New Journal of Chemistry

Supplementary Information for

"An ion pair receptor facilitating extraction of chloride salt from aqueous to organic phase"

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. 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 or 500 spectrometer using a residual protonated solvent as internal standard.

High resolution mass spectra (HRMS) were measured on a Quattro LC Micromass unit using ESI technique.

UV-VIS EXPERIMENTS

General procedure: The UV-Vis titration was performed using Thermo Spectronic Unicam UV500 Spectrophotometer at 298K in acetonitrile. $NaClO_4$ were dried under high vacuum at 30−45 °C prior to use. In this case, a 2500 μL of freshly prepared 1.75×10^{-5} M solution of receptor **1** was added to a cuvette. Small aliquots of TBAX, containing **1** at constant concentration, were added and a spectrum was acquired after each addition. In the case of ion pair titration receptor 1 was firstly pretreated with one equivalent of $NaClO_4$ (refers to receptor).Titration isotherms for NH protons were fitted to a 1:1 binding model using HypSpec program.

Fig. S1. Representative UV-Vis Titration Spectra
(Host: Receptor 1; Guest: TBAAc)

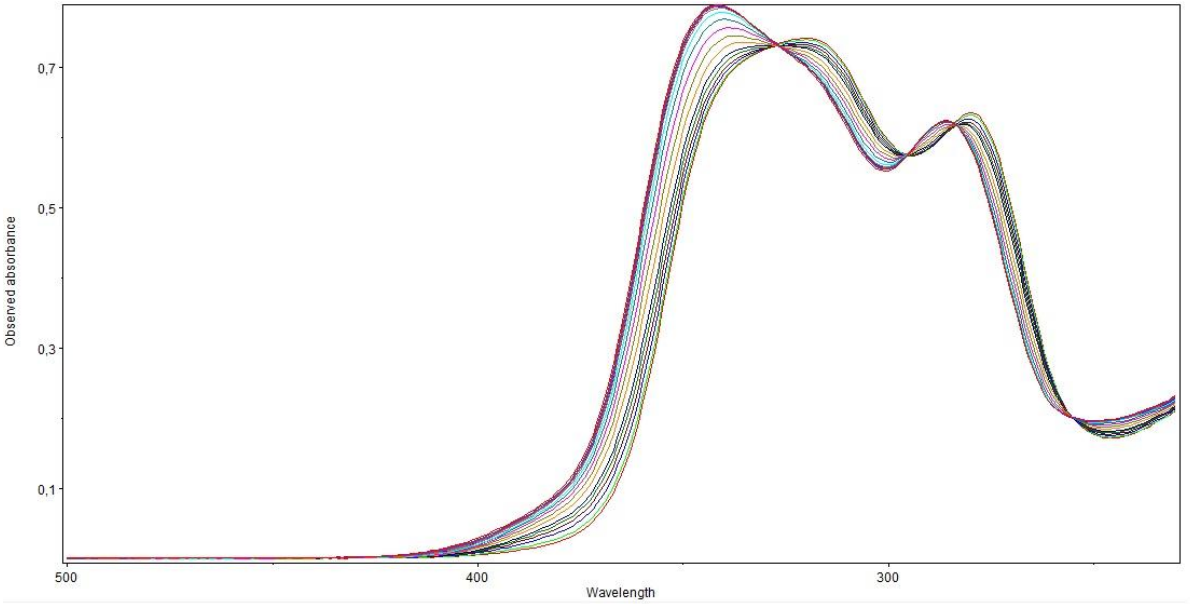


Fig. S2: Dilution curve of receptor **1**.

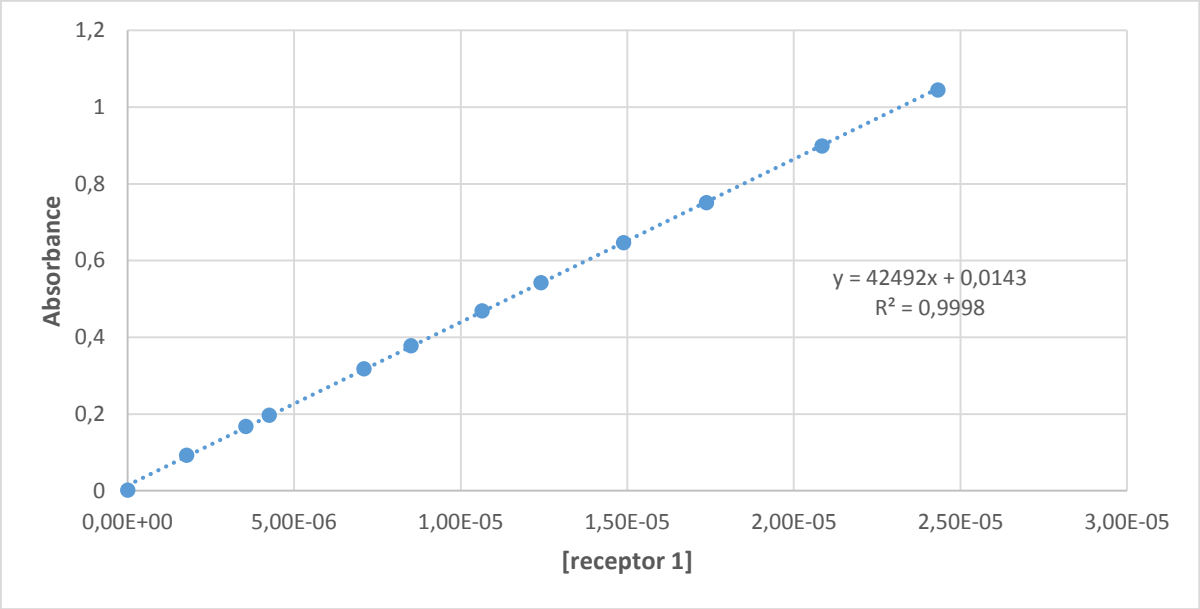


Fig. S3: Job plot (Host: Receptor **1**, guest: Cl^-)

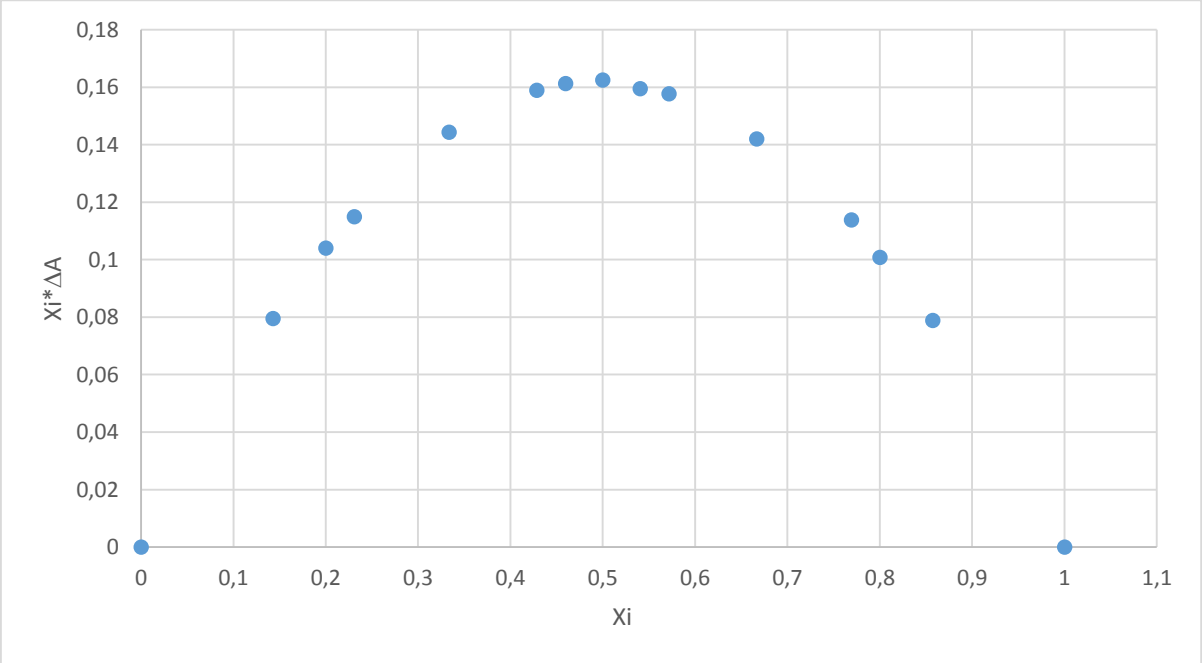


Fig. S4. UV-Vis titration binding isotherms of receptor 1 with TBACl and TBACl in the presence of 1 equivalent of $NaClO_4$.

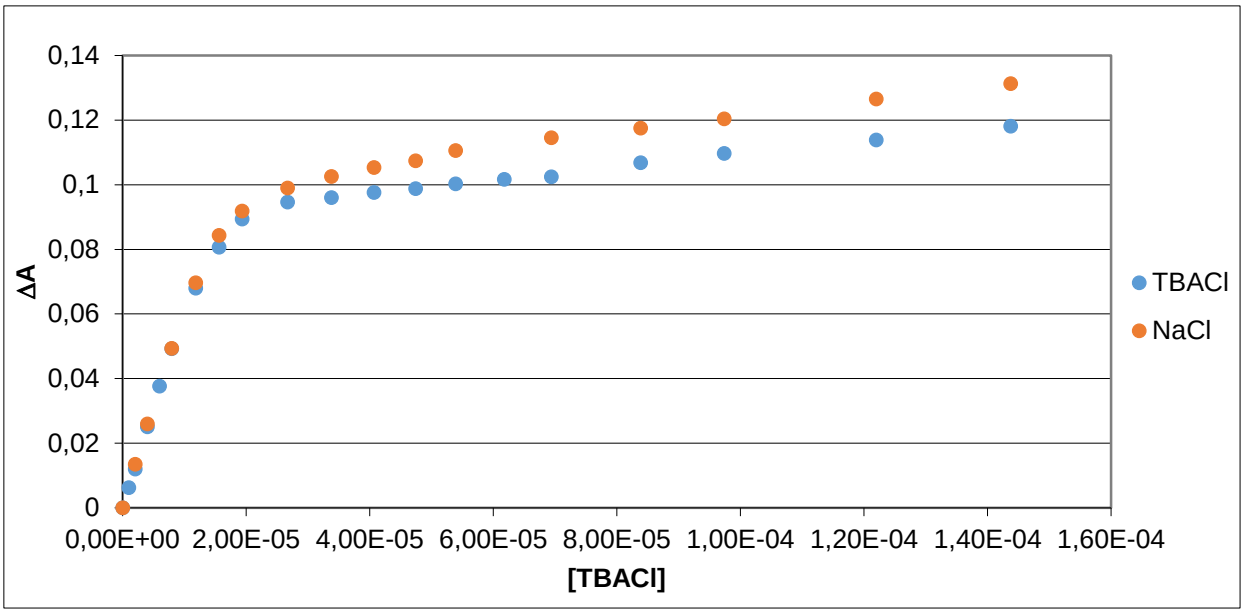


Fig. S5. UV-Vis titration binding isotherms of receptor 1 with $TBA^+CH_3COO^-$ and $TBA^+CH_3COO^-$ in the presence of 1 equivalent of $NaClO_4$.

