Supporting Information

Cooperative ion pair recognition by multitopic L-ornithine based salt receptors
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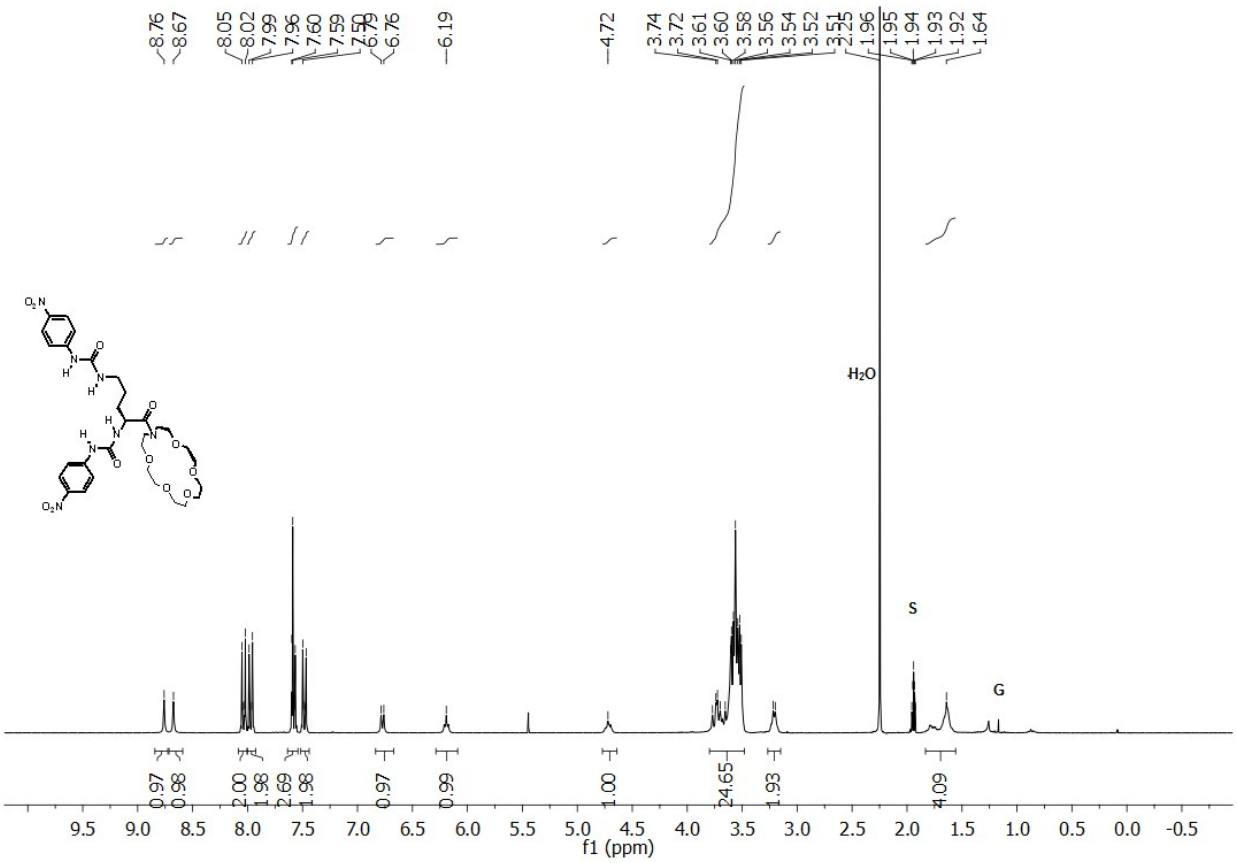
GENERAL INFORMATION

Unless specifically indicated, all other chemicals and reagents used in this study were purchased from commercial sources and used as received. Purification of products was performed using column chromatography on silica gel (Merck Kieselgel 60, 230-400 mesh) with mixtures of chloroform/methanol. Thin-layer chromatography (TLC) was performed on silica gel plates (Merck Kieselgel 60 F254).
^{1}H and ^{13}C NMR spectra used in the characterization of products were recorded on Bruker 300 spectrometer using a residual protonated solvent as internal standard. The following abbreviations are used to indicate the multiplicity: s - singlet; d - doublet; t - triplet; q - quartet; m - multiplet, b – broad signal.
High resolution mass spectra (HRMS) were measured on a Quattro LC Micromass unit using ESI technique.
UV-vis analyses were performed using Thermo Spectronic Unicam UV500 Spectrophotometer.

NMR SPECTRA

Fig. S1 and S2: ^{1}H and ^{13}C NMR of receptor **1.**



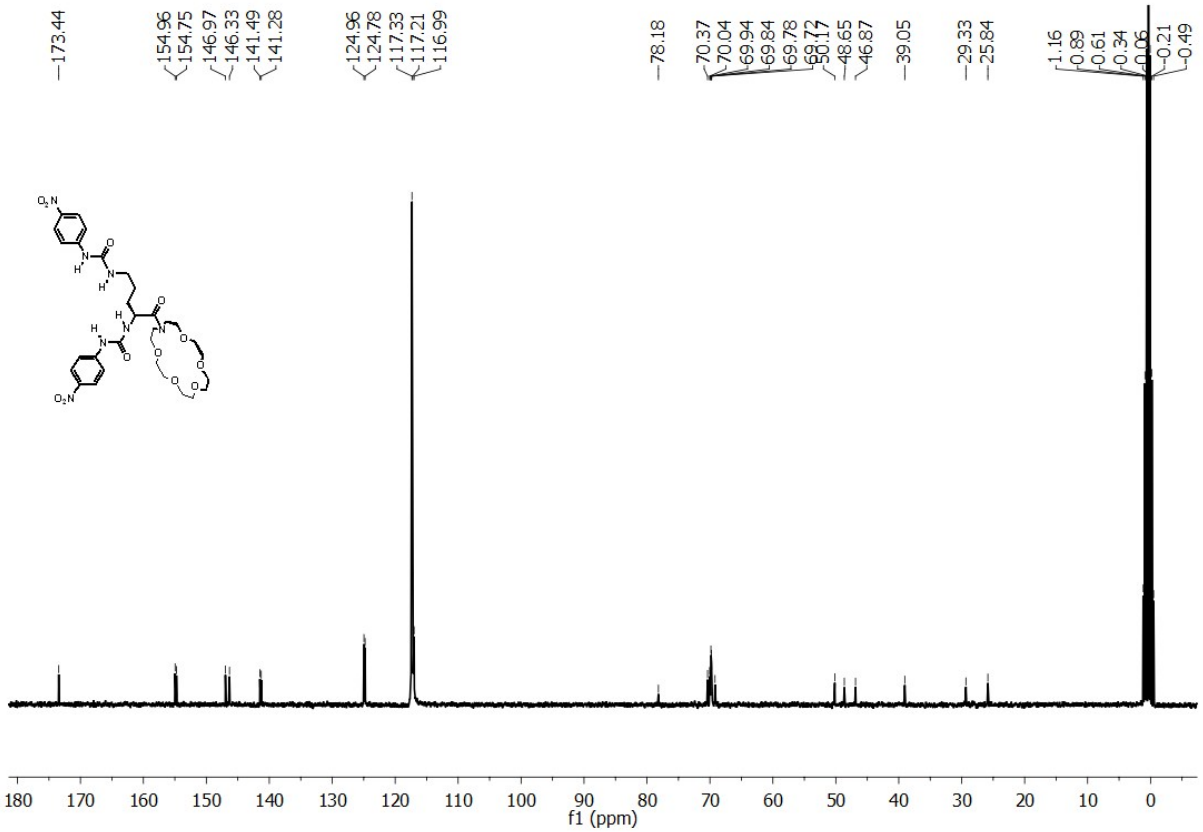
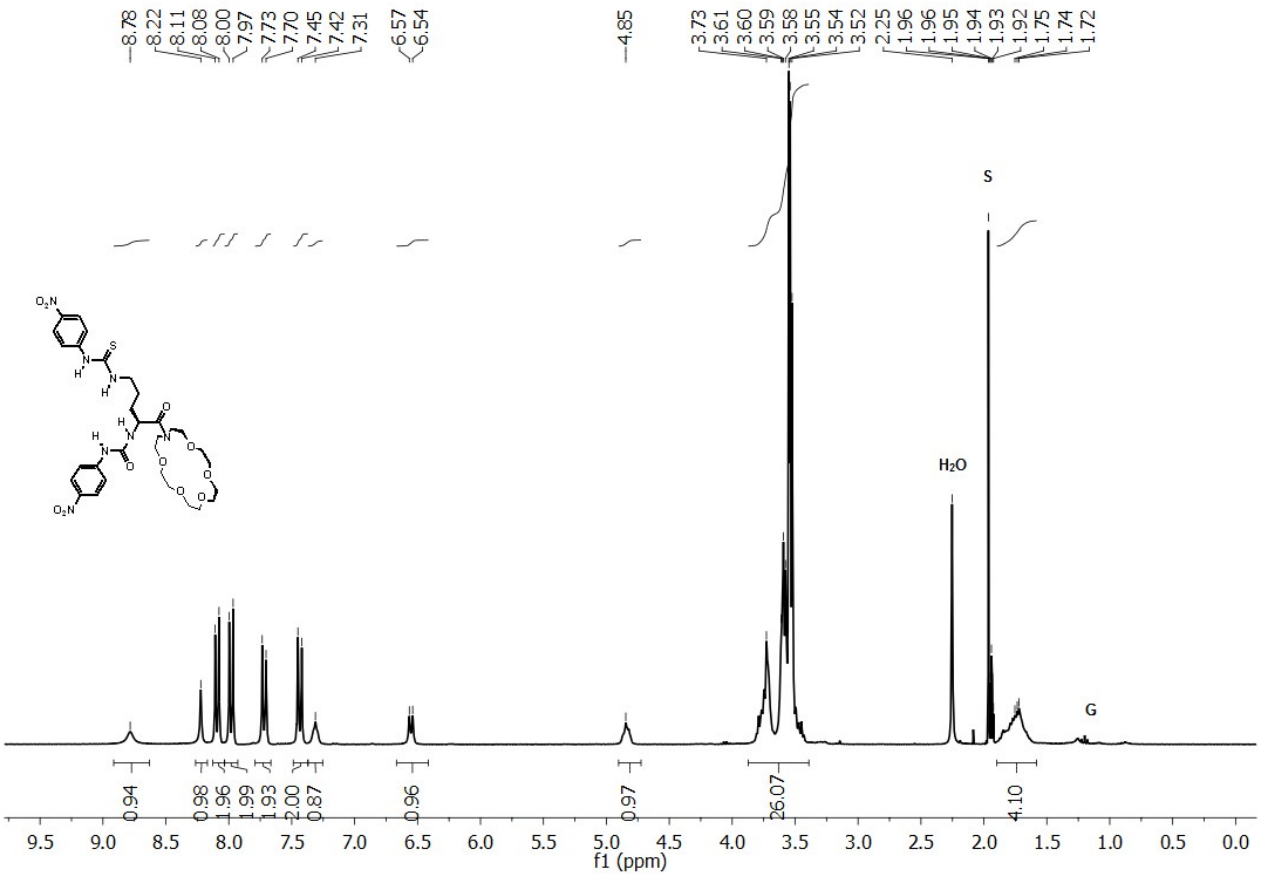


