Supporting Information

Anion-pair receptor comprising urea groups and N-benzyl-aza-18-crown-6: Effective Recognition and Liquid-Liquid Extraction of KCl salt.

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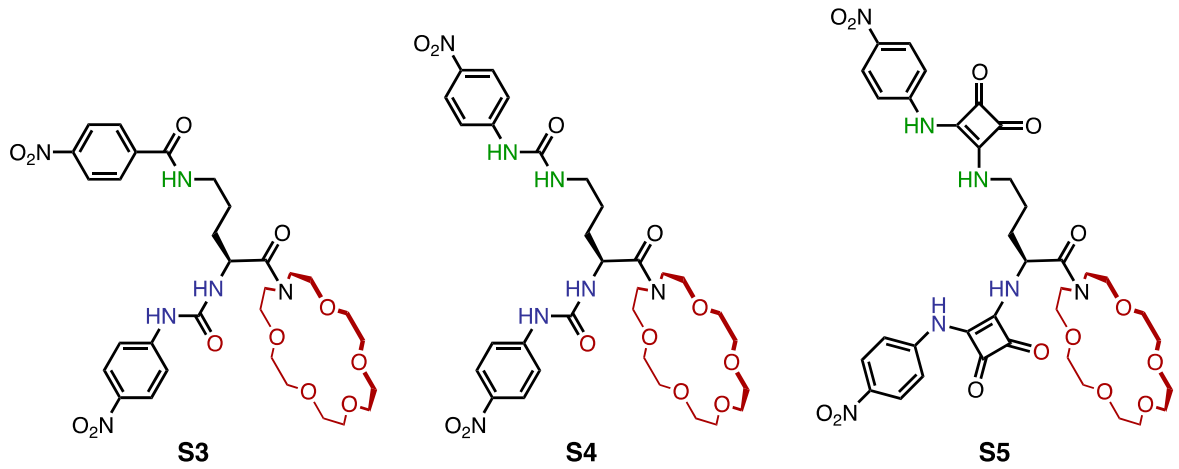
1. Previous results



	S3	S4	S5
TBA^+Cl^-	**3** 900	**18** 200	**1 6**20 000
$Na^+ClO_4^-$	>**50** 000[b]	**15** 200[b]	-
Na^+Cl^-	**8** 900	**33** 500	**1 5**80 000
K_{TBA}/K_{Na}	**2.3**	**1.8**	**1.0**

Figure 1 Association constants (Ka) for interactions between receptors **S3**-**S5** and chloride anions, sodium cations and chloride anions in the presence of one equivalent of sodium cations as well as

cooperativity factors defined as K_{TBA}/K_{Na}. UV-Vis titrations, solvent CH_3CN, temperature 293 K, $C_{receptor}$=1.75-2.5 x10^{-5}M, anions added as TBA salts. [b]Data from NMR titration experiment.

