Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Phenolic oxime based receptors for selective detection of fluoride

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A. Instrumentation and reagents:

Melting points were recorded on a JSCW melting point apparatus. Infrared spectra were recorded with a Nicolet Impact I-410 FT-IR spectrometer as KBr diluted discs. Elemental analysis was done by using Perkin Elmer PR 2400 series analyzer. The ^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on a 'JEOL' NMR spectrophotometer in DMSO-d_6 at room temperature. In NMR spectra, chemical shifts are reported in parts per million (ppm) downfield of Me_4Si (TMS) as internal standard. ^{1}H NMR spectroscopy based titration studies were carried out on a Bruker Avance-400 MHz FT NMR spectrometer in CD_3CN. The diffraction data was obtained with a Bruker Smart APEX- II diffractometer with Mo-K_{α} rotating anode generator, and Smart CCD detector. Structures were solved and refined using SHELXL-97 with anisotropic displacement parameters for non-H atoms. The hydrogen atoms on O and N were located from the Fourier map in all of the crystal structures. All C–H atoms were fixed geometrically. Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. A check of the final CIF file using PLATONS3 did not show any missed symmetry. UV-visible data were recorded with a Shimadzu UV-2450 spectrophotometer. CV measurements were performed on an electrochemical work station Sycopel AEW2-10 with an Ag/AgCl reference electrode, a platinum wire as a counter electrode.

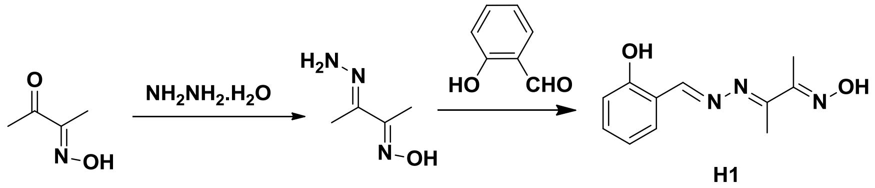
^{1}H NMR spectroscopy based titration studies were carried out on a Bruker Avance-400 MHz FT NMR spectrometer in acetonitrile-d_3.

UV-visible titrations were carried out in dimethylsulphoxide solution. All tetrabutylammonium salts for NMR and UV-visible titration were purchased from Sigma-Aldrich® and used as such. All anions were used in the form of their tetrabutyl ammonium salts (fluoride as its trihydrate). The receptor solutions were titrated by adding known quantities of concentrated solution of the anions in question. The anion solutions used to effect the titrations contained the receptor at the same concentration as the receptor solutions into which they were being titrated so as to nullify the dilution effect.

All tetrabutylammonium salts for NMR and UV-visible titration were purchased from Sigma-Aldrich® and were directly used in the titration experiment.

B. Synthesis procedure

Synthesis of H1



Step 1: Synthesis of Diacetyl monoxime hydrazine

Diacetyl monoxime (500 mg, 4.94 mmol) was dissolved in 20 mL of CH_3OH and stirred for 10 minute. To the above solution, hydrazine hydrate (275 mg, 5.49 mmol) was added drop wise with constant stirring. The reaction is highly exothermic and results a hot orange solution from which white needle shaped crystals start separated within 10 minute. The reaction mixture was left in the air for 2 h. The crystals were filtered, washed with cold ethanol and dried in vacuum.

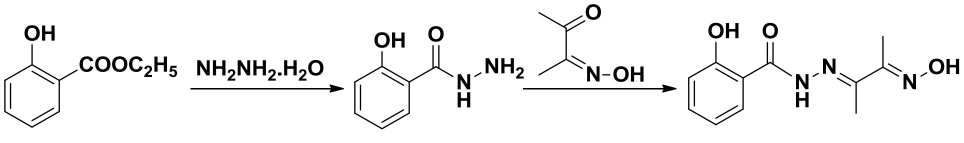
FT-IR (KBr): $\tilde{\nu}$ = 3389(m), 3307(m), 3222(s), 3008(w), 2842(w), 1639(w), 1575(m), 1432(m), 1365(s), 1127(w),1004(m).

*Step 2: Synthesis of **H1***

A mixture of salicylaldehyde (122 mg, 1 mmol) and diacetyl monoxime hydrazone (115 mg, 1 mmol) was taken in a round bottom flask and dissolved in 50 mL ethanol. The solution was refluxed for 4 h with continuous stirring. The resultant solution was cooled to room temperature and filtered. The yellow coloured filtrate was kept undisturbed in a beaker for crystallization at room temperature. Yellow block shaped crystals were observed after 2 days at the bottom of the beaker. The solvent was decanted and the solid was dried in air which yield 127 mg of **H1** as light yellow solid.

Yield: 127 mg (58% based on diacetyl monoxime hydrazone); m.p.:122-124 °C; FT-IR (KBr, cm^{-1}): 3201(br), 3052(w), 1964(w), 1612(s), 1543(w), 1492(w), 1359(m), 1267(m), 1202(m), 1147(m), 1011(m), 941(m), 796(w), 750(m), 702(m), 649(w); ^{1}H NMR (DMSO-d_6, 400 MHz, δ in ppm): 11.92 (s, 1H), 11.28 (s, 1H), 8.71 (s, 1H) 7.64 (d, J=7.32 Hz, 1H), 7.35 (t, J=7.76 Hz, 1H), 6.9 (m, 2H), 2.18 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, δ in ppm): 162.16, 156.78, 155.15, 131.33, 120.33, 40.22, 40.02, 39.81, 11.70, 9.85 164.60, 161.23, 159.25, 155.24, 133.55, 131.71, 120.07, 118.96, 116.94, 13.48, 9.89. Elemental analysis % calculated for $C_{11}H_{13}N_3O_2$: C = 60.27, H = 5.98, N = 19.16; Found: C = 59.93, H = 5.99, N = 15.10. UV-vis: (λ_{max}, nm):294, 338.

Synthesis of compound H2:



H2

Step 1: Synthesis of 2-Hydroxybenzohydrazide

A mixture of 16.6 g (0.1 mole) ethyl salicylate and 0.2 mole (10 mL) hydrazine hydrate were refluxed in 50 mL ethanol for 15 h. The resultant mixture was concentrated, cooled and poured into crushed ice. The solid mass thus separated out was filtered, ried and purified by recrystallization from ethanol.

Step 2: Synthesis of ***H2***

Diacetylmonoxime (200 mg, 2 mmol) was dissolved in 30 mL of ethanol in a 100 mL round bottom flask. To the solution, 2-hydroxybenzohydrazide (300 mg, 2 mmol) was added and the solution was refluxed overnight with continuous stirring. The resultant solution was evaporated in vacuum which yield 367 mg **H2** as white solid.

Yield: 78%; m.p.: 276.0-279.4 ºC; FT-IR (KBr, cm^{-1}): 3283 (w), 3104 (br), 2717(m), 2575(m), 1927(w), 1811(w), 1651(s), 1547(s), 1495(w), 1452(s), 1373(s), 1299(s), 1227(s), 1150(s), 1101(w), 1023(m), 985(w), 944(s), 828(w), 745(s), 619(s), 565(m), 503(m), 456(m), 414(w); ^{1}H NMR (DMSO-d_6, 400 MHz, δ in ppm): 11.69(s, 1H) , 11.59(s, 1H), 11.28(s, 1H), 7.94-7.92 (d, J = 7.96 Hz, 1H), 7.73(s, 1H), 7.38-7.36 (d, J = 7.16 Hz, 1H), 6.98-6.92 (m, 1H), 2.22-2.12(d, J =39.68, 3H), 2.09-1.99 (d, J = 36.52, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz, δ in ppm) : 162.16, 156.78, 155.15, 131.33, 120.33, 40.22, 40.02, 39.81, 11.70, 9.85; Elemental analysis % calculated for $C_{11}H_{13}N_3O_3$: C = 59.15, H = 5.87, N = 18.83; Found: C = 56.28 , H = 5.22 , N =17.77; UV-Vis : (λ_{max}, nm): 280, 375.