Fig. S3 and S3: ^{1}H and ^{13}C NMR of receptor **2.**



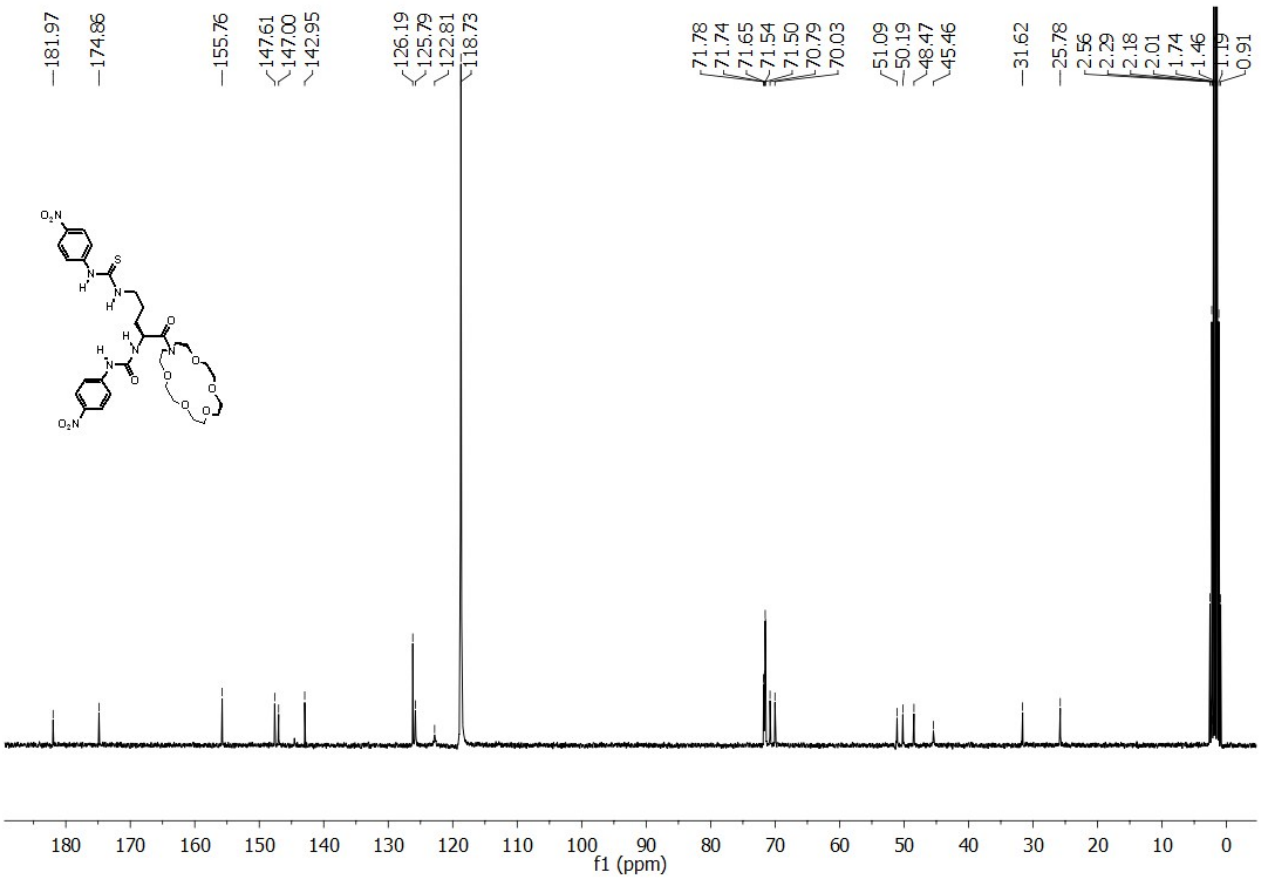
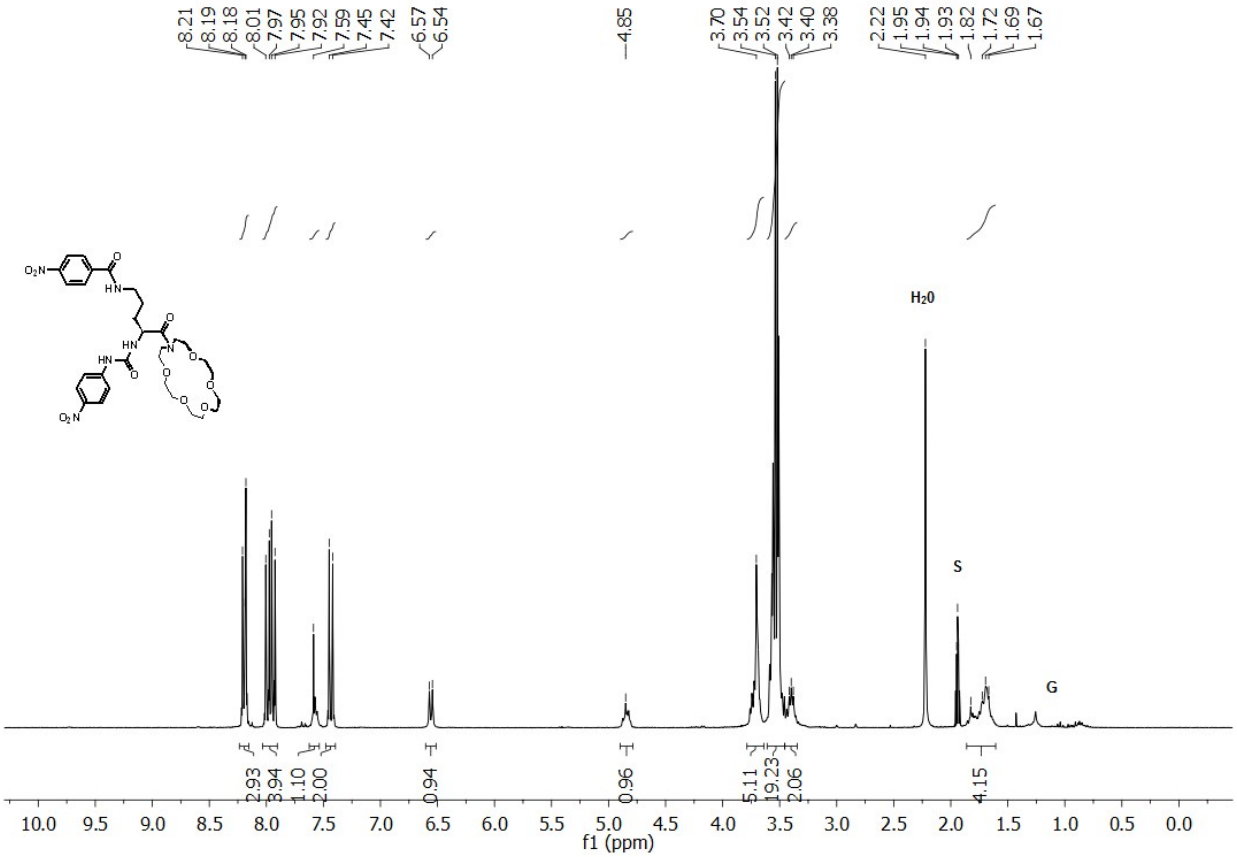


