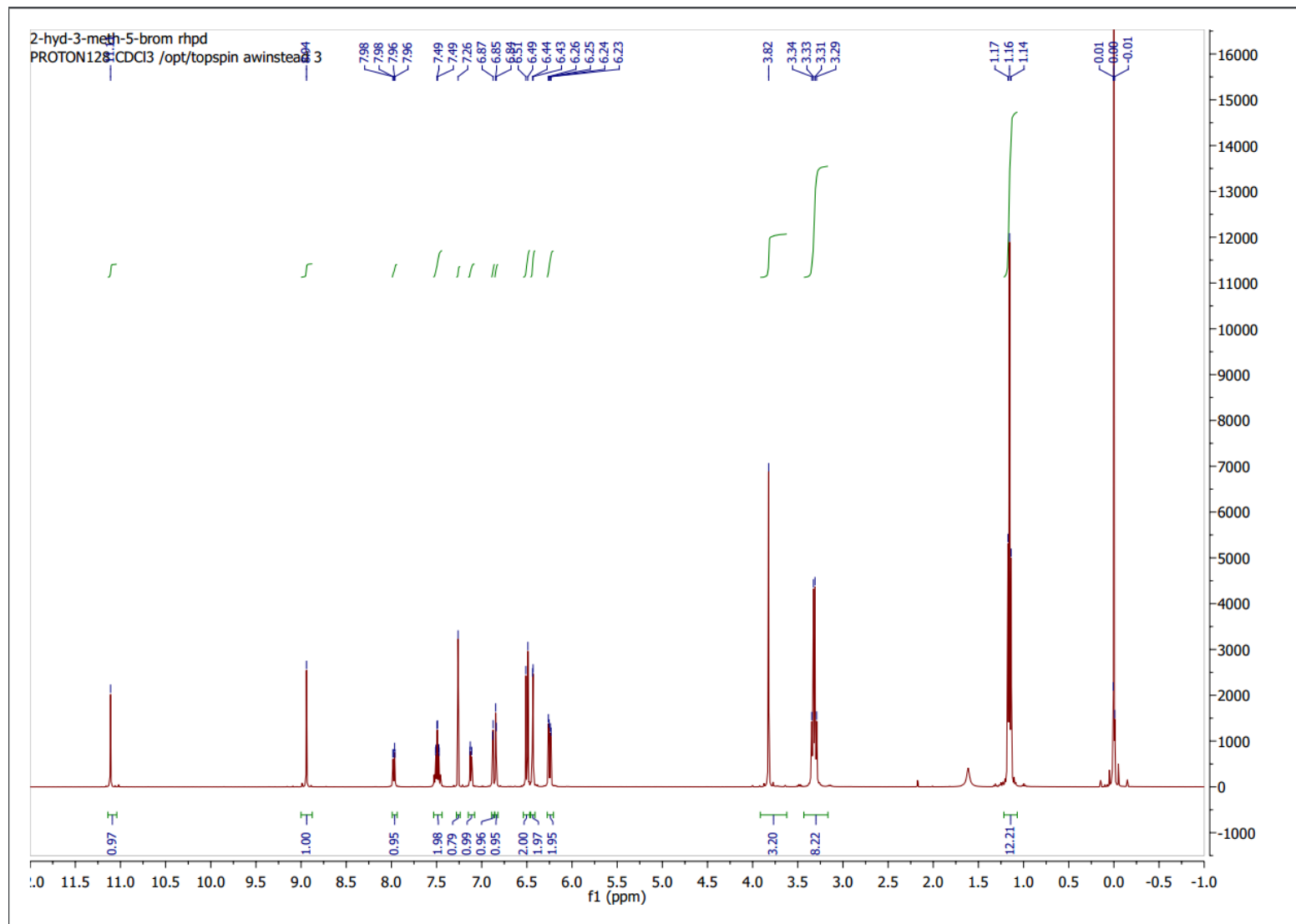


Figure S10: $^1\text{H-NMR}$ spectrum of compound L_2 (CDCl_3 , 400MHz)

