Supporting Information

Encapsulation of $[X_2(H_2O)_4]^{2-}$ (X = F/Cl) clusters by pyridyl terminated tripodal amide receptor in aqueous medium: Single crystal X-ray structural evidence

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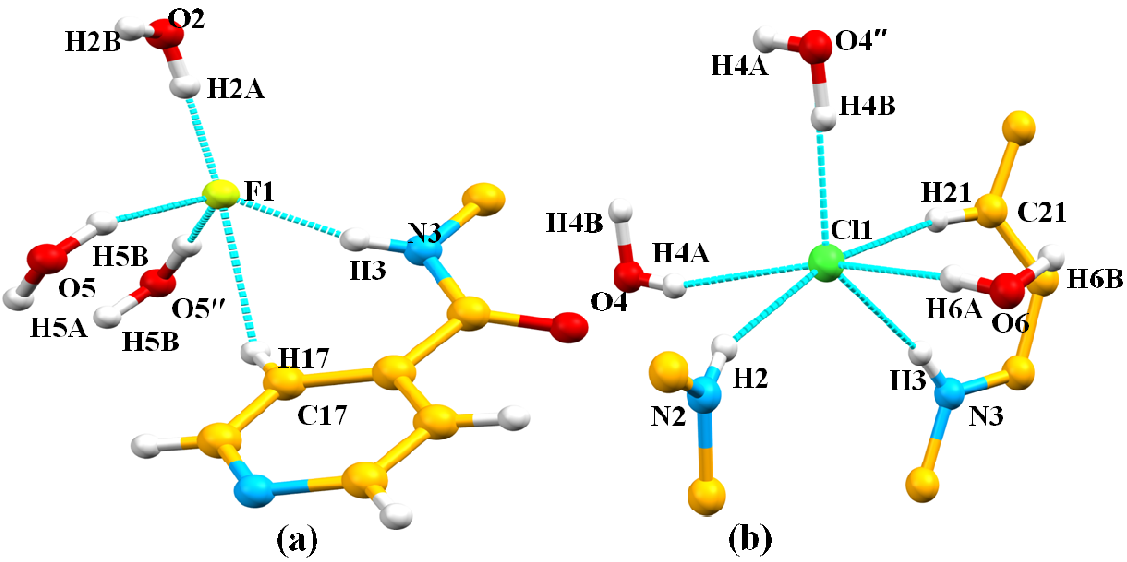


Fig. 1S: Coordination number and geometry of (a) complex **1**. In such distorted TBP arrangement F1 sits 1.047Å above the plane containing O5-N3-O5″ and distance of F1 from the centroid of plane containing O5-N3-O5″ is 1.166 Å. The plane containing O2-F1-C17 and O5-N3-O5″ dissects each other with an angle of 78.81° which means these planes are distorted by -11.19° compared to perfect TBP arrangement.

(b) Complex **2**. Here Cl1 sits just 0.326 Å above the centroid of plane containing O4-N2-O6-C21. In perfect octahedral arrangement the angle between axial atoms has to be 180° but in complex **2**, ∠O4″-Cl1-N3= 139.22° which means the structure is more axially distorted by -40.78°. The angle between axial (O4″-Cl1-N3) and equatorial planes (O4-N2-O6-C21) in complex **2**, is 88.67° which is slightly distorted by -1.33°.

Color codes of the crystal pictures are yellow: carbon, cyan: nitrogen, gray: hydrogen, red: oxygen, lighy green: fluoride, green: chloride.

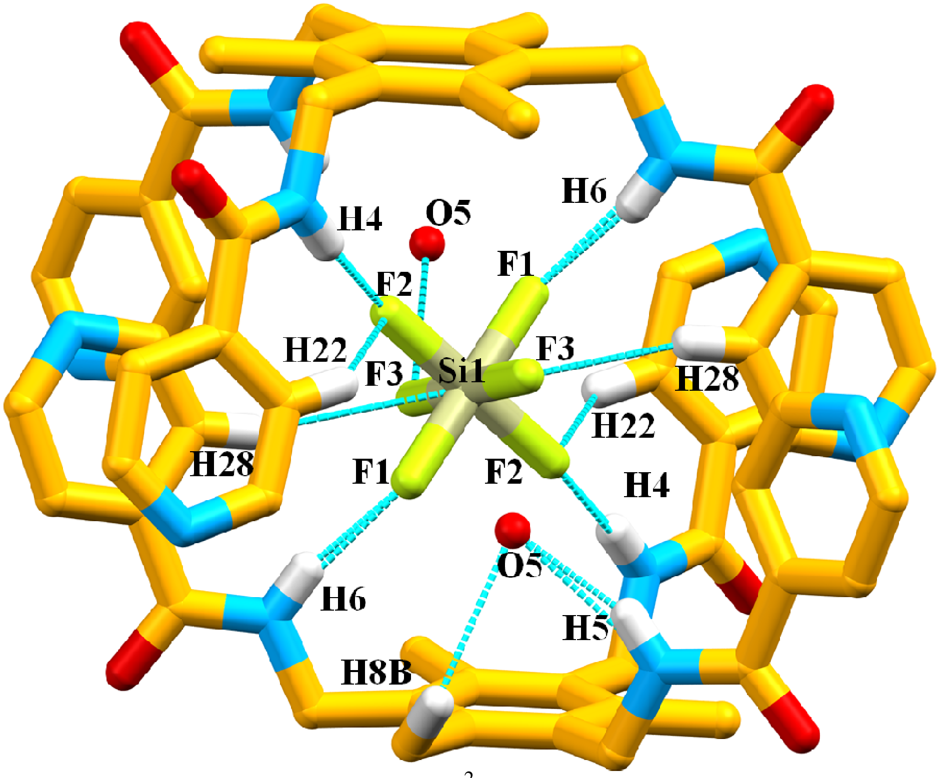


Fig. 2S: Labelled structure of complex **3**, SiF_6^{2-} encapsulated dimeric capsule. Color codes of the crystal picture are yellow: carbon, cyan: nitrogen, gray: hydrogen, red: oxygen, light green: fluoride.

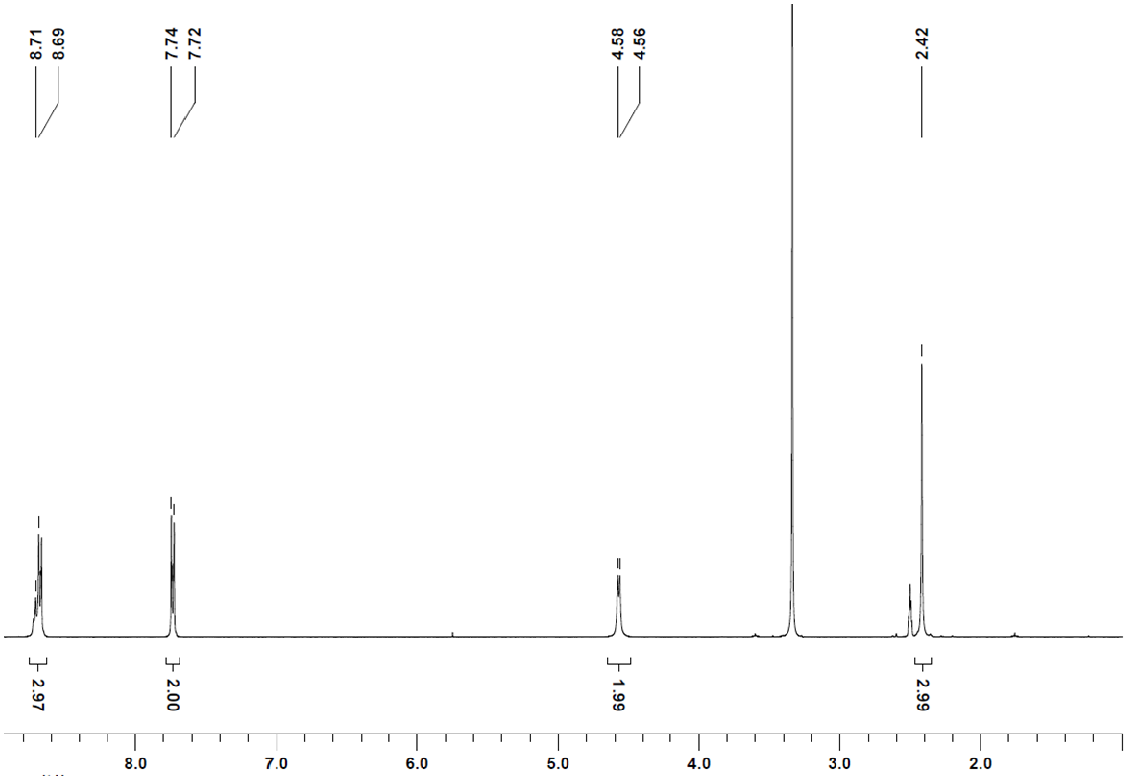


Fig. 3S: ^{1}H NMR (300 MHz) spectrum of receptor **L** in DMSO-d_6 at 25°C.

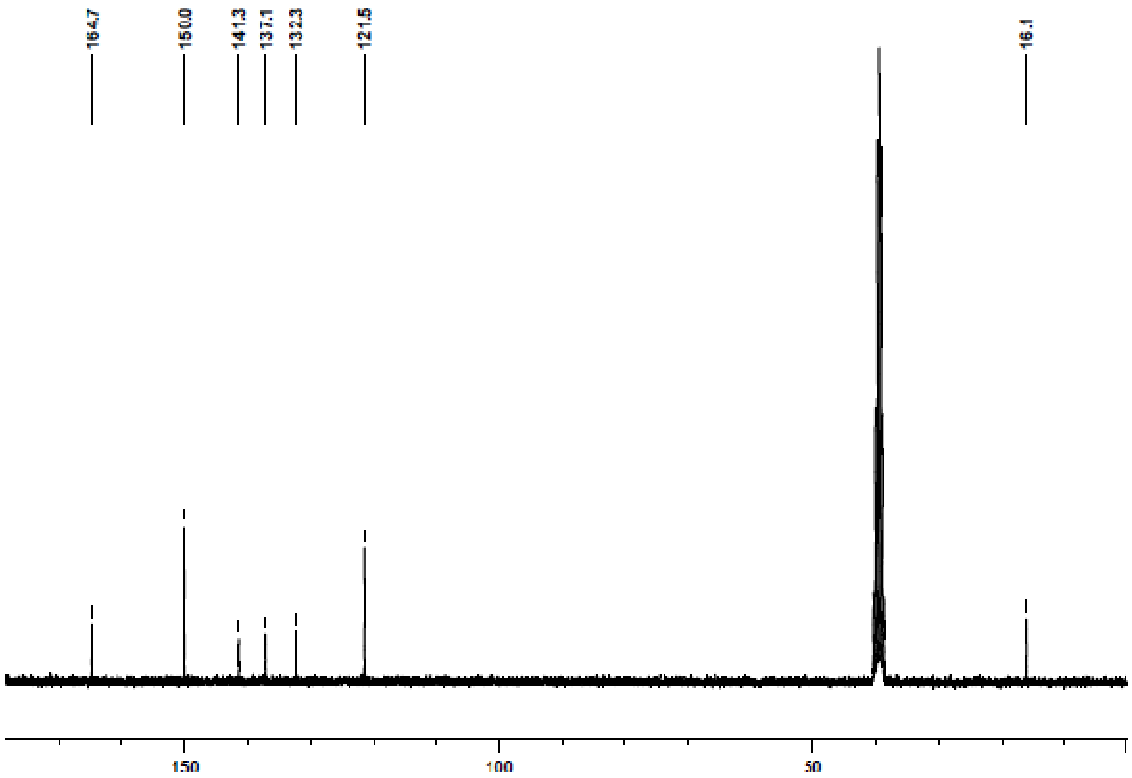


Fig. 4S: ^{13}C NMR (75 MHz) spectrum of receptor **L** in DMSO-d_6 at 25°C.