Fig. S5 and S6: ^{1}H and ^{13}C NMR of receptor **5.**



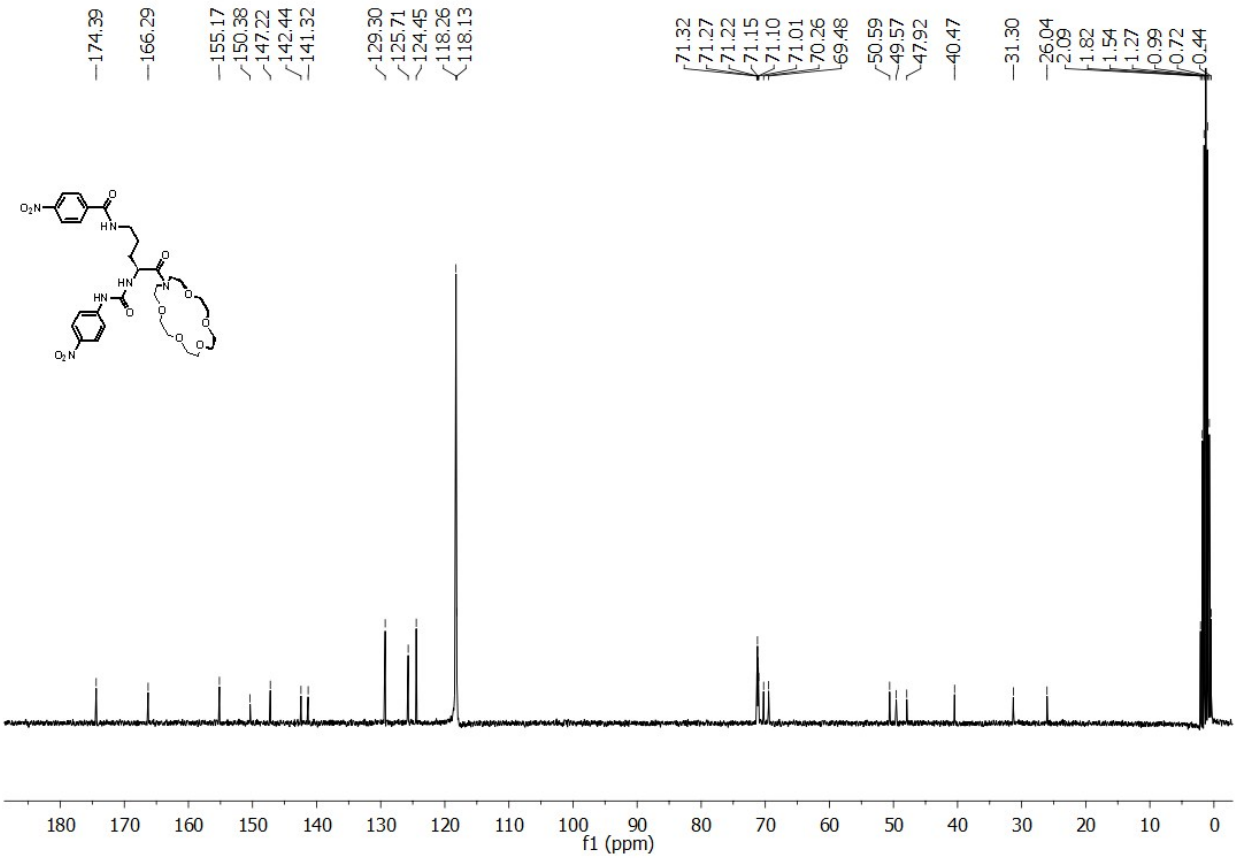
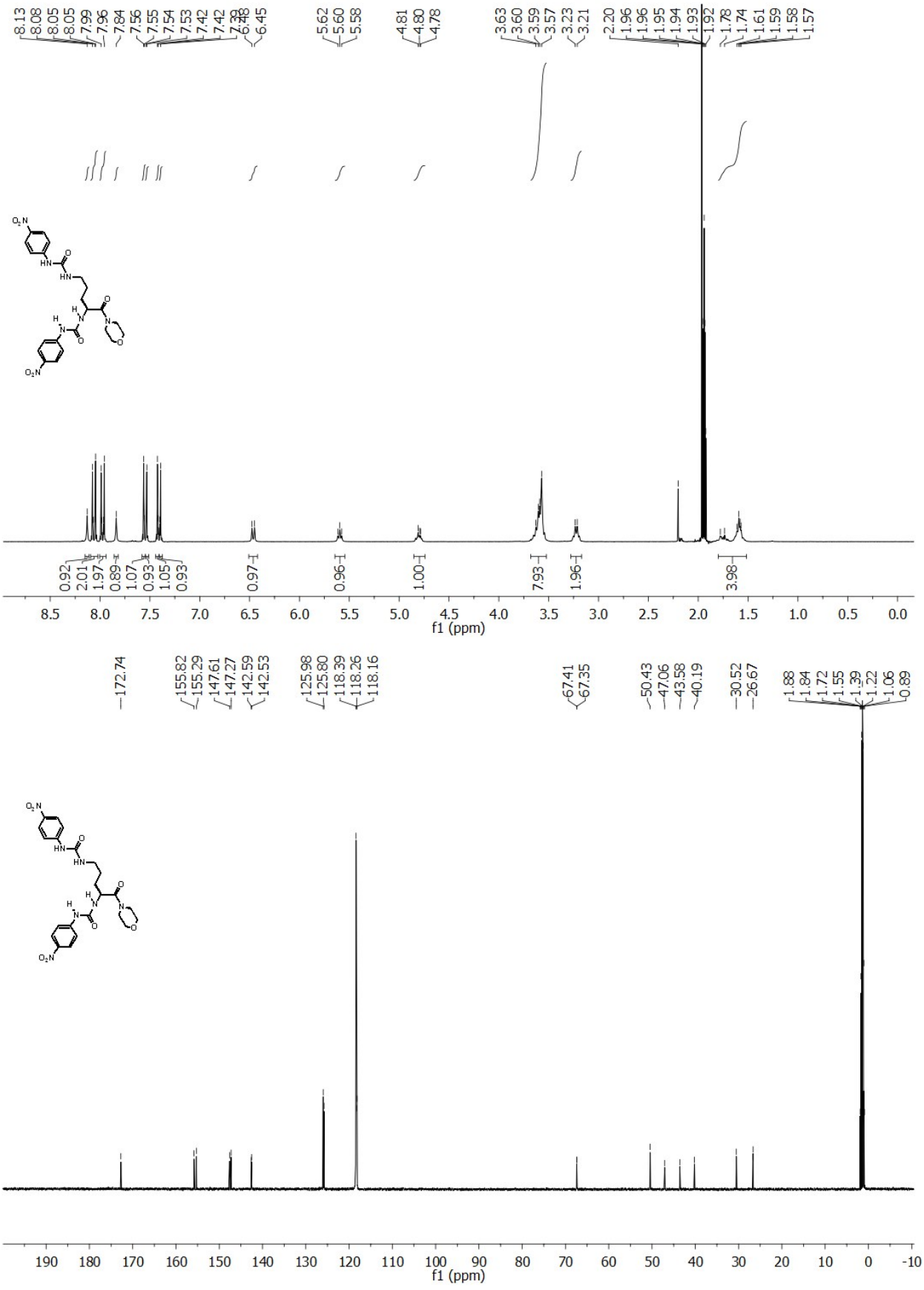


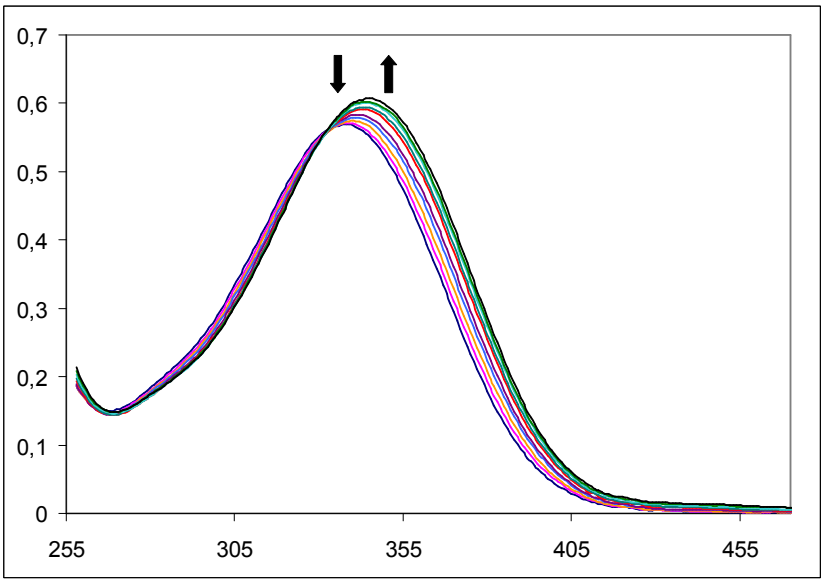
Fig. S7 and S8: ^{1}H and ^{13}C NMR of receptor **6.**



„S"- solvent, „G"- grease

UV-VIS EXPERIMENTS

Fig. S9: Representative Uv-Vis Titration Spectra



DILUTION AND JOB PLOTS.

Fig. S10: Dilution curve of receptor **1**.

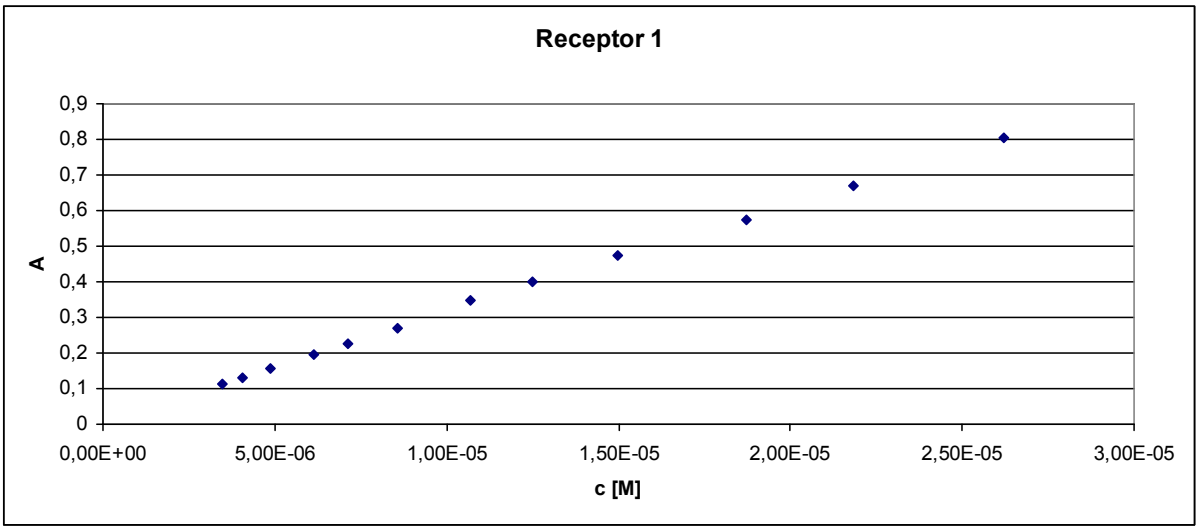


Fig. S11: Job plot (Host: Receptor **1**, guest: Cl^-)

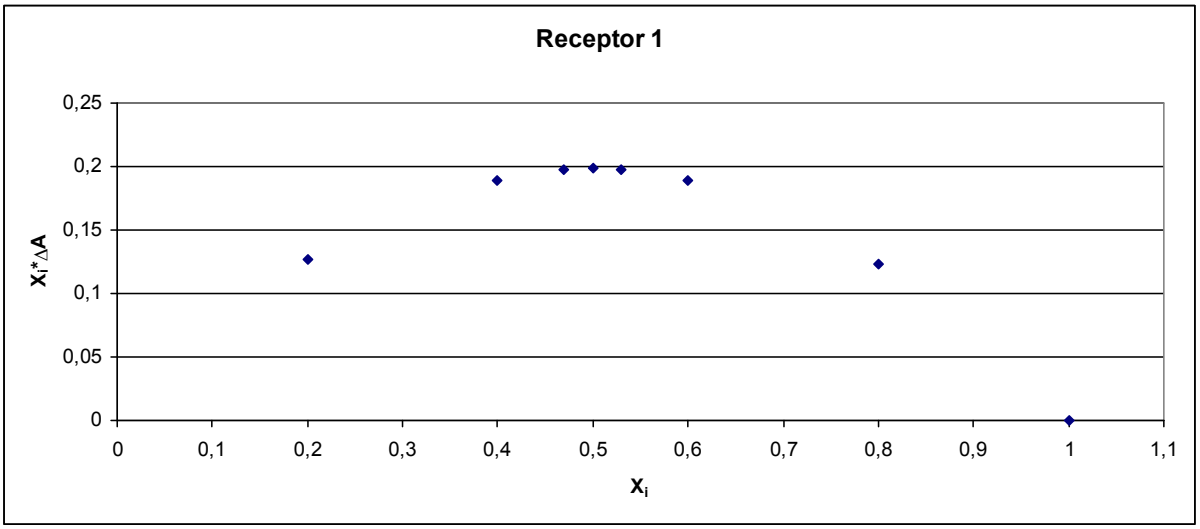


Fig. S12: Dilution curve of receptor **2**.