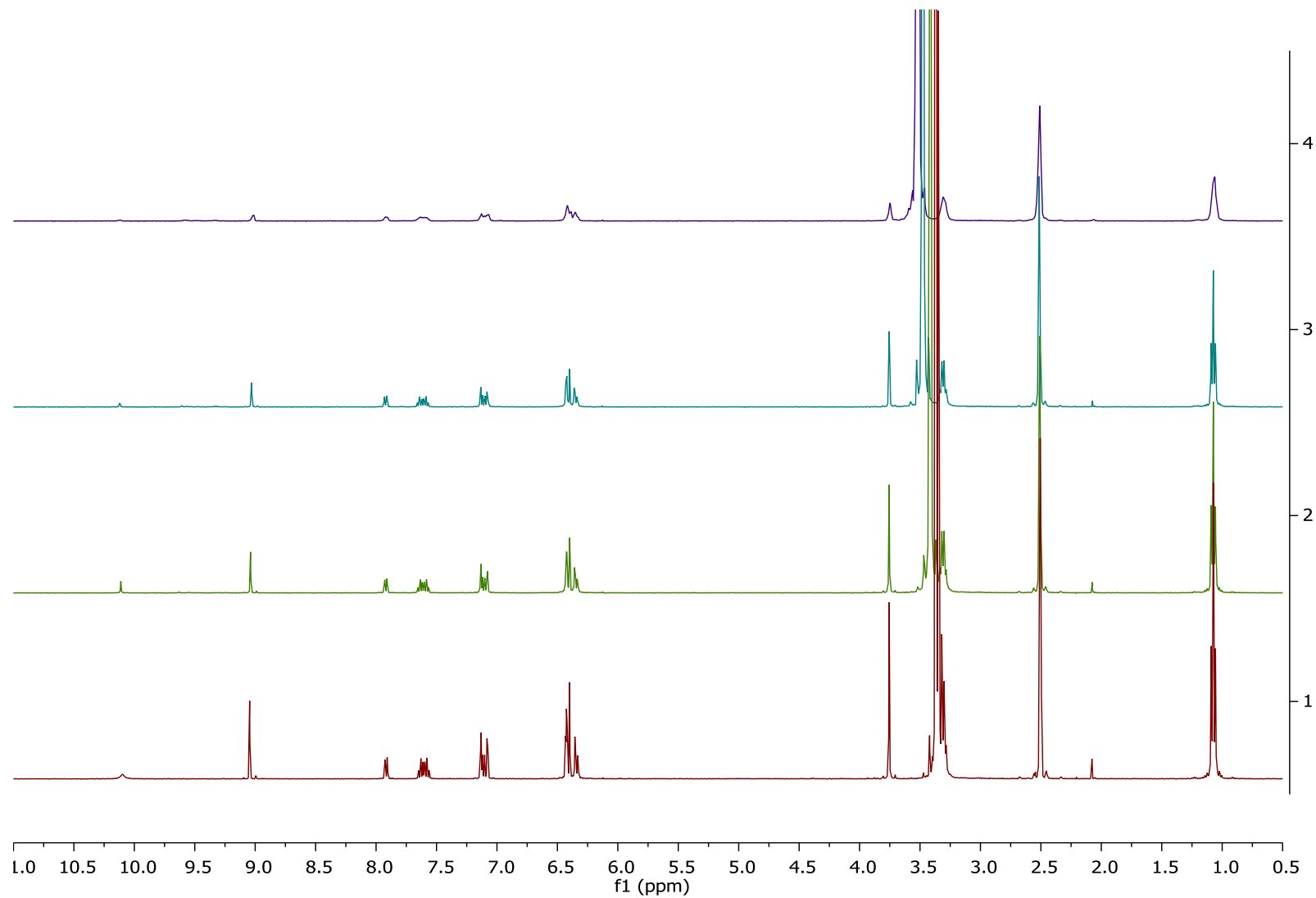


Figure S11: ^1H -NMR spectrum of compound $\text{L}_2\text{-Al}^{3+}$ (DMSO-d_6 , 400MHz)

