Electronic supporting information:

Tris(indolyl)methene molecule as an anion receptor and colorimetric chemosensor: tunable selectivity and sensitivity for anions

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This work was supported by the National Natural Science Foundational of China (Grant No. 0672121) and the open fund of State Key Laboratory of Oxo Synthesis & Selective Oxidation (Grant No. OSSO2008kjk6).

General methods

^{1}H NMR spectra were recorded at 400 MHz with TMS as an internal standard. High resolution mass spectra were obtained by Fourier-transform ion cyclotron resonance mass spectrometer, all new compounds were further characterized by HRMS. Melting points are uncorrected. UV-vis spectra were recorded at room temperature. The tetra-n-butylammonium fluoride was purchased from Fluka, the other tetra-n-butylammonium (Bu_4N^+) salts of different anions were purchased from Alfa Aesar. CH_3CN was used the chromatographically pure.

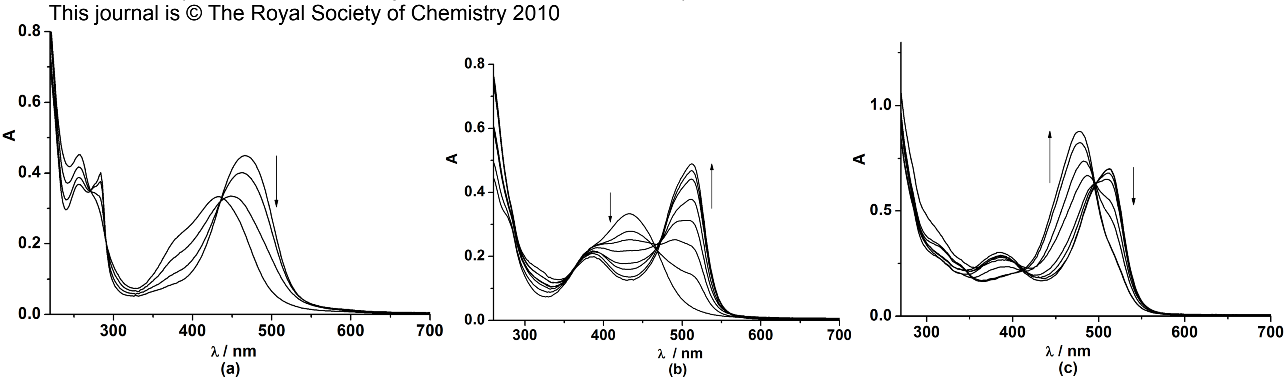


Fig. S1 The changes in UV-vis spectra of **1** recorded in CH_3CN (2.5×10^{-5} M) after addition of: (a) 0, 0.2, 0.6, 1 equiv. of OH^-; (b) 1, 5, 10, 15, 20, 25, 30, 35 equiv. of OH^-; (c) 35, 40, 45, 50, 55, 60, 80, 100 equiv. of OH^-.

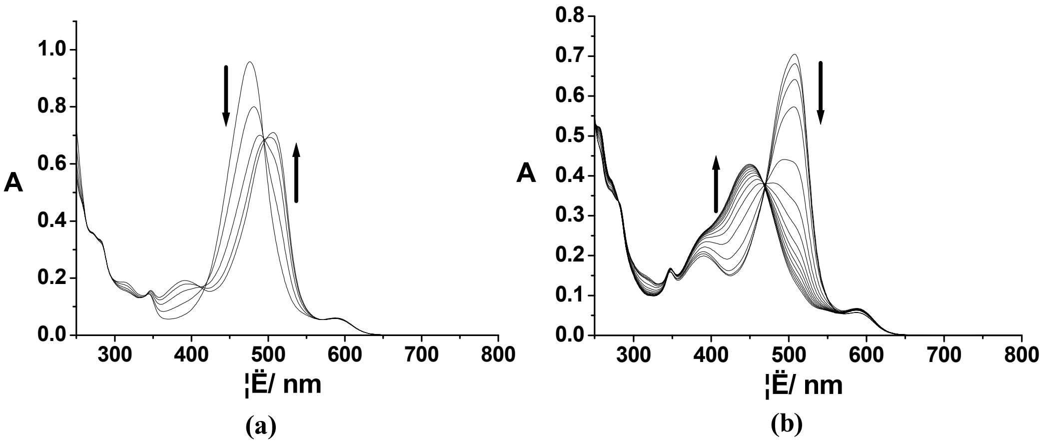


Fig. S2. Changes in UV-Vis spectra of **1** +200 equiv F^- recorded in CH_3CN (2.5×10^{-5} M) after addition of (a) 0, 1 (328.4 equiv), 2, 3, 4 μL of CH_3OH; (b) 5, 6, 7, 10, 12.5, 15, 17.5, 20, 22.5, 25, 27.5, 30, 32.5, 35, 37.5 μL of CH_3OH.

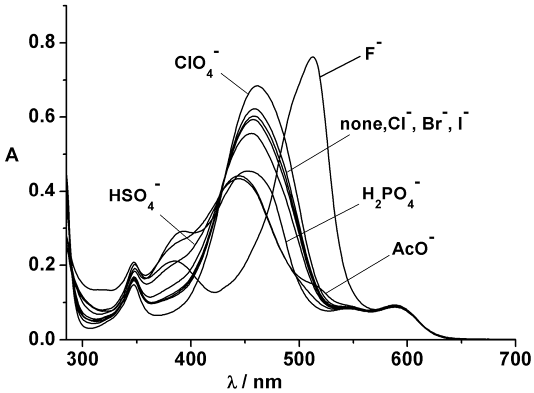


Fig. S3. UV-vis spectra of **1** recorded in CH_3CN (2.5×10^{-5} M) after addition of 25 equiv of various anions (none, F^-, AcO^-, Cl^-, Br^-, I^-, HSO_4^-, ClO_4^-, $H_2PO_4^-$).

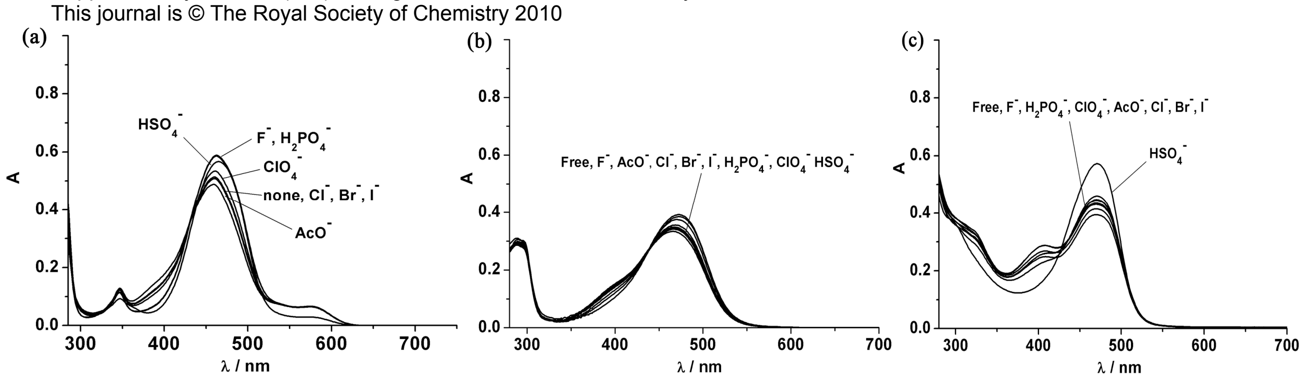


Fig. S4. UV-vis spectra of **1** (a), **2** (b), and **3** (c) recorded in CH_3CN/H_2O (4:1, v/v, 2.5×10^{-5} M) after addition of 25 equiv of various anions (none, F^-, AcO^-, Cl^-, Br^-, I^-, HSO_4^-, ClO_4^-, $H_2PO_4^-$).

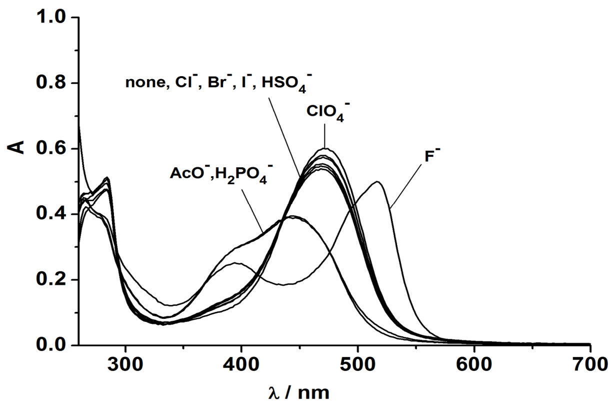


Fig. S5. UV-vis spectra of **1** recorded in DMSO (2.5×10^{-5} M) after addition of 25 equiv of various anions (none, F^-, AcO^-, Cl^-, Br^-, I^-, HSO_4^-, ClO_4^-, $H_2PO_4^-$).

