Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supporting Information

For

Mononuclear Zn(II)- and Cu(II)-Complexes of a Hydroxynaphthalene Derived Dipicolylamine: Fluorescent Sensing Behaviours toward Pyrophosphate Ions

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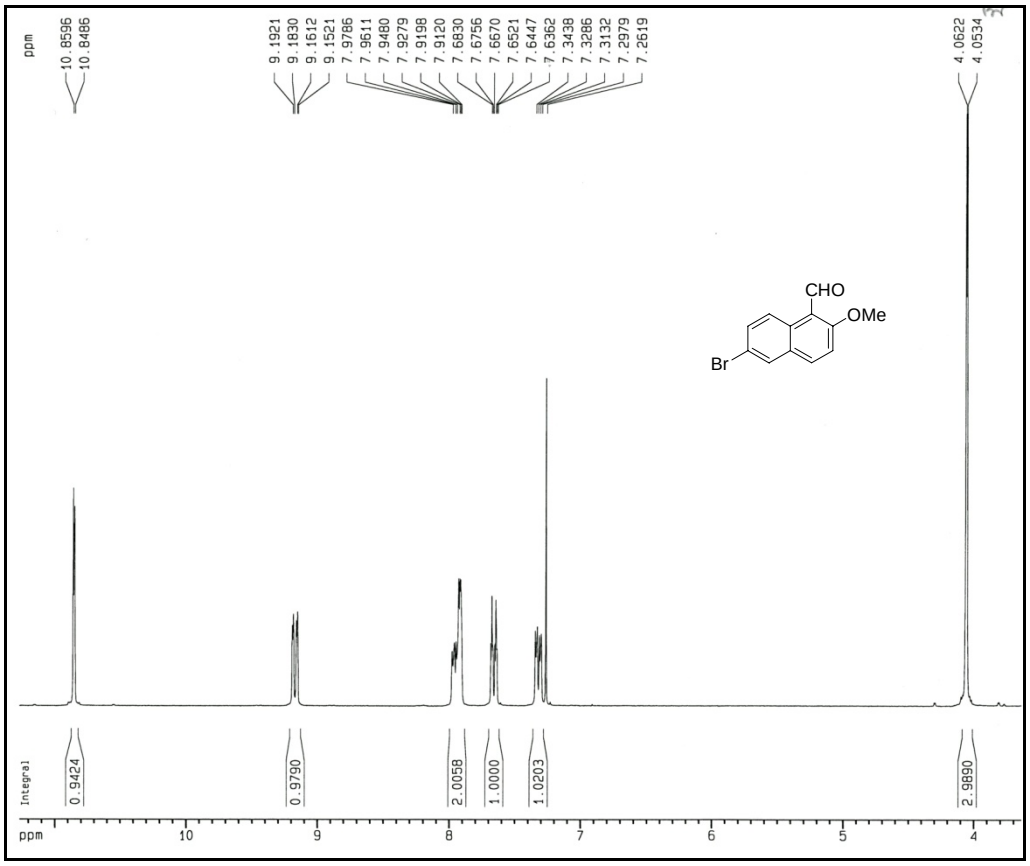
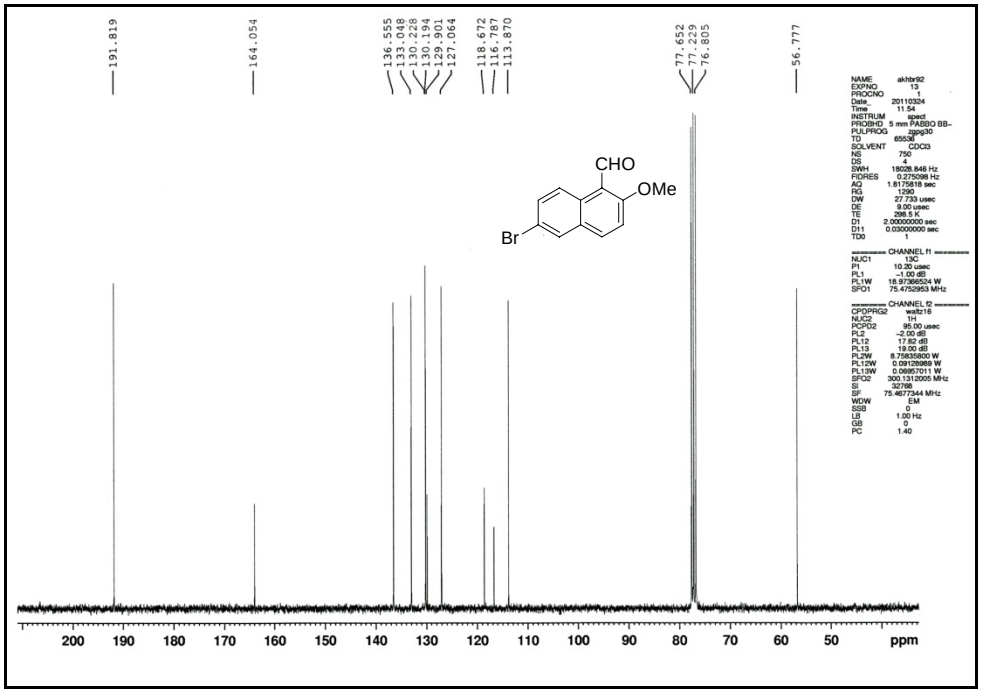
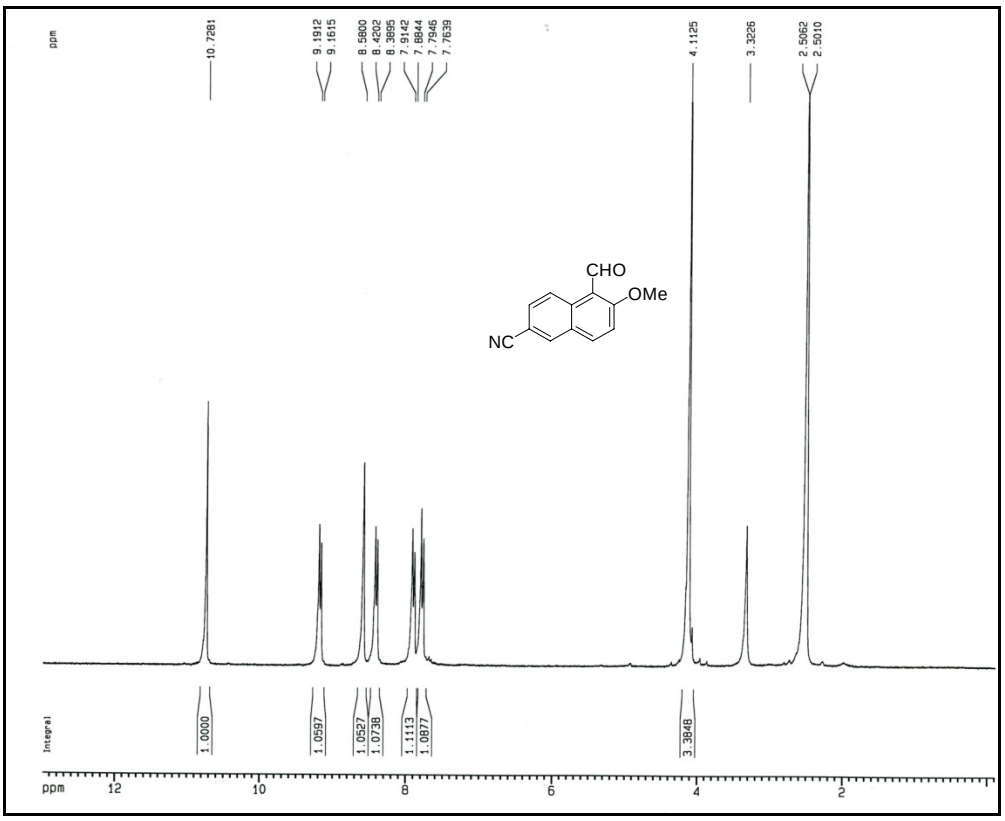
General methods

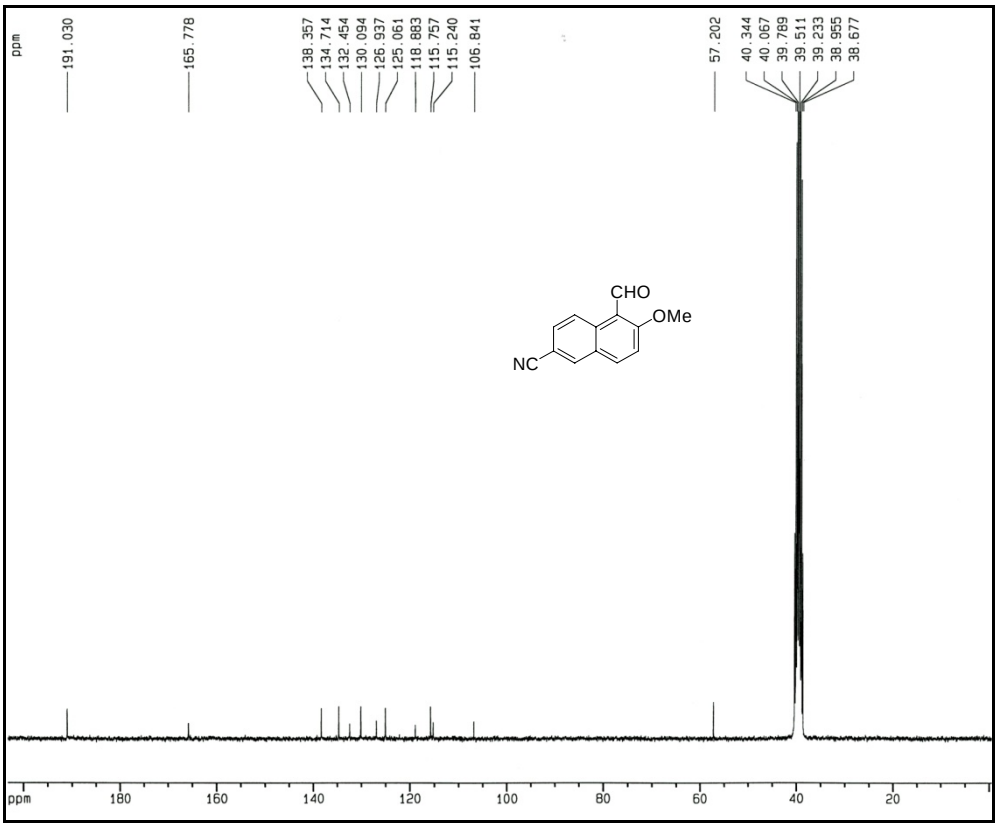
Chemicals from Sigma-Aldrich were used without further purification. All reactions were performed under argon atmosphere unless otherwise stated. Analytical TLC was performed on Merck silica gel (60 F254) plates (0.25 mm) and visualized with ultraviolet light. ^{1}H and ^{13}C NMR spectra were measured with a Bruker DPX-300 spectrometer. Coupling constants (*J* value) are reported in Hertz. The chemical shifts are shown in ppm. UV/Vis absorption spectra were obtained using a HP 8453 UV/Vis spectrophotometer. FTIR spectra were recorded at a spectral resolution of 4 cm^{-1} with a BRUKER VERTEX 70 spectrometer. Fluorescence spectra were recorded on a Photon Technology International fluorimeter. High-resolution mass spectra were recorded on a JEOL JMS-700 spectrometer. Solutions of each analytes (PPi, Pi, ATP, ADP, and others) were prepared by dissolving sodium salt of the anionic species in deionized water. Stock solutions of **1**·Zn(II), **1**·Cu(II) and **6** were prepared by dissolving them separately in deionized water (each 1.0 mM).