2. Synthetic route to receptors **1** and **2**

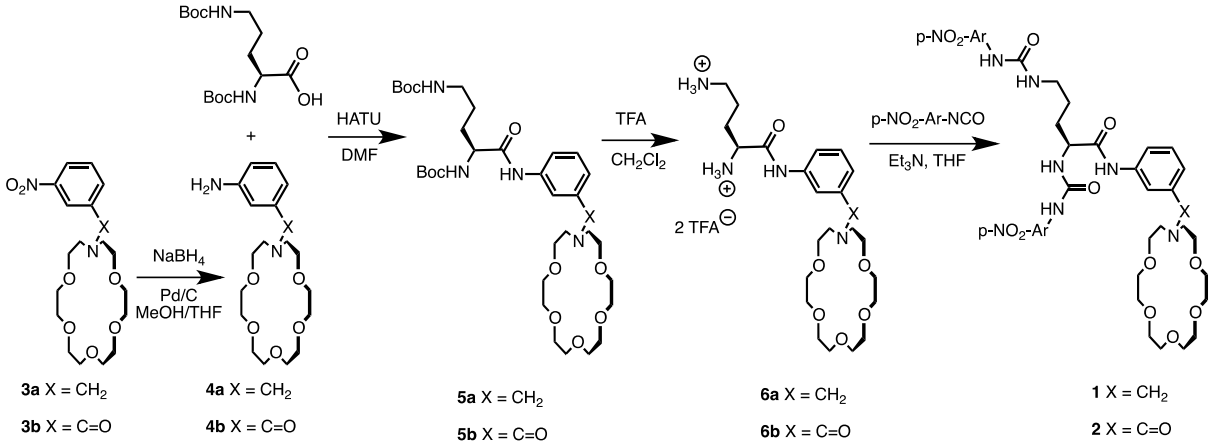


Figure 2 Synthetic route to receptors 1 and 2

3. ^{1}H and ^{13}C NMR spectra

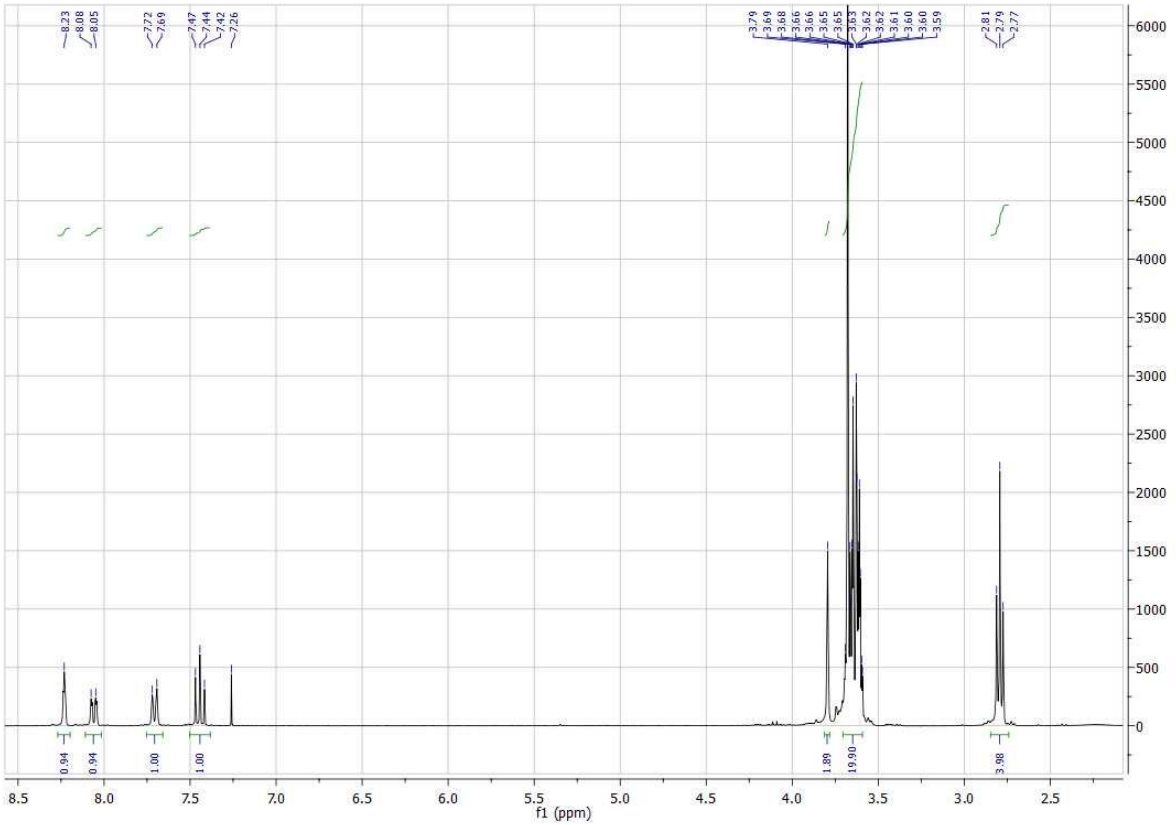


Figure 3 ^{1}H NMR of compound **3a**

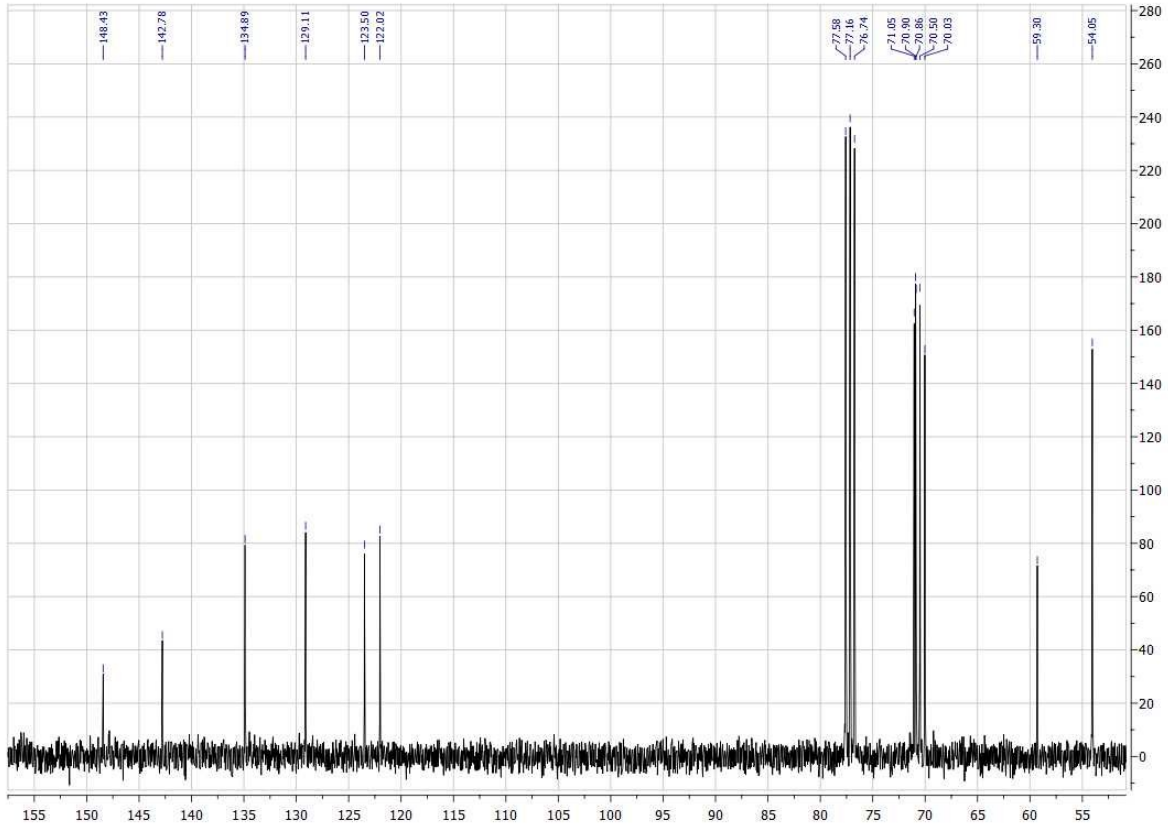


Figure 4 ^{13}C NMR of compound **3a**

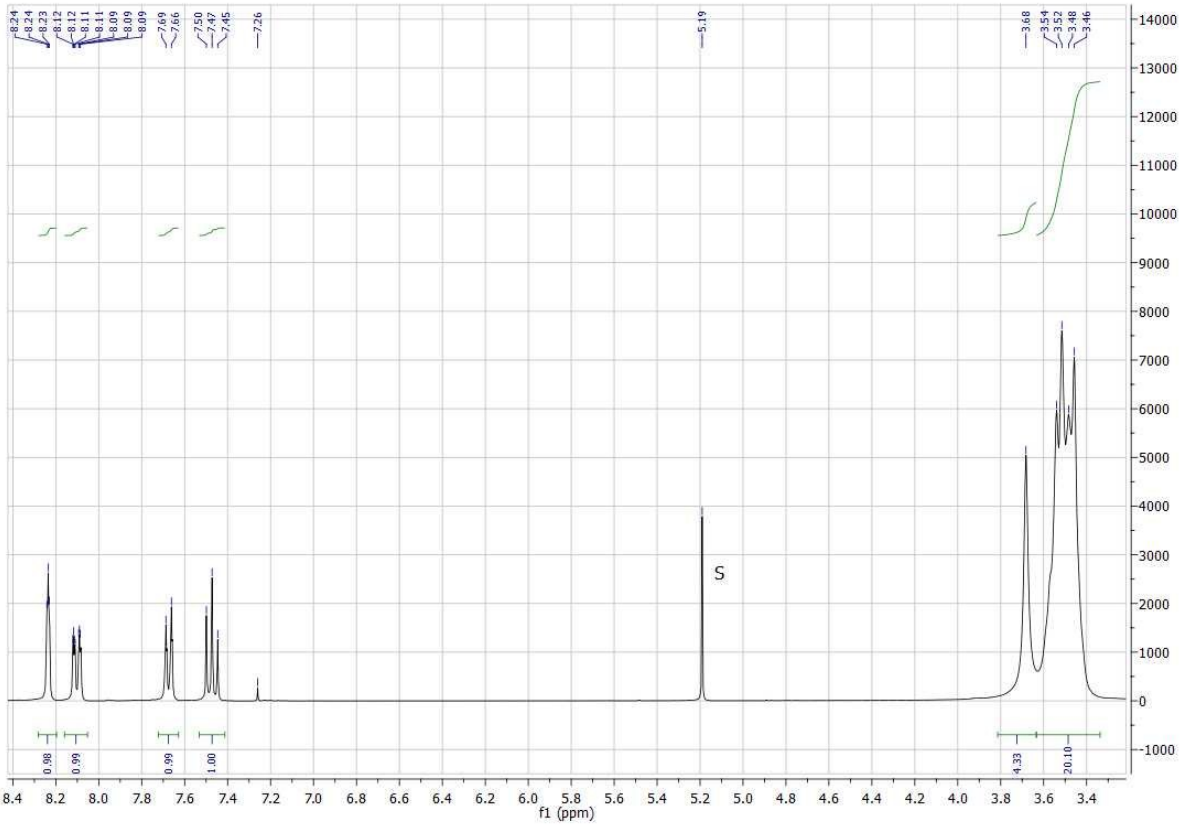


Figure 5 ^{1}H NMR of compound **3b**

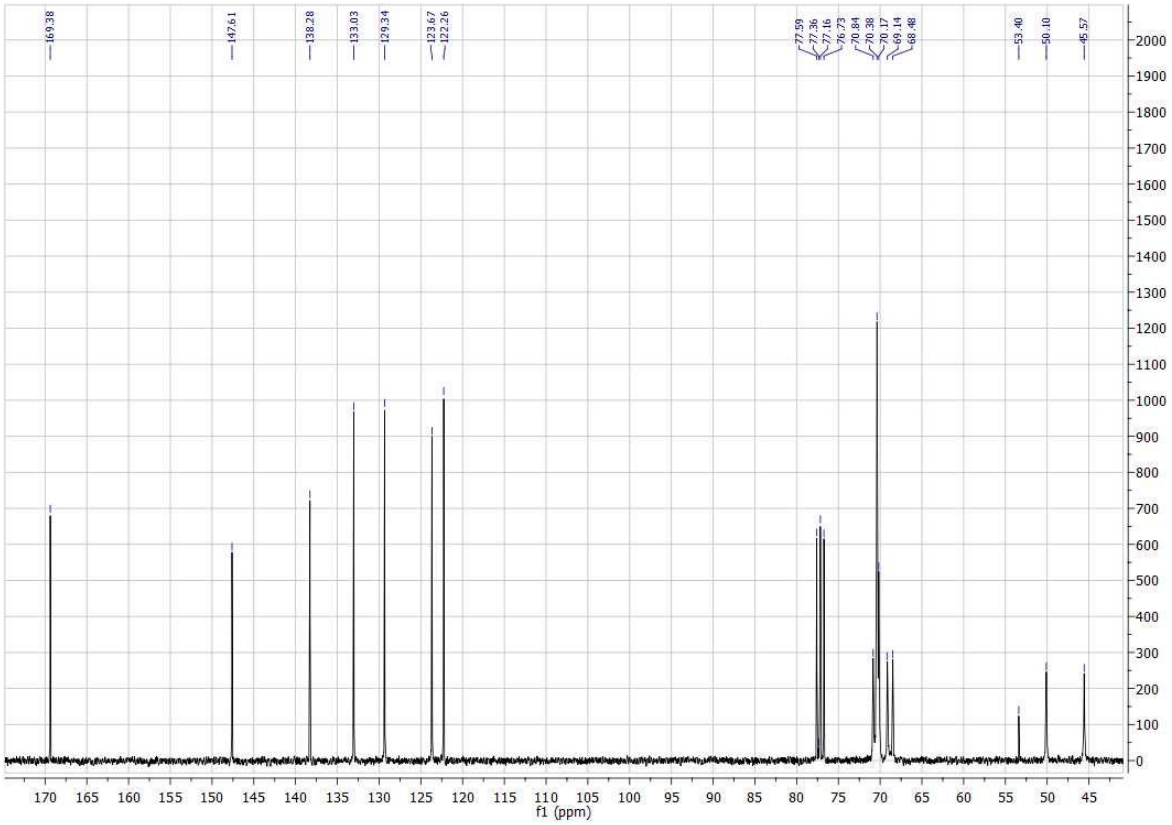


Figure 5 ^{13}C NMR of compound **3b**

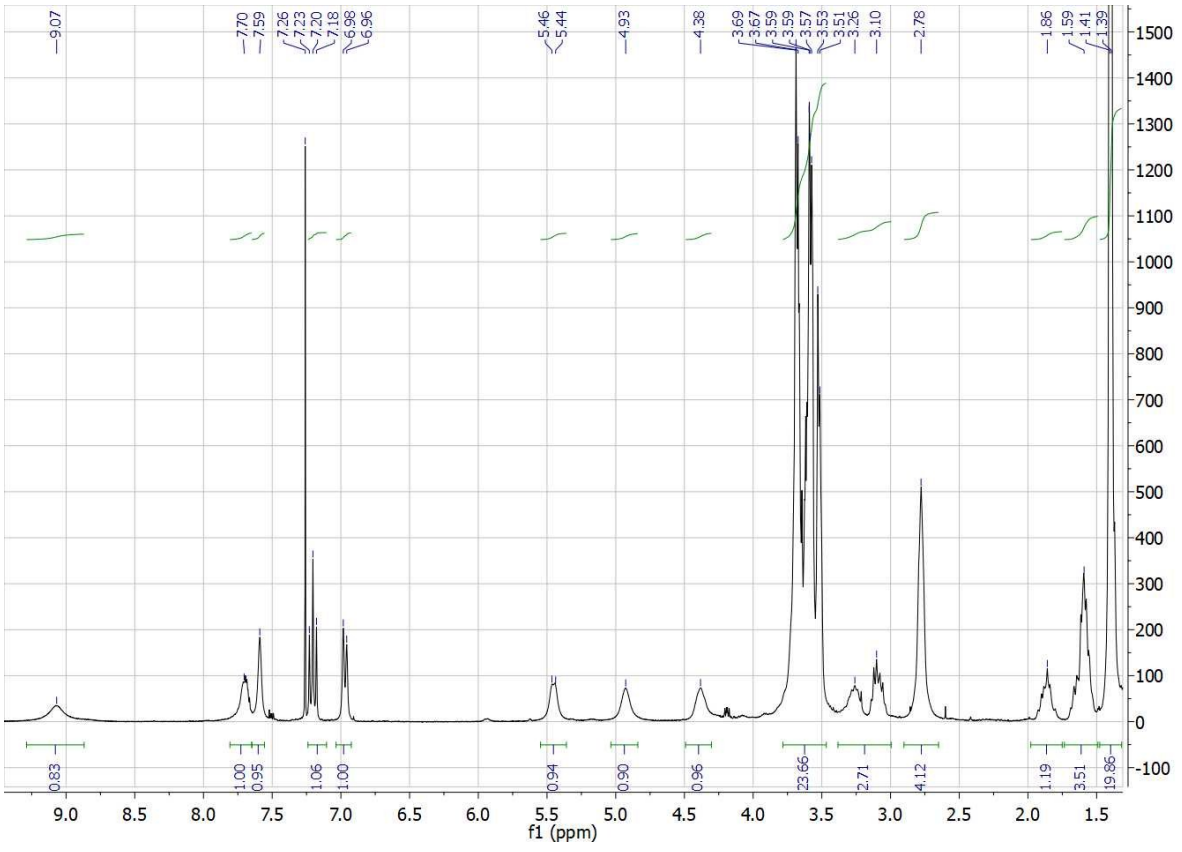


Figure 6 ^{1}H NMR of compound **5a**

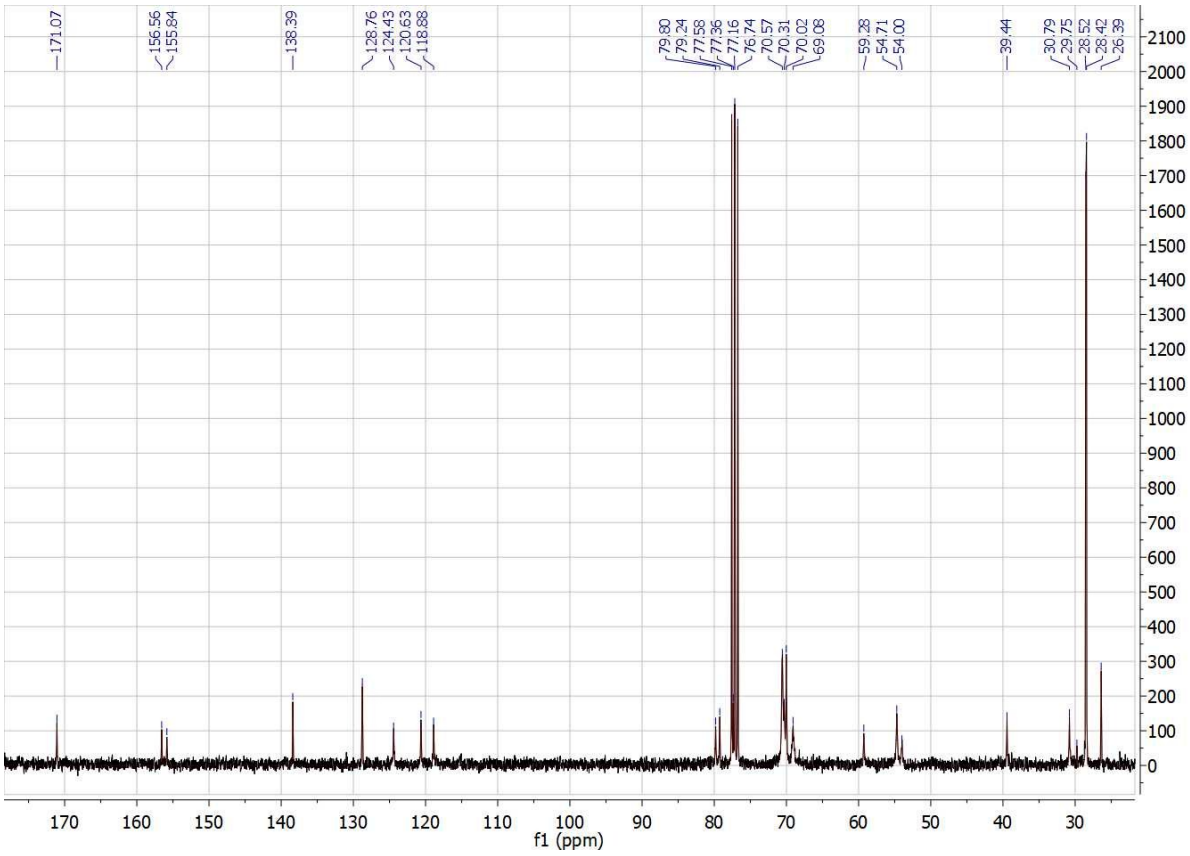


