

Supporting Information

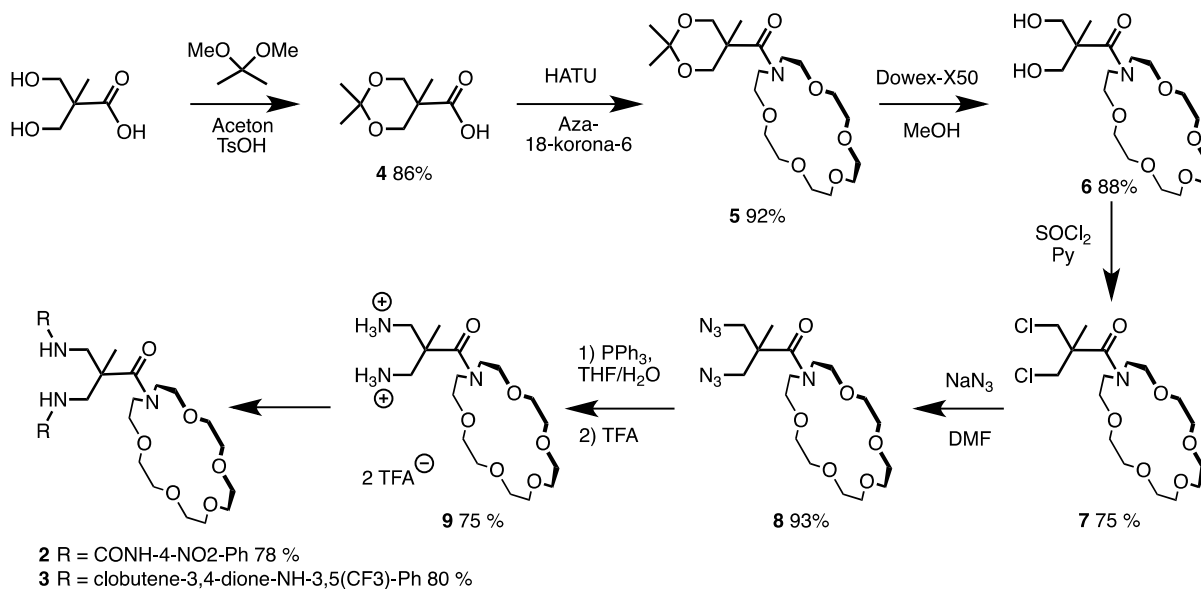
Highly effective ion-pair receptors based on 2,2-Bis(aminomethyl) propionic acid

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Synthetic route to receptors **2** and **3**.



NMR SPECTRA

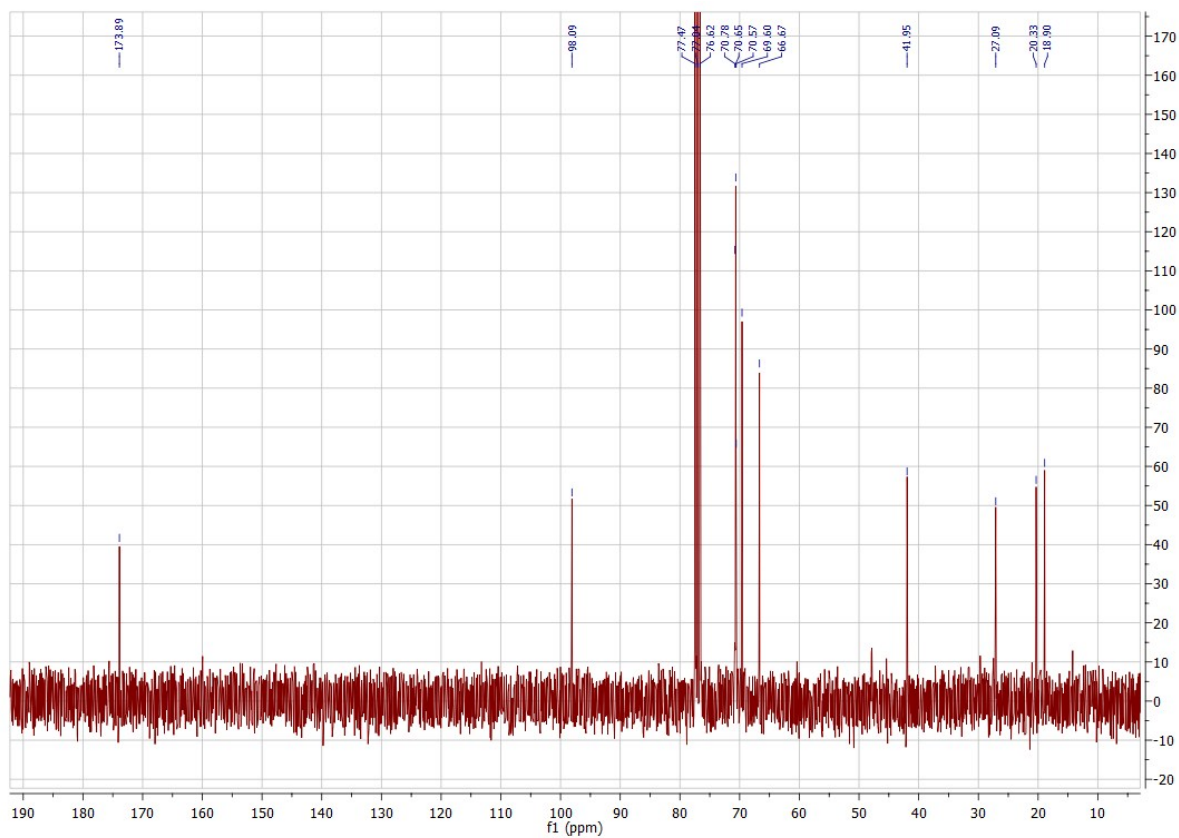
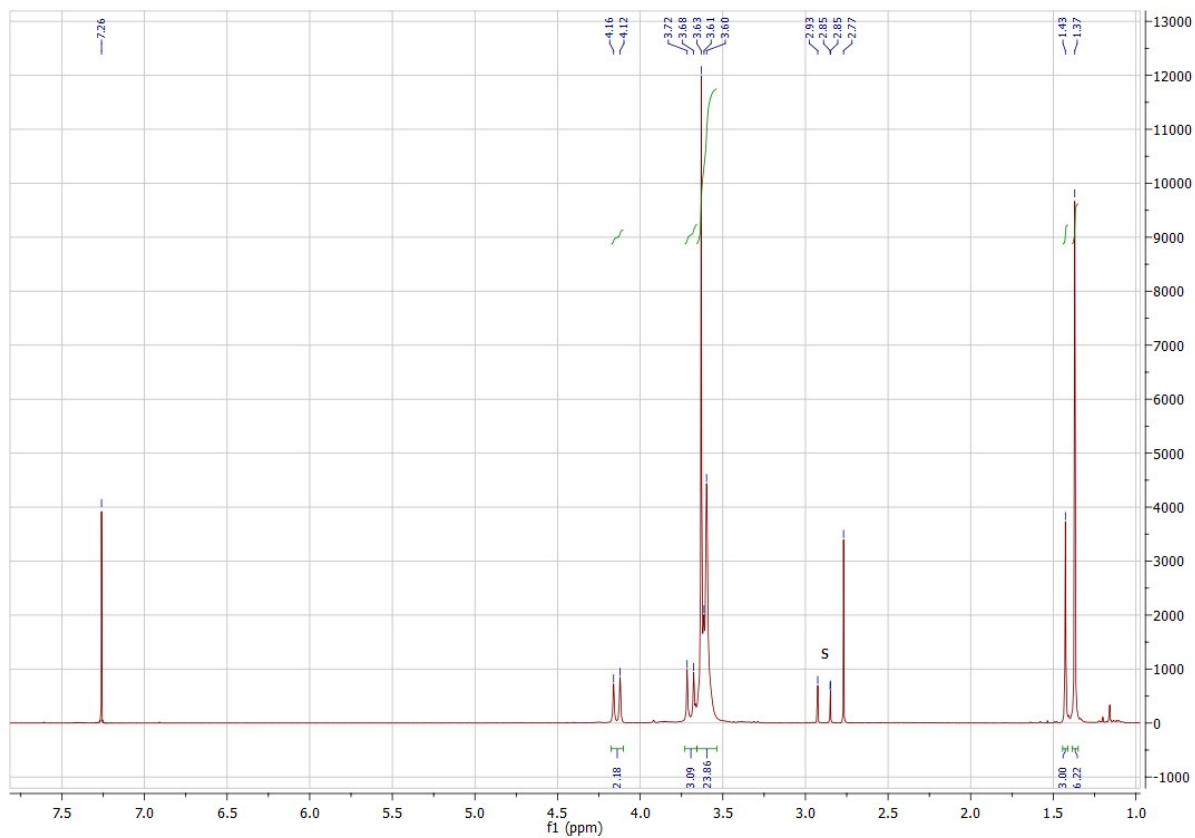


Figure S1. ^1H and ^{13}C NMR of compound 5.