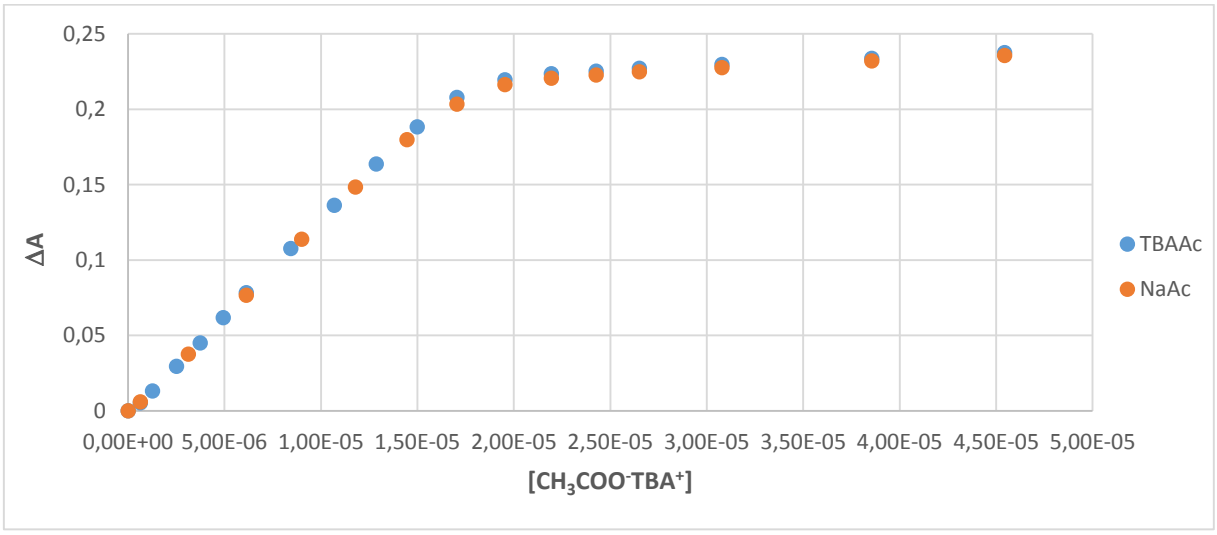


Fig. S6. UV-Vis titration binding isotherms of receptor 1 with TBA^+PhCOO^- and TBA^+PhCOO^- in the presence of 1 equivalent of $NaClO_4$.

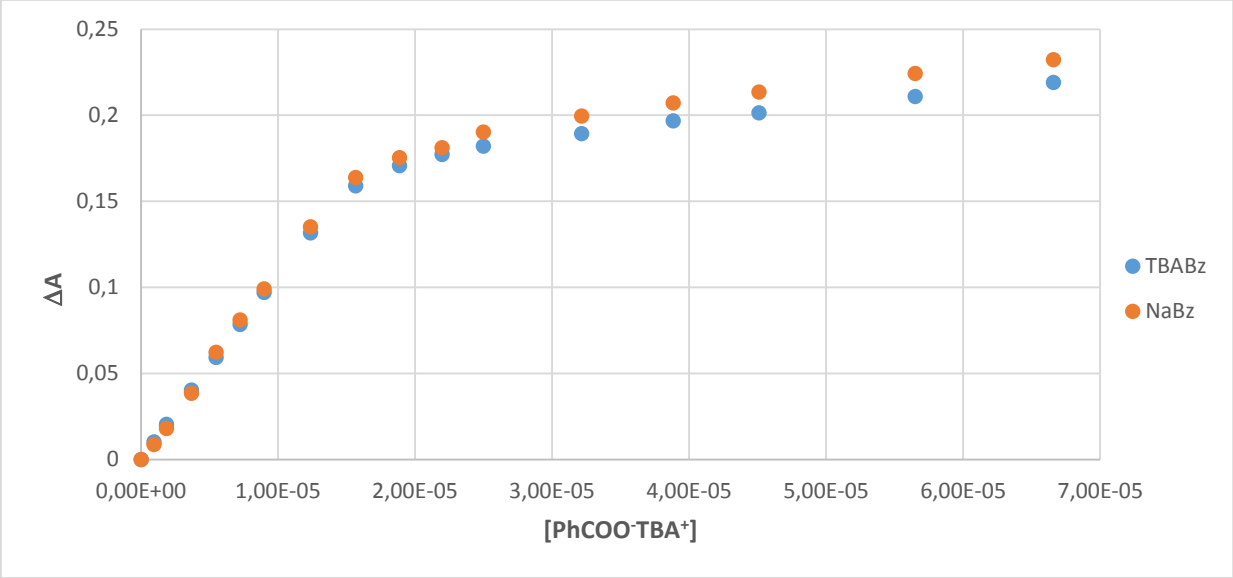


Fig. S7. UV-Vis titration binding isotherms of receptor 1 with TBABr and TBABr in the presence of 1 equivalent of $NaClO_4$.

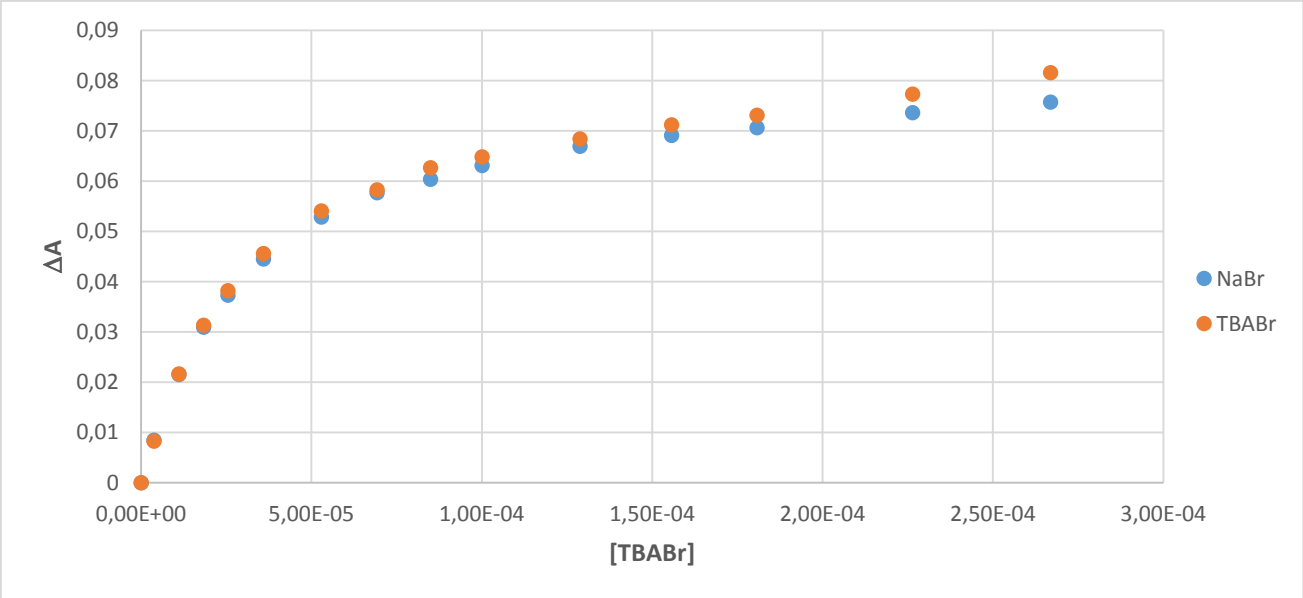


Fig. S8. UV-Vis titration binding isotherms of receptor 1 with $TBANO_2$ and $TBANO_2$ in the presence of 1 equivalent of $NaClO_4$.

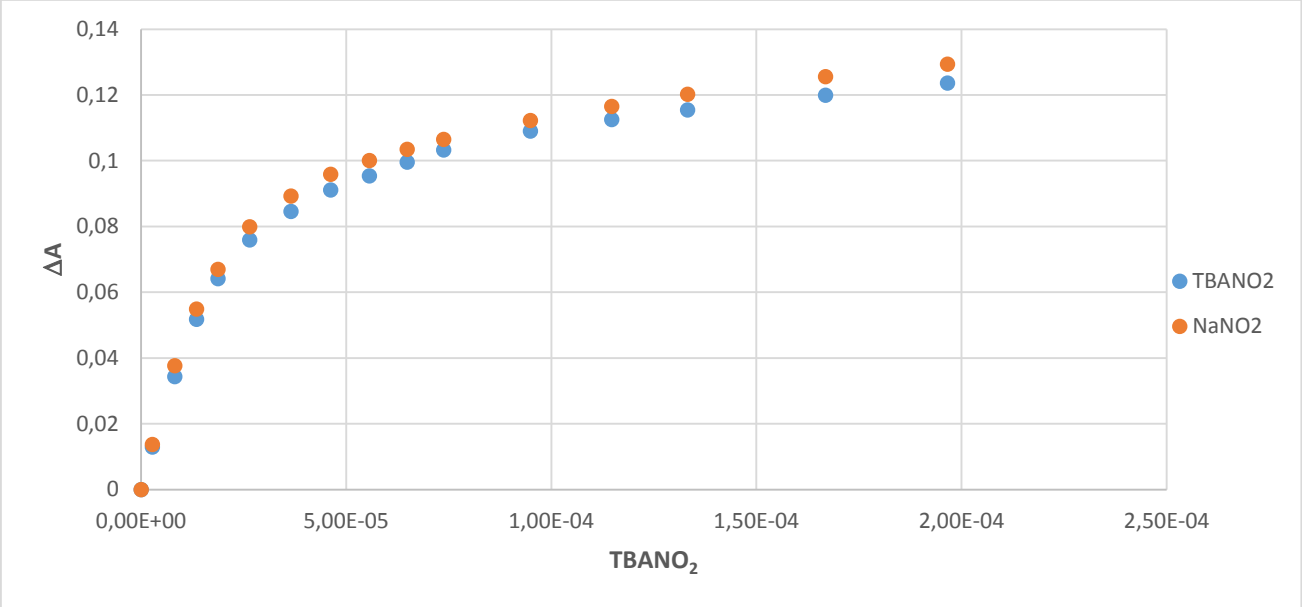


Fig. S9. Representative UV-Vis Titration Spectra (Host: Receptor 3; Guest: TBACl)

