Supplementary materials (ESI) for New Journal of Chemistry

A new class of functionalized calix[4]arenes as neutral receptors for colorimetric detection of fluoride ions

Har Mohindra Chawla,* Rahul Shrivastava and Satya Narayan Sahu

Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi-110016, India

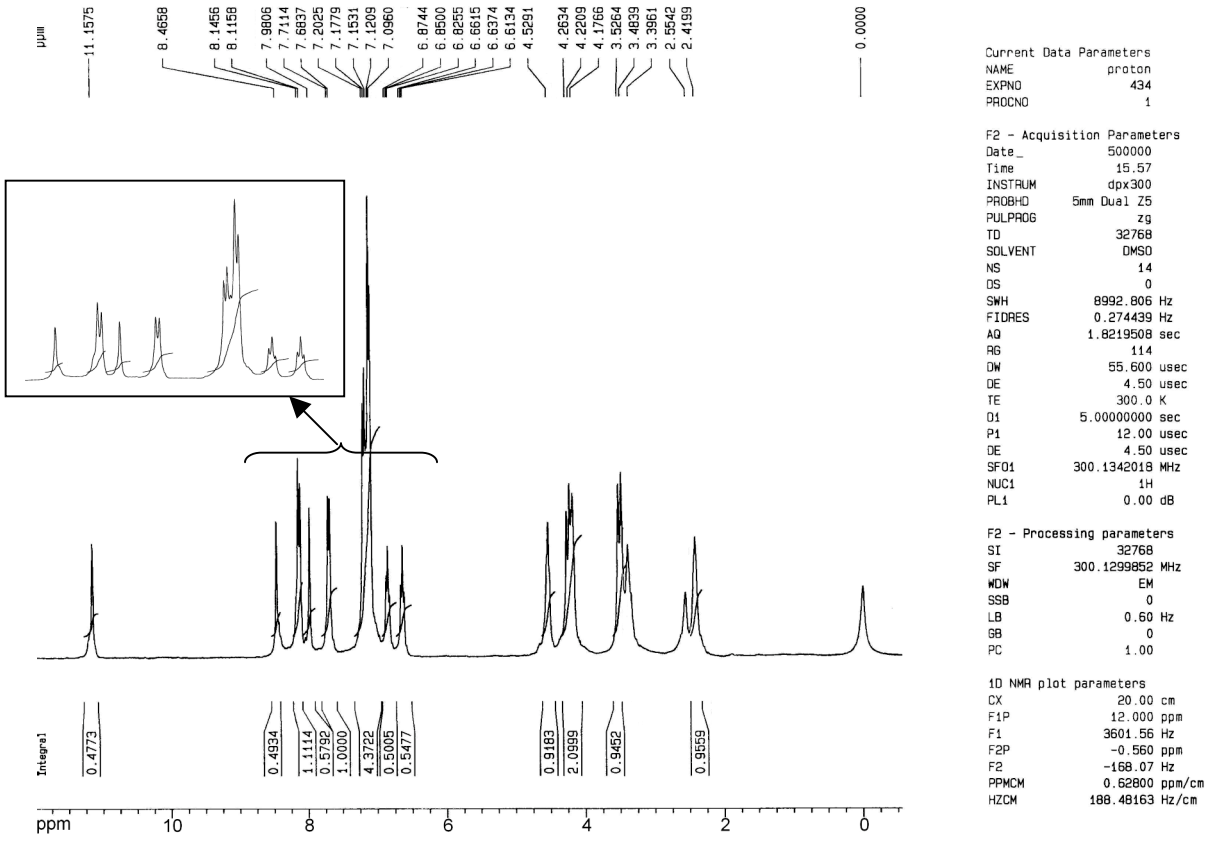
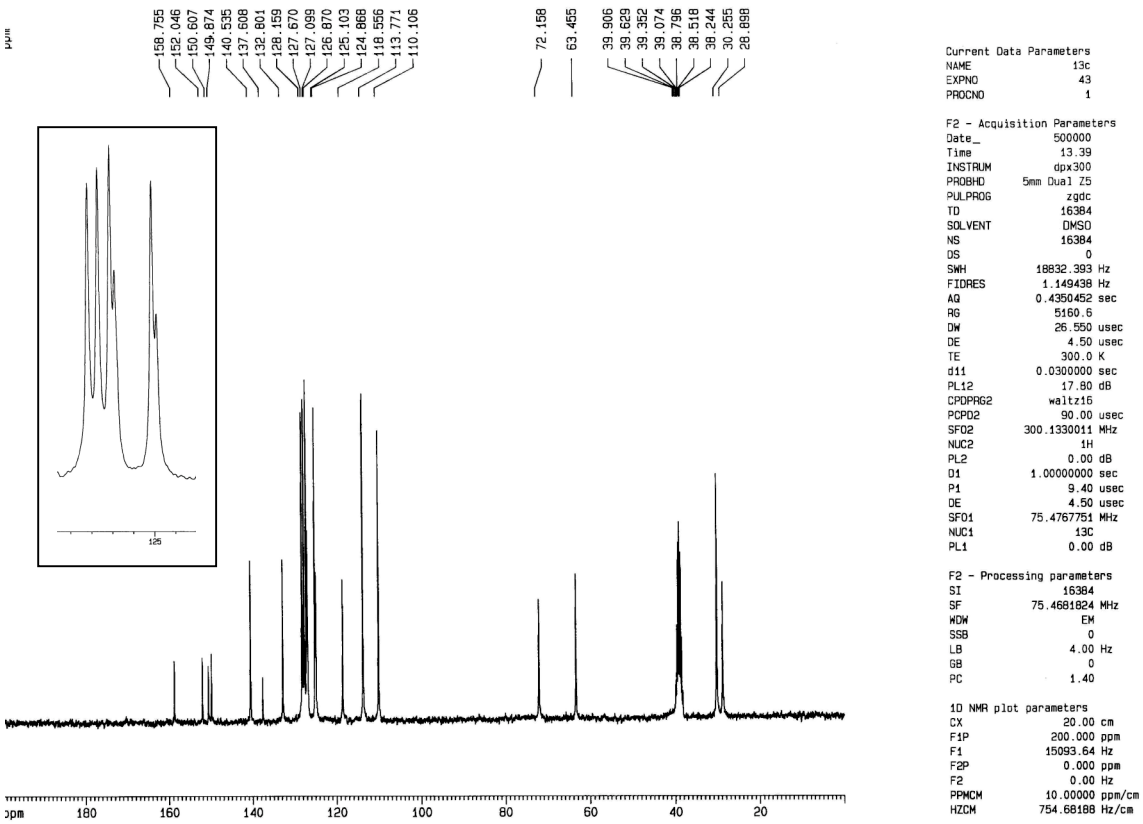