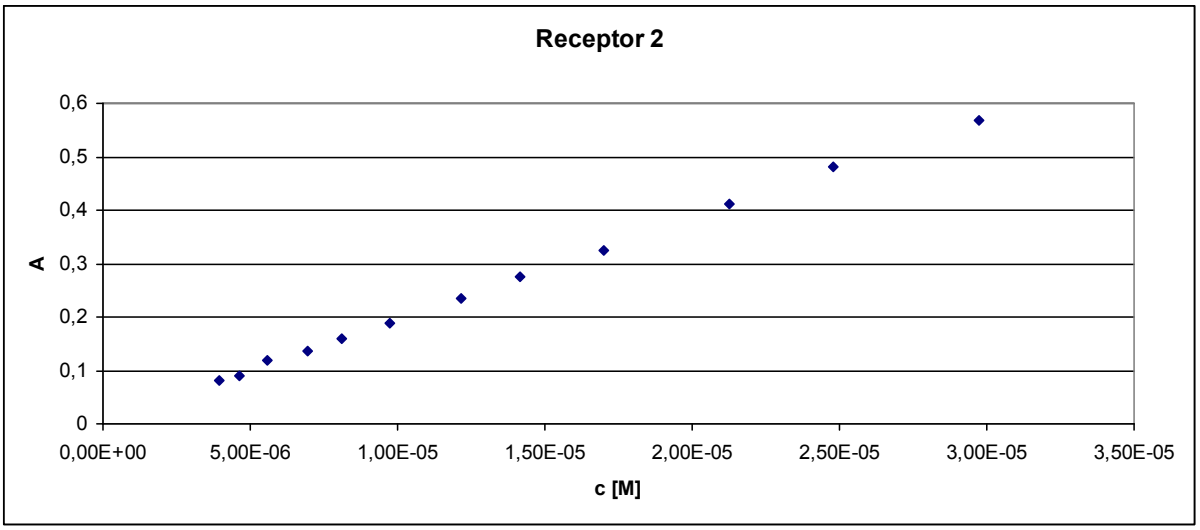


Fig. S12: Job plot (Host: Receptor **2**, guest: Cl^-)

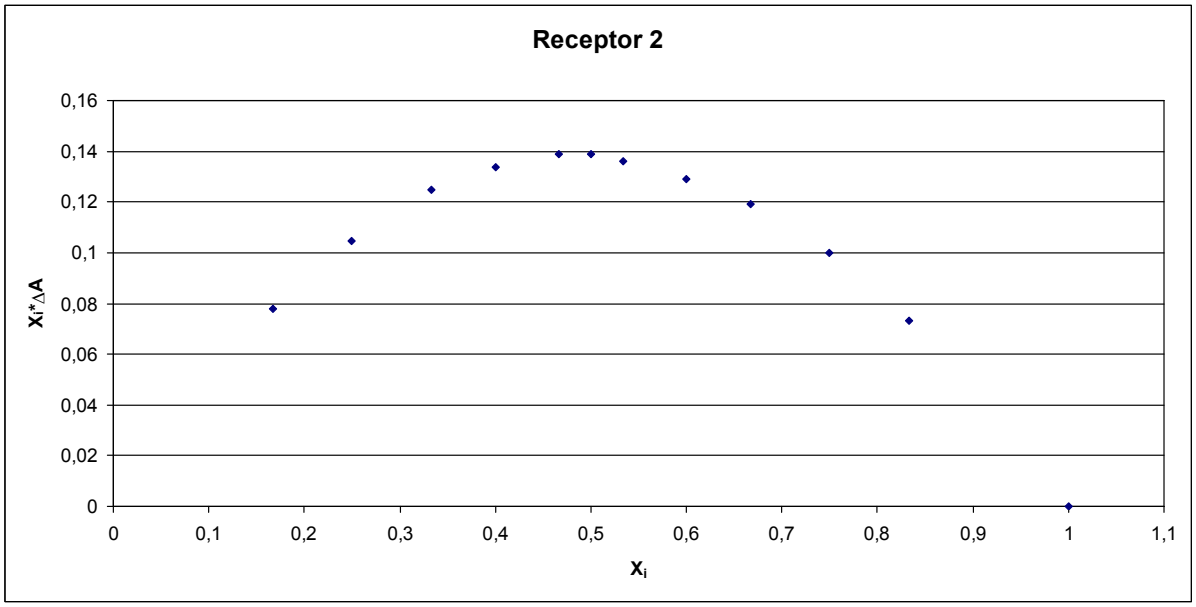


Table S1: Association Constants.

	Receptor 1			Receptor 2		
	TBA^+	Na^+	K_{Na}/K_{TBA}	TBA^+	Na^+	K_{Na}/K_{TBA}
NO_2^-	3 800	7 800	2,05	7 200	18 500	1,82
Br^-	3 400	5 100	1,5	3 700	4 700	1,27
Cl^{-*}	18 200	33 500	1,84	46 800	85 500	2,57
$PhCOO^-$	460 000	161 000	0,35	$1{,}19 \cdot 10^6$	526 000	0,44
Ac^-	$3{,}5 \cdot 10^6$	280 000	-	deprotonation	deprotonation	-

***** Association constants for interactions of receptors **4** and **5** with chloride. Receptor **4**: K_{TBACl}= 1700 M^{-1}, K_{NaCl}= 5100 M^{-1}; Receptor **5**: K_{TBACl}= 3900 M^{-1}, K_{NaCl}= 8900 M^{-1}

Fig. S13: UV-Vis titration binding isotherms of receptor **1** with TBACl and TBACl in the presence of 1 equivalent of $NaPF_6$. Experimental data (points), fitted curve (line).

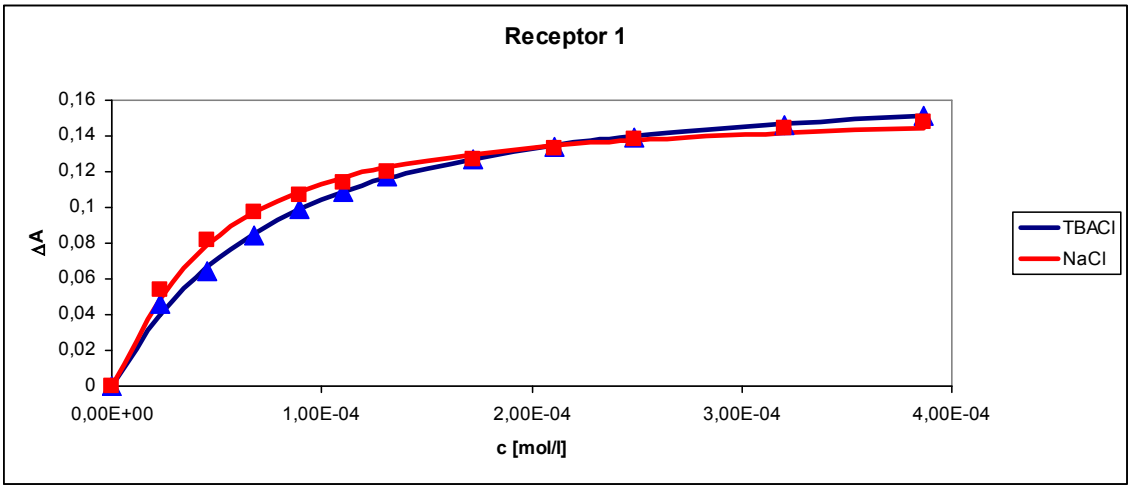


Fig. S14: UV-Vis titration binding isotherms of receptor **2** with TBACl and TBACl in the presence of 1 equivalent of $NaPF_6$. Experimental data (points), fitted curve (line).

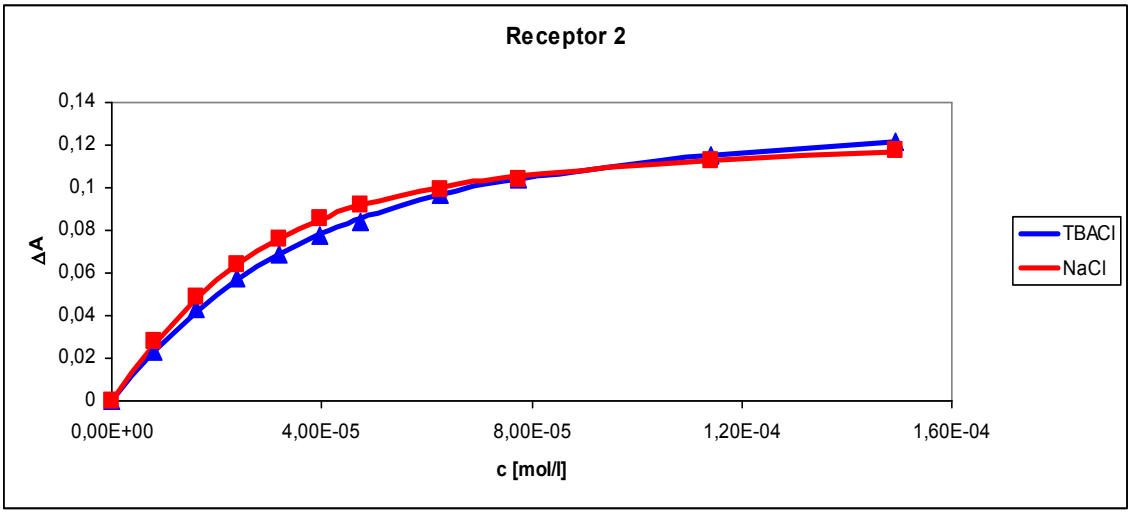


Fig. S15: UV-Vis titration binding isotherms of receptor **4** with TBACl and TBACl in the presence of 1 equivalent of $NaPF_6$. Experimental data (points), fitted curve (line).

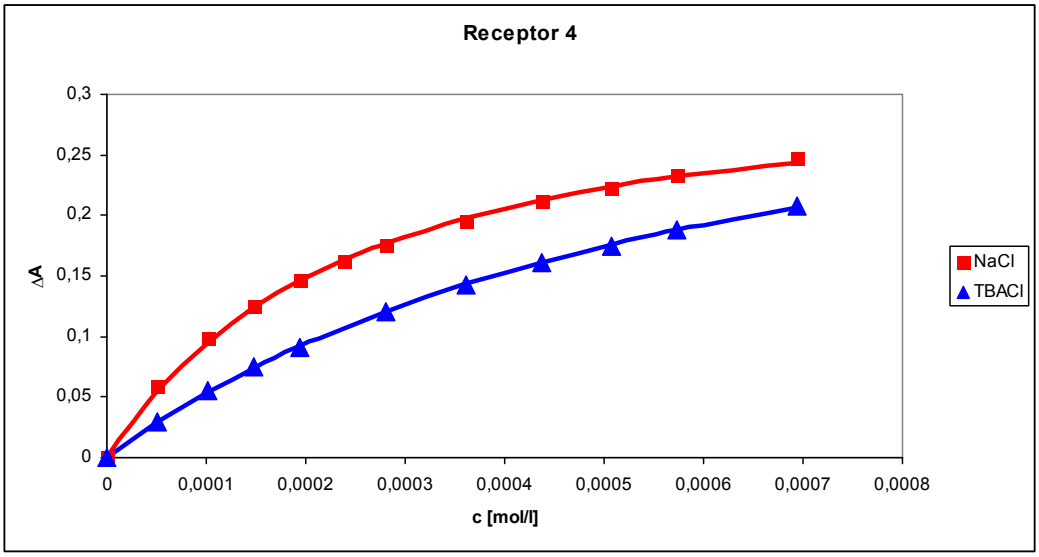


Fig. S16: UV-Vis titration binding isotherms of receptor **5** with TBACl and TBACl in the presence of 1 equivalent of $NaPF_6$. Experimental data (points), fitted curve (line).

