

Supporting Information

A fluorescence enhancement-based sensor for hydrogen sulfate ion

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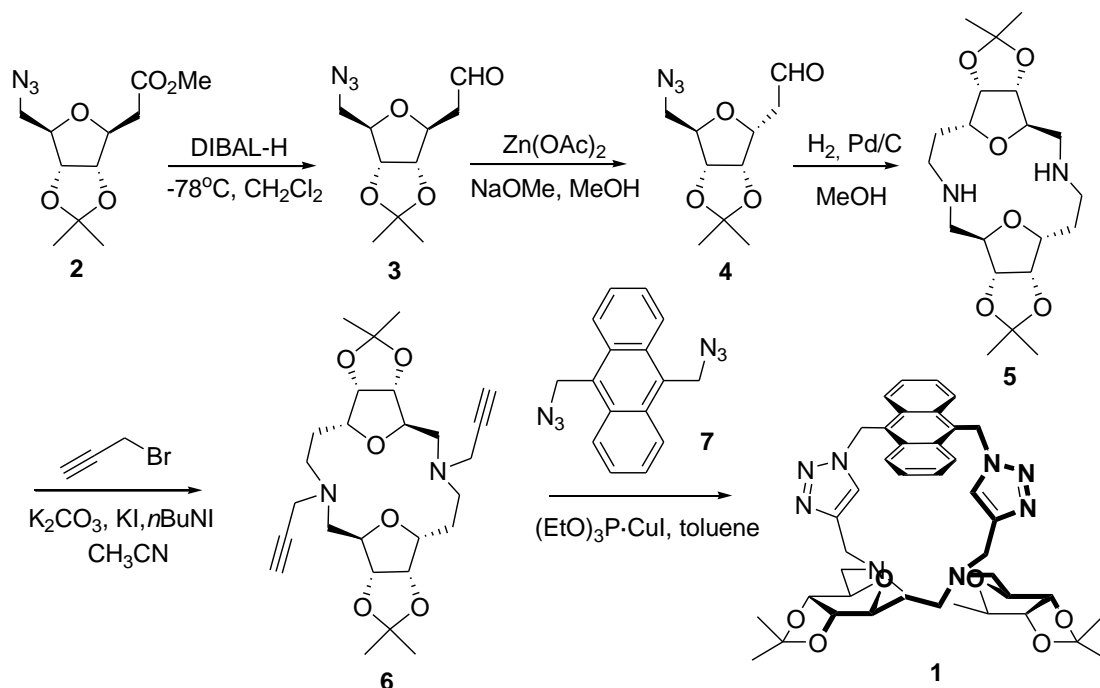
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- S16 Partial plots of ¹H NMR spectra of **1** on addition of HSO₄⁻ ion in MeOD solution. (**Figure S14**)

1. Experimental

1.1. General Methods

All reagents were obtained from commercial suppliers and were used without further purification. DCM was distilled over CaH₂. MeOH was distilled over magnesium and iodine. Analytical thin-layer chromatography was performed using silica gel 60 F254 plates (Merck). The ¹H and ¹³C NMR spectra were recorded with a Bruker AM 300 spectrometer. Chemical shifts are given in ppm with residual CHCl₃ or CD₃OD as reference. Mass spectra were recorded under fast atom bombardment (FAB) or electrospray interface (ESI) conditions. Microwave reactions were carried out in a Milestone Start S with a maximum power of 300W and 50 mL process flask.



Methyl 2-C-(5-azido-5-deoxy-2,3-di-O-isopropylidene-β-D-ribofuranosyl)acetaldehyde (3)

To a solution of **2** (3.58 g, 13 mmol) in dry CH₂Cl₂ (100 mL) was added 1 M solution of DIBALH (30 mL, 2.5 equiv.) at -78 °C. The reaction mixture was stirred at the temperature for 1 h. MeOH (16 mL) was added and stirred for 10 min at -78 °C. Saturated NaCl (2 mL), Et₂O (50 mL) and MgSO₄ (1.07 g) were subsequently added. The mixture was stirred at room temperature for 1 h and then filtered through Celite. The solvent was removed and the crude was purified by chromatography (Hexanes/EtOAc 5:1) to give **3** (2.01 g, 64%) as a colorless oil; *R*_f 0.34 (EtOAc/Hexanes 1:2.5); ¹H NMR (300 MHz, CDCl₃) δ: 9.71 (t, *J* = 1.5 Hz, 1H), 4.54 (dd, *J* = 6.9, 4.5 Hz, 1H), 4.40 (dd, *J* = 6.6, 5.1 Hz, 1H), 4.30-4.25 (m, 1H), 4.03 (q, *J* = 4.2 Hz, 1H), 3.49 (dd, *J* = 13.2, 3.6 Hz, 1H), 3.28 (dd, *J* = 13.2, 4.5 Hz, 1H), 2.74-2.69 (m, 2H), 1.47 (s, 3H), 1.27 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ: 199.3, 115.1, 84.2, 82.9, 81.8, 79.4, 52.0, 46.8, 27.2, 25.3; HRMS (FAB): Calcd for C₁₀H₁₆N₃O₄ (M+H), *m/z* 242.1141; found *m/z* 242.1138.

Methyl 2-C-(5-azido-5-deoxy-2,3-di-O-isopropylidene-α-D-ribofuranosyl)

acetaldehyde (**4**)

To a solution of **3** (1.04 g, 4.32 mmol) and Zn(OAc)₂ (4.7 g, 6.0 equiv.) were added 0.7 M solution of NaOMe in MeOH (15 mL). The mixture was stirred overnight, and then neutralized by adding HOAc. The mixture was extracted by ethyl acetate, filtered, and concentrated. The resulting residue was purified by silica column chromatography (Hexanes/EtOAc 5:1) to give **4** (0.78 g, 75%) as a colorless oil; R_f 0.34 (Hexanes/EtOAc 2.5:1); ¹H NMR (300 MHz, CDCl₃) δ: 9.78 (d, *J* = 1.2 Hz, 1H), 4.77-4.60 (m, 2H), 4.42-4.16 (m, 2H), 3.39-3.28 (m, 2H), 2.86-2.83 (m, 2H), 1.44 (s, 3H), 1.30 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ: 199.9, 112.9, 83.2, 82.6, 81.2, 76.2, 51.6, 43.6, 26.1, 24.7; HRMS (FAB): Calcd for C₁₀H₁₆N₃O₄ (M+H), *m/z* 242.1141; found *m/z* 242.1135.