Figure 7 ^{13}C NMR of compound **5a**

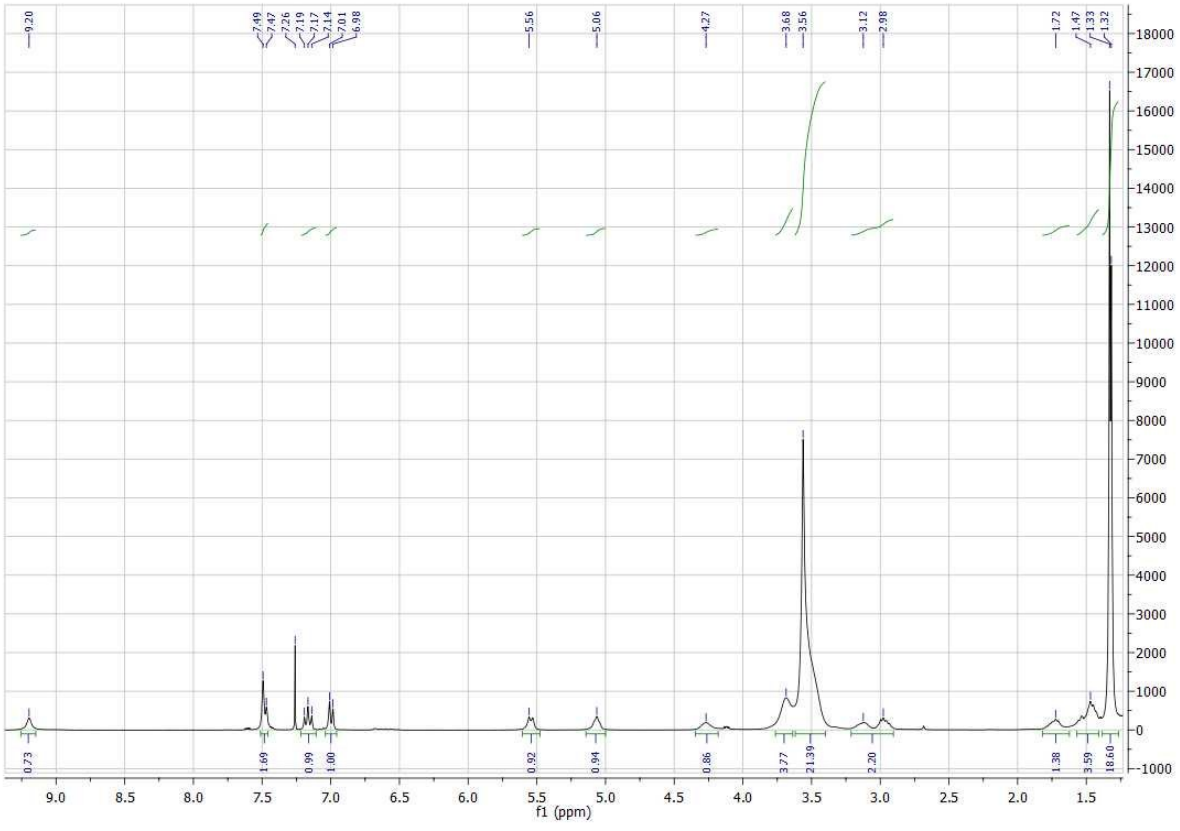


Figure 8 ^{1}H NMR of compound **5b**

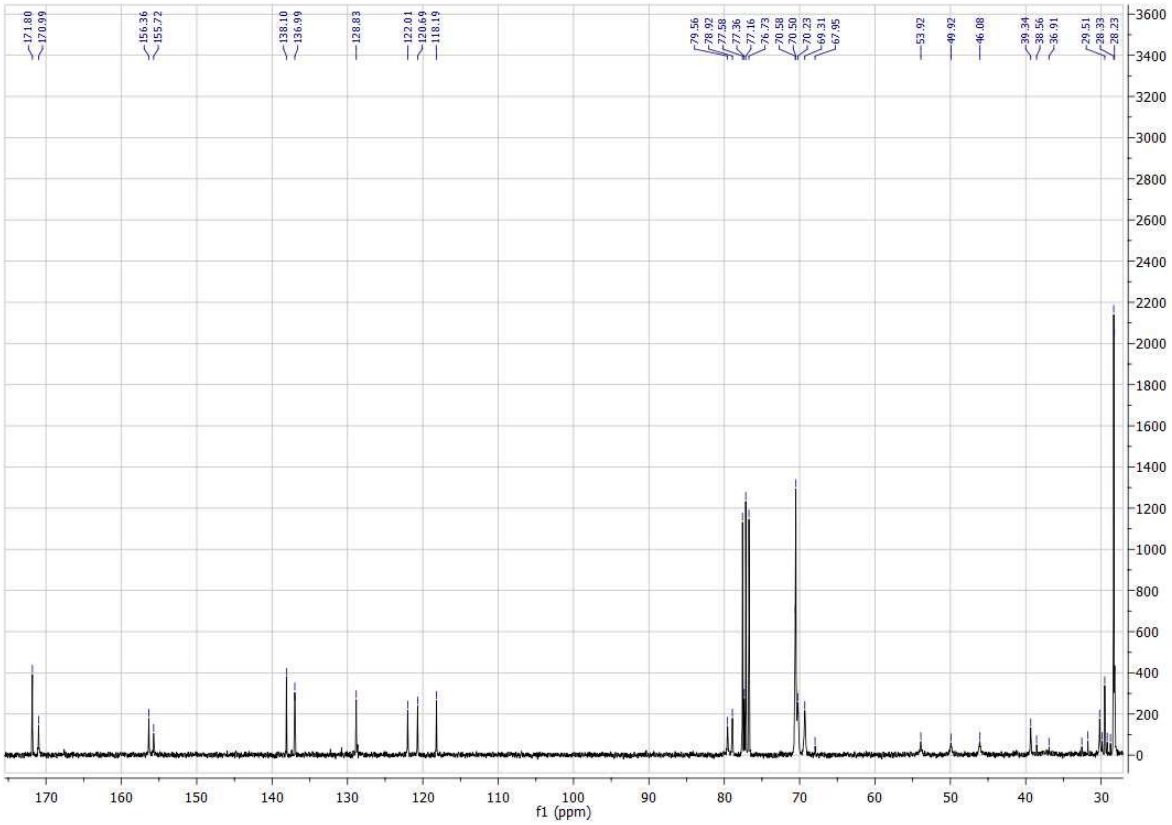


Figure 9 ^{13}C NMR of compound **5b**

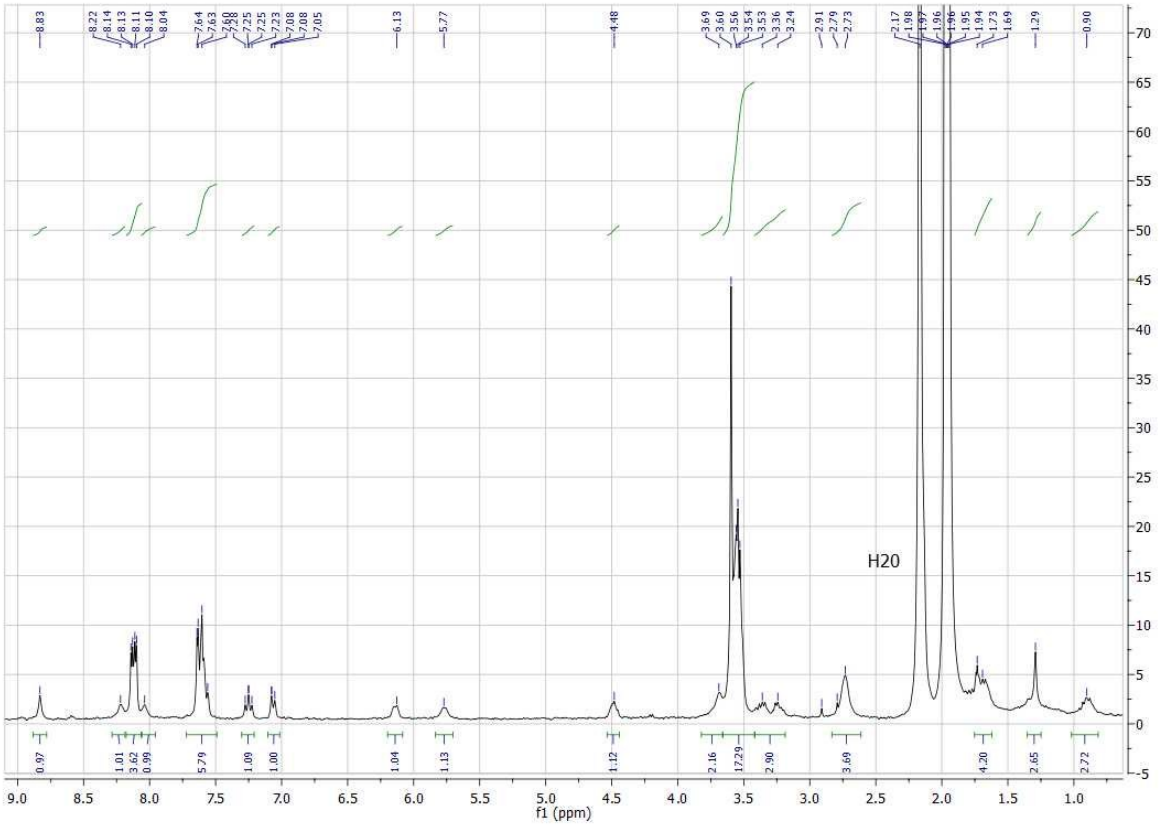


Figure 10 ^{1}H NMR of compound **1**

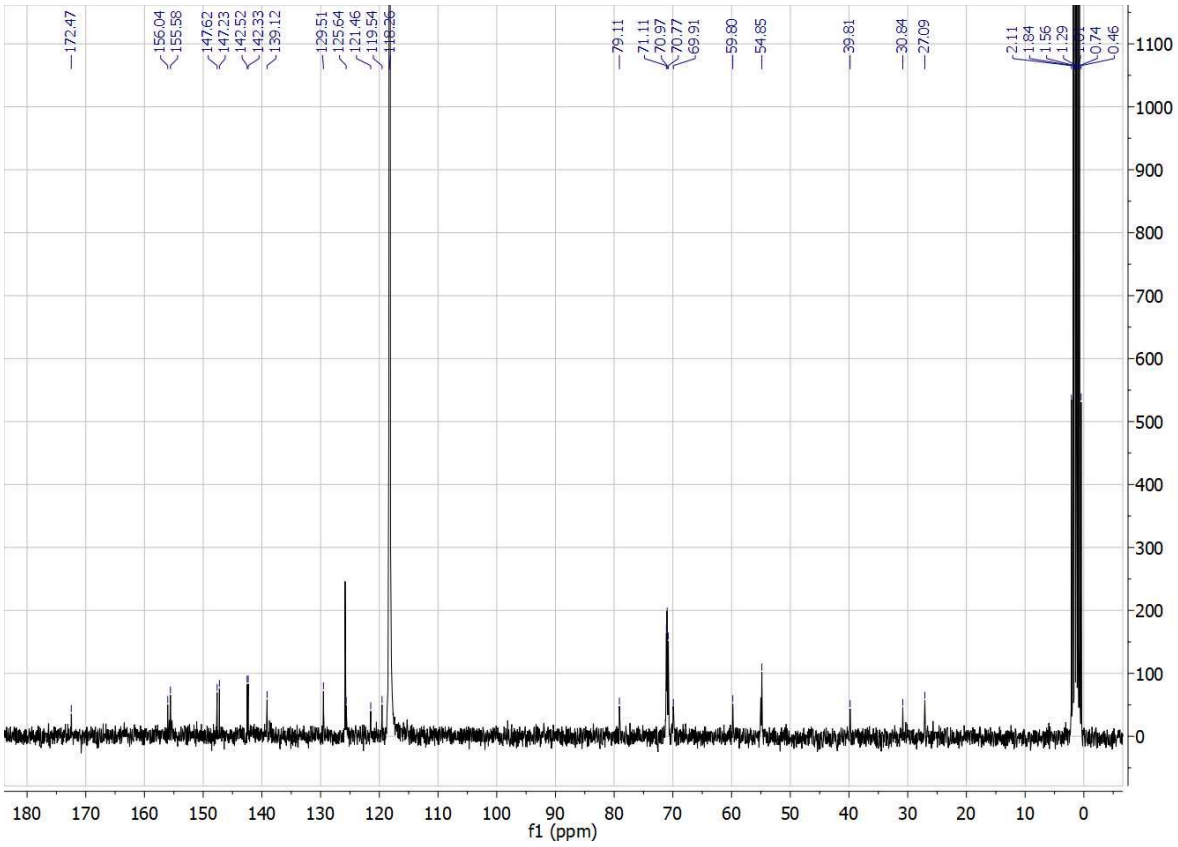


Figure 11 ^{13}C NMR of compound **1**

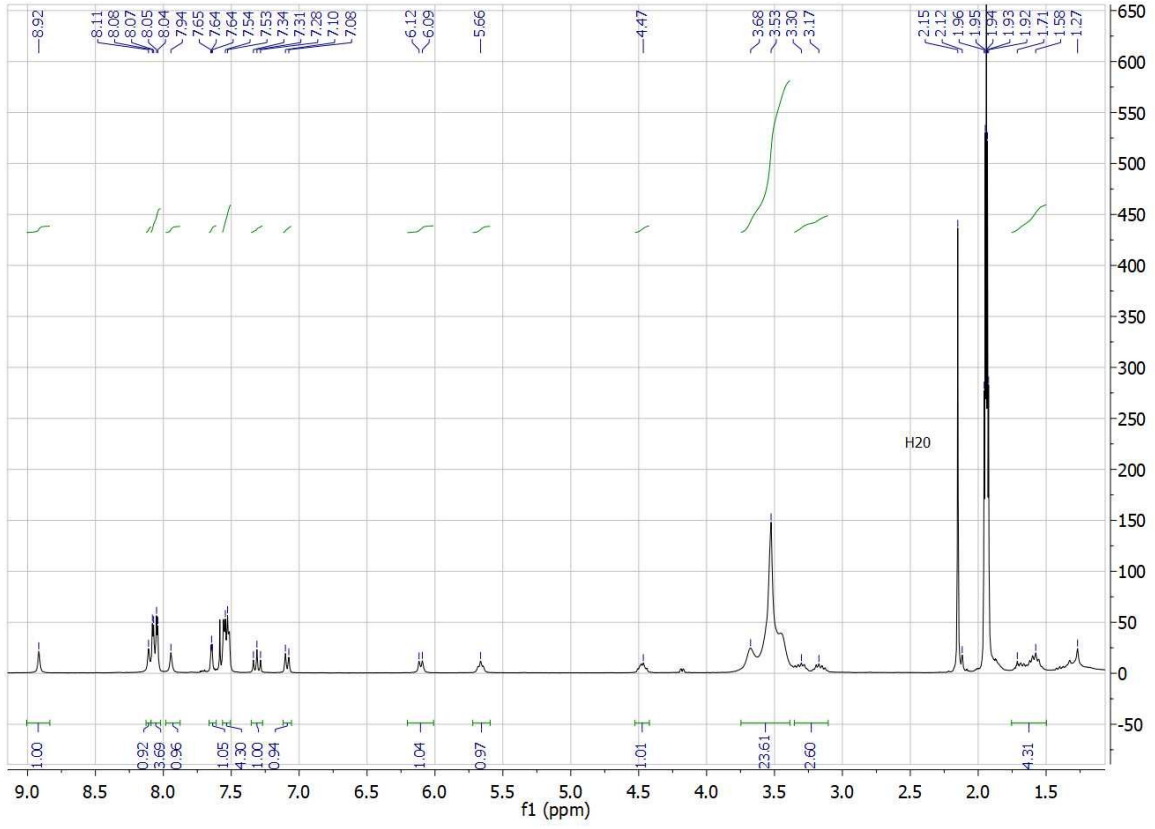


Figure 12 ^{1}H NMR of compound **2**

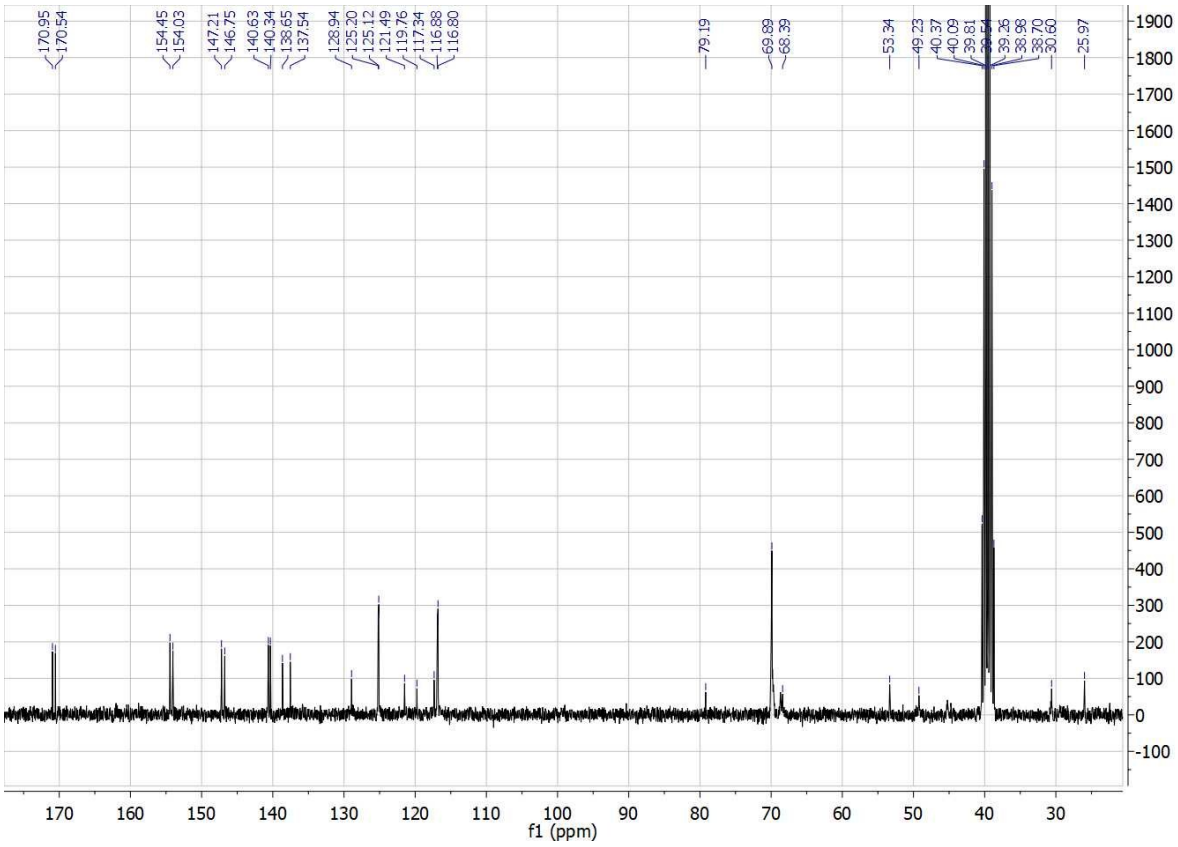


Figure 13 ^{13}C NMR of compound **2**

4. UV-Vis titration experiments

UV-Vis experiment general procedure

UV-Vis titration experiments were performed on a Thermo SpectronicUnicam UV500 spectrophotometerin CH_3CN solution at 298K. To 10 mm cuvette was added 2.5 mL of 2.0 x 10^{-5} M solution of studied receptor and in case of salts binding studies 1 mol equivalent of cation (KPF_6, $NaClO_4$ or NH_4PF_6). Small aliquots of ~5.0 x 10^{-4} M guest solution (anion or cation) containing receptor 1 or 2 at the same concentration as in cuvette, were added and a spectrum was acquired. The resulting titration data were analysed by the HypSpec program to obtain the association constant (K_a). The stoichiometry determination was done using continuous variation method (Job plot).

Job plots:

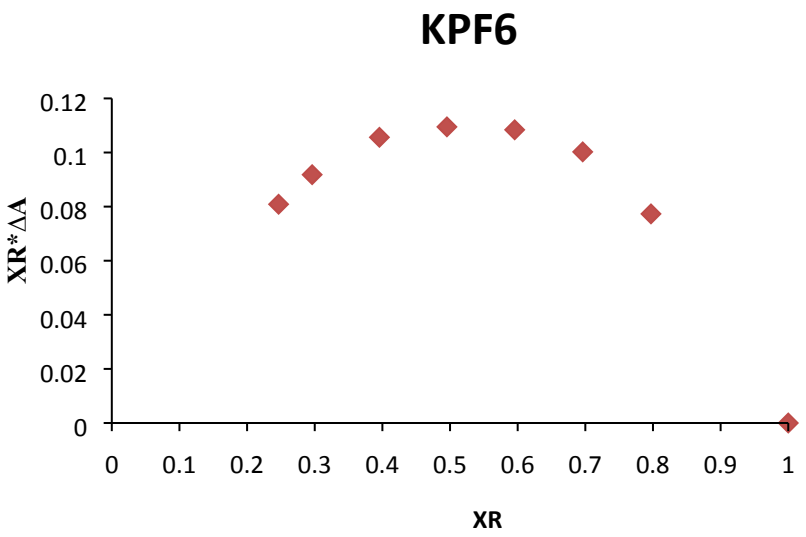


Figure 14 Job plot analysis of receptor **1** in the presence of KPF_6

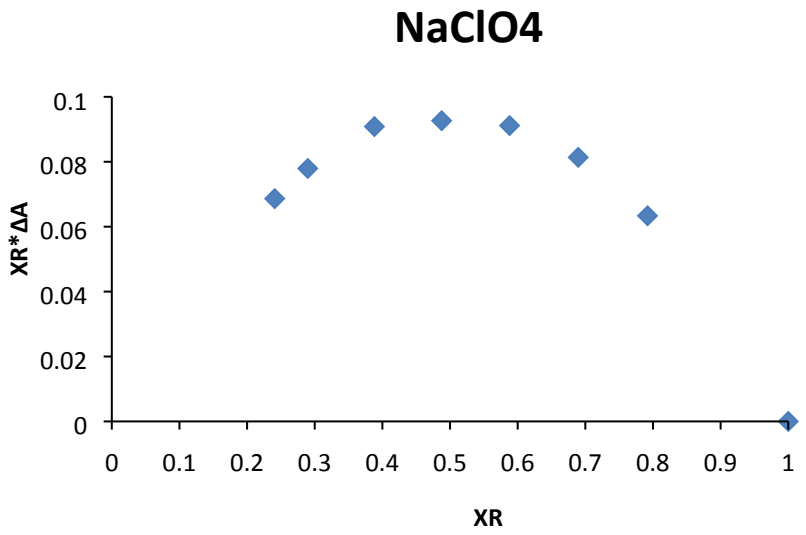


Figure 15 Job plot analysis of receptor **1** in the presence of $NaClO_4$

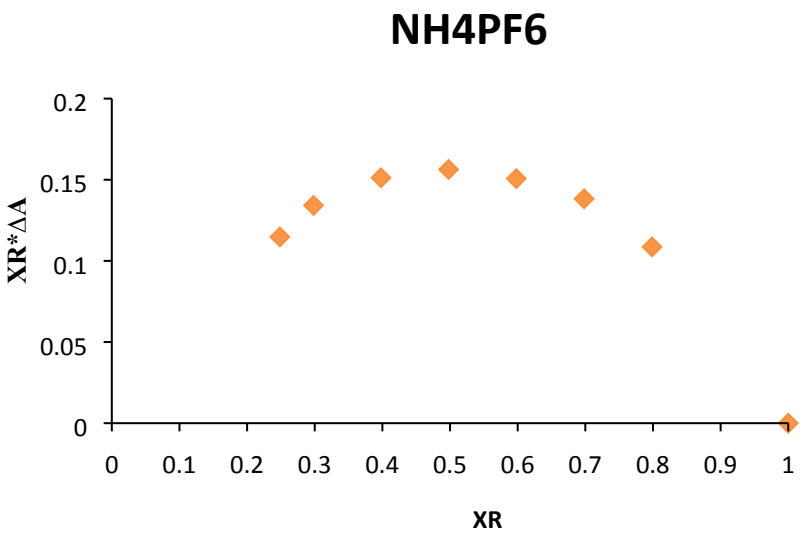


Figure 16 Job plot analysis of receptor **1** in the presence of NH_4PF_6

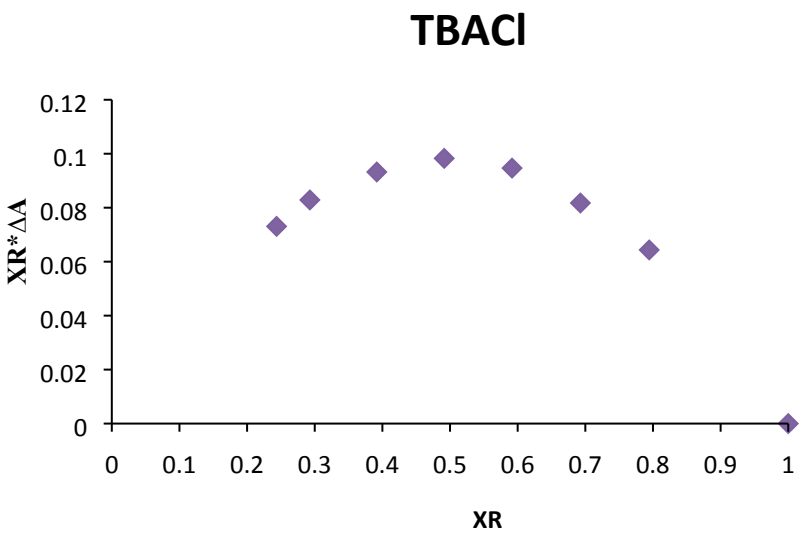


Figure 17 Job plot analysis of receptor **1** in the presence of TBACl

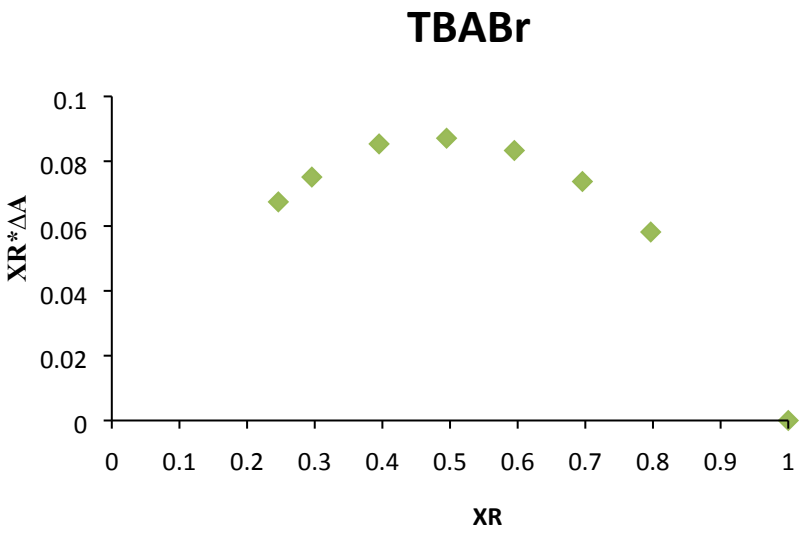


Figure 18 Job plot analysis of receptor **1** in the presence of TBABr

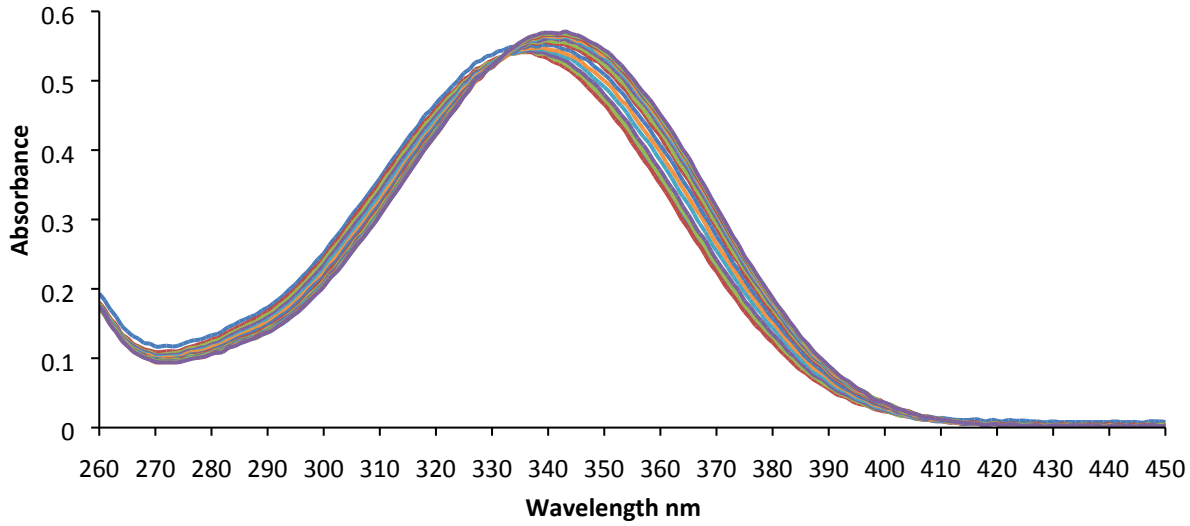


Figure 19 UV-Vis **1** spectrum changes upon titrant (TBACl) addition (293 K, CH_3CN solution, $C_{titrant}$=5.5 x10^{-4}M, $C_{receptor}$=2.0 x10^{-5}M)

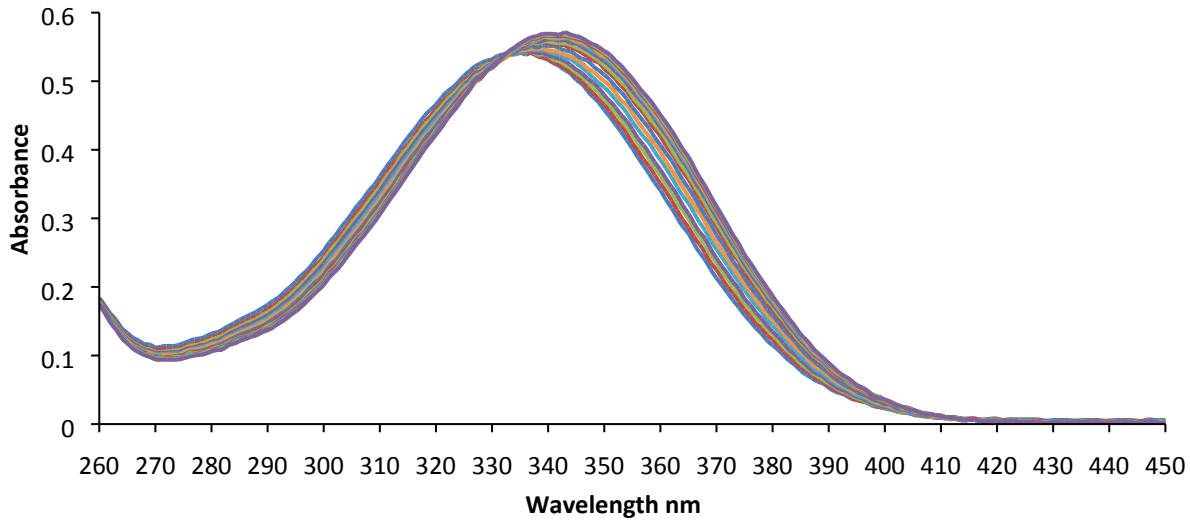


Figure 20 UV-Vis **1** spectrum changes upon titrant (TBACl) addition in presence of 1 eq. $NaClO_4$ (293 K, CH_3CN solution, $C_{titrant}$=5.5 x10^{-4}M, $C_{receptor}$=2.0 x10^{-5}M)

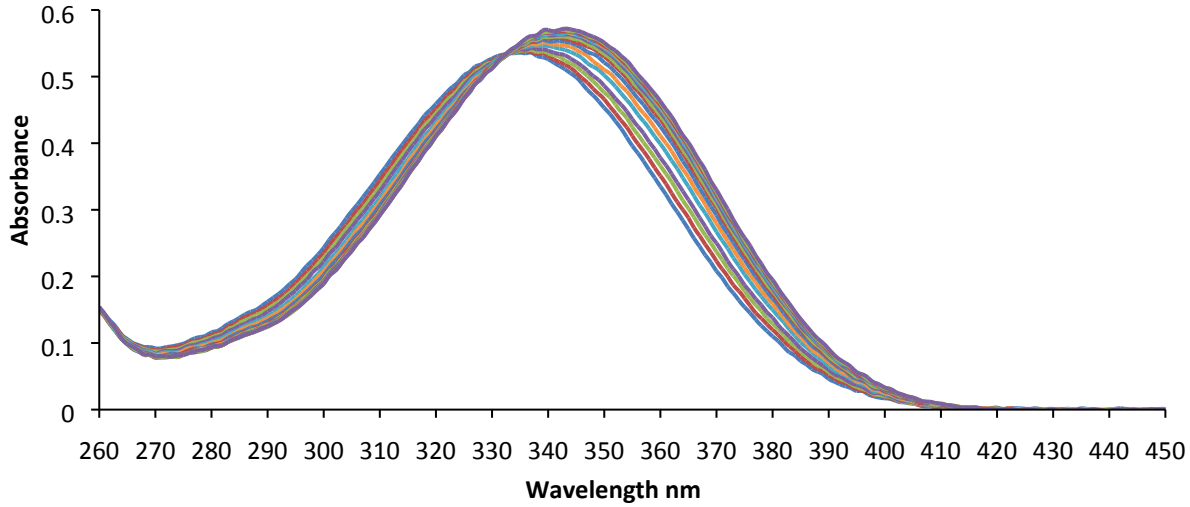


Figure 21 UV-Vis **1** spectrum changes upon titrant (TBACl) addition in presence of 1 eq. KPF_6 (293 K, CH_3CN solution, $C_{titrant}$=5.5 x10^{-4}M, $C_{receptor}$=2.0 x10^{-5}M)

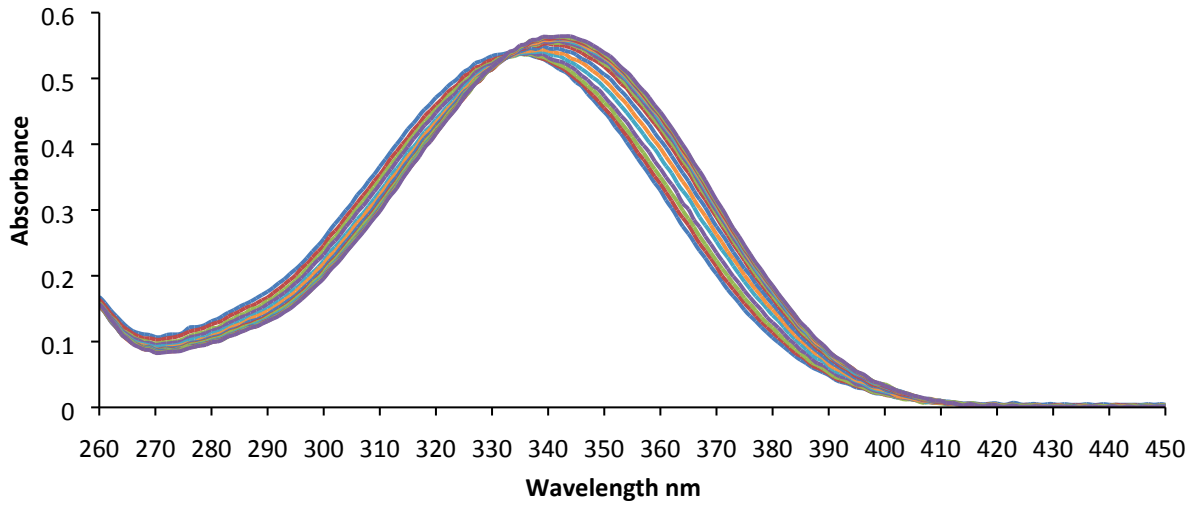


Figure 22 UV-Vis **1** spectrum changes upon titrant (TBACl) addition in presence of 1 eq. NH_4PF_6 (293 K, CH_3CN solution, $C_{titrant}$=5.5 x10^{-4}M, $C_{receptor}$=2.0 x10^{-5}M)

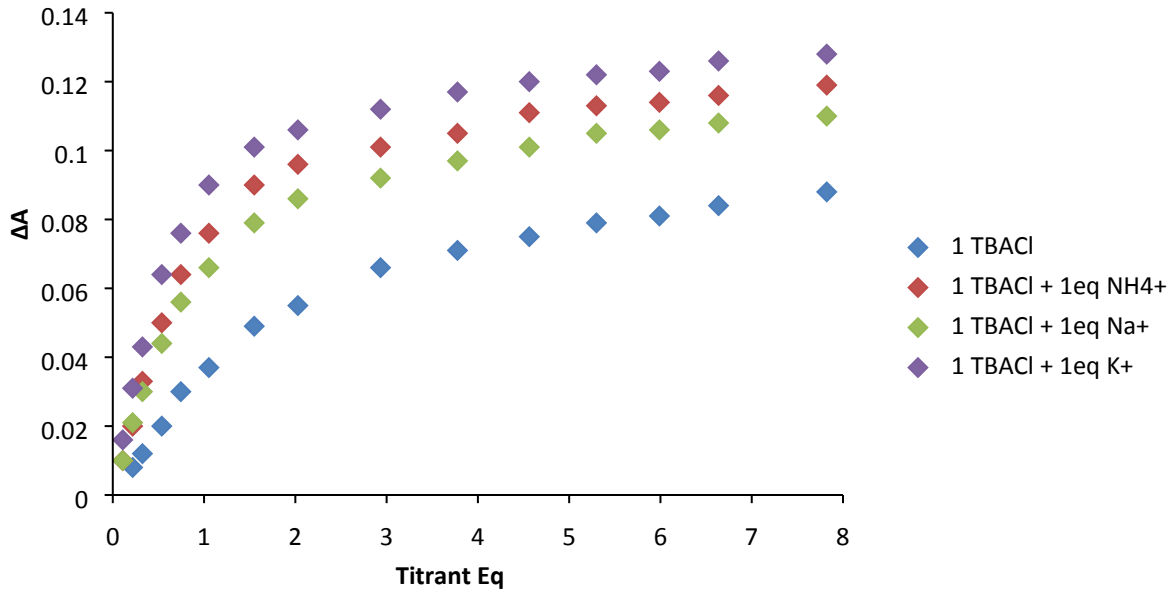


Figure 23 UV-Vis titration binding isotherms of **1** at 360 nm wavelength**,** with TBACl in the presence or absence of 1 eq. of cation

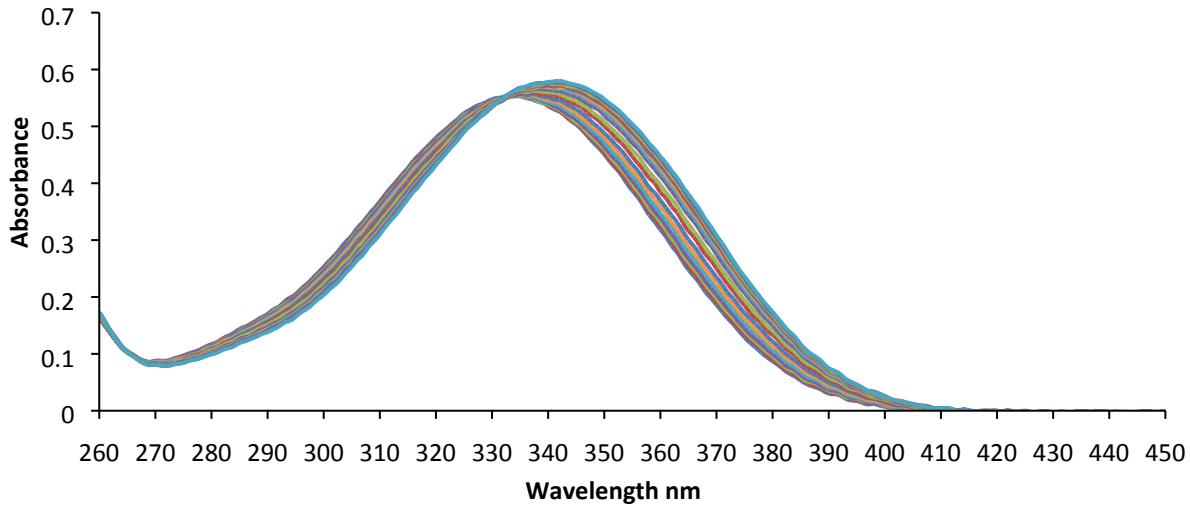


Figure 24 UV-Vis **2** spectrum changes upon titrant (TBACl) addition (293 K, CH_3CN solution, $C_{titrant}$=5.3 x10^{-4}M, $C_{receptor}$=2.0 x10^{-5}M)

