Electronic Supplementary Material (ESI) for Analyst

O- tert- butyldiphenylsilyl coumarin and dicoumarol: A case toward selective sensing of F^- ions in organic and aqueous environments

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1. Change in emission of receptor 1 with various anions in $CHCl_3$.

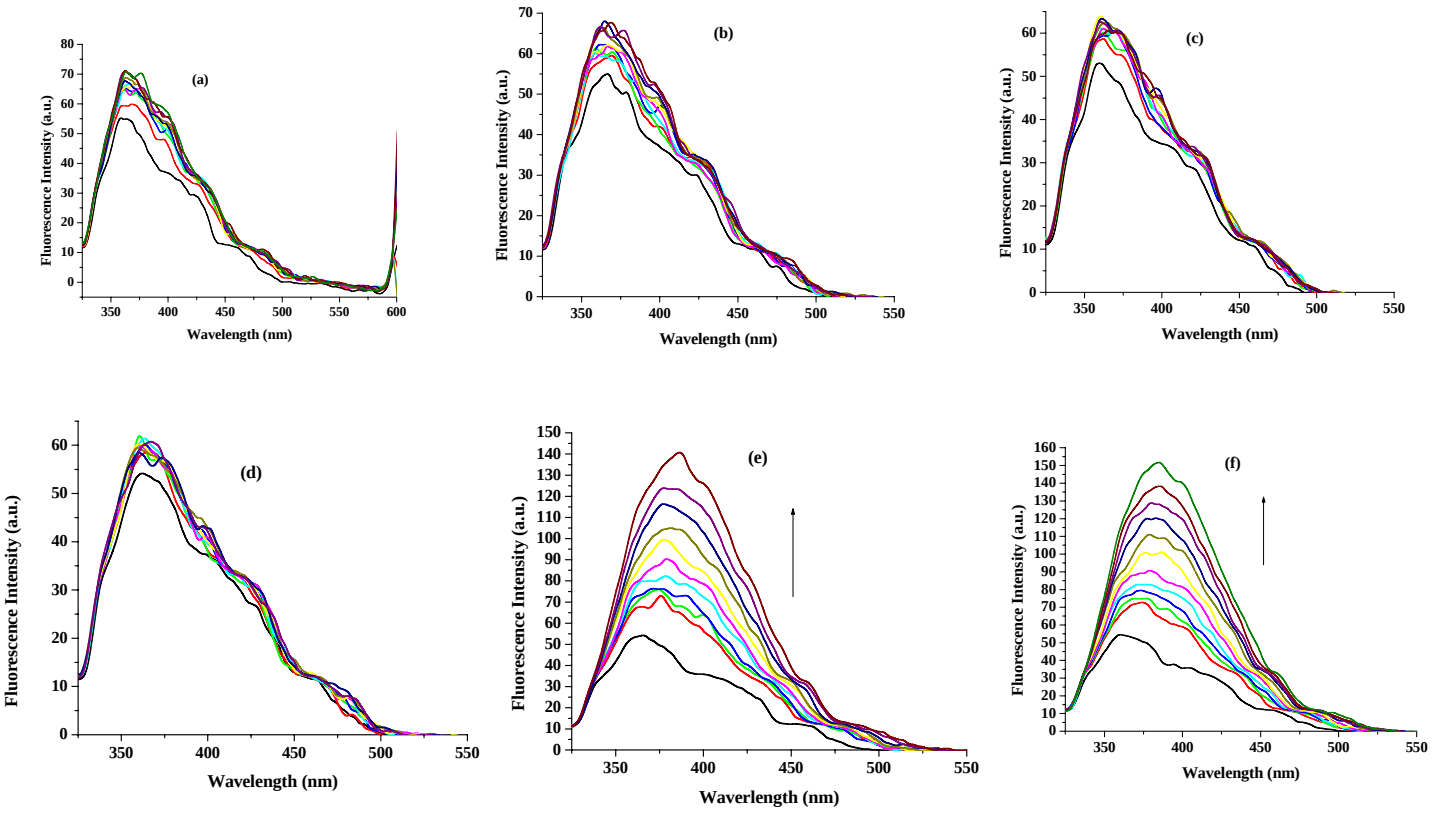


Figure S1. Fluorescence titration spectra for **1** (c = 7.01 x 10^{-5} M) with (a) HSO_4^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) AcO^- (f) $H_2P0_4^-$ in $CHCl_3$ (in all cases [anion] = 1x 10^{-3} M).

2. Change in absorbance of receptor 1 with various anions in $CHCl_3$.

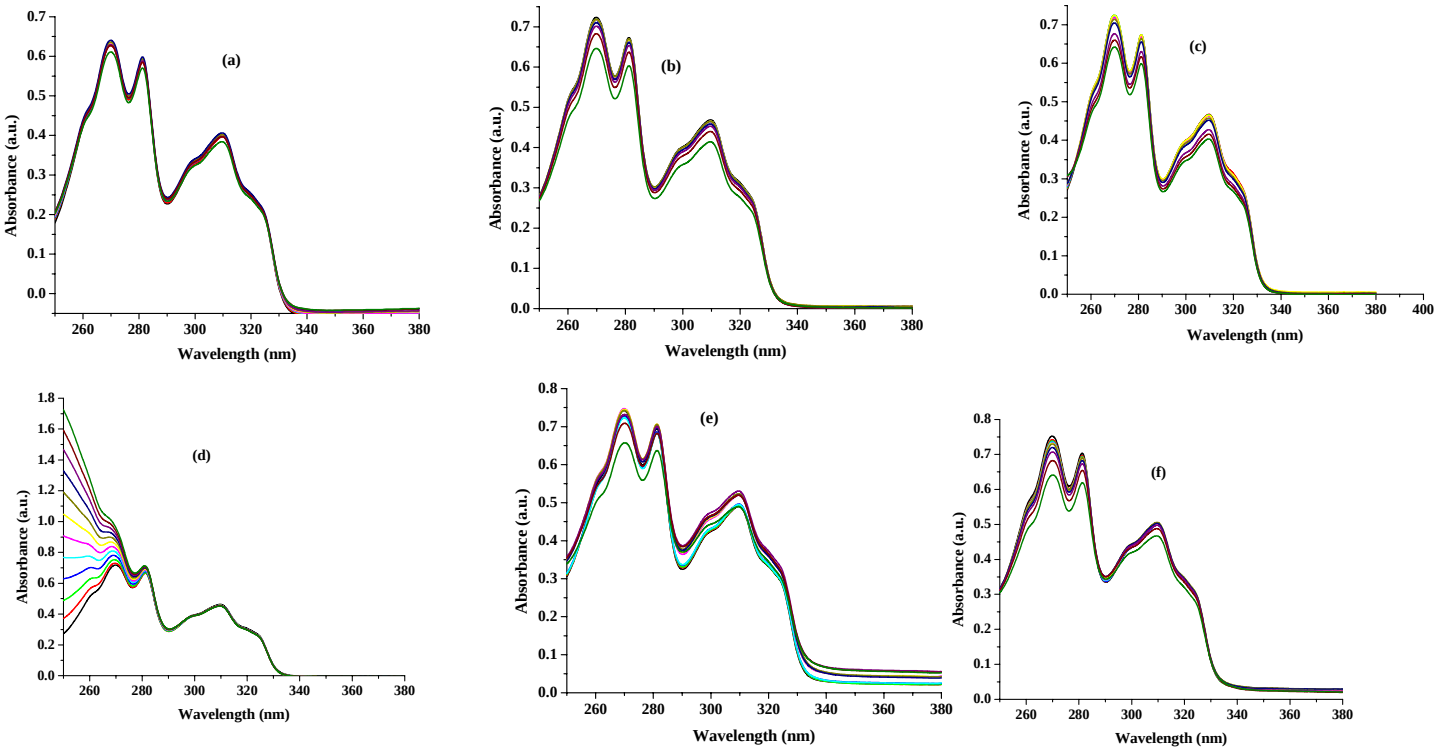
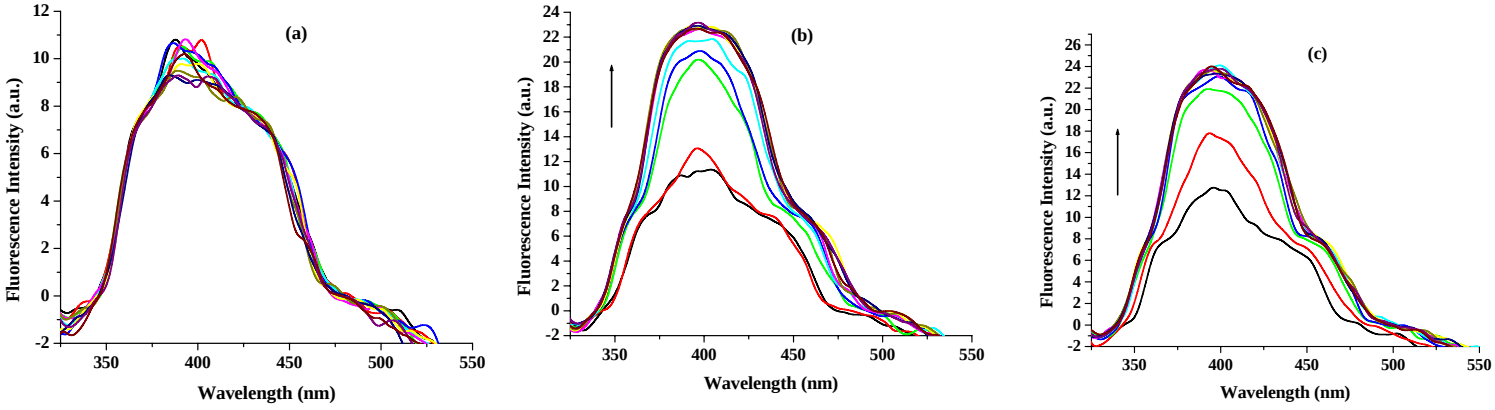


Figure S2. Change in absorbance of receptor **1** (c = 7.01 x 10^{-5} M) with (a) HSO_4^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) AcO^- (f) $H_2PO_4^-$ in $CHCl_3$ (in all cases [anion] = 1x 10^{-3} M).

3. Change in emission of receptor 1 with various anions in CH_3CN.



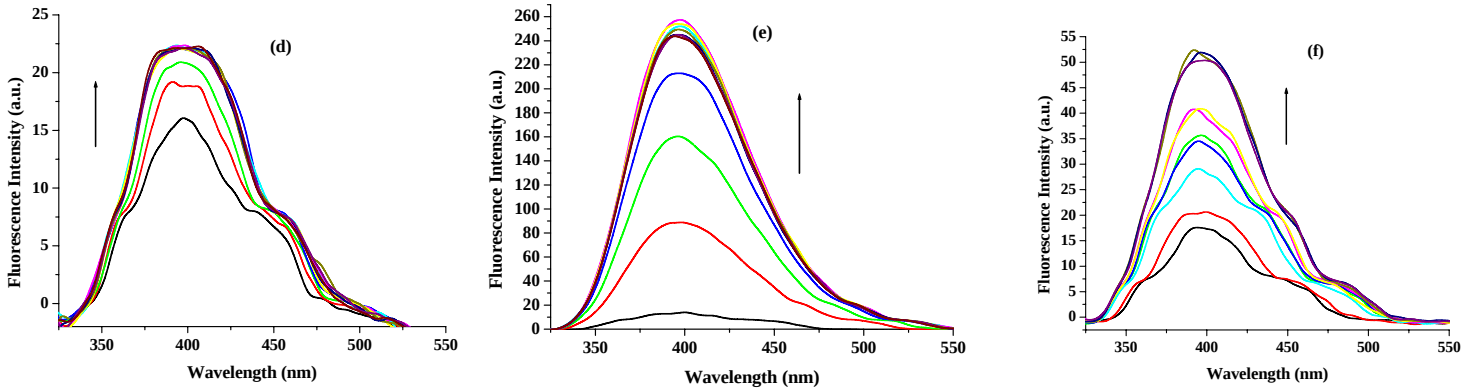


Figure S3. Fluorescence titration spectra for **1** (c = 9.92 x 10^{-5} M) with (a) HSO_4^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) AcO^- (f) $H_2P0_4^-$ in CH_3CN (in all cases [anion] = 1x 10^{-3} M).

4. Change in absorbance of receptor 1 with various anions in CH_3CN.

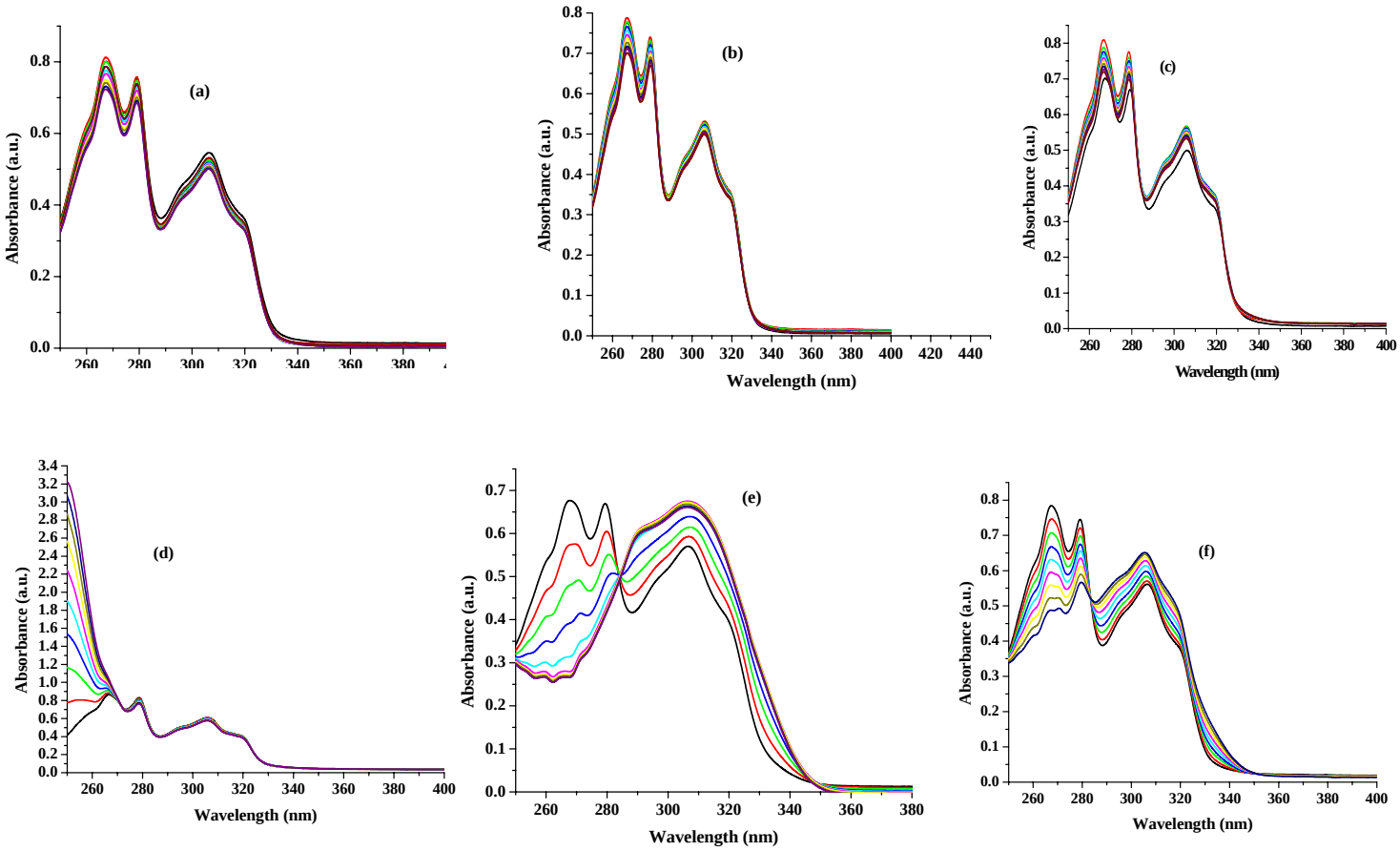


Figure S4. Change in absorbance of receptor **1** (c = 9.92 x 10^{-5} M) with (a) HSO_4^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) AcO^- (f) $H_2PO_4^-$ in CH_3CN (in all cases [anion] = 1x 10^{-3} M).

5. Emission profiles for 1a with the anions in $CHCl_3$ and CH_3CN.

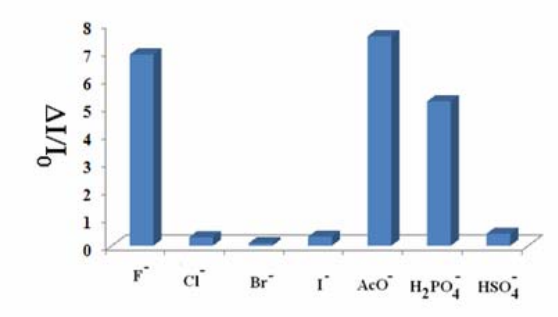


Figure S5. Change in fluorescence ratio at 382 nm for **1a** (c = 5.15 x 10^{-5} M) upon addition of 2 equiv of TBA salt of various anions in $CHCl_3$ (λ_{ex} = 310 nm).

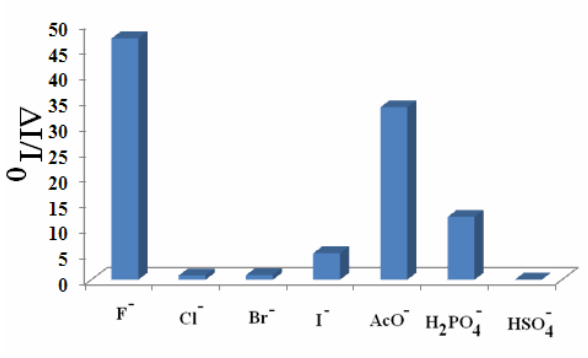


Figure S6. Change in fluorescence ratio at 395 nm for **1a** (c = 6.53 x 10^{-5} M) upon addition of 2 equiv of TBA salt of various anions in CH_3CN (λ_{ex} = 310 nm).

6. Relative emission change of 1 (taken in CH_3CN) upon addition of aq. solutions of potassium salts of different anions.

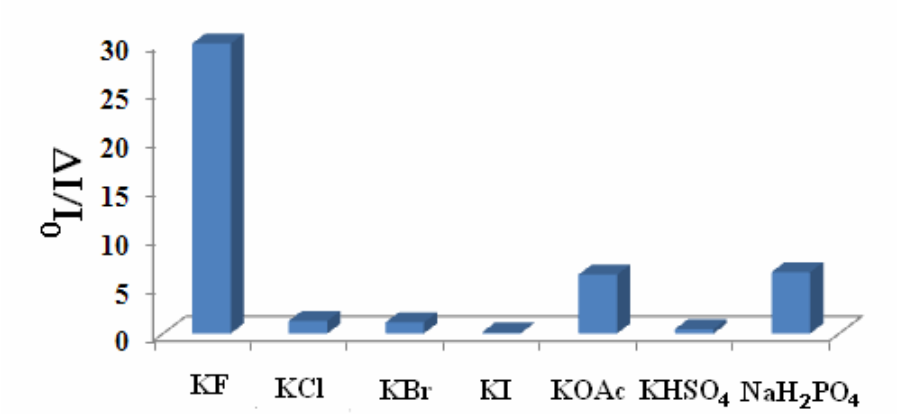


Figure S7. Relative fluorescence changes of **1** (c = 5.92 x 10^{-5} M) in CH_3CN after treatment with 1 equiv amounts of aqueous solution of different salts of various anion (λ_{ex} = 315 nm).

7. Selectivity study in aq. CH_3CN with **1**.

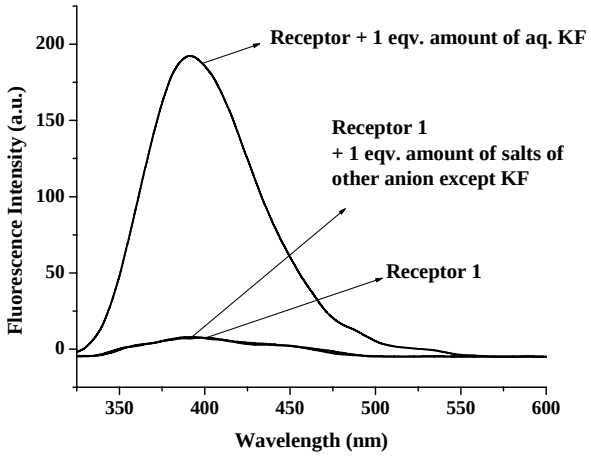


Figure S8. Change in emission of **1** (c = 5.92 x 10^{-5} M) in CH_3CN in presence and absence of 1 equivalent amounts of aqueous solution of fluoride and other anions (taken as their potassium salts).

8. Change in absorbance of receptor 2 with various anions in $CHCl_3$.

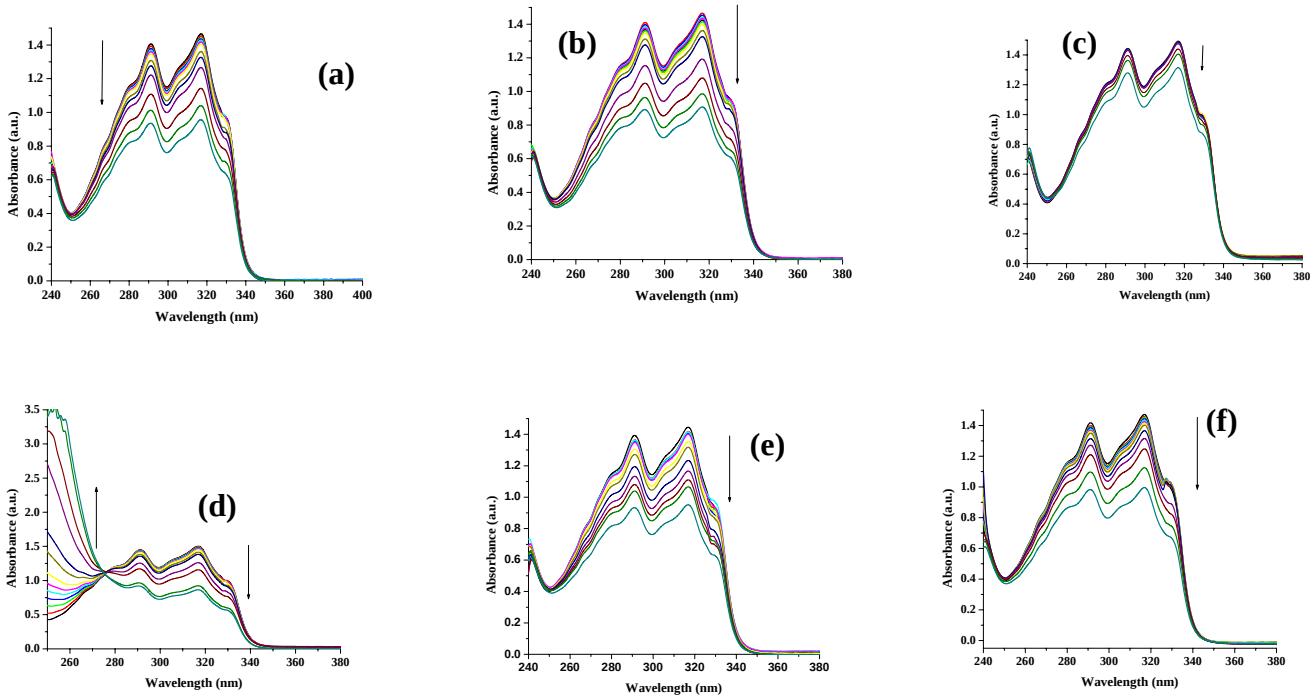


Figure S9. Change in absorbance of receptor **2** (c = 6.50 x 10^{-5} M) with (a) HSO_4^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) AcO^- (f) $H_2PO_4^-$ in $CHCl_3$ (in all cases [anion] = 1x 10^{-3} M).

9. Change in emission of receptor 2 with various anions in $CHCl_3$.

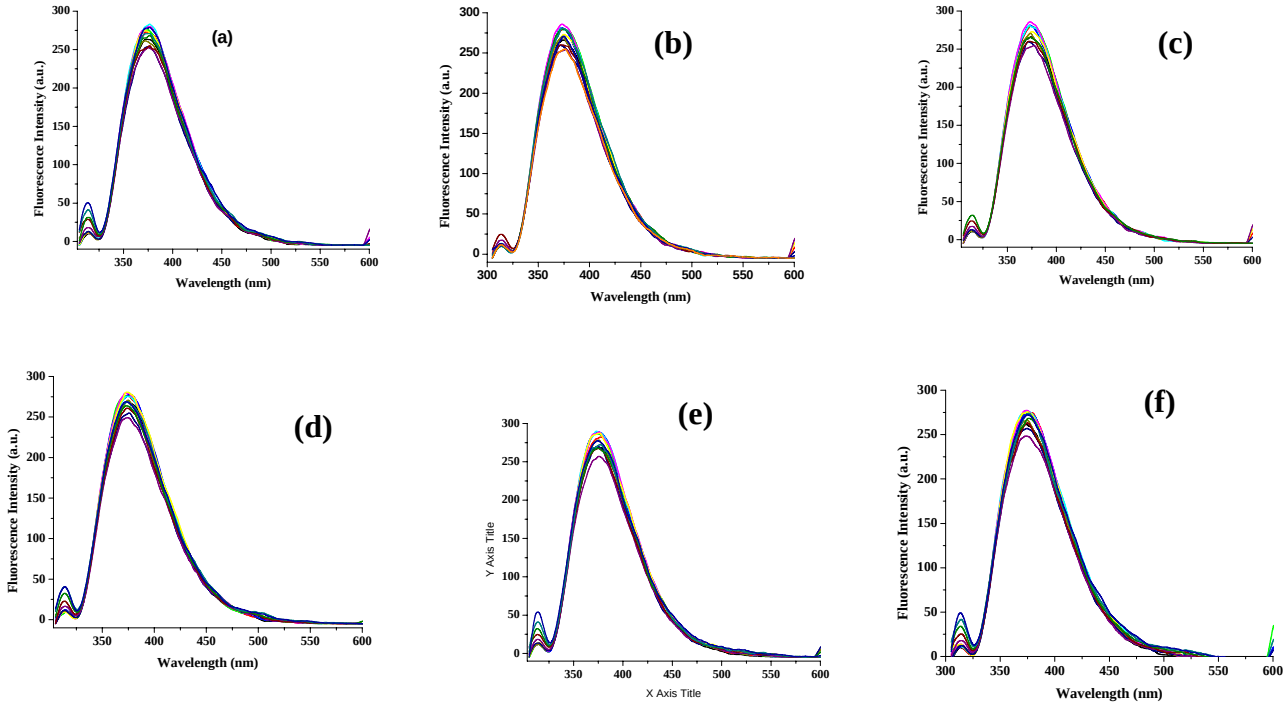


Figure S10. Fluorescence titration spectra for **2** (c = 6.50 x 10^{-5} M) with (a) HSO_4^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) AcO^- (f) $H_2P0_4^-$ in $CHCl_3$ (in all cases [anion] = 1x 10^{-3} M).

10. Color change for 2 and 2a in $CHCl_3$

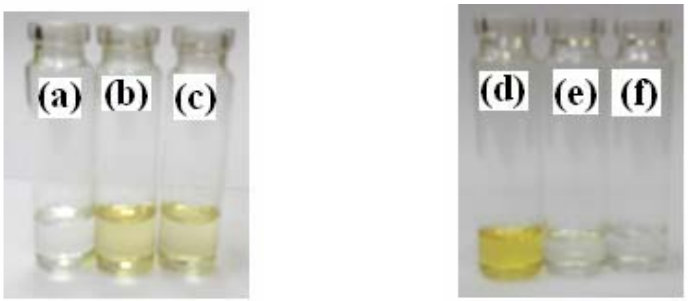


Figure S11. (a) Dicoumarol **2a** (c = 6.15x10^{-3} M) in $CHCl_3$, (b) Dicoumarol **2a** (c = 5.85x10^{-3} M) with 10 equivalent amounts of tetrabutylamonium hydroxide (c = 1x10^{-3} M) ion in $CHCl_3$, (c) dicumarol **2a** (c = 5.78x10^{-3} M) with 10 equivalent amounts of tetrabutylamonium fluoride (c = 1x10^{-3} M) in $CHCl_3$, (d) compound **2** (c= 6.28x10^{-3} M) with 10 equivalent amounts of tetrabutylamonium fluoride ion (c = 1x10^{-3} M) in $CHCl_3$, (e) Compound **2** (c = 6.36 x 10^{-3} M) in $CHCl_3$, (f) compound **2** (c = 6.28 x 10^{-3} M) with 10 equivalent amounts of tetrabutylamonium hydroxide ion (c = 1 x 10^{-3} M) in $CHCl_3$.

11. Change in emission of 2 and 2a in the presence of large excess of F^- in $CHCl_3$.

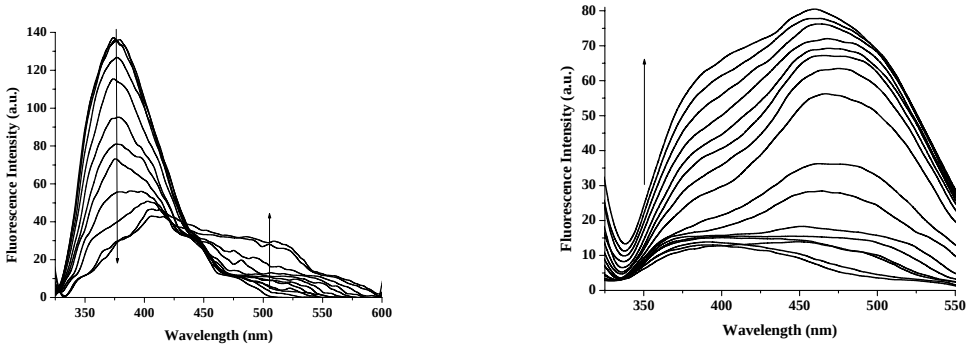


Figure S12. (a) Change in emission of **2** (c = 5.85 x 10^{-5} M) in the presence of 43 equivalent amounts of tetrabutylammonium salts of F^- in $CHCl_3$; (b) Change in emission of **2a** (c = 6.01 x 10^{-5} M) in the presence of 15 equivalent amounts of tetrabutylammonium fluoride.

12. Change in absorbance of receptor 2 with various anions in CH_3CN.

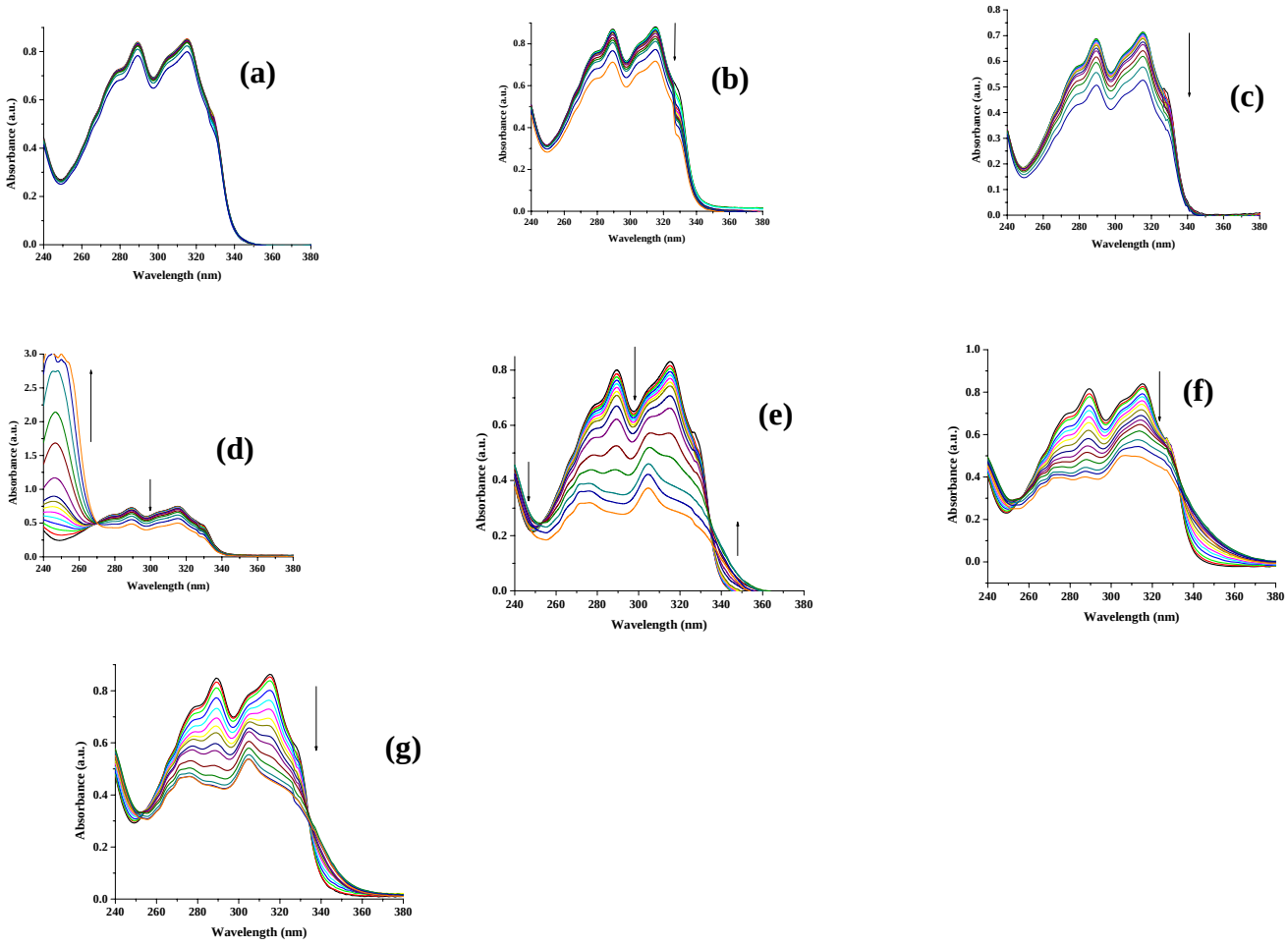


Figure S13. Change in absorbance of receptor **2** (c = 3.50 x 10^{-5} M) with (a) HSO_4^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) F^-, (f) AcO^- and (g) $H_2P0_4^-$ in CH_3CN (in all cases [anion] = 1x 10^{-3} M).

13. Change in emission of receptor 2 with various anions in CH_3CN.

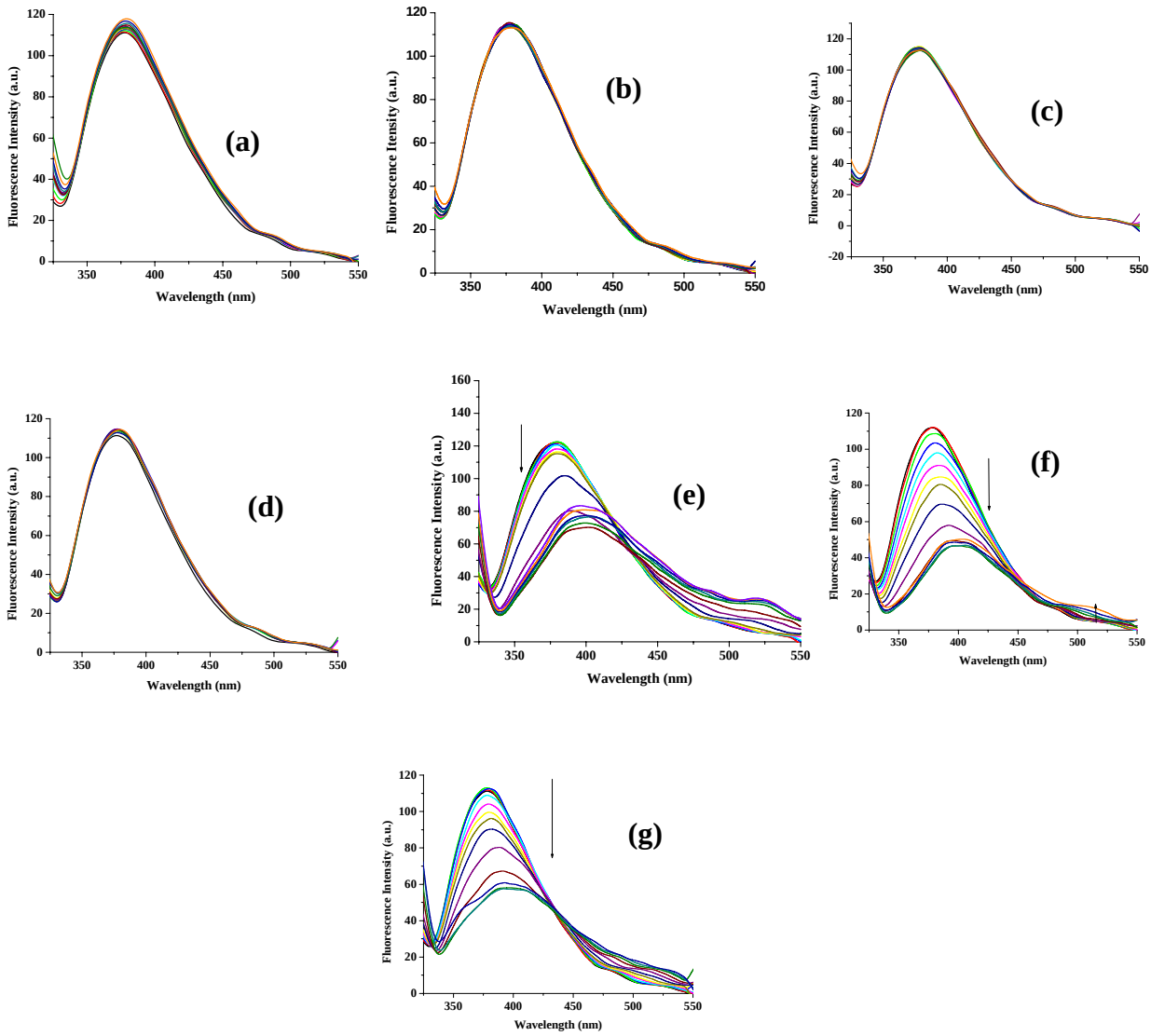


Figure S14. Fluorescence titration spectra for **2** (c = 3.50 x 10^{-5} M) with (a) HSO_4^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) F-(f)AcO^-, (g) $H_2P0_4^-$ in CH_3CN (in all cases [anion] = 1x 10^{-3} M).

14. Color change for 2 in CH_3CN

Figure S15. The photographs of solutions under ambient light of (a) **2** (c = 5.68 x 10^{-3} M) itself and in presence of 15 equivalent amounts of tetrabutylammonium salts of different anions in CH_3CN.

15. Selectivity study in $CHCl_3$ with 2.

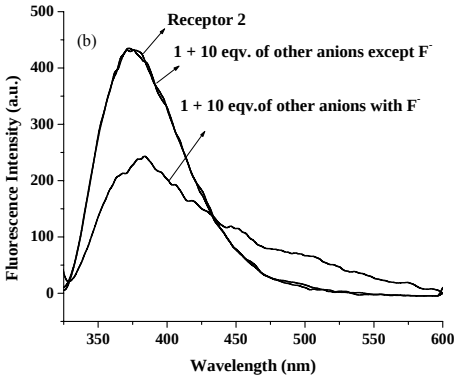


Figure S16. Change in emission of **2** (c = 6.10 x 10^{-5} M) in presence and absence of 10 equivalent amounts of fluoride and other anions (taken as their tetrabutylammonium salts) in $CHCl_3$.

16. Change in fluorescence ratio for 2 and 2a in CH_3CN

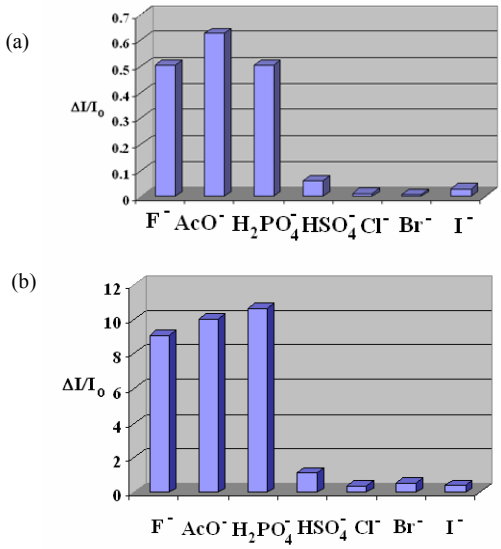


Figure S17. (a) Change in fluorescence ratio at 378 nm for (a) **2** (c = 3.5 x 10^{-5} M) and (b) **2a** (c = 6.19 x 10^{-5} M) upon addition of 15 equiv of TBA salt of various anions in CH_3CN (λ_{ex} for **2** and **2a** are 315 nm and 310 nm, respectively).

17. Selectivity study in aq. CH_3CN with 2.

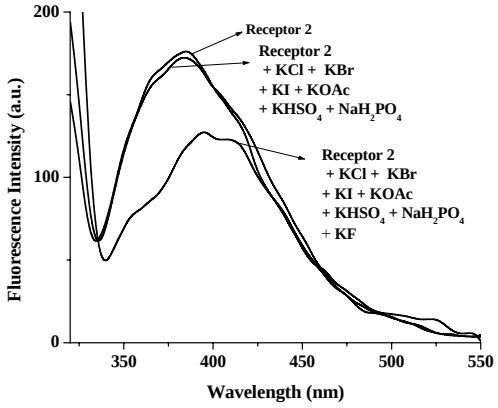


Figure S18. Change in emission of **2** (6.35 x 10^{-5} M) in CH_3CN upon addition of 10 equiv. amounts of aq. solution of KF (c = 2 x 10^{-3} M) to **2** containing other anions in 5 equivalent amounts.

18. ^{1}H NMR change for 1 with F^- in $CDCl_3$.

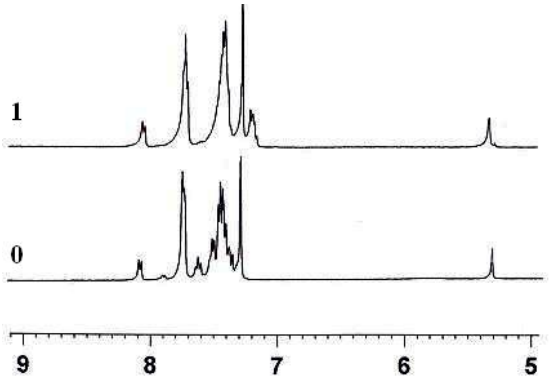


Figure S19..Partial ^{1}H NMR (400 MHz) of **1** (*c* = 3.85 x 10^{-3} M) in the absence and presence of equivalent amount of tetrabutylammonium fluoride in $CDCl_3$. (the number indicates the equivalent amounts added)

19. **Rate constant determination for 2 in aq. CH_3CN**

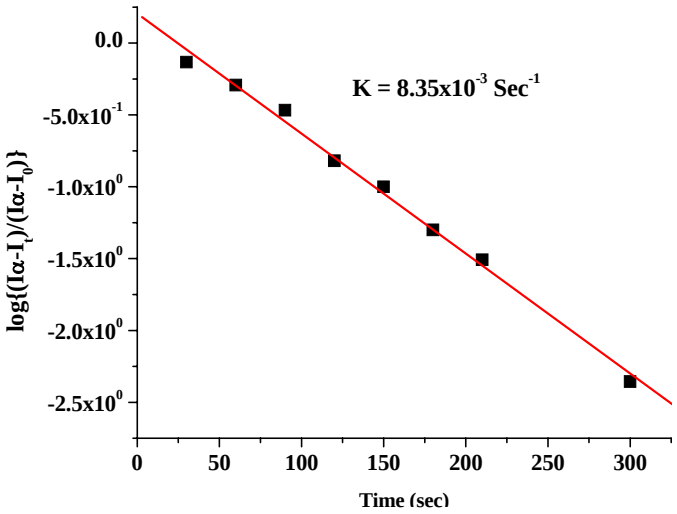


Figure S20. Plot for first order reaction of **2** with F^- in aq. CH_3CN.

20. **Rate constant determination for 2 in $CHCl_3$**

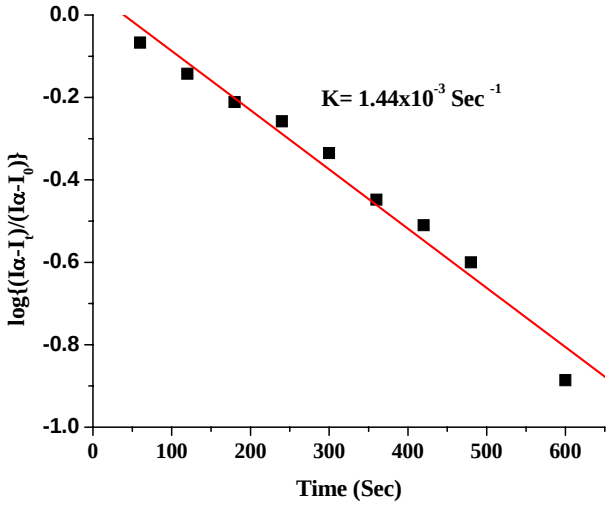


Figure S21. Plot for first order reaction of **2** with F^- in $CHCl_3$.

21. Fluorescence profile of 1 with different concentrations of aq. KF.

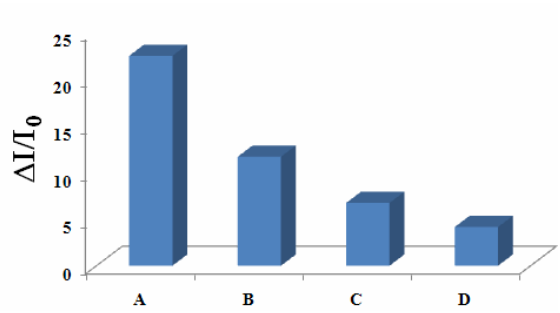


Figure S22. Change in fluorescence ratio ($\Delta I/I_0$) of **1** upon addition of 1 equivalent amount of aqueous solution of KF of different concentrations (A = 2 x 10^{-3} M; B = 2 x 10^{-4} M; C= 10^{-5} M; D = 2 x 10^{-6} M).

22. Fluorescence profile of 1 with different concentrations of aq. KF.

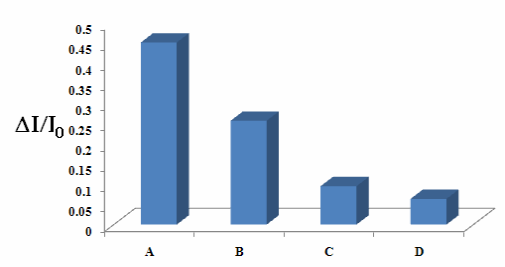


Figure S23. Change in fluorescence ratio ($\Delta I/I_0$) of receptor **2** upon addition of 2.5 equivalent amounts of aqueous solution of KF of different concentrations (A = 2 x 10^{-3} M; B = 2 x 10^{-4} M; C= 10^{-5} M; D = 2 x 10^{-6} M).

23. DST optimized geometries.

(a) (b)

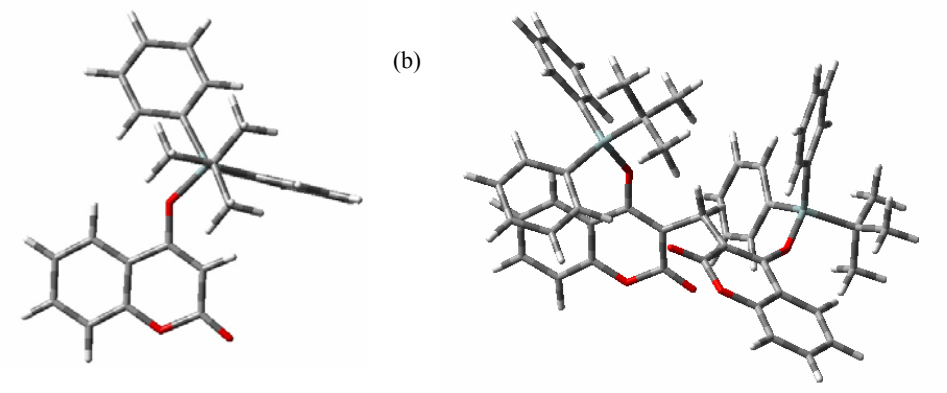


Figure S24. DFT optimized geometries of (a) **1** and (b) **2** in gas phase.

24. MTT assay.

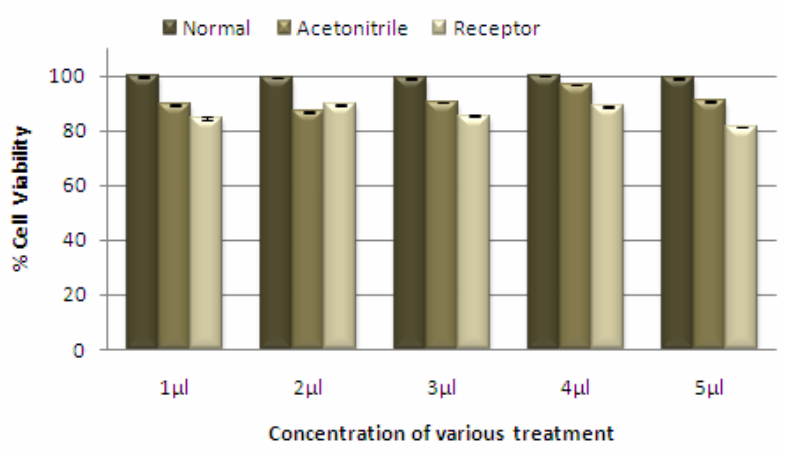


Figure S25. MTT assay for receptor **1**.

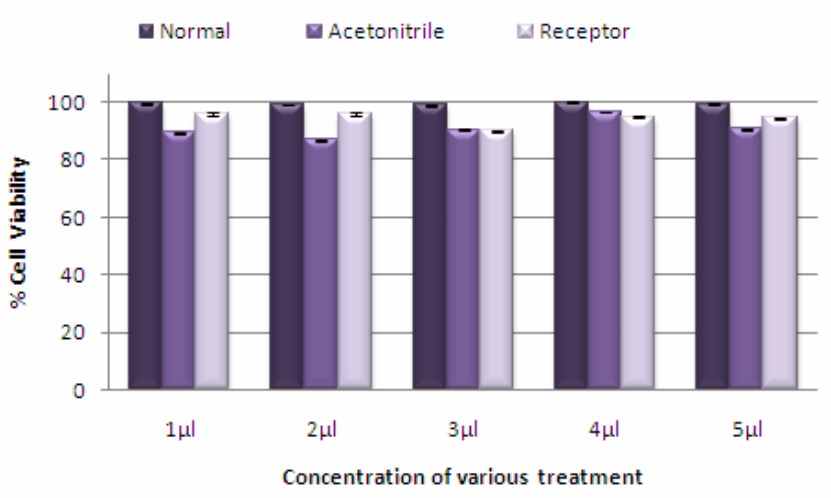
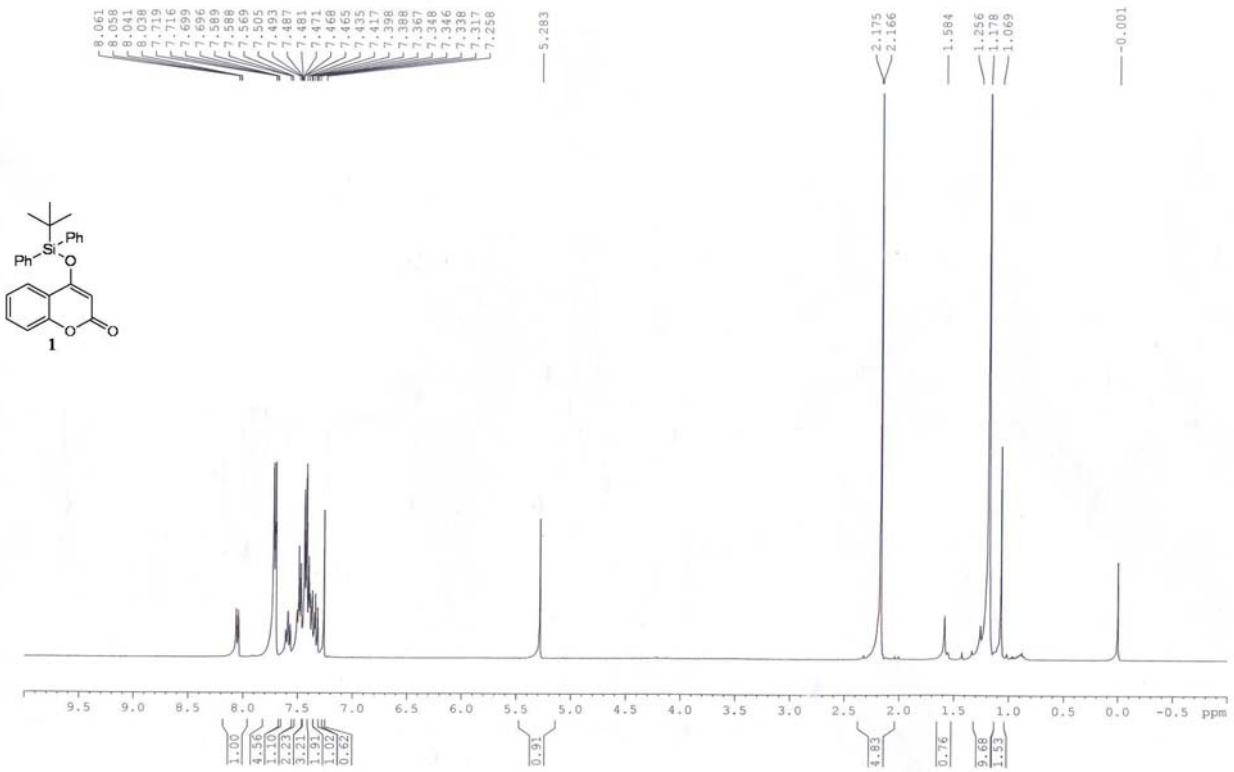
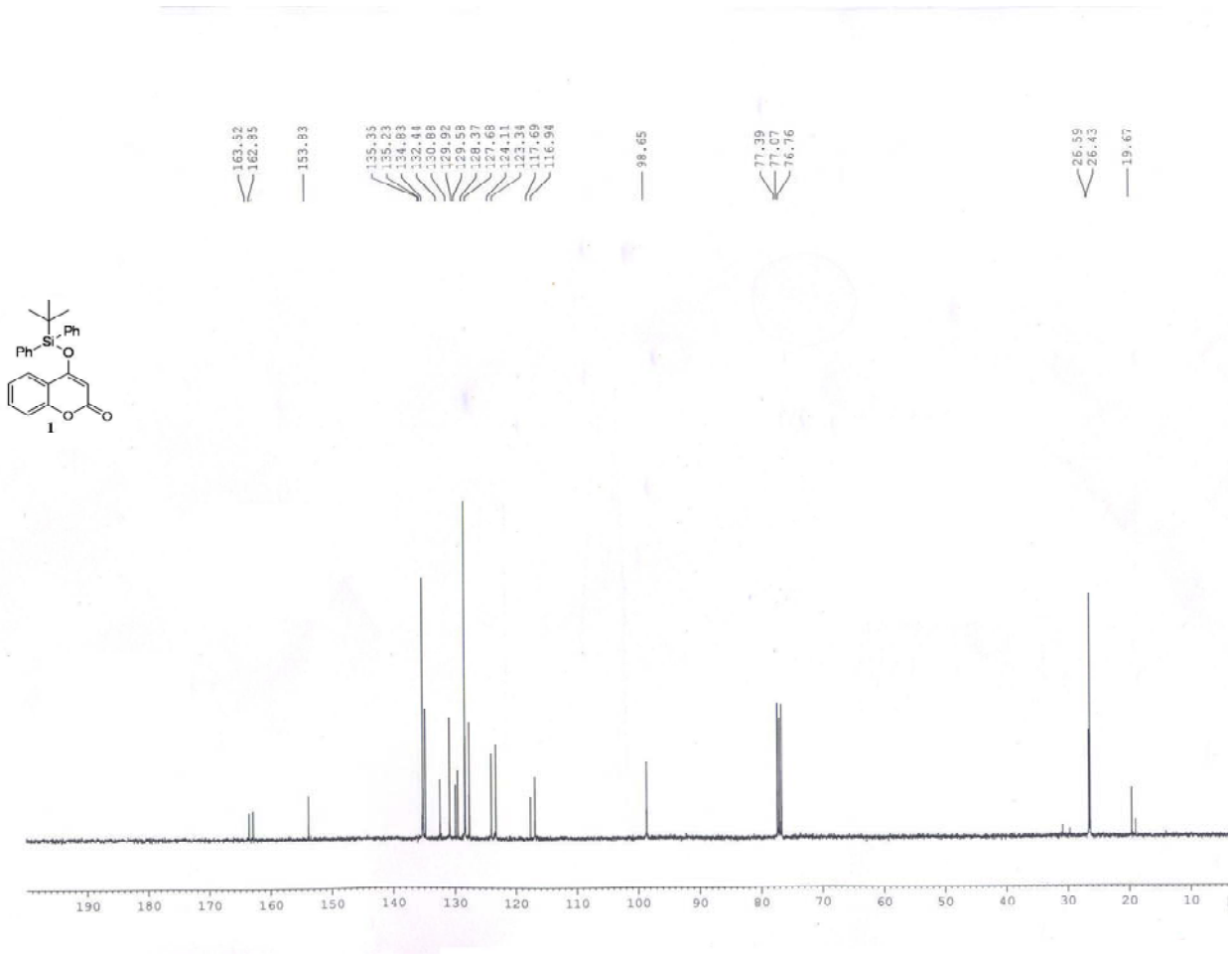


Figure S26.MTT assay for receptor **2**.

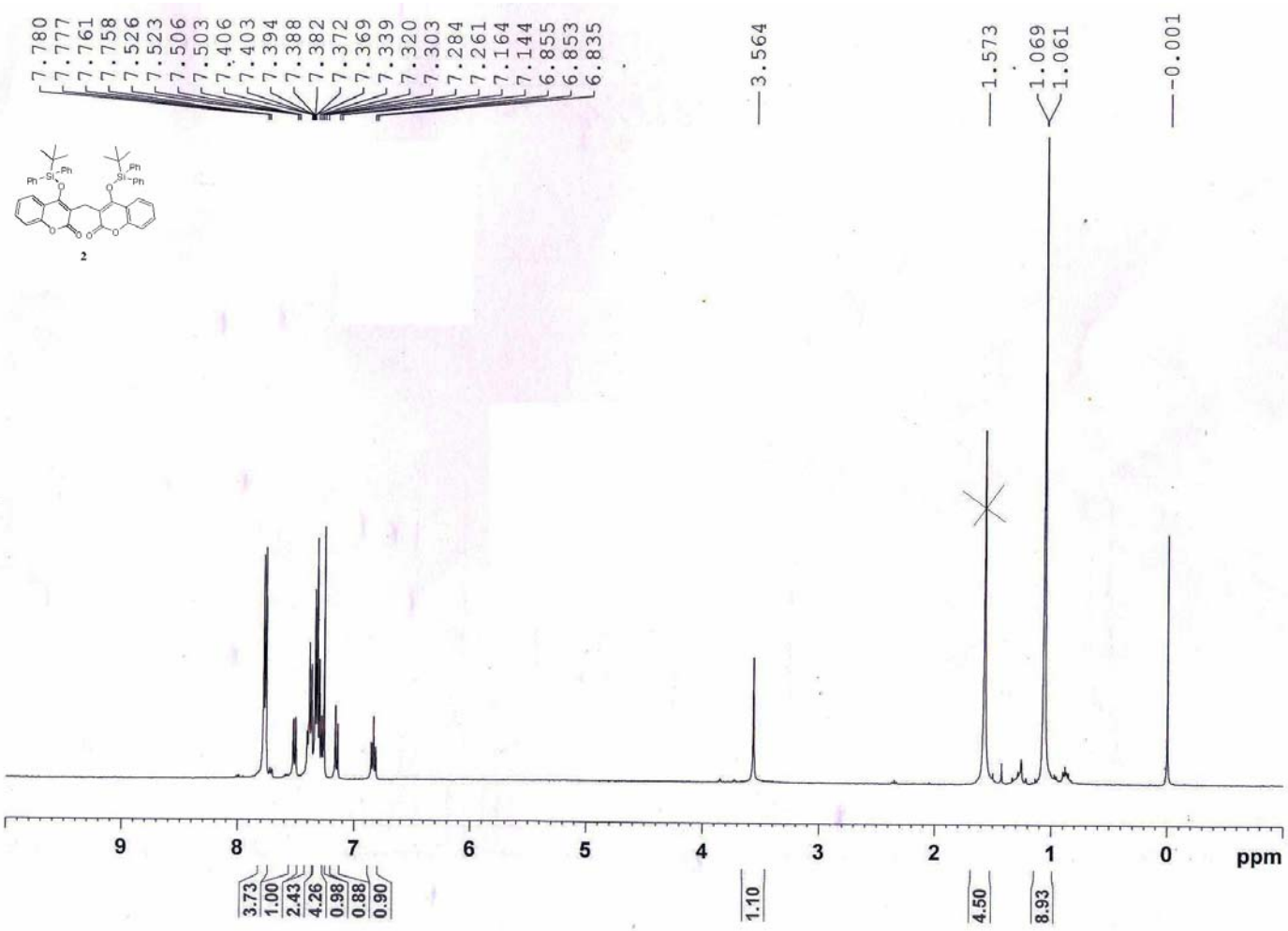
^{1}H NMR (400 MHz, $CDCl_3$) of 1



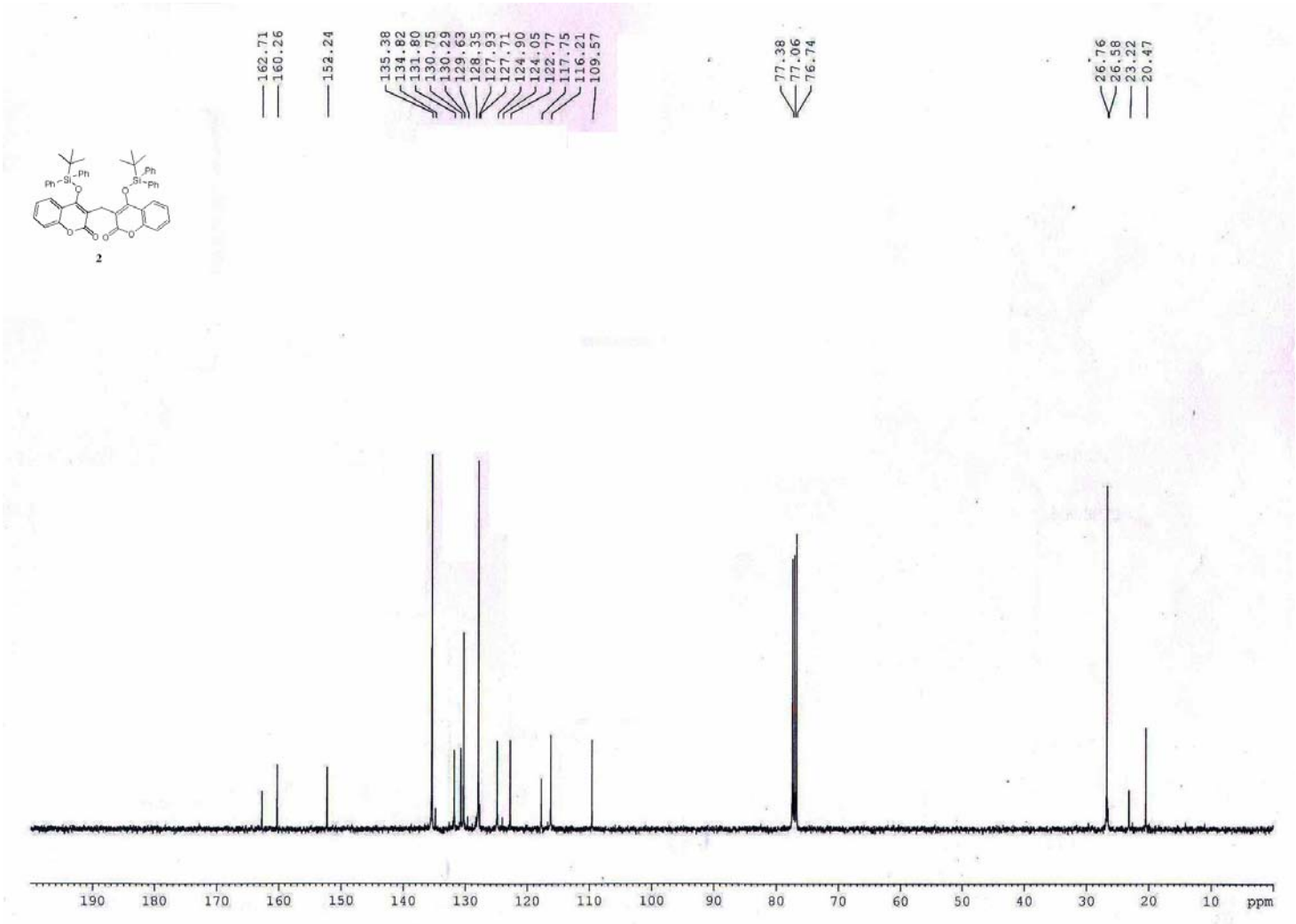
^{13}C NMR (100 MHz, $CDCl_3$) of 1



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



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



Mass of 2