Supplementary Information for:

A subtle interplay of C-H hydrogen bonds in complexation of anions of varied dimensionality by a nitro functionalized tripodal podand

*Sandeep Kumar Dey, Bimlesh Ojha and Gopal Das**

Department of Chemistry, Indian Institute of Technology Guwahati, Assam-781039, India.

E-mail: gdas@iitg.ernet.in

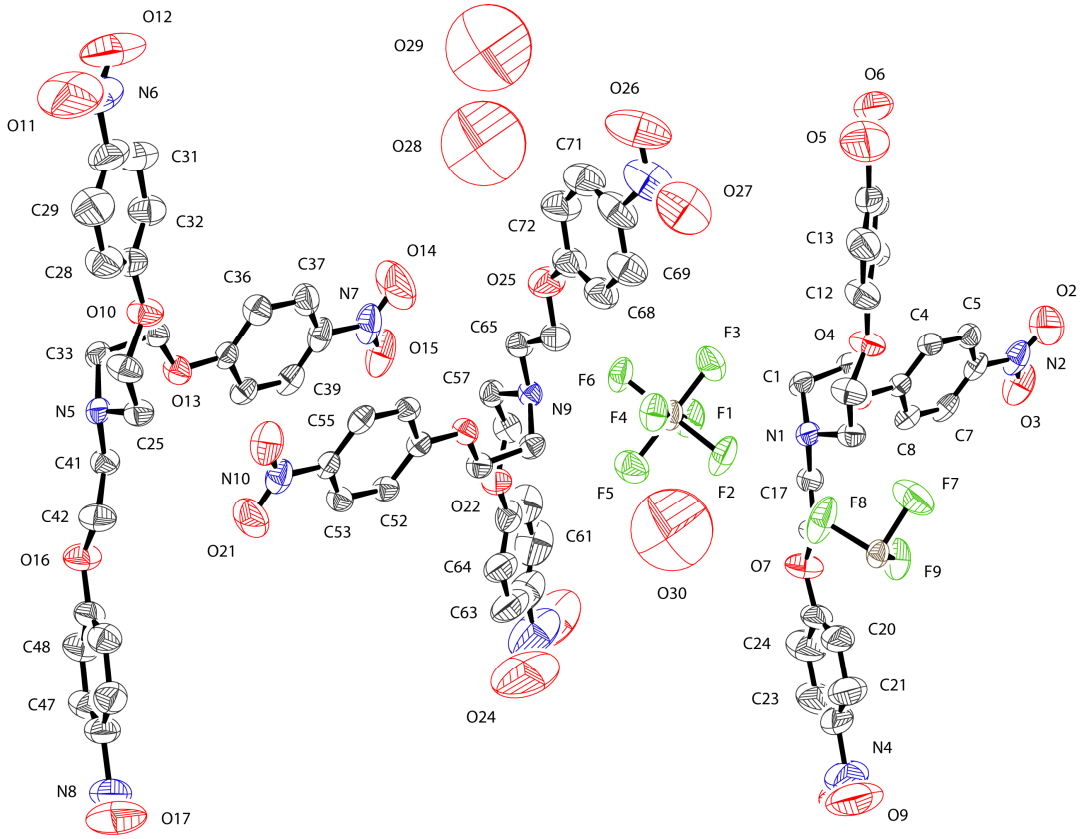

Figure S1. ORTEP plot (50 % probability ellipsoids) of [H**L**$^{+}$]•[SiF_6^{-}]•1.3 H_20 (**6**) along with atom numbering scheme.

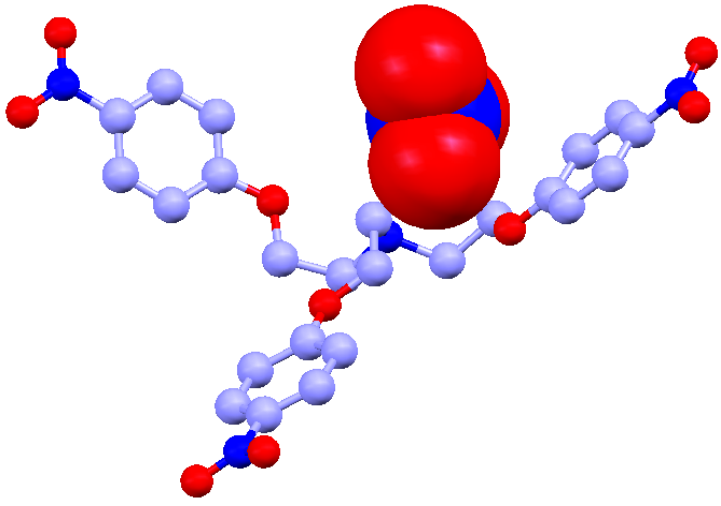

Figure S2. Crystal structure of [H**L**$^{+}$]•[NO_3^{-}] (**3**) depicting the tripodal cleft shaped cavity in H**L**$^{+}$ unit with the nitrate being placed within the tripodal cleft.

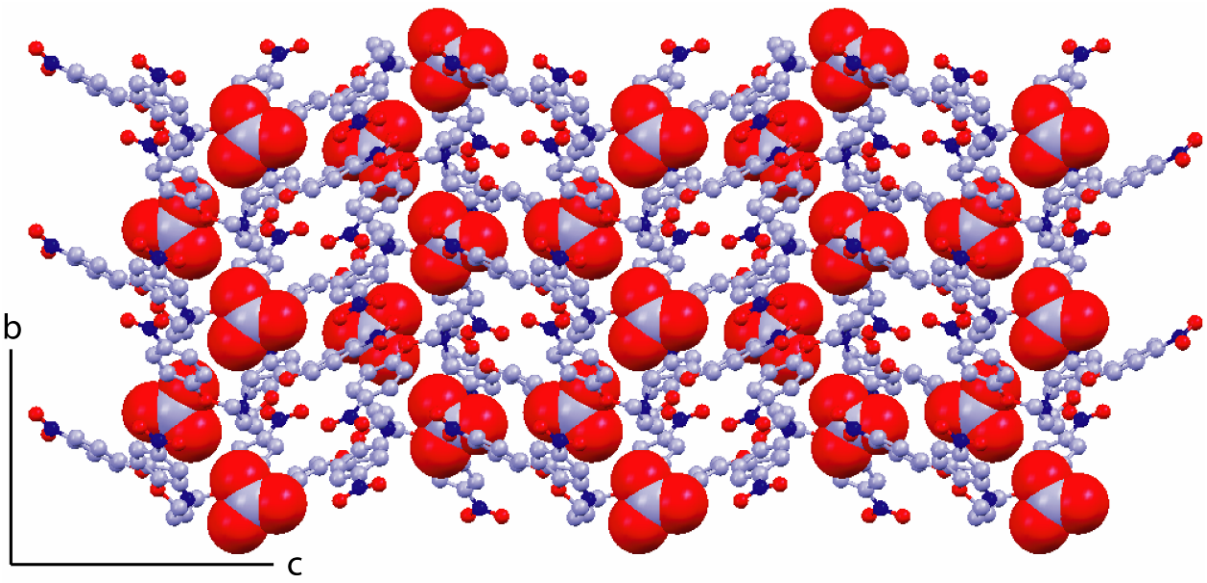

Figure S3. Crystal packing diagram of [H**L**$^{+}$]•[NO_3^-] (**3**) as viewed down the crystallographic *a*-axis showing the zigzag arrangement of the nitrate anions along *b*-axis.

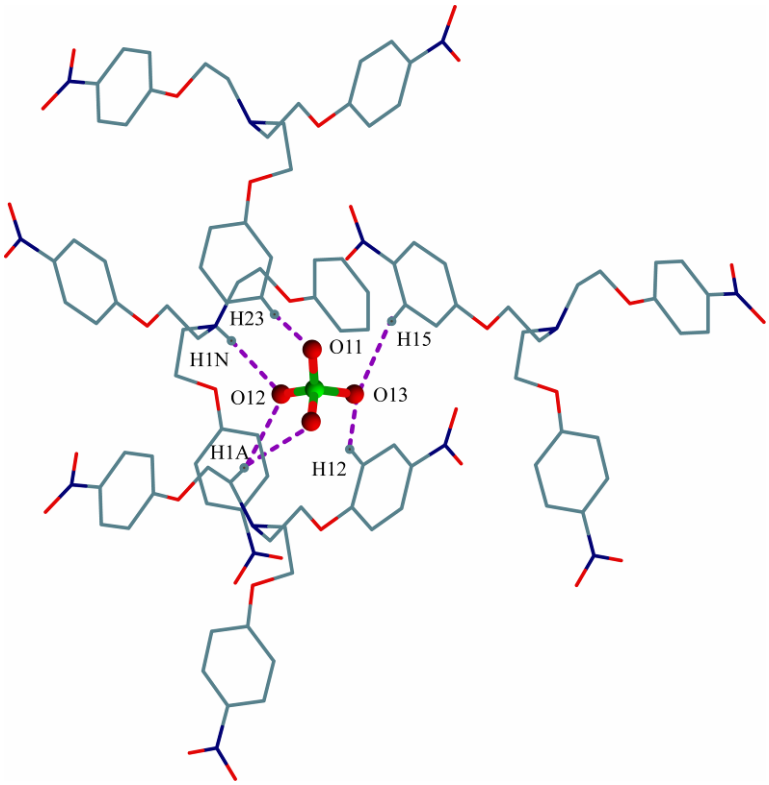

Figure S4. Close-up view of perchlorate binding by four encircling H**L**$^{+}$ tripodal receptor molecules in complex [H**L**$^{+}$]•[ClO_4^-] (**4**).

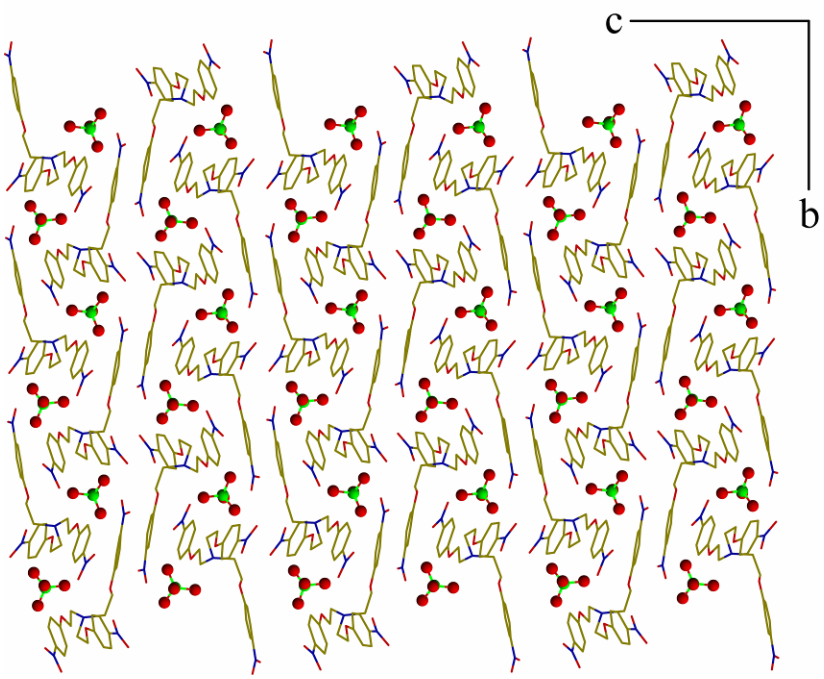

Figure S5. Crystal packing diagram of [H**L**$^{+}$]•[ClO_4^-] (**4**) as viewed down the crystallographic *a*-axis showing the zigzag arrangement of the perchlorate anions along *b*-axis.