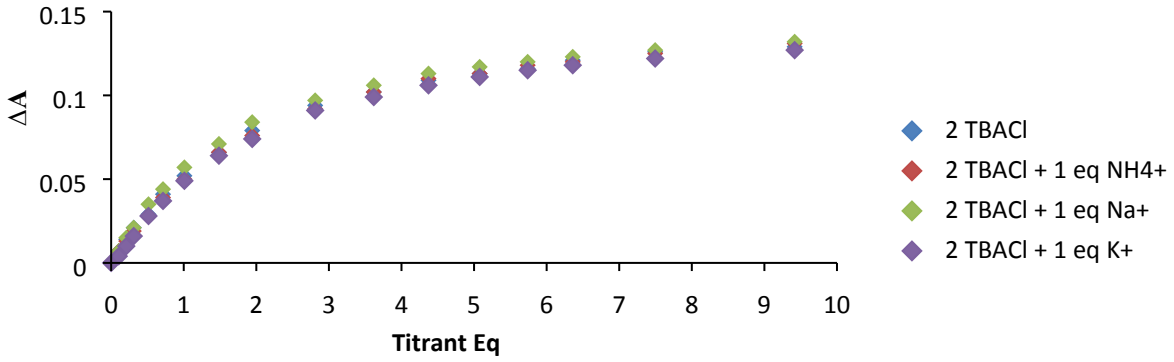


Figure 25 UV-Vis titration binding isotherm of **2** at 360 nm wavelength, with TBACl in the presence or absence of 1 eq. of cation

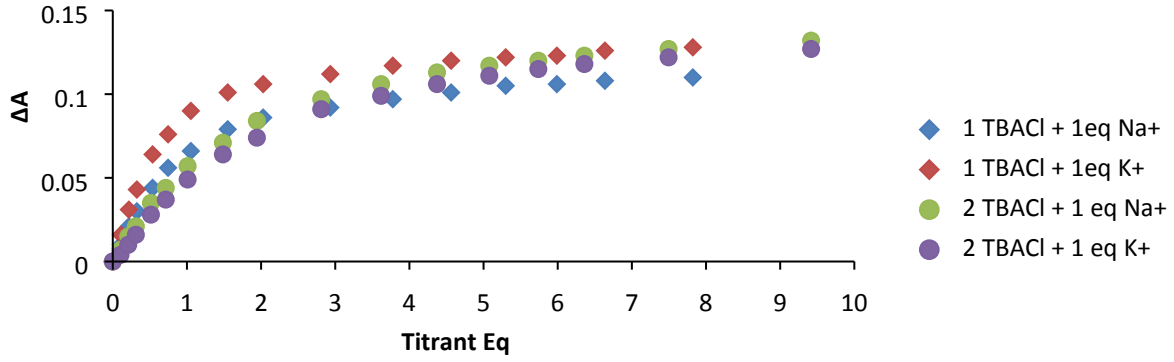


Figure 26 UV-Vis titration binding isotherm of **1** and **2** at 360 nm wavelength**,** with TBACl in the presence or absence of 1 eq. of potassium and sodium cation

5. Association constants and errors

	TBA^+	Na^+	K_{Na}/K_{TBA}	K^+	K_K/K_{TBA}	NH_4^+	K_{NH4}/K_{TBA}
AcO^-	227 000 (0.83%)	110 000 (0.6%)	0.49	104 000 (0.9%)	0.46	12 000 (1.5%)	[b]
BzO^-	268 000 (0.71%)	123 000 (0.63%)	0.5	128 000 (0.73%)	0.5	13 800 (1.3%)	[b]
Cl^-	70 000 (0.99%)	166 000 (0.64%)	2.4	370 000 (0.98%)	5.3	270 000 (0.81%)	3.9
Br^-	4 370 (0.6%)	21 000 (0.9%)	4.8	18 500 (0.57%)	4.3	31 500 (0.56%)	7.2
NO_2^-	10 300 (1.8%)	24 800 (0.49%)	2.4	38 800 (0.55%)	3.8	13 500 (0.44%)	1.3
NO_3^-	50 (15%)	4 10 (9.3%)	8.2	1 500 (0.96%)	33	5 900 (0.67%)	128

Figure 27 UV-Vis spectroscopy K_{obs} values for interactions of **1** with various ion-pair combinations[a] [a]UV-Vis [b]Spectral changes during the titration indicate dislodging of anions from the receptor **1**.

	Na^+	K^+	NH_4^+
3a	5.22 (1.4%)	6.60 (12%)	5.55 (3.2%)
3b	4.07 (1.7%)	-	-

Figure 28 $LogK_a$ for interactions of aza-crown ethers **3a** and **3b** with cations ($NaClO_4$, KPF_6, NH_4PF_6 salts) in acetonitrile

	AcO^-	BzO^-	$H_2PO_4^-$	Cl^-	Br^-	NO_2^-	NO_3^-
K_a	227 000 (0.83%)	268 000 (0.71%)	220 000 (0.78%)	70 000 (0.99%)	4 370 (0.6%)	10 300 (1.8%)	50 (15%)

Figure 29 Association constants (K_a) values for interactions of **1** with various anions (TBA salts) in acetonitrile

	TBA^+	Na^+	K_{Na}/K_{TBA}	K^+	K_K/K_{TBA}	NH_4^+	K_{NH4}/K_{TBA}
Cl^-	41 000 (0.17%)	51 000 (0.21%)	1.2	44 000 (0.49%)	1	36 000 (0.14%)	0.9
Br^-	1 500 (0.7%)	1 300 (1.2%)	0.9	3 400 (0.43%)	2.3	3 450 (0.66%)	2.3

Figure 30 UV-Vis spectroscopy K_{obs} values for interactions of **2** with halogens ion-pair combinations

6. The calculated structure of 1•KCl complex

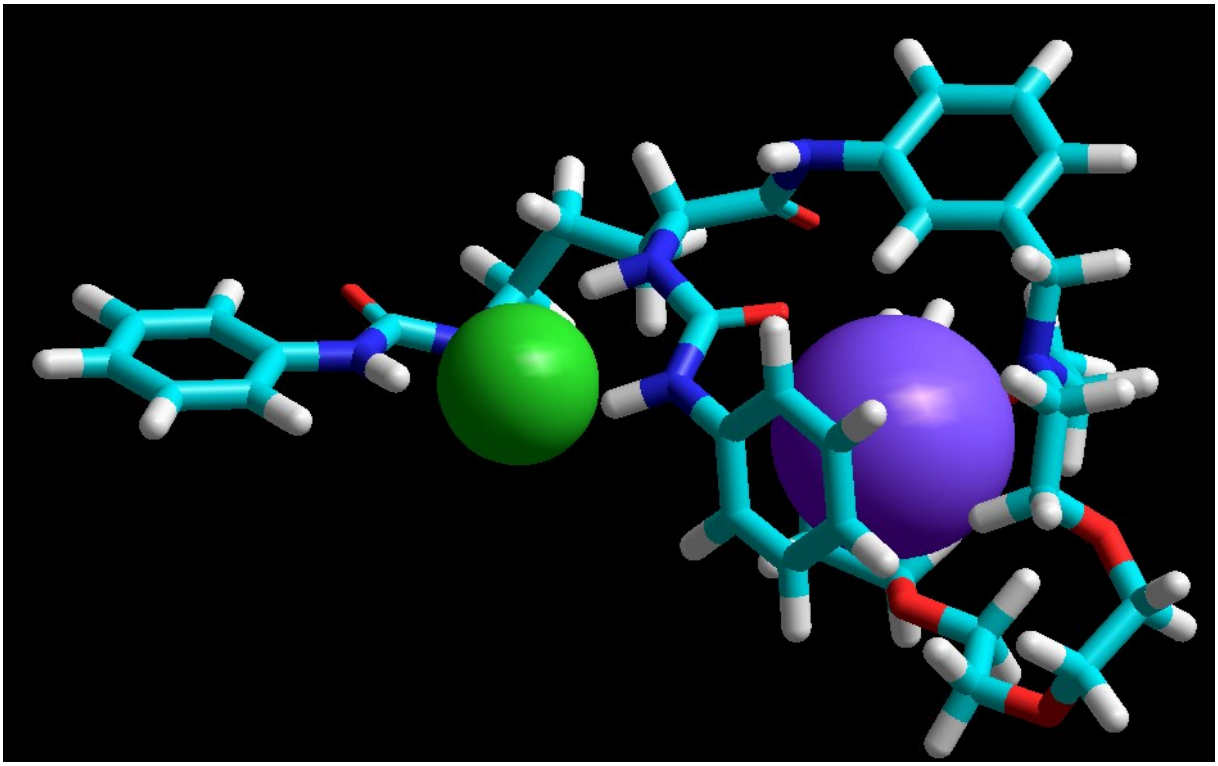
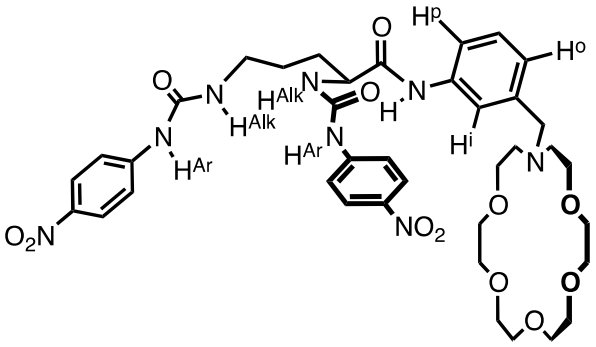


Figure 31 The calculated of **1**•KCl complex structure using semi-empirical method AM1

7. NMR titration experiments

NMR experiment general procedure

^{1}H NMR titration experiments were performed on a 300 MHz BrukerAvance spectrometer, at 298K, in CD_3CN solution. In each case 0.5 mL of 1.5-1.6 x 10^{-3} solution of receptor **1** was added to 5 mm NMR tube. Where applicable the solution also contained 1 mol equivalent of cation (KPF_6) in receptor solution was added. After each addidion of titrant as tetrabutyloamonium salt in receptor solution, a spectrum was registered. The resulting titration date were analysed by HypNMR.