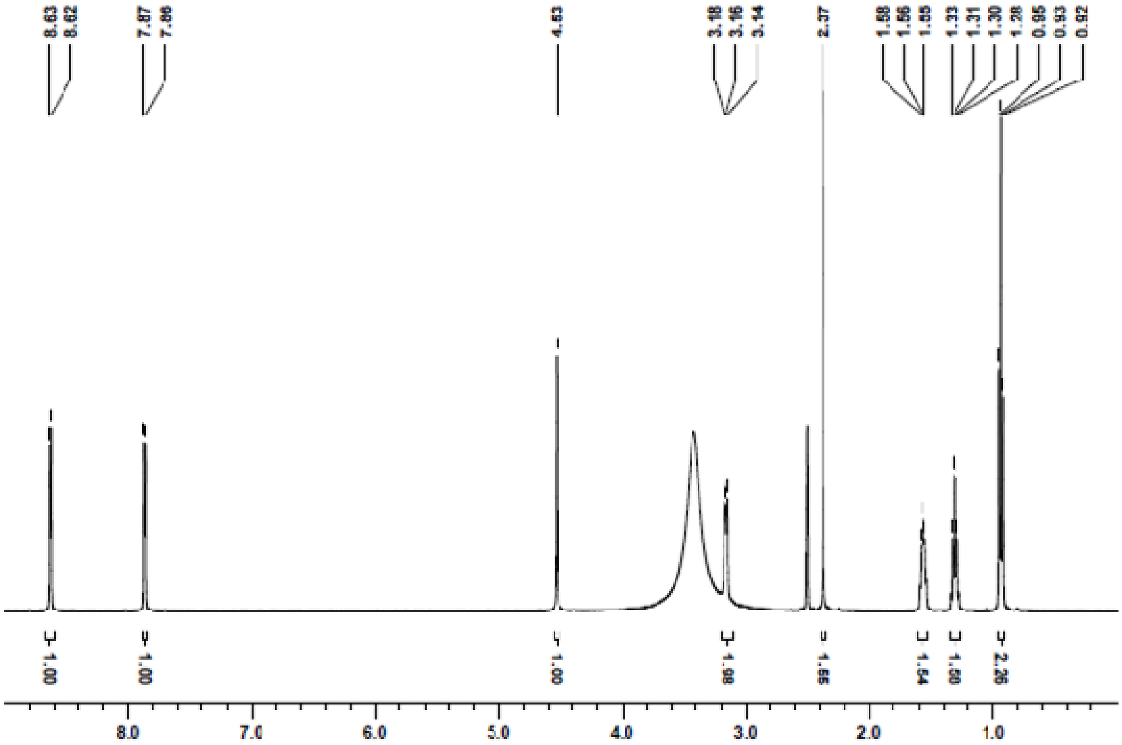


Fig. 5S: ^{1}H NMR (300 MHz) spectrum of complex **1** in DMSO-d_6 at 25°C.

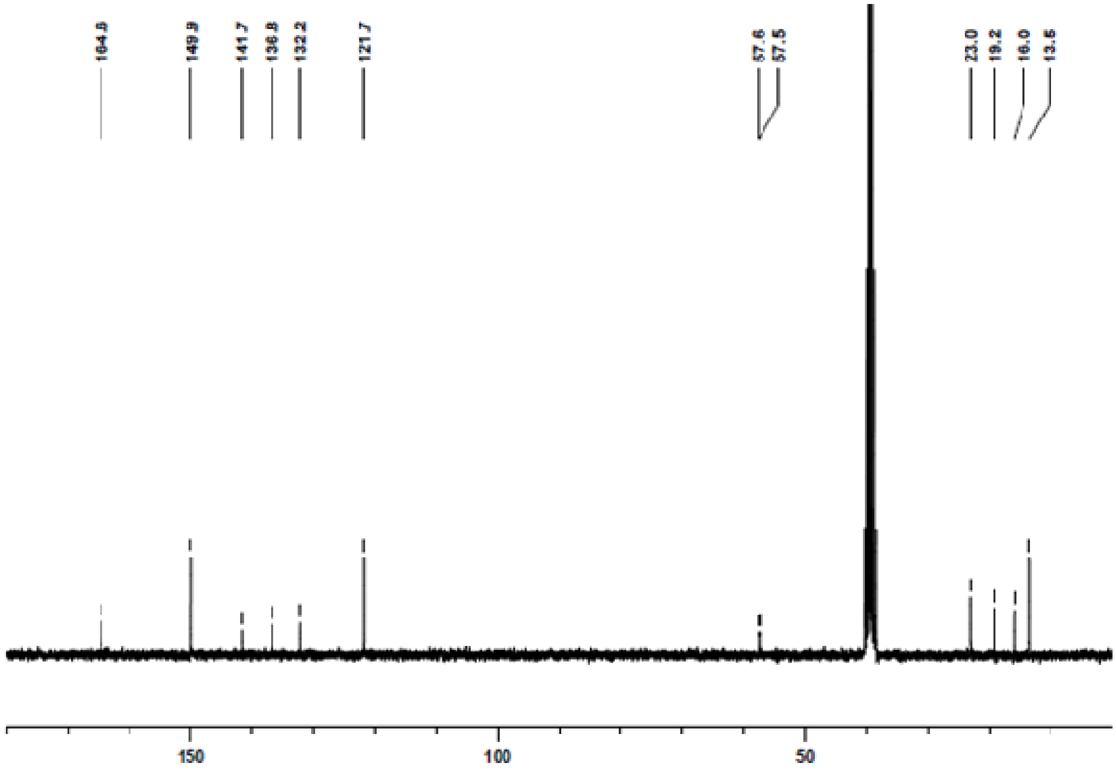


Fig. 6S: ^{13}C NMR (75 MHz) spectrum of complex **1** in DMSO-d_6 at 25°C.

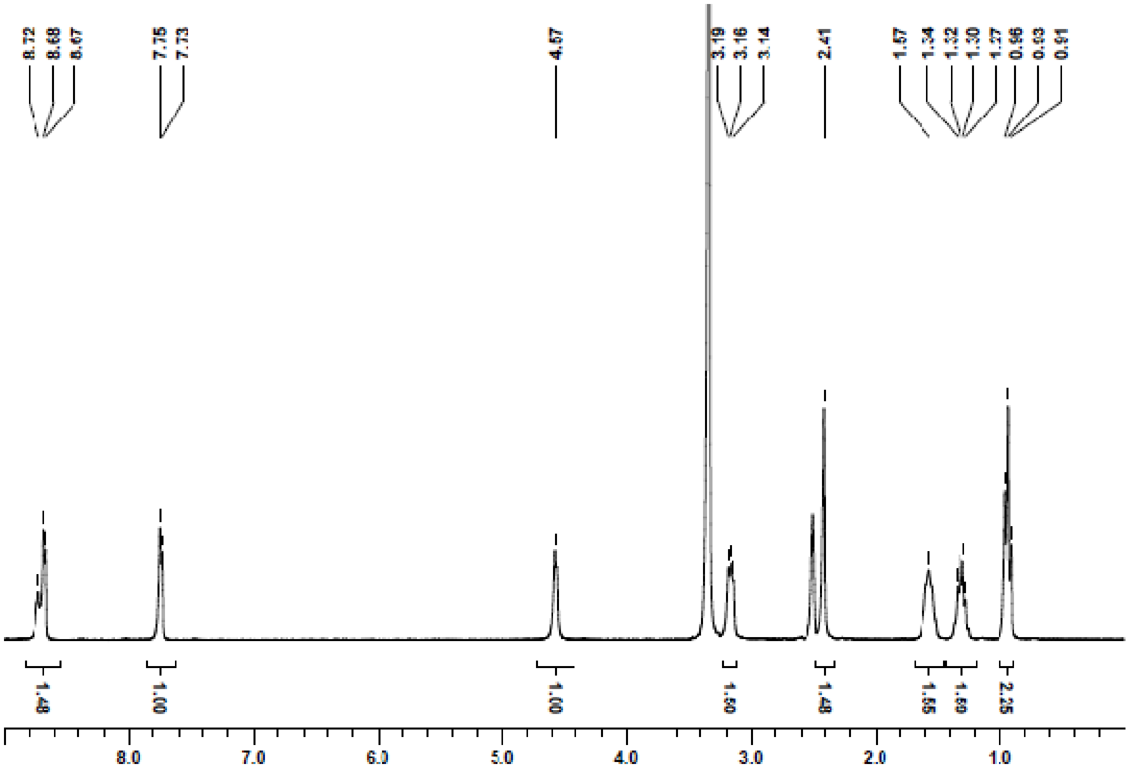


Fig. 7S: ^{1}H NMR (300 MHz) spectrum of complex **2** in DMSO-d_6 at 25°C.

