Electronic Supplementary Information

Hydrogen and Halogen Bonding in a Concert Act of Anion Recognition: F^- Induced Atmospheric CO_2 Uptake by an Iodophenyl Functionalized Simple Urea Receptor

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Characterization of receptor L_1:

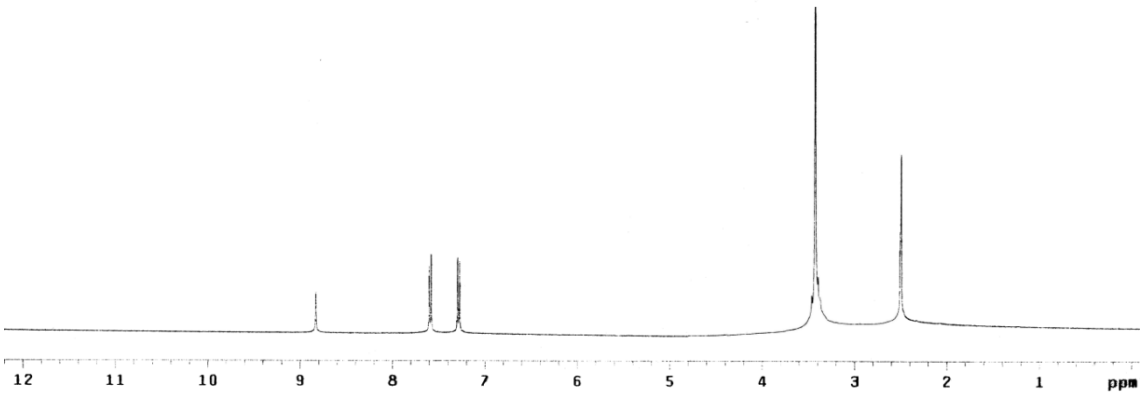

Figure S1: ^{1}H NMR spectrum of receptor $\mathbf{L_1}$ in DMSO-d_6 (Varian-400 MHz) at 298 K, δ (ppm), 7.28 (d, 4H, ArH), 7.59 (d, 4H, ArH), 8.832 (s, 2H, –NH).

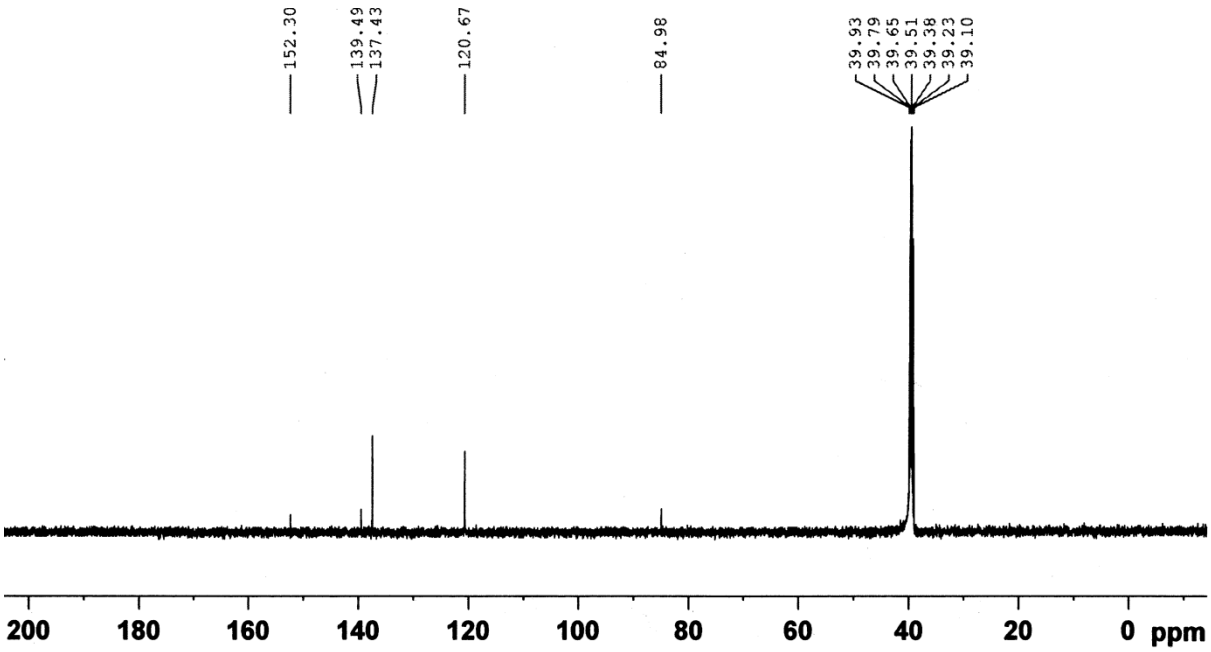

Figure S2: ^{13}C NMR spectrum of receptor $\mathbf{L_1}$ in DMSO-d_6 (Bruker-150 MHz) at 298 K. δ (ppm), 84.98 (2C, ArH), 120.67 (4C, ArH), 137.43 (4C, ArH), 139.49 (2C, ArH), 152.30 (1C, C=O).

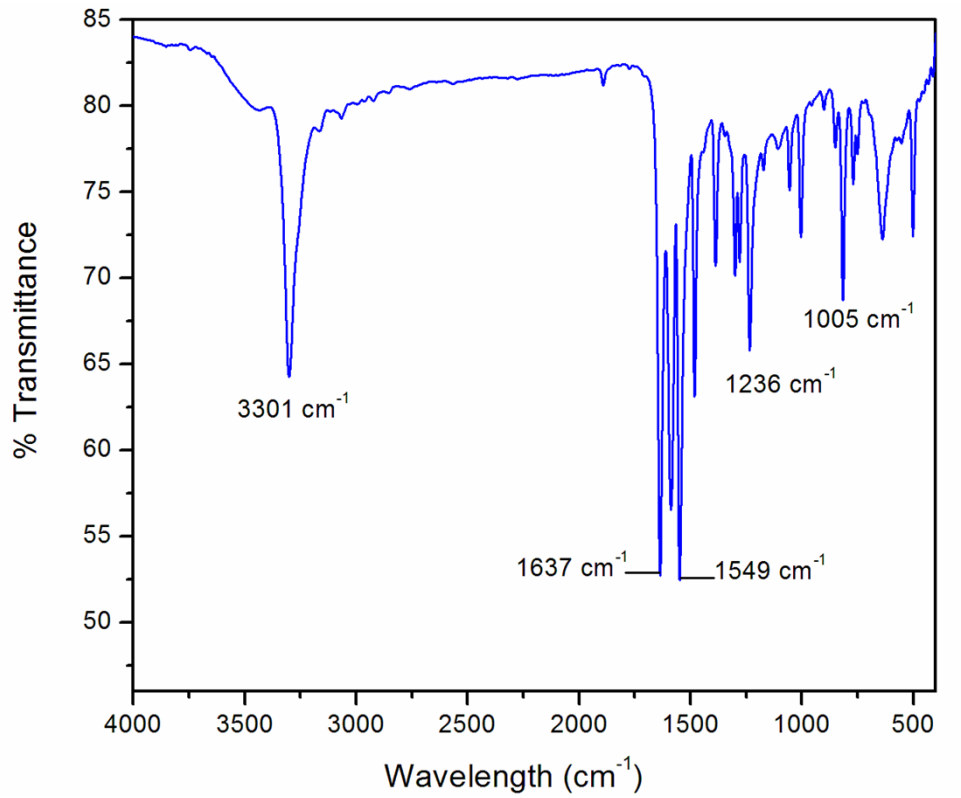

Figure S3. FT-IR spectrum of receptor $\mathbf{L_1}$ recorded in KBr pellet. υ cm^{-1}: 1005 (C-I), 1236 (C-N), 1549 (C=C), 1637 (-C=O), 3301 (N-H).

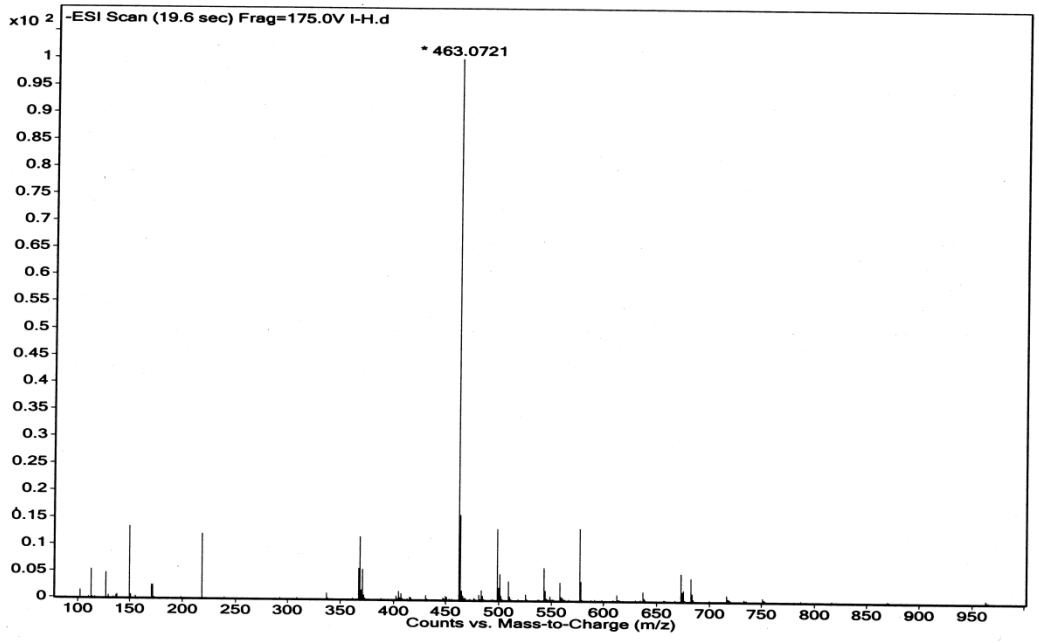

Figure S4. ESI-Mass spectrum of $\mathbf{L_1}$ recorded in acetonitrile (MeCN) at 298 K showing m/z = 463.07 corresponds to $[M]^+$.

Characterization of receptor L_2:

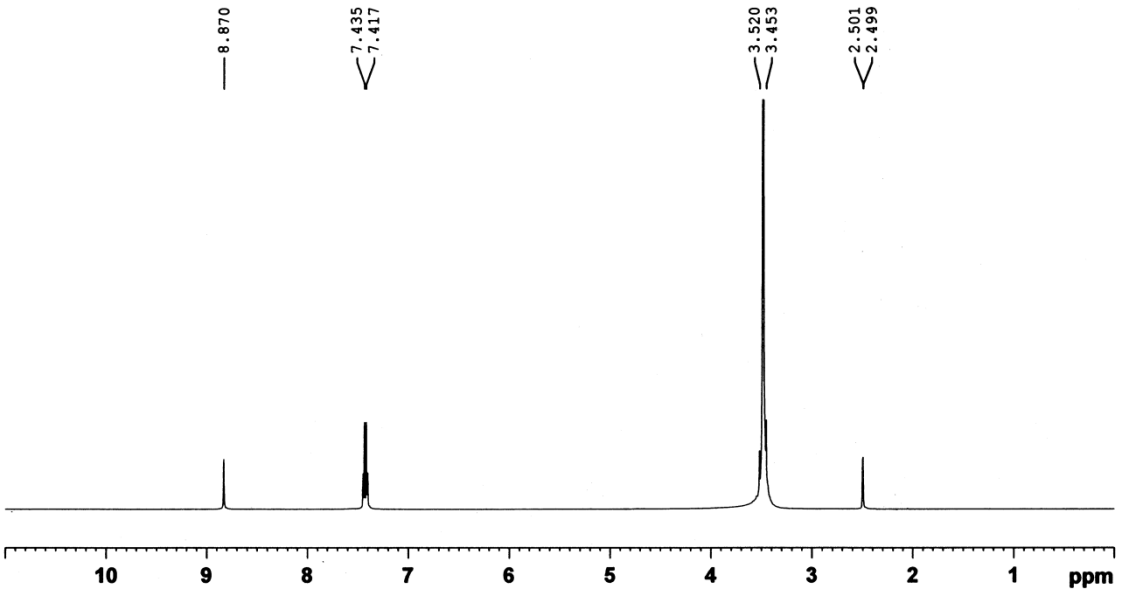

Figure S5: ^{1}H NMR spectrum of receptor $\mathbf{L_2}$ in DMSO-d_6 (Bruker-600 MHz) at 298 K, δ (ppm), 7.417 (d, 4H, ArH), 7.435 (d, 4H, ArH), 8.870 (s, 2H, –NH).

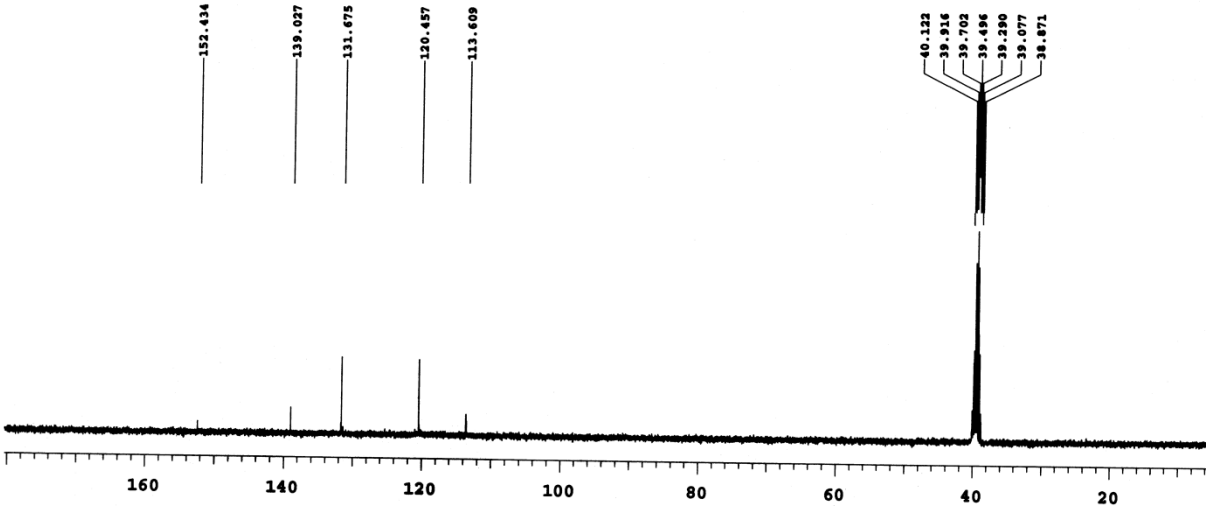

Figure S6: ^{13}C NMR spectrum of receptor $\mathbf{L_2}$ in DMSO-d_6 (Bruker-150 MHz) at 298 K. δ (ppm), 113.609 (2C, ArH), 120.457 (4C, ArH), 131.675 (4C, ArH), 139.027 (2C, ArH), 152.434 (1C, C=O).

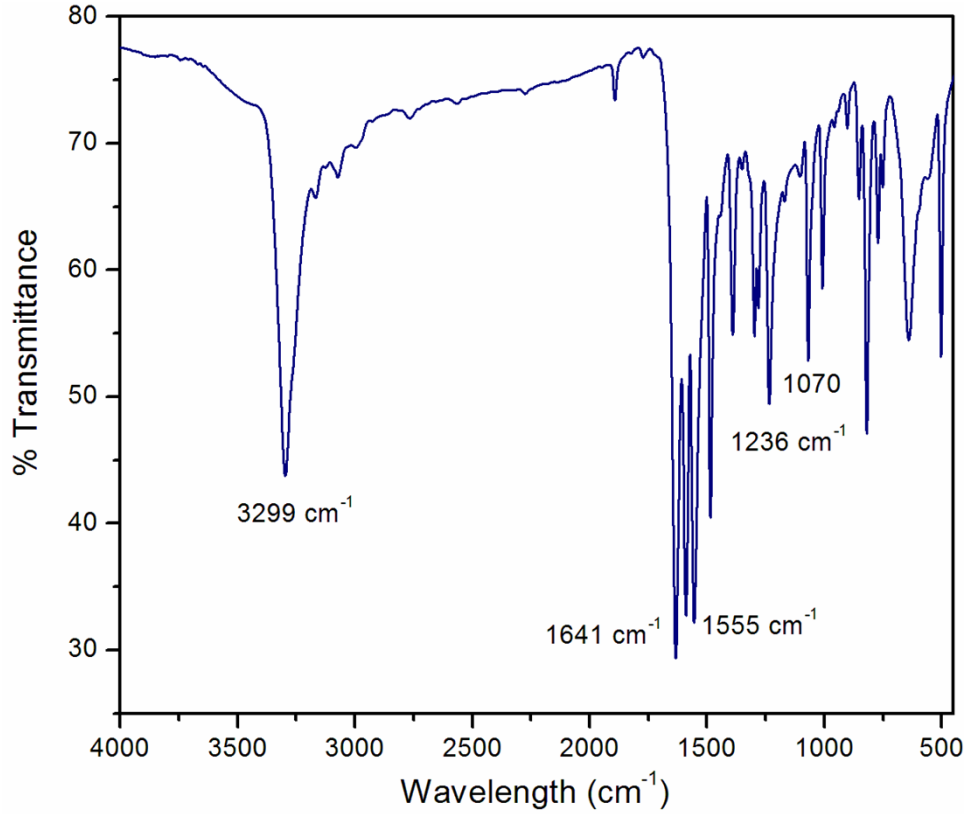

Figure S7. FT-IR spectrum of receptor $\mathbf{L_2}$ recorded in KBr pellet. υ cm^{-1}: 1070 (C-Br), 1236 (C-N), 1555 (C=C), 1641 (-C=O), 3299 (N-H).

