**Novel calix[4]arene based metallo-supramolecular complex for recognition of CN- ions in aqueous medium**

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**Material and Methods:**

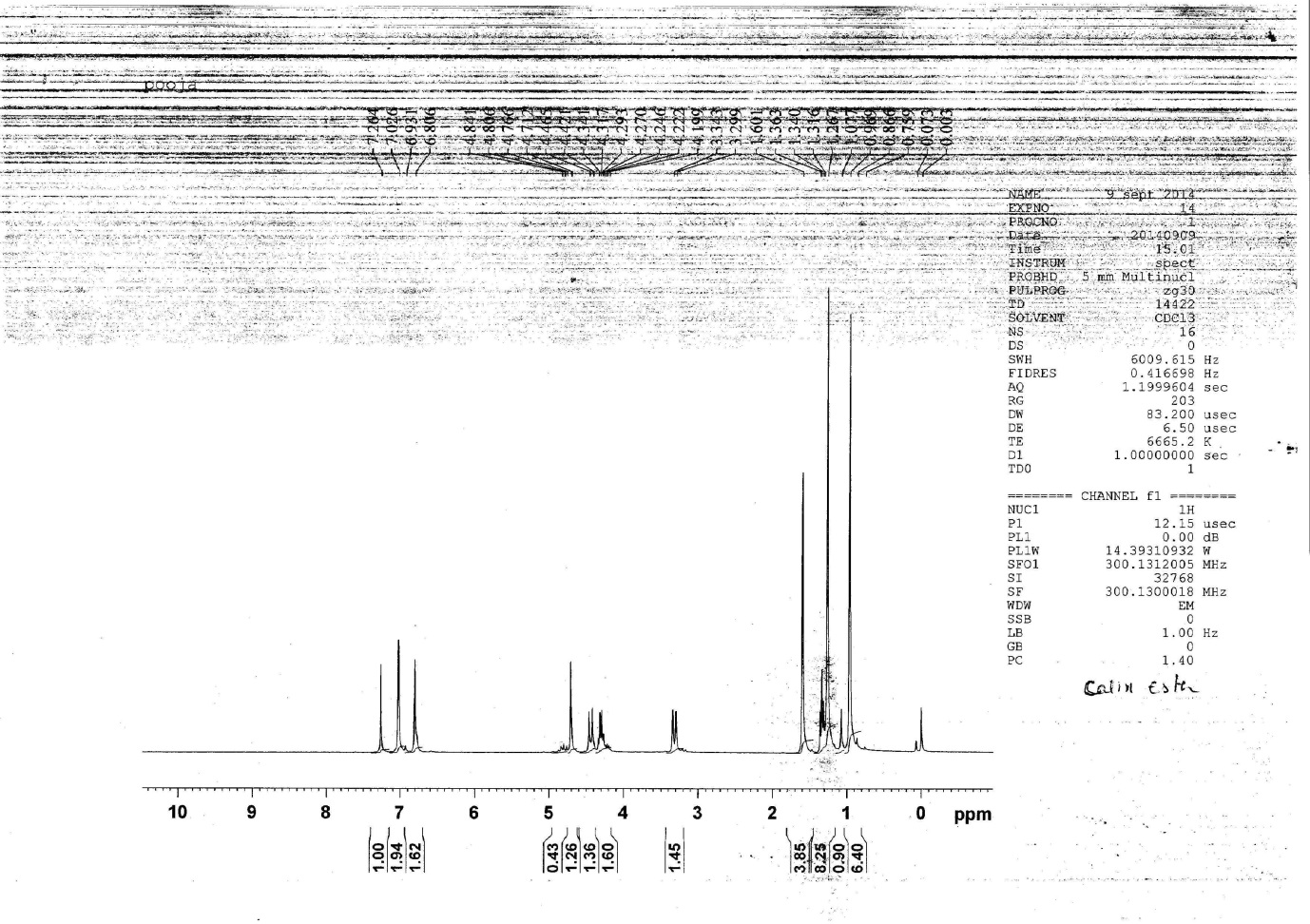
All the reagents and solvents were purchased from Merck and Sigma-Aldrich and were used without any further purification. IR spectra in KBr were recorded on Agilent/ Perkin Elmer FT-IR spectrometer. 1H NMR spectra (chemical shifts in δ ppm) were recorded on a Bruker 300 FT–NMR (300 MHz) spectrometer, using TMS as internal standard. The UV-Vis absorption spectra were recorded on Perkin Elmer Lambda 35 spectrophotometer using a quartz curette (path length = 1 cm). Fluorescence spectra were recorded on a Horiba Fluoromax 4 spectrophotometer. HRMS were recorded on Brukar MICROTOF Q II in aqueous acetonitrile.

