Supporting Information

Arsenate recognition in aqueous media by a simple tripodal urea

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MATERIALS AND METHODS

Materials: Tris-(2-aminoethyl)-amine (TREN), pentafluorophenyl isocyanate, tetrabutylammonium iodide were purchased from Sigma-Aldrich and were used as received. Dichloromethane (DCM) was freshly distilled with Calcium hydride. Sodium hydrogenarsenate (Na_2HAsO_4), sodium sulfate (Na_2SO_4) and sodium dihydrogenphosphate (NaH_2PO_4) were purchased from Merck, India and were used as received. All solvents were procured from Merck.

Methods: FTIR was recorded on SHIMADZU FTIR-8400S infrared spectrophotometer with KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a 500/300 MHz and 125/75 MHz BrukerDPX-500 MHz NMR and BrukerAvance300 Spectrometer. Transmission Electron Microscope-Energy Dispersive X-ray (TEM-EDX) analyses were carried out on a JEOL JEM-2010 electron microscope operated at an accelerating voltage of 100 kV. pH measurements are performed in Metrohm glass electrode.

^{1}H-NMR titration studies: All ^{1}H-NMR titration experiments for **L** with different anions were conducted on a Bruker300 MHz at 298 K respectively. Stock solution of host was prepared in DMSO-*d*$_6$:D_2O (9:1, v/v) solvent mixture. Sodium salts of arsenate ($HAsO_4^{2-}$), sulfate (SO_4^{2-}), dihydrogenphosphate ($H_2PO_4^-$) and carbonate (CO_3^{2-}) were used to prepared the stock solution of anion in DMSO-*d*$_6$: D_2O (1:1.1) solvent system. To evaluate the association constants and stoichiometry of binding in cases of these four anions with **L**, ^{1}H-NMR titrations were performed at 298 K. Aliquots of anions were added from a standard stock solution of anion to the solution of **L**. The association constants, *K*, were calculated by fitting the change in the CH_c chemical shift with a 1:1 association model with non-linear least square analysis. Job's plot revealed a best fit for 1:1 host to guest binding mode.The equation $\Delta\delta = \{([A]_0+[L]_0+1/K)\pm(([A]_0+[L]_0+1/K)^2-4[L]_0[A]_0)^{1/2}\}\Delta\delta_{max}/2[L]_0$ was used for calculating association constants.

pH measurement experiment:

GC grade dimethyl sulfoxide (DMSO) and double distilled water is used for all the pH measurement experiment. Stock solution of anion i.e. arsenate and phosphate are buffered by mixing borax (10 mM)/boric acid (200 mM) in DMSO-H_2O (1:1.1, v/v) solvent mixture. Solution of **L** is buffered by mixing borax (2 mM)/boric acid (200mM) in DMSO-H_2O (9:1, v/v) solvent mixture. Na_2HAsO_4 and NaH_2PO_4 salts are used to prepare the stock solution of respective anion. Further the concentration of anion is maintained as that the scale of ^{1}H NMR titration experiment scale i.e 30 mM for anion and ~ 3 mM for **L**. The pH of buffered stock solution for arsenate and phosphate are measured as 9.5 and 8.5 respectively. All the pH experiments are performed thrice.

X-ray Crystallography: Crystals suitable for single crystal X-ray diffraction studies were 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 crystals of complex **1**was collected using MoK_α (λ = 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 SAMRT 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. Graphics were generated using PLATON[6]and MERCURY 2.4.[7]The non-hydrogen atoms were refined anisotropically till the convergence. In the case of complex **1**, all the hydrogen atoms were located from the difference Fourier map and refined isotropically. One tetrabutylammonium cation and one dimethyl sulfoxide solvent molecules in complex **1** are disordered. Disordered S1 atoms of the dimethyl sulfoxide over three positions are treated by FVAR command. C72, C73, C74, C79, C81, C84, C85, C86, C87 and C88 are isotropically refined. CCDC-**910790** (complex **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

SYNTHESIS

Synthesis of Complex **1**:60 mg (0.08 mmol) of **L** was dissolved in DMSO/H_2O (20:1 v/v) and then 58 mg (2 equiv.) of *n*-$Bu_4N^+I^-$and excess $Na_2HAsO_4$was added to the above solution. Then the mixture was stirred at room temperature for 10 minutes and then heated to 60ºC. The mixture was then filtered allowed to evaporate for crystallization. After 3-4 days, colorless diamond like crystals of complex [$\mathbf{L}_2(HAsO_4^{2-})\cdot(n\text{-}Bu_4N^+)_2.(DMSO)_2$] (**1**) suitable for single crystal X-ray diffraction analysis were obtained in 80% yield. ^{1}H NMR (500 MHz, DMSO-*d*$_6$):δ 0.927 (t, 12H,$NCH_2CH_2CH_2CH_3$,*J*= 7.25 Hz), 1.294-1.322 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.558 (8H, $NCH_2CH_2CH_2CH_3$), 2.375 (6H, NCH_2CH_2), 2.950 (6H, NCH_2CH_2), 3.134-3.168 (m, 8H, $NCH_2CH_2CH_2CH_3$), 8.041 (br, 3H, N*H*$_b$), 9.506(br, 3H, N*H*$_a$); ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ 13.4 (NCH2CH2CH2*C*H3), 19.2(NCH2CH2*C*H2CH3), 23.0 (NCH2*C*H2CH2CH3) 38.1(N*C*H2), 54.8 (NCH2*C*H2), 57.5 (N*C*H2CH2CH2CH3), 115.8 (m of s, Ar*C*CF, J_{CCF} = 15.3 Hz), 134.8-135.7 (m of d, Ar*C*F),138.2-138.9 (m of d, Ar*C*F), 140.9-141.2 (m of d, Ar*C*F), 144.3-144.5 (m of d, Ar*C*F), 155.2 (s, *C*=O).

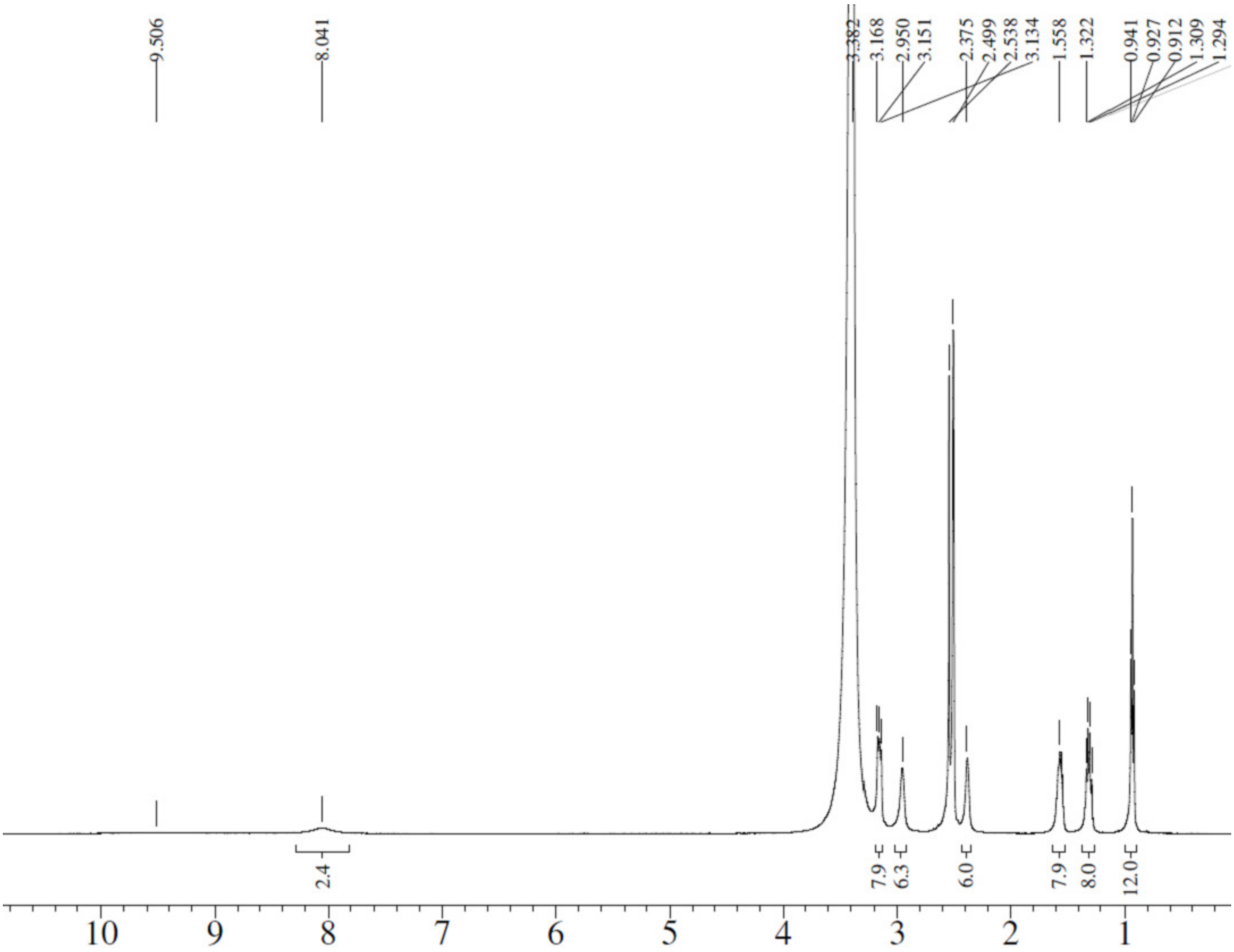


Fig. 1S. ^{1}H-NMR spectra of complex **1** in DMSO-d_6 at 298K.

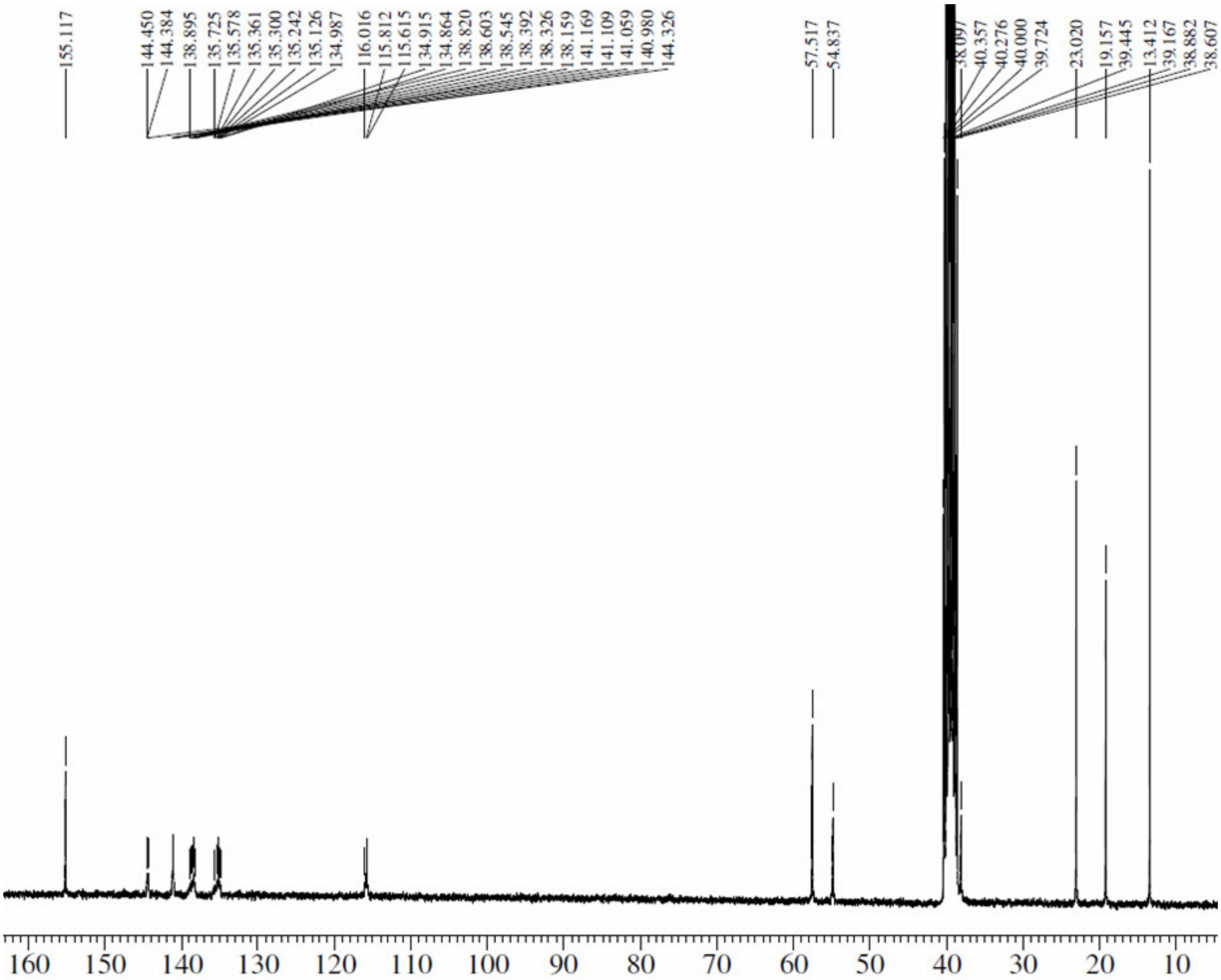


Fig. 2S. ^{13}C-NMR spectra of complex **1** in DMSO-d_6 at 298K.

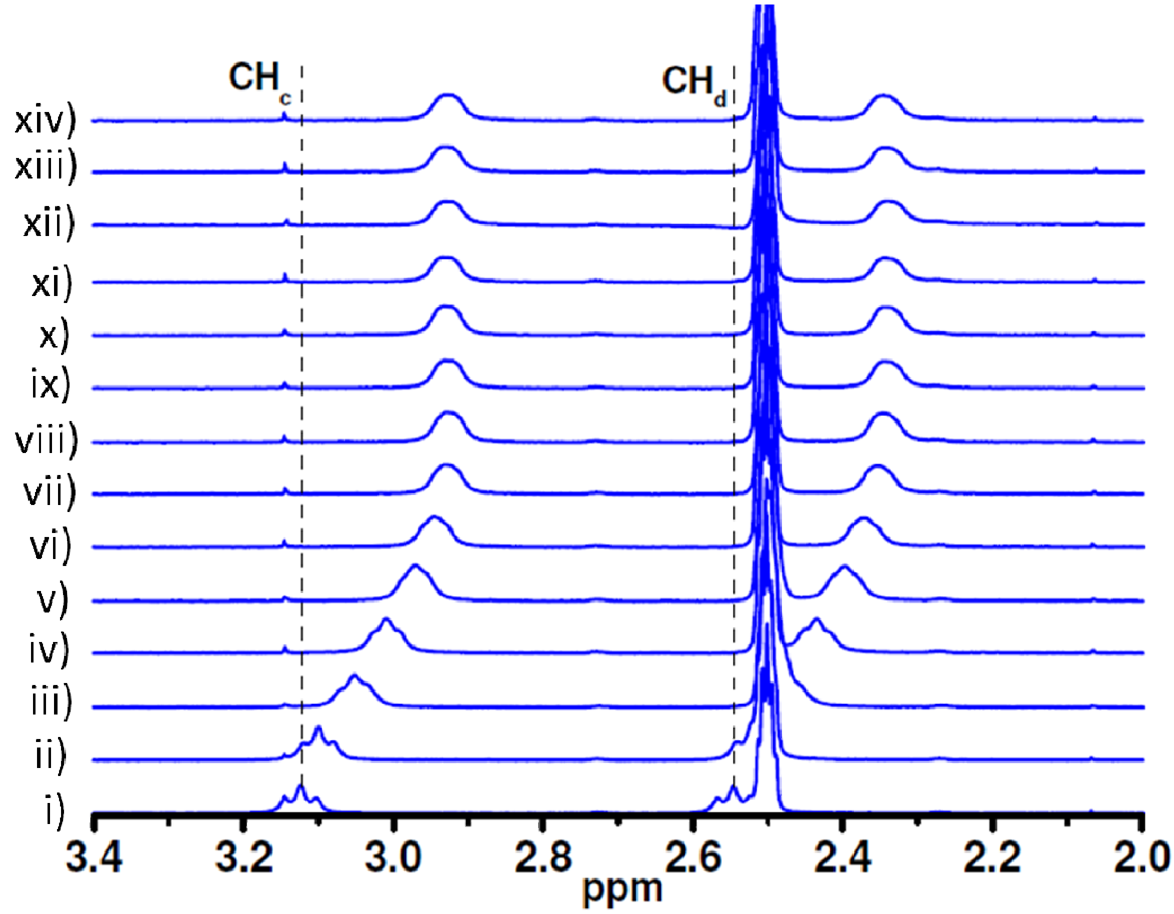


Fig. 3S. Partial ^{1}H-NMR (300 MHz) spectral changes of **L** in DMSO-d_6/D_2O(9:1)(v/v) with added standard Na_2HAsO_4 solution in DMSO-d_6/D_2O (1:1.1)(v/v) ([**L**]$_0$ = 27.97mM). Ratio of concentration [$HAsO_4^{2-}$]/[**L**]: (i) 0, (ii) 0.19, (iii) 0.38, (iv) 0.57, (v) 0.77, (vi) 0.96, (vii) 1.15, (viii) 1.34, (ix) 1.53, (x) 1.72, (xi) 2.30, (xii) 3.06, (xiii) 4.12 and (xiv) 4.50 ([**L**] is varied from 2.92 to 1.99 mM by the addition of aliquots of 27.97mM Na_2HAsO_4).