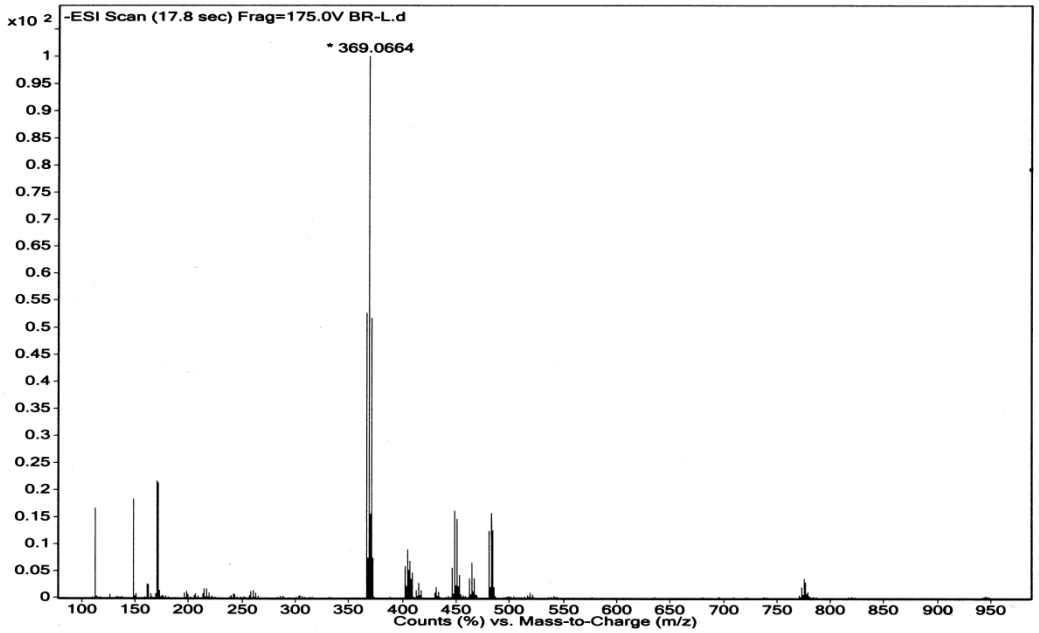

Figure S8. ESI-Mass spectrum of $\mathbf{L_2}$ recorded in acetonitrile (MeCN) at 298 K showing m/z = 369.06 corresponds to $[M]^+$.

***Characterization of complex 1a*:**

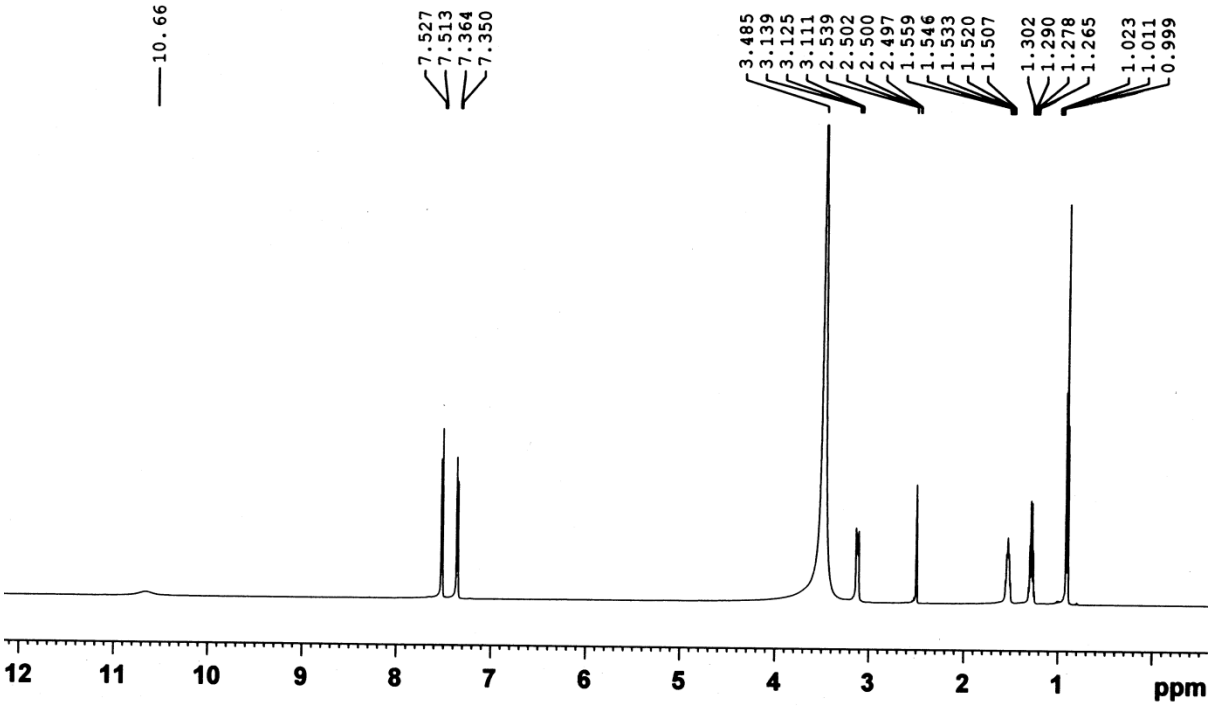

Figure S9: ^{1}H NMR spectrum of complex **1a** in DMSO-d_6 (Bruker-600 MHz) at 298 K, δ(ppm), 1.011 (t, 12H, n–TBA-CH_3), 1.28 (q, 8H, n–TBA-CH_2), 1.533 (q, 8H, n–TBA-CH2), 3.125 (t, 8H, n–TBA-N^+CH_2), 7.57 (d, 4H, ArH), 7.520 (d, 4H, ArH), 10.67 (s, 2H, –NH).

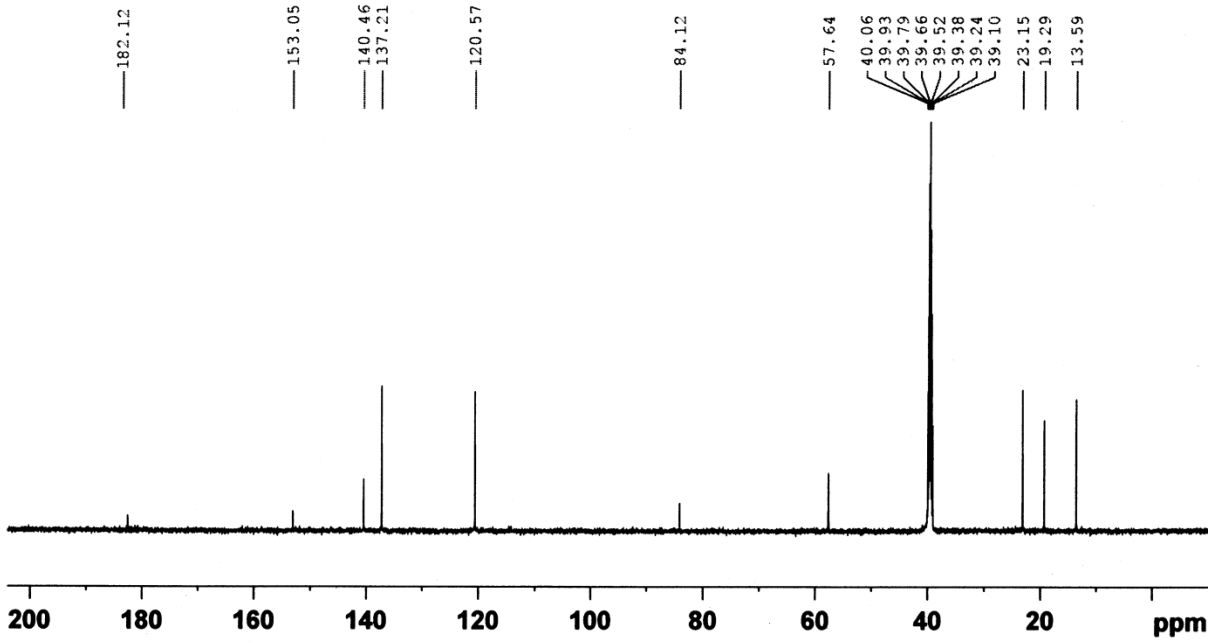

Figure S10: ^{13}C NMR spectrum of complex **1a** in DMSO-d_6 (Bruker-150 MHz) at 298 K. δ (ppm), 13.59 (4C, n–TBA-CH_3), 19.29 (4C, n–TBA-CH_2), 23.15 (4C, n–TBA-CH_2), 57.64

(4C, n–TBA-N^+CH_2), 84.12 (2C, ArH), 120.15 (4C, ArH), 137.21 (4C, ArH), 140.46 (2C, ArH), 153.05 (1C, C=O), and 182.12 (1C, HCO_3^- anion).

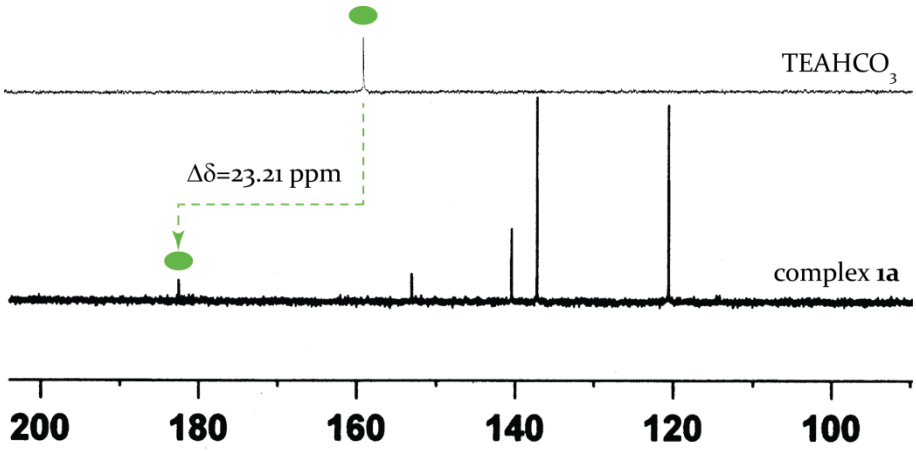

Figure S11. Partial ^{13}C NMR spectrum of complex **1a** (below) showing the huge downfield shift of the HCO_3^- resonance relative to the (TEA)HCO_3 salt (above).

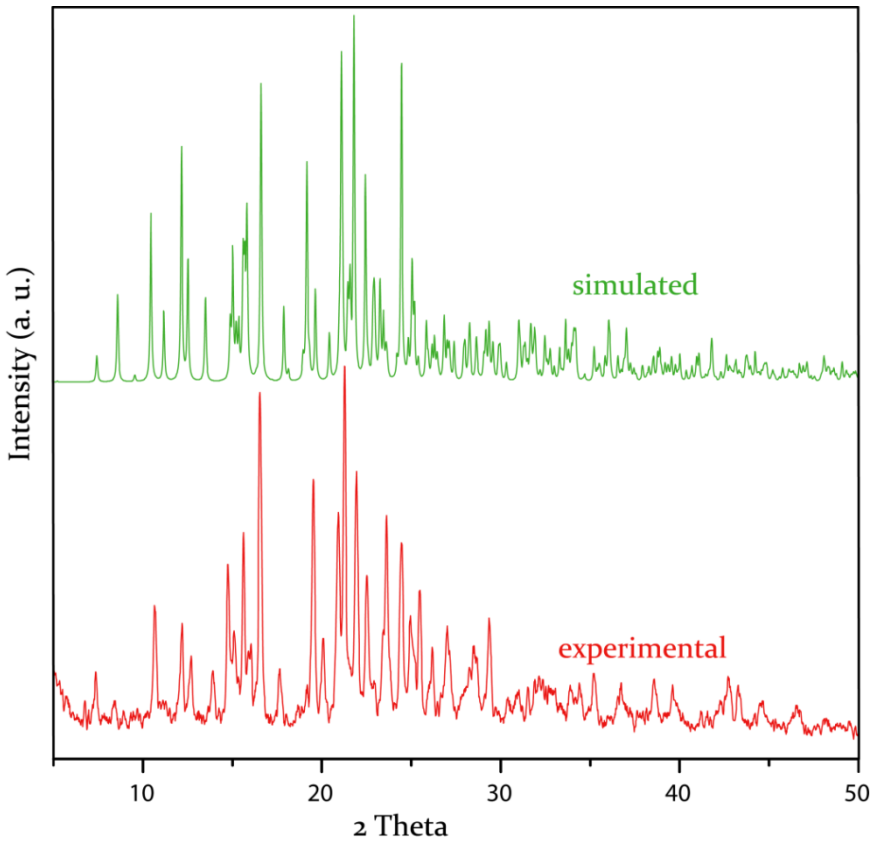

Figure S12. Powder X-ray diffraction patterns of isolated crystals of **1a:** experimental is in green colour and simulated pattern is in red colour.

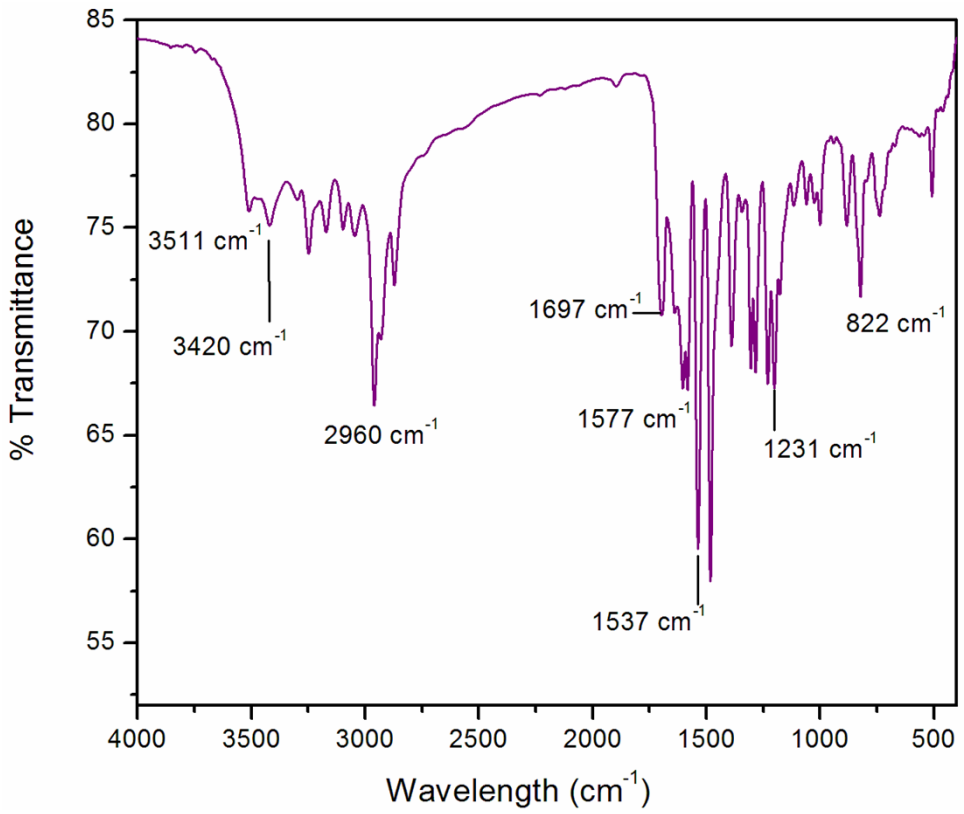

Figure S13. FT-IR spectrum of complex **1a** recorded in KBr pellet. υ cm^{-1}: 822 (HCO_3^{-1}), 1231 (C-N), 1537 (C=C), 1577(C-O), 1697 (-C=O), 2960 (C-H), 3420 (N-H), 3511(O-H).

***Characterization of complex 1b*:**

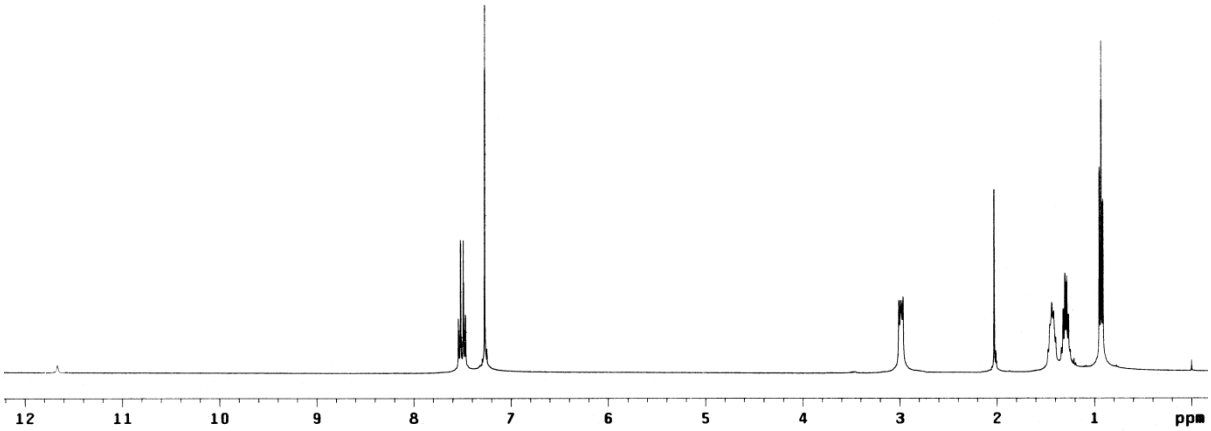

Figure S14: ^{1}H NMR spectrum of complex **1b** in $CDCl_3$ (Varian-400 MHz) at 298 K, δ (ppm), 0.93 (t, 12H, n–TBA-CH_3), 1.294 (q, 8H, n–TBA-CH_2), 1.43 (t, 8H, n–TBA-CH2), 2.029 (s, Acetate–CH_3), 2.987 (t, 8H, n–TBA-N^+CH_2), 7.485 (d, 4H, ArH), 7.53 (d, 4H, ArH), 11.67 (s, 2H, –NH).