The fluorescence titration data were employed to estimate the binding affinity for 1:1 and 1:2 stoichiometry by modified Benesi-Hildebrand method employing equations given below--

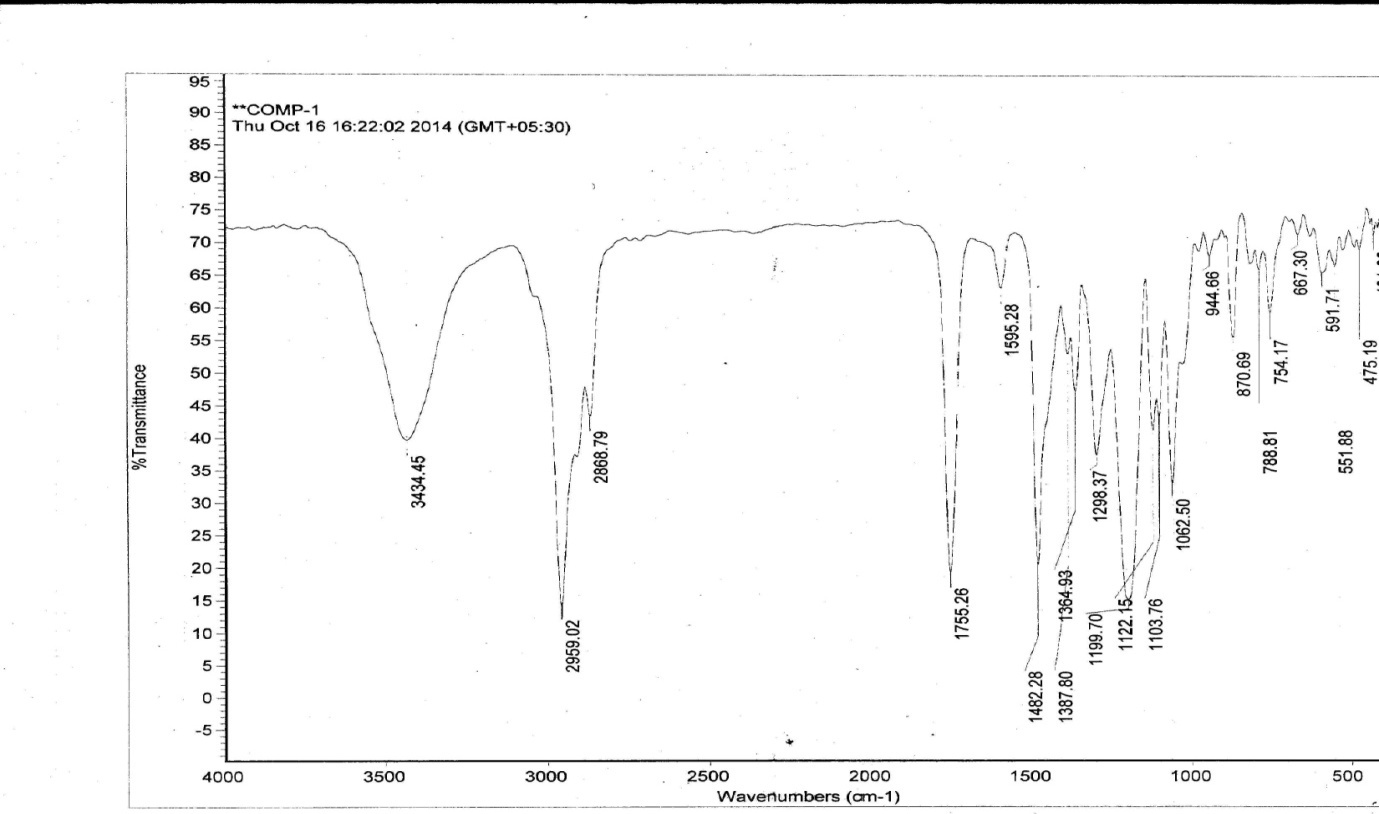
**1/(*I* - *Io*) = 1/(*I* - *I*f) + 1/K (*I* - *I*f) [M] (1)**