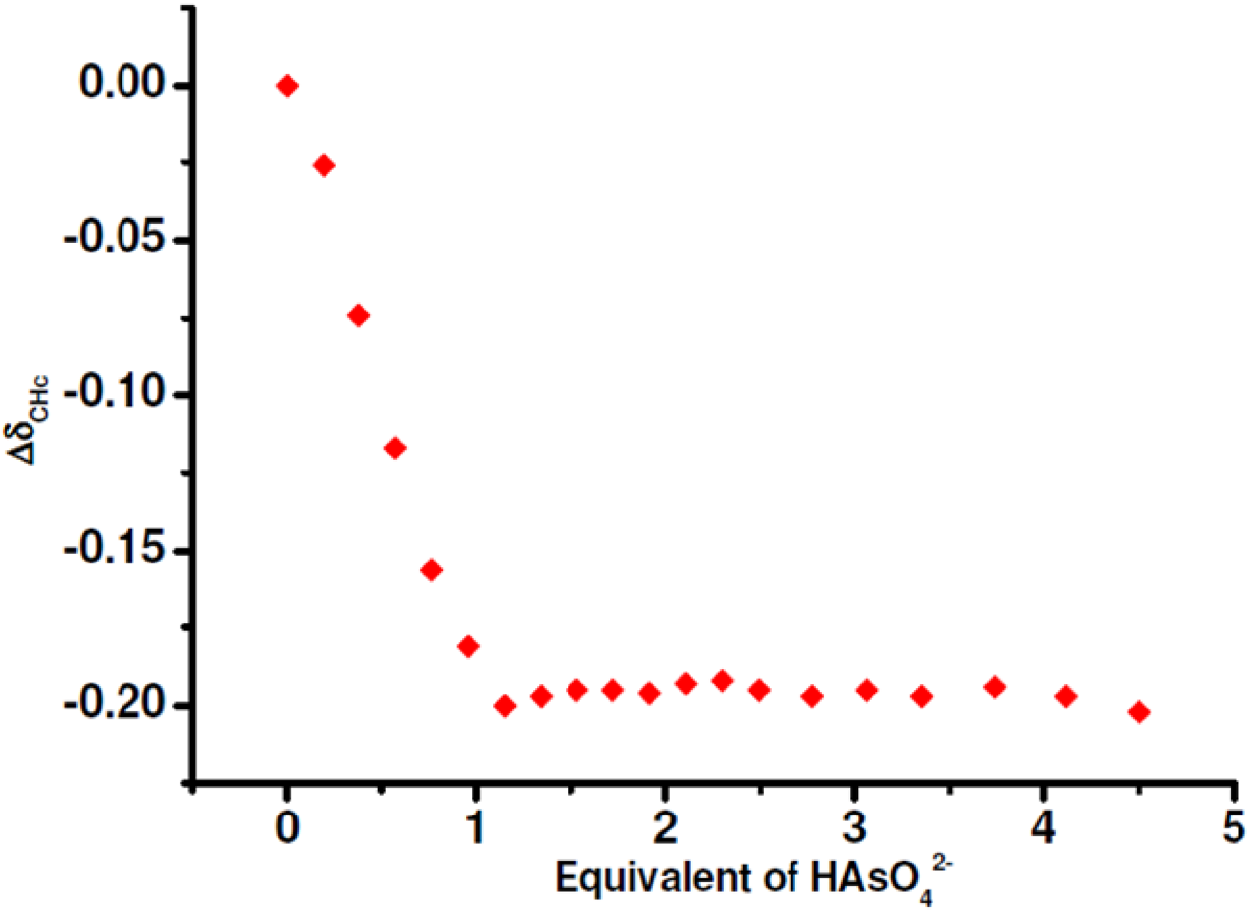


Fig. 4S. Plot shows the change in chemical shift of the –CH_c of **L** with increasing amounts of standard Na_2HAsO_4 solution at 298K.

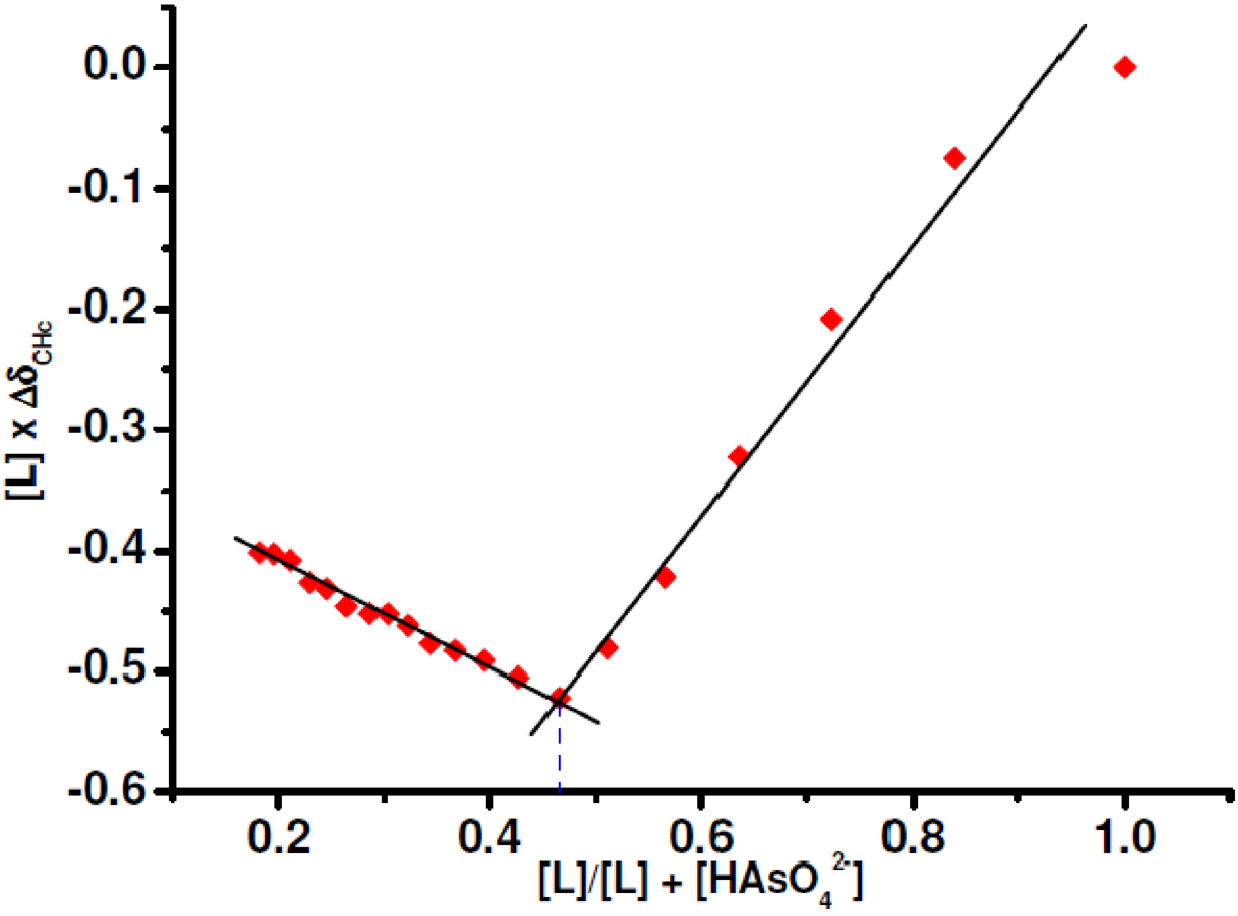


Fig. 5S. Job's plot of **L** with Na_2HAsO_4 in DMSO-d_6/D_2O (1:1.1)(v/v) at 298K.

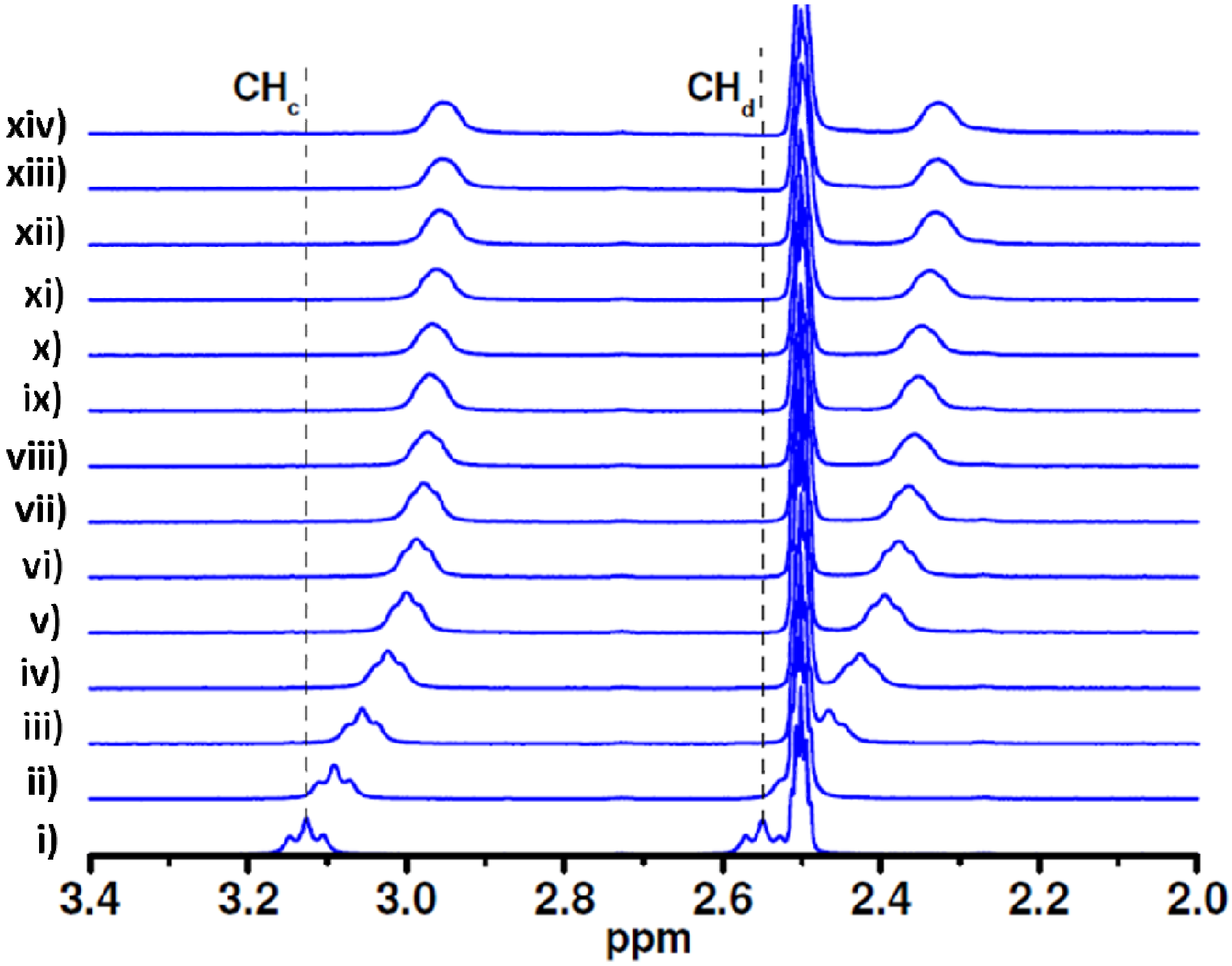


Fig. 6S. Partial ^{1}H-NMR (300 MHz) spectral changes of **L** in DMSO-$d_6$with added standard Na_2SO_4 solution in DMSO-d_6/D_2O(1:1.1)(v/v) ([**L**]$_0$ = 4.27 mM). Ratio of concentration [SO_4^{2-}]/[**L**]: (i) 0, (ii) 0.14, (iii) 0.27, (iv) 0.41, (v) 0.55, (vi) 0.69, (vii) 0.82, (viii) 0.96, (ix) 1.10, (x) 1.23, (xi) 1.64, (xii) 2.15, (xiii) 2.74 and (xiv) 2.97 ([**L**] is varied from 4.27 to 3.39 mM by the addition of aliquots of 48.68 mM Na_2SO_4).

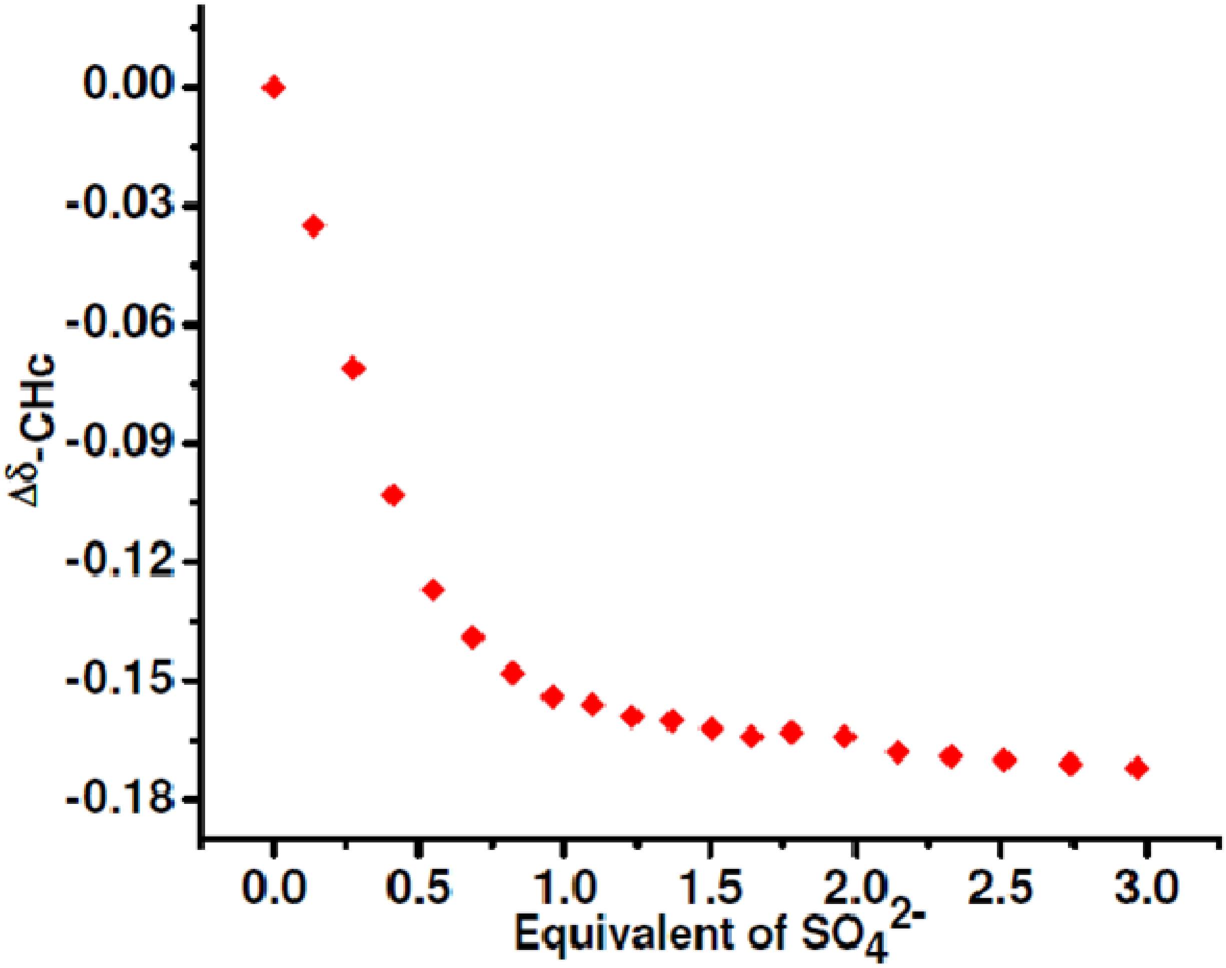


Fig. 4S. Plot shows the change in chemical shift of the –CH_c of **L** with increasing amounts of standard Na_2SO_4 solution at 298K.

