Supporting Information

Design and chemical synthesis of a novel coumarin-based framework as a potential chemosensor of a neurotoxic insecticide, azamethiphos

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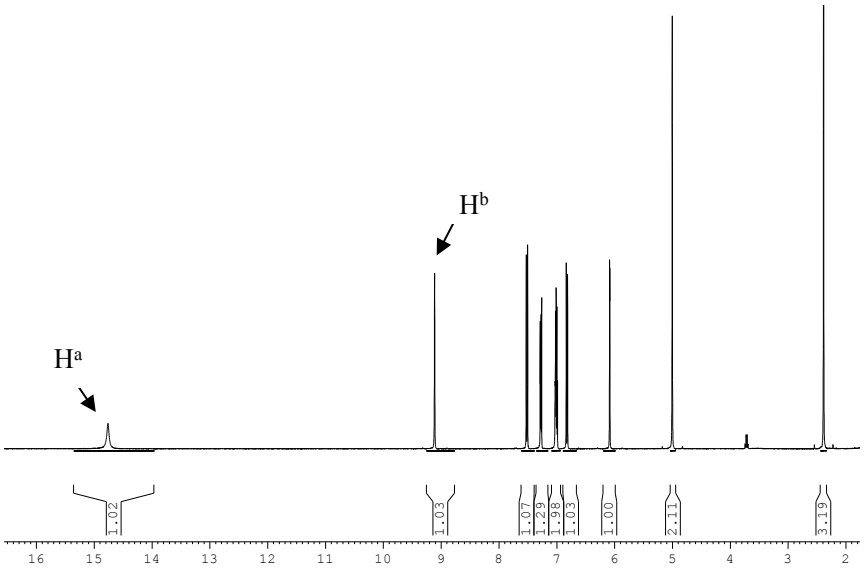

Figure S1. ^{1}H NMR spectrum of ligand L in dmso-*d6* (H^a and H^b denote hydroxyl and iminic protons, respectively).[31]

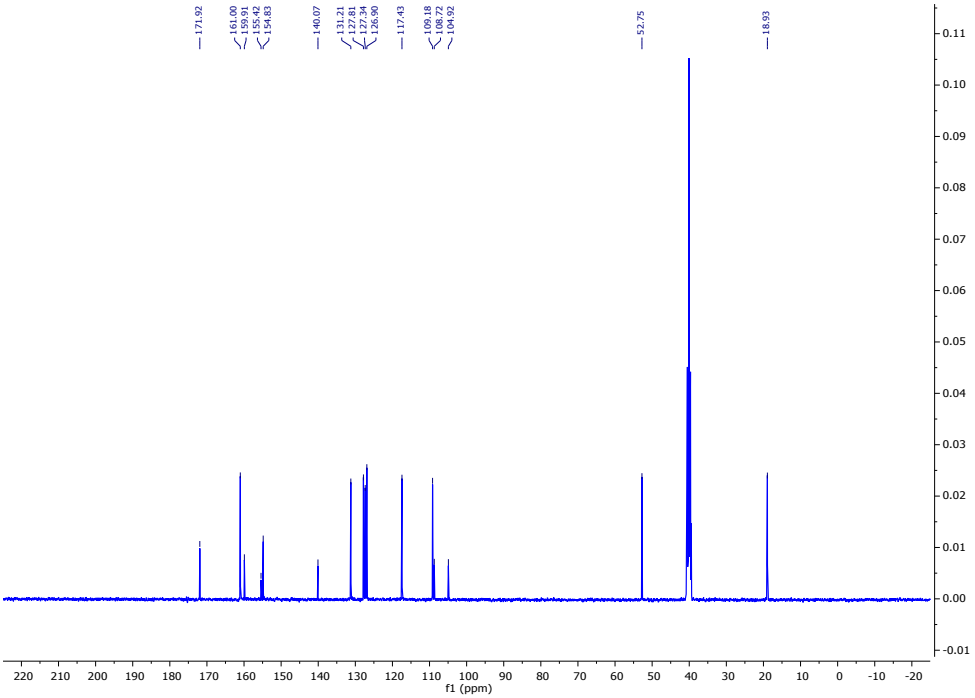

Figure S2.^{13}C NMR spectrum of ligand L in dmso-*d6*.