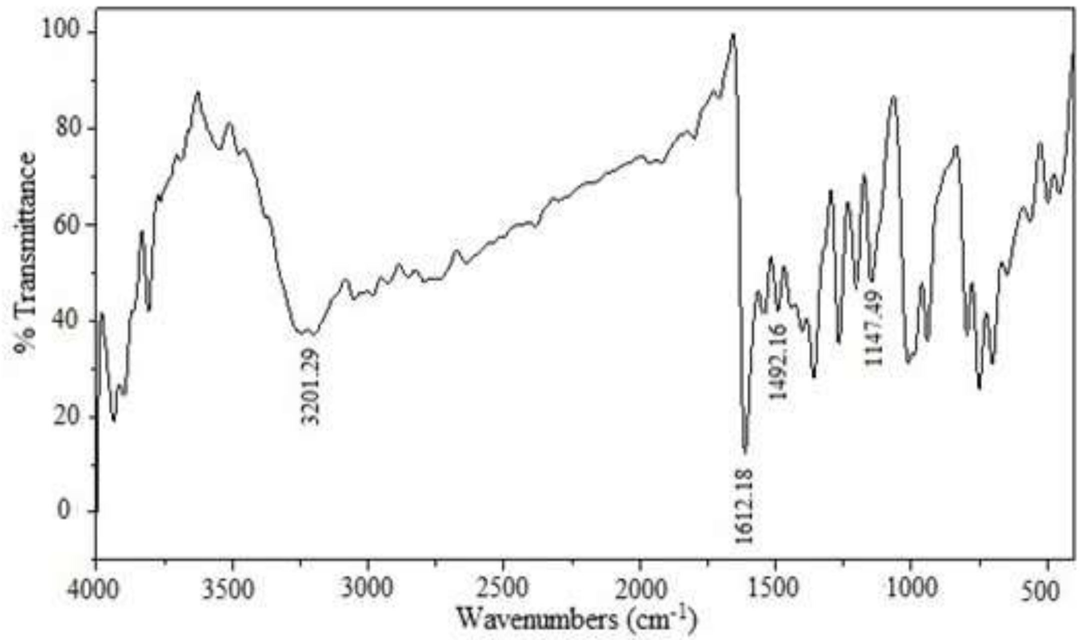


Figure S1: FTIR spectrum of compound **H1**

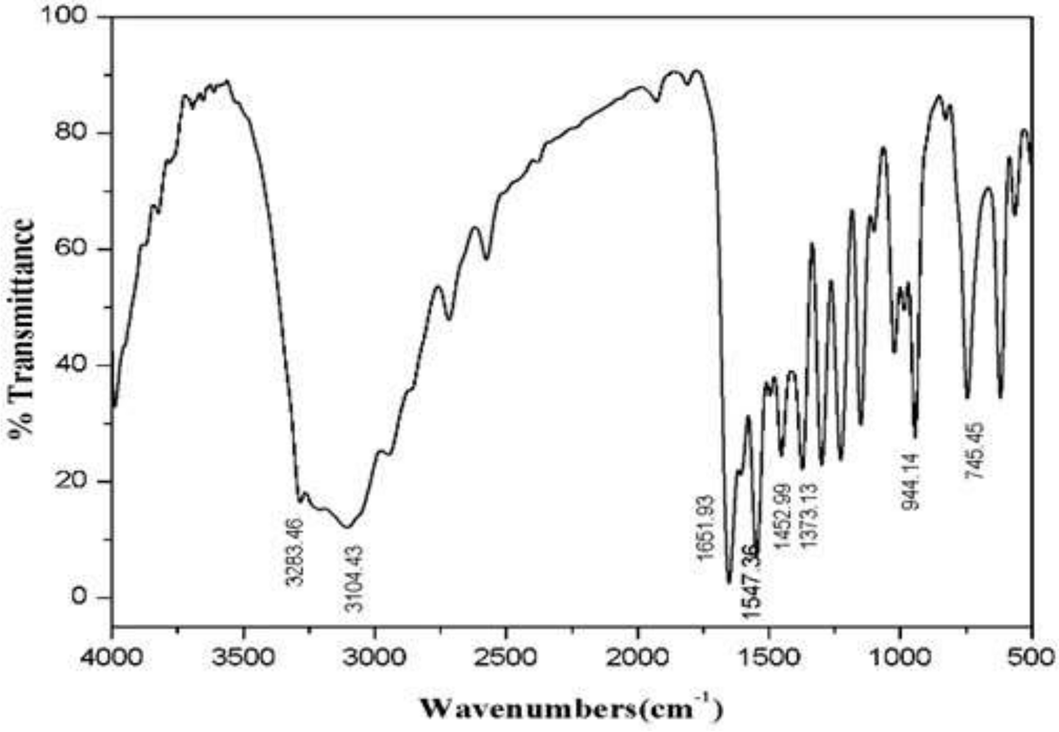
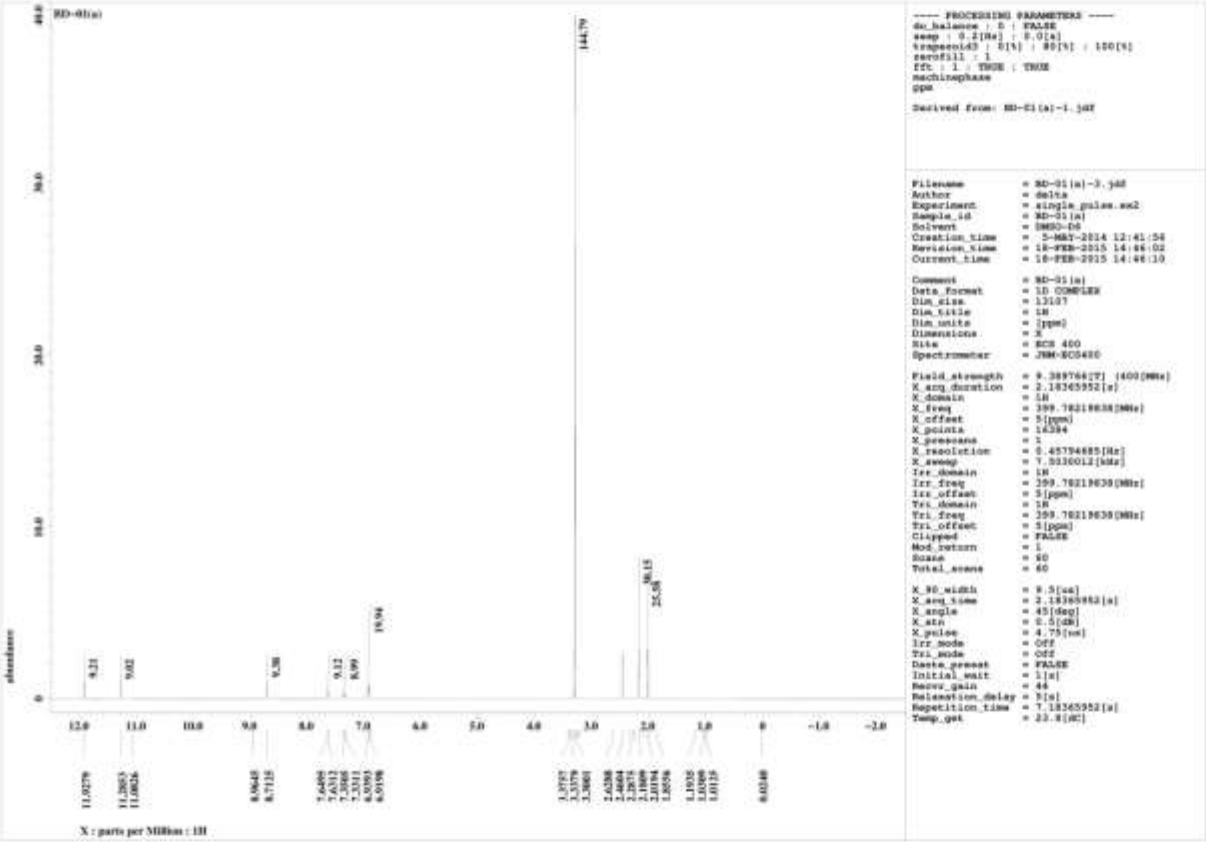


Figure S2: FTIR spectrum of compound **H2**



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ppm

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X_pulse            = 4.75[us]
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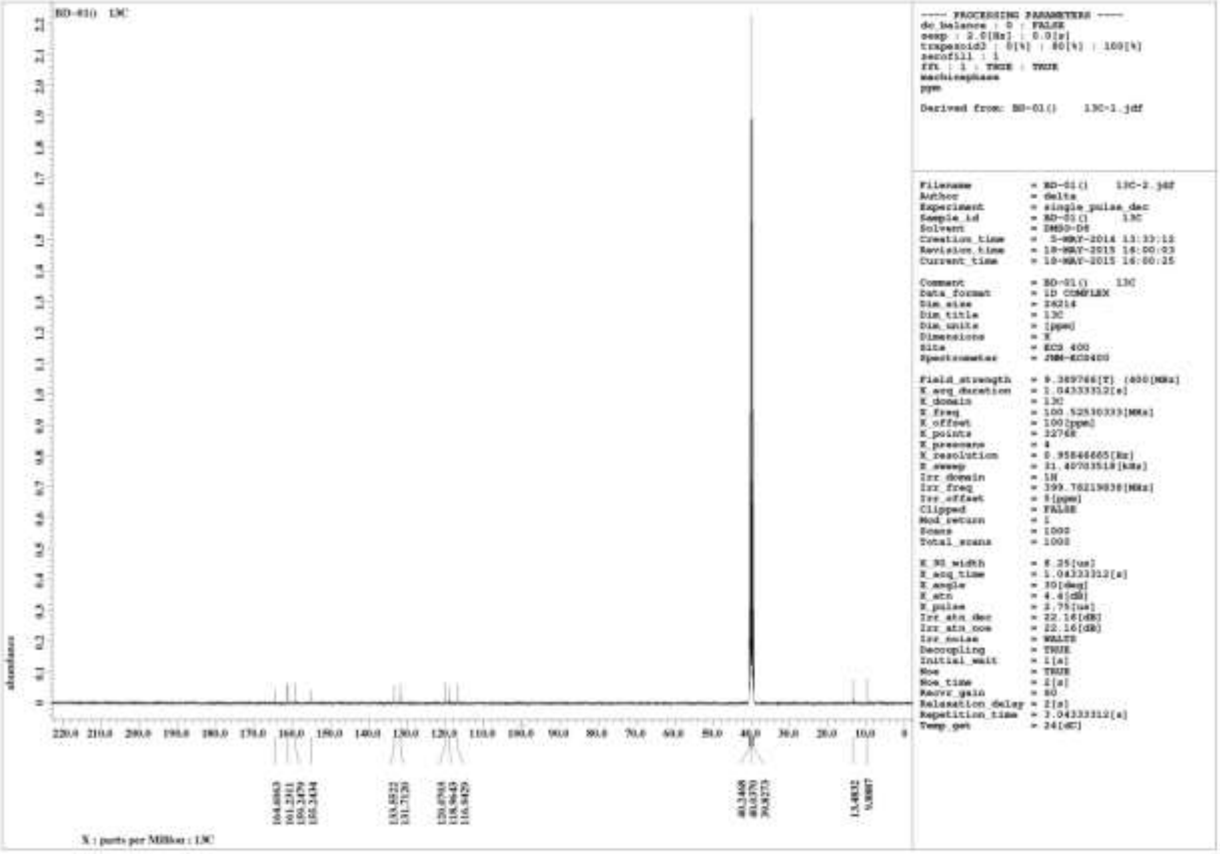
Figure S3: ^{1}H-NMR spectrum of compound **H1**.



