Electronic Supplementary Information

Effect of Substitution on Halide/Hydrated Halide Binding: A Case Study of Neutral Bis Urea Receptors

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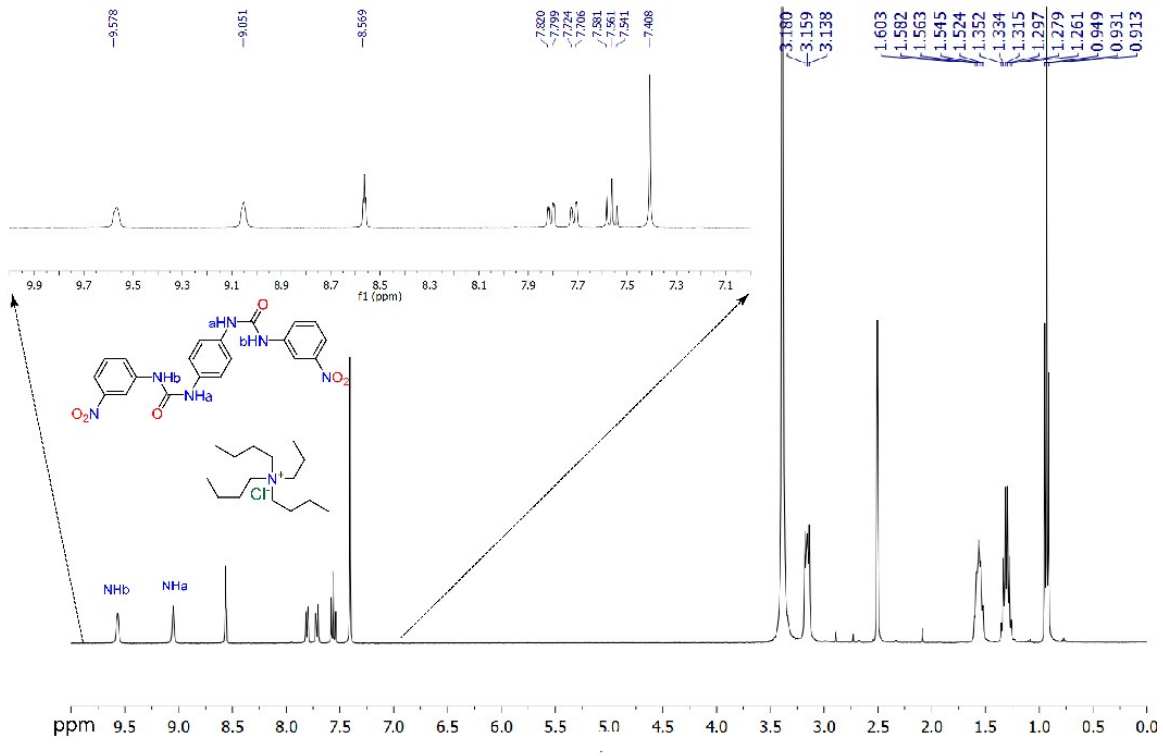

Figure S1: Integrated ^{1}H-NMR spectrum (full as well as expanded) of Chloride complex of $\mathbf{L_1}$ in DMSO-d_6 at 25ºC.

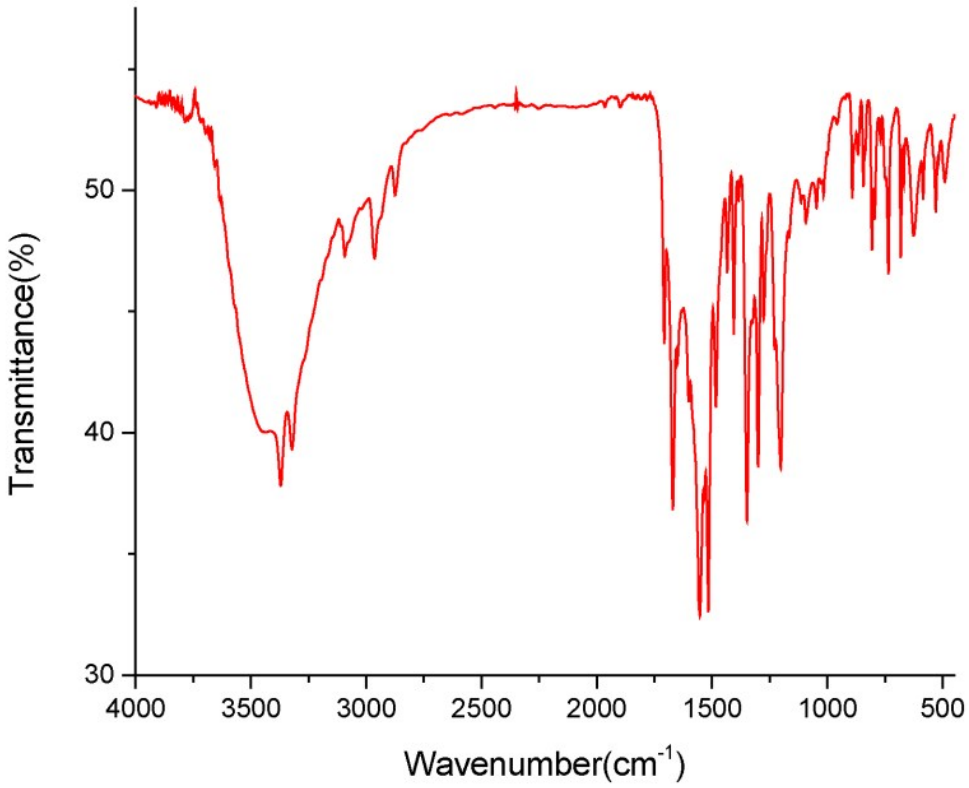

Figure S2: FT-IR spectrum of Chloride complex of receptor $\mathbf{L_1}$ recorded in KBr pellet.

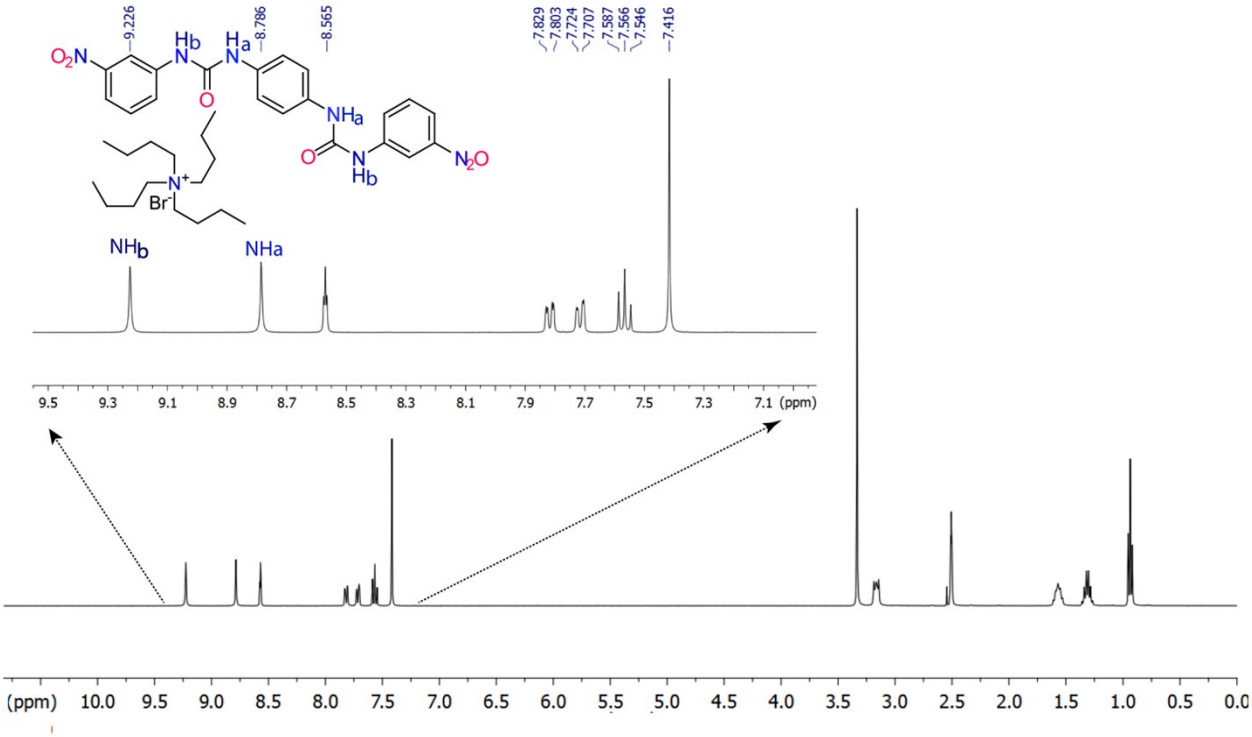

Figure S3: Integrated ^{1}H-NMR spectrum (full as well as expanded) of Bromide complex of $\mathbf{L_1}$ in DMSO-d_6 at 25ºC.

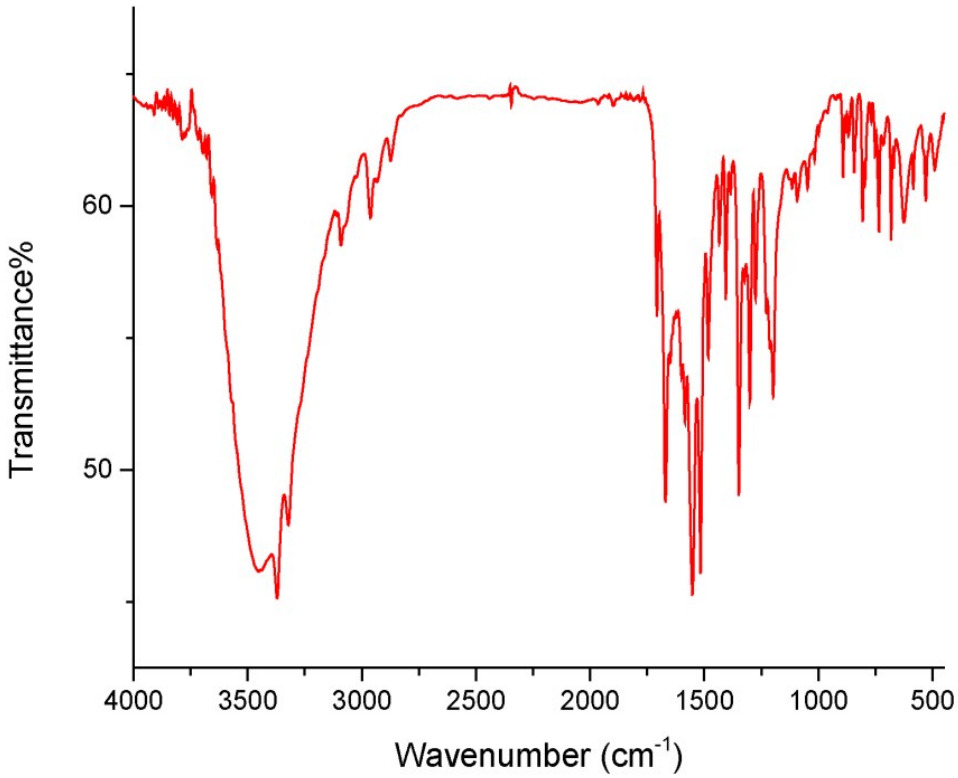

Figure S4: FT-IR spectrum of Bromide complex of receptor $\mathbf{L_1}$ recorded in KBr pellet.

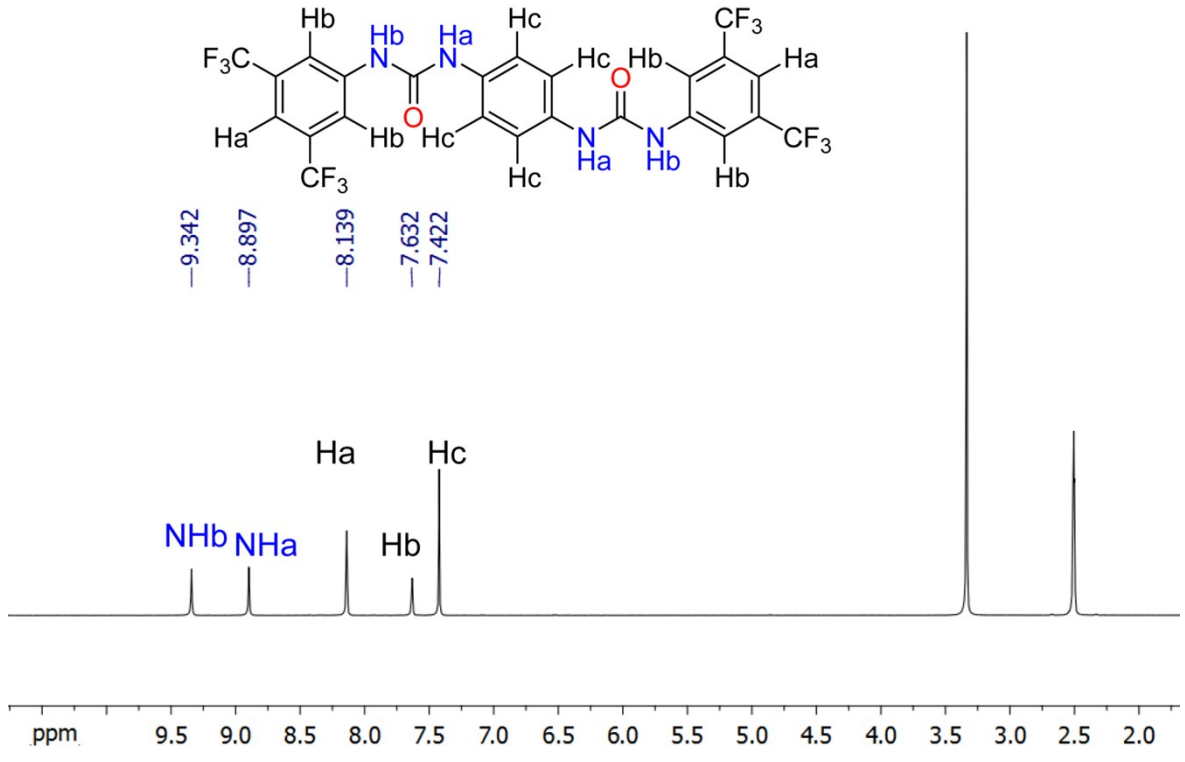

Figure S5: Integrated ^{1}H-NMR spectrum (full as well as expanded) and explanation of all hydrogen atoms of free dipodal receptor $\mathbf{L_2}$ in DMSO-d_6 at 25ºC.