Furanoid Sugar-Aza-Crown (**5**)

A mixture of **4** (0.95 g, 3.94 mmol) and 10% Pd-C (0.1 g) in methanol (20 mL) was stirred under H₂ atmosphere (balloon pressure) for 24 h until the starting material was completely consumed. The reaction mixture was filtered and the filtrate was concentrated. Purification by chromatography (EtOAc/MeOH 3:1) gave **5** (0.63 g, 80%) as a pale yellow solid; m.p: 182 °C; R_f 0.21 (EtOAc/MeOH 1:2); ¹H NMR (300 MHz, CDCl₃) δ: 4.57 (dd, *J* = 6.0, 5.7 Hz, 2H), 4.38 (d, *J* = 6.0 Hz, 2H), 4.27 (dd, *J* = 12.6, 3.9 Hz, 2H), 3.68 (d, *J* = 9.9 Hz, 2H), 3.11-3.05(m, 3H), 2.63 (dd, *J* = 12.0, 3.9 Hz, 2H), 2.49-2.47 (m, 4H), 2.04-1.99 (m, 3H), 1.83-1.78 (m, 2H), 1.43 (s, 6H), 1.24 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ: 112.6, 83.5, 82.7, 81.8, 79.4, 48.7, 48.4, 27.7, 26.2, 25.3; HRMS (FAB): Calcd for C₂₀H₃₄N₂O₆ (M+H), *m/z* 398.2417; found *m/z* 399.2501.

N-Propargyl Furanoid Sugar-Aza-Crown (**6**)

To a solution of **5** (0.648 g, 1.63 mmol) in CH₃CN (10 mL) was added K₂CO₃ (0.56 g, 4.06 mmol) and propargyl bromide (0.36 mL, 4.06 mmol) and the reaction mixture

was refluxed for 6 h. After removal of the solvent, the residue was dissolved in ether, washed with aq NaHCO₃, and dried over MgSO₄. Chromatographic separation (MeOH-EtOAc 1:20) led to **6** (0.603 g, 78%) as a yellow solid; m.p: 150 °C; ¹H NMR (300 MHz, CDCl₃) δ: 4.63 (t, *J* = 4.8 Hz, 2H), 4.47 (dd, *J* = 1.8, 6.3 Hz, 2H), 4.14-4.06 (m, 4H), 3.40 (q, *J* = 17.7 Hz, 5H), 2.86 -2.83 (m, 2H), 2.72 -2.47 (m, 7H), 2.13 (s, 2H), 1.82-1.68 (m, 6H), 1.46 (s, 6H), 1.30 (s, 6H); ; ¹³C NMR (75 MHz, CDCl₃) δ: 113.0, 83.8, 82.1, 81.0, 78.6, 77.3, 72.8, 56.3, 49.7, 42.6, 27.3, 26.3, 25.0; HRMS (FAB): Calcd for C₂₆H₃₉N₂O₆ (M+H), m/z 475.2808; found m/z 475.2811.

Receptor 1

A solution of dialkyne **6** (0.492 g, 1.04 mmol), diazide **7** (0.475 g, 1.65 mmol), and the copper catalyst [Ph₃P · CuI] (0.039 g, 0.087 mmol) in toluene (20 mL) was stirred at 85 °C for 15 min by microwave irradiation (300 W) (Milestone Start S). After evaporation of the solvent, the resulting mixture solid was filtered and washed with EtOAc. Then the solvent was removed and the residue was purified by chromatography (EtOAc/MeOH 15:1) to give **1** (0.25 g, 35%) as a yellow solid. m.p 198 °C; *R_f* = 0.23 (EtOAc/MeOH 8:1); ¹H NMR (300 MHz, CDCl₃) δ: 4.63 (t, *J* = 4.8 Hz, 2H), 4.47 (dd, *J* = 1.8, 6.3 Hz, 2H), 4.14 – 4.06 (m, 4H), 3.40 (q, *J* = 17.7 Hz, 5H), 2.86 – 2.83 (m, 2H), 2.72 – 2.47 (m, 7H), 2.13 (s, 2H), 1.82 – 1.68 (m, 6H), 1.46 (s, 6H), 1.30 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ: 113.0, 83.8, 82.1, 81.0, 78.6, 77.3, 72.8, 56.3, 49.7, 42.6, 27.3, 26.3, 25.0; HRMS (FAB): Calcd for C₄₂H₅₁N₈O₆ (M+H), m/z 763.3932, found m/z 763.3941.

