Supporting Information

Non-multimacrocyclic heteroditopic receptor that cooperatively binds and effectively extracts KAcO salt

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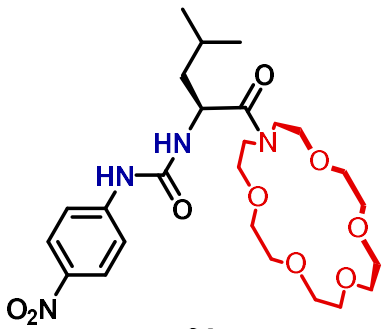
1. Previous results

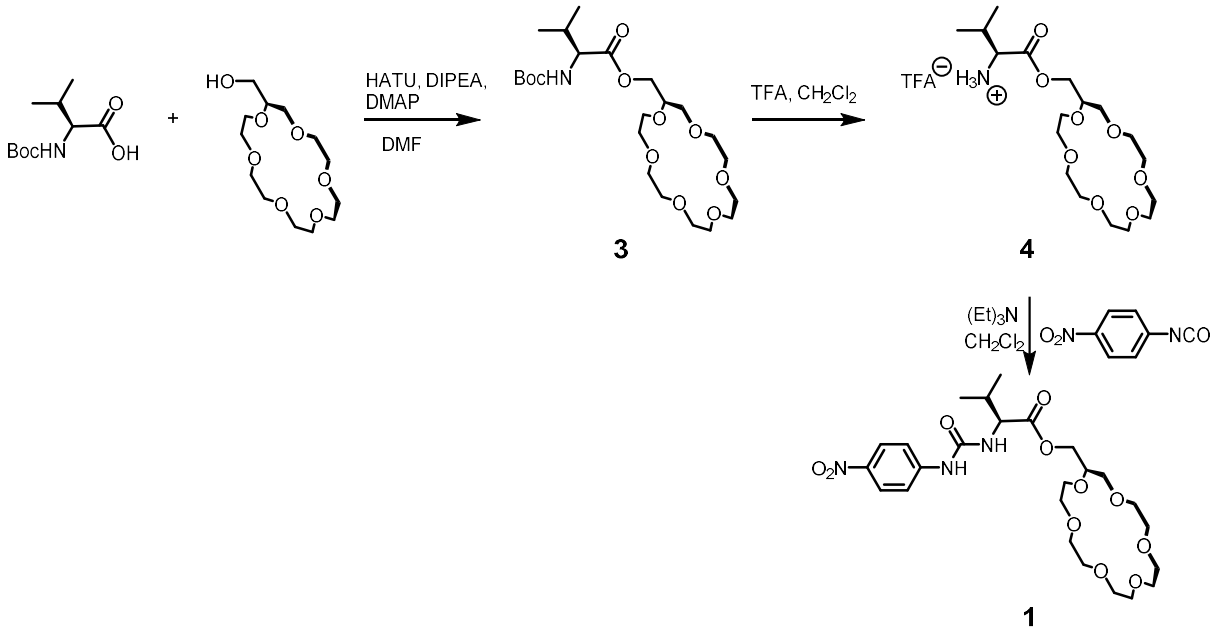


S4

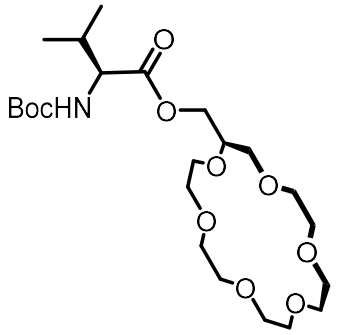
	TBA$^+$	$NaClO_4$
Cl^-	1 700	5 100
K_M/K_{TBACl}	-	3.0

Table 1. The association constants (K_a) values (298 K, CH_3CN solution) for interactions of **S4** with chloride anion in the absence and presence of one molar equivalent of sodium cation

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



2-Hydroxymethyl-18-crown-6 ester of Boc-L-valine



The solution of Boc-L-valine 0.15 g (0.69 mmol), 0.3 g (0.79 mmol) HATU, 0.19 g (0.25 mL, 1.4 mmol) DIPEA and catalytic amount of DMAP, dissolve in 2 mL of dry DMF, was stirred under argon atmosphere in room temerature for one hour. Then the solution of 0.2 g (0.68 mmol) 2-hydroxymethyl-18-crown-6 in 2 mL of dry DMF was added. The reaction mixture was stirred at room temerature for 24h. After this time the solvent was evaporated under reduce pressure, the oil resiude was dissolve in $CHCl_3$ and washed with amonium chloride and water. The organic phase was dryed over $MgSO_4$, filtered and the solvent was eveporated. The oil was purified by column chromatography on silica gel with 50% hexane/ethyl acetate then ethyl acetate as eluents to give 0.18 g (0.37 mmol) of product **3** as oil in 54% of yield. R_f (10% MeOH/DCM) = 0.3 ^{1}H NMR (300 MHz, $CDCl_3$,δ_{ppm}): 5.01 (d, J=9 Hz, 1H), 4.14 (m, 3H), 3.69 (m, 3H), 3.62 (m, 22H), 2.02 (m, 1H), 1.33 (s, 9H), 0.85 (d, J=6Hz, 3H), 0.78 (d, J=6Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$,δ_{ppm}): 172.07, 155.49, 79.47, 76.78, 70.86, 70.82, 70.77, 70.72, 70.62, 70.56, 70.51, 69.78, 69.67, 64.63, 64.12, 58.42, 31.18, 28.18, 18.87, 17.43.

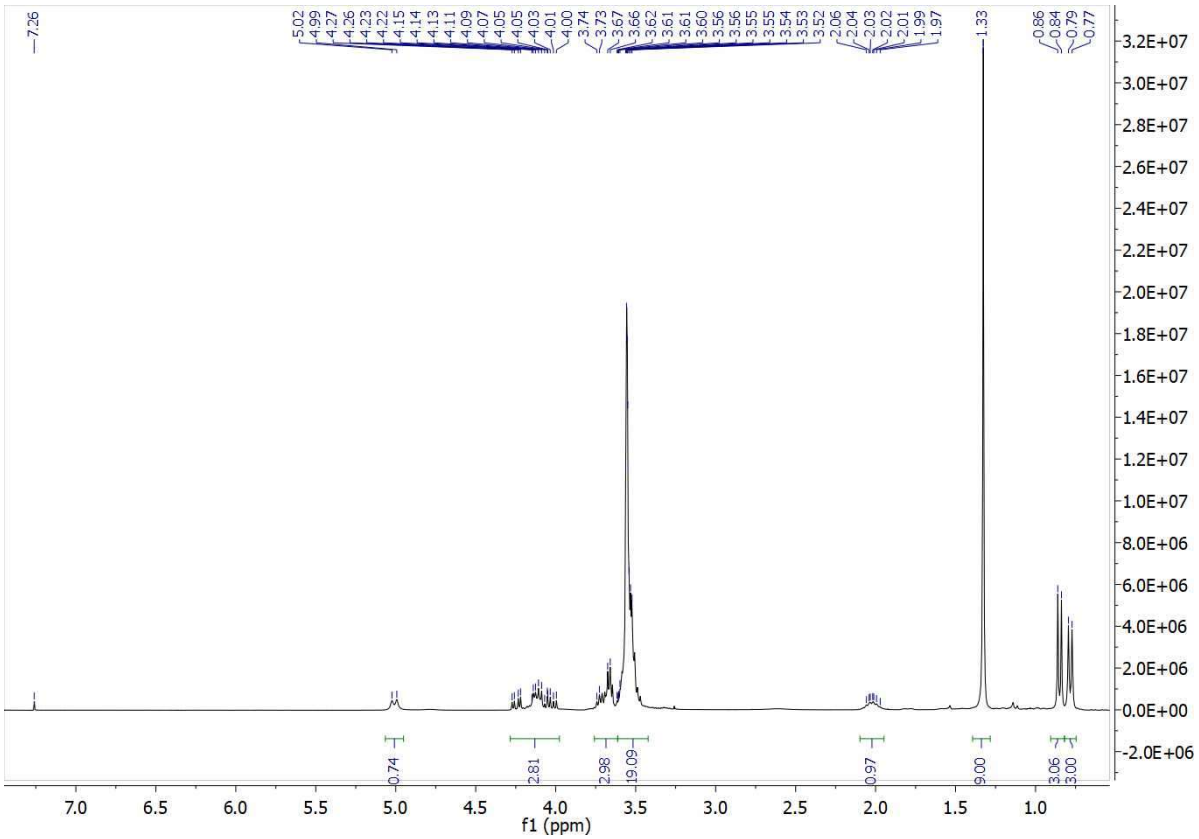


Figure 1. ^{1}H NMR of compound **3**

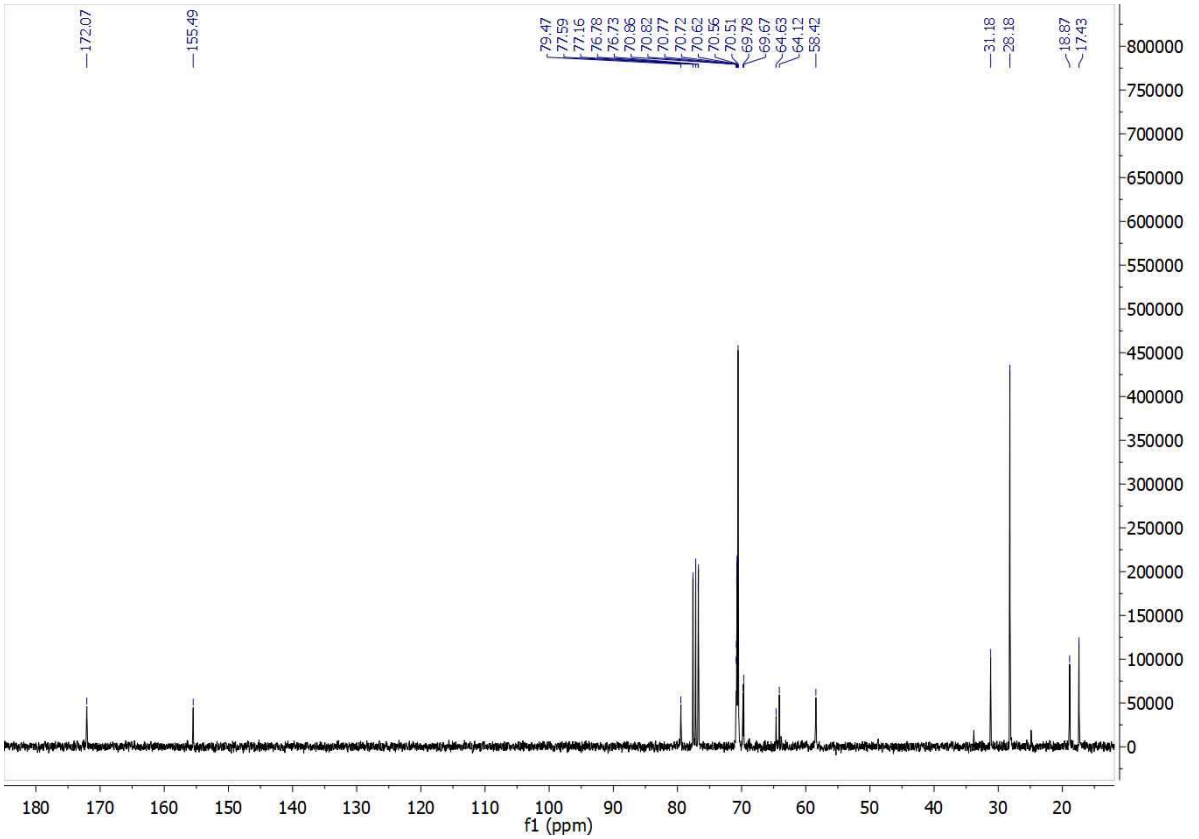
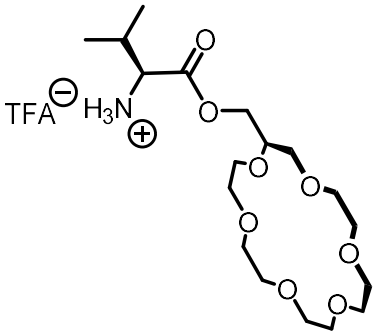


Figure 2. ^{13}C NMR of compound **3**

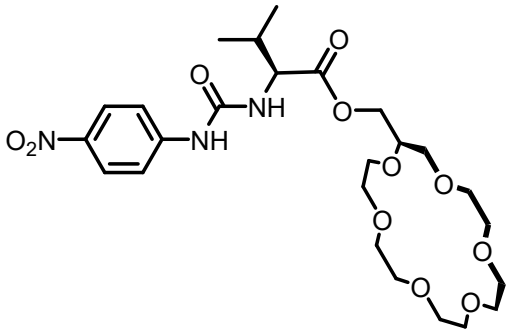
Trifluoroacetic acid salt of 2-Hydroxymethyl-18-crown-6 ester of L-valine



4

The solution of **3** 0.18 g (0.37mmol) in 2 mL 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

To the solution of **4** 0.19 g (0.37 mmol) in 5 mL of DCM, 0.6 mL (0.83 g, 4 mmol, 10 eq) of triethylamine was added. Then solution of 0.067 g (0.41 mmol, 1.1 eq) 4-nitrophenyl isothiocyanate in 2 mL of DCM was added. The reaction was stirred overnight in room temperature. Then the solvent was evaporated and the resulting oil was dissolved in chloroform and washed twice with water. The organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated. Receptors were purified by column chromatography on silica gel with chloroform then 5% MeOH/$CHCl_3$. To remove any inorganic salts absorbed during the work-up, receptor **1** was dissolved in chloroform and washed with distilled water. Evaporation of the solvent (without drying) gave 0.14 g (0.25 mmol) of desired receptor as a yellow oil in 68% of yield. R_f (10% MeOH/DCM) = 0.2. ^{1}H NMR (300 MHz, $CDCl_3$,δ_{ppm}): 8.51 (d, J=24 Hz, 1H), 8.10 (d, J=6 Hz, 2H), 7.63 (dd, J_1=3 Hz, J_2=6 Hz, 2H), 6.28 (dd, J_1=9 Hz, J_2=15 Hz, 1H), 4.46 (m, 1H), 4.21 (m, 2H), 3.69 (m, 22H), 3.31 (m, 1H), 2.16 (m, 1H), 0.97 (dd, J_1=3 Hz, J_2=6 Hz, 3H), 0.90 (d, J=6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$,δ_{ppm}): 172.47, 154.87, 146.19, 141.86, 125.28, 117.83, 70.92, 70.76, 70.54, 69.87, 64.35, 58.20, 31.20, 19.17, 17.80. HR-MS (ESI): m/z = 580.2464 $[M+Na]^+$ (calc. for $C_{25}H_{39}N_3O_{11}Na$: 580.2482).