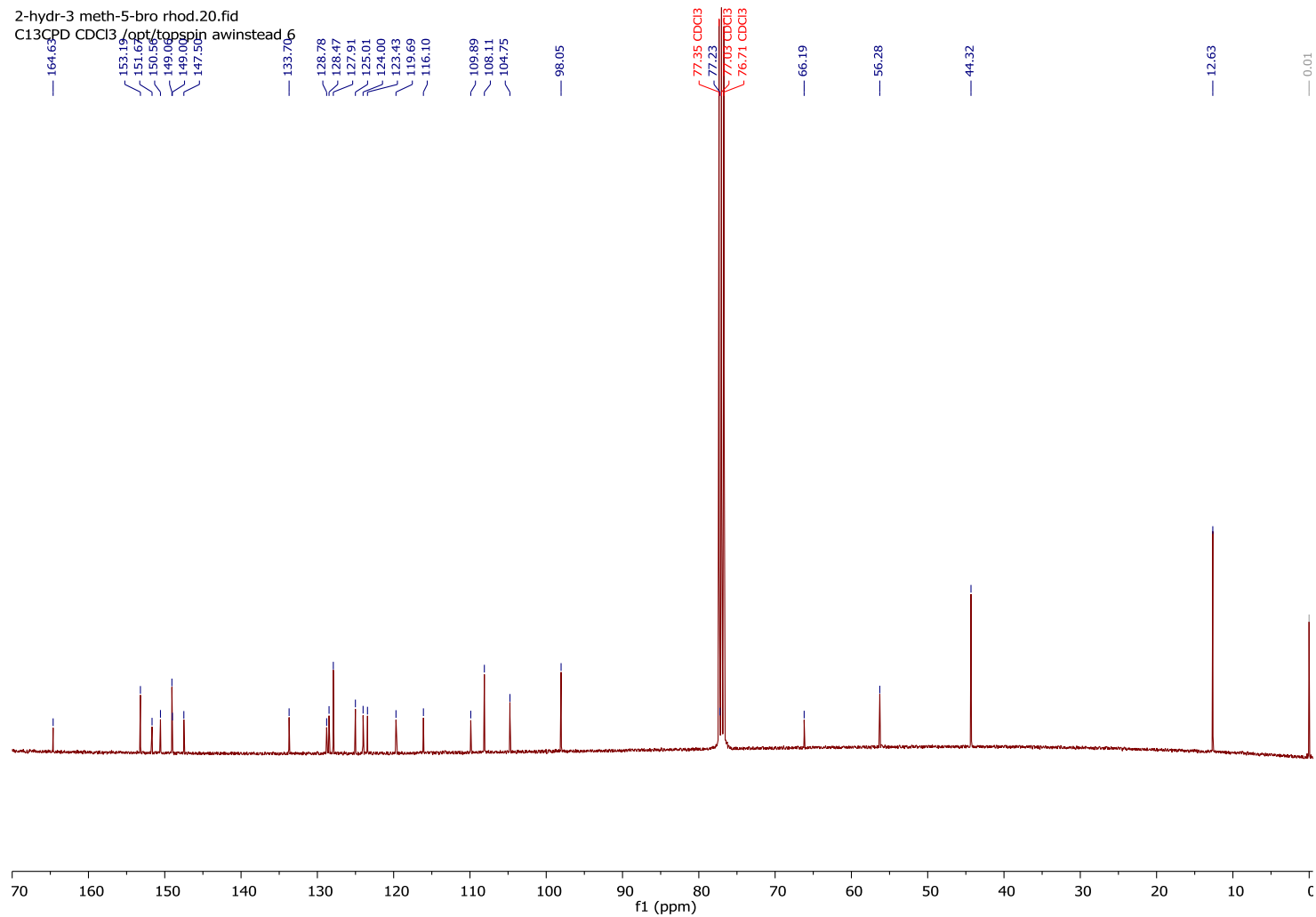


Figure S12: ^{13}C -NMR spectrum of compound **L2** in $\text{CDCl}_3\text{-d}$

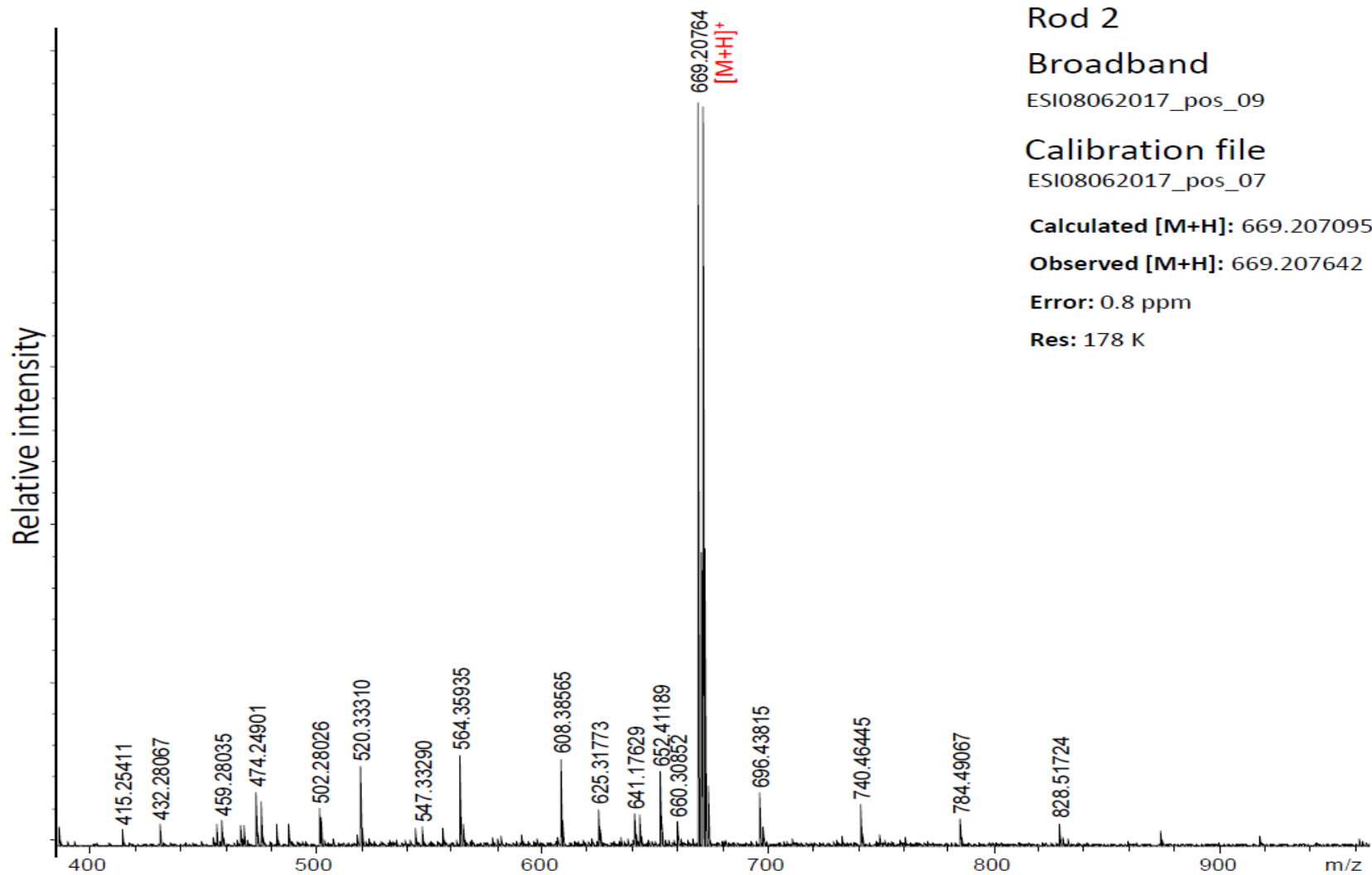


Figure S13: HRMS (ESI) spectrum of L₂

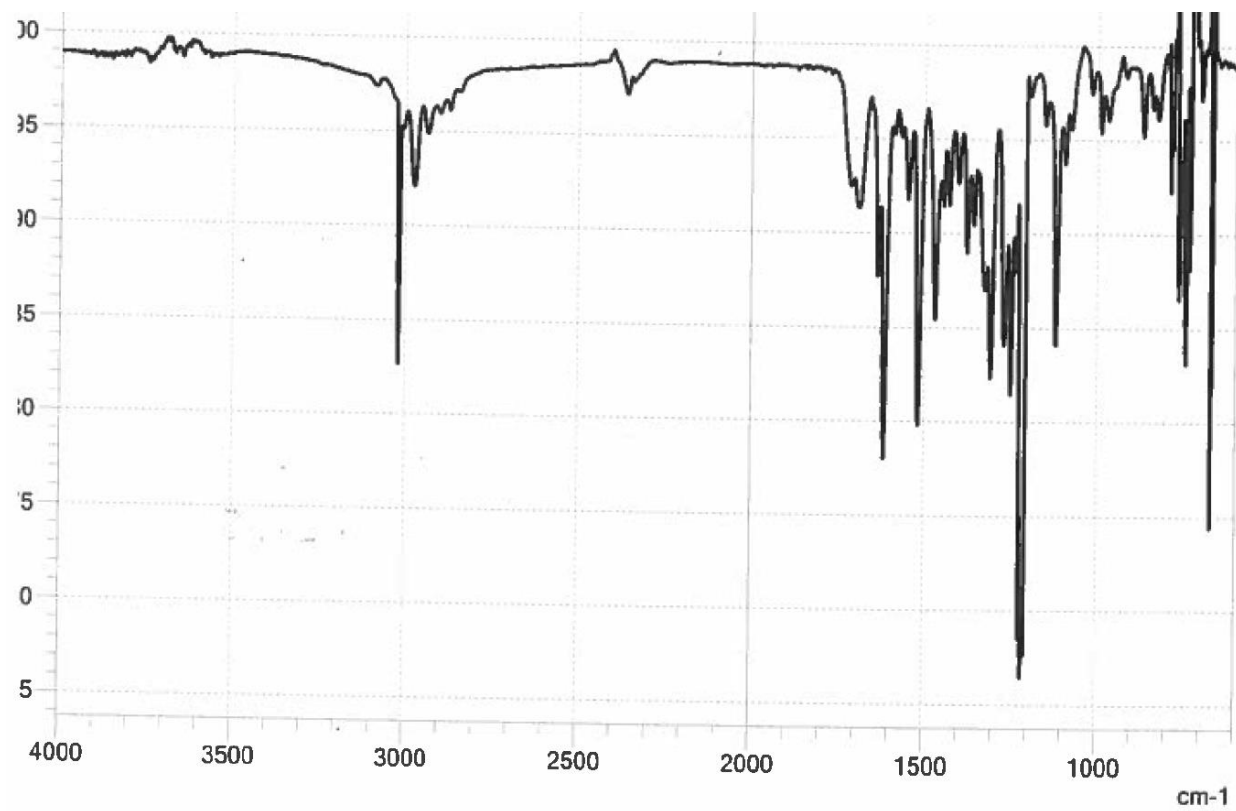


Figure S14: FTIR spectrum of compound **L₂**

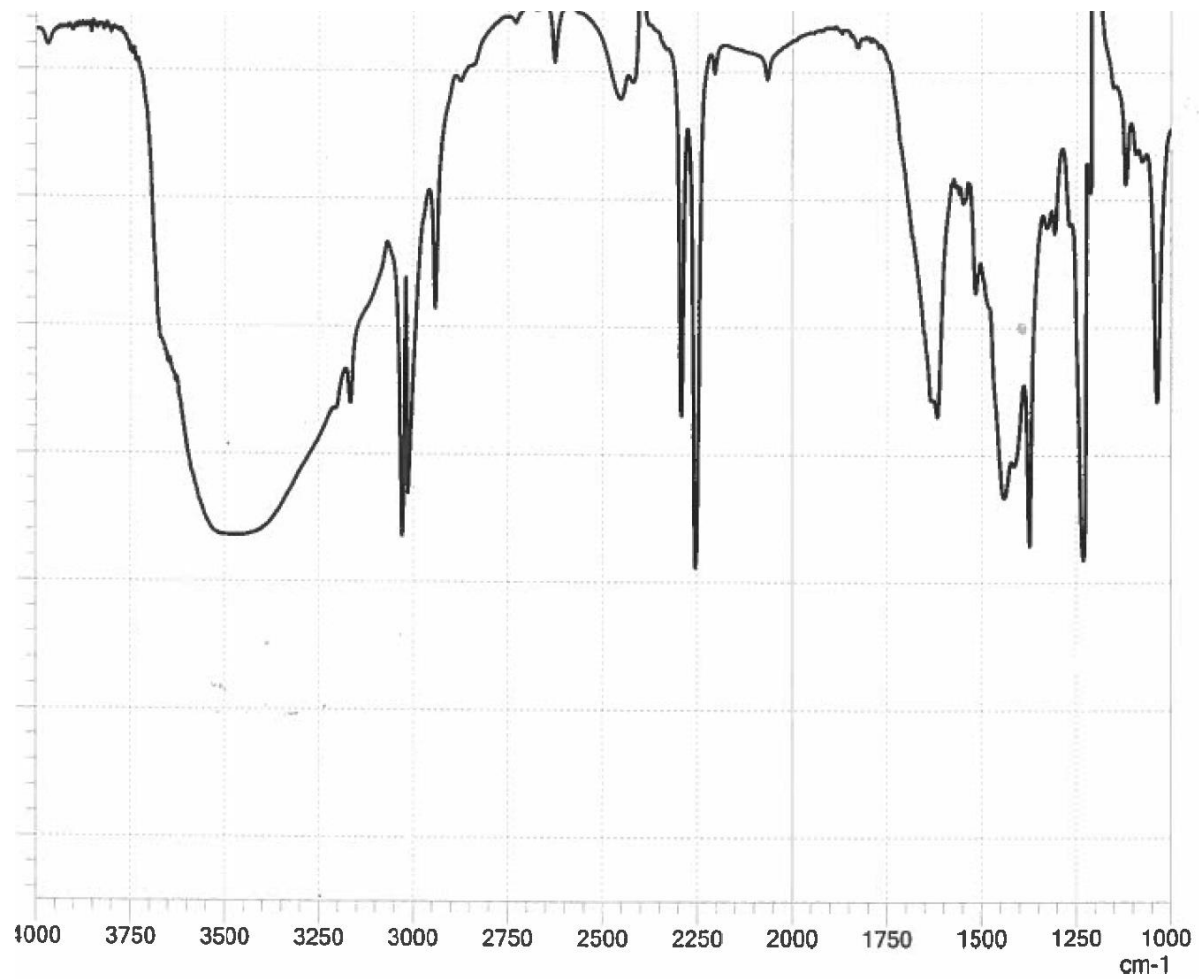


Figure S14-1: FTIR spectrum of compound L_2+Al^{3+}

Table S1: DF B3LYP/6-31G (d) HOMO -LUMO Energy of the cis and trans conformations of **L₁** and the Corresponding Al-Complexes

Component	E HOMO (eV)	E LUMO (eV)	Frontier Orbital Energy Gap (eV)
Cis	- 5.03	-1.35	3.68
L ₁ -Al ³⁺ Complex	-7.77	-4.95	2.82
Trans	-4.81	-1.34	3.47
L ₁ -Al ³⁺ Salt Complex	-5.35	-2.95	2.40

Table S2: DF B3LYP/6-31G (d) HOMO -LUMO Energy of the cis and trans confirmation of **L₂** and the Corresponding Al⁺³ -Complexes

