Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

A new 1,2,3-triazole-decorated imino-phenol: Selective sensing of Zn^{2+}, Cu^{2+} and picric acid under different experimental conditions

Sumit Ghosh, Nabajyoti Baildya and Kumaresh Ghosh*

Department of Chemistry, University of Kalyani, Kalyani-741235, India.
Email: ghosh_k2003@yahoo.co.in; kumareshchem18@klyuniv.ac.in

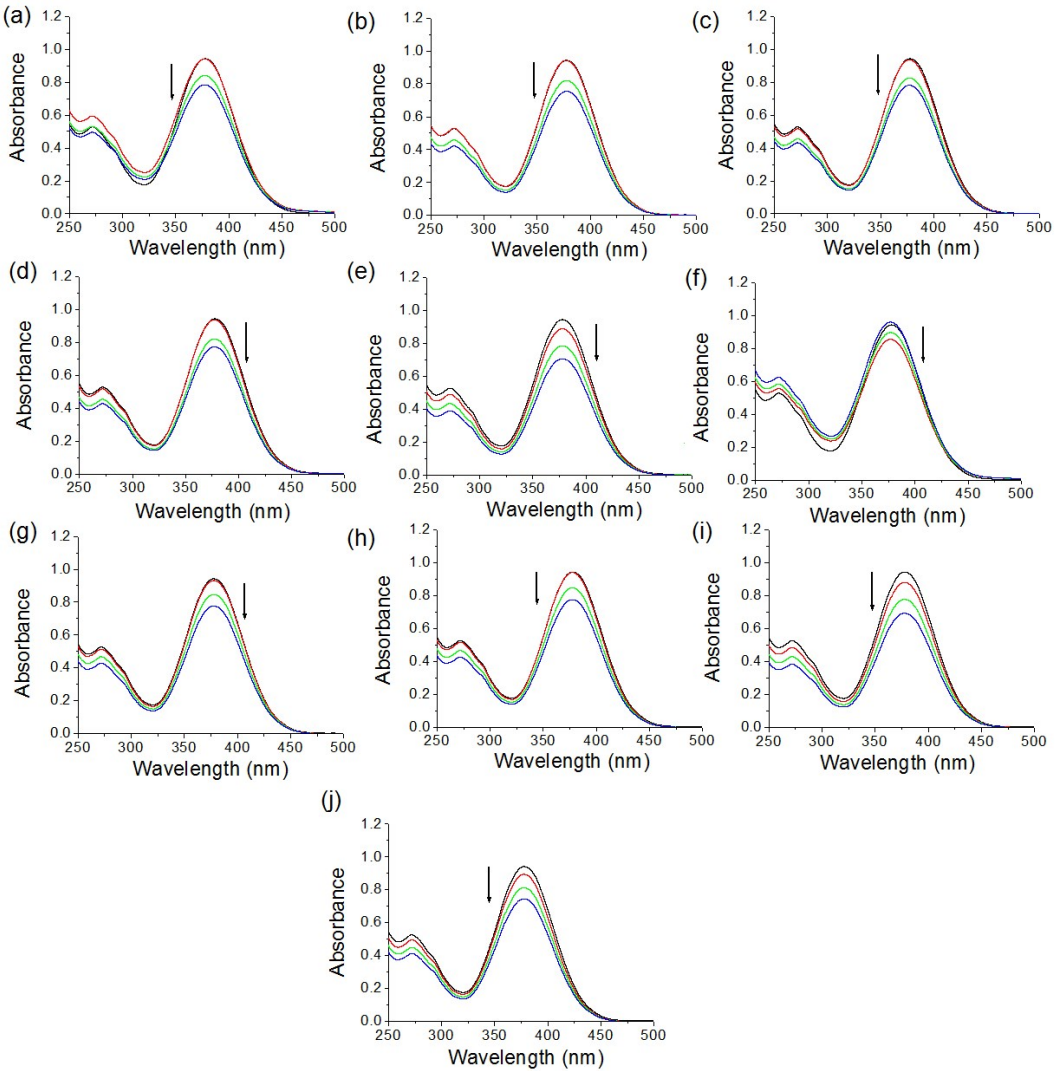


Figure S1. Change in absorbance of **1** (c = 2.5 x 10^{-5} M) in CH_3CN-H_2O (3:1, v/v, 10 mM HEPES, pH = 6.8, containing 1% DMSO) upon addition of 3 equiv. amounts of (a) Ag^{+}, (b) Al^{3+}, (c) Ca^{2+}, (d) Cd^{2+}, (e) Co^{2+}, (f) Fe^{2+}, (g) Fe^{3+}, (h),Hg^{2+}, (i) Ni^{2+} and (j) Pb^{2+} [concentration of metal ions were 1 x 10^{-3} M; all metal ions were used as their perchlorate salts].

