Supporting Information

Acid/Base Controlled Size Modulation of Capsular Phosphates, Hydroxide Encapsulation, Quantitative and Clean Extraction of Sulfate with Carbonate Capsules of a Tripodal Urea Receptor

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Materials and Methods

Materials: All the tetrabutylammonium anions (F^-, Cl^-, Br^-, I^-, OH^-, $H_2PO_4^-$, CH_3COO^-, NO_3^-, ClO_4^-, SO_4^{2-}) and tetraethylammonium bicarbonate, NMR solvents ($CDCl_3$ and DMSO-d_6), Triphenylphosphine, Hexafluorobenzene were purchased from Sigma-Aldrich, USA and were used without further purification. Potassium sulfate, potassium dihydrogenphosphate and potassium nitrate were purchased from Merck. Chloroform, Acetonitrile and Dimethylsulfoxide (DMSO) were purchased from Spectrochem, Ltd., India.

Methods: The isothermal titration calorimetric (ITC) experiment was performed on a MicroCal VP-ITC instrument. FT-IR was recorded on SHIMADZU FTIR-8400S infrared spectrophotometer with KBr pellets. ^1H, ^{13}C, ^{19}F, ^{31}P- NMR spectra were recorded on a Bruker DPX 300 FT-NMR and DPX 500 FT-NMR spectrometer. Chemical shifts for ^1H,^{13}C , ^{19}F, ^{31}P- NMR were reported in parts per million (ppm), calibrated to the residual solvent peak set, with coupling constants reported in Hertz (Hz). Hexafluorobenzene, triphenylphosphine were used as internal standard in ^{19}F-NMR and ^{31}P-NMR studies respectively. X-ray powder patterns were collected on a Bruker D8 SWAX X-ray diffractometer (CuKα = 1.5418 Å) with a scan rate of 0.3 min/deg in the $5^o < 2\theta < 55^o$ range with a step size of 0.05º. Energy Dispersive X-ray (EDX) analyses were carried out on a field emission scanning electron microscope (FE-SEM) using JEOL, JSM-6700F equipment operated with the accelerating voltage 5 kV. Gravimetric analysis of precipitated $BaSO_4$ was carried out by taking on a G-4 gauche-crucible. In each case before taking weight, it was dried in hot air oven for 12 hour followed by 3 hour in vacuum desiccator.

Isothermal Titration Calorimetric (ITC) studies: The ligand **L** was prepared by our reported procedure.[1] Titration was carried out at 298 K in dry dimethyl sulfoxide (DMSO). Solution of anion in DMSO was taken in the measuring cell. This solution was then titrated with 30 injections of 10 µl of **L** solution prepared in DMSO. An interval of 220 seconds was allowed between each injection, and the stirring speed was set at 329 rpm. The obtained data was processed using Origin 7.0 software supplied with the instrument and fitted to a one site binding model. Blank titration of **L** into solvent was also performed and subtracted from the corresponding titration to remove any effect from the heats of dilution from the titrant. The studies of the effect of the various anions was repeated twice with two different batches of **L** and showed good reproducibility.

Figure1S: Chloride (1.754 mM **L** + 0.060mM chloride)

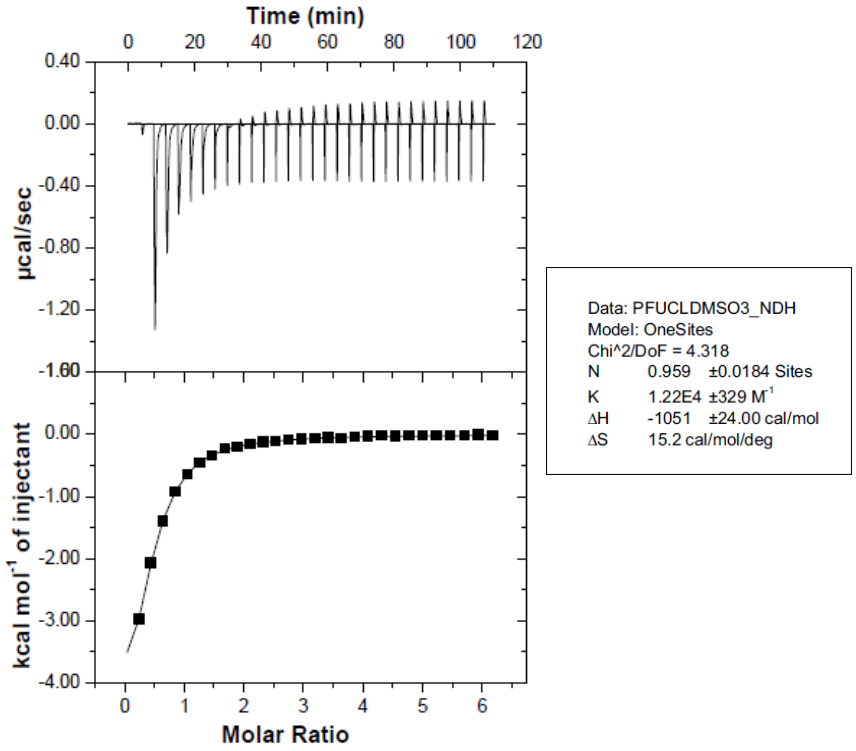


Figure2S: Bromide (1.454 mM **L**+ 0.062 mM bromide)

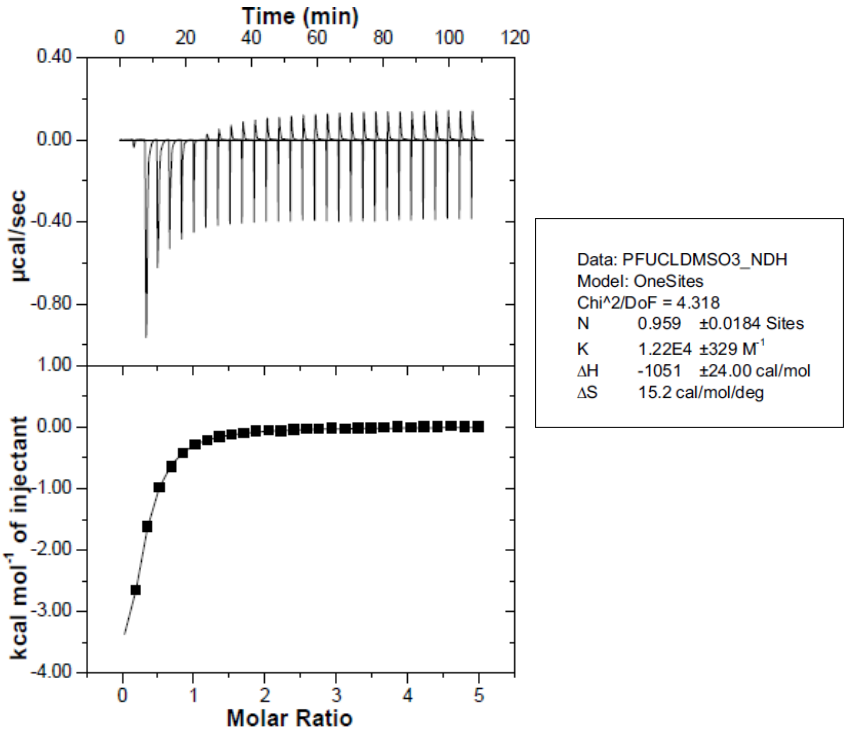


Figure3S: Sulfate (1.89 mM **L**+ 0.051 mM sulfate)

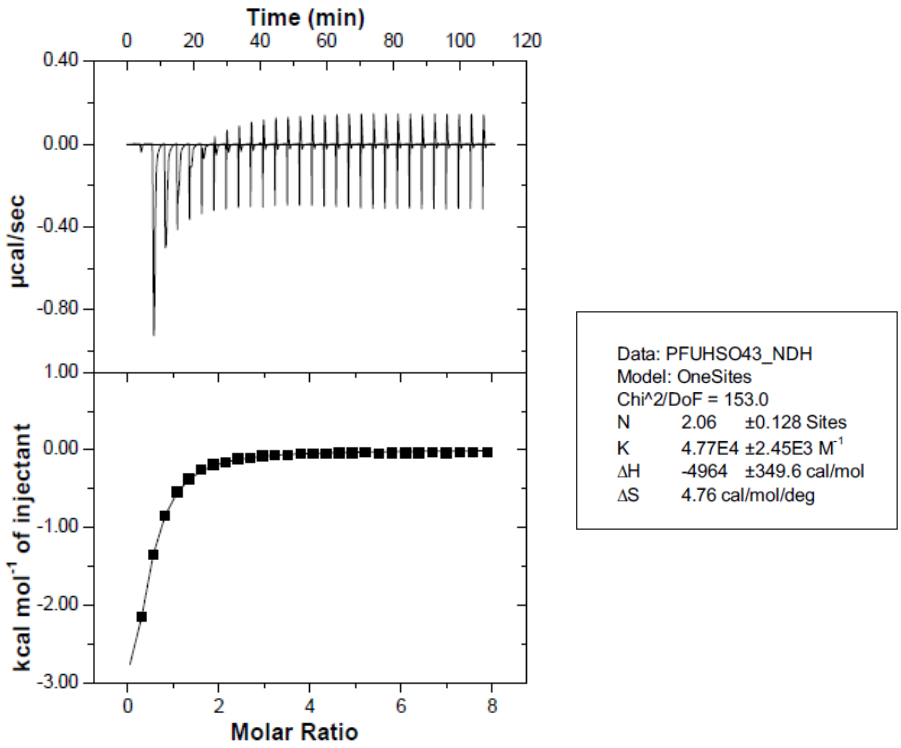
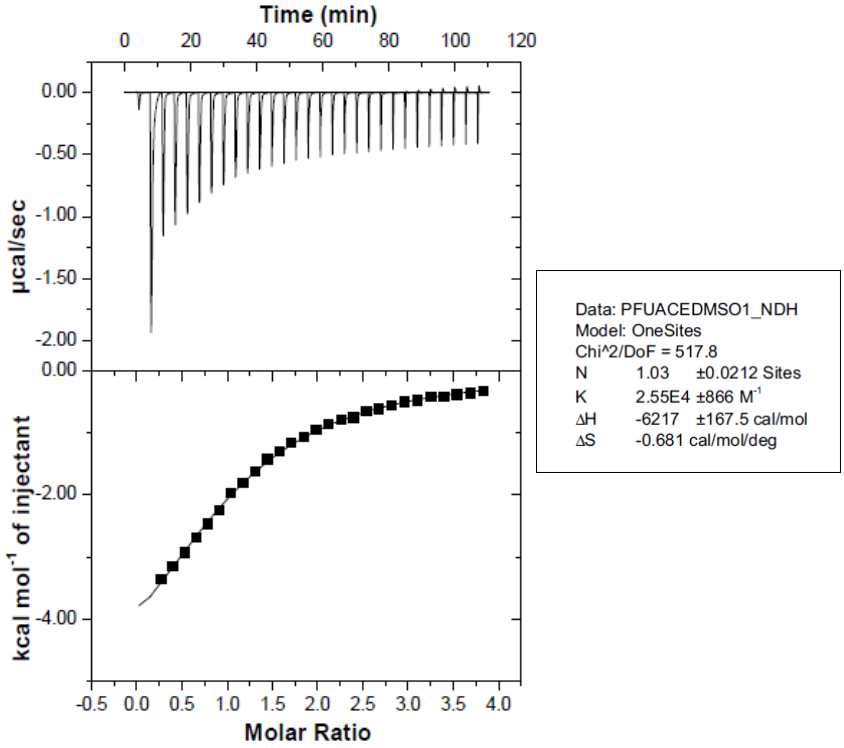


Figure4S: Acetate (1.045 mM **L**+ 0.058 mM acetate)



Synthetic Procedure for Complex 5 and Complex 6:

Complex 5: Complex 5 was synthesized by reacting **L**, *n*-$Bu_4NH_2PO_4$ and *n*-Bu_4NOH or addition of *n*-Bu_4NOH to the isolated crystals of complex **1** in DMSO. 75 mg of **L** was dissolved in 10 mL of DMSO in a 25 mL beaker. *n*-$Bu_4NH_2PO_4$ (2 m mole) and *n*-Bu_4NOH (2 m mole) were added to the DMSO solution of **L** whereas, in other case 2 m mole of *n*-Bu_4NOH was added in one shot to the 10 mL DMSO solution of **1**. In both cases, the mixtures were stirred for 5 min at room temperature and warmed slightly for few minutes. After cooling to room temperature, both the resulting solutions were filtered using a filter paper. Filtrates were collected in 25 mL beaker and allowed to crystallize at room temperature. From both the solutions colourless crystals of the monohydrogenphosphate complex of **L**, $[\mathbf{L}_2(HPO_4)][N(n\text{-}Bu)_4]_2$ (**5**), suitable for X-ray diffraction was obtained after three days. Isolated Yield in form of crystal is low (10%), but the isolated mass is 80%. ^{1}H NMR (125 MHz, DMSO-d_6) (Figure 12S): δ 0.91 (t, 3H, $NCH_2CH_2CH_2CH_3$), 1.29 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.54 (m, 2H, $NCH_2CH_2CH_2CH_3$), 2.33 (s, 6H, NCH_2), 2.89 (s, 6H, NCH_2CH_2), 3.14 (m, 2H, $NCH_2CH_2CH_2CH_3$), 8.18 (br, 3H, NH_b), 9.45 (br, 3H, NH_a). ^{13}C NMR (125 MHz, DMSO-d_6) (Figure 13S): δ 13.9 ($NCH_2CH_2CH_2CH_3$), 19.7 ($NCH_2CH_2CH_2CH_3$), 23.6 ($NCH_2CH_2CH_2CH_3$) 38.6 (NCH_2), 55.4 (NCH_2CH_2), 58.1 ($NCH_2CH_2CH_2CH_3$), 115.8 (Ar, CF), 136.3 (Ar, *C*F), 138.2 (Ar, *C*F), 143.3 (Ar, *C*F), 155.8 (*C*=O).

