Supplementary Material (ESI) for Chemical Communications
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Anion binding *vs* deprotonation in colorimetric pyrrolylamido(thio)urea based anion sensors

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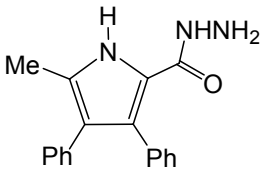
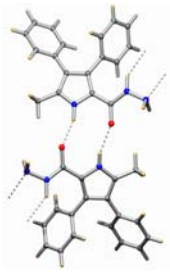
Supplementary information

Experimental procedures

5-Methyl-3,4-diphenyl-1H-pyrrole-2 carbohydrazide **6**.

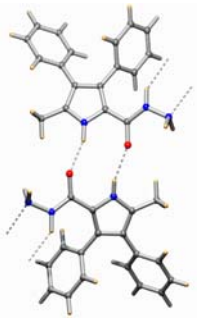




5-Methyl-3,4-diphenyl-1H-pyrrole-2 carboxylic acid ethyl ester (1g, 3.46mmol) was added to a large excess of hydrazine hydrate (5mL, 100eq). To this was then added enough ethanol to produce dissolution. The reaction was heated to reflux for 48 hrs, and then allowed to cool to room temperature. Water was added inducing precipitation of the product. This was collected by filtration, washed with water (3 x 10mL) and dried. A white crystalline solid was produced, 717mg, 71% yield. Solubility precluded the acquisition of a ^{13}C NMR spectrum, however the structure was confirmed by X-ray crystallography (Table S1).

^{1}H ($CDCl_3$): δ 9.67 (br. s, 1H, pyrrole NH), δ 7.26 – 6.91 (m, 10H, Ar. H), δ 6.62 (br. s, 1H, NH), δ 3.79 (br. s, 2H, NH_2), δ 2.29 (s, 3H, CH_3).
MS (ES^+): 605.1 ($2M + Na^+$)

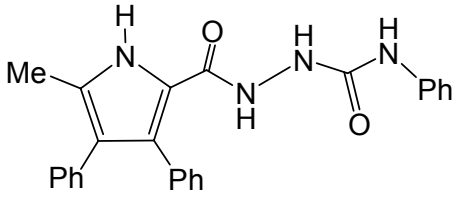
Table S1. Crystal data and structure refinement details for compound **6**.



Empirical formula	$C_{18}H_{17}N_3O$
Formula weight	291.35
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 10.990(4) Å
	b = 18.366(9) Å
	c = 15.123(4) Å
Volume	3033(2) Å^3
Z	8 (2 molecules in the asymmetric unit)
Density (calculated)	1.276 Mg / m^3
Absorption coefficient	0.081 mm^{-1}
F(000)	1232
Crystal	Block; Colourless
Crystal size	0.2 × 0.1 × 0.1 mm^3
θ range for data collection	2.93 – 27.12°
Index ranges	$-13 \le h \le 14$, $-22 \le k \le 23$, $-19 \le l \le 19$
Reflections collected	27627
Independent reflections	6610 [R_{int} = 0.1582]
Completeness to θ = 27.12°	98.5 %
Absorption correction	Semi–empirical from equivalents
Max. and min. transmission	0.9919 and 0.9839
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6610 / 0 / 432
Goodness-of-fit on F^2	0.941
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0685, $wR2$ = 0.1249
R indices (all data)	$R1$ = 0.2330, $wR2$ = 0.1765
Extinction coefficient	0.0043(7)
Largest diff. peak and hole	0.267 and –0.335 e Å^{-3}

Diffractometer: *Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *asymmetric unit*). **Cell determination:** DirAx (Duisenberg, A.J.M.(1992). J. Appl. Cryst. 25, 92-96.) **Data collection:** Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). **Data reduction and cell refinement**: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction**: Sheldrick, G. M. SADABS - Bruker Nonius area detector scaling and absorption correction - V2.10 S**tructure solution**: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473). S**tructure refinement**: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany). **Graphics:** Cameron - A Molecular Graphics Package. (D. M. Watkin, L. Pearce and C. K. Prout, Chemical Crystallography Laboratory, University of Oxford, 1993).

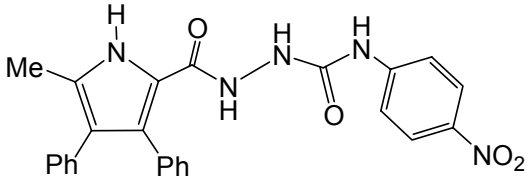
2-(5-Methyl-3,4-diphenyl-1H-pyrrole-2-carbonyl)-N-phenylhydrazinecarboxamide **1**.



Phenyl isocyanate (76μL, 0.70mmol) was dissolved in chloroform, and the solution degassed for 10 mins. Then, 5-methyl-3,4-diphenyl-1H-pyrrole-2 carbohydrazide (203mg, 0.70mmol) was added, and the reaction stirred at room temperature for 24 hours. A precipitate is formed, which was collected by filtration, washed with DCM (3 x 10mL) and dried. A white solid was produced, 137mg, yield of 46%.

^{1}H (DMSO): δ 11.67 (s, 1H, NH), δ 8.72 (s, 1H, NH), δ 8.30 (br. s, 1H, NH), δ 8.10 (s, 1H, NH), δ 7.48 (m, 2H, Ar. H), δ 7.25 (m, 10H, Ar. H), δ 7.04 (m, 2H, Ar. H), δ 2.31 (s, 3H, CH_3).
^{13}C (DMSO): δ 180.5, 160.6, 138.9, 134.8, 134.6, 130.7, 129.8, 128.9, 128.2, 127.9, 127.0, 126.6, 125.6, 124.9, 122.4, 118.7, 11.7.
MS ES^+: 433.2 ($M + Na^+$), 843.4 ($2M + Na^+$), 1253.8 ($3M + Na^+$). ES^-: 409.3 (M - H).
Microanalysis: Calc. for $C_{25}H_{22}O_2N_4.H_2O$: C: 70.08; H: 5.65; N: 13.08. Found C: 70.11; H: 5.20; N: 13.11.

2-(5-methyl-3,4-diphenyl-1H-pyrrole-2-carbonyl)-N-(4-nitrophenyl) hydrazinecarboxamide **2**.

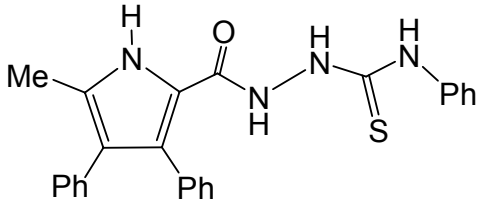


4-Nitrophenyl isocyanate (115mg, 0.70mmol) was dissolved in chloroform (10mL) and degassed for 10 mins. Then, 5-methyl-3,4-diphenyl-1H-pyrrole-2 carbohydrazide (204mg, 0.70mmol) was added and the reaction stirred at room temperature for 24

hours. A precipitate formed, which was collected by filtration, washed with DCM (3 x 10mL) and dried. A cream powder was produced, 280mg, 87% yield.