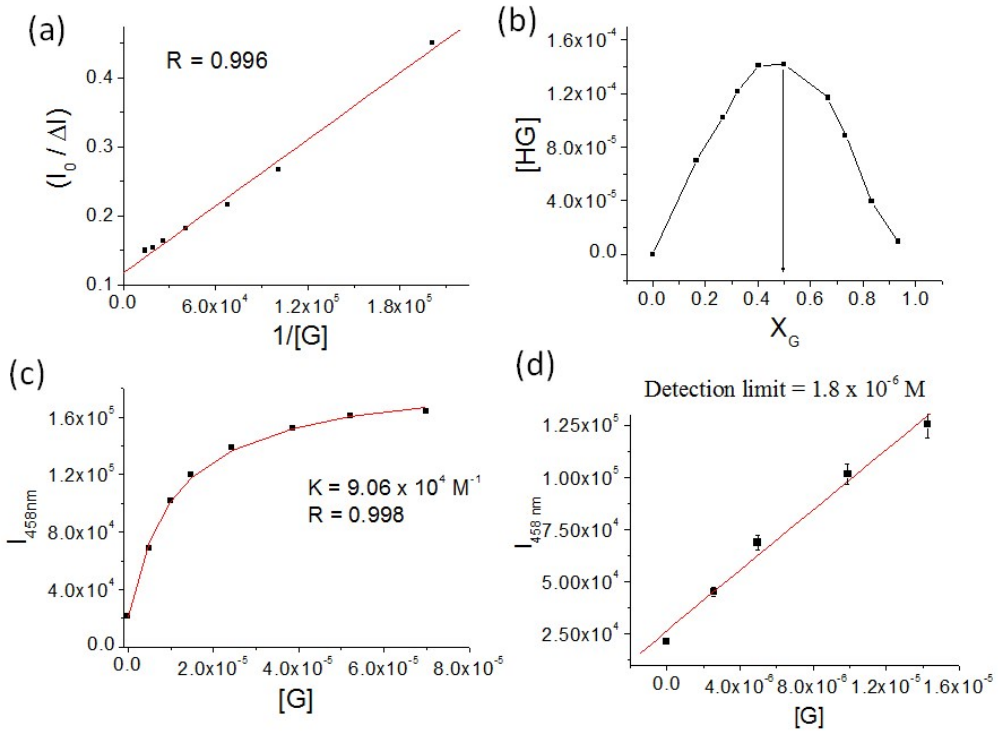


Figure S2. (a) Benesi-Hildebrand plot for **1** (c = 2.5 x 10^{-5} M) with Zn^{2+}; (b) Fluorescence (λ_{ex} = 380 nm) Job plot at 458 nm for **1** with Zn^{2+} ions in CH_3CN-H_2O (3:1, v/v, 10 mM HEPES, pH = 6.8, containing 1% DMSO) where [H] = [G] = 2.5 x 10^{-5} M; (c) Non liner binding constant curve for **1** (*c* = 2.5 x 10^{-5} M) with Zn^{2+} (*c* = 1.0 x 10^{-3} M) and (d) Detection limit for **1** (*c* = 2.5 x 10^{-5} M) with Zn^{2+} ([Zn^{2+}] = 1 x 10^{-3} M) at 458 nm in CH_3CN-H_2O (3:1, v/v, 10 mM HEPES, pH = 6.8, containing 1% DMSO) from emission titration.

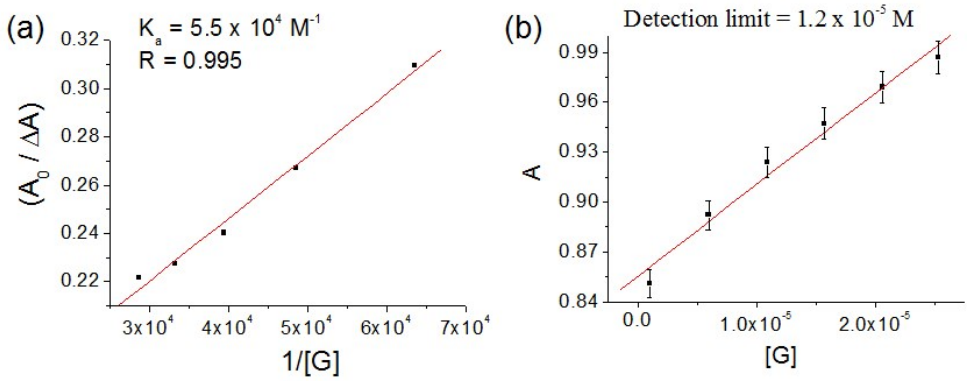


Figure S3. (a) Binding constant curve and (b) detection limit for compound **1** (c = 1.7 x 10^{-5} M) with Zn^{2+} ([Zn^{2+}] = 1 x 10^{-3} M) at 390 nm in CH_3CN-H_2O (3:1, v/v, 10 mM HEPES, pH = 6.8, containing 1% DMSO) from absorbance study.

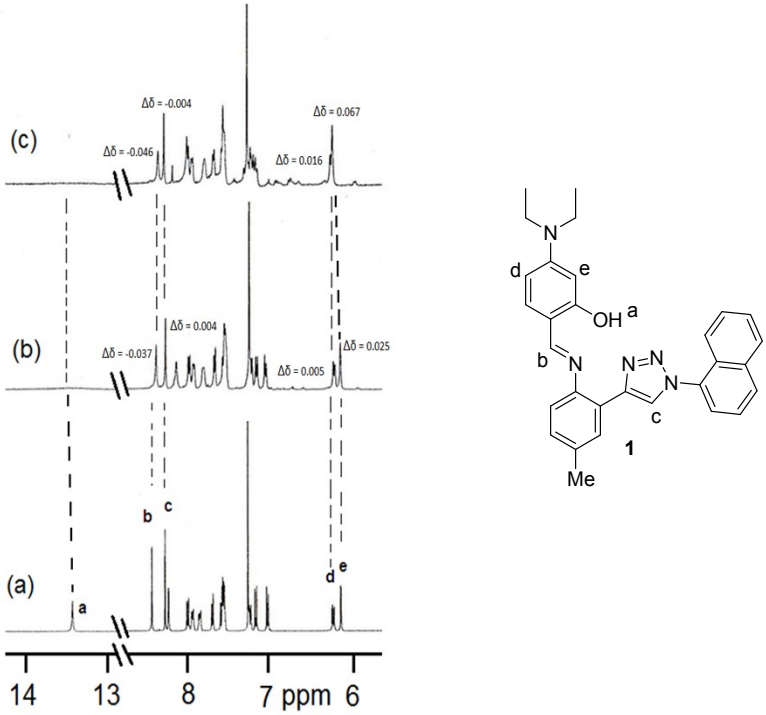


Figure S4. Partial ^{1}H NMR ($CDCl_3$, 400 MHz) of (a) **1** (c = 0.004 M) , (b) **1** with 1 equiv. amount of Zn^{2+} and (c) **1** with 2 equiv. amount of Zn^{2+}.

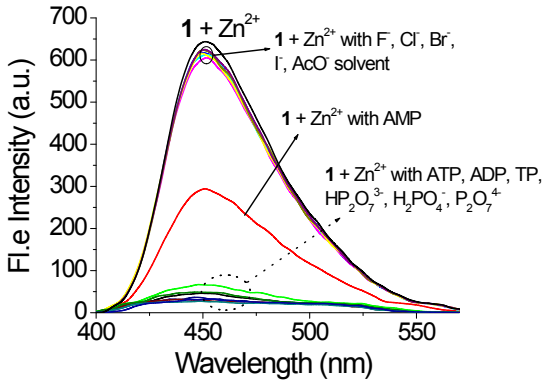


Figure S5. Change in emission of the zinc-ensemble of **1** (c = 2.5 x 10^{-5} M) upon gradual addition 5 equiv. amounts of different anions (c = 1 x 10^{-3} M) in CH_3CN/H_2O (3: 1, v/v, pH = 6.8, 10 mM HEPES buffer, containing 1% DMSO).

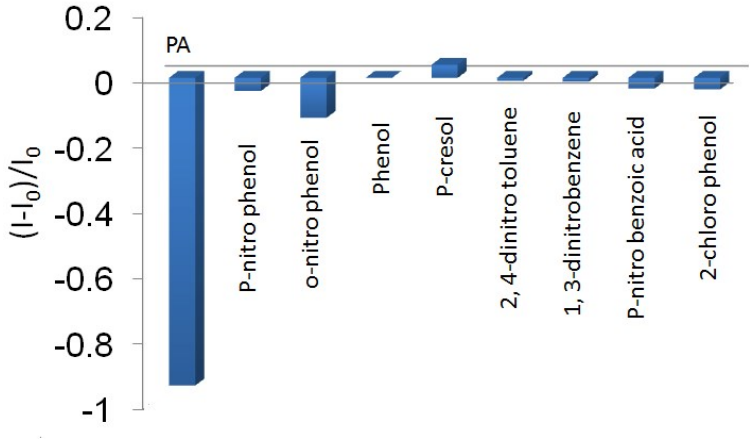


Figure S6. Change in fluorescence ratio of **1**.Zn^{2+} (c = 2.5×10^{-5} M) at 458 nm in the presence of 5 equiv. amounts of different nitroaromatics in CH_3CN/H_2O (3: 1, v/v, pH = 6.8, 10 mM HEPES buffer, containing 1% DMSO).