**1/(*I* - *Io*) = 1/(*I* - *I*f) + 1/K (*I* - *I*f) [M]2 (1I)**

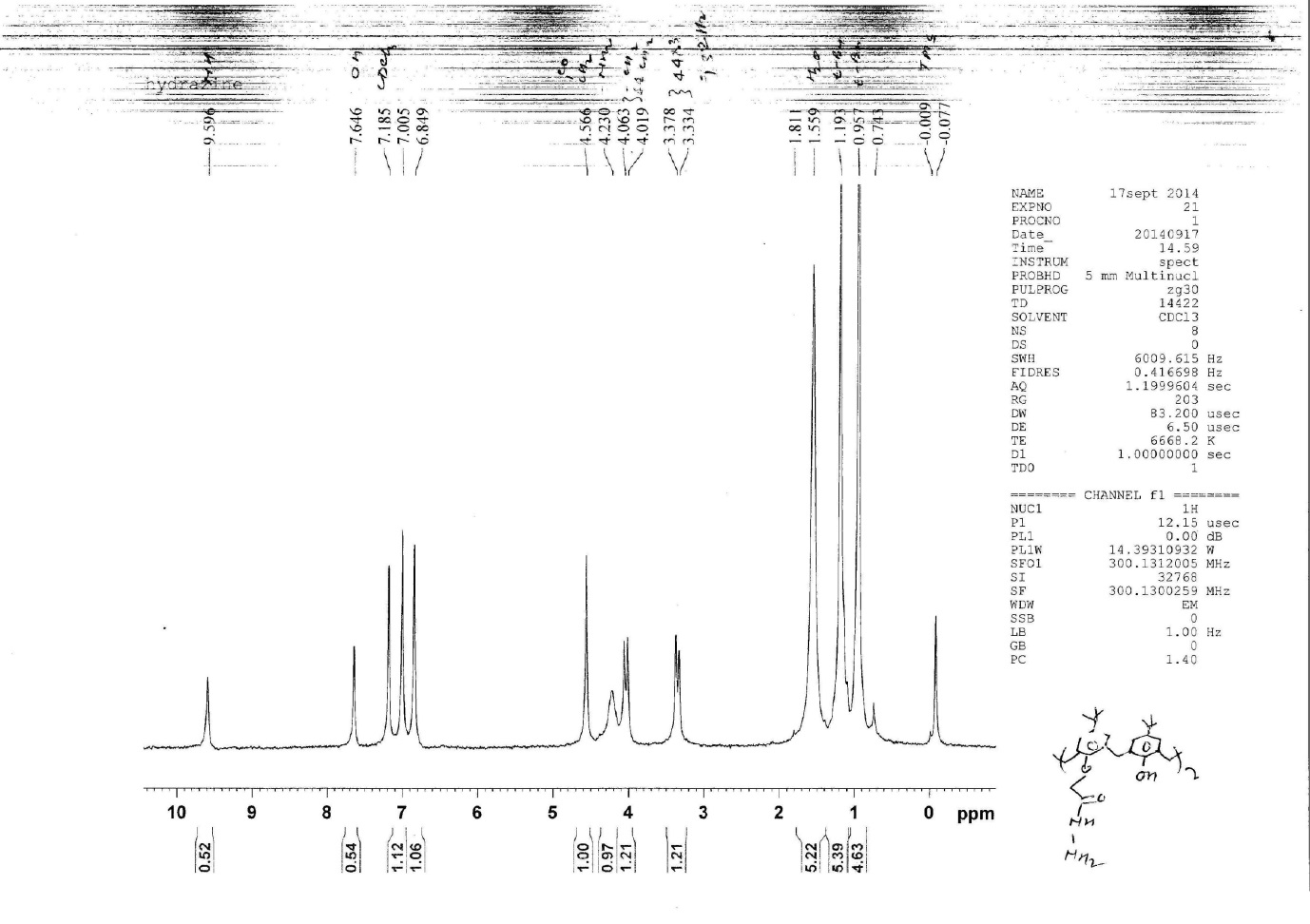
Where, K is the association constant, *I* is fluorescence intensity/absorbance of free receptor **4**, *I*o is the observed fluorescence intensity/absorbance of complex, **4-Cu2+** and *I*f is the fluorescence intensity/absorbance at saturation.



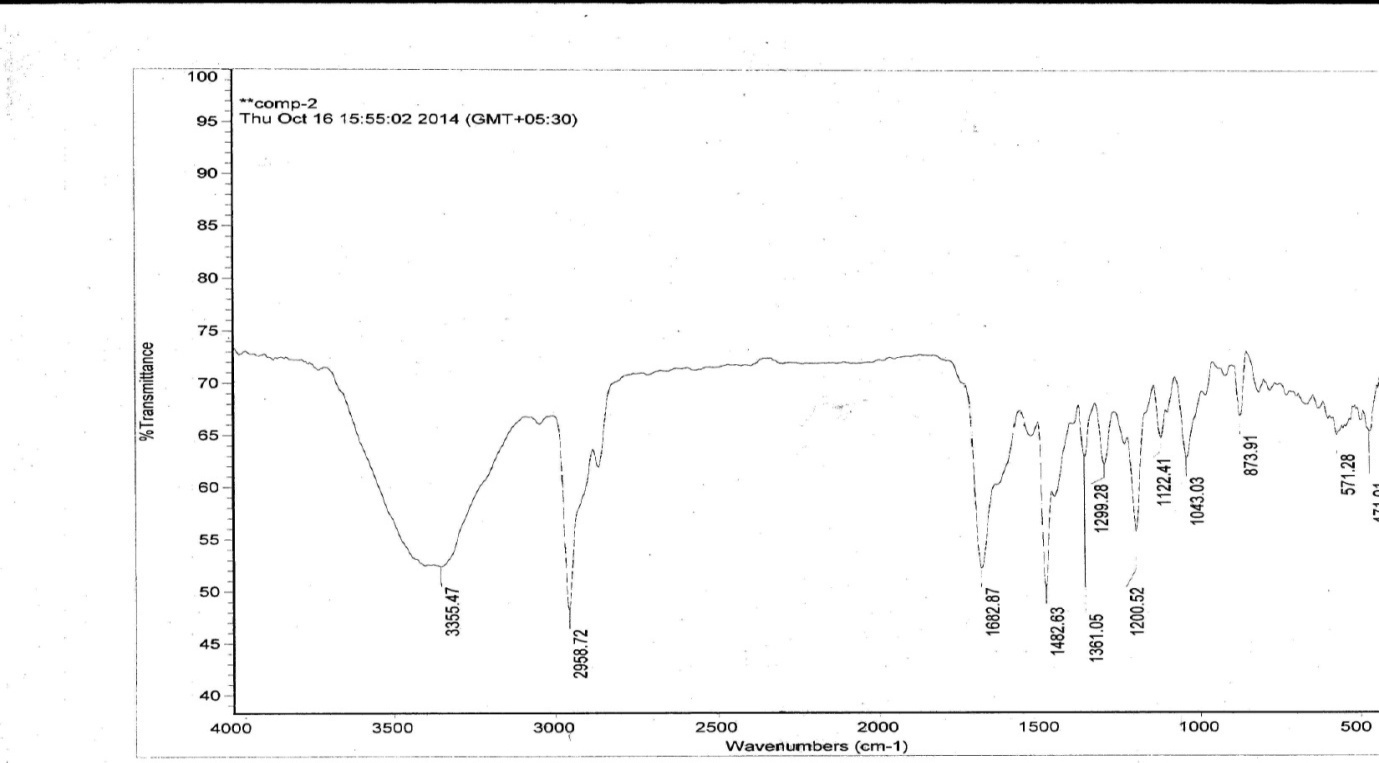
**Figure S1:** 1H NMR spectrum of compound **2** in CDCl3.