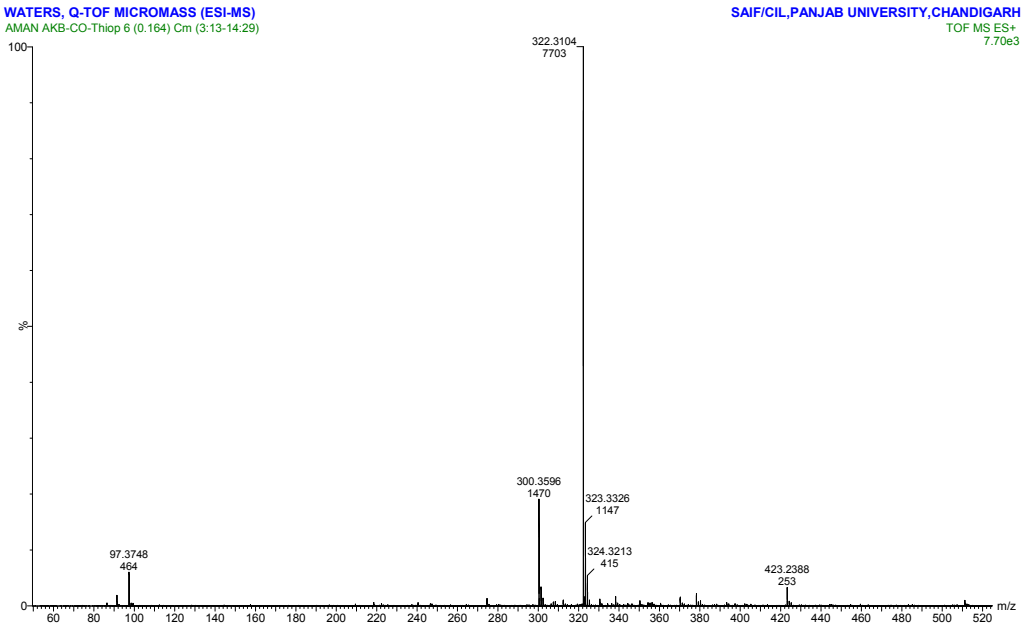

Figure S3. Mass spectrum of ligand L via electrospray ionization technique (positive mode)

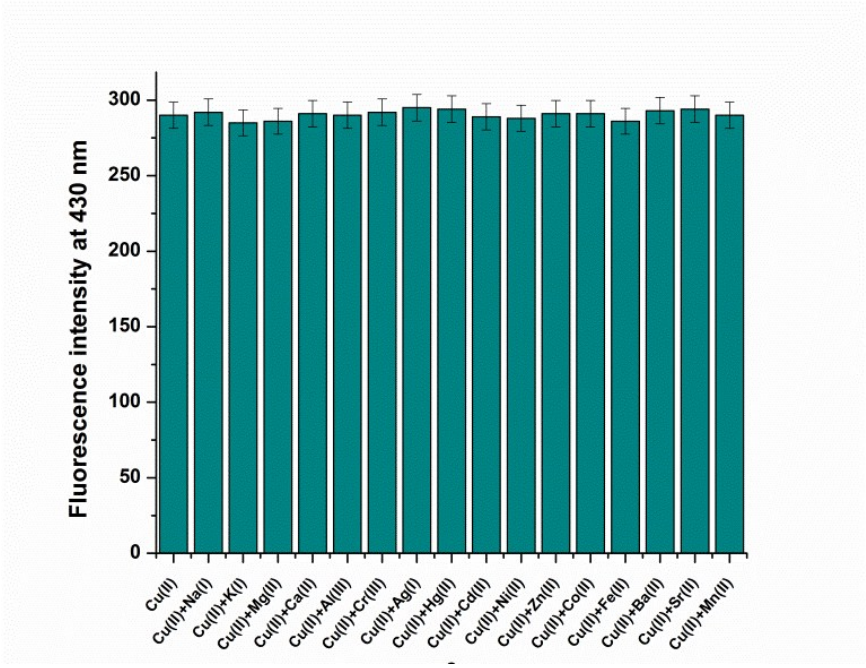

Figure S4. Competitive binding experiment of title ligand **A1** with Cu^{2+} in the presence of competing select metal ions.

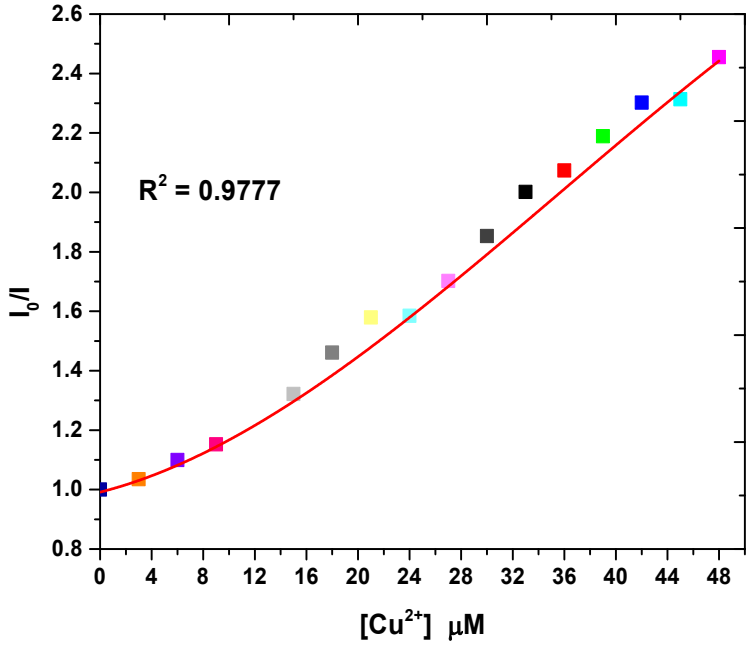

Figure S5. Stern-Volmer plot for determination of association constant (K_a) between Cu^{2+} and organic nanoparticles **A1**