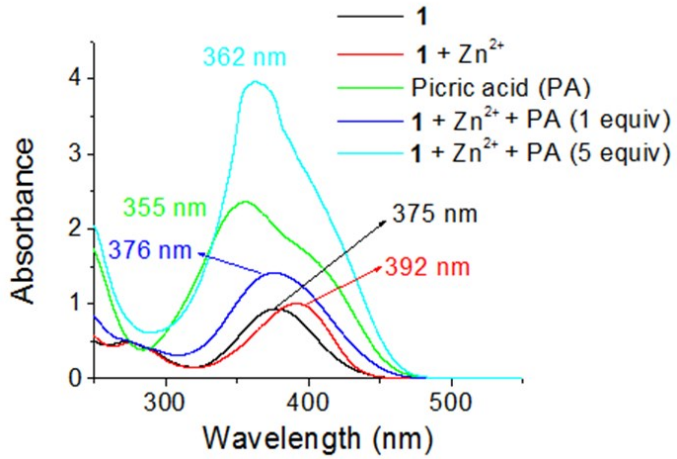


Figure S7. Change in emission of the ensemble **1**.Zn^{2+} [prepared by mixing **1** (c = 2.5×10^{-5} M) with 3 equiv. amounts of Zn^{2+} (c = 1×10^{-3} M)] upon addition of picric acid (PA) (c = 1×10^{-3} M) in CH_3CN/H_2O (3 : 1, v/v, pH = 6.8, 10 mM HEPES buffer, containing 1 % DMSO).

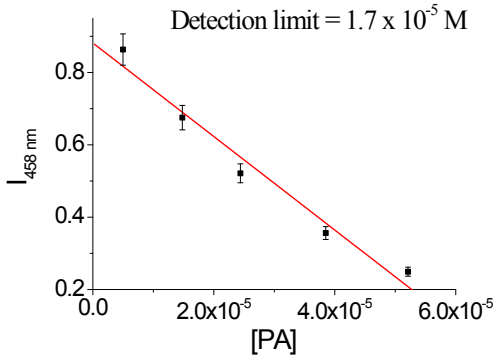


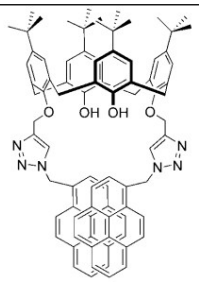
Figure S8. Detection limits for **1**-Zn^{2+} ensemble (c = 2.5 x 10^{-5} M) with picric acid (PA) ([PA] = 1 x 10^{-3} M) at 458 nm in CH_3CN-H_2O (3:1, v/v, 10 mM HEPES, pH = 6.8, containing 1% DMSO) from emission titration.

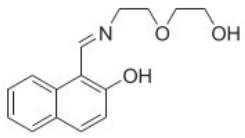
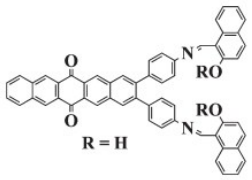
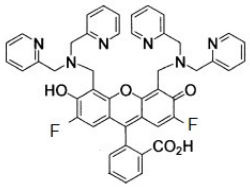
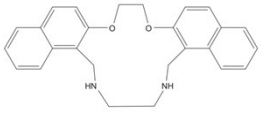
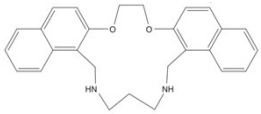
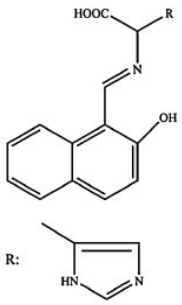
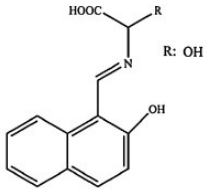
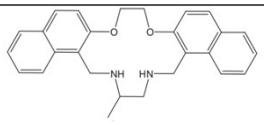
Table S1: Simulated absorption wavelengths (λ_{max} in nm), oscillator strengths (***f***), and the composition of the corresponding electronic transitions (H = HOMO; L = LUMO) calculated using B3LYP/6-31g(d) level of theory

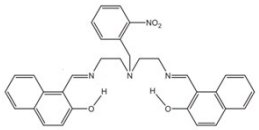
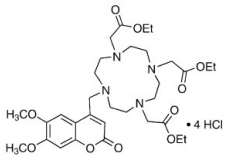
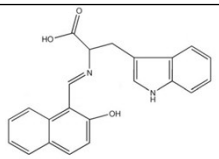
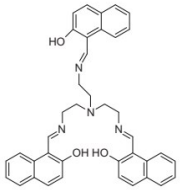
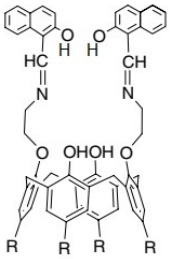
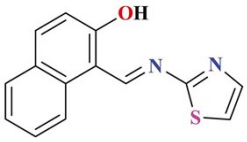
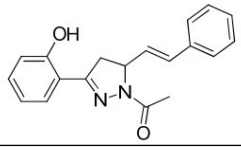
Compound	λ_{max}	***f***	ε (10^4)	**Main compositions (contribution)**
1 in CH_3CN-H_2O	356 (376)[a]	1.13	2.81	H→L+1 (94%)
	294	0.20	3.39	H-3→L (87%)
1-Zn^{2+} in CH_3CN-H_2O	380 (392)[a]	1.10	2.63	H→L (95%)
	306	0.21	3.27	H-1→L+1 (84%)

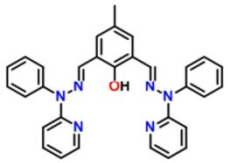
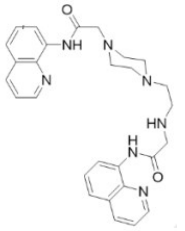
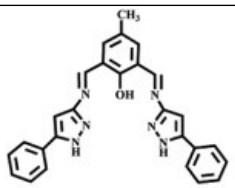
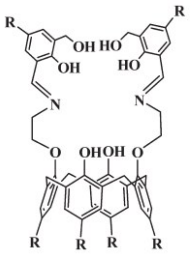
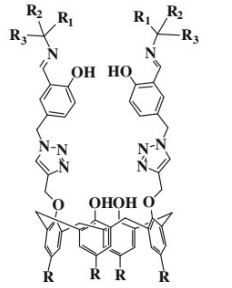
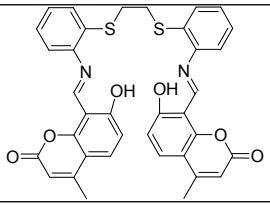
*a indicates the experimental values