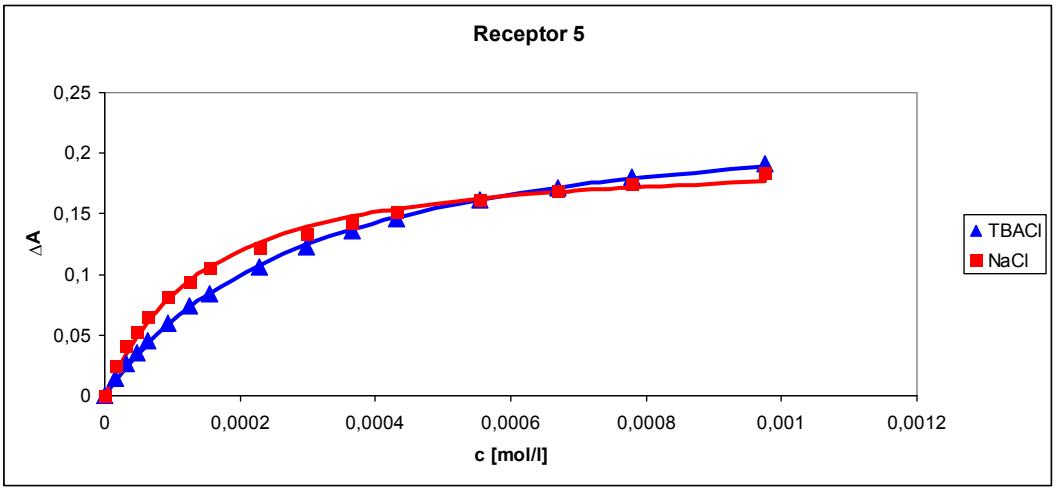


Fig. S17: UV-Vis titration binding isotherms of receptor **1** with $TBANO_2$ and $TBANO_2$ in the presence of 1 equivalent of $NaPF_6$. Experimental data (points), fitted curve (line).

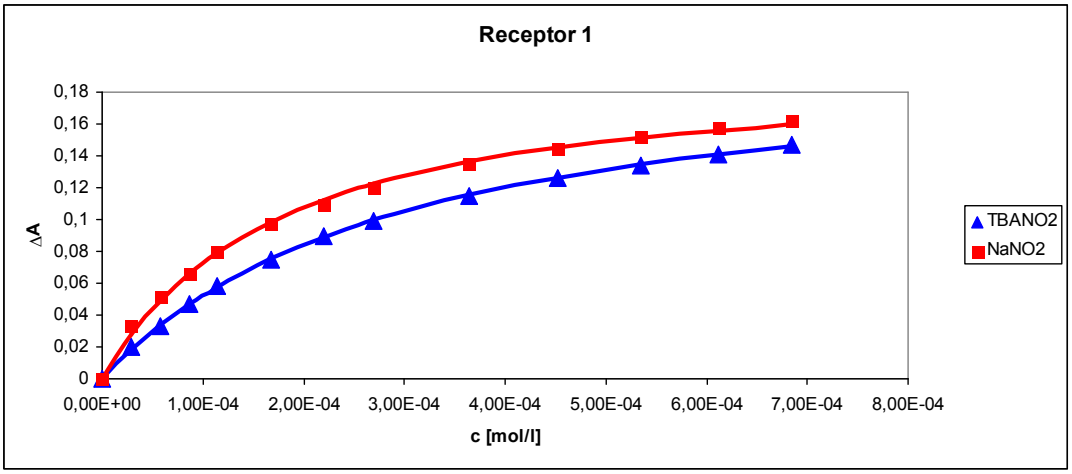


Fig. S18: UV-Vis titration binding isotherms of receptor **2** with $TBANO_2$ and $TBANO_2$ in the presence of 1 equivalent of $NaPF_6$. Experimental data (points), fitted curve (line).

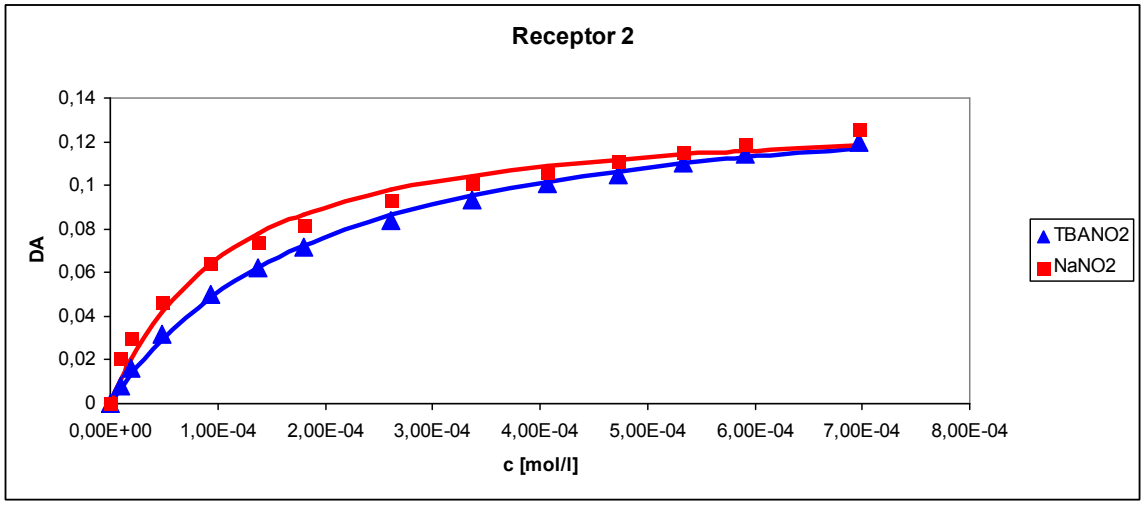


Fig. S19: UV-Vis titration binding isotherms of receptor **1** with TBABr and TBABr in the presence of 1 equivalent of $NaPF_6$. Experimental data (points), fitted curve (line).

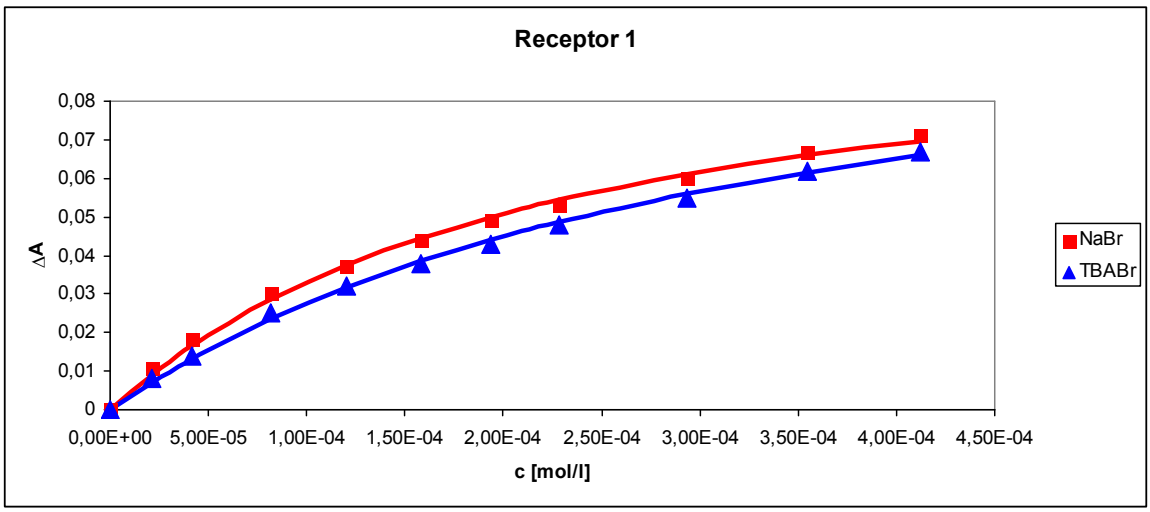


Fig. S20: UV-Vis titration binding isotherms of receptor **2** with TBABr and TBABr in the presence of 1 equivalent of $NaPF_6$. Experimental data (points), fitted curve (line).

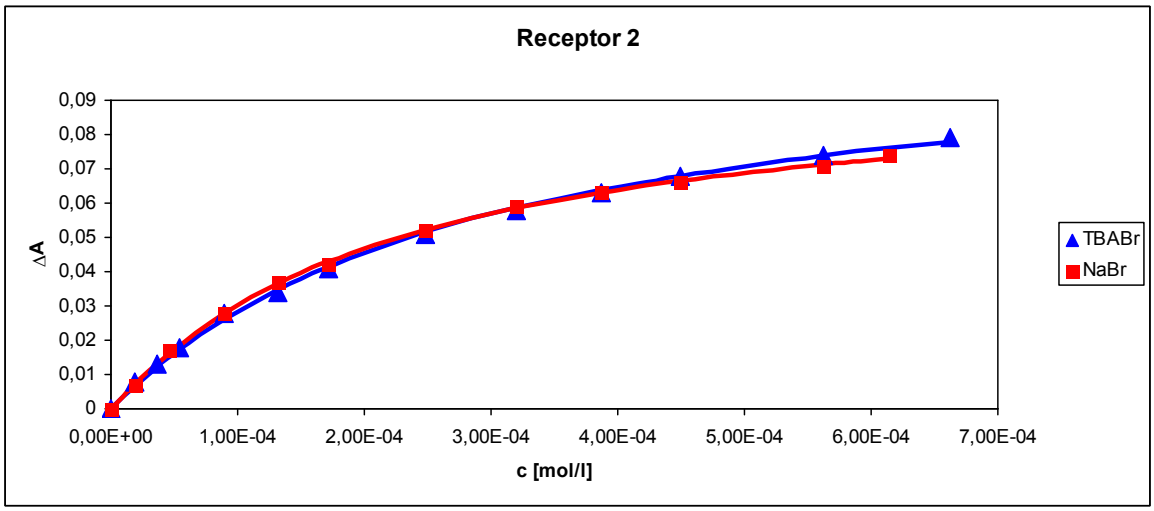


Fig. S21: UV-Vis titration binding isotherms of receptor **1** with PhCOOTBA and PhCOOTBA in the presence of 1 equivalent of $NaPF_6$. Experimental data (points), fitted curve (line).

