Electronic Supplementary Information

Neutral host-guest capsular associations by homologous halophenyl substituted organic tris-urea receptor series: Solid and solution state studies

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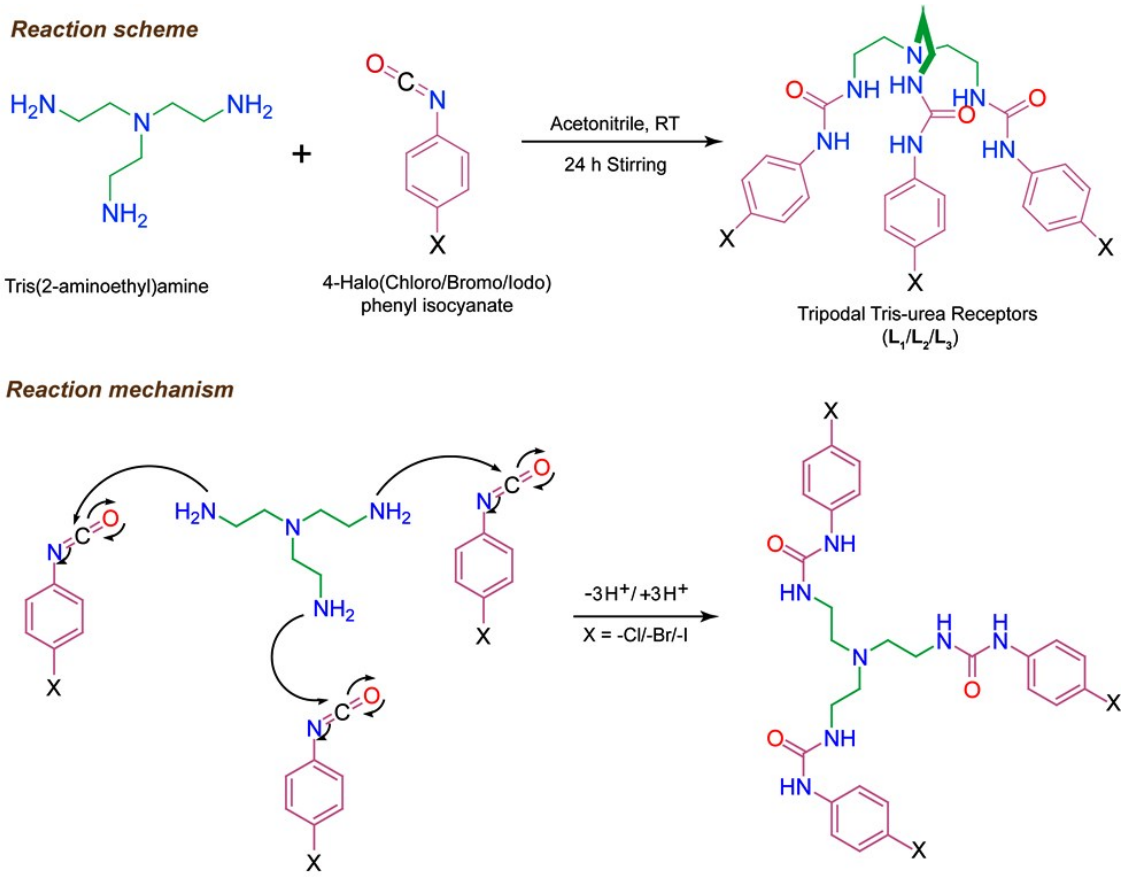


Scheme S1: Synthetic pathway and reaction mechanism for preparation of three tris-urea receptors **L_1, L_2** and **L_3**.

Characterization of free receptors L_1, L_2 and L_3:

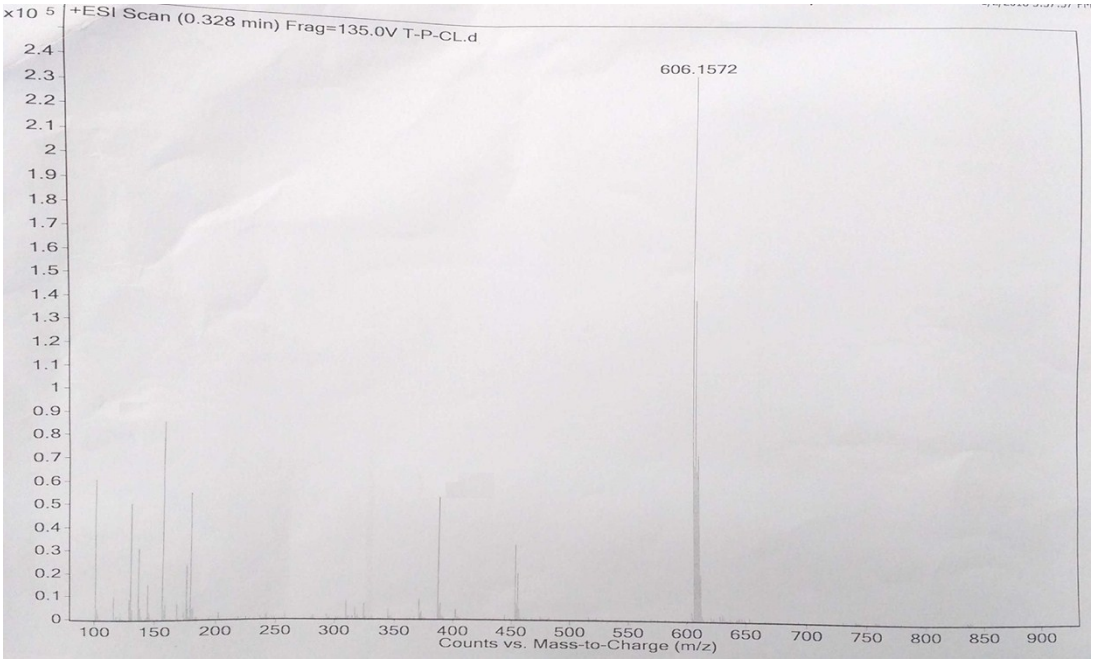


Figure S1: ESI-mass spectrum of tris([(4-chlorophenyl)amino]ethyl)-urea receptor **L_1**.

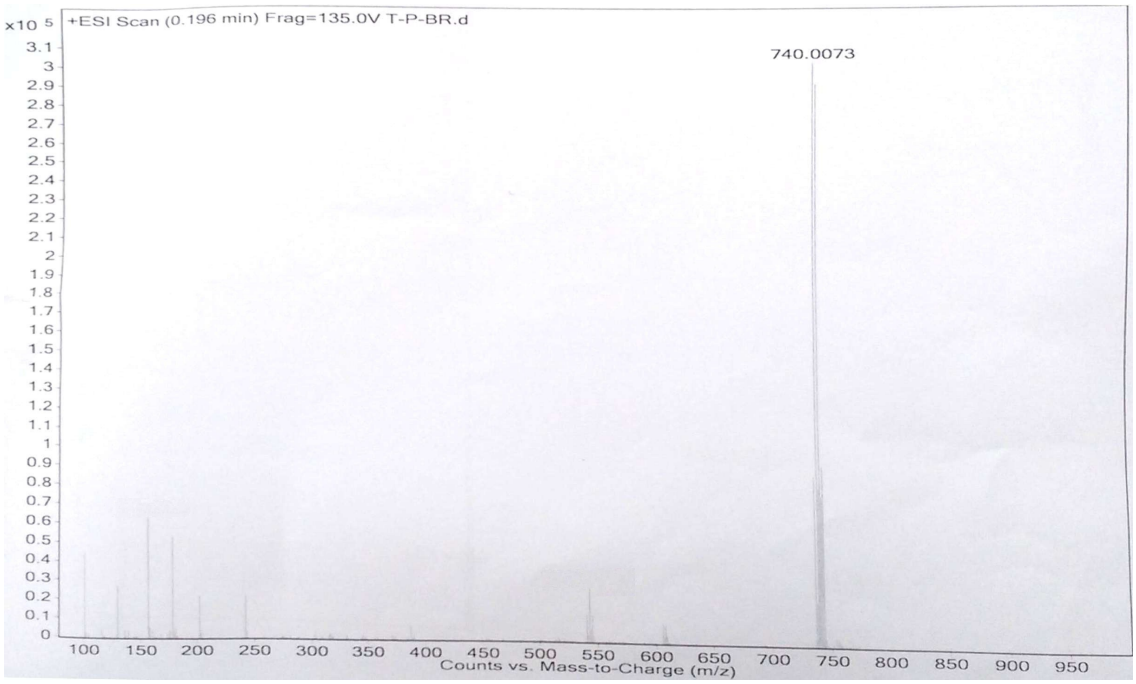


Figure S2: ESI-mass spectrum of tris([(4-bromophenyl)amino]ethyl)-urea receptor $\mathbf{L_2}$.

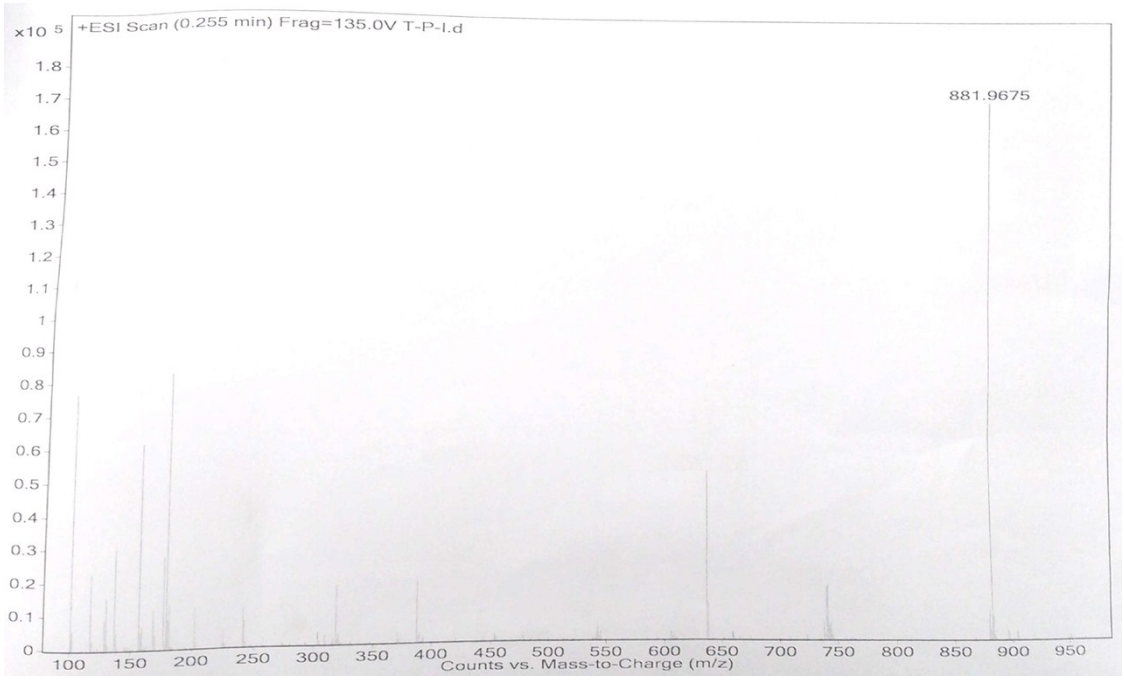


Figure S3: ESI-mass spectrum of tris([(4-iodophenyl)amino]ethyl)-urea receptor $\mathbf{L_3}$.

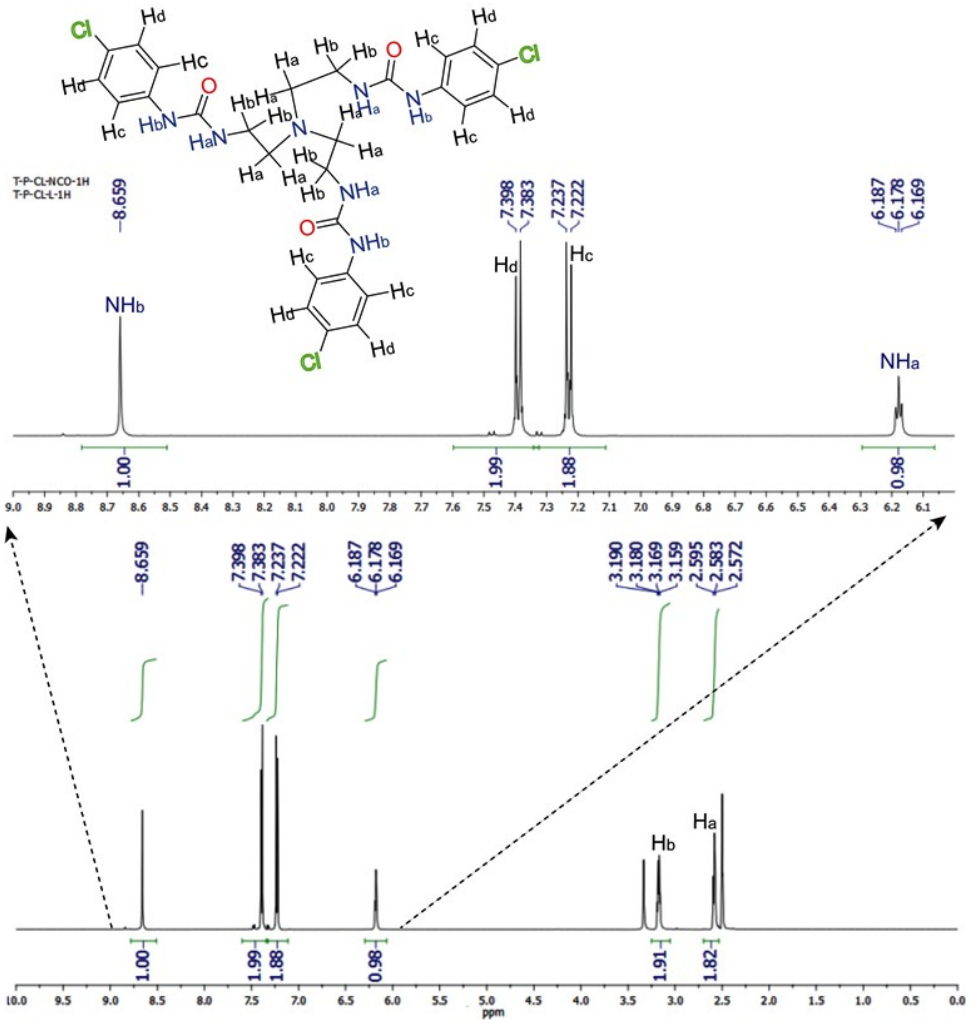


Figure S4: Integrated ^{1}H-NMR spectrum (full as well as expanded) and interpretation of all hydrogen atoms of free tripodal tris-urea receptor $\mathbf{L_1}$ in DMSO-d_6 at 25ºC.