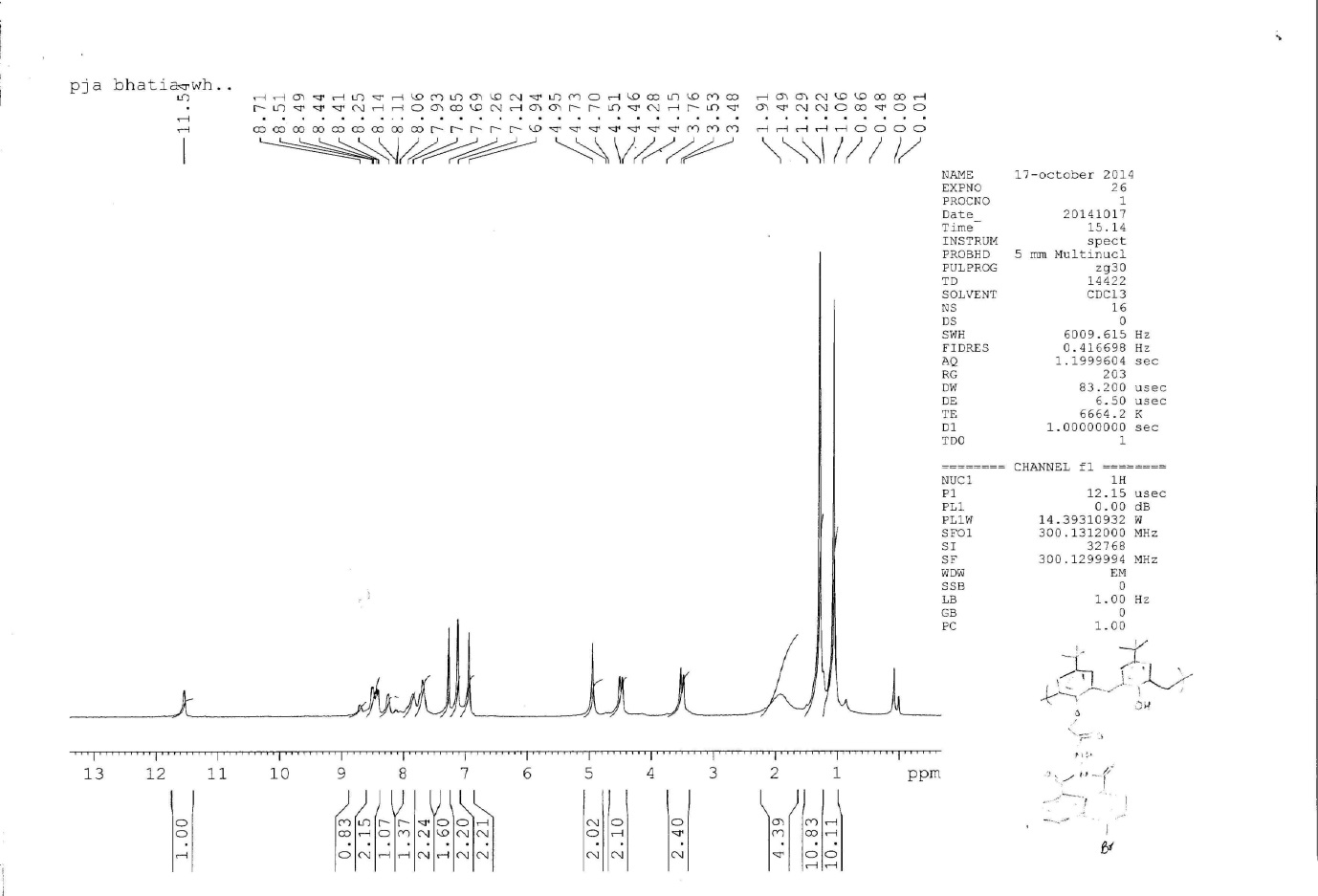
**Figure S2:** FT-IR spectrum of compound **2**.



