Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information for:

Bis- and Tris- Naphthoimidazolium Derivatives for the Fluorescent Recognition of ATP and GTP in 100% Aqueous Solution

Zhaochao Xu, [‡,a,c] Na Ri Song, [‡,b], Jong Hun Moon,[d] Jin Yong Lee,[*d] and Juyoung Yoon[*,a,b]

[a] *Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750,Korea, Fax: (+82) 2-3277-2384*
[b] *Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea*
[c] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*
[d] *Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea*

[‡] These authors contributed equally to this work

jyoon@ewha.ac.kr

Experimental Section

General methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Thin layer chromatography (TLC) was carried out using Merck 60 F_{254} plates with thickness of 0.25 mm. Preparative TLC was performed using Merck 60 F_{254} plates with the thickness of 1 mm.Melting points were measured using a Büchi 530 melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker 250 MHz or Varian 500 MHz. Chemical shifts were given in ppm and coupling constants (*J*) in Hz. Mass spectra were obtained using a JMS-HX 110A/110A Tandem Mass Spectrometer (JEOL). UV absorption spectra were obtained on UVIKON 933 Double Beam UV/VIS Spectrometer. Fluorescence emission spectra were obtained using RF-5301/PC Spectrofluorophotometer (Shimadzu).

Preparation of fluorometric anion titration solutions

Stock solutions (1 mM) of the sodium salts of $CH_3CO_2^-$, $H_2PO_4^-$, CN^-, F^-, Cl^-, Br^-, I^-, NO_3^-, and pyrophosphate (PPi) in double distilled water and sodium salts of ATP, ADP, AMP, CTP, GTP, TTP, UTP in adequate buffer solution (pH 7.4, 20 mM, HEPES) were prepared. Stock solution of compounds (0.1 mM) was also prepared in adequate buffer solution. Test solutions were prepared by placing 4-40 μL of the probe stock solution into a test tube, adding an appropriate aliquot of each anion stock, and diluting the solution to 4 mL with buffer solution. For all measurements, excitation was at 326 nm; emission was measured at 460 nm. Both excitation and emission slit widths were 3nm/5nm for **1** and **2** and 3nm/3nm for **3**.

Preparation of NMR titration solutions

The solution of receptors as 2 mM in D_2O-DMSO-d_6 (2:8, v/v) was titrated by adding known quantities of concentrated solution (4 mM) of anions in the form of their sodium salts. All sodium anions were purchased from Aldrich. All titration were repeated at least once to get the consistent values.

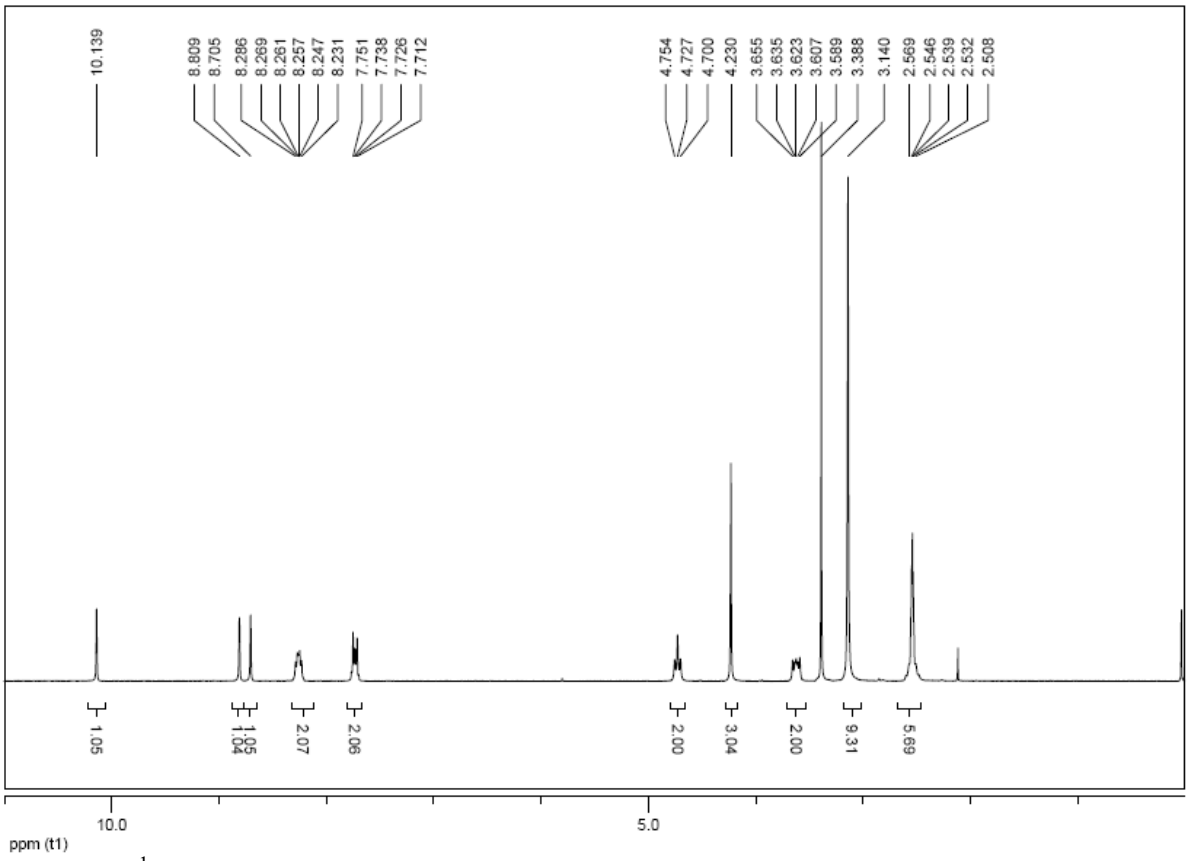

Figure S1. ^{1}H-NMR of compound **1** in DMSO–d_6.

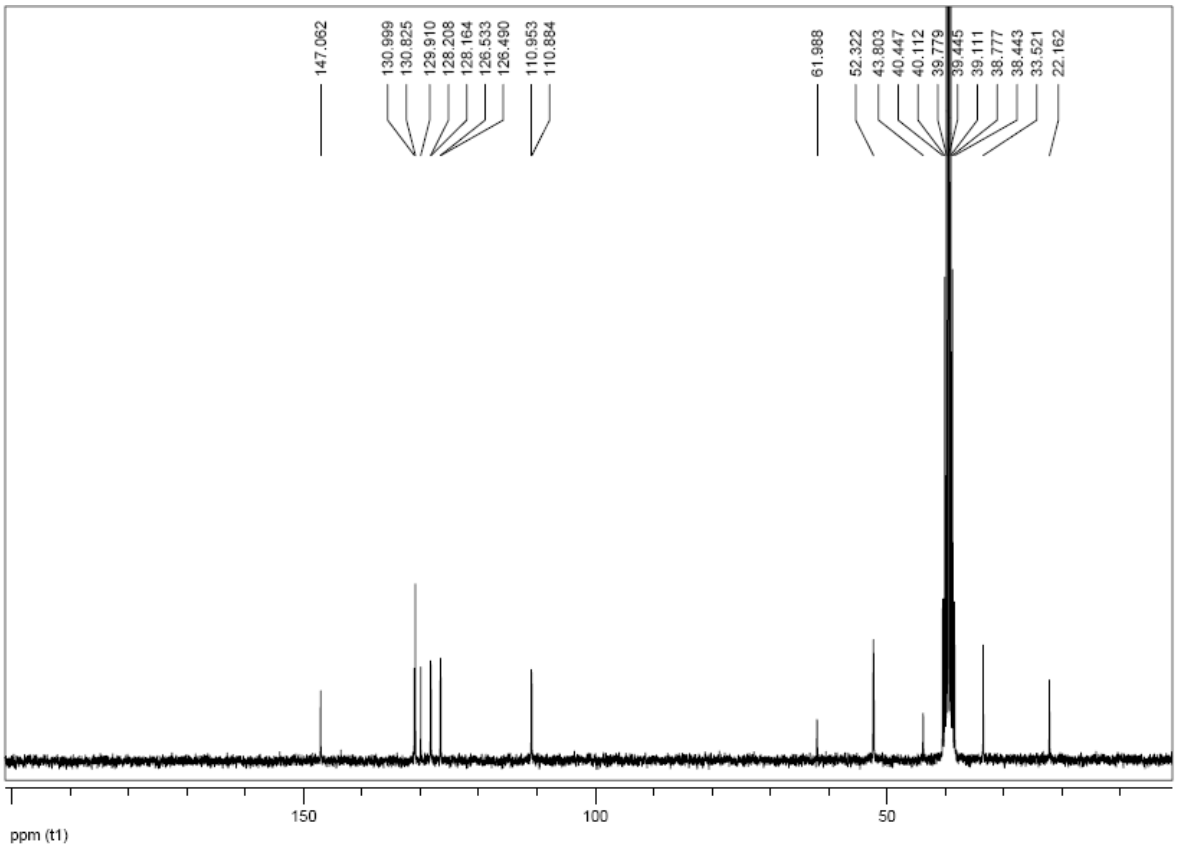

Figure S2. ^{13}C-NMR of compound **1** in DMSO–d_6.