Complex 6: Complex 6 was synthesized by reacting **L** with *n*-Bu_4NCN in DMSO. 75 mg of **L** was dissolved in 10 mL of DMSO in a 25 mL beaker. *n*-Bu_4NCN (1 m mole) were added in one shot to the 10 mL DMSO solution of **L**. The mixtures were stirred for 5 min at room temperature and warmed slightly for few minutes. After cooling to room temperature, both the resulting solutions were filtered using a filter paper. Filtrates were collected in 25 mL beaker and allowed to crystallize at room temperature in aerobic condition. From the solution colourless crystals of the monohydrogenphosphate complex of **L**, [**L** (OH)][N (n-Bu)$_4$] (6), suitable for X-ray diffraction was obtained after five days. Isolated Yield in form of crystal is 90%. ^{1}H NMR (75 MHz, $CDCl_3$) (Figure 14S): δ 0.95 (t, 12H, $NCH_2CH_2CH_2CH_3$), 1.35 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.55 (m, 8H, $NCH_2CH_2CH_2CH_3$), 2.48 (s, 6H, NCH_2), 3.16 (m, 8H, $NCH_2CH_2CH_2CH_3$), 3.17 (s, 6H, NCH_2CH_2). ^{13}C NMR (125 MHz, $CDCl_3$) (Figure 15S): δ 12.745 ($NCH_2CH_2CH_2CH_3$), 14.296 ($NCH_2CH_2CH_2CH_3$), 19.806 ($NCH_2CH_2CH_2CH_3$), 23.841 ($NCH_2CH_2CH_2CH_3$), 58.879 (NCH_2CH_2), 136.064 (Ar, CF), 139.162(Ar, *C*F),

141.612 (Ar, *C*F), 144.983 (Ar, *C*F), 155.739 (*C*=O). ^{19}F NMR (125 MHz, $CDCl_3$) (Figure 16S): -148.43 (Ar, *C*F), -165.41 (Ar, *C*F), -168.26 (Ar, *C*F).

X-ray crystallographic refinement details:

X-ray Crystallography: Crystal suitable for single crystal X-ray diffraction studies 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 the crystal of complex **5** and **6** were collected using Mo*K*α (l = 0.7107 Å) radiation on a Bruker SMART APEX II diffractometer equipped with CCD area detector at 100 K. The data integration and reduction were processed with SAINT[2] software provided with the software package of SMART APEX II. An empirical absorption correction was applied to the collected reflections with SADABS[3]. The structures were solved by direct methods using SHELXTL[4] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[5] program package. The non-hydrogen atoms were refined anisotropically till convergence. The hydrogen atoms were geometrically fixed at idealized positions whereas the hydrogen atoms attached to the nitrogen atoms were located from the difference Fourier map and refined isotropically till convergence is attained. Graphics were generated using PLATON[6] and MERCURY 2.3.[7]

Table1S. Single crystal X-ray crystallographic table of complex **5** and complex **6**

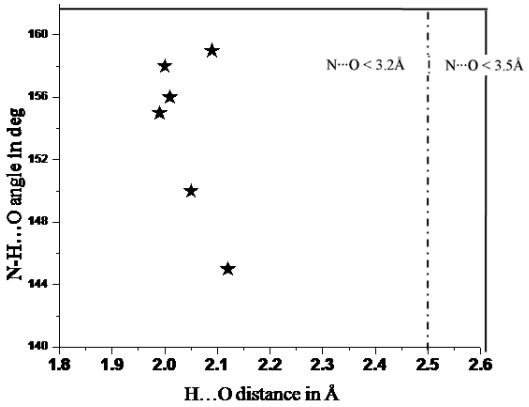
Parameters	**Complex 5**	**Complex 6**
Empirical formula	C86 H109 F30 N16 O10 P	C43 H54 F15 N8 O4
Formula weight	2127.86	1031.94
crystal system	ORTHORHOMBIC	TRICLINIC
Space group	P212121	P-1
***a* (Å)**	19.210(4)	13.939(2)
***b* (Å)**	20.782(4)	14.194(5)
***c* (Å)**	25.120(5)	14.511(3)
α (deg)	90.00	93.624(3)
β (deg)	90.00	118.198(2)
γ (deg)	90.00	96.509(3)
***V* (Å^3)**	10029(3)	2491.6(10)
Z	4	2
d_{calc} (g/cm^3)	1.409	1.375
Crystal size (mm^3)	0.36x0.21x0.12	0.26x0.12x0.05
Diffractometer	Smart CCD	Smart CCD
***F*(000)**	4408	1070
μ MoKα (mm^{-1})	0.146	0.127
***T* (K)**	100(2)	100(2)
θ max	21.05	24.16
ObservedReflections	10636	7919
Parameters refined	1289	659
R_1; WR_2	0.0542; 0.1036	0.0633; 0.1769
GOF (F2)	1.482	1.047

Table2S. Hydrogen bonding interactions of encapsulated hydrogen phosphate in the cavity of **L** in complex **5.**

Phosphate atom	D-H···A	d(H···A)Å	d(D···A)Å	∠DHA °
O1	N10-H10···$O1_b$	2.07	2.908(5)	165
	O1-H1···$N4_c$	2.28	3.075(5)	162
	N4-H4...$O1_a$	2.39	3.074(6)	137
O2	N5-H5···$O2_a$	1.89	2.743(5)	168
	N6-H6···$O2_a$	2.04	2.901(5)	174
	N12-H12···$O2_b$	2.05	2.899(6)	168
	N4-H4...$O2_a$	2.50	3.175(6)	136
O3	N9-H9···$O3_b$	2.06	2.778(5)	140
	N11-H11···$O3_b$	1.98	2.800(6)	158
	N13-H13···$O3_b$	1.98	2.815(5)	163
	N10-H10...$O3_b$	2.55	3.193(6)	132
O4	N2-H2···$O4_a$	2.16	2.941(4)	151
	N3-H3···$O4_a$	2.14	2.833(6)	138
	N7-H7···$O4_a$	2.07	2.872(5)	154
	N14-H14···$O4_b$	2.03	2.863(5)	163

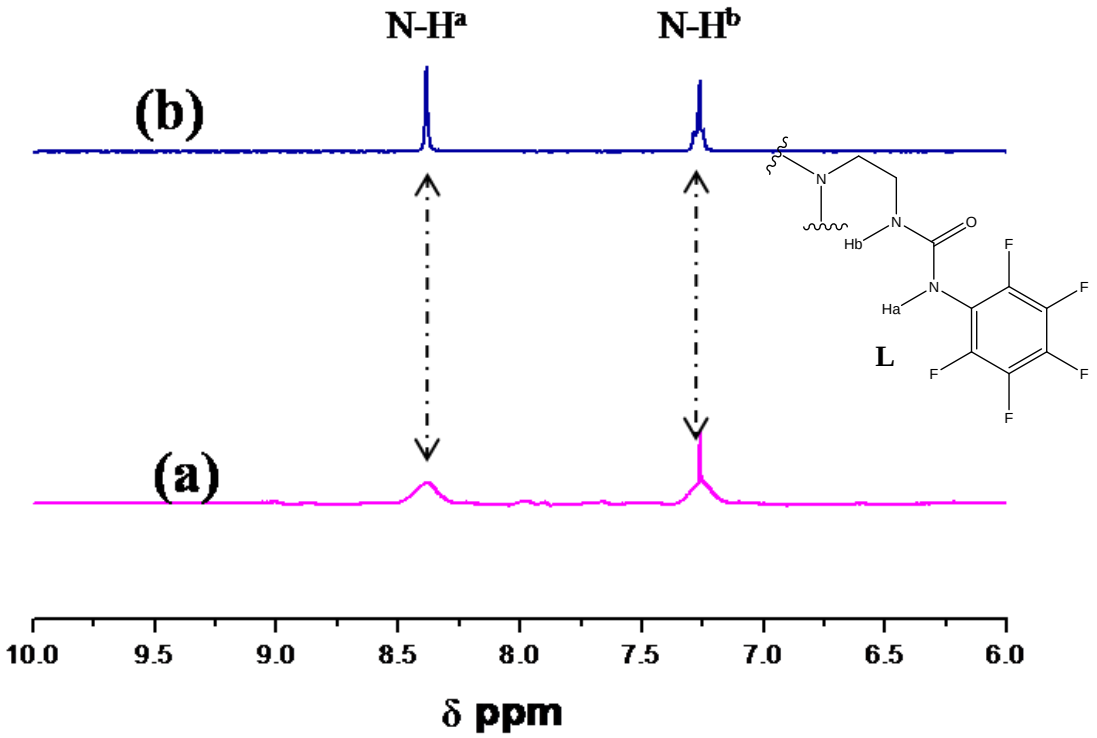
Symmetry operation: a= -x,1/2+y,1/2-z; b = 1/2-x,-y,1/2+z; c= -x,-1/2+y,1/2-z

Figure5S. The scatter plot of N–H…O angle *vs.* H…O distance of the hydrogen bonds in complex **6**



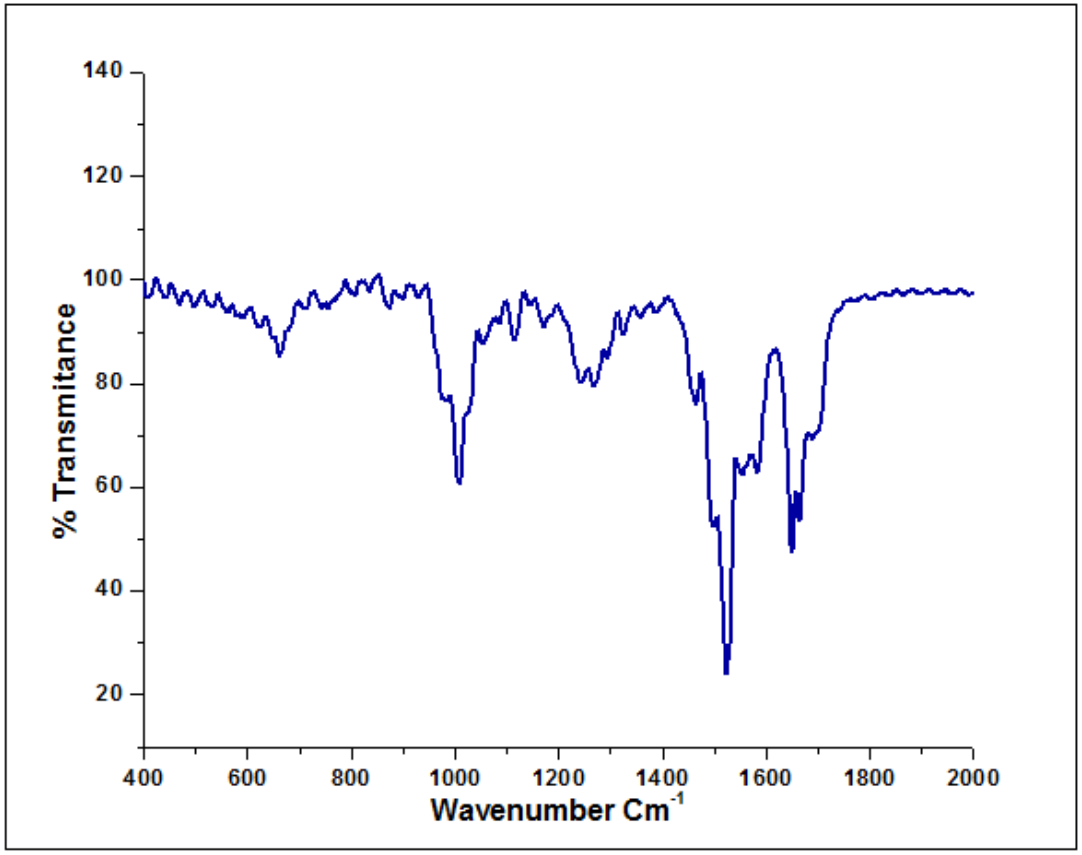
A correlation of the N‑H···O angle *vs.* H···O distance showed that all are in the strong hydrogen bonding interaction region of $d_{H\cdots O}$ < 2.5 A° and $d_{N\cdots O}$ < 3.5 Å.

