Ion-pair induced supramolecular assembly formation for selective extraction and sensing of potassium sulfate

by

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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. If necessary 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. DOSY experiments were conducted at 298 K on Varian VNMRS 600 MHz instruments with a residual solvent signal as an internal standard.

Mass spectra were measured on Quattro LC Micromass or Shimadzu LCMS-IT-TOF unit.

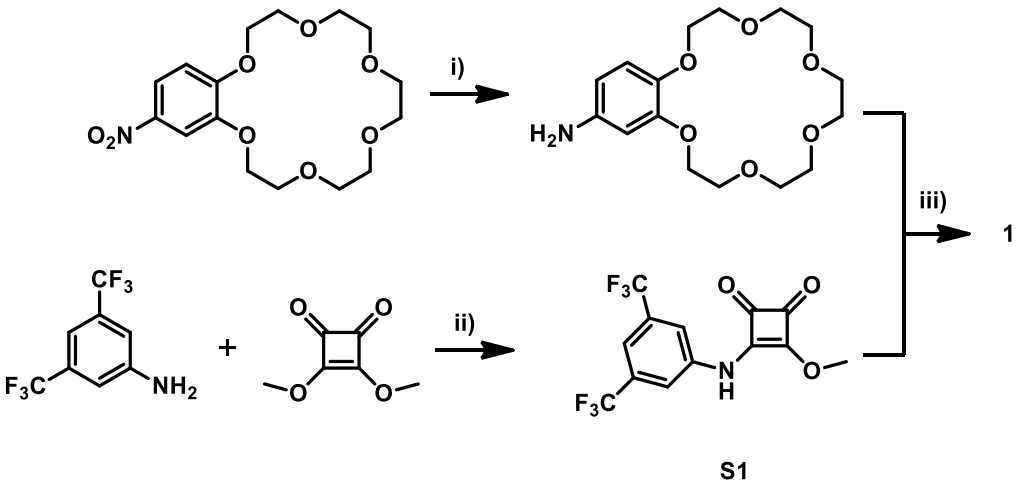
UV-vis analyses were performed using Thermo Spectronic Unicam UV500 Spectrophotometer.

Atomic emission measurements were performed using Perkin Elmer AAnalyst 300 spectometer.

Dynamic Light Scattering analyses were performed using a Malvern Zetasizer Nano ZS (Malvern Instruments Ltd, UK) at 25ºC and a 173° angle relative to the source. The hydrodynamic diameter distributions were obtained by volume using the software package of the apparatus. Each curve represents the average of 3 measurements (16 runs each). Prior to analysis, all solutions were filtered and degassed.

Synthesis

All reagents and chemicals were of reagent grade quality and purchased commercially. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer. ^{1}H NMR chemical shifts δ are reported in ppm referenced to residual solvent signal (DMSO-d_6 or CD_3CN).



Scheme S1. Synthesis of receptor **1**. Reagents and conditions: i) H_2, Pd/C, MeOH-THF, 12h, rt, quantitative; (ii) methanol, 72 h, rt, 95%; (iii) methanol, 48 h, rt, 90%.

Preparation of compound S1. To a solution of 3,4-dimethoxy-3-cyclobutane-1,2-dione (2.00 g, 14.1 mmol) in MeOH (20 ml) was added 3,5-bis(trifluoromethyl)aniline (2.40 ml, 15.5 mmol, 1.1equiv) was added at room temperature. After being stirred for 3 days the

reaction mixture was filtered, and the collected solid material was washed with MeOH. The obtained light yellow solid was dried *in vacuo* to give desired product **S1** (4.54 g, 13.4 mmol, 95%).

HRMS (ESI): calcd for $C_{13}H_7F_6NO_3Na$ $[M+ Na]^+$: 362.0228, found: 362.0225.

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.19 (s, 1H), 8.05 (s,2H), 7.78 (s, 1H), 4.41 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 187.4, 184.5, 179.9, 169.1, 140.2, 131.2 (q, J= 33 Hz), 123,1 (q, J= 271 Hz), 119.2, 116.1, 61.0.

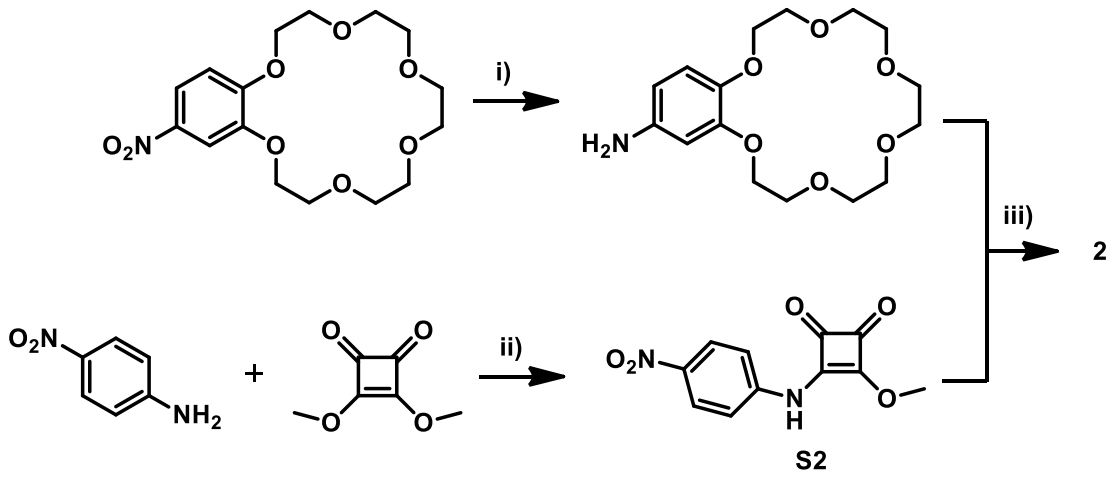
Preparation of receptor 1. To a degassed solution of 4-nitrobenzo-18-crown-6-ether (645 mg, 1.80 mmol) in 30 ml of THF/MeOH (1:4) 25 mg of 10% Pd/C was added. The reaction mixture was kept under H_2 atmosphere (balloon pressure) at room temperature overnight. The catalyst was removed by filtration through a pad of Celite and washed with MeOH. The filtrate was concentrated under reduced pressure to give the crude product in quantitative yield (590 mg). The amine was used in next step without further purification.

To the solution of amine (590 mg, 1.80 mmol) in MeOH (10 ml) was added a compound **S1** (644 mg, 1.90 mmol) at room temperature. The mixture was stirred at room temperature for 2 days. The reaction mixture was filtered, and the collected solid material was washed with MeOH. The obtained white solid was dried *in vacuo* to give desired receptor containing residual molecule of methanol. The residual solvent was removed by dissolving of receptor in chloroform and evaporation of the solvent under reduced pressure. Receptor 1 was obtained as white solid in a 90% yield (1028 mg, 1.62 mmol).

HRMS (ESI): calcd for $C_{28}H_{28}F_6N_2O_8K$ $[M + K]^+$: 673.1387, found: 673.1375.

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.21 (s, 1H), 9.97 (s, 1H), 8.05 (s, 2H), 7.72 (s, 1H), 7.20 (s, 1H), 7.00 – 6.90 (m, 1H), 6.85 – 6.75 (m, 1H), 4.23 – 3.94 (m, 4H), 3.76 (s, 4H), 3.68 – 3.42 (m, 12H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 183.6, 181.9, 166.8, 164.4, 149.1, 145.3, 141.2, 132.4, 132.0 (q, *J*= 32 Hz), 123.6 (q, *J*= 271 Hz), 119.0, 115.8, 114.2, 111.3, 105.7, 70.3, 69.2, 69.0, 68.9, 68.5.



Scheme S2. Synthesis of receptor **2**. Reagents and conditions: i) H_2, Pd/C, MeOH-THF, 12h, rt, quantitative; (ii) methanol, 72 h, rt, 85%; (iii) methanol, 48 h, rt, 75%.

Preparation of compound S2. To a solution of 3,4-dimethoxy-3-cyclobutane-1,2-dione (2.00 g, 14.1 mmol) in MeOH (20 ml) was added 4-nitroaniline (1.95 g, 14.1 mmol) at room temperature. After being stirred for 3 days the reaction mixture was filtered and the collected solid material was washed with MeOH. The obtained red solid was dried *in vacuo* to give desired product **S2** (2.97 g, 12.0 mmol, 85%).

HRMS (ESI): calcd for $C_{11}H_8N_2O_5Na$ $[M+ Na]^+$: 271.0331, found: 271.0339.

^{1}H NMR (300 MHz, DMSO-d_6) δ 11.23 (s, 1H), 8.30 – 8.20 (m, 2H), 7.65 – 7.50 (m, 2H), 4.43 (s, 3H).

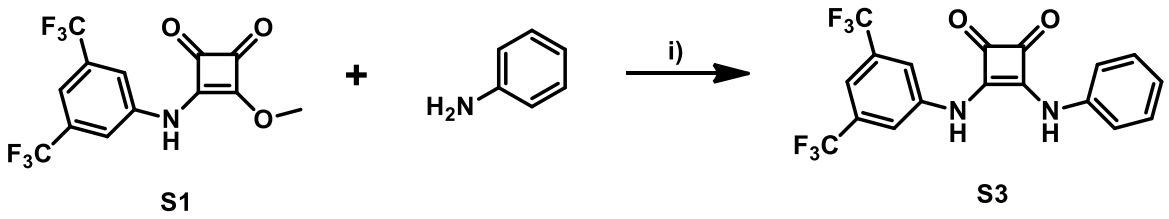
^{13}C NMR (75 MHz, DMSO-d_6) δ 187.7, 185.4, 180.9, 169.5, 144.8, 143.0, 125.8, 119.42, 61.5.

Preparation of receptor 2. To the solution of 4-aminobenzo-18-crown-6-ether (590 mg, 1.80 mmol) in MeOH (10 ml) was added a compound **S2** (447 mg, 1.80 mmol) at room temperature. After being stirred for 2 days, the reaction mixture was filtered, and the collected solid material was washed with MeOH. The obtained deep orange solid was dried *in vacuo* to give desired in a 75% yield (978 mg, 1.35 mmol).

HRMS (ESI): calcd for $C_{26}H_{29}N_3O_{10}K$ $[M+ K]^+$: 582.1940, found: 583.1473

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.28 (s, 1H), 9.97 (s, 1H), 8.34 - 8.22 (m, 2H), 7.71 - 7.61 (m, 2H), 7.23 (s, 1H), 7.03 - 6.78 (m, 2H), 4.20 - 3.95 (m, 4H), 3.88 - 3.69 (m, 4H), 3.69 - 3.38 (m, 12H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 181.2, 167.2, 164.2, 149.0, 145.3, 142.2, 132.0, 126.0, 118.4, 114.2, 111.2, 105.6, 70.3, 70.2, 69.2, 69.0, 68.9, 68.5.



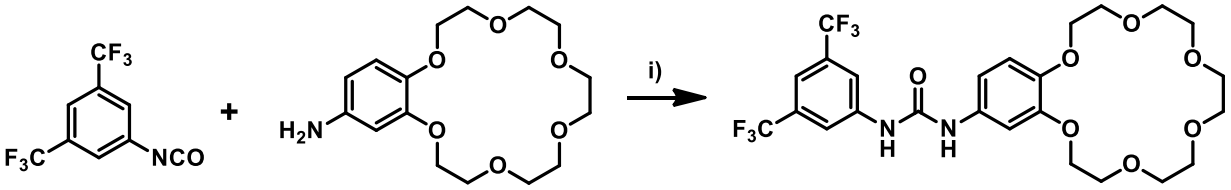
Scheme S3. Synthesis of receptor **S3**. Reagents and conditions: (i) methanol, 48 h, rt, 71%.

Preparation of receptor S3. To a solution of compound S1 (204 mg, 0.60 mmol) in MeOH (5 mL) was added aniline (56 mg, 0.60 mmol) at room temperature. The mixture was stirred for 2 days. Then the reaction mixture was filtered, and the collected solid material was washed with MeOH. The obtained white solid was dried *in vacuo* to give the desired receptor (170 mg, 0.425 mmol, 71%):

HRMS (ESI): calcd for $C_{13}H_7F_6NO_3Na$ $[M+ Na]^+$: 362.0228, found: 362.0225.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.31 (s, 2H), 7.96 (s,2H), 7.66 (s, 1H), 7.43 - 7.34 (m, 4H), 7.22 - 7.12 (m, 1H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 182.5, 181.9, 166.5, 164.4, 140.5, 137.9, 131.1 (q, *J*= 32 Hz), 128.9, 123.4, 120.9, 118.6, 118.4, 114.9.



S4

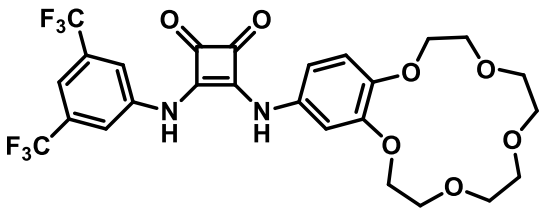
Scheme S4. Synthesis of receptor **S4**. Reagents and conditions: (i) CH_2Cl_2, TEA, 12 h, rt, 73%.

Preparation of receptor S4. To a solution of 4-aminobenzo-18-crown-6-ether (580 mg, 1.77 mmol) and trimethylamine (251 μl, 1.80 mmol) in methylene dichloride (10 mL) was added 3,5-trifluoromethylisocyanate (300 μL, 1.76 mmol) at room temperature. After being stirred for 12 h, the reaction mixture was concentrated and the residue was purified on column chromatography (5% methanol in chloroform) to give the title product as a slightly pink solid (748 mg, 1.28 mmol, 73% yield).

HRMS (ESI): calcd for $C_{25}H_{28}F_6N_2O_7K$ $[M+K]^+$: 621.1438, found: 621.1411.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.38 (s, 1H), 8.83 (s, 1H), 8.13 (s, 2H), 7.61 (s, 1H), 7.21 (s, 1H), 6.99 - 6.81 (m, 2H), 4.16 - 3.95 (m, 4H), 3.87 - 3.68 (m, 4H), 3.69 - 3.44 (m, 12H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 153.0, 148.7, 144.3, 142.5, 131.1 (q, J= 32 Hz), 123.8 (q, J= 271 Hz), 118.3, 114.5, 114.2, 111.8, 106.2, 70.3, 69.3, 69.2, 68.9, 68.6.

Receptor S5 was prepared according to previously reported procedure.[1]



S5

UV-vis titration experiments

The UV-Vis titration was performed using Thermo Spectronic Unicam UV500 Spectrophotometer at 298K in acetonitrile. In each case, a 2500 μL of freshly prepared 3.14×10^{-5} M solution of receptor was added to a cuvette and small aliquots of TBAX, containing constant concentration of the receptor, were added and a spectrum was acquired after each addition. In the case of ion pair titration receptor was firstly pretreated with one equivalent of KPF_6 or $NaClO_4$ (refers to receptor). The resulting titration data were analyzed using BindFit (v0.5) package, available online at http://supramolecular.org

DILUTION

Fig. S1. Dilution curve of receptor **1**.

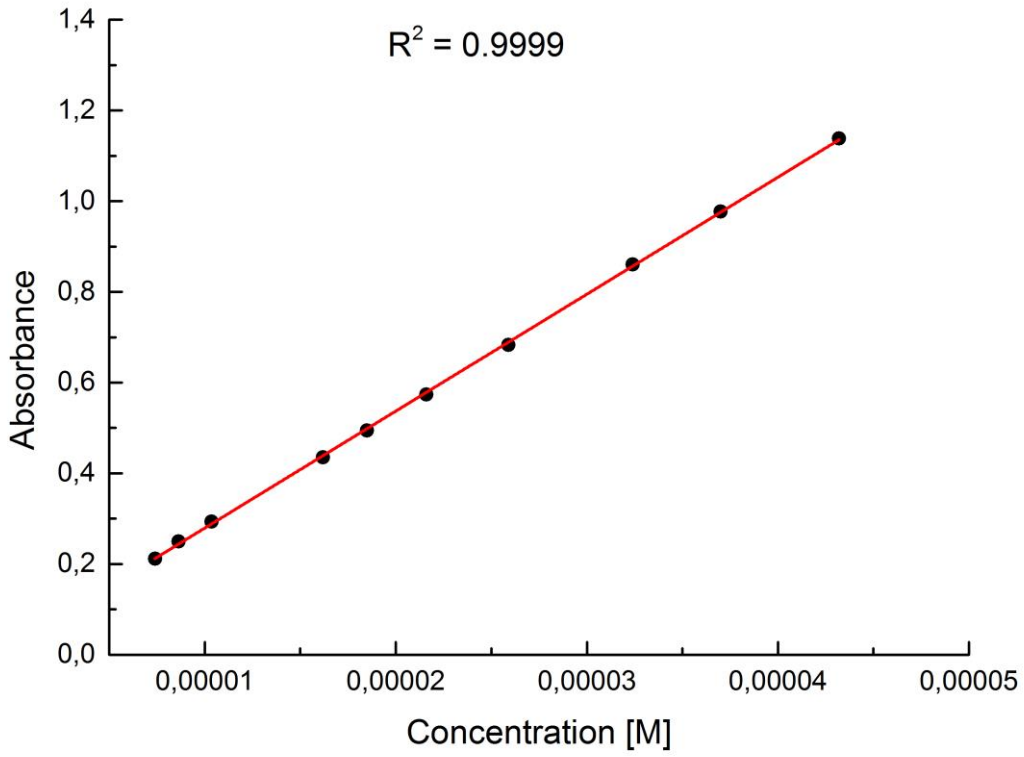


Fig. S2. UV-Vis titration of receptor **1** with TBACl in 0.5% H_2O (pH=3) in MeCN and selected binding isotherms.

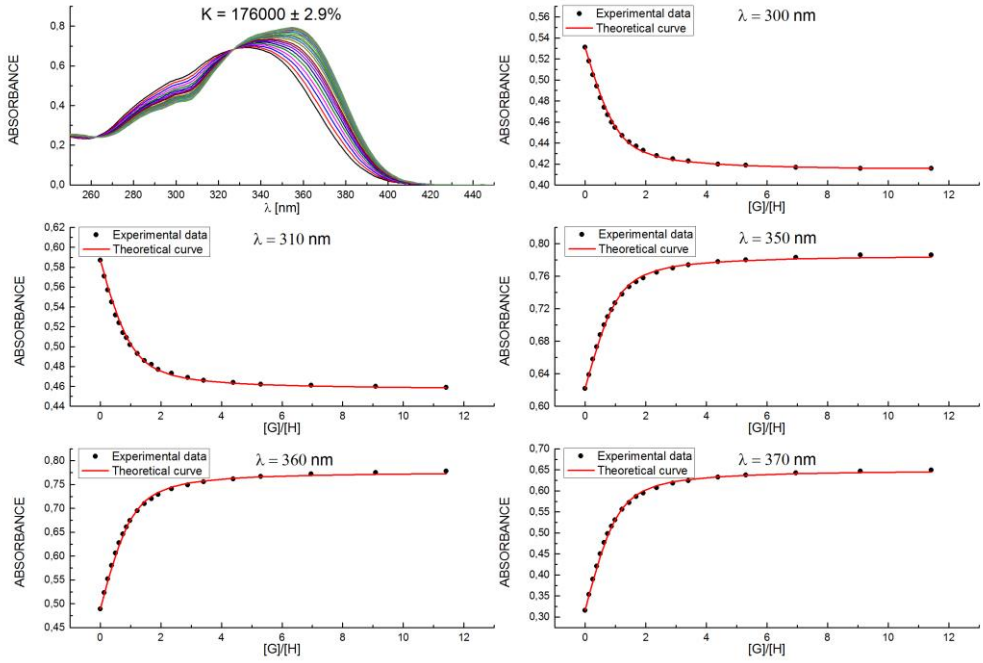


Fig. S3. UV-Vis titration of receptor **1** with TBACl in 0.5% H_2O (pH=3) in the presence of 1 equivalent of $NaClO_4$ and selected binding isotherms.

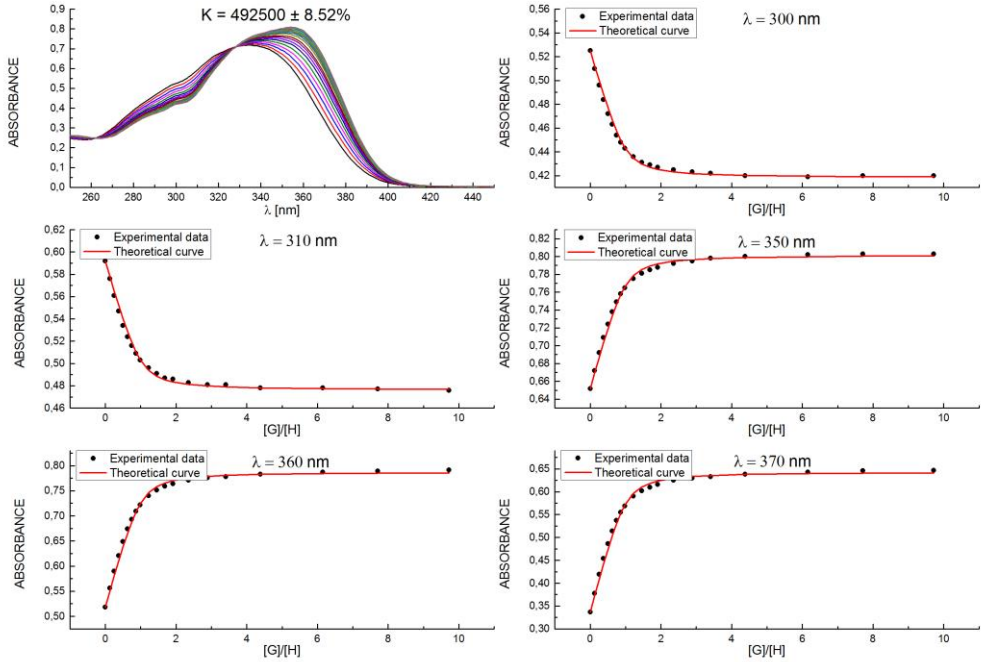


Fig. S4. UV-Vis titration of receptor **1** with TBACl in 0.5% H_2O (pH=3) in the presence of 1 equivalent of KPF_6 and selected binding isotherms.

