SUPPORTING INFORMATION

Manuscript title: **Allosteric binding properties of a 1,3-*alternate* thiacalix[4]arene-based receptor having phenylthiourea and 2-pyridylmethyl moieties on opposite faces**

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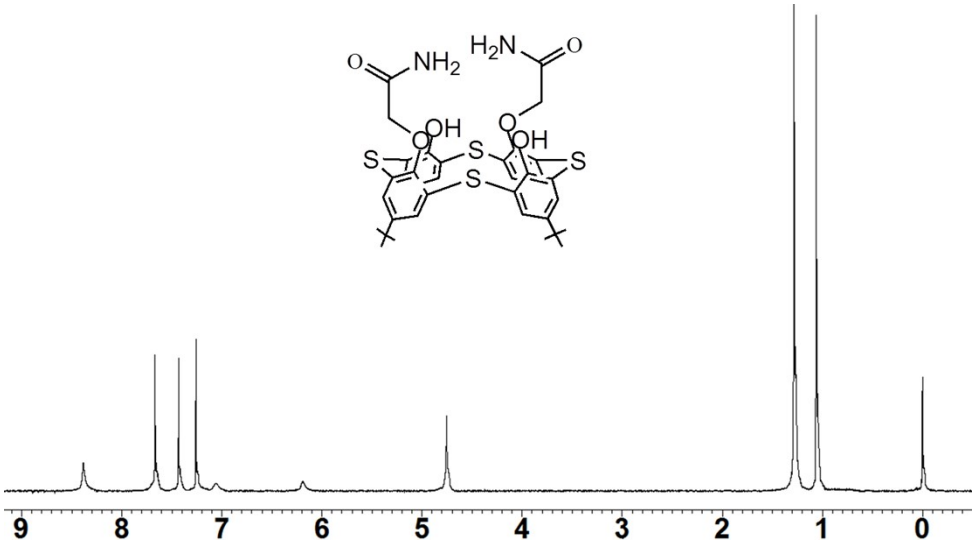


Figure S1. ^{1}H–NMR spectrum of **2** (300 MHz, $CDCl_3$, 293 K).

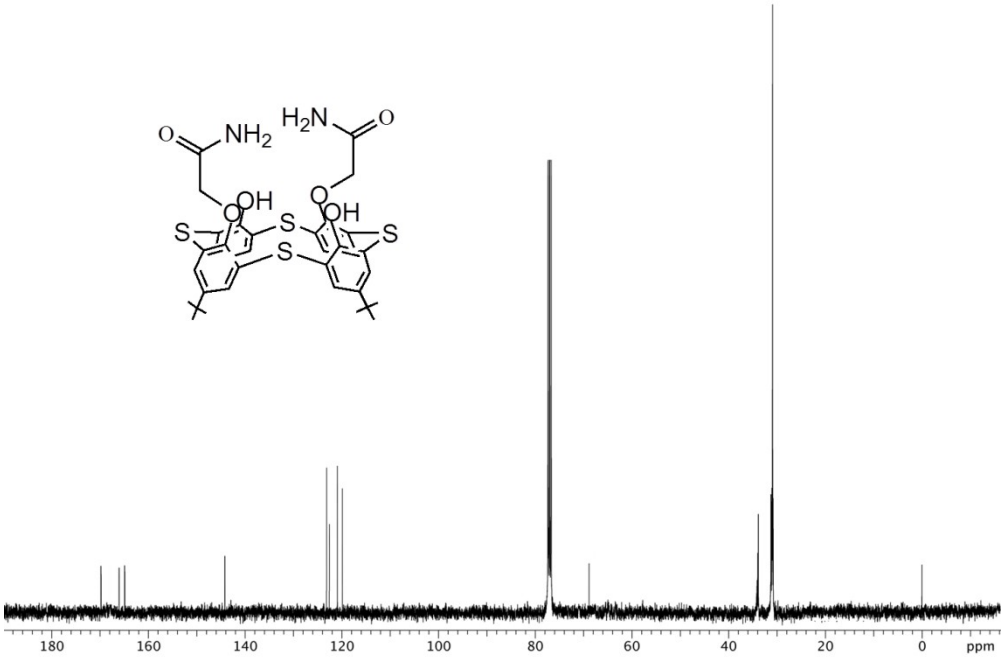


Figure S2. ^{13}C–NMR spectrum of **2** (100 MHz, $CDCl_3$, 293 K).

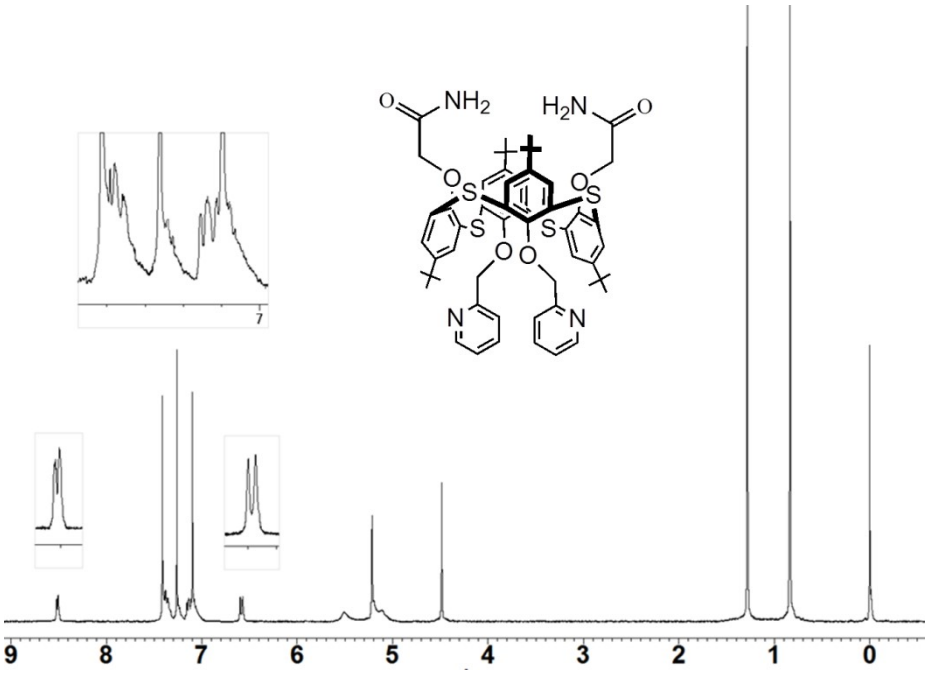


Figure S3. ^{1}H–NMR spectrum of **3** (300 MHz, $CDCl_3$, 293 K).

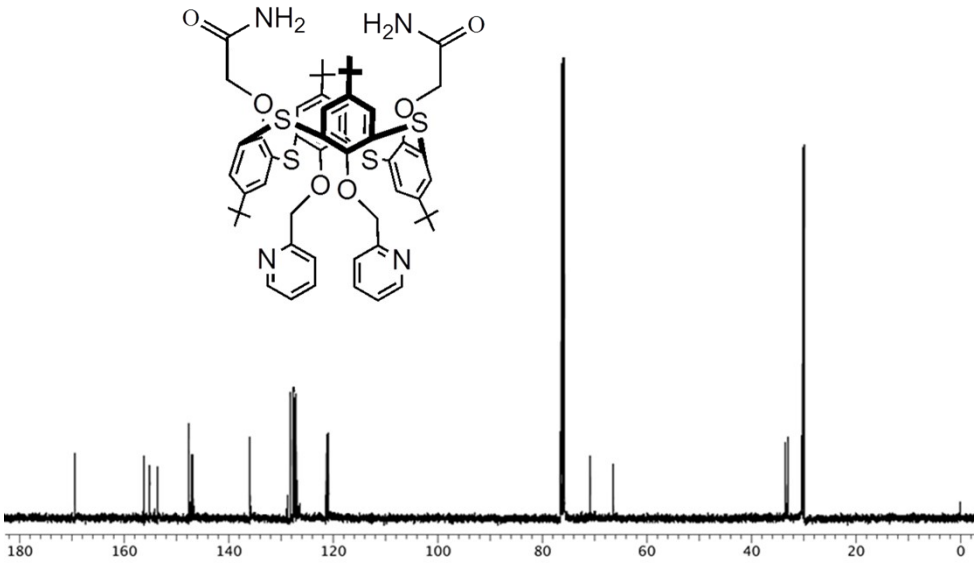


Figure S4. ^{13}C–NMR spectrum of **3** (100 MHz, $CDCl_3$, 293 K).

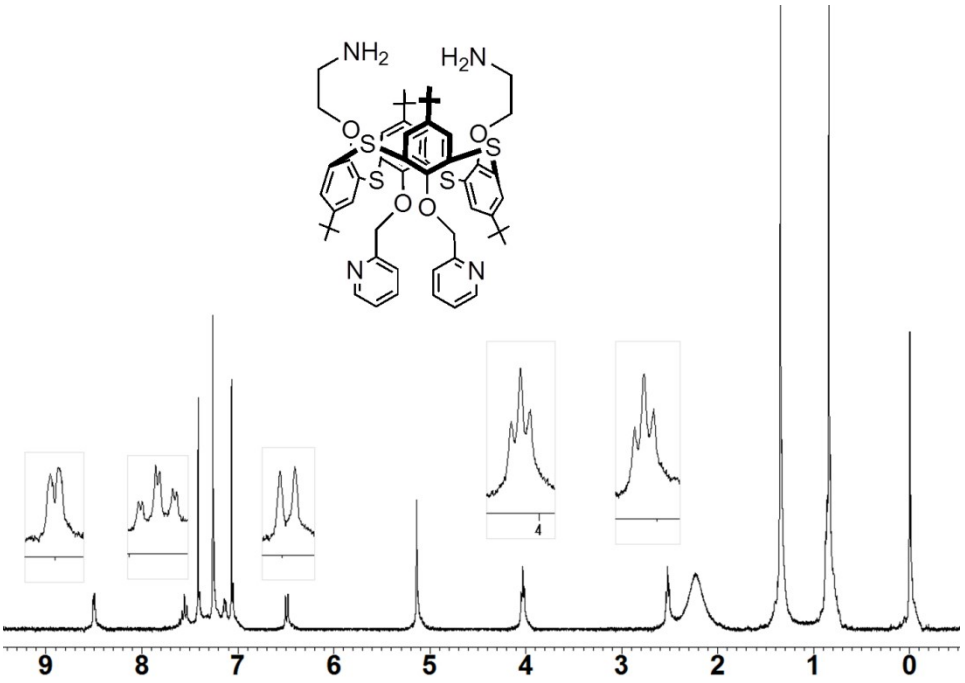


Figure S5. ^{1}H–NMR spectrum of **4** (300 MHz, $CDCl_3$, 293 K).

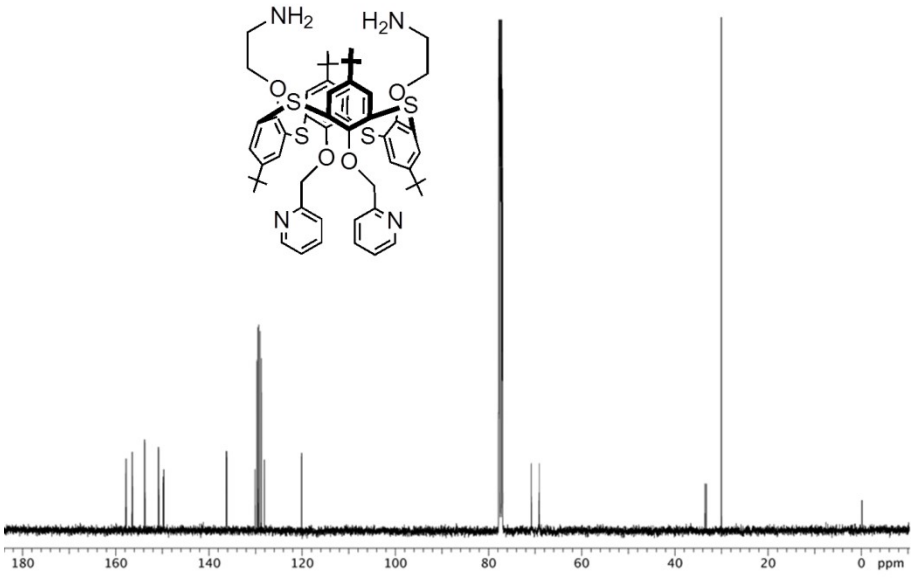


Figure S6. ^{13}C–NMR spectrum of **4** (100 MHz, $CDCl_3$, 293 K).

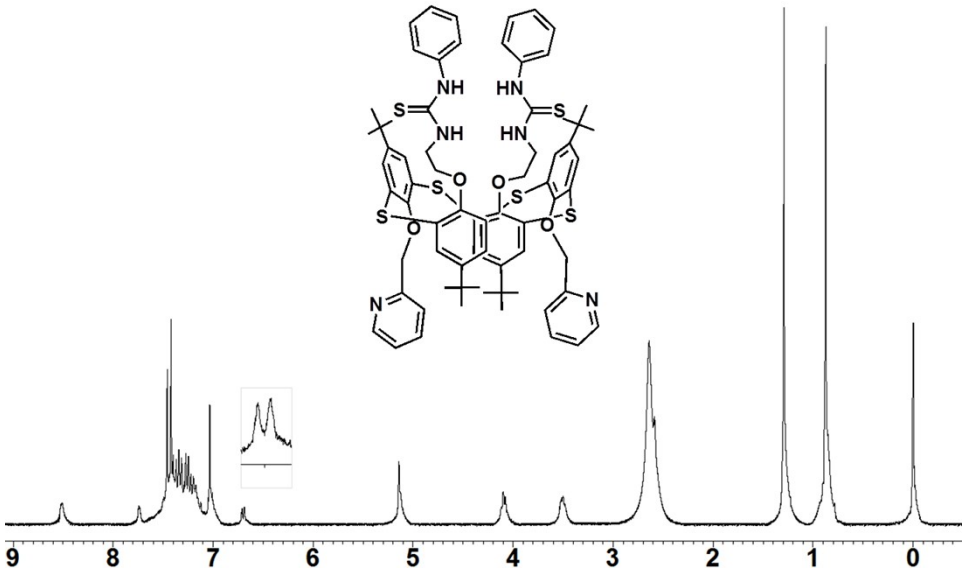


Figure S7. ^{1}H–NMR spectrum of **5a** (300 MHz, $CDCl_3$, 293 K).

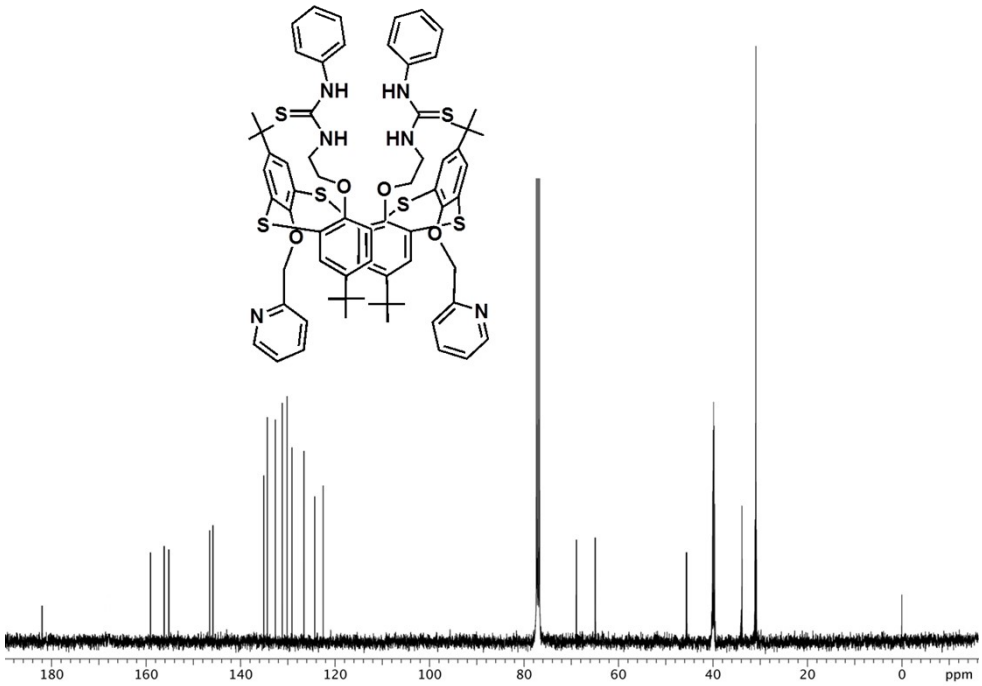


Figure S8. ^{13}C–NMR spectrum of **5a** (100 MHz, $CDCl_3$–DMSO-d_6, 293 K).

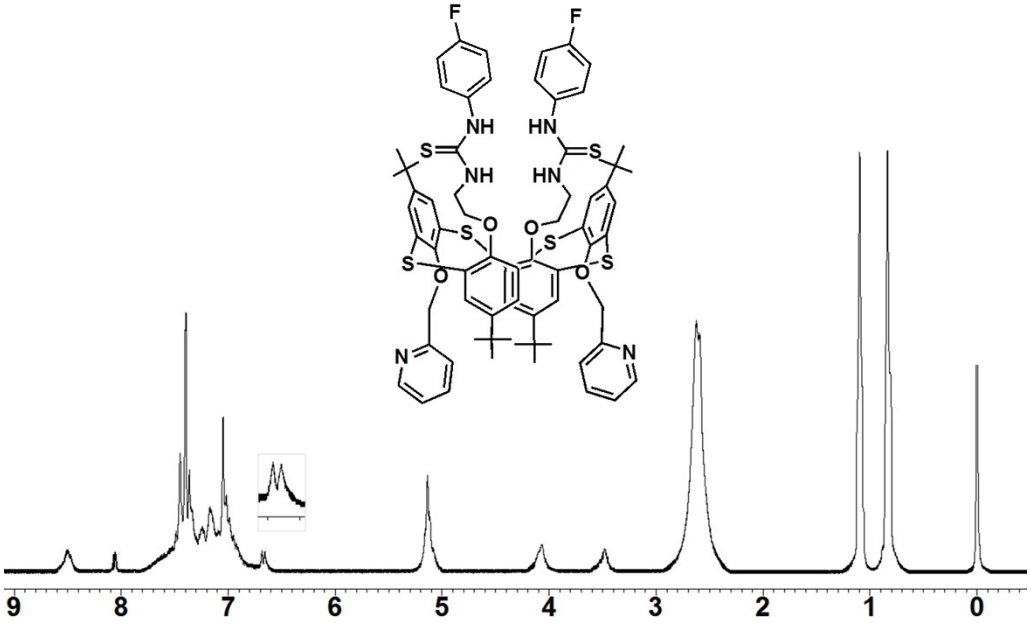


Figure S9. ^{1}H–NMR spectrum of **5b** (300 MHz, $CDCl_3$–DMSO-d_6, 293 K).

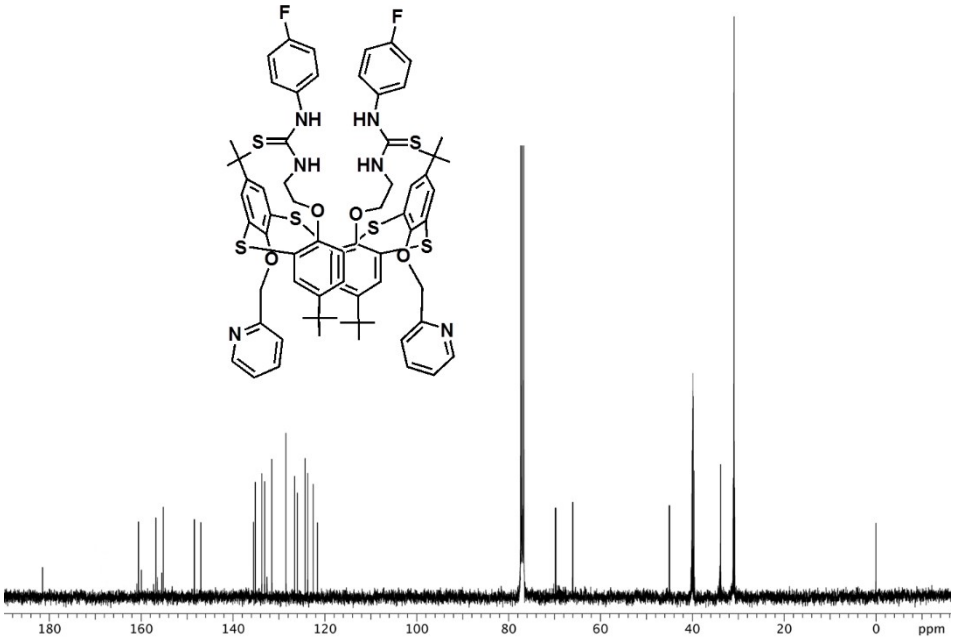


Figure S10. ^{13}C–NMR spectrum of **5b** (100 MHz, $CDCl_3$–DMSO-d_6, 293 K).

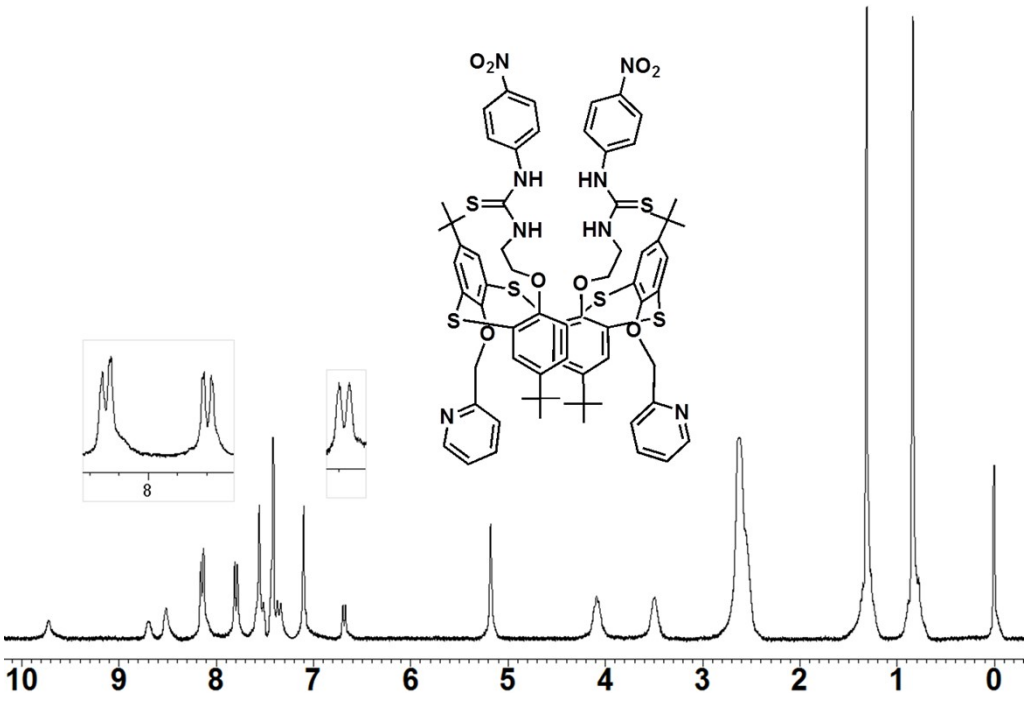


Figure S11. ^{1}H–NMR spectrum of **5c** (300 MHz, $CDCl_3$–DMSO-d_6, 293 K).

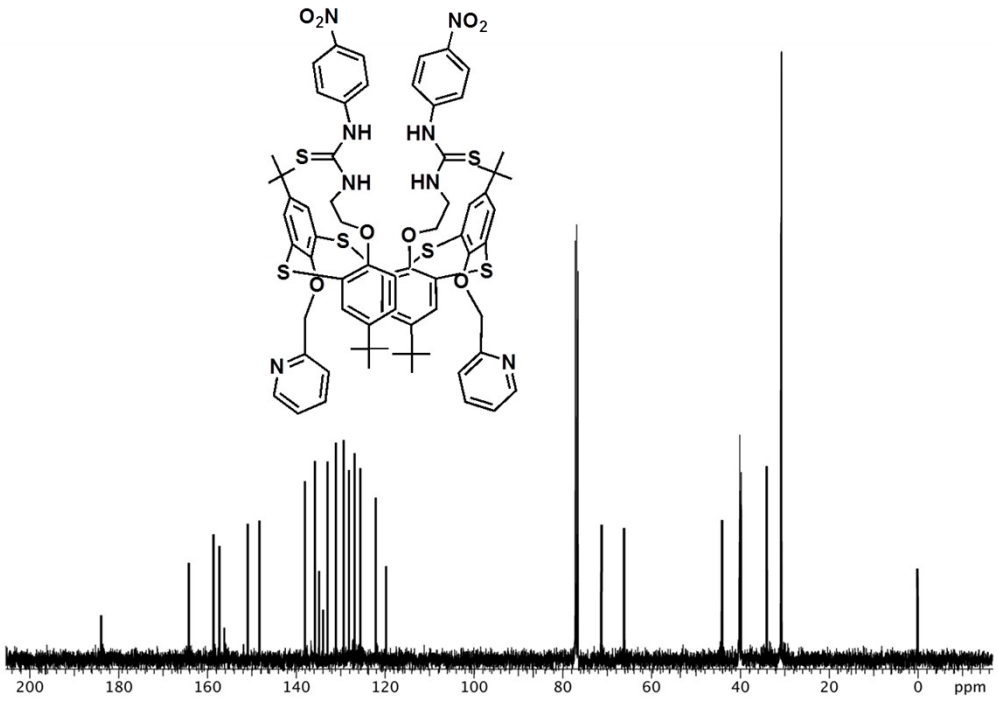


Figure S12. ^{13}C–NMR spectrum of **5c** (100 MHz, $CDCl_3$–DMSO-d_6, 293 K).

X–ray crystal structure of receptor 5a

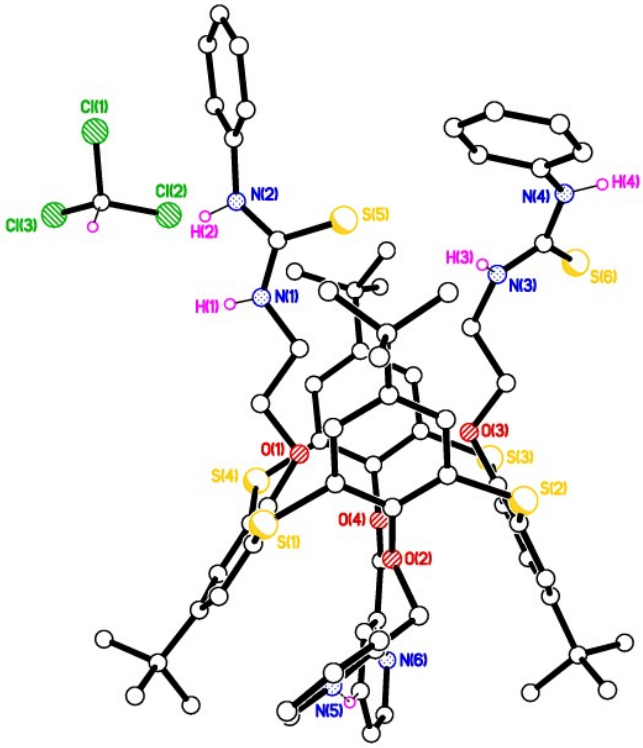


Figure S13. The first thiacalixarene in the asymmetric unit with the chloroform solvent of crystallization, showing intramolecular C–H···N hydrogen bonding between opposing pyridine rings. Minor disorder components and H atoms not involved in H-bonding are omitted for clarity.

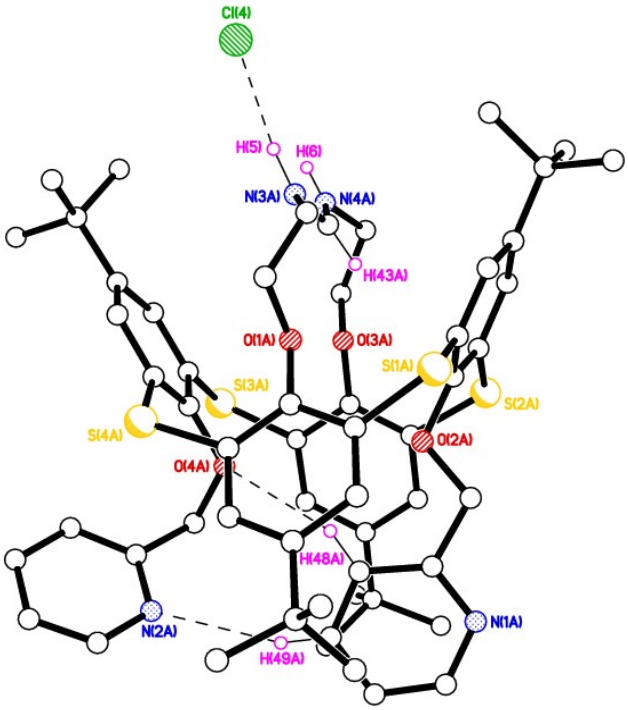


Figure S14. The second, modified, thiacalixarene in the asymmetric unit, showing intramolecular hydrogen between opposing pyridine groups and the charge-assisted N–H^+···Cl^- hydrogen bonding at the top of the figure. Most H atoms not involved in H-bonding are omitted for clarity.

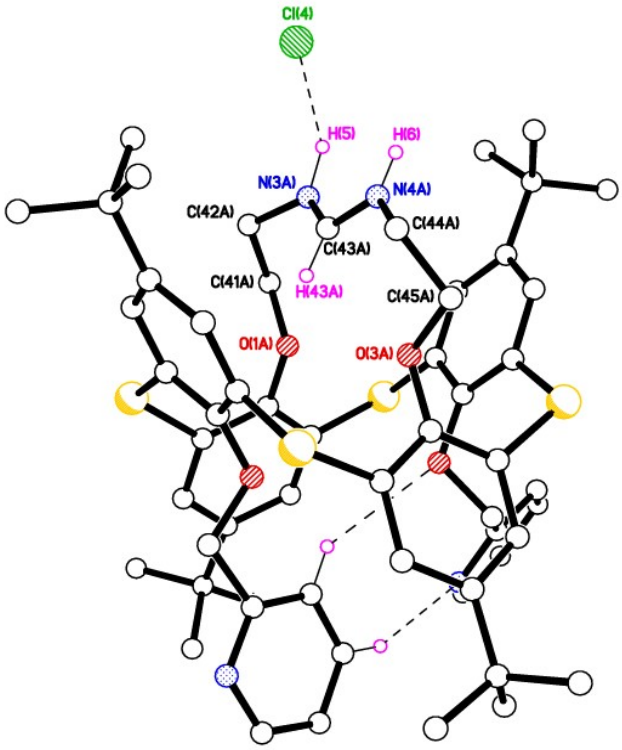


Figure S15. Alternative view of the second thiacalixarene in the asymmetric unit, emphasizing the novel functional group at the top of the molecule exhibiting a delocalized positive charge, acting as a counter cation for Cl^- anion capture. H atoms not involved in H-bonding are omitted for clarity.

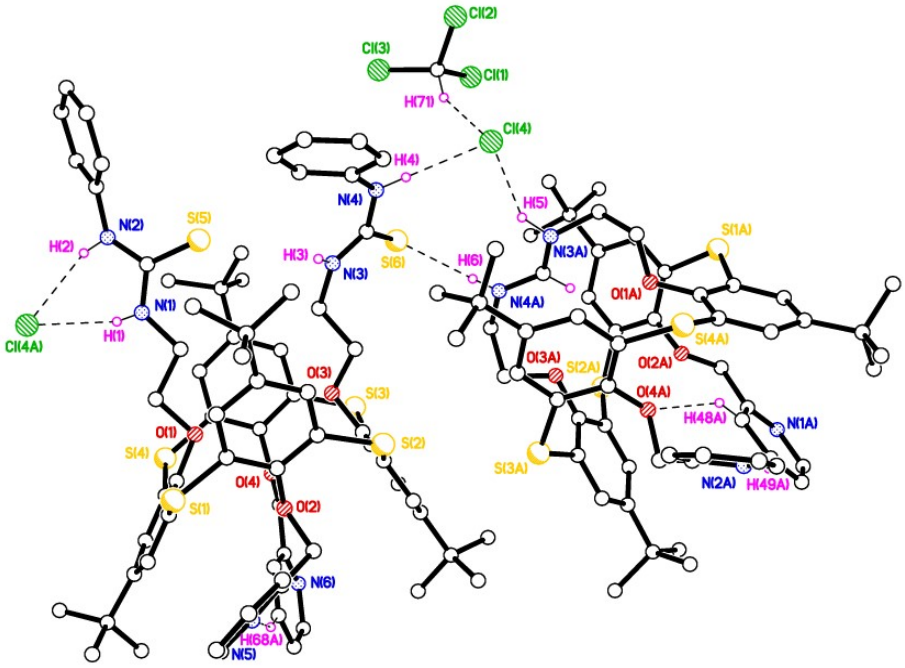


Figure S16. The asymmetric unit of **5a**, showing the intermolecular S···H–N hydrogen bonding between the two thiacalixarenes and the N–H···Cl interactions between each thiacalixarene and the Cl^- anion. Minor disorder components and H atoms not involved in H-bonding are omitted for clarity.

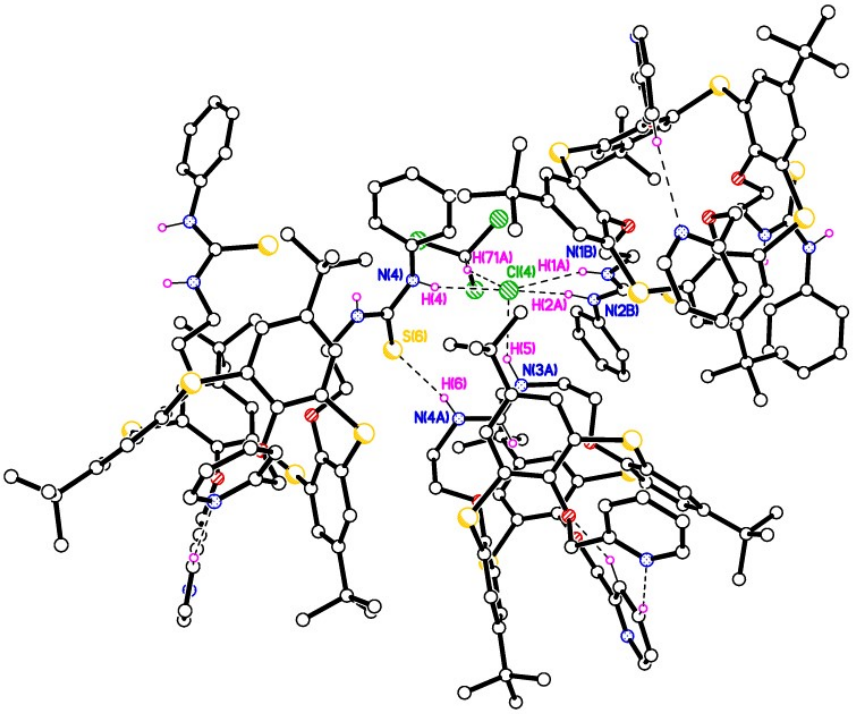
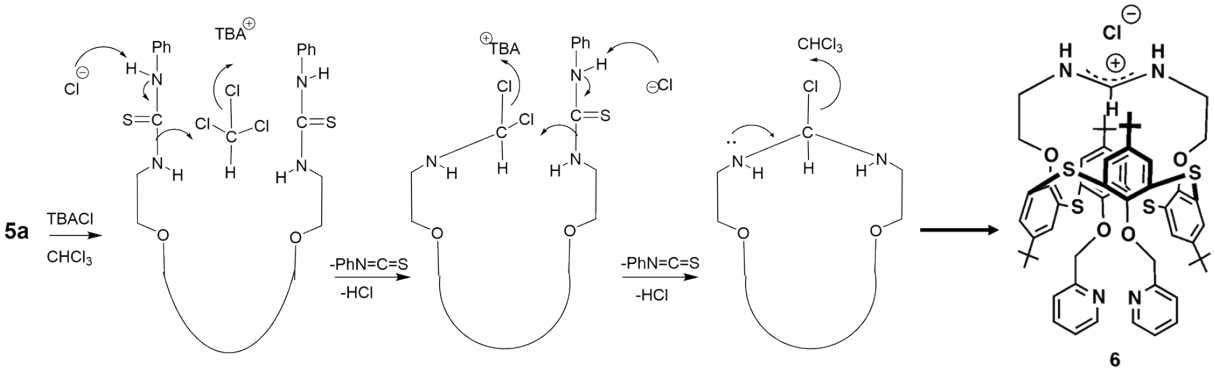
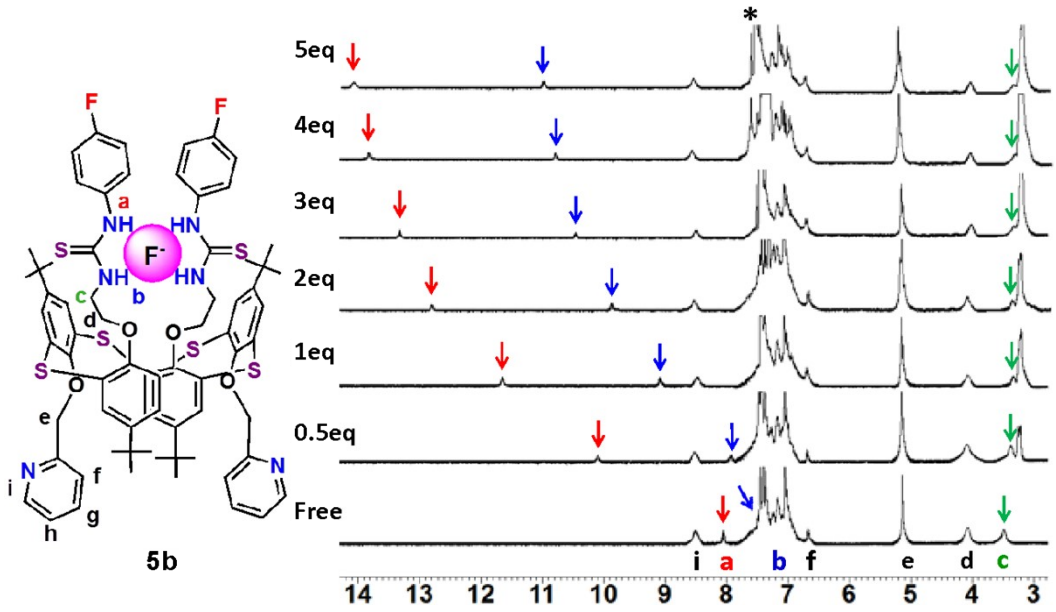


Figure S17. X-Ray crystal structure of **5a**, highlighting the capture of the Cl^- anion between three thiacalixarenes via N–H···Cl hydrogen bonding and the (disordered) chloroform solvent of crystallization. Minor disorder components and H atoms not involved in H-bonding are omitted for clarity.



Scheme S1. Schematic representation of possible mechanism of the formation of **6** from **5a** in the presence of TBACl in $CHCl_3$.



5a (mol^{-1})	**F**$^{-}$ (mol^{-1})	NH_a Proton (ppm)	NH_b Proton (ppm)
4.00E-03	0	8.050	7.600
4.00E-03	2.00E-03	10.090	8.420
4.00E-03	4.00E-03	11.550	9.100
4.00E-03	8.00E-03	12.750	9.820
4.00E-03	1.20E-02	13.300	10.415
4.00E-03	1.60E-02	13.800	10.750
4.00E-03	2.00E-02	13.850	10.810

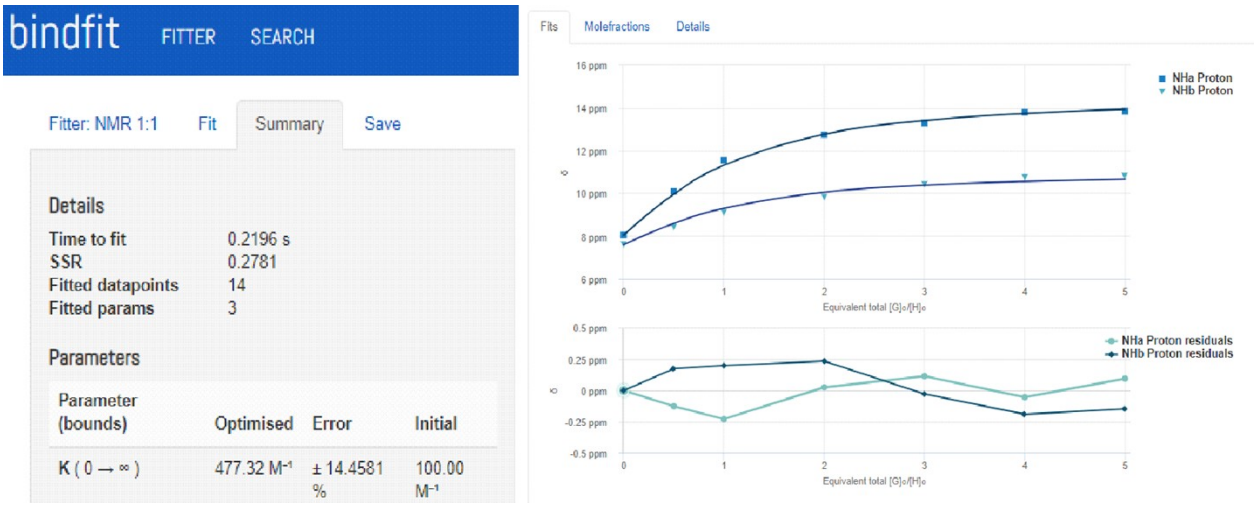
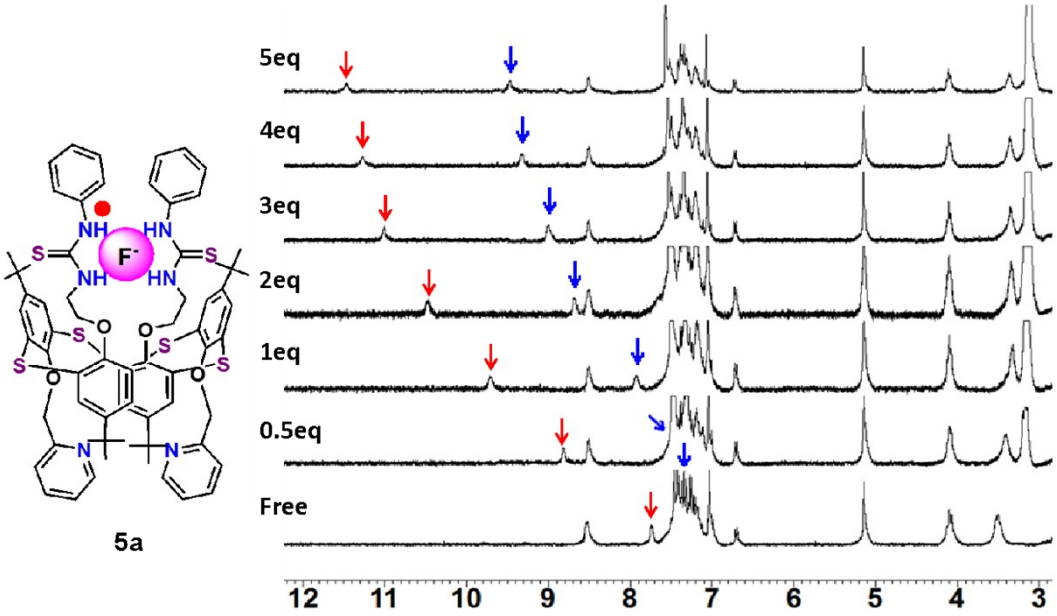


Figure S18. ^{1}H NMR spectroscopic stack plot of a $CDCl_3$–DMSO-d_6 (10:1, v/v) solution of **5b** (4.0×10^{-3} M) upon addition of TBAF in CD_3CN. ($K_a = 477 \pm 14$ M^{-1}) and the screen capture from the **1:1** global fit analysis using http://supramolecular.org.



5a (mol^{-1})	F^- (mol^{-1})	NH_a Proton (ppm)	NH_b Proton (ppm)
4.00E-03	0	7.720	7.150
4.00E-03	2.00E-03	8.800	7.550
4.00E-03	4.00E-03	9.700	7.900
4.00E-03	8.00E-03	10.500	8.640
4.00E-03	1.20E-02	11.000	8.980
4.00E-03	1.60E-02	11.250	9.340
4.00E-03	2.00E-02	11.400	9.440

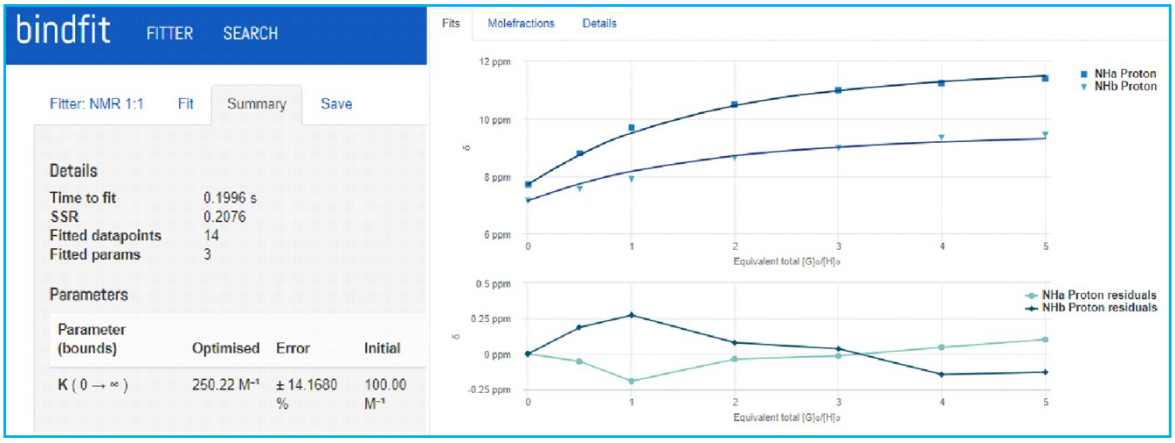


Figure S19. ^{1}H NMR spectroscopic stack plot of a $CDCl_3$–DMSO-d_6 (10:1, v/v) solution of **5a** (4.0×10^{-3} M) upon addition of TBAF in CD_3CN. (($K_a = 250 \pm 14$ M^{-1}). and the screen capture from the **1:1** global fit analysis using http://supramolecular.org.

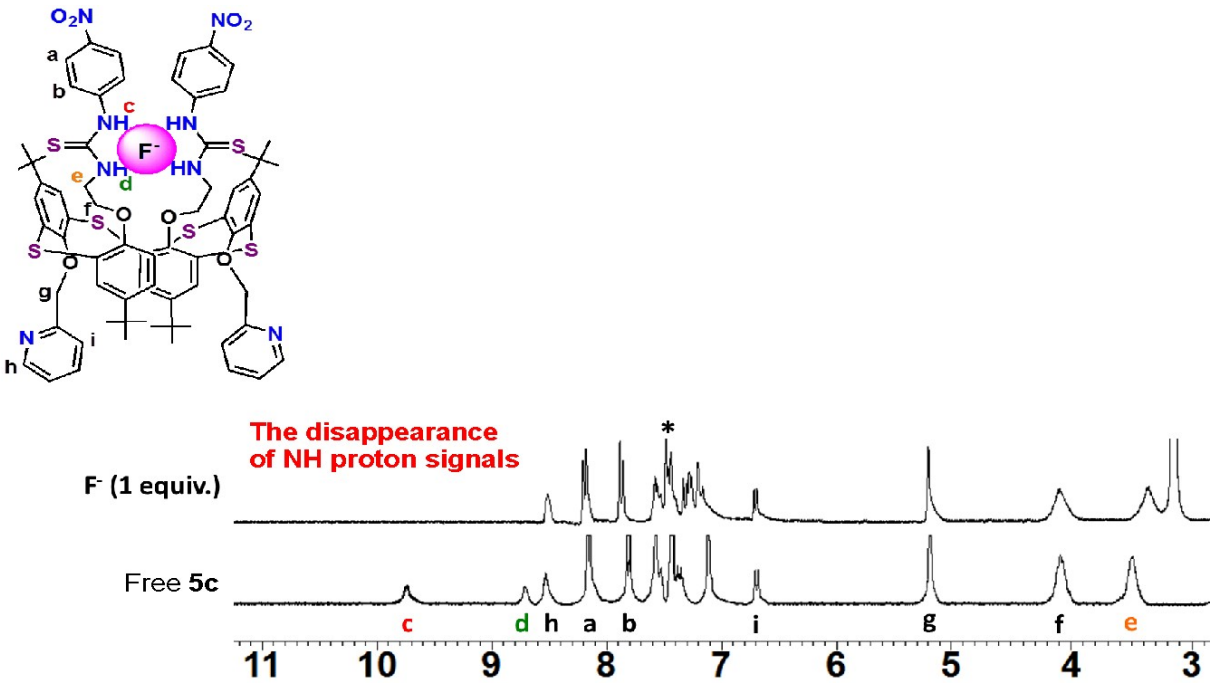


Figure S20. ^{1}H NMR spectroscopic stack plot of a $CDCl_3$–DMSO-d_6 (10:1, v/v) solution of **5c** (4.0×10^{-3} M) upon addition of TBAF in CD_3CN.

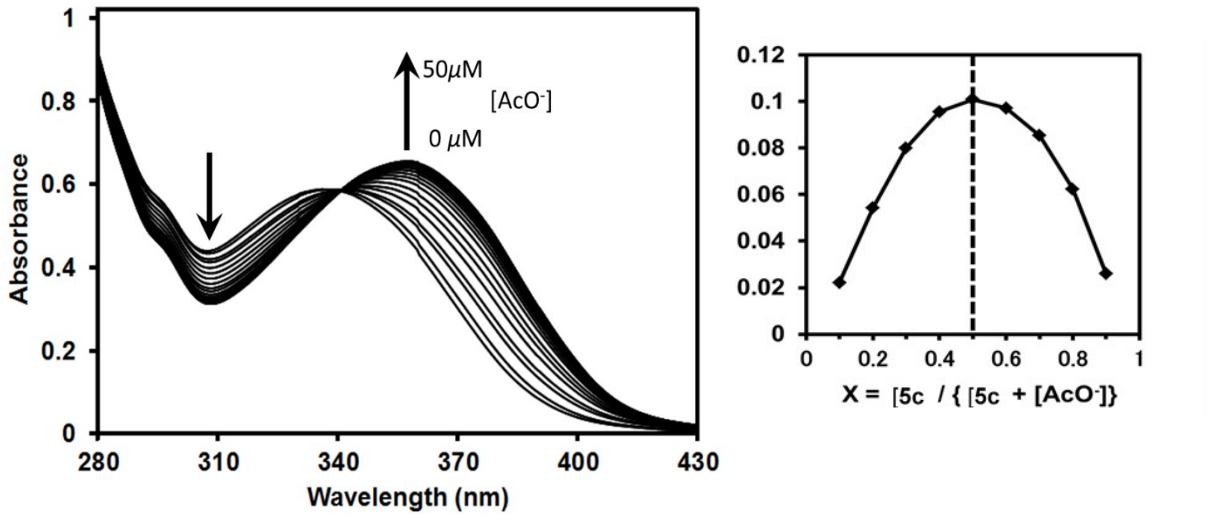


Figure S21. *Left*: UV–vis absorption spectra changes of **5c** (2.5 μM) upon the addition of AcO^- ion (0–50 μM) as its tetrabutylammonium salt in CH_2Cl_2–DMSO (10:1, v/v) at 298 K. *Right*: Job plot showing the 1:1 binding of **5c** to AcO^- ion from the UV-vis titration method at 358 nm in CH_2Cl_2–DMSO (10:1, v/v).

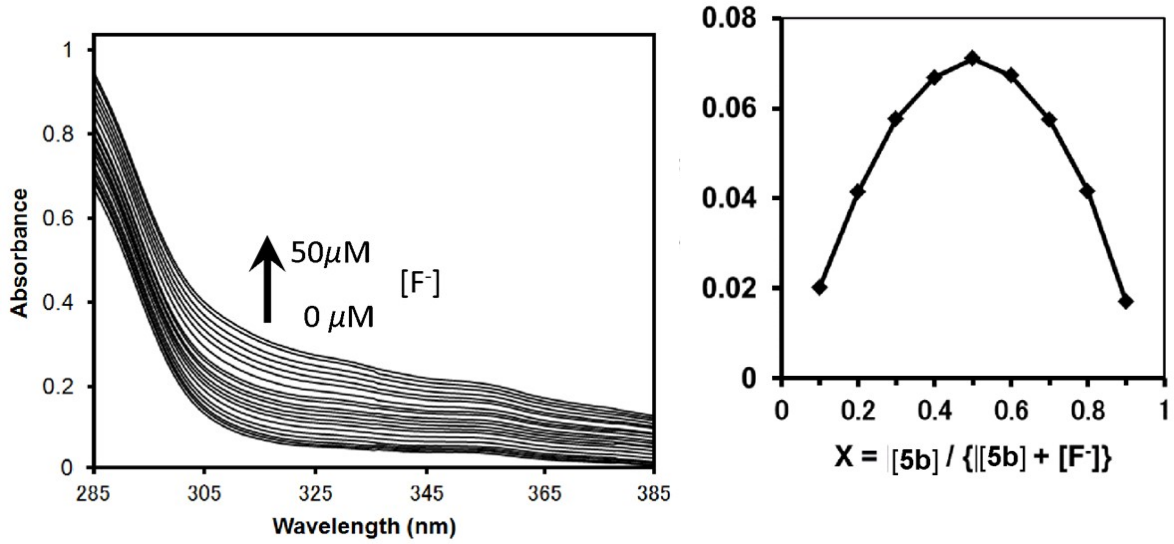


Figure S22. *Left*: UV–vis absorption spectra changes of **5b** (2.5 μM) upon the addition of F^- ion (0–50 μM) at 298 K as a TBAF salt in CH_2Cl_2–DMSO (10:1, v/v). *Right*: Job's plot showing the 1:1 binding of **5b** to F^- ion from the UV-vis titration method at 358 nm in CH_2Cl_2–DMSO (10:1, v/v).

Table S1. The DFT interaction energies ΔIE (kJ mol^{-1}) calculated from the geometry optimized structure of receptors **L** (*For*: **5a**: R= H; **5b**: R= F; and **5c**: R= NO_2**)** and complexes with the anions (F^-, Cl^-, AcO^-, and $H_2PO_4^-$) and cation Ag^+ using B3LYP/LANL2DZ basis set in gas phase, dichloromethane (DCM) and dimethyl sulfoxide (DMSO) solvent system using *Gaussian 16*[1] at the B3LYP level of DFT and the LANL2DZ basis set.[2].

Complex	ΔIE (kJ mol^{-1}) in gas phase			ΔIE (kJ mol^{-1}) in DCM solvent			ΔIE (kJ mol^{-1}) in DMSO solvent		
	5a (R= H)	**5b** (R= F)	**5c** (R= NO_2)	**5a** (R= H)	**5b** (R= F)	**5c** (R= NO_2)	**5a** (R= H)	**5b** (R= F)	**5c** (R= NO_2)
L⊃F^-	-484.91	-505.38	-551.35	-242.11	-249.53	-274.69	-206.34	-225.79	-231.55
L⊃Cl^-	-296.45	-317.00	-362.33	-112.51	-118.86	-138.44	-82.87	-101.32	-100.61
L⊃AcO^-	-294.52	-314.05	-361.34	-125.67	-132.34	-155.99	-95.96	-115.25	-104.33
L⊃$H_2PO_4^-$	-268.66	-289.58	-339.47	-119.77	-126.41	-136.37	-91.63	-105.16	-101.83
L⊃Ag^+	-440.17	-436.59	-436.38	–	–	–	v	–	–
L⊃Ag^+	–	-435.64	–	–	-169.28	–	–	-146.90	–
Ag^+⊂**L**⊃F^-	–	-1090.11	–	v	-417.73	–	v	-364.91	–

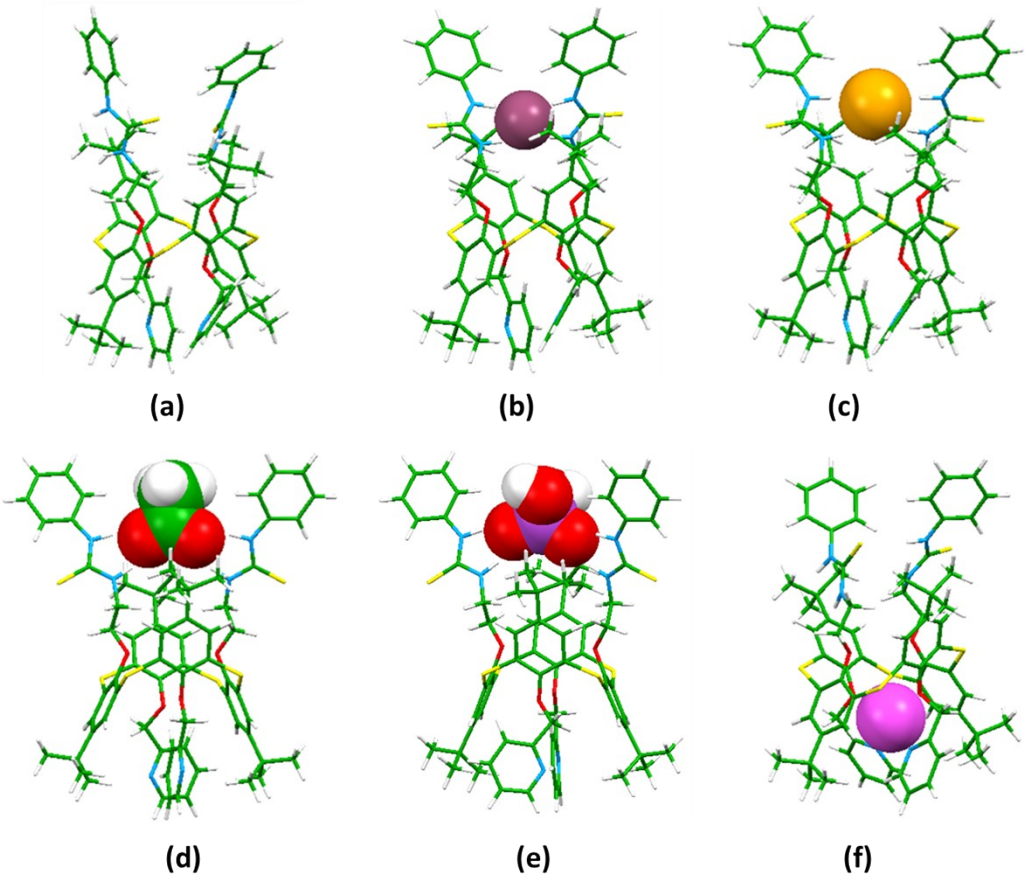


Figure S23. Geometry-optimized (PBE0/LANL2DZ) structures of receptor **5a** (R= H) and complexes with the anions (b-e) (F^-, Cl^-, AcO^-, and $H_2PO_4^-$) and Ag^+(f) ion by using B3LYP/LANL2DZ basis set in gas phase. Colour code: carbon atoms = green, oxygen atoms = red, nitrogen atoms = blue, and Ag^+ = magenta. F^- = purple; Cl^- = orange; Hydrogen atoms = white; phosphorus atom= light purple.

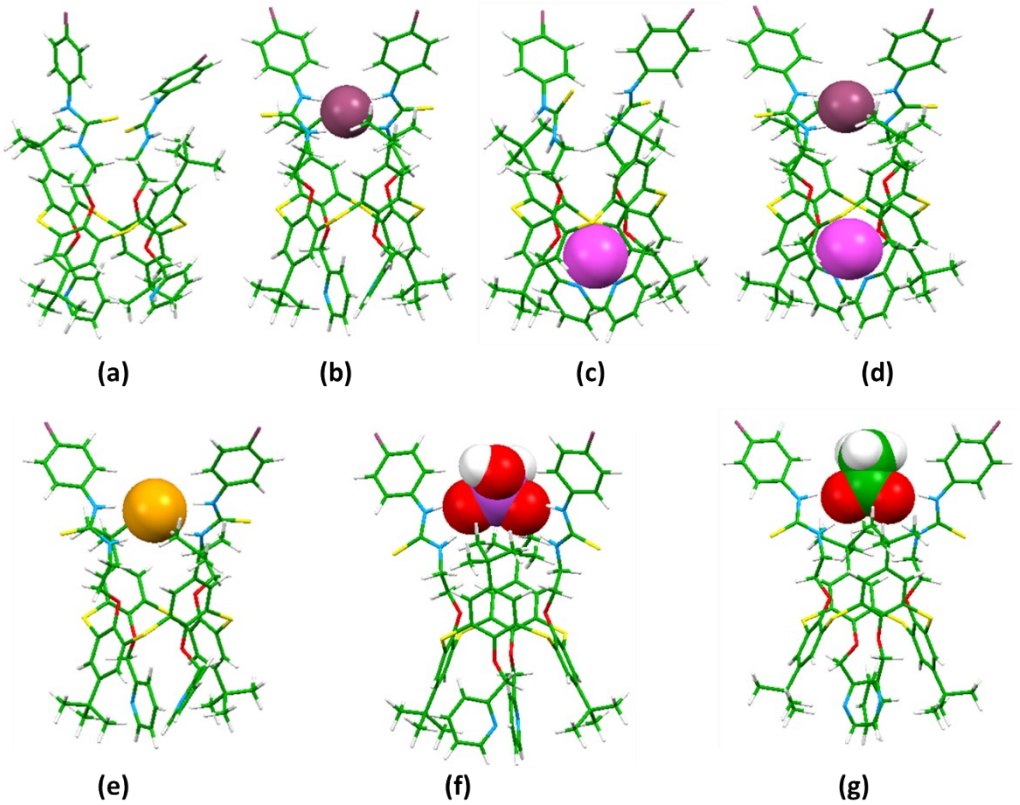


Figure S24. Geometry-optimized (PBE0/LANL2DZ) structures of receptor **5b** (R= F) and complexes with the anions (F^-, Cl^-, AcO^-, and $H_2PO_4^-$), Ag^+ ion (c) and Cl^- in presence of Ag^+ ion (d) by using B3LYP/LANL2DZ basis set in gas phase. Colour code: carbon atoms = green, oxygen atoms = red, nitrogen atoms = blue, and Ag^+ = magenta. F^- = purple; Cl^- = orange; Hydrogen atoms = white; phosphorus atom= light purple.

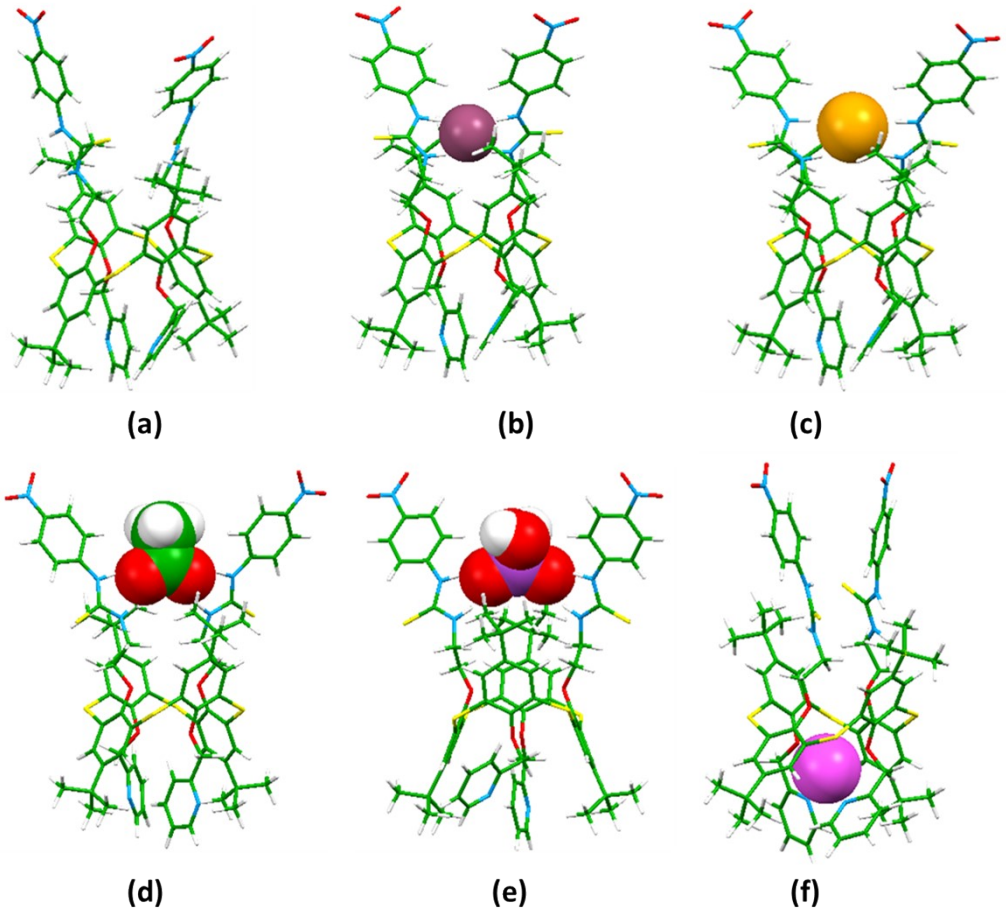


Figure S25. Geometry-optimized (PBE0/LANL2DZ) structures of receptor **5c** (R= NO_2) and complexes with the anions (F^-, Cl^-, AcO^-, and $H_2PO_4^-$) and Ag^+ ion by using B3LYP/LANL2DZ basis set in gas phase. Colour code: carbon atoms = green, oxygen atoms = red, nitrogen atoms = blue, and Ag^+ = magenta. F^- = purple; Cl^- = orange; Hydrogen atoms = white; phosphorus atom= light purple.

References:

1. M. J. Frisch, *et al*., *Gaussian 16*, Revision C.01 Gaussian, Inc., Wallingford CT, 2019.
2. (a) J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, **77**, 3865; (b) J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1997, **78**, 1396.