Figure6S. Comparison of partial ^{1}H-NMR (300 MHz) spectra of (a) extracted mass (extraction of SO_4^{2-} with **L** + excess TBACl) and (b) **L** in presence of excess TBACl in $CDCl_3$ at 298 K.



In both the cases (a) and (b) the respective urea N-H protons (N-H^a and N-H^b) appear at same positions clearly indicate that sulfate was not extracting at all when extraction was done with **L** in presence of excess TBACL.

Figure7S. Partial (400-2000 Cm^{-1}) FT-IR spectra of extracted mass (extraction of SO_4^{2-} with **L** in presence of excess TBACl) in KBr discs



This FT-IR study on the extracted mass which showed no characteristic peak of SO_4^{2-} at 1100 cm^{-1} (symmetric stretching frequencies of sulfate) clearly showed no binding of SO_4^{2-} with L.

Figure8S. Comparison of partial ^{1}H-NMR (300 MHz) spectra of (a) **L** in presence of excess TBACl (b) extracted mass (extraction of SO_4^{2-} with **L** + 1 equivalent TBACl) and (c) complex **3** in $CDCl_3$ at 298 K.

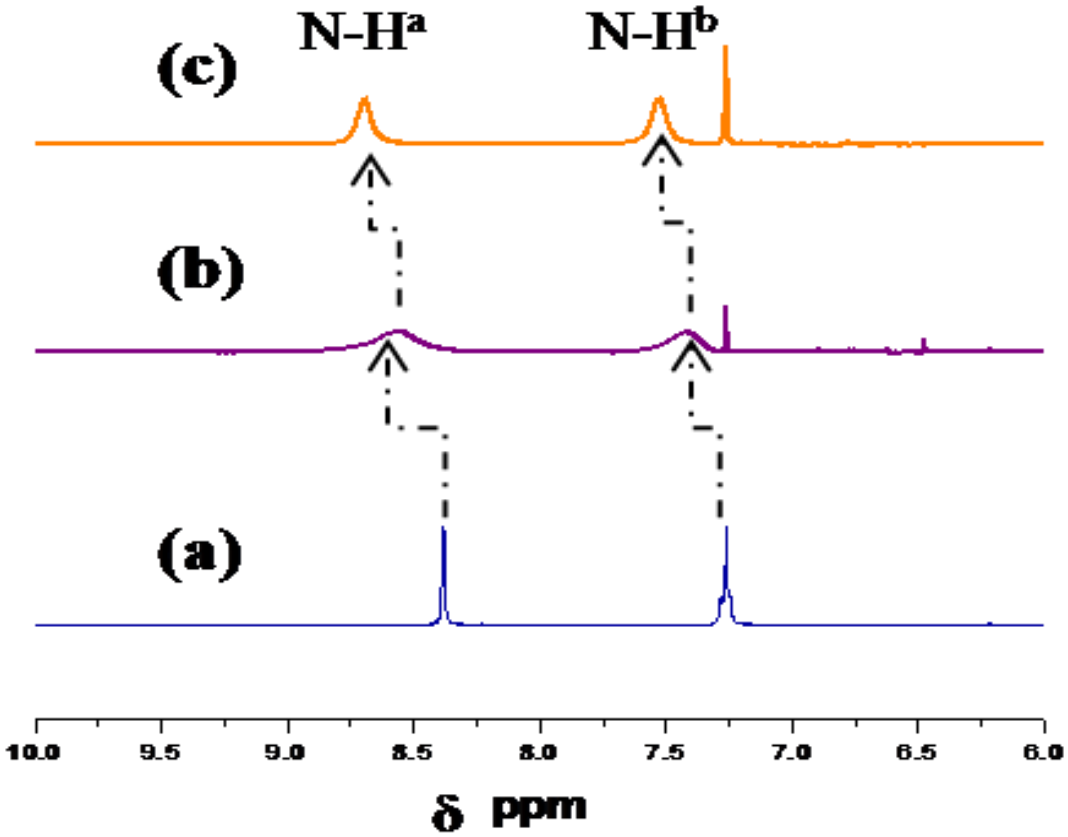


Figure9S. Energy Dispersive X-ray spectroscopy (EDX) of extracted mass (extraction of SO_4^{2-} with **L** + 1 equivalent TBACl), depicting the presence of Cl ions along with S ions**.**

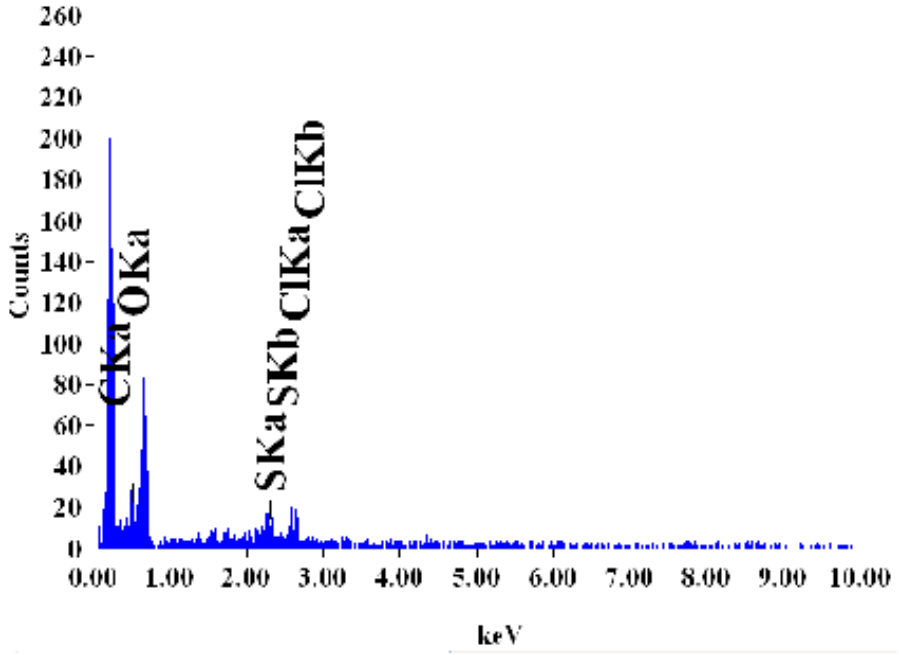
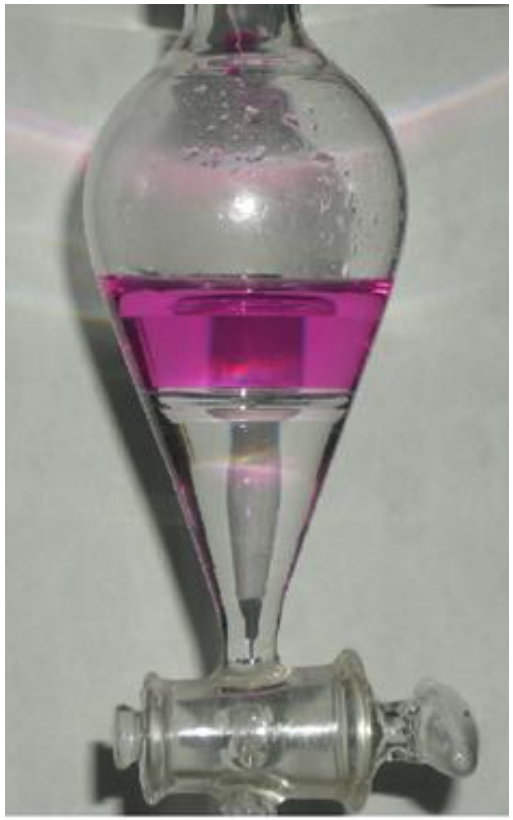
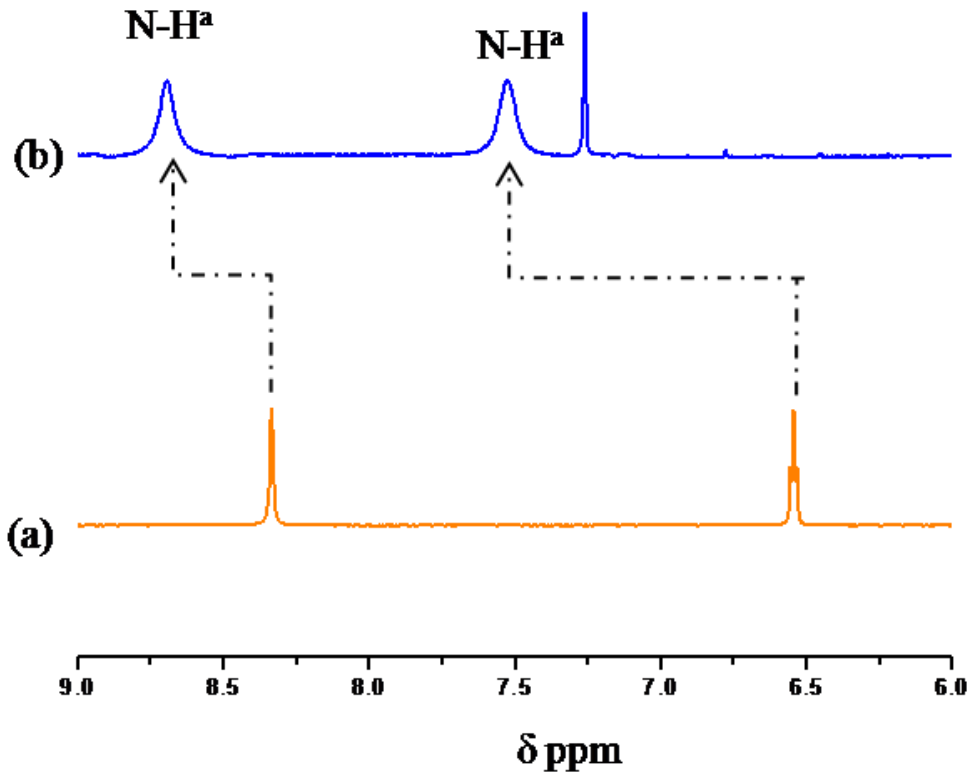


Figure10S. Visual detection of sulfate extraction (extraction of SO_4^{2-} with complex **4**)



The addition of phenolphthalein indicator to the aqueous layer showed a dark pink color supports its basic nature due to the exchange of carbonate anions from organic layer to aqueous layer and simultaneous transport of sulfate anions from aqueous to organic layer.

Figure11S. Comparison of partial ^{1}H-NMR (500 MHz) spectra of **L** in DMSO(d_6) with ^{1}H-NMR (300 MHz) spectra of complex **3** in $CDCl_3$ at 298 K.



