Electronic Supplementary Material (ESI) for Analyst

An Al^{3+} and $H_2PO_4^-/HSO_4^-$ selective conformational arrest and bail to pyrimidine-naphthalene anchored molecular switch

Ajit Kumar, Virendra Kumar and K. K. Upadhyay*

Department of Chemistry (Centre for Advanced Study), Faculty of Science, Banaras Hindu University, Varanasi-221005, India

**E-mail: drkaushalbhu@yahoo.co.in, Tel: +91 542 670 2488*

TABLE OF CONTENTS

1. EXPERIMENTAL

1.1 Apparatus:

The IR Spectra for the receptors **1** was recorded on JASCO-FTIR Spectrophotometer while ^{1}H NMR spectra for the same were recorded on a 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 pharmaspec spectrophotometer with quartz cuvette (path length=1 cm). Emission spectra were recorded on Varian Cary Eclipse Fluorescence spectrophotometer/ JY HORIBA Fluorescence spectrophotometer.

1.2 Materials:

All reagents for synthesis were purchased from Sigma-Aldrich and were used without further purification.

1.3 General Methods:

All titration experiments were carried at room temperature. All the cations were used as their chloride salts while anions were used as their tetrabutyl ammonium (TBA) salts. The ^{1}H NMR spectra were recorded by using tetramethylsilane (TMS) as an internal reference standard. For the ^{1}H NMR spectra of receptor **1**, $5x10^{-3}$ M solutions was prepared in DMSO-d_6 while the stock solution of Al^{3+} and HSO_4^- was prepared in DMSO-d_6:D_2O (95:5, v/v). For fluorescence titration experiment the solution of cations were prepared in aqueous medium. Due to insufficient solubility of receptor **1** in pure water its stock solution of 0.25 M was prepared in ethanol which was used for fluorescence titration experiment in water at 1 μM concentration through dilution.

The detection limit of receptor **1** towards Al^{3+} or receptor 1+Al^{3+} ensemble towards $H_2PO_4^-$ and HSO_4^- was determined from a plot of fluorescence intensity as a function of the

concentration of the added metal ions or anion. To determine the S/N ratio, the fluorescence intensity of receptor **1** in absence of any analyte 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 analyte) divided by the slope of calibration plot between analyte concentration and fluorescence intensity.

1.4. Theoretical studies:

All DFT calculations were carried out with the Gaussian 03 program. The structures of receptor **1** in the absence and presence of anions were fully optimized in gaseous phase using B3LYP functional with the 6-31g** basis set. To visualize the optimized structures Gauss View software was used.

2. FIGURES AND CAPTIONS:

Figure S1: Naked-eye color change of 10μ M aqueous solution of receptor 1 upon addition of 2 equivalent of Al^{3+}

Figure S2: Perturbation of UV-visible spectrum of 10 μM aqueous solution of receptor **1** with different metal ions (2 equiv. each)

Figure S3: Job's Plot of Al^{3+} with receptor **1** showing 1:1 stoichiometry

Figure S4: Non-linear fitting of fluorescence titration data between receptor **1** and Al^{3+}

Figure S5: Effect of various anions (30 equiv. each) on the emission spectrum of 1μM aqueous solution of receptor **1**+Al^{3+} ensemble

Figure S6: ^{1}H NMR spectrum of 1×10^{-3} M solution (DMSO-d_6) of receptor **1** in the absence and presence of HSO_4^- (D_2O)

Figure S7: Revival of quenched fluorescence intensity of 1 μM aqueous solution of receptor 1+Al^{3+}+HSO_4^- upon addition of Al^{3+}

Figure S8: Non-linear fitting of fluorescence titration data between receptor 1+Al^{3+} ensemble and (a) $H_2PO_4^-$ (b) HSO_4^-

Figure S1: Naked-eye color change of 10μM aqueous solution of receptor **1** upon addition of 2 equivalent of Al^{3+}

Figure S2: Perturbation of UV-visible spectrum of 10 µM aqueous solution of receptor **1** with different metal ions (2 equiv. each)

