Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Development of effective potassium acetate extractant

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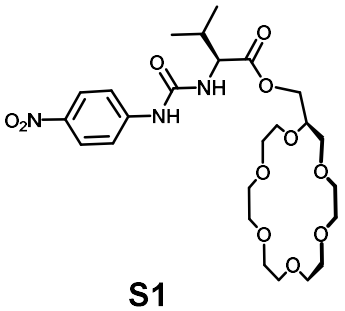
Table of Contents:

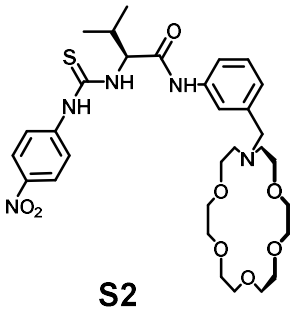
General Information

All solvents and starting materials were purchased from Merc or Fluorochem. All commercial-grade chemicals were used without further purification. The TBA AcO salt and cation ClO_4^- or PF_6^- salts were dried under high vacuum at 30–45 °C before using. ^1H and ^{13}C NMR spectra as well as titration experiments were performed on a 300 MHz Bruker Avance spectrometer. ^1H NMR chemical shifts δ are reported in ppm with reference to the tetramethylsilane ($CDCl_3$) or protonated residual solvent signal (CD_3CN). (3-Nitrobenzyl)-aza-18-crown-6 and (3-aminobenzyl)-aza-18-crown-6 were prepared according to our literature report.[1]

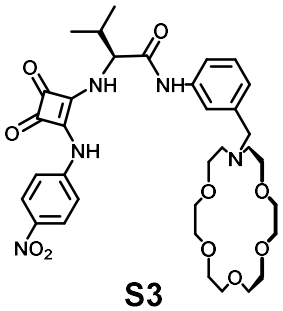
1. Structures of similar compunds



S1

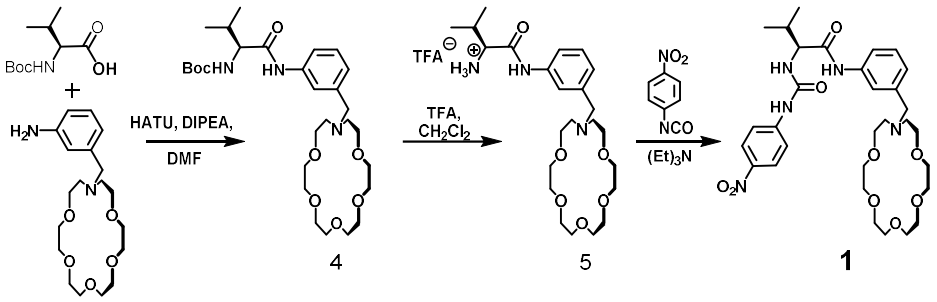


S2

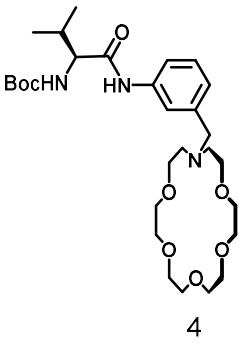


S3

2. Synthetic route to the receptors 1 and 2 with experimental procedures and NMR spectra



(3-aminobenzyl)-aza-18-crown-6 amide of N-Boc-L-valine



The solution of N-Boc-L-valine 0.23 g (1.06 mmol), 0.40g (1.06 mmol) HATU, 1.40 g (1.8 mL, 1.1 mmol) DIPEA, dissolved in 8 mL of dry DMF, was stirred under argon atmosphere at room temperature for 1h. Then 0.32g (0.87 mmol) of (3-aminobenzyl)-aza-18-crown-6 was added. The reaction mixture was then stirred at room temperature overnight. Then the solvent was evaporated. The oily residue was dissolved in chloroform and washed two times with distilled water. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated. The oil was purified by column chromatography on silica gel with chloroform then 4% methanol/chloroform as eluents to give 0.35 g (0.62 mmol) of an amorphous solid 77% of yield; R_f (10% MeOH/DCM) = 0.53 ^{1}H NMR (300 MHz; $CDCl_3$; δppm): 8.77 (s; 1H), 7.97 (s; 1H), 7.41 (s; 1H), 7.33 (t, J = 12 Hz, 1H), 7.17 (d, J=6 Hz, 1H), 5.37 (s, 1H), 4.31 (s, 2H), 4.09 (m, 1H), 3.77-3.60 (m, 20H), 3.33 (s, 4H), 2.14 (m, 1H), 1.41 (s, 9H), 0.98 (m, 6H); ^{13}C NMR (300 MHz; $CDCl_3$; δppm): 171.25; 156.11; 138.97; 130.09; 127.03; 79.94; 77.34; 70.05; 64.03; 60.70; 53.94; 31.50; 28.37; 19.57; 17.84

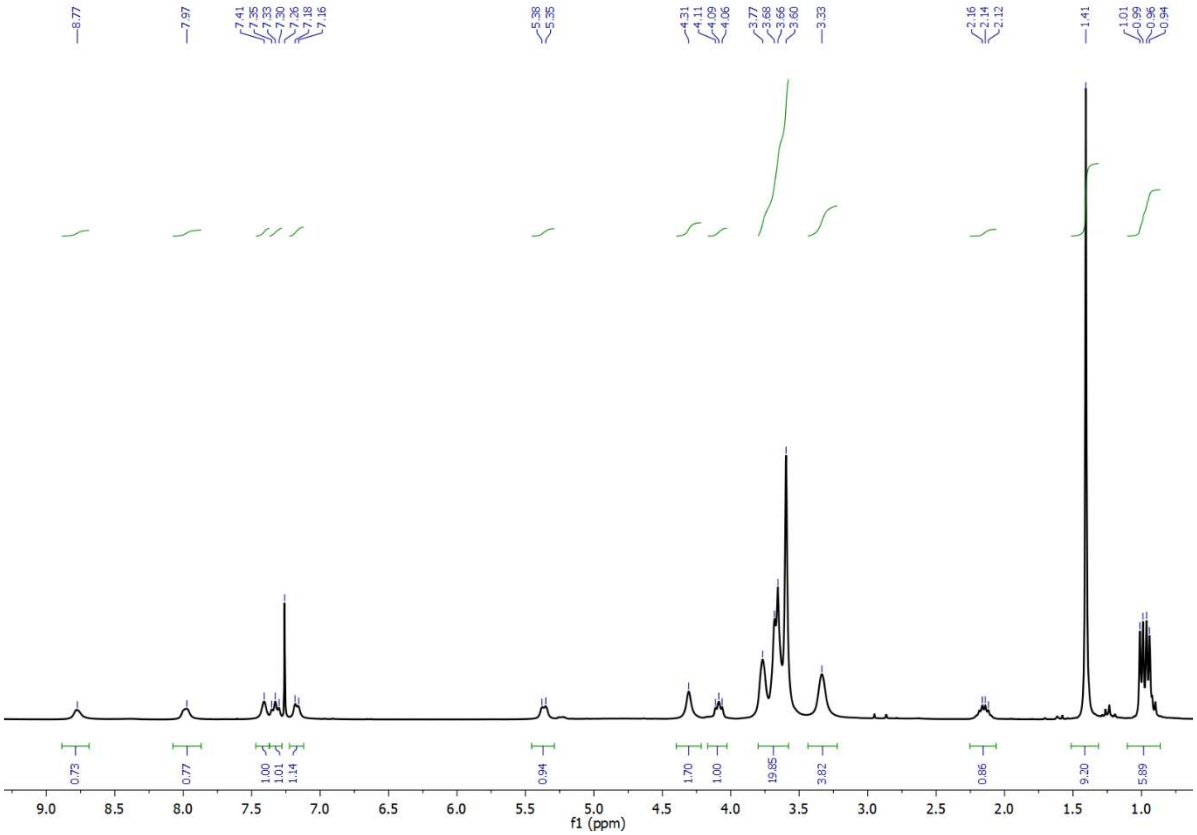


Figure 1.[1]H NMR of compound **4**

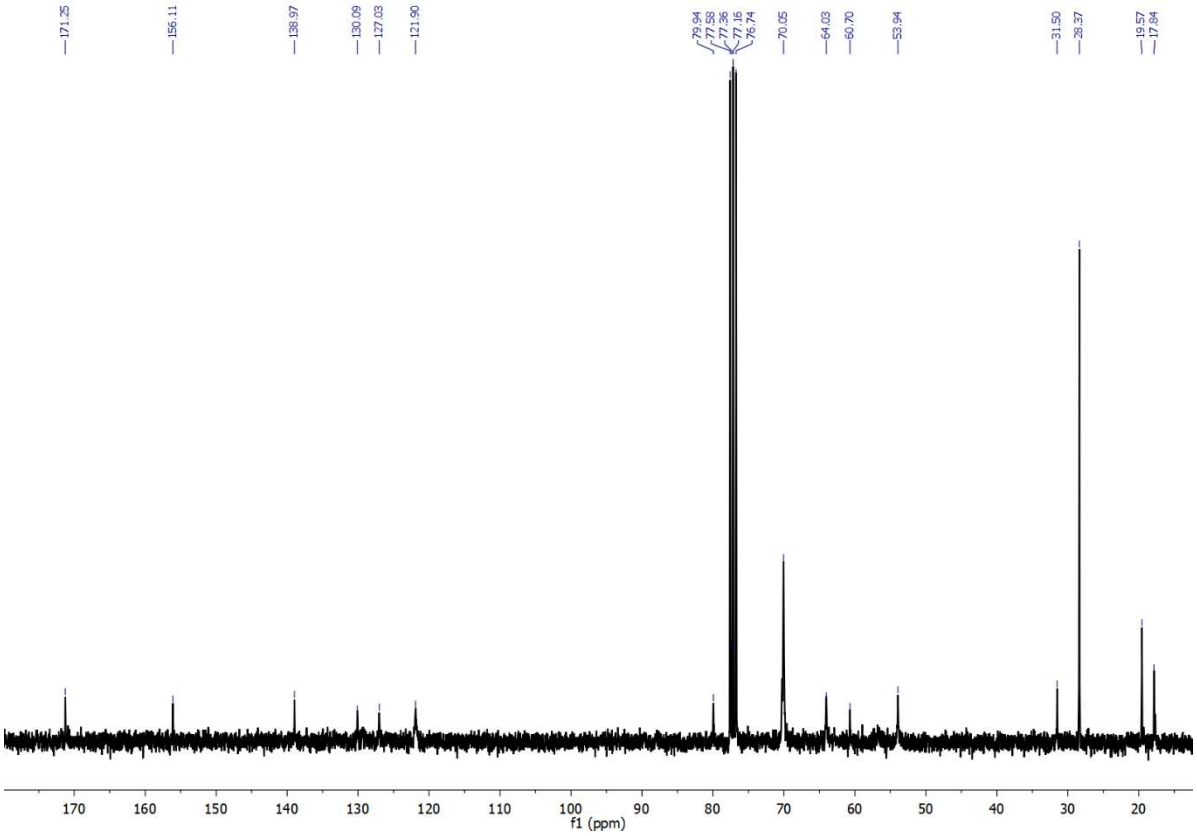
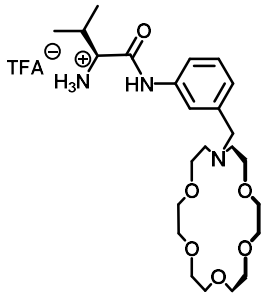


Figure 2.[13]C NMR of compound **4**

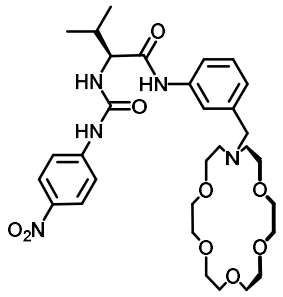
Trifluoroacetic acid salt of (3-aminobenzyl)-aza-18-crown-6 amide of N-Boc-L-valine



5

The solution of **4** 0.35 g (0.62 mmol) in 2mL DCM was cooled to 0 °C using dry ice/water bath. To this solution 1.5 mL of trifluoroacetic acid was added. Then cooling bath was removed and the reaction mixture was stirred at room temperature for 1h. The full conversion of the substrate was confirmed by TLC analysis in 10% MeOH/DCM. Then the volatiles were evaporated and the residue was dried under high vacuum to give desired compound in form of TFA salts. These compounds were used in the next step without further purification.

Receptor 1



1

In round bottom flask the 0.35 g (0.6 mmol) of compound **5** and 0.6 mL (0.44 g, 4 mmol) of triethylamine were dissolved in 15 mL of dry THF. To the resulting mixture 0.12 g (0.73 mmol) of 4-nitrophenyl isothiocyanate was added under argon atmosphere. The reaction mixture was stirred overnight at room temperature. Then the solvent was evaporated and the resulting oil was dissolved in chloroform and washed two times with distilled water. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated. The receptors were purified by column chromatography on silica gel with 10% MeOH/DCM as eluents to give 0.20 g (0.32 mmol) of an amorphous solid 53% of yield; R_f (10% MeOH/DCM) = 0.2. To remove any inorganic salts absorbed during the work-up, the receptor **1** was dissolved in chloroform and washed with distilled water. The evaporation of the solvent (without drying) gave desired receptor.^{1}H NMR (300 MHz; DMSO δppm): 10.16 (s, 1H), 9.46 (s, 1H), 8.14 (d, J= 9Hz, 2H), 7.60 (d, J= 9Hz, 2H), 7.54- 7.52 (bs, 2H), 7.23 (t, J=4 Hz, 1H), 7.01 (d, J=4 Hz, 1H), 6.74 (d, J= 9 Hz, 1H), 4.31 (dd, J_1=9 Hz, J_2=4 Hz, 1H), 3.59 (s, 2H), 3.54- 3.48 (m, 20H) 2.66 (t, J=4 Hz, 4H), 2.06 (m, 1H), 0.93 (m, 6H); ^{13}C NMR (300 MHz; $CDCl_3$; δppm): 172.62, 172.52, 155.07, 145.91, 141.70, 141.65, 137.32, 128.74, 124.95, 124.87, 121.74, 117.48, 71.14, 70.80, 70.73, 70.15, 59.46, 55.17, 32.56, 19.77, 18.31;HR-MS (ESI): m/z = 654.3119 $[M+Na]^+$ (calc. for $C_{31}H_{45}N_5O_9Na$: 654.3109)

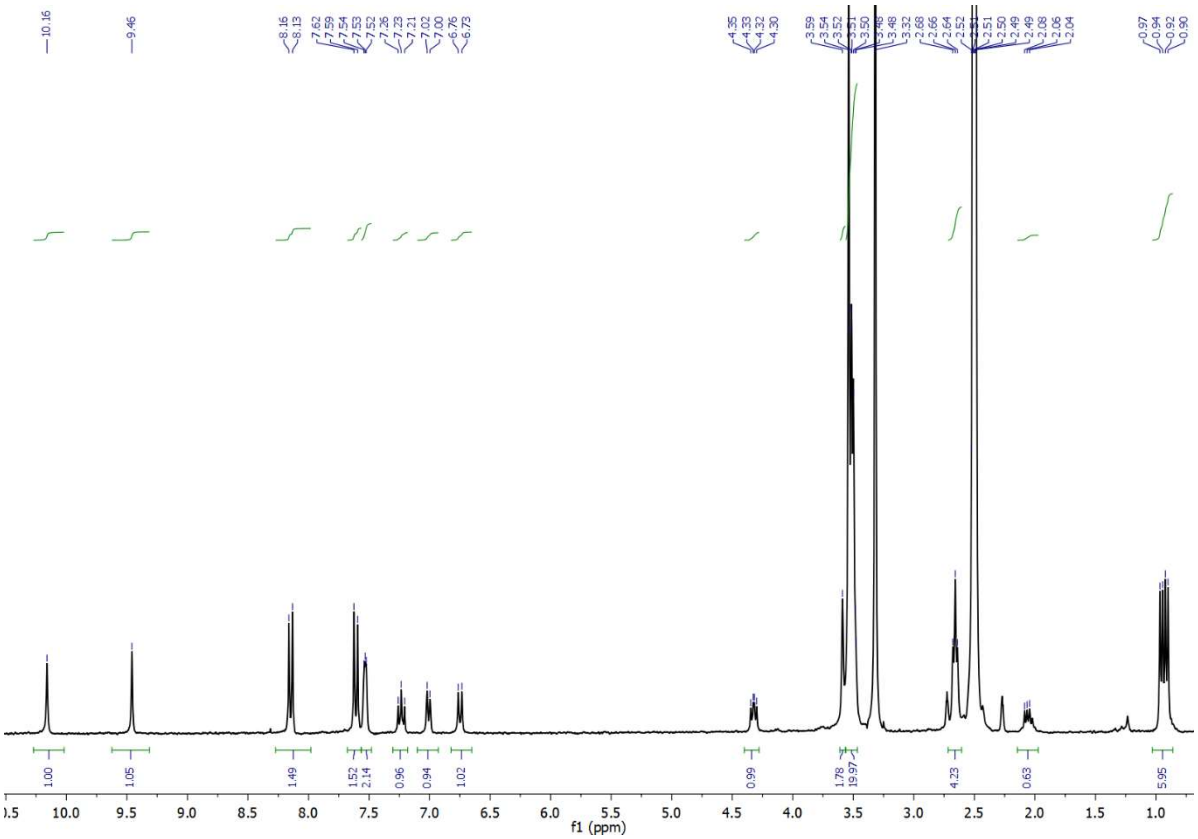


Figure 3. ^{1}H NMR of compound **1**

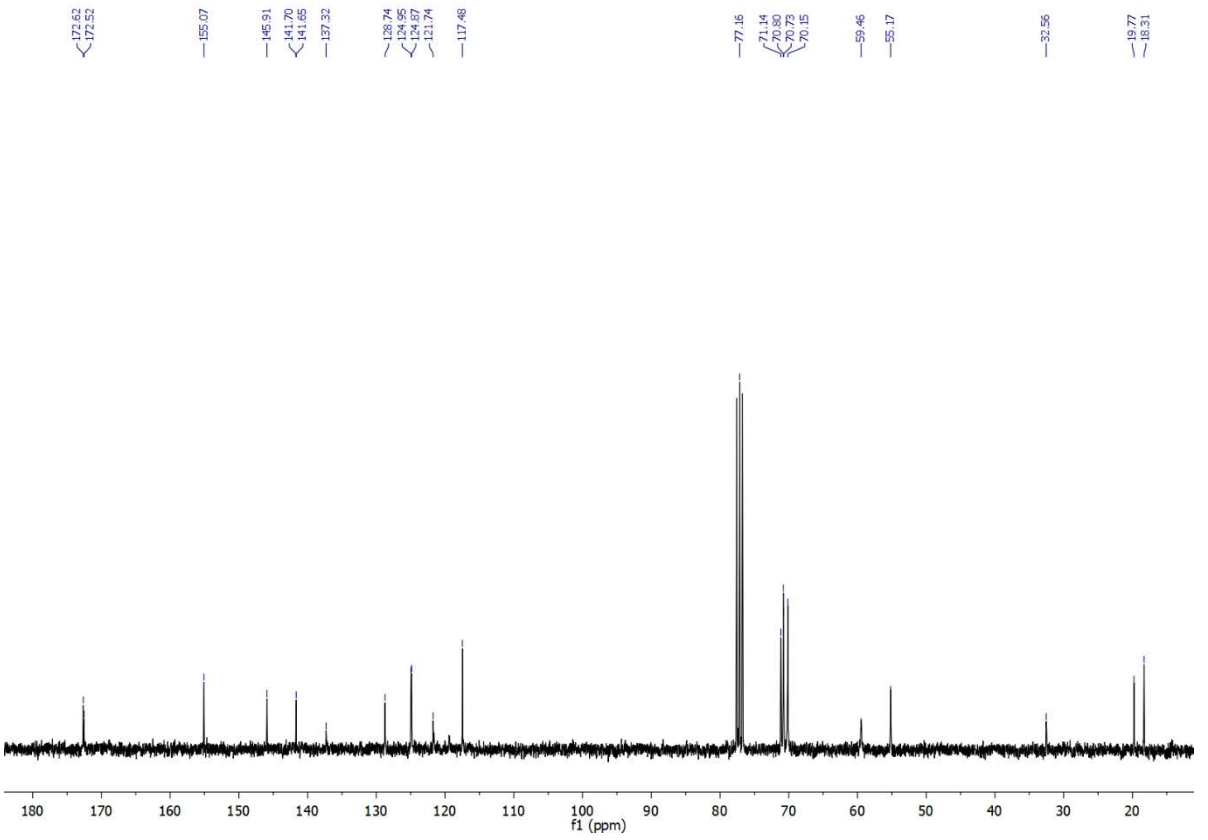


Figure 4. ^{13}C NMR of compound **1**

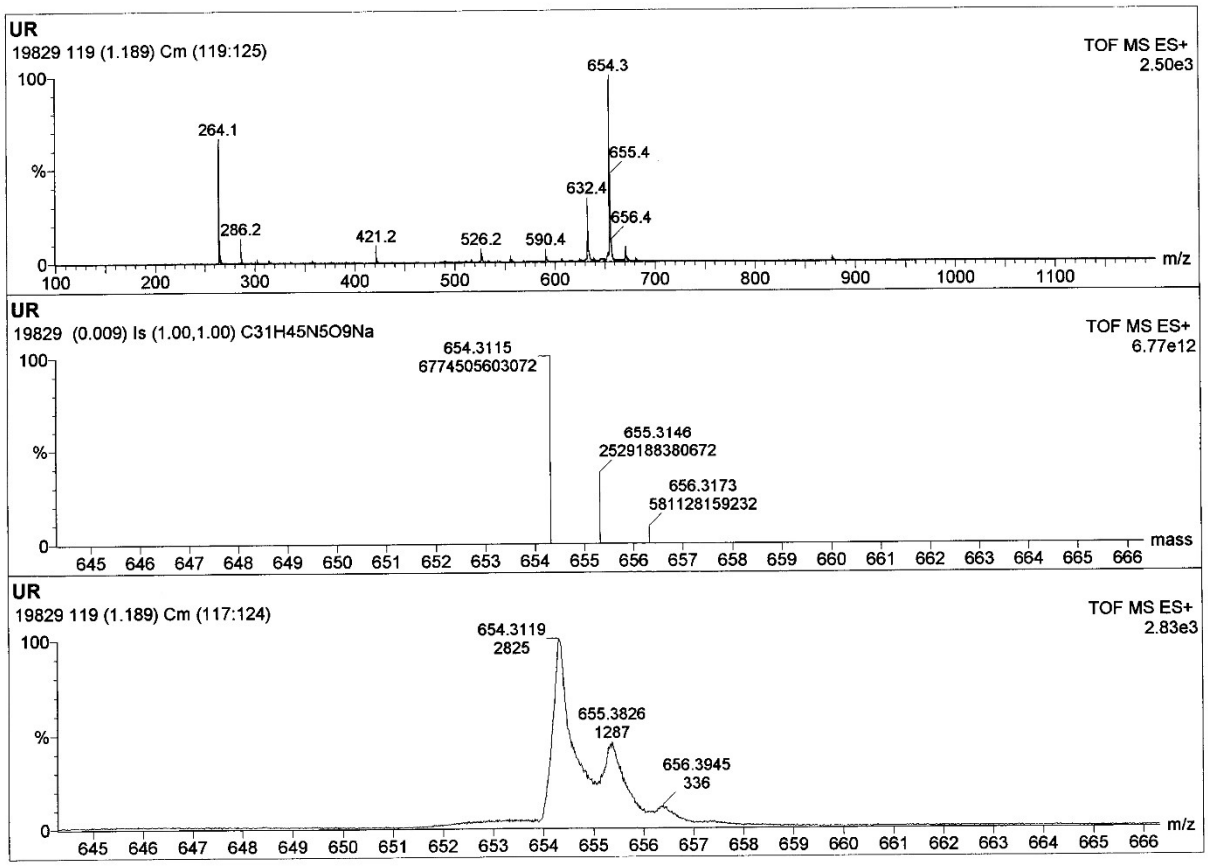
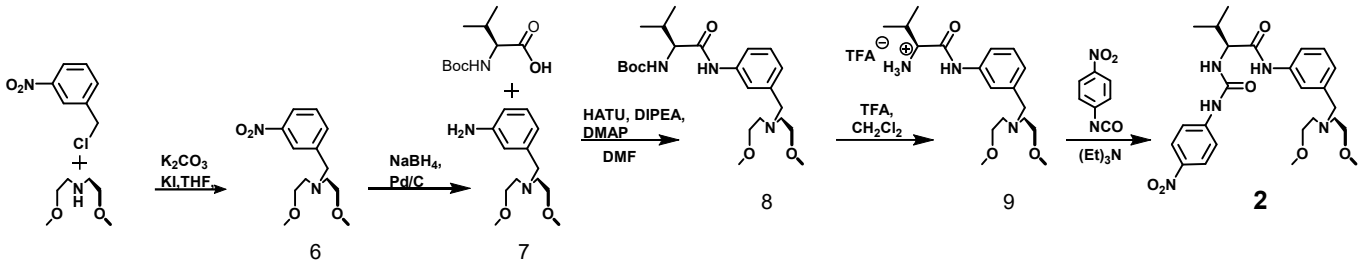
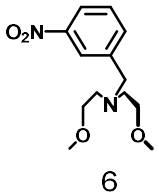


Figure 5. HR-MS of compound **1**

Synthetic route of the compound **2** is analogous to the synthetic route of the compound **1** with the same procedures and purification methods.