^{1}H-NMR study of complex **3** shows a large downfield chemical shift of both the urea –NH signals ($\Delta\delta$= 0.34 and 0.98 ppm) *w.r.t.* **L**, indicative of sulfate encapsulation in the cleft of **L.**

Figure12S. ^{1}H-NMR (500 MHz, DMSO-d_6, 298 K) spectrum of complex **5**

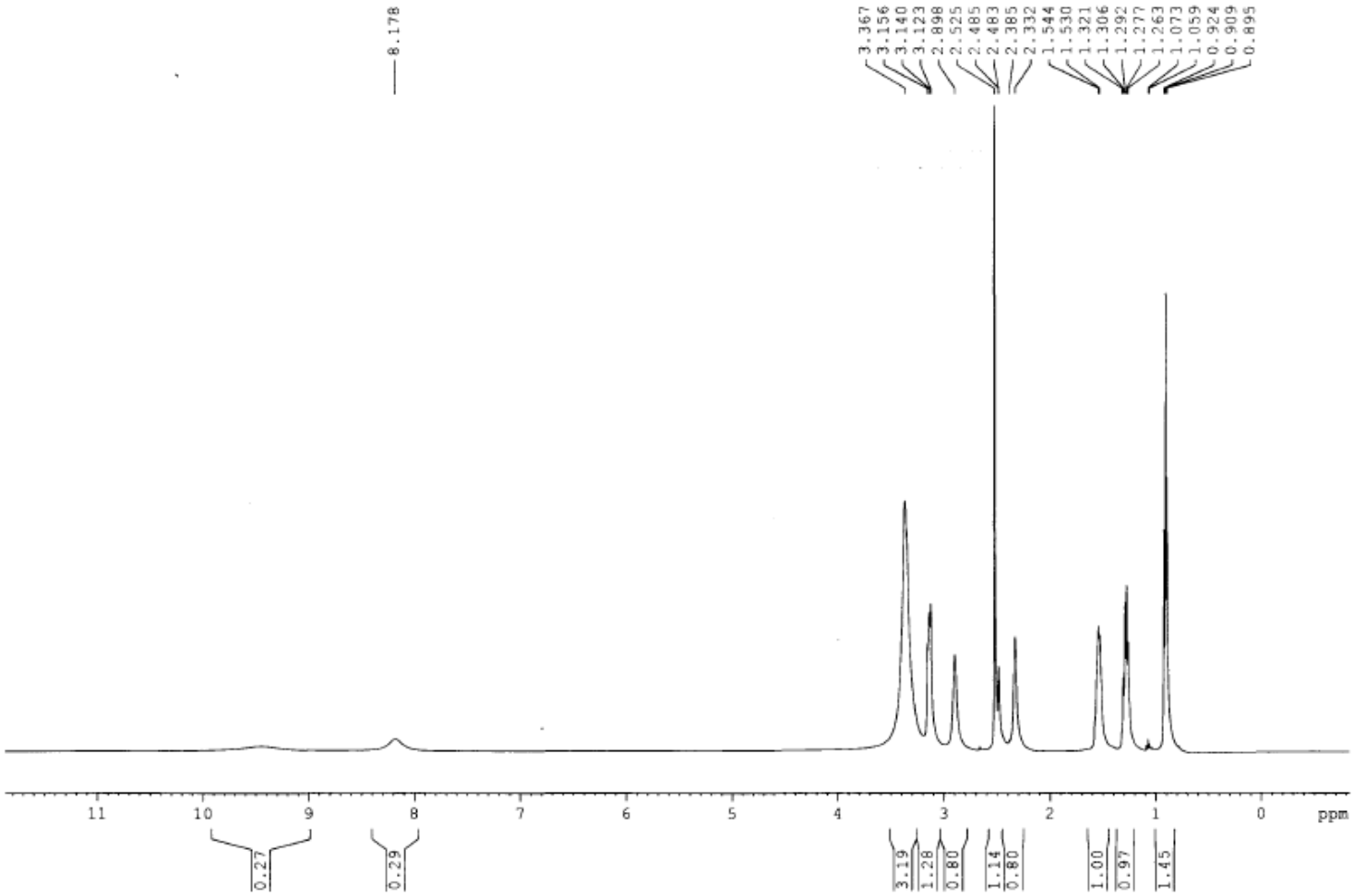


Figure13S. ^{13}C-NMR (500 MHz, DMSO-d_6, 298 K) spectrum of complex **5**

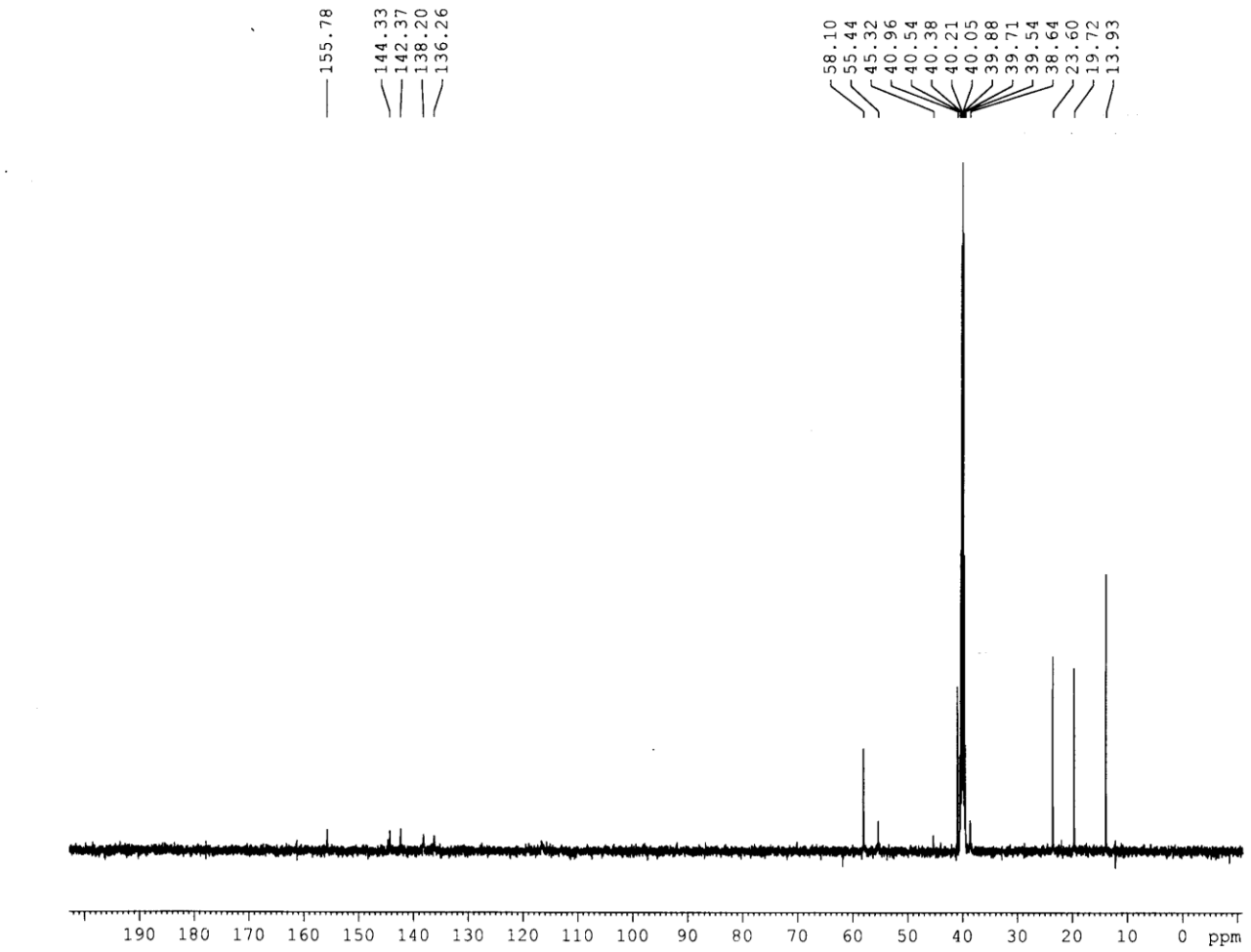


Figure14S. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) spectrum of complex **6**