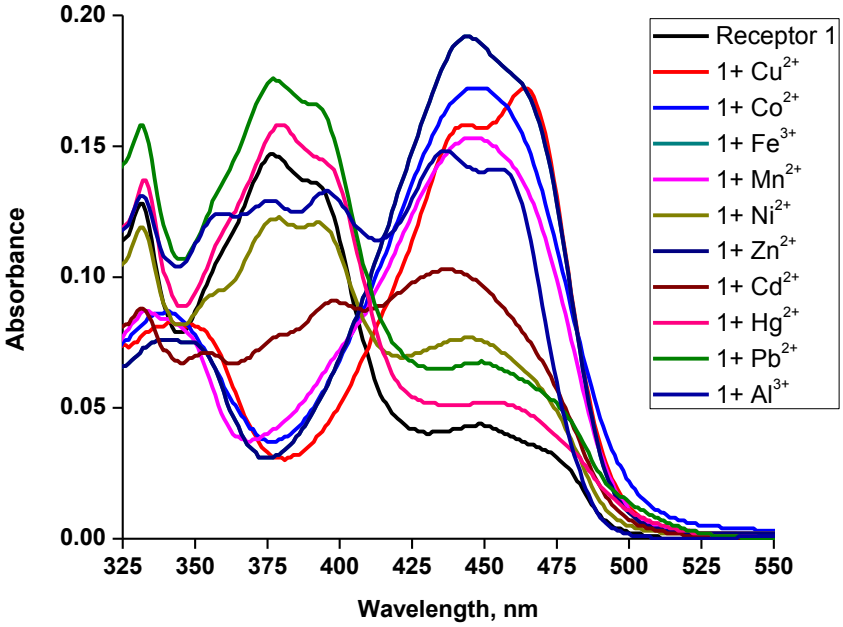


Figure S3: Job's Plot of Al^{3+} with receptor **1** showing 1:1 stoichiometry

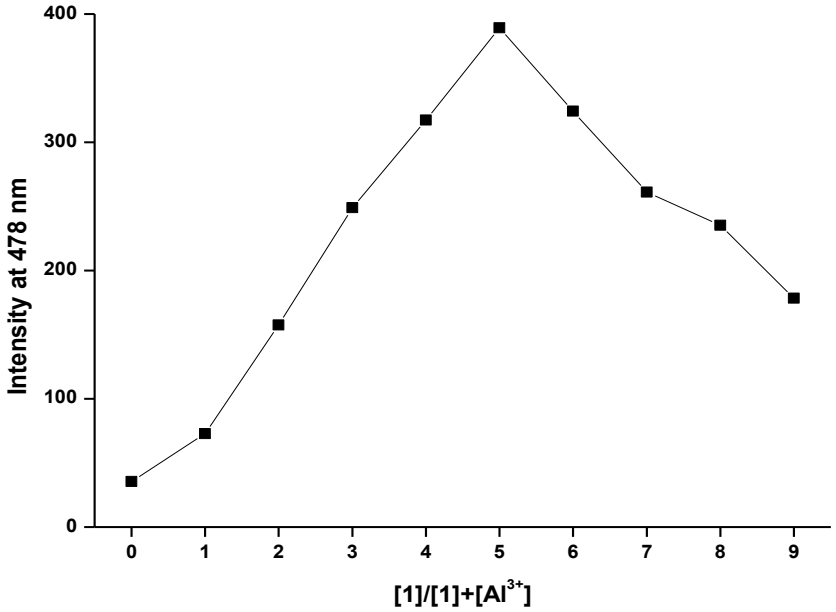


Figure S4: Non-linear fitting of fluorescence titration data between receptor **1** and Al^{3+}