Component	HOMO (eV)	LUMO (eV)	Difference (eV)	Corresponding Wavelength (nm)
Cis	-5.05	-1.22	3.83	317
Trans	-4.86	-1.29	3.57	340
L ₂ - Al ⁺³ Complex	-4.86	-2.64	2.22	547

Table S3: TD-DFT/6-31G (d) calculations of HOMO-LUMO energy of trans-L₁, trans-L₂ and their corresponding Al complexes in H₂O

Component	HOMO (eV)	LUMO (eV)	Difference (eV)
Trans- L ₁	-5.02	-1.81	3.21
Trans-L ₁ -Al ³⁺ complex	-5.49	-2.70	2.79
Trans- L ₂	-5.03	-1.73	3.03
Trans- L ₂ -Al ³⁺ complex	-5.46	-2.66	2.80

Table S4: TD-DFT/6-31G(d) energies of key HOMO-LUMOs of trans-**L1** and **L1-Al³⁺** salt complex in H₂O

<u>trans-L₁</u>		<u>trans-L₁-Al³⁺ salt complex</u>	
MO's	Energy (eV)	MO's	Energy (eV)
LUMO +1	-1.0	LUMO+1	-1.8
LUMO	-1.81	LUMO	-2.70
HOMO	-5.02	HOMO	-5.49
HOMO-1	-5.2	HOMO-1	-5.7
HOMO-2	-5.4	HOMO-2	-6.3
HOMO-3	-5.9	HOMO-3	-6.5
HOMO-4	-6.4	HOMO-4	-6.6
HOMO-5	-6.6	HOMO-5	-6.6

Table S5: Vertical excitation energies (VE_e), excitation wavelengths (λ_{exc}) oscillator strengths (f) and transitions of the lowest few excited singlets obtained from TD-DFT/6-31G(d) calculations of trans **L1** in H₂O

Vertical Excitation (VE _e) (eV)	$\lambda_{\text{excitation}}$ (λ_{exc}) (nm)	Oscillator Strength (f)	Key transitions	$\lambda_{\text{expt.}}$ (nm)
3.6804	336.88	0.0004	HOMO-1 → LUMO+1	95%
3.5546	348.80	0.0004	HOMO-3 → LUMO	97%
3.5487	349.38	0.0061	HOMO → LUMO +1	98%
3.2693	379.24	0.4632	HOMO-2 → LUMO	97%
2.8969	427.99	0.0004	HOMO-1 → LUMO	99%
2.7541	450.18	0.0145	HOMO → LUMO	99%

Table S6: Vertical excitation energies (VE_e), excitation wavelengths ($\lambda_{exc.}$) oscillator strengths (f) and transitions of the lowest few excited singlets obtained from TD-DFT/6-31G(d) calculations of trans **L₁-Al³⁺** salt complex in H₂O

Vertical Excitation (VE_e) (eV)	$\lambda_{excitation}$ ($\lambda_{exc.}$) (nm)	Oscillator Strength (f)	Key transition	$\lambda_{expt.}$ (nm)
3.2871	375.11	0.0313	HOMO-4 → LUMO HOMO-3 → LUMO HOMO-5 → LUMO	45% 30% 13%
3.2663	379.59	0.1208	HOMO-1 → LUMO+1	78%
3.1969	387.83	0.0344	HOMO → LUMO+1	86%
3.1922	388.40	0.0579	HOMO-2 → LUMO	71%
2.9341	422.57	1.0951	HOMO → LUMO	89%
2.5619	483.96	0.0069	HOMO-1 → LUMO	97%

Table S7: TDDFT/6-31G(d) energies of key HOMO-LUMOs of trans-L₂ and L₂-Al³⁺ complex

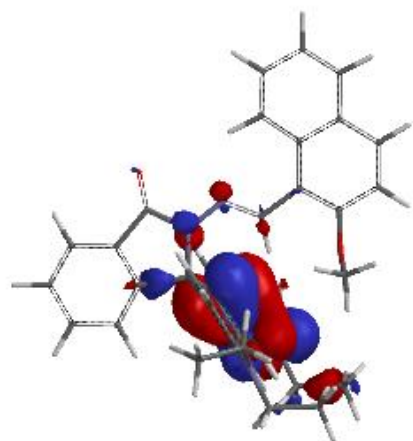
MO's	Energy (eV)	MO's	Energy (eV)
LUMO +1	-0.8	LUMO+1	-1.9
LUMO	-1.73	LUMO	-2.66
HOMO	-5.03	HOMO	-5.46
HOMO-1	-5.2	HOMO-1	-5.5
HOMO-2	-5.8	HOMO-2	-6.0
HOMO-3	-5.9	HOMO-3	-6.2
HOMO-4	-6.1	HOMO-4	-6.8
HOMO-5	-6.8	HOMO-5	-7.1

Table S8: Vertical excitation energies (VE_e), excitation wavelengths ($\lambda_{exc.}$) oscillator strengths (f) and transitions of the lowest few excited singlets obtained from TDDFT/6-31G(d) calculations of trans L_2 in H_2O

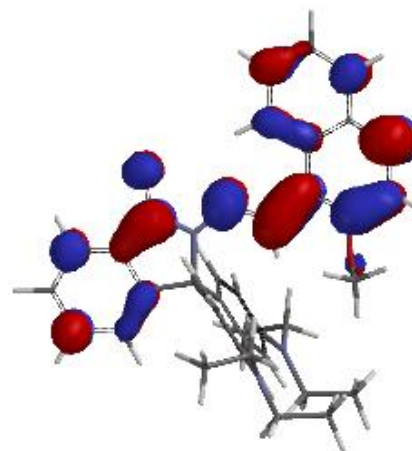
Vertical Excitation (VE_e) (eV)	$\lambda_{excitation}$ ($\lambda_{exc.}$) (nm)	Oscillator Strength (f)	Key transition	λ_{expt} (nm)
3.8804	319.51	0.0012	HOMO-1 \rightarrow LUMO+1	96%
3.7523	330.42	0.0067	HOMO \rightarrow LUMO+1	97%
3.6050	343.92	0.0011	HOMO-3 \rightarrow LUMO	99%
3.6008	344.32	0.3152	HOMO-2 \rightarrow LUMO	93%
2.9489	420.44	0.0004	HOMO-1 \rightarrow LUMO	99%
2.8101	441.21	0.0088	HOMO \rightarrow LUMO	100 %