2-methoxy-N-(2-methoxyethyl)-N-(3-nitrobenzyl)ethan-1-amine



6

To a solution of 4 g (30 mmol) bis(2-methoxyethyl)amine in 150 mL of anhydrous THF, 12.5g (90 mmol) potassium carbonate, catalytic amount of potassium iodide and 5.7 g (33.3 mmol) 3-nitrobenzyl chloride was added. The reaction mixture was stirred at 66 °C (oil bath) for 72h. Then the solvent was evaporated. The oily residue was dissolved in chloroform and washed two times with distilled water. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated. The oil was purified by column chromatography on silica gel with

chloroform as eluents to give 4.47g (16.67 mmol) of product **6** as oil in 55% of yield. R_f (10% MeOH/DCM) = 0.4; ^{1}H NMR (300 MHz, $CDCl_3$,δ_{ppm}): 8.21 (s, 1H), 8.03 (d,J=9 Hz, 1H), (7.66 (d,J=9 Hz, 1H), 7.43 (m, 1H), 3.80 (s, 2H), 3.45 (t, J=6Hz, 4H), 3.27 (s, 6H), 2.73 (t, J=6Hz, 4H);^{13}C NMR (75 MHz, $CDCl_3$,δ_{ppm}): 148.30, 142.57, 134.69, 128.98, 123.36, 121.88, 71.25, 58.83, 58.76, 53.85.

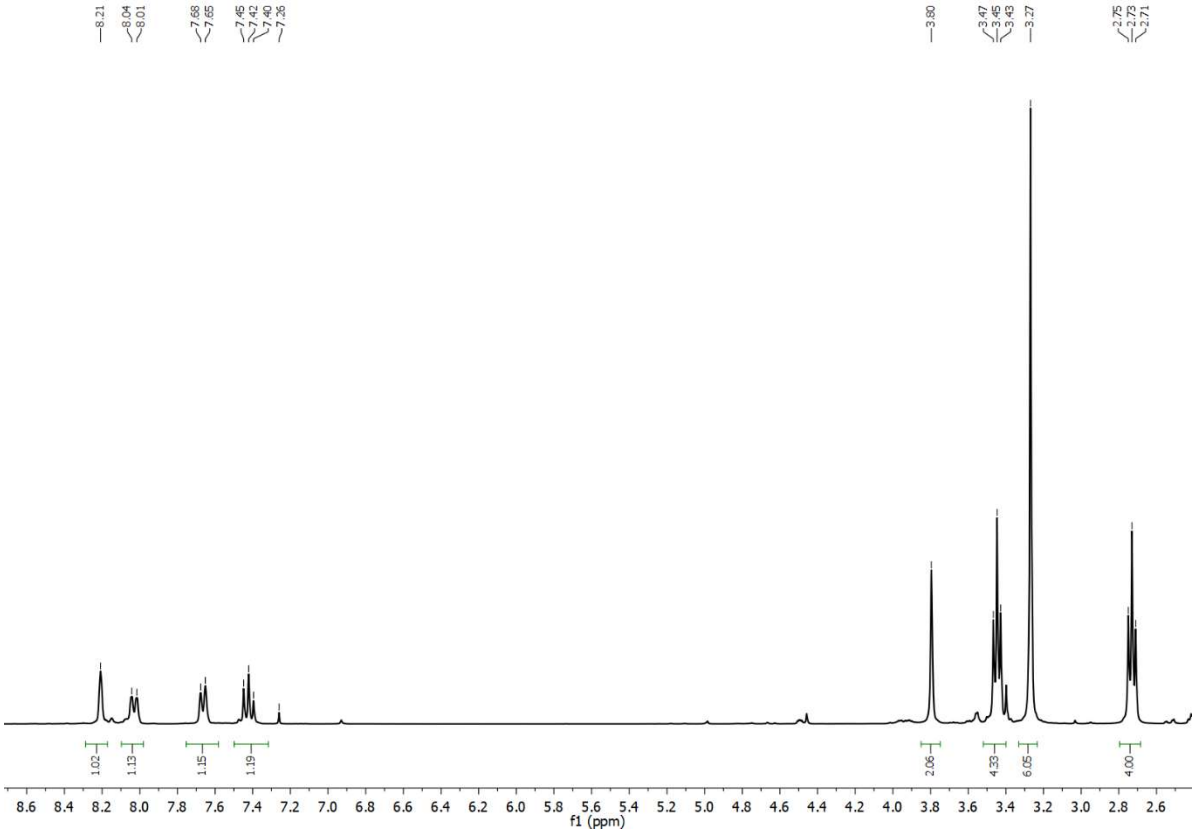


Figure 6.^{1}H NMR of compound **6**

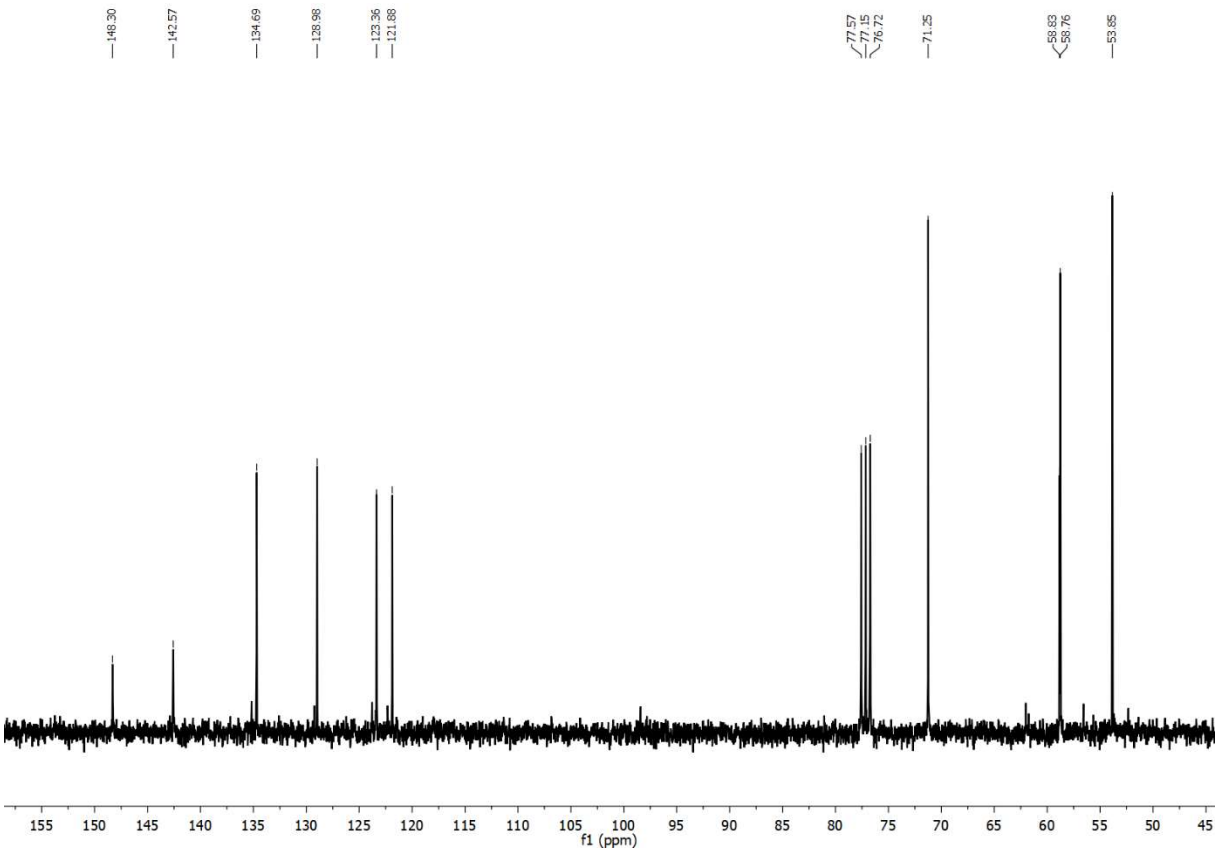
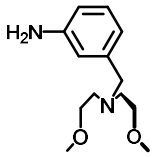


Figure 7. ^{13}C NMR of compound **6**

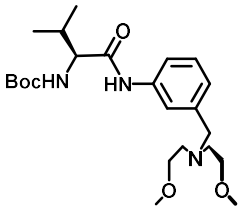
3-((bis(2-methoxyethyl)amino)methyl)aniline



7

To a solution of **6** (0.45 g, 1.68 mmol) in 4mL of THF and 4 mL of MeOH, 0.5g of 10% palladium on carbon was added under argon atmosphere. Then to vigorously stirred reaction mixture 0.14 g (3.7 mmol) of sodium borohydride was added. The resulting mixture was stirred at room temperature for one hour. Then the catalyst was removed by filtration through a pad of Celit and the solvents were evaporated. The oily residue was dissolved in chloroform and washed two times with distilled water. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated to give 0.4 g (1.67 mmol) of **7** as colourless oil 99% of yield. This compound was used in the next step without further purification.

N-(3-((bis(2-methoxyethyl)amino)methyl)phenyl)amide of N-Boc-L-valine



8

The solution of N-Boc-L-valine 0.4 g(1.84 mmol), 0.7g (1.84 mmol) HATU, 2.5g (3.2mL, 2.0 mmol) triethylamine, dissolved in 8 mL of dry DMF, was stirred under argon atmosphere at room temperature for 1h. Then 0.4g (1.7mmol) of **7** was added. The reaction mixture was then stirred at room temperature overnight. Then the solvent was evaporated. The oily residue was dissolved in chloroform and washed two times with distilled water. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated. The oil was purified by column chromatography on silica gel with chloroform then 4% methanol/chloroform as eluents to give 0.51 g (1.17 mmol) of an amorphous solid 68% of yield; R_f (10% MeOH/DCM) = 0.55; ^{1}H NMR (300 MHz; CD_3CN; δppm): 8.70 (s, 1H); 7.52 (s, 1H), 7.46 (d, J=9Hz, 1H), 7.22 (t, J=9Hz, 1H), 7.05 (d, J=9Hz, 1H), 5.80 (bs, 1H), 4.03 (m, 1H), 3.60 (s, 2H), 3.41 (t, J=6Hz, 4H), 3.24 (s, 6H), 2.64 (t, J=6Hz, 4H), 1.41 (s, 9H), 0.97 (m, 6H); ^{13}C NMR (300 MHz; CD_3CN; δppm): 171.76, 157.01, 142.09, 139.22, 129.47, 125.32, 120.96, 119.24, 79.90, 71.92, 61.71, 60.17, 58.82, 54.50, 31.86, 28.62, 19.79, 18.54.

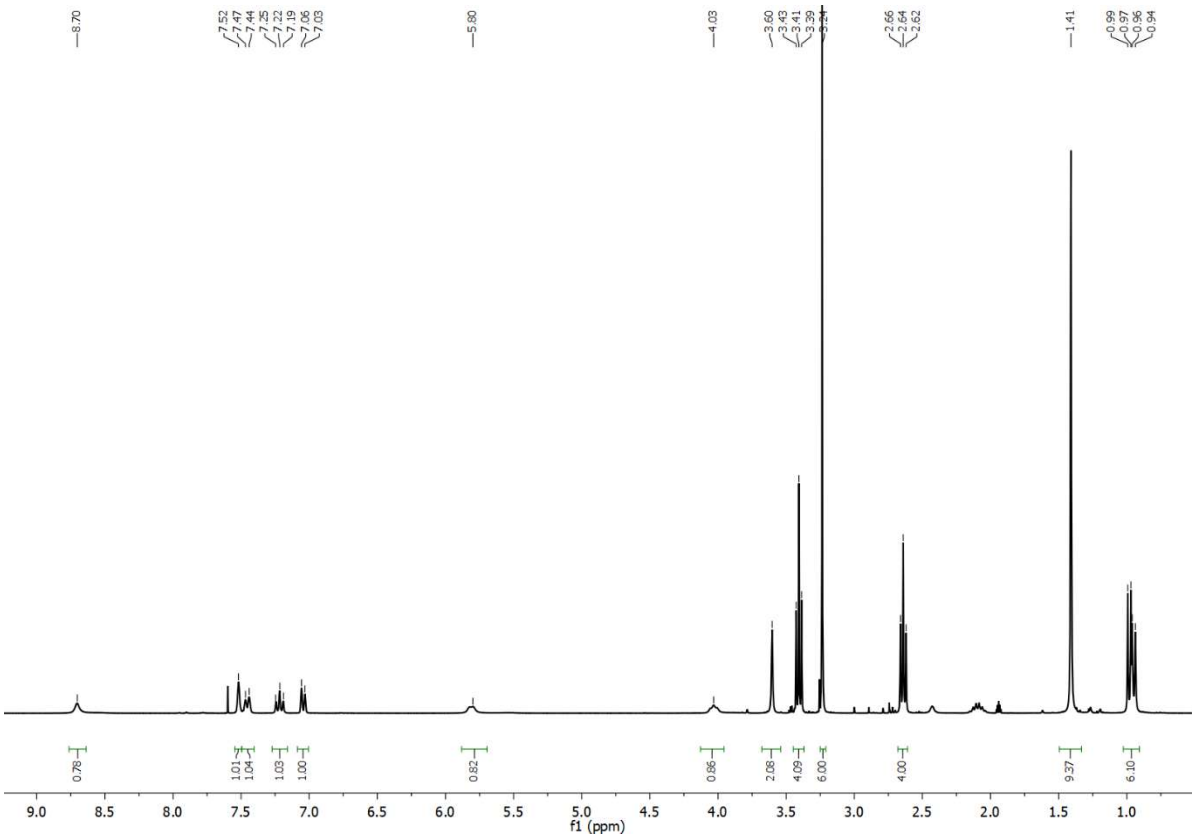


Figure 8. ^{1}H NMR of compound **8**

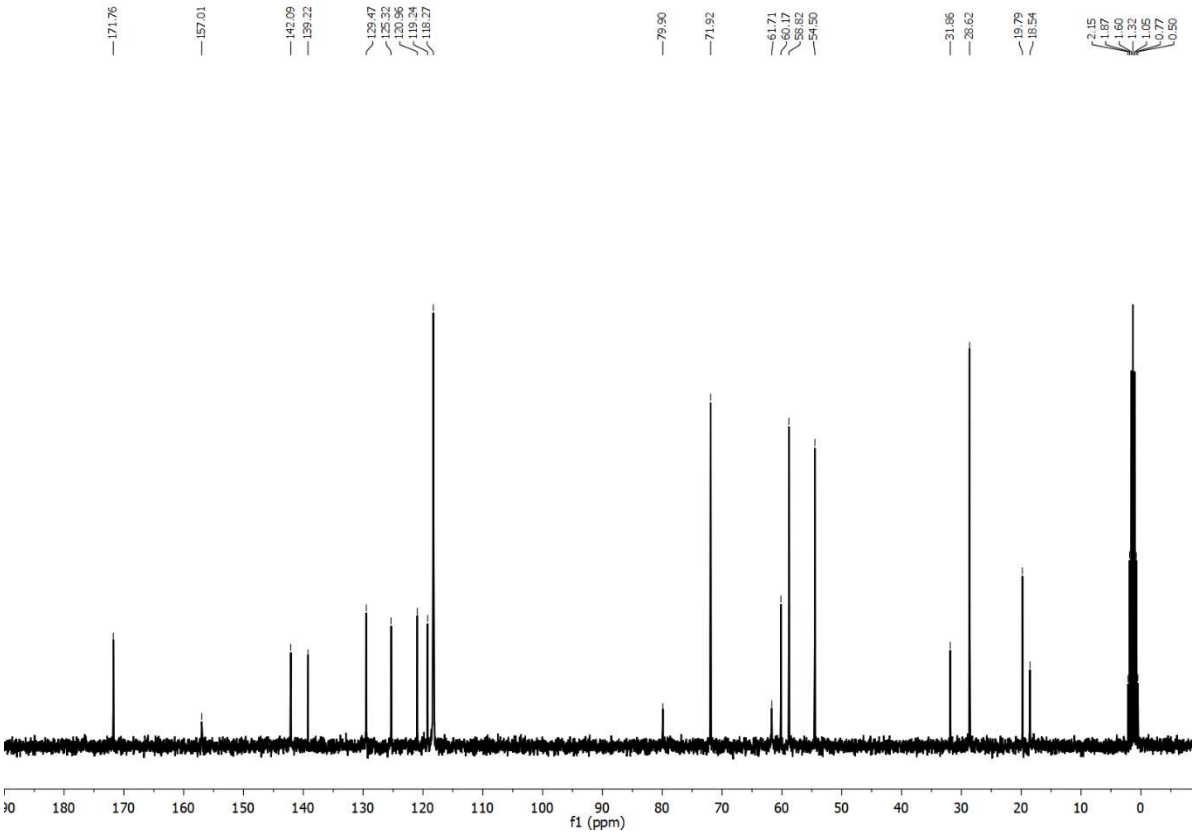
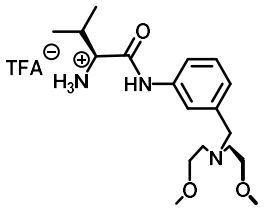


Figure 9.^{13}C NMR of compound **8**

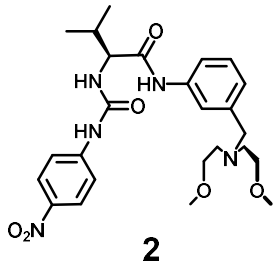
Trifluoroacetic acid salt of (3-aminobenzyl)-aza—bis-2-methoxyethyl amide of N-Boc-L-valine



9

The solution of **8** 0.51 g (1.17 mmol) in 4mL DCM was cooled to 0 °C using dry ice/water bath. To this solution 3.0 mL of trifluoroacetic acid was added. Then cooling bath was removed and the reaction mixture was stirred at room temperature for 1h. The full conversion of the substrate was confirmed by TLC analysis in 10% MeOH/DCM. Then the volatiles were evaporated and the residue was dried under high vacuum to give the desired compound in form of TFA salts. These compounds were used in the next step without further purification.