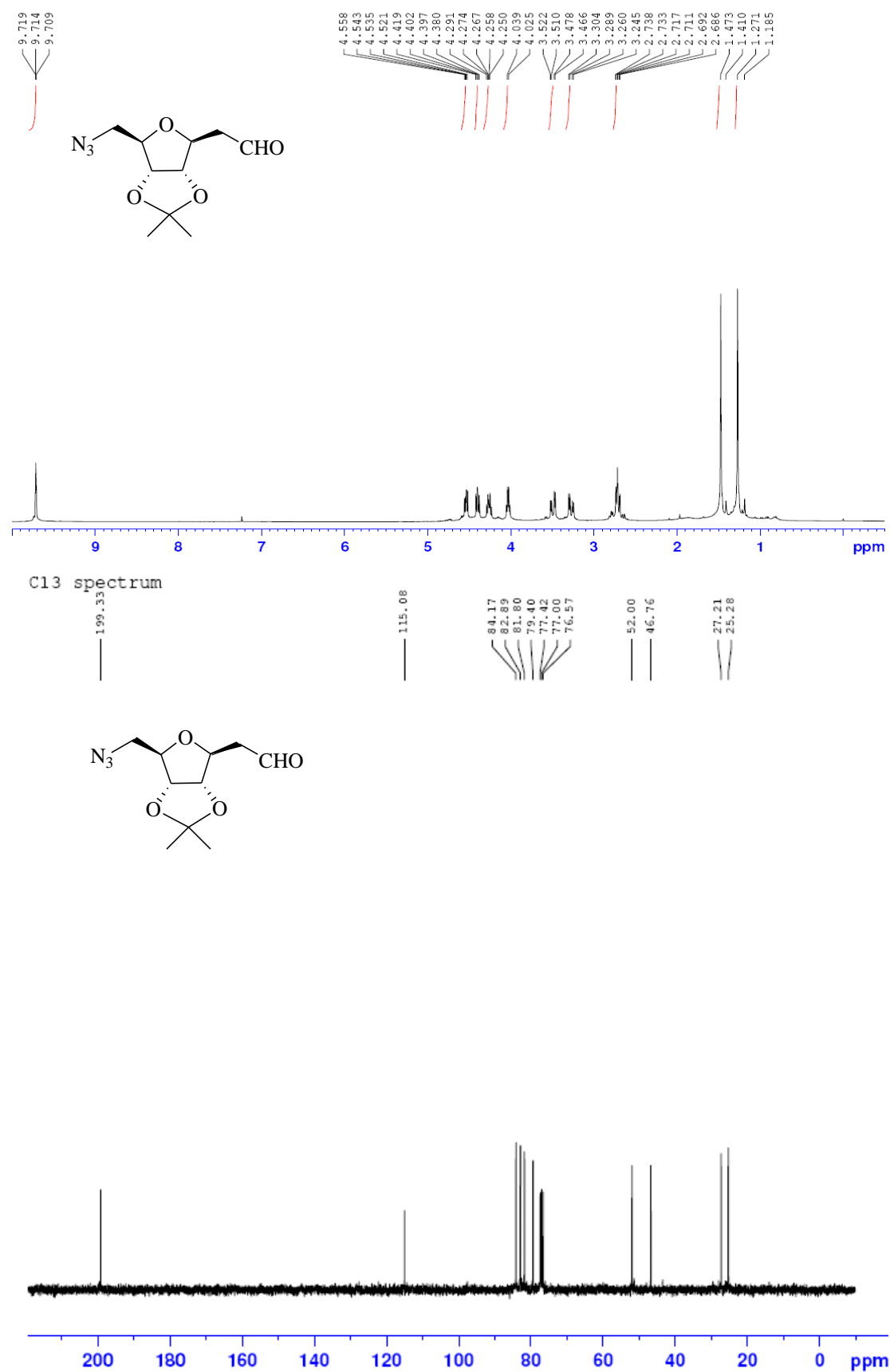


Figure S1. ¹H and ¹³C NMR Spectra of **3**.

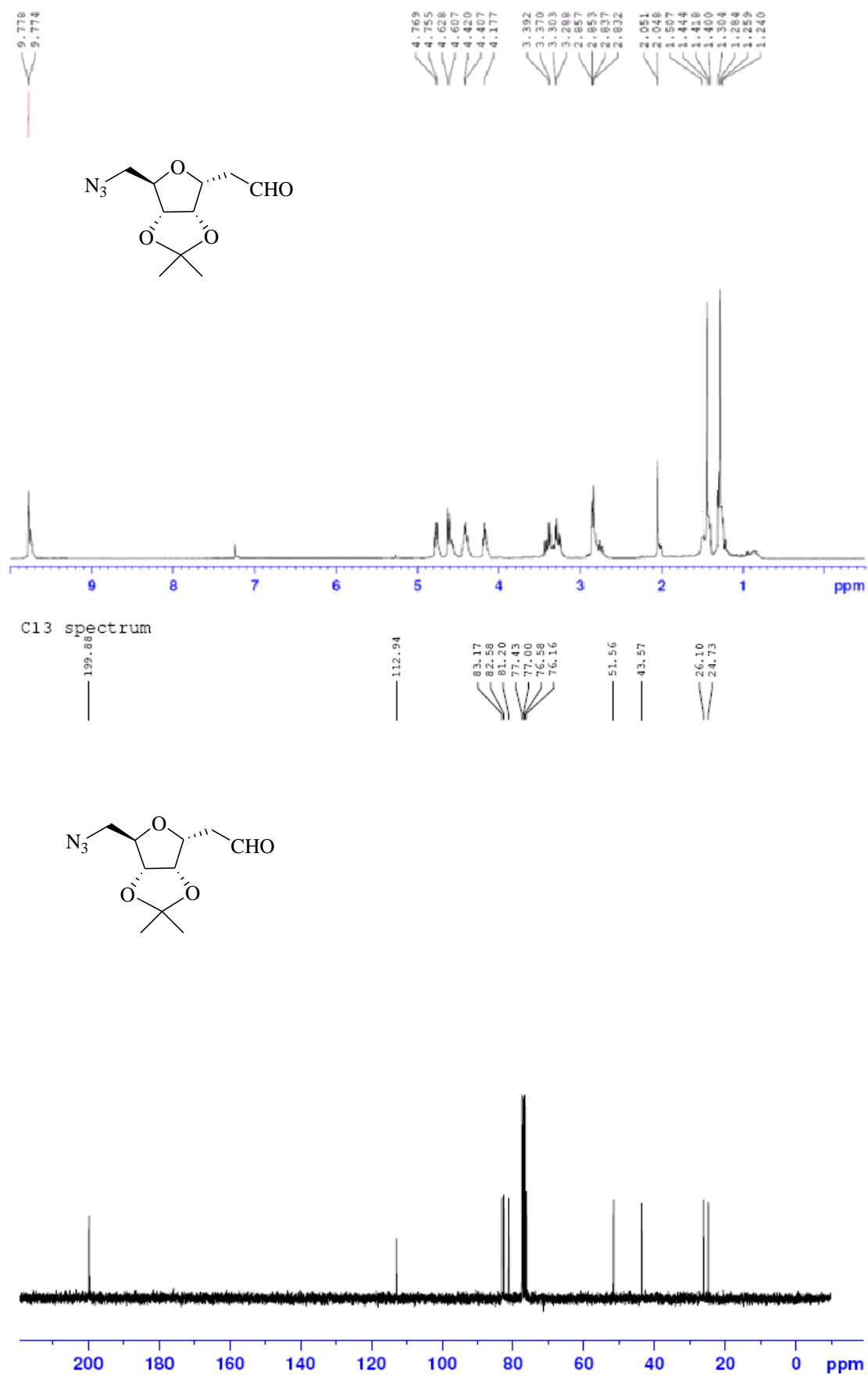
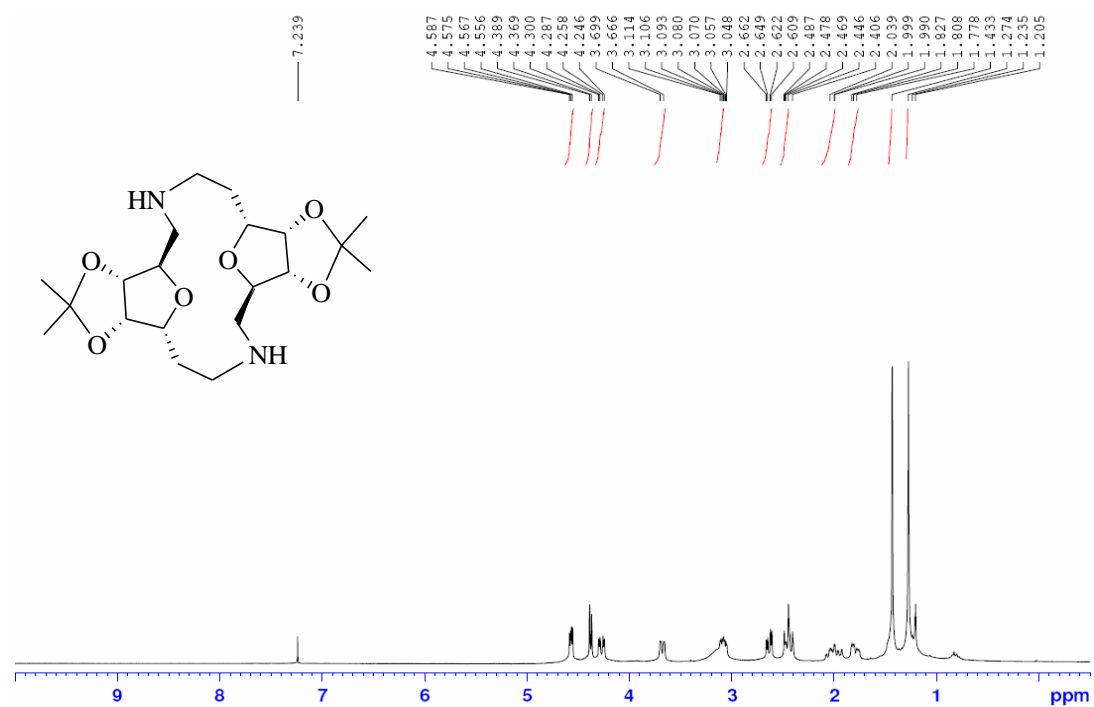


Figure S2. ¹H and ¹³C NMR Spectra of 4.