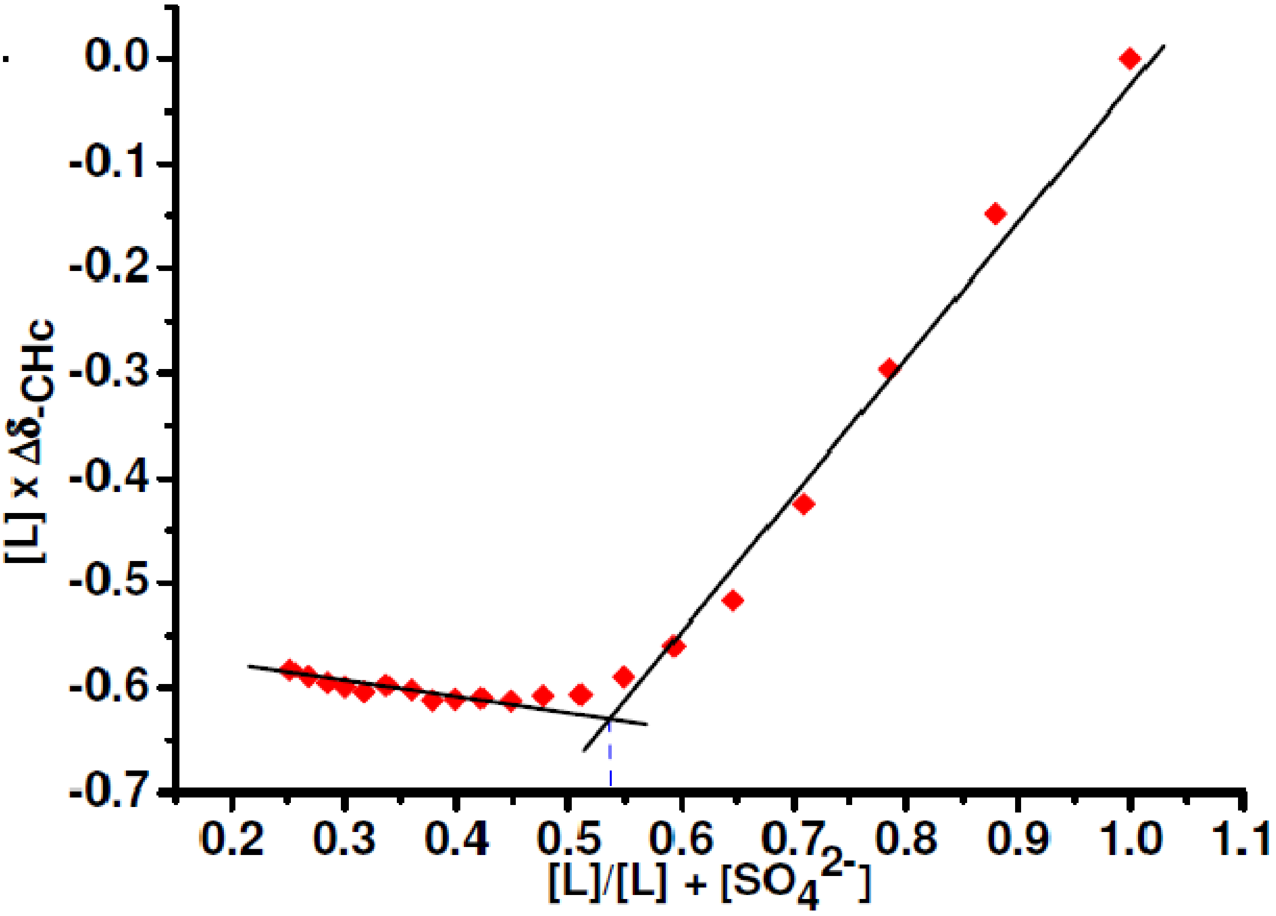


Fig. 8S. Job's plot of **L** with Na_2SO_4 in DMSO-d_6/D_2O (1:1.1)(v/v) at 298K.

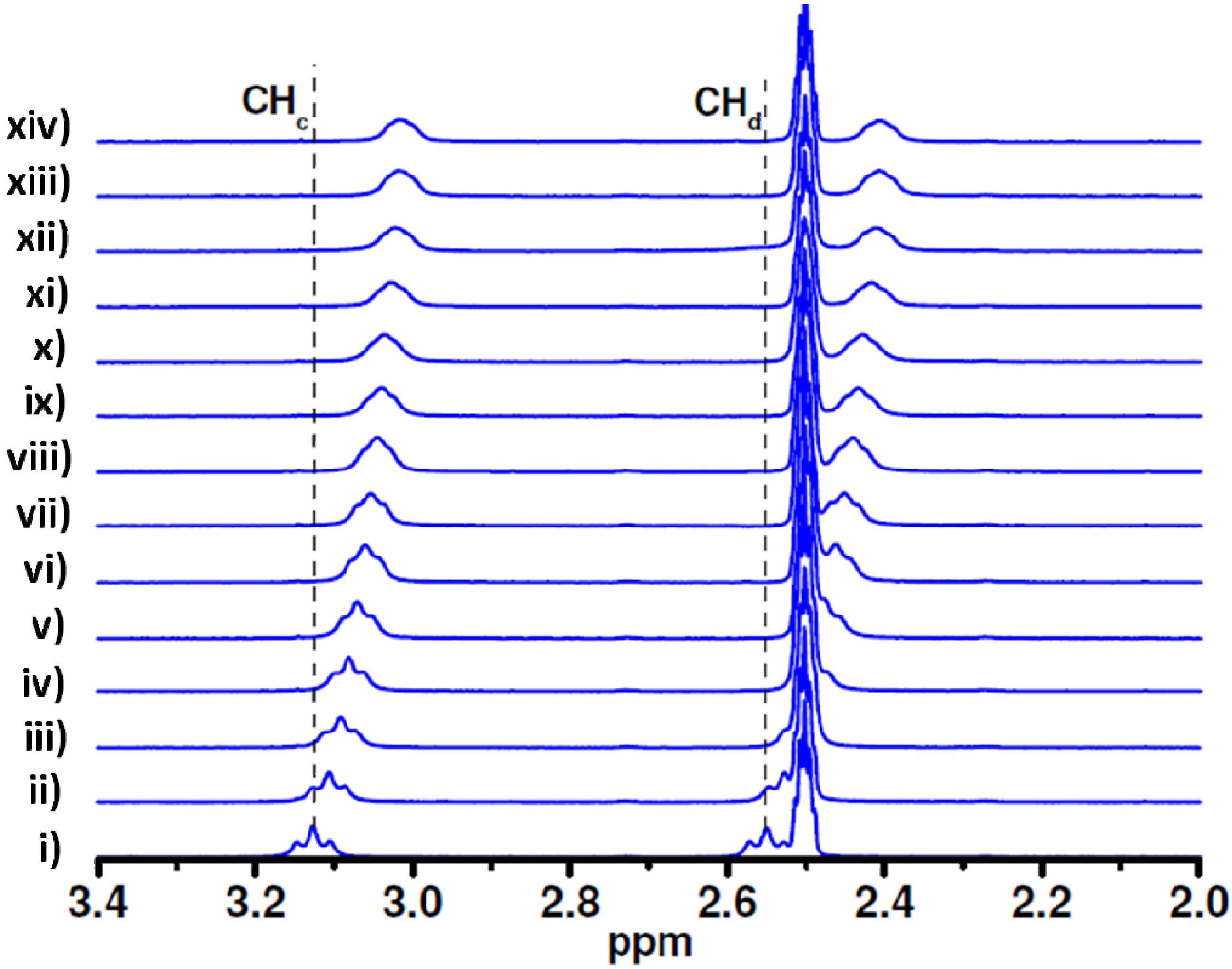


Fig. 9S. Partial ^{1}H-NMR (300 MHz) spectral changes of **L** in DMSO-d_6/D2O (9:1)(v/v) with added standard NaH_2PO_4 solution in DMSO-d_6/D_2O (1:1.1)(v/v) ([**L**]$_0$ = 4.01mM). Ratio of concentration [$H_2PO_4^-$]/[**L**]: (i) 0, (ii) 0.11, (iii) 0.22, (iv) 0.33, (v) 0.43, (vi) 0.54, (vii) 0.65, (viii) 0.76, (ix) 0.87, (x) 0.98, (xi) 1.30, (xii) 1.70, (xiii) 2.21 and (xiv) 2.39([**L**] is varied from 4.01 to 3.17 mM by the addition of aliquots of 36.26 mM NaH_2PO_4).

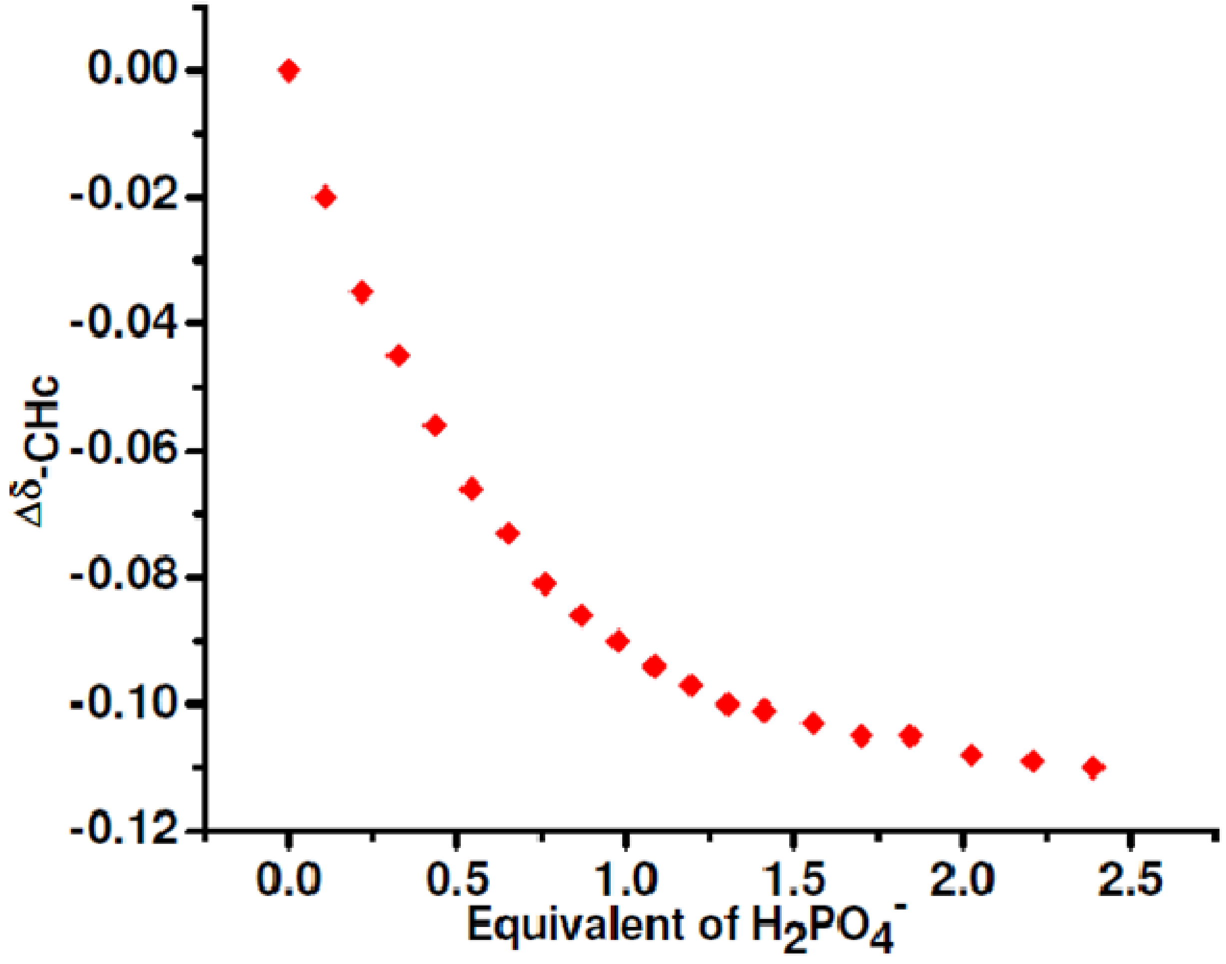


Fig. 10S. Plot shows the change in chemical shift of the –CH_c of **L** with increasing amounts of standard NaH_2PO_4 solution at 298K.

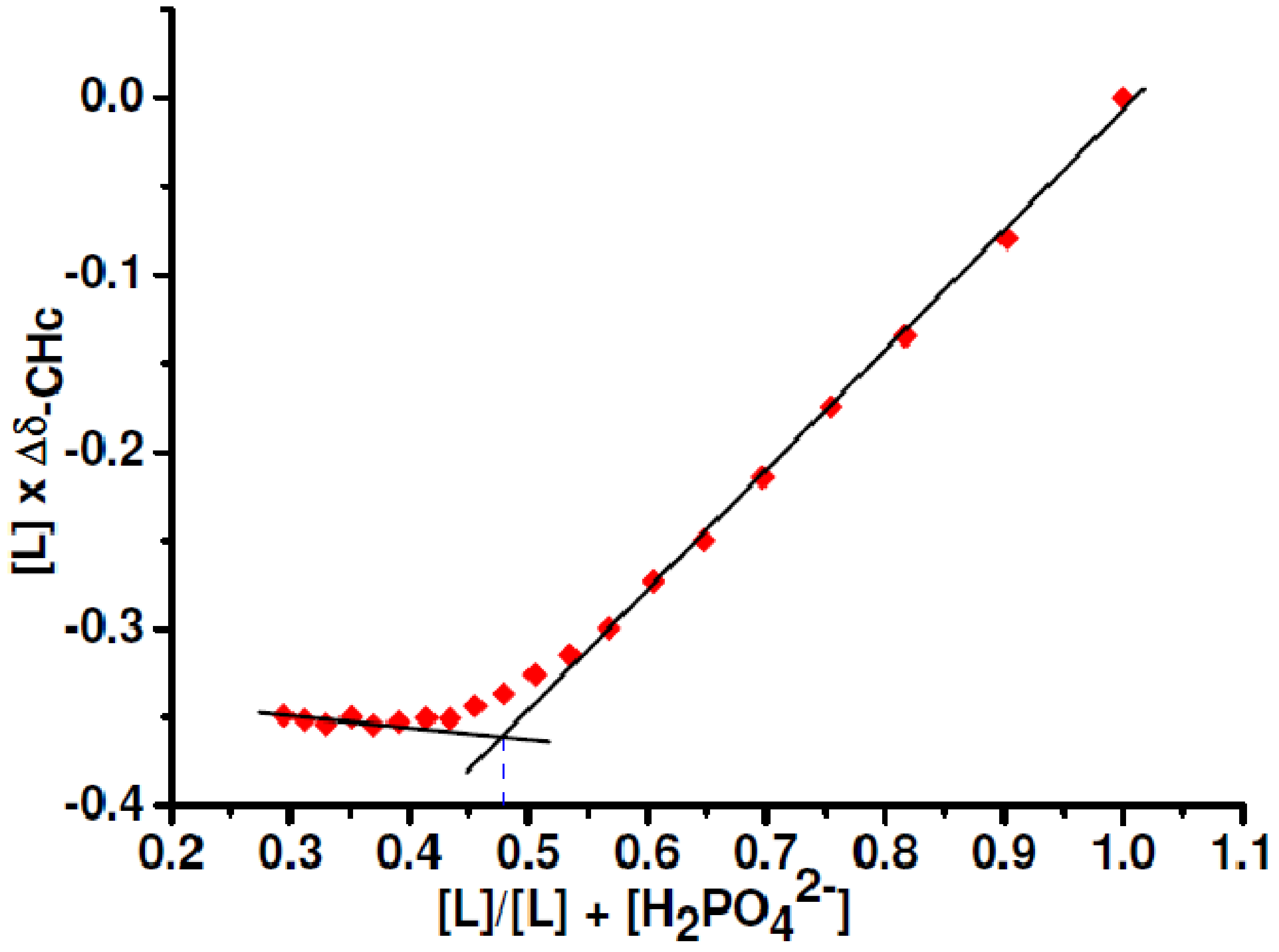


Fig. 11S. Job's plot of **L** with NaH_2PO_4 in DMSO-d_6/D_2O (1:1.1)(v/v) at 298K.