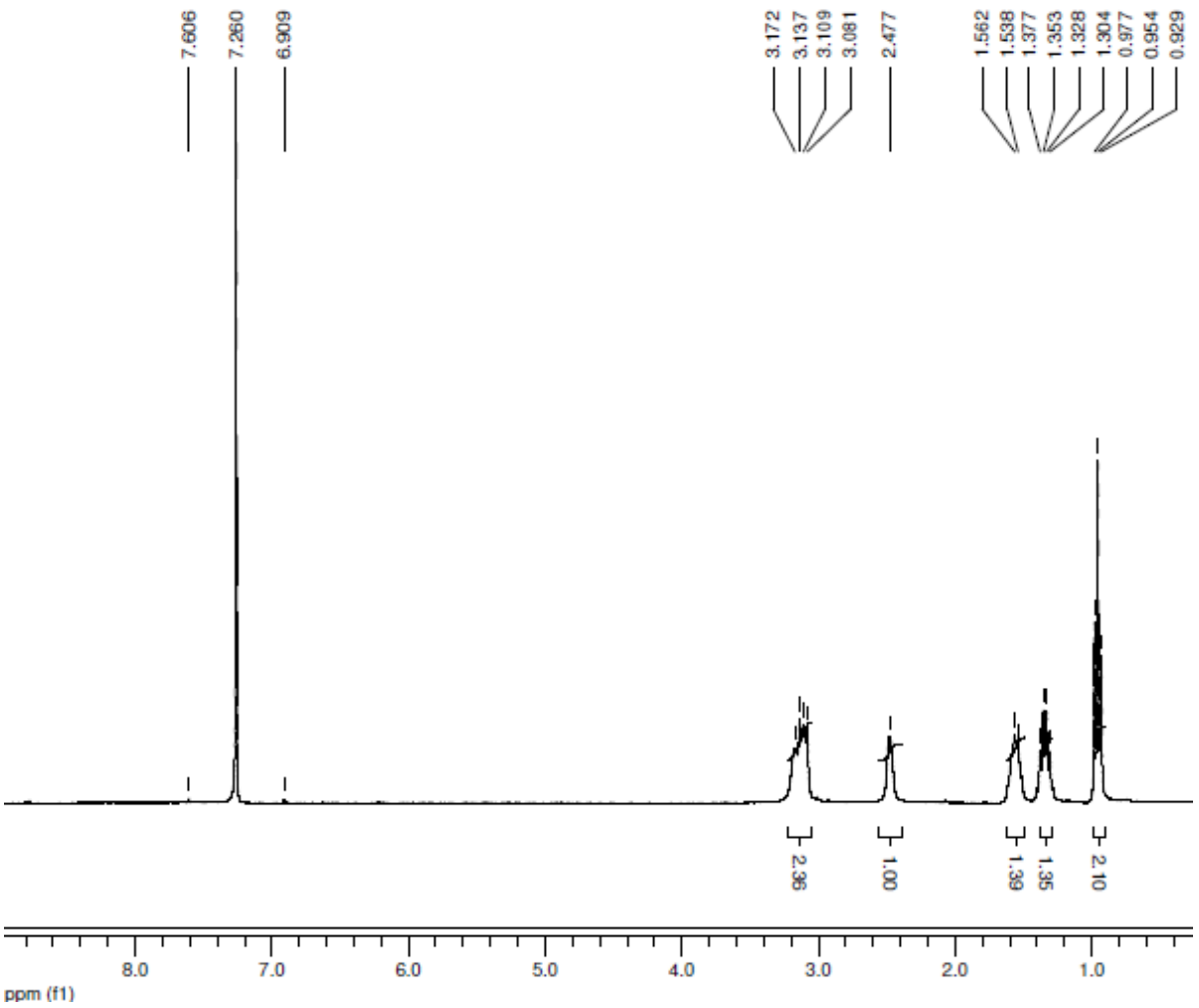


Figure15S. ^{13}C-NMR (300 MHz, $CDCl_3$, 298 K) spectrum of complex **6**

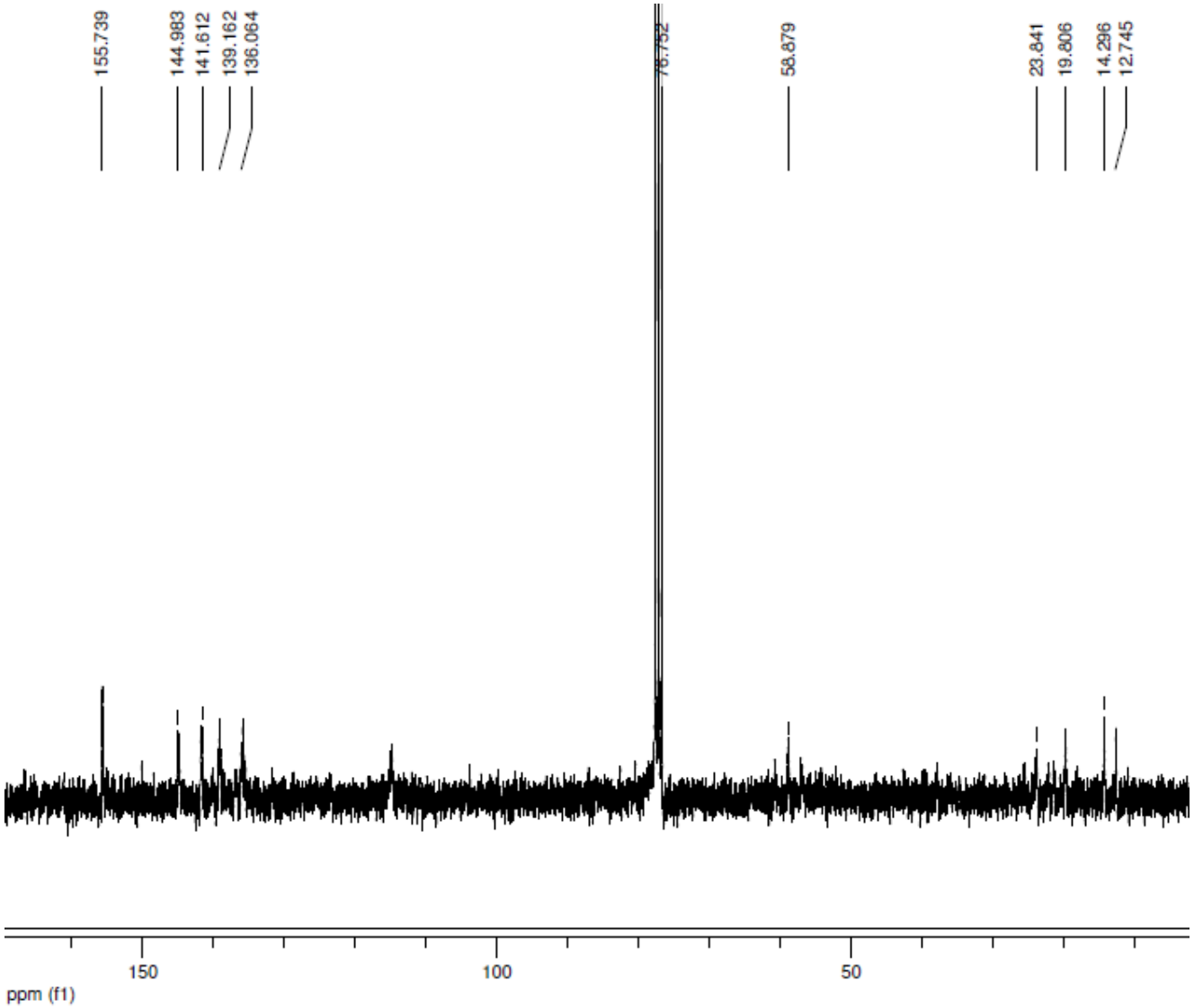


Figure16S. ^{19}F-NMR (500 MHz, $CDCl_3$, 298 K) spectrum of complex **6**

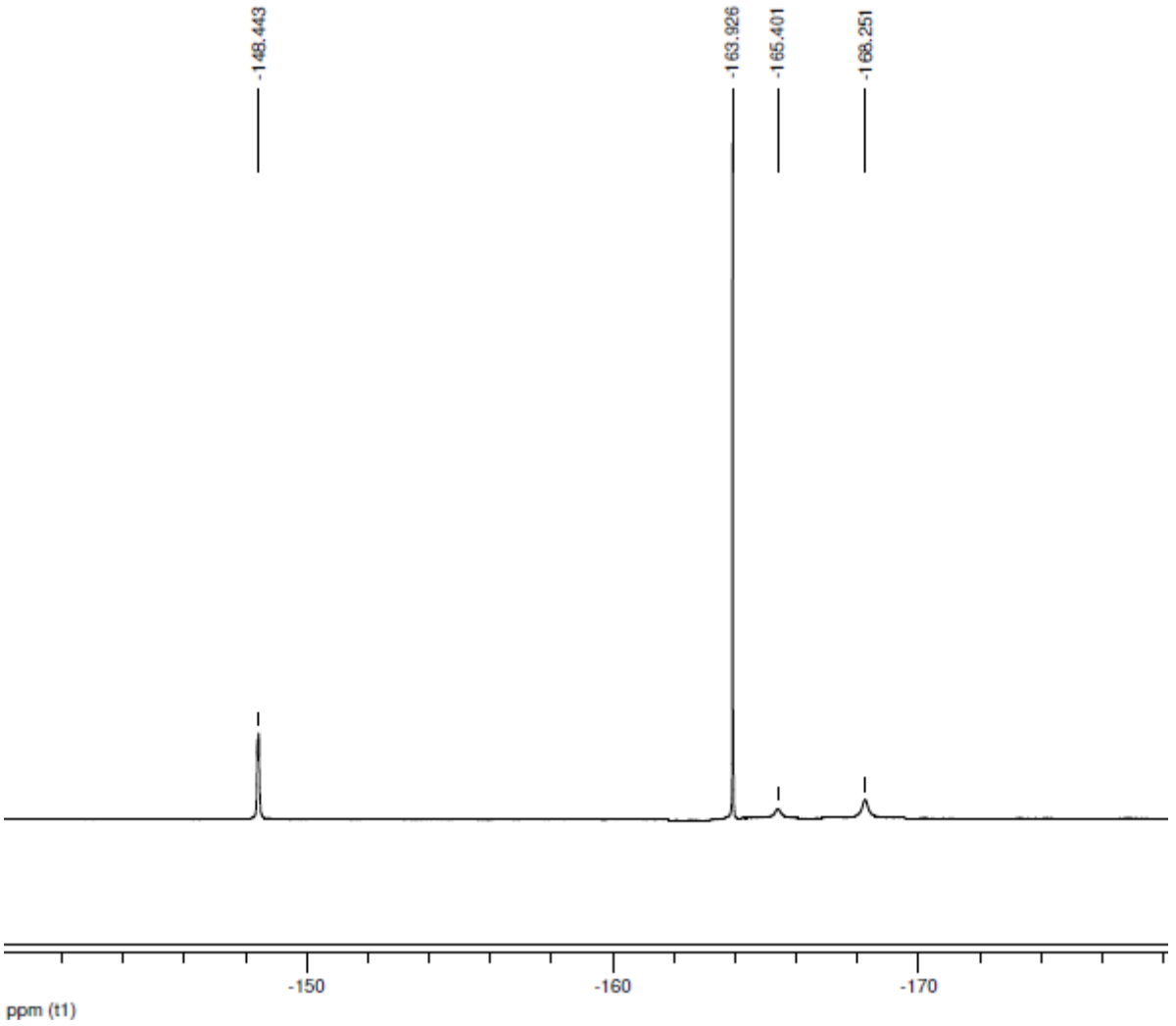


Figure17S. Partial ^{31}P NMR spectra (500 MHz, DMSO-d_6, 298 K) of *n*-$Bu_4NH_2PO_4$ and downfield shift of ^{31}P resonance upon addition of **L**

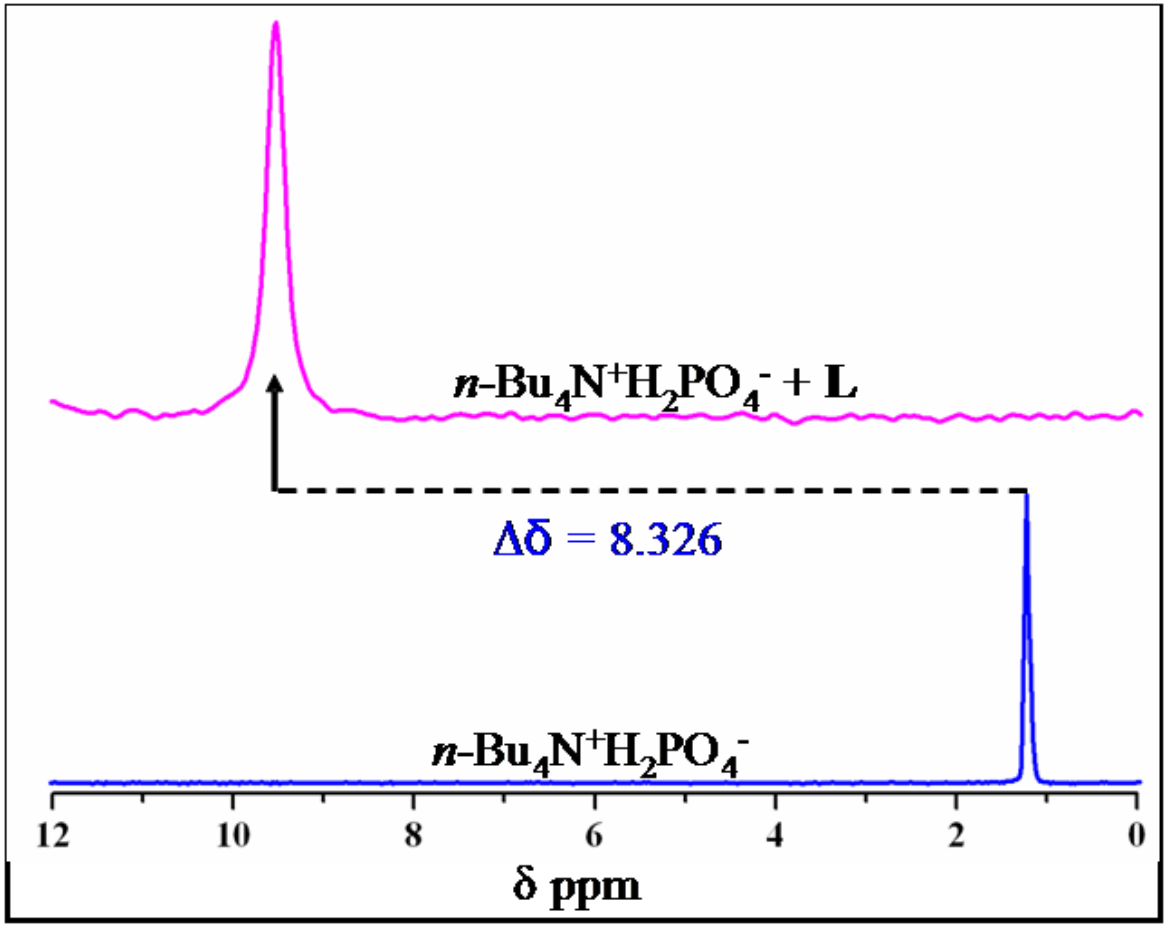


Figure18S. Partial ^{31}P NMR spectra (500 MHz, DMSO-d_6, 298 K) of *n*-$Bu_4NH_2PO_4$ + *n*-Bu_4NOH and downfield shift of ^{31}P resonance upon addition of **L**

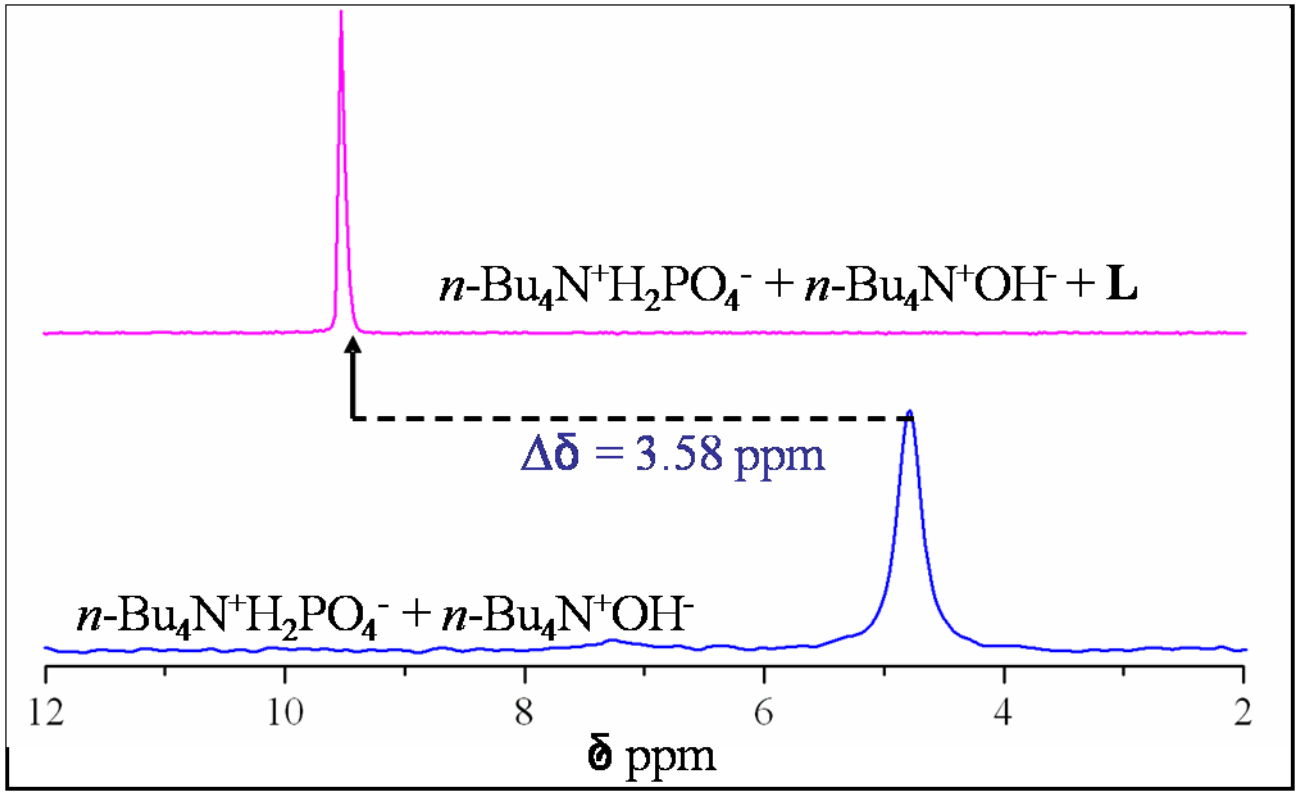


Figure19S. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) spectrum of **L** in presence excess TBACl.

