Electronic Supplementary Information (ESI)

Unexpected halide anion binding mode in *meso*-bis-ethynyl picket-calix[4]pyrroles: Effects of *meso* - π (ethynyl) extension

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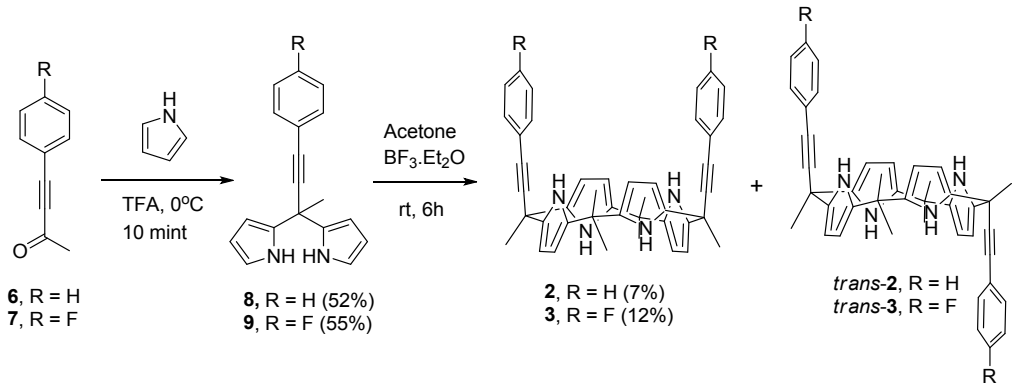
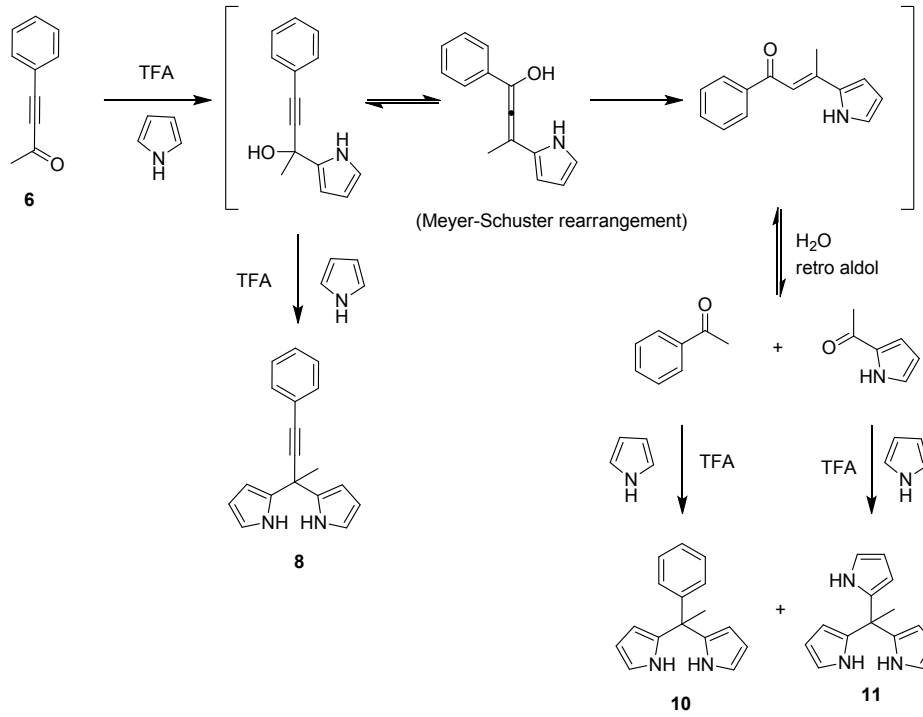
Content

Materials and methods: All commercially available compounds were used as received. Transformation- and oxygen-sensitive compounds were performed under a nitrogen atmosphere. The reaction progress was monitored by thin layer chromatography (TLC) on glass sheets that were coated with silica gel 60 F254 (MN), with detection by a UV Lamp. Product purification was performed by column chromatography on silica (230–400 mesh, MN). The identity and purity of the prepared compounds were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy (Bruker 400/300 MHz). Mass spectra were recorded on Voyager DE-STR MALDI-TOF and JEOL JMS-700 GC mass spectrometer. Binding constants corresponding to the host-guest interaction were determined using isothermal titration calorimetry (ITC). For the ITC measurements, the host compound was dissolved in acetonitrile to give 0.333-0.865 mM stock solutions. These host solutions were titrated into tetrabutylammonium salt solutions (2.17 – 9.08 mM) of the anion in question contained in the insulated cell (1.4584 mL) of a fully computer operated VP-ITC MicroCalorimeter.



Scheme S1. Synthesis of calix[4]pyrroles **2** and **3**



Scheme S2. Synthesis of key building block **8** and unexpected rearrangement products **10** and **11**

Synthesis of compound 8

To a mixture of 4-Phenyl-3-butyn-2-one (**6**) (0.145 mg, 1 mmol) and pyrrole (0.35 ml, 5 equiv.), trifluoroacetic acid (80µl, 1 equiv.) was added dropwise at 0^0C. The mixture was then stirred for 10 minute at 0°C under inert atmosphere in absence of light. The reaction was quenched by adding aqueous NaOH (0.1 N) before being extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The resulting yellow liquid was purified by column chromatography over silica gel (10:1 hexane/ethyl acetate, eluent). Yield: 52%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.19 (bs, 2H, NH), 7.45 (d, J = 4.8 Hz, 2H, Ar-C*H*), 7.33-7.31 (m, 3H, Ar-C*H*), 6.70 (m, 2H, pyr-*H*), 6.17 (m, 4H, pyr-*H*), 1.99 (s, 3H, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): 134.7, 131.7, 128.3, 122.9, 117.2, 108.4, 104.7, 91.9, 82.7, 36.3 and 30.2 ppm. Exact mass calculated for $C_{18}H_{16}N_2$ 260.131 found 260.0 $(M)^+$.

Synthesis of calix[4]pyrrole 2

To a solution of **8** (1.06 g) in acetone (500 ml), $BF_3.Et_2O$ (0.48 ml, 1 equiv.) was added dropwise under inert atmosphere. The reaction mixture was then allowed to stir for six hour under protection from light at room temperature. It was then quenched with excess of triethylamine. Excess solvent was then removed and the crude was extracted repeatedly with dichloromethane. It was then washed with water and the combined organic layer was dried over Na_2SO_4. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel using hexane/dichloromethane (7:3, v/v) as eluent to afford **2** and *trans*-**2** in 7% and 5% yields respectively.

2: ^{1}H NMR (CD_3CN, 400 MHz): δ (ppm) 7.94 (bs, 4H, NH), 7.45-7.41 (m, 4H, Ar-C*H*), 7.37-7.34 (m, 6H, Ar-C*H*), 6.03 (dd, J = 2.8, 3.2 Hz, 4H, pyr-*H*), 5. 87 (dd, J = 2.8, 3.2 Hz, 4H, pyr-*H*), 1.88 (s, 6H, C*H*$_3$), 1.55 (s, 6H, C*H*$_3$), 1.54 (s, 6H, C*H*$_3$); ^{13}C NMR (CD_3CN, 100 MHz) 138.9, 133.8, 131.1, 128.2, 127.9, 122.8, 103.6, 102.6, 92.5, 81.4, 35.4, 34.6, 27.8, 27.4 and 27.3 ppm; MALDI-TOF: exact mass calculated for $C_{42}H_{40}N_4$ 600.325 found 601.199 $(M+H)^+$. *Trans*-**2**: ^{1}H NMR (CD_3CN, 400 MHz): δ (ppm) 7.98 (bs, 4H, N*H*), 7.43-7.40 (m, 4H, Ar-C*H*), 7.37-7.34 (m, 6H, Ar-C*H*), 6.02 (dd, J = 2.8, 3.2 Hz, 4H, pyr-*H*), 5.87 (dd, J = 2.8, 3.2 Hz, 4H, pyr-*H*), 1.90 (s, 6H, C*H*$_3$), 1.55 (s, 12H, CH_3).

Synthesis of compound 9

Compound **9** is synthesized following the same protocol as that of compound **8**, using 4-*para*fluorophenyl-3-butyn-2-one (**7**)[S1] as the starting material. Yield: 55%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.14 (bs, 2H, NH), 7.43-7.42 (m, 2H, Ar-C*H*), 7.02 (t, J = 8 Hz, 2H, Ar-C*H*), 6.69-6.67 (m, 2H, pyr-*H*), 6.18-6.15 (m, 4H, pyr-*H*), 1.98 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 162.8, 161.3, 134.7, 133.7, 133.6, 119.0, 117.4, 115.8, 115.6, 108.5, 104.8, 91.7, 81.7, 36.3 and 30.2 ppm. Exact mass calculated for $C_{18}H_{1f}FN_2$ 278.32 found 278.0 $(M)^+$.

Synthesis of calix[4]pyrrole 3

Calix[4]pyrrole **3** is synthesized following the same protocol as that of calix[4]pyrrole **2**, using compound **9** as the building block. Yield: 12%. **3**: ^{1}H NMR (CD_3CN, 400 MHz): δ (ppm) 7.89 (bs, 4H, NH), 7.05-7.10 (m, 4H, Ar-C*H*), 6.00 (t, J = 2.8 Hz, 4H, pyr-*H*), 5. 87 (t, J = 3.2 Hz, 4H, pyr-*H*), 1.84 (s, 6H, CH_3), 1.52 (s, 6H, CH_3), 1.51 (s, 6H, CH_3); ^{13}C NMR (CD_3CN, 100 MHz) 163.6, 161.2, 139.4, 134.1, 133.7, 133.6, 119.57, 115.7, 115.5, 104.0, 102.9, 92.5, 80.6, 35.7, 35.0, 31.3, 28.8, 28.1, 27.8 and 27.7 ppm; MALDI-TOF: exact mass calculated for $C_{42}H_{48}F_2N_4$ 636.306 found 637.349 $(M+H)^+$.

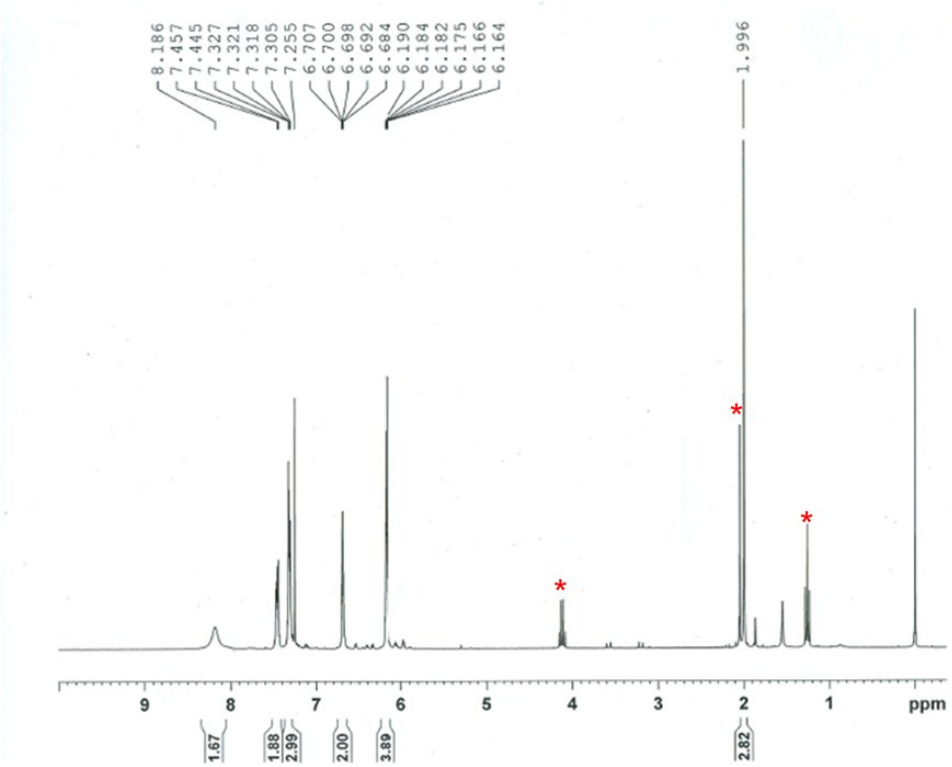


Figure S1: ^{1}H NMR spectrum of **8** in $CDCl_3$ (* indicates residual solvent peaks)

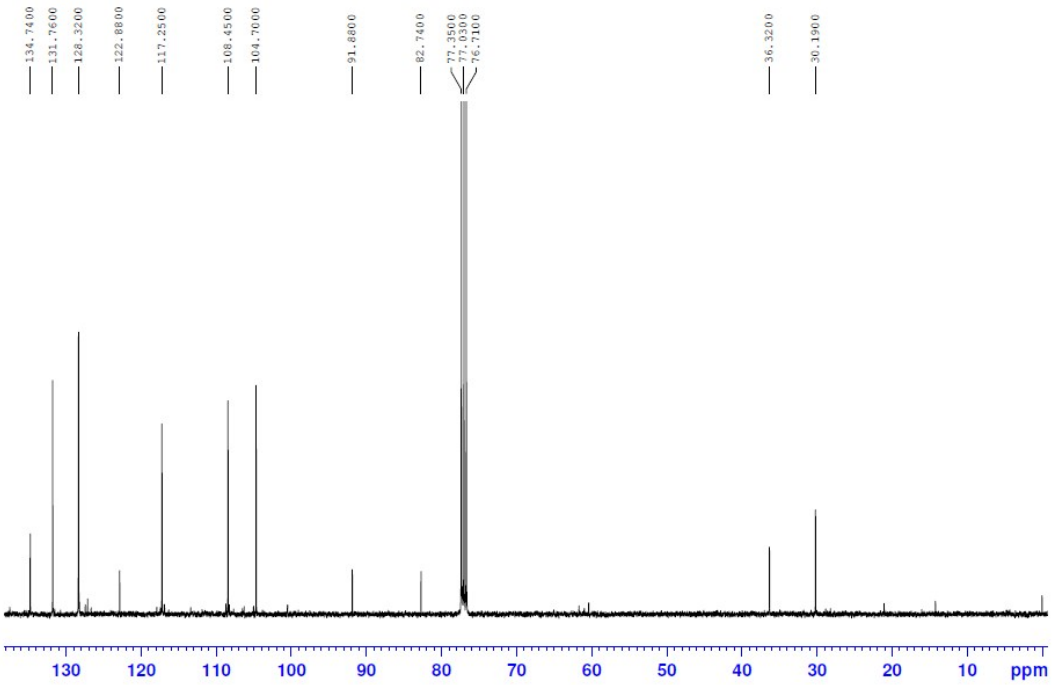


Figure S2: ^{13}C NMR spectrum of compound **8** in $CDCl_3$

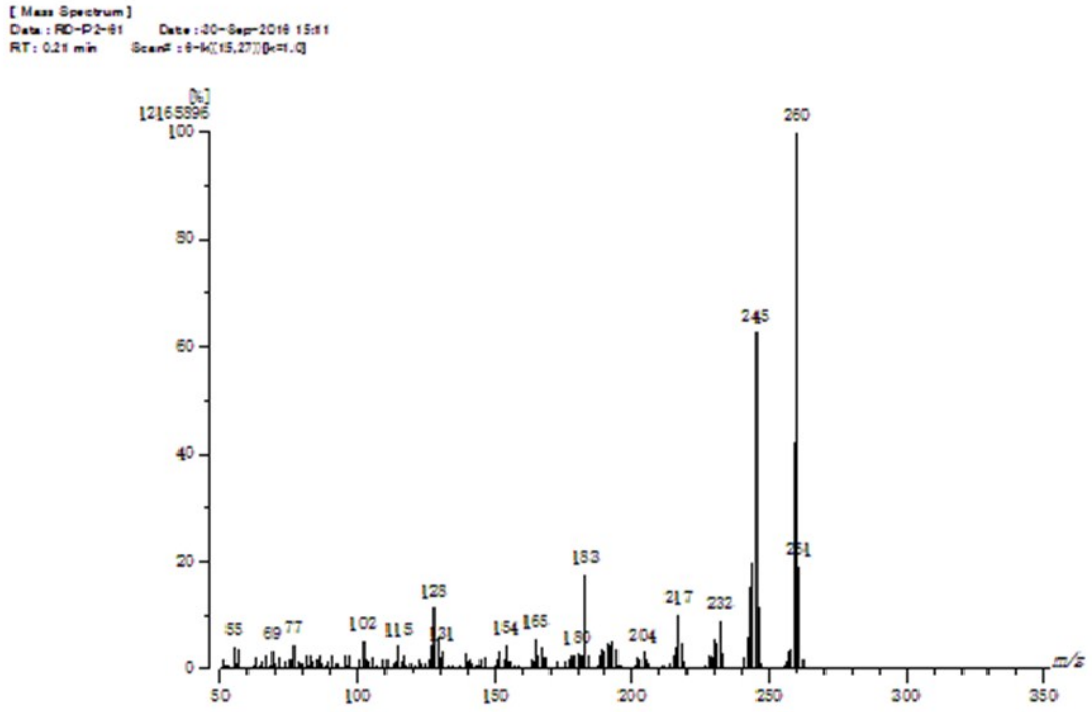


Figure S3: Mass spectrum of compound **8**

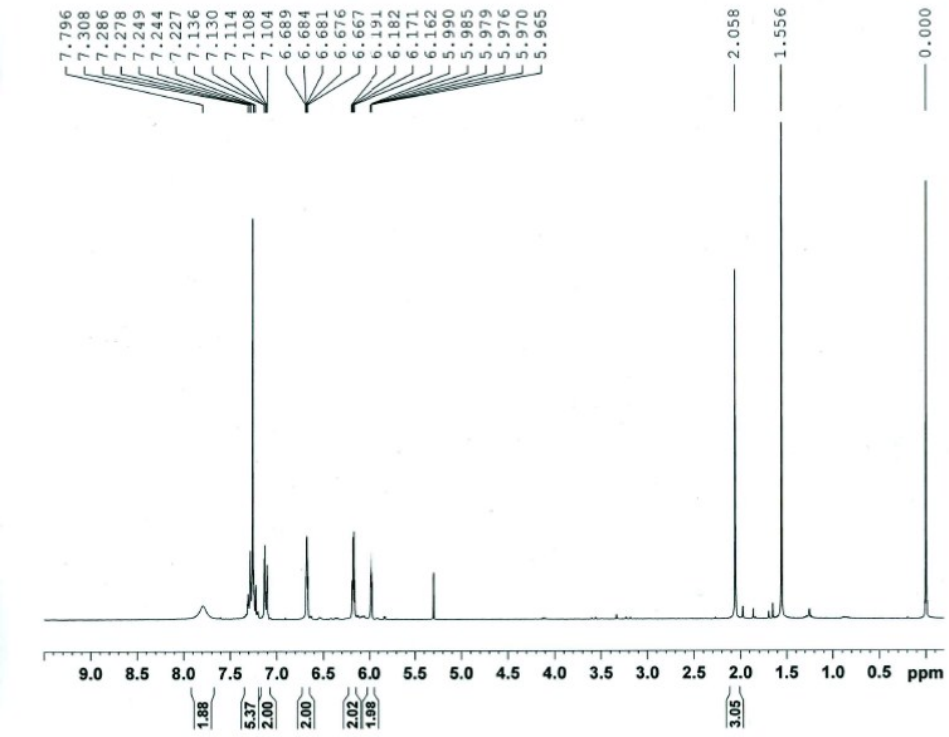


Figure S4: ^{1}H NMR spectrum of **10** in $CDCl_3$

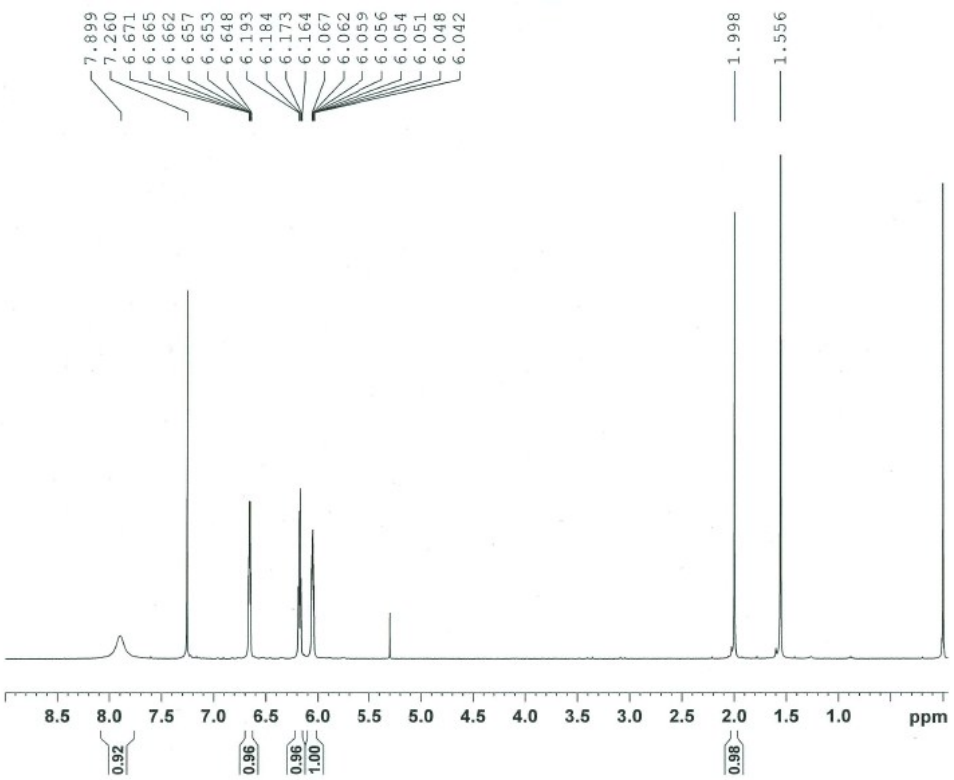


Figure S5. ^{1}H NMR spectrum of **11** in $CDCl_3$

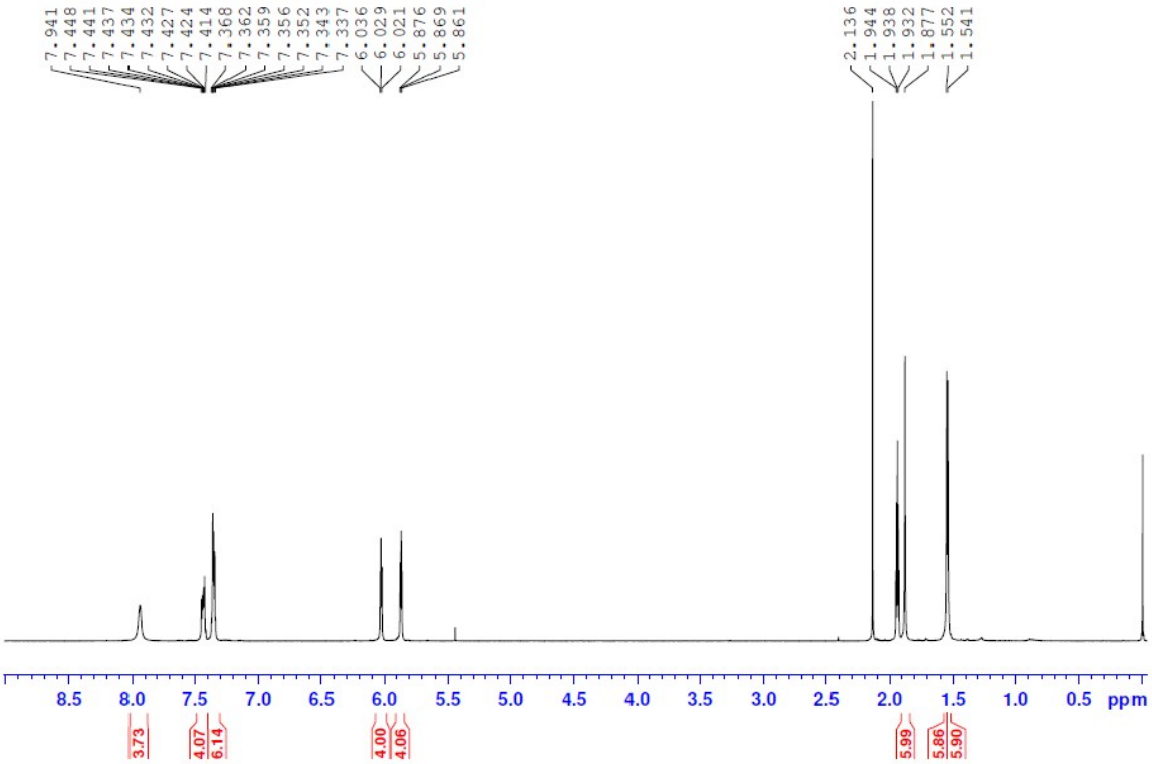


Figure S6: ^{1}H NMR spectrum of calix[4]pyrrole **2** in CD_3CN

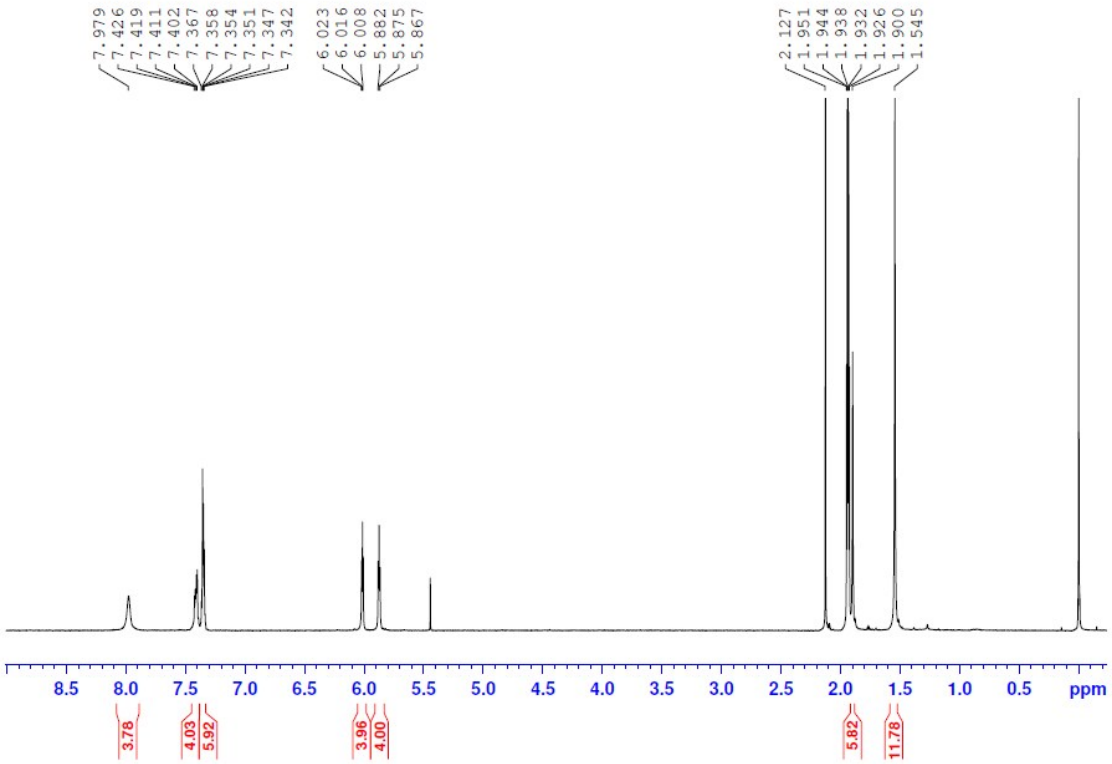


Figure S7: ^{1}H NMR spectrum of calix[4]pyrrole *trans*-**2** in CD_3CN

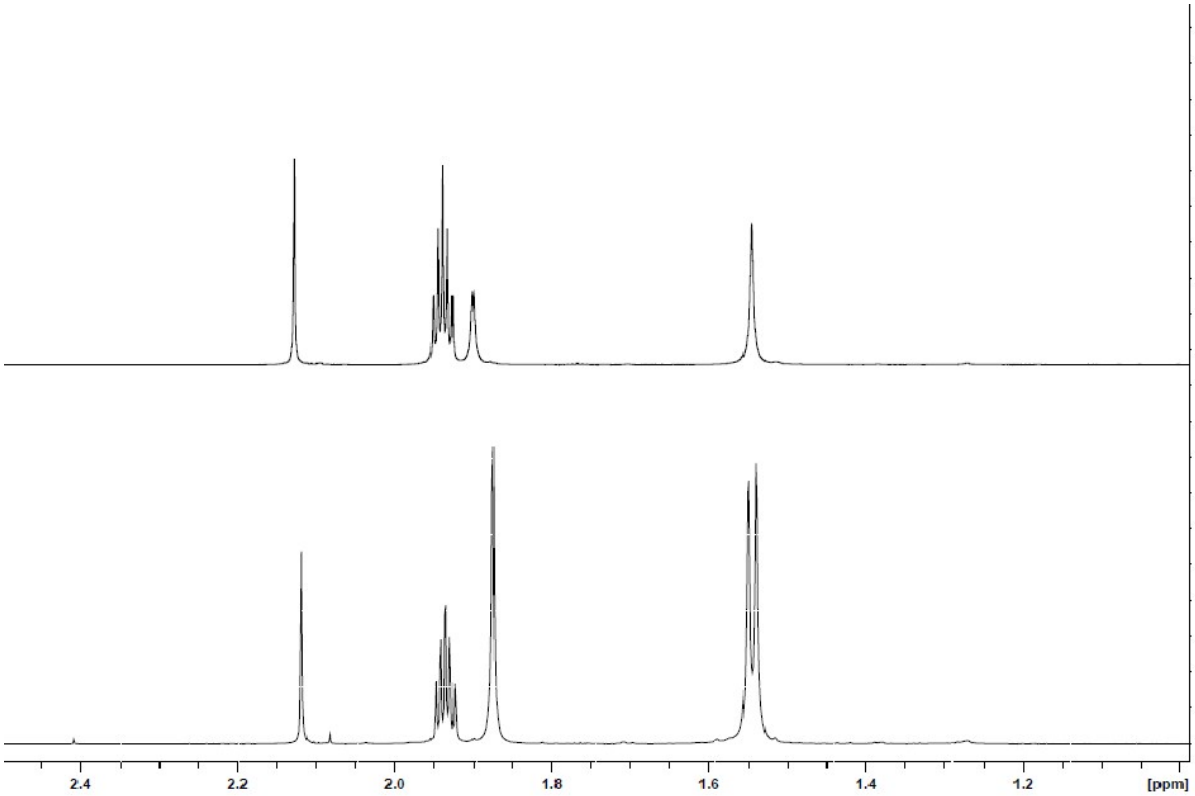


Figure S8: Comparative partial ^{1}H NMR spectra of *cis*-**2** (bottom) and *trans*-**2** (top) in CD_3CN

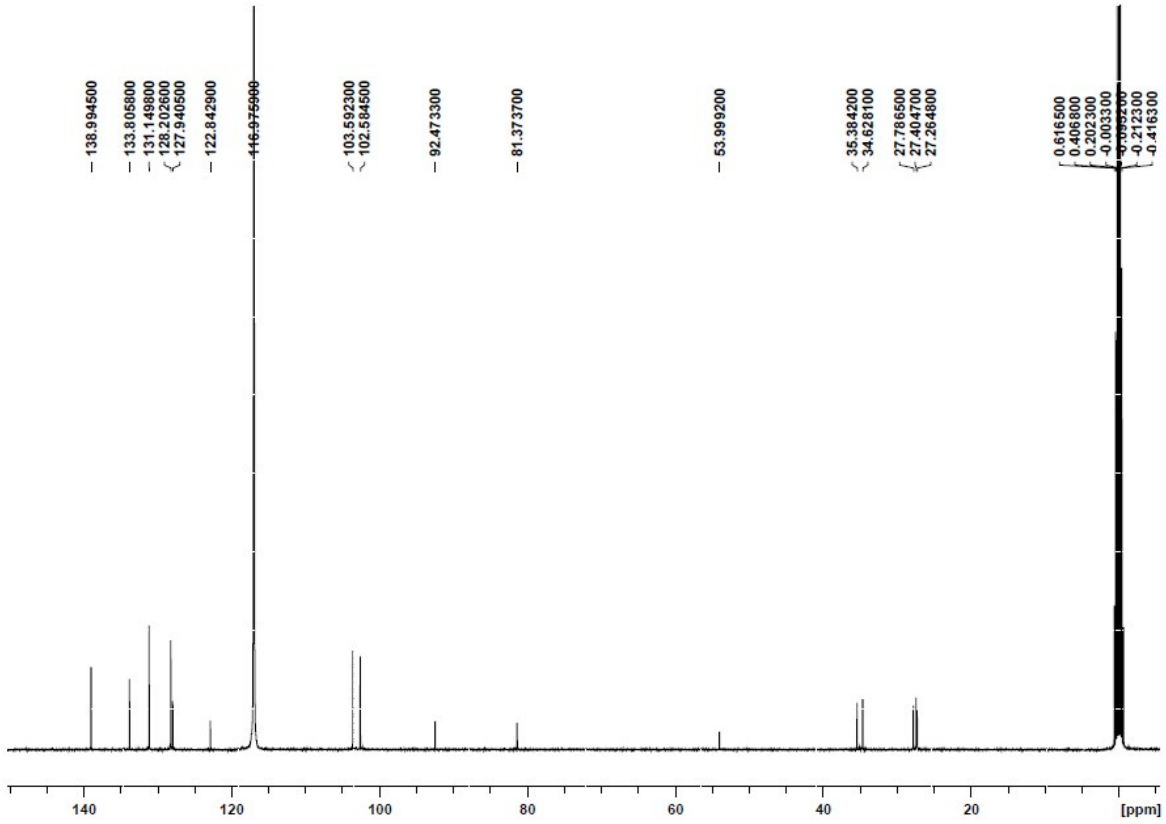


Figure S9: ^{13}C NMR spectrum of calix[4]pyrrole **2** in CD_3CN

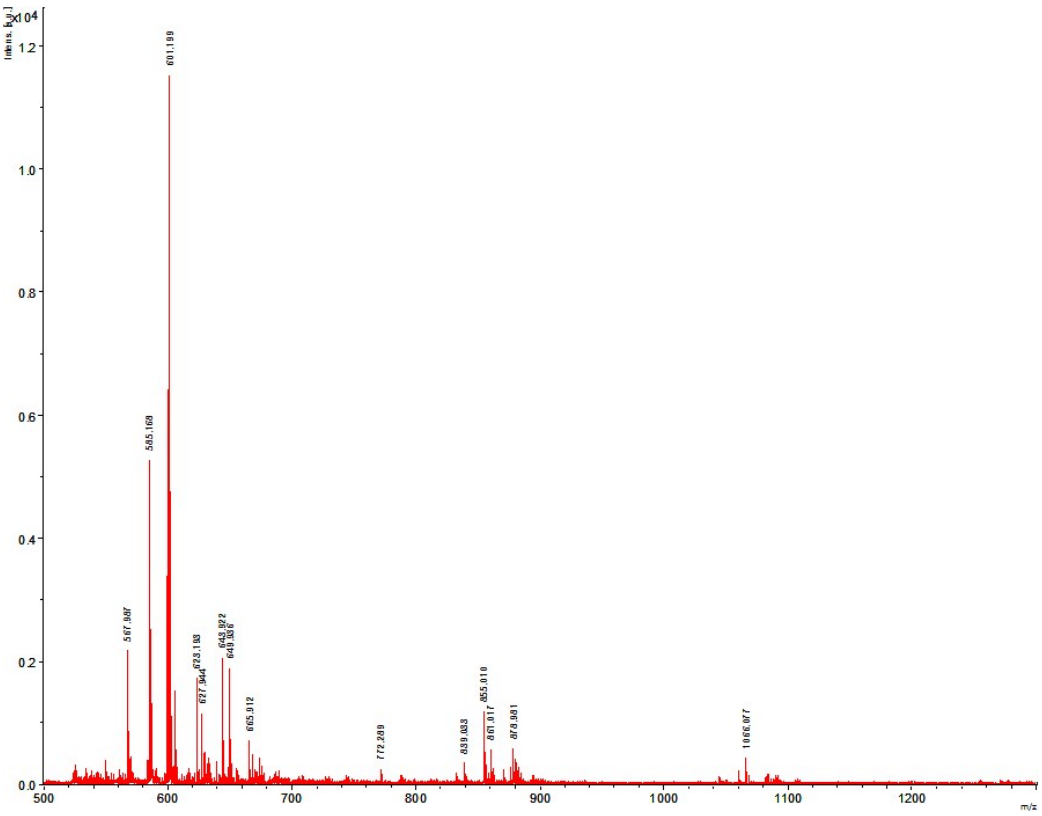


Figure S10: MALDI-TOF spectrum of calix[4]pyrrole **2**

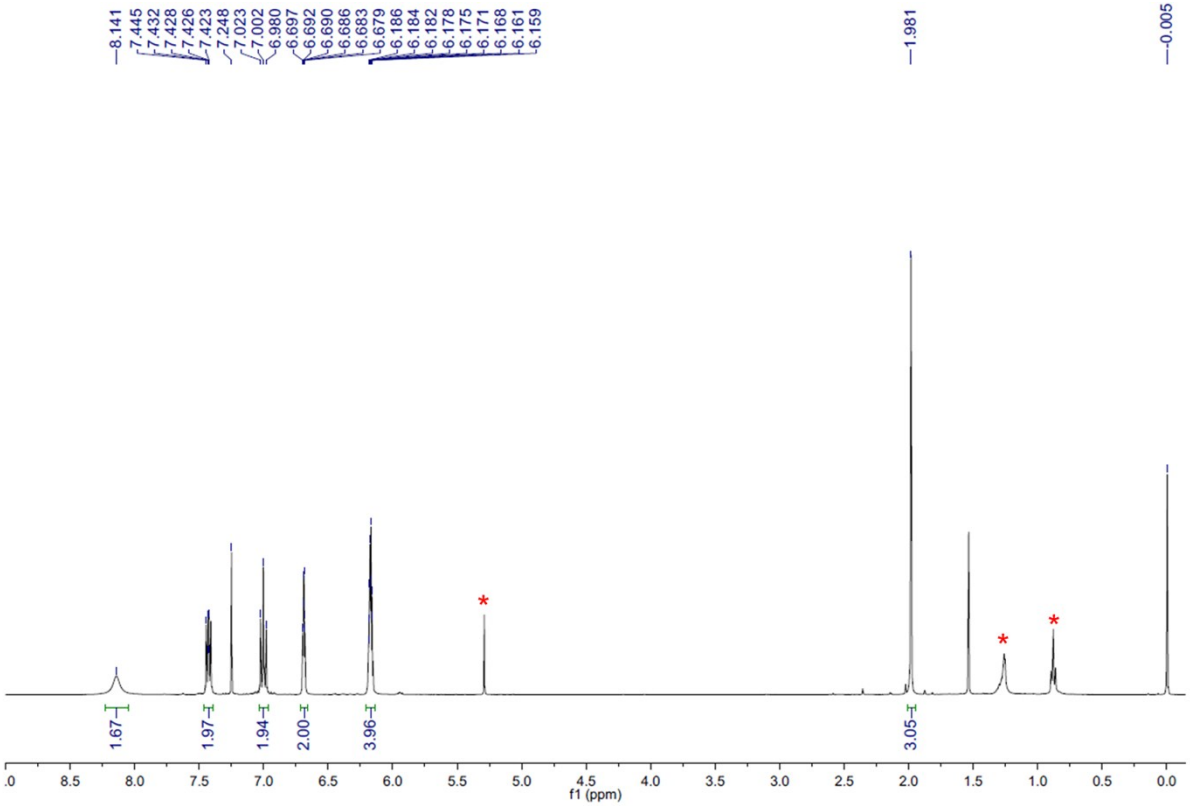


Figure S11: ^{1}H NMR spectrum of compound **9** in $CDCl_3$ (* indicates residual solvents)

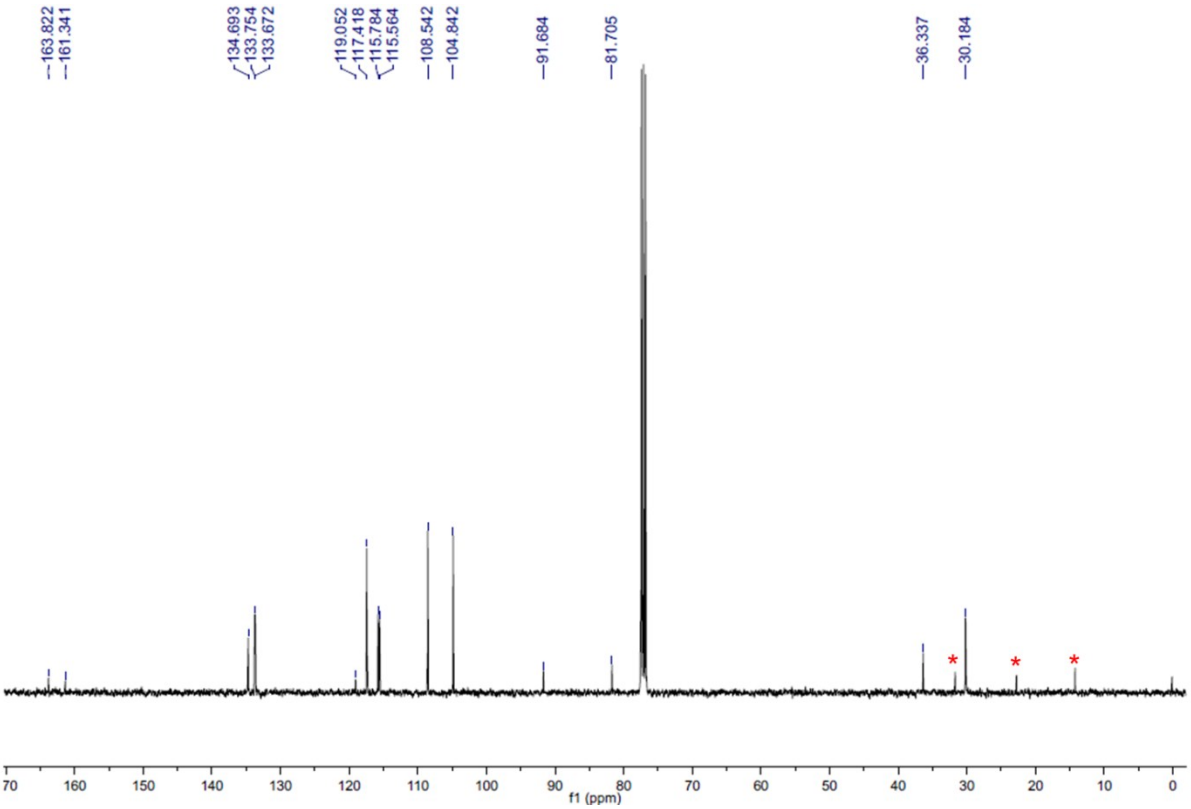


Figure S12: ^{13}C NMR spectrum of compound **9** in $CDCl_3$ (* indicates residual solvents)

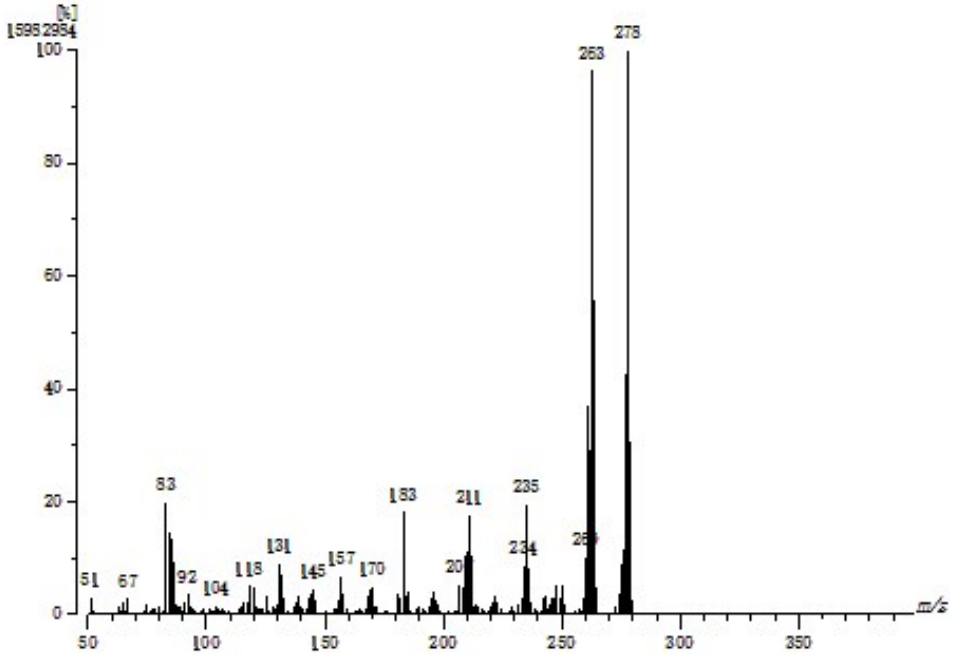


Figure S13: Mass spectrum of compound **8**

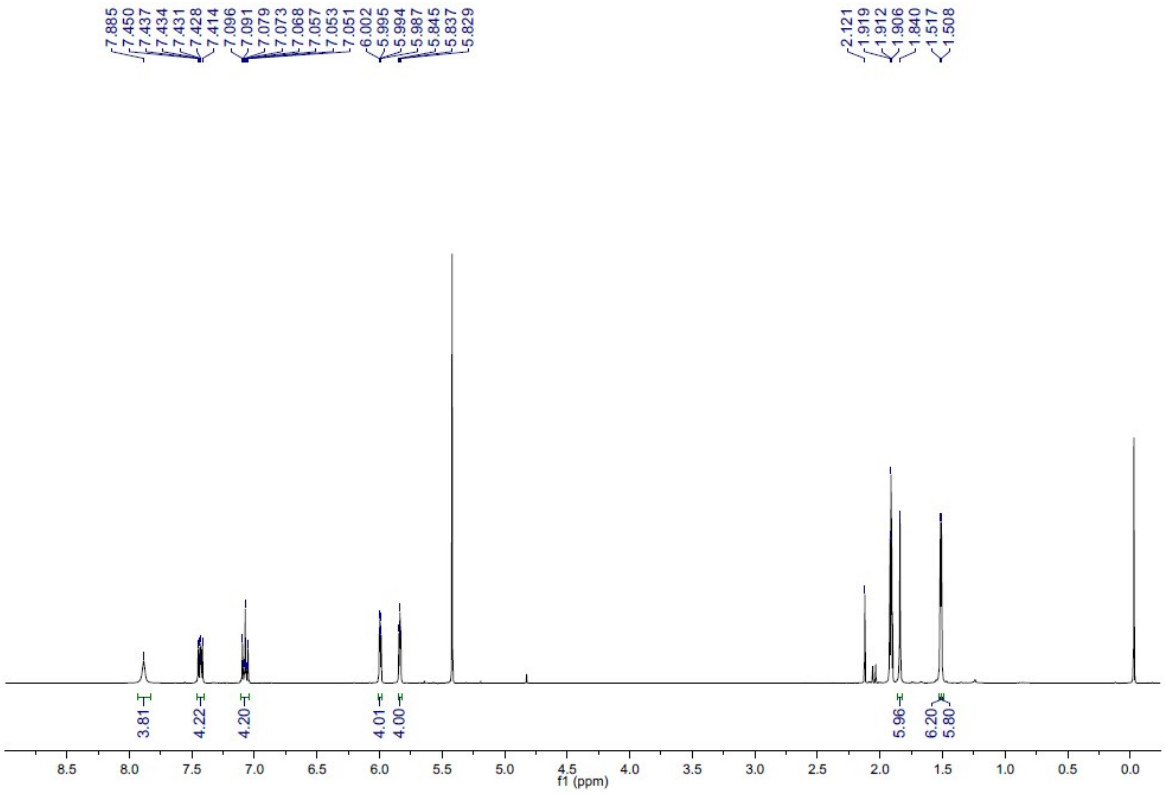


Figure S14: ^{1}H NMR spectrum of calix[4]pyrrole **3** in CD_3CN

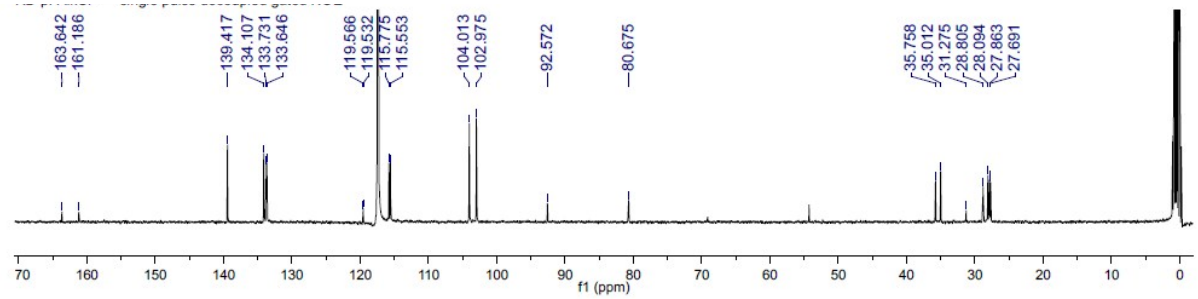


Figure S15: ^{13}C NMR spectrum of calix[4]pyrrole **3** in CD_3CN

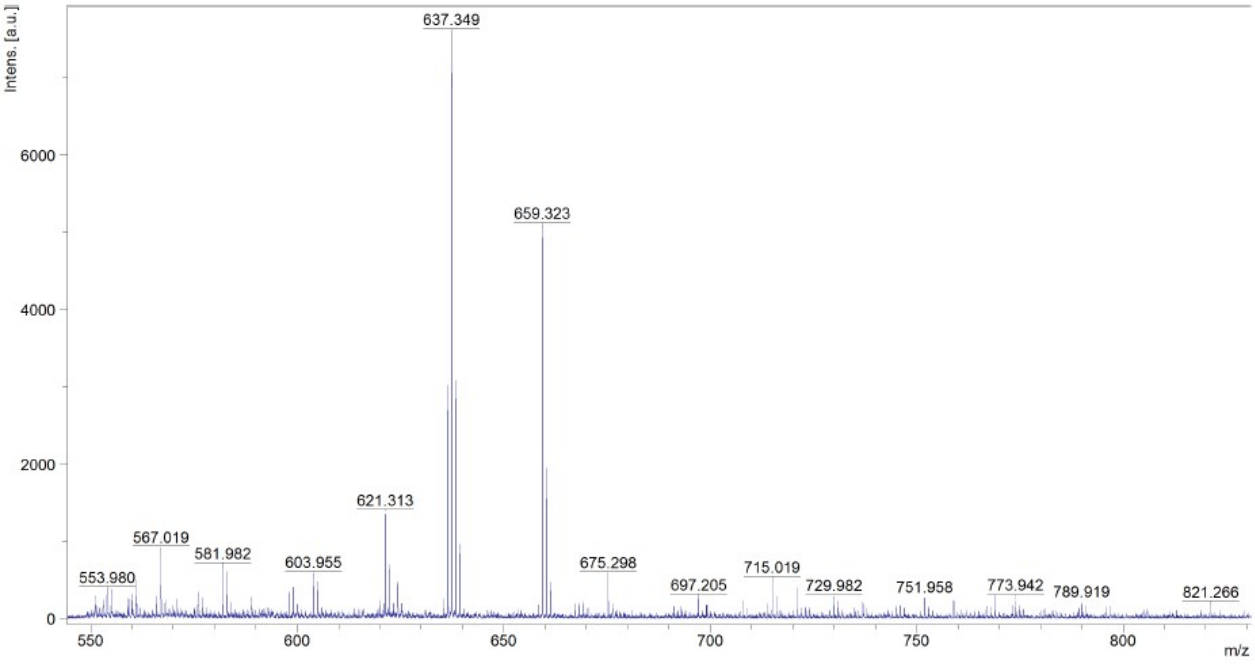
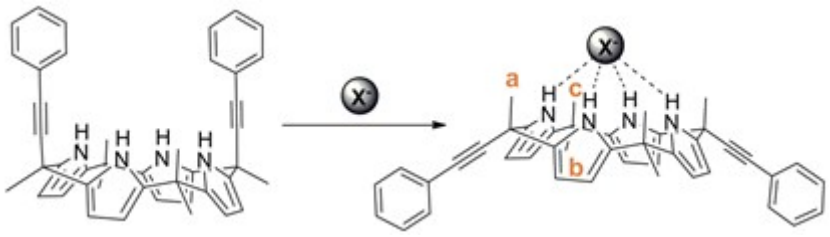


Figure S16: MALDI-TOF spectrum of calix[4]pyrrole **3**



Proposed halide recognition mode in calix[4]pyrrole **2** (X^- = halides)

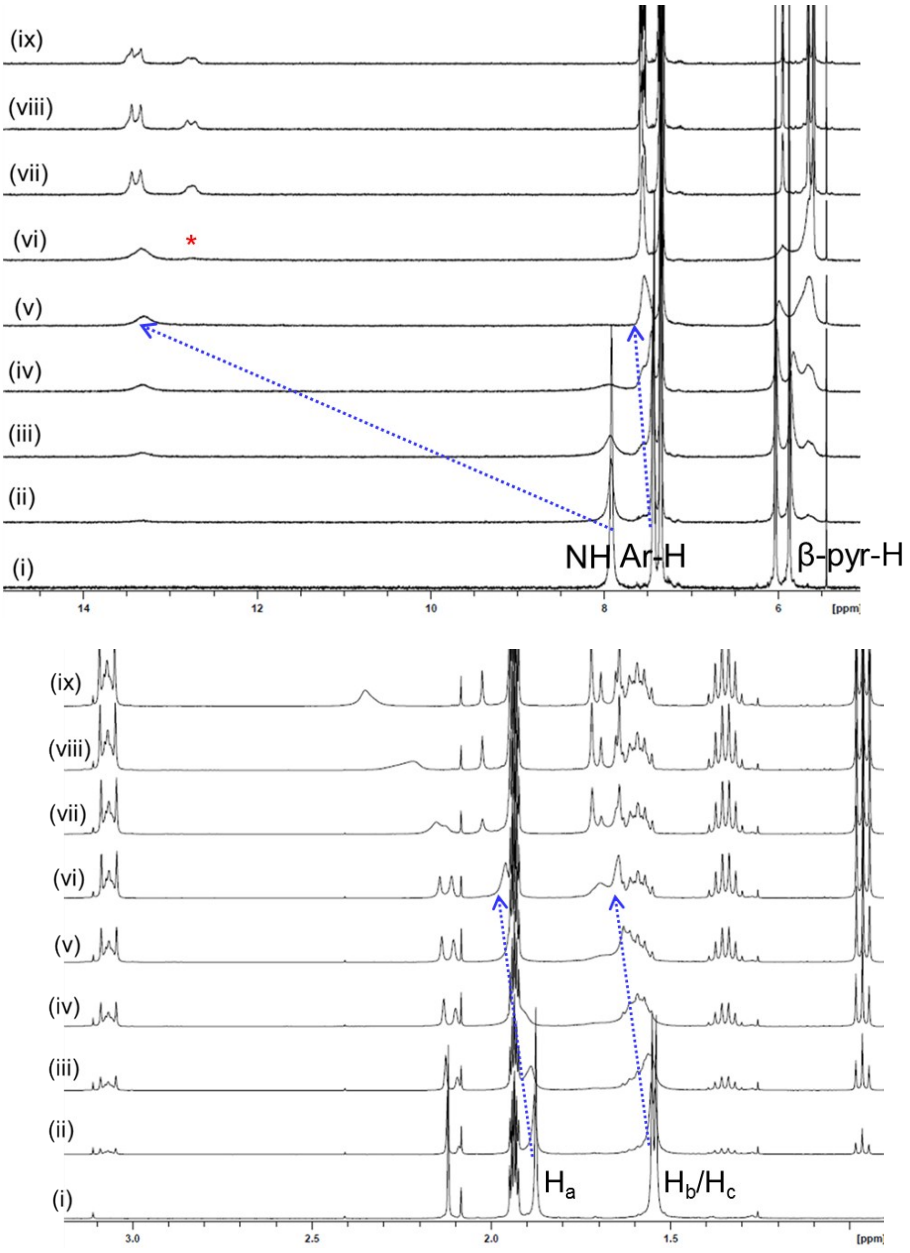


Figure S17: Partial ^{1}H NMR titration spectra of **2** (10.82 mM) with TBAF in CD_3CN (top and bottom): (i) **2,** (ii) **2** + 0.25 equiv. F^-, (iii) **2** + 0.5 equiv. F^-, (iv) **2** + 0.75 equiv. F^-, (v) **2** + 1.0 eqv. F^-, (vi) **2** + 1.25 equiv. F^-, (vii) **2** + 1.5 equiv. F^-, (viii) **2** + 1.75 equiv. F^- and (ix) **2** + 2.0 equiv. F^-.

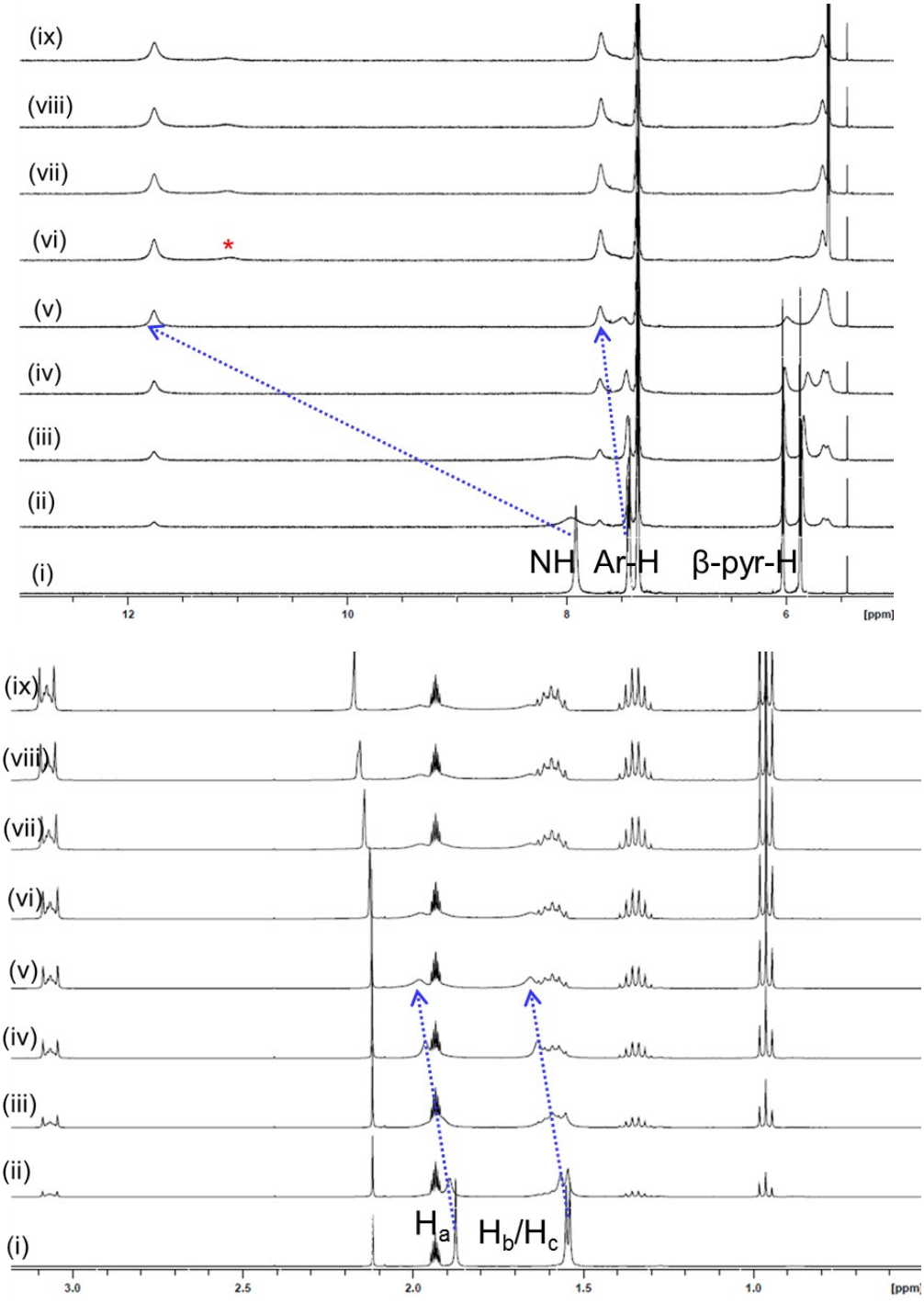


Figure S18: Partial ^{1}H NMR titration spectra of **2** (12.15 mM) with TBACl in CD_3CN (top and bottom). (i) **2,** (ii) **2** + 0.25 equiv. Cl^-, (iii) **2** + 0.5 equiv. Cl^-, (iv) **2** + 0.75 equiv. Cl^-, (v) **2** + 1.0 equiv. Cl^-, (vi) **2** + 1.25 equiv. Cl^-, (vii) **2** + 1.5 equiv. Cl^-, (viii) **2** + 1.75 equiv. Cl^- and (ix) **2** + 2.0 equiv. Cl^-.

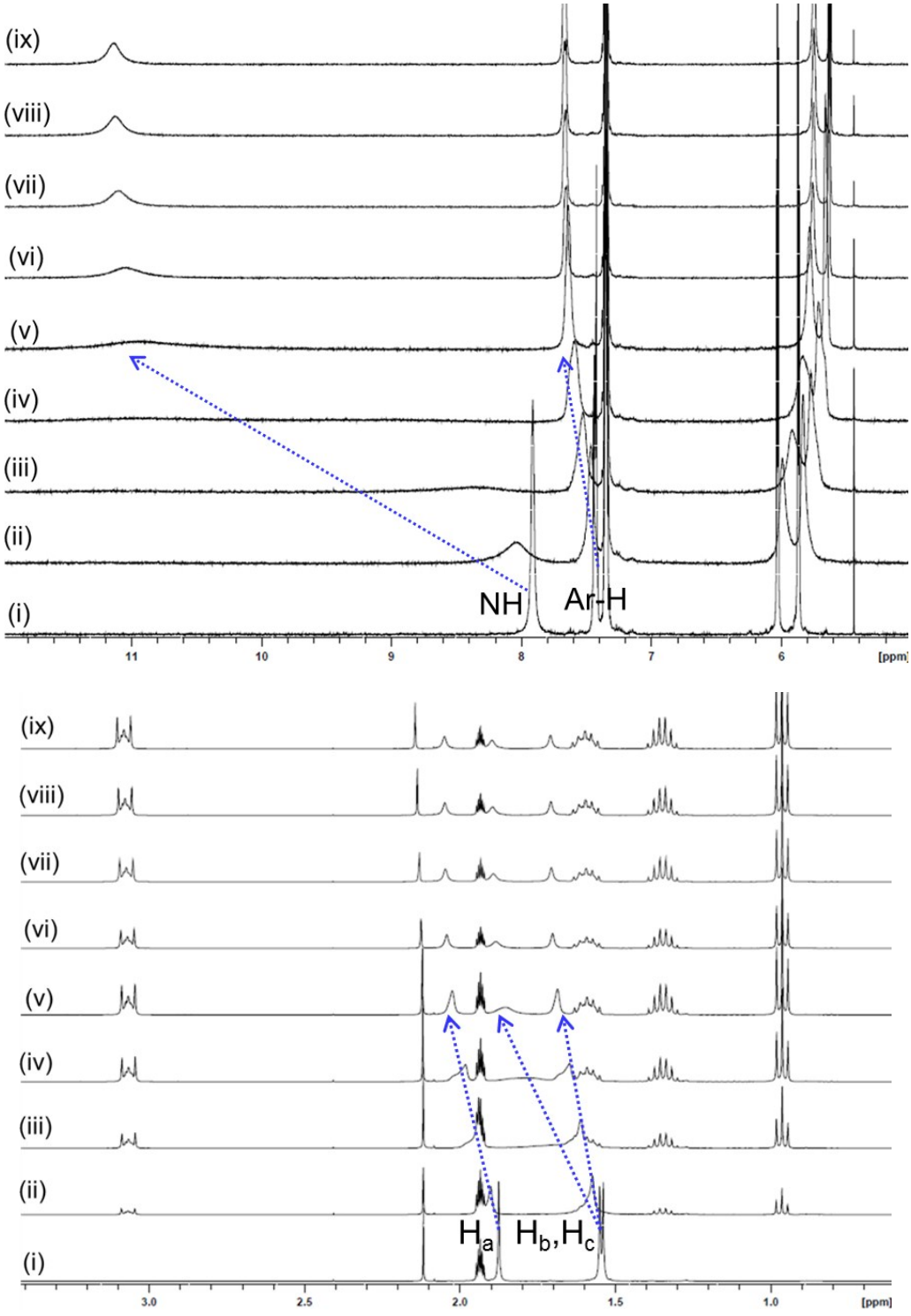


Figure S19: Partial ^{1}H NMR titration spectra of **2** (11.98 mM) with TBABr in CD_3CN (top and bottom). (i) **2**, (ii) **2** + 0.26 equiv. Br^-, (iii) **2** + 0.52 equiv. Br^-, (iv) **2** + 0.78 equiv. Br^-, (v) **2** + 1.04 equiv. Br^-, (vi) **2** + 1.3 equiv. Br^-, (vii) **2** + 1.56 equiv. Br^-, (viii) **2** + 1.82 equiv. Br^- and (ix) **2** + 2.08 equiv. Br^-.

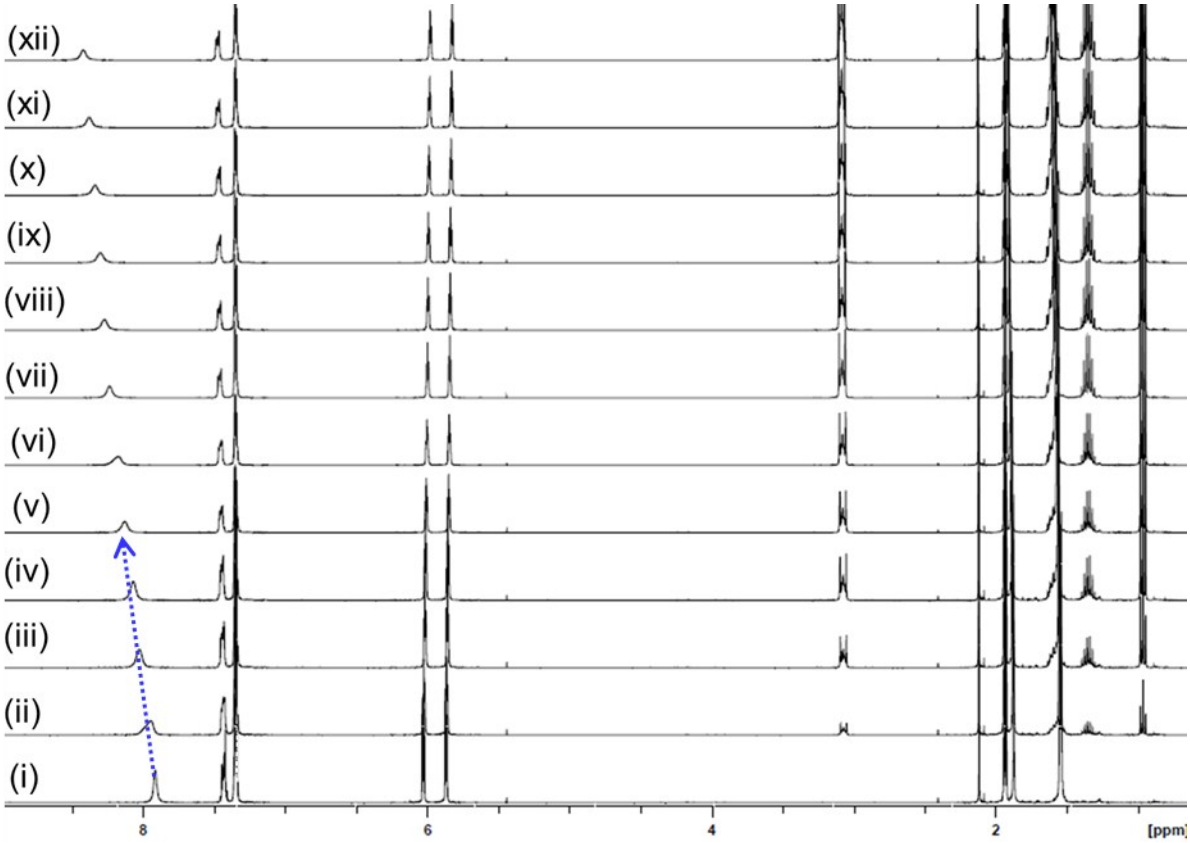


Figure S20. Partial ^{1}H NMR titration spectra of **2** (11.32 mM) with TBAI in CD_3CN. (i) **2**, (ii) **2** + 0.15 equiv. I^-, (iii) **2** + 0.3 equiv. I^-, (iv) **2** + 0.45 equiv. I^-, (v) **2** + 0.6 equiv. I^-, (vi) **2** + 0.75 equiv. I^-, (vii) **2** + 1.0 equiv. I^-, (viii) **2** + 1.15 equiv. I^-, (ix) **2** + 1.3 equiv. I^-, (x) **2** + 1.45 equiv. I^-, (xi) **2** + 1.6 equiv. I^- and (xii) **2** + 1.75 equiv. I^-.

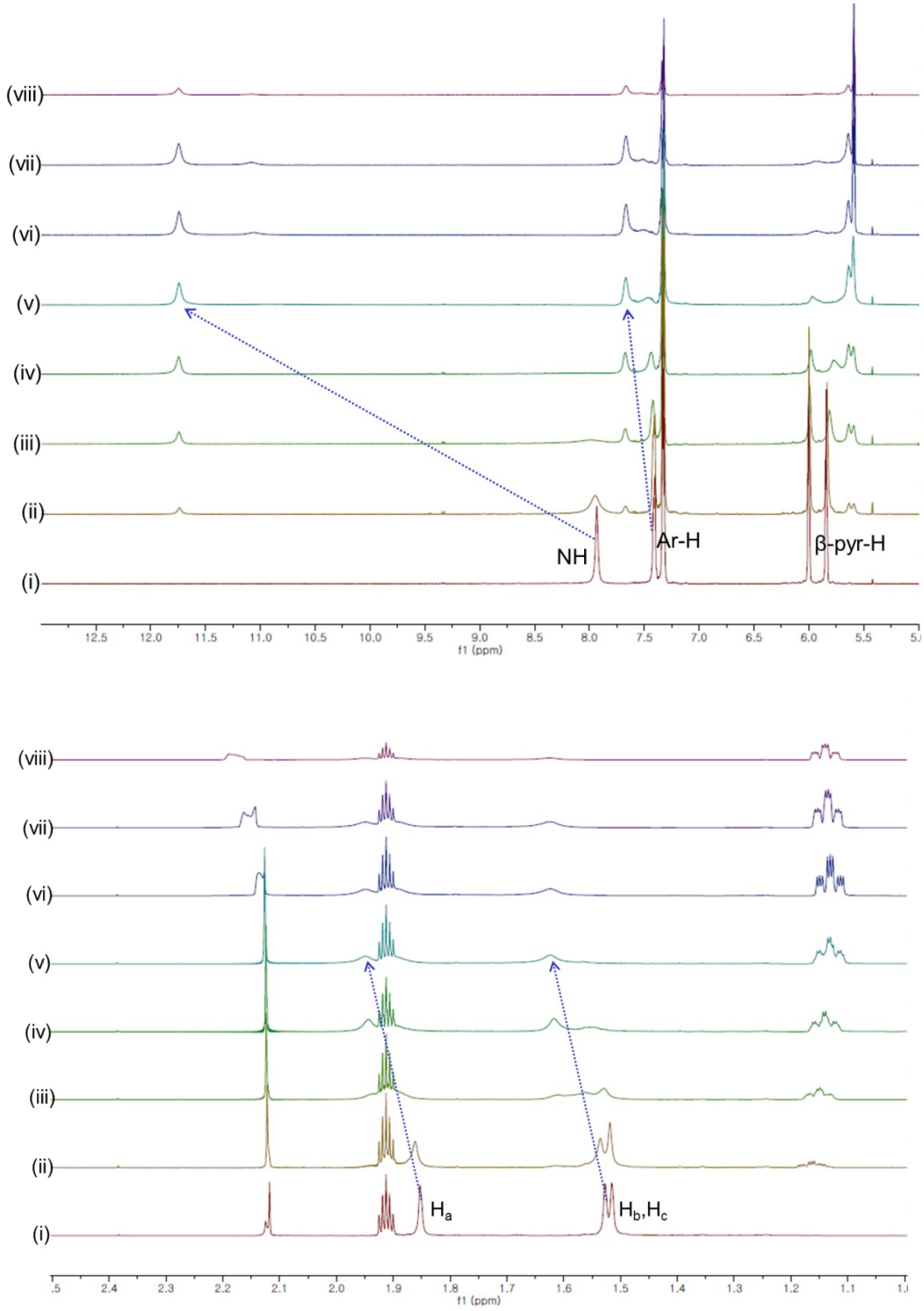
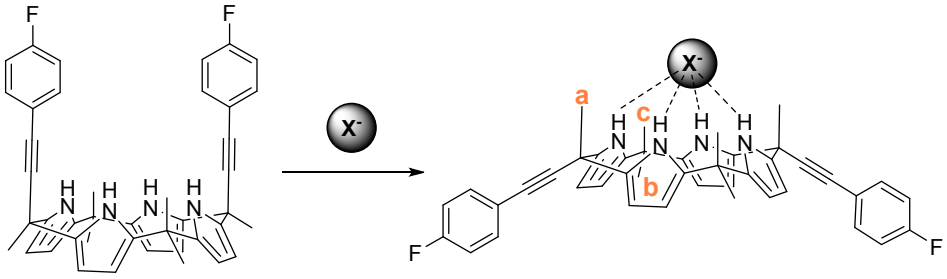
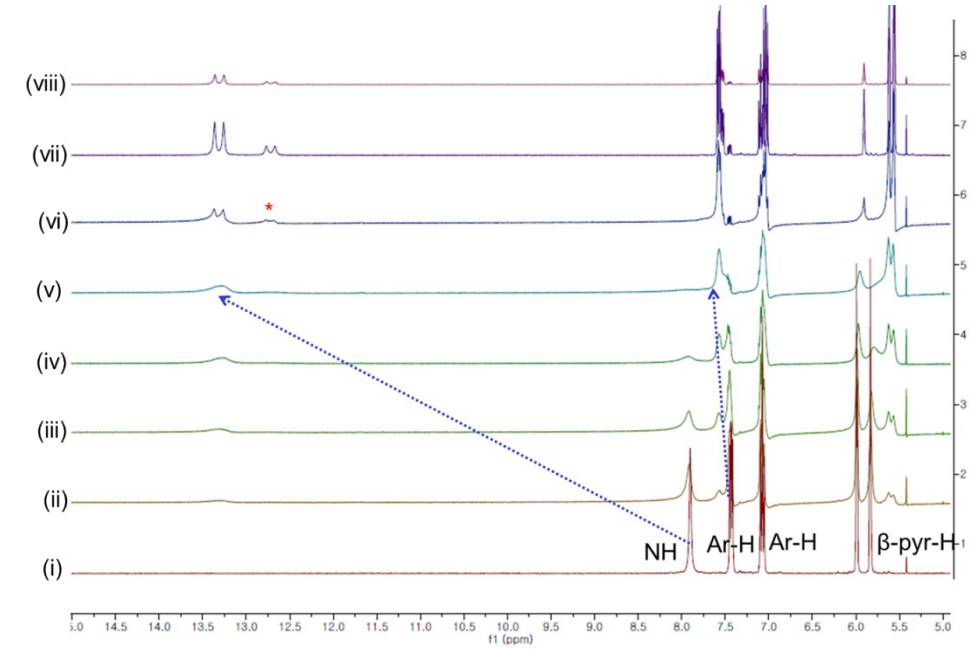


Figure S21: Partial ^{1}H NMR titration spectra of **2** (9.98 mM) with TEACl in CD_3CN (top and bottom). (i) **2**, (ii) **2** + 0.27 equiv. Cl^-, (iii) **2** + 0.54 equiv. Cl^-, (iv) **2** + 0.81 equiv. Cl^-, (v) **2** + 1.08 equiv. Cl^-, (vi) **2** + 1.5 equiv. Cl^- and (vii) **2** + 2.08 equiv. Cl^-.



Proposed halide recognition mode in calix[4]pyrrole **3** (X^- = halides)



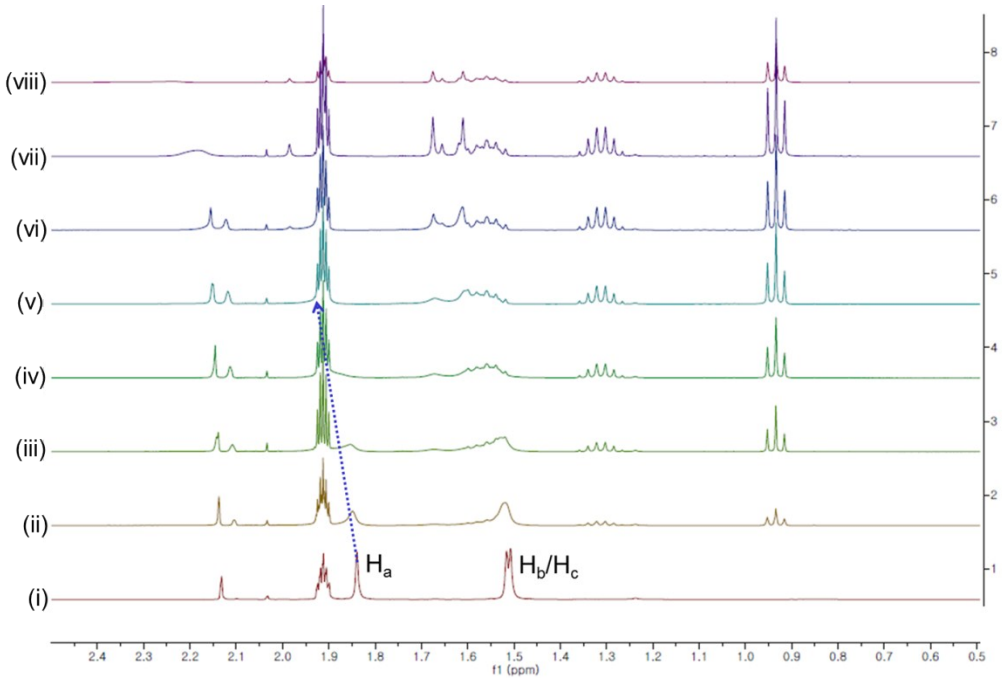


Figure S22: Partial ^{1}H NMR titration spectra of **3** (12.15 mM) with TBAF in CD_3CN (top and bottom). (i) **3,** (ii) **3** + 0.27 equiv. F^-, (iii) **3** + 0.55 equiv. F^-, (iv) **3** + 0.83 equiv. F^-, (v) **3** + 1.10 equiv. F^-, (vi) **3** + 1.38 equiv. F^-, (vii) **3** + 1.69 equiv. F^-, (viii) **3** + 2.03 equiv. F^-.

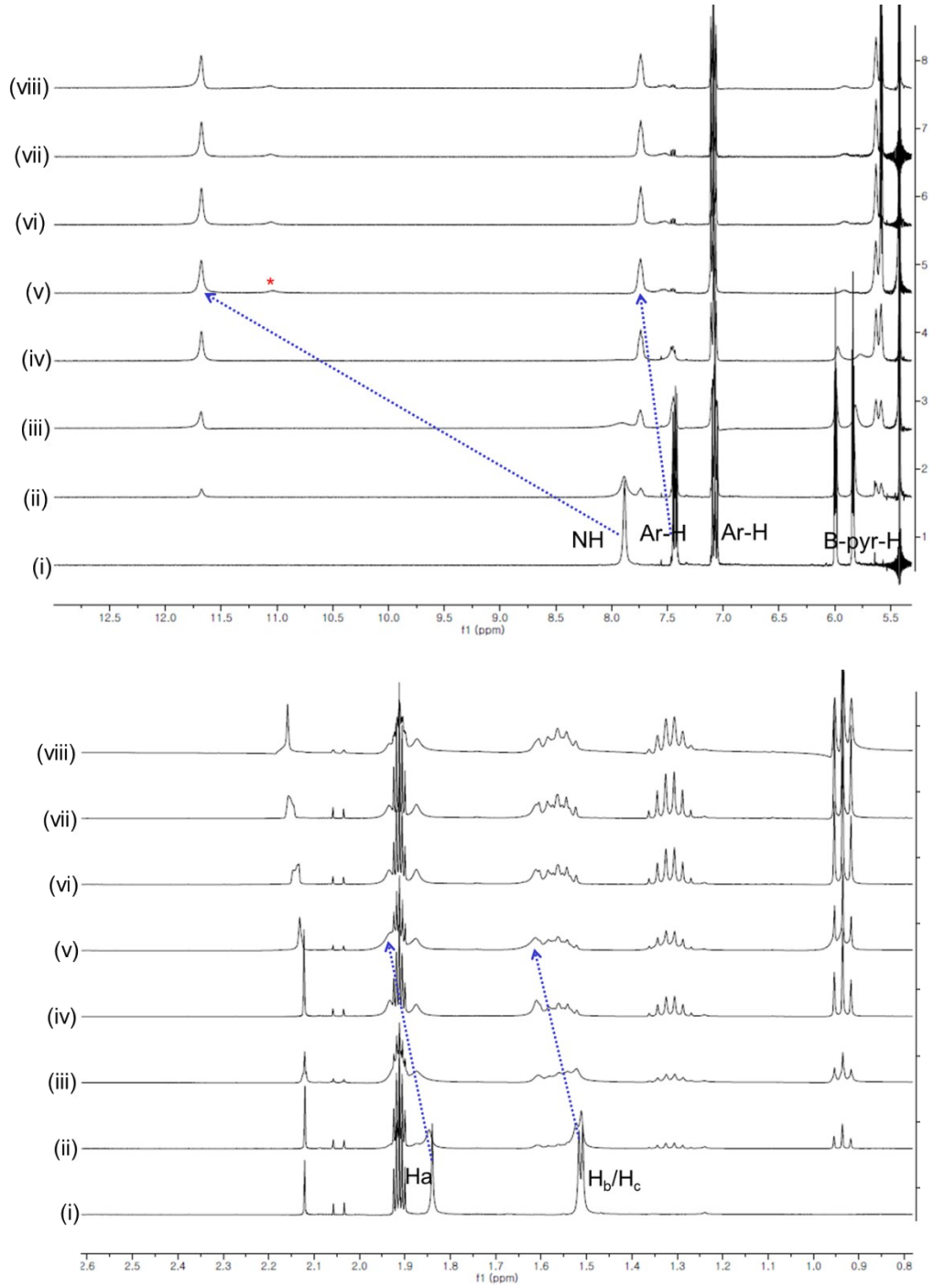


Figure S23: Partial ^{1}H NMR titration spectra of **3** (7.54 mM) with TBACl in CD_3CN (top and bottom). (i) **3,** (ii) **3** + 0.27 equiv. Cl^-, (iii) **3** + 0.54 equiv. Cl^-, (iv) **3** + 0.81 equiv. Cl^-, (v) **3** + 1.08 equiv. Cl^-, (vi) **3** + 1.37 equiv. Cl^-, (vii) **3** + 1.68 equiv. Cl^-, (viii) **3** + 2.01 equiv. Cl^-.

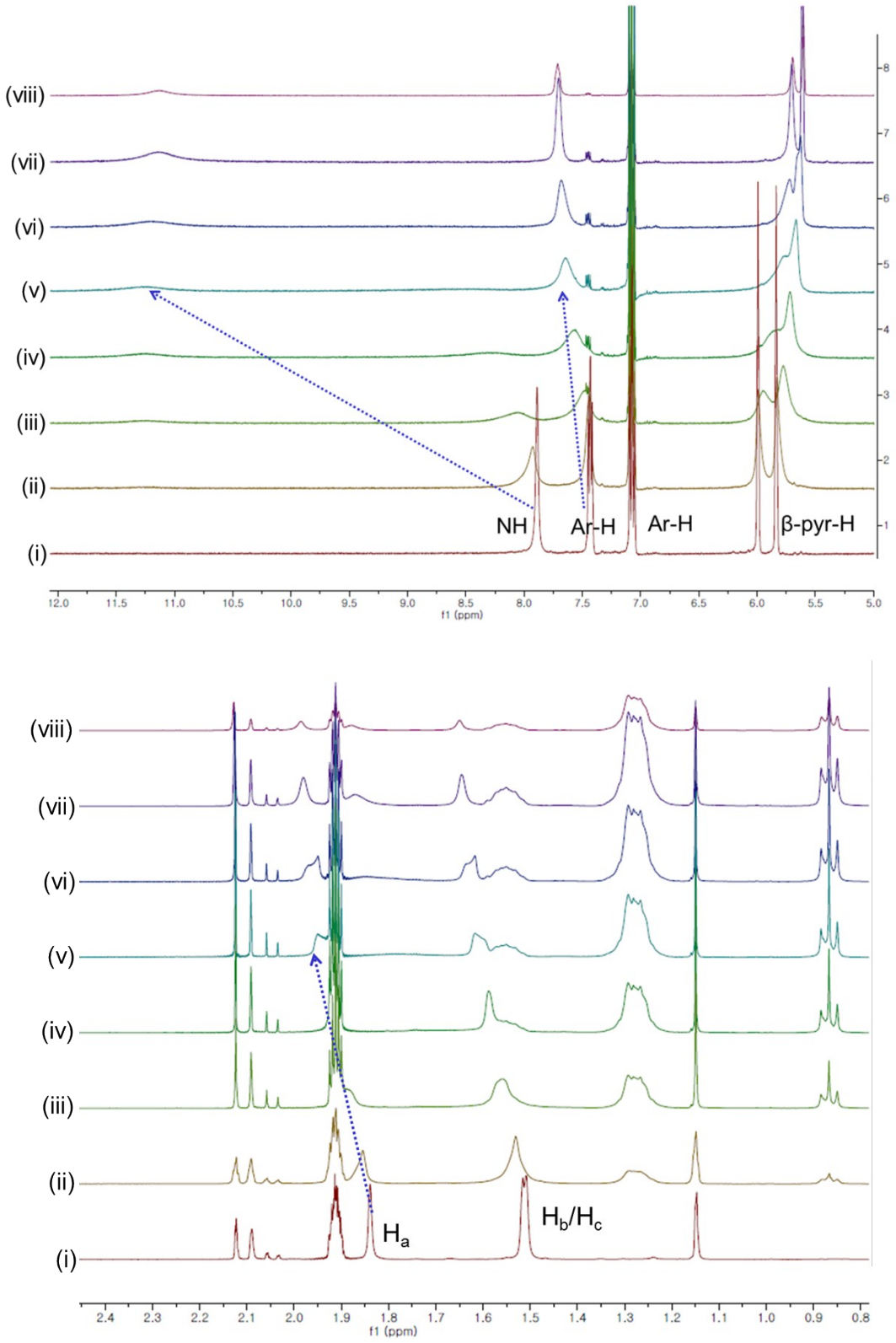
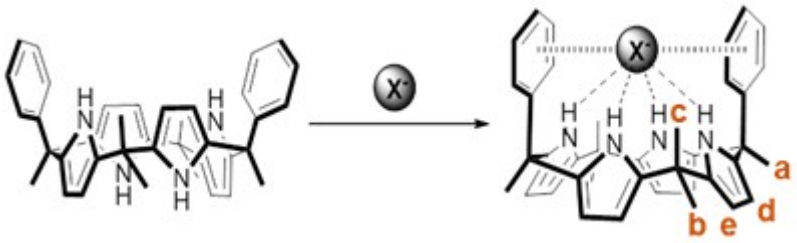


Figure S24: Partial ^{1}H NMR titration spectra of **3** (7.54 mM) with TBABr in CD_3CN (top and bottom). (i) **3,** (ii) **3** + 0.27 equiv. Br^-, (iii) **3** + 0.54 equiv. Br^-, (iv) **3** + 0.81 equiv. Br^-, (v) **3** + 1.08 equiv. Br^-, (vi) **3** + 1.35 equiv. Br^-, (vii) **3** + 1.68 equiv. Br^-, (viii) **3** + 2.0 equiv. Br^-.



Proposed halide anions binding mode in calix[4]pyrrole **4** (X^- = halides)

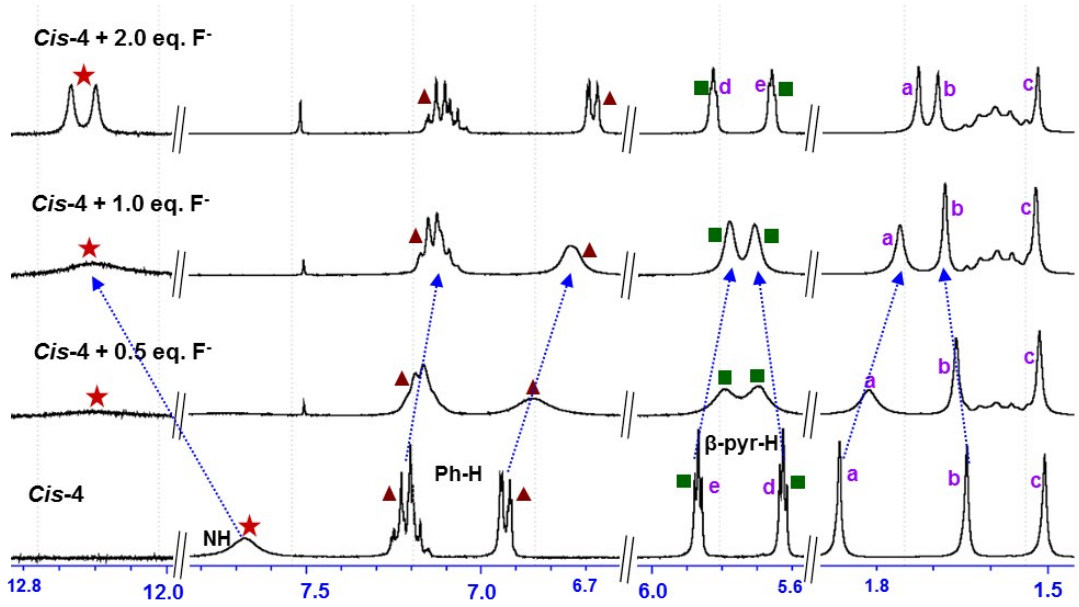


Figure S25: ^{1}H NMR titration spectra of calix[4]pyrrole **4** with TBAF in CD_3CN

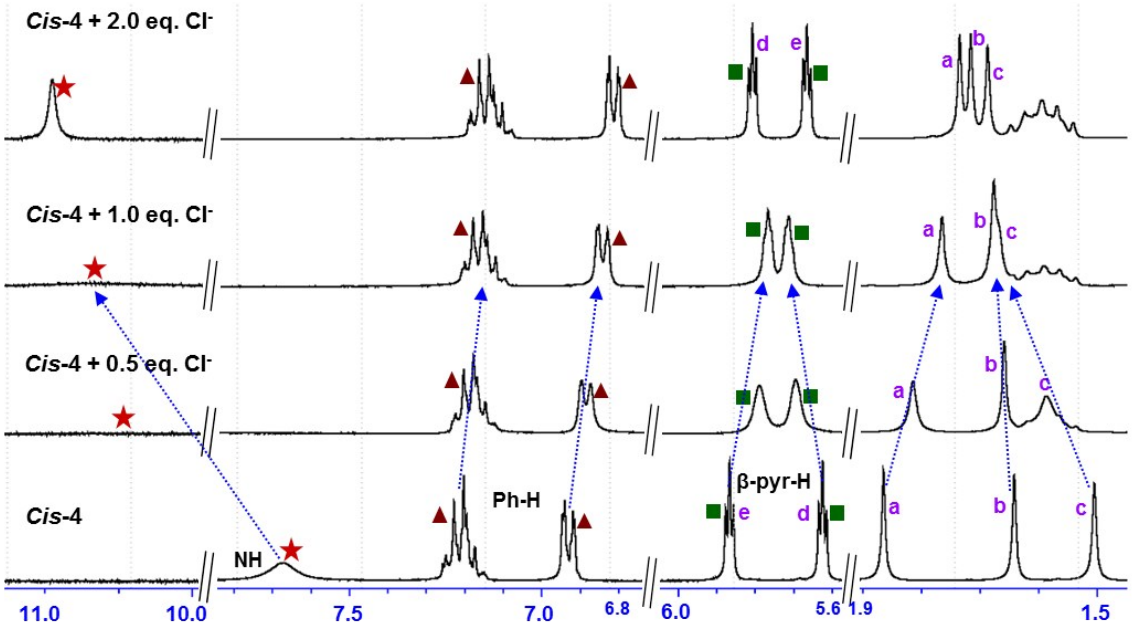


Figure S26: ^{1}H NMR titration spectra of calix[4]pyrrole **4** with TBACl in CD_3CN

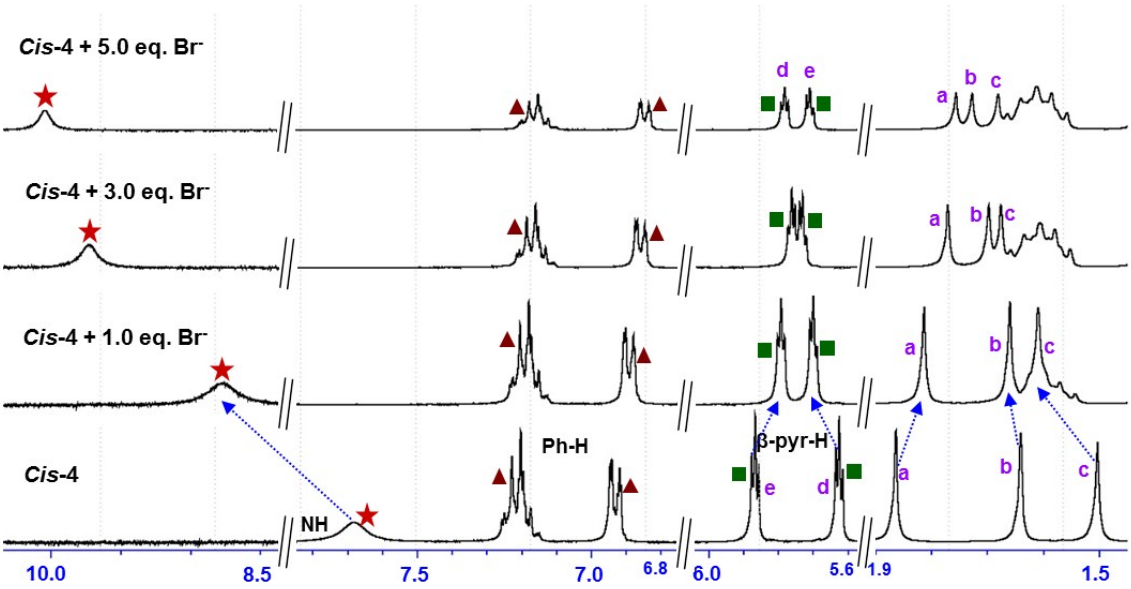
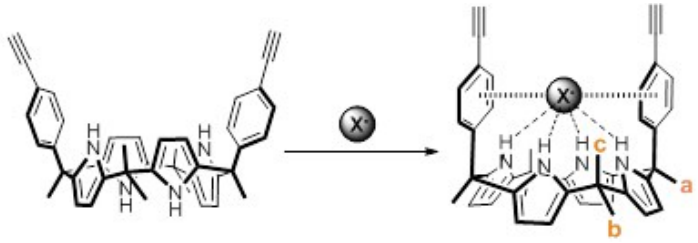
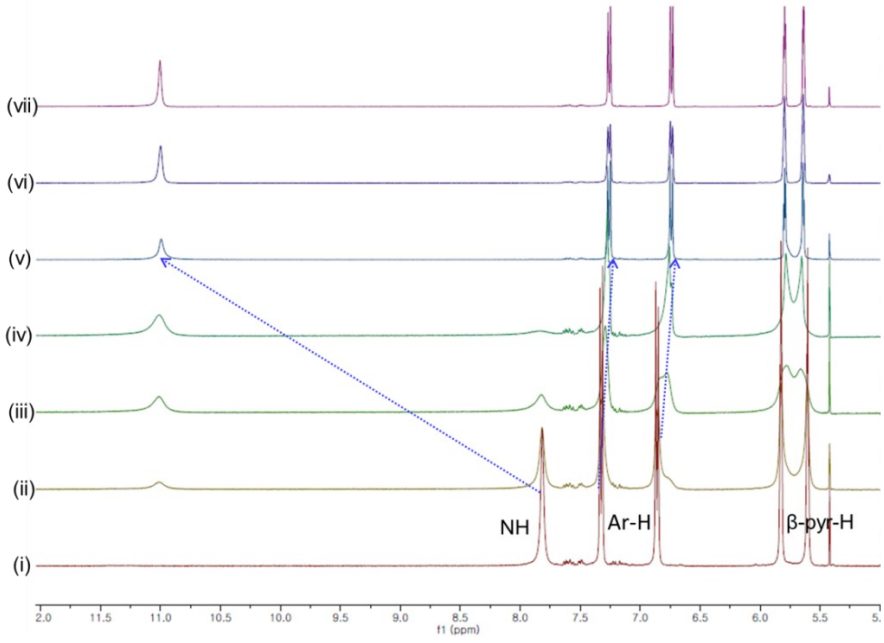


Figure S27: ^{1}H NMR titration spectra of calix[4]pyrrole **4** with TBABr in CD_3CN



Proposed halide anions binding mode in calix[4]pyrrole **5** (X^- = halides)



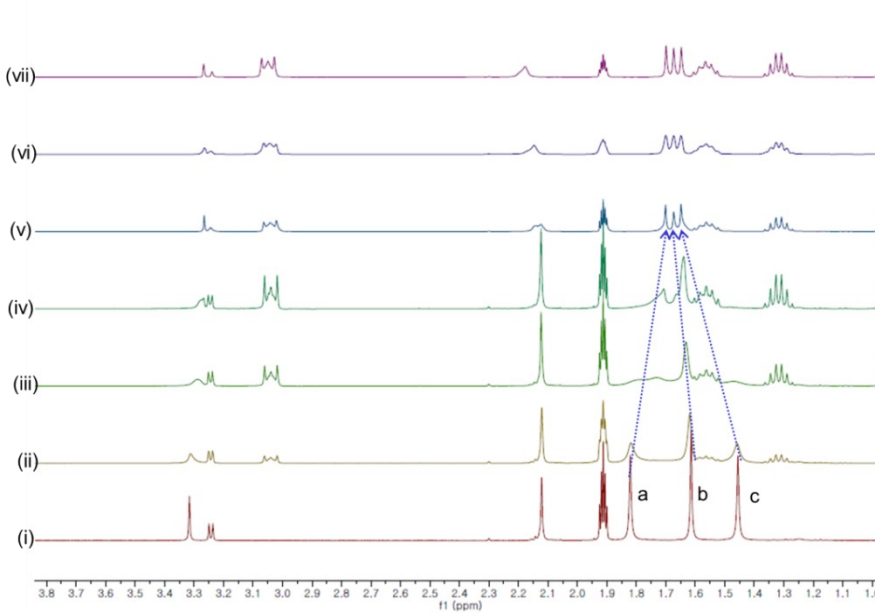
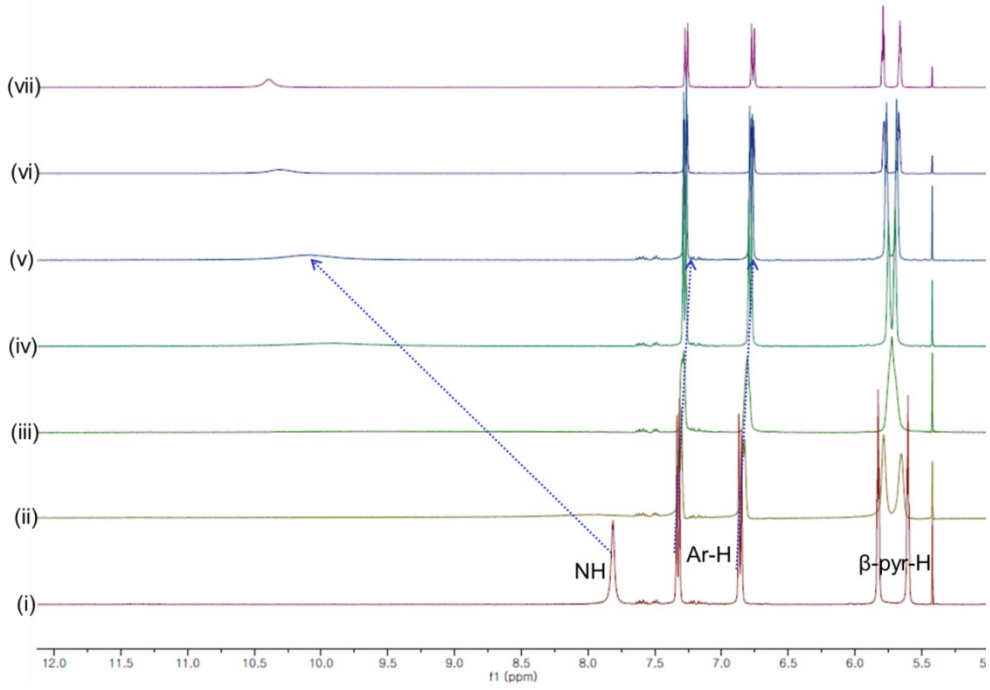


Figure S28: Partial ^{1}H NMR titration spectra of **5** (10.98 mM) with TBACl in CD_3CN (top and bottom). (i) **5**, (ii) **5** + 0.26 equiv. Cl^-, (iii) **5** + 0.52 equiv. Cl^-, (iv) **5** + 0.78 equiv. Cl^-, (v) **5** + 1.04 equiv. Cl^-, (vi) **5** + 1.56 equiv. Cl^- and (vii) **5** + 2.08 equiv. Cl^-.



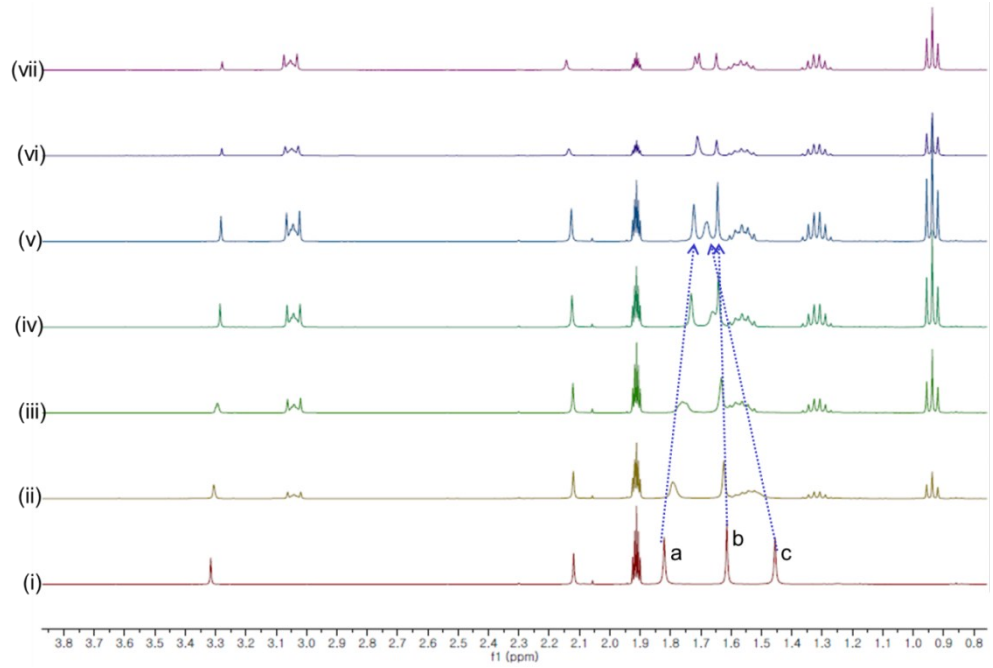


Figure S29: Partial ^{1}H NMR titration spectra of **5** (9.98 mM) with TBABr in CD_3CN (top and bottom). (i) **5**, (ii) **5** + 0.27 equiv. Br^-, (iii) **5** + 0.54 equiv. Br^-, (iv) **5** + 0.81 equiv. Br^-, (v) **5** + 1.08 equiv. Br^-, (vi) **5** + 1.52 equiv. Br^- and (vii) **5** + 2.01 equiv. Br^-.

Note: ^{1}H NMR titrations of fluoride and chloride with receptors **2** and **3** indicate a possible slow equilibrium between the *bis*-axial and *bis*-equatorial complexes. Observed new NH peak (marked with *in **Figures S17**, **S18**, **S22** and **S23**) is probably for the less stable *bis*-axial complex which becomes visible at higher anion concentrations.

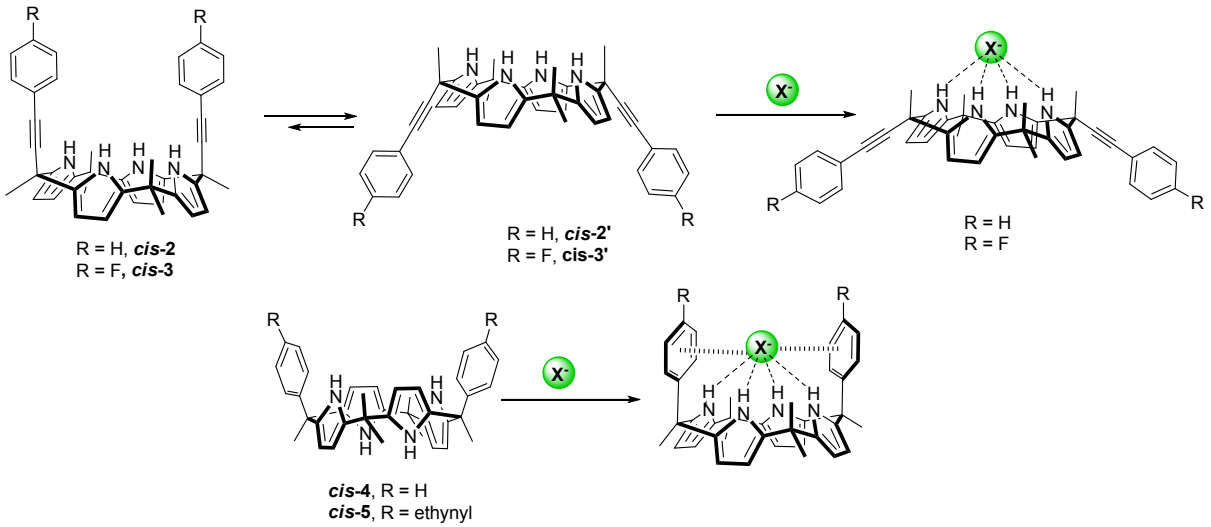


Figure S30: Proposed halide binding modes in calix[4]pyrroles **2**, **3** (top) and **4, 5** (bottom).(X = halide).

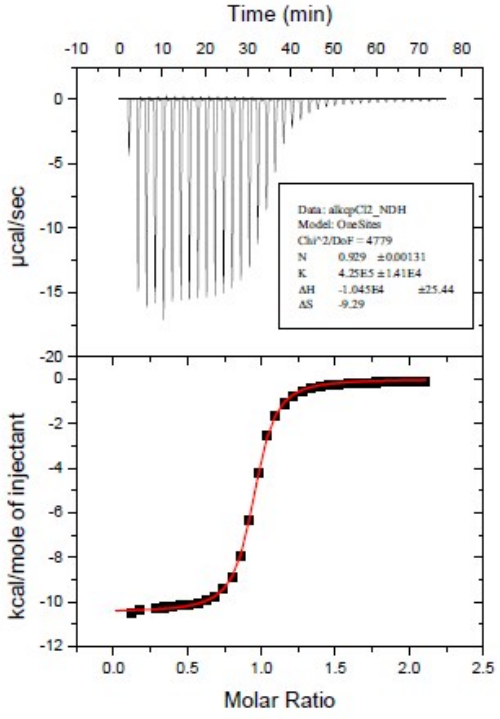


Figure S31: ITC profile for the titration of **2** (0.416 mM) with TBACl (4.02 mM) in acetonitrile at 298 K.

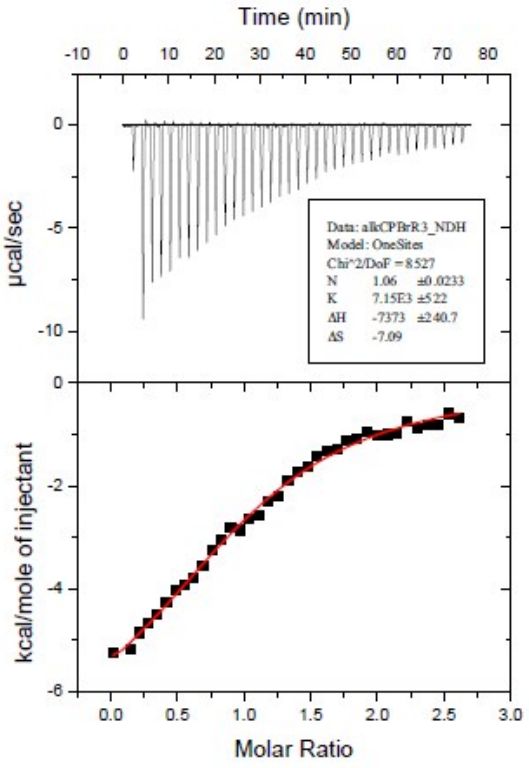


Figure S32: ITC profile for the titration of **2** (0.339 mM) with TBABr (3.97 mM) in acetonitrile at 298 K.

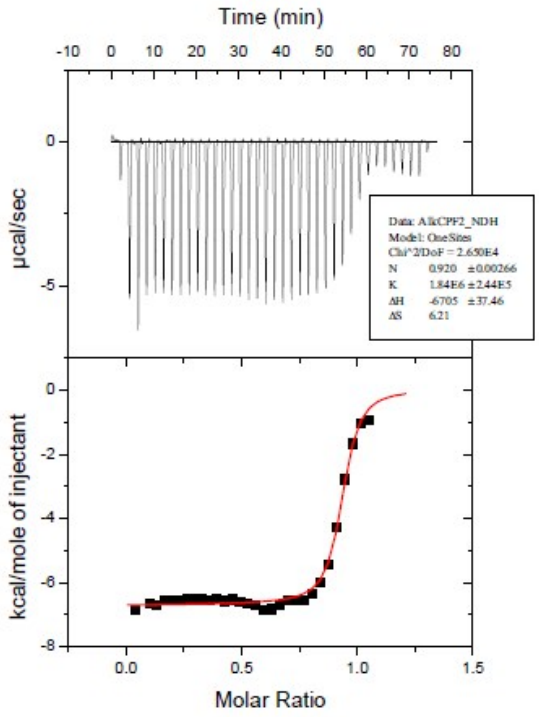


Figure S33: ITC profile for the titration of **2** (0.392 mM) with TBAF (2.17 mM) in acetonitrile at 298 K.

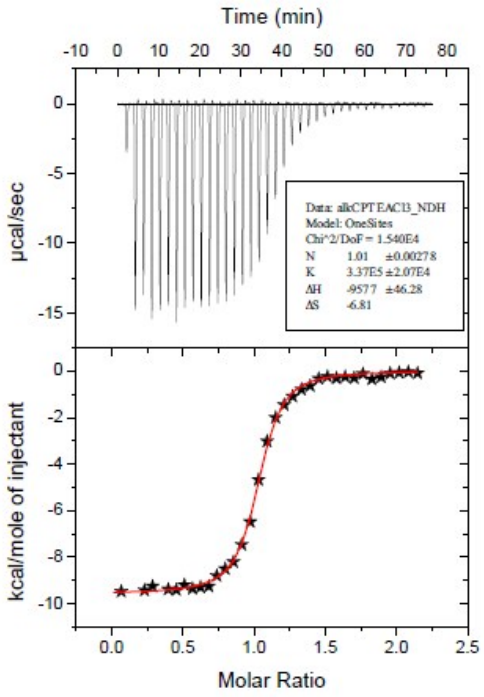


Figure S34: ITC profile for the titration of **2** (0.333 mM) with TEACl (3.61 mM) in acetonitrile at 298 K

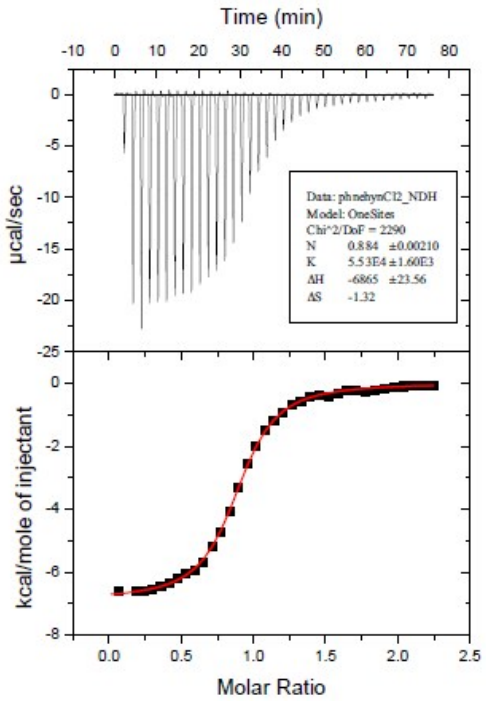


Figure S35: ITC profile for the titration of **5** (0.832 mM) with TBACl (8.366 mM) in acetonitrile at 298 K

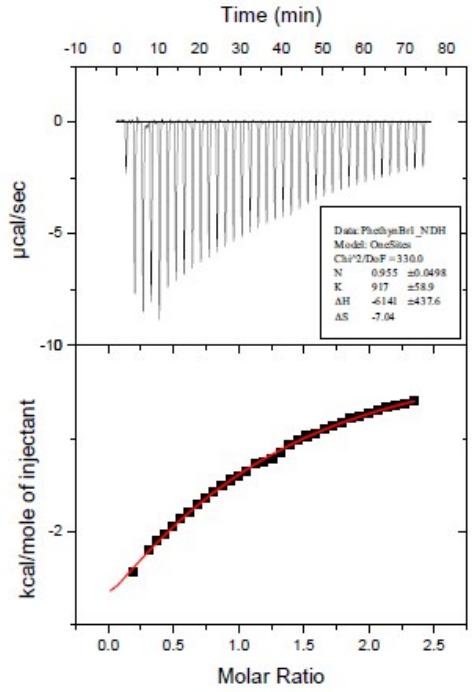


Figure S36: ITC profile for the titration of **5** (0.865 mM) with TBABr (9.084 mM) in acetonitrile at 298 K

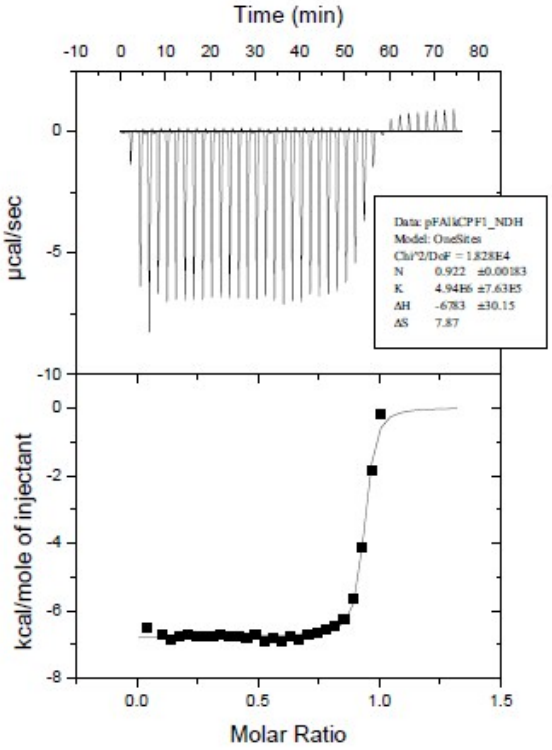


Figure S37: ITC profile for the titration of **3** (0.454 mM) with TBAF (2.677 mM) in acetonitrile at 298 K

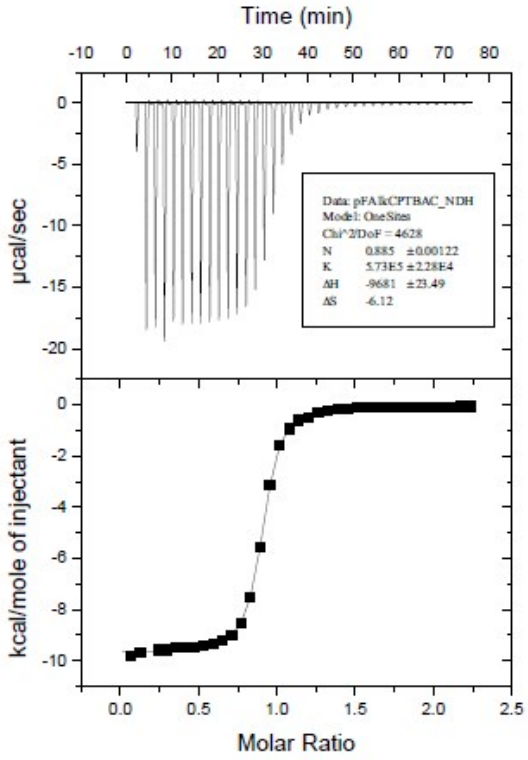


Figure S38: ITC profile for the titration of **3** (0.497 mM) with TBACl (4.986 mM) in acetonitrile at 298 K

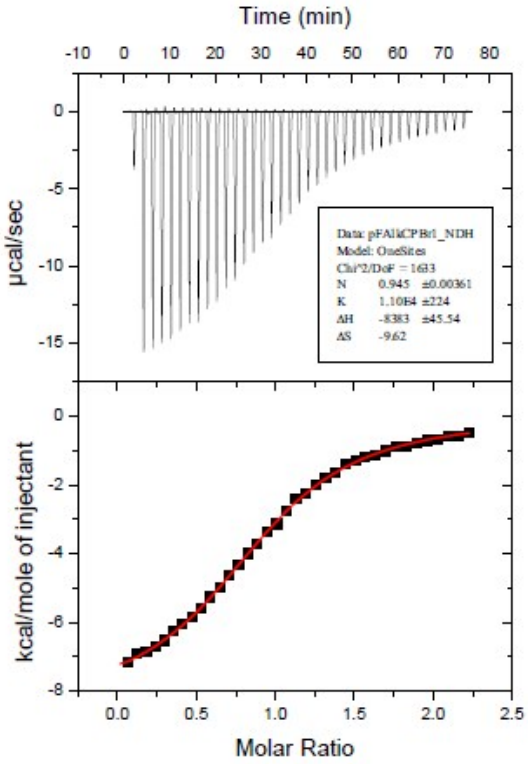


Figure S39: ITC profile for the titration of **3** (0.597 mM) with TBABr (5.95 mM) in acetonitrile at 298 K

Table S1: Binding affinities and thermodynamic parameters for the binding of various anions (as their tetrabutylammonium salts) with host **2** measured by isothermal titration calorimetry at 298 K in CH_3CN (* Calculated from ^1H NMR titration).

Anion	K_a	ΔH (kacl/mol)	TΔS (kcal/mol)	ΔG (kcal/mol)
TBAF	$1.84 \times 10^6 \pm 2.44 \times 10^5$	-6.705	1.85	-8.550
TBACl	$4.25 \times 10^5 \pm 1.41 \times 10^4$	-10.45	-2.768	-7.681
TEACl	$3.37 \times 10^5 \pm 2.07 \times 10^4$	-9.577	-2.029	-7.548
TBABr	$7.15 \times 10^3 \pm 5.22 \times 10^2$	-7.373	-2.112	-5.260
TBAI	38.7*	-	-	-2.16

Table S2: Binding affinities and thermodynamic parameters for the binding of various anions (as their tetrabutylammonium salts) with host **3** measured by isothermal titration calorimetry at 298 K in CH_3CN

Anion	K_a	ΔH (kacl/mol)	TΔS (kcal/mol)	ΔG (kcal/mol)
TBAF	$4.94 \times 10^6 \pm 7.63 \times 10^5$	-6.783	2.345	-9.128
TBACl	$5.73 \times 10^5 \pm 2.28 \times 10^4$	-9.681	-1.823	-7.858
TBABr	$1.10 \times 10^4 \pm 2.24 \times 10^2$	-8.383	-2.866	-5.517

Table S3: Binding affinities and thermodynamic parameters for the binding of various anions (as their tetrabutylammonium salts) with host **5** measured by isothermal titration calorimetry at 298 K in CH_3CN

Anion	K_a	ΔH (kacl/mol)	TΔS (kcal/mol)	ΔG (kcal/mol)
TBACl	$5.53 \times 10^4 \pm 1.60 \times 10^3$	-6.865	-0.393	-6.472
TBABr	$0.917 \times 10^3 \pm 0.589 \times 10^2$	-6.141	-2.097	-4.044

Single Crystal X-ray Diffraction. Single crystal X-ray diffraction data of $C_{42}H_{40}N_4$ (*Cis*-**2**), $[C_{42}H_{40}N_4][C_8H_{20}N]Cl$ (Complex **1**), Complex **2** and $C_{42}H_{40}N_4{\cdot}2C_3H_6O{\cdot}H_2O$ (*Cis*-**2**) were collected at 203, 203, 203 and 296 K respectively with a Bruker SMART BREEZE diffractometer (Mo Kα radiation). Synchrotron X-ray diffraction data (0.70000 Å radiation) for $C_{42}H_{40}N_4{\cdot}2CH_3CN$ (*trans*-**2**) was collected at 100 K with an ADSC Quantum 210 CCD diffractometer on 2D Supramolecular Crystallography (2D-SMC) Beamline, Pohang Accelerator Laboratory (PAL; Pohang, Republic of Korea). The data were solved and refined using SHELXS-2013 and SHELXL-2013, respectively.[S2,S3] All atoms except for hydrogen were refined with anisotropic displacement parameters and converged for $I > 2\sigma(I)$. All calculations were performed with the WinGX-2014 crystallographic software package.[S4] Crystallographic data, atomic parameter and selective bond lengths of $C_{42}H_{40}N_4$, $[C_{42}H_{40}N_4][C_8H_{20}N]Cl$ and $C_{42}H_{40}N_4{\cdot}2C_3H_6O{\cdot}H_2O$ are listed in Tables S1-9. **CCDC 1827178-1827181** and **1846661**

Table S4. Crystallographic table

Compound	$C_{42}H_{40}N_4$	$[C_{42}H_{40}N_4][C_8H_{20}N]Cl$	$C_{42}H_{40}N_4{\cdot}2C_3H_6O{\cdot}H_2O$	$C_{42}H_{40}N_4{\cdot}2CH_3CN$
empirical formula	$C_{42}H_{40}N_4$	$[C_{42}H_{40}N_4][C_8H_{20}N]Cl$	$C_{42}H_{40}N_4{\cdot}2C_3H_6O{\cdot}H_2O$	$C_{42}H_{40}N_4{\cdot}2CH_3CN$
fw	600.78	766.48	734.95	682.89
crystal system	Rhombohedral	Monoclinic	Monoclinic	Monoclinic
space group	$R\bar{3}$	$P2_1$	$P2_1/c$	$P2_1/c$
a (Å)	26.1757(5)	10.1635(19)	16.8622(6)	11.270(2)
b (Å)	26.1757(5)	20.791(4)	9.5715(4)	14.844(3)
c (Å)	31.6025(9)	10.5547(19)	26.4871(9)	12.708(3)
α (°)	90	90	90	90
β (°)	90	102.641(2)	90.972(2)	114.23(3)
γ (°)	120	90	90	90
V (Å^3)	18752.0(9)	2176.3(7)	4274.3(3)	1938.7(8)
Z	18	2	4	2
λ (Å)	0.71073	0.71073	0.71073	0.70000
T (K)	203	203	296	100
ρ_{calcd} (g·cm^{-3})	0.958	1.17	1.142	1.170
$R(F_o)$[a]	0.1056	0.0488	0.0586	0.0531
$R_w(F_o^2)$[b]	0.2558	0.0825	0.1144	0.0998

Table S5. Crystallographic Data for $C_{60}H_{77}F_3N_6O_{0.29}$

Compound	$C_{60}H_{77}F_3N_6O_{0.29}$
empirical formula	$C_{60}H_{77}F_3N_6O_{0.29}$
fw	943.27
crystal system	Triclinic
space group	$P\bar{1}$
a (Å)	11.5785(7)
b (Å)	13.3678(9)
c (Å)	19.1989(10)
α (°)	80.990(3)
β (°)	73.141(3)
γ (°)	82.786(4)
V (Å^3)	2798.7(3)
Z	2
λ (Å)	0.71073
T (K)	203(2)
ρ_{calcd} (mg·m^{-3})	1.119
$R(F_o)^a$	0.0522
$R_w(F_o^2)^b$	0.1497

Table S6. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $C_{42}H_{40}N_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	6638(2)	2130(2)	2364(1)	38(1)
C(2)	6718(2)	2532(2)	2661(1)	43(1)
C(3)	7195(2)	2630(2)	2925(1)	40(1)
C(4)	7404(2)	2276(2)	2783(1)	36(1)
C(5)	6175(2)	1835(2)	2023(1)	45(1)
C(6)	5705(2)	1215(2)	2170(2)	74(2)
C(7)	5875(2)	2209(2)	1951(1)	59(1)
C(8)	6440(2)	1794(2)	1606(1)	44(1)
C(9)	6254(2)	1357(2)	1309(2)	52(1)
C(10)	6616(2)	1587(2)	948(2)	59(1)
C(11)	7026(2)	2155(2)	1026(1)	47(1)
C(12)	7504(2)	2619(2)	749(1)	57(1)
C(13)	7573(2)	2325(3)	374(2)	69(2)
C(14)	7628(2)	2110(3)	60(2)	72(2)
C(15)	7654(3)	1823(4)	-334(2)	82(2)
C(16)	8063(4)	2150(4)	-632(2)	134(3)

C(17)	8067(6)	1861(7)	-1002(3)	188(6)
C(18)	7674(7)	1306(8)	-1088(4)	185(6)
C(19)	7282(5)	969(5)	-778(3)	157(4)
C(20)	7274(4)	1231(4)	-395(2)	125(3)
C(21)	8092(2)	2960(2)	979(1)	51(1)
C(22)	8494(3)	3549(2)	982(2)	63(1)
C(23)	8983(2)	3631(2)	1220(2)	60(1)
C(24)	8884(2)	3095(2)	1357(1)	47(1)
C(25)	9241(2)	2905(2)	1617(1)	48(1)
C(26)	8916(2)	2578(2)	2010(1)	41(1)
C(27)	9004(2)	2185(2)	2238(2)	52(1)
C(28)	8644(2)	2002(2)	2585(1)	27(1)
C(29)	8314(2)	2271(2)	2590(1)	38(1)
C(30)	7891(2)	2179(2)	2943(1)	42(1)
C(31)	7633(2)	1571(2)	3101(1)	47(1)
C(32)	7433(2)	1072(2)	3221(1)	51(1)
C(33)	7187(2)	462(2)	3348(2)	57(1)
C(34)	7338(3)	99(3)	3129(2)	86(2)
C(35)	7107(3)	-486(3)	3242(2)	112(3)
C(36)	6731(4)	-707(3)	3584(2)	115(3)
C(37)	6588(3)	-351(3)	3806(2)	89(2)
C(38)	6813(2)	232(2)	3694(2)	66(1)
C(39)	7311(3)	3064(2)	600(2)	77(2)
C(40)	9393(2)	2505(2)	1342(2)	68(2)
C(41)	9821(2)	3456(2)	1741(2)	76(2)
C(42)	8224(2)	2619(2)	3307(1)	57(1)
N(1)	7056(2)	1969(2)	2444(1)	45(1)
N(2)	6914(2)	2281(2)	1429(1)	49(1)
N(3)	8335(2)	2686(2)	1205(1)	50(1)
N(4)	8481(2)	2633(2)	2238(1)	70(1)

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[C_{42}H_{40}N_4][C_8H_{20}N]Cl$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U*(eq)
C(1)	8136(3)	9798(2)	3499(3)	33(1)
C(2)	8747(3)	10302(2)	4223(3)	43(1)
C(3)	7881(4)	10517(2)	5022(3)	43(1)

C(4)	6758(3)	10136(2)	4779(3)	34(1)
C(5)	5488(3)	10148(2)	5318(3)	37(1)
C(6)	5399(3)	9560(2)	6153(3)	32(1)
C(7)	5518(3)	9497(2)	7464(3)	39(1)
C(8)	5303(3)	8839(2)	7732(3)	39(1)
C(9)	5057(3)	8514(2)	6572(3)	32(1)
C(10)	4713(3)	7812(2)	6252(3)	34(1)
C(11)	5853(3)	7435(2)	5889(3)	33(1)
C(12)	6642(3)	6954(2)	6507(3)	39(1)
C(13)	7486(3)	6741(2)	5683(3)	39(1)
C(14)	7196(3)	7097(2)	4580(3)	34(1)
C(15)	7738(3)	7078(2)	3345(3)	38(1)
C(16)	8563(3)	7671(2)	3215(3)	34(1)
C(17)	9919(3)	7756(2)	3285(3)	42(1)
C(18)	10147(3)	8414(2)	3034(3)	40(1)
C(19)	8933(3)	8718(2)	2814(3)	34(1)
C(20)	8544(3)	9408(2)	2428(3)	36(1)
C(21)	4237(3)	10176(2)	4185(3)	45(1)
C(22)	5494(4)	10753(2)	6145(3)	46(1)
C(23)	3438(3)	7759(2)	5138(3)	41(1)
C(24)	6550(4)	7035(2)	2156(3)	49(1)
C(25)	8620(4)	6477(2)	3376(4)	53(1)
C(26)	7378(3)	9416(2)	1198(3)	42(1)
C(27)	4362(3)	7508(2)	7407(3)	39(1)
C(28)	3945(3)	7267(2)	8259(3)	39(1)
C(29)	3291(3)	7004(2)	9232(3)	35(1)
C(30)	3227(3)	7366(2)	10329(3)	43(1)
C(31)	2507(4)	7142(2)	11199(3)	55(1)
C(32)	1843(4)	6562(2)	10999(4)	56(1)

C(33)	1913(4)	6197(2)	9925(4)	53(1)
C(34)	2637(3)	6414(2)	9040(3)	46(1)
C(35)	9726(3)	9713(2)	2072(3)	39(1)
C(36)	10650(3)	9931(2)	1691(3)	39(1)
C(37)	11752(3)	10170(2)	1170(3)	38(1)
C(38)	11933(4)	10821(2)	1004(3)	53(1)
C(39)	12990(5)	11035(2)	487(4)	70(1)
C(40)	13866(5)	10602(3)	124(4)	68(1)
C(41)	13699(4)	9957(2)	287(4)	59(1)
C(42)	12658(3)	9737(2)	827(3)	46(1)
C(43)	9589(3)	8119(2)	6598(3)	42(1)
C(44)	10452(3)	7523(2)	6849(4)	53(1)
C(45)	10042(3)	8400(2)	8968(3)	51(1)
C(46)	8793(4)	8053(2)	9167(4)	60(1)
C(47)	8928(3)	9176(2)	7249(3)	44(1)
C(48)	9180(4)	9769(2)	8103(3)	53(1)
C(49)	11393(3)	8909(2)	7598(3)	49(1)
C(50)	11527(4)	9249(2)	6371(4)	56(1)
N(1)	6927(3)	9698(1)	3846(3)	36(1)
N(2)	5122(3)	8958(1)	5620(3)	34(1)
N(3)	6207(3)	7529(1)	4712(3)	36(1)
N(4)	7971(3)	8264(1)	2926(3)	36(1)
N(5)	9984(2)	8651(2)	7605(2)	39(1)
Cl(1)	4766(1)	8580(1)	2564(1)	38(1)

Table S8. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $C_{42}H_{40}N_4 \cdot 2C_3H_6O \cdot H_2O$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U*(eq)
C(1)	2020(1)	1951(2)	2791(1)	32(1)
C(2)	2442(1)	3127(2)	2679(1)	42(1)
C(3)	3242(1)	2725(2)	2603(1)	41(1)
C(4)	3293(1)	1315(2)	2669(1)	33(1)
C(5)	3996(1)	333(2)	2623(1)	36(1)
C(6)	4185(1)	-444(2)	3109(1)	35(1)
C(7)	4761(1)	-239(2)	3468(1)	47(1)
C(8)	4679(1)	-1279(3)	3841(1)	50(1)
C(9)	4057(1)	-2111(2)	3710(1)	36(1)
C(10)	3738(1)	-3438(2)	3941(1)	39(1)
C(11)	2842(1)	-3422(2)	3961(1)	35(1)
C(12)	2281(1)	-4374(2)	3802(1)	41(1)
C(13)	1524(1)	-3847(2)	3930(1)	40(1)
C(14)	1632(1)	-2588(2)	4166(1)	33(1)
C(15)	1045(1)	-1577(2)	4392(1)	34(1)
C(16)	1045(1)	-175(2)	4124(1)	33(1)
C(17)	913(1)	1142(2)	4300(1)	41(1)
C(18)	919(1)	2064(2)	3884(1)	41(1)
C(19)	1055(1)	1308(2)	3457(1)	33(1)
C(20)	1150(1)	1767(2)	2912(1)	35(1)
C(21)	3817(1)	-730(2)	2226(1)	38(1)
C(22)	3675(1)	-1637(2)	1931(1)	40(1)
C(23)	3515(1)	-2785(2)	1595(1)	39(1)
C(24)	3677(1)	-2699(3)	1082(1)	49(1)
C(25)	3519(2)	-3813(3)	766(1)	57(1)
C(26)	3204(1)	-5025(3)	957(1)	54(1)
C(27)	3053(1)	-5138(3)	1464(1)	51(1)

C(28)	3206(1)	-4022(3)	1781(1)	43(1)
C(29)	4728(1)	1183(2)	2468(1)	49(1)
C(31)	4001(1)	-4694(2)	3624(1)	53(1)
C(32)	4081(1)	-3594(3)	4483(1)	55(1)
C(33)	238(1)	-2216(2)	4350(1)	39(1)
C(34)	-402(1)	-2733(2)	4335(1)	42(1)
C(35)	-1187(1)	-3348(2)	4339(1)	46(1)
C(36)	-1687(2)	-3272(3)	3916(1)	60(1)
C(37)	-2452(2)	-3844(3)	3935(2)	79(1)
C(38)	-2692(2)	-4481(3)	4380(2)	91(1)
C(39)	-2196(2)	-4587(3)	4789(1)	88(1)
C(40)	-1453(2)	-4024(3)	4768(1)	67(1)
C(41)	1239(1)	-1361(3)	4960(1)	47(1)
C(42)	761(1)	699(2)	2549(1)	44(1)
C(43)	729(1)	3176(2)	2837(1)	49(1)
C(44)	1246(1)	6573(3)	1667(1)	44(1)
C(45)	1412(2)	7910(3)	1408(1)	72(1)
C(46)	983(1)	5370(3)	1349(1)	58(1)
C(47)	3460(1)	1073(3)	4464(1)	47(1)
C(48)	4165(2)	1877(3)	4663(1)	85(1)
C(49)	3017(1)	1663(3)	4030(1)	62(1)
N(1)	2543(1)	846(2)	2781(1)	33(1)
N(2)	3756(1)	-1596(2)	3262(1)	35(1)
N(3)	2437(1)	-2336(2)	4181(1)	34(1)
N(4)	1128(1)	-65(2)	3610(1)	32(1)
O(1)	1307(1)	6454(2)	2123(1)	57(1)
O(2)	3271(1)	-24(2)	4657(1)	63(1)
O(1W)	2029(1)	7848(2)	2908(1)	46(1)

Table S9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $C_{42}H_{40}N_4 \cdot 2CH_3CN$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U*(eq)
C(1)	4385(1)	7061(1)	27(1)	19(1)
C(2)	4978(2)	7694(1)	-381(1)	23(1)
C(3)	6331(2)	7505(1)	103(1)	23(1)
C(4)	6533(1)	6762(1)	787(1)	17(1)
C(5)	7779(1)	6243(1)	1450(1)	19(1)
C(6)	7856(1)	5403(1)	799(1)	17(1)
C(7)	8488(1)	5257(1)	92(1)	22(1)
C(8)	8223(1)	4364(1)	-316(1)	22(1)
C(9)	7445(1)	3974(1)	147(1)	18(1)
C(10)	2988(1)	6989(1)	-118(1)	22(1)
C(11)	2094(2)	7447(2)	-1253(2)	37(1)
C(12)	2845(2)	7486(2)	893(2)	35(1)
C(13)	8953(2)	6852(1)	1617(2)	28(1)
C(14)	7857(1)	5991(1)	2603(1)	22(1)
C(15)	7958(2)	5793(1)	3548(1)	24(1)
C(16)	8091(2)	5564(1)	4691(1)	26(1)
C(17)	9268(2)	5734(1)	5645(1)	35(1)
C(18)	9392(2)	5545(2)	6751(2)	44(1)
C(19)	8347(3)	5184(2)	6907(2)	50(1)
C(20)	7183(3)	5011(2)	5976(2)	45(1)
C(21)	7056(2)	5198(1)	4865(2)	34(1)
C(22)	3794(2)	3369(1)	2358(2)	29(1)
C(23)	4495(1)	4057(1)	2025(1)	22(1)
N(1)	5343(1)	6491(1)	742(1)	17(1)
N(2)	7226(1)	4619(1)	830(1)	17(1)

N(3)	5061(1)	4601(1)	1790(1)	27(1)

Table S10. Selected Bond Distances (Å) for $C_{42}H_{40}N_4$

C(1)-C(2)	1.348(5)	C(19)-C(20)	1.395(11)
C(1)-N(1)	1.376(5)	C(21)-C(22)	1.363(6)
C(1)-C(5)	1.512(5)	C(21)-N(3)	1.373(5)
C(2)-C(3)	1.414(5)	C(22)-C(23)	1.405(7)
C(3)-C(4)	1.367(5)	C(23)-C(24)	1.363(6)
C(4)-N(1)	1.375(5)	C(24)-N(3)	1.379(5)
C(4)-C(30)	1.504(5)	C(24)-C(25)	1.505(6)
C(5)-C(8)	1.518(6)	C(25)-C(26)	1.506(6)
C(5)-C(6)	1.538(6)	C(25)-C(41)	1.533(6)
C(5)-C(7)	1.547(6)	C(25)-C(40)	1.557(6)
C(8)-C(9)	1.369(6)	C(26)-C(27)	1.366(6)
C(8)-N(2)	1.376(5)	C(26)-N(4)	1.414(5)
C(9)-C(10)	1.411(7)	C(27)-C(28)	1.365(5)
C(10)-C(11)	1.352(6)	C(28)-C(29)	1.359(5)
C(11)-N(2)	1.383(5)	C(29)-N(4)	1.381(5)
C(11)-C(12)	1.513(6)	C(29)-C(30)	1.505(5)
C(12)-C(13)	1.474(7)	C(30)-C(31)	1.471(6)
C(12)-C(21)	1.524(7)	C(30)-C(42)	1.551(5)
C(12)-C(39)	1.556(6)	C(31)-C(32)	1.200(6)
C(13)-C(14)	1.183(6)	C(32)-C(33)	1.449(7)
C(14)-C(15)	1.474(8)	C(33)-C(34)	1.384(7)
C(15)-C(16)	1.358(9)	C(33)-C(38)	1.388(6)
C(15)-C(20)	1.376(9)	C(34)-C(35)	1.381(7)
C(16)-C(17)	1.396(11)	C(35)-C(36)	1.378(8)
C(17)-C(18)	1.322(16)	C(36)-C(37)	1.358(8)
C(18)-C(19)	1.374(15)	C(37)-C(38)	1.380(7)

Table S11. Selected Bond Distances (Å) for $[C_{42}H_{40}N_4][C_8H_{20}N]Cl$

C(1)-C(2)	1.365(4)	C(19)-N(4)	1.383(4)
C(1)-N(1)	1.373(4)	C(19)-C(20)	1.521(5)
C(1)-C(20)	1.520(4)	C(20)-C(35)	1.477(4)
C(2)-C(3)	1.418(5)	C(20)-C(26)	1.555(4)
C(3)-C(4)	1.366(5)	C(27)-C(28)	1.185(4)
C(4)-N(1)	1.380(4)	C(28)-C(29)	1.447(4)
C(4)-C(5)	1.520(4)	C(29)-C(34)	1.389(5)
C(5)-C(6)	1.521(5)	C(29)-C(30)	1.394(5)
C(5)-C(22)	1.531(4)	C(30)-C(31)	1.376(5)
C(5)-C(21)	1.545(4)	C(31)-C(32)	1.375(6)
C(6)-C(7)	1.369(4)	C(32)-C(33)	1.379(6)
C(6)-N(2)	1.376(4)	C(33)-C(34)	1.385(5)
C(7)-C(8)	1.423(5)	C(35)-C(36)	1.190(4)
C(8)-C(9)	1.372(4)	C(36)-C(37)	1.440(4)
C(9)-N(2)	1.376(4)	C(37)-C(38)	1.383(5)
C(9)-C(10)	1.523(5)	C(37)-C(42)	1.390(5)
C(10)-C(27)	1.485(4)	C(38)-C(39)	1.381(5)
C(10)-C(11)	1.516(4)	C(39)-C(40)	1.378(6)
C(10)-C(23)	1.551(4)	C(40)-C(41)	1.367(6)
C(11)-C(12)	1.356(4)	C(41)-C(42)	1.385(5)
C(11)-N(3)	1.381(4)	C(43)-C(44)	1.509(5)
C(12)-C(13)	1.420(4)	C(43)-N(5)	1.526(4)
C(13)-C(14)	1.357(4)	C(45)-C(46)	1.513(5)
C(14)-N(3)	1.377(4)	C(45)-N(5)	1.520(4)
C(14)-C(15)	1.522(4)	C(47)-C(48)	1.516(5)
C(15)-C(16)	1.515(4)	C(47)-N(5)	1.518(4)
C(15)-C(25)	1.533(5)	C(49)-C(50)	1.508(5)

C(15)-C(24)	1.542(5)	C(49)-N(5)	1.530(4)
C(16)-C(17)	1.375(4)	N(1)-H(1)	0.91(4)
C(16)-N(4)	1.376(4)	N(2)-H(2)	0.90(3)
C(17)-C(18)	1.423(5)	N(3)-H(3)	0.93(3)
C(18)-C(19)	1.360(4)	N(4)-H(4)	0.96(4)

Table S12. Selected Bond Distances (Å) for $C_{42}H_{40}N_4 \cdot 2C_3H_6O \cdot H_2O$

C(1)-C(2)	1.367(3)	C(19)-N(4)	1.381(3)
C(1)-N(1)	1.378(2)	C(19)-C(20)	1.521(3)
C(1)-C(20)	1.516(3)	C(20)-C(43)	1.535(3)
C(2)-C(3)	1.421(3)	C(20)-C(42)	1.542(3)
C(3)-C(4)	1.363(3)	C(21)-C(22)	1.190(3)
C(4)-N(1)	1.379(2)	C(22)-C(23)	1.437(3)
C(4)-C(5)	1.519(3)	C(23)-C(28)	1.388(3)
C(5)-C(21)	1.490(3)	C(23)-C(24)	1.394(3)
C(5)-C(6)	1.516(3)	C(24)-C(25)	1.378(3)
C(5)-C(29)	1.540(3)	C(25)-C(26)	1.375(3)
C(6)-C(7)	1.360(3)	C(26)-C(27)	1.374(3)
C(6)-N(2)	1.383(2)	C(27)-C(28)	1.380(3)
C(7)-C(8)	1.411(3)	C(33)-C(34)	1.187(3)
C(8)-C(9)	1.357(3)	C(34)-C(35)	1.448(3)
C(9)-N(2)	1.375(2)	C(35)-C(40)	1.389(3)
C(9)-C(10)	1.512(3)	C(35)-C(36)	1.392(3)
C(10)-C(11)	1.513(3)	C(36)-C(37)	1.403(4)
C(10)-C(31)	1.536(3)	C(37)-C(38)	1.394(4)
C(10)-C(32)	1.545(3)	C(38)-C(39)	1.361(4)
C(11)-C(12)	1.374(3)	C(39)-C(40)	1.367(3)
C(11)-N(3)	1.378(3)	C(44)-O(1)	1.216(3)
C(12)-C(13)	1.419(3)	C(44)-C(45)	1.480(3)

C(13)-C(14)	1.368(3)	C(44)-C(46)	1.491(3)
C(14)-N(3)	1.379(2)	C(47)-O(2)	1.214(3)
C(14)-C(15)	1.515(3)	C(47)-C(49)	1.473(3)
C(15)-C(33)	1.495(3)	C(47)-C(48)	1.503(3)
C(15)-C(16)	1.518(3)	N(1)-H(1N)	0.91(2)
C(15)-C(41)	1.549(3)	N(2)-H(2N)	0.88(2)
C(16)-C(17)	1.363(3)	N(3)-H(3N)	0.88(2)
C(16)-N(4)	1.375(3)	N(4)-H(4N)	0.87(2)
C(17)-C(18)	1.412(3)	O(1W)-H(1W)	0.90(4)
C(18)-C(19)	1.365(3)	O(1W)-H(2W)	0.87(3)

Table S13. Selected Bond Distances (Å) for $C_{42}H_{40}N_4 \cdot 2CH_3CN$

C(1)-C(2)	1.372(2)	C(12)-H(16)	1.012(19)
C(1)-N(1)	1.3796(19)	C(12)-H(17)	1.03(2)
C(1)-C(10)	1.512(2)	C(13)-H(5)	0.98(2)
C(2)-C(3)	1.419(2)	C(13)-H(6)	1.06(2)
C(2)-H(3)	1.001(19)	C(13)-H(7)	1.004(19)
C(3)-C(4)	1.364(2)	C(14)-C(15)	1.196(2)
C(3)-H(4)	1.003(18)	C(15)-C(16)	1.438(2)
C(4)-N(1)	1.3788(17)	C(16)-C(21)	1.384(3)
C(4)-C(5)	1.518(2)	C(16)-C(17)	1.405(2)
C(5)-C(14)	1.479(2)	C(17)-C(18)	1.383(3)
C(5)-C(6)	1.517(2)	C(17)-H(10)	1.09(2)
C(5)-C(13)	1.544(2)	C(18)-C(19)	1.381(3)
C(6)-N(2)	1.3719(19)	C(18)-H(11)	1.04(2)
C(6)-C(7)	1.374(2)	C(19)-C(20)	1.383(3)
C(7)-C(8)	1.411(2)	C(19)-H(12)	0.99(3)
C(7)-H(8)	1.001(19)	C(20)-C(21)	1.387(3)
C(8)-C(9)	1.369(2)	C(20)-H(13)	0.94(2)

C(8)-H(9)	0.982(18)	C(21)-H(14)	0.909(19)
C(9)-N(2)	1.3809(19)	C(22)-C(23)	1.456(2)
C(9)-C(10)#1	1.506(2)	C(22)-H(21)	0.95(2)
C(10)-C(11)	1.538(2)	C(22)-H(22)	1.00(2)
C(10)-C(12)	1.546(2)	C(22)-H(23)	1.02(3)
C(11)-H(18)	1.02(2)	C(23)-N(3)	1.142(2)
C(11)-H(19)	1.03(2)	N(1)-H(1)	0.87(2)
C(11)-H(20)	1.02(3)	N(2)-H(2)	0.935(18)
C(12)-H(15)	1.07(2)		

Table S14. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $C_{60}H_{77}F_3N_6O_{0.29}$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U*(eq)
C(1)	3365(2)	1120(1)	8879(1)	33(1)
C(2)	3516(2)	569(1)	9512(1)	40(1)
C(3)	4202(2)	1129(1)	9794(1)	40(1)
C(4)	4466(2)	2004(1)	9324(1)	33(1)
C(5)	5163(2)	2878(1)	9360(1)	35(1)
C(6)	6346(2)	2925(1)	8750(1)	34(1)
C(7)	7526(2)	2697(2)	8762(1)	42(1)
C(8)	8273(2)	2937(2)	8038(1)	41(1)
C(9)	7533(2)	3303(1)	7601(1)	33(1)
C(10)	7793(2)	3699(1)	6788(1)	34(1)
C(11)	7682(2)	2877(1)	6351(1)	33(1)
C(12)	8547(2)	2313(2)	5894(1)	43(1)
C(13)	7952(2)	1648(2)	5638(1)	49(1)
C(14)	6735(2)	1821(2)	5943(1)	43(1)
C(15)	5675(2)	1371(2)	5829(1)	55(1)
C(16)	4924(2)	802(2)	6528(1)	46(1)
C(17)	4753(2)	-202(2)	6712(1)	59(1)
C(18)	3904(2)	-333(2)	7412(1)	53(1)
C(19)	3567(2)	601(1)	7640(1)	36(1)
C(20)	2690(2)	911(1)	8349(1)	34(1)
C(21)	4378(2)	3893(2)	9291(1)	45(1)

C(22)	5446(2)	2728(2)	10103(1)	50(1)
C(23)	6945(2)	4657(1)	6663(1)	40(1)
C(24)	9060(2)	3981(1)	6522(1)	38(1)
C(25)	10065(2)	4241(1)	6294(1)	38(1)
C(26)	11278(2)	4555(1)	6083(1)	36(1)
C(27)	11687(2)	5256(1)	5469(1)	37(1)
C(28)	12826(2)	5603(2)	5306(1)	42(1)
C(29)	13538(2)	5234(2)	5763(1)	42(1)
C(30)	13188(2)	4533(2)	6367(1)	47(1)
C(31)	12048(2)	4192(2)	6525(1)	44(1)
C(32)	4863(2)	2206(2)	5527(1)	82(1)
C(33)	6215(3)	605(3)	5267(2)	103(1)
C(34)	1839(2)	1849(1)	8190(1)	41(1)
C(35)	1955(2)	42(1)	8702(1)	38(1)
C(36)	1367(2)	-660(2)	8983(1)	40(1)
C(37)	711(2)	-1537(1)	9325(1)	36(1)
C(38)	-548(2)	-1487(2)	9493(1)	44(1)
C(39)	-1162(2)	-2340(2)	9823(1)	48(1)
C(40)	-508(2)	-3225(2)	9984(1)	44(1)
C(41)	735(2)	-3316(2)	9822(1)	48(1)
C(42)	1343(2)	-2463(2)	9491(1)	43(1)
C(43)	-191(2)	6873(1)	7859(1)	42(1)
C(44)	-186(2)	5740(2)	7859(1)	51(1)
C(45)	-1012(2)	5268(2)	8570(1)	64(1)
C(46)	-2340(3)	5551(2)	8648(2)	89(1)
C(47)	1902(2)	7043(2)	7009(1)	45(1)
C(48)	2494(2)	7048(2)	7615(1)	49(1)
C(49)	3851(2)	6755(2)	7356(1)	68(1)
C(50)	4477(2)	6671(2)	7957(2)	77(1)
C(51)	398(2)	8557(1)	7273(1)	44(1)
C(52)	1129(2)	9284(2)	6669(1)	49(1)
C(53)	742(2)	10372(2)	6823(1)	54(1)
C(54)	1541(2)	11130(2)	6287(1)	68(1)
C(55)	179(2)	7282(2)	6497(1)	46(1)
C(56)	-1125(2)	7597(2)	6511(1)	58(1)
C(57)	-1410(2)	7219(2)	5876(1)	68(1)
C(58)	-2710(2)	7467(2)	5852(2)	88(1)
C(59)	6584(2)	10546(2)	7962(2)	78(1)
C(60)	6956(2)	9480(2)	8060(1)	63(1)
N(1)	3943(1)	1993(1)	8767(1)	32(1)
N(2)	6358(1)	3290(1)	8038(1)	33(1)

N(3)	6575(1)	2583(1)	6378(1)	36(1)
N(4)	4185(1)	1294(1)	7097(1)	37(1)
N(5)	577(1)	7442(1)	7158(1)	40(1)
N(6)	7243(2)	8639(2)	8137(1)	102(1)
F(3)	4486(1)	3191(1)	7420(1)	38(1)
F(1)	14649(1)	5584(1)	5620(1)	64(1)
F(2)	-1109(1)	-4061(1)	10321(1)	67(1)
O(1W)	2497(5)	4545(4)	8092(3)	68(2)

Table S15. Selected Bond Distances (Å) for $C_{60}H_{77}F_3N_6O_{0.29}$

C(1)-C(2)	1.365(3)	C(24)-C(25)	1.195(2)
C(1)-N(1)	1.375(2)	C(25)-C(26)	1.441(2)
C(1)-C(20)	1.525(2)	C(26)-C(27)	1.391(2)
C(2)-C(3)	1.417(3)	C(26)-C(31)	1.395(3)
C(3)-C(4)	1.369(3)	C(27)-C(28)	1.386(2)
C(4)-N(1)	1.377(2)	C(28)-C(29)	1.370(3)
C(4)-C(5)	1.521(2)	C(29)-F(1)	1.3624(19)
C(5)-C(6)	1.523(2)	C(29)-C(30)	1.367(3)
C(5)-C(22)	1.532(3)	C(30)-C(31)	1.385(3)
C(5)-C(21)	1.546(3)	C(35)-C(36)	1.193(2)
C(6)-C(7)	1.368(2)	C(36)-C(37)	1.442(2)
C(6)-N(2)	1.374(2)	C(37)-C(38)	1.395(2)
C(7)-C(8)	1.419(3)	C(37)-C(42)	1.397(3)
C(8)-C(9)	1.365(3)	C(38)-C(39)	1.386(3)
C(9)-N(2)	1.377(2)	C(39)-C(40)	1.365(3)
C(9)-C(10)	1.521(2)	C(40)-F(2)	1.363(2)
C(10)-C(24)	1.482(2)	C(40)-C(41)	1.375(3)
C(10)-C(11)	1.521(2)	C(41)-C(42)	1.383(3)
C(10)-C(23)	1.545(3)	C(43)-C(44)	1.513(3)
C(11)-C(12)	1.360(3)	C(43)-N(5)	1.528(2)
C(11)-N(3)	1.372(2)	C(44)-C(45)	1.516(3)
C(12)-C(13)	1.412(3)	C(45)-C(46)	1.505(4)
C(13)-C(14)	1.365(3)	C(47)-C(48)	1.512(3)
C(14)-N(3)	1.378(2)	C(47)-N(5)	1.520(2)
C(14)-C(15)	1.517(3)	C(48)-C(49)	1.524(3)
C(15)-C(16)	1.519(3)	C(49)-C(50)	1.515(3)
C(15)-C(32)	1.522(4)	C(51)-C(52)	1.514(3)
C(15)-C(33)	1.550(3)	C(51)-N(5)	1.520(2)
C(16)-C(17)	1.357(3)	C(52)-C(53)	1.516(3)
C(16)-N(4)	1.379(2)	C(53)-C(54)	1.516(3)

C(17)-C(18)	1.416(3)	C(55)-C(56)	1.509(3)
C(18)-C(19)	1.362(3)	C(55)-N(5)	1.523(2)
C(19)-N(4)	1.375(2)	C(56)-C(57)	1.523(3)
C(19)-C(20)	1.525(3)	C(57)-C(58)	1.512(3)
C(20)-C(35)	1.483(2)	C(59)-C(60)	1.436(4)
C(20)-C(34)	1.543(3)	C(60)-N(6)	1.130(3)

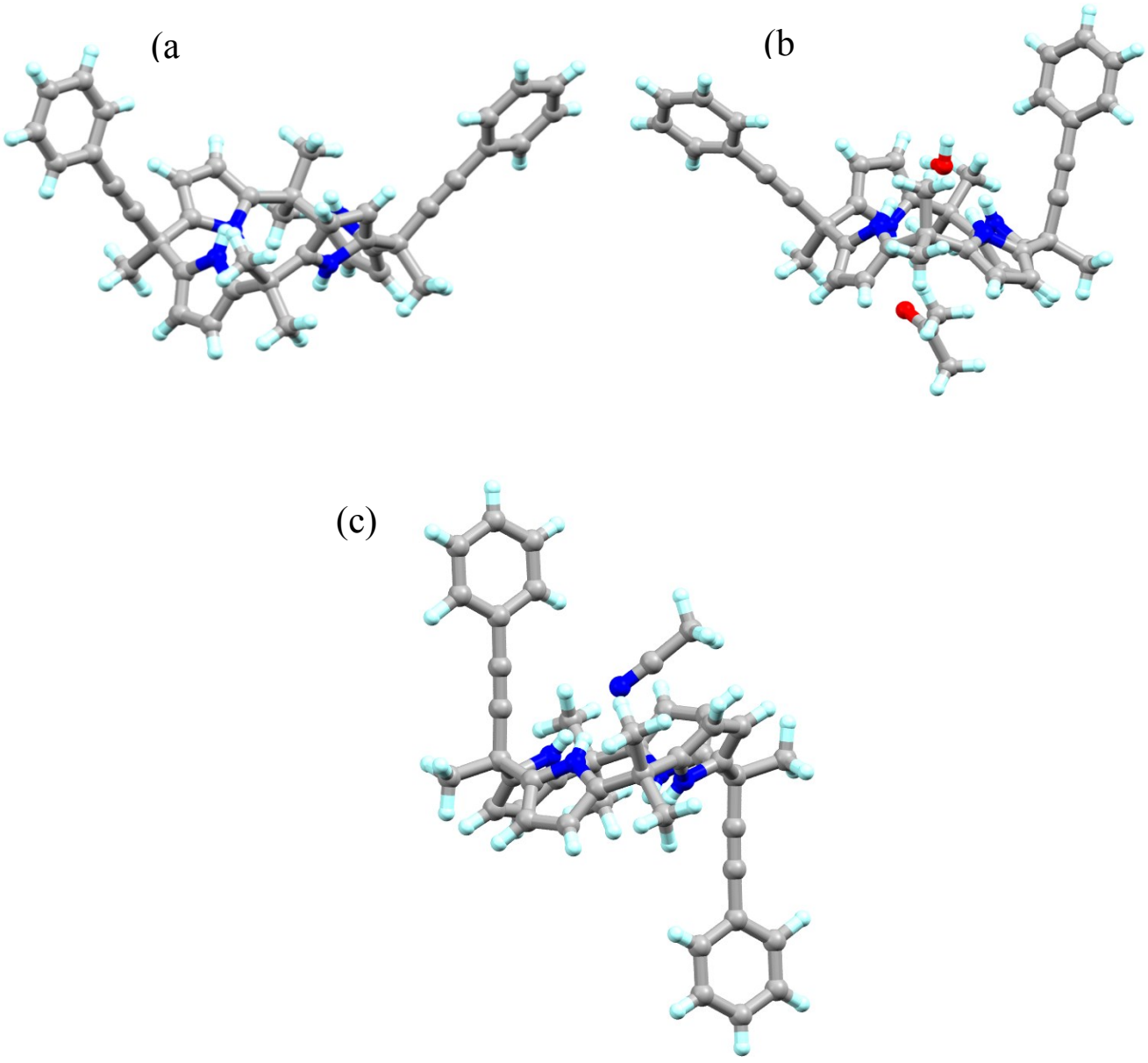


Figure S40. Single crystal X-ray structures of (a) **2** (1,3-alternate conformation), (b) **2** (partial cone conformation) with bound acetone and water and (c) *trans*-**2** (1,2-alternate conformation) with bound acetonitrile

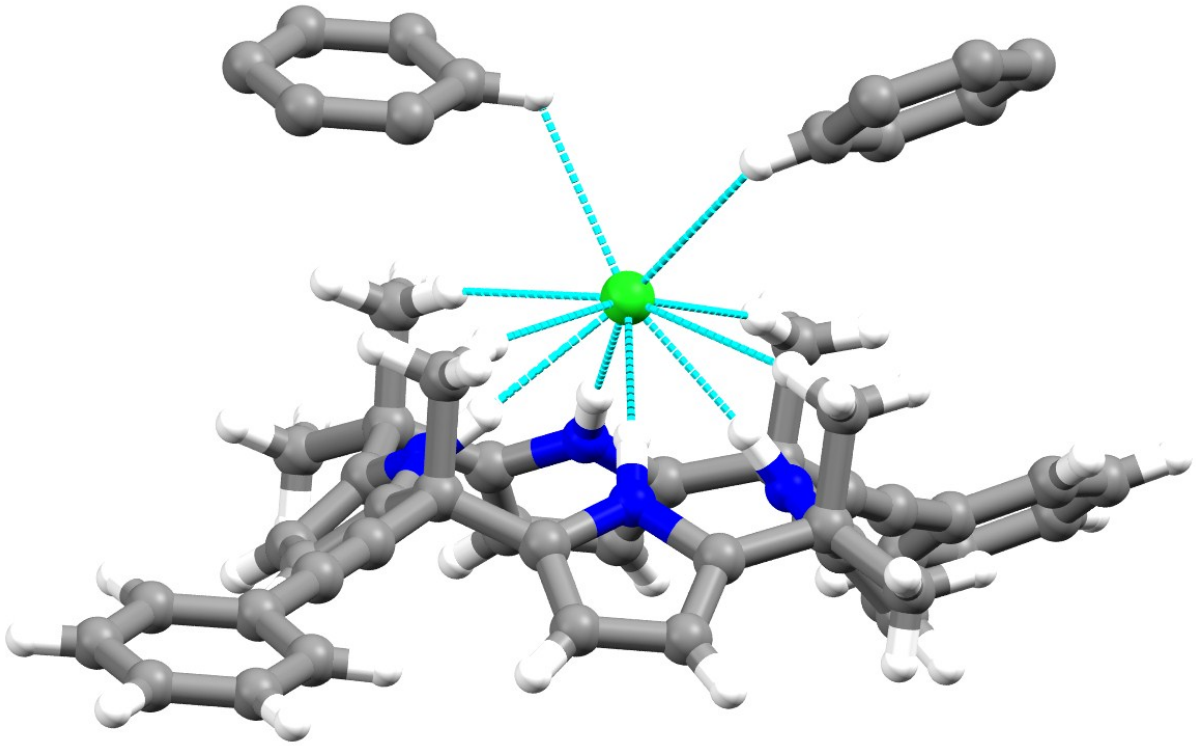


Figure S41: Close-up view of the hydrogen bonding interactions in complex **1**. Countercations are omitted for clarity.

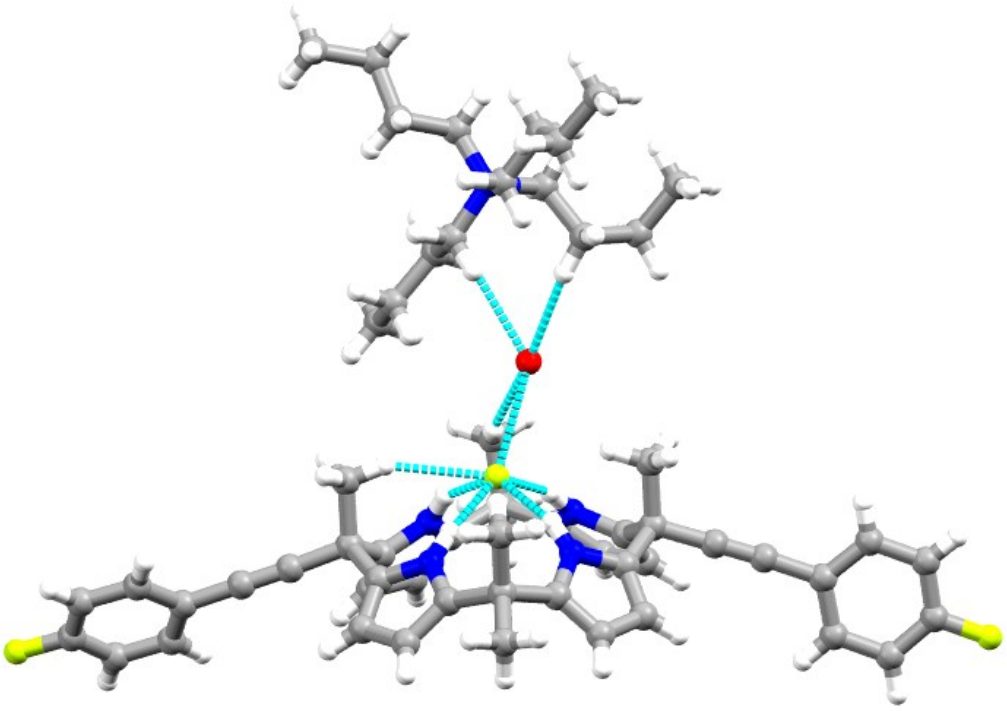


Figure S42: Close-up view of the hydrogen bonding interactions in complex **2**. Solvent molecules are omitted for clarity.

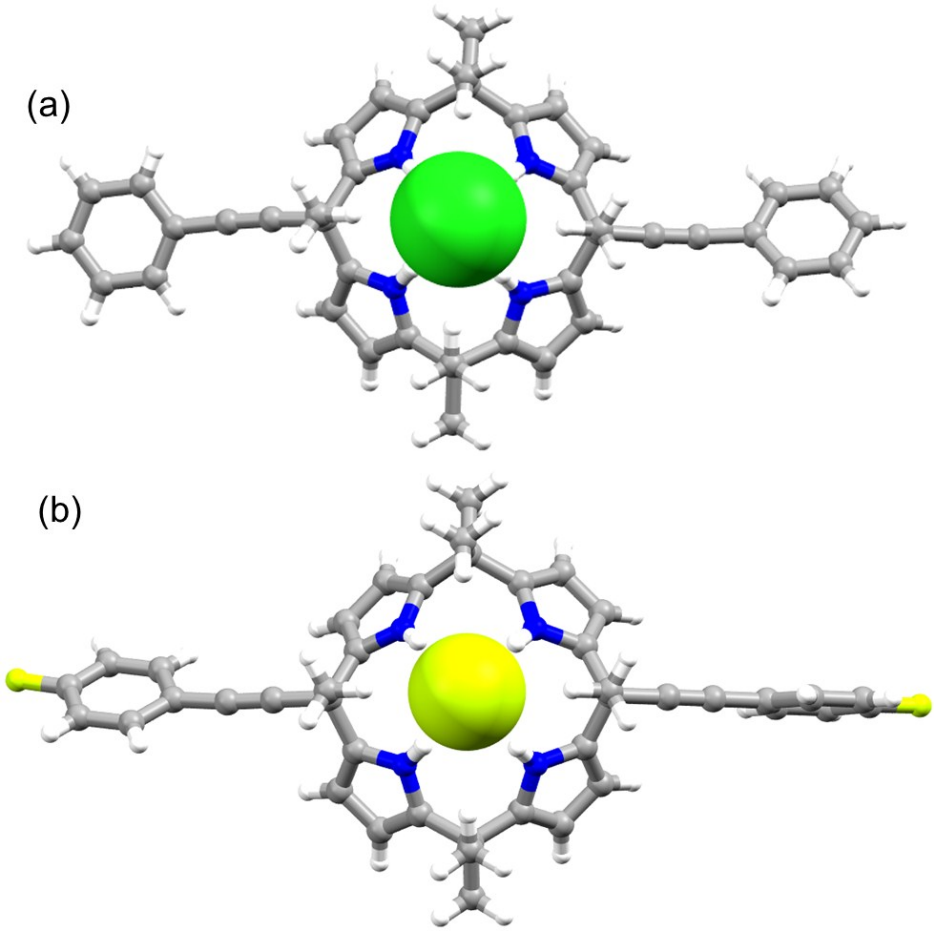


Figure S43: Top view of crystal structures of (a) complex **1** and (b) complex **2**. Solvent molecules and countercations are omitted for clarity.

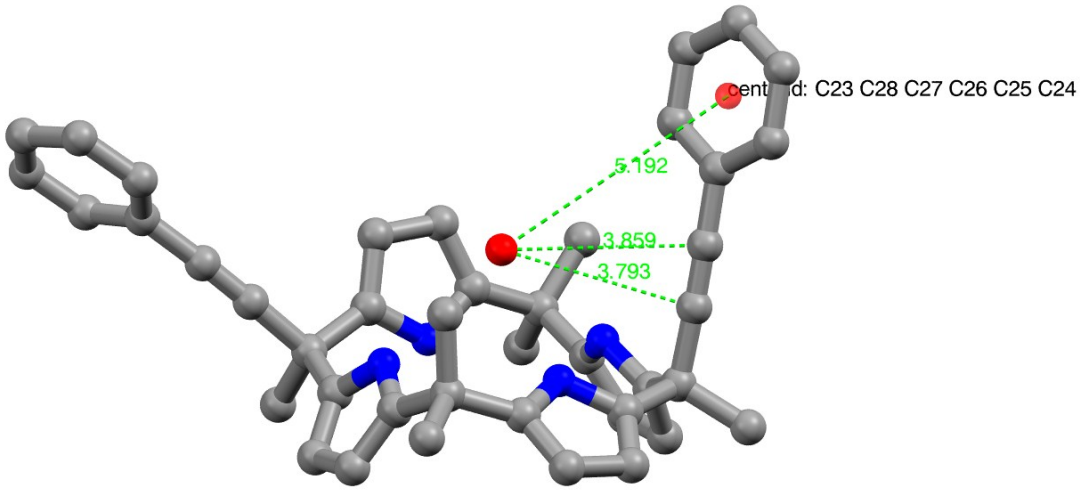


Figure S44: Close-up view of the distances (in Å) of bound water molecule to triple bond and the centroid of phenyl ring of **2**.

Table S16. Hydrogen bonding parameters for complex **1**

D-H•X	$d_{H•X}$ (Å)	$d_{D•X}$ (Å)	∟D-H•X (º)
N1-H1•Cl1	2.37(4)	3.280(3)	178(5)
N2-H2•Cl1	2.37(3)	3.262(3)	173(3)
N3-H3•Cl1	2.33(3)	3.257(3)	174(3)
N4-H4•Cl1	2.31(4)	3.263(3)	172(3)
C23-H23A	2.76	3.704(3)	165
C24-H24C	2.81	3.760(4)	167
C26-H26A	2.77	3.719(3)	165
C30-H30	2.81	3.573(4)	139

Table S17. Hydrogen bonding parameters for complex **2**

D-H•X	$d_{H•X}$ (Å)	$d_{D•X}$ (Å)	∟D-H•X (º)
N1-H1•F3	1.93	2.7677(17)	160
N2-H2•F3	2.00	2.7824(18)	150
N3-H3•F3	1.93	2.7784(18)	164
N4-H4•F3	1.98	2.7875(18)	154

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