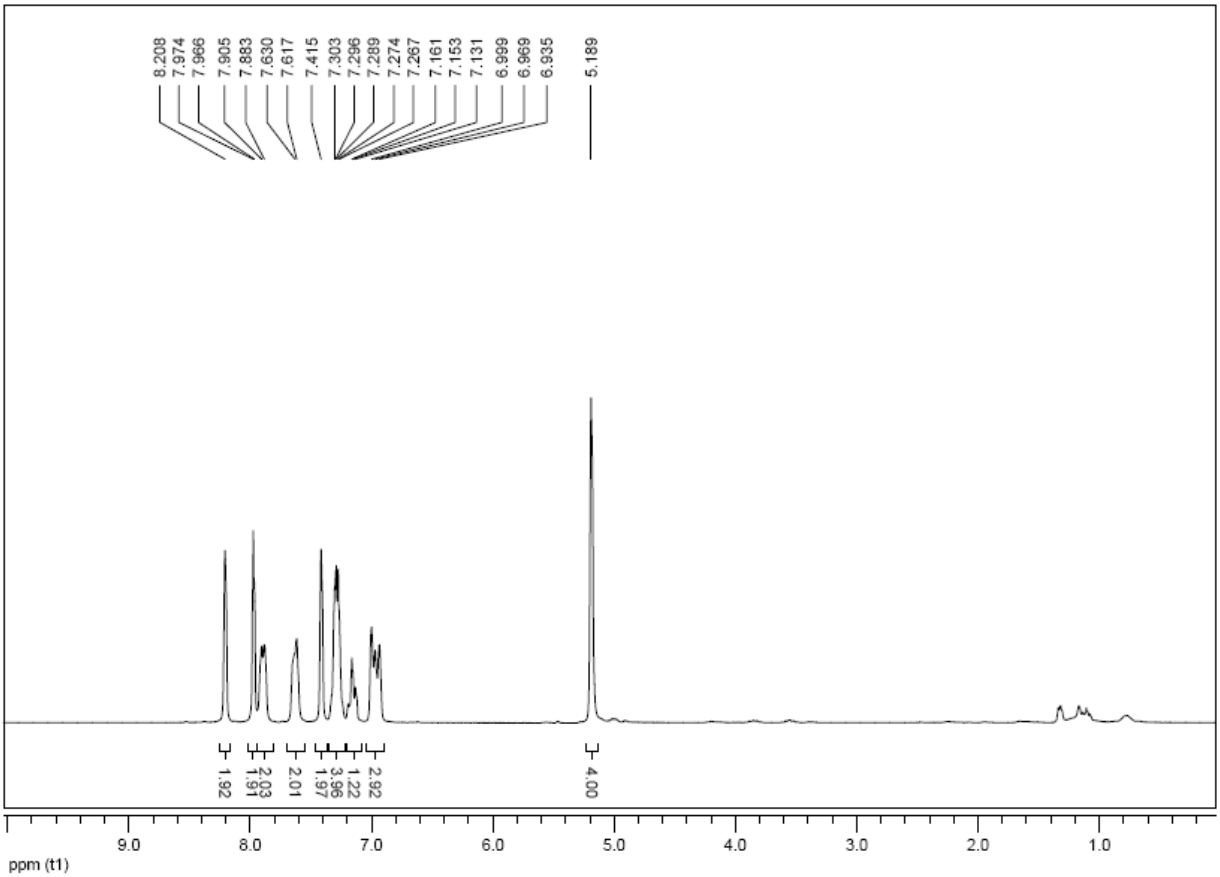

Figure S3. ^{1}H-NMR of compound **8** in $CDCl_3$.

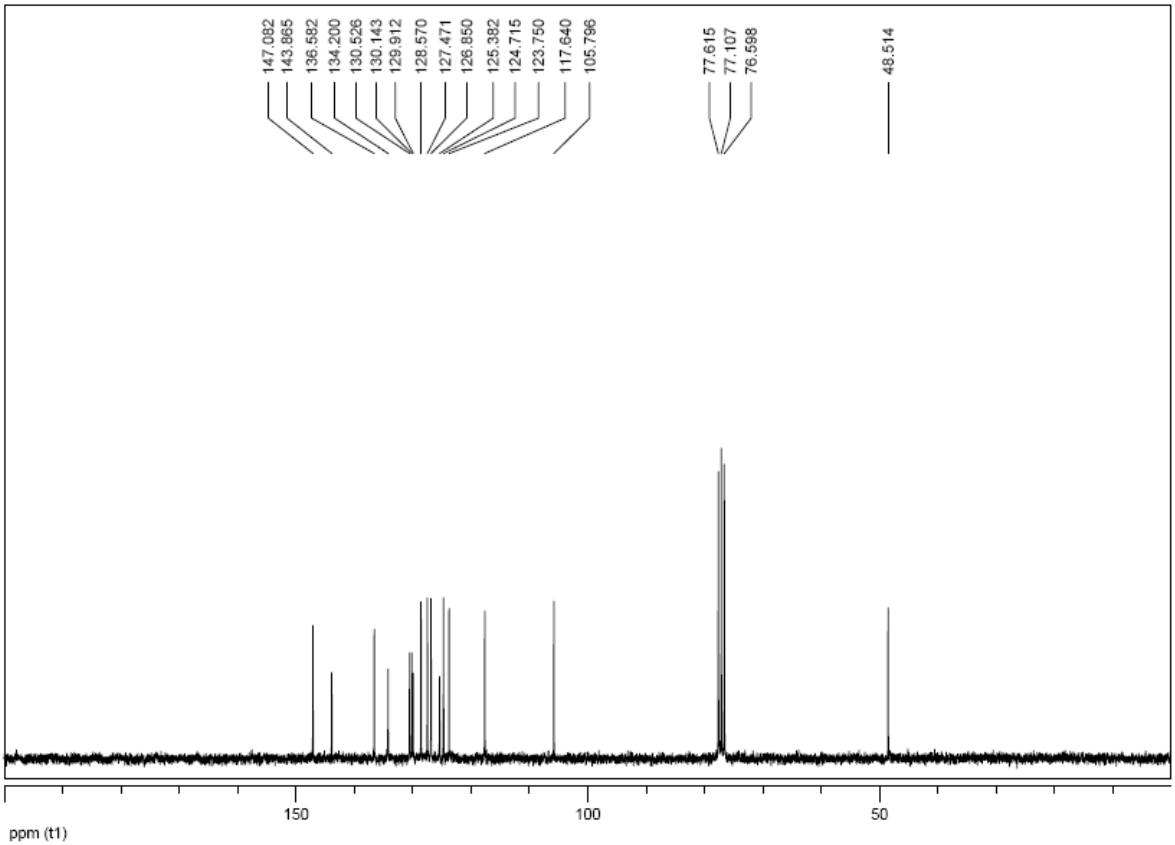

Figure S4. ^{13}C-NMR of compound **8** in $CDCl_3$.