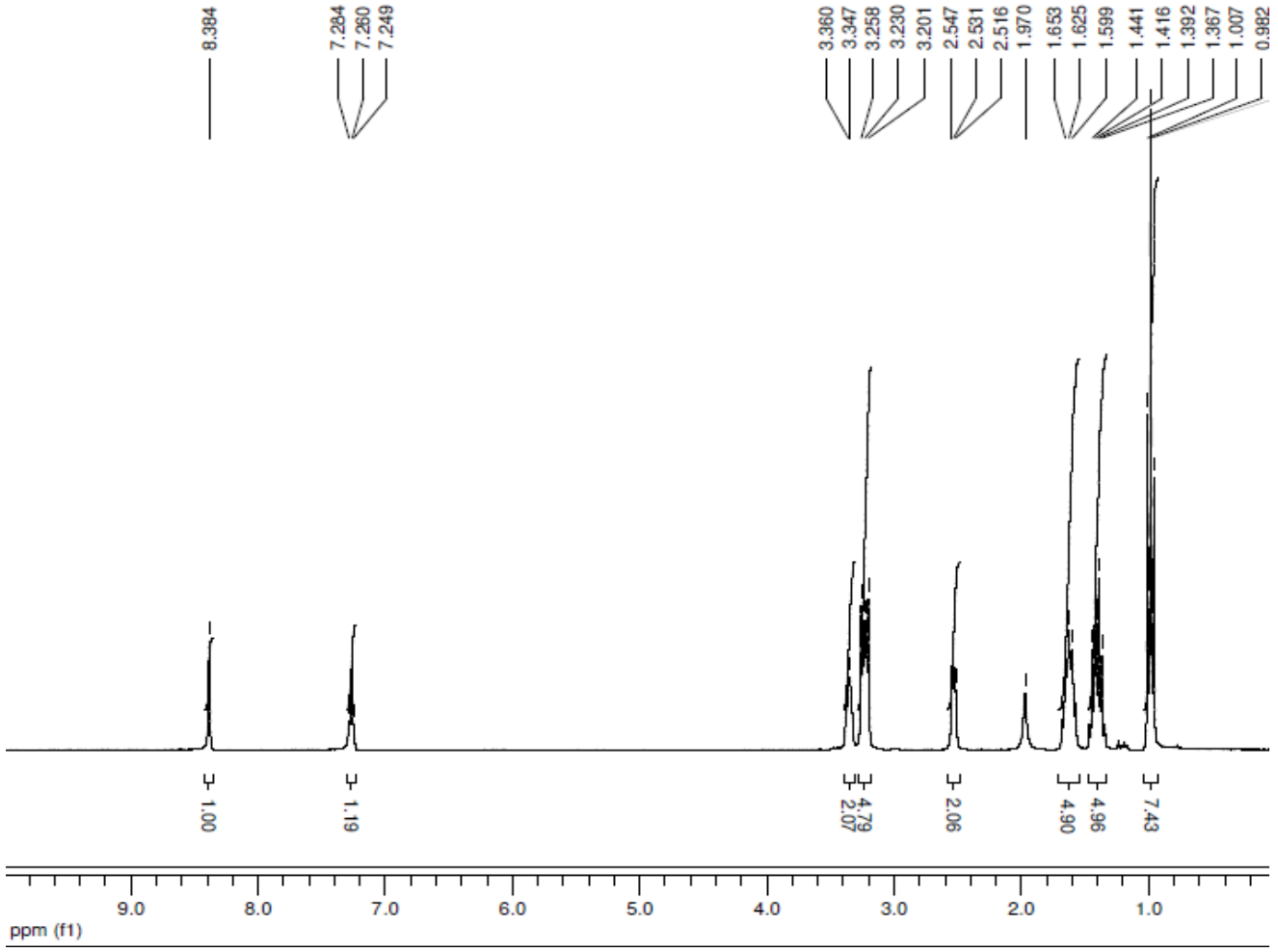


Figure20S. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) spectrum of extracted mass (extraction of SO_4^{2-} with L in presence of excess TBACl)

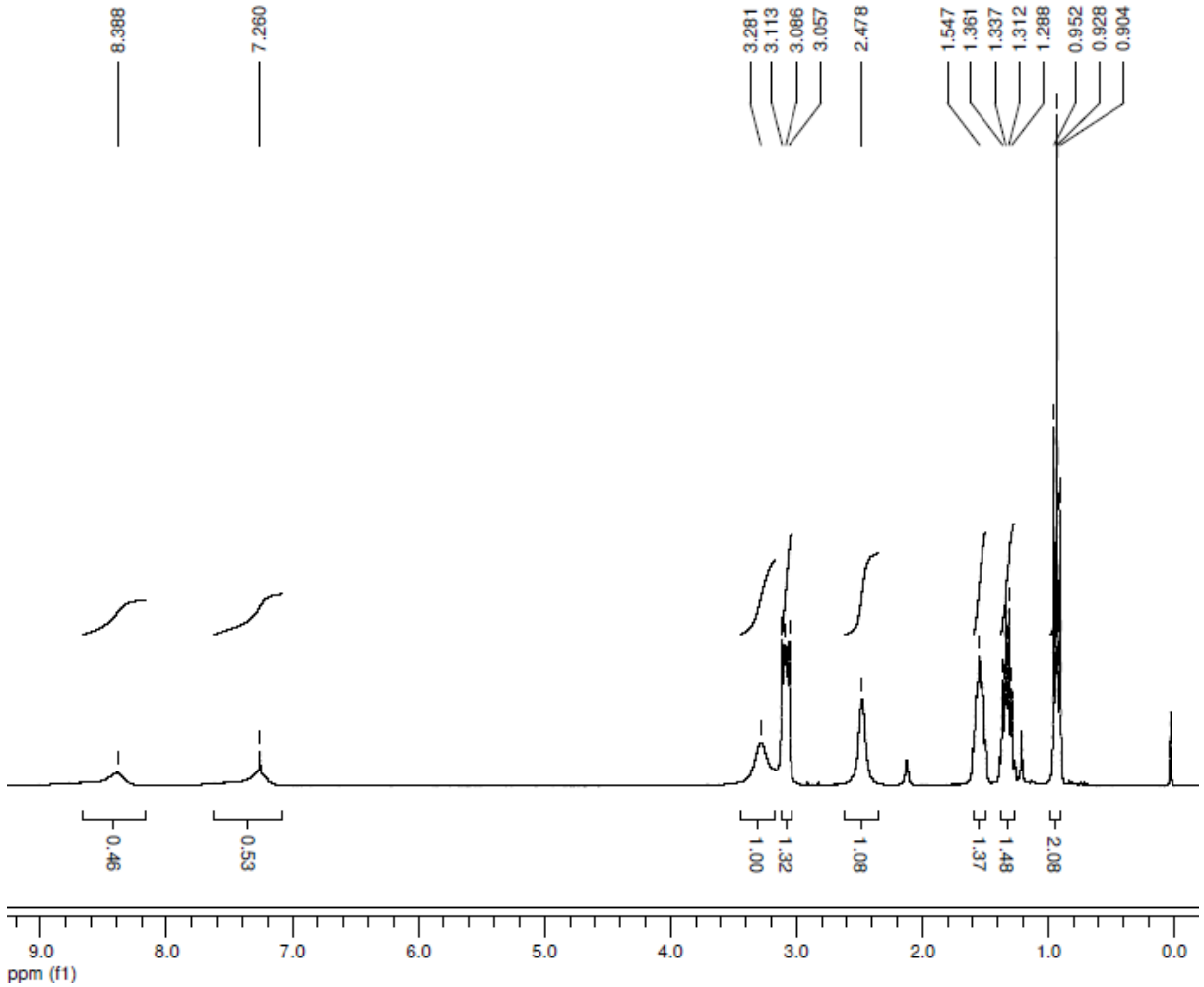


Figure21S. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) spectrum of extracted mass (extraction of SO_4^{2-} with **L** in presence of 1 equivalent TBACl)

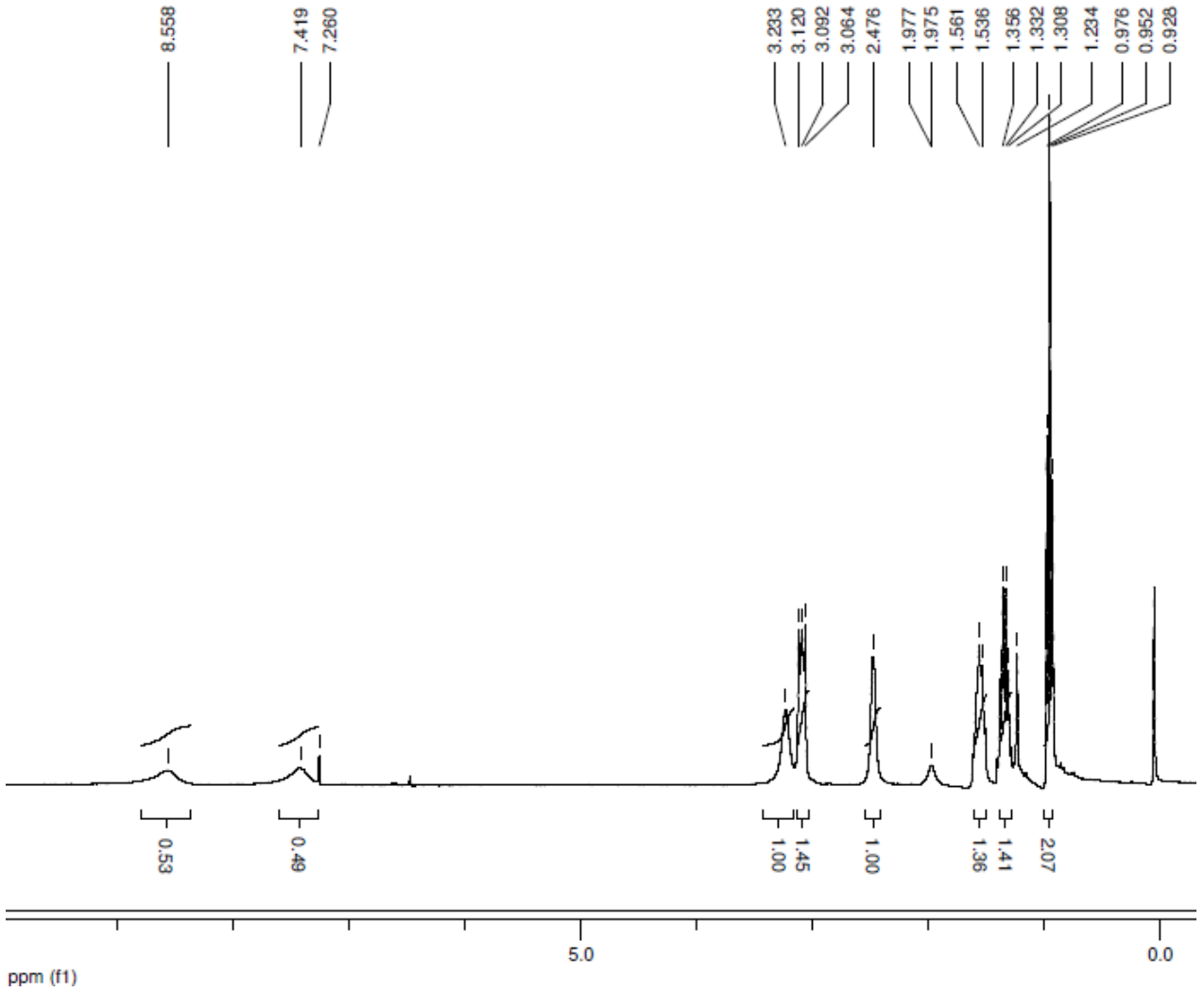


Figure22S. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) spectrum of complex **3**