Table S9: Vertical excitation energies (VE_e), excitation wavelengths ($\lambda_{exc.}$) oscillator strengths (f) and transitions of the lowest few excited singlets obtained from TD-DFT/6-31G(d) calculations of trans L_2 - Al^{3+} complex in H_2O

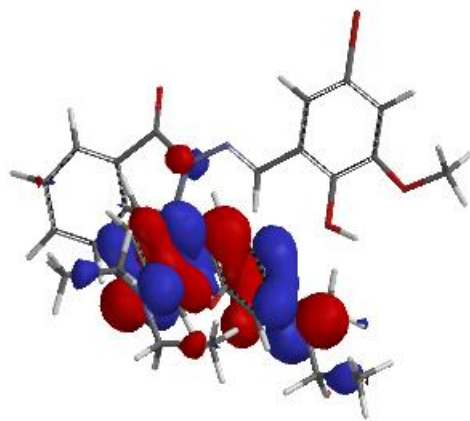
Vertical Excitation (VE_e) (eV)	$\lambda_{excitation}$ ($\lambda_{exc.}$) (nm)	Oscillator Strength (f)	Key transitions	λ_{expt} (nm)
3.1863	389.12	0.0123	HOMO-1 \rightarrow LUMO+1	81%
			HOMO \rightarrow LUMO+1	17%
3.1448	394.25	0.1193	HOMO \rightarrow LUMO+1	57%
			HOMO-3 \rightarrow LUMO	26%
3.1103	398.63	0.0808	HOMO-3 \rightarrow LUMO	64%
			HOMO \rightarrow LUMO+1	23%
2.9374	422.09	0.0035	HOMO-2 \rightarrow LUMO	96%
2.7178	456.19	0.7824	HOMO-1 \rightarrow LUMO	75%
			HOMO \rightarrow LUMO	23%
2.4053	515.47	0.0009	HOMO \rightarrow LUMO	74%
			HOMO-1 \rightarrow LUMO	23%



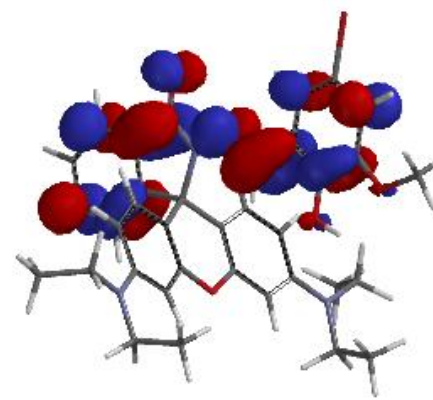
HOMO of cis L1



LUMO of cis L1

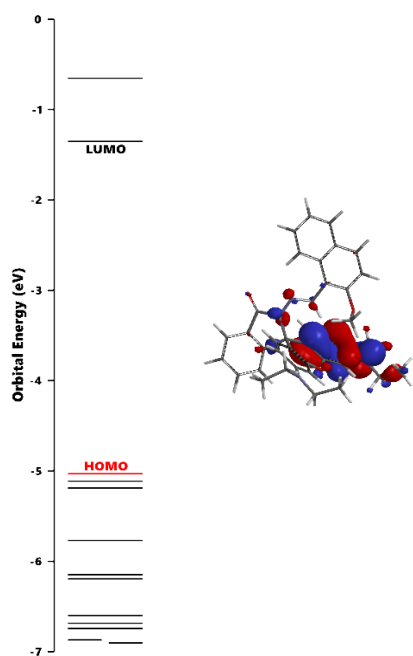


HOMO of cis L2

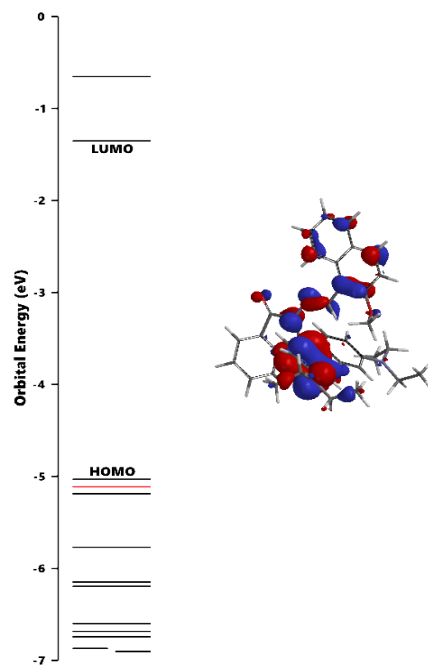


LUMO of cis L2

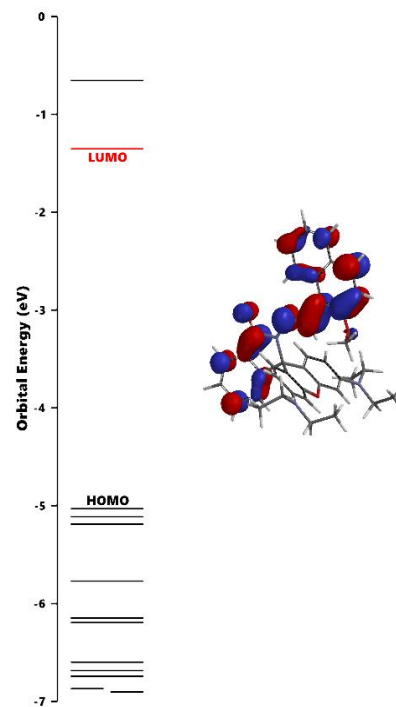
Figure S15: HOMO-LUMO of L1 cis and L2 cis confirmation