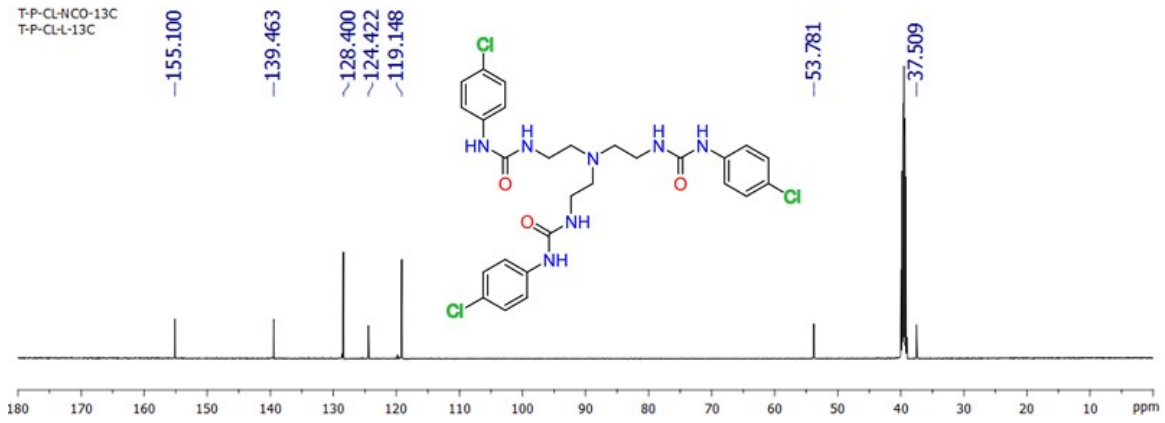


Figure S5: Integrated ^{13}C-NMR spectrum (full as well as expanded) free tripodal urea receptor $\mathbf{L_1}$ in DMSO-d_6 at 25ºC.

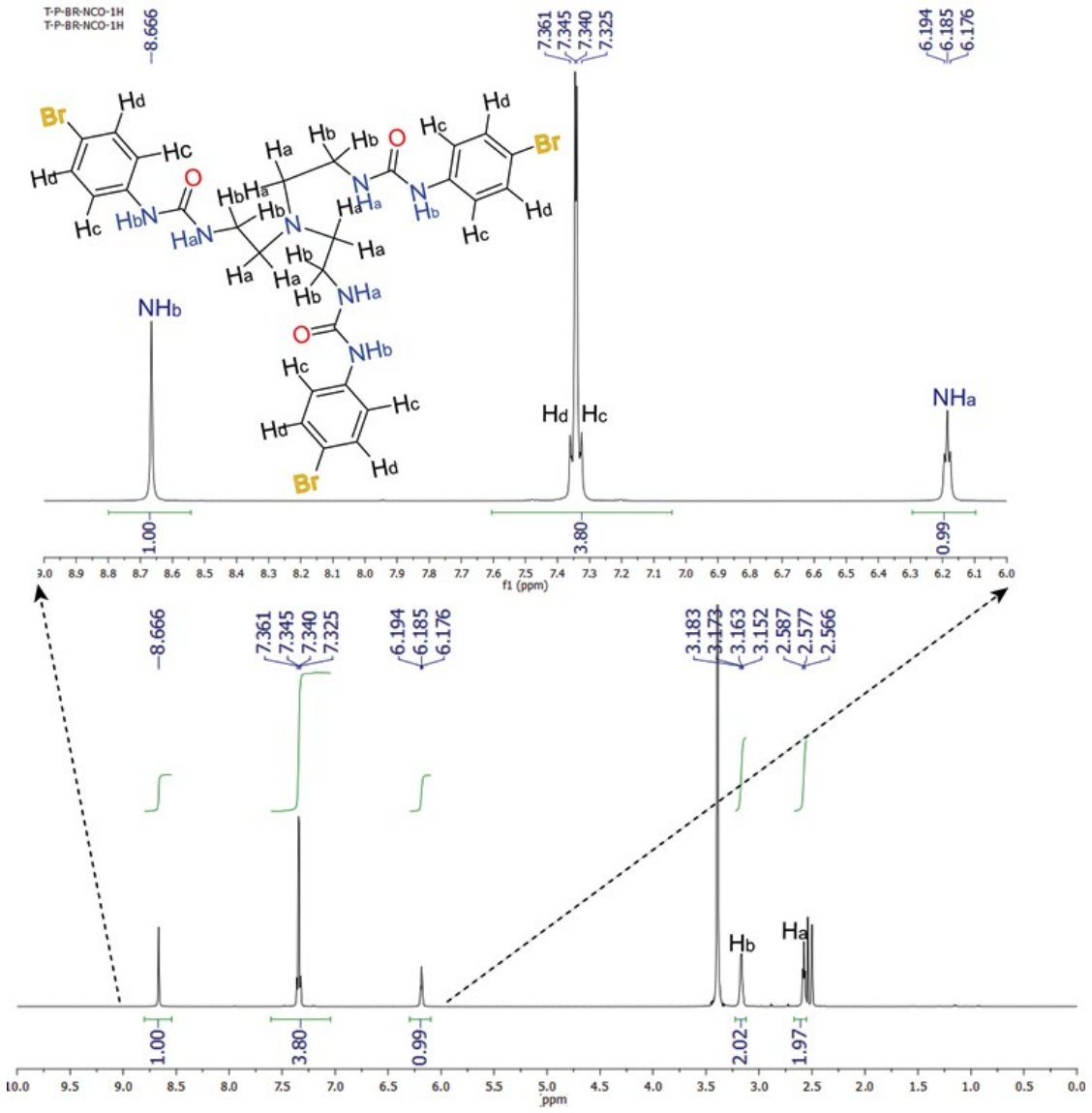


Figure S6: Integrated ^{1}H-NMR spectrum (full as well as expanded) and interpretation of all hydrogen atoms of free tripodal tris-urea receptor $\mathbf{L_2}$ in DMSO-d_6 at 25ºC.

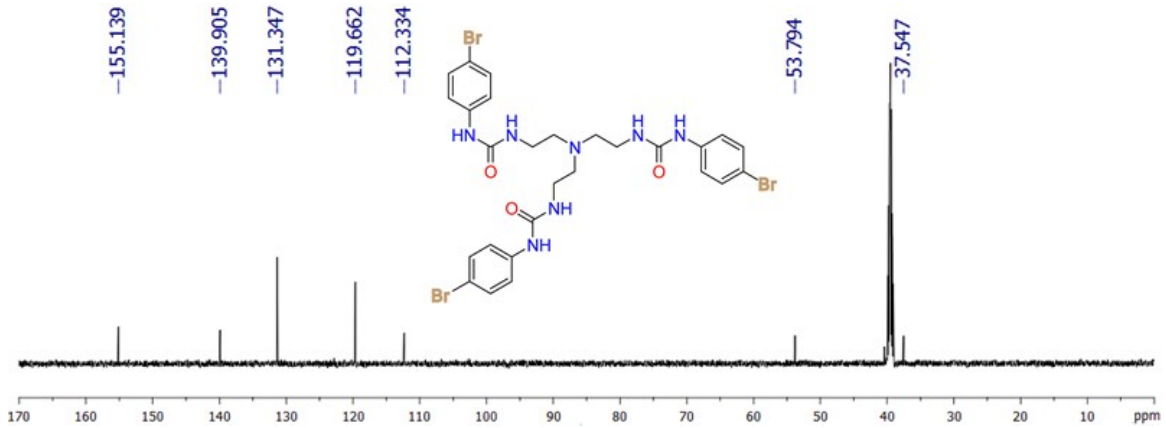


Figure S7: Integrated ^{13}C-NMR spectrum (full as well as expanded) free tripodal urea receptor $\mathbf{L_2}$ in DMSO-d_6 at 25ºC.

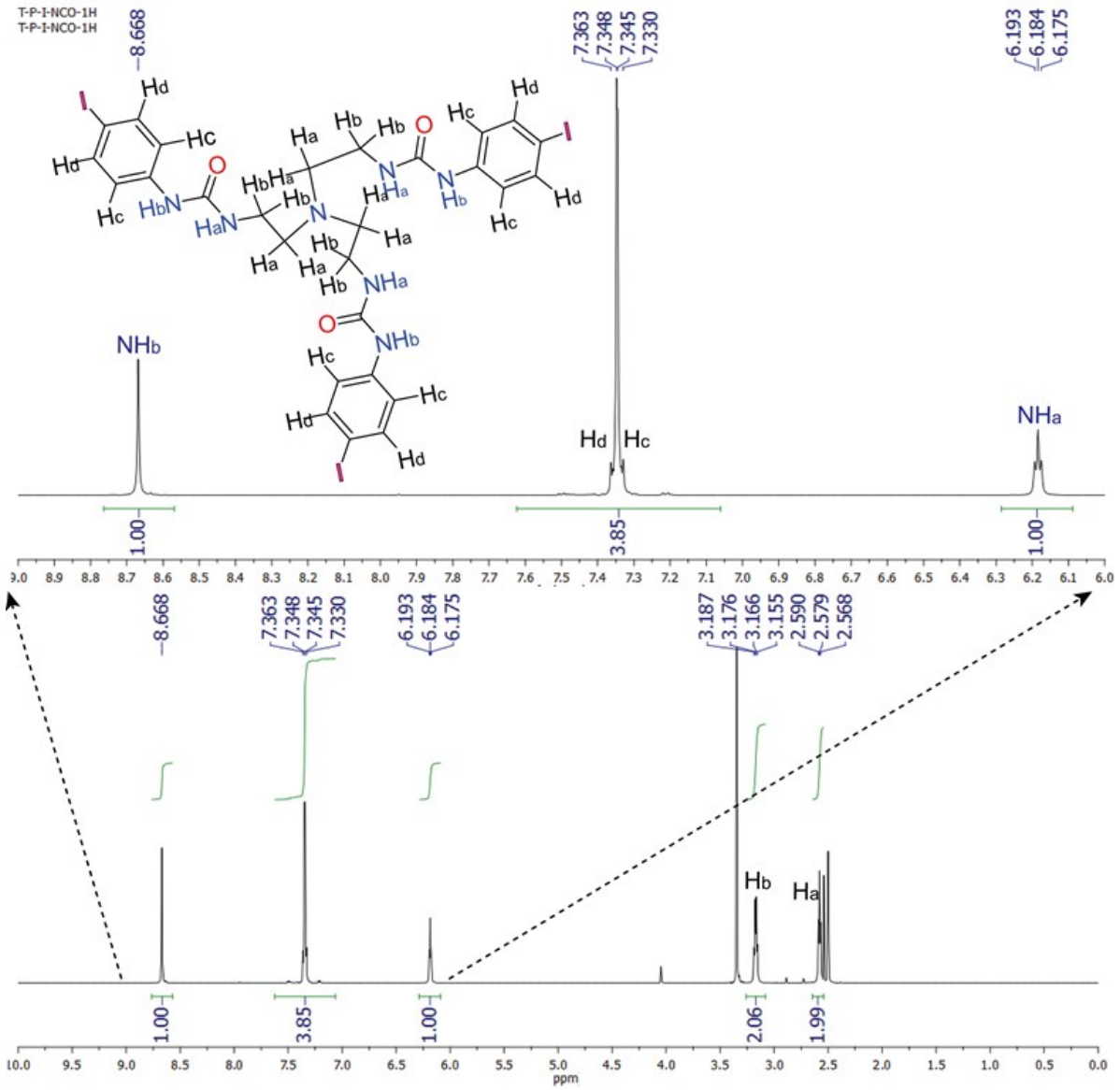


Figure S8: Integrated ^{1}H-NMR spectrum (full as well as expanded) and interpretation of all hydrogen atoms of free tripodal tris-urea receptor **L_3** in DMSO-d_6 at 25ºC.