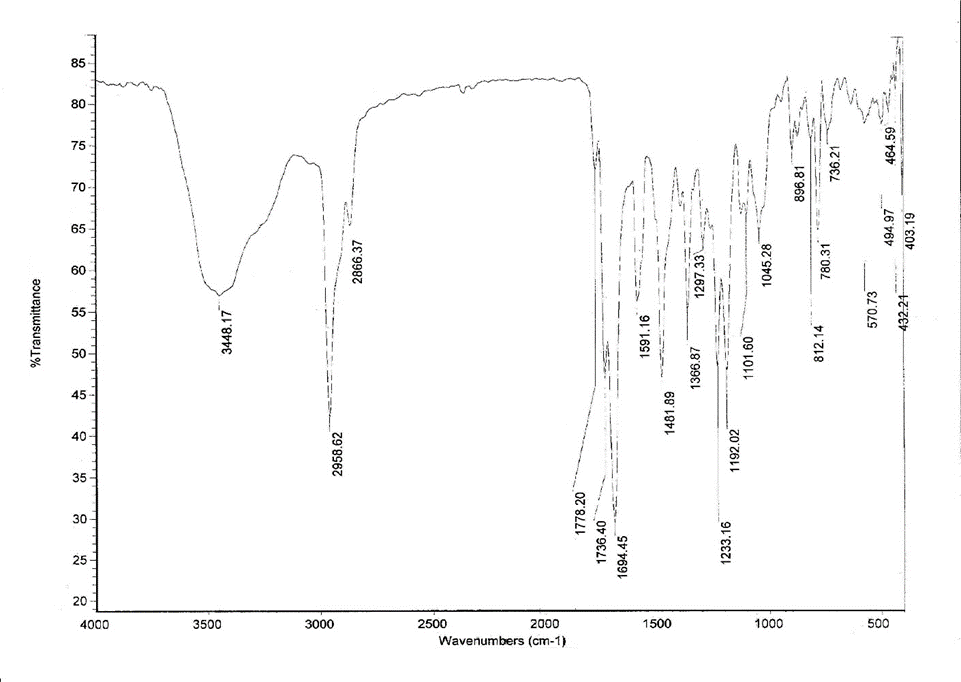
**Figure S3:** 1H NMR spectrum of compound **3** in CDCl3.



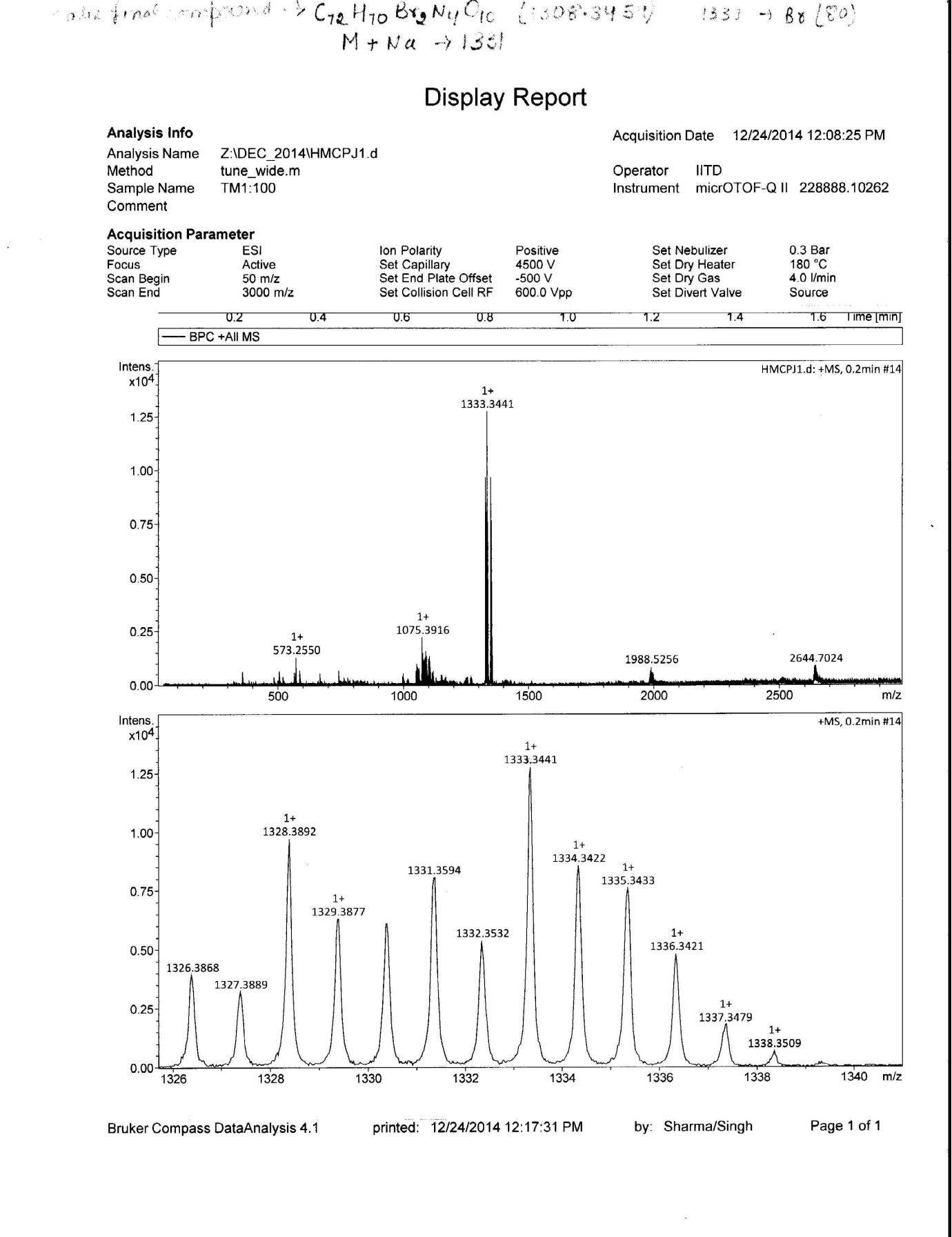
**Figure S4:** FT-IR spectrum of compound **3**.