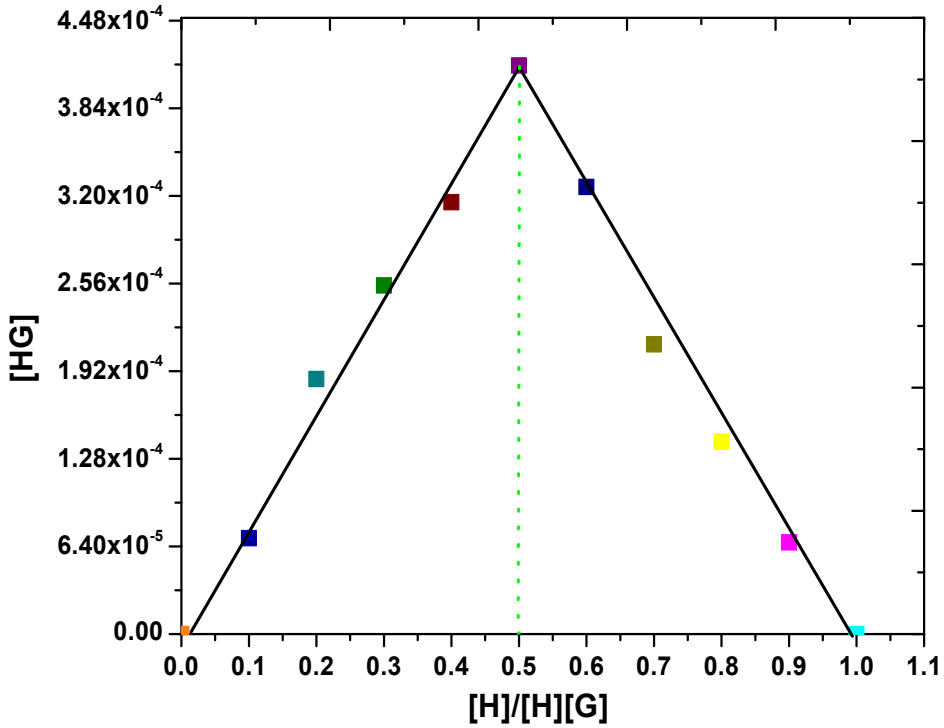

Figure S6. Job plot to determine the stoichiometry of the chemical coordination between the host ligand **A1** and guest metal ion Cu^{2+}.

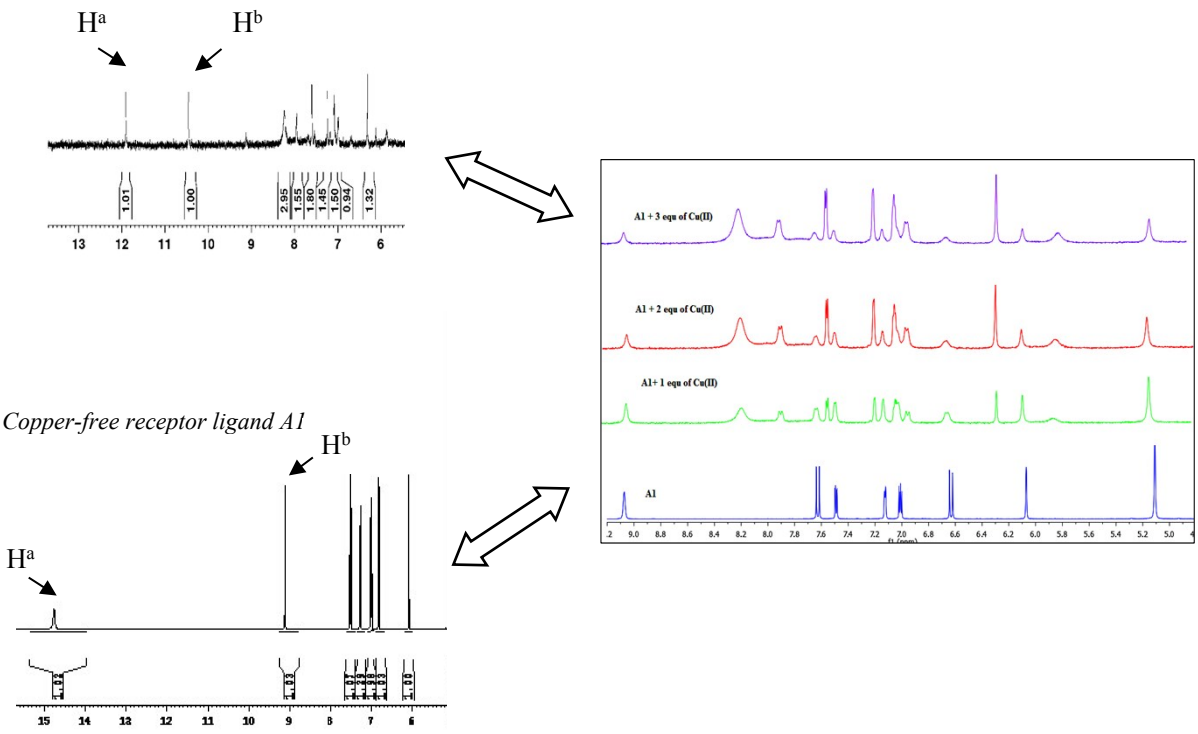

Figure S7.1 ^{1}H NMR titration of **A1** in presence and absence of Cu^{2+} in dmso-*d6* (H^a and H^b denote hydroxyl proton and iminic hydrogen of **A1**, respectively)