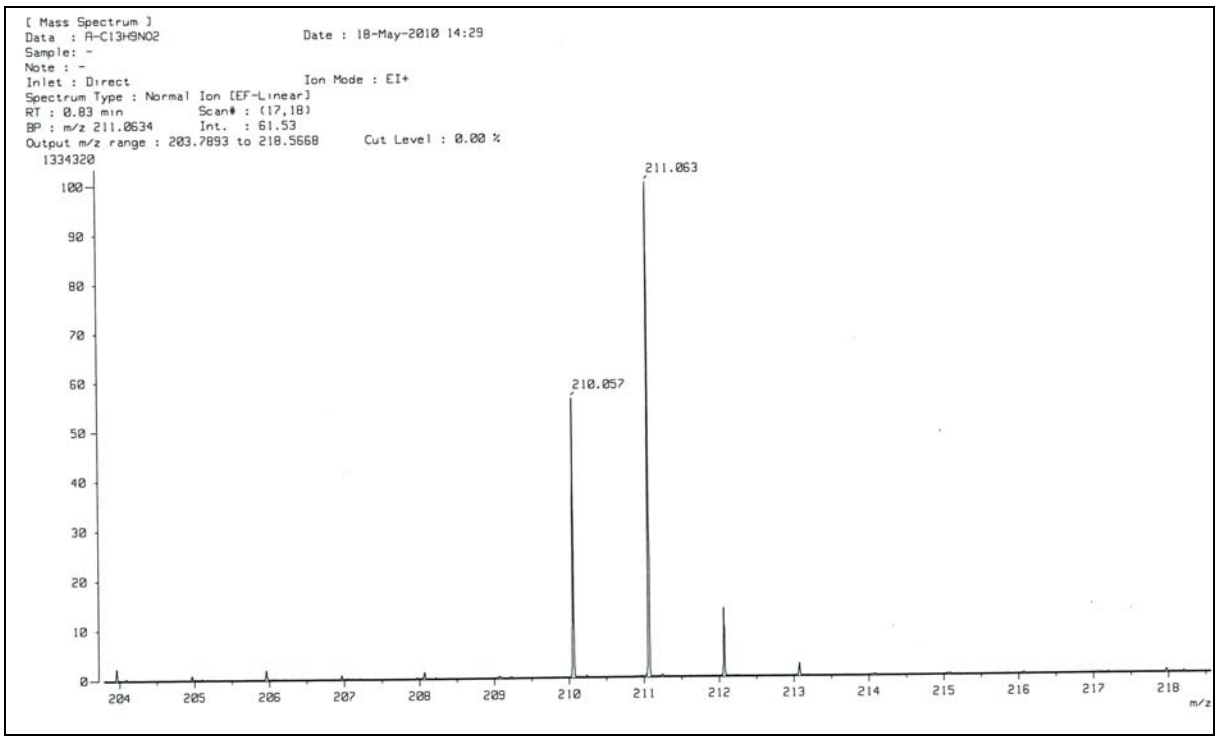


^{1}H and ^{13}C NMR spectra of compound **2**.

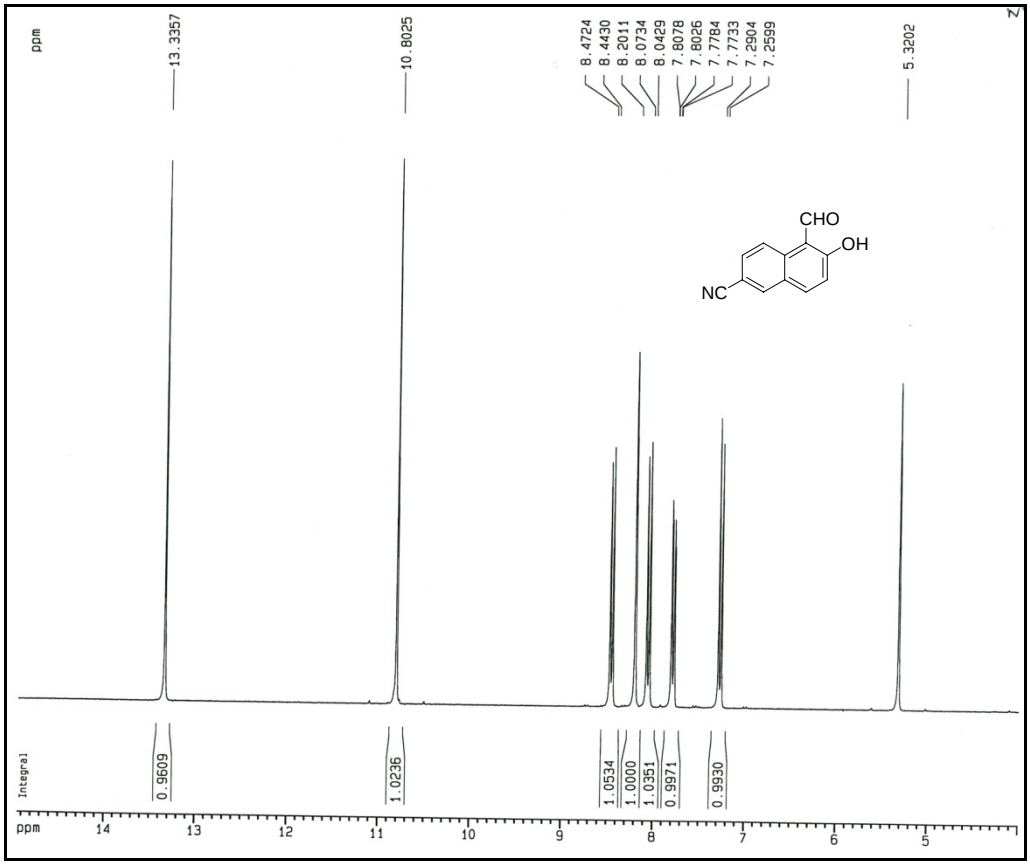


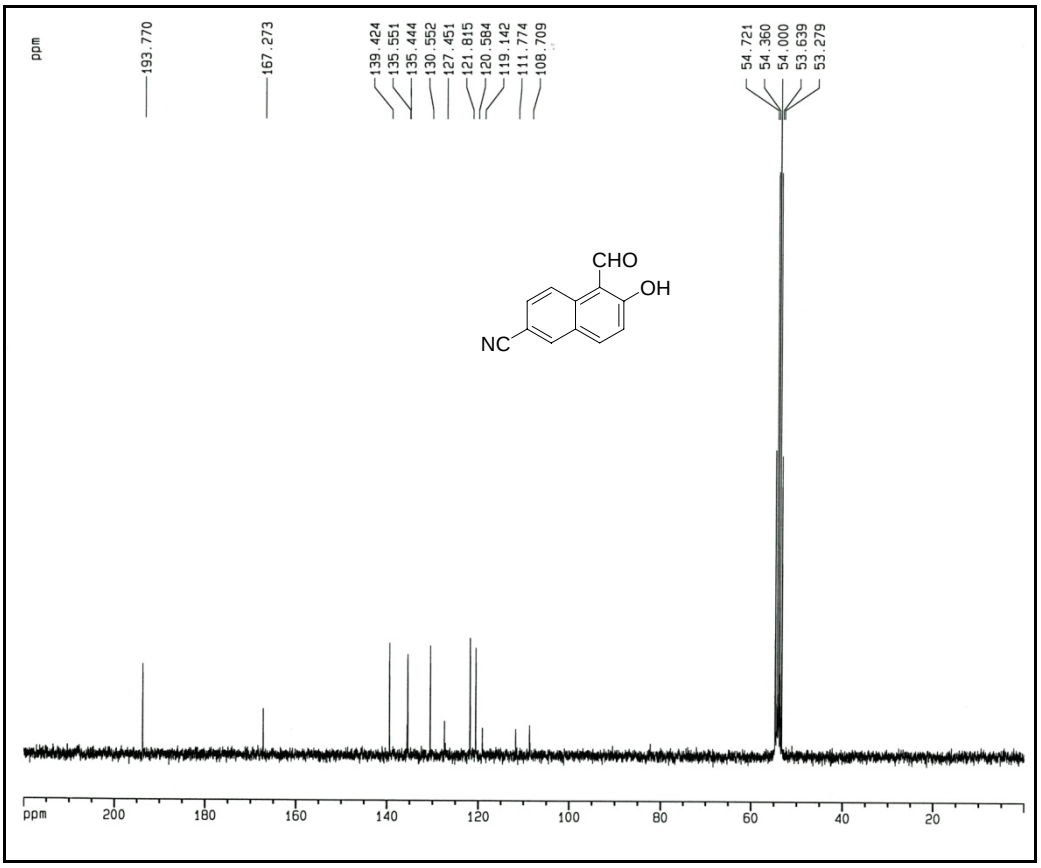


^{1}H and ^{13}C NMR spectra of compound **3**.