C13 spectrum

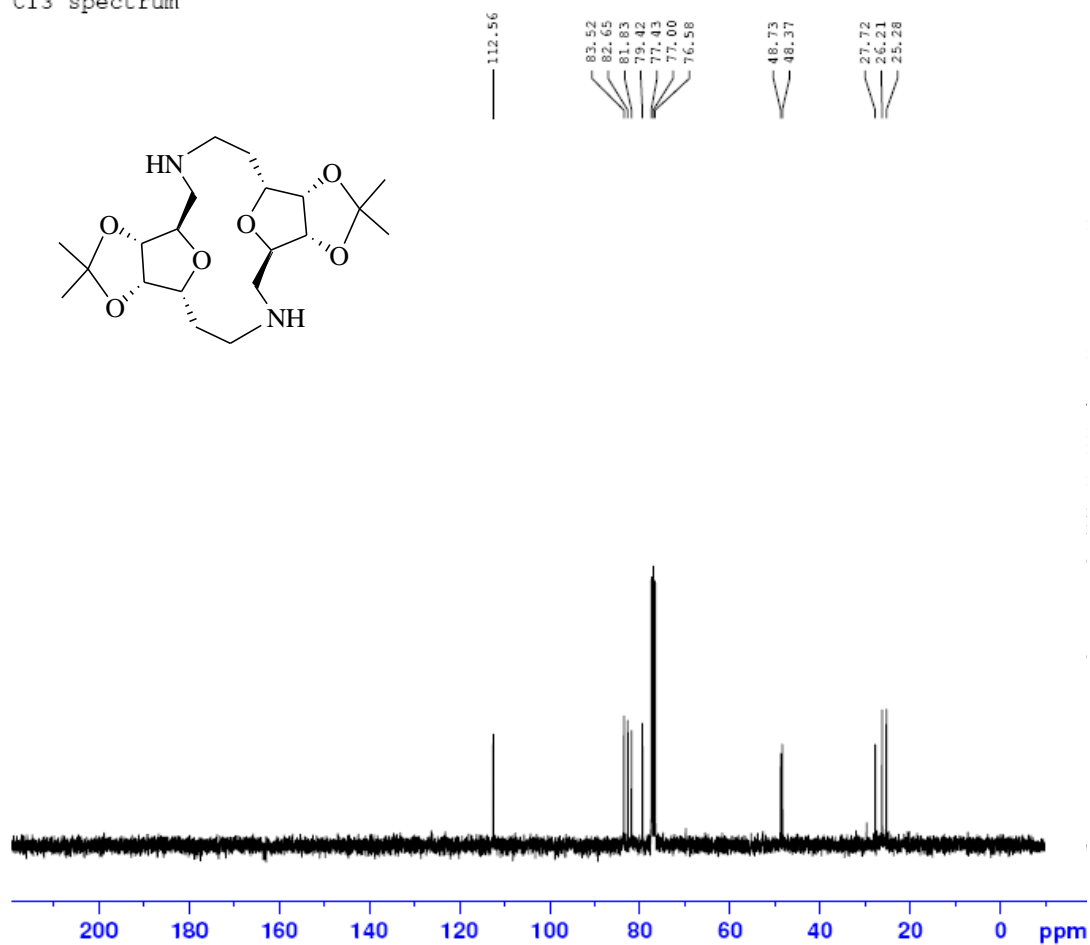


Figure S3. ¹H and ¹³C NMR Spectra of 5

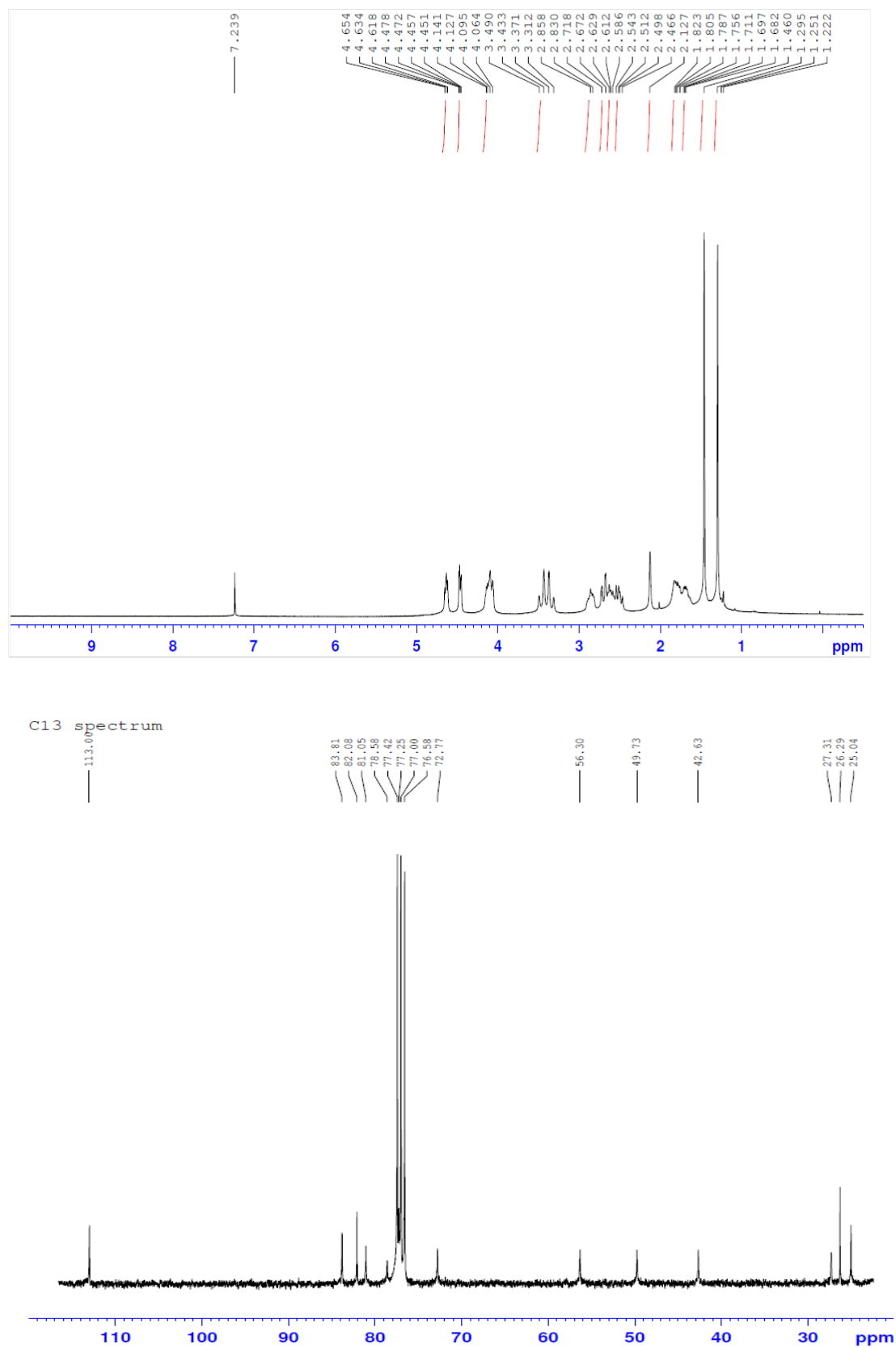


Figure S4. ^1H and ^{13}C NMR Spectra of **6**.

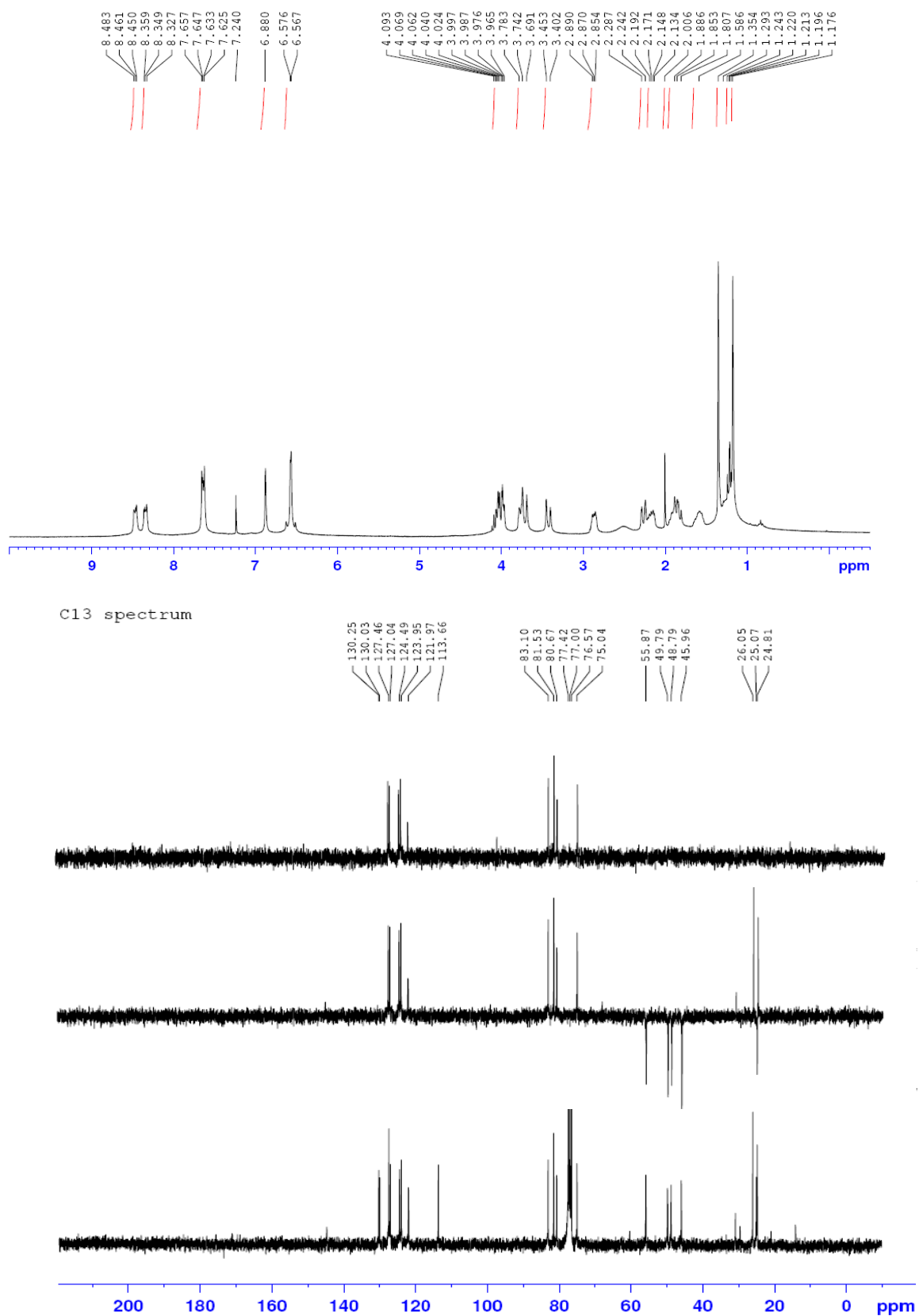


Figure S5. ^1H and ^{13}C NMR Spectra of **1**.

[Elemental Composition]
Data : FAB-H-451 Date : 25-Nov-72 18:23 Page: 1
Sample: up-peggy(NBA)
Note : *
Inlet : Direct Ion Mode : FAB+
RT : 8.09 min Scan#: (47,52)
Elements : C 80/0, 1H 80/0, D 0/0, O 6/1, N 8/0
Mass Tolerance : 10ppm, 5mmu if m/z < 500, 20mmu if m/z > 2000
Unsaturation (U.S.) : -0.5 - 22.0

Observed m/z	Int%	Err(ppm / mmu)	U.S. Composition
763.3941	100.0	+1.2 / +0.9	21.5 C 42 1H 51 O 6 N 8