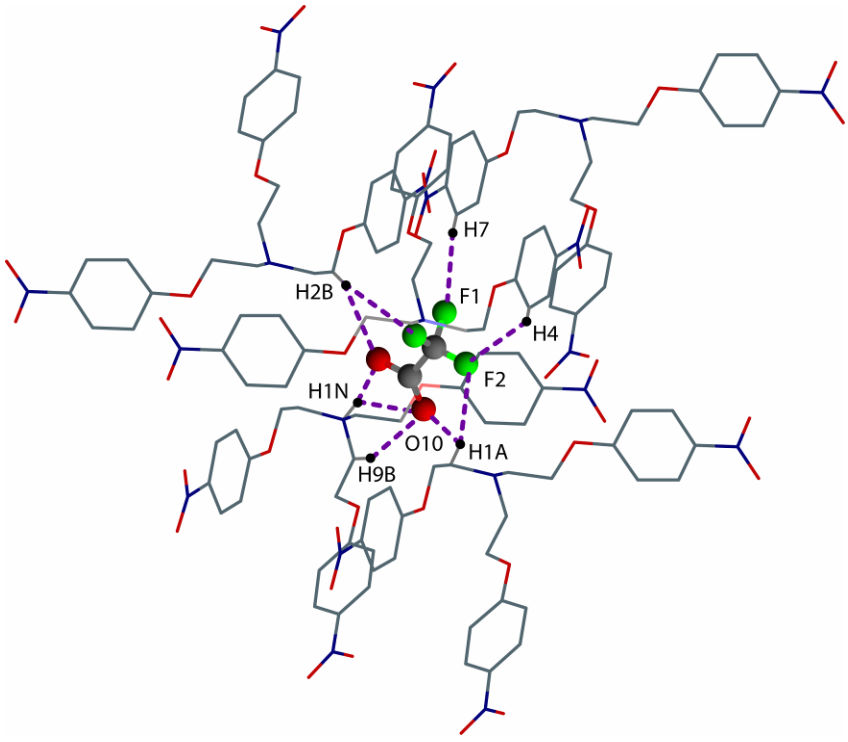

Figure S6. Close-up view for binding of trifluoroacetate by five encircling cationic H**L**$^{+}$ tripodal receptor molecules in complex [H**L**$^{+}$]•[CF_3COO^-] (**5**).

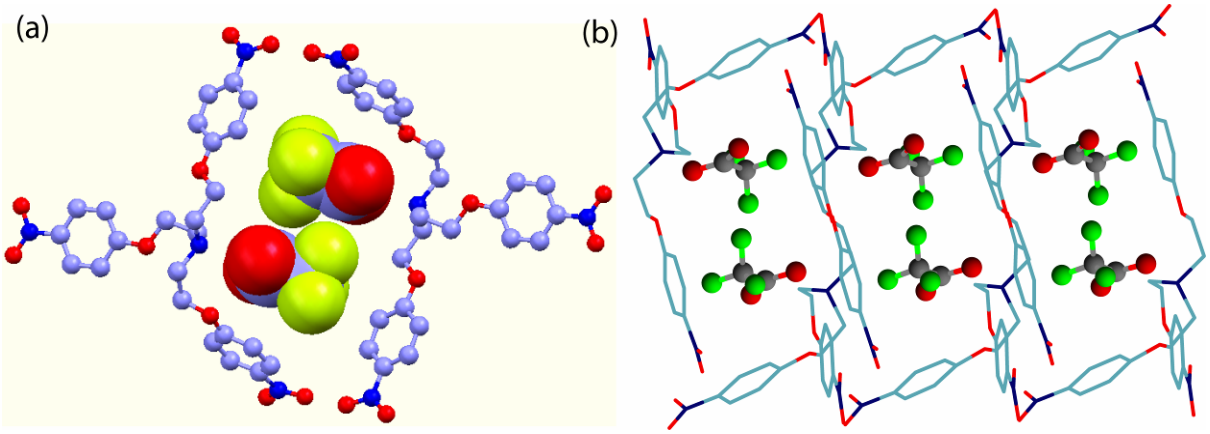

Figure S7. Close-up views for the encapsulation of dimeric trifluoroacetate anions within the tripodal cleft of H**L**$^{+}$ units in [H**L**$^{+}$]•[CF_3COO^{-}] (**5**) (Ball and stick representation).

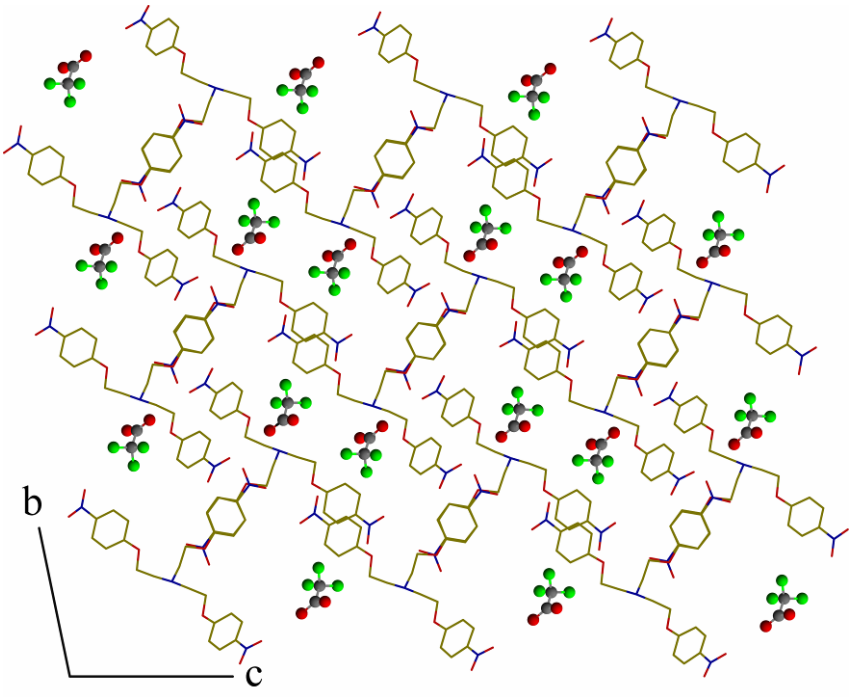

Figure S8. Crystal packing diagram of [H**L**$^{+}$]•[CF_3COO^{-}] (**5**) as viewed down the crystallographic *a*-axis.

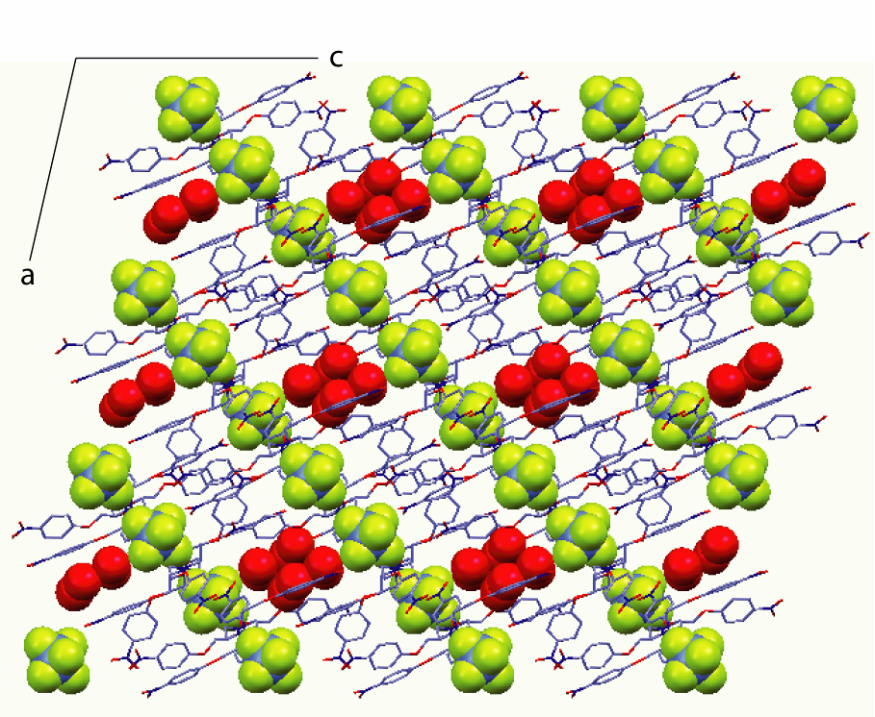

Figure S9. Crystal packing diagram of [2H**L**$^{+}$]•[SiF_6^{-2}]•2 H_2O (**6**) as viewed down the crystallographic *b*-axis showing the linear arrangement of SiF_6^{-} ions diagonally along the ac-plane and cluster of water molecules are positioned in the available space between the adjacent tripodal arrays.

