

SUPPORTING INFORMATION

# Encapsulation of $[F_4(H_2O)_{10}]^{4-}$ in a Dimeric Assembly of an Unidirectional Arene Based Hexapodal amide Receptor

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## Experimental Section

**Compound L:** Hexakis(aminomethyl)benzene (0.303 g, 1.2 mmol) and 1 ml triethylamine was dissolved in 200 ml dry tetrahydrofuran and stirred at 0°C using ice-bath for 20 minutes under N<sub>2</sub> atmosphere. 3-nitrobenzoyl chloride (1.56 g, 8.4 mmol, 7 eq) was added batch-wise to the reaction mass under N<sub>2</sub> atmosphere with constant stirring. Formation of off-white precipitate was observed immediately. The temperature of the reaction was gradually brought to room temperature and continued stirring for 24hrs. Filtered the solid and washed with THF. The residue was washed with plenty of water to remove triethylammonium chloride followed by diethyl ether and air dried to give 1.05 g (76%) of L as off-white powder. <sup>1</sup>H NMR, 500 MHz (DMSO-*d*<sub>6</sub>) δ 4.82 (s, 12H, -CH<sub>2</sub>), 7.47 (t, 6H, -CH), 8.09 (d, 12H, -CH), 8.39 (s, 6H, -CH), 8.95 (s, 6H, -NH); <sup>13</sup>C NMR, 125.8 MHz (DMSO-*d*<sub>6</sub>) δ 39.5, 121.97, 125.98, 130.07, 134.14, 135.29, 137.90, 147.69, 163.87. HRMS (ESI): m/z 1169.1154 [L+Na]<sup>+</sup>, 1147.1666 [L+H]<sup>+</sup>. Elemental analysis: Calcd. for L: C, 56.55; H, 3.69; N, 14.65; O, 25.11. Found: C, 56.36; H, 3.97; 14.05.

**Complex 1:** Complex 1 was prepared by charging excess (10eq.) of tetrabutylammonium fluoride to the solution of L (115 mg, 100 μM) in 25 ml dioxane. Two weeks later, after complete evaporation of dioxane, few colorless crystals of 1 was found among the semi-

solid residue. The crystal was analyzed for single crystal X-ray crystallography and the semi-solid residue was washed with water, dried and analyzed for NMR spectroscopy.  $^1\text{H}$  NMR (500 MHz, Acetone- $d_6$ ):  $\delta$  (ppm) 0.94 (t,  $J = 7.5$  Hz, 28H,  $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.43 (q,  $J = 7.5$  Hz, 16H,  $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.57 (m, 16H,  $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.46 (16H,  $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.85 (s, 12H,  $-\text{NH}-\text{CH}_2$ ), 7.25 (t,  $J = 8$  Hz, 6H,  $\text{CH}$ ), 7.93 (d,  $J = 6.5$  Hz, 6H,  $\text{CH}$ ), 8.47 (d,  $J = 8$  Hz, 6H,  $\text{CH}$ ), 8.64 (s, 6H,  $\text{CH}$ ).  $^{13}\text{C}$  NMR, 125.8 MHz (Acetone- $d_6$ )  $\delta$  13.03, 19.54, 23.63, 39.61, 58.52, 122.80, 124.24, 128.84, 133.77, 136.28, 137.50, 147.75, 163.19.

**Complex 2:** Complex **2** was prepared by charging excess (10 eq.) of tetrabutylammonium acetate to the solution of **L** (115 mg, 100  $\mu\text{M}$ ) in 50 ml acetone-dioxane (1:1 V/V) binary solvent mixture. After a week, colorless crystals of **2** were formed and the crystal was analyzed for single crystal X-ray crystallography and the semi-solid residue was washed with water, dried and analyzed for NMR spectroscopy.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.89 (t,  $J = 6.5$  Hz, 24H,  $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.18 (q,  $J = 6.5$  Hz, 22H,  $-\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.32 (m, 16H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.78 (s, 6H,  $\text{CH}_3\text{COO}^-$ ), (t, 16H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.74 (s, 12H,  $-\text{NH}-\text{CH}_2$ ), 7.05 (t, 6H,  $-\text{CH}_{\text{Ar}}$ ), 7.89 (d, 6H,  $-\text{CH}_{\text{Ar}}$ ), 8.16 (d, 6H,  $-\text{CH}_{\text{Ar}}$ ), 8.74 (s, 6H,  $-\text{CH}_{\text{Ar}}$ ), 10.23 (b,  $-\text{NH}$ ).  $^{13}\text{C}$  NMR (125.8, MHz  $\text{CDCl}_3$ ):  $\delta$  13.52, 19.61, 23.80, 24.24, 39.90, 58.63, 122.92, 124.79, 128.80, 133.85, 135.59, 136.90, 147.67, 164.14, 176.75.

Crystal data for **1** and **2** were collected with a SMART APEX II diffractometer equipped

with a CCD area detector and a  $M_oK\alpha$  radiation source ( $\lambda = 0.7107 \text{ \AA}$ ). A crystal was selected from the semi solid residue, immersed in partone oil, and then mounted. Data collection, data reduction, and structure solution/refinement were carried out using the software package SMART APEX. Graphics were generated with MERCURY 2.3. Empirical absorption corrections were performed using equivalent reflections with the program SADABS. The structure was solved by direct methods and refined in a routine manner. Non-hydrogen atoms were treated anisotropically in all cases. All the hydrogen atoms were geometrically fixed for complex **1** and **2**. Lattice dioxane molecule in complex **1** was disordered at two sites and the disorder was modeled using PART command of the SHELXTL program.