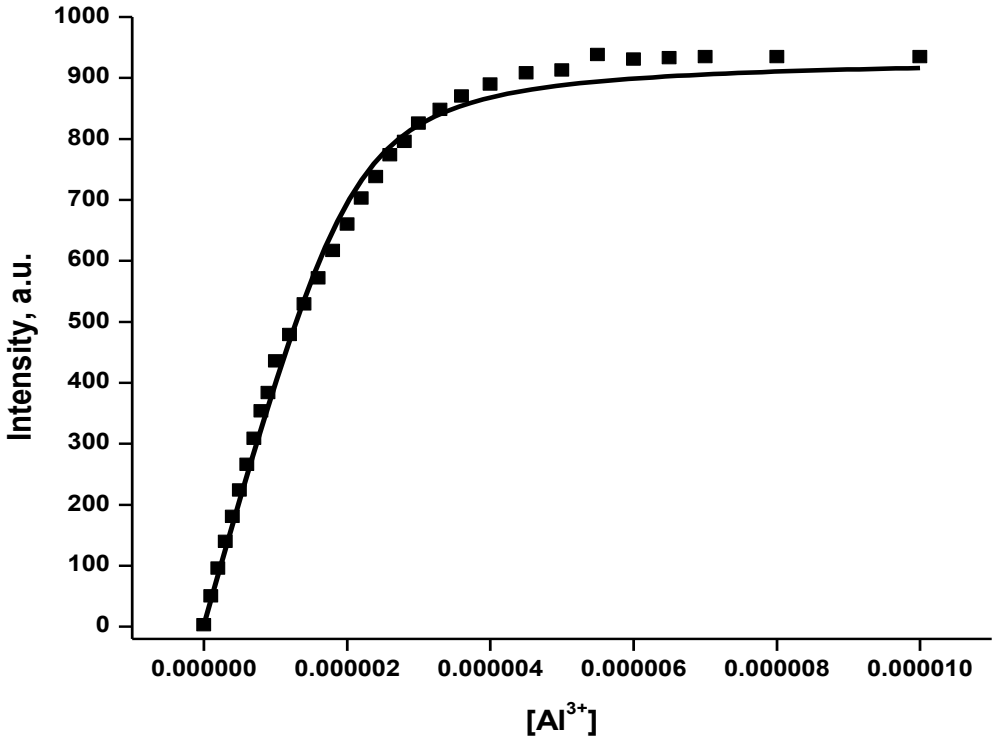


Figure S5: Effect of various anions (30 equiv. each) on the emission spectrum of 1µM aqueous solution of receptor **1**+Al^{3+} ensemble

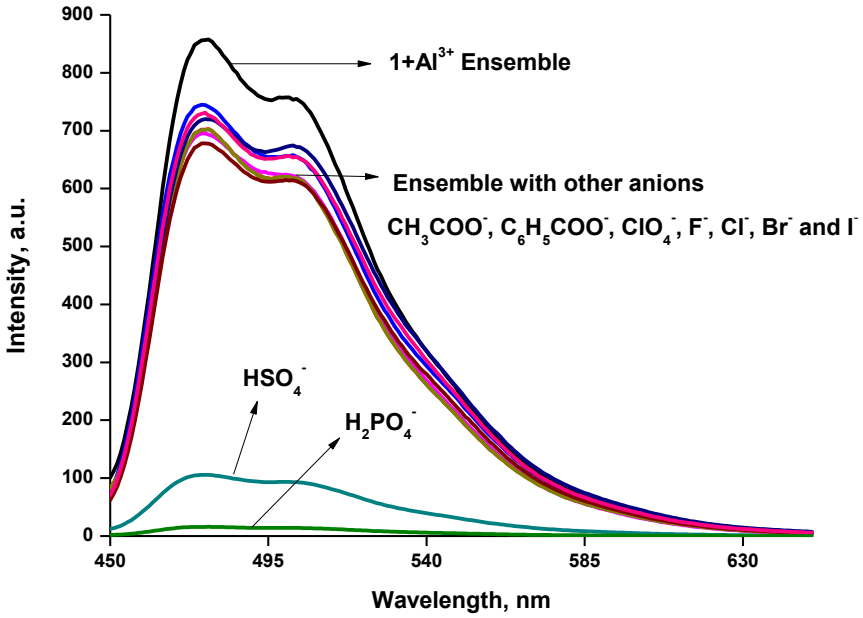


Figure S6: ^{1}H NMR spectrum of 1×10^{-3} M solution (DMSO-d_6) of receptor **1** in the absence and presence of HSO_4^- (D_2O)