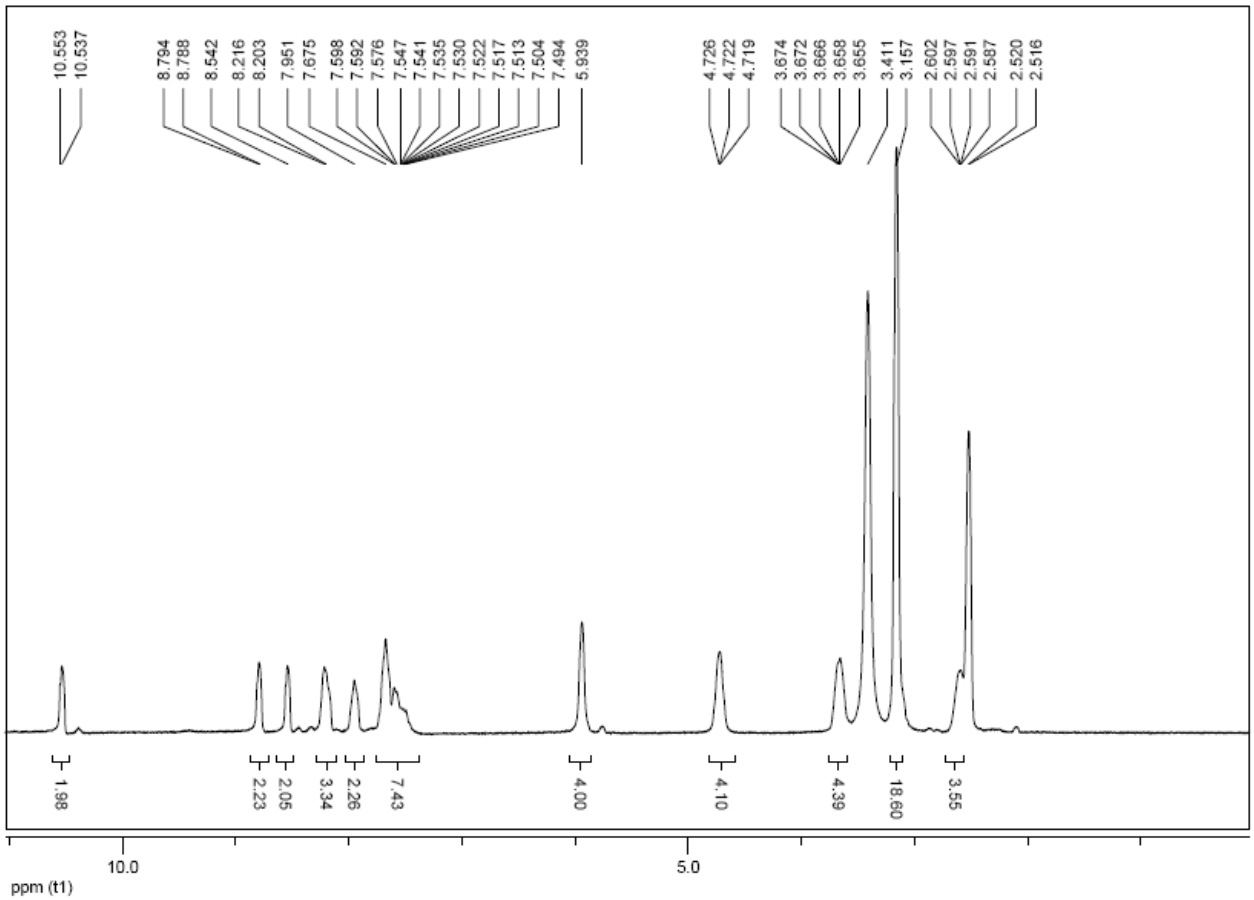

Figure S5. ^{1}H-NMR of compound **2** in DMSO–d_6.

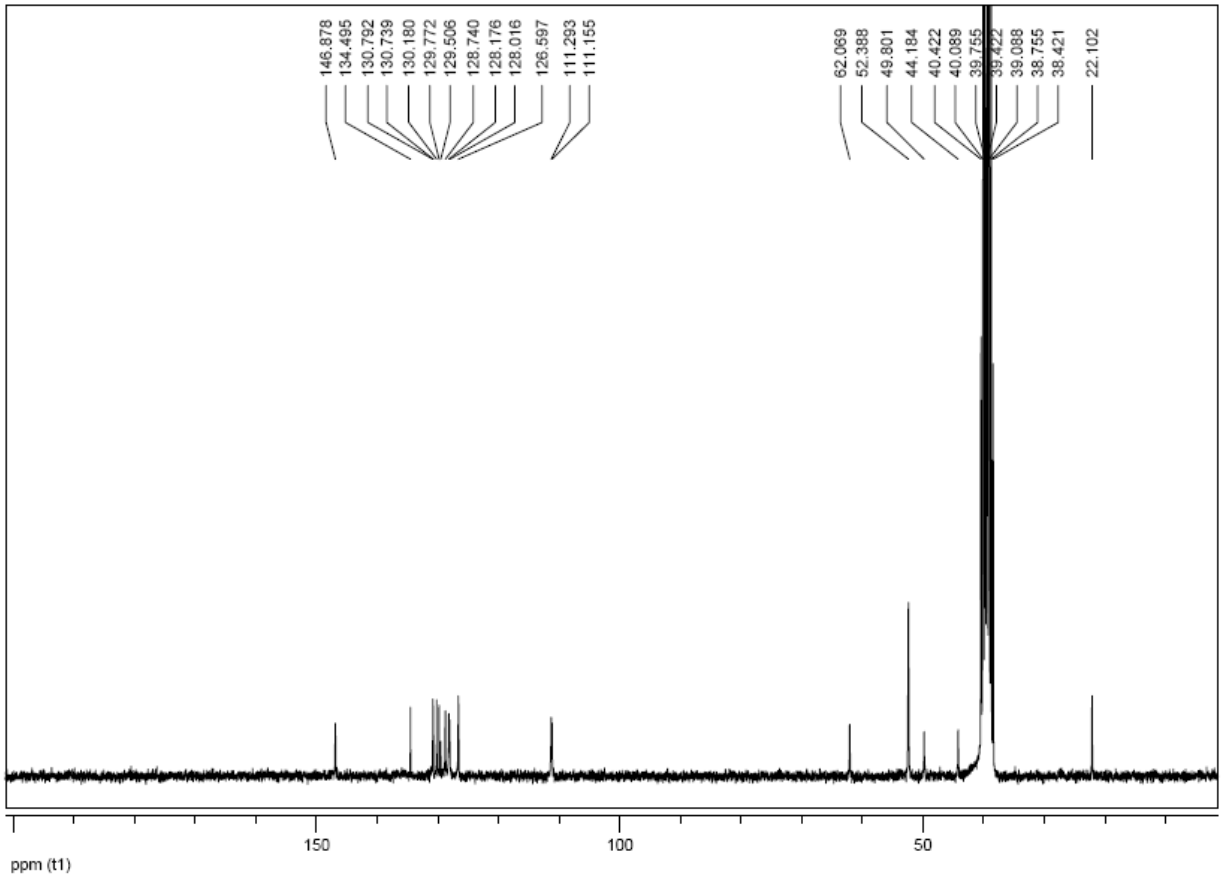

Figure S6. ^{13}C-NMR of compound **2** in DMSO–d_6.

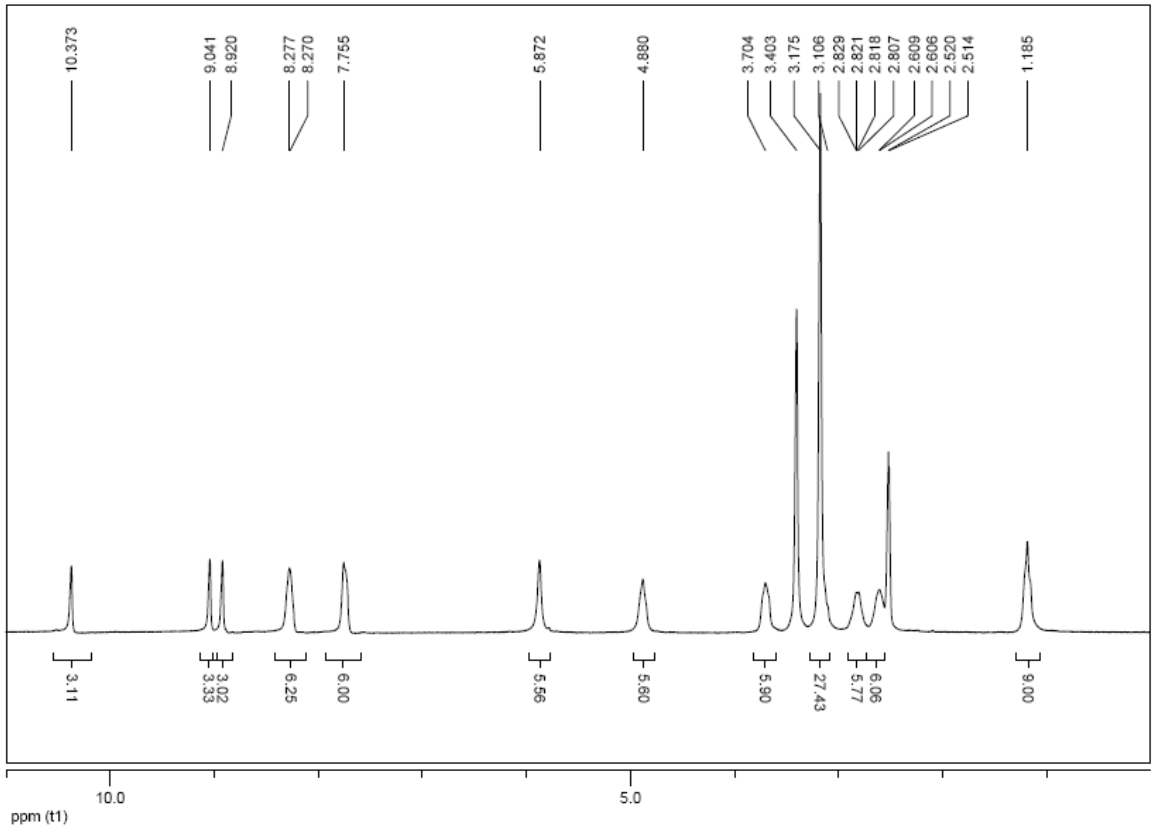

Figure S7. ^{1}H-NMR of compound **3** in DMSO–d_6.