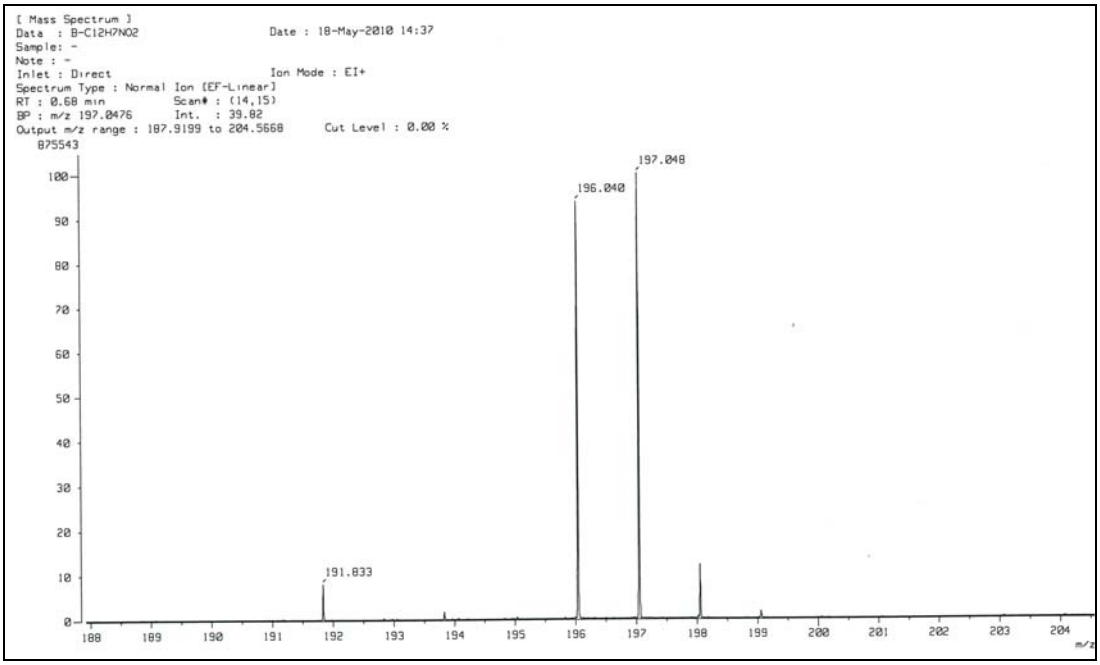


FAB (+) HRMS of compound **3**.

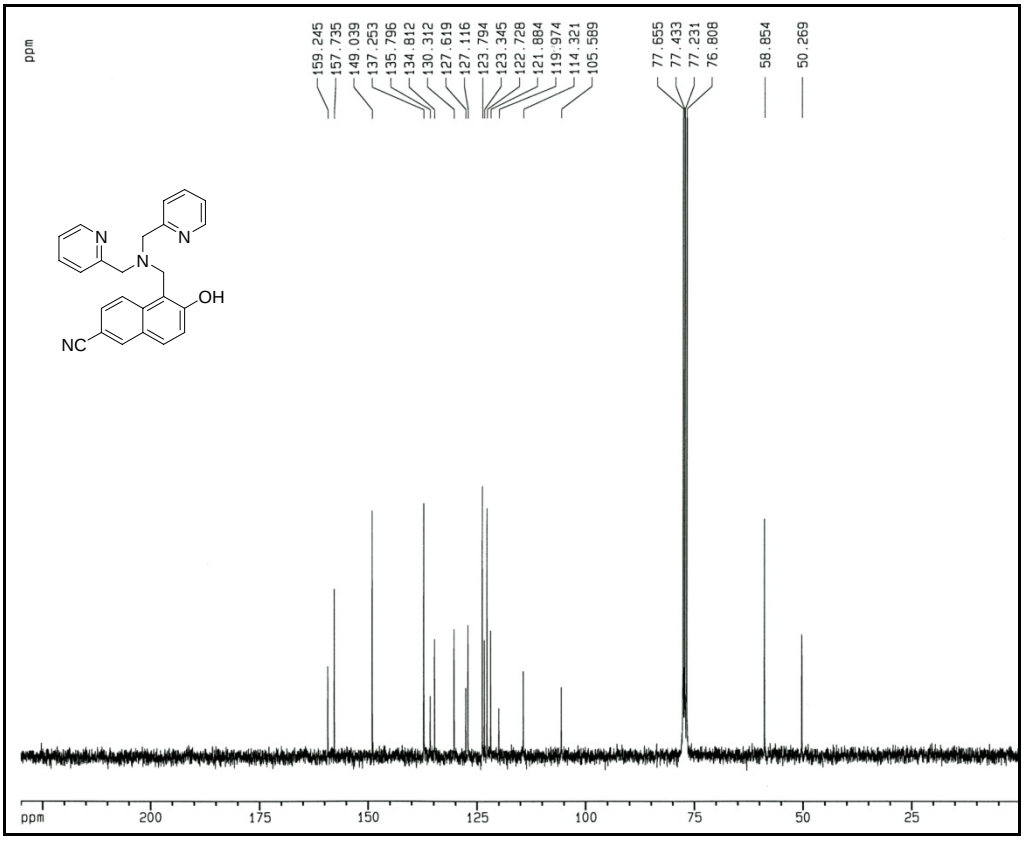




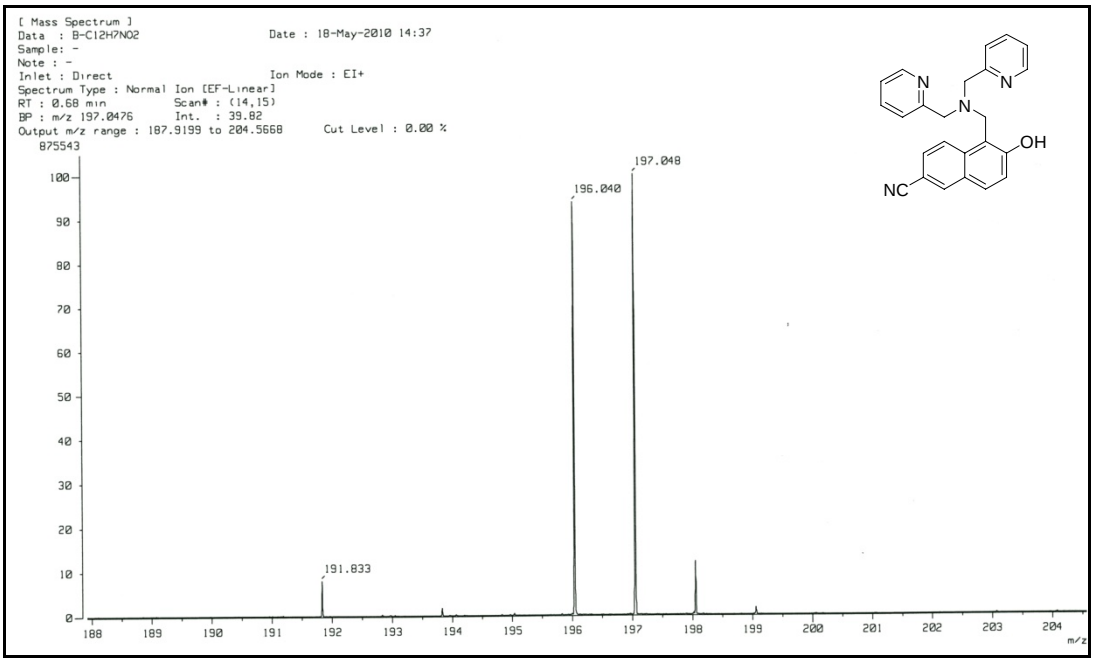
^{1}H and ^{13}C NMR spectra of compound **4**.



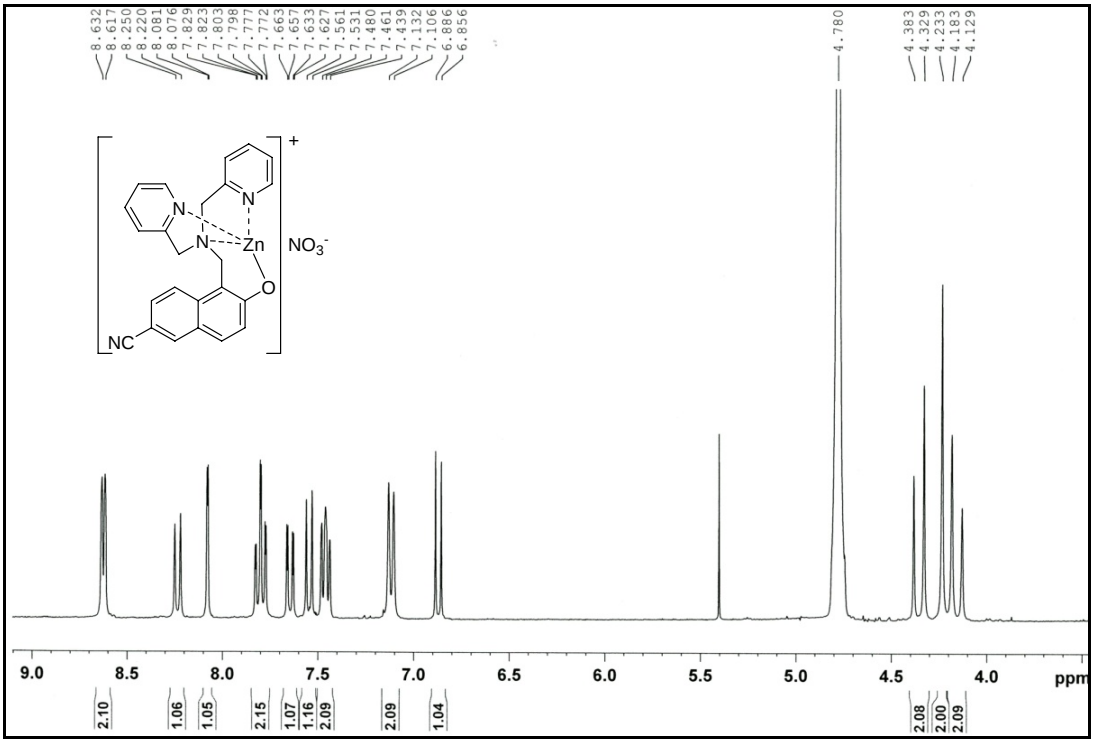
FAB (+) HRMS of compound **4**.