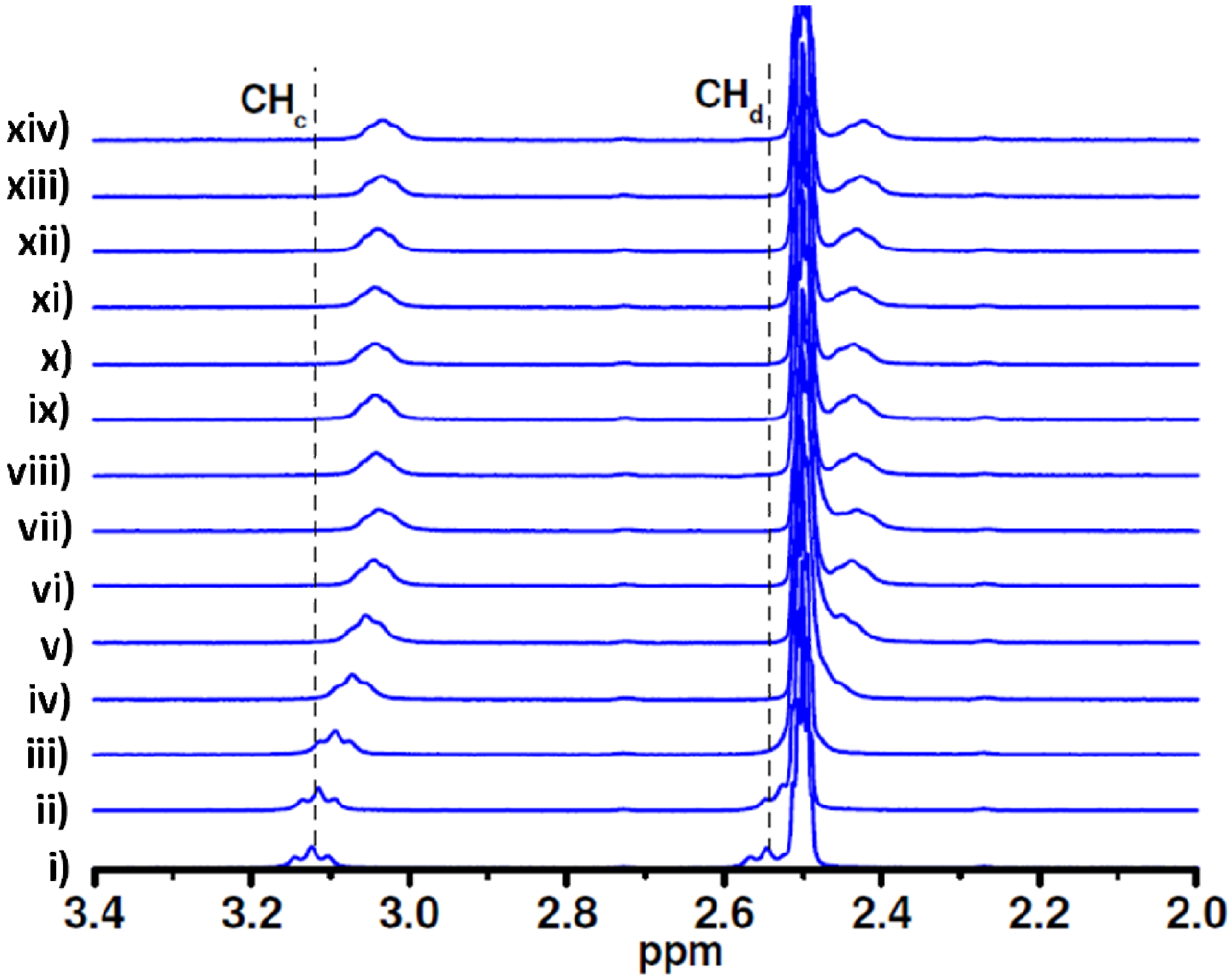


Fig. 12S. Partial ^{1}H-NMR (300 MHz) spectral changes of **L** in DMSO-d_6/D_2O (9:1)(v/v) with added standard Na_2CO_3 solution in DMSO-d_6/D_2O (1:1.1)(v/v) ([**L**]$_0$ = 2.46 mM). Ratio of concentration [CO_3^-]/[**L**]: (i) 0, (ii) 0.13, (iii) 0.25, (iv) 0.38, (v) 0.51, (vi) 0.63, (vii) 0.76, (viii) 0.88, (ix) 1.01, (x) 1.14, (xi) 1.52, (xii) 1.94, (xiii) 2.53 and (xiv) 2.74([**L**] is varied from 2.46 to 1.94 mM by the addition of aliquots of 25.88 mM Na_2CO_3).

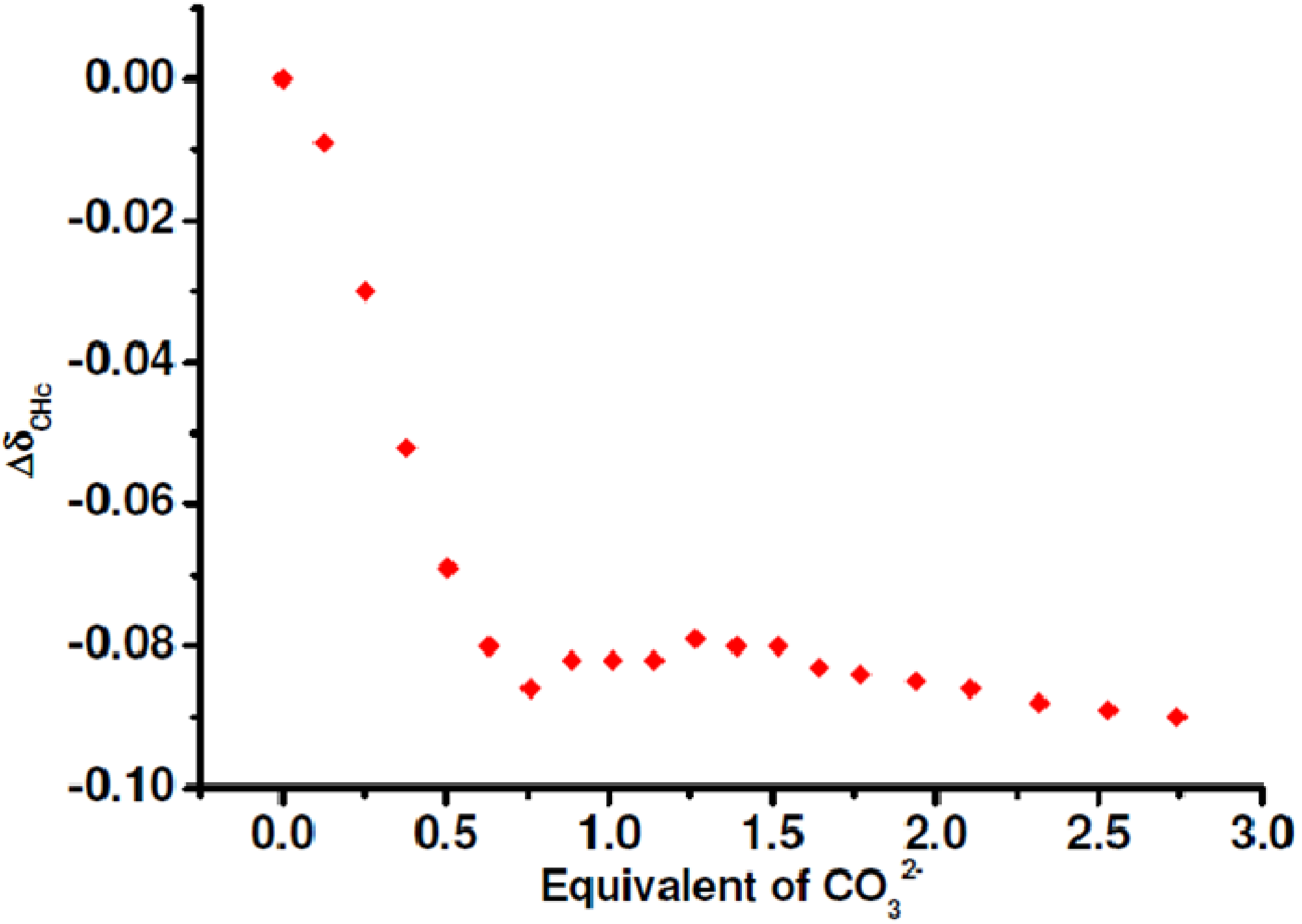


Fig. 13S. Plot shows the change in chemical shift of the –CH_c of **L** with increasing amounts of standard Na_2CO_3 solution at 298K.

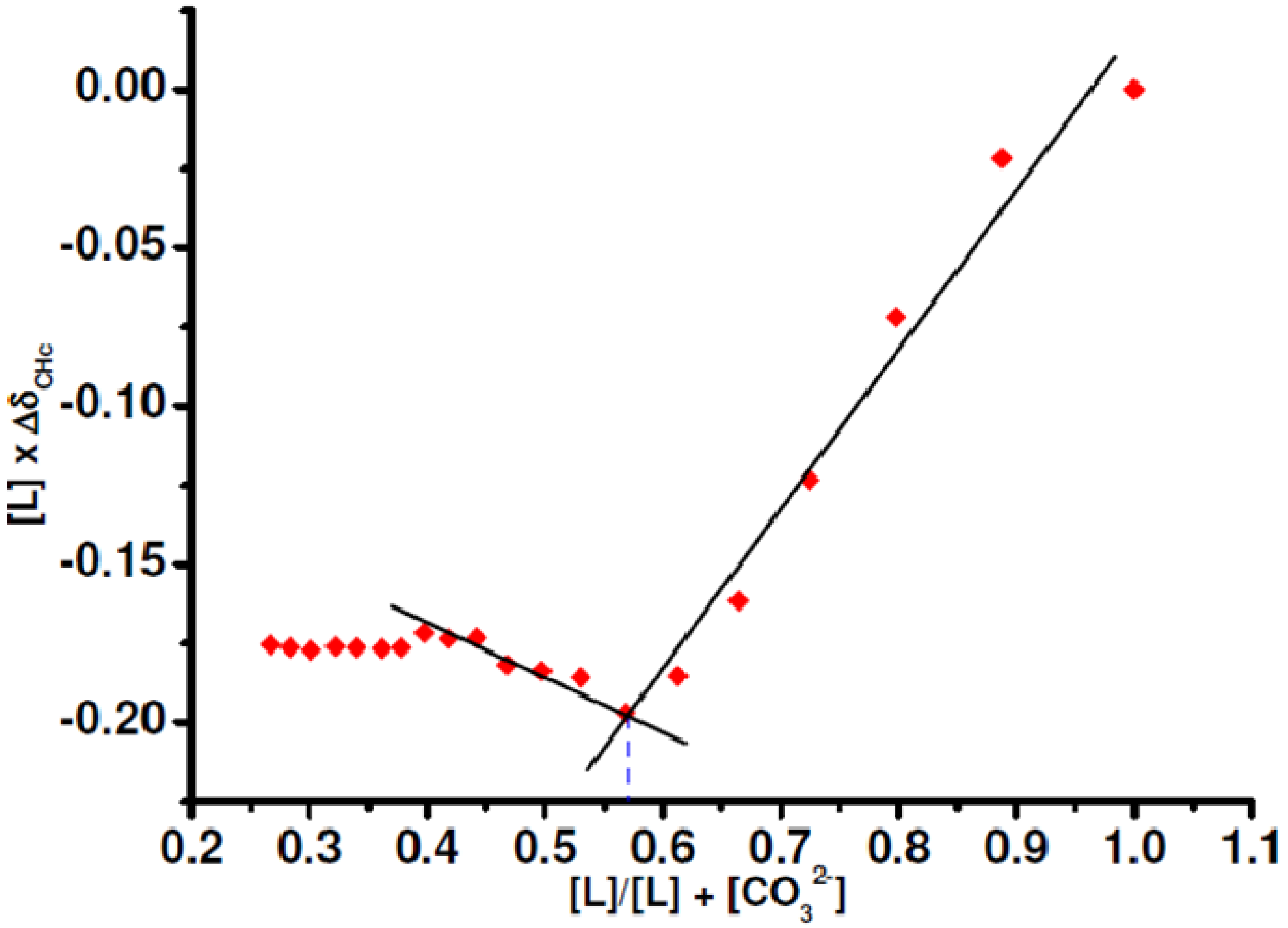


Fig. 14S. Job's plot of **L** with Na_2CO_3in DMSO-d_6/D_2O (1:1.1)(v/v) at 298K.

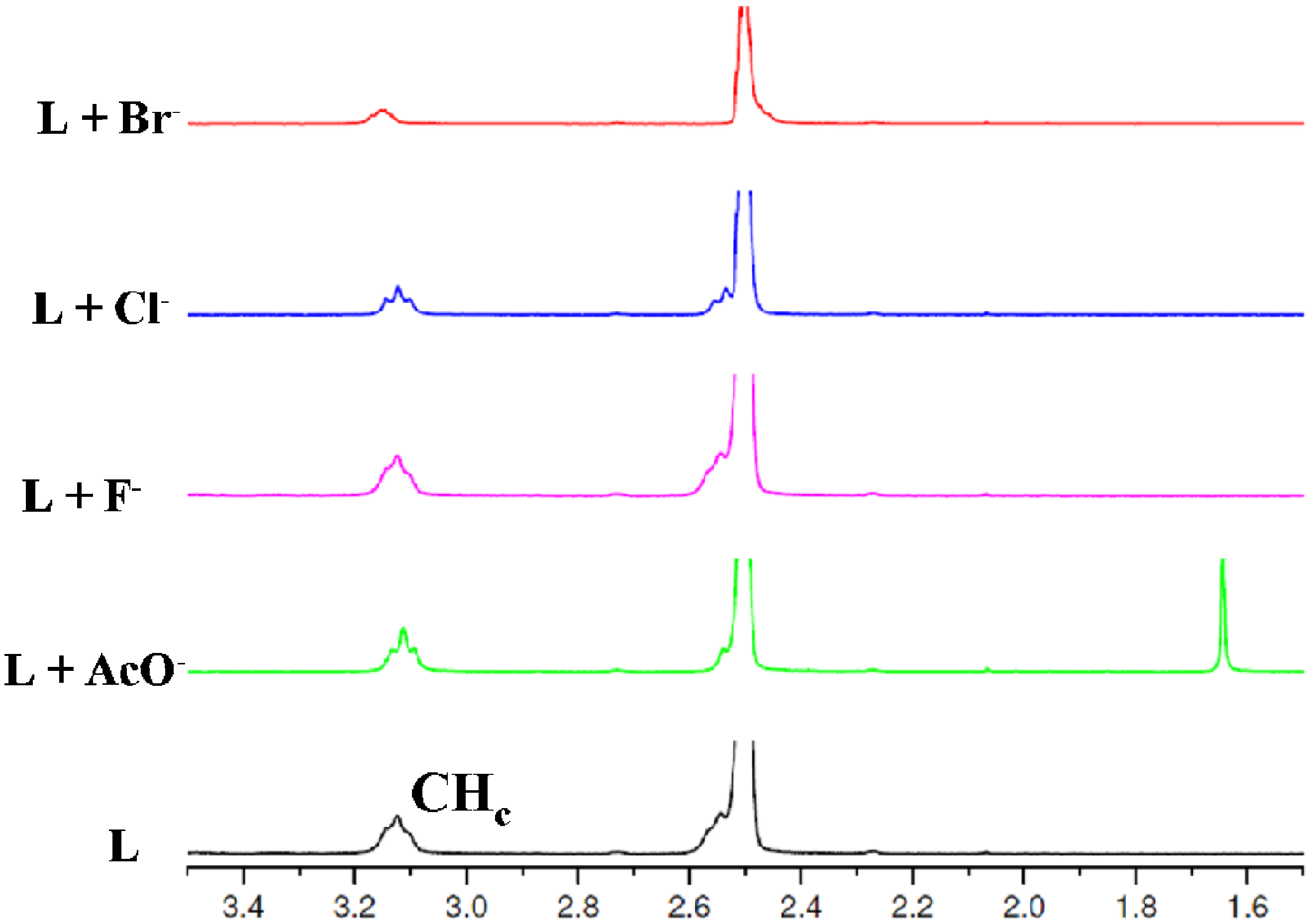


Fig. 15S. Partial ^{1}H-NMR spectra of **L** (DMSO-d_6/D_2O, 9:1, v/v) with excess of AcO$^-$, F$^-$, Cl$^-$ and Br$^-$ (DMSO-d_6/D_2O, 1.1:1, v/v).