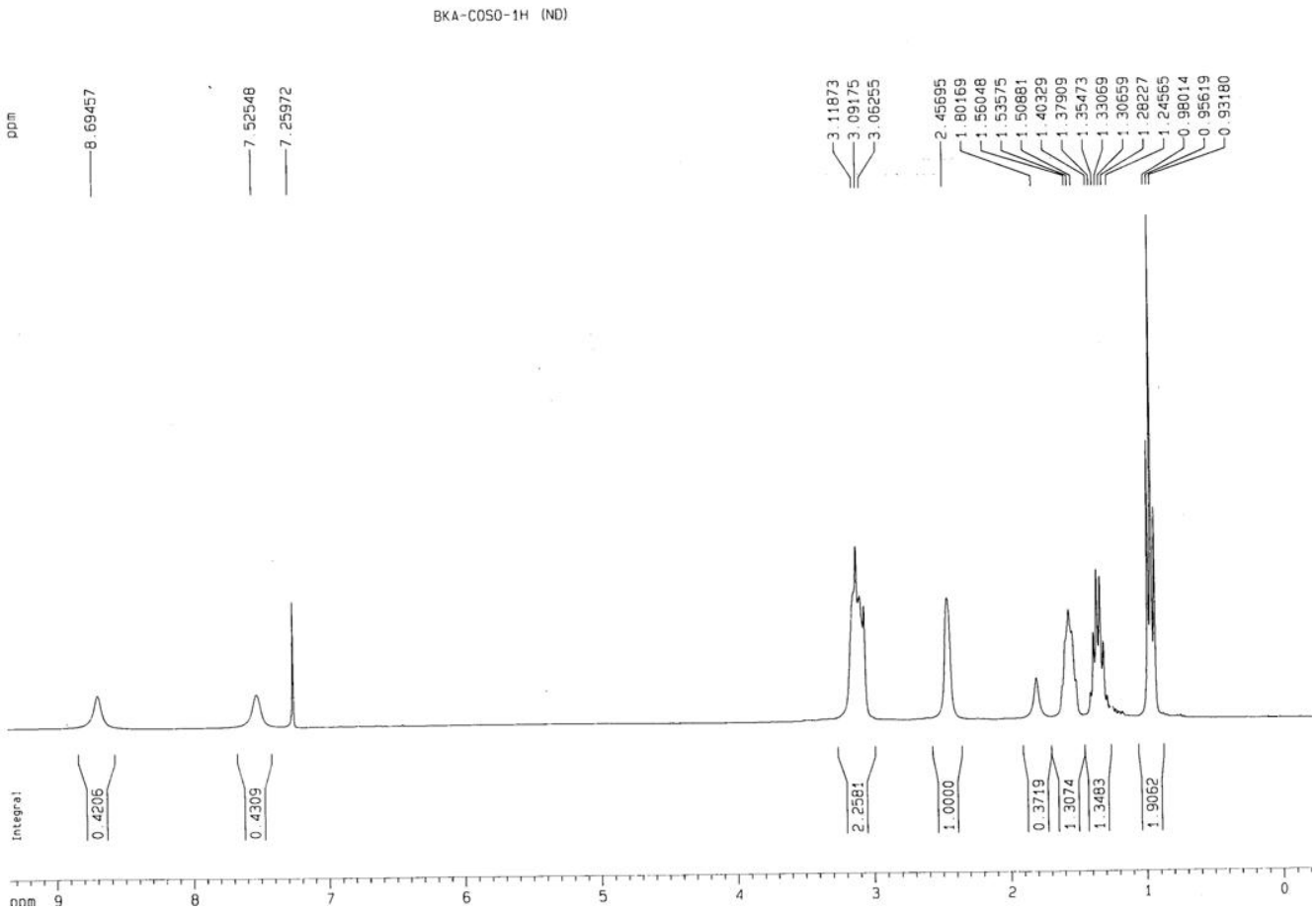


Figure23S. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) spectrum of extracted mass (extraction of SO_4^{2-} with complex **4**)

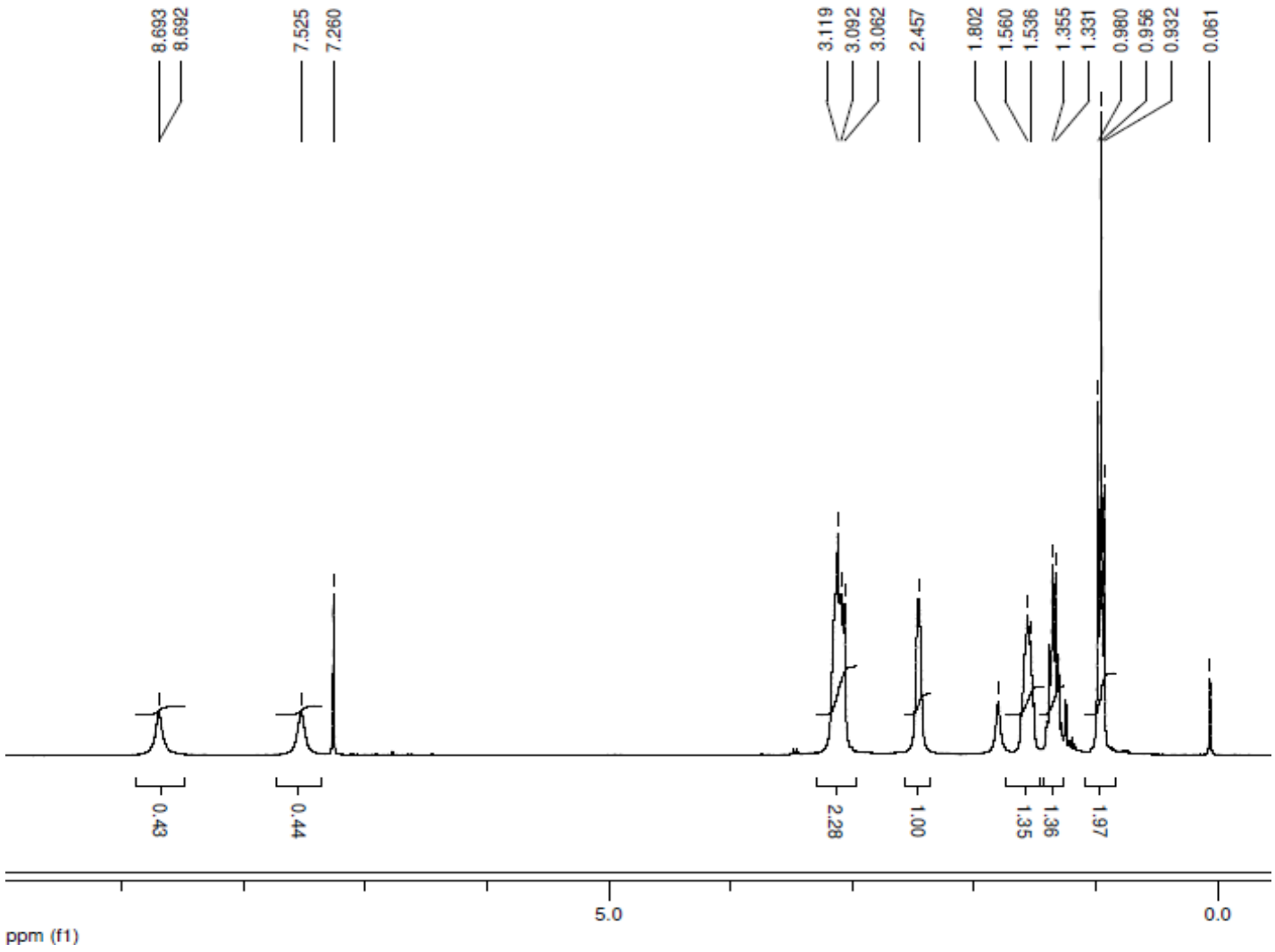
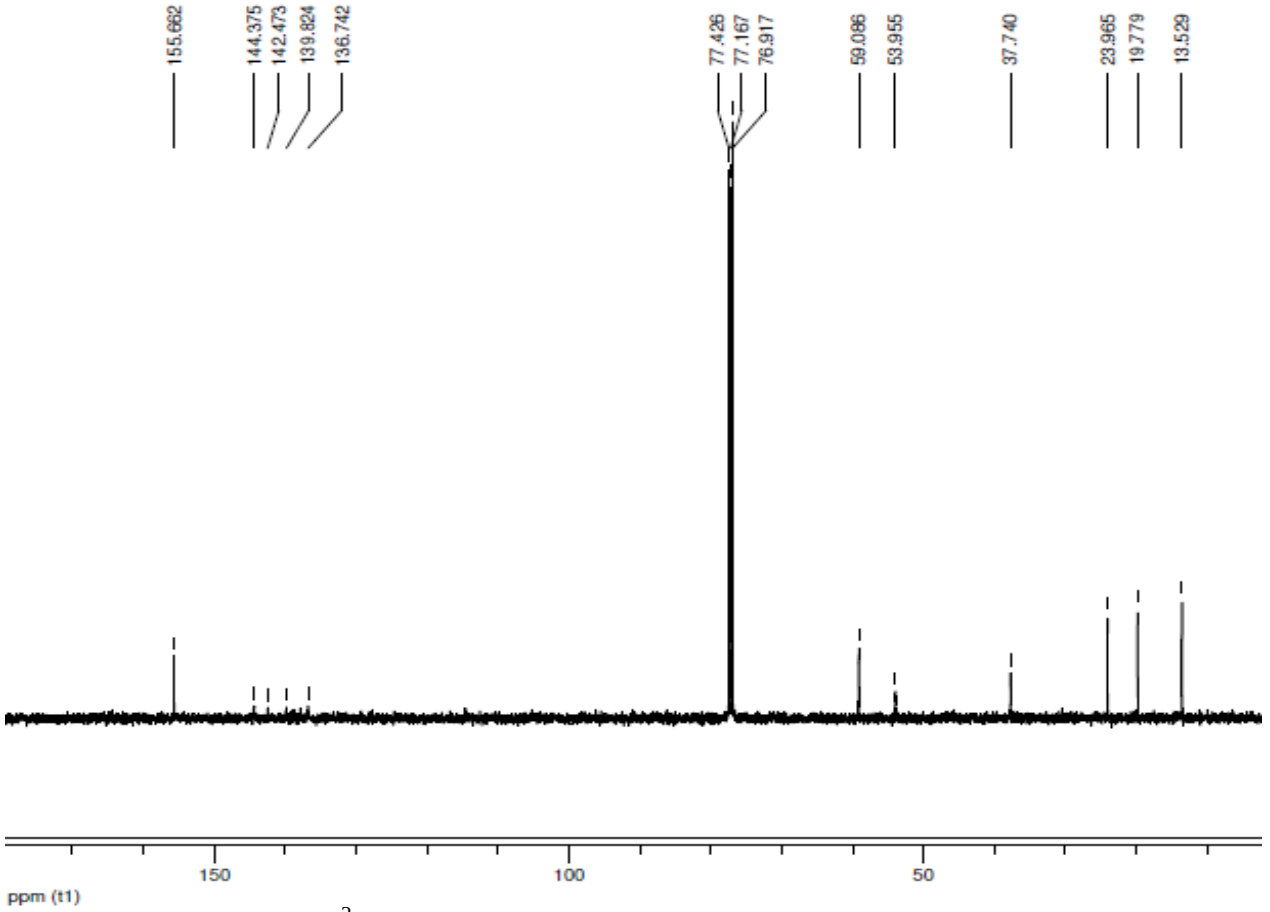


Figure24S. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) spectrum of extracted mass (extraction of SO_4^{2-} with complex **4**)



The absence of peak at 269.63 (carbon atom of CO_3^{2-}) depicted the 100% conversion of carbonate complex **4** to sulfate complex **3**.

