

Supporting information

Syntheses, crystal structures and photophysical properties of Cu(II) complexes: Fine tuning of coordination sphere for selective binding of Azamethiphos.

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Table of Content:

Figure S1. ¹H NMR spectrum of ligand L1

Figure S2. ¹³C NMR spectrum of ligand L1

Figure S3. ¹H NMR spectrum of ligand L2

Figure S4. ¹³C NMR spectrum of ligand L2

Figure S5. FTIR Spectrum of ligand L1

Figure S6. FTIR Spectrum of ligand L2

Figure S7. ESI-mass spectrum of ligand L1

Figure S8. ESI-mass spectrum of ligand L2

Figure S9. FTIR Spectrum of complex C1

Figure S10. FTIR Spectrum of complex C2

Figure S11 (A): The powder XRD pattern of C1 (simulated from single crystal data and synthesized in bulk), (B) The powder XRD pattern of C2 (simulated from single crystal data and synthesized in bulk).

Figure S12: The solid state emission spectrum of C1 and C2 (bulk synthesis).

Figure S13. The emission spectrum of C2 (10 μM) in presence of tested organophosphate (30 μM)

Figure S14. Jobs plot of C1 in presence of azamethiphos.

Figure S15. ^{31}P NMR spectrum of Azamethiphos and copper complex of Azamethiphos in DMSO- d_6 .

Figure S16. The ESI-Mass spectrum of copper: azamethiphos complex.

Figure S17. The change in the emission spectrum on addition of Cu^{2+} ion (0-10 μM) in C1: azamethiphos solution.

Figure S18. Reversible switching cycles of fluorescence intensity ($\lambda_{\text{em}} = 430 \text{ nm}$) by alternate addition of azamethiphos and copper ion

Table S1. Selected bond lengths and angles (\AA , $^\circ$) for C1

Table S2. Hydrogen bonding parameters (\AA , $^\circ$) of C1

Table S3. Selected bond lengths and angles (\AA , $^\circ$) for C2

Table S4. Hydrogen bonding parameters (\AA , $^\circ$) of C2

Table S5. Comparisons table between literatures reported sensors and present sensor of organophosphates.