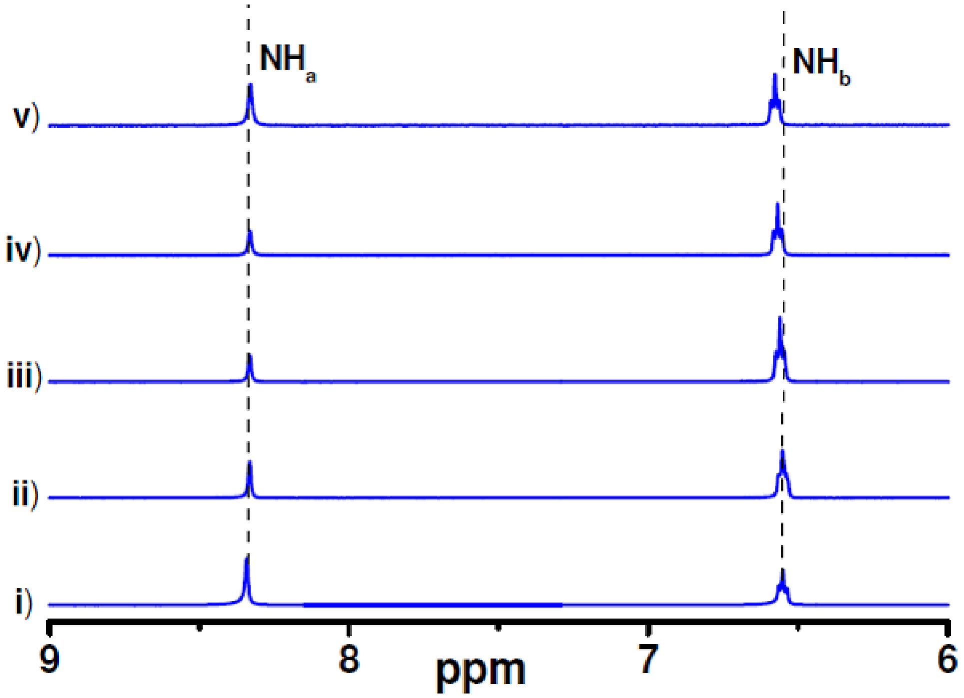


Fig. 16S. Partial ^{1}H-NMR (300 MHz) spectral changes of **L** in DMSO-d_6 with added solution of DMSO-d_6/D_2O (1:1.1)(v/v) solvent. Volume of added solvent: i) 0µl, ii) 10µl, iii) 20 µl, iv) 40 µl, v) 60 µl.

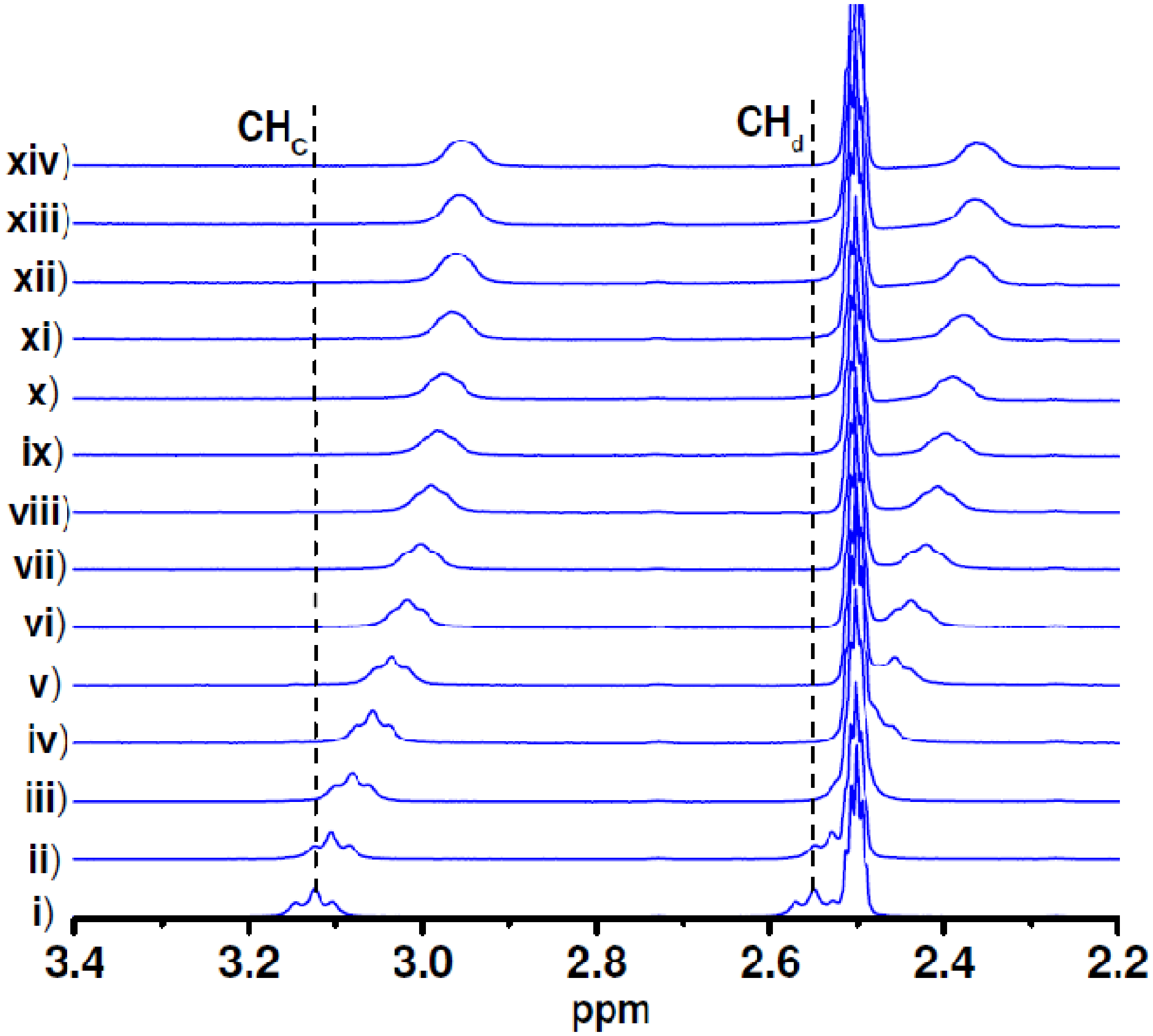


Fig. 17S. Partial ^{1}H-NMR (300 MHz) spectral changes of **L** in DMSO-d_6/D_2O (9:1)(v/v)/borax/boric acid with added standard Na_2HAsO_4 solution in borax (10 mM)/boric acid (200 mM) in DMSO-d_6/D_2O (1:1.1)(v/v) ([**L**]$_0$ = 2.89 mM). Ratio of concentration [$HAsO_4^{2-}$]/[**L**]: (i) 0, (ii) 0.098, (iii) 0.197, (iv) 0.296, (v) 0.395, (vi) 0.493, (vii) 0.592, (viii) 0.691, (ix) 0.789, (x) 0.888, (xi) 1.08, (xii) 1.28, (xiii) 1.55 and (xiv) 2.07([**L**] is varied from 2.89 to 2.27 mM by the addition of aliquots of 23.81 mM Na_2HAsO_4).

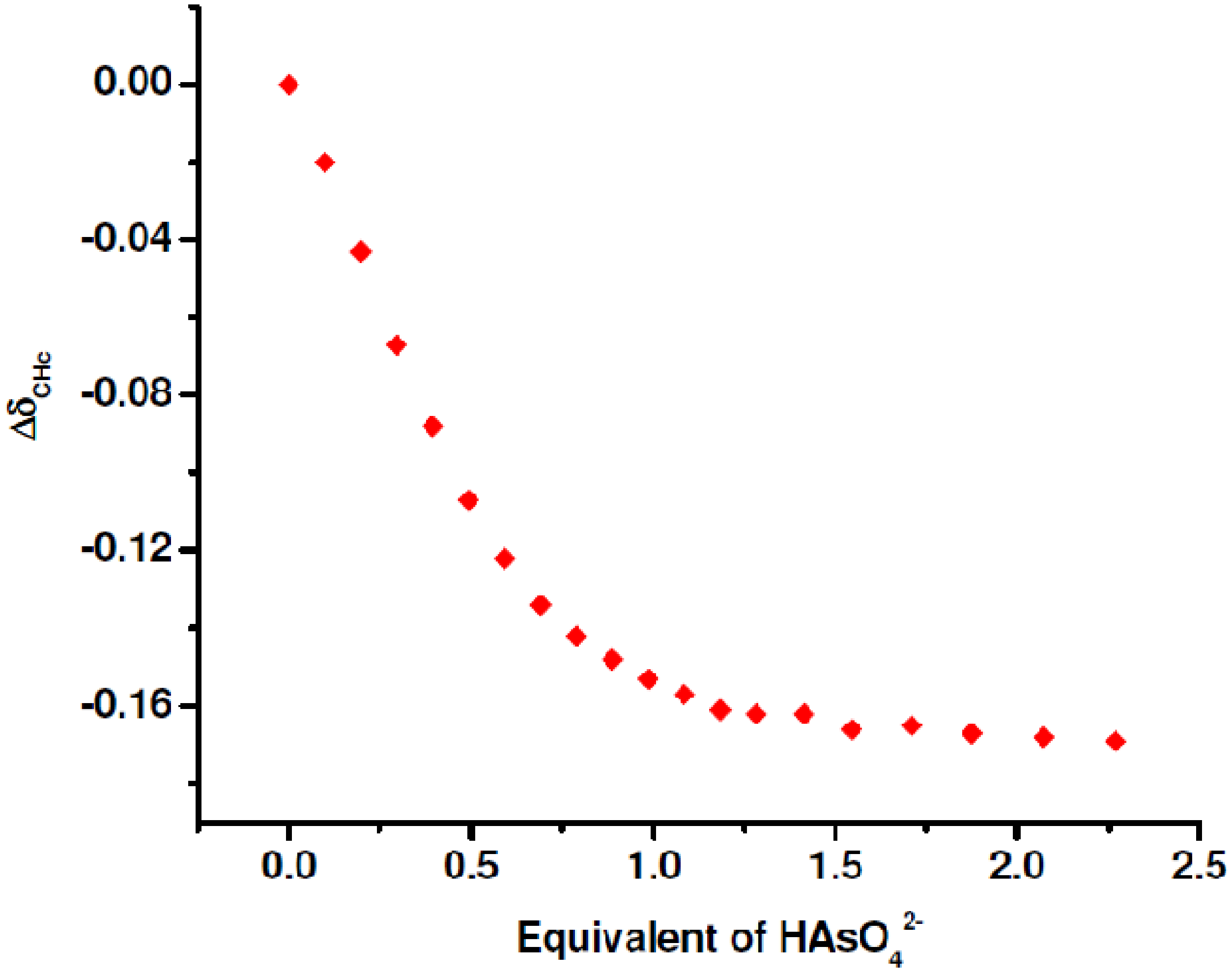


Fig. 18S. Plot shows the change in chemical shift of the –CH_c of **L** with increasing amounts of standard Na_2HAsO_4 solution at 298K in borax/boric acid buffer.

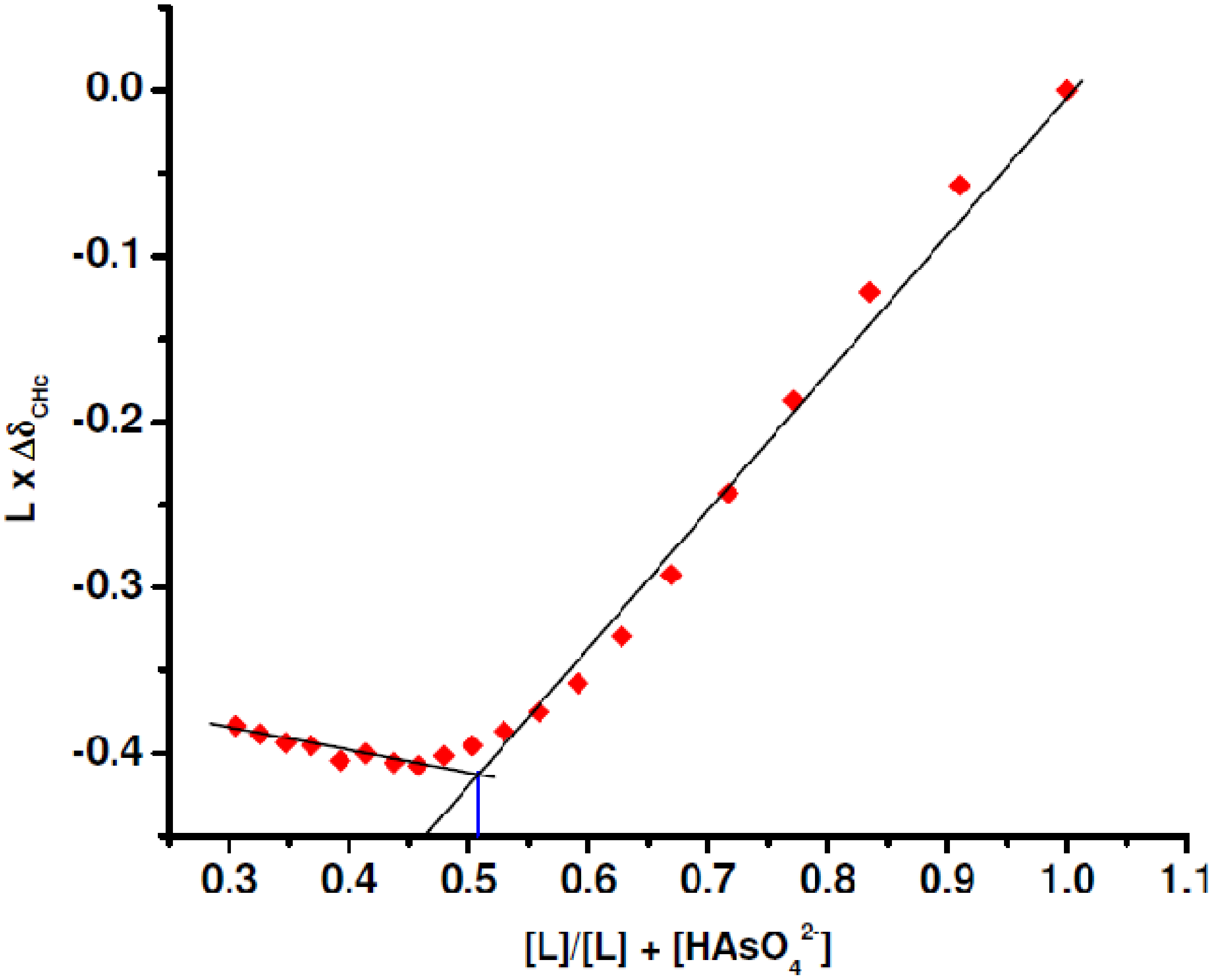


Fig. 19S. Job’s plot of **L** with Na_2HAsO_4 in DMSO-d_6/D_2O (1:1.1)(v/v) at 298K in borax/boric acid buffer.