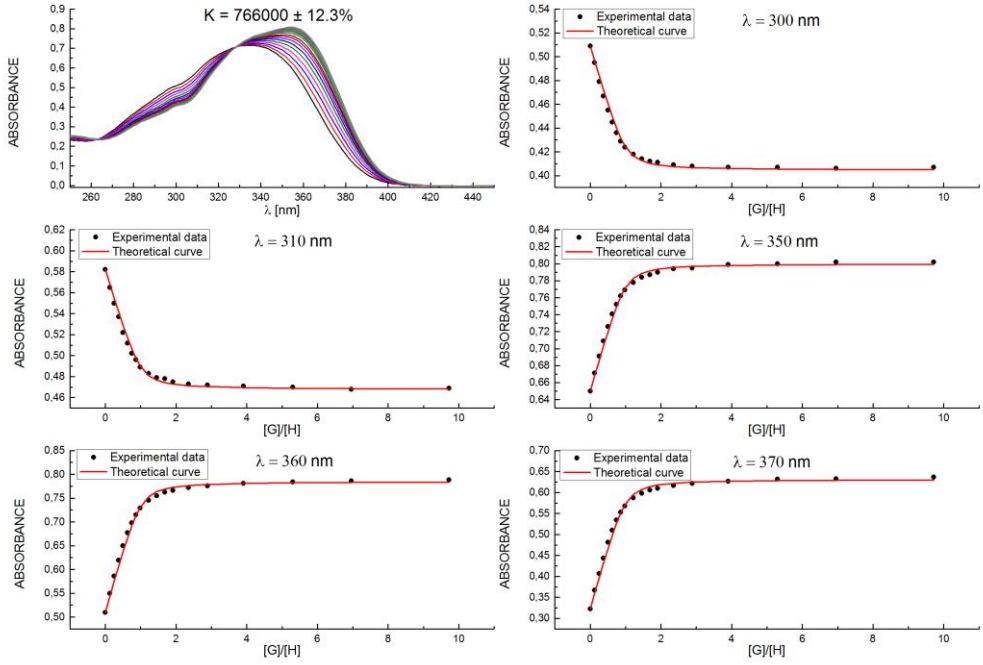


Fig. S5. UV-Vis titration of receptor **1** with TBABr in MeCN and selected binding isotherms.

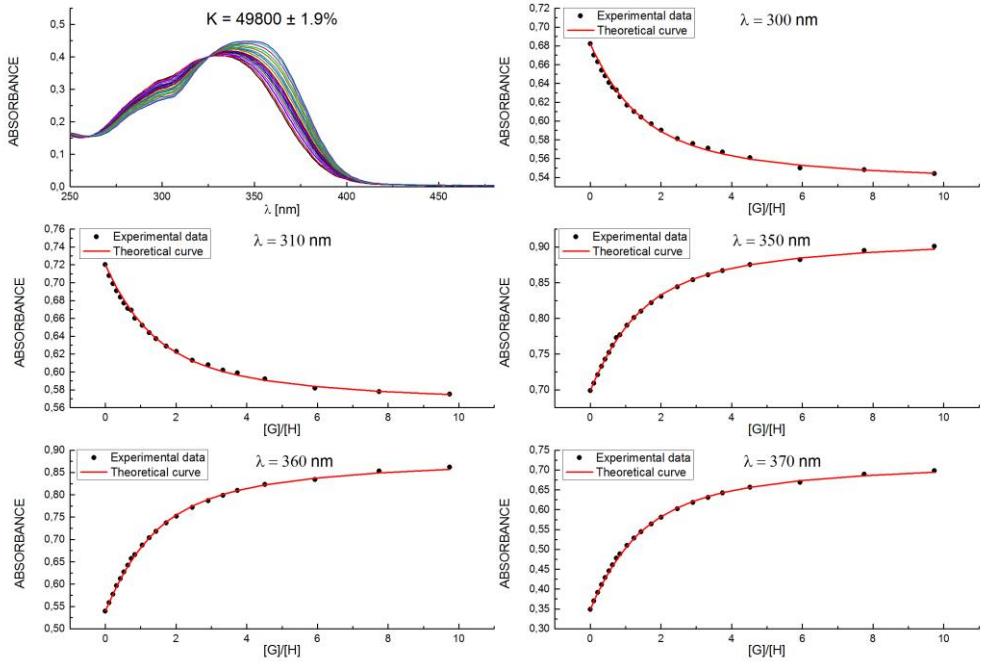


Fig. S6. UV-Vis titration of receptor **1** with TBABr in the presence of 1 equivalent of $NaClO_4$ and selected binding isotherms.

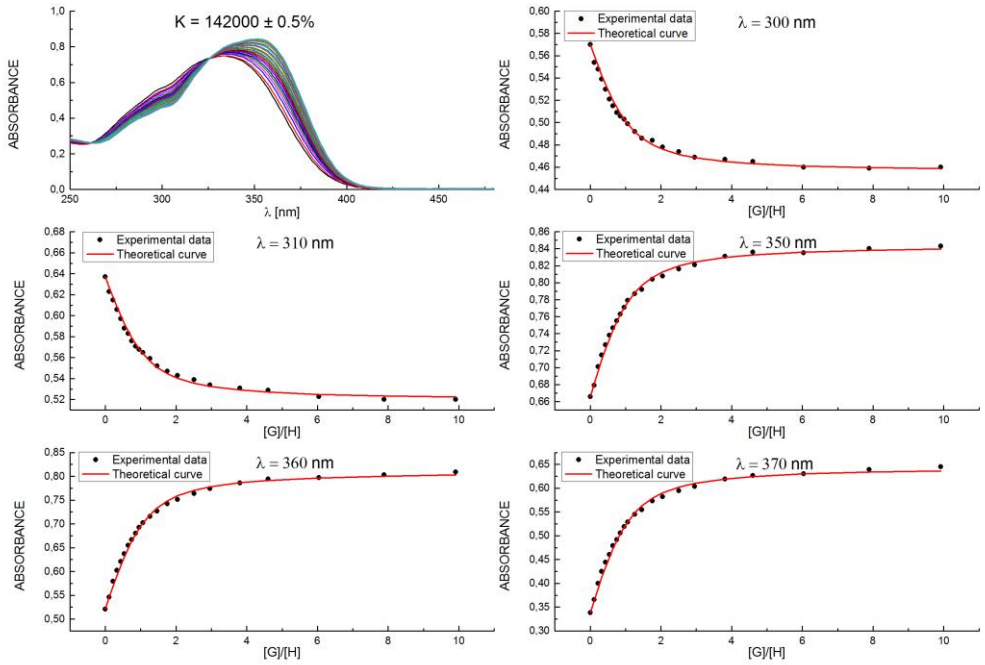


Fig. S7. UV-Vis titration of receptor **1** with TBABr in the presence of 1 equivalent of KPF_6 and selected binding isotherms.

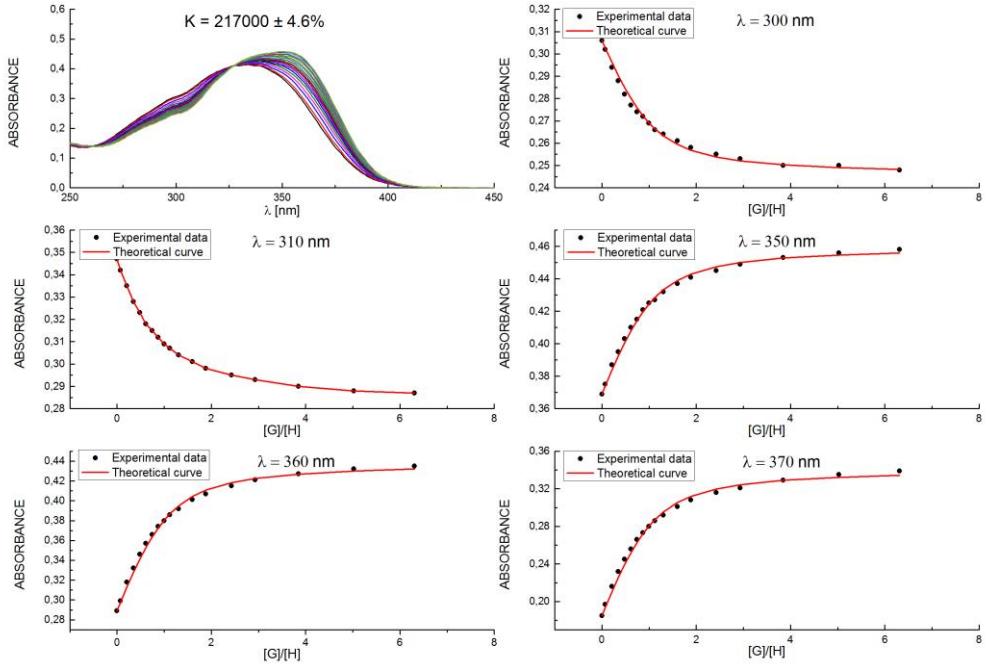


Fig. S8. UV-Vis titration of receptor **1** with TBAI and selected binding isotherms.

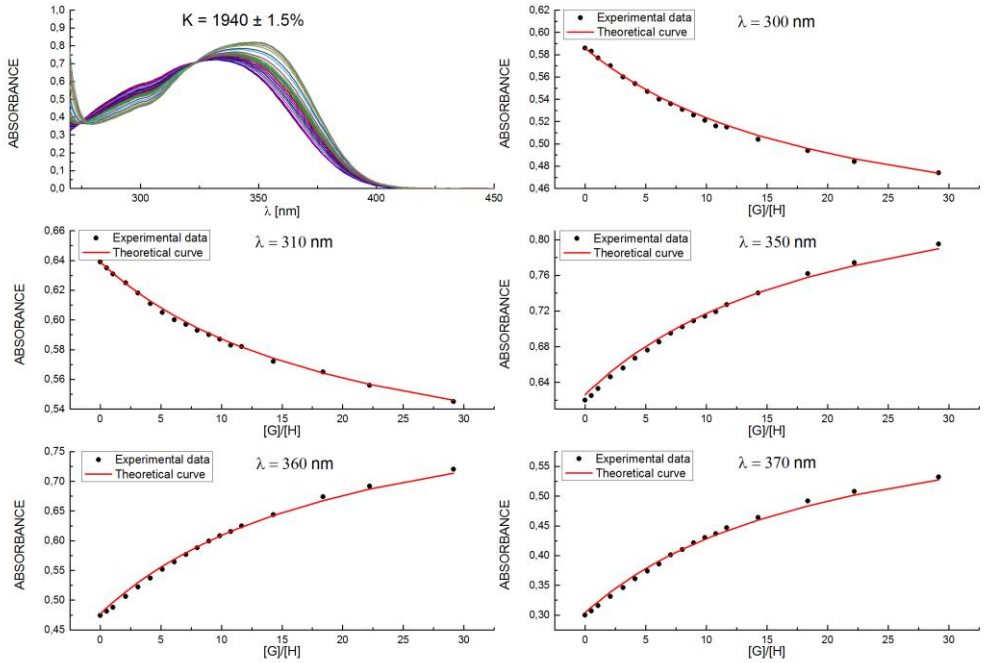


Fig. S9. UV-Vis titration of receptor **1** with TBAI in the presence of 1 equivalent of $NaClO_4$ and selected binding isotherms.

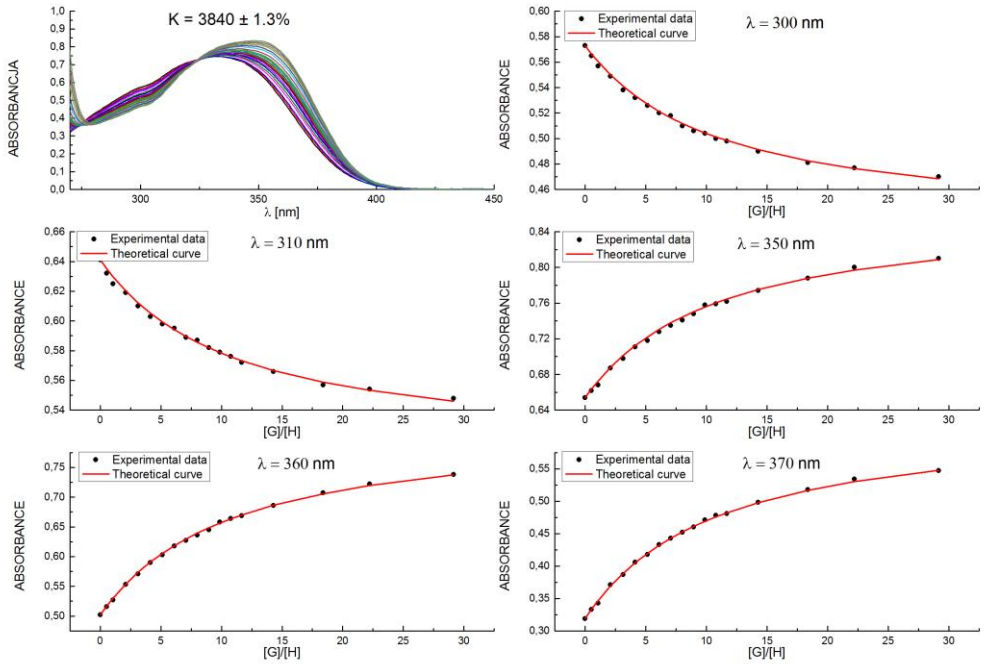


Fig. S10. UV-Vis titration of receptor **1** with TBAI in the presence of 1 equivalent of KPF_6 and selected binding isotherms.

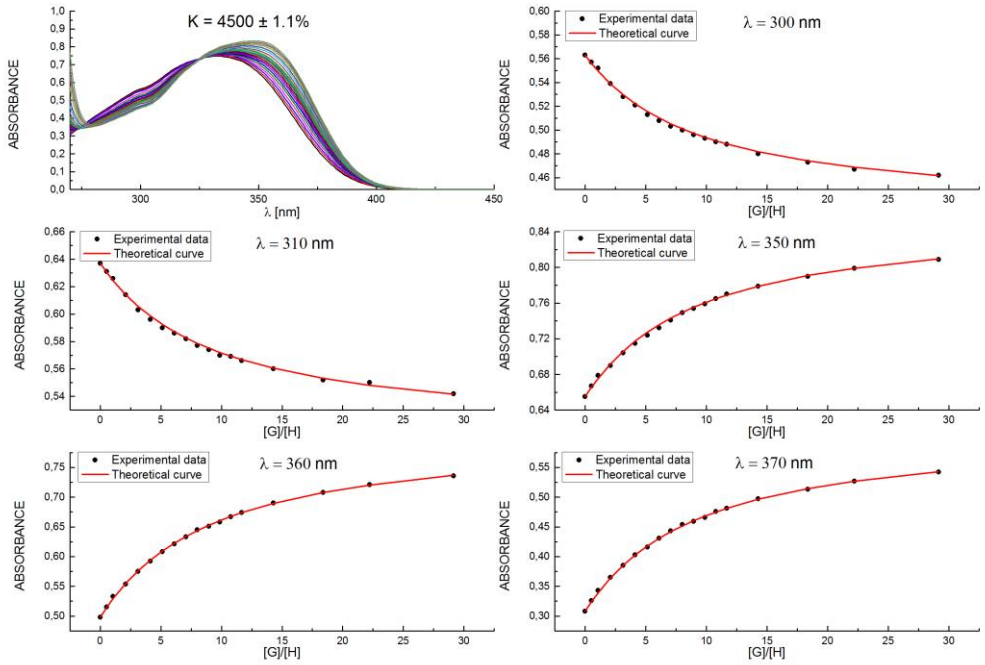


Fig. S11. UV-Vis titration of receptor **1** with $TBANO_2$ and selected binding isotherms.

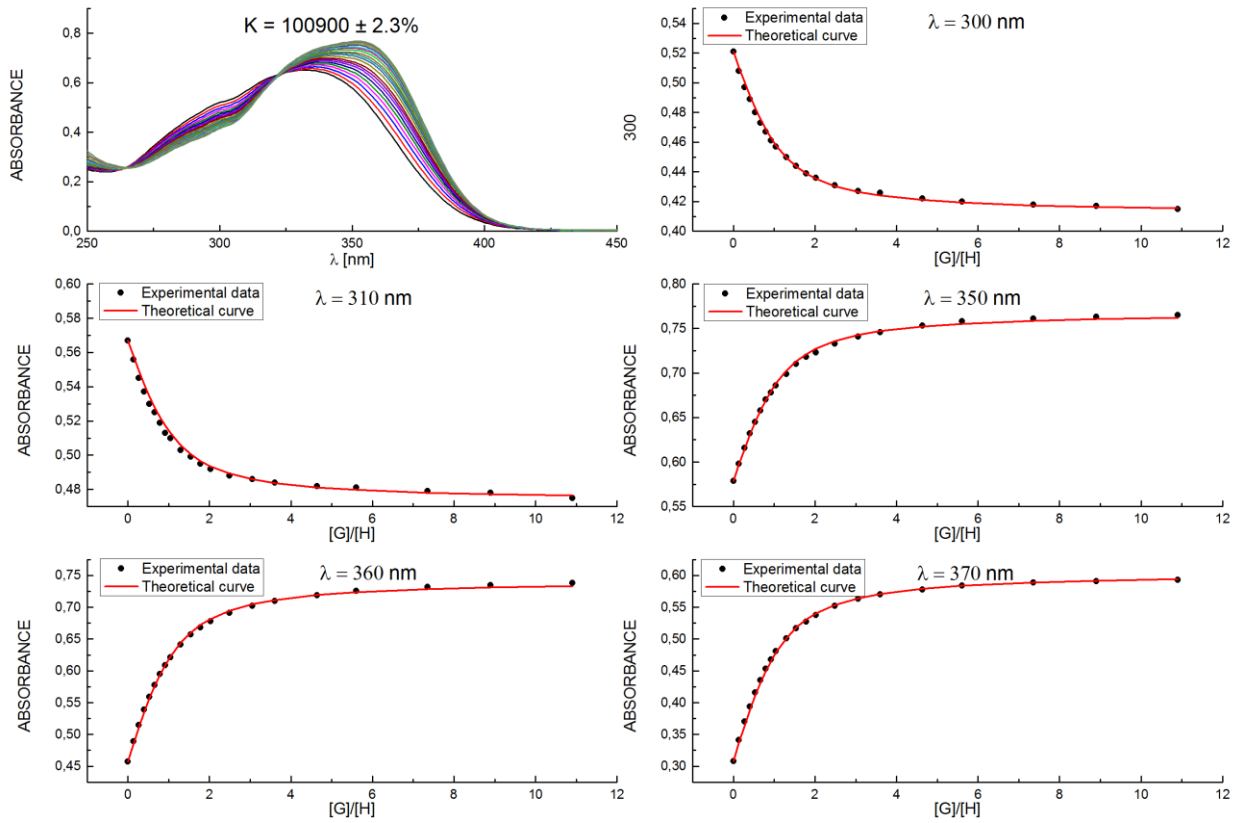


Fig. S12. UV-Vis titration of receptor **1** with $TBANO_2$ in the presence of 1 equivalent of $NaClO_4$ and selected binding isotherms.

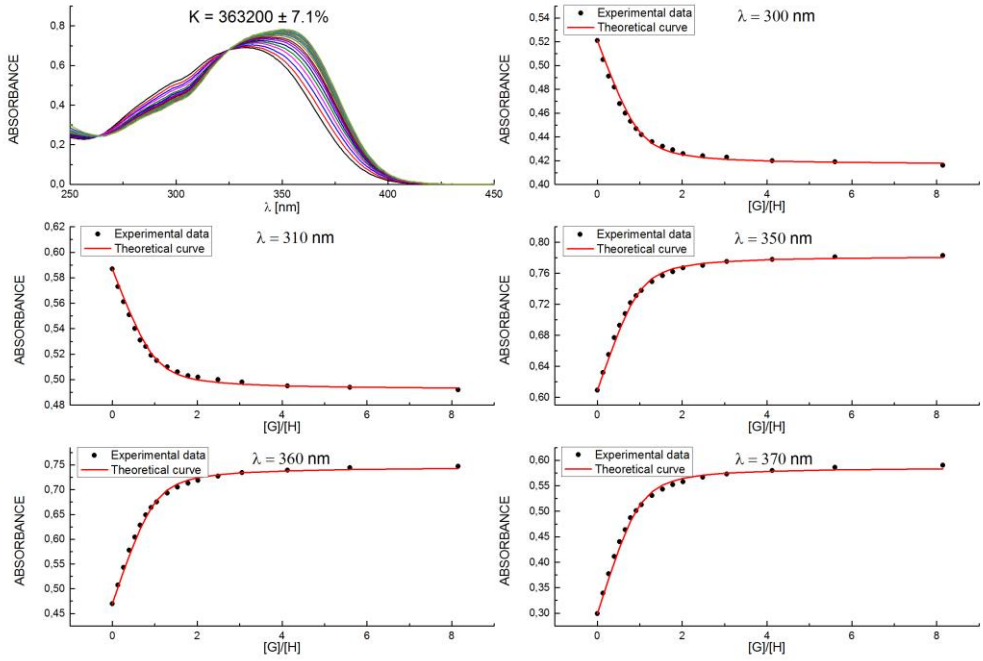


Fig. S13. UV-Vis titration of receptor **1** with $TBANO_2$ in the presence of 1 equivalent of KPF_6 and selected binding isotherms.