^{1}H (DMSO): δ 11.62 (s, 1H, NH), δ 9.43 (br. s, 1H, NH), δ 8.43 (br. s, 1H, NH), δ 8.33 (br. s, 1H, NH), δ 8.17 (d, 2H, Ar. H, J=9.15Hz), δ 7.71 (d, 2H, Ar. H, J=9.15Hz), δ 7.18 (m, 8H, Ar. H), δ 6.99 (m, 2H, Ar. H), δ 2.27 (s, 3H, CH_3).
^{13}C (DMSO): δ 160.9, 146.2, 141.1, 134.8, 134.7, 130.6, 129.8, 129.0, 127.8, 126.8, 126.6, 125.6, 125.0, 122.3, 118.6, 117.7, 11.7.
MS ES$^+$: 478.2 (M + Na^+), 933.5 (2M + Na^+). ES-: 454.3 (M - H), 909.5 (2M - H).
Microanalysis: Calc. for: $C_{25}H_{21}N_5O_4$: C: 65.93; H: 4.65; N: 15.37. Found: C: 65.54; H: 4.61; N: 15.05.

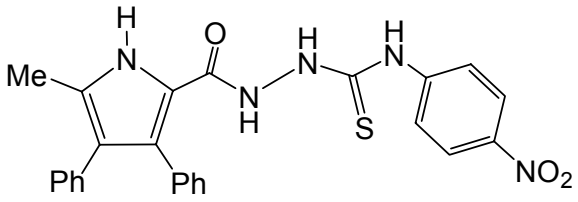
2-(5-methyl-3,4-diphenyl-1H-pyrrole-2-carbonyl)-N-phenylhydrazinecarbothioamide **3**:



The pyrrole carbonyl hydrazine (200mg, 0.686mmol), was added to a degassed solution of phenylisothiocyanate (82μL, 0.69 mmol) in chloroform (10mL). The reaction was stirred at room temperature for 72 hours after which time a white precipitate had formed. This was collected by filtration, washed with DCM and dried to produce 214mg of product, 73% yield.

^{1}H (DMSO-d_6): δ 11.60 (s, 1H, pyrrole NH), δ 9.62 (br. s, 1H, NH), δ 9.52 (br. s, 1H, NH), δ 8.86 (br.s, 1H, NH), δ 7.46 (d, 2H, CH, J = 7.92Hz), δ 7.33 (m, 2H, Ar. H), δ 7.19 (m, 9H, Ar. H), δ 6.97 (d, 2H, Ar. H, J = 6.78), δ 2.26 (s, 3H, CH_3).
^{13}C (DMSO-d_6): δ 180.5, 160.6, 138.9, 134.8, 134.6, 130.7, 129.8, 128.9, 128.2, 127.9, 127.0, 126.6, 125.6, 124.9, 122.4, 118.7, 11.7.
Microanalysis: Calc. for: $C_{25}H_{22}N_4OS$: C: 70.40; H: 5.20; N: 13.14. Found: C: 70.64; H: 5.31; N: 13.05.

2-(5-methyl-3,4-diphenyl-1H-pyrrole-2-carbonyl)-N-(4-nitrophenyl) hydrazinecarbothioamide **4**:



Pyrrole carbonyl hydrazine (400mg, 1.37mmol) was added to a degassed solution of 4-nitrophenylisothiocyanate (248mg, 1.38mmol) in chloroform (15mL). The reaction was stirred at room temperature for 24 hours during which time a yellow precipitate formed. The solution was filtered and the precipitate washed with DCM and dried to produce 550mg of product, 85% yield.

^{1}H (Acetone-d_6): δ 11.92 (s, 1H, pyrrole NH), δ 9.60 (s, 1H, NH), δ 9.02 (s, br, 1H, NH), δ 8.09 (m, 5H, CH and NH), δ 7.21 (m, 10H, CH), δ 2.37 (s, 3H, CH_3).
^{13}C (DMSO): δ 161.4, 146.3, 144.6, 135.8, 135.7, 131.7, 131.5, 131.0, 129.7, 128.8, 128.5, 128.0, 126.7, 124.8, 124.5, 123.3, 119.7, 12.0.
MSES^{+}: 471.9 (M^{+}), 535.0 (M + Na^{+} + CH3CN), 965.1 (2M + Na^{+}).
Microanalysis: Calc. for: $C_{25}H_{21}N_5O_3S$: C: 63.68; H: 4.49; N: 14.85. Found: C: 63.66; H: 4.47; N: 14.86.

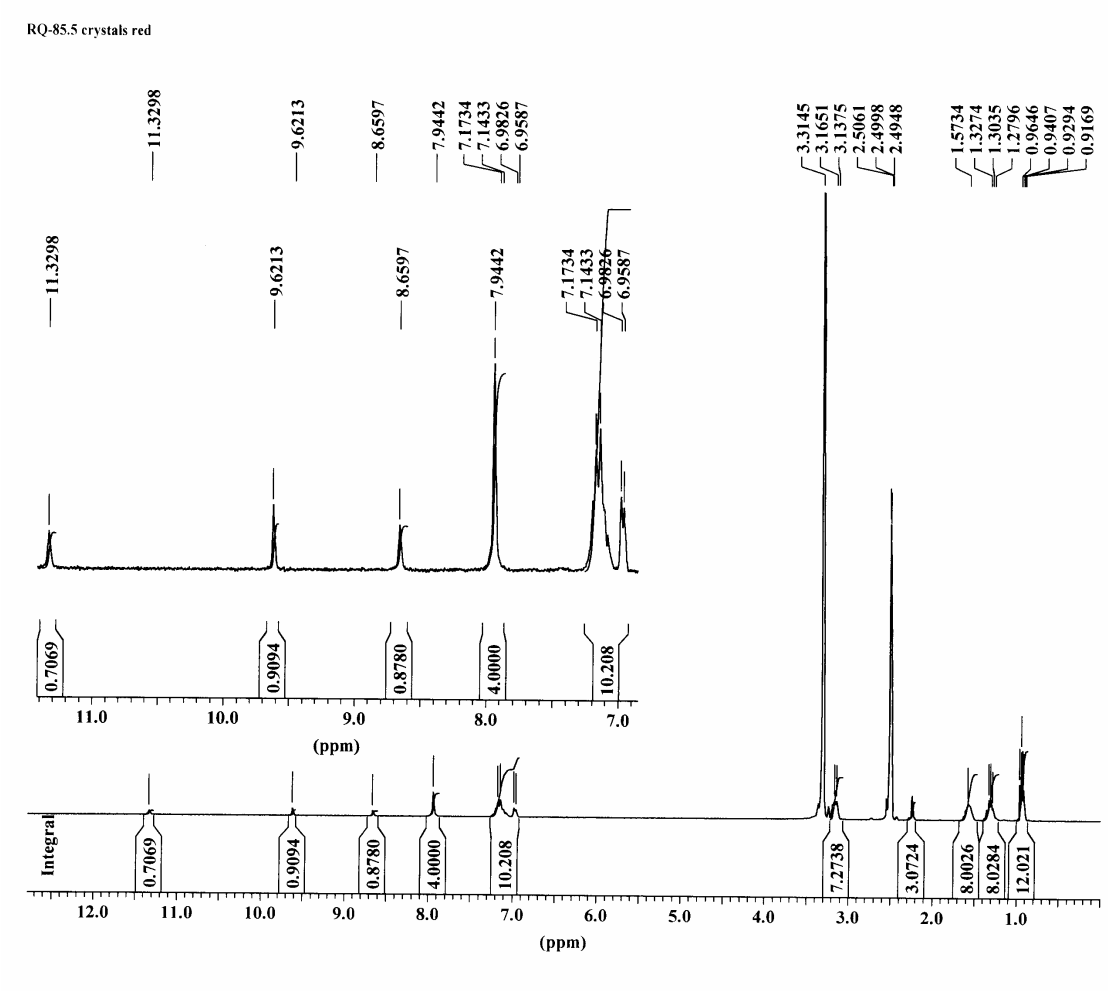


Figure S1 ^{1}H NMR spectra of the TBA salt of deprotonated compound **4** in DMSO-d_6 .