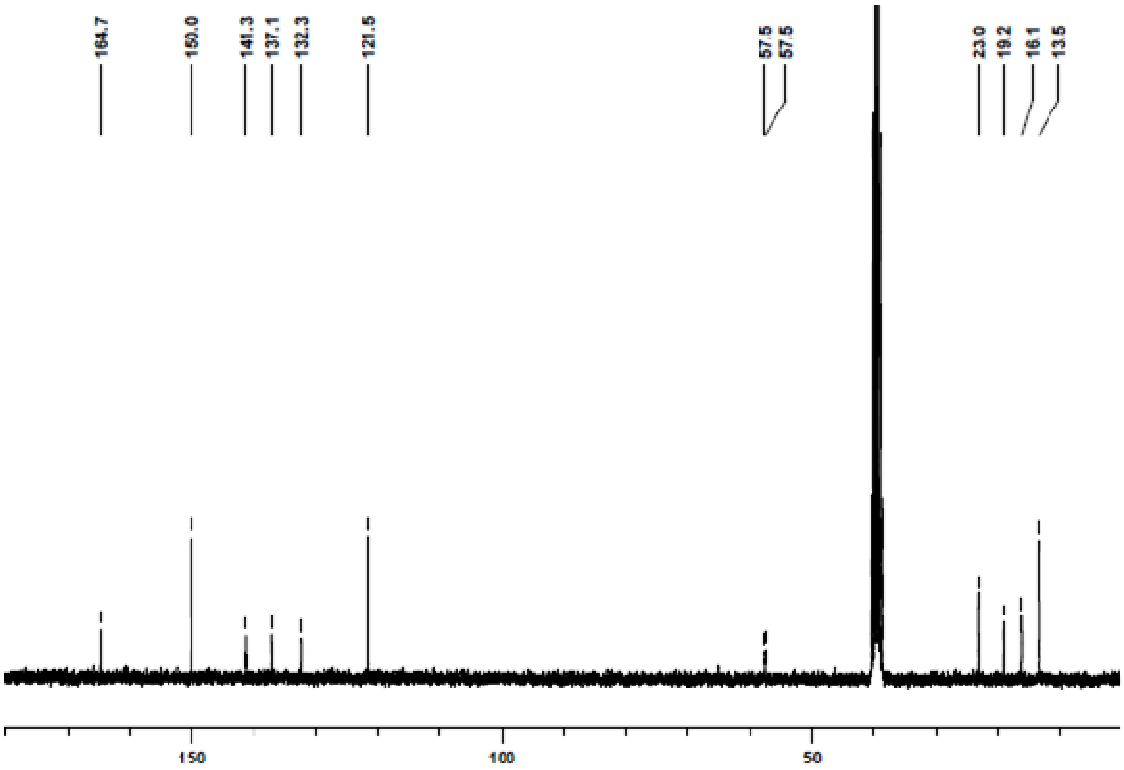


Fig. 8S: ^{13}C NMR (75 MHz) spectrum of complex **2** in DMSO-d_6 at 25°C.

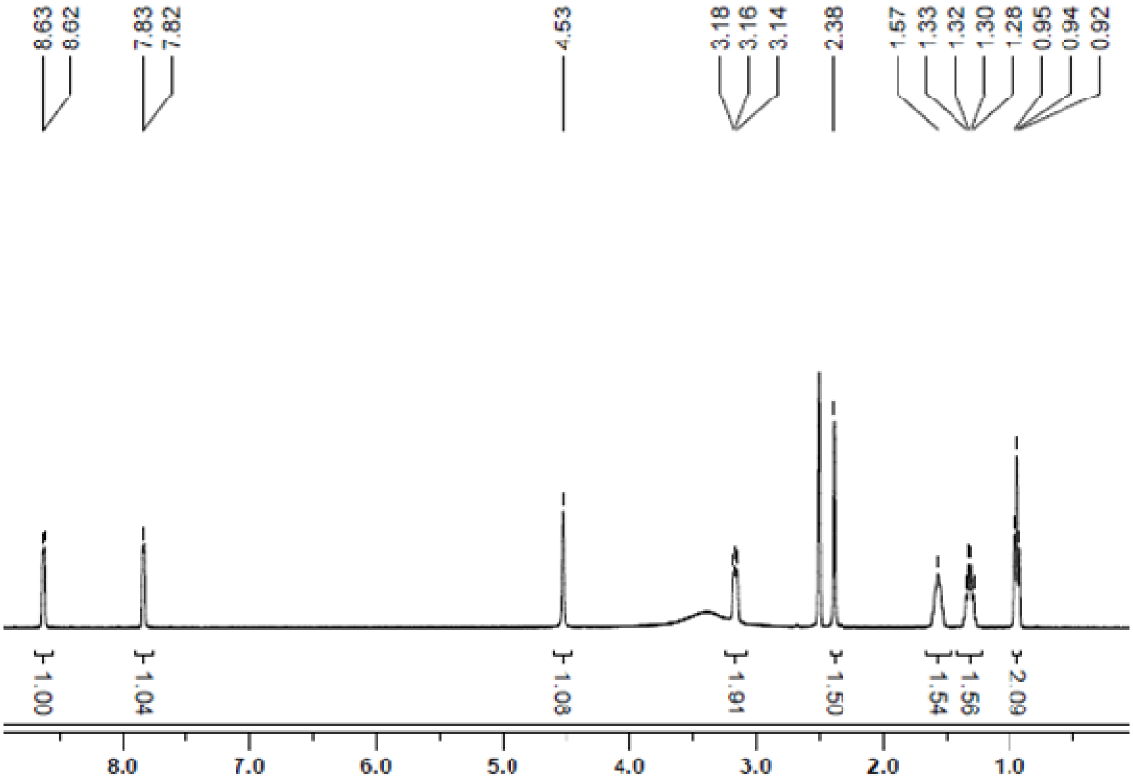


Fig. 9S: ^{1}H NMR (300 MHz) spectrum of complex **3** in DMSO-d_6 at 25°C.

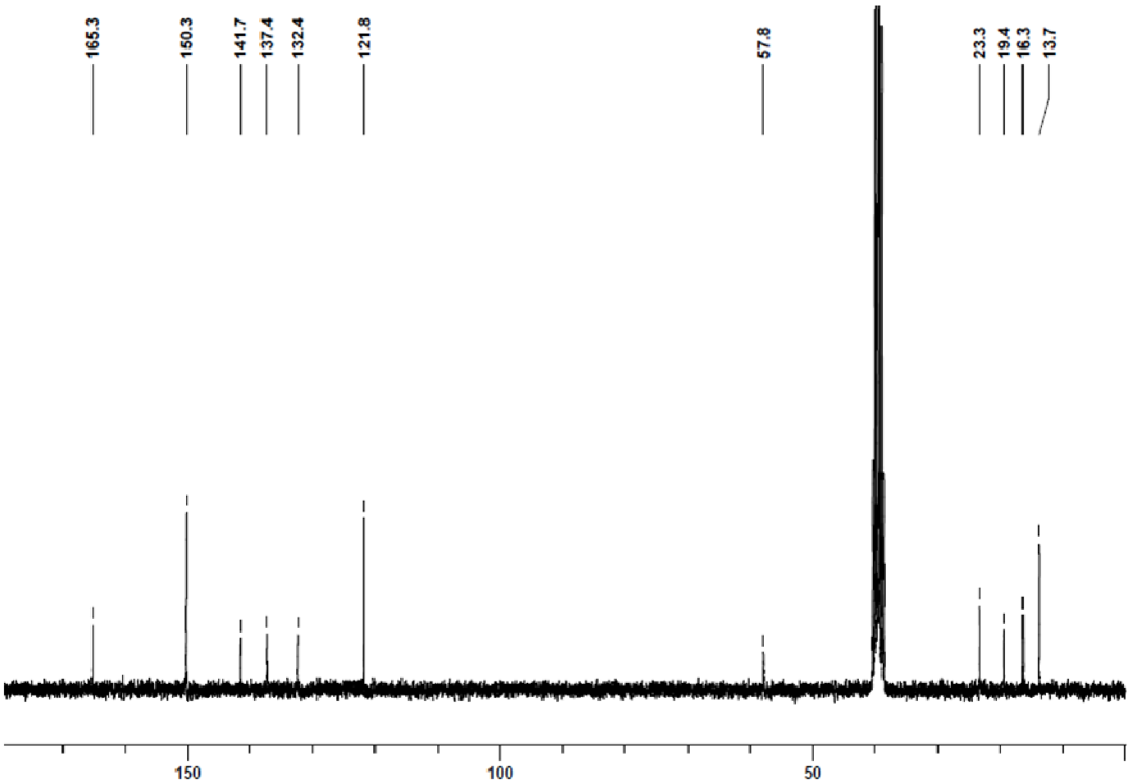


Fig. 10S: ^{13}C NMR (75 MHz) spectrum of complex **3** in DMSO-d_6 at 25°C.

Table 1S: Selected H-bonding parameters of complex **1**

D-H···A	**H···A (Å)**	**D···A (Å)**	**∠D-H···A (°)**
N1-H1···O5^{1}	1.9800	2.821(7)	165.00
O2-H2A···F1^{1}	1.78(5)	2.647(7)	171(7)
N3-H3···F1^{2}	1.8400	2.683(6)	165.00
O4-H4B···O11^{3}	2.06(7)	2.847(6)	154(6)
N5-H5···O2^{2}	2.0400	2.878(7)	163.00
O5-H5A···F1^{2}	1.71(10)	2.702(6)	165(7)
O5-H5B···F1^{4}	1.71(9)	2.618(6)	159(7)
O6-H6A···O4^{5}	2.06(9)	2.869(8)	174(11)
O6-H6B···N2^{6}	1.96(9)	2.871(8)	164(7)
C10-H10···O5^{1}	2.4500	3.254(8)	145.00
Symmetry codes: (1) x, y, z (2) x, y, -1+z (3) x, y, 1+z (4) 2-x, 1-y, 1-z (5) 1-x, 1-y, 1-z (6) -1+x, y, z.			

Table 2S: Selected H-bonding parameters of complex **2**

D-H···A	**H···A (Å)**	**D···A (Å)**	**∠D-H···A (°)**
N1-H1···O4^{1}	2.1600	2.974(3)	157.00
N2-H2···Cl1^{2}	2.6100	3.429(2)	159.00
N3-H3···Cl1^{2}	2.5900	3.419(2)	161.00
O4-H4A···Cl1^{2}	2.61(3)	3.375(2)	161(4)
O5-H5B···O1^{3}	2.52(4)	2.942(3)	112(4)
C3-H3B···N1^{1}	2.6000	3.311(4)	132.00
C12-H12A···O3^{1}	2.3900	2.732(3)	100.00
C37-H37B···O3^{4}	2.5900	3.384(3)	139.00
C41-H41B···O2^{5}	2.4700	3.421(3)	166.00
Symmetry codes: (1) x, y, z (2) x, y, 1+z (3) x, y, -1+z (4) 1-x, 1-y, 1-z (5) 2-x, 1-y, 1-z.			

