Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

Chloride Ion Recognition Using Thiourea/Urea Based Receptors Incorporated into 1,3-Disubstituted Calix[4]arenes

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General Experimental Procedures

All reagents were purchased from aldrich and used without further purification. THF was dried over sodium and benzophenone and kept over molecular sieves overnight before use. UV Spectra was recorded on SCHIMADZU UV-1700 spectrophotometer, with a quartz cuvette (path length: 1 cm). The cell holder was thermostatted at 25 ^{o}C. ^{1}H and ^{13}C NMR spectra were recorded on JEOL-FT NMR-AL 300MHz spectrophotometer using $CDCl_3$/ DMSO-d_6 as solvent and TMS as internal standards. Solutions of compound **3, 5, 7** and various tetrabutylammonium anions for UV studies were prepared in THF AR grade. All spectrophotometric titration curve were fitted with SPECFIT\32 software

UV-Vis Titrations

UV-Vis titrations were performed on $5x10^{-5}$ M solution of ligands **3**, **5** and **7** in THF. Typically, aliquots of freshly prepared Bu_4NX (X=CN^-, F^-, Cl^-, Br^-, I, OAc^- and NO_3^-) standard solutions (10^{-1}-$5x10^{-3}$ M in THF) were added and the UV-Vis spectra of the samples were recorded.

^{1}H NMR Titration and Job's Plot for Stoichiometry Determination of Compound 3-5 and 7-8 with Various Anions:

Stock solution (10mM) of compounds **3-5** and **7-8** were prepared in $CDCl_3$. Similarly, Stock solution (20mM) of anions (Fluoride, Chloride, Bromide, Iodide, Acetate, Cyanide and Nitrate as their tetrabutylammonium salts) were prepared in $CDCl_3$ for the ^{1}H NMR experiments.

ISE Membrane preparation and potential measurement[12a]

Membranes were prepared using DOS (plasticizer), PVC, ionophore (**3-5** / **7-8**) and N-Butyl-3-Methylimidazolium hexafluorophosphate (additive) dissolved in dry THF and evaporated slowly. The amounts of the various constituents of the membrane are given in Table S13

The potentiometric cell used was Ag|AgCl|1.031022 M NaCl|PVC membrane|test solution|Ag|AgCl. Membranes were conditioned in 0.01 M sodium chloride for 12 h and deionised water for half an hour prior to ISE titrations, unless stated otherwise. The pH of the solutions were varied using HNO_3/ Hexamine solutions.