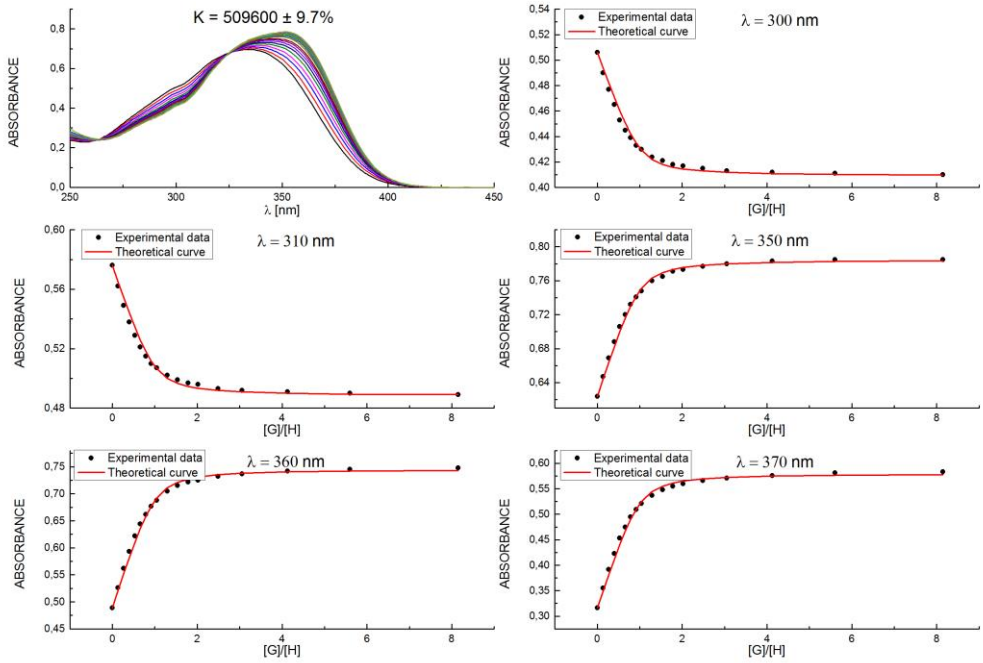


Fig. S14. UV-Vis titration of receptor **1** with $TBANO_3$ and selected binding isotherms.

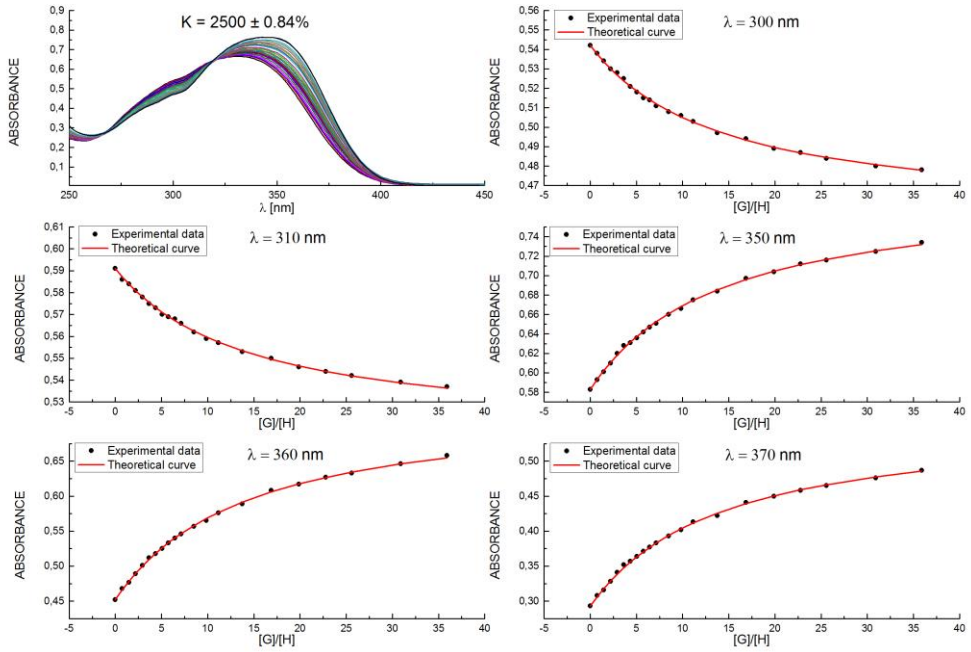


Fig. S15. UV-Vis titration of receptor **1** with $TBANO_3$ in the presence of 1 equivalent of $NaClO_4$ and selected binding isotherms.

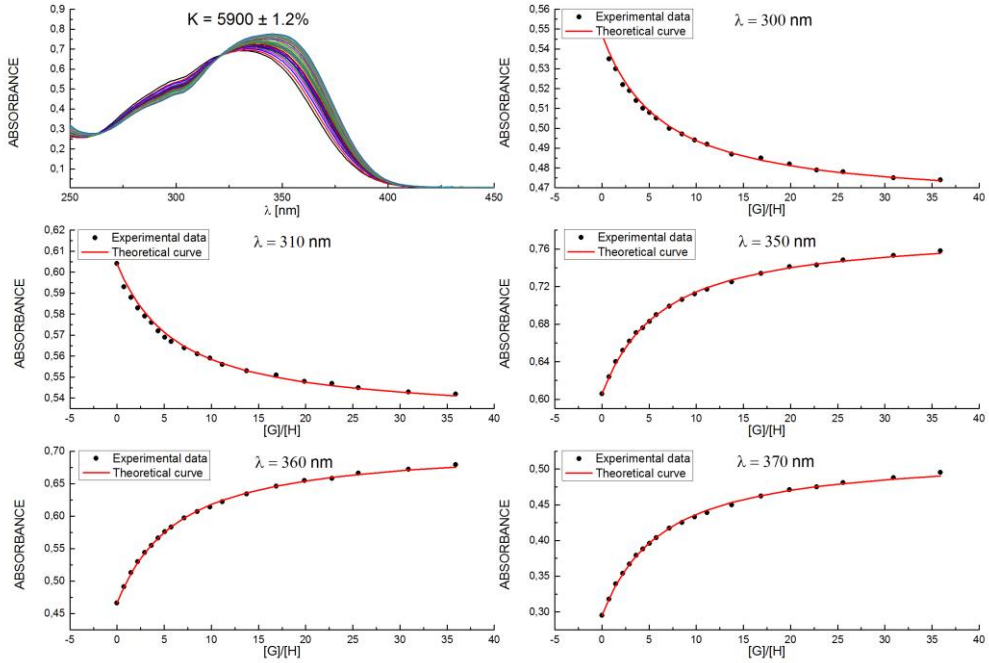


Fig. S16. UV-Vis titration of receptor **1** with $TBANO_3$ in the presence of 1 equivalent of KPF_6 and selected binding isotherms.

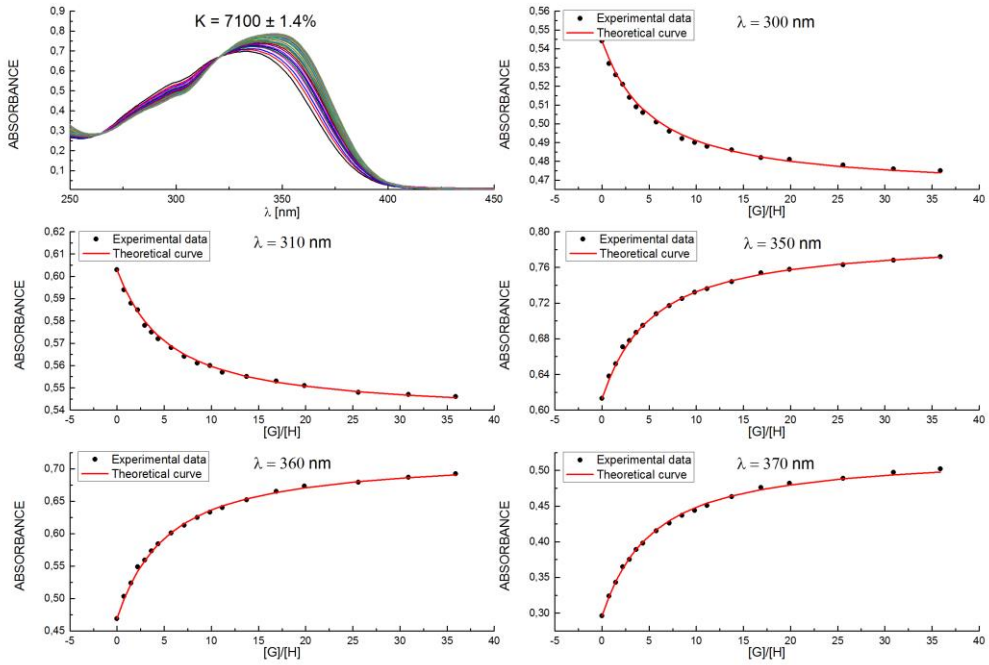


Fig. S17. UV-Vis titration of receptor **1** with TBA_2SO_4 and selected binding isotherms. 2:1 Fitting.

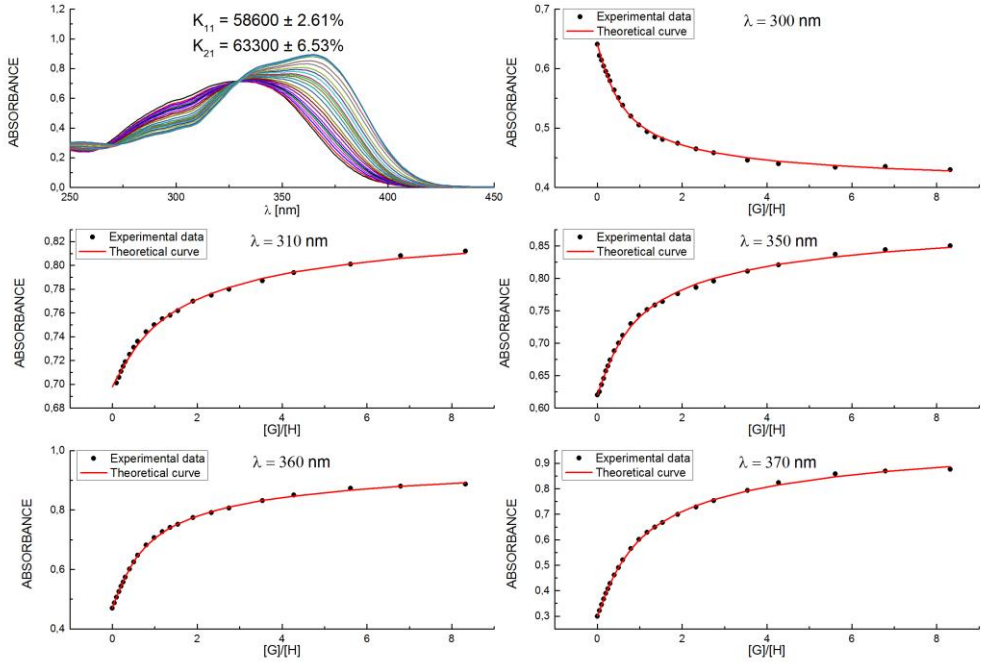


Fig. S18. UV-Vis titration of receptor **1** with $TBAHSO_4$ and selected binding isotherms. 2:1 Fitting.

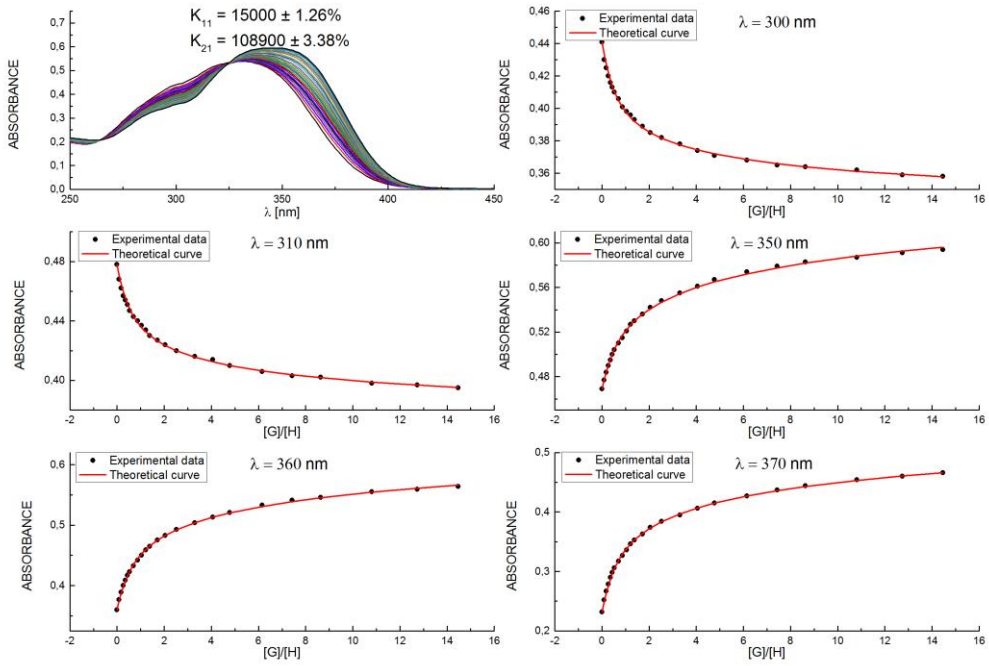


Fig. S19. UV-Vis titration of receptor **1** with $NaClO_4$ and selected binding isotherms.

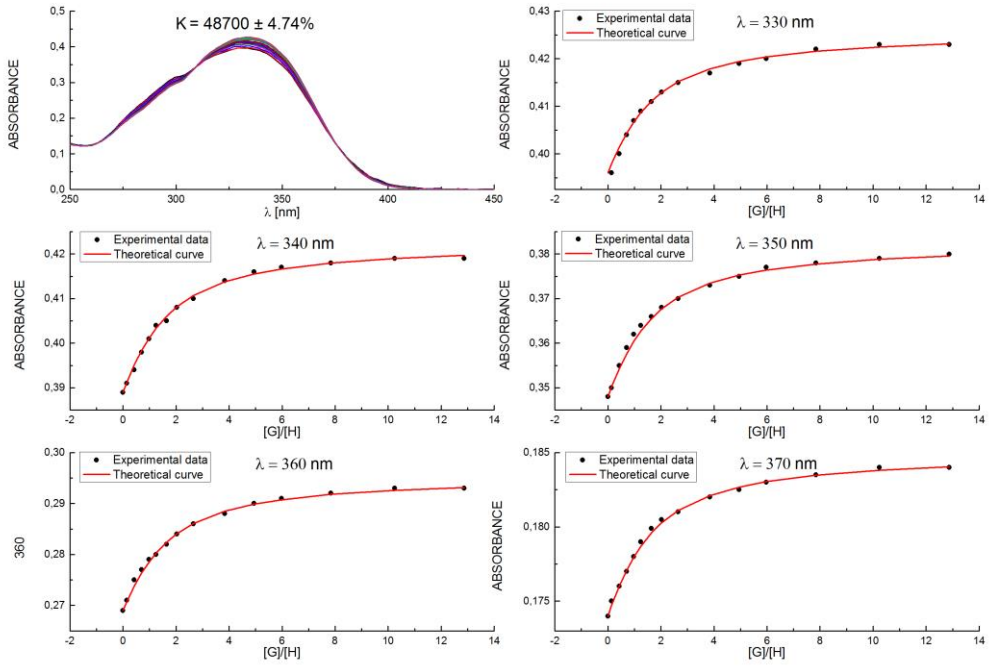


Fig. S20. UV-Vis titration of receptor **1** with KPF_6 and selected binding isotherms.

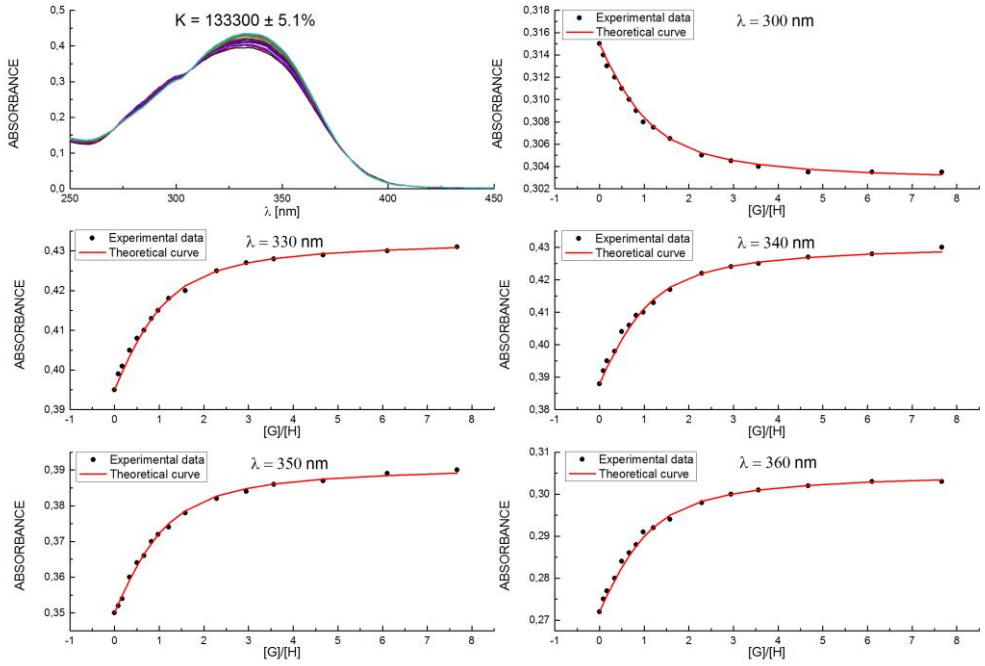


Fig. S21. UV-Vis titration of receptor **1** with NaCl in 5% H_2O (pH=3) in MeCN and selected binding isotherms.

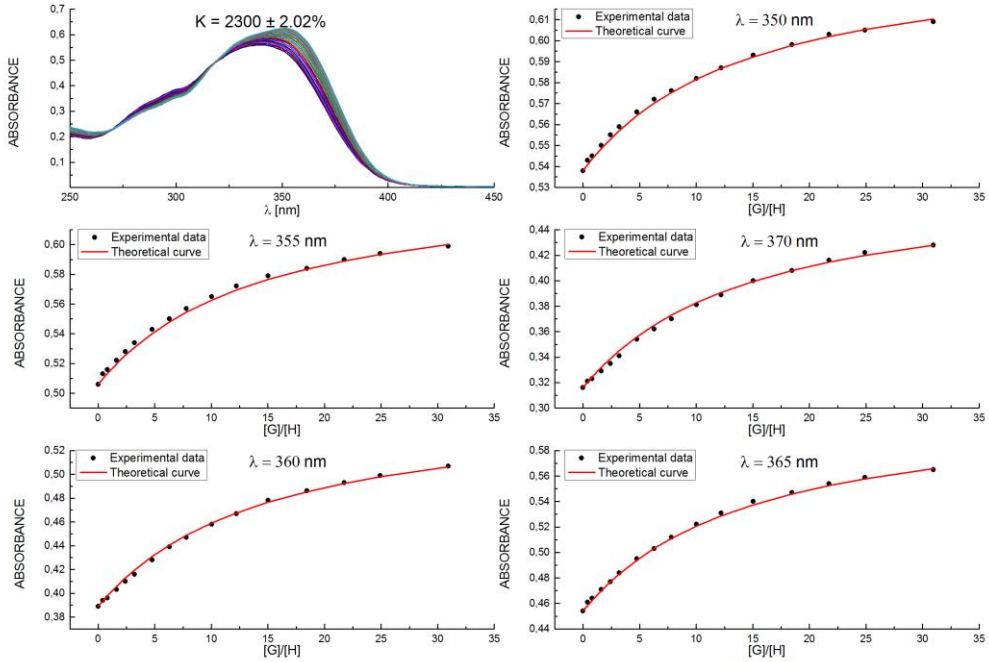


Fig. S22. UV-Vis titration of receptor **1** with KCl in 5% H_2O (pH=3) in MeCN and selected binding isotherms.

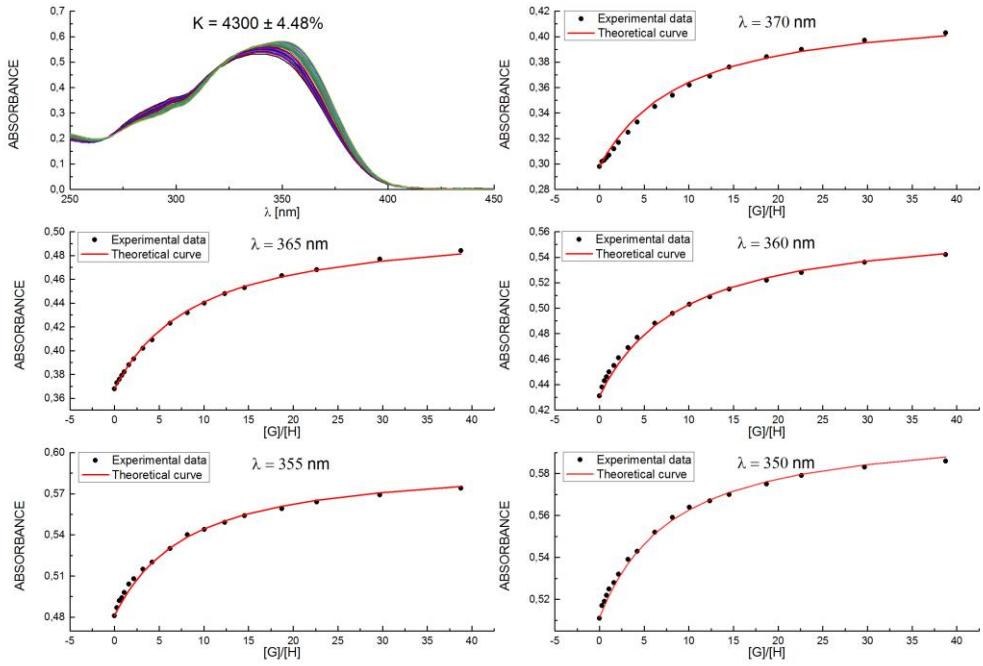


Table S1. Association constants for interactions between receptors **1** with selected anions and apparent association constants for interactions between **1** with anions in the presence of one equivalent of sodium perchlorate and potassium hexafluorophosphate[a].

	1	**1+ 1 eq. $NaClO_4$**	**1 + 1 eq. KPF_6**
Cl^-	176000[b]	492500[b]	766000[b]
Br^-	49800	142000	217000
I^-	1940	3840	4500
NO_2^-	100900	363200	509600
NO_3^-	2500	5900	7100
HSO_4^-	K_{11} = 15000 K_{21} = 108900	-[c]	-[c]
SO_4^{2-}	K_{11} = 58600 K_{21} = 63300	-[c]	-[c]
CH_3COO^-	-[d]	-[d]	-[d]

[a]UV-Vis, solvent CH_3CN, 293 K, [1] = 3.14×10^{-5} M, anions added as TBA salts, where [TBAX] ~ 3×10^{-3} M, M^{-1}, errors < 10%. [b] titrations performed in 0.5% water (pH=3) in acetonitrile; [c] fitting produced a high error rate, the results obtained does not match to any of models; [d] deprotonation.