Figure S1. ^{1}H NMR spectrum of **4b** in DMSO-d_6.



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F2 - Processing parameters

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1D NMR plot parameters

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F1	15093.64 Hz
F2P	0.000 ppm
F2	0.00 Hz
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HZCM	754.68188 Hz/cm

Figure S2. ^{13}C NMR spectrum **4b** in DMSO-d_6.

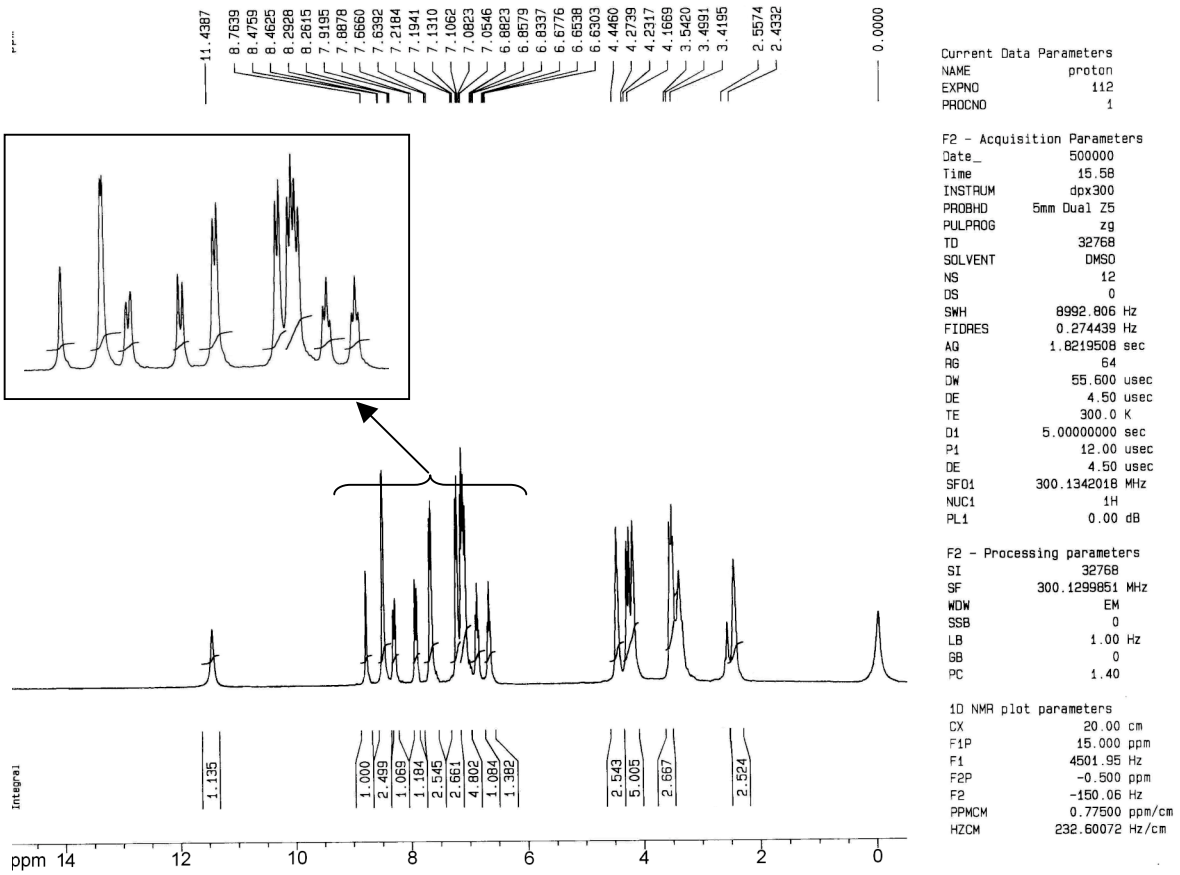
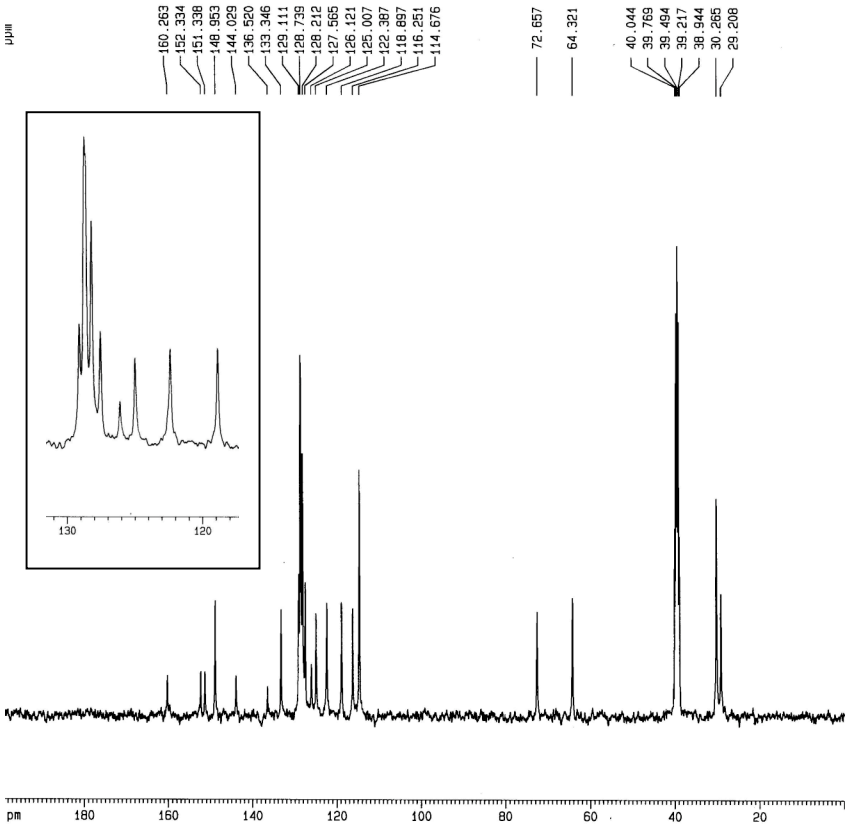


Figure S3. ^{1}H NMR spectrum of **4c** in DMSO-d_6.

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NUC1                13C
PL1                0.00 dB

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1D NMR plot parameters
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F1              15093.56 Hz
F2P                0.000 ppm
F2                 0.00 Hz
PPMCM          10.00000 ppm/cm
HZCM          754.67810 Hz/cm
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Figure S4. ^{13}C NMR spectrum of **4c** in DMSO-d_6

^{1}H-^{1}H COSY spectra of 4b

The 2D COSY correlation spectrum of **4b** (**Figure S5**) indicated that H_a protons are correlated with H_b protons at the *ortho*-position of the nitro group which exhibited a moderate upfield shift ($\Delta\delta$= - 0.22) upon addition of tetrabutylammonium fluoride ions (5.0 equiv.) as depicted in **Figure S6**.

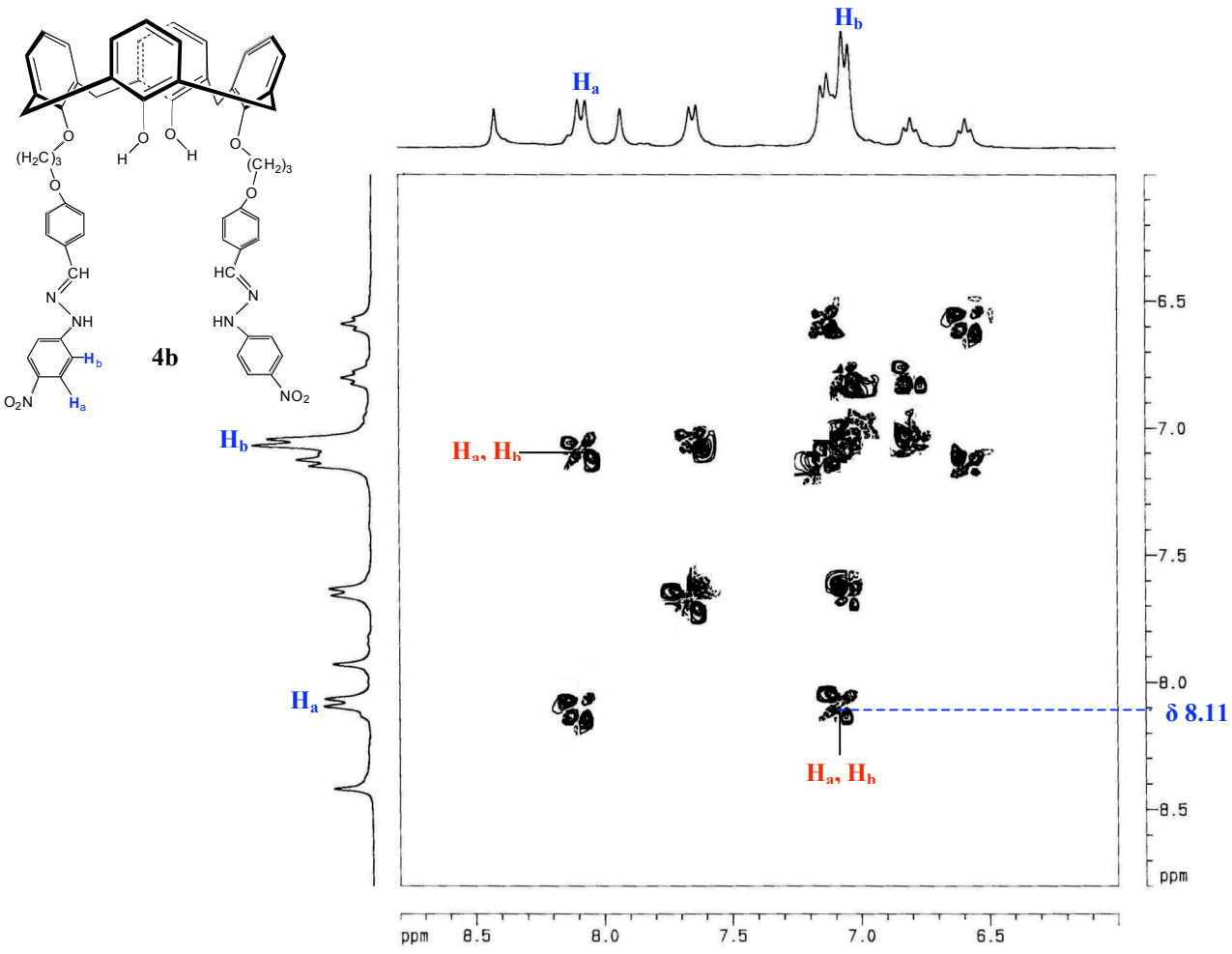

Figure S5. ^{1}H-^{1}H COSY spectrum of **4b** in DMSO-d_6.