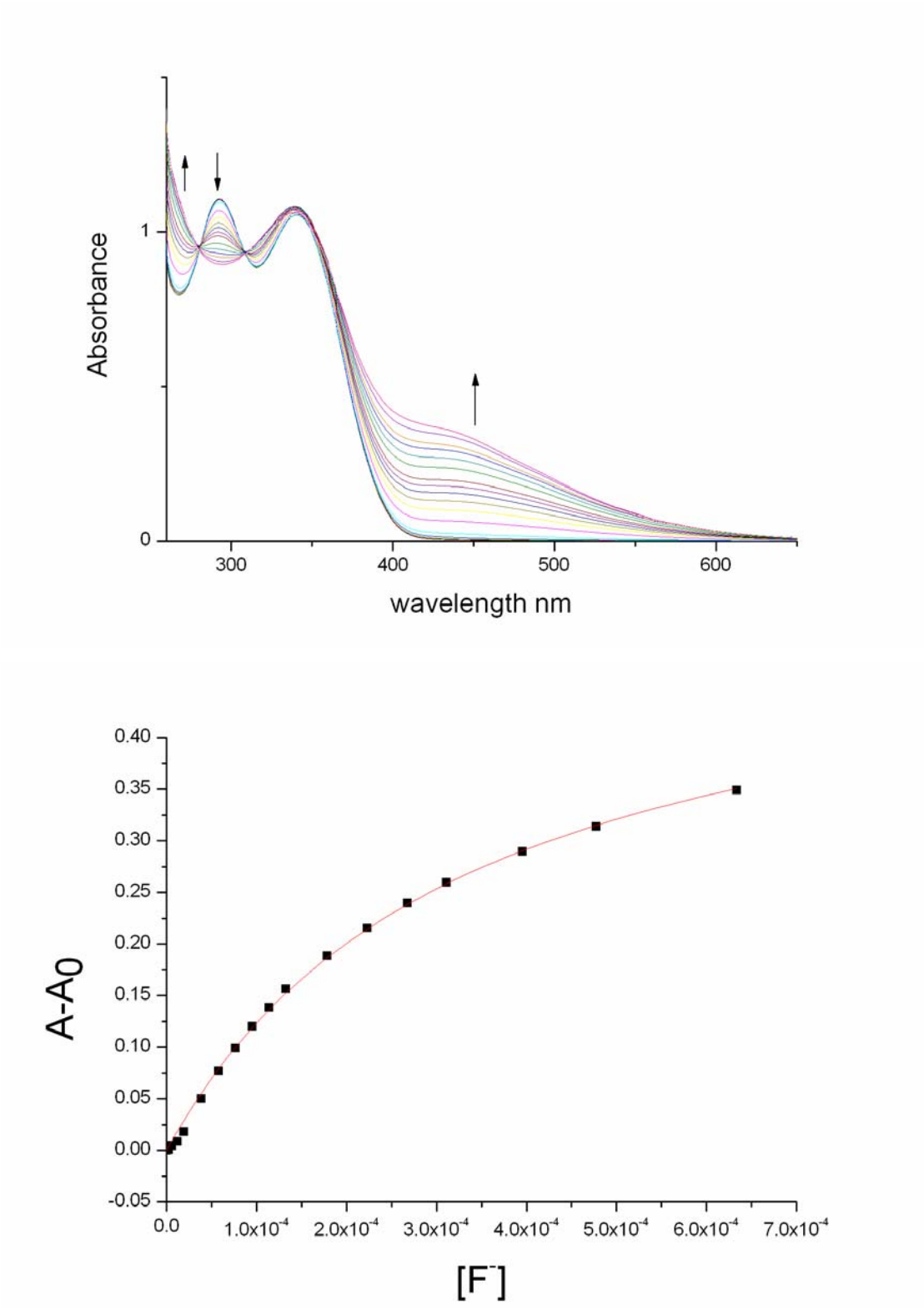


Figure S2 a) UV–vis absorption spectrophotometric titration of compound **2** with TBA fluoride in DMSO at 25 ºC. b) Variation of absorbance at 390 nm versus concentration of anion. The trend line is the result of the non linear least-square fit of the experimental data according to $A-A_0=B\times[F^-]/(1+(K\times[F^-])$

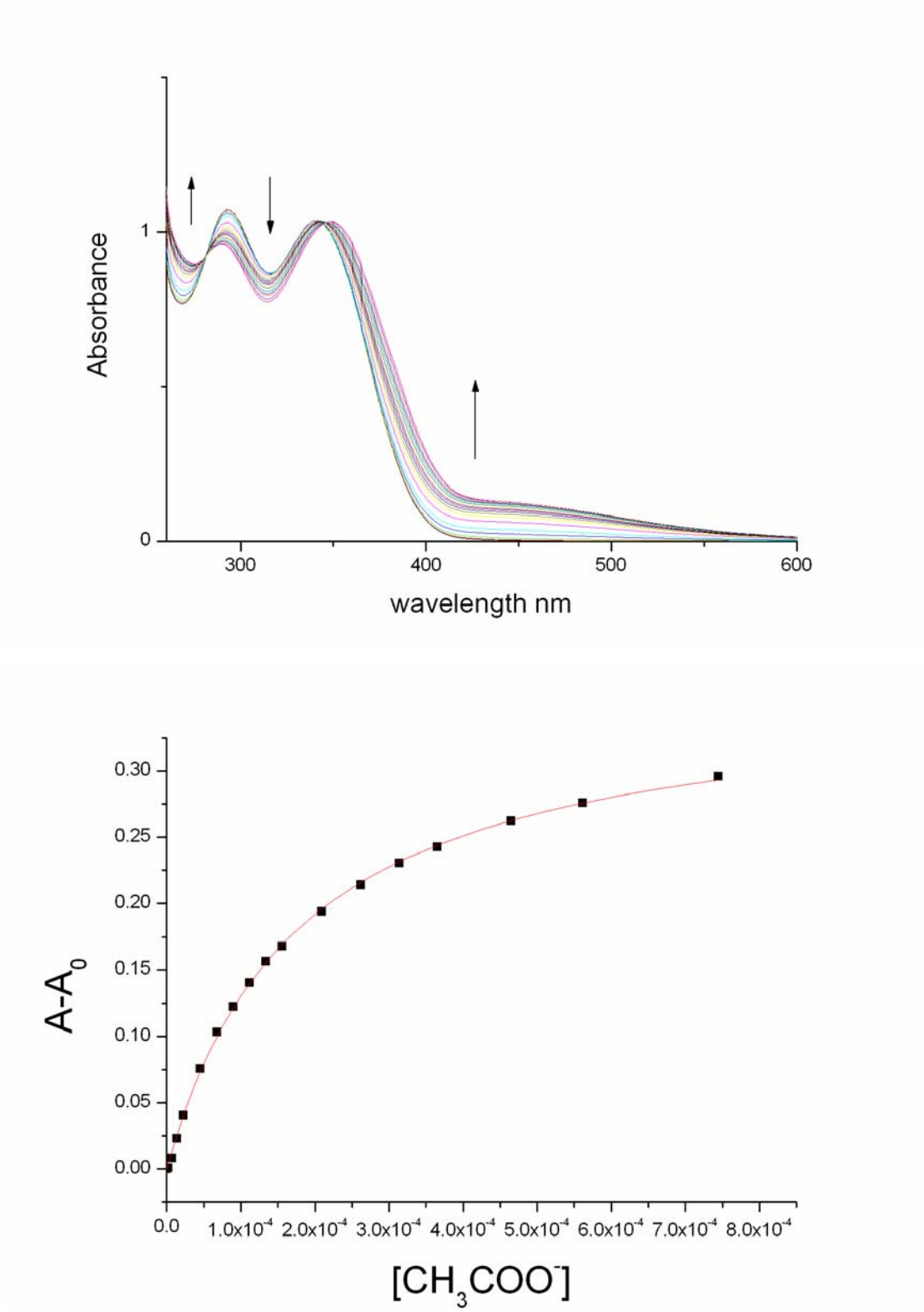


Figure S3 a) UV–vis absorption spectrophotometric titration of compound **2** with TBA acetate in DMSO at 25 ºC. b) Variation of absorbance at 390 nm versus concentration of anion. The trend line is the result of the non linear least-square fit of the experimental data according to $A-A_0=B\times[G^-]/(1+(K\times[G^-])$

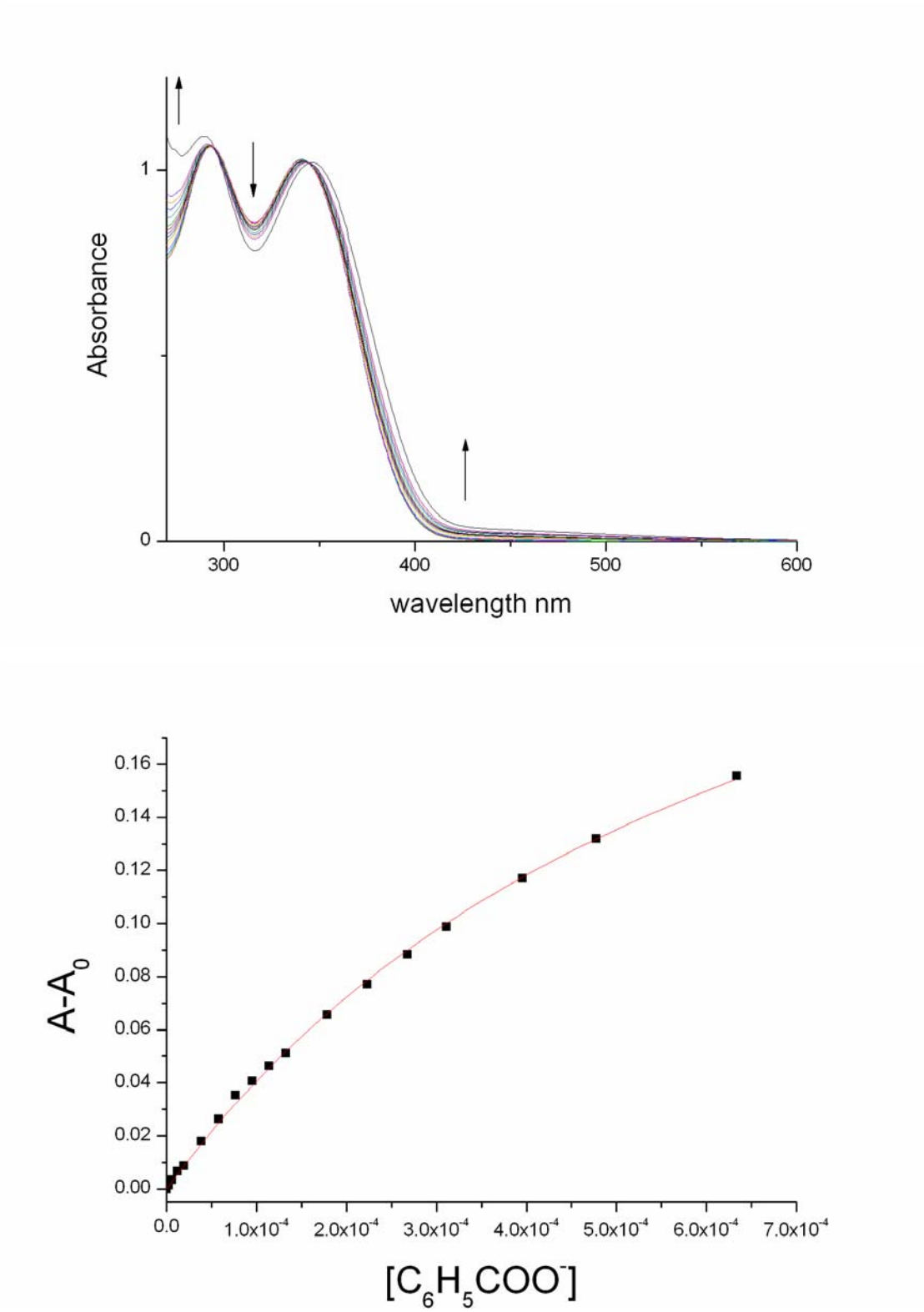


Figure S4 a) UV–vis absorption spectrophotometric titration of compound **2** with TBA benzoate in DMSO at 25 ºC. b) Variation of absorbance at 390 nm versus concentration of anion. The trend line is the result of the non linear least-square fit of the experimental data according to $A\text{-}A_0=B\times[G^-]/(1+(K\times[G^-])$

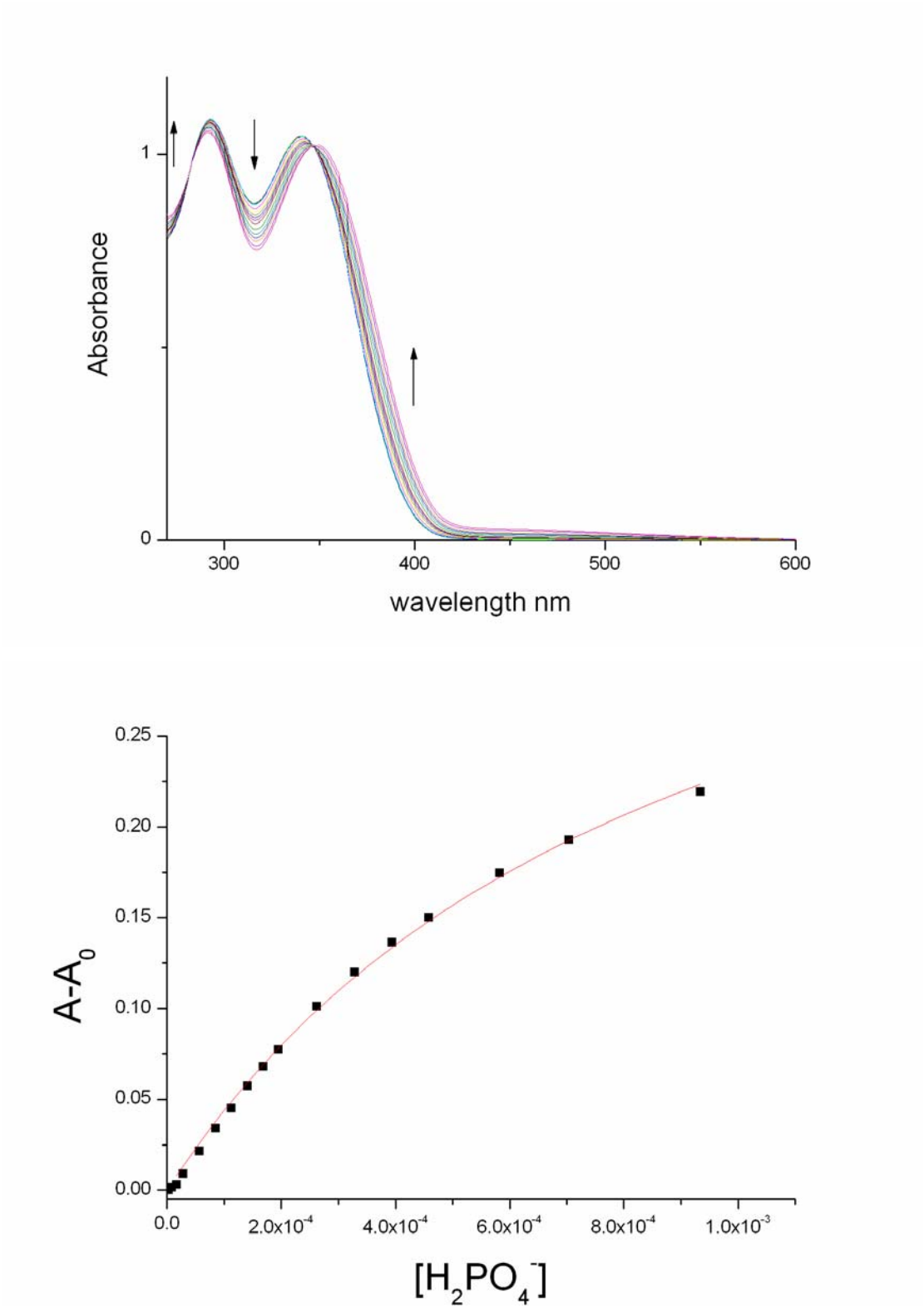


Figure S5 a) UV–vis absorption spectrophotometric titration of compound **2** with TBA dihydrogenphosphate in DMSO at 25 ºC. b) Variation of absorbance at 390 nm versus concentration of anion. The trend line is the result of the non linear least-square fit of the experimental data according to $A\text{-}A_0=B\times[G^-]/(1+(K\times[G^-])$

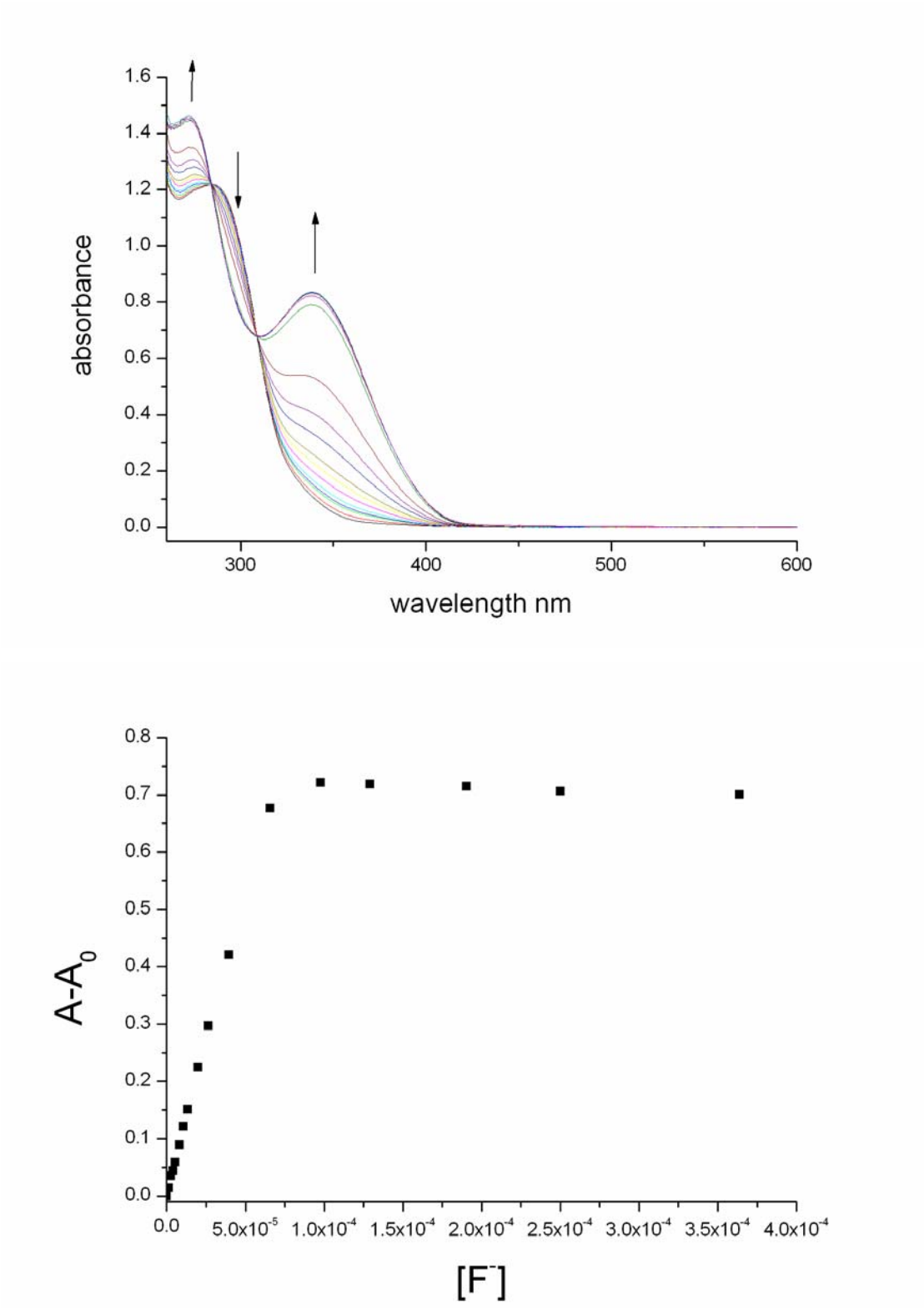


Figure S6 a) UV–vis absorption spectrophotometric titration of compound **3** with TBA fluoride in DMSO at 25 ºC. b) Variation of absorbance at 360 nm versus concentration of anion.

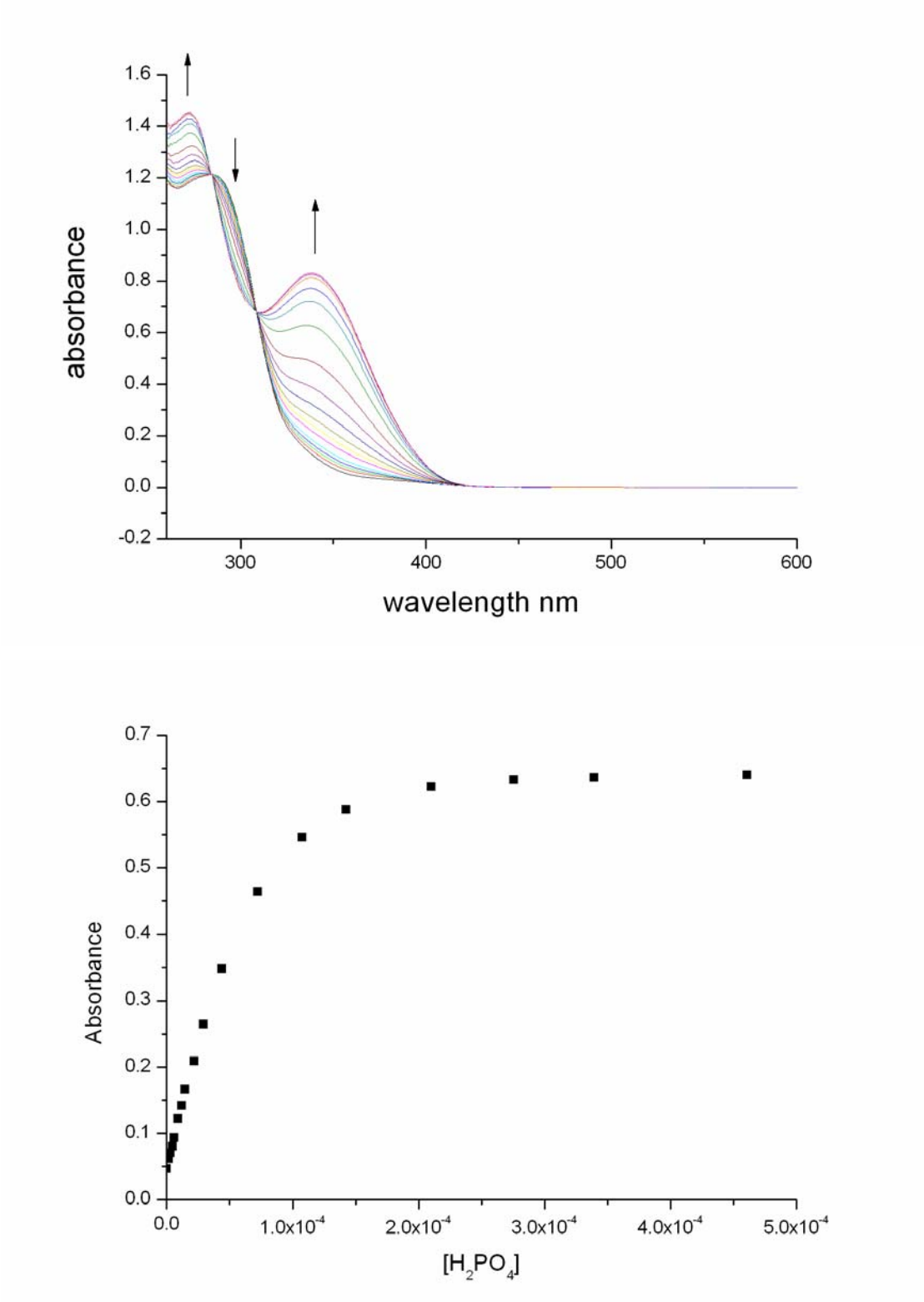


Figure S7 a) UV–vis absorption spectrophotometric titration of compound **3** with TBA dihydrogenphosphate in DMSO at 25 ºC. b) Variation of absorbance at 360 nm versus concentration of anion.

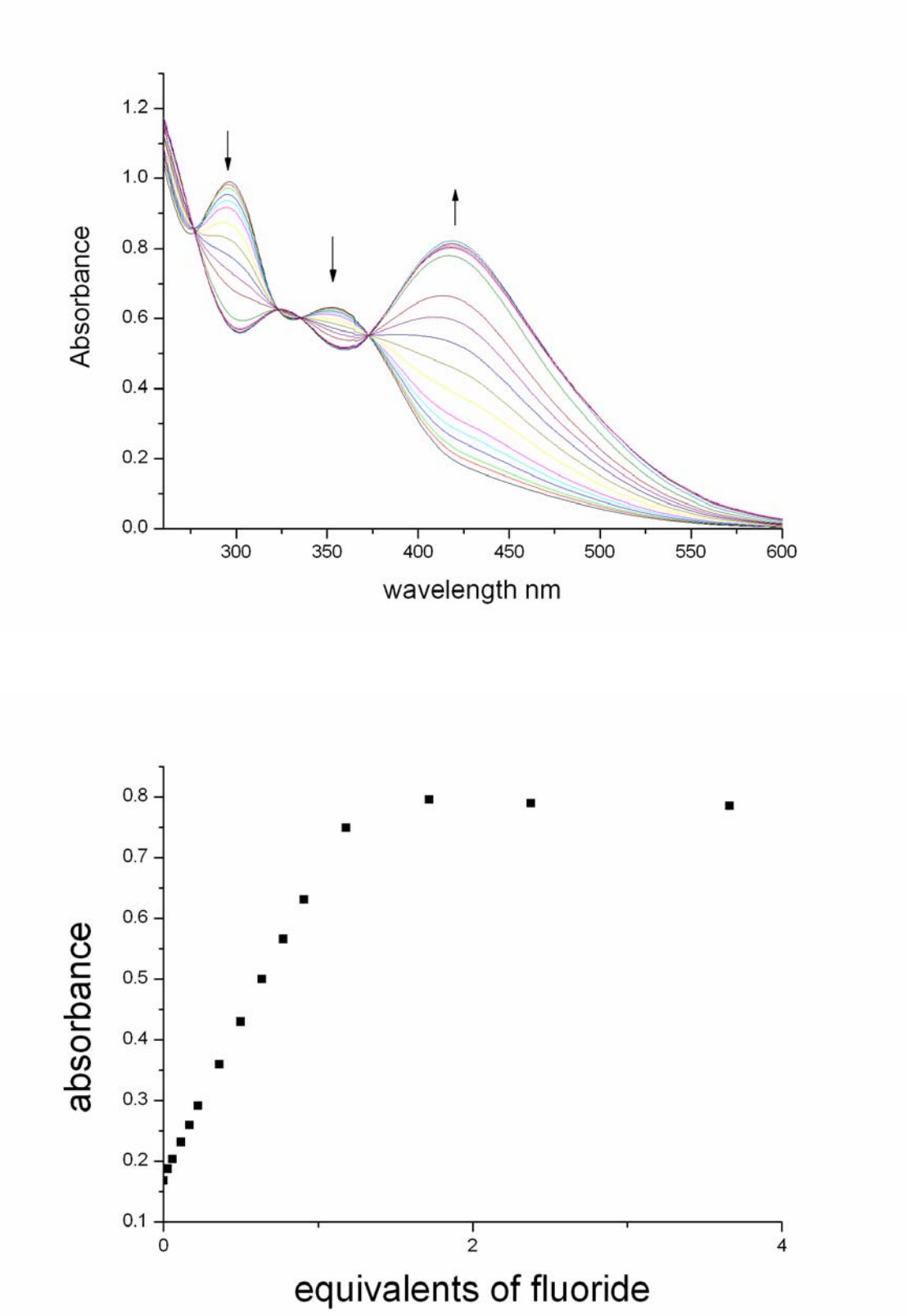


Figure S8 a) UV–vis absorption spectrophotometric titration of compound **4** with TBA fluoride in DMSO at 25 ºC. b) Variation of absorbance at 360 nm versus equivalents of fluoride.

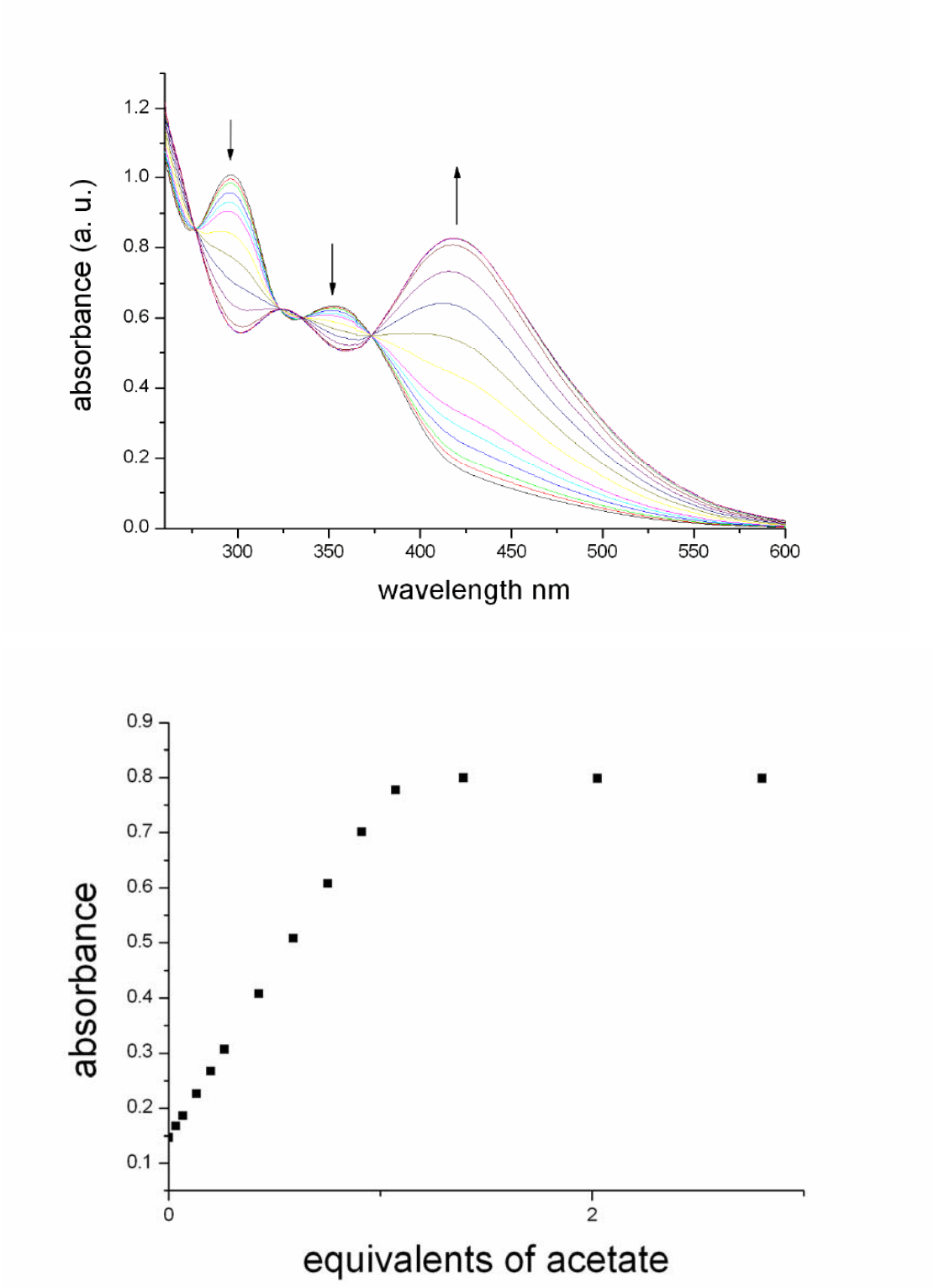


Figure S9 a) UV–vis absorption spectrophotometric titration of compound **4** with TBA acetate in DMSO at 25 ºC. b) Variation of absorbance at 450 nm versus equivalents of acetate.

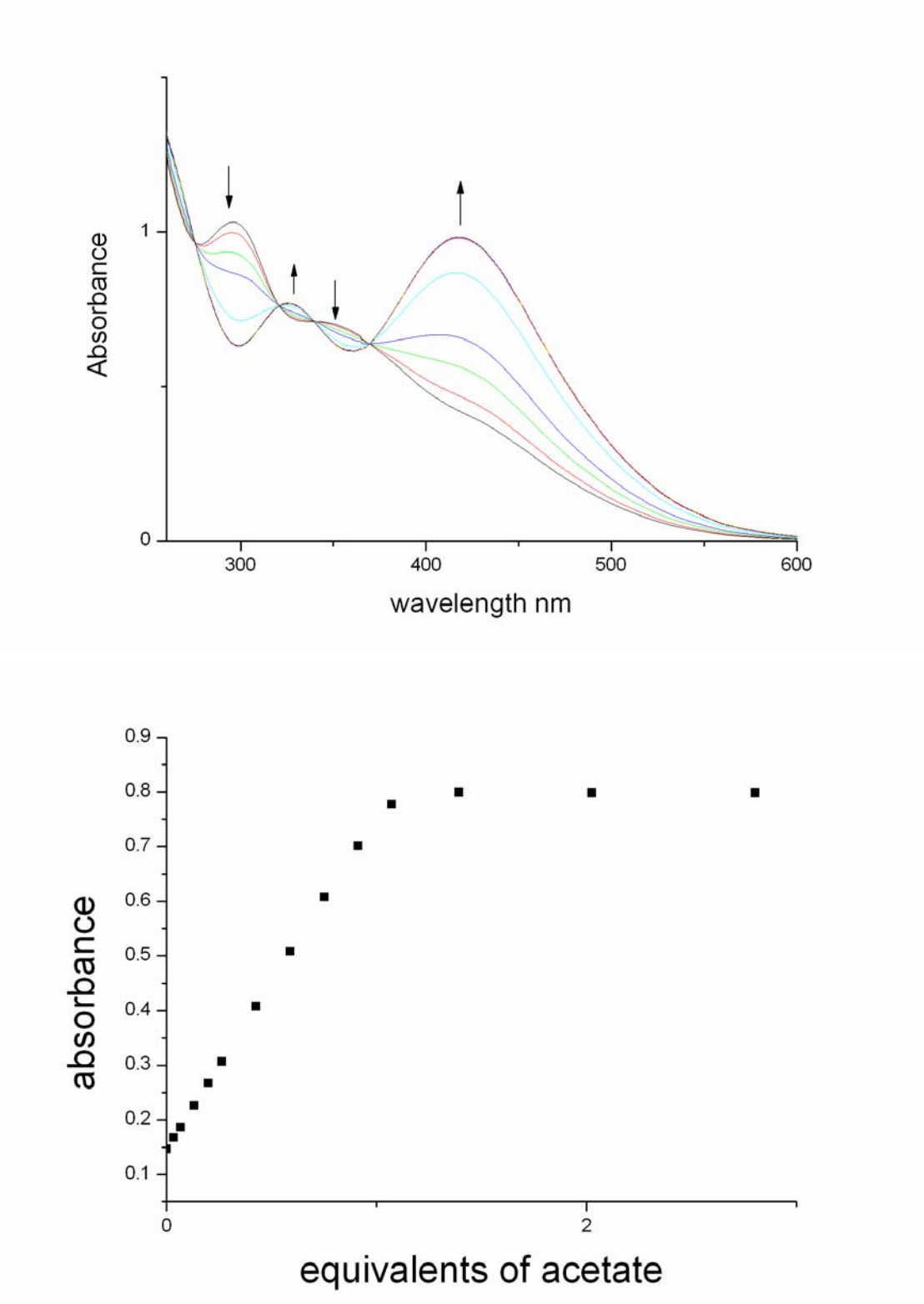


Figure S10 a) UV–vis absorption spectrophotometric titration of compound **4** with TBA acetate in DMSO/ water 9:1 at 25 ºC. b) Variation of absorbance at 450 nm versus equivalents of acetate.

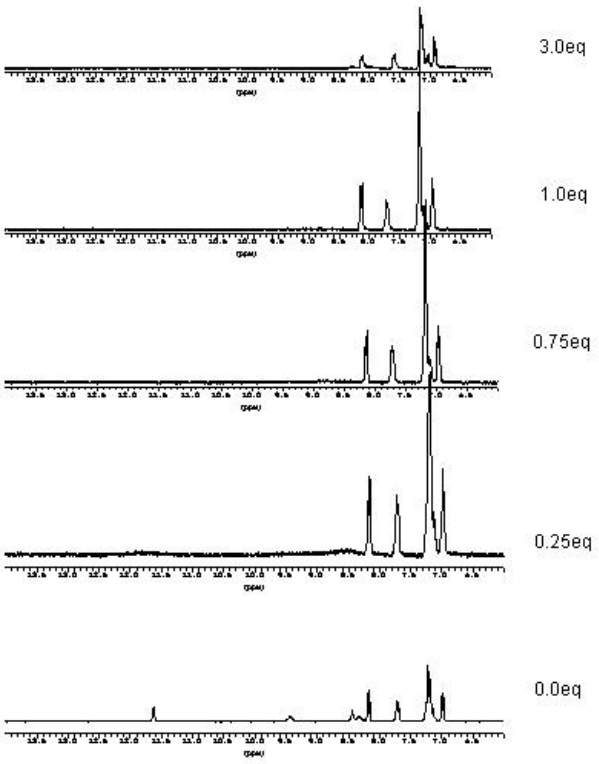


Figure S11 Stack plot of ^{1}H NMR spectra of compound **2** in the presence of increasing amounts of TBAF recorded in DMSO-d_6 .

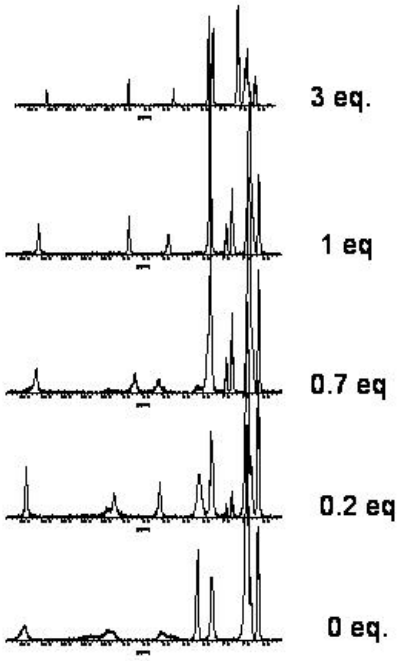


Figure S12 Stack plot of ^{1}H NMR spectra of compound **4** in the presence of increasing amounts of TBA Benzoate recorded in DMSO-d_6 .

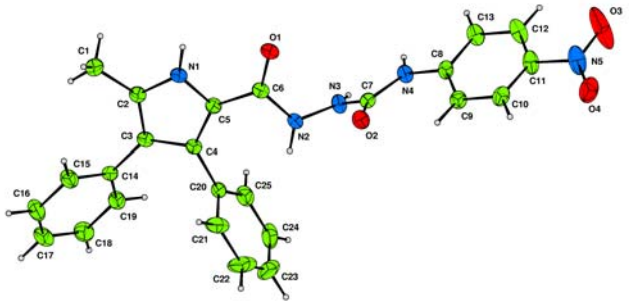


Figure S13 X-Ray crystal structure of compound **2**. Thermal ellipsoids are drawn at the 50% probability level.

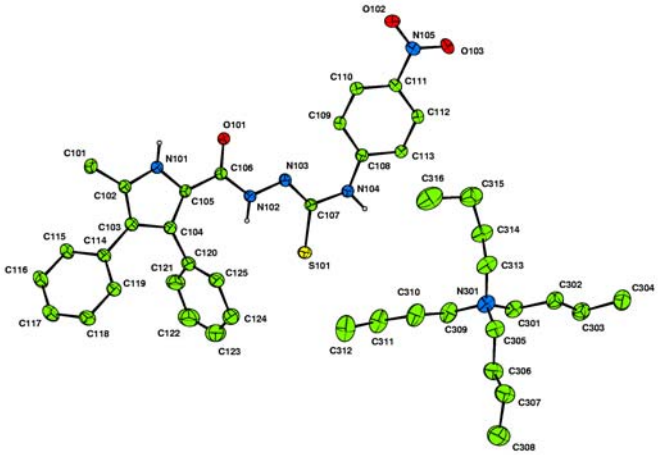


Figure S14 X-Ray crystal structure of tetrabutylammonium (**4**-H^+)$^-$. Thermal ellipsoids are drawn at the 35% probability level. From the asymmetric unit one anion and the tetrabutylammonium cation in the general position are shown.