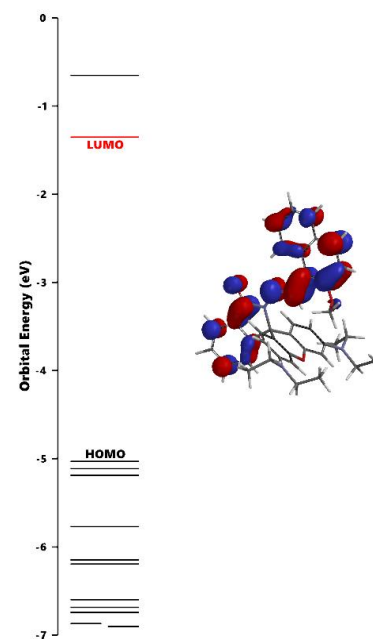
HOMO



HOMO-1



LUMO

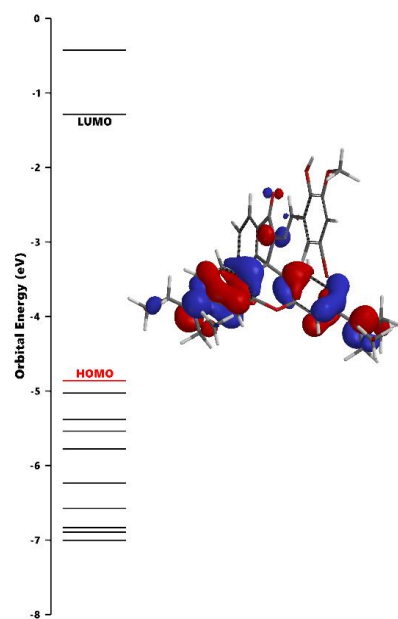


LUMO +1

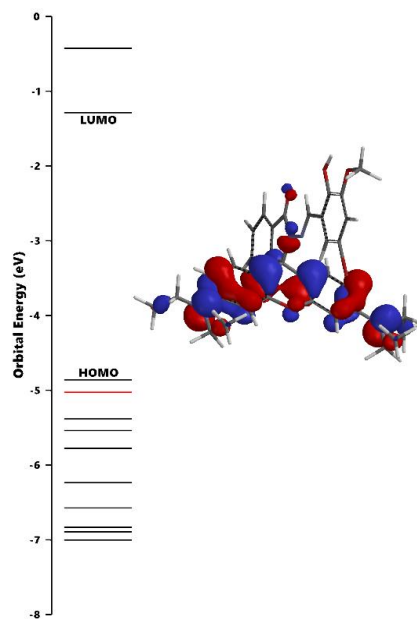
HOMO and **HOMO-1** are shown below for **L₁** (cis)

LUMO and **LUMO +1** are shown below for **L₁** (cis)

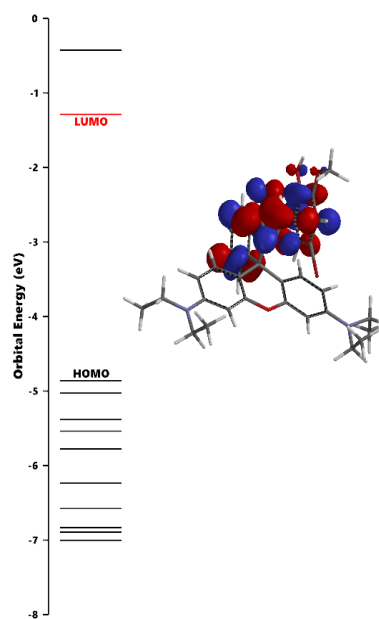
Figure S16: HOMO-LUMO-1 of **L₁** cis confirmation



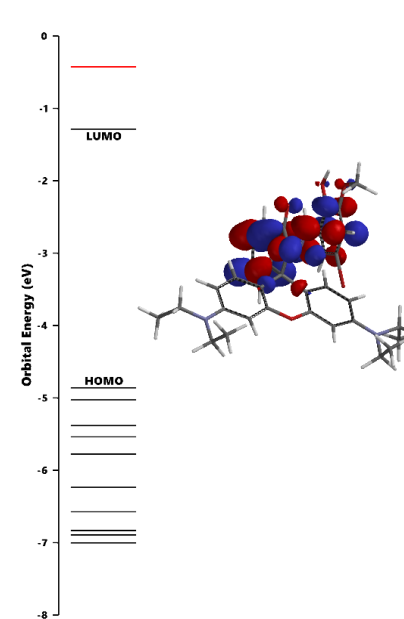
HOMO



HOMO-1



LUMO

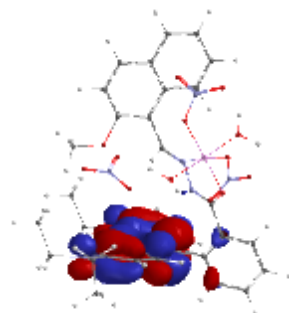


LUMO +1

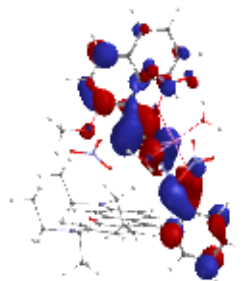
HOMO and **HOMO-1** are shown below for L_2 (trans conformation)

LUMO and **LUMO +1** are shown below for L_2 (trans)

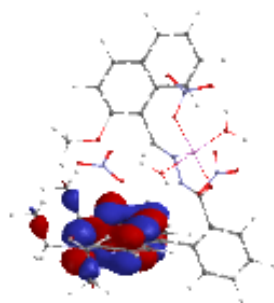
Figure S17: HOMO-LUMO of L_2 trans confirmation