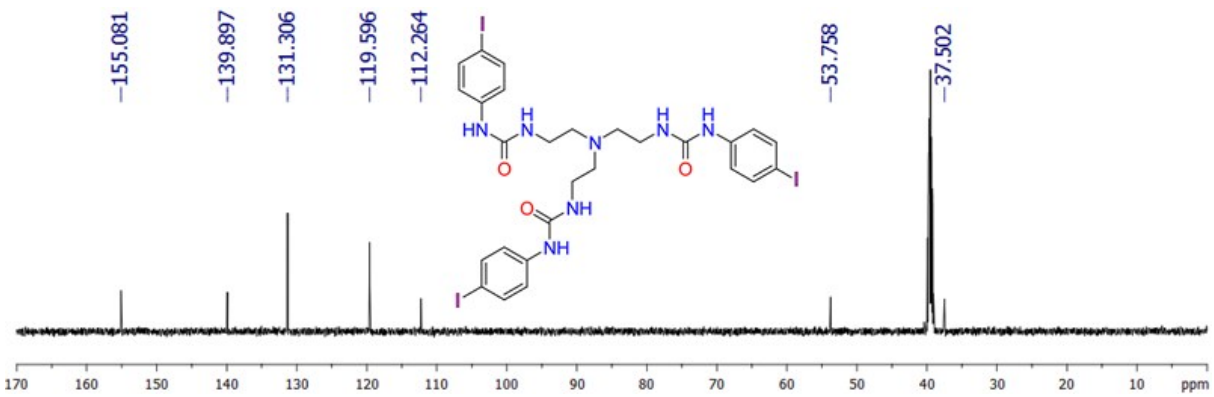


Figure S9: Integrated ^{13}C-NMR spectrum (full as well as expanded) free tripodal urea receptor **L_3** in DMSO-d_6 at 25ºC

Characterization of anion complexes of receptors:

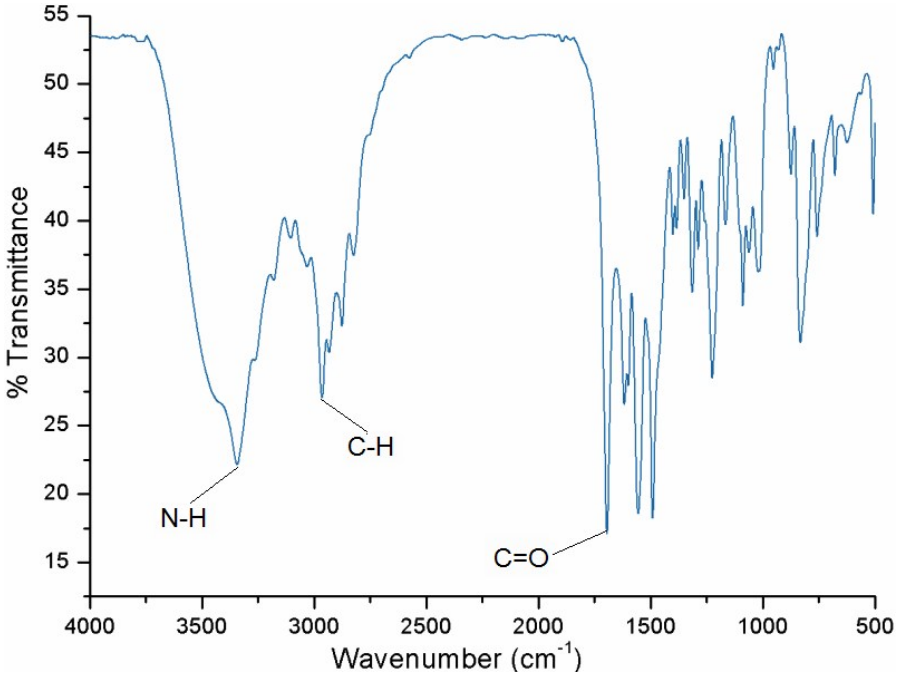


Figure S10: FT-IR spectrum of fluoride encapsulated complex **1a** of $\mathbf{L_1}$ recorded in KBr pellet.

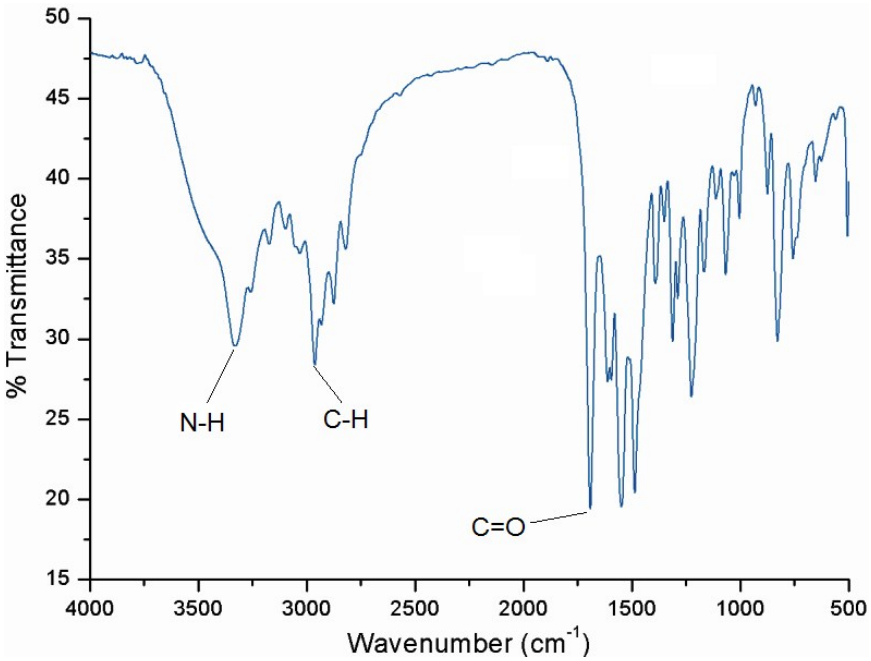


Figure S11: FT-IR spectrum of fluoride encapsulated complex **2a** of $\mathbf{L_2}$ recorded in KBr pellet.

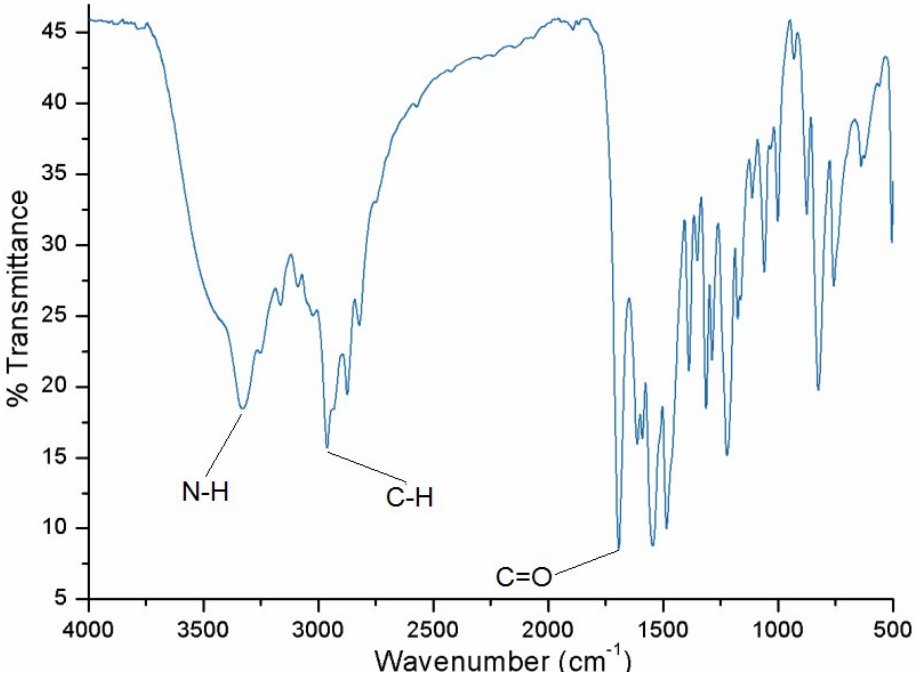


Figure S12: FT-IR spectrum of fluoride encapsulated complex **3a** of $\mathbf{L_3}$ recorded in KBr pellet.

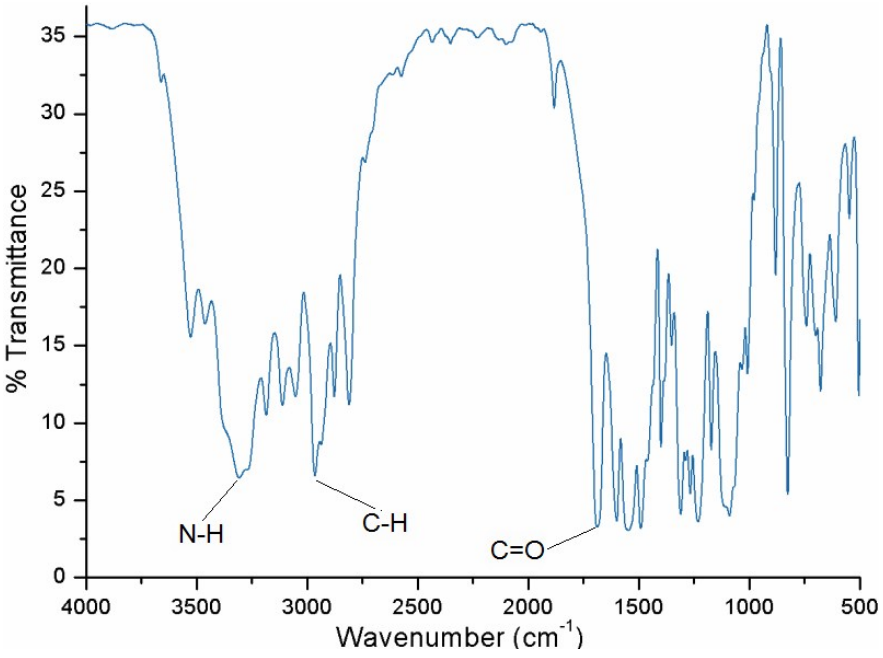


Figure S13: FT-IR spectrum of divalent sulphate encapsulated complex **1b** of $\mathbf{L_1}$ recorded in KBr pellet.

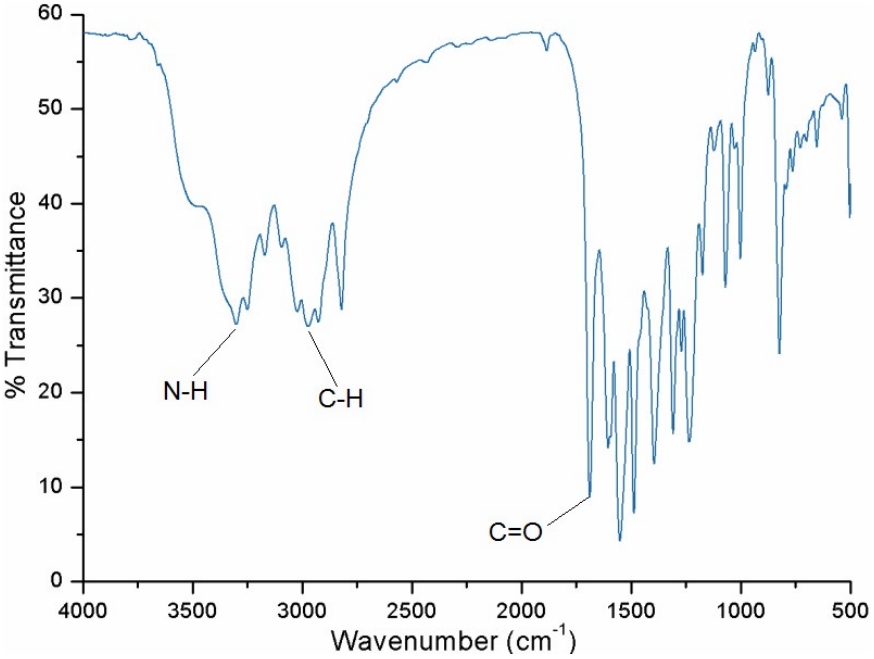


Figure S14: FT-IR spectrum of divalent carbonate encapsulated complex **2b** of $\mathbf{L_2}$ recorded in KBr pellet.

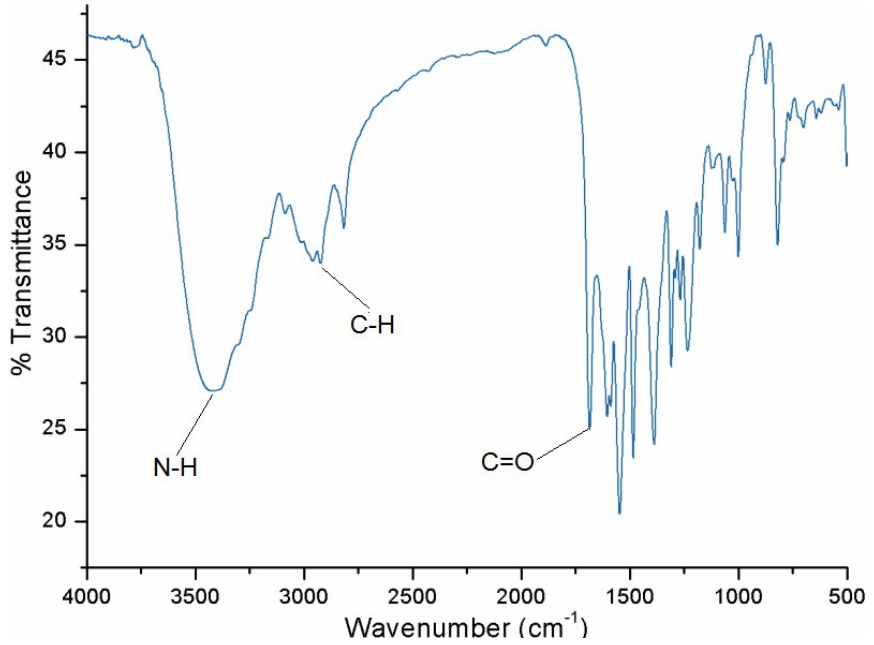


Figure S15: FT-IR spectrum of divalent carbonate encapsulated complex **3b** of $\mathbf{L_3}$ recorded in KBr pellet.