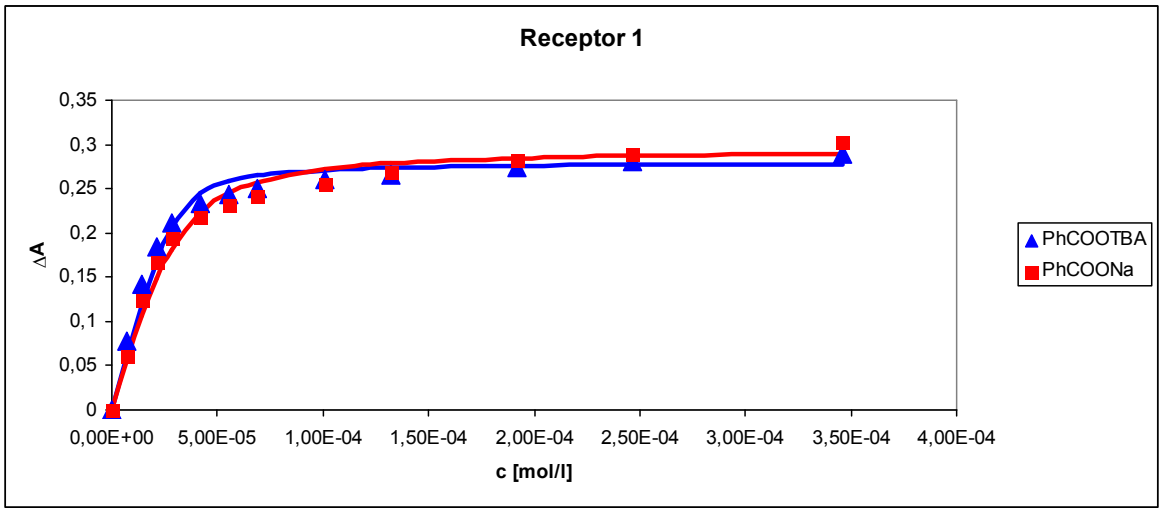


Fig. S22: UV-Vis titration binding isotherms of receptor **2** with PhCOOTBA and PhCOOTBA in the presence of 1 equivalent of $NaPF_6$. Experimental data (points), fitted curve (line).

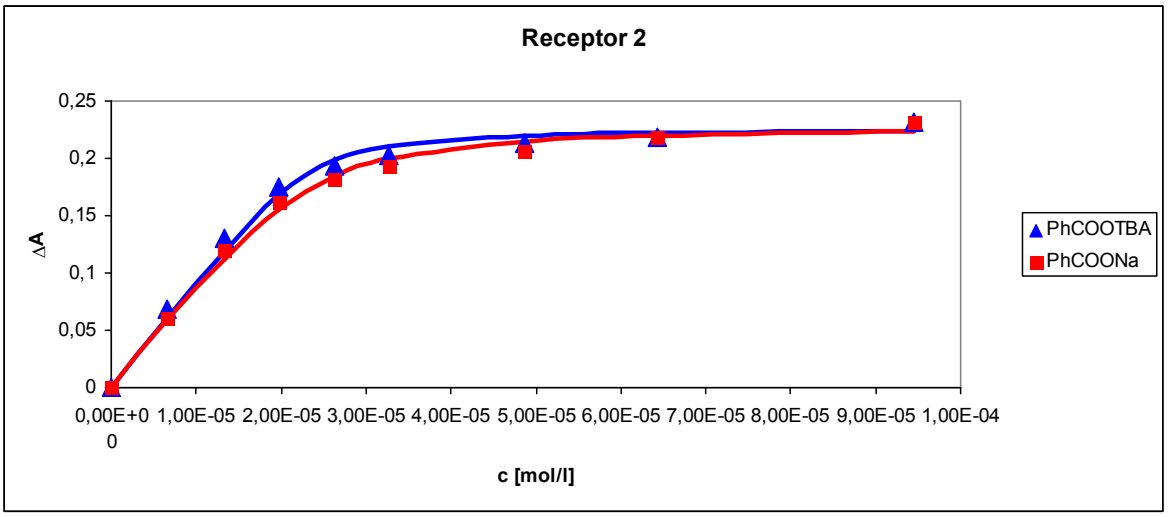
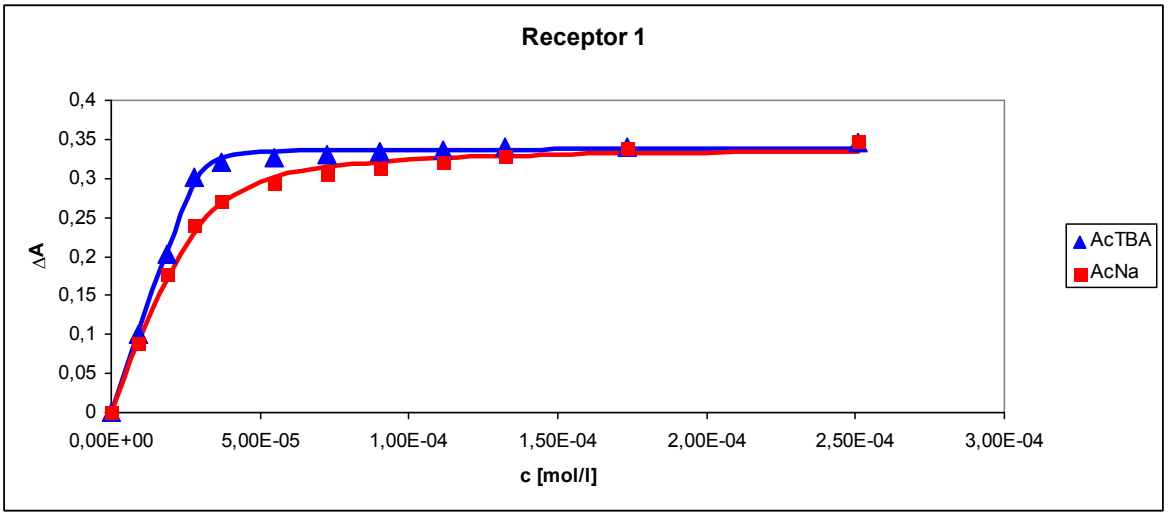


Fig. S23: UV-Vis titration binding isotherms of receptor **1** with AcTBA and AcTBA in the presence of 1 equivalent of $NaPF_6$. Experimental data (points), fitted curve (line).



NMR TITRATIONS

The ^{1}H NMR titrations were performed on a Varian UnityPlus 200 MHz spectrometer, at 298K in CD_3CN. The anion TBA and cation PF6 salts were dried under high vacuum at 30−45 °C prior to use. In each case, a 500 μL of freshly prepared 2.56 or 2.66 mM solution of receptor **1** or **2** was added to a 5mm NMR tube. Where applicable the solution also contained 1 molar equivalent of sodium hexafluorophosphate. Small aliquots of 60 mM solution of tetrabutylammonium bromide salts, containing **1** or **2** at 2.56 or 2.66 mM concentration, were added and a spectrum was acquired after each addition. Titration isotherms for NH protons were fitted to a 1:1 binding model using the HypNMR 2000 program.

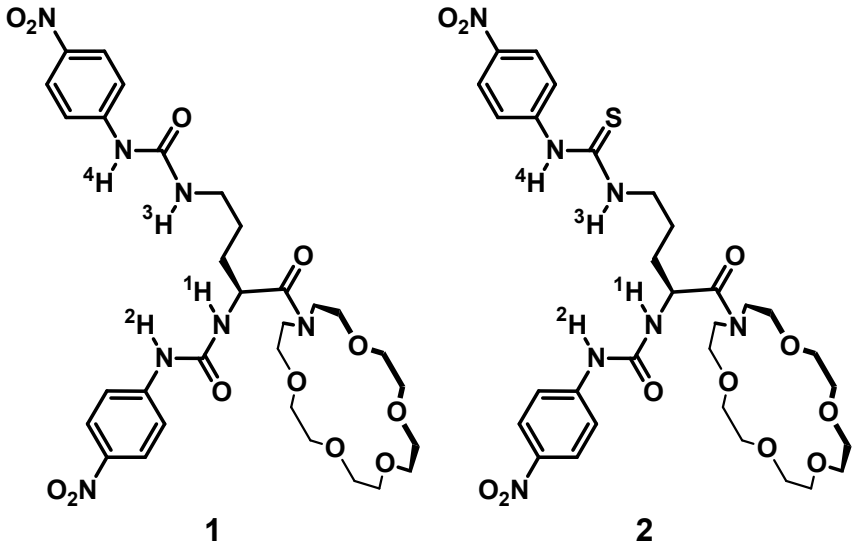


Fig. S24: ^{1}H NMR titrations of receptors **1** and **2** with TBABr and TBABr in the presence of 1 equivalent of $NaPF_6$. Profiles based on the chemical shift (δ, ppm) of urea H^1 proton.

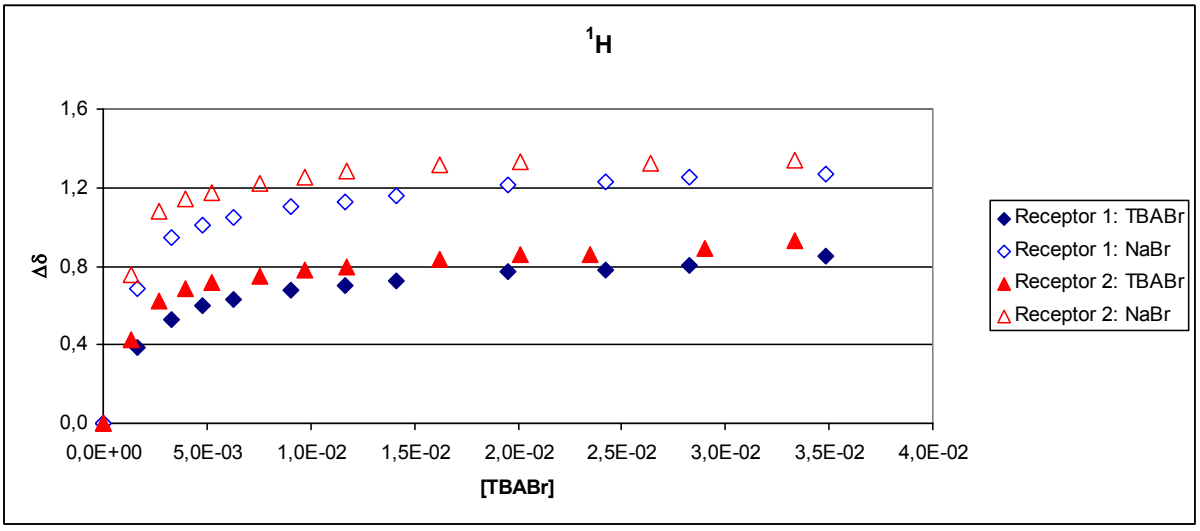


Fig. S25: ^{1}H NMR titrations of receptors **1** and **2** with TBABr and TBABr in the presence of 1 equivalent of $NaPF_6$. Profiles based on the chemical shift (δ, ppm) of urea H^2 proton.