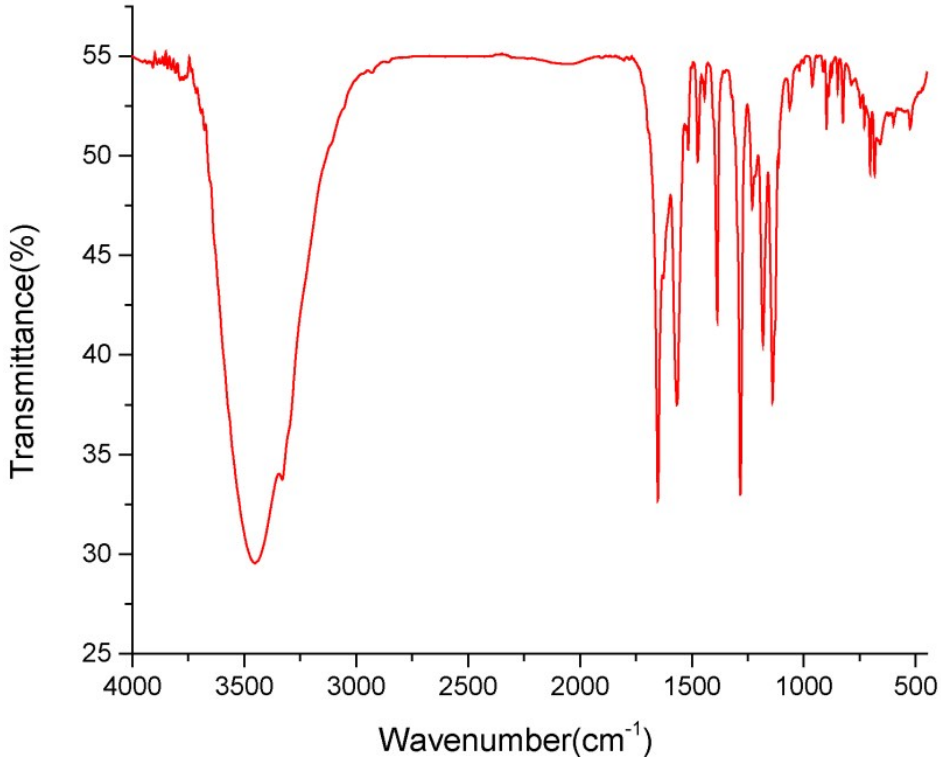

Figure S6: FT-IR spectrum of receptor $\mathbf{L_2}$ recorded in KBr pellet.

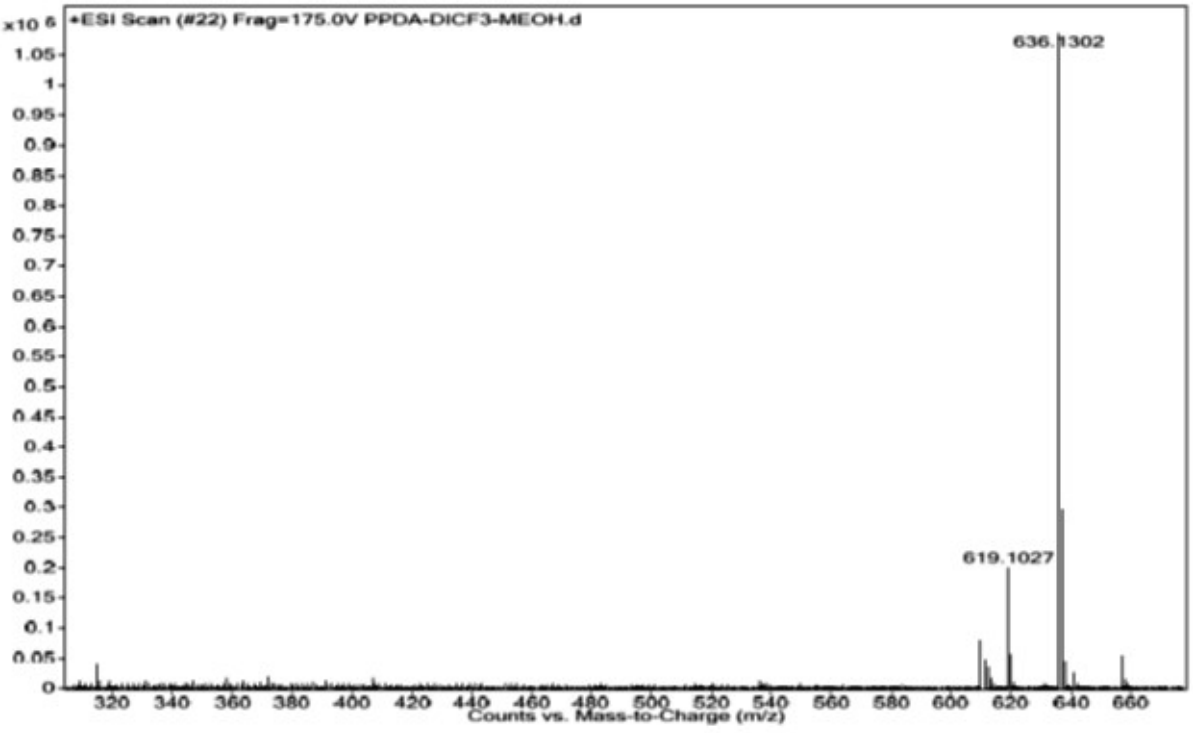

Figure S7: ESI-Mass spectrum of dipodal receptor $\mathbf{L_2}$.

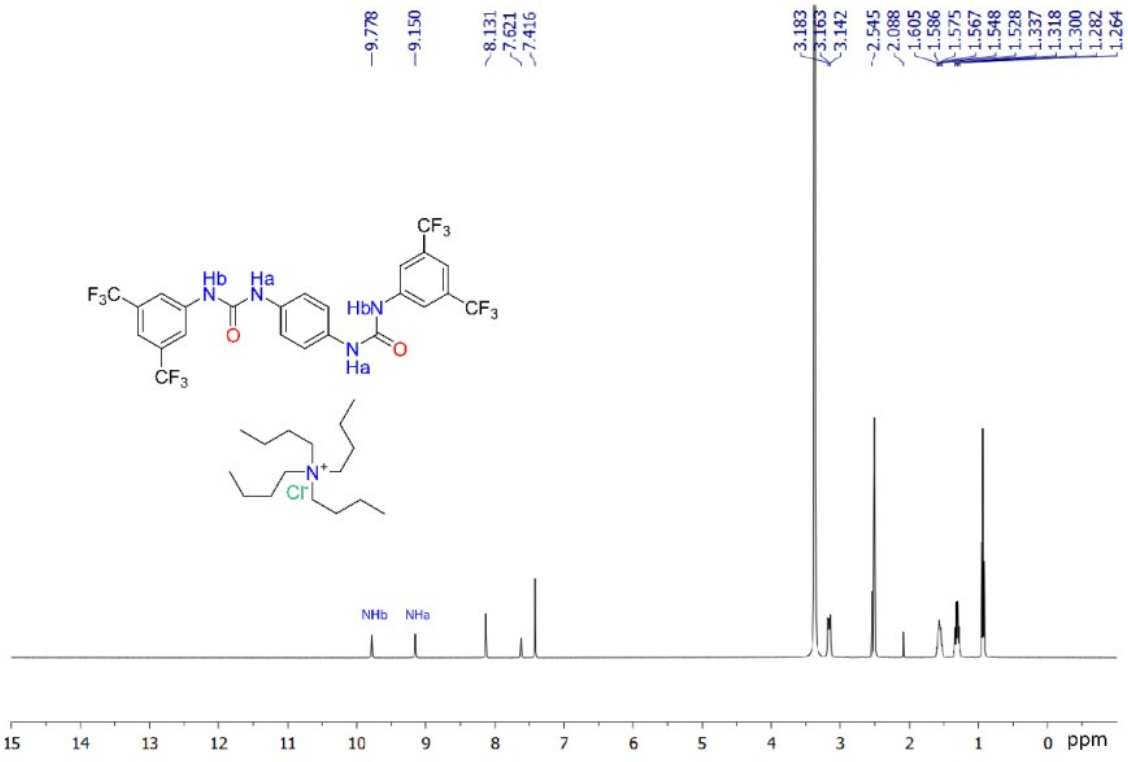

Figure S8: Integrated ^{1}H-NMR spectrum (full as well as expanded) of Chloride complex of receptor $\mathbf{L_2}$ in DMSO-d_6 at 25ºC.

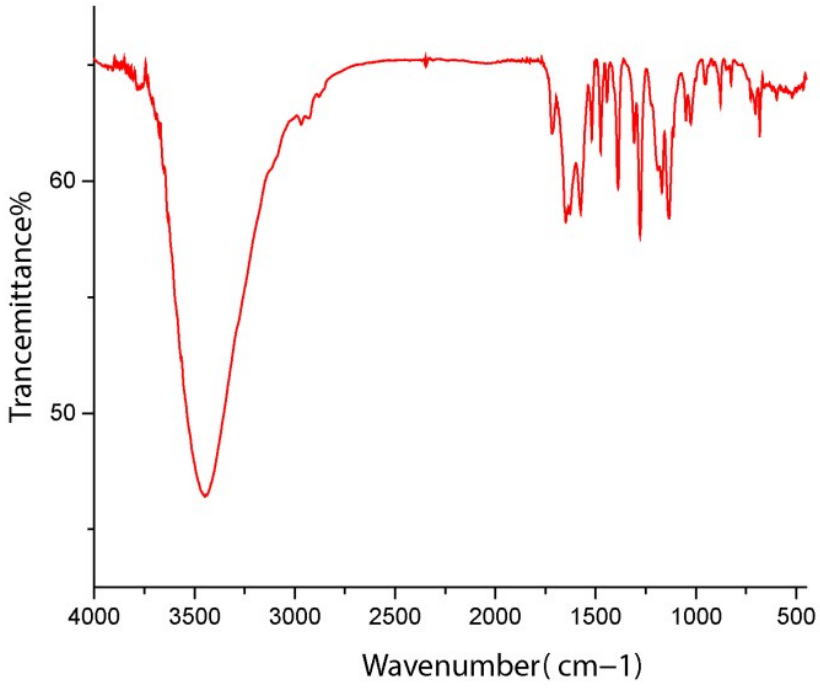

Figure S9: FT-IR spectrum of Chloride complex of receptor $\mathbf{L_2}$ recorded in KBr pellet.

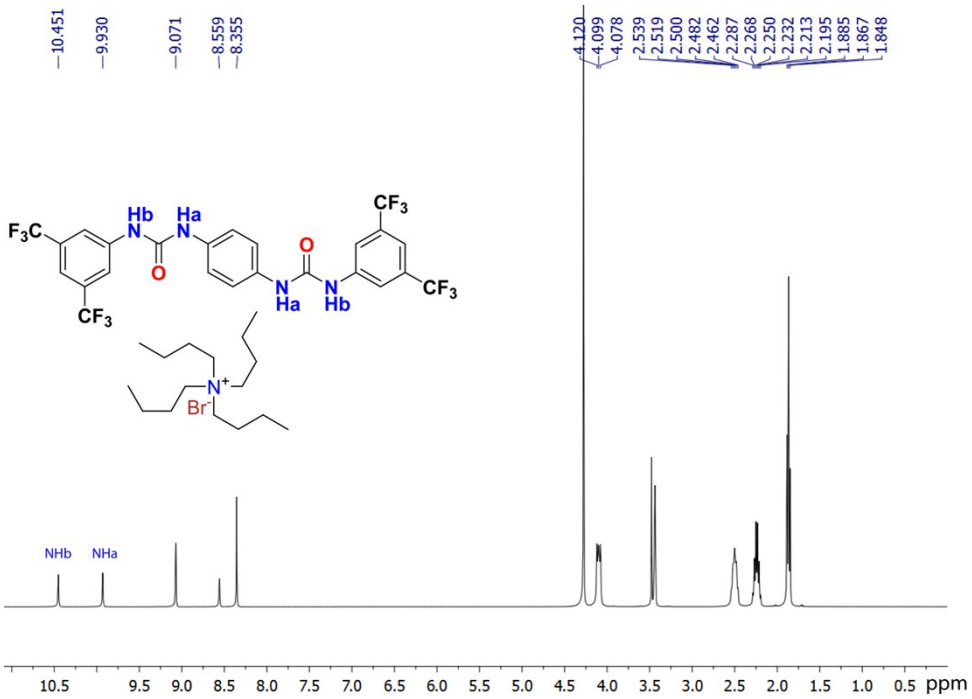

Figure S10: Integrated ^{1}H-NMR spectrum (full as well as expanded) of Bromide complex of receptor L_2 in DMSO-d_6 at 25ºC.