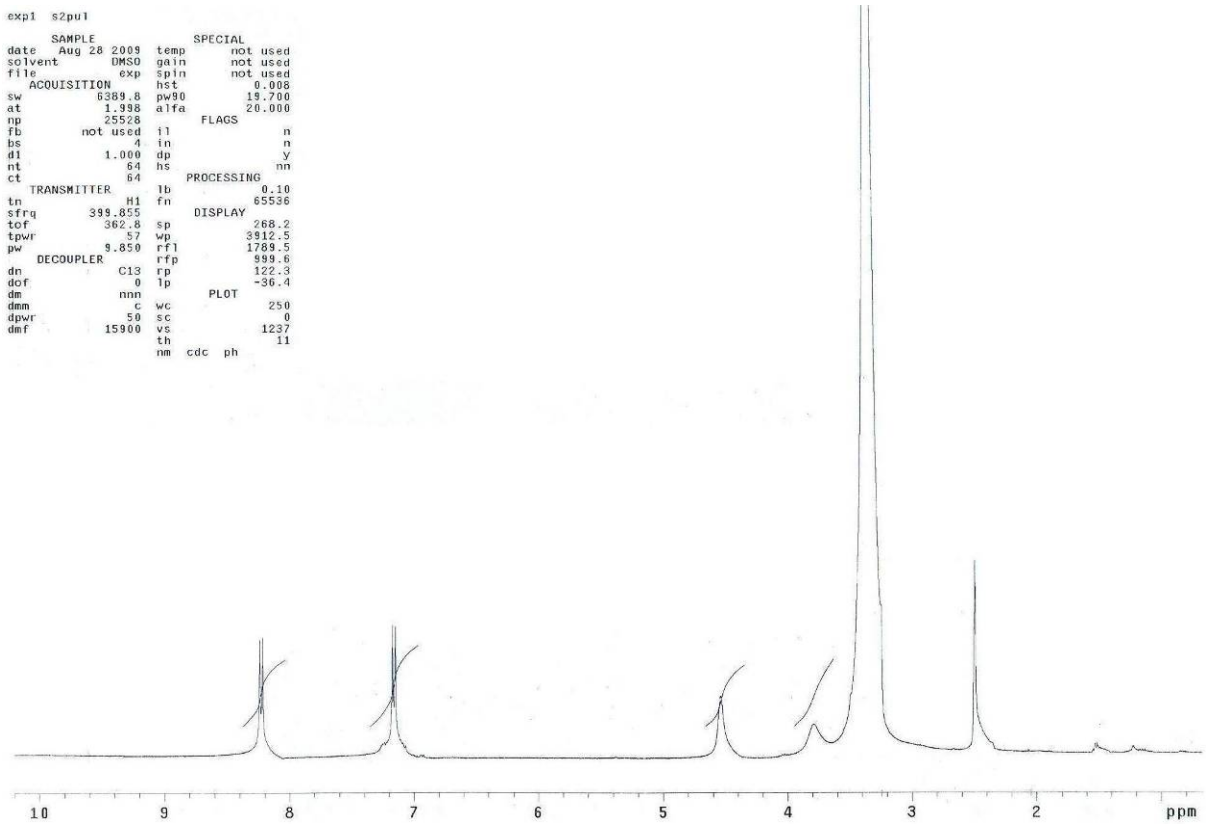

Figure S10. ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) of [H**L**$^{+}$]•[Cl^{-}] (**1**) in DMSO-d_6.

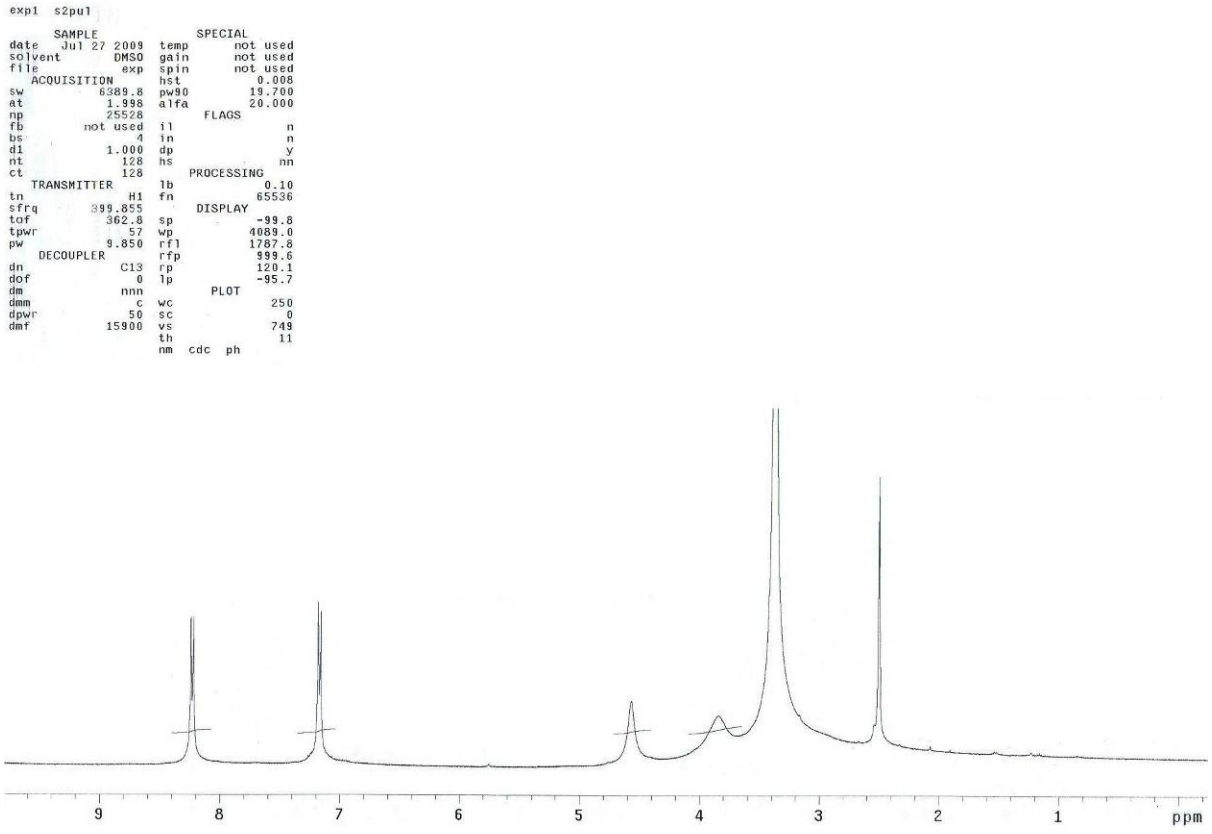

Figure S11. ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) of [H**L**$^{+}$]•[Br^{-}] (**2**) in DMSO-d_6.

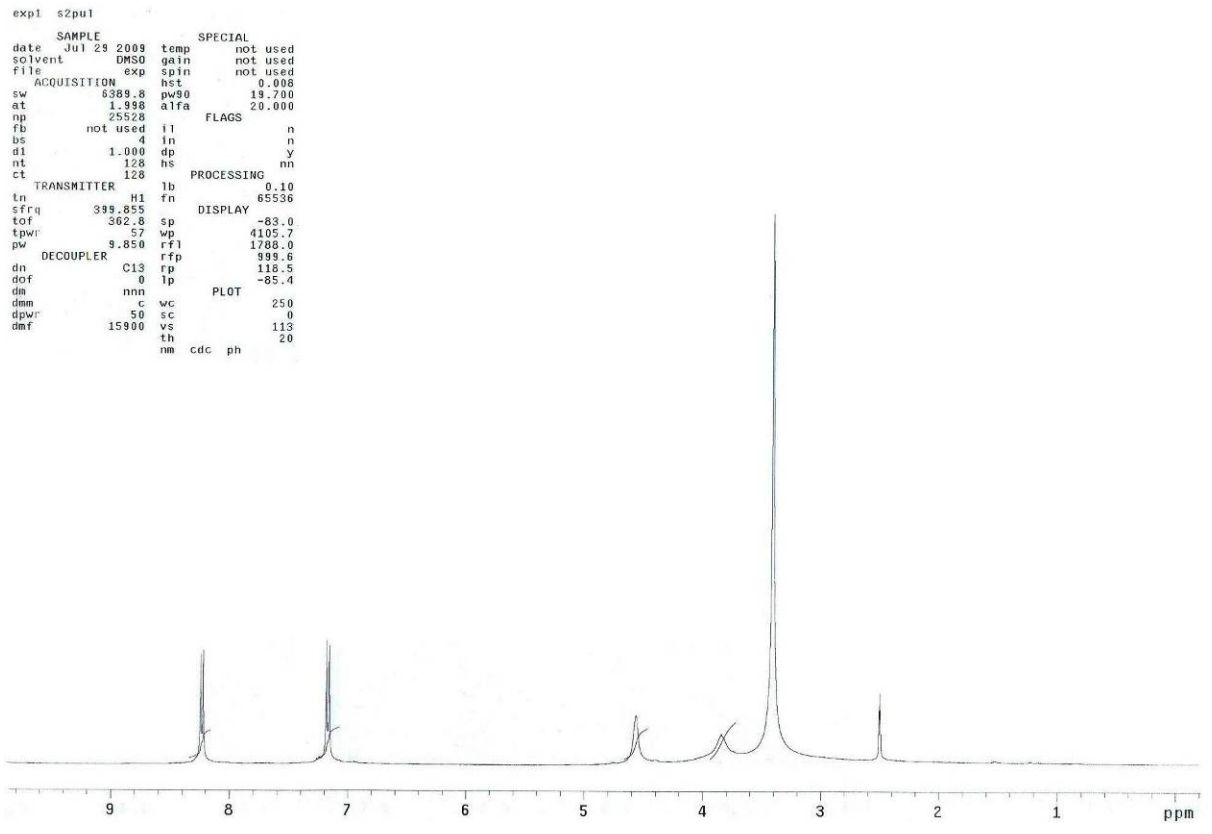

Figure S12. ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) of [H**L**$^{+}$]•[NO_3^{-}] (**3**) in DMSO-d_6.

