

Electronic Supplementary Information
for

**Pyrimidine based highly sensitive fluorescent receptor for Al³⁺
showing dual signaling mechanism**

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1. Experimental:

1.1 Apparatus:

The IR Spectrum for the receptor 1 was recorded on JASCO-FTIR Spectrophotometer while ¹H NMR spectra were recorded on a Bruker-400 Avance NMR Spectrometer and JEOL AL 300 FT NMR Spectrometer. Mass spectrometric analysis was carried out on a MDS Sciex API 2000 LCMS spectrometer. Electronic spectra were recorded at room temperature (298 K) on a UV-1700 pharماسpec spectrophotometer with quartz cuvette (path length=1 cm). Emission spectra were recorded on Varian Cary Eclipse Fluorescence spectrophotometer.

1.2 Materials:

All reagents for synthesis were purchased from Sigma-Aldrich and were used without further purification. The DMSO of HPLC grade for UV-visible experiments was purchased from Spectrochem pvt. Ltd. Mumbai, India.

1.3 General Methods:

All titration experiments were carried at room temperature. For the UV-visible titrations a 10 μM solution of the receptor solution and chloride salt of metals were prepared in DMSO as well as in aqueous media respectively. The ¹H NMR titrations were carried out in DMSO-d₆ using tetramethylsilane (TMS) as an internal reference standard. For the ¹H NMR spectral titrations the 5x10⁻³ M solutions of the receptor 1 and the stock solution of Al³⁺ as its chloride salt were

prepared separately in DMSO- d_6 . Fluorescence titration of receptor **1** with Al^{3+} was performed in 0.5 μ M DMSO solution of receptor. The chloride salt of metals were prepared in DMSO as well as in aqueous media. For fluorescence titration experiment the solution of cations were prepared in aqueous medium. Due to insufficient solubility of receptor **1** in water its stock solution of 0.25 M was prepared in DMSO which was used for fluorescence titration experiment in water at 0.5 μ M concentration through dilution. The detection limit of receptor **1** and **3** as a fluorescent sensor for the analysis of Al^{3+} was determined from a plot of fluorescence intensity as a function of the concentration of the added metal ions. To determine the S/N ratio, the fluorescence intensity of both receptors without Al^{3+} was measured by 10 times and the standard deviation of blank measurements was determined. The detection was calculated as three times the standard deviation from the blank measurement (in the absence of Al^{3+} ion) divided by the slope of calibration plot between Al^{3+} ion concentration and fluorescence intensity.

Figure 1: Effect of concomitant additions of various metal ions (0-5 equivalents) on the UV-visible spectra of 10 μ M DMSO solution of receptor 1:

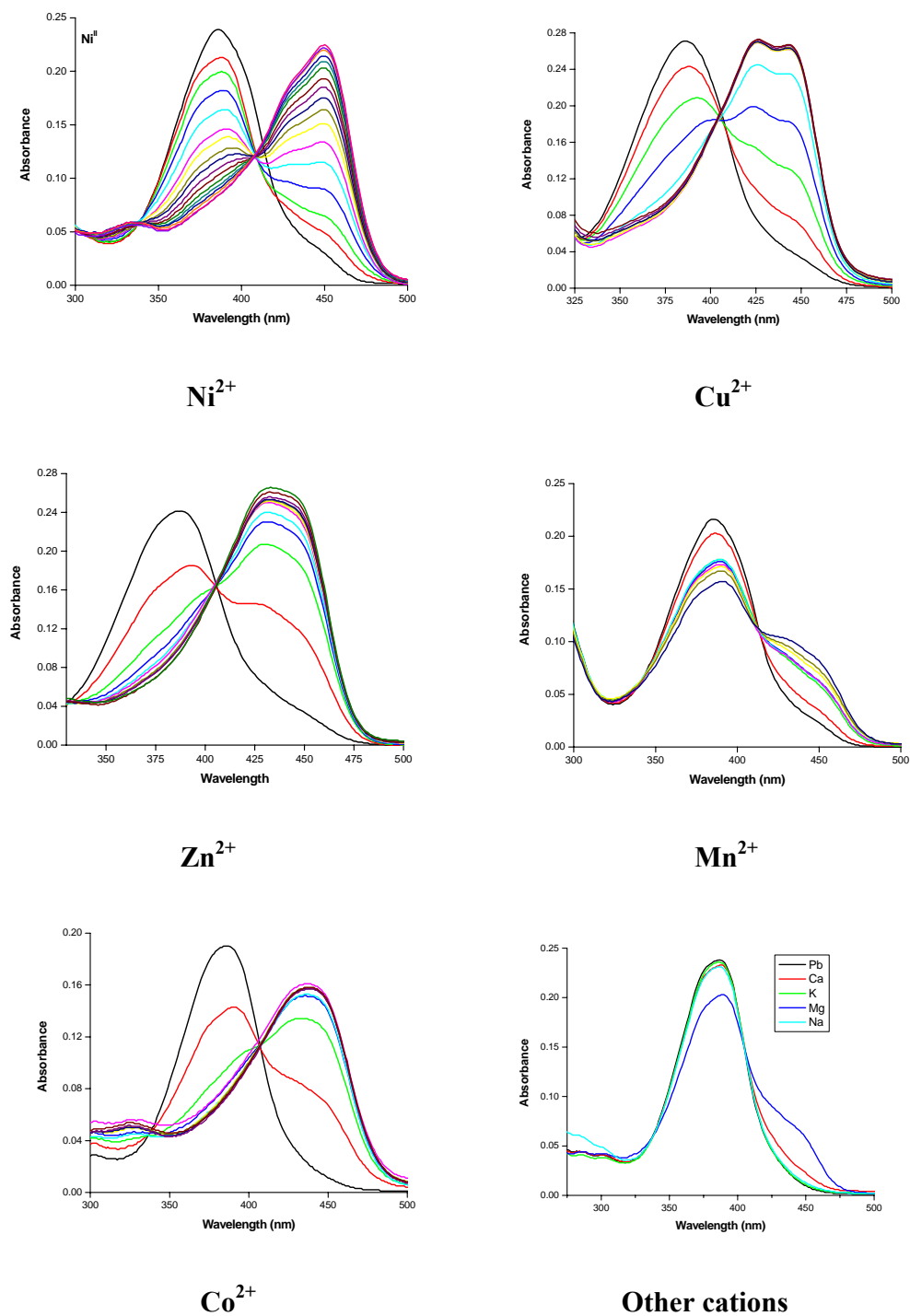


Figure 2: Color changes of receptor 1 (50 μM DMSO solution) with various metal ions (5 equivalents each):

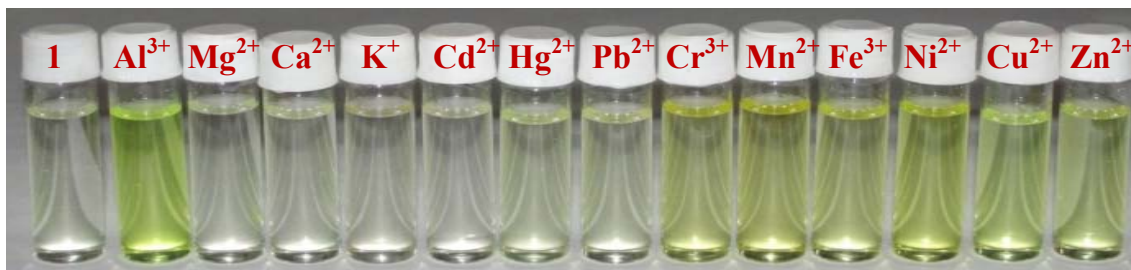


Figure 3: Job's Plot of Al^{3+} with receptor 1 showing 1:1 stoichiometry:

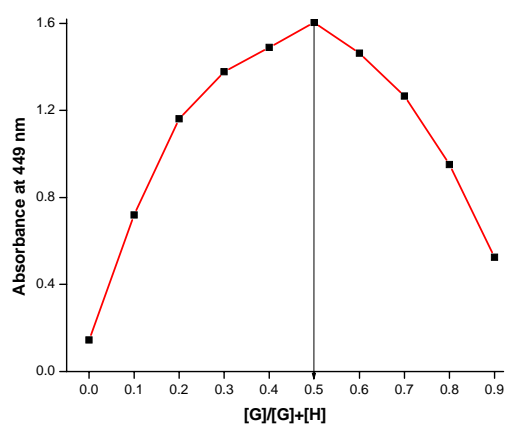


Figure 4: Mass spectrum of receptor 1+ Al^{3+} complex:

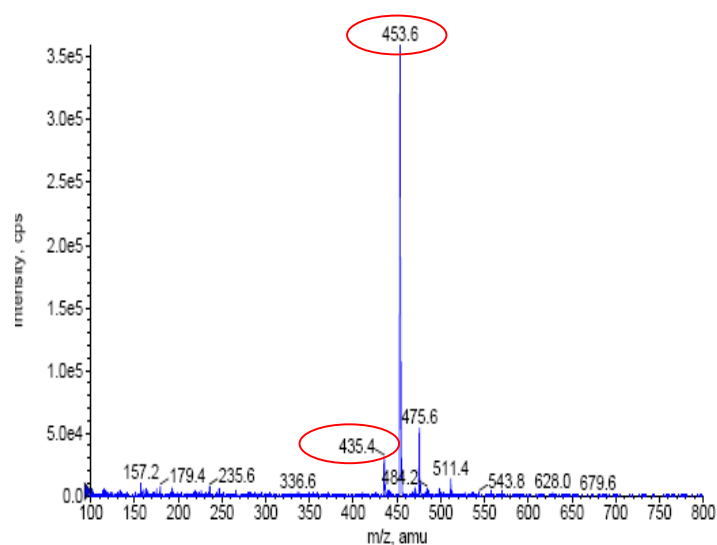


Figure 5: Non linear fitting of UV-visible titration data:

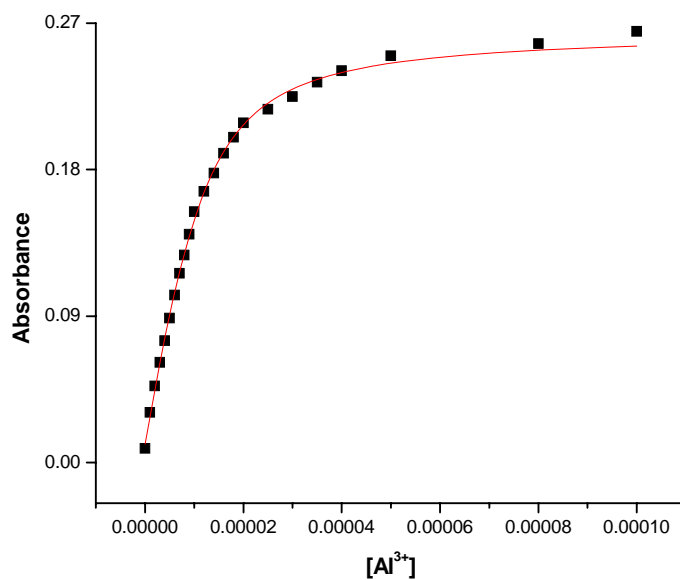


Figure 6: Effect of Al^{3+} (5 equivalents) on the UV-visible spectra of 10 μ M DMSO solution Receptor 3:

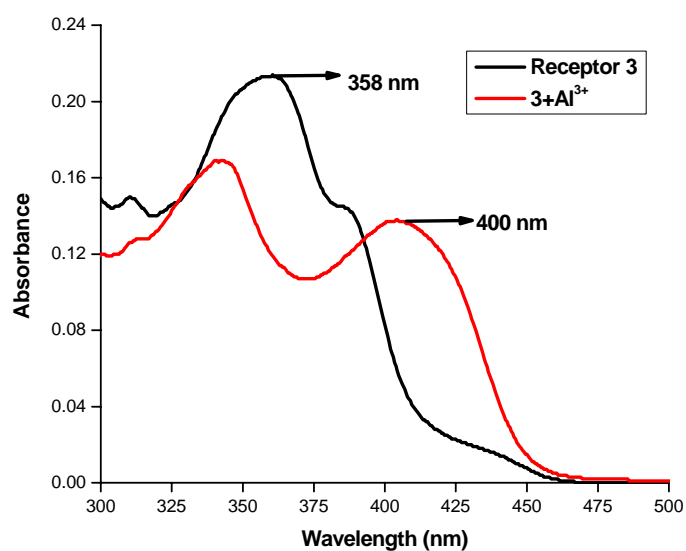


Figure 7: Determination of detection limit and calibration curves of receptor with Al^{3+} :

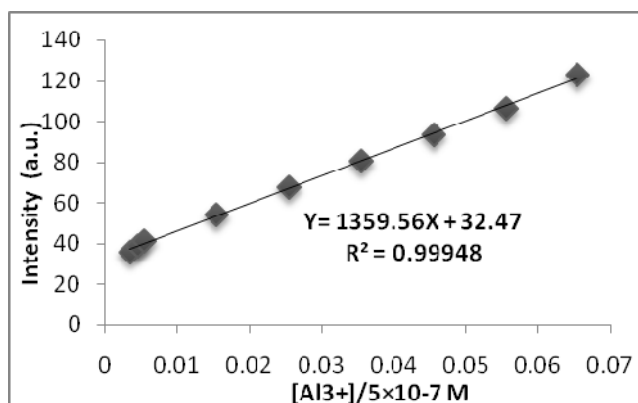


Figure7a: Receptor 1 (in DMSO)

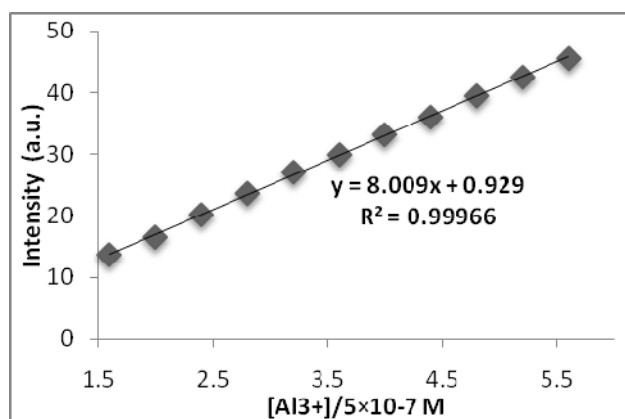


Figure7b: Receptor 1 (in Water)

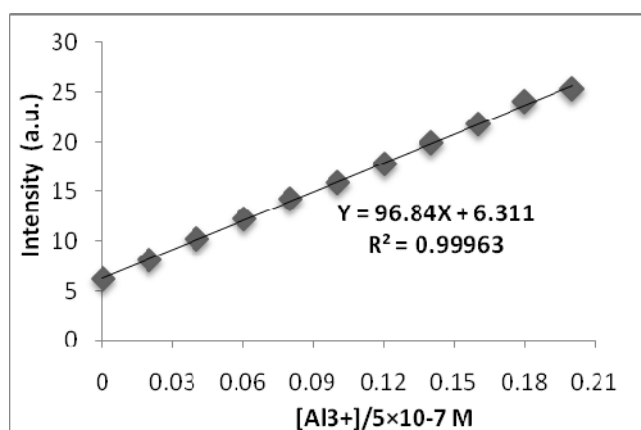
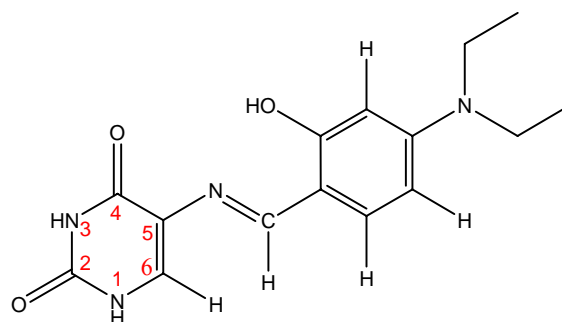