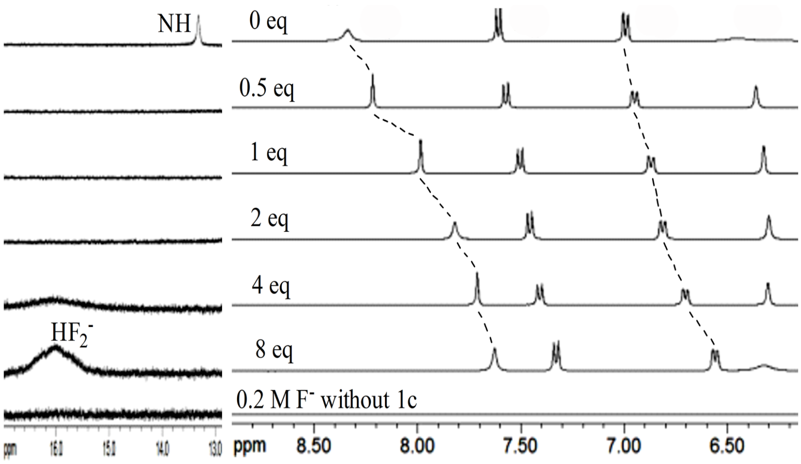


Fig. S6. ^{1}H NMR titration spectra of receptor **2** (2.5×10^{-2} M) in DMSO-d_6 solution with F^- (0, 0.5, 1, 2, 4, 8 equiv) and F^- alone (bottom), the dashed lines track the shift of the H_1 and H_3 signals.

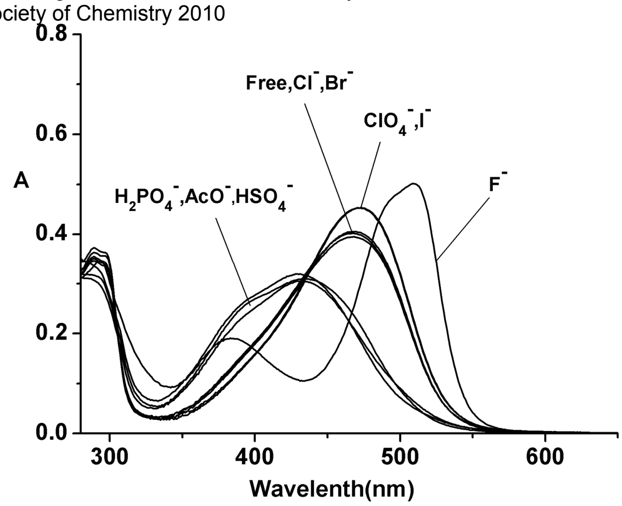


Fig. S7. UV-vis spectra of **2** recorded in CH_3CN (2.5×10^{-5} M) after addition of 25 equiv of various anions (none, F^-, AcO^-, Cl^-, Br^-, I^-, HSO_4^-, ClO_4^-, $H_2PO_4^-$).

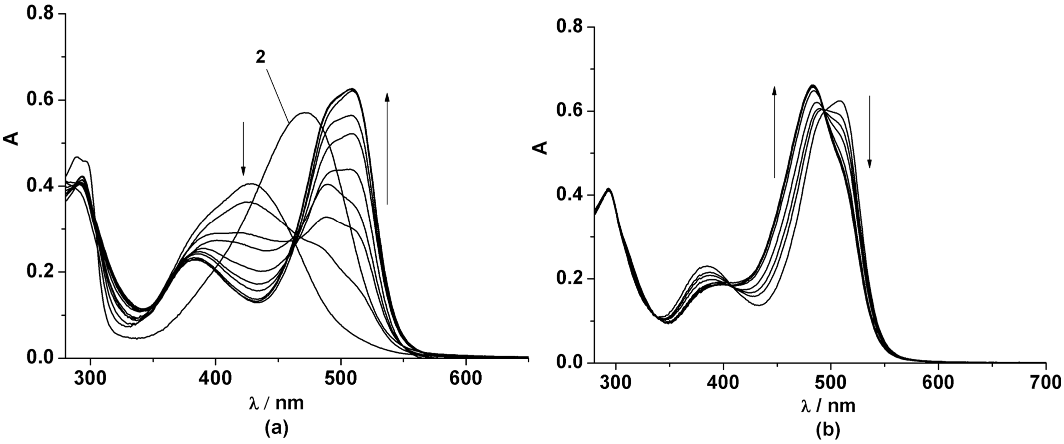
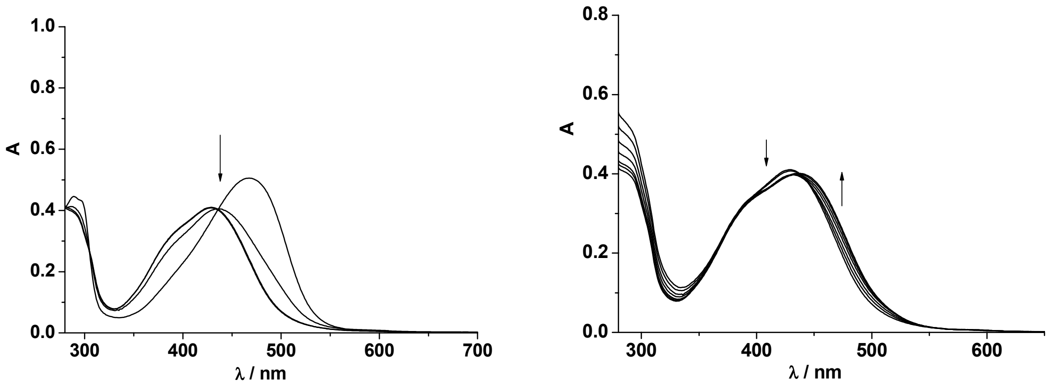
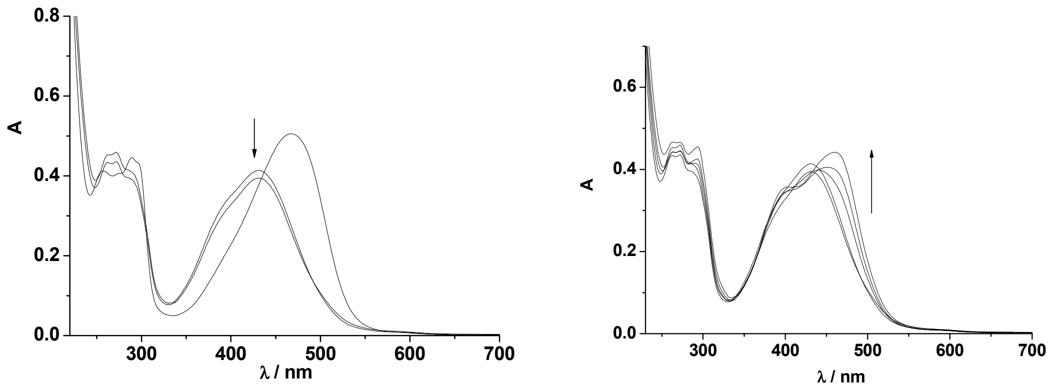


Fig. S8. The changes in UV-vis spectra of **2** recorded in CH_3CN (2.5×10^{-5} M) after addition of: (a) 0, 2, 4, 6, 8, 10, 15, 20, 30, 40, 60 equiv of F^-; (b) 60, 80, 100, 120, 140, 160, 180, 200 equiv of F^-.



(a) (b)

Fig. S9. The changes in UV-vis spectra of **2** (2.5×10^{-5} M) measured in MeCN after addition of (a) 0, 0.5, 1, 2 equiv of AcO^-; (b) 2, 10, 30, 60, 100, 150, 200 equiv of AcO^-.



(a) (b)

Fig. S10. The changes in UV-vis spectra of **2** (2.5×10^{-5} M) measured in MeCN after addition of (a) 0, 0.5, 1, 2 equiv of $H_2PO_4^-$; (b) 2, 10, 50, 100, 200 equiv of $H_2PO_4^-$.