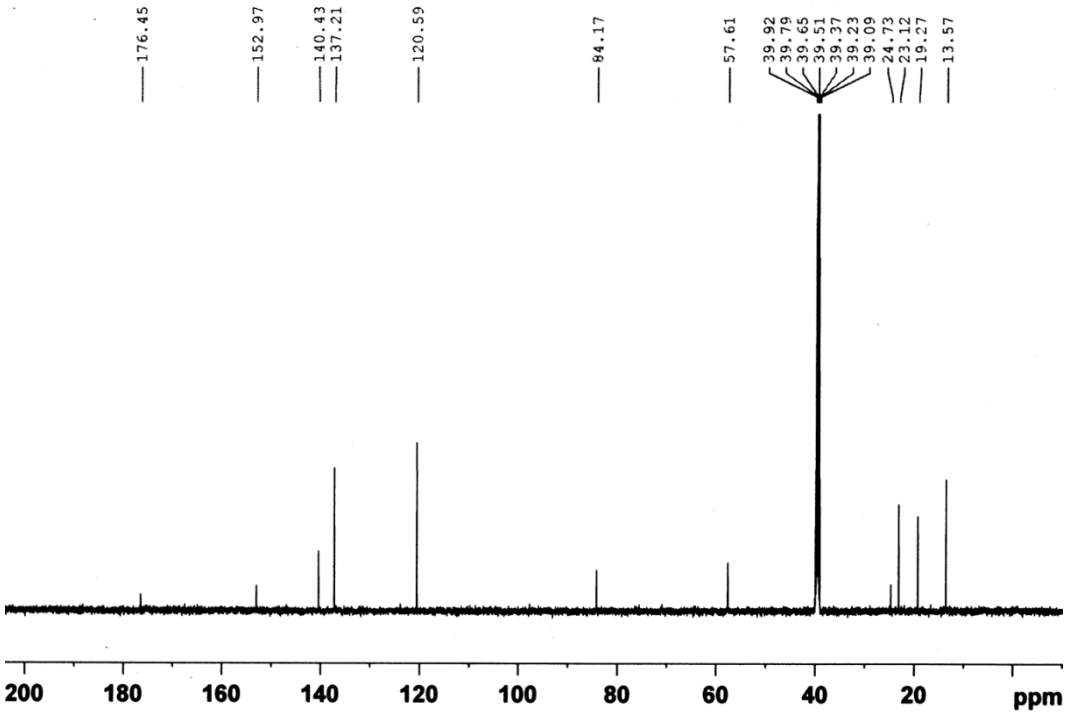

Figure S15: ^{13}C NMR spectrum of complex **1b** in DMSO-d_6 (Bruker-150 MHz) at 298 K, 13.57 (4C, n–TBA-CH_3), 19.27 (4C, n–TBA-CH_2), 23.12 (4C, n–TBA-CH_2), 24.73 (1C, Acetate–CH_3), 57.61 (4C, n–TBA-N^+CH_2), 84.17 (2C, ArH), 120.59 (4C, ArH), 137.21 (4C, ArH), 140.43 (2C, ArH), 152.97 (1C, C=O) and 176.53 (Acetate–COO^-).

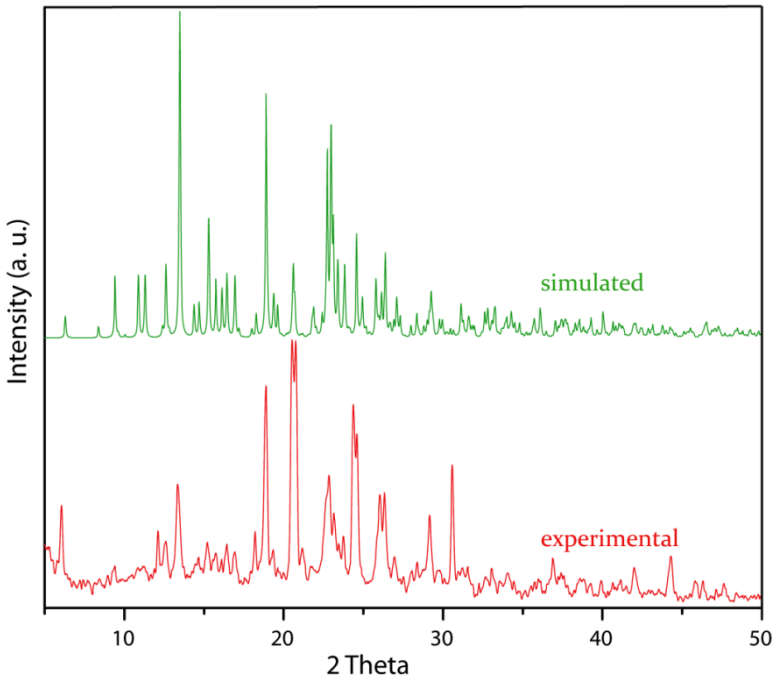

Figure S16. Powder X-ray diffraction patterns of isolated crystals of **1b:** experimental is in green colour and simulated pattern is in red colour.

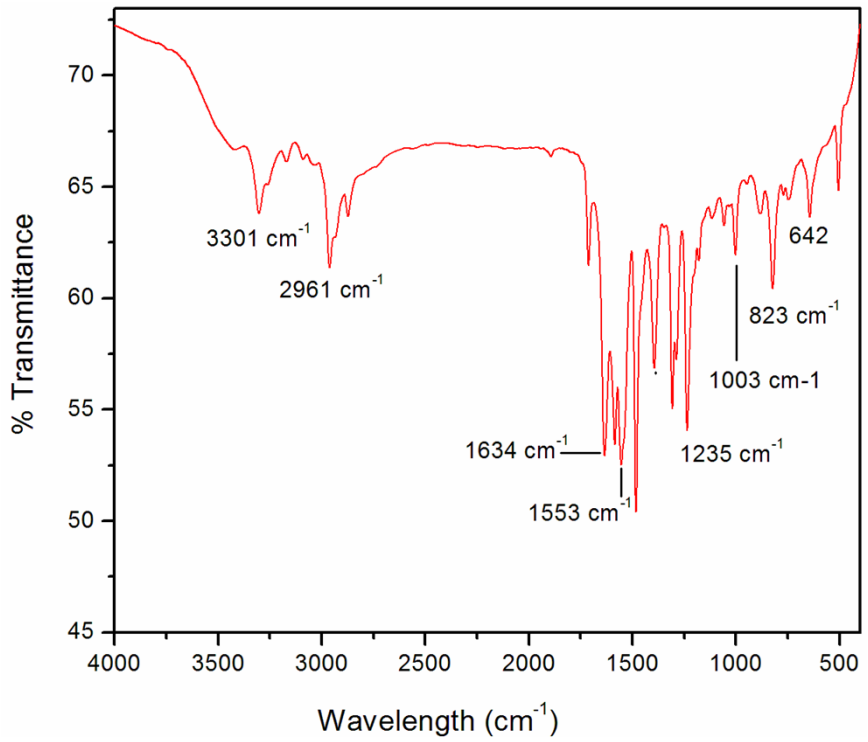

Figure S17. FT-IR spectrum of complex **1b** recorded in KBr pellet. υ cm^{-1}: 642(-COO deformation), 823 (-COO), 1003(C-I), 1235 (C-N), 1553 (C=C), 1634 (-C=O), 2961 (C-H), 3301 (N-H).

***Characterization of complex 2a*:**

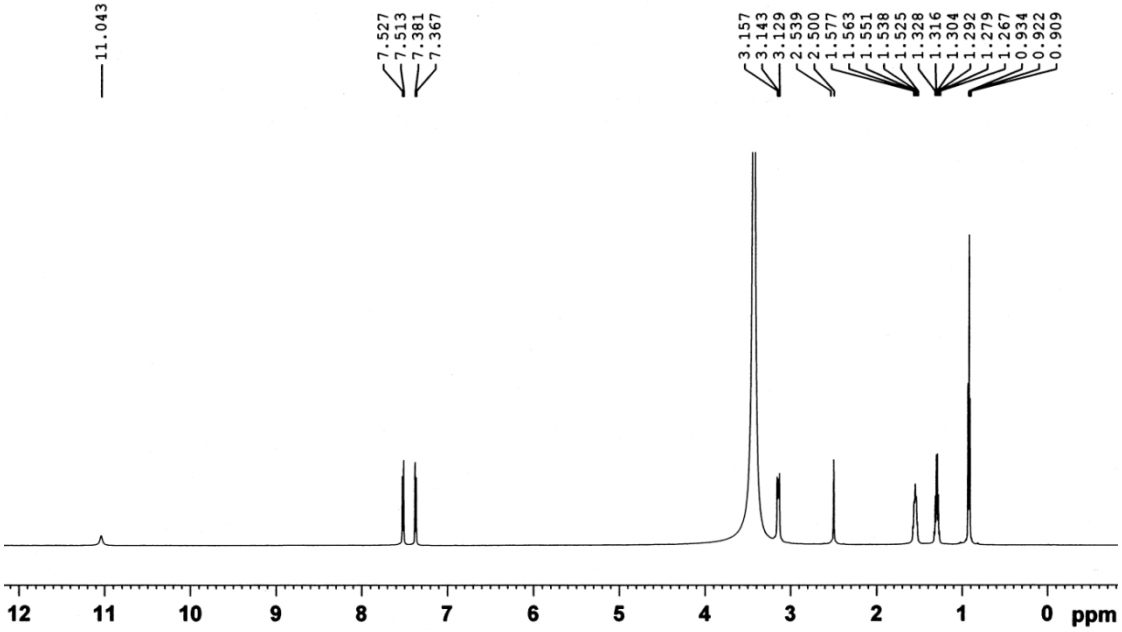

Figure S18: ^{1}H NMR spectrum of complex **2a** in DMSO-d_6 (Bruker-600 MHz) at 298 K, δ (ppm), 0.922 (t, 12H, n–TBA-CH_3), 1.30 (s, 8H, n–TBA-CH_2), 1.55 (p, 8H, n–TBA-CH2), 3.143 (s, 8H, n–TBA-N^+CH_2), 7.374 (d, 4H, ArH), 7.52 (d, 4H, ArH), 11.043 (s, 2H, –NH).

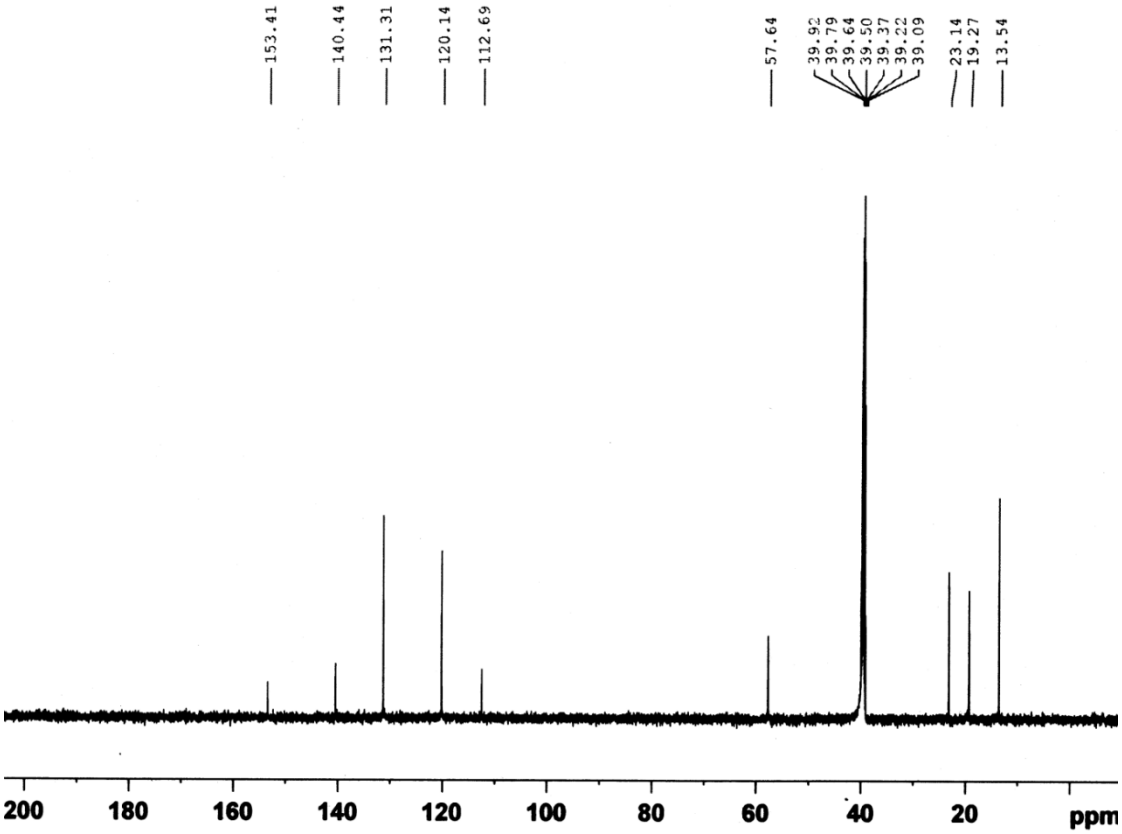

Figure S19: ^{13}C NMR spectrum of complex **2a** in DMSO-d_6 (Bruker-150 MHz) at 298 K. δ (ppm) 13.54 (4C, n–TBA-CH_3), 19.27 (4C, n–TBA-CH_2), 23.14 (4C, n–TBA-CH_2), 57.64 (4C, n–TBA-N^+CH_2), 112.69 (2C, ArH), 120.14 (4C, ArH), 131.31 (4C, ArH), 140.44 (2C, ArH) and 153.41 (1C, C=O).

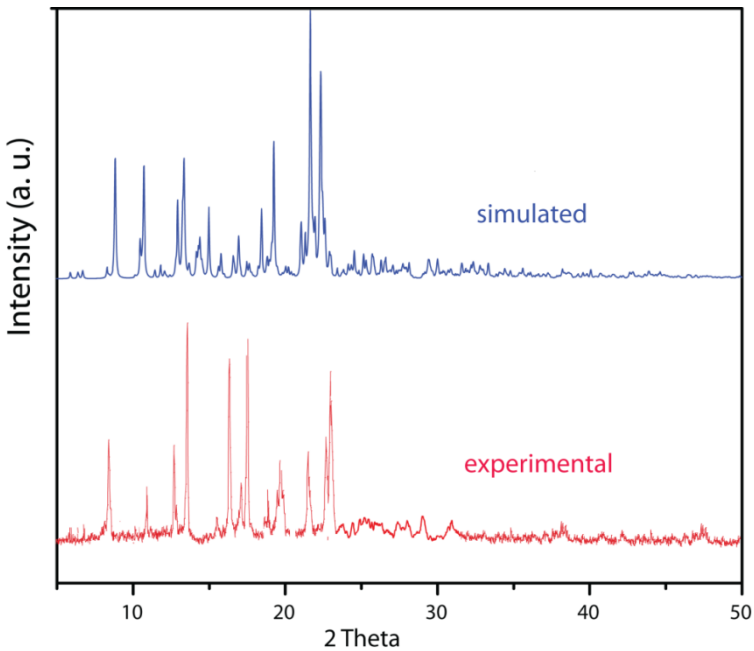

Figure S20. Powder X-ray diffraction patterns of isolated crystals of **2a**: experimental is in blue colour and simulated pattern is in red colour.