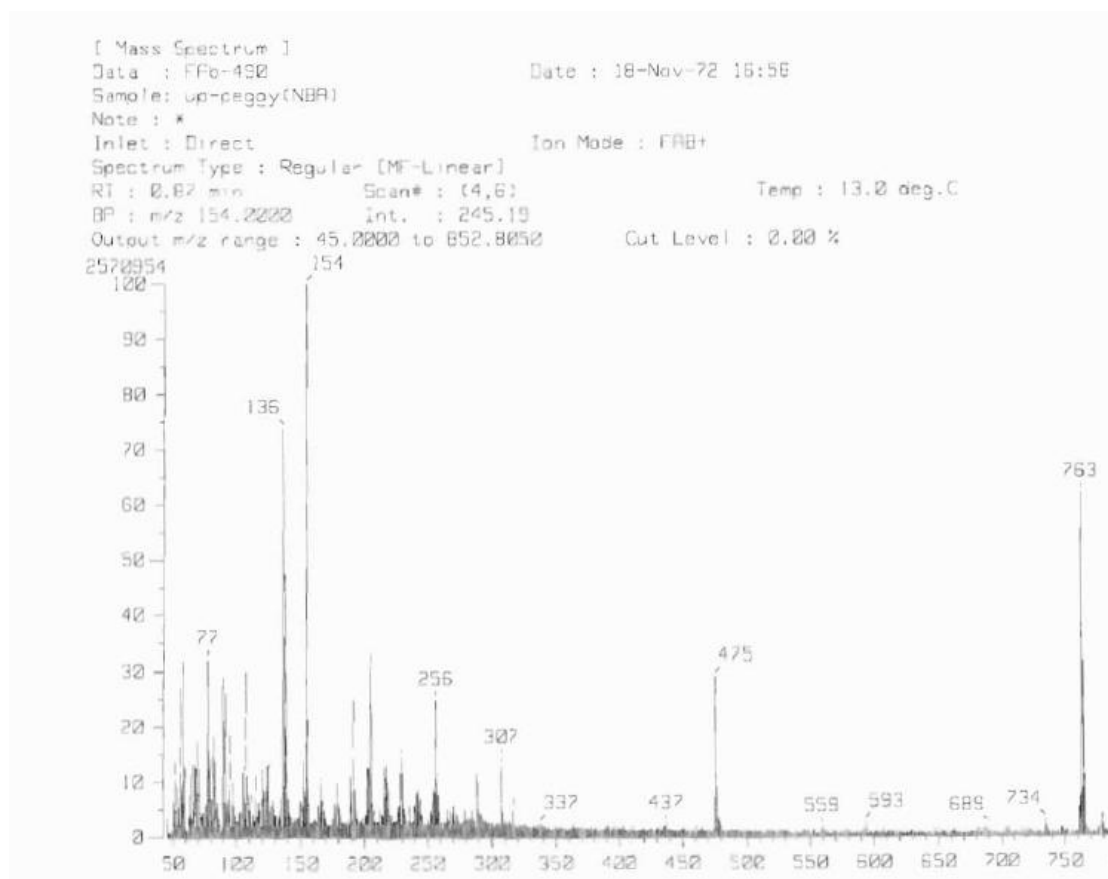


Figure S6. High-resolution mass data and low-resolution Mass Spectrum of **1**.

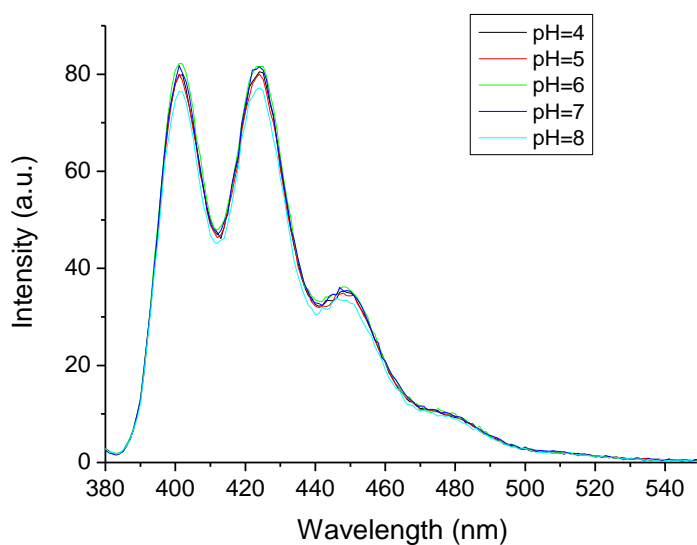


Figure S7. Variation of fluorescence spectra of **1** (8.9 μM) in MeOH as a function of pH at 423 nm; $\lambda_{\text{ex}}=374$ nm

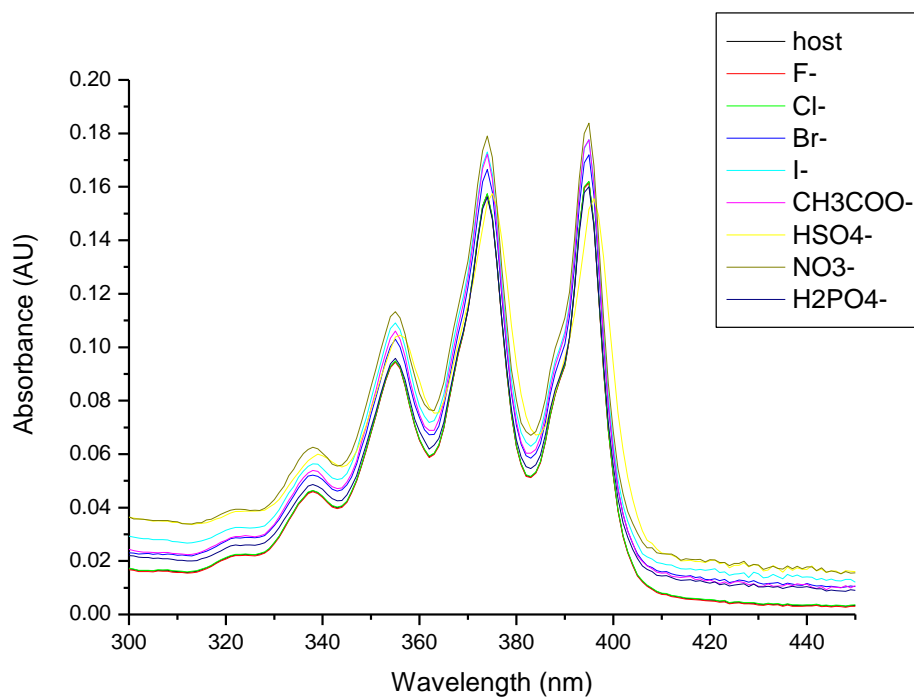


Figure S8. UV/vis spectra of **1** recorded in MeOH (2.4×10^{-5} M) after addition of 10 equiv of various anions.