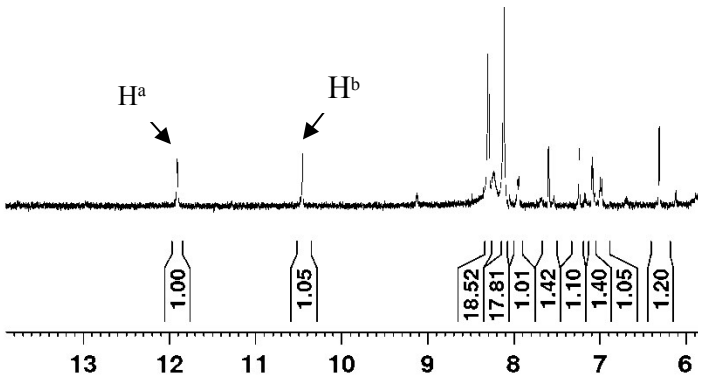

Figure S7.2 ^{1}H NMR titration of **A1** in presence of $Cu^{2+}$and azamethiphos in dmso-*d6* (H^a and H^b denote hydroxyl proton and iminic hydrogen of **A1**, respectively)

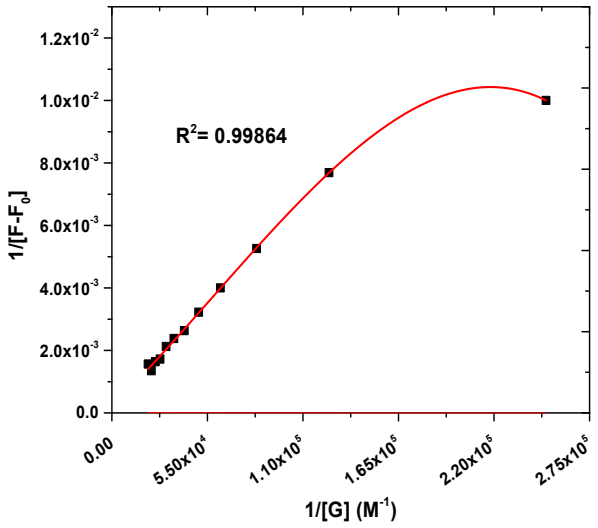

Figure S8. Benesi-Hildebrand plot to determine the binding constant between Cu^{2+}·**A1** with azamethiphos where F_0 and F denote the fluorescence emission intensity of the copper-bound receptor complex Cu^{2+}·**A1** in the absence and presence of azamethiphos (analyte), respectively.[G] represents the molar concentration of azamethiphos.

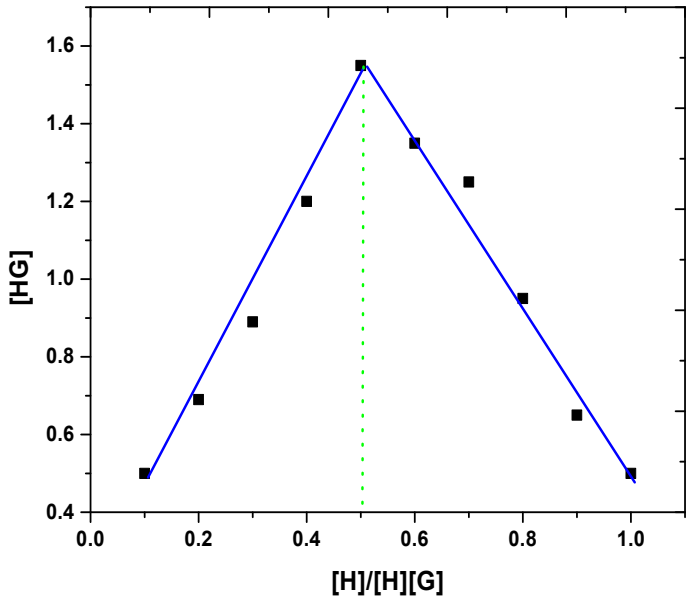

Figure S9. Job plot to determine the stoichiometry of the binding interaction between the host complex Cu^{2+}·**A1** and azamethiphos (analyte). [H] and [G] represent the molar concentration of the host complex Cu^{2+}·**A1** and azamethiphos, respectively

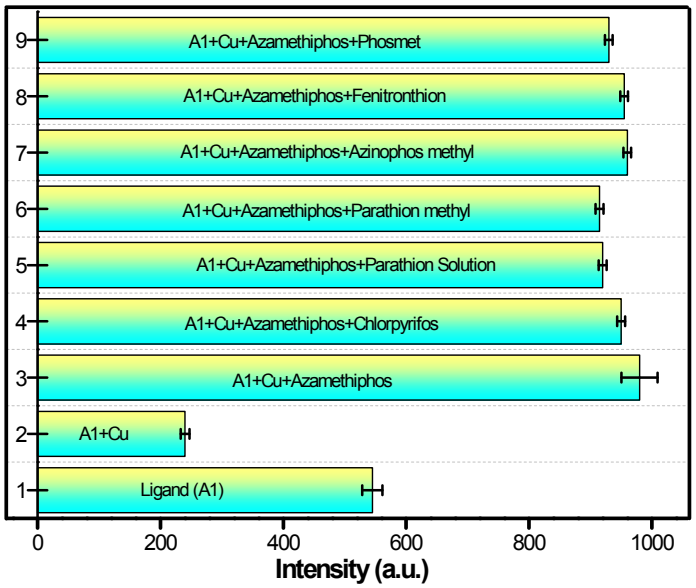

Figure S10. Competitive binding experiment of copper:ligand ensemble (Cu^{2+}·**A1** ; λ_{em} = 440 nm) towards azamethiphos in the presence of select organophosphate pesticides