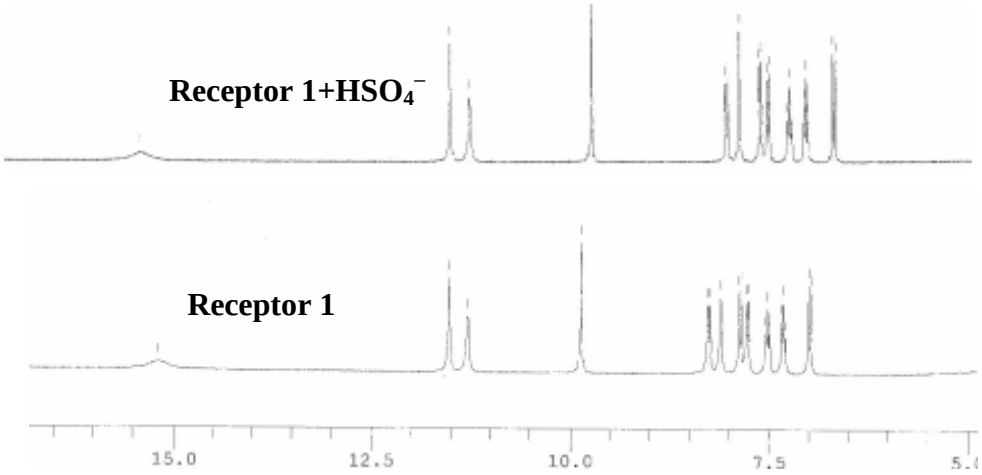


Figure S7: Revival of quenched fluorescence intensity of 1 µM aqueous solution of receptor $1+Al^{3+}+HSO_4^-$ upon addition of Al^{3+}

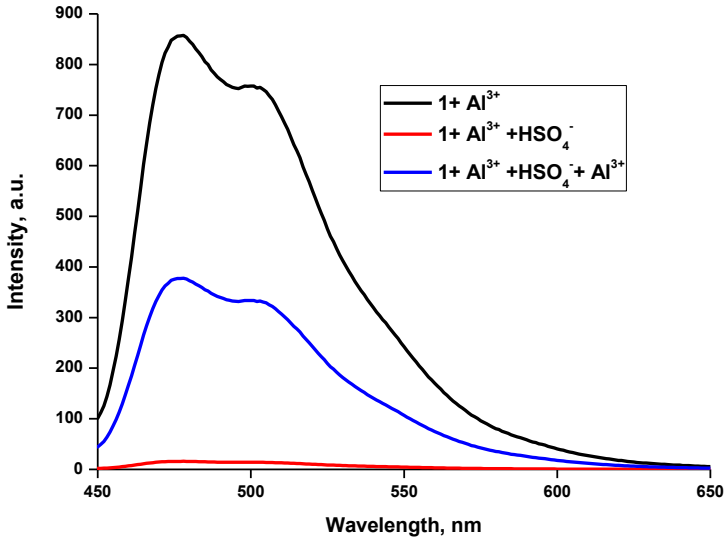
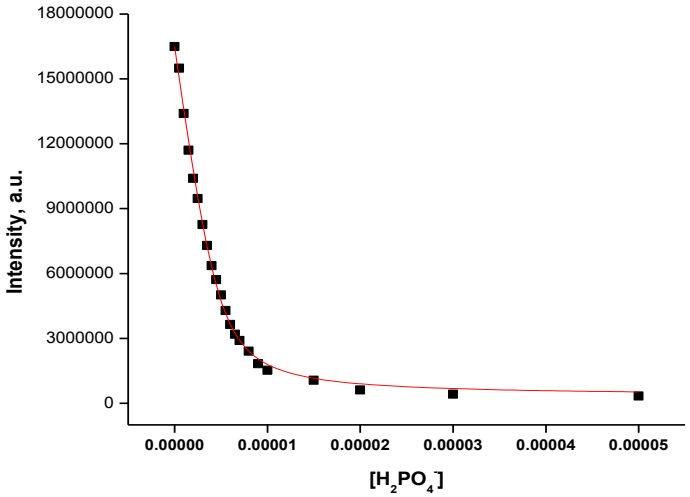
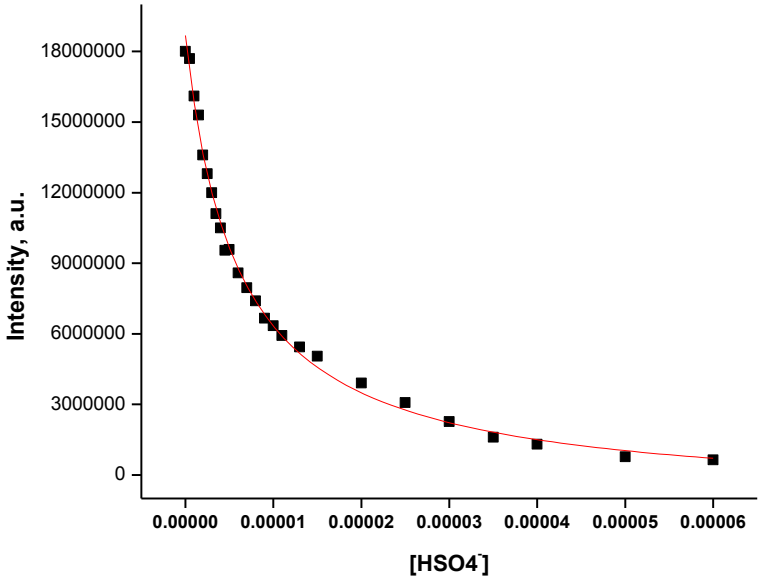