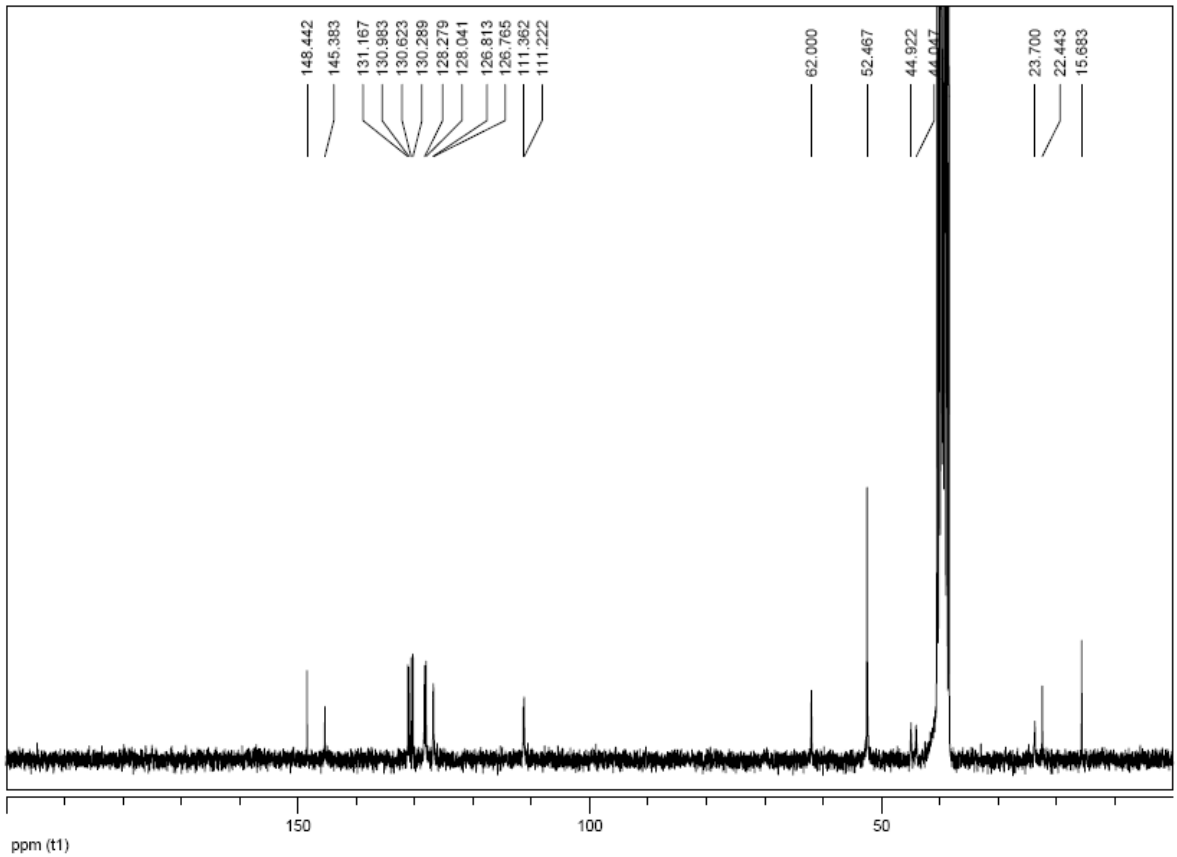

Figure S8. ^{13}C-NMR of compound **3** in DMSO–d_6.

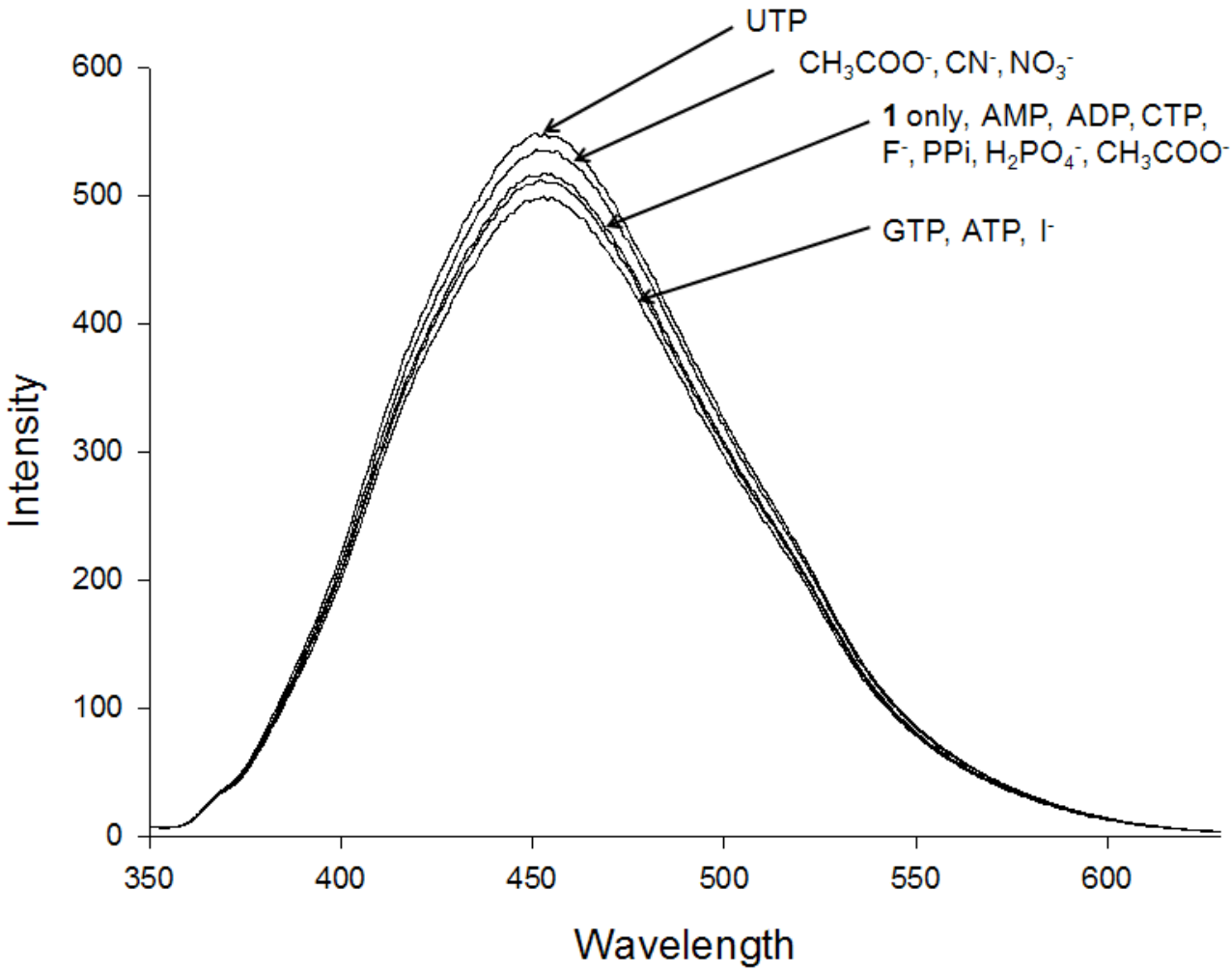

Figure S9. Fluorescent emission changes of **1** (6 μM) upon addition of $CH_3CO_2^-$, $H_2PO_4^-$, CN^-, F^-, Cl^-, Br^-, I^-, NO_3^-, and pyrophosphate (PPi) and nucleotides, such as ATP, GTP, CTP, TTP, UTP, ADP and AMP (10 equiv.) at pH 7.4 (20 mM HEPES) (excitation at 326 nm).