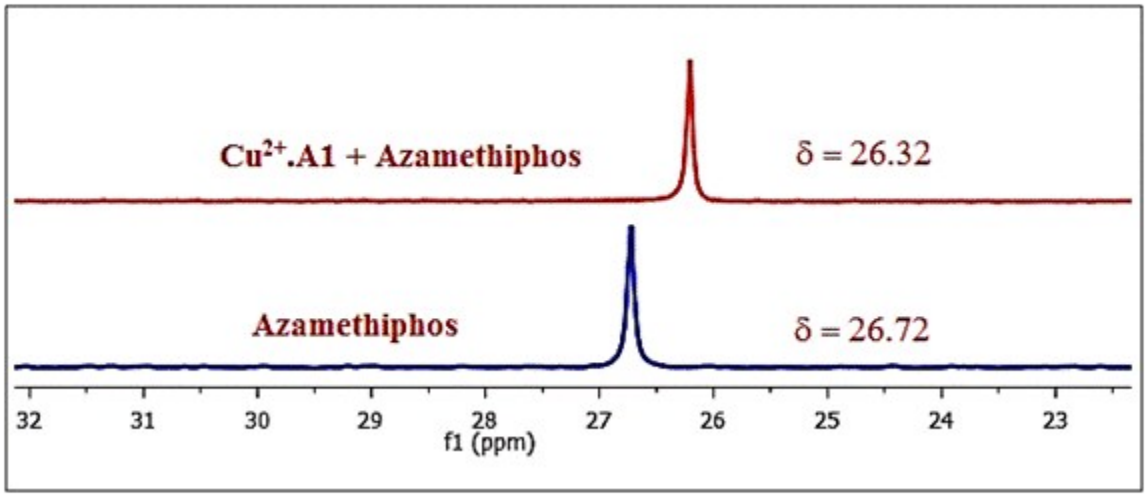

Figure S11. ^{31}P NMR spectrum of azamethiphos in the presence and absence of copper-ligand ensemble, Cu^{2+}·**A1**

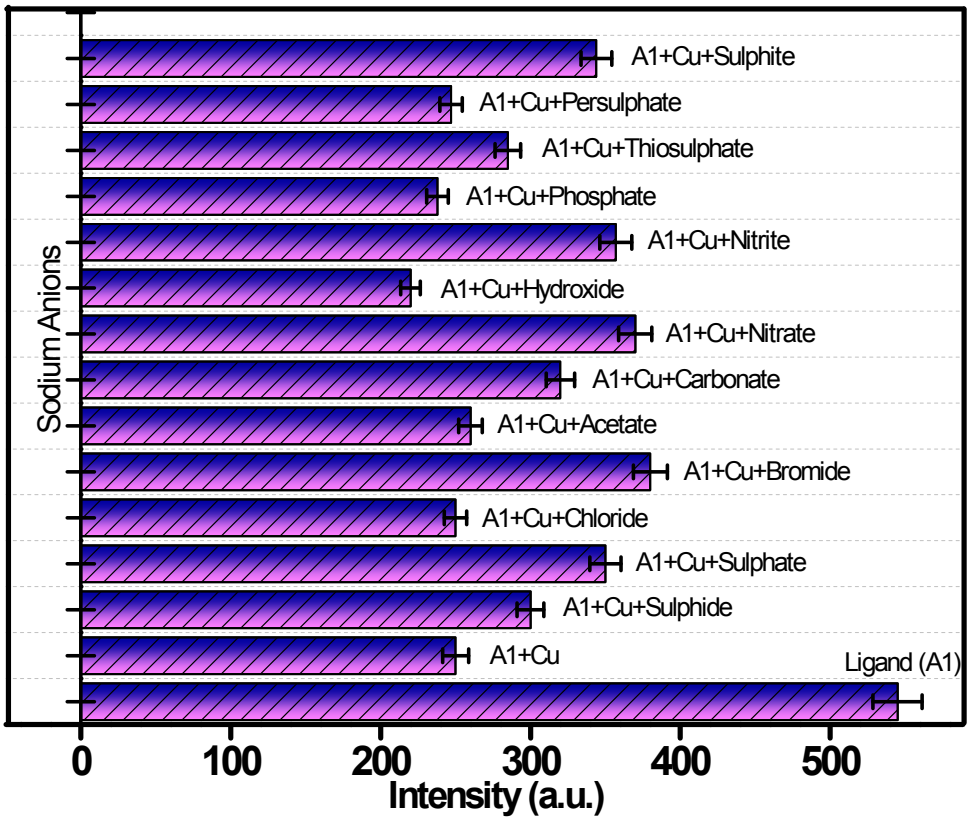

Figure S12. Fluorescence profile of Cu^{2+}-**A1** (50μM ; λ_{em} = 430nm) in presence of a library of select anions (50μM) in aqueous medium.