Figure S8: Non-linear fitting of fluorescence titration data between receptor 1+Al^{3+} ensemble and (a) $H_2PO_4^-$ (b) HSO_4^-

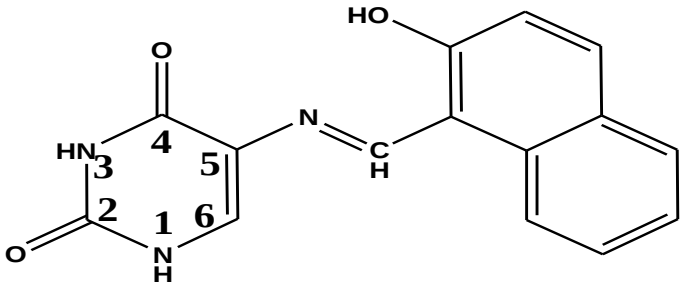


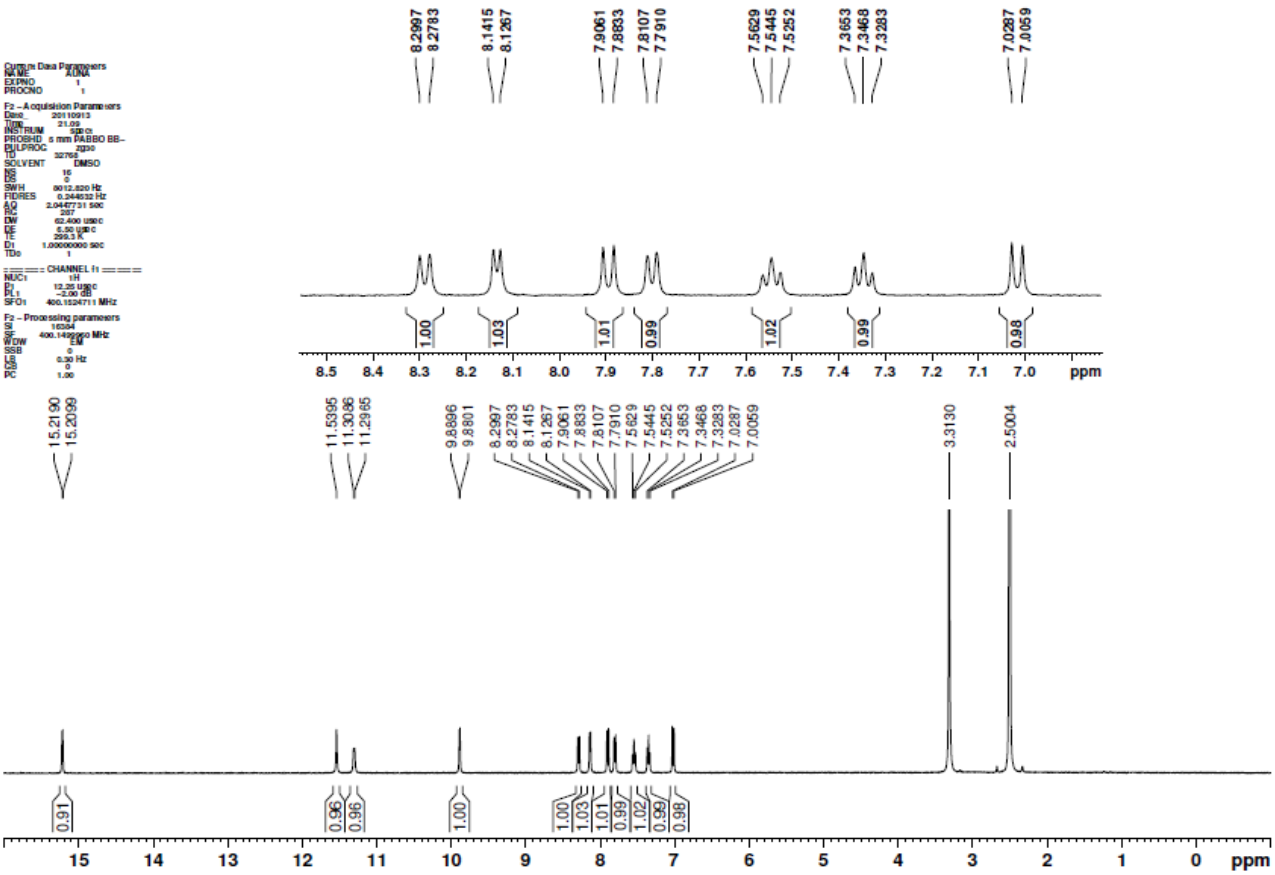
(a) $H_2PO_4^-$



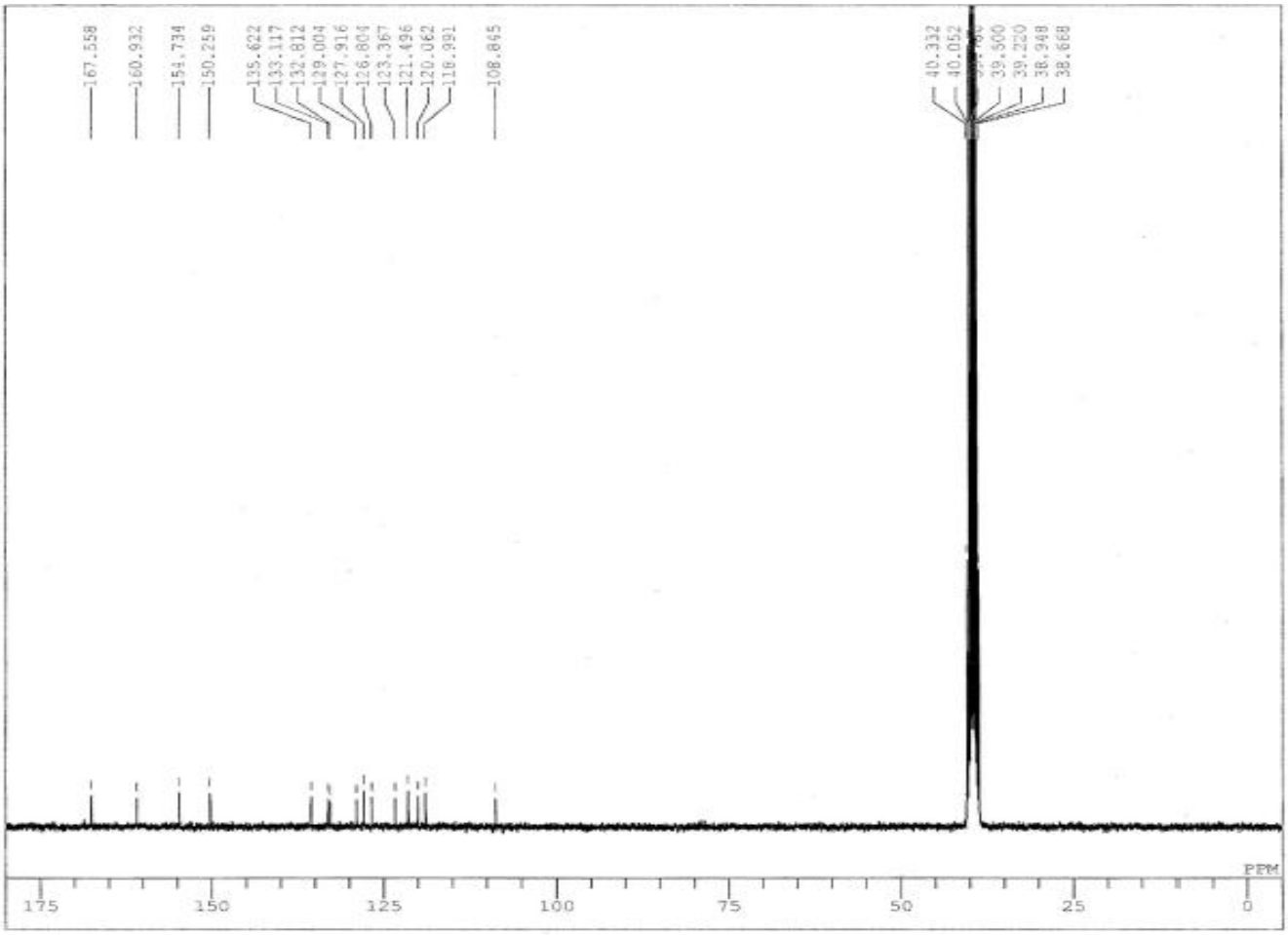
(b) HSO_4^-

^{1}H NMR spectrum of Receptor 1

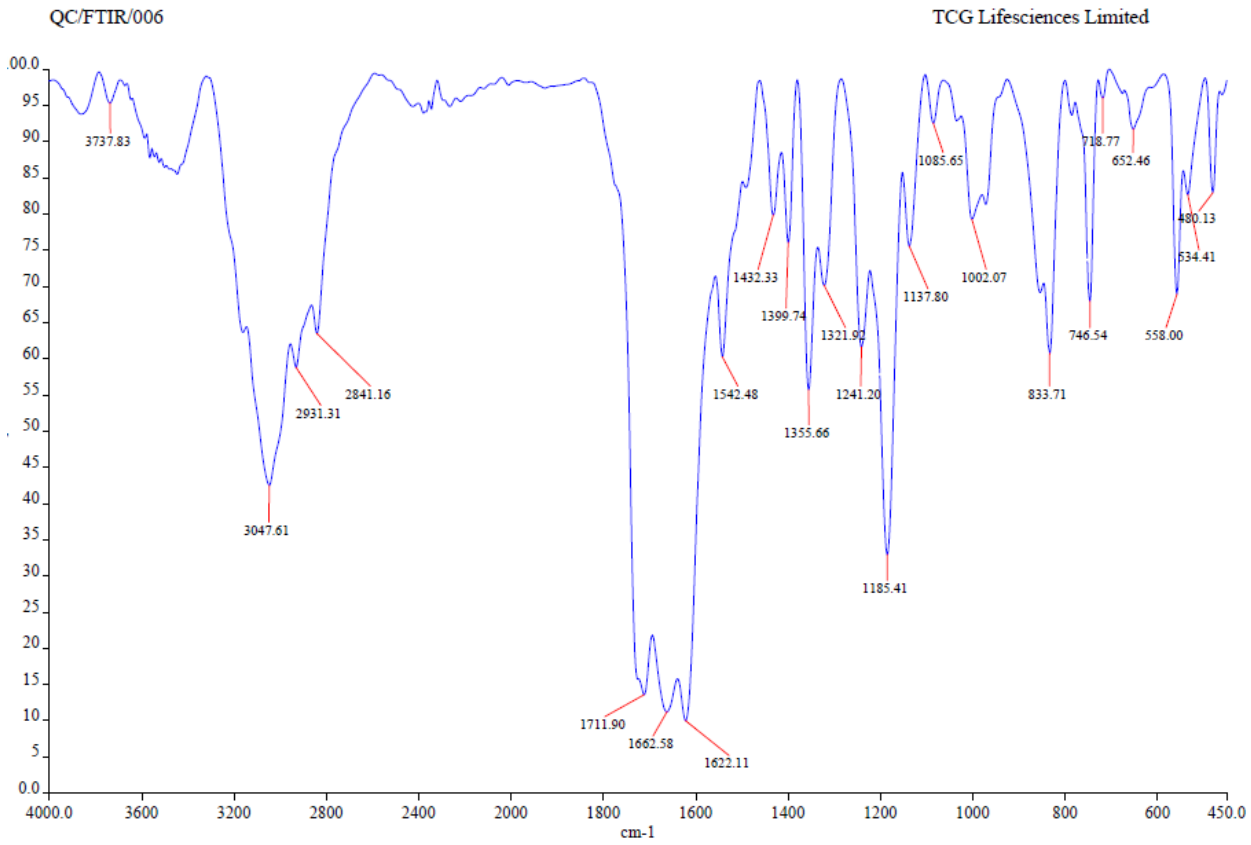




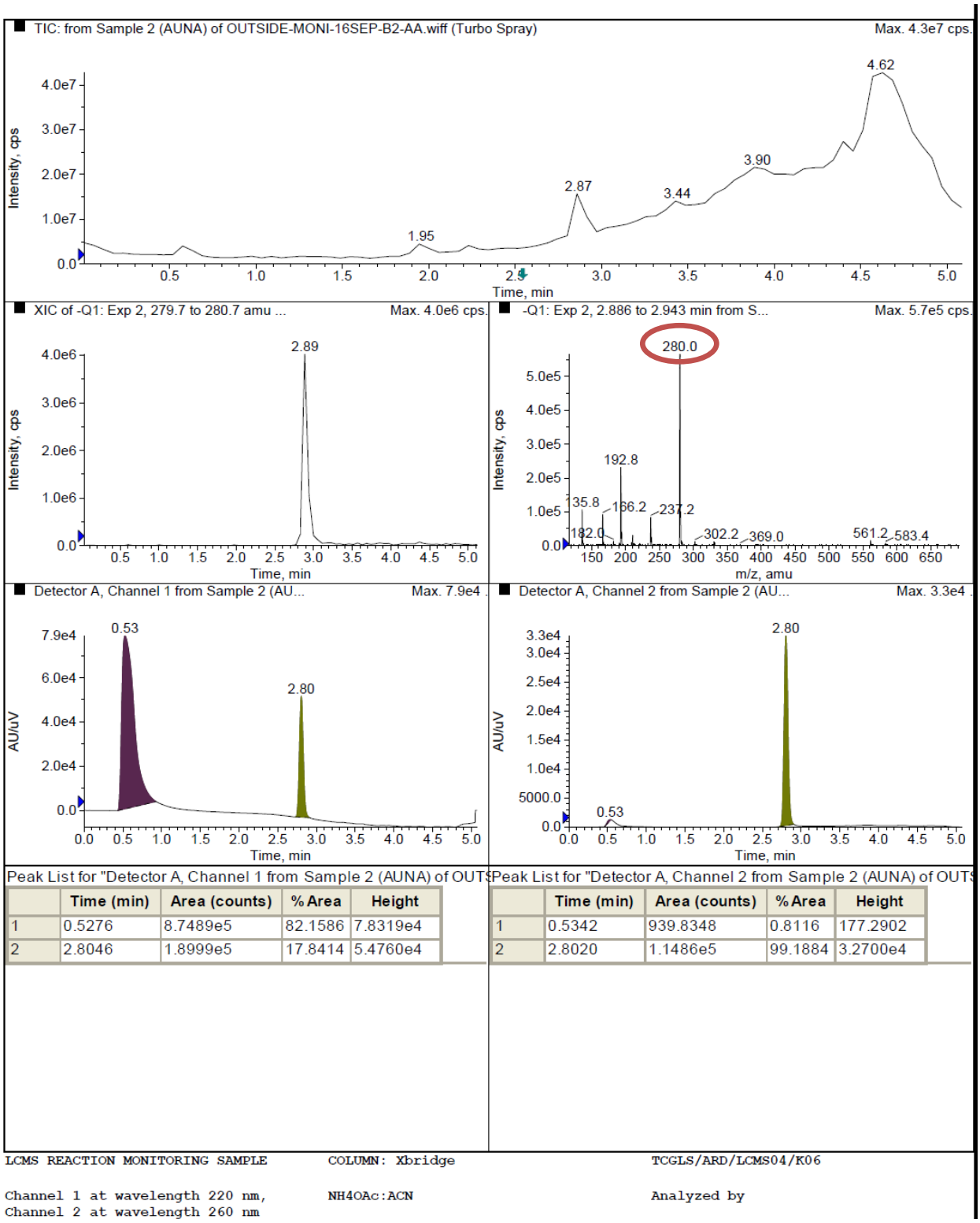
^{13}C NMR spectrum of Receptor 1



IR spectrum of Receptor 1



Mass spectrum of Receptor 1



Peak List for "Detector A, Channel 1 from Sample 2 (AUNA) of OUTS

	Time (min)	Area (counts)	% Area	Height
1	0.5276	8.7489e5	82.1586	7.8319e4
2	2.8046	1.8999e5	17.8414	5.4760e4

Peak List for "Detector A, Channel 2 from Sample 2 (AUNA) of OUTS

	Time (min)	Area (counts)	% Area	Height
1	0.5342	939.8348	0.8116	177.2902
2	2.8020	1.1486e5	99.1884	3.2700e4

LCMS REACTION MONITORING SAMPLE COLUMN: Xbridge TCGLS/ARD/LCMS04/K06

Channel 1 at wavelength 220 nm, NH4OAc:ACN Analyzed by
Channel 2 at wavelength 260 nm