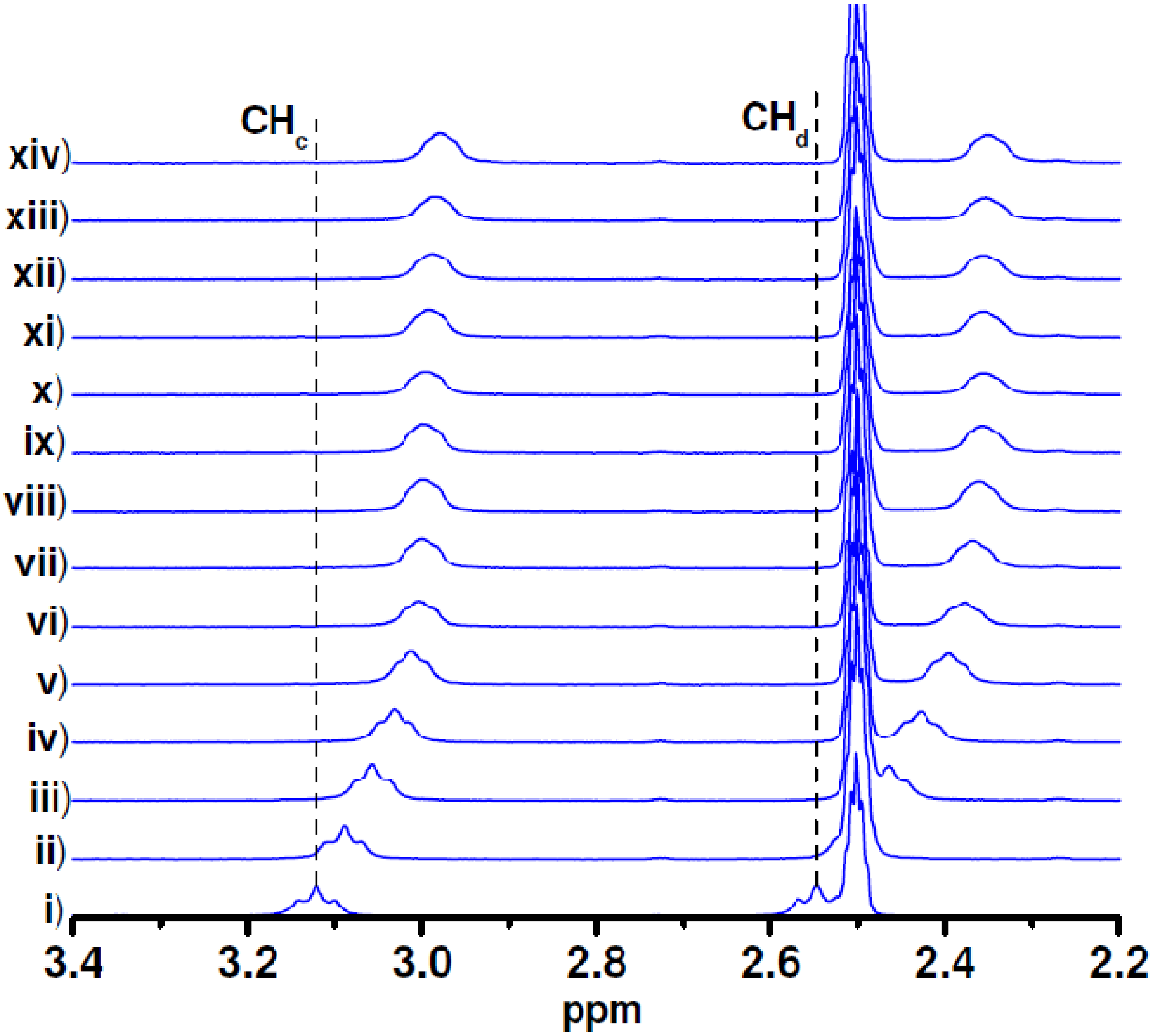


Fig. 20S. Partial ^{1}H-NMR (300 MHz) spectral changes of **L** in DMSO-d_6/D_2O (9:1)(v/v)/borax/boric acid with added standard Na_2SO_4 solution in borax (10 mM)/boric acid (200 mM) in DMSO-d_6/D_2O (1:1.1)(v/v) ([**L**]$_0$ = 2.97mM). Ratio of concentration [SO_4^{2-}]/[**L**]: (i) 0, (ii) 0.15, (iii) 0.30, (iv) 0.45, (v) 0.61, (vi) 0.76, (vii) 0.91, (viii) 1.06, (ix) 1.21, (x) 1.36, (xi) 1.67, (xii) 1.97, (xiii) 2.37 and (xiv) 3.18 ([**L**] is varied from 2.97 to 2.33 mM by the addition of aliquots of 37.55 mM Na_2SO_4).

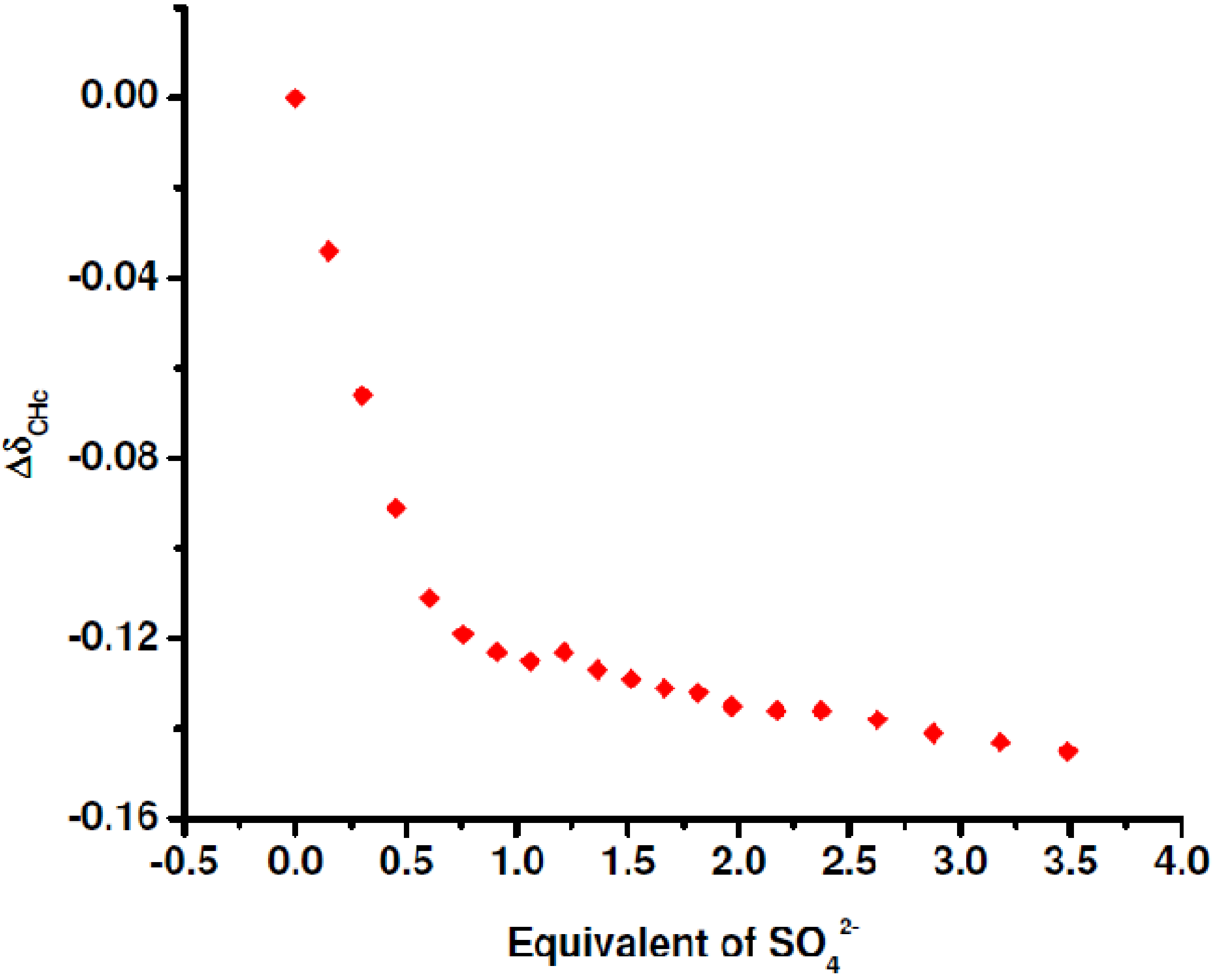


Fig. 21S. Plot shows the change in chemical shift of the –CH_c of **L** with increasing amounts of standard Na_2SO_4 solution at 298K in borax/boric acid buffer.

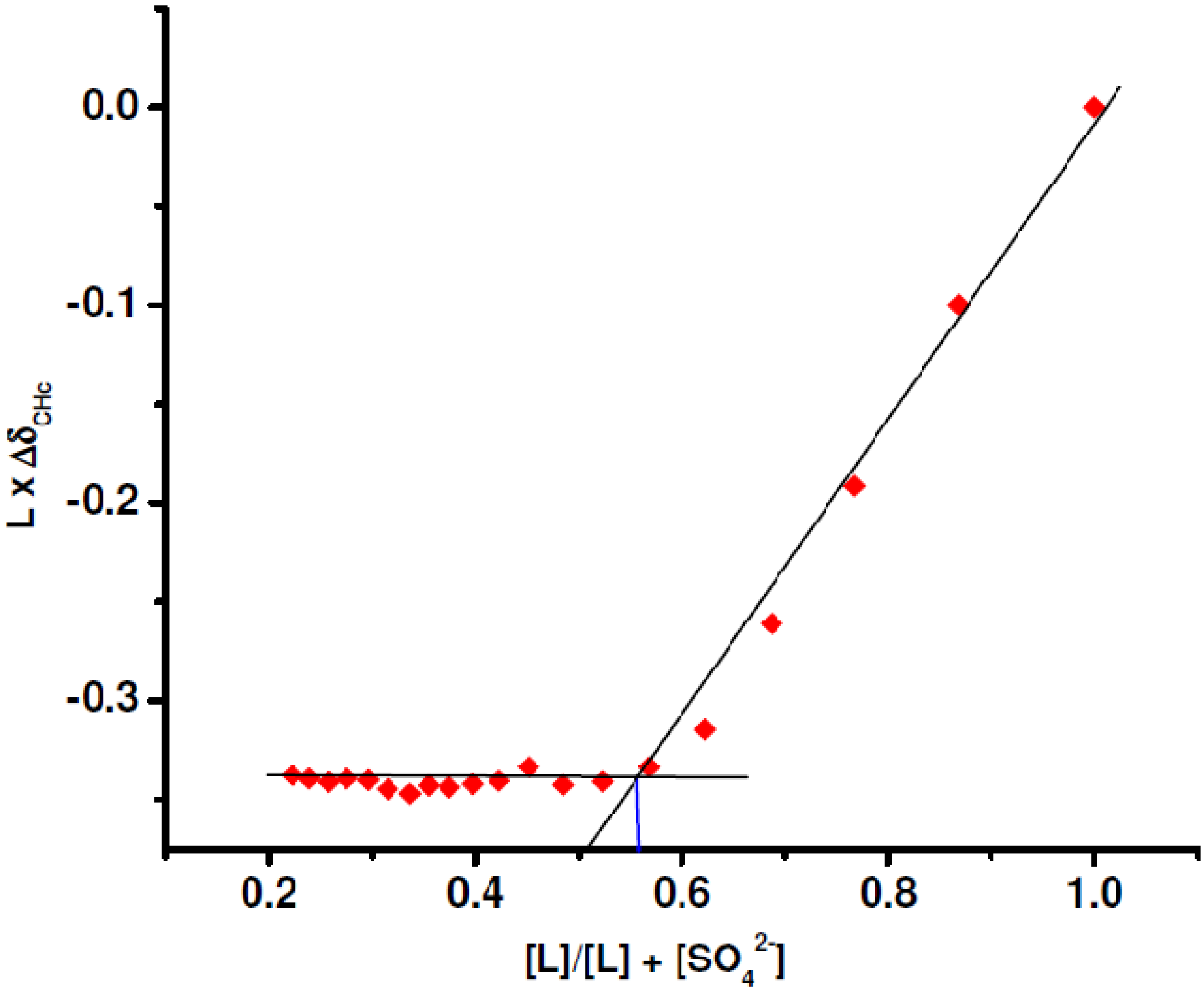


Fig. 22S. Job's plot of **L** with Na_2SO_4 in DMSO-d_6/D_2O (1:1.1)(v/v) at 298K in borax/boric acid buffer.

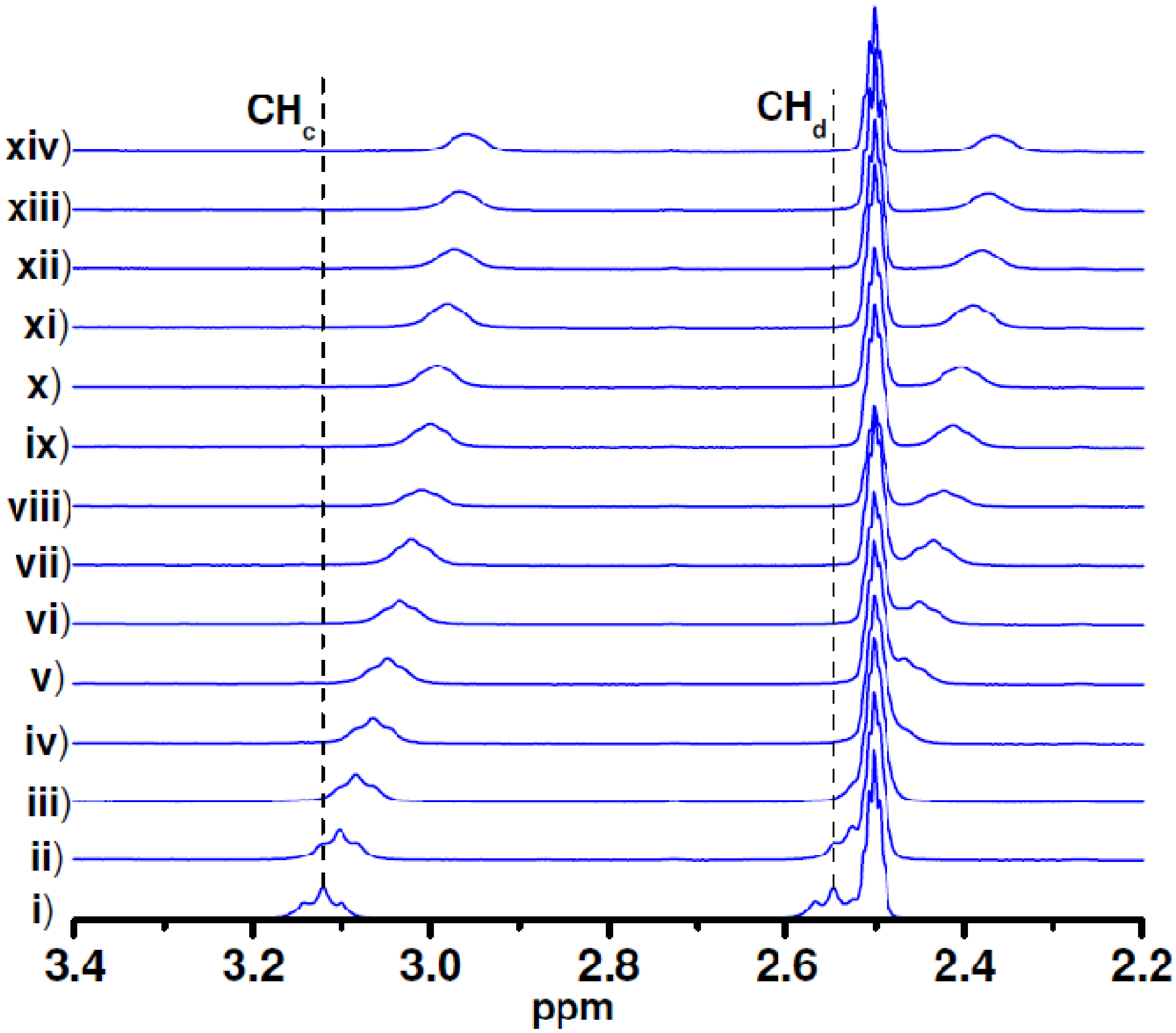


Fig. 23S. Partial ^{1}H-NMR (300 MHz) spectral changes of **L** in DMSO-d_6/D_2O (9:1)(v/v)/borax/boric acid with added standard NaH_2PO_4 solution in borax (10 mM)/boric acid (200 mM) in DMSO-d_6/D_2O (1:1.1)(v/v) ([**L**]$_0$ = 3.75 mM). Ratio of concentration [$H_2PO_4^-$]/[**L**]: (i) 0, (ii) 0.11, (iii) 0.21, (iv) 0.32, (v) 0.42, (vi) 0.53, (vii) 0.64, (viii) 0.75, (ix) 0.85, (x) 0.96, (xi) 1.17, (xii) 1.39, (xiii) 1.67 and (xiv) 2.24([**L**] is varied from 3.75 to 2.93 mM by the addition of aliquots of 33.33 mM NaH_2PO_4).