Table 3S: Selected H-bonding parameters of complex **3**

D-H···A	**H···A (Å)**	**D···A (Å)**	**∠D-H···A (°)**
N4-H4···F2^{1}	2.0100	2.854(3)	166.00
N5-H5···O5^{2}	2.0600	2.880(3)	158.00
N6-H6···F1^{1}	2.0000	2.844(3)	167.00
C9-H9B···O1^{3}	2.5900	3.429(3)	145.00
C22-H22···F2^{1}	2.5300	3.252(4)	135.00
C28-H28···F3^{1}	2.5300	3.442(7)	165.00
Symmetry codes: (1) x, 1+y, z (2) x, y, z (3) -x, 1-y, 2-z			

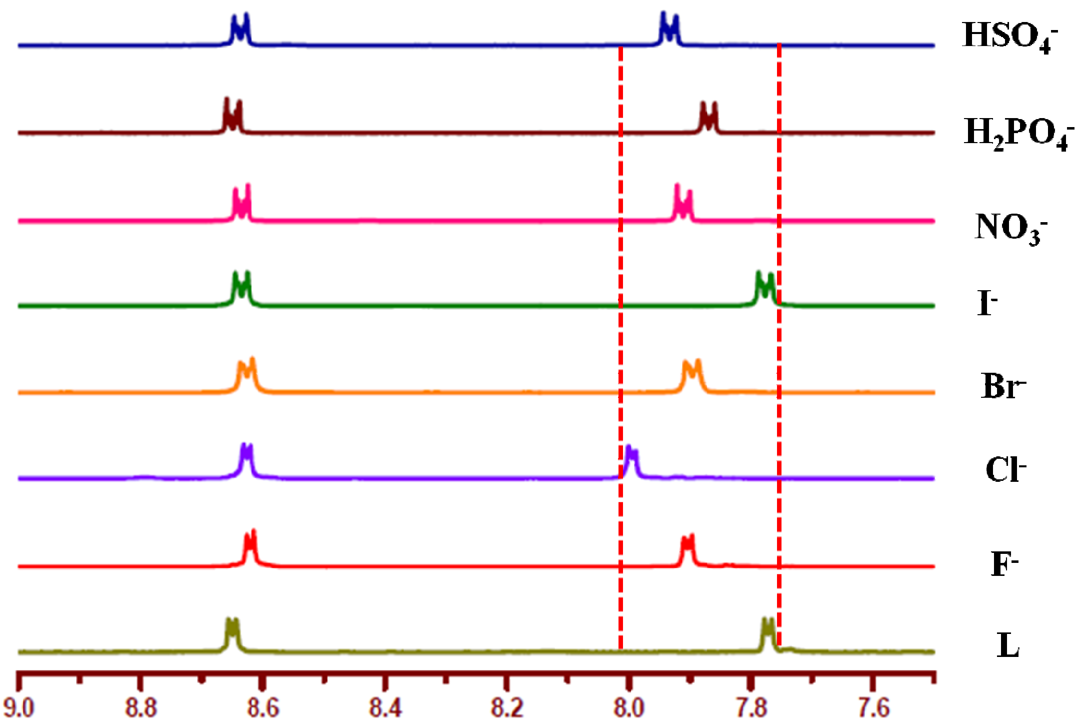


Fig. 11S: Comparative partial ^{1}H NMR (300 MHz) spectra of **L**(~ 4 mM) in D_2O-acetone-d_6 (1:19, v/v) after addition of excess amount (~ 3 equivalent) of TBA salts of different anions.

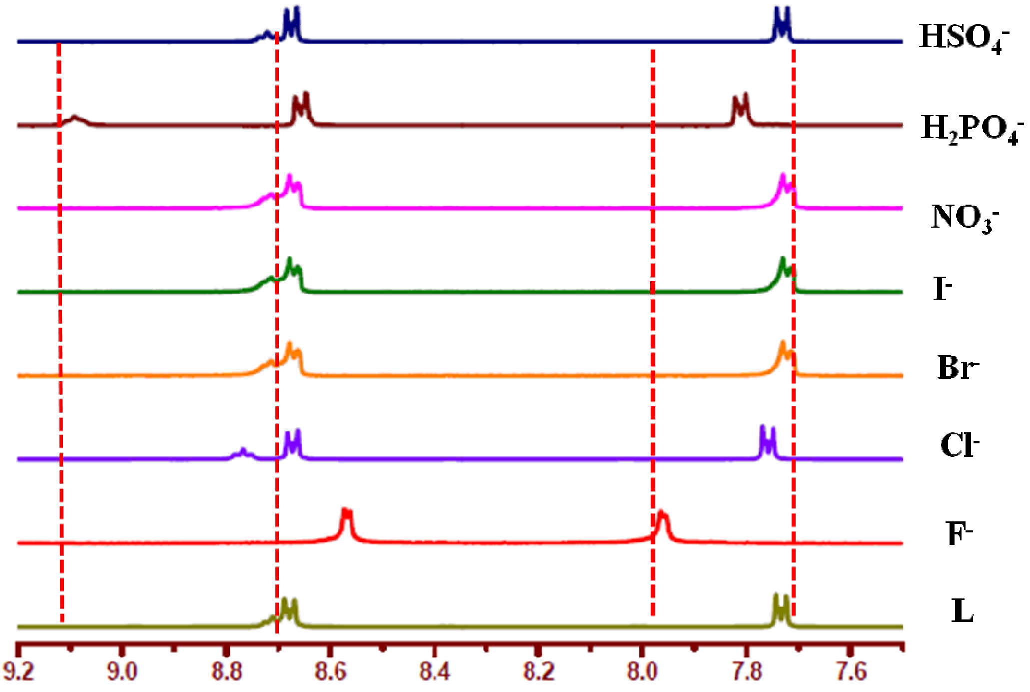


Fig. 12S: Comparative partial ^{1}H NMR (300 MHz) spectra of **L**(~ 4 mM) in DMSO-d_6 after addition of excess amount (~ 3 equivalent) of TBA salts of different anions.

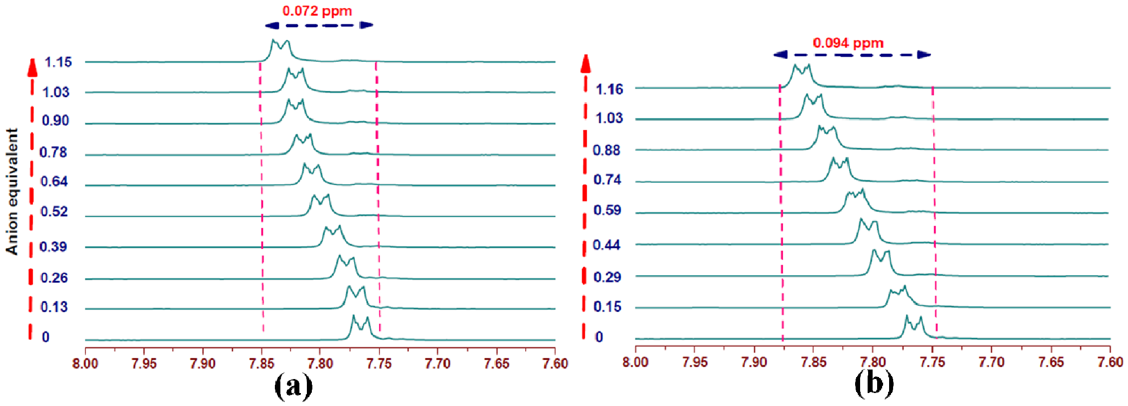


Fig. 13S: Partial ^{1}H NMR (300 MHz) titration profiles (a) Spectral change of **L** after adding TBAF in D_2O-acetone-d_6 (1:19, v/v) upto 1.15 equivalents. (b) Spectral change of **L** after adding TBACl in D_2O-acetone-d_6 (1:19, v/v) upto 1.16 equivalents.

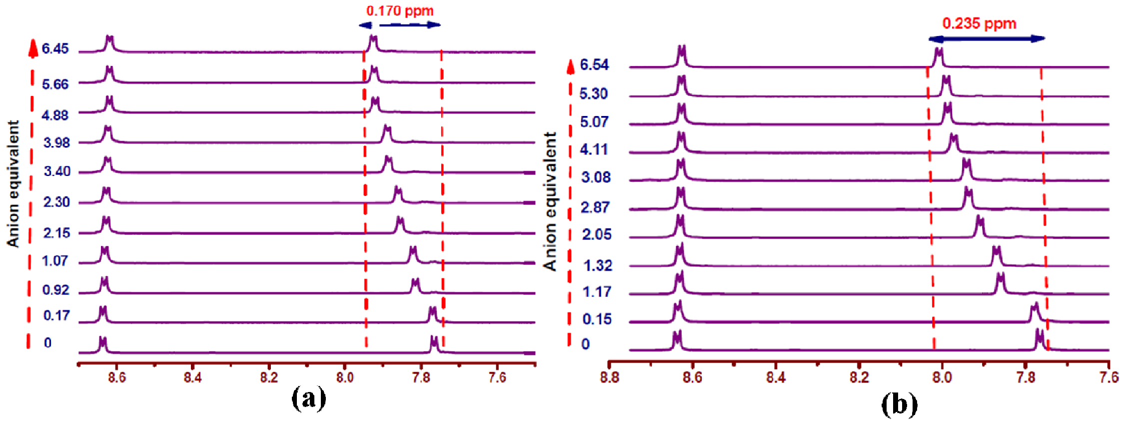
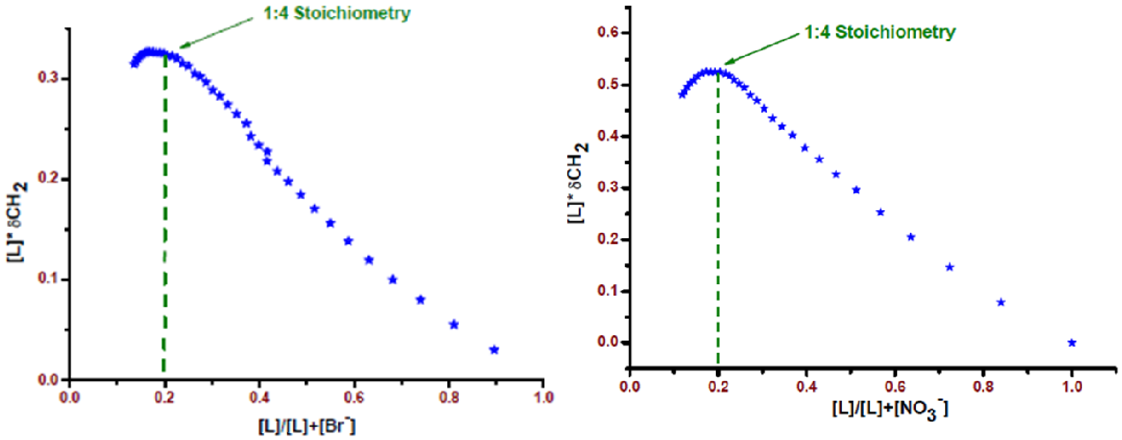
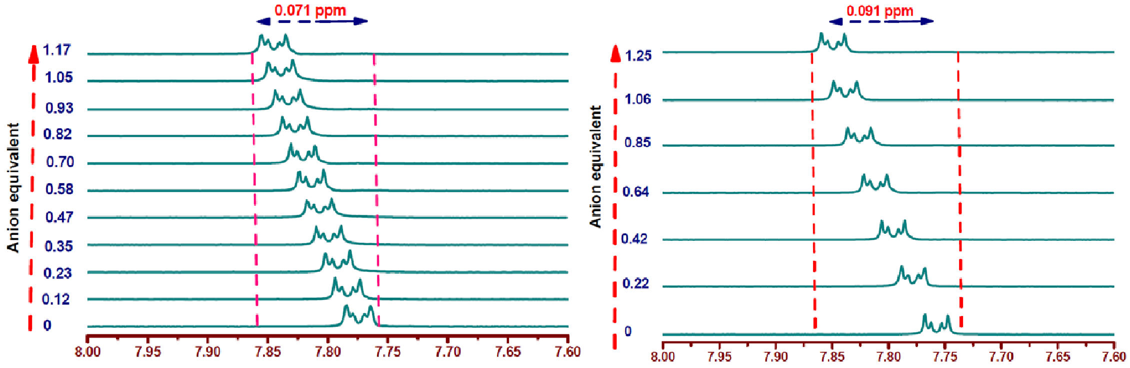