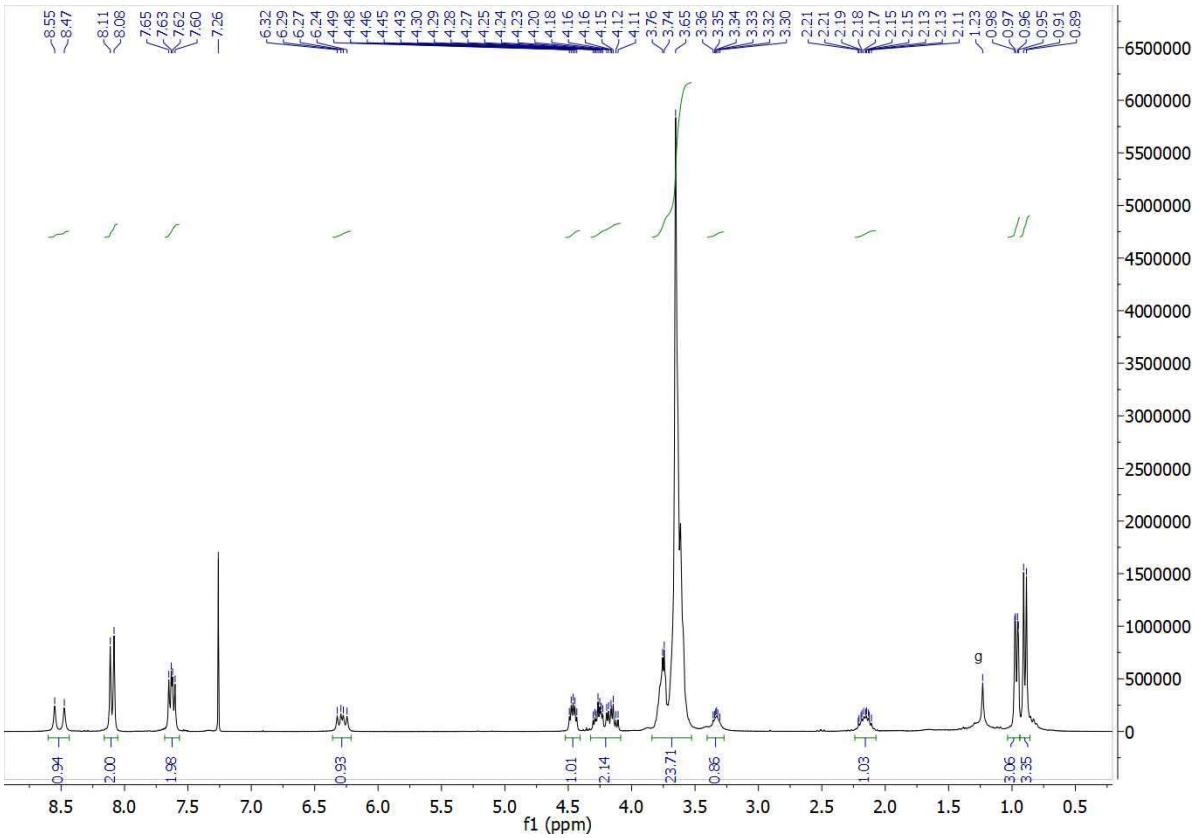


Figure 3. ^{1}H NMR of compound **1**

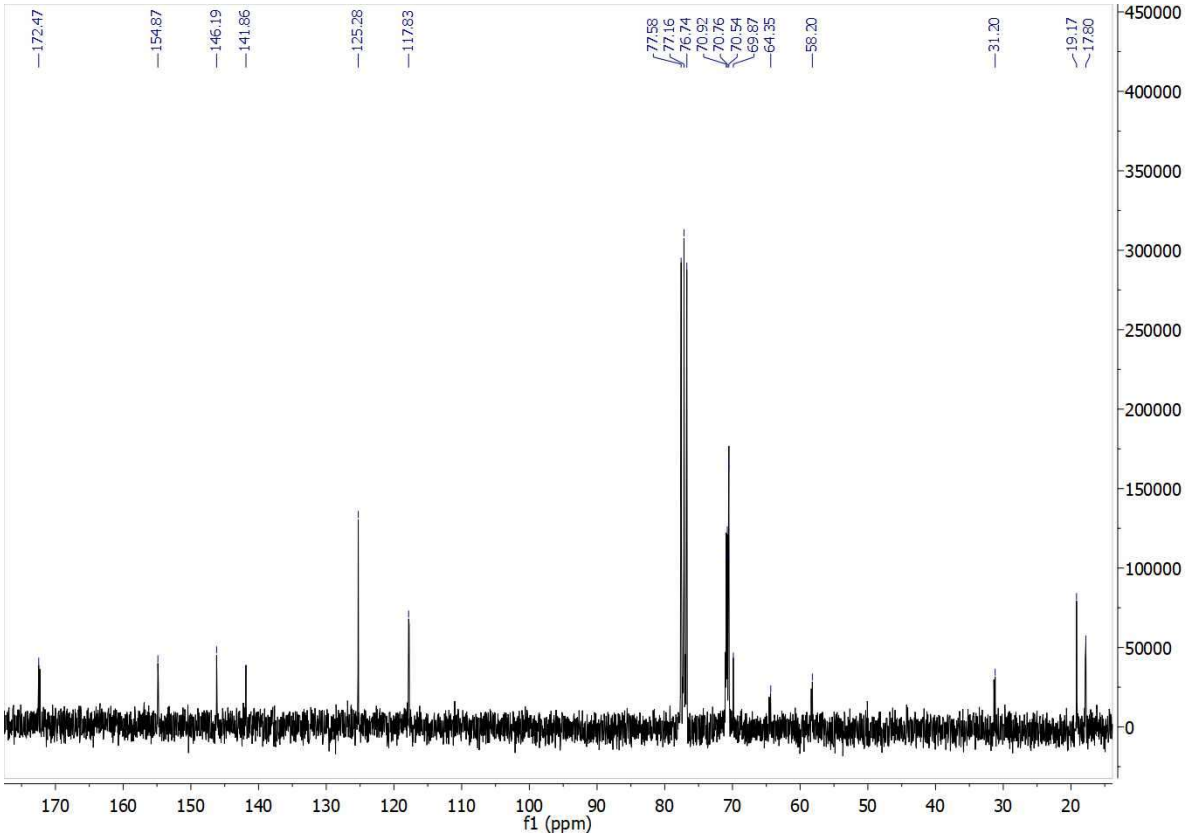
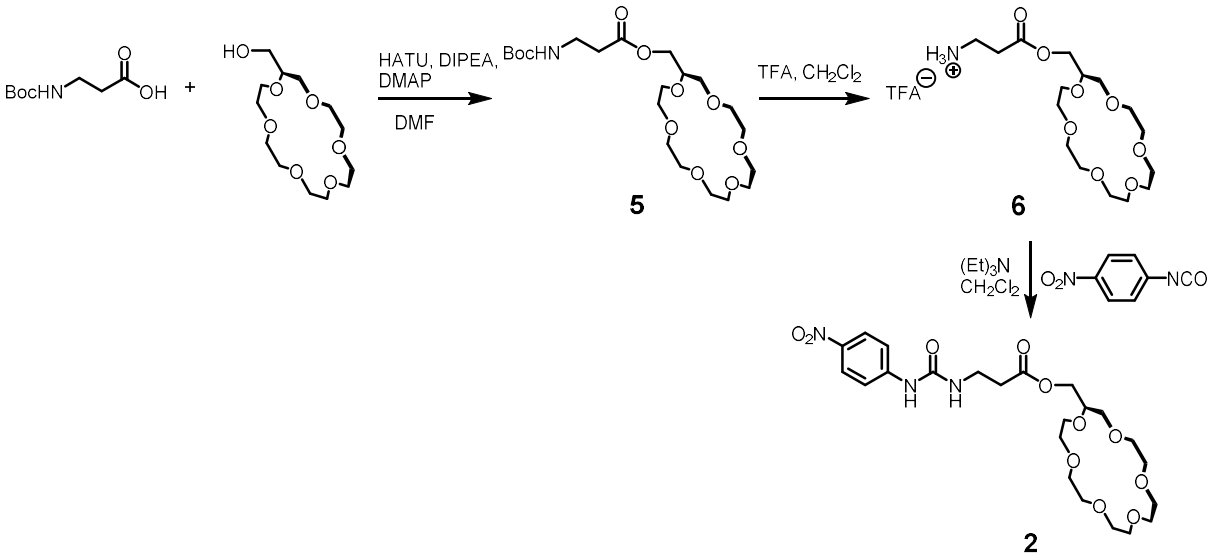
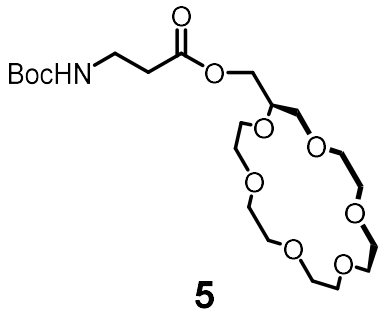


Figure 4. ^{13}C NMR of compound **1**



2-Hydroxymethyl-18-crown-6 ester of Boc-β-alanine



The solution of Boc-β-alanine 0.27g (1.45 mmol), 0.46g (1.2 mmol) HATU, 0.40g (0.55 mL, 3.1 mmol) DIPEA and catalytic amount of DMAP, dissolve in 4 mL of dry DMF, was stirred under argon atmosphere in room temerature for one hour. Then the solution of 0.36g (1.2 mmol) 2-hydroxymethyl-18-crown-6 in 2 mL of dry DMF was added. The reaction mixture was stirred at room temerature for 24h. After this time the solvent was evaporated under reduce pressure, the oil resiude was dissolve in $CHCl_3$ and washed with amonium chloride and water. The organic phase was dryed over $MgSO_4$, filtered and the solvent was eveporated. The oil was purified by column chromatography on silica gel with chloroform then 5% MeOH/$CHCl_3$ as eluents to give 0.42 g (0.91 mmol) of product **5** as oil in 63% of yield. R_f (10% MeOH/DCM) = 0.33. ^{1}H NMR (300 MHz, $CDCl_3$,δ_{ppm}): 5.19 (t, J=6 Hz, 1H), 4.13 (dd, J_1=6 Hz, J_2=12 Hz, 1H), 3.97 (dd, J_1=6 Hz, J_2=12 Hz, 1H), 3.67 (m, 1H), 3.62 (m, 2H), 3.49 (m, 20H), 3.20 (m, 2H), 2.39 (t, J=6 Hz, 2H), 1.26 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$,δ_{ppm}): 171.85, 155.59, 78,89, 76.61, 70.75, 70.63, 70.56, 70.44, 70.38, 70.35, 69.47, 63.75, 35.95, 34.49, 28.17.

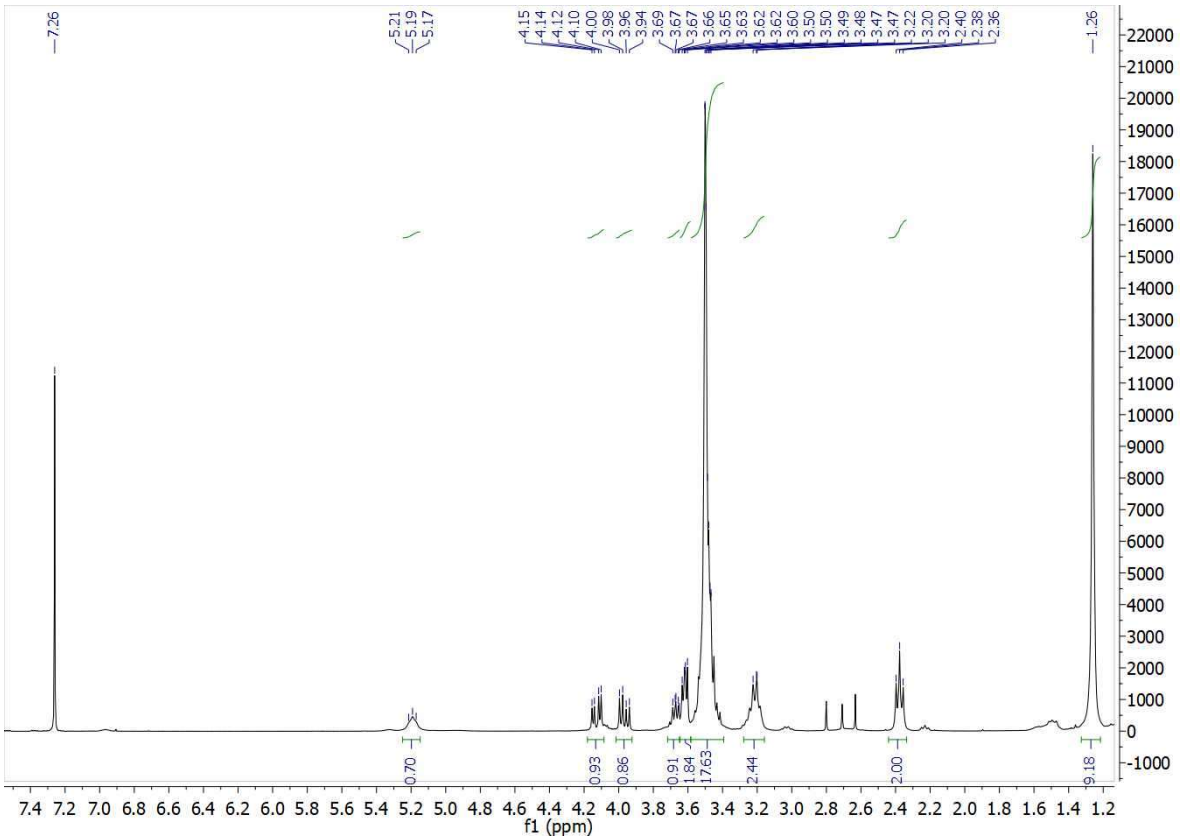


Figure 5. ^{1}H NMR of compound **5**

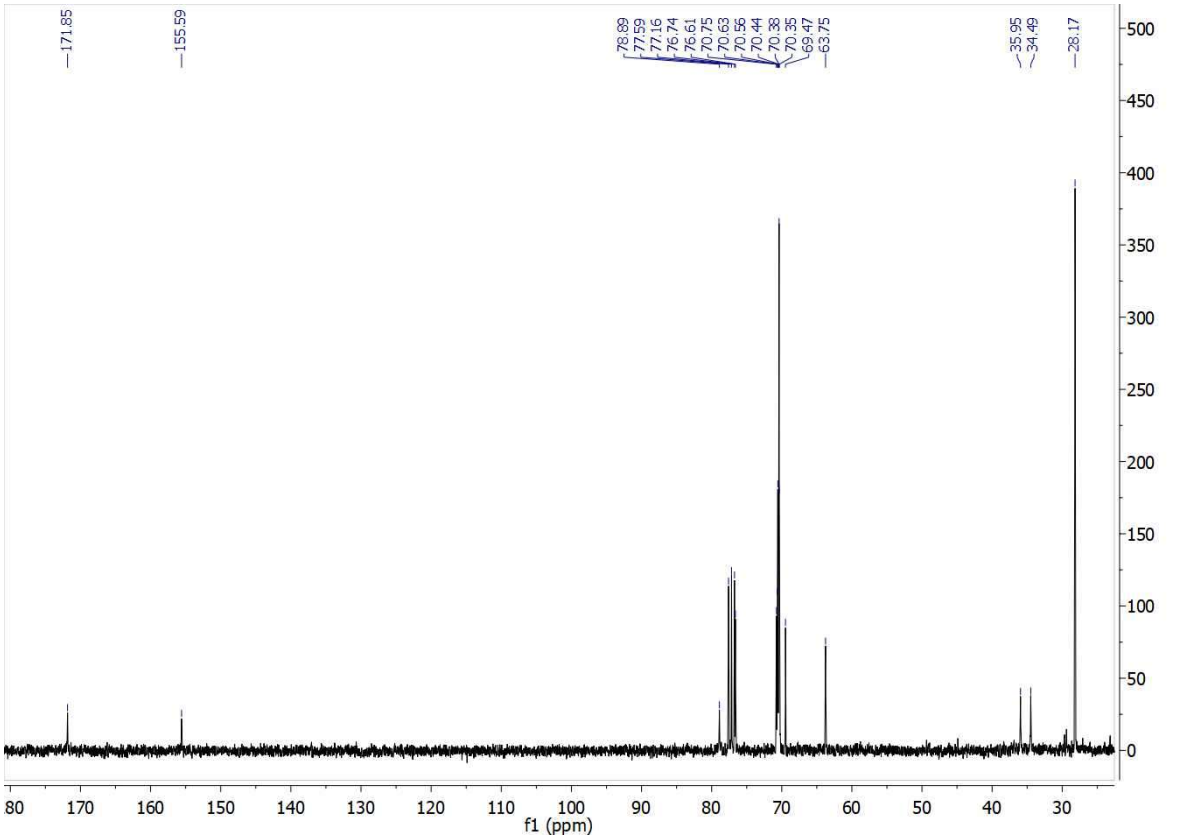
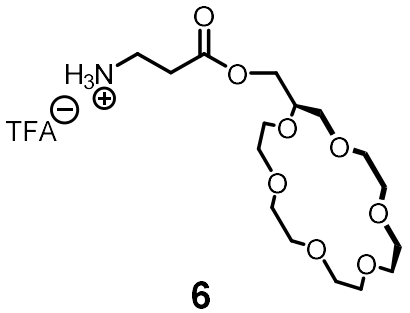


Figure 6. ^{13}C NMR of compound **5**

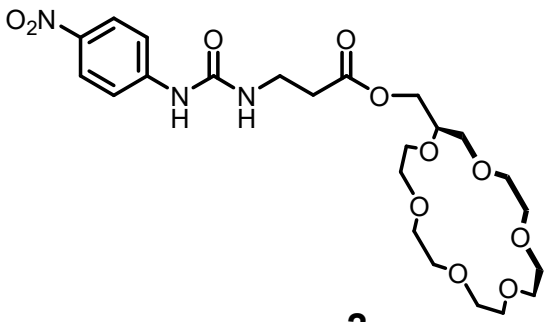
Trifluoroacetic acid salt of 2-Hydroxymethyl-18-crown-6 ester of β-alanine



6

The solution of **5** 0.27g (0.58 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 2



2

To the solution of **6** 0.27 g (0.58 mmol) in 5 mL of DCM, 1.0 mL (0.73 g, 7 mmol, 12 eq) of triethylamine was added. Then solution of 0.11 g (0.67 mmol, 1.2 eq) 4-nitrophenyl isothiocyanate in 2 mL of DCM was added. The reaction was stirred overnight in room temperature. Then the solvent was evaporated and the resulting oil was dissolved in chloroform and washed twice with water. The organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated. Receptors were purified by column chromatography on silica gel with chloroform then 5% MeOH/$CHCl_3$. To remove any inorganic salts absorbed during the work-up, receptor **2** was dissolved in chloroform and washed with distilled water. Evaporation of the solvent (without drying) gave 0.20 g (0.37 mmol) of desired receptor as a yellow oil in 64% of yield. R_f (10% MeOH/DCM) = 0.3.^{1}H NMR (300 MHz, $CDCl_3$,δ_{ppm}): 8.90 (s, 1H), 8.11 (d, J=9 Hz, 2H), 7.71 (d, J=9 Hz, 2H), 6.15 (t, J=6 Hz, 1H), 4.69 (m, 1H), 3.89 (m, 2H), 3.60 (m, 22H), 2.57 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$,δ_{ppm}): 172.20, 155.06, 146.73, 141.57, 125.18, 117.65, 77.03, 71.72, 70.87, 70.81, 70.74, 70.62, 70.33, 70.30, 70.03, 69.18, 62.42, 36.66, 35.59. HR-MS (ESI): m/z = 552.2144 $[M+Na]^+$ (calc. for $C_{23}H_{35}N_3O_{11}Na$: 552.2169).

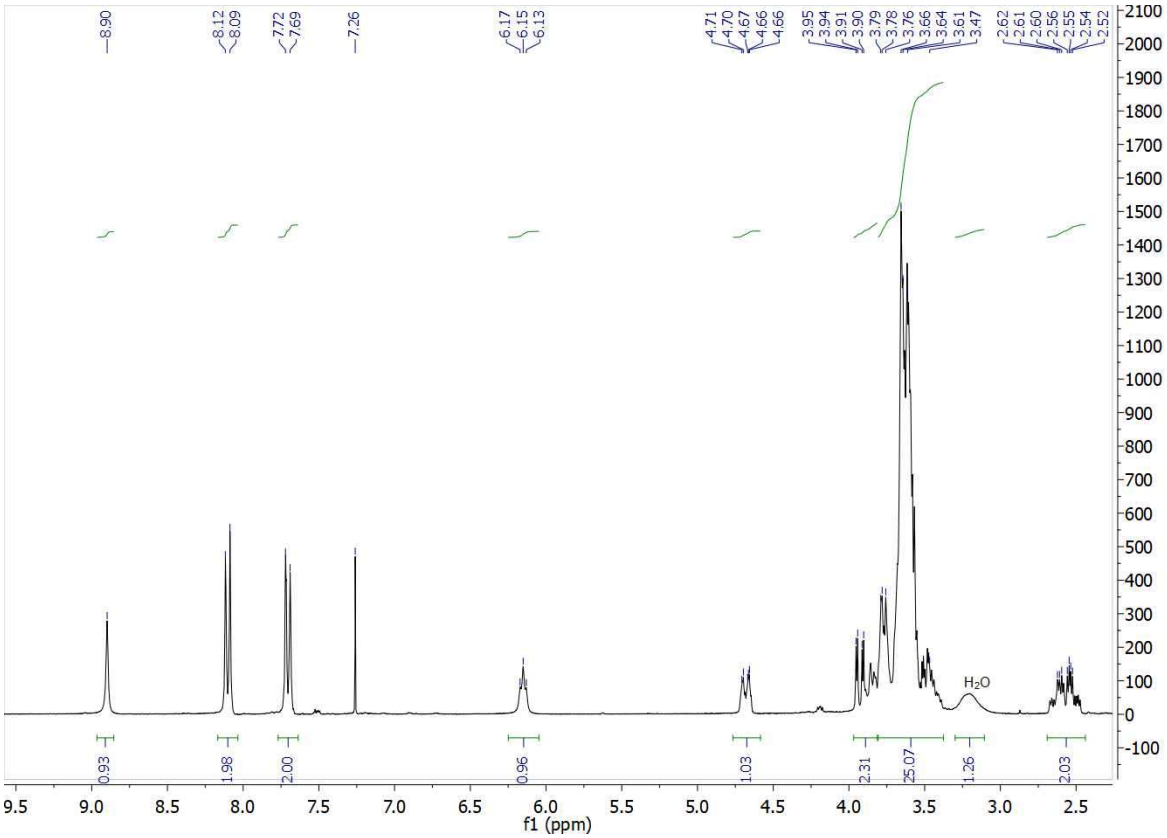


Figure 7. ^{1}H NMR of compound **2**

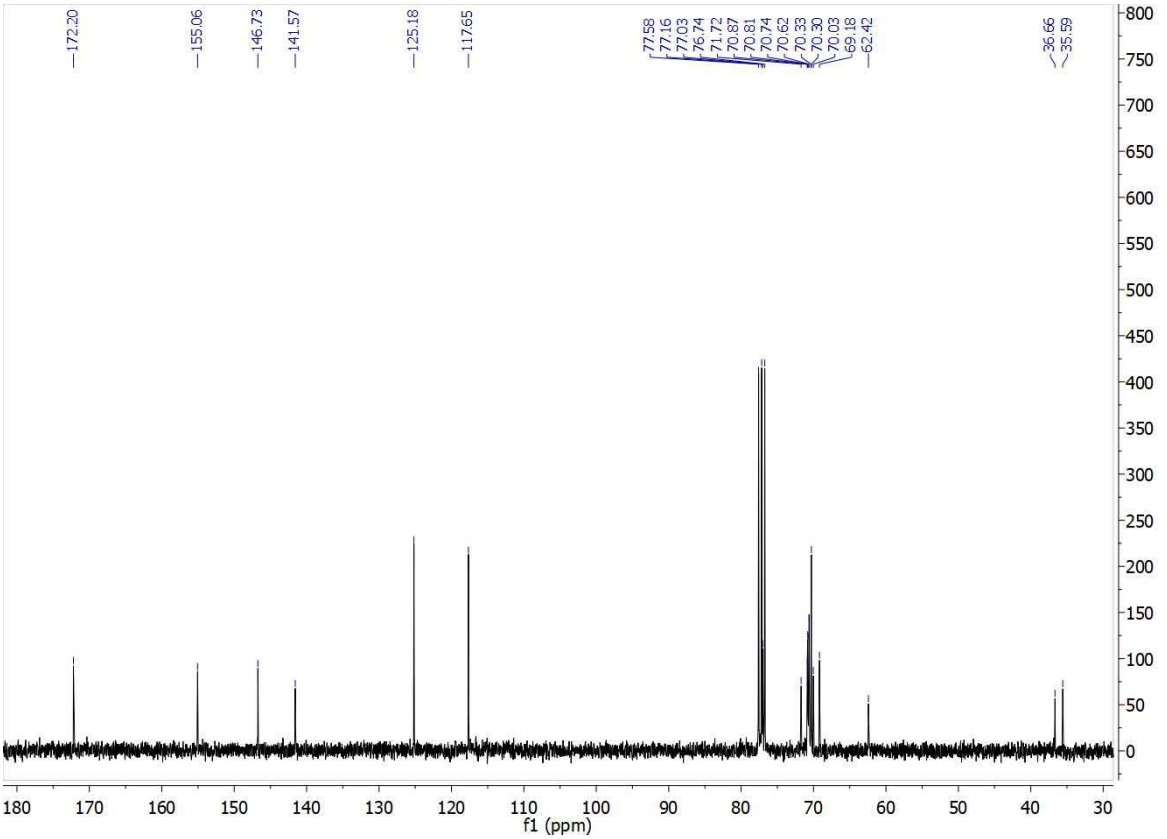


Figure 8. ^{13}C NMR of compound **2**

3. The calculated structure of 1•KCl complex

Geometrical optimizations analyses were carried out with the Gaussian09 [1] suite of programs at the ωB97X-D functional at 6-311G(2df,2p) basis set[2].

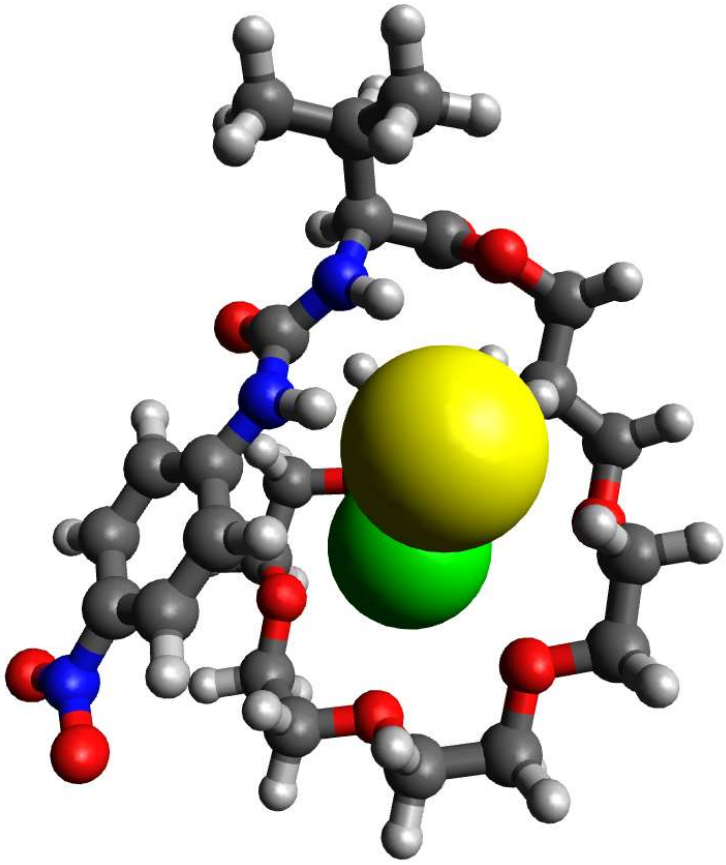


Figure 9. The structure of the receptor **1** in complex with KCl salt

Atom-ion	Distance [Å]
$K^+ \cdots$ O(crown)	2.91
$K^+ \cdots$ O(crown)	2.82
$K^+ \cdots$ O(crown)	2.82
$K^+ \cdots$ O(crown)	2.74
$K^+ \cdots$ O(crown)	3.25
$K^+ \cdots$ O(crown)	2.75
$Cl^- \cdots$ HN(Urea)	2.13
$Cl^- \cdots$ HN(Urea)	2.74
$K^+ \cdots Cl^-$	3.12

Table 2. Distances between ions and atoms

4. UV-Vis titration experiments

UV-Vis titration experiments were performed on a Thermo SpectronicUnicam UV500 spectrophotometer in CH_3CN solution at 298K. To 10 mm cuvette was added 2.5 mL of 5.0 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 ~5.0 x 10^{-3} 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).

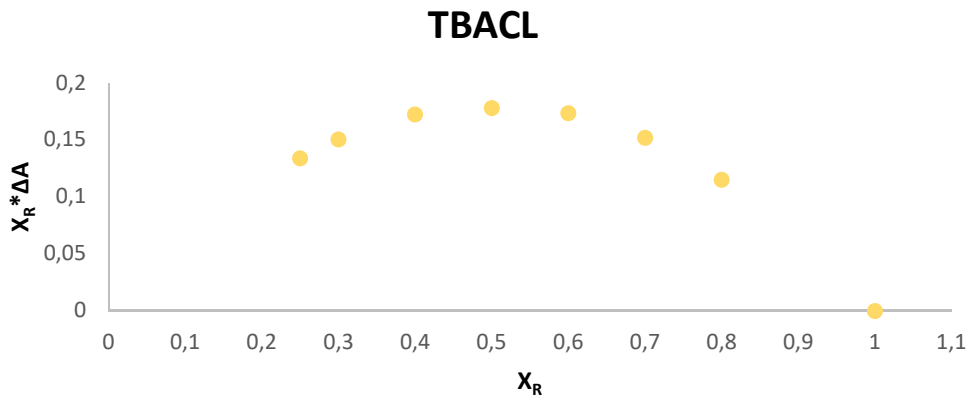


Figure 10. Job plot analysis of the receptor **1** in the presence of TBACl

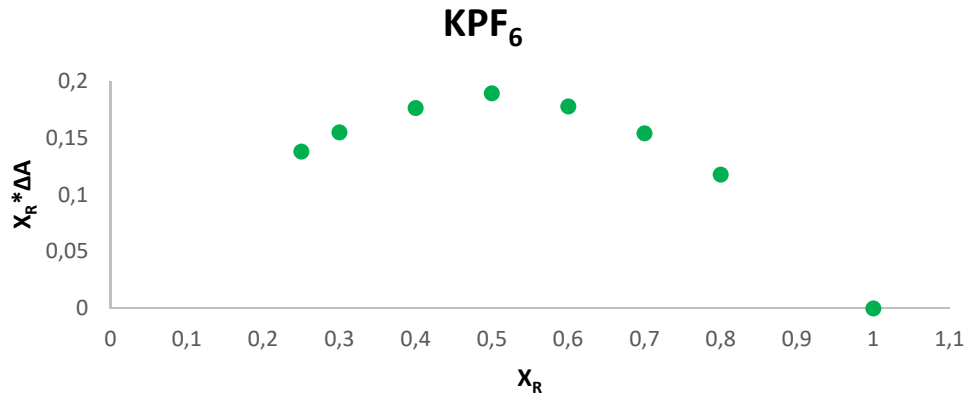


Figure 11. Job plot analysis of the receptor **1** in the presence of KPF_6

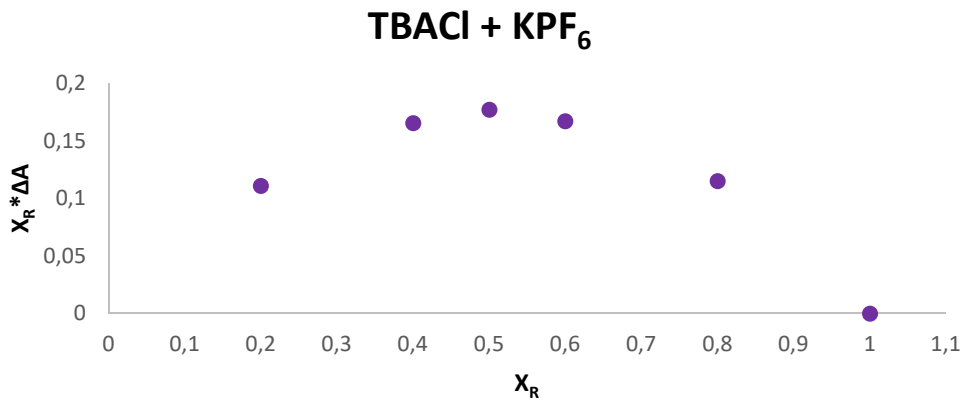


Figure 12. Job plot analysis of the receptor **1** in the presence of TBACl and KPF_6

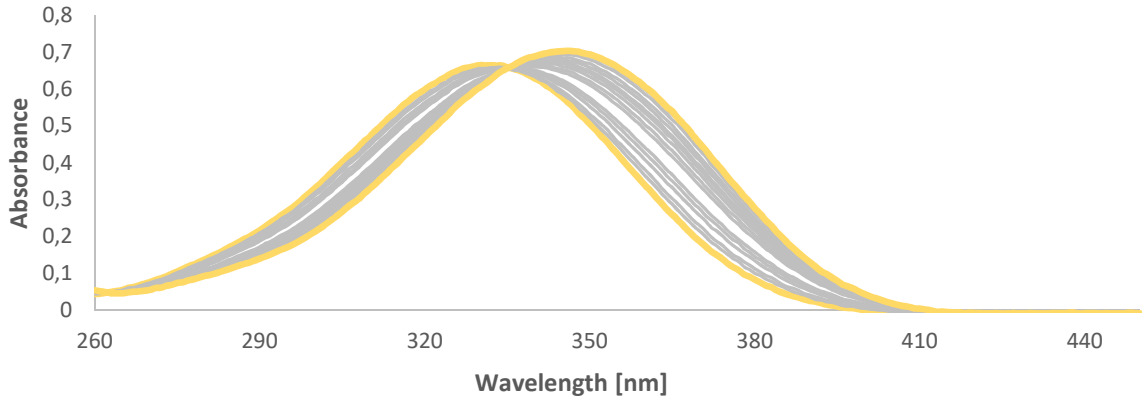


Figure 13. UV-Vis **1** spectrum changes upon titrant (TBACl) addition (293 K, CH_3CN solution, $C_{titrant}$=5.9x10^{-3} M, $C_{receptor}$=5.4 x10^{-5} M)

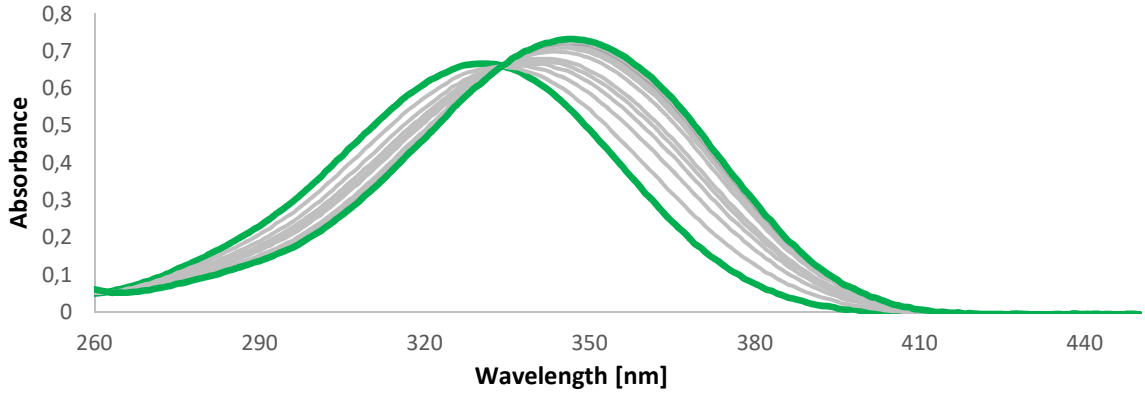


Figure 14. UV-Vis **1** spectrum changes upon titrant (TBACl) addition in presence of 1 eq. KPF_6 (293 K, CH_3CN solution, $C_{titrant}$=5.9 x10^{-3} M, $C_{receptor}$=5.4 x10^{-5} M)

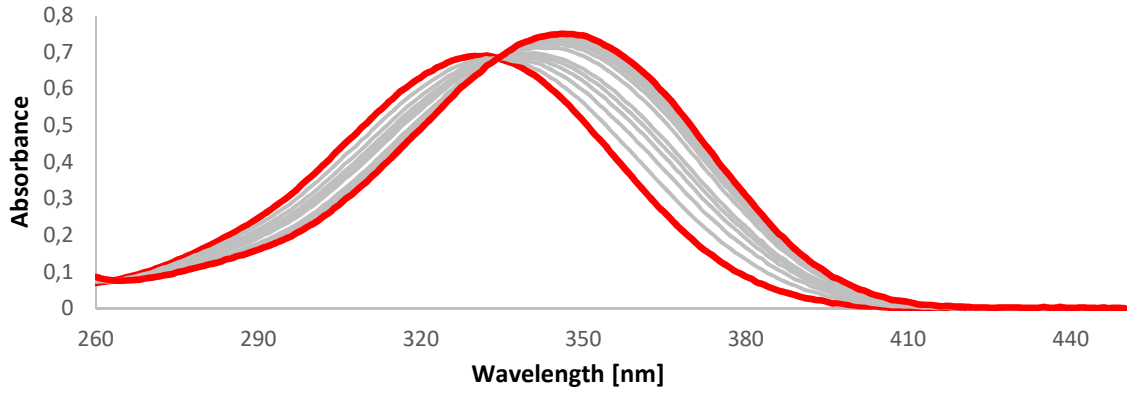


Figure 15. UV-Vis **1** spectrum changes upon titrant (TBACl) addition in presence of 1 eq. $NaClO_4$ (293 K, CH_3CN solution, $C_{titrant}$=5.9 x10^{-3} M, $C_{receptor}$=5.4 x10^{-5} M)

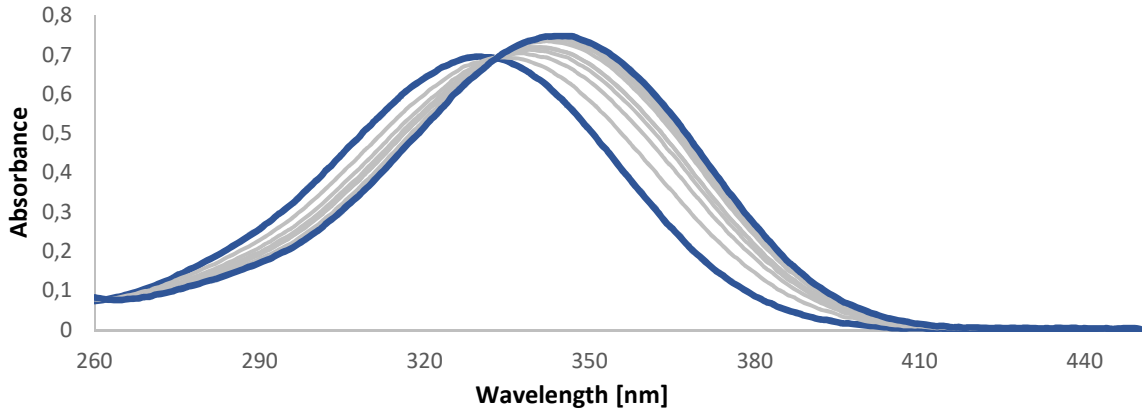


Figure 16. UV-Vis **1** spectrum changes upon titrant (TBACl) addition in presence of 1 eq. NH_4PF_6 (293 K, CH_3CN solution, $C_{titrant}$=5.9 x10^{-3} M, $C_{receptor}$=5.4 x10^{-5} M)

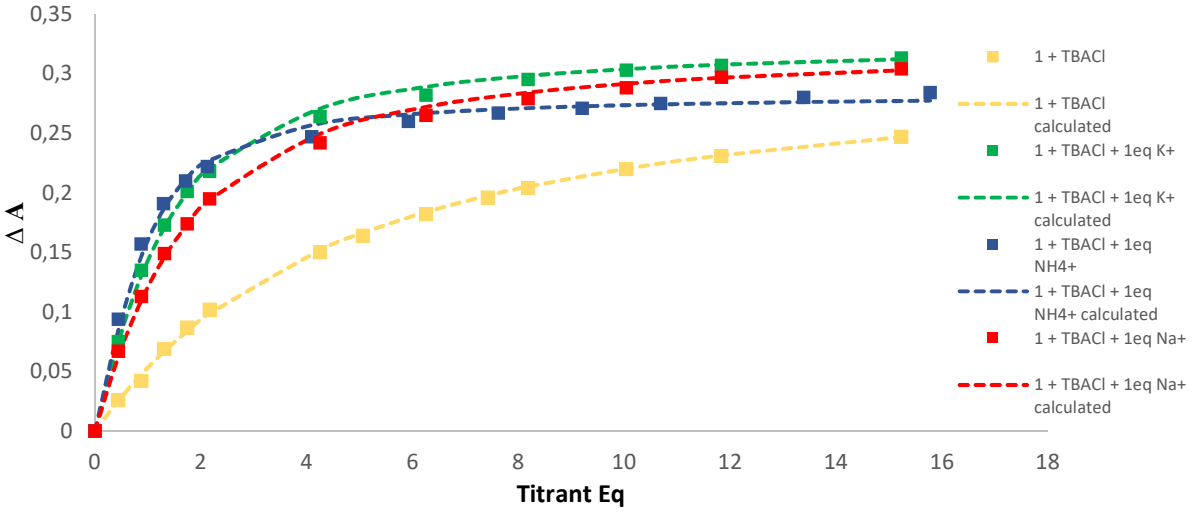


Figure 17. UV-Vis titration binding isotherms (experimental and calculated) of the receptor **1** with TBACl in the presence of one equivalent of cations (λ=360 nm)

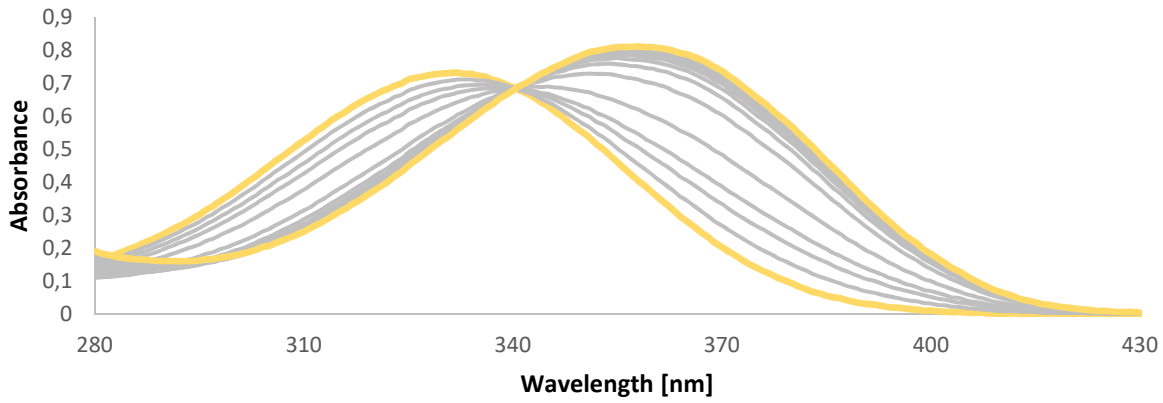


Figure 18. UV-Vis **1** spectrum changes upon titrant (TBABzO) addition (293 K, CH_3CN solution, $C_{titrant}$=1.9 x10^{-3} M, $C_{receptor}$=4.9 x10^{-5} M)

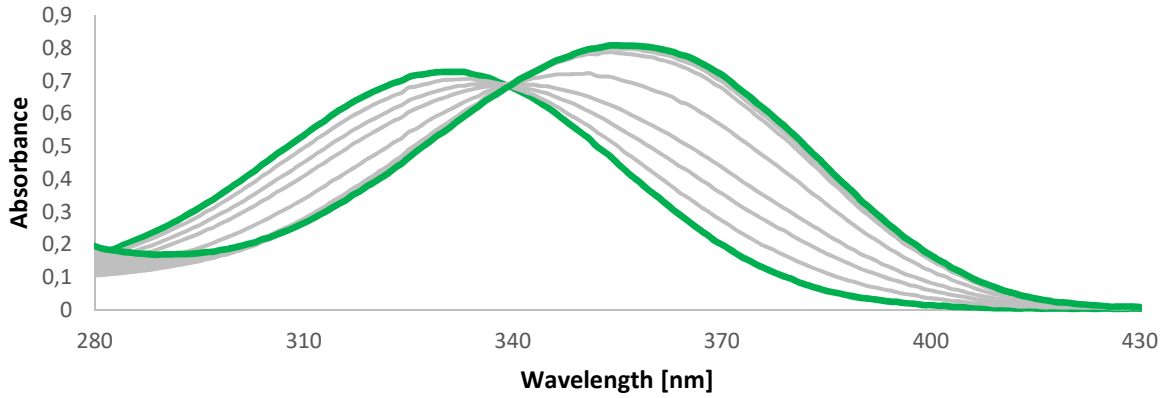


Figure 19. UV-Vis **1** spectrum changes upon titrant (TBABzO) addition in presence of 1 eq. KPF_6 (293 K, CH_3CN solution, $C_{titrant}$=1.9 x10^{-3} M, $C_{receptor}$=4.9 x10^{-5} M)

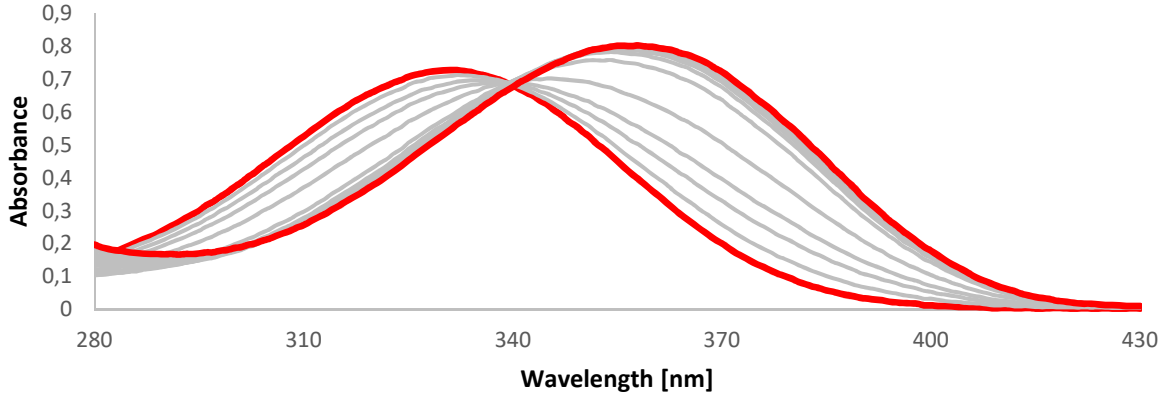


Figure 20. UV-Vis **1** spectrum changes upon titrant (TBABzO) addition in presence of 1 eq. NaClO4 (293 K, CH3CN solution, $C_{titrant}$=1.9 x10^{-3} M, $C_{receptor}$=4.9 x10^{-5} M)

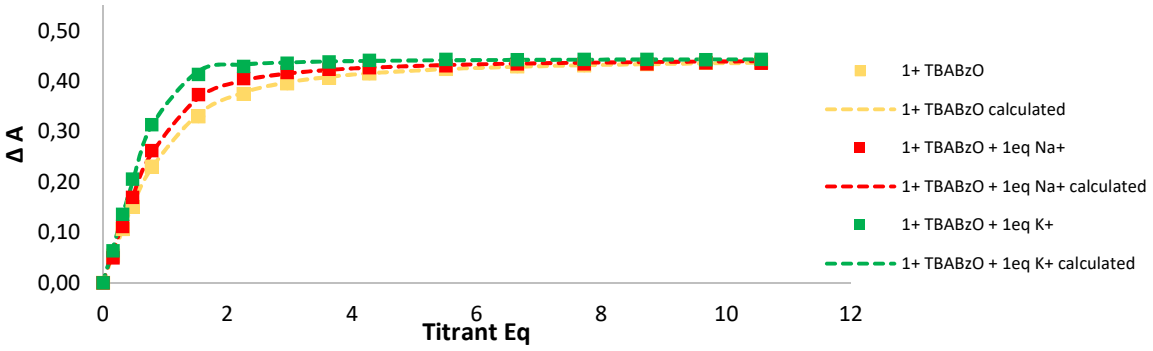


Figure 21. UV-Vis titration binding isotherms (experimental and calculated) of the receptor **1** with TBABzO in the presence of one equivalent of cations (λ=360 nm)

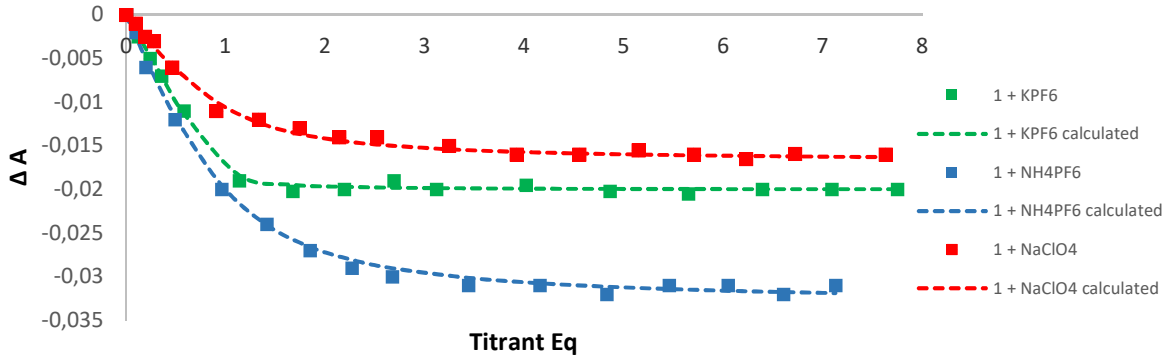


Figure 22. UV-Vis titration binding isotherms (experimental and calculated) of the receptor **1** with $NaClO_4$, KPF_6 and NH_4PF_6 (293K, CH_3CN solution, λ=357 nm, C_{NaClO4}=1.2 x10^{-3} M, C_{KPF6}=1.5 x10^{-3} M, C_{NH4PF6}=1.2 x10^{-3} M $C_{receptor}$=4.9 x10^{-5} M)

	TBA^+	$NaClO_4$	KPF_6	NH_4PF_6
Cl^-	4 500 (0.11%)	17 500 (0.13%)	25 600 (0.13%)	55 000 (0.34%)
K_M/K_{TBACl}	-	3.9	5.7	12.2
Br^-	1 040 (0.51%)	3 800 (0.14%)	4 420 (0.15%)	7 470 (0.12%)
K_M/K_{TBABr}	-	3.7	4.3	7.2
I^-	-[b]	360 (0.88%)	120 (1.9%)	400 (0.94%)
$K_M/K_{TBA\ I}$	-	7.2	2.4	8.0
AcO^-	252 000 (0.31%)	2 700 000 (8.3%)	>10 000 000 (22%)	-[c]
$K_M/K_{TBA\ AcO}$	-	11	>40	-
BzO^-	75 000 (0.27%)	130 000 (0.48%)	570 000 (0.97%)	-[c]
$K_M/K_{TBA\ BzO}$	-	1.7	7.6	-

L-BocPhe$^-$	21 000 (0.29%)	67 000 (0.16%)	130 000 (0.27%)	-[c]
$K_M/K_{TBA\ LBocPhe}$	-	3.2	6.2	-

Table 3. UV-Vis spectroscopy K_{obs}[a] values (298 K, CH_3CN solution) for interactions of **1** with various ion-pair combinations and standard errors values in parentheses, [b] K_a value too small to be calculated, to estimate cooperation factor, K_a values= 50 M^{-1} was assume, [c]Spectral changes during the titration indicate dislodging of anions from the receptor **1**.

$Na^+ClO_4^-$	$K^+PF_6^-$	$H_4N^+PF_6^-$
92 000 (3.4%)	924 000 (6.9%)	77 000 (1.1%)

Table 4.UV-Vis spectroscopy K_{obs} values (298 K, CH_3CN solution) for interactions of **1** with cations and standard errors values in parentheses

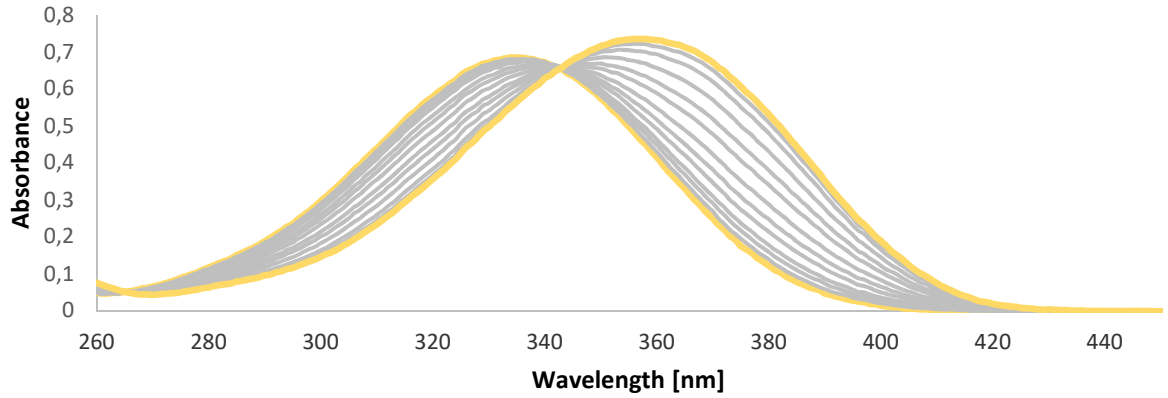


Figure 23. UV-Vis **2** spectrum changes upon titrant (TBAAcO) addition (293 K, CH_3CN solution, $C_{titrant}$=1.9 x10^{-3} M, $C_{receptor}$=5.0 x10^{-5} M)

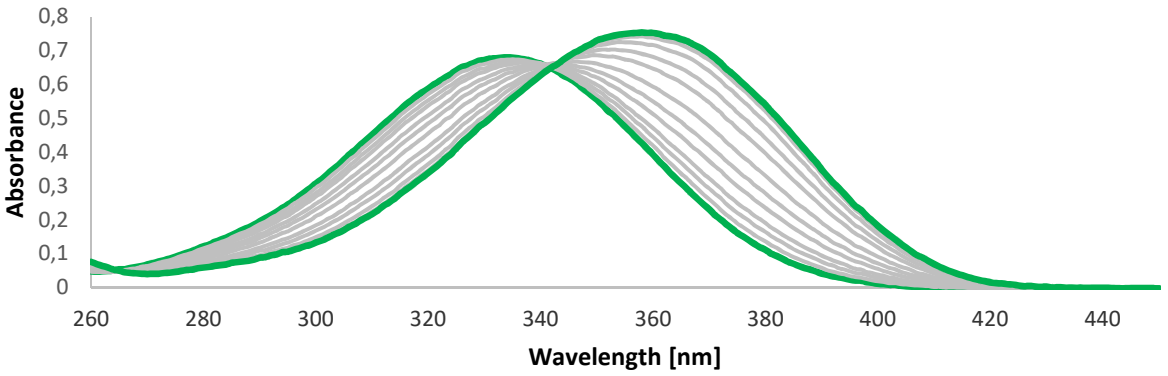


Figure 24. UV-Vis **2** spectrum changes upon titrant (TBAcO) addition in presence of 1 eq. KPF_6 (293 K, CH_3CN solution, $C_{titrant}$=1.9 x10^{-3} M, $C_{receptor}$=5.0 x10^{-5} M)

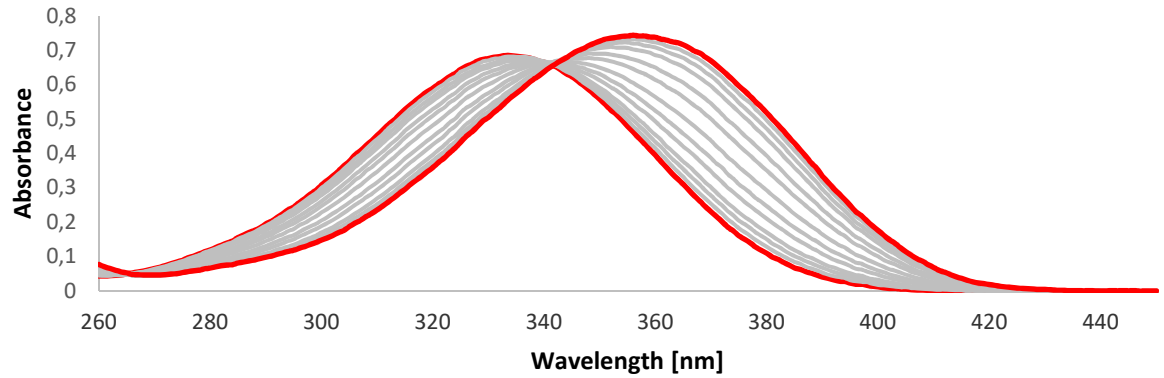


Figure 25. UV-Vis **2** spectrum changes upon titrant (TBAAcO) addition in presence of 1 eq. $NaClO_4$ (293 K, CH_3CN solution, $C_{titrant}$=1.9 x10^{-3} M, $C_{receptor}$=5.0 x10^{-5} M)

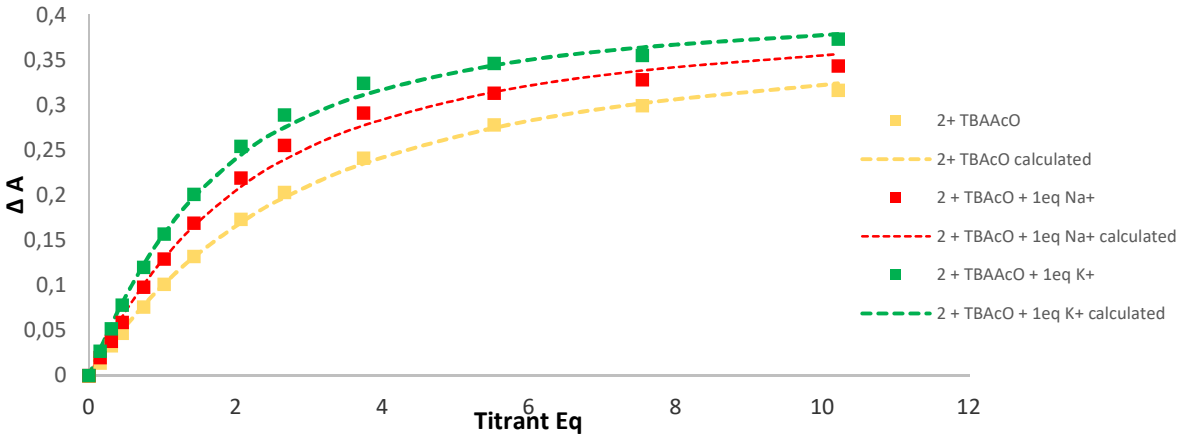


Figure 26. UV-Vis titration binding isotherms (experimental and calculated) of the receptor **2** with TBAAcO in the presence of one equivalent of cations (λ=360 nm)

	TBA^+	$NaClO_4$	KPF_6
AcO^-	9 100 (0.15%)	12 600 (0.71%)	21 200 (0.63%)
K_M/K_{TBAAcO}	-	1.4	2.3

Table 5. UV-Vis spectroscopy K_{obs} values (298 K, CH_3CN solution) for interactions of **2** with acetate ion-pairs and standard errors values in parentheses

5. NMR titration experiments

^{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 3.2 x 10^{-3} M solution of receptor **1** was added to 5 mm NMR tube. The receptor solution contains or not 1 mol eq. of sodium, potassium or ammonium cation. Then to the receptor solution titrant solution of tetrabutylammonium bromide in receptor solution (6.5 x10^{-2} M) was added. After each addition of titrant, a spectrum was registered. The resulting titration date were analyzed by HypNMR.

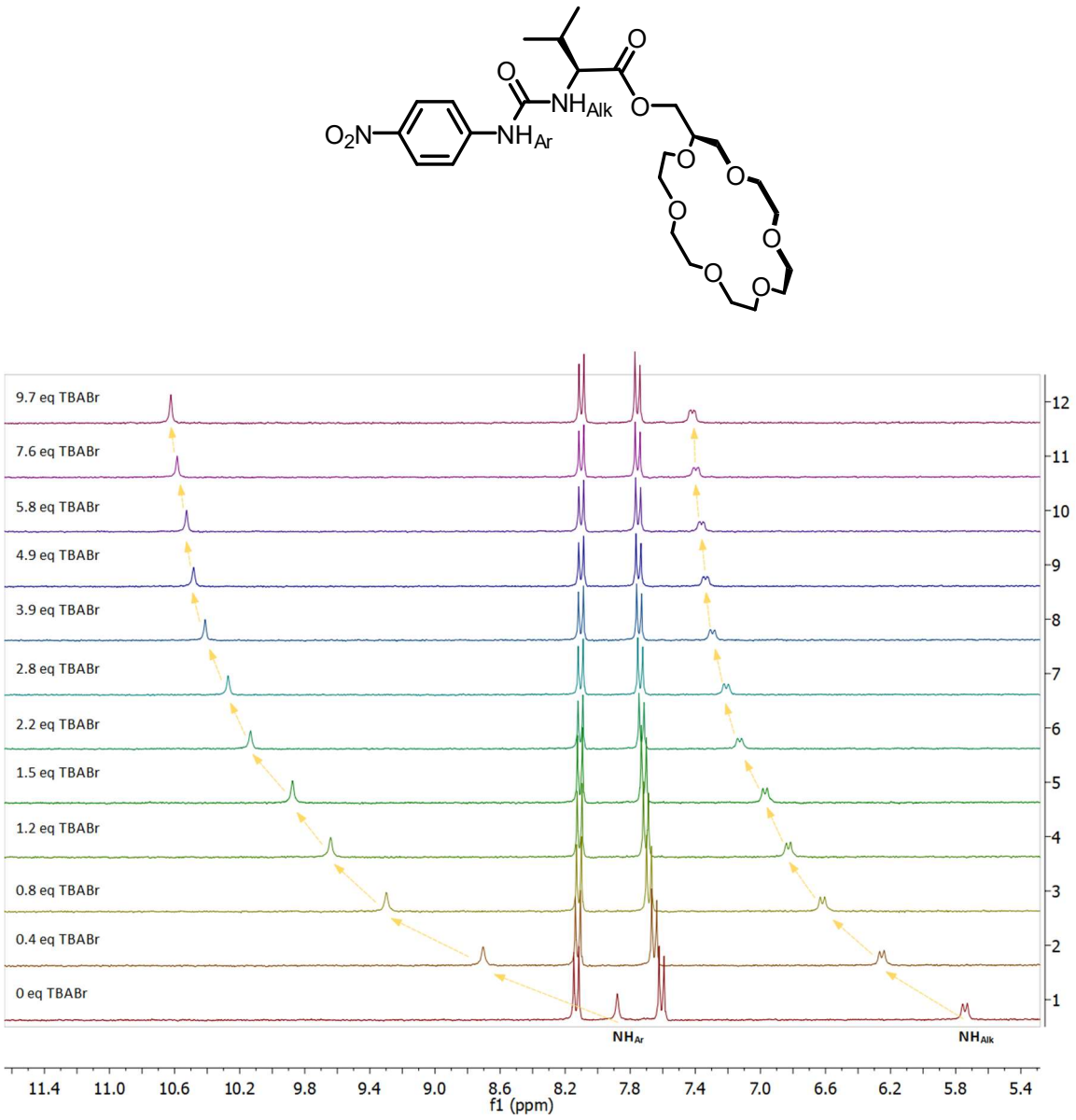


Figure 27. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBABr) addition, (293 K, CD_3CN solution, $C_{titrant}$=6.5 x10^{-2} M, $C_{receptor}$=3.2 x10^{-3} M)

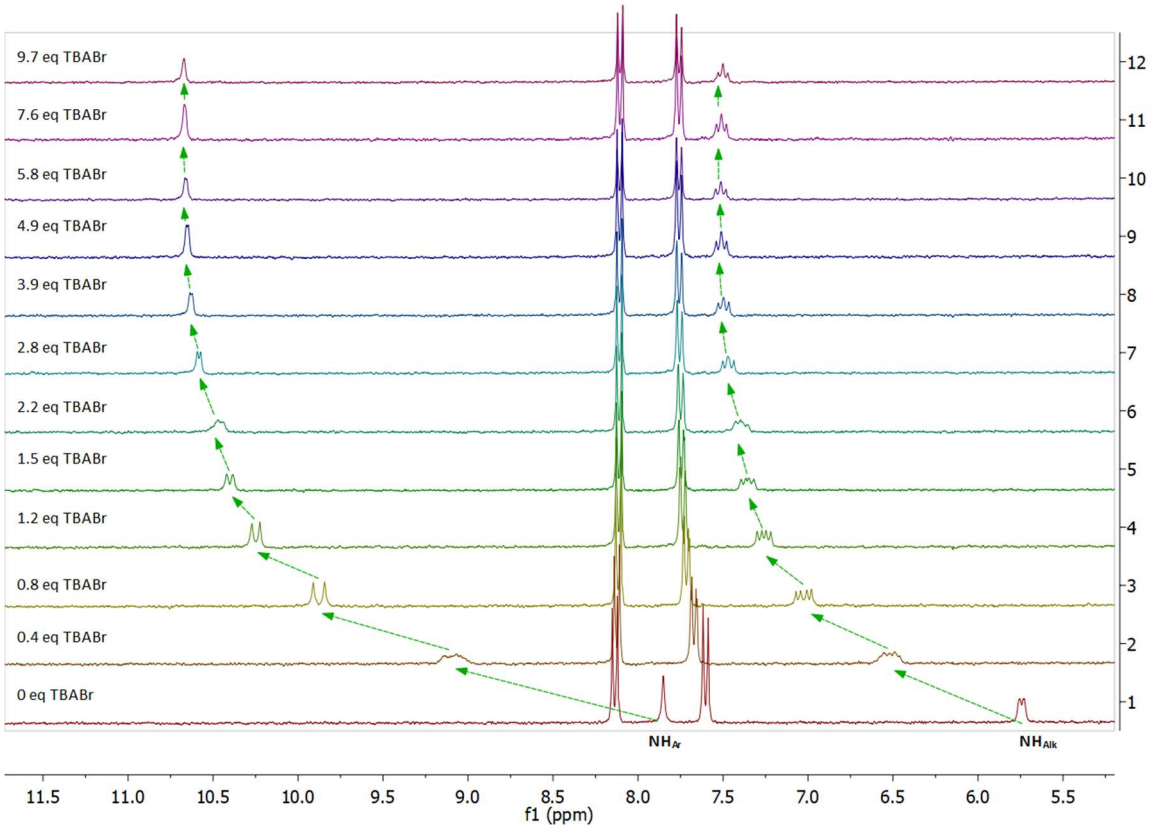


Figure 28. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBABr) addition in presence of 1eq. KPF_6, (293 K, CD_3CN solution, $C_{titrant}$=6.5 x10^{-2} M, $C_{receptor}$=3.2 x10^{-3} M)

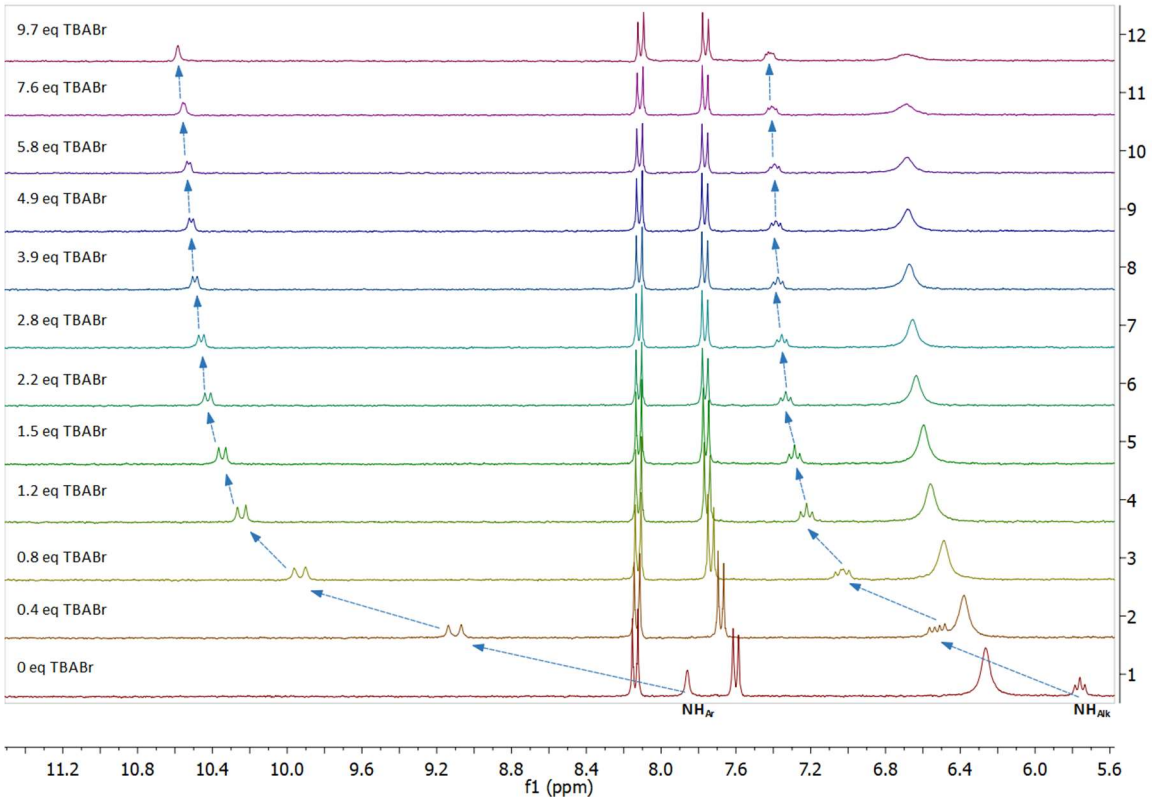


Figure 29. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBABr) addition in presence of 1eq. NH_4PF_6, (293 K, CD_3CN solution, $C_{titrant}$=6.5 x10^{-2} M, $C_{receptor}$=3.2 x10^{-3} M)

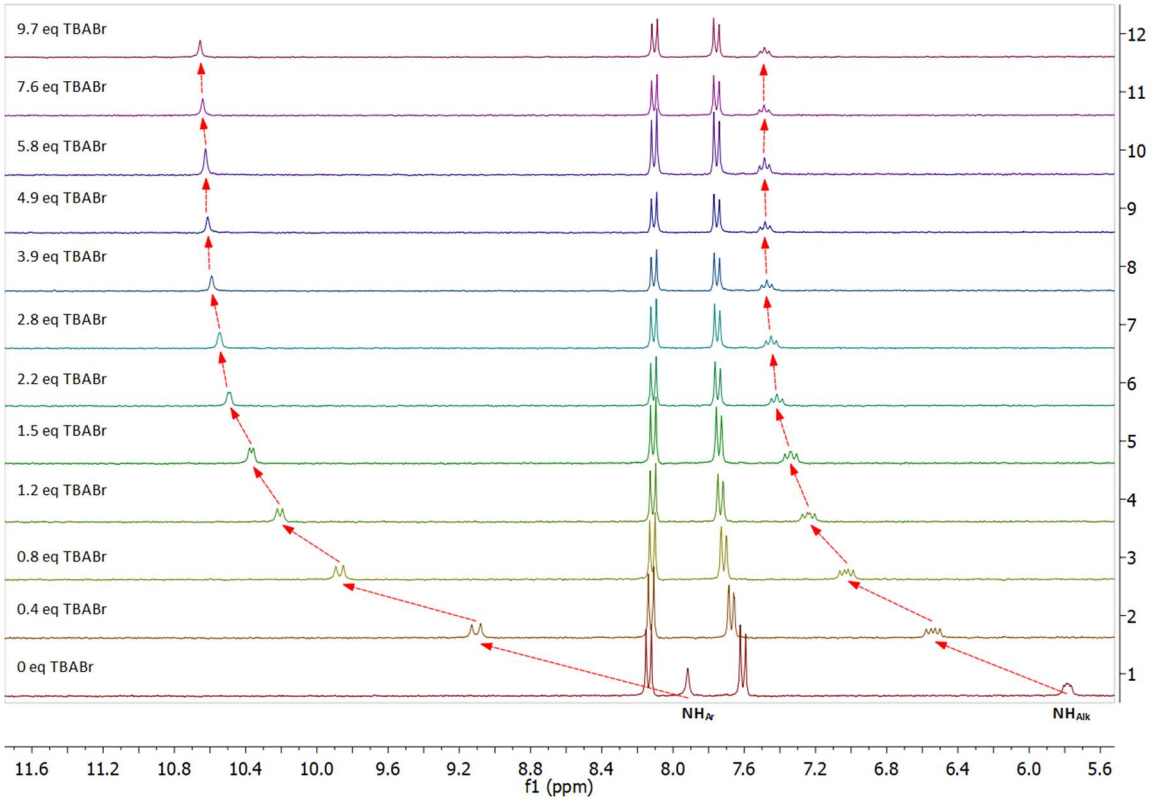


Figure 30. Partial ^{1}H NMR titration experiment of **1** upon titrant (TBABr) addition in presence of 1eq. $NaClO_4$, (293 K, CD_3CN solution, $C_{titrant}$=6.5 x10^{-2} M, $C_{receptor}$=3.2 x10^{-3} M)

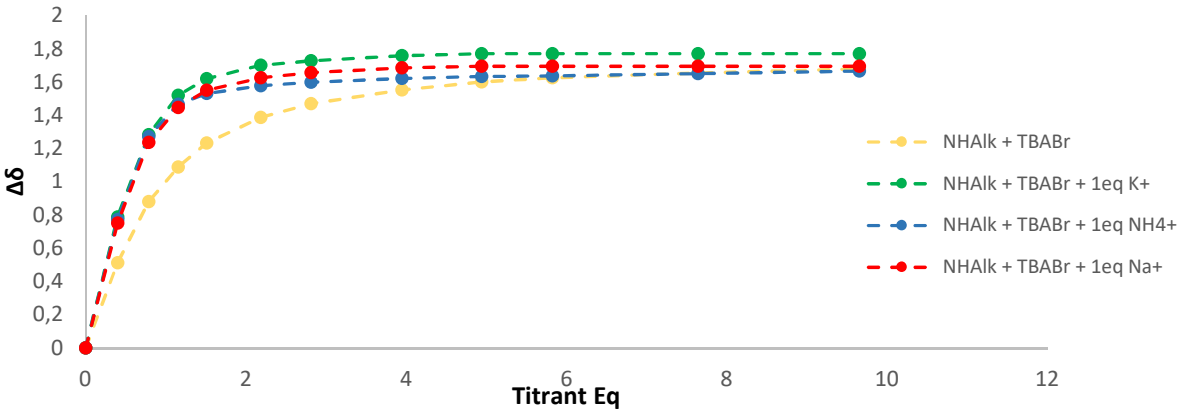


Figure 31. ^{1}H NMR titration binding isotherm of **1** with TBABr in the presence or absence of 1 eq. of cations

	TBA^+	$NaClO_4$	KPF_6	NH_4PF_6
Br^-	1 000 (0.04%)	6 900 (0.29%)	7 400 (0.29%)	15 500 (0.62%)
K_M/K_{TBACl}	-	6.9	7.4	15.5

Table 6. ^{1}H NMR spectroscopy K_{obs} values (298 K, CD_3CN solution) for interactions of **1** with bromide ion-pairs and standard errors values in parentheses

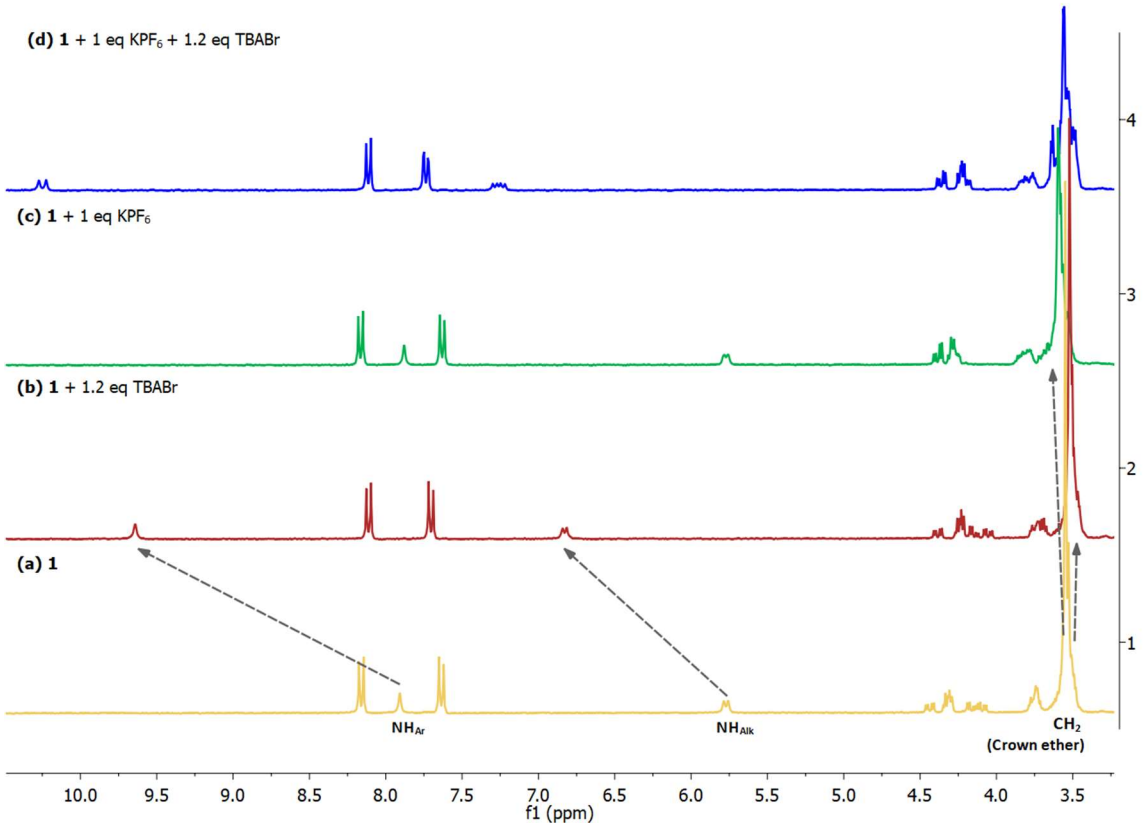


Figure 32. Partial ^{1}H NMR spectra of compound **1** $C_{receptor}$=3.2 x10^{-3} M (a) on the addition of 1.2 equivalent of TBABr (b) on the addition of 1 equivalent of KPF_6 (c) and on the addition of 1 equivalent of KPF_6 and 1.2 equivalent of TBABr (d)

6. Extraction studies

Extraction studies were performed using ^{1}H NMR spectroscopy on a 300 MHz BrukerAvance spectrometer, at 298K, in $CDCl_3$ solution. The solution of 7.96 mg of **1** in 0.6 ml of $CDCl_3$ in 0.5 mm NMR tube $C_{receptor1}$=2.4x10^{-2} was washed with destilated water, the spectrum was aquaierd, then the water phase was removed. Next chloroform solution was extracted (vigorous shaking for 10 minutes) with 0.5 ml aquoues solution of potasium acetate C_{AcOK} =5.63 M - which corresponds to 195 molar equivalents, the spectrum was acquired without aqueous phase removed. Then the water phase was removed and the organic phase was back-extracted with H_2O and the ^{1}H NMR spectra was aquaired.

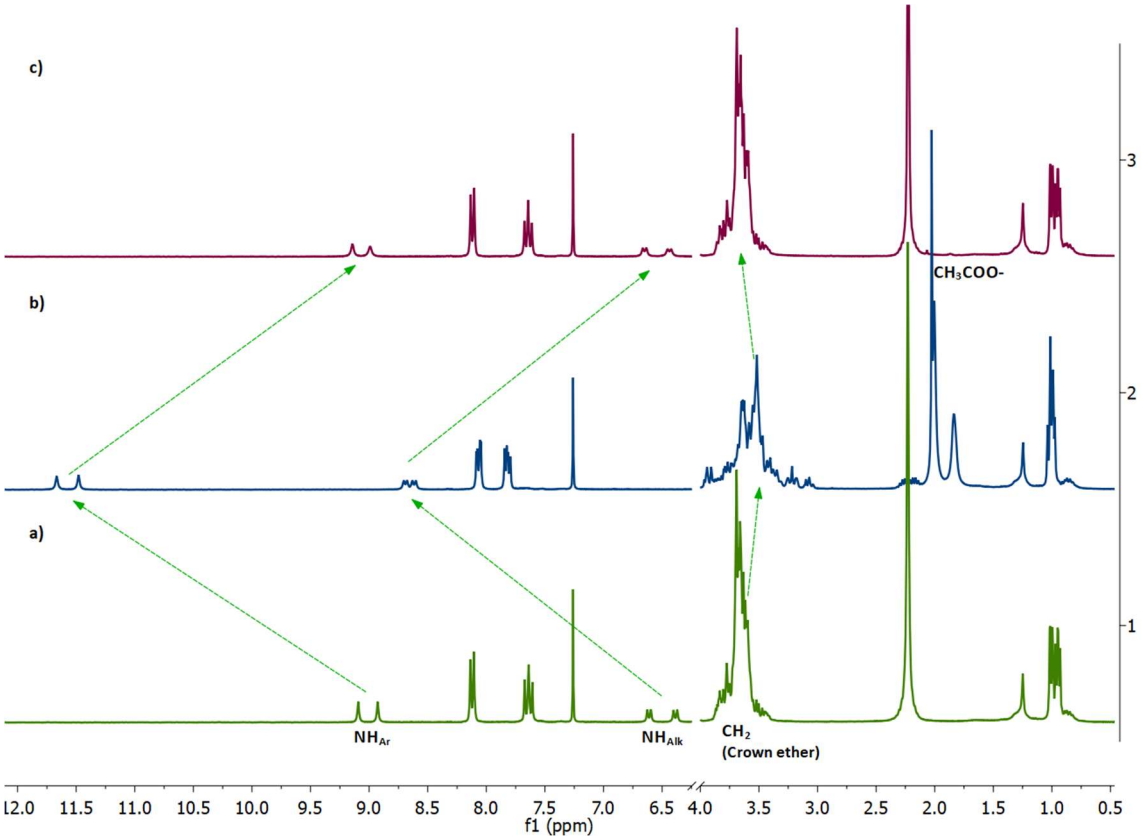


Figure 33. Partial ^{1}H NMR spectra of the compound **1** $C_{receptor}$=2.4 x10^{-2} M: (a) $C_{receptor}$=2.4 x10^{-2} M in wet $CDCl_3$, (b) after extraction of CH_3COOK from aqua solution $C_{CH3COOK}$=5.6 M, (c) after back-extraction with distilled water

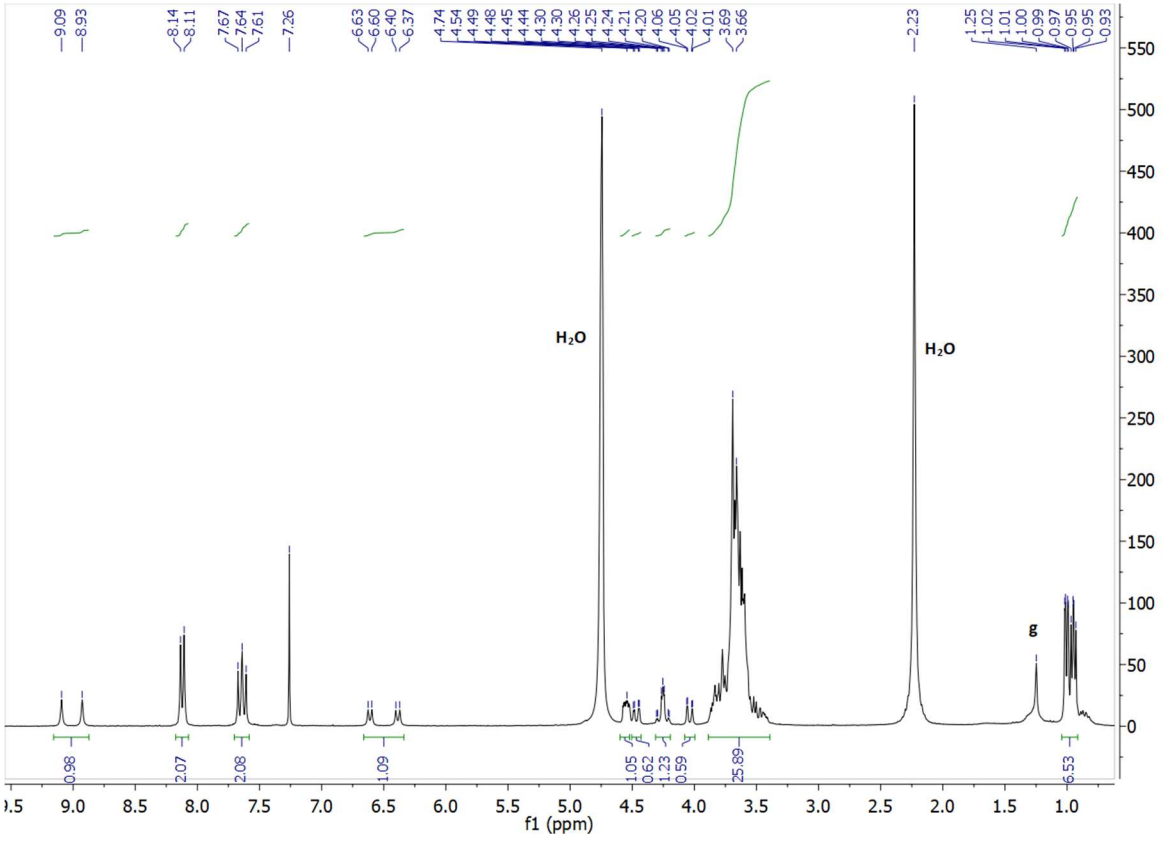


Figure 34. ^{1}H NMR spectra of compound **1** $C_{receptor}$=2.4 x10^{-2} M in wet $CDCl_3$

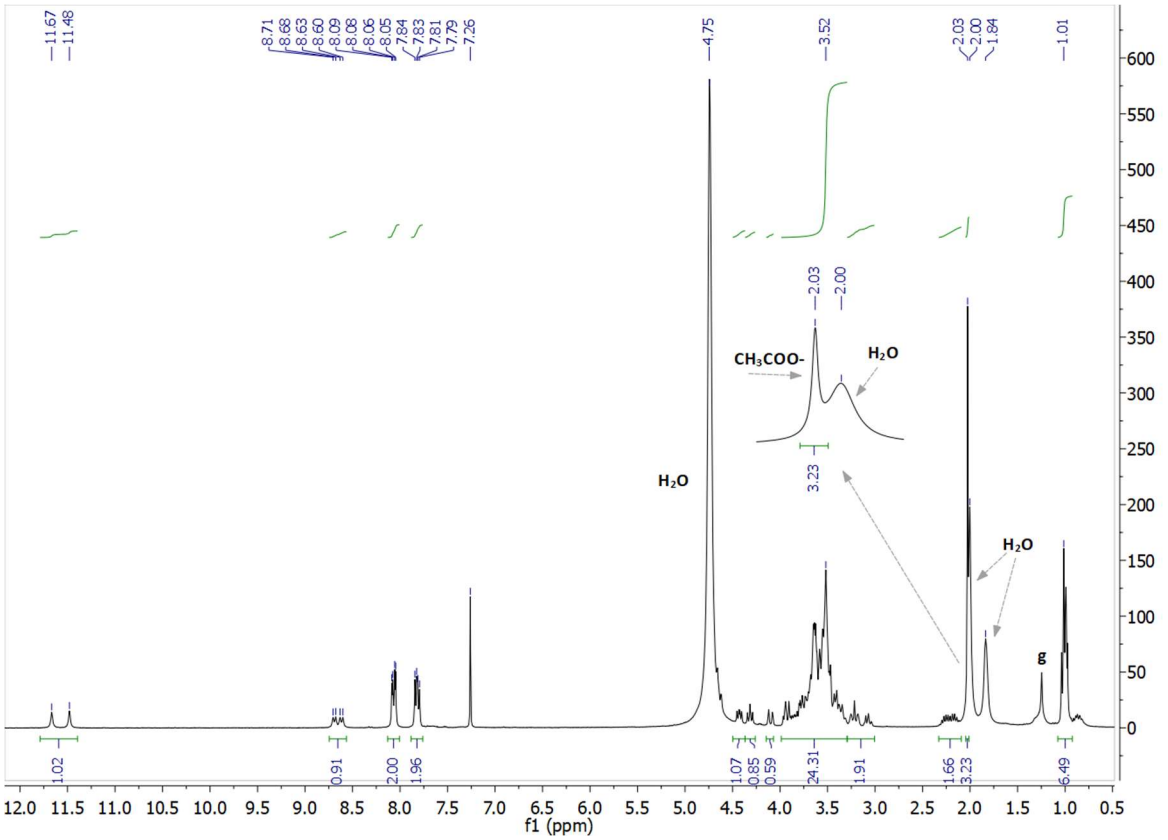


Figure 35. ^{1}H NMR spectra of compound **1** $C_{receptor}$=2.4 x10^{-2} M after extraction of CH_3COOK from aqua solution $C_{CH3COOK}$=5.6 M, n_1=0.0144, $n_{CH3COOK}$=2.8, 194 eq.

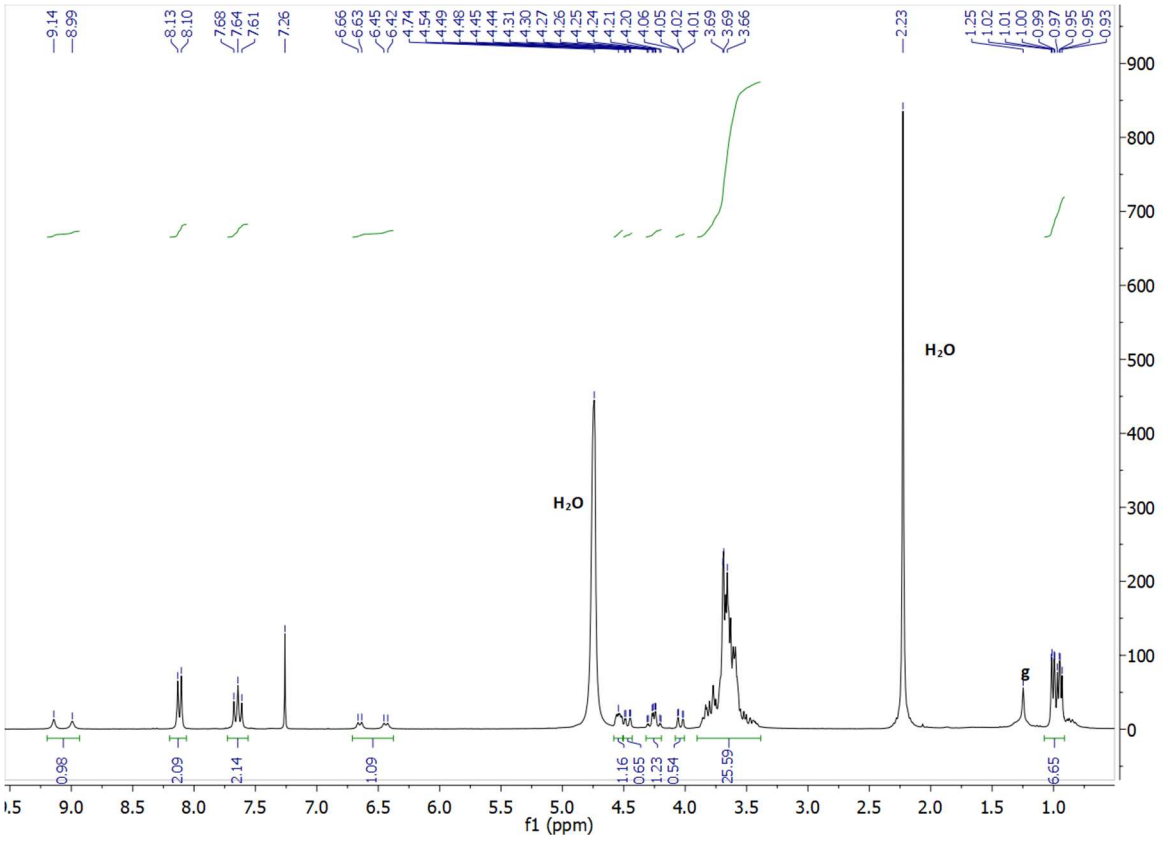


Figure 36. ^{1}H NMR spectra of compound **1** $C_{receptor}$=2.4 x10^{-2} M after back-extraction with distilled water

7. References

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