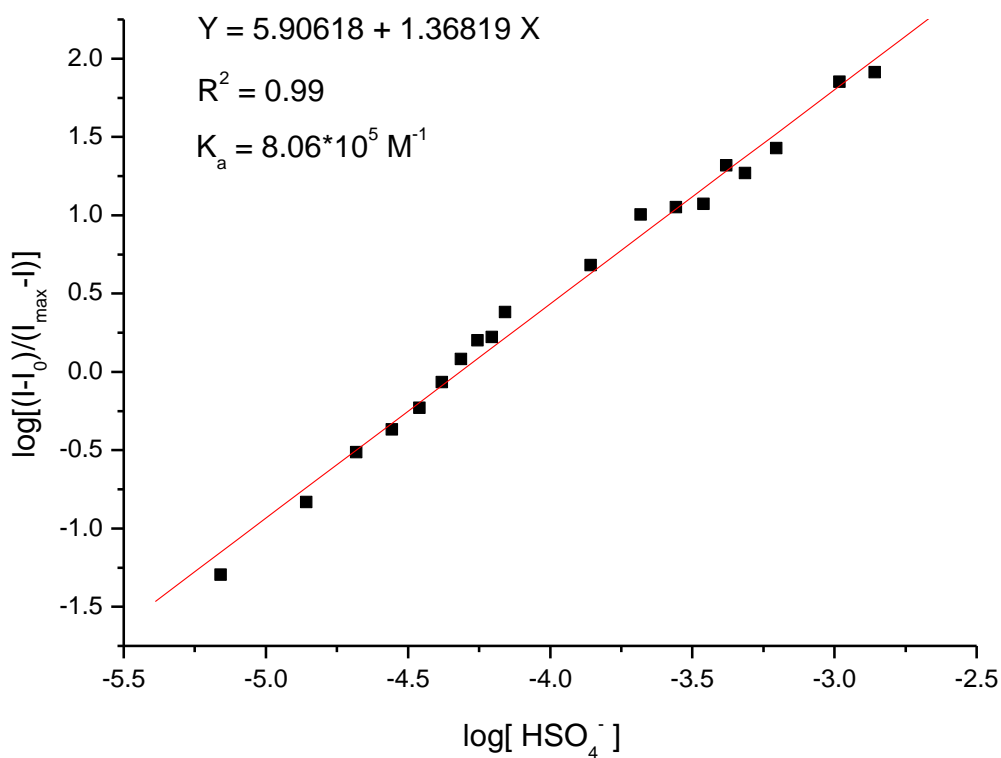


Figure S9. Hill plot

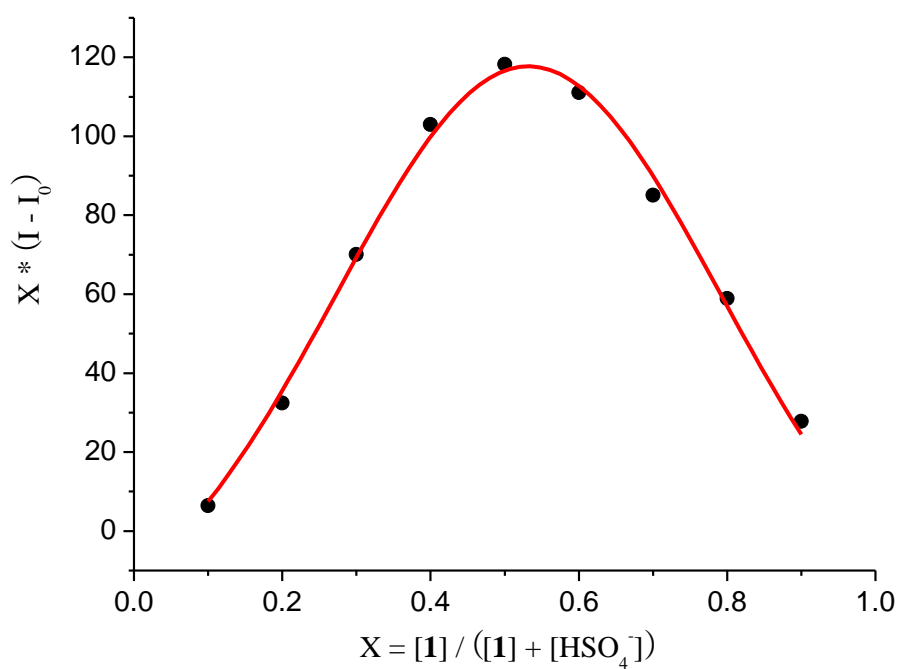


Figure S10. Job plot of a 1:1 complex of **1** ($2.40 \times 10^{-3} \text{ M}$) with HSO₄⁻.

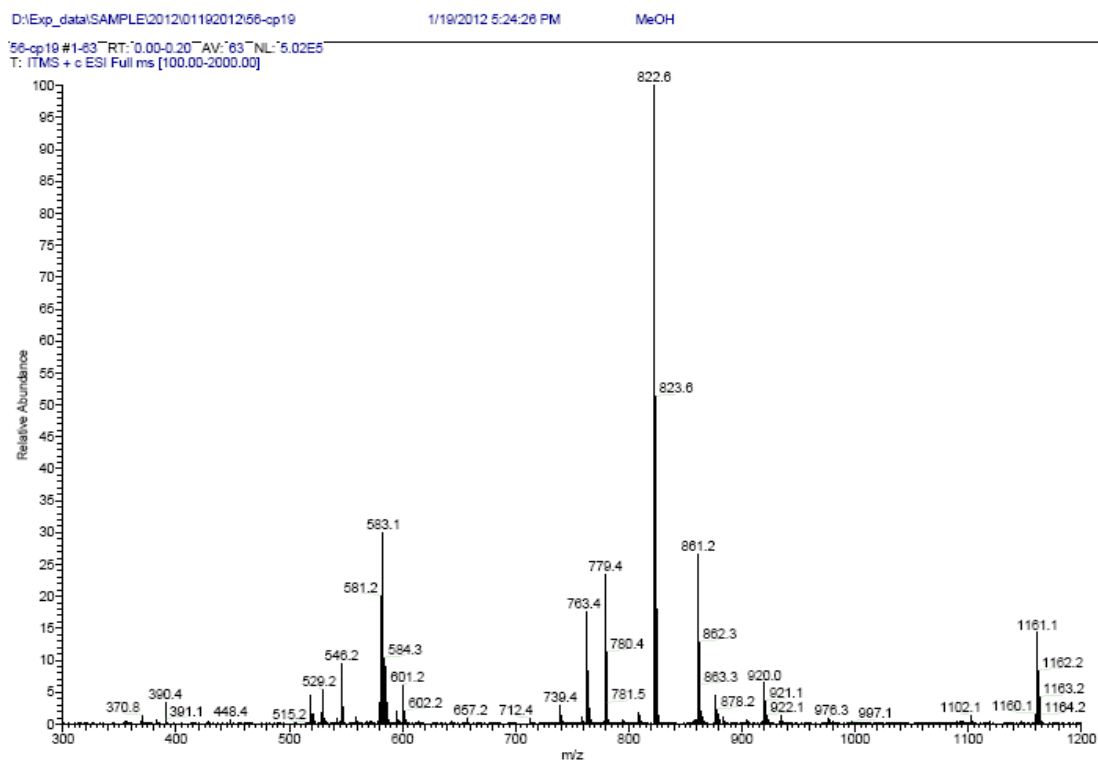


Figure S11 ESI Mass spectrum for **1-HSO₄⁻** complex

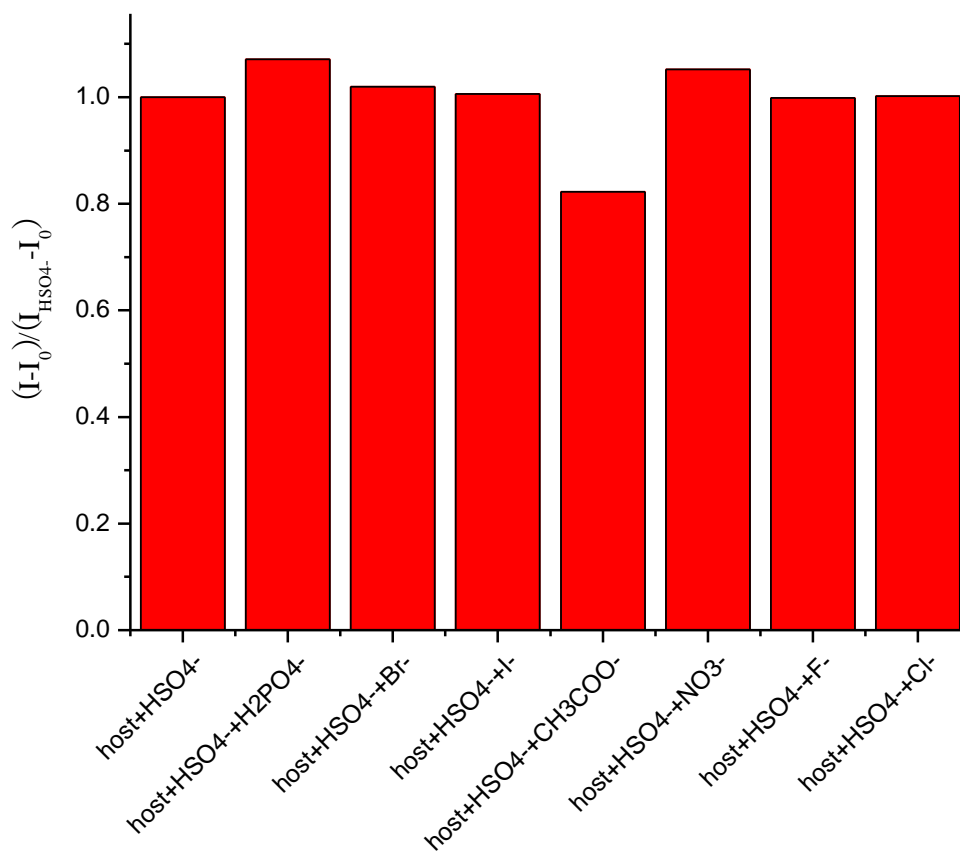


Figure S12. Competitive experiments in the **1** + HSO₄⁻ system with interfering anions. [1] = 69 μM, [HSO₄⁻] = 690 μM, and [Xⁿ⁻] = 690 μM in MeOH. λ_{ex} = 374 nm.

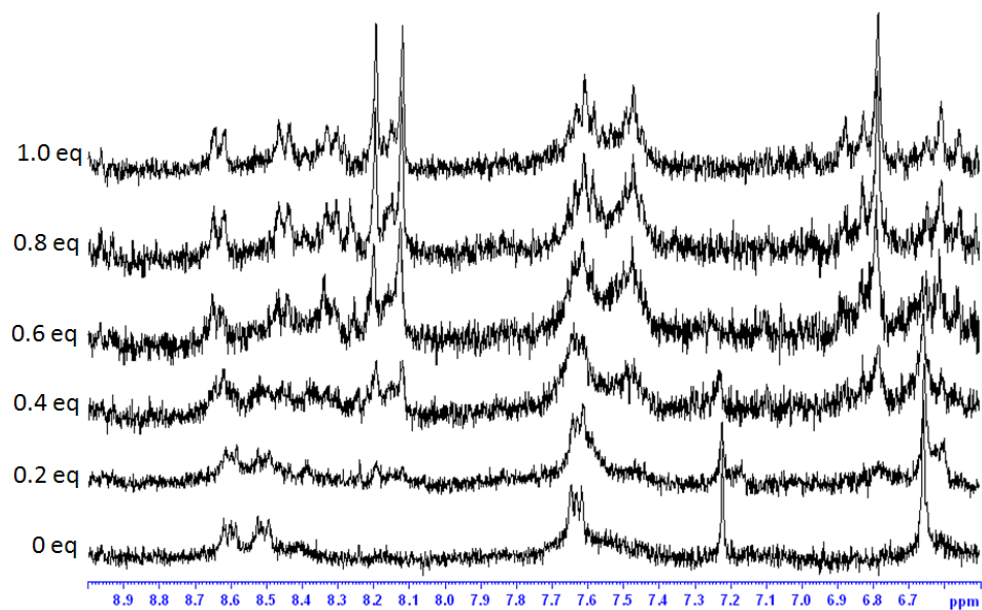


Figure S13. Partial plots of ^1H NMR spectra of **1** on addition of HSO_4^- ion in MeOD solution.

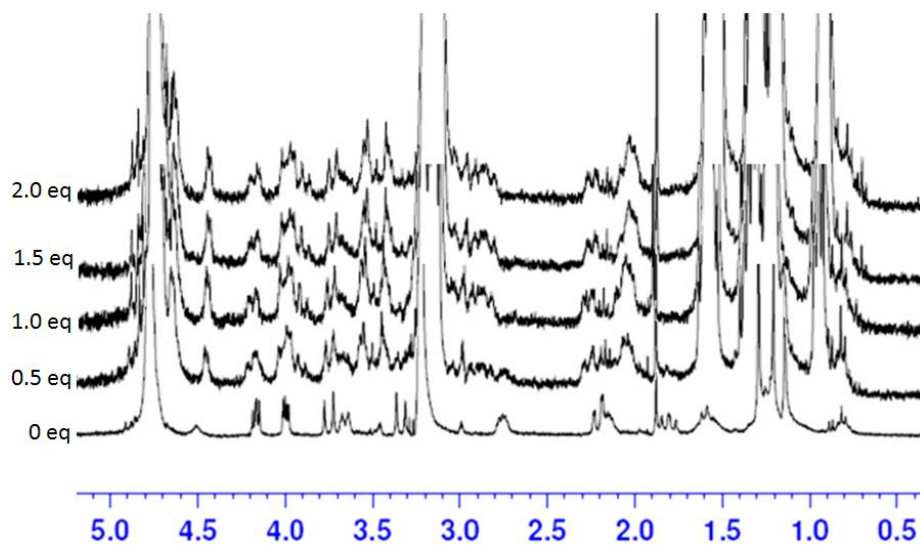


Figure S14. Partial plots of ^1H NMR spectra of **1** on addition of HSO_4^- ion in MeOD solution.