Fig. 14S: Partial ^{1}H NMR (300 MHz) titration profiles (a) Spectral change of **L** in D_2O-acetone-d_6 (1:19, v/v) after adding TBAF (6. 45 equivalent) in D_2O-acetone-d_6 (1:19, v/v) (b) Spectral change of **L** in D_2O-acetone-d_6 (1:19, v/v) after adding TBACl (6.54 equivalent).



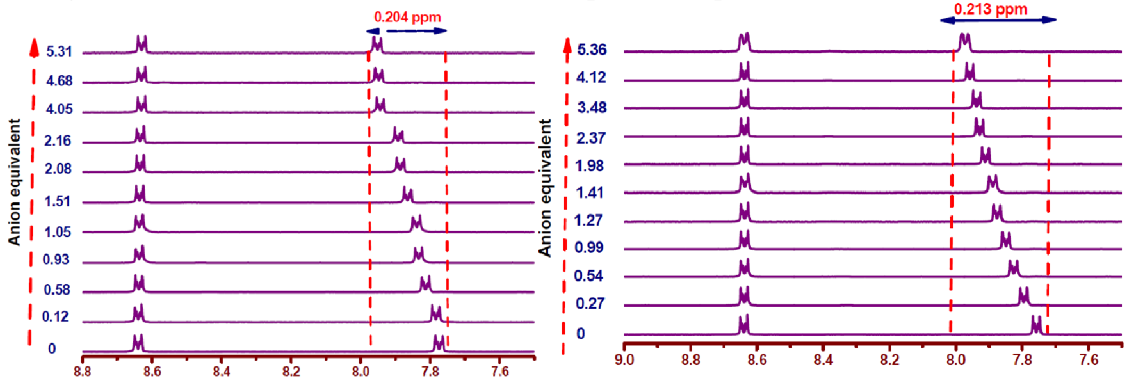
(a) **(b)**

Fig. 15S (a) Job's plot analysis of **L** in D_2O-acetone-d_6 (1:19, v/v) after adding TBABr in acetone-d_6. (b) Job's plot for analysis of **L** in D_2O-acetone-d_6 (1:19, v/v) after adding $TBANO_3$ in acetone-d_6.



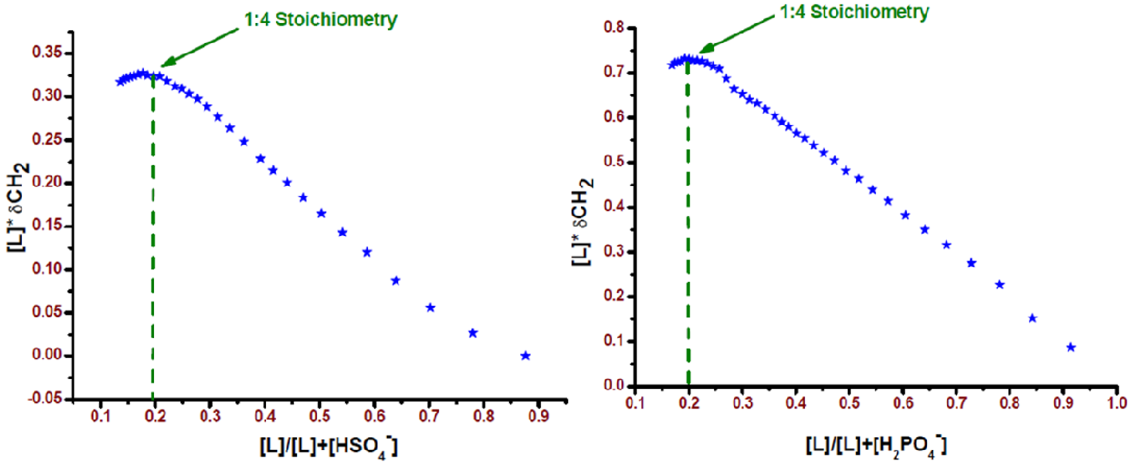
(a) **(b)**

Fig. 16S: Partial ^1H NMR (300 MHz) titration profiles (a) Spectral change of **L** after adding TBABr in D_2O-acetone-d_6 (1:19, v/v) upto 1.17 equivalents. (b) Spectral change of **L** after adding $TBANO_3$ in D_2O-acetone-d_6 (1:19, v/v) upto 1.25 equivalents.



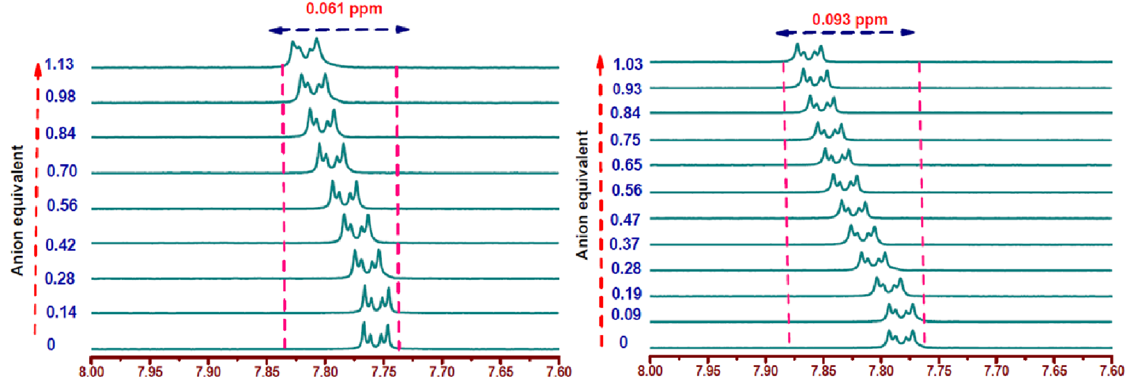
(a) **(b)**

Fig. 17S: Partial ^1H NMR (300 MHz) titration profiles (a) Spectral change of **L** in D_2O-acetone-d_6 (1:19, v/v) after adding TBABr (5. 31 equivalent) in D_2O-acetone-d_6 (1:19, v/v) (b) Spectral change of **L** in D_2O-acetone-d_6 (1:19, v/v) after adding $TBANO_3$ (5.36 equivalent).



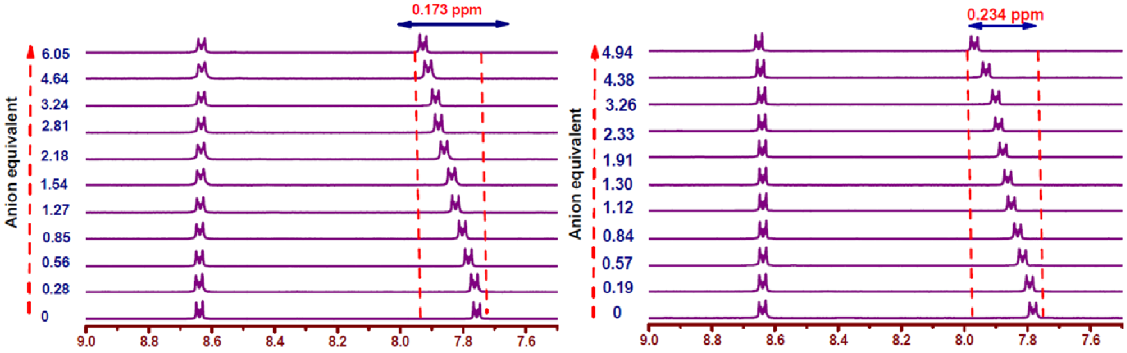
(a) **(b)**

Fig. 18S: (a) Job's plot analysis of **L** in D$_2$O-acetone-d_6 (1:19, v/v) after adding TBAHSO$_4$ in D$_2$O-acetone-d_6 (1:19, v/v). (b) Job's plot for analysis of **L** in D$_2$O-acetone-d_6 (1:19, v/v) after adding TBAH$_2$PO$_4$ in acetone-d_6.



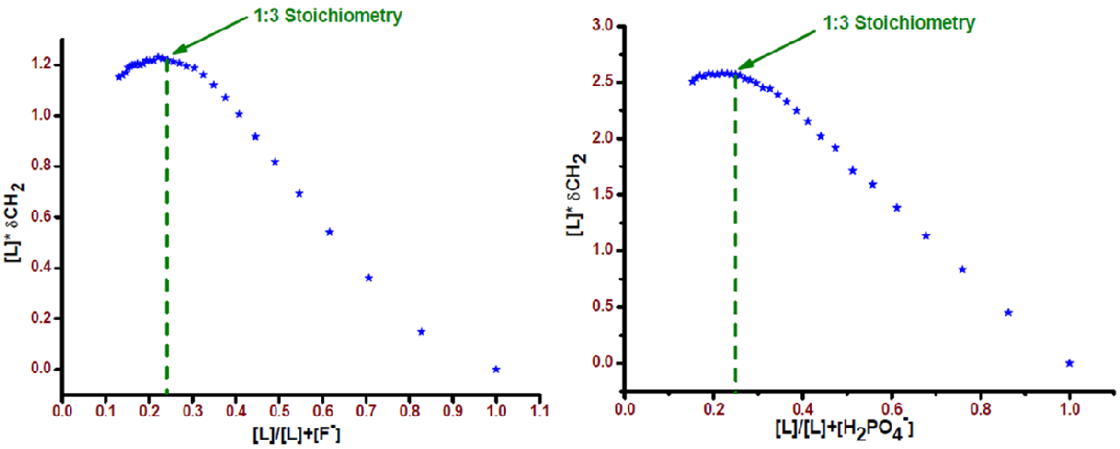
(a) **(b)**

Fig. 19S: Partial ^{1}H NMR (300 MHz) titration profiles (a) Spectral change of **L** after adding TBAHSO$_4$ in D$_2$O-acetone-d_6 (1:19, v/v) upto 1.13 equivalent. (b) Spectral change of **L** after adding TBAH$_2$PO$_4$ in D$_2$O-acetone-d_6 (1:19, v/v) upto 1.03 equivalent.