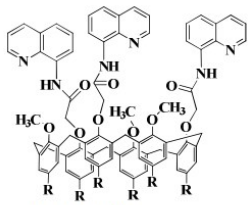
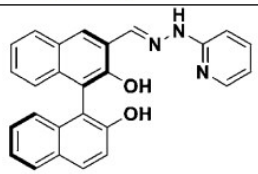
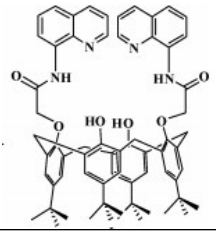
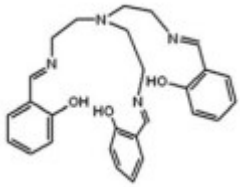
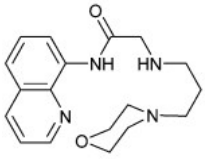
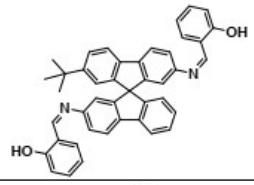
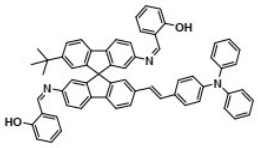
Table S2 : Reported structures for Zn^{2+} sensing in solution phase.

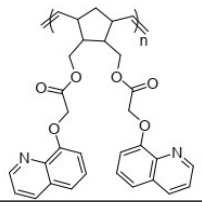
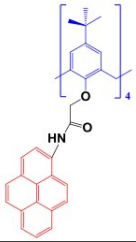
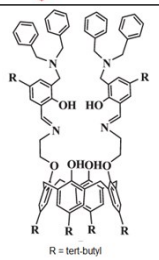
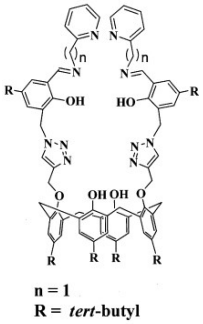
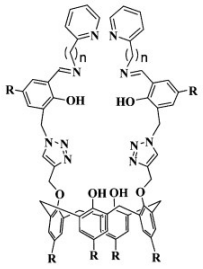
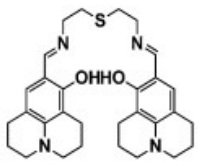
Entry	Structure of sensor	solvent	Detection limit	Interference from other metal ions	Ref.
1		CH_3CN	-	Cd^{2+}	1

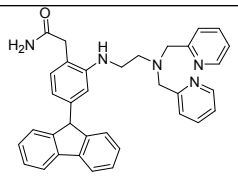
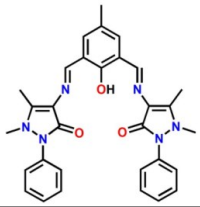
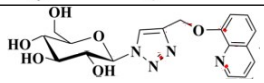
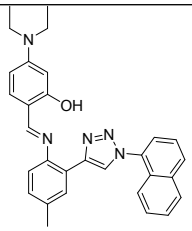
2		EtOH:H_2O (9:1, v/v)	1 x 10^{-8} M	-	2
3		THF	3.5 x 10^{-9} M	-	3
4		50 mM PIPES, 100 mM KCl (pH 7)	~ 5 x 10^{-6} M	-	4
5		**CH_3CN: DMF (9:1, v/v)**	1 x 10^{-7} M	Fe^{3+}, Cu^{2+}, Ni^{2+}	5
6		**CH_3CN: DMF (9:1, v/v)**	-	Cd^{2+}	5
7		buffer solution (10 mM, Tris–HCl, distilled water)	**2.4x10^{-6}M**	Cd^{2+}	6
8		buffer solution (10 mM, Tris–HCl, distilled water)	**1 ×10^{-6} M**	Cd^{2+}	6
9		**CH_3CN: DMF (1:1, v/v)**	**5 ×10^{-8} M**	Cu^{2+}, Fe^{3+}	7

10		**CH_3CN: DMF (1:1, v/v)**	**1×10^{-7} M**	-	8
11		50 mM PIPES buffer, 100 mM KCl, pH 7	**1×10^{-6} M**	Hg^{2+}, Pb^{2+}, Cd^{2+}	9
12		buffer solution (10 mM, Tris–HCl, pH 7.5)	**-**	-	10
13		EtOH:H_2O (95:5, v/v)	**4.89×10^{-8} M**	Cu^{2+}	11
14		MeOH	**60 ppb**	Cu^{2+}	12
15		DMSO/ H_2O, v/v, 1:9; 5 mM, HEPES buffer: pH 7.0	**3.1×10^{-4} M**	-	13
16		EtOH:H_2O (1:1, v/v)	**2.9×10^{-8} M**	Cu^{2+}, Fe^{3+}	14

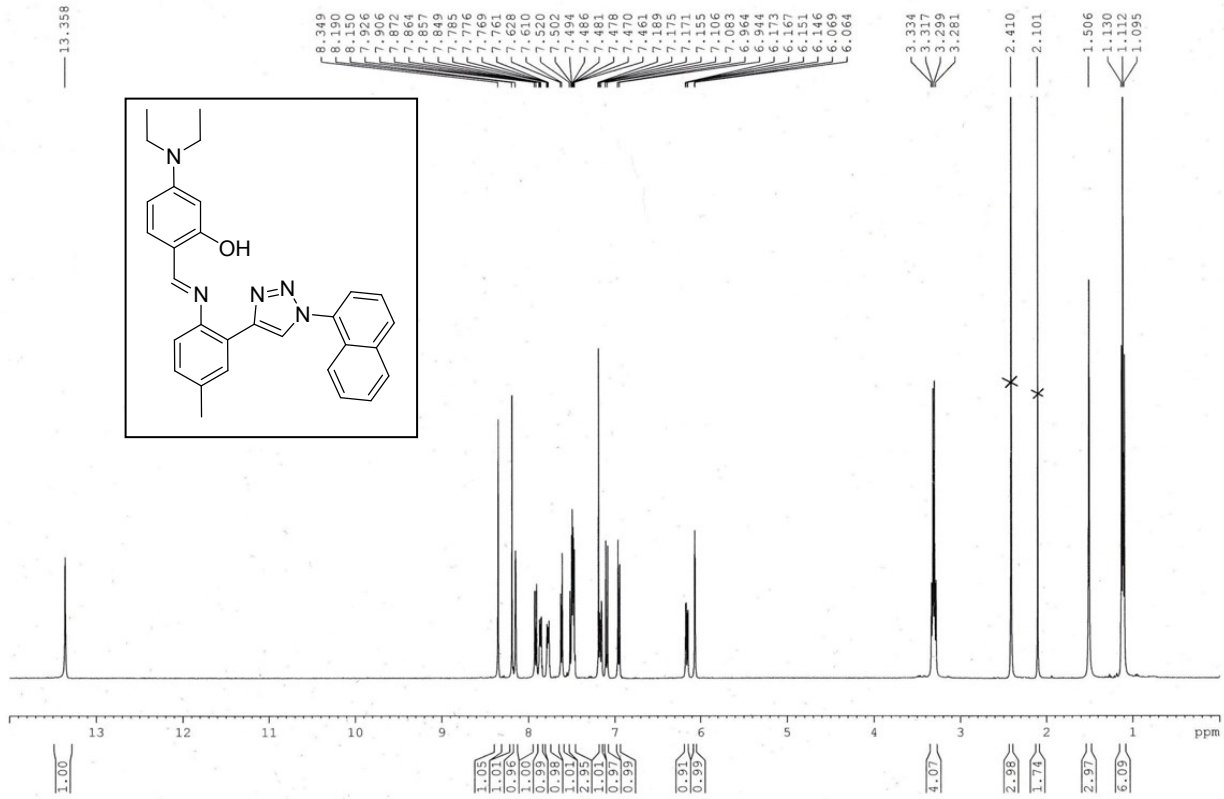
17		DMSO: H_2O (1:1, v/v)	-	-	15
18		bis-tris buffer solution (pH 7.0) containing DMSO	9 x 10^{-4} M	-	16
19		DMSO	27.80 nM	-	17
20	 R = tert-butyl	MeOH	192 ppb	-	18
21	 R: t-butyl; R_1: CH_3; R_2: CH_2OH; R_3: CH_2OH	MeOH	174 ppb	-	19
22		MeOH: H_2O (2:1, v/v)	0.068× 10^{-6} M	-	20

23	 R = tert-butyl	MeOH	-	Cu^{2+}	21
24		CH3CN/ HEPES (10 mM, pH = 7.4) = 1 : 1 (v/v)	2.2×10^{-6} M	Fe^{3+}, Al^{3+}	22
25		MeOH	183 ppb	Fe^{2+}, Cu^{2+}, Hg^{2+}	23
26		10 mM HEPES buffer–CH_3OH (99 : 1, v/v)	1.1×10^{-6} M	Co^{2+}, Cu^{2+}	24
27		DMSO	0.29×10^{-6} M	-	25
28		DMF:H_2O (9:1, v/v)	300nM	Cu^{2+}, Hg^{2+}	26
29		DIOX:H_2O (13:7, v/v)	63nM	-	26

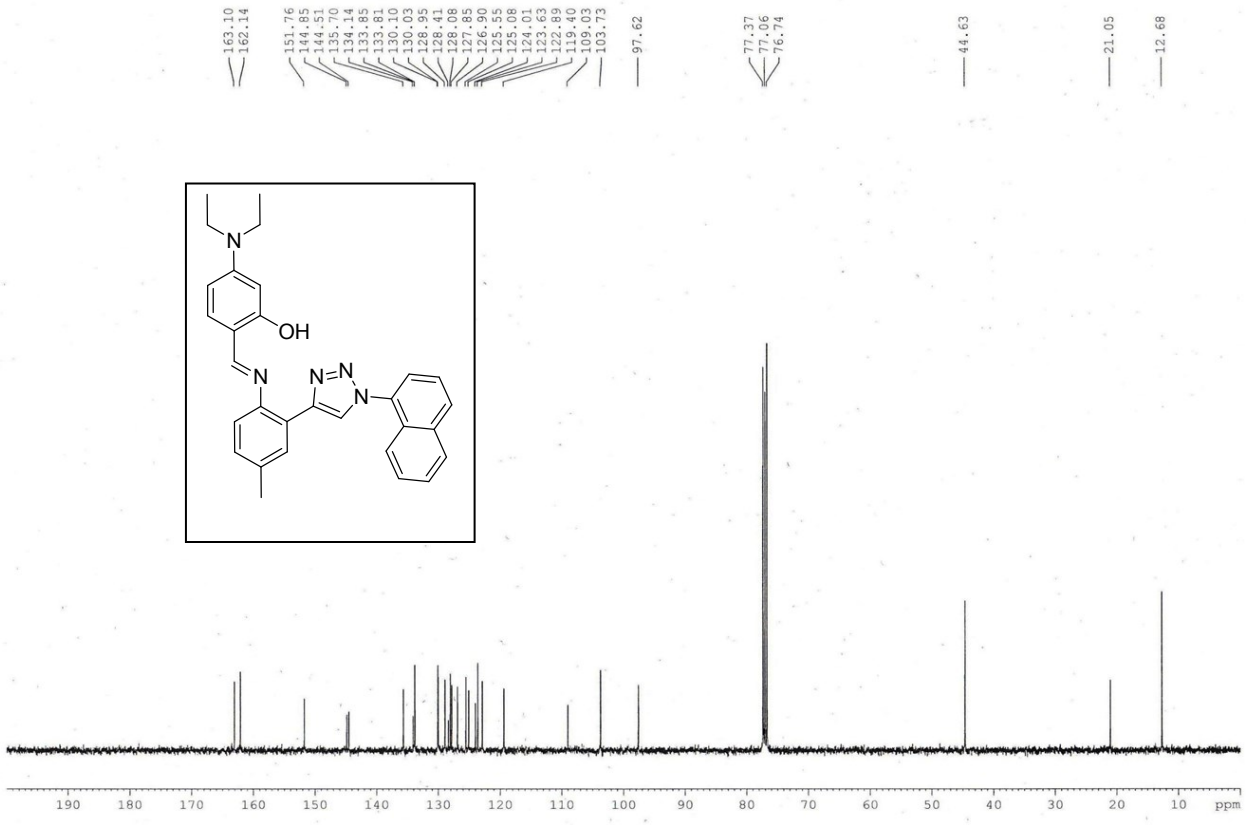
30		CH_3CN	2.04×10^{-7} M	Cd^{2+}	27
31		CH_3CN	6.43 nM	Hg^{2+}	28
32		MeOH	6.9×10^{-7} M	Ni^{2+}, Cu^{2+}, Fe^{2+}	29
33		MeOH: H_2O (2:1, v/v)	31 ppb	-	30
34		MeOH: H_2O (2:1, v/v)	112 ppb	-	30
35		DMF	1.5×10^{-6} M	Al^{3+}	31

36		HEPES buffer (10 mM, pH 7.4)	-	Cd^{2+}, Co^{2+}, Cu^{2+}	32
37		MeOH	1.74×10^{-6} M	Al^{3+}	33
38		HEPES buffer	-	Hg^{2+}, Cd^{2+}	34
This work		**CH_3CN: H_2O (3:1, v/v** pH = 6.8, 10 mM HEPES buffer, containing 1% DMSO)	1.8×10^{-6} M	Cu^{2+}	-