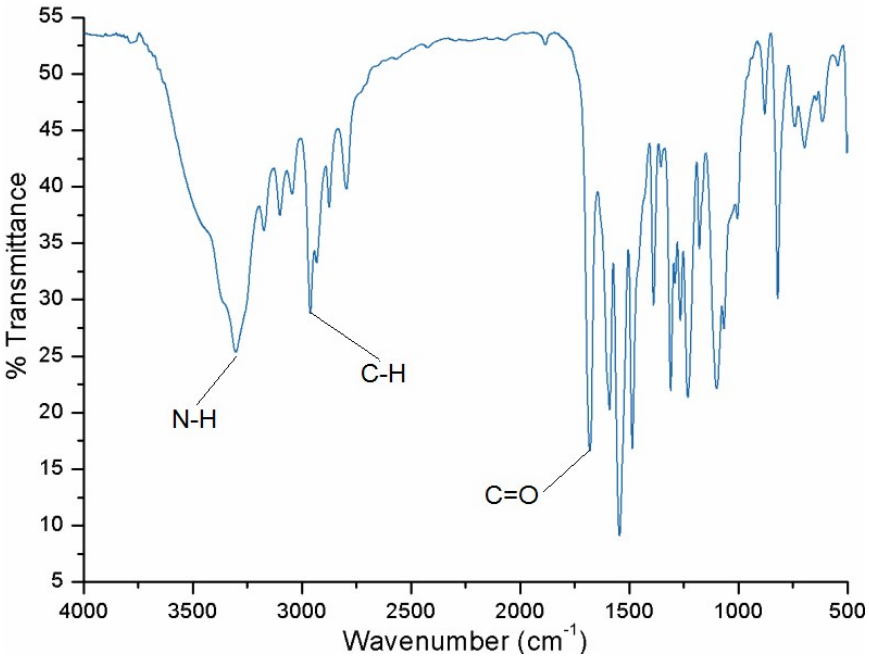


Figure S16: FT-IR spectrum of divalent sulphate encapsulated complex **3c** of $\mathbf{L_3}$ recorded in KBr pellet.

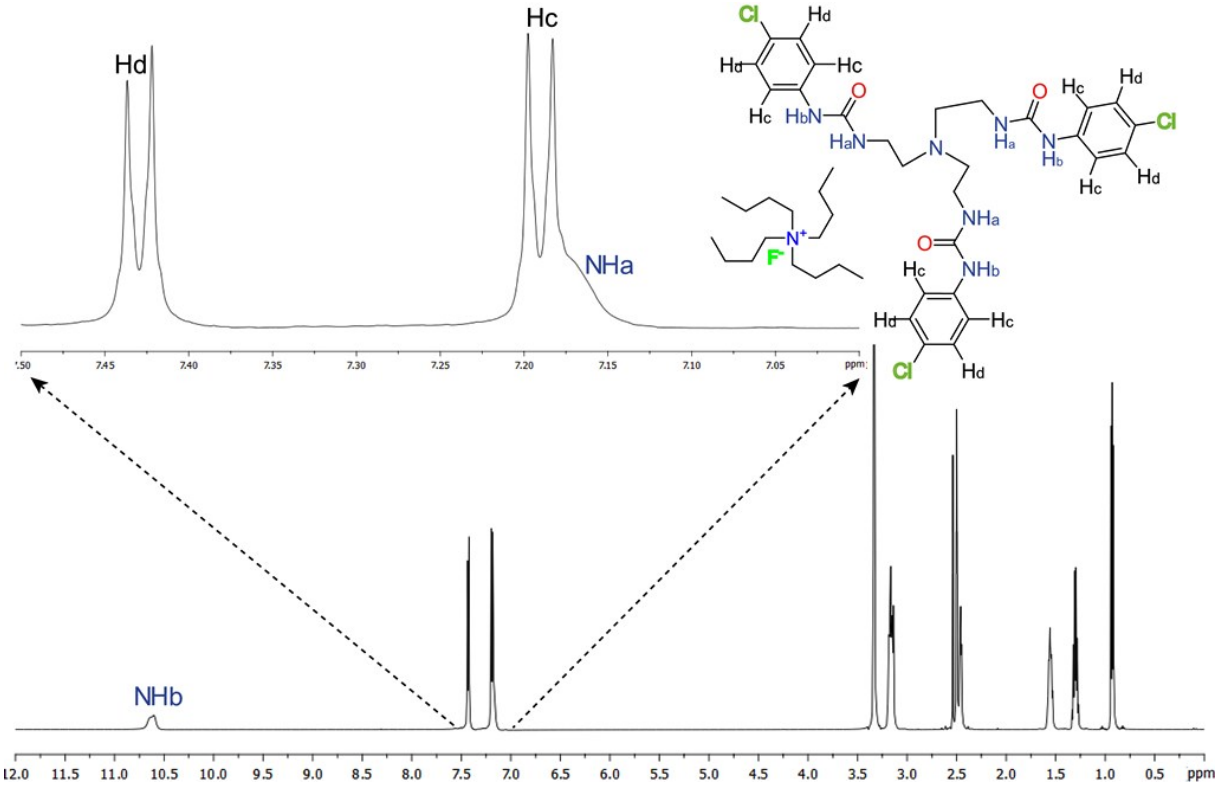


Figure S17: ^{1}H NMR full and expanded spectrum of fluoride complex **1a** as recorded in DMSO-d_6 at 298 K.

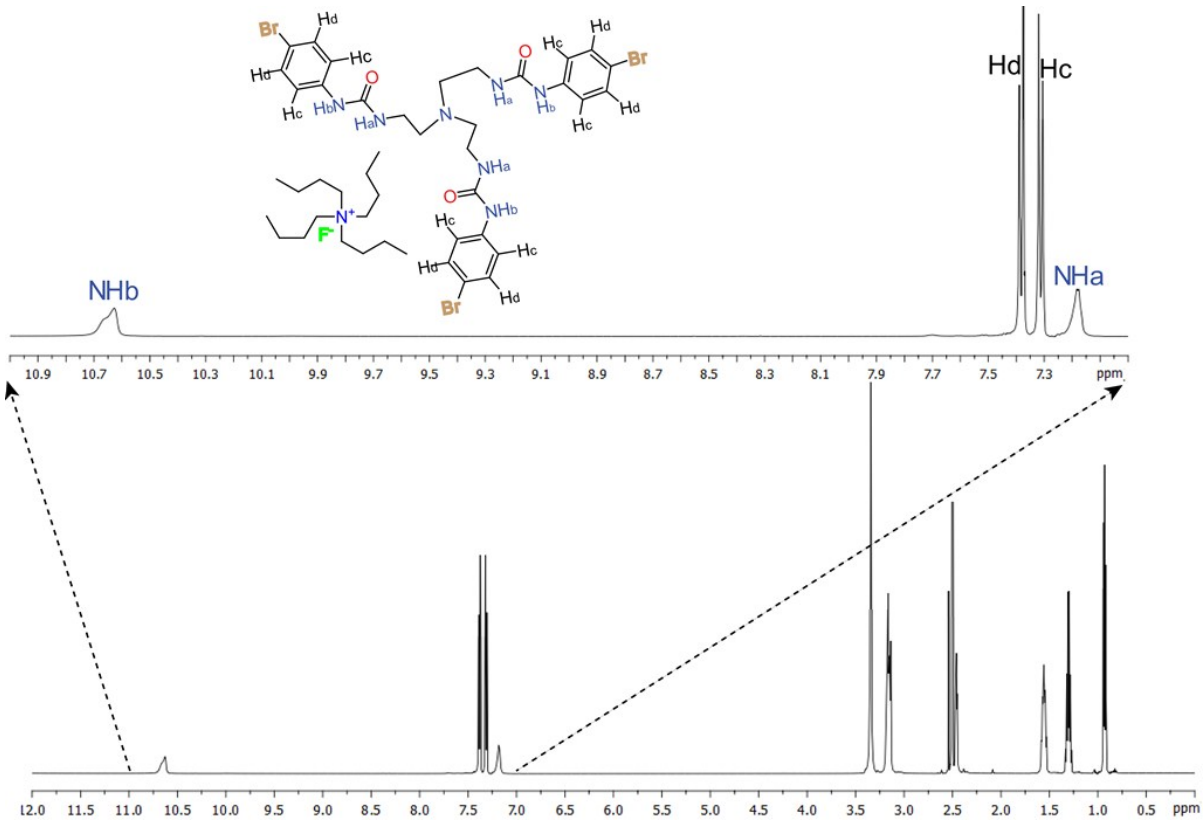


Figure S18: ^{1}H NMR full and expanded spectrum of fluoride complex **2a** as recorded in DMSO-d_6 at 298 K.

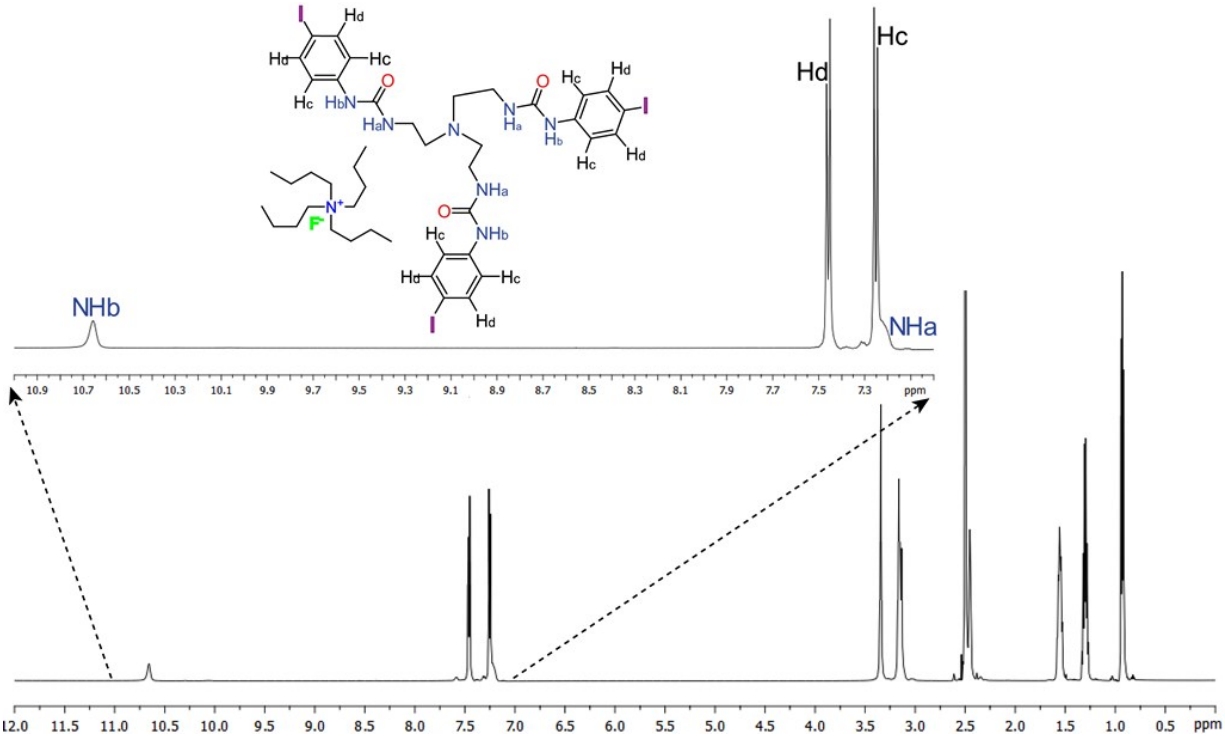


Figure S19: ^{1}H NMR full and expanded spectrum of fluoride complex **3a** as recorded in DMSO-d_6 at 298 K.

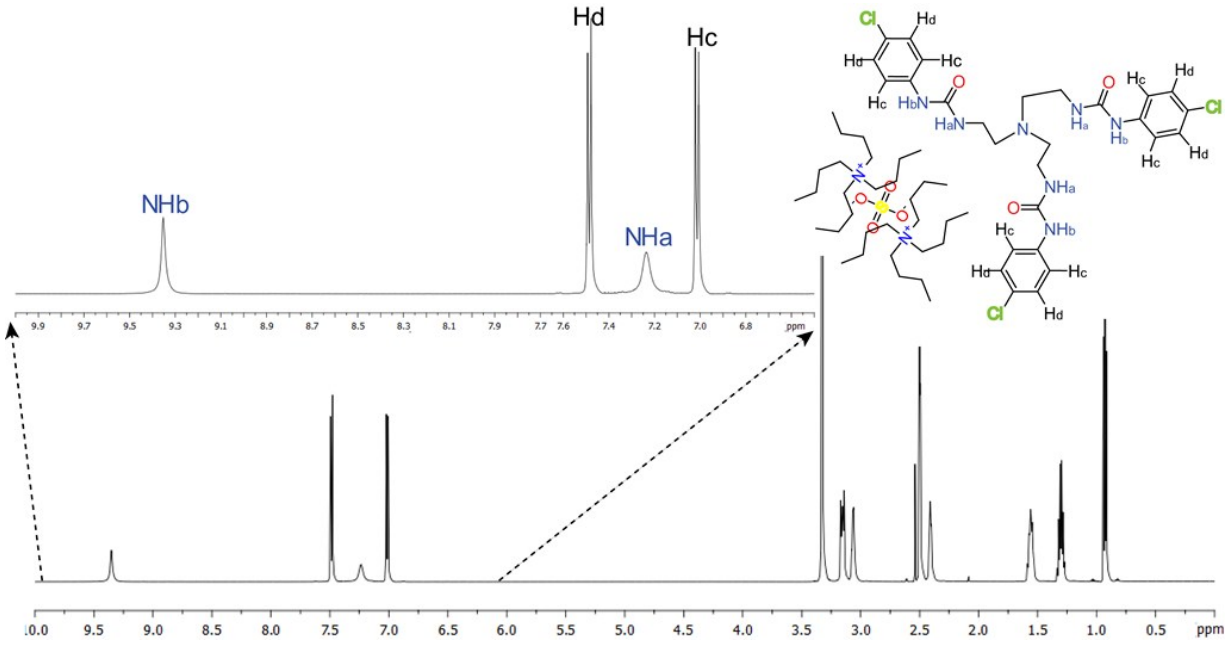


Figure S20: ^{1}H NMR full and expanded spectrum of sulphate complex **1b** as recorded in DMSO-d_6 at 298 K.

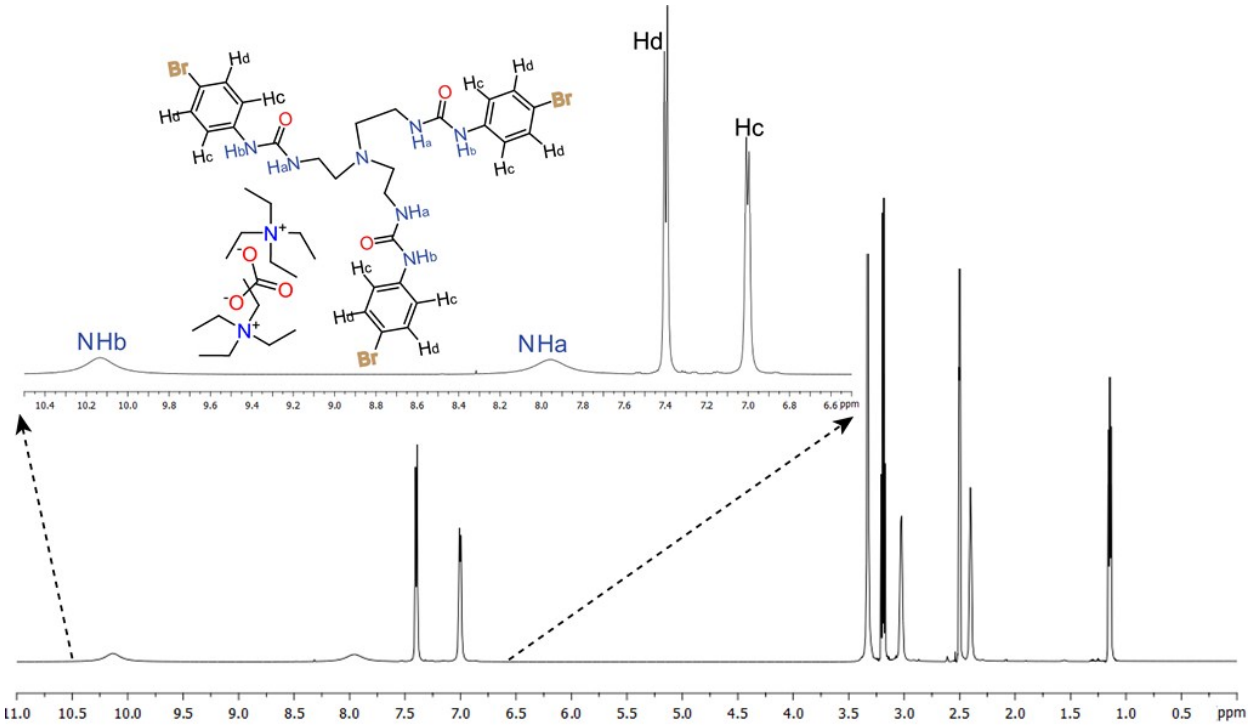


Figure S21: ^{1}H NMR full and expanded spectrum of carbonate complex **2b** as recorded in DMSO-d_6 at 298 K.

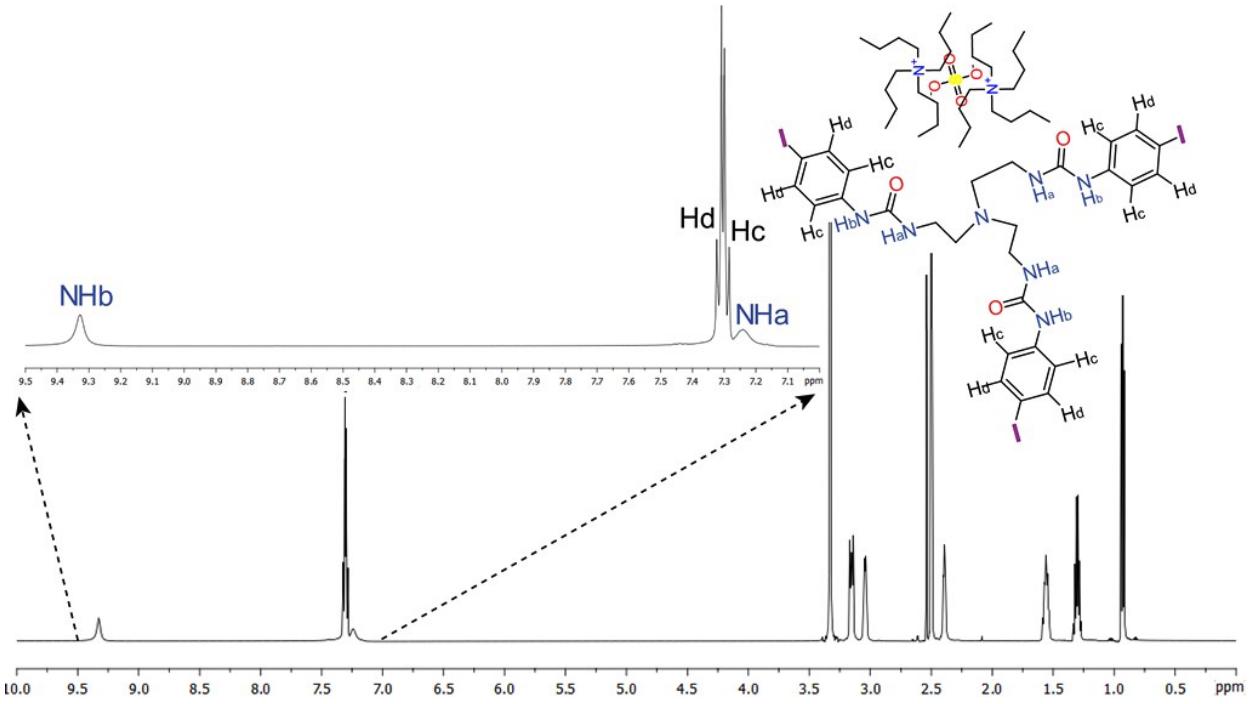


Figure S22: ^{1}H NMR full and expanded spectrum of fluoride complex **3c** as recorded in DMSO-d_6 at 298 K.

Solution state anion binding studies:

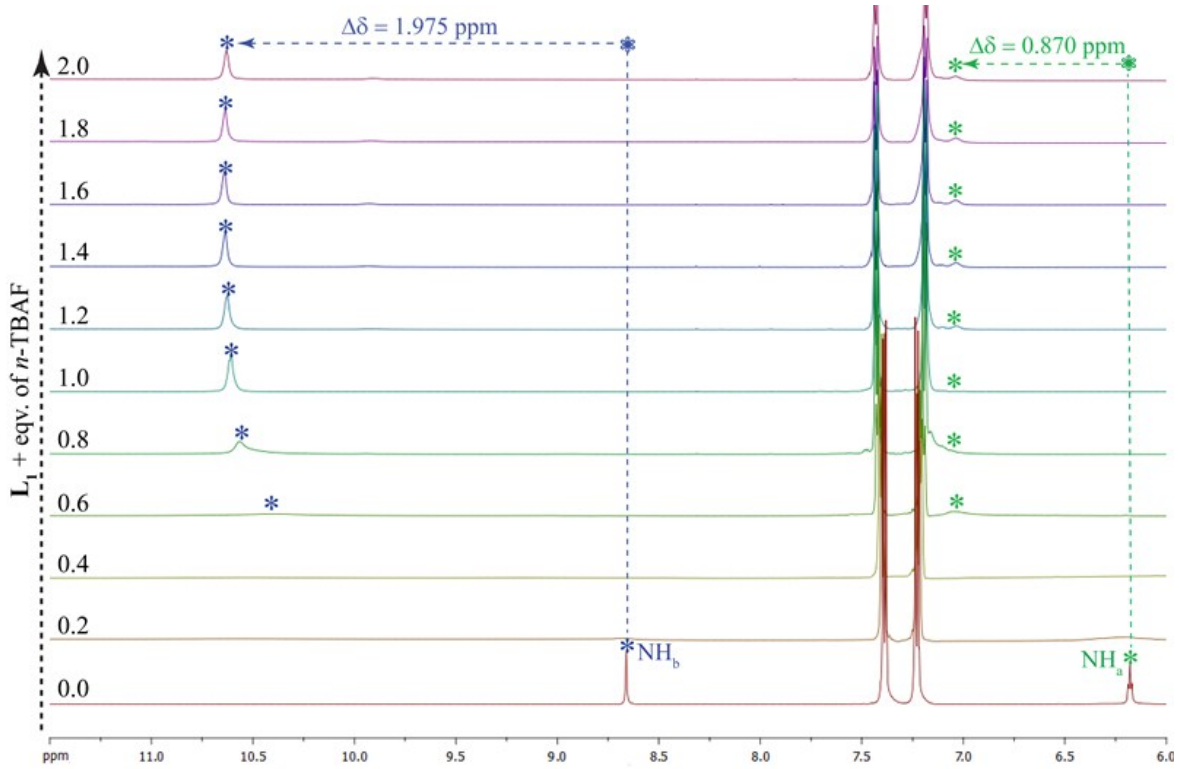


Figure S23: Expanded partial ^{1}H NMR stack plot of $\mathbf{L_1}$ upon titration with standard *n*-TBAF in DMSO-d_6.

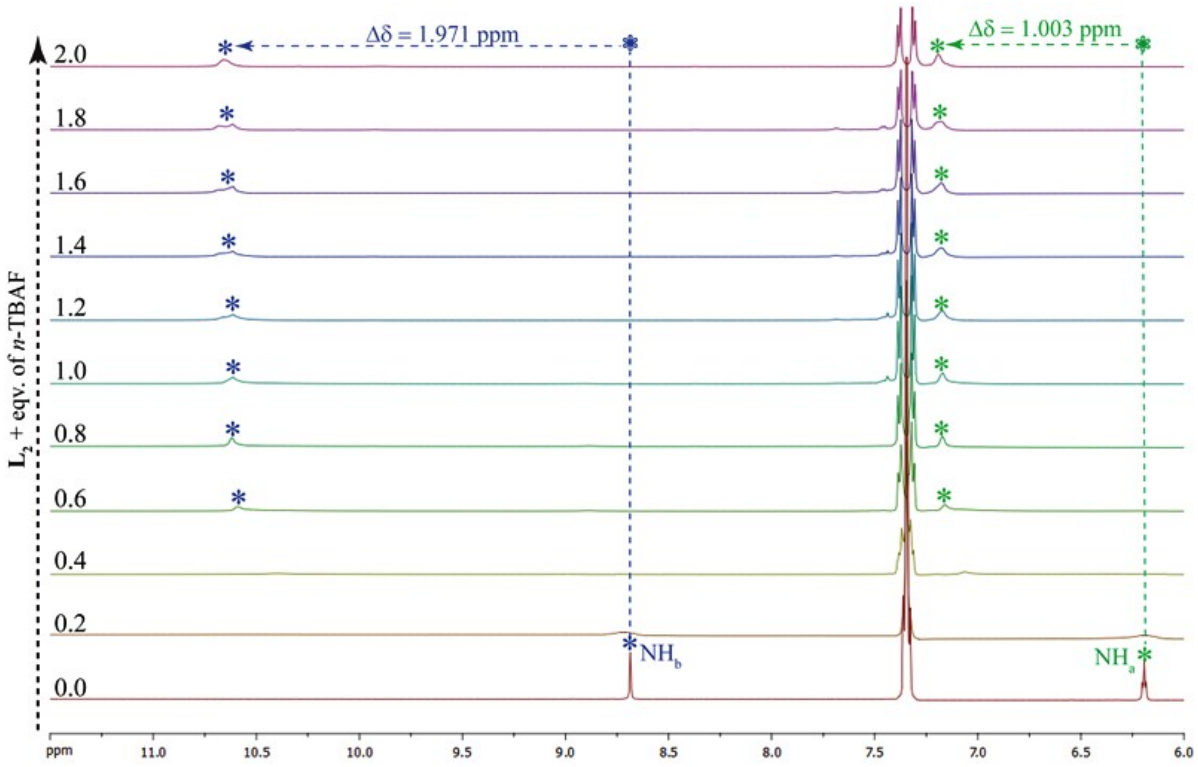


Figure S24: Expanded partial ^{1}H NMR stack plot of $\mathbf{L_2}$ upon titration with standard *n*-TBAF in DMSO-d_6.

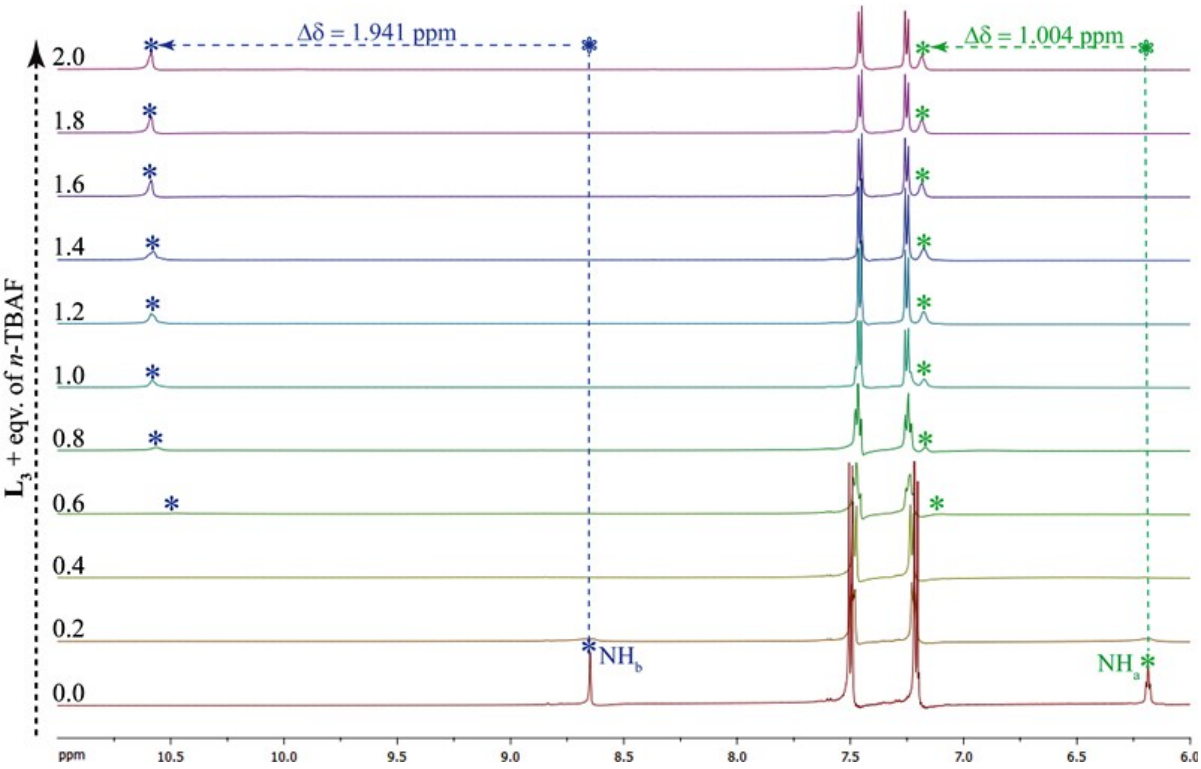


Figure S25: Expanded partial ^{1}H NMR stack plot of $\mathbf{L_3}$ upon titration with standard *n*-TBAF in DMSO-d_6.

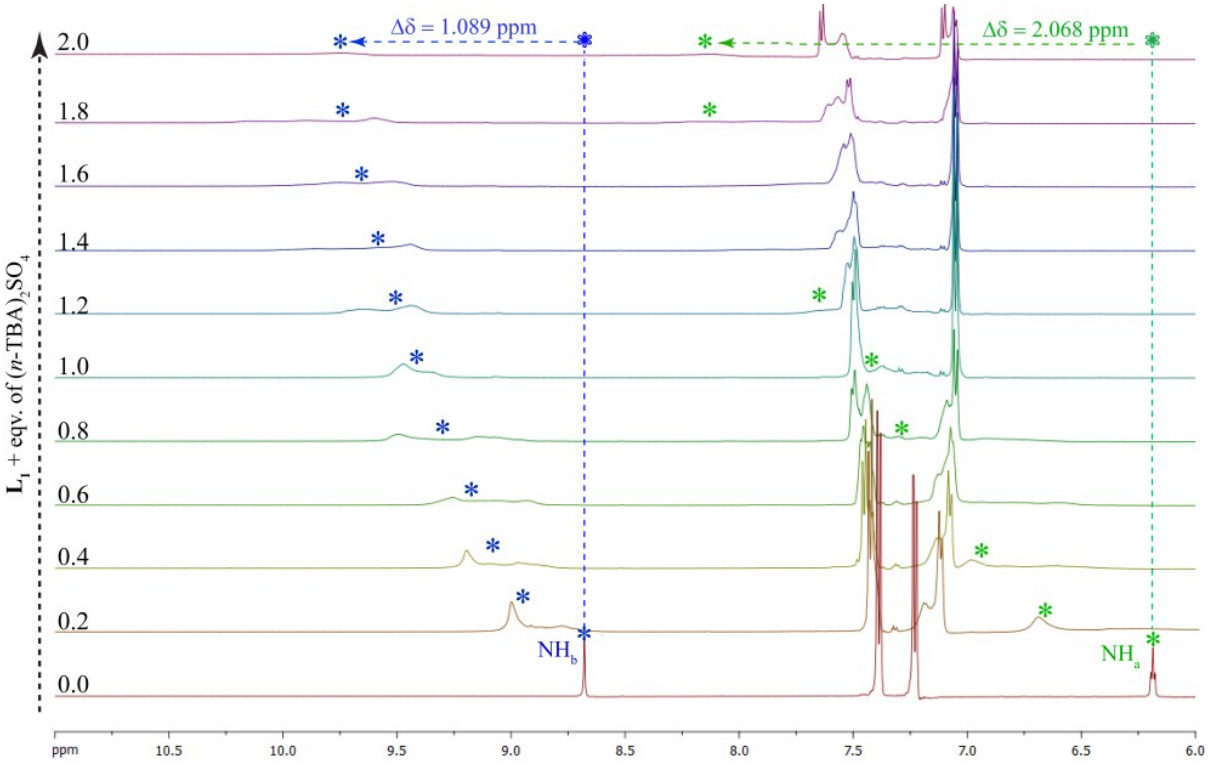


Figure S26: Expanded partial ^{1}H NMR stack plot of $\mathbf{L_1}$ upon titration with standard $(n\text{-TBA})_2SO_4$ in DMSO-d_6.

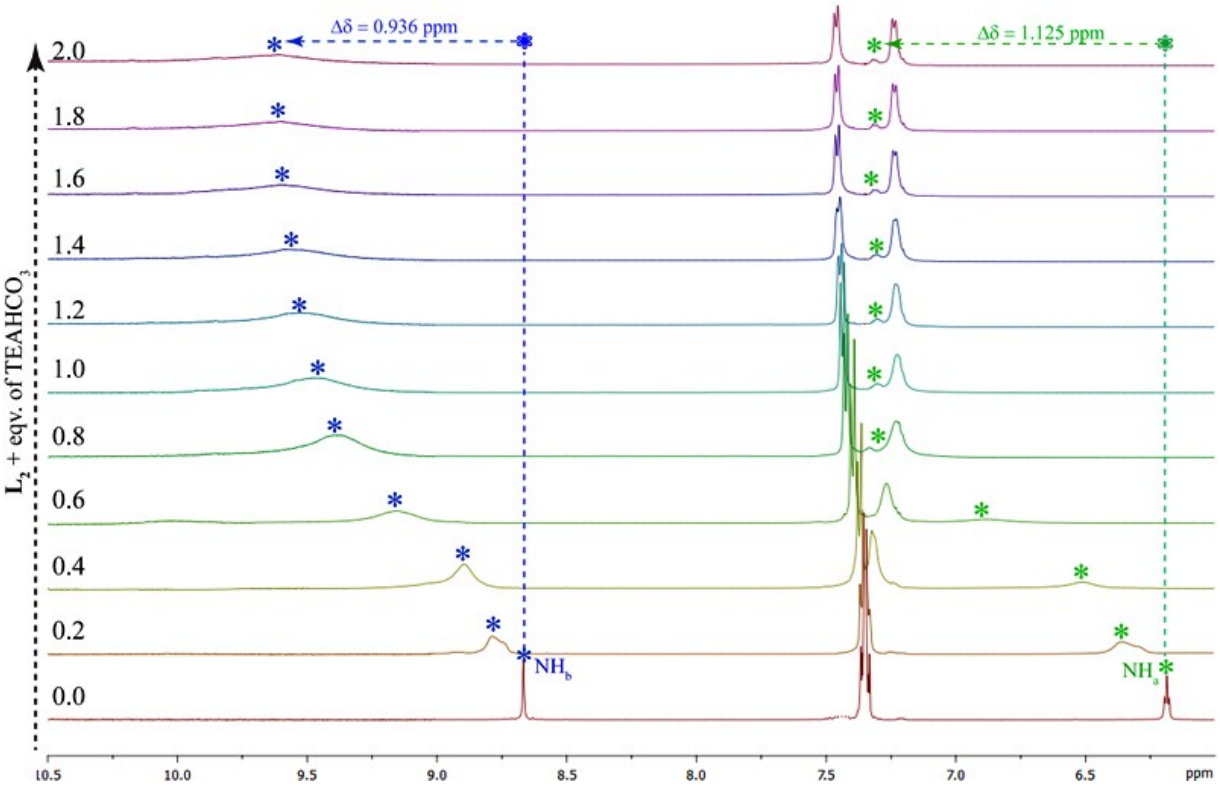


Figure S27: Expanded partial ^{1}H NMR stack plot of $\mathbf{L_2}$ upon titration with standard $TEAHCO_3$ in DMSO-d_6.

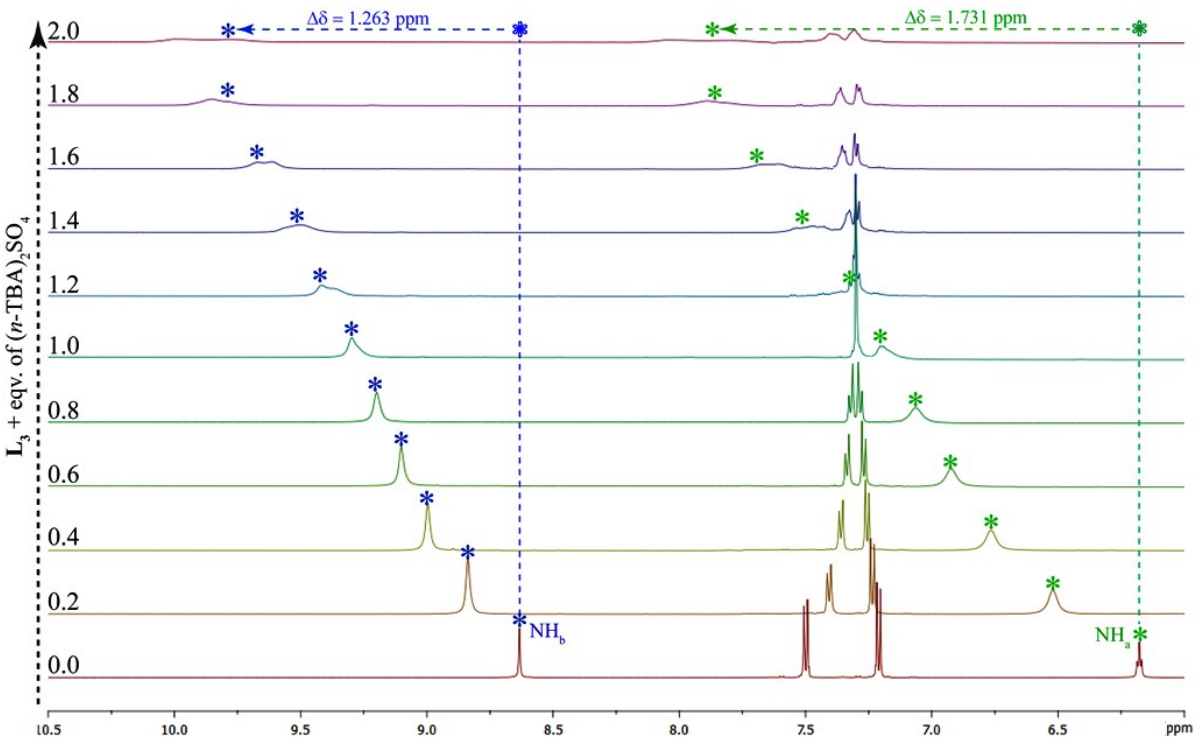


Figure S28: Expanded partial ^{1}H NMR stack plot of $\mathbf{L_3}$ upon titration with standard $(n\text{-TBA})_2SO_4$ in DMSO-d_6.

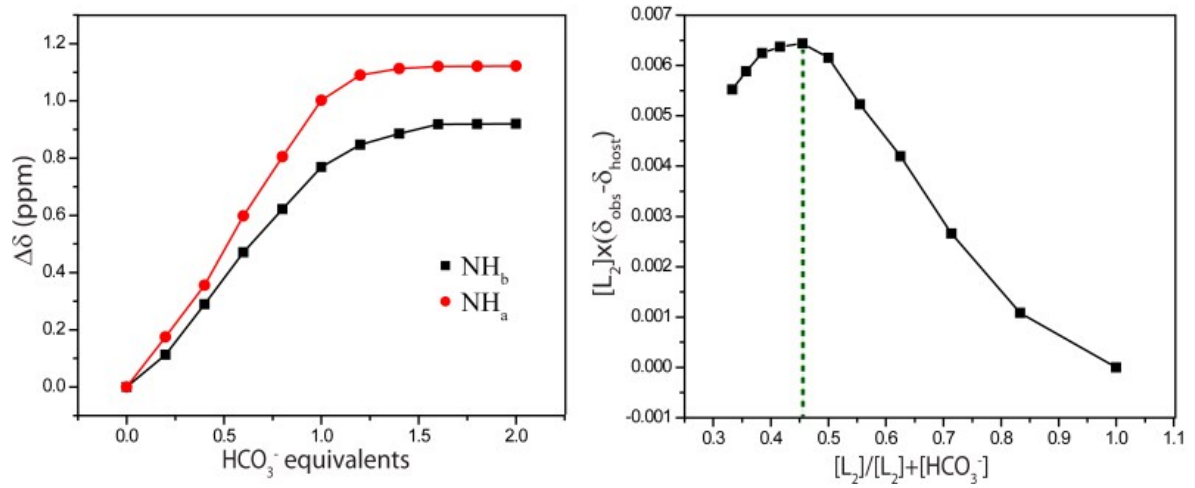


Figure S29: Change in chemical shift of –NH resonances of $\mathbf{L_2}$ (10 mM) with increasing concentration of standard HCO_3^- solution (50 mM) in DMSO-d_6 at 298 K and the corresponding Job's plot.

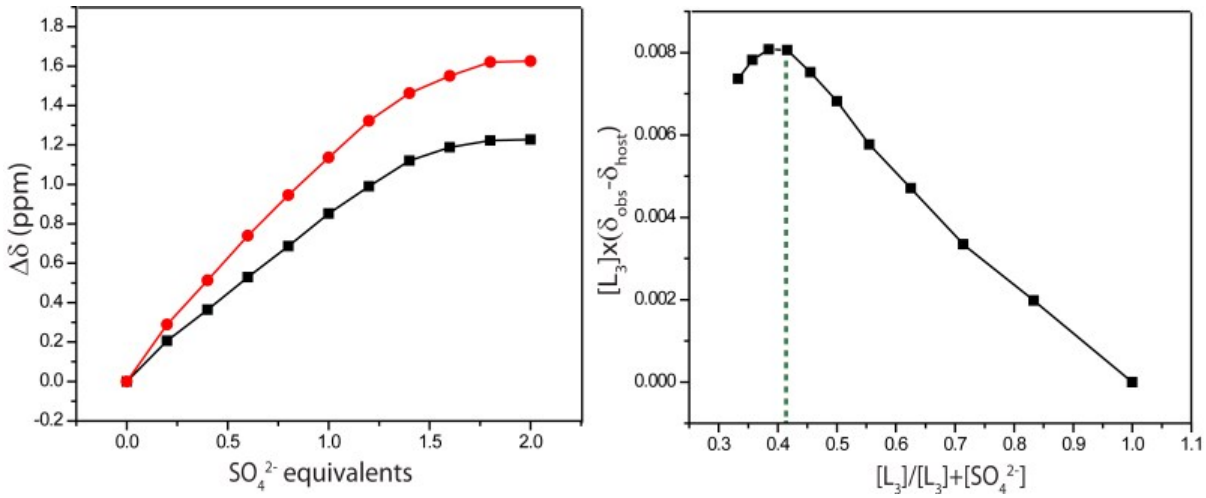
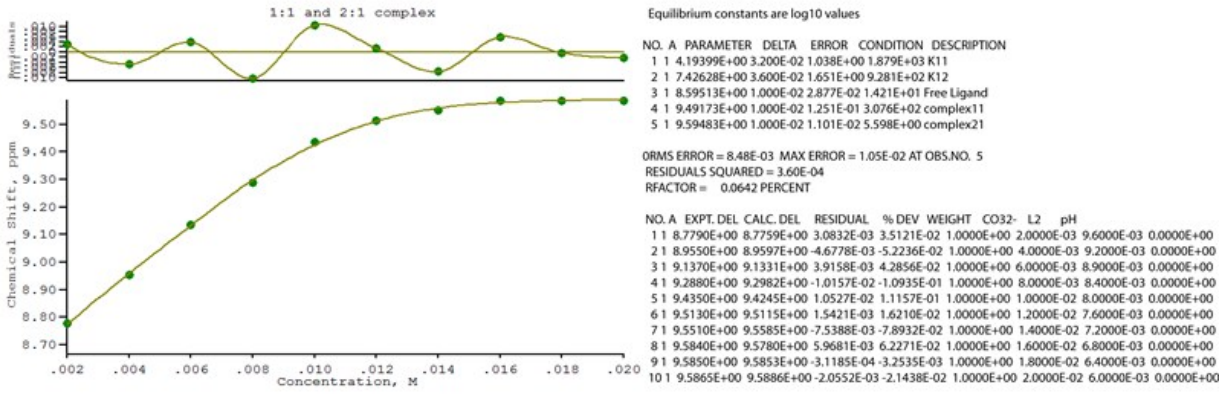


Figure S30: Change in chemical shift of –NH resonances of $\mathbf{L_3}$ (10 mM) with increasing concentration of standard SO_4^{2-} solution (50 mM) in DMSO-d_6 at 298 K and the corresponding Job's plot.



Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes
Program run at 00:45:21 on 06/13/2018

1:1 and 2:1 complex

Equilibrium constants are log10 values

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	4.19399E+00	3.200E-02	1.038E+00	1.879E+03	K11
2	1	7.42628E+00	3.600E-02	1.651E+00	9.281E+02	K12
3	1	8.59513E+00	1.000E-02	2.877E-02	1.421E+01	Free Ligand
4	1	9.49173E+00	1.000E-02	1.251E-01	3.076E+02	complex11
5	1	9.59483E+00	1.000E-02	1.101E-02	5.598E+00	complex21

0RMS ERROR = 8.48E-03 MAX ERROR = 1.05E-02 AT OBS.NO. 5
RESIDUALS SQUARED = 3.60E-04
RFACTOR = 0.0642 PERCENT

NO.	A	EXPT. DEL	CALC. DEL	RESIDUAL	% DEV	WEIGHT	CO32-	L2	pH
1	1	8.7790E+00	8.7759E+00	3.0832E-03	3.5121E-02	1.0000E+00	2.0000E-03	9.6000E-03	0.0000E+00
2	1	8.9550E+00	8.9597E+00	-4.6778E-03	-5.2236E-02	1.0000E+00	4.0000E-03	9.2000E-03	0.0000E+00
3	1	9.1370E+00	9.1331E+00	3.9158E-03	4.2856E-02	1.0000E+00	6.0000E-03	8.9000E-03	0.0000E+00
4	1	9.2880E+00	9.2982E+00	-1.0157E-02	-1.0935E-01	1.0000E+00	8.0000E-03	8.4000E-03	0.0000E+00
5	1	9.4350E+00	9.4245E+00	1.0527E-02	1.1157E-01	1.0000E+00	1.0000E-02	8.0000E-03	0.0000E+00
6	1	9.5130E+00	9.5115E+00	1.5421E-03	1.6210E-02	1.0000E+00	1.2000E-02	7.6000E-03	0.0000E+00
7	1	9.5510E+00	9.5585E+00	-7.5388E-03	-7.8932E-02	1.0000E+00	1.4000E-02	7.2000E-03	0.0000E+00
8	1	9.5840E+00	9.5780E+00	5.9681E-03	6.2271E-02	1.0000E+00	1.6000E-02	6.8000E-03	0.0000E+00
9	1	9.5850E+00	9.5853E+00	-3.1185E-04	-3.2535E-03	1.0000E+00	1.8000E-02	6.4000E-03	0.0000E+00
10	1	9.5865E+00	9.5886E+00	-2.0552E-03	-2.1438E-02	1.0000E+00	2.0000E-02	6.0000E-03	0.0000E+00

TOLERANCE ON SUM OF SQUARES 0.0100
TOLERANCE ON EIGEN VALUES 0.0001
CONVERGANCE AFTER 26 ITERATIONS

Figure S31: Change in chemical shift of urea resonances of $\mathbf{L_2}$ (10 mM) with increasing concentration of standard HCO_3^- solution (50 mM) in DMSO-d_6 (left) and the output file from WINEQNMR programme of $\mathbf{L_2}$-HCO_3^- titrations (right).

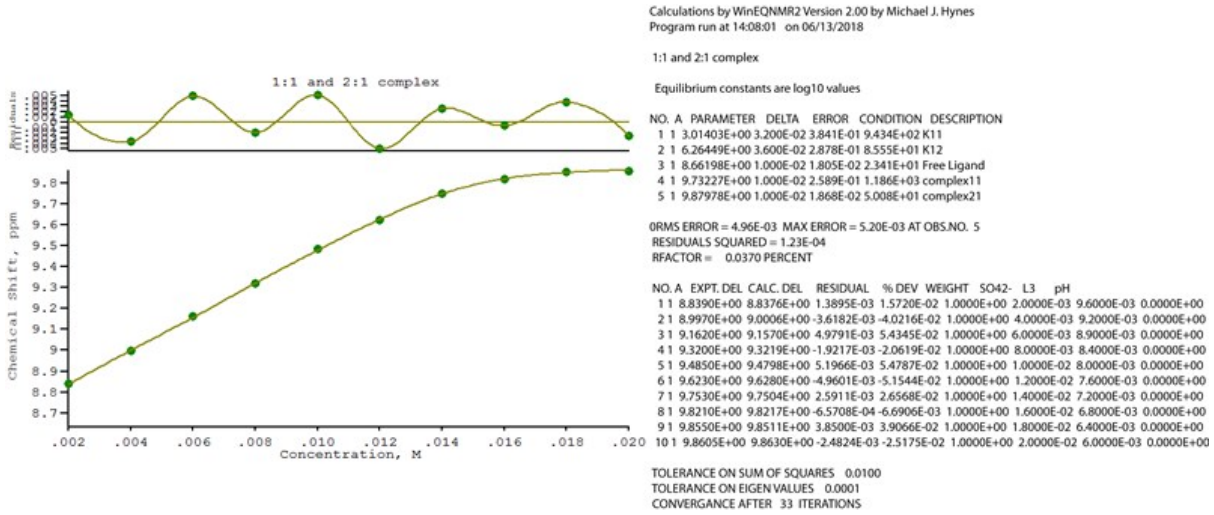


Figure S32: Change in chemical shift of urea resonances of $\mathbf{L_3}$ (10 mM) with increasing concentration of standard SO_4^{2-} solution (50 mM) in DMSO-d_6 (left) and the output file from WINEQNMR programme of $\mathbf{L_3}$-SO_4^{2-} titrations (right).

Table S1. Hydrogen bonding distances (Å) and Bond angles (°) in the anion complexes of **L**:

Complex	D–H···A	*d*(D···H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	<D–H···A/°	Symmetry codes
$\mathbf{L_1}$	N2-H2N···O2	0.86	2.15	2.950(3)	156	x,y,z
	N3-H3N···O2	0.86	2.13	2.931(3)	155	x,y,z
	N4-H4N···O3	0.86	2.04	2.876(3)	162	1-x,-y,1-z
	N5-H5N···O3	0.86	2.34	3.102(3)	149	1-x,-y,1-z
	N6-H6N···O1	0.86	2.25	2.997(3)	145	-x,1-y,1-z
	N7-H7N···O1	0.86	2.05	2.878(3)	155	-x,1-y,1-z
$\mathbf{L_2}$	N2-H1N···O2	0.86	2.04	2.872(7)	163	-x,1-y,2-z
	N3-H2N···O2	0.86	2.35	3.111(8)	148	-x,1-y,2-z
	N4-H3N···O3	0.86	2.29	3.039(9)	146	1-x,-y,2-z
	N5-H4N···O3	0.86	2.02	2.838(7)	159	1-x,-y,2-z
	N6-H5N···O1	0.86	2.14	2.946(8)	155	x,y,z
	N7-H6N···O1	0.86	2.12	2.923(9)	155	x,y,z
$\mathbf{L_3}$	N2-H2N···O2	0.86	2.14	2.944(9)	156	x,y,z
	N3-H3N···O2	0.86	2.16	2.960(9)	154	x,y,z
	N4-H4N···O3	0.86	2.08	2.901(8)	160	1-x,-y,1-z
	N5-H5N···O3	0.86	2.30	3.083(8)	151	1-x,-y,1-z
	N6-H6N···O1	0.86	2.44	3.164(9)	143	-x,1-y,1-z
	N7-H7N···O1	0.86	2.01	2.843(8)	164	-x,1-y,1-z
1a	N2-H2N···F1	0.86	2.17	2.928(4)	147	x,y,z
	N3-H3N···F1	0.86	1.93	2.740(3)	156	x,y,z
	N4-H4N···F1	0.86	2.09	2.880(4)	152	x,y,z

	N5-H5N···F1	0.86	1.95	2.779(4)	161	x,y,z
	N6-H6N···F1	0.86	2.26	2.998(4)	143	x,y,z
	N7-H7N···F1	0.86	1.88	2.719(4)	167	x,y,z
	C8-H8···F1	0.93	2.41	3.329(5)	168	x,1+y,z
	C19-H19A···O1	0.97	2.42	3.322(5)	154	x,-1+y,z
1b	N2-H2N···O10	0.86	2.38	3.144(6)	149	x,y,z
	N3-H3N··· O10	0.86	2.13	2.965(6)	165	x,y,z
	N4-H4N···O9	0.86	2.28	3.053(5)	149	x,y,z
	N5-H5N···O9	0.86	2.01	2.834(5)	160	x,y,z
	N6-H6N···O7	0.86	2.19	2.985(5)	155	x,y,z
	N7-H7N···O7	0.86	2.19	3.000(6)	157	x,y,z
	N9-H9N···O8	0.86	2.09	2.887(5)	154	x,y,z
	N10-H10N···O9	0.86	2.10	2.939(5)	165	x,y,z
	N11-H11N···O8	0.86	2.23	2.909(6)	136	x,y,z
	N12-H12N···O10	0.86	2.30	3.142(6)	168	x,y,z
	N13-H13N···O8	0.86	2.13	2.926(6)	155	x,y,z
	N14-H14N···O7	0.86	2.07	2.911(5)	164	x,y,z
	C32-H32···O9	0.93	2.48	3.266(7)	142	x,y,z
	C55-H55B···O2	0.97	2.46	3.352(6)	152	1+x,y,z
	C56-H56A···O6	0.97	2.48	3.450(7)	155	x,y,z
	C64-H64A···O2	0.97	2.53	3.494(6)	175	1+x,y,z
	C83-H83A···O3	0.97	2.35	3.258(6)	156	-1/2+x,1/2-y,-1/2+z
	C83-H83B···O1	0.97	2.36	3.326(6)	173	1/2-x,-1/2+y,1/2-z
2a	N2-H2N···F1	0.86	2.19	2.935(7)	145	x,y,z
	N3-H3N···F1	0.86	1.92	2.751(6)	163	x,y,z
	N4-H4N···F1	0.86	2.09	2.883(6)	152	x,y,z
	N5-H5N···F1	0.86	2.03	2.837(6)	155	x,y,z
	N6-H6N···F1	0.86	2.28	3.005(7)	143	x,y,z
	N7-H7N···F1	0.86	1.92	2.761(6)	166	x,y,z
	C8-H8···F1	0.93	2.40	3.315(8)	167	1+x,y,z
	C19-H19B···O1	0.97	2.50	3.423(8)	160	-1+x,y,z
2b	N2-H2N···O5	0.86	2.49	3.347(14)	177	1-x,y,1/2-z
	N3-H3N··· O4	0.86	1.98	2.801(17)	159	x,y,z
	N4-H4N··· O5	0.86	2.30	3.157(14)	178	x,y,z
	N5-H5N··· O5	0.86	2.01	2.804(14)	153	1-x,y,1/2-z
	N6-H6N··· O4	0.86	2.40	3.253(11)	172	x,y,z
	N7-H7N··· O5	0.86	2.03	2.844(13)	159	x,y,z
	C34-H34B···O3	0.97	2.50	3.390(2)	153	x,y,z
3a	N2-H2N···F1	0.86	2.08	2.867(9)	152	x,y,z
	N3-H3N···F1	0.86	1.96	2.779(9)	159	x,y,z
	N4-H4N···F1	0.86	2.25	2.988(9)	145	x,y,z
	N5-H5N···F1	0.86	1.90	2.725(8)	162	x,y,z

	N6-H6N···F1	0.86	2.20	2.952(10)	147	x,y,z
	N7-H7N···F1	0.86	1.92	2.738(9)	159	x,y,z
	N9-H9N···F2	0.86	2.05	2.849(8)	155	x,y,z
	N10-H10N···F2	0.86	2.05	2.854(10)	156	x,y,z
	N11-H11N···F2	0.86	2.20	2.942(9)	144	x,y,z
	N12-H12N···F2	0.86	1.99	2.756(8)	148	x,y,z
	N13-H13N···F2	0.86	2.22	2.984(9)	149	x,y,z
	N14-H14N···F2	0.86	1.93	2.762(8)	161	x,y,z
	C10-H10B···O3	0.97	2.46	3.318(12)	147	-1+x,y,z
	C24-H24···F1	0.93	2.51	3.435(12)	170	1+x,y,z
	C44-H44···F2	0.93	2.48	3.404(11)	172	-1+x,y,z
	C46-H46B···F2	0.97	2.47	3.333(10)	149	1+x,y,z
	C53-H53···O2	0.93	2.52	3.381(13)	155	1-x,1-y,-z
	C63-H63A···O4	0.97	2.53	3.478(13)	165	-1+x,y,z
	C63-H63B···O1	0.97	2.50	3.425(12)	160	-x,1-y,1-z
3b	N2-H2N···O4	0.86	2.45	3.301(5)	170	x,y,z
	N3-H3N···O5	0.86	2.06	2.869(8)	156	x,y,z
	N4-H4N···O5	0.86	2.27	3.125(9)	177	x,y,z
	N5-H5N···O5	0.86	2.01	2.791(9)	150	-x,y,1/2-z
	N6-H6N···O5	0.86	2.60	3.455(9)	174	x,y,z
	N7-H7N···O4	0.86	1.99	2.810(8)	159	x,y,z
3c	N2-H2N···O17B	0.86	2.27	3.050(3)	151	1-x,1/2+y,1-z
	N2-H2N···O19A	0.86	2.11	2.920(18)	157	1-x,1/2+y,1-z
	N3-H3N···O19A	0.86	2.23	3.019(17)	153	1-x,1/2+y,1-z
	N3-H3N···O20B	0.86	2.03	2.807(3)	165	1-x,1/2+y,1-z
	N4-H4N···O17B	0.86	2.35	3.120(3)	149	1-x,1/2+y,1-z
	N4-H4N···O18A	0.86	2.21	2.990(2)	151	1-x,1/2+y,1-z
	N5-H5N···O18A	0.86	2.12	2.933(19)	159	1-x,1/2+y,1-z
	N5-H5N···O19B	0.86	2.21	3.040(2)	162	1-x,1/2+y,1-z
	N6-H6N···O17B	0.86	2.25	3.000(3)	147	1-x,1/2+y,1-z
	N6-H6N···O20A	0.86	2.19	3.000(2)	157	1-x,1/2+y,1-z
	N7-H7N···O18B	0.86	2.06	2.890(3)	161	1-x,1/2+y,1-z
	N7-H7N···O20A	0.86	2.21	3.031(19)	159	1-x,1/2+y,1-z
	N9-H9N···O13B	0.86	2.43	3.190(3)	148	1-x,-1/2+y,-z
	N9-H9N···O14A	0.86	2.16	2.877(17)	141	1-x,-1/2+y,-z
	N10-H10N···O13B	0.86	2.07	2.920(2)	169	1-x,-1/2+y,-z
	N10-H10N···O15A	0.86	2.29	3.112(19)	159	1-x,-1/2+y,-z
	N11-H11N···O14A	0.86	2.11	2.932(16)	158	1-x,-1/2+y,-z
	N11-H11N···O15B	0.86	2.20	2.940(3)	144	1-x,-1/2+y,-z
	N12-H12N···O15B	0.86	2.00	2.810(4)	156	1-x,-1/2+y,-z
	N12-H12N···O16A	0.86	2.14	2.988(17)	170	1-x,-1/2+y,-z
	N13-H13N···O14A	0.86	2.18	2.940(18)	147	1-x,-1/2+y,-z
	N13-H13N···O16B	0.86	2.10	2.910(3)	156	1-x,-1/2+y,-z
	N14-H14N···O13A	0.86	2.18	3.018(17)	166	1-x,-1/2+y,-z

N14-H14N···O16B	0.86	2.15	2.960(3)	156	1-x,-1/2+y,-z
N16-H16N···O17A	0.86	2.17	2.899(18)	143	x,y,z
N16-H16N···O19B	0.86	2.28	3.070(2)	152	x,y,z
N17-H17N···O18A	0.86	2.27	3.068(19)	155	x,y,z
N17-H17N···O19B	0.86	2.07	2.910(3)	164	x,y,z
N18-H18N···O17A	0.86	2.21	3.010(18)	154	x,y,z
N18-H18N···O20B	0.86	2.00	2.810(2)	155	x,y,z
N19-H19N···O19A	0.86	2.06	2.901(16)	166	x,y,z
N19-H19N···O20B	0.86	2.26	3.010(2)	145	x,y,z
N20-H20N···O17A	0.86	2.22	2.948(18)	142	x,y,z
N20-H20N···O18B	0.86	2.13	2.920(3)	152	x,y,z
N21-H21N···O18B	0.86	2.13	2.930(3)	155	x,y,z
N21-H21N···O20A	0.86	2.33	3.064(17)	162	x,y,z
N23-H23N···O14B	0.86	2.35	3.110(3)	147	x,y,z
N23-H23N···O16A	0.86	2.14	2.935(17)	153	x,y,z
N24-H24N···O15B	0.86	2.04	2.900(3)	176	x,y,z
N24-H24N···O16A	0.86	2.24	3.040(17)	155	x,y,z
N25-H25N···O13A	0.86	2.23	3.011(18)	150	x,y,z
N25-H25N···O14B	0.86	2.18	2.960(4)	149	x,y,z
N26-H26N···O13A	0.86	2.04	2.868(17)	160	x,y,z
N26-H26N···O16B	0.86	2.31	3.130(3)	161	x,y,z
N27-H27N···O14B	0.86	2.38	3.130(4)	146	x,y,z
N27-H27N···O15A	0.86	2.23	3.053(19)	159	x,y,z
N28-H28N···O13B	0.86	2.01	2.870(3)	174	x,y,z
N28-H28N···O15A	0.86	2.31	3.120(2)	156	x,y,z
C129-H12A···O3	0.97	2.46	3.410(2)	167	x,y,z
C125-H12G···O5	0.97	2.50	3.414(14)	156	x,1+y,z
C14-H14···O19B	0.93	2.29	3.130(2)	151	1-x,1/2+y,1-z
C149-H14H···O1	0.97	2.40	3.320(16)	159	x,y,z
C161-H16D···O8	0.97	2.32	3.260(16)	163	2-x,1/2+y,1-z
C162-H16K···O9	0.97	2.50	3.457(18)	170	x,y,z
C54-H54···O13A	0.93	2.54	3.312(19)	141	1-x,-1/2+y,-z
C63-H63···O18A	0.93	2.40	3.200(2)	144	x,y,z
C77-H77···O20A	0.93	2.49	3.300(19)	145	x,y,z
C95-H95···O16B	0.93	2.53	3.340(3)	145	x,y,z

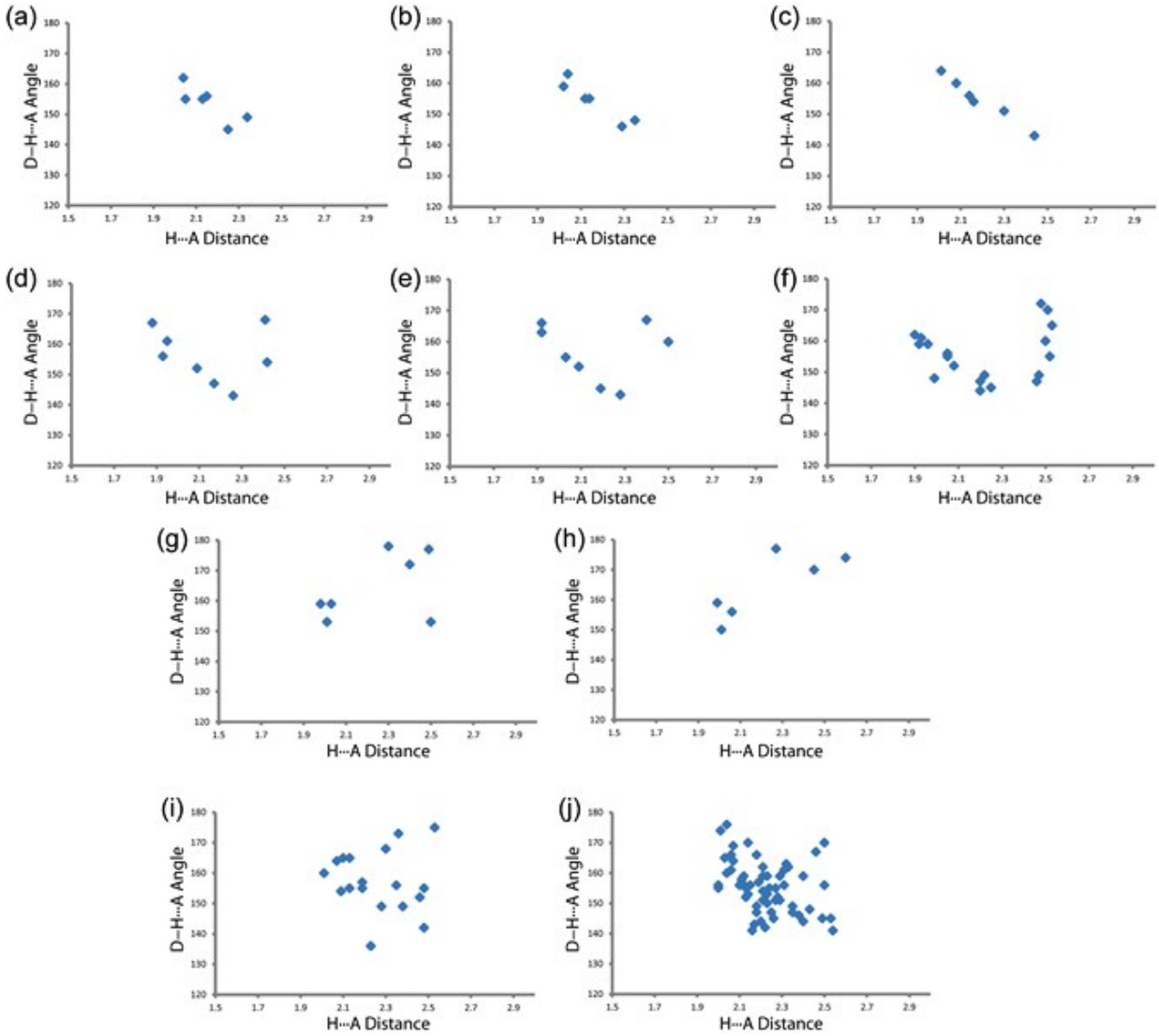


Figure S33. The scatter plot of D–H···A angles *vs*. H···A distances of the hydrogen bonds in free receptors (a) $\mathbf{L_1}$, (b) $\mathbf{L_2}$, (c) $\mathbf{L_3}$ and in anion-receptor complexes (d) **1a**, (e) **2a**, (f) **3a**, (g) **2b**, (h) **3b**, (i) **1b** and (j) **3c**.