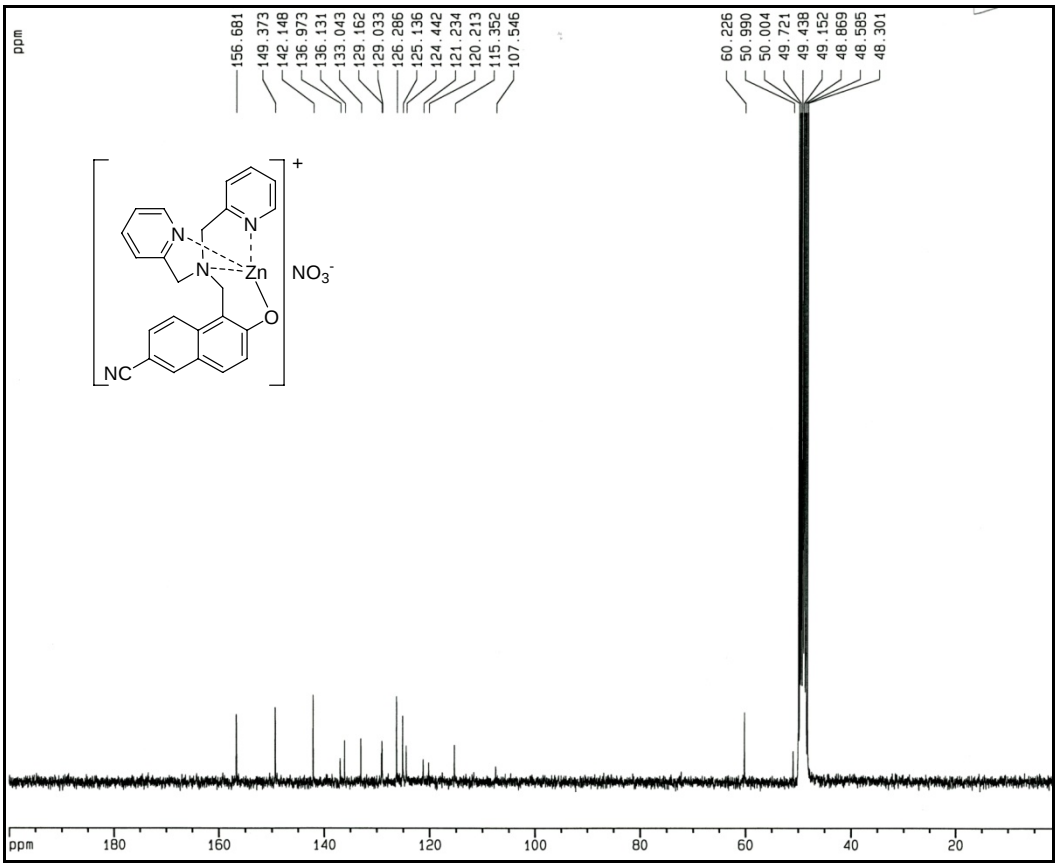
^{1}H and ^{13}C NMR spectra of compound **1**.



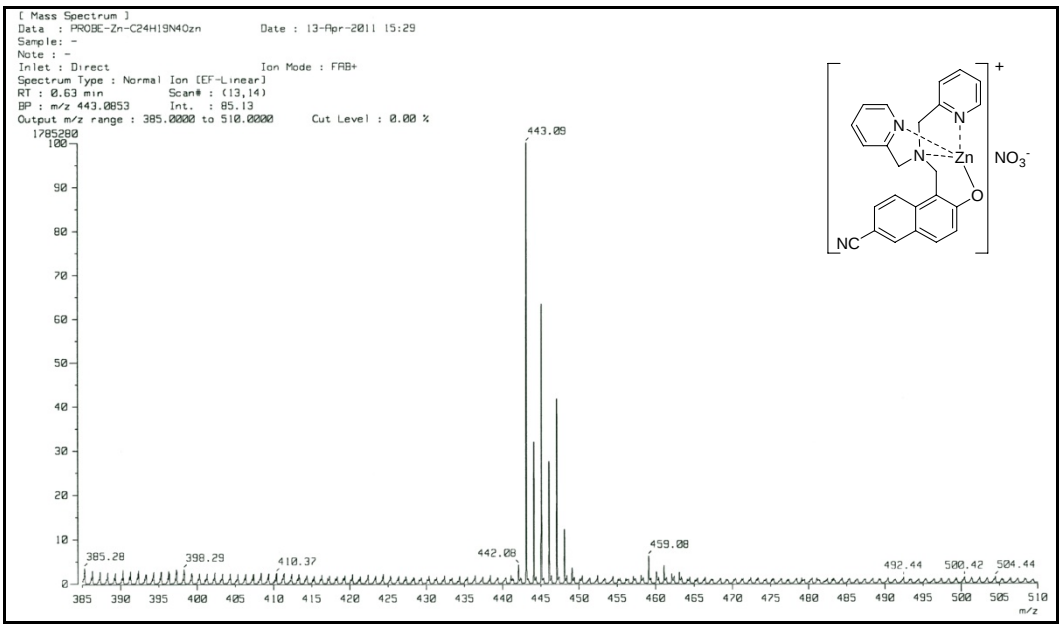
FAB (+) HRMS of compound **1**.



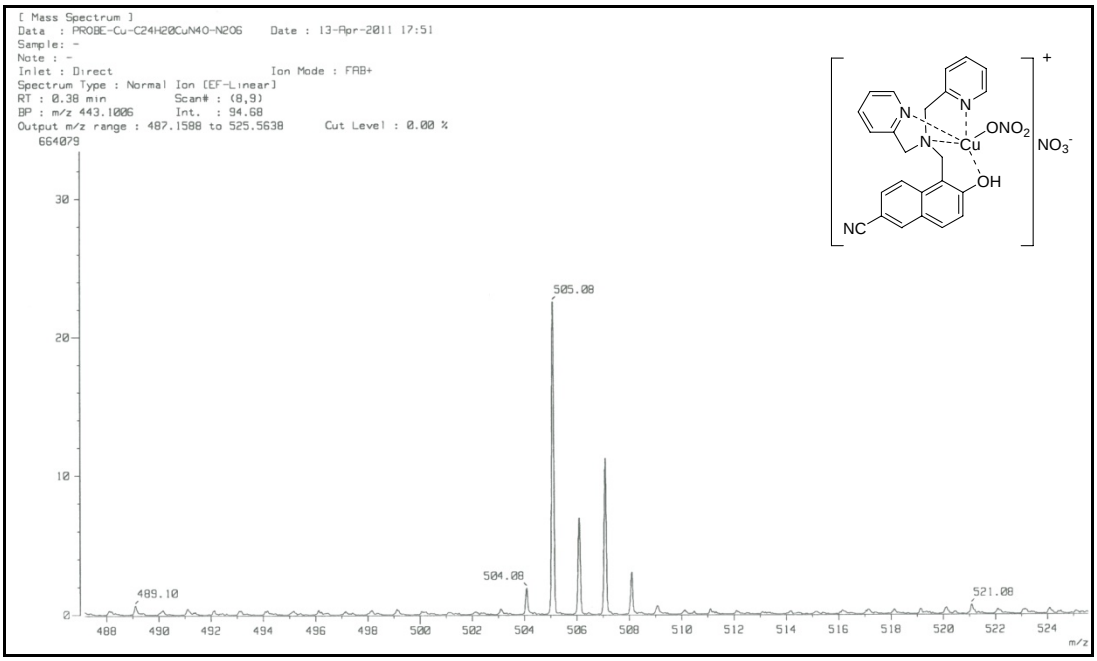
^{1}H NMR spectrum of complex **1**·Zn(II).



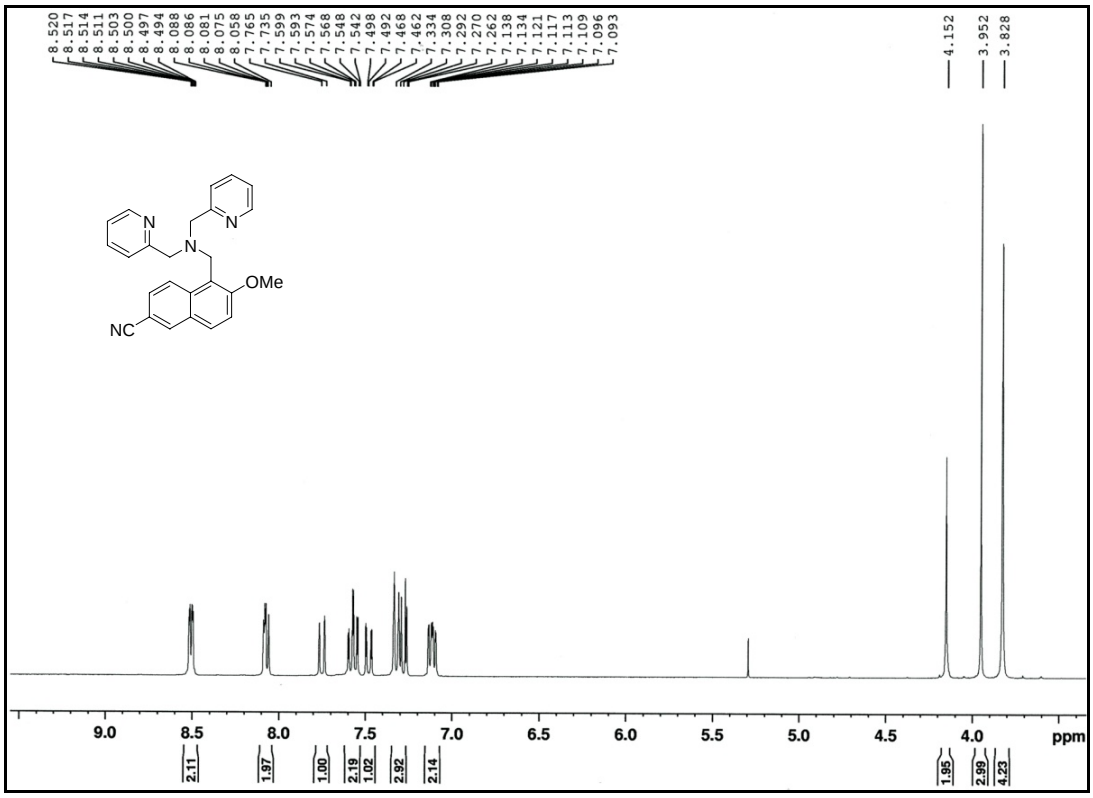
^{13}C NMR spectrum of complex **1**·Zn(II).