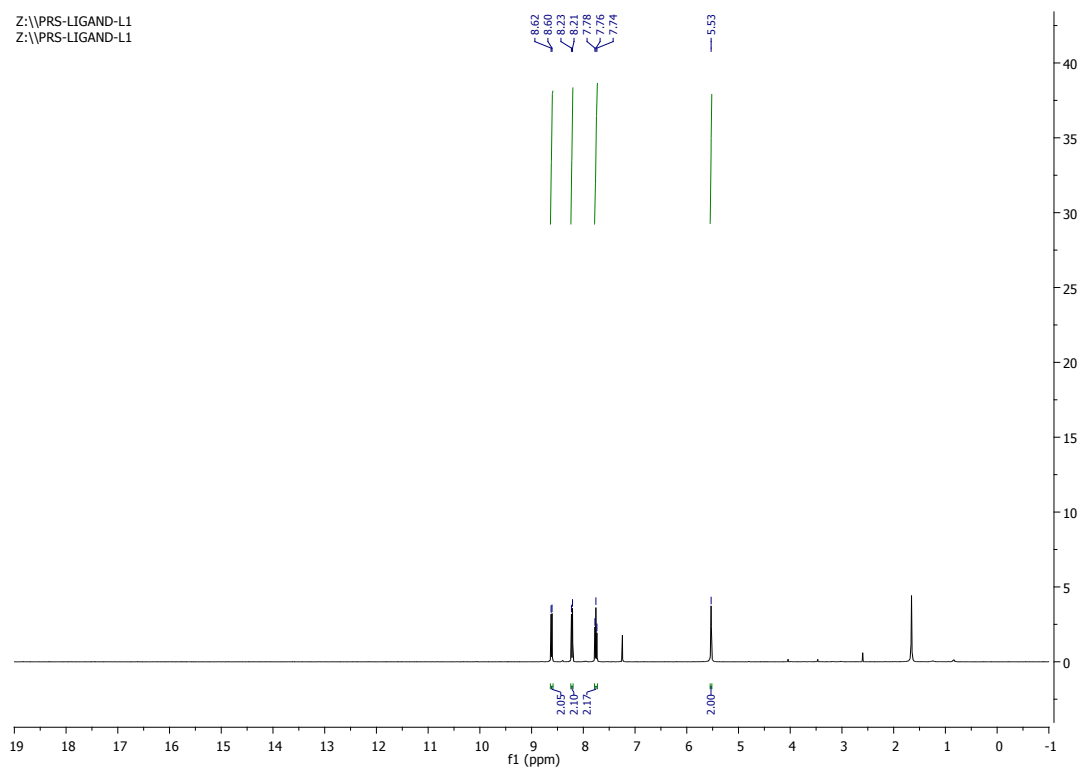


Figure S1. ^1H NMR spectrum of ligand **L1** in CDCl_3

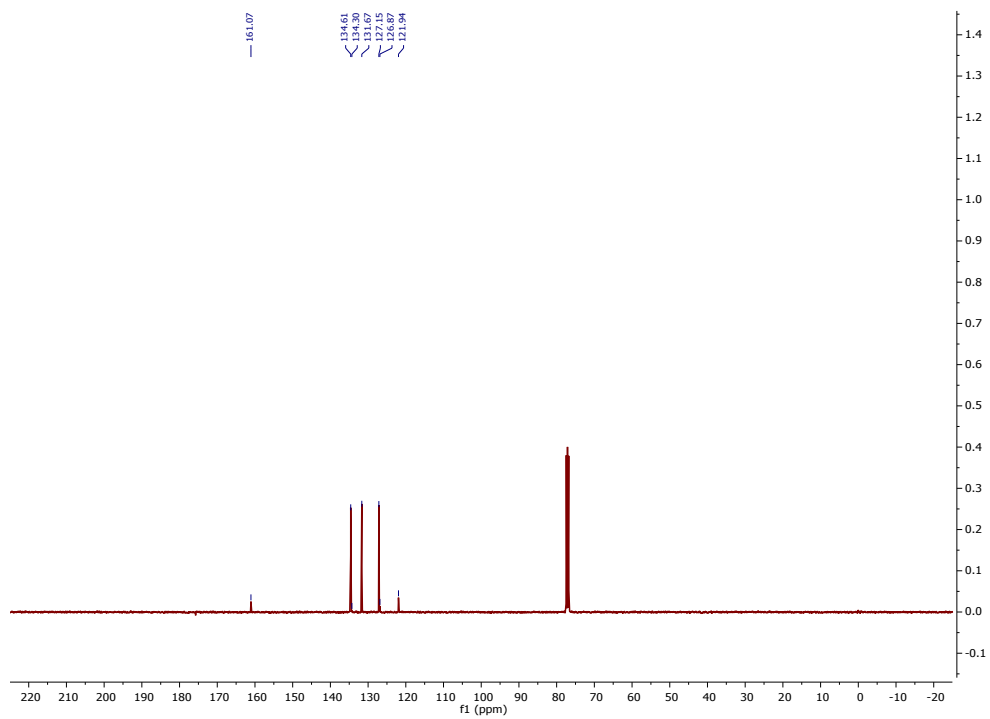


Figure S2. ¹³C NMR spectrum of ligand L1 in CDCl₃

Z:\PRS-LIGAND-L2
Z:\PRS-LIGAND-L2

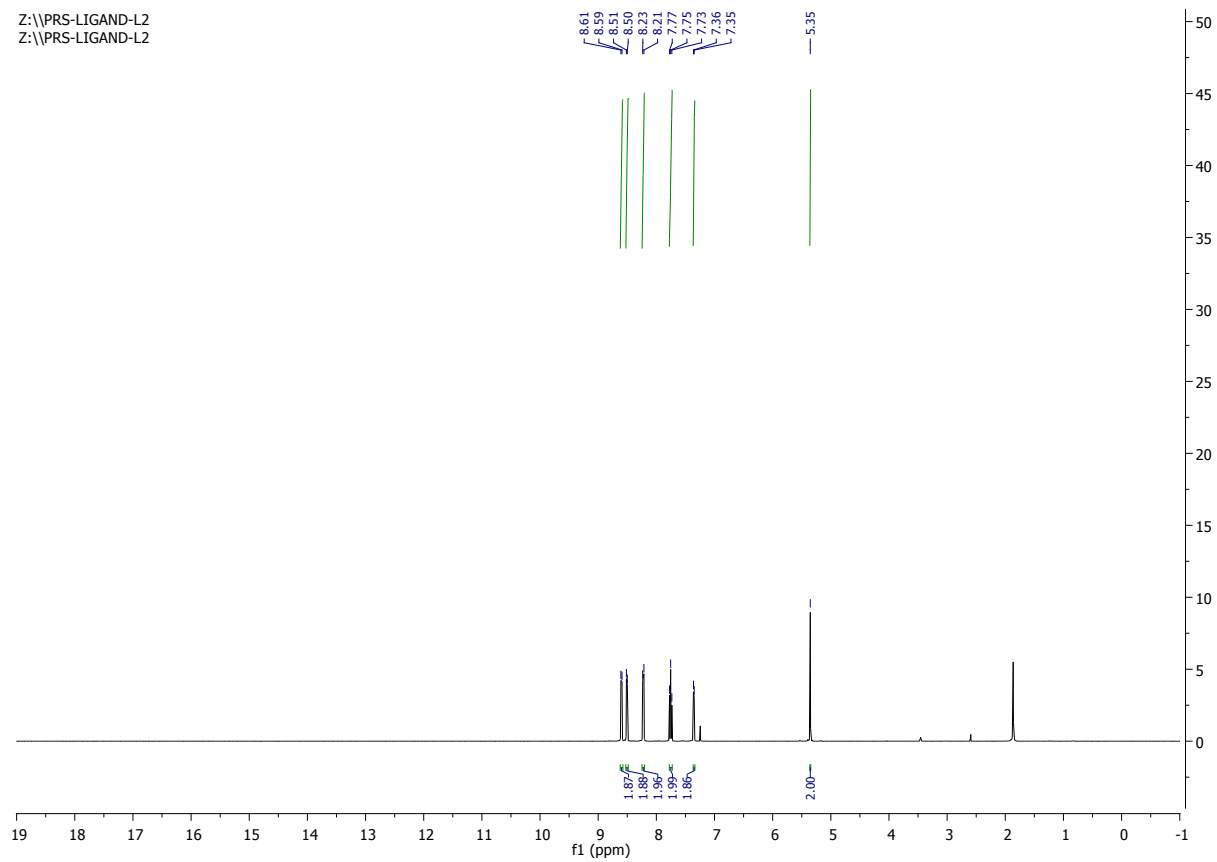


Figure S3. ^1H NMR spectrum of ligand L2 in CDCl_3