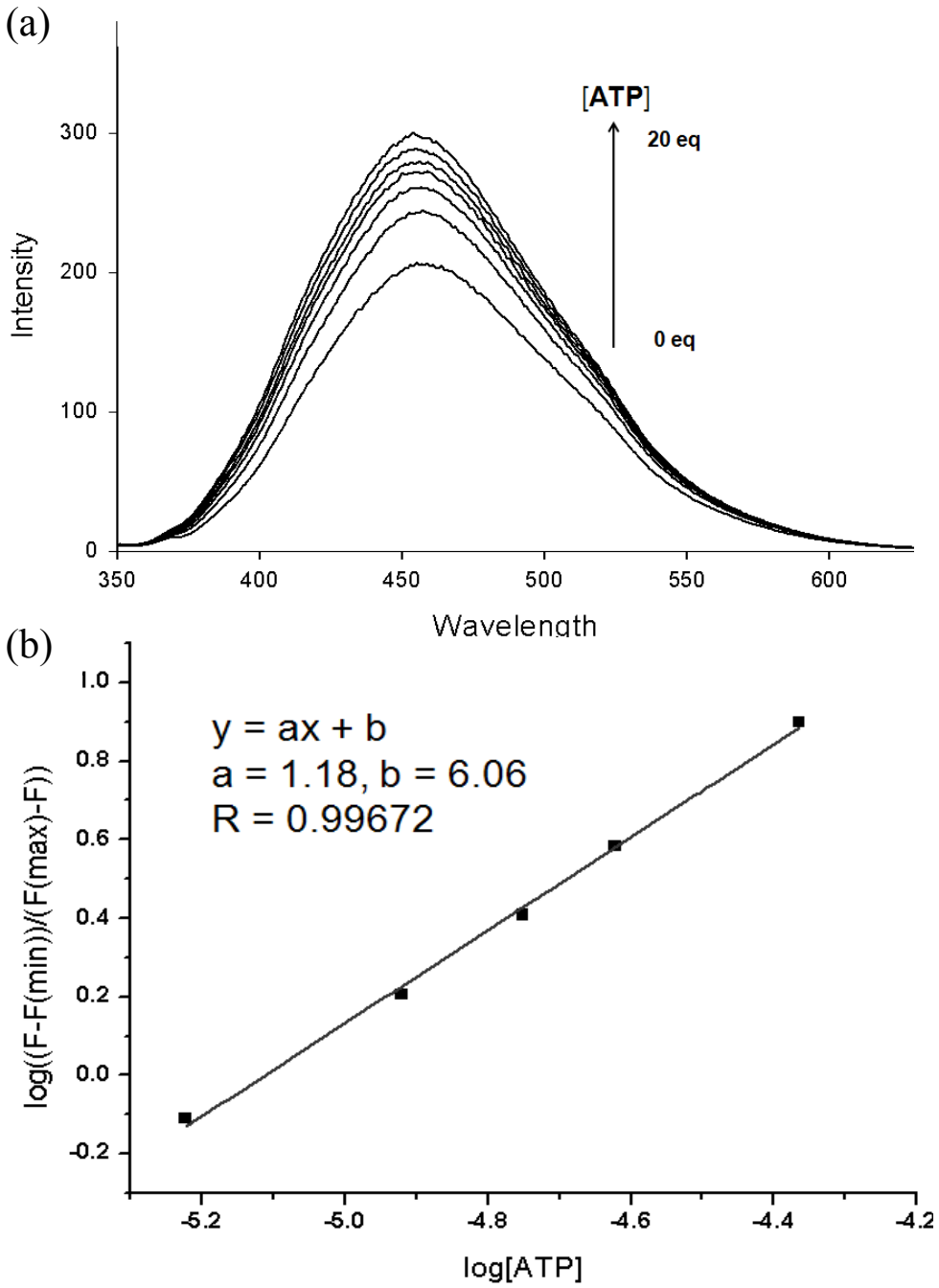

Figure S10. Fluorescent titrations of **3** (6 μM) upon addition of sodium salt of ATP(a) at pH 7.4 (20 mM HEPES)(excitation at 326 nm) and its Hill-plot(b).

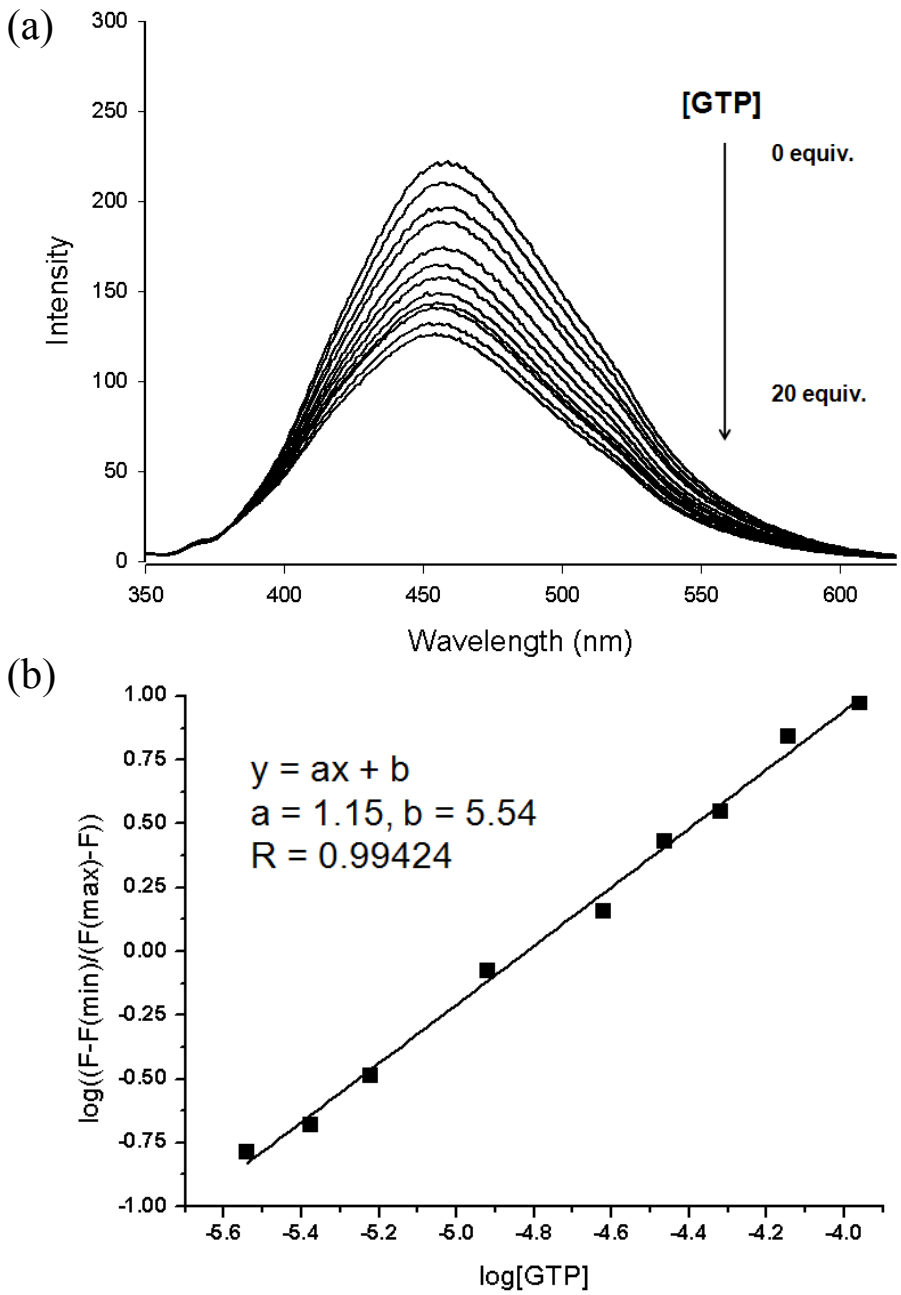

Figure S11. Fluorescent titrations of **3** (6 μM) upon addition of sodium salt of GTP(a) at pH 7.4 (20 mM HEPES)(excitation at 326 nm) and its Hill-plot(b).