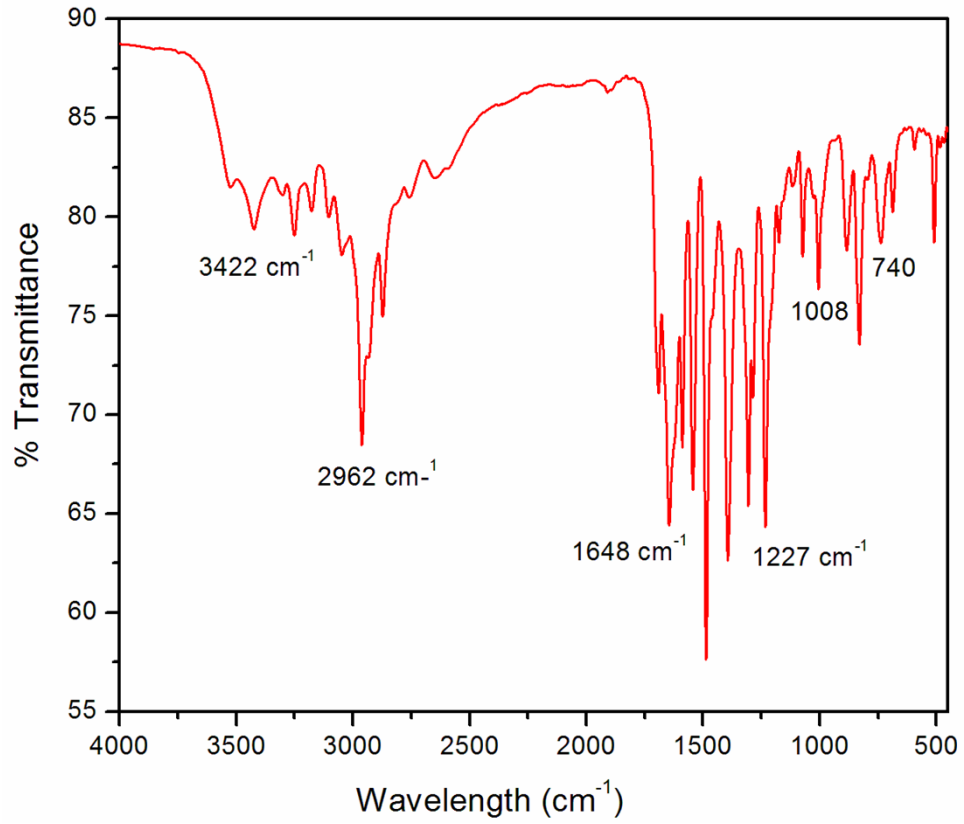

Figure S21. FT-IR spectrum of complex **2a** recorded in KBr pellet. υ cm^{-1}: 740(SiF_6^{2-}), 1008(C-Br), 1227 (C-N), 1648 (-C=O), 2962 (C-H), 3422 (N-H).

***Characterization of complex 2b*:**

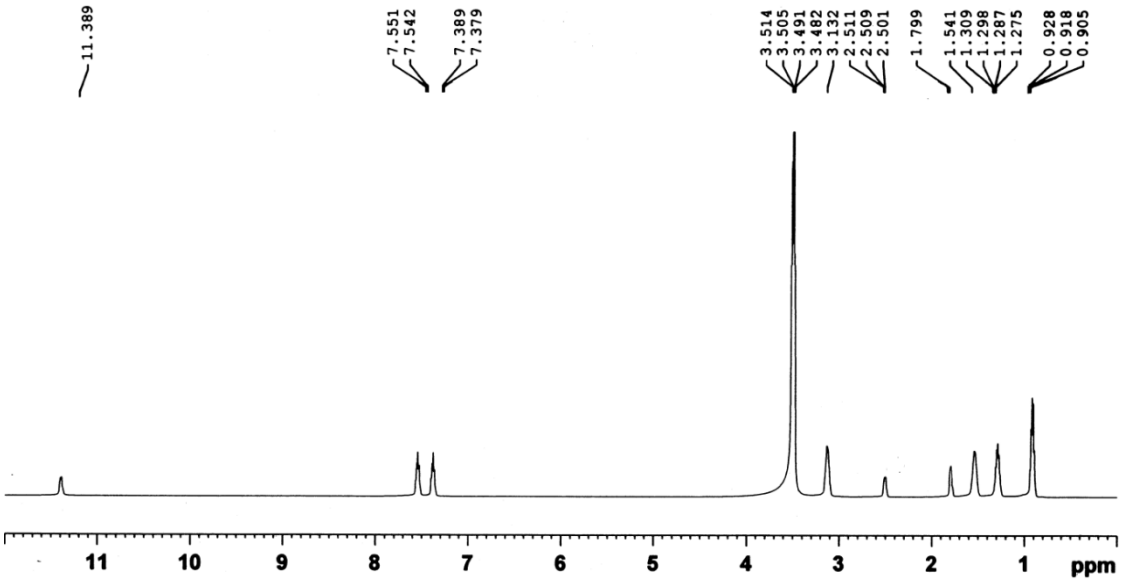

Figure S22: ^{1}H NMR spectrum of complex **2b** in DMSO-d_6 (Bruker-600 MHz) at 298 K, δ (ppm), 0.91 (t, 12H, n–TBA-CH_3), 1.293 (q, 8H, n–TBA-CH_2), 1.541 (s, 8H, n–TBA-CH2), 1.799 (s, Acetate–CH_3), 3.132 (s, 8H, n–TBA-N^+CH_2), 7.384 (d, 4H, ArH), 7.547 (d, 4H, ArH), 11.39 (s, 2H, –NH).

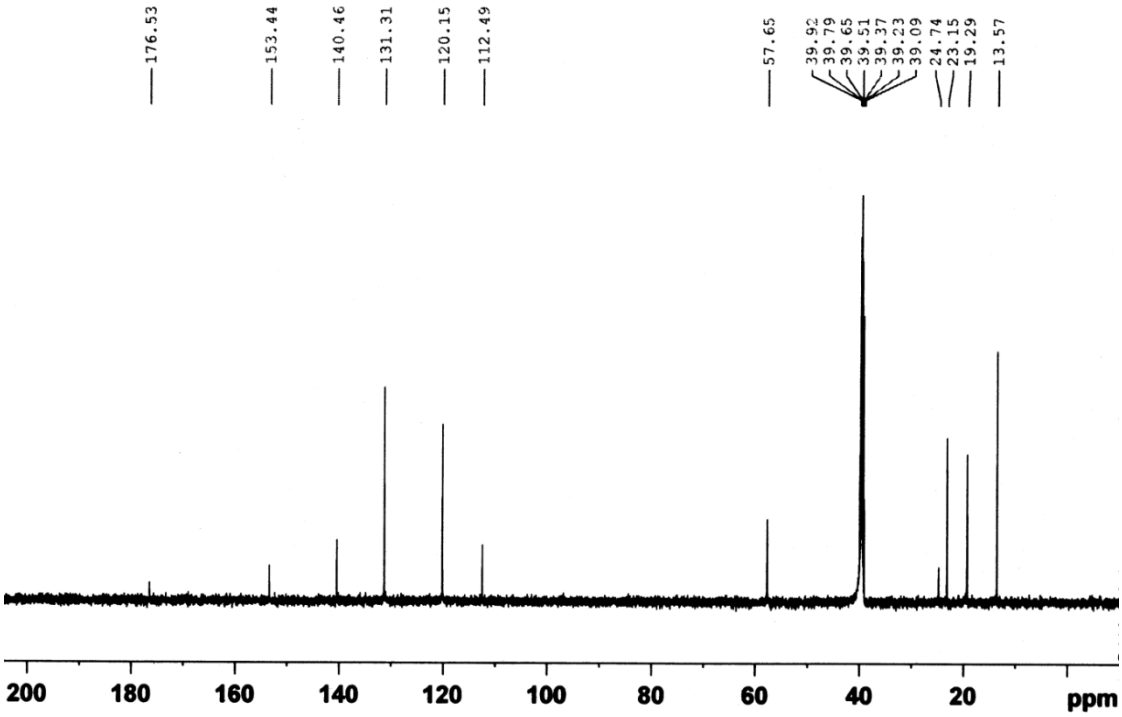

Figure S23: ^{13}C NMR spectrum of complex **2b** in DMSO-d_6 (Bruker-150 MHz) at 298 K. δ (ppm) 13.57 (4C, n–TBA-CH_3), 19.29 (4C, n–TBA-CH_2), 23.15 (4C, n–TBA-CH_2), 24.74 (1C, Acetate–CH_3), 57.65 (4C, n–TBA-N^+CH_2), 112.49 (2C, ArH), 120.15 (4C, ArH), 131.31 (4C, ArH), 140.46 (2C, ArH), 153.44 (1C, C=O) and 176.53 (Acetate–COO^-).

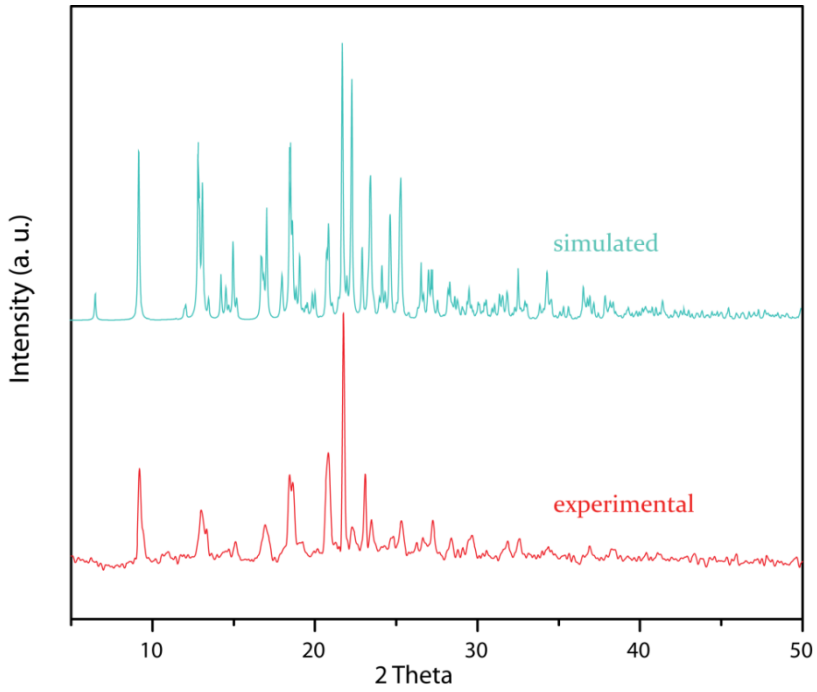

Figure S24. Powder X-ray diffraction patterns of isolated crystals of **2b:** experimental is in green colour and simulated pattern is in red colour.

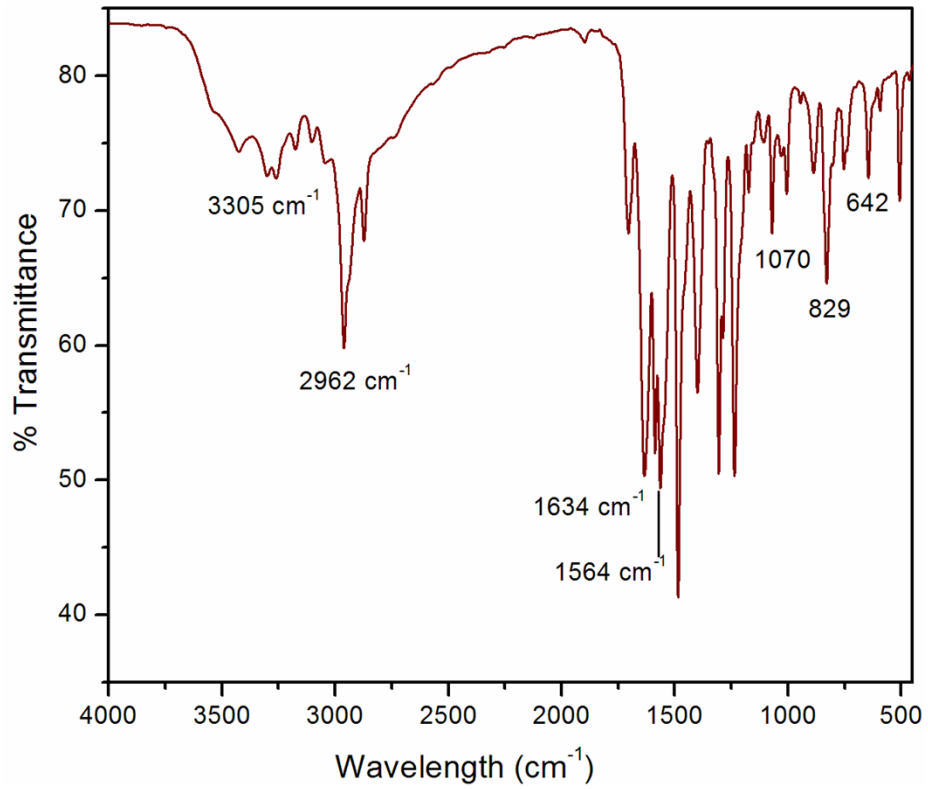

Figure S25. FT-IR spectrum of complex **2b** recorded in KBr pellet. υ cm^{-1}: 642(-COO deformation), 829 (-COO), 1070(C-Br), 1236 (C-N), 1564 (C=C), 1634 (-C=O), 2962 (C-H), 3305 (N-H).

Table S1. Crystallographic parameters and refinement details.

Parameters	L_1	1a	1b	L_2	2b
CCDC	973820	973821	973822	973823	973825
Formula	$C_{13}H_{10}I_2N_2O$	$C_{30}H_{47}I_2N_3O_4$	$C_{31}H_{49}I_2N_3O_3$	$C_{13}H_{10}Br_2N_2O$	$C_{31}H_{49}Br_2N_3O_3$
Fw	464.03	767.51	765.53	370.03	671.53
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C 2	P 21/c	C2/c	P 21/c
a/Å	29.2420(9)	23.9471(7)	8.8809(3)	28.0636(16)	9.5024(5)
b/Å	4.6414(10)	8.3931(2)	21.0697(6)	4.6085(3)	18.9054(10)
c/Å	10.1031(3)	17.0344(5)	18.9452(6)	10.0857(6)	19.3877(13)
α/°	90.00	90.00	90.00	90.00	90.00
β/°	94.122(2)	96.4510(10)	97.815(2)	95.469(4)	99.771(5)
γ/°	90.00	90.00	90.00	90.00	90.00

V/Å^3	1367.68(7)	3402.07(16)	3512.06(19)	1298.46(14)	3432.4(3)
Z	4	4	4	4	4
Dc/g cm^{-3}	2.254	1.498	1.448	1.893	1.299
μ Mo Kα/mm^{-1}	4.588	1.884	1.823	6.231	2.394
T/K	298(2)	298(2)	298(2)	298(2)	298(2)
θ max.	28.30	23.64	23.12	26.00	23.23
Total no.of reflections	9542	19895	43647	8968	15160
Independent reflections	1694	8369	8711	1596	8817
Observed reflections	1541	4435	4605	1040	5893
Parameters refined	83	384	358	83	426
R_1, $I > 2\sigma(I)$	0.0292	0.0421	0.0612	0.0377	0.0590
wR_2, $I > 2\sigma(I)$	0.0996	0.1107	0.1786	0.1119	0.1226
R_1, (all data)	0.0315	0.0604	0.1155	0.0697	0.1794
wR_2 (all data)	0.1052	0.1203	0.2080	0.1397	0.1652
GOF (F^2)	0.909	1.074	1.082	0.920	1.003

Table S2. Details of Hydrogen Bonding contacts in the Complexes **1a-b** and **2a-b.**

complex	D–H···A[a]	d(D···A)/Å	d(H···A)/Å	∠D–H···A/°
1a	N1–H···O2	2.761(7)	1.921(5)	165.2(4)
	N2–H···O3	2.909(6)	2.104(4)	155.4(3)
	C6–H···O2	3.292(7)	2.571(4)	134.6(4)
	C13–H···O3	3.382(6)	2.644(4)	136.8(4)
1b	N1–H···O3	2.835(6)	1.985(4)	169.3(3)
	N2–H···O2	2.833(5)	1.974(4)	175.8(3)
	C3–H···O3	3.384(8)	2.648(5)	136.4(4)
	C9–H···O2	3.449(7)	2.723(4)	135.4(4)
2b	N1–H···O3	3.454(5)	2.728(4)	142.8(3)
	N2–H···O3	2.809 (5)	1.976(4)	162.5(3)
	N1–H···O2	2.778(5)	1.962(3)	157.8(3)
	C3–H···O2	3.315(7)	2.661(4)	128.0(3)

[a] D= Donor, A=Aceptor

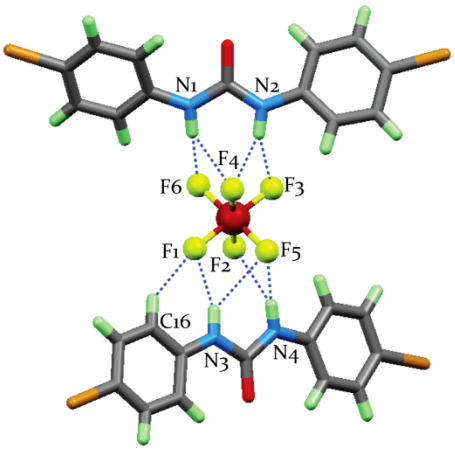

Figure S26. Ball-and-stick representation depicting the H-bonding contacts of complex **2a** (CCDC no. 973824) on SiF_6^{2-} (*n*-TBA cations are omitted for clarity of the presentation).

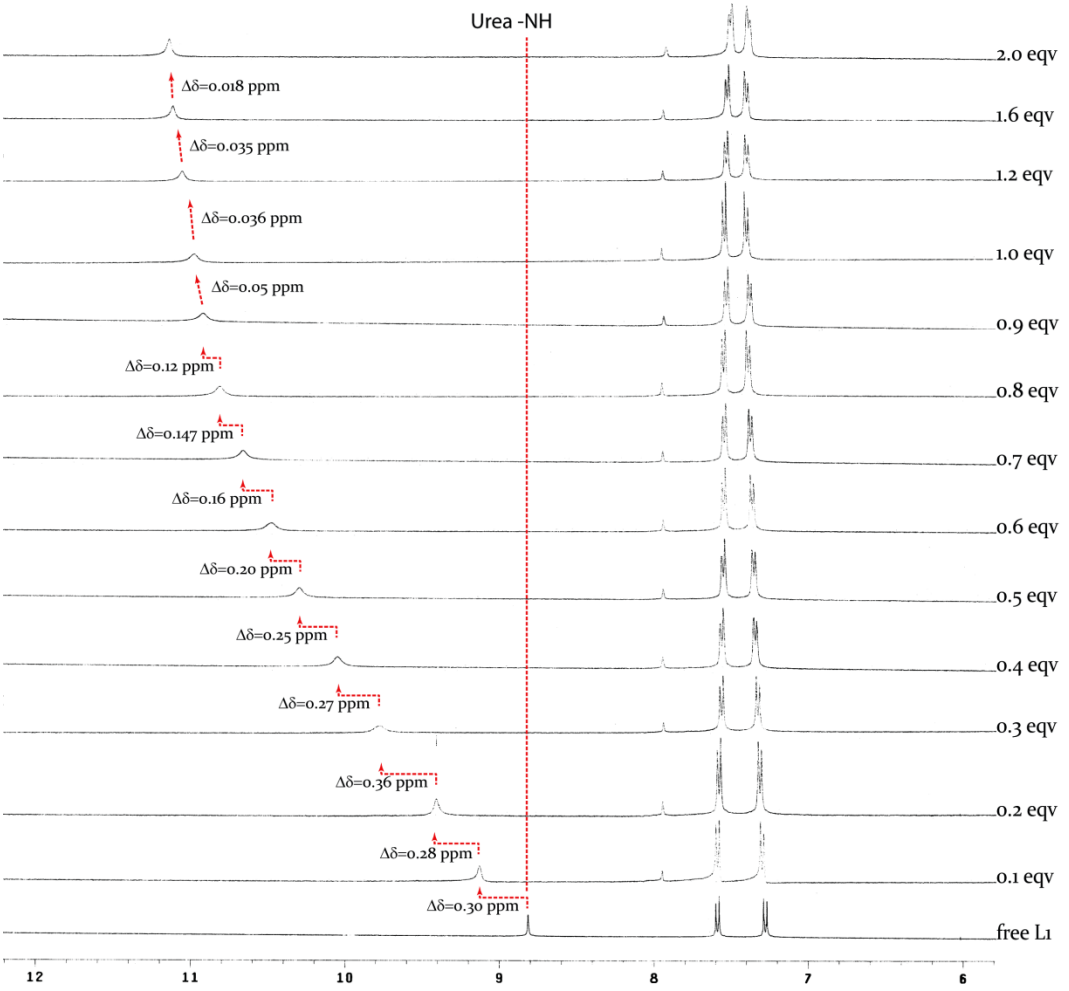

Figure S27. Expanded partial ^{1}H NMR spectra of $\mathbf{L_1}$ upon titration with HCO_3^-(TEA) in DMSO-d_6.

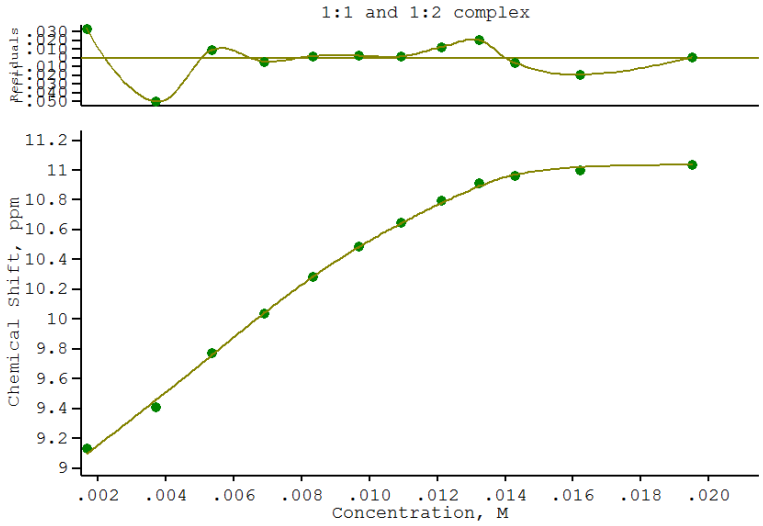

Figure S28. Fit plot obtained in the determination of K_a using urea-NH resonance by WinEQNMR2 for $\mathbf{L_1}$ and bicarbonate anion.

Calculations for the titration of $\mathbf{L_1}$ with the bicarbonate anion.

```
                                        out
Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes
Program run at 16:21:30   on 01/08/2014

 1:1 and 1:2 complex

  Equilibrium constants are log10 values

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  5.15685E+00 3.200E-02 7.732E-01 1.962E+02 K11
   2  1  9.06291E+00 3.600E-02 1.194E+00 1.245E+02 K12
   3  1  8.81662E+00 1.000E-02 3.401E-02 2.376E+00 Free Ligand
   4  1  1.04618E+01 1.000E-02 9.592E-02 3.082E+01 complex11
   5  1  1.10428E+01 1.000E-02 3.004E-02 5.233E+00 complex12

0RMS ERROR = 2.58E-02  MAX ERROR = 4.98E-02 AT OBS.NO.  2
 RESIDUALS SQUARED = 4.67E-03
 RFACTOR =     0.1898 PERCENT

 NO. A   EXPT. DEL  CALC. DEL     RESIDUAL     % DEV   WEIGHT      HCO3-
L1          pH
   1 1  9.1320E+00  9.0992E+00  3.2840E-02  3.5961E-01  1.0000E+00  1.6667E-03
9.6154E-03  0.0000E+00
   2 1  9.4100E+00  9.4598E+00 -4.9824E-02 -5.2948E-01  1.0000E+00  3.7037E-03
9.2593E-03  0.0000E+00
   3 1  9.7730E+00  9.7635E+00  9.5291E-03  9.7504E-02  1.0000E+00  5.3571E-03
8.9286E-03  0.0000E+00
   4 1  1.0039E+01  1.0043E+01 -4.2152E-03 -4.1989E-02  1.0000E+00  6.8966E-03
8.6207E-03  0.0000E+00
   5 1  1.0288E+01  1.0286E+01  1.9436E-03  1.8892E-02  1.0000E+00  8.3333E-03
8.3333E-03  0.0000E+00
   6 1  1.0487E+01  1.0485E+01  2.2364E-03  2.1325E-02  1.0000E+00  9.6774E-03
8.0645E-03  0.0000E+00
   7 1  1.0647E+01  1.0646E+01  1.4744E-03  1.3848E-02  1.0000E+00  1.0937E-02
7.8125E-03  0.0000E+00
   8 1  1.0794E+01  1.0781E+01  1.2708E-02  1.1773E-01  1.0000E+00  1.2121E-02
7.5758E-03  0.0000E+00
   9 1  1.0913E+01  1.0893E+01  2.0475E-02  1.8762E-01  1.0000E+00  1.3235E-02
7.3529E-03  0.0000E+00
  10 1  1.0965E+01  1.0971E+01 -5.5246E-03 -5.0384E-02  1.0000E+00  1.4286E-02
7.1429E-03  0.0000E+00
  11 1  1.1001E+01  1.1020E+01 -1.9384E-02 -1.7621E-01  1.0000E+00  1.6216E-02
6.7568E-03  0.0000E+00
  12 1  1.1035E+01  1.1034E+01  7.3433E-04  6.6545E-03  1.0000E+00  1.9512E-02
6.0976E-03  0.0000E+00

 TOLERANCE ON SUM OF SQUARES    0.0100
 TOLERANCE ON EIGEN VALUES    0.0001
 CONVERGANCE AFTER   38  ITERATIONS
```

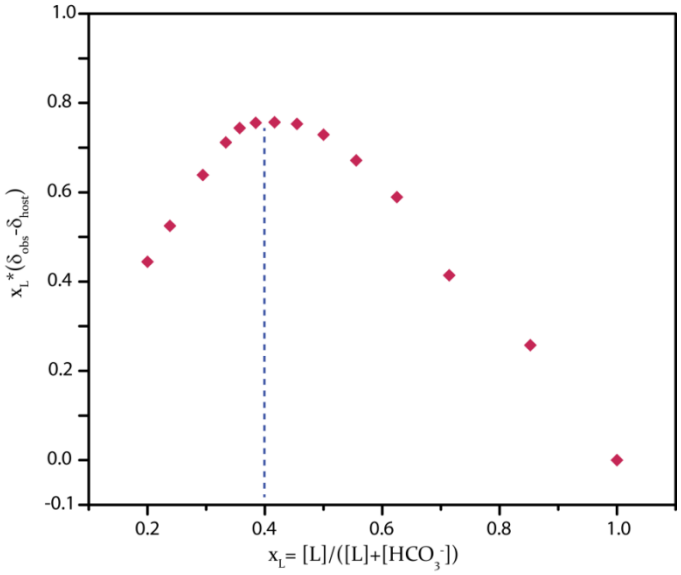

Figure S29. Job plot using urea-NH resonances for $\mathbf{L_1}$ and bicarbonate anion, showing a maximum at 0.4 mole fraction value of the receptor for the multiple equilibria existing between 1: 1 and 1 : 2 complexes.

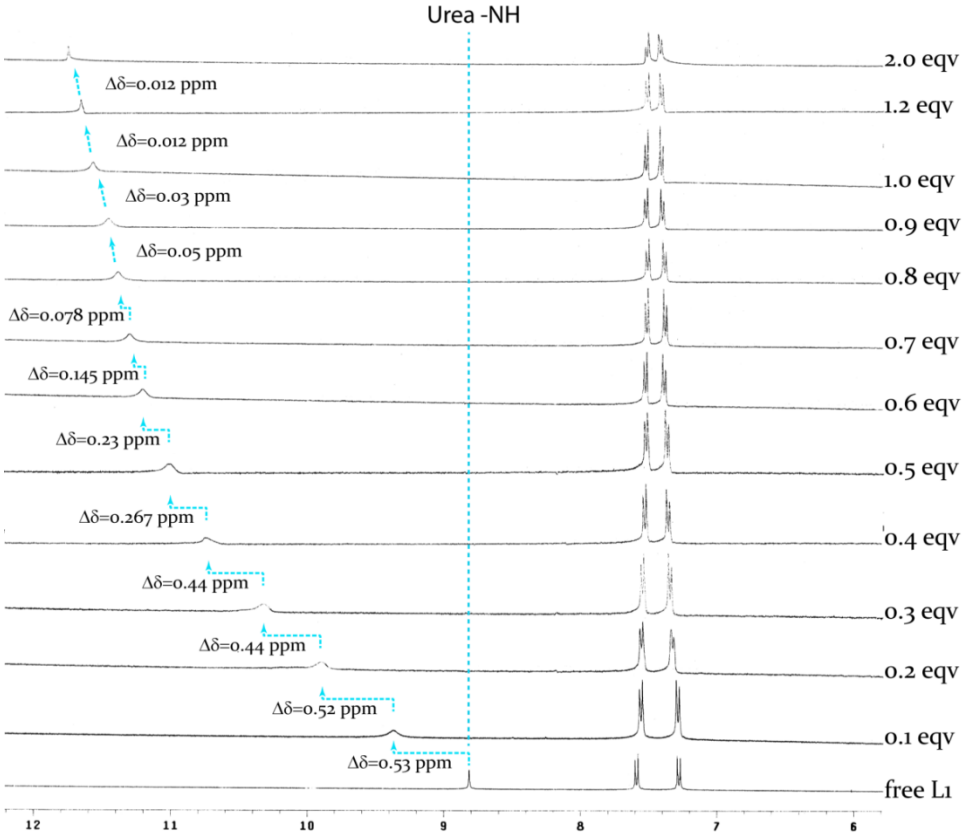

Figure S30. Expanded partial ^{1}H NMR spectra of $\mathbf{L_1}$ upon titration with AcO^-(n-TBA) in DMSO-d_6.

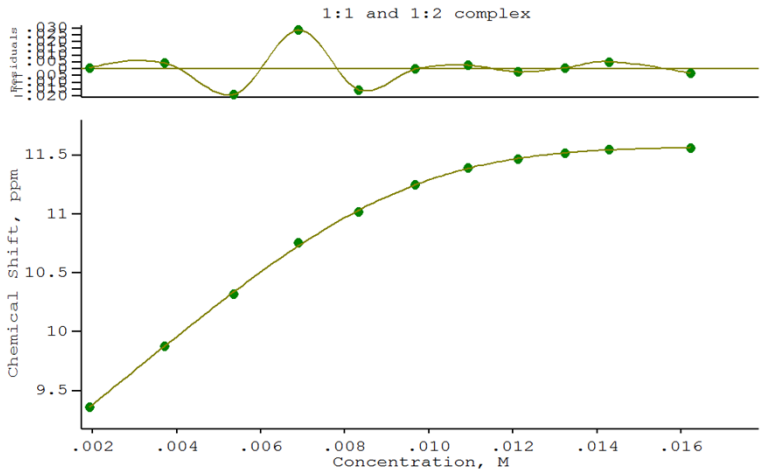

Figure S31. Fit plot obtained in the determination of K_a using urea-NH resonance by WinEQNMR2 for $\mathbf{L_1}$ and acetate anion.

Calculations for the titration of $\mathbf{L_1}$ with the acetate anion.

```
                                        out
Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes
Program run at 16:49:45   on 01/08/2014

 1:1 and 1:2 complex

  Equilibrium constants are log10 values

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  3.69465E+00 3.200E-02 2.886E-01 9.752E+02 K11
   2  1  6.33635E+00 3.600E-02 5.488E-01 4.350E+02 K12
   3  1  8.80631E+00 1.000E-02 3.919E-02 9.090E+00 Free Ligand
   4  1  1.17029E+01 1.000E-02 1.717E-01 3.103E+02 complex11
   5  1  1.15518E+01 1.000E-02 6.628E-02 2.386E+01 complex12

0RMS ERROR = 1.58E-02  MAX ERROR = 2.88E-02 AT OBS.NO.  4
 RESIDUALS SQUARED = 1.49E-03
 RFACTOR =     0.1065 PERCENT

 NO. A   EXPT. DEL  CALC. DEL     RESIDUAL     % DEV   WEIGHT      AcO-           L1
         pH
   1 1  9.3600E+00  9.3595E+00  5.3883E-04  5.7567E-03  1.0000E+00  1.9231E-03
9.6154E-03  0.0000E+00
   2 1  9.8800E+00  9.8757E+00  4.2715E-03  4.3234E-02  1.0000E+00  3.7037E-03
9.2593E-03  0.0000E+00
   3 1  1.0320E+01  1.0339E+01 -1.8932E-02 -1.8345E-01  1.0000E+00  5.3571E-03
8.9286E-03  0.0000E+00
   4 1  1.0759E+01  1.0730E+01  2.8756E-02  2.6728E-01  1.0000E+00  6.8966E-03
8.6207E-03  0.0000E+00
   5 1  1.1019E+01  1.1034E+01 -1.5468E-02 -1.4037E-01  1.0000E+00  8.3333E-03
8.3333E-03  0.0000E+00
   6 1  1.1249E+01  1.1249E+01 -1.8978E-04 -1.6871E-03  1.0000E+00  9.6774E-03
8.0645E-03  0.0000E+00
   7 1  1.1392E+01  1.1390E+01  2.4824E-03  2.1791E-02  1.0000E+00  1.0937E-02
7.8125E-03  0.0000E+00
   8 1  1.1470E+01  1.1472E+01 -2.3661E-03 -2.0628E-02  1.0000E+00  1.2121E-02
7.5758E-03  0.0000E+00
   9 1  1.1520E+01  1.1519E+01  6.9904E-04  6.0681E-03  1.0000E+00  1.3235E-02
7.3529E-03  0.0000E+00
  10 1  1.1550E+01  1.1545E+01  5.1756E-03  4.4810E-02  1.0000E+00  1.4286E-02
7.1429E-03  0.0000E+00
  11 1  1.1562E+01  1.1565E+01 -3.2415E-03 -2.8036E-02  1.0000E+00  1.6216E-02
6.7568E-03  0.0000E+00

 TOLERANCE ON SUM OF SQUARES    0.0100
 TOLERANCE ON EIGEN VALUES    0.0001
 CONVERGANCE AFTER   22  ITERATIONS
```

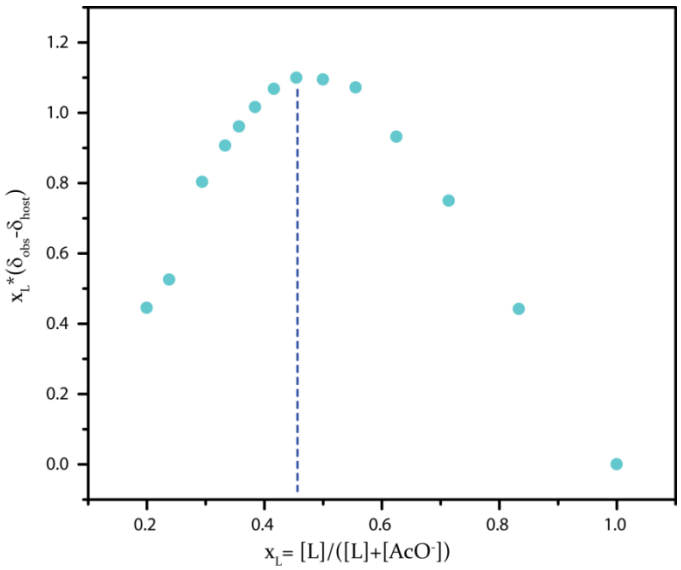

Figure S32. Job plot using urea-NH resonances for $\mathbf{L_1}$ and acetate anion, showing a maximum at 0.45 mole fraction value of the receptor for the multiple equilibria existing between 1: 1 and 1 : 2 complexes.

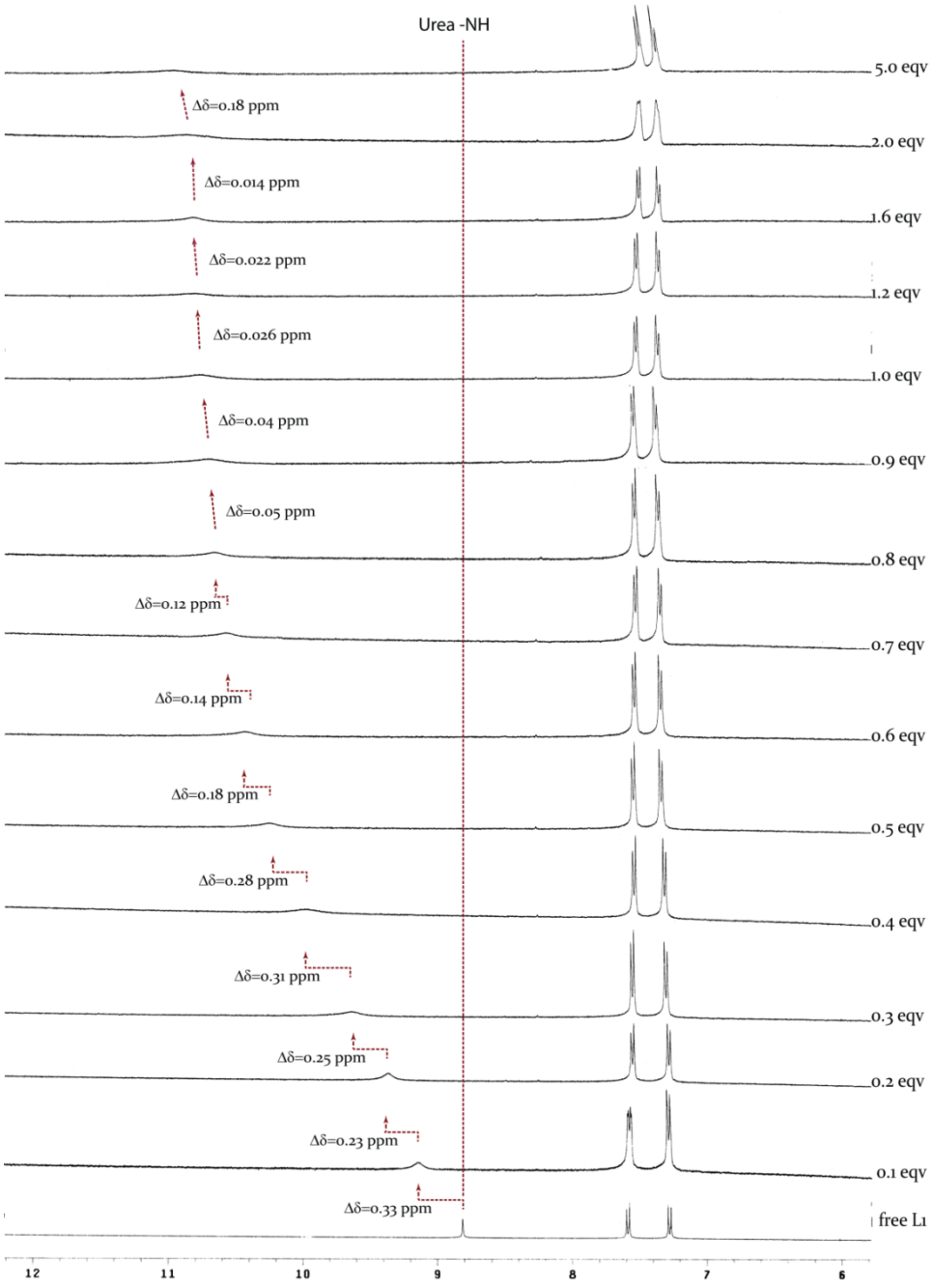

Figure S33. Expanded partial ^{1}H NMR spectra of $\mathbf{L_1}$ upon titration with F^-(n-TBA) in DMSO-d_6.

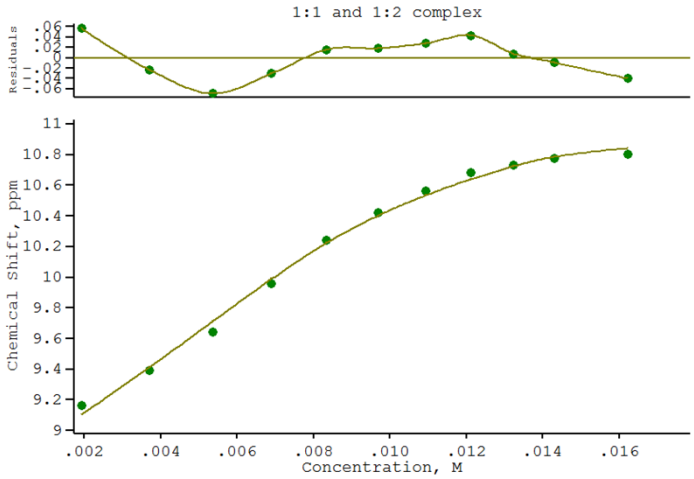

Figure S34. Fit plot obtained in the determination of K_a using urea-NH resonance by WinEQNMR2 for $\mathbf{L_1}$ and fluoride anion.

Calculations for the titration of $\mathbf{L_1}$ with the fluoride anion.

```
                                        out
Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes
Program run at 18:23:40   on 01/08/2014

 1:1 and 1:2 complex

  Equilibrium constants are log10 values

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  4.95144E+00 3.200E-02 2.394E+00 3.708E+02 K11
   2  1  8.37534E+00 3.600E-02 4.120E+00 4.244E+02 K12
   3  1  8.79251E+00 1.000E-02 7.171E-02 2.734E+00 Free Ligand
   4  1  1.03681E+01 1.000E-02 1.756E-01 3.463E+01 complex11
   5  1  1.08952E+01 1.000E-02 2.520E-01 6.255E+01 complex12

0RMS ERROR = 4.91E-02  MAX ERROR = 6.90E-02 AT OBS.NO.  3
 RESIDUALS SQUARED = 1.45E-02
 RFACTOR =     0.3544 PERCENT

 NO. A   EXPT. DEL  CALC. DEL     RESIDUAL     % DEV   WEIGHT      F-           L1
      pH
   1 1  9.1630E+00  9.1053E+00  5.7686E-02  6.2955E-01  1.0000E+00  1.9231E-03
9.6154E-03  0.0000E+00
   2 1  9.3910E+00  9.4135E+00 -2.2460E-02 -2.3916E-01  1.0000E+00  3.7037E-03
9.2593E-03  0.0000E+00
   3 1  9.6430E+00  9.7120E+00 -6.8969E-02 -7.1522E-01  1.0000E+00  5.3571E-03
8.9286E-03  0.0000E+00
   4 1  9.9600E+00  9.9897E+00 -2.9698E-02 -2.9818E-01  1.0000E+00  6.8966E-03
8.6207E-03  0.0000E+00
   5 1  1.0241E+01  1.0225E+01  1.6071E-02  1.5693E-01  1.0000E+00  8.3333E-03
8.3333E-03  0.0000E+00
   6 1  1.0420E+01  1.0402E+01  1.8230E-02  1.7496E-01  1.0000E+00  9.6774E-03
8.0645E-03  0.0000E+00
   7 1  1.0564E+01  1.0536E+01  2.8188E-02  2.6683E-01  1.0000E+00  1.0937E-02
7.8125E-03  0.0000E+00
   8 1  1.0685E+01  1.0642E+01  4.3401E-02  4.0618E-01  1.0000E+00  1.2121E-02
7.5758E-03  0.0000E+00
   9 1  1.0734E+01  1.0726E+01  8.1882E-03  7.6283E-02  1.0000E+00  1.3235E-02
7.3529E-03  0.0000E+00
  10 1  1.0777E+01  1.0786E+01 -8.7833E-03 -8.1501E-02  1.0000E+00  1.4286E-02
7.1429E-03  0.0000E+00
  11 1  1.0803E+01  1.0843E+01 -3.9724E-02 -3.6772E-01  1.0000E+00  1.6216E-02
6.7568E-03  0.0000E+00

 TOLERANCE ON SUM OF SQUARES    0.0100
 TOLERANCE ON EIGEN VALUES    0.0001
 CONVERGANCE AFTER   12  ITERATIONS
```

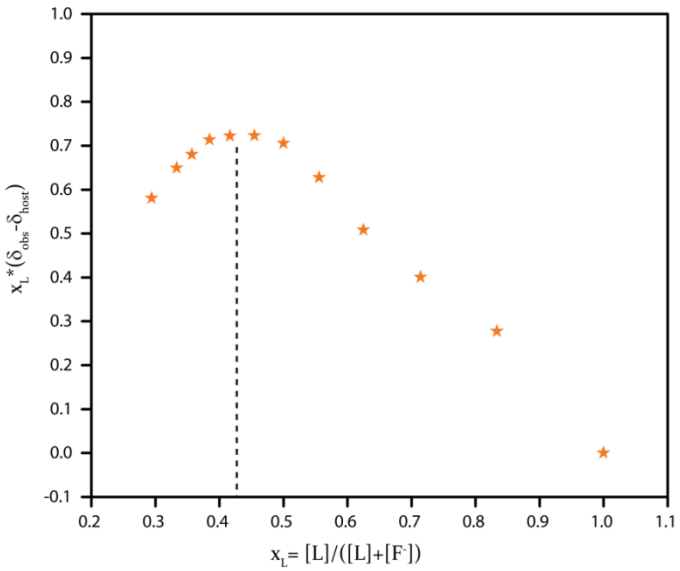

Figure S35. Job plot using urea-NH resonances for $\mathbf{L_1}$ and fluoride anion, showing a maximum at 0.43 mole fraction value of the receptor for the multiple equilibria existing between 1: 1 and 1 : 2 complexes.

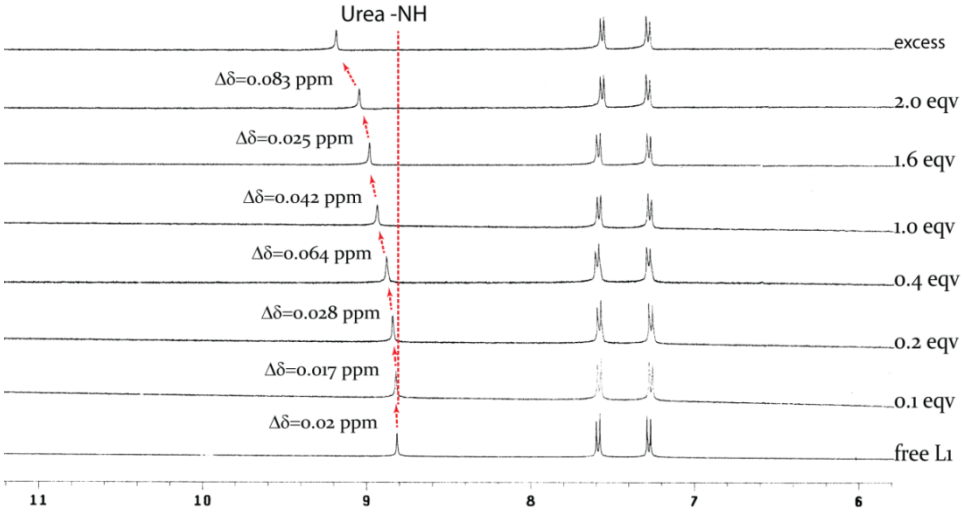

Figure S36. Expanded partial ^{1}H NMR spectra of $\mathbf{L_1}$ upon titration with Cl^-(TEA) in DMSO-d_6.

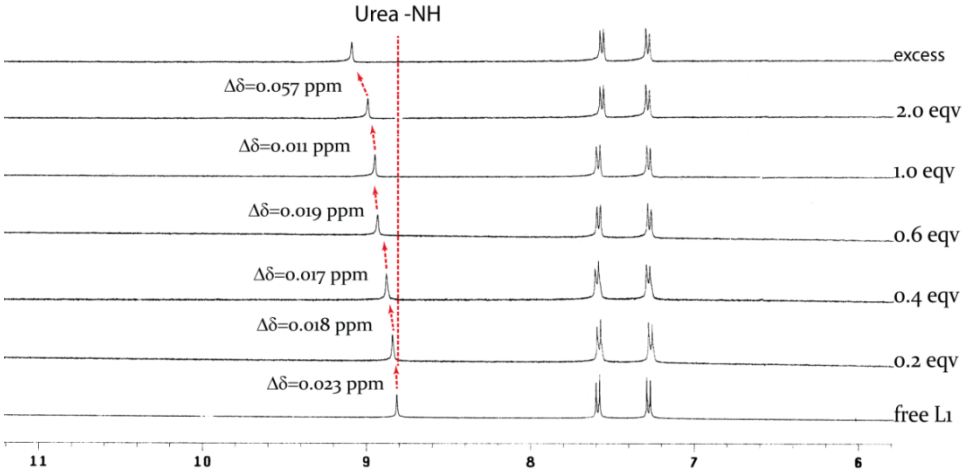

Figure S37. Expanded partial ^{1}H NMR spectra of $\mathbf{L_1}$ upon titration with Br^-(n-TBA) in DMSO-d_6.

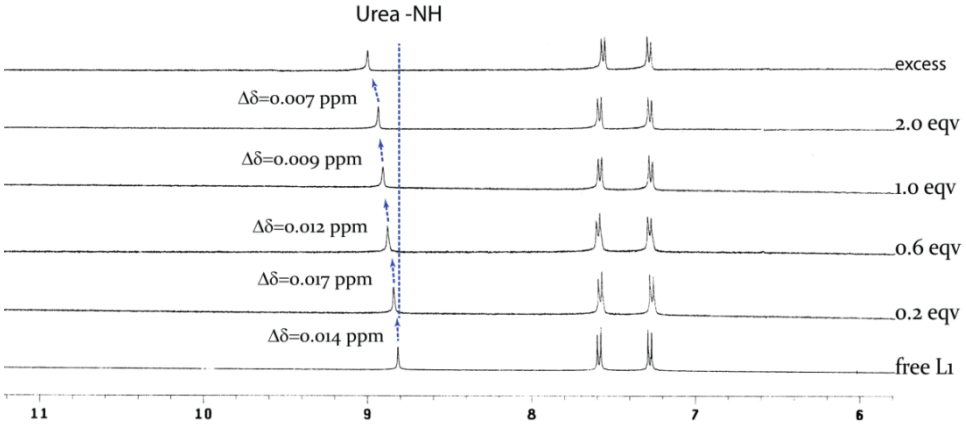

Figure S38. Expanded partial ^{1}H NMR spectra of $\mathbf{L_1}$ upon titration with I^-(n-TBA) in DMSO-d_6.

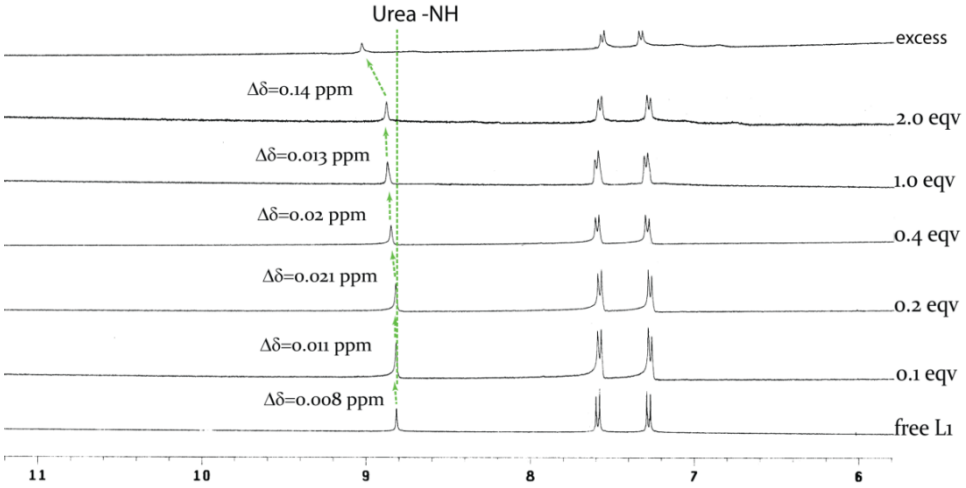

Figure S39. Expanded partial ^{1}H NMR spectra of $\mathbf{L_1}$ upon titration with HSO_4^-(n-TBA) in DMSO-d_6.

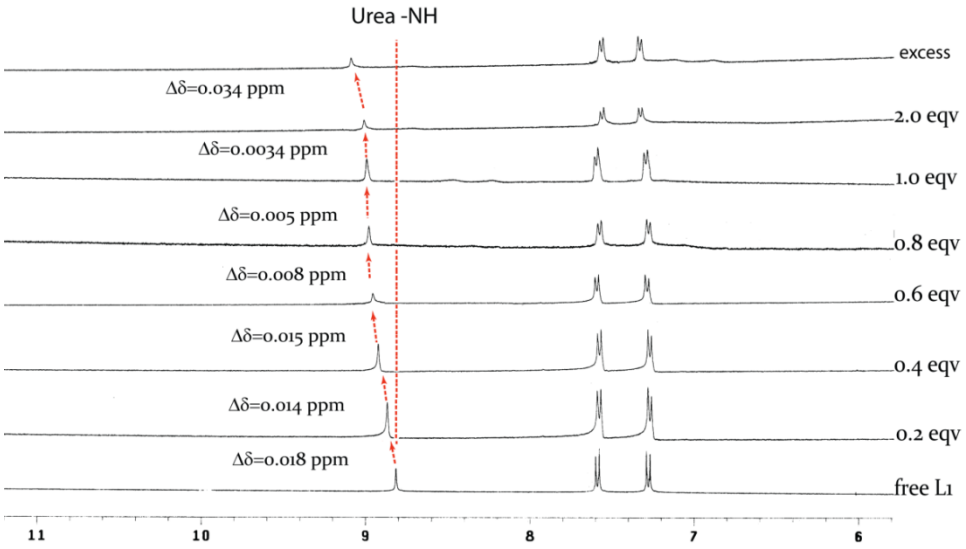

Figure S40. Expanded partial ^{1}H NMR spectra of $\mathbf{L_1}$ upon titration with $H_2PO_4^-$(n-TBA) in DMSO-d_6

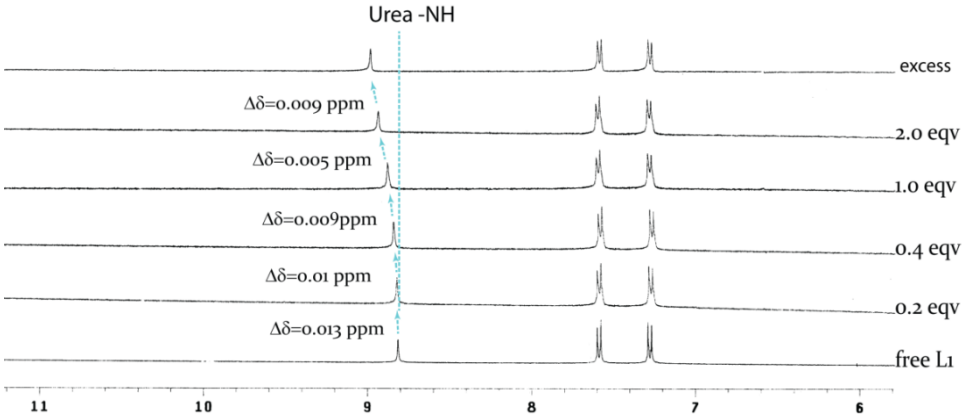

Figure S41. Expanded partial ^{1}H NMR spectra of $\mathbf{L_1}$ upon titration with NO_3^-(TEA) in DMSO-d_6.

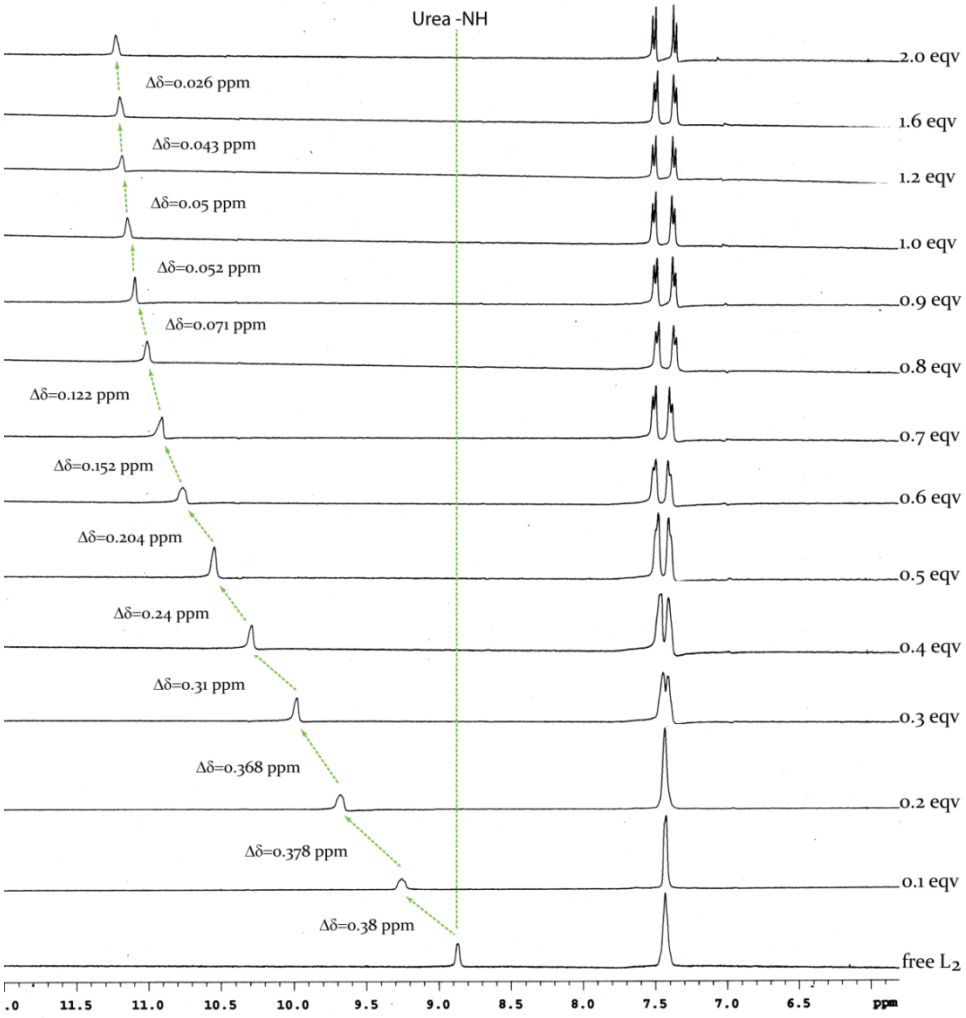

Figure S42. Expanded partial ^{1}H NMR spectra of $\mathbf{L_2}$ upon titration with AcO^-(n-TBA) in DMSO-d_6.

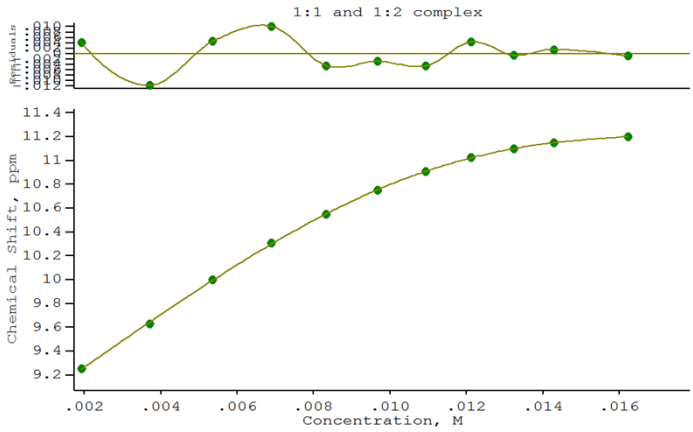

Figure S43. Fit plot obtained in the determination of K_a using urea-NH resonance by WinEQNMR2 for $\mathbf{L_2}$ and acetate anion.

Calculations for the titration of L_2 with the acetate anion.

```
                                        out
Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes
Program run at 17:11:38   on 01/08/2014

 1:1 and 1:2 complex

  Equilibrium constants are log10 values

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  3.66075E+00 3.200E-02 2.202E-01 1.322E+03 K11
   2  1  6.53355E+00 3.600E-02 3.391E-01 4.054E+02 K12
   3  1  8.82052E+00 1.000E-02 2.464E-02 1.627E+01 Free Ligand
   4  1  1.10966E+01 1.000E-02 1.299E-01 5.727E+02 complex11
   5  1  1.12669E+01 1.000E-02 3.217E-02 3.256E+01 complex12

0RMS ERROR = 7.62E-03  MAX ERROR = 1.16E-02 AT OBS.NO.  2
 RESIDUALS SQUARED = 3.48E-04
 RFACTOR =     0.0533 PERCENT

 NO. A   EXPT. DEL  CALC. DEL     RESIDUAL     % DEV   WEIGHT      AcO-           L
         pH
   1 1  9.2540E+00  9.2499E+00  4.1151E-03  4.4468E-02  1.0000E+00  1.9231E-03
9.6154E-03  0.0000E+00
   2 1  9.6320E+00  9.6436E+00 -1.1618E-02 -1.2062E-01  1.0000E+00  3.7037E-03
9.2593E-03  0.0000E+00
   3 1  1.0000E+01  9.9954E+00  4.6263E-03  4.6263E-02  1.0000E+00  5.3571E-03
8.9286E-03  0.0000E+00
   4 1  1.0310E+01  1.0300E+01  1.0186E-02  9.8799E-02  1.0000E+00  6.8966E-03
8.6207E-03  0.0000E+00
   5 1  1.0549E+01  1.0553E+01 -4.4279E-03 -4.1975E-02  1.0000E+00  8.3333E-03
8.3333E-03  0.0000E+00
   6 1  1.0753E+01  1.0756E+01 -2.7552E-03 -2.5622E-02  1.0000E+00  9.6774E-03
8.0645E-03  0.0000E+00
   7 1  1.0905E+01  1.0910E+01 -4.5233E-03 -4.1479E-02  1.0000E+00  1.0937E-02
7.8125E-03  0.0000E+00
   8 1  1.1027E+01  1.1023E+01  4.4870E-03  4.0691E-02  1.0000E+00  1.2121E-02
7.5758E-03  0.0000E+00
   9 1  1.1098E+01  1.1099E+01 -5.9128E-04 -5.3278E-03  1.0000E+00  1.3235E-02
7.3529E-03  0.0000E+00
  10 1  1.1150E+01  1.1148E+01  1.5745E-03  1.4121E-02  1.0000E+00  1.4286E-02
7.1429E-03  0.0000E+00
  11 1  1.1200E+01  1.1201E+01 -8.4114E-04 -7.5102E-03  1.0000E+00  1.6216E-02
6.7568E-03  0.0000E+00

 TOLERANCE ON SUM OF SQUARES    0.0100
 TOLERANCE ON EIGEN VALUES    0.0001
 CONVERGANCE AFTER   35  ITERATIONS
```

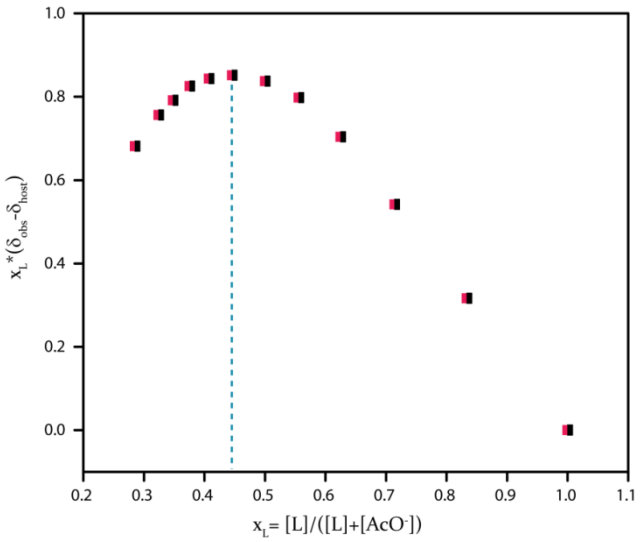

Figure S44. Job plot using urea-NH resonances for L_2 and acetate anion, showing a maximum at 0.45 mole fraction value of the receptor for the multiple equilibria existing between 1: 1 and 1 : 2 complexes.

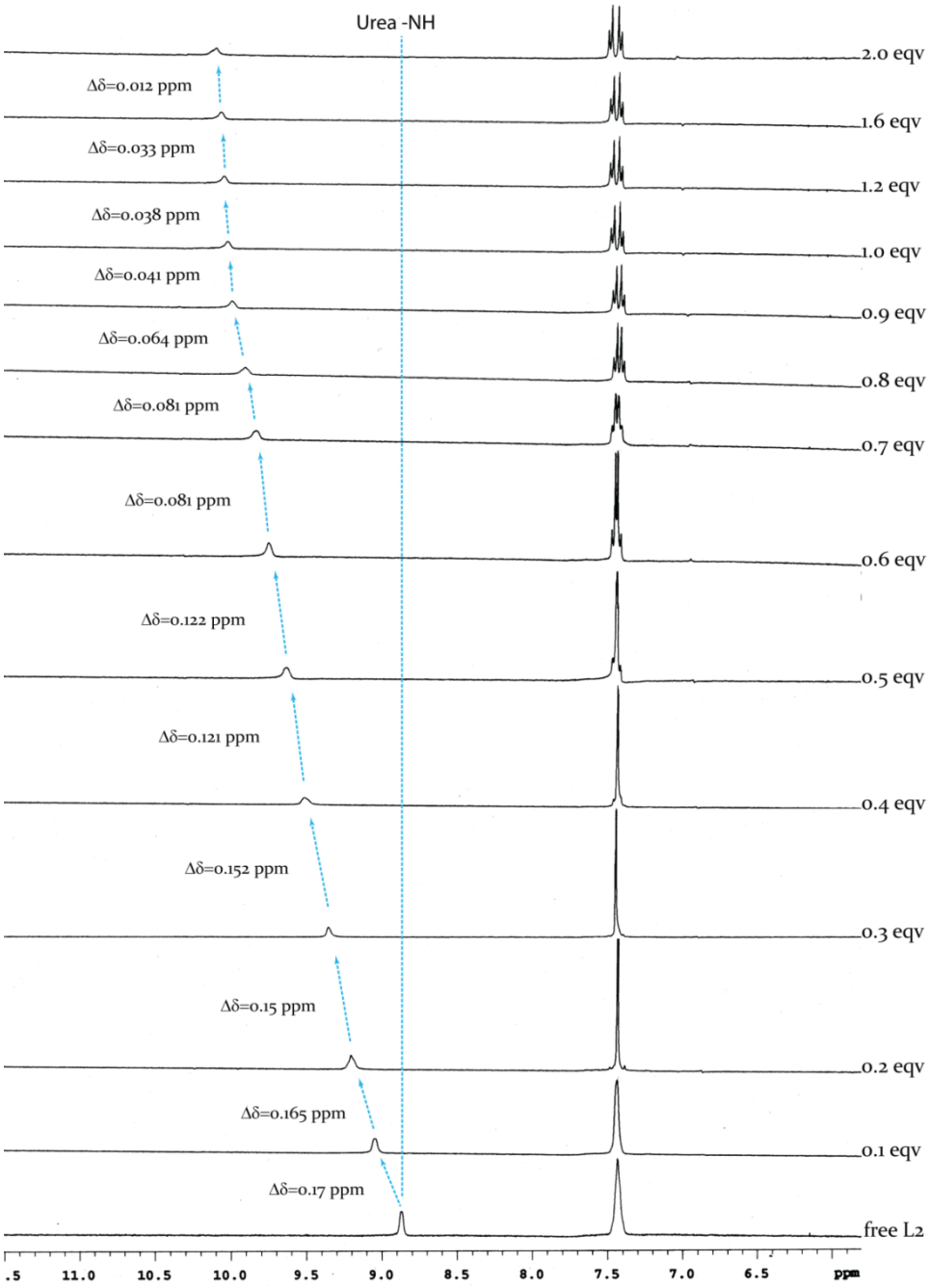

Figure S45. Expanded partial ^{1}H NMR spectra of $\mathbf{L_2}$ upon titration with HCO_3^-(TEA) in DMSO-d_6.

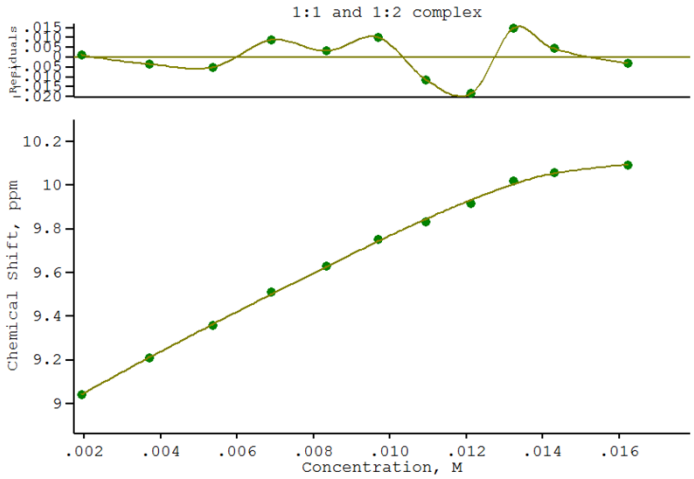

Figure S46. Fit plot obtained in the determination of K_a using urea-NH resonance by WinEQNMR2 for $\mathbf{L_2}$ and bicarbonate anion.

Calculations for the titration of L_2 with the bicarbonate anion.

```
                                        out
Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes
Program run at 18:30:16   on 01/08/2014

 1:1 and 1:2 complex

  Equilibrium constants are log10 values

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  3.31956E+00 3.200E-02 1.596E+00 7.560E+03 K11
   2  1  6.78632E+00 3.600E-02 1.339E+00 7.126E+02 K12
   3  1  8.83889E+00 1.000E-02 9.227E-02 1.098E+02 Free Ligand
   4  1  1.00942E+01 1.000E-02 1.259E+00 6.274E+03 complex11
   5  1  1.01112E+01 1.000E-02 8.686E-02 1.405E+02 complex12

0RMS ERROR = 1.26E-02  MAX ERROR = 1.83E-02 AT OBS.NO.  8
 RESIDUALS SQUARED = 9.47E-04
 RFACTOR =     0.0958 PERCENT

 NO. A   EXPT. DEL  CALC. DEL     RESIDUAL     % DEV   WEIGHT      HCO3-
L2          pH
   1 1  9.0440E+00  9.0429E+00  1.1396E-03  1.2601E-02  1.0000E+00  1.9231E-03
9.6154E-03  0.0000E+00
   2 1  9.2090E+00  9.2125E+00 -3.4571E-03 -3.7540E-02  1.0000E+00  3.7037E-03
9.2593E-03  0.0000E+00
   3 1  9.3590E+00  9.3641E+00 -5.0631E-03 -5.4098E-02  1.0000E+00  5.3571E-03
8.9286E-03  0.0000E+00
   4 1  9.5110E+00  9.5023E+00  8.7280E-03  9.1768E-02  1.0000E+00  6.8966E-03
8.6207E-03  0.0000E+00
   5 1  9.6320E+00  9.6288E+00  3.2377E-03  3.3614E-02  1.0000E+00  8.3333E-03
8.3333E-03  0.0000E+00
   6 1  9.7540E+00  9.7437E+00  1.0272E-02  1.0531E-01  1.0000E+00  9.6774E-03
8.0645E-03  0.0000E+00
   7 1  9.8350E+00  9.8463E+00 -1.1306E-02 -1.1495E-01  1.0000E+00  1.0937E-02
7.8125E-03  0.0000E+00
   8 1  9.9160E+00  9.9343E+00 -1.8341E-02 -1.8496E-01  1.0000E+00  1.2121E-02
7.5758E-03  0.0000E+00
   9 1  1.0021E+01  1.0006E+01  1.4876E-02  1.4845E-01  1.0000E+00  1.3235E-02
7.3529E-03  0.0000E+00
  10 1  1.0059E+01  1.0054E+01  4.5424E-03  4.5157E-02  1.0000E+00  1.4286E-02
7.1429E-03  0.0000E+00
  11 1  1.0092E+01  1.0095E+01 -3.1137E-03 -3.0854E-02  1.0000E+00  1.6216E-02
6.7568E-03  0.0000E+00

 TOLERANCE ON SUM OF SQUARES    0.0100
 TOLERANCE ON EIGEN VALUES    0.0001
 CONVERGANCE AFTER   16  ITERATIONS
```

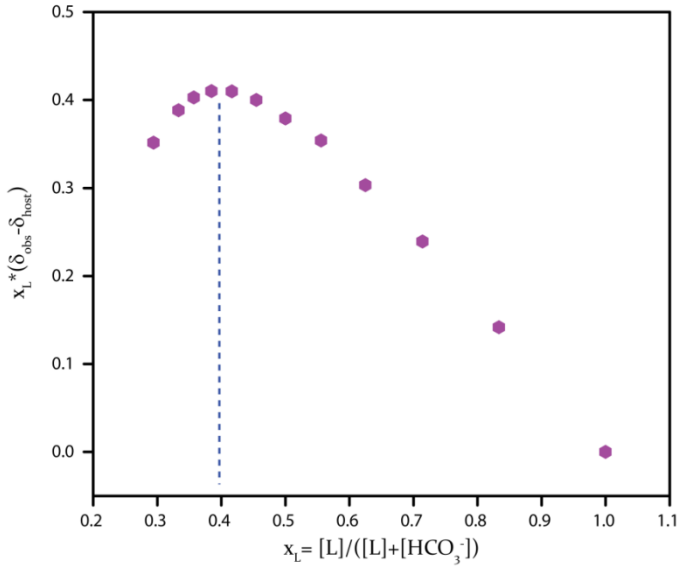

Figure S47. Job plot using urea-NH resonances for L_2 and bicarbonate anion, showing a maximum at 0.4 mole fraction value of the receptor for the multiple equilibria

existing between 1: 1 and 1 : 2 complexes.

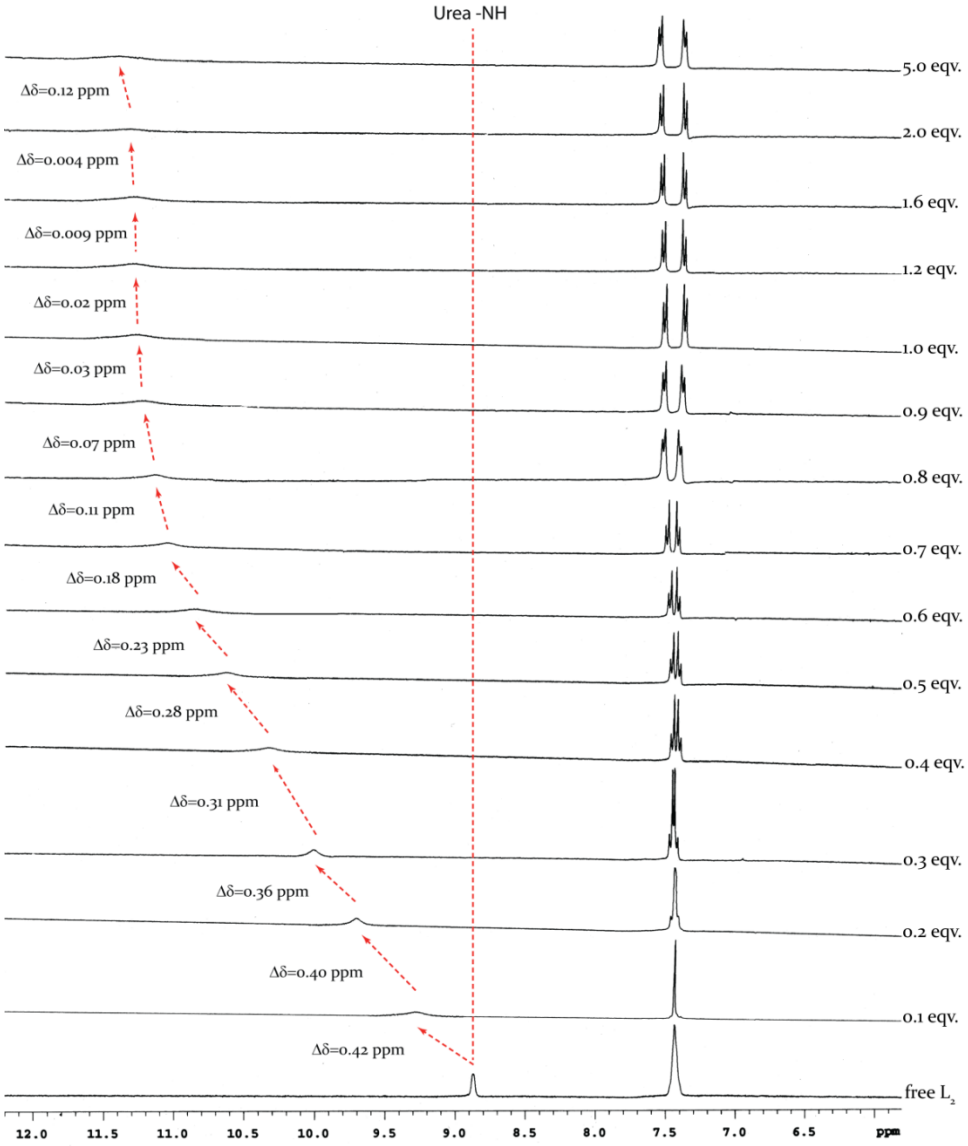

Figure S48. Expanded partial ^{1}H NMR spectra of $\mathbf{L_2}$ upon titration with F^-(n-TBA) in DMSO-d_6.

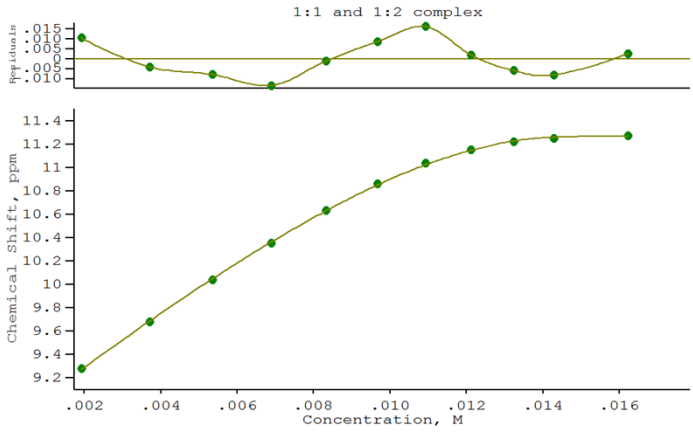

Figure S49. Fit plot obtained in the determination of K_a using urea-NH resonance by WinEQNMR2 for $\mathbf{L_2}$ and fluoride anion.

Calculations for the titration of L_2 with the fluoride anion.

```
                                        out
Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes
Program run at 18:38:25   on 01/08/2014

 1:1 and 1:2 complex

  Equilibrium constants are log10 values

NO.  A   PARAMETER    DELTA     ERROR    CONDITION   DESCRIPTION
   1  1  4.39668E+00 3.200E-02 1.177E+00 2.276E+04 K11
   2  1  8.24536E+00 3.600E-02 2.073E+00 1.599E+04 K12
   3  1  8.80584E+00 1.000E-02 4.867E-02 2.747E+01 Free Ligand
   4  1  1.12942E+01 1.000E-02 3.078E-01 9.149E+02 complex11
   5  1  1.12707E+01 1.000E-02 1.622E-02 5.927E+00 complex12

0RMS ERROR = 1.17E-02  MAX ERROR = 1.62E-02 AT OBS.NO.  7
 RESIDUALS SQUARED = 8.16E-04
 RFACTOR =     0.0809 PERCENT

 NO. A   EXPT. DEL  CALC. DEL     RESIDUAL     % DEV   WEIGHT      F-           L2
       pH
   1 1  9.2840E+00  9.2734E+00  1.0628E-02  1.1447E-01  1.0000E+00  1.9231E-03
9.6154E-03  0.0000E+00
   2 1  9.6840E+00  9.6879E+00 -3.8710E-03 -3.9973E-02  1.0000E+00  3.7037E-03
9.2593E-03  0.0000E+00
   3 1  1.0044E+01  1.0052E+01 -7.8545E-03 -7.8201E-02  1.0000E+00  5.3571E-03
8.9286E-03  0.0000E+00
   4 1  1.0354E+01  1.0367E+01 -1.3257E-02 -1.2804E-01  1.0000E+00  6.8966E-03
8.6207E-03  0.0000E+00
   5 1  1.0634E+01  1.0635E+01 -9.0122E-04 -8.4749E-03  1.0000E+00  8.3333E-03
8.3333E-03  0.0000E+00
   6 1  1.0864E+01  1.0855E+01  8.8148E-03  8.1138E-02  1.0000E+00  9.6774E-03
8.0645E-03  0.0000E+00
   7 1  1.1044E+01  1.1028E+01  1.6241E-02  1.4706E-01  1.0000E+00  1.0937E-02
7.8125E-03  0.0000E+00
   8 1  1.1154E+01  1.1152E+01  1.9102E-03  1.7126E-02  1.0000E+00  1.2121E-02
7.5758E-03  0.0000E+00
   9 1  1.1224E+01  1.1230E+01 -5.8193E-03 -5.1847E-02  1.0000E+00  1.3235E-02
7.3529E-03  0.0000E+00
  10 1  1.1254E+01  1.1262E+01 -7.9689E-03 -7.0810E-02  1.0000E+00  1.4286E-02
7.1429E-03  0.0000E+00
  11 1  1.1274E+01  1.1271E+01  2.6150E-03  2.3195E-02  1.0000E+00  1.6216E-02
6.7568E-03  0.0000E+00

 TOLERANCE ON SUM OF SQUARES    0.0100
 TOLERANCE ON EIGEN VALUES    0.0001
 CONVERGANCE AFTER   39  ITERATIONS
```

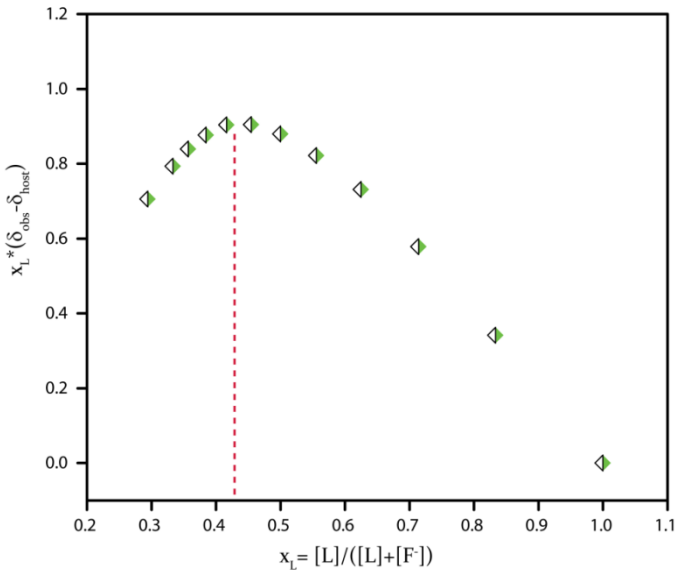

Figure S50. Job plot using urea-NH resonances for $\mathbf{L_2}$ and fluoride anion, showing a maximum at 0.43 mole fraction value of the receptor for the multiple equilibria existing between 1: 1 and 1 : 2 complexes.

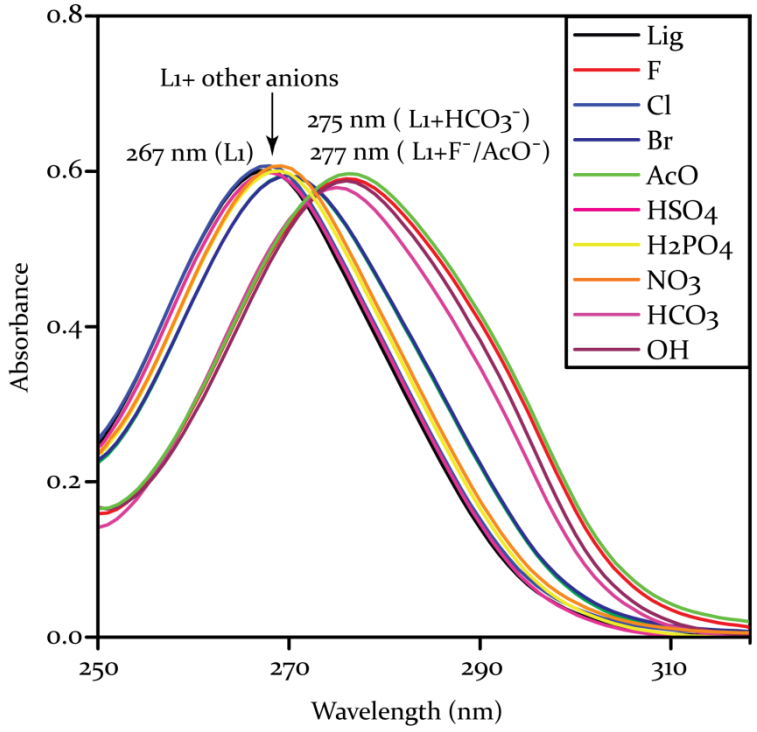

Figure S51. Changes in the UV/Vis spectrum of $\mathbf{L_1}$ in MeCN upon addition of *n*-TBA salts of anions (20 equiv.)

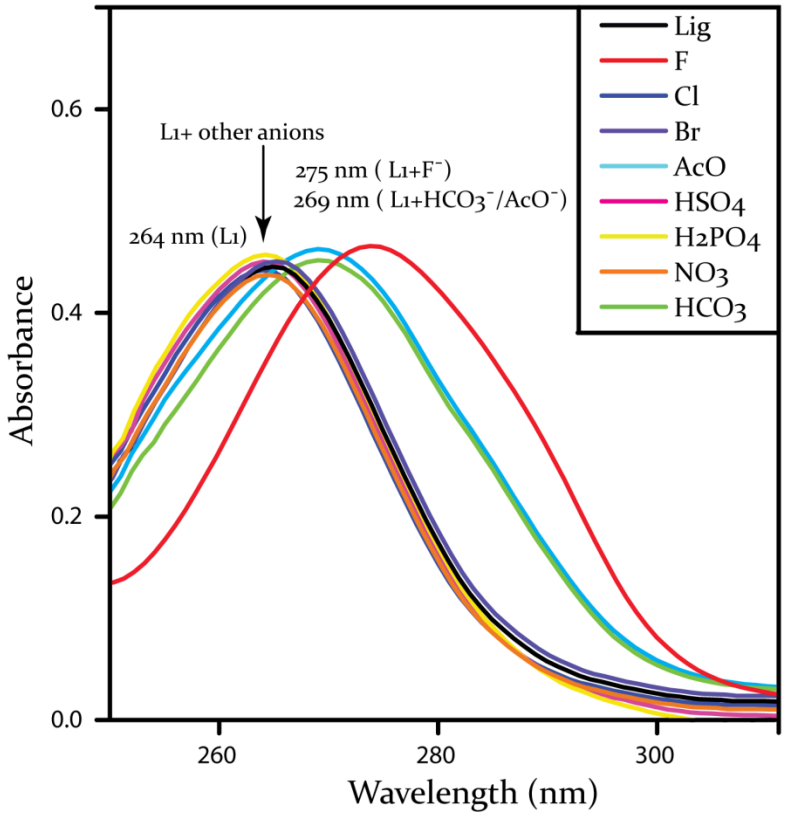

Figure S52. Changes in the UV/Vis spectrum of $\mathbf{L_2}$ in MeCN upon addition of *n*-TBA salts of anions (20 equiv.)

References

1. Hynes, M.J., EQNMR: A computer program for the calculation of stability constants from nuclear magnetic resonance chemical shift data, *J. Chem. Soc., Dalton Trans*. **1993** 311-312.