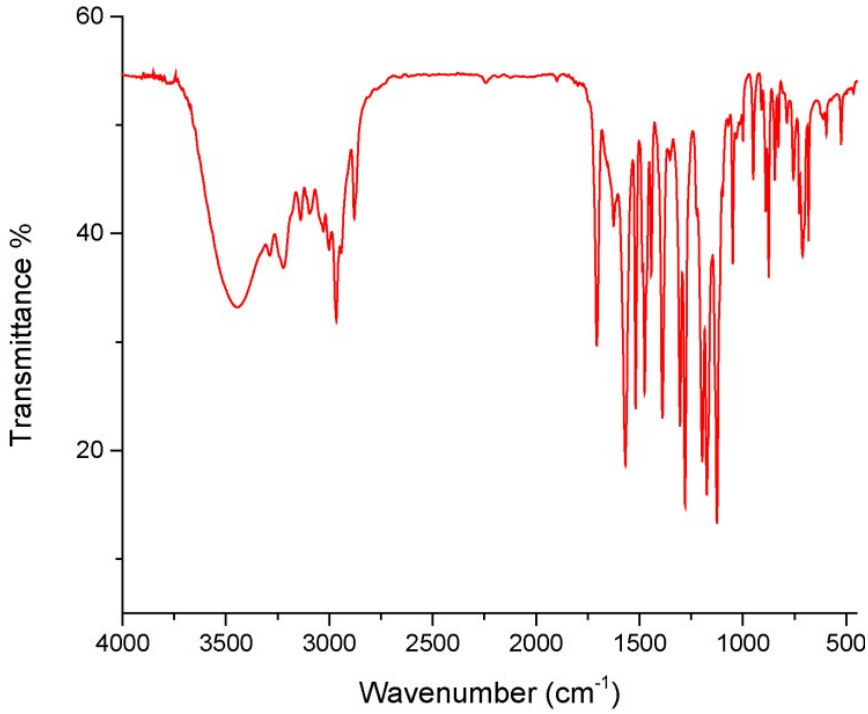

Figure S11: FT-IR spectrum of Bromide complex of receptor $\mathbf{L_2}$ recorded in KBr pellet.

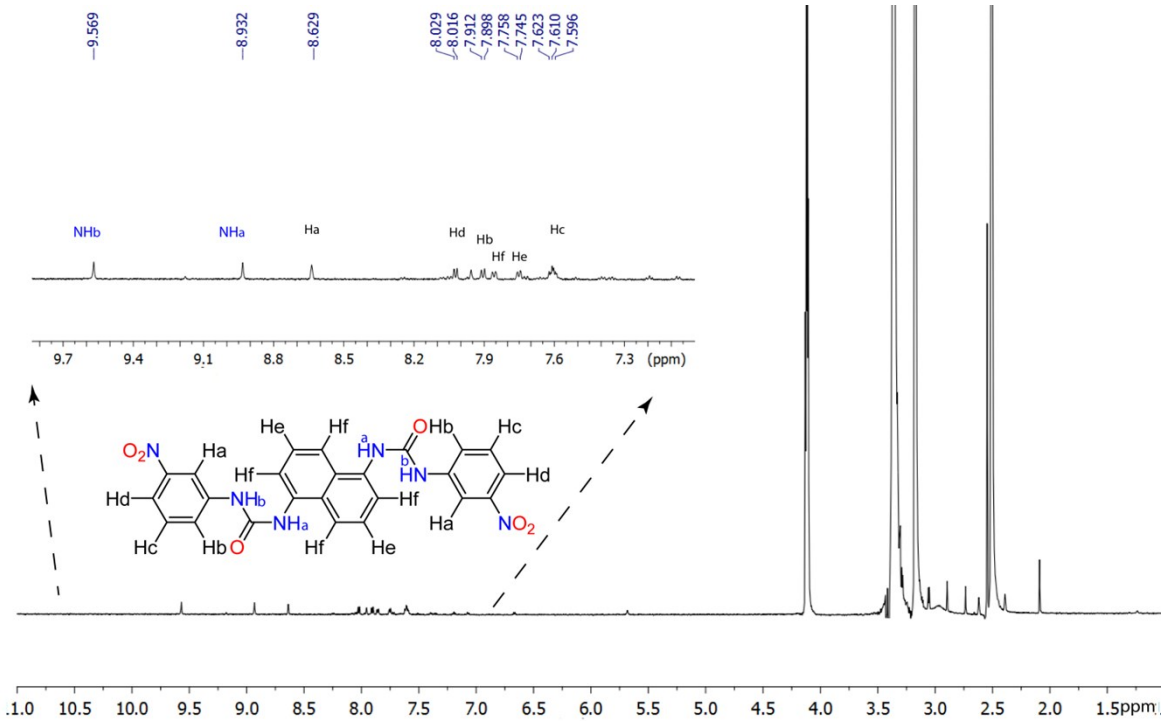

Figure S12: Integrated ^{1}H-NMR spectrum (full as well as expanded) and explanation of all hydrogen atoms of free dipodal bis-urea receptor $\mathbf{L_3}$ in DMSO-d_6 at 25ºC.

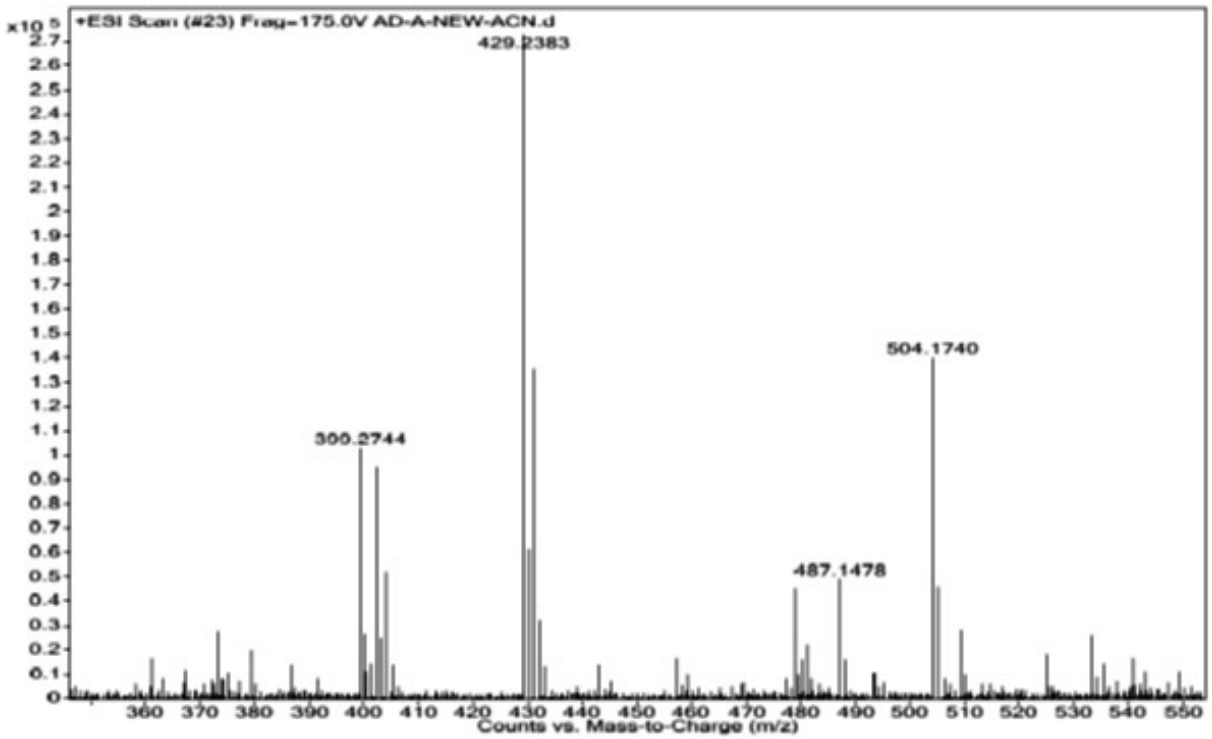

Figure S13: ESI-Mass spectrum of dipodal receptor $\mathbf{L_3}$.

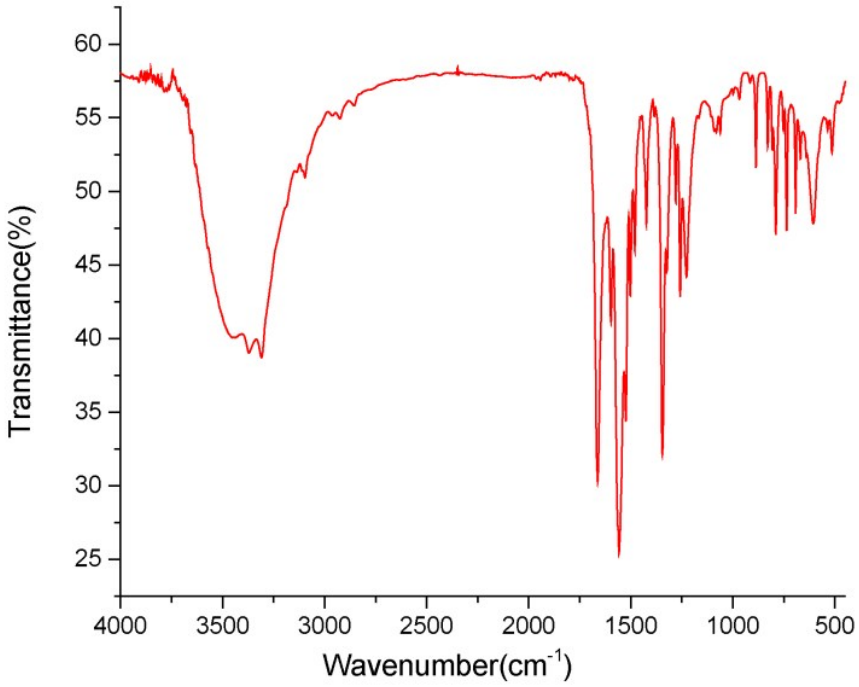

Figure S14: FT-IR spectrum of receptor $\mathbf{L_3}$recorded in KBr pellet.

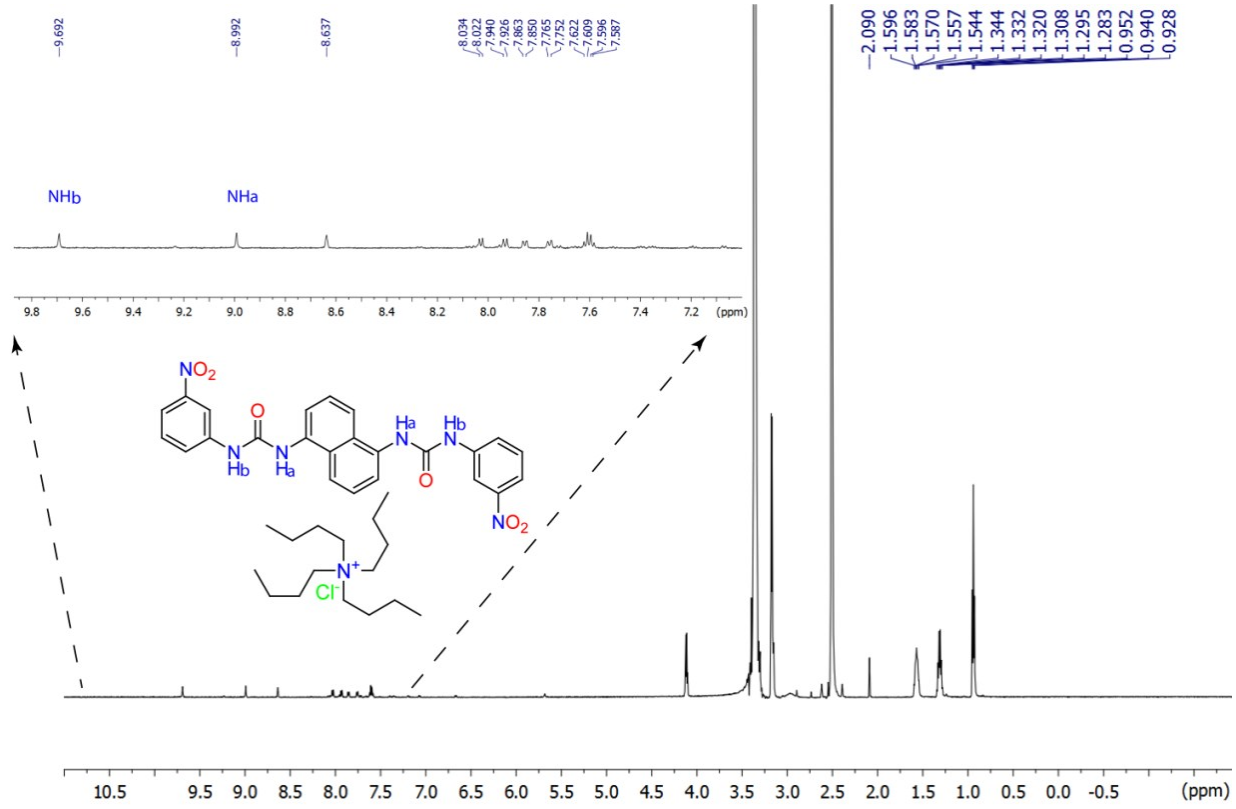

Figure S15: Integrated ^{1}H-NMR spectrum (full as well as expanded) of Chloride complex of receptor $\mathbf{L_3}$ in DMSO-d_6 at 25ºC.

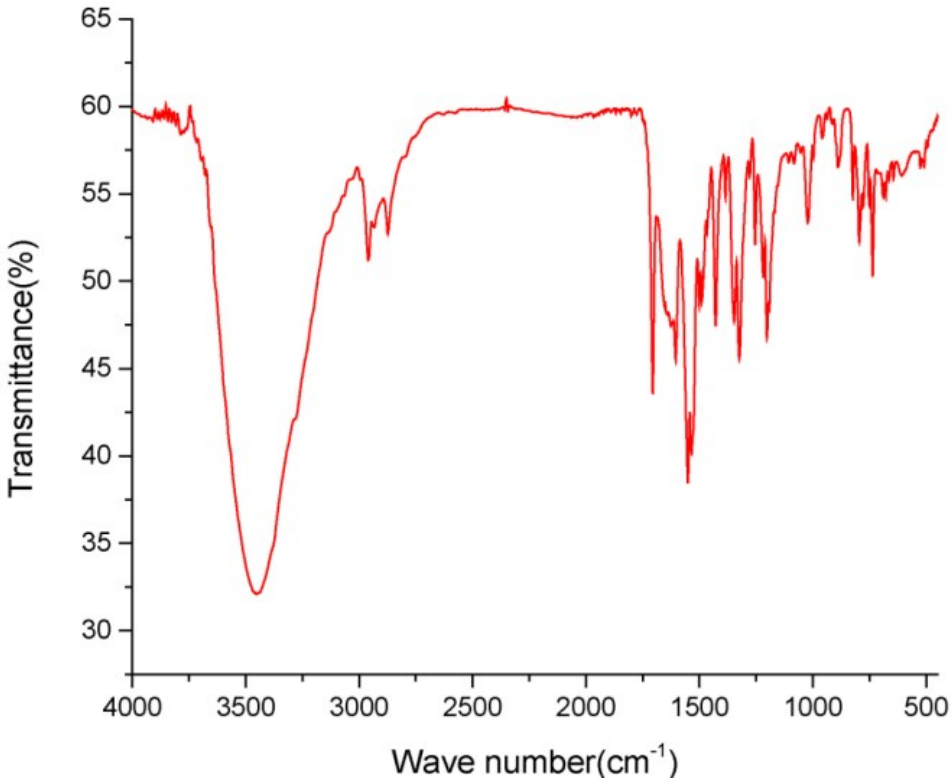

Figure S16: FT-IR spectrum of Chloride complex of receptor $\mathbf{L_3}$ recorded in KBr pellet.

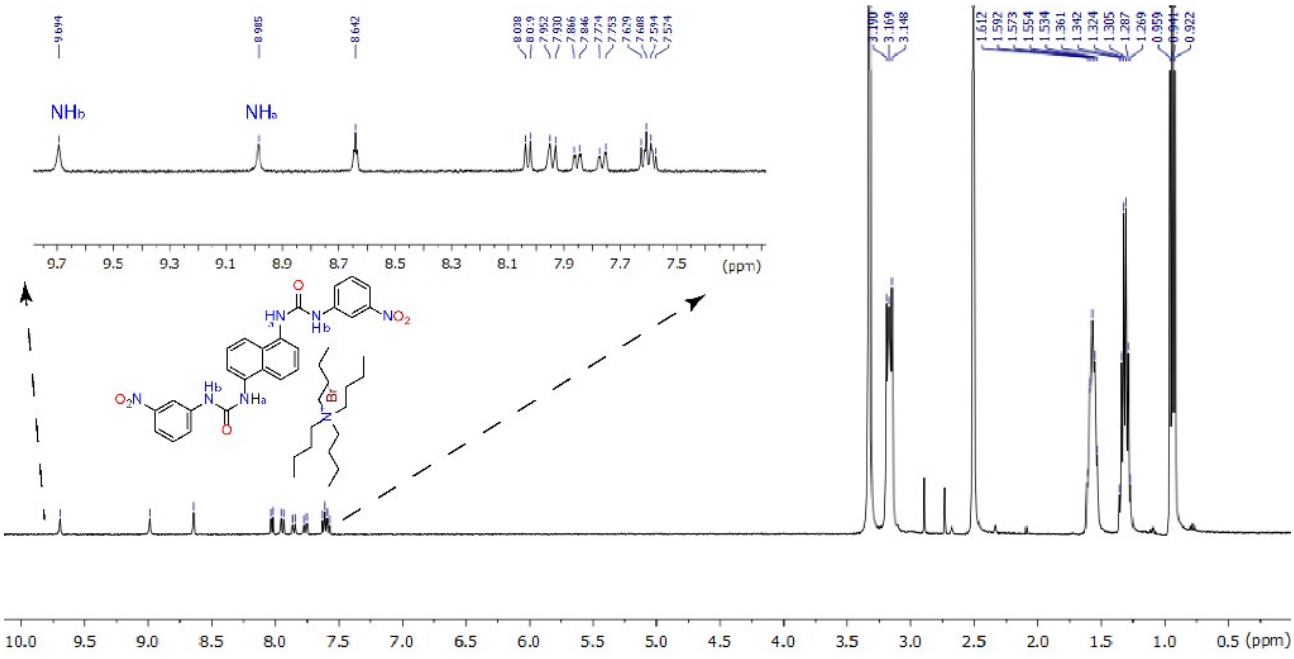

Figure S17: Integrated ^{1}H-NMR spectrum (full as well as expanded) of Bromide complex of receptor $\mathbf{L_3}$ in DMSO-d_6 at 25ºC.

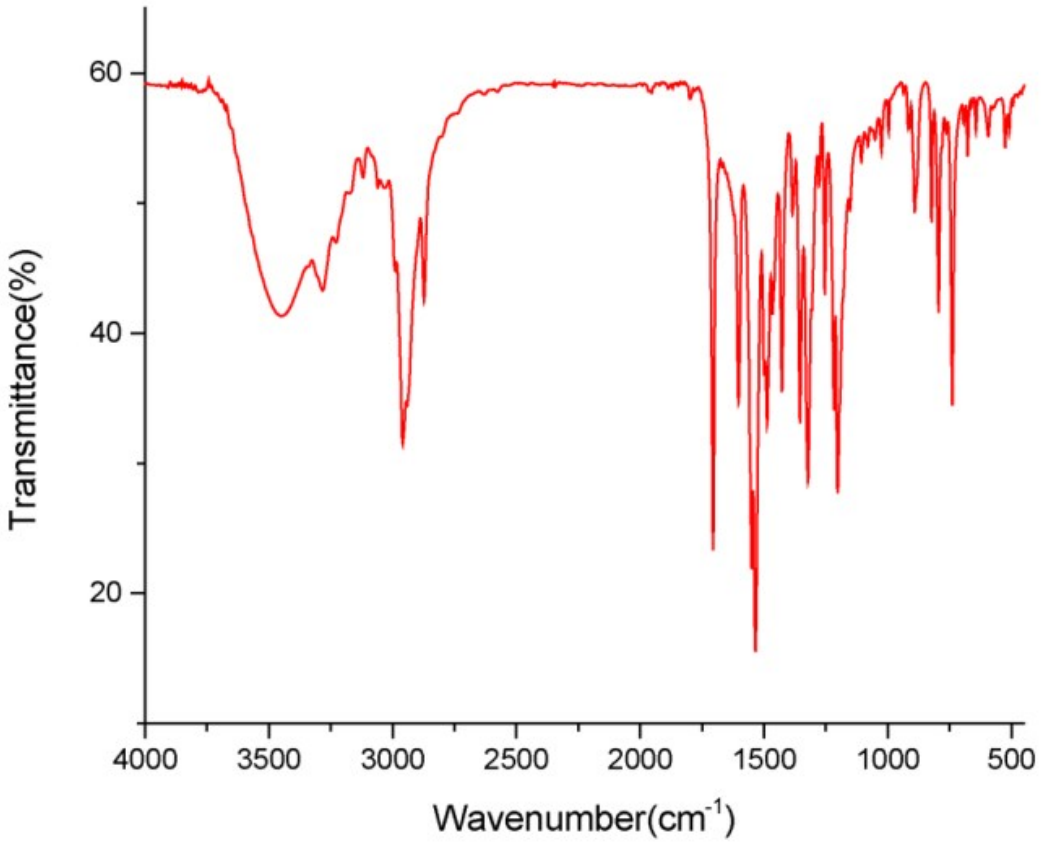

Figure S18: FT-IR spectrum of Bromide complex of receptor $\mathbf{L_3}$ recorded in KBr pellet.

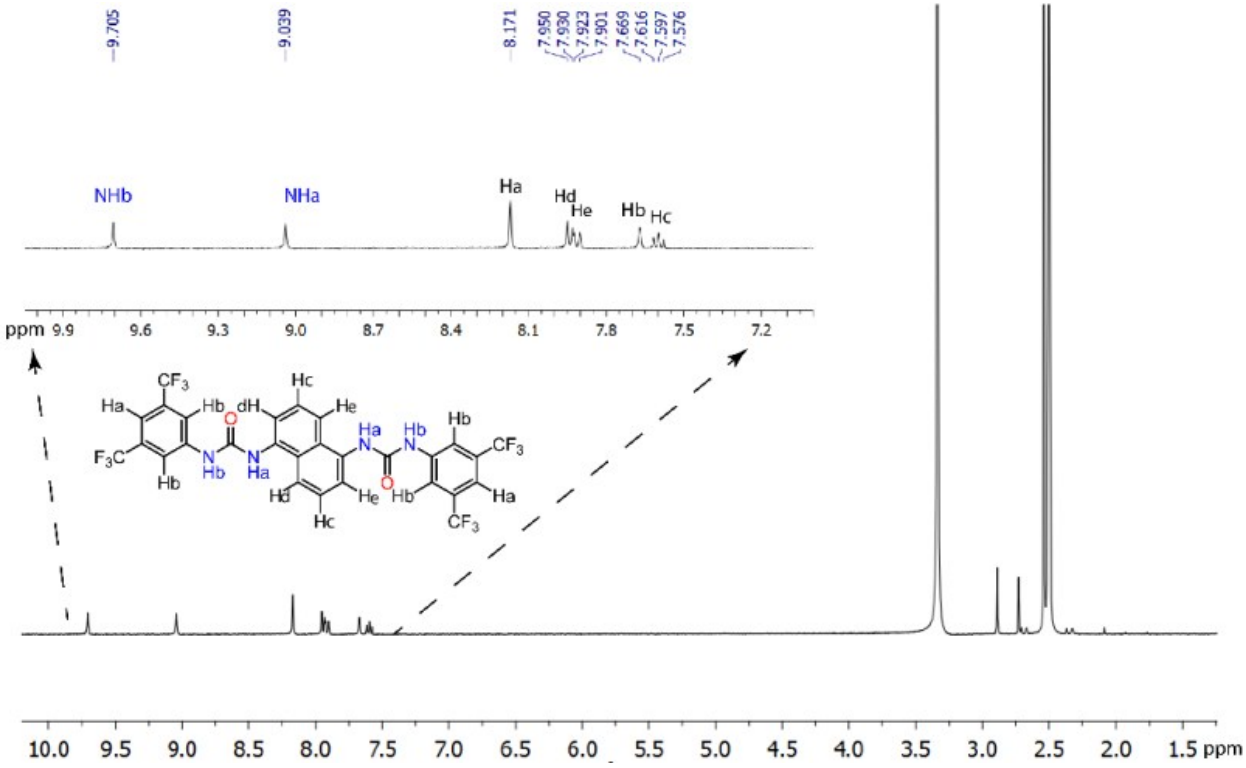

Figure S19: Integrated ^{1}H-NMR spectrum (full as well as expanded) and explanation of all hydrogen atoms of free dipodal bis urea receptor $\mathbf{L_4}$ in DMSO-d_6 at 25ºC.

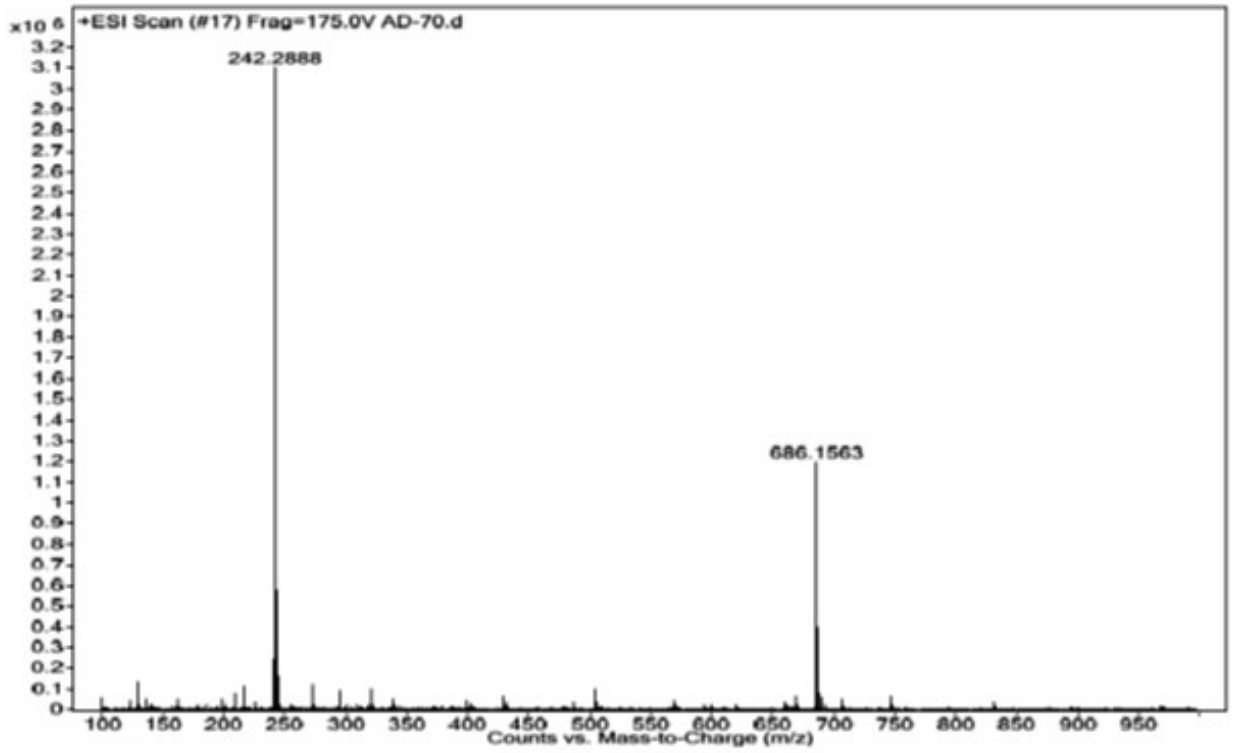

Figure S20: ESI-Mass spectrum of dipodal receptor $\mathbf{L_4}$.

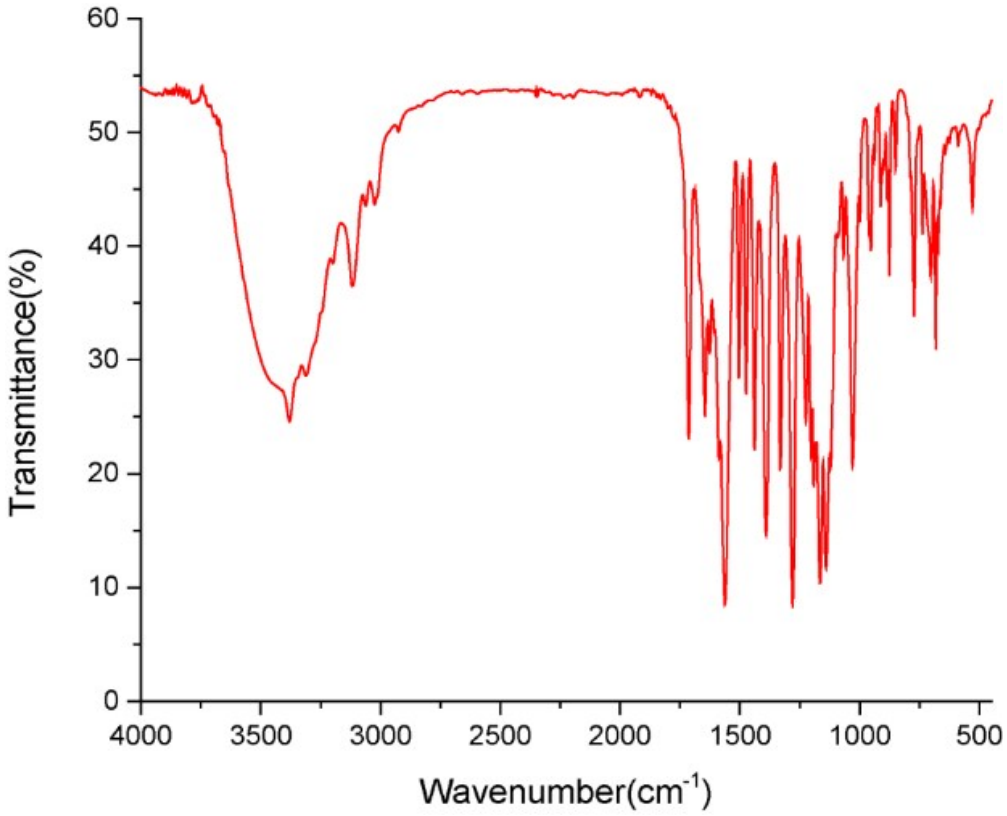

Figure S21: FT-IR spectrum of receptor $\mathbf{L_4}$ recorded in KBr pellet.

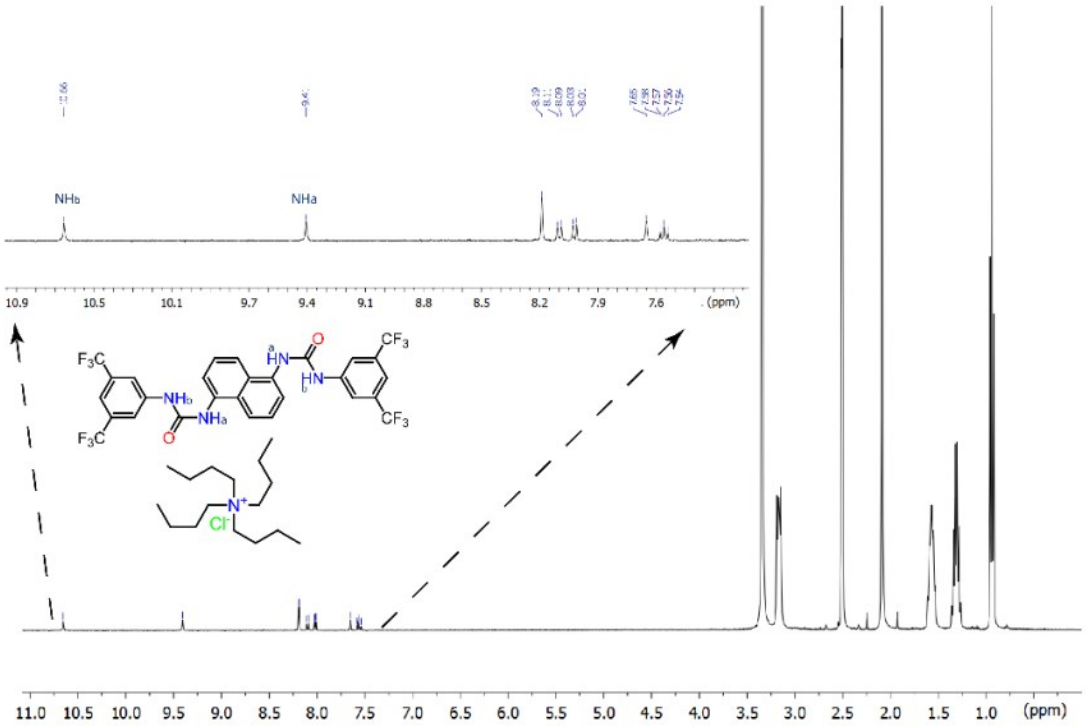

Figure S22: Integrated ^{1}H-NMR spectrum (full as well as expanded) and explanation of all hydrogen atoms of Chloride complex of receptor $\mathbf{L_4}$ in DMSO-d_6 at 25ºC.

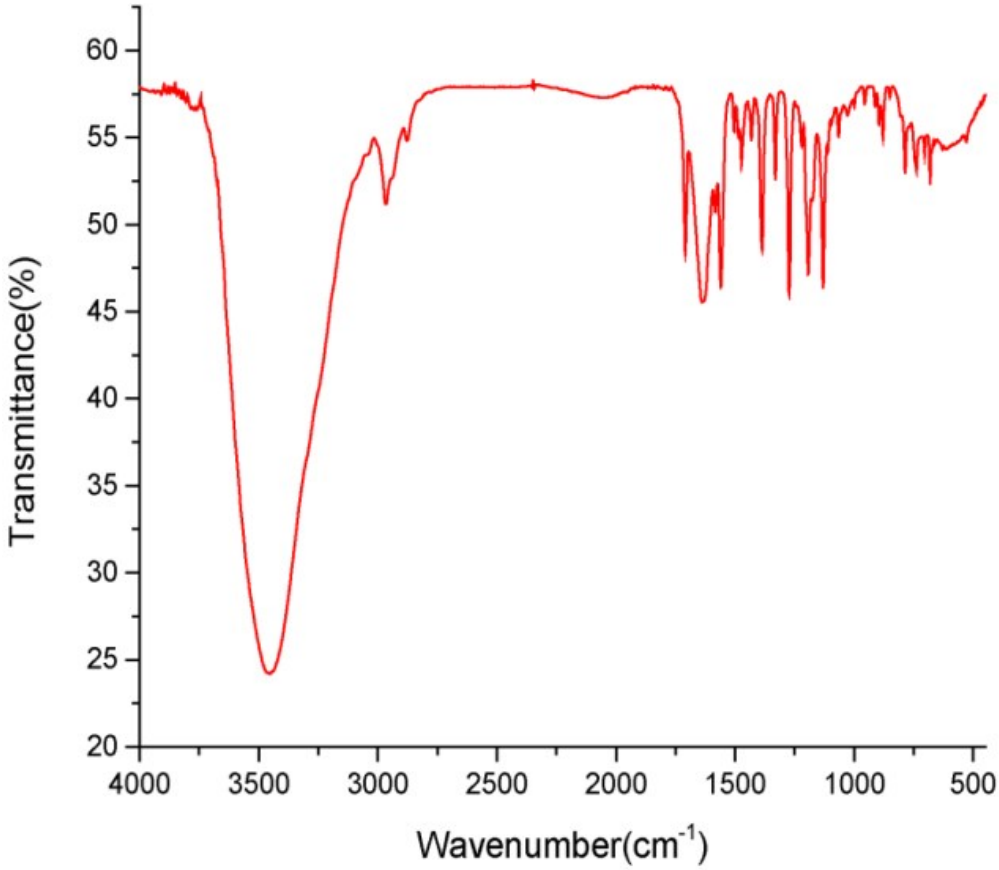

Figure S23: FT-IR spectrum of Bhloride complex of receptor $\mathbf{L_4}$ recorded in KBr pellet.

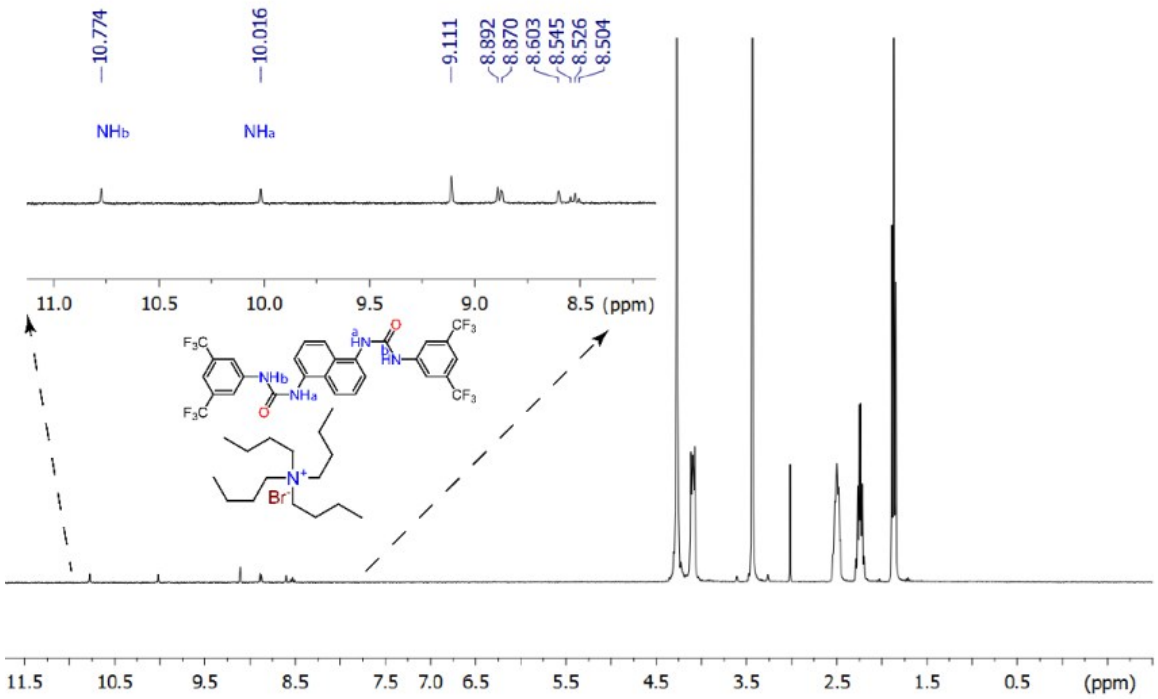

Figure S24: Integrated ^{1}H-NMR spectrum (full as well as expanded) Bromide complex of receptor $\mathbf{L_4}$ in DMSO-d_6 at 25ºC.

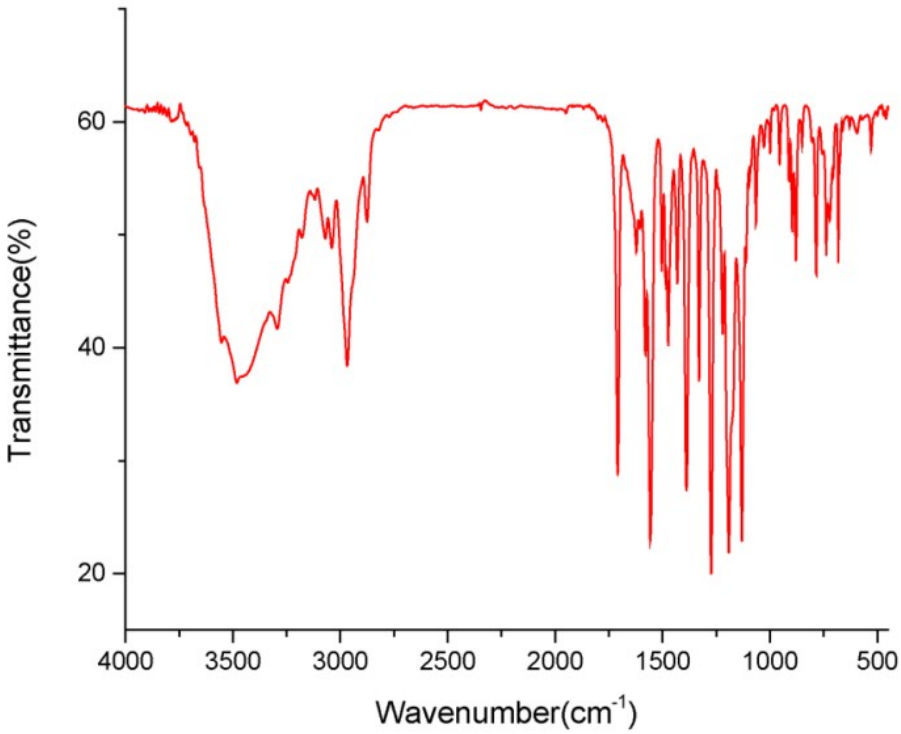

Figure S25: FT-IR spectrum of Bromide complex of dipodal receptor $\mathbf{L_4}$ recorded in KBr pellet.

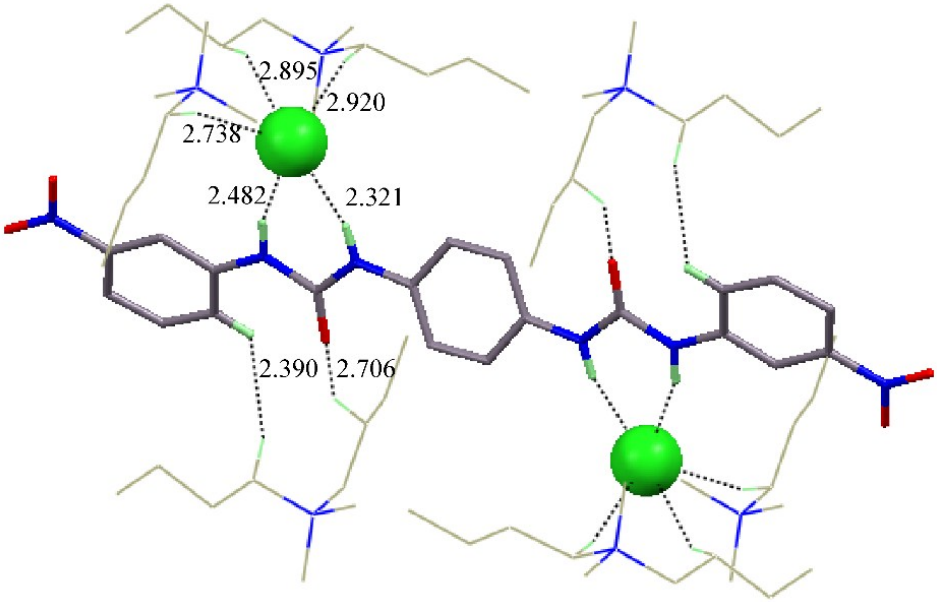

Figure S26: X-ray structure analysis of complex **1a** showing coordination environment of anion as well as extra stabilization through C-$H_{aliphatic}$···O_{urea} and C-$H_{aliphatic}$··· $\pi_{aromatic}$ interaction with proper bond distances in Angstrom.

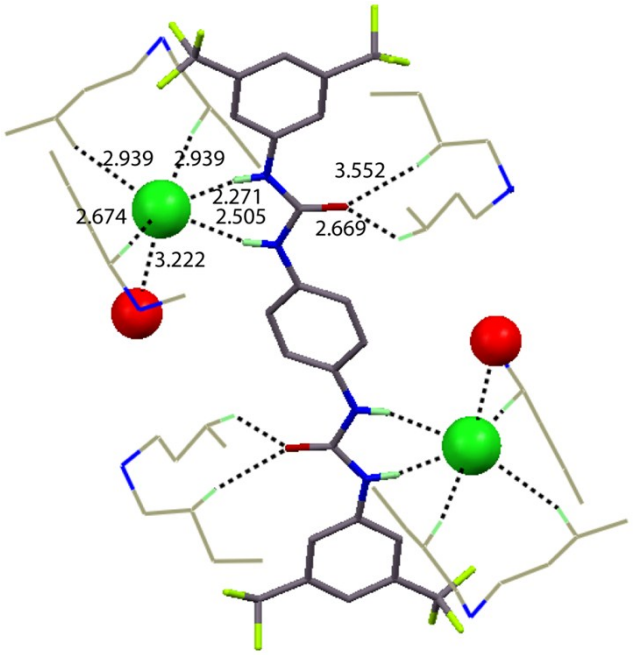

Figure S27: X-ray structure analysis of complex **2a** showing coordination environment of anion as well as extra stabilization through two C-$H_{aliphatic}$···O_{urea} with proper bond distances in Angstrom.

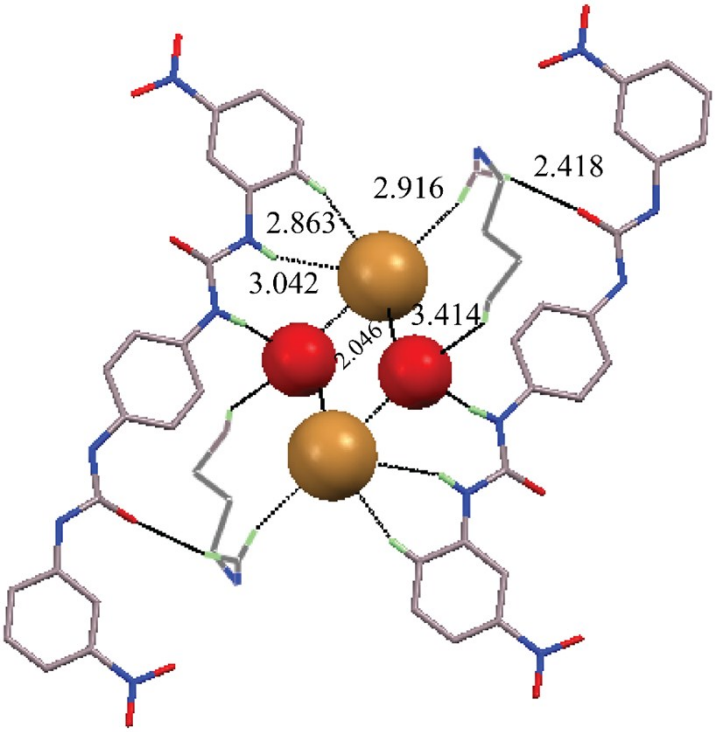

Figure S28: X-ray structure analysis of complex **1b** showing coordination environment of anion as well as extra stabilization through C-$H_{aliphatic}$···O_{urea}, C-$H_{aliphatic}$··· $\pi_{aromatic}$ C-$H_{aliphatic}$···O_{water} interaction with proper bond distances in Angstrom.

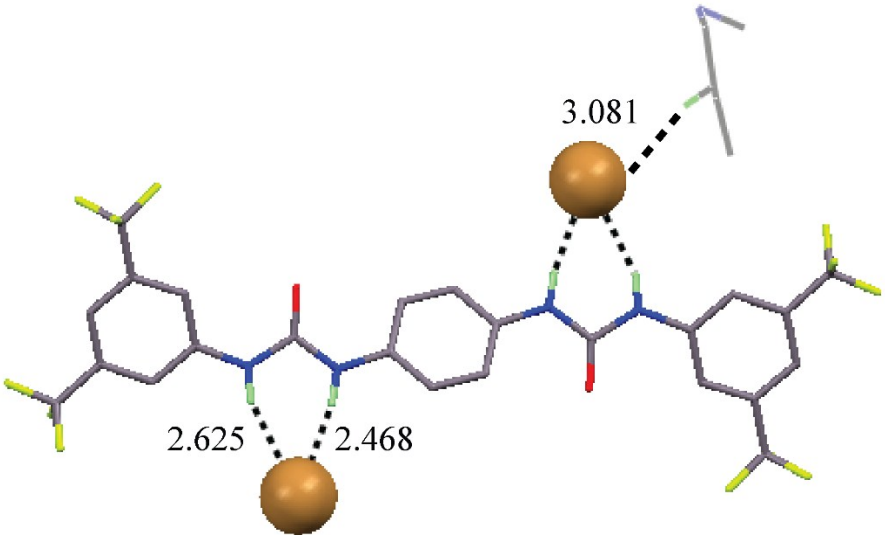

Figure S29: X-ray structure analysis of complex **2b** showing coordination environment of anion as well as extra stabilization through C-$H_{aliphatic}$···O_{urea}, with proper bond distances in Angstrom.

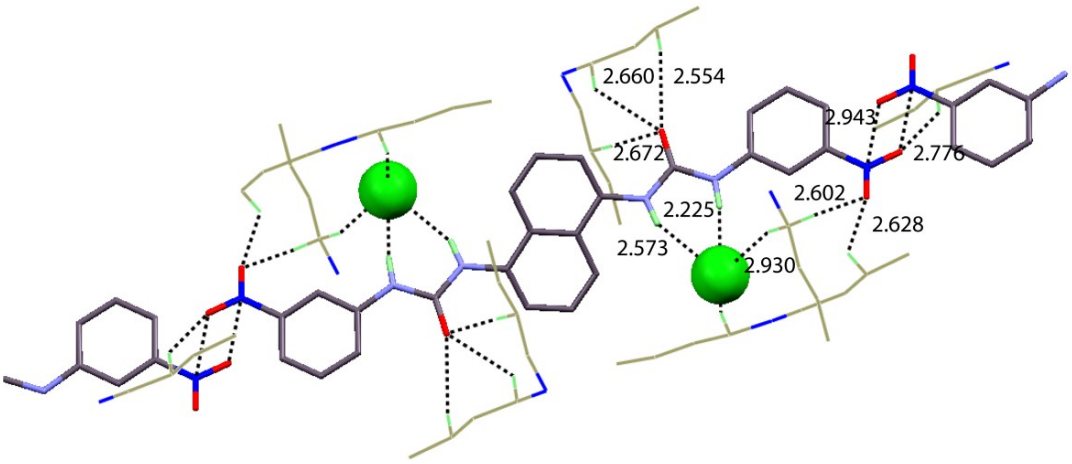

Figure S30: X-ray structure analysis of complex **3a** showing coordination environment of anion as well as extra stabilization through three C-H $_{aliphatic}$···O $_{urea}$, four C-H $_{aliphatic}$···O interaction from two different oxygen of substituted NO_2 group and one cross connected parallel C-H···O interaction between two NO_2 groups of each host site with proper bond distances in Angstrom.

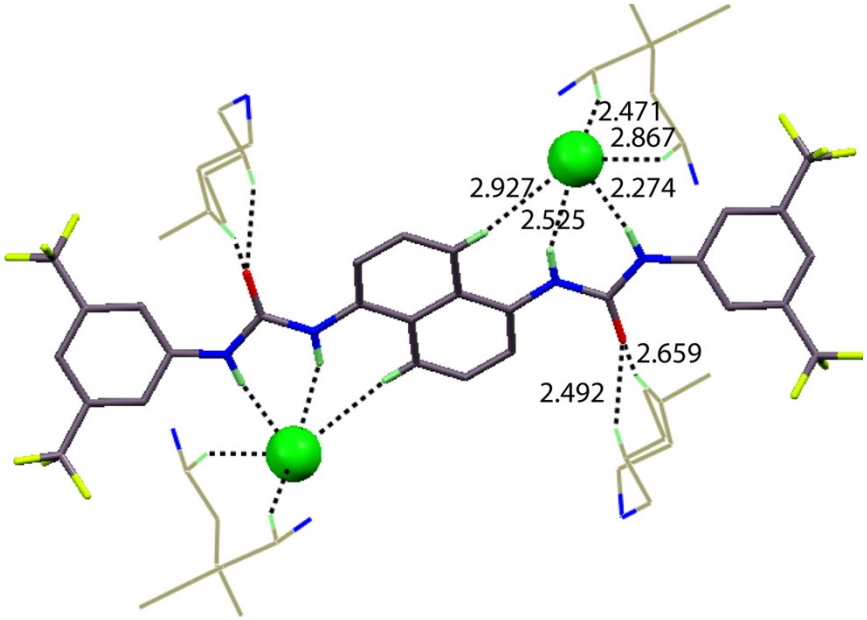

Figure S31: X-ray structure analysis of complex **4a** showing coordination environment of anion as well as extra stabilization through two C-H $_{aliphatic}$···O $_{urea}$ interaction with proper distances in Angstrom.

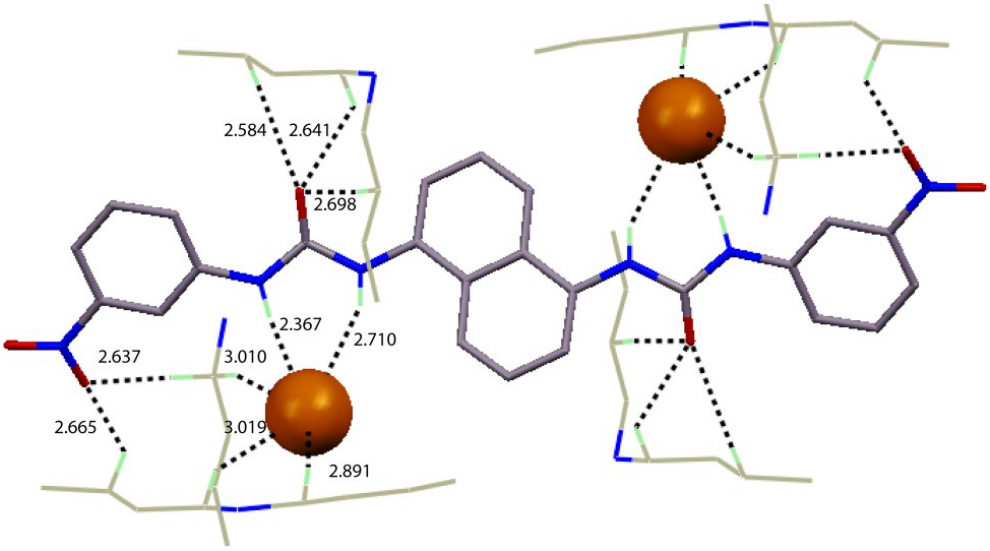

Figure S32: X-ray structure analysis of complex **3b** showing coordination environment of anion as well as extra stabilization through three C-H $_{aliphatic}$···O $_{urea}$, two C-H $_{aliphatic}$···O interaction involving one oxygen atom of substituted NO_2 group with proper bond distances in Angstrom.

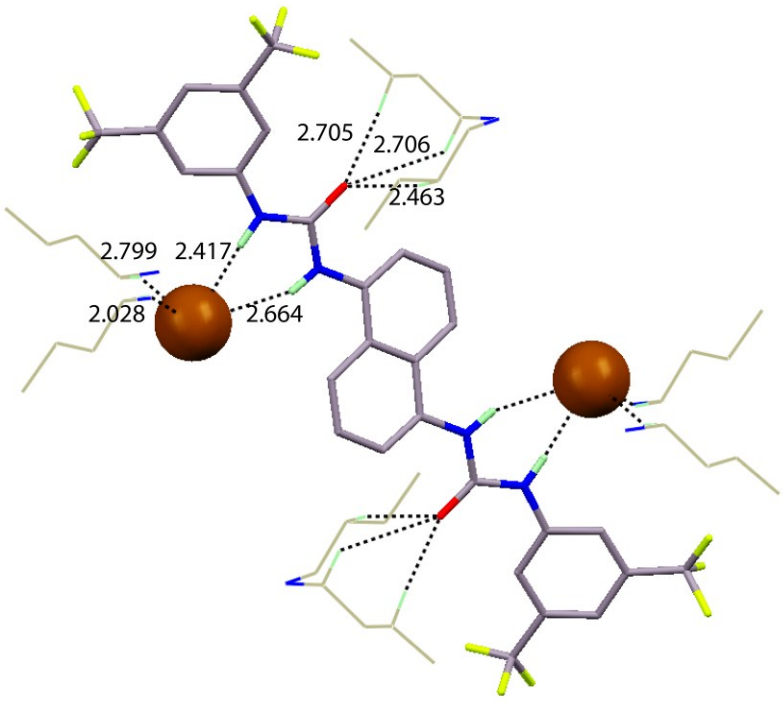

Figure S33: X-ray structure analysis of complex **4b** showing coordination environment of anion as well as extra stabilization through three C-$H_{aliphatic}$···O $_{urea}$ interaction with proper distances in Angstrom.

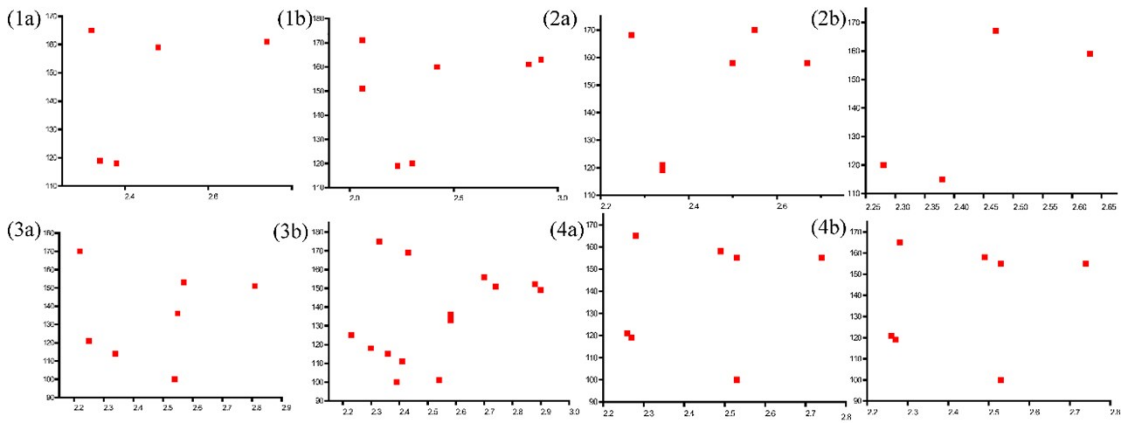

Figure S34: The scatter plot of N−H···A angle vs. H···A distance of the hydrogen bonds in the complexes (**1a**, **1b, 2a, 2b, 3a, 3b, 4a** and **4b**).

Anion binding analysis by ^{1}H-NMR titrations **—** The ^{1}H NMR titration of the compounds was performed in DMSO-d_6 solvent. The stock solutions of the compound (10 mM), tetrabutyl ammonium Chloride (TBACl; 2 M) and tetrabutyl ammonium Bromide (TBABr; 2 M) were prepared in DMSO-d_6. The TBACl and TBABr were used as the source of Cl^- and Br^- ion. The changes in chemical shift (Δδ) value of the N-H protons of the urea-moieties were analysed. Significant extents of chemical shift (Δδ) of both N-H protons were observed. All ^{1}H NMR spectra were stacked through the MestReNova software. Changes in chemical shift against the concentration of Cl^- as well as Br^- ions were fitted using BindFit v0.5 program.[1]

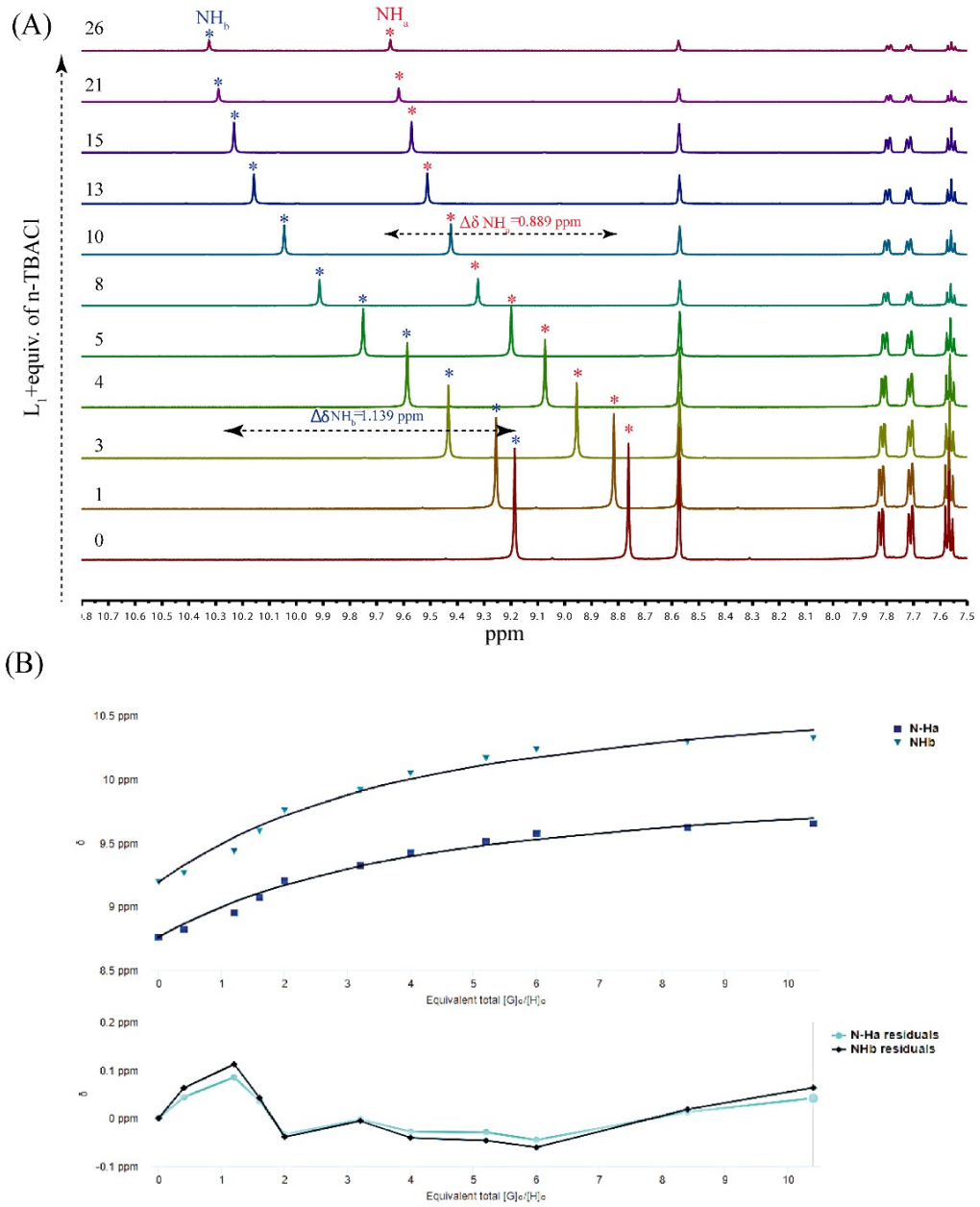

Figure S35: (A) Expanded partial ^{1}H NMR spectra of $\mathbf{L_1}$ upon titration with n-TBACl in DMSO-d_6. (B) Showing the raw vs. fitted data (fitted to 1**:**1 NMR binding data) (top) and the corresponding residual plot (bottom). Binding constant (K) = 24.36 M^{-1} (Ref. 2).

(http://app.supramolecular.org/bindfit/view/a04aa7b4-1b10-4ec4-b62a-004488bc153d)

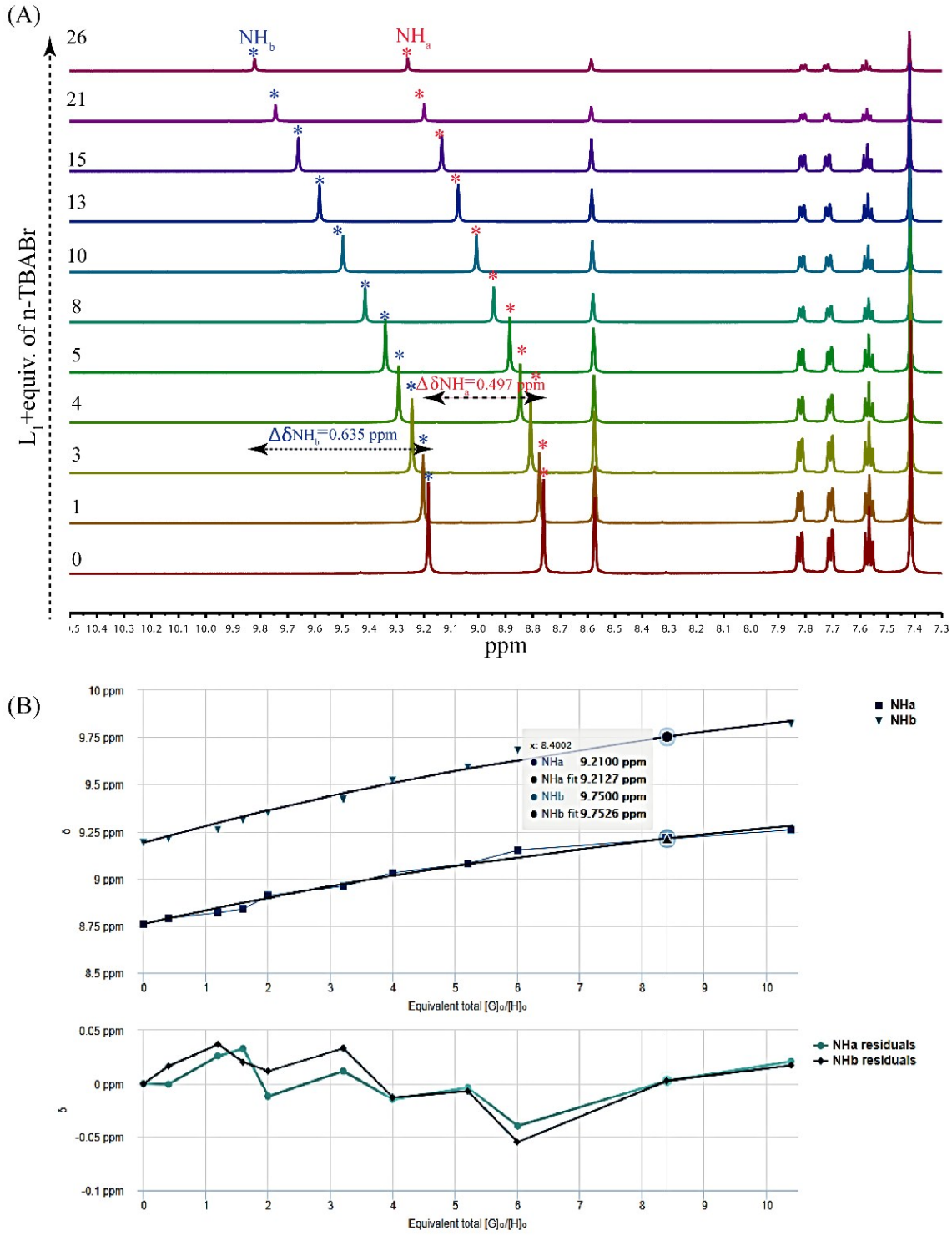

Figure S36: (A) Expanded partial ^{1}H NMR spectra of $\mathbf{L_1}$ upon titration with n-TBABr in DMSO-d_6. (B) Showing the raw vs. fitted data (fitted to 1:1 NMR binding data) (top) and the corresponding residual plot (bottom). Binding constant (K) = 2.85 M^{-1} (Ref 2).

(http://app.supramolecular.org/bindfit/view/2f704e70-704c-4c4a-b586-861ec75747dc)

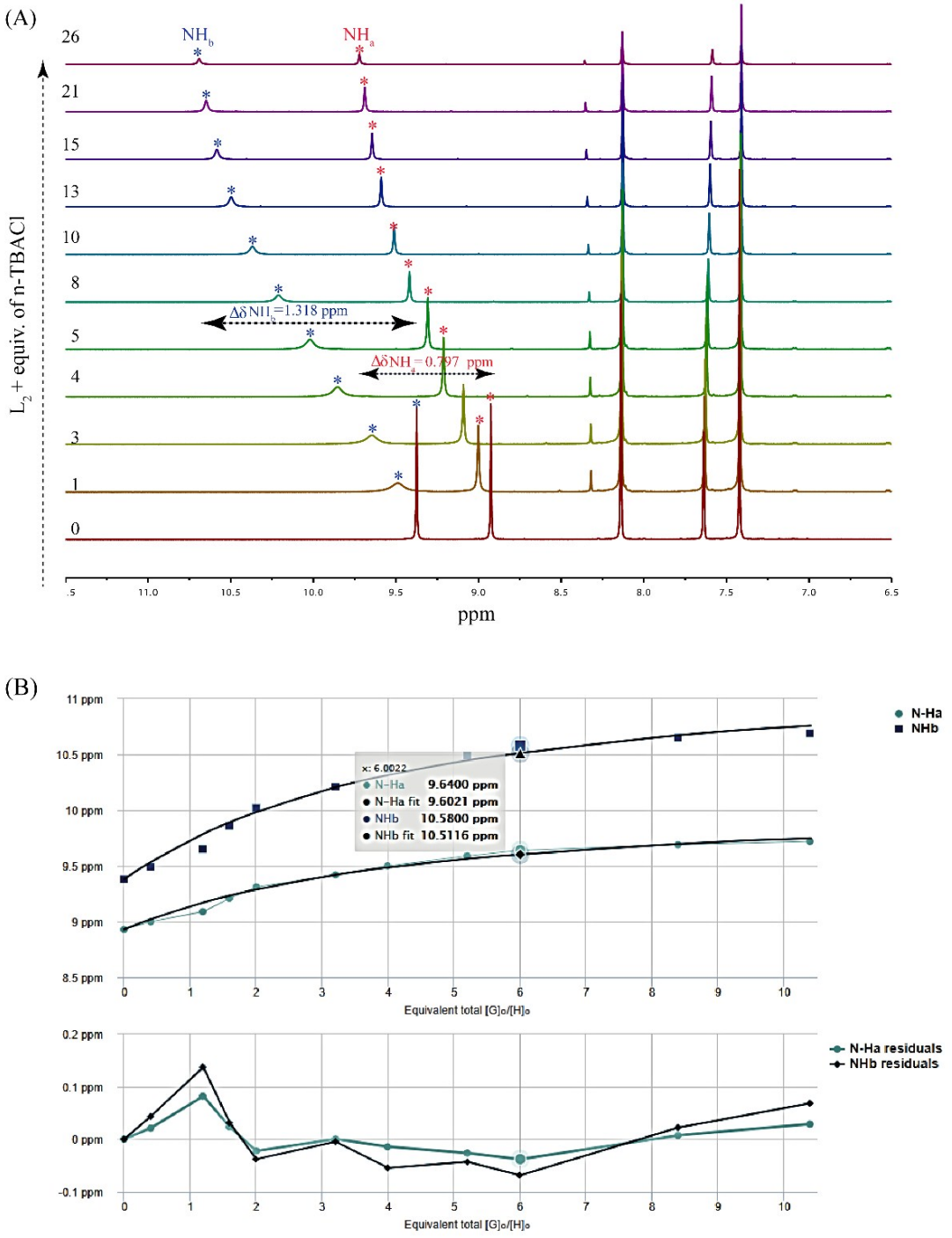

Figure S37: (A) Expanded partial ^{1}H NMR spectra of **L_2** upon titration with n-TBACl in DMSO-d_6. (B) Showing the raw vs. fitted data (fitted to 1**:**1 NMR binding data) (top) and the corresponding residual plot (bottom). Binding constant (K) = 24.43 M^{-1} (Ref 2).

(http://app.supramolecular.org/bindfit/view/ee741007-4a26-4279-9860-6c57eaca46fb)

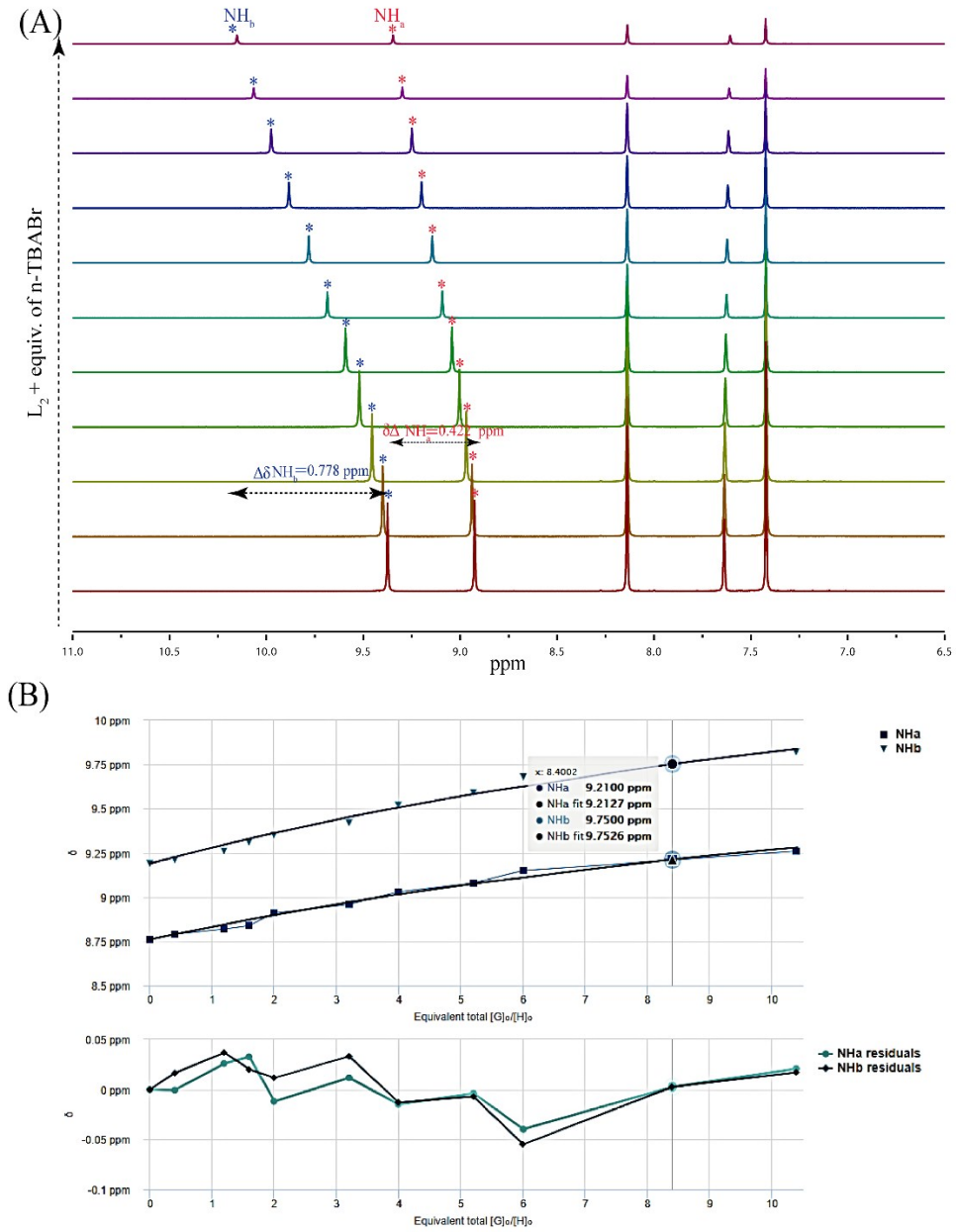

Figure S38: (A) Expanded partial ^{1}H NMR spectra of **L_2** upon titration with n-TBABr in DMSO-d_6. (B) Showing the raw vs. fitted data (fitted to 1:1 NMR binding data) (top) and the corresponding residual plot (bottom). Binding constant (K) = 2.72 M^{-1} (Ref 2)

(http://app.supramolecular.org/bindfit/view/c24e85bf-7407-49e2-87cb-19270479e6fd))

Table S1: Hydrogen bonding distances (Å) and Bond angles (º) in the neutral anion-receptor complexes:

Complex	D−H···A	d(D···H)/Å	d(H···A)/Å	d(D···A)/Å	<D−H···A/°	Symmetry codes
1a	N2-H2N···Cl1	0.86	2.48	3.299(5)	159	1-x,1/2+y,1/2-z
	N3-H3N···Cl1	0.86	2.32	3.159(5)	165	1-x,1/2+y,1/2-z
	C6-H6···O3	0.93	2.34	2.901(9)	119	x, y, z
	C10-H10···O3	0.93	2.38	2.934(9)	118	x, y, z
	C16-H16B···O1	0.97	2.61	3.515(1)	154	x, y, z
	C15-H15A···Cl1	0.97	2.92	3.861(7)	163	x, y, z
	C11-H11A···Cl1	0.97	2.74	3.669(7)	161	x, y, z
	C20-H20B···Cl1	0.97	2.89	3.748(8)	147	x, y, z
1b	N2-H2N···Br1	0.86	2.06	3.838(6)	151	-x,1-y,-z
	N3-H3N···O4	0.86	2.05	2.898(8)	170	1-x,1-y,-z
	C4-H4···Br1	0.93	2.86	3.753(8)	161	x,y,z
	C6-H6···O3	0.93	2.23	2.798(8)	119	x,y,z
	C10-H10···O3	0.93	2.29	2.867(9)	119	x,y,z
	C18-H18A···O3	0.97	2.42	3.348(10)	161	x,-1+y,z
	O4-H4A···Br1	0.85	2.70	3.413(7)	143	x,y,z
	O4-H4B···Br1	0.85	2.37	3.206(6)	167	1-x,1-y,-z
	C18-H18B···Br1	0.97	2.92	3.851(10)	162	x,y,z
2a	N1-H1···Cl1	0.86	2.27	3.115(6)	168	x,y,z
	N2-H2···Cl1	0.86	2.50	3.317(6)	158	x,y,z
	C8-H8···O1	0.93	2.34	2.908(7)	119	x,y,z
	C12-H12···O1	0.93	2.34	2.929(7)	121	x,y,z
	C14-H14B···O1	0.97	2.55	3.510(8)	170	x,1-y,1/2+z
	C24-H24A···Cl1	0.97	2.67	3.589(6)	158	x,y,z
2b	N1-H1N···Br1	0.86	2.63	3.441(4)	159	x,y,z
	N2-H2N···Br1	0.86	2.47	3.312(4)	167	x,y,z
	C6-H6···O1	0.93	2.28	2.855(6)	120	x,y,z
	C11-H11···O1	0.93	2.38	2.894(6)	115	x,y,z
3a	N1-H1N···Cl1	0.86	2.57	3.360(2)	153	x,y,z
	N2-H2N···Cl1	0.86	2.22	3.076(2)	170	x,y,z
	C4-H4···O1	0.93	2.25	2.850(3)	121	x,y,z
	C9-H9···O1	0.93	2.34	2.854(3)	114	x,y,z
	C11-H11···N1	0.93	2.54	2.850(3)	100	1-x,1-y,1-z
	C14-H14A···O1	0.97	2.55	3.318(4)	136	x,y,z
	C20-H20B···Cl1	0.97	2.81	3.691(4)	152	x,-1+y,z
	N2-H2N···Br1	0.86	2.36	2.367(4)	173	1+x,1+y,z

3b	N3-H3N··· Br1	0.86	2.70	2.709(5)	154	1+x,1+y,z
	C16-H16···Br1	0.97	2.89	3.767(3)	150	1+x, y, z
	C22-H22B···O3	0.97	2.58	2.584(2)	134	x, y, z
	C22-H22A···O2	0.97	2.66	3.334(5)	126	x, y, z
	C23-H23A···O1	0.97	2.66	3.534(3)	149	x, y, z
	C24-H24A···O3	0.97	2.64	3.394(4)	134	x, y, z
	C27-H27A···O3	0.97	2.69	3.666(4)	175	x, y, z
	C28-H28A···O2	0.97	2.63	3.522(4)	151	x, y, z
4a	N1-H1N···Cl1	0.86	2.28	3.115(4)	165	x,y,z
	N2-H2N···Cl1	0.86	2.53	3.326(4)	155	x,y,z
	C7-H7···O1	0.93	2.27	2.835(6)	119	x,y,z
	C11-H11···O1	0.93	2.26	2.852(6)	121	x,y,z
	C13-H13···N2	0.93	2.53	2.841(5)	100	-x,1-y,-z
	C17-H17A···O1	0.97	2.49	3.414(6)	158	x,1-y,1/2+z
	C22-H22B···Cl1	0.97	2.74	3.642(5)	155	x,y,z
4b	N10-H10N···Br1	0.86	2.67	3.472(4)	157	x,y,z
	N17-H17N···Br1	0.86	2.42	3.258(4)	166	x,y,z
	C5-H5···O25	0.93	2.29	2.856(7)	119	x,y,z
	C24-H24···O25	0.93	2.26	2.851(8)	121	x,y,z
	C28-H28B···O25	0.97	2.47	3.390(9)	159	x,1-y,1/2+z
	C29-H29A···Br(1)	0.97	2.93	3.803(6)	151	x,1+y,z
	C35-H35A···Br(1)	0.97	2.80	3.702(6)	155	x,y,z
	C57-H57···N10	0.93	2.53	2.841(7)	100	x,y,z

Table S2: Contact contributions from the d_{norm} surface areas of dipodal segments in free receptors and in anion complexes**.**

Bond	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
C···H	21.4	16.9	11.8	9.5	20.3	19.9	15.2	14.7
O···H	19.6	27.6	10.5	3.4	20.5	20.3	116	11.8
F···H	0	0	24.8	36.4	0	0	24.6	24
N···H	4	4.6	2.4	1.7	3.9	3.9	2.4	2.4
H···H	37.8	33.6	21.4	22.3	41.2	41.2	25.1	25
Cl···H	12.7	0	19.2	0	11.2	0	8.5	0
Br···H	0	13.4	0	12.7	0	12.4	0	9.3

References:

1. D. Brynn Hibbert and P. Thordarson, Chem Commun, 2016, **52**, 12792-12805.

2**.** http://supramolecular.org.