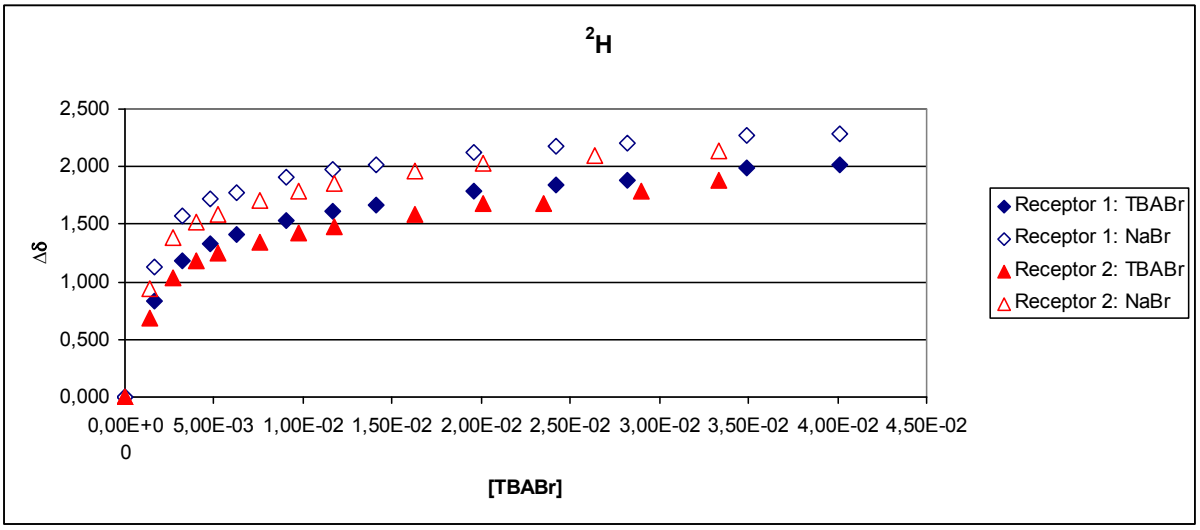


Fig. S26: ^{1}H NMR titrations of receptors **1** and **2** with TBABr and TBABr in the presence of 1 equivalent of $NaPF_6$. Profiles based on the chemical shift (δ, ppm) of (thio)urea H^3 proton.

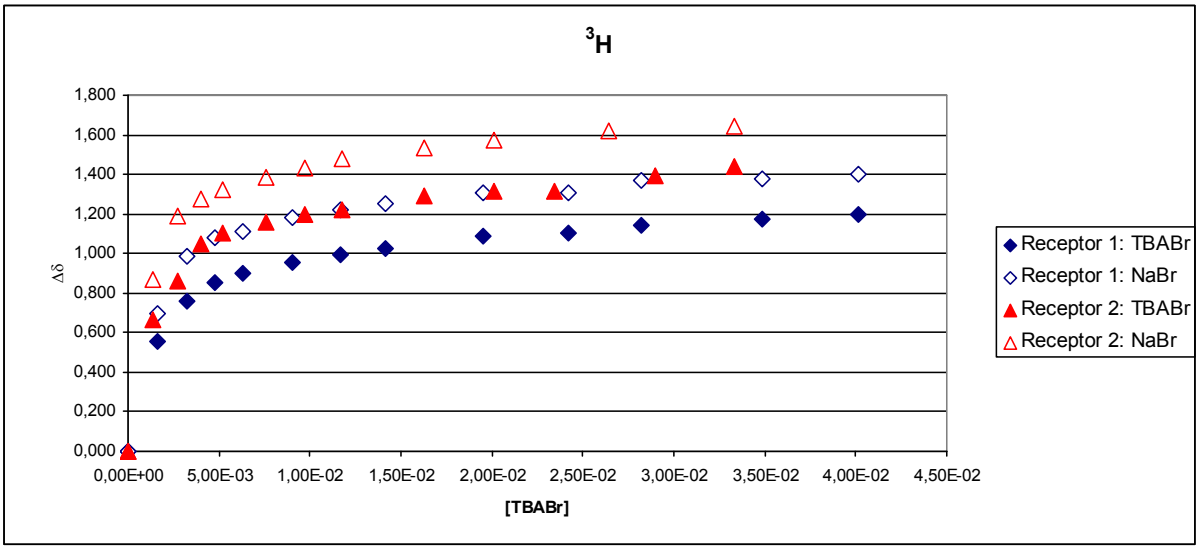


Fig. S27: ^{1}H NMR titrations of receptors **1** and **2 w**ith TBABr and TBABr in the presence of 1 equivalent of $NaPF_6$. Profiles based on the chemical shift (δ, ppm) of (thio)urea H^4 proton.

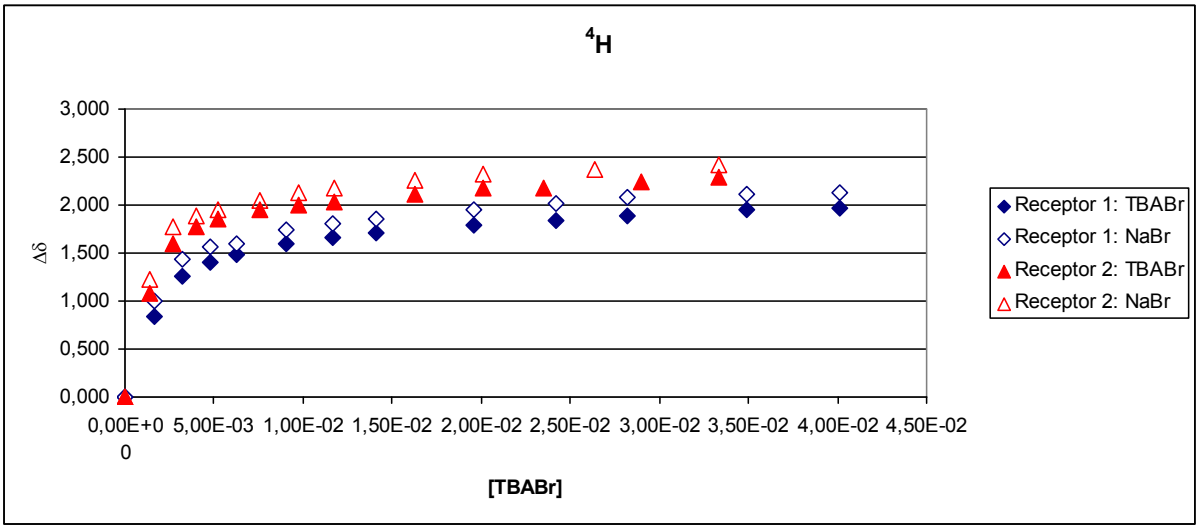


Fig S 28:. Partial ^{1}H NMR spectra (200 MHz, 298 K) of receptor **1** upon addition of 0, 0.6, 1.1, 1.6, 2.1, 3, 3.9, 4.7, 6.5, 8, 10.6, 13,3 of TBABr.

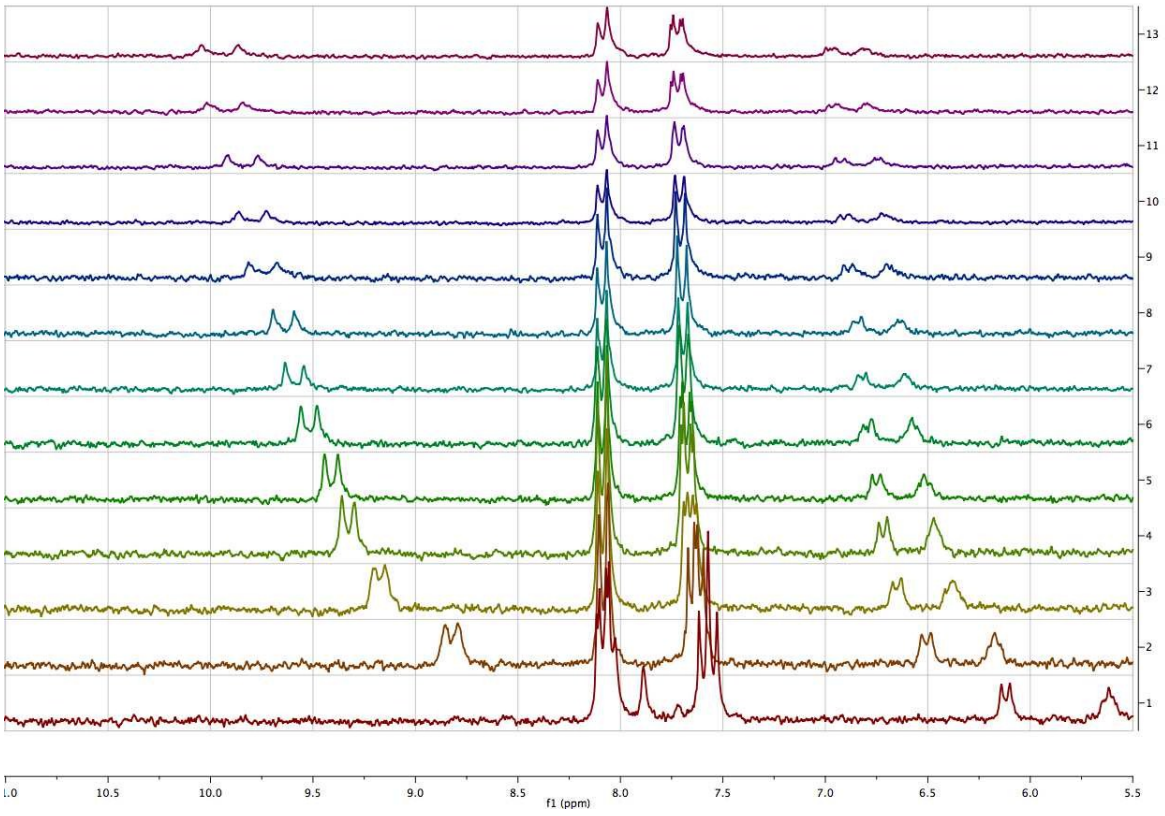


Fig S29: Partial ^{1}H NMR spectra (200 MHz, 298 K) of receptor **1** in the presence of 1eq. of $NaPF_6$ upon addition of 0, 0.6, 1.1, 1.6, 2.1, 3, 3.9, 4.7, 6.5, 8, 10.6, 13,3 of TBABr.