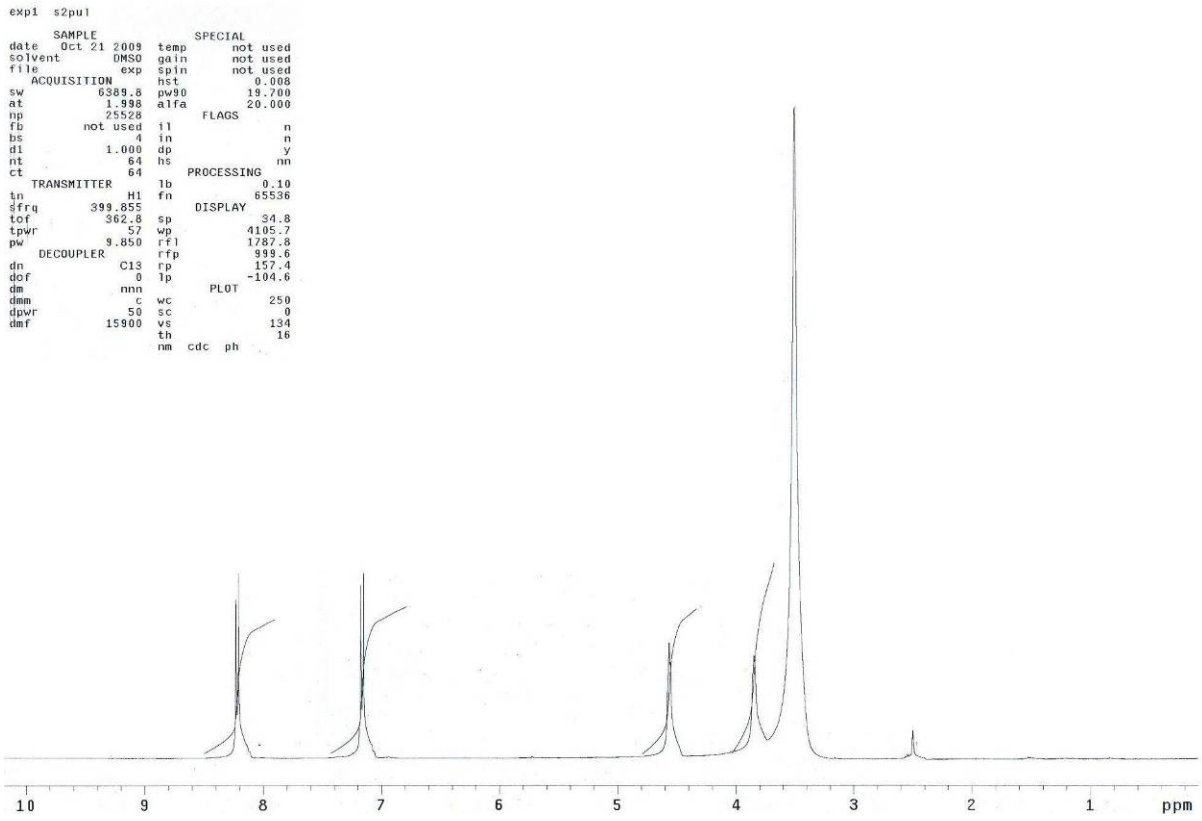

Figure S13. ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) of [H**L**$^{+}$]•[ClO_4^-] (**4**) in DMSO-d_6.

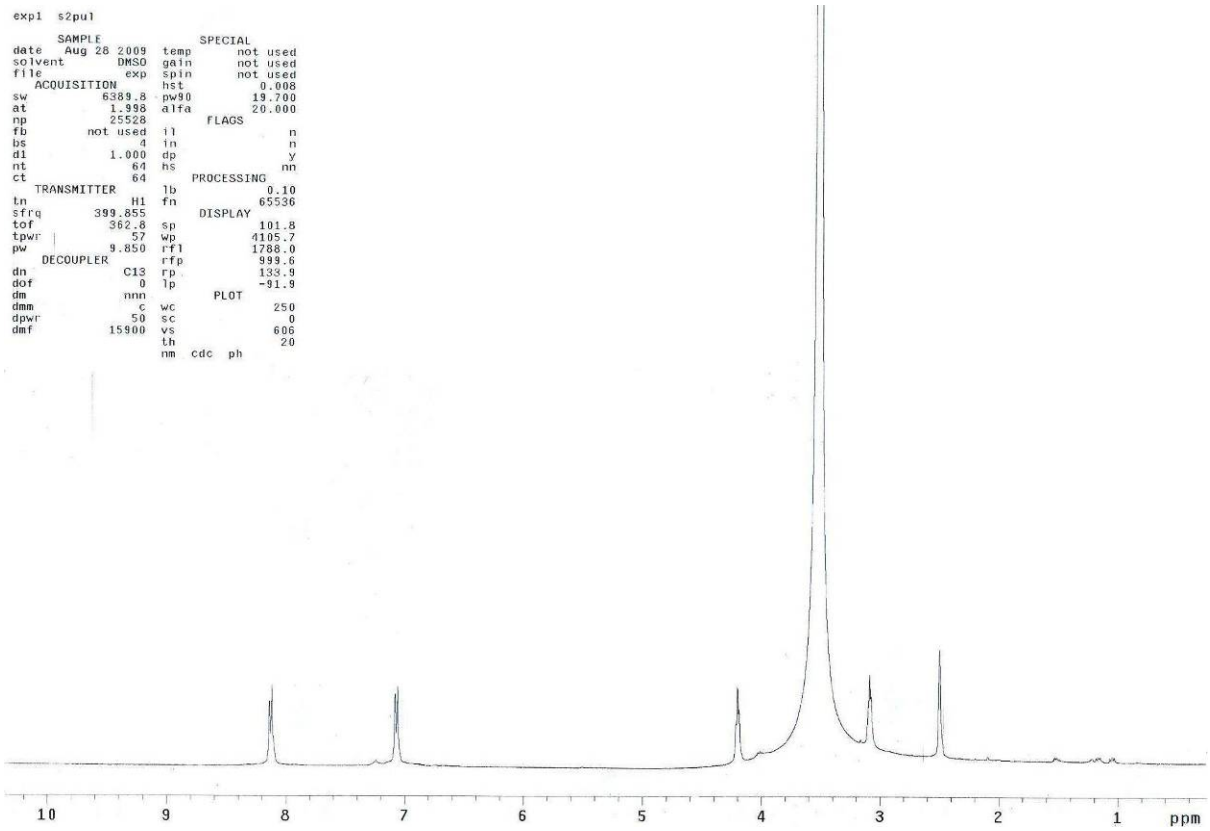

Figure S14. ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) of [H**L**$^{+}$]•[CF_3COO^-] (**5**) in DMSO-d_6.

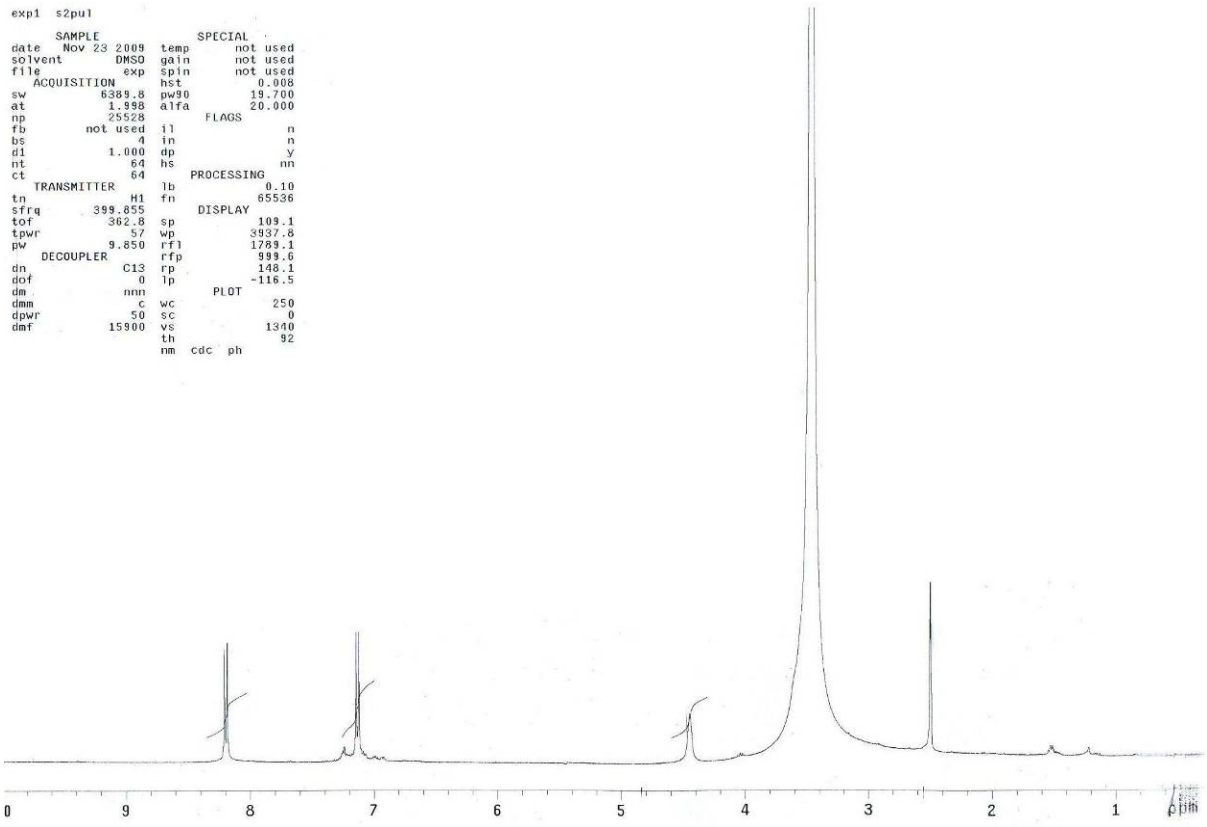

Figure S15. ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) of [H**L**$^{+}$]•[SiF_6^{-}] (**6**) in DMSO-d_6.

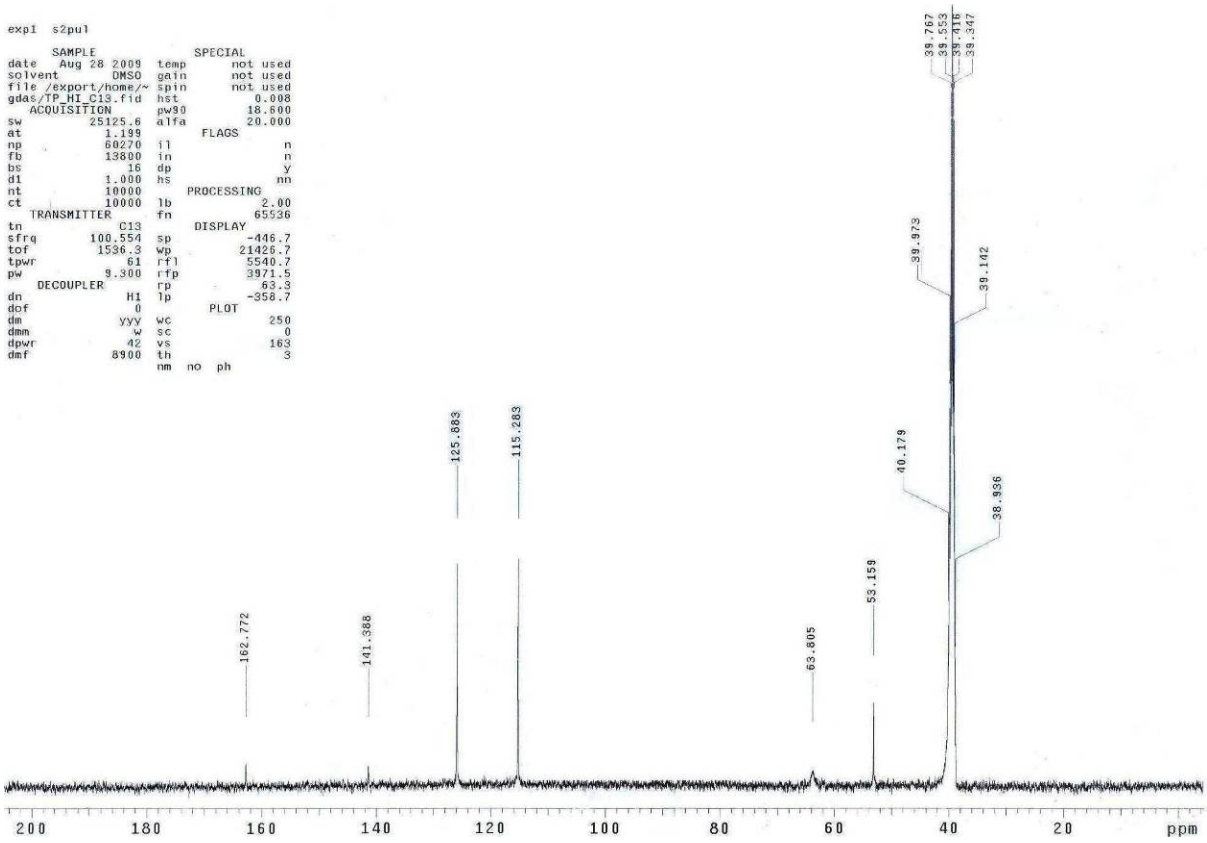

Figure S16. ^{13}C-NMR spectrum (100 MHz, DMSO-d_6) of [H**L**$^{+}$]•[Cl^{-}] (**1**) in DMSO-d_6.