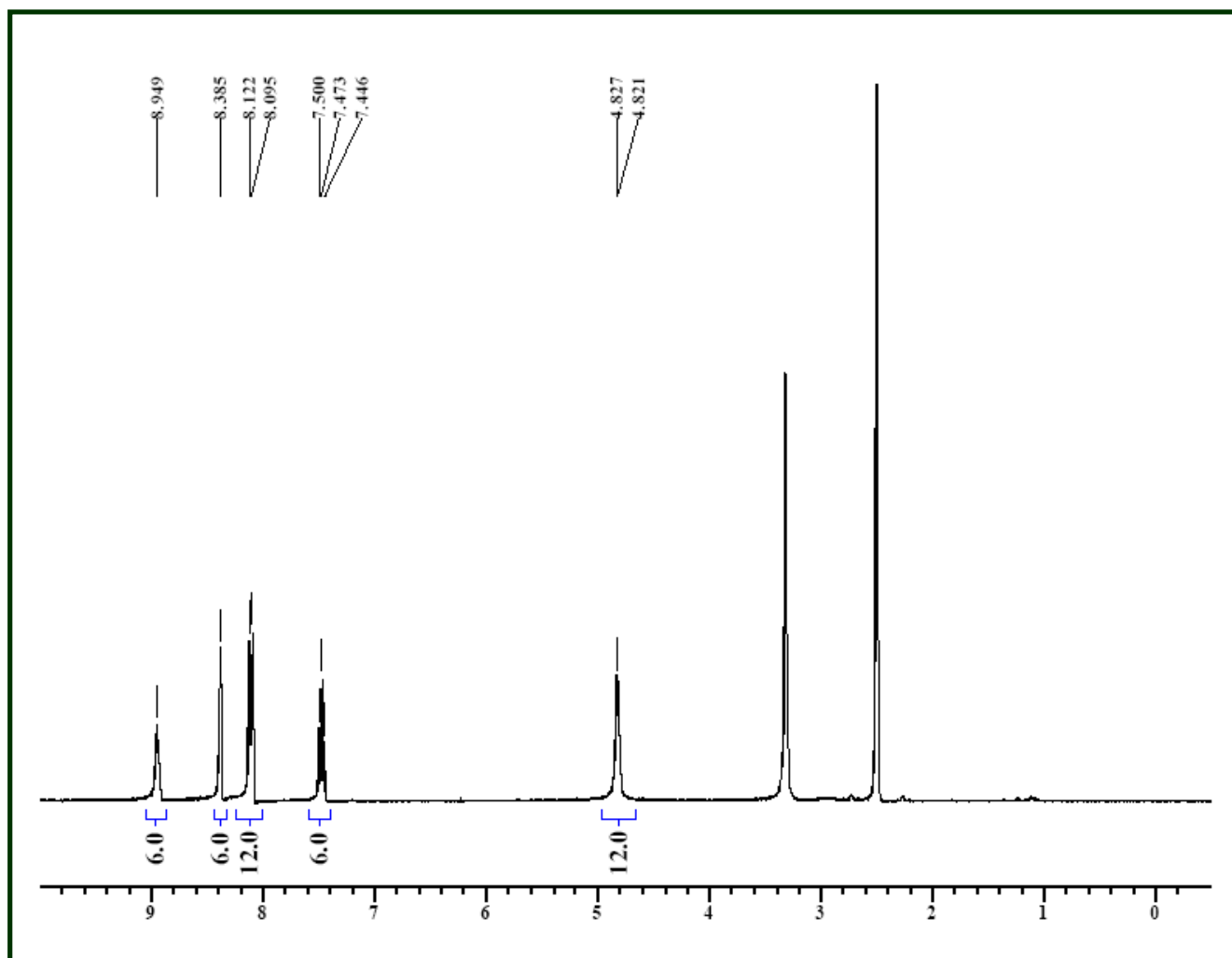


Figure S1.  $^1\text{H-NMR}$  spectra of ligand L in  $\text{DMSO-}d_6$  at  $25^\circ\text{C}$

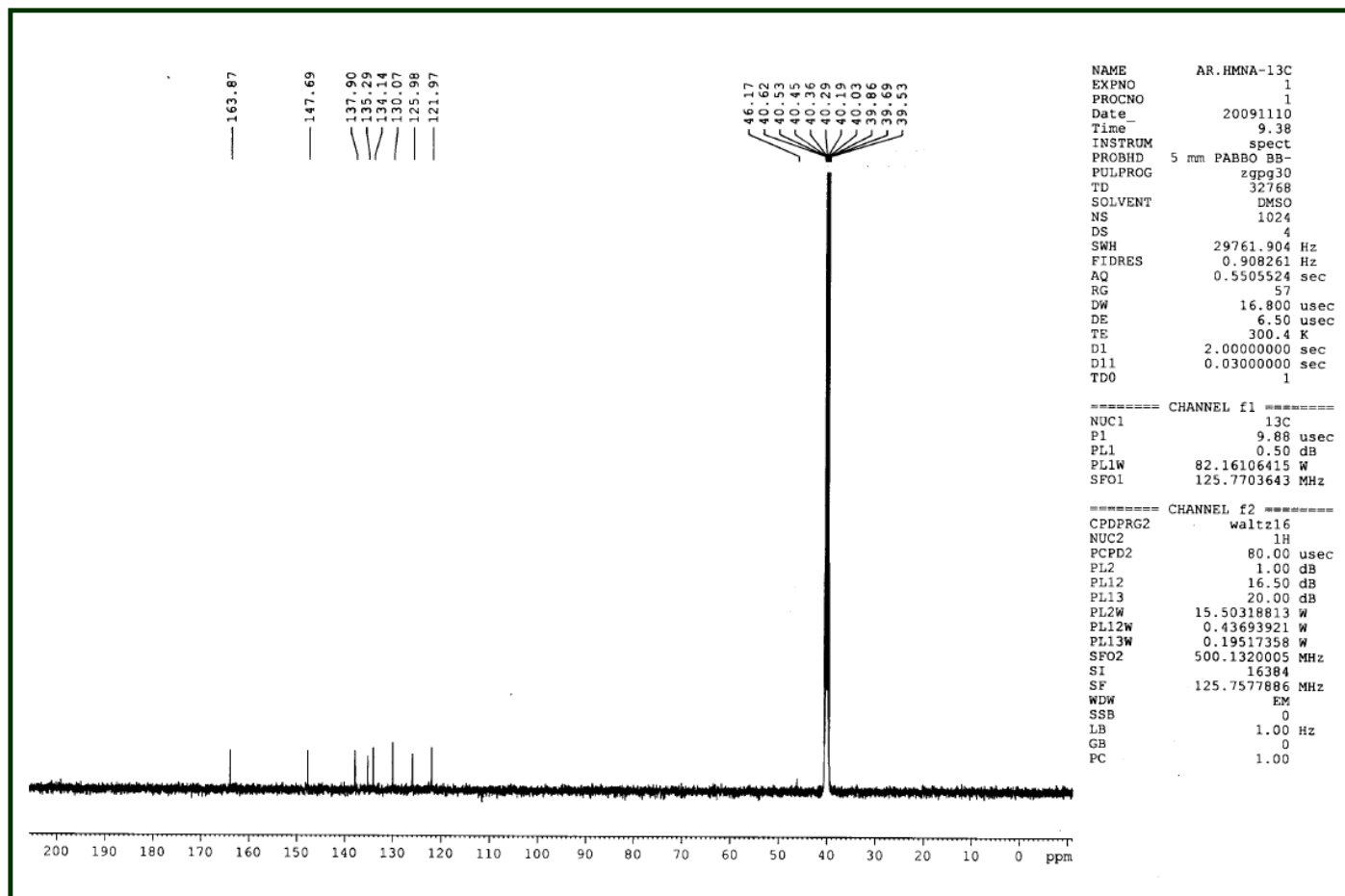


Figure S2.  $^{13}\text{C}$ -NMR spectra of ligand L in  $\text{DMSO-}d_6$  at  $25^\circ\text{C}$