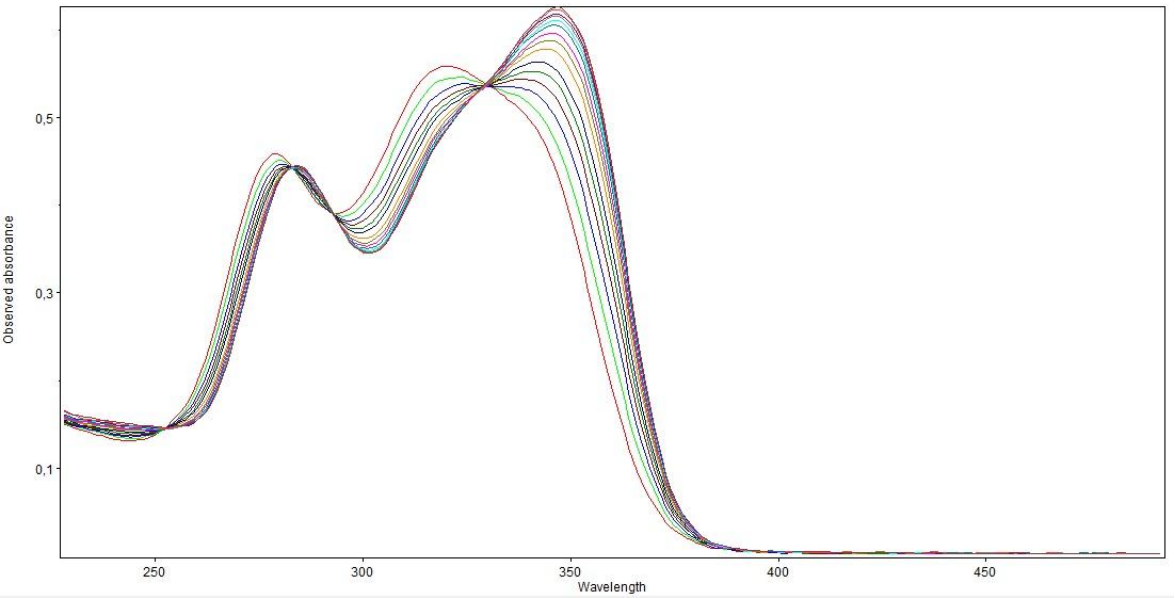


Fig. S10. UV-Vis titration binding isotherms of receptor 3 with TBACl and TBACl in the presence of 1 equivalent of $NaClO_4$.

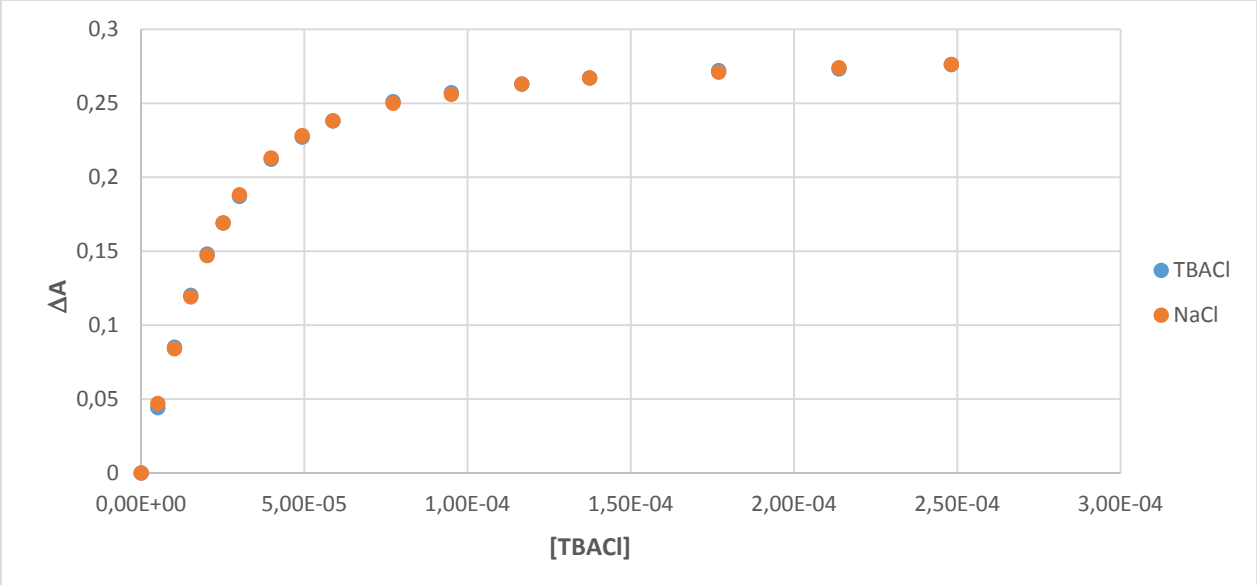


Fig. S11. Representative UV-Vis Titration Spectra (Host: Receptor 2; Guest: TBACl)

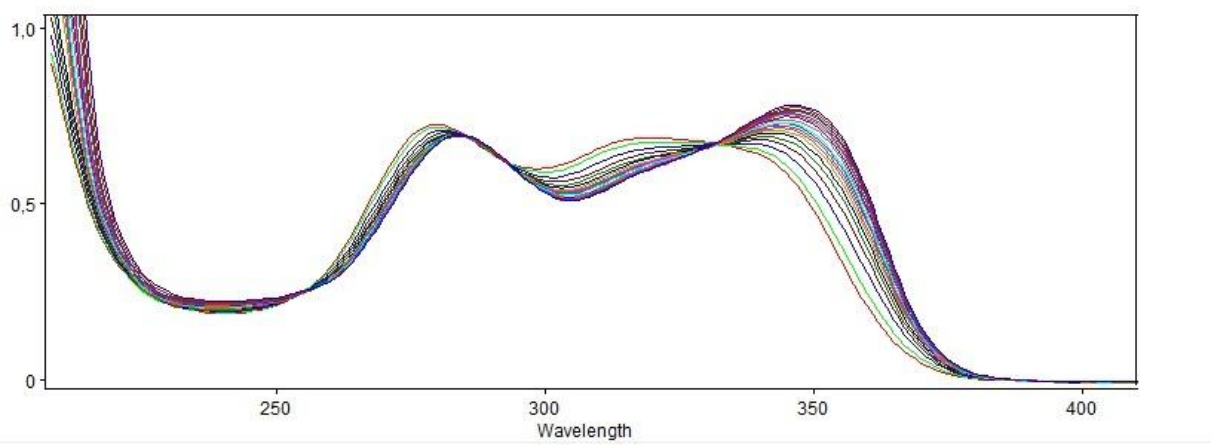
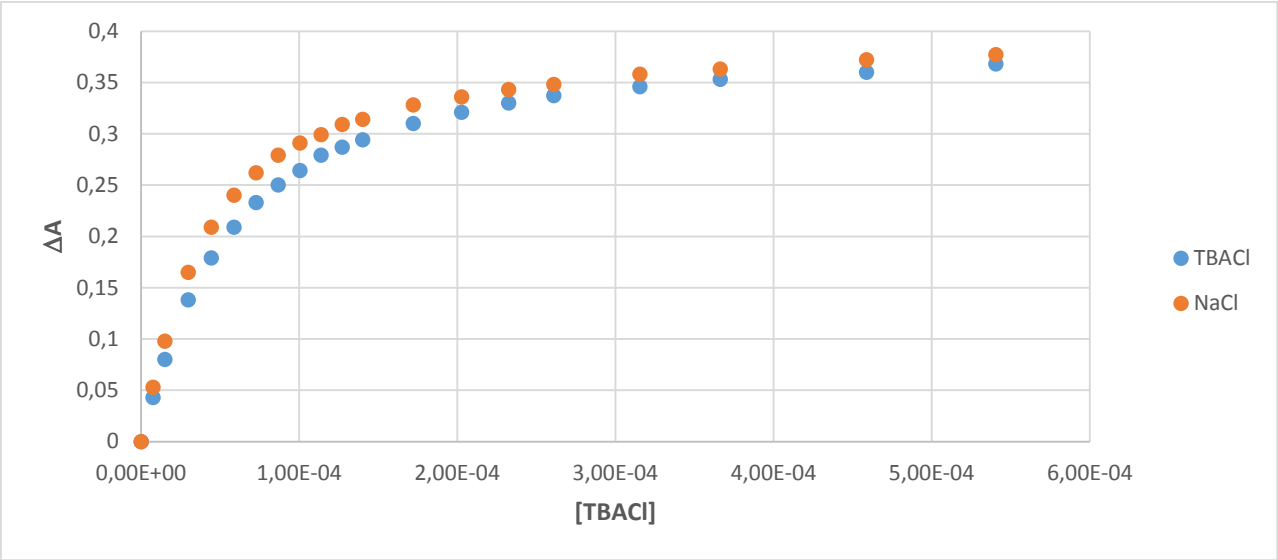
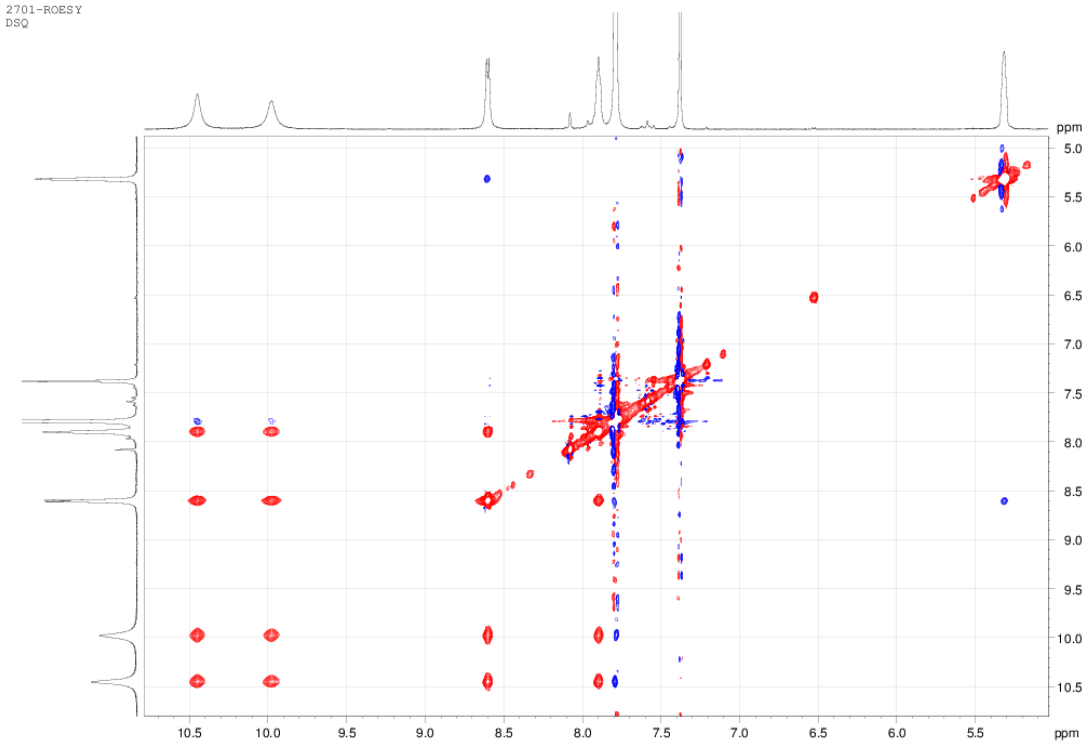


Fig. S12. UV-Vis titration binding isotherms of receptor 2 with TBACl and TBACl in the presence of 1 equivalent of $NaClO_4$.