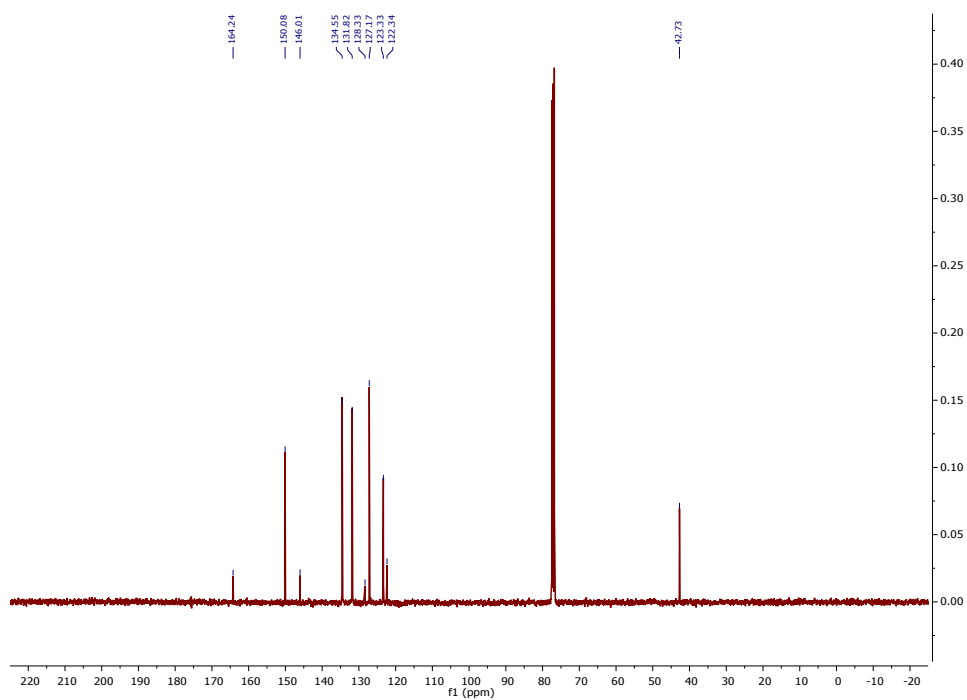


Figure S4. ^{13}C NMR spectrum of ligand L2 in CDCl_3

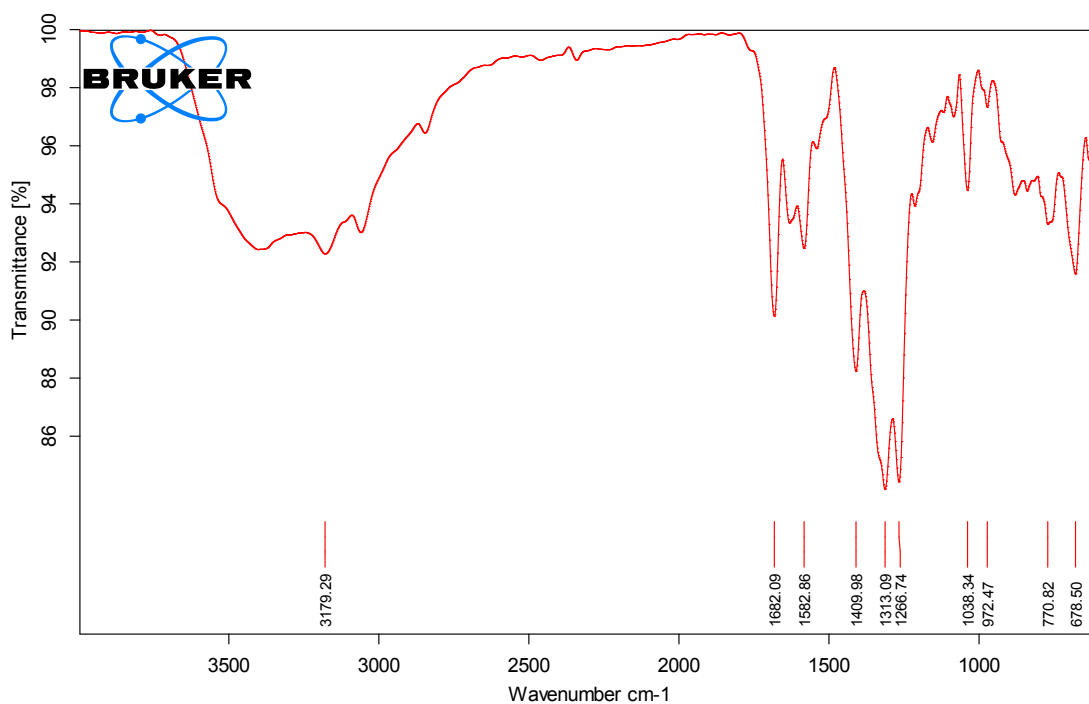


Figure S5. FTIR Spectrum of ligand L1

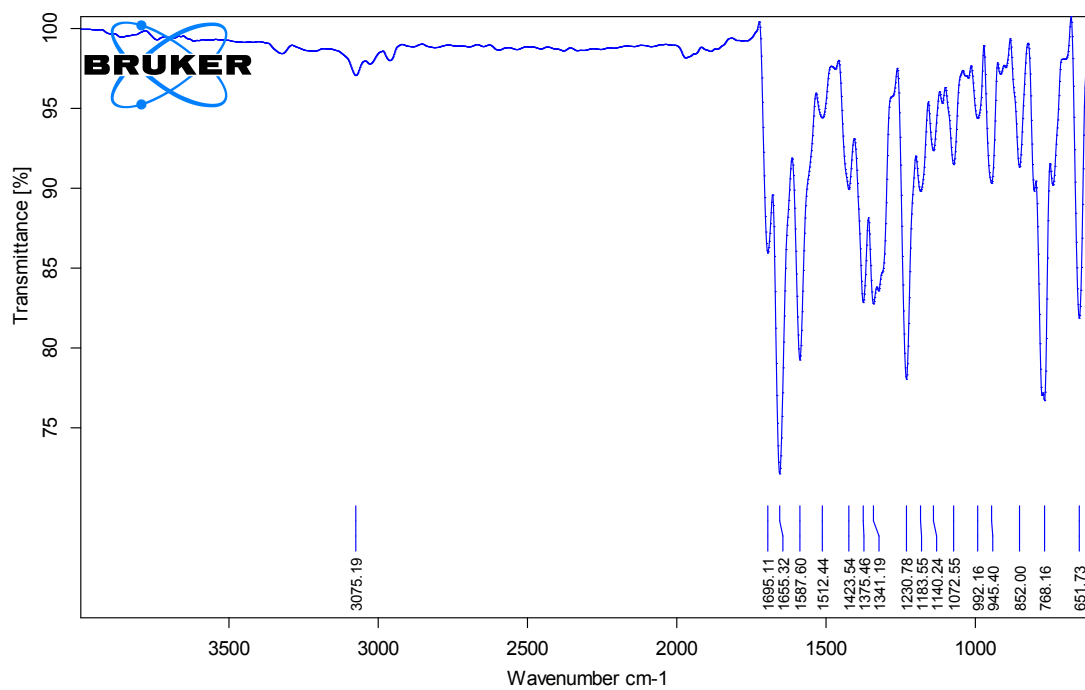


Figure S6. FTIR Spectrum of ligand L2

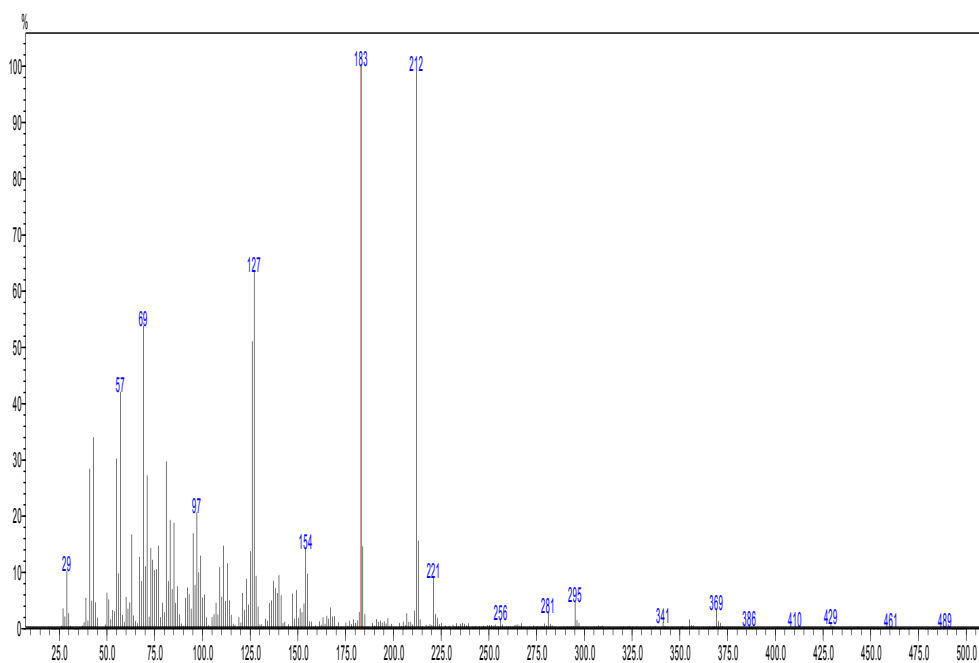