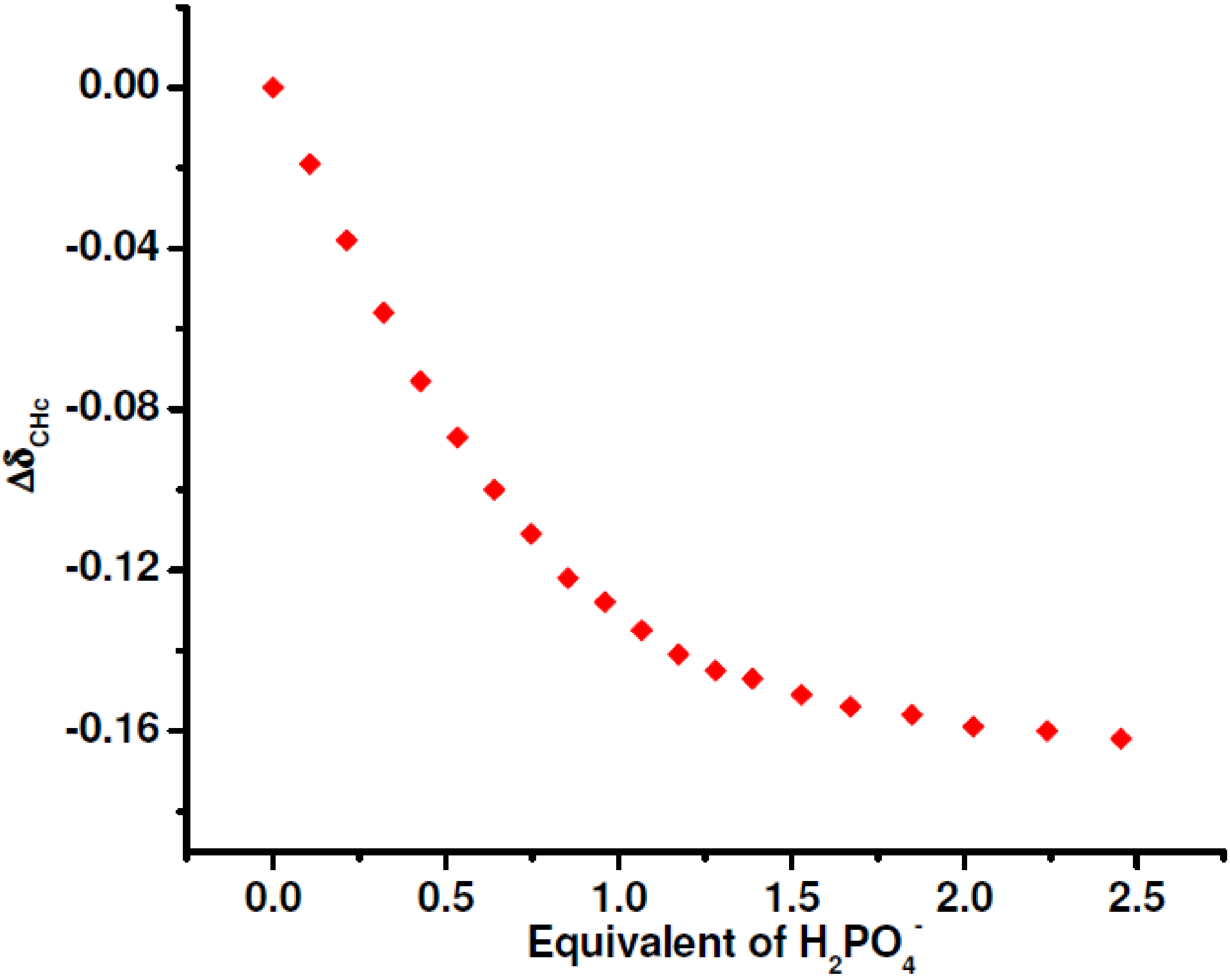


Fig. 24S. Plot shows the change in chemical shift of the –CH_c of **L** with increasing amounts of standard NaH_2PO_4 solution at 298K in borax/boric acid buffer.

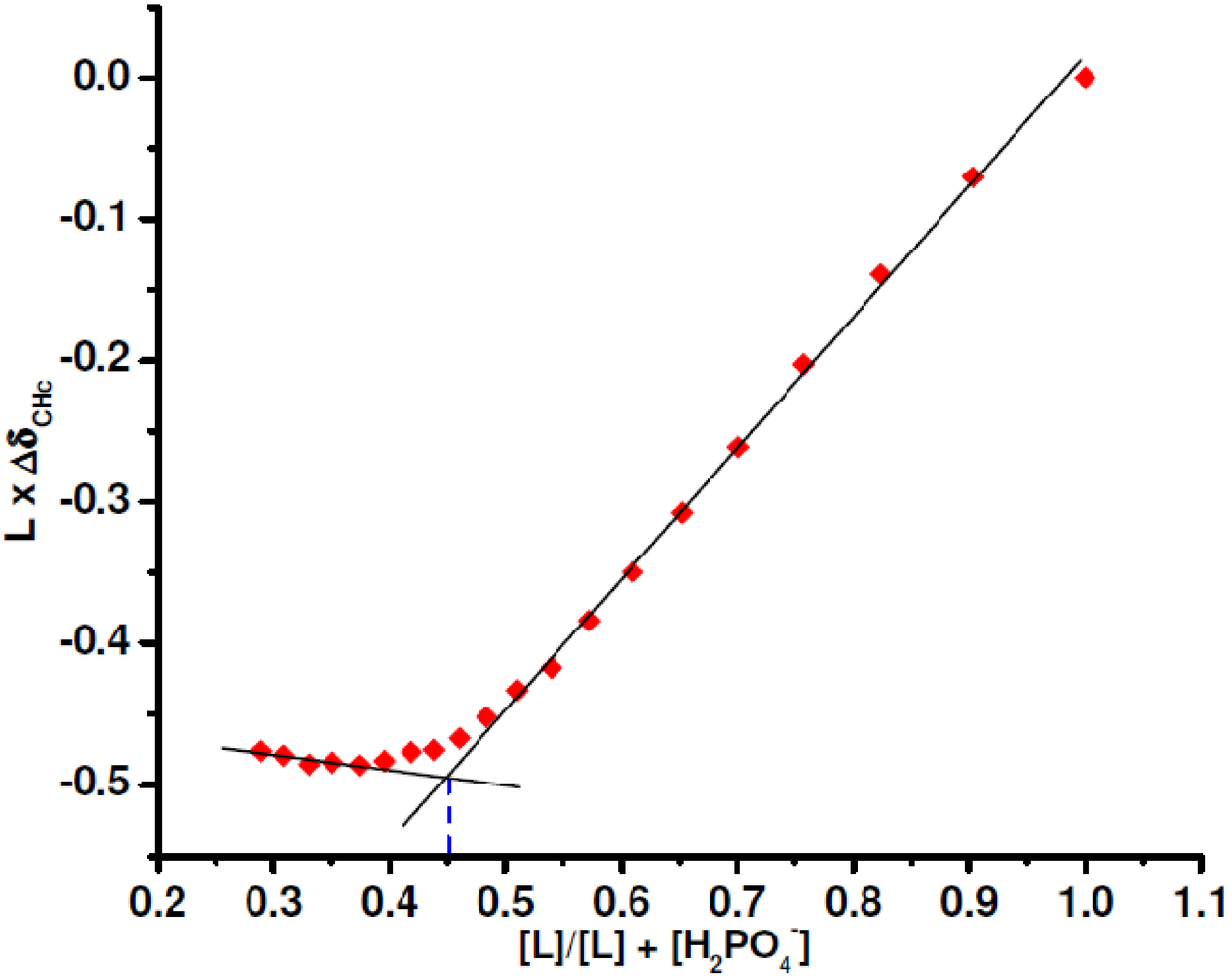


Fig. 25S. Job's plot of **L** with NaH_2PO_4 in DMSO-d_6/D_2O (1:1.1)(v/v) at 298K in borax/boric acid buffer .

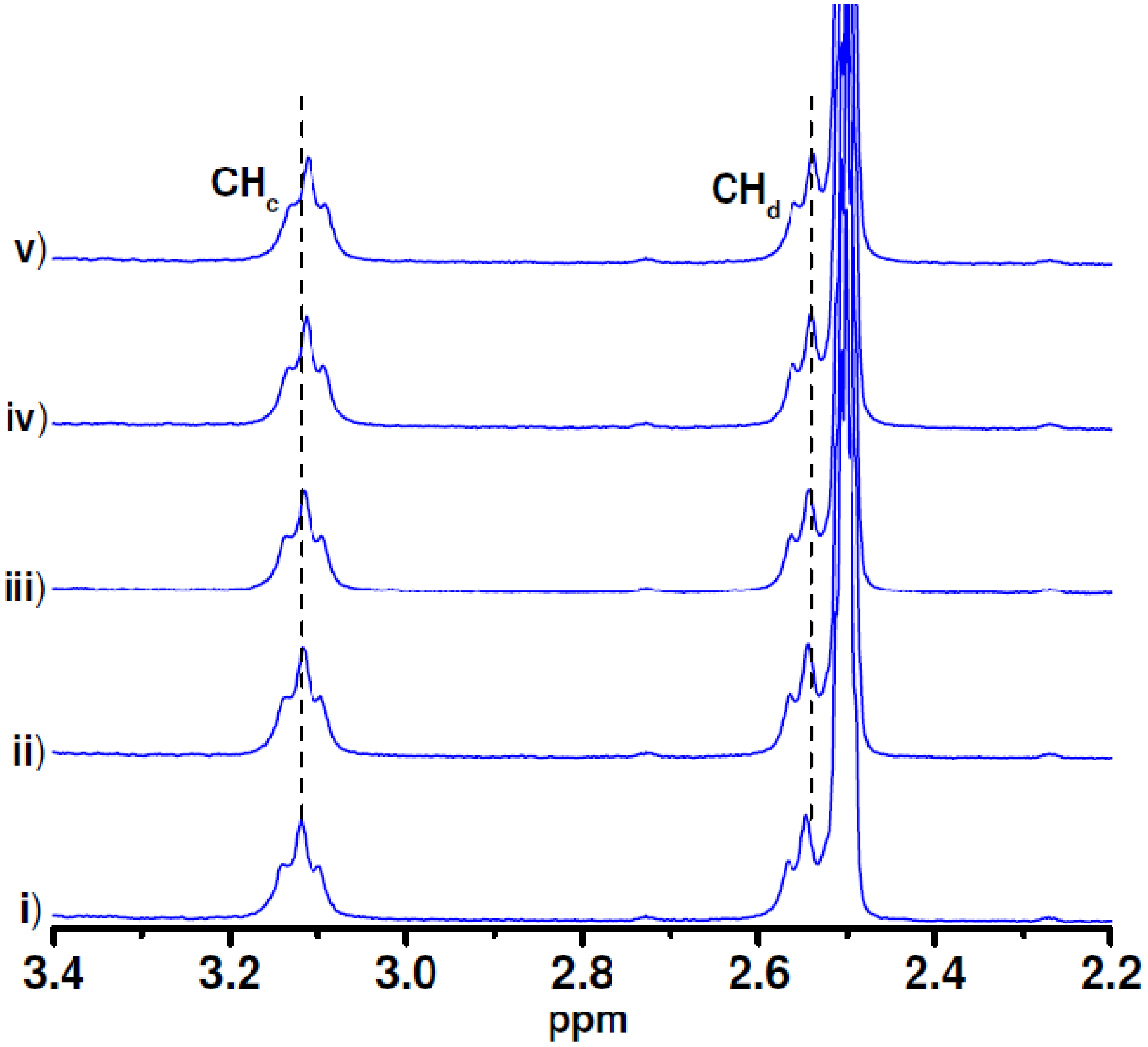


Fig. 26S. Partial ^{1}H-NMR (300 MHz) spectral changes of **L** in DMSO-d_6 with added solution of DMSO-d_6/D_2O (1:1.1)(v/v) solvent in borax/boric acid buffer. Volume of added solvent: i) 0μl, ii) 10μl, iii) 20 μl, iv) 40 μl, v) 60 μl.

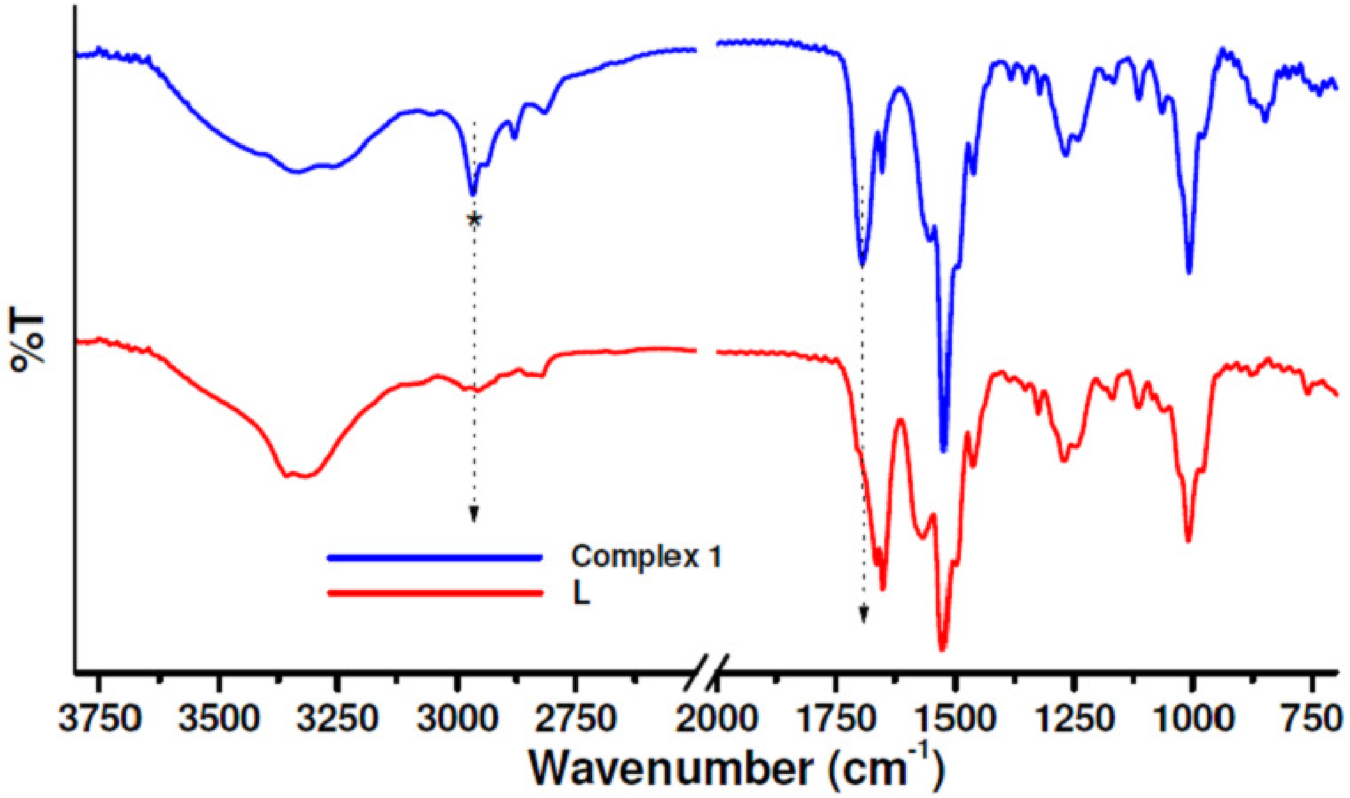
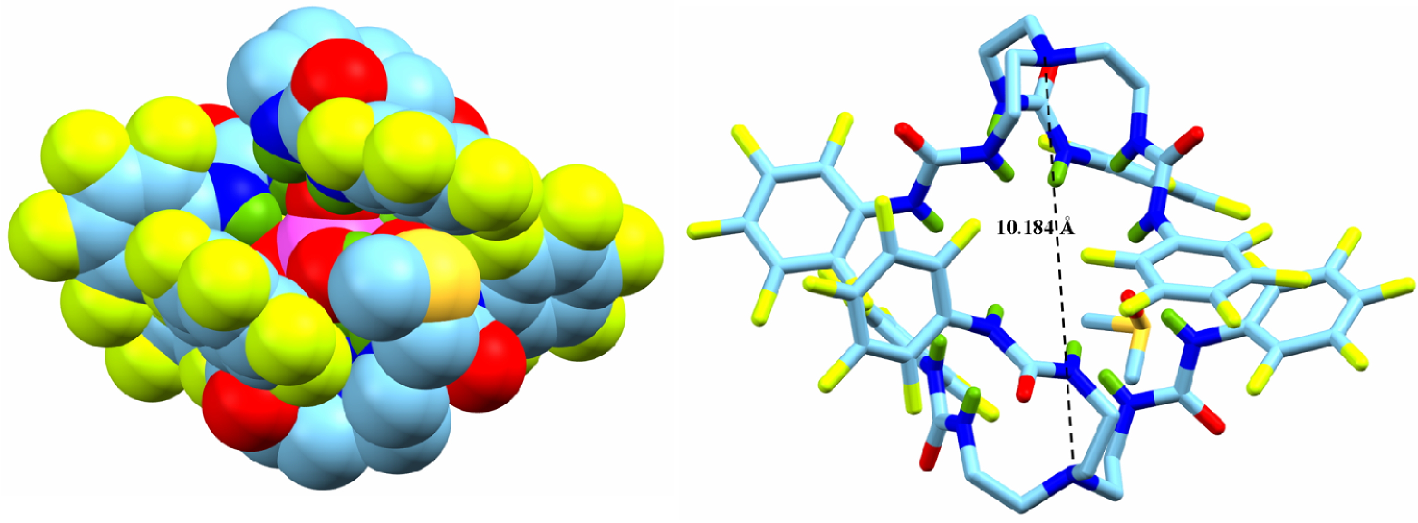


Fig.27S. Comparative FT-IR analyses of **L** (red) and complex **1** (blue) in KBr discs ('*' indicates the C-H stretching frequency of tetrabutylammonium cation in complex **1**).