**Figure S5:** 1H NMR spectrum of compound **4** in CDCl3.



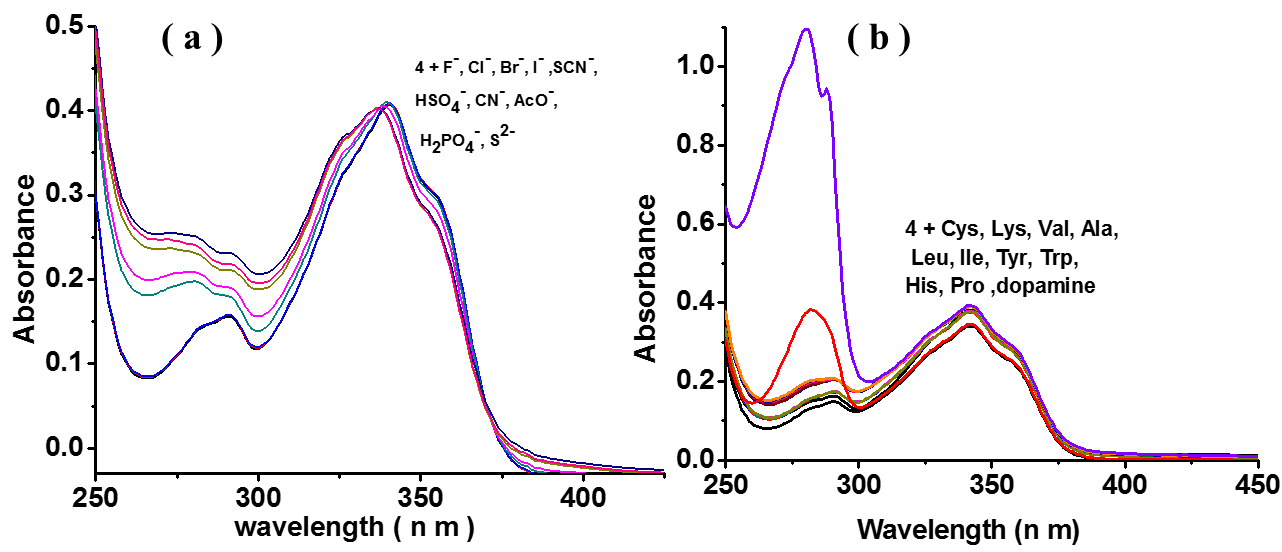
**Figure S6:** FT-IR spectrum of compound **4**.



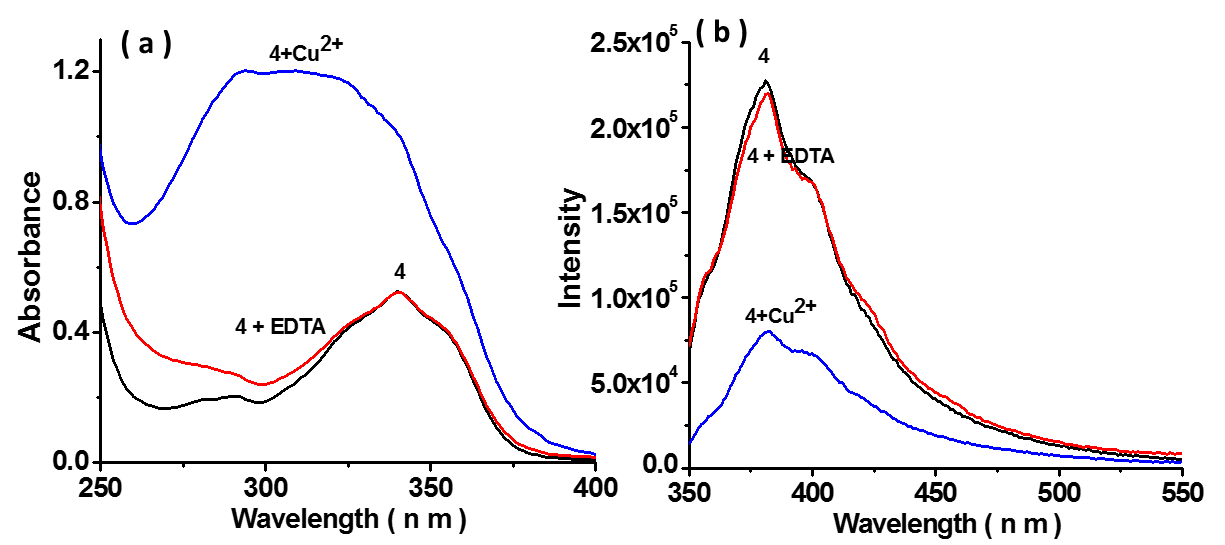
**Figure S7:** HRMS mass spectrum of compound **4.**



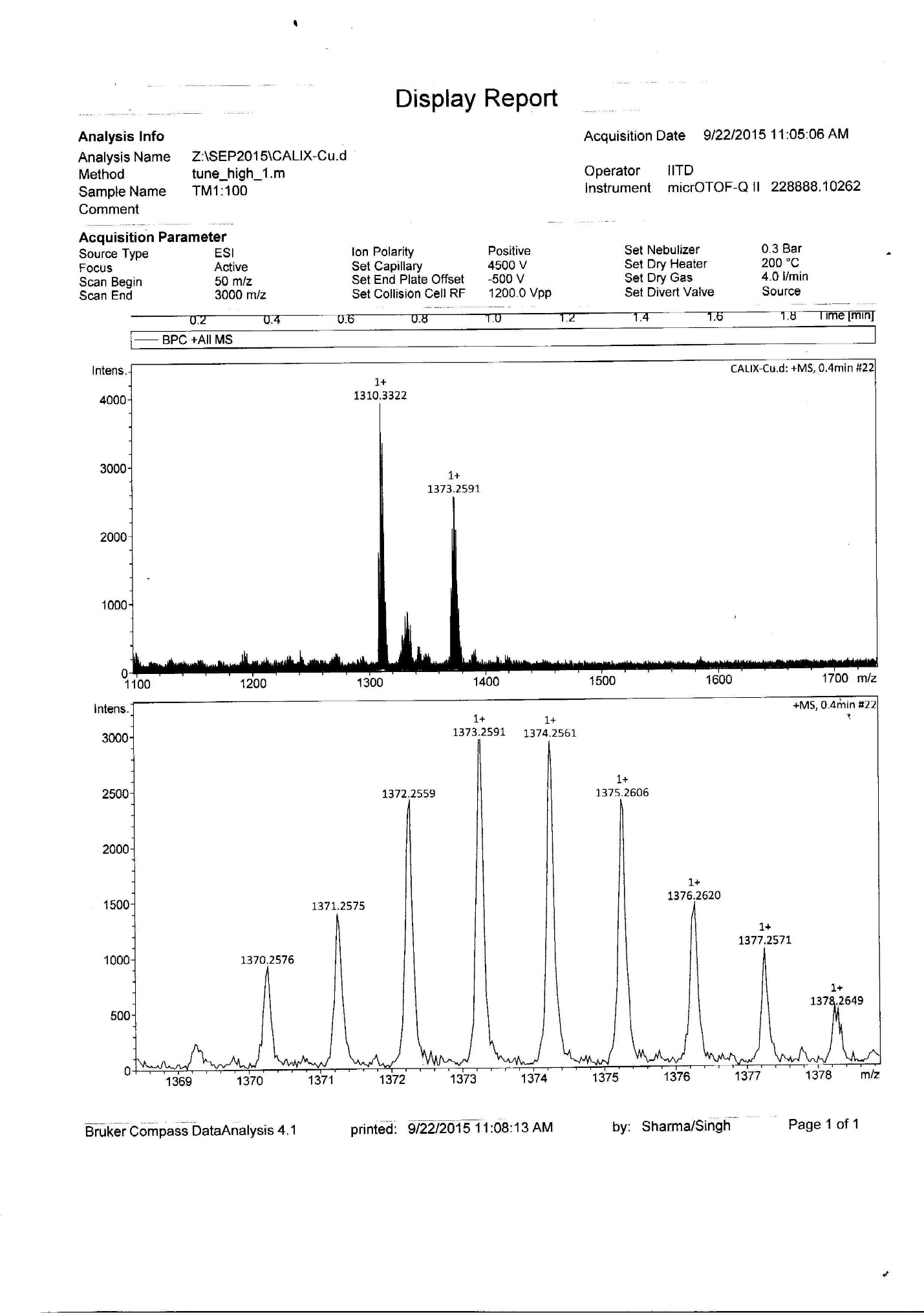
**Figure S8:** Interference studies on **4** with different metal ions (20 equiv) in aqueous-acetonitrile solution (20%, v/v).



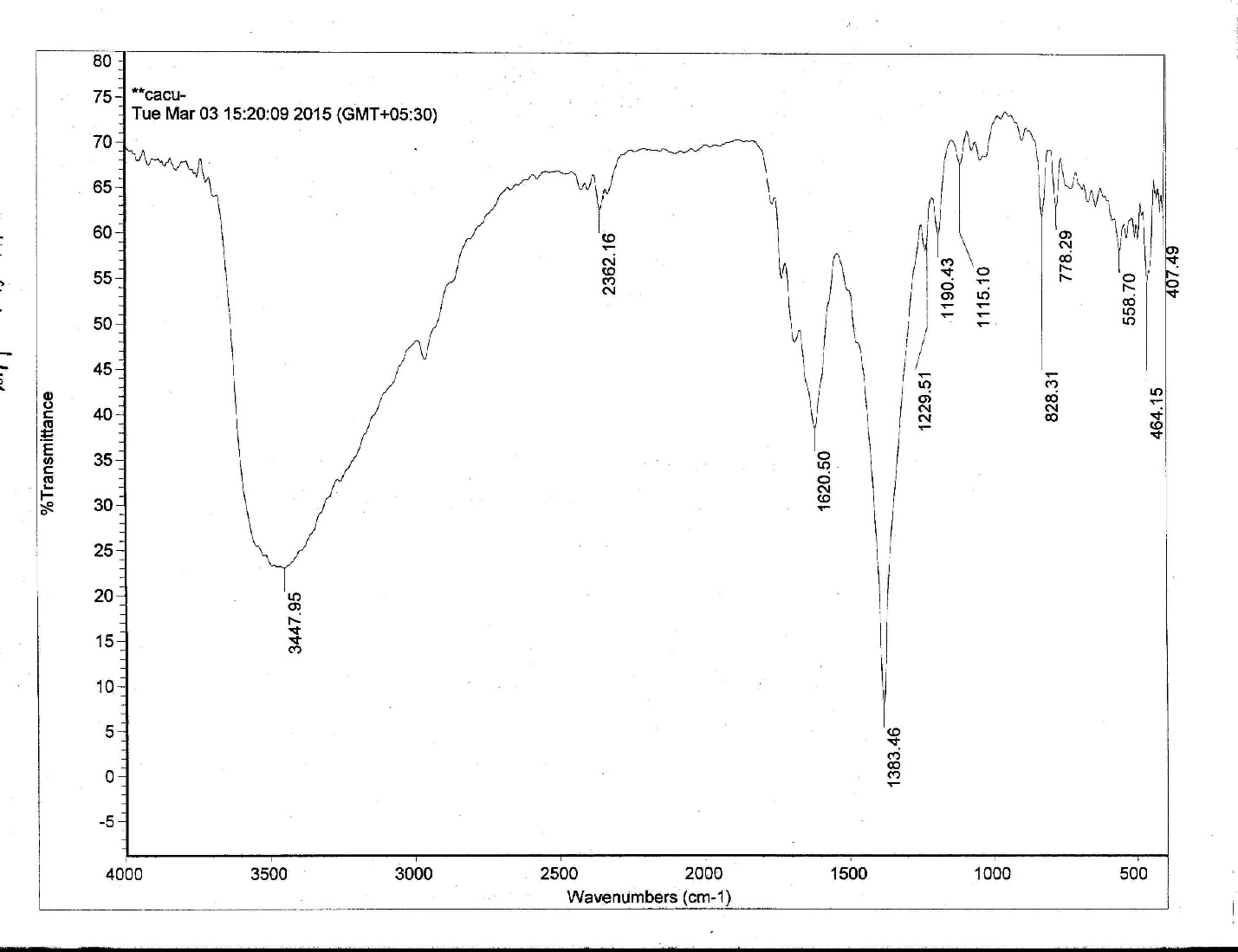
**Figure S9:** Interaction of **4** (10 µM) with different (a) anions (20 equiv) and (b) amino acids (20 equiv) in aqueous-acetonitrile solution (20%, v/v).



**Figure S10:** Re-usability of **4**, **4**-Cu2+ on treatment with EDTA in aqueous-acetonitrile solution (20%).

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**Figure S11:** HRMS spectrum of **4-Cu2+** which showed the molecular ion peak at m/z 1373.2591; 1371.2575, calculated for [C72H70Br2N4O10Cu]+ m/z = 1373.2834; 1371.2844.



**Figure S12:** FT-IR spectrum of **4**-Cu2+ complex in KBr.



**Figure S13:** Interaction studies on **4-Cu2+** complex with different anions (20 equiv) in aqueous-acetonitrile solution (20%, v/v).



**Figure S14:** Fluorescence interaction of **4-Cu2+**with anions(20 equiv) in aqueous-acetonitrile solution (20%, v/v).