Attempts were made to fit the data from sulfate titrations to 4:1 binding mode using HypSpec however no reliable data were obtained. Although we could fit the data well with low error the calculated stability constants vary significantly depending on initial stability constants estimated.

Fig. S23. UV-Vis titration of receptor **1** with TBA_2SO_4 in the presence of 1 equivalent of KPF_6 and selected binding isotherms (λ=360, 365 and 370 nm).

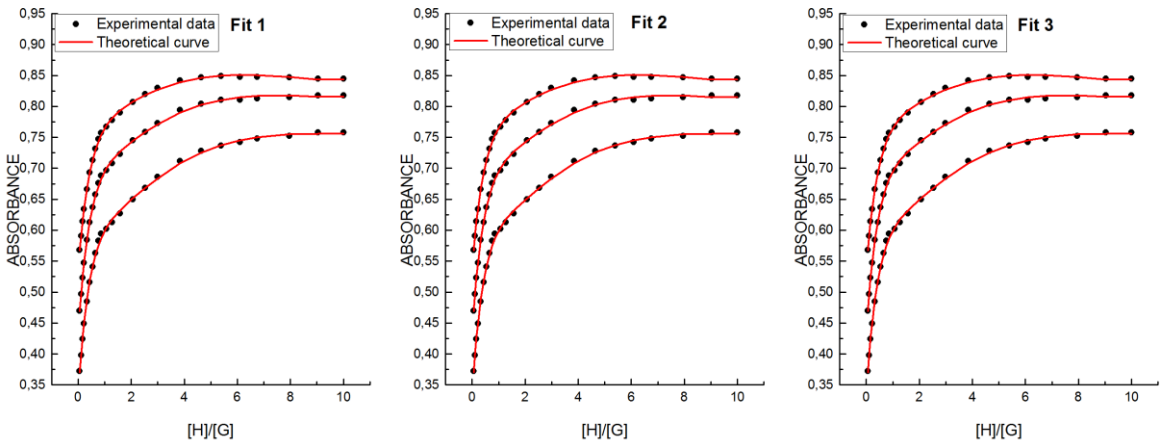


Table S2. Selected set of association constants for interactions between receptors **1** with TBA_2SO_4 in the presence of 1 equivalent of KPF_6.

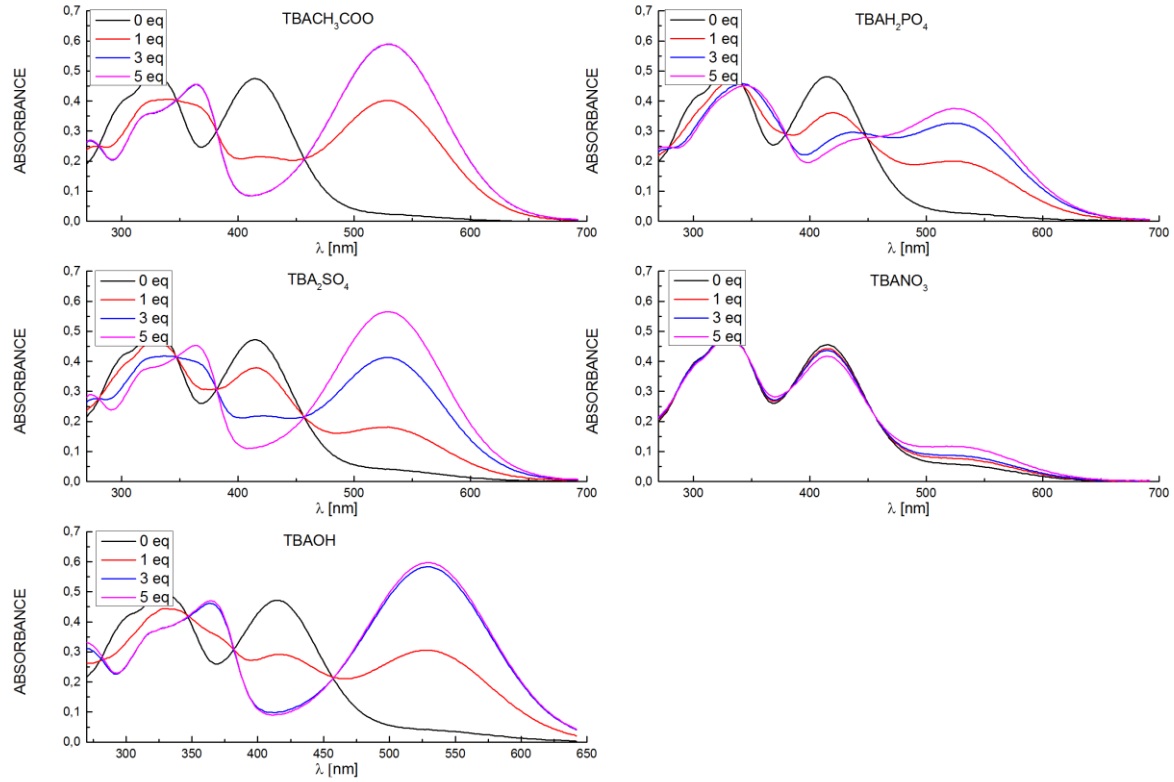
	Fit 1	**Fit 2**	**Fit 3**
$logK_{11}$	4.16	4.16	4.17
$logK_{21}$	3.38	2.83	3.49
$logK_{31}$	3.89	2.15	4.01
$logK_{41}$	5.11	2.87	5.42
σ	$9.96 \cdot 10^{-4}$	$1.13 \cdot 10^{-3}$	$1.08 \cdot 10^{-3}$

Table S3. Association constants for interactions between receptors **1** with sodium chloride and potassium chloride[a].

	NaCl	**KCl**
1	2300	4300

[a]UV-Vis, 5% water (pH=3) in acetonitrile, 293 K, [1] = 3.10×10^{-5} M, [NaCl] = 6.37×10^{-3} M, [KCl] = 4.26×10^{-3} M, M^{-1}, errors < 10%.

Fig. S24. UV-Vis titration spectra of receptor **2** (upon gradual addition of selected salts).



NMR TITRATION

The ^{1}H NMR titration was performed on a Bruker 300 spectrometer, at 298K in CD_3CN. In each case, a 500 μL of freshly prepared 3.55 mM solution of receptor **1** was added to a 5mm NMR tube. In the case of ion pair titration receptor was firstly pretreated with one equivalent of KPF_6 (refers to receptor). Then small aliquots of solution of TBAX, containing **1** at constant concentration, were added and a spectrum was acquired after each addition. The resulting titration data were analyzed using BindFit (v0.5) package, available online at http://supramolecular.org

Fig. S25. $^{1}HNMR$ spectra recorded upon titration of receptor 1 in CD_3CN with $TBANO_3$.

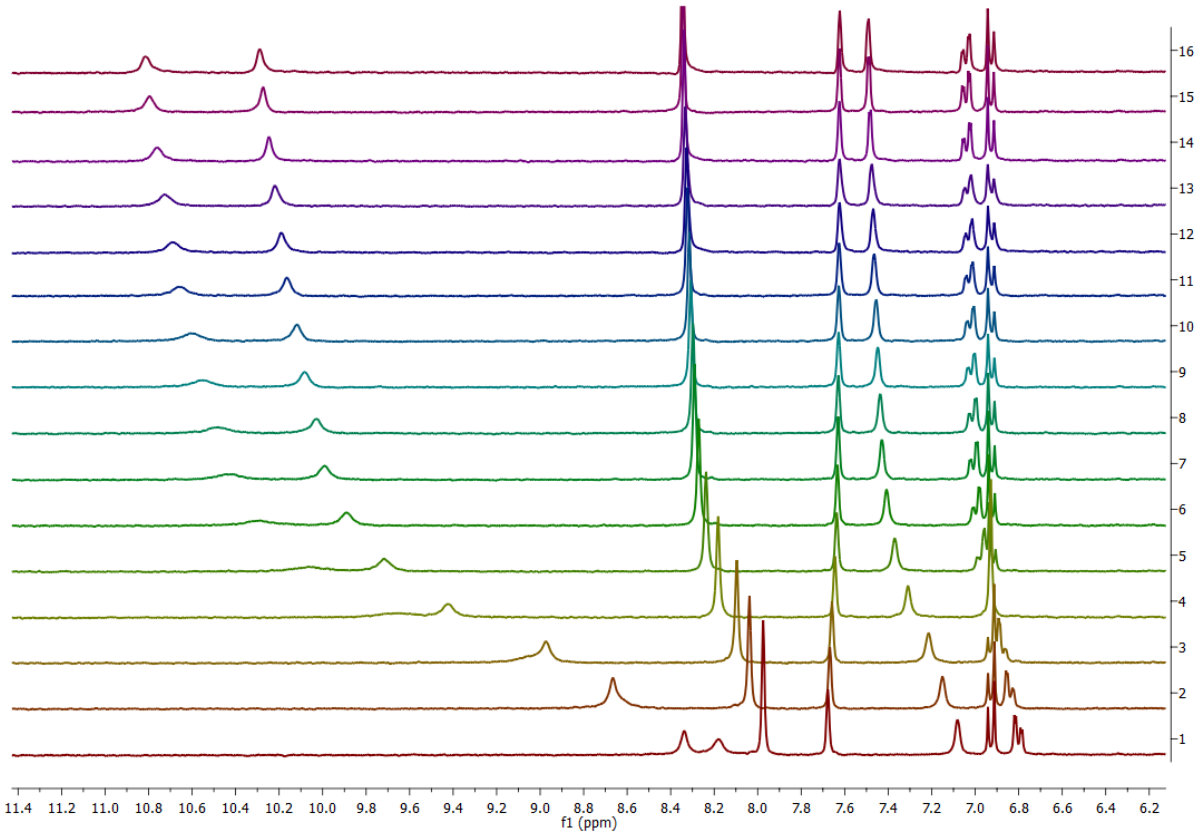


Fig. S26. ^{1}HNMR titration binding isotherms of receptor 1 (3.12×10^{-3}M) in CD_3CN upon addition of increasing amounts of $TBANO_3$.

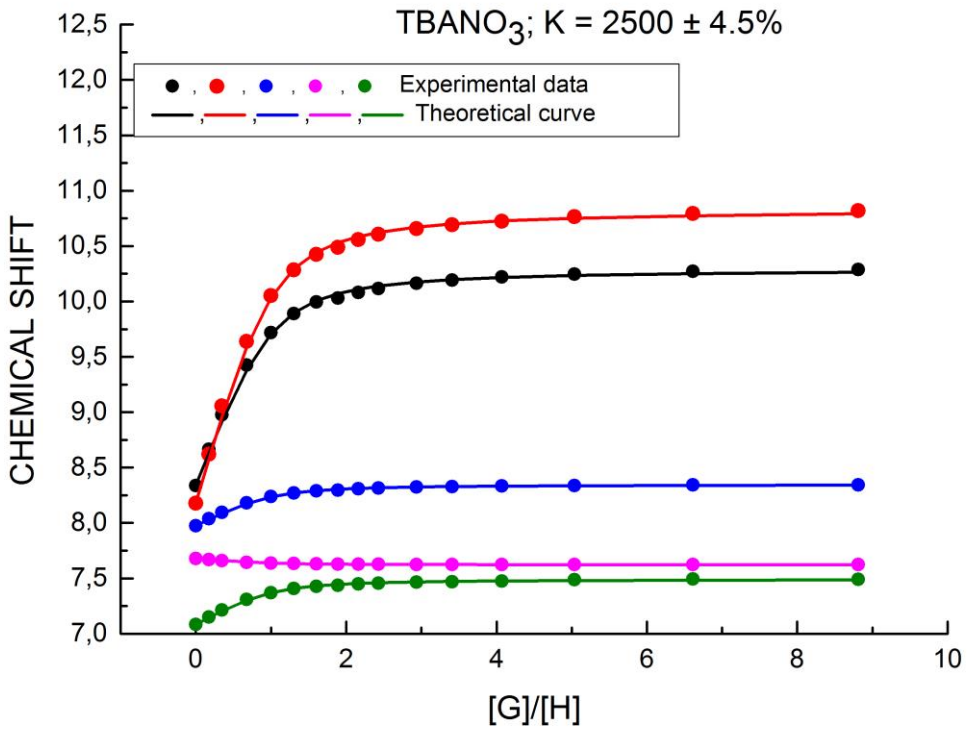


Fig. S27. ^{1}HNMR spectra recorded upon titration of receptor 1 in CD_3CN with $TBANO_3$ in the presence of 1 eq. KPF_6.

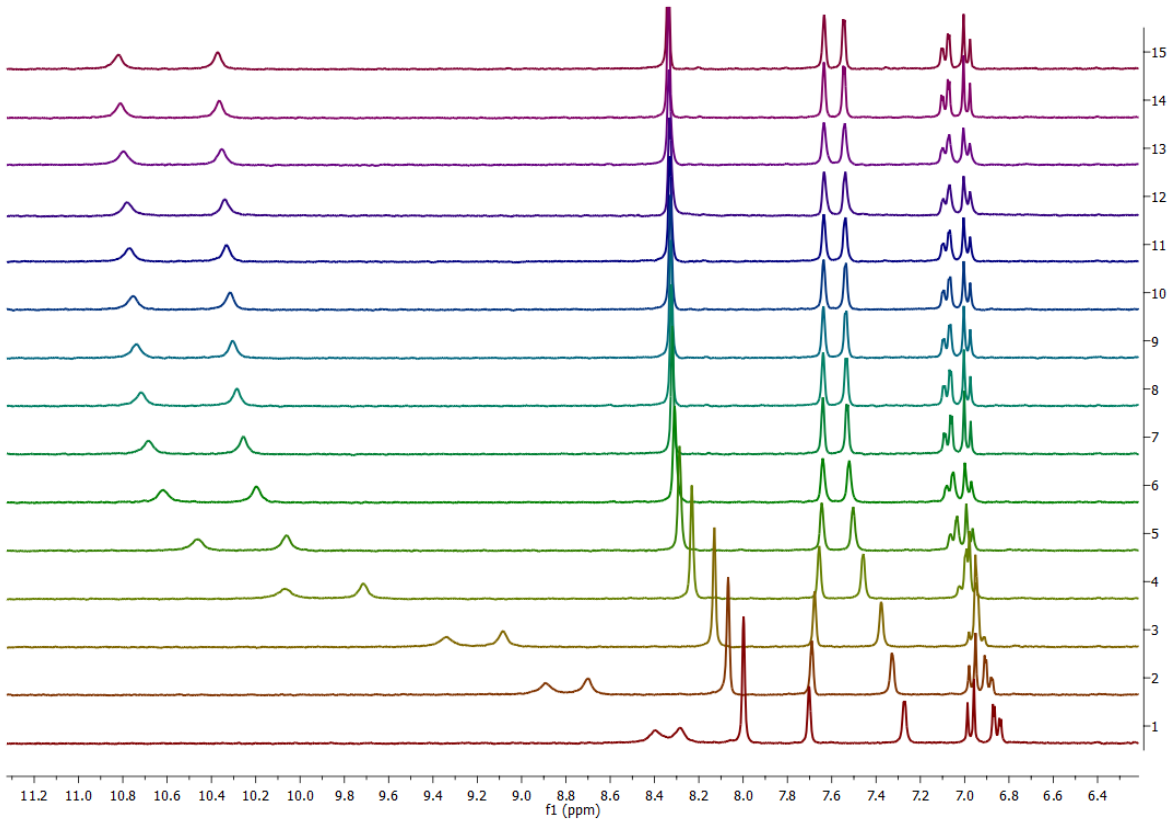


Fig. S28. ^{1}HNMR titration binding isotherms of receptor 1 (3.12×10^{-3}M) in CD_3CN upon addition of increasing amounts of $TBANO_3$ in the presence of 1 eq. KPF_6.

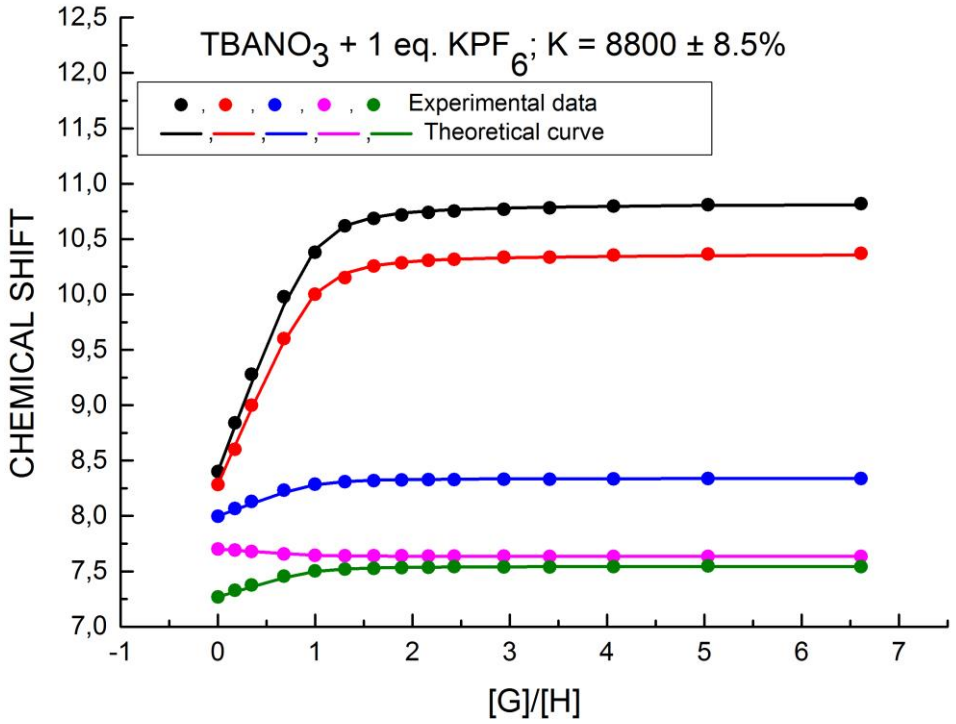


Fig. S29. ^{1}HNMR spectra recorded upon titration of receptor **1** (3.12×10^{-3}M) in CD_3CN with TBA_2SO_4 (Signals corresponding to amide and phenyl protons). Left figure - titration performed in the range from 0.0 equiv. to 7.22 equiv, right figure - titration performed in the range from 0.0 equiv. to 0.43 equiv.

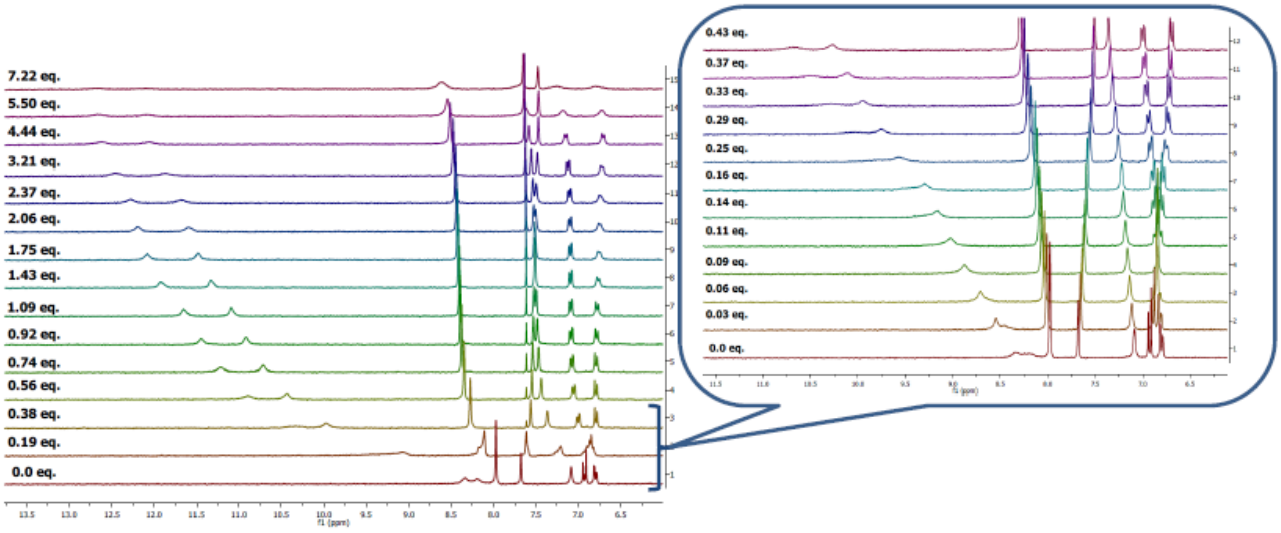


Fig. S30. ^{1}HNMR spectra recorded upon titration of receptor **1** (3.12×10^{-3}M) in CD_3CN with TBA_2SO_4 (Signals corresponding to crown ether). Left figure - titration performed in the range from 0.0 equiv. to 7.22 equiv, right figure - titration performed in the range from 0.0 equiv. to 0.43 equiv.