Figure7c: Receptor 3 (in DMSO)

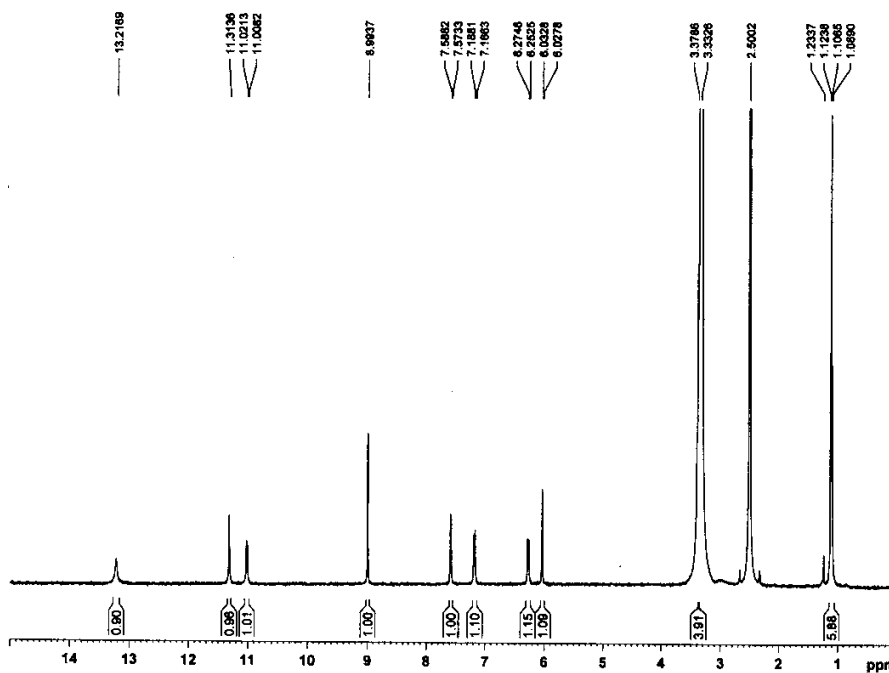
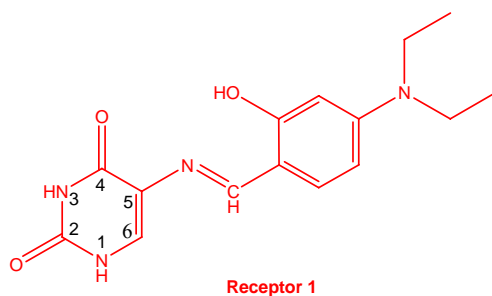
Table 1: Changes in Chemical shifts (δ ppm) of receptor 1 during ^1H NMR titration experiment upon concomitant additions of AlCl_3 :

$[\text{Al}^{3+}]$ Equiv.	-OH	-N ₃ H	-N ₁ H	-CH=N-	Ar-H	Ar-H	Ar-H	-C ₆ H	-CH ₂	-CH ₃
0.00	13.209	11.325	11.031	8.994	7.598	7.190	6.278	6.034	3.397	1.125
0.25	13.207	11.331	11.037	8.991	7.604	7.199	6.281	6.035	3.381	1.124
0.50	13.139	11.346	11.053	8.984	7.615	7.194	6.292	6.041	3.385	1.123
1.00	13.074	11.366	11.068	8.973	7.624	7.205	6.305	6.048	3.389	1.127
1.50	13.048	11.385	11.079	8.964	7.650	7.216	6.314	6.055	3.392	1.129
2.00	12.958	11.399	11.090	8.956	7.658	7.211	6.308	6.063	3.338	1.131