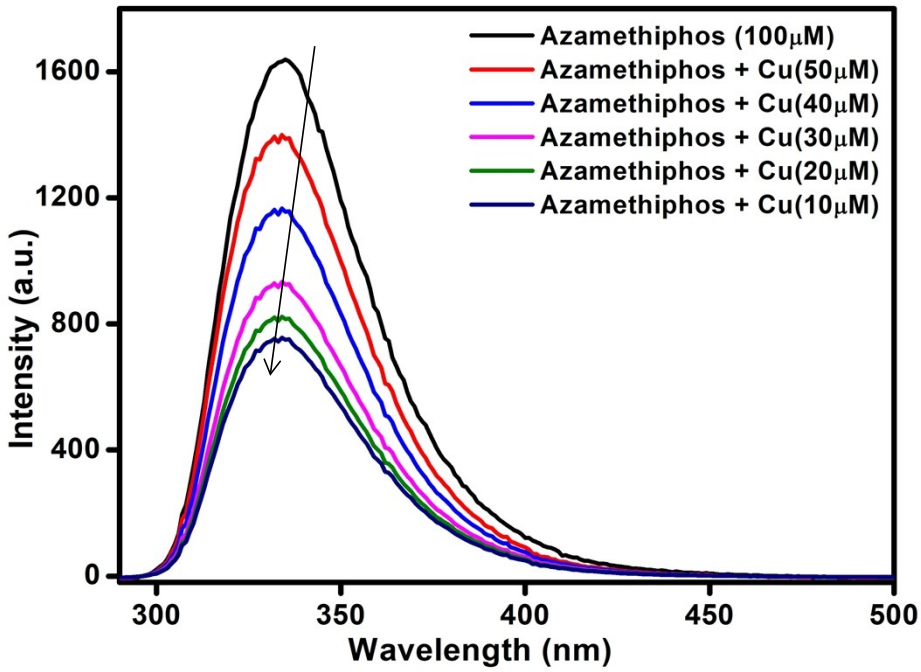

Figure S13. Fluorescence titration studies of azamethiphos (100 μM; λ_{em} = 330 nm) with Cu^{2+} (0-50 μM)

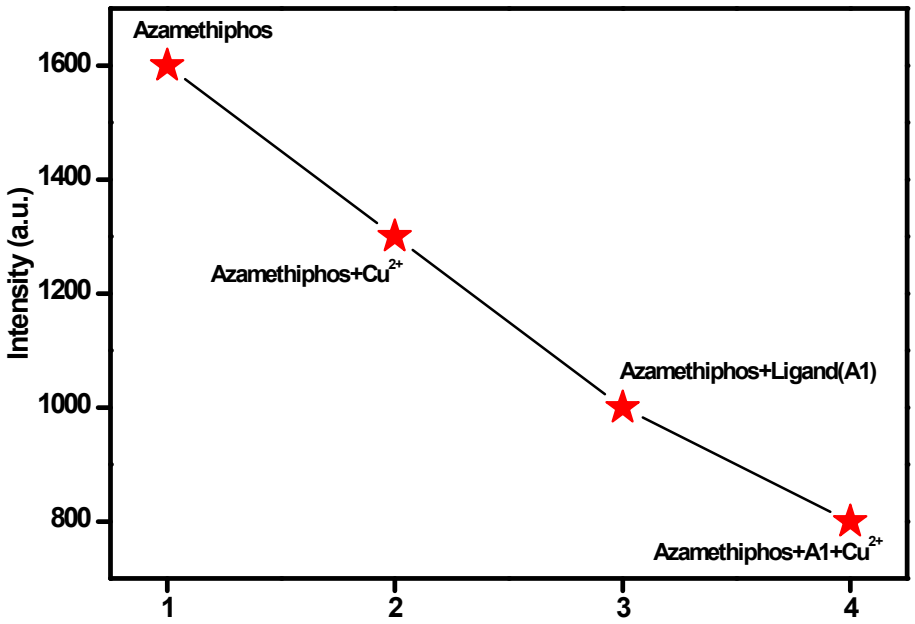

Figure S14. Fluorescence profile of azamethiphos (λ_{em} = 330 nm) in the presence of (i) Cu^{2+} (ii) ligand (**A1**) and (iii) ligand-copper ensemble (**A1**·Cu^{2+})

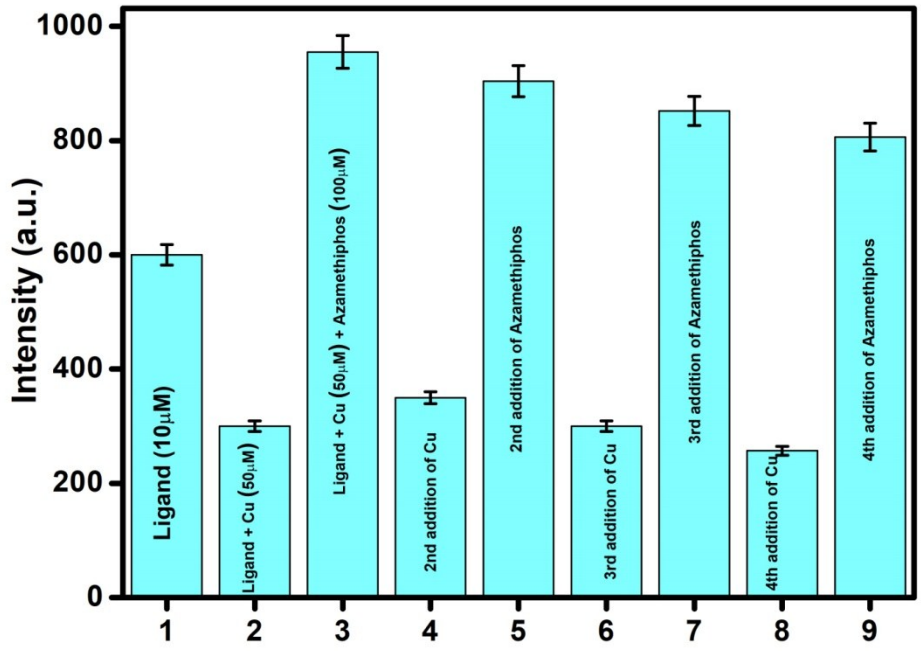

Figure S15. Cyclical fluctuations in fluorescence intensity of ligand **A1**(λ_{em} = 430 nm; 10μM) upon sequential dosage of azamethiphos (100 - 40 μM) and Cu^{2+} (50-20 μM) in an alternate pattern.

