Electronic Supplementary Material (ESI) for RSC Advances.

Dipicolylamine coupled rhodamine dyes: New clefts for highly selective naked eye sensing of Cu^{2+} and CN^- ions

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1. Packing diagram

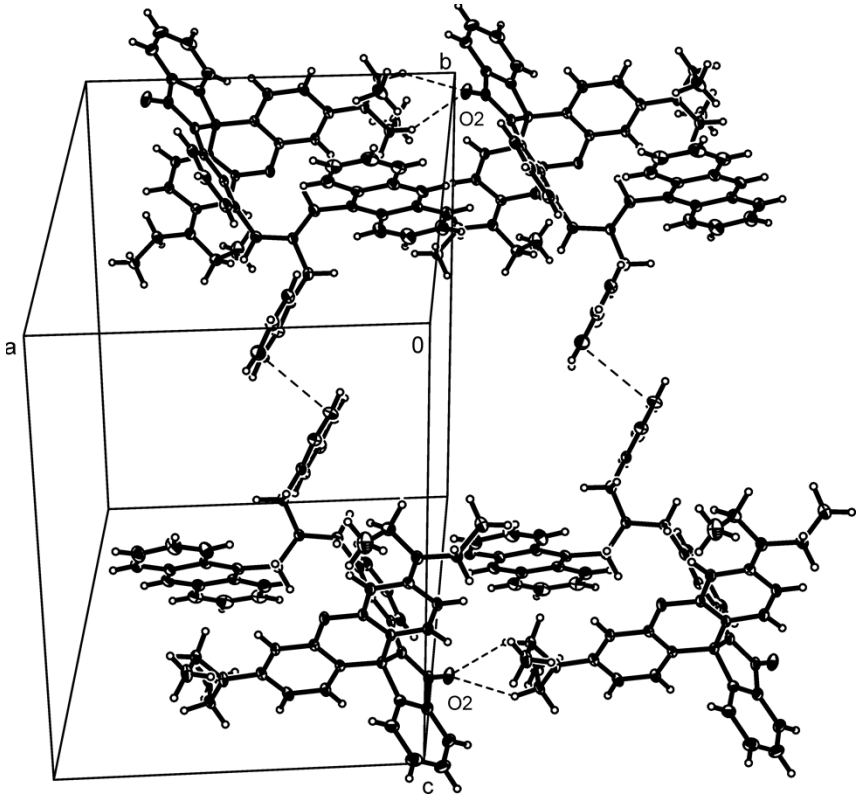
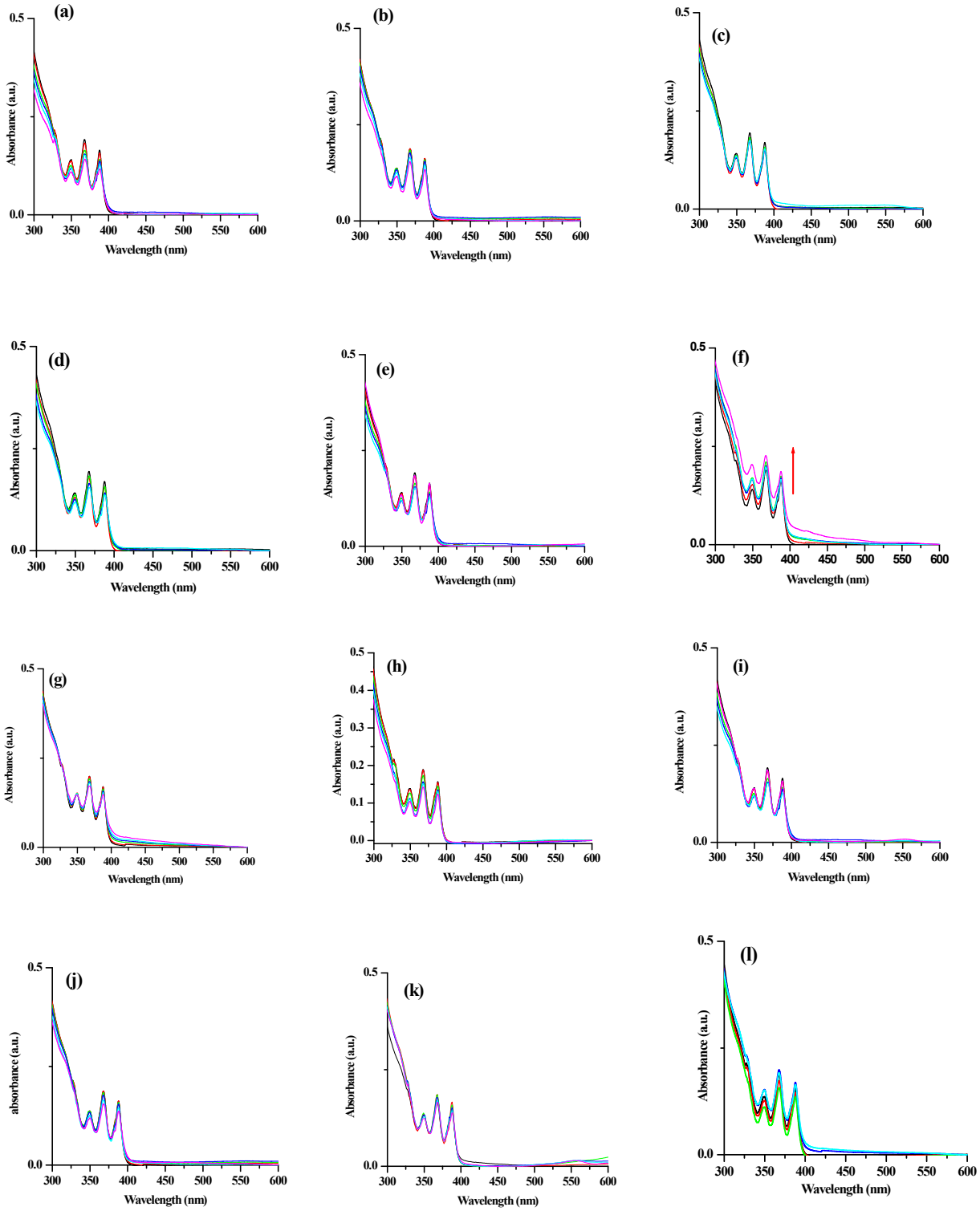


Figure 1S. Packing plot for **1**.

2. Change in absorbance of receptor 1 with various metal ions in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer).



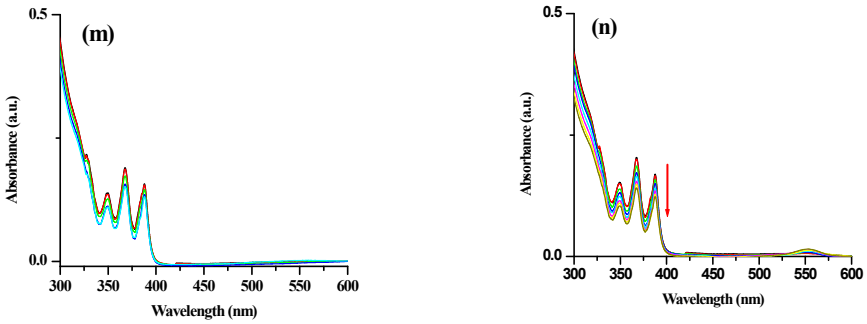


Figure 2S. Change in absorbance of **1** (c = 2.5 x 10^{-5} M) in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) upon addition of 10 equiv. of (a) $AgClO_4$, (b) $Al(ClO_4)_3$, (c) $Cd(ClO_4)_2$ (d) $Co(ClO_4)_2$, (e) $Fe(ClO_4)_2$, (f) $Fe(ClO_4)_3$, (g) $Hg(ClO_4)_2$, (h) $Mg(ClO_4)_2$ (i) $Mn(ClO_4)_2$, (j) $NaClO_4$, (k) $Ni(ClO_4)_3$, (l) $Pb(ClO_4)_2$, (m) $Pd(ClO_4)_2$, (n) $Zn(ClO_4)_2$ [concentration of metal salts were 1 x 10^{-3} M].

3. Detection limit of receptor 1 with Cu^{2+}:

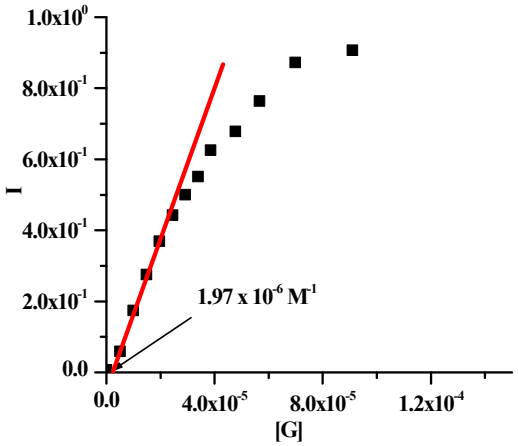


Figure 3S. Detection limit of receptor **1** in $CH_3CN–H_2O$ (4:1, v/v, pH = 7.2, 10 mM Tris-HCl buffer).

4. Change in absorbance of 1 upon addition of $Cu(ClO_4)_2$ in $EtOH–H_2O$ (7 : 3, v/v, pH = 7.2, 10 mM Tris-HCl buffer).

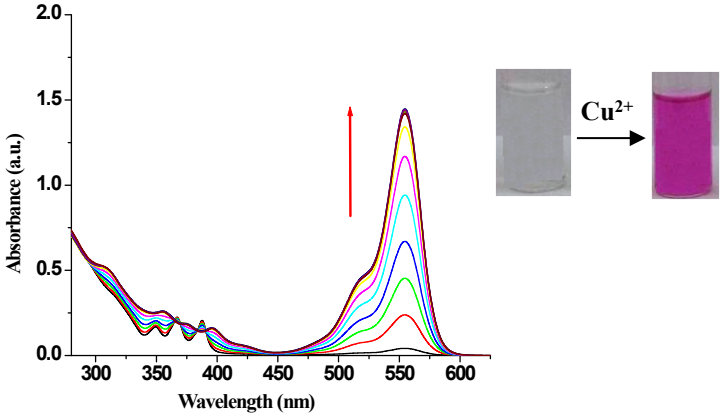


Figure 4S. Change in absorbance of **1**(c = 2.5x10^{-5} M) upon addition of $Cu(ClO_4)_2$ (c = 1 x 10^{-3} M) in $EtOH–H_2O$ (7 : 3, v/v, pH = 7.2, 10 mM Tris-HCl buffer). Inset shows the colour change of **1** (c = 2.5x10^{-5} M) in presence of 2 equiv. of $Cu(ClO_4)_2$ (c = 1 x 10^{-3} M).

5. Change in absorbance of 1 upon addition of various metal ions in EtOH–H_2O (7 : 3, v/v, pH = 7.2, 10 mM Tris-HCl buffer).

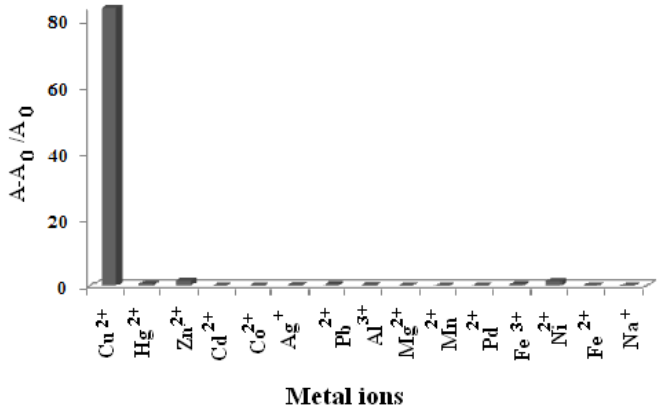
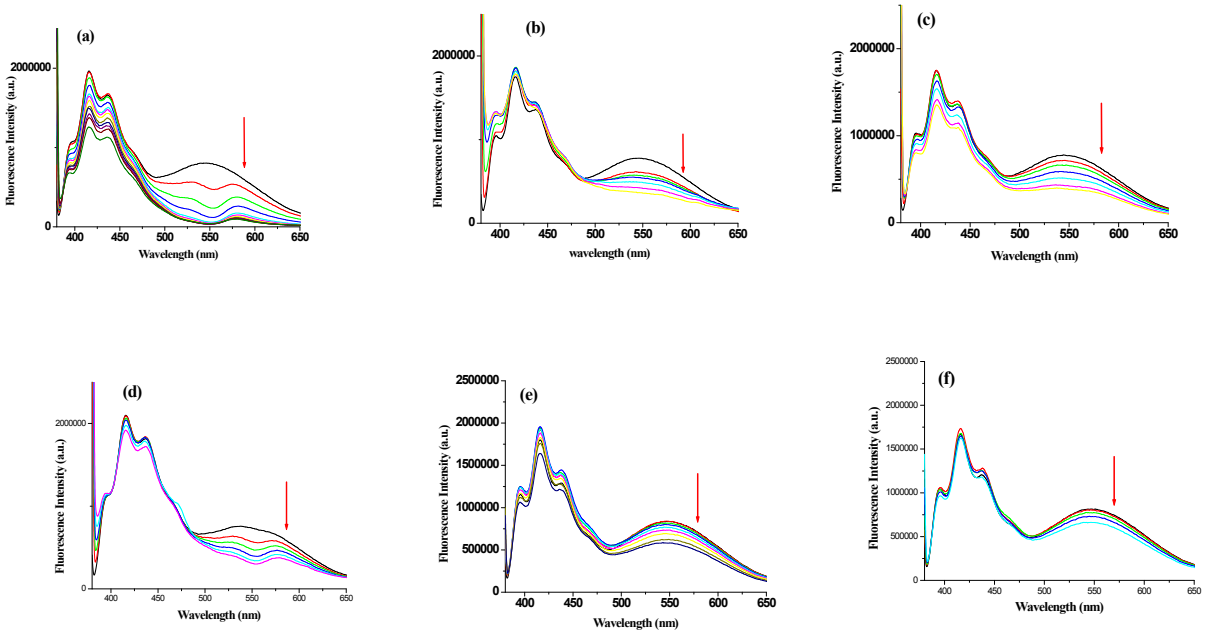


Figure 5S. Bar plot showing change in absorbance for receptor **1** (c = 2.5 x 10^{-5} M) upon addition of 5 equiv. of various metal ions (c = 1 x 10^{-3} M) in EtOH–H_2O (7 : 3, v/v, pH = 7.2, 10 mM Tris-HCl buffer).

6. Change in emission of receptor 1 with various metal ions in CH_3CN–H_2O (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer).



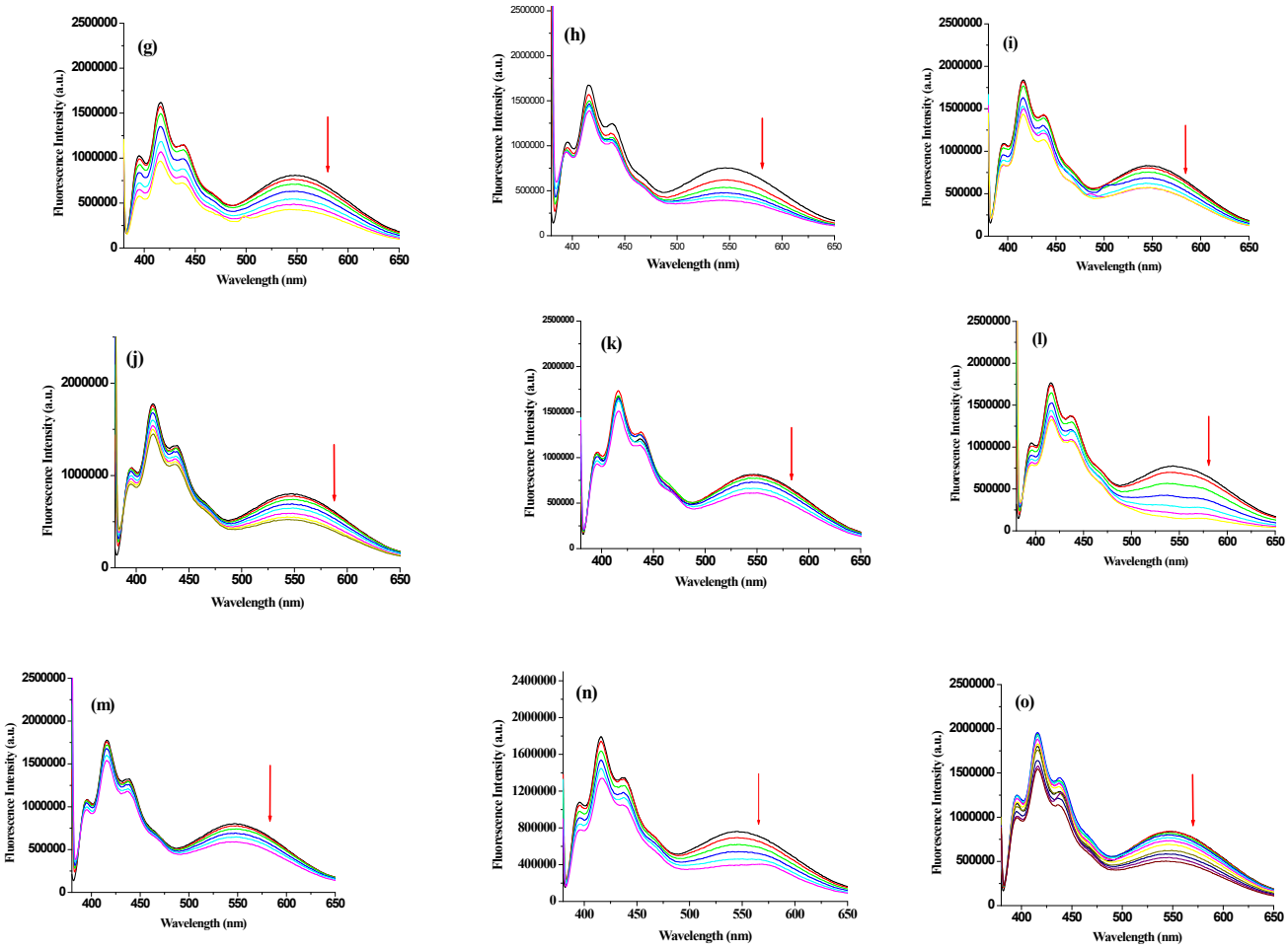


Figure 6S. Change in emission of **1** (c = 2.5 x 10^{-5} M) in CH_3CN–H_2O (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) upon addition of 15 equiv. of (a) $Cu(ClO_4)_2$, (b) $AgClO_4$, (c) $Al(ClO_4)_3$, (d) $Cd(ClO_4)_2$ (e) $Co(ClO_4)_2$, (f) $Fe(ClO_4)_2$, (g) $Fe(ClO_4)_3$, (h) $Hg(ClO_4)_2$, (i) $Mg(ClO_4)_2$ (j) $Mn(ClO_4)_2$, (k) $NaClO_4$, (l) $Ni(ClO_4)_3$, (m) $Pb(ClO_4)_2$, (n) $Pd(ClO_4)_2$, (o) $Zn(ClO_4)_2$ [concentration of metal salts were 1 x 10^{-3} M] (λ_{exc} = 370 nm)..