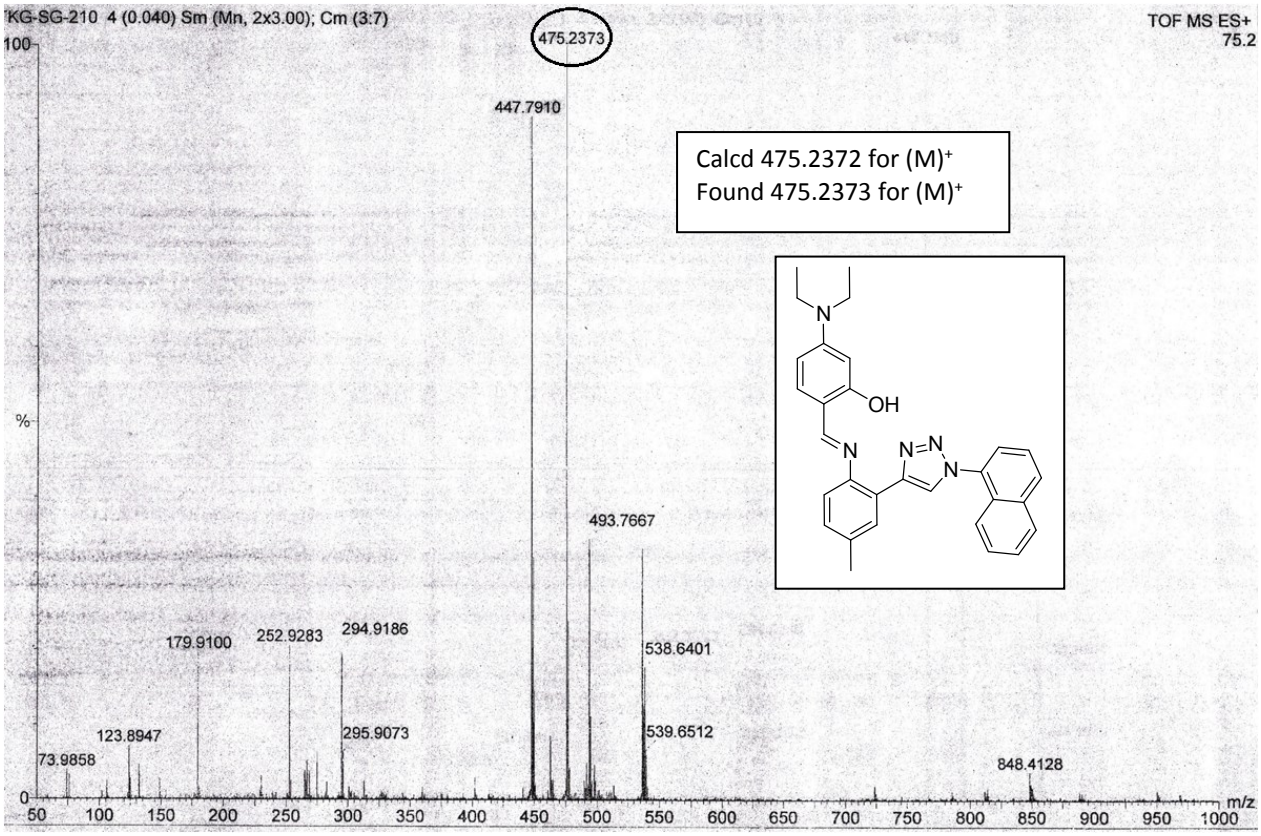
^{1}H NMR ($CDCl_3$, 400 MHz) of 1



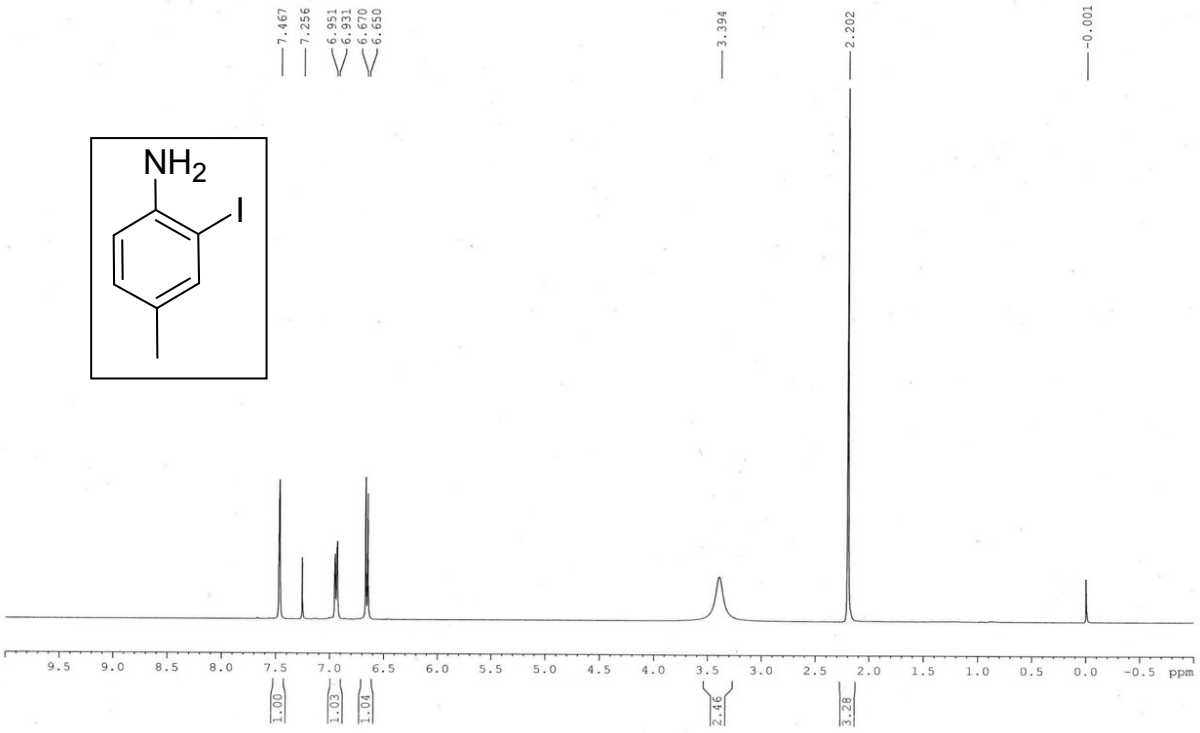
^{13}C NMR ($CDCl_3$, 100 MHz) of 1



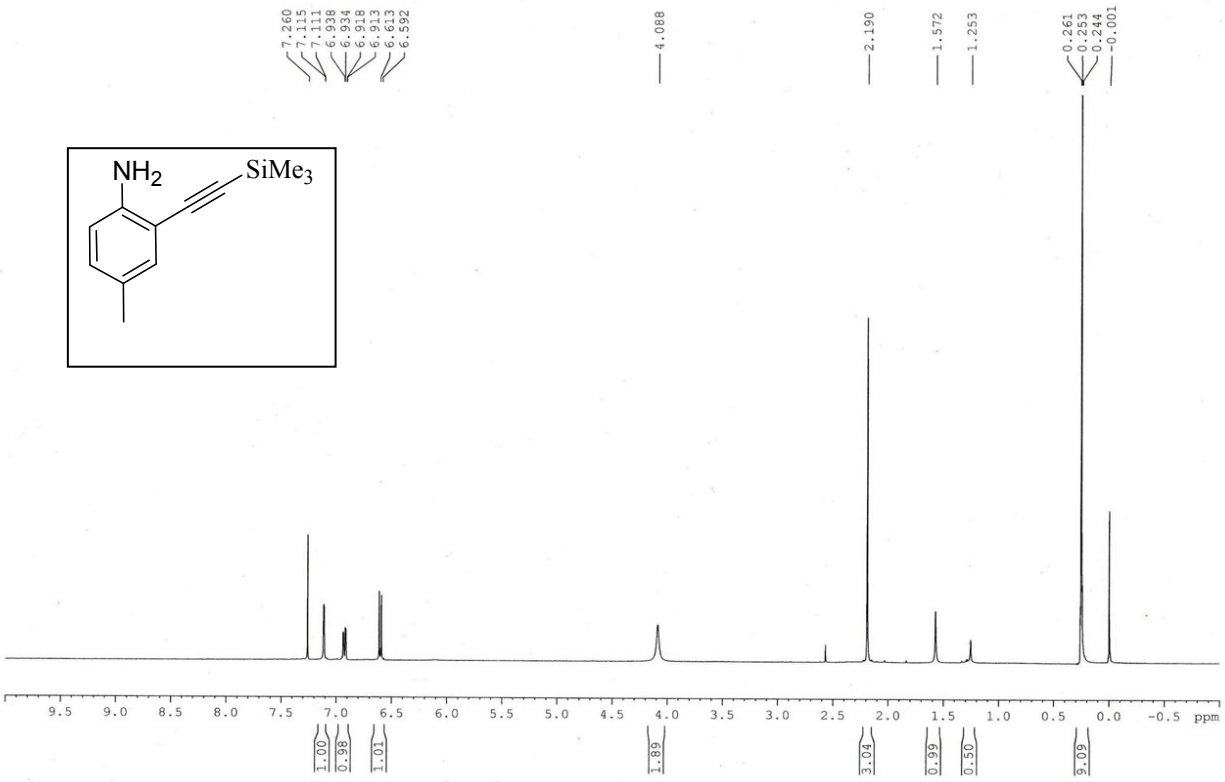
$^{-}$Mass ($CDCl_3$, 100 MHz) of 1



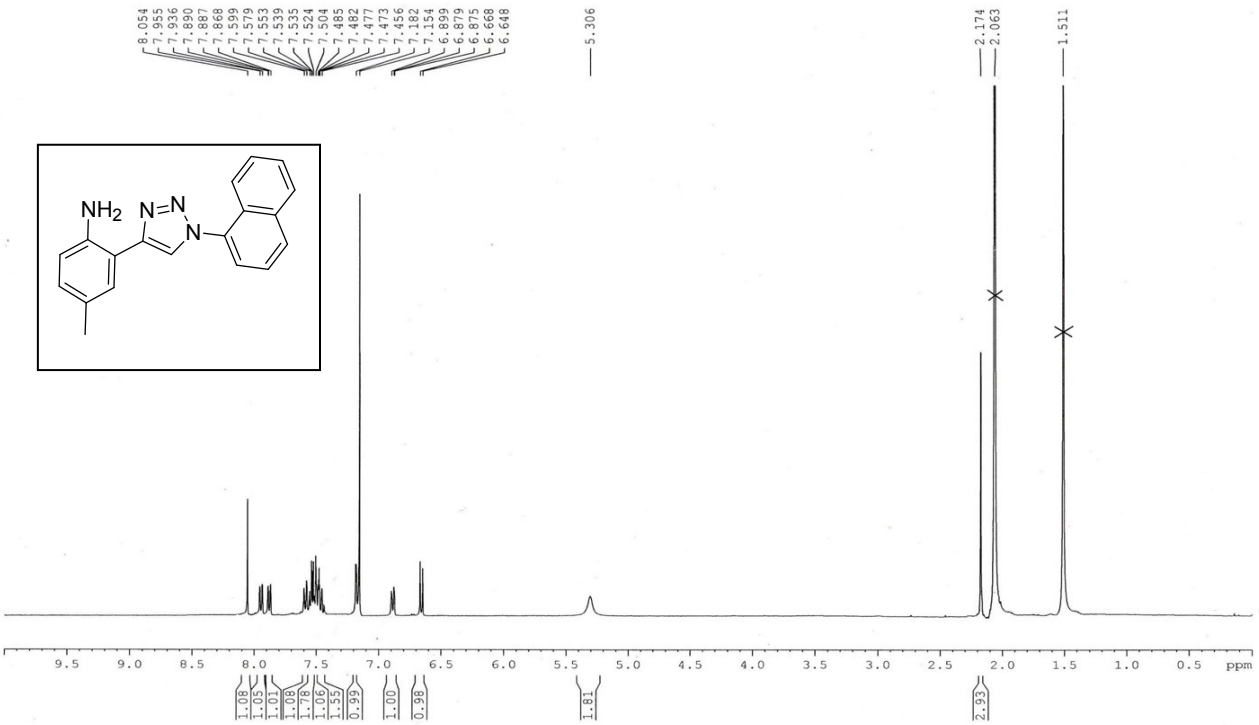
^{1}H NMR ($CDCl_3$, 400 MHz) of 2



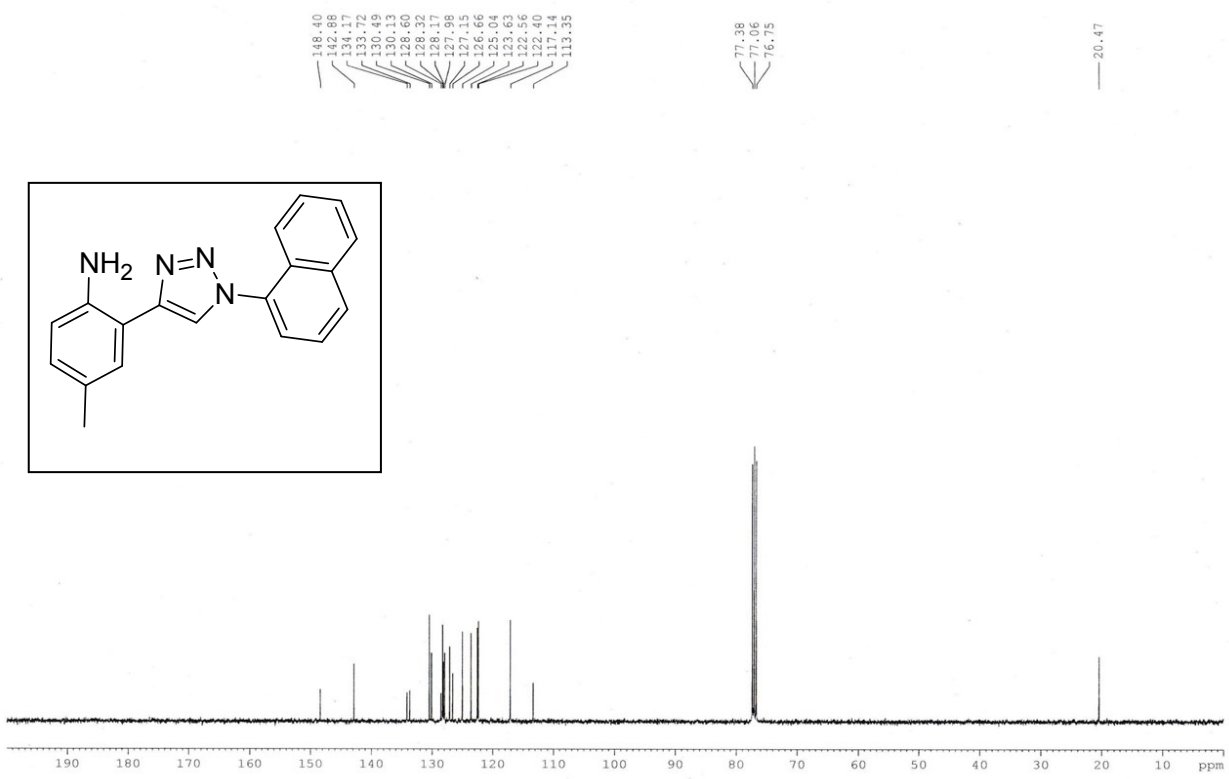
^{1}H NMR ($CDCl_3$, 400 MHz) of 3



^{1}H NMR ($CDCl_3$, 400 MHz) of 6



^{13}C NMR ($CDCl_3$, 100 MHz) of 6



Reference

1. S. Y. Park, J. H. Yoon, C. S. Hong, R. Souane, J. S. Kim, S. E. Matthews and J. Vicens, *J. Org. Chem.,* 2008, **73**, 8212.
2. H. Y. Lin, T. Y. Chen, C. K. Liu and A. T. Wu, *Luminescence*, 2016, **31**, 236.
3. V. Bhalla, Roopa and M. Kumar, *Dalton Trans.*, 2013, **42**, 975.
4. C. J. Chang, E. M. Nolan, J. Jaworski, S. C. Burdette, M. Sheng and S. J. Lippard, *Chemistry & Biology*, 2004, **11**, 203.
5. R. Azadbakht, H. Keypour, H. A. Rudbari, A. H. Mohammad and Z. S. Menati, *J. Lumin.*, 2012, 132, 1860.
6. L. Li, F. Liu and H. W. Li, *Spectrochim. Acta A*, 2011, **79**, 1688.
7. R. Azadbakht, M. Parviz, E. Tamari, H. Keypour and R. Golbedaghi, *Spectrochim. Acta A*, 2011, **80**, 200.

8. R. Azadbakht and H. Keypour, *Spectrochim. Acta A*, 2012, **85**, 293.