NMR MEASUREMENTS

Fig. S13 ^{1}H-^{1}H ROESY of receptor **1**. (Assignment of squaramide protons)



NMR Titration: The ^{1}H NMR titration was performed on a Bruker 300 spectrometer, at 298K in 10% DMSO-d_6 in CD_3CN . $NaClO_4$ were dried under high vacuum at 30−45 °C prior to use. In this case, a 500 μL of freshly prepared 2.30 mM solution of receptor **1** was added to a 5mm NMR tube. Small aliquots of 42 mM solution of TBACl, containing **1** at 2.30 mM concentration, were added and a spectrum was acquired after each addition. In the case of ion pair titration of receptor 1 one equivalent of $NaClO_4$ (refers to receptor) was introduced to NMR tube. Titration isotherms for NH protons were fitted to a 1:1 binding model using the BindFit v0.5 program (http://supramolecular.org/).

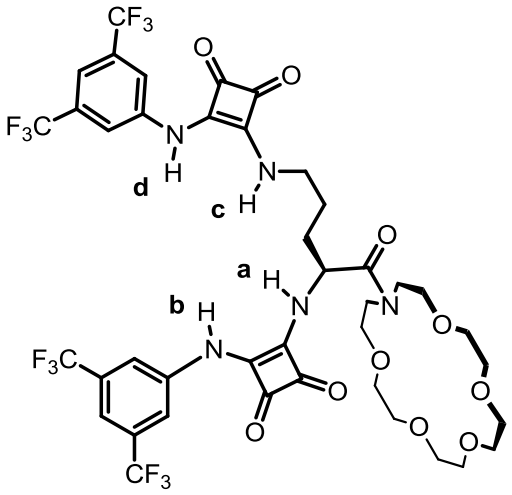


Fig. S14. Variation of the ^{1}HNMR spectrum of receptor 1 in CD_3CN upon addition of increasing amounts of TBACl

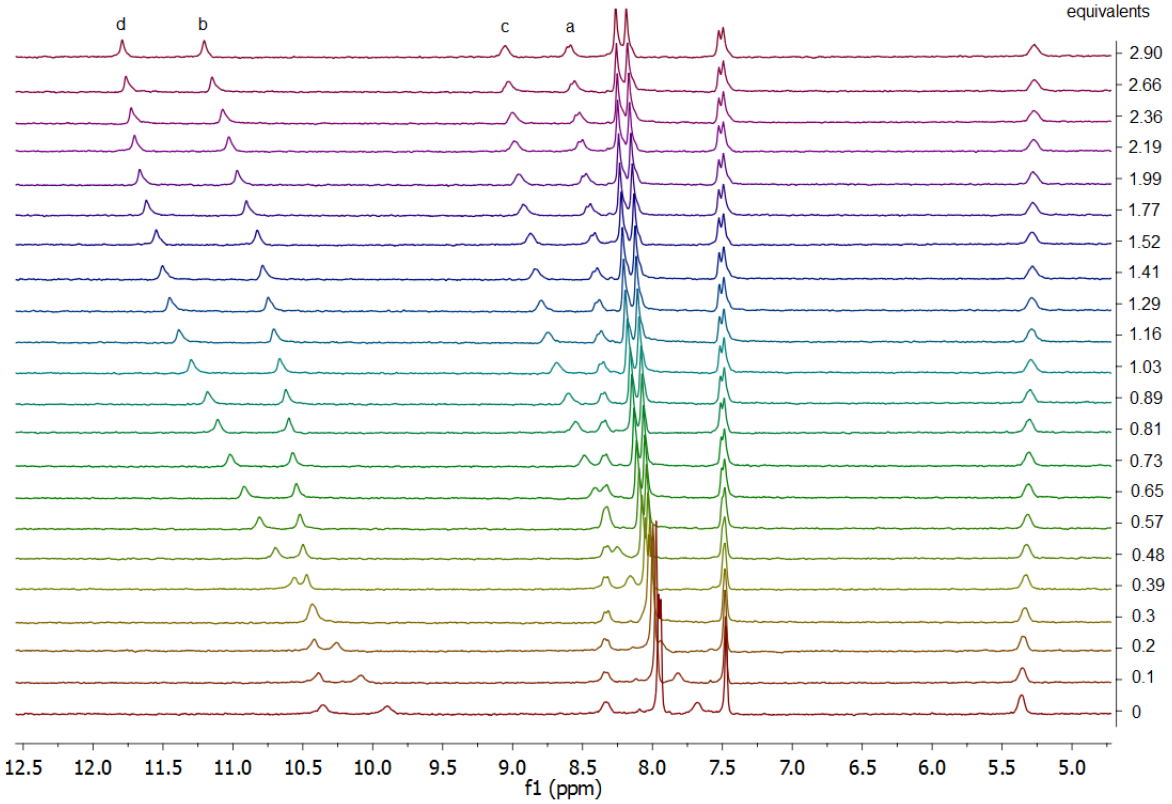
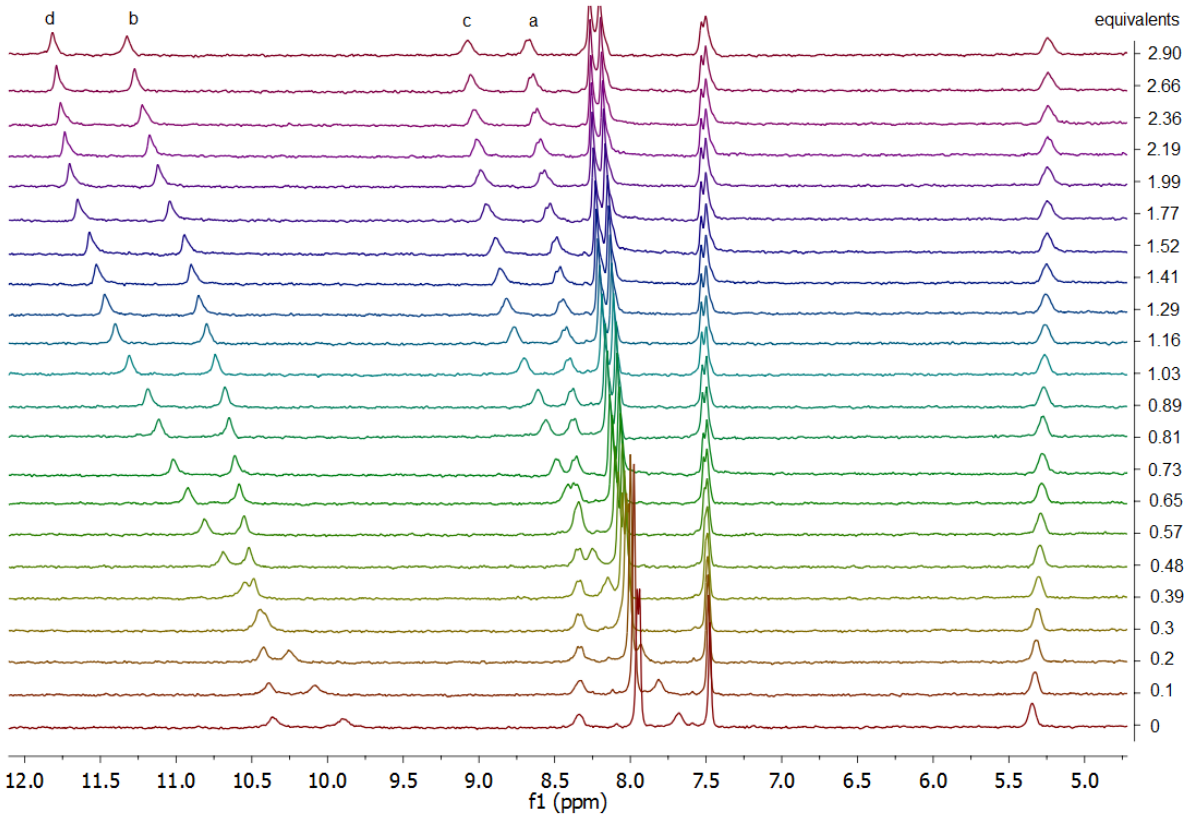


Fig. S15. Variation of the ^{1}HNMR spectrum of receptor 1 in CD_3CN upon addition of increasing amounts of TBACl in the presence of 1 equivalent of sodium perchlorate



EXTRACTION EXPERIMENTS

First toluidine blue was dissolved in water and extracted several times with chloroform up to disappearance of colour in organic phase. The aqueous phase was separated and the water was evaporated *in vacuo.* Then 2 ml of 5×10^{-5} M toluidine blue solution was extracted with 2 ml suspension containing 1, 10 and 50 equivalents of receptor **1** in 20 % n-butanol in chloroform and after phase separation (two homogenous phases) the concentration of dye in aqueous phases were monitored using UV-vis measurements. Calibration curve was generated using a standard solution of toluidine blue in water and is presented below. Absorbance was taken for wavelength 626 nm, which corresponds to the maximum.