7. Change in emission and absorbance with change of pH of the medium

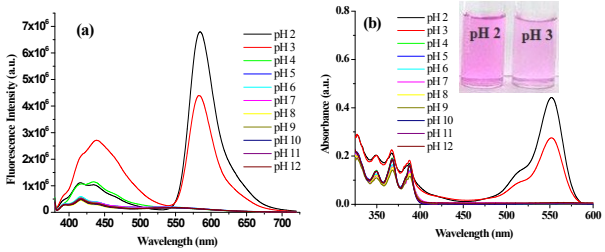


Figure 7S. Change in (a) emission (λ_{exc} = 370 nm) and (b) absorbance of **1** at different pHs in CH_3CN–H_2O (4: 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer).

8. Change in fluorescence spectra of 3 with pH in EtOH–H_2O (7 : 3, v/v, pH = 7.2, 10 mM Tris-HCl buffer).

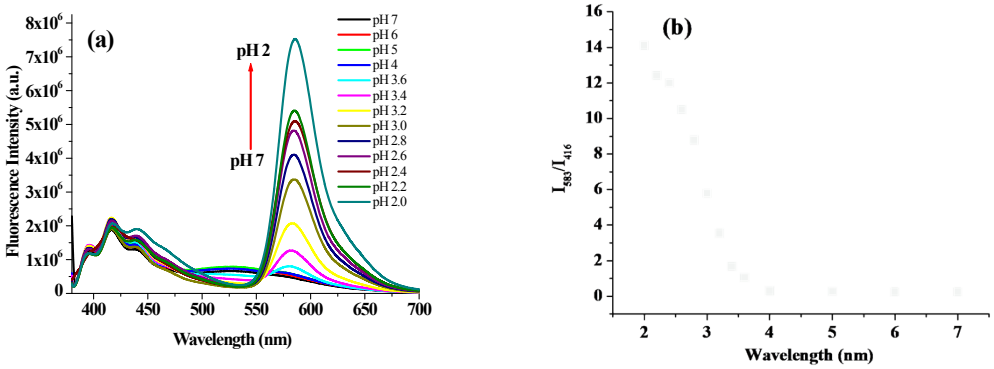


Figure.8S. (a) Fluorescence spectra of receptor **1** (c = 2.5x10^{-5} M) in EtOH–H_2O (7 : 3, v/v, pH = 7.2, 10 mM Tris-HCl buffer) at different pH values (λ_{exc} = 370 nm), (b) the change of fluorescence emission ratios (I_{583}/I_{416}) by pH values.

9. Partial IR Spectra:

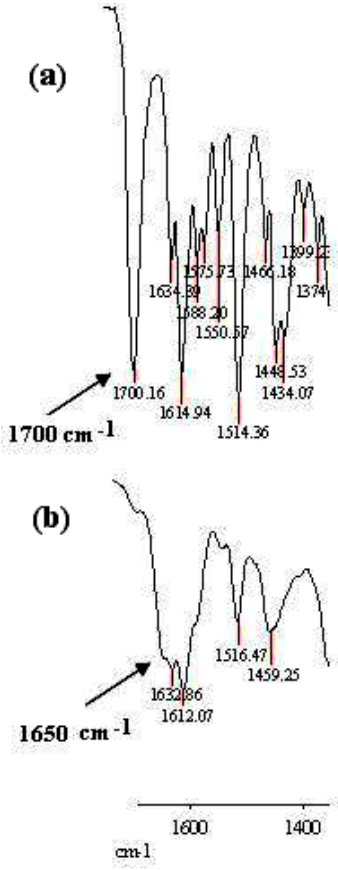
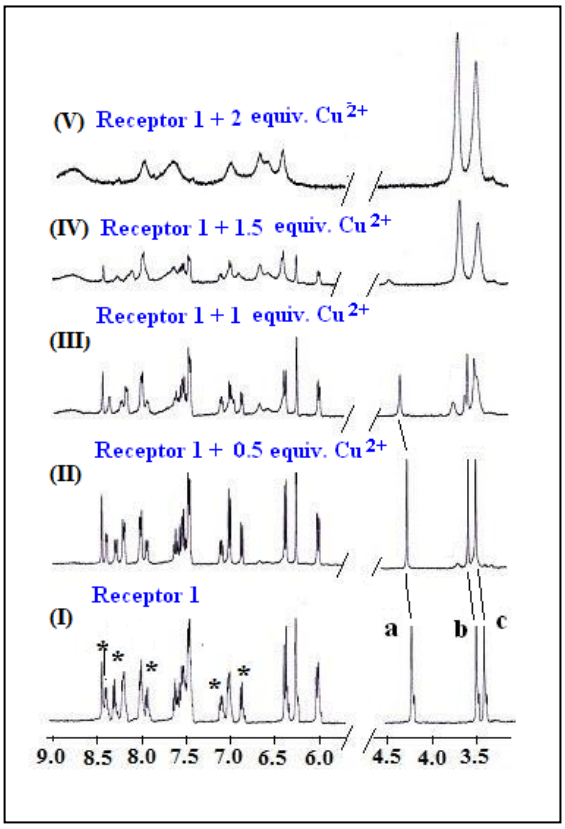


Figure 9S: Partial FT IR (ν in cm^{-1}, KBr) Spectra of (a) Receptor **1**; (b) **1**+ $Cu(ClO_4)_2$.

10. Partial ^{1}H NMR spectra of 1 upon gradual addition of Cu^{2+}:



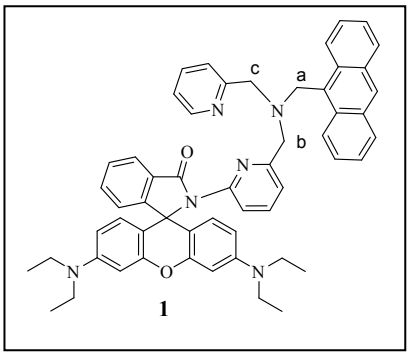
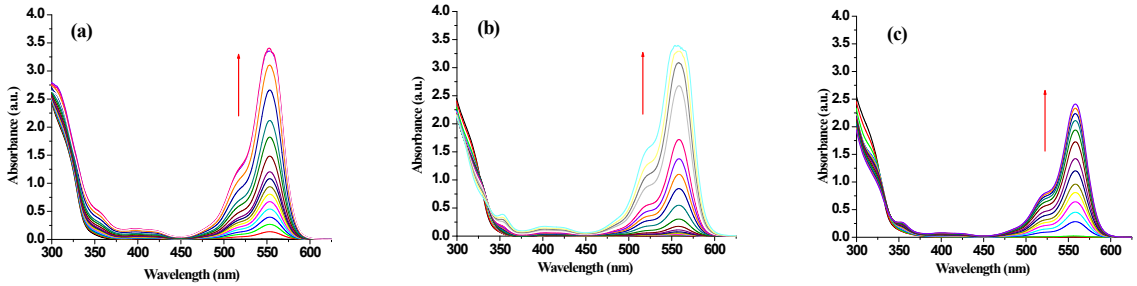
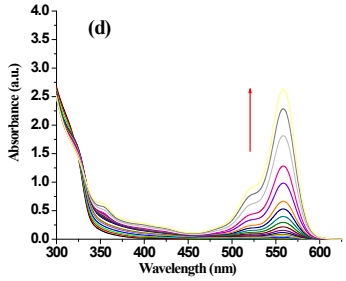
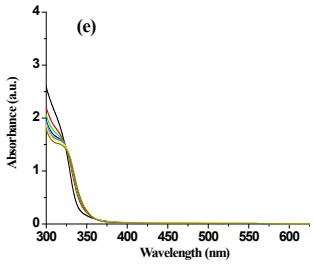


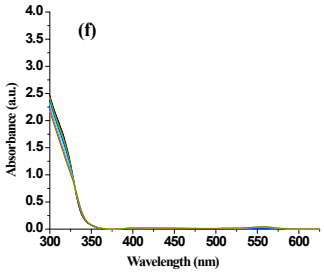
Figure 10S. Partial ^{1}H NMR Spectra of receptor **1** in presence of various equiv. amounts of $Cu(ClO_4)_2$ in CD_3CN: (I) **1,** (II) **1** + 0.5 equiv. $Cu(ClO_4)_2$, (III) **1** + 1 equiv. $Cu(ClO_4)_2$, (IV) **1** + 1.5 equiv. $Cu(ClO_4)_2$ and (V) **1** + 2 equiv. $Cu(ClO_4)_2$ (* indicates some pyridyl ring protons).

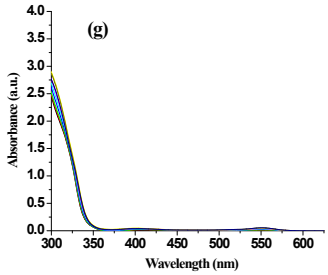
11. Change in absorbance of receptor 3 with various metal ions in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer).

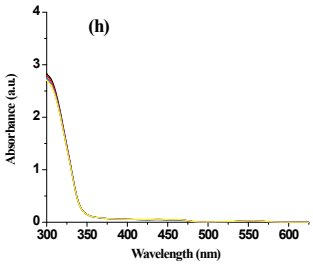


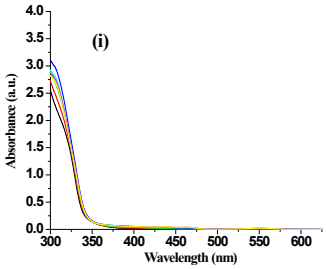

(d)
Absorbance (a.u.)
Wavelength (nm)

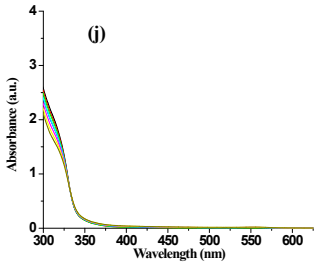

(e)
Absorbance (a.u.)
Wavelength (nm)

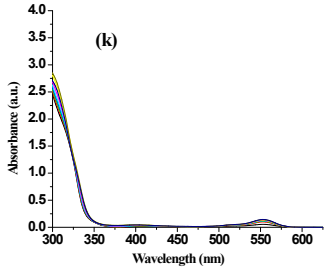

(f)
Absorbance (a.u.)
Wavelength (nm)

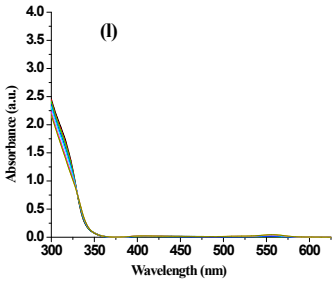

(g)
Absorbance (a.u.)
Wavelength (nm)

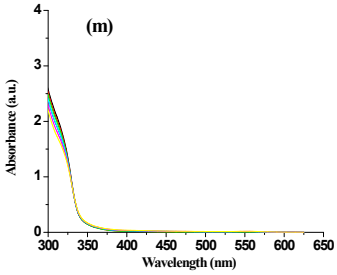

(h)
Absorbance (a.u.)
Wavelength (nm)

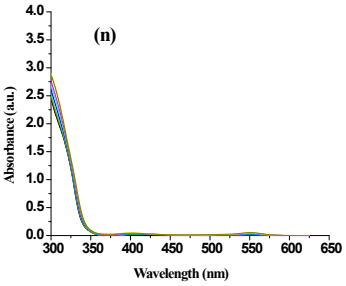

(i)
Absorbance (a.u.)
Wavelength (nm)


(j)
Absorbance (a.u.)
Wavelength (nm)


(k)
Absorbance (a.u.)
Wavelength (nm)


(l)
Absorbance (a.u.)
Wavelength (nm)


(m)
Absorbance (a.u.)
Wavelength (nm)


(n)
Absorbance (a.u.)
Wavelength (nm)

(o)

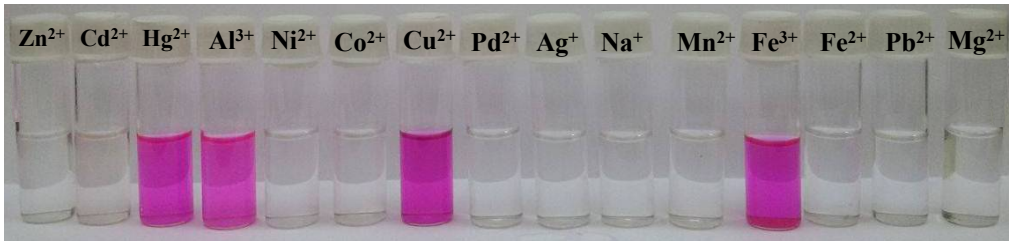
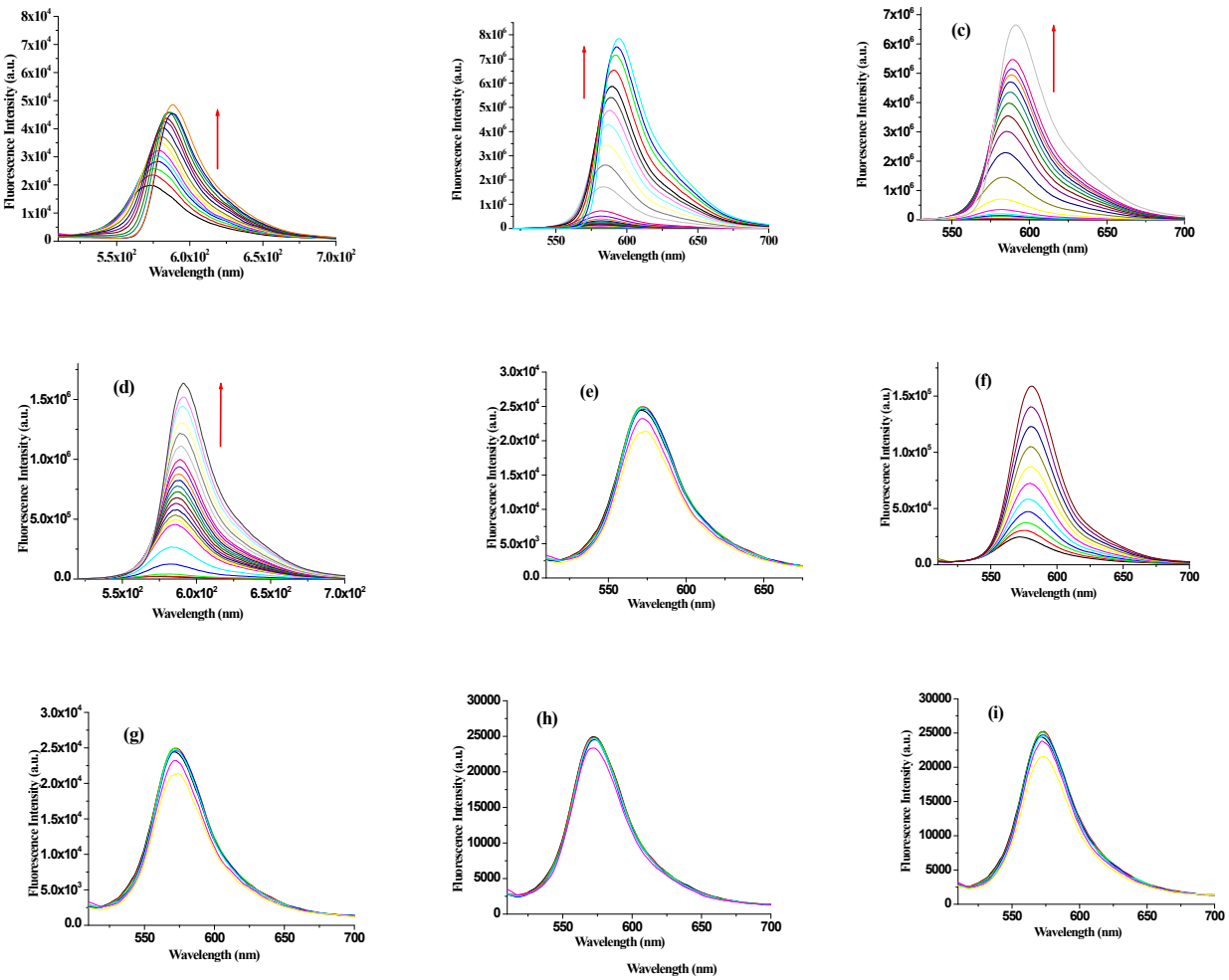


Figure 11S. Change in emission of **3** (c = 2.5 x 10^{-5} M) in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) upon addition of 5 equiv. of (a) $Cu(ClO_4)_2$, (b) $Hg(ClO_4)_2$, (c) $Al(ClO_4)_3$, (d) $Fe(ClO_4)_3$, (e) $AgClO_4$, (f) $Cd(ClO_4)_2$, (g) $Co(ClO_4)_2$, (h) $Fe(ClO_4)_2$ (i) $Ni(ClO_4)_2$, (j) $Pb(ClO_4)_2$, (k) $Zn(ClO_4)_2$, (l) $Mg(ClO_4)_2$, (m) $Pd(ClO_4)_2$, (n) $NaClO_4$ [concentration of metal salts were 1 x 10^{-3} M], (o) Photographs shows the color change of the solution of **3** (c = 2.5 x 10^{-5} M) in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) in presence of 5 equiv. amounts of metal ions studied.

