Supporting Information

Unusual Recognition of $(n\text{-}Bu_4N)_2SO_4$ by a Cyanuric Acid based Host via Contact Ion-Pair Interactions

*I. Ravikumar, and Pradyut Ghosh**

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, 2A & B Raja S. C. Mullick Road, Kolkata 700 032. India.

E-mail: *icpg@iacs.res.in*

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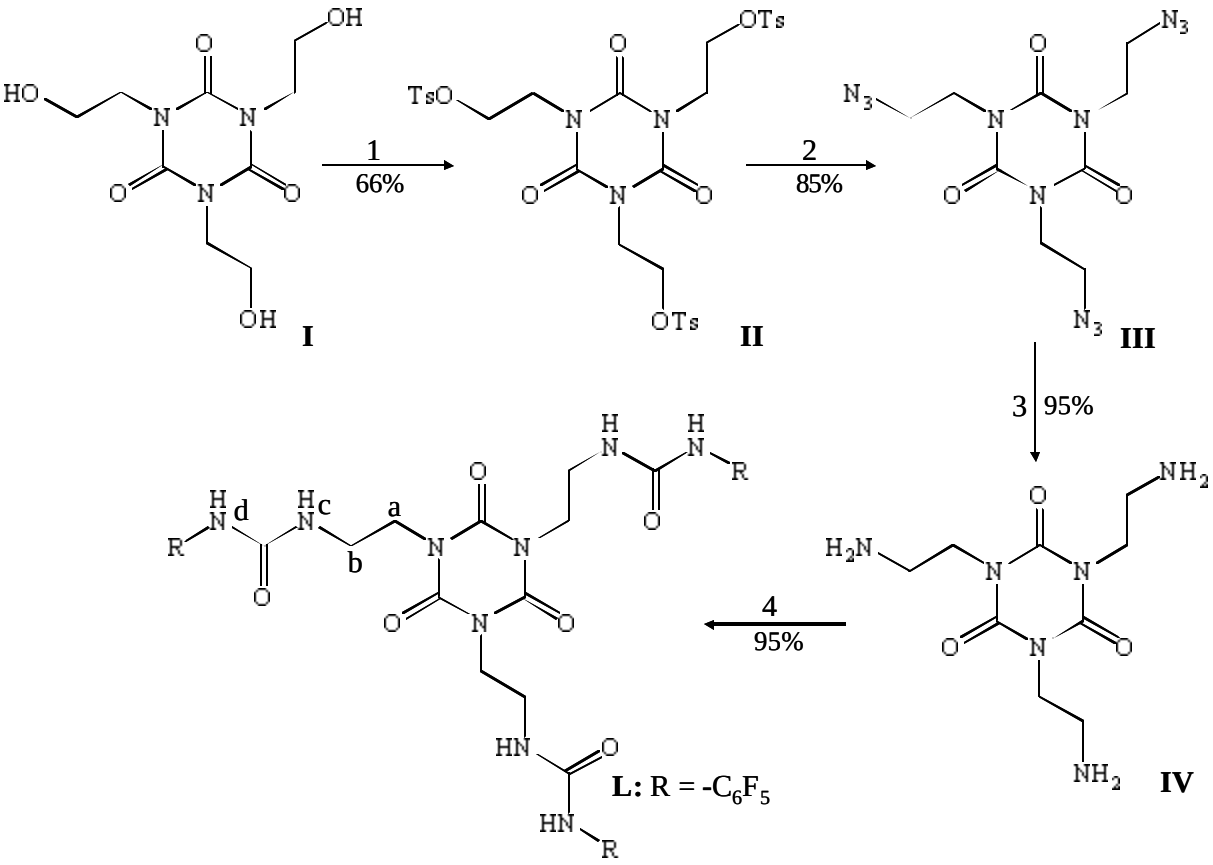
1. Materials and Methods :

1,3,5-Tris(2-hydroxyethyl)-1,3,5-triazine-2,4,6-trione (**I**), pentafluorophenyl isocyanate, tetrabutylammonium salts of fluoride, chloride, bromide, iodide, nitrate, acetate, sulfate, dihydrogenphosphate, and perchlorate were purchased from Sigma-Aldrich, USA and were used as purchased without further purification. Dichloromethane (DCM), Tetrahydrofuran (THF), diethylether, ethylacetate, dimethylformamaide (DMF) and dimethylsulfoxide (DMSO) were purchased from Spectrochem Ltd., India. ^{1}H-NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker DPX 300 FT-NMR spectrometer. Chemical shifts for ^{1}H- and ^{13}C-NMR were reported in parts per million (ppm), calibrated to the residual solvent peak set, with coupling constants reported in Hertz (Hz). 19F-NMR (500 MHz) were recorded on a Bruker AVII 500 MHz spectrometer with trifluorotoluene as an external standard.

2. Scheme for syntheis of L



3. Synthesis of 1,3,5-Tris(2-tosylethyl)-1,3,5-triazine-2,4,6-trione (II):

2.0 g (7.6 mmol) of trialcohol was taken in a 250 ml two neck round bottom flask. It was suspended in 100 ml of dry THF and was cooled to 0°C by an ice bath. 3.0 ml of freshly distilled triethylamine was added to the reaction mixture. The reaction mixture was allowed to stir at 0°C for 30 min. 5.1 g (26.7 mmol) of tosyl chloride dissolved in 50 ml of dry THF was taken in a pressure equalizing funnel and added slowly for a period of 1-2 hrs to the reaction mixture at 0°C. The reaction mixture was allowed to stir at 0-5°C for 3 hrs and at RT for 2 days at nitrogen atmosphere. The precipitate so formed was filtered and washed with cold THF (5ml x 5 times). The filtrate was evaporated to dryness under reduced pressure. The crude semi solid product obtained was dissolved in 100 ml of DCM. The organic layer was washed with 2 x 50 ml of water, 1 x 100 ml of 5% $NaHCO_3$ and again twice with 2 x 50 ml of water. The organic layer was collected and dried over sodium sulfate. The solvent was removed under vacuum to yield a semi solid mass. The product was kept in the freezer for overnight to obtain a colorless solid. The crude colorless solid was stirred with 100 ml of diethyl ether for 4 hrs and filtered off. The precipitate was washed several times with cold diethyl ether. The pure product was isolated as colorless solid in 66 % yield by column chromatography (silica gel: $CHCl_3$ eluent). The ditosylate product was isolated by

column chromatography (silica gel: ehtylacetate:$CHCl_3$ (1:4 v/v)) eluent. HRMS (ESI): 724.2229 [M+H^+] (100%).^{1}H NMR (300 MHz, CD_3CN): d 2.40 (s, 9H, Ar-CH_3), 3.94 (t, 6H, NCH_2, J = 5 Hz), 4.19 (t, 6H, NCH_2CH_2, J = 5 Hz), 7.38 (d, 6H, Ts-*H*, J = 8 Hz), 7.72 (d, 6H, Ts-*H*, J = 8 Hz). ^{13}C NMR (75.47 MHz, CD_3CN): d 20.67 (Ts-CH_3), 41.41 (NCH_2CH_2), 66.66 (NCH_2CH_2), 127.71 (Ts-CH),), 130.04 (Ts-CH),), 132.44 (Ts-*C*),), 145.65 (Ts-*C*), 148.29 (s, *C*=O).

4. Synthesis of 1,3,5-Tris(2-azidoethyl)-1,3,5-triazine-2,4,6-trione (III):

Tritosylate (1.0 g, 1.38 mmole) was dissolved in 20 ml of dry DMF. Sodium azide (0,36 g, 5.5 mmole) was added the solution. The reaction mixture was stirred at 75°C for two days in nitrogen atmosphere. After two days of continuous stirring, the reaction mixture was cooled to room temperature and poured in to ice cold water (600 ml). The aqueous solution was extracted with ethylacetate (150 ml) thrice. The combined organic layers were washed with water and dried over anhydrous sodium sulfate. The solvent was removed under vacuum to give colorless semisolid. The crude product was re-dissolved in diethylether and covered with a parafilm. The beaker was kept in the refrigerator at 4°C. A crystal of triazide (2) was obtained upon slow evaporation at 4°C after three days. In 85% yield HRMS (ESI): 358.8098 [M+Na^+] (100%).^{1}H NMR (300 MHz, $CDCl_3$): d 3.58 (t, 6H, NCH_2, J = 3.6 Hz), 4.16 (t, 6H, NCH_2CH_2, J = 3.6 Hz). ^{13}C NMR (75.47 MHz, $CDCl_3$): d 41.79 (NCH_2), 48.43 (NCH_2CH_2), 148.69 (s, *C*=O).

5. Synthesis of 1,3,5-Tris(2-aminoethyl)-1,3,5-triazine-2,4,6-trione (IV):

400 mg (0.12 mmole) of triazide was dissolved in 50 ml of dry ethanol in a 200 ml flask. 200 mg of 10% Pd on activated charcoal was added. Hydrogenation was performed at RT in 60 psi of hydrogen pressure for 12 hrs. After this time, the Pd on charcoal was filtered through a filter paper and washed several times with ethanol. The filtrate was evaporated under reduced pressure to give a colorless oily mass. Acetonitrile (10 ml) was added to the semi solid and sonicated for few minutes. A colorless solid precipitates out. The precipitate was washed with CH_3CN and then with diethylether and finally dried in a dessicator to yield a colorless solid in 95% yield. HRMS (ESI): 259.0164 [M+H^+] .^{1}H NMR (300 MHz, CD_3CN): d 2.71 (t, 6H, NCH_2, J = 6 Hz), 3.43 (t, 6H, NCH_2CH_2, J = 6 Hz), 5.42 (t, 6H, NH_2).

6. Synthesis of Compound L:

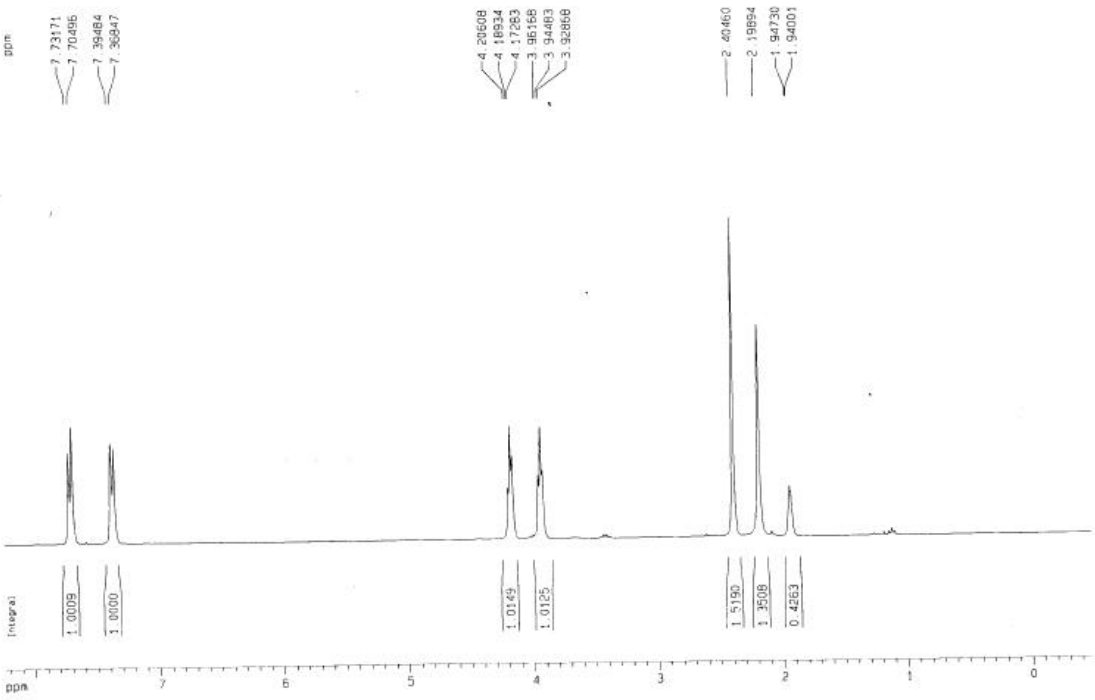
Triamine, (516 mg, 0.2 mmol) was taken in a 100 mL round bottomed flask, and dissolved in 50 mL of dry tetrahydrofuran (THF). The reaction mixture was allowed to stir at room temperature in nitrogen

atmosphere for 15 min for complete dissolution. 0.125 g (0.6 mmol) of 2,3,4,5,6-pentafluorophenyl isocyanate was dissolved in another 50 mL of dry THF and taken in a 100 mL pressure equalizing funnel. This solution was added dropwise for a period of 1 hour at constant stirring in room temperature. After the addition, the reaction mixture was allowed to stir at room temperature in nitrogen atmosphere for another 14 h. The white precipitate formed was filtered out, and washed three times with cold THF. The colorless solid was washed again with diethylether and to yield the required product as colorless solid (yield: 95%). ESI (–ve mode): 884.0 [M-H^+] (100%).^{1}H NMR (300 MHz, DMSO-d_6): d 3.24 (t, 6H, NCH_2, J = 6 Hz), 3.81 (t, 6H, NCH_2CH_2, J = 6 Hz), 6.55 (t, 3H, N*H*), 8.29 (s, 3H, N*H*). ^{13}C NMR (75.47 MHz, DMSO-d_6): d 38.40 (N*C*H_2), 53.68 (NCH_2*C*H_2), 112.68 (m of s, Ar, *C*C-F, J_{CCF} = 15Hz), 137.87 (m of d, Ar, *C*-F, J_{CF} = 252 Hz), 142.20 (m of d, Ar, *C*-F J_{CF} = 252 Hz), 144.16 (m of d, Ar, *C*-F, J_{CF} = 249 Hz), 157.88 (s, *C*=O). ^{19}F NMR (500 MHz, CD_3CN): d -164.94 (t, 2Ar-*F*, J_{F-F} = 23 Hz), -161.06 (t, Ar-*F*, J_{F-F} = 23 Hz), -147.25 (d, 2 Ar-*F*, J_{F-F} = 23 Hz). Elemental analysis: Calculated:- C-40.69, H-2.05, N-14.24 %, Experimental:- C-40.77, H-2.05, N-14.30 %.