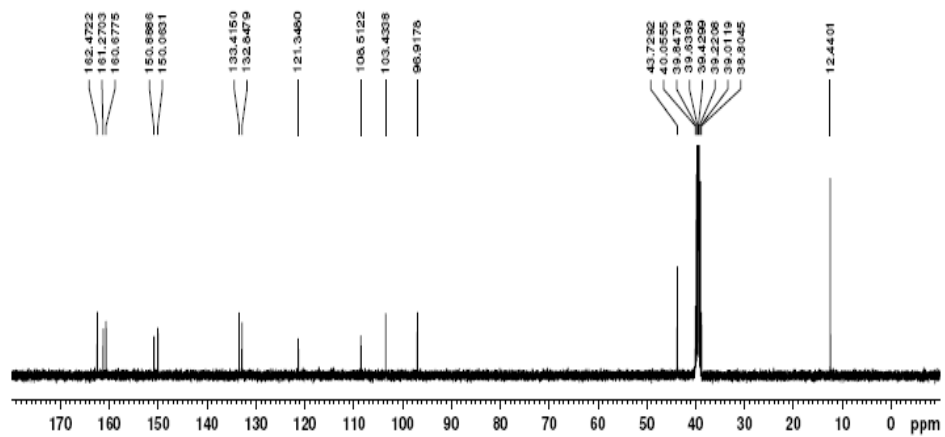


Receptor 1

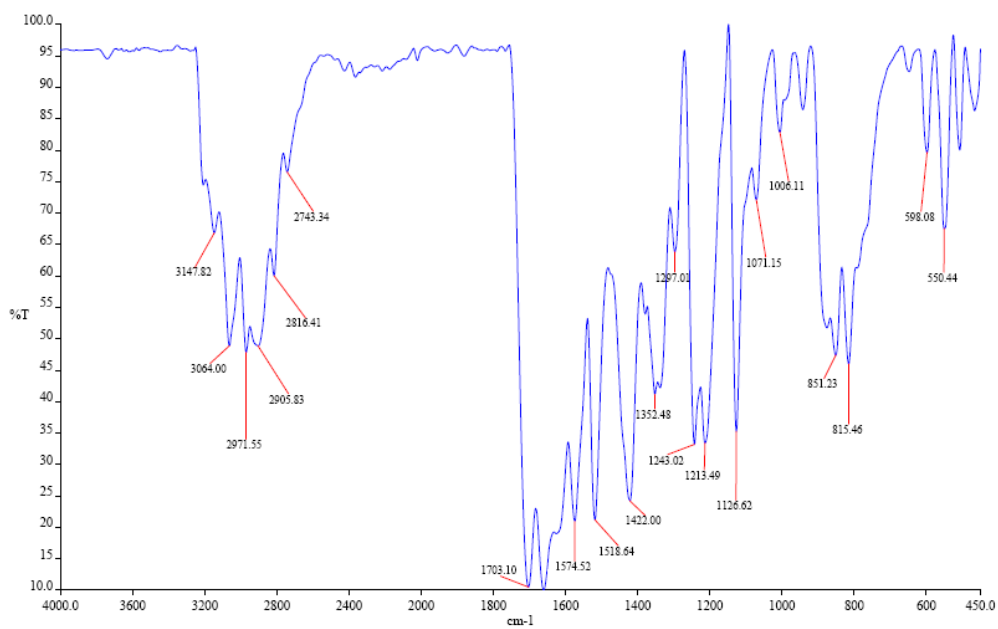
¹H NMR SPECTRA OF RECEPTOR 1



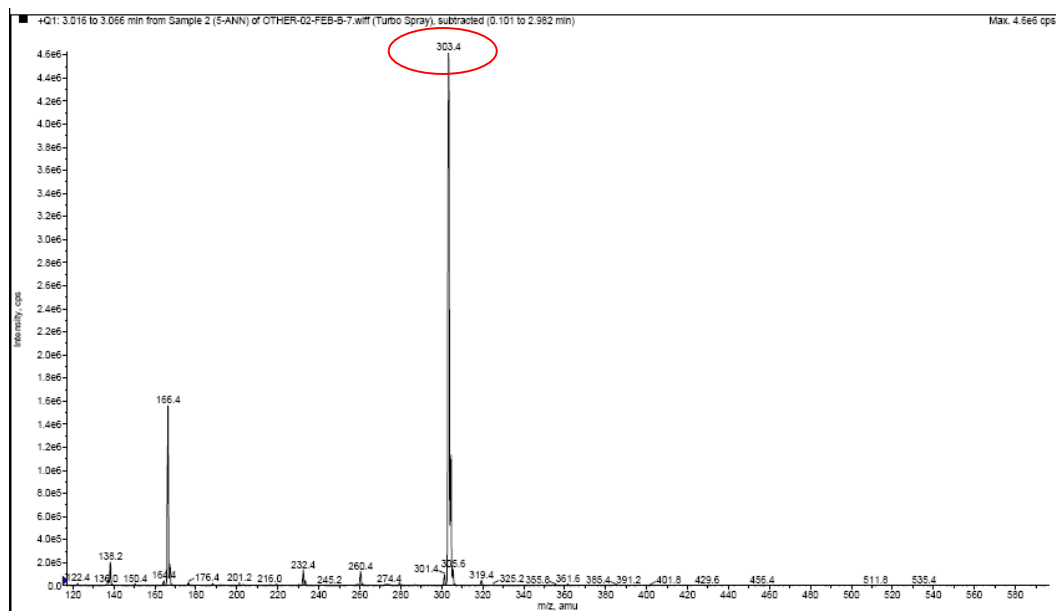
^{13}C NMR SPECTRA OF RECEPTOR 1



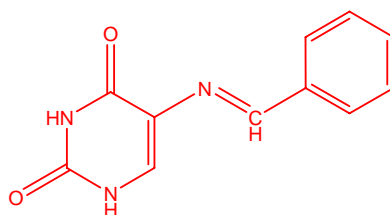