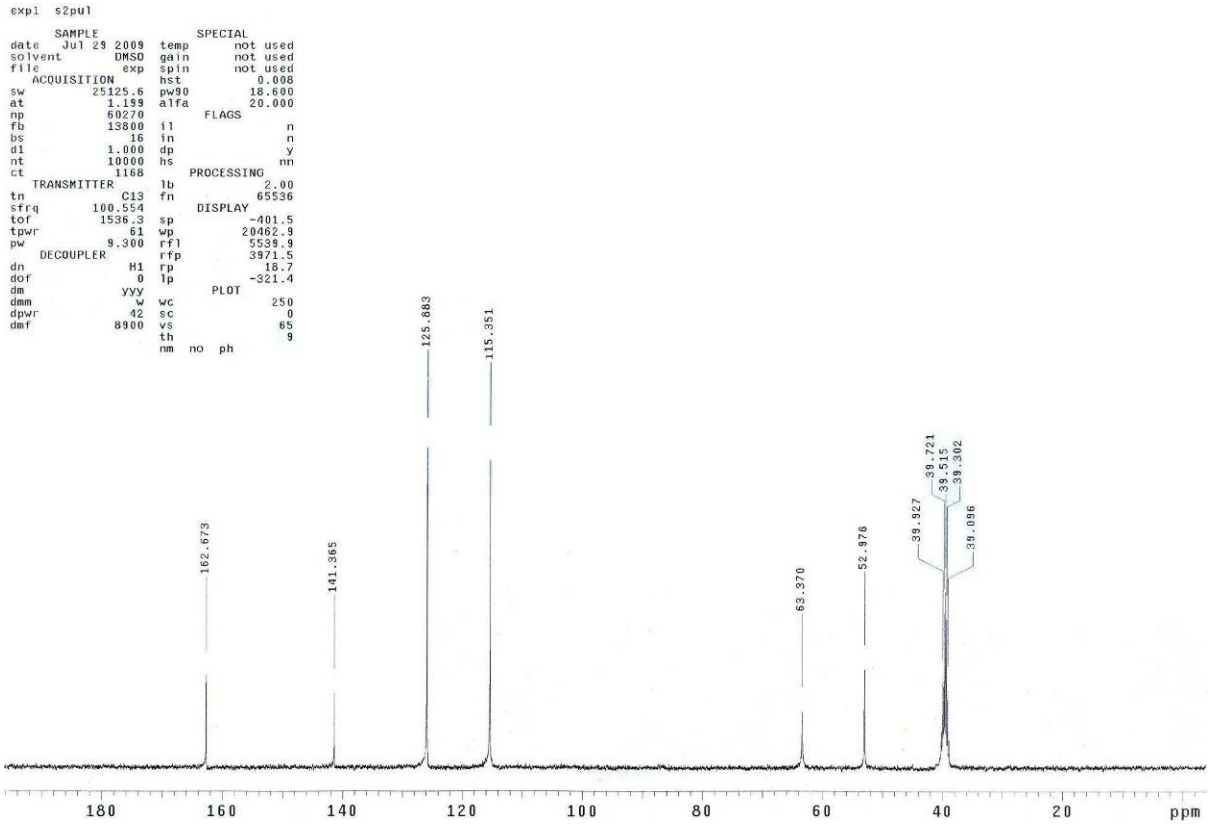

Figure S17. ^{13}C-NMR spectrum (100 MHz, DMSO-d_6) of [H**L**$^+$]•[Br$^-$] (**2**) in DMSO-d_6.

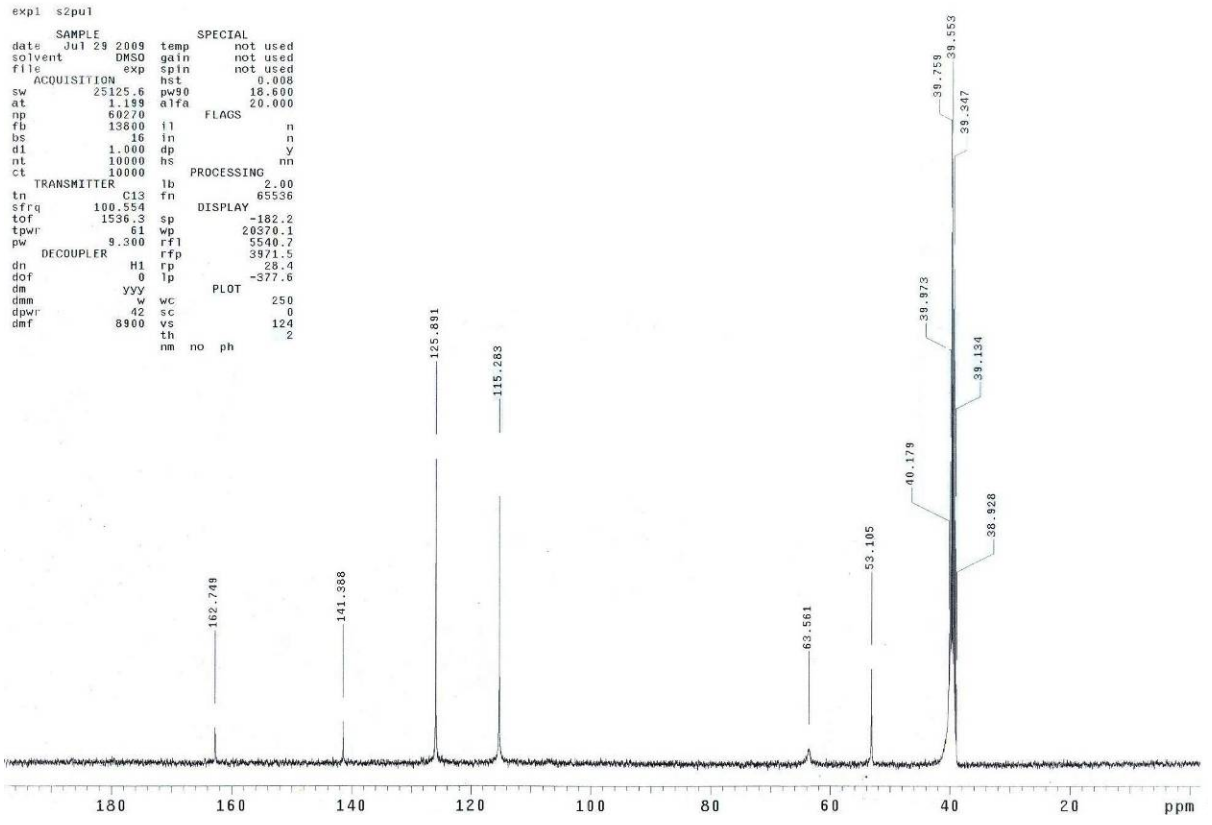

Figure S18. ^{13}C-NMR spectrum (100 MHz, DMSO-d_6) of [H**L**$^+$]•[NO$_3^-$] (**3**) in DMSO-d_6.

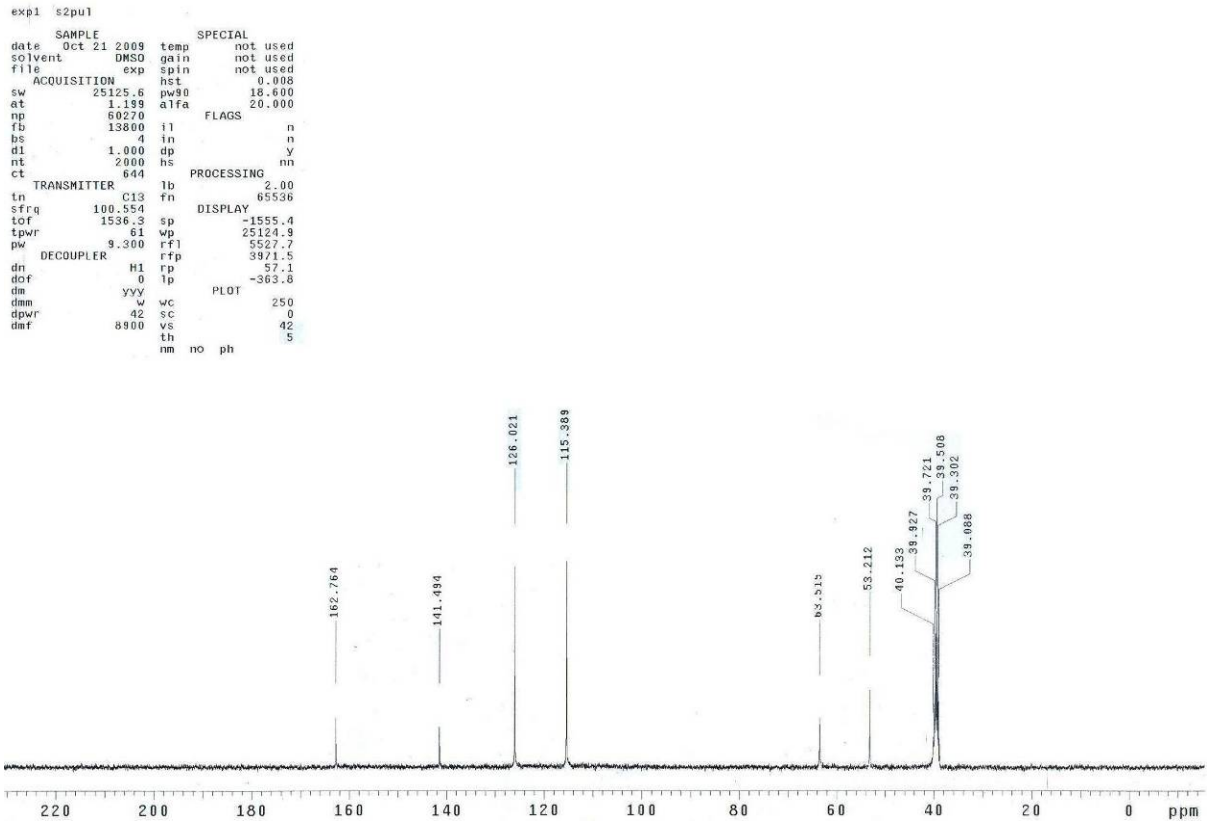

Figure S19. ^{13}C-NMR spectrum (100 MHz, DMSO-d_6) of [H**L**$^+$]•[ClO_4^-] (**4**) in DMSO-d_6.