Table 1S. Crystallographic table of complex **1**

Parameters	Complex **1**
Emperical formula	$C_{360}H_{320}F_{120}N_{64}O_{44}S_8As_8$
Formula weight	2212.03
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	21.4103(19)
b (Å)	26.030(2)
c (Å)	20.5147(18)
α (°)	90.00
β (°)	111.082(2)
γ (°)	90.00
V ($Å^3$)	10667.8(16)
Z	4
d_{calc} (g/cm^3)	1.377
Crystal size (mm^3)	0.45 x 0.20 x 0.18
F(000)	4505
μ Mo Kα (mm^{-1})	0.451
T(K)	150 (2)
θ range (deg)	0.99-25.00
Independent Reflections	18770
Observed Reflections	14429
Parameters	1283
R1;wR2	0.0997, 0.2890
GOF (F^2)	0.850



a) b)

Fig. 28S. a) Space-fill representation of HAsO$_4^{2-}$encapsulateddimeric capsular assembly of complex **1**; b) ball-stick representation showing the dimension of complex **1**capsule.

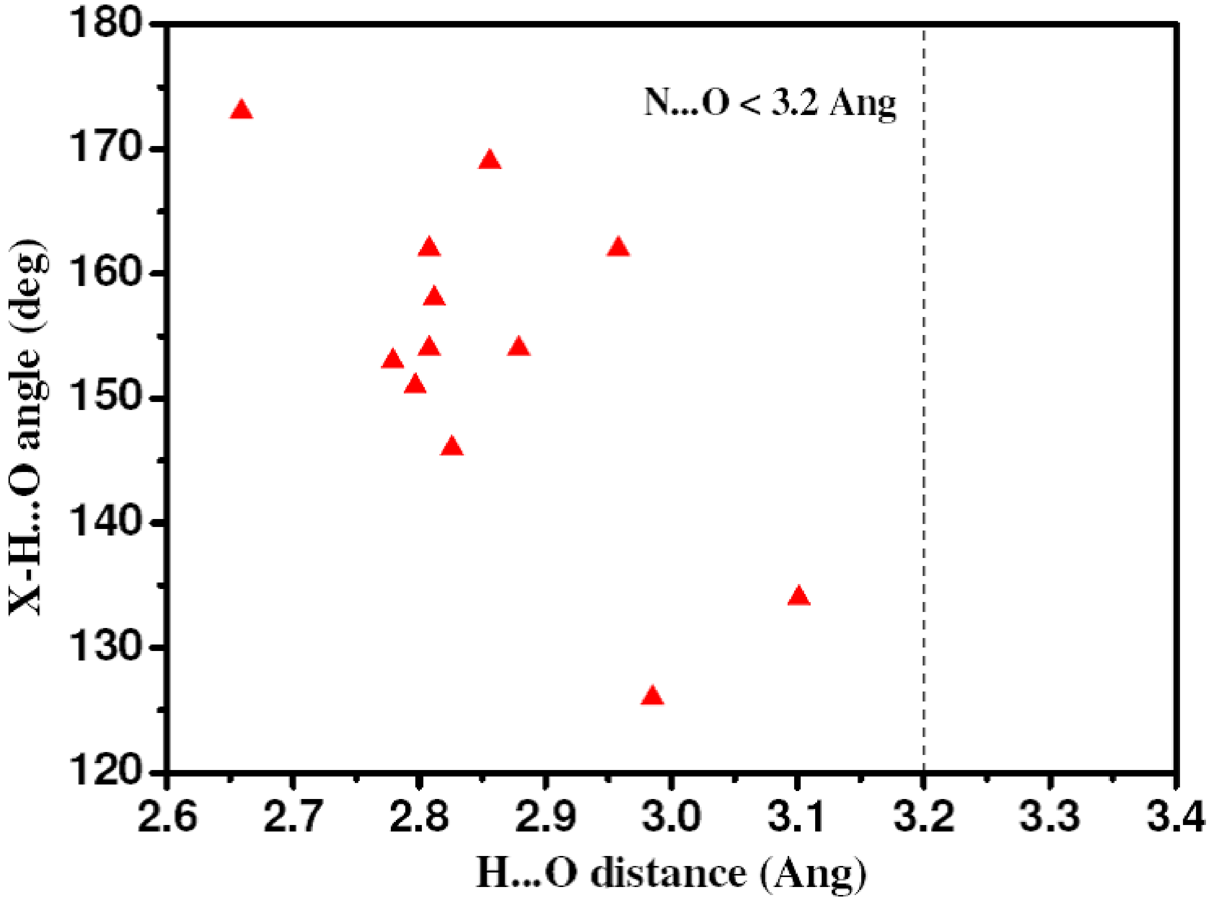


Fig.29S. The scatter plot of X–H¨O *vs.* H¨O distances of the hydrogen bonds in complex **1**(X = N/O).

Table 2S. Inter-atomic distances, and angles for the H-bonding Interactions of the encapsulated $HAsO_4^{2-}$ in complex **1**.

D-H···A	**d (H···A), Å**	**d (D···A), Å**	**< D-H-A °**
N3-H3···O7[a]	2.010	2.808(8)	154
N4-H4···O10[a]	2.010	2.856(7)	169
N5-H5···O7[a]	2.000	2.812(7)	158
N6-H6···O10[a]	2.440	3.101(7)	134
N7-H7···O10[a]	1.990	2.776(9)	153
O8-H8···O11[a]	1.840	2.659(10)	173
N9-H9···O9[b]	2.080	2.879(8)	154
N10-H10···O10[b]	1.980	2.808(8)	162
N11-H11···O9[b]	2.400	2.985(9)	126
N12-H12···O9[b]	2.070	2.826(7)	146
N13-H13···O9[b]	2.130	2.958(7)	162
N14-H14···O7[b]	2.010	2.797(7)	151
[a] x, y, z; [b] 1-x,-1/2+y,3/2-z			

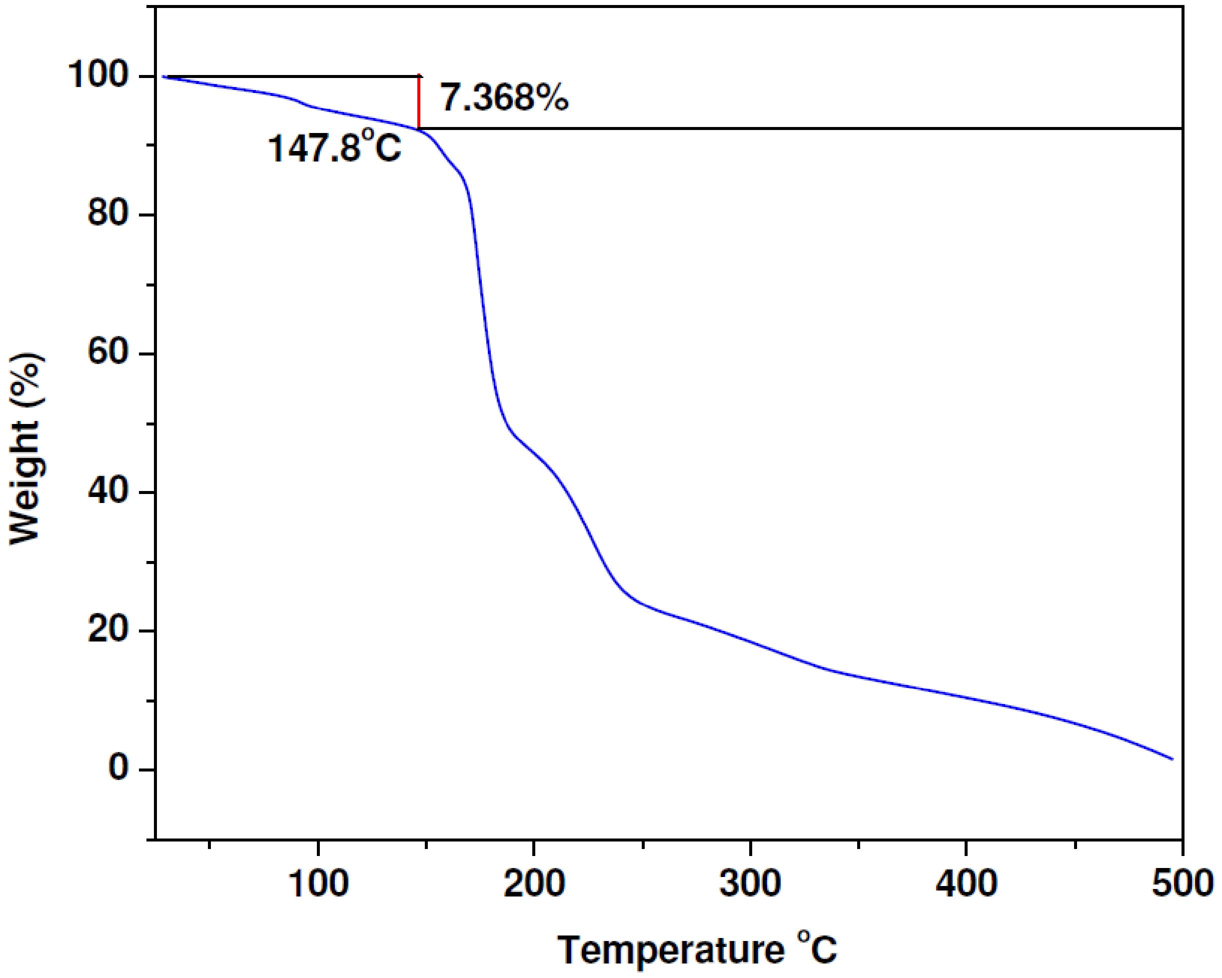


Fig. 30S. The TGA analysis of complex**1** shows weight loss of 7.368% within around 150°C, which corresponds to the loss of two dimethyl sulfoxide and one water molecule.

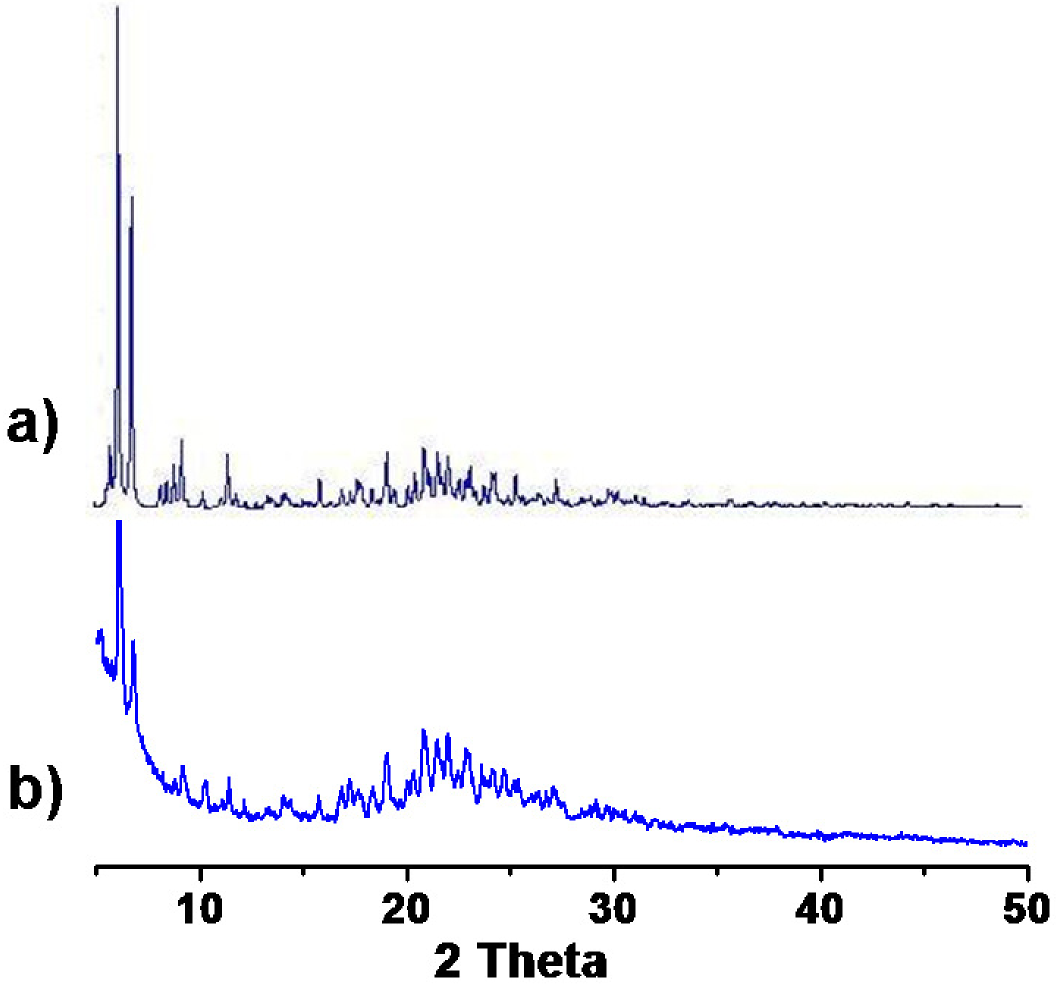


Fig. 31S. (a) PXRD pattern of the crystal of complex **1** (simulated) and (b) PXRD pattern of complex **1** (experimental pattern).

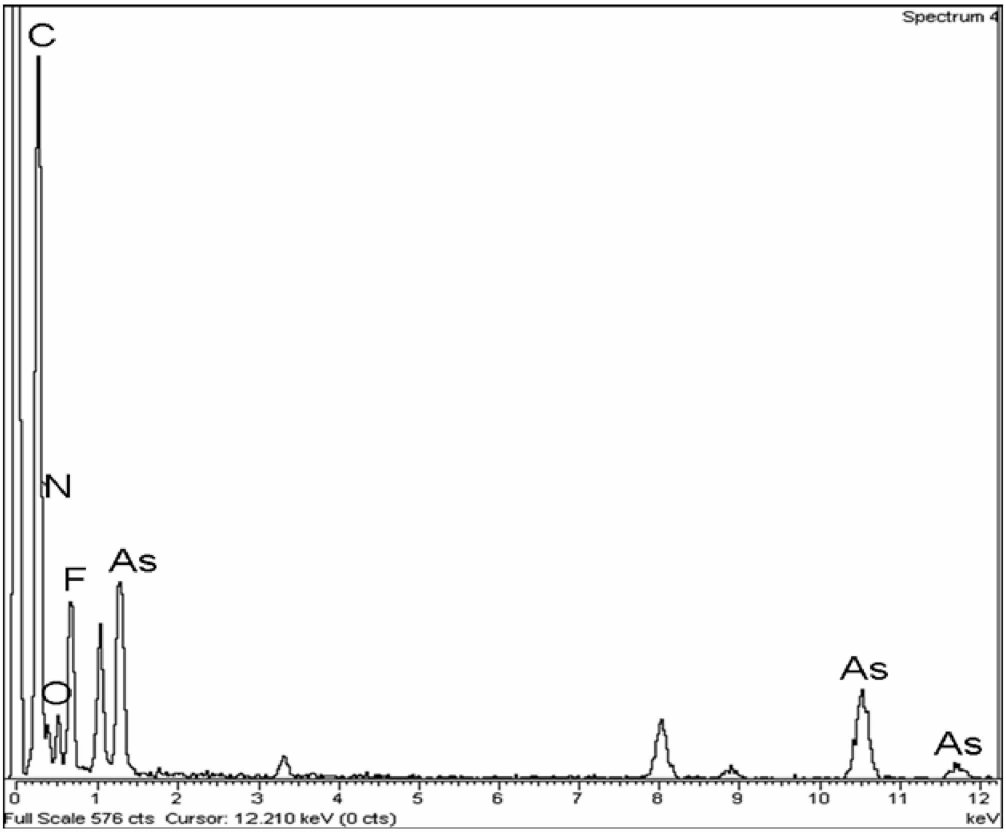


Fig. 32S.TEM-EDX profile of complex **1**.

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