^{1}H and ^{13}C NMR Data of Compounds 3-5 and 7-8

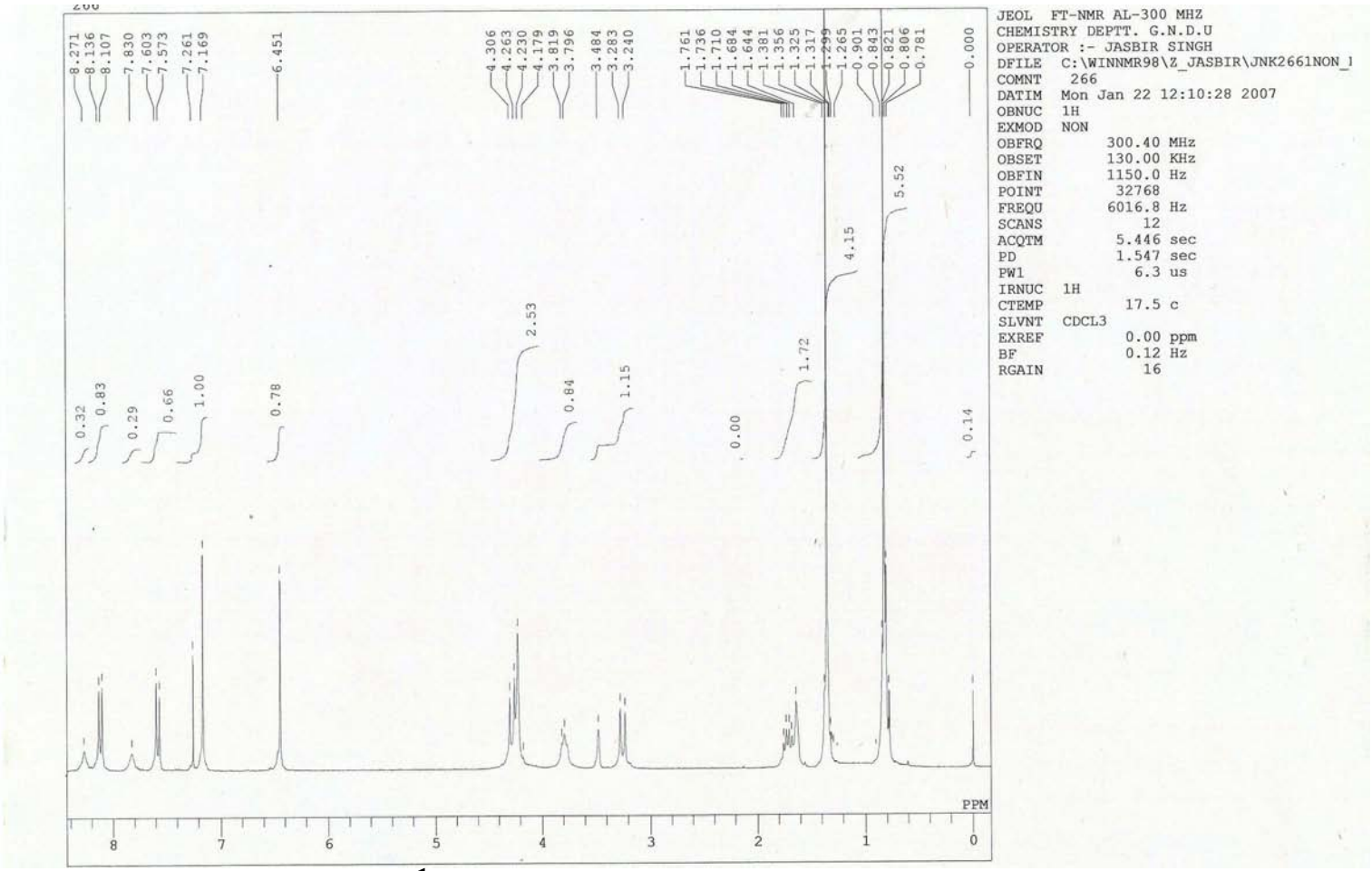

Figure S1: ^{1}H NMR Spectra of Compound 3

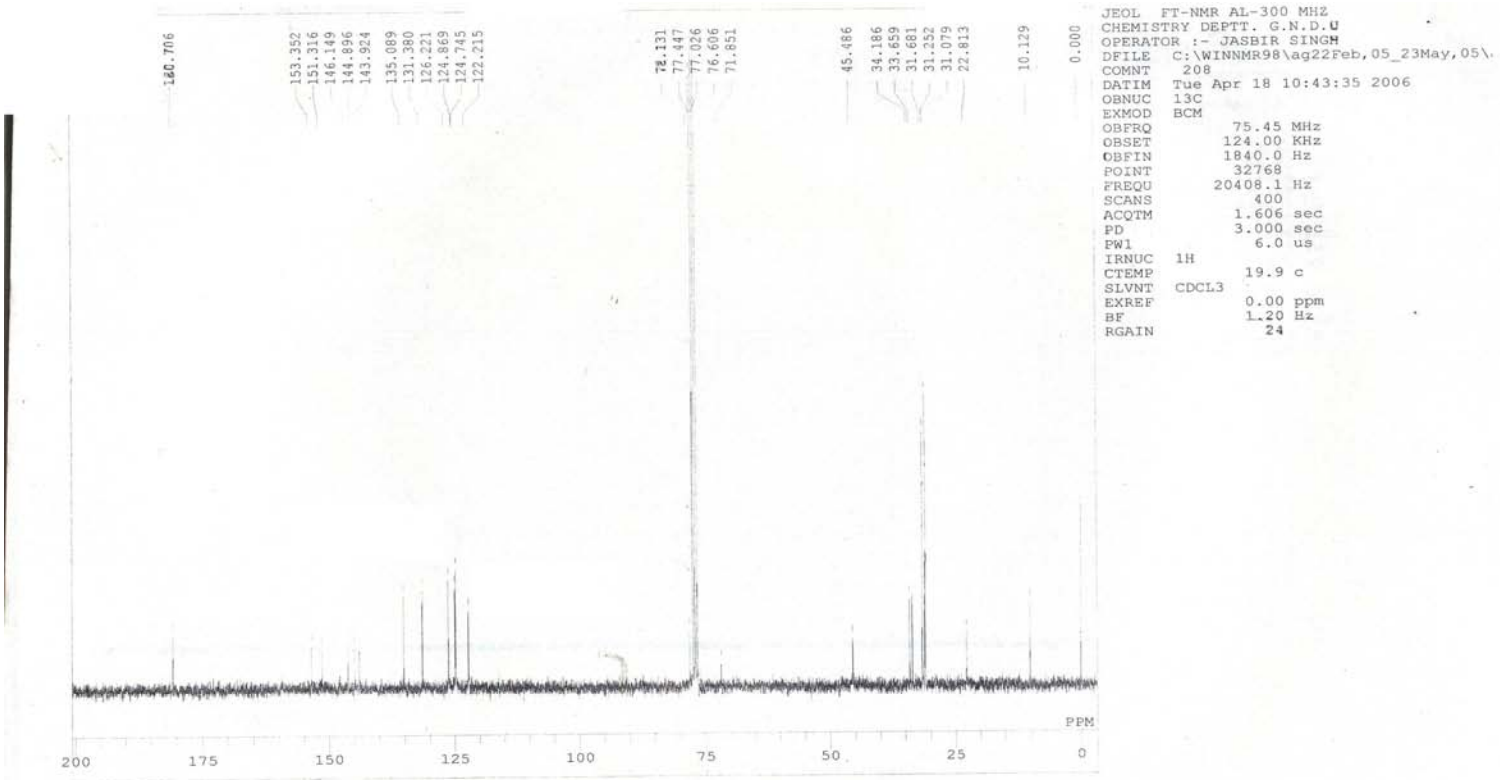

Figure S2: ^{13}C NMR Spectra of Compound 3

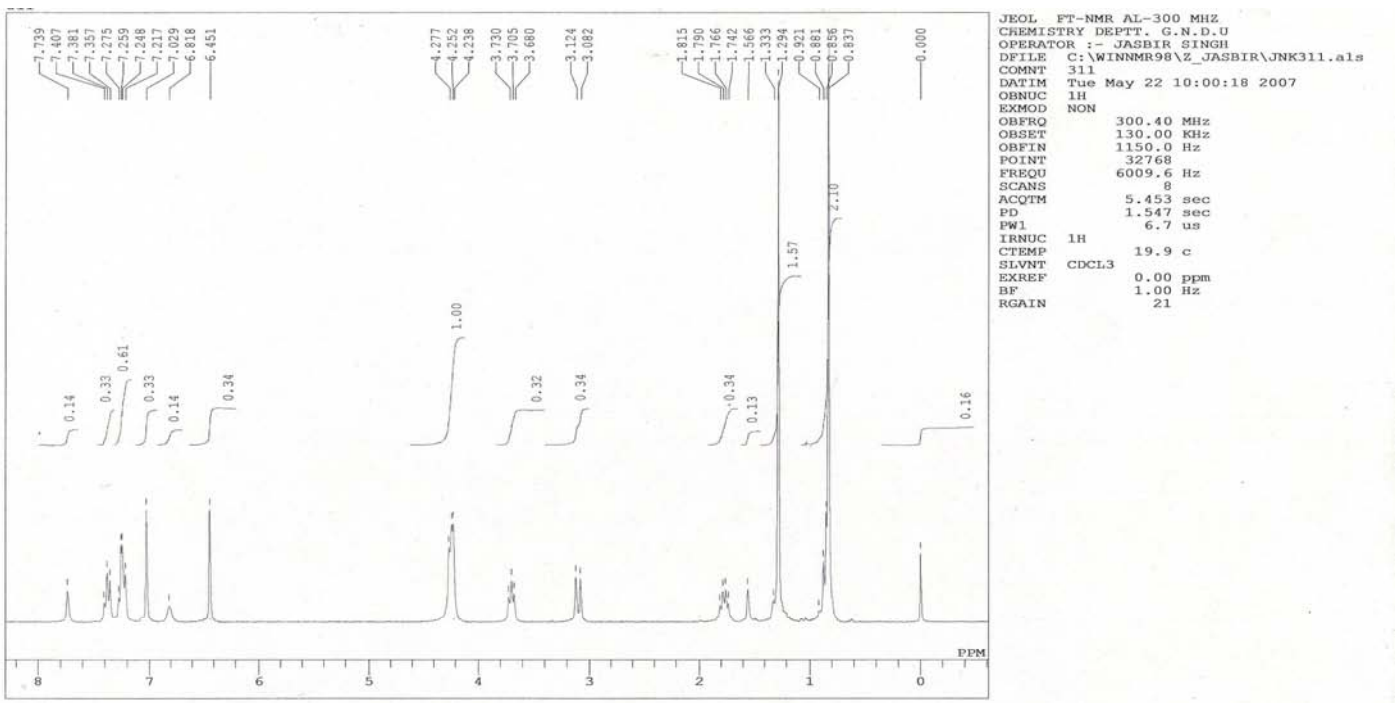