Figure S7. ESI-mass spectrum of ligand L1

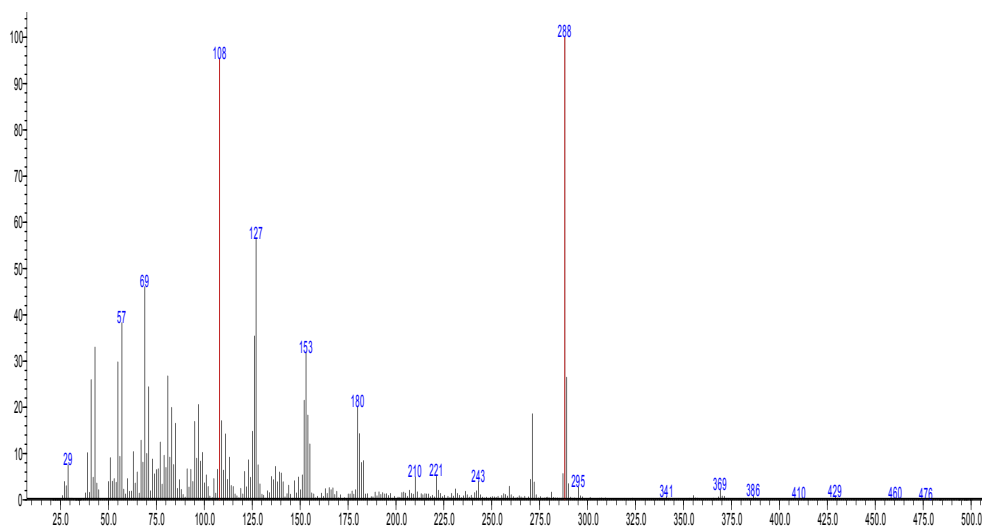


Figure S8. ESI-mass spectrum of ligand L2

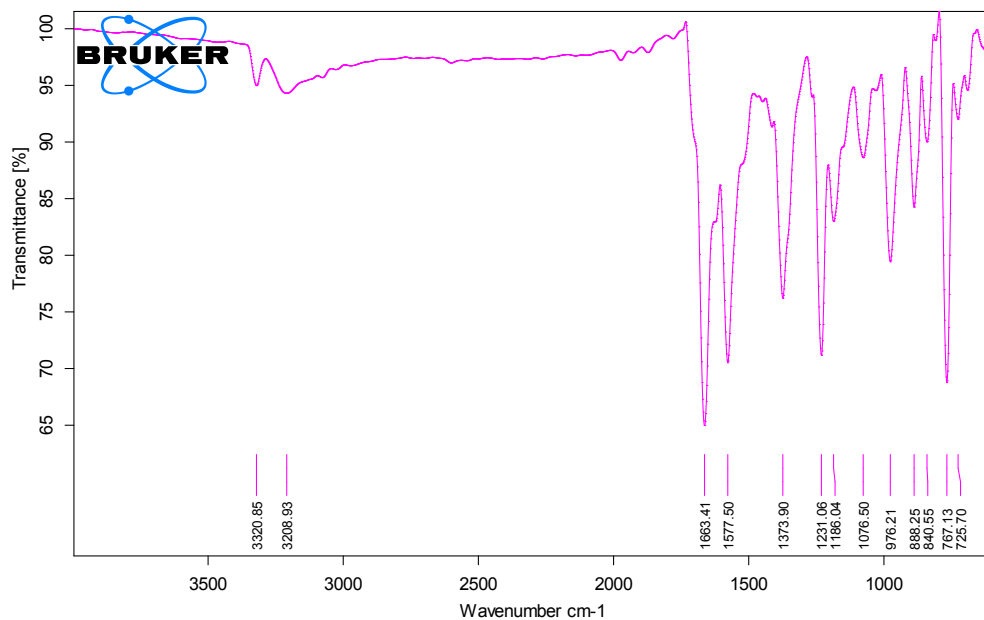


Figure S9. FTIR Spectrum of complex C1

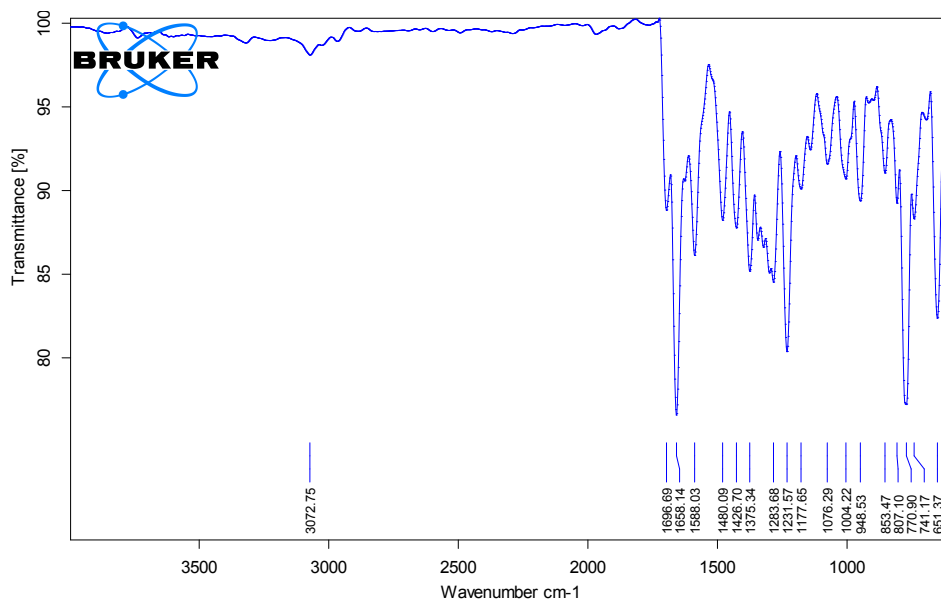


Figure S10. FTIR Spectrum of complex C2

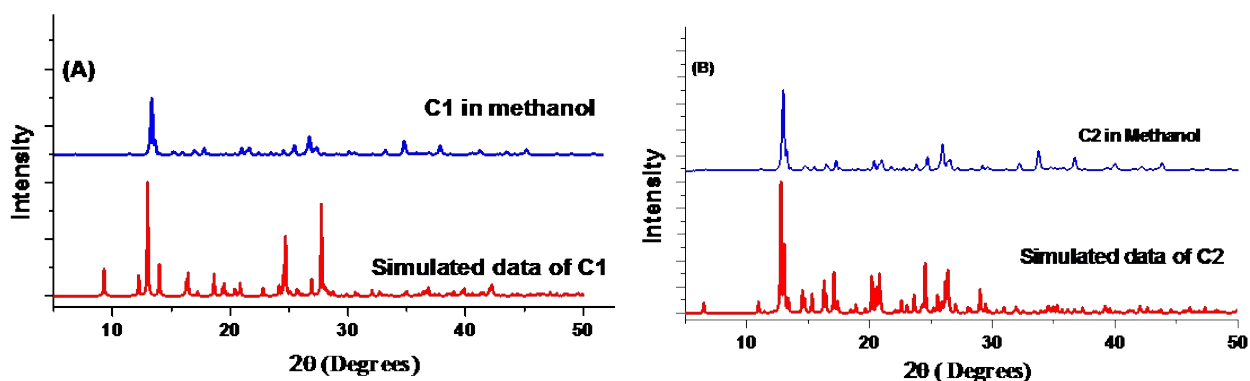