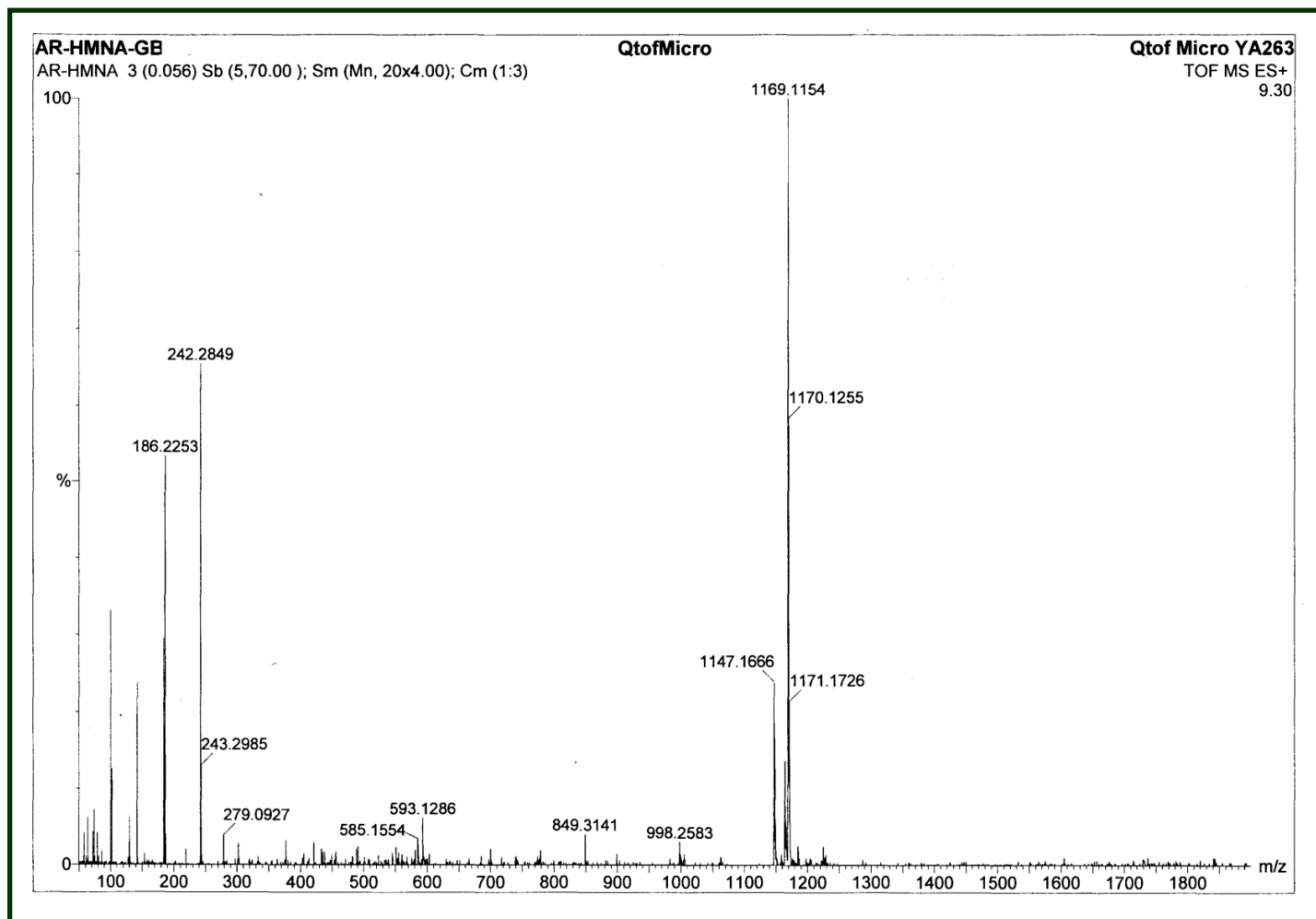


Figure S3. HRMS (ESI) of L

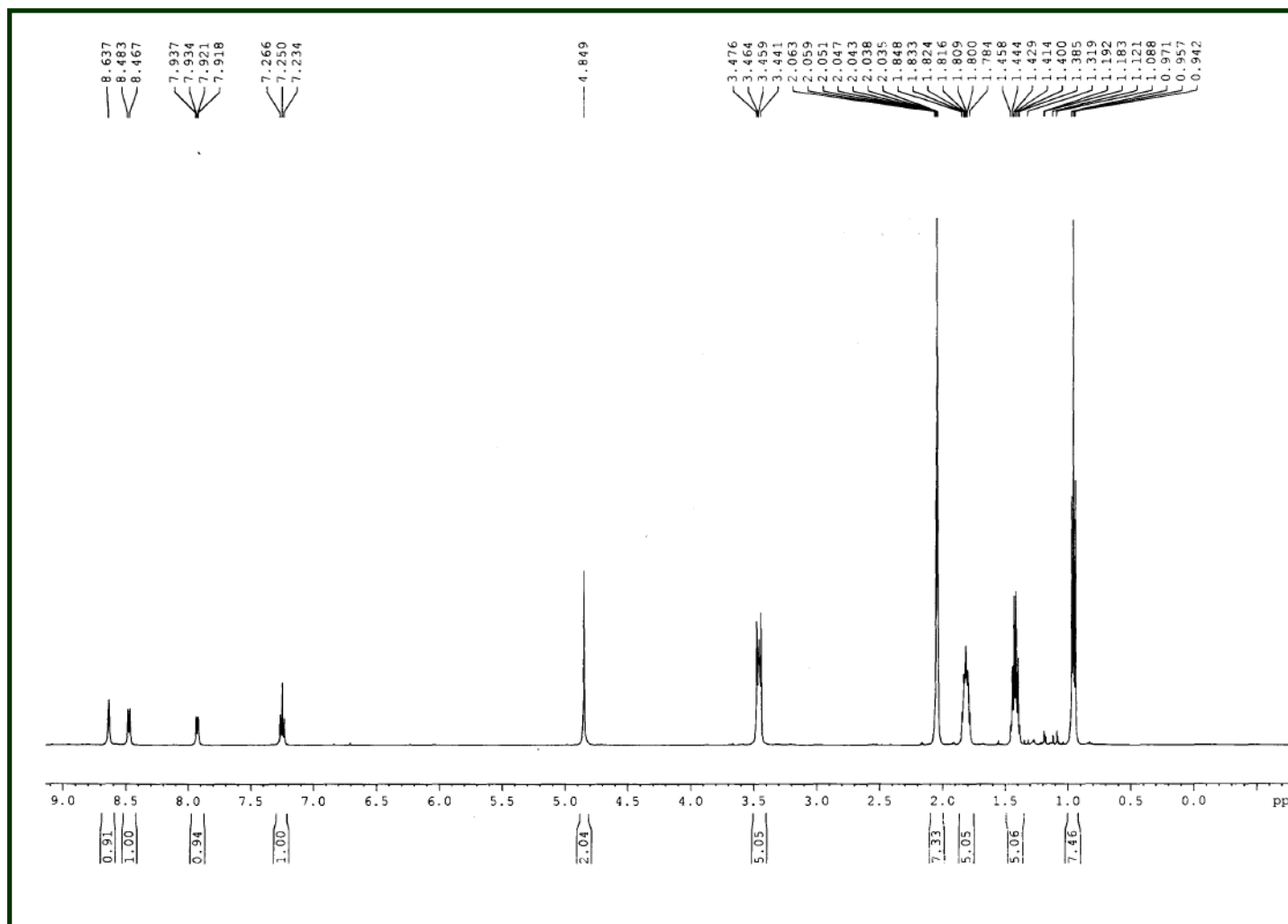
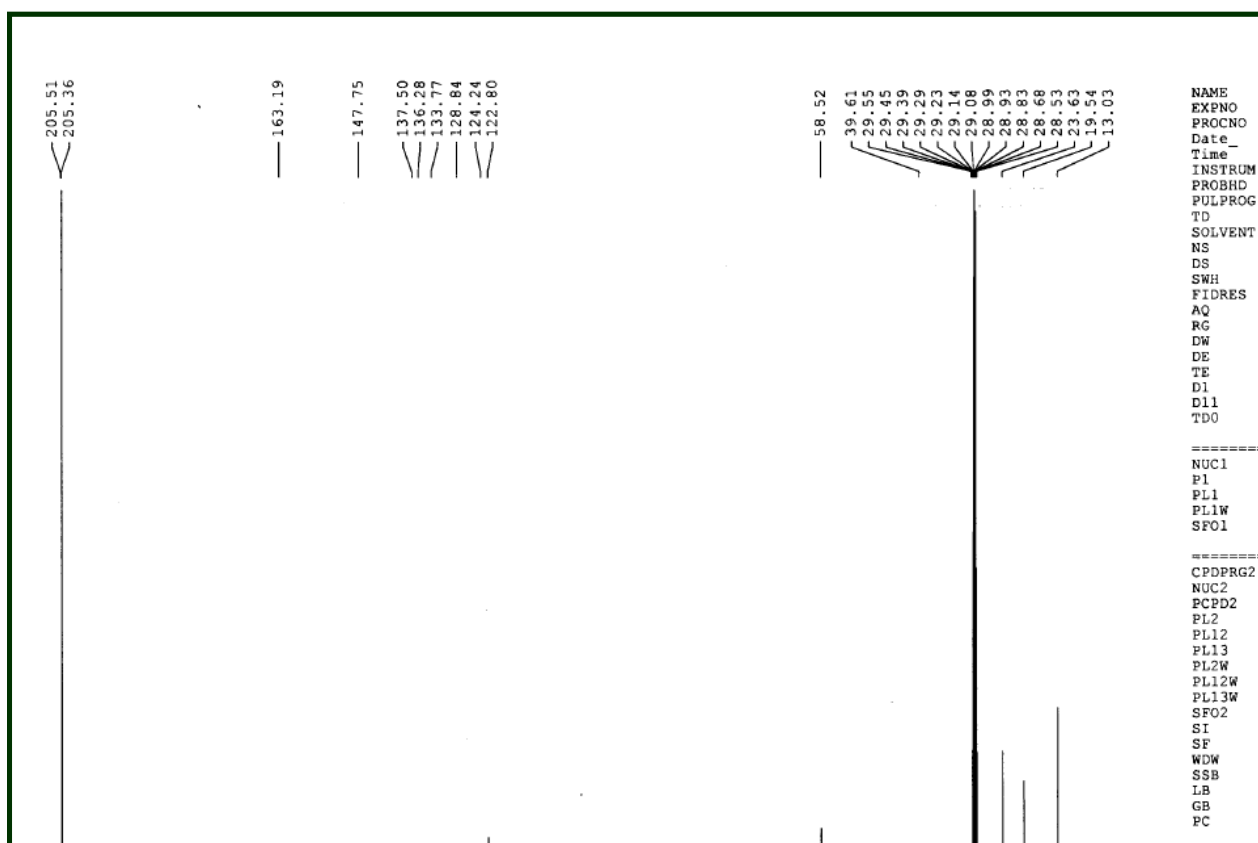