Figure S3: ^{1}H NMR Spectra of Compound 4

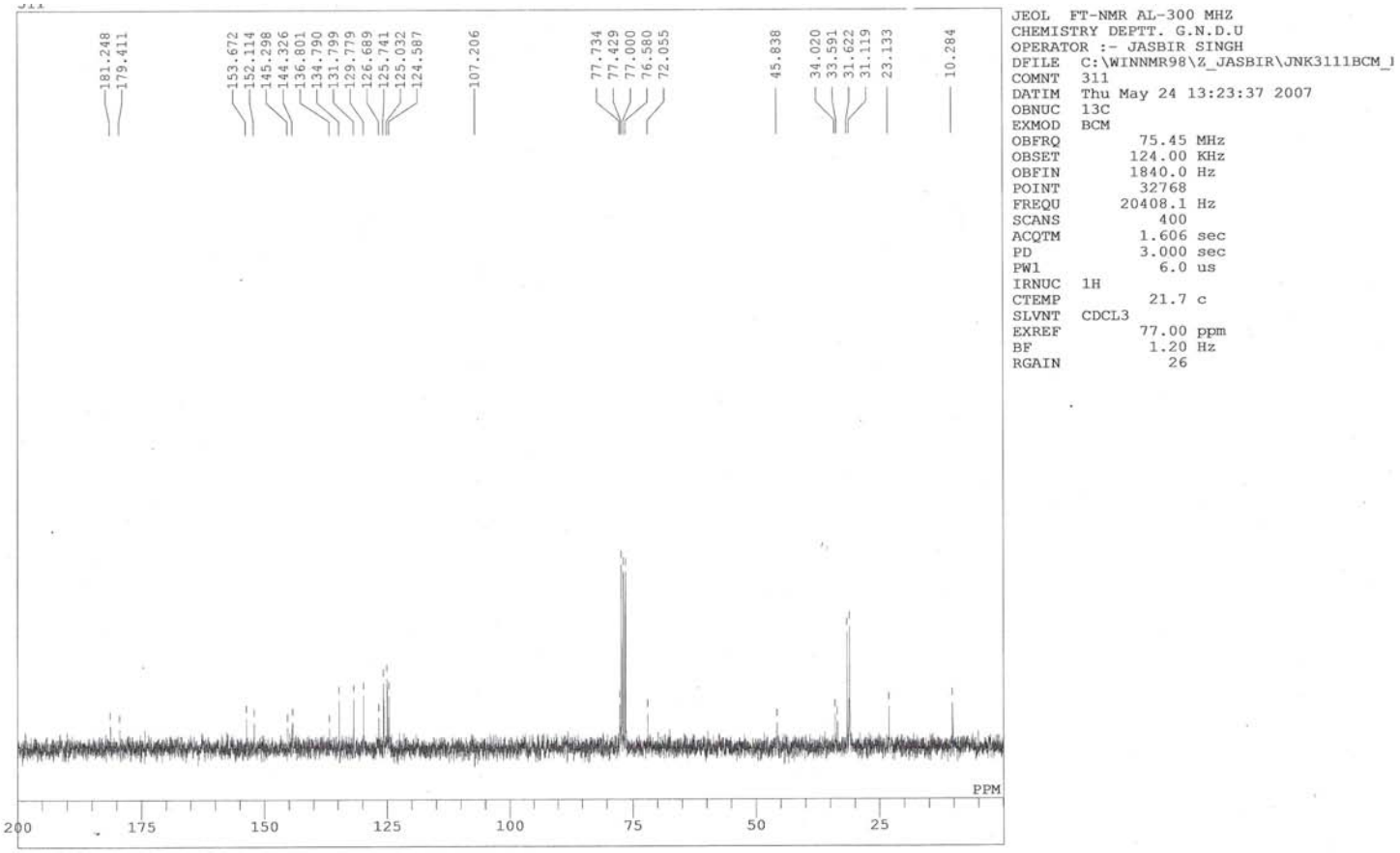

Figure S4: ^{13}C NMR Spectra of Compound 4

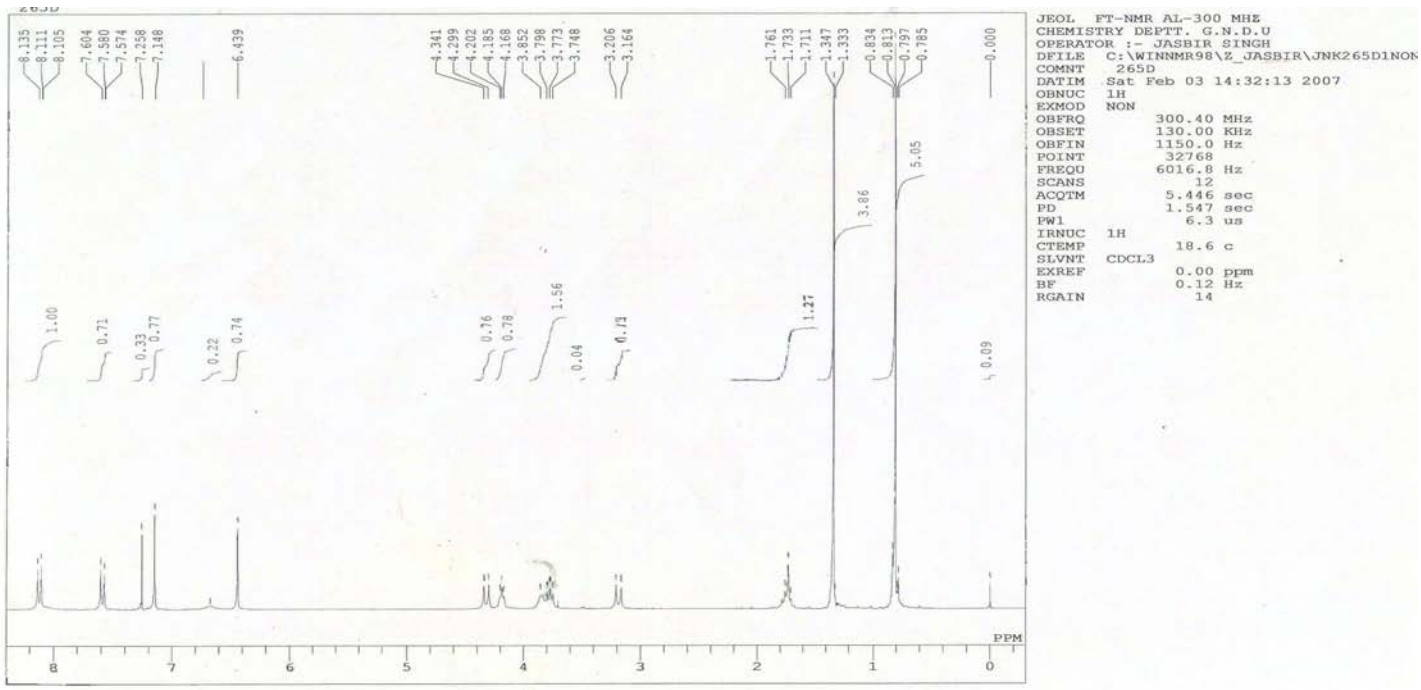

Figure S5: ^{1}H NMR Spectra of Compound 5

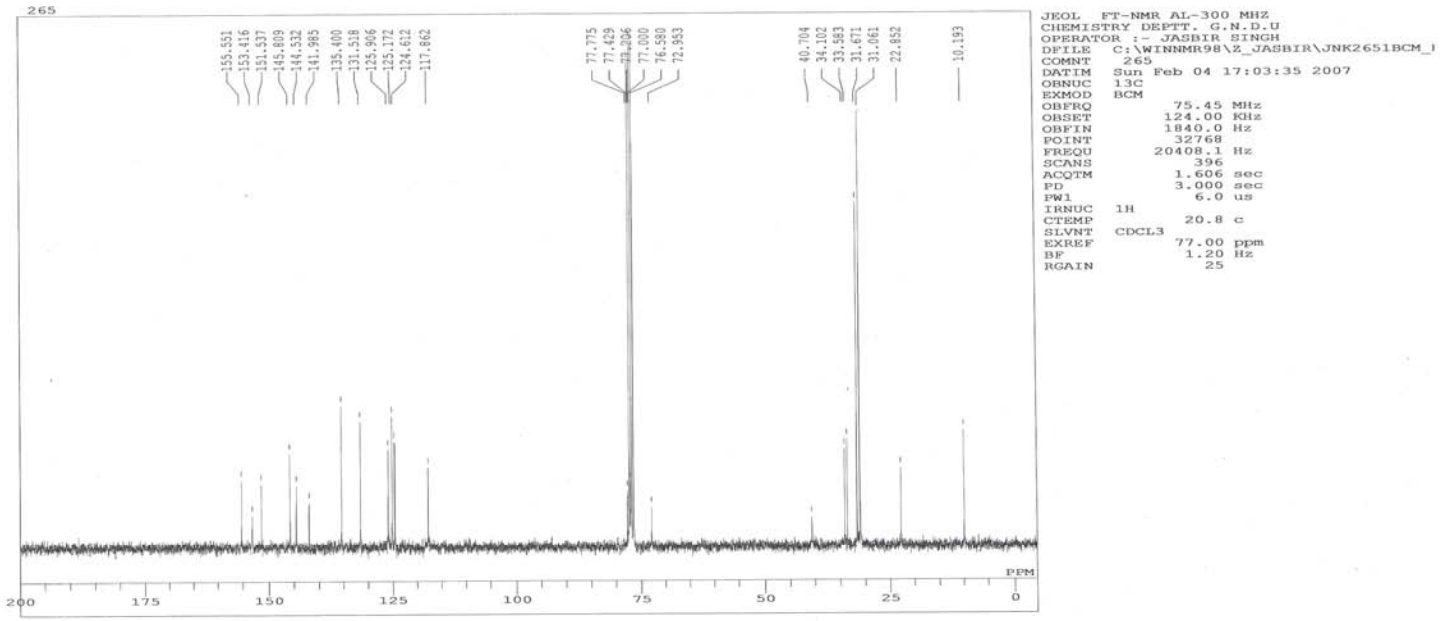

Figure S6: ^{13}C NMR Spectra of Compound 5