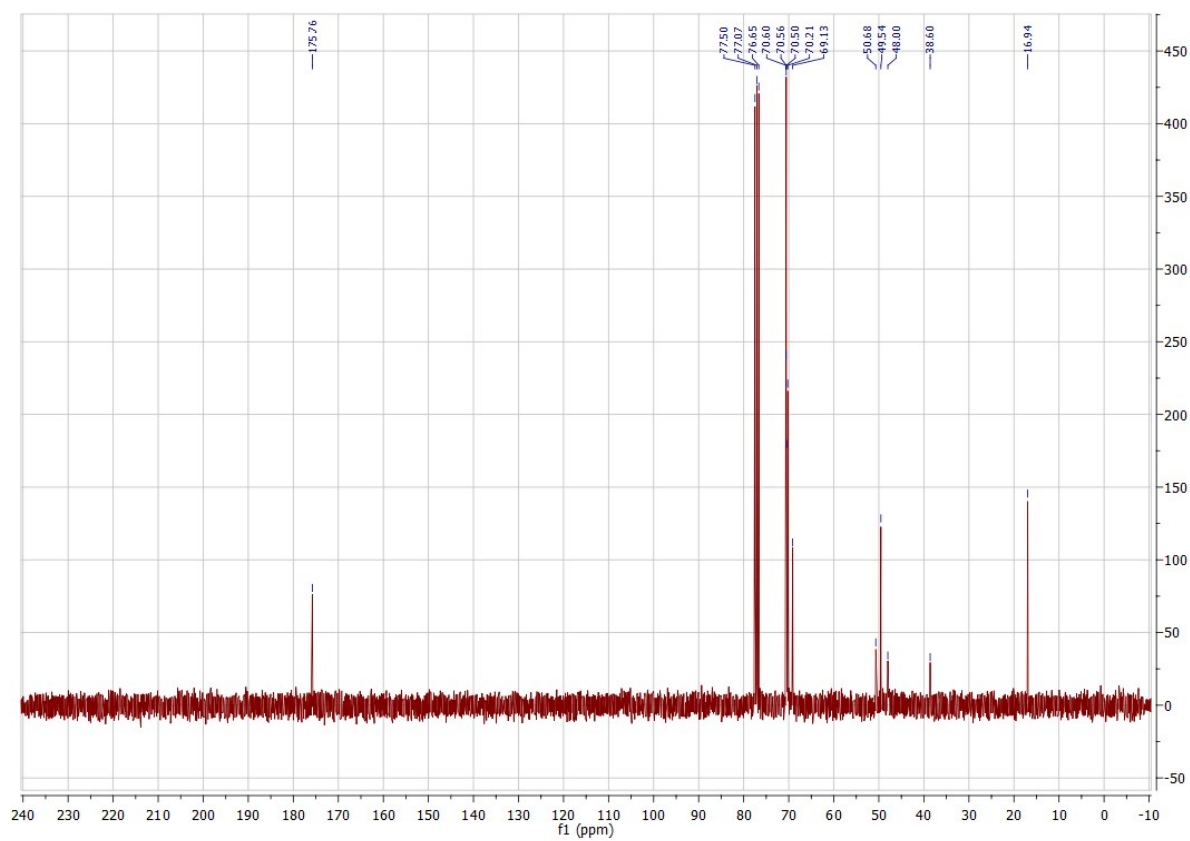
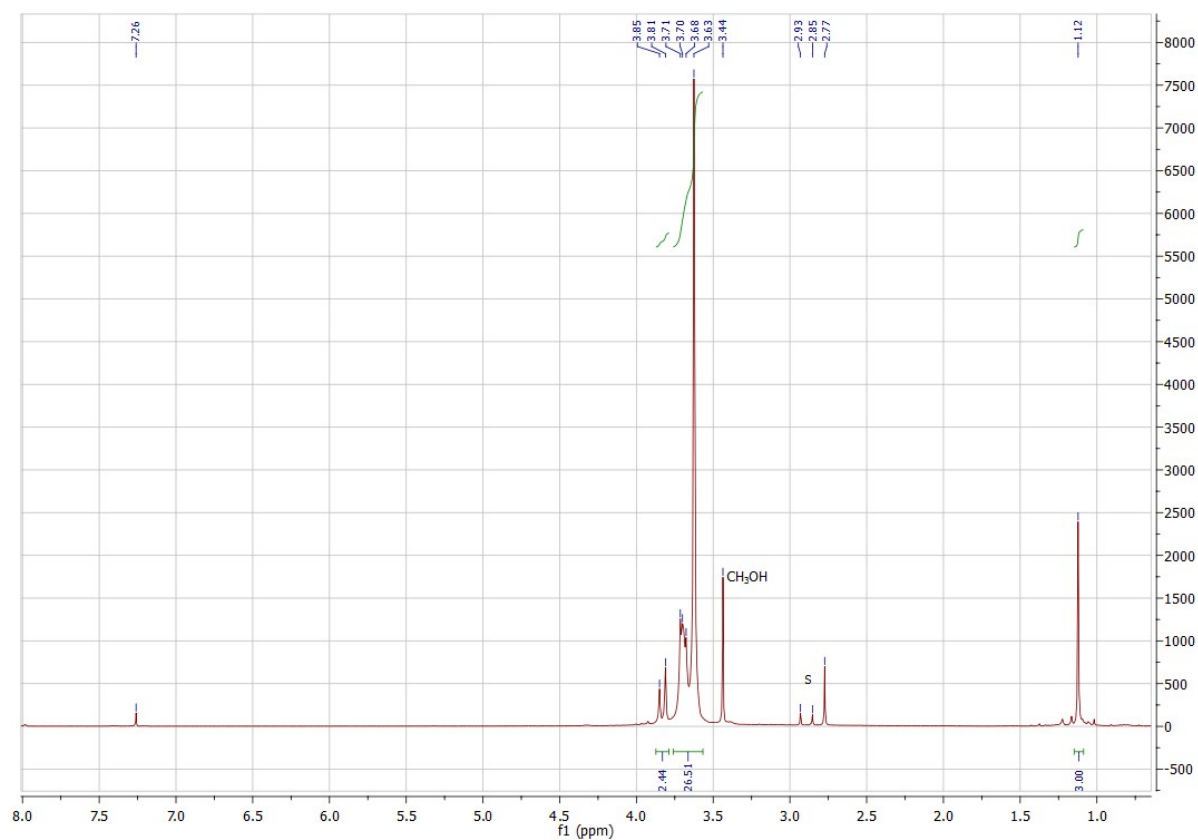


Figure S2. ^1H and ^{13}C NMR of diol 6.

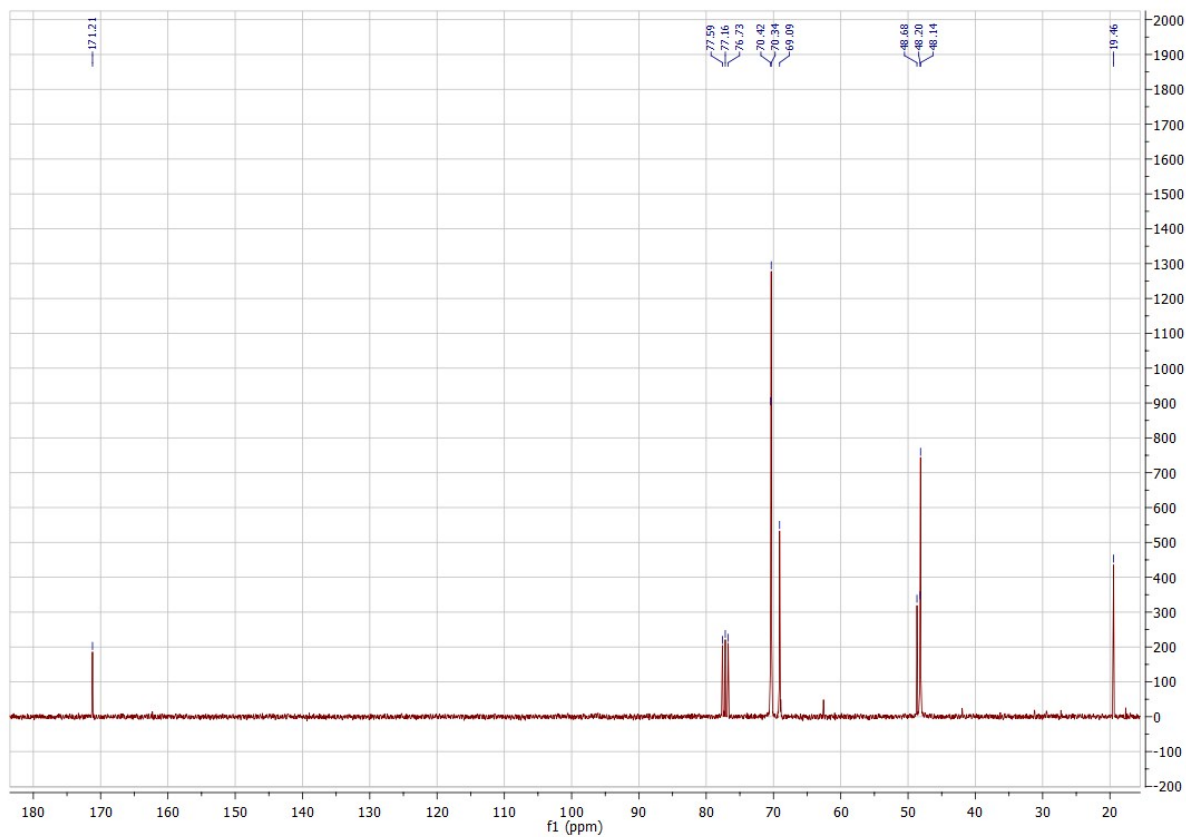
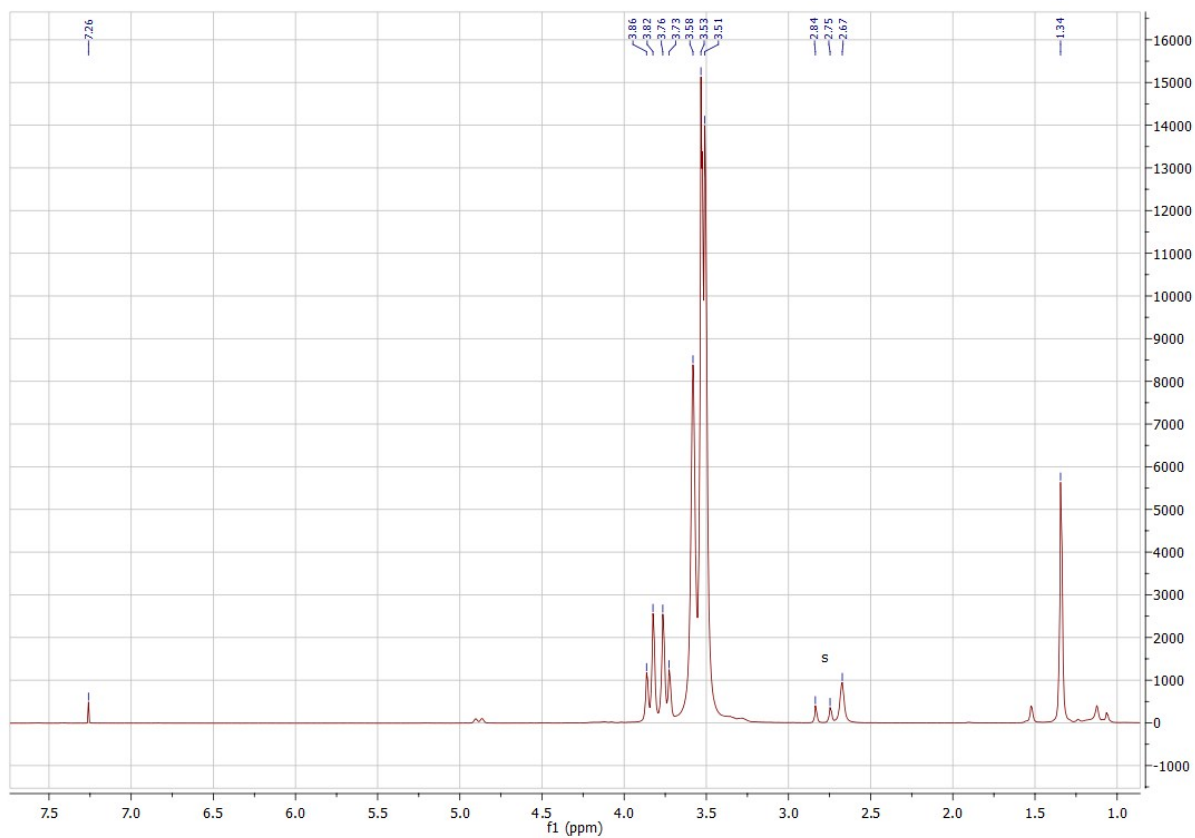


Figure S3. ¹H and ¹³C NMR of compound bischloride 7.

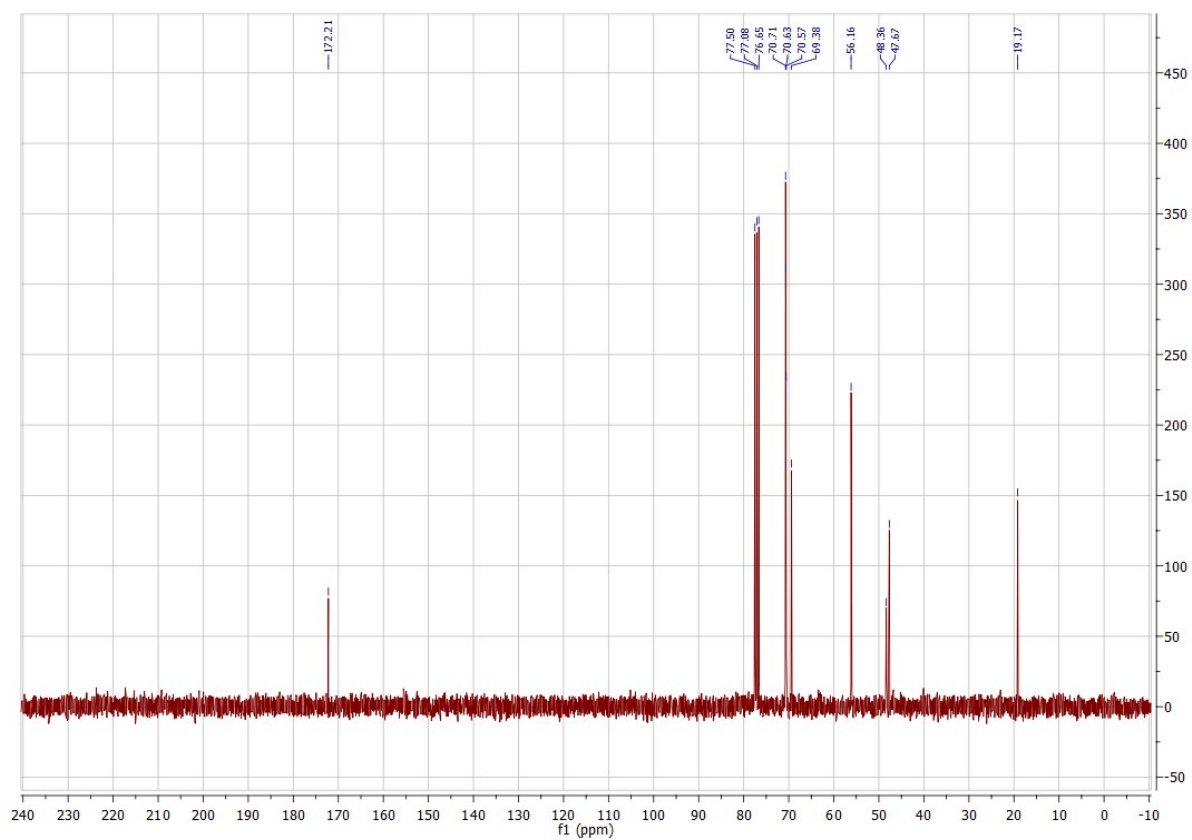
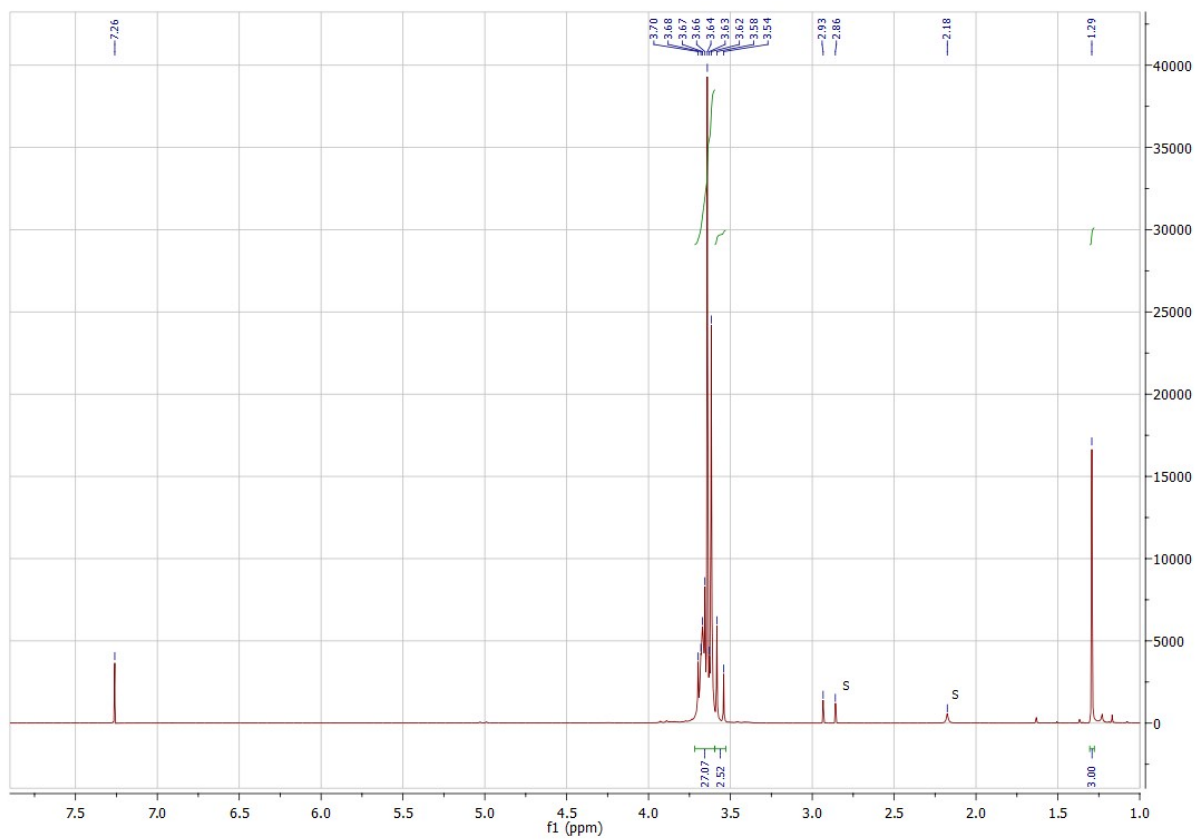


Figure S4. ^1H and ^{13}C NMR of bisazide **8**.

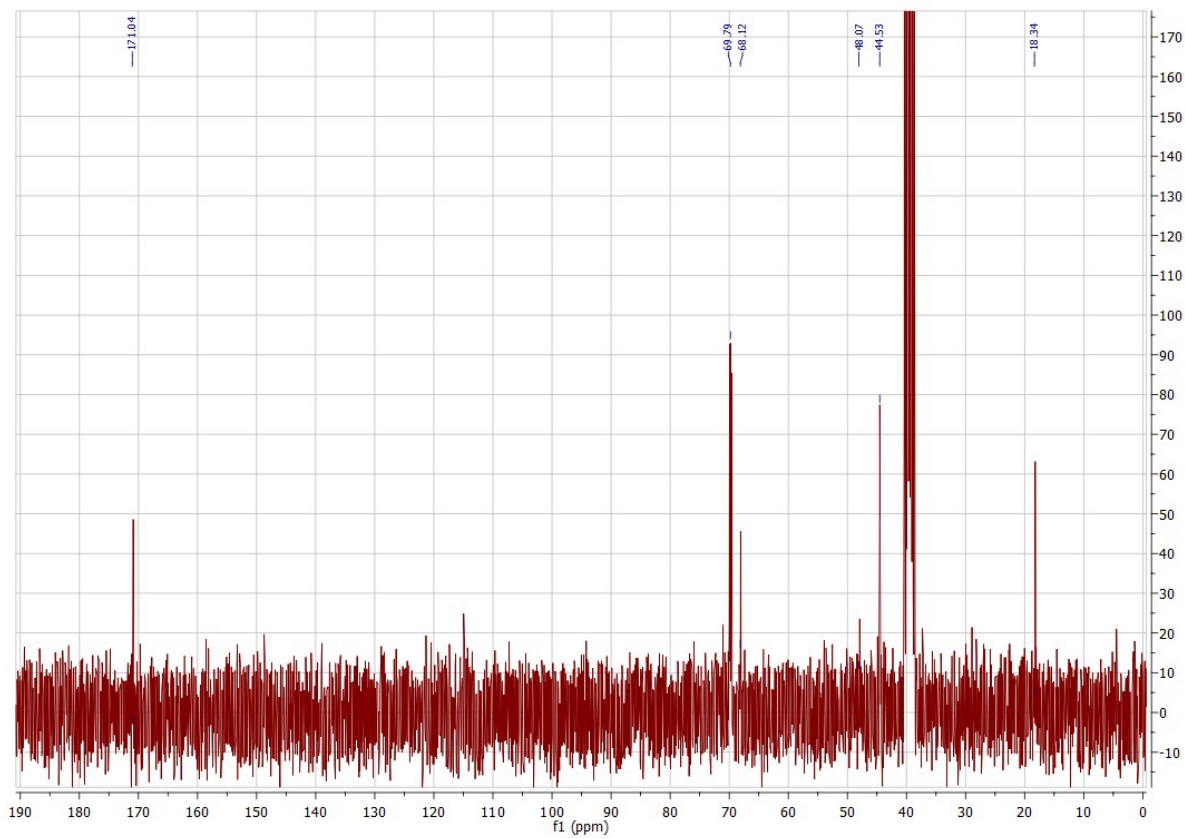
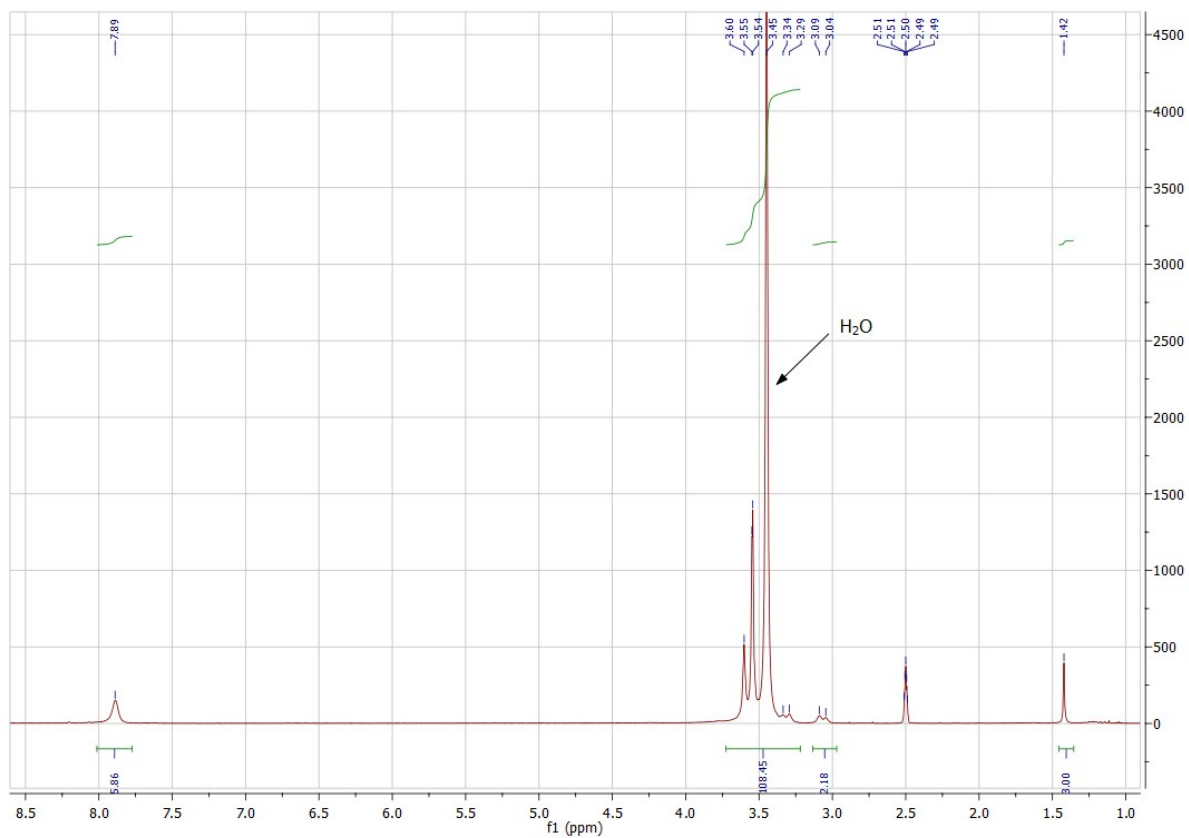


Figure S5. ¹H and ¹³C NMR of bisammonium salt **9** in DMSO-d₆.

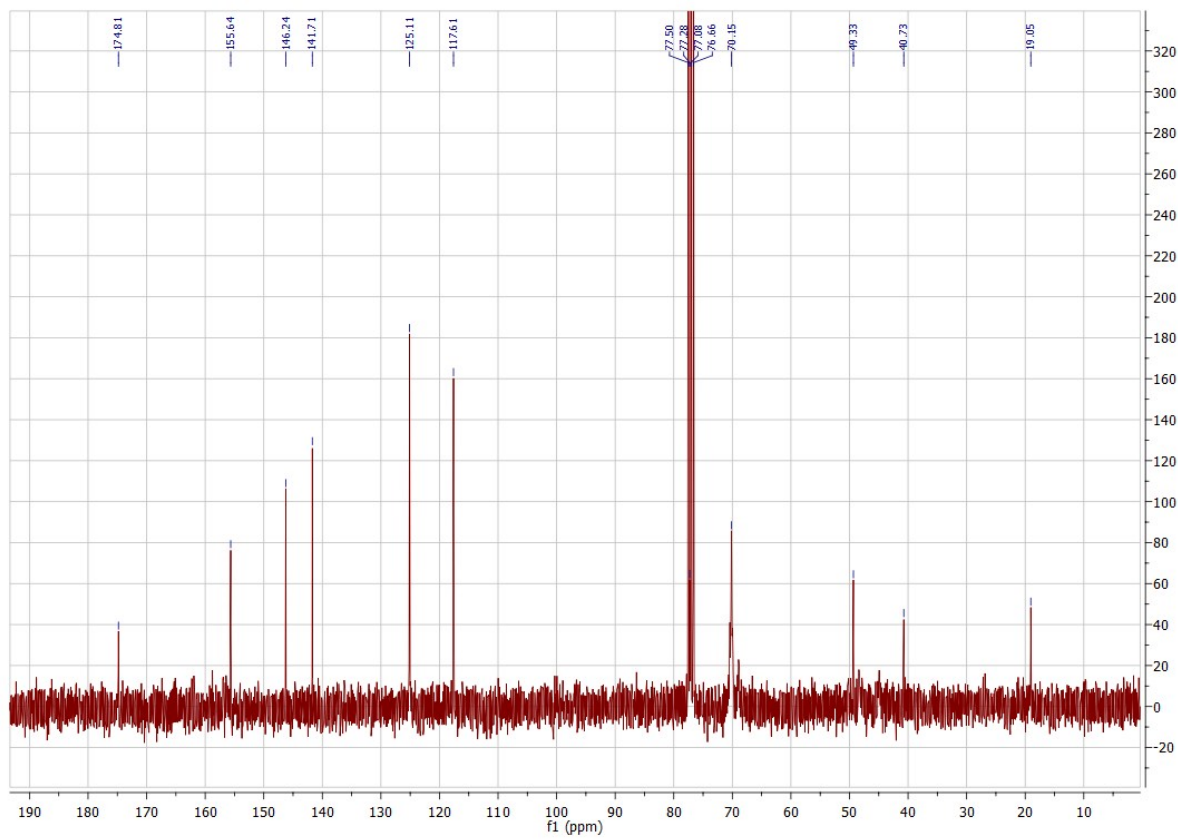
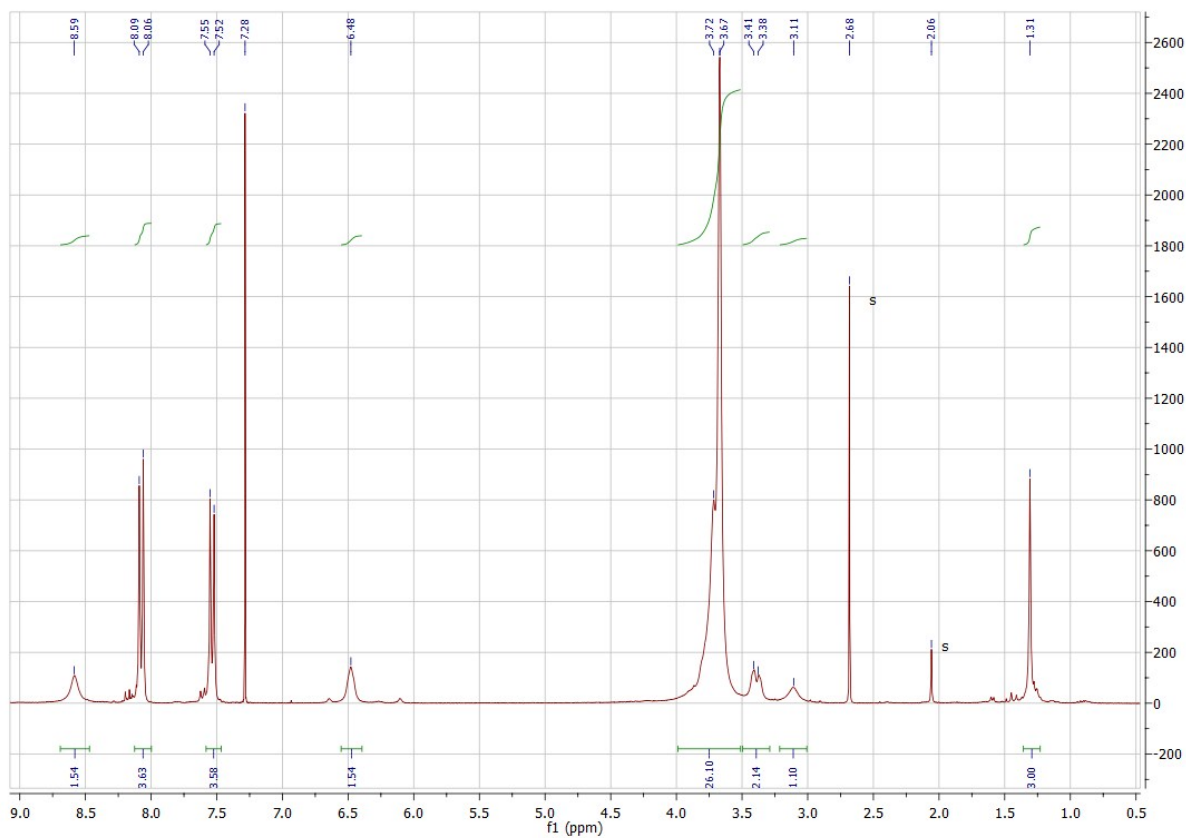


Figure S6. ¹H and ¹³C NMR of urea group containing receptor 2.

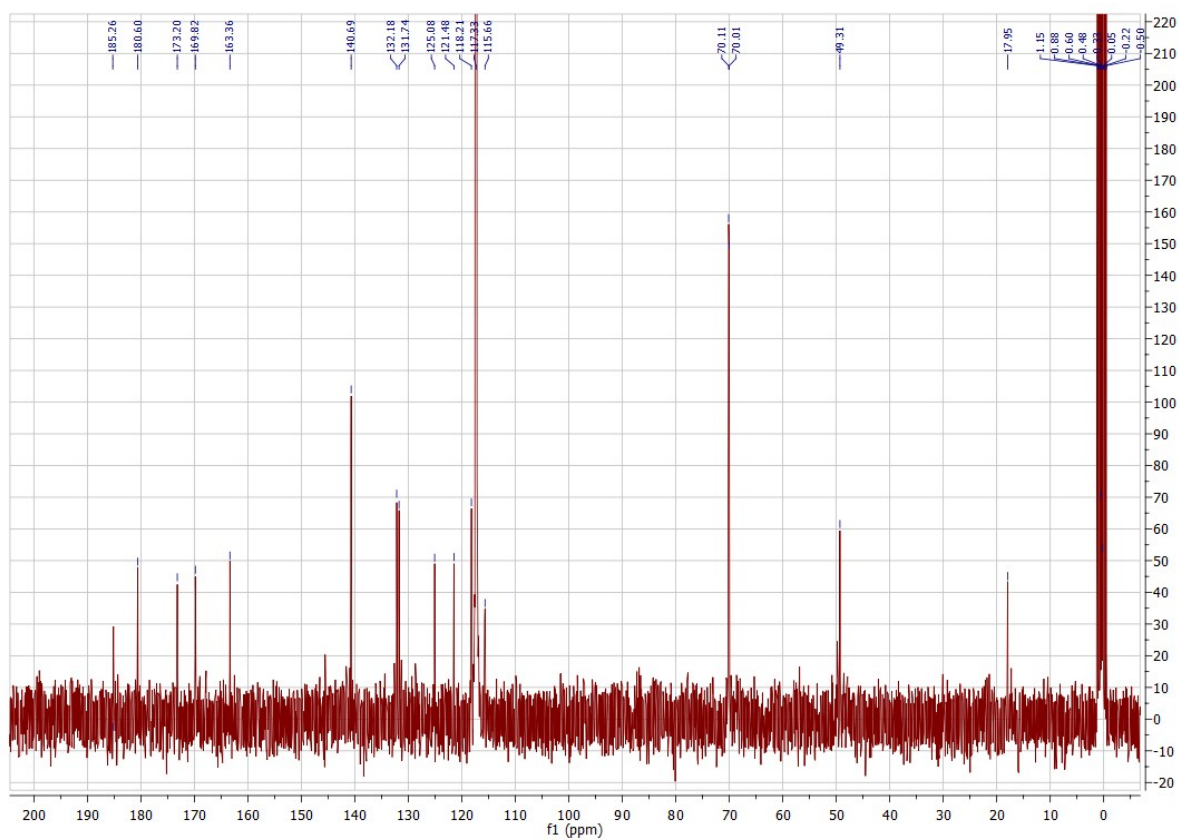
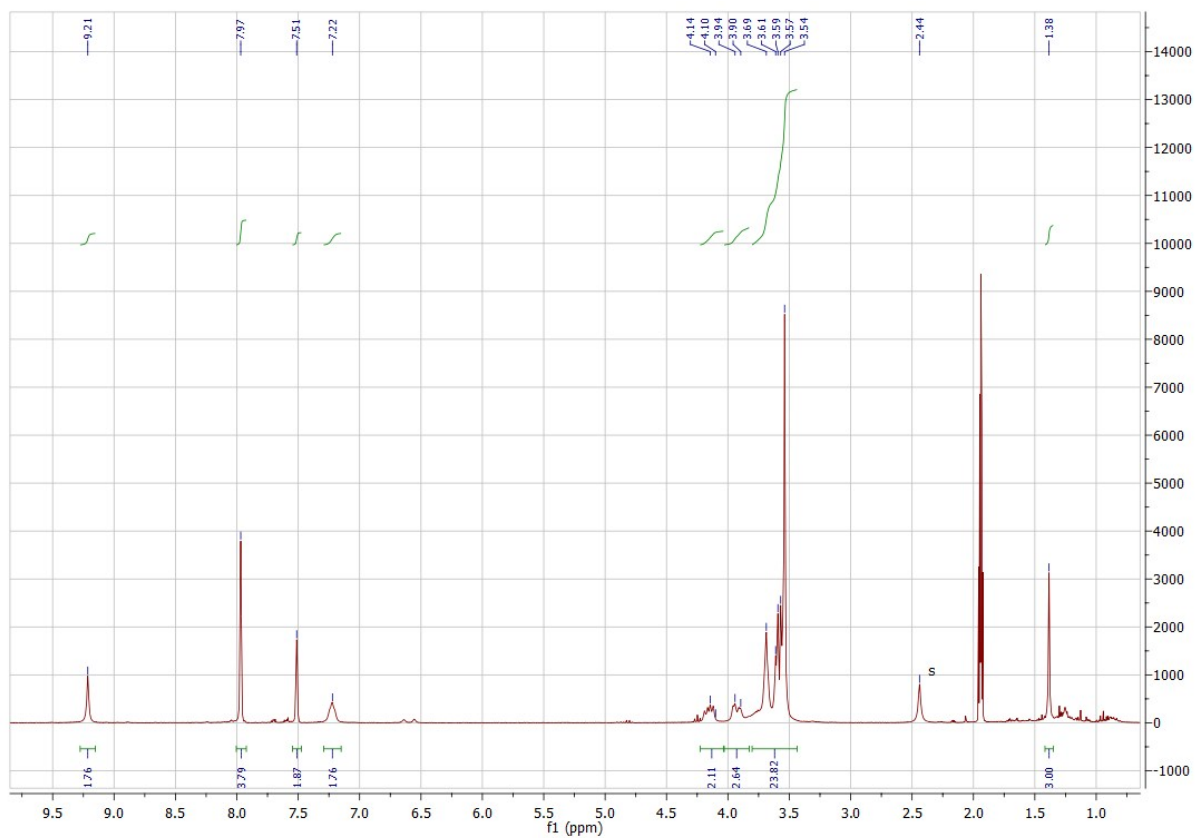