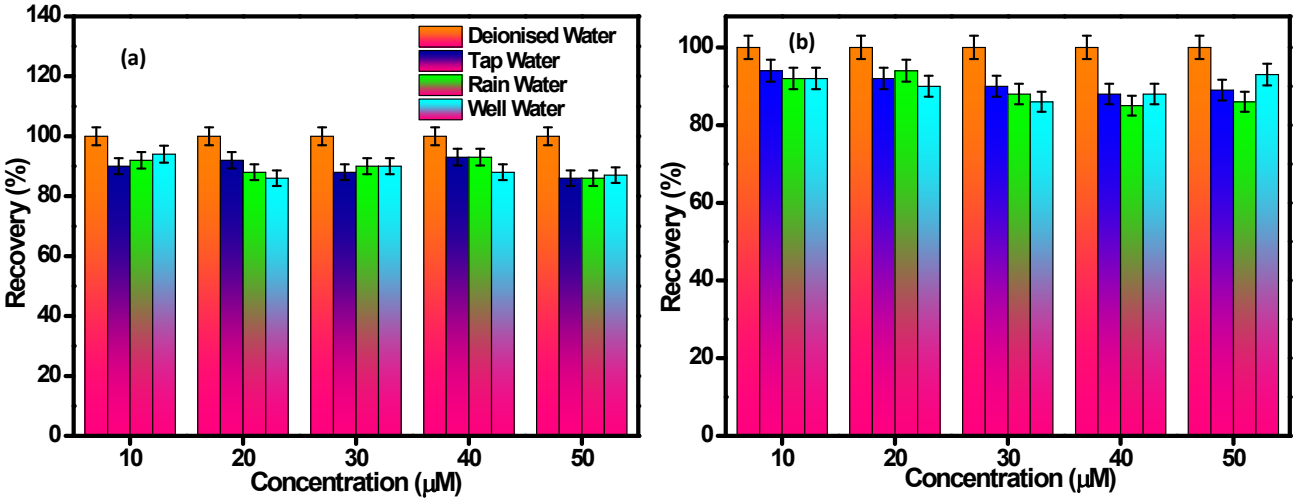

Figure S16. Fluorescence studies in deionized water and select real water samples (tap water, rain water and well water) of (a) **A1** (λ_{em} = 430 nm) upon spiking with Cu^{2+} (10, 20, 30, 40 and 50 μM) and (b) **A1**·Cu^{2+} (λ_{em} = 440 nm) upon spiking with azamethiphos (10, 20, 30, 40 and 50 μM)

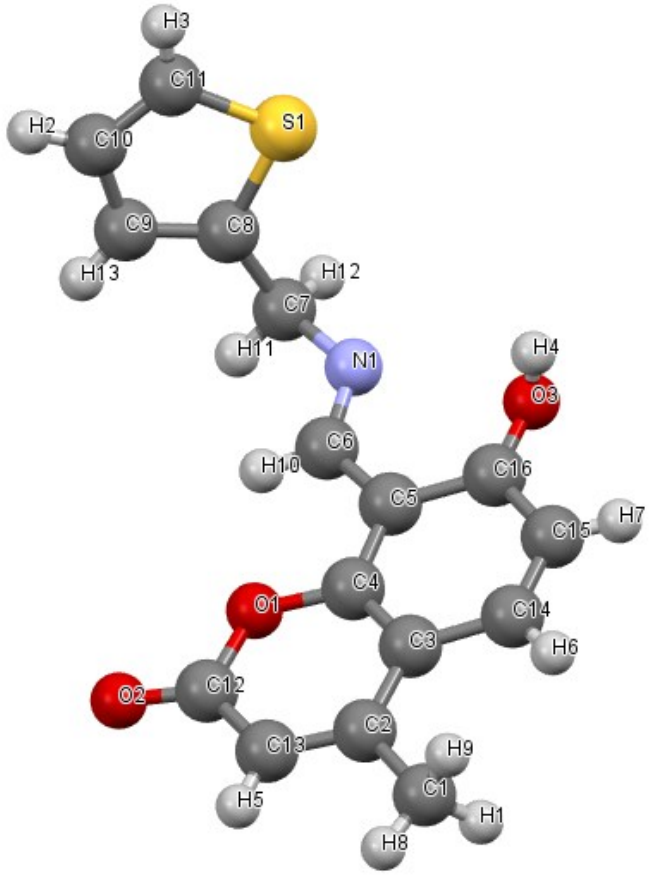

Figure S17. Fully labeled molecular structure of ligand L

Table S1. Crystal data and structure refinement for ligand L

Chemical formula	**$C_{16}H_{13}NO_3S$**	
Formula weight	**299.33**	
Temperature	**296(2) K**	
Wavelength	**0.71073 Å**	
Crystal system	**Triclinic**	
Space group	**P -1**	
Unit cell dimensions	**a = 7.518(7) Å**	**α = 70.671(10)°**
	b = 9.118(9) Å	**β = 71.668(11)°**
	c = 11.293(11) Å	**γ = 78.323(11)°**
Volume	**689.2(11) $Å^3$**	
Z	**2**	
Density (calculated)	**1.442 g/cm^3**	
Absorption coefficient	**0.244 mm^{-1}**	
F(000)	**312**	