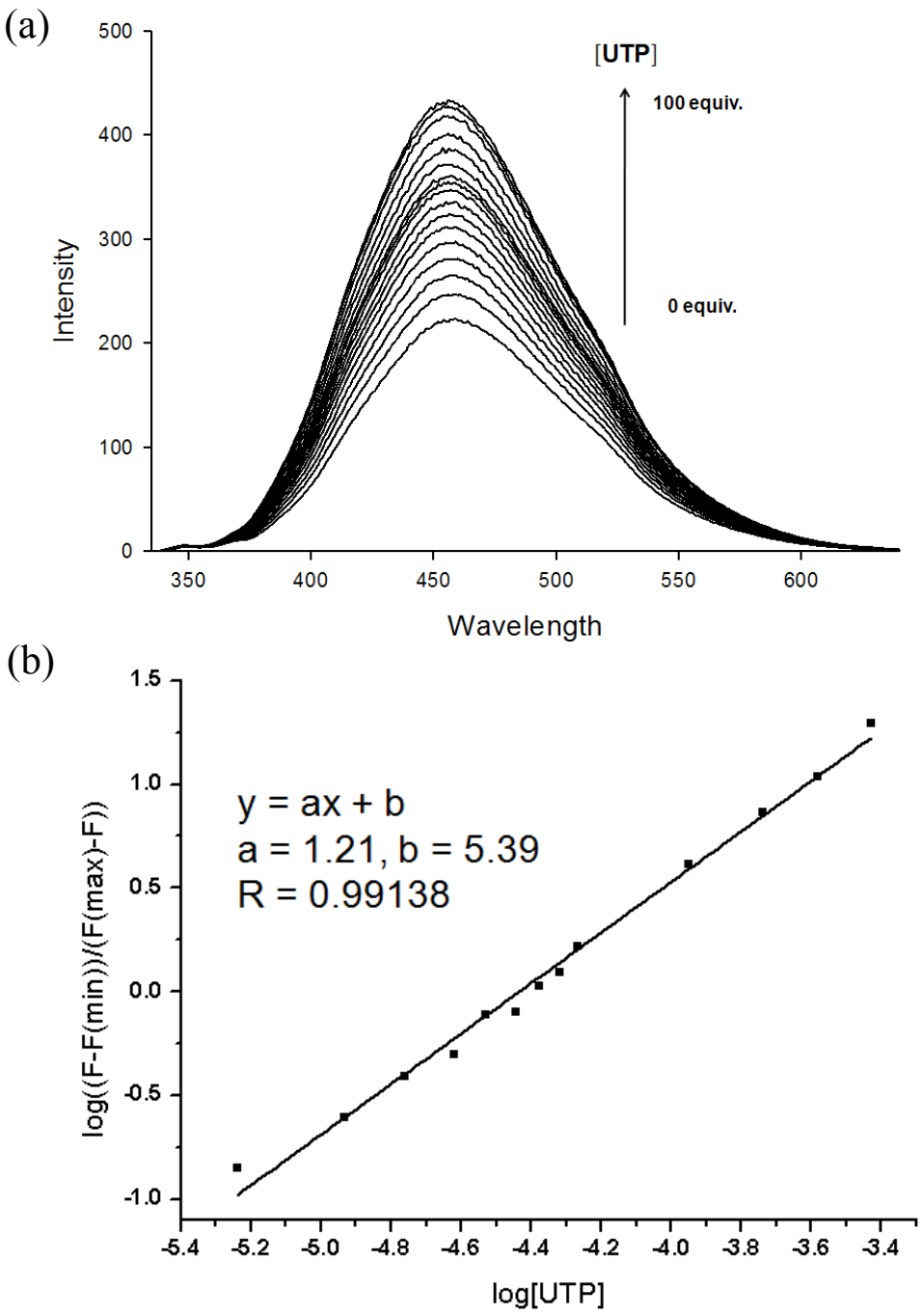

Figure S12. Fluorescent titrations of **3** (6 μM) upon addition of sodium salt of UTP(a) at pH 7.4 (20 mM HEPES)(excitation at 326 nm) and its Hill-plot(b).

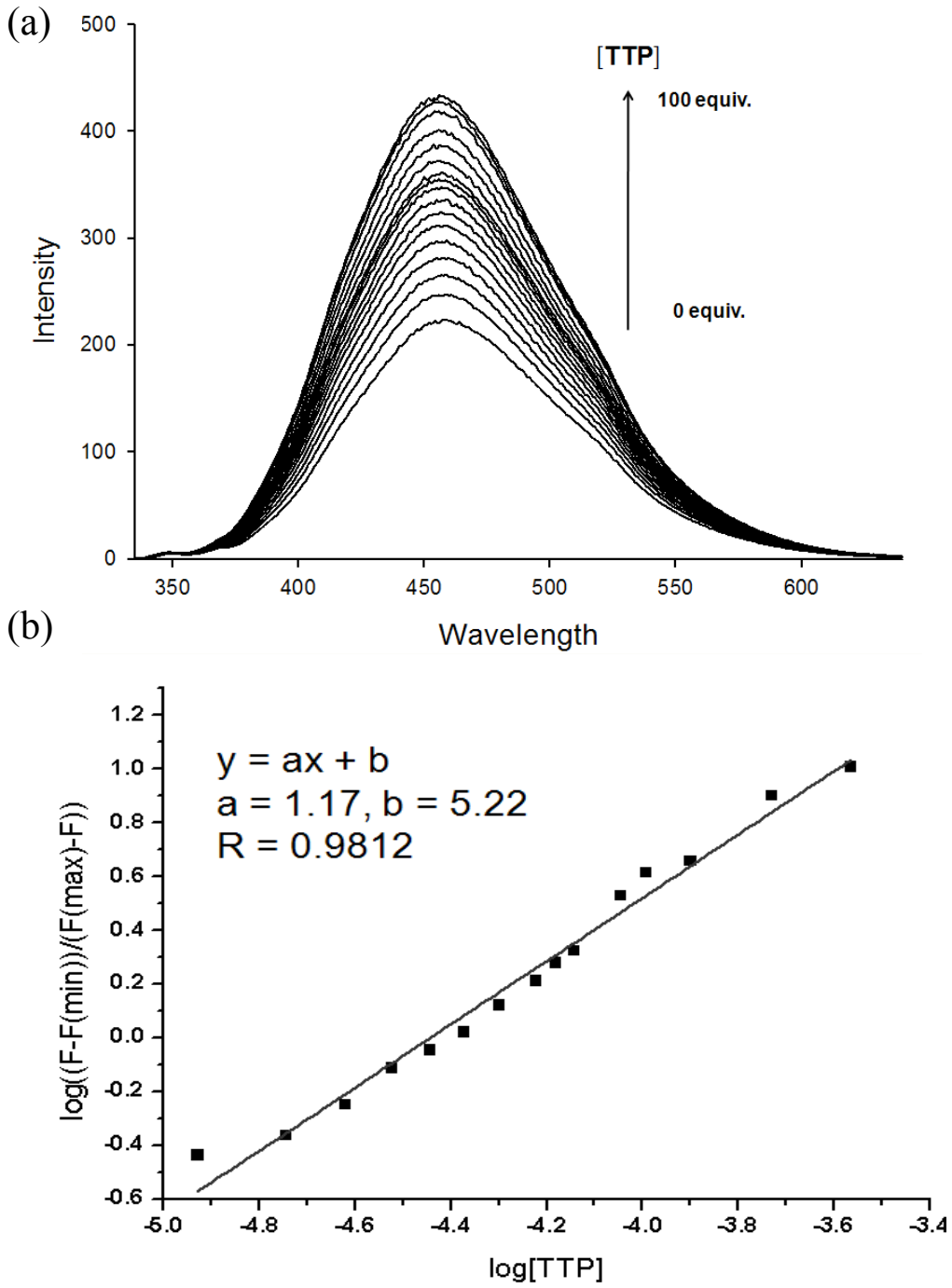

Figure S13. Fluorescent titrations of **3** (6 μM) upon addition of sodium salt of TTP(a) at pH 7.4 (20 mM HEPES)(excitation at 326 nm) and its Hill-plot(b).