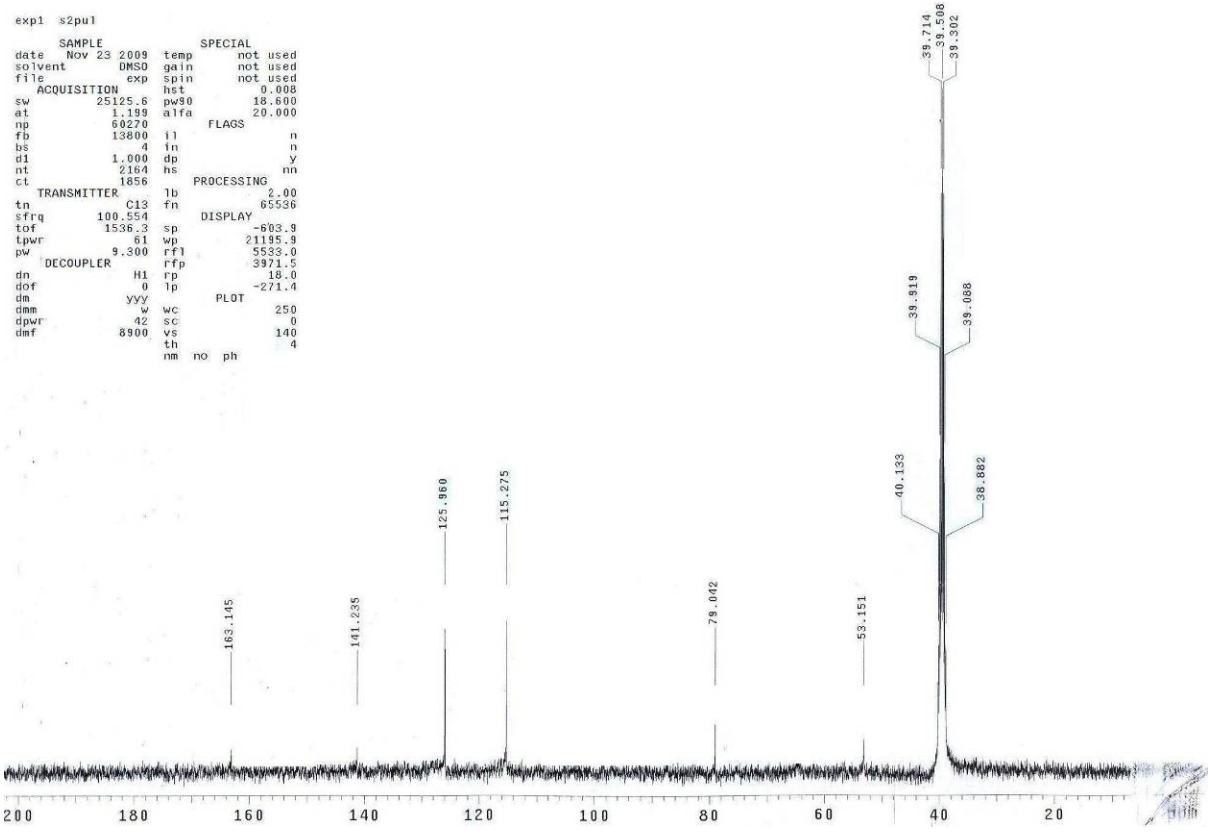

Figure S20. ^{13}C-NMR spectrum (100 MHz, DMSO-d_6) of [H**L**$^+$]•[CF_3COO^-] (**5**) in DMSO-d_6.

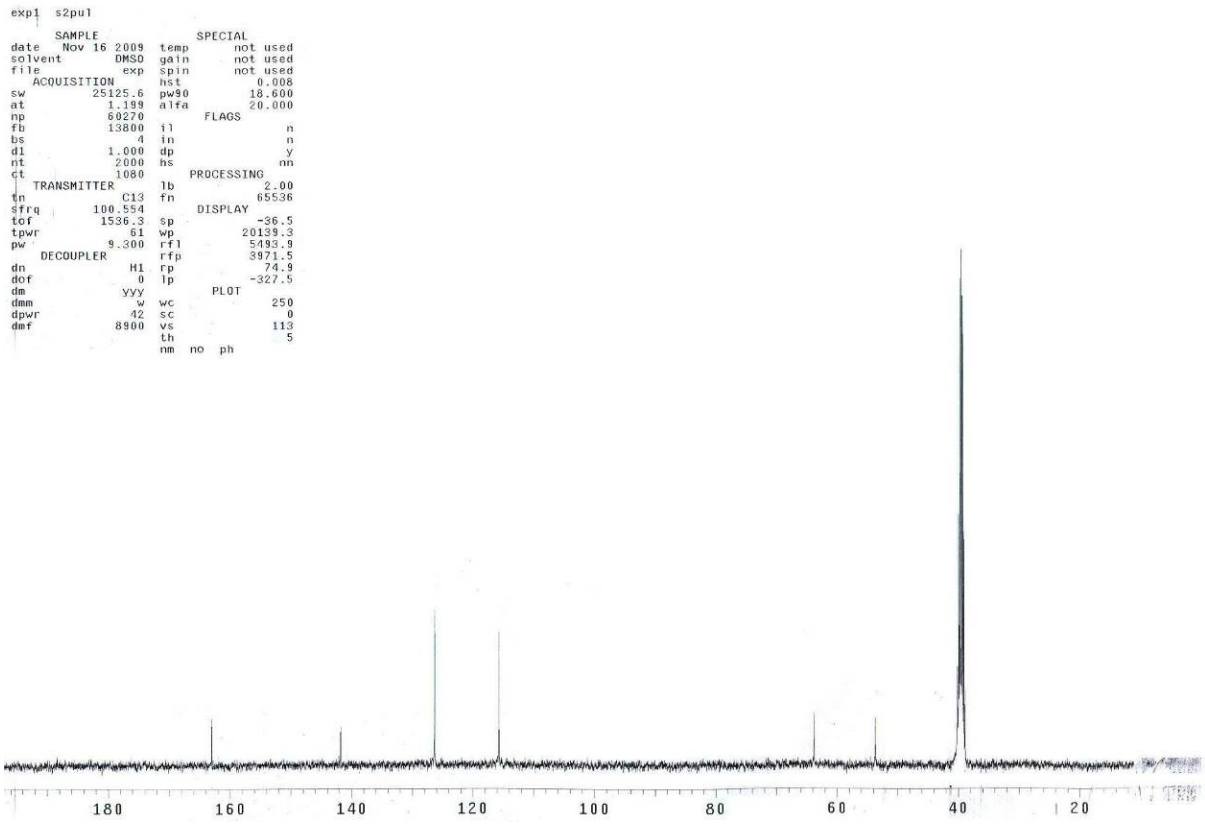

Figure S21. ^{13}C-NMR spectrum (100 MHz, DMSO-d_6) of [H**L**$^+$]•[SiF_6^-] (**6**) in DMSO-d_6.

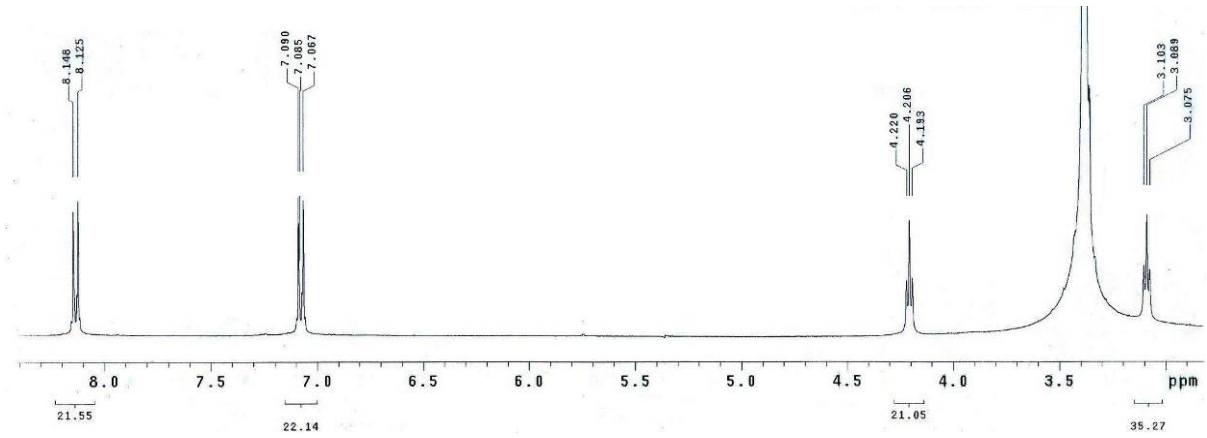

Figure S22. Selected region of the ^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of receptor **L.**

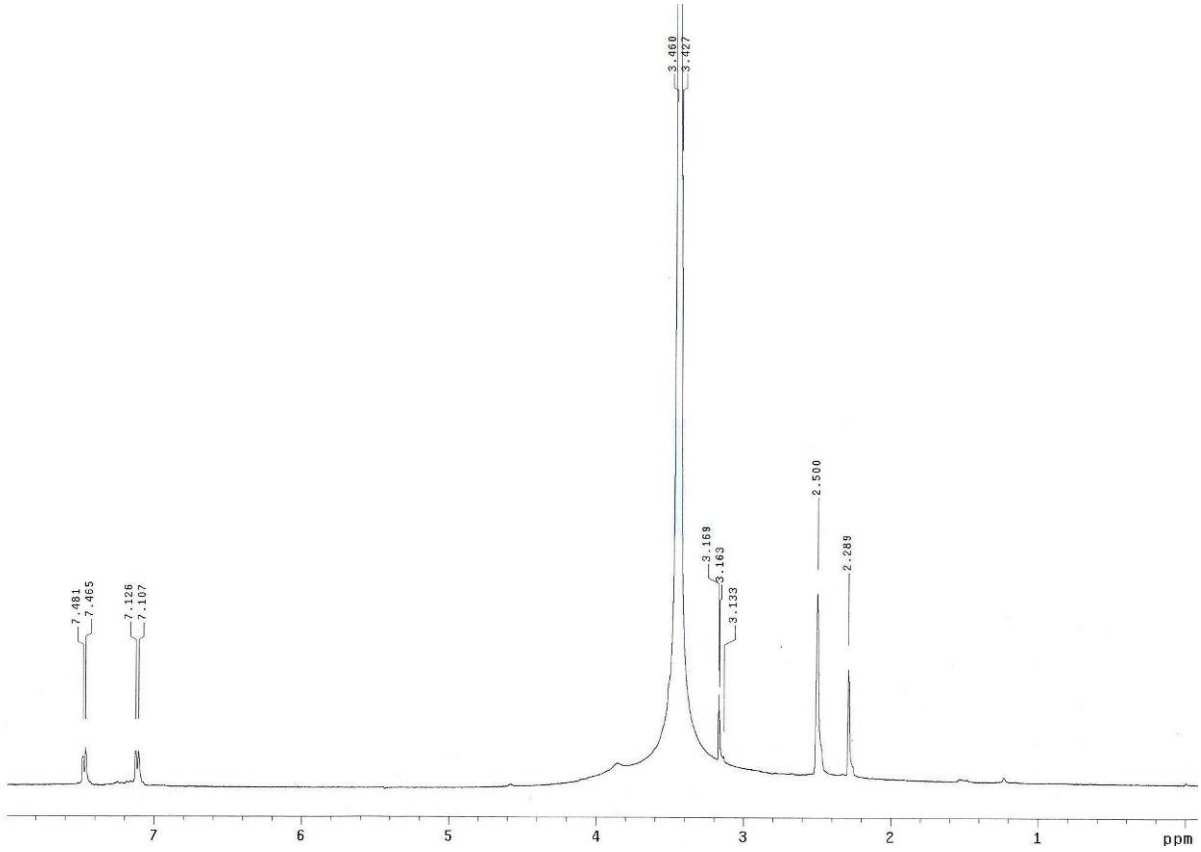

Figure S23. ^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of receptor **L** with 1 equivalent of *p*-toluene sulphonic acid (PTSA), [H**L**$^{+}$]•[OTs] salt**.**

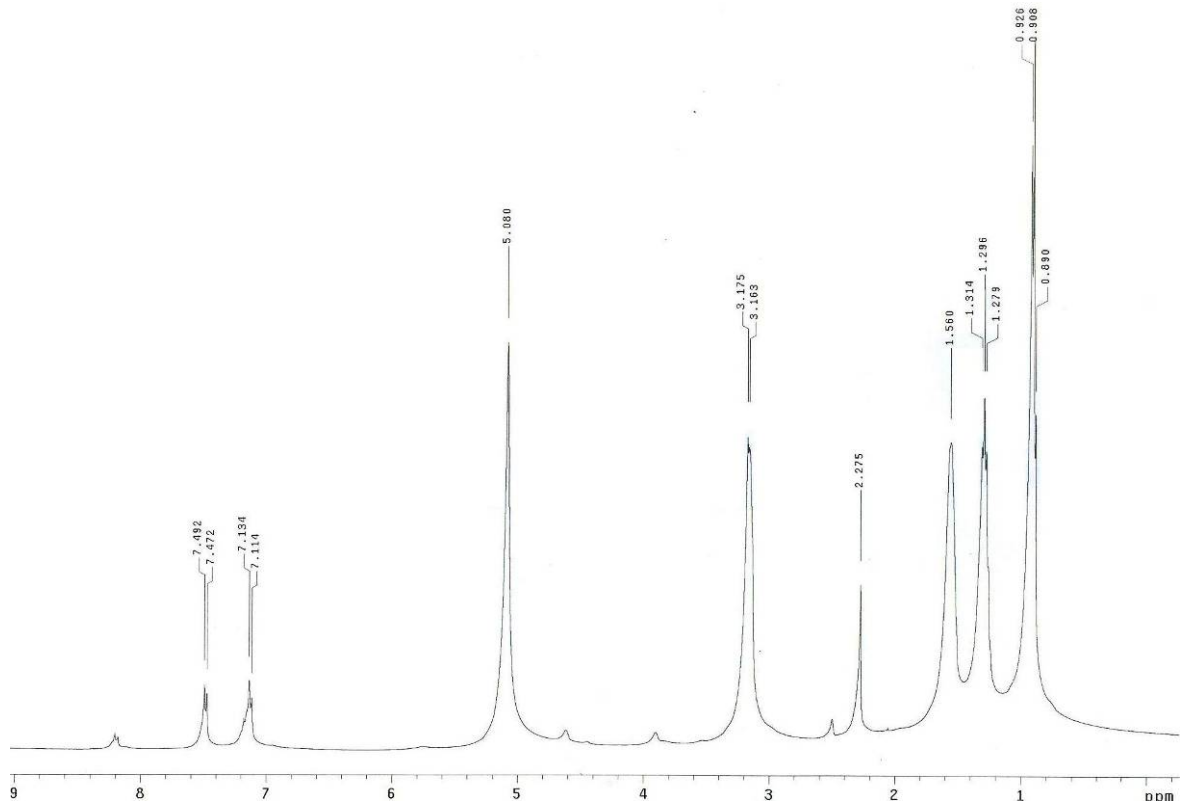

Figure S24. ^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of [H**L**$^{+}$]•[OTs] salt, doped with 1.2 equivalent of tetrabutyl ammonium bromide.

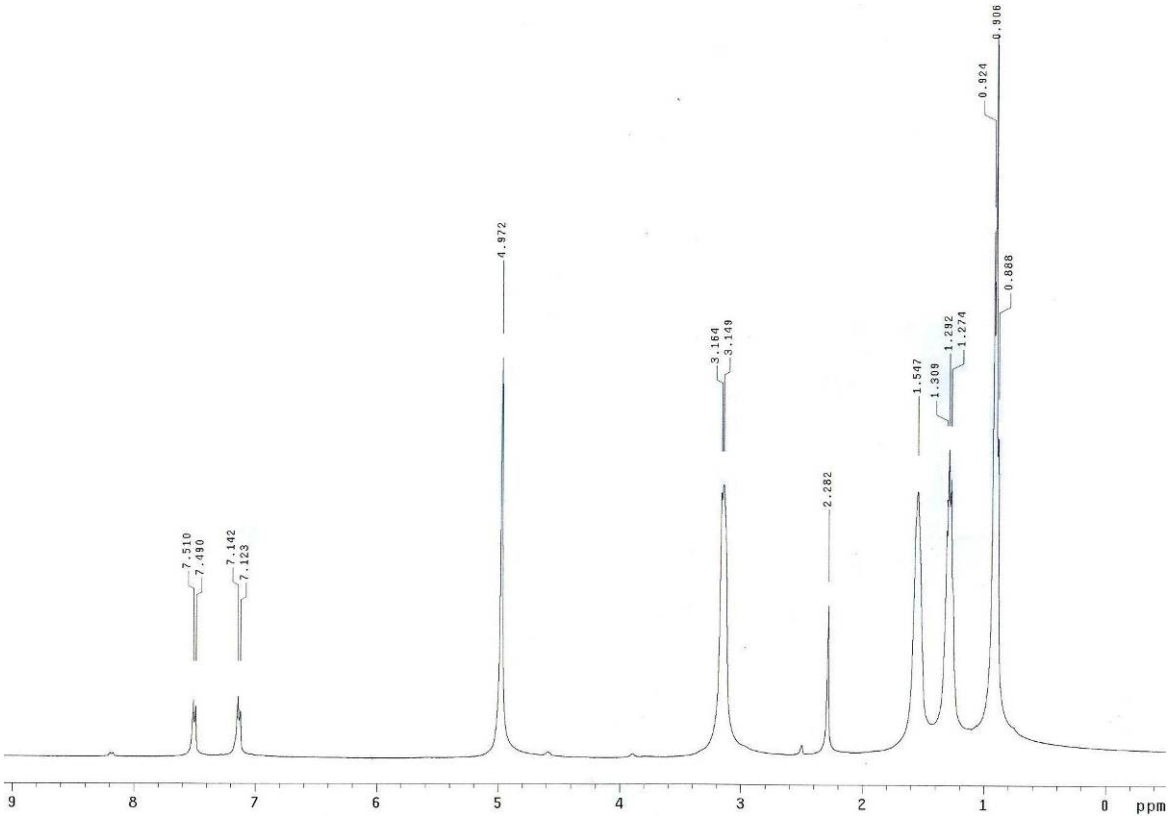

Figure S25. ^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of [H**L**$^{+}$]•[OTs] salt, doped with 1.2 equivalent of tetrabutyl ammonium nitrate.