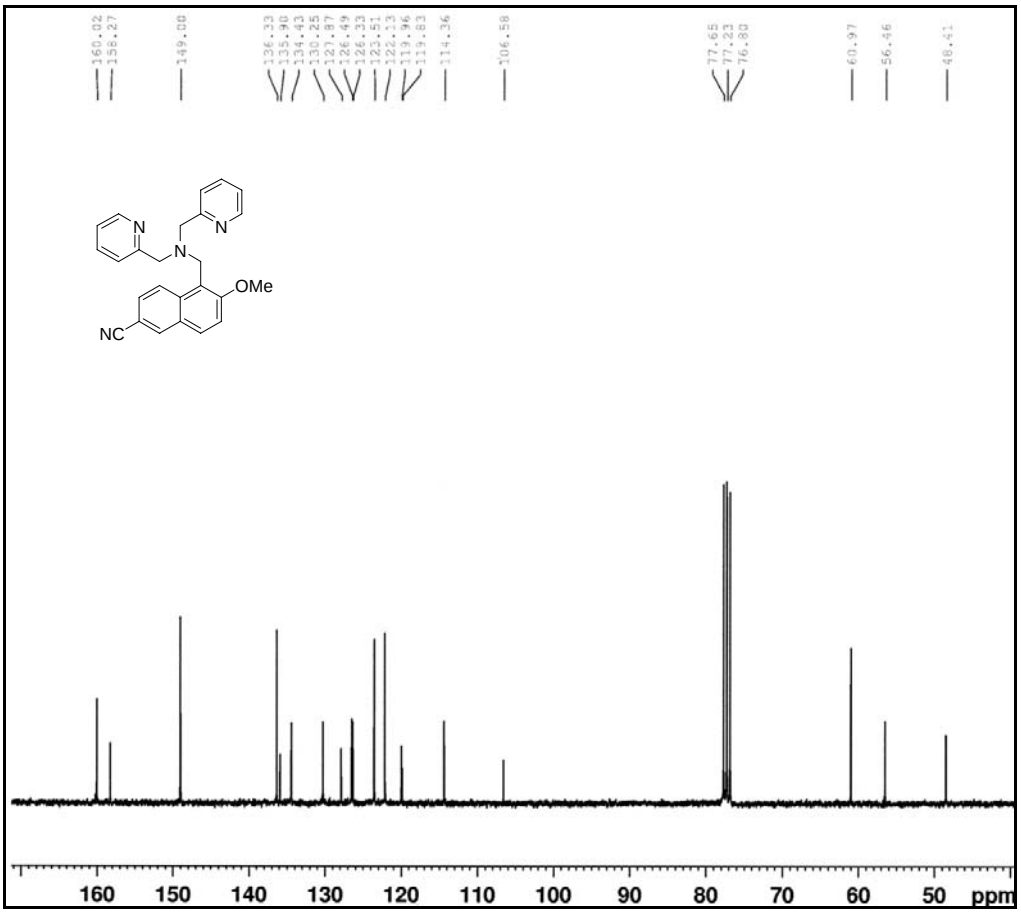


FAB (+) HRMS of complex **1**·Zn(II).

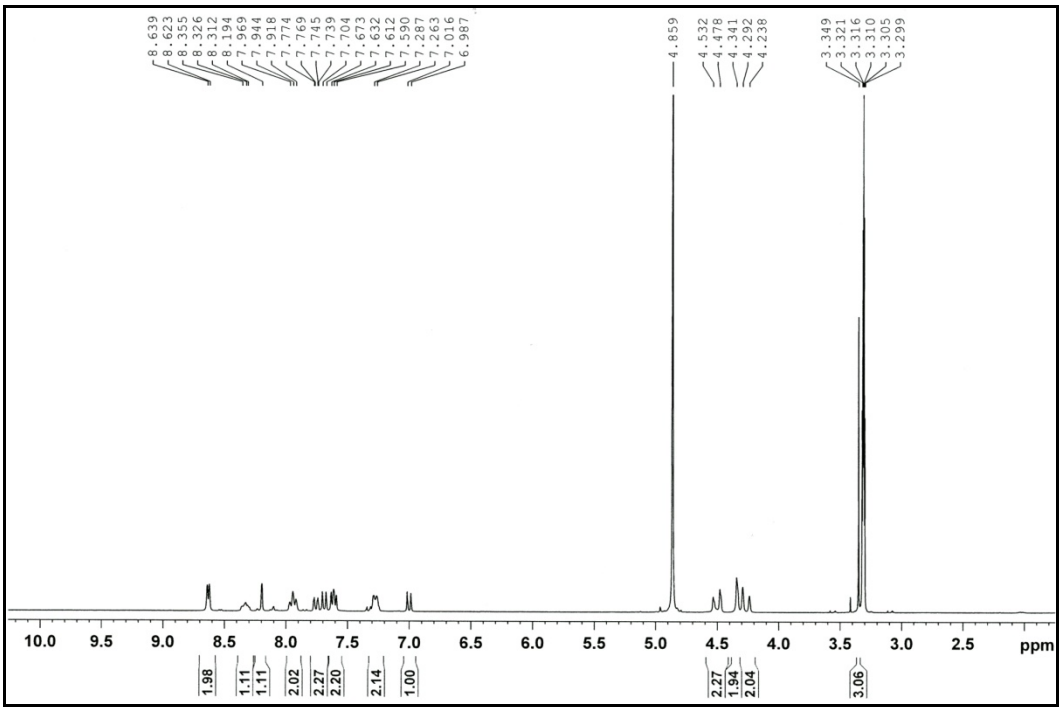


FAB (+) HRMS of complex **1**·Cu(II).

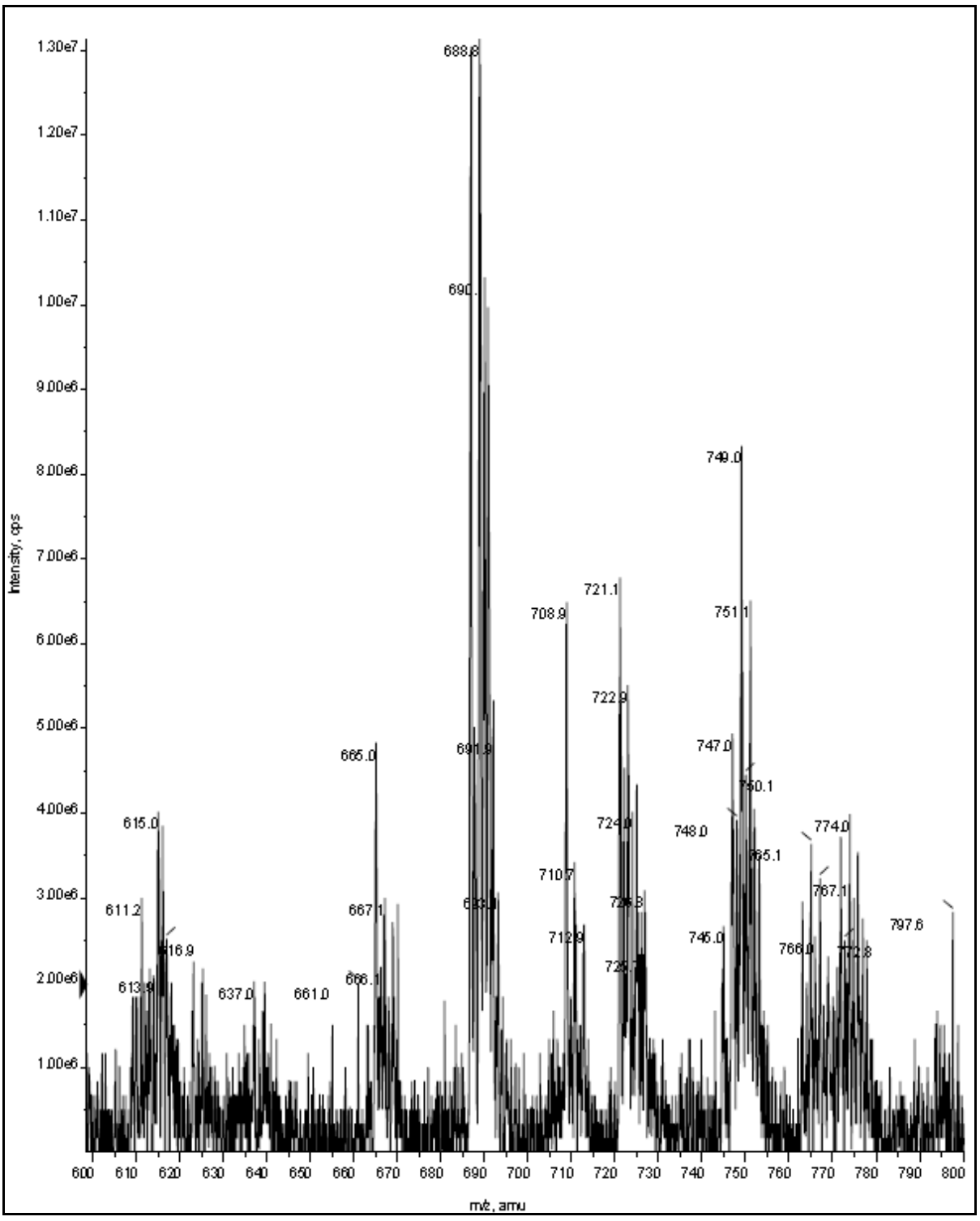




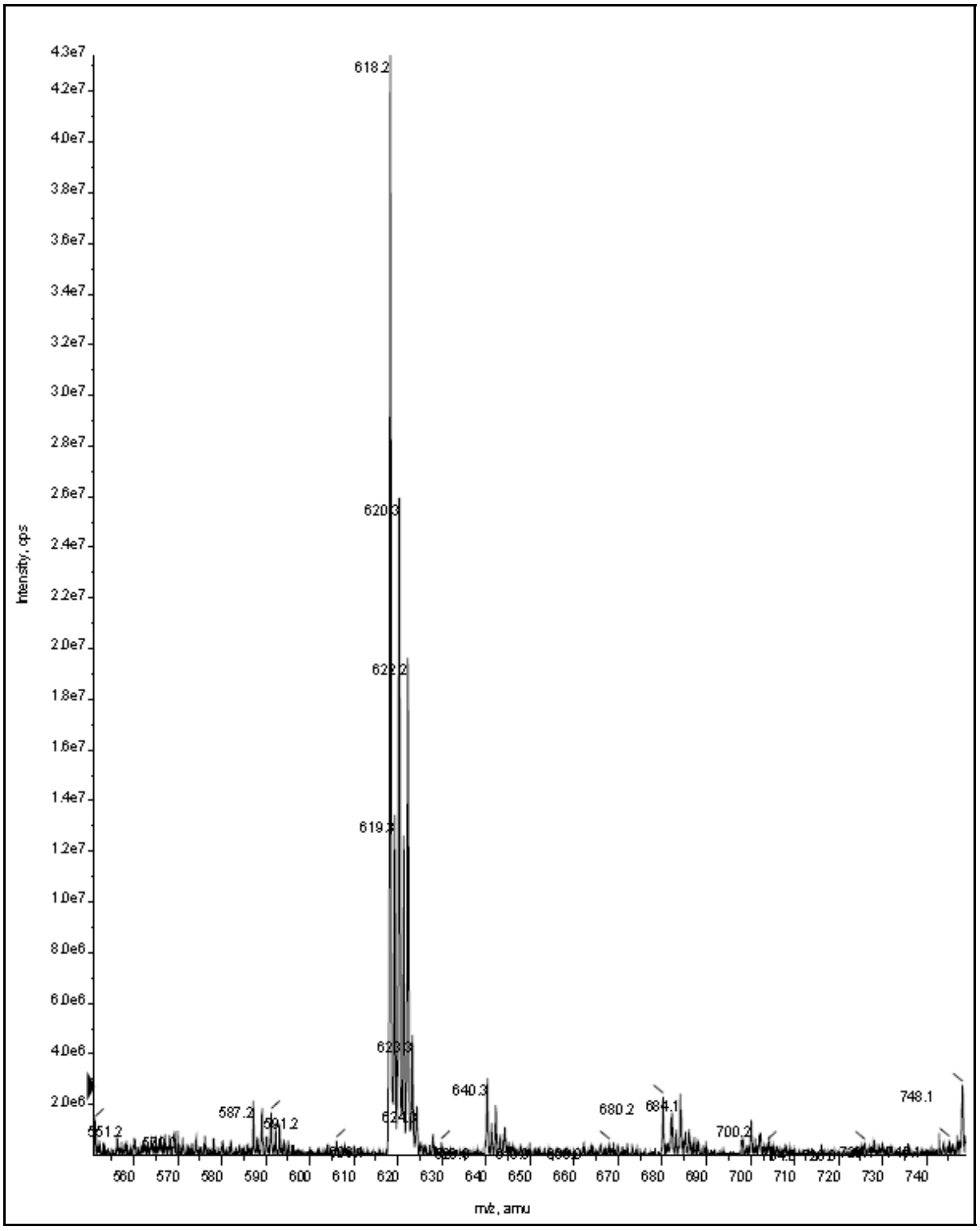
^{1}H and ^{13}C NMR spectrum of **5**.