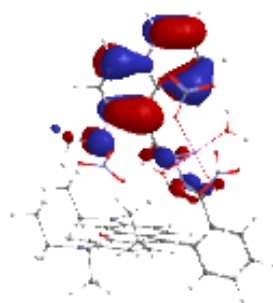
LUMO



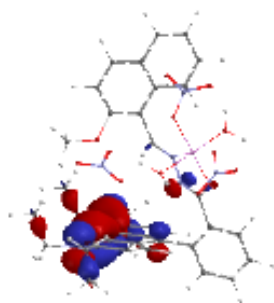
LUMO+1



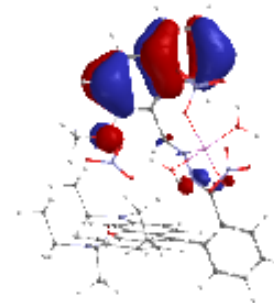
HOMO



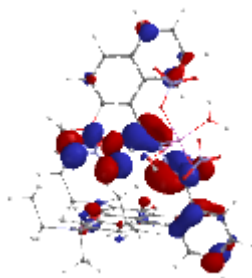
HOMO-1



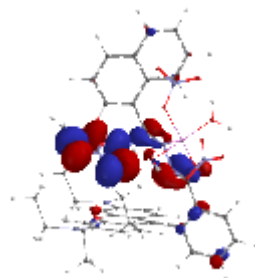
HOMO-2



HOMO-3

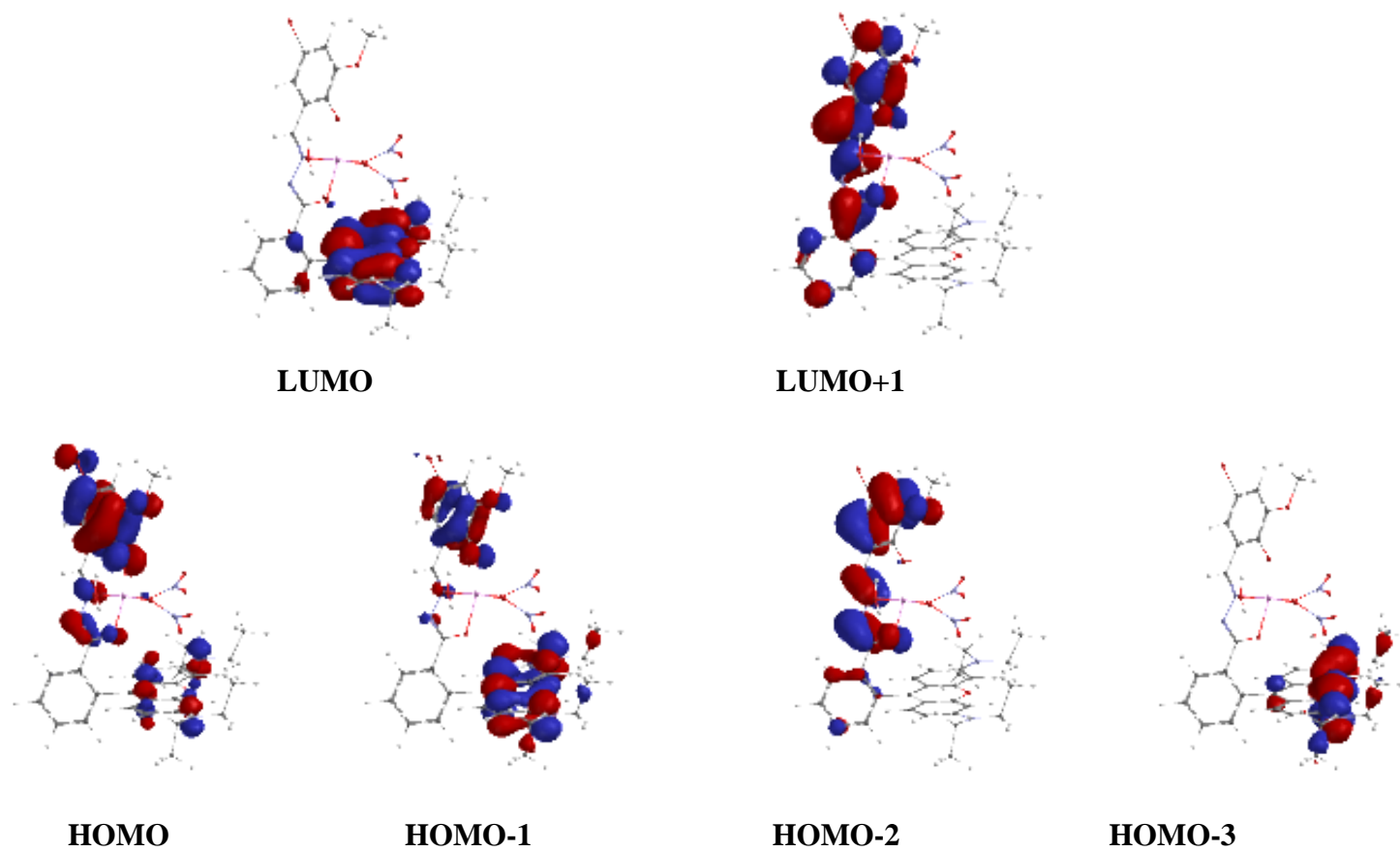


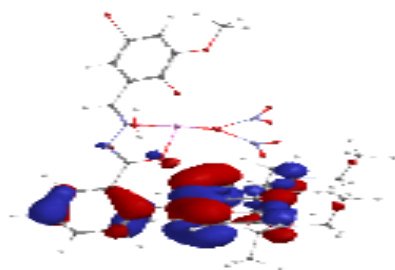
HOMO-4



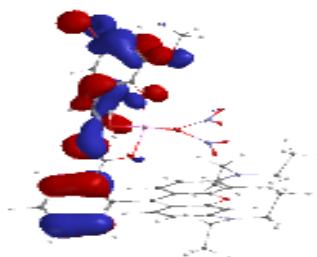
HOMO-5

Figure S18 Some TD-DFT HOMO and LUMO's of trans- L_1-Al^{3+} salt complex in H_2O





HOMO-4



HOMO-5

Figure 19 Some TD-DFT HOMO and LUMO's of trans- L_2-Al^{+3} complex in H_2O