IR SPECTRA OF RECEPTOR 1



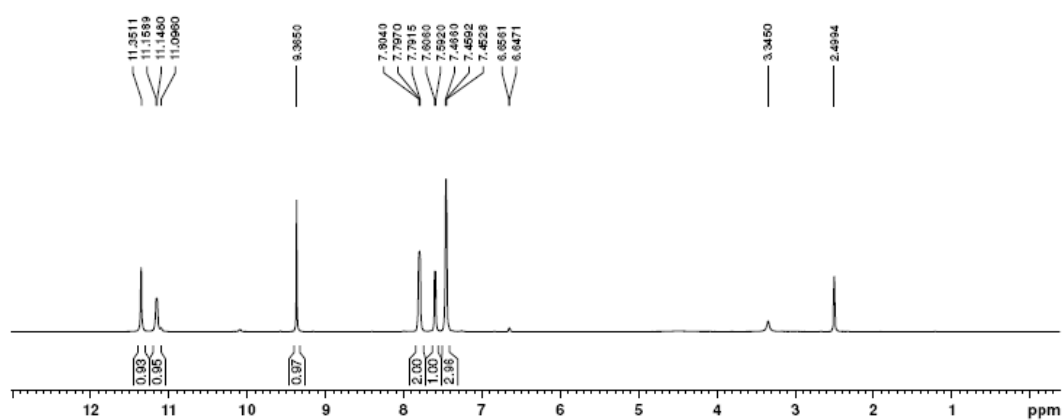
MASS SPECTRA OF RECEPTOR 1



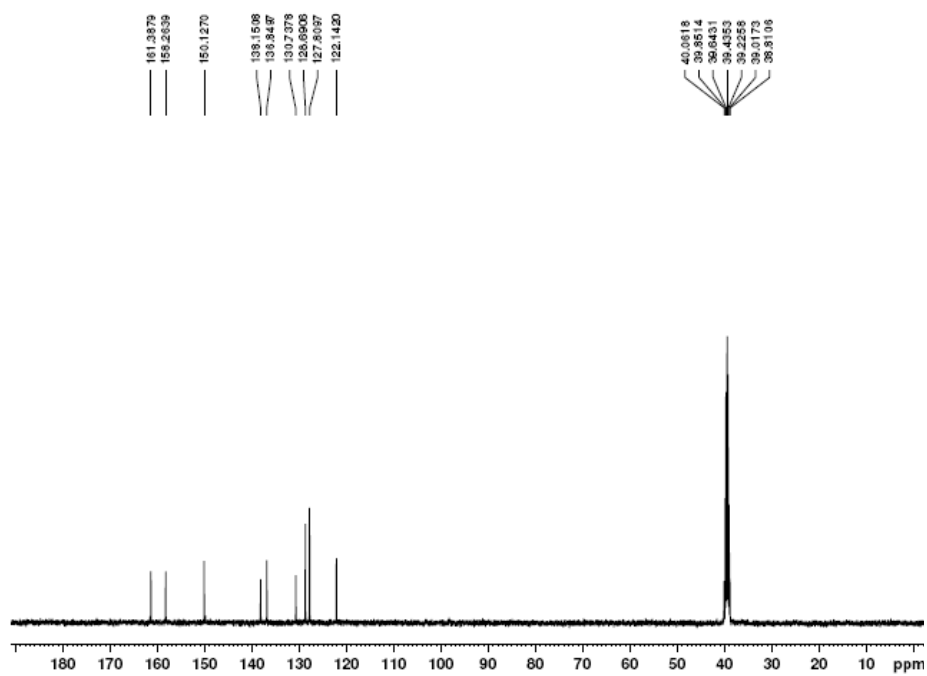
¹H NMR SPECTRA OF RECEPTOR 2



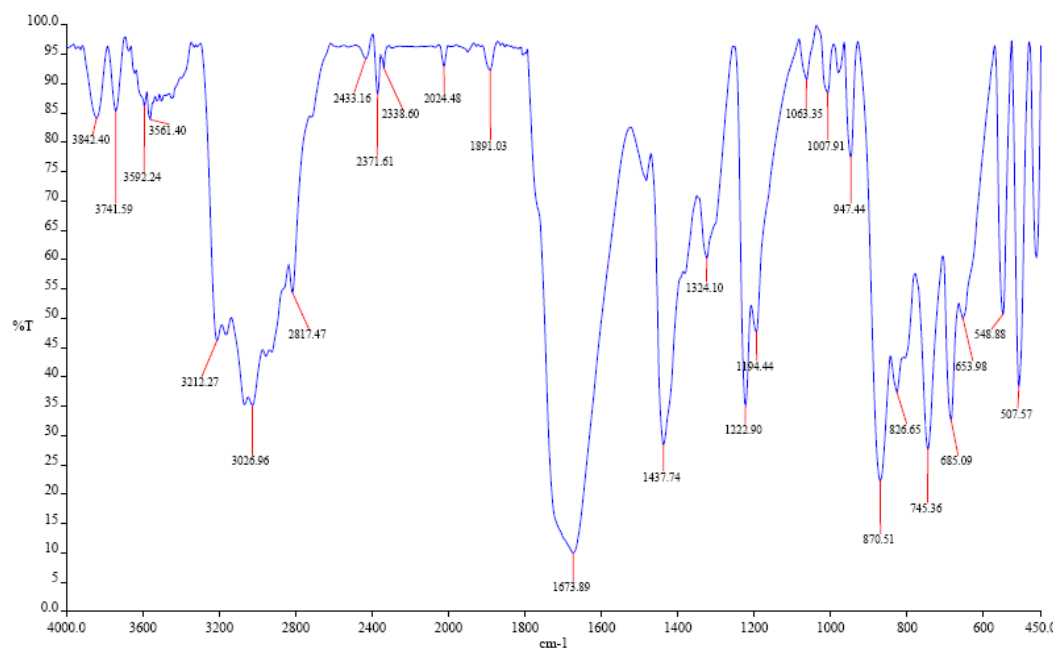