^{1}H NMR spectrum of Zn(II) complex **6**.



ES-(+) Mass spectrum of **1**·Zn(II)–PPi adduct.



ES-(-) Mass spectrum of **1**·Zn(II)–PPi adduct.

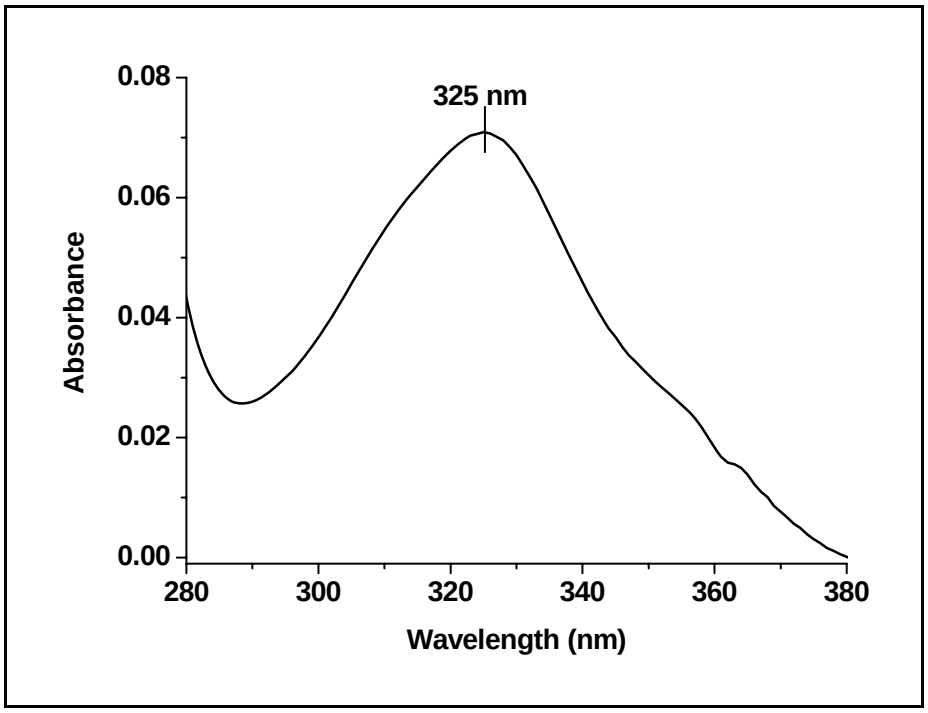


Fig S1. Absorption spectrum of **1**·Zn(II) (10 μM) in 10 mM HEPES buffer of pH 7.4.

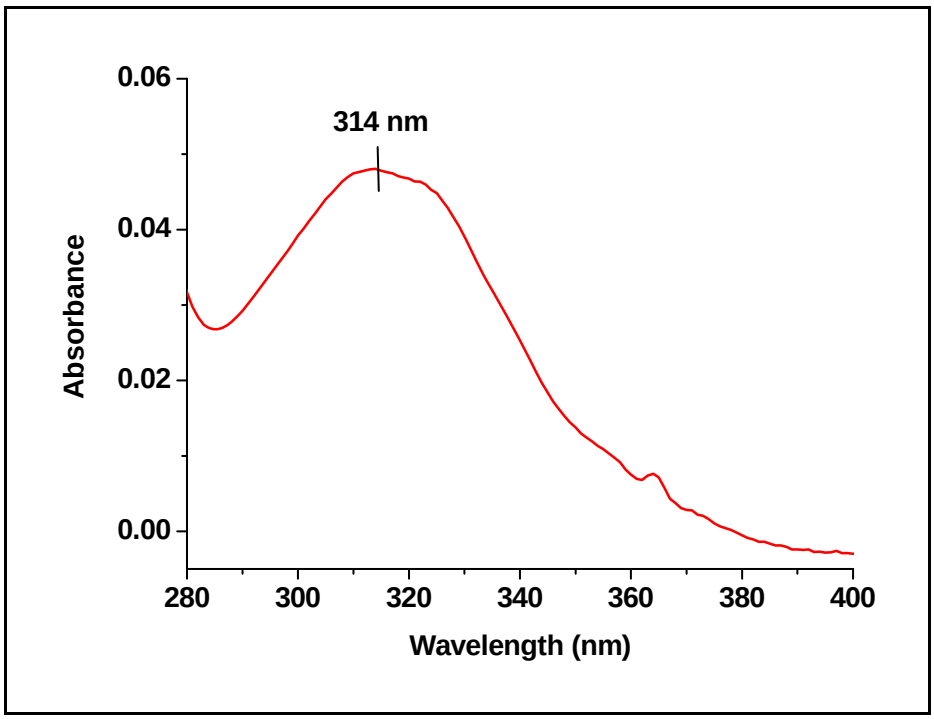


Fig S2. Absorption spectrum for a mixture of **1**·Zn(II) (10 μM) and 200 equivalents of PPi in 10 mM HEPES buffer of pH 7.4.

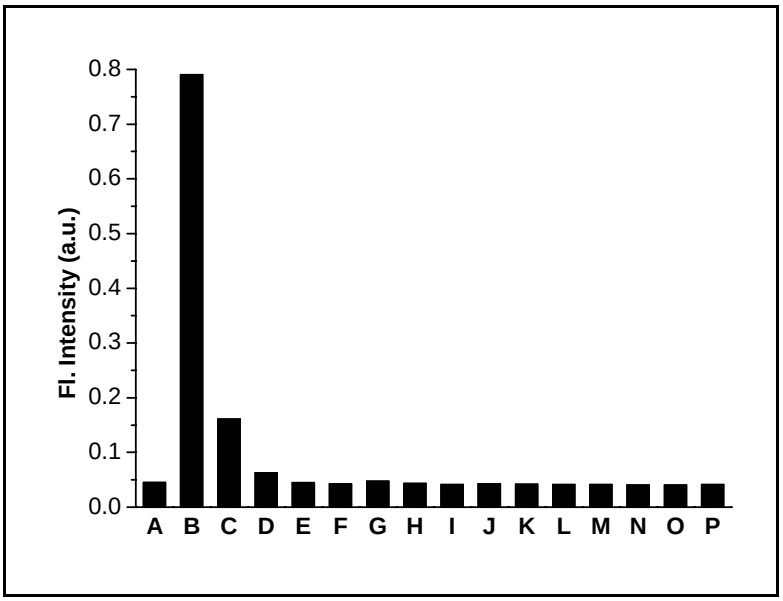


Fig S3. A bar chart presenting fluorescence response of **1**·Zn(II) (10 μM) toward each of various anions (250 equivalents; A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, and P are **1**·Zn(II)**,** PPi, ATP, ADP, $H_2PO_4^-$, AcO^-, PO_4^{3-}, HSO_4^-, ClO_4^-, F^-, I^-, Br^-, Cl^-, N_3^-, NO_2^- and NO_3^- respectively) as their sodium salts in 10 mM HEPES buffer of pH 7.4; measured after 6 h of addition of the analyte (excitation at 310 nm; intensity was estimated by the peak height at λ = 435 nm).

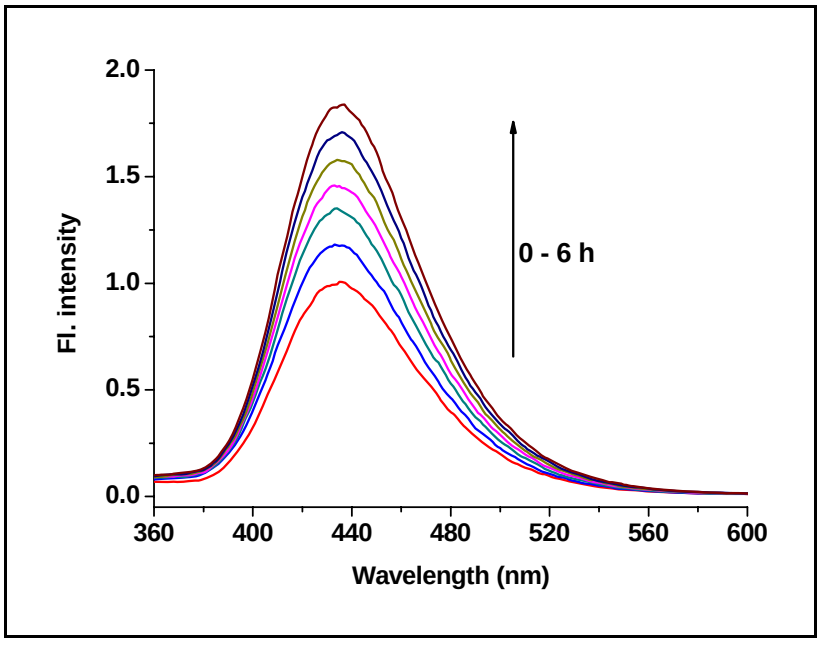


Fig S4. Time-dependent fluorescence enhancement of **1**·$Zn(ClO_4)_2$ (10 μM) in presence of 300 equivalents of PPi in 10 mM HEPES buffer of pH 7.4 (excitation at 310 nm).