12. Change in emission of receptor 3 with various metal ions in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer).



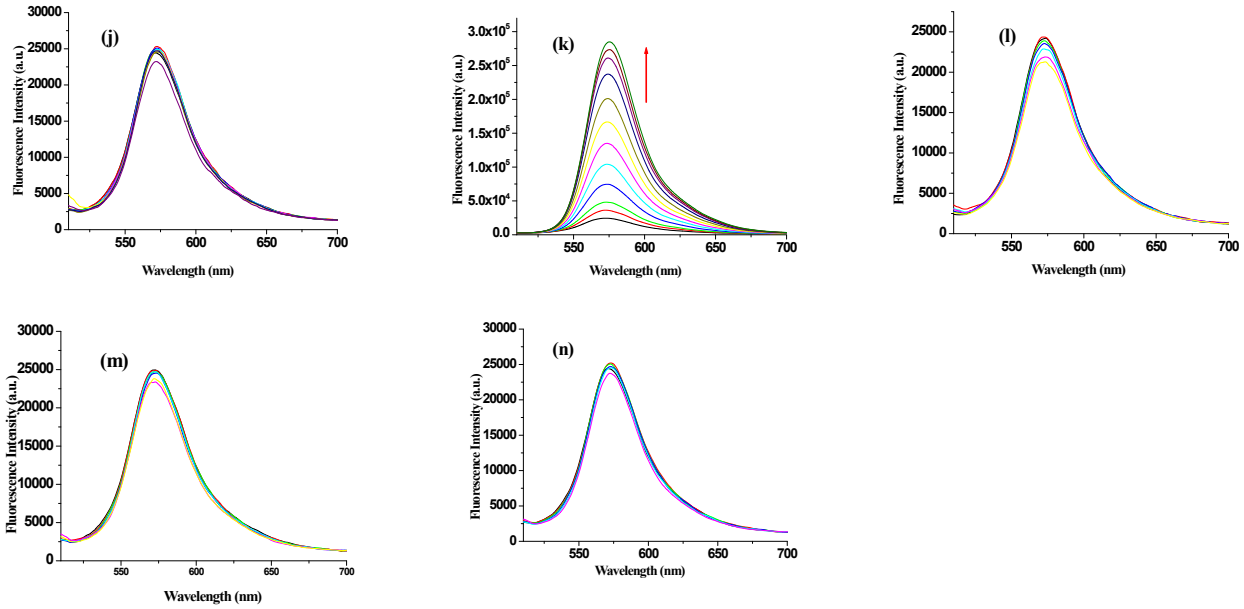


Figure 12S. Change in emission of **1** (c = 2.5 x 10^{-5} M) in CH_3CN–H_2O (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) upon addition of 10 equiv. of (a) $Cu(ClO_4)_2$, (b) $Hg(ClO_4)_2$, (c) $Al(ClO_4)_3$, (d) $Fe(ClO_4)_3$, (e) $AgClO_4$, (f) $Cd(ClO_4)_2$, (g) $Co(ClO_4)_2$, (h) $Fe(ClO_4)_2$ (i) $Ni(ClO_4)_2$, (j) $Pb(ClO_4)_2$, (k) $Zn(ClO_4)_2$, (l) $Mg(ClO_4)_2$, (m) $Pd(ClO_4)_2$, (n) $NaClO_4$ [concentration of metal salts were 1 x 10^{-3} M] (λ_{exc} = 500 nm).

13. Reversible binding of receptor 1 towards $Cu(ClO_4)_2$ with EDTA

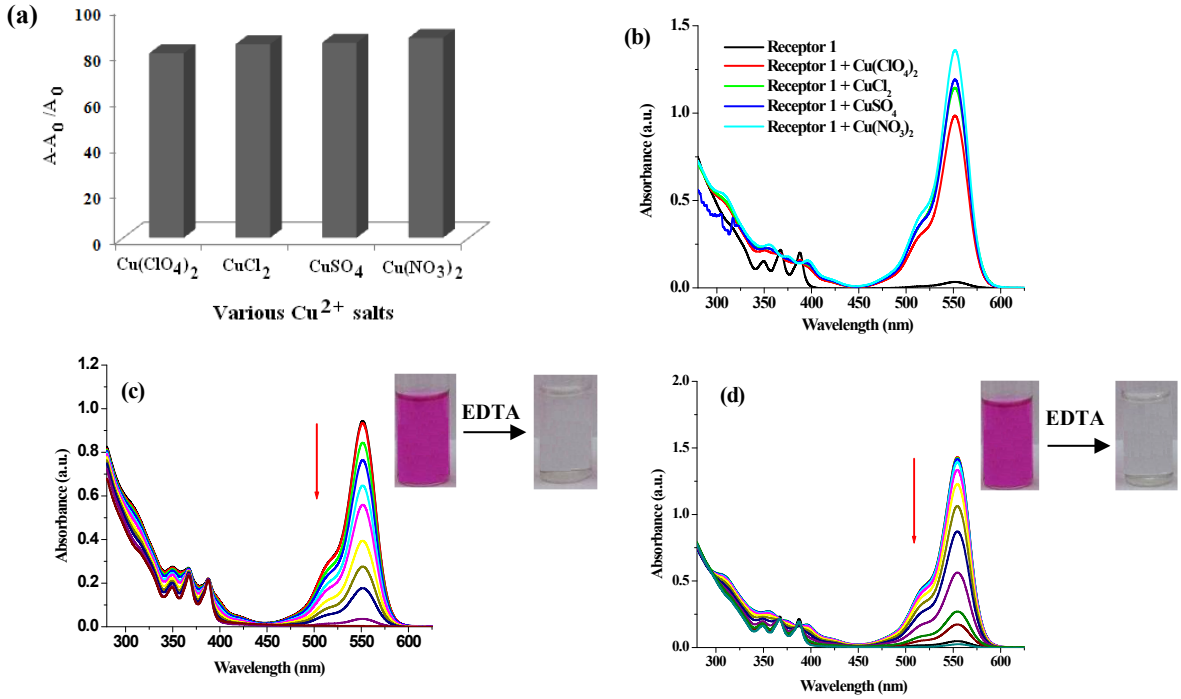
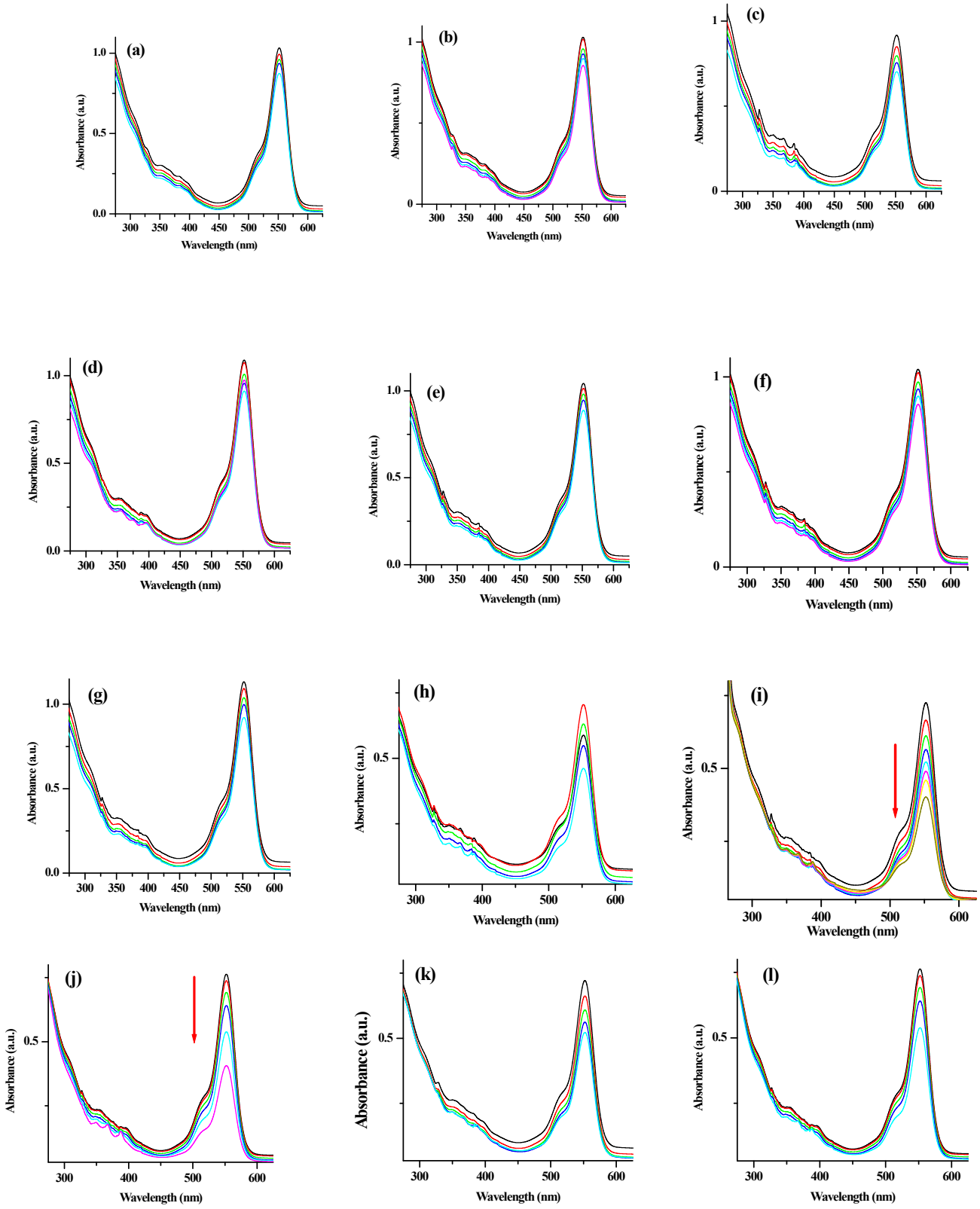


Figure 13S. (a) Bar plot showing the change in absorbance ratio of **1** (c = 2.5 x 10^{-5} M) upon addition of various Cu^{2+} salts (c = 1 x 10^{-3} M) and (b) Change in absorbance of **1** (c = 2.5x10^{-5} M) upon addition of 2 equiv. amounts of various Cu^{2+} salts (c = 1 x 10^{-3} M) in CH_3CN–H_2O (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer); Change in absorbance of '**1**.Cu^{2+}' (1+ 2 equiv. Cu^{2+}) ensemble upon addition of 2 equiv. amounts of EDTA in (c) CH_3CN–H_2O (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) and (d) EtOH–H_2O (7 : 3, v/v, pH = 7.2, 10 mM Tris-HCl buffer).

14. Change in absorbance of "1-Cu^{2+}" ensemble upon addition of various anions in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer).



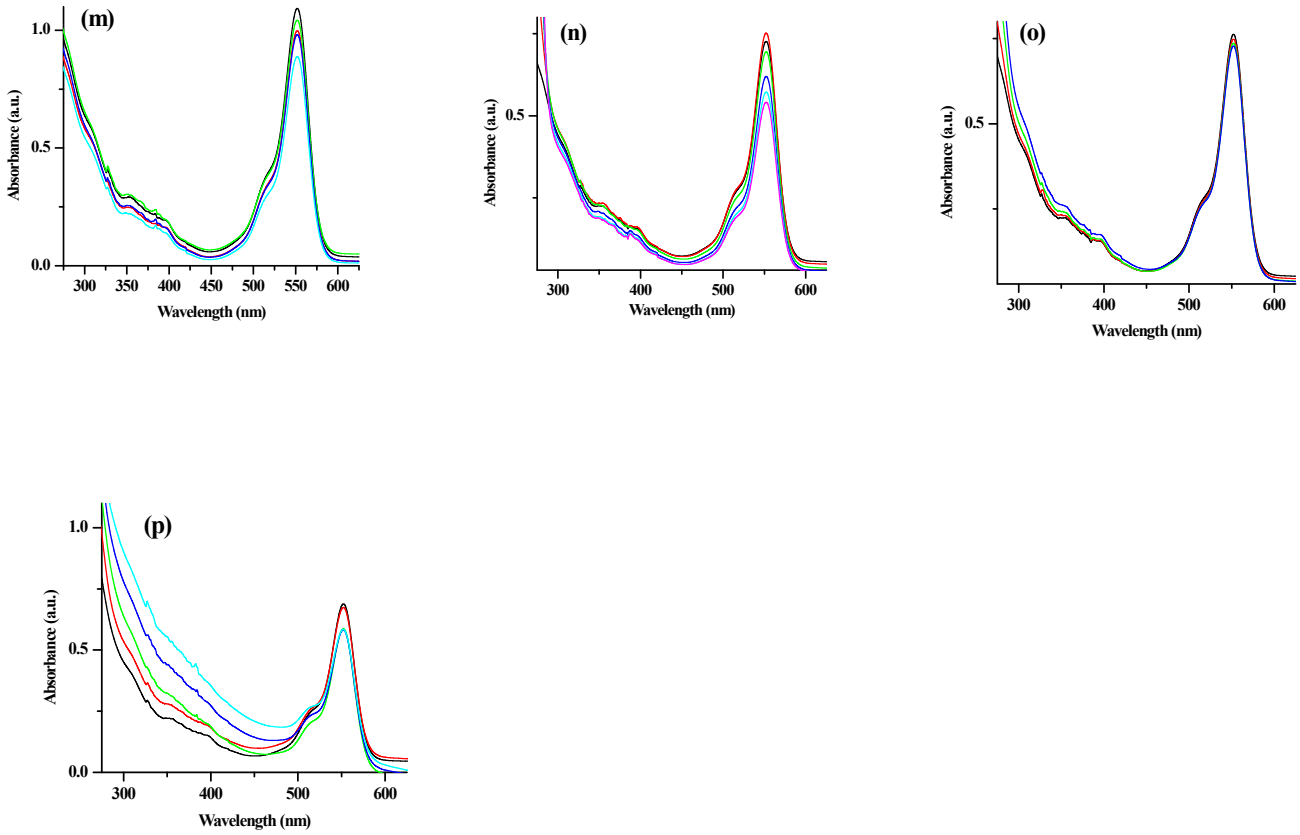


Figure 14S. Absorption spectra of **1.Cu**$^{2+}$ complex in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) upon addition of 12 equiv. amounts of (a) F^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) HSO_4^-, (f) NO_3^-, (g) OAc^-, (h) PO_4^{3-}, (i) $P_2O_7^{4-}$, (j) $HP_2O_7^{3-}$, (k) $H_2PO_4^-$, (l) ClO_4^-, (m) HPO_4^{2-}, (n) ADP, (o) ATP, (p) AMP.

15. Change in absorbance of 2 with different metal ions

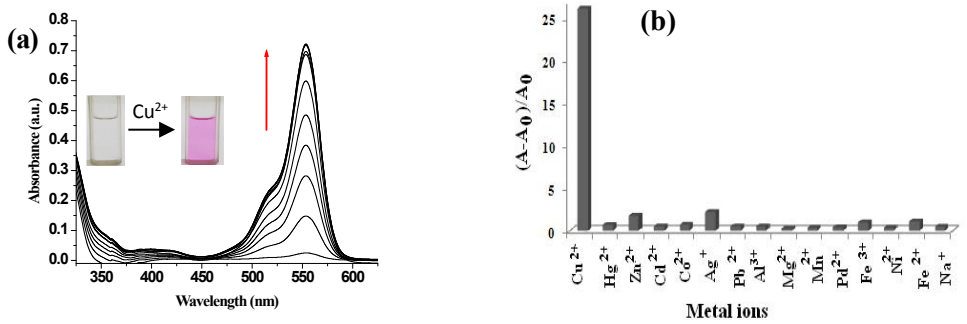


Figure 15S. (a) Change in absorbance of **2** (c = 2.5 x 10^{-5} M) in $CH_3CN–H_2O$ (4: 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) upon gradual addition of 2 equiv. of Cu^{2+} (c = 1 x 10^{-3} M), inset shows the colour change of **2** in presence of 2 equiv. amounts of Cu^{2+} (left); (b) Change in absorption ratio (A- A_0/A_0) of **2** (c = 2.5 x 10^{-5} M) at 554 nm upon addition of 2 equiv. amounts of various metal ions in $CH_3CN–H_2O$ (4: 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer).