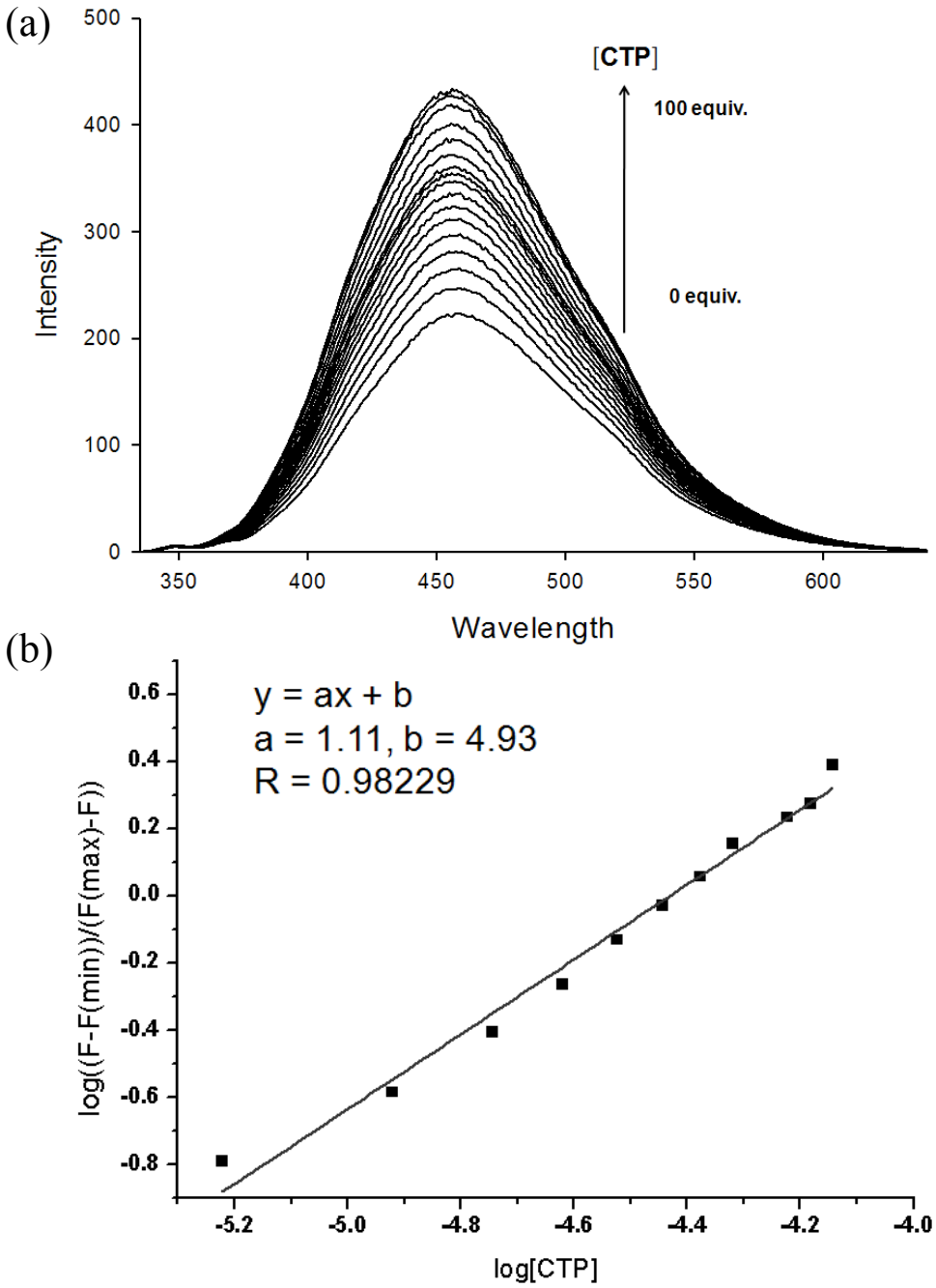

Figure S14. Fluorescent titrations of **3** (6 μM) upon addition of sodium salt of CTP(a) at pH 7.4 (20 mM HEPES)(excitation at 326 nm) and its Hill-plot(b).

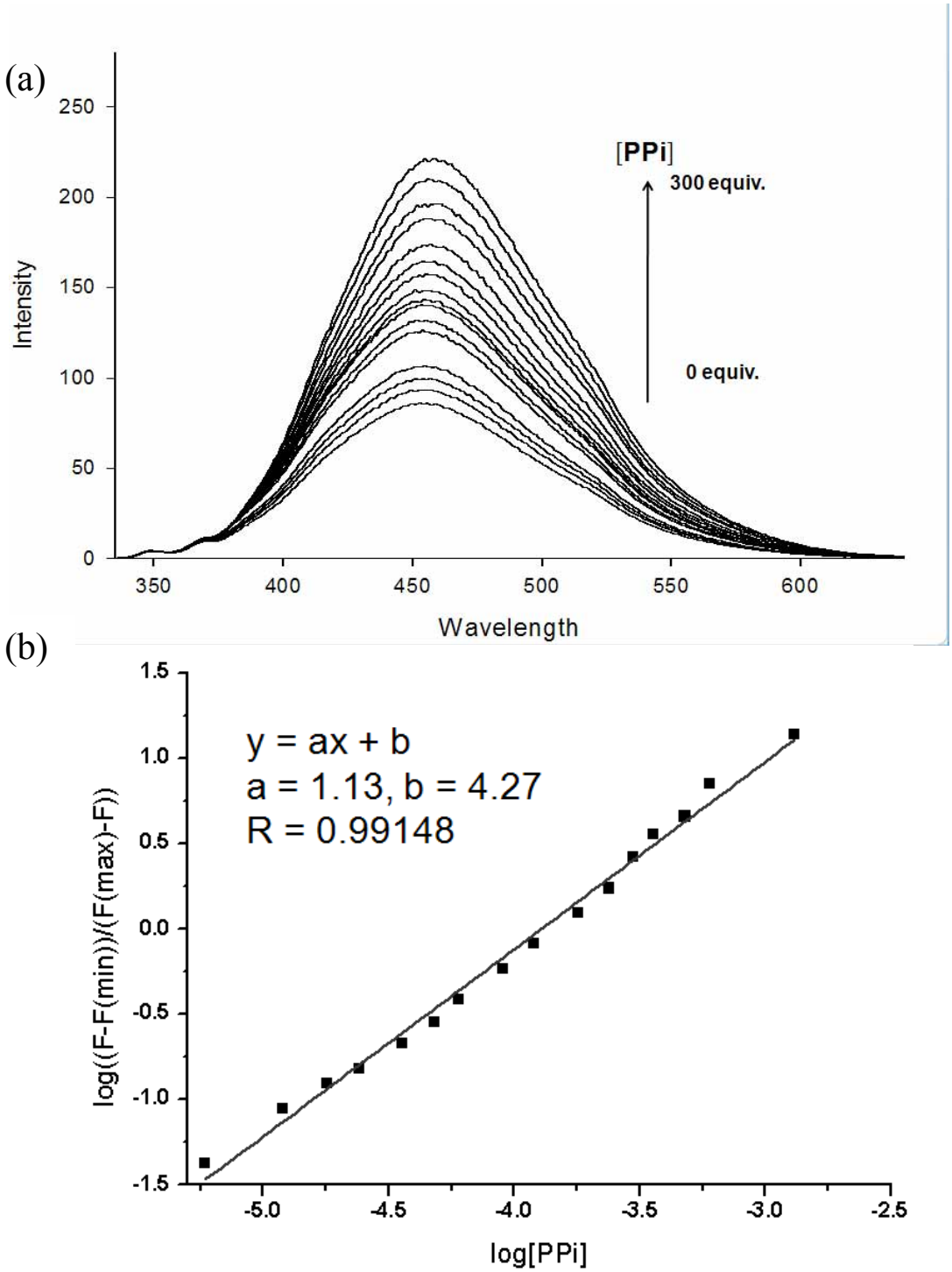

Figure S15. Fluorescent titrations of **3** (6 μM) upon addition of sodium salt of PPi(a) at pH 7.4 (20 mM HEPES)(excitation at 326 nm) and its Hill-plot(b).

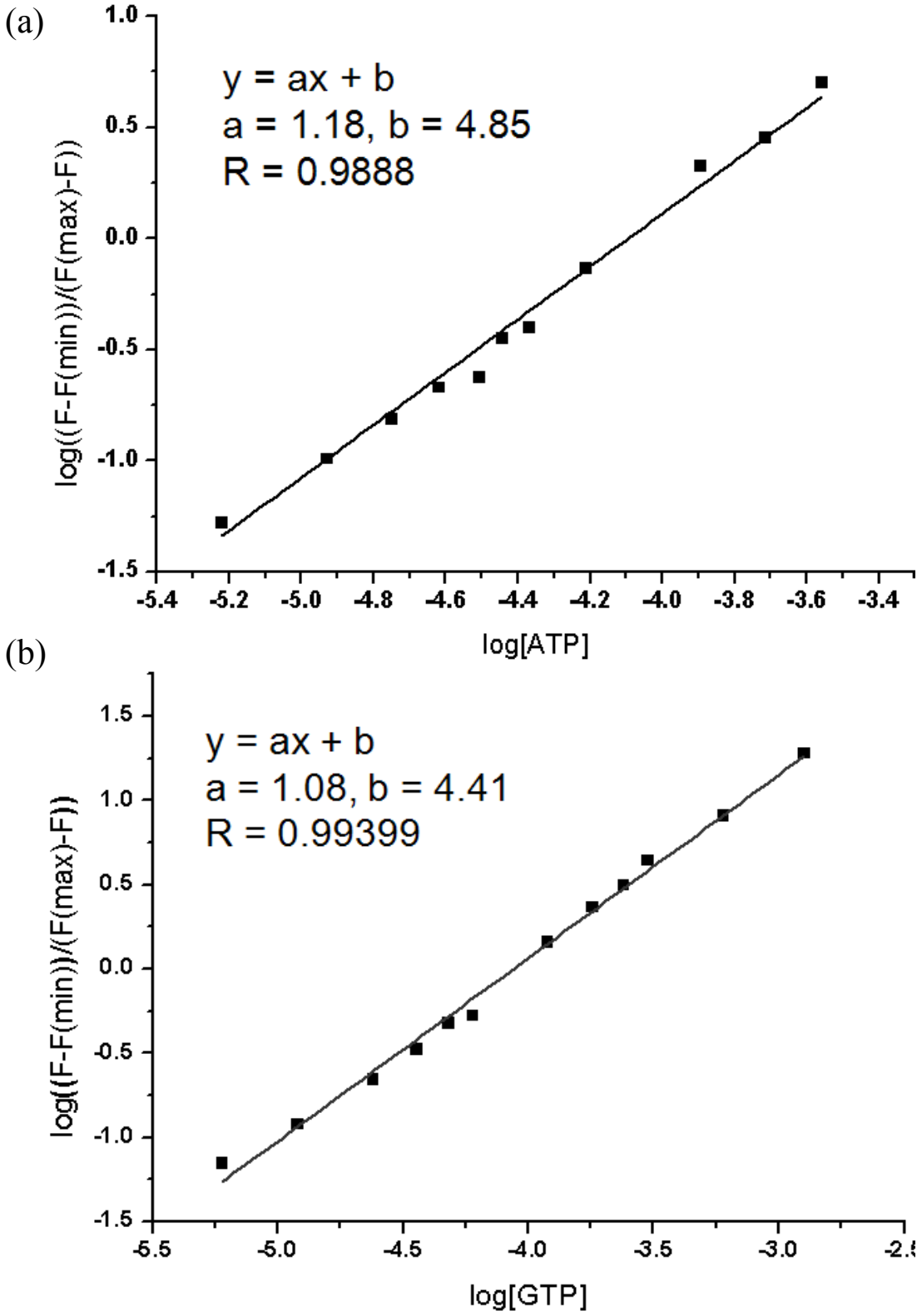

Figure S16. Hill-plot of compound **2** from the fluorescence titration of sodium salt of ATP(a) and GTP(b)