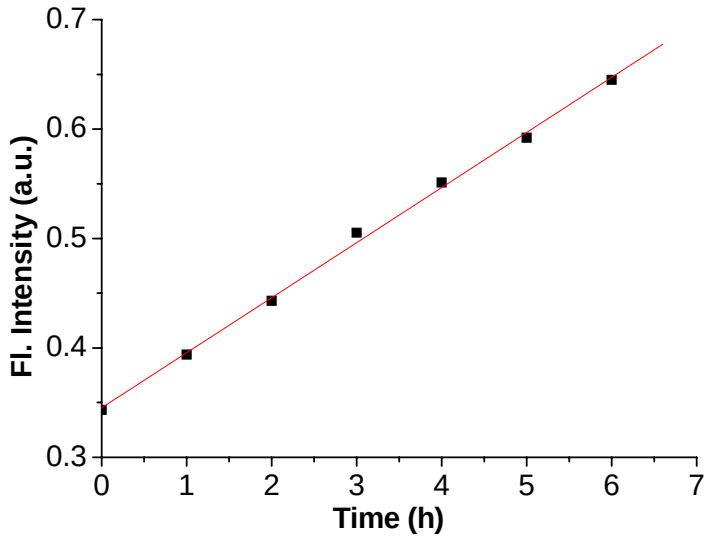


Fig S5. Time-dependent fluorescence enhancement of **1**·Cu(II) **(**10 mM) in presence of PPi (400 equiv.) in a HEPES buffer (10 mM, pH 7.4) (excitation at 325 nm; intensity was estimated by the peak height at λ = 437 nm).

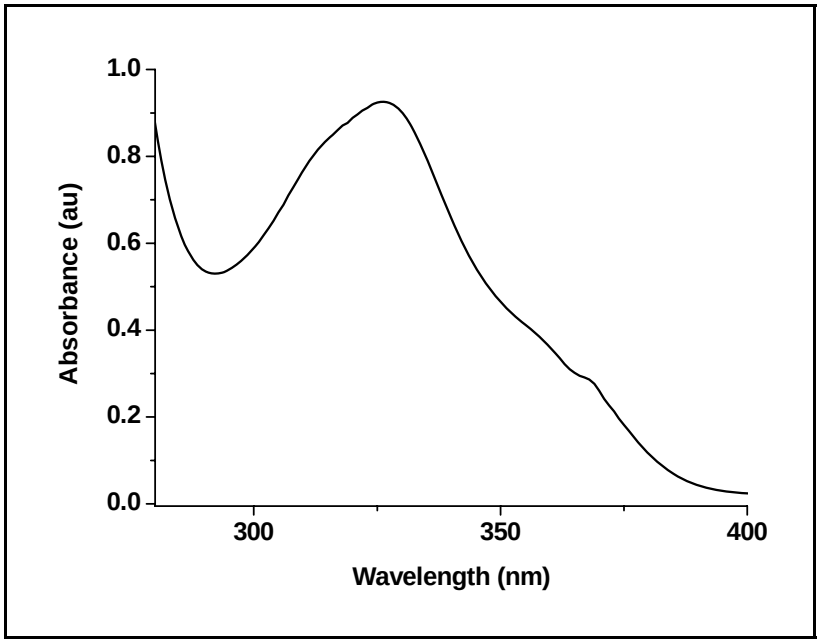


Fig S6. Absorption spectrum of **1**·Cu(II) (10 μM) in 10 mM HEPES buffer of pH 7.4.

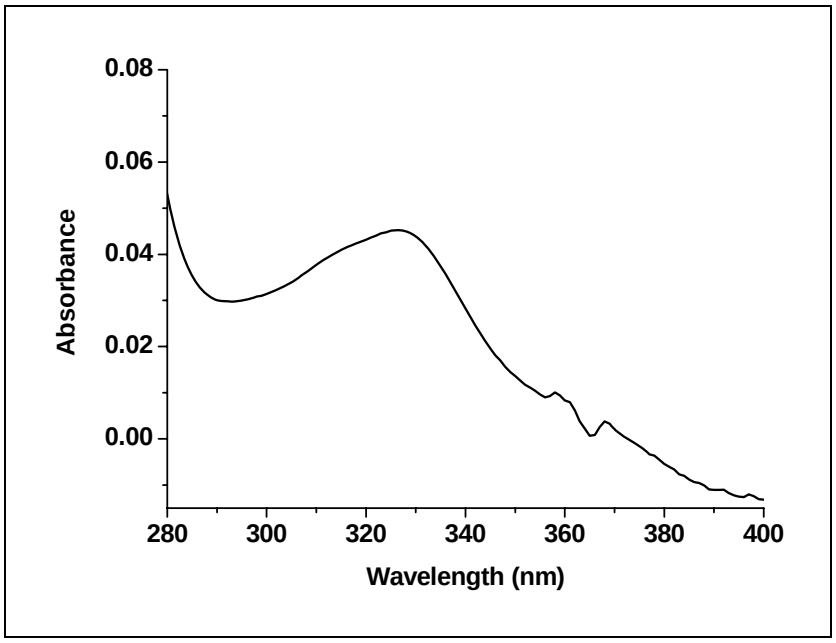


Fig S7. Absorption spectrum of for a mixture of **1**·Cu(II) (10 μM) and 700 equivalents of PPi in 10 mM HEPES buffer of pH 7.4.

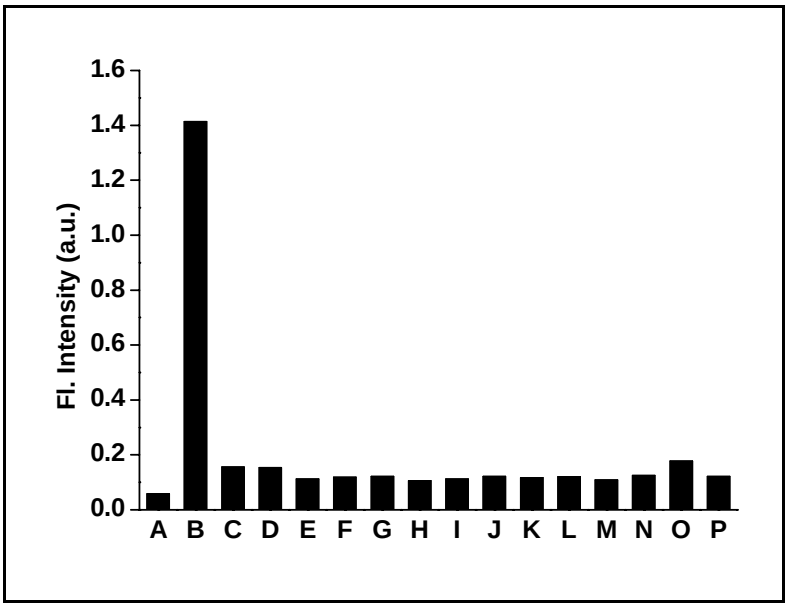


Fig S8. A bar chart presenting fluorescence response of **1**·Cu(II) (10 μM) toward each of various anions (900 equivalents; A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, and P are **1**·Cu(II)**,** PPi, ATP, ADP, PO_4^{3-}, $H_2PO_4^-$, AcO^-, F^-, I^-, Br^-, Cl^-, N_3^-, NO_2^-, NO_3^-, HSO_4^-, and ClO_4^- respectively) as their sodium salts in 10 mM HEPES buffer of pH 7.4; measured after 6 h of addition of the analyte (excitation at 325 nm; intensity was estimated by the peak height at λ = 437 nm).

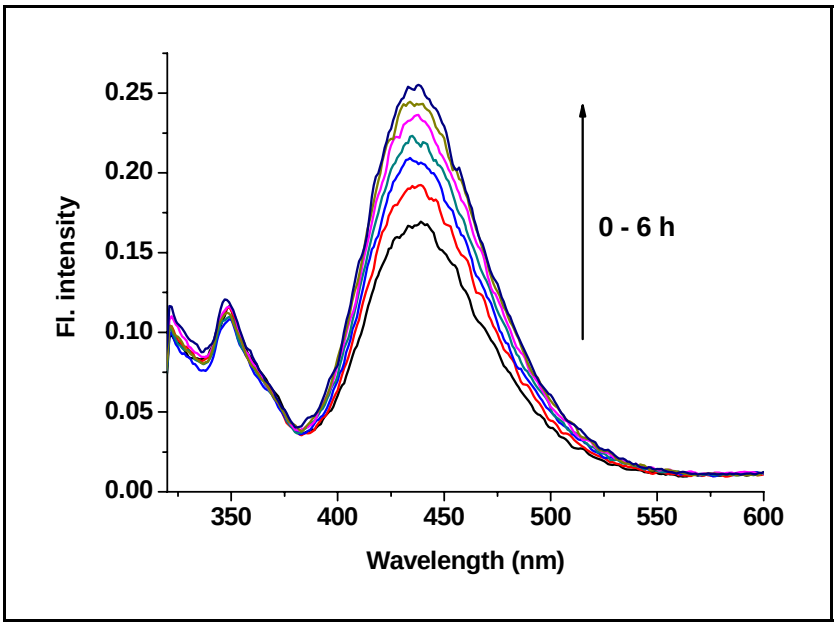


Fig S9. Time-dependent fluorescence enhancement of **1**·$Cu(ClO_4)_2$ (10 μM) in presence of 300 equivalents of PPi in 10 mM HEPES buffer of pH 7.4 (excitation at 325 nm).

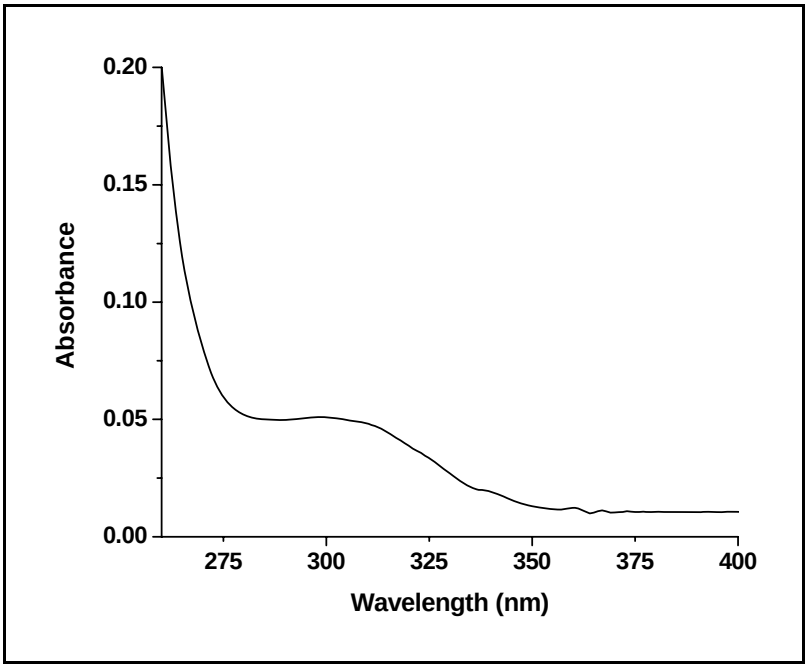


Fig S10. Absorption spectrum of [**5**·$Cu(NO_3)_2$] complex (10 μM) in 10 mM HEPES b uffer of pH 7.4.

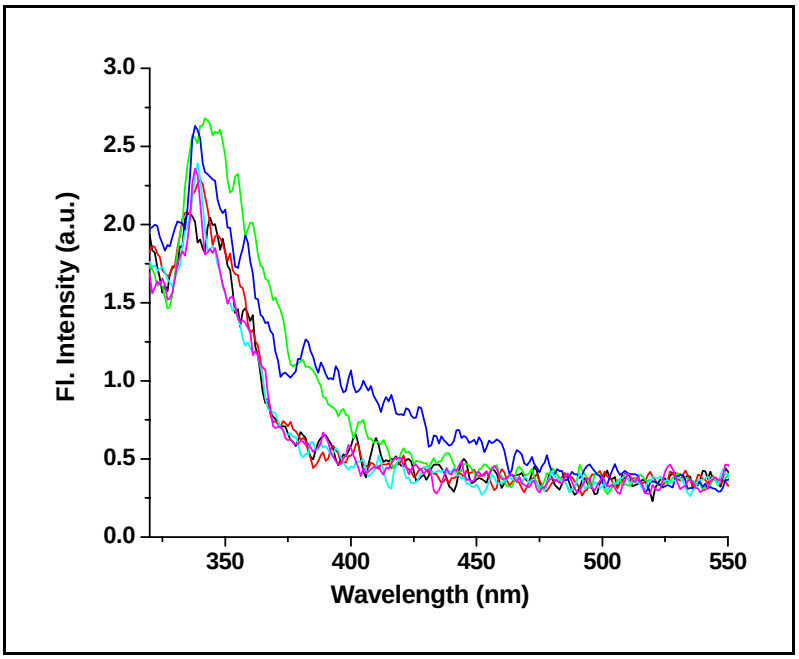


Fig S11. Fluorescence response of [**5**·$Cu(NO_3)_2$] complex (10 μM) toward 200 equivalent of each of various anions (PPi, ATP, ADP, and PO_4^{3-}) in 10 mM HEPES buffer of pH 7.4, taken after 6 h of addition of analyte; excitation at 300 nm).

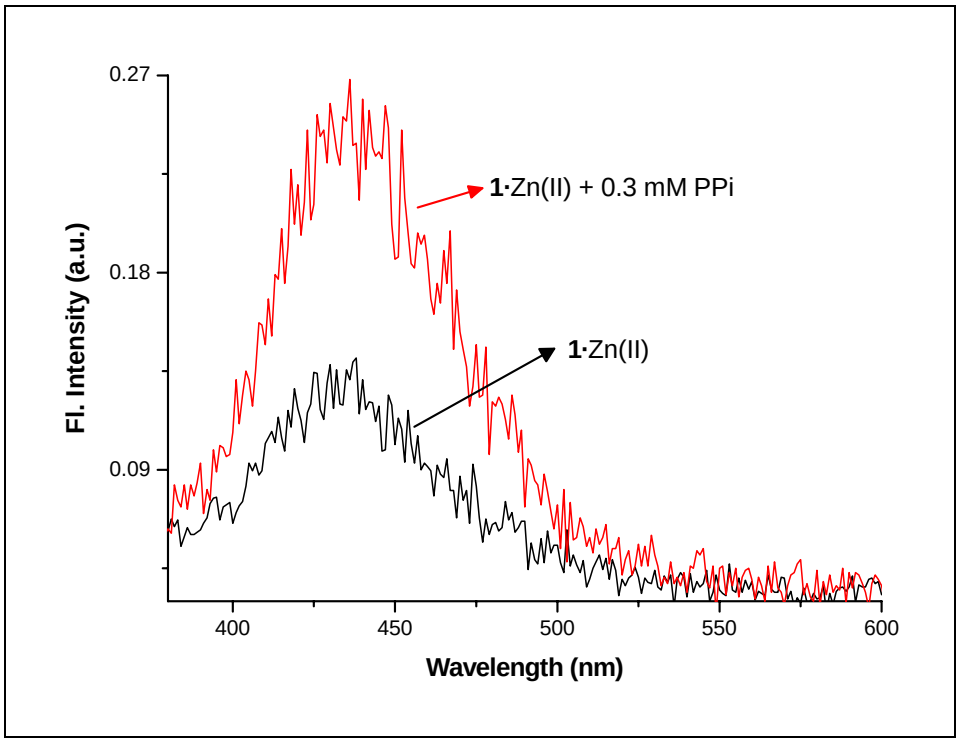


Fig S12. Determination of detection limit of PPi (10 μM **1**·Zn(II)) in 10 mM HEPES buffer of pH 7.4, taken after 6 h of addition of analyte (excitation at 310 nm).

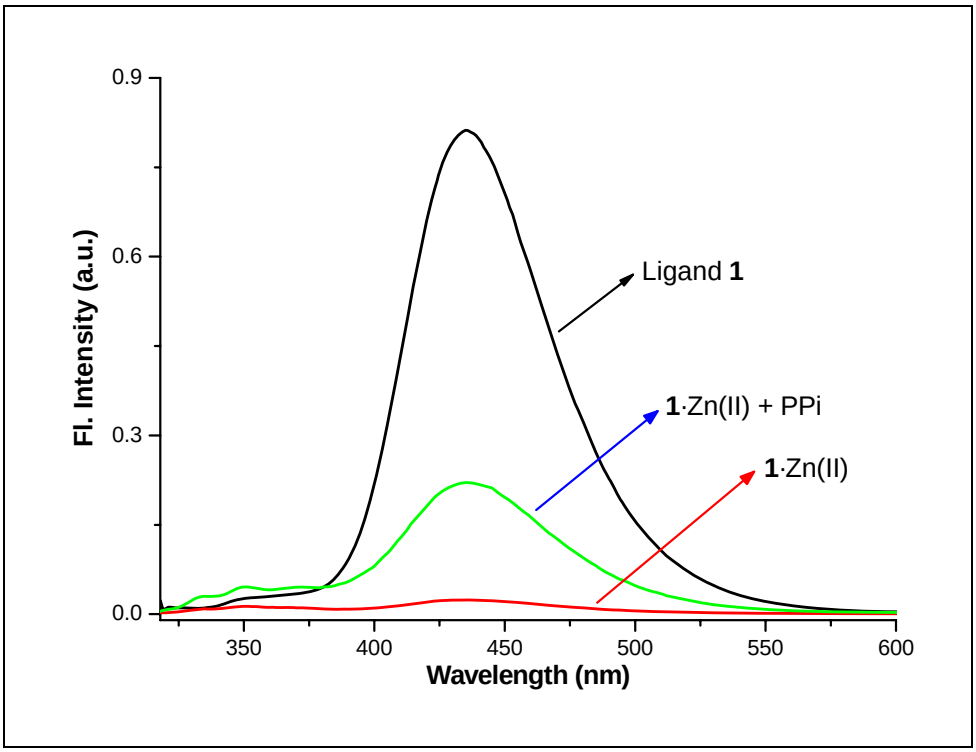


Fig S13. A comparison of fluorescence emission of **1**, **1**·Zn(II) and **1**·Zn(II)+PPi (10 μ M each in 10 mM HEPES buffer of pH 7.4; excitation at 310 nm).

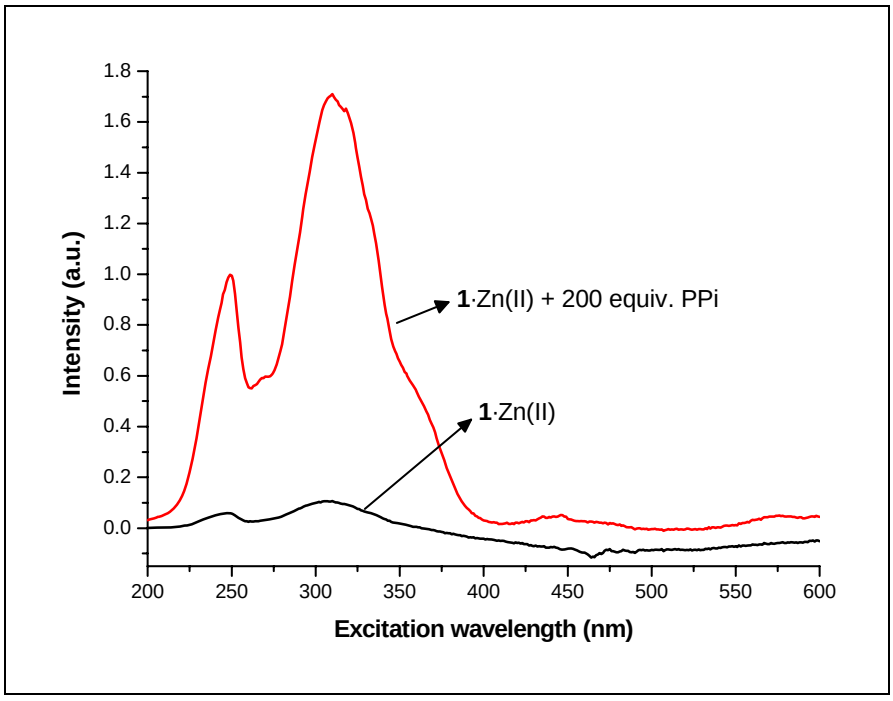


Fig S14. Excitation spectra recorded with probe **1**·Zn(II) (10 μM) and probe **1**·Zn(II) (10 μM) + 200 equivalent PPi (measured after 6 h of addition of the analyte) in 10 m mol HEPES buffer of pH 7.4.