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ppm

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Spectrometer      = JNM-ECS400

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X_sweep           = 31.40703518[kHz]
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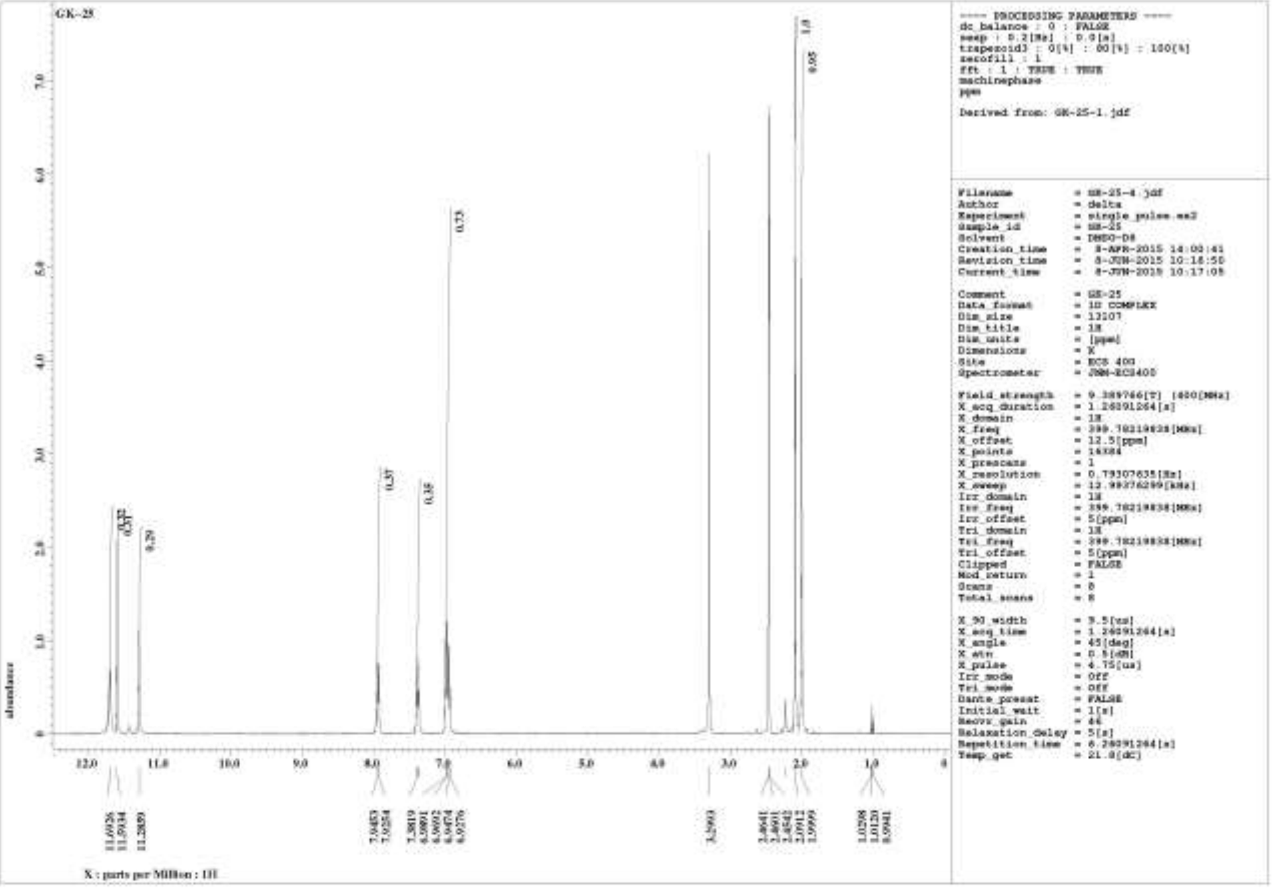
Figure S4: ^{13}C-NMR spectrum of compound **H1**.



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Spectrometer      = JNM-ECS400

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X_sweep           = 12.99376299[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
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X_atn             = 0.5[dB]
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Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
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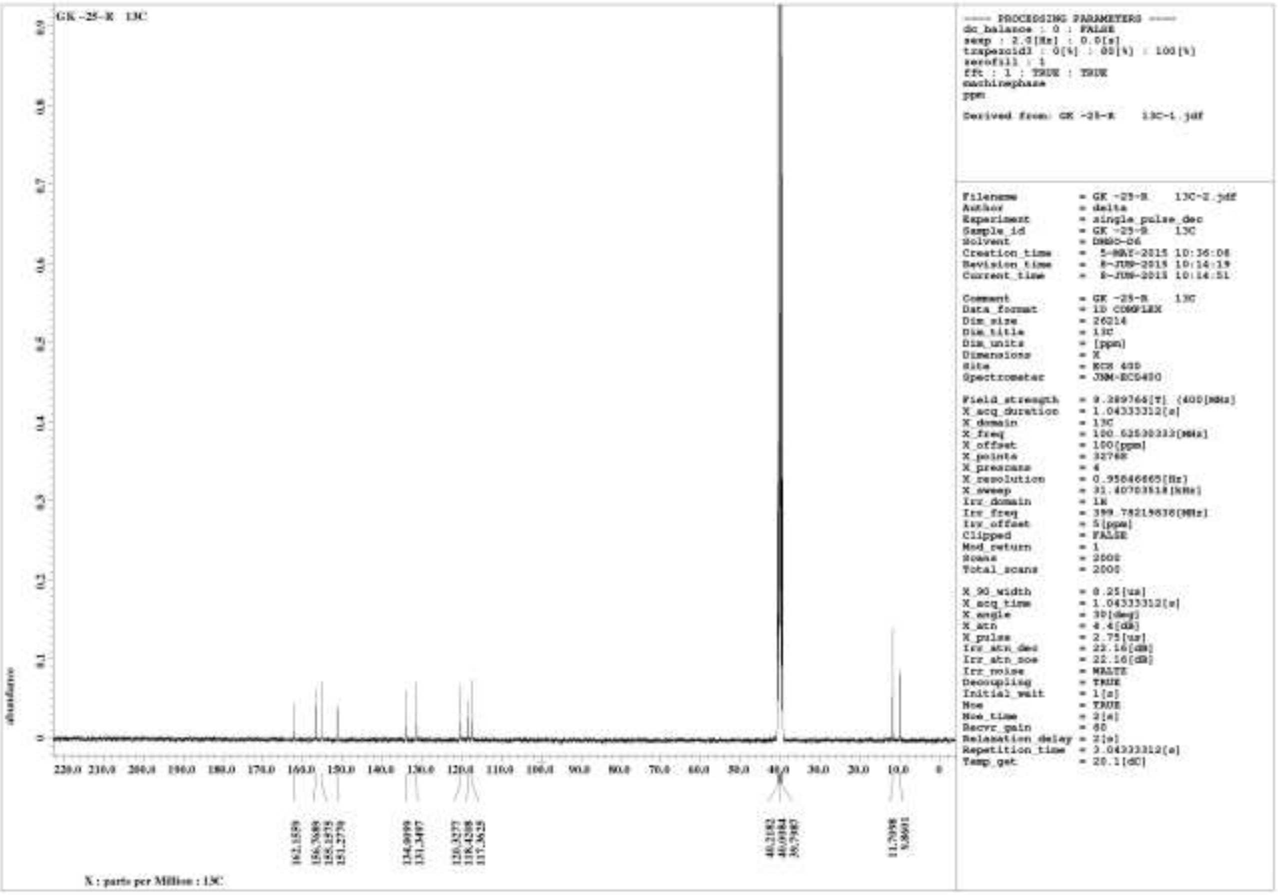
Figure S5: ^{1}H-NMR spectrum of compound **H2**.



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ppm

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Figure S6: ^{13}C-NMR spectrum of compound **H2**.

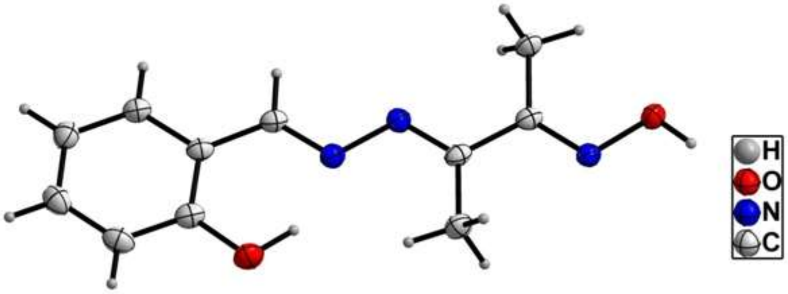

Figure S7: ORTEP diagram of **H1**, with the displacement ellipsoid drawn at the 35% probability level. Crystal data: $C_{11}H_{13}N_3O_2$, a = 19.7074 (7) Å, b = 4.4839(5) Å, c = 12.7541 (5) Å, $\alpha = \gamma$ = 90˚, β = 107.994˚ (2), V = 1071.91 (8), T = 296 K, Monoclinic, Space group P2(1)/n, z = 4. Colour code: red: O, blue: N, grey ellipsoid: C, grey sphere: H.

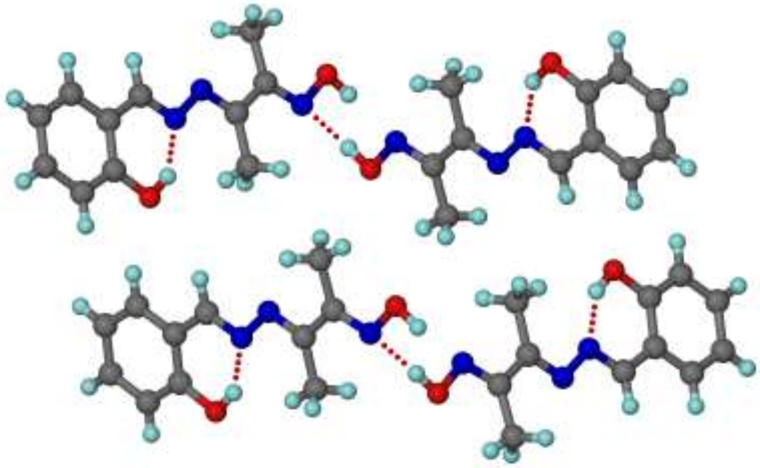

Figure S8: POV ray picture of Hydrogen bonding pattern of **H1** in solid state.

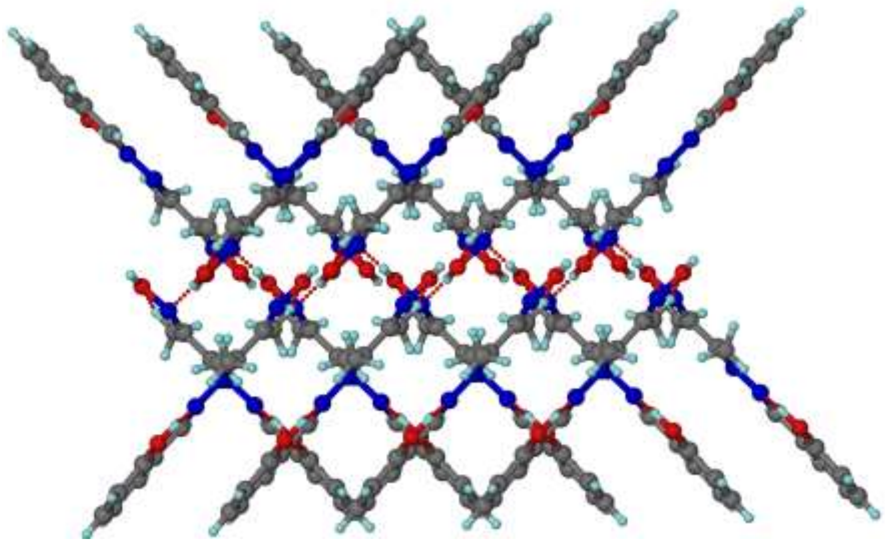

Figure S9: POV ray picture of packing pattern of **H1** in solid state showing Herringbone packing pattern.

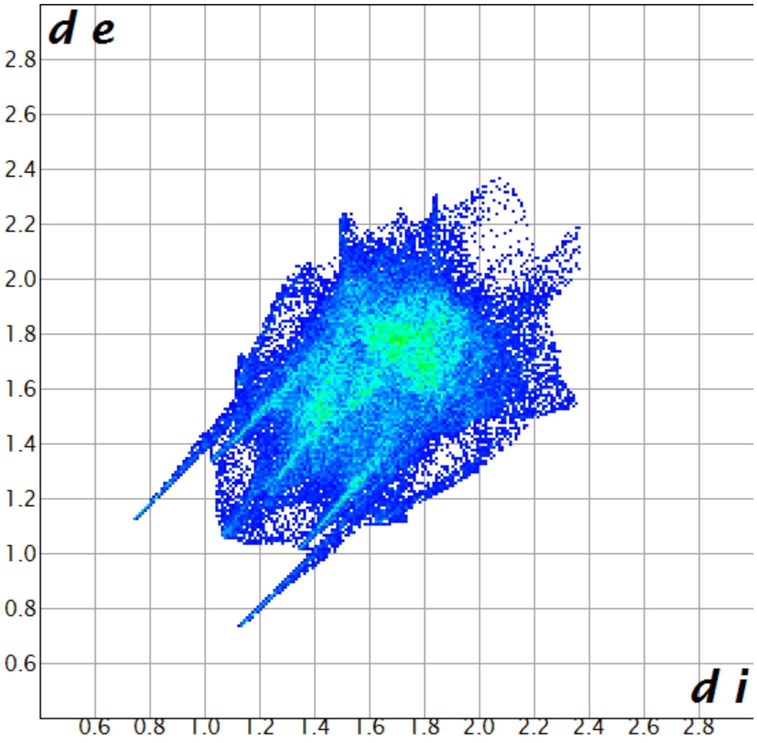

Figure S10: Two-dimensional fingerprint plots of **H1** for Hirshfeld surfaces.

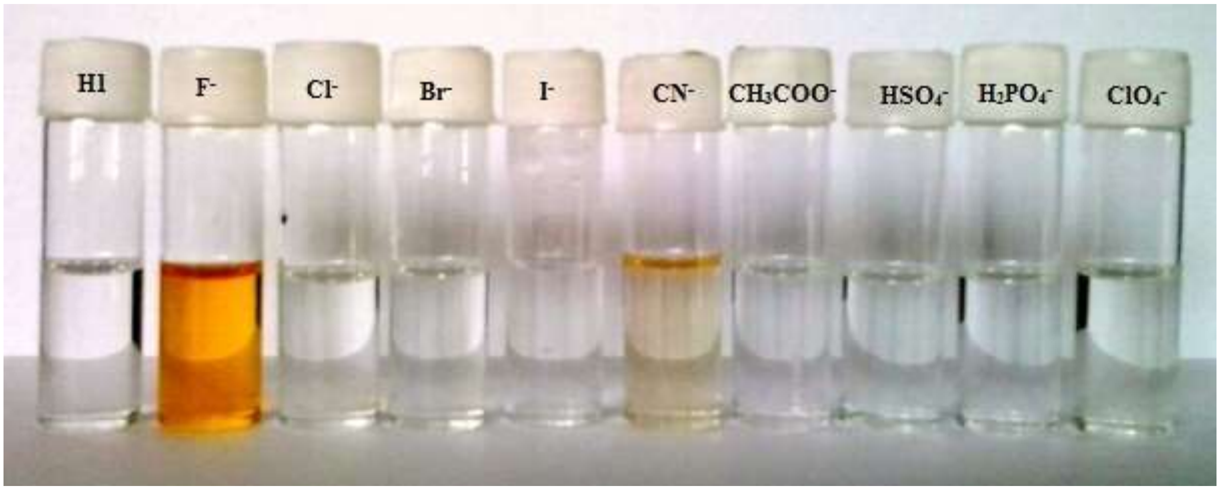

Figure S11: Naked eye view of the colour change while addition of different anions as its tetrabutyl ammonium salt to the solution of **H1** in dimethyl sulphoxide.

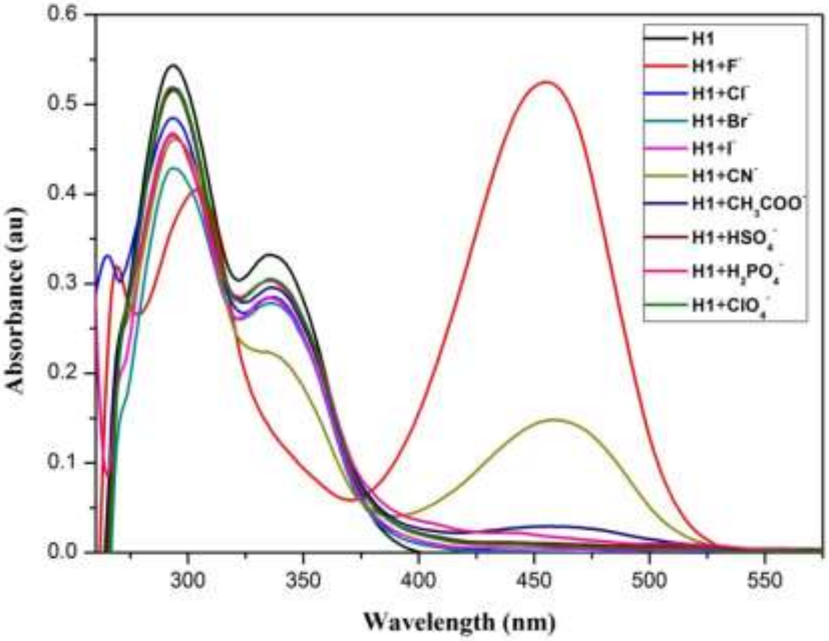

Figure S12: UV-visible absorption spectra of **H1** in dry DMSO (20 μM) after addition of 10 equiv. of different anions in the form of TBA salts.

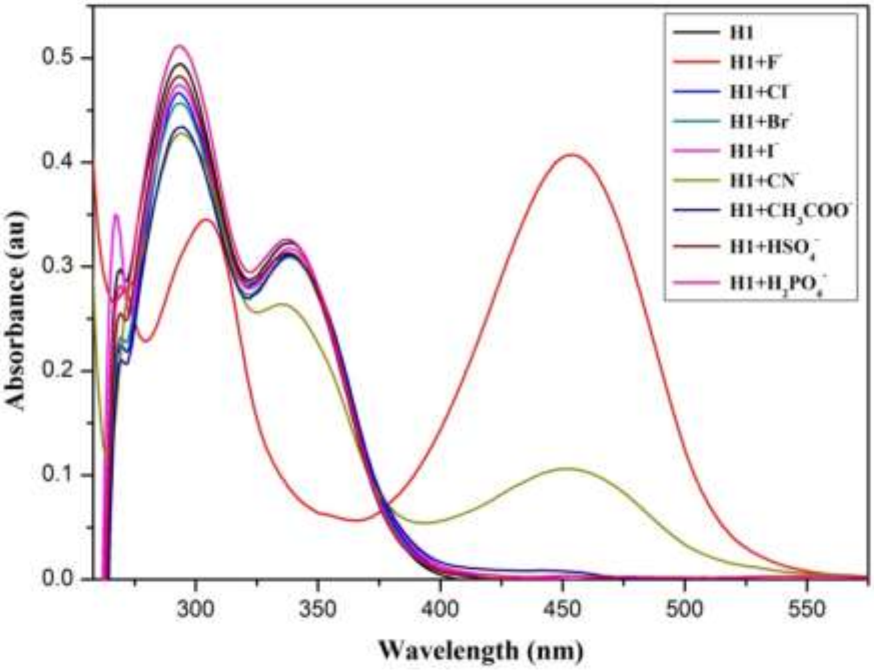

Figure S13: UV-visible absorption spectra of **H1** in dry DMSO (20 μM) after addition of 10 equiv. of different anions in the form of TBA salt solution in water.

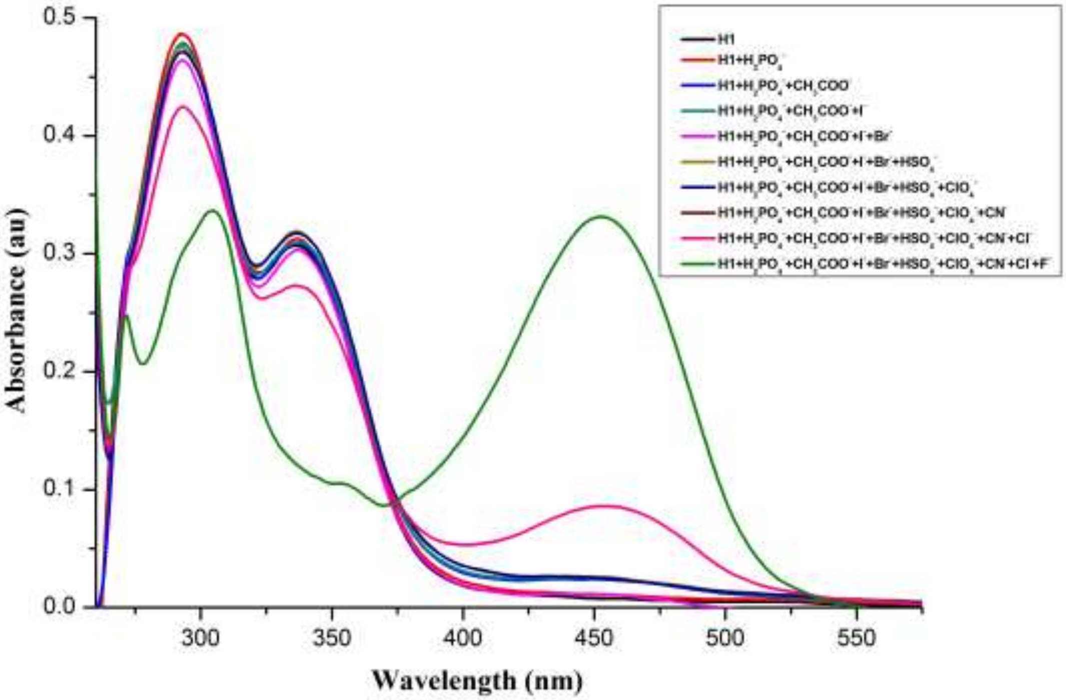

Figure S14: UV-visible absorption spectra of **H1** with sequential addition of different anions in the form of their tetra butyl ammonium salt; blue: **H1** in DMSO, Pink: CN^- in **H1** combined with other anions Green: F^- in **H1** combined with other anions including CN^-**.**

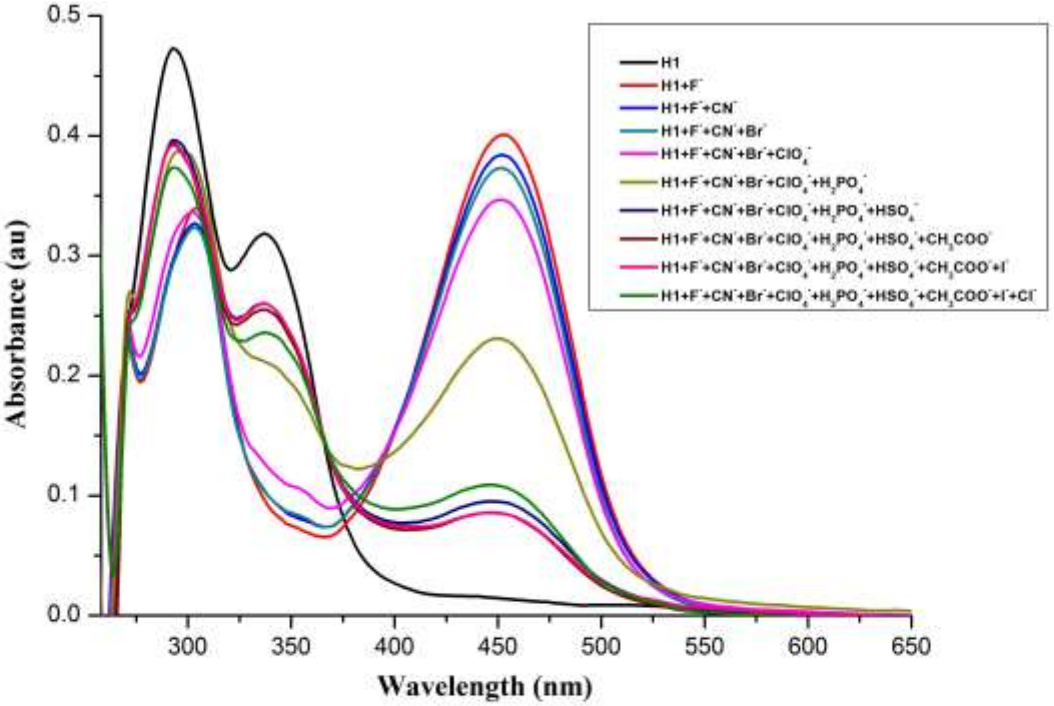

Figure S15: UV-visible absorption spectra of **H1:F**$^-$ in dry DMSO with addition of different anions in the form of their tetra butyl ammonium salt; Black: **H1** red: **H1:F**$^-$**;** Other spectra: **H1:F**$^-$ in presence of other anions**.**

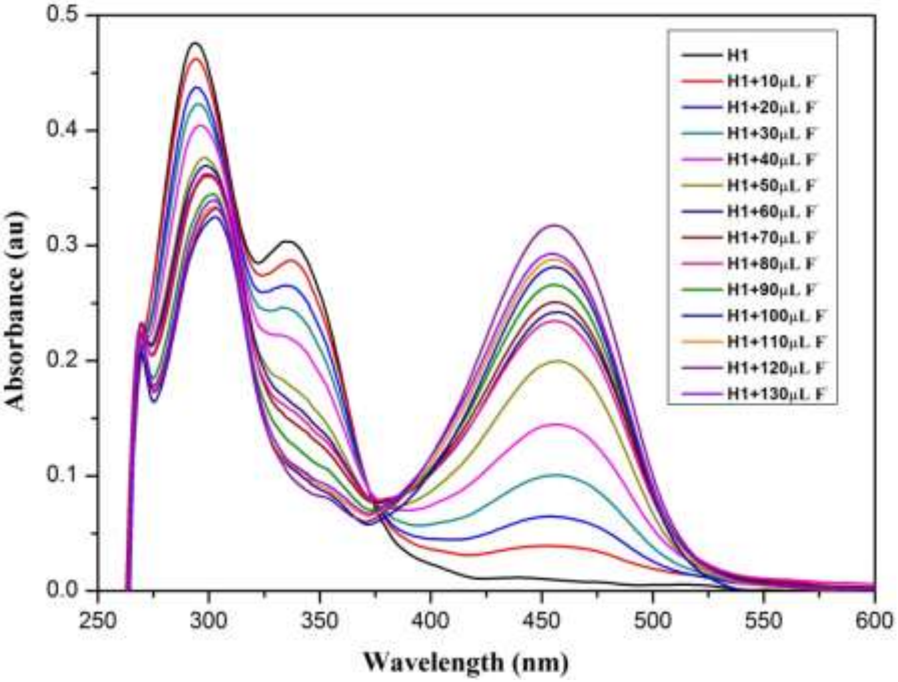

Figure S16: Evolution of UV-visible spectra of **H1 (20** μM) in DMSO upon gradual addition of TBAF solution (14 mmol) in DMSO.

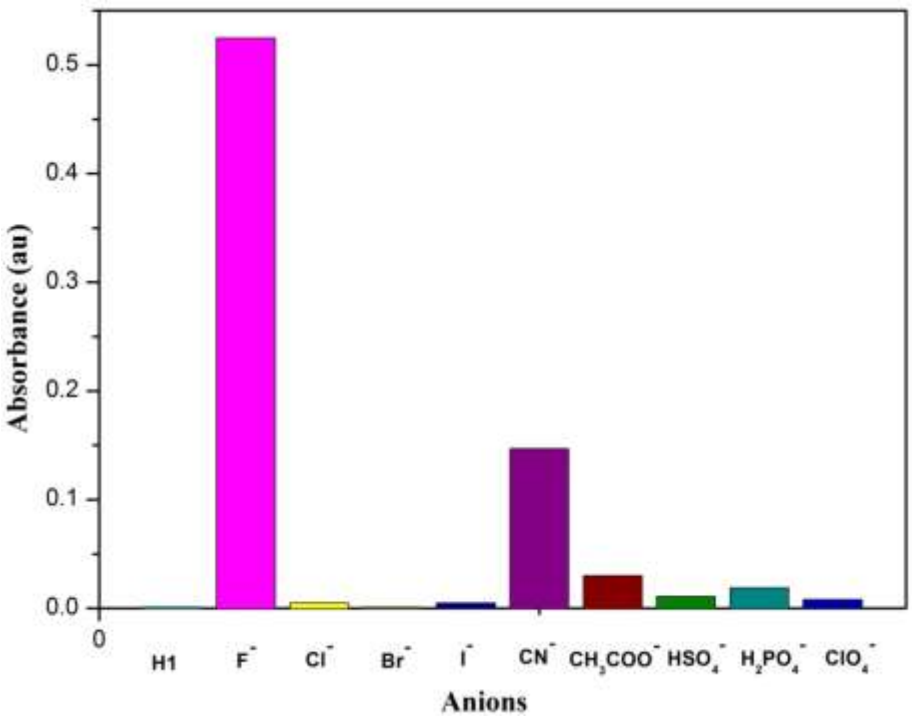

Figure S17: Intensity of the new 445 nm peak of **H1** after addition of 10 equiv. of different anions in the form of their TBA salt.

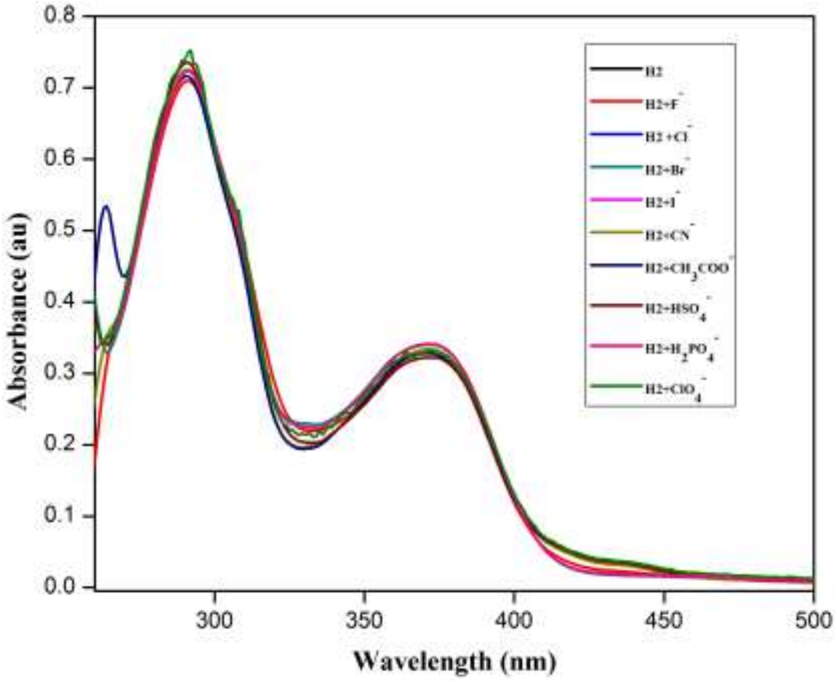

Figure S18: UV-visible spectra of **H2** (20 μM) in DMSO after addition of 10 equiv. of different anions in the form of TBA salt solution.

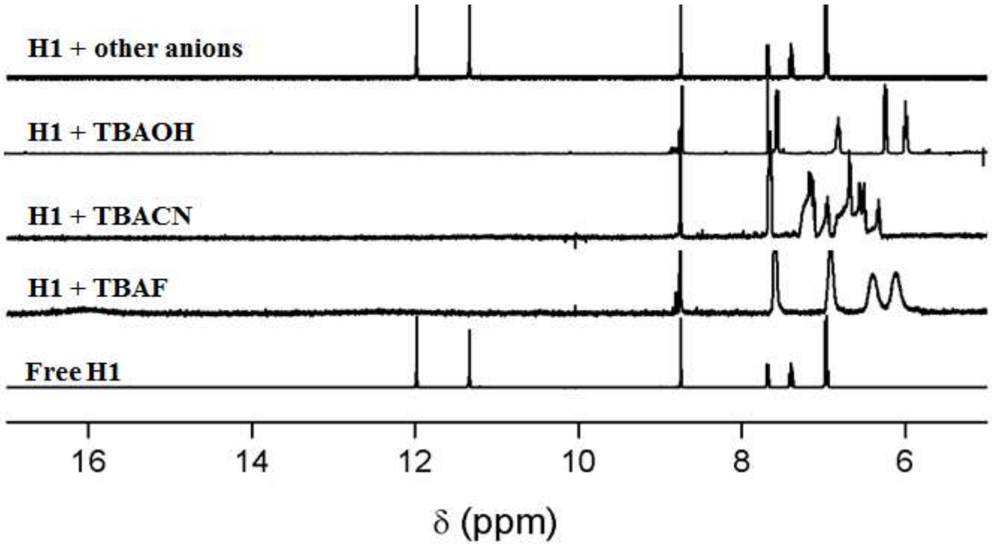

Figure S19: ^{1}H NMR titration plot of **H1** vs. tetrabutyl ammonium salt of different anions in $CDCl_3$.

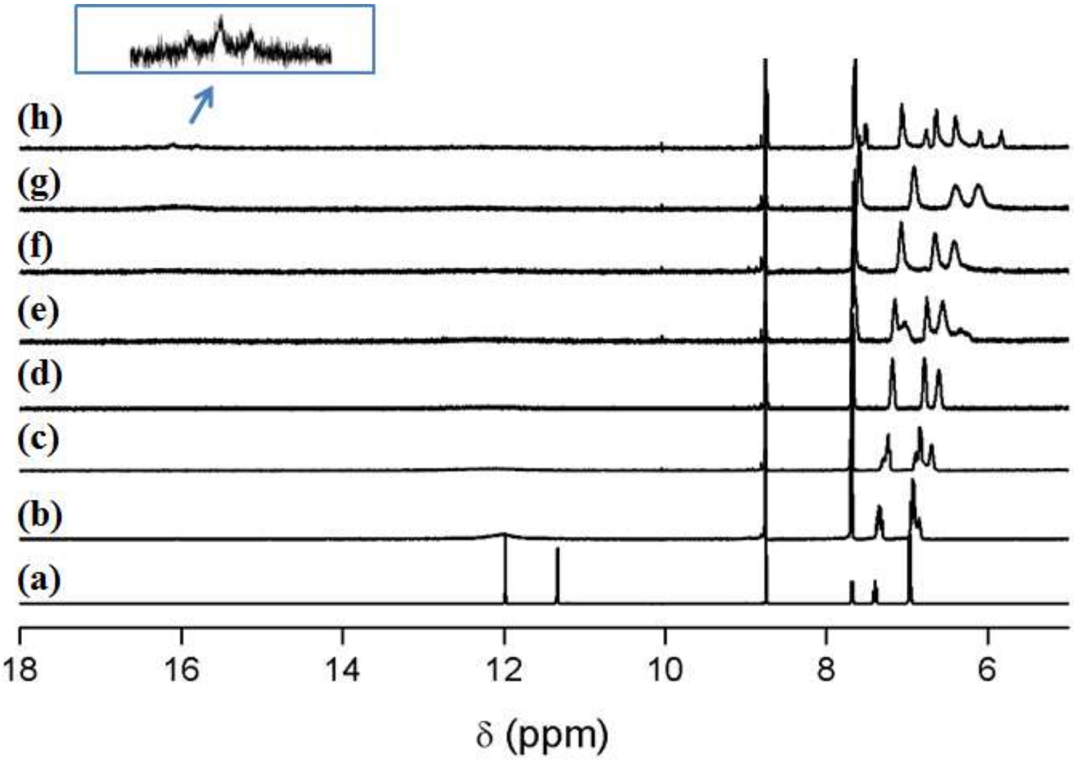

Figure S20: ^{1}H NMR titration plot of **H1** vs. tetrabutyl ammonium fluoride in DMSO-d_6.

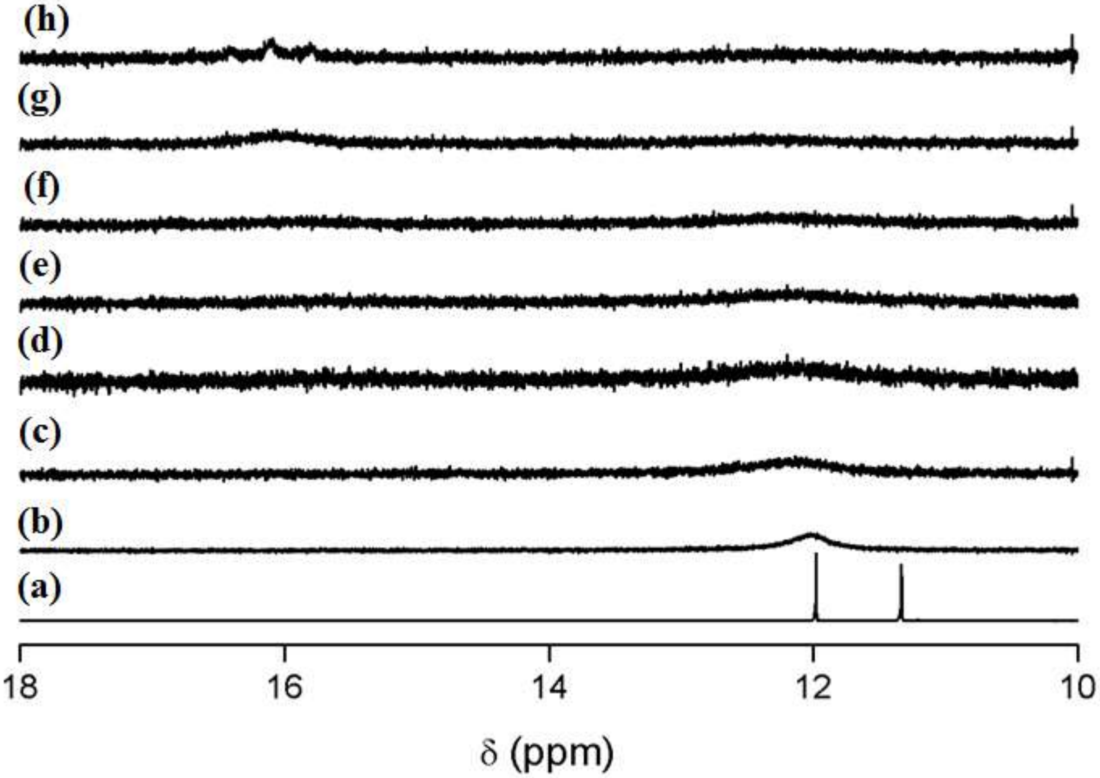

Figure S21: Expanded view of ^{1}H NMR titration plot of **H1** vs. tetrabutyl ammonium fluoride in DMSO-d_6.