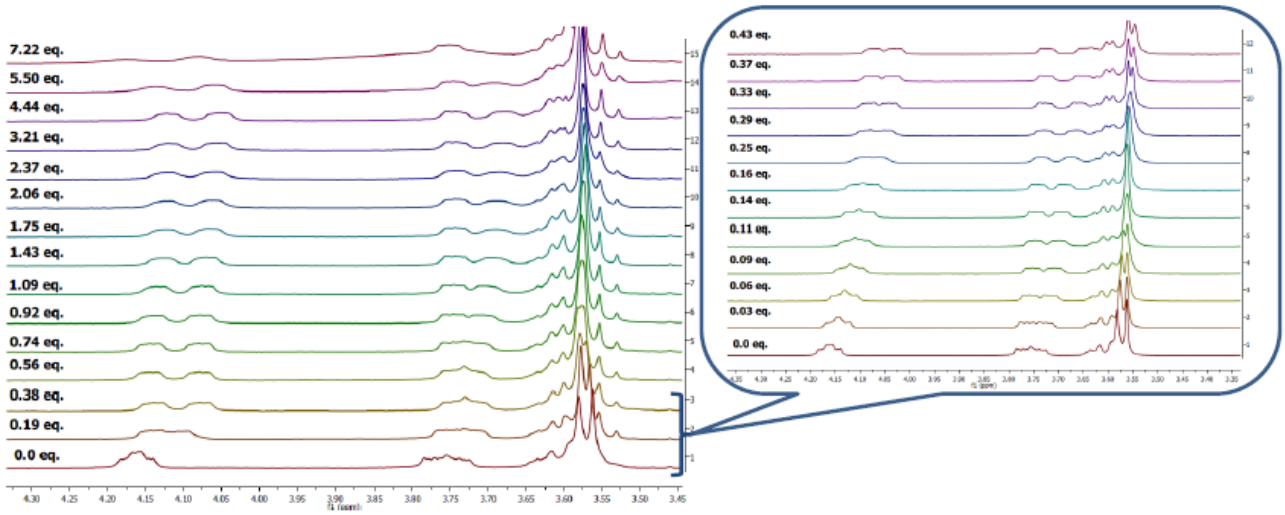


Fig. S31. ^{1}HNMR spectra recorded upon titration of receptor **1** (3.12×10^{-3}M) in CD_3CN with TBA_2SO_4 in the presence of 1 equiv. KPF_6 (Signals corresponding to amide and phenyl protons). Left figure - titration performed in the range from 0.0 equiv. to 7.22 equiv, right figure - titration performed in the range from 0.0 equiv. to 0.43 equiv.

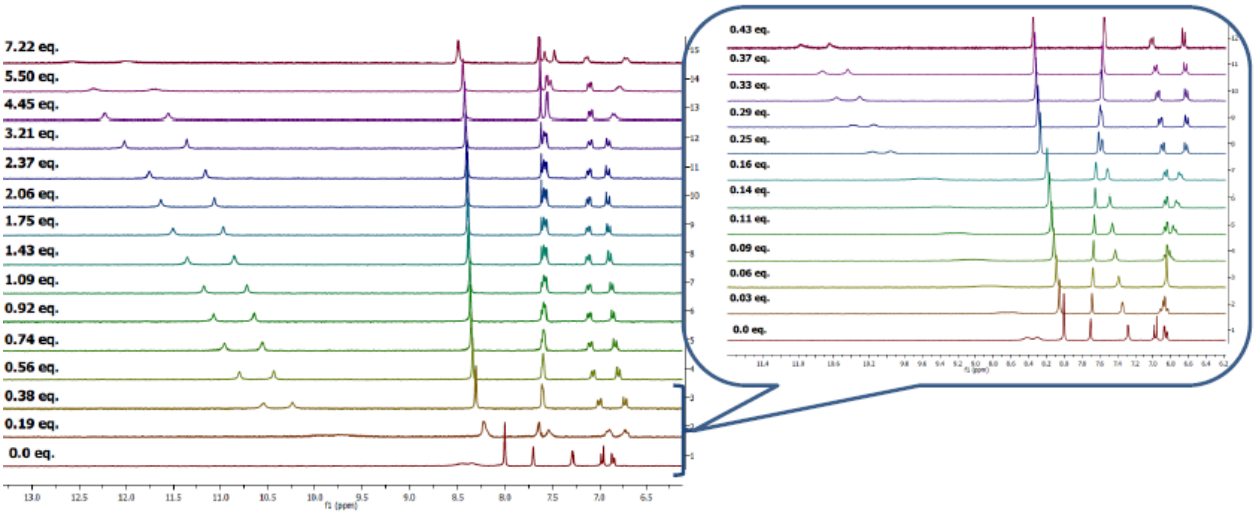


Fig. S32. ^{1}HNMR spectra recorded upon titration of receptor **1** (3.12×10^{-3}M) in CD_3CN with TBA_2SO_4 in the presence of 1 equiv. KPF_6 (Signals corresponding to crown ether protons). Left figure - titration performed in the range from 0.0 equiv. to 7.22 equiv, right figure - titration performed in the range from 0.0 equiv. to 0.43 equiv.

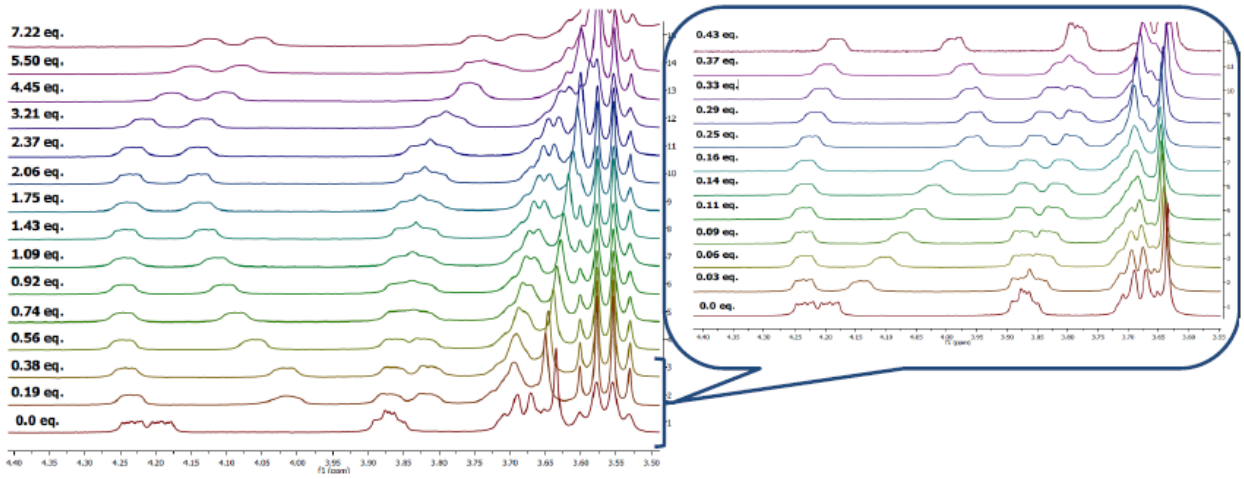
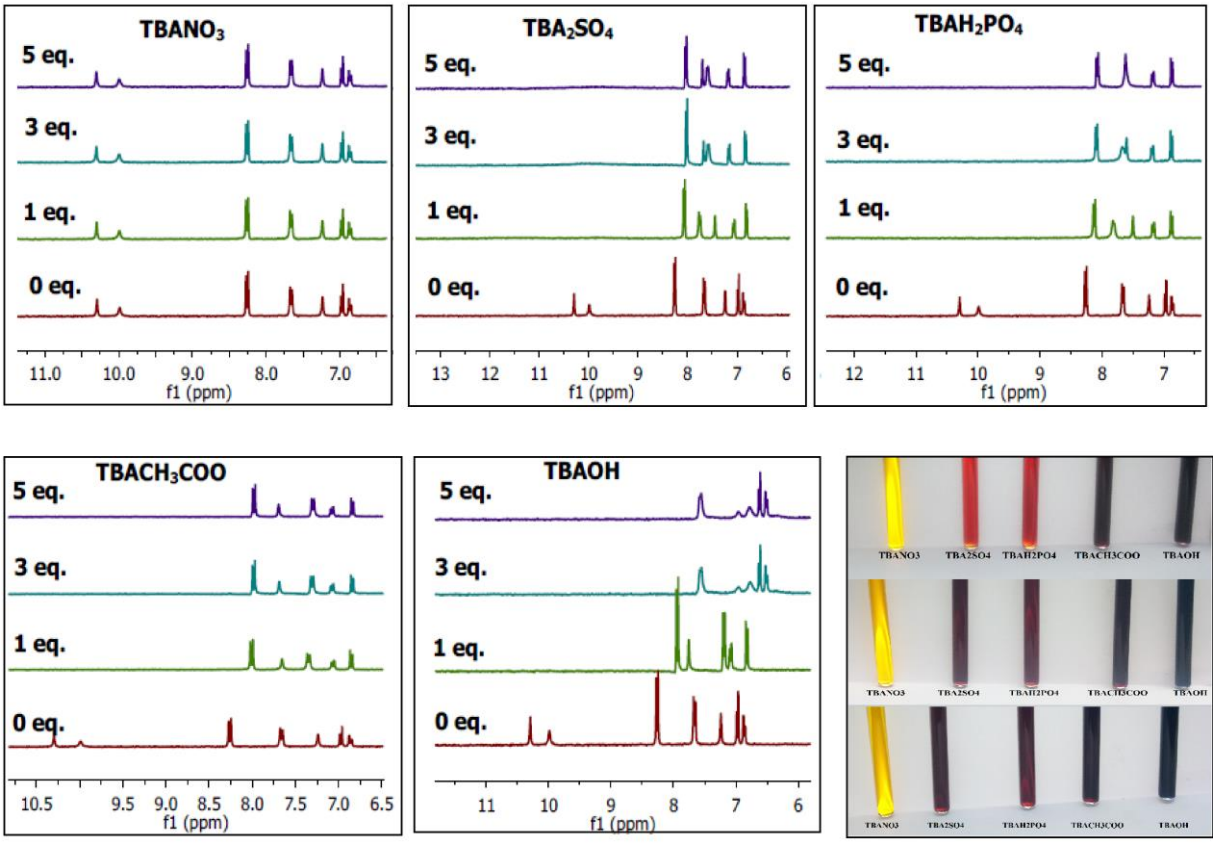


Fig. S33. Partial ^{1}H NMR spectra of receptor **2** (upon gradual addition of selected salts). Color changes upon addition of these salts into receptor **1** solution (from top: 1, 3 and 5 equivalents).



EXTRACTION EXPERIMENTS - ATOMIC EMISSION SPECTROSCOPY

General procedure: A solution of receptor in chloroform (1 ml, 2 mM) and 0.5 M aqueous K_2SO_4 were mixed thoroughly for 5 minutes in a vial (prolongation of the extraction time had no effect on the results obtained). The vial was allowed to stand to fully separate the two phases. Then 0.5 mL of organic phase was taken and diluted to 5 mL with ethyl acetate. The potassium concentration in organic phase was determined by atomic emission spectroscopy (AES). For receptor 1 back extraction experiment was also performed. Specifically, separated organic phase (1 ml) after extraction with 0.5 M aqueous K_2SO_4 solution was mixed thoroughly with deionized water (1 ml) for 5 min. After phase separation the organic phase was taken (0.5 ml), diluted to 5 mL with ethyl acetate and analyzed.

Fig. S34. Calibration curve generated using a standard solution of KPF_6 in solvent mixture, $V_{chloroform}/V_{ethyl\ acetate}$ = 1/9.

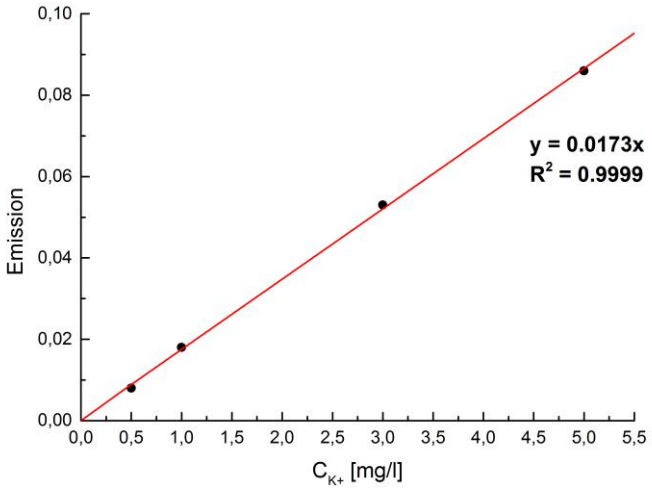


Table S4. Results of potassium extraction experiments

	C_{K^+} [mg/L][a]	Extraction efficiency/ Receptor occupation [%]
Receptor 1[2 mM]		
Extraction from aq. solution of K_2SO_4	2.86	36
Back extraction	1.36	17[b]
Receptor S3[2 mM]		
Extraction from aq. solution of K_2SO_4	0.04	-
Receptor S3 / 4-nitrobenzo-18-crown-6-ether [2 mM / 2 mM]		
Extraction from aq. solution of K_2SO_4	0.62	8
Receptor S4[2 mM]		
Extraction from aq. solution of K_2SO_4	0.08	1
Blank (chloroform)		
Extraction from aq. solution of K_2SO_4	0.01	-

[a] concentration after ten times dilution with ethyl acetate

[b] receptor occupation after back extraction (once washing with water); after three cycles the occupation decreases to 1%

EXTRACTION EXPERIMENTS – MASS SPECTROMETRY

Fig. S35. MS of chloroformic solution of **1** after aq. K_2SO_4 extraction (positive ion mode)

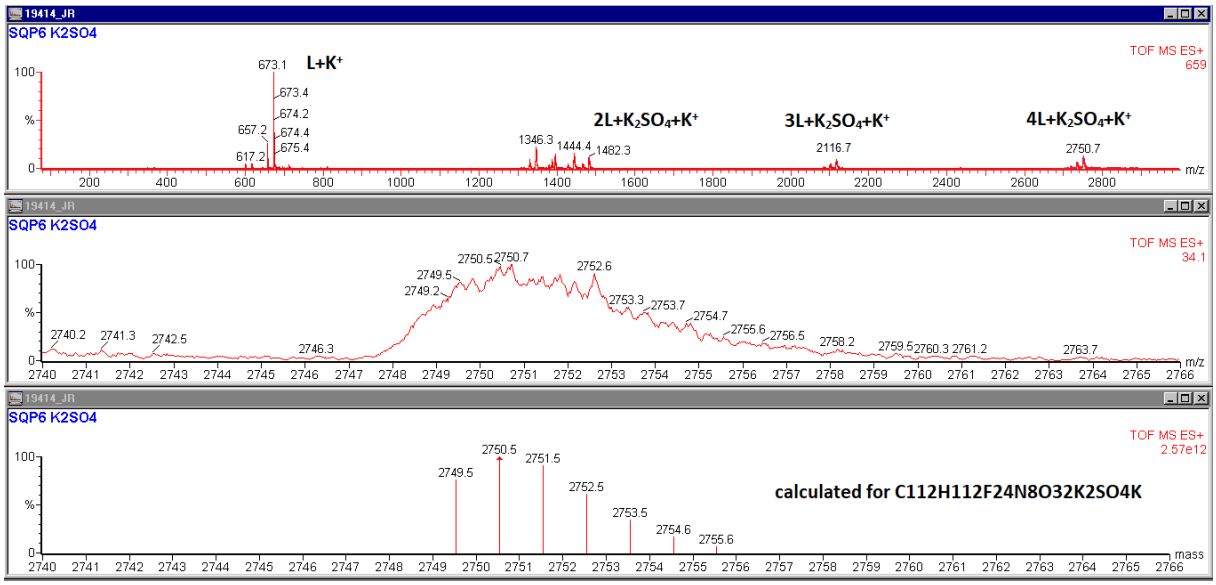
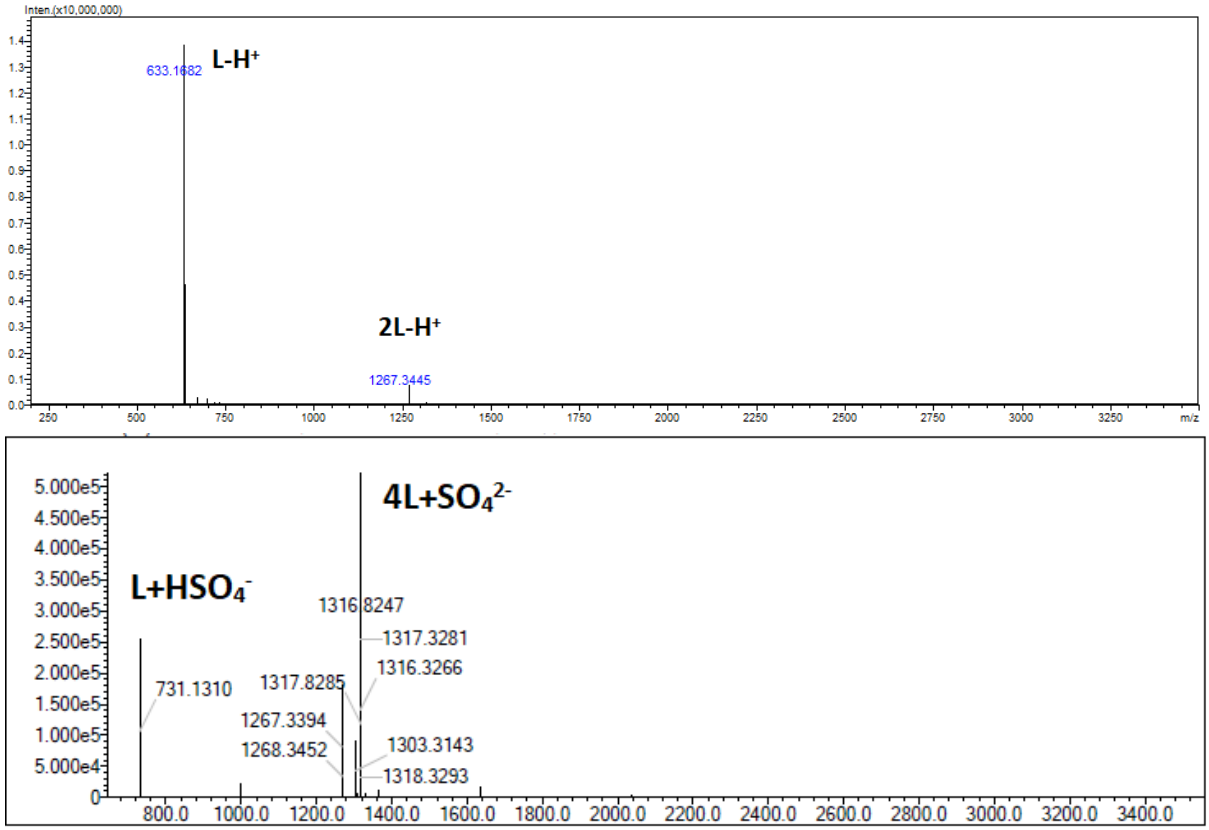
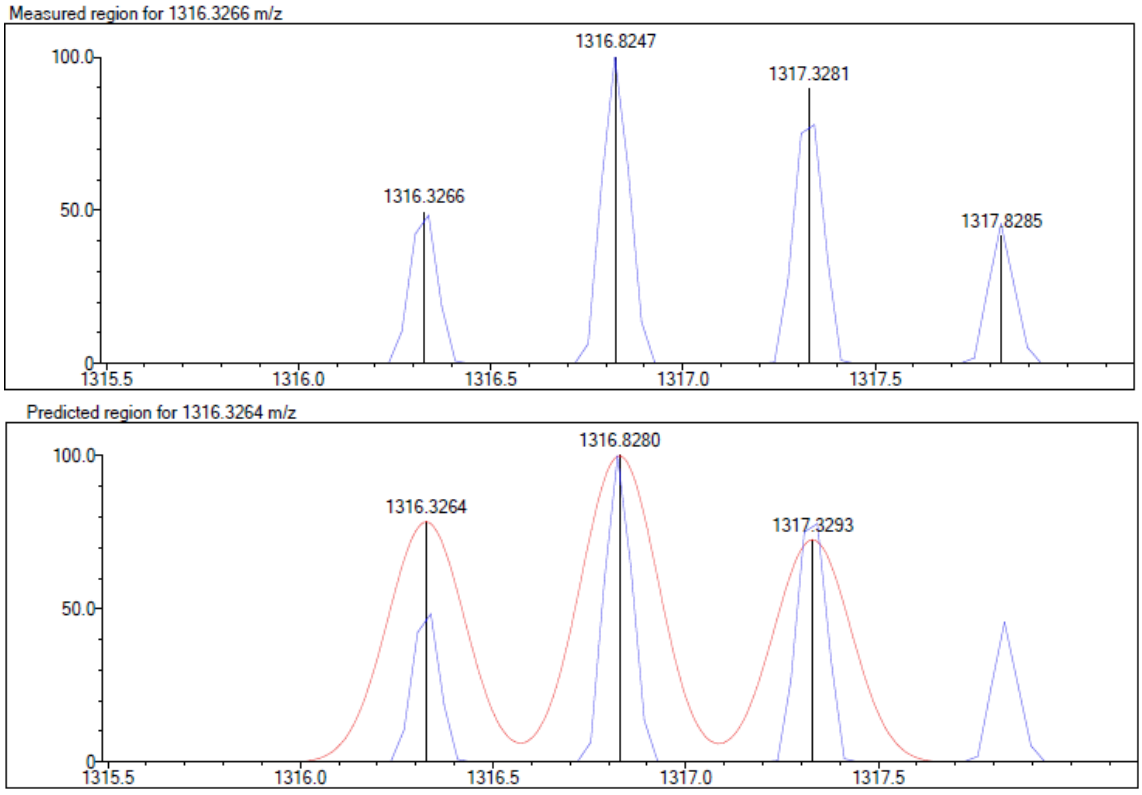


Fig. S36. MS of chloroformic solution of **1** after aq. K_2SO_4 extraction (negative ion mode)




Measured region for 1316.3266 m/z
1316.8247
1317.3281
1316.3266
1317.8285
100.0
50.0
0
1315.5
1316.0
1316.5
1317.0
1317.5
Predicted region for 1316.3264 m/z
1316.8280
1316.3264
1317.3293
100.0
50.0
0
1315.5
1316.0
1316.5
1317.0
1317.5

EXTRACTION EXPERIMENTS - ION CHROMATOGRAPHY

General procedure: A solution of receptor **1** in chloroform (2 ml, 5 mM or 20 mM) was intensive shaking with aqueous mixture (pH 6.0-7.5 depending of the salts used; above pH 8 there is no phase separation probably due to the receptor deprotonation. This eliminates direct use of basic salts such as hydrogen phosphates or phosphates) of suitable salts 5 mM each (2 ml) for 5 minutes. Then 1 mL of aqueous phase was taken and tenfold diluted. The concentration of chloride, bromide, nitrite, nitrate and sulfate anions in aqueous phase was determined by high performance ion chromatography (HPIC). In the case of back extraction 1 ml of organic phase after extraction was taken and intensive shaking with deionized water (4 x 2 ml). Collected aqueous phases were combined, diluted to 10 ml and analyzed. Differences in retention times (Fig.37 and Fig.38-39) result from the use of other equipment.