Fig. S16. Calibration curve generated using a standard solution of toluidine blue in water

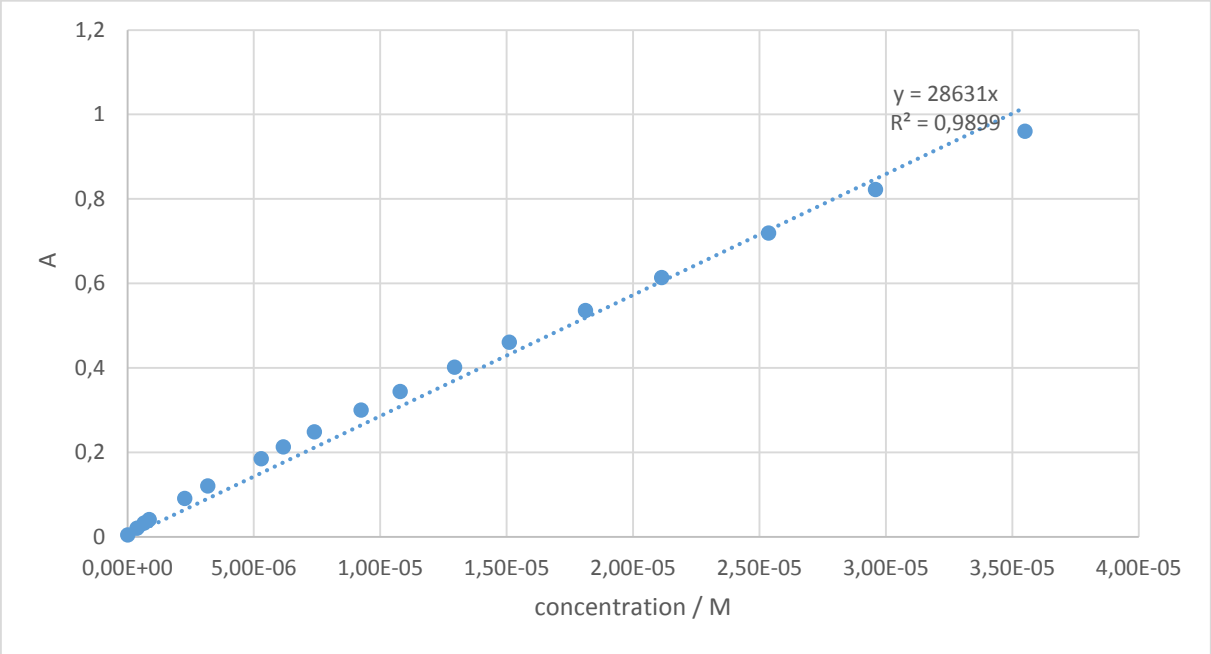
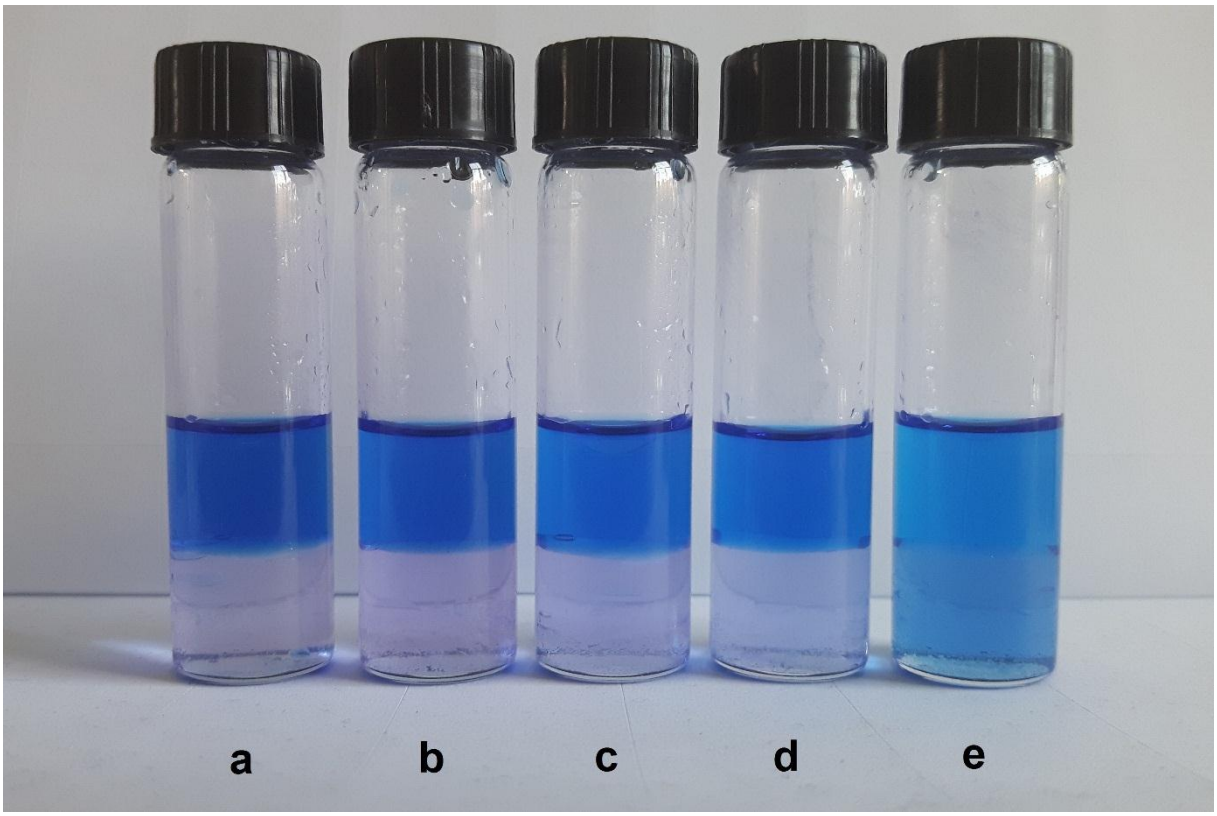
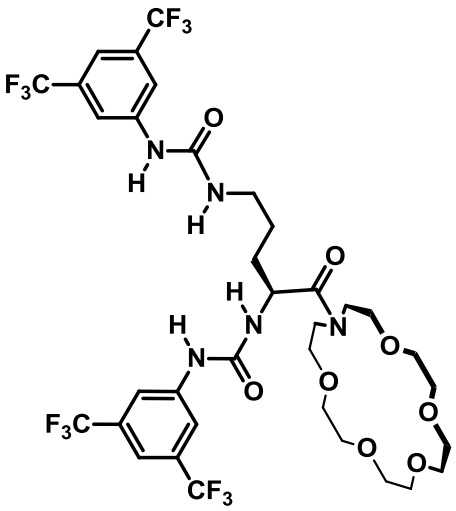


Fig. S17. Extraction of aqueous solution of toluidine blue (top layers) with solution of 20% n-butanol in chloroform and 50 equivalents of: a) 15-crown-5; b) urea based receptor (see structure below); c) receptor 2; d) receptor 3; e) receptor 1 (bottom layers).





urea based receptor investigated in extraction experiment

CRYSTAL DATA

The X-ray measurement of receptor **1** was performed at 100(2) K on a Bruker D8 Venture Photon100 CMOS diffractometer equipped with a TRIUMPH monochromator and a MoKα fine focus sealed tube (λ=0.71073 Å). A total of 2890 frames were collected with Bruker APEX2 program [1]. The frames were integrated with the Bruker SAINT software package [2] using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 40481 reflections to a maximum θ angle of 26.00° (0.81 Å resolution), of which 10005 were independent (average redundancy 4.046, completeness = 100.0%, R_{int}=1.91%, R_{sig}=1.74%) and 9686 (96.81%) were greater than $2\sigma(F^2)$. The final cell constants of a=8.8305(17) Å, b=9.1614(18) Å, c=16.760(3) Å, α=75.104(5)°, β=81.510(5)°, γ=77.835(5)°, V=1274.6(4) Å^3, are based upon the refinement of the XYZ-centroids of 9916 reflections above 20 $\sigma(I)$ with 4.678° < 2θ < 52.21°. Data were corrected for absorption effects using the multi-scan method (SADABS) [3]. The ratio of minimum to maximum apparent transmission was 0.958. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8870 and 0.9750.

The structure was solved and refined using SHELXTL Software Package [4] using the space group P1, with Z=1 for the formula unit, $C_{45}H_{53}F_{12}N_5O_{12}S_2$ and the Flack parameter equal to 0.088(14) [5]. The final anisotropic full-matrix least-squares refinement on F^2 with 705 variables converged at R1=2.33%, for the observed data and wR2=5.59% for all data. The goodness-of-fit was 1.039. The largest peak in the final difference electron density synthesis was 0.253 e$^-$/Å^3 and the largest hole was -0.169 e$^-$/Å^3 with an RMS deviation of 0.034 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.496 g/cm^3 and F(000), 594 e$^-$.

All non-hydrogen atoms were refined anisotropically. Most of hydrogen atoms were placed in calculated positions and refined within the riding model. Coordinates of hydrogen atoms engaged in hydrogen bonds were refined together with their isotropic temperature parameters. The temperature factors of the constrained hydrogen atoms were not refined and were set to be equal to 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 [6]. Molecular graphics was prepared using program Diamond 3.2 [7]. Thermal ellipsoids parameters are presented at 50% probability level.

Acknowledgements

The X-ray structure was determined in the Advanced Crystal Engineering Laboratory (aceLAB) at the Chemistry Department of the University of Warsaw by dr Lukasz Dobrzycki.