Figure S4. <sup>1</sup>H-NMR spectra of complex 1 in acetone-*d*<sub>6</sub> at 25°C





**Figure S5.**  $^{13}\text{C}$ -NMR spectra of complex **1** in acetone- $d_6$  at 25°C

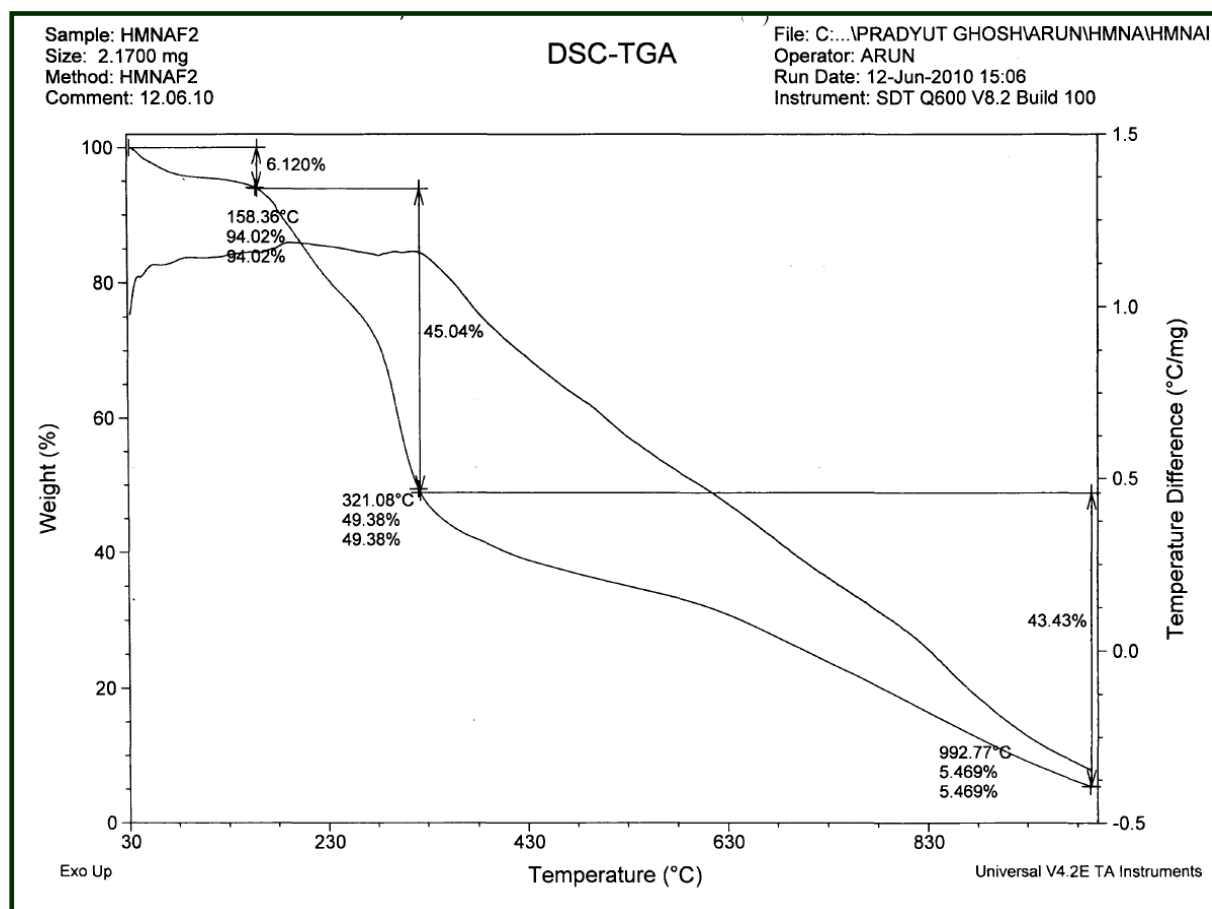


