Supplementary Information's

Uncovering the true mechanism of Optical detection of HSO_4^- in water by Schiff Base receptors - Hydrolysis *vs.* Hydrogen Bonding

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1. EXPERIMENTAL

1.1 Apparatus: The IR Spectra for the receptors (**1, 3 and 4**) were recorded on JASCO-FTIR Spectrophotometer while ^{1}H NMR spectra were recorded on a Bruker-400 Avance NMR Spectrometer and JEOL AL 300 FT NMR Spectrometer. Mass spectrometric analysis were 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.

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 anions were used as their tetrabutylammonium (TBA) salts while metal ions were used as their chloride salts. The ^{1}H NMR titrations were carried out by using tetramethylsilane (TMS) as an internal reference standard.

1.4. X-ray diffraction studies: Single crystal X-ray data of receptor 4 was collected on an Oxford Diffraction Xcalibur system with a Ruby CCD detector. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo-Kα radiation (λ= 0.71073 A°). Data for the receptor was collected at room temperature. The structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least squares method. All the calculations were carried out with the SHELX-97 program.

2. DISCUSSIONS

To prove the exact mechanism of HSO_4^- sensing through Schiff base type receptors in aqueous medium four fluorescent receptors (receptor **1-4**) were already discussed in the main text. Now we are elaborating four more receptors (**receptor 5-8**) of colorimetric type to strengthen the discussed mechanism;

In this context first of all we took the colorimetric Schiff base receptor reported by Wei et al. (receptor **5**) recently [3b]. The receptor was synthesized by the authors through Schiff base condensation between *5–(p–nitro-phenylazo)–salicylaldehyde* and *5–amino–1,3,4–thiadiazol–2–carboxylic acid*. The two characteristic absorption bands in UV–visible spectrum of receptor **5** were found at 488 nm and 376 nm. The receptor **5** underwent bleaching with HSO_4^- as reported by authors in H_2O/DMSO (3.8:6.2, v/v) solution. Upon the addition of HSO_4^- anion, there was a prominent change in the form of vanishing of the band at 488 nm while a new strong absorption band at 370 nm was appeared. The appearance of new absorption band at 370 nm in the presence of HSO_4^- ion was explained by authors in terms of formation of hydrogen bonded species between receptor and anion. However bathochromic shifting has been reported for the real hydrogen bonded cases of anions with similar receptors. The corresponding aldehyde i.e., *5–(p–nitro-phenylazo)–salicylaldehyde* is also reported to absorb at ~376 nm [12] which further supported above hydrolytic proposal. Hence here also on the basis of above UV-visible spectral changes we concluded that once again the hydrolysis of Schiff base occurred, which was reflected in terms of UV-visible band at 370 nm, which is the absorption band for aldehyde counterpart i.e., *5–(p–nitro-phenylazo)–salicylaldehyde*. Hence the colorimetric sensing of HSO_4^- ion by receptor **5** through the hydrogen bonding between them as claimed by authors is once again not convincible.

Moreover, Wei et al. as co-author with Zhang et al. [3c] reported a series of Schiff base receptors **(6a-d)** previously also for colorimetric detection of HSO_4^- ion in H_2O-DMSO (5/95, v/v) solution. The aldehyde counterpart i.e., *5–(p–nitro-phenylazo)–salicylaldehyde* in receptors **6c & d** were same as it was for receptor **5** while they took *5-(phenylazo)-salicylaldehyde* for receptor **6a & b**. According to the authors no hydrogen bonding as claimed above for receptor **5** by Wei et al., was responsible for the drastic color change (in receptor **6c & d**). However the protonation of the Ar–OH along with the configurational transformation upon addition of HSO_4^- was considered responsible for the same. In contrast to receptor **6c & d**, the addition of HSO_4^- to the solutions of the less conjugated receptors **6a** and **6b** did not induce a color change. Accordingly authors claimed that the most conjugated receptors **6d** along with **6c** displayed high selectivity either for basic anions or for HSO_4^- in a water-containing medium and proposed classical Bronsted acid-base reaction.

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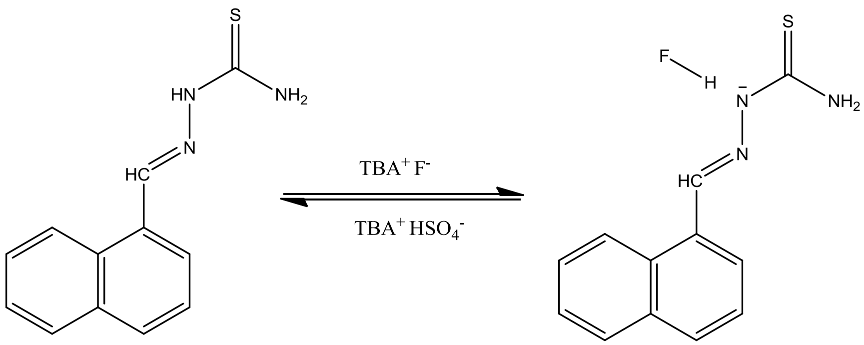
Although Zhang et al. proposed the acidic nature of HSO_4^- ion as the responsible factor for sensing but the site of protonation according to them was phenolic –OH not the imine nitrogen. They tried to support their argument by the fact that on protonation of phenolic –OH by HSO_4^- the blue shift took place. If receptor **6c & d** were prone towards protonation than the same must be the case for receptors **6a-b.** However no change in color or UV-visible spectrum of receptors **6a & b** not having any $–NO_2$ groups were observed. Nevertheless the perusal of the spectra of **6a & b** clearly proved that in both the cases hydrolysis of imine bond took place on addition of HSO_4^- leading to formation of starting material i.e., aldehyde and amine. The blue shifting in absorption band of receptors **6a & b** at ~340 nm while for **6c & d** were at ~374 nm upon addition of HSO_4^- ion. These absorption bands can be assigned to the corresponding aldehyde counterparts i.e., *5-(phenylazo)-salicylaldehyde* and *5–(p–nitro-phenylazo)–salicylaldehyde* respectively [12]. Hence even though Zhang et al. accepted the acidic nature of HSO_4^- as responsible for the sensing of same yet his proposal of protonation of phenolic –OH of receptor is not convincing one. Thus we are not out rightly opposing the protonation phenomenon of receptor in the presence of HSO_4^- ion but definitely the species proposed by authors are not the species responsible for the color change of receptors **6c-d**.

Author's case has further weakened by the fact that in spite of the different amine counterparts in the receptors **(5**, **6c-d)**, UV-visible band and color of the receptors in the presence of HSO_4^- ion were same. Furthermore in spite of having few same authors in both the cases but in one case they take an account of basic nature of HSO_4^- ion [3b] while in other the acidic nature even though the type of Schiff base receptor is almost similar [3c]. Here it is worth to mention that all these receptors **(6a-d)** underwent hydrolysis but the chromogenic responses were observed only for the (**6c & 6d**). Presence of electron withdrawing nitro group in receptor **6c** & **d** made them an efficient ICT probe and hence they absorbed at higher wavelengths (towards visible region) while receptors without nitro substituents absorbed towards lower wave length (towards UV region). Upon addition of HSO_4^- ion to these receptors the cleavage of Schiff base took place and a higher extent of blue shift was possible for **5**, **6c** & **6d** leading to a visible color change while receptors without nitro substituent produced only a meager amount of blue shift and although hydrolysis took place but no obvious color change were observed in these cases.

Furthermore two more colorimetric receptors (**receptor 7 & 8)** reported by Jiang et al. [3d,e] may be further helpful in understanding the above sensing mechanism. Jiang et al. reported a simple Schiff base receptor **7** based on thiosemicarbazide derivative of 1-naphthaldehyde. This receptor showed fluoride induced chromogenic changes which can be totally reversed with addition of HSO_4^-. In the continuation of above study later they synthesized a polymeric form of receptor **7** to develop new polymerbased sensory materials **(Receptor 8)**. Both of the receptor **7** and **8**, gave fluoride-induced chromogenic responses which were totally reversed by adding 1 equiv. of proton (aqueous hydrochloric acid solution) or adding HSO_4^- anions. The complete sensing process involves fluoride induced deprotonation of receptor **7/8** and reversal of color and UV-visible spectrum once again on the addition of HSO_4^-. Actually the addition of HSO_4^- to receptor-fluoride complex protonated the receptor replacing the fluoride in the form of HF or HF_2^-.



Receptor 7 **Receptor 7+F⁻**

Receptor 7 reported by Jiang et al. and effect of TBAF and TBAHSO$_4$ on receptor 7

Hence the above example also indicated towards the acidic nature of HSO_4^- ion and explained the reversal of the color of receptor + fluoride complex. In short the whole sensing process discussed above is an acid-base indicator. The H^+ and F^- ions competes with each other only and no option for hydrolysis of Schiff base was possible here as the same was observed in other Schiff base receptor in the presence of HSO_4^- ion. However, this study clearly established the acidic nature of HSO_4^- ion in aqueous/semi aqueous medium which was not considered by Kim et al. and Wei et al. leading to proposal of an improper sensing mechanism for interaction of Schiff bases with HSO_4^- ion. The hydrolytic action of HSO_4^- was further supported when Schiff base receptor **1** and **4** produced almost similar observations as in the case of HSO_4^- when they were treated individually with very small amount of dilute mineral acids like HCl, H_2SO_4 etc. (see Figures below).

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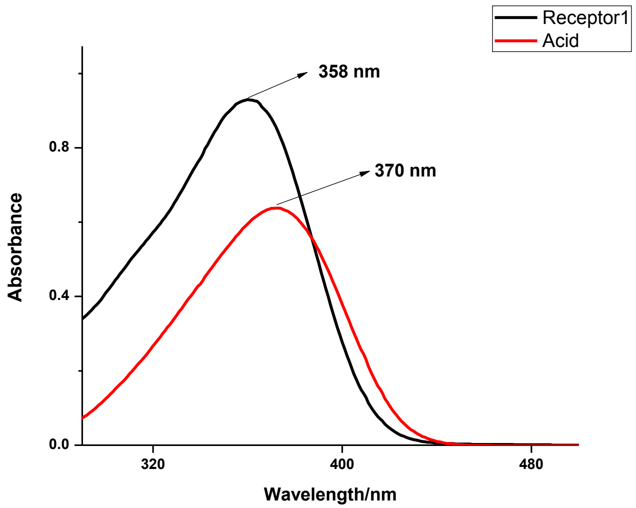
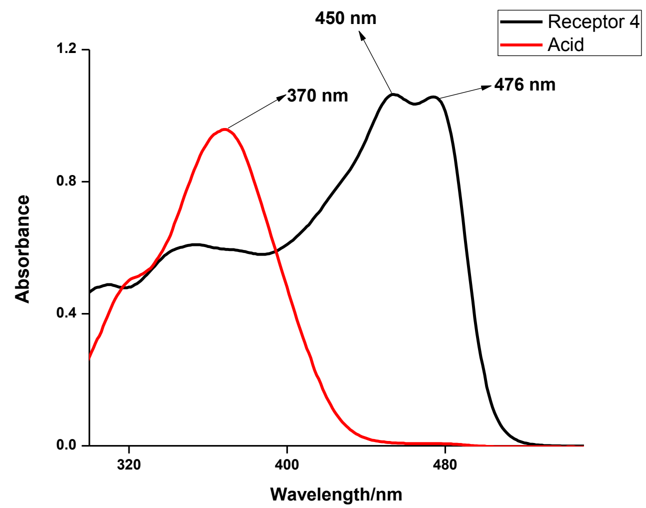




Effect of Mineral acid (HCl, 1 drop) on UV-visible spectra of Receptor 1 and 4

Note: The references cited in above discussion are same as it was in the manuscript.

3. FIGURES AND CAPTIONS

Figure S1: ^{1}H NMR spectrum of Receptor 1 and Receptor 1 + HSO_4^- in CD_3CN- D_2O

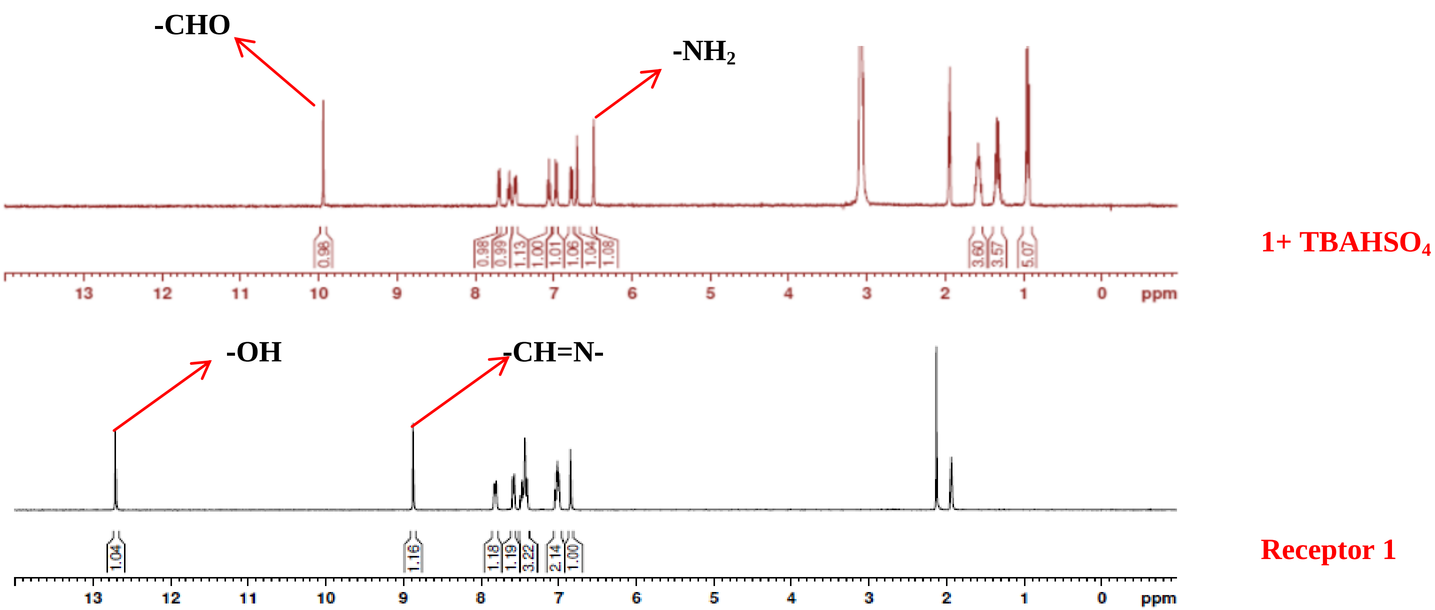


Figure S2: ^{1}H NMR spectrum of isolated product as *7-amino-4-trifluoromethyl coumarin* from the reaction between receptor 1 + HSO_4^- in $CDCl_3$

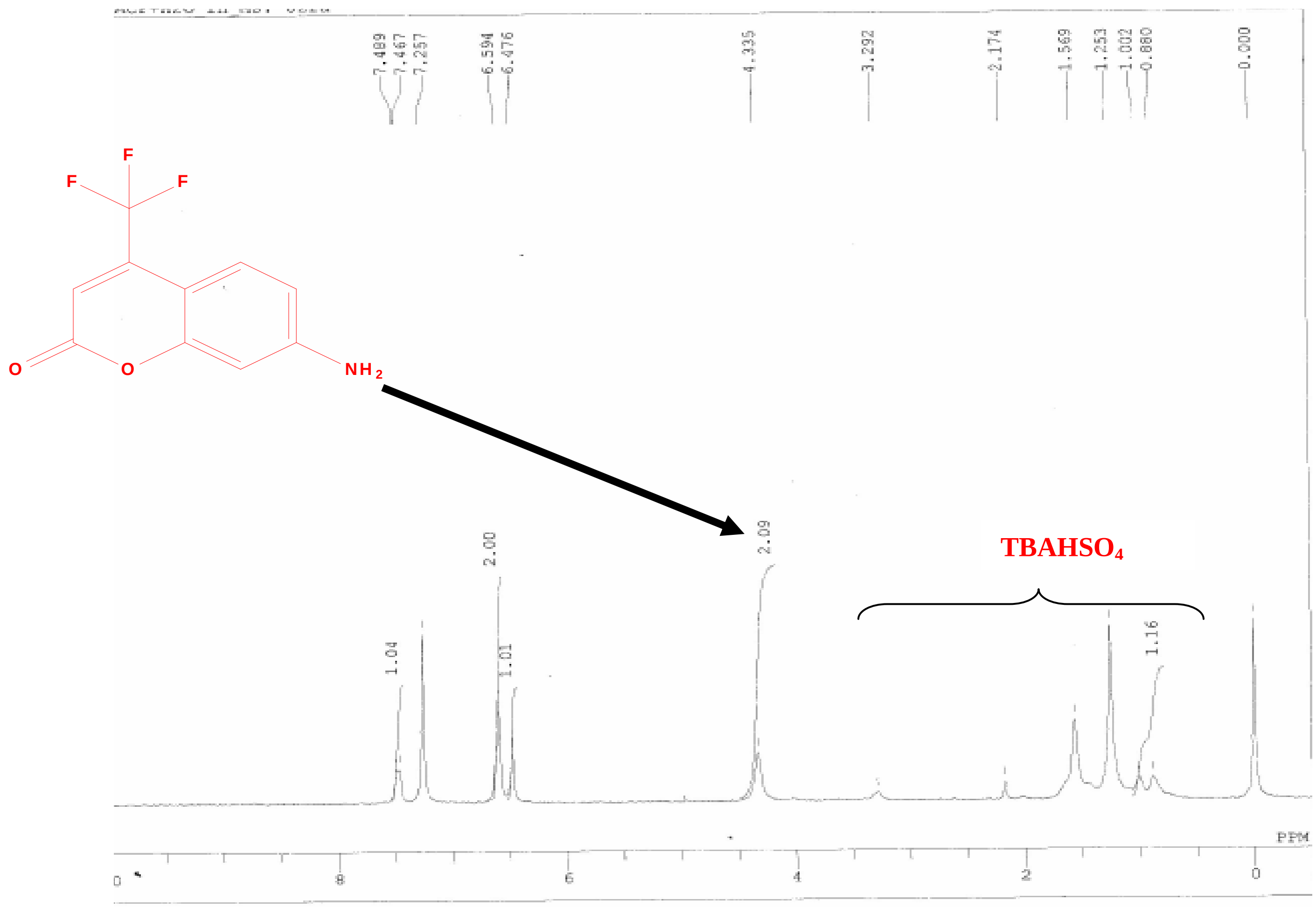
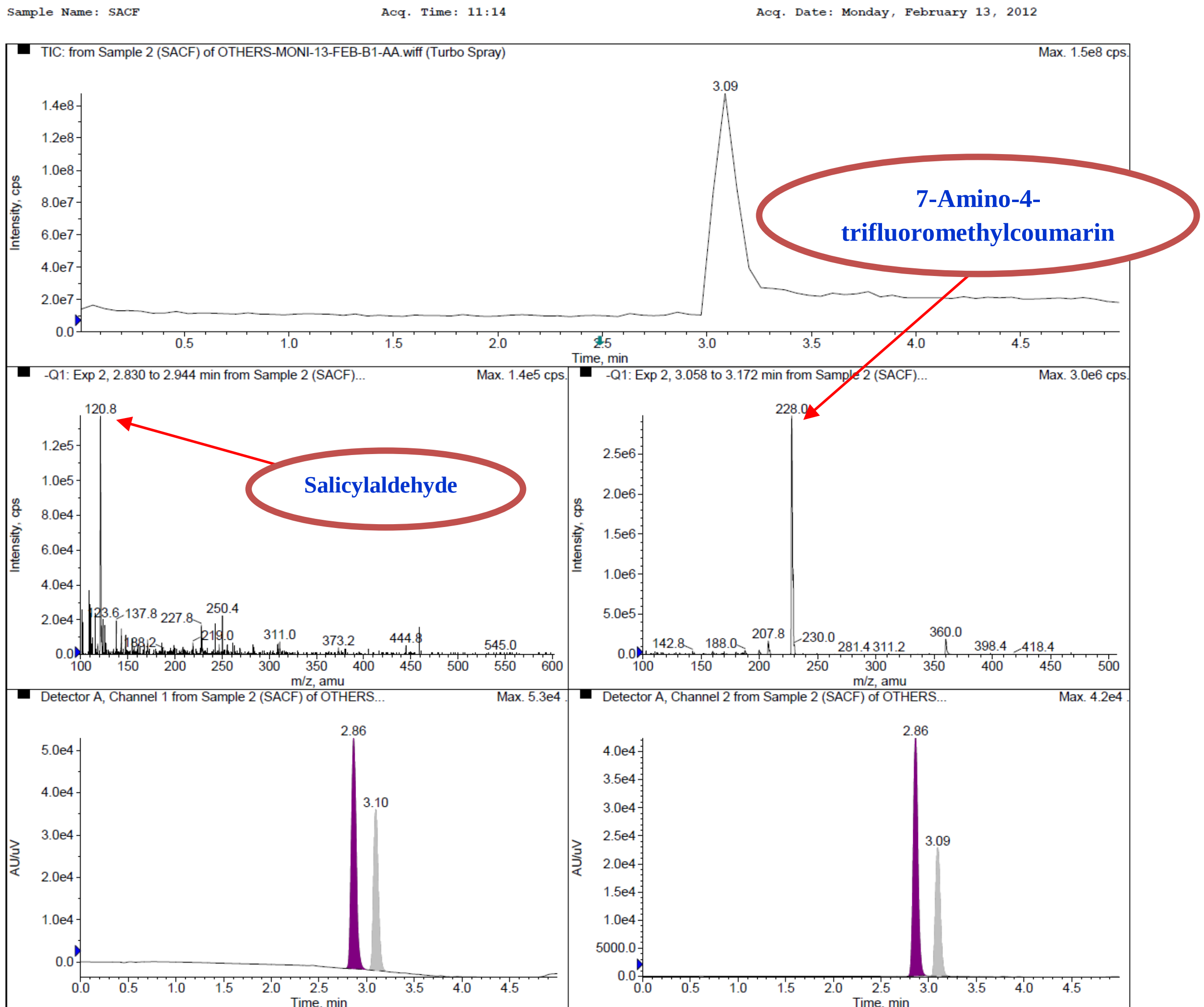


Figure S3: ESI-Mass spectrum (M–H) of Receptor 1 + HSO_4^- showing peaks for corresponding aldehyde and amine



Peak List for "Detector A, Channel 1 from Sample 2 (SACF) of OTHERS-MONI-13-FE

	Time (min)	Area (counts)	%Area	Height	%Height
1	2.8624	1.9080e5	60.4336	5.4504e4	58.9052
2	3.0954	1.2492e5	39.5664	3.8025e4	41.0948

Peak List for "Detector A, Channel 2 from Sample 2 (SACF) of OTHERS-MONI-13-FEE

	Time (min)	Area (counts)	%Area	Height	%Height
1	2.8623	1.4187e5	64.4048	4.2330e4	64.9618
2	3.0942	7.8411e4	35.5952	2.2832e4	35.0382

Figure S4: ^{1}H NMR spectrum of Receptor 4 in CD_3CN

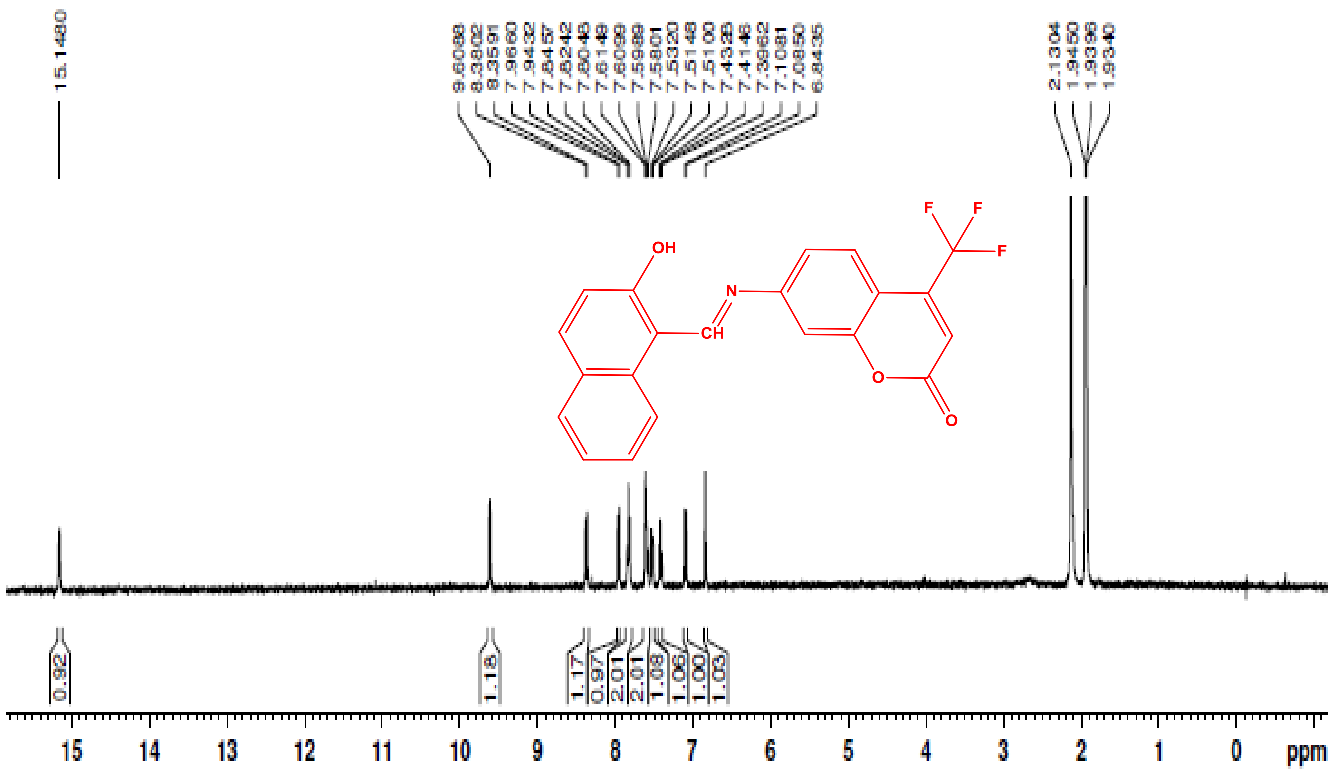


Figure S5: ^{13}C NMR spectrum of Receptor 4 in $CDCl_3$

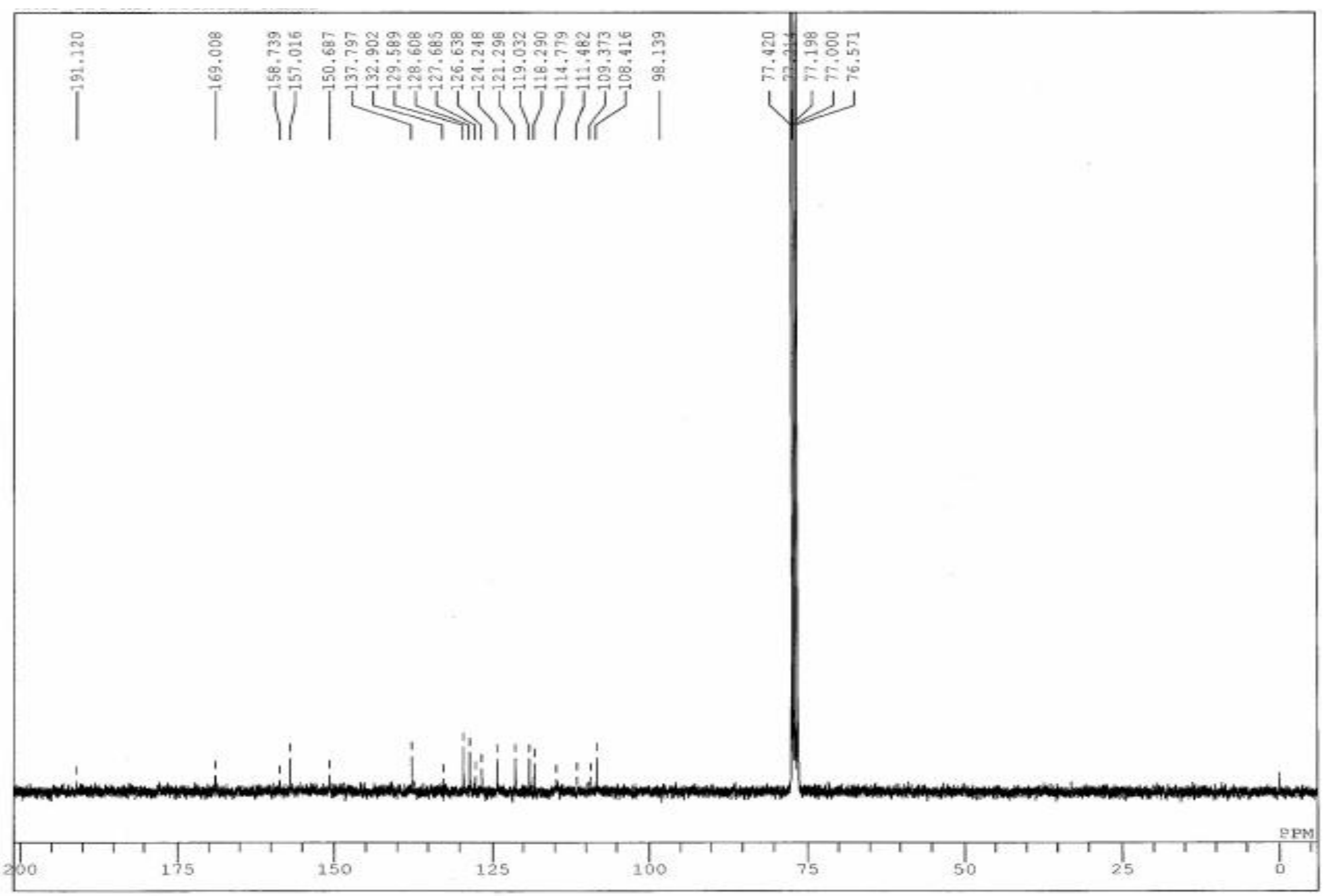


Figure S6: IR spectrum of Receptor 4

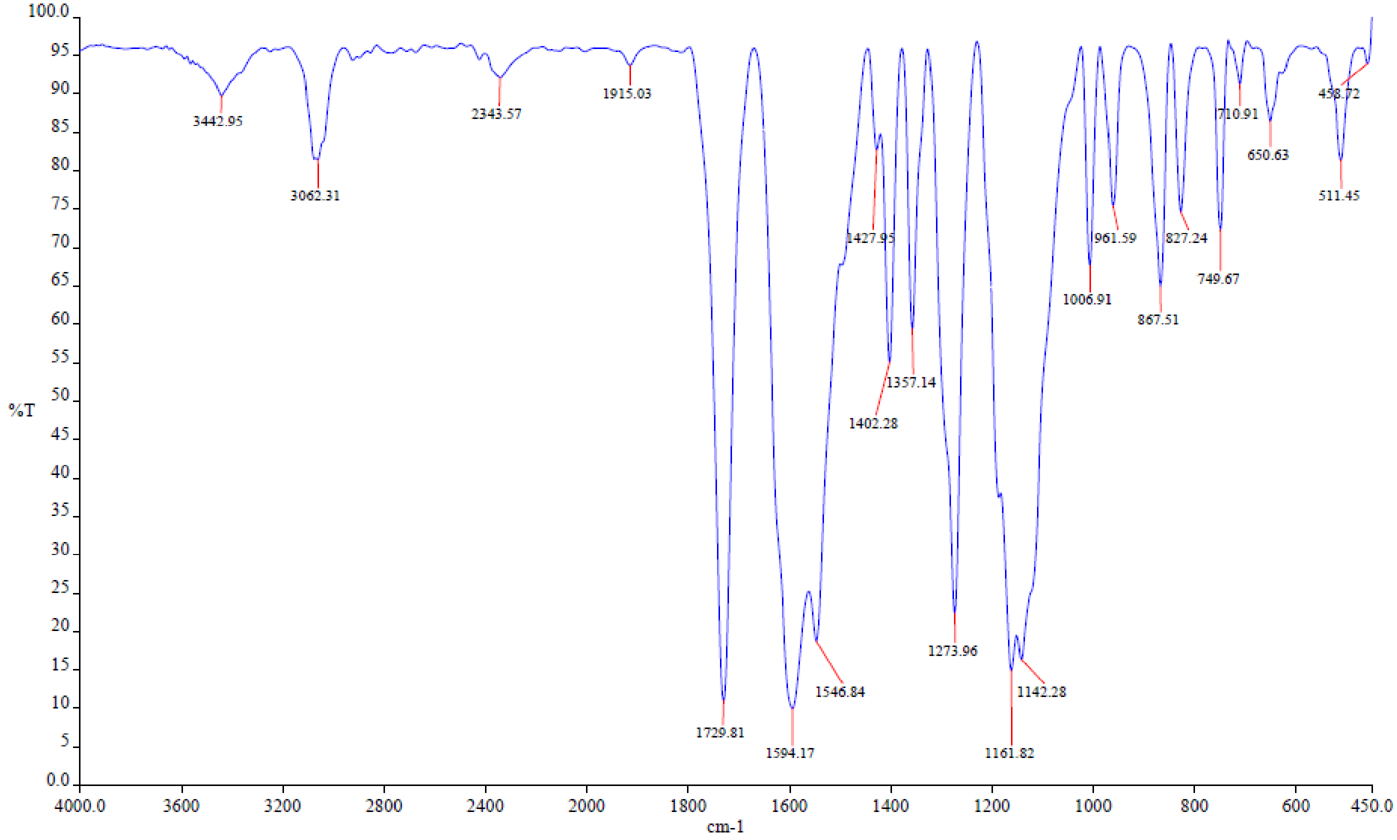
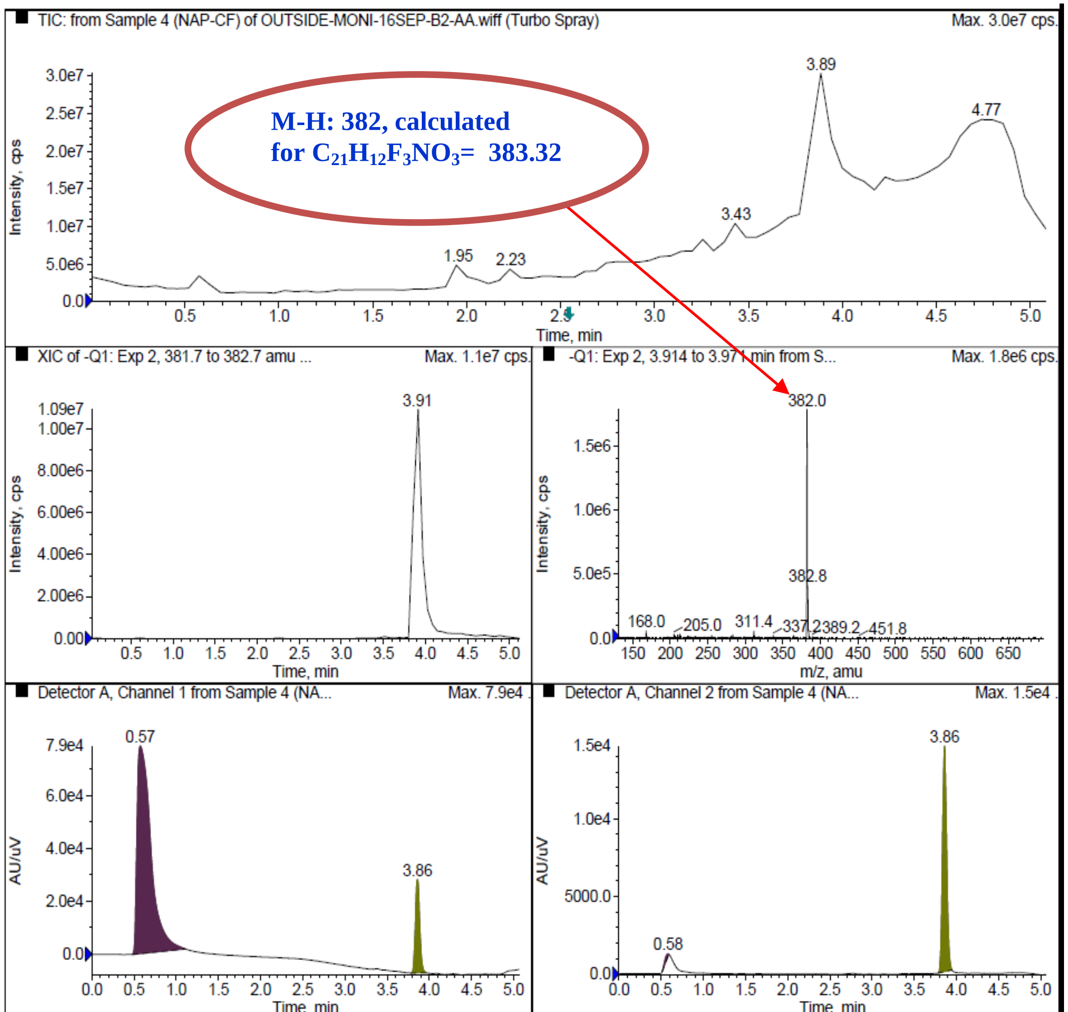


Figure S7: ESI Mass spectrum (M–H) of Receptor 4



Peak List for "Detector A, Channel 1 from Sample 4 (NAP-CF) of OU

	Time (min)	Area (counts)	% Area	Height
1	0.5735	9.0399e5	87.6897	7.8459e4
2	3.8596	1.2691e5	12.3103	3.5329e4

Peak List for "Detector A, Channel 2 from Sample 4 (NAP-CF) of OU

	Time (min)	Area (counts)	% Area	Height
1	0.5808	943.2496	1.8439	171.8660
2	3.8590	5.0212e4	98.1561	1.4537e4

Figure S8: X-ray crystal structure of Receptor 4 (Ortep diagram with 30% ellipsoid probability)

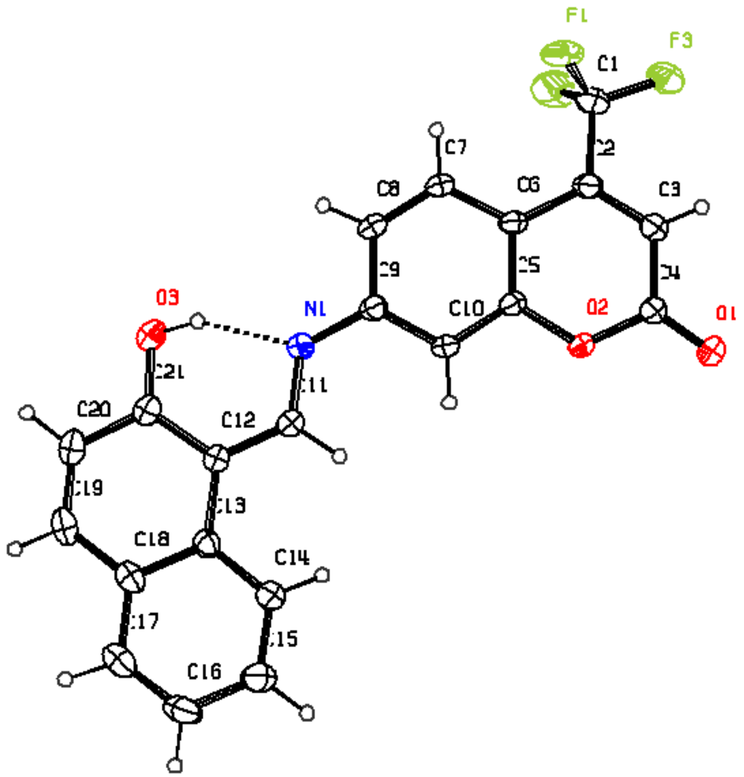
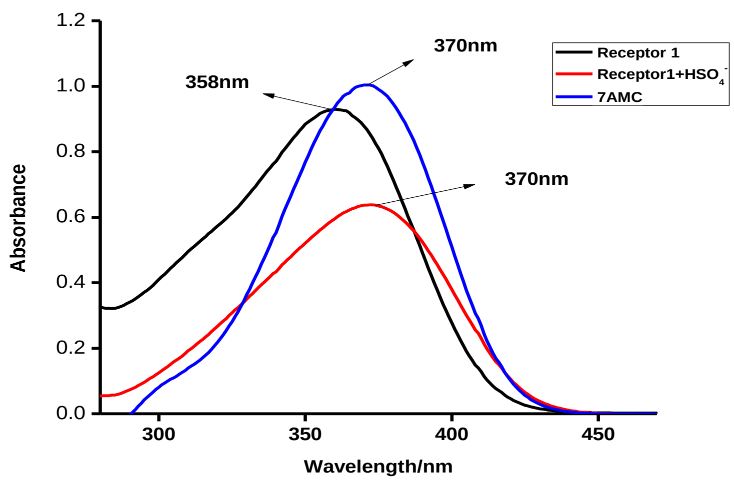
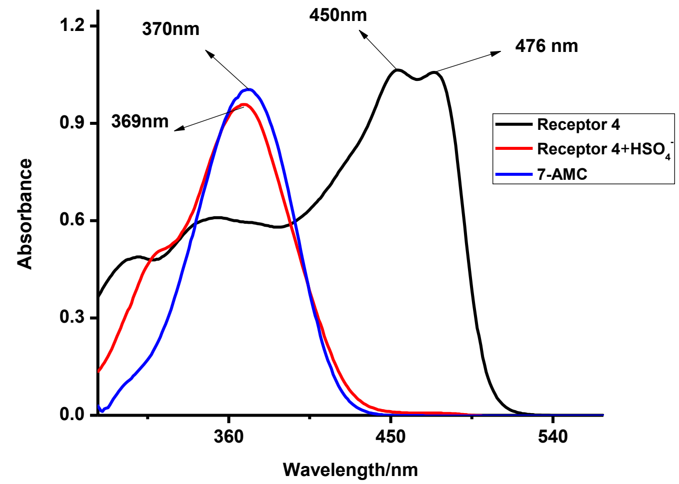


Figure S9: UV-visible spectra of receptor 1 and 4 with and without HSO_4^- along with 7-amino-4-trifluoromethyl coumarin (7-AMC); in 50 µM CH_3CN-H_2O (1:1, v/v) solution

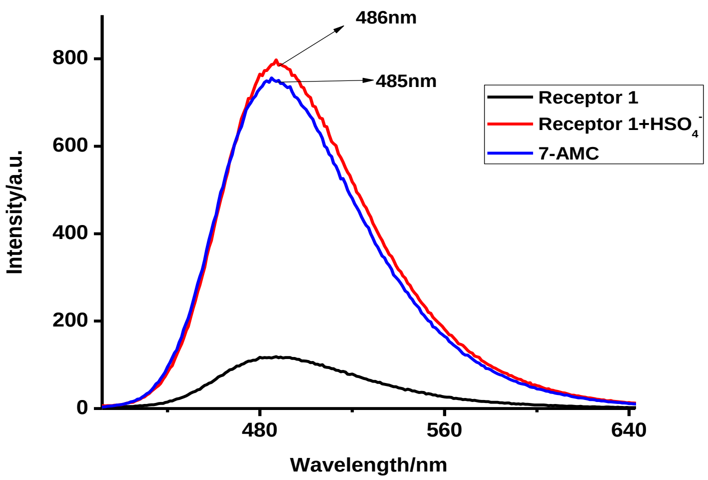


Receptor 1

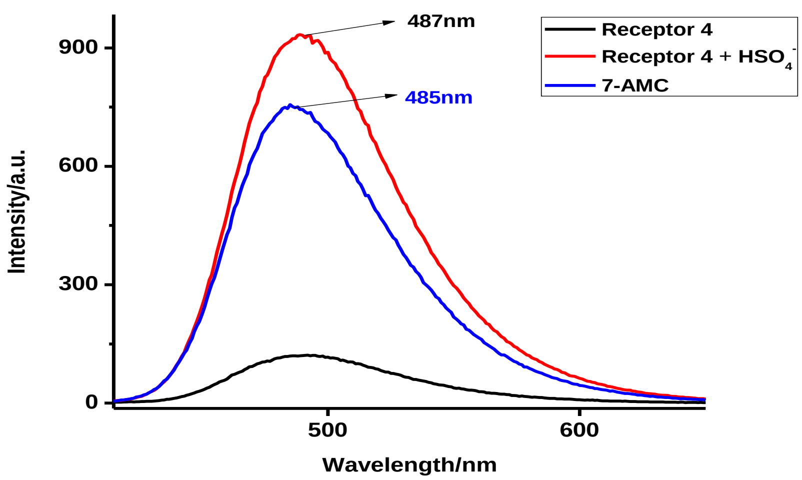


Receptor 4

Figure S10: Fluorescence spectra of receptor 1 and 4 with and without HSO_4^- along with 7-amino-4-trifluoromethyl coumarin (7-AMC); in 3 μM CH_3CN-H_2O (1:1, v/v) solution



Receptor 1



Receptor 4

Figure S11: ^{1}H NMR spectrum of Receptor 4 and Receptor 4 + HSO_4^- in CD_3CN- D_2O

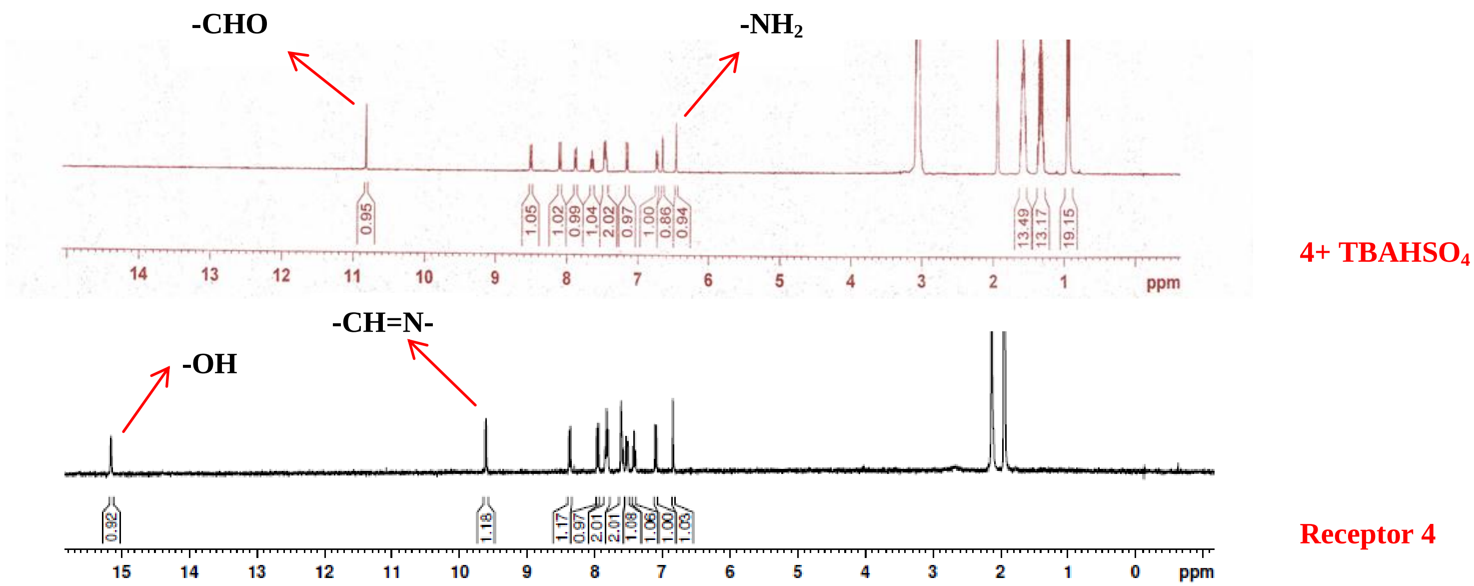


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Figure S12: ^{1}H NMR spectrum of isolated product as 7-amino-4-trifluoromethyl coumarin and 2-hydroxy napthaldehyde from the reaction between receptor 4 + HSO_4^- in $CDCl_3$

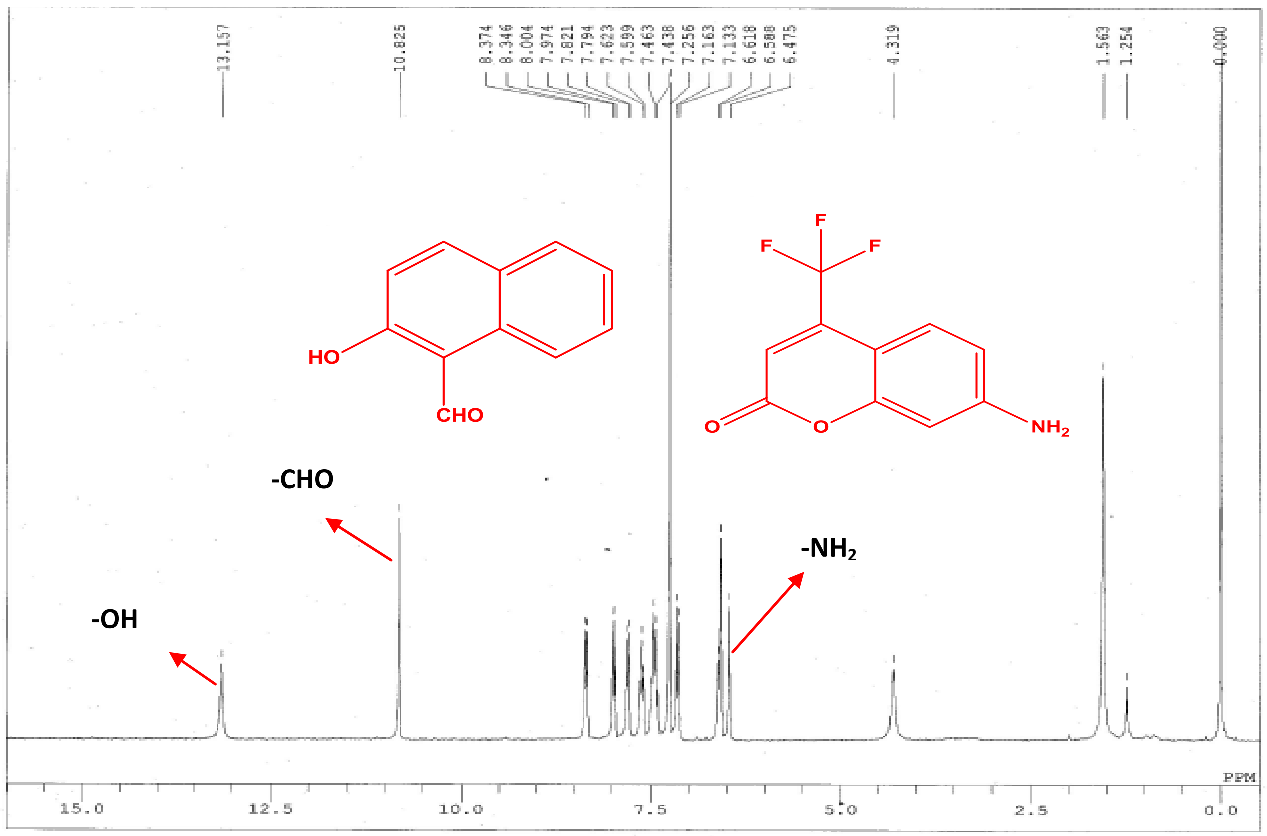
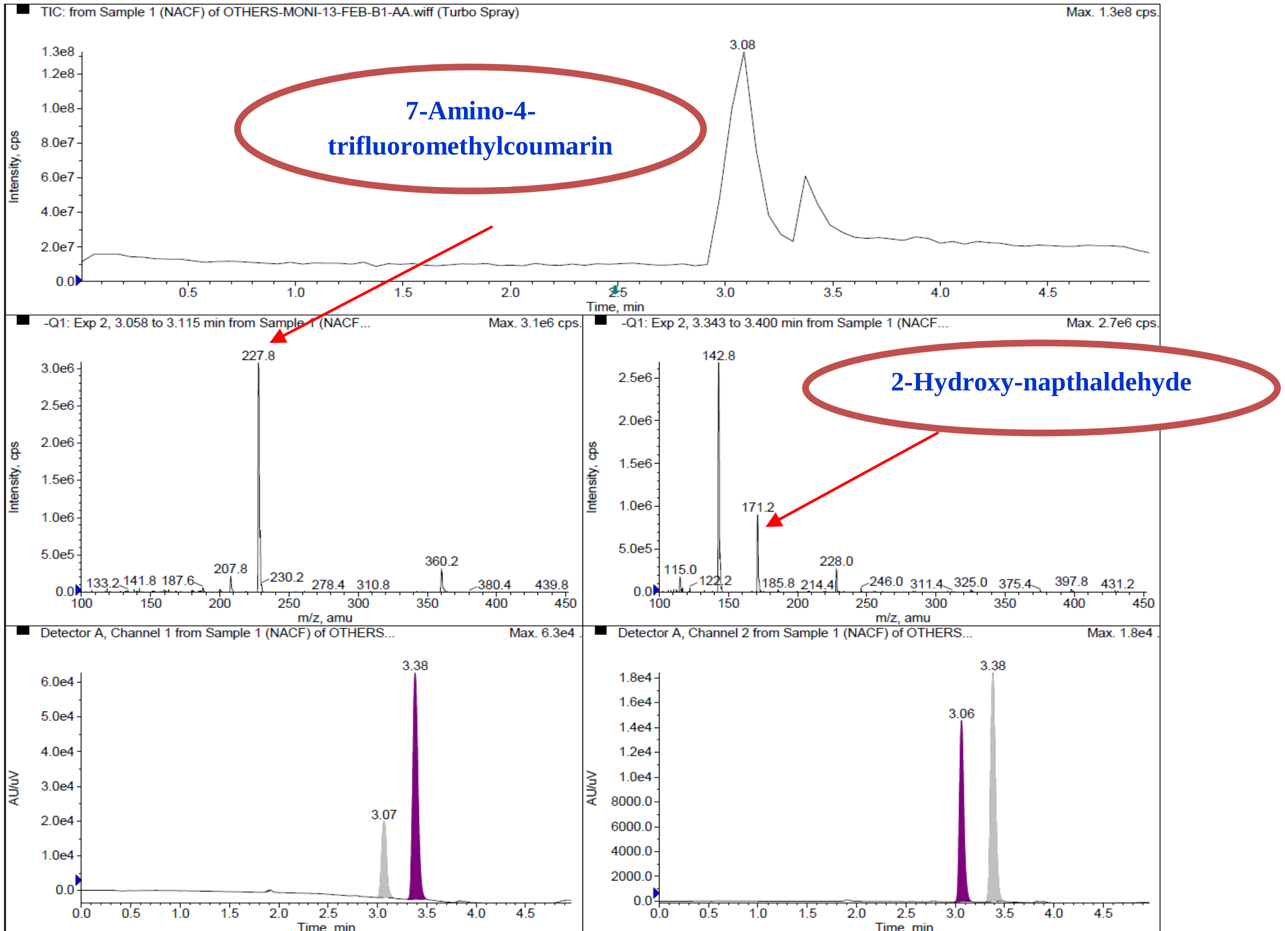


Figure S13: ESI-Mass spectrum (M–H) of Receptor 4 + HSO_4^- showing peaks for corresponding aldehyde and amine



Peak List for "Detector A, Channel 1 from Sample 1 (NACF) of OTHERS-MONI-13-FE

	Time (min)	Area (counts)	%Area	Height	%Height
1	1.9083	337.1127	0.1085	149.1268	0.1704
2	3.0661	7.4172e4	23.8722	2.1959e4	25.0912
3	3.3805	2.3584e5	75.9041	6.5234e4	74.5404
4	3.8321	358.0092	0.1152	173.1985	0.1979

Peak List for "Detector A, Channel 2 from Sample 1 (NACF) of OTHERS-MONI-13-FE

	Time (min)	Area (counts)	%Area	Height	%Height
1	3.0636	4.4845e4	42.1728	1.4612e4	44.2171
2	3.3819	6.1492e4	57.8272	1.8434e4	55.7829

Figure S14: Absorption spectra of Receptor 3 and 3+HSO_4^- in CH_3CN-H_2O (9:1, v/v) solution:

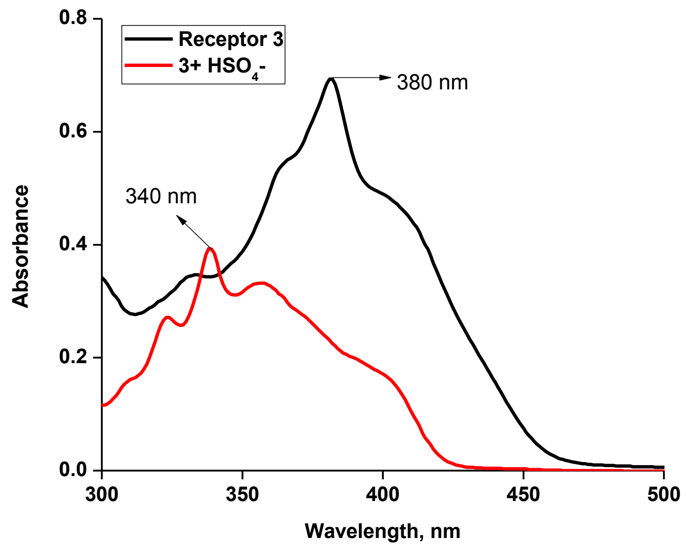


Figure S15: Emission spectra of 1-Aminopyrene

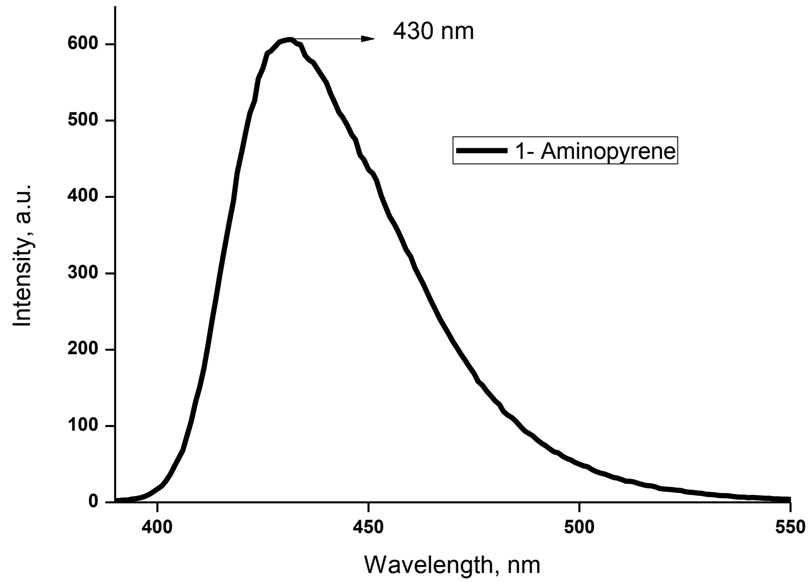
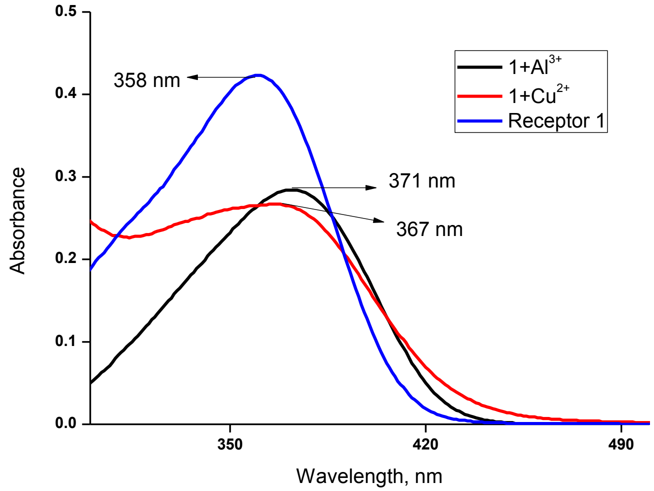
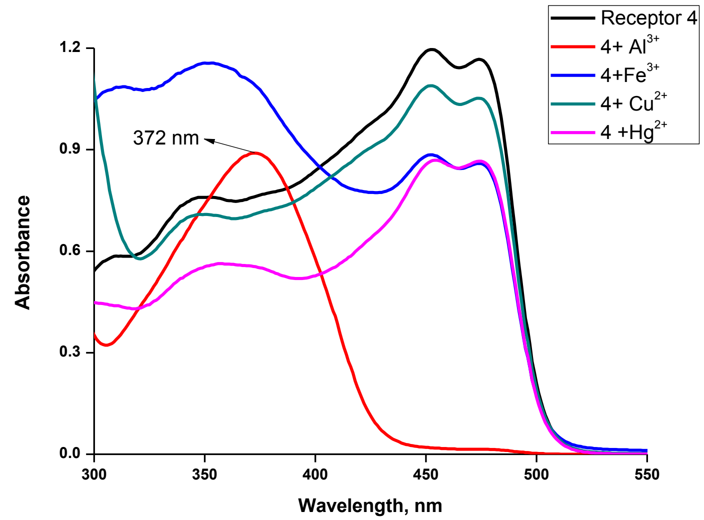


Figure S16: Effect of metal ions on Receptor 1 and 4

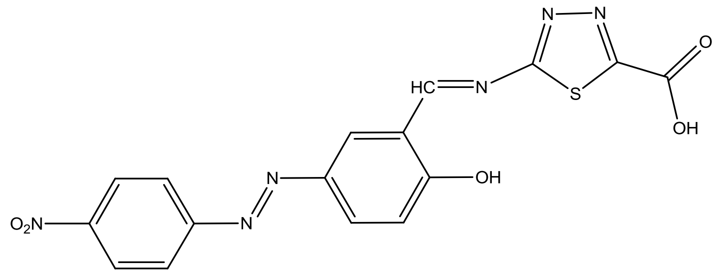




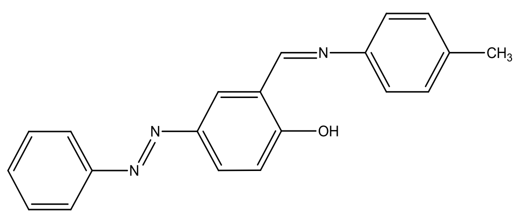
Receptor 1

Receptor 4

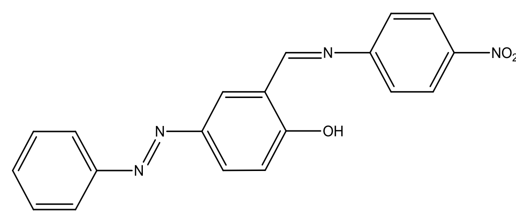
Figure S17 Colorimetric receptors 5 and 6a-d for HSO_4^- reported by Wei et al. and Zhang et al. respectively



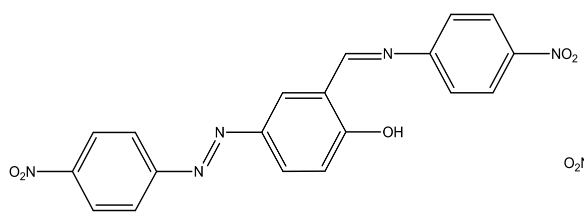
Receptor 5



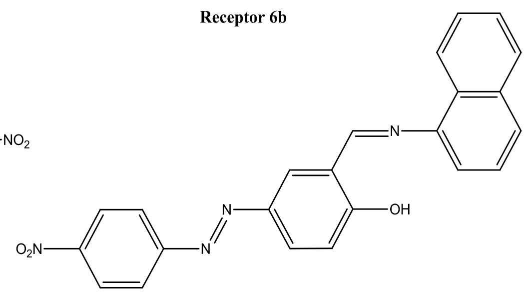
Receptor 6a



Receptor 6b



Receptor 6c



Receptor 6d

Receptor 6a-d

Figure S18: ^{1}H NMR spectrum of Receptor 1 in CD_3CN

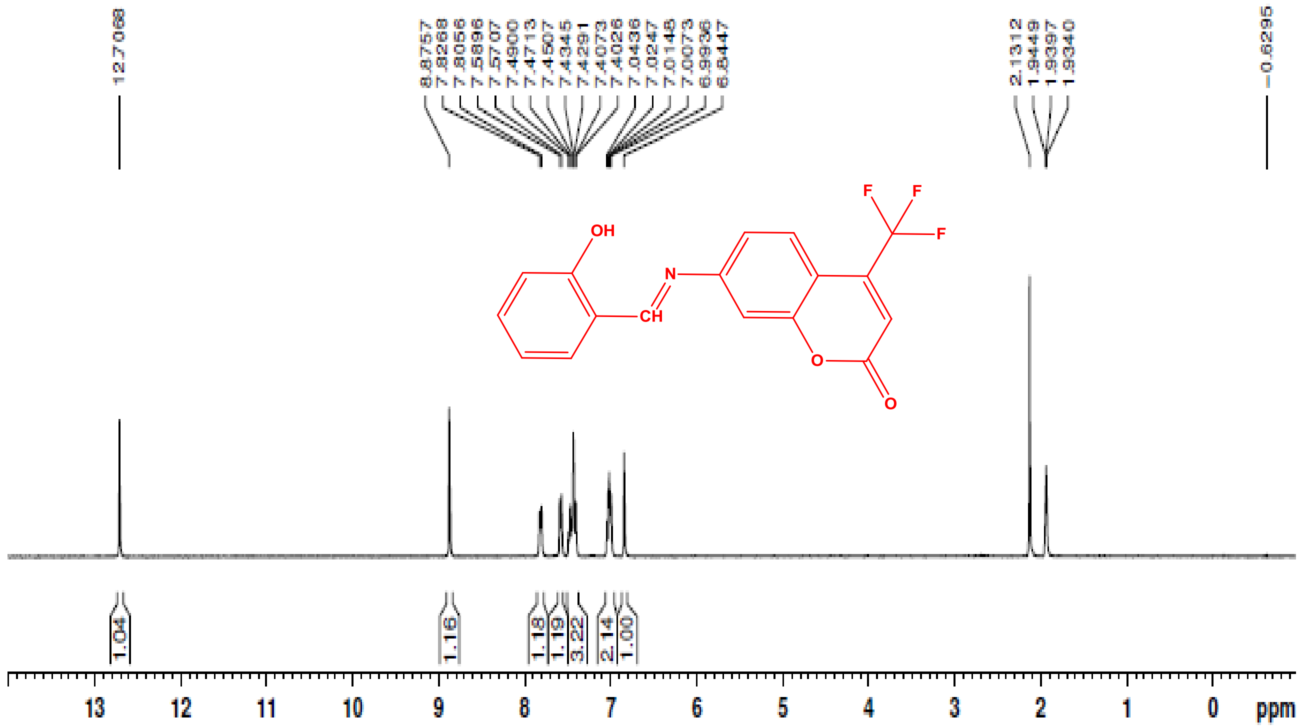


Figure S19: IR spectrum of Receptor 1

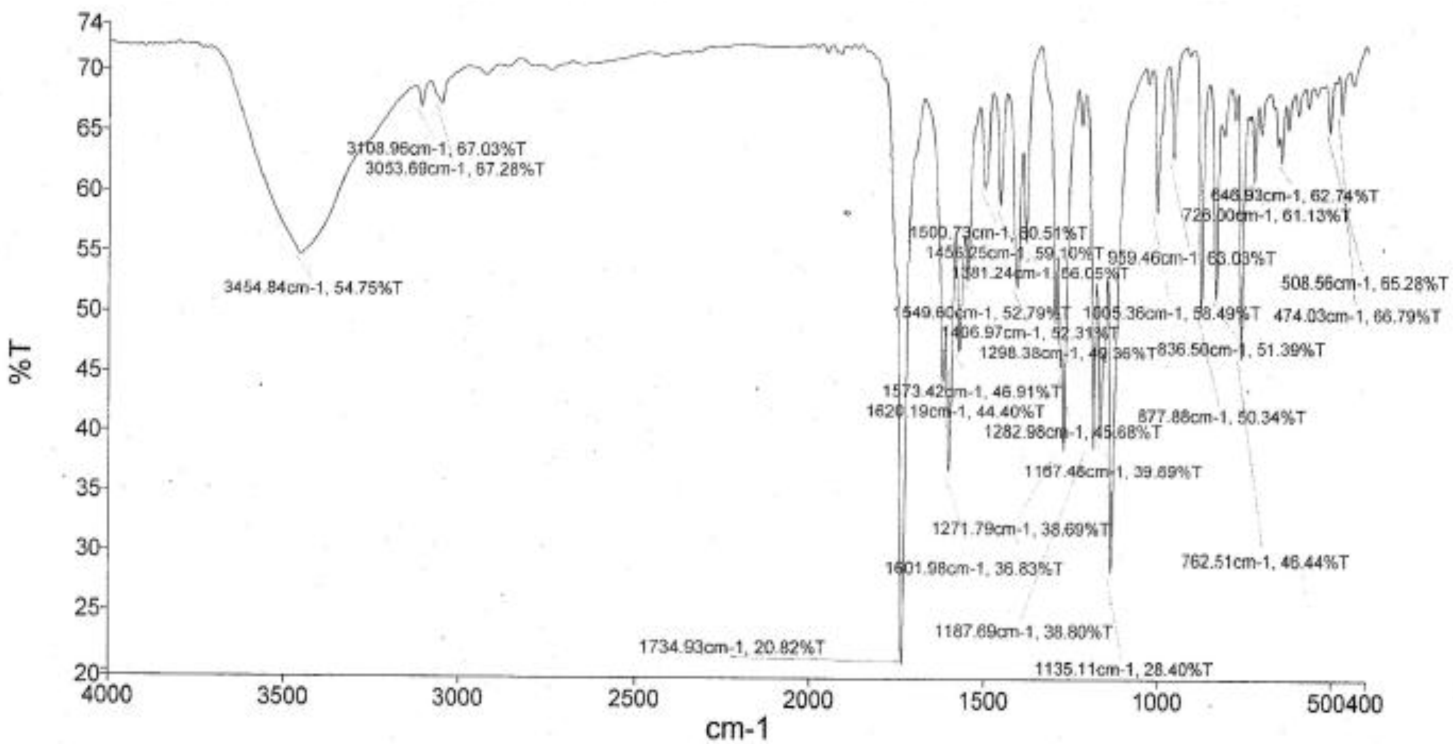
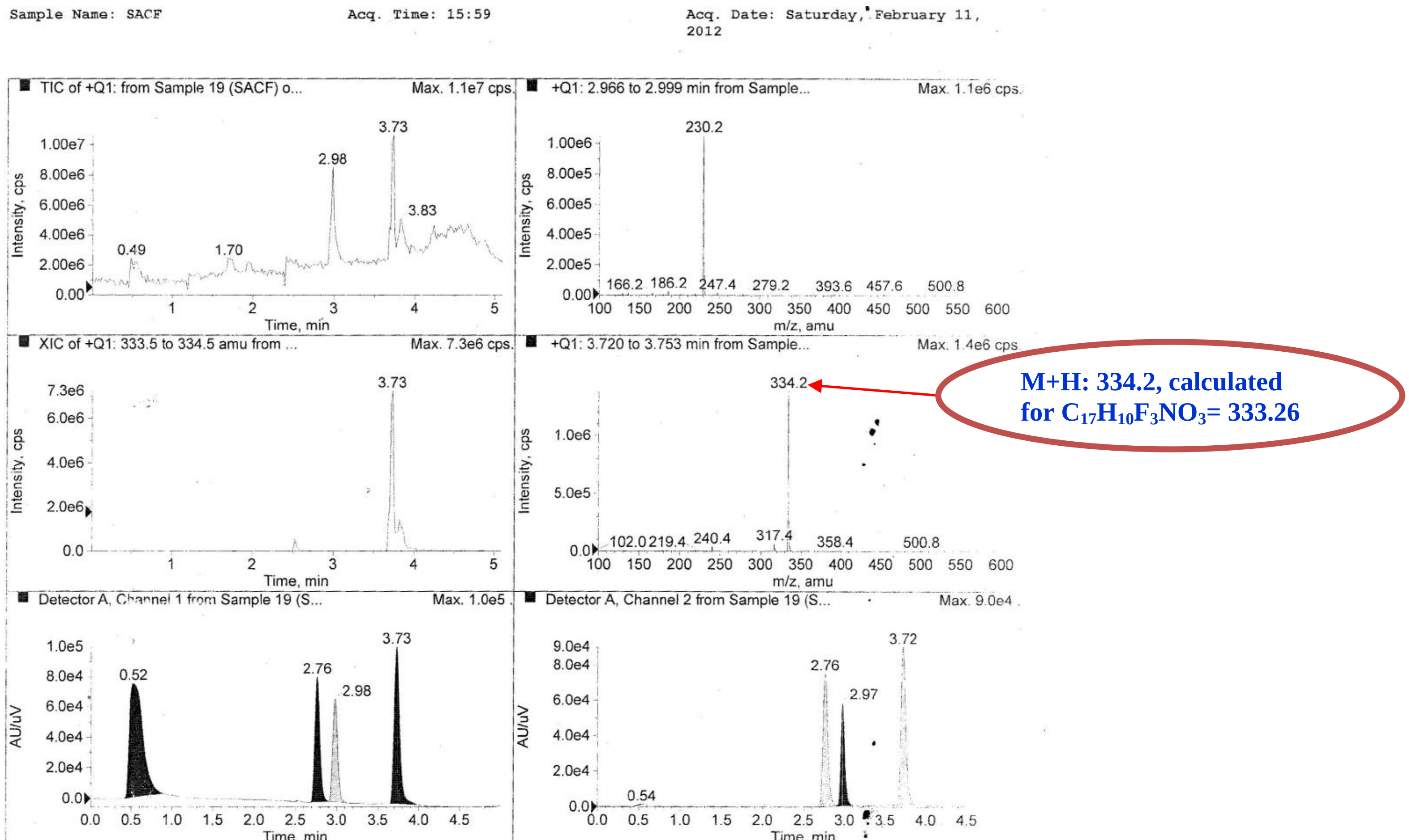


Figure S20: ESI-Mass spectrum (M+H) of Receptor 1



	Time (min)	Area (counts)	%Area	Height
1	0.5245	8.8156e5	43.6640	7.4672e4
2	2.5329	426.0902	0.0211	219.7453

	Time (min)	Area (counts)	%Area	Height
1	0.5375	1325.4670	0.1486	219.1135
2	2.7599	3.1322e5	35.1253	7.4982e4

Figure S21: [1]H NMR spectrum of Receptor 3 in $CDCl_3$

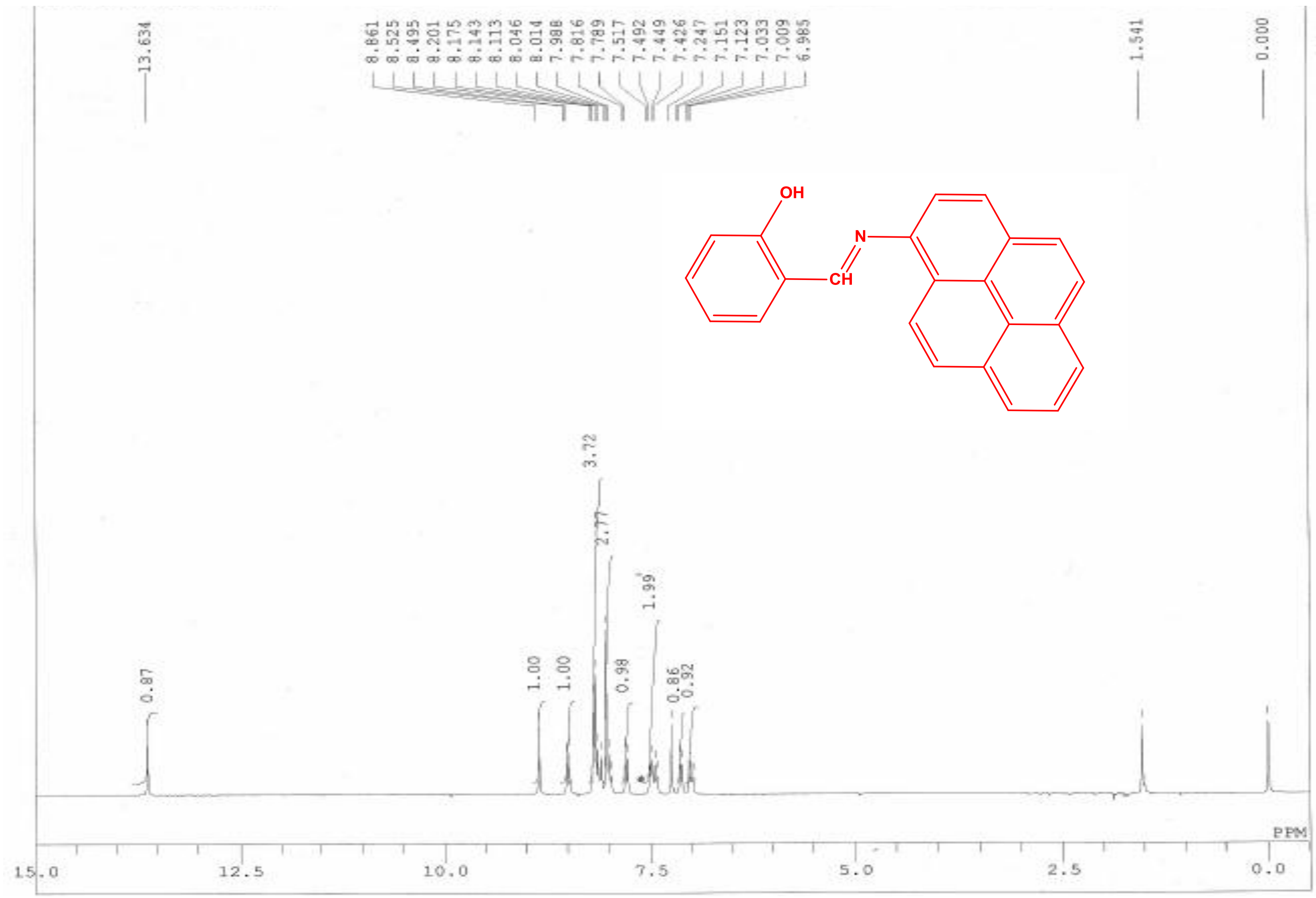
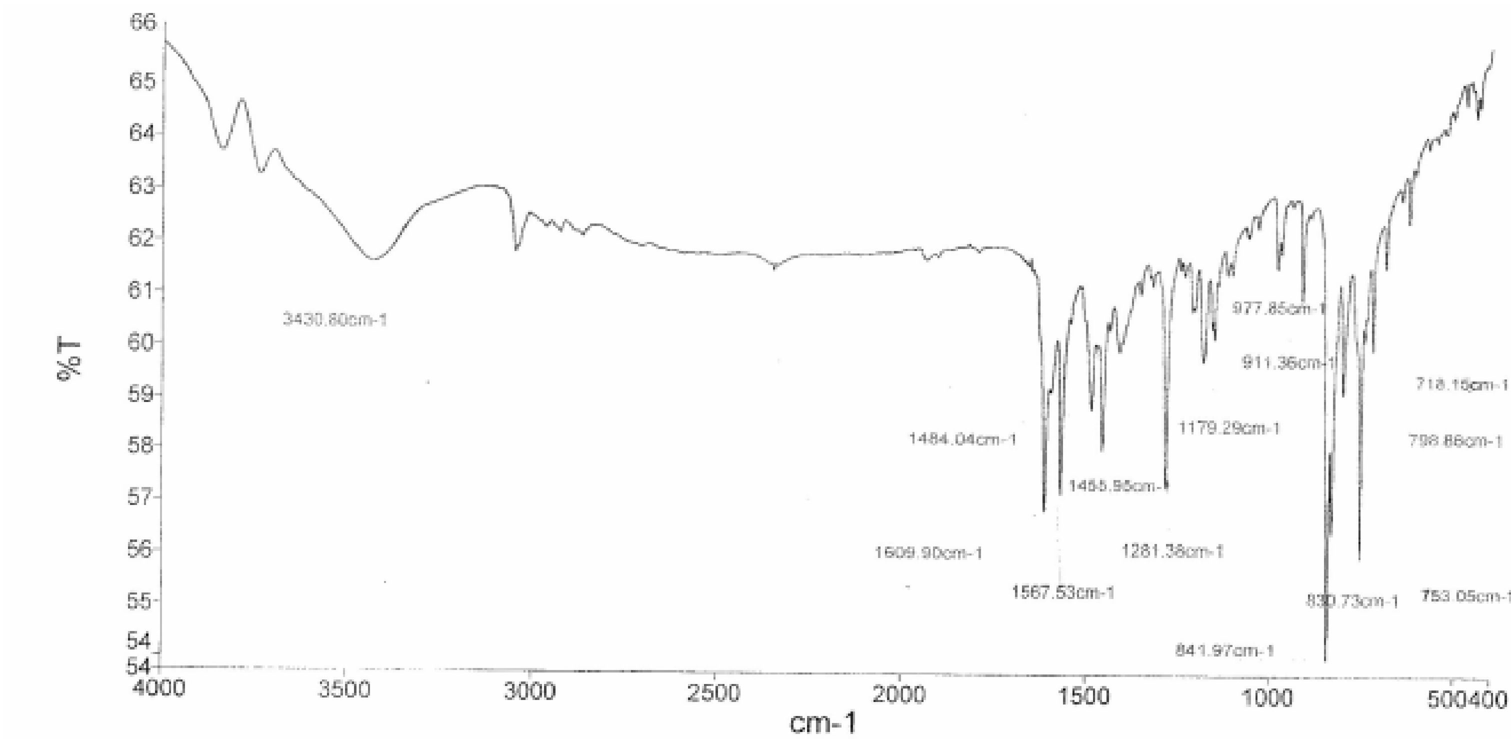
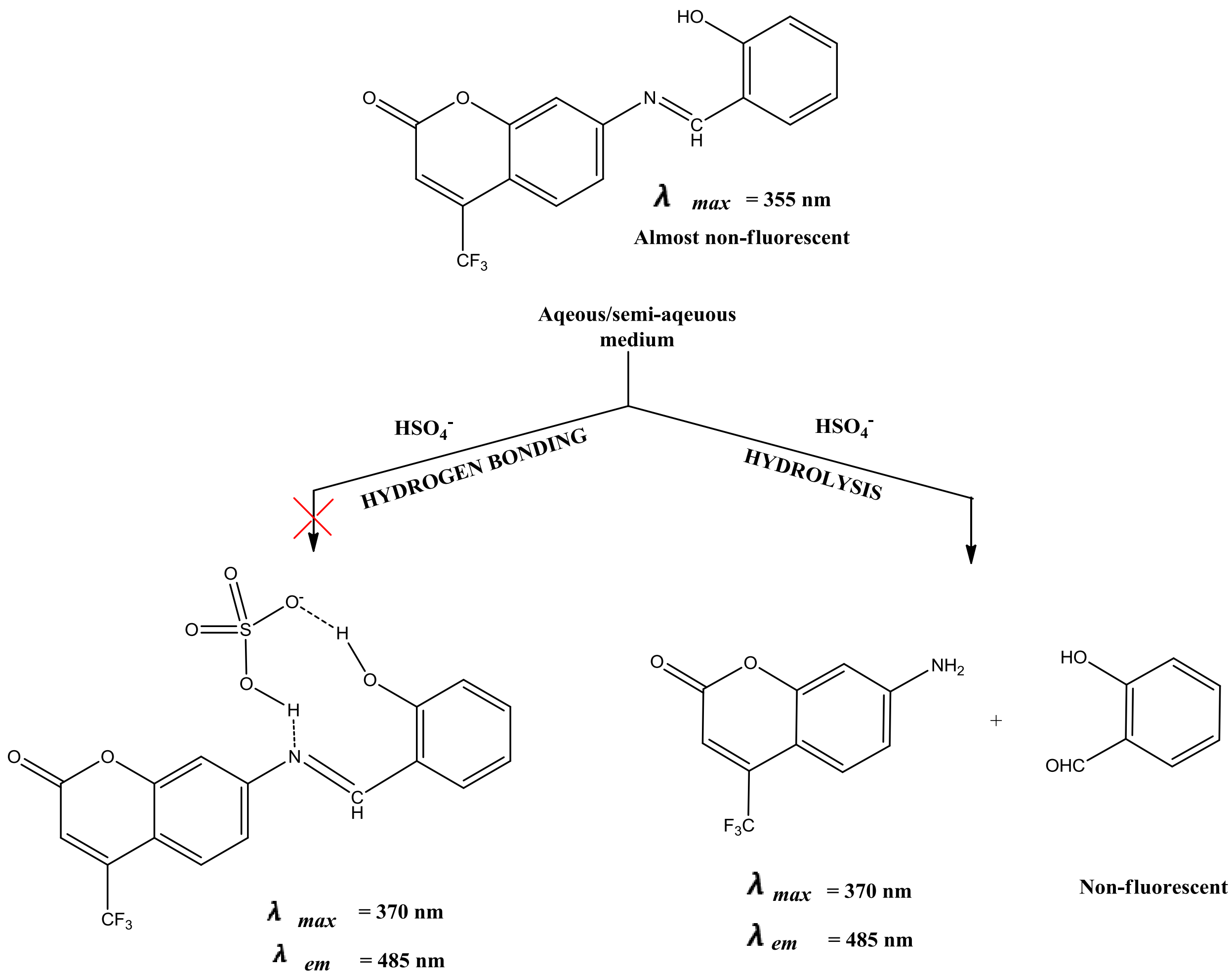


Figure S22: IR spectrum of Receptor 3



Scheme 1: Hydrogen bonding *vs.* Hydrolysis of Schiff base receptor 1 in the presence of HSO_4^-



Scheme 2: Hydrogen bonding *vs.* Hydrolysis of Schiff base receptor 3 in the presence of HSO_4^- and Hg^{2+}/Al^{3+}

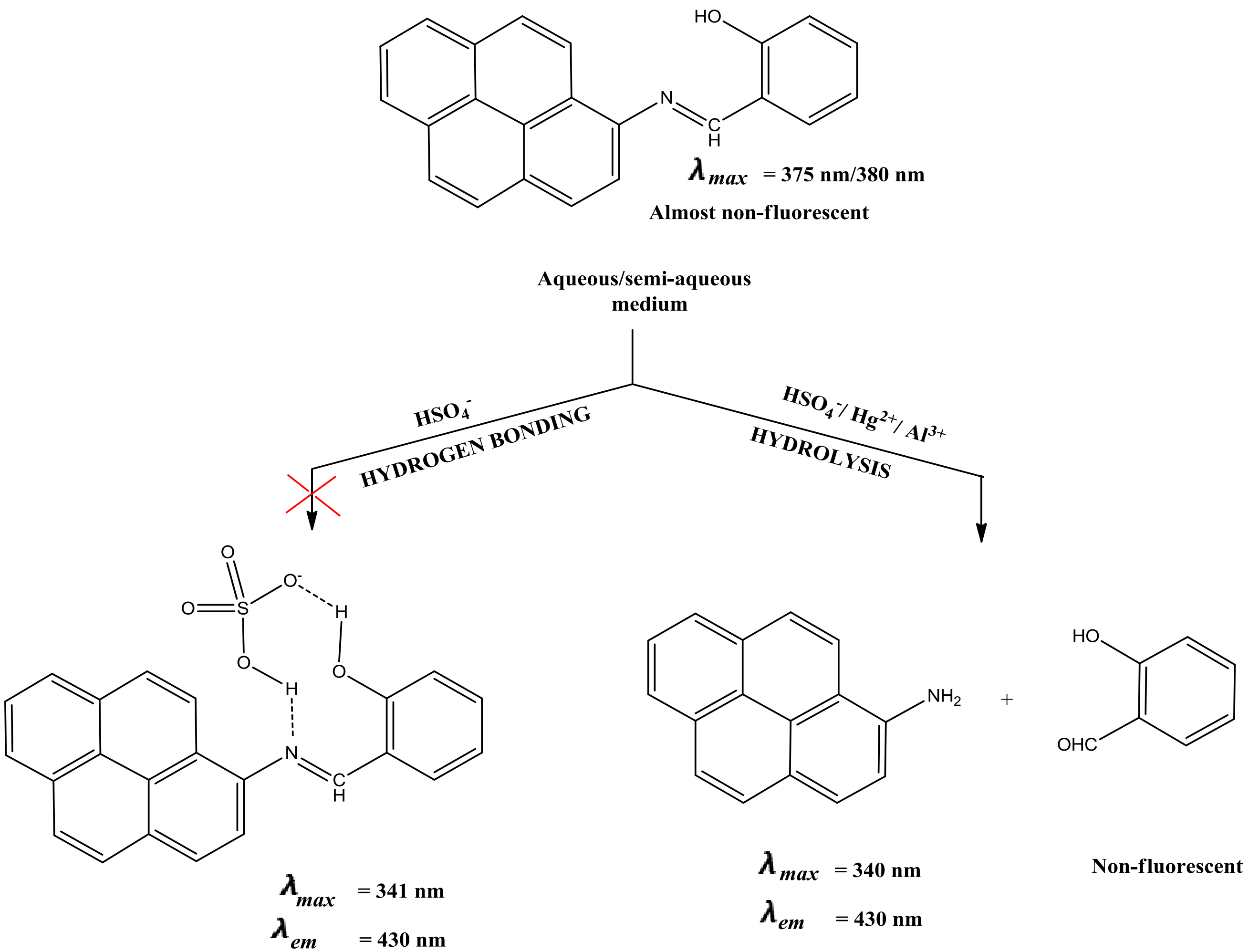


Table S1- Crystal data of receptor 4

CCDC No.	**873622**
Identification code	Receptor 4
Empirical formula	$C_{21} H_{15} F_3 N O_3$
Formula weight	386.34
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
space group	P -1
Unit cell dimensions	a = 6.2911(7) Å α = 109.076(10)° b = 11.5341(13) Å β = 99.931(9)° c = 12.3473(13) Å γ = 91.579(9)°
Volume	830.66(16) A^3
Z	2
Density (calculated)	1.545 Mg/m^3
Absorption coefficient	0.126 mm^{-1}
F(000)	398
Crystal size	0.24 x 0.22 x 0.18 mm
Crystal color and habit	Red Rectangular
Diffractometer	'Xcalibur, Eos
Theta range for data collection	3.30 to 29.01°
Limiting indices	-8<=h<=5, -15<=k<=15, -16<=l<=15
Reflections collected / unique	6250 / 3759 [R(int) = 0.0216]
Completeness to theta = 25.00°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.94287
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3759 / 0 / 285
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0530, wR2 = 0.1288
R indices (all data)	R1 = 0.0862, wR2 = 0.1540
Largest diff. peak and hole	0.385 and -0.211 $e.Å^{-3}$