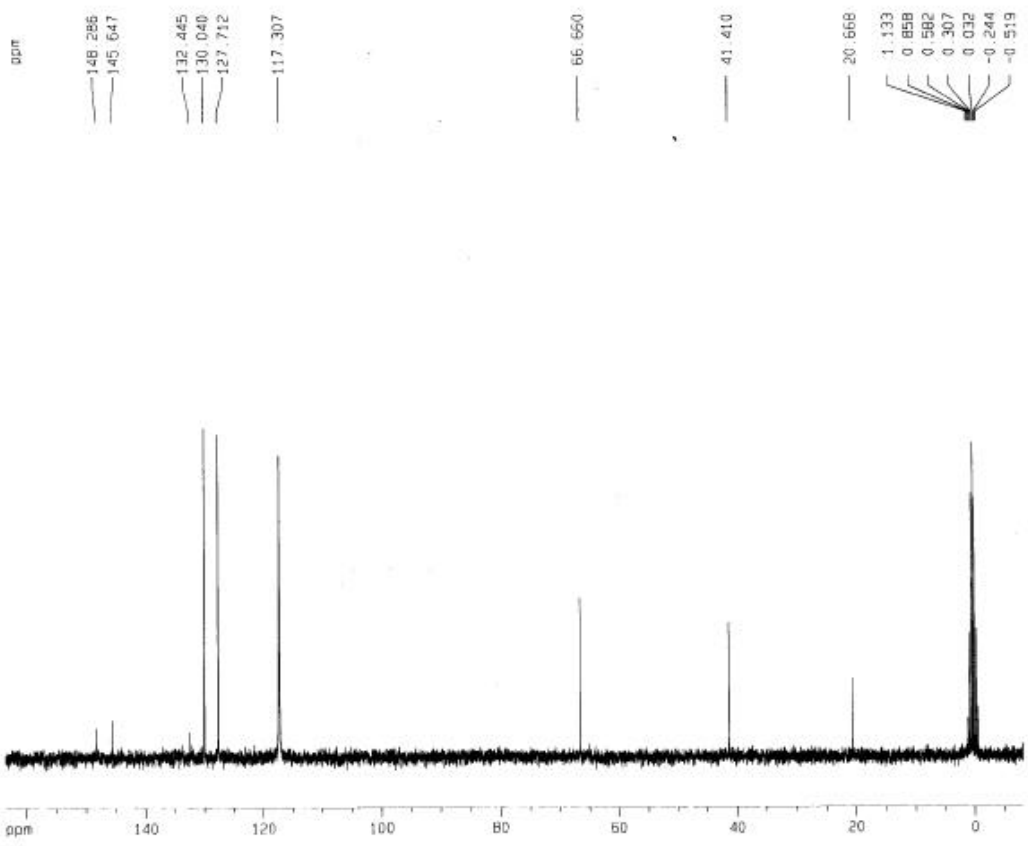
7. Synthesis of Complex 1:

83 mg (0.01 mmol) of **L** was dissolved in 10 ml of DMF and then 10.0 mg (0.03 mmol) of *n*-$Bu_4N^+HSO_4^-$ was added to the above solution. Then the mixture was stirred at room temperature for 10 minutes. Then, the mixture was filtered and allowed to evaporate for crystallization. After a week, colorless crystals of complex [**L**(SO_4^{2-})]·2 *n*-Bu_4N^+·DMF (**1**) suitable for X-ray diffraction studies were obtained in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (m, 3H, $NCH_2CH_2CH_2CH_3$), 1.35 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.55 (m, 2H, $NCH_2CH_2CH_2CH_3$), 2.89 (d, 3H, NCH_3), 2.97 (d, 3H, NCH_3), 3.21 (m, 2H, $NCH_2CH_2CH_2CH_3$), 3.51 (m, 6H, NCH_2CH_2), 4.11 (m, 6H, NCH_2CH_2), 8.018 (br, 1H, N*H*) 8.66 (br, 3H, N*H*), 10.02 (br, 3H, N*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$): d 13.48 ($NCH_2CH_2CH_2CH_3$), 19.65 ($NCH_2CH_2CH_2CH_3$), 23.95 ($NCH_2CH_2CH_2CH_3$), 31.46 (NCH_3), 36.52 (NCH_3), 37.22 (NCH_2CH_2), 42.05 (NCH_2CH_2), 58.65 ($NCH_2CH_2CH_2CH_3$), 112.68 (m of s, Ar, *C*C-F, J_{CCF} = 15Hz), 137.87 (m of d, Ar, *C*-F, J_{CF} = 252 Hz), 142.20 (m of d, Ar, *C*-F J_{CF} = 252 Hz), 144.16 (m of d, Ar, *C*-F, J_{CF} = 249 Hz), 157.88 (s, *C*=O). ^{19}F NMR (500 MHz, $CDCl_3$): d -165.26 (br, 2Ar-*F*), -158.48 (br, Ar-*F*), -145.38 (br, 2 Ar-*F*). Elemental analysis: calculated: C – 50.71%, H – 6.35%, N – 10.92% and experimental: C – 50.66%, H – 6.33%, N – 10.89%.

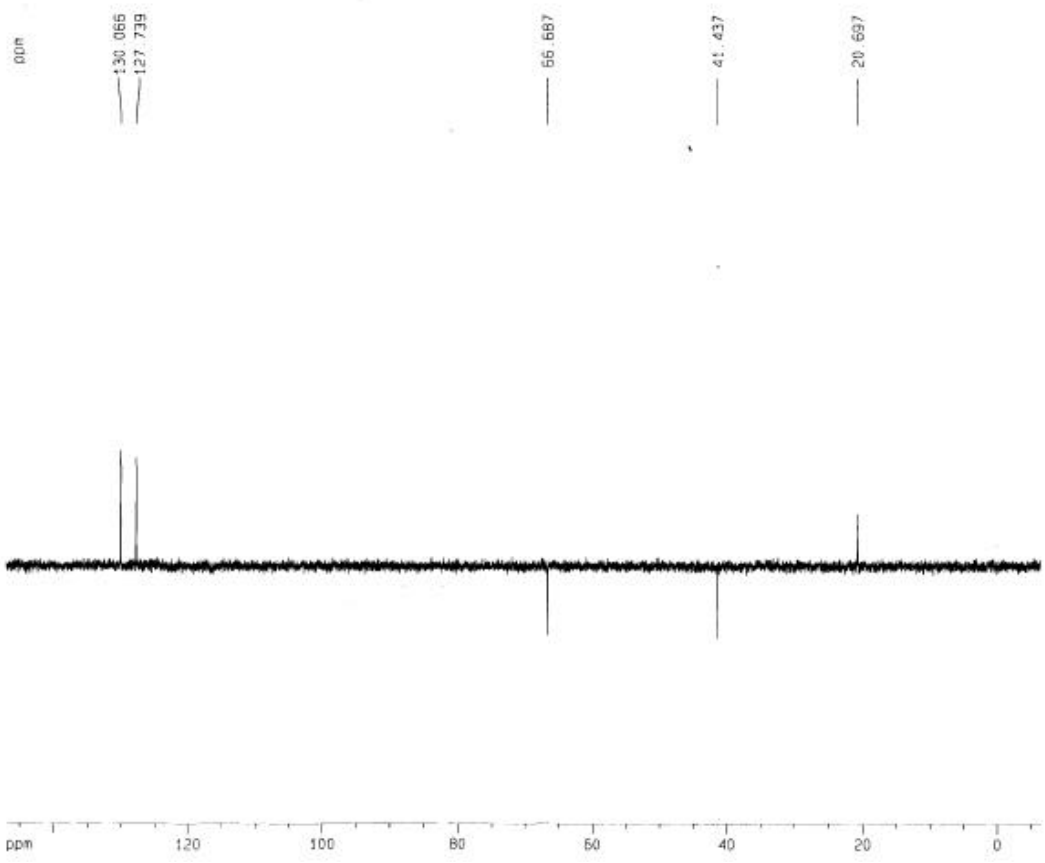
8. **Figure 1S**. ^{1}H-NMR Spectra of **II** in CD_3CN at 25ºC.



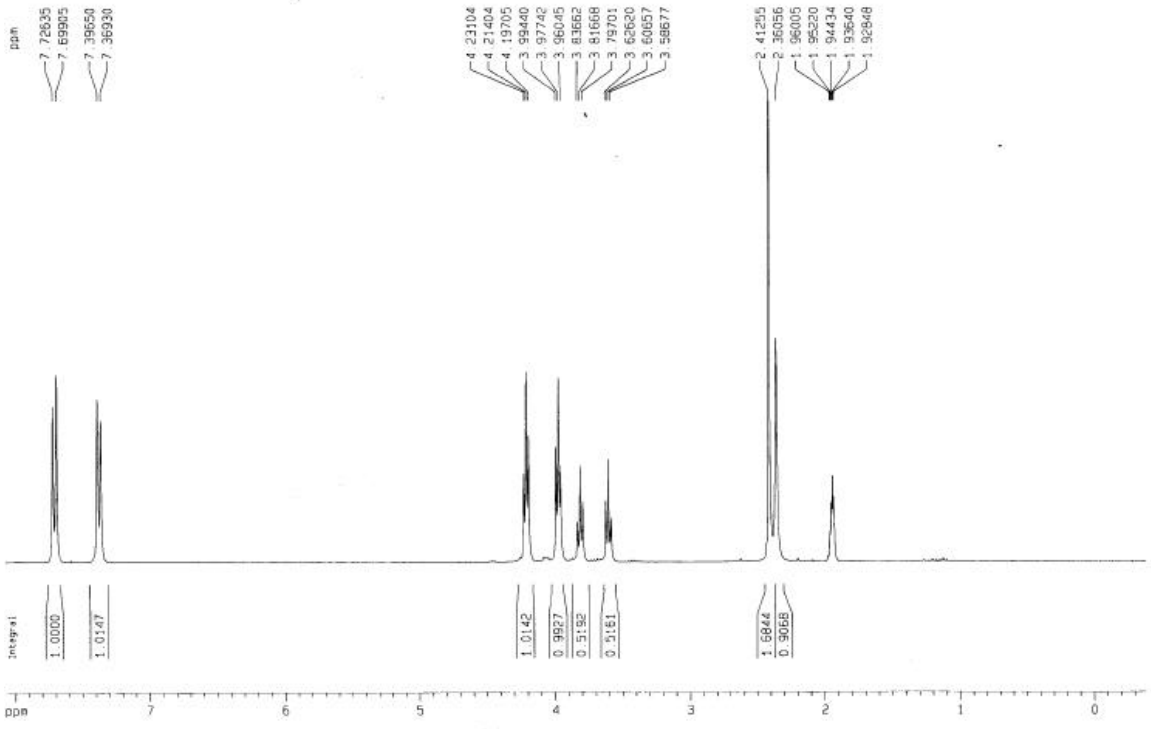
9. **Figure 2S**. ^{13}C-NMR Spectra of **II** in CD_3CN at 25ºC.



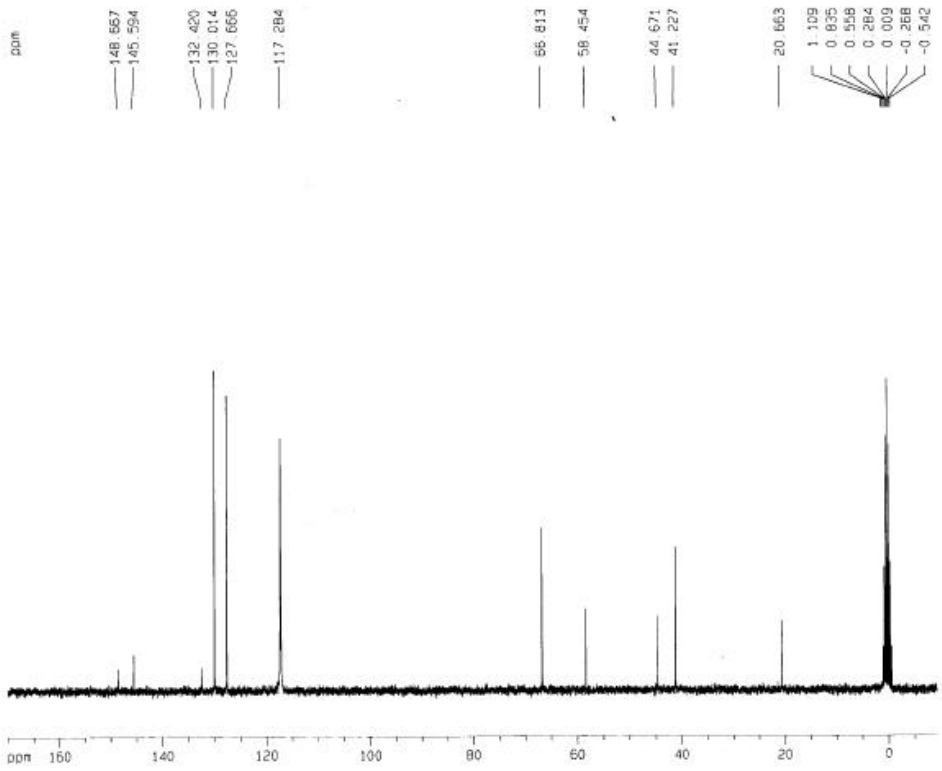
10. **Figure 3S**. DEPT-NMR Spectra of **II** in CD_3CN at 25ºC.



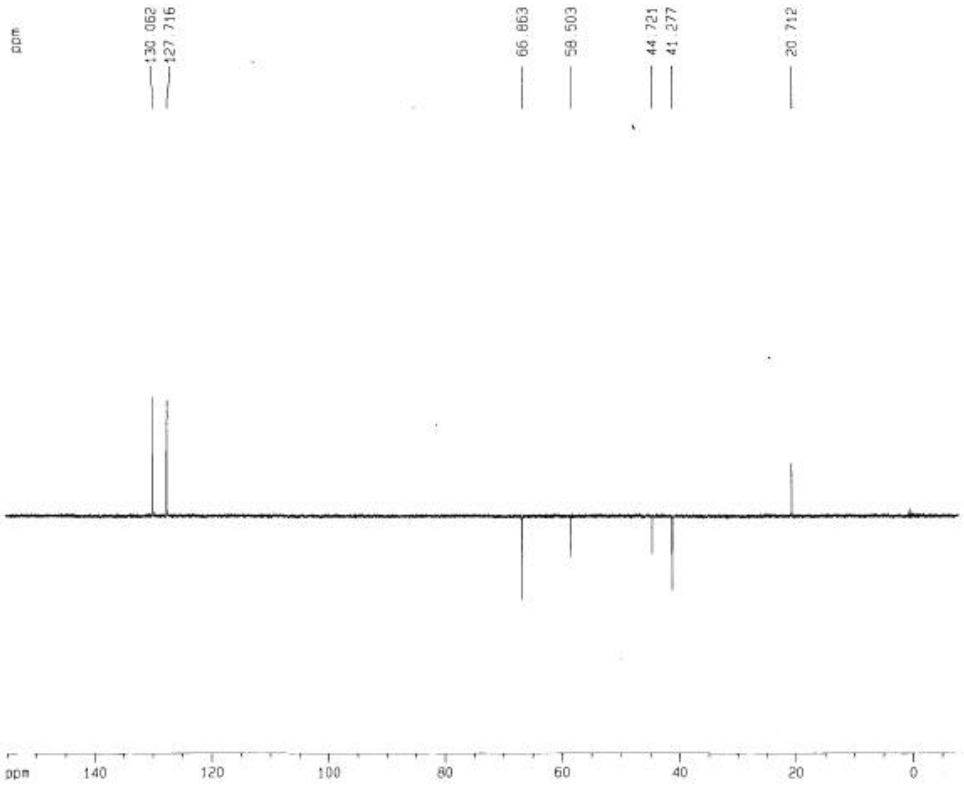
11. **Figure 4S**. ^{1}H-NMR Spectra of **IIa** in CD_3CN at 25ºC.



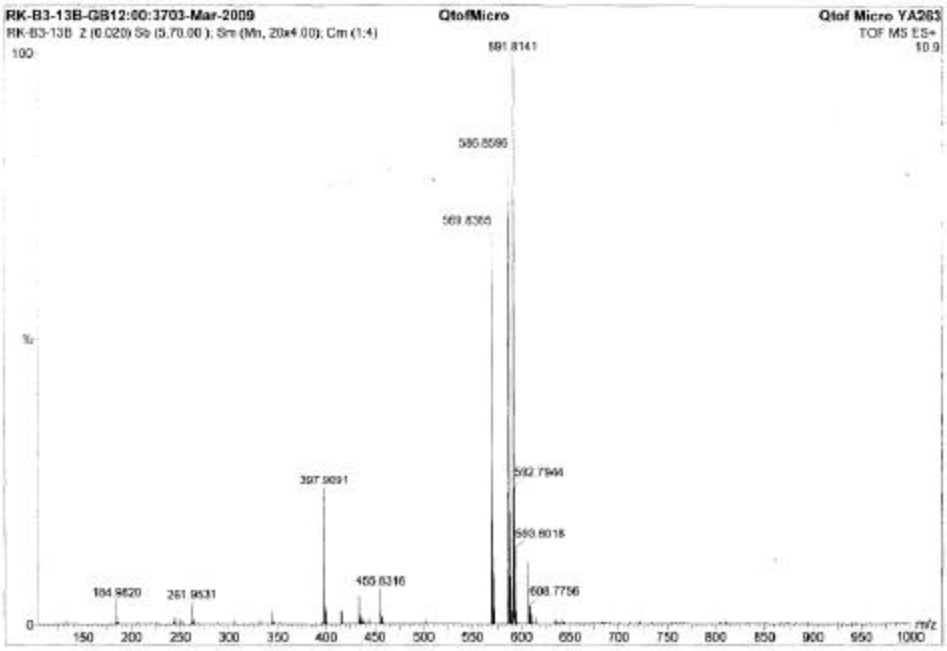
12. **Figure 5S**. ^{13}C-NMR Spectra of **IIa** in CD_3CN at 25ºC.



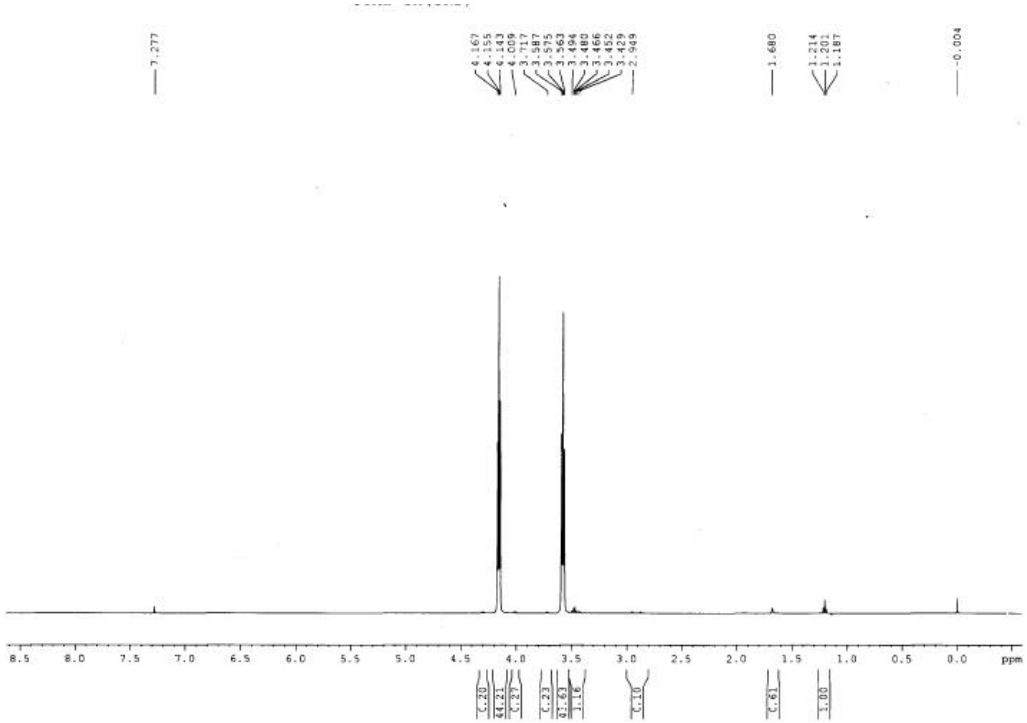
13. **Figure 6S**. DEPT-NMR Spectra of **IIa** in CD_3CN at 25ºC.



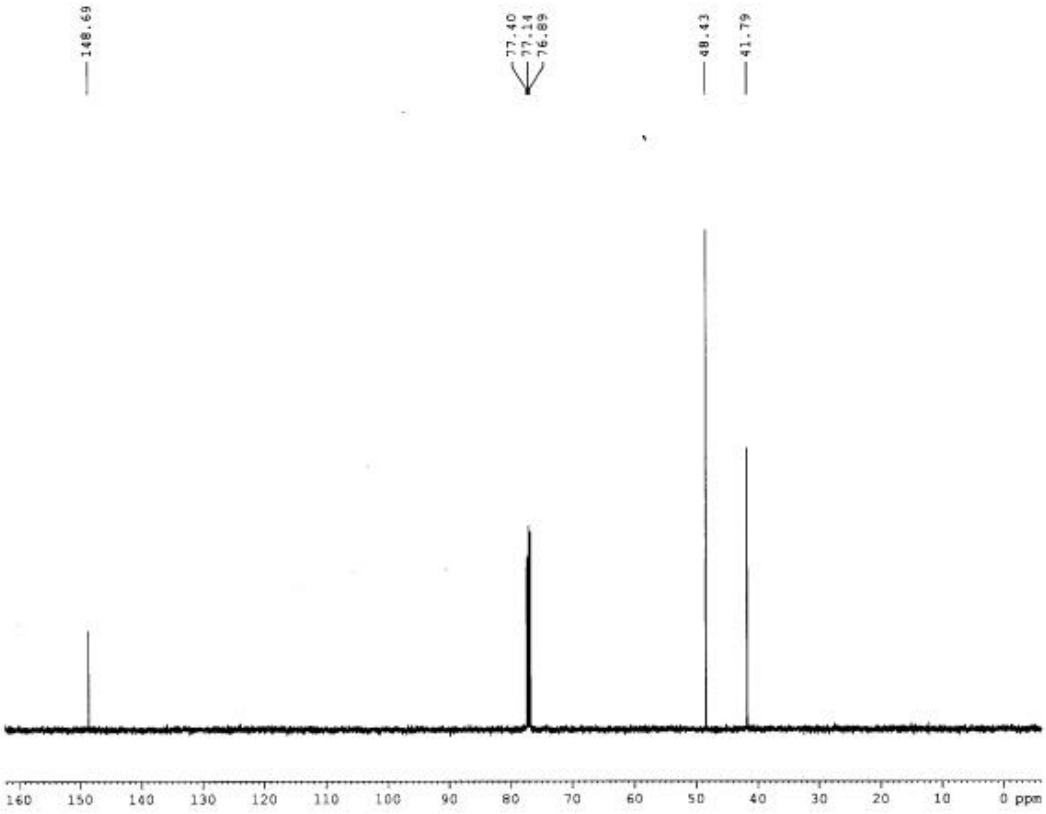
14. **Figure 7S**. HRMS Spectra of **IIa**.



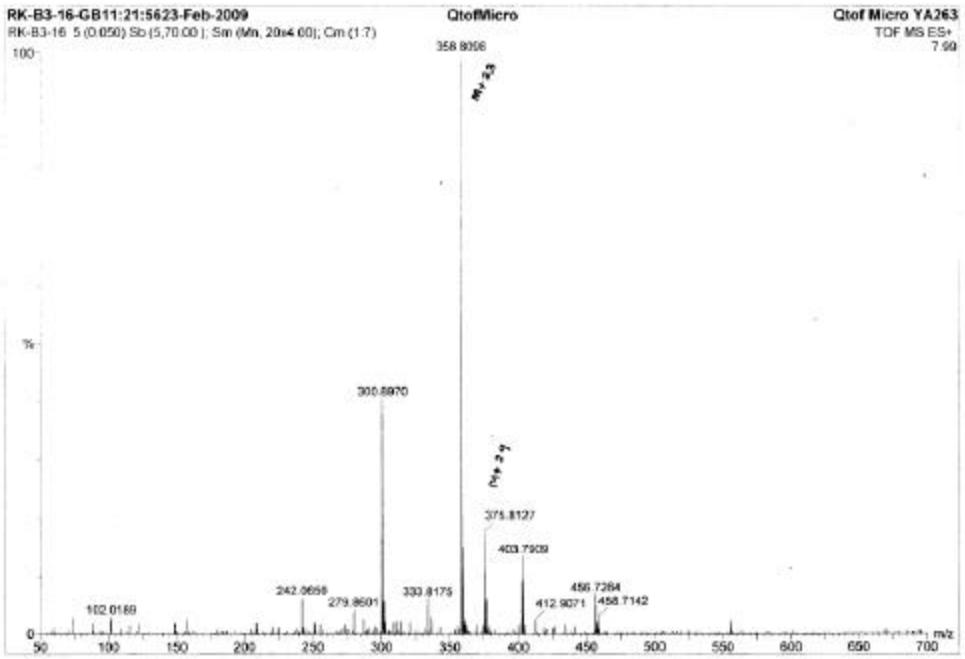
15. **Figure 8S**. ^{1}H-NMR Spectra of **III** in $CDCl_3$ at 25ºC.



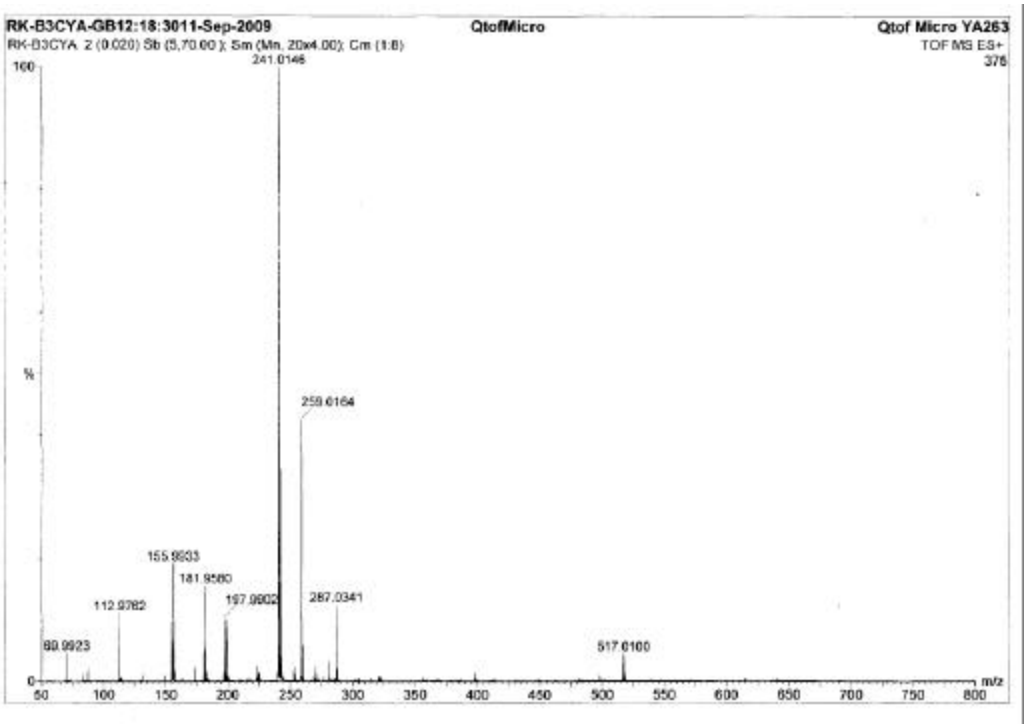
16. **Figure 9S**. ^{13}C-NMR Spectra of **III** in $CDCl_3$ at 25ºC.



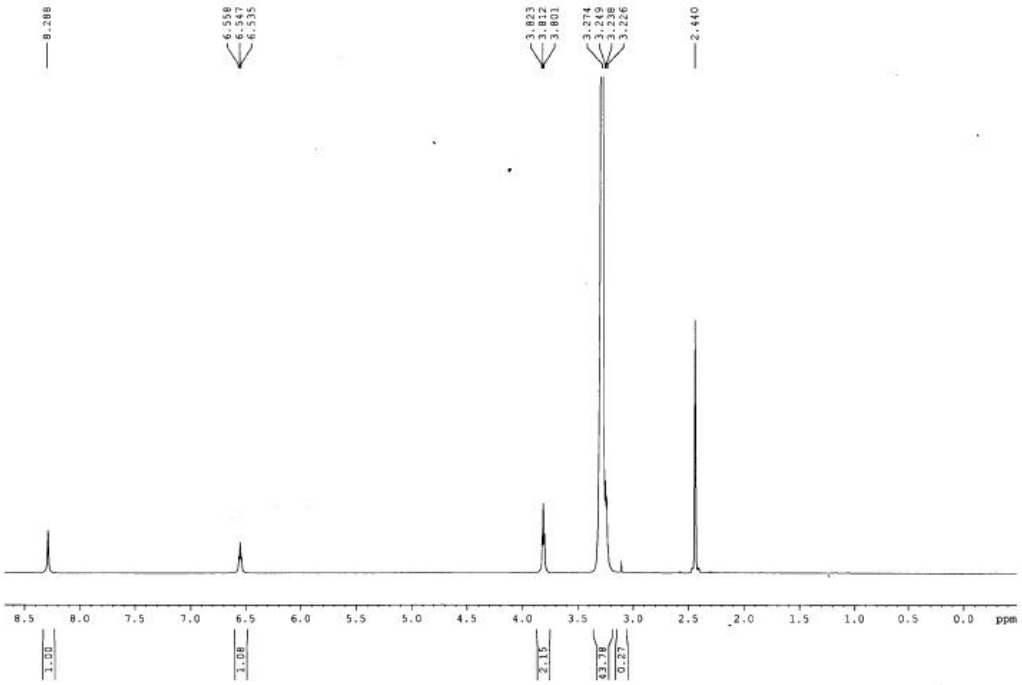
17. **Figure 10S**. HRMS Spectra of 1,3,5-Tris(2-azidoethyl)-1,3,5-triazine-2,4,6-trione **III**.



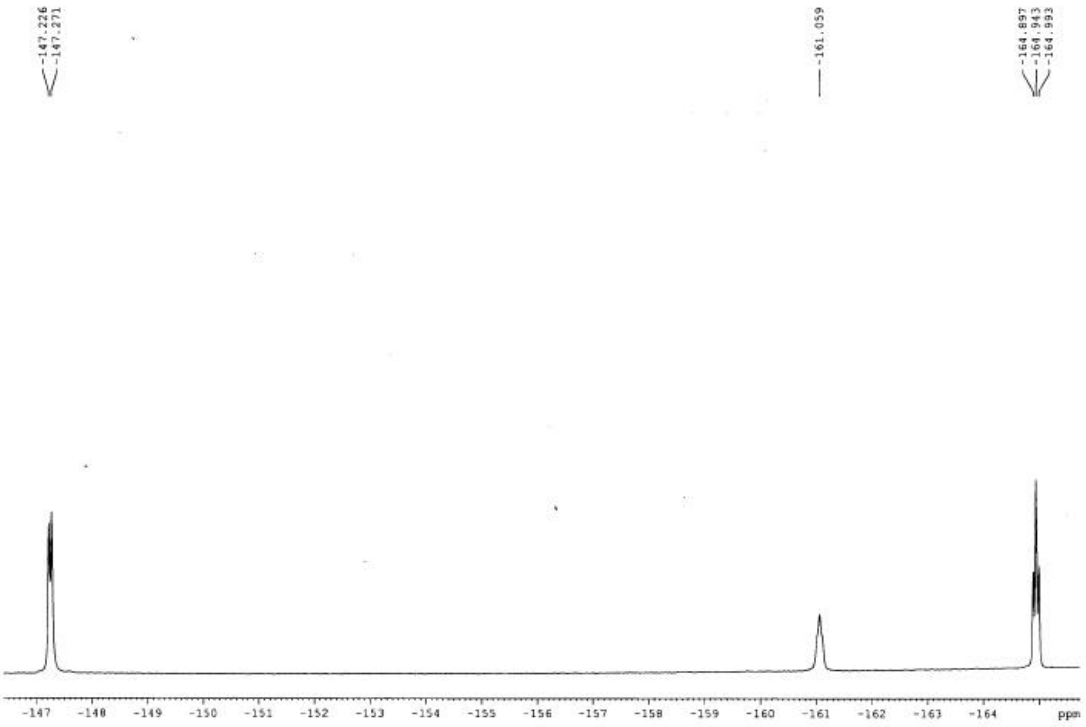
18. **Figure 11S**. HRMS Spectra of 1,3,5-Tris(2-aminoethyl)-1,3,5-triazine-2,4,6-trione **IV**.



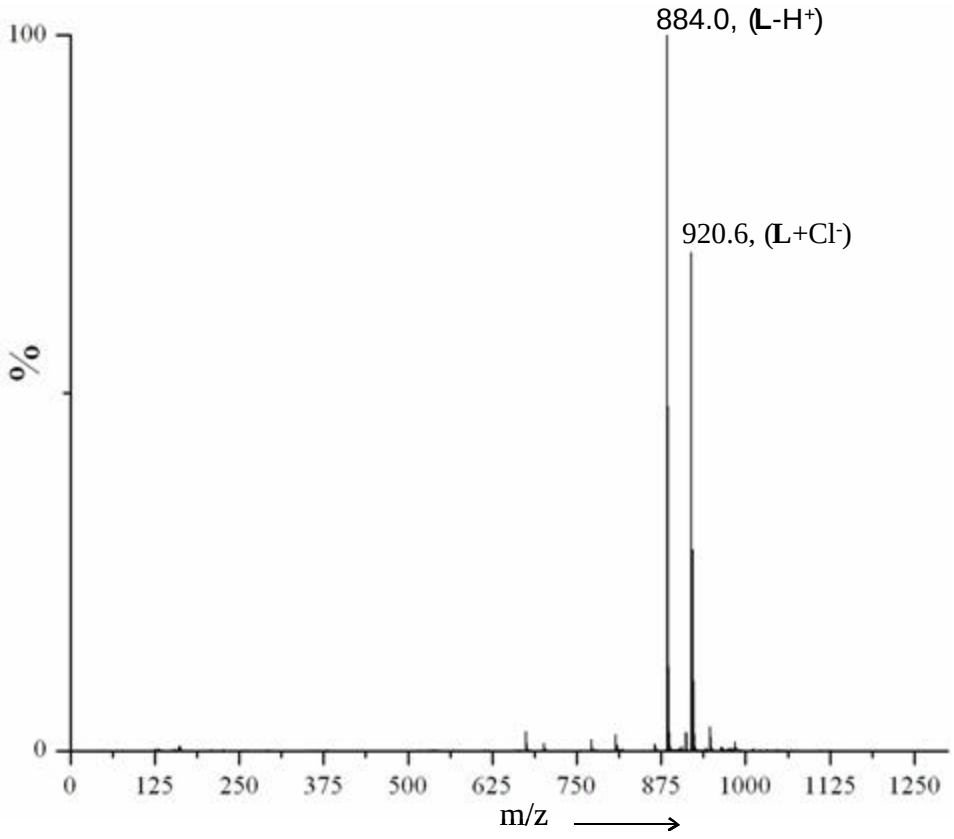
19. **Figure 12S**. ^{1}H-NMR Spectra of receptor, **L** in DMSO-d_6 at 25ºC.



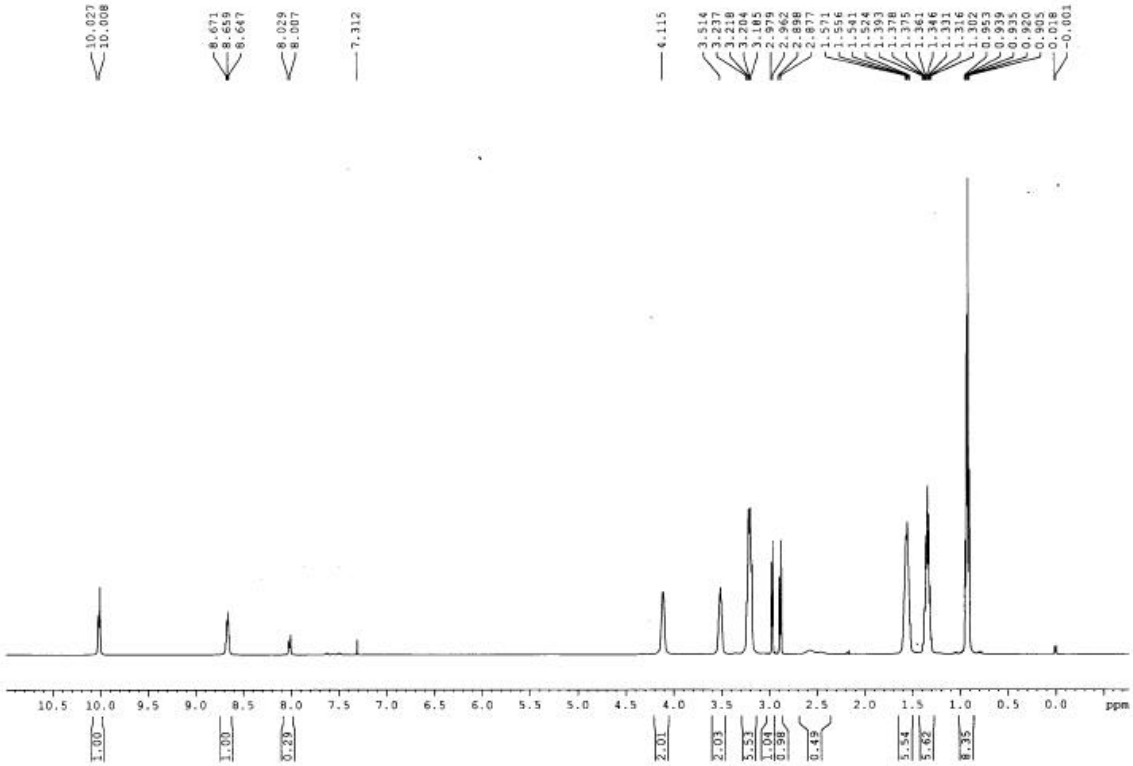
20. **Figure 13S**. ^{19}F-NMR Spectra of receptor, **L** in DMSO-d_6 at 25ºC.



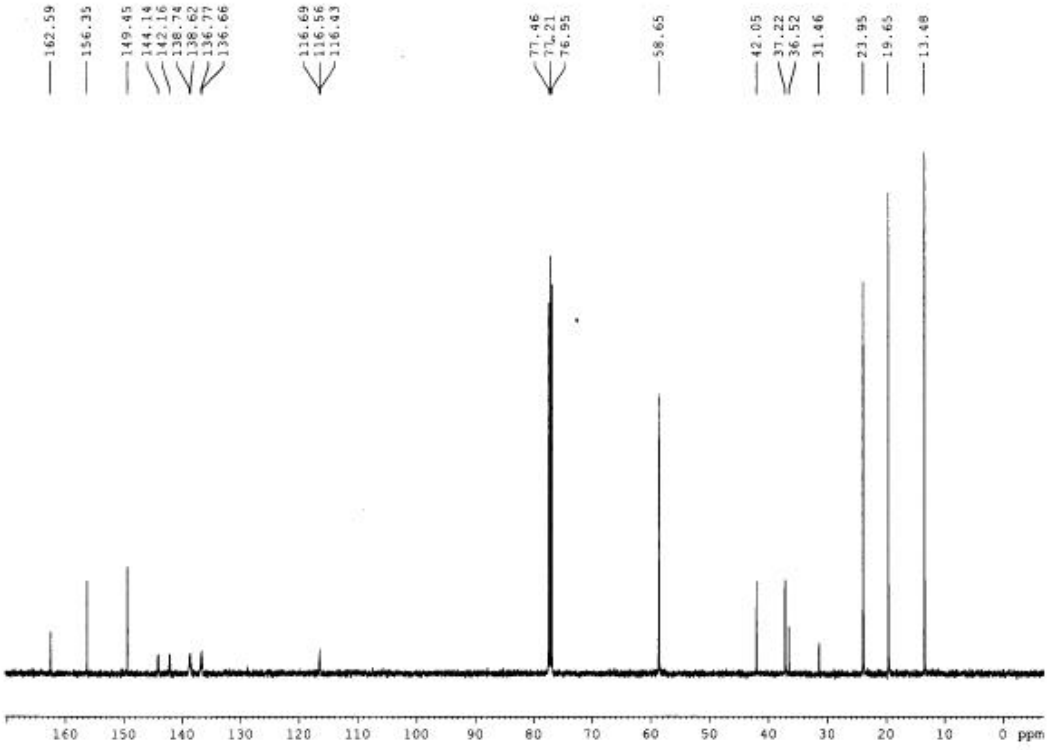
21. **Figure 14S**. ESI mass (negative mode) spectra of receptor, **L**.



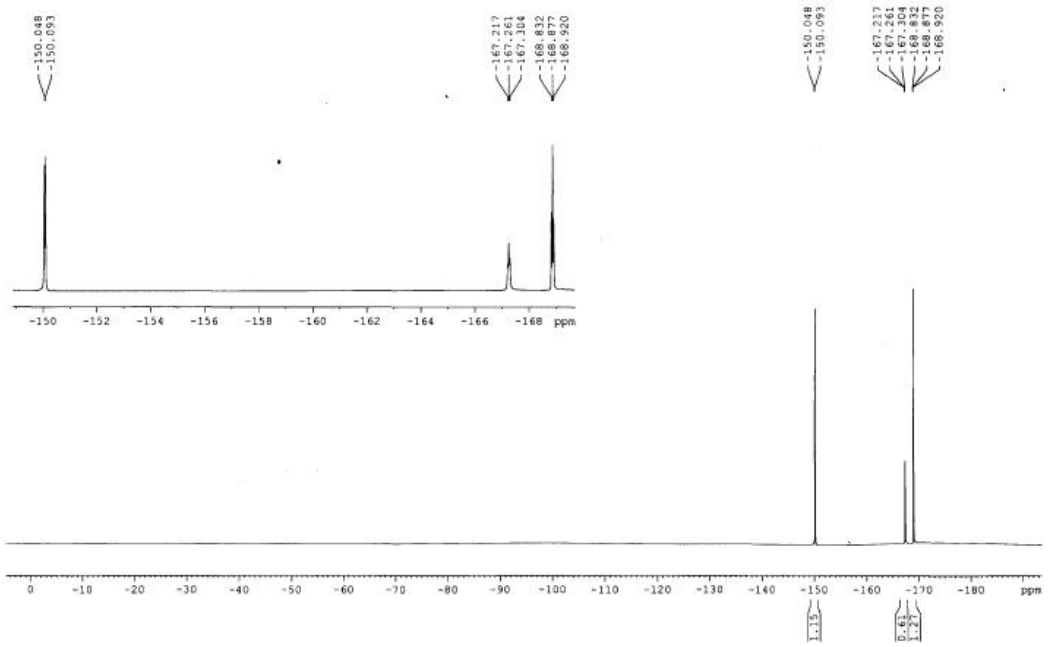
22. **Figure 15S**. ^{1}H-NMR Spectra of complex, **1** in DMSO-d_6 at 25ºC.



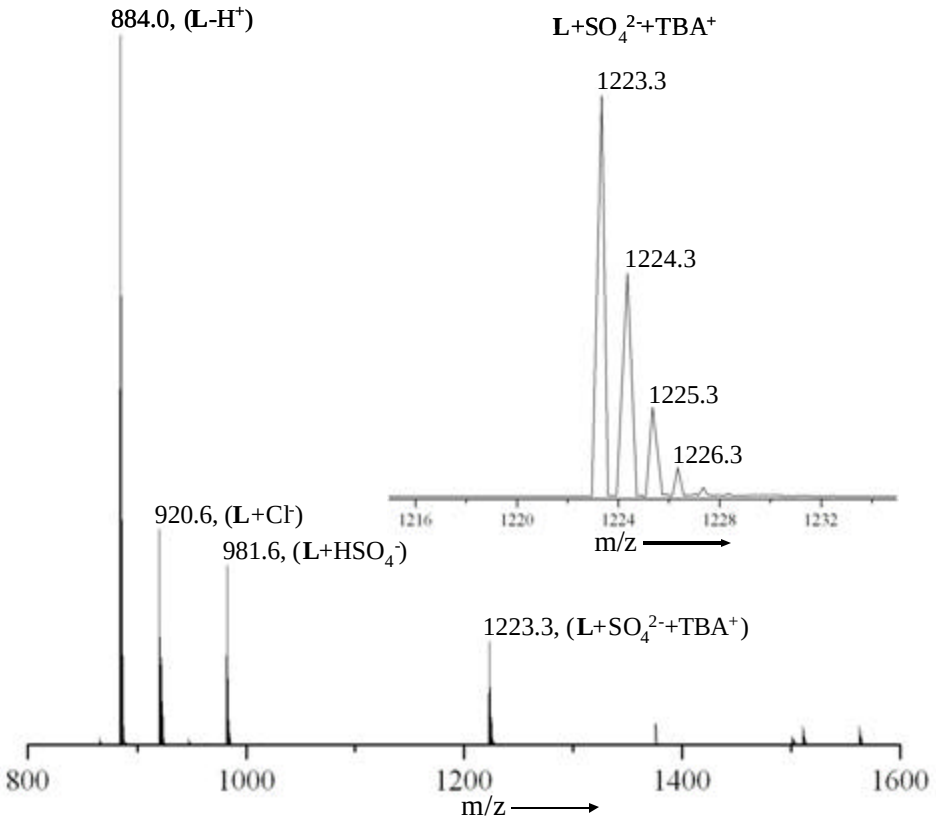
23. **Figure 16S**. ^{13}C-NMR Spectra of complex, **1** in DMSO-d_6 at 25ºC.



24. **Figure 17S**. ^{19}F-NMR Spectra of complex, **1** in DMSO-d_6 at 25ºC.



25. **Figure 18S**. ESI mass (negative mode) spectra of complex, **1**.



26. Single-crystal X-ray studies:

The crystallographic data and details of data collection and refinement for complex **1** is listed below. In the present case, a single crystal of suitable size was selected from the mother liquor and immersed in paratone oil and then mounted on the tip of a glass fibre and cemented using epoxy resin. Intensity data for this crystal was collected using MoK a (? = 0.7107 Å) radiation on a Bruker SMART APEX II diffractometer equipped with CCD area detector at 100 K. Reflections were measured from a hemisphere of data collected with each frame covering 0.5º in ?. The data integration, reduction and structure solutions/refinements were carried out using the software package of Bruker SMART APEX. Graphics were generated using PLATON 97[1] and MERCURY 2.2.[2] In complex **1**, the non-hydrogen atoms were refined anisotropically until convergence. All the hydrogen atoms in this complex were geometrically fixed at idealized positions and refined isotropically.

Reference:

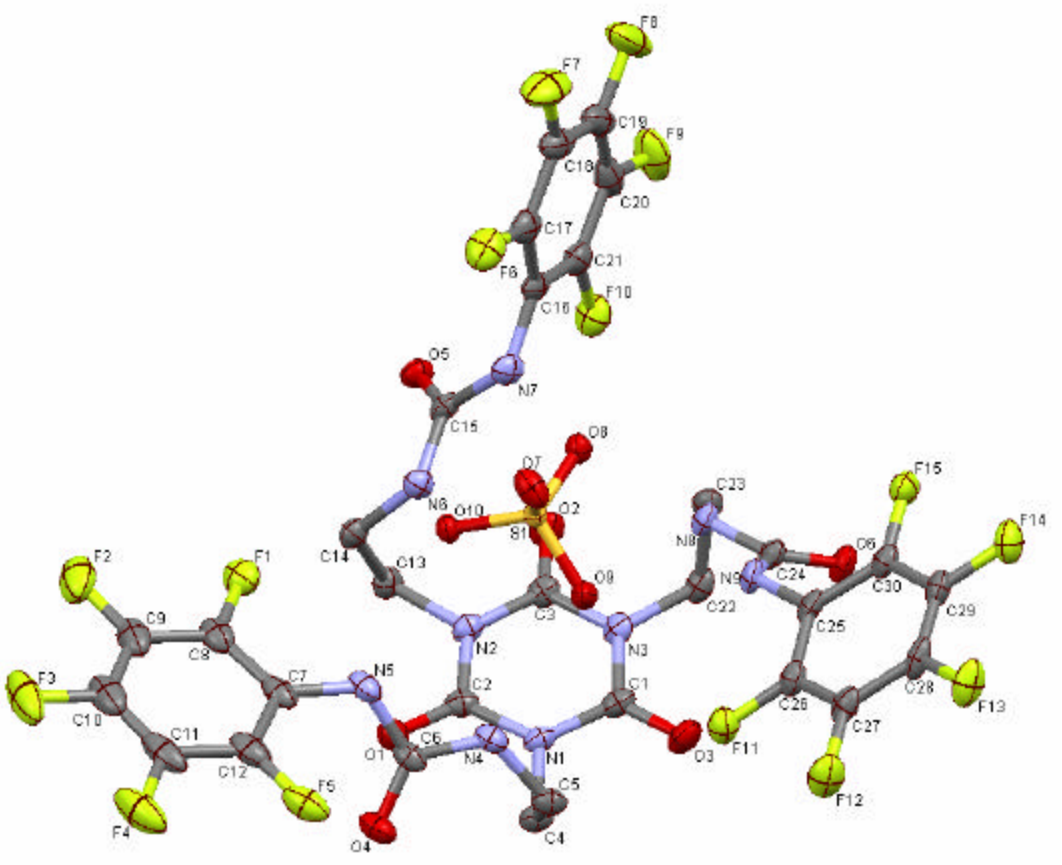
[1]. Spek, A. L. *PLATON-97*; University of Utrecht: Utrecht, The Netherlands, 1997.

[2]. *Mercury 1.3*, supplied with Cambridge Structural Database;CCDC: Cambridge, UK, 2003-2004.

27. **Table 1S**. Crystallographic table for complex **1**.

	1
Chemical formula	$C_{65}H_{97}F_{15}N_{12}O_{11}S$
Formula weight	1539.61
Temperature (K)	100
Radiation type	Mo Ka
Radiation wavelength	0.71073
Crystal system	Monoclinic
Space group	Cc
a (Å)	32.400(12)
b (Å)	12.936(5)
c (Å)	23.066(15)
a (deg)	90.00
ß (deg)	126.879(8)
? (deg)	90.00
Cell volume ($Å^3$)	7733(6)
Z	4
Calcd density (g/cm^3)	1.322
Absorption coefficient, µ (mm^{-1})	0.140
F(000)	3240
Crystal color	colorless
Crystal size (mm^3)	0.40 x 0.22 x 0.12
Data collection method	Bruker Apex II CCD diffractometer ? rotation with narrow frames
? range for data collection	1.57º to 25.00º
Index ranges	h -37 to 38; k -15 to 15; l -25 to 25
Completeness to ? = 25.00 º	99.6%
Relfns collected	25676
Independent Reflns	12215 (R_{int} = 0.0567)
Reflections with $F^2>2s$	9834
Absorption correction	semiempirical from equivalents
Min. and max. transmission	0.9462 and 0.9834
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Weighting parameters a, b	0.0990, 1.3050
Data/restraints/params	12215/2/937
Final *R* indices [$F^2>2s$]	R1 = 0.0545, WR2 = 0.1468
R indices (all data)	R1 = 0.0715 , WR2 = 0.1641
Goodness-of-fit of F^2	1.021
Largest and mean shift (su)	0.001 and 0.000
Largest diff. peak and hole (e $Å^{-3}$)	0.440 and -0.347

28. **Figure 19S**. ORTEP diagram of complex **1** with 50% probability of thermal ellipsoids. Two TBA^+ and DMF molecules in the asymmetric unit are omitted for clarity.



29. **Table 2S**. Hydrogen bonding interactions of encapsulated sulfate with the receptor **L** and tetrabutylammonium cations.

D-H···A	H···A (Å)	D···A (Å)	<D-H···A (deg)
N4-H4···O9[1]	2.14(7)	2.783(6)	160(7)
N5-H5···O10[1]	1.98(6)	2.821(5)	172(6)
N6-H6···O10[1]	2.18(6)	2.886(5)	160(6)
N7-H7···O8[1]	1.96(4)	2.744(5)	165(4)
N8-H8···O8[1]	2.38(5)	2.994(6)	160(5)
N9-H9···O9[1]	1.95(4)	2.733(5)	168(4)
C31-H31B···O7[2]	2.39	3.304(5)	157
C39-H39A···O7[2]	2.59	3.486(6)	154
C47-H47B···O7[3]	2.47	3.417(7)	164
C55-H55B···O8[3]	2.41	3.368(7)	171
C36-H36B···O10[2]	2.60	3.523(8)	159

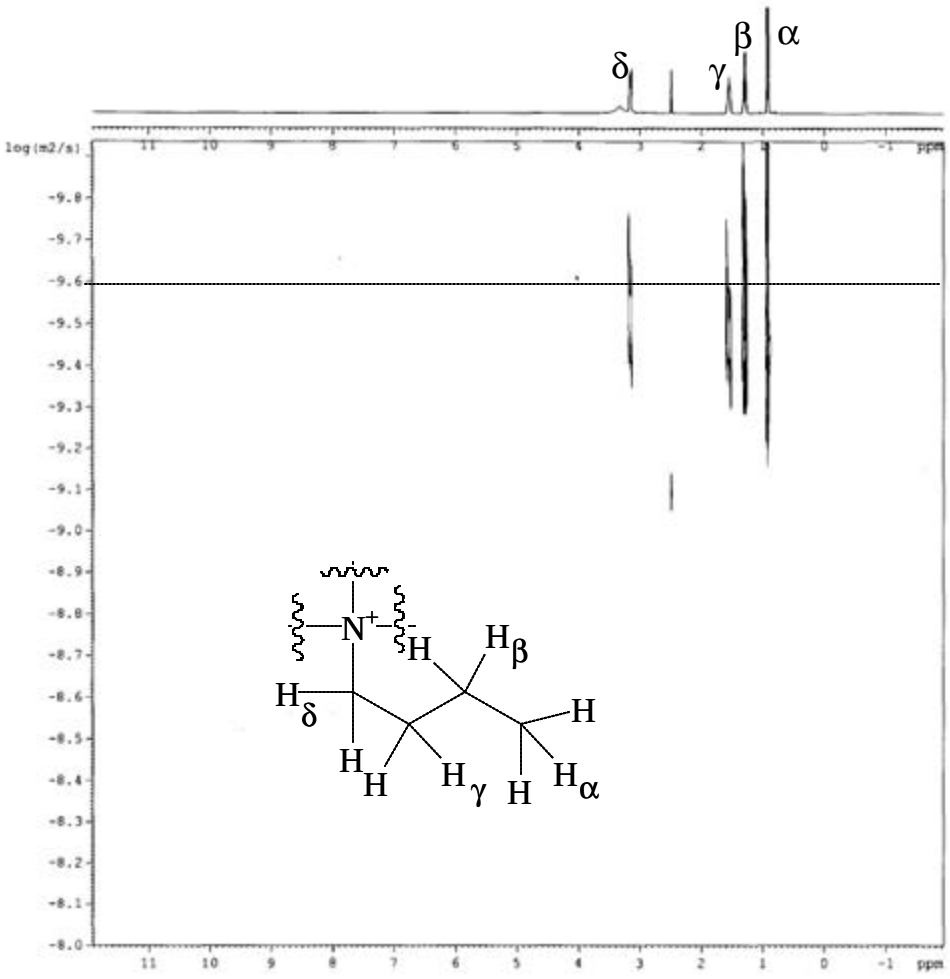
30. Diffusion measurements:

All 2D-DOSY experiments were performed on a Bruker AVII 500 MHz spectrometer. Data analyses were performed using tools within TOPSPIN 2.1 software. Sample volumes were 500 µL and the concentration of the sample was 5 mM. Anions were added as their tetrabutylammonium salts. All the experiments were performed in DMSO-d_6 solvent. Diffusion coefficients and hydrodynamic radii are correlated theoretically by the Stokes-Einstein relation.

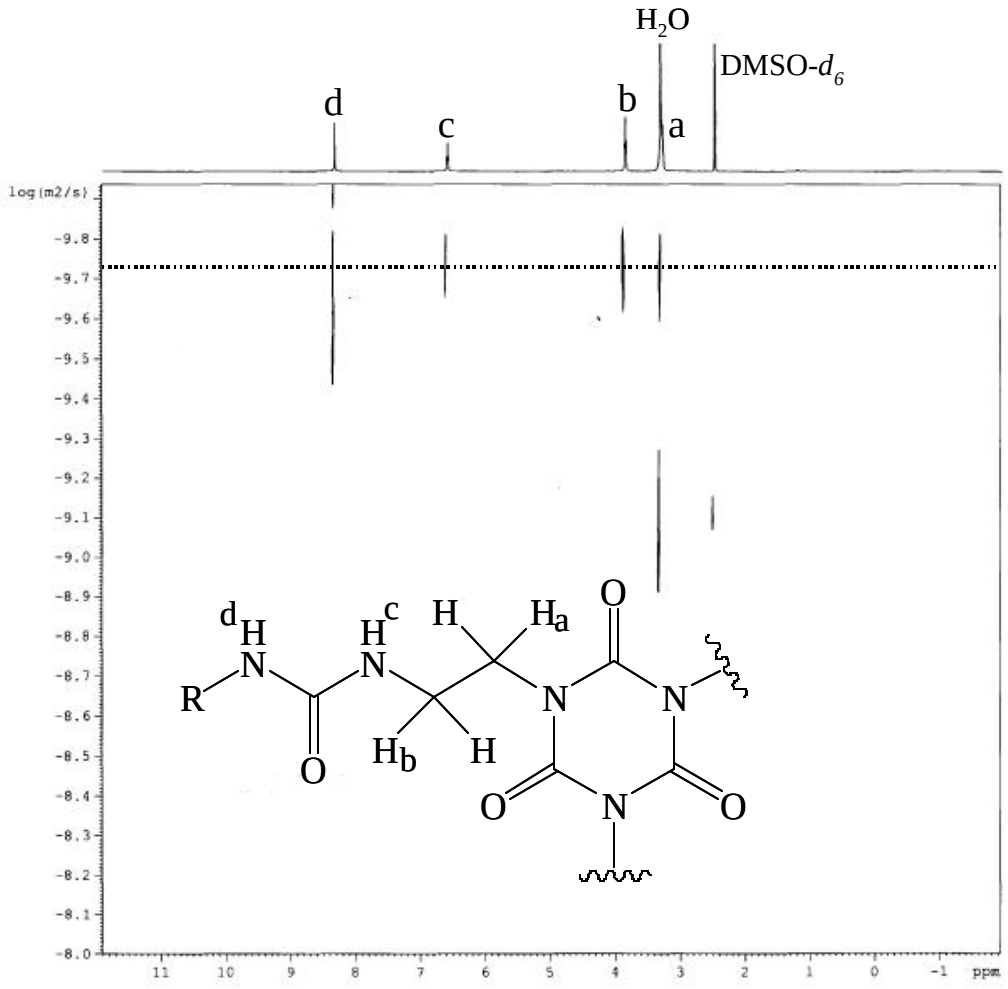
$$D = \frac{kT}{6\pi\eta r_s} \Rightarrow r_s = \frac{kT}{6\pi\eta D}$$

D is the diffusion coefficient; k is the Boltzmann constant (1.3807 x 10^{-23} $m^2Kgs^{-2}K^{-1}$); T is the temperature in Kelvin; ? is the viscosity of the solution (DMSO 1.991 x 10^{-2} $gcm^{-1}s^{-1}$); rs is the hydrodynamic radius of the molecular sphere.

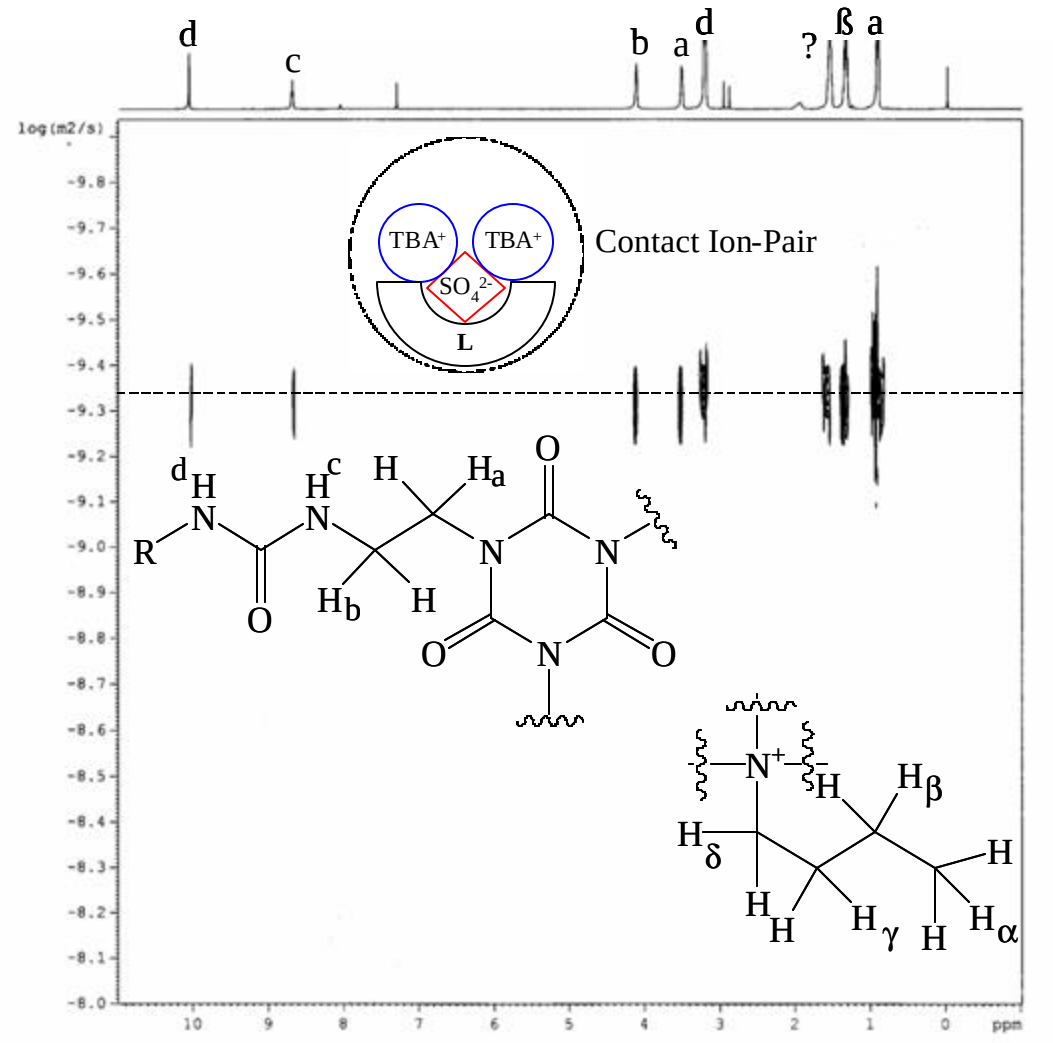
31. **Figure 20S**. ^{1}H-DOSY-NMR Spectra of $(n\text{-}Bu_4N^+)_2SO_4^{2-}$ in DMSO-d_6 at 298 K.



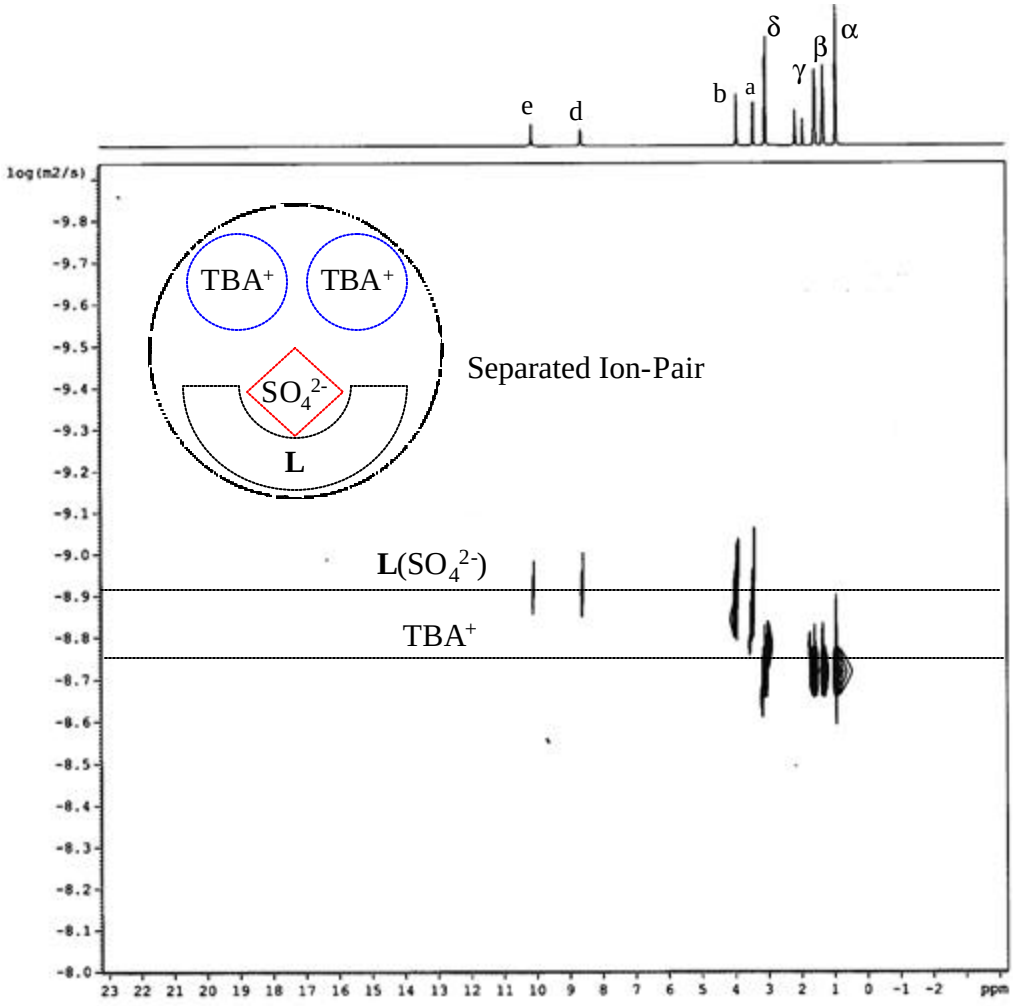
32. **Figure 21S**. ^{1}H-DOSY-NMR Spectra of receptor, **L** in DMSO-d_6 at 298 K.



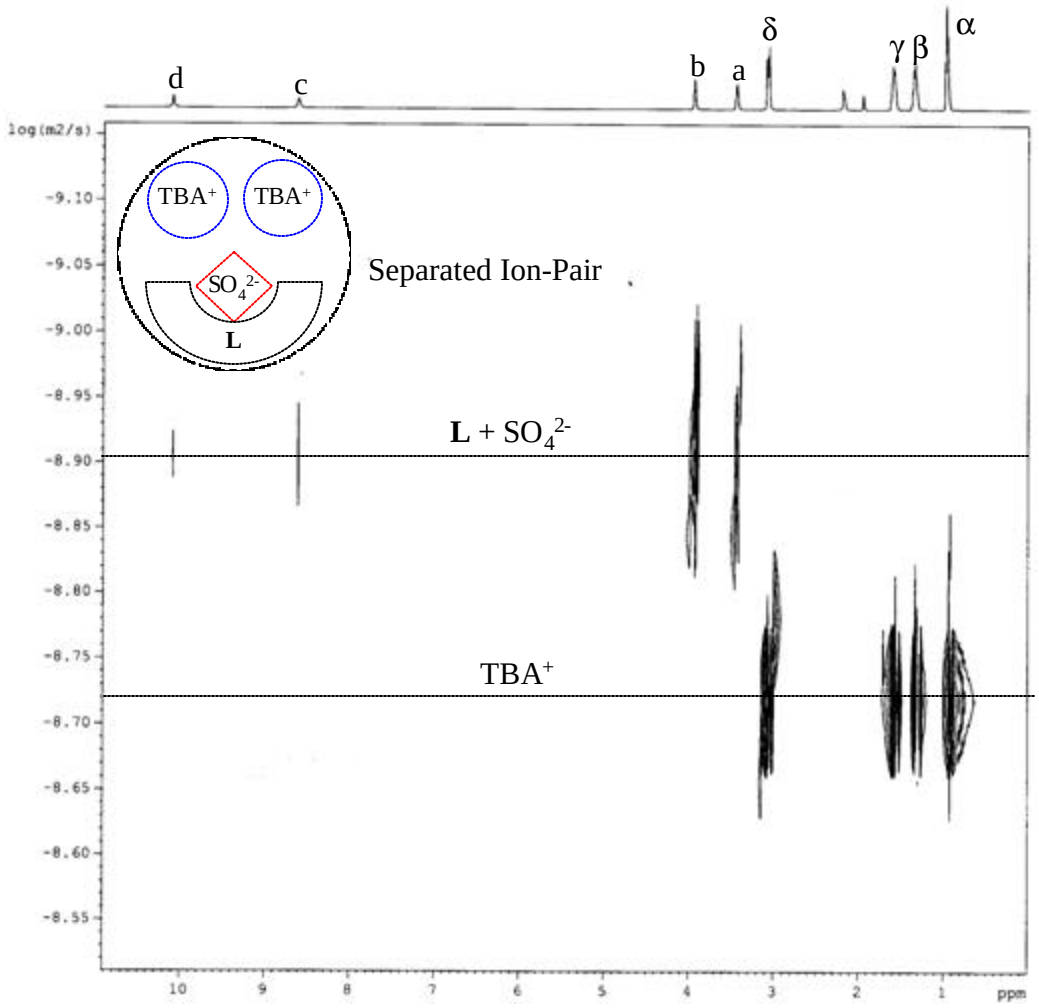
33. **Figure 22S**. ^{1}H-DOSY-NMR Spectra of complex, **1** in DMSO-d_6 at 298 K.



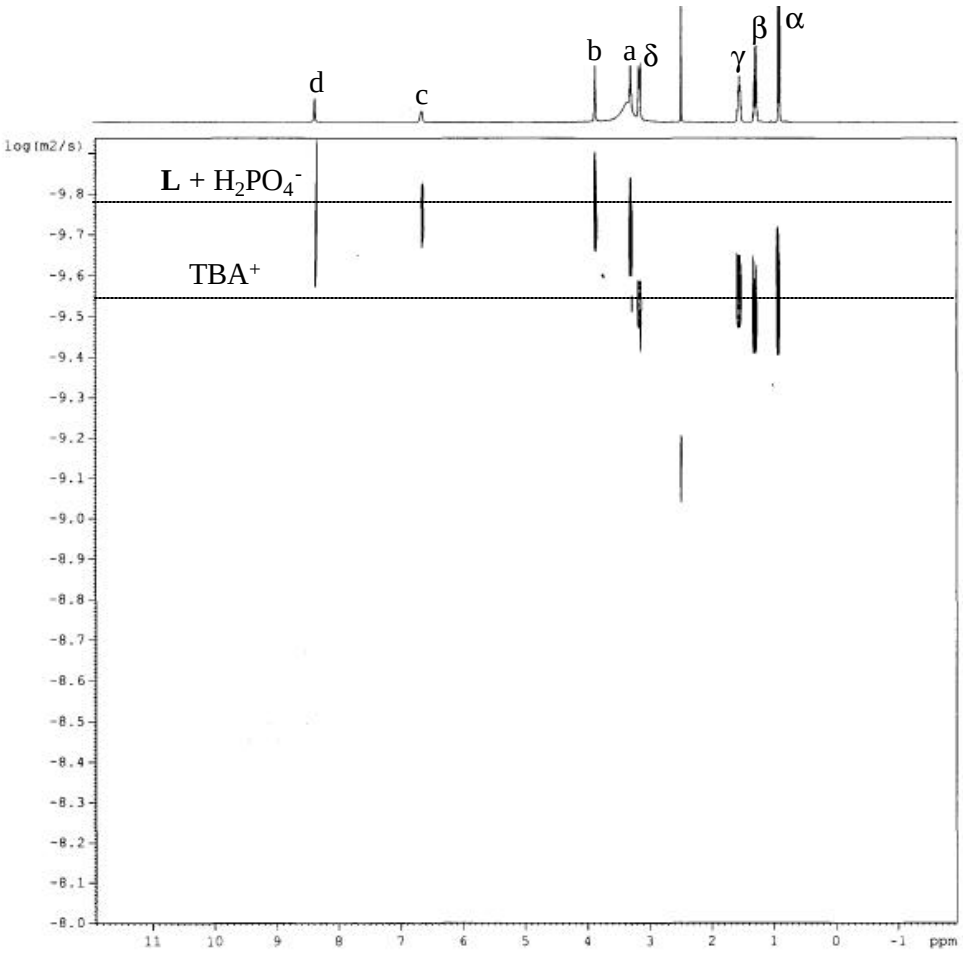
34. **Figure 23S**. ^{1}H-DOSY-NMR Spectra of complex, **1** in DMSO-d_6 at 313 K.



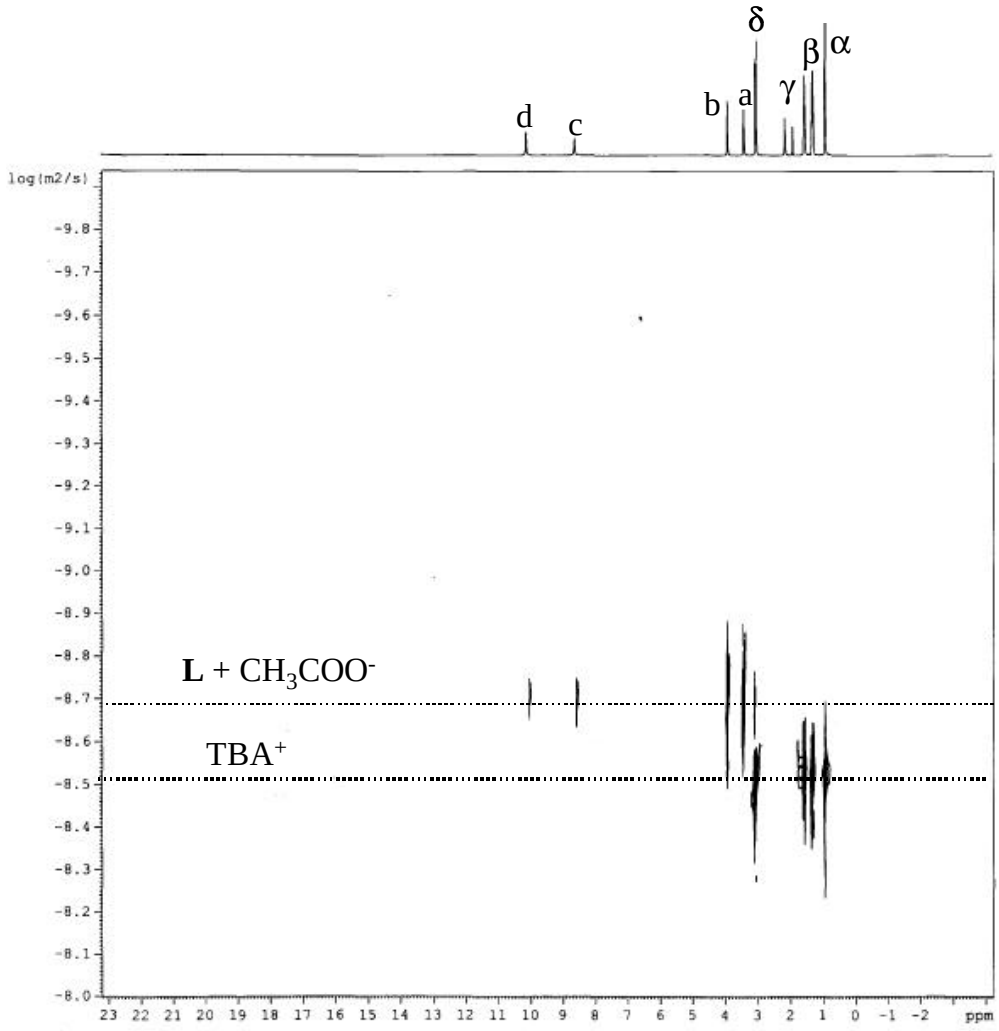
35. **Figure 24S**. ^{1}H-DOSY-NMR Spectra of complex, **1** in DMSO-d_6 at 333 K.



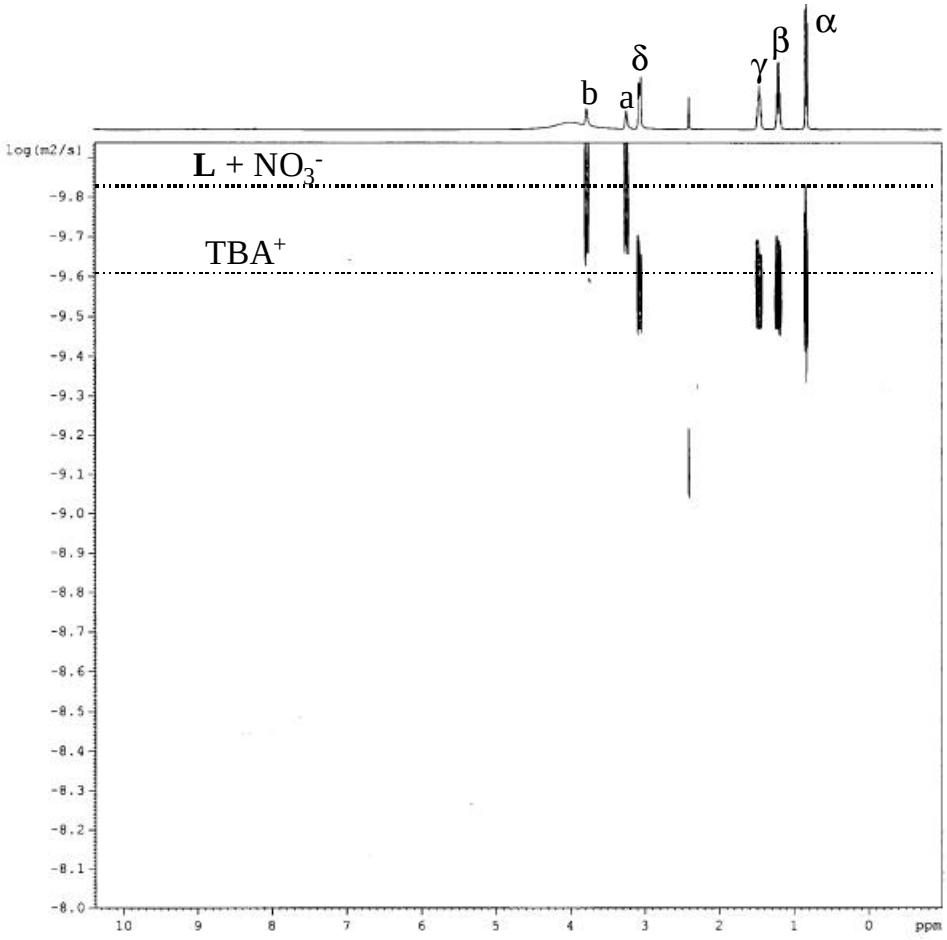
36. **Figure 25S**. ^{1}H-DOSY-NMR Spectra of receptor, **L** in the presence of *n*-$Bu_4N^+H_2PO_4^-$ in DMSO-d_6 at 298 K.



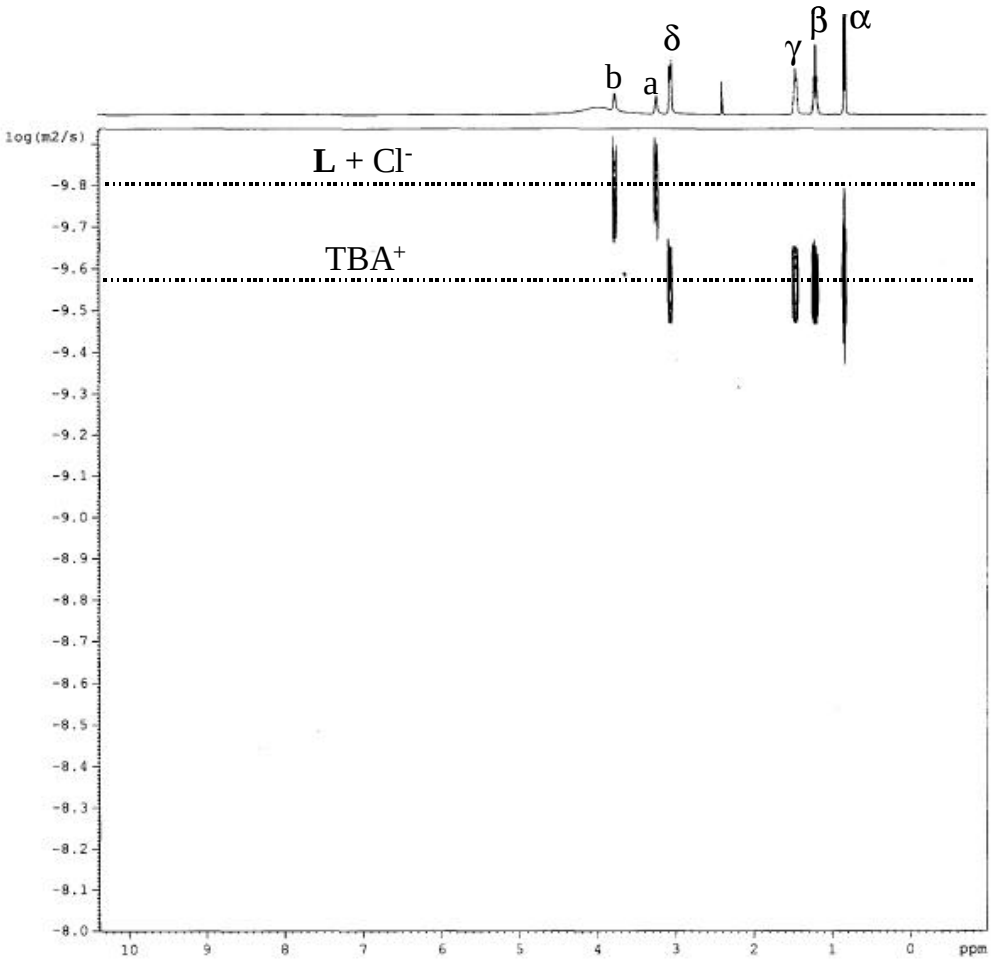
37. **Figure 26S**. ^{1}H-DOSY-NMR Spectra of receptor, **L** in the presence of *n*-$Bu_4N^+CH_3COO^-$ in DMSO-d_6 at 298 K.



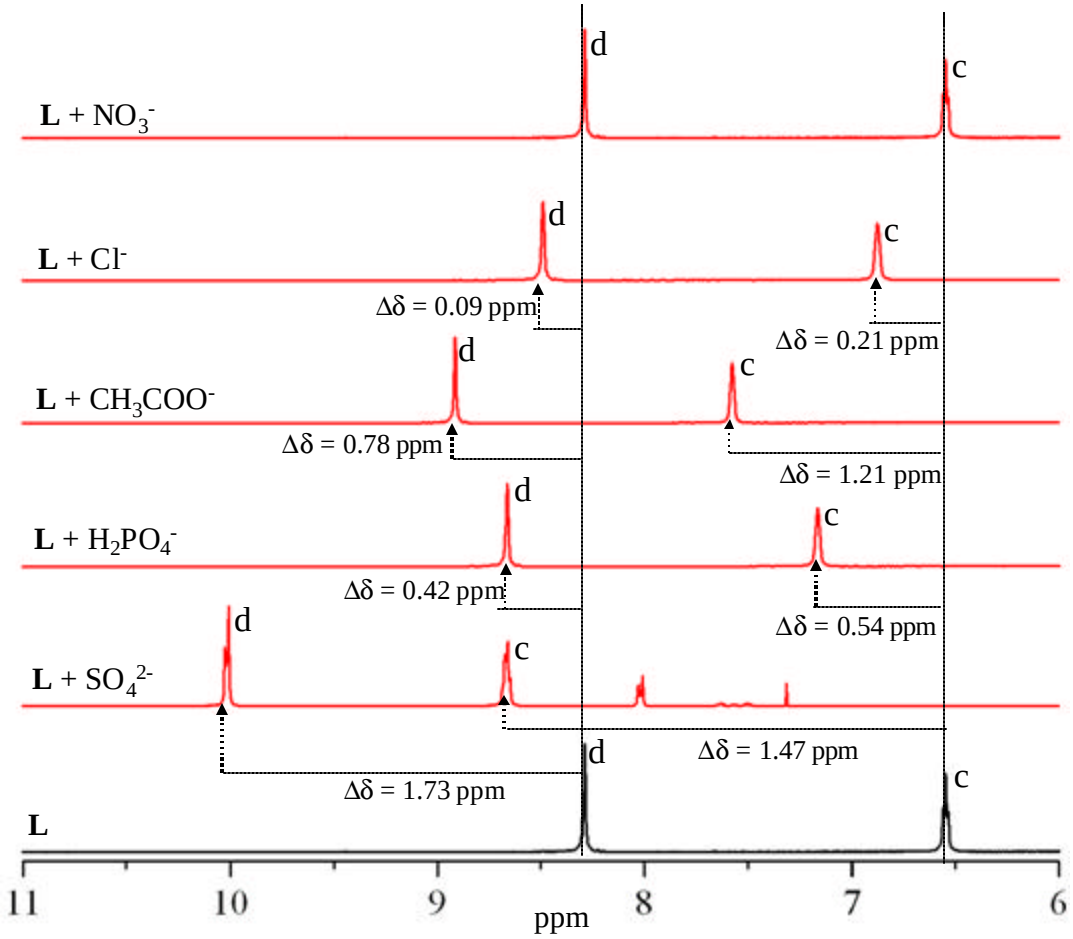
38. **Figure 27S**. ^{1}H-DOSY-NMR Spectra of receptor, **L** in the presence of *n*-$Bu_4N^+NO_3^-$ in DMSO-d_6 at 298 K.



39. **Figure 28S**. ^{1}H-DOSY-NMR Spectra of receptor, **L** in the presence of *n*-$Bu_4N^+Cl^-$ in DMSO-d_6 at 298 K.

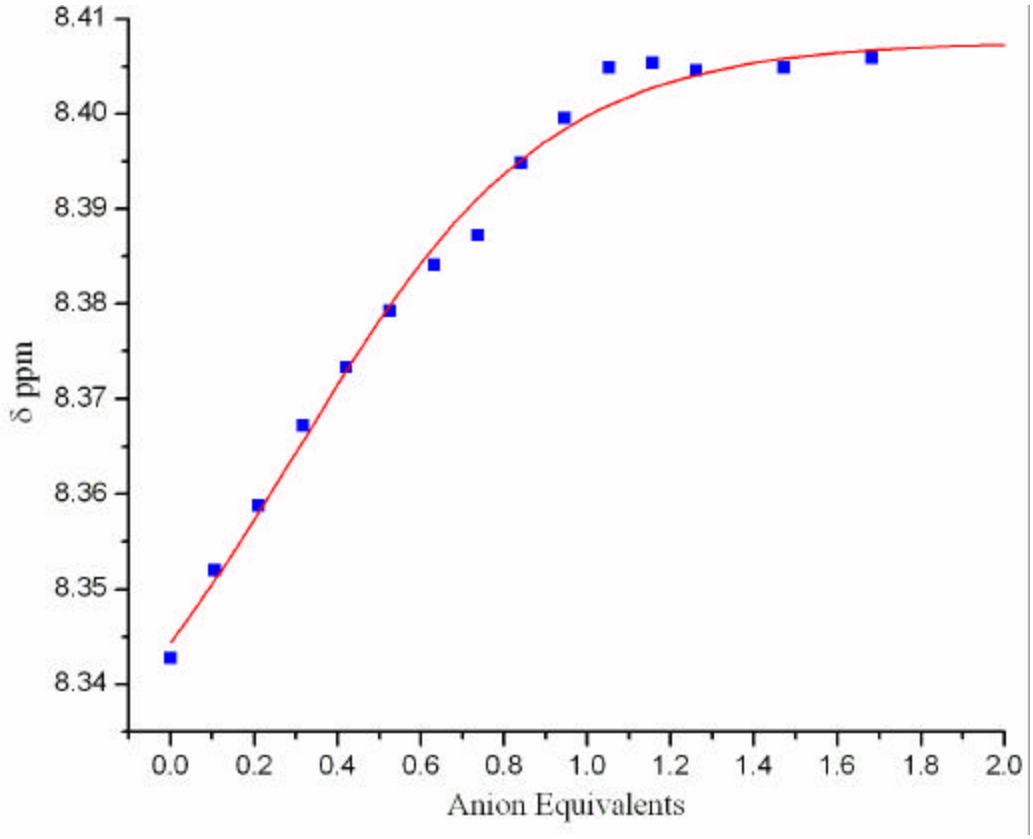


40. **Figure 29S**. Partial 1H-NMR spectra of L and downfield shift urea NH groups upon addition of different anions as tetrabutylammonium salts in DMSO-d_6 at 298 K.

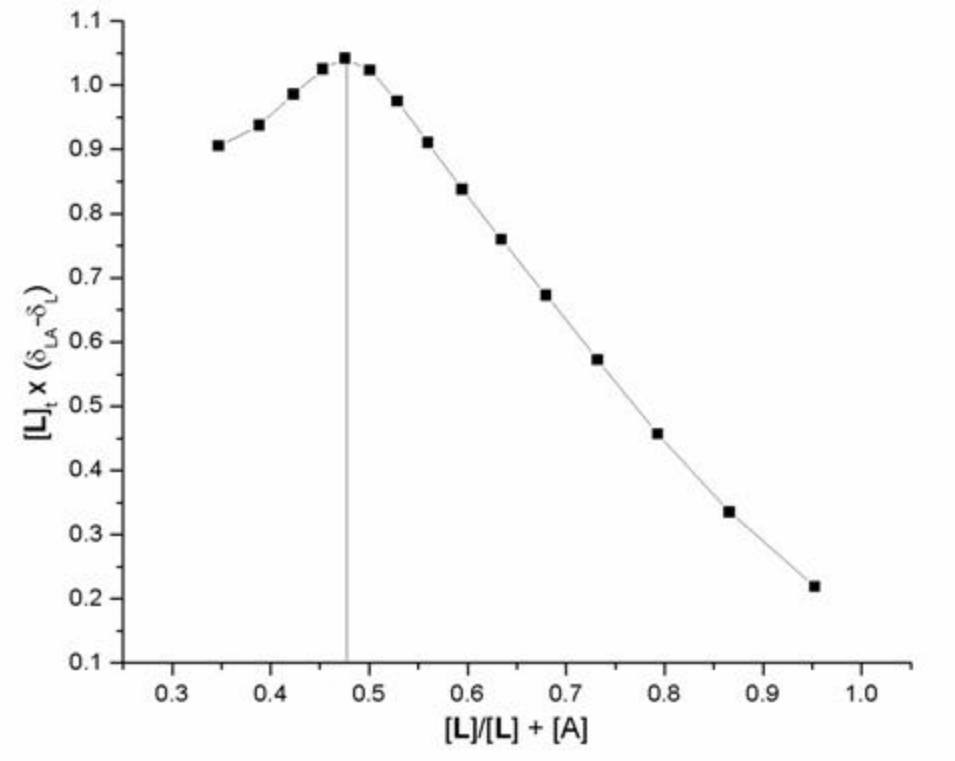


The large downfield shift of the urea protons Δδ -NH_c 1.47 and –NH_d 1.73 ppm in the case of sulfate; Δδ -NH_c 0.54 and –NH_d 0.42 ppm for dihydrogen phosphate; Δδ -NH_c 1.21 and –NH_d 0.78 ppm for acetate; Δδ -NH_c 0.21 and –NH_d 0.09 ppm for chloride are observed. The addition of *n*-$Bu_4N^+F^-$ to the DMSO-d_6 solution of the receptor **L** showed the disappearance of both the urea –NH_c and –NH_d signals. This observation may be attributed to the deprotonation of acidic urea protons by more basic fluoride anions. This prohibited us to evaluate the association constant for **L** with this anion. There are no considerable changes in the chemical shift of the urea protons of **L** with Br^-, I^-, ClO_4^- and NO_3^- observed, suggesting energetically unfavorable interaction of **L** with these anions in solution.

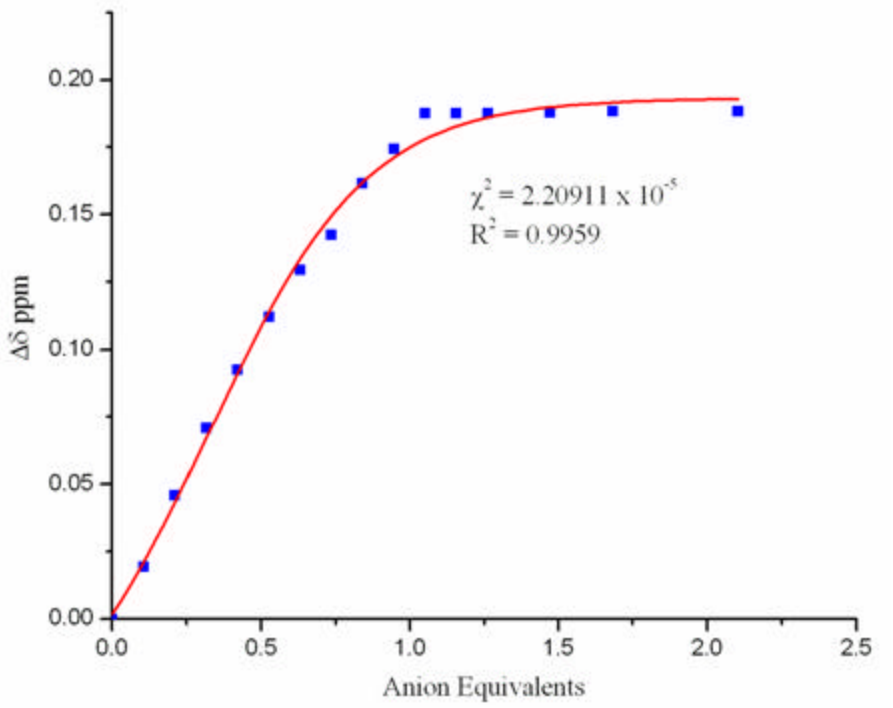
41. **Figure 30S**. Plot of change in chemical shift of urea -NH groups of **L** with increasing amounts of $(n\text{-}Bu_4N^+)_2SO_4^{2-}$ in DMSO-d_6 at 25ºC.



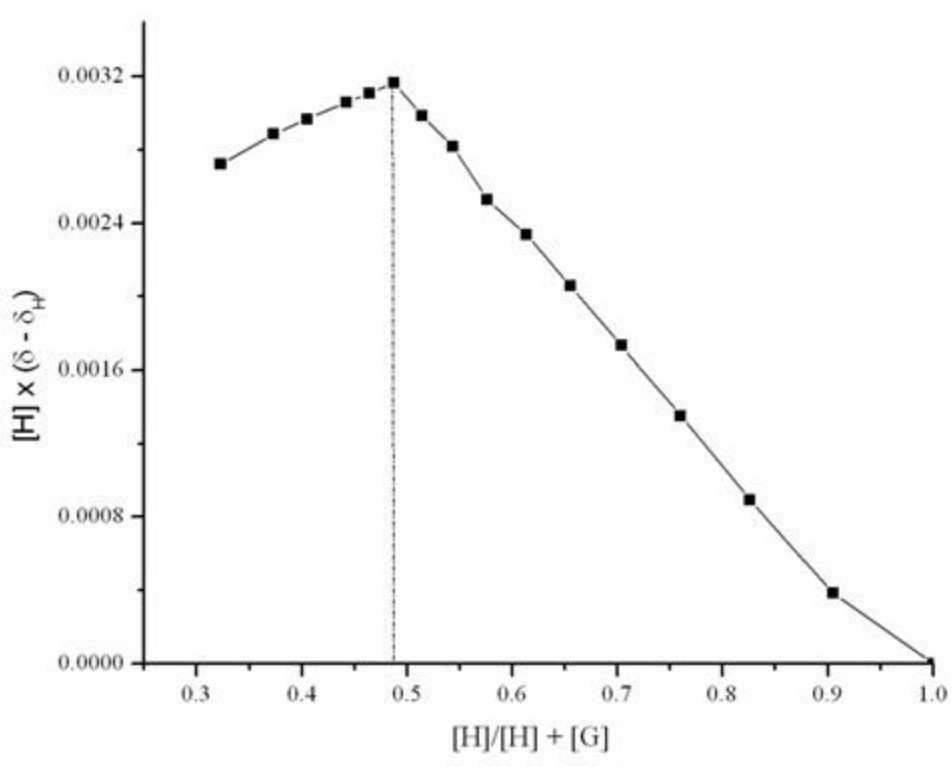
42. **Figure 31S**. Job's Plot of **L** with $(n\text{-}Bu_4N^+)_2SO_4^{2-}$ in DMSO-d_6 at 25ºC.



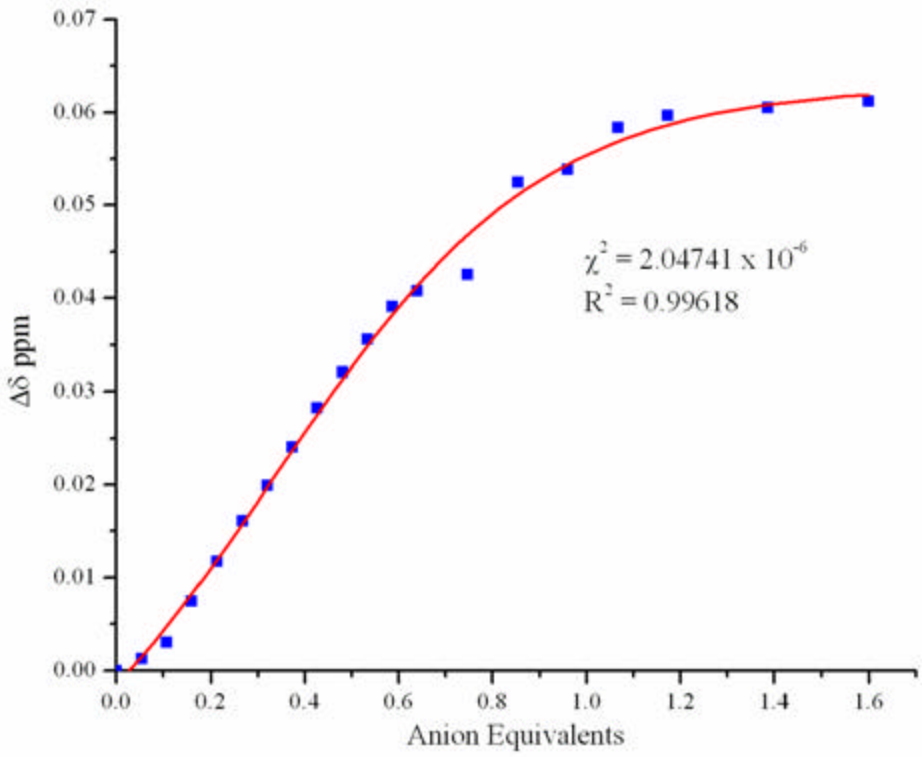
43. **Figure 32S**. Plot of change in chemical shift of urea -NH groups of **L** with increasing amounts of *n*-$Bu_4N^+H_2PO_4^-$ in DMSO-d_6 at 25ºC.



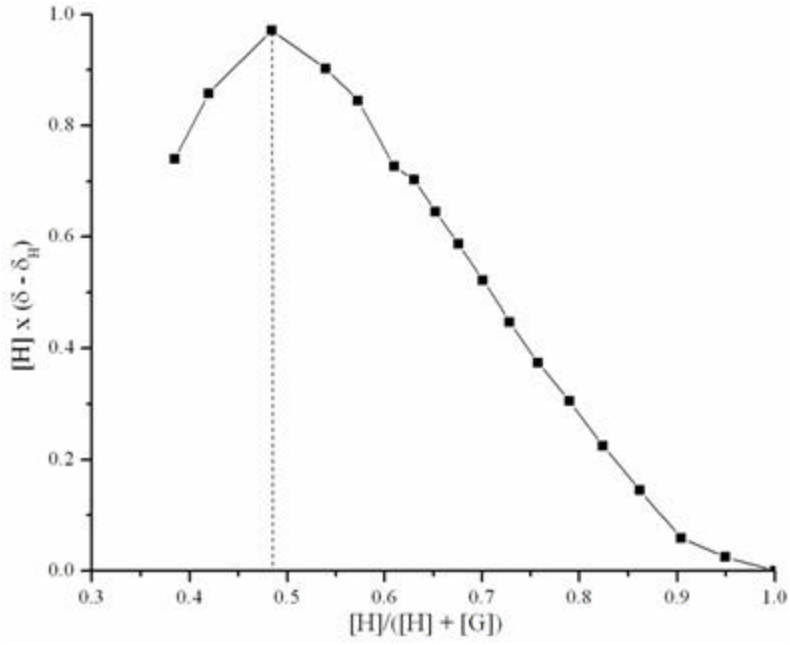
44. **Figure 33S**. Job's Plot of **L** with *n*-$Bu_4N^+H_2PO_4^-$ in DMSO-d_6 at 25ºC.



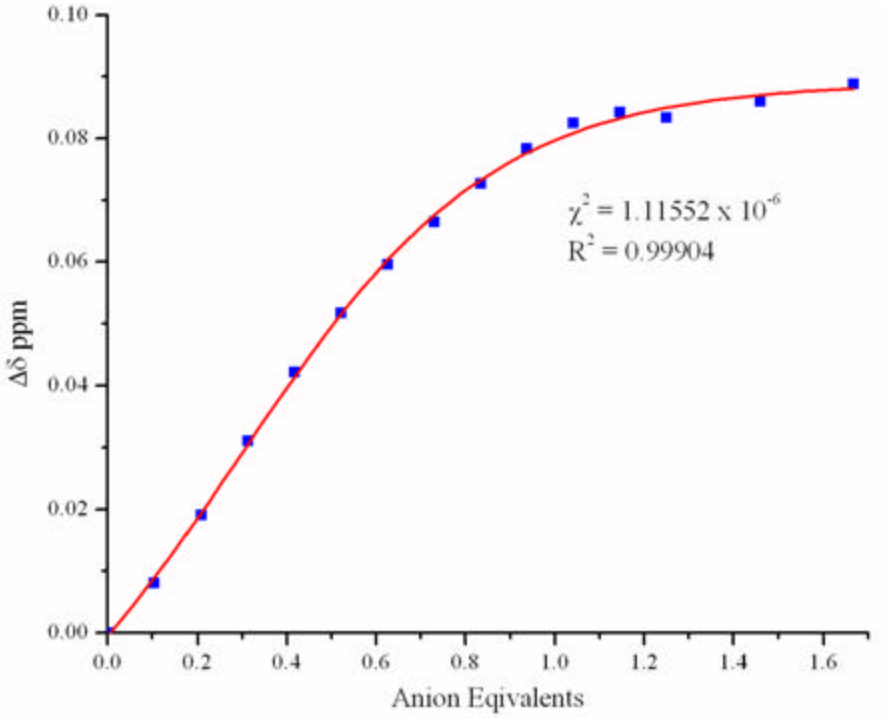
45. **Figure 34S**. Plot of change in chemical shift of urea -NH groups of **L** with increasing amounts of *n*-$Bu_4N^+CH_3COO^-$ in DMSO-d_6 at 25ºC.



46. **Figure 35S**. Job's Plot of **L** with *n*-$Bu_4N^+CH_3COO^-$ in DMSO-d_6 at 25ºC.



47. **Figure 36S**. Plot of change in chemical shift of urea -NH groups of **L** with increasing amounts of *n*-$Bu_4N^+Cl^-$ in DMSO-d_6 at 25ºC.



48. **Figure 37S**. Job's Plot of **L** with *n*-$Bu_4N^+Cl^-$ in DMSO-d_6 at 25ºC.