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SUPPLEMENTARY INFORMATION

A sensitive colorimetric detection of CN^- and AcO^- anions in semi-aqueous environment through a coumarin–naphthalene conjugate azo dye

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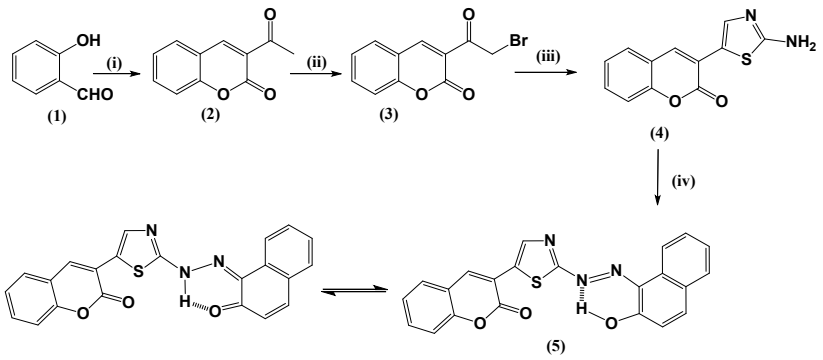
Materials and Chemicals: All the reagent and solvents were purchased from Sigma-Aldrich Chemical Pvt. Ltd. Stored in a desiccator under vacuum containing self-indicating silica, and used without any further purification. Solvent were purified prior to use. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda-35 UV-vis spectrophotometer using a quartz cuvette (path length = 1cm). Infrared (IR) spectra were recorded in potassium bromide (KBr) on Varian-3100 FT-IR spectrometer. ^{1}H NMR spectra were recorded (chemical shift in δ ppm) on a JEOL AL 300 and 500 FT-NMR (300 and 500MHz) spectrometer, using tetramethylsilane (TMS) as internal standard. All the spectroscopy experiments were carried out at room temperature. The stock solution of probe 5 (1 x 10^{-3}) were prepared in EtOH and diluted to obtained 10 μM in mixture of EtOH and H_2O (1:1, v/v) for absorption measurement. The stock solution of different anions (1 x 10^{-1} M) was prepared by dissolving their inorganic salt in water. The anion interaction studies were performed by addition of 1 x 10^{-1} M of different anions.

Estimation of Binding Constant: The absorption experimental data were utilized to calculate association constants by Benesi-Hildebrand method (B-H method) employing equations (1) for 1:1 stoichiometry.

$$\mathbf{1/(\mathit{I} - \mathit{I}_o) = 1/(\mathit{I} - \mathit{I}_f) + 1/K(\mathit{I} - \mathit{I}_f)[M]} \qquad \mathbf{(1)}$$

Where K is the association constant, I is the absorbance of the free probe **5**, I_o is the observed absorbance of the **5+CN**$^-$ and 5+AcO$^-$ in equation (1) complex, and I_f is the absorbance at saturation level.



Scheme S1: (i) Ethylacetoacetate/piperidine/EtOH/Δ, (ii) $Br_2/CHCl_3$/EtOH/r.t., (iii) thiourea/EtOH/r.t., (iv) a. H_2SO_4/AcOH, b. $NaNO_2/H_2O$/0°C, c. alk. β-naphthol.

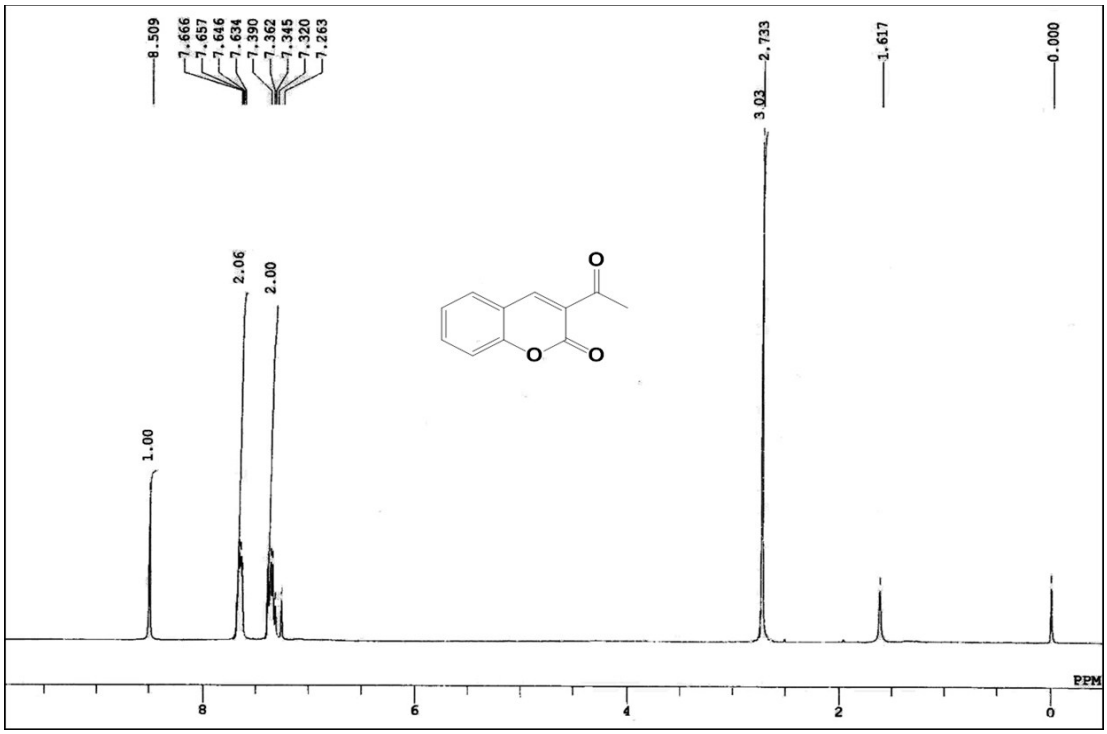


Figure S1: ^{1}H NMR spectrum of **2** in $CDCl_3$.

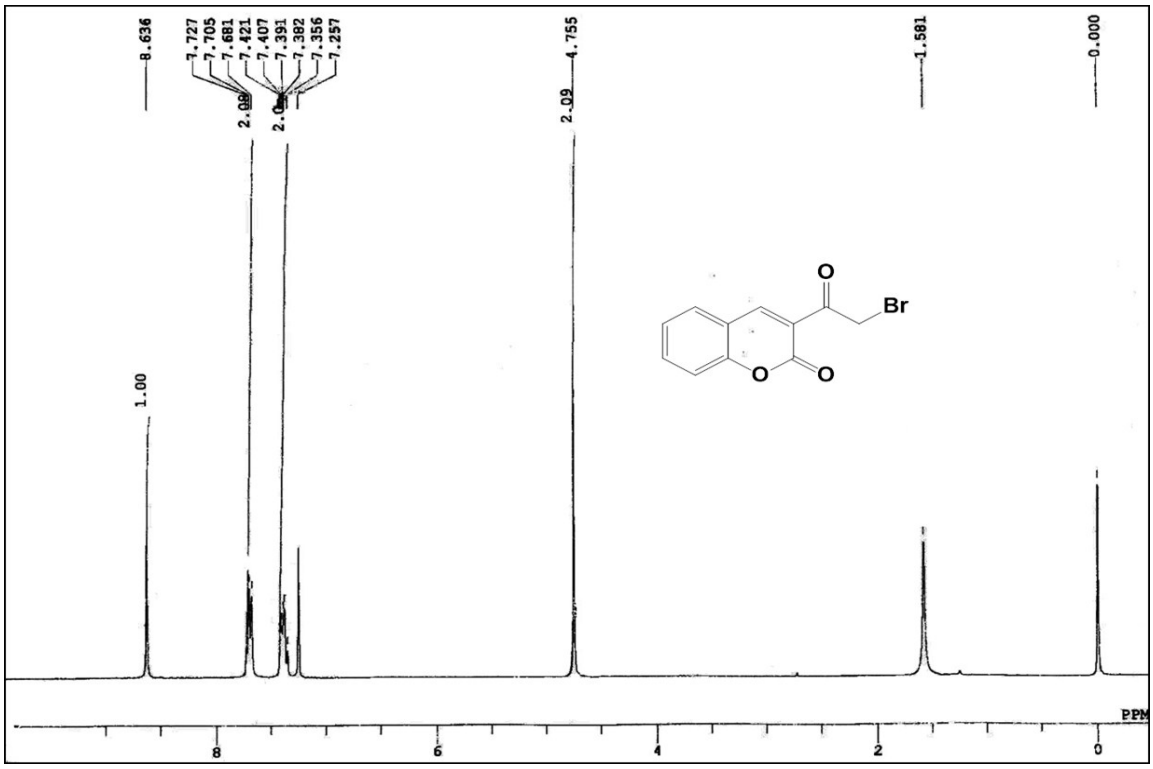


Figure S2: ^{1}H NMR spectrum of **3** in $CDCl_3$.

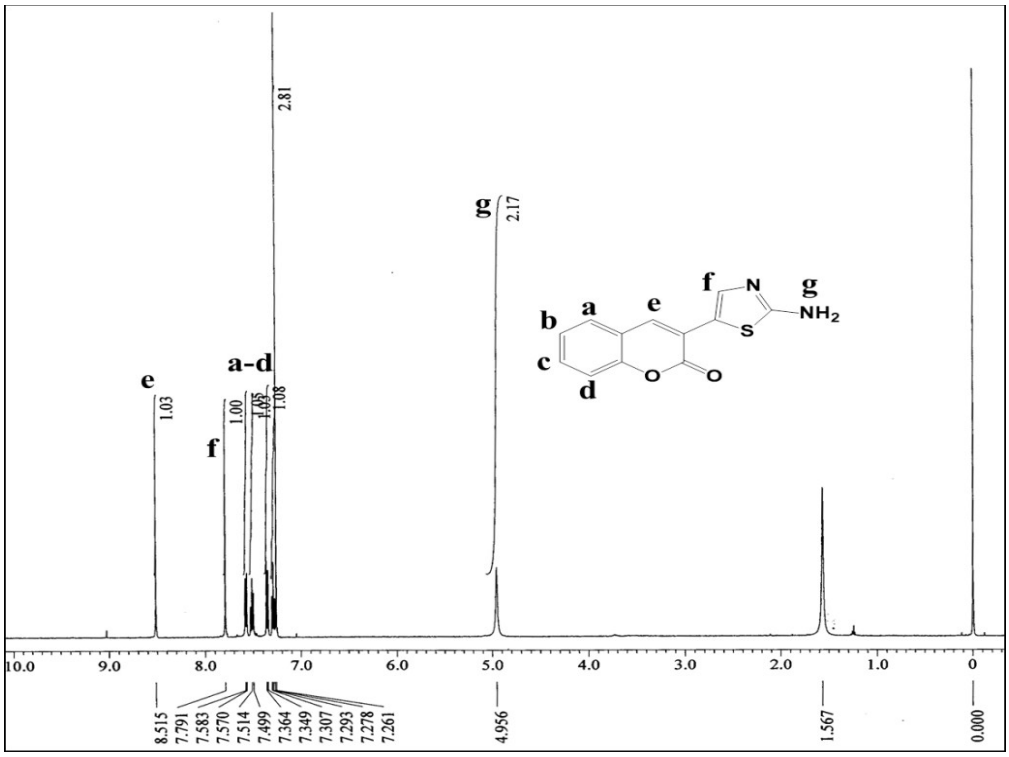


Figure S3: ^{1}H NMR spectrum of **4** in $CDCl_3$.

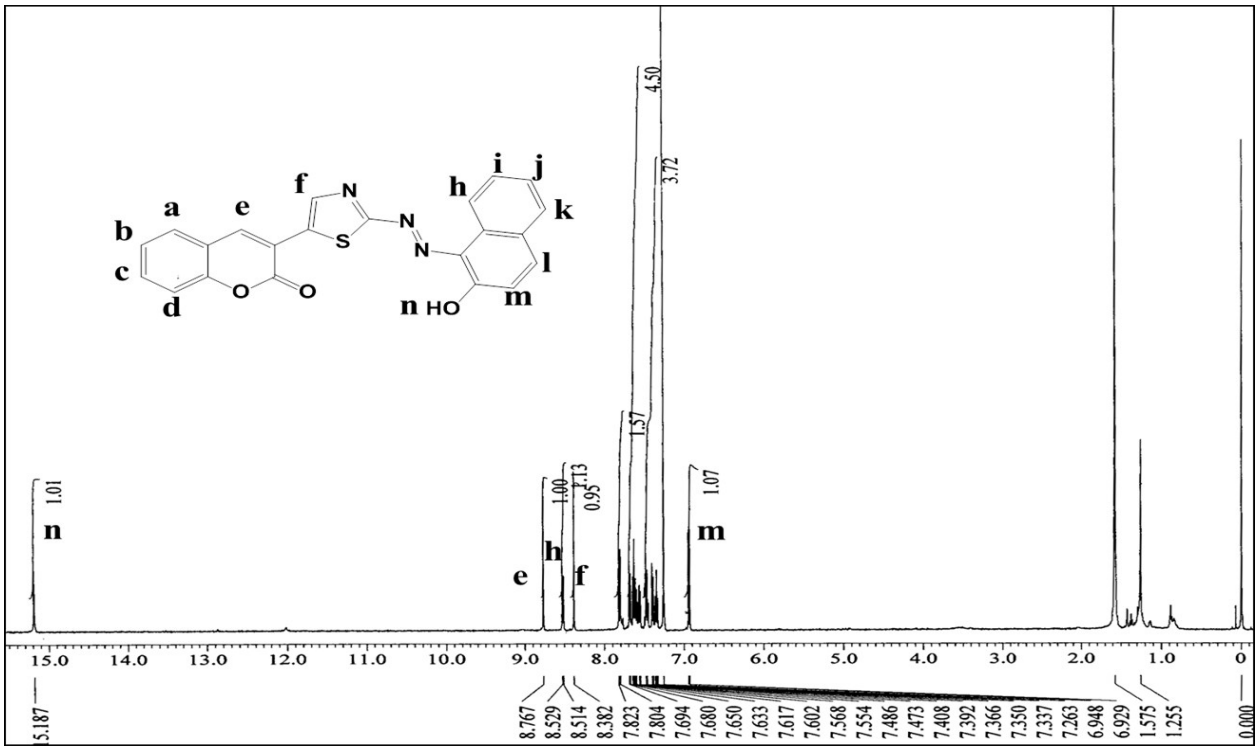


Figure S4: ^{1}H NMR spectrum of **5** in $CDCl_3$.

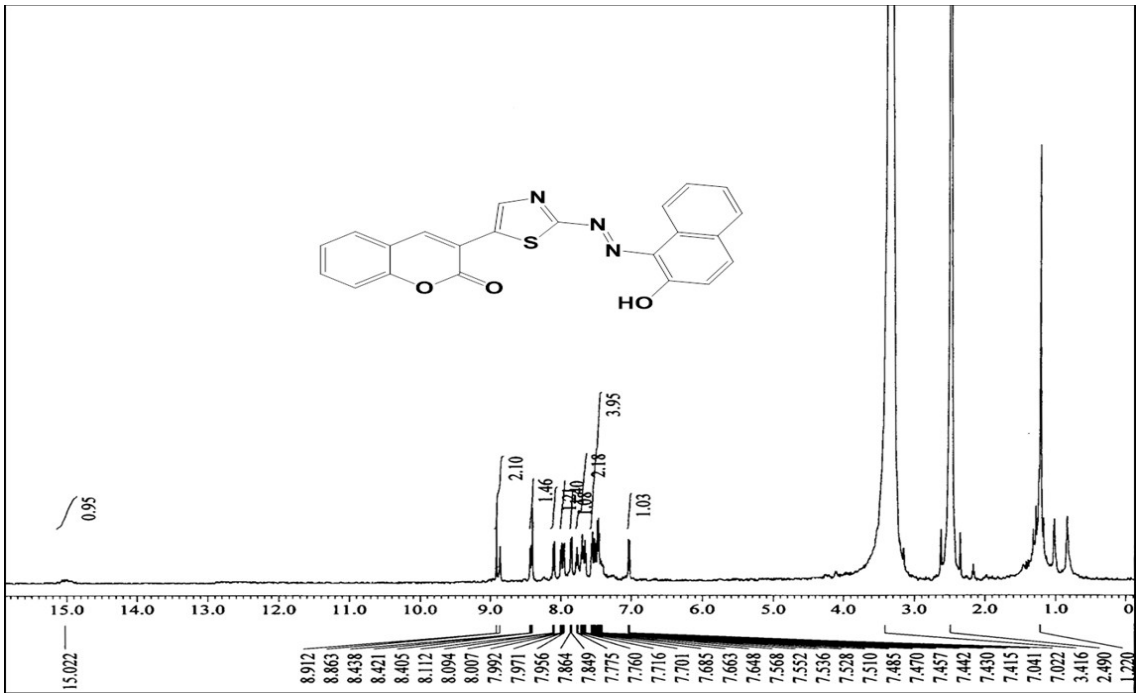


Figure S5: ^{1}H-NMR spectrum of probe **5** in DMSO-d_6.

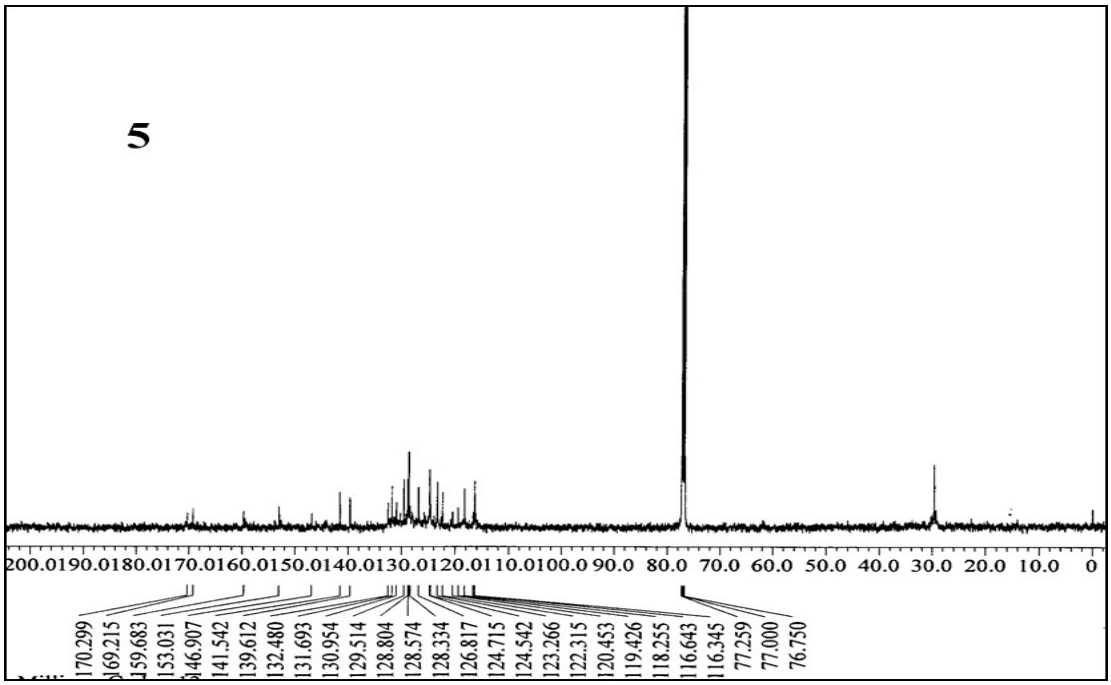


Figure S6: ^{13}C NMR spectrum of **5** in $CDCl_3$.

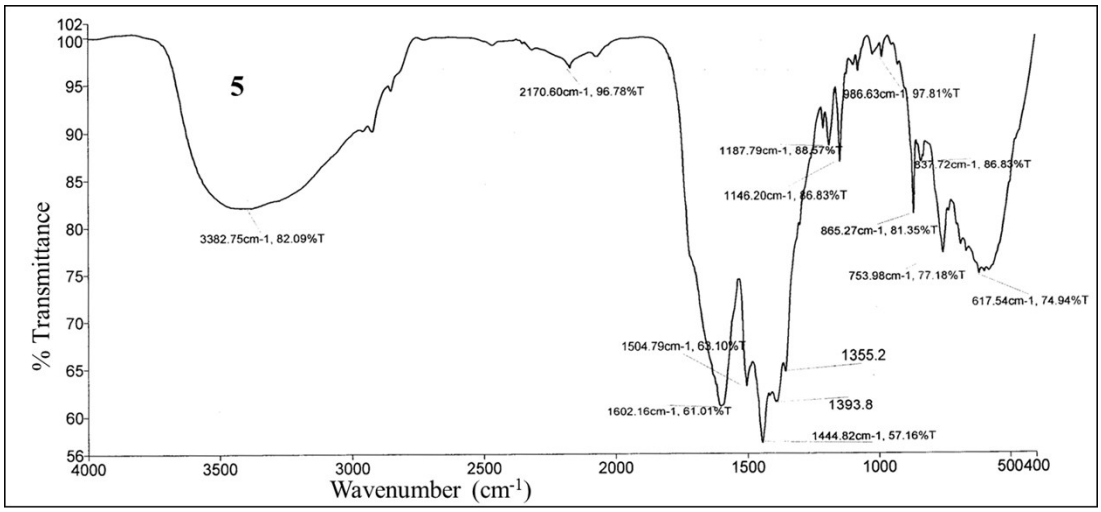


Figure S7: FT-IR spectrum of probe **5**.

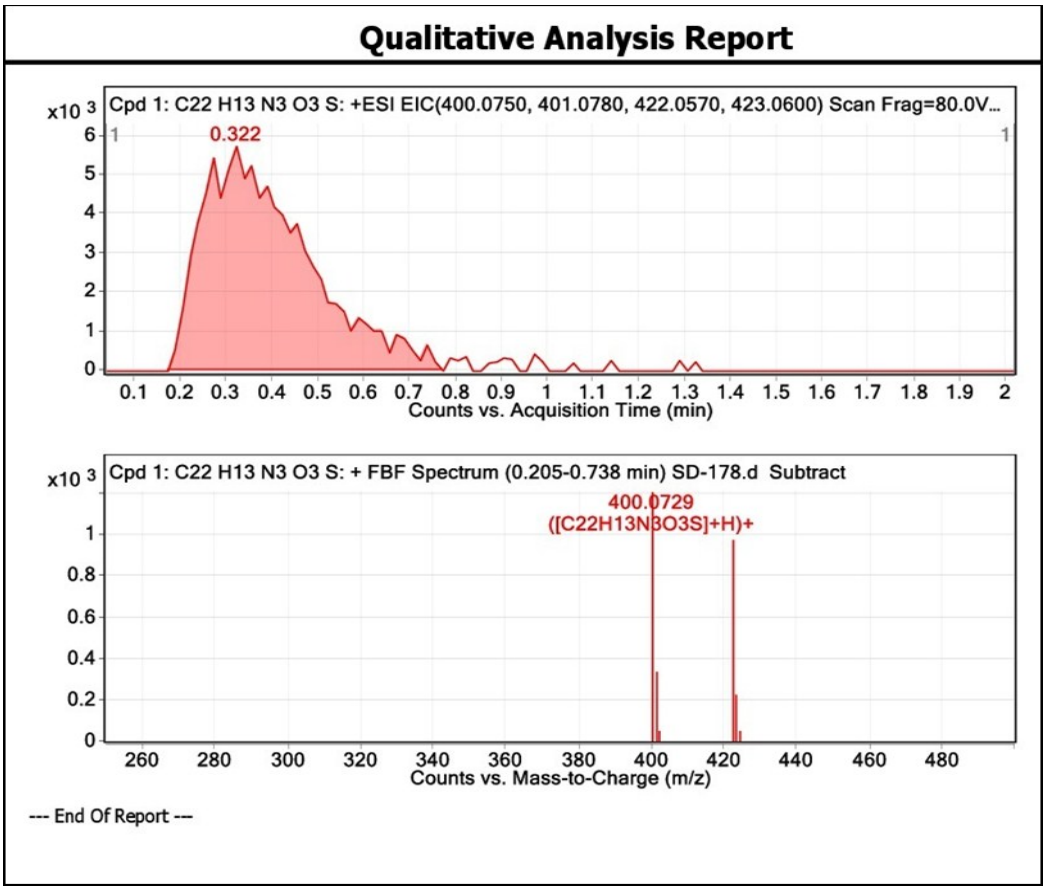


Figure S8: ESI-MS spectrum of probe **5**.

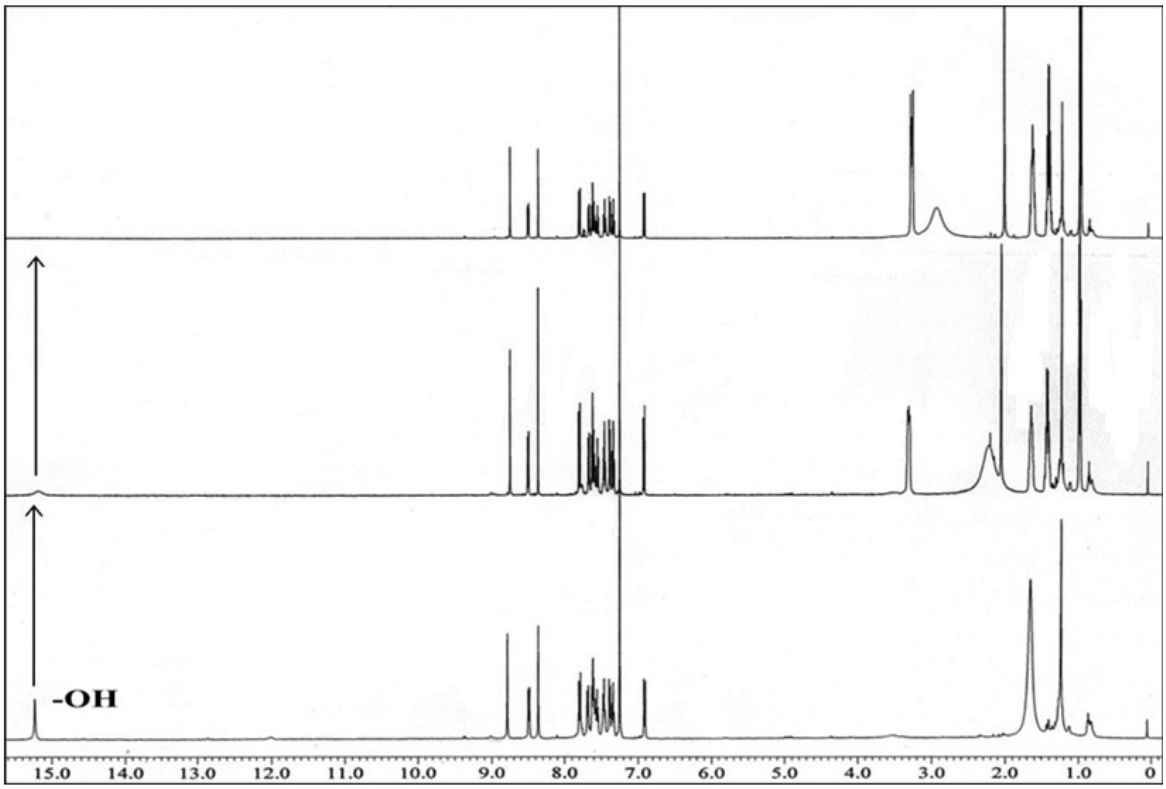


Figure S9: Stacked ^{1}H NMR spectra of probe **5** (2.0 x 10^{-2} M) upon addition of AcO^{-} (0 - 2.0 equiv) in $CDCl_3$.

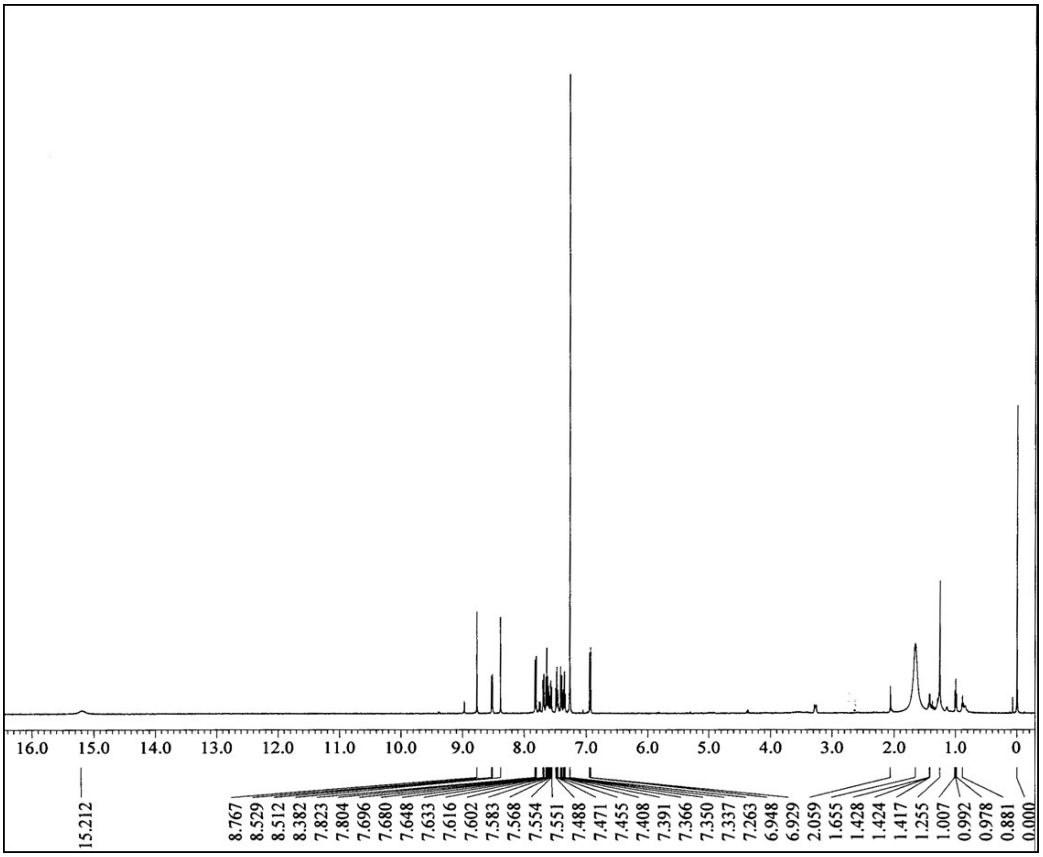


Figure S10: ^{1}H NMR spectra of probe **5** upon addition 0.5 equiv. of CN^{-} in $CDCl_3$.

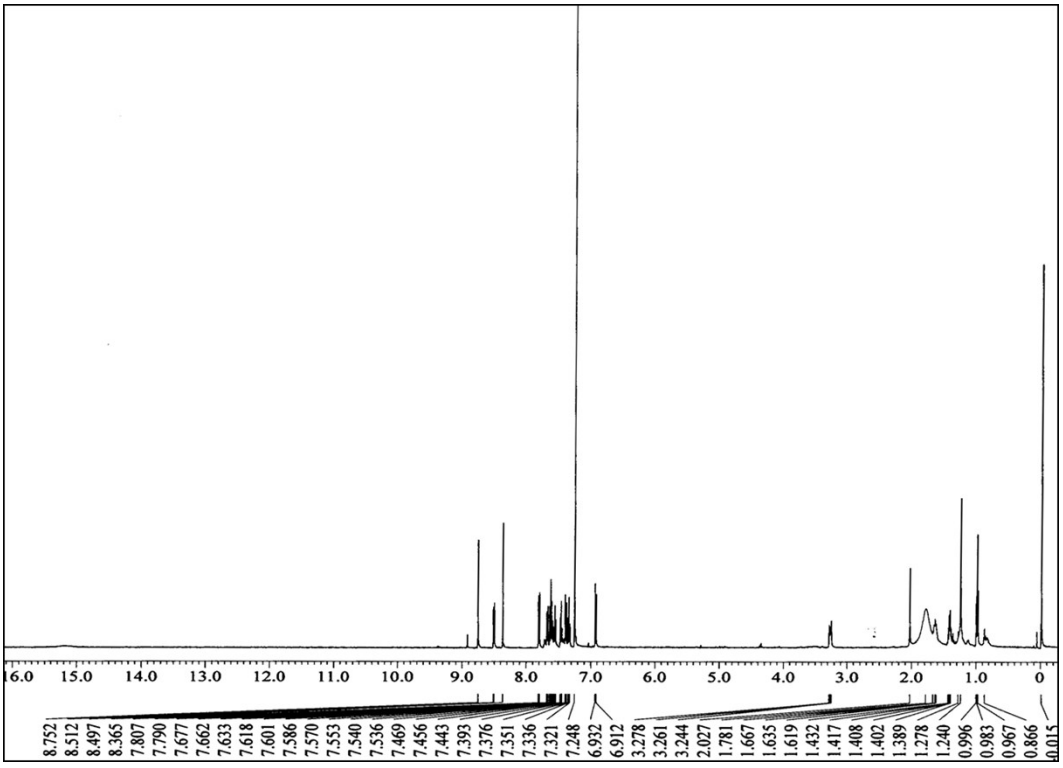


Figure S11: ^{1}H NMR spectra of probe **5** upon addition 1.0 equiv. of CN^{-} in $CDCl_3$.

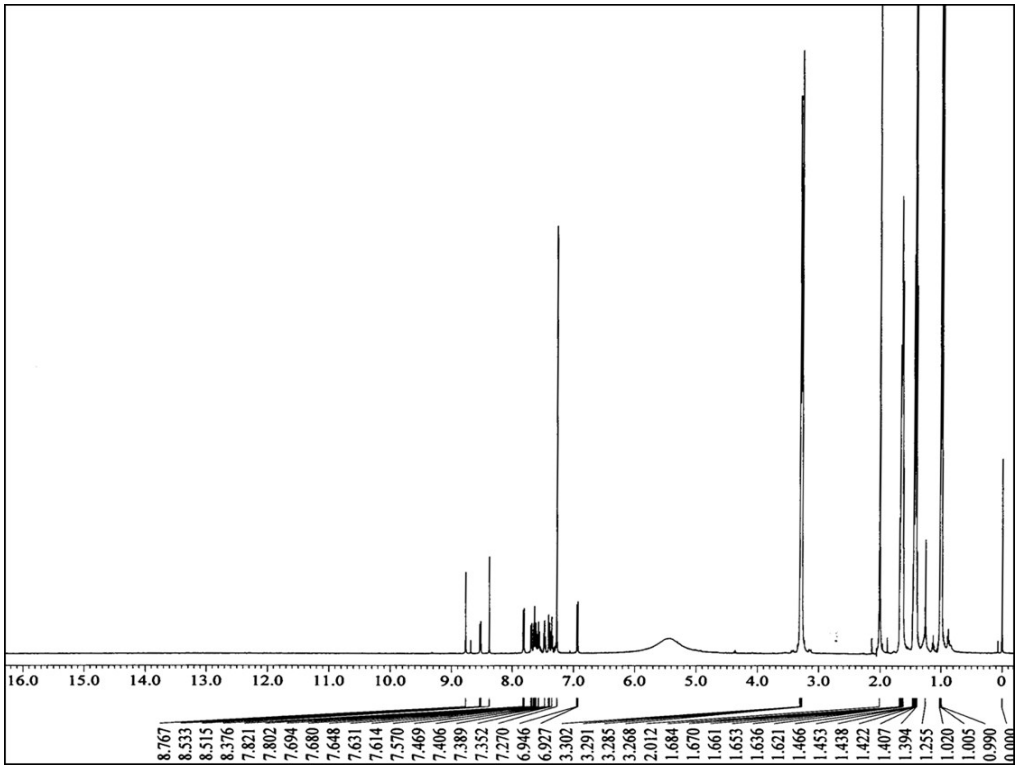


Figure S12: ^{1}H NMR spectra of probe **5** upon addition 2.0 equiv. of CN^{-} in $CDCl_3$.

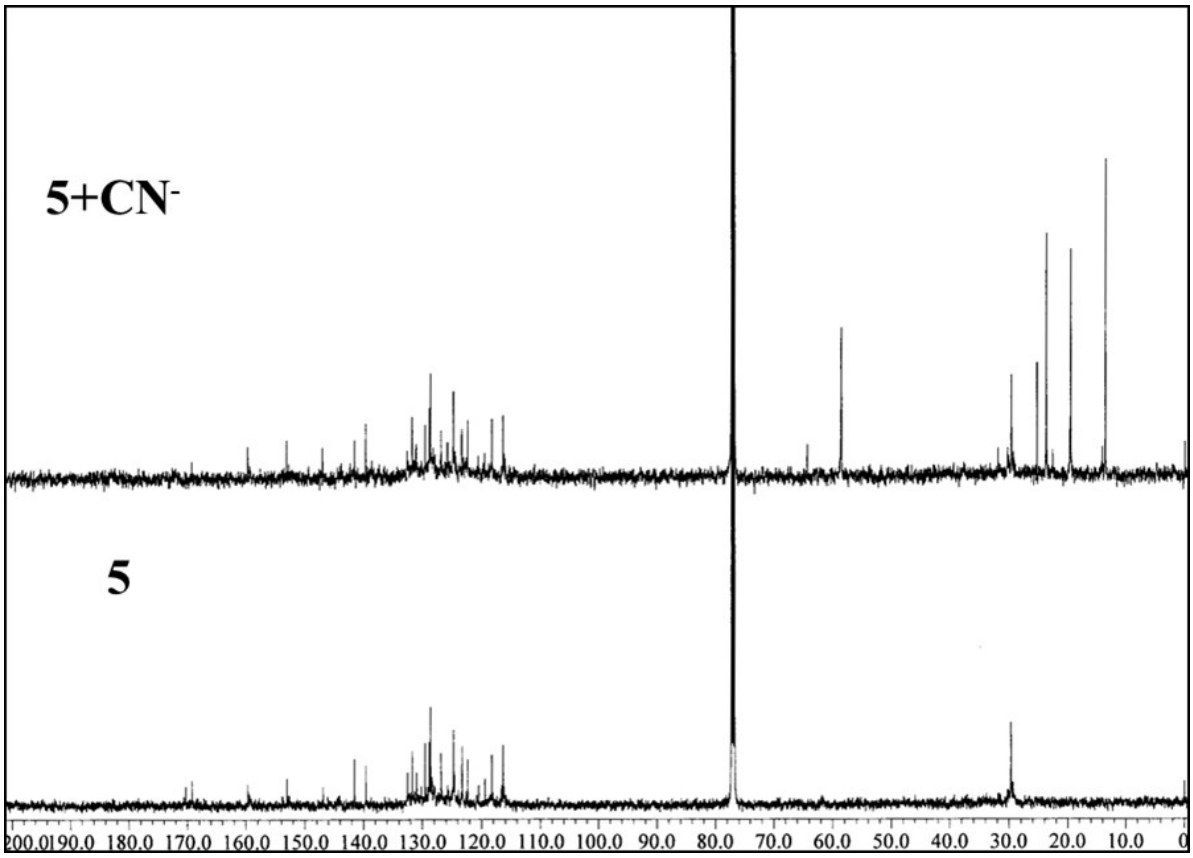


Figure S13: Stacked ^{13}C NMR spectra of probe **5** and **5+CN**$^{-}$ in $CDCl_3$.

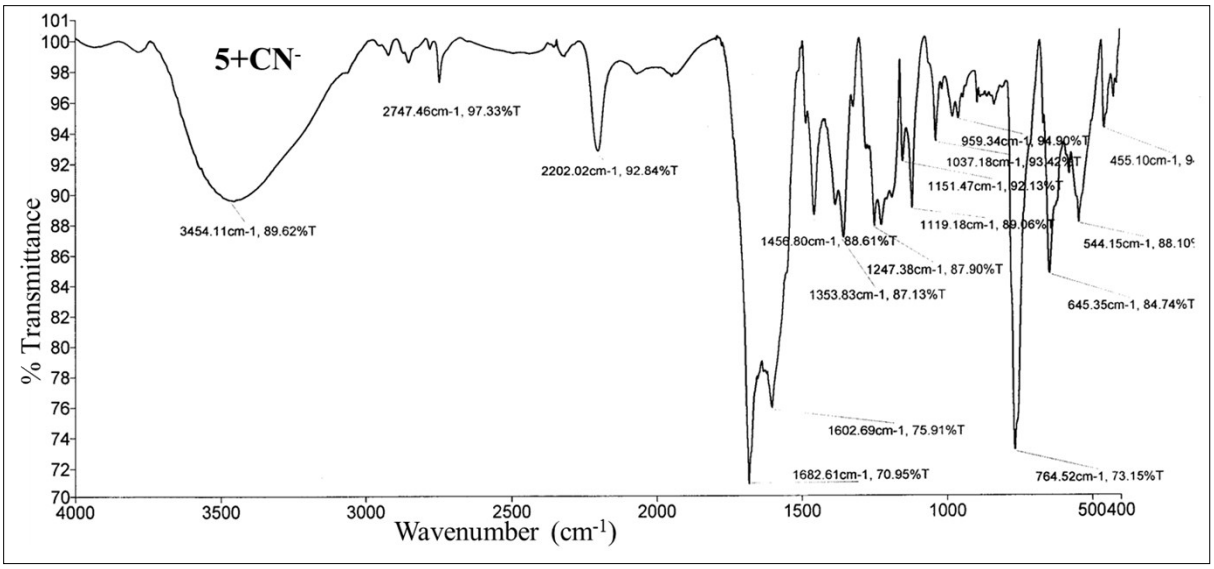


Figure S14: FT-IR spectrum of **5+CN**$^{-}$.

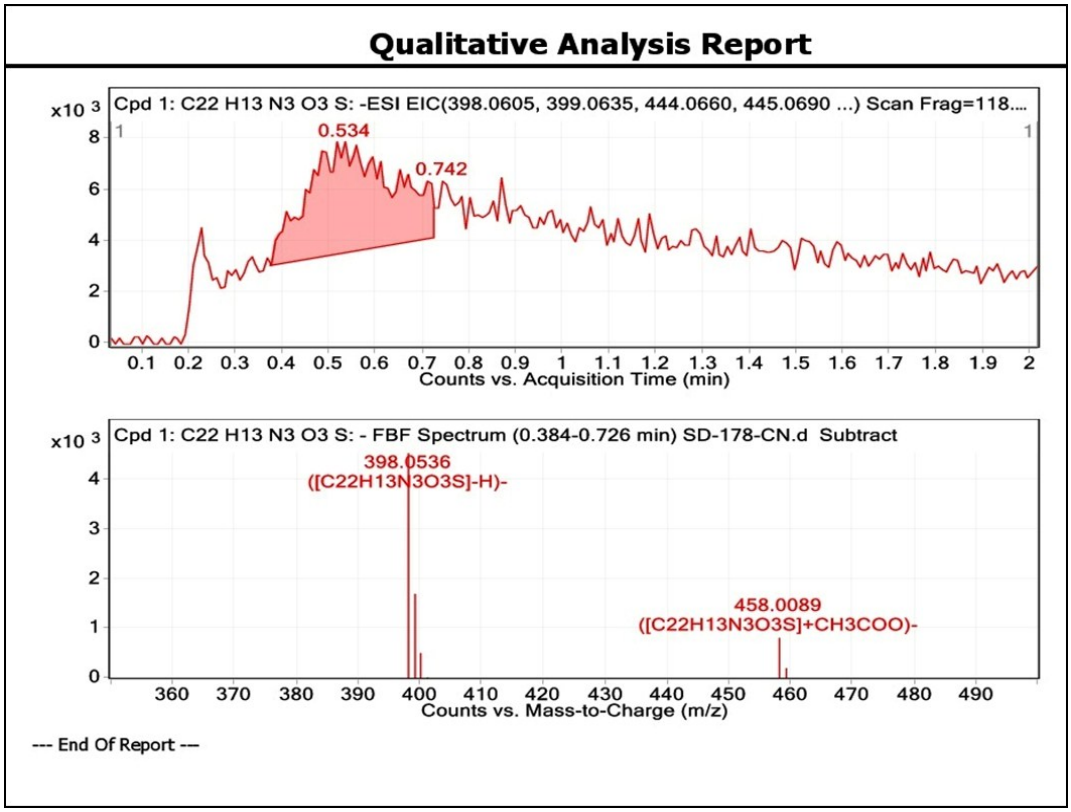


Figure S15: ESI-MS spectrum of **5**+CN^-.

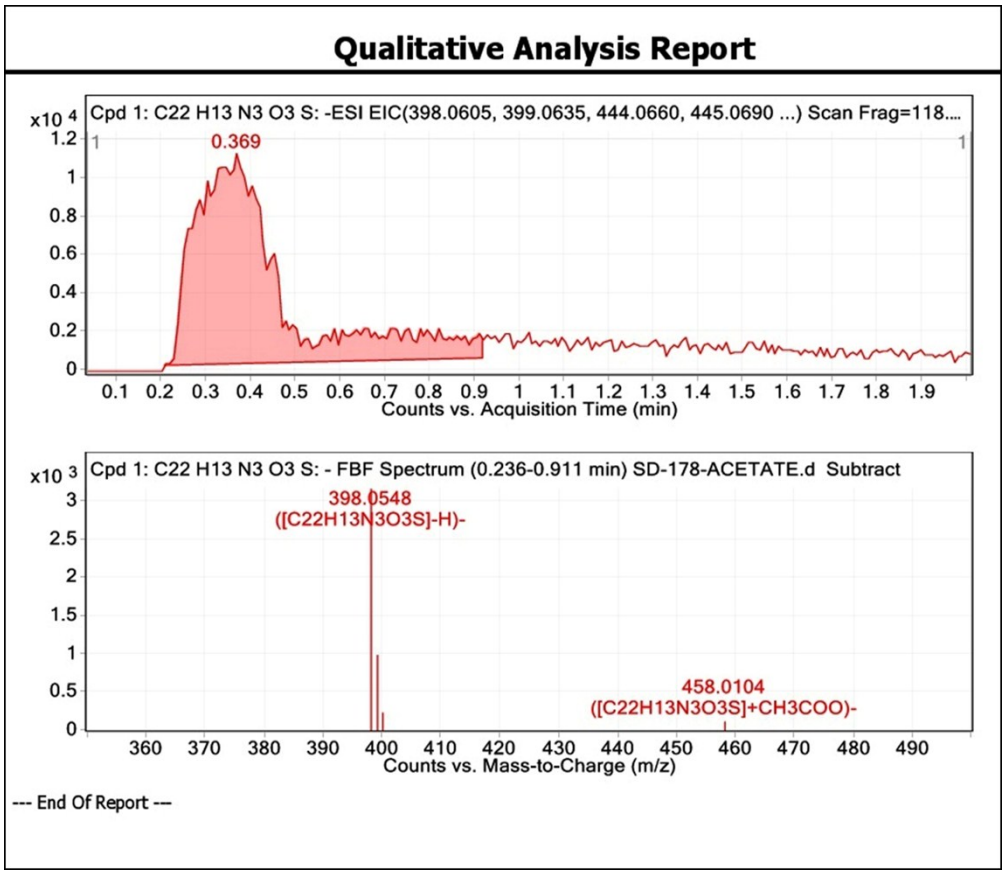


Figure S16: ESI-MS spectrum of **5**+**AcO**$^{-}$.

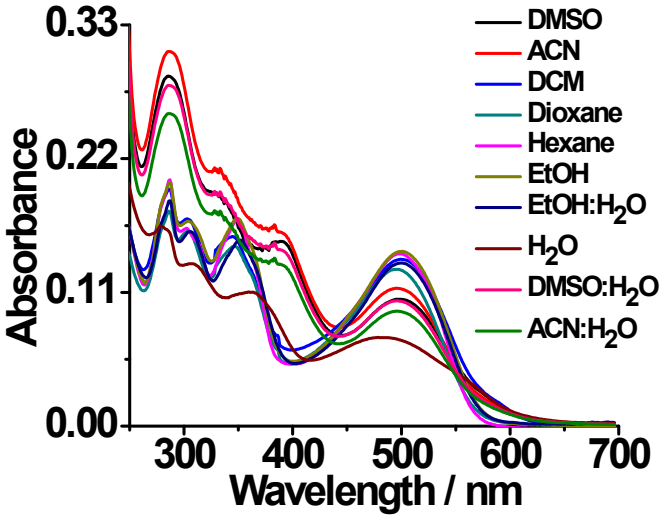


Figure S17: Absorption spectra of probe **5** in solvent of different polarity.

Table-S1: Photophysical property of probe **5** in solvent of different polarity.

Properties	λ_{max}	ε ($cm^{-1}M^{-1}$)
Hexane	283, 299, 346, 496	2.0148 x 10^4, 1.6219 x 10^4, 1.6983 x 10^4, 1.4167 x 10^4
DMSO	284, 329, 390, 502	2.8858 x 10^4, 1.9112 x 10^4, 1.5106 x 10^4 , 1.0403 x 10^4
DCM	286, 302, 344, 498	1.9461 x 10^4, 1.7070 x 10^4, 1.5609 x 10^4, 1.3732 x 10^4
H_2O	280, 309, 365, 481	1.6209 x 10^4, 1.3306 x 10^4, 1.1003 x 10^4, 0.7277 x 10^4
Dioxane	286, 303, 348 ,499	1.9479 x 10^4, 1.6896 x 10^4, 1.6722 x 10^4, 1.4419 x 10^4
MeCN	287, 333, 389, 499	3.0822 x 10^4, 2.1164 x 10^4, 1.5870 x 10^4 , 1.1193 x 10^4
EtOH	284, 303, 348, 499	1.8554 x 10^4, 1.5935 x 10^4, 1.6983 x 10^4, 1.4322 x 10^4
EtOH-H_2O	285, 304, 350, 498	1.5435 x 10^4, 1.5870 x 10^4, 1.5183 x 10^4, 1.3393 x 10^4
DMSO-H_2O	287, 331, 386, 498	2.8006 x 10^4, 1.9287 x 10^4, 1.44193 x 10^4, 1.0229 x 10^4
ACN-H_2O	287, 321, 387, 499	2.5693 x 10^4, 1.7661 x 10^4, 1.3393 x 10^4, 0.9464 x 10^4

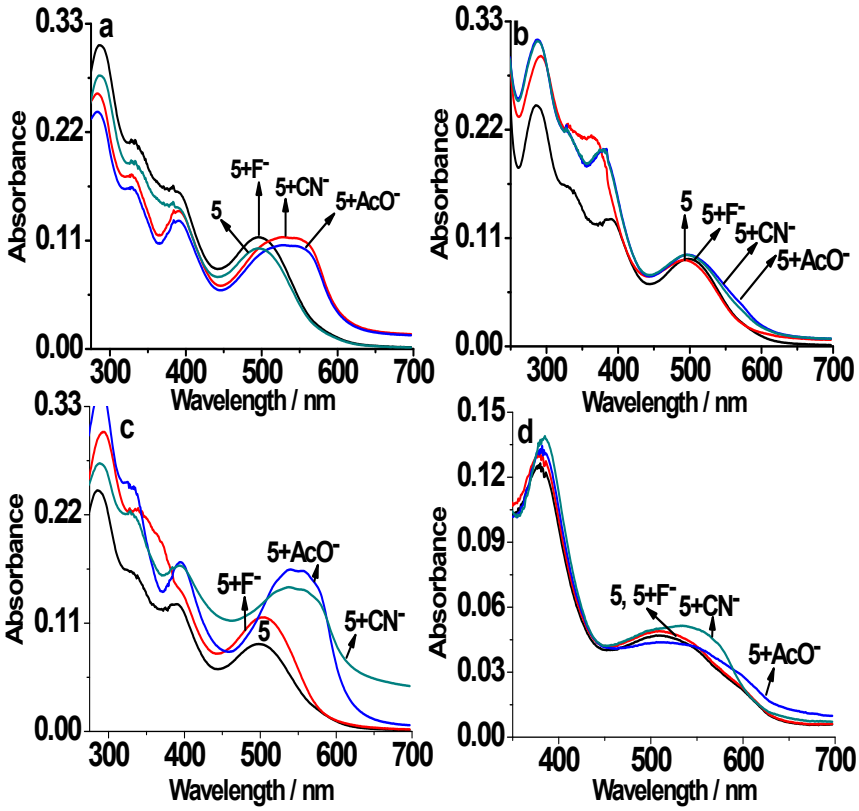


Figure S18: Absorption spectra of probe **5** (10 μM) after interaction with F^-, CN^-, AcO^- in (a) acetonitrile, (b) acetonitrile:H_2O (1:1, v/v), (c) DMSO and (d) DMSO:H_2O (1:1, v/v).

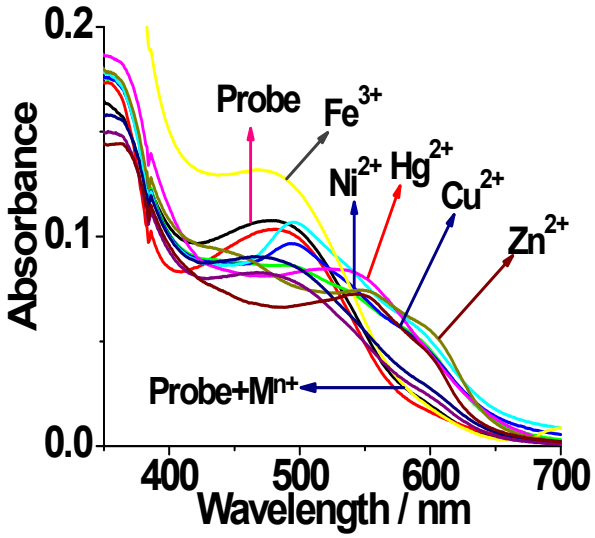


Figure S19: Interaction of probe **5** with different metal ions in aqueous ethanol (1:1; v/v).

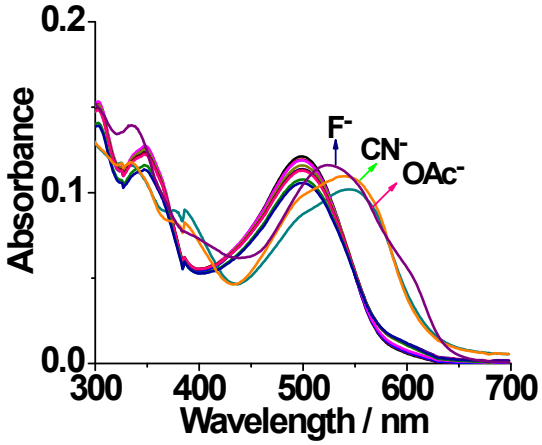


Figure S20: Interaction of probe **5** (10 μM) with different anions in pure ethanol.

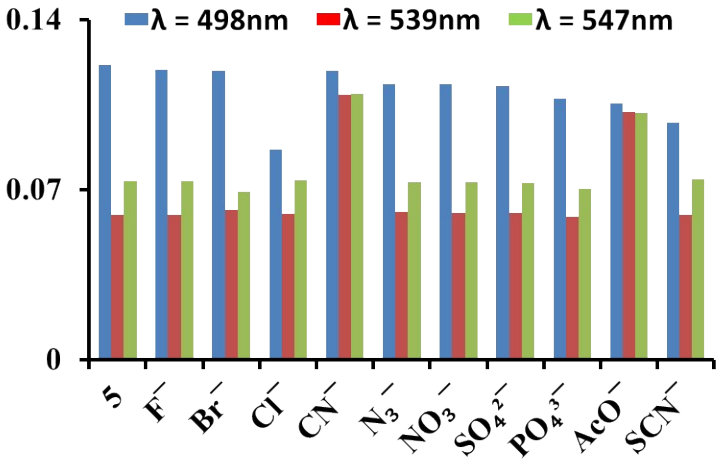


Figure S21: Bar Diagram of probe **5** (10 μM) after interaction with different anions.

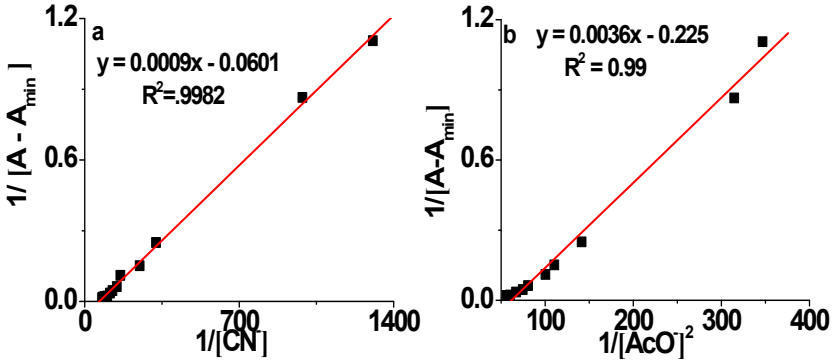


Figure S22: Benesi-Hildebrand plot of probe **5** (10 μM) with (a) CN^- and (b) AcO^- ions.

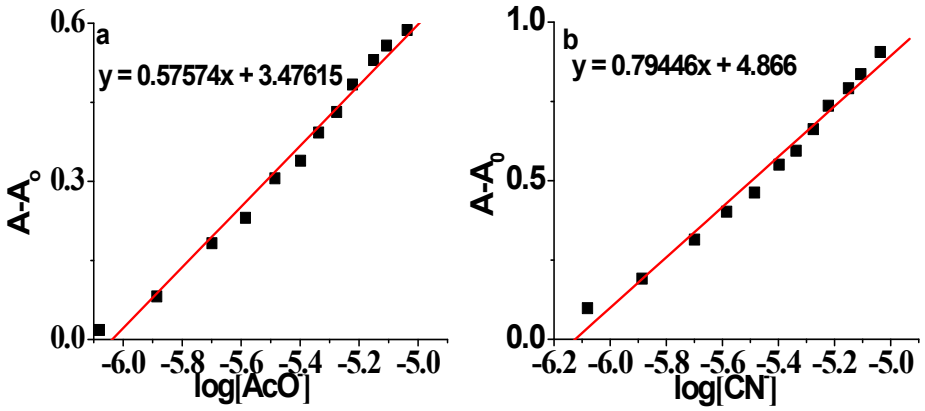


Figure S23: Change in absorption spectra of probe **5** (10 μM) upon addition of different concentration of (a) AcO^- (b) CN^-.

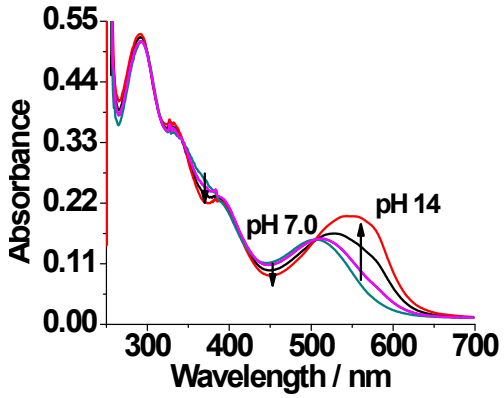


Figure S24: Change in absorption spectra of probe **5** (10 μM) at different pH in HEPES buffer (DMSO:H_2O; 9:1 v/v).

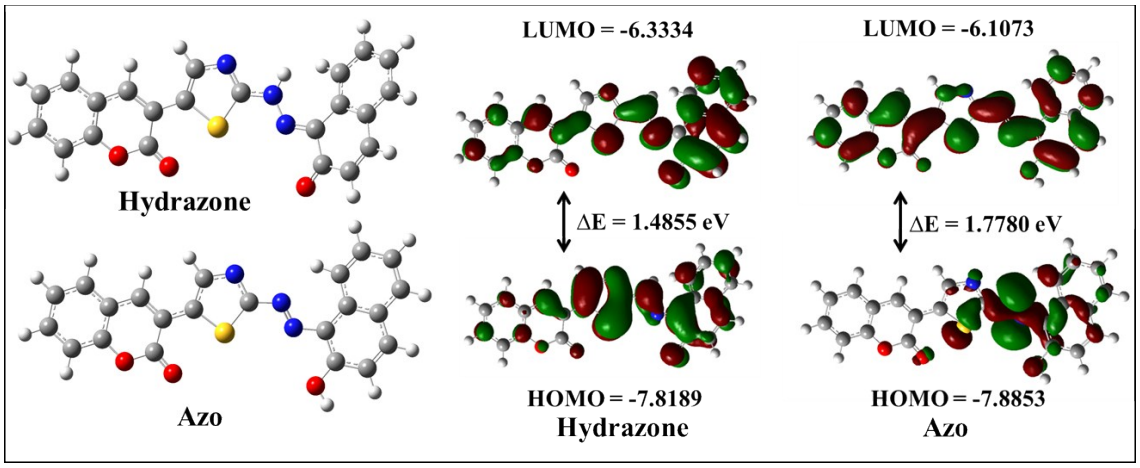


Figure S25: DFT method optimized minimum energy structure for azo and hydrazone form and HOMO-LUMO energy level for probe **5**.