Figure S11 (A): The powder XRD pattern of C1 (simulated from single crystal data and synthesized in bulk), (B) The powder XRD pattern of C2 (simulated from single crystal data and synthesized in bulk).

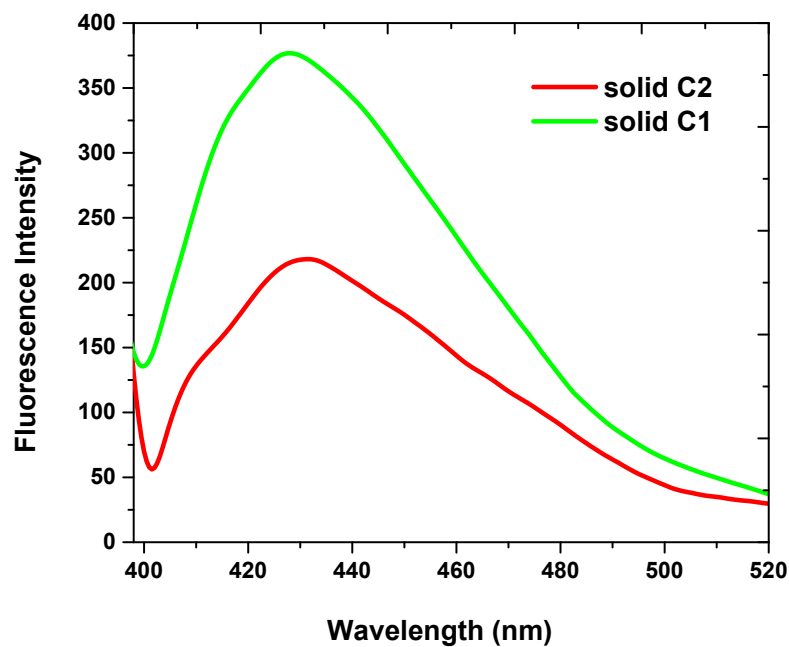


Figure S12: The solid state emission spectrum of C1 and C2 (bulk synthesis).