ORTEP plots and packing diagrams for receptor 1

Fig. S18. ORTEP (*P*=50%) of receptor 1

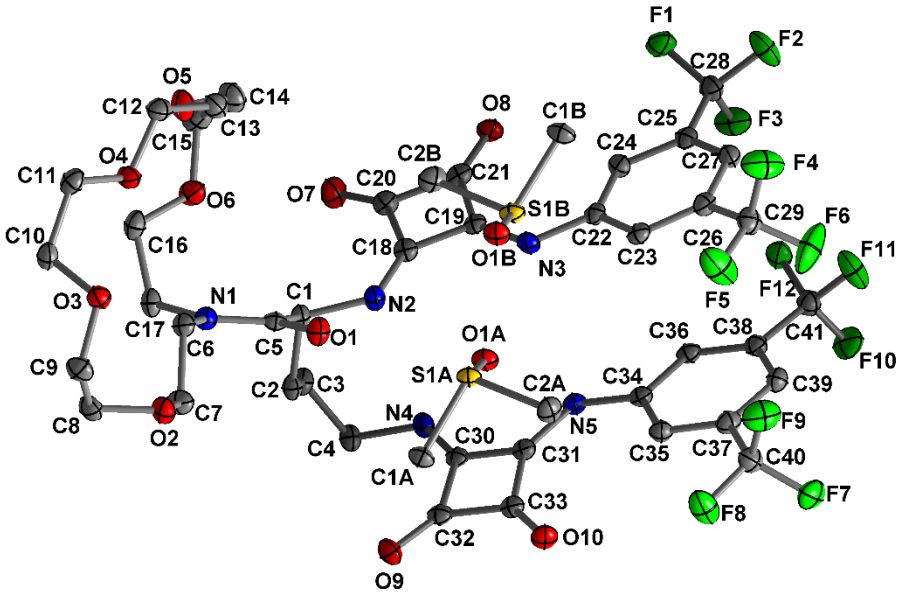
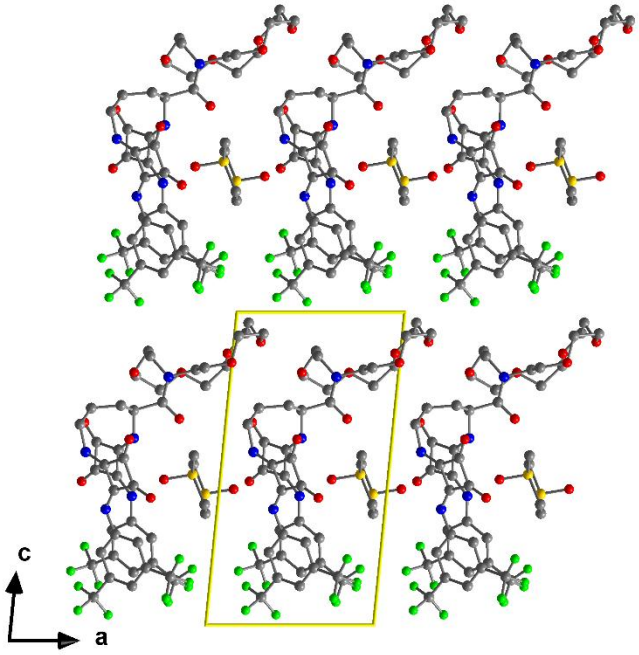
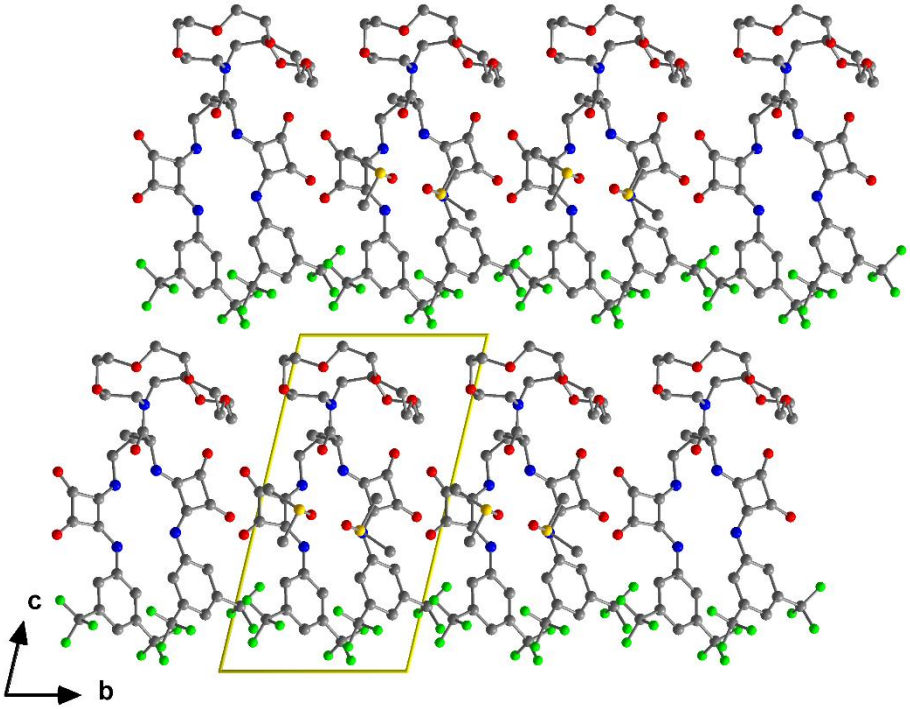
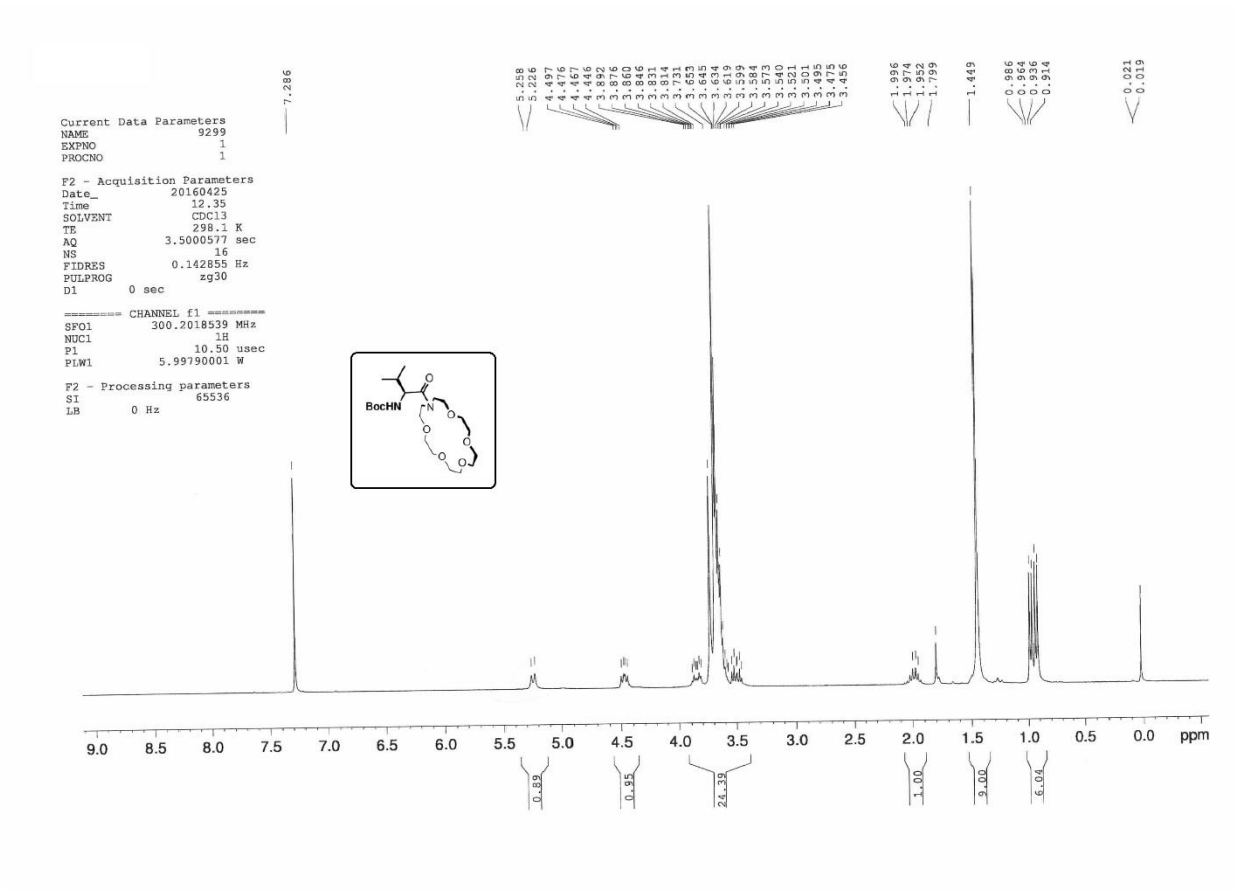