Figure S7. ¹H and ¹³C NMR of squaramide group containing receptor **3**.

UV-vis experiments:

Representative Job plots:

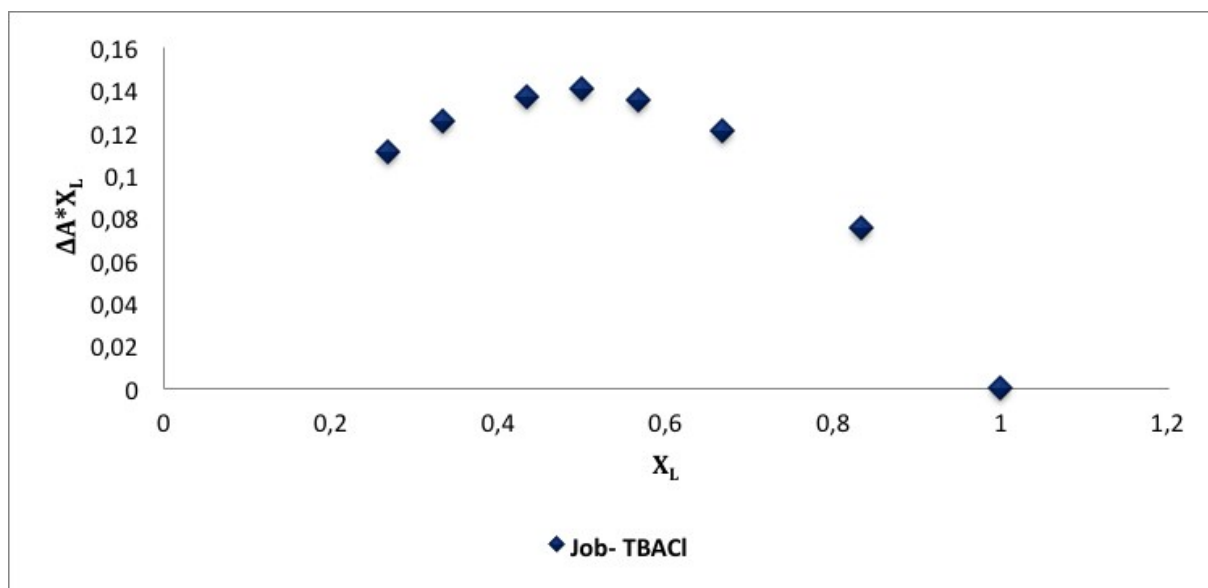


Figure S8. Job plot analysis of receptor 2 in the presence of TBACl.

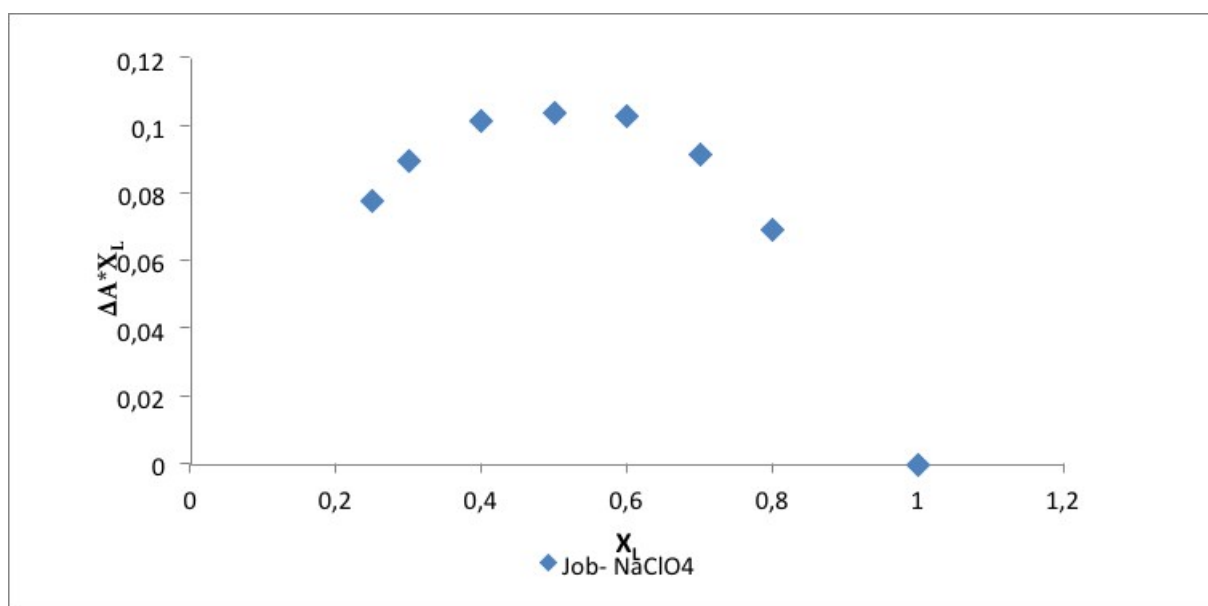


Figure S9. Job plot analysis of receptor 2 in the presence of NaClO₄.

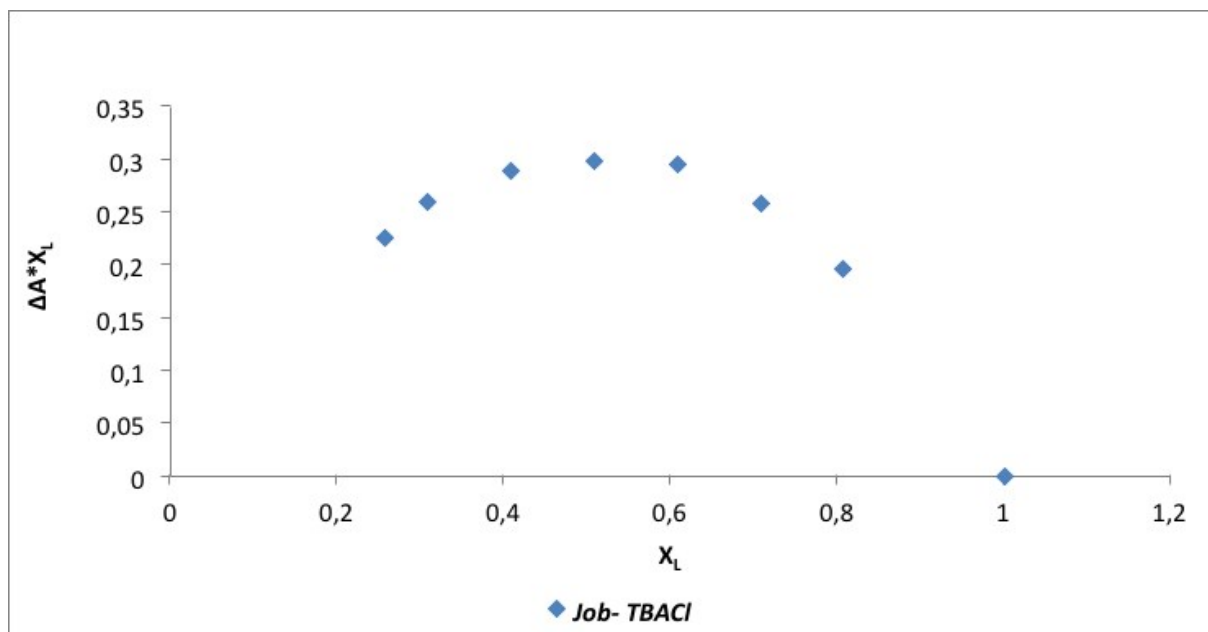


Figure S10. Job plot analysis of receptor **3** in the presence of TBACl.

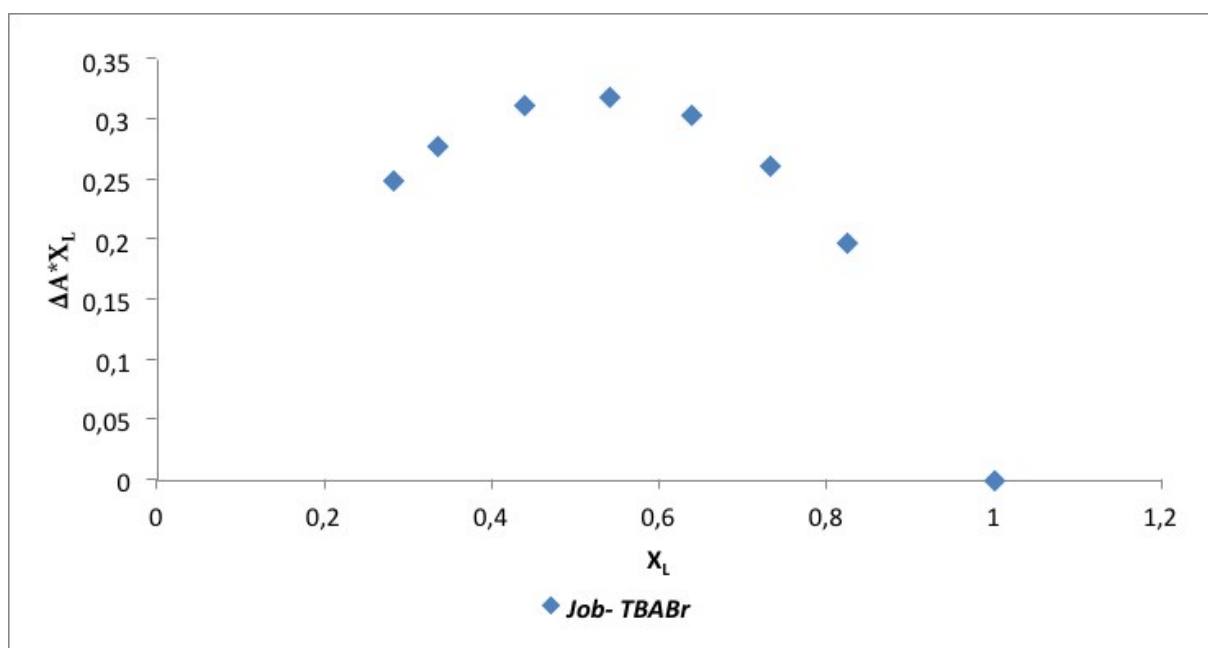
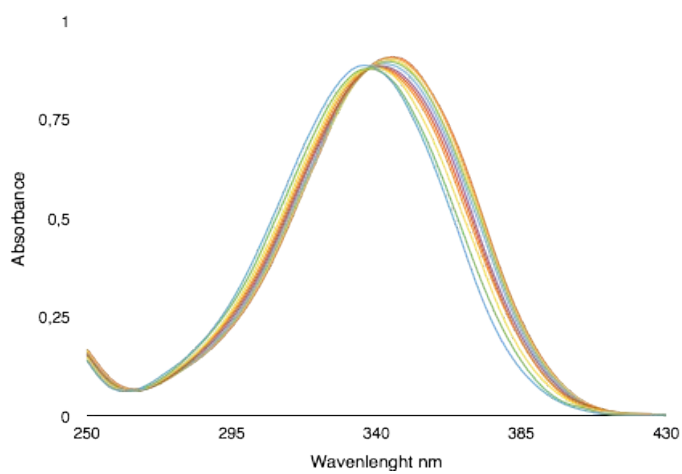


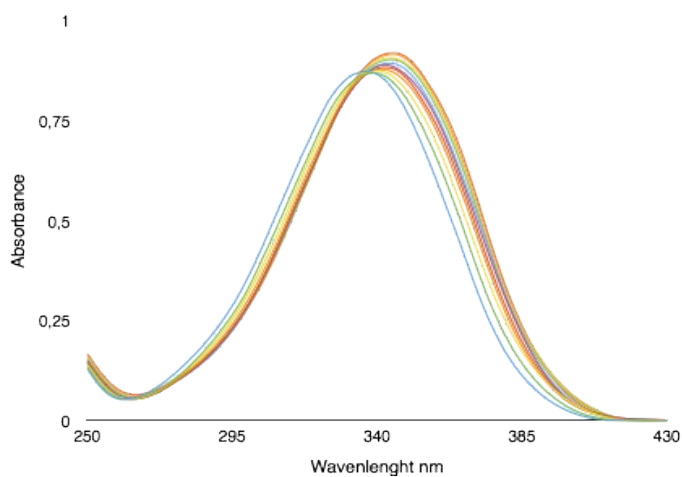
Figure S11. Job plot analysis of receptor **3** in the presence of TBABr.

Representative UV-vis titrations:

a)



b)



c)

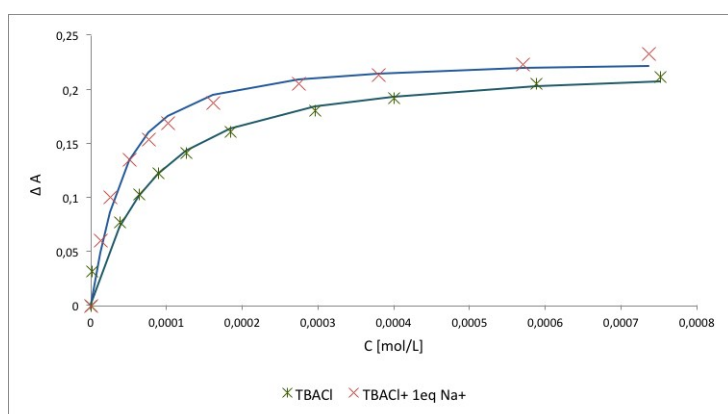


Figure S 12. UV-vis spectrum modulation upon the addition of TBACl to the CH₃CN solution of 2: in the absence (a) and presence (b) of 1eq of NaClO₄ (solvent CH₃CN, temperature 293 K, [2] = 31 μ M, titrant [TBACl] = 1 mM) and (c) the resulting binding isotherms.

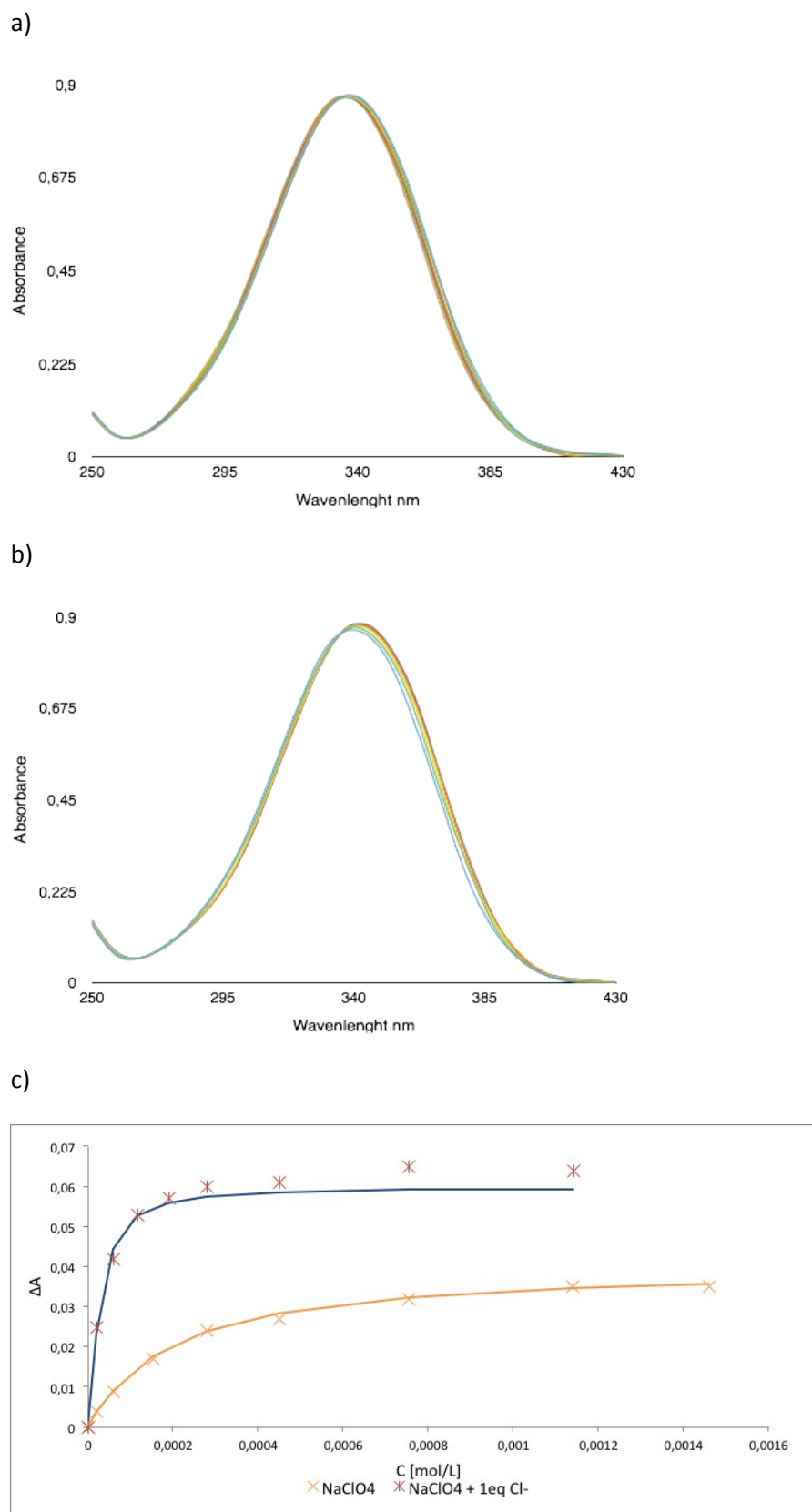


Figure S 13. UV-vis spectrum modulation upon the addition of NaClO₄ to the CH₃CN solution of **2**: in the absence (a) and presence (b) of 1eq of TBACl (solvent CH₃CN, temperature 293 K, [2] = 31 μM, titrant [TBACl] = 1 mM) and (c) the resulting binding isotherms.

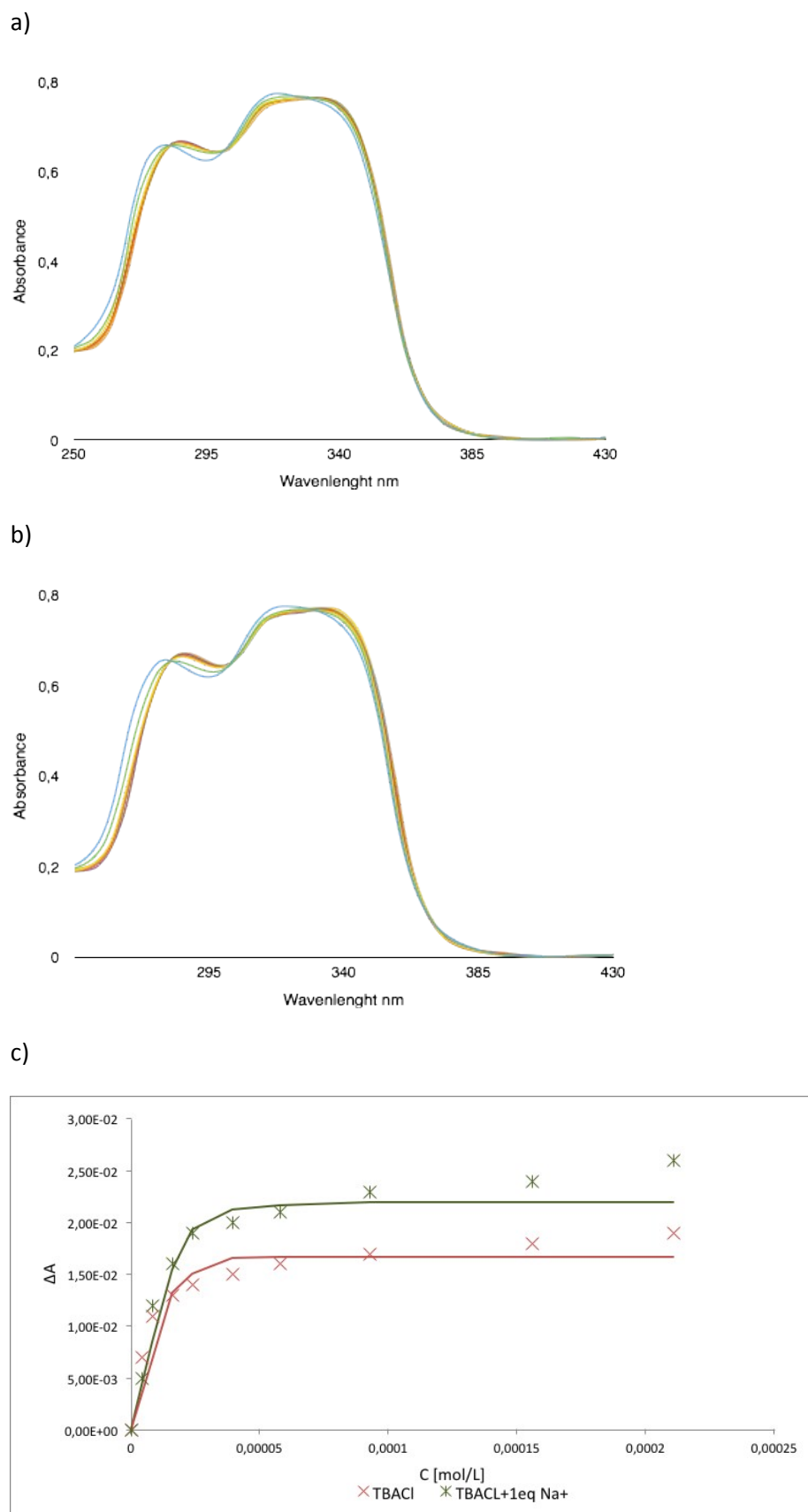


Figure S 14. UV-vis spectrum modulation upon the addition of TBACl to the CH_3CN solution of **3**: in the absence (a) and presence (b) of 1eq of NaClO_4 (solvent CH_3CN , temperature 293 K, $[\text{2}] = 31 \mu\text{M}$, titrant $[\text{TBACl}] = 1 \text{ mM}$) and (c) the resulting binding isotherms.

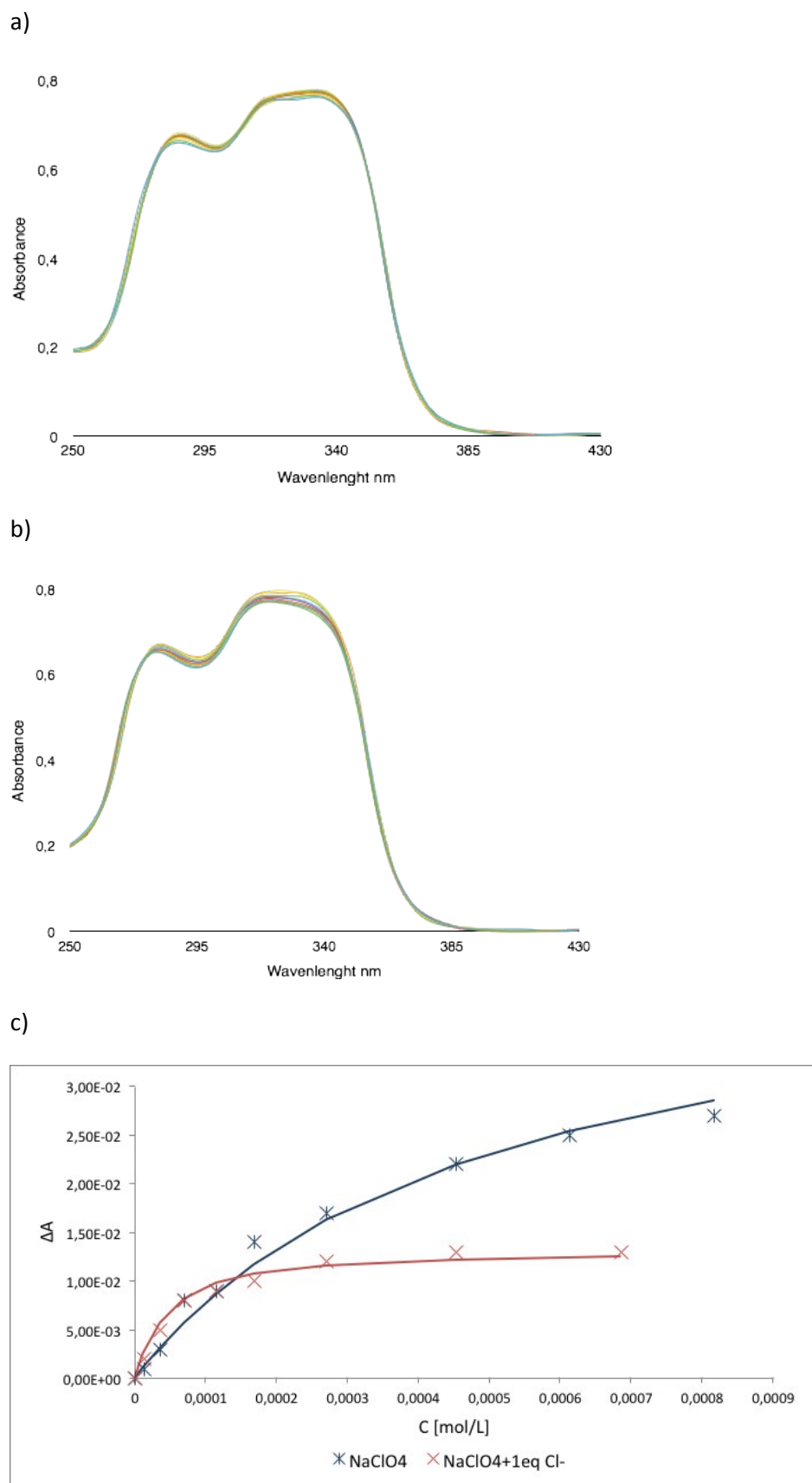


Figure S 15. UV-vis spectrum modulation upon the addition of NaClO₄ to the CH₃CN solution of **2**: in the absence (a) and presence (b) of 1eq of TBACl (solvent CH₃CN, temperature 293 K, [2] = 31 μM, titrant [TBACl] = 3.15 mM) and (c) the resulting binding isotherms.

¹H NMR titration experiments

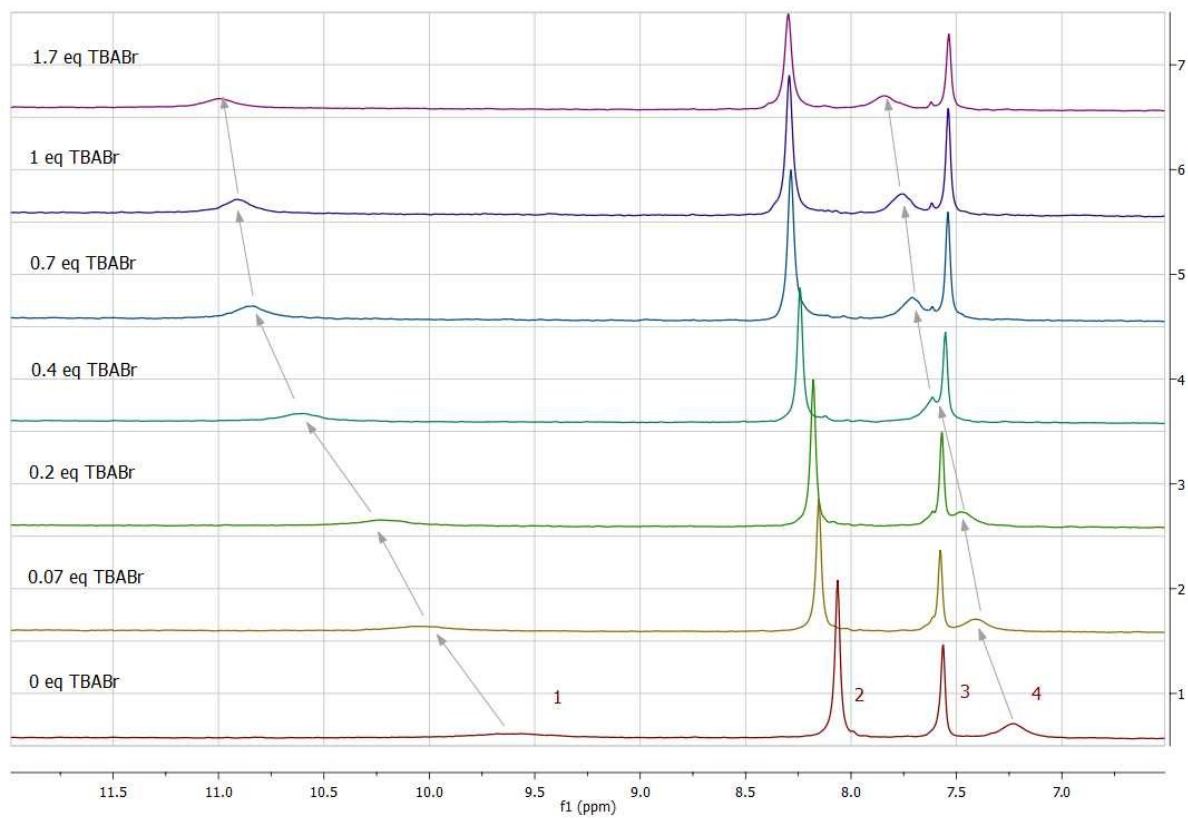
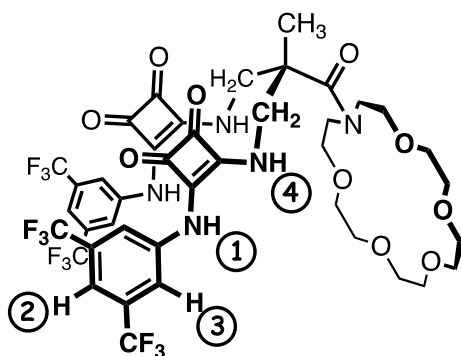


Figure S 16. Partial ¹H NMR spectra (300 MHz, 298 K) of receptor **3** upon addition of TBABr.

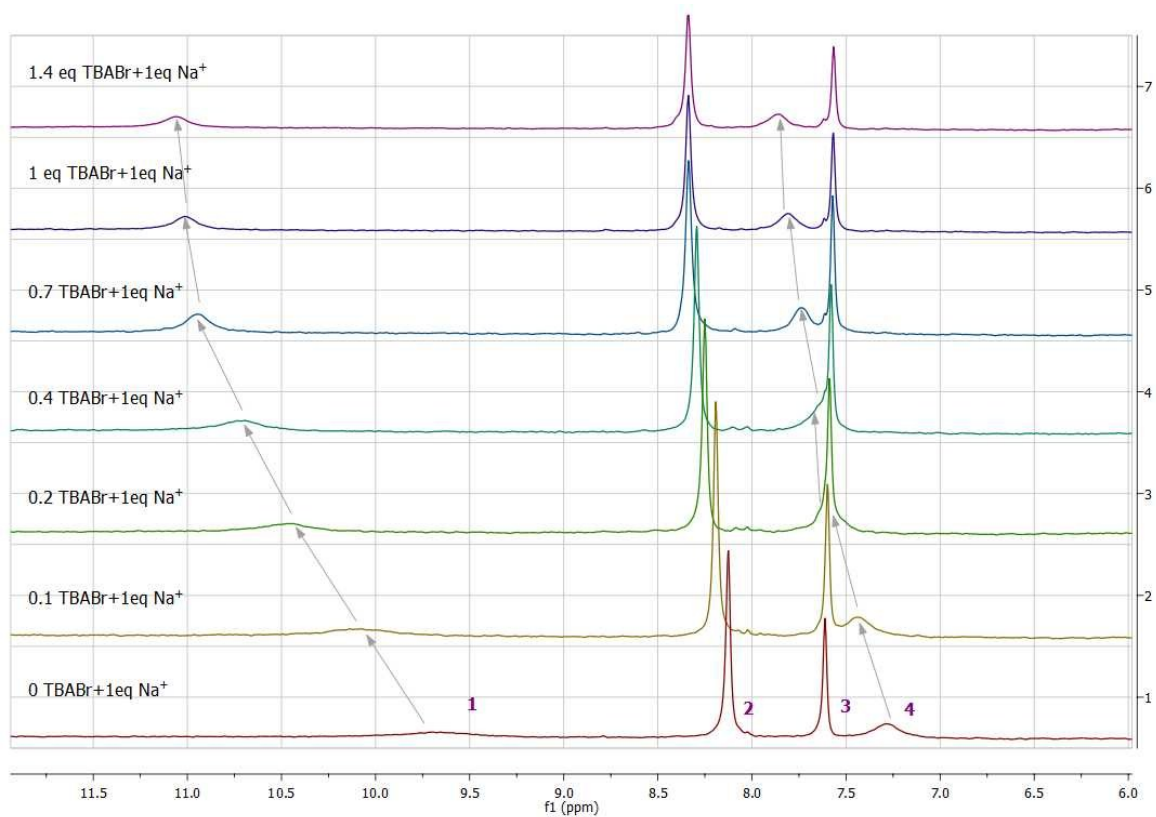


Figure S 17. Partial ^1H NMR spectra (300 MHz, 298 K) of receptor **3** + 1eq of NaClO_4 upon addition of TBABr.

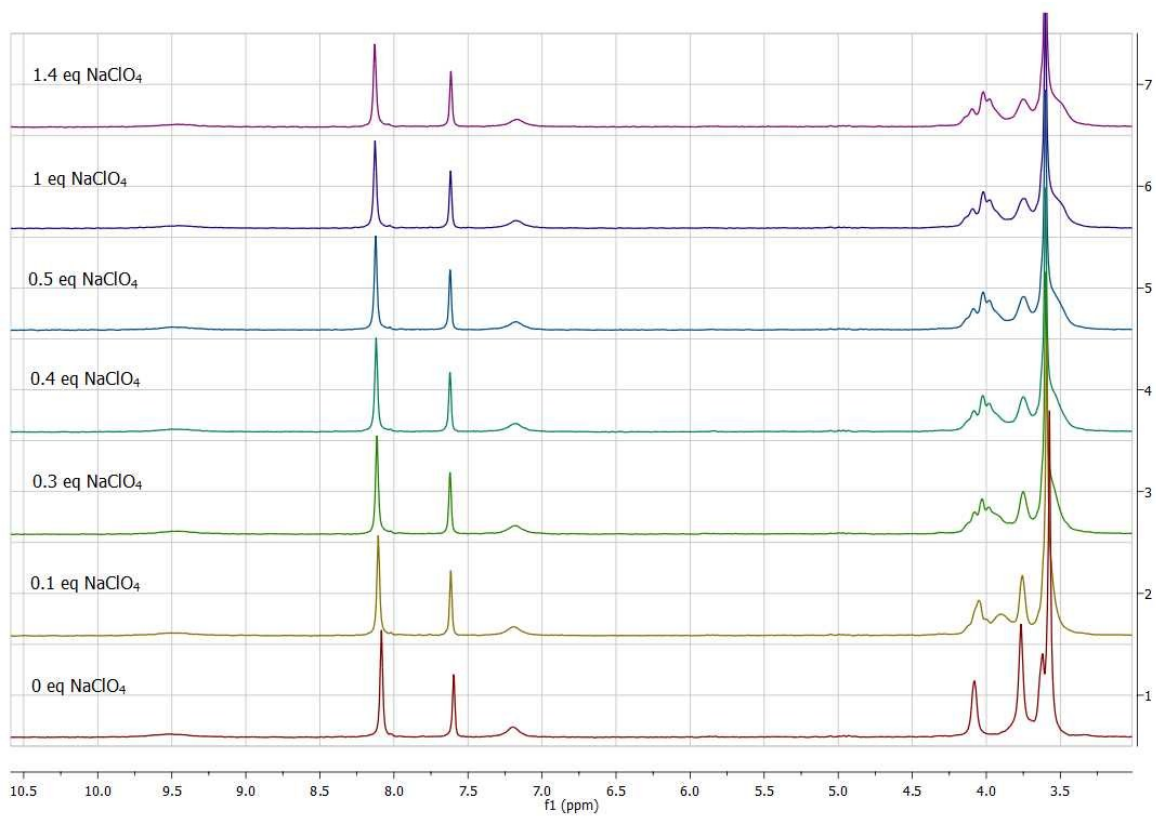


Figure S 18. Partial ^1H NMR spectra (300 MHz, 298 K) of receptor **3** upon addition of NaClO_4 .

Crystallographic Data

The X-ray measurement of receptor **3** was performed at 100(2) K on a Bruker D8 Venture Photon100 diffractometer equipped with a mirror monochromator and a CuK α INCOATEC μ S micro-focus source ($\lambda = 1.54178 \text{ \AA}$). A total of 3296 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 monoclinic unit cell yielded a total of 30421 reflections to a maximum θ angle of 55.00° (0.94 \AA resolution), of which 6140 were independent (average redundancy 4.955, completeness = 99.5%, $R_{\text{int}} = 6.62\%$, $R_{\text{sig}} = 4.68\%$) and 4624 (75.31%) were greater than $2\sigma(F_2)$. The final cell constants of $a = 20.6125(14) \text{ \AA}$, $b = 9.4687(7) \text{ \AA}$, $c = 26.8611(18) \text{ \AA}$, $\beta = 110.255(2)^\circ$, $V = 4918.4(6) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9934 reflections above $20 \sigma(I)$ with $6.921^\circ < 2\theta < 110.0^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS) [3]. The ratio of minimum to maximum apparent transmission was 0.726. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6080 and 0.9430.

The structure was solved and refined using SHELXTL Software Package [4] using the space group P21/c, with $Z = 2$ for the formula unit, C₈₂H₉₀F₂₄N₁₀O₃₁.20. The final anisotropic full-matrix least-squares refinement on F_2 with 827 variables converged at $R_1 = 10.48\%$, for the observed data and $wR_2 = 30.21\%$ for all data. The goodness-of-fit was 1.054. The largest peak in the final difference electron density synthesis was $0.492 \text{ e}/\text{\AA}^3$ and the largest hole was $-0.293 \text{ e}/\text{\AA}^3$ with an RMS deviation of $0.073 \text{ e}/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.466 g/cm^3 and $F(000)$, 2235 e $^-$.

The size of the measured crystal was very small and weakly diffracting what in combination with severe disorder of the molecules in the crystal lattice did not allow to collect reflections above 0.94 \AA resolution. This result in most of A, B and C level alerts in checkCIF report.

The crown ether fragment is disordered with atoms occupying alternative two or three positions with occupancy ratio equal to 0.7:0.3 or 0.7:0.2:0.1. All by one CF₃ groups are also disordered over two positions with occupancy ratio equal to either 0.8:0.2 or 0.7:0.3. Unidentified solvent molecules in the structures were modeled by partial occupancy O atoms.

The non-hydrogen atoms, except the disordered ones with lower occupancy, were refined anisotropically. Most of hydrogen atoms were placed in calculated positions and refined within the riding model. Hydrogen atoms of 100% occupancy water molecules (O1S and O2S) were refined together with their isotropic temperature factors. To preserve reasonable geometry of these H₂O molecules O-H and H...H distance restraints were used. The temperature factors of other 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 [5]. Molecular graphics was prepared using program Diamond 3.2 [6]. Thermal ellipsoids parameters are presented at 30% probability level.

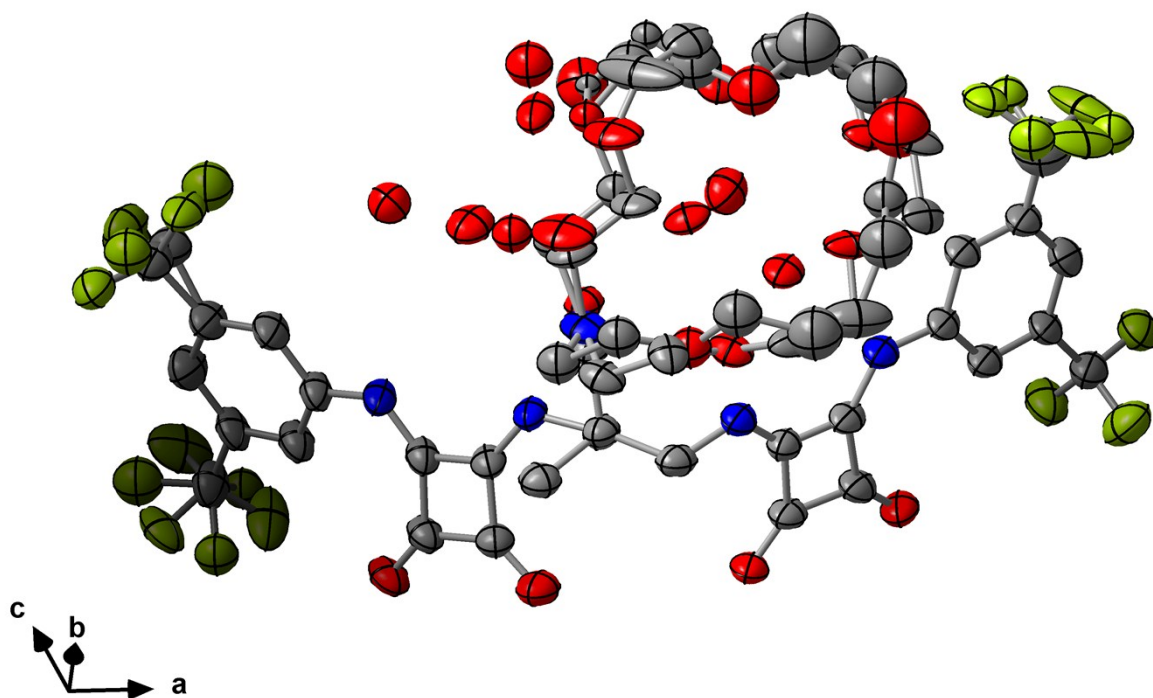


Figure S 19. Thermal ellipsoid plot of the single crystal structure of **3** at 30% probability.

References

- [1] APEX2,. Bruker AXS Inc., Madison, Wisconsin, USA, **2013**.
- [2] SAINT,. Bruker AXS Inc., Madison, Wisconsin, USA, **2013**.
- [3] SADABS,. Bruker AXS Inc., Madison, Wisconsin, USA, **2012**.
- [4] G. M. Sheldrick, *Acta Crystallogr.* **1990**, A46, 467-473; Sheldrick, G. M. *Acta Cryst.*, **2008**, A64, 112–122.
- [5] *International Tables for Crystallography*, Ed. A. J. C. Wilson, Kluwer: Dordrecht, **1992**, Vol.C.
- [6] Diamond – Crystal and Molecular Structure Visualization Crystal Impact – K. Brandenburg & H. Putz GbR, Rathausgasse 30, D-53111 Bonn, **2012**