

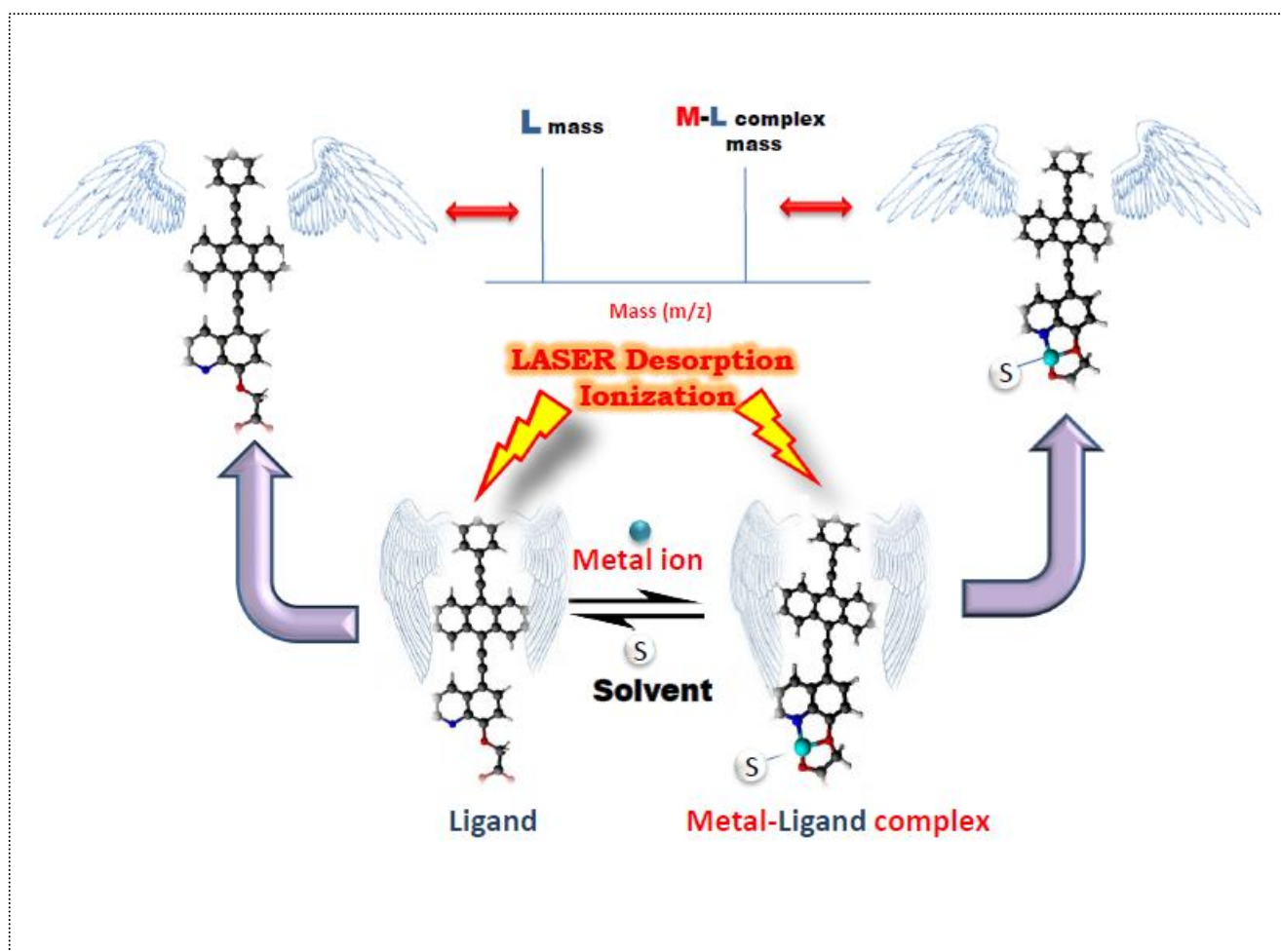
Electronic Supporting Information

Polyaromatic Label-Assisted External Matrix-free Mass Spectrometry: A New Analytical Technique for Selective Detection of Zinc

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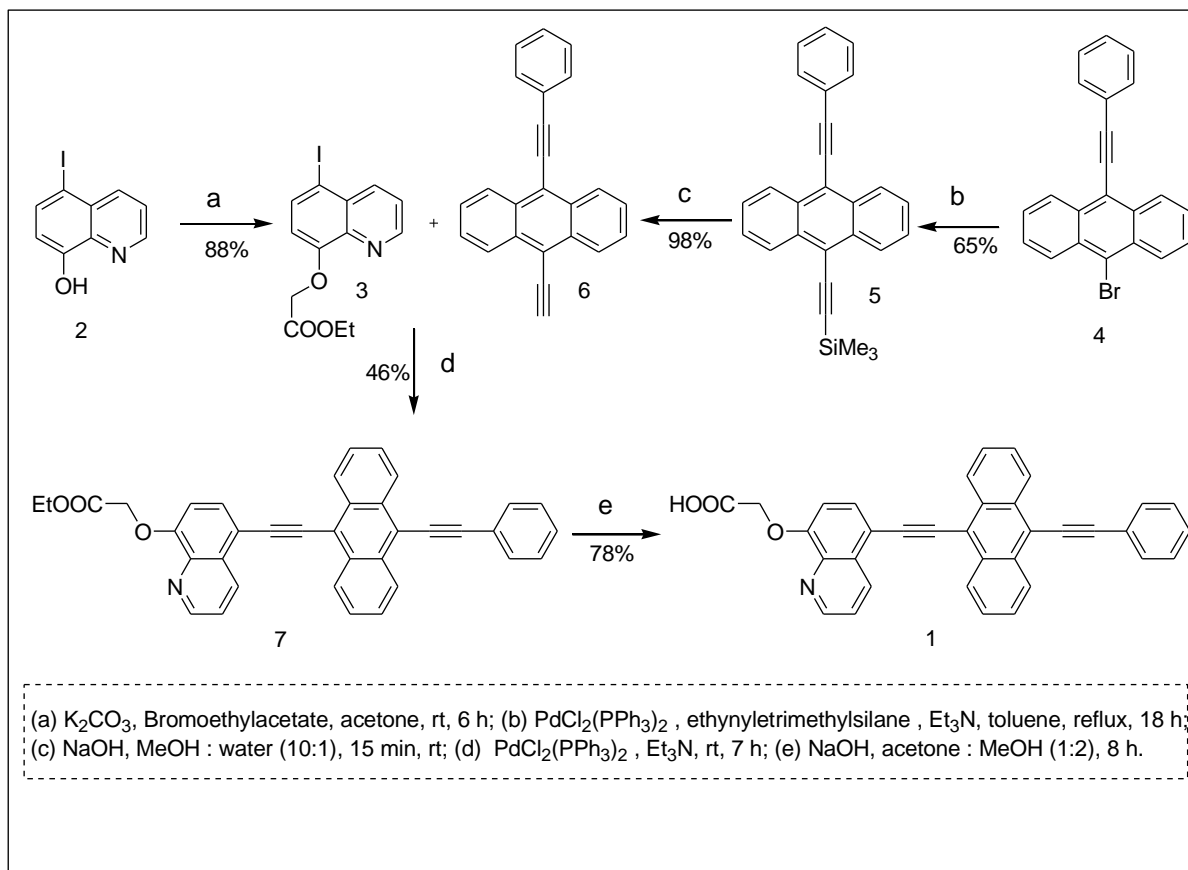
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Experimental Section

Reaction procedure:



Preparation of (5-Iodo-quinolin-8-yloxy)-acetic acid ethyl ester (3): 5-Iodo-quinolin-8-ol (**2**) (400 mg, 1.5 mmol) was dissolved in 50 ml of anhydrous acetone and (400 mg, 2.9 mmol) K_2CO_3 added to it. This mixture was stirred for 10 min at room temperature. Then (200 μ l, 0.22 mmol) bromoethylacetate was added to it and the stirring was another continued for 6 h at rt. After completion of the reaction solvent was evaporated and the reaction was quenched with water and extracted with ethylacetate. Then the organic layer was dried over Na_2SO_4 and concentrated. The residue was then purified by column chromatography (Hexane: Ethyl acetate/ 4:1) to afford (5-Iodo-quinolin-8-yloxy)-acetic acid ethyl ester (**2**) as white solid; yield: 370 mg (69 %) ; R_f = 0.35 (hexane : ethylacetate); 1H -NMR (400 Mz, $CDCl_3$): 8.91 (1H, bs), 8.33(1H, d, J = 8.2 Hz), 8.96 (1H, d, J = 8.2 Hz), 7.52-7.49 (1H, m), 6.75 (1H, d, J = 8Hz), 4.93 (2H, s), 4.25 (2H, q, J = 6.8 Hz), 1.25 (3H, t, J = 6.8 Hz); ^{13}C -NMR (100 MHz, $CDCl_3$): 168.6, 154.8, 150.3, 141.1, 140.6, 137.2, 131.1, 123.6, 111.4, 88.5, 66.4, 61.8, 14.4. . HRMS Calcd for $C_{13}H_{12}INO_3 + H^+$ 357.9935 found 357.9928.

Trimethyl-(10-phenylethynyl-anthracen-9-ylethynyl)-silane (5):

To a solution of 9-Bromo-10-phenylethynyl-anthracene (**4**) (700mg, 2.05 mmol) in a mixed solvent of triethylamine (40 mL) and Toluene (30 ml) was added ethynyletrimethylsilane (0.9 ml, 6.17 mmol), PdCl₂(PPh₃)₂ (40 mg, 0.06 mmol) under N₂. The reaction mixture was refluxed for 18 h at 90 °C and cooled to room temperature. 20 ml saturated solution of NH₄Cl was added and stirred for 30 min. Aqueous layer was extracted with EtOAc (100 mL×2), and the organic layer was washed with H₂O and brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (Hexane/EtOAc = 3:1) to afford desired compound as yellow gummy mass; yield 398 mg (54 %, 87 % on the basis of recovery of starting material); R_f = 0.8 (Hexane); ¹H-NMR (400 Mz, CDCl₃): 8.68 (2H, dd, J₁ = 4 Hz, J₂ = 2.8 Hz), 8.60 (2H, dd, J₁ = 2.8 Hz, J₂ = 4 Hz), 7.78 (2H, dd, J₁ = 1.6 Hz, J₂ = 8 Hz), 7.64 – 7.61 (4H, m), 7.48 – 7.42 (3H, m), 0.43 (9H, s). ¹³C-NMR (100 MHz, CDCl₃): 132.4, 131.9, 131.7, 128.7, 128.6, 127.3, 127.2, 126.9, 126.8, 123.4, 118.7, 118.3, 108.2, 102.4, 101.6, 86.4, 0.2. HRMS Calcd for C₂₇H₂₂Si + H⁺ 375.1564 found 375.1548.

9-Ethynyl-10-phenylethynyl-anthracene (6): Trimethyl-(10-phenylethynyl-anthracen-9-ylethynyl)-silane (**5**) (200 mg, .56 mmol) is taken in methanol (10 ml). A solution of (32 mg, 0.56 mmol) KOH in (1 ml) water was added to the previous solution and the mixture was stirred for 15 min. The solvent was evaporated and 20% HCl solution (5 ml) was added to it followed by the addition of EtOAc. Then the organic layer was dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography (hexane) to afford the desired product as yellow solid; yield 141 mg (88%); R_f = 0.6 (Hexane); ¹H-NMR (400 Mz, CDCl₃): 6.89 (2H, dd, J₁ = 2.4 Hz, J₂ = 4 Hz), 8.63 (2H, dd, J₁ = 2.4 Hz, J₂ = 4 Hz), 7.78 (2H, dd, J₁ = 1.2 Hz, J₂ = 8 Hz), 7.65 – 7.62 (4H, m), 7.48 – 7.43 (3H, m), 4.08 (1H, s), ¹³C-NMR (100 MHz, CDCl₃): 132.7, 132.5, 131.9, 131.7, 131.6, 129.2, 128.8, 128.6, 128.4, 127.2, 127.1, 126.8, 123.3, 119.1, 117.1, 102.5, 89.7, 86.2, 80.4. HRMS Calcd for C₂₄H₁₄ + H⁺ 303.1168 found 303.1154.

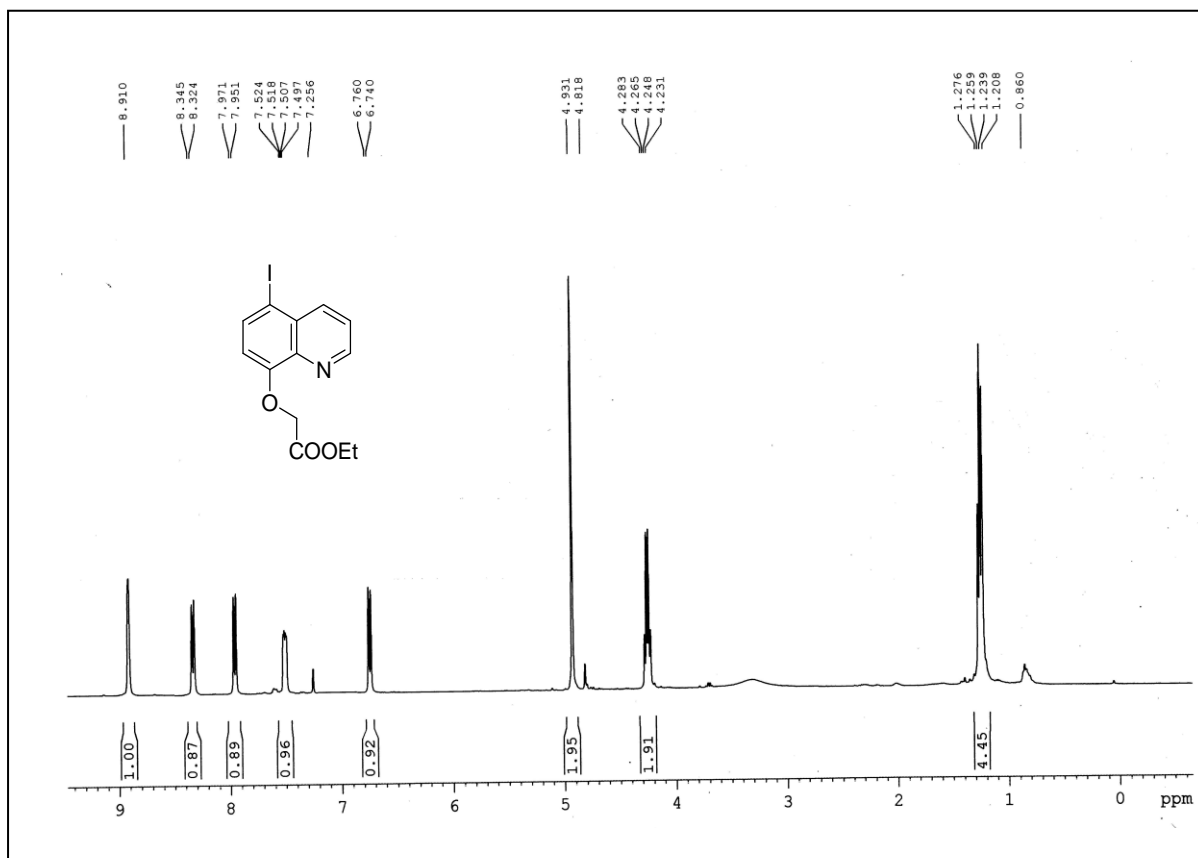
[5-(10-Phenylethynyl-anthracen-9-ylethynyl)-quinolin-8-yloxy]-acetic acid ethyl ester

(7): In 10 ml triethyl amine compound **3** (100 mg, 0.28) was taken. To this solution PdCl₂(PPh₃)₂ was added and the mixture was stirred for 10 min. Finally to this mixture catalytic amount of CuI was added followed by the addition of compound **6** (0.95 mg, 0.33) was added and stirred for another 7 h. Finally the reaction was quenched with water and it is diluted with ethyl acetate. Then organic layer was washed with brine and dried over Na₂SO₄. The residue was purified by Flash column Chromatography (silica mesh size 230-400). (Hexane/EtOAc 7:1) to afford compound xx as red coloured powder; yield 80 mg (54 %); R_f = 0.4 (Hexane/ethyl acetate = 3:1); ¹H-NMR (400 Mz, CDCl₃): 9.05 (1H, bs), 8.93 (1H, d, J = 8.4 Hz), 8.72 – 8.70 (4H, m), 7.95 (1H, d, J = 7.6 Hz), 7.77 (2H, d, J = 7.2 Hz), 7.64 (5H, bs), 7.43 (2H, J = 7.2 Hz), 7.42 (1H, s), 7.03 (1H, d, J = 8 Hz), 5.02 (2H, s), 4.29 (2H, q, J = 6.8 Hz), 1.26 (3H, t, J = 6.8 Hz). ¹³C-NMR (100 MHz, CDCl₃): 168.6, 154.6, 150.1, 135.3,

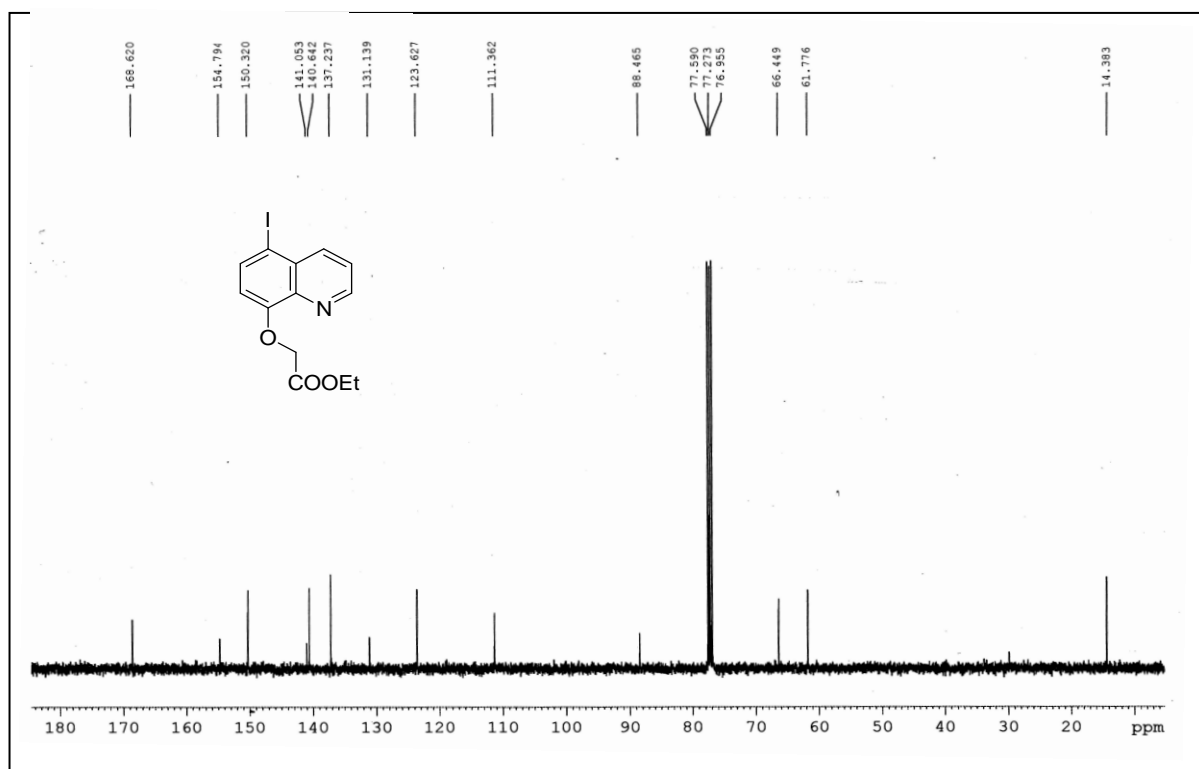
132.4, 132.3, 131.9, 131.7, 130.0, 129.0, 128.8, 128.6, 127.6, 127.3, 127.1, , 123.6, 122.9, 119.0, 118.4, 114.7, 109.7, 102.9, 99.2, 91.0, 86.6, 66.5, 61.9, 22.9, 14.35. HRMS Calcd for $C_{37}H_{25}NO_3 + H^+$ 532.1907 found 532.1896.

[5- (10 – Phenylethynyl – anthracen – 9 - ylethynyl) – quinolin – 8 - yloxy] – acetic acid

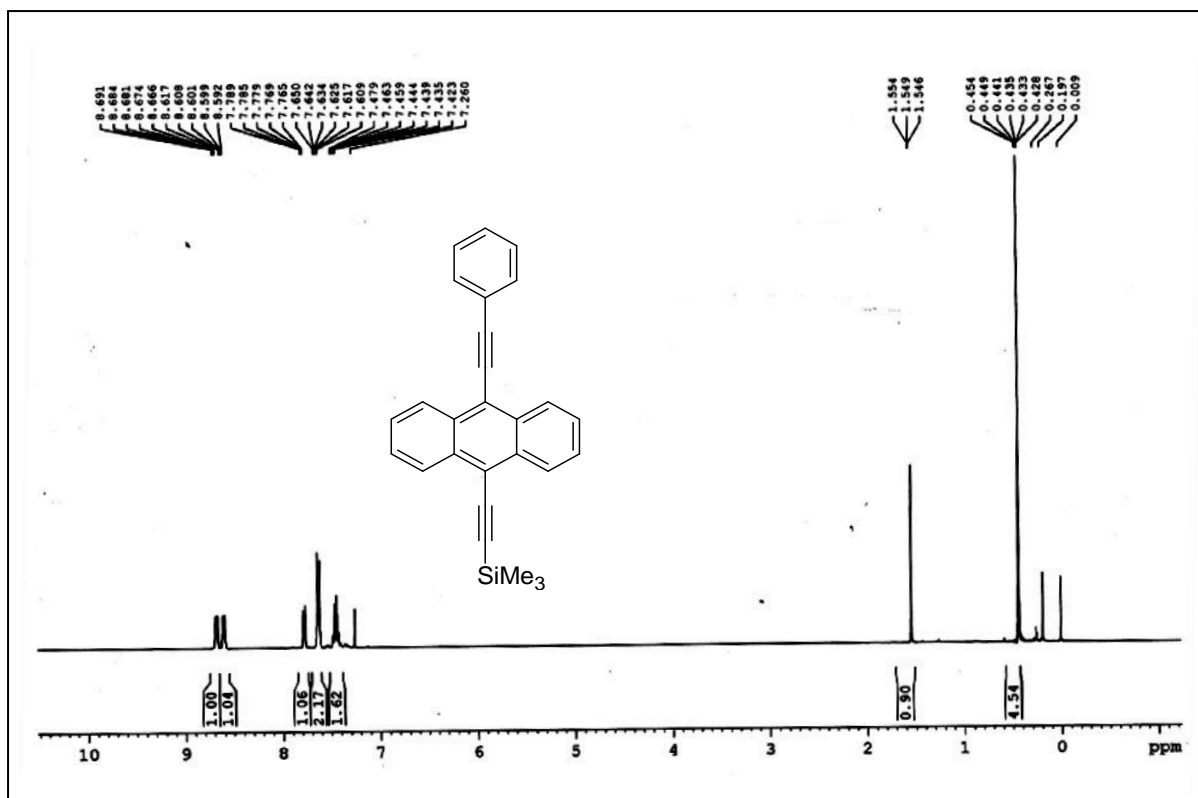
(1) : compound **7** (50 mg, 0.1 mmol) was taken in 7 ml mixed solvent [acetone:methanol = 1:2]. To this solution NaOH was added and stirred for 8 h. Then the reaction mixture was quenched with 20% HCl. Then the compound was extracted twice with ethyl acetate. Then the compound was further purified by precipitation from ethyl acetate petether solution. The product obtained as red solid; yield: 35 mg (72 %). 1H -NMR (400 Mz, d_6 -DMSO): 9.09 (1H, bs), 9.01 (1H, d, $J = 8$ Hz), 8.76-8.69 (4H, m), 8.24 (1H, d, $J = 8.1$ Hz), 7.95 (1H, bs), 7.89 – 7.82 (5H, m), 7.53 (3H, s), 7.39 (1H, d, $J = 8.1$ Hz), 5.1 (2H, s). ^{13}C -NMR (100 MHz, d_6 -DMSO): 170.2, 154.4, 149.7, 133.5, 132.2, 132.0, 131.8, 129.9, 129.5, 129.3, 129.2, 128.5, 128.3, 127.4, 125.4, 124.1, 123.6, 123.2, 122.7, 118.2, 112.8, 111.3, 103.4, 100.0, 90.6, 86.3, 66.0. HRMS: Calcd for $C_{35}H_{22}NO_3 + H^+$ 504.1594 found 504.1608.



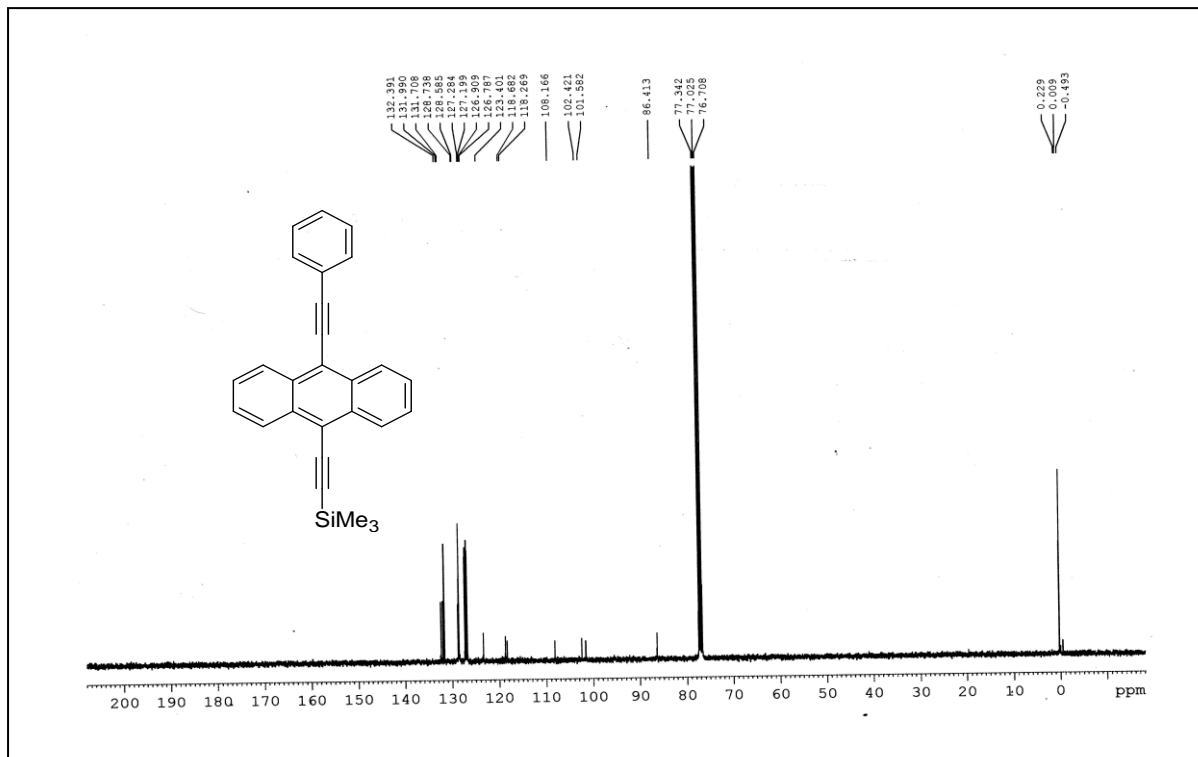
¹H-NMR(400 MHz, CDCl₃) of compound 2



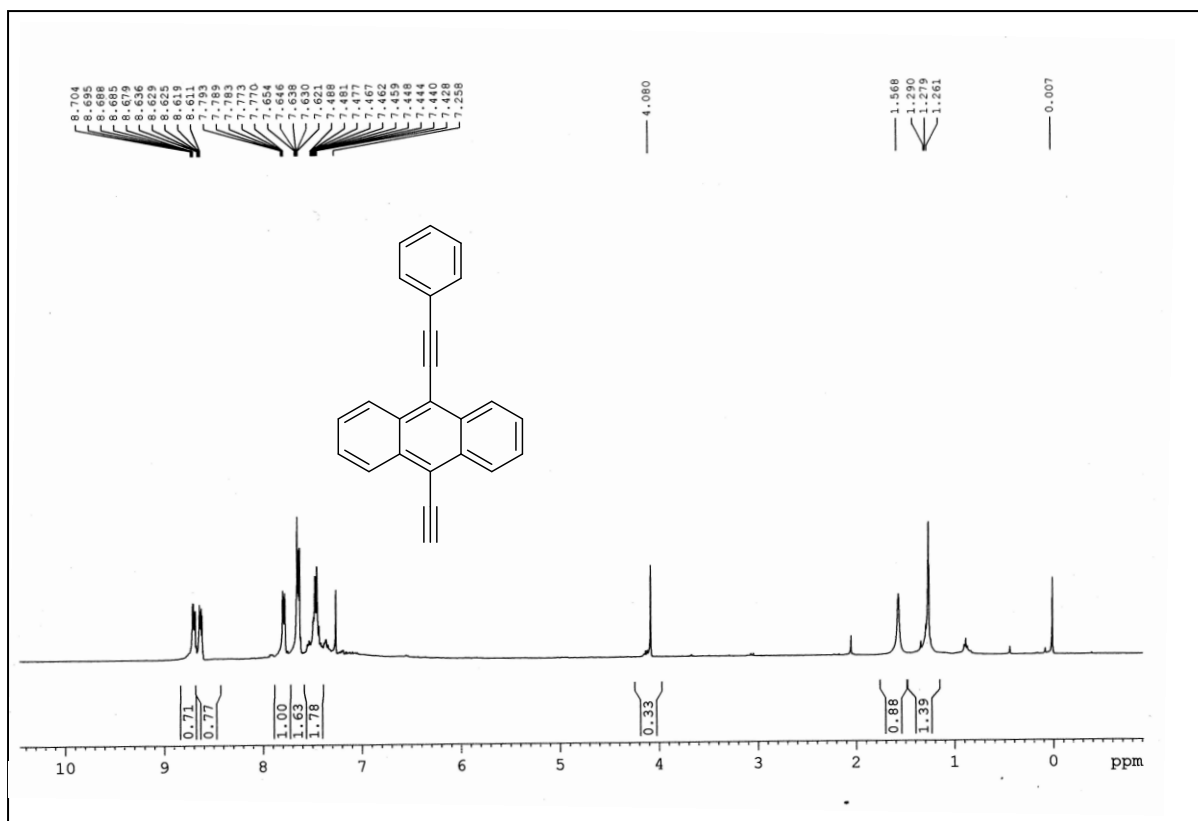
¹³C-NMR (100 MHz, CDCl₃) of compound 2



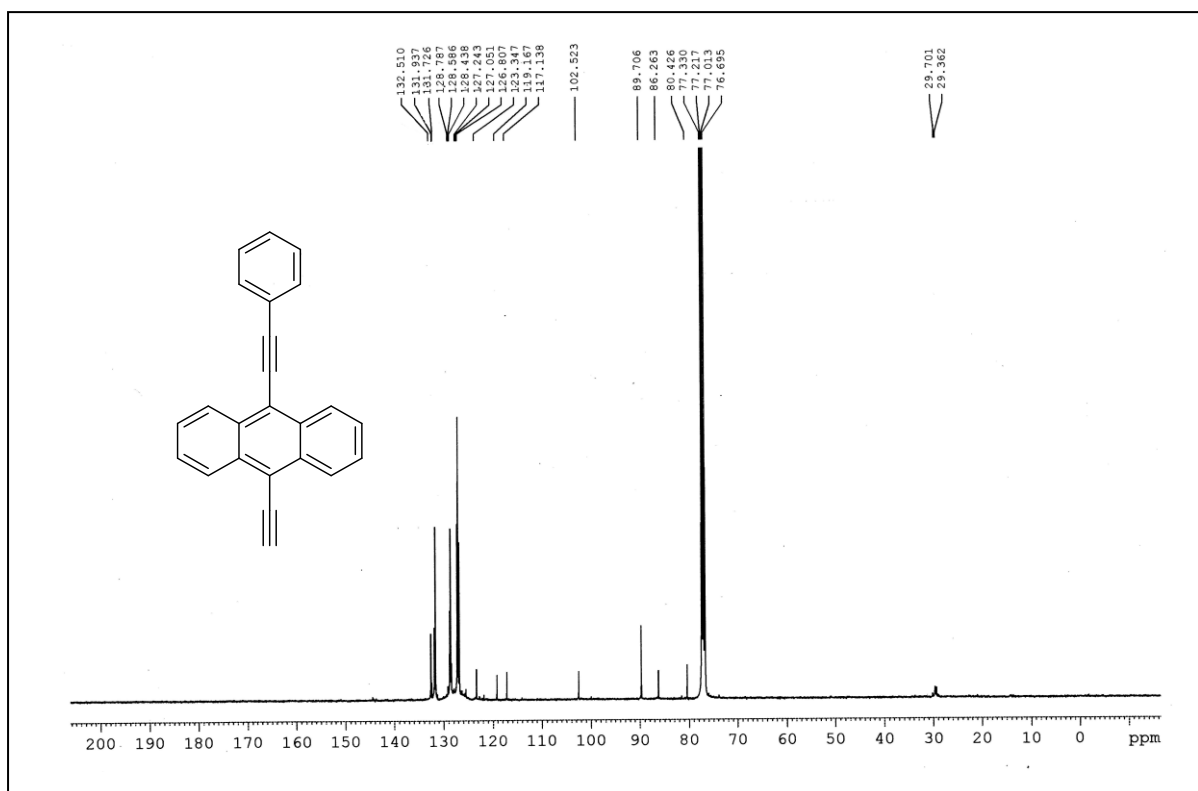
¹H-NMR(400 MHz, CDCl₃) of compound 5



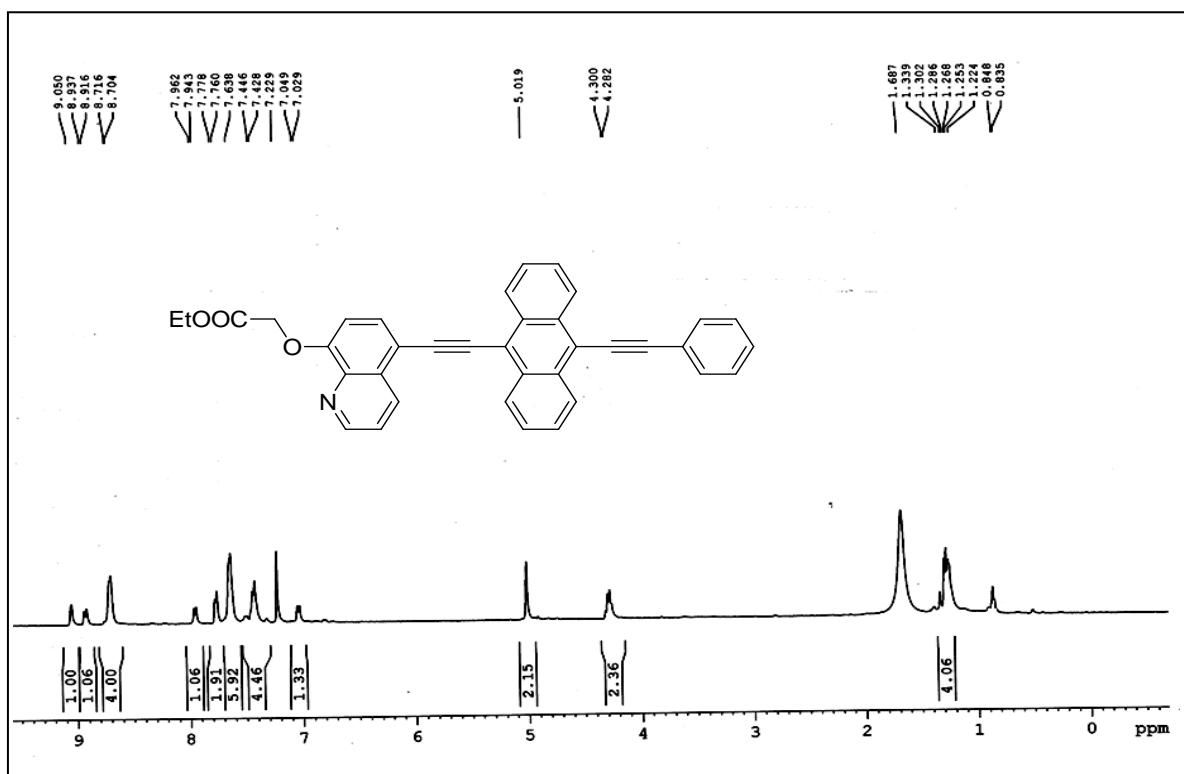
¹³C-NMR (100 MHz, CDCl₃) of compound 5



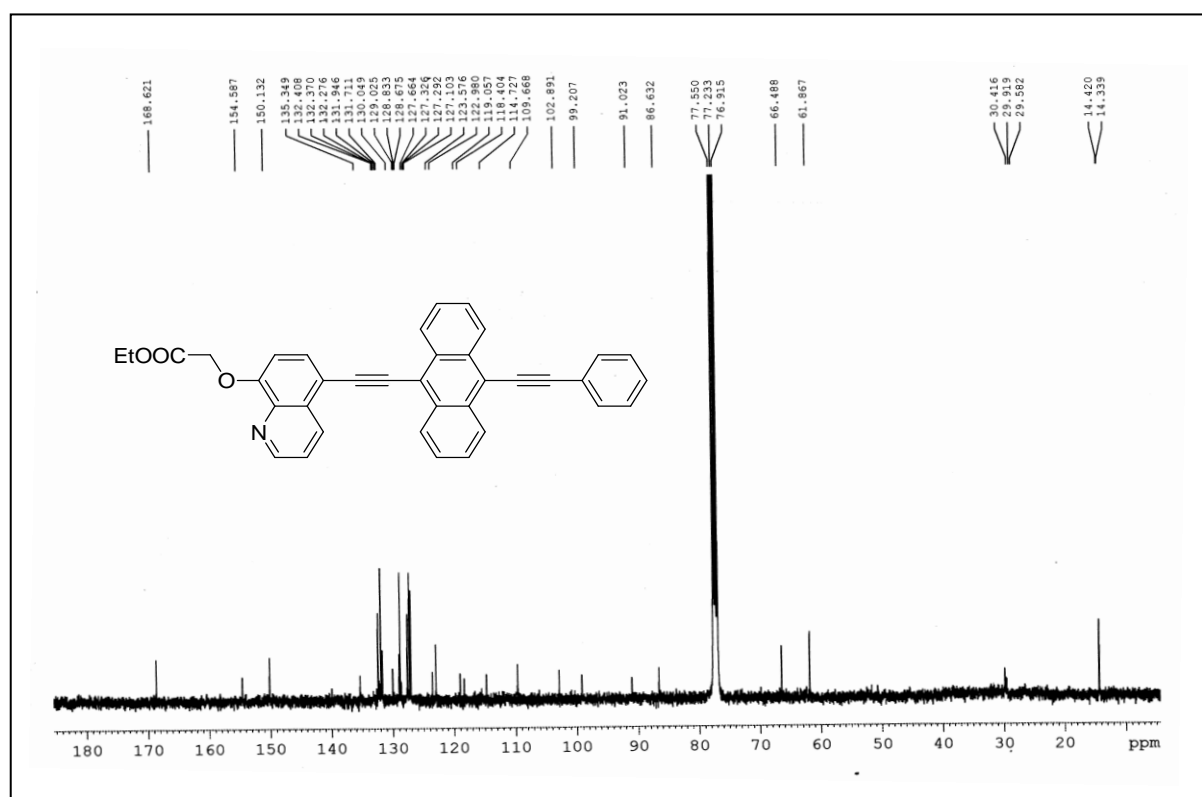
¹H-NMR(400 MHz, CDCl₃) of compound 6



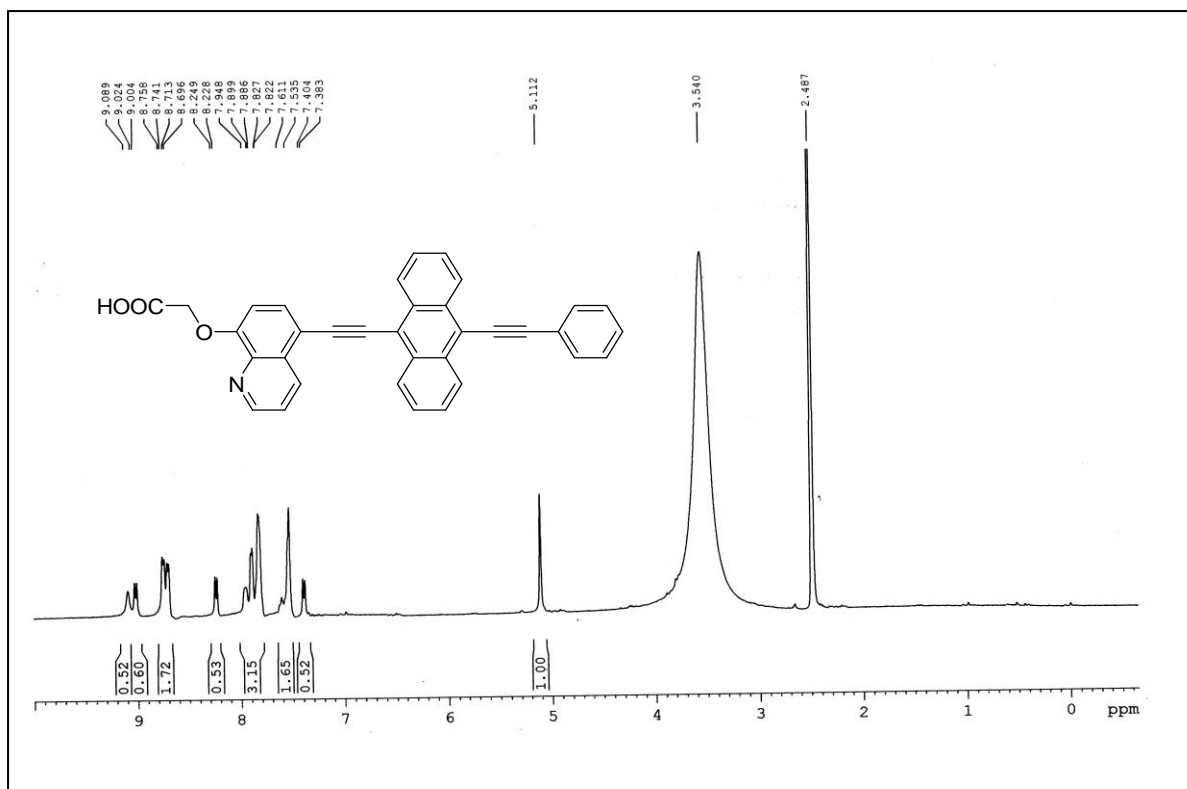
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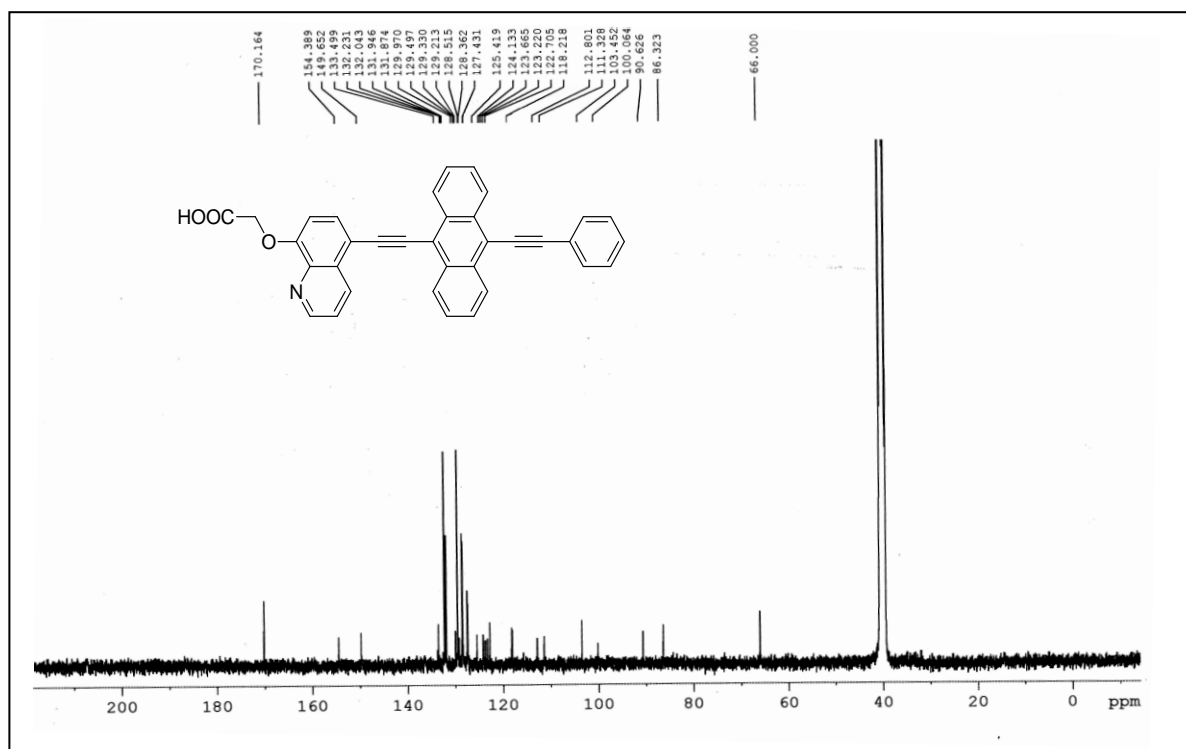
¹H-NMR(400 MHz, CDCl₃) of compound 7



¹³C-NMR (100 MHz, CDCl₃) of compound 7



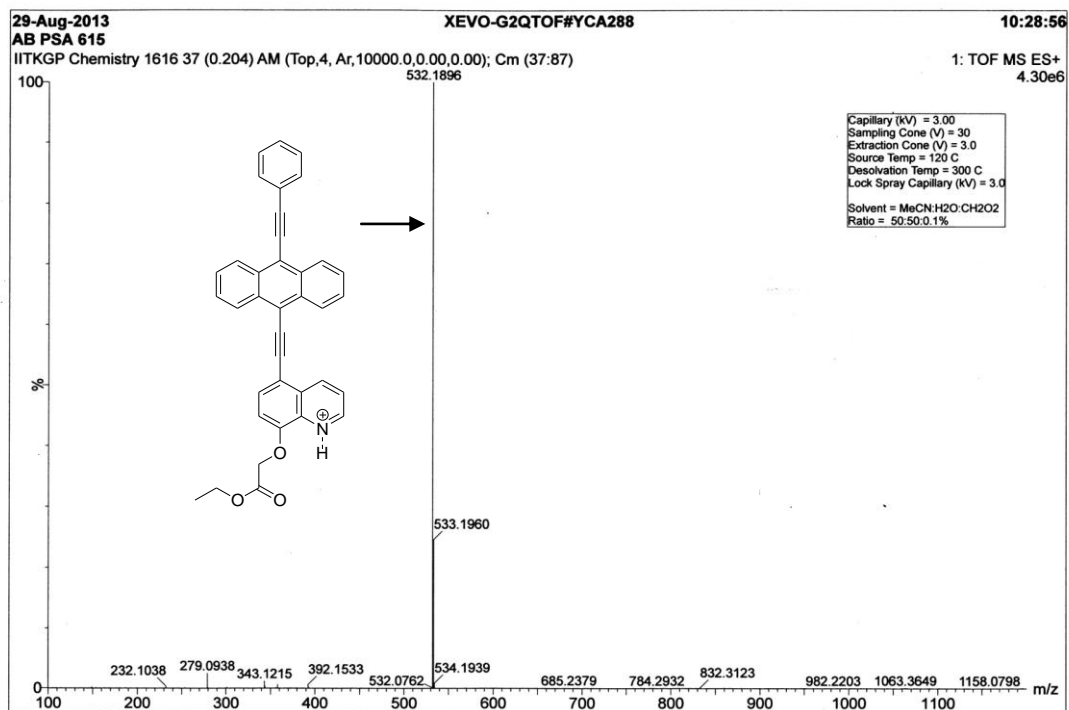
¹H-NMR(400 MHz, d₆-DMSO) of compound 1



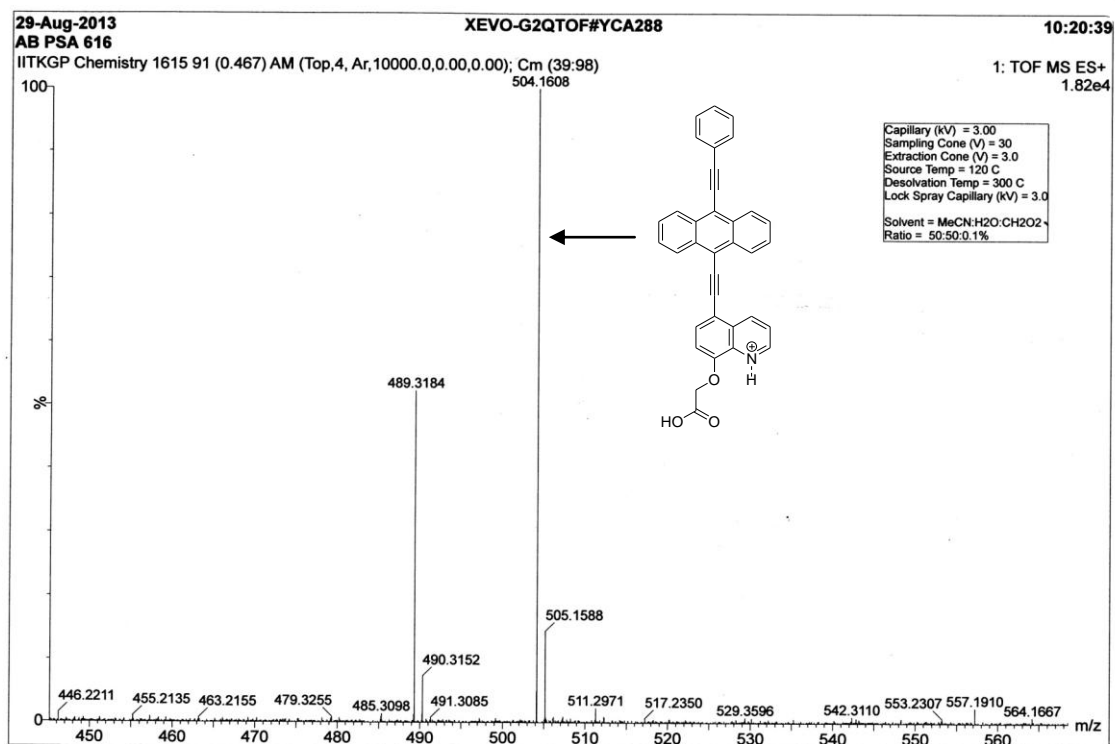
¹³C-NMR (100 MHz, d₆-DMSO) of compound 1

Ligand = Compound1

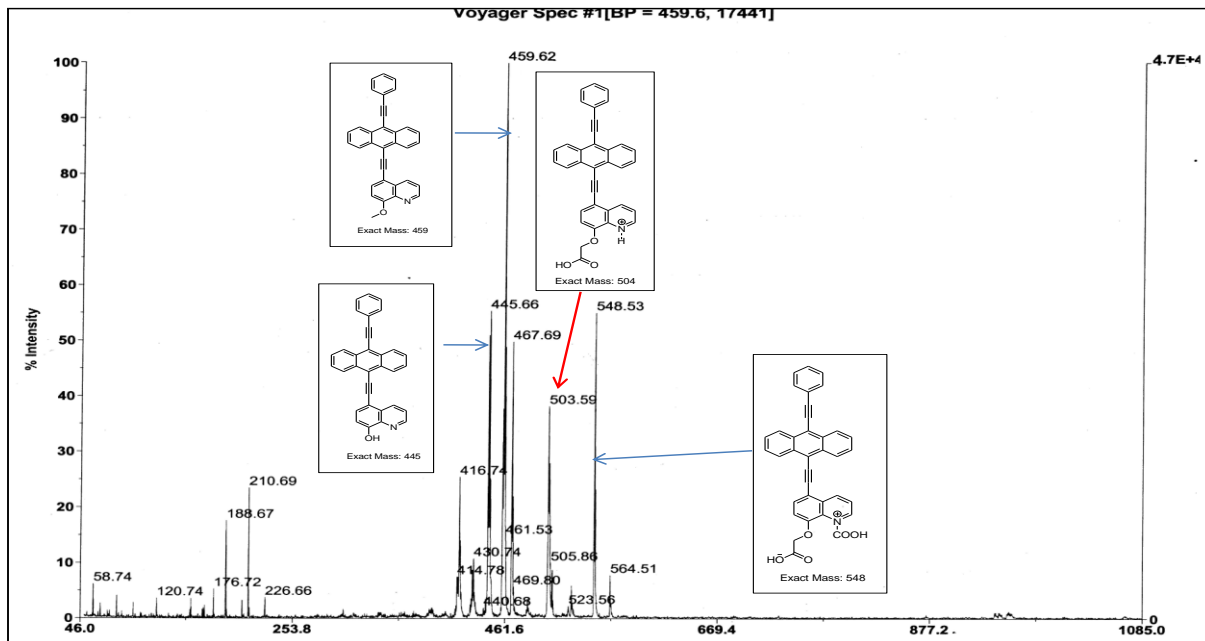
HRMS SPECTRUM OF SYNTHESISED LIGAND PRECURSOR:



HRMS SPECTRUM OF SYNTHESISED LIGAND:

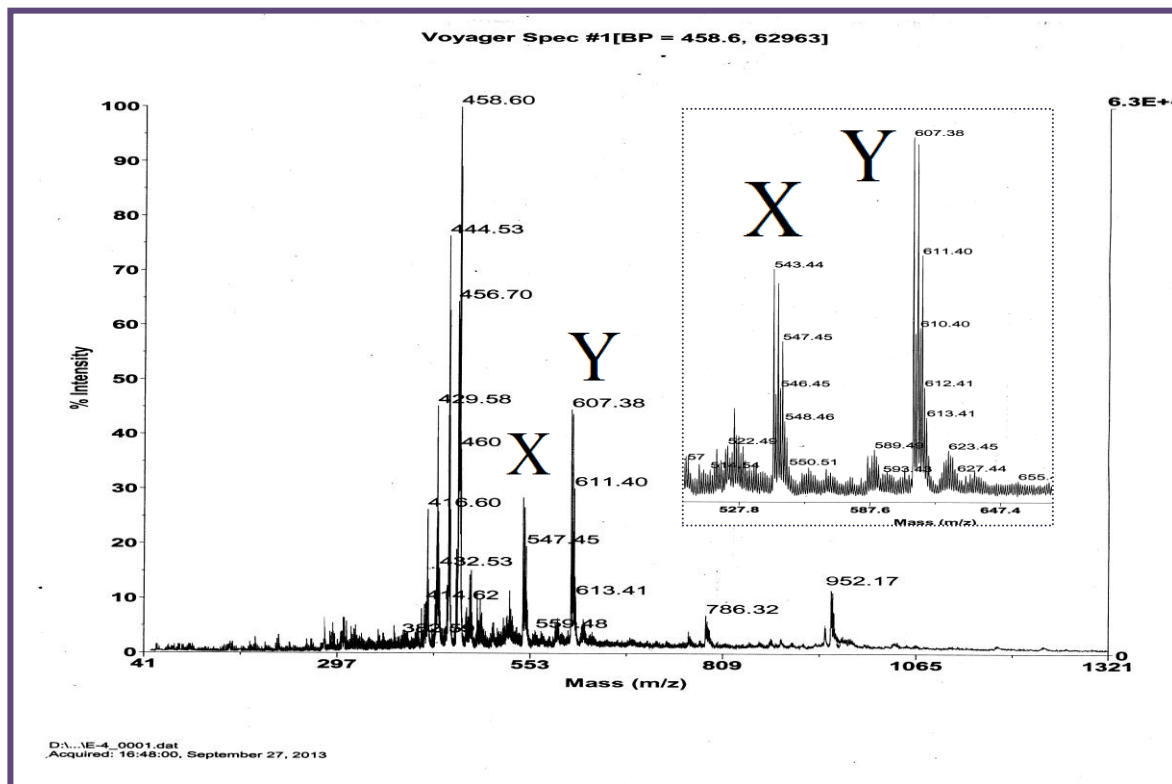


Laser Desorption Ionization Spectrum of Ligand:

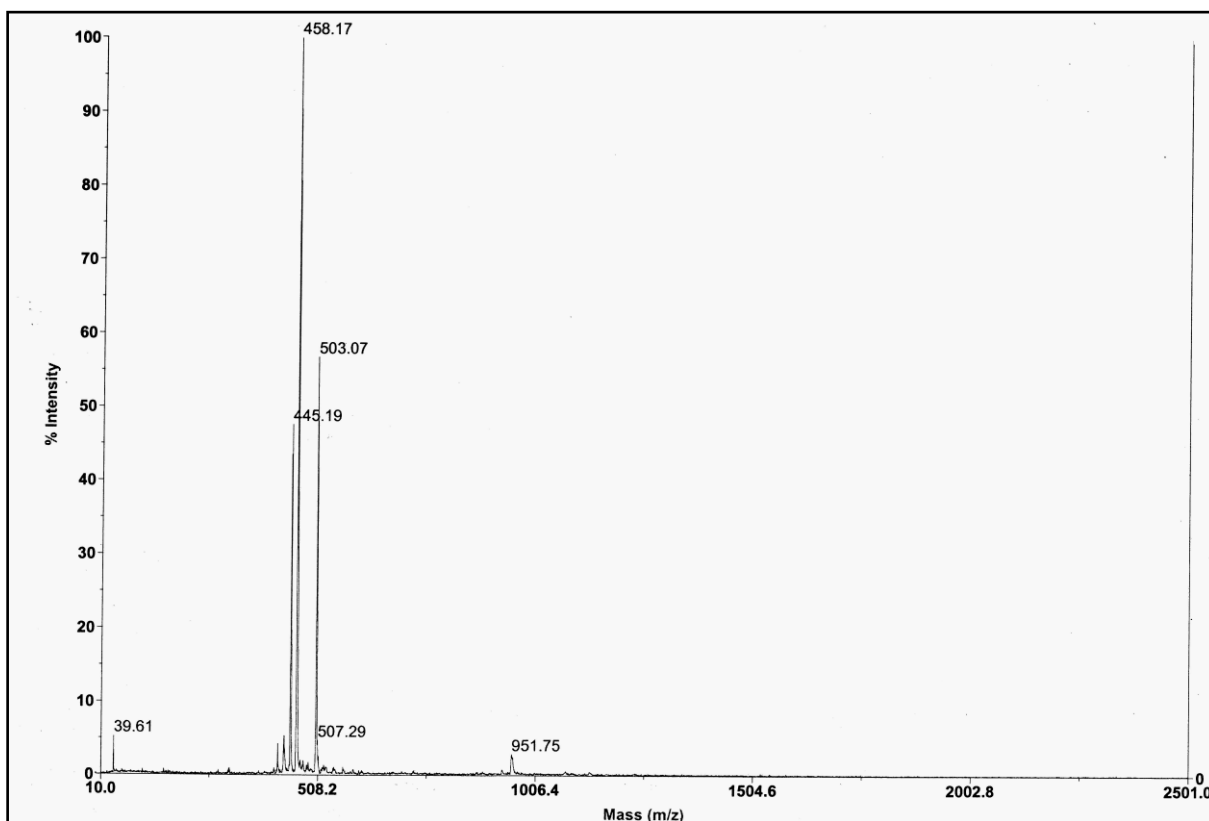


Concentration of the ligand was 1×10^{-5} (M). 2 μ l was spotted in the well.

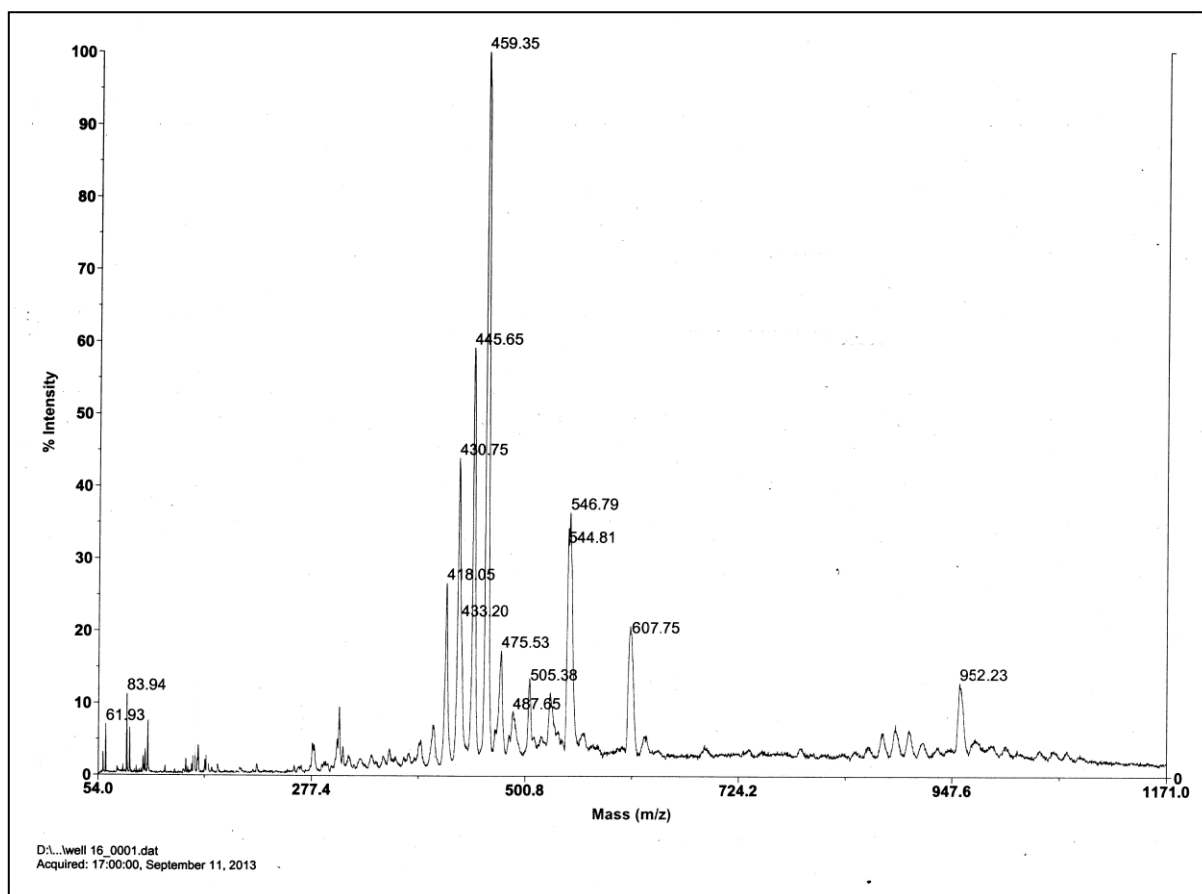
Ligand incubated with Zinc perchlorate : (X = 2:1 and Y = 1:1 (ligand:metal)complex.



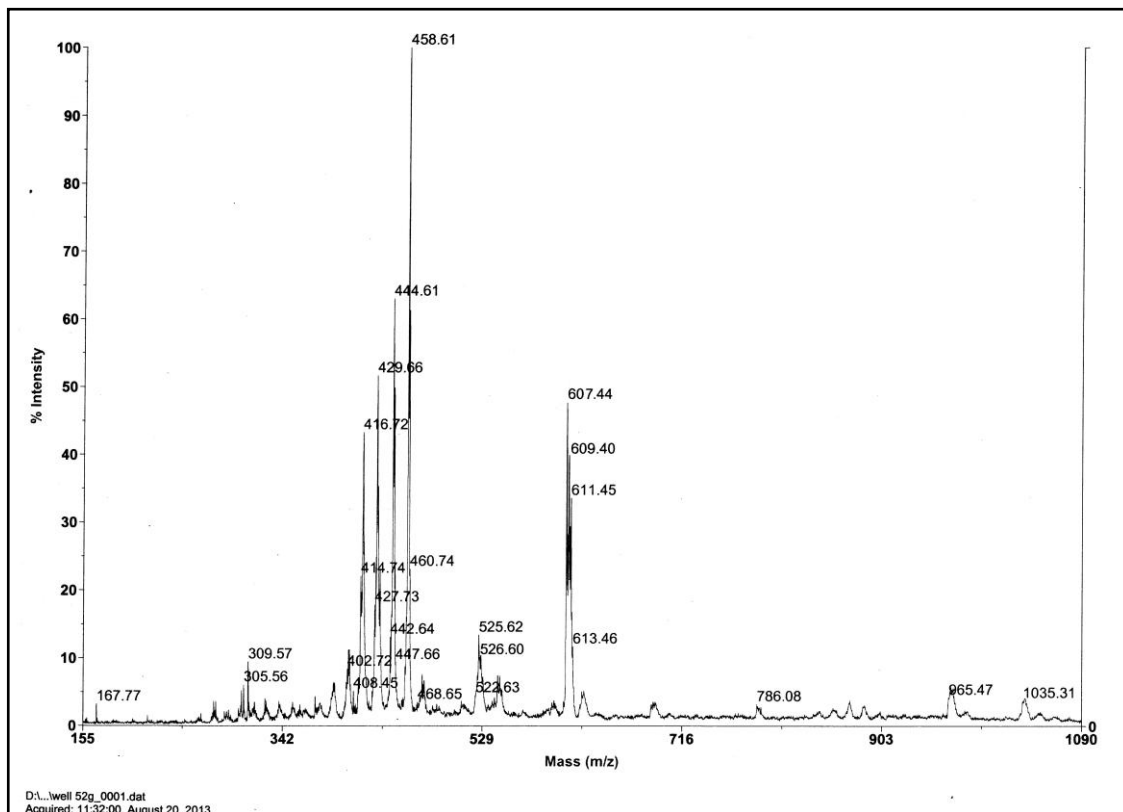
Ligand (Compound 1) incubated with Cu²⁺:



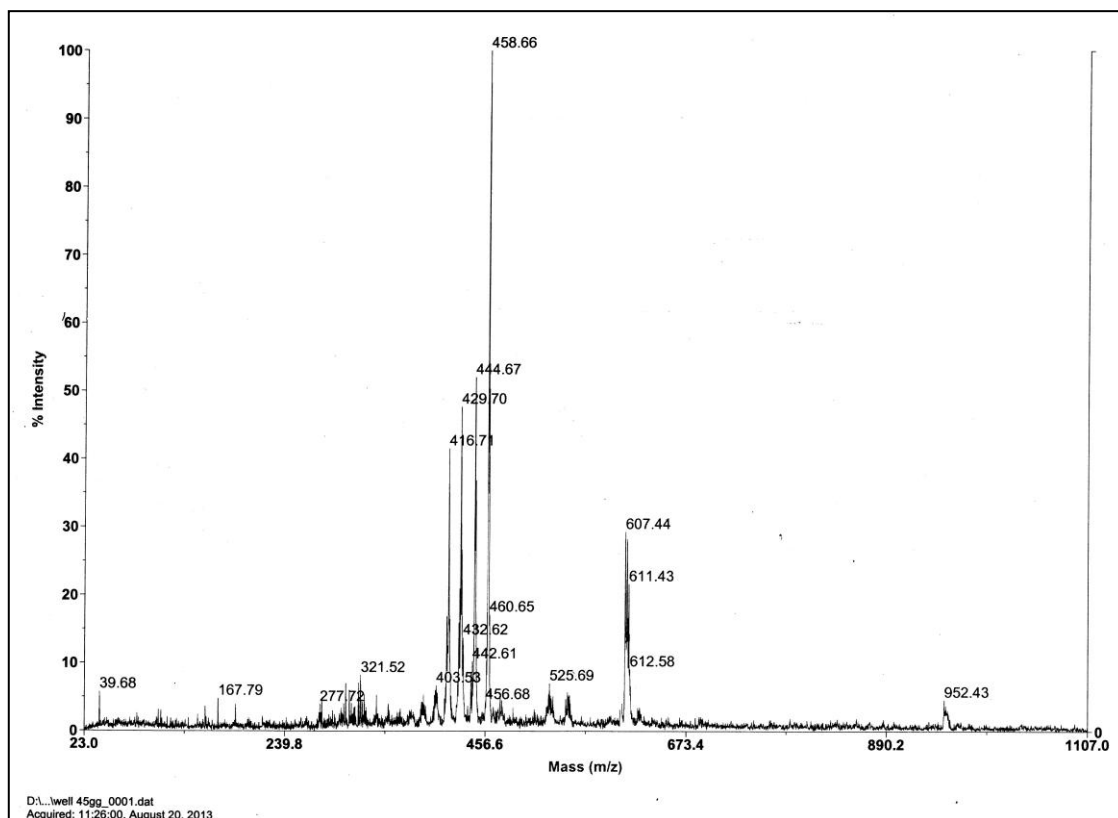
Ligand incubated with Cu²⁺ + Zn²⁺:



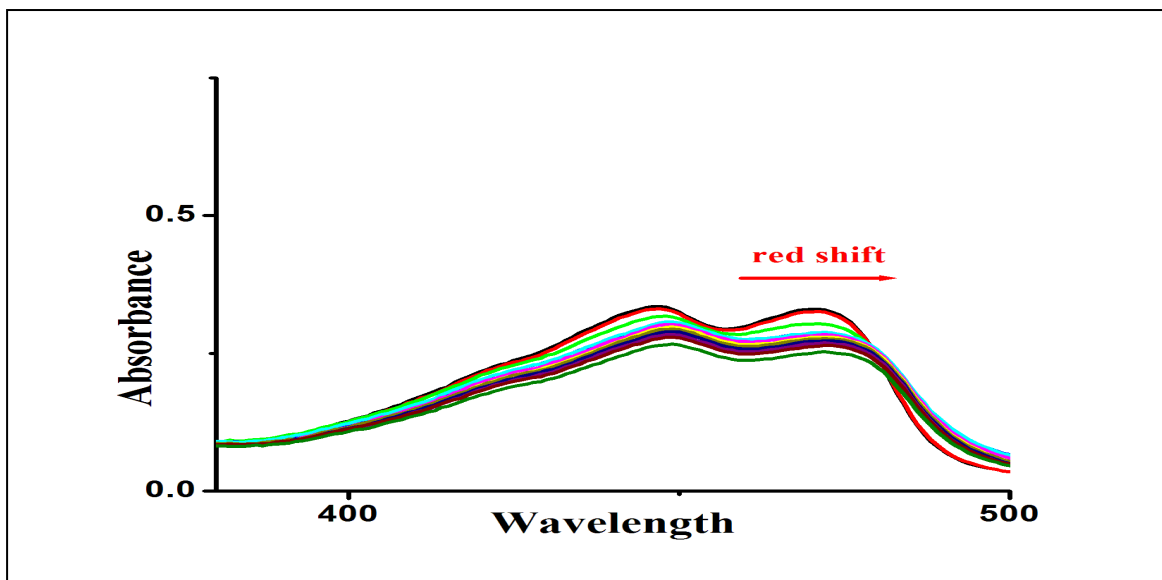
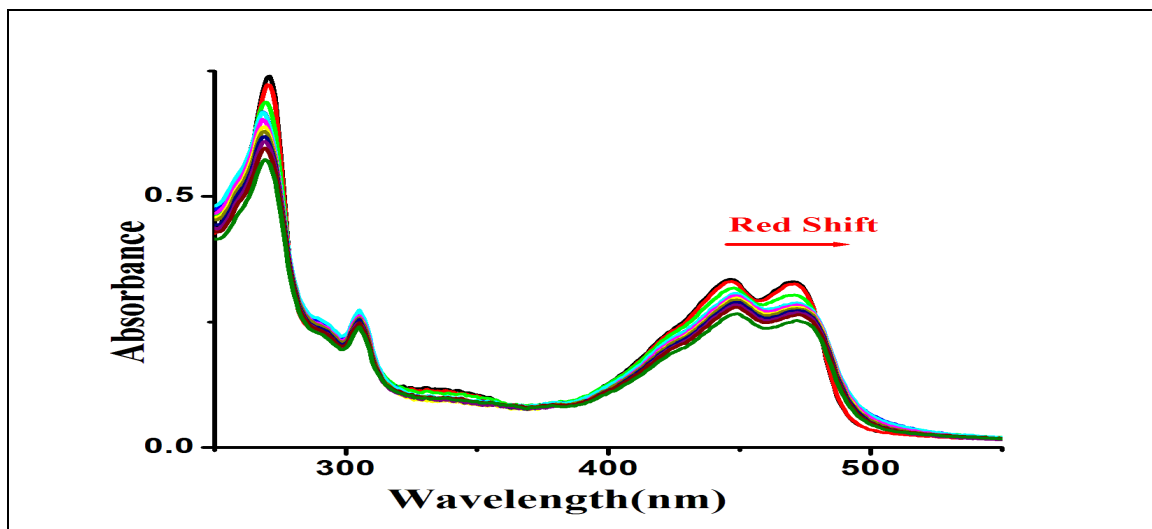
Ligand incubated with Zn²⁺ + Fe³⁺:



Ligand incubated with Zn²⁺ + Cd²⁺:

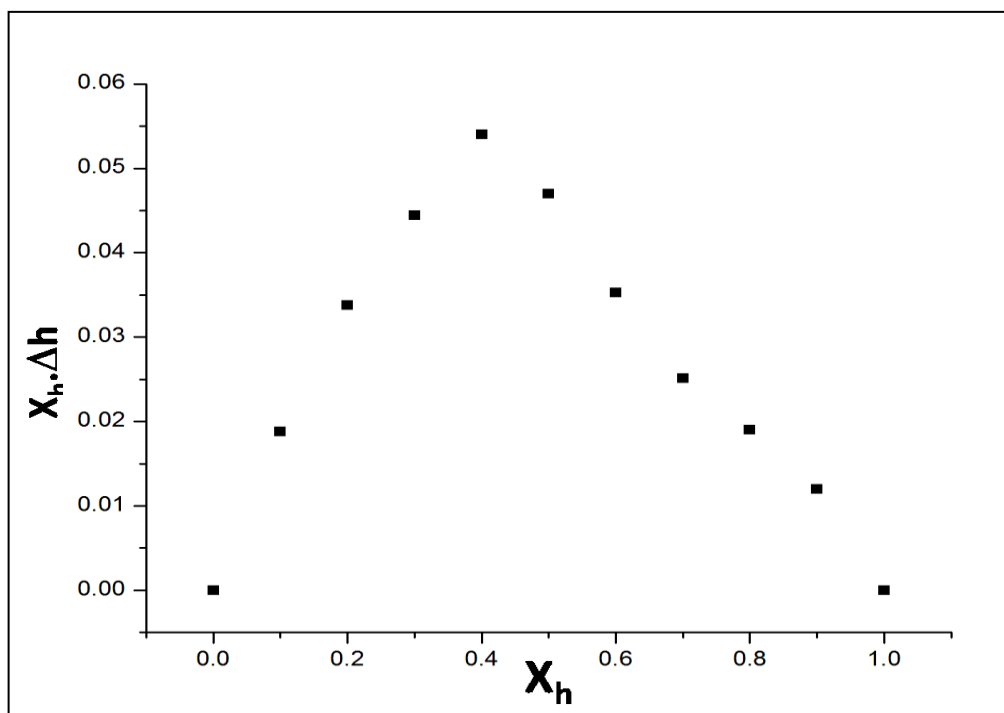


UV-vis Behaviour: The binding behaviour of the ligand/receptor with different cations was studied in CH₃CN-HEPES buffer (8/2, v/v, 25°C) at pH = 7.4. The UV-vis titration experiment was carried out in mixed aqueous media at 1 x10⁻⁵ M concentration of receptor solution upon addition of incremental amount of 7 equiv of Zn²⁺ (2 x10⁻⁴ M). The UV-vis spectrum of the receptor exhibits peaks at 487nm and 500nm. Upon gradual increase of the Zn²⁺ ion concentration, exhibits a red shift from 487 nm and 500nm.



JOB'S PLOT:

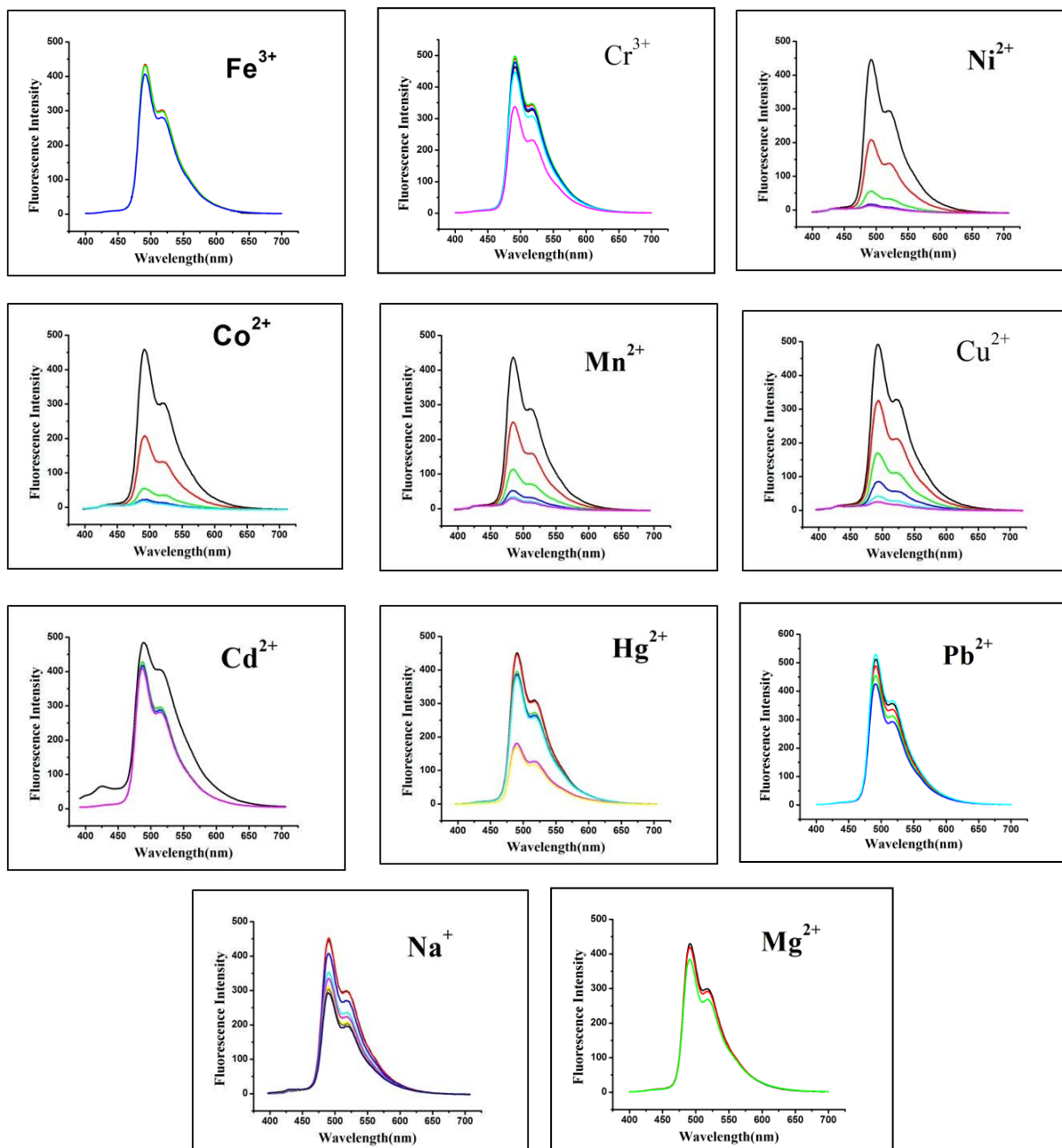
Job plot shows a maxima at 0.4 mole fraction of the receptor. This value indicates compound 1 and Zn^{2+} exists in a multiple equilibrium between a 1:1 and 1:2 complex.



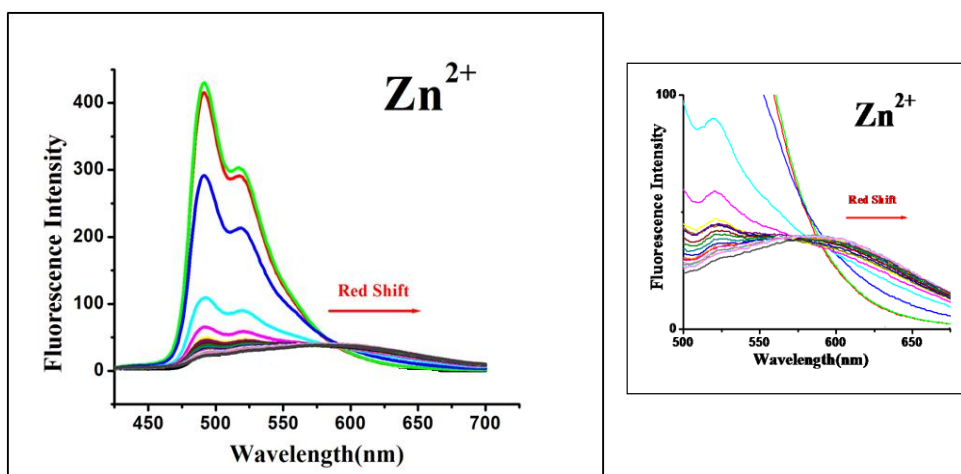
Job's plot diagram of the ligand for Zn^{2+} (where X_h is the mole fraction of the host and Δh indicates the change of the absorbance).

Fluorescence titration:

For fluorescence titrations, stock solution of the sensor ($c = 1 \times 10^{-5}$ M) was prepared for the titration of cations in CH_3CN -HEPES buffer (6/4, v/v, 25°C) at pH 7.4. The solution of the guest cations using their chloride (Fe, Cr, Mg, Hg, Pb, Al, Cd) and perchlorate (Zn, Ni, Mn, Cu, Na) salts in the order of $200 \mu\text{M}$ were also prepared. Solutions of various concentrations containing sensor and increasing concentrations of cations were prepared separately. The spectra of these solutions were recorded by means of fluorescence methods.



Fluorescent Behaviour in presence of Zn²⁺ ion:



Fluorescence Behaviour of Compound 1 in Presence of Various Metal Ions:

