Supporting Information

Selective Detection of Guanosine-5′-triphosphate and Iodide by Fluorescent Benzimidazolium-based Cyclophanes

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1. NMR and MASS spectral analysis:

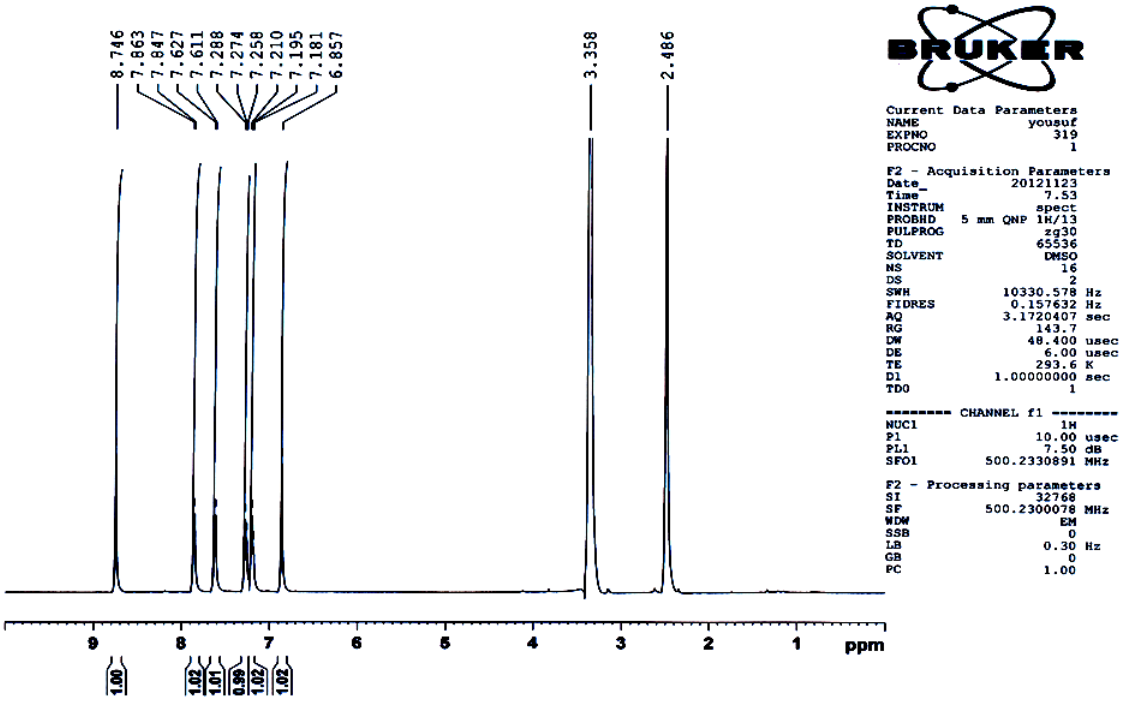

Figure S1. ^{1}H NMR spectrum of compound (**a**) in DMSO-d_6

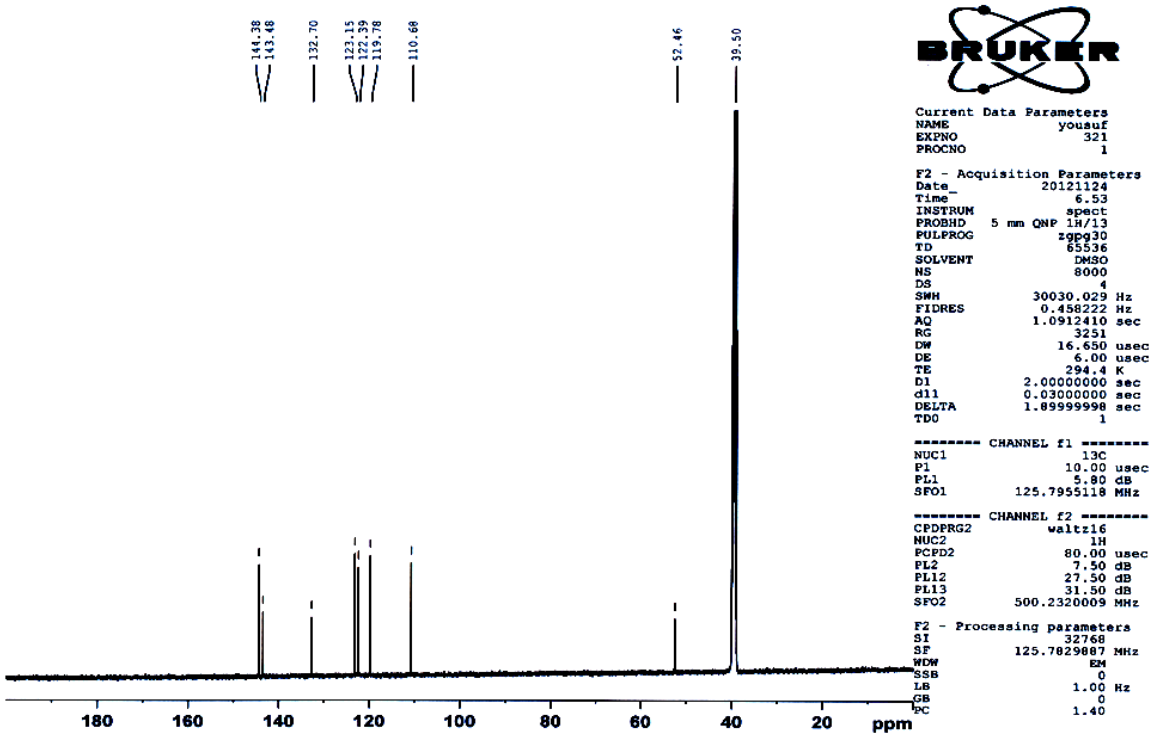

Figure S2. ^{13}C NMR spectrum of compound (**a**) in DMSO-d_6

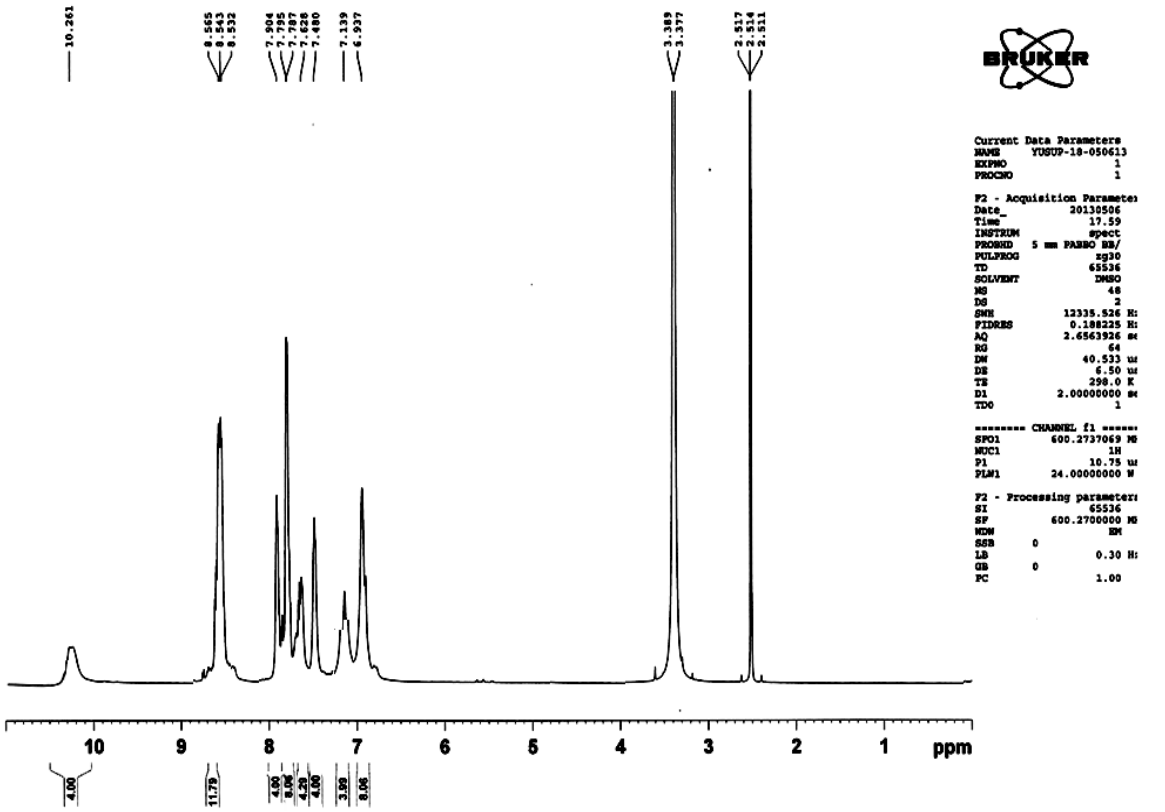

Figure S3. ^{1}H NMR spectrum of compound (**1**) in DMSO-d_6

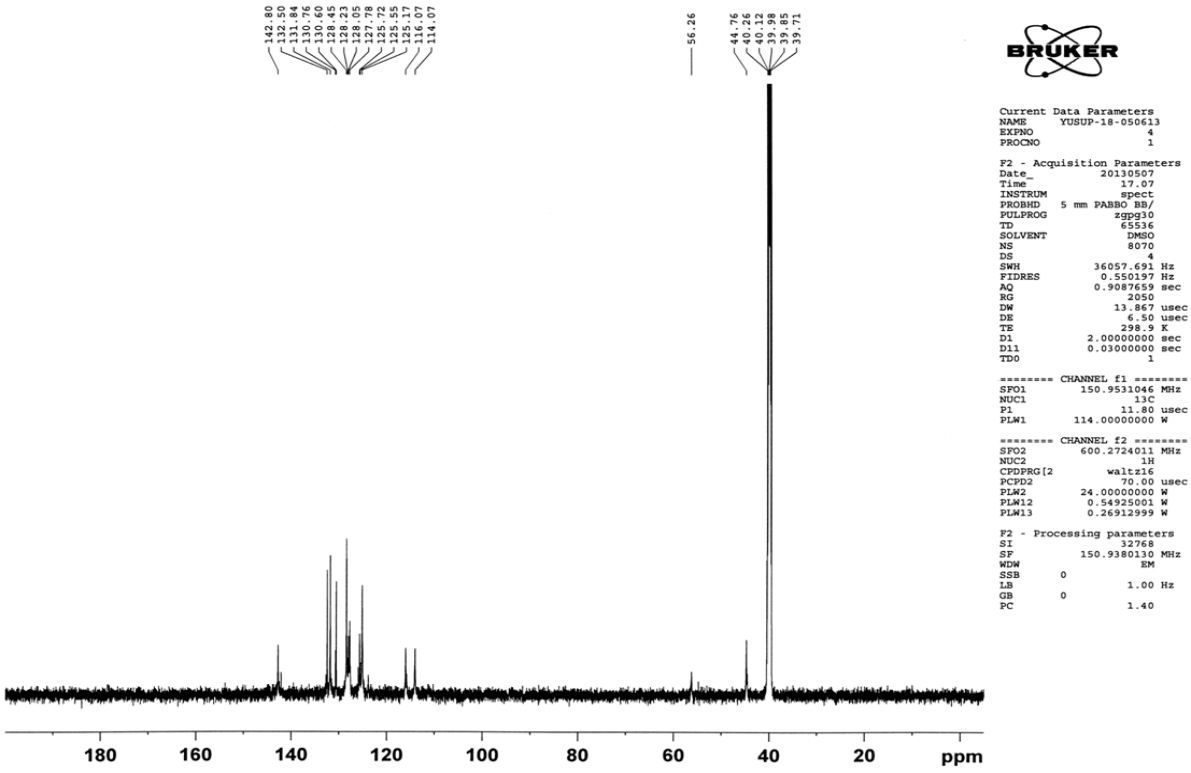

Figure S4. ^{13}C NMR spectrum of compound (**1**) in DMSO-d_6

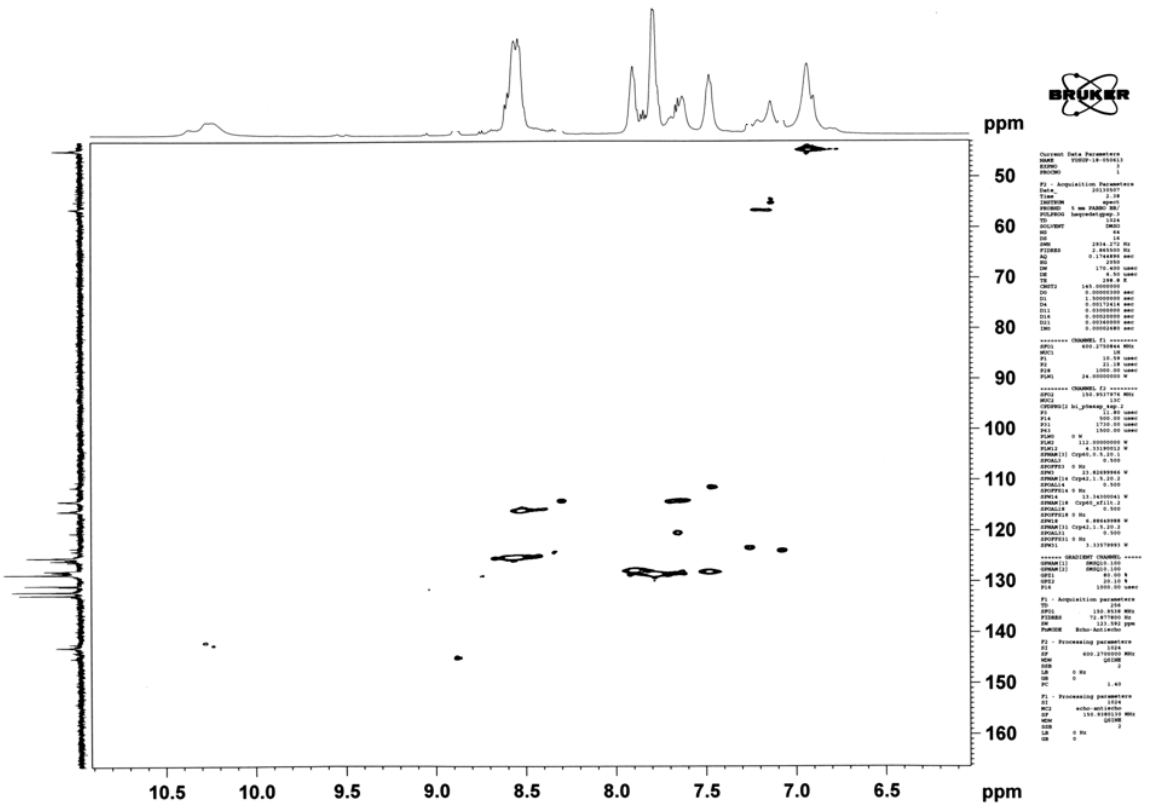

Figure S5. HSQC spectrum of compound (**1**) in DMSO-d_6

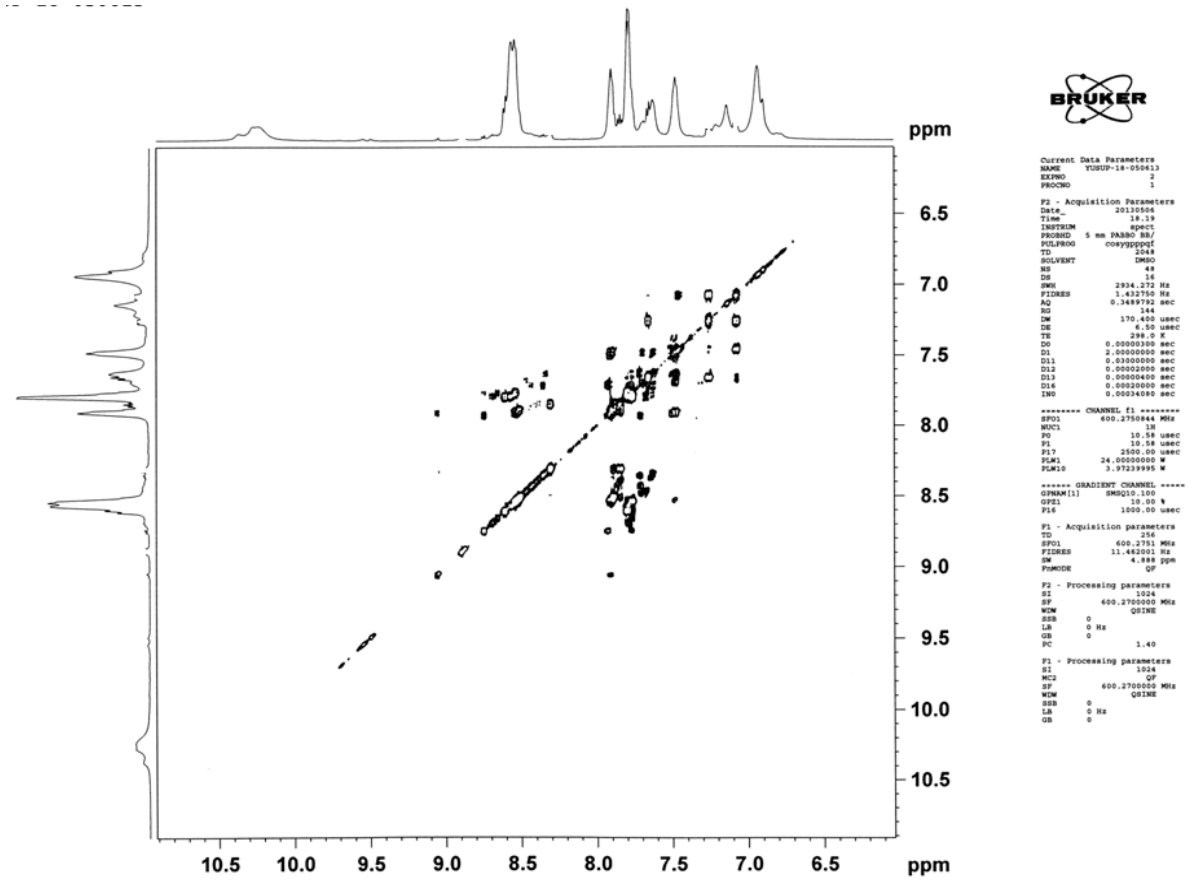

Figure S6. ^{1}H COSY spectrum of compound (**1**) in DMSO-d_6

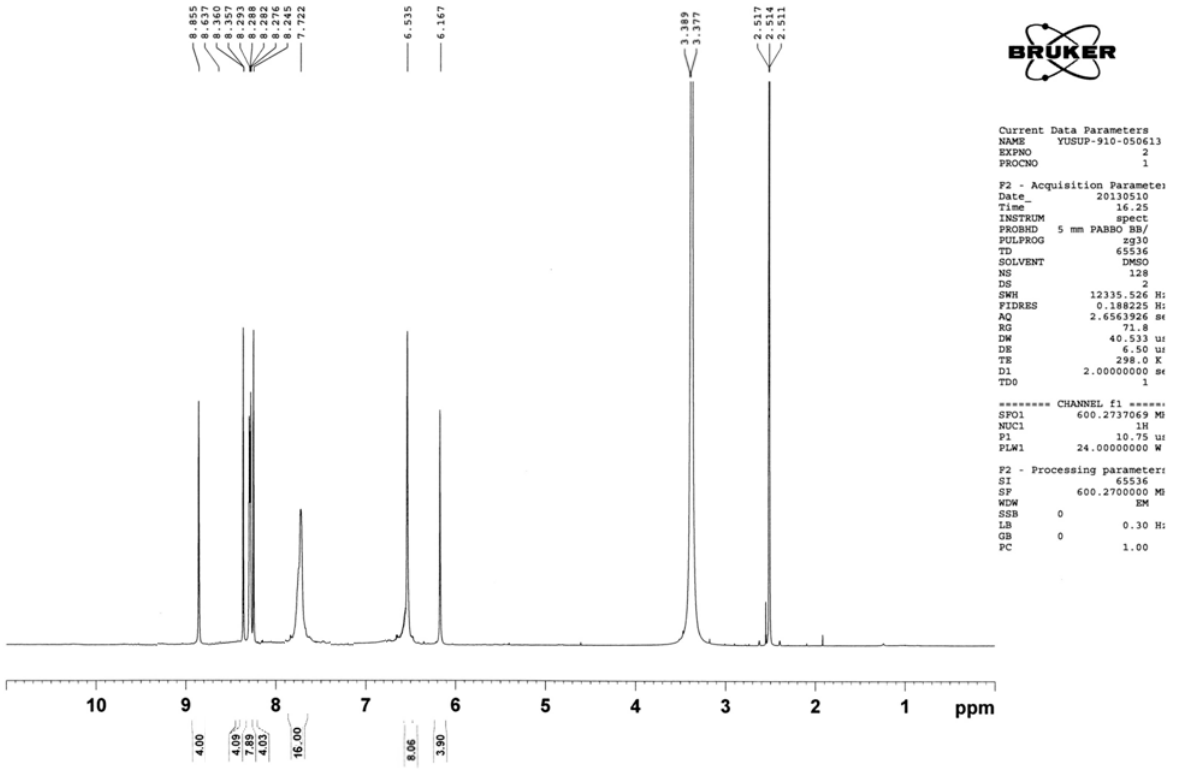

Figure S7. ^{1}H NMR spectrum of compound (**2**) in DMSO-d_6

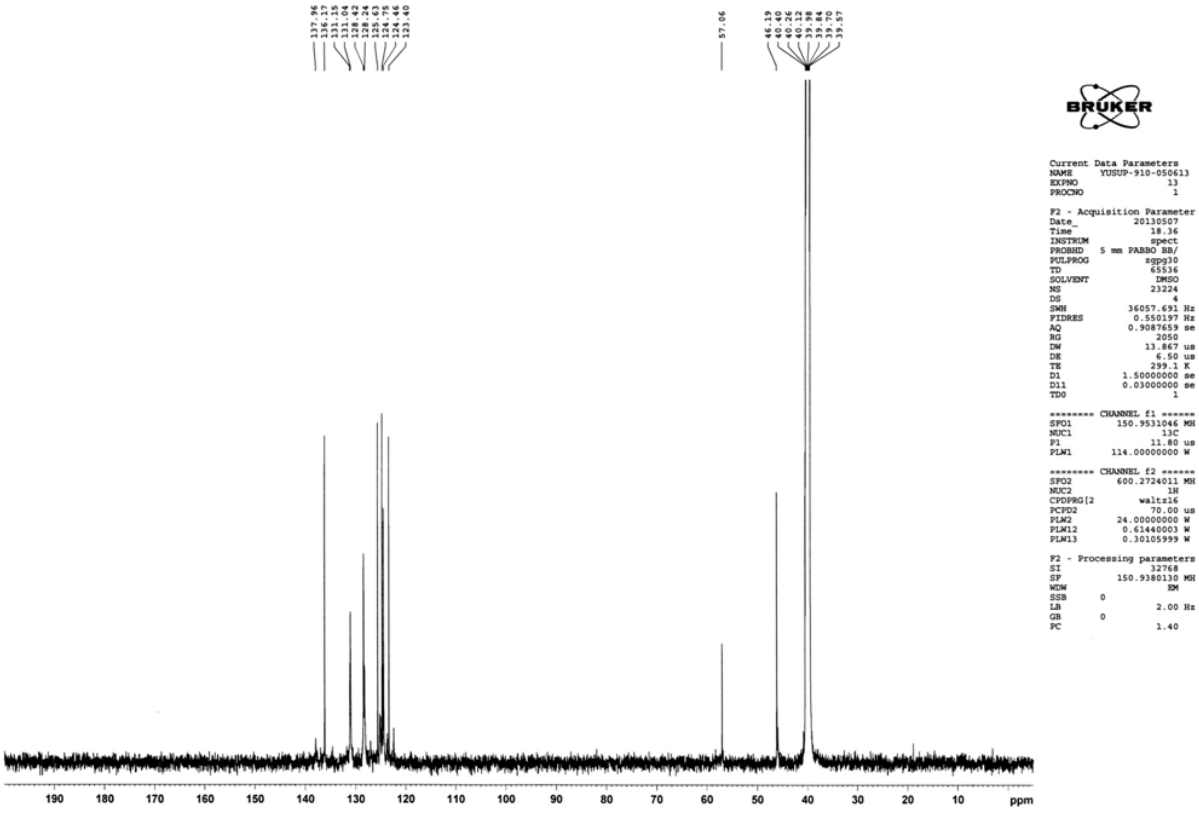

Figure S8. ^{13}C NMR spectrum of compound (**2**) in DMSO-d_6

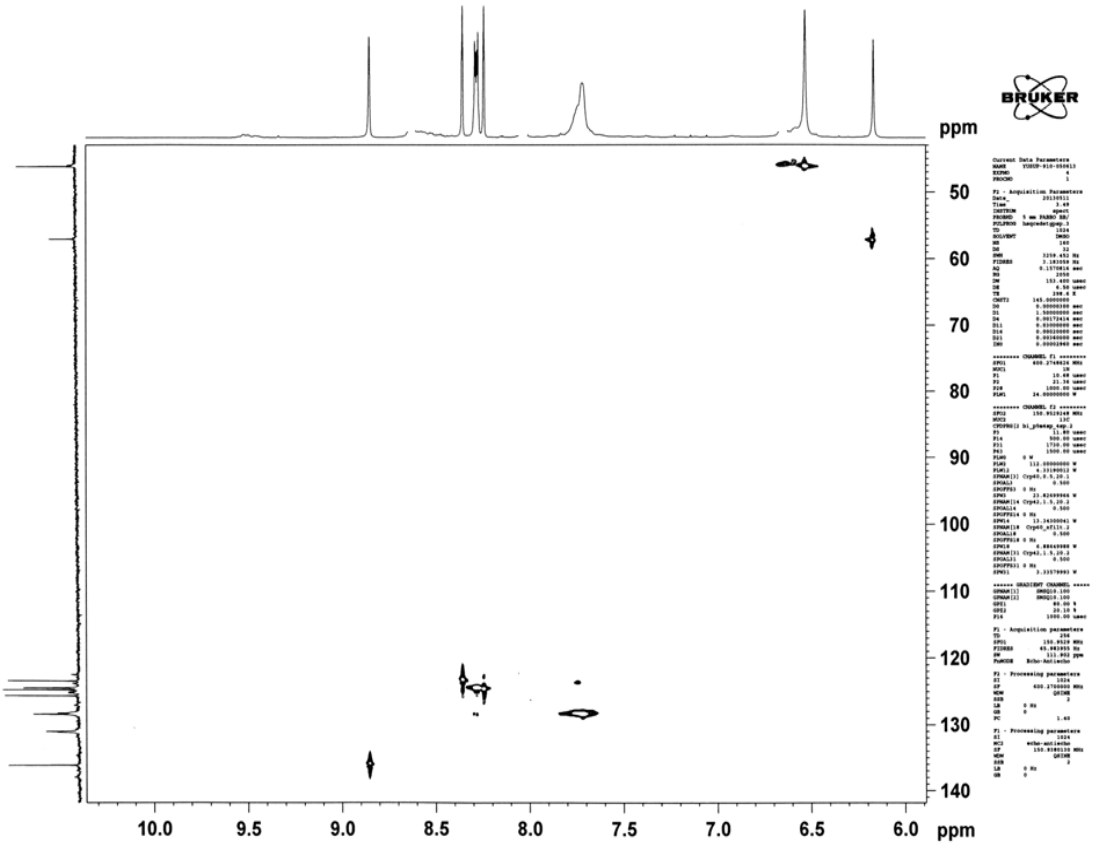

Figure S9. HSQC spectrum of compound (**2**) in DMSO-d_6

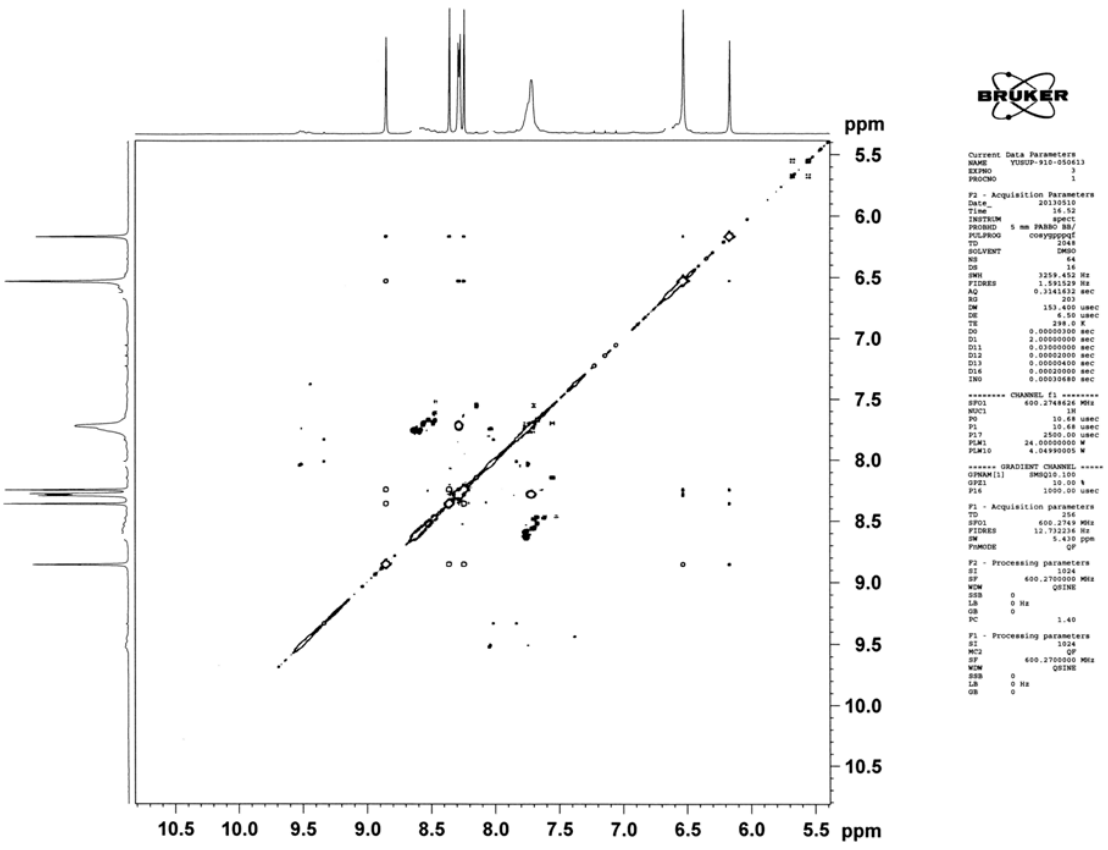

Figure S10. ^{1}H COSY spectrum of compound (**2**) in DMSO-d_6

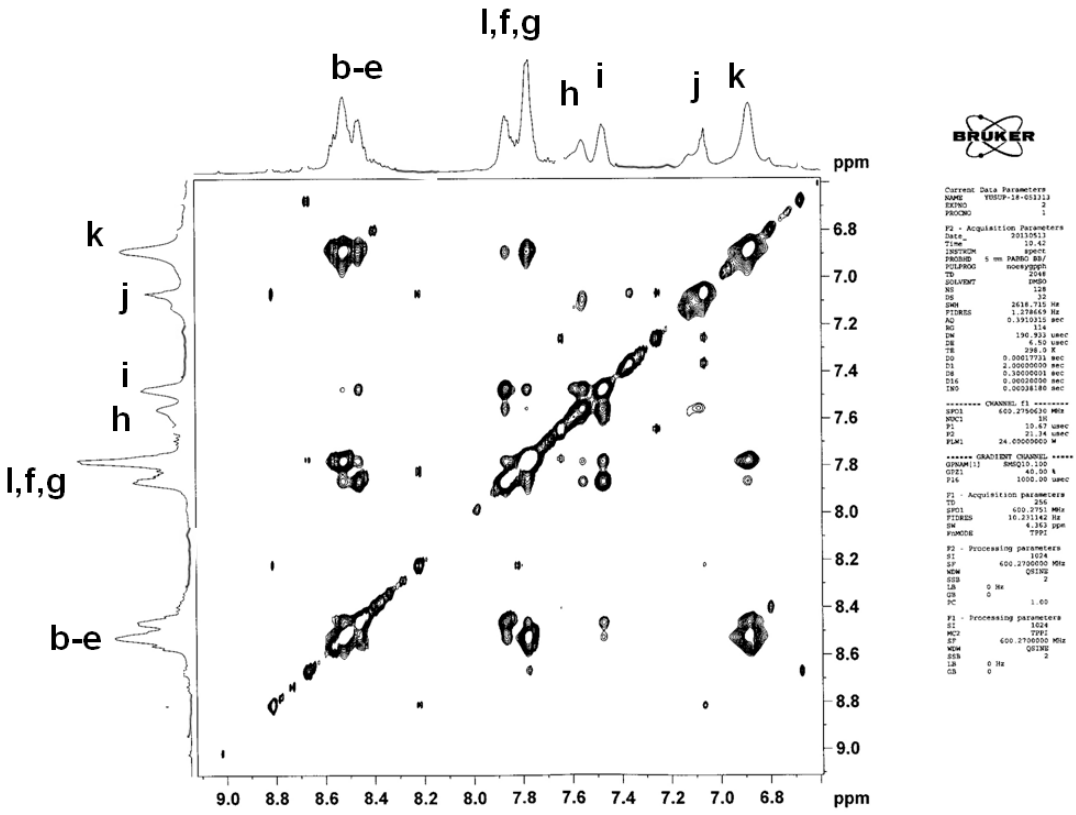

Figure S11. 600 MHz NOESY spectrum of **1** with 1 eq. of GTP in DMSO-*d*6.

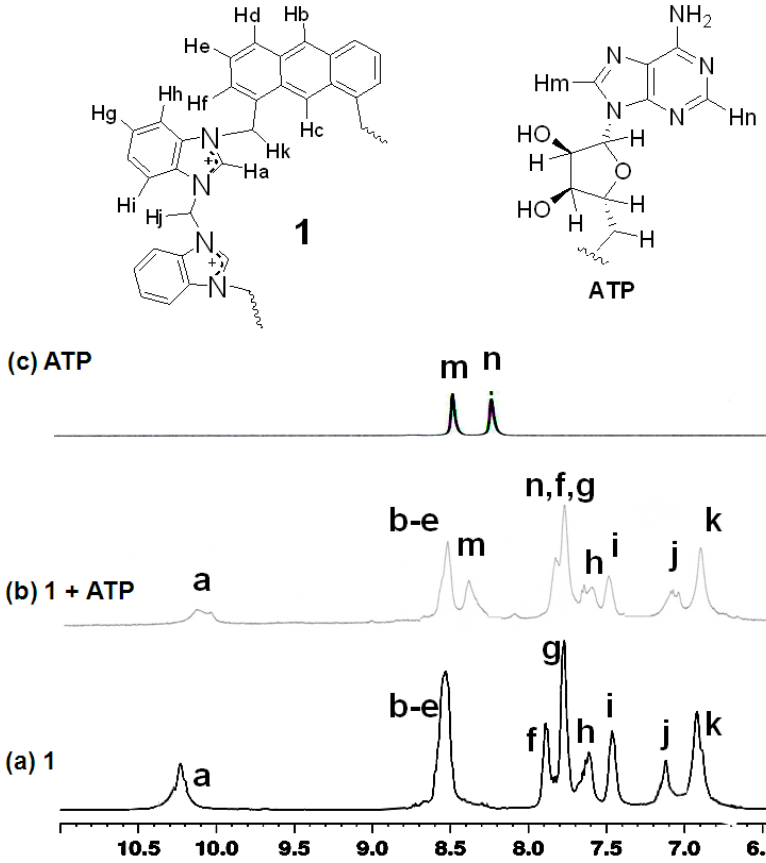

Figure S12. Partial 600 MHz ^{1}H NMR spectra for (a) **1** (2 mM), (b) **1**-ATP (1 equiv) (c) ATP. ATP was dissolved in D_2O as stock solution.

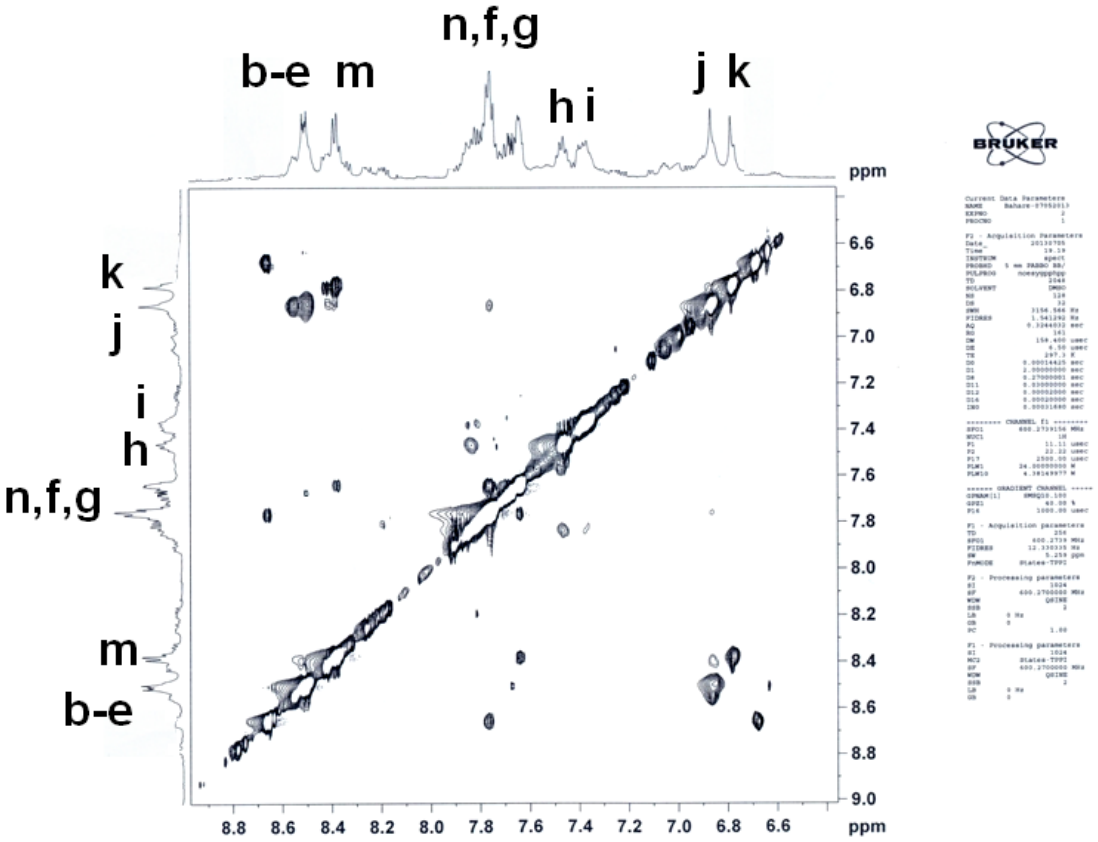

Figure S13. 600 MHz NOESY spectrum of **1** with 1 eq. of ATP in DMSO-*d*6.

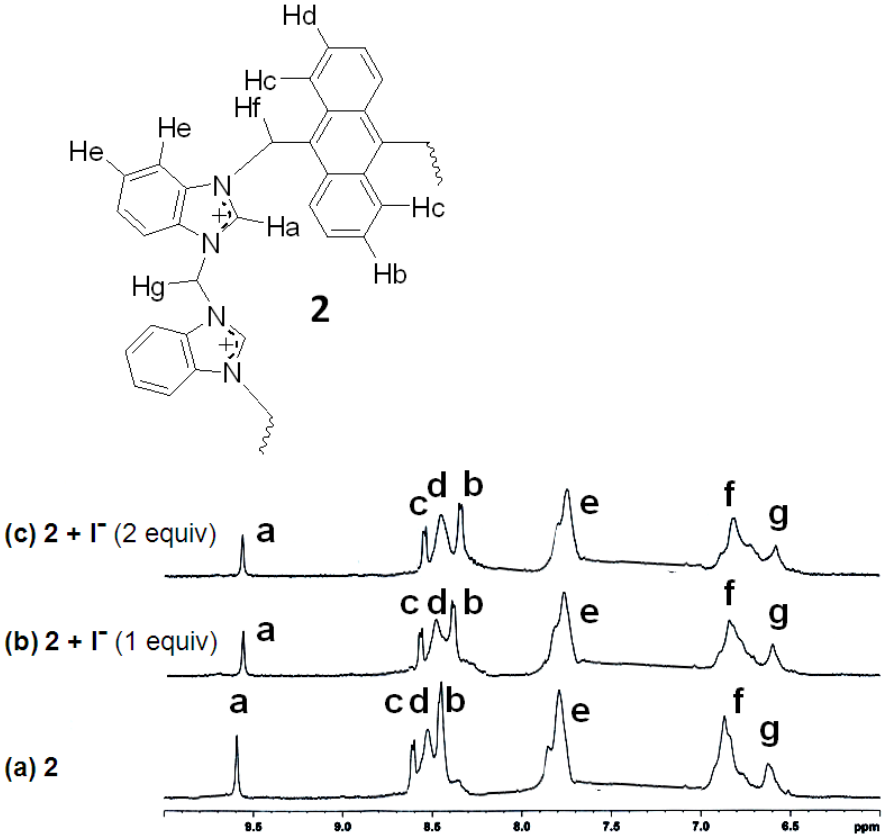

Figure S14. Partial 500 MHz ^{1}H NMR spectra for (a) **2** as PF_6^- (2 mM), (b,c) **2**-I^- (1 and 2 equiv). I^- was dissolved in D_2O as stock solution.

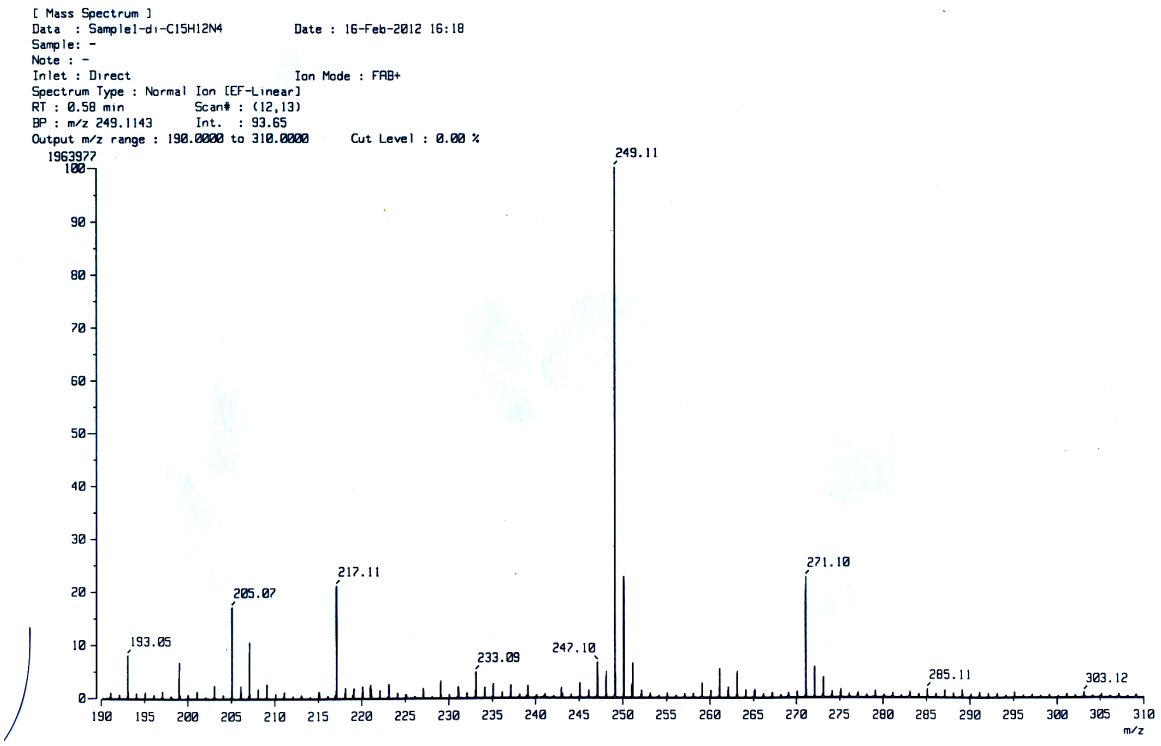

Figure S15. HRMS (FAB) Spetrum of compound (**a**).

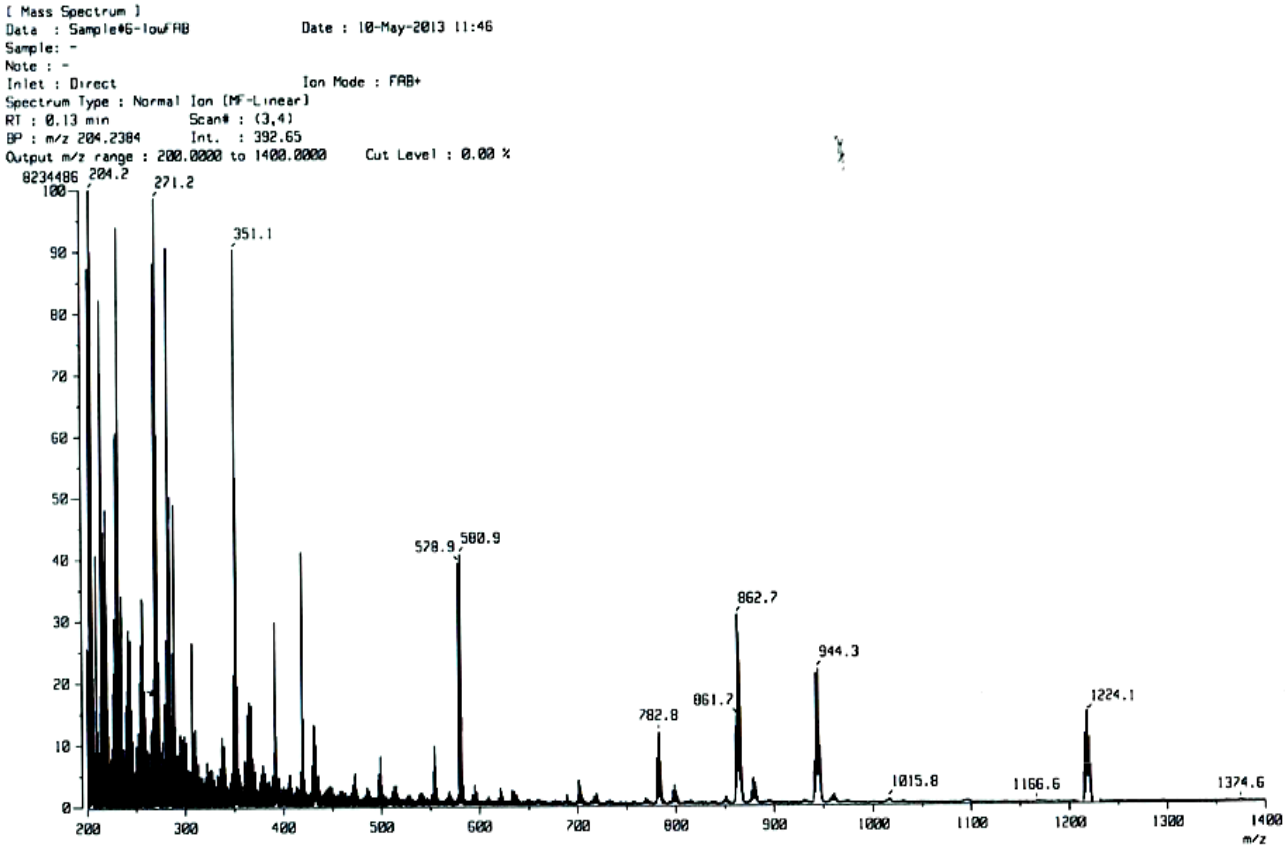

Figure S16. MS (FAB) Spetrum of compound (**1**).

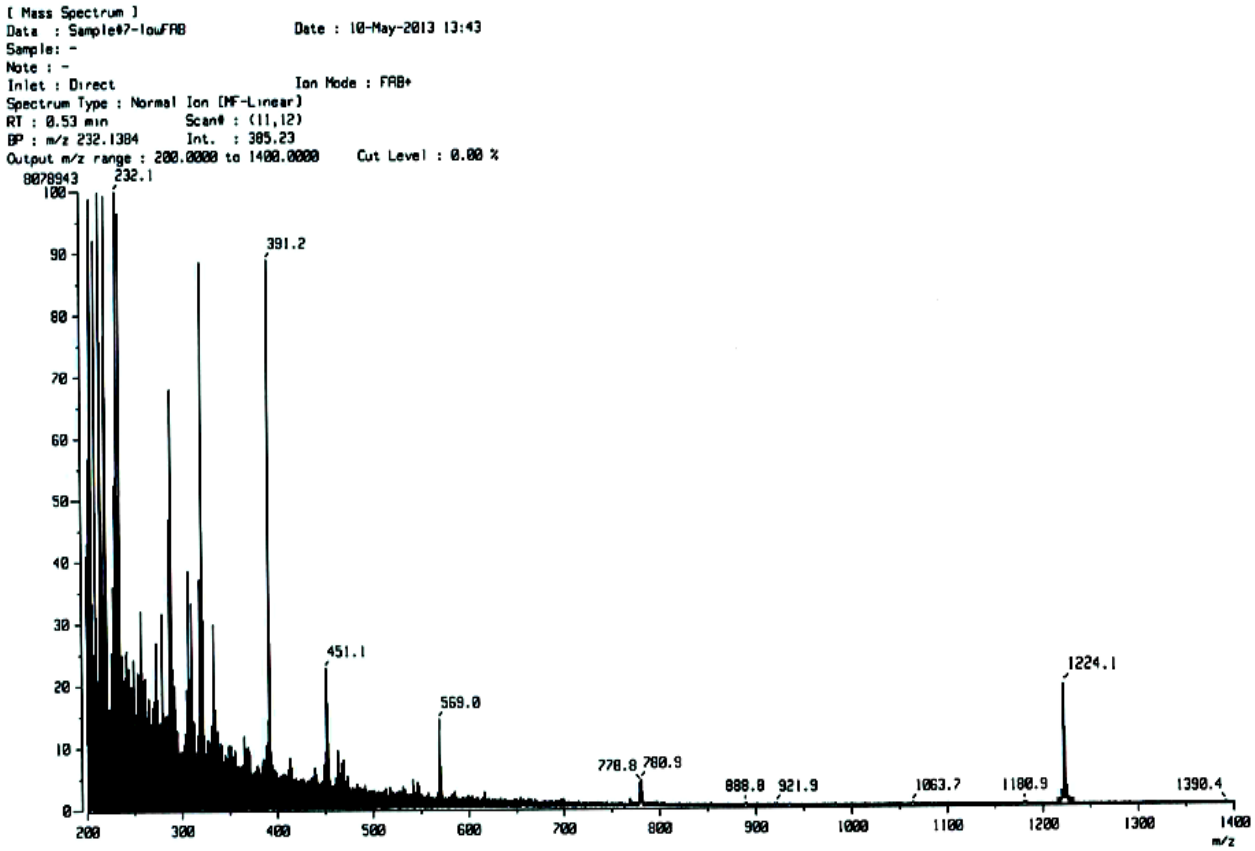

Figure S17. MS (FAB) Spetrum of compound (**2**).

2. UV-visible Absorbance

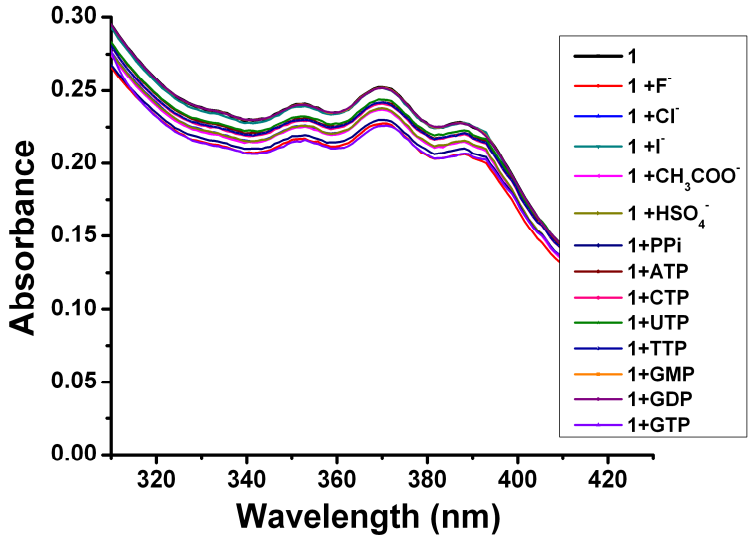

Figure S18. Absorption spectra of **1** (5 μM) upon addition of *n*-tetrabutylammomonium (*n*-TBA) salts; of F^-, Cl^-, I^-, CH_3COO^-, HSO_4^- (100 equiv) and sodium salts of phosphate anions; pyrophosphate (PPi), CTP, TTP, UTP, ATP and GTP (100 equiv) at pH 7.4 (10 mM HEPES buffer).

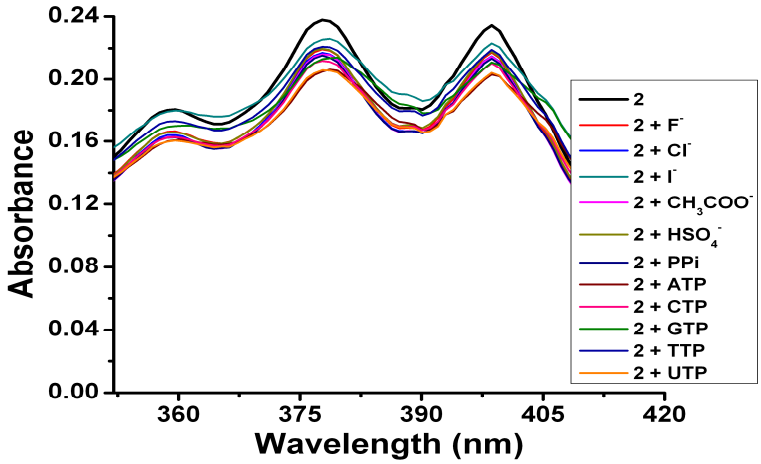

Figure S19. Absorption spectra of **2** (5 μM) upon addition of *n*-tetrabutylammomonium (*n*-TBA) salts; of F^-, Cl^-, I^-, CH_3COO^-, HSO_4^- (100 equiv) and sodium salts of phosphate anions; pyrophosphate (PPi), CTP, TTP, UTP, ATP and GTP (100 equiv) at pH 7.4 (10 mM HEPES buffer).

3. **Fluorometric Analysis:**

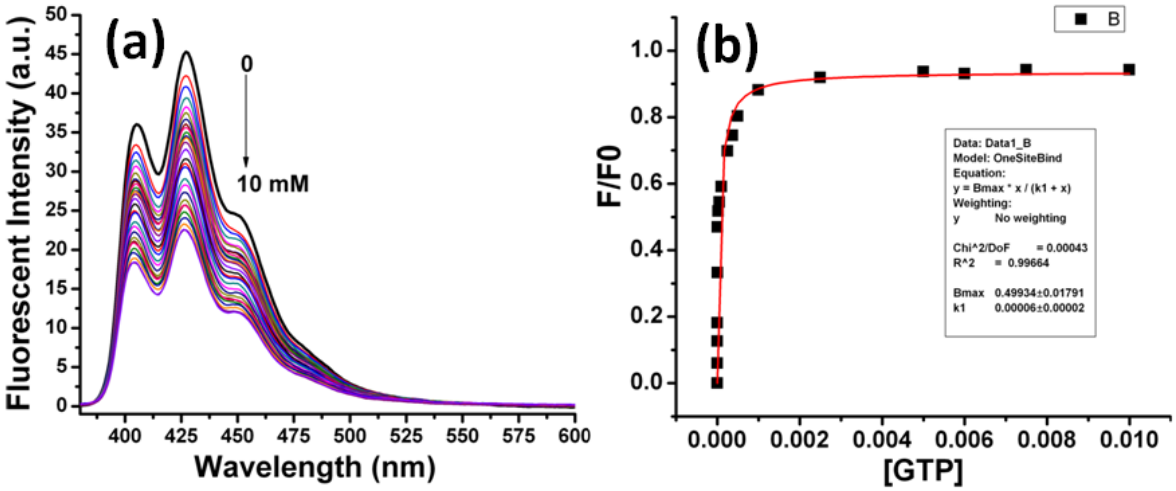

Figure S20. Emission spectra (excitation at 367 nm) of receptor **1** (5 µM) upon addition of sodium salt of GTP at pH 7.4 (10 mM HEPES buffer) and the corresponding binding isotherm.

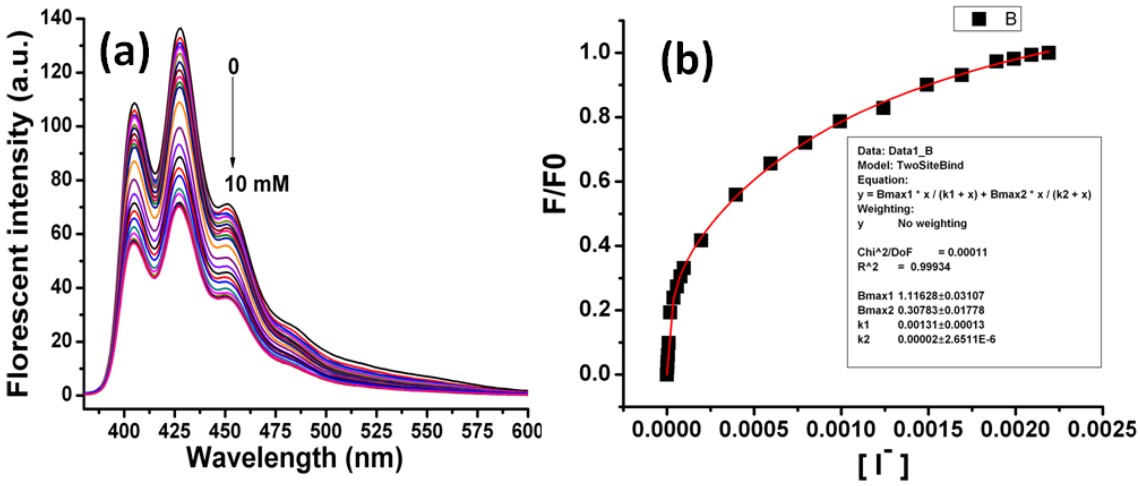

Figure S21. Emission spectra (excitation at 367 nm) of receptor **2** (5 μM) upon addition of *n*-tetrabutylammomonium (*n*-TBA) salt of I^- at pH 7.4 (10 mM HEPES buffer) and the corresponding binding isotherm.

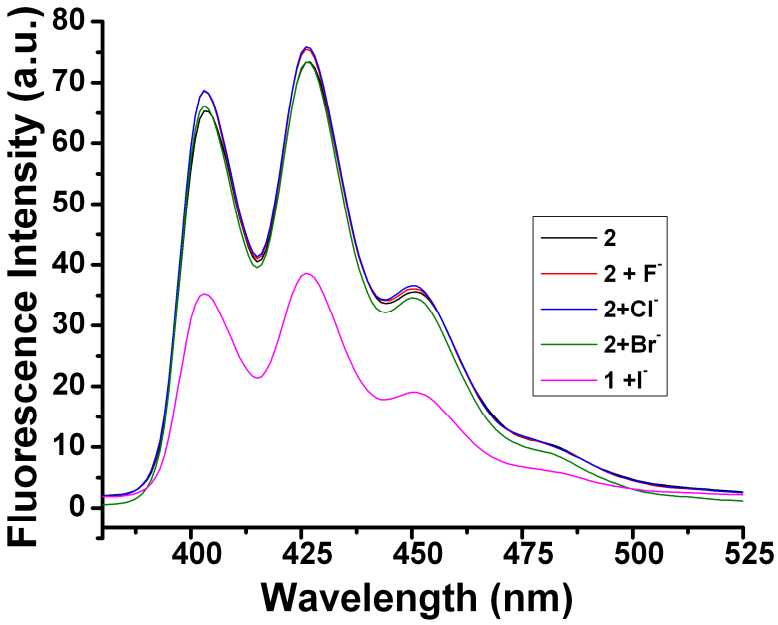

Figure S22. Fluorescent emission changes of PF_6^- salt of **2** (**2**.4PF_6^-) (5 μM) upon the addition of *n*-tetrabutylammomonium (*n*-TBA) salts of F^-, Cl^-, Br^- and I^- (100 equiv) in 10 mM HEPES buffer (pH 7.0) CH_3CN/H_2O (5:1, v/v) (slit width =1.5 nm; excitation at 367 nm).

4. Studies of receptor-anion complex stoichiometry (Job plot)

Job plot analysis was performed using fluorescence emission spectroscopy. The plots were constructed in the usual way and were found to exhibit maxima at 0.5 for GTP in case of receptor **1**, and 0.33 for I^- in case of receptor **2**. Such findings support the proposal that receptor **1** forms a 1:1 complex with the GTP and receptor **2** forms a 1:2 complex with I^-.

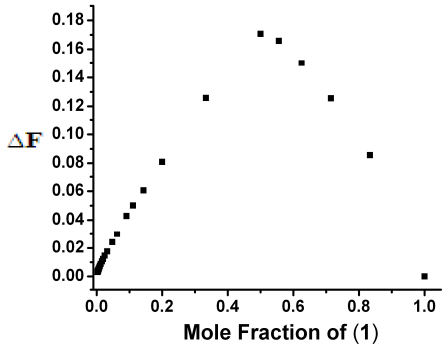

Figure S23. Assessment of the stoichometry of the GTP complex of **1** via Job plot analysis; [**1**] + [GTP] = 5 μM, pH 7.4 (10 mM HEPES buffer), 25ºC.

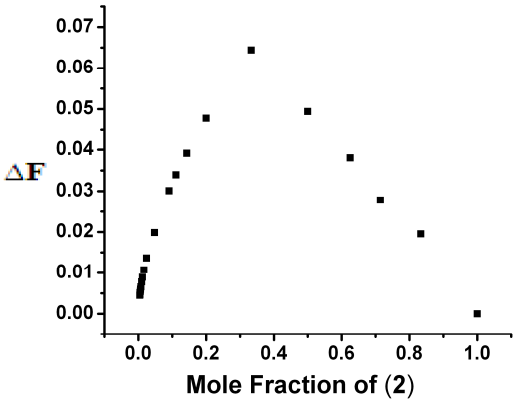

Figure S24. Assessment of the stoichometry of the $\mathbf{I}^-$ complex of **2** via Job plot analysis; [**2**] + [I^-] = 5 μM, pH 7.4 (10 mM HEPES buffer), 25ºC.

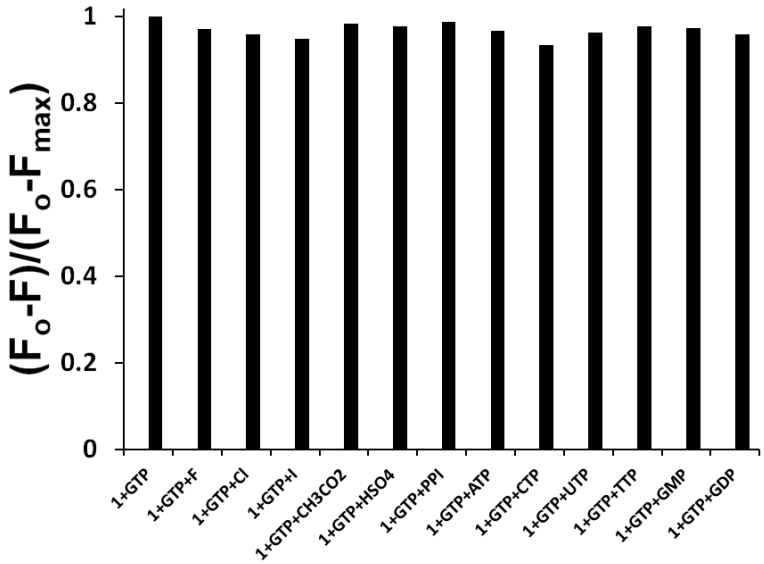

Figure S25. Competitive experiment in the **1** + GTP with interfering anions.[**1**]= 5 μM , [GTP] = 0.5 mM, and [A^-]= 0.5 mM in 10 mM HEPES buffer. (slit width = 3 nm; λ_{ex} = 367)

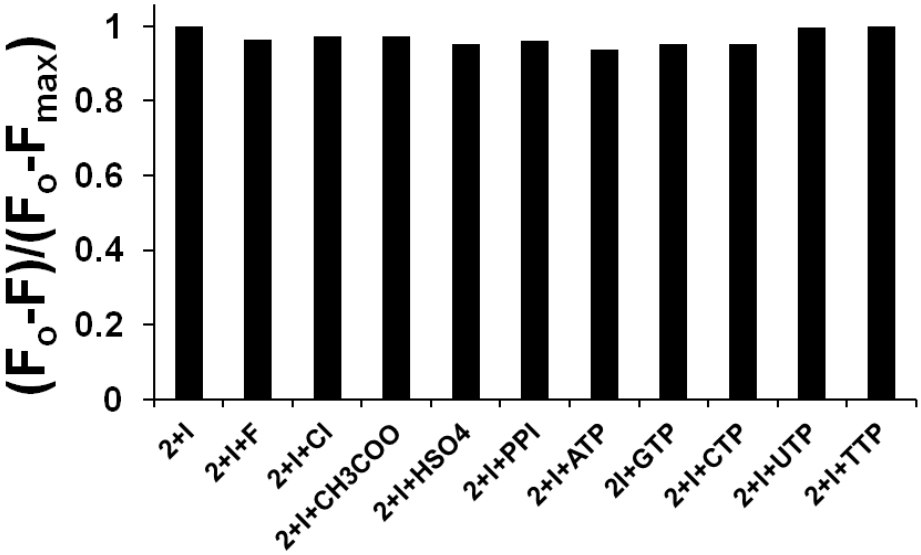

Figure S26. Competitive experiment in the **2** + I^- with interfering anions.[**2**] = 5 μM , [I^-] = 0.5 mM, and [A^-]= 0.5 mM in 10 mM HEPES buffer. (slit width = 3 nm; λ_{ex} = 367).

5. **Theoretical calculation: Role of Br^- anions in receptors**

The receptors **1** and **2** are sensing GTP and I^-, respectively. Therefore, the ultimate purpose is proposing the structure of each sensor molecule when it interacts with the anions. One issue to be considered is the role of Br^-. In the case of **1**-4Br^-, one of 4Br^- anions is inside the cavity. After adding GTP, the sensor **1** interacts with GTP, while most Br^- anions are replaced by GTP. Even the Br^- anion inside the cavity is replaced, as the four benzimidazolium moieties in **1** change their orientations and structures to easily interact with the GTP. In the case of **2**-2I^-, it is unnecessary to add two more anions, 2Br^-, to balance the charge. There are two reasons: 1) The two exra Br^- anions do not participate in the bonding, but are solvated in the aqueous solution. 2) One I^- anion interacts with four benzimidazolium moieties and another one interacts weakly with two anthracene moieties. The 2Br^- would not be bound to **2** because none of the four benzimidazolium moieties are available.