16. Competitive selectivity and Job plot

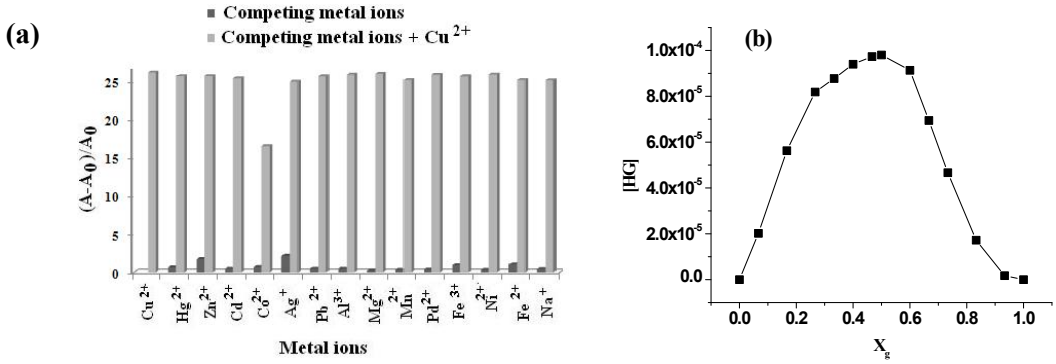


Figure 16S. (a) Competitive selectivity of **2** (c = 2.5 x 10^{-5} M) towards Cu^{2+} (*c* = 1 x 10^{-3} M) in presence of 2 equiv. amounts of other metal ions in $CH_3CN–H_2O$ (4:1, v/v, pH = 7.2, 10 mM Tris-HCl buffer); (b) UV-Vis Job plot of receptor **2** with Cu^{2+} at 554 nm in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) where [H] = [G] = 2.5 x 10^{-5} M.

17. Binding constant curve of receptor 2 with Cu^{2+}

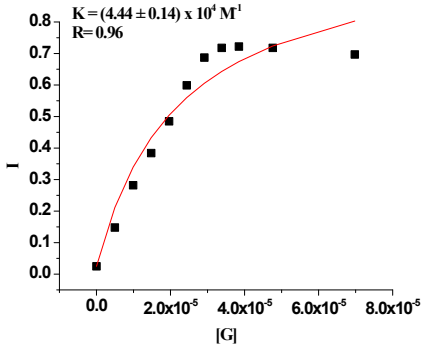


Figure 17S. Binding constant curve for **2** with Cu^{2+} from non-linear fitting of UV-vis titration data.

18. Detection limit of receptor 2 with Cu^{2+}

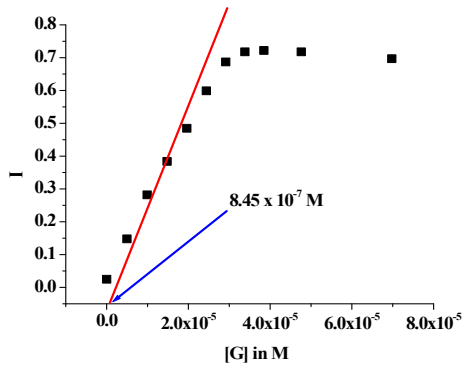


Figure 18S. Detection limit of receptor **2** in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) in sensing of Cu^{2+} ion.

19. Change in emission ratio (I- I_0/I_0) of 2 with some selected metal ions

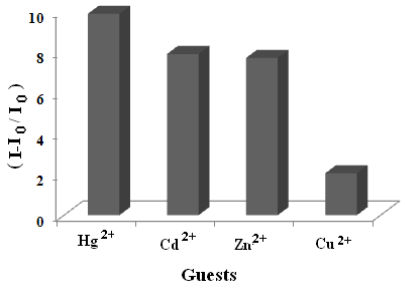


Fig 19S. Change in emission ratio (I- I_0/I_0) of **2** (c = 2.5 x 10^{-5} M) at 580 nm upon addition of 2 equiv. amounts of various metal ions in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer)

20. Change in fluorescence spectra of receptor 2 with selective metal ions by excitation at 370 nm.

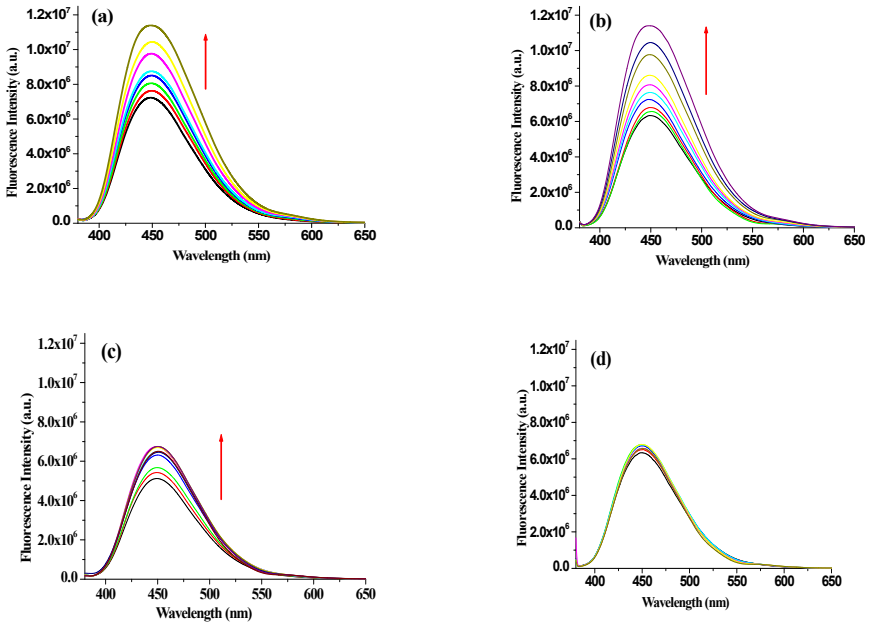


Figure 20S. Change in emission of **2** (c = 2.5 x 10^{-5} M) in $CH_3CN–H_2O$ (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) upon addition of 10 equiv. of (a) $Cd(ClO_4)_2$, (b) $Hg(ClO_4)_2$, (c) $Zn(ClO_4)_2$ and (d) $Cu(ClO_4)_2$, [concentration of metal salts were 1 x 10^{-3} M] [λ_{ex} = 370 nm].

21. Change in emission and absorbance of 2 at different pHs

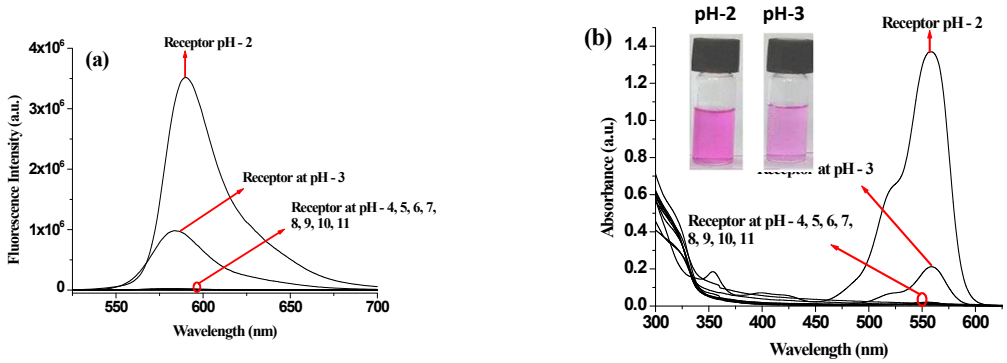


Figure 21S. (a) Change in emission of **2** at different pHs in CH_3CN/H_2O (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer) (λ_{exc} = 500 nm), (b) Change in absorbance of **2** at different pHs in CH_3CN/H_2O (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer).

22. Copper ensemble of 2 and its anion sensing

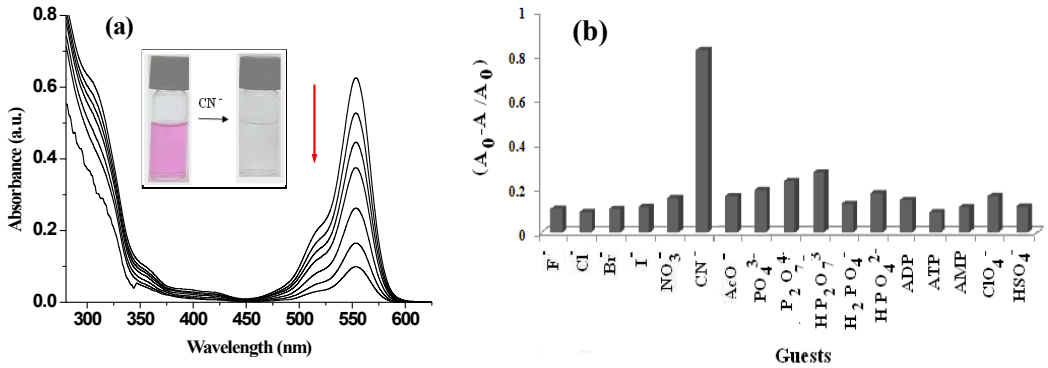


Figure 22S. (a) Absorption spectra for **2**.Cu^{2+} ensemble on gradual addition of 15 equiv. amounts of CN^- in CH_3CN-H_2O (4: 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer), (b) Change in absorbance ratio at 552 nm for '**2**.Cu^{2+}' ensemble upon addition of 15 equiv. of various anions (c = 1 x 10^{-3} M) in CH_3CN-H_2O (4: 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer).

23. Detection limit of various 2.Cu^{2+} ensemble

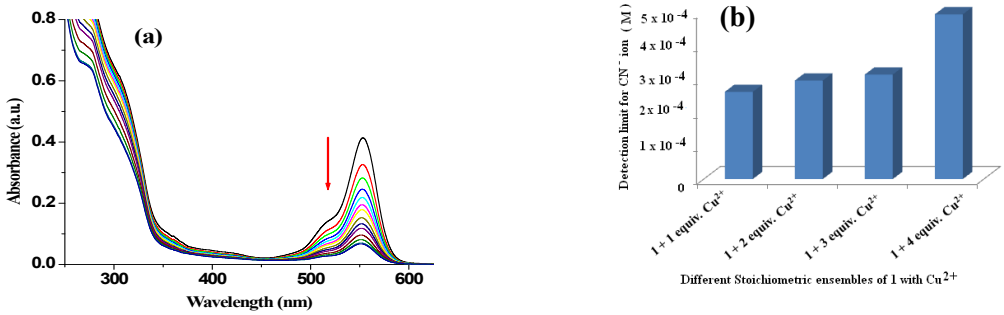


Fig. 23S. (a) Emission spectra for **2**.Cu^{2+} ensemble (receptor **2** + 1 equiv. of Cu^{2+}) upon gradual addition of 12 equiv. amounts of CN^- (c = 1 x 10^{-3} M) in CH_3CN–H_2O (4 : 1, v/v, pH = 7.2, 10 mM Tris-HCl buffer); (b) change in detection limit towards CN^- ion for different stoichiometric ensembles of **2**.Cu^{2+}.

24. MTT assay of receptors 1 and 2

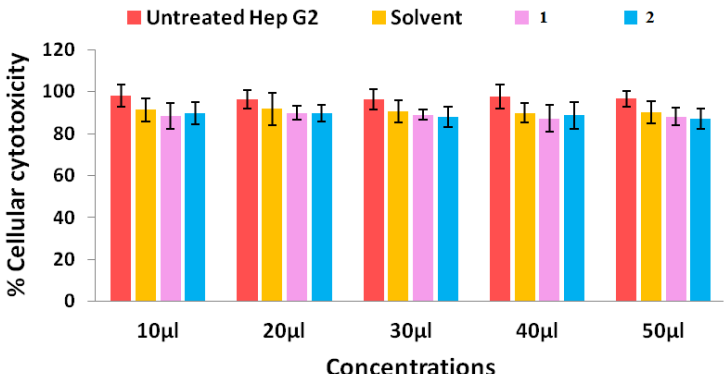


Figure 24S. MTT assay of receptors **1** and **2**.

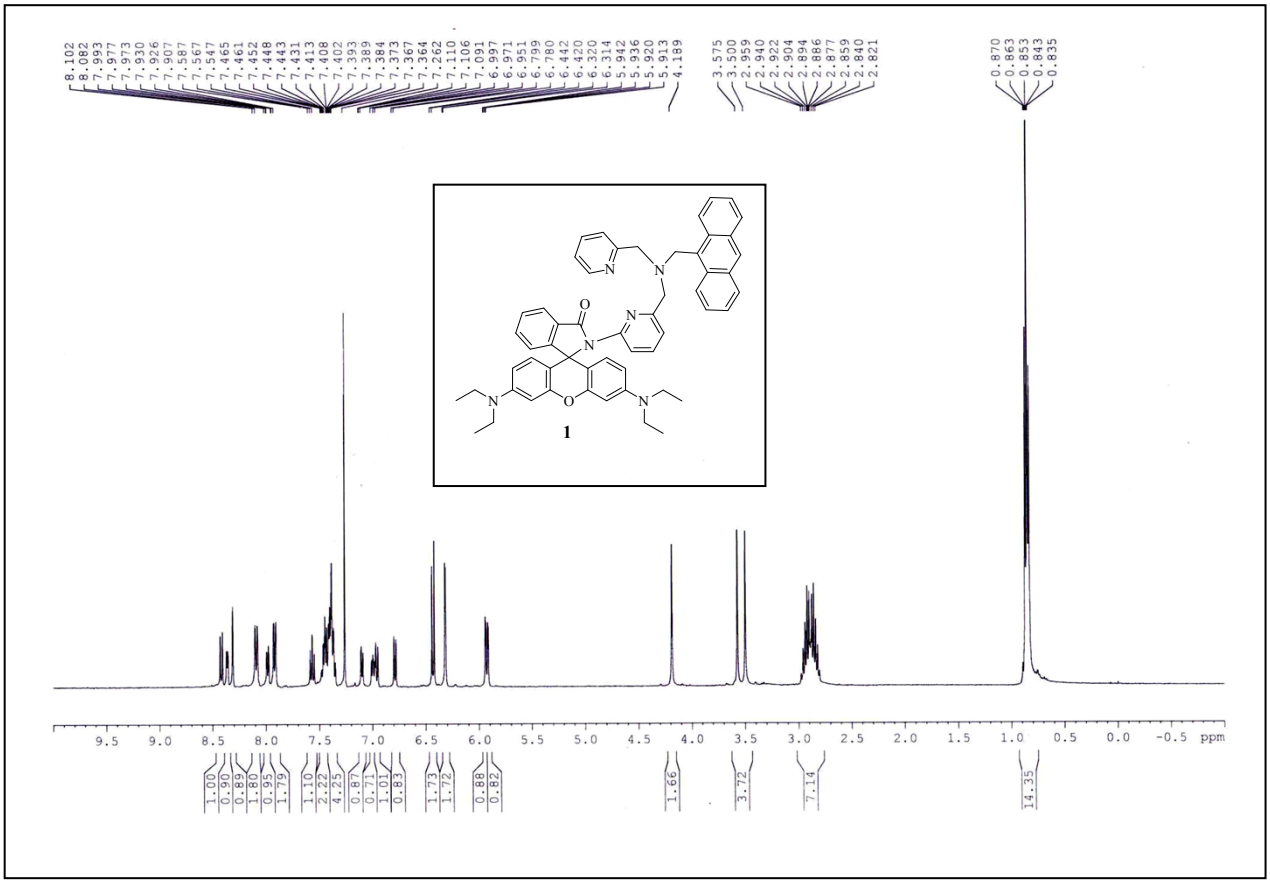
General procedure for fluorescence and UV-vis titrations:

Stock solutions of the receptors were prepared in CH_3CN/aqueous Tris-HCl buffer (4: 1, v/v, pH = 7.2) (or in EtOH/aqueous Tris-HCl buffer (7: 3, v/v, pH = 7.2)) in the concentration range of ~10^{-5} M. An amount of 2 mL of the receptor solution was taken in a cuvette. Stock solutions of guests in the concentration range of ~10^{-3} M were prepared in the same solvent and were individually added in different amounts to the receptor solution. Upon addition of metal ions, the change in emission of the receptor was noted. The same stock solutions for receptor and guests were used to perform the UV-vis titration experiment.