Theta range for data collection	**1.98 to 25.16°**	
Index ranges	**-8<=h<=8, -10<=k<=10, -13<=l<=13**	
Reflections collected	**8677**	
Independent reflections	**2461 [R(int) = 0.0180]**	
Coverage of independent reflections	**99.9%**	
Absorption correction	**multi-scan**	
Structure solution technique	**direct methods**	
Structure solution program	**SHELXS-97 (Sheldrick, 2008)**	
Refinement method	**Full-matrix least-squares on F^2**	
Refinement program	**SHELXL-97 (Sheldrick, 2008)**	
Function minimized	**$\Sigma w(F_o^2 - F_c^2)^2$**	
Data / restraints / parameters	**2461 / 0 / 192**	
Goodness-of-fit on F^2	**1.051**	
Final R indices	**2186 data; I >2σ (I)** **all data**	**R1 = 0.0460, wR2 = 0.1408** **R1 = 0.0503, wR2 = 0.1461**
Weighting scheme	**$w=1/[\sigma^2(F_o^2)+(0.0917P)^2+0.2923P]$ where $P=(F_o^2+2F_c^2)/3$**	
Largest diff. peak and hole	**0.652 and -0.494 eÅ^{-3}**	

Table S2. Bond lengths (Å) of L

S1-C8	1.718(3)	S1-C11	1.716(3)
O1-C4	**1.370(2)**	**O1-C12**	**1.394(2)**
O2-C12	**1.210(3)**	**O3-C16**	**1.256(3)**
O3-H4	**0.82**	**N1-C6**	**1.301(3)**
N1-C7	**1.476(2)**	**C1-C2**	**1.498(3)**
C1-H8	**0.96**	**C1-H9**	**0.96**
C1-H1	**0.96**	**C2-C13**	**1.356(3)**
C2-C3	**1.437(3)**	**C3-C4**	**1.385(3)**
C3-C14	**1.431(3)**	**C4-C5**	**1.418(3)**
C5-C6	**1.413(3)**	**C5-C16**	**1.457(3)**
C6-H10	**0.93**	**C7-C8**	**1.498(3)**
C7-H11	**0.97**	**C7-H12**	**0.97**
C8-C9	**1.381(3)**	**C9-C10**	**1.406(4)**
C9-H13	**0.93**	**C10-C11**	**1.332(4)**
C10-H2	**0.93**	**C11-H3**	**0.93**
C12-C13	**1.428(3)**	**C13-H5**	**0.93**
C14-C15	**1.353(3)**	**C14-H6**	**0.93**

C15-C16	**1.441(3)**	**C15-H7**	**0.93**

Table S3. Bond angles (º) of L

C8-S1-C11	92.10(13)	C4-O1-C12	121.98(14)
C16-O3-H4	**109.5**	**C6-N1-C7**	**122.80(16)**
C2-C1-H8	**109.5**	**C2-C1-H9**	**109.5**
H8-C1-H9	**109.5**	**C2-C1-H1**	**109.5**
H8-C1-H1	**109.5**	**H9-C1-H1**	**109.5**
C13-C2-C3	**119.12(17)**	**C13-C2-C1**	**120.65(18)**
C3-C2-C1	**120.23(18)**	**C4-C3-C14**	**116.83(18)**
C4-C3-C2	**118.65(18)**	**C14-C3-C2**	**124.51(17)**
O1-C4-C3	**121.11(17)**	**O1-C4-C5**	**115.37(15)**
C3-C4-C5	**123.53(17)**	**C6-C5-C4**	**120.25(17)**
C6-C5-C16	**121.06(17)**	**C4-C5-C16**	**118.68(16)**
N1-C6-C5	**124.29(17)**	**N1-C6-H10**	**117.9**
C5-C6-H10	**117.9**	**N1-C7-C8**	**112.65(16)**
N1-C7-H11	**109.1**	**C8-C7-H11**	**109.1**
N1-C7-H12	**109.1**	**C8-C7-H12**	**109.1**
H11-C7-H12	**107.8**	**C9-C8-C7**	**126.54(19)**
C9-C8-S1	**110.08(16)**	**C7-C8-S1**	**123.37(16)**
C8-C9-C10	**112.5(2)**	**C8-C9-H13**	**123.7**
C10-C9-H13	**123.7**	**C11-C10-C9**	**113.8(2)**
C11-C10-H2	**123.1**	**C9-C10-H2**	**123.1**
C10-C11-S1	**111.5(2)**	**C10-C11-H3**	**124.2**
S1-C11-H3	**124.3**	**O2-C12-O1**	**115.57(17)**
O2-C12-C13	**127.85(18)**	**O1-C12-C13**	**116.58(17)**
C2-C13-C12	**122.53(18)**	**C2-C13-H5**	**118.7**
C12-C13-H5	**118.7**	**C15-C14-C3**	**122.29(17)**
C15-C14-H6	**118.9**	**C3-C14-H6**	**118.9**
C14-C15-C16	**122.17(18)**	**C14-C15-H7**	**118.9**
C16-C15-H7	**118.9**	**O3-C16-C15**	**122.47(18)**
O3-C16-C5	**121.03(17)**	**C15-C16-C5**	**116.49(18)**