Fig. S19. Packing in crystal of receptor 1




c
b

NMR SPECTRA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PLW1 5.99790001 W
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0.019
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9.00
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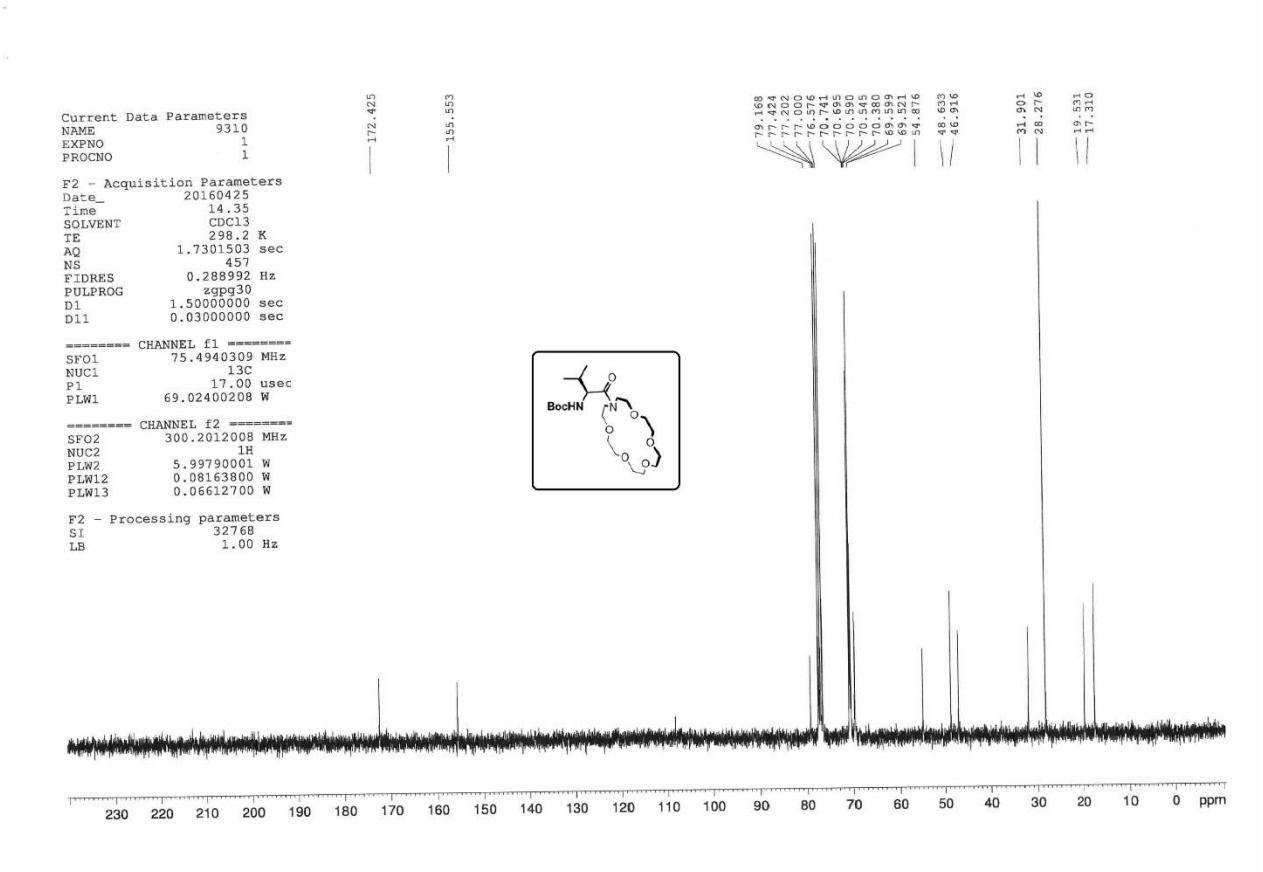
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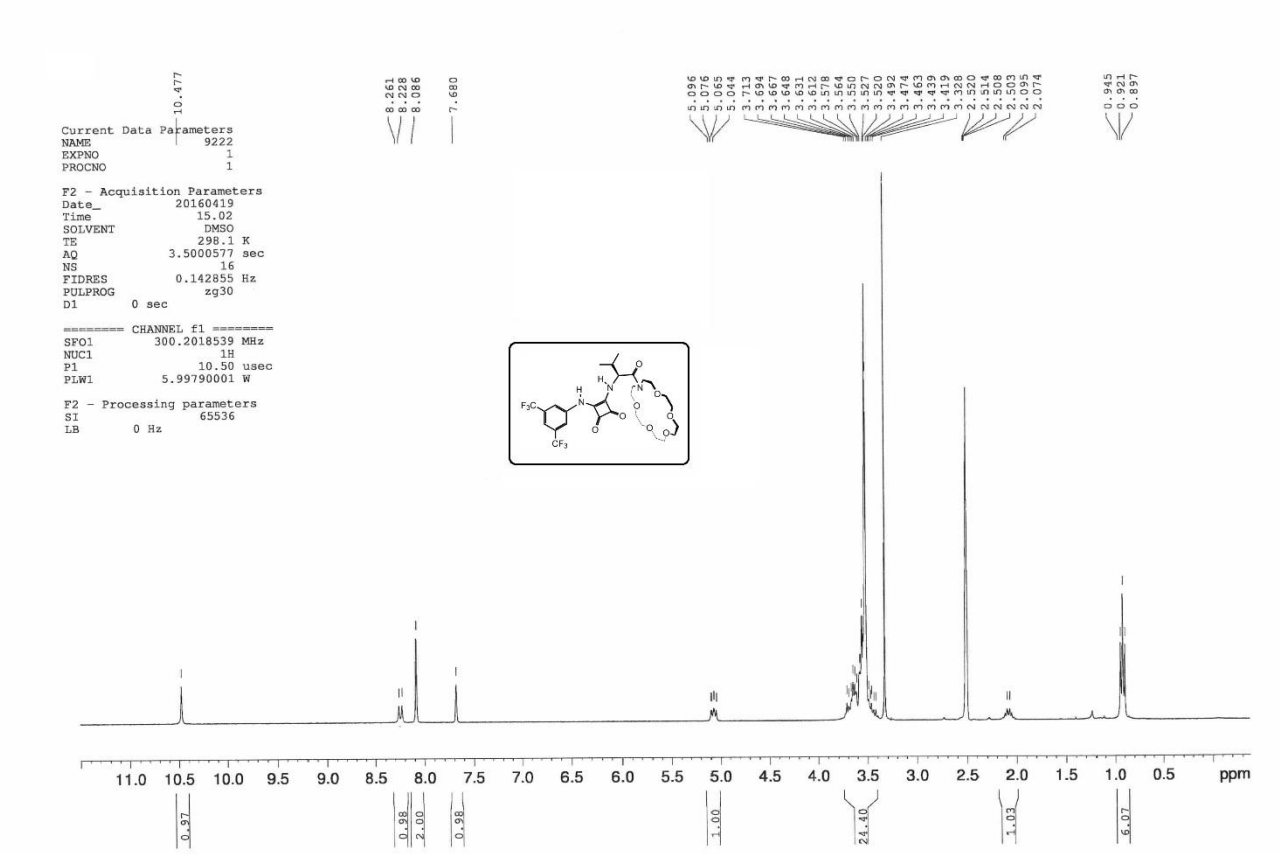
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2.503
2.095
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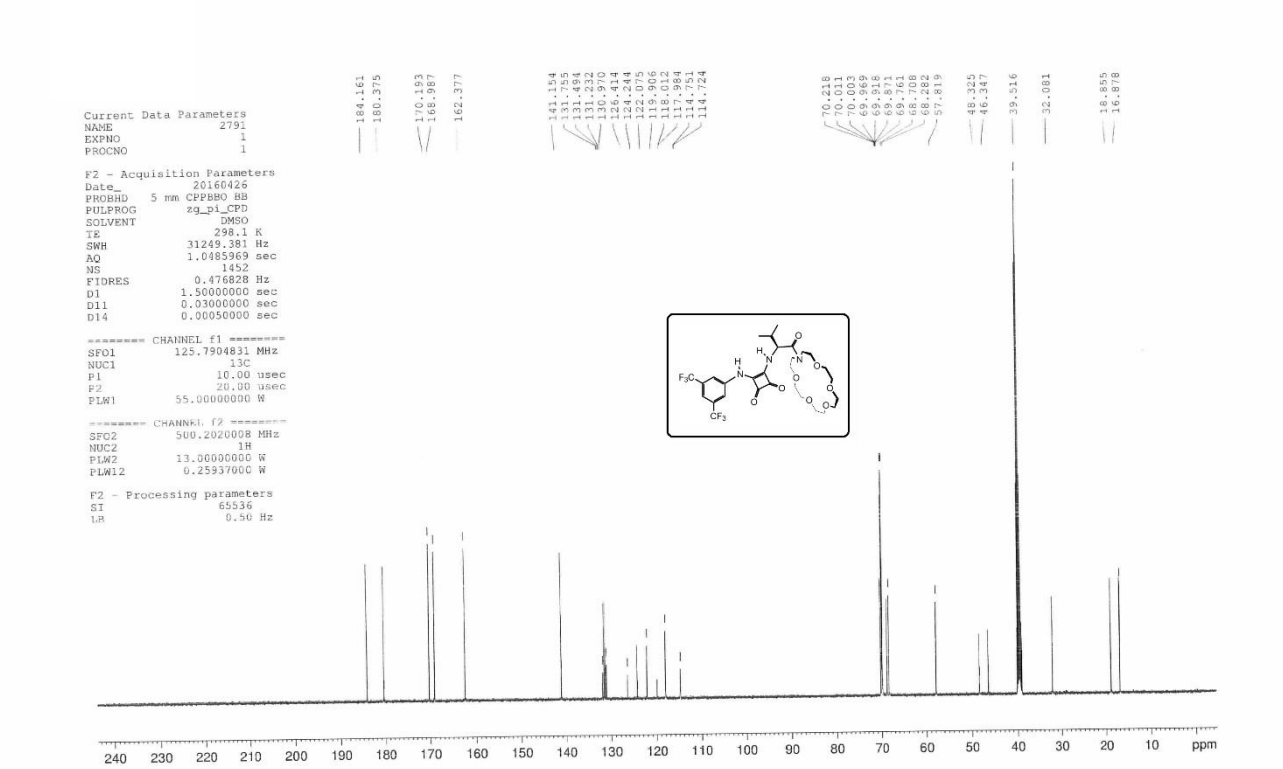
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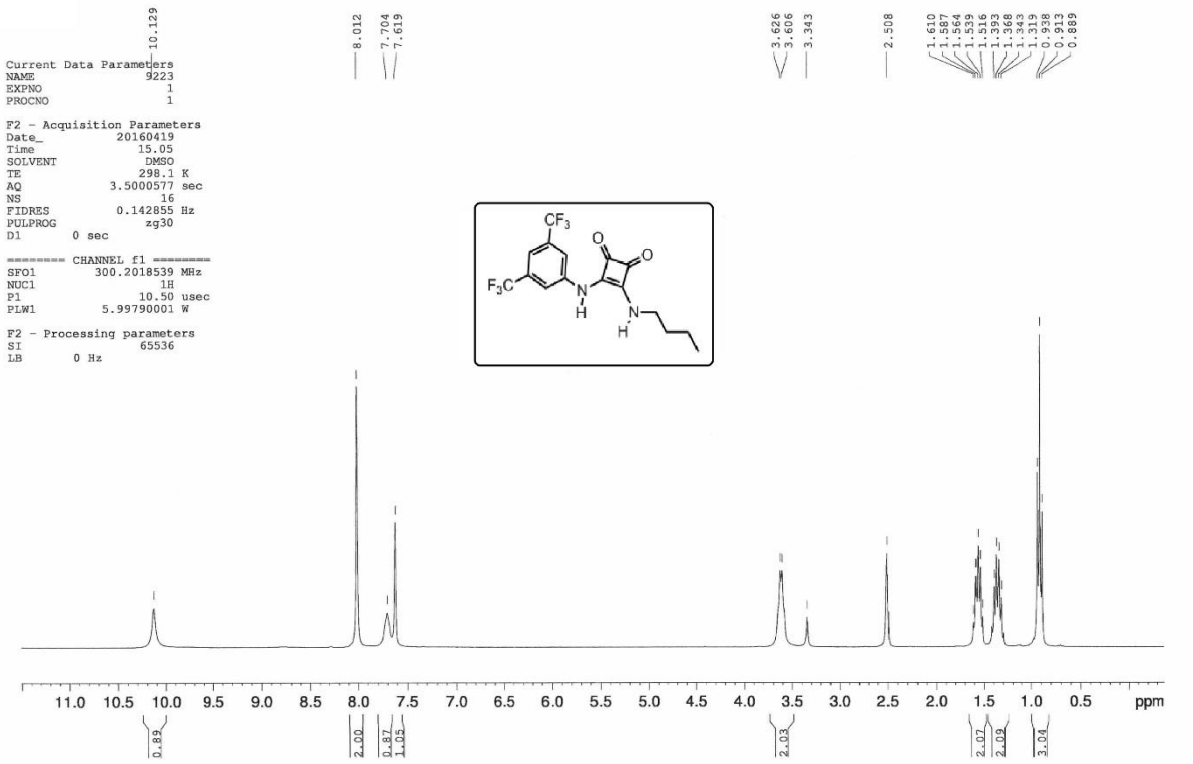
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P1 10.50 usec
PLW1 5.99790001 W
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N
H
N
H
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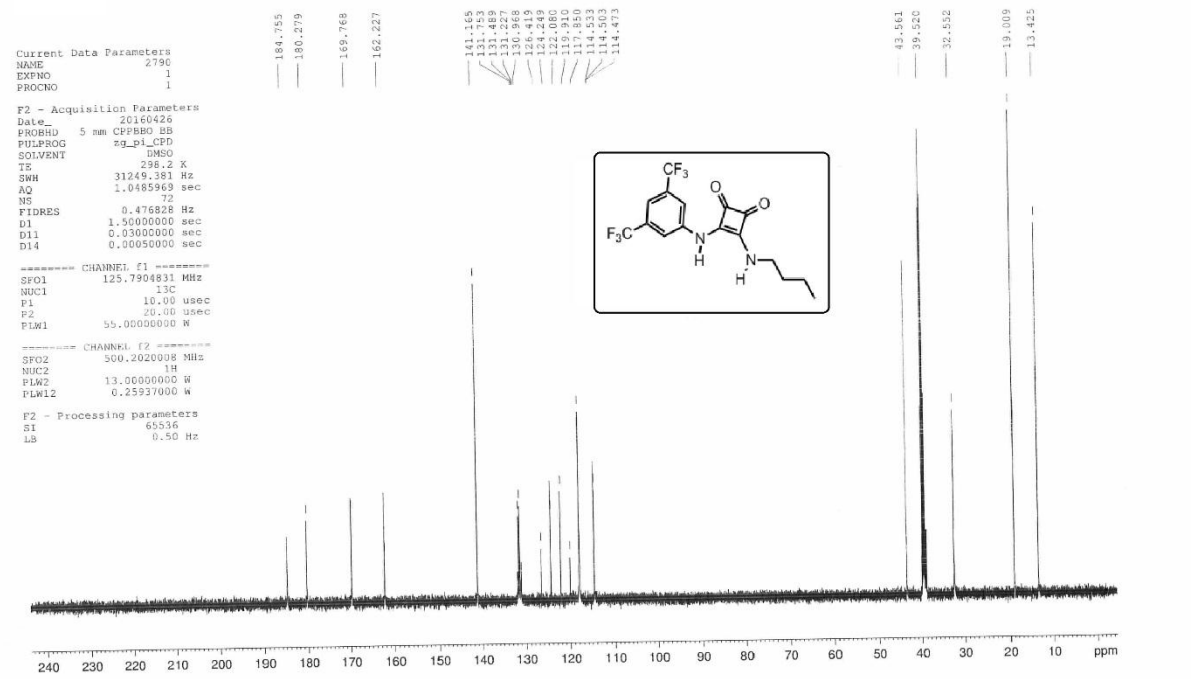
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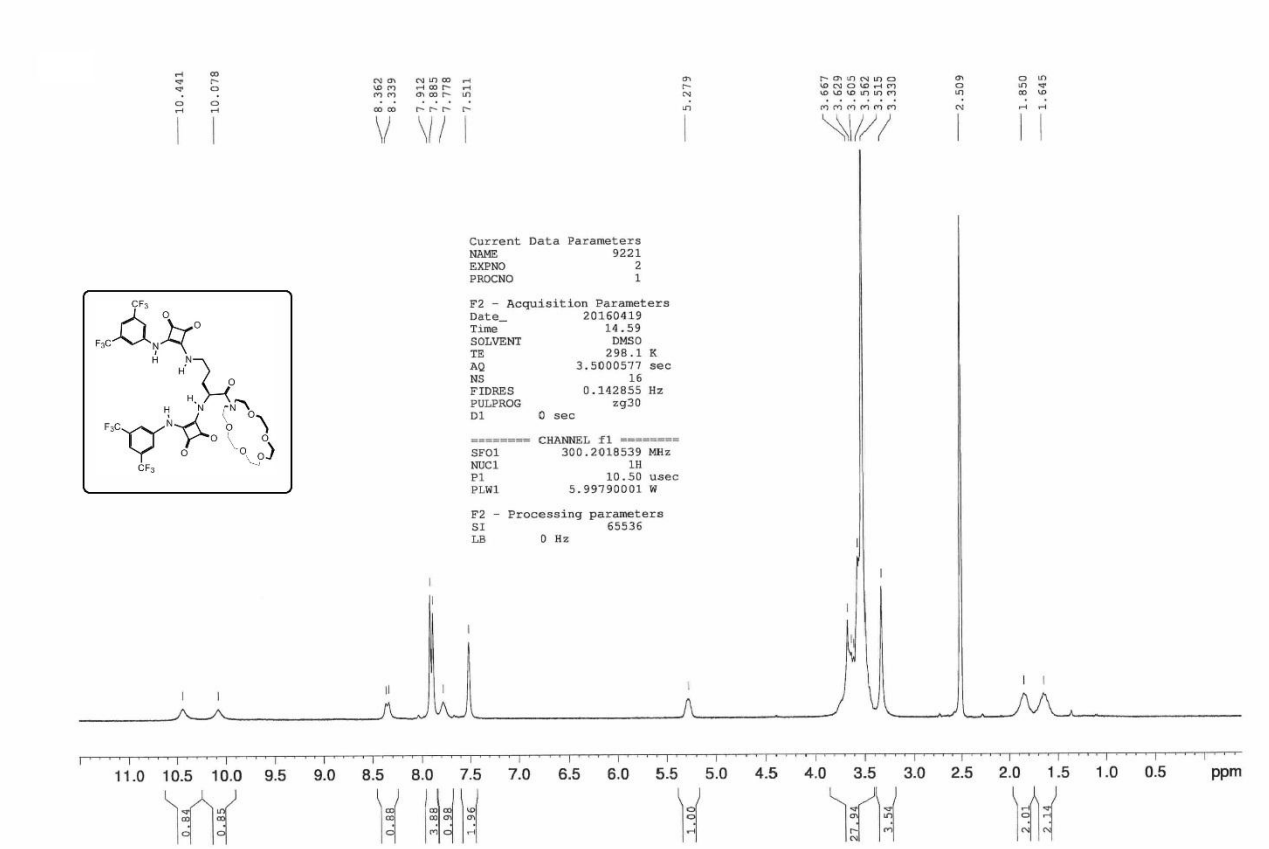
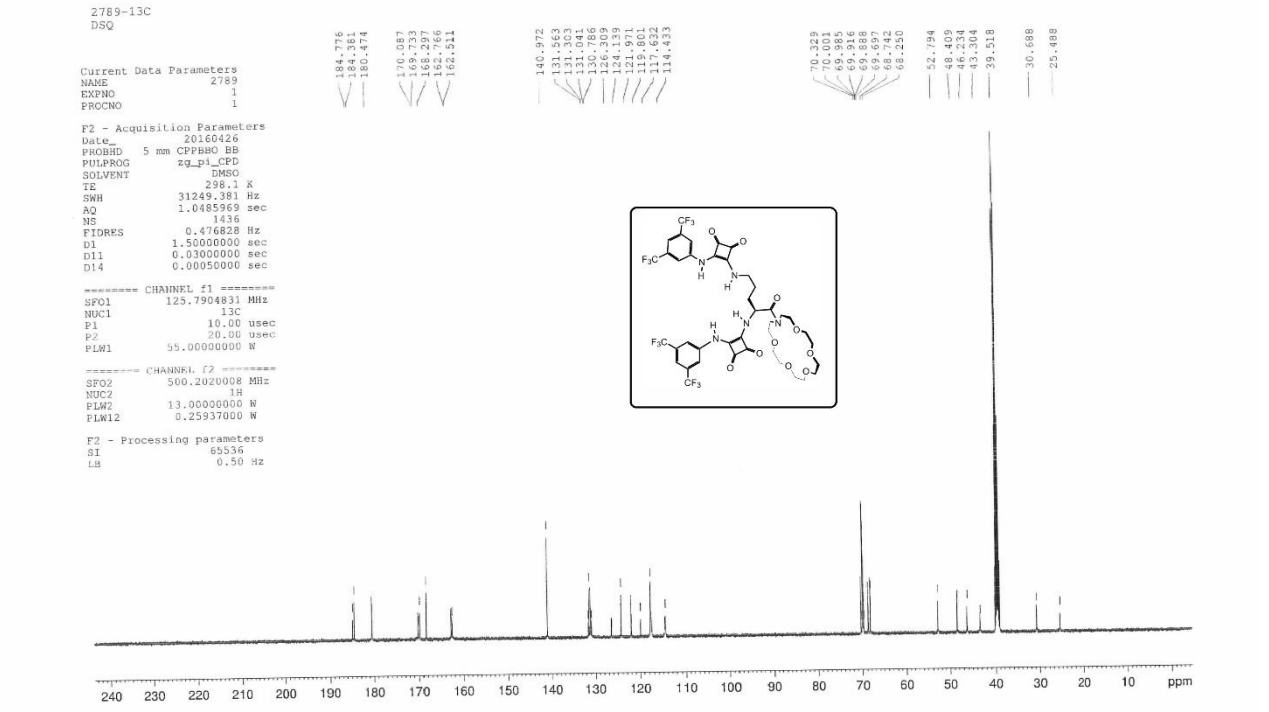
F2 - Acquisition Parameters
Date_ 20160426
PROBHD 5 mm CPPBBO BB
PULPROG zg_pl_CPD
SOLVENT DMSO
TE 298.2 K
SWH 31249.381 Hz
AQ 1.0485969 sec
NS 72
FIDRES 0.476828 Hz
D1 1.50000000 sec
D11 0.03000000 sec
D14 0.00050000 sec
======== CHANNEL f1 ========
SFO1 125.7904831 MHz
NUC1 13C
P1 10.00 usec
P2 20.00 usec
PLW1 55.00000000 W
======== CHANNEL f2 ========
SFO2 500.2020008 MHz
NUC2 1H
PLW2 13.00000000 W
PLW12 0.25937000 W
F2 - Processing parameters
SI 65536
LB 0.50 Hz
CF3
F3C
O
O
N
H
N
H
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