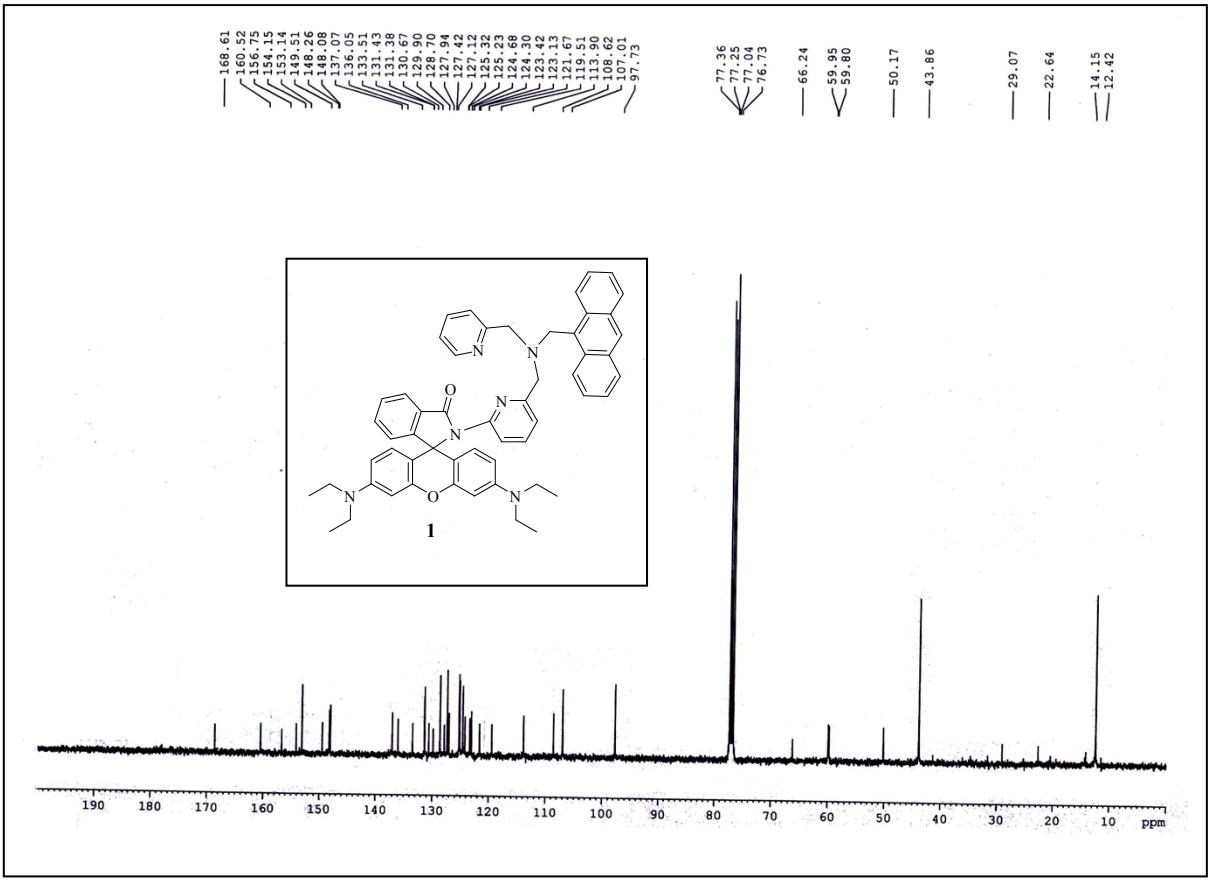
Job's plot

The stoichiometry was determined by the continuous variation method (Job Plot).[10] In this method, solutions of receptor and guest cations of equal concentrations were prepared in the solvent used in the experiment. Then receptor and guest solutions were mixed in different proportions maintaining a total volume of 3 mL of the mixture. All the prepared solutions were kept for 1 h with occasional shaking at room temperature. Then emission and absorbance of the solutions of different compositions were recorded. The concentration of the complex i.e., [HG] was calculated using the equation [HG] = $\Delta A/A_0$ x [H] where $\Delta A/A_0$ indicates the relative absorbance intensities. [H] Corresponds to the concentration of the pure receptor. Mole fraction of the guest (X_G) was plotted against concentration of the complex [HG]. In the plot, the mole fraction of the guest at which the concentration of the receptor–guest complex [HG] is maximum, gives the stoichiometry of the complex.

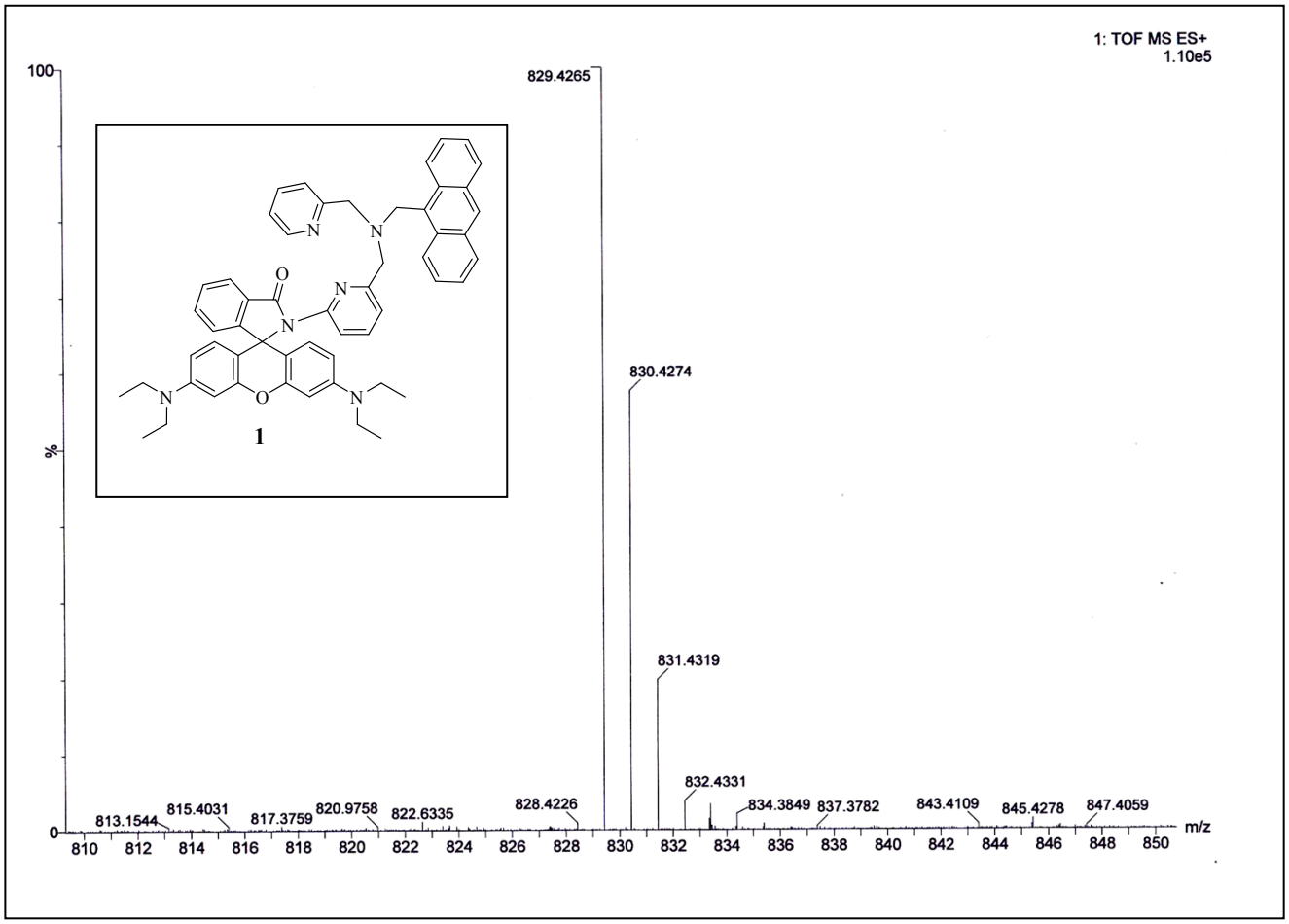
^{1}H NMR of 1 (400 MHz, $CDCl_3$):



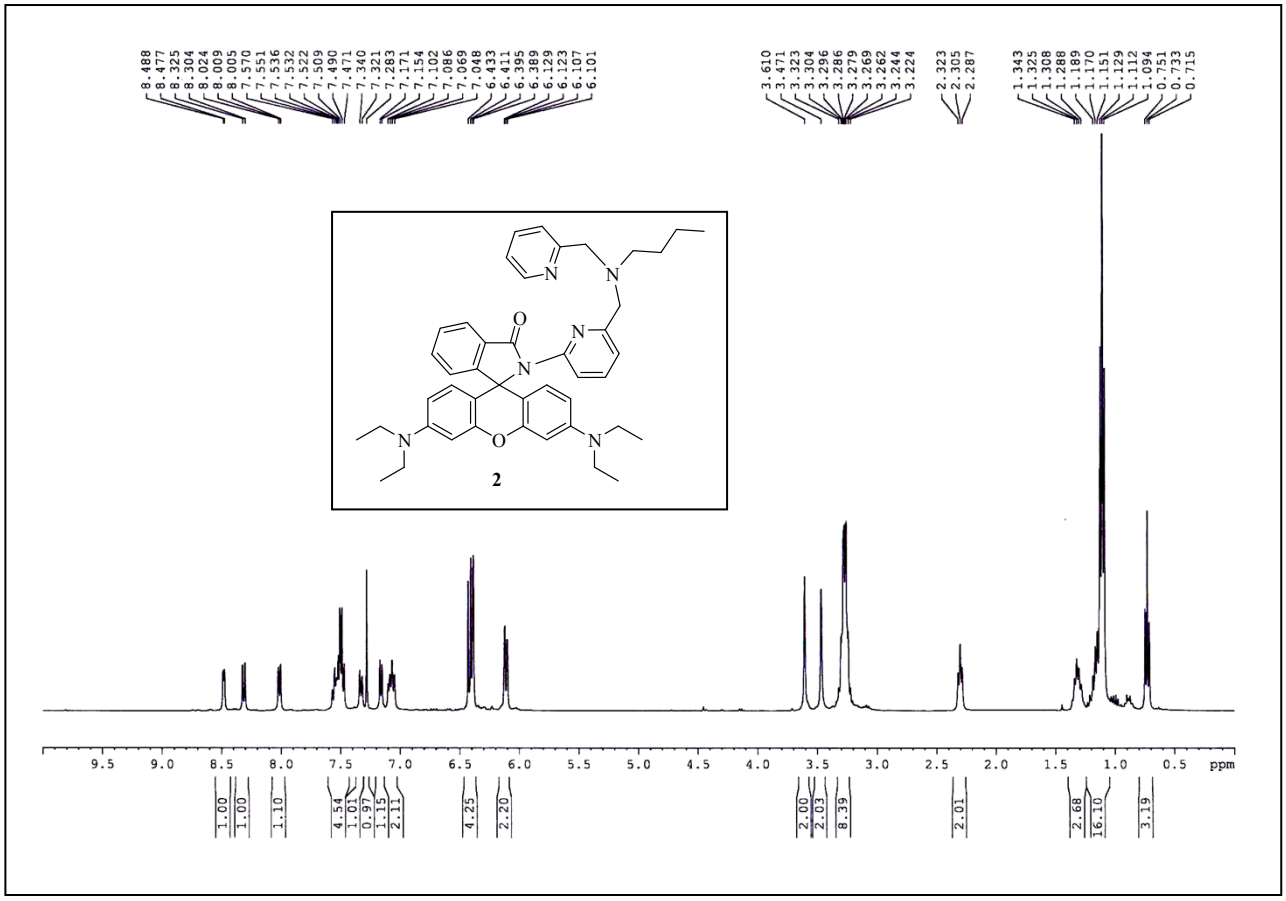
^{13}C NMR of 1 (100 MHz, $CDCl_3$):



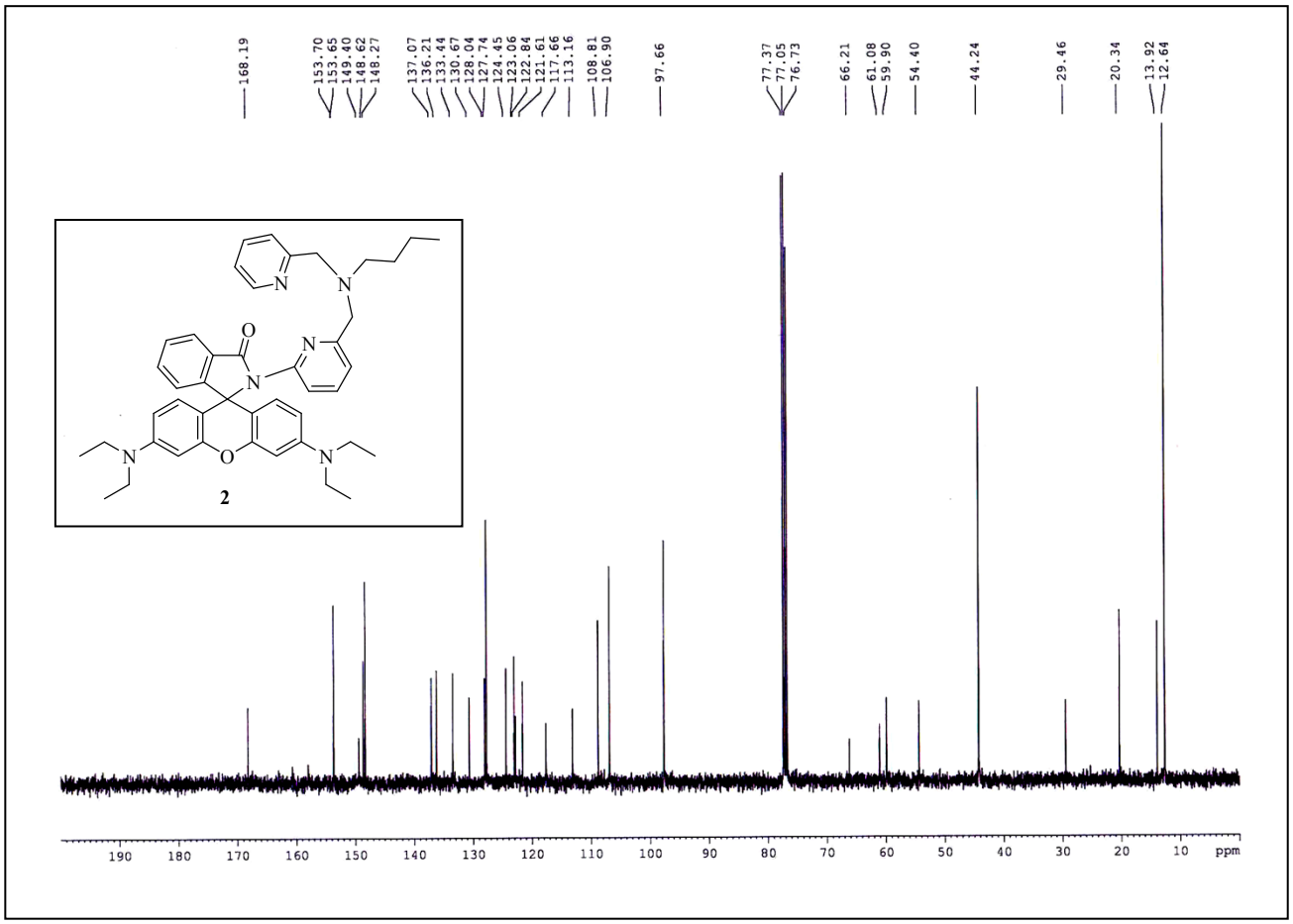
HRMS OF 1:


1: TOF MS ES+
1.10e5
100
%
0
829.4265
830.4274
831.4319
832.4331
813.1544
815.4031
817.3759
820.9758
822.6335
828.4226
834.3849
837.3782
843.4109
845.4278
847.4059
m/z
810
812
814
816
818
820
822
824
826
828
830
832
834
836
838
840
842
844
846
848
850
1

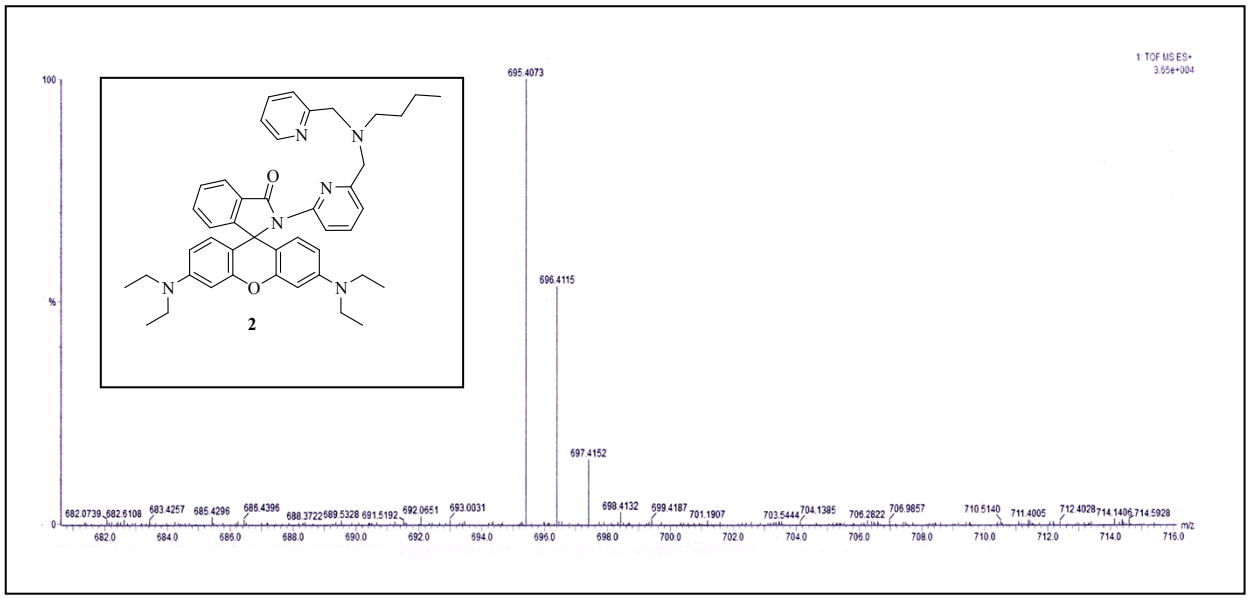
^{1}H NMR of 2 (400 MHz, $CDCl_3$):



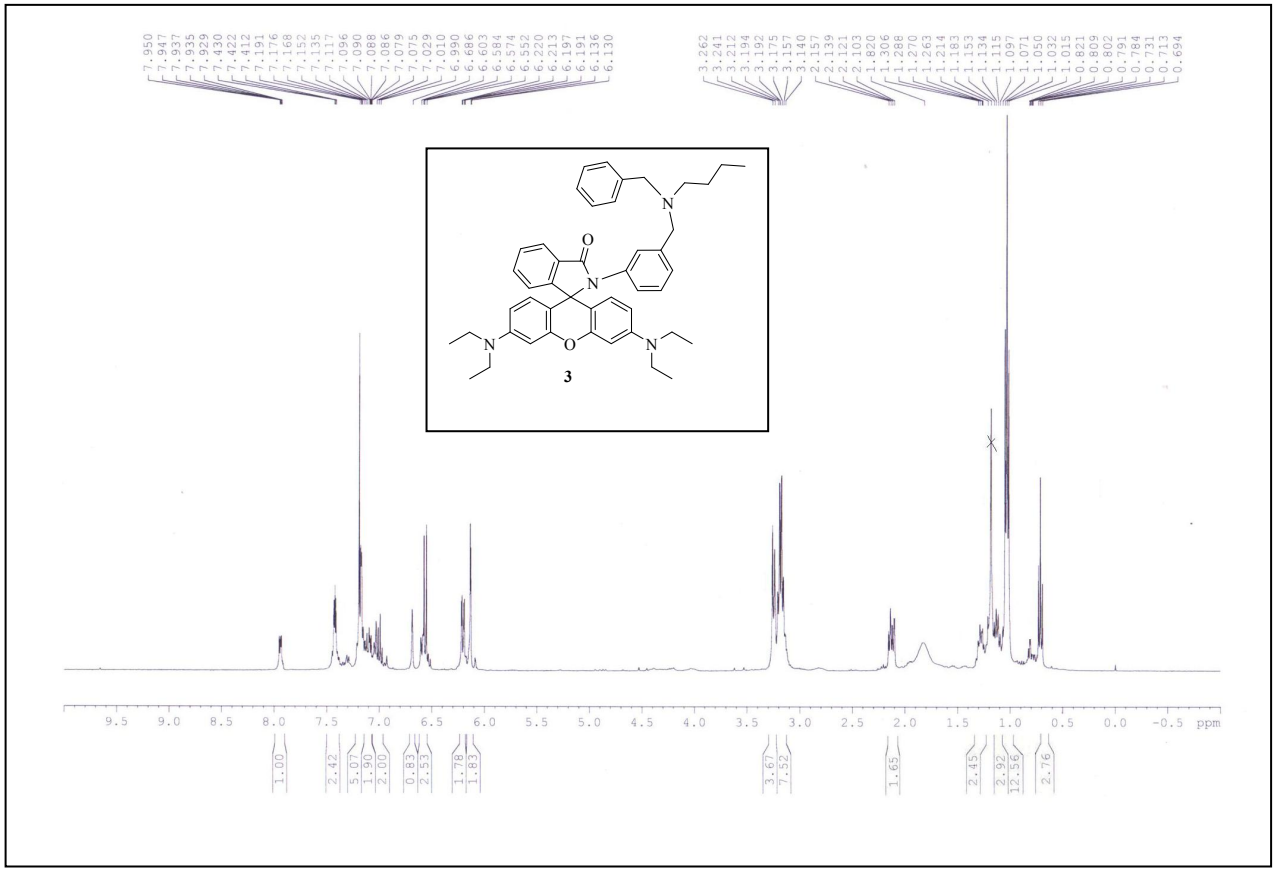
^{13}C NMR of 2 (100 MHz, $CDCl_3$):



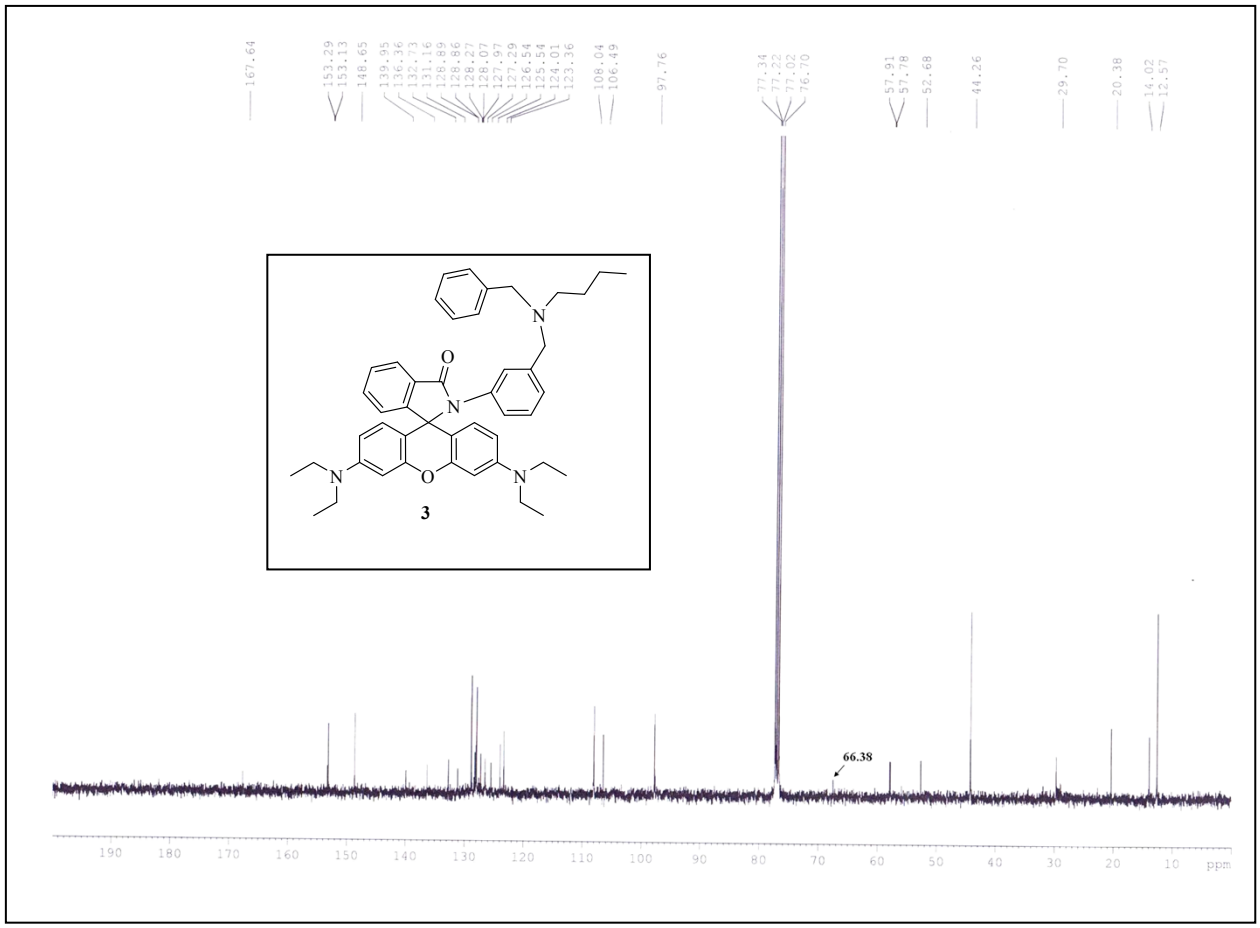
HRMS of 2:


1: TOF MS ES+
3.65e+004
100
%
0
695.4073
696.4115
697.4152
682.0739
682.6108
683.4257
685.4296
686.4396
688.3722
689.5328
691.5192
692.0651
693.0031
698.4132
699.4187
701.1907
703.5444
704.1385
706.2822
706.9857
710.5140
711.4005
712.4028
714.1406
714.5928
m/z
682.0
684.0
686.0
688.0
690.0
692.0
694.0
696.0
698.0
700.0
702.0
704.0
706.0
708.0
710.0
712.0
714.0
716.0
O
N
2

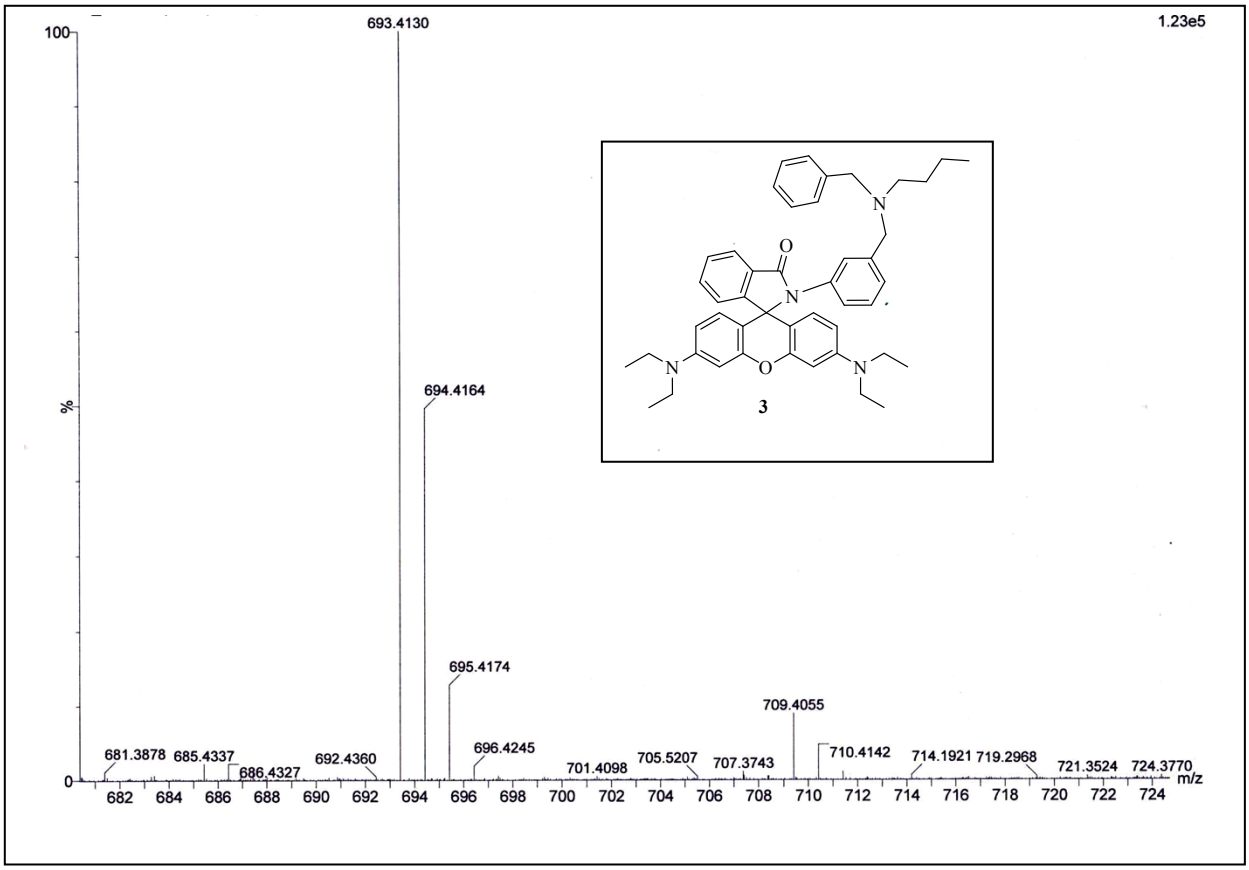
^{1}H NMR of 3 (400 MHz, $CDCl_3$):



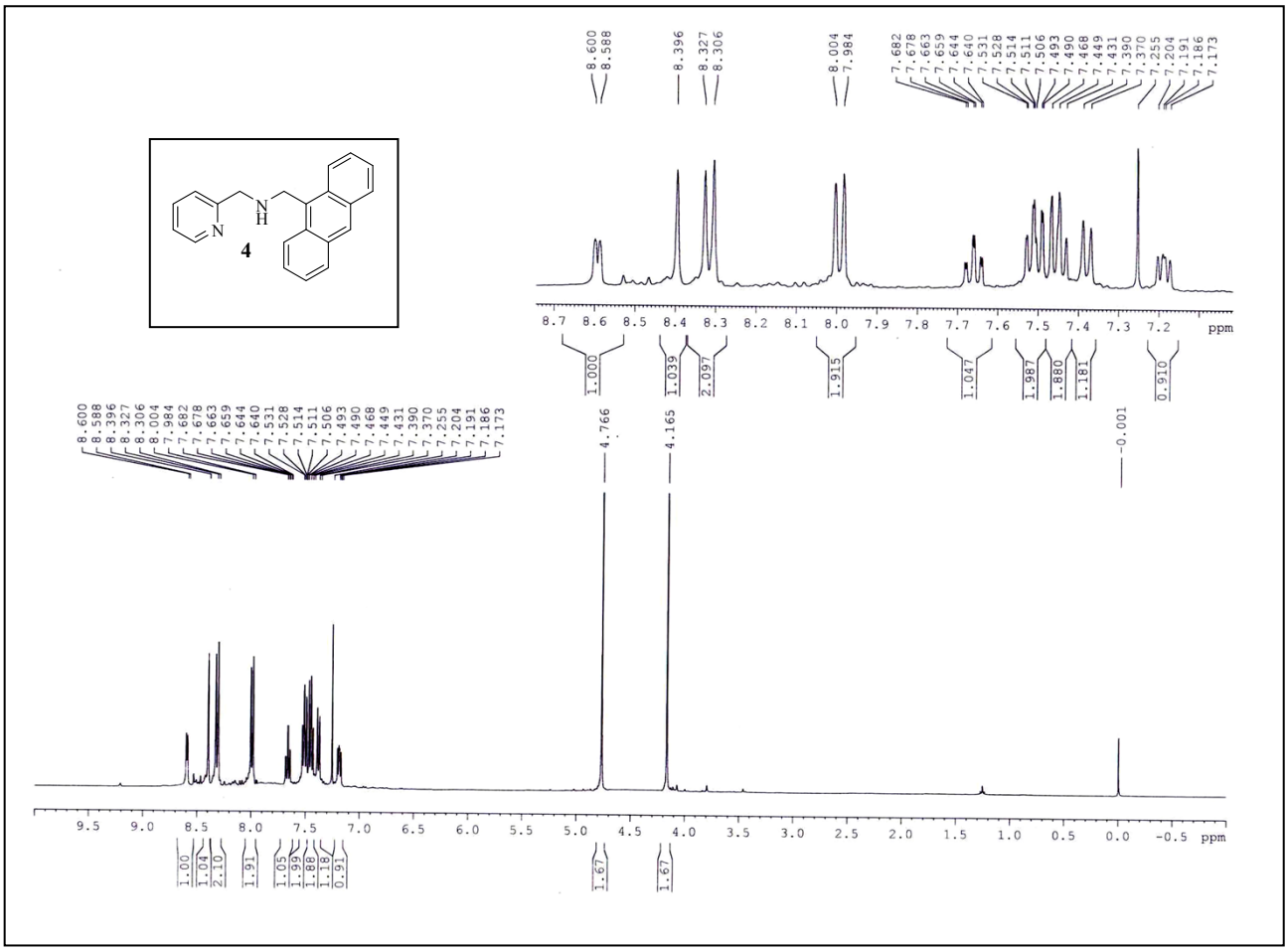
^{13}C NMR of 3 (100 MHz, $CDCl_3$):



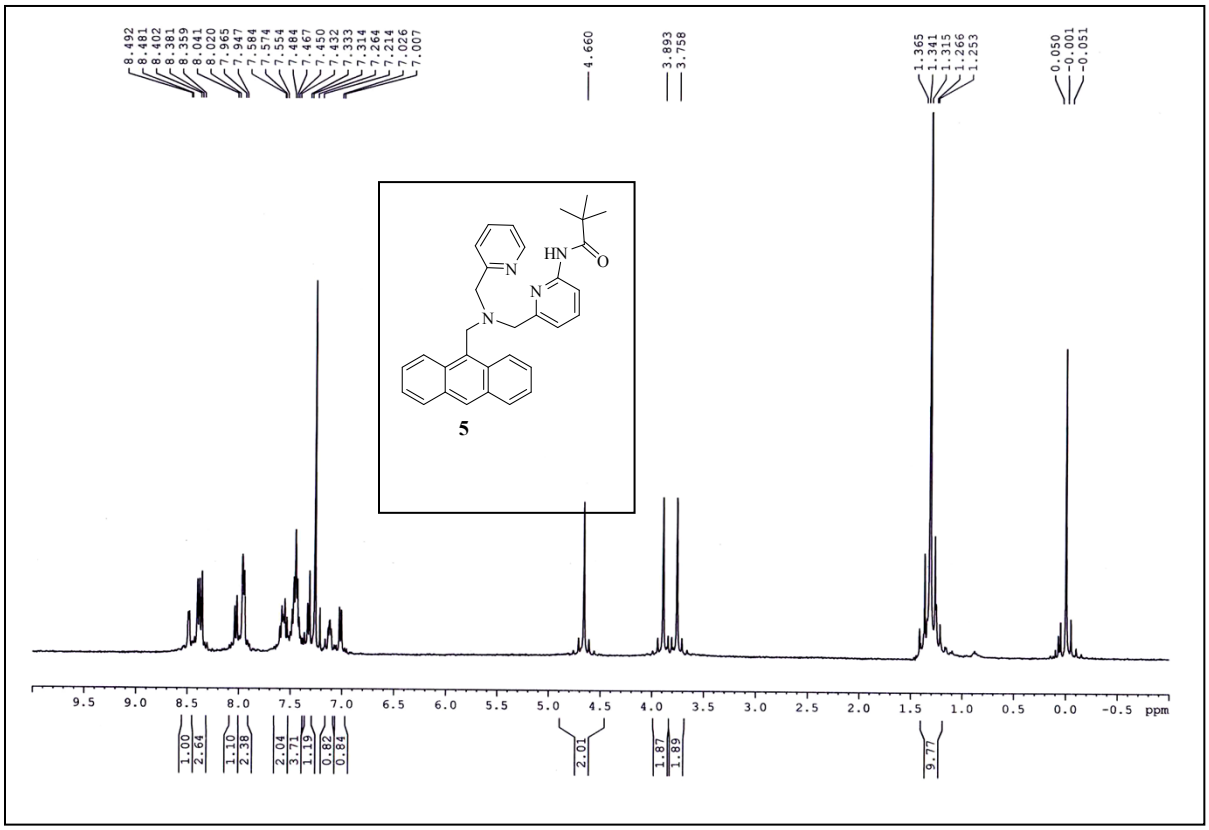
HRMS OF 3:


693.4130
1.23e5
100
%
0
694.4164
695.4174
709.4055
681.3878
685.4337
686.4327
692.4360
696.4245
701.4098
705.5207
707.3743
710.4142
714.1921
719.2968
721.3524
724.3770
m/z
682
684
686
688
690
692
694
696
698
700
702
704
706
708
710
712
714
716
718
720
722
724
O
N
N
O
N
3

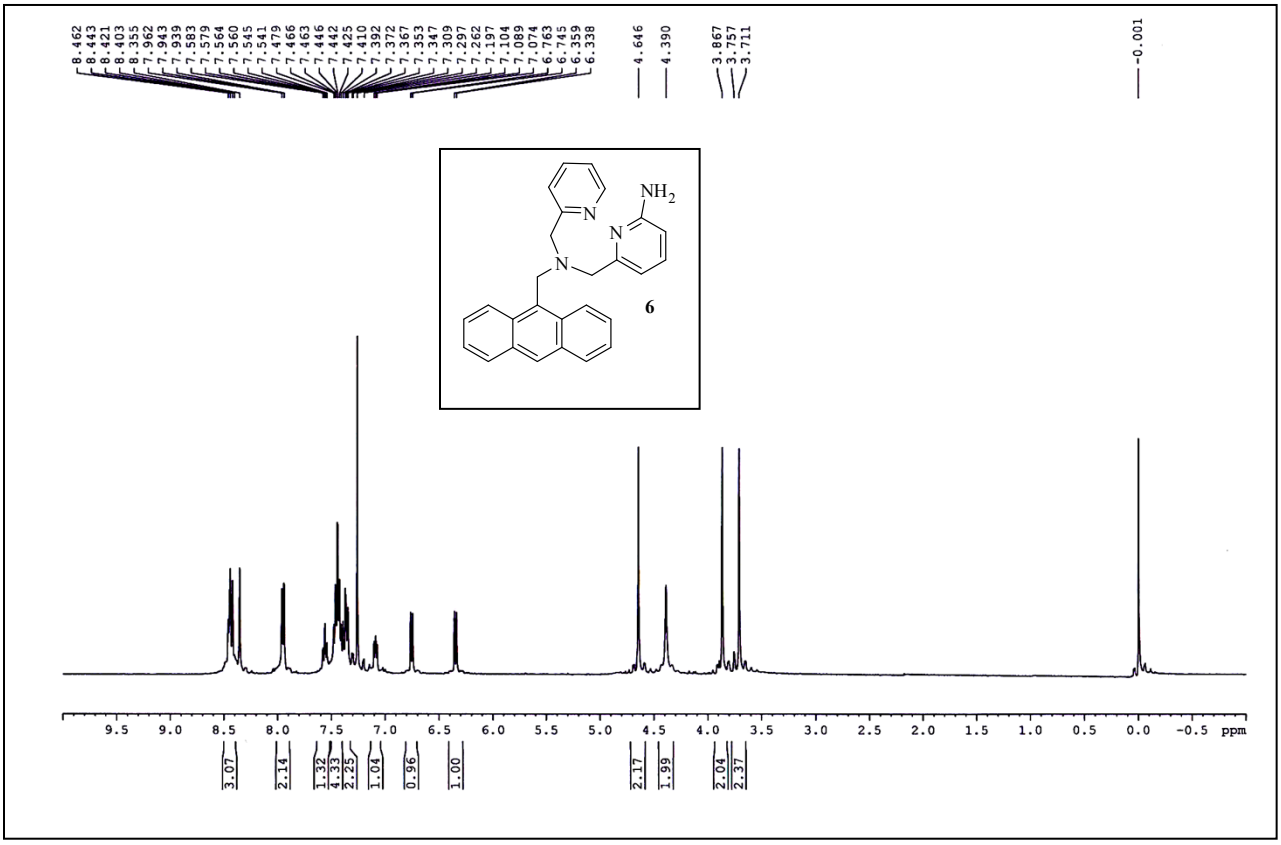
^{1}H NMR of 4 (400 MHz, $CDCl_3$):



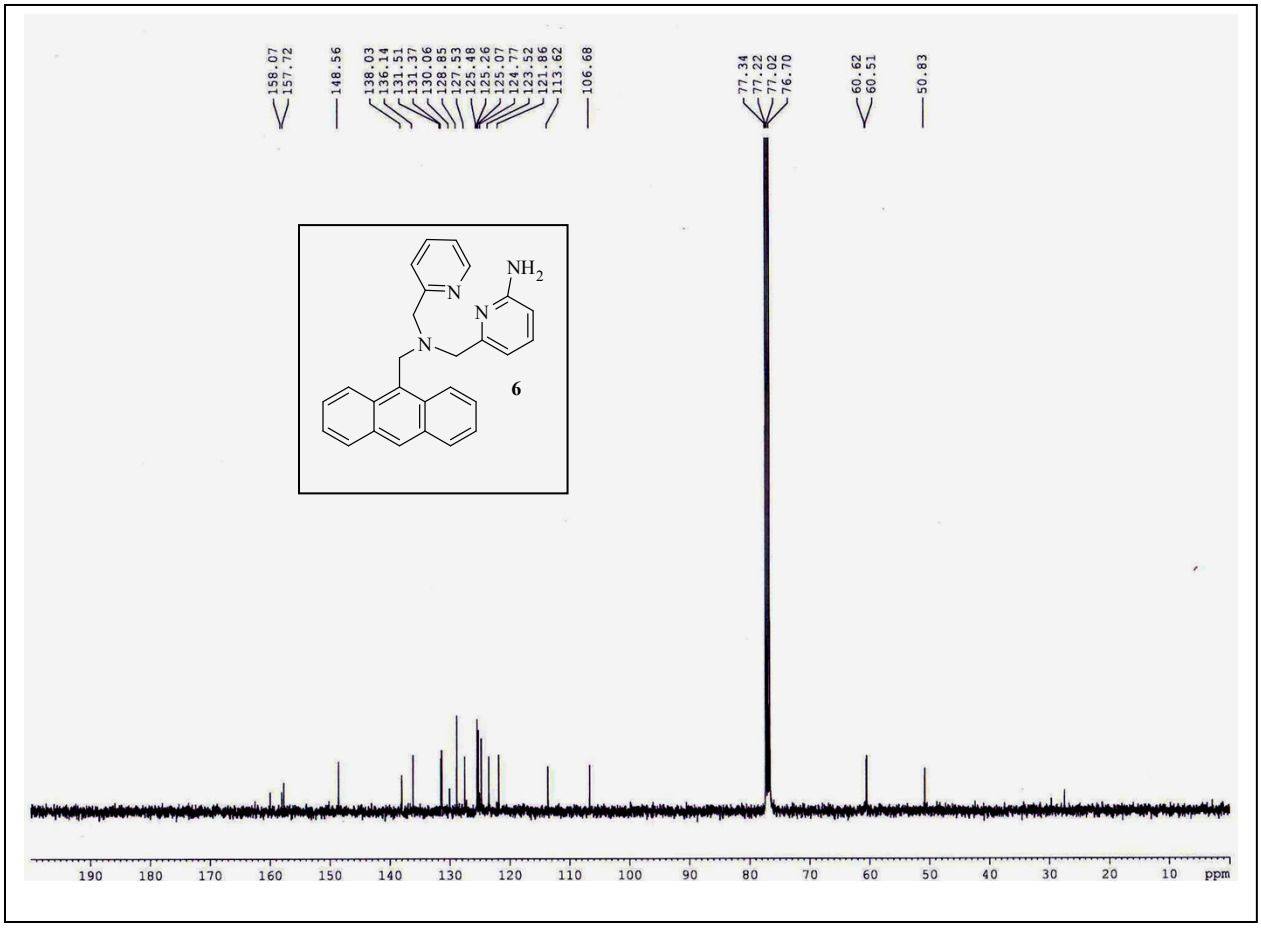
^{1}H NMR of 5 (400 MHz, $CDCl_3$):



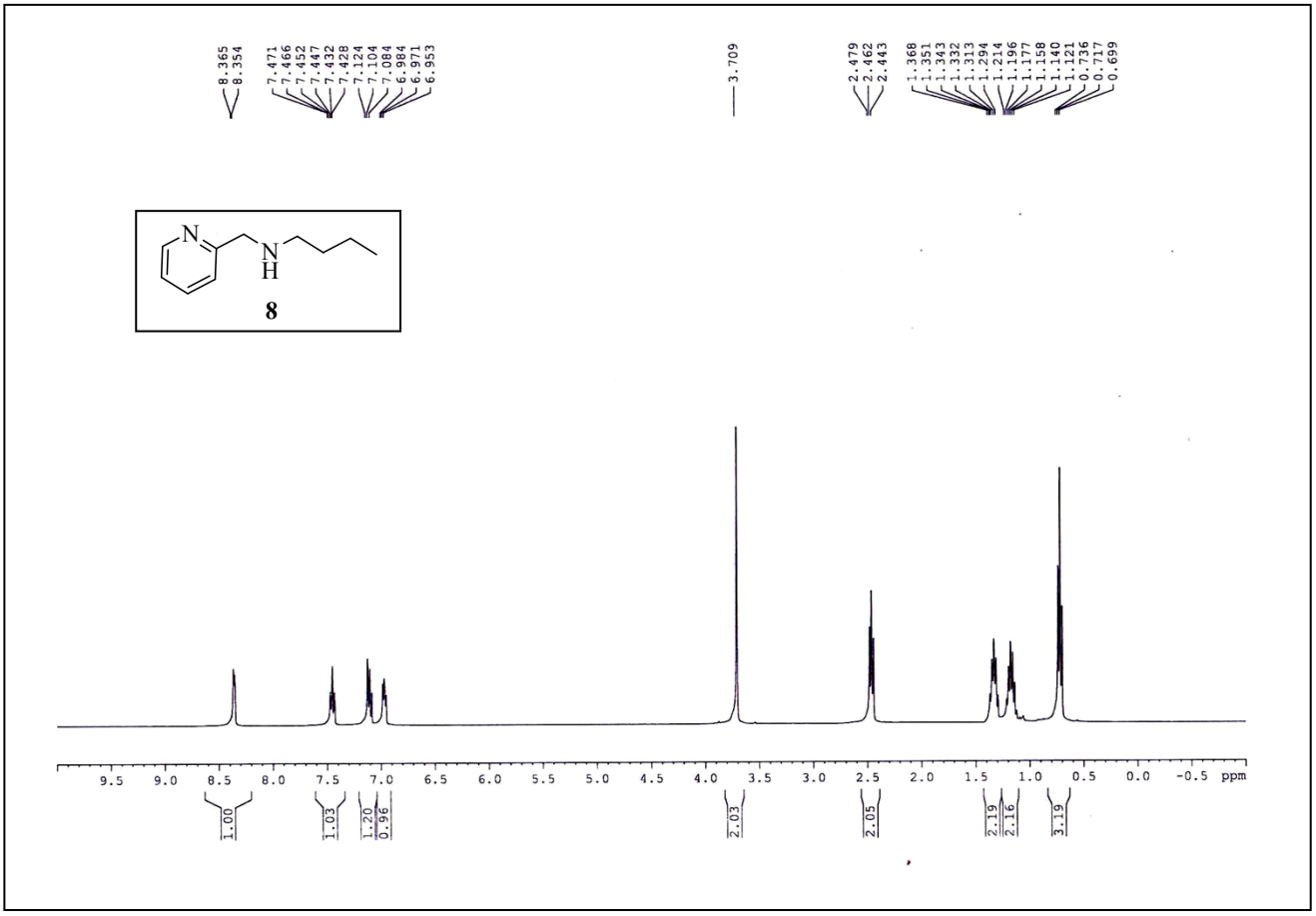
^{1}H NMR of 6 (400 MHz, $CDCl_3$):



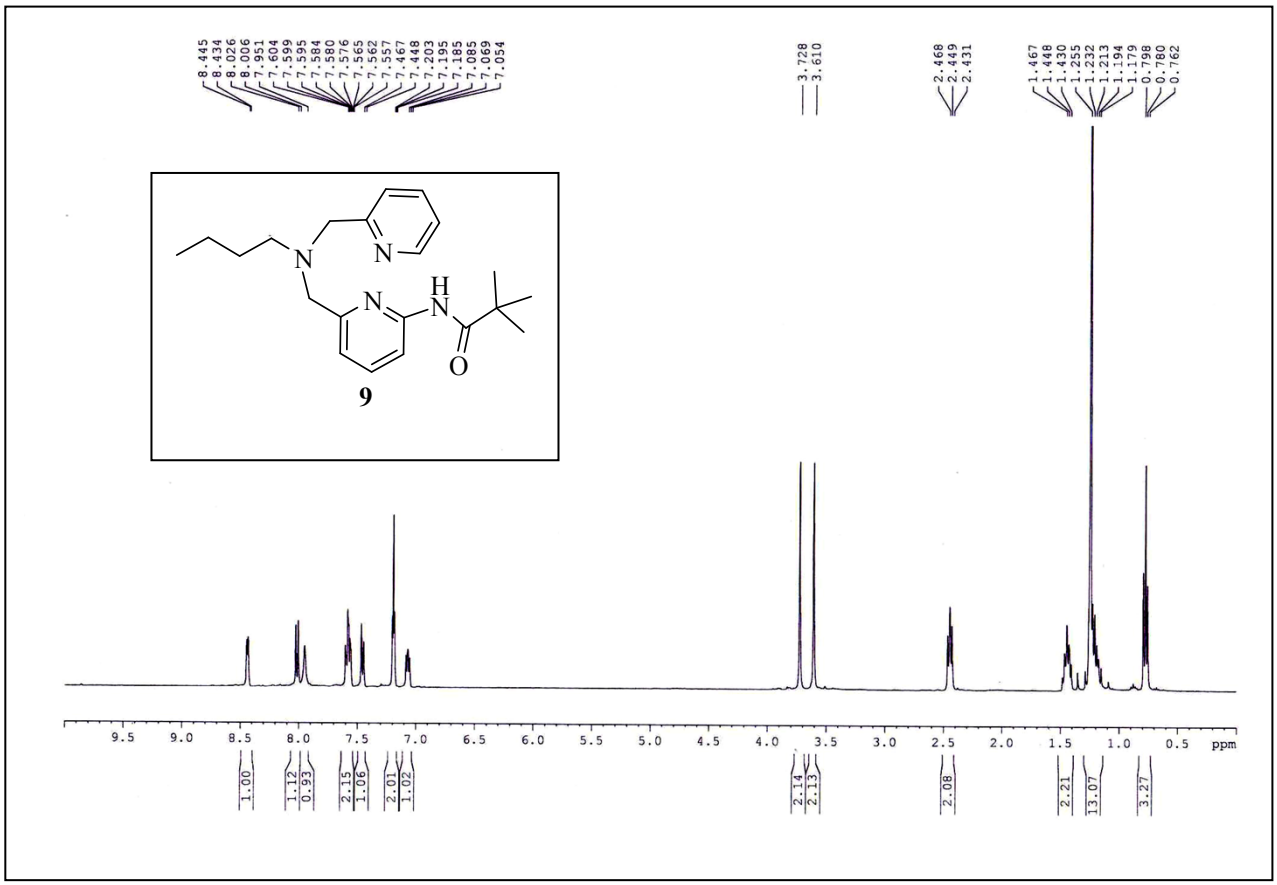
^{13}C NMR of 6 (100 MHz, $CDCl_3$):