Monotopic receptor **2**



2

In round bottom flask the 0.51 g (1.17 mmol) of the compound **9** and 2.5 mL (1.83g, 17 mmol) of triethylamine were dissolved in 10 mL of dry THF. To the resulting mixture 0.21 g (1.29 mmol) of 4-nitrophenyl isothiocyanate was added under argon atmosphere. The reaction mixture was stirred overnight at room temperature. Then the solvent was evaporated and the resulting oil was dissolved in chloroform and washed two times with distilled water. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated. Receptors were purified by column chromatography on silica gel with 10% MeOH/DCM as eluents to give 0.29 g (0.57 mmol) of an amorphous solid 49% of yield; R_f (10% MeOH/DCM) = 0.22. To remove any inorganic salts absorbed during the work-up, the receptor **2** was dissolved in chloroform and washed with distilled water. The evaporation of the solvent (without drying) gave the desired receptor.^{1}H NMR (300 MHz; CD_3CN; δppm): 8.76 (s, 1H), 8.15 (s, 1H), 8.03 (bt, J_1=6Hz, J_2=9Hz, 1H), 7.53 (s, 1H), 7.51 (s, 1H), 7.47 (d, J=9Hz, 1H), 7.42 (s, 1H), 7.23 (bt, J_1=6Hz, J_2=9Hz, 1H), 7.05 (d, J=6Hz, 1H), 6.24 (m, 1H), 4.34 (t, J=6Hz, 1H), 3.59 (s, 2H), 3.38 (t, J=6Hz, 4H), 3.21 (s, 6H), 2.61 (t, J=6Hz, 4H), 2.23-2.14 (m, 1H), 1.05-0.97 (m, 6H); ^{13}C NMR (300 MHz; $CDCl_3$; δppm): 172.04, 155.60, 147.25, 142.66, 142.26, 138.93, 129.58, 125.86, 125.70, 121.35, 119.60, 71.87, 60.49, 60.07, 58.79, 54.47, 32.35, 19.81, 18.20; HR-MS (ESI): m/z = 524.2485 $[M+Na]^+$ (calc. for $C_{25}H_{35}N_5O_6Na$: 524.2480)

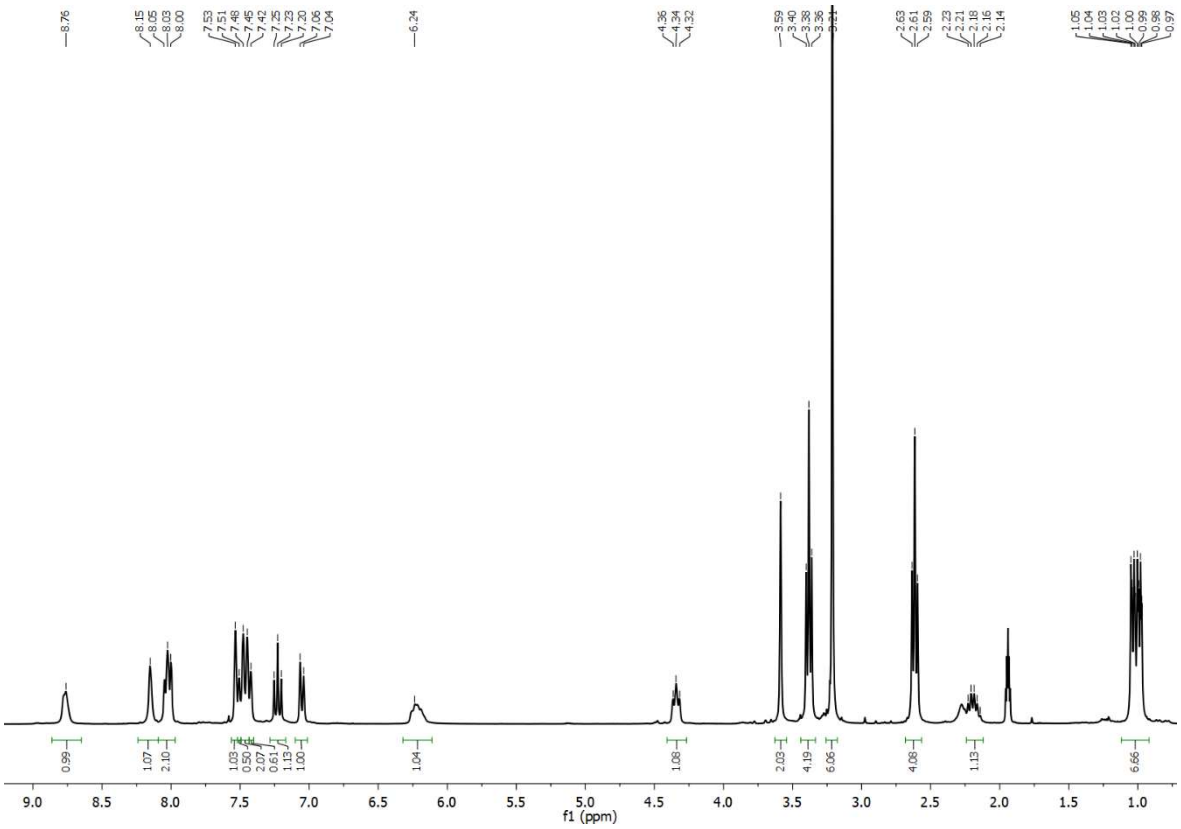


Figure 10. ^{1}H NMR of compound **2**

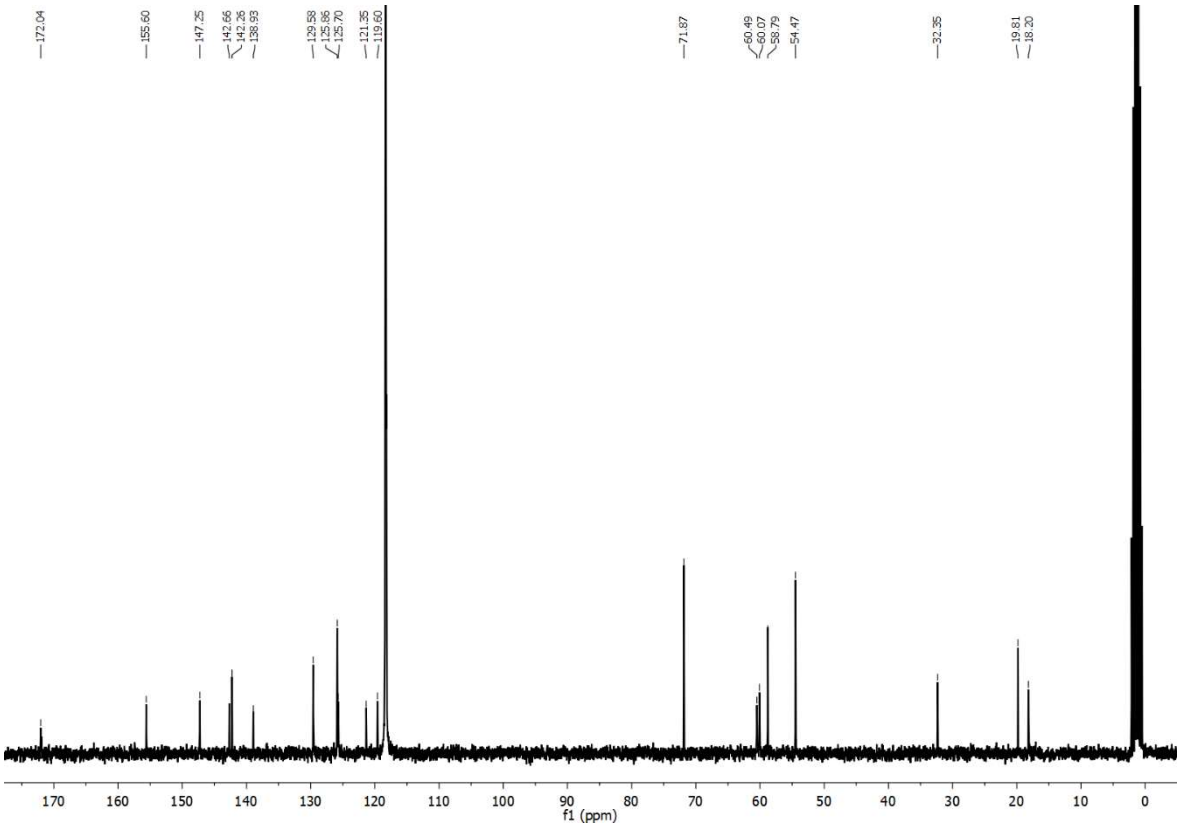


Figure 11.[13]C NMR of compound **2**

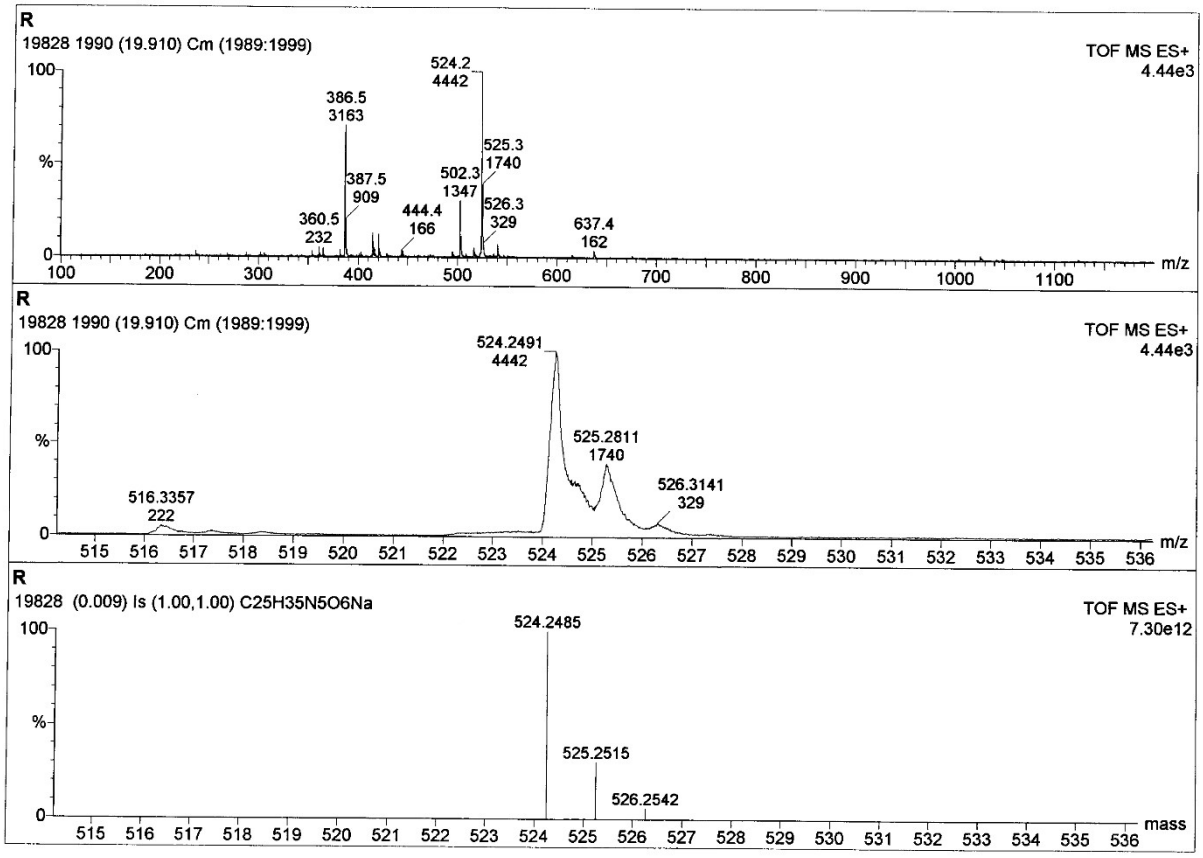


Figure 12. HR-MS of compound **2**

3. UV-Vis titration experiments

UV-Vis titration experiments were performed on a Thermo SpectronicUnicam UV 500 spectrophotometer in CH_3CN solution at 298K. To 10 mm cuvette was added 2.5 mL of 4.0 x 10^{-5} M solution of studied receptor and in case of salts binding studies 1 molar equivalent of cation (KPF_6, $NaClO_4$ or NH_4PF_6) was added. Small aliquots of ~1.5 x 10^{-3} M guest solution (anion or cation) containing the receptor **1** 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).

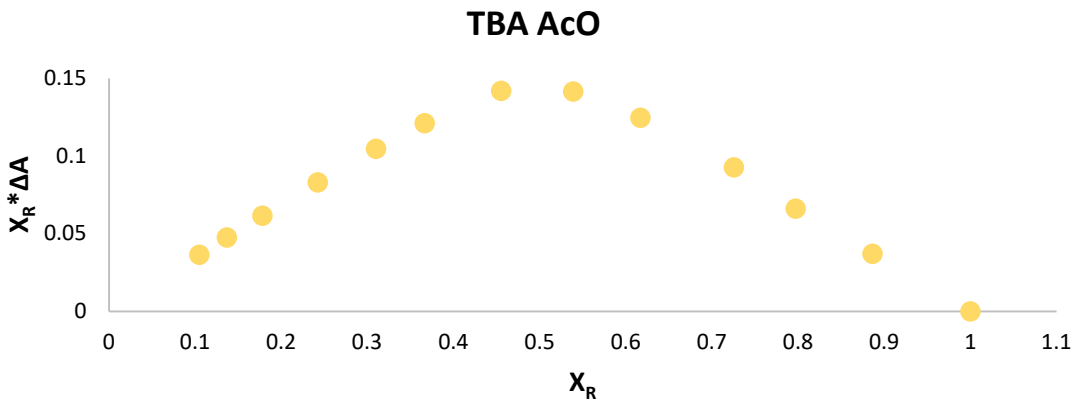


Figure 13. Job plot analysis of the receptor **1**in the presence of TBA AcO

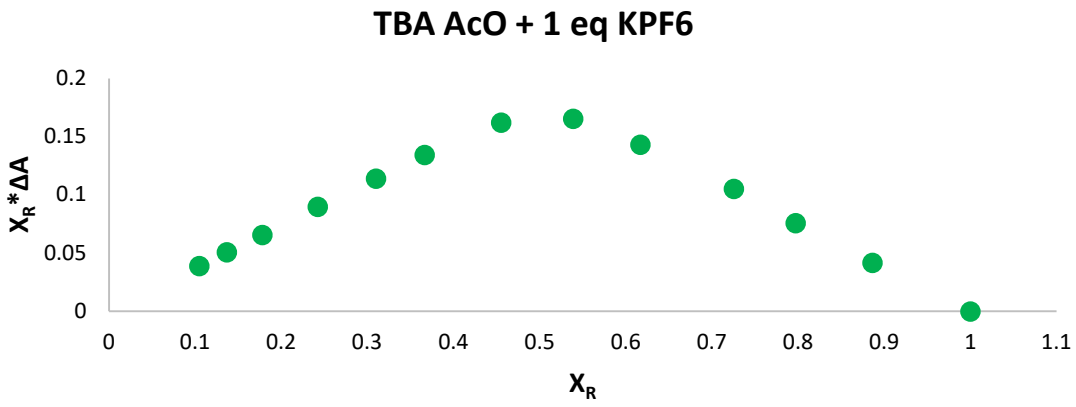


Figure 14. Job plot analysis of the receptor **1** in the presence of TBA AcO in presence of 1 eq KPF_6

- CH_3CN solution

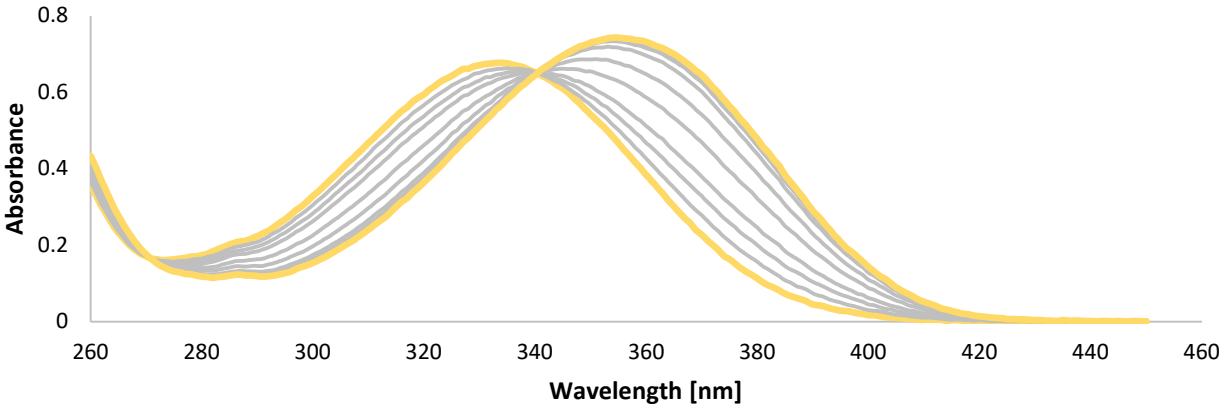


Figure 15. UV-Vis **1** spectrum changes upon titrant (TBA AcO) addition (293 K, CH_3CN solution, $C_{titrant}$=1.3 x10^{-3}M, $C_{receptor}$=4.0 x10^{-5}M)

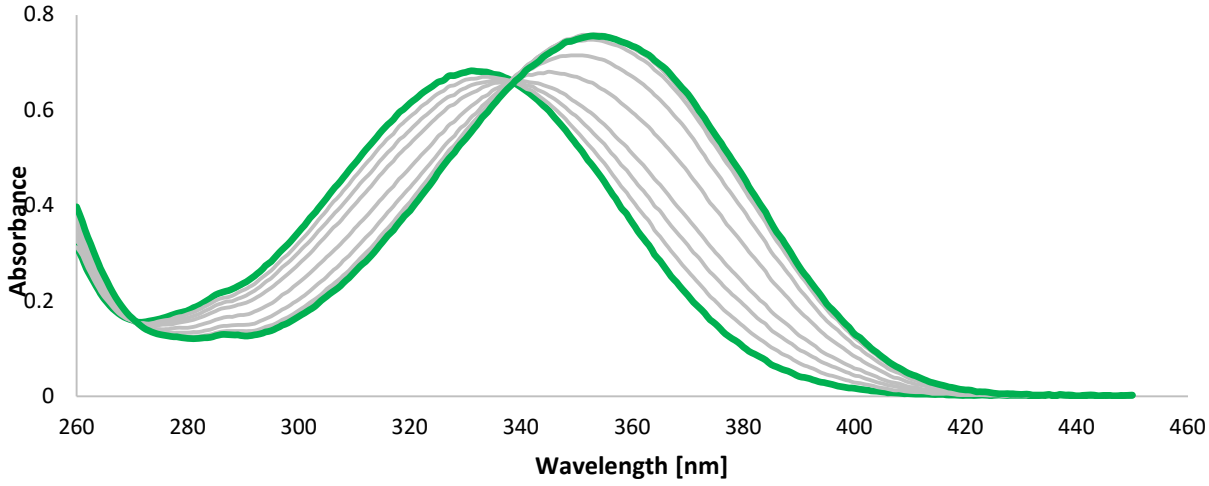


Figure 16. UV-Vis **1** spectrum changes upon titrant (TBA AcO) addition in presence of 1 eq. KPF_6 (293 K, CH_3CN solution, $C_{titrant}$=1.3 x10^{-3}M, $C_{receptor}$=4.0 x10^{-5}M)

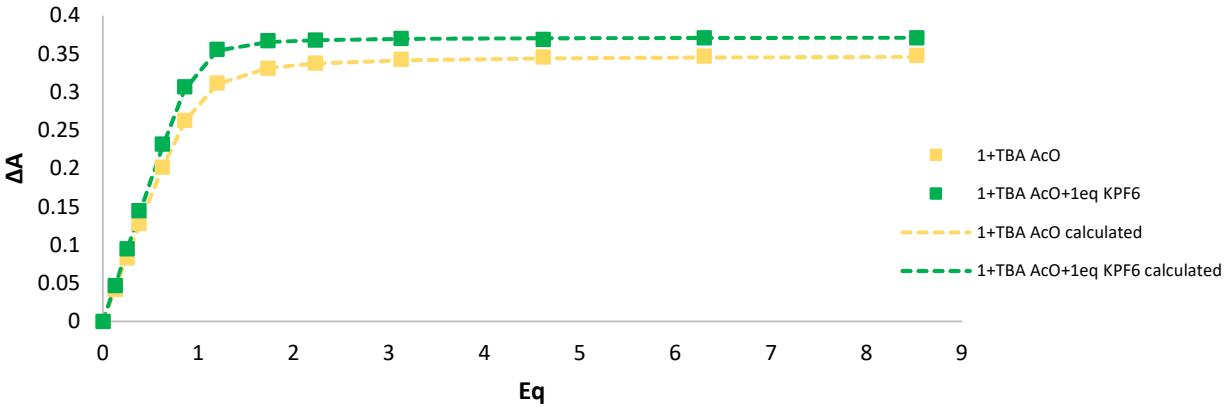


Figure 17. UV-Vis titration binding isotherms (experimental and calculated) of the receptor **1** with TBA AcO in the presence of one equivalent of cations (λ=360 nm) (293 K, CH_3CN solution)

- 1% H_2O/CH_3CN solution

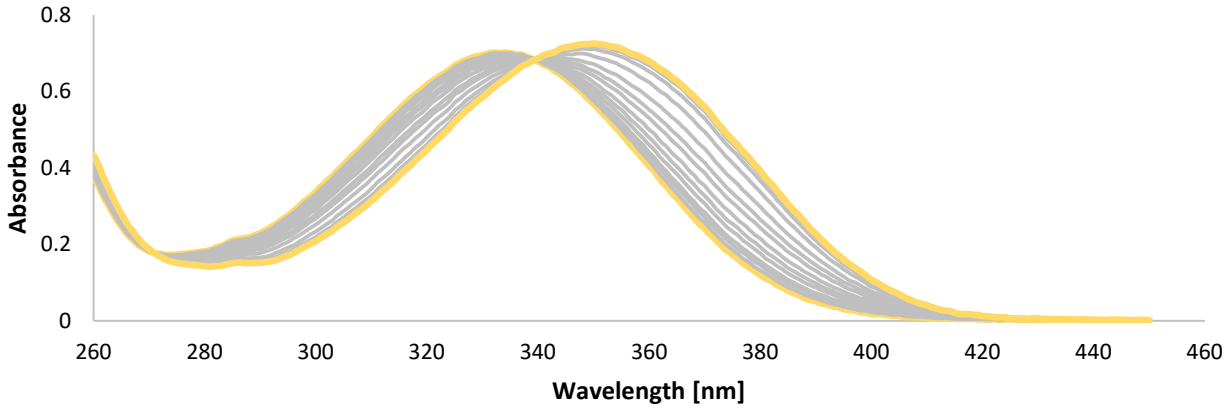


Figure 18. UV-Vis **1** spectrum changes upon titrant (TBA AcO) addition (293 K, 1% H_2O/CH_3CN solution, $C_{titrant}$=1.2 x10^{-3}M, $C_{receptor}$=4.1 x10^{-5}M)

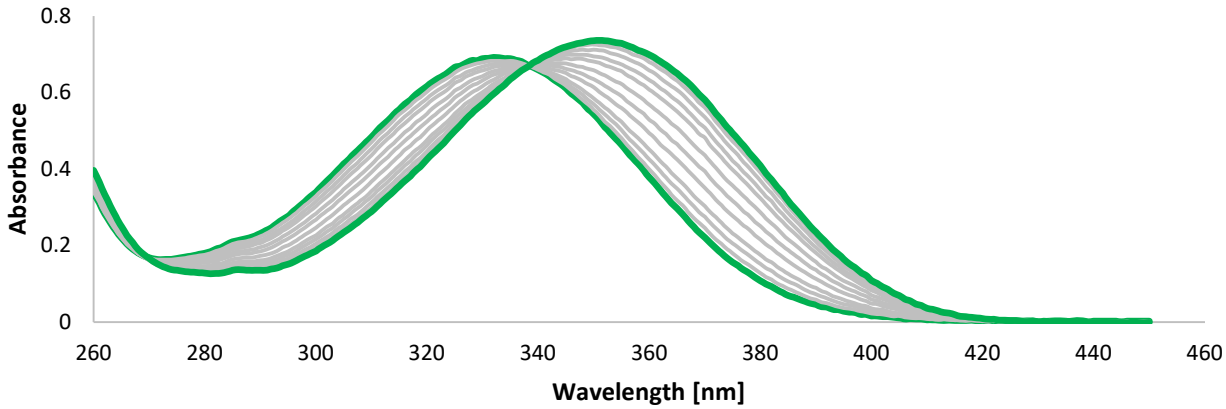


Figure 19. UV-Vis **1** spectrum changes upon titrant (TBA AcO) addition in presence of 1 eq. KPF_6 (293 K, 1% H_2O/CH_3CN solution, $C_{titrant}$=1.2 x10^{-3}M, $C_{receptor}$=4.1 x10^{-5}M)

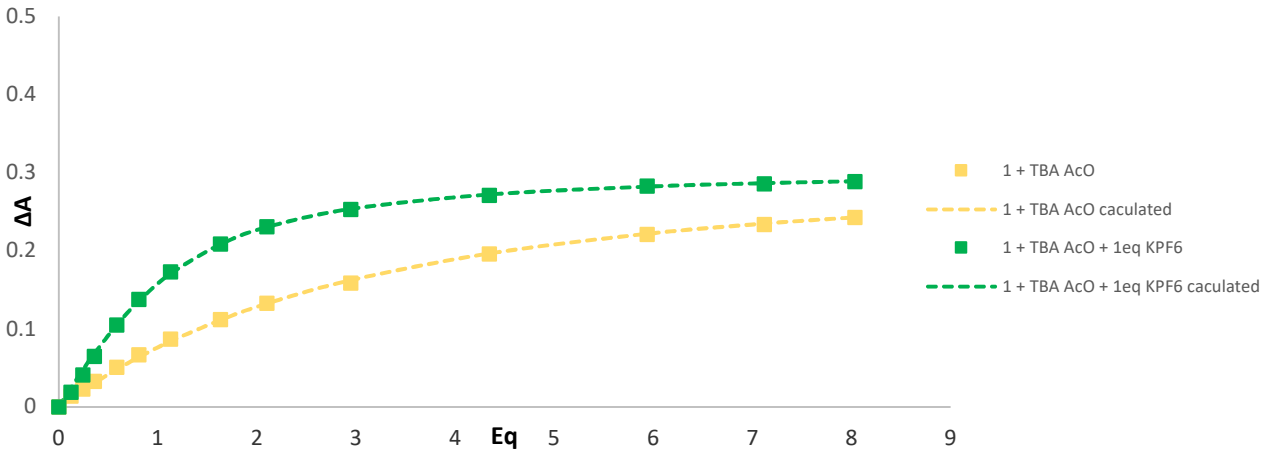


Figure 20. UV-Vis titration binding isotherms (experimental and calculated) of the receptor **1** with TBA AcO in the presence of one equivalent of cations (λ=360 nm) (293 K, 1% H_2O/CH_3CN solution)