Fig. S37. Chromatograms obtained during extraction experiments after tenfold dilution (a) source phase: aqueous solution of potassium salts of chlorides, bromides, nitrates, nitrites and sulfates (b) after extraction with 5 mM of **1** in $CHCl_3$ (c) after extraction with 20 mM of **1** in $CHCl_3$.

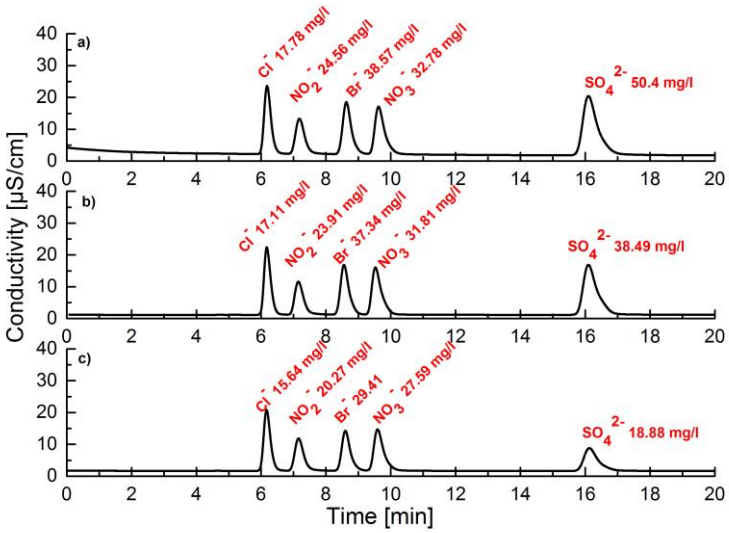


Fig. S38. Chromatograms obtained during extraction experiments after tenfold dilution (a) source phase: aqueous solution of potassium sulfate and potassium dihydrogen phosphate (b) after extraction with 5 mM of **1** in $CHCl_3$. In the chromatograms PO_4^{3-} is reported due to existing of this form in pH of eluent.

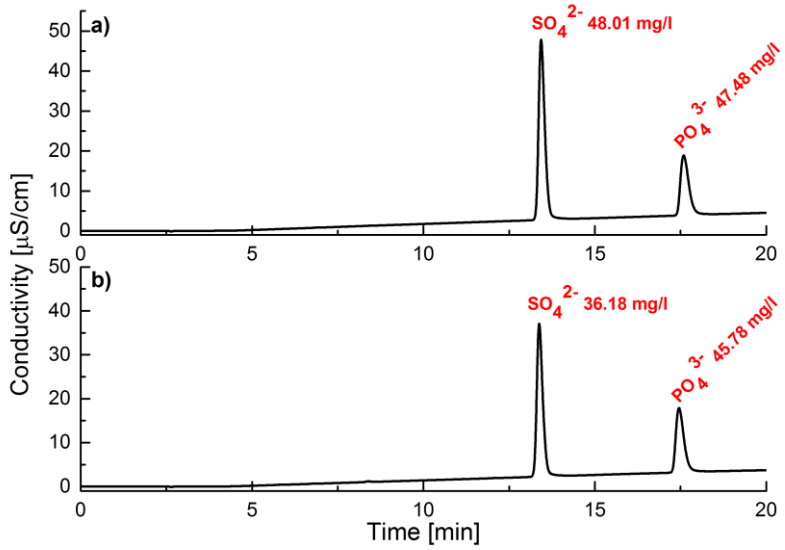
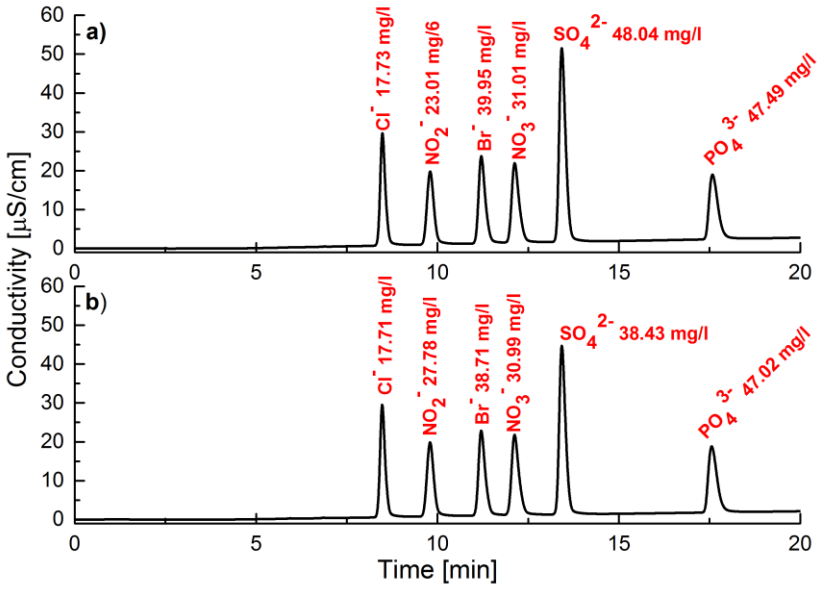


Fig. S39. Chromatograms obtained during extraction experiments after tenfold dilution (a) source phase: aqueous solution of potassium salts of chlorides, bromides, nitrates, nitrites, sulfates dihydrogen phosphates (b) after extraction with 5 mM of **1** in $CHCl_3$. In the chromatograms PO_4^{3-} is reported due to existing of this form in pH of eluent.



CRYSTAL DATA

Single crystal X-ray diffraction

The final crystal data and structure refinement parameters for crystals **[1×Na_2SO_4]**, **[1×KNO_3]** and **[1×H_2O]** are collected in **Table S3**. The numbering scheme of all heavy atoms in the ligand molecule used for each X-ray structure is presented in **Figure S40**. Thermal ellipsoid plots for each structure are collected in **Figure S41**.

Table S5. Crystal data and structure refinement parameters for **[1×Na_2SO_4]**, **[1×KNO_3]** and **[1×H_2O]**.

Identification code	**[1×Na_2SO_4]**	**[1×KNO_3]**	**[1×H_2O]**
Formula	$C_{238.88}H_{234}F_{48}N_{19.29}Na_4O_{87.20}S_2$	$C_{58.59}H_{61.07}F_{12}K_2N_{6.71}O_{22.30}$	$C_{28}H_{30}F_6N_2O_9$
M_x**/ g·mol^{-1}**	5838.34	1522.15	652.54
***T*/ K**	104(2)	130(2)	125(2)
***λ*/ Å**	0.71073	0.71073	0.71073
Crystal size/ mm	0.174×0.354×0.609	0.142×0.179×0.404	0.047×0.116×0.291
Space group	*Cc*	$P\bar{1}$	$P2_1/c$
Unit cell dimensions	*a* = 38.656(4) Å *b* = 18.5689(19) Å *c* = 22.026(2) Å *β* = 115.432(3)°	*a* = 11.6762(5) Å *b* = 14.1244(7) Å *c* = 20.8720(10) Å *α* = 100.7753(16)° *β* = 91.7229(17)° *γ* = 99.9343(17)°	*a* = 21.627(4) Å *b* = 15.667(3) Å *c* = 8.4646(18) Å *β* = 100.217(6)°
V*/ Å^3, *Z	14278.(2), 2	3323.9(3) , 2	2822.6(10) , 4
D$_x$/ g·cm^{-3}	1.358	1.521	1.536
***μ*/ mm^{-1}**	0.142	0.258	0.139
***F*(000)**	6016	1568	1352
θ_{min}, θ_{max}	2.17°, 25.05°	2.24°, 26.00°	2.87°, 25.06°
Index ranges	-46≤*h*≤45 -22≤*k*≤22 -26≤*l*≤26	-14≤*h*≤14 -17≤*k*≤17 -25≤*l*≤25	0≤*h*≤25 -18≤*k*≤0 -10≤*l*≤9
Reflections collected	68818	94264	39121
Independent reflections	23682 [R_{int} = 0.0656]	13061 [R_{int} = 0.0267]	4981 [R_{int} = 0.0772]
Completeness	99.2%	99.9%	99.5%
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
T_{max}, T_{min}	0.976, 0.919	0.964, 0.903	0.993, 0.961
Refinement method	Full-matrix LSQ on F^2	Full-matrix LSQ on F^2	Full-matrix LSQ on F^2
Data / restraints / parameters	23682 / 1327 / 2577	13061 / 117 / 1039	4981 / 9 / 437
Goodness-of-fit on F^2	1.437	1.032	1.031
Final *R* indices	13039 data; $I>2\sigma(I)$ $R1$ = 0.0934, $wR2$ = 0.2267 all data $R1$ = 0.1639, $wR2$ = 0.2684	11238 data; $I>2\sigma(I)$ $R1$ = 0.0363, $wR2$ = 0.0849 all data $R1$ = 0.0441, $wR2$ = 0.0901	4093 data; $I>2\sigma(I)$ $R1$ = 0.0429, $wR2$ = 0.0962 all data $R1$ = 0.0596, $wR2$ = 0.1026
Absolute structure parameter	0.09(8)	-	-
Extinction	0.0016(2)	-	0.0044(9)
ρ_{max}, ρ_{min}	0.471 e·Å^{-3}, -0.332 e·Å^{-3}	0.436 e·Å^{-3}, -0.407 eÅ^{-3}	0.217 e·Å^{-3}, -0.223 eÅ^{-3}

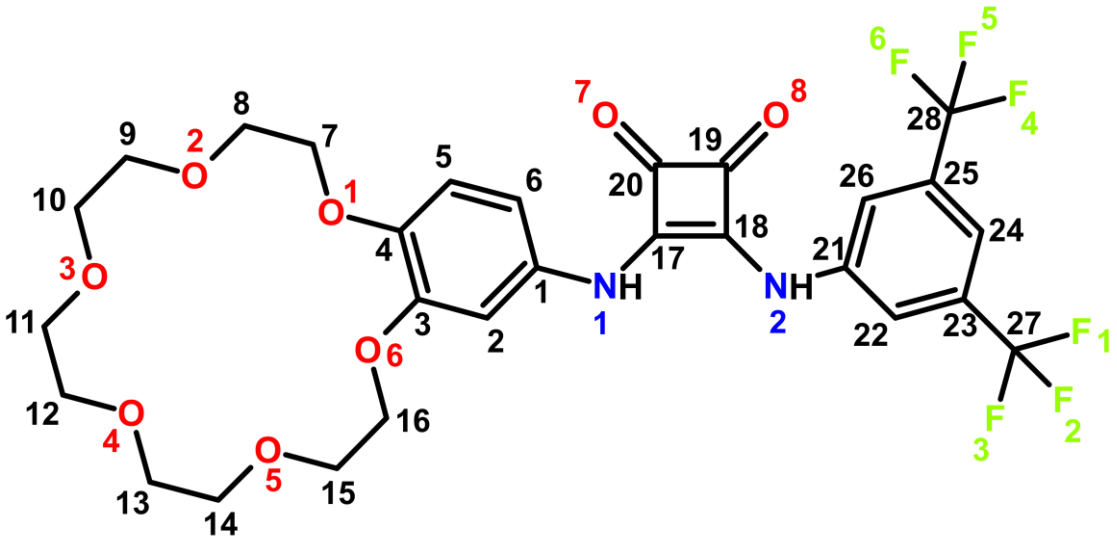


Fig. S40. Basic numbering scheme of non-H atoms in ligand **1** used in all crystal structures.

[1×Na_2SO_4]

The X-ray measurement of pale yellow prism-like specimen of **[1×Na_2SO_4]** with approximate dimensions 0.174×0.354×0.609 mm was performed at 104(2) K on a Bruker D8 Venture PhotonII diffractometer equipped with a TRIUMPH monochromator and a MoKα fine focus sealed tube (λ = 0.71073 Å). A total of 846 frames were collected with Bruker APEX3 program.[2] The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.[3] The integration of the data using a monoclinic unit cell yielded a total of 68818 reflections to a maximum θ angle of 25.05° (0.84 Å resolution), of which 23682 were independent (average redundancy 2.906, completeness = 99.2%, R_{int} = 6.56%, R_{sig} = 9.13%) and 13039 (55.06%) were greater than $2\sigma(F^2)$. The final cell constants of a = 38.656(4) Å, b = 18.5689(19) Å, c = 22.026(2) Å, β = 115.432(3)°, V = 14278.(2) Å^3, are based upon the refinement of the XYZ-centroids of 9986 reflections above 20 $\sigma(I)$ with 4.639° < 2θ < 45.76°. Data were corrected for absorption effects using the Multi-Scan method (SADABS).[4] The ratio of minimum to maximum apparent transmission was 0.735. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.919 and 0.976.

The structure was solved and refined using SHELX[6,7] software package using the space group *Cc*, with Z = 2 for the formula unit, $C_{238.88}H_{234}F_{48}N_{19.29}Na_4O_{87.20}S_2$ and Flack parameter[8] yielding 0.09(8). The final anisotropic full-matrix least-squares refinement on F^2 with 2577 variables converged at $R1$ = 9.34%, for the observed data and $wR2$ = 26.84% for all data. The

goodness-of-fit was 1.437. The largest peak in the final difference electron density synthesis was 0.471 $e^-/Å^3$ and the largest hole was -0.332 $e^-/Å^3$ with an RMS deviation of 0.083 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.358 g/cm^3 and $F(000)$, 6016 e^-.

The structure in the asymmetric part of the unit cell contains four ligand molecules (denoted from A to D), two sodium cations, one sulfate anion and non stoichiometric amount of solvent species: acetonitrile, water, methanol and diethyl ether. Two ligands (A and C) have Na ions coordinated in the crown ether fragment. The cations are additionally coordinated by two water species in molecule A, whereas in the molecule C the cation is coordinated by H_2O and acetonitrile moieties. The structure is severely disordered. All ligand are located in two alternative positions with refined occupancy ratios equal to 0.601(13):0.399(13), 0.776(14):0.224(14), 0.644(10):0.356(10) and 0.809(16):0.191(16) for A, B, C and D molecules respectively. In addition in the molecules A and B the CF_3 groups are disordered over three sites with refined occupancies yielding 100% in total. The only ordered moiety in the structure is SO_4^{2-} anion coordinated by four ligands, however thermal ellipsoids of the atoms are slightly elongated suggesting the anion might be disordered as well. Every ligand molecule forms two N-H…O hydrogen bonds with each O moiety in the sulfate anion thus the encapsulated SO_4^{2-} is stabilized by eight hydrogen bonds in the centre of supramolecular core-shell-like aggregate of four ligands.

During the structure refinement number of restraints were applied to preserve reliable geometry of the molecules. Because disordered fragments are in relative close proximity restraints for atomic displacement parameters of selected C, O, and F atoms were also used. All major component non-hydrogen atoms were refined anisotropically. hydrogen atoms were placed in calculated positions and refined within the riding model. The temperature factors of hydrogen atoms were not refined and were set to be equal to 1.2 or 1.5 times larger than U_{eq} of the corresponding heavy atom. The atomic scattering factors were taken from the International Tables.[9] Molecular graphics was prepared using program Mercury 3.9[10] and Diamond 4.[11] Thermal ellipsoids parameters are presented at 30% probability level in **Figure S41 a)** separately for molecules A to D.

Due to the severe disorder of the highly defected crystal resulting in its relatively weak scattering power and necessity of use of large number of refined parameters two Alerts level B are present in the check CIF, whereas the final discrepancy factor is quite high. This is however justified in case of such heavily disordered and relatively large structure.

[1×KNO_3]

The X-ray measurement of pale yellow prism-like specimen of [**1×KNO_3]** with approximate dimensions 0.142×0.179×0.404 mm was performed at 130(2) K on a Bruker D8 Venture Photon100 diffractometer equipped with a TRIUMPH monochromator and a MoKα fine focus sealed tube (λ = 0.71073 Å). A total of 2420 frames were collected with Bruker APEX3 program.[2] The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.[3] The integration of the data using a triclinic unit cell yielded a total of 94264 reflections to a maximum θ angle of 26.00° (0.81 Å resolution), of which 13061 were independent (average redundancy 7.217, completeness = 99.9%, R_{int} = 2.67%, R_{sig} = 1.72%) and 11238 (86.04%) were greater than $2\sigma(F^2)$.The final cell constants of a = 11.6762(5) Å, b = 14.1244(7) Å, c = 20.8720(10) Å, α = 100.7753(16)°, β = 91.7229(17)°, γ = 99.9343(17)°, V = 3323.9(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9804 reflections above 20 $\sigma(I)$ with 5.035° < 2θ < 52.65°.Data were corrected for absorption effects using the Multi-Scan method (SADABS).[4] The ratio of minimum to maximum apparent transmission was 0.951. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.903 and 0.964.

The structure was solved and refined using SHELX[6,7] software package using the space group $P\bar{1}$, with Z = 2 for the formula unit, $C_{58.59}H_{61.07}F_{12}K_2N_{6.71}O_{22.30}$. The final anisotropic full-matrix least-squares refinement on F^2 with 1039 variables converged at $R1$ = 3.63%, for the observed data and $wR2$ = 9.01% for all data. The goodness-of-fit was 1.032. The largest peak in the final difference electron density synthesis was 0.436 $e^-/Å^3$ and the largest hole was -0.407 $e^-/Å^3$ with an RMS deviation of 0.042 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.521 g/cm^3 and F(000), 1568 e^-.

The asymmetric part of the unit cell consists of two ligands (denoted A and B) and two KNO_3 ionic pairs. In the structure three out of four CF_3 groups are disordered over three positions. The occupancy ratio of these fragments were refined. Moreover, symmetry independent part of the cell contains disordered solvent molecules identified as diethyl ether and acetonitrile sharing the same place. The latter molecule has two alternative orientation. As the sum occupancy of the disordered solvent molecules is set to be 1 with each component free to refine the sum formula of the crystal is non stoichiometric.

The non-hydrogen atoms, including major component disordered moieties, were refined anisotropically. Most of hydrogen atoms were placed in calculated positions and refined within the riding model. Position and temperature factors of four hydrogen atoms engaged in hydrogen bonds were refined. The temperature factors of all other hydrogen atoms were not

refined and were set to be either 1.2 or 1.5 times larger than U_{eq} of the corresponding heavy atom. The atomic scattering factors were taken from the International Tables[9]. Molecular graphics was prepared using program Mercury 3.9[10] and Diamond 4[11]. Thermal ellipsoids parameters are presented at 50% probability level in **Figure S41 b)** separately for molecules A and B.

[1×H₂O]

The X-ray measurement of colorless plate-like specimen of **[1×H₂O]** with approximate dimensions 0.291×0.116×0.047 mm was performed at 125(2) K on a Bruker D8 Venture PhotonII diffractometer equipped with a TRIUMPH monochromator and a MoKα fine focus sealed tube (λ = 0.71073 Å). A total of 1100 frames were collected with Bruker APEX3 program[2]. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm[3]. The integration of the data using a monoclinic unit cell yielded a total of 39121 reflections to a maximum θ angle of 25.06° (0.84 Å resolution), of which 4981 were independent (average redundancy 7.854, completeness = 99.5%, R_{int} = 7.72%, R_{sig} = 5.70%) and 4093 (82.17%) were greater than $2\sigma(F^2)$. The final cell constants of a = 21.627(4) Å, b = 15.667(3) Å, c = 8.4646(18) Å, β = 100.217(6)°, V = 2822.6(10) Å^3, are based upon the refinement of the XYZ-centroids of 8019 reflections above 20 $\sigma(I)$ with 6.137° < 2θ < 49.65°. Data were corrected for absorption effects using the Multi-Scan method (TWINABS).[6] The ratio of minimum to maximum apparent transmission was 0.685. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.961 and 0.993.

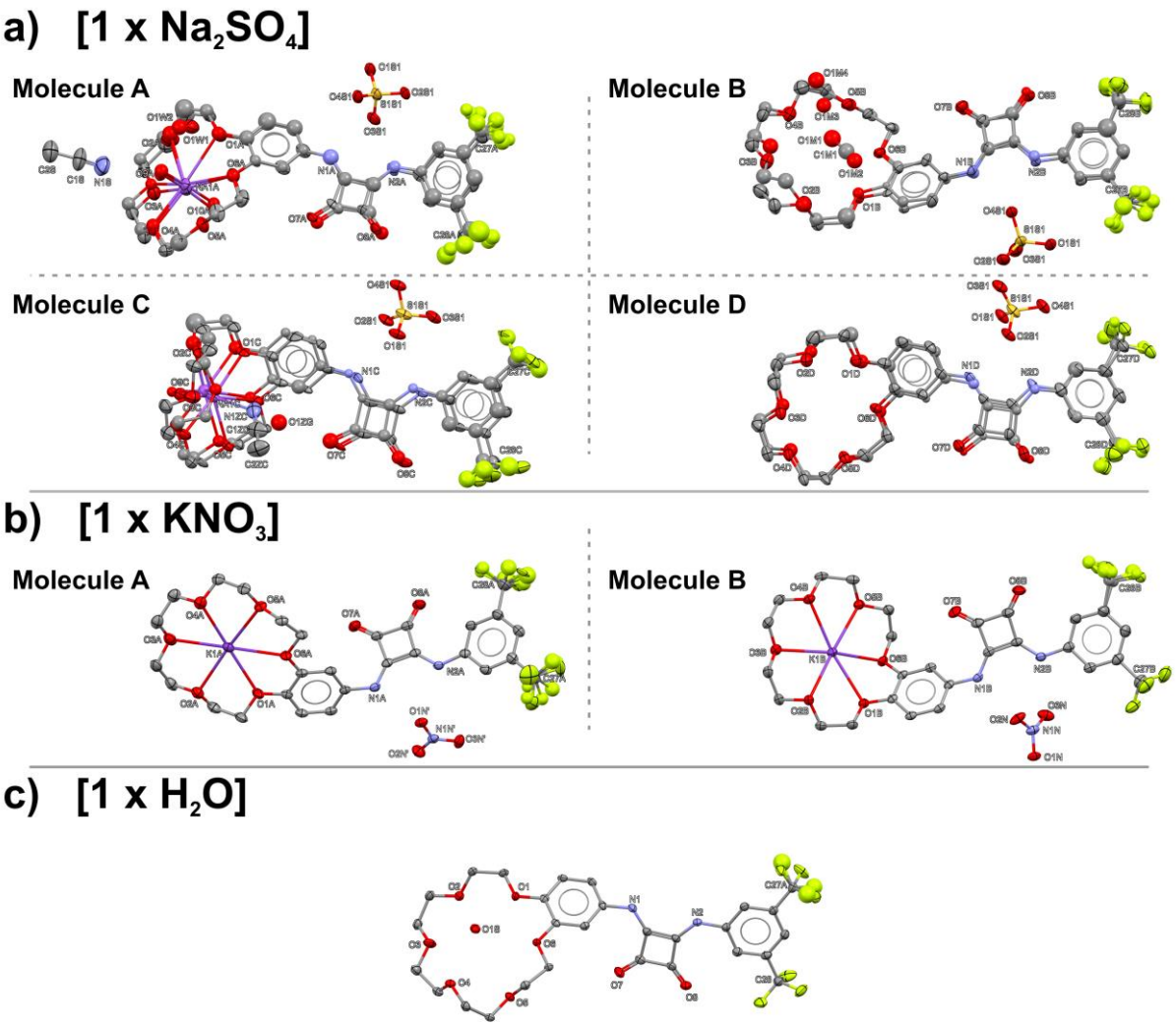
The structure was solved and refined using SHELX[7,8] software package using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{28}H_{30}F_6N_2O_9$. The final anisotropic full-matrix least-squares refinement on F^2 with 437 variables converged at $R1$ = 4.29%, for the observed data and $wR2$ = 10.26% for all data. The goodness-of-fit was 1.031. The largest peak in the final difference electron density synthesis was 0.217 e$^-$/Å^3 and the largest hole was -0.223 e$^-$/Å^3 with an RMS deviation of 0.054 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.536 g/cm^3 and F(000), 1352 e$^-$.