Figure25S. After $BaSO_4$ precipitation ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) spectrum of Cl^- containing extracted mass.

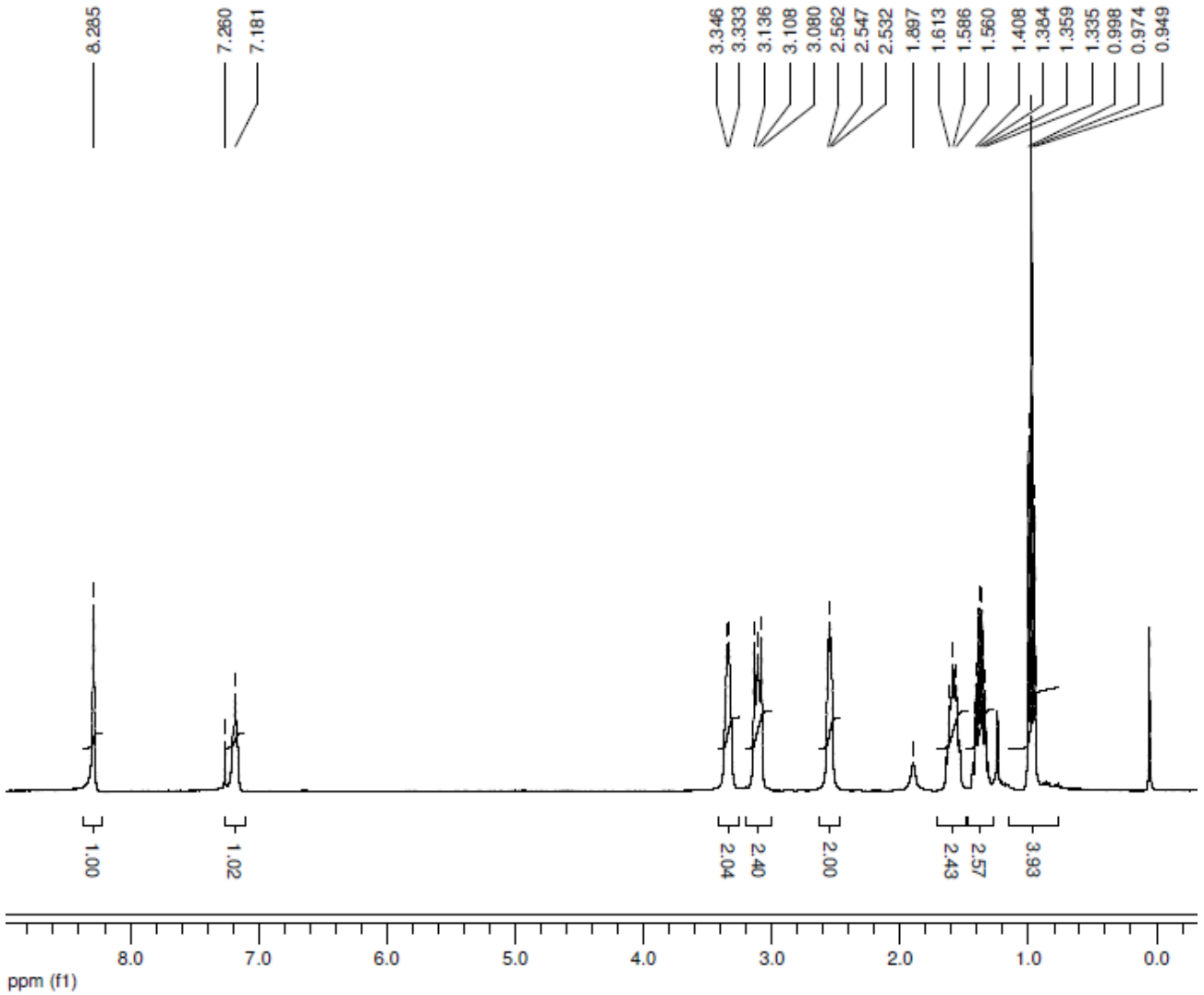


Figure26S. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) spectrum of extracted mass (extraction of SO_4^{2-} with Cl^- containing $CHCl_3$ solution obtained up on $BaSO_4$ precipitation)

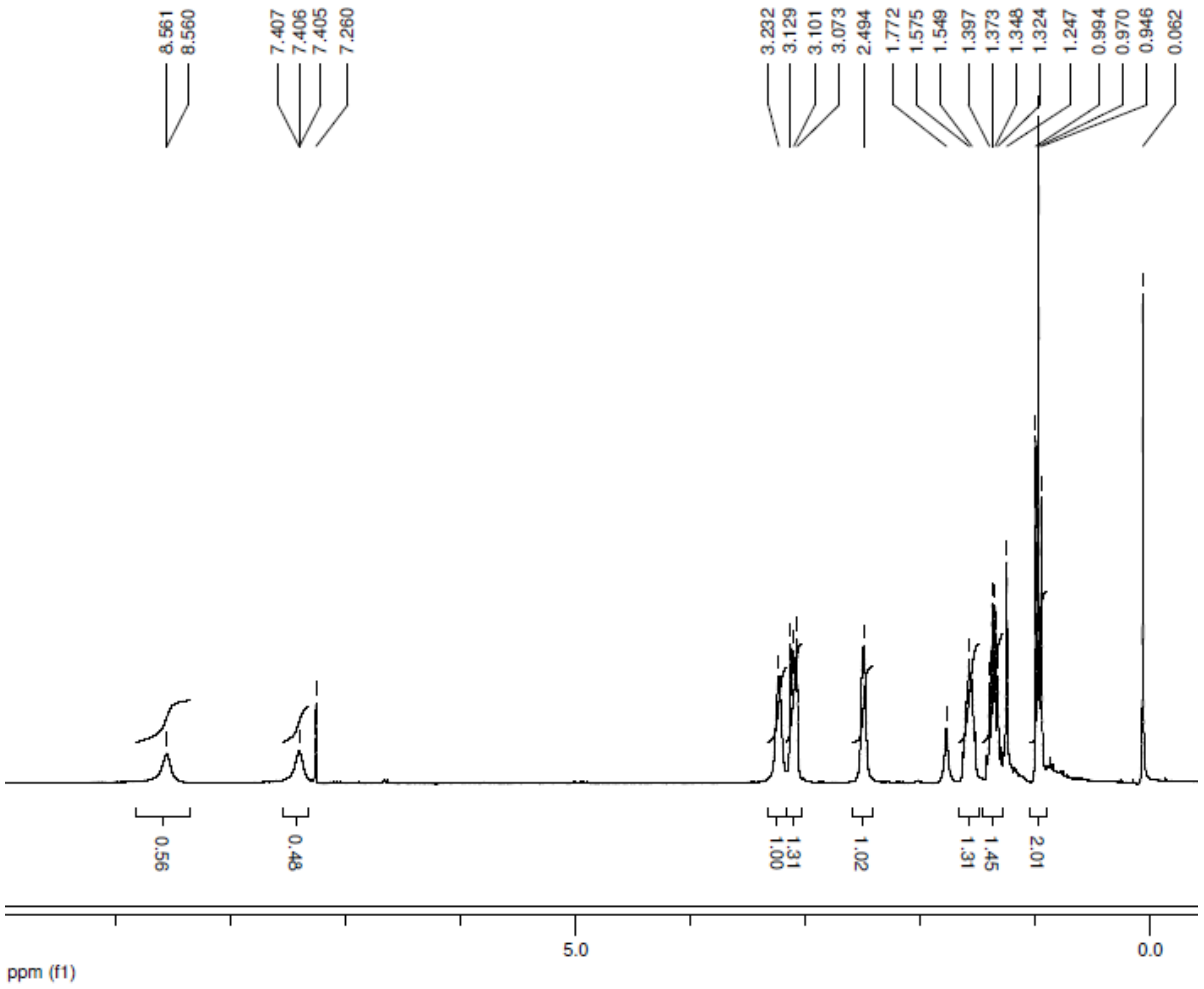
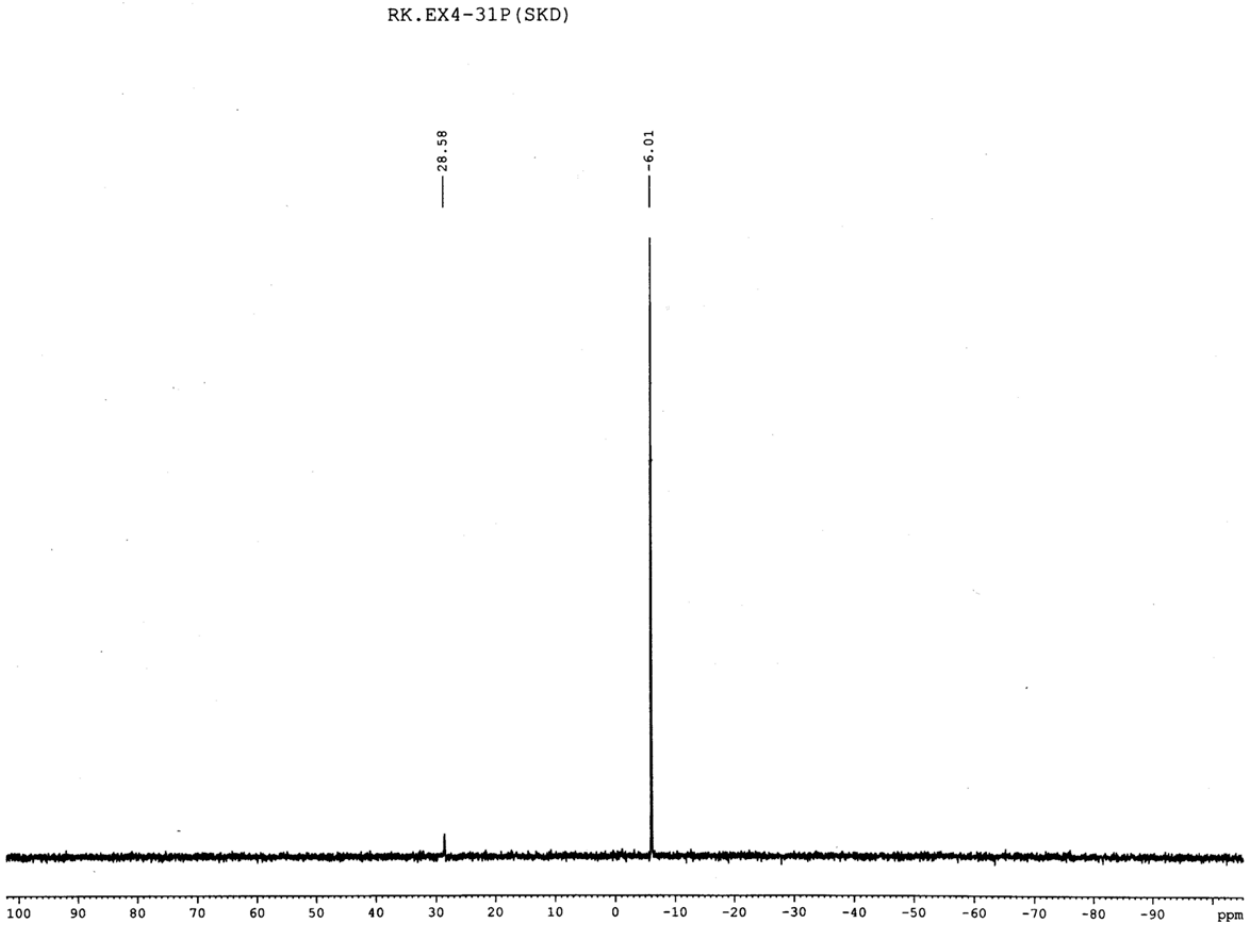


Figure27S. ^{31}P-NMR (500 MHz, DMSO (d_6), 298 K) spectrum of extracted mass (extraction of SO_4^{2-} with complex **4** in presence of equivalent amount of KH_2PO_4)



References:

1) Lakshminarayanan, P. S.; Ravikumar, I.; Suresh, E.; Ghosh, P. *Chem. Commun.* **2007**, 5214.

2) SAINT and *XPREP*, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995. G. M. Sheldrick.

2) *SADABS, empirical absorption Correction Program*; University of Göttingen: Göttingen, Germany,1997.

4) G. M. Sheldrick, *SHELXTL Reference Manual:* V*ersion 5.1*; Bruker AXS: Madison, WI, 1997.

5) G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

6) A. L. Spek, *PLATON-97*; University of Utrecht: Utrecht, The Netherlands, 1997.

7) Mercury 2.3 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2006.