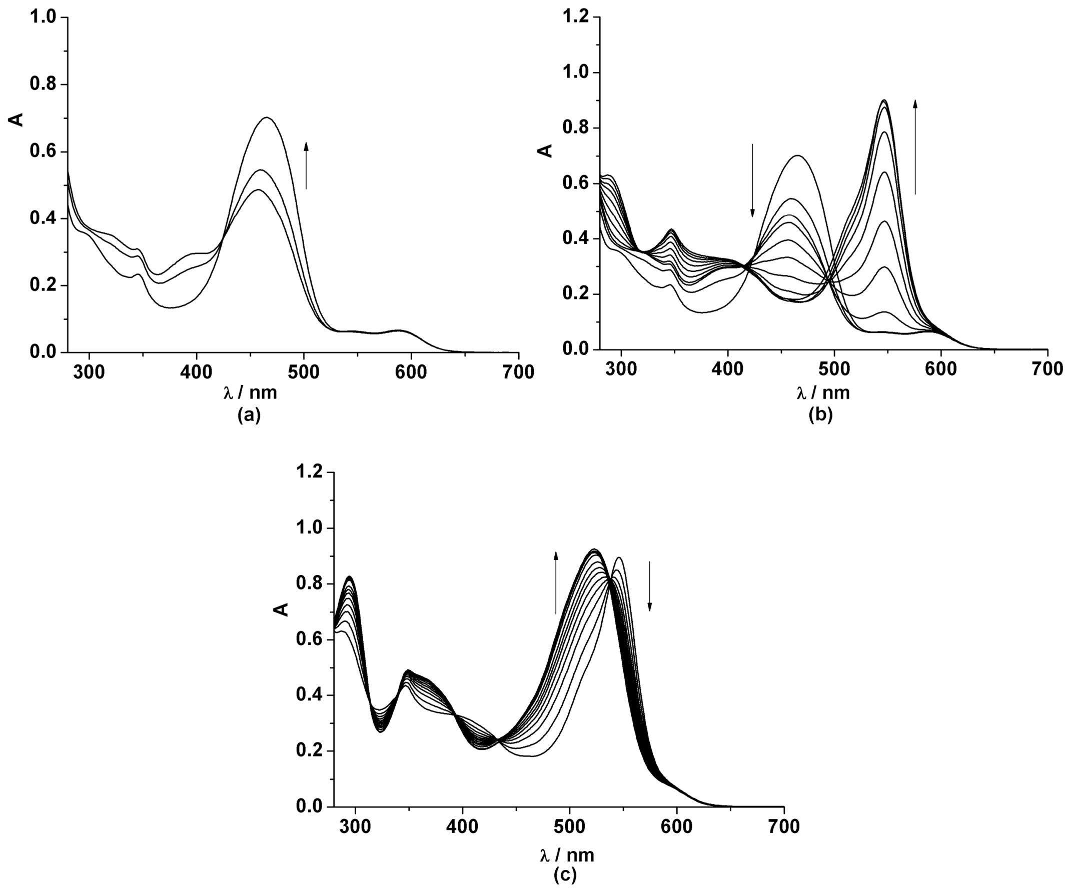
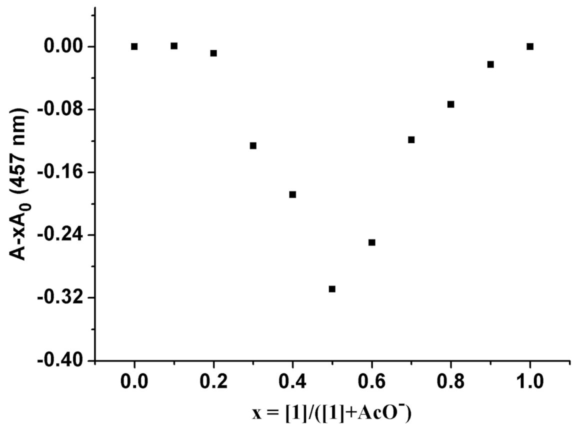


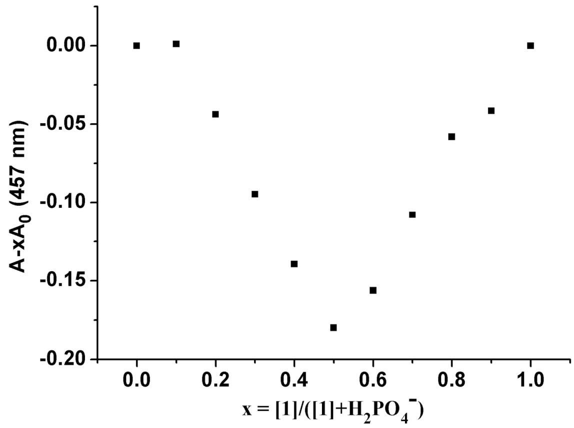
Fig. S11. The changes in UV-vis spectra of **3** recorded in CH_3CN (2.5×10^{-5} M) after addition of: (a) 0, 0.2, 0.4 equiv of F^-; (b) 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, 2 equiv of F^-; (c) 2, 2.5, 3, 3.5, 4, 6, 8, 10, 20, 50, 100 equiv of F^-.

The Job's plots and the equilibrium constants of receptors 1-3 with three basic anions.

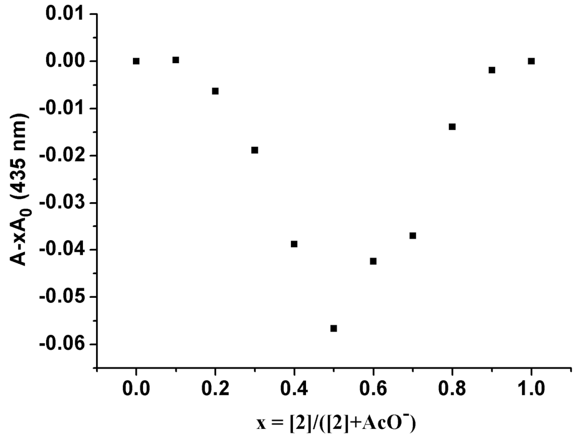
1. The Job's plots of the receptors with AcO^- and $H_2PO_4^-$.[1-2]

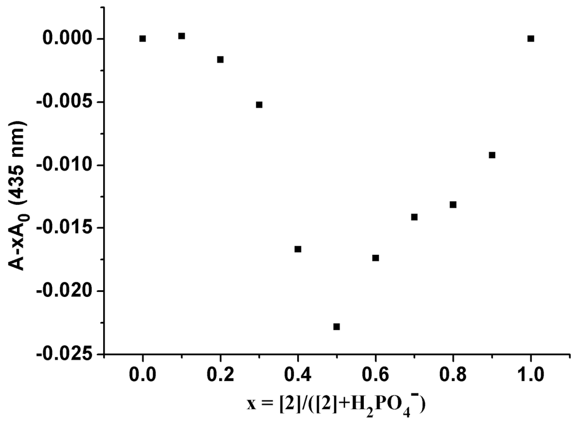
(1) Job's plot of **1** with AcO^- and $H_2PO_4^-$ by UV-vis spectroscopy in CH_3CN at 25 ºC. [1] + [Anion] = 10^{-4} M.



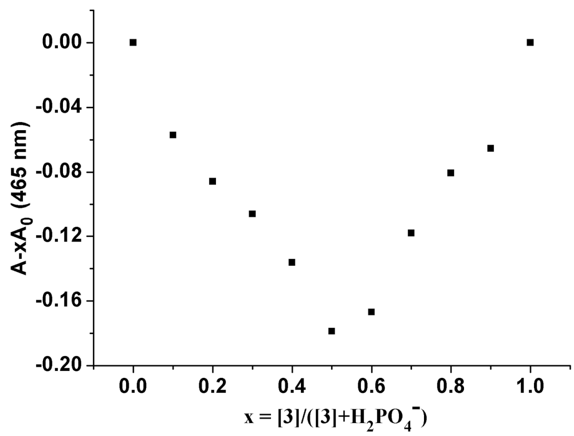


(2) Job's plot of **2** with AcO^- and $H_2PO_4^-$ by UV-vis spectroscopy in CH_3CN at 25 ºC. [**2**] + [Anion] = 10^{-4} M.





(3) Job's plot of **3** with $H_2PO_4^-$ by UV-vis spectroscopy in CH_3CN at 25 ºC. [**3**] + [Anion] = 10^{-4} M.



2. The equilibrium constants of receptors **1-3** with three basic anions.

(1) The fitting method of the equilibrium constants.

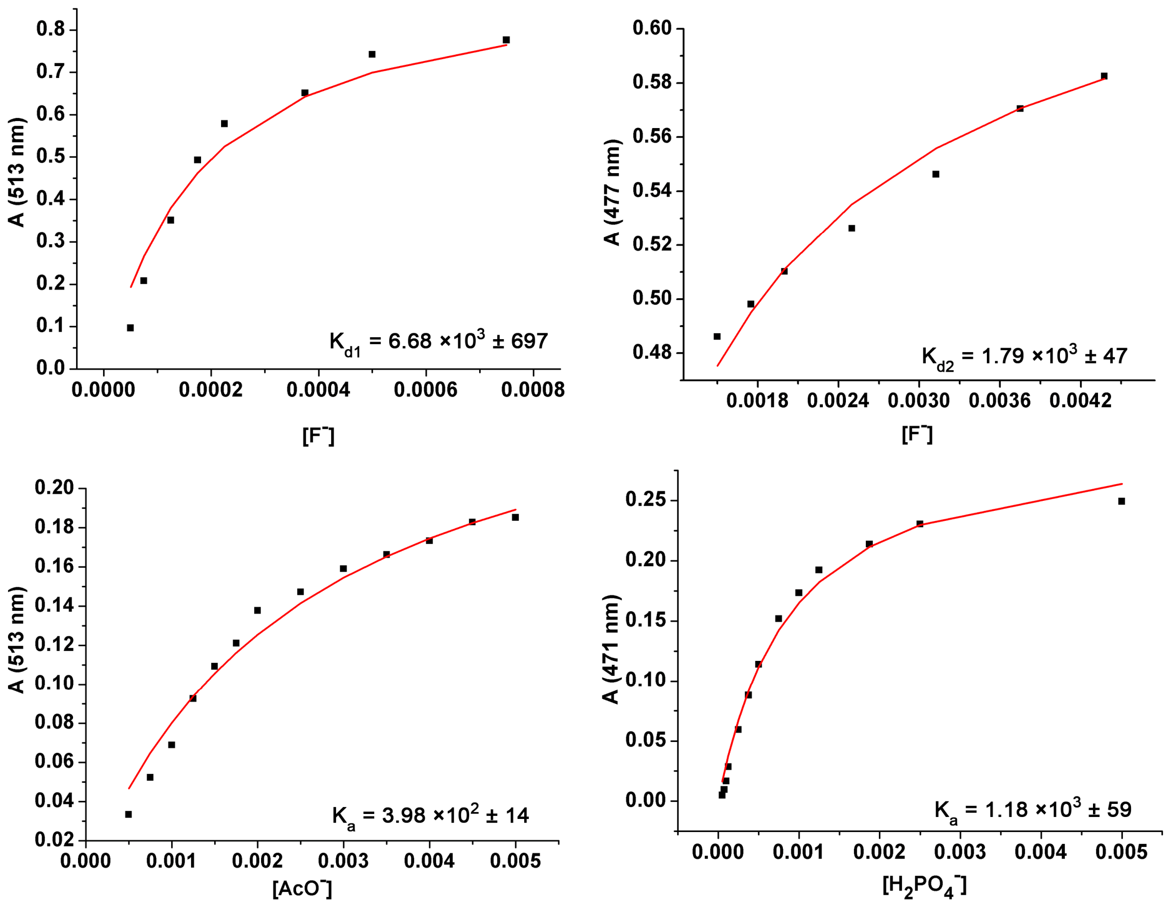
The stepwise disassociation constants of receptors **1-3** with F^- or AcO^- were calculated according to the following two equilibria developed by Fabbrizzi's group and Gunnlaugsson's group:[3-4]

$$[LH_2\cdots X]^- + X^- \overset{K_{d1}}{\rightleftharpoons} [LH]^- + [HX_2]^- \quad (1)$$

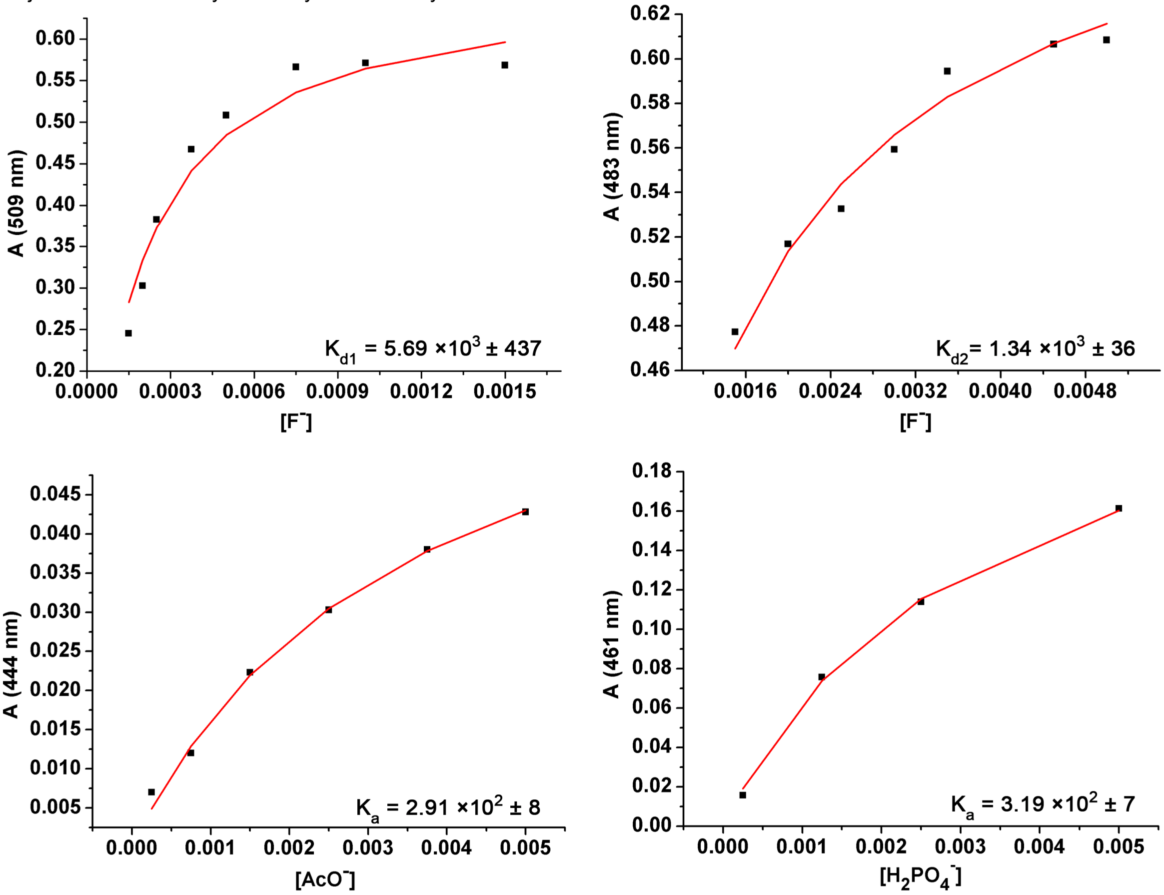
$$[LH\cdots X]^{2-} + X^- \overset{K_{d2}}{\rightleftharpoons} [L]^{2-} + [HX_2]^- \quad (2)$$

The disassociation and association constants of the receptors **1-3** with three anions were evaluated through nonlinear least squares fitting by origin software according to 1:1 stoichiometry.[5]

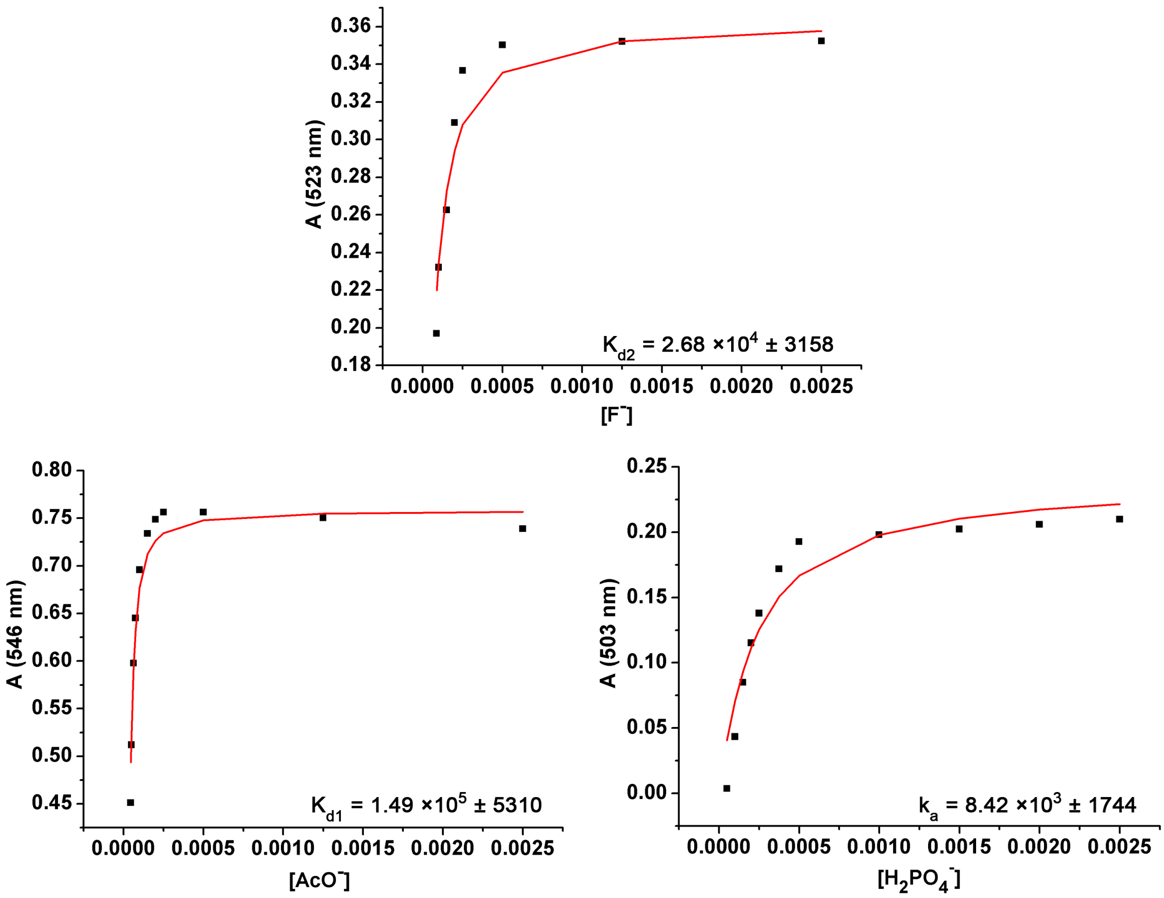
(2) The calculated equilibrium constants of receptors **1** with three basic anions (red line represents calculated result).



(3) The calculated equilibrium constants of receptors **2** with three basic anions (red line represents calculated result).

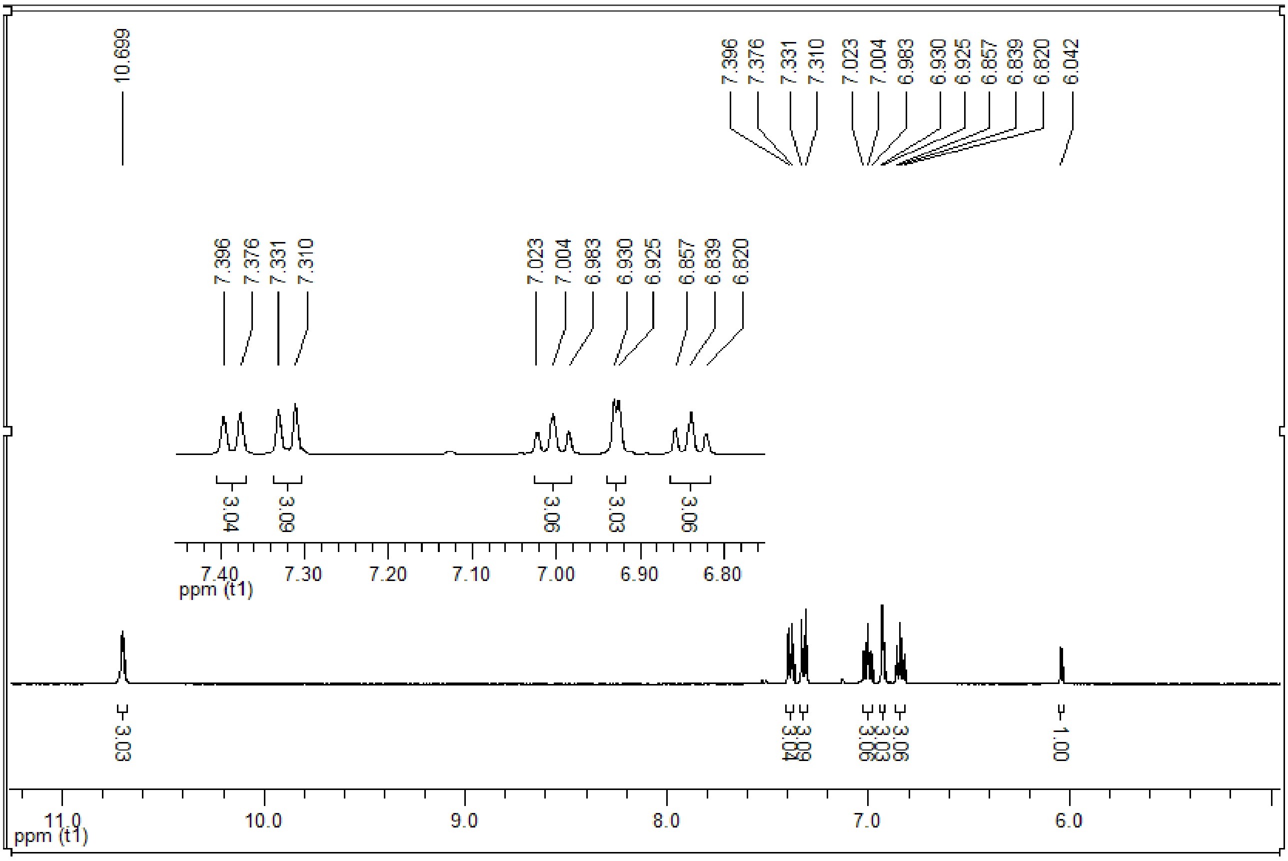


(4) The calculated equilibrium constants of receptors **3** with three basic anions (red line represents calculated result).

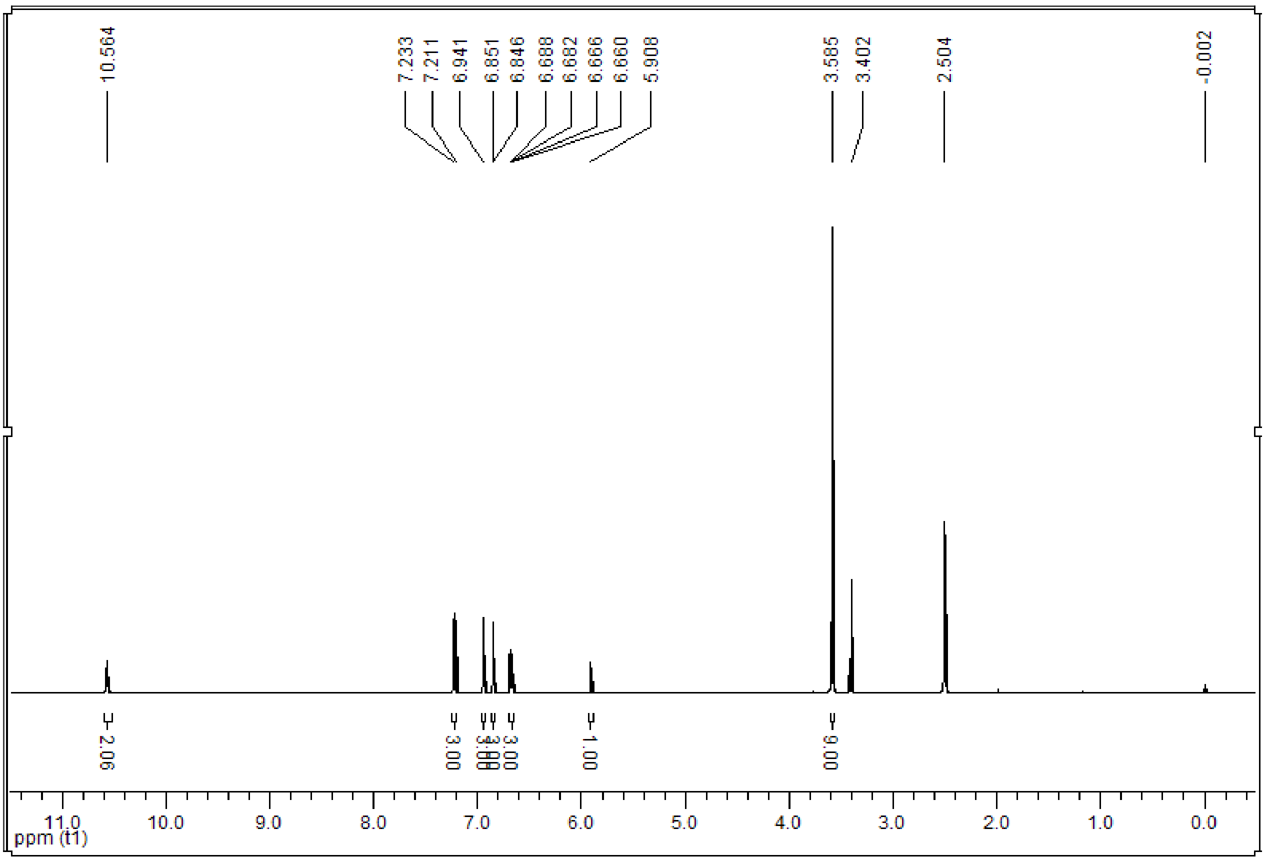


[1]H NMR spectra of 1-3

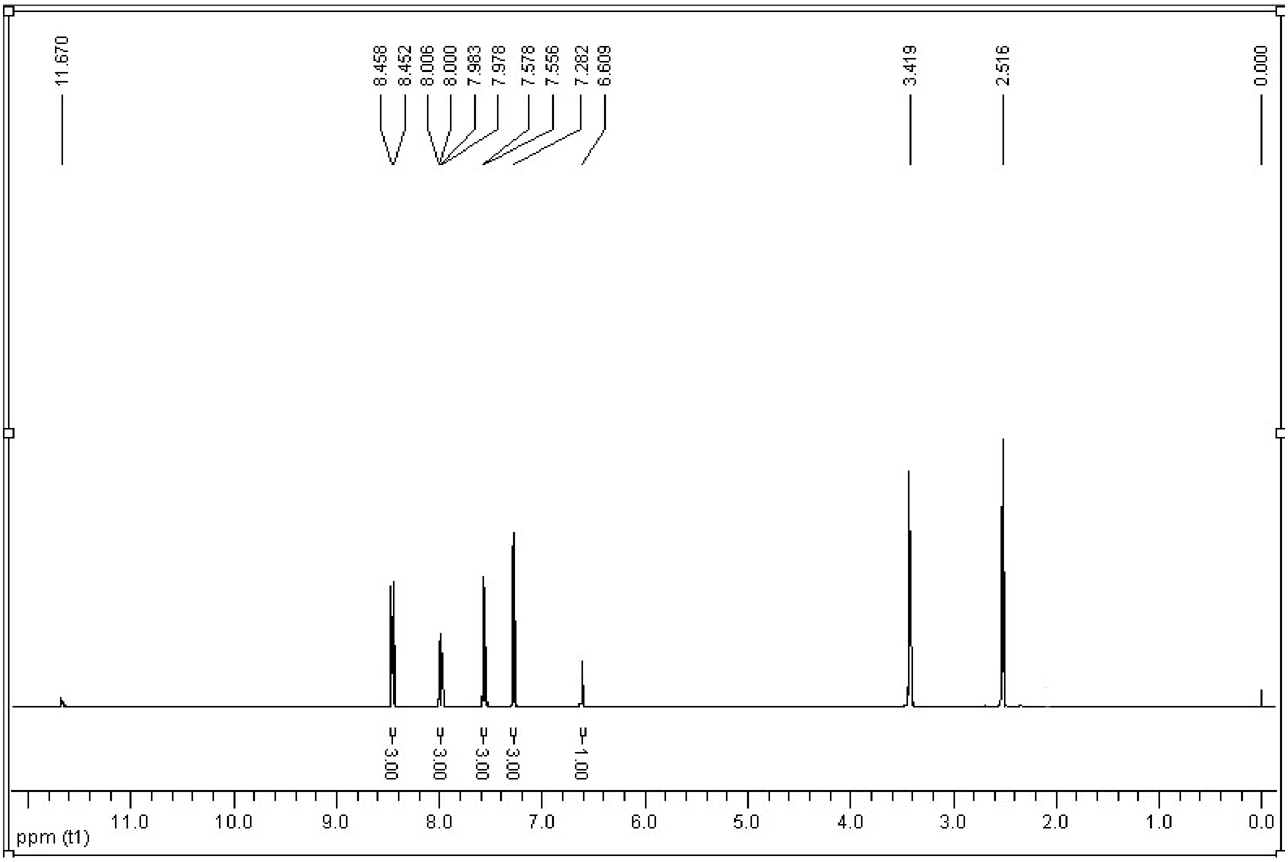
[1]H NMR of spectra of **1a** (400MHz, DMSO-d_6)



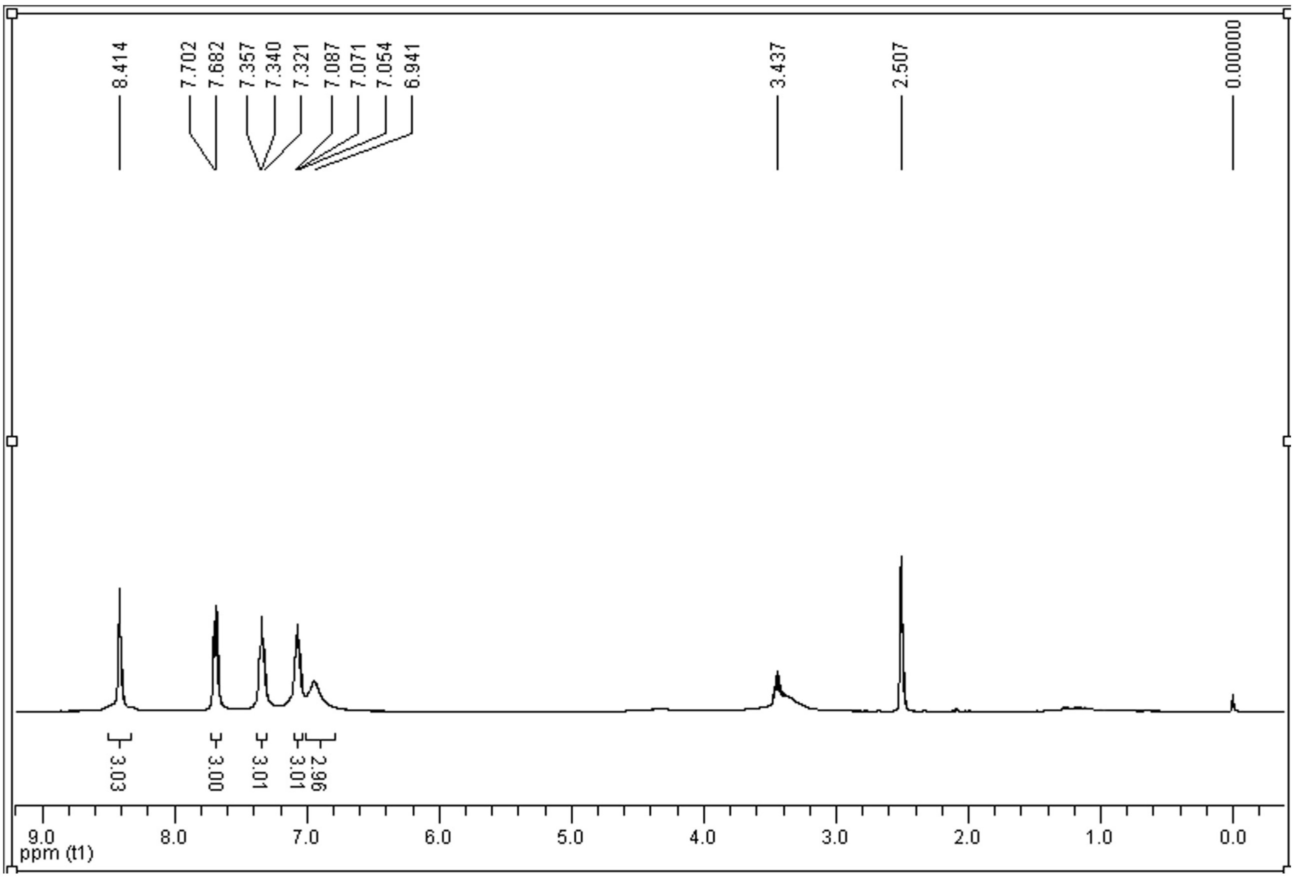
[1]H NMR of spectra of **2a** (400MHz, DMSO-d_6)



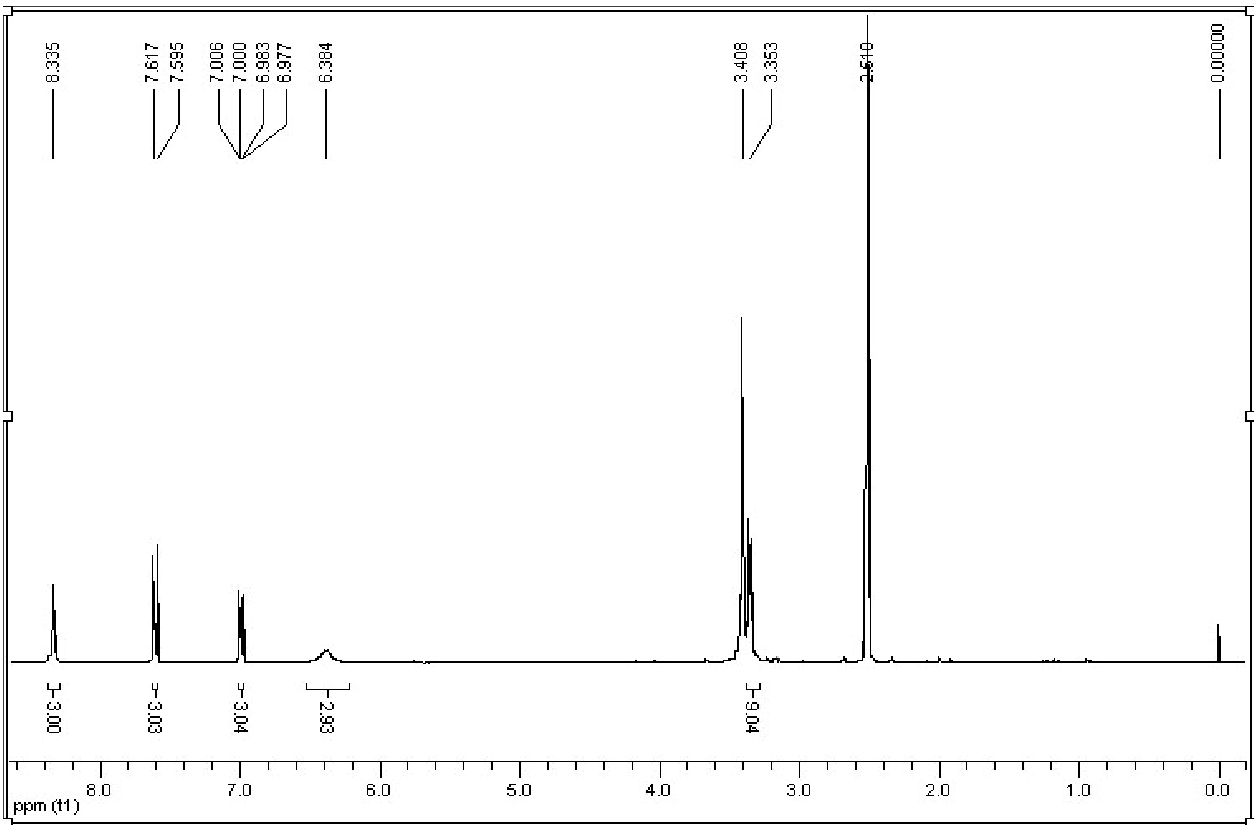
^{1}H NMR spectra of 3a (400MHz, DMSO-d_6)



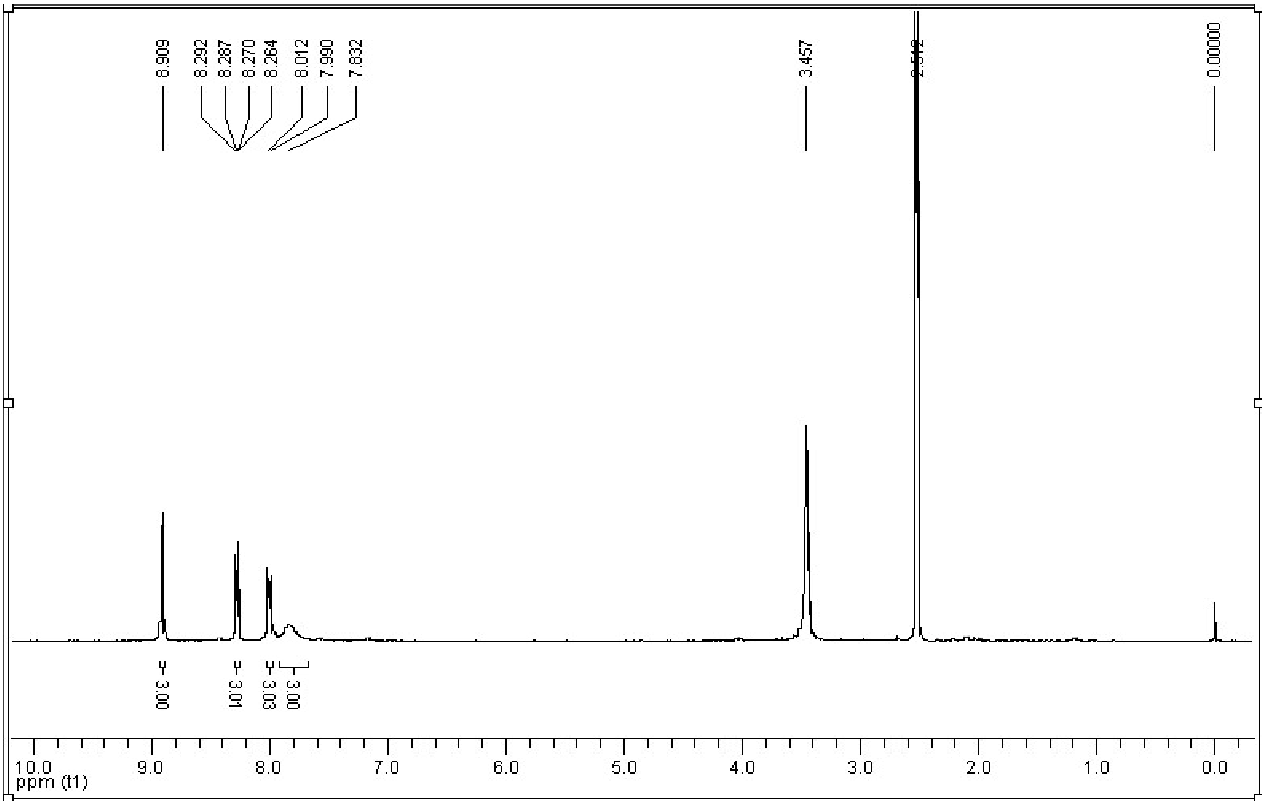
^{1}H NMR spectra of 1 (400MHz, DMSO-d_6)



^{1}H NMR of spectra of 2 (400MHz, DMSO-d_6)

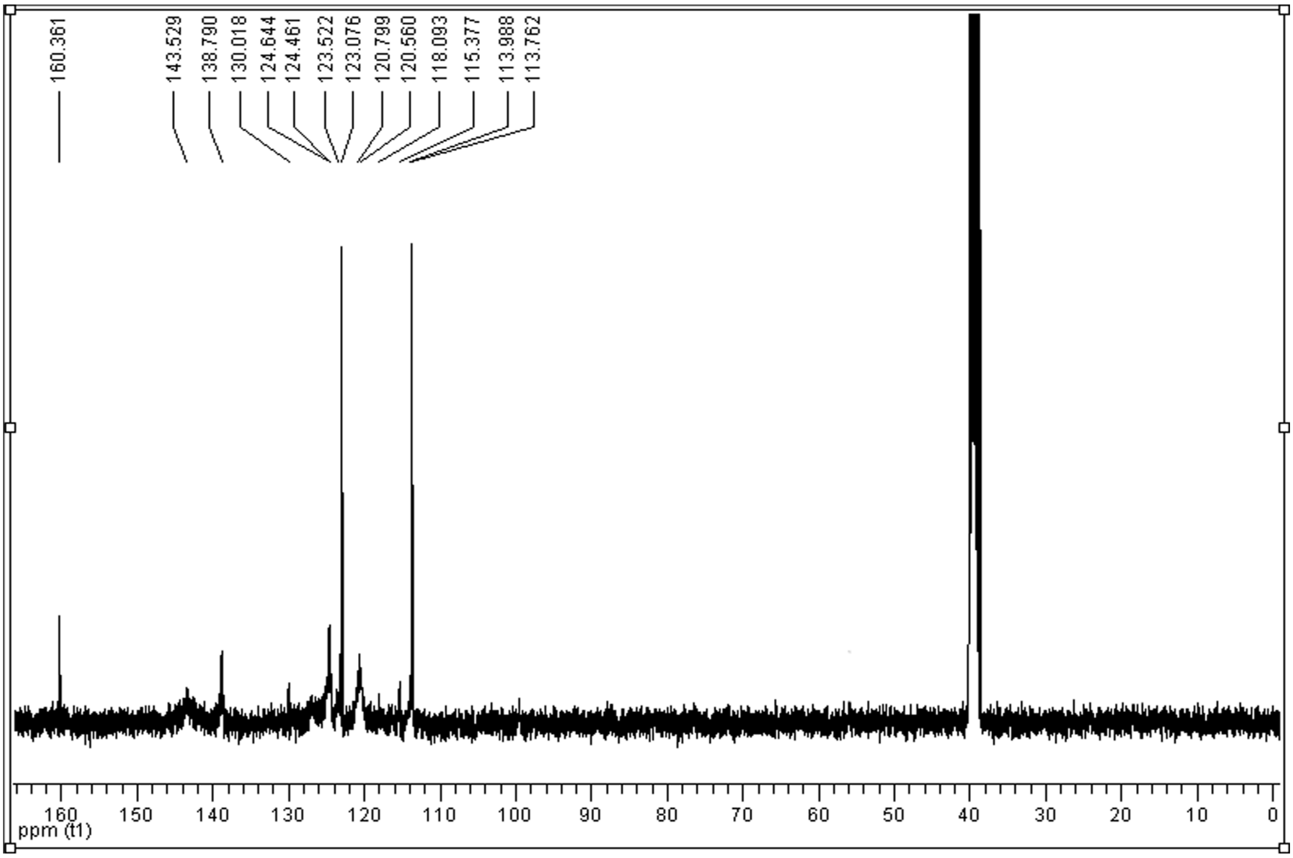


^{1}H NMR spectra of 3 (400MHz, DMSO-d_6)

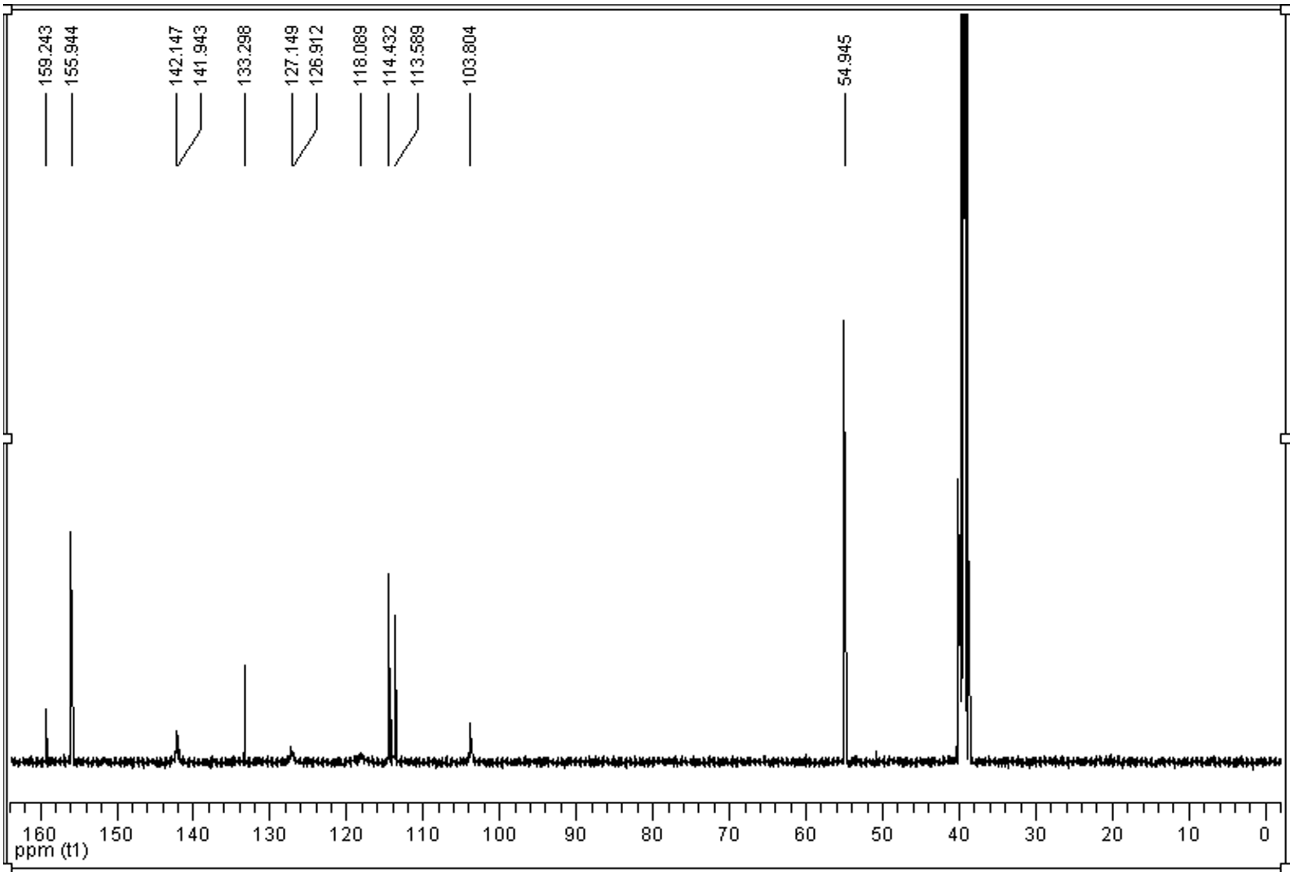


^{13}C NMR spectra of 1-3

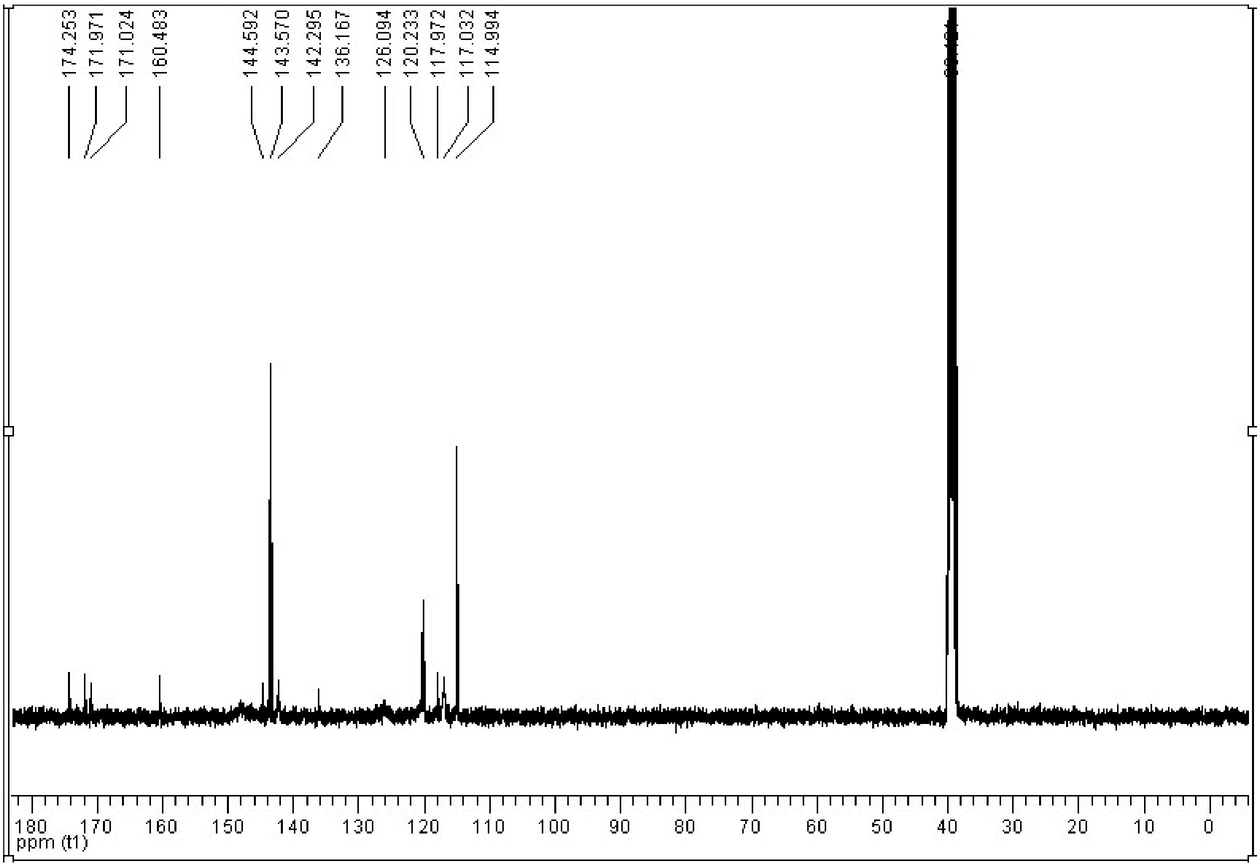
^{13}C NMR of spectra of 1 (400MHz, DMSO-d_6)



^{13}C NMR of spectra of 2 (400MHz, DMSO-d_6)



^{13}C NMR of spectra of 3 (400MHz, DMSO-d_6)



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