Receptor 2



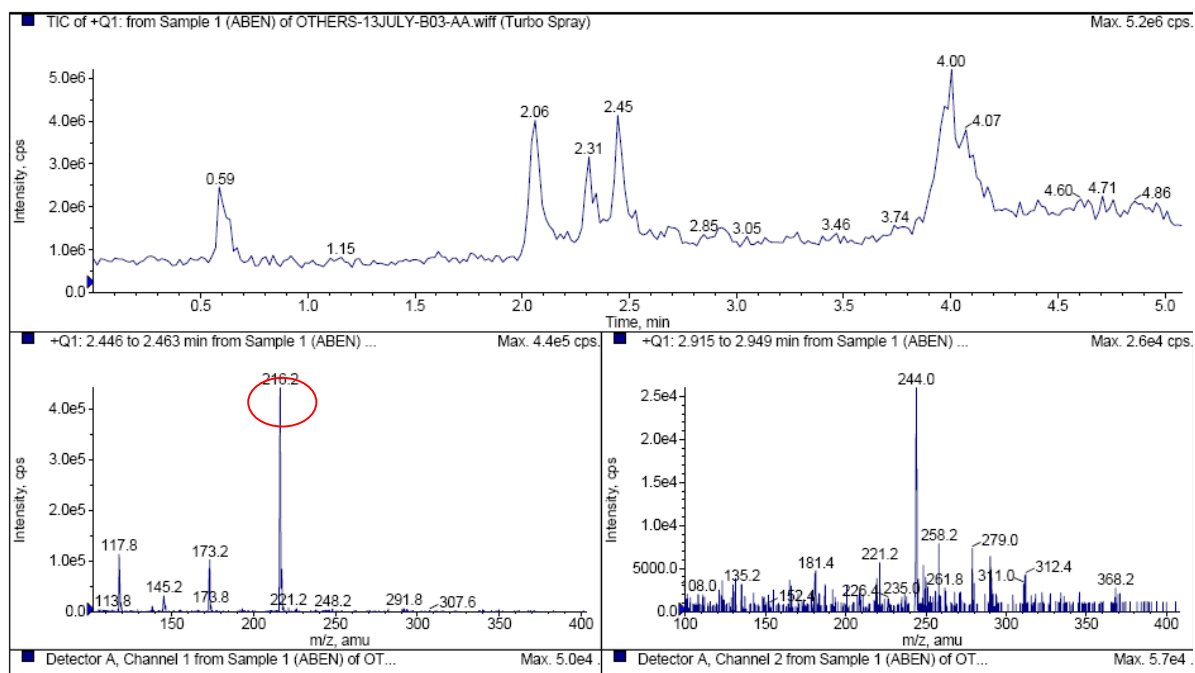
¹³C NMR SPECTRA OF RECEPTOR 2



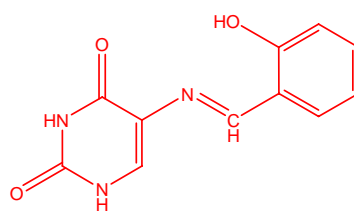
IR SPECTRA OF RECEPTOR 2



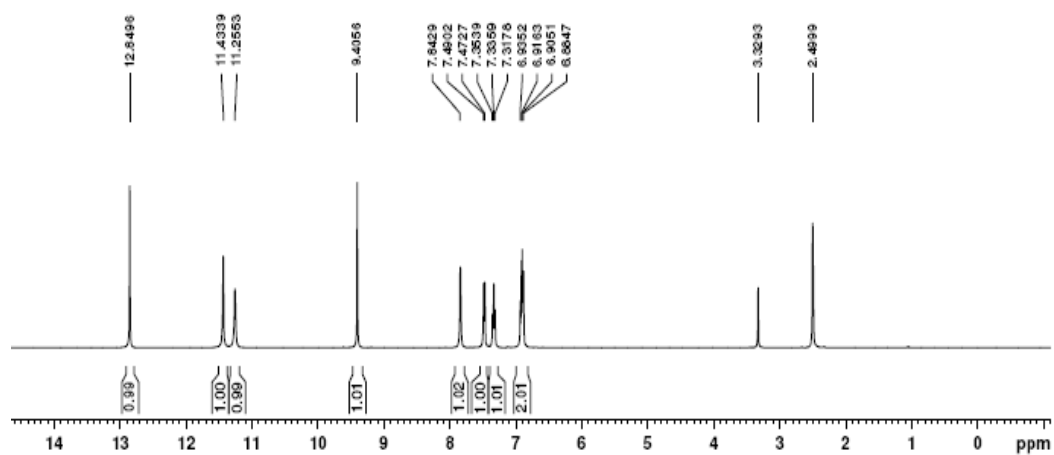
MASS SPECTRA OF RECEPTOR 2



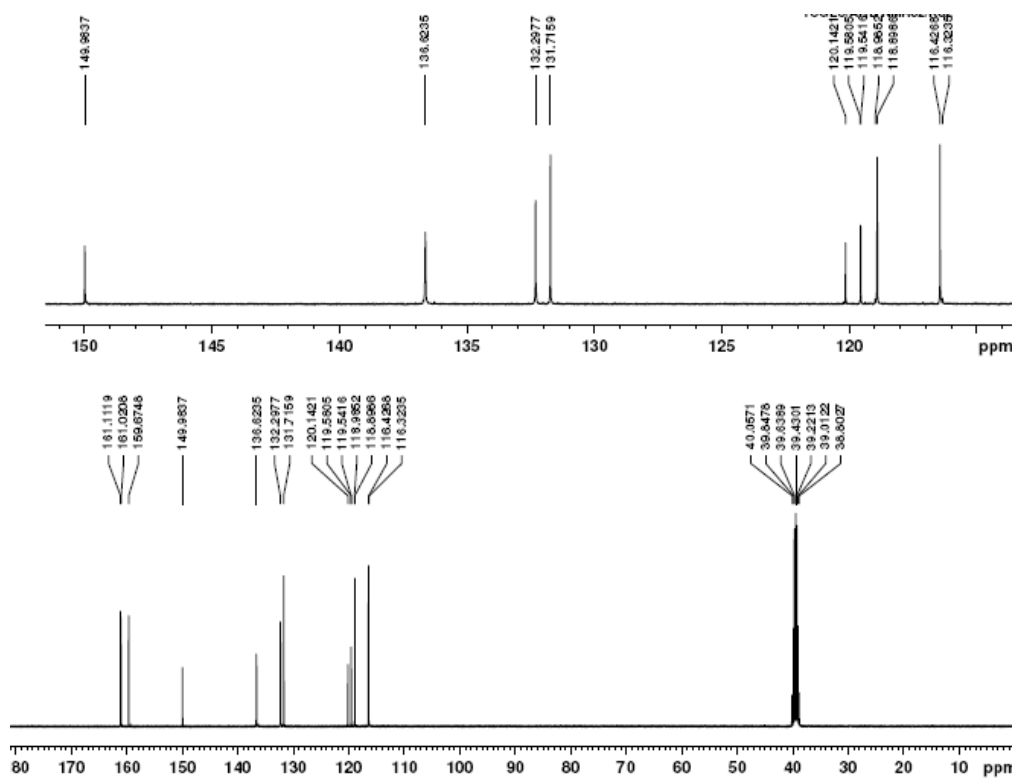
¹H NMR SPECTRA OF RECEPTOR 3



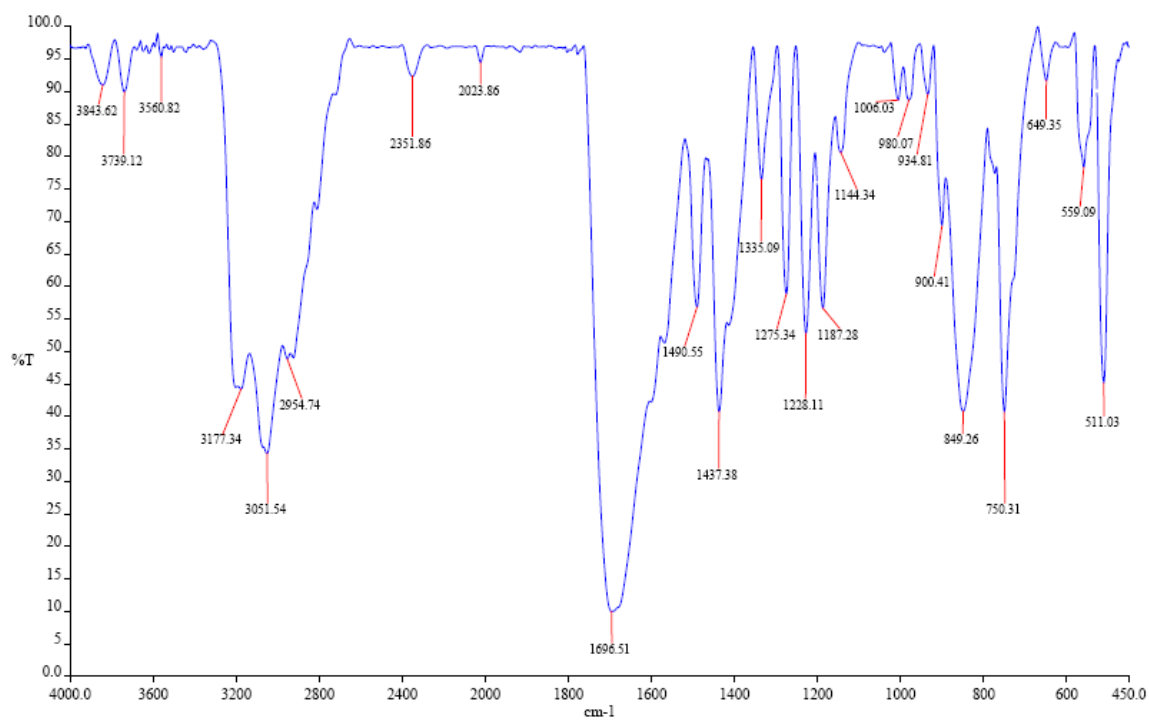
Receptor 3



¹³C NMR SPECTRA OF RECEPTOR 3



IR SPECTRA OF RECEPTOR 3



MASS SPECTRA OF RECEPTOR 3