9. N. C. Lim, L. Yao, H. C. Freakeb and C. Bruckner, *Bioorg. Med. Chem. Lett.*, 2003, 13, 2251.
10. L. Li, Y. Q. Dang, H. W. Li, B. Wang and Y. Wu, *Tetrahedron Lett.*, 2010, 51, 618.
11. W. H. Hsieh, C. F. Wan, D. J. Liao and A. T. Wu, *Tetrahedron Lett.*, 2012, 53, 5848.
12. J. Dessingou, R. Joseph and C. P. Rao, *Tetrahedron Lett.*, 2005, **46**, 7967.
13. A. A. A. Aziz, *J. Braz. Chem. Soc.*, 2020, DOI: 10.21577/0103-5053.20200049.
14. Y. Yang, C. Ma, Y. Zhang, Q. Xue, J. ru, X. Liu and H. Guo, *Anal. Methods.*, 2018, **10**, 1833.
15. K. Ghosh, K. Mawai, S. nathani, P. Roy and U. P. singh, *Dalton Trans.*, 2018, **47**, 6421.
16. J. M. Jung, J. H. Kang, J. Han, H. Lee, M. H. Lim, K. T. Kim and Cheal Kim, *Sens. Actuators B Chem.,* 2018, **267**, 58.
17. S. Lohar, S. Pal, M. Mukherjee, A. Maji, N. Demitri and P. Chattopadhyay, *RSC Adv.*, 2017, **7**, 25528.
18. R. Joseph, J. P. Chinta and C. P. Rao, *J. Org. Chem.*, 2010, **75**, 3387.
19. R. K. Pathak, S. M. Ibrahim and C. P. Rao, *Tetrahedron **Lett**.*, 2009, 50, 2730.
20. C. Sinha, C. Patra, A. K. Bhanja, A. Mahapatra, S. Mishra and K. D. Saha, *RSC Adv.*, 2016, **6**, 76505.
21. V.V. S. Mummidivarapu, S. Bandaru, D. S. Yarramala , K. Samanta, D. S. Mhatre and C. P. Rao, *Anal. Chem.*, 2015, **87**, 4988.