- 3% H_2O/CH_3CN solution

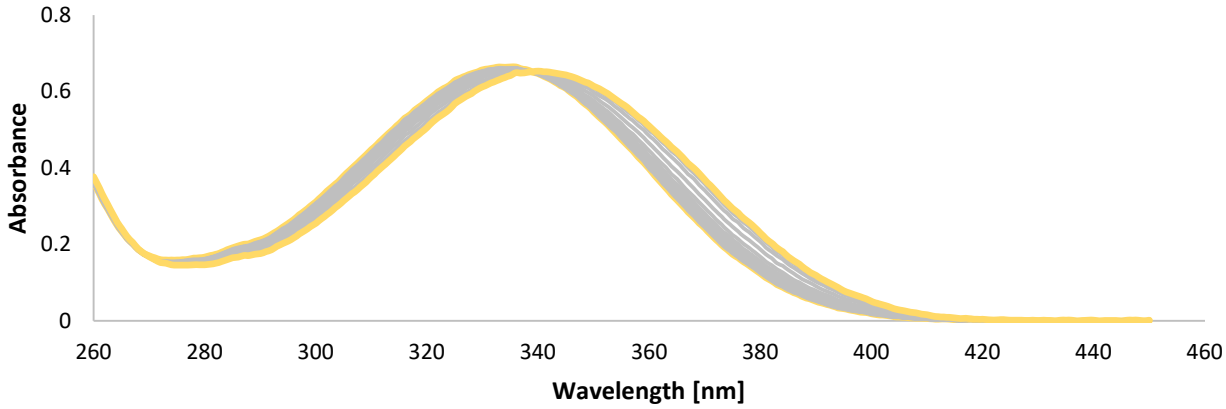


Figure 21. UV-Vis **1** spectrum changes upon titrant (TBA AcO) addition (293 K, 1% H_2O/CH_3CN solution, $C_{titrant}$=2.8 x10^{-3}M, $C_{receptor}$=3.9 x10^{-5}M)

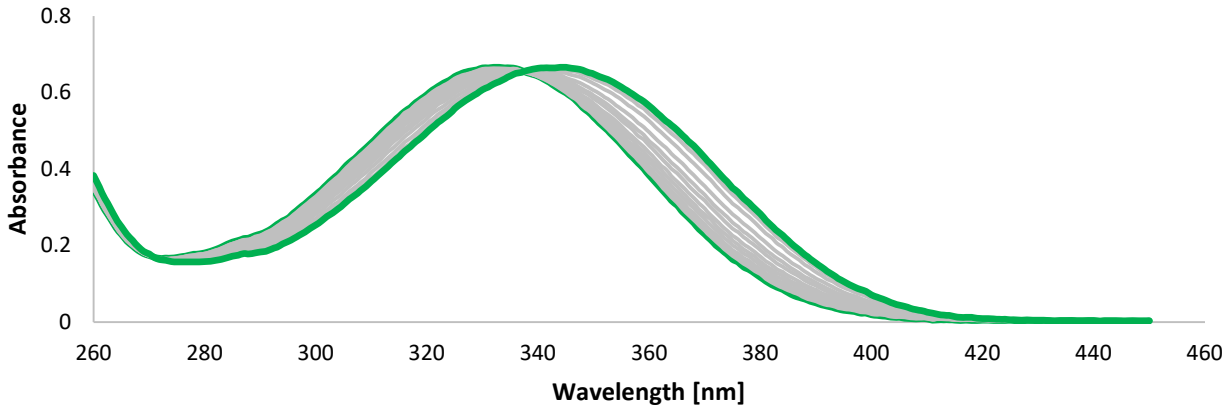


Figure 22. UV-Vis **1** spectrum changes upon titrant (TBA AcO) addition in presence of 1 eq. KPF_6 (293 K, 3% H_2O/CH_3CN solution, $C_{titrant}$=2.8 x10^{-3}M, $C_{receptor}$=3.9 x10^{-5}M)

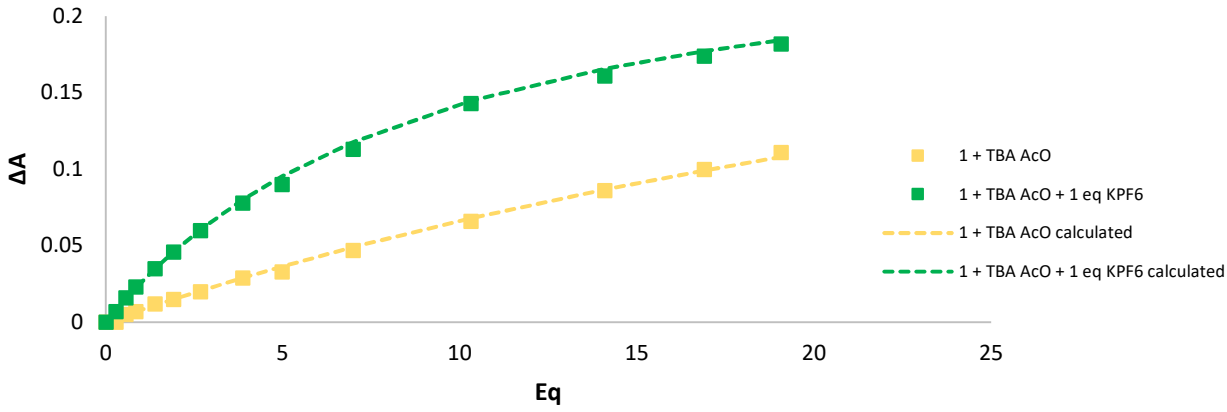


Figure 23. UV-Vis titration binding isotherms (experimental and calculated) of the receptor **1** with TBA AcO in the presence of one equivalent of cations (λ=360 nm) (293 K, 3% H_2O/CH_3CN solution)

Solvent	Ion	TBA^+	KPF_6
CH_3CN	**AcO^-**	580 000 (0.25%)	1 700 000 (0.64%)
	$K_M/K_{TBA\ AcO}$	-	2.93
1% H_2O/CH_3CN	**AcO^-**	11 000 (0.09%)	52 000 (0.12%)
	$K_M/K_{TBA\ AcO}$	-	4.72
3% H_2O/CH_3CN	**AcO^-**	970 (0.57%)	3400 (0.11%)
	$K_M/K_{TBA\ AcO}$		3.51

Figure 24. UV-Vis spectroscopy K_{obs} values (298 K) for interactions of **1** with AcO^- in present or absence of potassium cationand standard errors values in parentheses

4. NMR titration experiments

^{1}H NMR titration experiments were performed on a 300 MHz Bruker Avance spectrometer, at 298K, in CD_3CN solution. In each case 0.5 mL of 3.2 x 10^{-3} M solution of the receptor **1** was added to 5 mm NMR tube. The receptor solution contains or not 1 mol eq. of sodium, potassium cation or ammonium cation. Then to the receptor solution the titrant solution of tetrabutylammonium acetate in the receptor solution (1.9 x10^{-1}M) was added. After each addition of the titrant, a spectrum was registered. The resulting titration data were analyzed by Bindfit.[2]

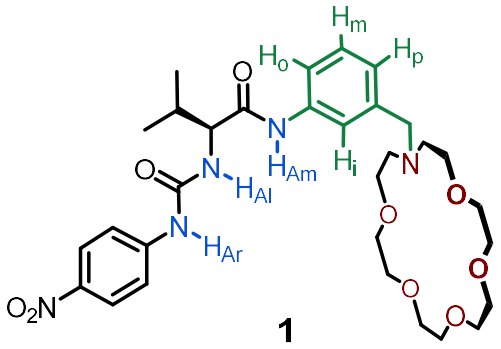


Figure 25. Structure of receptor **1** with description.

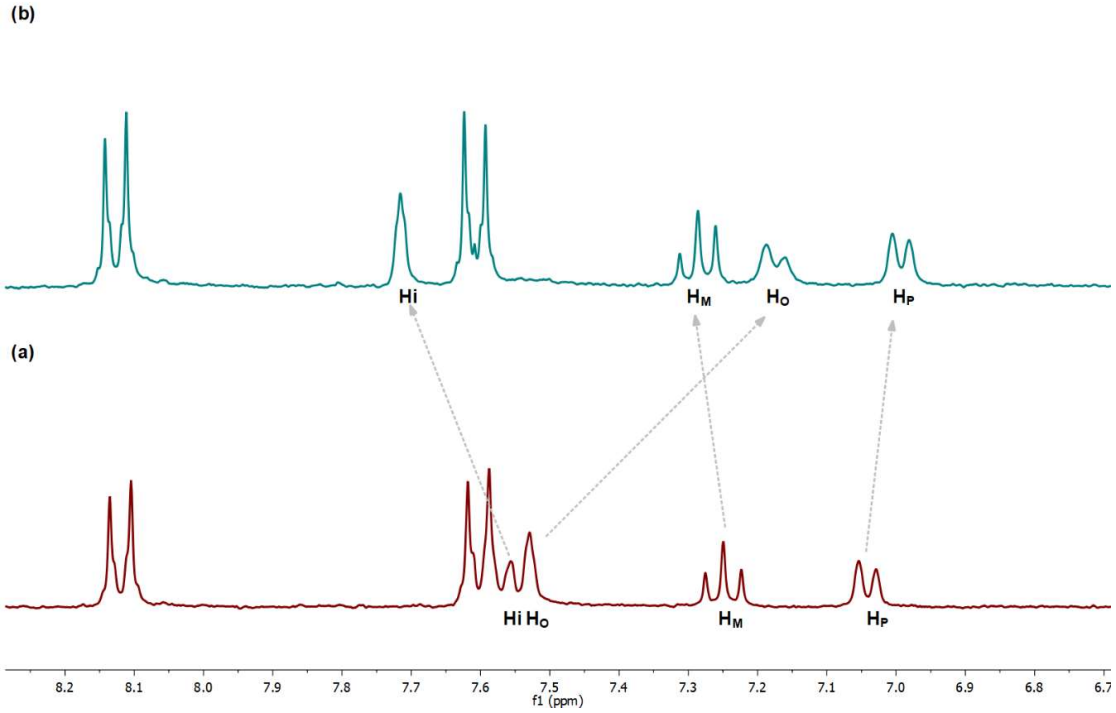


Figure 26. Partial ^{1}H NMR titration experiment of **1** (a) spectrum without cation addition (b) spectrum after addition of 1 eq KPF_6 (293 K, 3%H_2O/CD_3CN solution, C_{KPF6}=1.8 x10^{-1}M, $C_{receptor}$=3.8 x10^{-3} M)

- 3% H_2O/CD_3CN

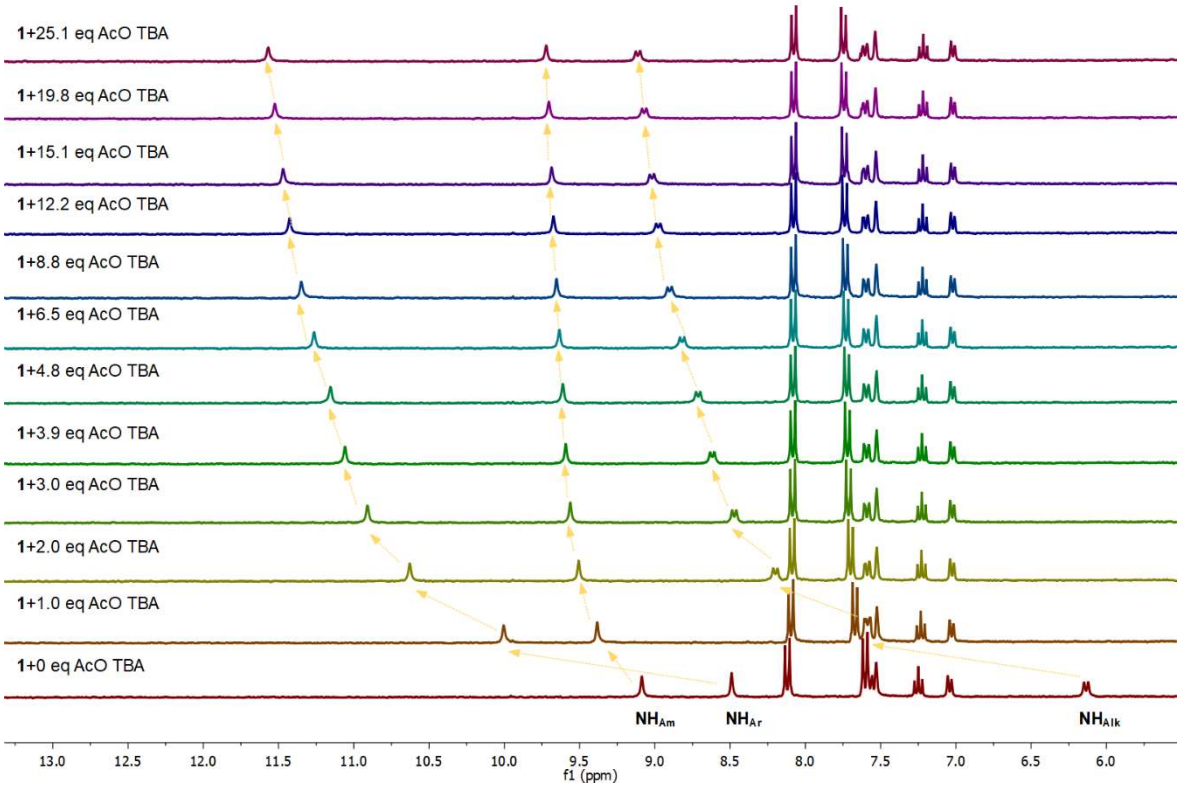


Figure 27. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBA AcO) addition, (293 K, 3%H_2O/CD_3CN solution, $C_{titrant}$=1.9 x10^{-1}M, $C_{receptor}$=3.8 x10^{-3} M)

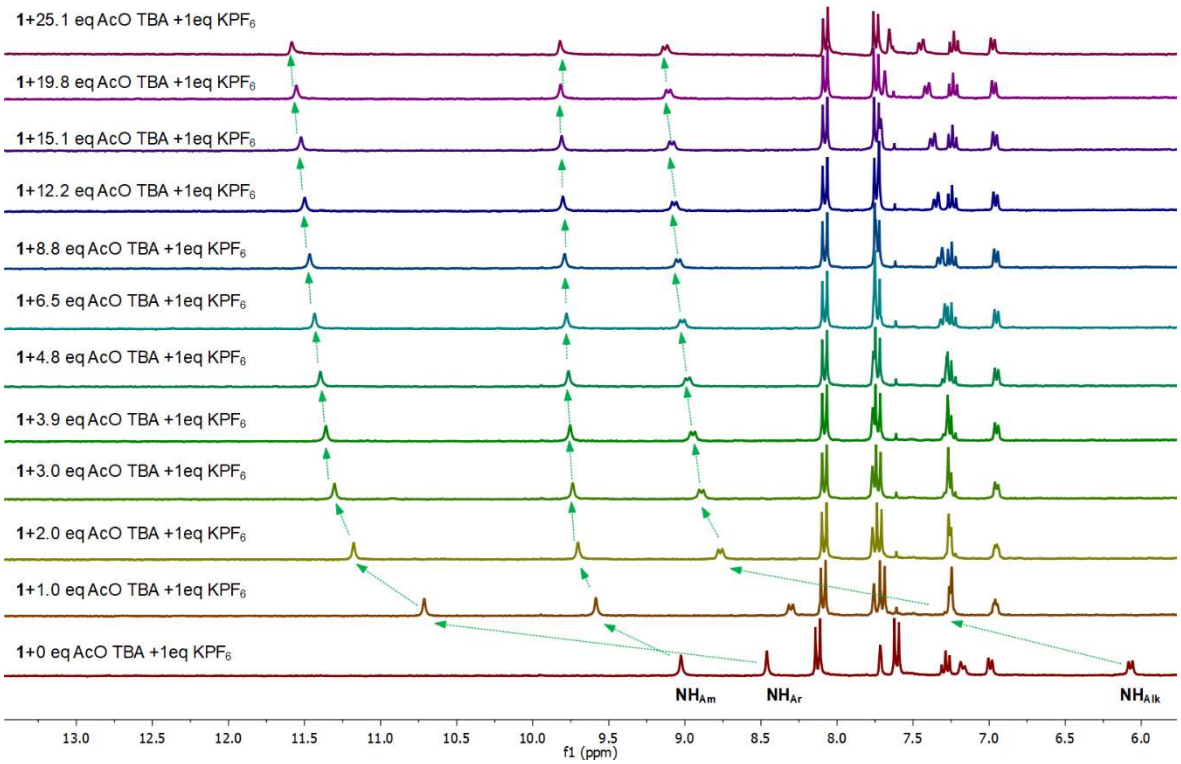


Figure 28. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBA AcO) addition in presence of 1eq. KPF_6,(293 K, 3%H_2O/CD_3CN solution, $C_{titrant}$=1.9 x10^{-1}M, $C_{receptor}$=3.8 x10^{-3} M)

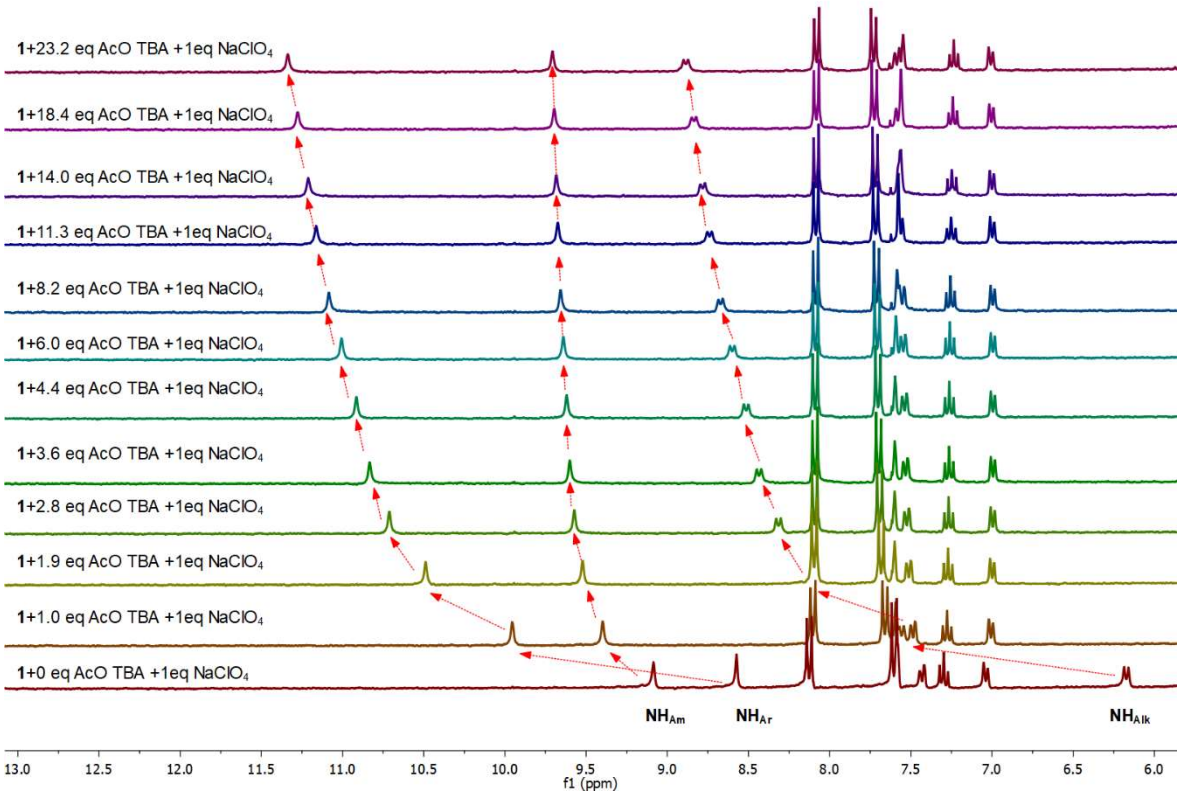


Figure 29. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBA AcO) addition in the presence of 1eq. $NaClO_4$, (293 K, 3%H_2O/CD_3CN solution, $C_{titrant}$=1.9 x10^{-1}M, $C_{receptor}$=3.9 x10^{-3} M)

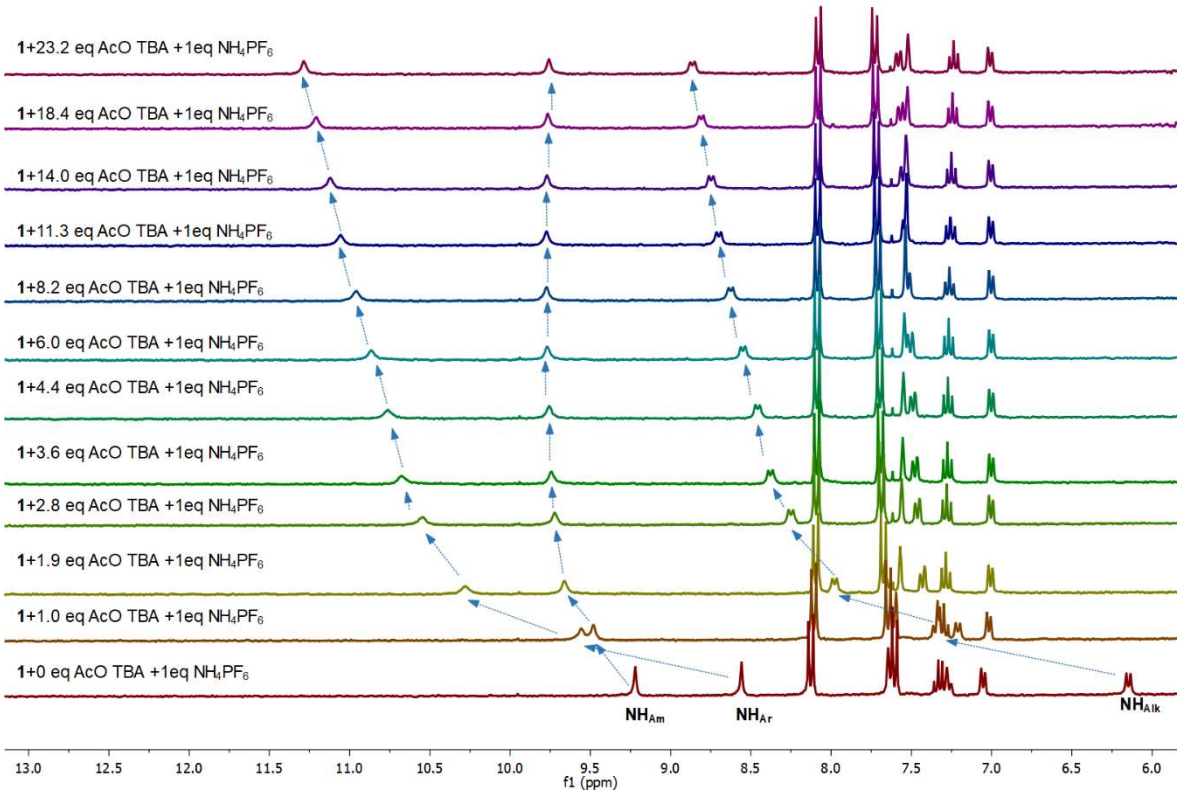


Figure 30. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBA AcO) addition in the presence of 1eq. NH_4PF_6,(293 K, 3%H_2O/CD_3CN solution, $C_{titrant}$=1.9 x10^{-1}M, $C_{receptor}$=3.9 x10^{-3} M)

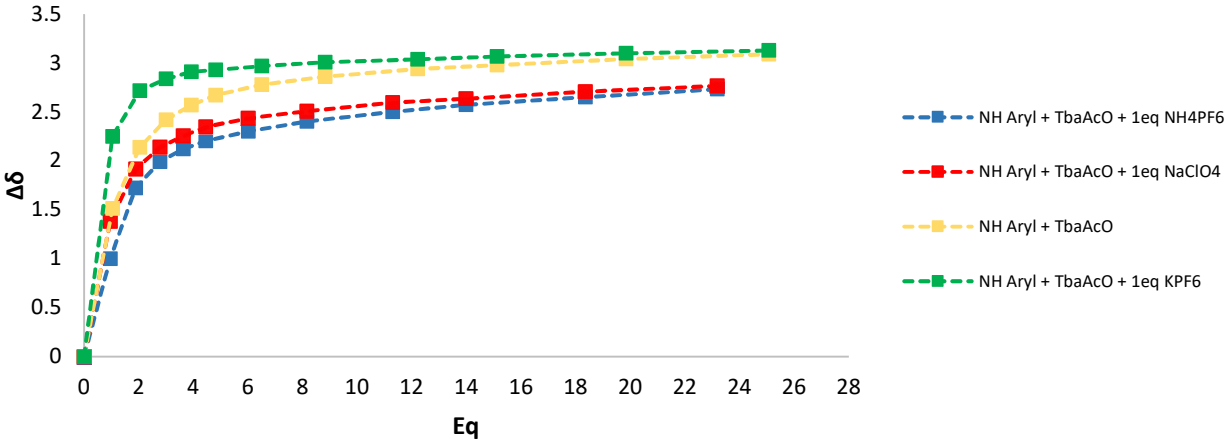


Figure 31.^{1}H NMR titration binding isotherm of **1** with TBA AcO in the presence or absence of 1 eq. of cations, 3%H_2O/CD_3CN solution

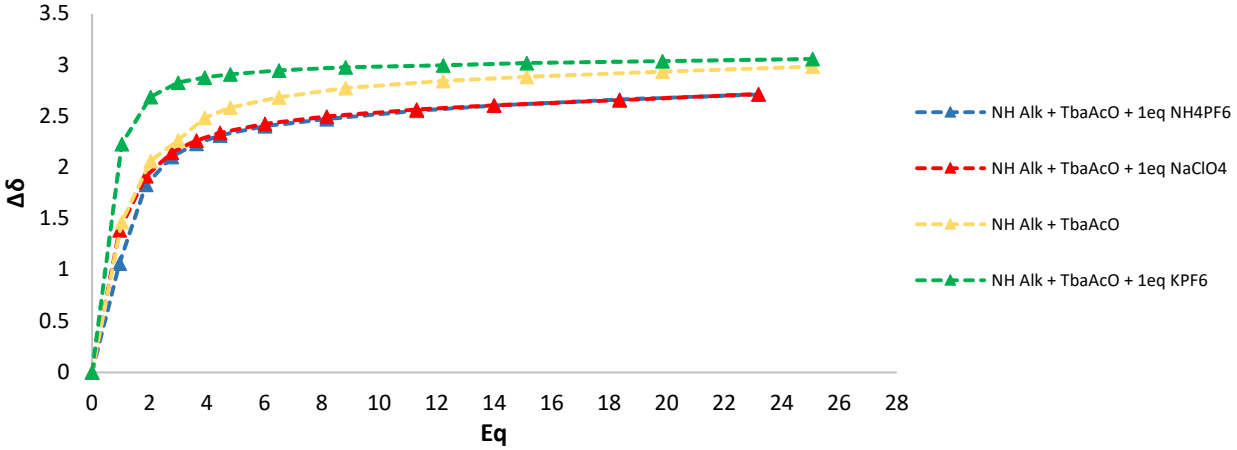


Figure 32 .[1]H NMR titration binding isotherm of **1** with TBA AcO in the presence or absence of 1 eq. of cations, 3%H_2O/CD_3CN solution

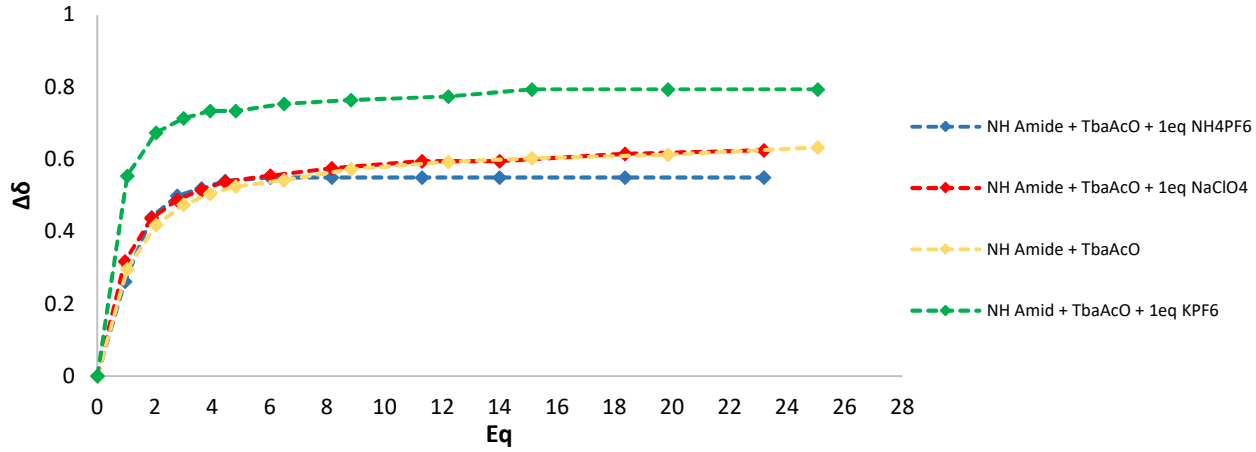


Figure 33.[1]H NMR titration binding isotherm of **1** with TBA AcO in the presence or absence of 1 eq. of cations, 3%H_2O/CD_3CN solution

Solvent	Ion	**TBA^+**	**$NaClO_4$**	**KPF_6**	**NH_4PF_6**
3% H_2O/CH_3CN	**AcO^-**	420 (4.9%)	500 (8.7%)	2060 (13.4%)	330 (9.1%)
	$K_M/K_{TBA\ AcO}$	-	1.19	4.90	0.79

Figure 34. NMR spectroscopy K_{obs} values (298 K) for interactions of **1** with AcO^- in the presence or absence of potassium cation and standard errors values in parentheses

5. NMR extraction experiments

[1]H NMR extraction experiments were performed on a 300 MHz Bruker Avance spectrometer, at 298K, in $CDCl_3$ solution. In each case 0.5 mL of 2.5 x 10^{-2} M solution of the receptor **1** was washed with water, then after phase separation, the receptor **1** solution was extracted with aqueous solution of salts for 1 minute. The equivalent of salt in water solution was calculated based on molarity of the receptor in chloroform phase. *For example: 0.5 ml of chloroform solution of the receptor **1** (2.5x10^{-2}) was extracted with 0.5 ml of AcOK water solution (2.5x10^{-1}) which corresponded to 10 eq.* Then chloroform phase

containing receptor-salt complex was washed with water ('back' extraction), to prove the reversibility of extraction process. After each step of the experiment ^{1}H NMR spectrum was registered. The efficiency of the extraction process was calculated on the basis ofthe carboxylate alkyl signals integration values, assuming the receptor as an internal standard. The 100% efficiency corresponds to fully salt loaded receptor.

- Control experiment checking salt affinity to aqueous phase. Conformation that AcOK in LLE experiment condition was not extracted with chloroform.

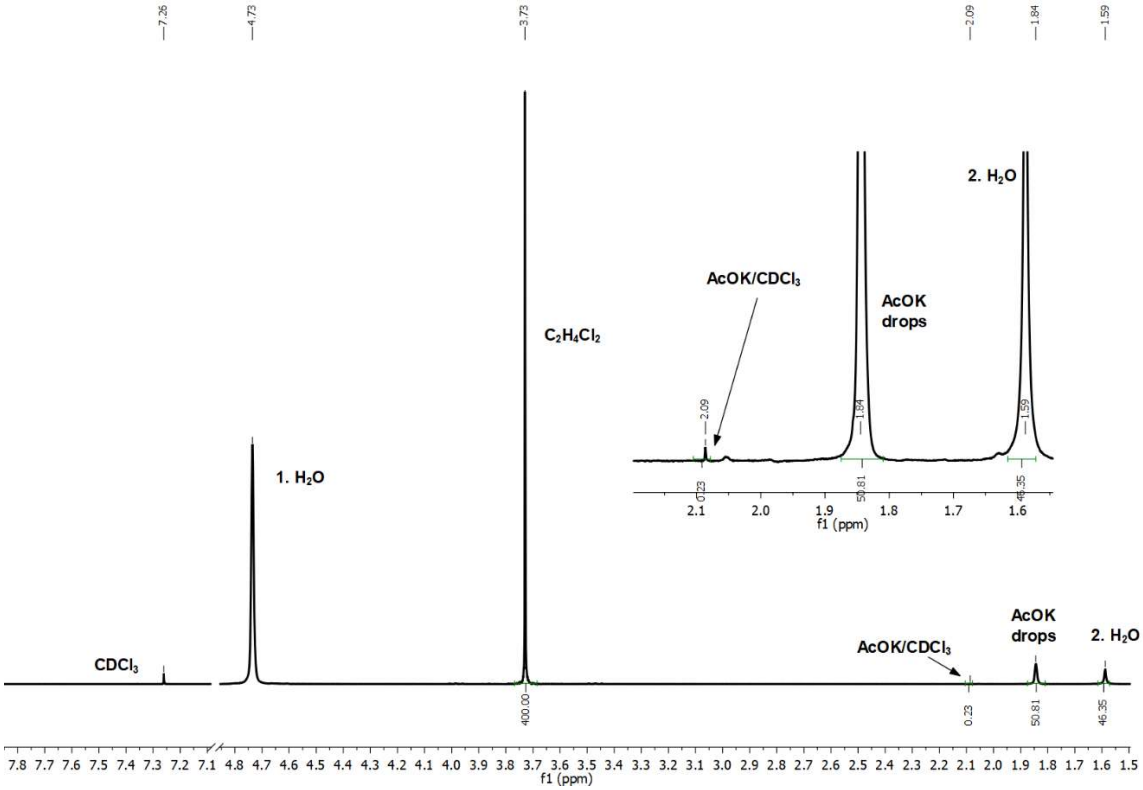


Figure 35. Liquid-Liquid extraction of AcOK aqua solution C=3.2 M which corresponds to 130 eq. when the receptor solution is present with $CDCl_3$. 1 H_2O is peak corresponding to water in drops on the NMR tubes walls. 2 H_2O is water in $CDCl_3$. Potasium acetate concentration was measured based on addition of 10 µL of 1,2-dichloroethane as internal standard and it was 1.93x 10^{-7}. The efficiency of this proces was 6x10^{-6}% based on internal standard.

- On the spectrum above and many spectras under the peak 1.84-1.88 can be observed. This peak corresponds to the potassium acetate in water droplets remaining on the walls of NMR tube. The intensity of this signal depended on the concentration of the potassium acetate in water and the quality of phase separation. Nevertheless, the presence of this signal does not affect extraction experiment efficiency and quality, because the peak of pottasium acetate in $CDCl_3$ has diferent chemical shift 2.09-.2.13.Moreover, we tried to simulate the most realistic conditions of the extraction proces therefore we did not perform any additional treatments of the NMR sample.

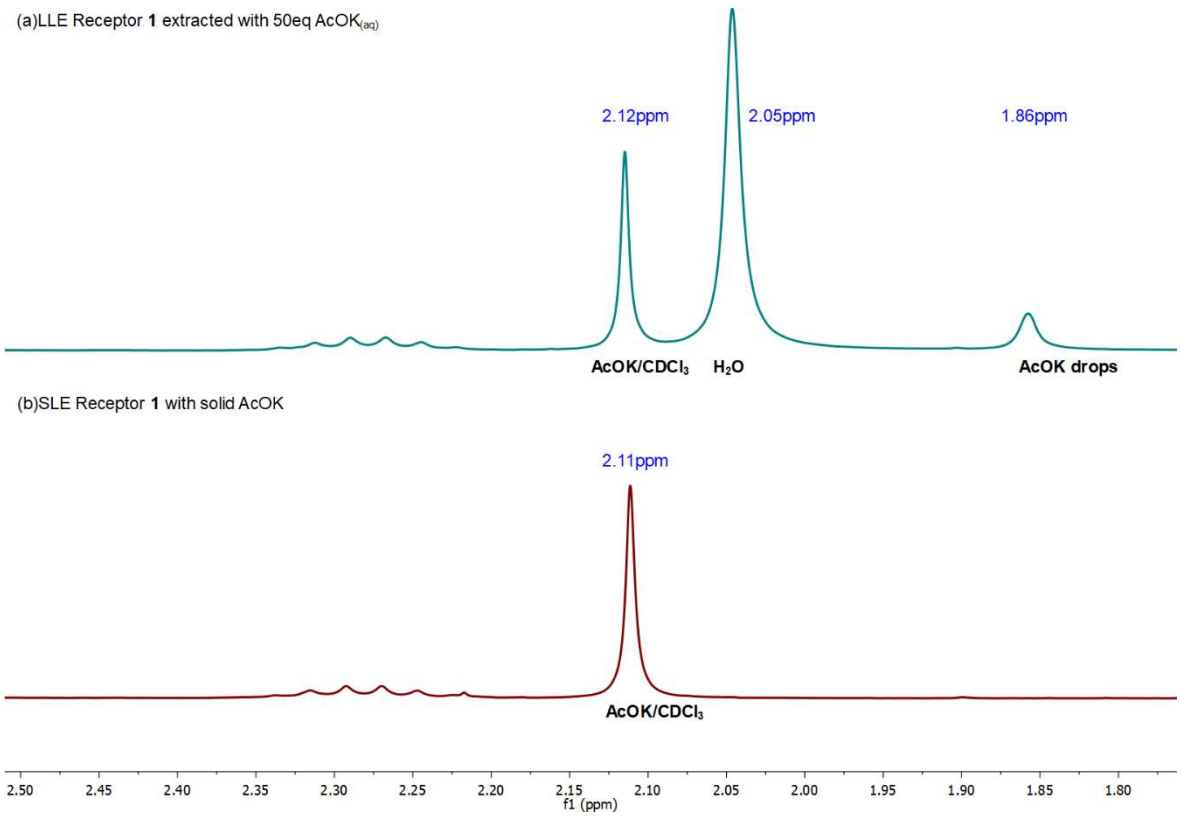


Figure 36. Partial ^{1}H NMR spectrum of the receptor **1** (a) LLE extraction $C_{receptor}$=2.5x10^{-2}M, C_{AcOK}=1.25M (b) SLE extraction $C_{receptor}$=2.5x10^{-2}M, solid AcOK was added.

- Control experiment checking receptor **1**●AcOK complex affinity to the organic phase and possible decline of the receptor was carried out.

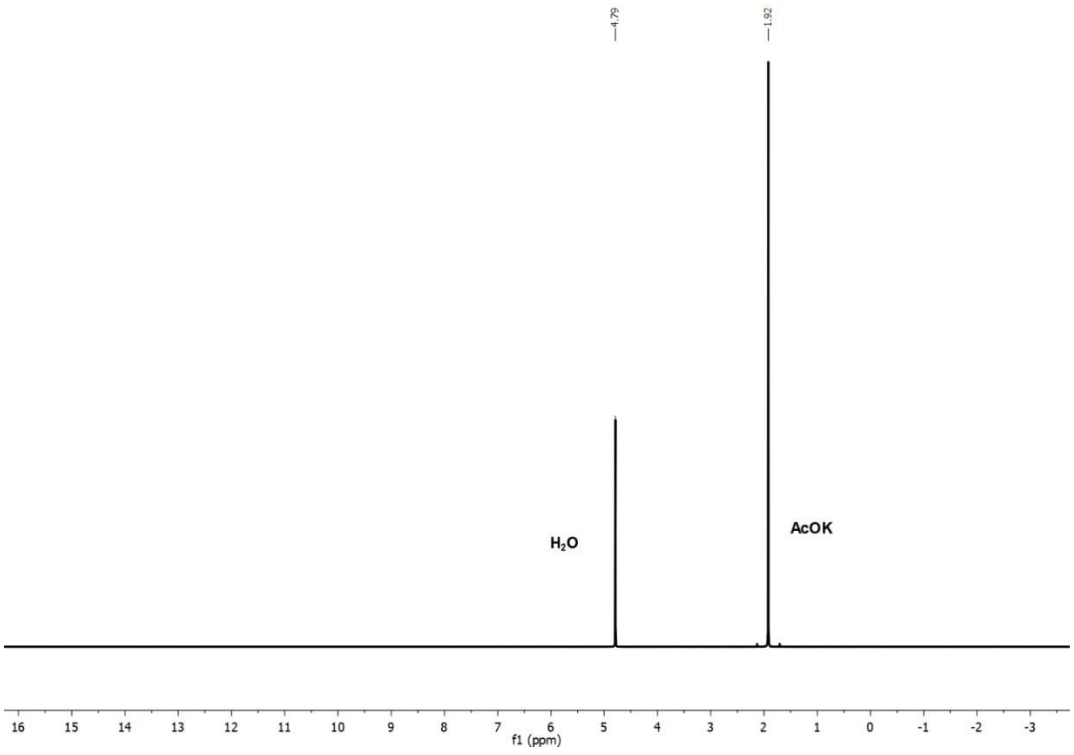


Figure 37.^{1}H NMR spectrum of D_2O phase used as 'back' extraction phase on receptor **1** $C_{receptor}$=2.5x10^{-2}M complex with AcOK. No receptor peaks were observed on this spectrum.

- Extraction studies

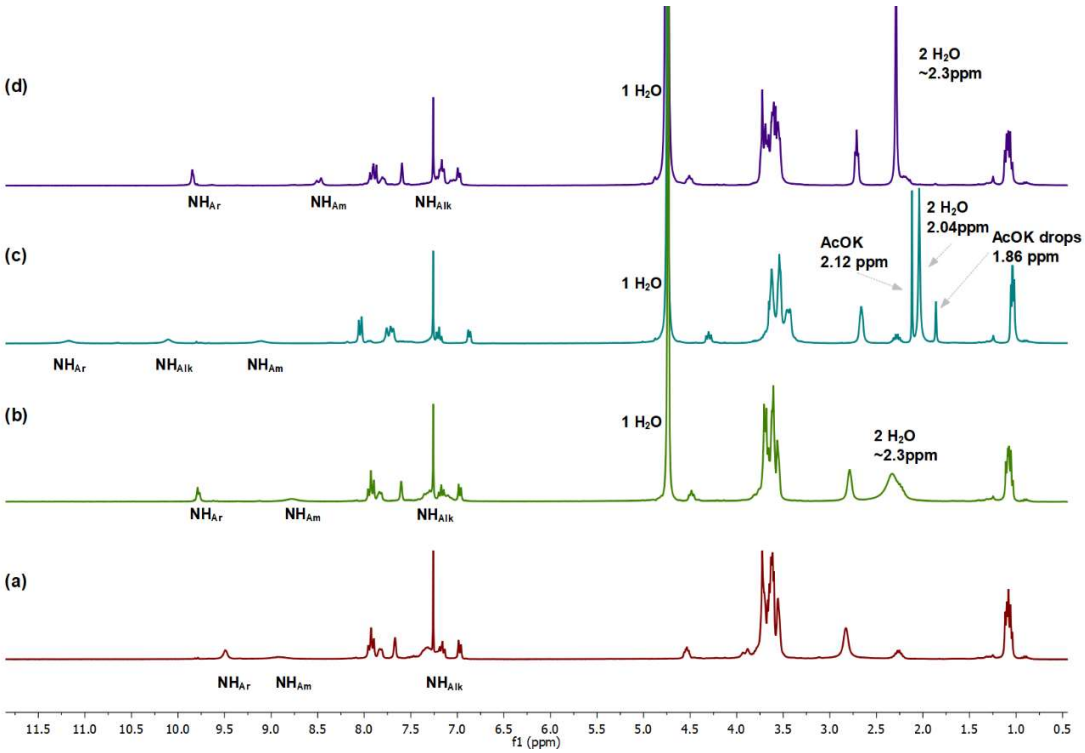


Figure 38. ^{1}H NMR spectrum stack of extraction experiment steps. (a) The receptor **1** dissolved in 'dry' $CDCl_3$ ($C_{receptor}$=2.5x10^{-2}M); (b) The receptor **1** solution after being washed with deionized water; (c) The receptor **1** solution after extraction with 50 eq AcOK aquaeus solution (C_{AcOK}=1.25M); (d) The receptor **1** solution after 'back extraction'- washed with deionized water. (1 H_2O- H_2O/H_2O; 2 H_2O-$H_2O/CDCl_3$)

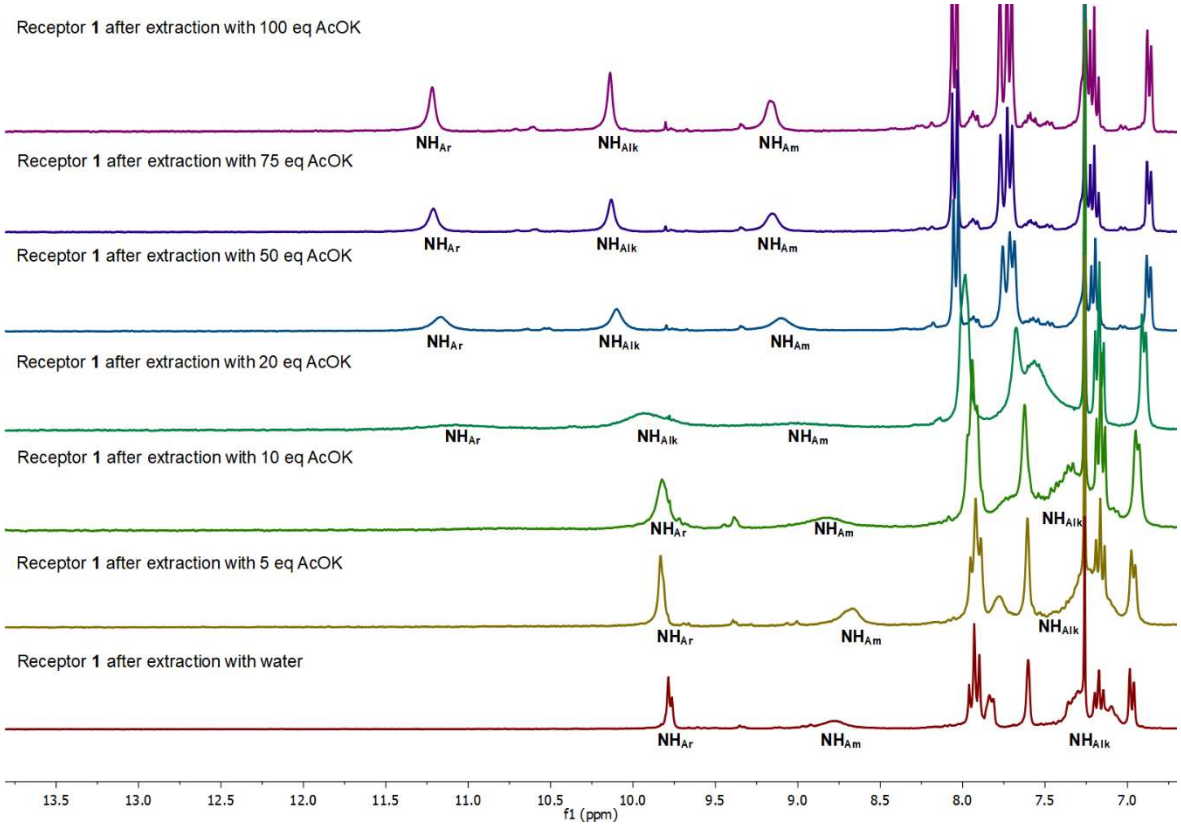


Figure 39. Partial ^{1}H NMR extraction experiment of **1** after 1 minute extraction with aqueous solutions of potassium acetate (293 K, $CDCl_3$,C_{AcOK}=0.125-2.5M, $C_{receptor}$=2.5 x10^{-2}M)

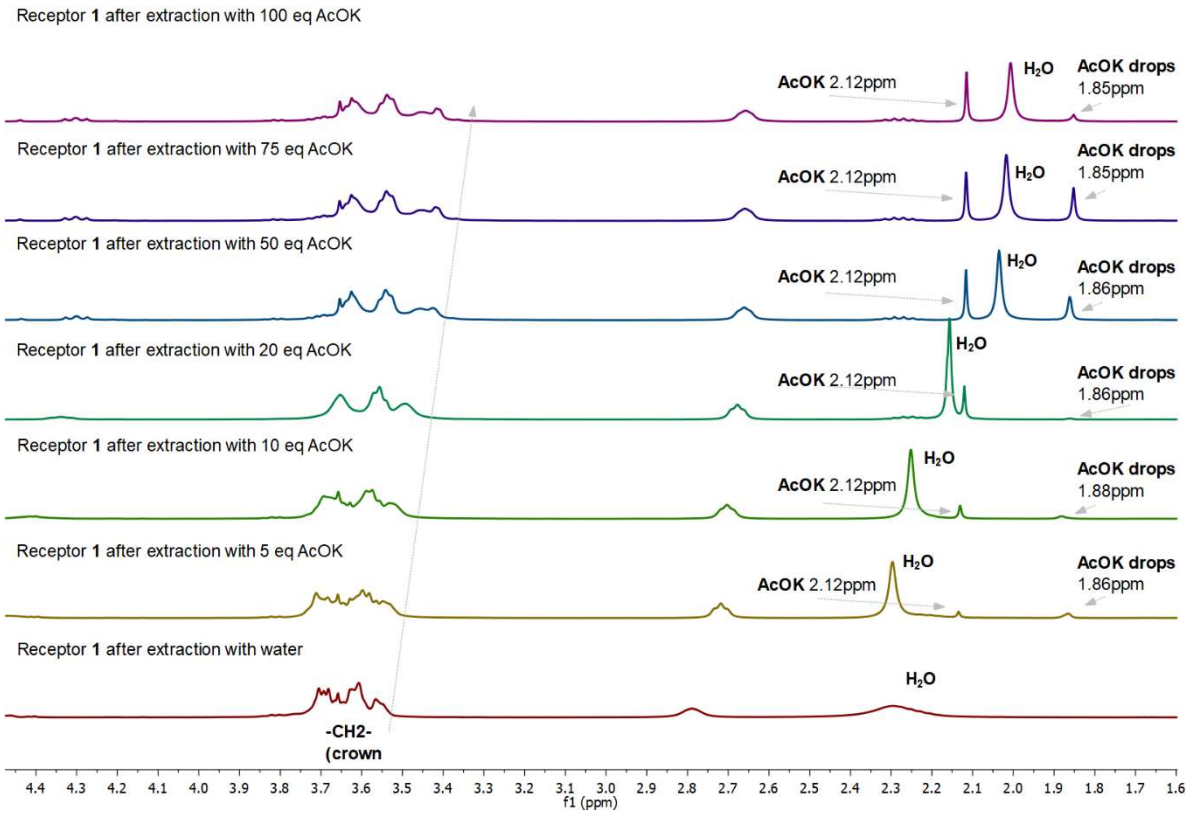


Figure 40. Partial ^{1}H NMR extraction experiment of **1** after 1 minute extraction with aqueous solutions of potassium acetate (293 K, $CDCl_3$,C_{AcOK}=0.125-2.5M, $C_{receptor}$=2.5 x10^{-2}M)

C_{AcOK}[mol/dm^3]	$C_{receptor}$[mol/dm^3]	Equivalent[a]	Extraction efficiency[b]
0.1250	0.0252	5	13 %
0.2500	0.0252	10	28 %
0.4963	0.0250	20	53 %
0.7444	0.0250	30	71 %
0.9925	0.0250	40	81 %
1.3127	0.0252	52	88 %
1.8753	0.0252	74	94 %
2.5178	0.0252	100	98 %
3.2732	0.0252	130	100 %
3.7767	0.0252	150	100 %
5.0356	0.0252	199	100 %

Figure 41. Results of ^{1}H NMR extraction experiments;[a]units of moles of salt vs. units of moles of the receptor in 0.5 ml of solutions; [b] Extraction efficiency calculated from the integral value of acetate methyl group. Assuming that 100% efficiency is the value of the integral 3.

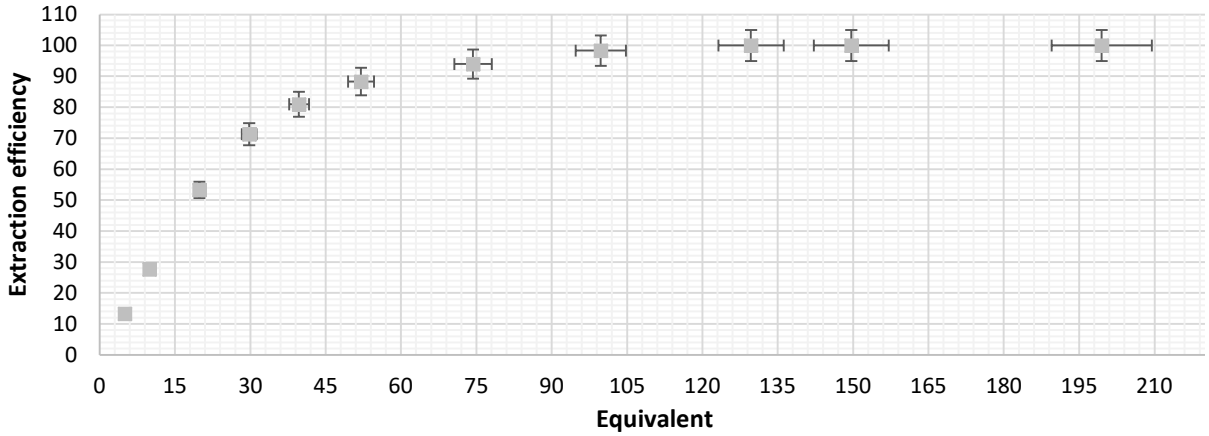


Figure 42. Efficiency of extraction process in function of salt concentration. Based on ^{1}H NMR extraction experiments.

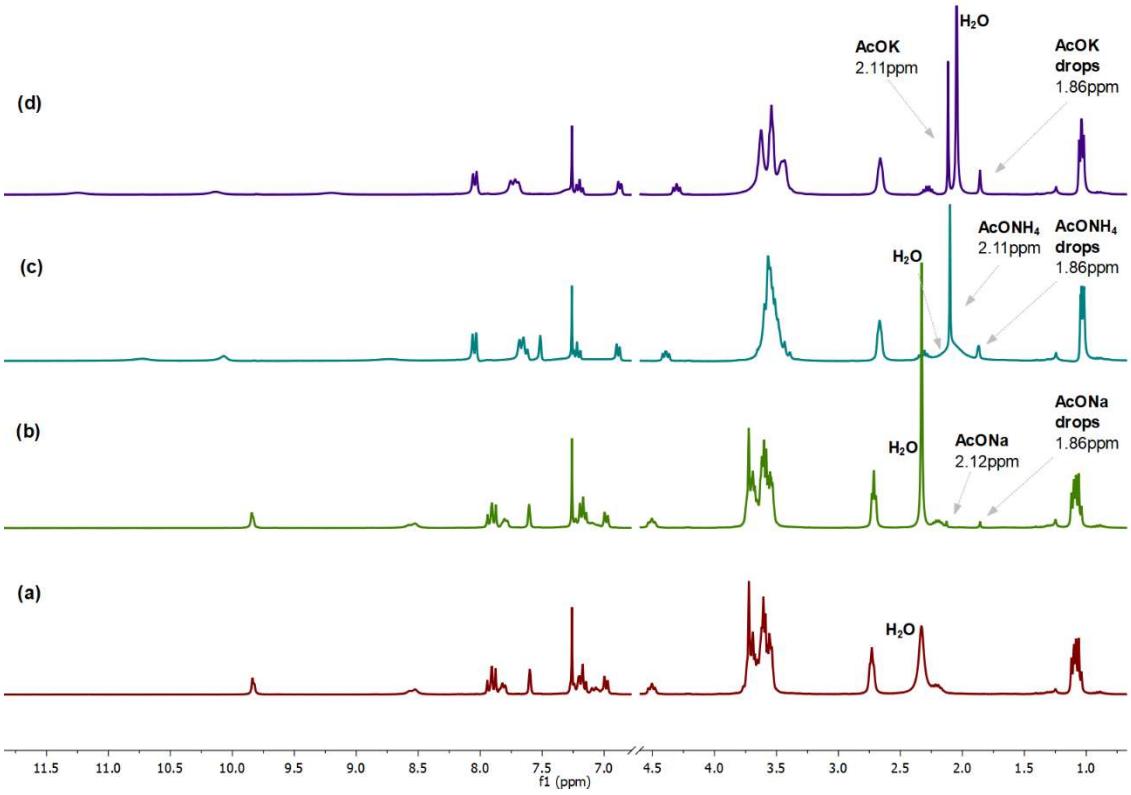


Figure 43. ^{1}H NMR spectrum stack of extraction experiment steps. ($C_{receptor}$=2.5x10^{-2}M); (a) The receptor **1** solution after being washed with deionized water; (b) The receptor **1** solution after extraction with 50 eq AcONa aqua solution (C_{AcOK}=1.25M); (c) The receptor **1** solution after extraction with 50 eq $AcONH_4$ aqua solution (C_{AcOK}=1.25M); (d) The receptor **1** solution after extraction with 50 eq AcOK aqua solution (C_{AcOK}=1.25M)

	50 eq AcOK	**50 eq AcONa**	**50 eq $AcONH_4$**
Extraction efficiency [(a)]	80%	4 %	~70%[(b)]

Figure 44. The results of ^{1}H NMR extraction experiments of receptor **1** with different acetates salts; [(a)] The extraction efficiency calculated from the integral value of acetate methyl group. Assuming that 100% efficiency is the value of the integral 3. [(b)]Estimated carefully, during experiment signal corresponding to water molecules rose up acetate methyl group integration value.

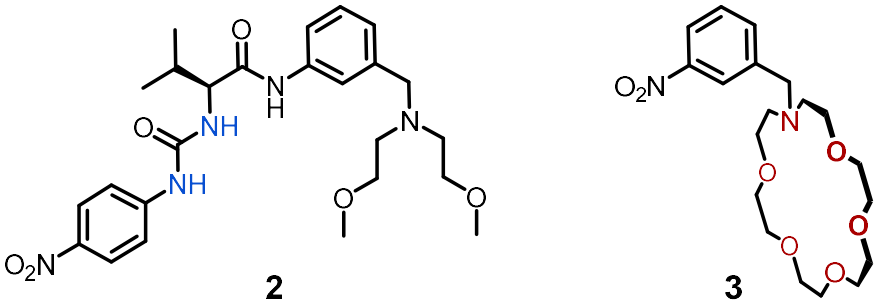


Figure 45. Structures of the monotopic receptors **2** and **3**

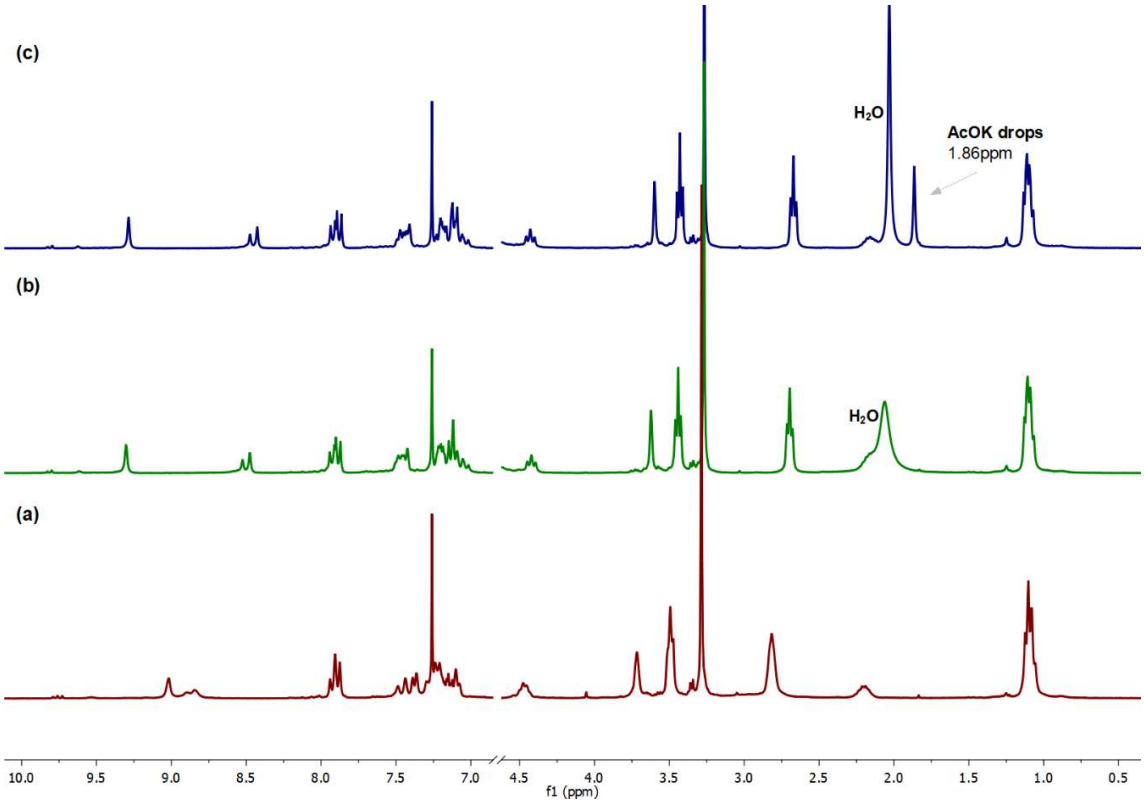


Figure 46. Partial ^{1}H NMR spectrum stack of Receptor **2**; (a) Receptor **2** dissolved in 'dry' $CDCl_3$ ($C_{receptor}$=2.5x10^{-2}M); (b) Receptor **2** solution after being washed with deionized water; (c) Receptor **2** solution after the extraction with 50 eq AcOK aqua solution (C_{AcOK}=1.25M)

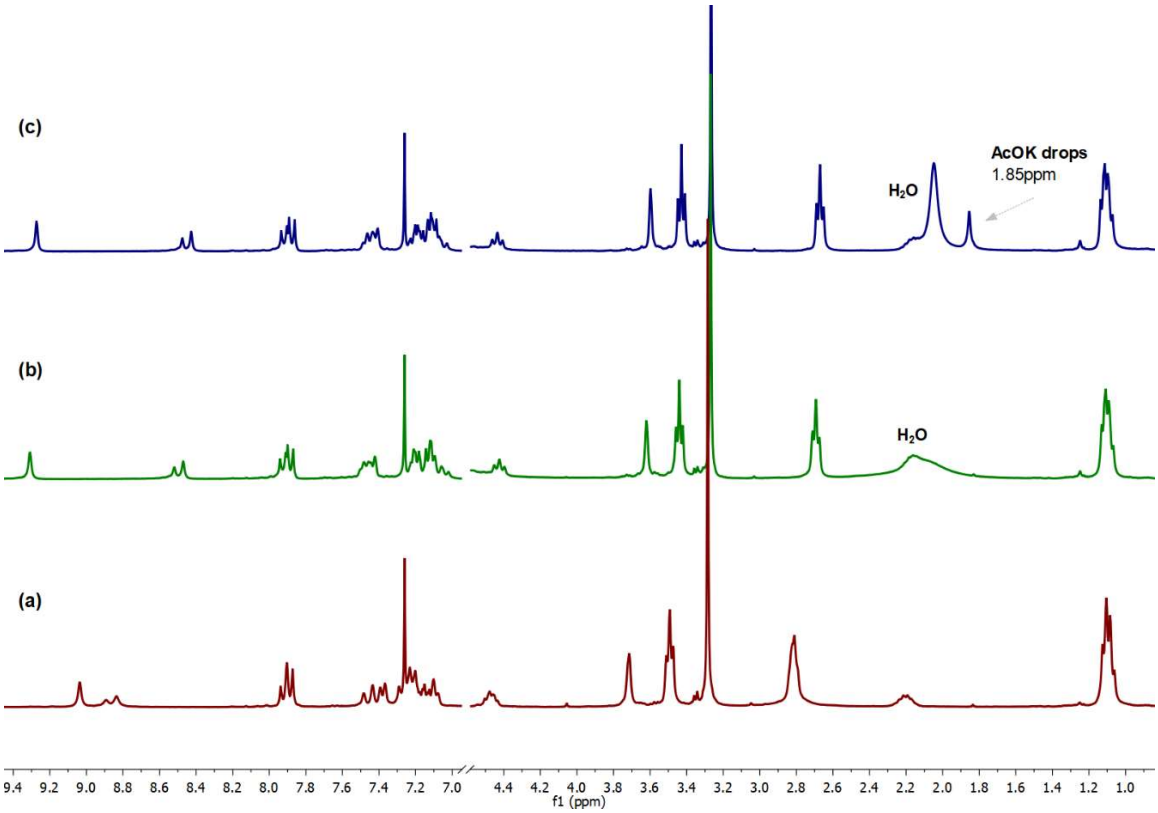


Figure 47. Partial ^{1}H NMR spectrum stack of Receptor **2**; (a) Receptor **2** dissolved in 'dry' $CDCl_3$ ($C_{receptor}$=2.5x10^{-2}M); (b) Receptor **2** solution after being washed with deionized water; (c) Receptor **2** solution after the extraction with 100 eq AcOK aqua solution (C_{AcOK}=2.5M)

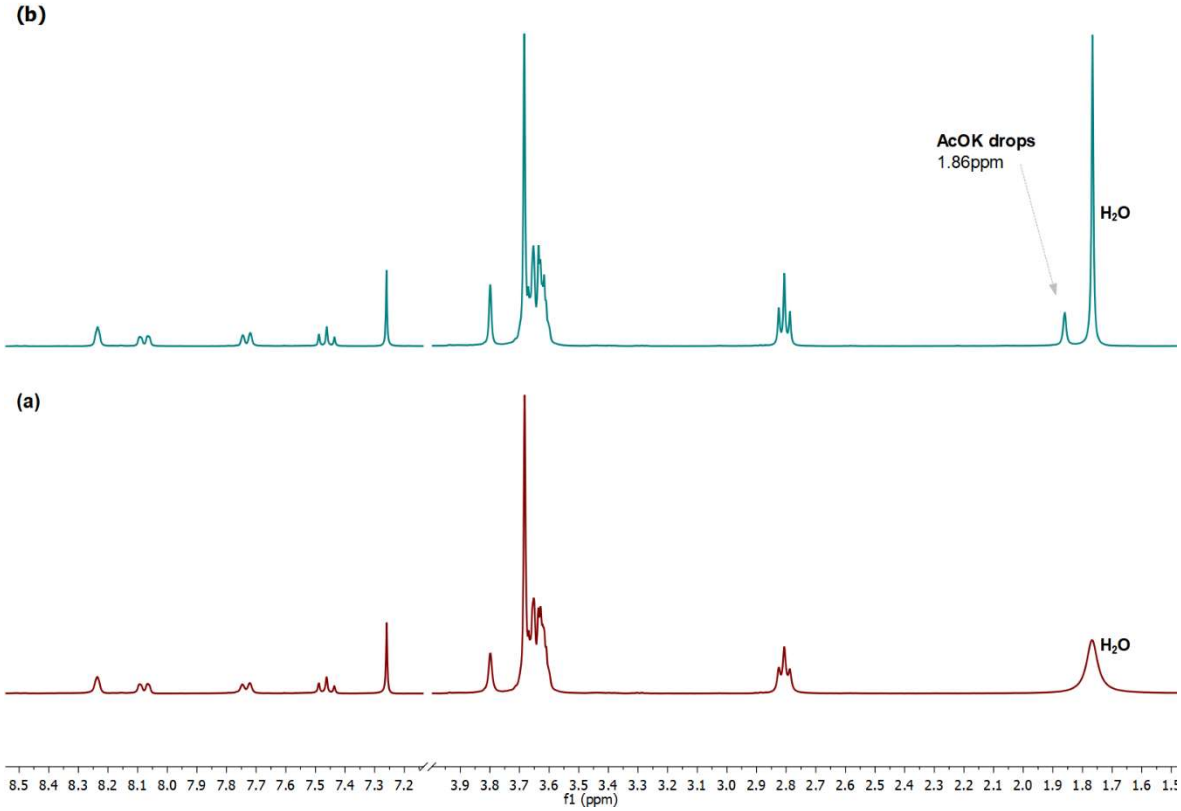


Figure 48. Partial ^{1}H NMR spectrum stack of Receptor **3**; (a) Receptor **3** solution after being washed with deionized water ($C_{receptor}$=2.5x10^{-2}M); (b) Receptor **3** solution after extraction with 50 eq AcOK aqua solution (C_{AcOK}=1.25M)

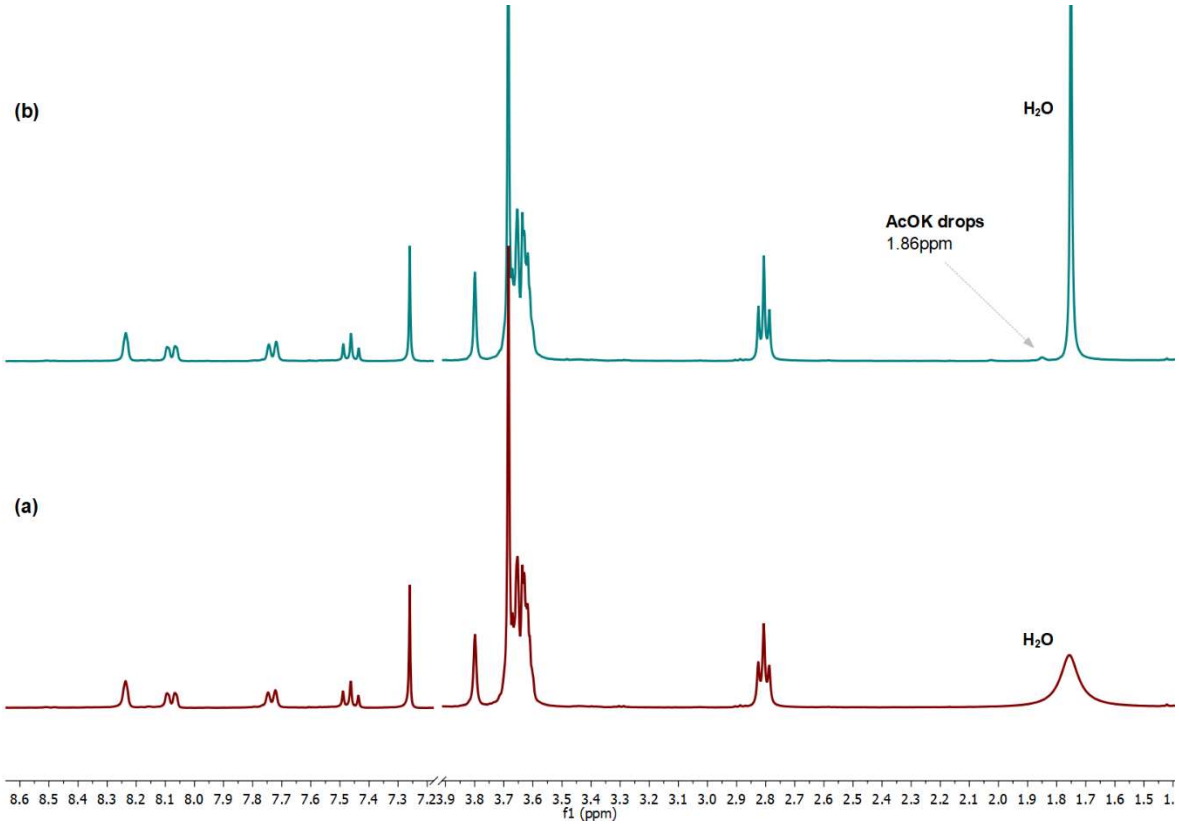


Figure 49. Partial ^{1}H NMR spectrum stack of Receptor **3**; (a) Receptor **3** solution after being washed with deionized water ($C_{receptor}$=2.5x10^{-2}M); (c) Receptor **3** solution after extraction with 100 eq AcOK aqua solution (C_{AcOK}=2.5M)

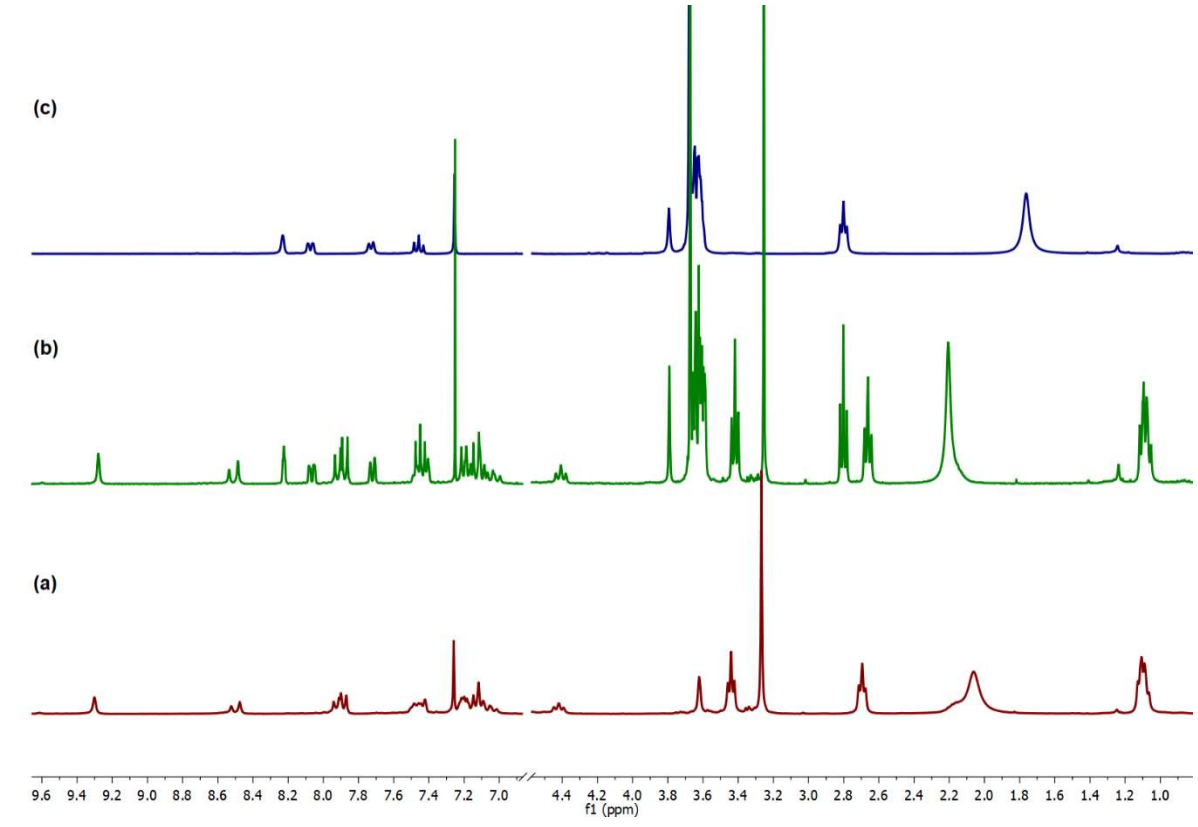


Figure 50. Partial ^{1}H NMR (a) Receptor **2** after being washed with deionized water ($C_{receptor}$=2.5x10^{-2}M); (b) Equimolar mixture of Receptors **2** and **3** after being washed with deionized water ($C_{receptor}$=2.5x10^{-2}M); (c) Receptor **3** after being washed with deionized water($C_{receptor}$=2.5x10^{-2}M)

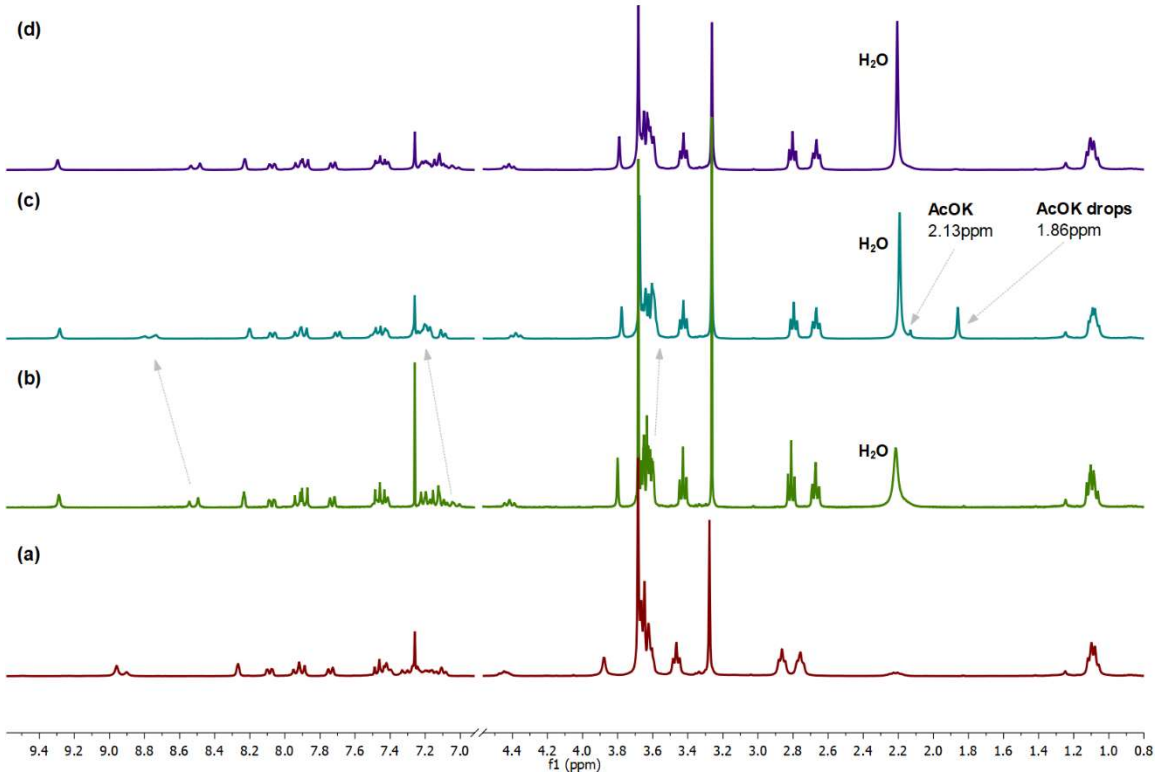


Figure 51. Partial ^{1}H NMR spectrum stack of extraction experiment steps. (a) Equimolar mixture of Receptors **2** and **3** dissolved in 'dry' $CDCl_3$ ($C_{receptors}$=2.5x10^{-2}M); (b) Equimolar mixture of Receptors **2** and **3** solution being washed with deionized water; (c) Equimolar mixture of Receptors **2** and **3** solution after extraction with 50 eq AcOK aqua solution (C_{AcOK}=1.25M); (d) Equimolar mixture of Receptors **2** and **3** solution after 'back extraction'- washed with deionized water.

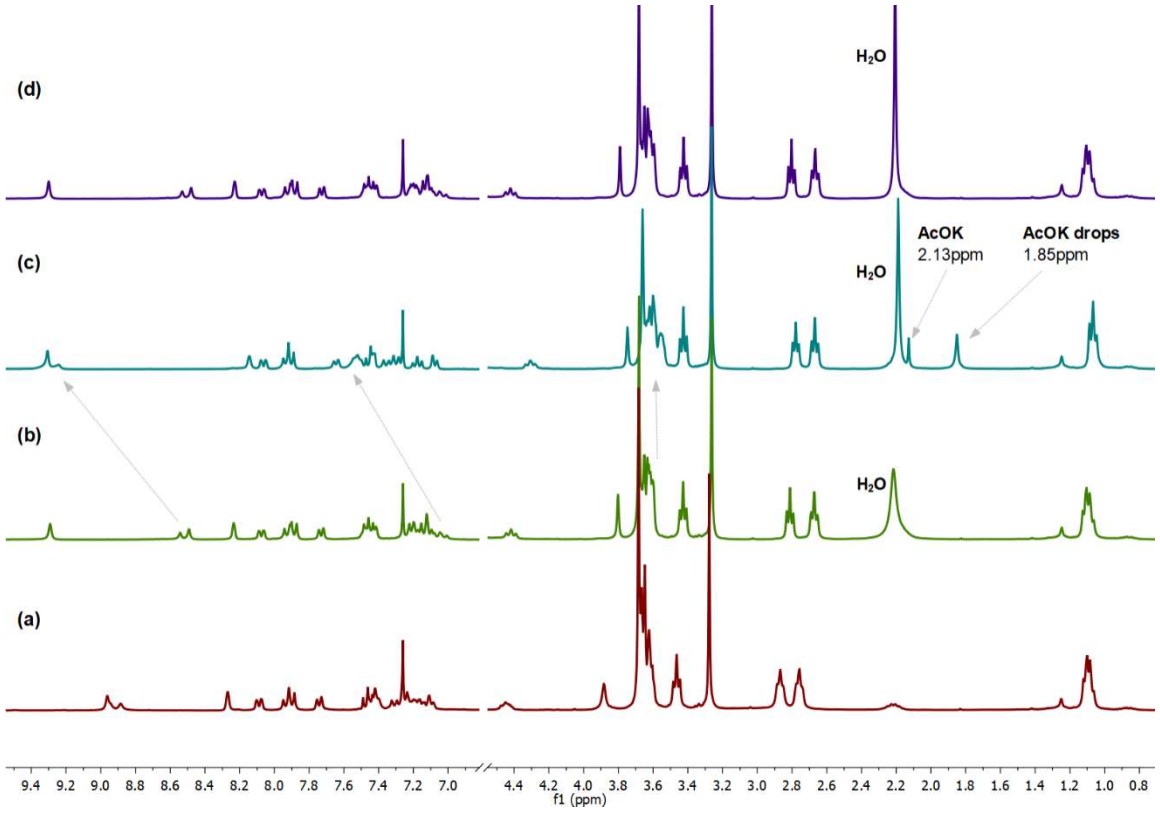


Figure 52. Partial^{1}H NMR spectrum stack of extraction experiment steps. (a) Equimolar mixture of Receptors **2** and **3** dissolved in 'dry' $CDCl_3$ ($C_{receptors}$=2.5x10^{-2}M); (b) Equimolar mixture of Receptors **2** and **3** solution after being washed with deionized

water; (c) Equimolar mixture of Receptors **2** and **3** solution after extraction with 100 eq AcOK aqua solution (C_{AcOK}=2.5M); (d) Equimolar mixture of Receptors **2** and **3** solution after 'back extraction'- washed with deionized water.

C_{AcOK}[mol/dm^3]	$C_{receptor}$[mol/dm^3]	Equivalent[a]	Extraction efficiency [b]
1.25	0.025	50	12 %
2.5	0.025	100	27 %

Figure 53. The results of ^{1}H NMR extraction experiments for equimolar mixture of receptors **2** and **3**; [a]units of moles of salt vs. units of moles of receptor in 0.5 ml of solutions; [b] Extraction efficiency calculated from the integral value of acetate methyl group. Assuming that 100% efficiency is the value of the integral 3.

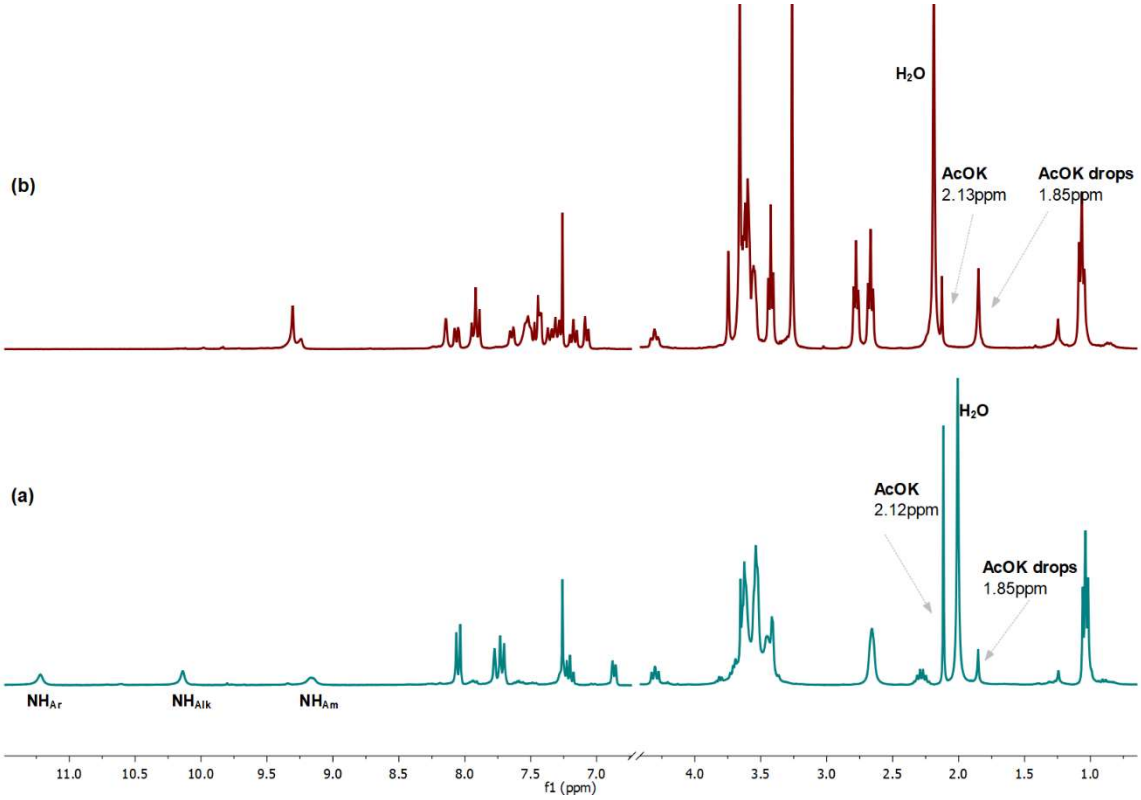


Figure 54. Partial ^{1}H NMR spectrum stack of extraction experiment steps. $C_{receptors}$=2.5x10^{-2}M (a) Receptor **1** solution after extraction with 100 eq AcOK aqua solution (C_{AcOK}=2.5M) (b) Equimolar mixture of Receptors **2** and **3** solution after extraction with 100 eq AcOK aqua solution (C_{AcOK}=2.5M); Extraction efficiency (a) ~100%; (b) ~27%

6. Extraction of potassium ibuprofenate

Extraction experiment of potassium ibuprofenate was performed using the same technique as in case of model potassium acetate. All extraction steps were carried out in NMR tube without any further refinement on the sample.

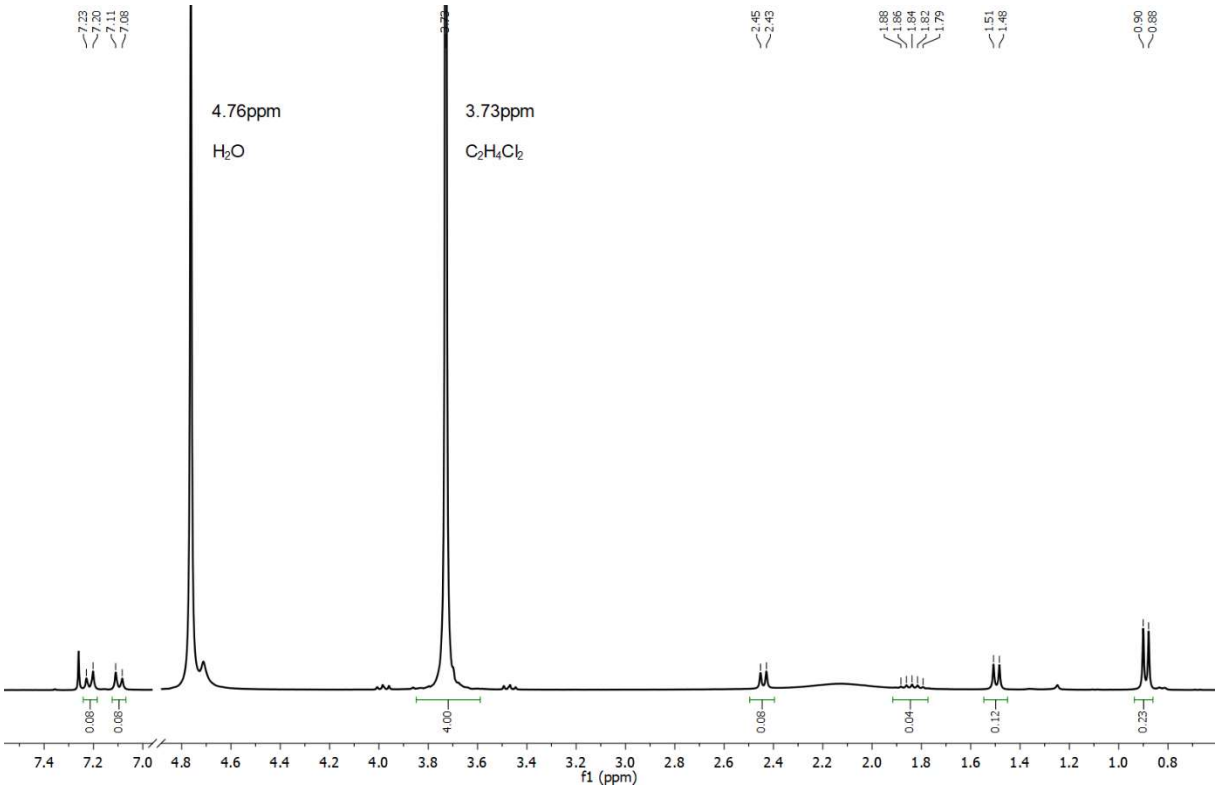


Figure 55. Liquid-Liquid extraction of potassium ibuprofenate aqueous solution C=0.2 M which corresponds to 8.1 eq. when the receptor solution is present with $CDCl_3$. Salt concentration was measured based on addition of 10 µL of 1,2-dichloroethane as internal standard and it was 4.82x 10^{-6}. The efficiency of this process was 3.83 % based on internal standard addition.

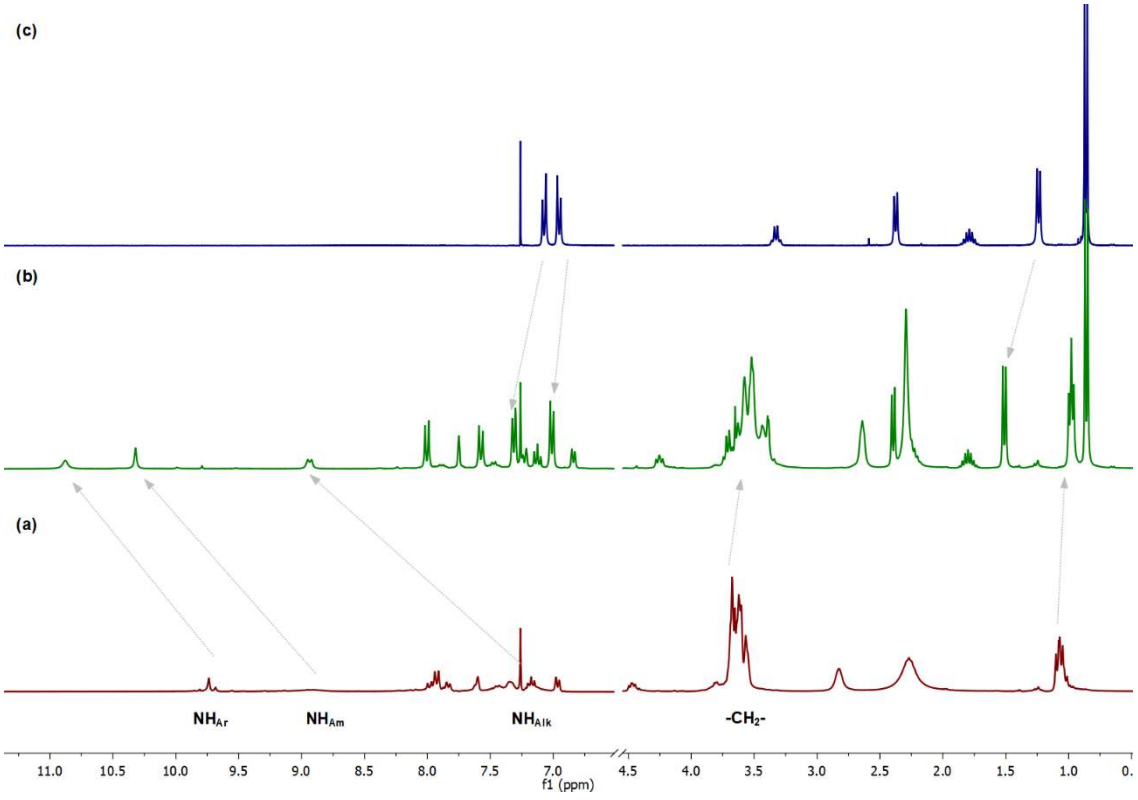


Figure 56. ^{1}H NMR spectrum stack of extraction experiment steps: (a) Receptor **1** solution after being washed with deionized water C_{rec}=2.5x10^{-2}; (b) Receptor **1** solution after extraction with 3.8eqpotassium ibuprofenate aqueous solution (C_{salt}=9.6x10^{-2}M); (c) $CDCl_3$ solution of potassium ibuprofenateextracted from solid to chloroform phase (SLE), after 30 minutes. Extraction efficiency estimated as 100%.

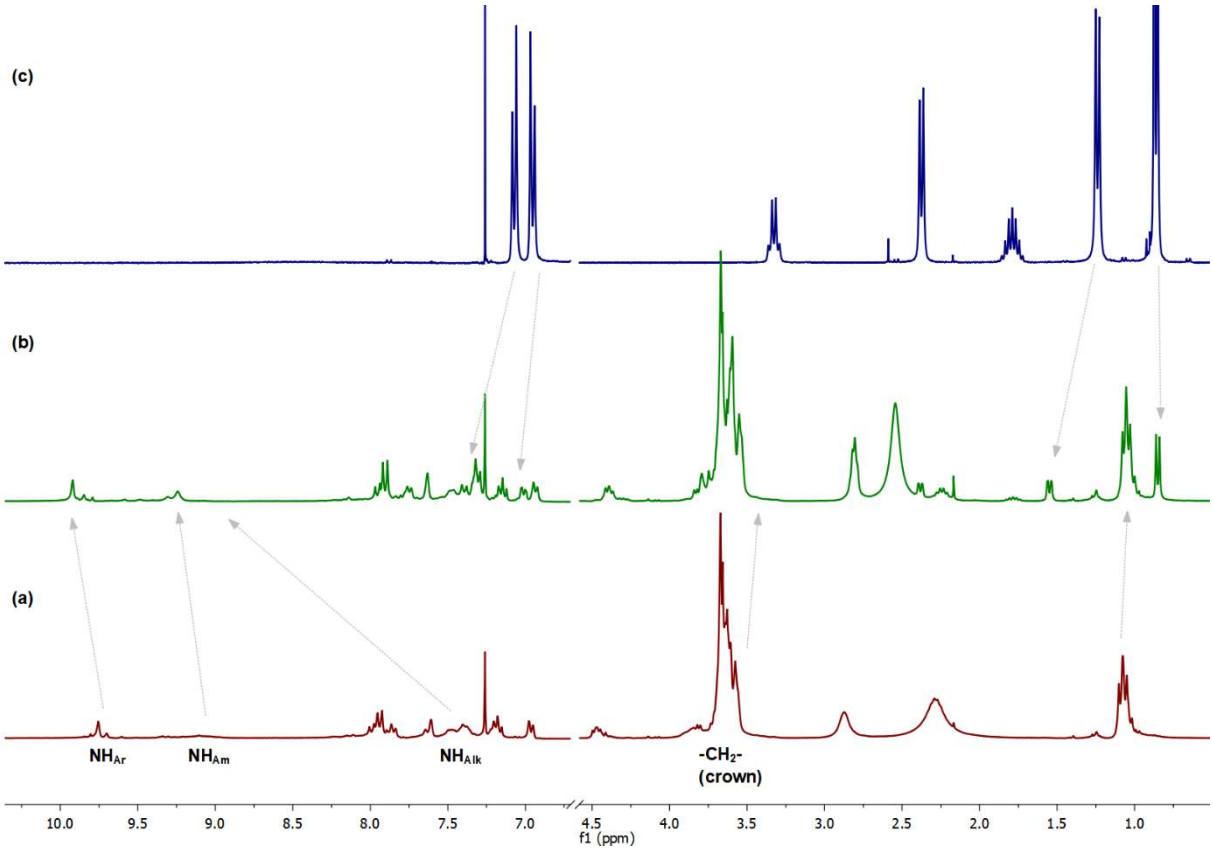
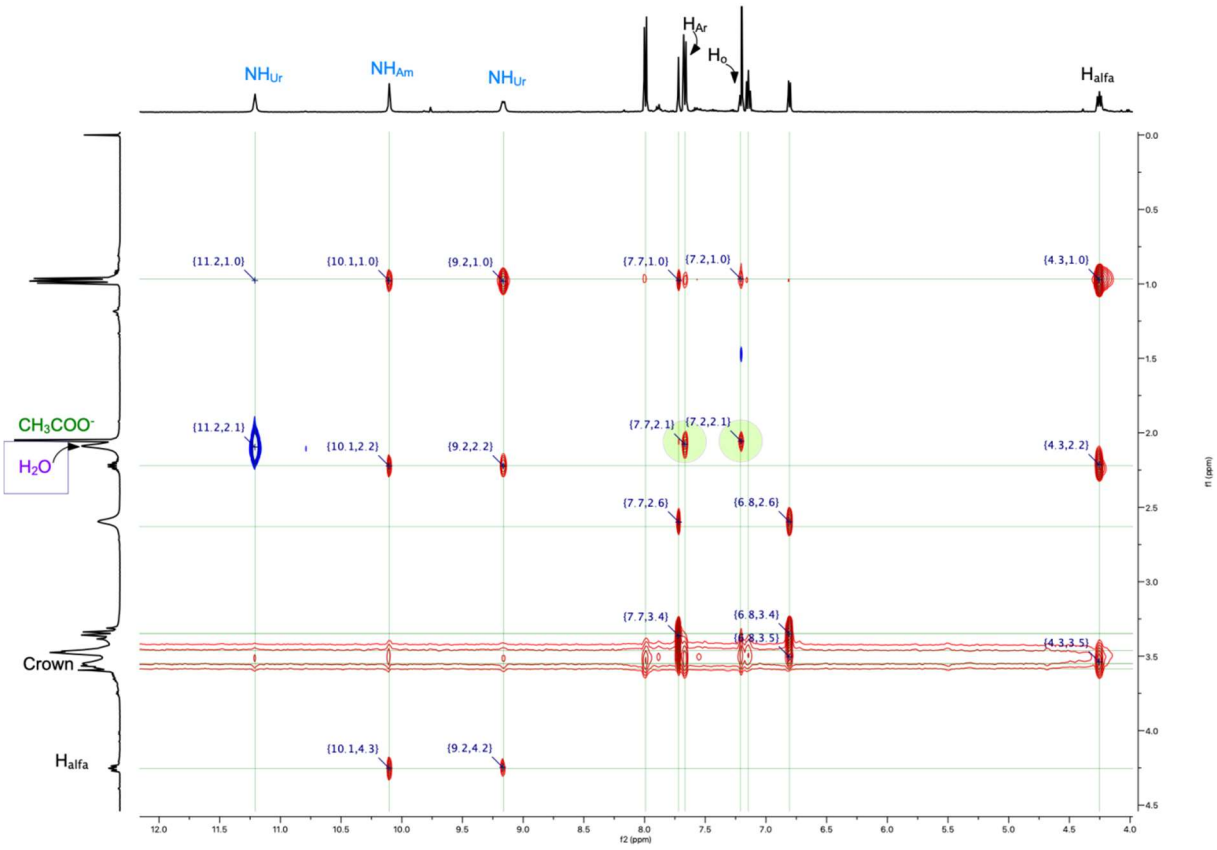


Figure 57. ^{1}H NMR spectrum stack of extraction experiment steps: (a) Receptor **1** solution after being washed with deionized water C_{rec}=2.5x10^{-2}; (b) Receptor **1** solution after extraction with 0.25 eq potassium ibuprofenate aqueous solution(C_{salt}=6.2x10^{-3}M); (c) $CDCl_3$ solution of potassium ibuprofenate extracted from solid to chloroform phase (SLE), after 30 minutes.

7. 2D NMR ROESY experiment

2D NMR ROESY experiment was performed on 500 MHz Varian spectrometer, at 298K in $CDCl_3$ solution. The receptor **1** solution $C_{receptor}$=3x10^{-2}M in chloroform was extracted with 100 eq AcOK aqueous solution C_{AcOK}=3M. Then after phase separation organic phase was retract through hydrophobic filter and placed in NMR tube. Filtration was performed to dispose water drops on the NMR tube's walls.



The results of 2D ROESY experiment have shown cross-peaks between protons H_{Ar} with potassium acetate methyl group and with benzyle linker's proton H_o. The presence of those cross-peaks confirmed close distance between the receptor and the salt in the ternery complex. The most important conclusion is that this tight fit is maintained in 'wet' chloroform solution in concentration similar to LLE experiments.

8. The calculated structure of 1•KCl complex

Theoretical calculations for **1**●AcOK were performed in Gaussian 09 (Revision D.01).[3] The initial (starting point) geometry has been established based on 2D ROESY NMR results and was obtained by preoptimization of **1**●AcOK with universal force field and steepest descent algorithm implemented in Avogadro 1.2.[4] Geometry optimization and frequency calculation were done with aim of the ωB97xD hybrid functional and 6-311G(2df,2p) basis set.[5] Ultrafine integration grid method was also applied. Stationary point was found with positive values of all calculated frequencies. Evaluated energy for obtained final geometry is -7844085.62766536kJ/mol and atomic coordinates are provided below.

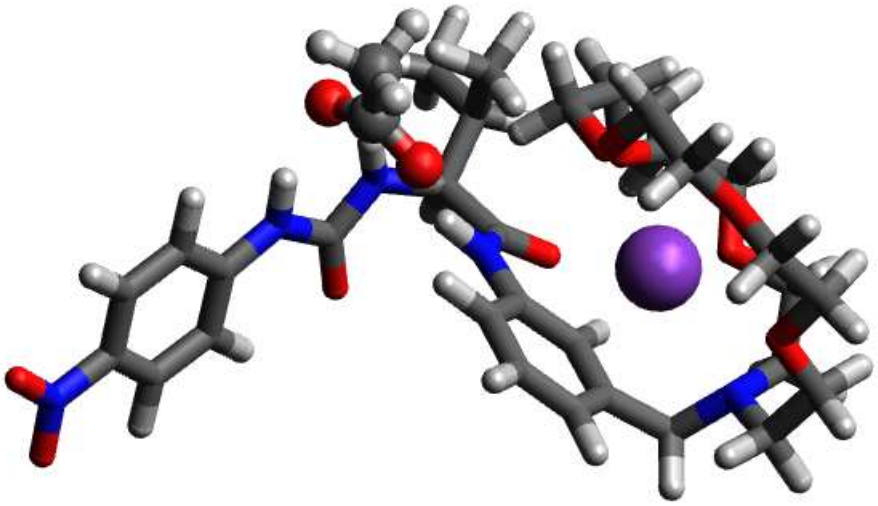


Figure 58. The structure of receptor **1** in complex with AcOK

Atoms	Distance [Å]
(Rec H_{Ar})H59---H95(CH_3COO^-)	4.896
(Rec H_{Ar})H59---H96(CH_3COO^-)	4.174
(Rec H_{Ar})H59---H97(CH_3COO^-)	5.461
(Rec H_{Ar})H56---H95(CH_3COO^-)	7.798
(Rec H_{Ar})H56---H96(CH_3COO^-)	7.620
(Rec H_{Ar})H56---H97(CH_3COO^-)	8.204
(Rec H_o)H83---H95(CH_3COO^-)	3.986
(Rec H_O)H83---H96(CH_3COO^-)	5.126
(Rec H_O)H83---H97(CH_3COO^-)	4.946
(CH_3COO^-)O93 Y-shape---K^+	7.134
(CH_3COO^-)O92 Y-shape---K^+	4.964
N9--O93	2.842; $\sphericalangle_{NHO}$ 160°
N9—O92	3.635; $\sphericalangle_{NHO}$ 120°
N3—O93	2.891; $\sphericalangle_{NHO}$ 155°
N3—O92	3.268; $\sphericalangle_{NHO}$ 120°
N43—O92	2.771; $\sphericalangle_{NHO}$150°
N43—O93	4.192; $\sphericalangle_{NHO}$ 160°
K98--O24	2.774
K98--O23	2.761
K98--O27	2.767
K98--O32	2.870
K98--O33	2.874
$Ar_{ring}\pi$-- K98	2.871

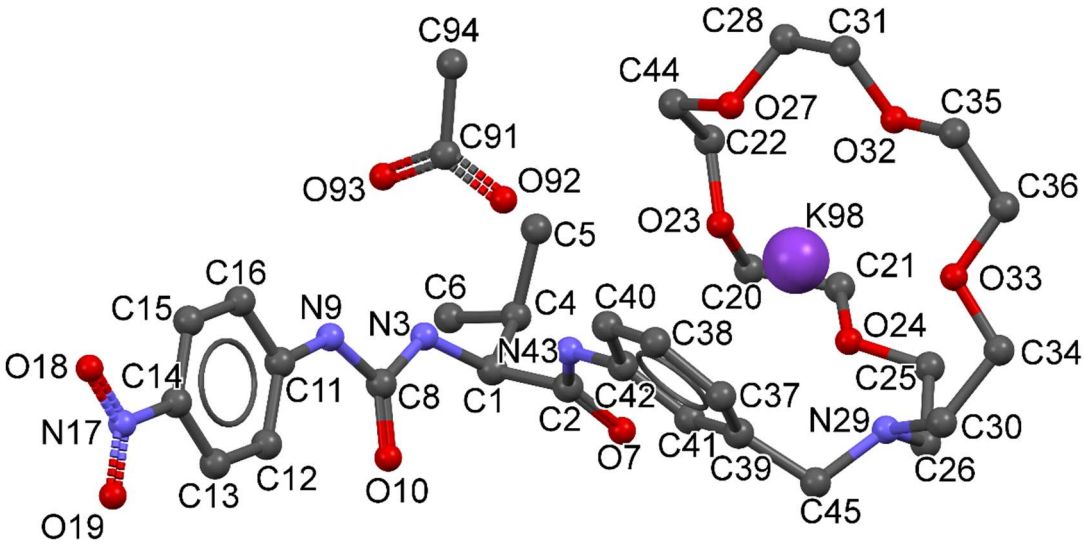


Figure 59. Numbered structure of receptor **1** scaffold in complex with AcOK

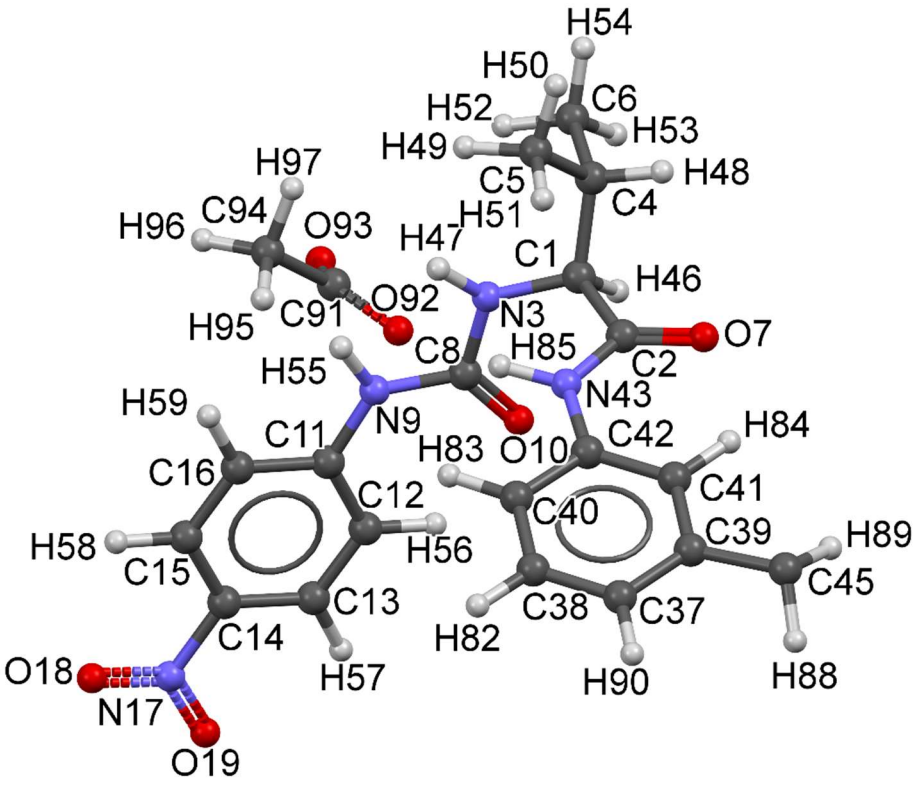


Figure 60. Partial numbered structure of receptor **1** scaffold in complex with AcOK. Anion coordination part.

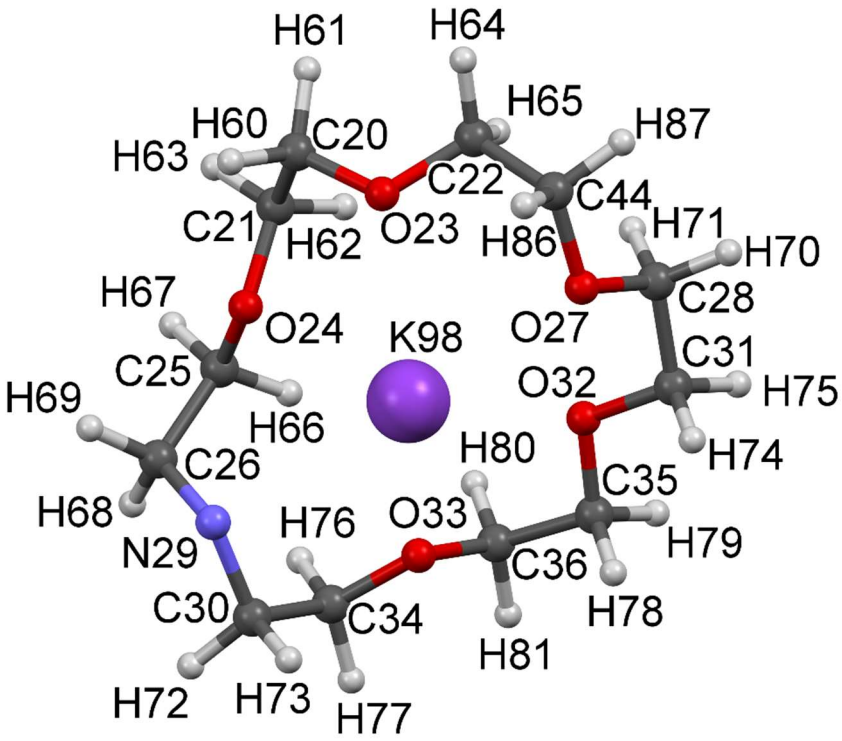


Figure 61. Partial numbered structure of receptor **1** scaffold in complex with AcOK. Cation coordination part.

Number	Label	X	Y	Z
1	C1	-1.8850	2.4576	-1.9775
2	C2	-0.7644	1.4063	-2.0254
3	N3	-2.9432	2.1658	-1.0547
4	C4	-1.2870	3.8517	-1.7265
5	C5	-0.7551	3.9929	-0.3000
6	C6	-2.2956	4.9472	-2.0526
7	O7	0.0193	1.4131	-2.9600
8	C8	-3.8173	1.1465	-1.3143
9	N9	-4.5688	0.8364	-0.1952
10	O10	-3.9033	0.5972	-2.3948
11	C11	-5.5136	-0.1543	-0.0523
12	C12	-5.9657	-0.9635	-1.1026
13	C13	-6.9158	-1.9337	-0.8607
14	C14	-7.4222	-2.1060	0.4164
15	C15	-6.9915	-1.3130	1.4690
16	C16	-6.0442	-0.3452	1.2334
17	N17	-8.4215	-3.1371	0.6610
18	O18	-8.8443	-3.2643	1.7950
19	O19	-8.7815	-3.8193	-0.2794
20	C20	2.5242	2.5462	-0.9766
21	C21	3.9209	2.1207	-1.3671
22	C22	2.1605	2.6512	1.3844
23	O23	2.0976	1.8875	0.2008
24	O24	3.8602	0.7607	-1.7306
25	C25	5.0714	0.2019	-2.1716
26	C26	4.7560	-1.0803	-2.9261
27	O27	2.4369	0.7047	2.8163
28	C28	3.4874	1.0114	3.6945
29	N29	4.0679	-2.0810	-2.1252
30	C30	4.9084	-3.1690	-1.6656
31	C31	4.3525	-0.2069	3.8627

32	O32	4.9844	-0.4950	2.6339	66	H66	5.7333	0.0136	-1.3150
33	O33	5.4940	-2.2189	0.4498	67	H67	5.5895	0.8932	-2.8478
34	C34	6.0293	-2.7507	-0.7412	68	H68	5.6916	-1.4768	-3.3433
35	C35	5.8543	-1.5963	2.7152	69	H69	4.1289	-0.8026	-3.7733
36	C36	6.4860	-1.8373	1.3713	70	H70	3.0932	1.3088	4.6740
37	C37	1.3792	-3.0654	-0.6134	71	H71	4.1010	1.8361	3.3127
38	C38	0.4594	-2.6583	0.3476	72	H72	5.3636	-3.7197	-2.5067
39	C39	1.6502	-2.2338	-1.6935	73	H73	4.2826	-3.8760	-1.1201
40	C40	-0.2006	-1.4498	0.2276	74	H74	3.7388	-1.0580	4.1811
41	C41	0.9692	-1.0306	-1.8368	75	H75	5.1029	-0.0149	4.6389
42	C42	0.0258	-0.6319	-0.8881	76	H76	6.6907	-2.0176	-1.2195
43	N43	-0.7311	0.5276	-0.9907	77	H77	6.6392	-3.6332	-0.5124
44	C44	1.5978	1.8102	2.5064	78	H78	5.3064	-2.4937	3.0283
45	C45	2.7726	-2.5488	-2.6498	79	H79	6.6447	-1.4063	3.4520
46	H46	-2.2954	2.4317	-2.9876	80	H80	6.9988	-0.9303	1.0269
47	H47	-2.8647	2.4485	-0.0805	81	H81	7.2357	-2.6306	1.4777
48	H48	-0.4471	3.9318	-2.4203	82	H82	0.2451	-3.2950	1.1962
49	H49	-1.5671	4.0613	0.4269	83	H83	-0.9063	-1.1204	0.9784
50	H50	-0.1554	4.9003	-0.2064	84	H84	1.1720	-0.3834	-2.6747
51	H51	-0.1418	3.1358	-0.0216	85	H85	-1.2796	0.7559	-0.1523
52	H52	-3.1767	4.8620	-1.4157	86	H86	0.6271	1.4062	2.2073
53	H53	-2.6232	4.8846	-3.0909	87	H87	1.4522	2.4305	3.3971
54	H54	-1.8581	5.9341	-1.8933	88	H88	2.8150	-3.6246	-2.8435
55	H55	-4.2855	1.3330	0.6511	89	H89	2.5725	-2.0677	-3.6066
56	H56	-5.5586	-0.8195	-2.0892	90	H90	1.8820	-4.0200	-0.5171
57	H57	-7.2732	-2.5662	-1.6591	91	C91	-2.2353	1.7971	2.2790
58	H58	-7.4037	-1.4668	2.4545	92	O92	-1.4364	1.0752	1.6328
59	H59	-5.6956	0.2828	2.0432	93	O93	-3.2532	2.3566	1.8136
60	H60	1.8336	2.2644	-1.7727	94	C94	-1.9101	2.0521	3.7466
61	H61	2.4841	3.6317	-0.8481	95	H95	-1.3886	1.2018	4.1826
62	H62	4.6239	2.2664	-0.5341	96	H96	-2.8133	2.2777	4.3084
63	H63	4.2675	2.7259	-2.2134	97	H97	-1.2527	2.9227	3.8070
64	H64	1.5550	3.5580	1.2848	98	K98	3.0683	-0.6794	0.5046
65	H65	3.1943	2.9608	1.5906					

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