Figure S6. TGA spectrum of complex 1

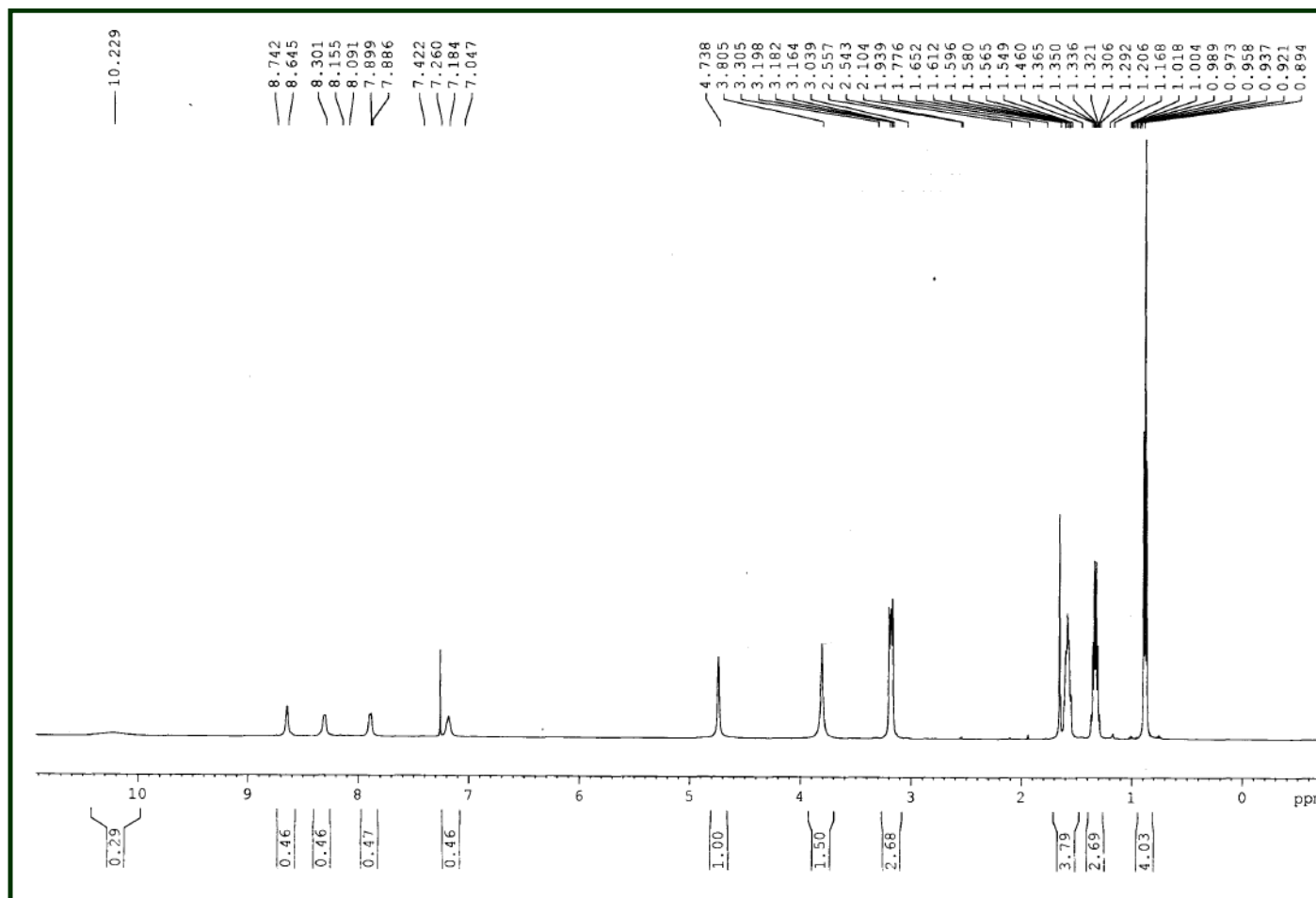
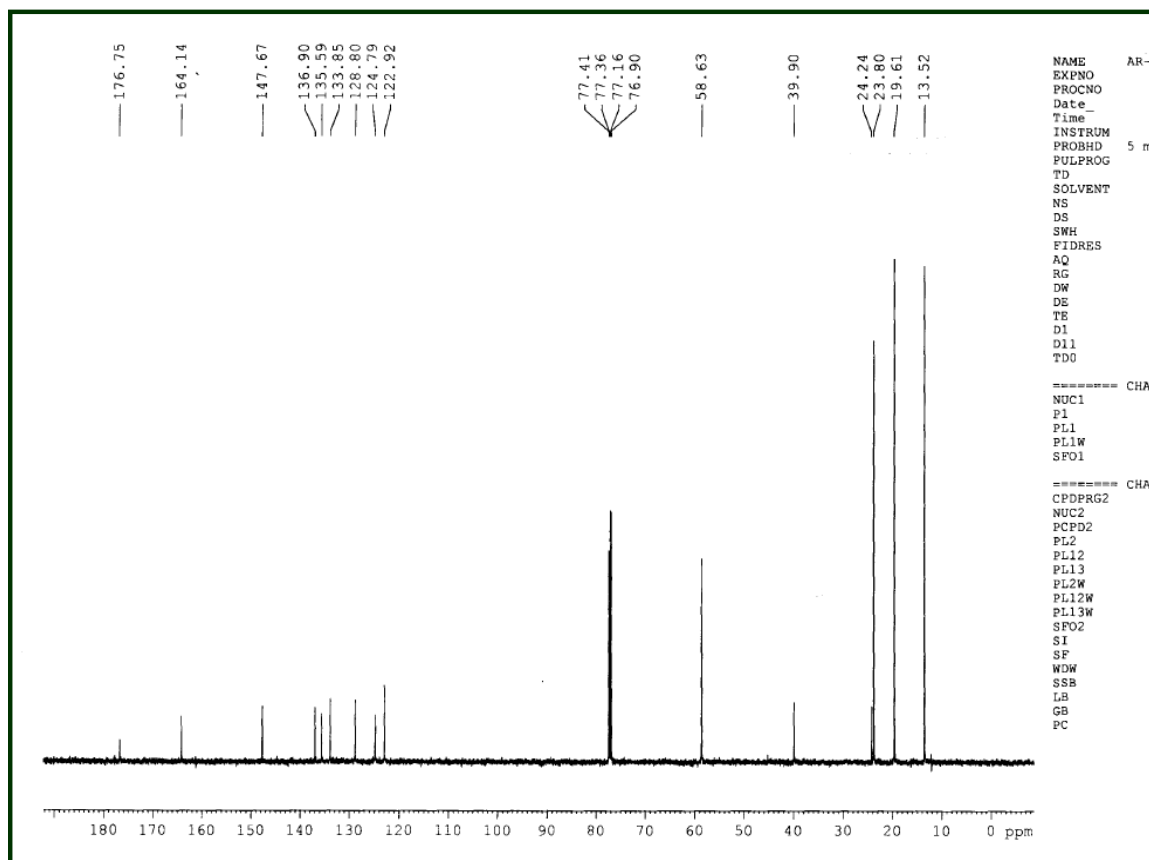


Figure S7.  $^1\text{H-NMR}$  spectra of complex **2** in  $\text{CDCl}_3$  at  $25^\circ\text{C}$

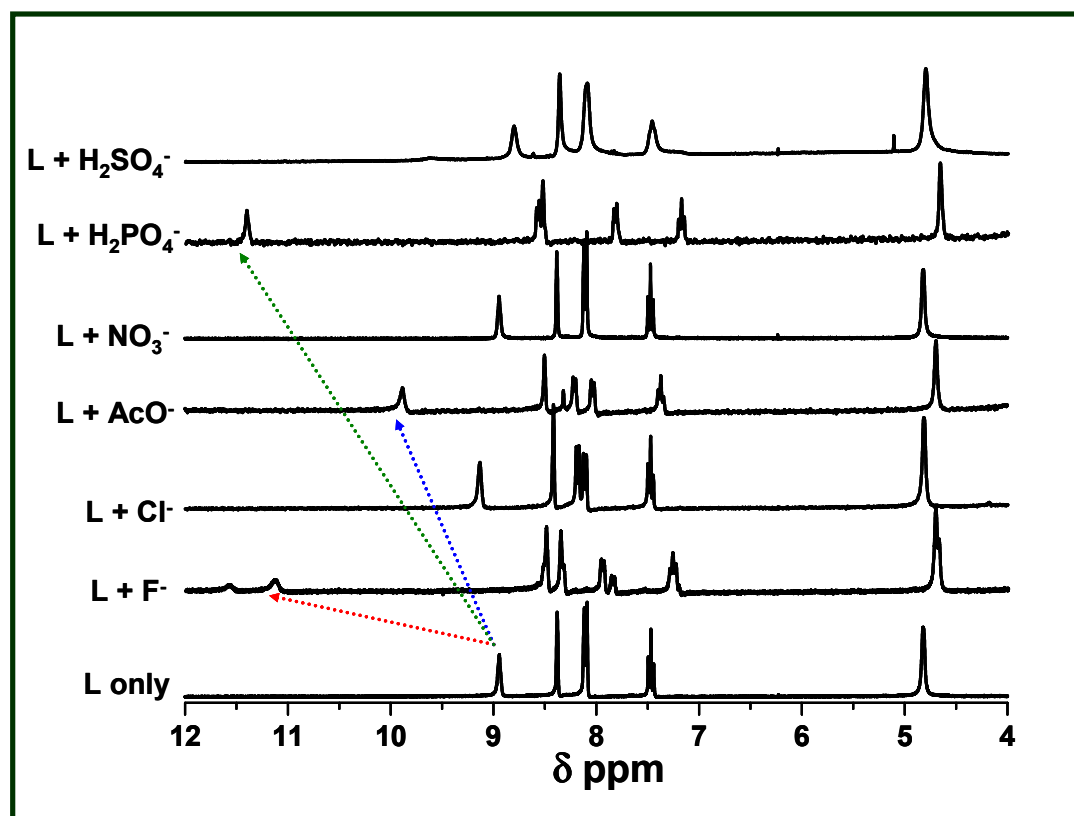


**Figure S8.**  $^{13}\text{C}$ -NMR spectra of complex **2** in  $\text{CDCl}_3$  at  $25^\circ\text{C}$

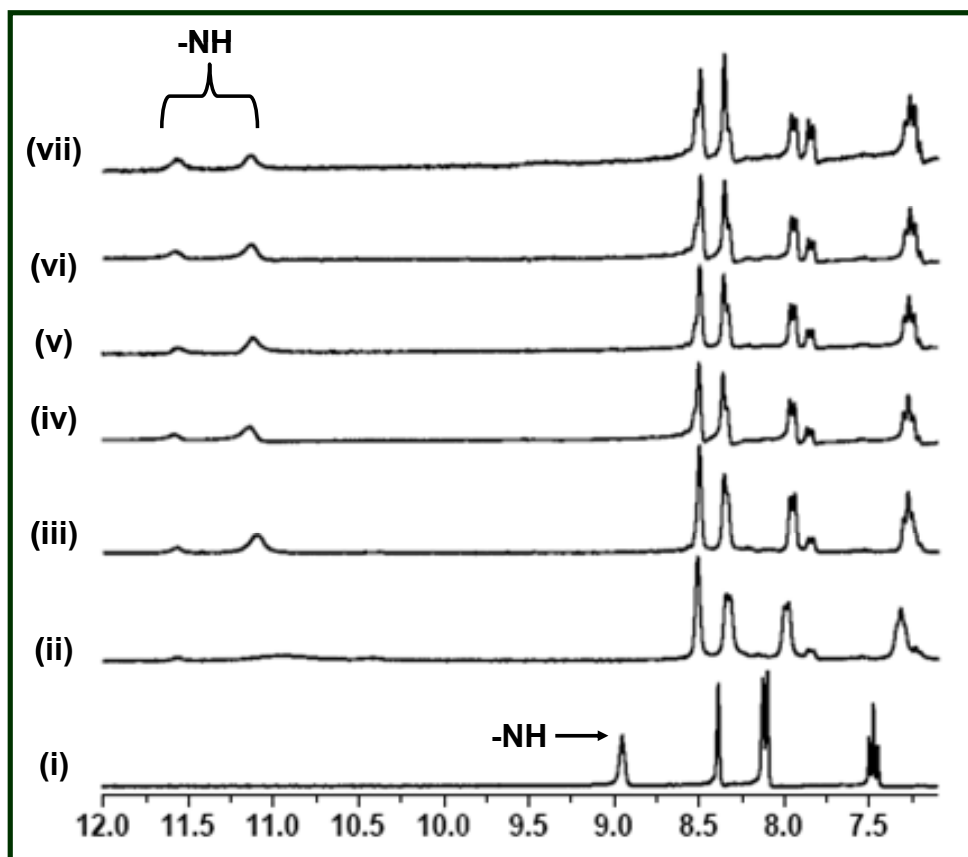
## Solution state anion binding studies of **L**

The anion binding ability of **L** in solution was validated by  $^1\text{H}$ -NMR experiments in  $\text{DMSO-}d_6$  at  $25^\circ\text{C}$  in the presence of tetrabutylammonium (TBA) salts of different anions. In qualitative  $^1\text{H}$ -NMR studies,  $\text{F}^-$ ,  $\text{AcO}^-$  and  $\text{H}_2\text{PO}_4^-$  showed huge changes in the NMR spectral pattern. These studies indicated the solution state binding of  $\text{F}^-$ ,  $\text{AcO}^-$  and  $\text{H}_2\text{PO}_4^-$  with **L**. For detailed solution state binding of these ions with **L**, we have carried out  $^1\text{H}$ -NMR titration experiments in  $\text{DMSO-}d_6$  at  $25^\circ\text{C}$ . Upon gradual addition of aliquots of TBA-F/TBA-OAc/TBA. $\text{H}_2\text{PO}_4^-$ , change in chemical shifts were observed for amide  $-\text{NH}$ , aryl  $-\text{CH}$  and  $-\text{CH}_2$  signals of **L**. In the case of  $\text{F}^-$ , the aryl  $-\text{CH}$  (singlet) signal is monitored for Job's plot analysis. The Job's plot for **L** with  $\text{F}^-$  showed host-guest stoichiometry 1:2. In addition to the parent signals, a set of new signals are generated after the addition of two equivalents of  $\text{F}^-$ . In cases of  $\text{AcO}^-$  the  $-\text{NH}$  proton signals were monitored for Job's plot analysis. Job's plot for **L** with  $\text{AcO}^-$  showed host-guest stoichiometry 1:4 along with a hump at 0.33 corresponds to the host-guest stoichiometry of 1:2. Thus titration experiments indicated that both  $\text{F}^-$  and  $\text{AcO}^-$  have multiple equilibria with **L** in the solution state. Whereas, the job's plot of **L** with  $\text{H}_2\text{PO}_4^-$  showed the prominent hump at 0.33 indicative of 1:2 **L**:  $\text{H}_2\text{PO}_4^-$  complexation in the solution. The association constants for the 1:2 (host: guest) complex for  $\text{H}_2\text{PO}_4^-$  was calculated by EQNMR. The overall association constants  $\log \beta_1$  and  $\log \beta_2$  for **L** with  $\text{H}_2\text{PO}_4^-$  are 2.39 and 4.44. Association constant calculation was not performed for  $\text{F}^-$  and

AcO<sup>-</sup> with L due to the existence of multiple equilibria in solution.

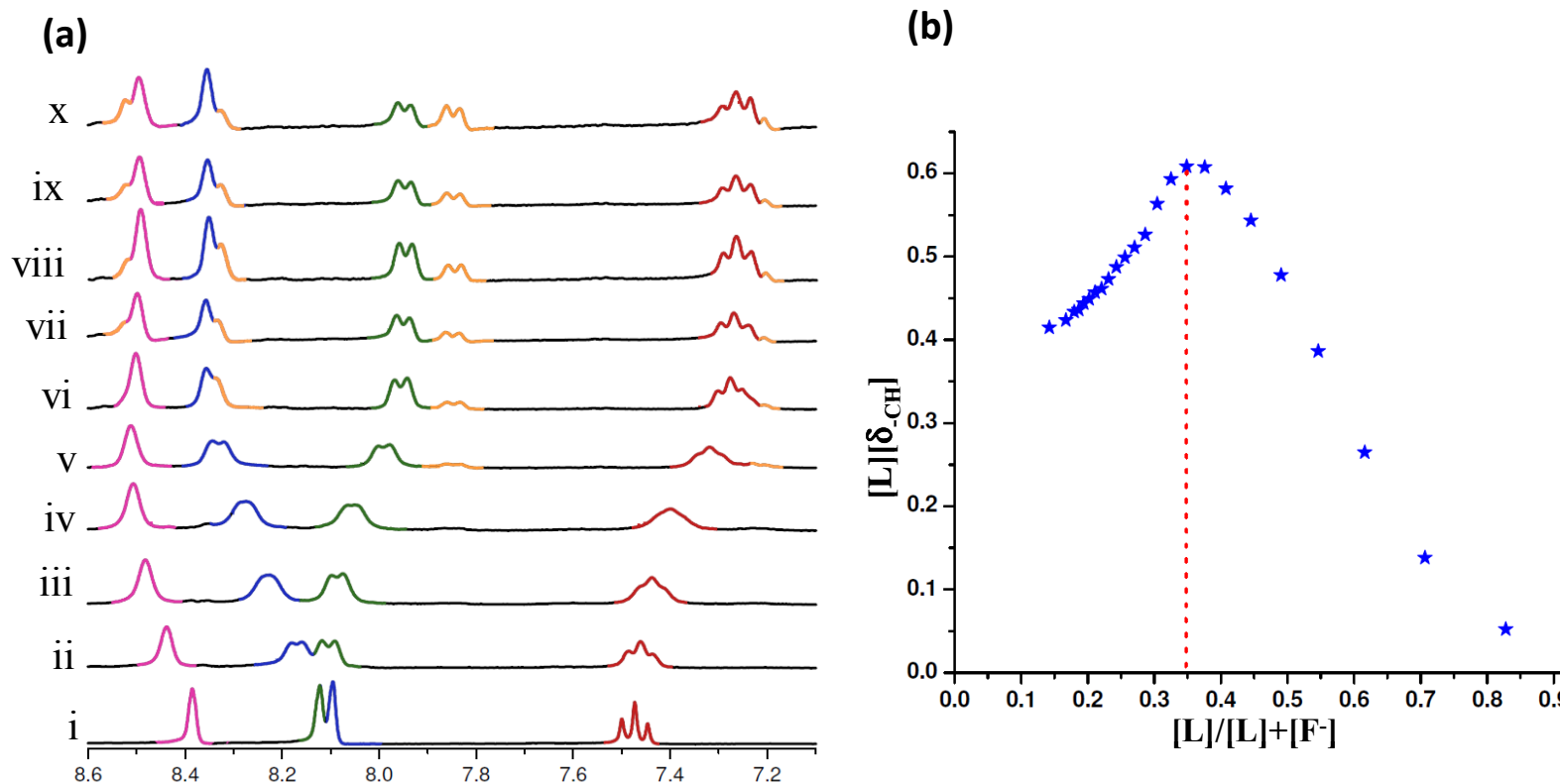


**Figure S9.** <sup>1</sup>H-NMR spectra showing change in chemical shift positions of L upon addition of excess of various anions in DMSO-*d*<sub>6</sub> at 25°C.



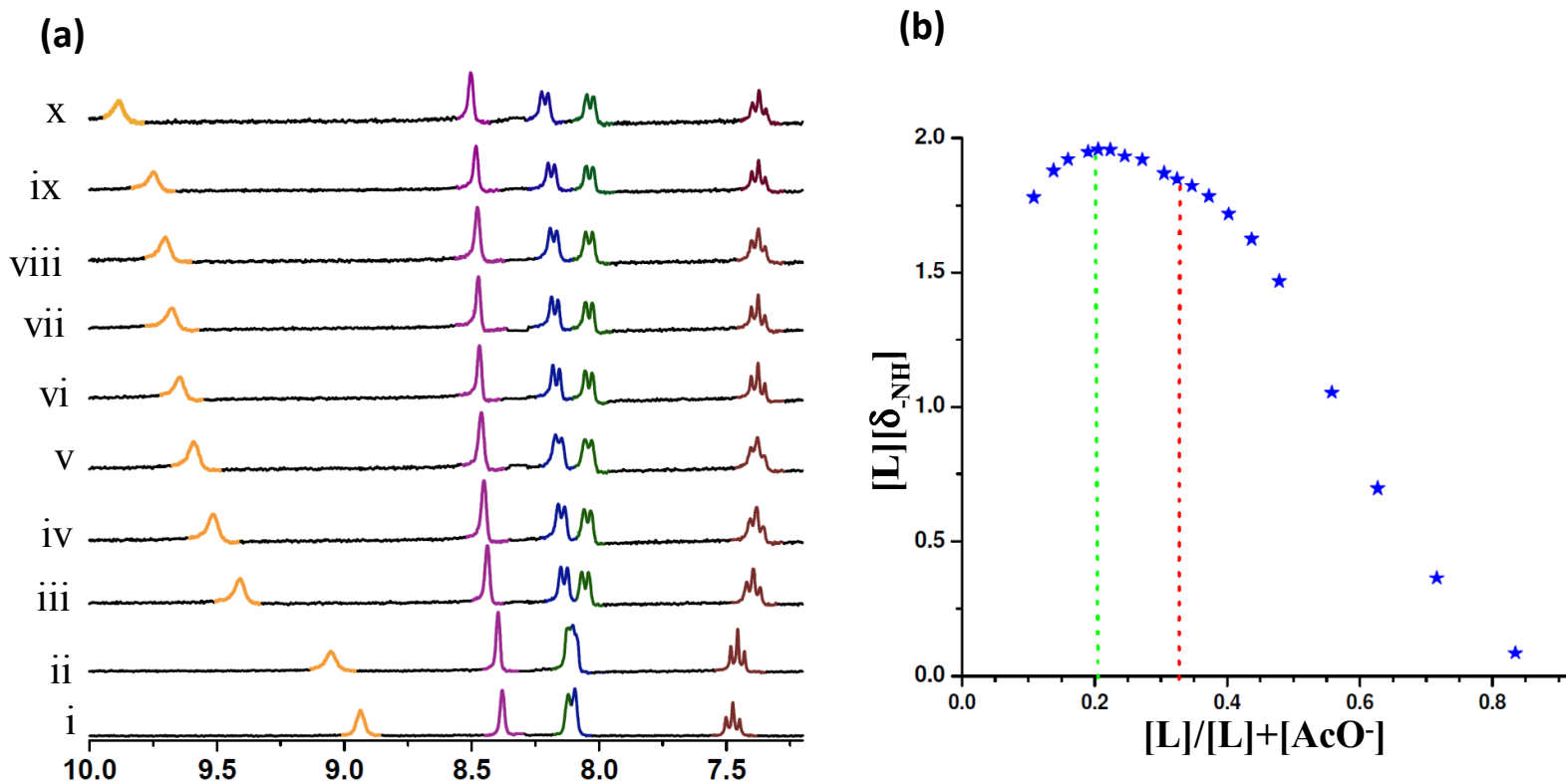
**Figure S10.**  $^1\text{H-NMR}$  spectral changes of L with added TBA-F in  $\text{DMSO-d}_6$