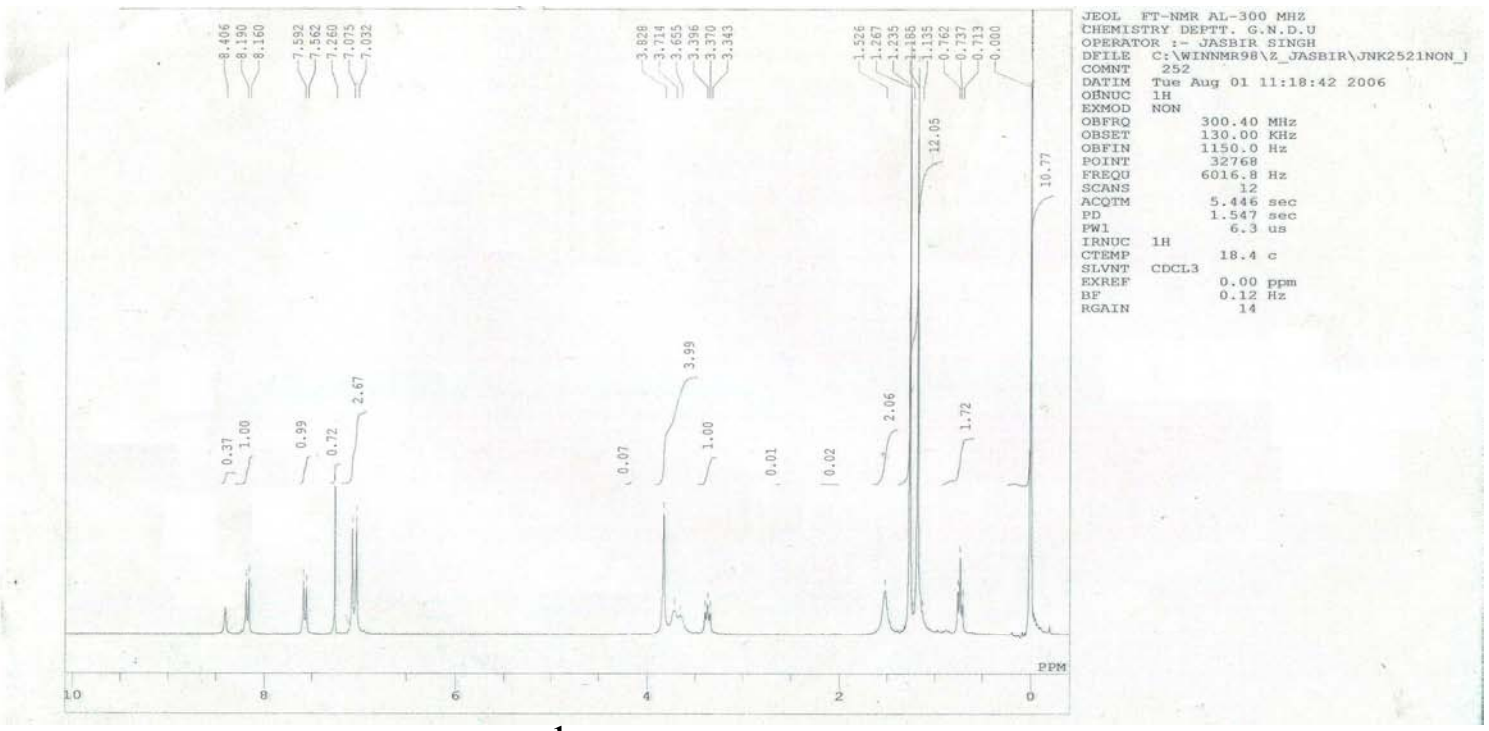

Figure S7: ^{1}H NMR Spectra of Compound 7

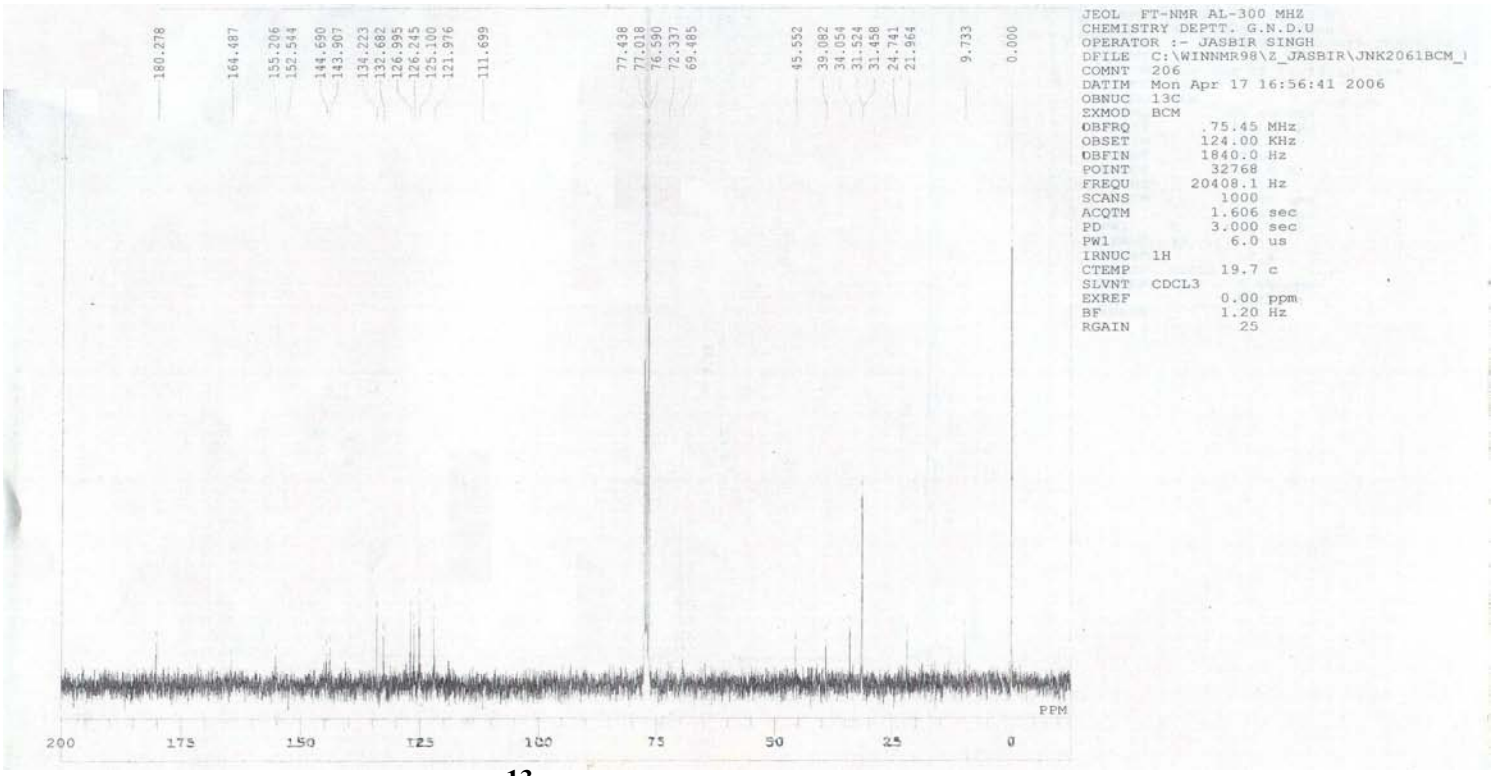

Figure S8: ^{13}C NMR Spectra of Compound 7

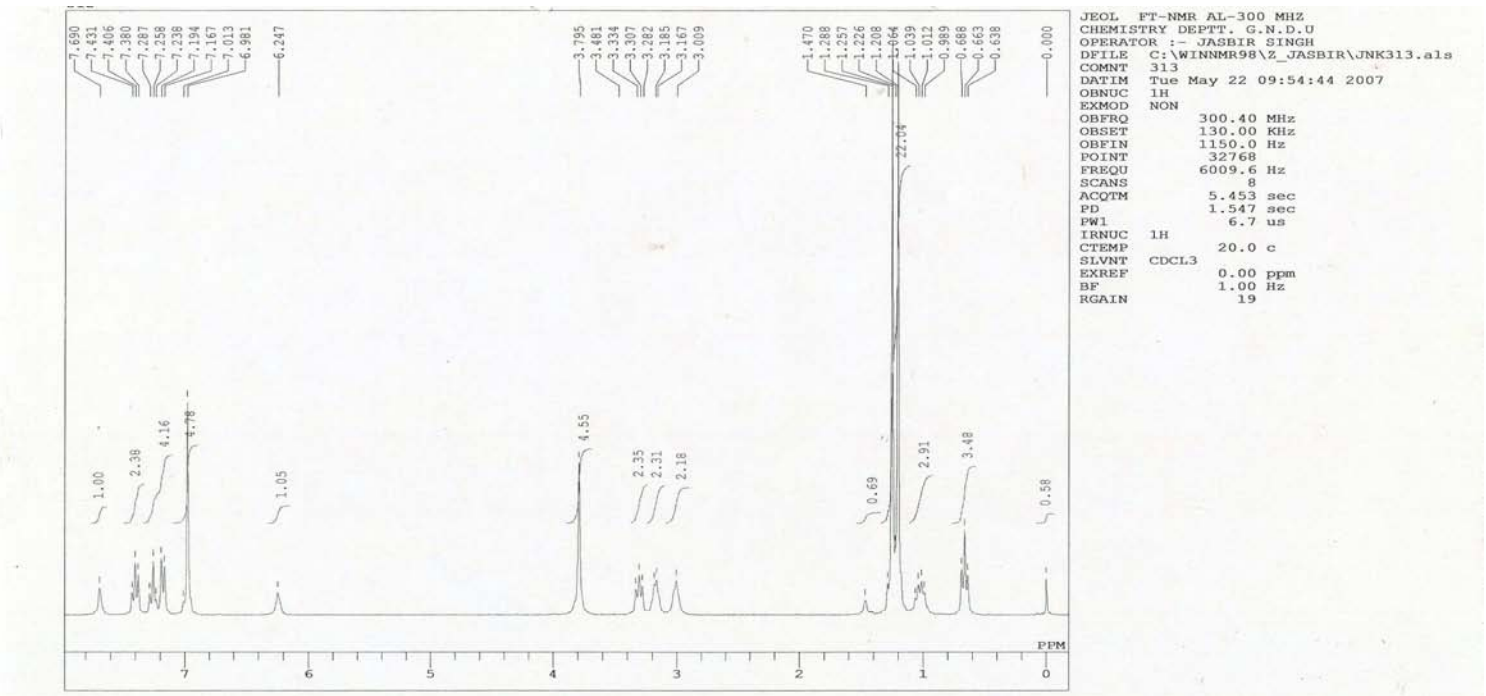

Figure S9: ^{1}H NMR Spectra of Compound 8

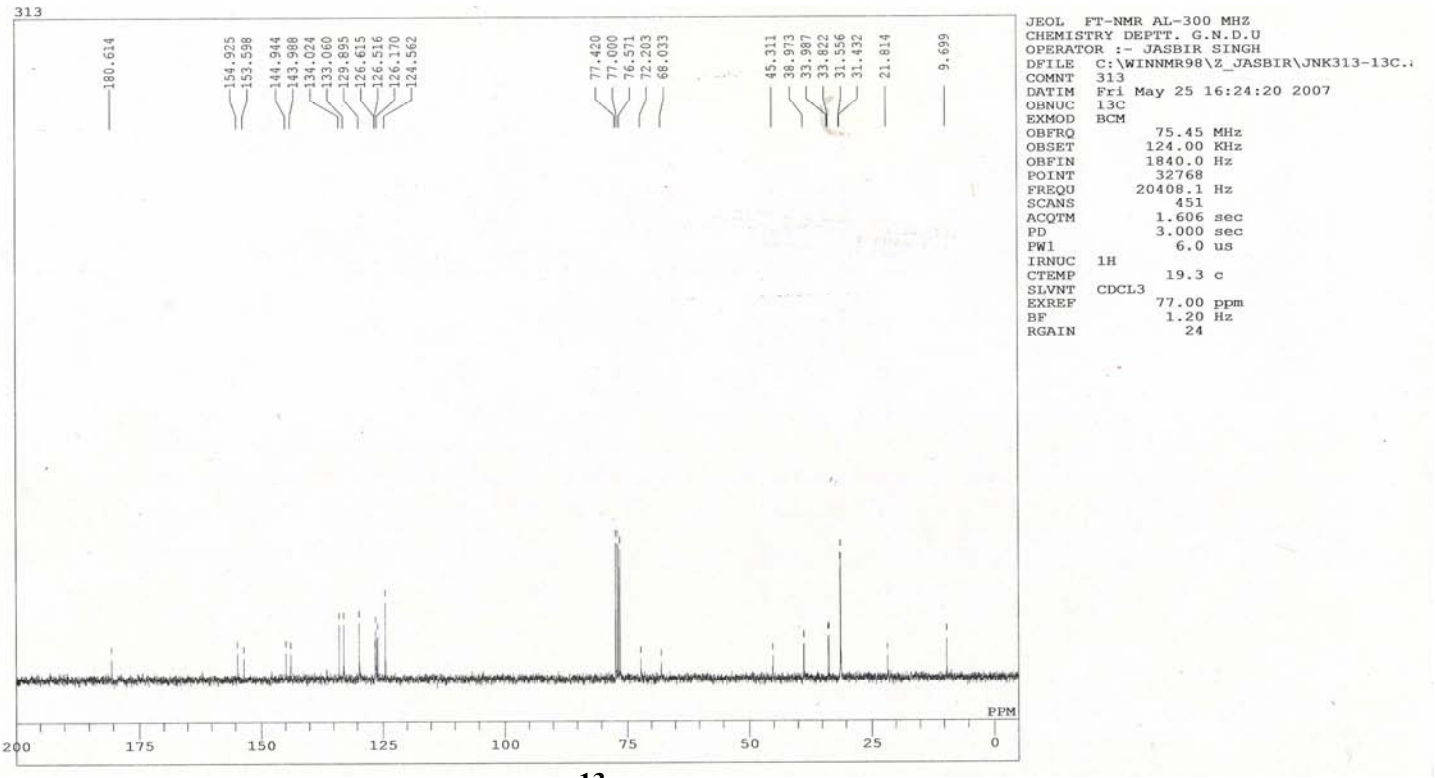

Figure S10: ^{13}C NMR Spectra of Compound 8

NMR Studies

Table S11 ^{1}H NMR induced shifts (Δδ in ppm) in thioureido / ureido derivative **3-5** (10 mM) in *cone* conformation upon complexation with various Tetrabutylammonium anions (F^-, Cl^-, Br^-, I^-, NO_3^- and OAc^-) (10 mM)

Entry	Anion		**3**		**4**		**5**	
		H_c	NH_a	NH_b	NH_a	NH_b	NH_a	NH_b
1	F^-	0.60	*	*	*	*	*	*
2	Cl^-	0.51	0.87	2.29	0.36	0.70	0.55	1.00
3	Br^-	0.54	0.71	2.04	0.21	0.24	0.52	0.92
4	I^-	0.23	0.52	1.05	0.10	0.12	0.47	0.81
5	NO_3^-	0.33	0.35	1.05	0.15	0.17	0.51	0.95
6	OAc^-	0.52	*	*	1.06	1.24	2.60	*

* Disappearence of peak

Table S12 ^{1}H NMR induced shifts (Δδ in ppm) in thioureido / ureido derivative **7-8** in 1,3-*alternate* conformation upon complexation with various Tetrabutylammonium anions (F^-, Cl^-, Br^-, I^-, NO_3^- and OAc^-) (10mM).