22. S. Y. Jiao, L. L. Peng, K. Li, Y. M. Xie, M. Z. Ao, X. Wang and X. Q. Yu, *Analyst*, 2013, **138**, 5762.
23. V. V. S. Mummidivarapu, K. Tabbasum, J. P. Chinta and C. P. Rao, *Dalton Trans.*, 2012, **41**, 1671.
24. K. B. Kim, H. Kim, E. J. Song, S. Kim, I. Nohb and C. Kim, *Dalton Trans.*, 2013, **42**, 16569.
25. D. Yun, J. B. Chae, H. So, H. Lee, K. T. Kim and C. Kim, *New J. Chem.,* 2020, **44**, 442.
26. J. wan, W. zhang, H. Guo, J. Liang, D. Huang and H. xiao*, J. Mater. Chem., C*, 2019, **7**, 2240.
27. P. Yao, Z. Liu, J. Ge, Y. Chen and Q. Cao*, Dalton Trans.*, 2015, **44**, 7470.
28. P. G. Sutariya, H. N. Soni, S. A. Gandhi and A. Pandya*, New J. Chem.*, 2019, **43**, 9855.
29. R. Joseph, J. P. Chinta, and C. P. Rao, *Inorg. Chem.*, 2011, **50**, 7050.
30. R. K. Pathak, V. K. Hinge, A. Rai, D. Panda and C. Pulla Rao, *Inorg. Chem.*, 2012, **51**, 4994.
31. Y. S. Kim, G. J. Park, J. J. Lee, S. Y. Lee, S. Y. Lee and C. Kim, *RSC Adv.*, 2015, **5**, 11229.
32. Q. c. Xu, X. f. Wang, G. w. Xing and Y. Zhang, *RSC Adv.*, 2013,**3**, 15834.
33. S. Dey, A. Maity, M. Shyamal, D. Das, S. Maity, P. K. Giri, N. Mudi, S. Samanta, P. Hazra and A. Misra*, Photochem. Photobiol. Sci.*, 2019, **18**, 2717.
34. S. Areti, S. Bandaru and C. P. Rao, *ACS Omega*, 2016, **1**, 626.