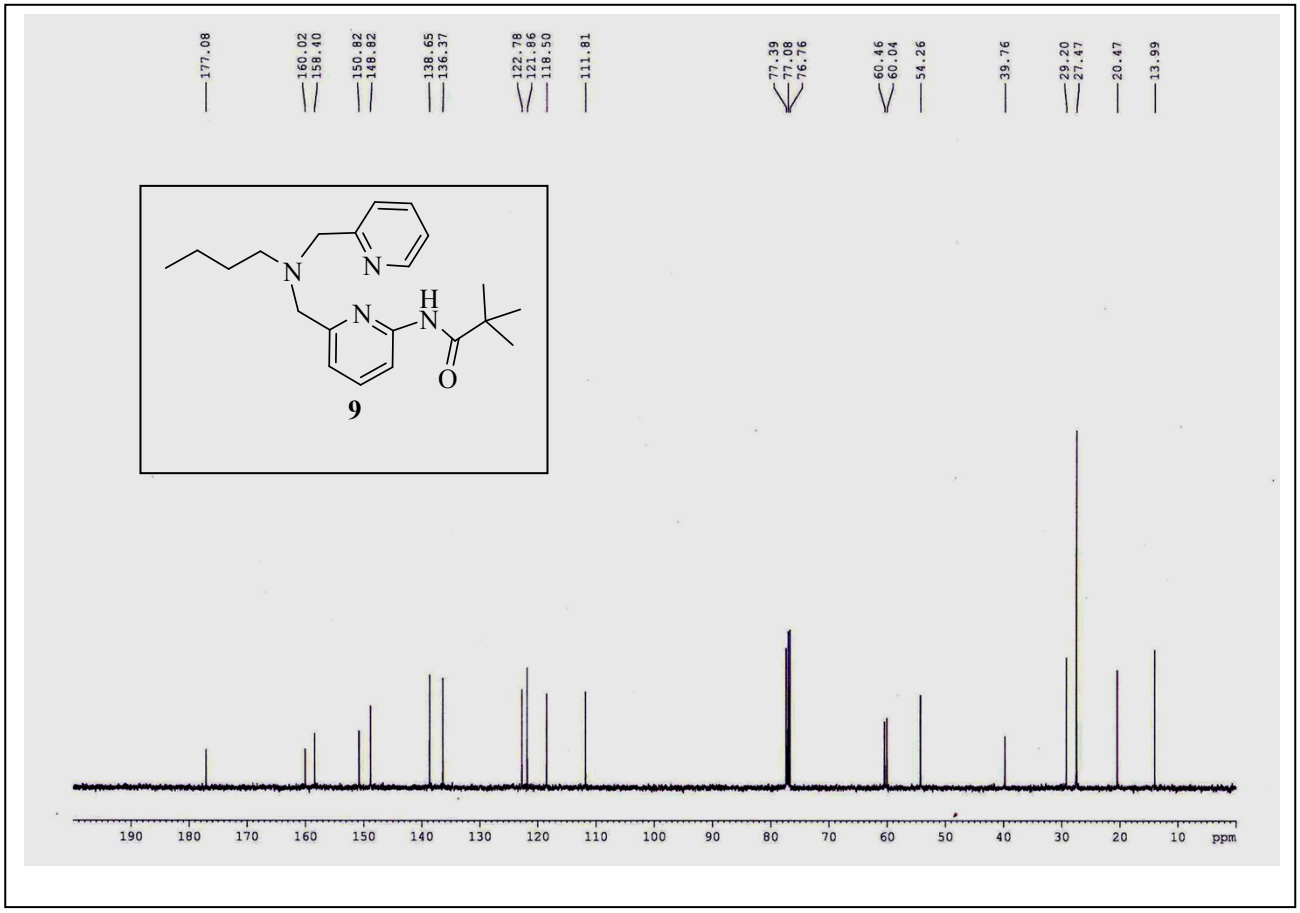
^{1}H NMR of 8 (400 MHz, $CDCl_3$):



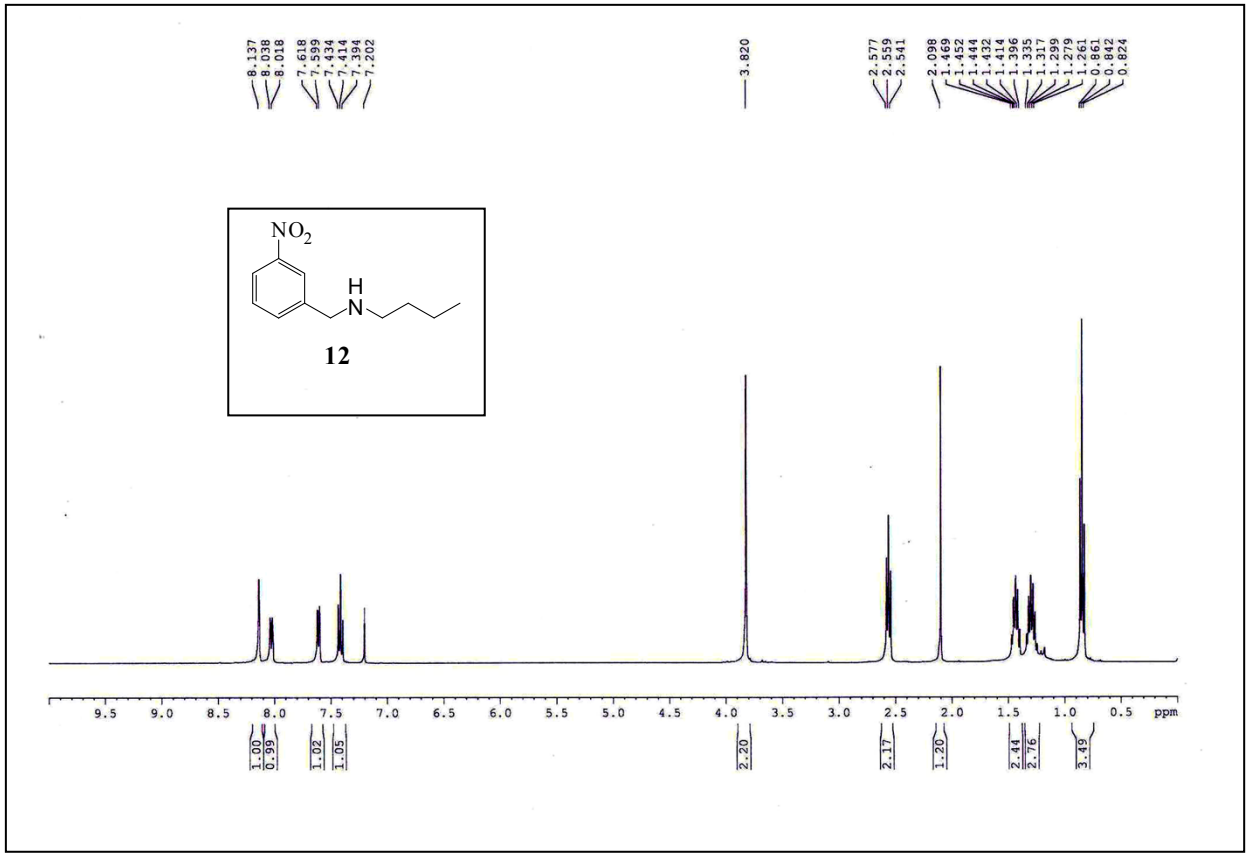
^{1}H NMR of 9 (400 MHz, $CDCl_3$):



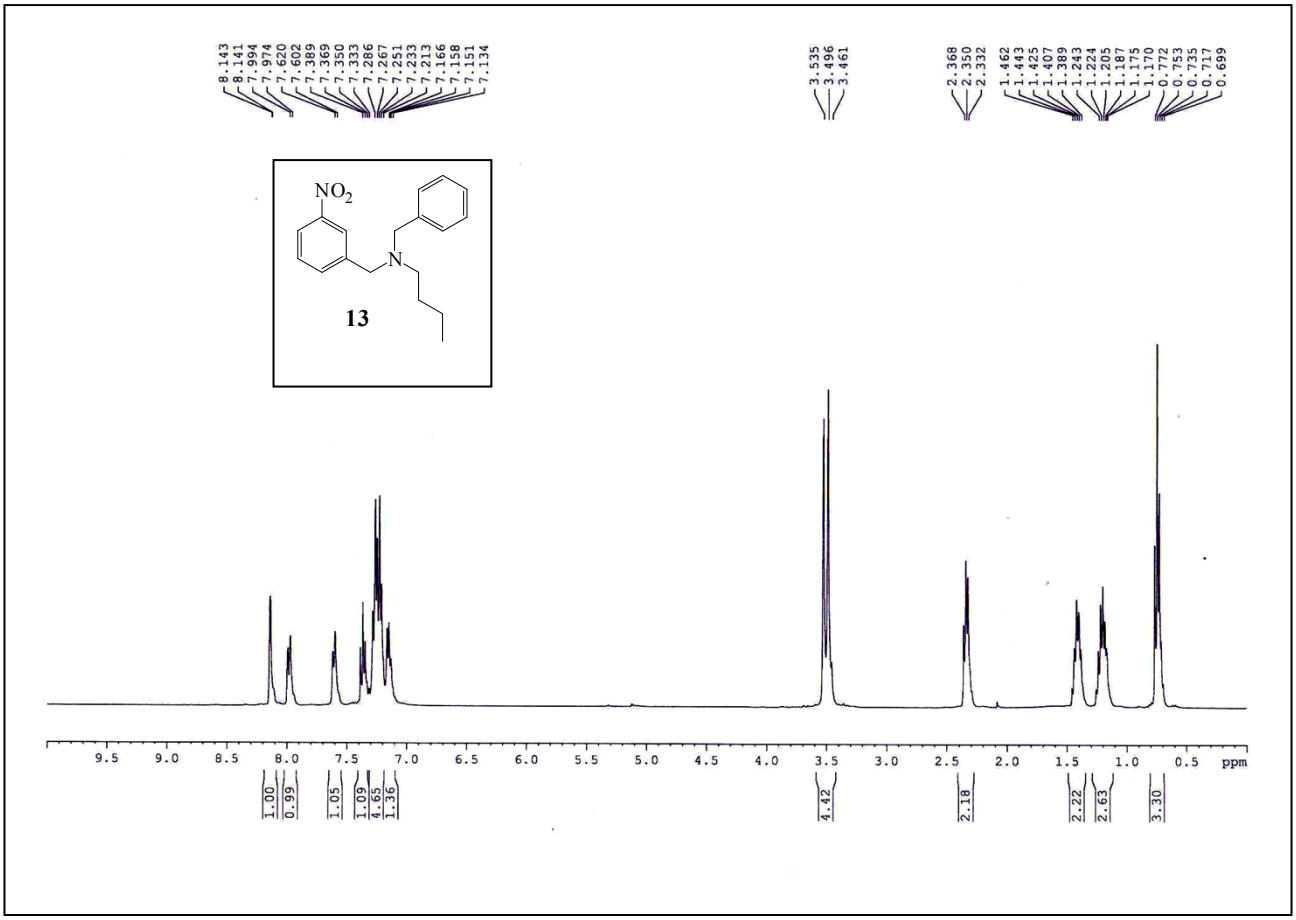
^{13}C NMR of 9 (100 MHz, $CDCl_3$):



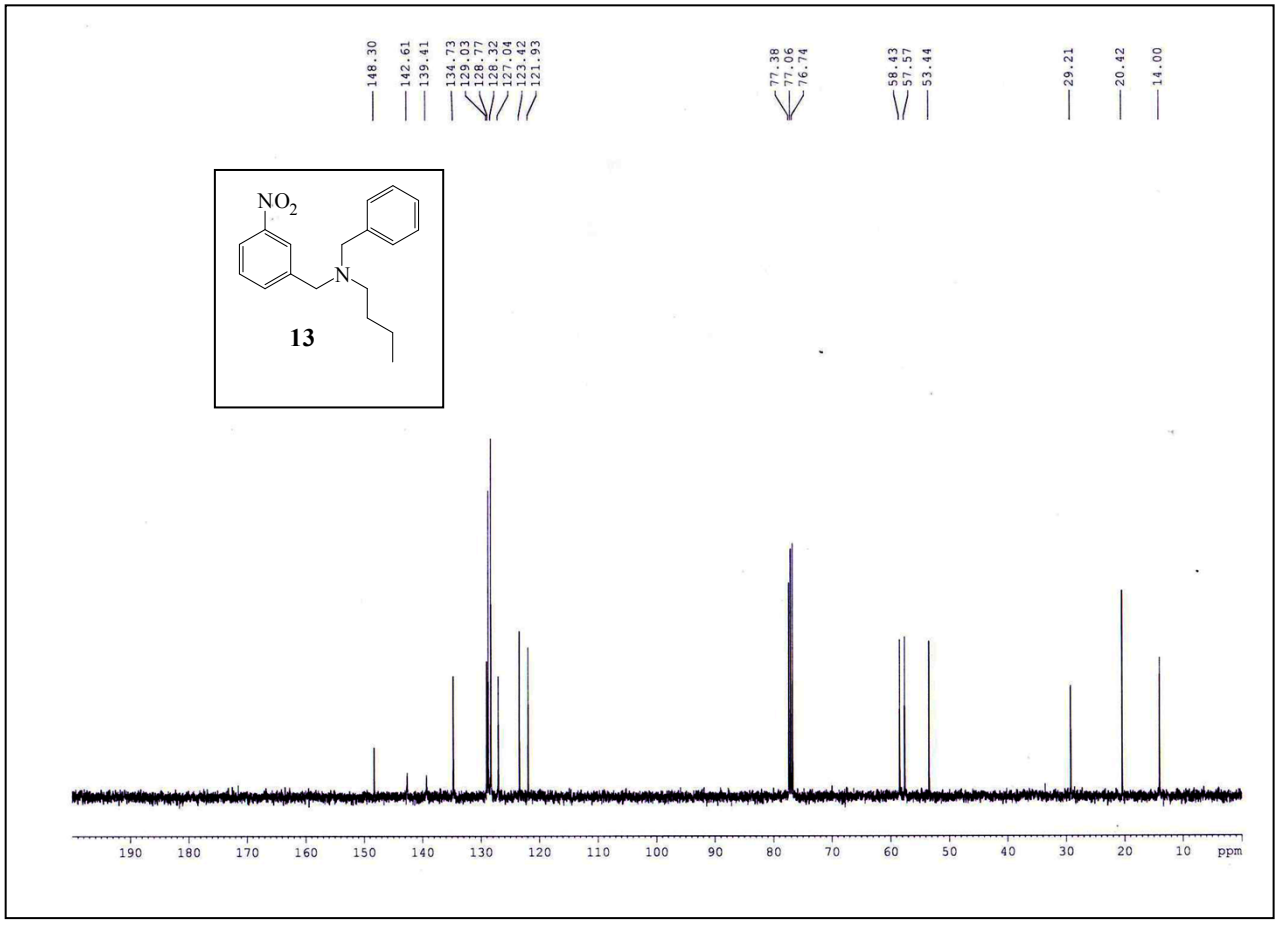
^{1}H NMR of 12 (400 MHz, $CDCl_3$):



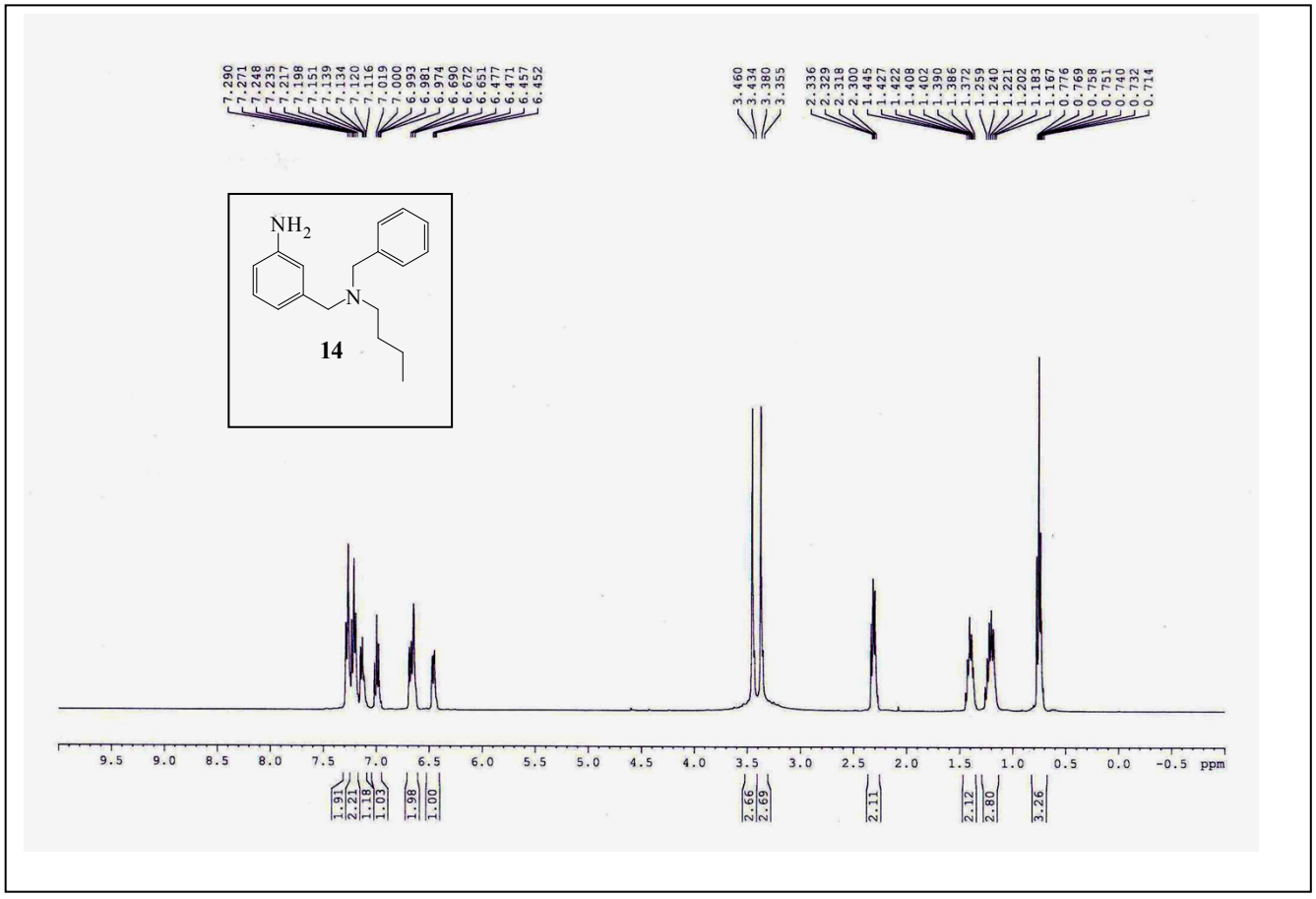
^{1}H NMR of 13 (400 MHz, $CDCl_3$):



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



^{1}H NMR of 14 (400 MHz, $CDCl_3$):



^{13}C NMR of 14 (100 MHz, $CDCl_3$):