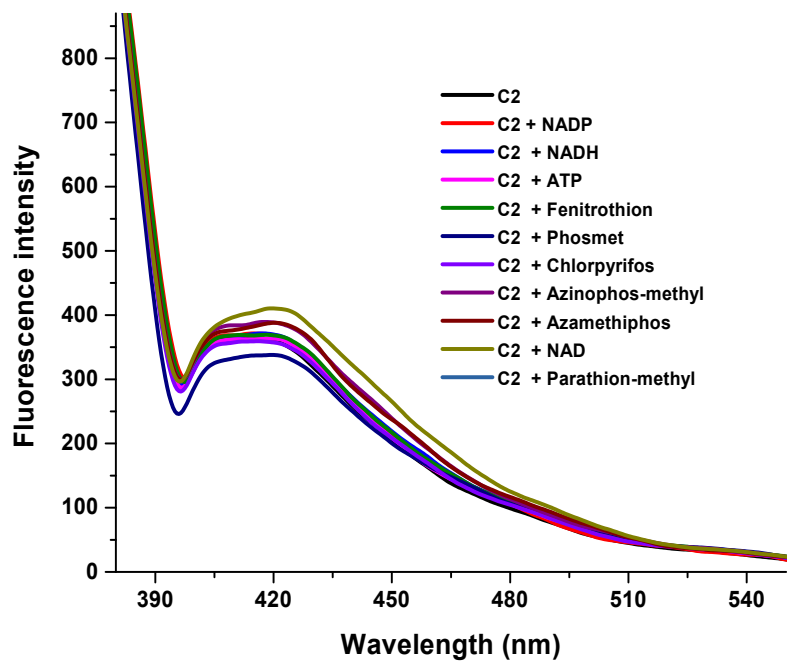


Figure S13. The emission spectrum of C2 (10 μM) in presence of tasted organophosphate (30 μM)

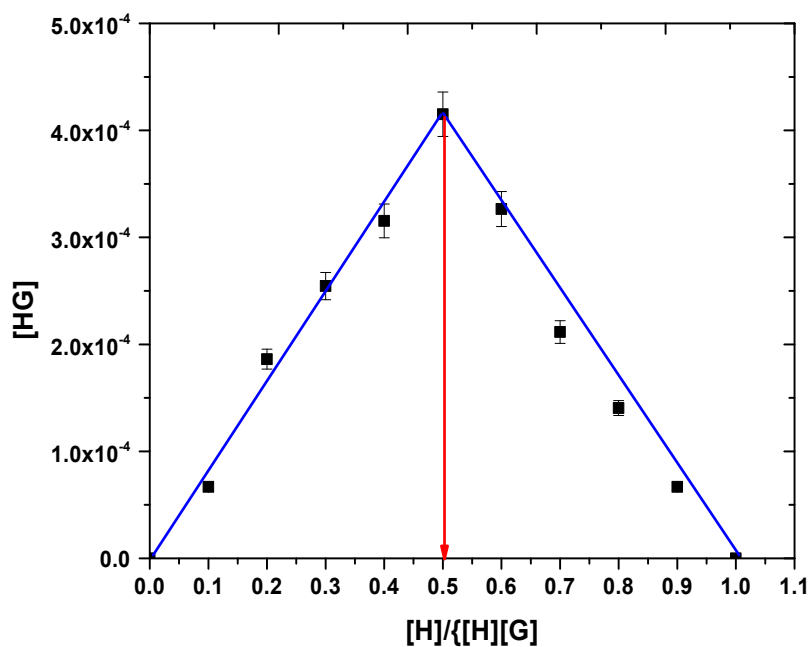


Figure S14. Jobs plot of C1 in presence of azamethiphos.

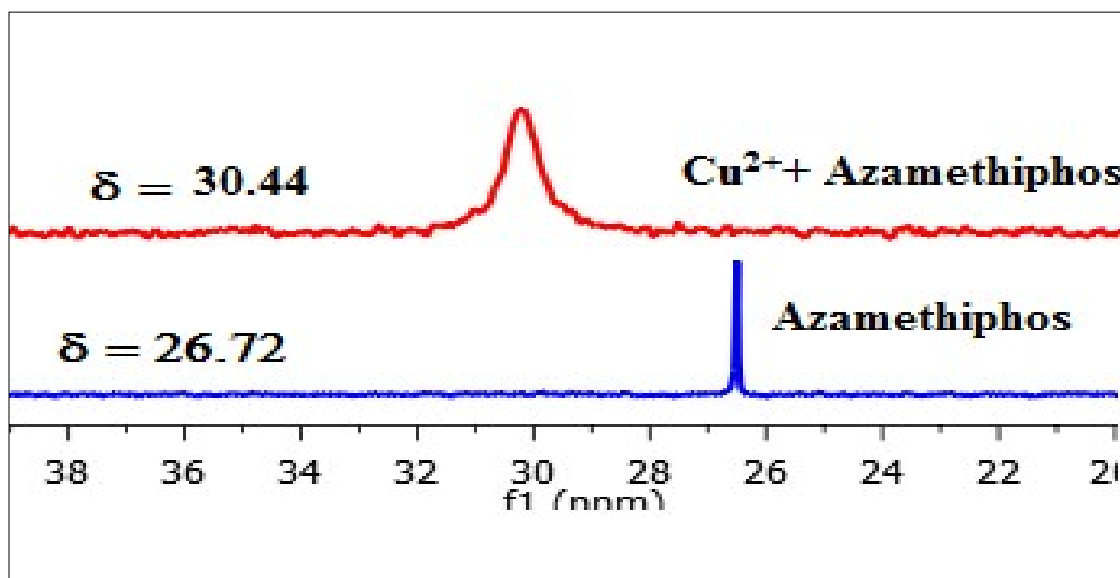


Figure S15. ³¹P NMR spectrum of Azamethiphos and copper complex of Azamethiphos in DMSO-d₆

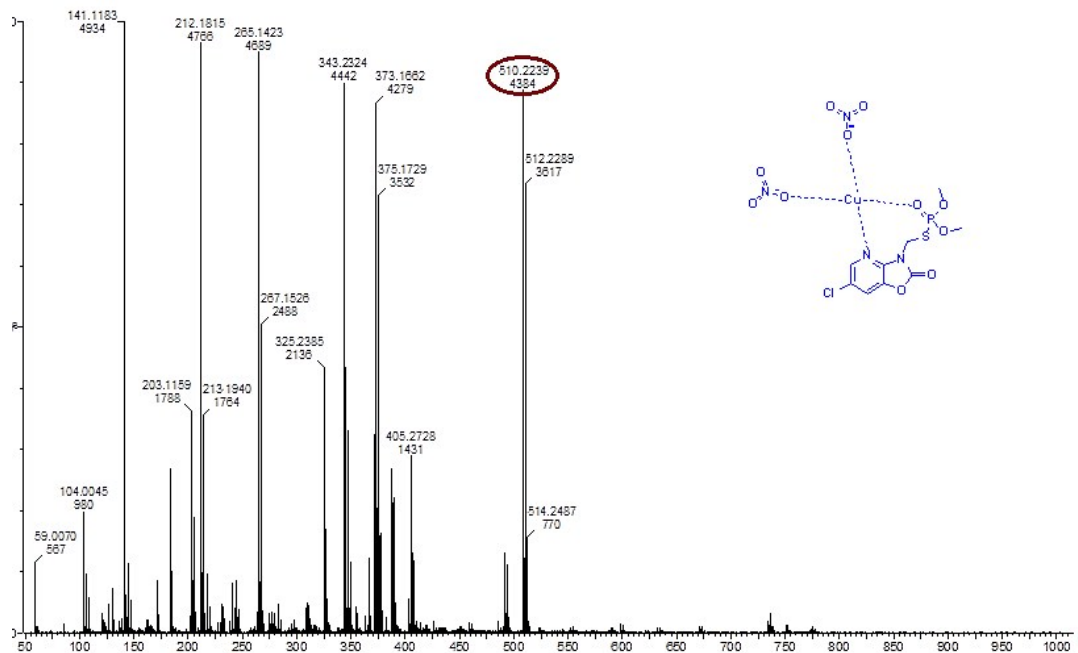


Figure S16. The ESI-Mass spectrum of copper: azamethiphos complex

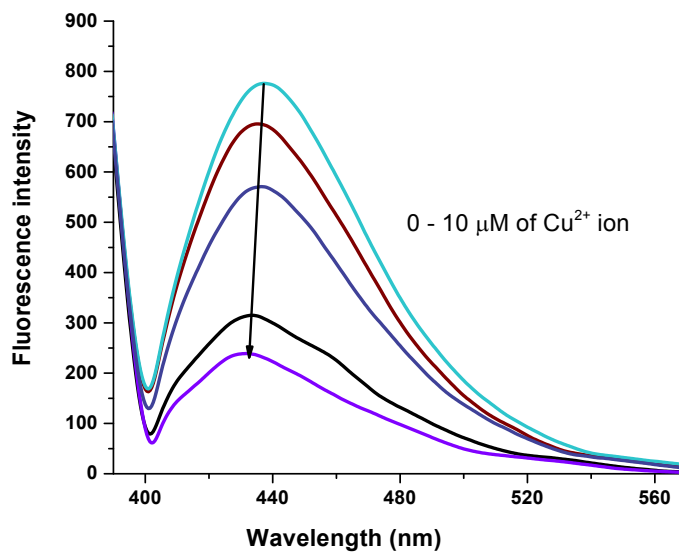


Figure S 17. The change in the emission spectrum on addition of Cu^{2+} ion (0-10 μM) in C1: azamethiphos (10:30 μM).

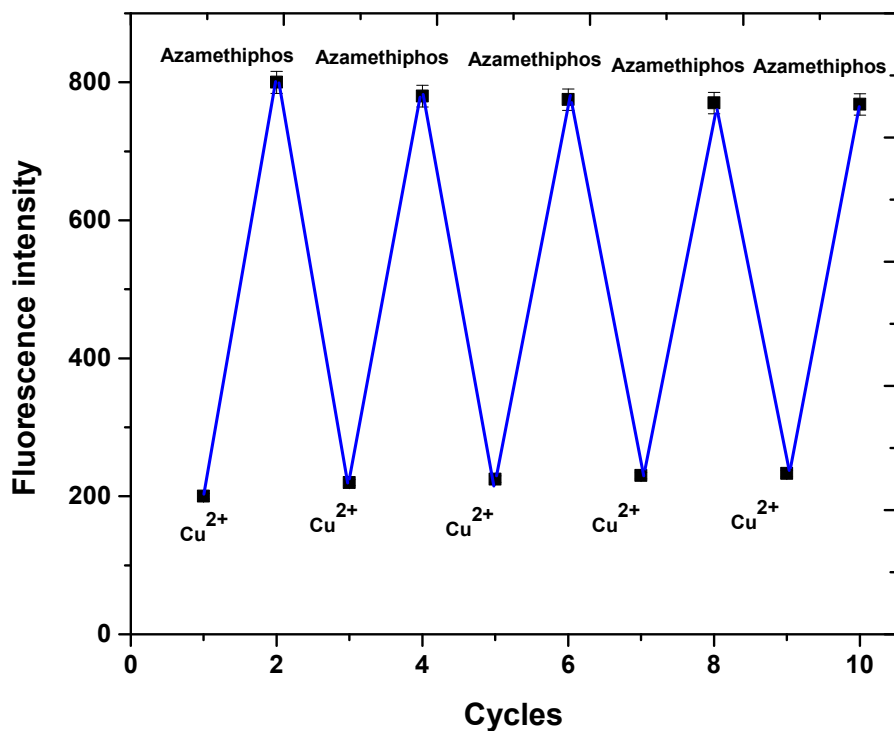


Figure S18. Reversible switching cycles of fluorescence intensity ($\lambda_{em} = 430$ nm) by alternate addition of azamethiphos and copper ion

Table S1. Selected bond lengths and angles (\AA , $^\circ$) for C1

Bond lengths(\AA)					
Cu(1)-N(2)	1.9814(18)	O(1)-C(1)	1.211(3)	O(4)-N(3)	1.246(3)
Cu(1)-O(2)	2.1307(15)	O(2)-C(12)	1.231(2)	O(5)-N(3)	1.220(2)
Cu(1)-O(3)	2.1632(17)	O(3)-N(3)	1.273(2)	N(1)-C(12)	1.387(3)
Bond angles($^\circ$)					
N(2)#1-Cu(1)-N(2)	180.0	O(2)-Cu(1)-O(2)#1	180.0	N(2)#1-Cu(1)-O(3)#1	96.38(8)
N(2)#1-Cu(1)-O(2)	99.70(6)	N(2)#1-Cu(1)-O(3)	83.62(8)	N(2)-Cu(1)-O(3)#1	83.62(8)
N(2)-Cu(1)-O(2)	80.30(6)	N(2)-Cu(1)-O(3)	96.38(8)	O(2)-Cu(1)-O(3)#1	81.45(6)
N(2)#1-Cu(1)-O(2)#1	80.30(6)	O(2)-Cu(1)-O(3)	98.55(6)	O(2)#1-Cu(1)-O(3)#1	98.55(6)
N(2)-Cu(1)-O(2)#1	99.70(6)	O(2)#1-Cu(1)-O(3)	81.45(6)	O(3)-Cu(1)-O(3)#1	180.0

Table S2. Hydrogen bonding parameters (Å, °) of C1

D-H...A	D...A/ Å	H...A/ Å	D-H...A/°
N2-H1A...O1 ⁱ	2.983(2)	2.178(3)	172.4(2)
N2-H1B...O4 ⁱⁱ	2.866(3)	2.033(3)	164.9(3)
C4-H4A...O5 ⁱⁱⁱ	3.251(3)	2.675(2)	120.7(2)

Equivalent positions: (i) -x,-y+1,-z+1, (ii) -x+1,-y,-z+1, (iii) -x+1,-y+1,-z, (iv) x,+y+1,+z-1,

Table S3. Selected bond lengths and angles (Å,°) for C2

Bond lengths(Å)					
Cu(1)-N(1)	1.9819(17)	Cu(1)-O(3)#1	1.9930(16)	N(1)-C(1)	1.338(3)
Cu(1)-N(1)#1	1.9819(17)	Cu(1)-O(5)	2.423(2)	N(1)-C(5)	1.339(3)
Cu(1)-O(3)	1.9930(16)	Cu(1)-O(5)#1	2.423(2)	N(2)-C(18)	1.395(3)
Bond angles(°)					
N(1)-Cu(1)-N(1)#1	91.50(10)	O(3)-Cu(1)-O(3)#1	90.53(10)	N(1)-Cu(1)-O(5)#1	104.15(7)
N(1)-Cu(1)-O(3)	92.22(7)	N(1)-Cu(1)-O(5)	107.83(8)	N(1)#1-Cu(1)-O(5)#1	107.83(8)
N(1)#1-Cu(1)-O(3)	160.65(7)	N(1)#1-Cu(1)-O(5)	104.15(7)	O(3)-Cu(1)-O(5)#1	89.63(8)
N(1)-Cu(1)-O(3)#1	160.65(7)	O(3)-Cu(1)-O(5)	56.71(7)	O(3)#1-Cu(1)-O(5)#1	56.71(7)
N(1)#1-Cu(1)-O(3)#1	92.22(7)	O(3)#1-Cu(1)-O(5)	89.63(8)	O(5)-Cu(1)-O(5)#1	133.53(11)

Table S4. Hydrogen bonding parameters (Å, °) of C2

D-H...A	D...A/ Å	H...A/ Å	D-H...A/°
C1-H1...O4 ⁱ	3.172(3)	2.571(3)	121.4(1)
C2-H2...O1	3.207(3)	2.576(2)	124.2(1)
C5-H5 ...O1 ⁱⁱ	3.273(3)	2.437(2)	146.7(1)

Equivalent positions: (i) -x+1,-y+1,-z+1, (ii)x,-y,+z-1/2

Reference: (S)

1. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, G. G.

Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 1999, 32, 115-119.

2. G. M. Sheldrick, *Acta Crystallogr. A* 71 (2015) 3-8.
3. L.J. Farrugia, *J. Appl. Crystallogr.* 32, 1999, 837.
4. M. Nardelli, *J. Appl. Crystallogr.* 28, 1995, 659.
5. W. T. Pennington, DIAMOND - Visual Crystal Structure Information System, *J. Appl. Cryst.* 32, 1999, 1028.

Table S5. Comparisons table between literatures reported sensors and present sensor of organophosphate.

S.NO	Material used	Technique used for sensing	Detection limit	Solvent System	Reference No.
1	Zirconium nanoparticles	electrochemical	9 ng/ml	Water	1
2	Organic receptor	Fluorescence	Not given	dichloromethane	2
3	Lysine modified carbon nanotubes	electrochemical	Microlevel	Ethanol/water	3
4	Metal complexes	Fluorescence	44 – 71 nM	Water	4
5	Organic receptor	NMR spectroscopy	Not given	DMSO-d6	5
6	Metal complex	Fluorescence	Not given	Chloroform: methanol	6
7	Organic receptor	Fluorescence	Not given	Methanol	7
8	Metal complexes	Fluorescence	Not given	Chloroform: acetonitrile	8
9	Metal complexes	Fluorescence	19 nM	Methanol	Present manuscript

References:

- 1 G. Liu and Y. Lin, 2005, **77**, 5894–5901.
- 2 S.-W. Zhang and T. M. Swager, *J. Am. Chem. Soc.*, 2003, **125**, 3420–3421.
- 3 P. M. Diakowski, Y. Xiao, M. W. P. Petryk and H.-B. Kraatz, *Anal. Chem.*, 2010, **82**, 3191–3197.
- 4 P. Raj, A. Singh, K. Kaur, T. Aree, A. Singh and N. Singh, *Inorg. Chem.*, 2016.
- 5 M. R. Sambrook, J. R. Hiscock, A. Cook, A. C. Green, I. Holden, J. C. Vincent and P. A.

- Gale, *Chem. Commun.*, 2012, **48**, 5605–5607.
- 6 S. Sarkar and R. Shunmugam, *Chem. Commun.*, 2014, **50**, 8511–8513.
- 7 T. J. Dale and J. Rebek, *J. Am. Chem. Soc.*, 2006, **128**, 4500–4501.
- 8 D. Knapton, M. Burnworth, S. J. Rowan and C. Weder, *Angew. Chemie*, 2006, **118**, 5957–5961.