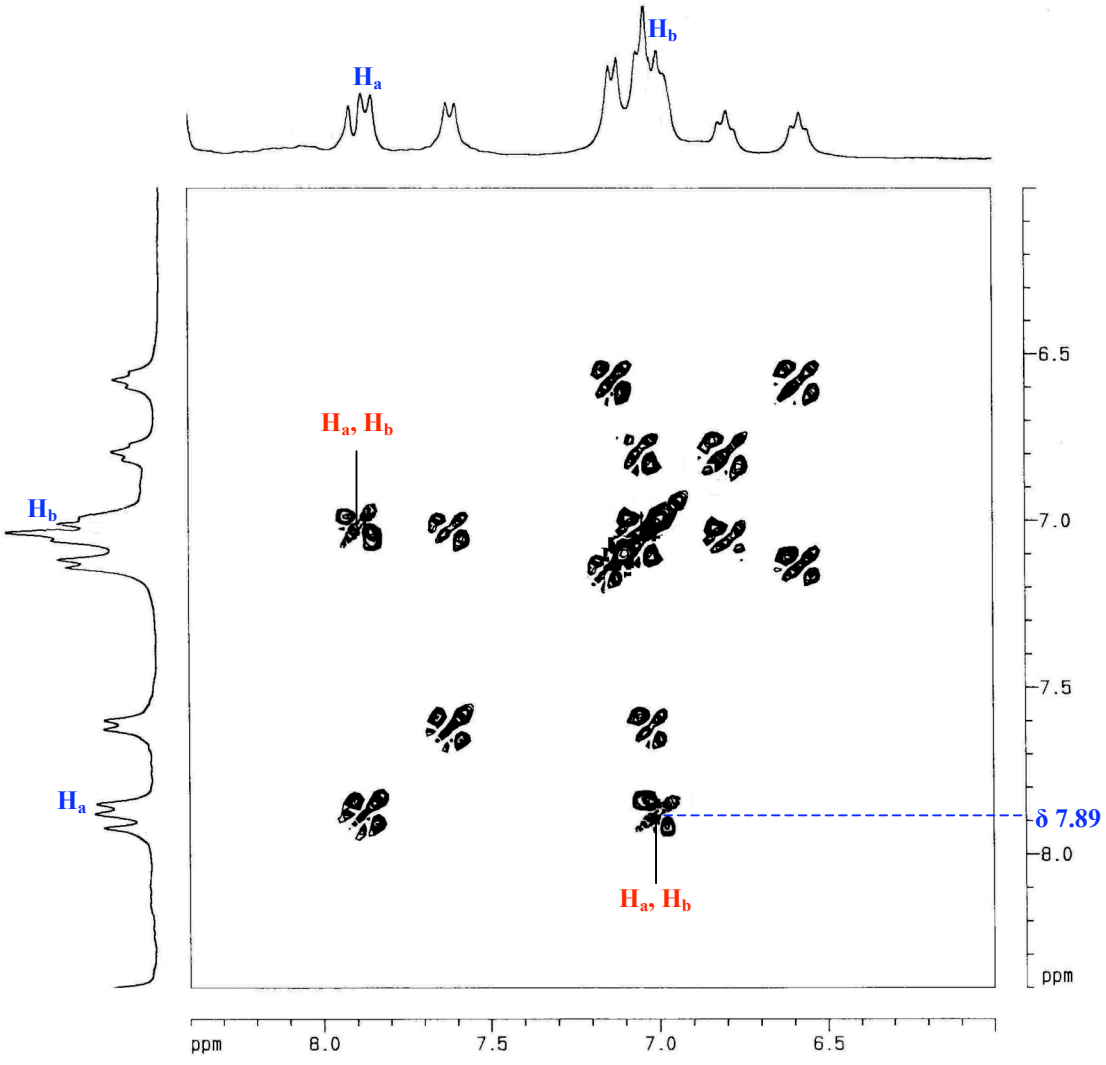

Figure S6. ^{1}H-^{1}H COSY spectrum of **4b** in DMSO-d_6 in the presence of 5.0 equiv of tetrabutylammonium fluoride.

Uv-visible spectra and absorbance titration curves

Note: The receptors **4d** and **4e** exhibited similar Uv-visible spectral changes and colorimetric observations with the examined anions as that observed for **4b** and **4c** respectively in analogous experimental set-ups.

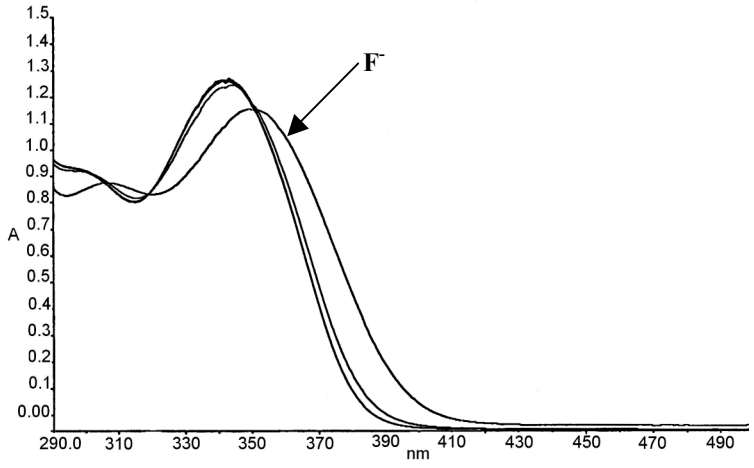

Figure S7. UV-visible spectra of **4a** (5×10^{-5} M) with different anions (1×10^{-4} M) (F^-, Cl^-, Br^-, I^-, HSO_4^-, $H_2PO_4^-$, AcO^-, ClO_4^-, PF_6^- in the form of tetrabutylammonium salts) in DMSO:CH_3CN (0.5:9.5 v/v).

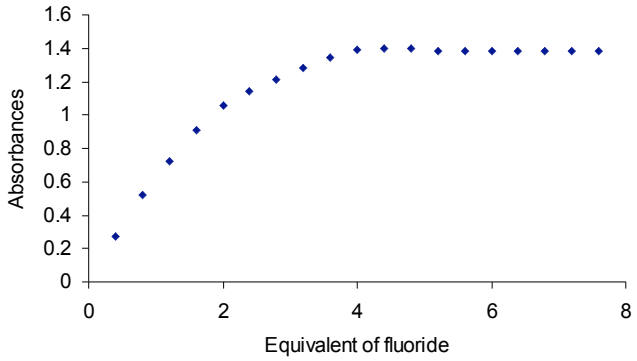

Figure S8. Absorbance changes for **4b** at 549 nm on addition of various equivalents of tetrabutylammonium fluoride.

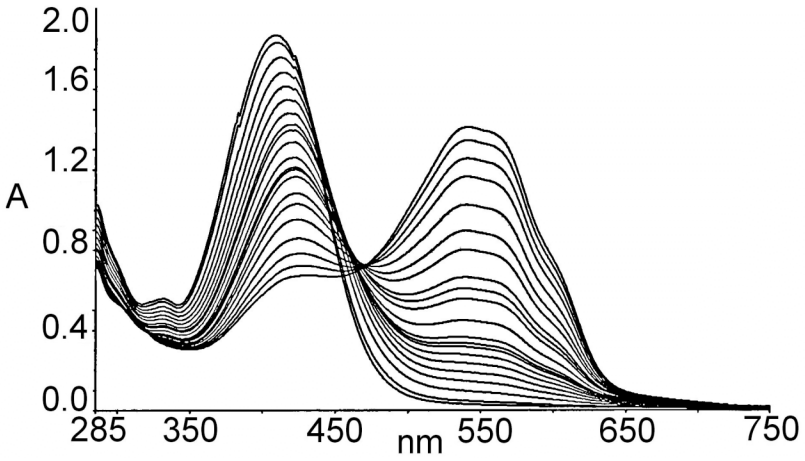

Figure S9. Changes in absorption spectra for **4b** (5×10^{-5} M) in DMSO:CH_3CN (0.5:9.5 v/v) with addition of tetrabutylammonium hydroxide from 0 to 4 equiv.

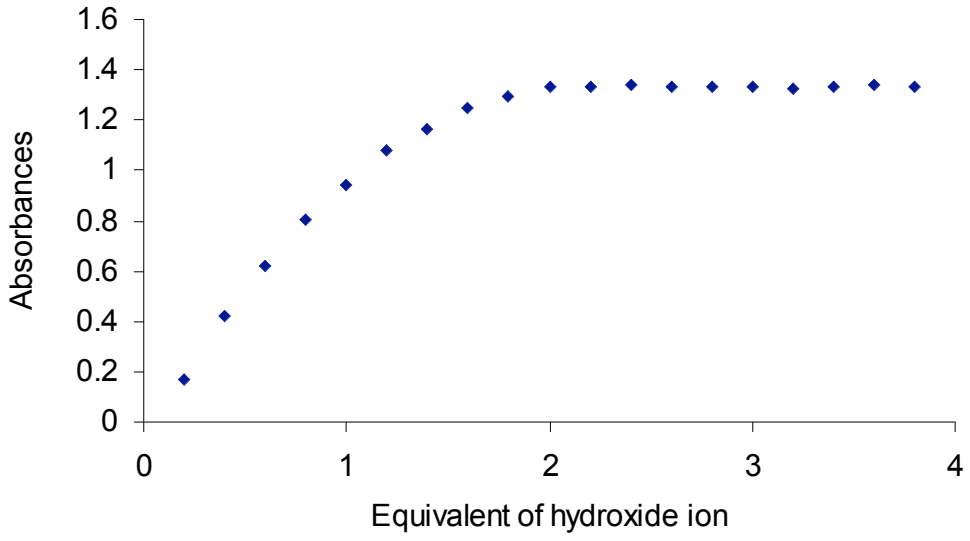

Figure S10. Absorbance changes for **4b** at 549 nm on addition of various equivalents of tetrabutylammonium hydroxide.

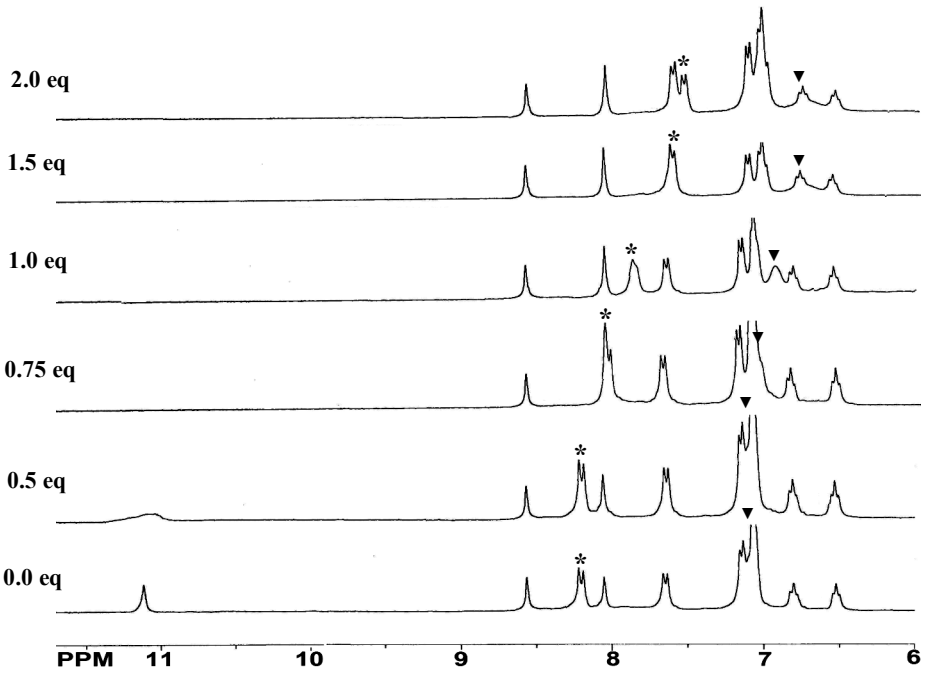

Figure S11 Partial ^{1}H NMR (300 MHz and 298 K) spectra of **4b** (10 mM) upon addition of various equiv. of TBA.OH (40 mM) in DMSO-d_6. Numbers at the left side indicate the equivalent amounts of OH^- added (* = ArH_a, ▼ = ArH_b).

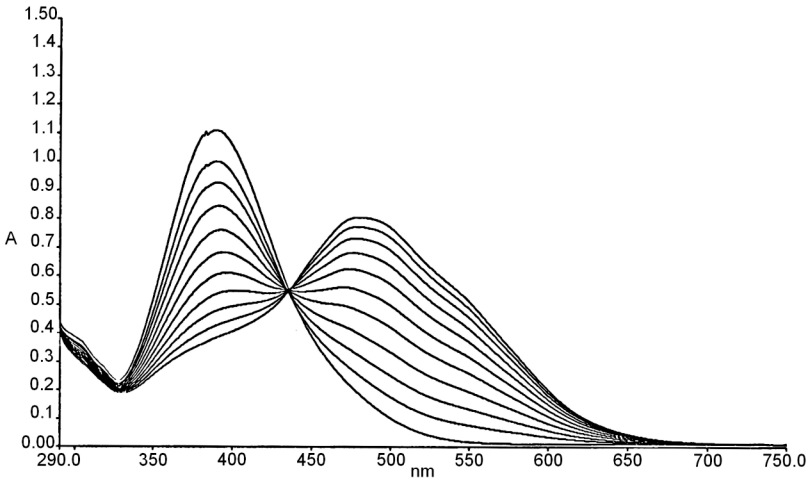

Figure S12. Changes in absorption spectra for **4c** (2×10^{-5} M) in DMSO:CH_3CN (0.5:9.5 v/v) with addition of tetrabutylammonium fluoride from 0 to 5 equiv.

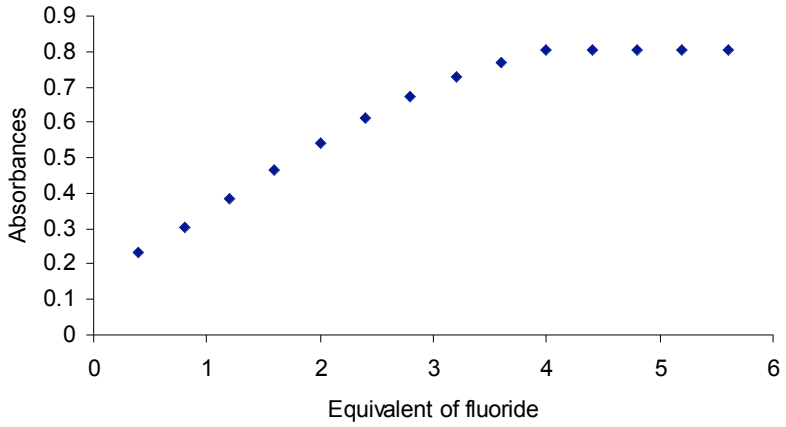

Figure S13. Absorbance changes for **4c** at 485 nm on addition of various equivalents of tetrabutylammonium fluoride.

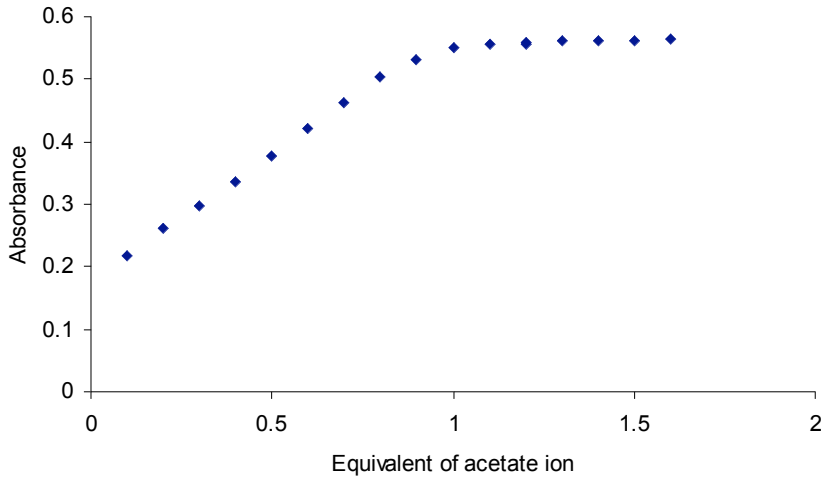

Figure S14. Absorbance changes for **4c** at 477 nm on addition of various equivalents of tetrabutylammonium acetate.

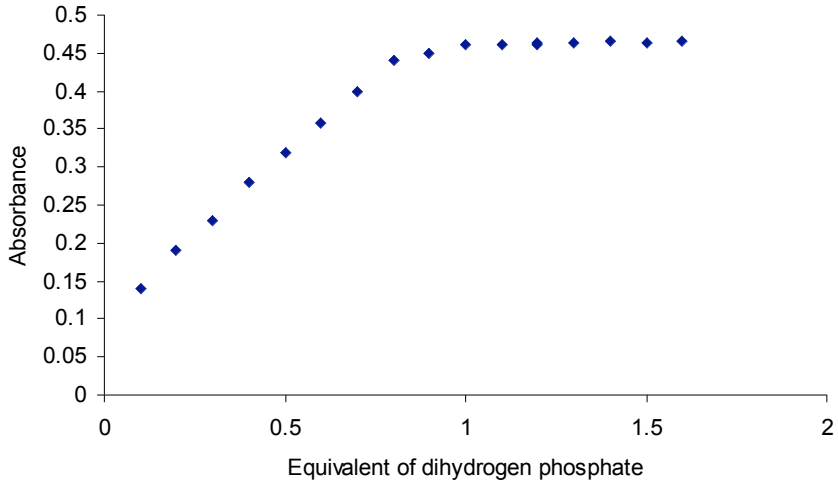

Figure S15. Absorbance changes for **4c** at 469 nm on addition of various equivalents of dihydrogen phosphate.

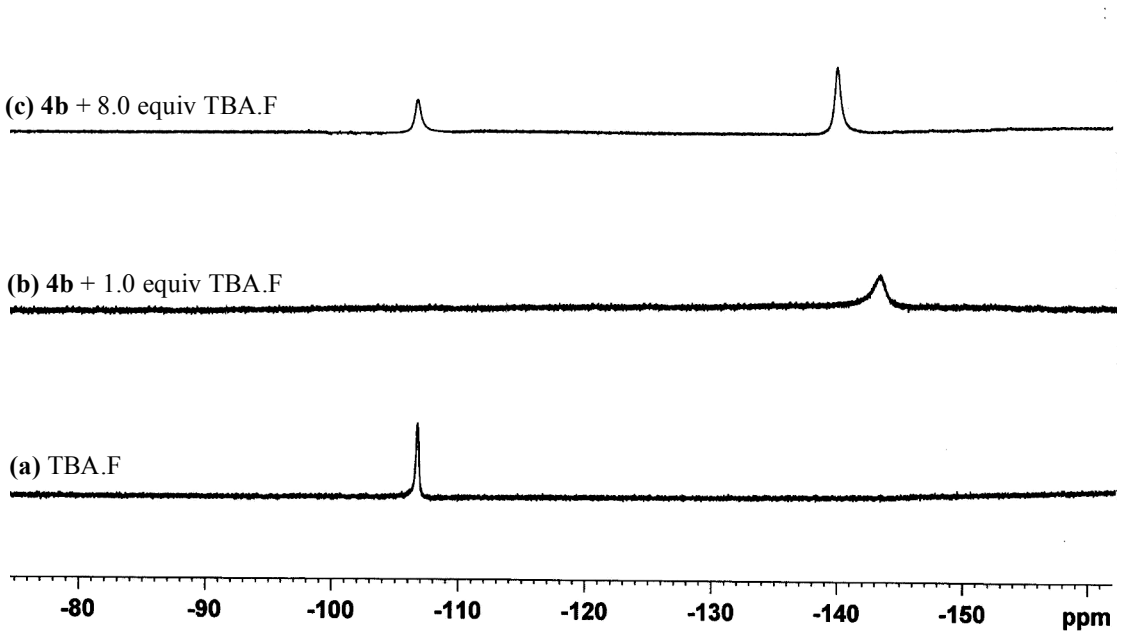

Figure S16. Partial ^{19}F NMR (300 MHz and 298 K) spectra of **4b** (10 mM) (a) only TBA.F (b) **4b**+1.0 eq TBA.F (c) **4b**+8.0 equiv TBA.F