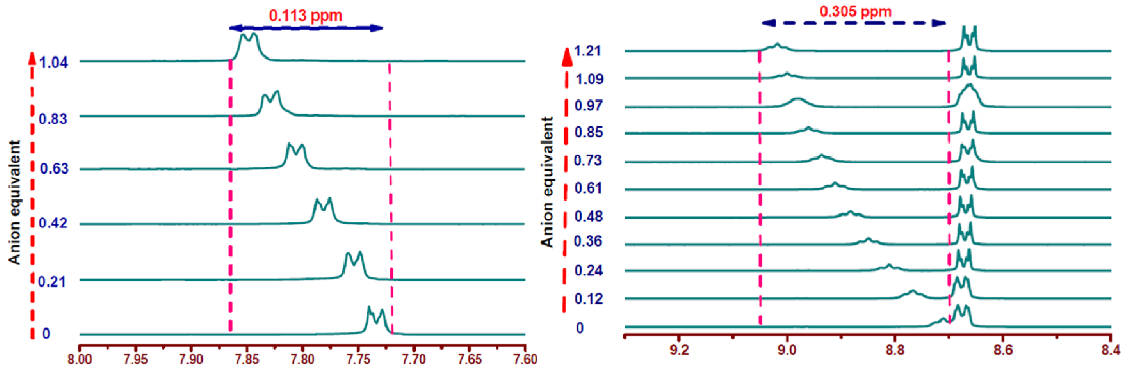
(a) **(b)**

Fig. 20S: Partial ^{1}H NMR (300 MHz) titration profiles (a) Spectral change of **L** in D$_2$O-acetone-d_6 (1:19, v/v) after adding TBAHSO$_4$ (6.05 equivalent) in D$_2$O-acetone-d_6 (1:19, v/v) (b) Spectral change of **L** in D$_2$O-acetone-d_6 (1:19, v/v) after adding TBAH$_2$PO$_4$ (4.94 equivalent).



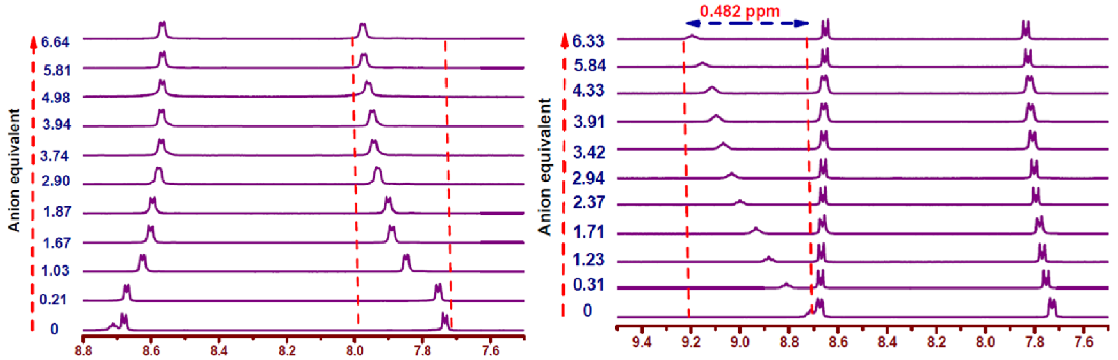
(a) **(b)**

Fig. 21S: (a) Job's plot analysis of **L** in D_2O-acetone-*d*$_6$ (1:19, v/v) after adding TBAF in DMSO-*d*$_6$ (b) Job's plot analysis of **L** in D_2O-acetone-*d*$_6$ (1:19, v/v) after adding $TBAH_2PO_4$ in DMSO-*d*$_6$.



(a) **(b)**

Fig. 22S: Partial ^{1}H NMR (300 MHz) titration profiles (a) Spectral change of **L** after adding TBAF in DMSO-*d*$_6$ upto 1.04 equivalent. (b) Spectral change of **L** after adding $TBAH_2PO_4$ in DMSO-*d*$_6$ upto 1.21 equivalent.



(a) **(b)**

Fig. 23S: Partial ^{1}H NMR (300 MHz) titration profiles (a) Spectral change of **L** in after adding TBAF (6.64 equivalent) in DMSO-*d*$_6$ (b) Spectral change of **L** in DMSO-*d*$_6$ after adding $TBAH_2PO_4$ (6.33 equivalent).

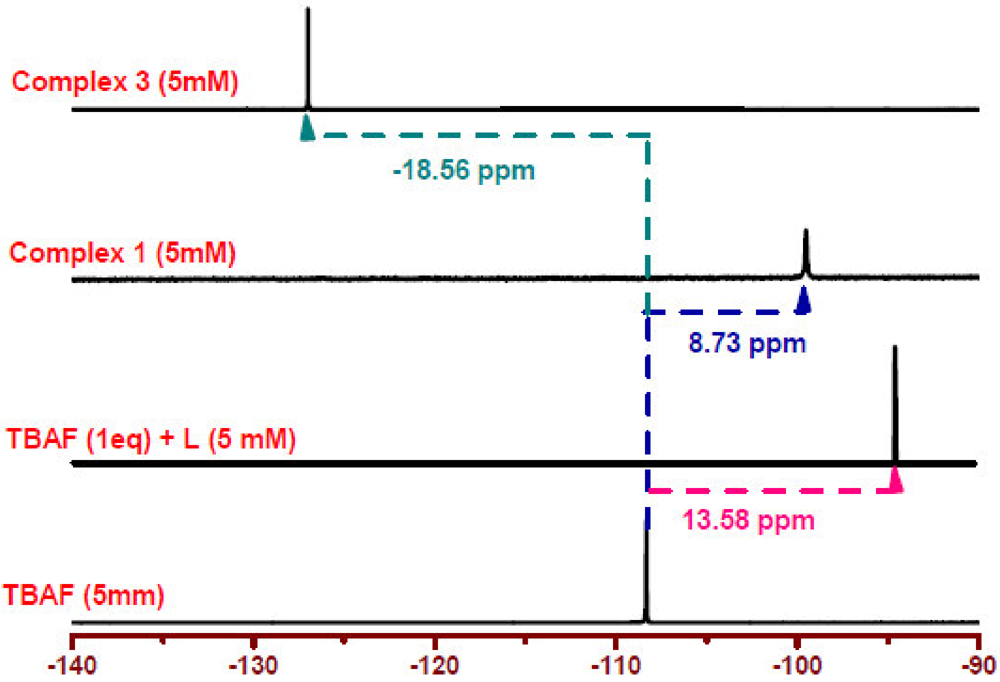


Fig. 24S: Comparative partial ^{19}F NMR spectra in DMSO-d_6 in 500 MHz.

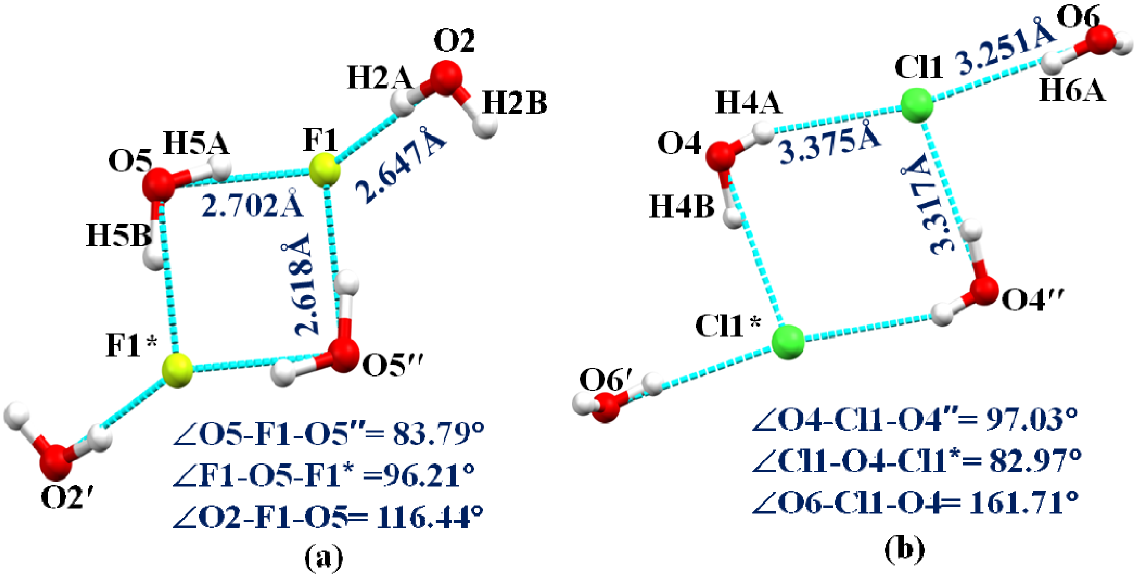


Fig. 25S: H-bonding distances and angles of the $[(X)_2(H_2O)_4]^{2-}$ cluster in (a) complex **1** (X=F) and (b) complex **2** (X=Cl).

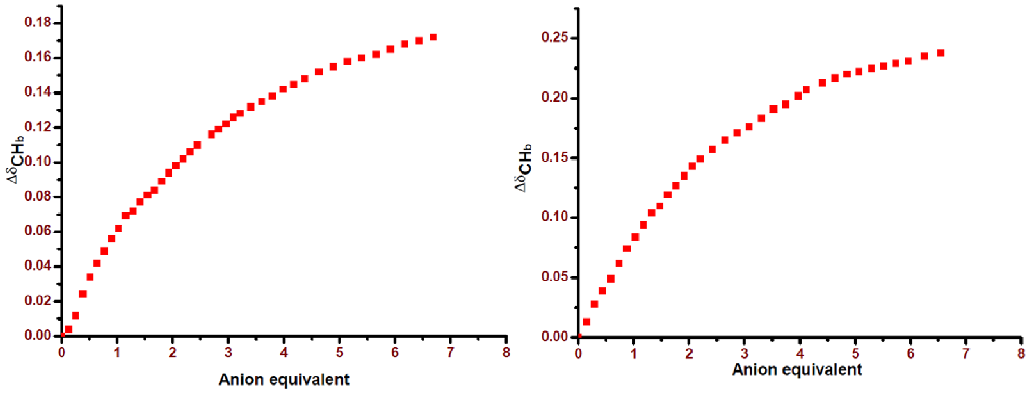


Fig. 26S: Anion equivalents plot of (a) change in chemical shift of **L** with increasing equivalent of TBAF in D_2O-acetone-d_6 (1:19, v/v) (b) change in chemical shift of **L** with increasing equivalent of TBACl in D_2O-acetone-d_6 (1:19, v/v).

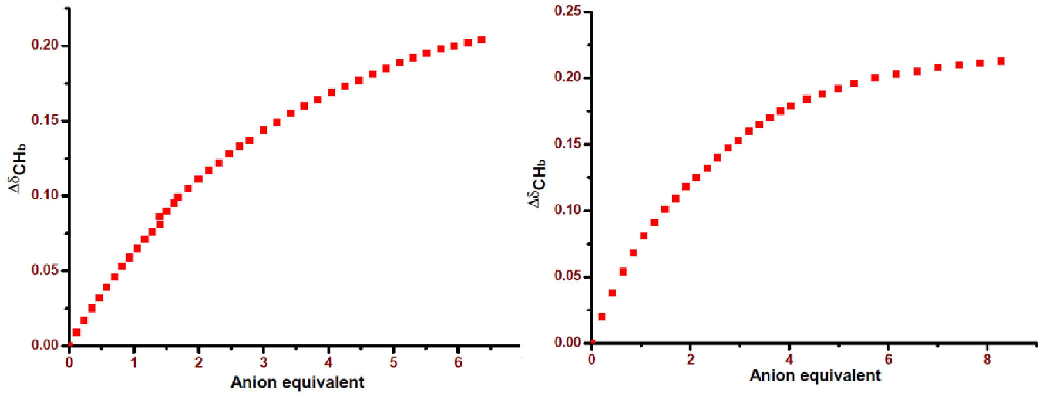


Fig. 27S: Anion equivalents plot of (a) change in chemical shift of **L** with increasing equivalent of TBABr in D_2O-acetone-d_6 (1:19, v/v) (b) change in chemical shift of **L** with increasing equivalent of TBANO3 in D_2O-acetone-d_6 (1:19, v/v).

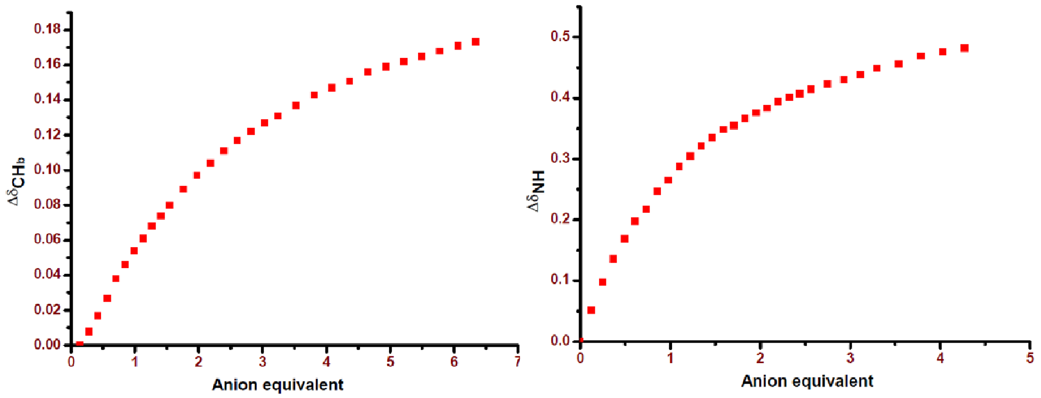


Fig. 28S: Anion equivalents plot of (a) change in chemical shift of **L** with increasing equivalent of $TBAHSO_4$ in D_2O-acetone-d_6 (1:19, v/v) (b) change in chemical shift of **L** with increasing equivalent of $TBAH_2PO_4$ in D_2O-acetone-d_6 (1:19, v/v).

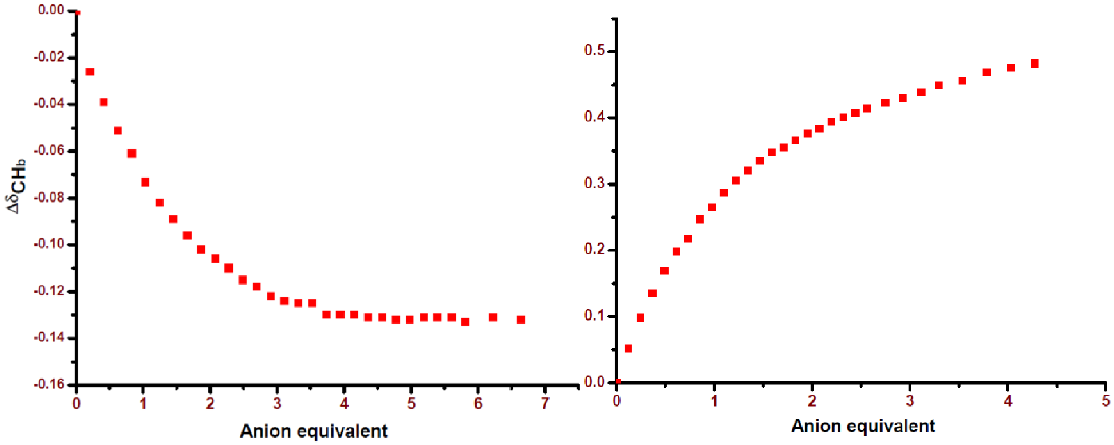


Fig. 29S: Anion equivalents plot of (a) change in chemical shift of **L** with increasing equivalent of TBAF in DMSO-d_6 (b) change in chemical shift of **L** with increasing equivalent of $TBAH_2PO_4$ in DMSO-d_6.

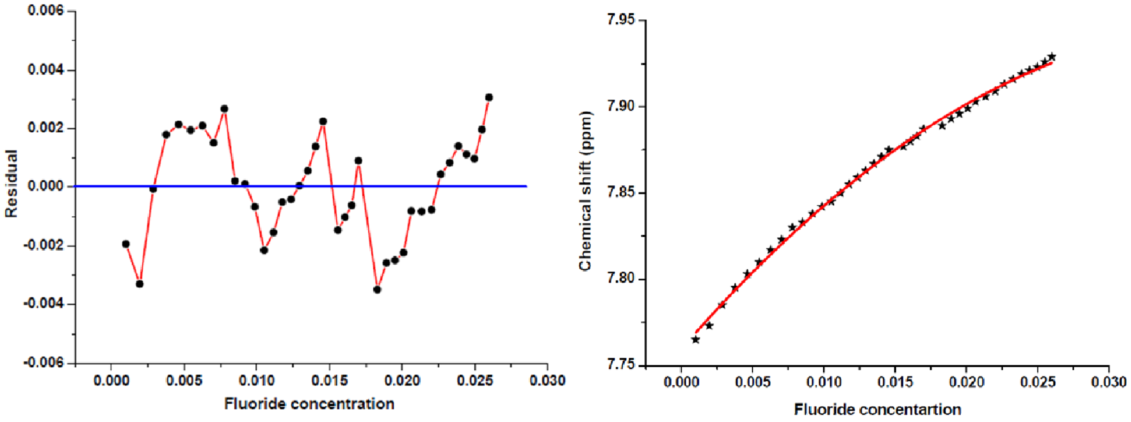


Fig. 30S: Fit plot of NMR titration of **L** with TBAF (Concentration in mole unit) in D_2O-acetone-d_6 (1:19, v/v).

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Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 11:14:42   on 10/08/2013

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

Reaction:   Sn + L = Sn(L)

FILE: TEST11.FIT (Measured shift is on 119Sn)

IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0

File prepared by M. J. Hynes, October 22 2000

Equilibrium constants are log10 values

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION

1  1  1.59245E+00 2.000E-01 2.920E-02 2.300E+02   K1

2  1  7.75683E+00 2.000E-01 1.168E-03 8.101E+00   SHIFT Sn

3  1  8.10416E+00 1.000E+00 1.141E-02 1.791E+02    SHIFT Sn(L)
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0RMS ERROR = 1.77E-03  MAX ERROR = 3.49E-03 AT OBS.NO. 25

RESIDUALS SQUARED = 1.10E-04

RFACTOR =     0.0216 PERCENT
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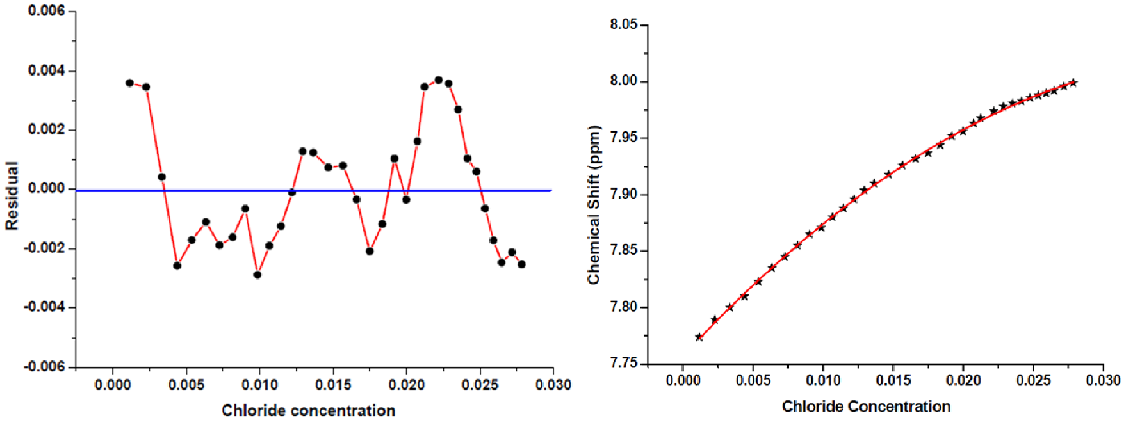

Fig. 31S: Fit plot of NMR titration of **L** with TBACl (Concentration in mole unit) in D_2O-acetone-d_6 (1:19, v/v).

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Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

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 Reaction:   Sn + L = Sn(L)

FILE: TEST11.FIT (Measured shift is on 119Sn)

IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0

File prepared by M. J. Hynes, October 22 2000

  Equilibrium constants are log10 values

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION

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  2  1  7.75398E+00 2.000E-01 1.508E-03 8.333E+00   SHIFT Sn

  3  1  8.25250E+00 1.000E+00 1.383E-02 1.783E+02    SHIFT Sn(L)

0RMS ERROR = 2.11E-03  MAX ERROR = 3.69E-03 AT OBS.NO. 25

RESIDUALS SQUARED = 1.37E-04

RFACTOR =     0.0254 PERCENT
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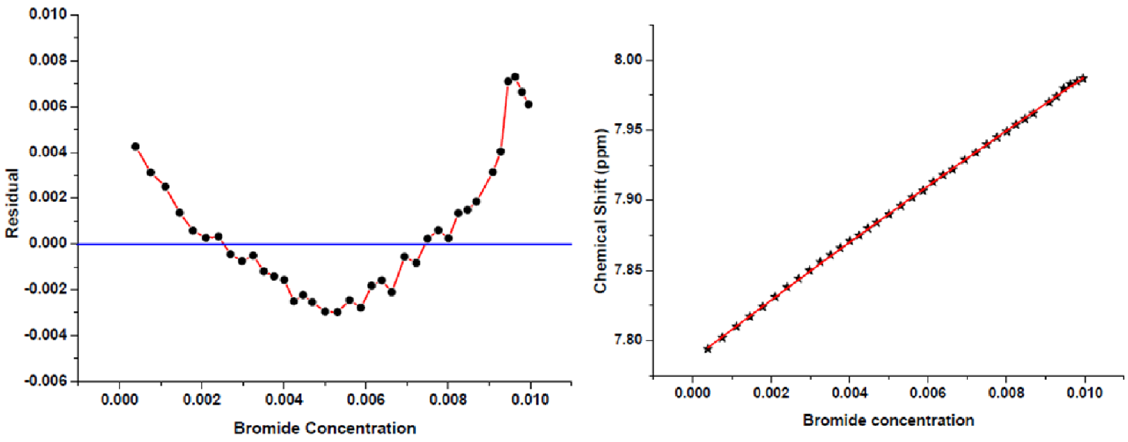

Fig. 32S: Fit plot of NMR titration of **L** with TBABr (Concentration in mole unit) in D_2O-acetone-d_6 (1:19, v/v).

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Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 12:37:03   on 10/08/2013

 IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

 Reaction:   Sn + L = Sn(L)

FILE: TEST11.FIT (Measured shift is on 119Sn)

IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0

File prepared by M. J. Hynes, October 22 2000

  Equilibrium constants are log10 values

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION

  1  1  1.56227E+00 2.000E-01 1.070E-01 1.069E+03   K1

  2  1  7.78004E+00 2.000E-01 2.910E-03 1.048E+01   SHIFT Sn

  3  1  8.55284E+00 1.000E+00 1.340E-01 9.312E+02    SHIFT Sn(L)

0RMS ERROR = 4.69E-03  MAX ERROR = 2.11E-02 AT OBS.NO. 38

RESIDUALS SQUARED = 7.70E-04

RFACTOR =     0.0570 PERCENT
```

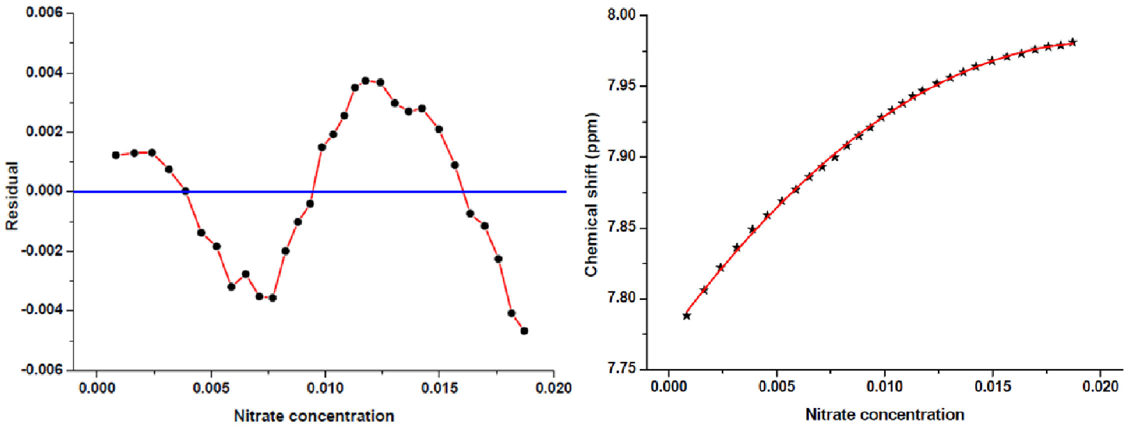

Fig. 33S: Fit plot of NMR titration of **L** with $TBANO_3$ (Concentration in mole unit) in D_2O-acetone-d_6 (1:19, v/v).

```
Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 15:15:23   on 10/08/2013

 IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

 Reaction:   Sn + L = Sn(L)

FILE: TEST11.FIT (Measured shift is on 119Sn)

IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0

File prepared by M. J. Hynes, October 22 2000

  Equilibrium constants are log10 values

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION

  1  1  2.02509E+00 2.000E-01 2.881E-02 9.054E+01   K1

  2  1  7.76675E+00 2.000E-01 2.210E-03 7.230E+00   SHIFT Sn

  3  1  8.10447E+00 1.000E+00 8.055E-03 6.202E+01    SHIFT Sn(L)

0RMS ERROR = 2.63E-03  MAX ERROR = 4.68E-03 AT OBS.NO. 30

RESIDUALS SQUARED = 1.86E-04

RFACTOR =     0.0315 PERCENT
```

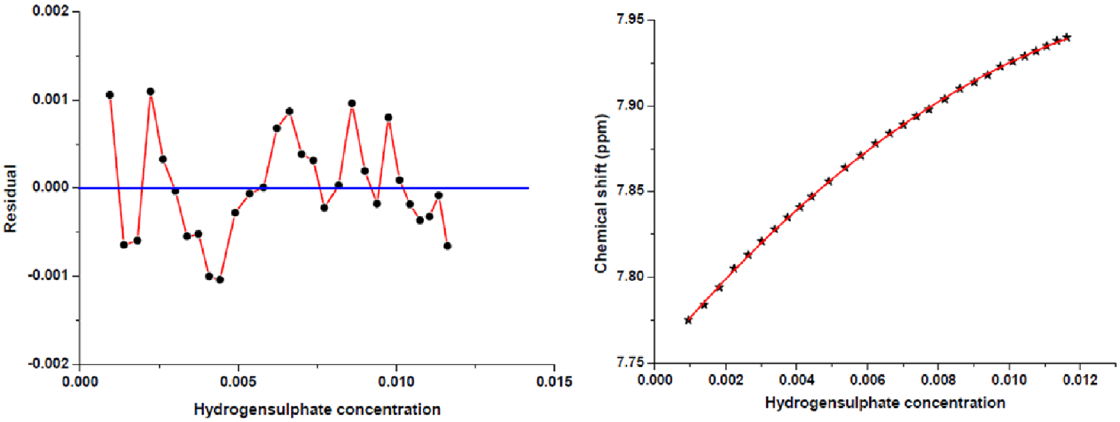

Fig. 34S: Fit plot of NMR titration of **L** with TBAHSO$_4$ (Concentration in mole unit) in D$_2$O-acetone-*d*$_6$ (1:19, v/v).

```
Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 15:43:37   on 10/08/2013

 IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

 Reaction:   Sn + L = Sn(L)

FILE: TEST11.FIT (Measured shift is on 119Sn)

IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0

File prepared by M. J. Hynes, October 22 2000

  Equilibrium constants are log10 values

NO.  A   PARAMETER    DELTA     ERROR   CONDITION   DESCRIPTION

  1  1  1.96887E+00 2.000E-01 1.111E-02 2.635E+02   K1

  2  1  7.74983E+00 2.000E-01 5.374E-04 1.050E+01   SHIFT Sn

  3  1  8.13070E+00 1.000E+00 4.574E-03 1.966E+02    SHIFT Sn(L)

0RMS ERROR = 6.14E-04  MAX ERROR = 1.10E-03 AT OBS.NO.  4

RESIDUALS SQUARED = 9.82E-06

RFACTOR =     0.0074 PERCENT
```

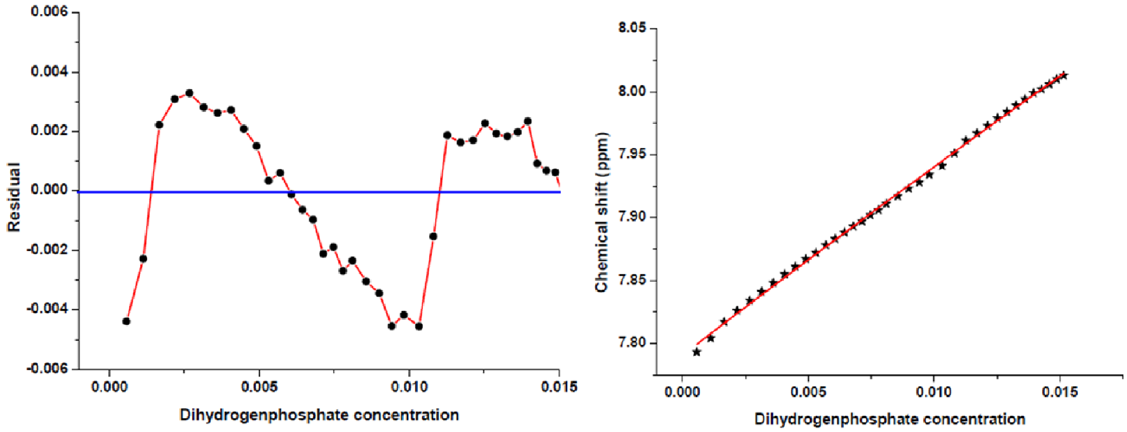

Fig. 35S: Fit plot of NMR titration of **L** with TBAH_2PO_4 (Concentration in mole unit) in D_2O-acetone-d_6 (1:19, v/v).

```
Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 16:33:57   on 10/08/2013

  IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)

  Reaction:   Sn + L = Sn(L)

 FILE: TEST11.FIT (Measured shift is on 119Sn)

 IDEAL DATA: K1 = 63.091; DELTA M = 20.0; DELTA ML = 120.0

 File prepared by M. J. Hynes, October 22 2000

   Equilibrium constants are log10 values

 NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION

   1  1  8.71083E-01 2.000E-01 1.239E-01 7.841E+03   K1

   2  1  7.78813E+00 2.000E-01 1.512E-03 1.182E+01   SHIFT Sn

   3  1  1.00450E+01 1.000E+00 5.536E-01 7.425E+03    SHIFT Sn(L)

 0RMS ERROR = 2.52E-03  MAX ERROR = 4.56E-03 AT OBS.NO. 24

 RESIDUALS SQUARED = 2.16E-04

 RFACTOR =     0.0306 PERCENT
```

References:

1. P. A. Gale, J. Garric, M. E. Light, B. A. McNally and Bradley D. Smith, *Chem. Commun.*, 2007, 1736-1738.