The crystal is twinned with partial overlap of reflections. During data integration two twin components were used. The final twin component ratio obtained during structure refinement yielded 0.574(1):0.426(1).

In the structure one CF_3 group is disordered over two sites with refined occupancy ratio yielding 0.937(6):0.063(6). All major component non-hydrogen atoms were refined

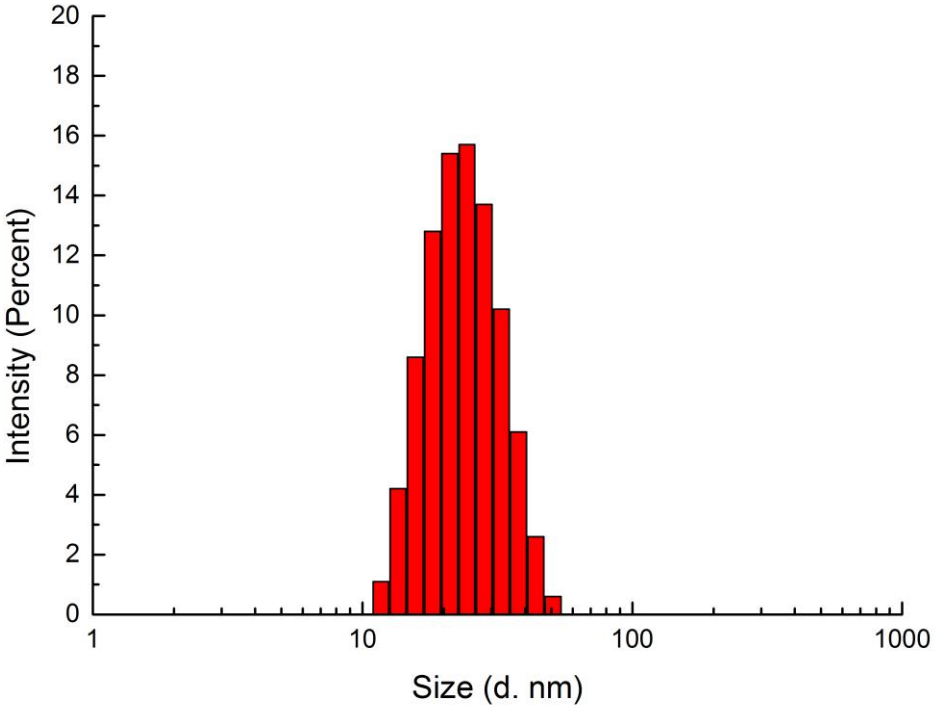
anisotropically. Most of hydrogen atoms were placed in calculated positions and refined within the riding model. Positions of O-H and N-H hydrogen atoms engaged in hydrogen bonds were refined. The temperature factors of hydrogen atoms, except O-H and N-H ones, were not refined and were set to be equal to 1.2 times larger than U_{eq} of the corresponding heavy atom. The atomic scattering factors were taken from the International Tables[9] Molecular graphics was prepared using program Mercury 3.9[10] and Diamond 4[11]. Thermal ellipsoids parameters are presented at 50% probability level in **Figure S41 c)**.

Fig. S41. Thermal ellipsoid plot of atoms in crystals of: **a) [1×Na_2SO_4]** presented at 30% probability level, only selected solvent molecules are visible **b) [1×KNO_3]** presented at 50% probability level and **c) [1×H_2O]** presented at 50% probability level. H atoms omitted for clarity. Only selected atoms are numbered.



DYNAMIC LIGHT SCATTERING MEASUREMENTS (DLS)

Fig. S42. Distribution of the hydrodynamic diameter of **1** (3.11 mM in CH_3CN) and 1 eq. KPF_6 and 5 eq. TBA_2SO_4.



^{1}H NMR DOSY EXPERIMENTS

Fig. S43. ^{1}H DOSY NMR spectrum of receptor **1** (3.04 mM) in CD_3CN.

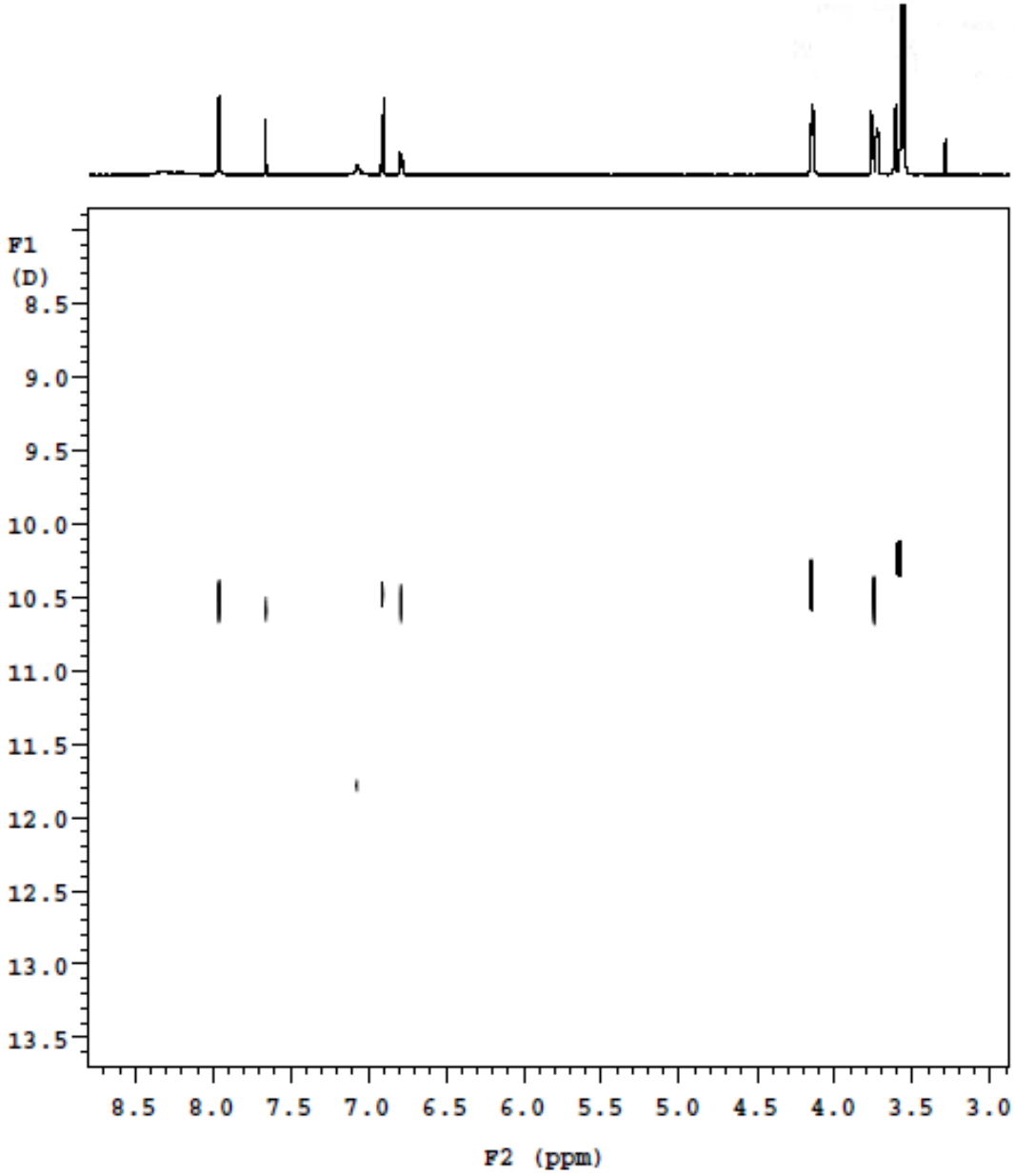


Fig. S44. ^{1}H DOSY NMR spectrum of receptor **1** (3.04 mM) with 1 eq. $TBAPF_6$ in CD_3CN.

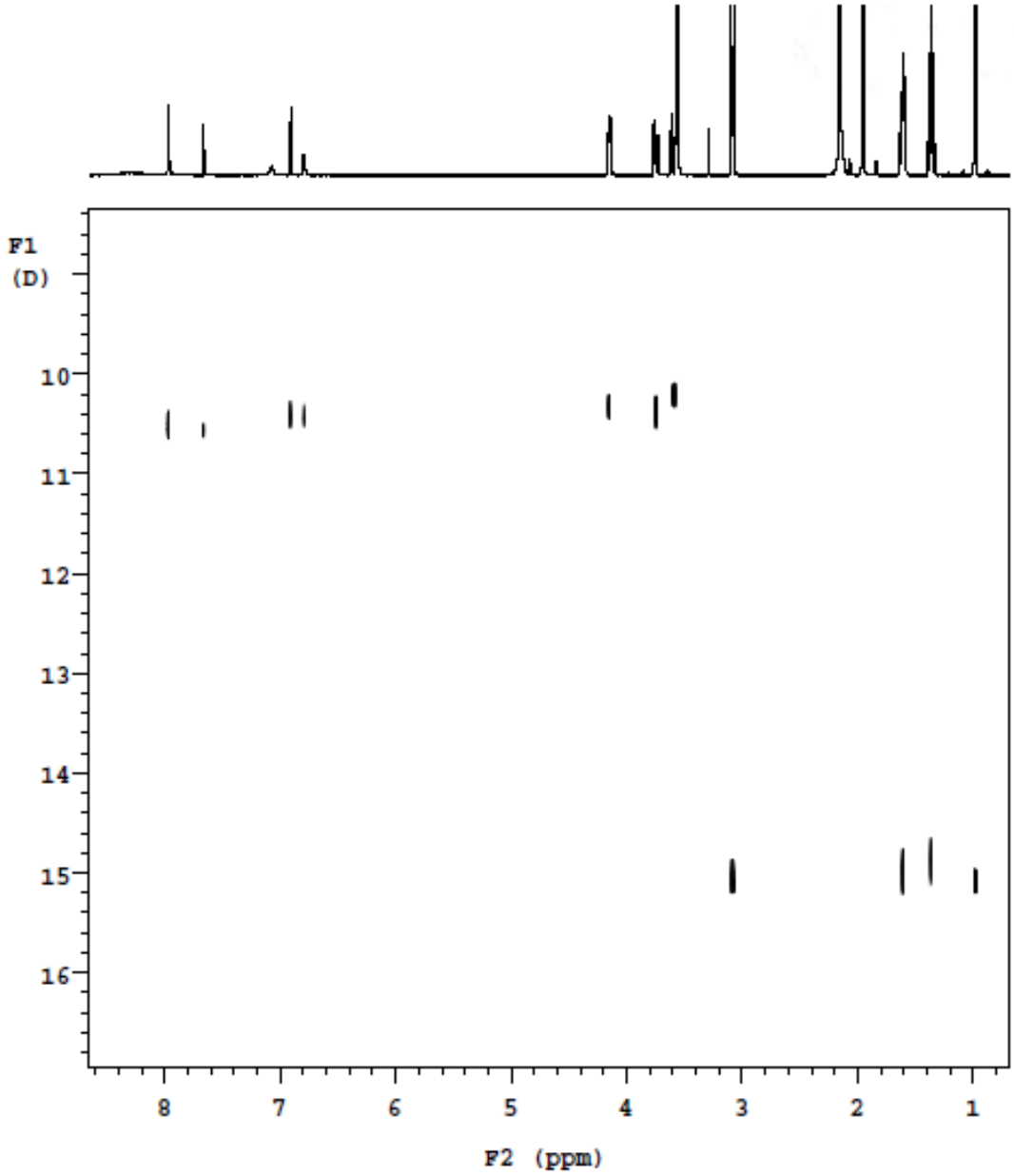
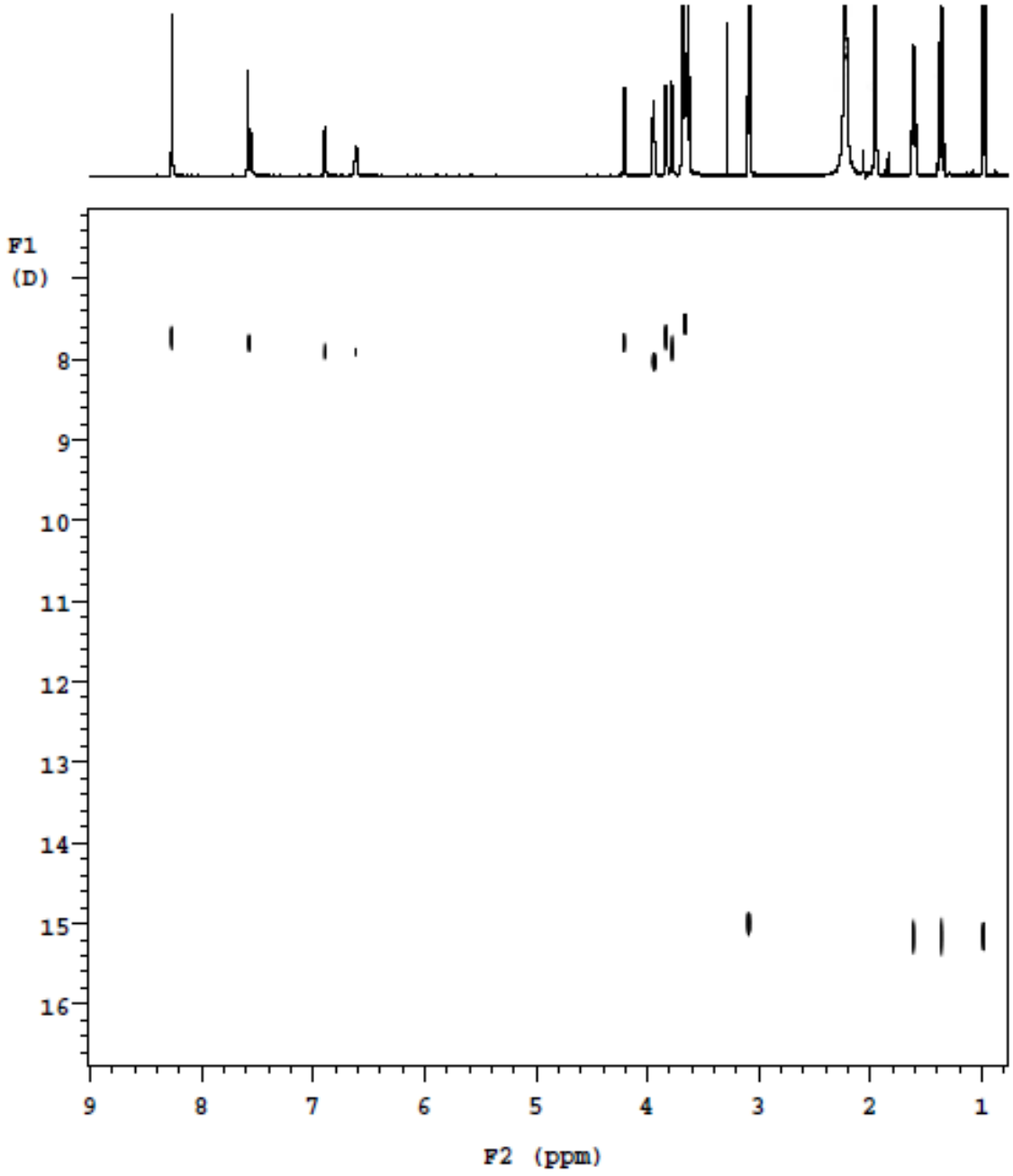
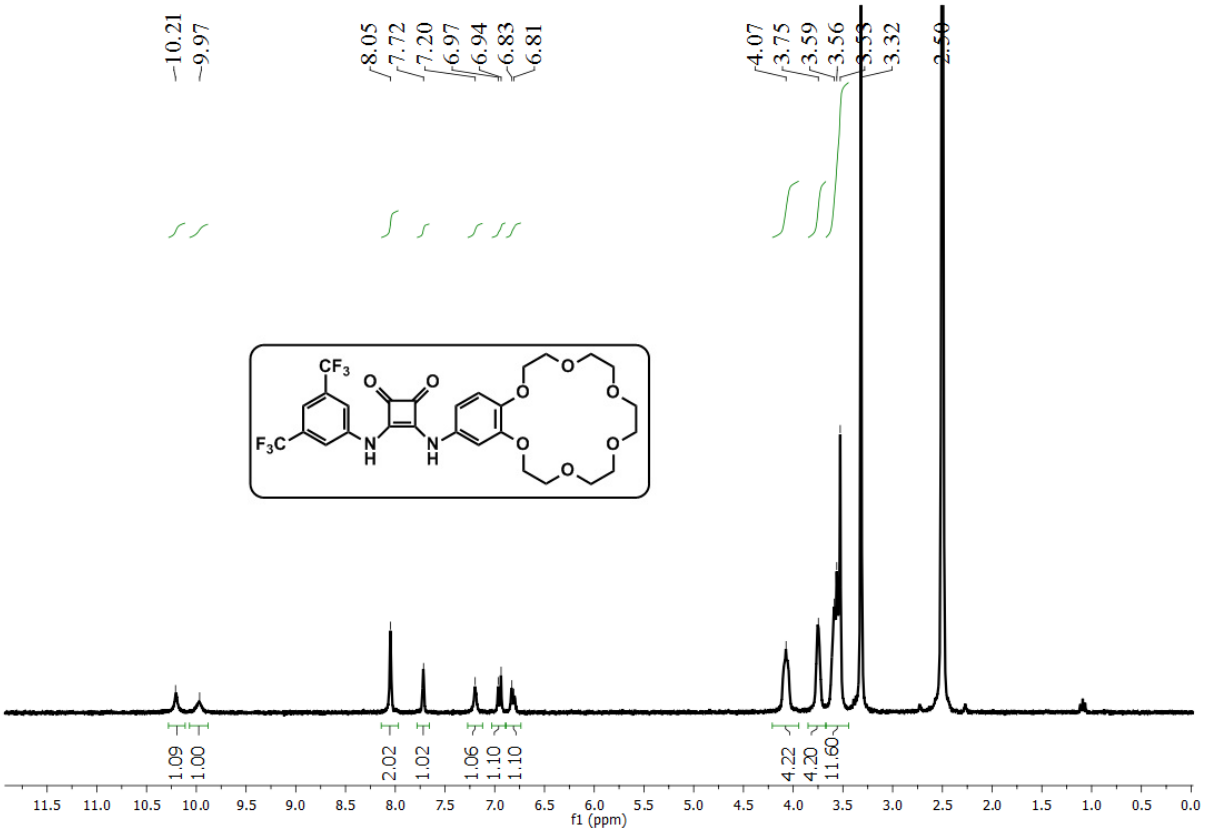


Fig. S45. ^{1}H DOSY NMR spectrum of receptor **1** (3.04 mM) with 1 eq. KPF_6 and 0.25 eq. TBA_2SO_4 in CD_3CN.