## $^1\text{H-NMR}$ titration experiments of **L** with TBA-F



**Figure S11.** (a)  $^1\text{H-NMR}$  spectral changes of **L** with added TBA-F ( $[\text{L}]$  is varied from 5.18 mM to 3.84 mM by the addition of aliquots of 100.03 mM TBA-F). Ratio of concentration  $[\text{L}]/[\text{F}^-]$ : (i) 0, (ii) 0.62, (iii) 1.04, (iv) 1.45, (v) 2.08, (vi) 2.49, (vii) 3.12, (viii) 3.53, (ix) 3.95, and (x) 6.02. (b) Job's plot for **L** with TBA-F. All spectra were recorded in  $\text{DMSO-}d_6$  at  $25^\circ\text{C}$ .

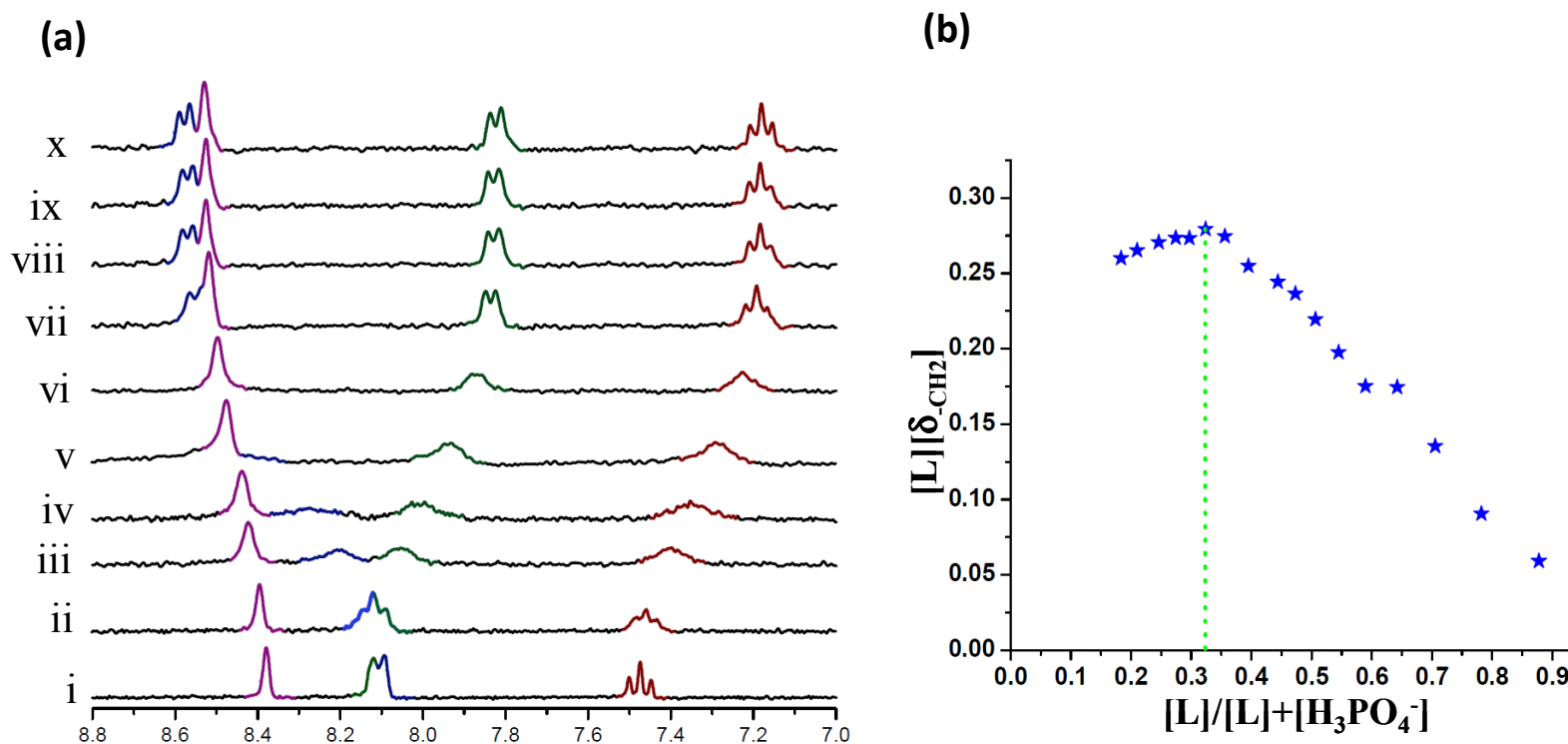
## $^1\text{H-NMR}$ titration experiments of **L** with TBA-OAc



**Figure S12.**(a)  $^1\text{H-NMR}$  spectral changes of **L** with added TBA-OAc. ( $[\text{L}]$  is varied from 3.45 mM to 1.89 mM by the addition of aliquots of 34.23 mM TBA-OAc). Ratio of concentration  $[\text{L}]/[\text{AcO}^-]$ : (i) 0, (ii) 0.40, (iii) 1.09, (iv) 1.49, (v) 2.08, (vi) 2.68, (vii) 3.07, (viii) 3.47, (ix) 4.26, and (x) 8.23. (b) Job's plot for **L** with TBA-OAc. All spectra were recorded in  $\text{DMSO-}d_6$  at  $25^\circ\text{C}$ .



## $^1\text{H-NMR}$ titration experiments of **L** with $\text{TBA-H}_2\text{PO}_4$



**Figure S13.**(a)  $^1\text{H-NMR}$  spectral changes of **L** with added  $\text{TBA-H}_2\text{PO}_4^-$ . ( $[\text{L}]$  is varied from 1.87 mM to 1.49 mM by the addition of aliquots of 32.46 mM  $\text{TBA-H}_2\text{PO}_4$ ). Ratio of concentration  $[\text{L}]/[\text{AcO}^-]$ : (i) 0, (ii) 0.28, (iii) 0.70, (iv) 0.97, (v) 1.53, (vi) 2.09, (vii) 2.64, (viii) 3.06, (ix) 3.76, and (x) 4.45. (b) Job's plot for **L** with  $\text{TBA-H}_2\text{PO}_4$ . All spectra were recorded in  $\text{DMSO-}d_6$  at  $25^\circ\text{C}$ .