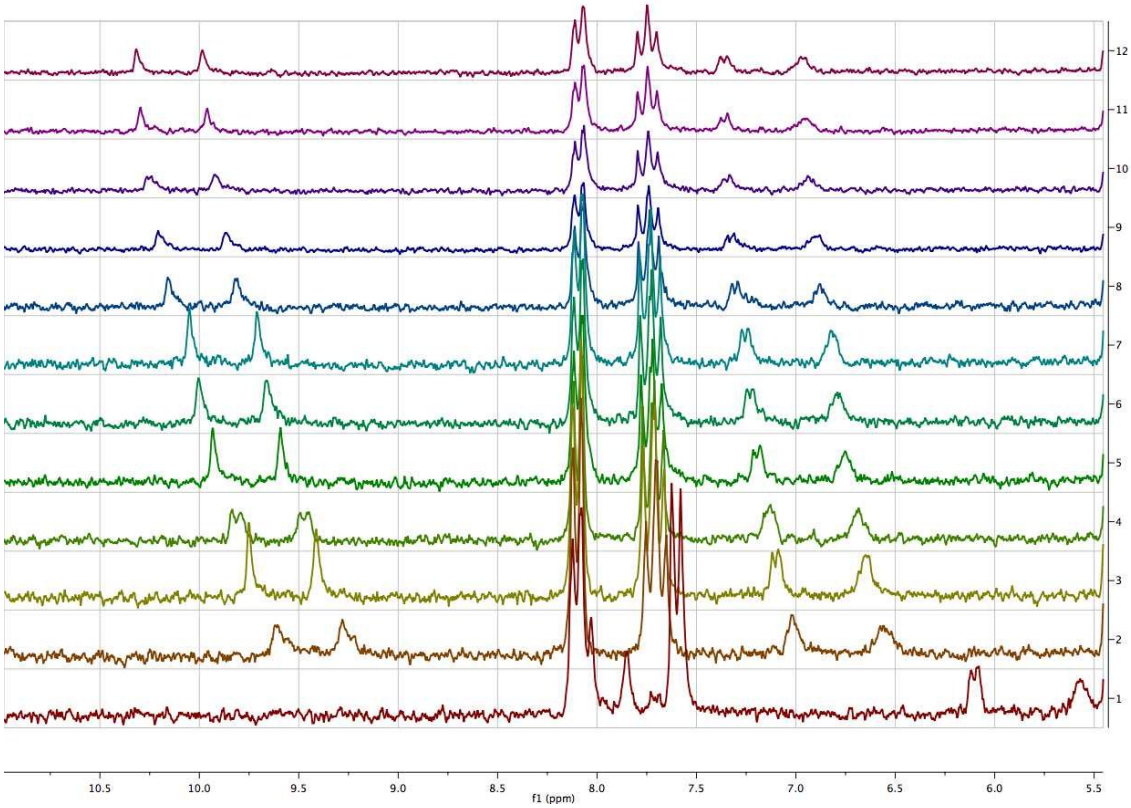


Fig S30: Partial ^{1}H NMR spectra (200 MHz, 298 K) of receptor **2** upon addition of 0, 0.6, 1.1, 1.6, 2.1, 3, 3.9, 4.7, 6.5, 8, 10.6, 13,3 of TBABr.

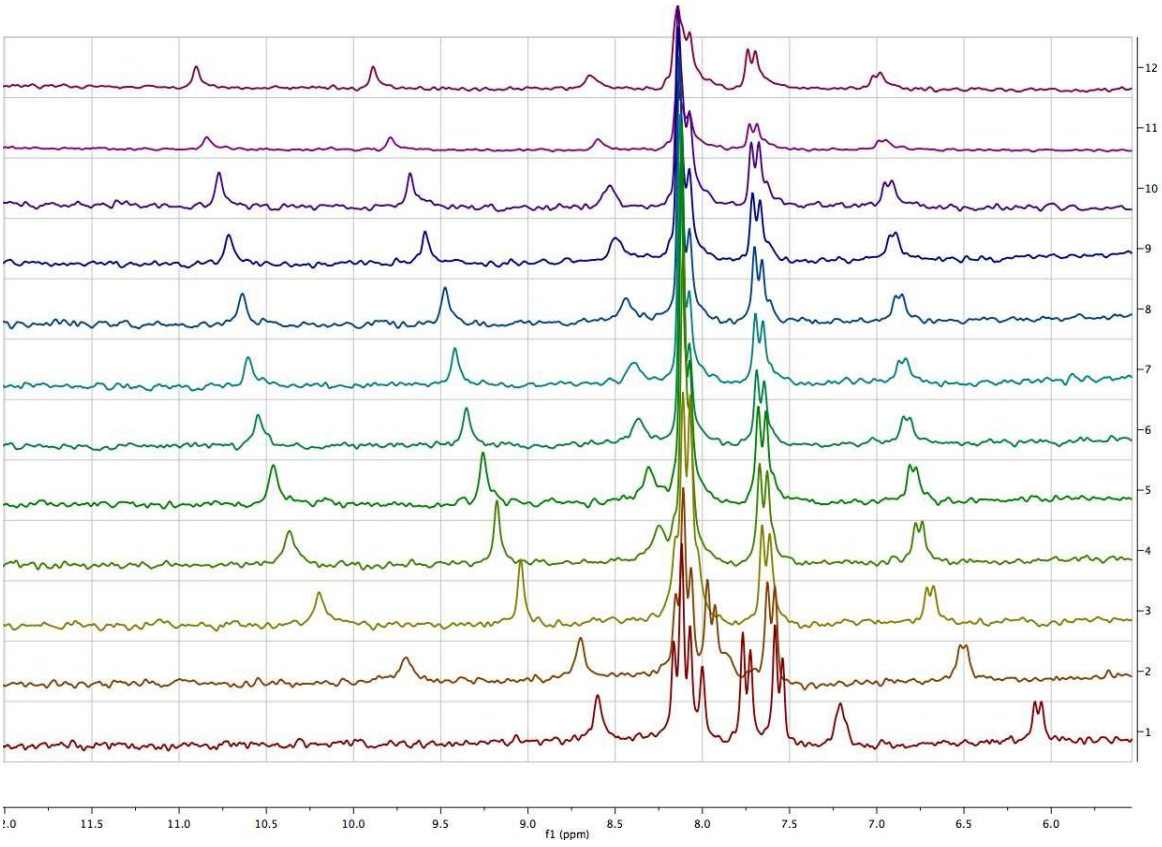


Fig. S31: Partial ^{1}H NMR spectra (300 MHz, 298 K) of receptor **2** in the presence of 1eq. of $NaPF_6$ upon addition of 0, 0.6, 1.1, 1.6, 2.1, 3, 3.9, 4.7, 6.5, 8, 10.6, 13,3 of TBABr.

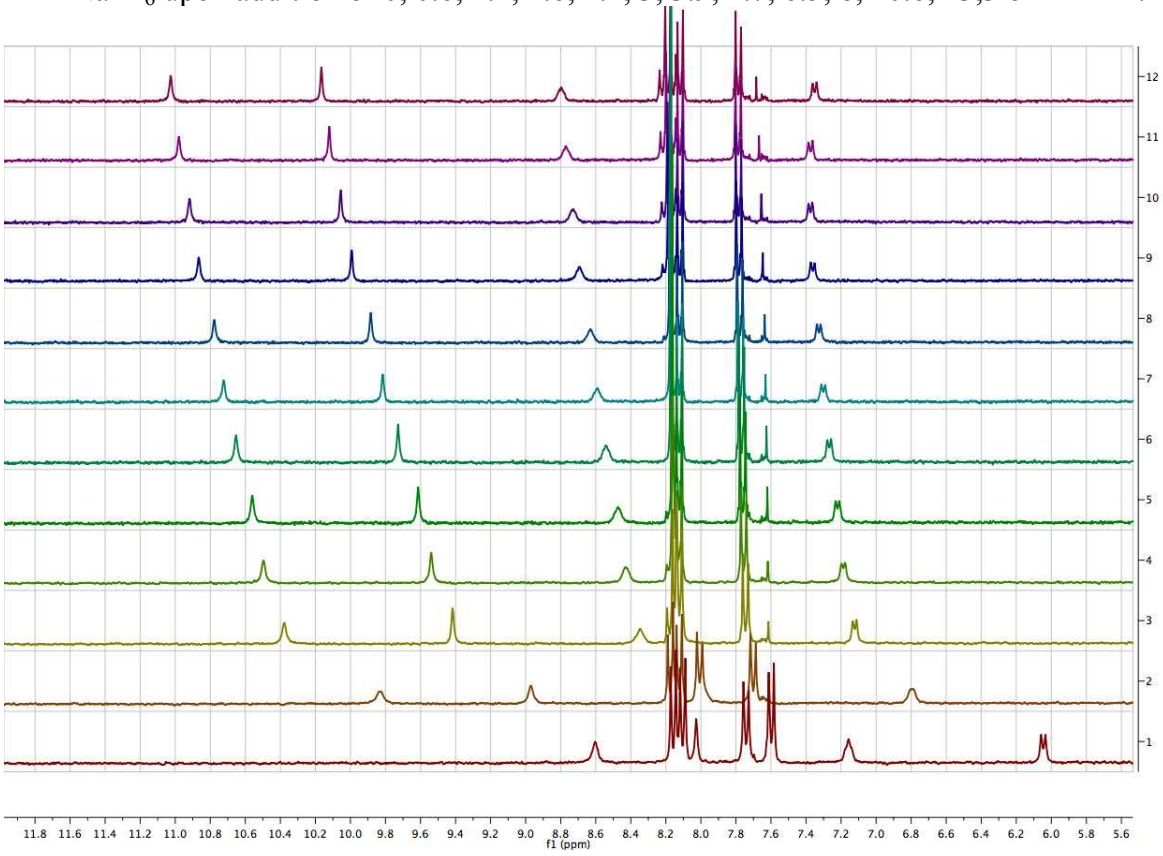


Fig. S32: NMR titration binding isotherms of receptor **1** with Na^{+} (K_a=15200M^{-1})