NMR SPECTRA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8.05
7.72
7.20
6.97
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6.83
6.81
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3.75
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3.56
3.53
3.32
2.50
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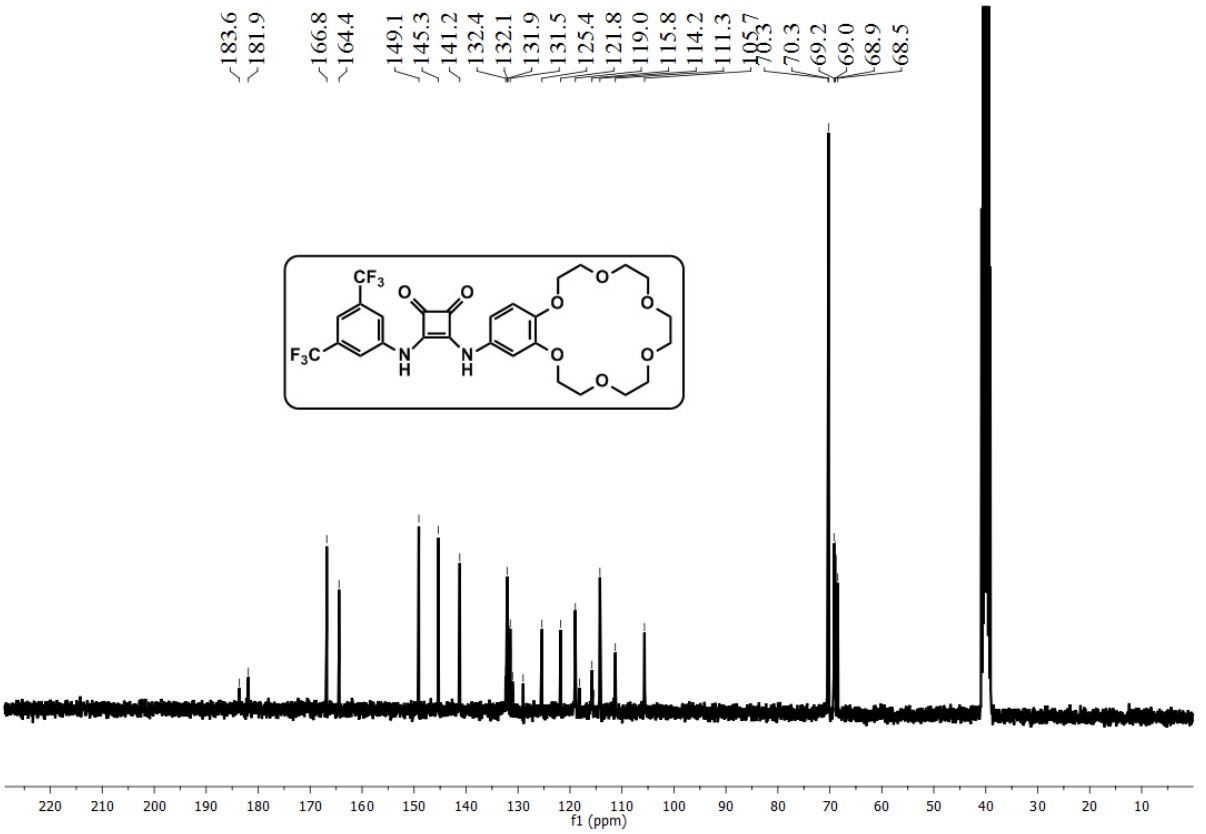
2.02
1.02
1.06
1.10
1.10
4.22
4.20
11.60
f1 (ppm)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166.8
164.4
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145.3
141.2
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131.9
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121.8
119.0
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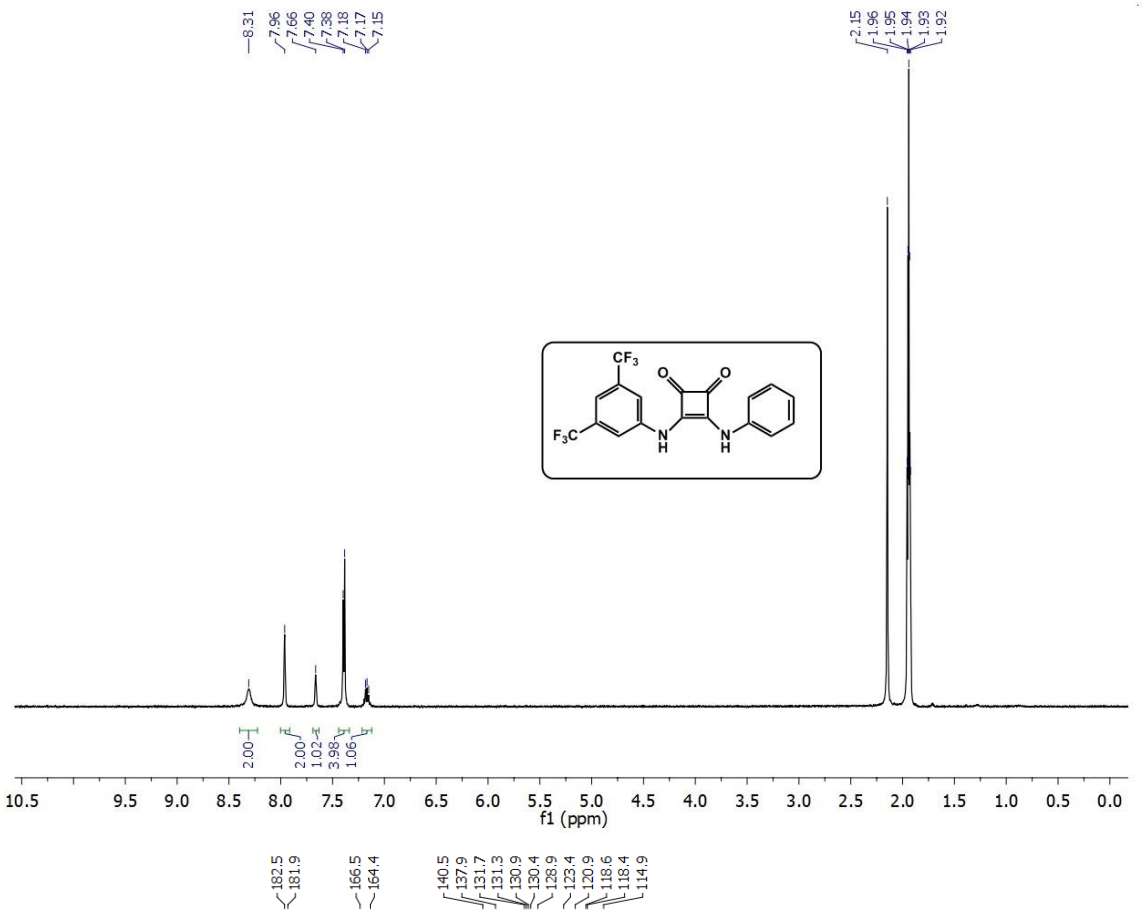
70.3
69.2
69.0
68.9
68.5
f1 (ppm)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1.92
CF3
F3C
O
O
N
H
N
H
2.00
2.00
1.02
3.98
1.06
10.5
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9.0
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8.0
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7.0
6.5
6.0
5.5
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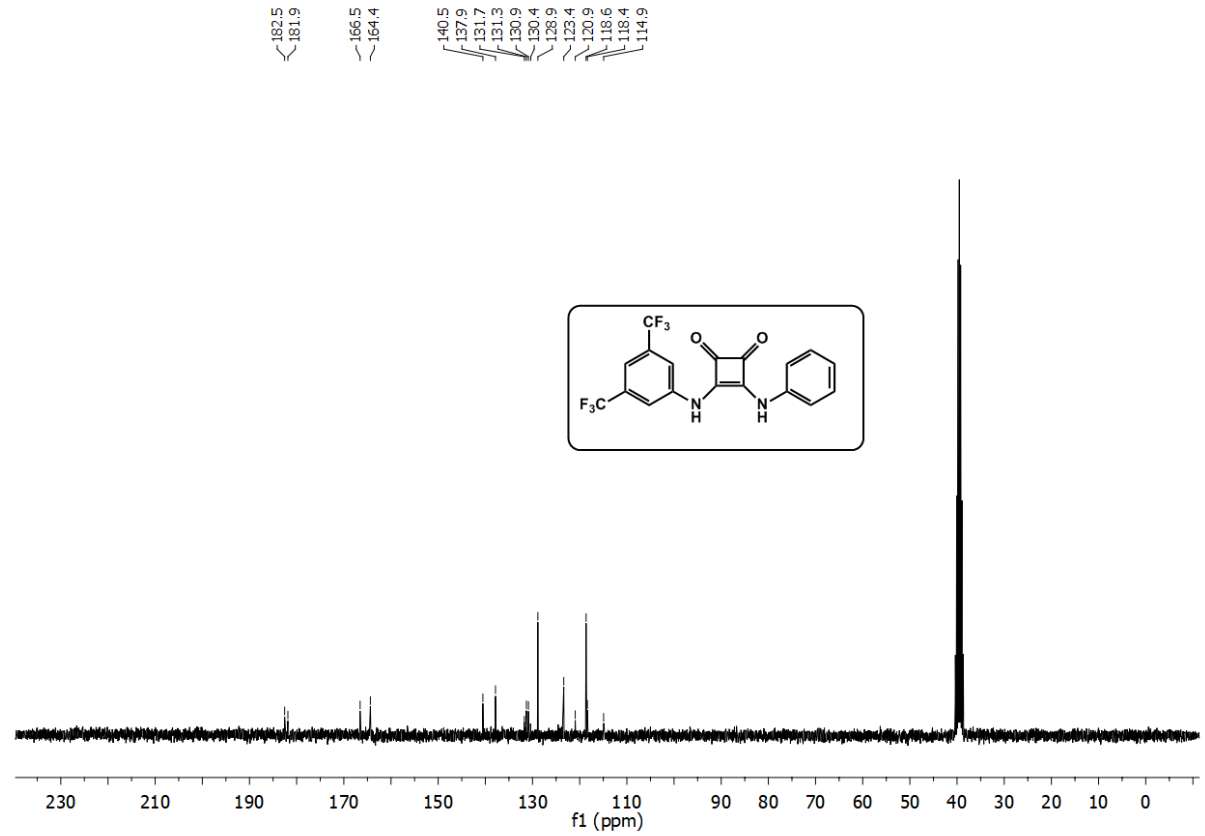
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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137.9
131.7
131.3
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130.4
128.9
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118.6
118.4
114.9
CF3
F3C
O
O
N
H
N
H
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170
150
130
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90
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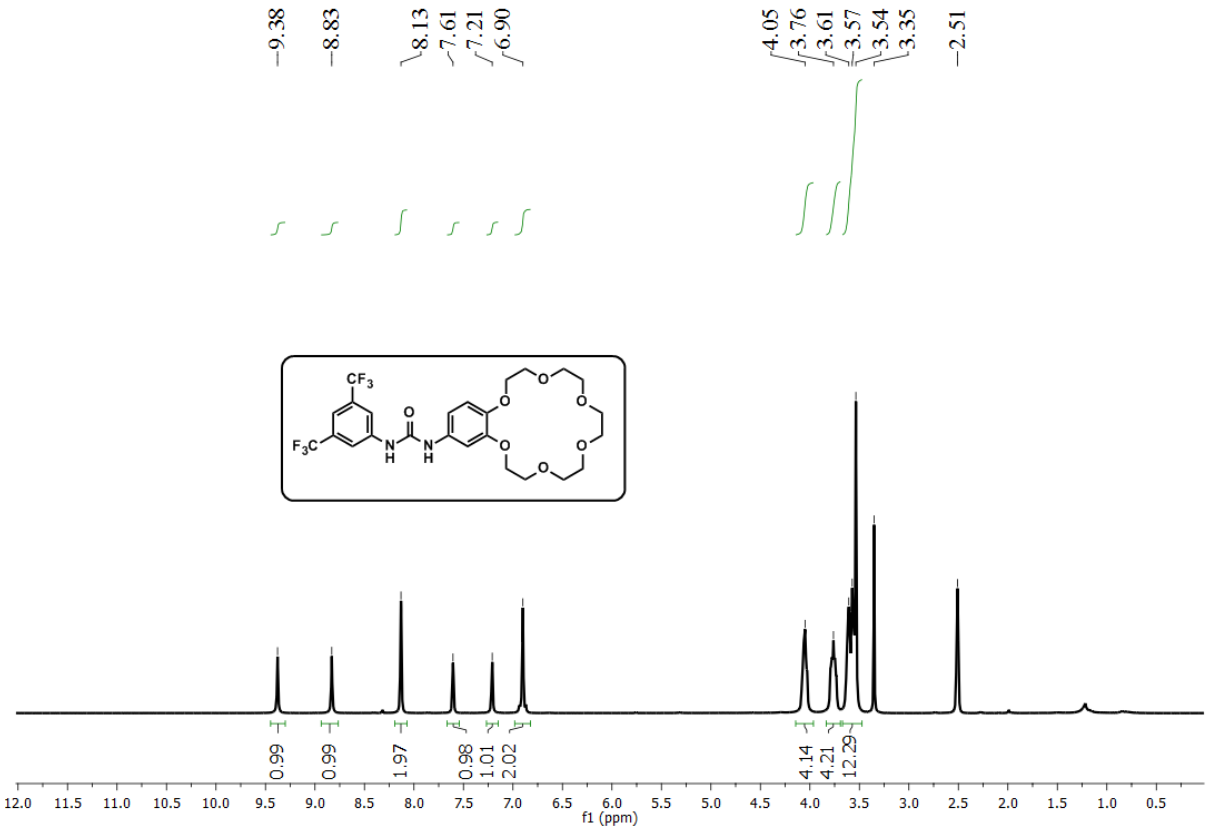
70
60
50
40
30
20
10
0
f1 (ppm)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3.76
3.61
3.57
3.54
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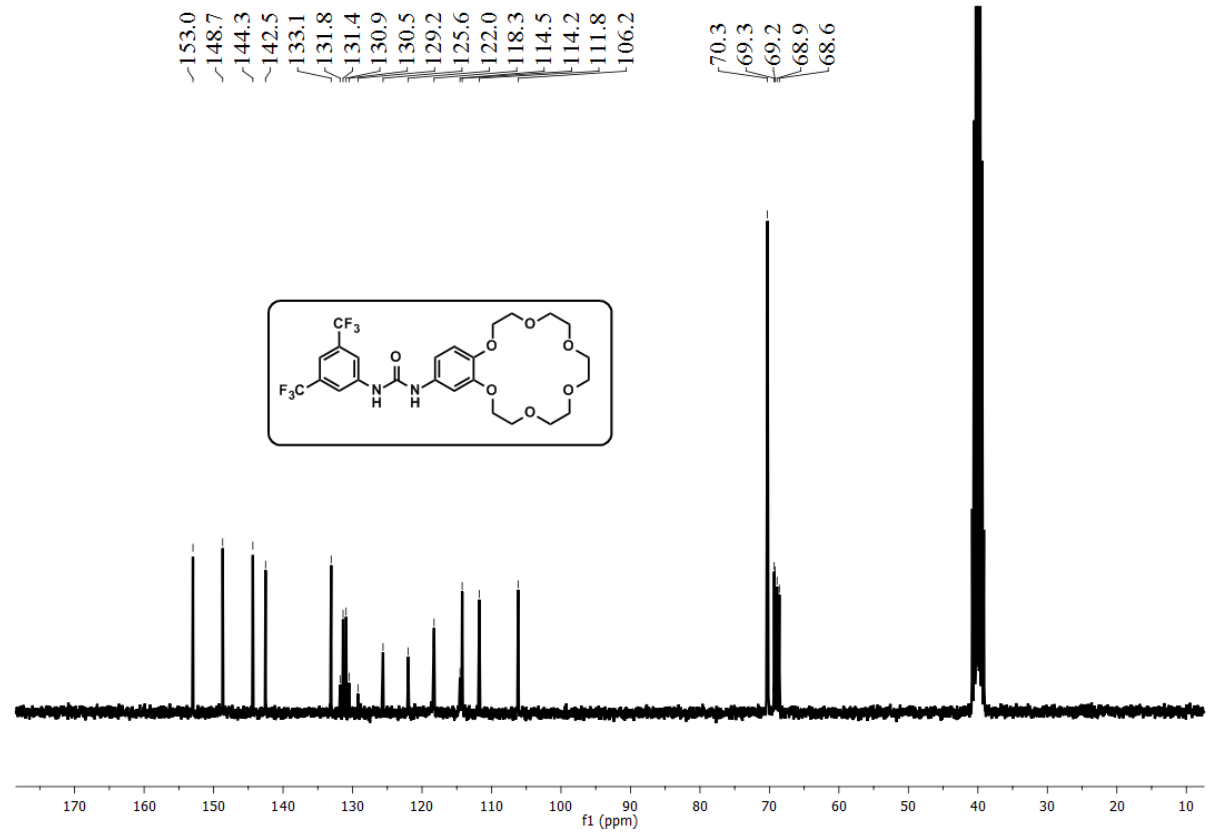
1.01
2.02
4.14
4.21
12.29
f1 (ppm)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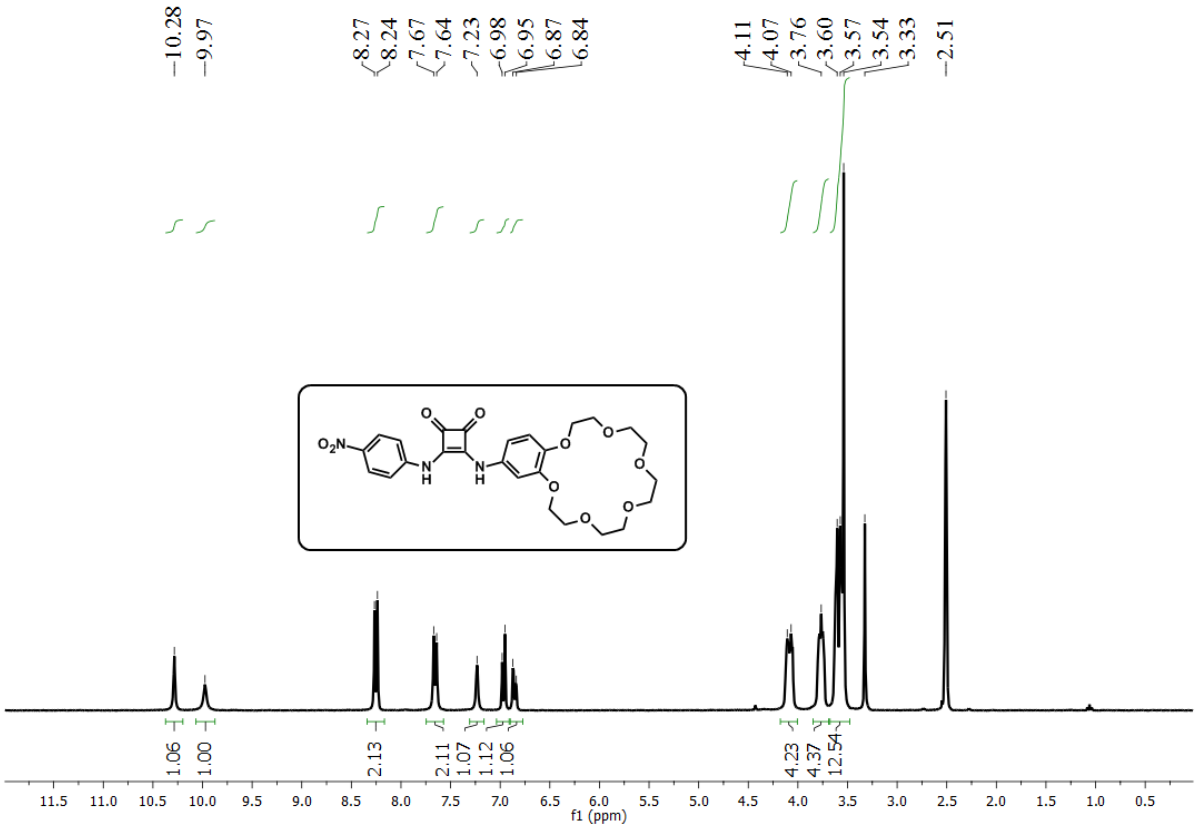
68.6
f1 (ppm)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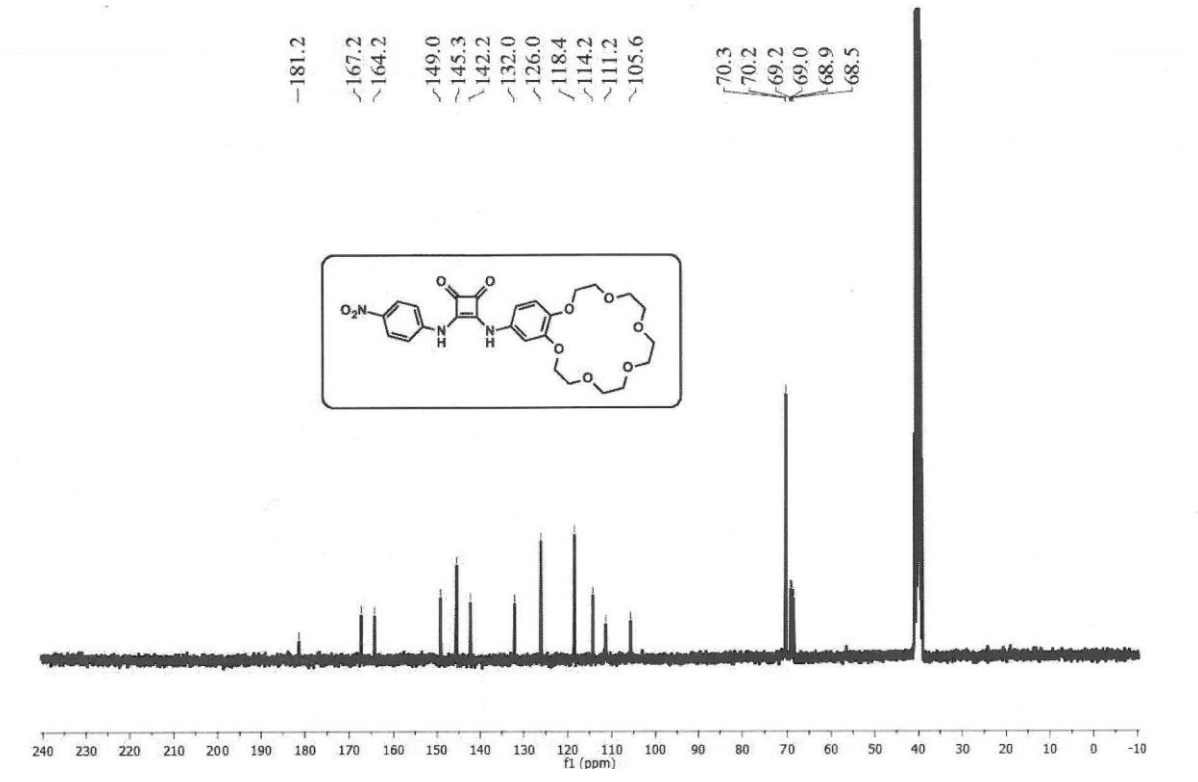
1.06
4.23
4.37
12.54
f1 (ppm)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167.2
164.2
149.0
145.3
142.2
132.0
126.0
118.4
114.2
111.2
105.6
70.3
70.2
69.2
69.0
68.9
68.5
f1 (ppm)

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