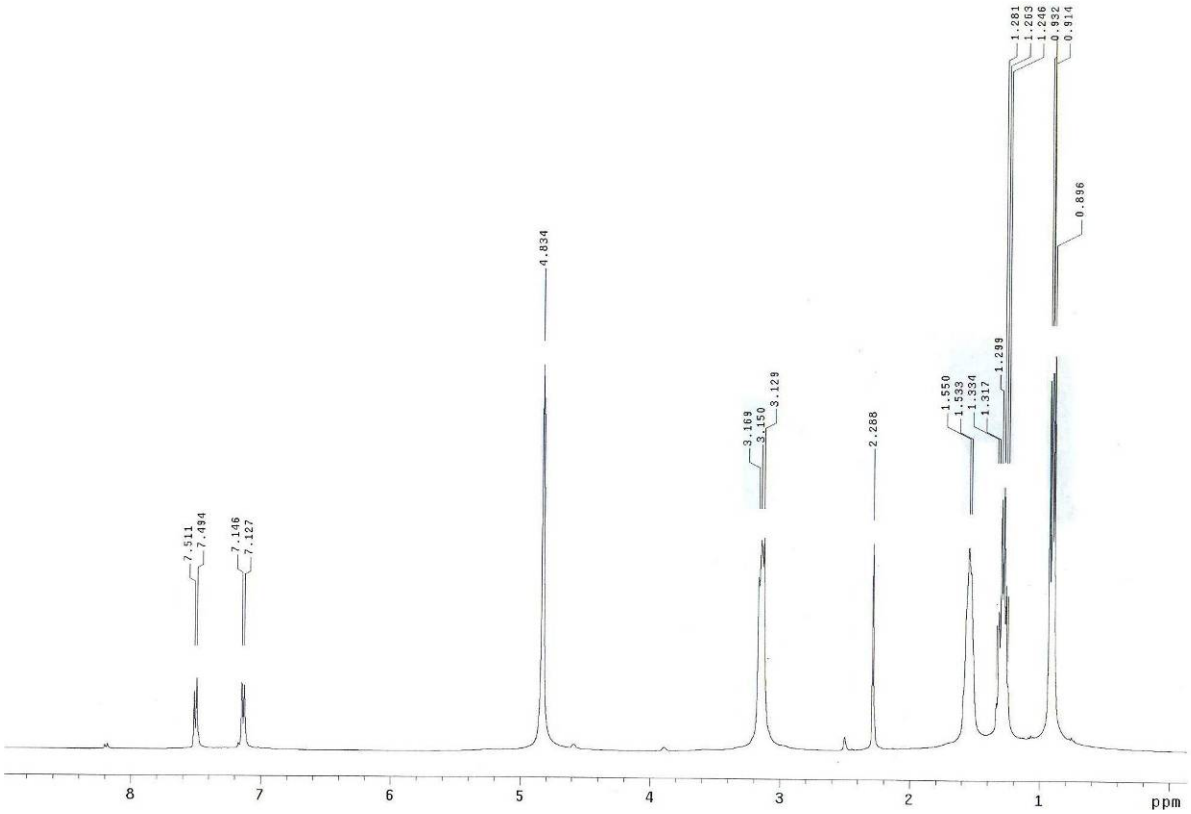

Figure S26. ^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of [H**L**$^{+}$]•[OTs] salt, doped with 1.2 equivalent of tetrabutyl ammonium perchlorate.

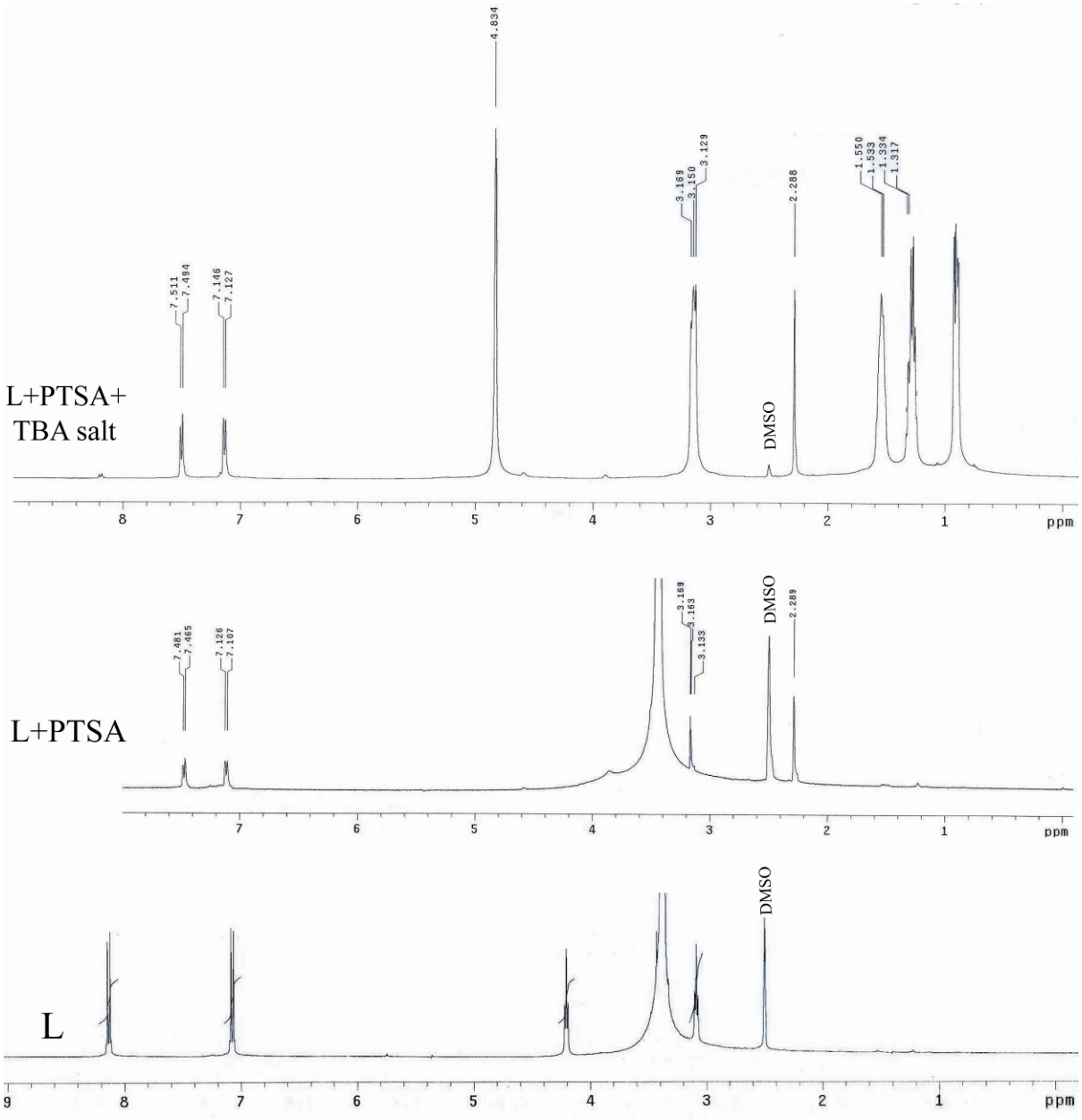

Figure S27. ^{1}H-NMR (400 MHz, DMSO-d_6) spectra of receptor **L** (below), **L** with 1 equivalent of *p*-toluene sulphonic acid (PTSA), [H**L**$^{+}$]•[OTs] salt (middle) and [H**L**$^{+}$]•[OTs] with 1.2 equivalent of tetrabutyl ammonium (TBA) salt of inorganic anions (above).

Table S1. Selected interligand non-covalent interactions among **L**H$^+$ units in anionic complexes **1**-**6**.

D-H····A	*d*(H····A) (Å)	*d*(D····A) (Å)	∠(DHA) (°)
[H**L**$^+$]•[Cl$^-$] (**1**)			
C16-H16····O2	2.51	3.390	156
C2-H2B····O3	2.60	3.229	121
C10-H10A····O3	2.59	3.560	178
C8-H8····O3	2.33	3.222	160
C17-H17B····O5	2.70	3.349	124
C20-H20····O6	2.52	3.428	164
C7-H7····C2g	3.037	3.970	157
C1g•••C1g		4.183	
C3g•••C3g		3.610	
C1g•••C3g		3.858	
[H**L**$^+$]•[Br$^-$] (**2**)			
C24-H24····O3	2.63	3.499	162
C2-H2A····O5	2.55	3.559	172
C10-H10A····O5	2.59	3.263	125
C16-H16····O5	2.42	3.328	163
C8-H8····O6	2.52	3.415	160
C23-H23····O9	2.70	3.504	150
C3g•••C3g		3.601	
C3g•••C2g		3.906	
C15-H15•••C1g	3.056	3.924	156
[H**L**$^+$]•[NO_3^-] (**3**)			
C1-H1B····O3	2.70	3.594	152
C24-H24····O3	2.60	3.323	134
C2-H2A····O5	2.60	3.472	148
C17-H17B····O5	2.67	3.644	175
C4-H4····O6	2.48	3.399	168
C10-H10A····O6	2.58	3.256	126
C8-H8····O9	2.40	3.089	130
[H**L**$^+$]•[ClO_4^-] (**4**)			
C17-H17A····O2	2.54	3.367	142
C10-H10B····O3	2.71	3.594	151
C17-H17B····O3	2.33	3.235	154
C9-H9B····O5	2.51	3.373	147
C24-H24····O6	2.54	3.431	
C8-H8····O8	2.68	3.563	157
[H**L**$^+$]•[CF_3COO^-] (**5**)			
C9-H9A····O2	2.56	3.324	135
C10-H10A····O3	2.67	3.620	164
C17-H17B····O5	2.68	3.615	160
C17-H17B····O6	2.66	3.497	143
C20-H20····O6	2.56	3.155	121
C1g •••C1g		3.726	
C2g •••C2g		3.518	
[2H**L**$^+$]•[SiF_6^{2-}]•2H_2O (**6**)			
C9-H9B····O3	2.55	3.372	149
C33-H33A····O3	2.60	3.364	135
C50-H50A····O5	2.66	3.592	159
C1-H1B····O6	2.57	3.290	131
C53-H53····O9	2.67	3.413	136
C55-H55····O11	2.60	3.521	169
C50-H50B····O12	2.60	3.348	133
C1-H1A····O15	2.61	3.371	135
C65-H65A····O15	2.58	3.487	154
C16-H16····O17	2.56	3.381	146
C25-H25B····O20	2.46	3.339	149

C49-H49B····O20	2.69	3.405	130
C68-H68····O21	2.51	3.380	155
C34-H34A····O24	2.65	3.605	166
C69-H69····O27	2.71	3.546	149
C1g····C1g		3.688	
C1g····C5g		3.544	
C5g····C7g		3.671	
C7g····C7g		3.507	
C4g····C4g		3.629	

C1g = Centroid of ring C3-C8
C2g = Centroid of ring C11-C16
C3g = Centroid of ring C19-C24
*C4g = Centroid of ring C27-C32
*C5g = Centroid of ring C35-C40
*C7g = Centroid of ring C51-C56
* = Present only in complex **6**

Table S2. Molecular conformation: Relevant Torsion Angles in anion complexes **1**-**6** (τ_{ether} = atoms involving N_{amino}-C-C-O_{ether} and τ_{amino} = atoms involving C-N_{amino}-C-C).

Complexes	**1**	**2**	**3**	**4**	**5**	**6**
(a) τ_{ether}						
N1-C1-C2-O1	-161.67	60.29	-70.56	-55.88	-83.38	72.40
N1-C9-C10-O4	-58.78	160.80	56.50	168.30	80.23	-77.81
N1-C17-C18-O7	-79.42	79.01	90.27	-65.60	-74.81	166.97
(b) τ_{amino}						
C1-N1-C9-C10	- 54.64	58.73	48.06	56.86	65.14	56.19
C1-N1-C17-C18	50.78	179.95	-59.10	157.30	174.07	-178.68
C9-N1-C1-C2	- 57.98	52.65	63.95	174.10	52.08	54.66
C9-N1-C17-C18	178.33	-50.86	169.58	-75.56	-57.34	50.36
C17-N1-C1-C2	67.36	-177.41	-62.41	-57.43	178.66	-74.07
C17-N1-C9-C10	177.07	-67.64	177.70	-72.54	-60.42	-175.05