Entry	Anion	**7**			**8**		**9**[14]	
		H_c	NH_a	NH_b	NH_a	NH_b	NH_a	NH_b
1	F^-	0.10[#]	2.56[#]	*	*	*	*	*
2	Cl^-	0.54	1.47	1.81	0.38	0.61	0.96	1.70
3	Br^-	0.53	1.11	1.50	0.12	0.24	0.79	1.36
4	I^-	0.43	0.98	1.15	0.15	0.16	0.65	0.84
5	NO_3^-	0.45	1.11	1.34	0.15	0.21	0.83	1.24
6	OAc^-	0.52	2.56	2.76	1.01	0.90	*	*

[*] Disappearence of peaks. [#] Proton NMR shifts recorded in DMSO-d_6

ISE Studies

Table S13: Composition and response charecteristics of chloride ion selective sensor **3-5** and **7-8**.

S.No	PVC (mg)	Plasticiser DOS (mg)	*n*-Butyl-3-methylimidazolium hexafluorophosphate (mg)	Ionophore (mg)	No. of Experiments	Internal solution (M)	Linear Range (M)	Detection Limit (M)	Slope (mV/dec)
3	39.5	28.2	24.3	8.2	3	1.0×10^{-2}	1.0×10^{-1}-5.0×10^{-5}	2.51×10^{-5}	-47.35
4	40.9	28.7	24.7	9.9	3	1.0×10^{-2}	1.0×10^{-1}-5.0×10^{-5}	2.51×10^{-5}	-42.36
5	40.6	28.8	24.4	9.9	3	1.0×10^{-2}	1.0×10^{-1}-5.0×10^{-5}	2.51×10^{-5}	-55.07
7	44.1	29.6	24.6	7.9	3	1.0×10^{-2}	1.0×10^{-1}-5.0×10^{-5}	2.51×10^{-5}	-49.97
8	41.4	28.5	26.8	9.9	3	1.0×10^{-2}	1.0×10^{-1}-5.0×10^{-5}	1.50×10^{-5}	-58.39

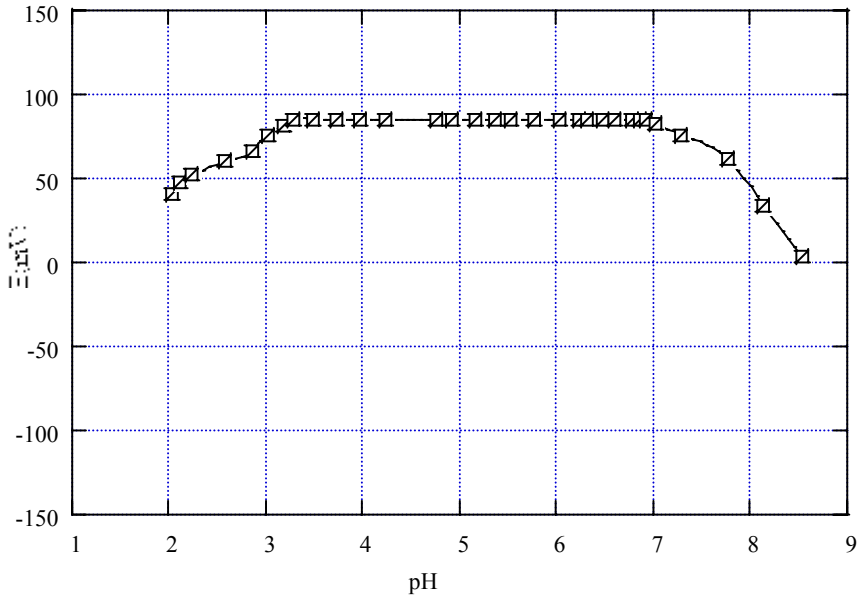

Figure S14: Effect of pH of potential response of chloride ion-selective electrodes based on receptor **8**

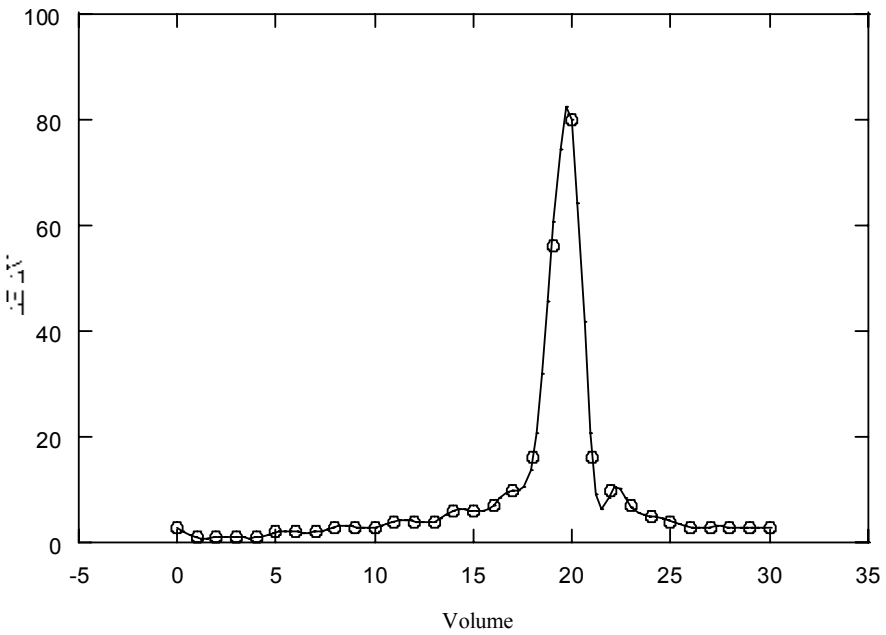

Figure S15: Derivative curve for titration of 1.0 x 10^{-2} M Ag^{+} solution with 1.0 x 10^{-2} M NaCl monitored using receptor **8**