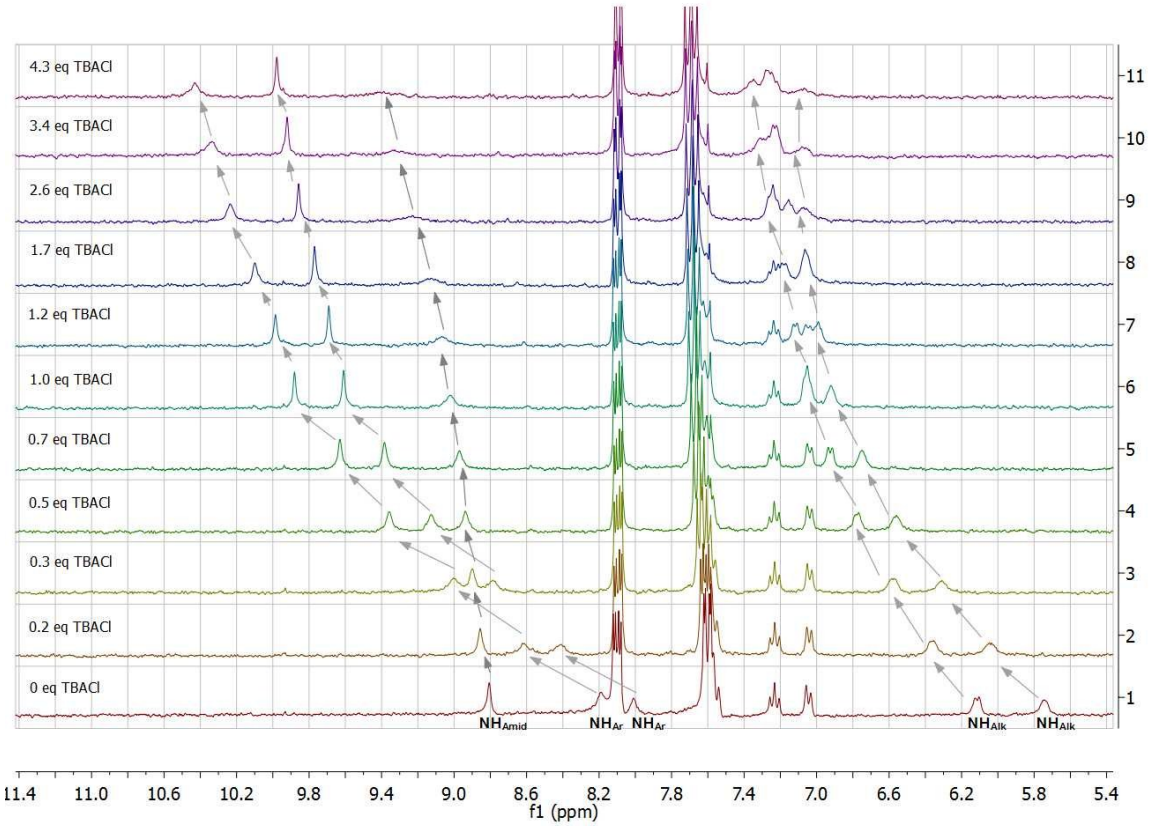


Figure 32 Partial ^{1}H NMR titration experiment of **1** upon titrant (TBACl) addition, (293 K, CD_3CN solution, $C_{titrant}$=1.4 x10^{-2}M,$C_{receptor}$=1.6 x10^{-3}M)

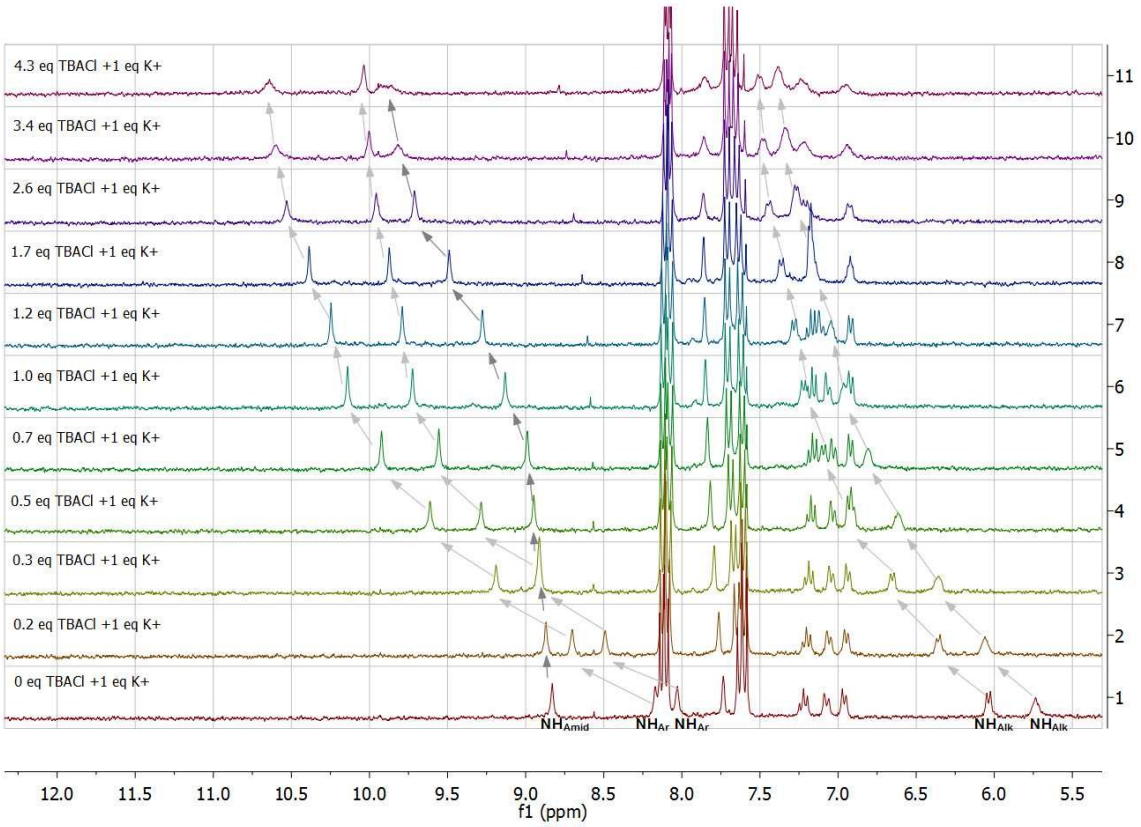


Figure 33 Partial ^{1}H NMR titration experiment of **1** upon titrant (TBACl) addition in presence of 1eq. KPF_6, (293 K, CD_3CN solution, $C_{titrant}$=1.4 x10^{-2}M, $C_{receptor}$=1.6 x10^{-3}M ^{3}M)

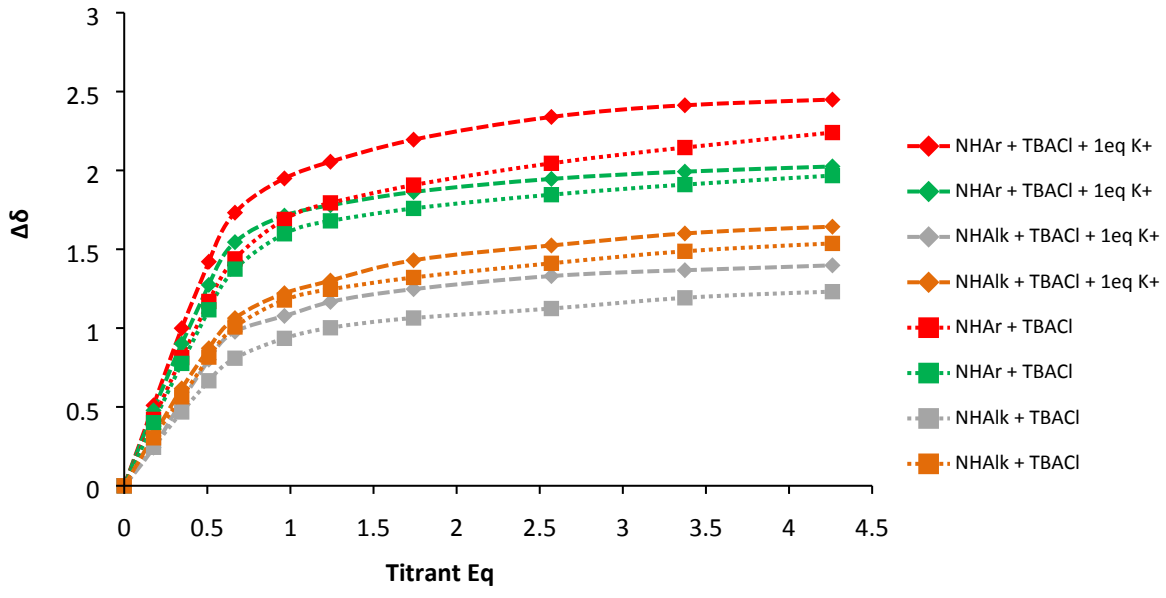


Figure 34 ^{1}H NMR titration binding isotherms of **1**, with TBACl in the presence or absence of 1 eq. potassium cation

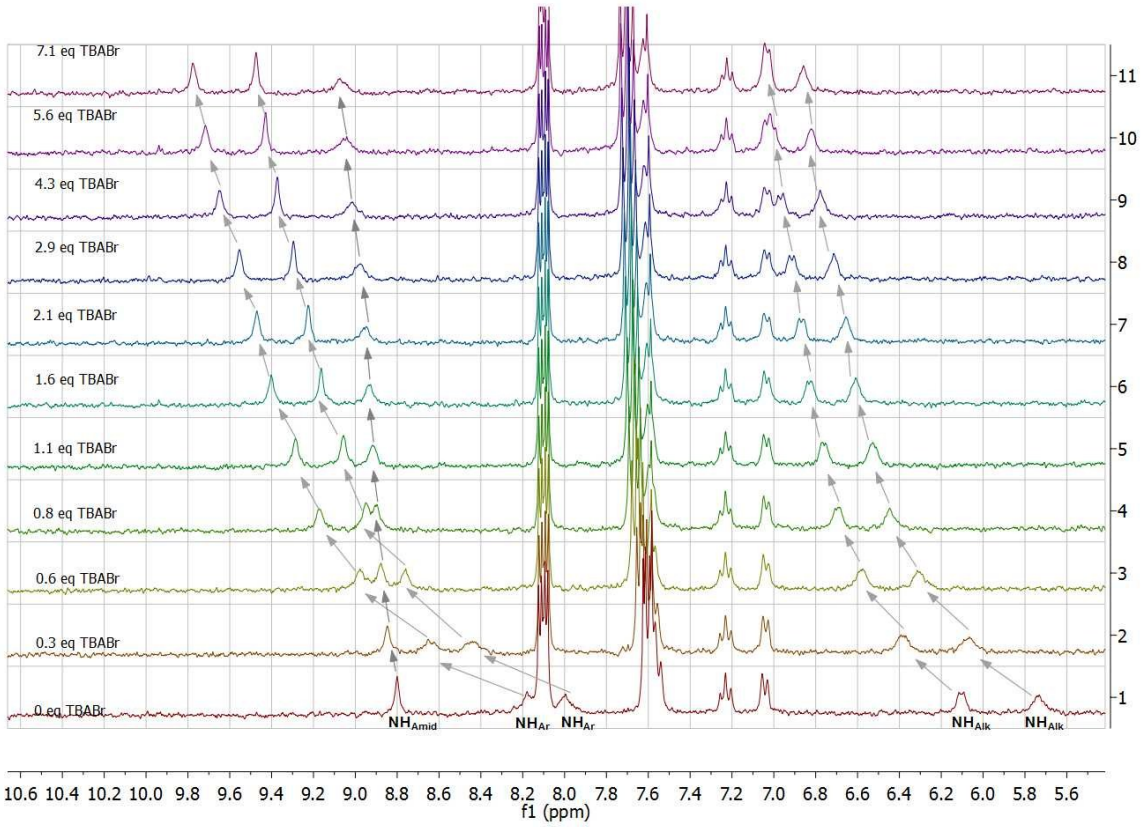


Figure 35 Partial ^{1}H NMR titration experiment of **1** upon titrant (TBABr) addition, (293 K, CD_3CN solution, $C_{titrant}$=2.3 x10^{-2}M,$C_{receptor}$=1.5 x10^{-3}M)

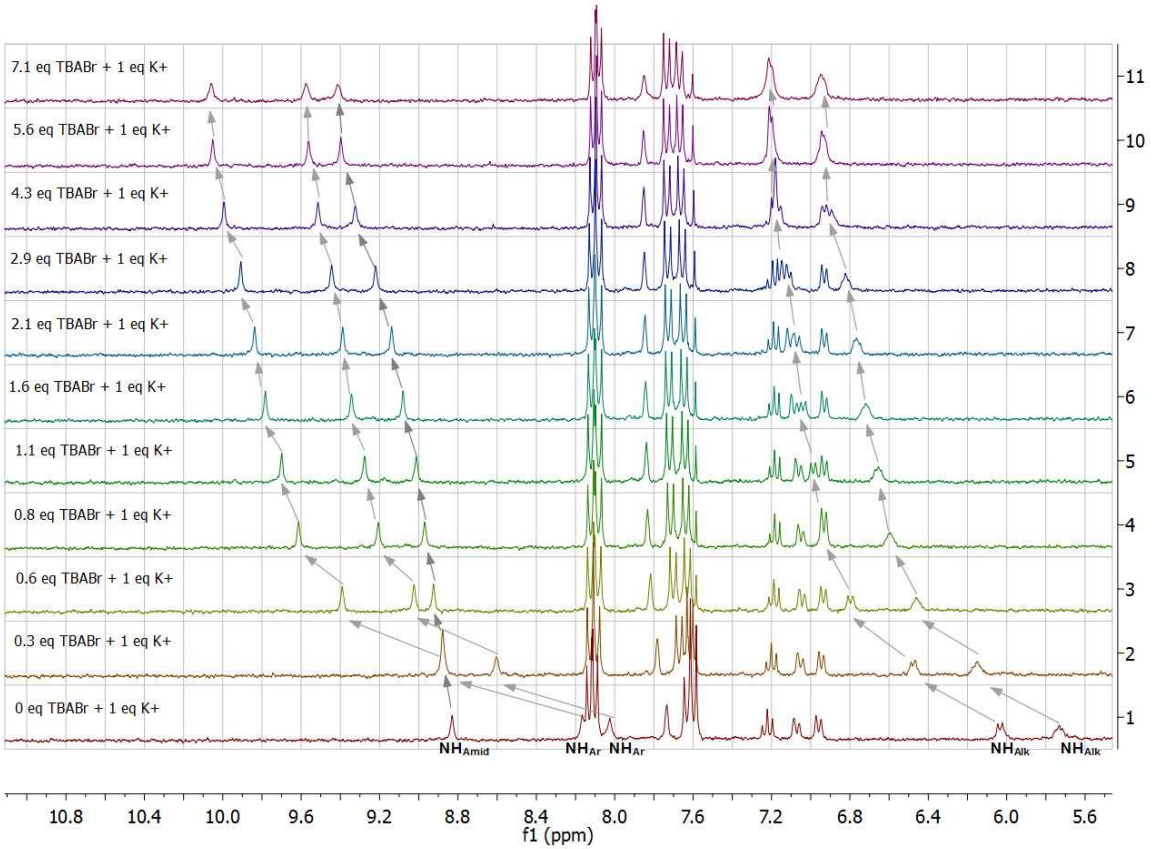


Figure 36 Partial ^{1}H NMR titration experiment of **1** upon titrant (TBABr) addition in presence of 1eq. KPF_6, (293 K, CD_3CN solution, $C_{titrant}$=2.3 x10^{-2}M, $C_{receptor}$=1.5 x10^{-3}M)