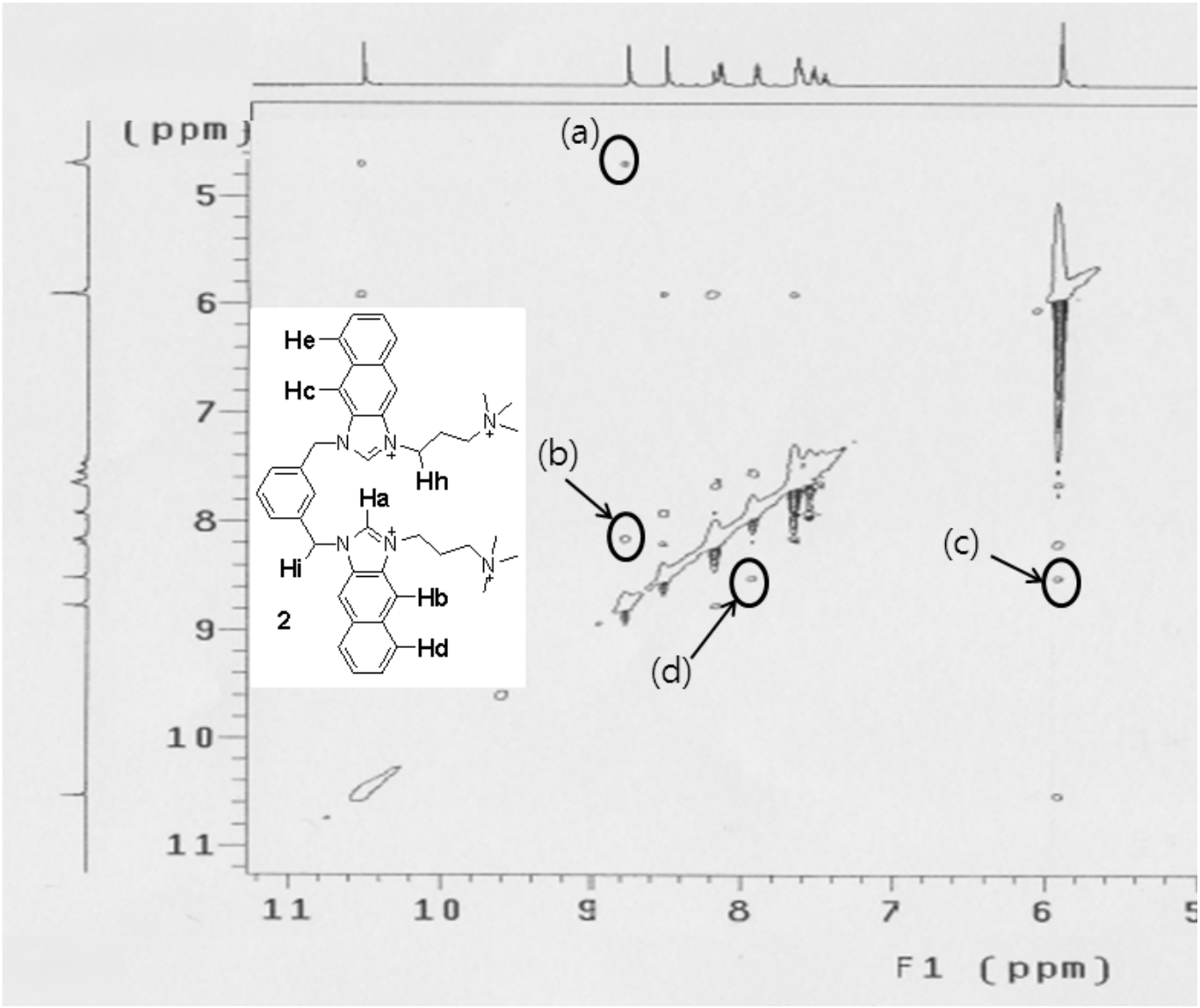

Figure S17. Partial 2D-NOESY NMR spectra of **2** in DMSO–d_6 cross peak **A** between Hb and Hh(a), cross peak **B** between Hb and Hd(b), cross peak **C** between Hc and Hi(c) and cross peak **D** between Hc and He(d).

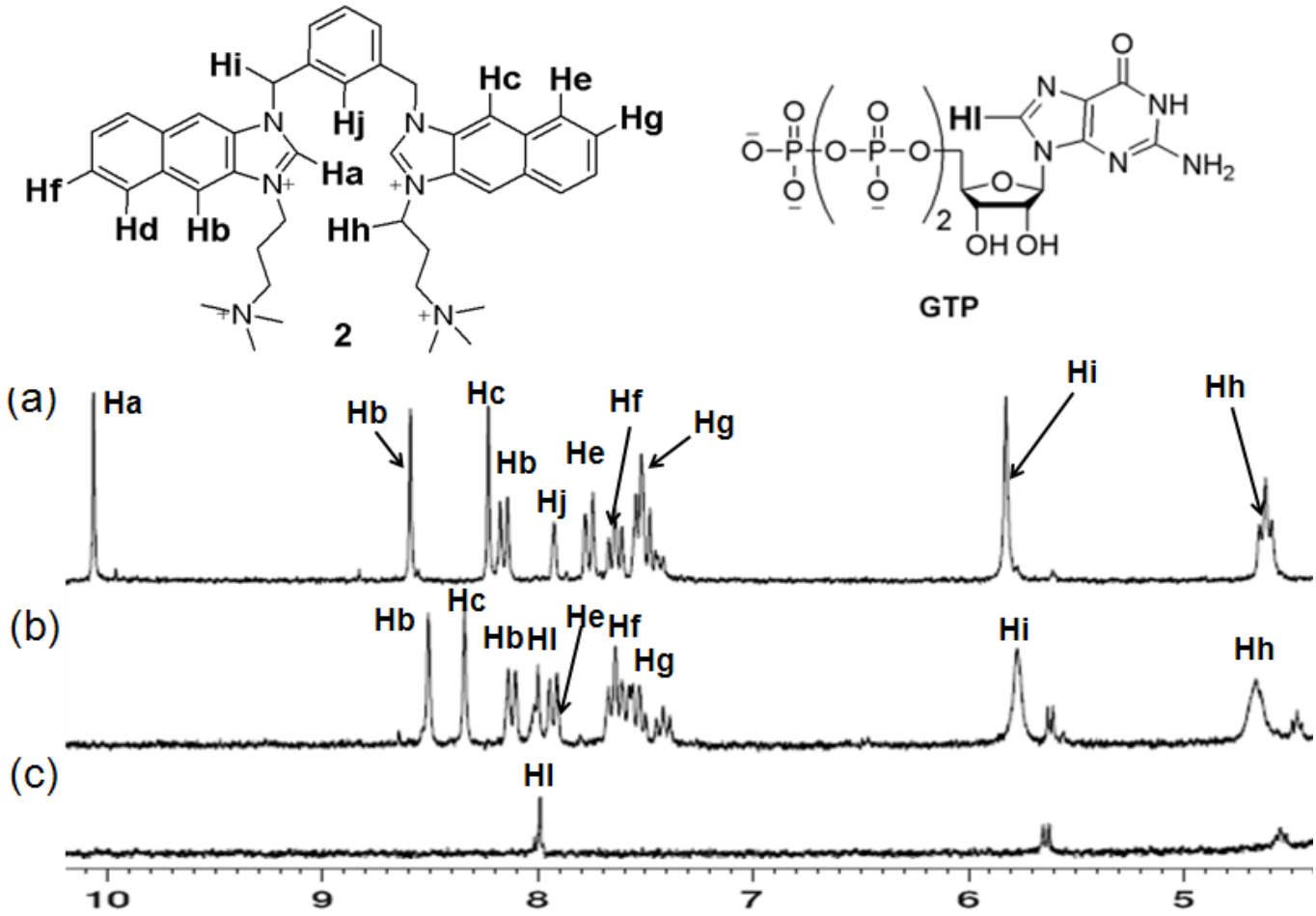

Figure S18. Partial NMR spectra for host **2** (2 mM)(a), **2**+ GTP (1.0 equiv.)(b) and GTP(c) in D_2O DMSO–d_6 (2:8, v/v).