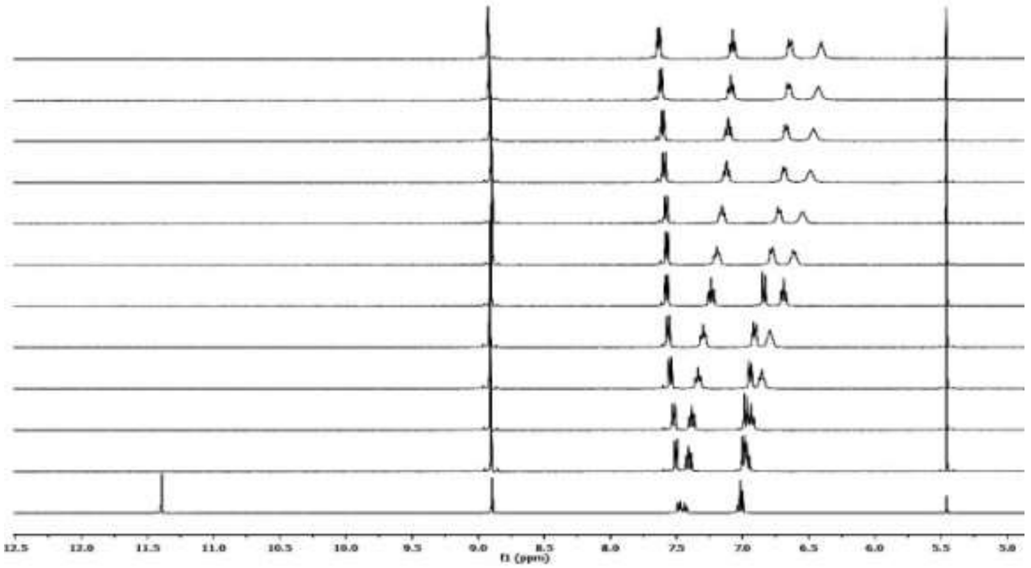

Figure S22: ^{1}H NMR titration plot of **H1** vs. tetrabutyl ammonium fluoride in acetonitrile-d_3.

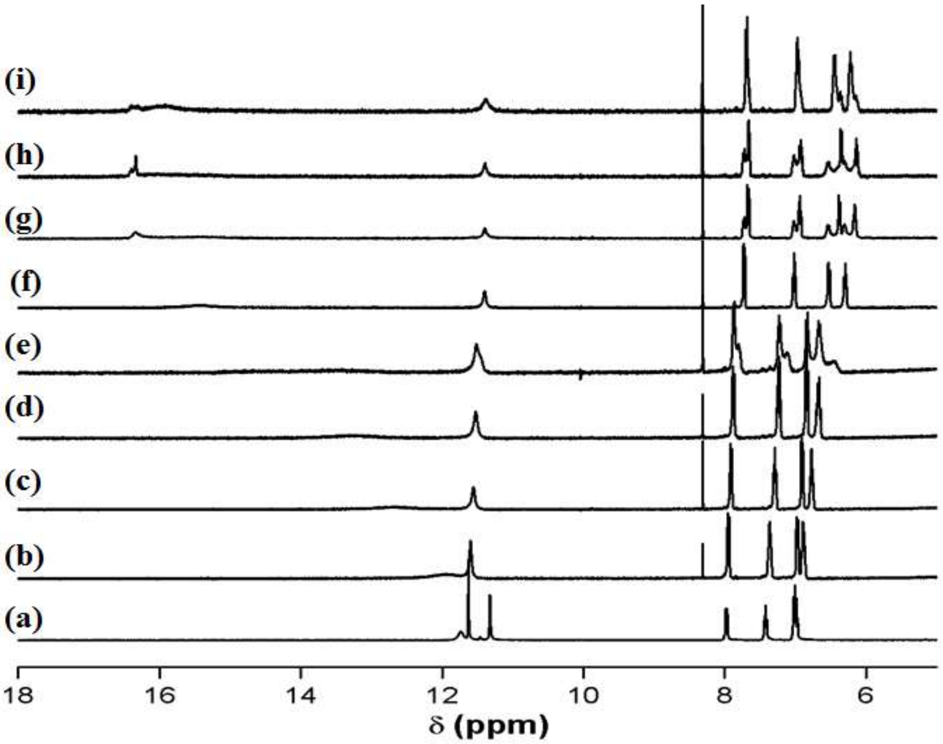

Figure S23: ^{1}H NMR titration plot of **H2** vs. tetrabutyl ammonium fluoride in DMSO-d_6.

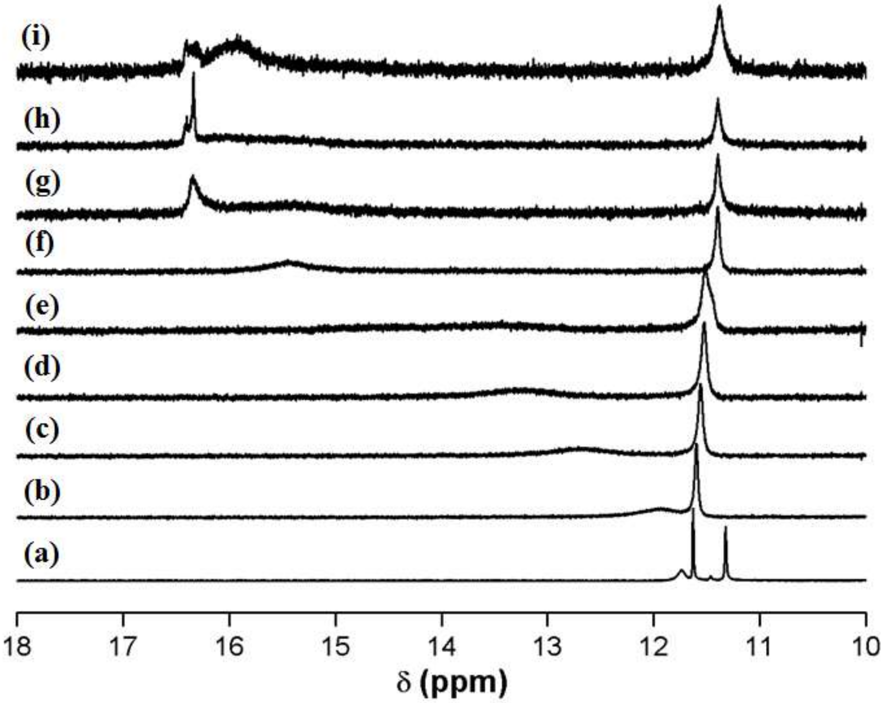

Figure S24: Expanded view of ^{1}H NMR titration plot of **H2** vs. tetrabutyl ammonium fluoride in DMSO-d_6.

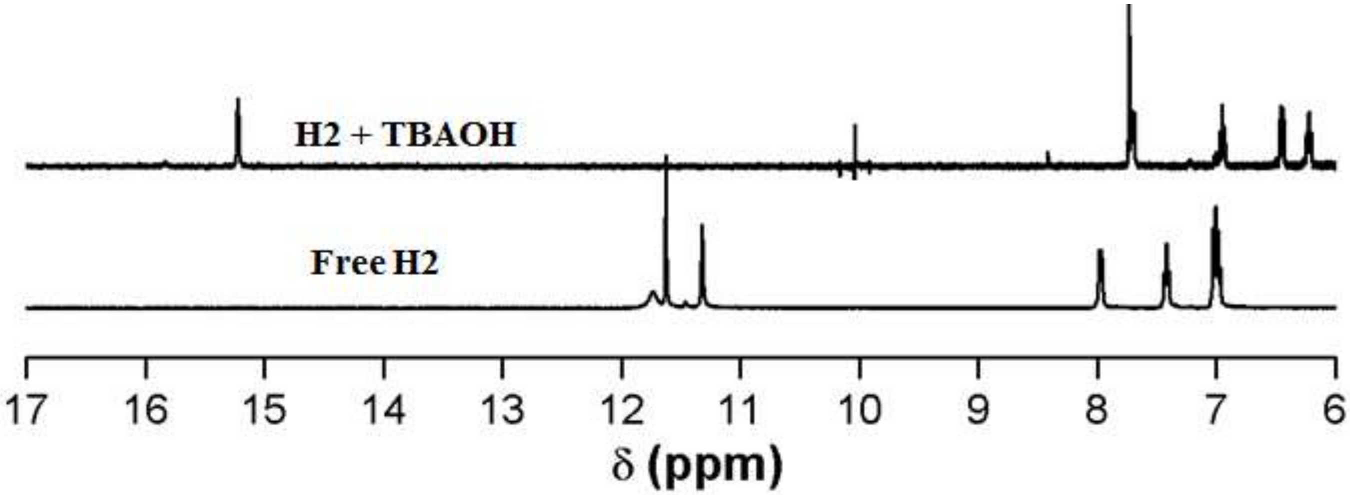

Figure S24: Change in ^{1}H NMR spectra of **H2** after addition of TBAOH in DMSO-d_6

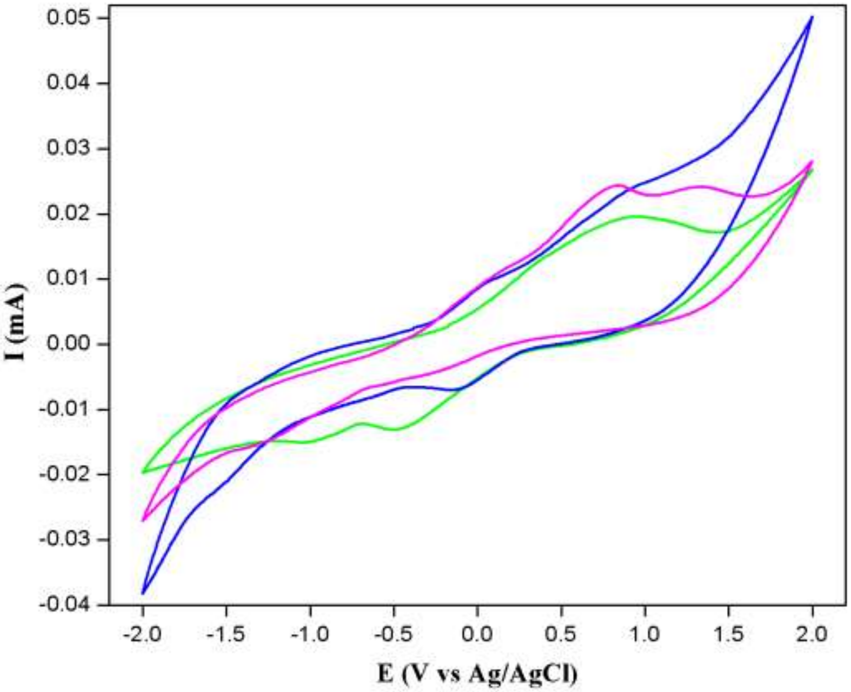

Figure S25: CVs recorded in *n*-Bu_4NClO_4/DMSO. Green: **H1** with $TBAClO_4$ as electrolyte; Pink: **H1** with TBAF as electrolyte; blue: **H1.F$^-$** with $TBAClO_4$ as electrolyte.

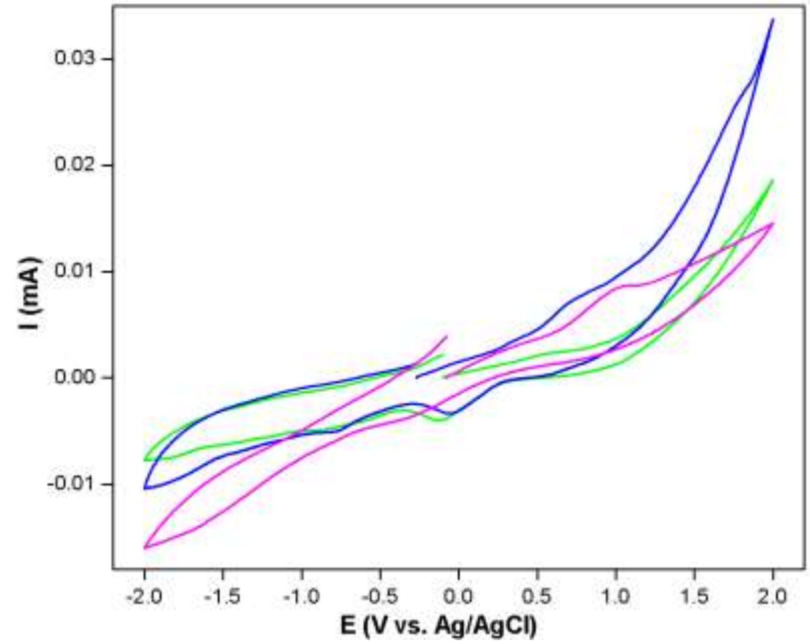

Figure S26: CVs recorded in *n*-Bu_4NClO_4/DMSO. Green: **H2** with $TBAClO_4$ as electrolyte; Pink: **H2** with TBAF as electrolyte; blue: **H2.F**$^-$ with $TBAClO_4$ as electrolyte.

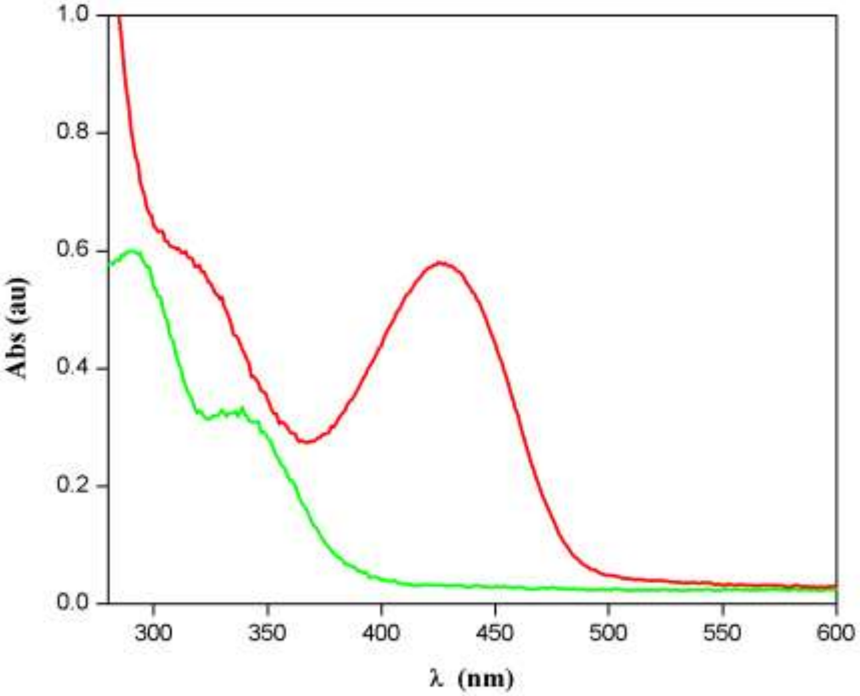

Figure S27: UV-visible spectra of **H1** (20 µM) in DMSO (green) and UV-visible spectra of **H2** after addition of TBAOH solution in methanol.

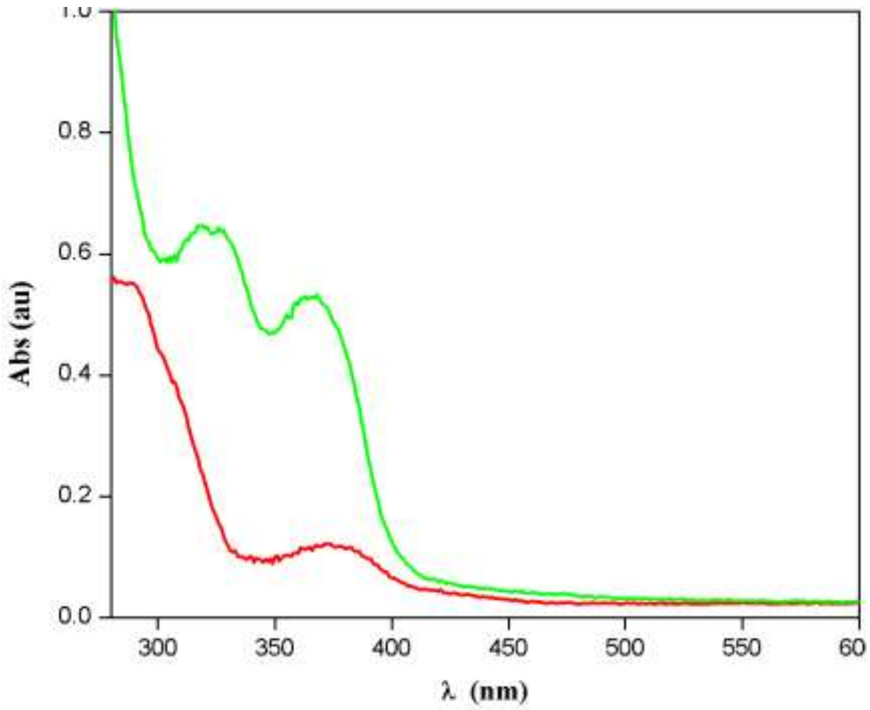

Figure S28: UV-visible spectra of **H2** (20 µM) in DMSO (green) and UV-visible spectra of **H2** after addition of TBAOH solution in methanol.

Tabl1 1: Crystal data and refinement parameters of **H1**.

Empirical formula	$C_{11}H_{13}N_3O_2$
Formula weight	219.14
Temperature/K	296(2)
Wavelength/ Å	0.71073
Crystal system	monoclinic
Space group	$P2_1/C$
Unit cell dimensions	a = 19.7074(7) Å
	b = 4.4839(2) Å
	c = 12.7541(5) Å
	α = 90º
	β = 107.994(2)
	ɣ = 90º
Volume/ $Å^3$	1071.90(7)
Z	4

Density (calculated)/Mgm^{-3}	1.359
Absorption coefficient/mm^{-1}	none
F(000)	464
Crystal size/mm^{3}	0.18 × 0.14 × 0.11
Theta range for data collection/º	1.09 to 26.18º
Index ranges	$-22 \leq h \leq 24$, $-5 \leq k \leq 5$, $-15 \leq l \leq 15$
Reflections collected	14556
Independent reflections	2139 [R(int) = 0.0536]
Completeness to $\theta = 26.18^{\circ}$	99.5%
Absorption correction	none
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2139 / 0 / 156
Goodness-of-fit on F^2	1.099
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0606$, $wR_2 = 0.1784$
R indices (all data)	$R_1 = 0.0734$, $wR_2 = 0.2028$
Largest diff. Peak and hole /e Å^{-3}	0.606 and -0.498