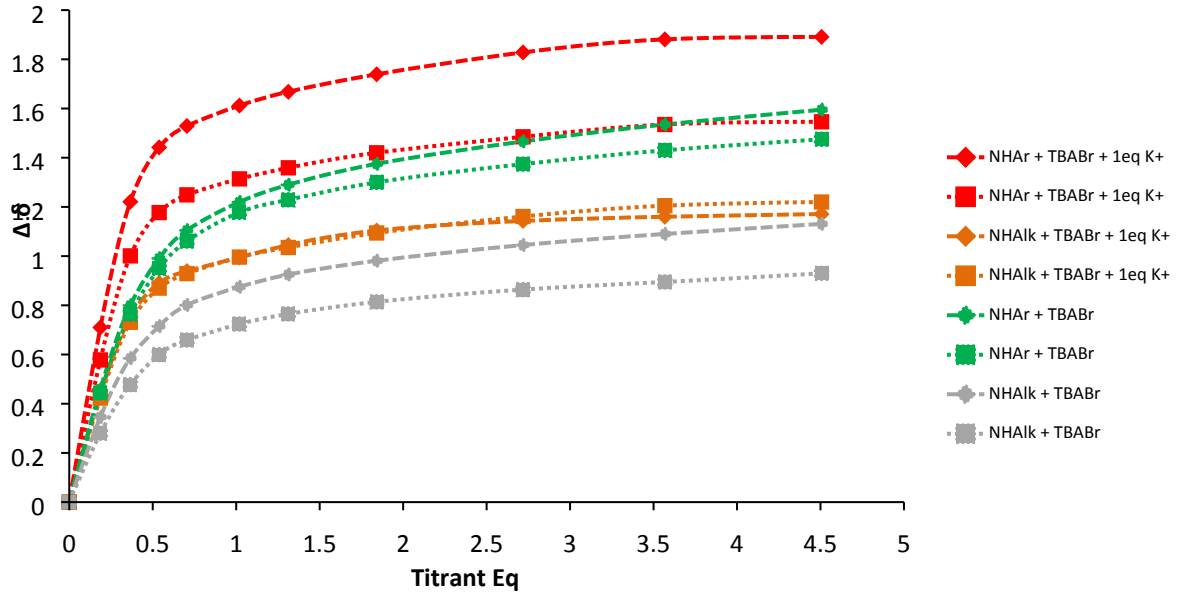


Figure 37 ^{1}H NMR titration binding isotherm of **1**, with TBABr in the presence or absence of 1 eq. potassium cation

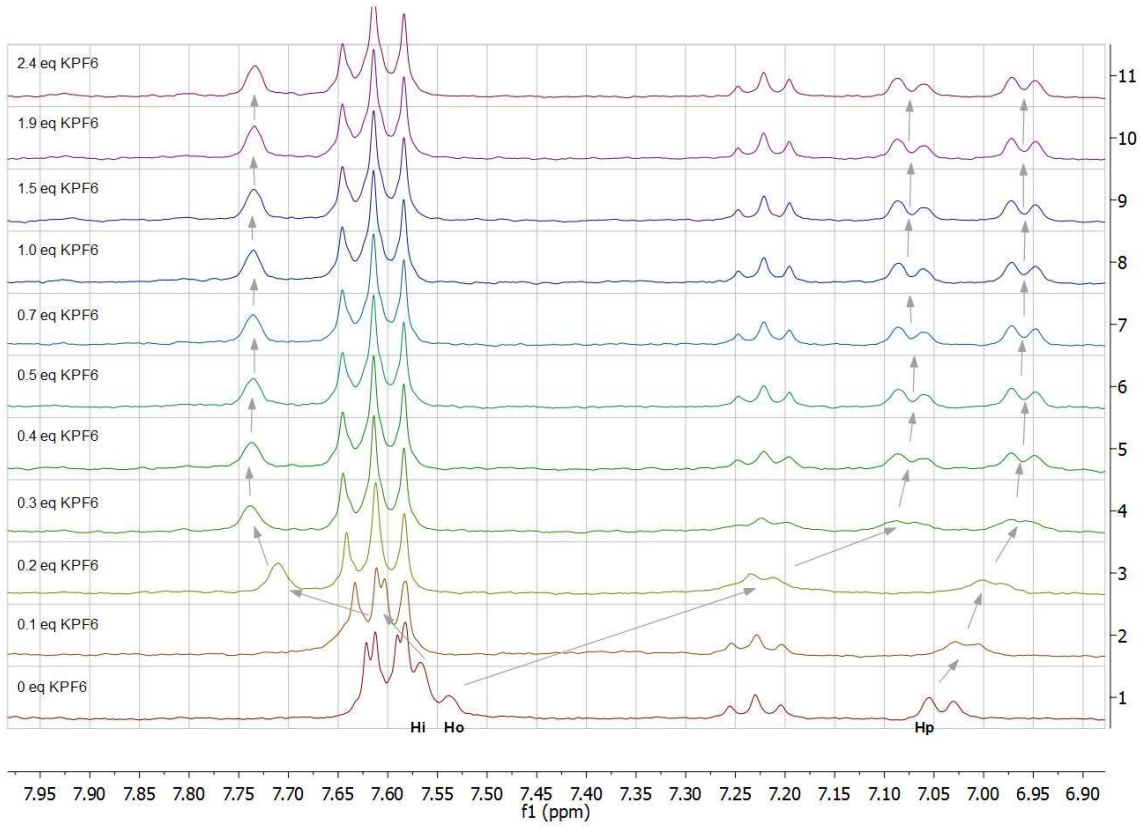


Figure 38 Partial ^{1}H NMR titration experiment of **1** upon titrant (KPF_6) addition, (293 K, CD_3CN solution, $C_{titrant}$=7.8 x10^{-3}M, $C_{receptor}$=1.5 x10^{-3}M)

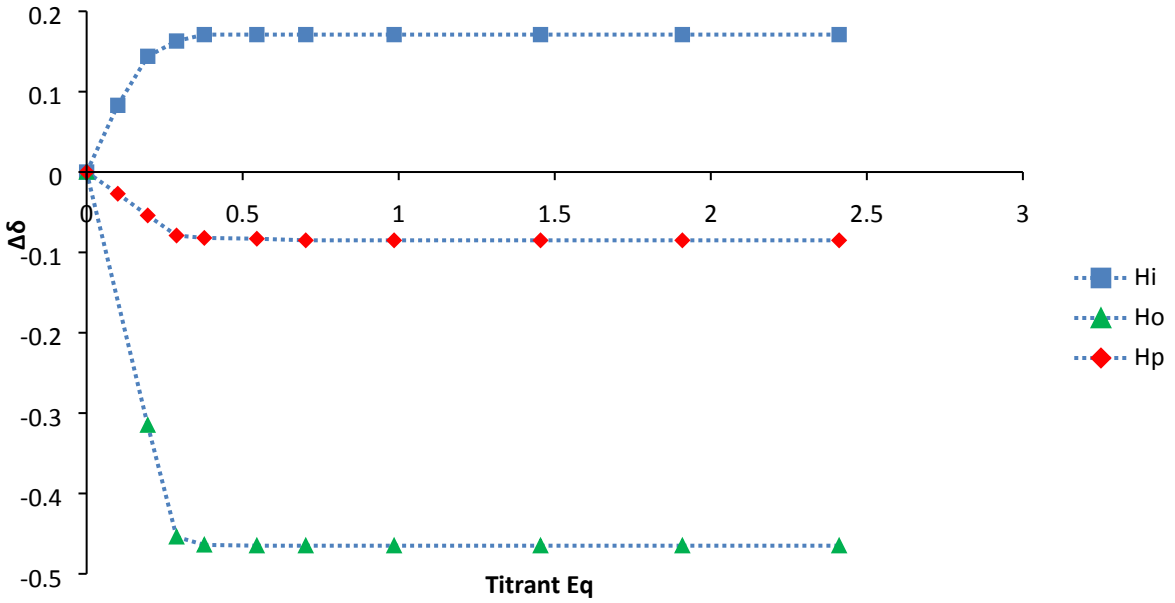


Figure 39 ^{1}H NMR titration binding isotherm of **1** with KPF_6

8. Extraction experiment

Chloride concentration in aqueous phase was measured using Zall, Fisher and Garner colorimetric method based on displacement of thiocyanate from mercury (II) thiocyanate on chloride anion. Thiocyanate anions in presence of iron (III) cations forms color complexes with max absorbance at 480 nm wavelength.

Salt extraction experiment were done using solution of 8.89 mg (0.011mmol) of the receptor **1** in 10 ml of chloroform and solution of 37.52 mg (0.50 mmol) KCl, or 30.36 mg (0.52 mmol) NaCl, or 27.29 mg (0.51 mmol) NH_4Cl in 10 ml of deionized water. Then 2.5 ml of receptor solution was shaken overnight with 2.5 ml of salt solution. After phase separation, 2.0 ml of chloroform solution was taken and shaken with 2.0 ml of deionized water. Then 1.2 ml of water phase was added to solution of 1.6 ml of $Fe(NO_3)_3$ (14.0 g of $Fe(NO_3)_3$ *9 H_2O in 125 ml of concentrated HNO_3 and 125 ml of H_2O), 0.6 ml of saturated $Hg(SCN)_2$ in 2.6 ml of deionized water. After 1 minute UV-Vis spectrum was acquired.

Calibration curve was received using potassium chloride solution and is presented below.

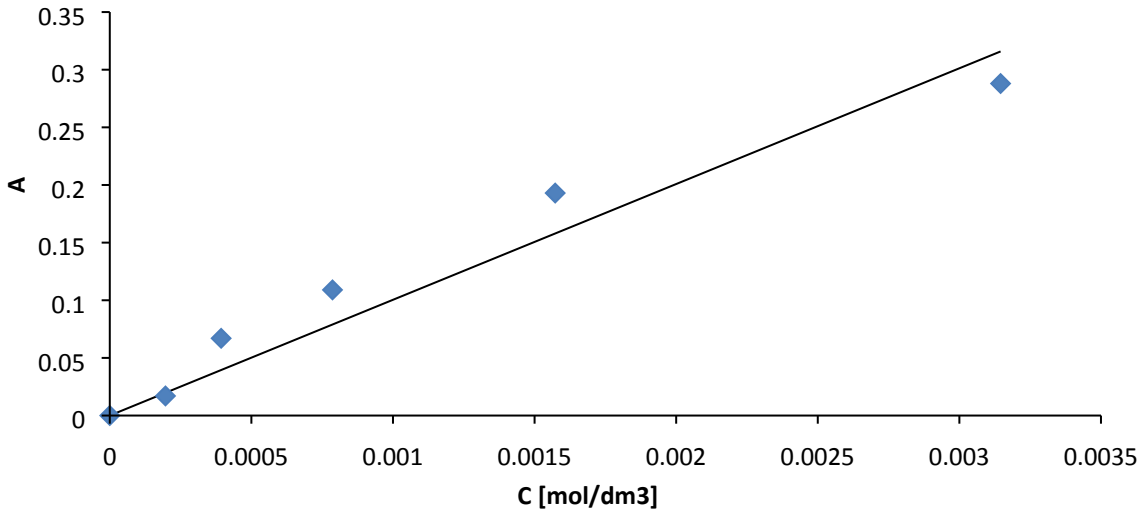


Figure 40 Chloride calibration curve

The extraction efficiency was calculated as the fraction of receptor molecules occupied by the complex in the organic phase. The blind sample was pure chloroform treated as samples contain receptors **1** and **2**.

Salt / Receptor	KCl	Nh_4Cl	NaCl
1	97%	93%	6%
2	0%	0%	0%
Blind	0%	0%	0%

Figure 41 The extraction efficiency