10.441
10.078
8.362
8.339
7.912
7.885
7.778
7.511
5.279
3.667
3.629
3.605
3.562
3.515
3.330
2.509
1.850
1.645
Current Data Parameters
NAME 9221
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160419
Time 14.59
SOLVENT DMSO
TE 298.1 K
AQ 3.5000577 sec
NS 16
FIDRES 0.142855 Hz
PULPROG zg30
D1 0 sec
======== CHANNEL f1 ========
SFO1 300.2018539 MHz
NUC1 1H
P1 10.50 usec
PLW1 5.99790001 W
F2 - Processing parameters
SI 65536
LB 0 Hz
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.84
0.85
0.88
3.88
0.98
1.96
1.00
27.94
3.54
2.01
2.14


2789-13C
DSQ
184.776
184.361
180.474
170.087
169.733
168.237
162.766
162.511
140.972
131.563
131.303
131.044
130.786
126.309
124.139
121.971
119.801
117.632
114.433
70.329
70.001
69.985
69.916
69.888
69.697
68.282
68.250
52.794
48.409
46.234
43.304
39.518
30.688
25.488
Current Data Parameters
NAME 2789
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160426
PROBHD 5 mm CPPBBO BB
PULPROG zg_pi_CPD
SOLVENT DMSO
TE 298.1 K
SWH 31249.381 Hz
AQ 1.0485969 sec
NS 1436
FIDRES 0.476828 Hz
D1 1.50000000 sec
D11 0.03000000 sec
D14 0.00050000 sec
======== CHANNEL f1 ========
SFO1 125.7904831 MHz
NUC1 13C
P1 10.00 usec
P2 20.00 usec
PLW1 55.00000000 W
======== CHANNEL f2 ========
SFO2 500.2020008 MHz
NUC2 1H
PLW2 13.00000000 W
PLW12 0.25937000 W
F2 - Processing parameters
SI 65536
LB 0.50 Hz
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm