A ferrocene functionalized rotaxane host system capable of the electrochemical recognition of chloride

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SUPPLEMENTARY INFORMATION

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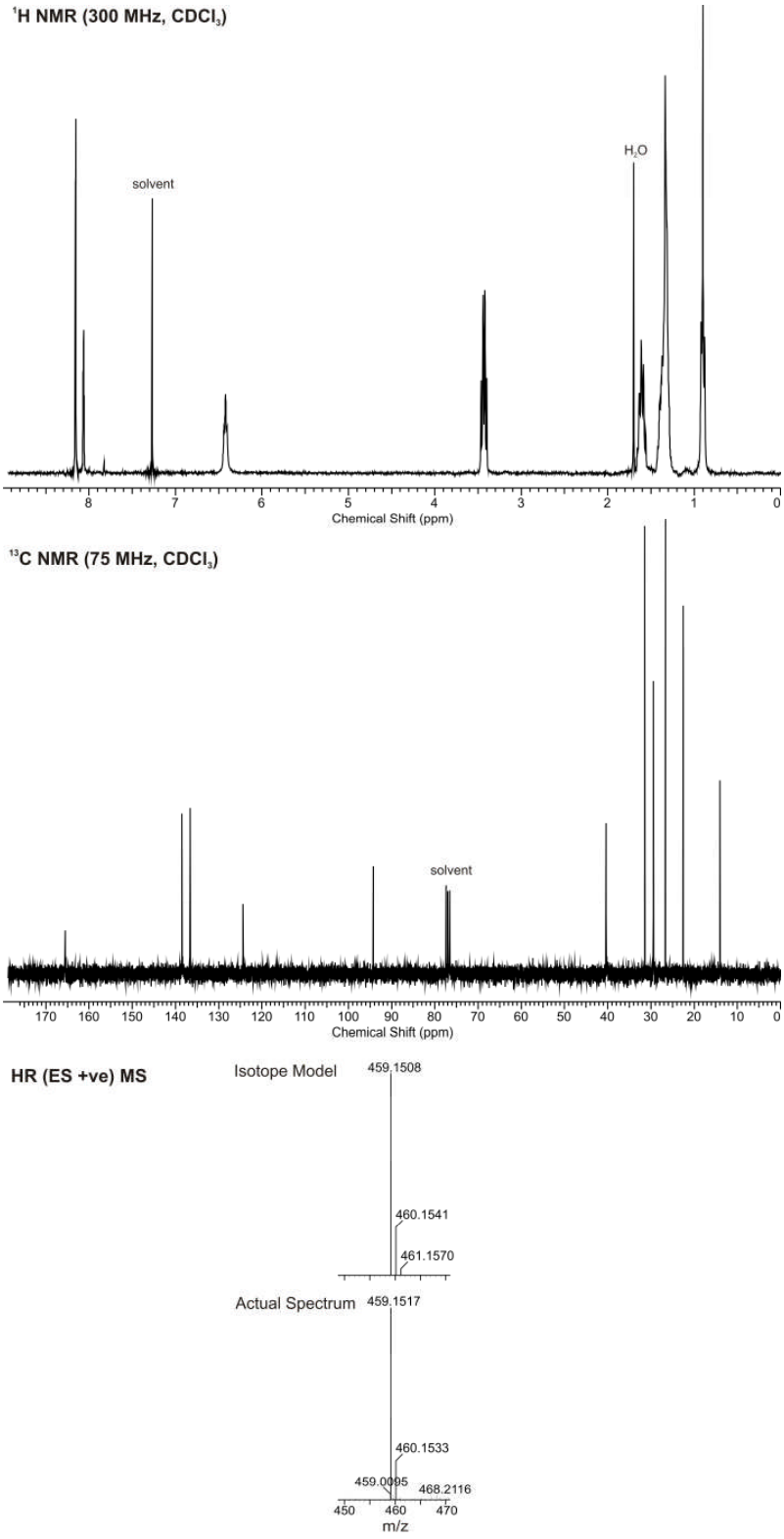
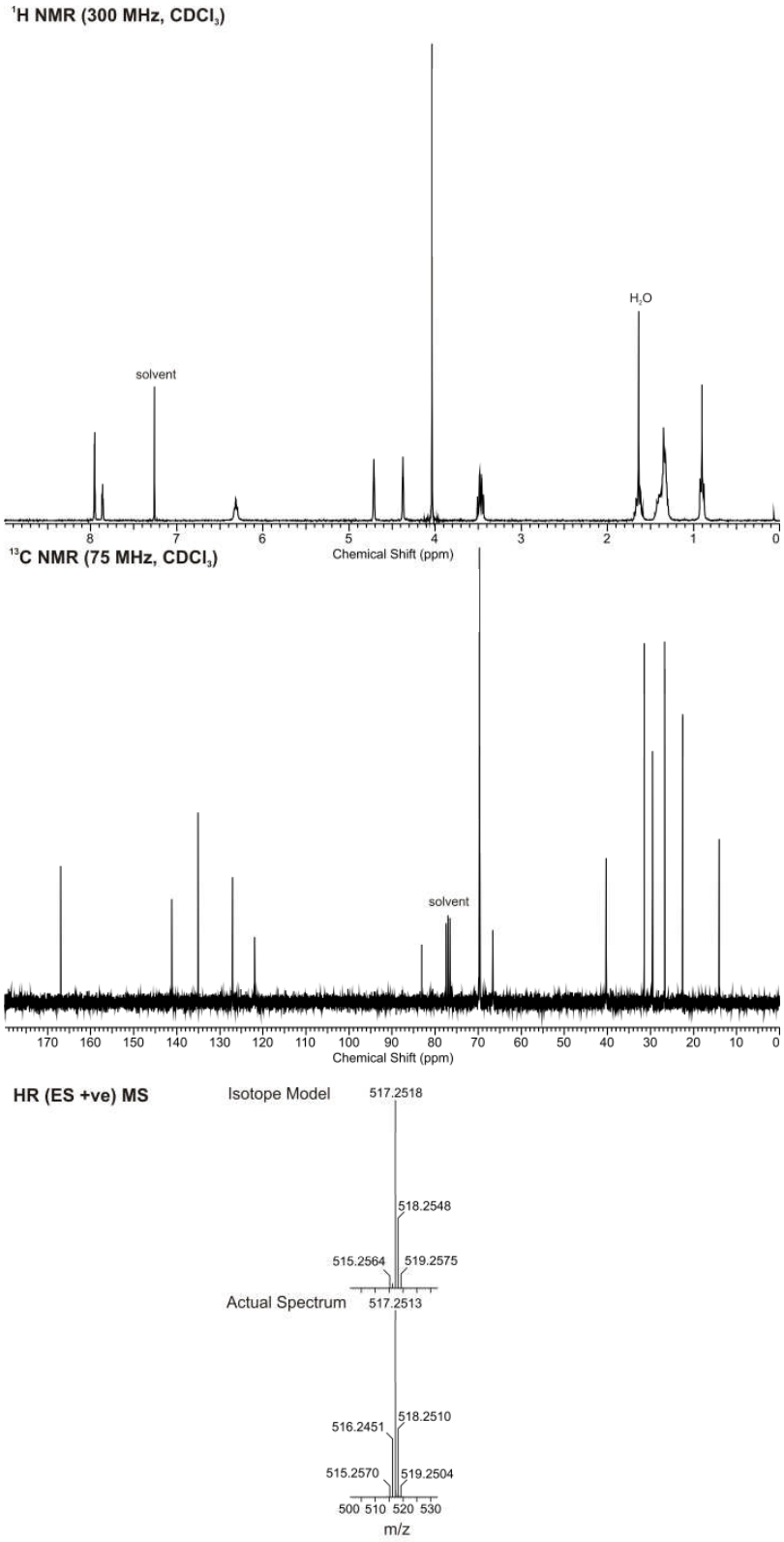
Part I: Spectral Characterization of Novel Compounds

Compound **2**



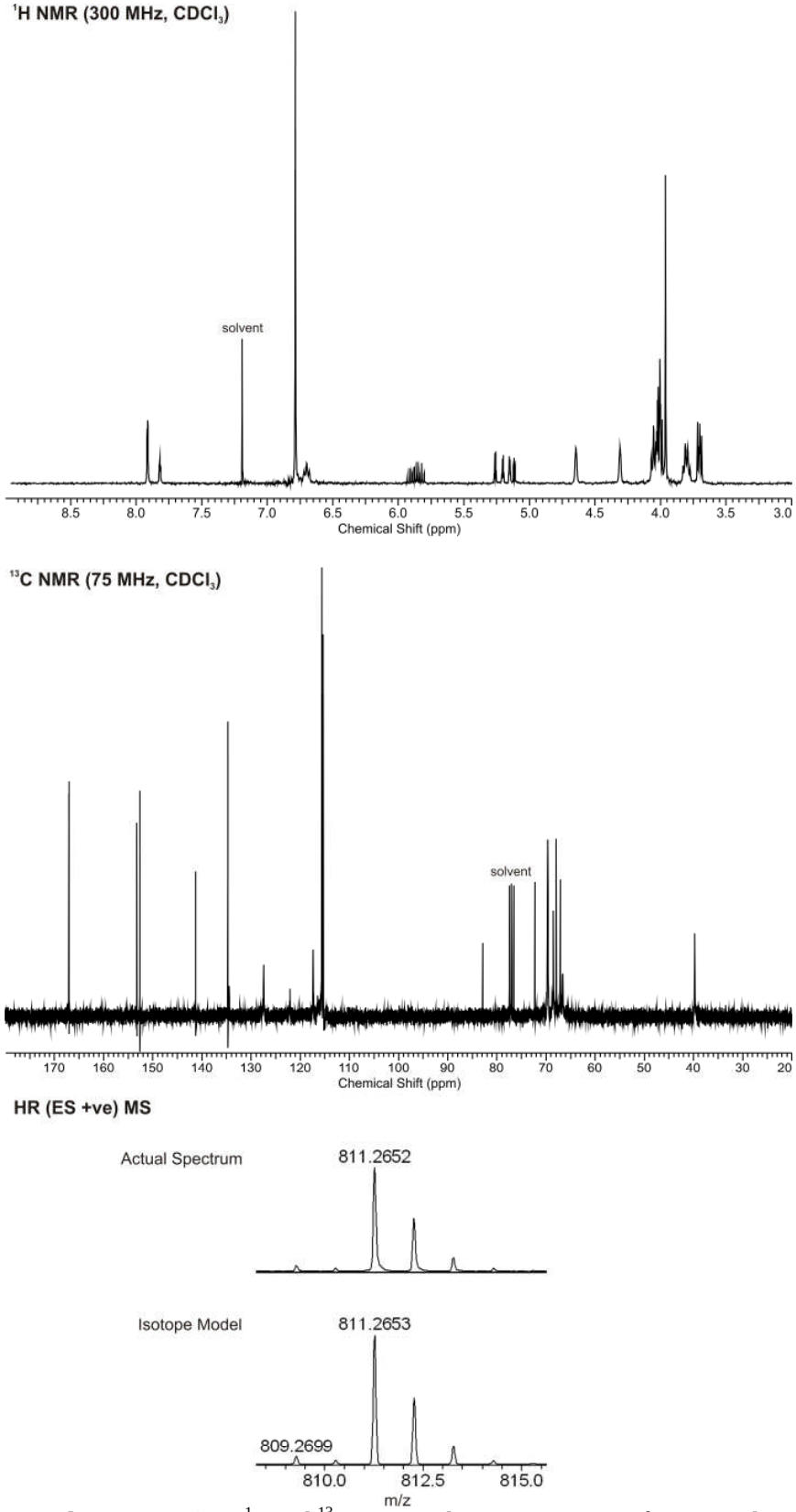
Supplementary Fig. 1 ^{1}H and ^{13}C NMR and HR mass spectra of compound **2**.

Model **3**



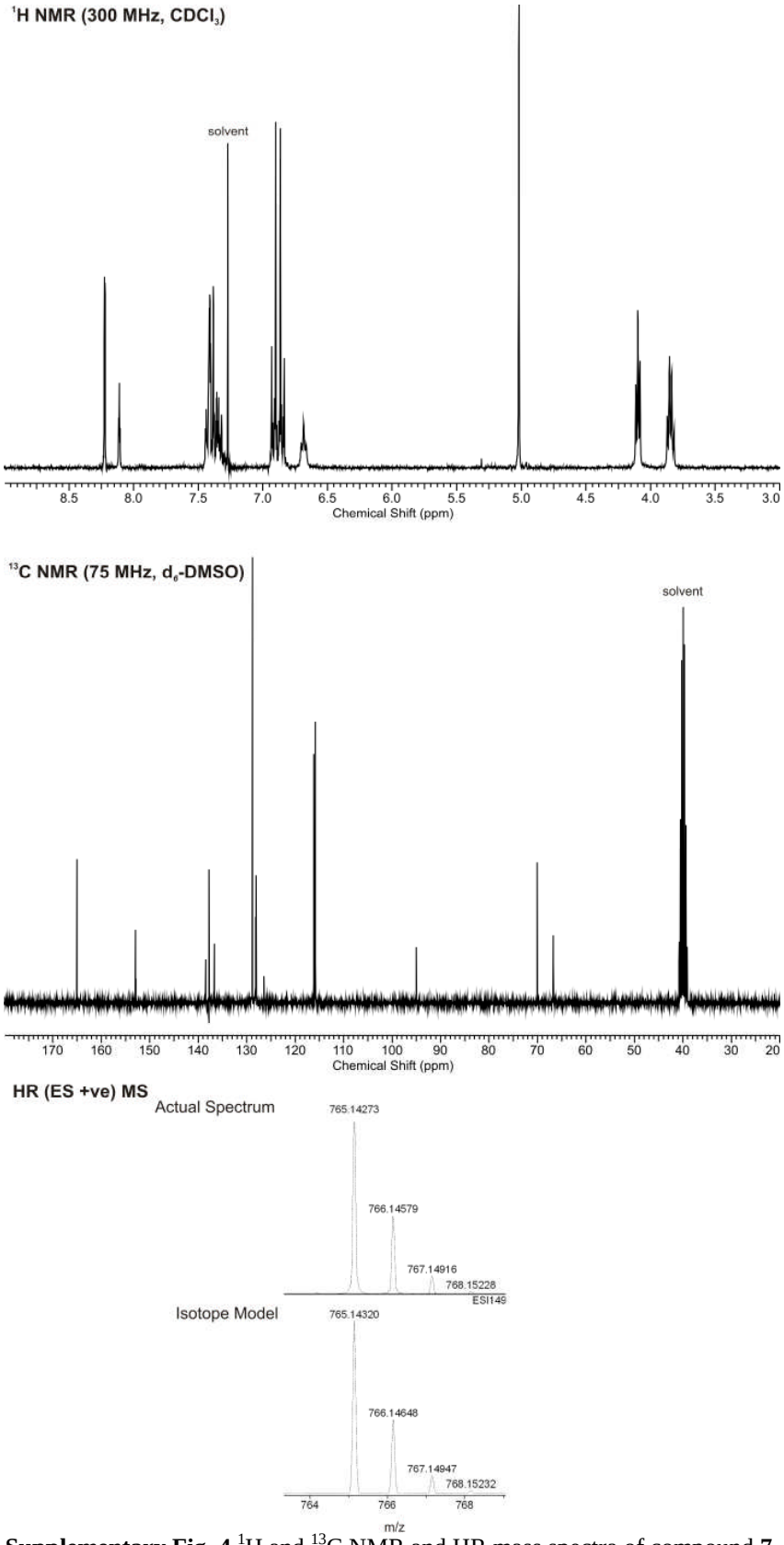
Supplementary Fig. 2 ^{1}H and ^{13}C NMR and HR mass spectra of model **3**.

Compound **5**



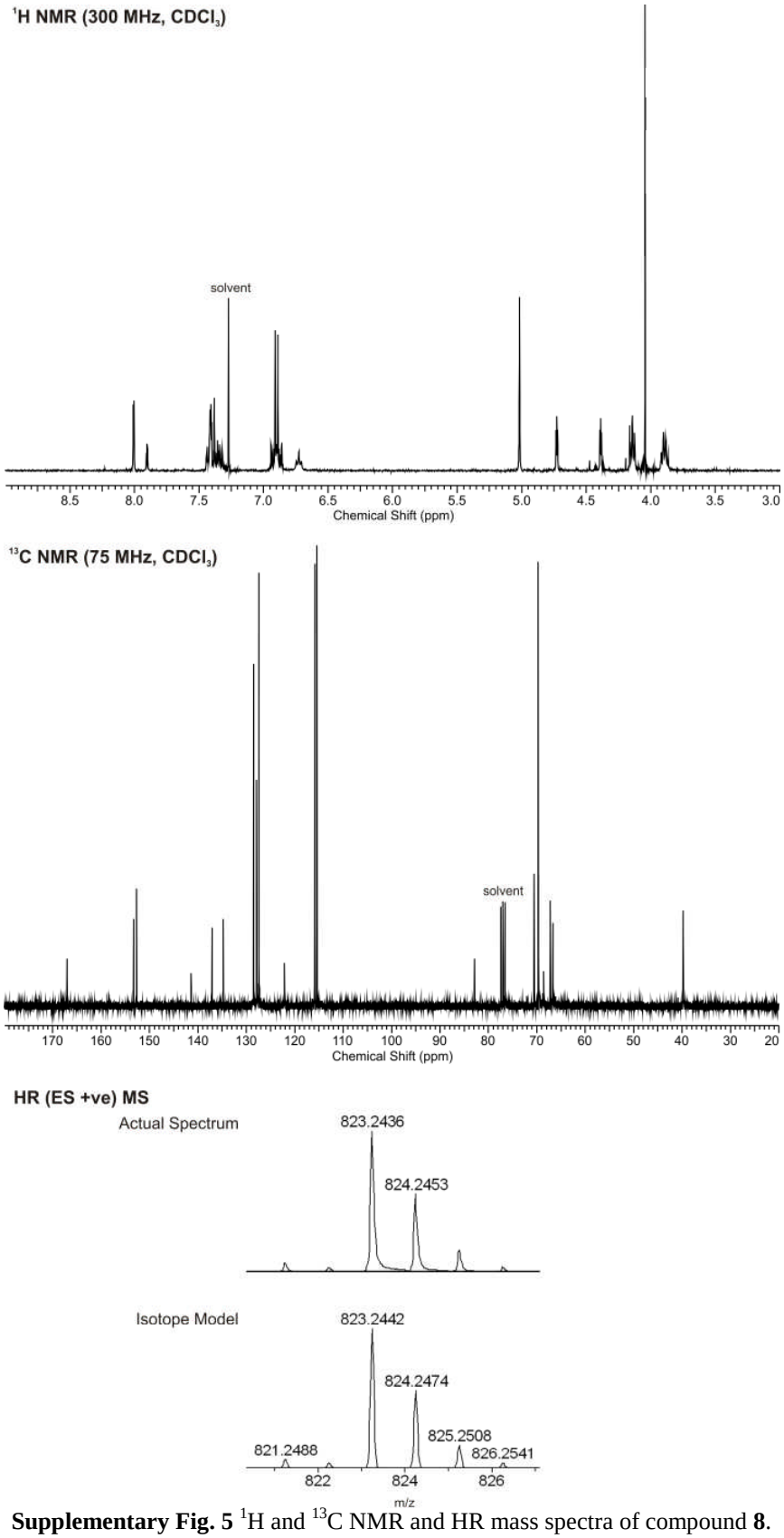
Supplementary Fig. 3 ^{1}H and ^{13}C NMR and HR mass spectra of compound **5**.

Compound **7**



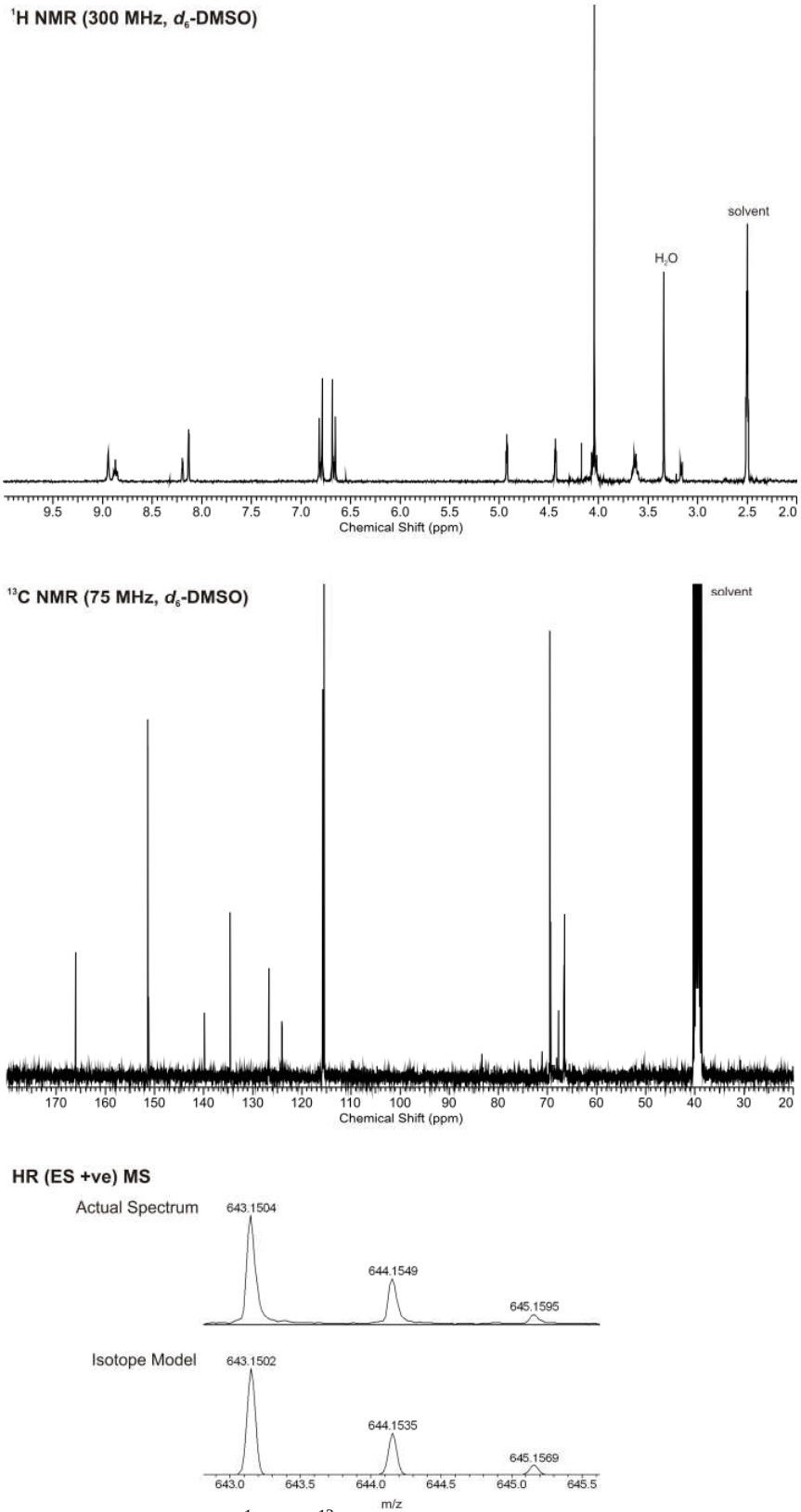
Supplementary Fig. 4 ^{1}H and ^{13}C NMR and HR mass spectra of compound **7**.

Compound **8**



Supplementary Fig. 5 ^{1}H and ^{13}C NMR and HR mass spectra of compound **8**.

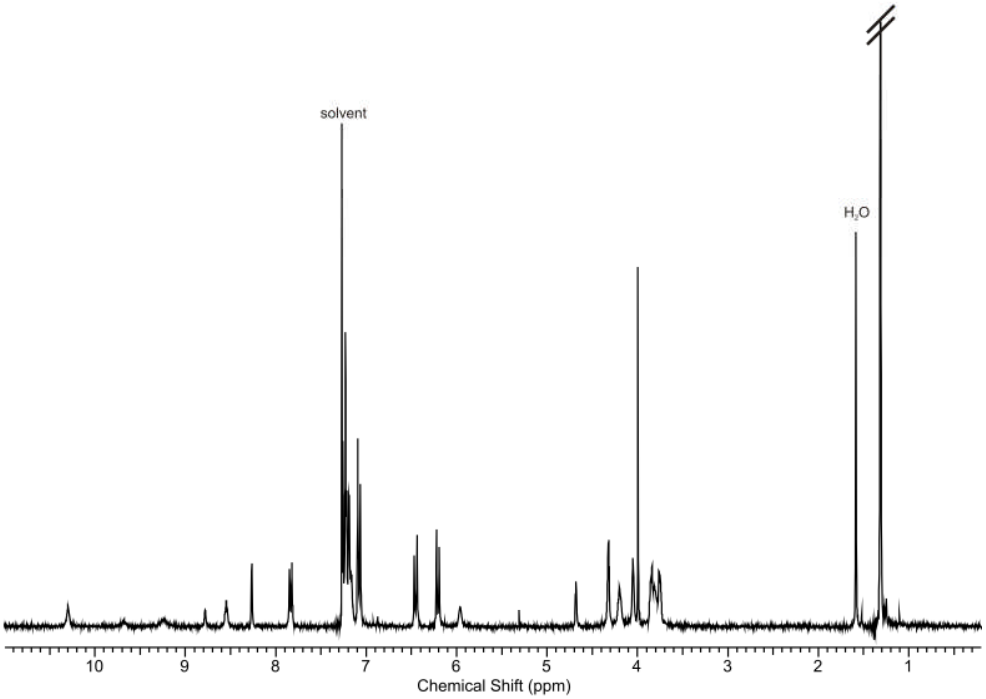
Compound **9**



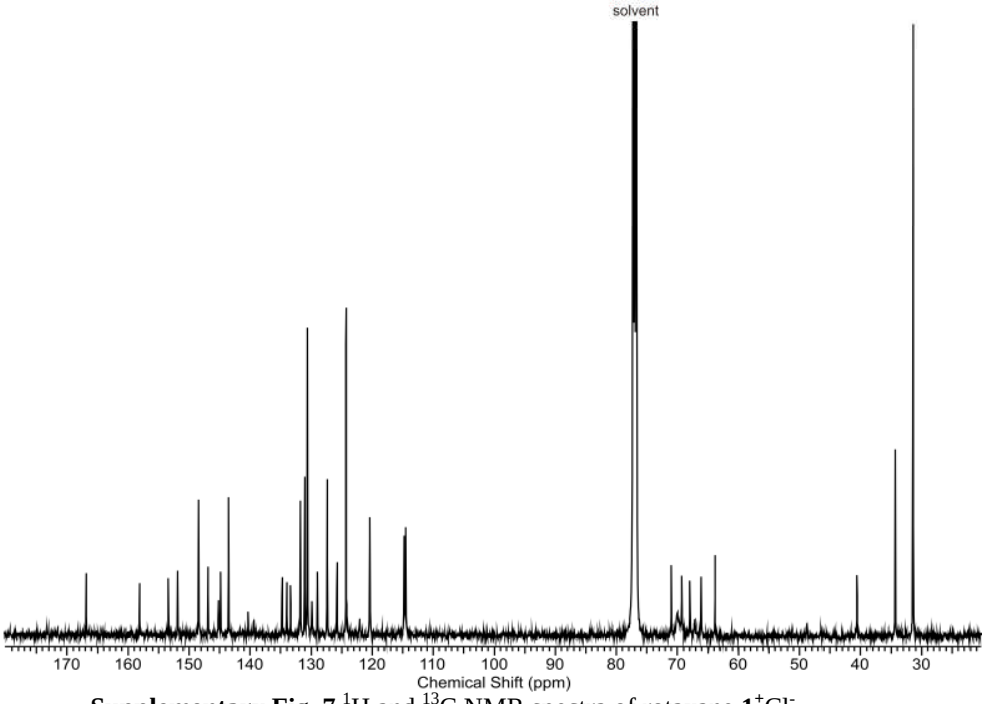
Supplementary Fig. 6 ^{1}H and ^{13}C NMR and HR mass spectra of compound **9**.

Rotaxane $\mathbf{1}^{+}Cl^{-}$

^{1}H NMR (300 MHz, $CDCl_3$)



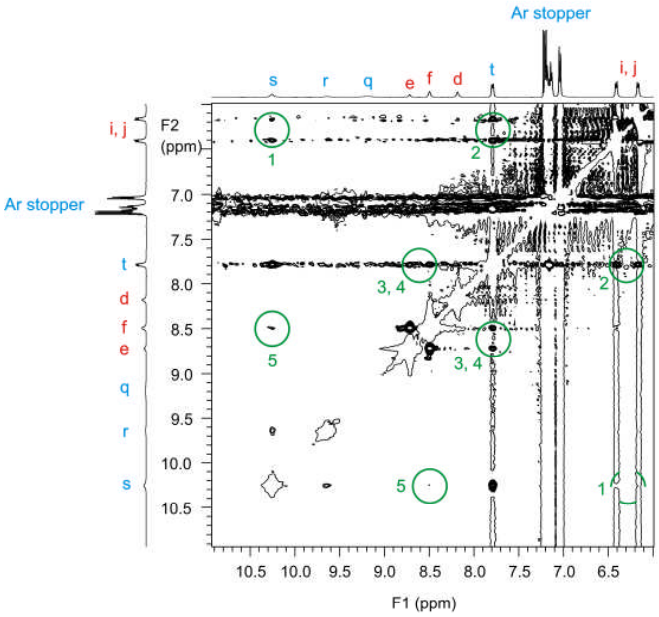
^{13}C NMR (125.8 MHz, $CDCl_3$)

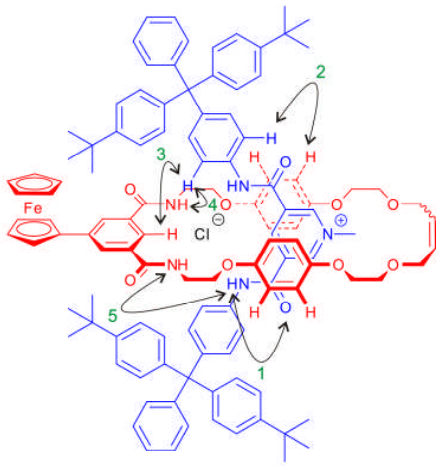


Supplementary Fig. 7 ^{1}H and ^{13}C NMR spectra of rotaxane $\mathbf{1}^{+}Cl^{-}$.

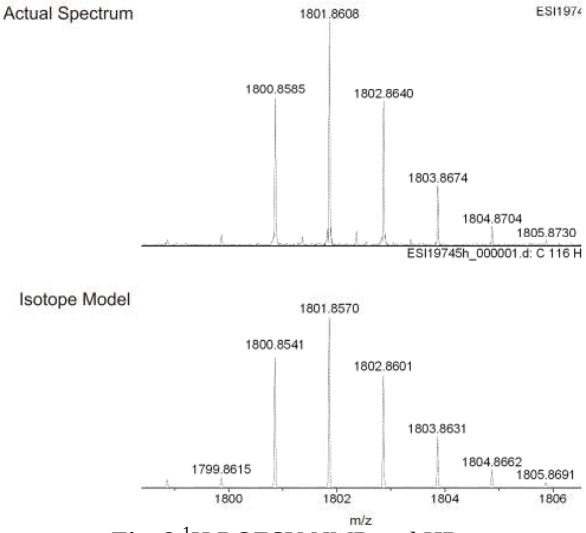
Rotaxane $\mathbf{1}^{+}Cl^{-}$ (cont.)

^{1}H ROESY NMR (500 MHz, $CDCl_3$)



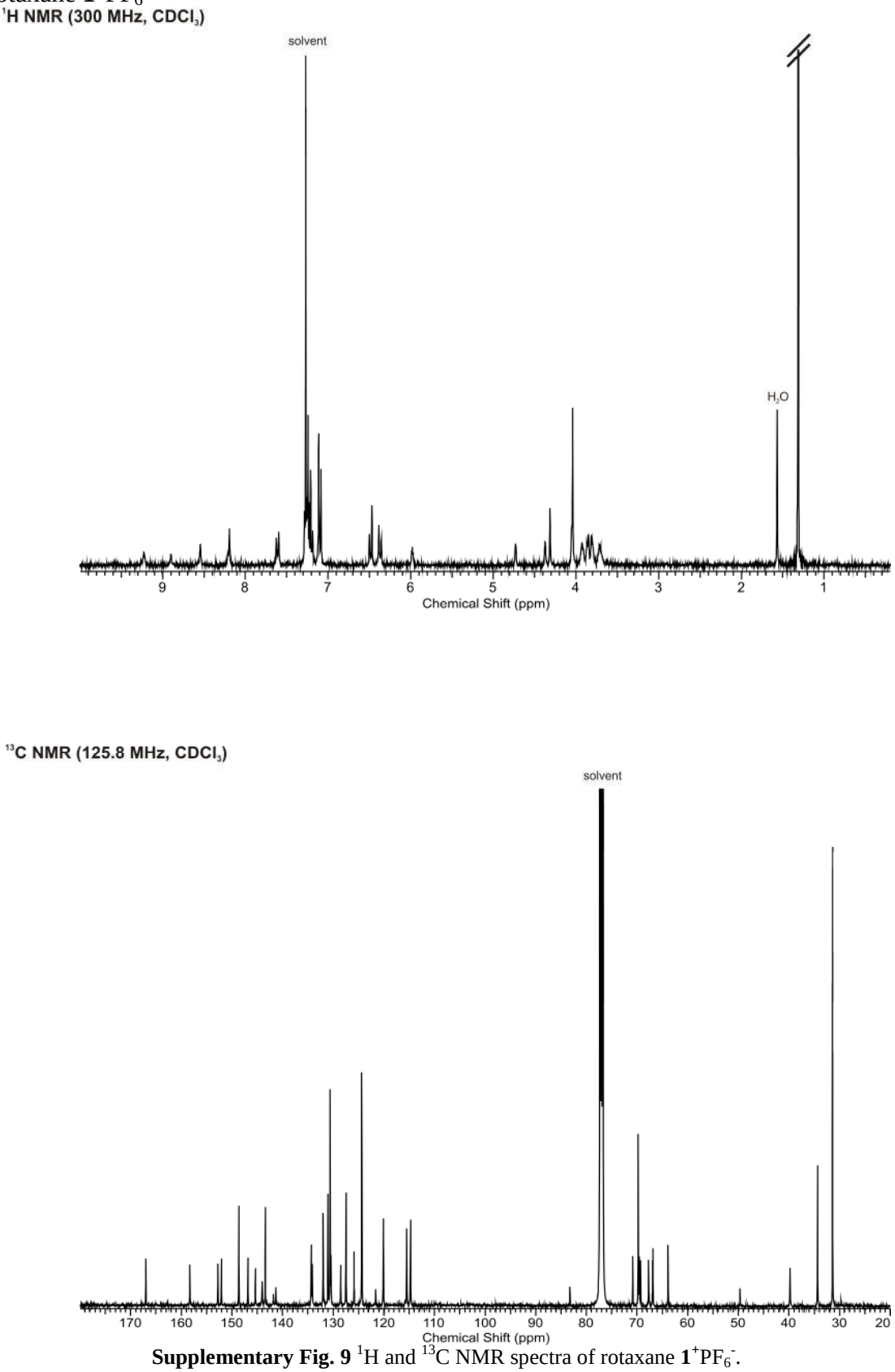


HR (ES +ve) MS



Supplementary Fig. 8 ^{1}H ROESY NMR and HR mass spectra of rotaxane $\mathbf{1}^{+}Cl^{-}$.

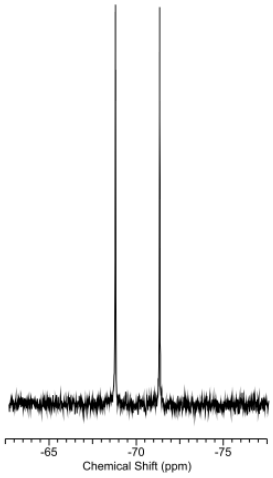
Rotaxane $\mathbf{1}^{+}PF_6^{-}$



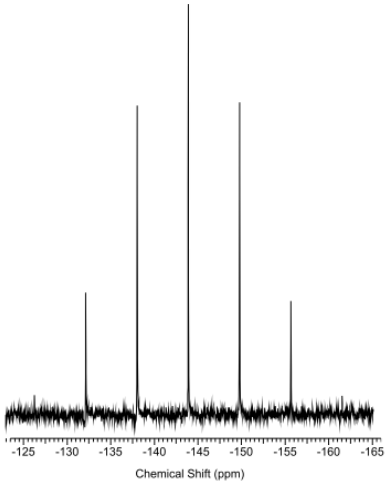
Supplementary Fig. 9 ^{1}H and ^{13}C NMR spectra of rotaxane $\mathbf{1}^{+}PF_6^{-}$.

Rotaxane $\mathbf{1}^{+}PF_6^{-}$ (cont.)

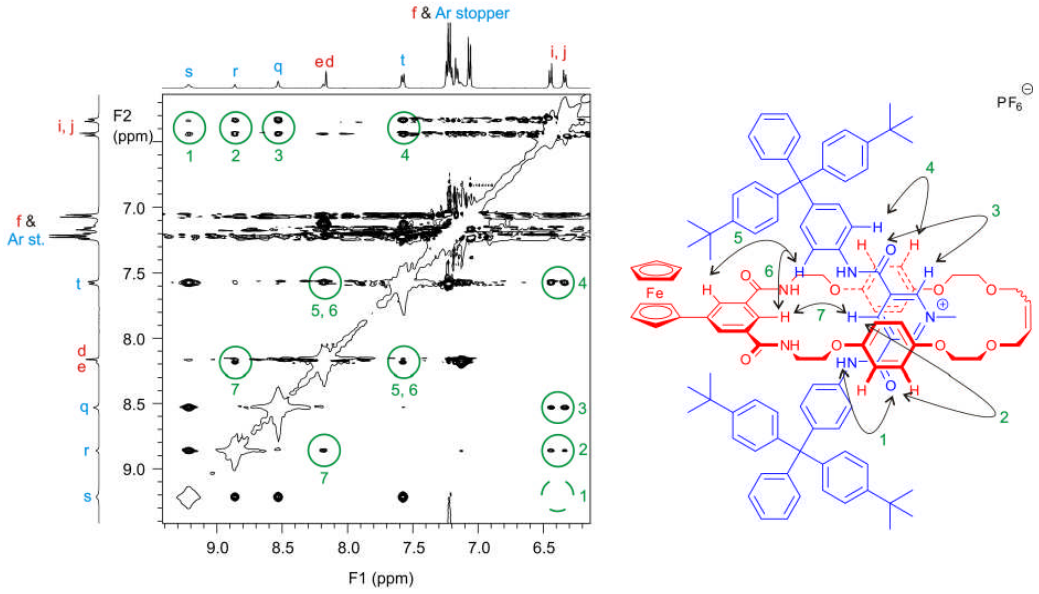
^{19}F NMR (282.4 MHz, $CDCl_3$)



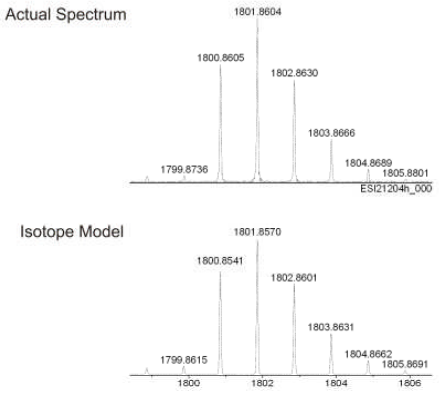
^{31}P NMR (121.5 MHz, $CDCl_3$)



^{1}H ROESY NMR (500 MHz, $CDCl_3$)



HR (ES +ve) MS



Supplementary Fig. 10 ^{19}F, ^{31}P and ^{1}H ROESY NMR and HR mass spectra of rotaxane $\mathbf{1}^{+}PF_6^{-}$.

Part II: Anion Recognition Studies

^{1}H NMR Titrations

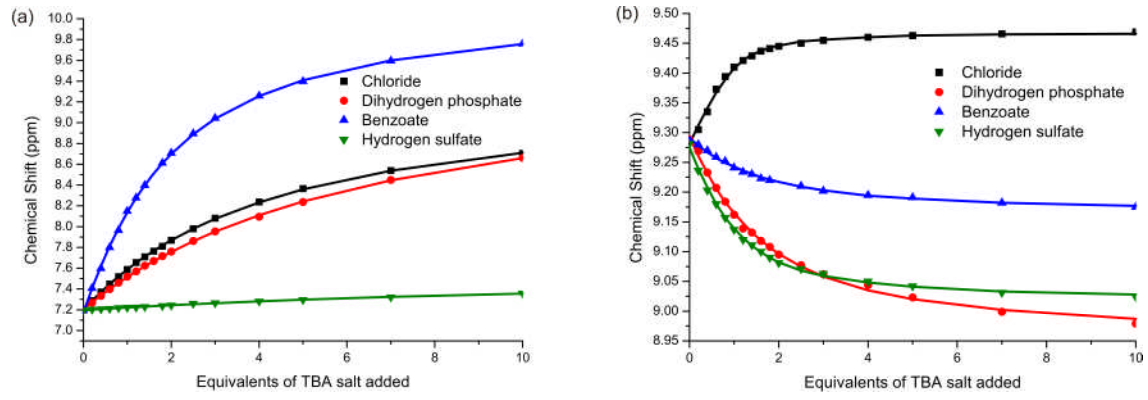
Protocol

^{1}H NMR spectra were recorded on a Varian Unity Plus 500 spectrometer. In a typical experiment, a solution of guest was added to a solution of the host at 293 K. The chemical shift of specific proton(s) was monitored for seventeen titration points (for 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10.0 equivalents of added guest), with the resulting data analysed using the WinEqNMR2 computer program[1], as the association of guest and host was found to be fast on the NMR timescale for all systems.

The anion binding titration experiments were carried out using salts of the non-complexing tetrabutylammonium (TBA) cation as the guest species, titrated into the dissolved host. A 0.075 M solution of anion was added to 0.50 mL of a 1.50 mM solution of host, i.e. 10 μL is 1 equivalent. The volumes of TBA salt added were 10 x 2 μL, 2 x 5 μL, 2 x 10 μL, 1 x 20 μL and 1 x 30 μL.

The values of the observed chemical shift and the guest concentration were entered into winEQNMR2 for every titration point and, estimates for the binding constant and limiting chemical shifts were made. The parameters were refined using non-linear squares analysis to obtain the best fit between observed and calculated chemical shifts for a 1:1 binding stoichiometry. The program plots the observed chemical shift versus the guest concentration, revealing the accuracy of the experimental data and the suitability of the model used. The input parameters were varied until the best-fit values of the stability constants, and their errors, converged.

Titration Curves



Supplementary Fig. 11 Plots of chemical shift versus equivalents of TBA salt added for: (a) Model **3** (amide proton) in CD_3CN and (b) Rotaxane $\mathbf{1}^+PF_6^-$ (cleft pyridinium proton) in 1:1 $CDCl_3$:CD_3OD, from which association constants were calculated using WinEqNMR2.

[1] M. J. Hynes, *J. Chem. Soc. Dalton Trans.*, 1993, 311.

Electrochemical Titrations

Protocol

Cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed on an Autolab Potentiostat/Galvanostat model PG-STAT 12, controlled by General Purpose Electrochemical System Software v. 4.9 (Eco Chemie). A standard one-compartment three-electrode electrochemical cell, located inside a Faraday cage, was used with a glassy carbon solid disc working electrode, a platinum wire auxiliary electrode and an Innovative Instruments, Inc. LF-2 leak-free silver/silver chloride reference electrode. A 0.5 mM ferrocene sample was used to check the reference electrode and internal resistance of the equipment. The electrolyte solution used in all experiments was 0.1 M $TBAPF_6$ in MeCN.

CVs were typically recorded with a 1 s equilibration time, a step potential of 1 mV and a scan rate of 100 mVs^{-1}. SWVs were typically recorded with a 1 s equilibration time, a step potential of 3 mV and a frequency of 30 Hz. The working electrode was cleaned between scans by polishing with commercially available microcloth.

In a typical experiment, the host (0.5 mM) was dissolved in 2.5 mL of a solution of $TBAPF_6$ (0.1 M) and cyclic and square wave voltammograms were recorded. For the cyclic voltammetry scan rates of 25, 50, 75, 100, 250 and 500 mVs^{-1} were used to test for reversibility. Anion binding experiments were performed by addition of 0, 0.5, 1, 2, 5 and 10 equivalents of anion (as a 0.25 M solution of TBAX salt in electrolyte solution, 5 µL is 1 equivalent) to a 2.5 mL aliquot of the receptor solution, stirred and the cyclic and square wave voltammograms recorded.

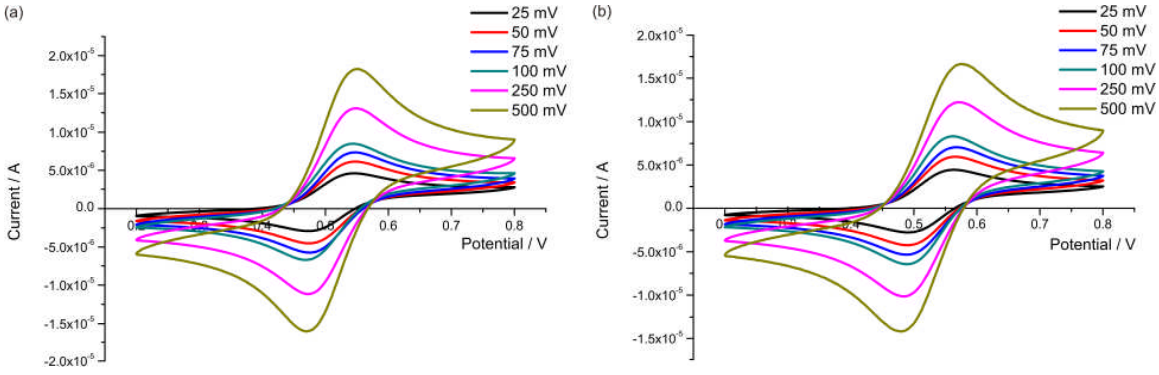
Electrochemical Data

I. Reversibility

For an electrochemical system (under fast kinetics) to be described as reversible, the following criteria must be satisfied:

(i) ΔE = 59/n mV (where n = number of electrons transferred in the redox process), so here where n = 1, ΔE should equal 59 mV;
(ii) E_{pa} and E_{pc} are independent of the scan rate;
(iii) $I_{pa} / I_{pc} = 1$;
(iv) I_{pa} and I_{pc} are proportional to the square root of the scan rate.

From CVs of model **3** and rotaxane $\mathbf{1}^{+}PF_6^{-}$ recorded at varying scan rates, it is best to describe model **3** and rotaxane $\mathbf{1}^{+}PF_6^{-}$ as being quasi-reversible electrochemical systems because the data almost fit the outlined criteria.

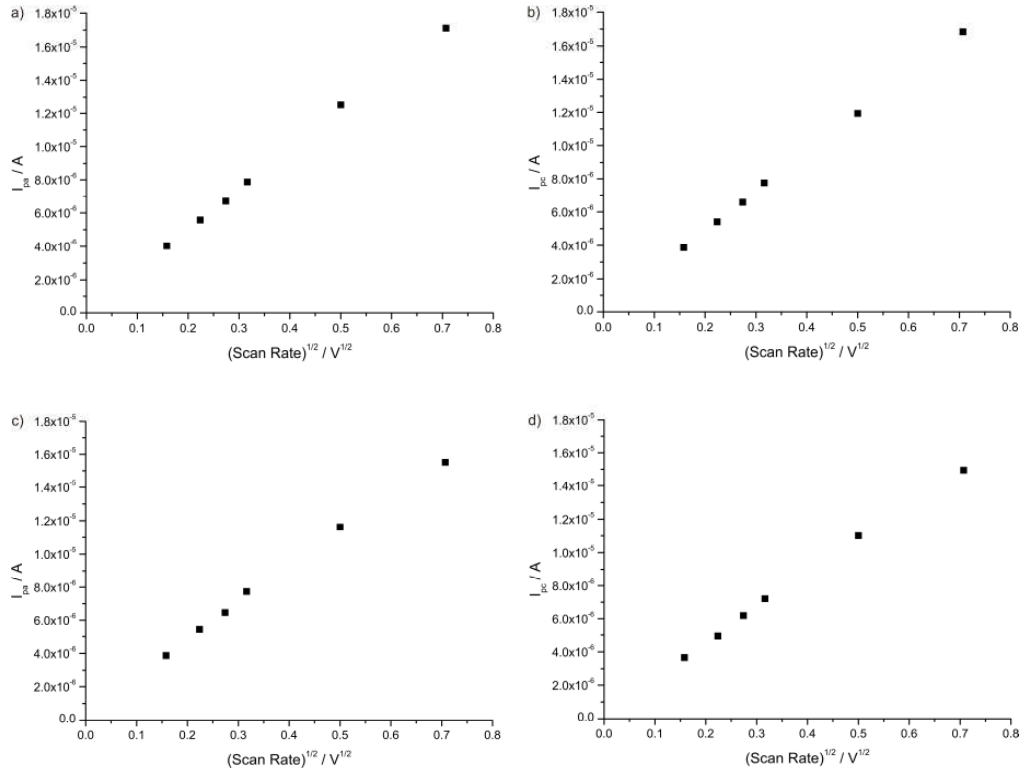


Supplementary Fig. 12 CVs of (a) Model **3** and (b) Rotaxane $\mathbf{1}^{+}PF_6^{-}$ in 0.1 M $TBAPF_6/CH_3CN$, with varying scan rates (Potential compared to Ag/AgCl reference).

Supplementary Table 1 ΔE, E_{pa}, E_{pc} and I_{pa}/I_{pc} data for model **3** and rotaxane $\mathbf{1}^{+}PF_6^{-}$ for various scan rates[a]

Scan Rate / mV	Model **3**				Rotaxane $\mathbf{1}^{+}PF_6^{-}$			
	ΔE / mV	E_{pa} /mV	E_{pc} /mV	I_{pa}/I_{pc}	ΔE / mV	E_{pa} /mV	E_{pc} /mV	I_{pa}/I_{pc}
25	0.067	0.543	0.476	1.04	0.068	0.562	0.494	1.06
50	0.066	0.545	0.479	1.03	0.067	0.561	0.494	1.10
75	0.066	0.543	0.477	1.02	0.071	0.563	0.492	1.04
100	0.067	0.540	0.473	1.02	0.067	0.560	0.493	1.07
250	0.070	0.547	0.477	1.05	0.084	0.571	0.487	1.06
500	0.074	0.547	0.473	1.02	0.088	0.574	0.486	1.04

[a] Electrolyte: 0.1 M $TBAPF_6/CH_3CN$. Potential compared to Ag/AgCl reference.

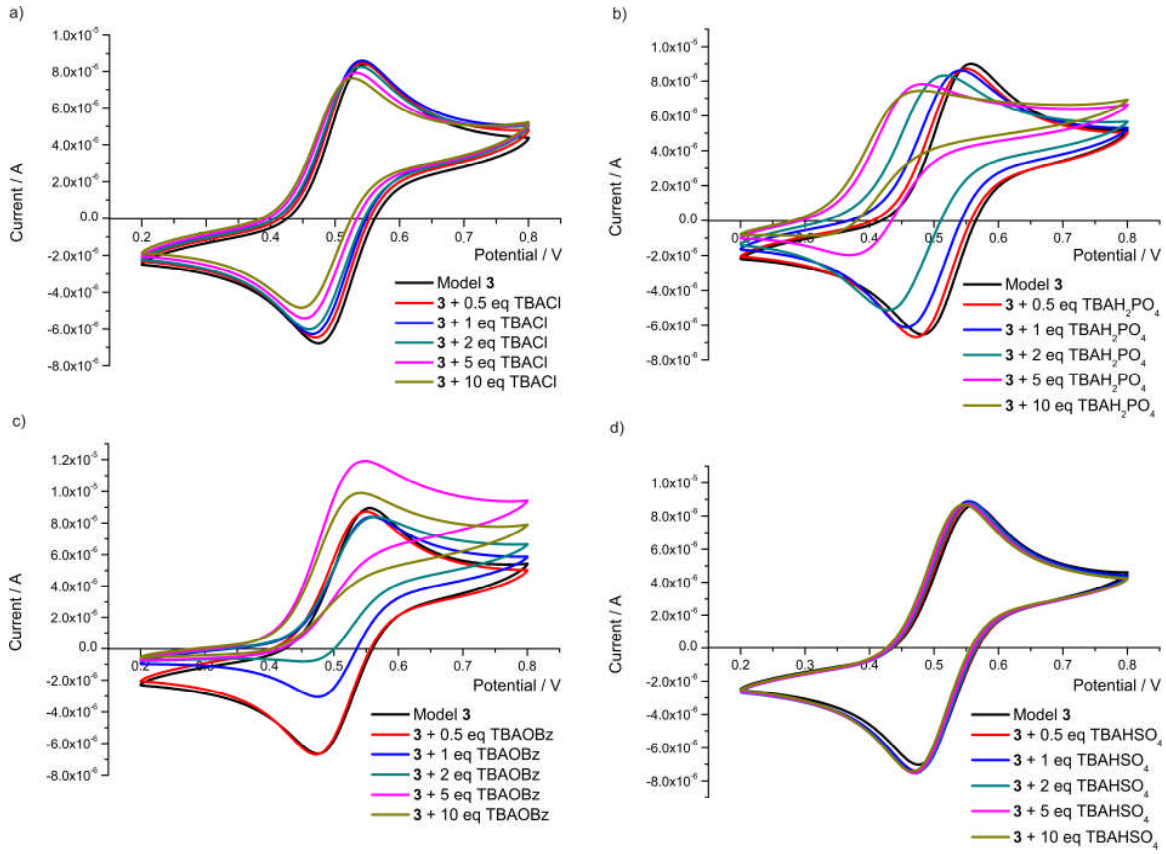


Supplementary Fig. 13 Plots of I_{pa} and I_{pc} against (scan rate)$^{1/2}$ for model **3** [(a) and (b)] and rotaxane $\mathbf{1}^{+}PF_6^{-}$ [(c) and (d)].

II. CVs and selected SWVs of anion titration experiments

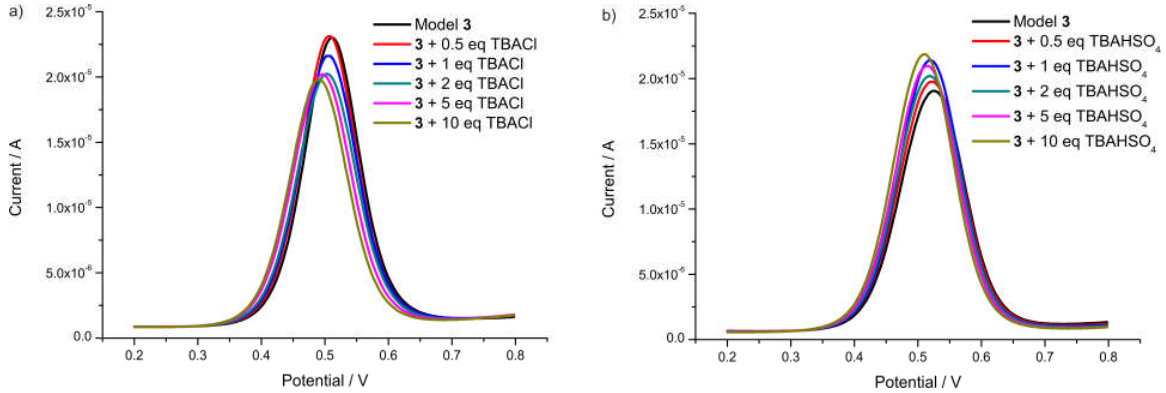
Model **3** ($E_{1/2}$ = + 85 mV relative to $E_{1/2(ferrocene)}$ = 0 V)

CVs



Supplementary Fig. 14 CVs of Model **3** in 0.1 M $TBAPF_6/CH_3CN$ upon the addition of aliquots of (a) TBACl, (b) $TBAH_2PO_4$, (c) TBAOBz and (d) $TBAHSO_4$ (Potential compared to Ag/AgCl reference).

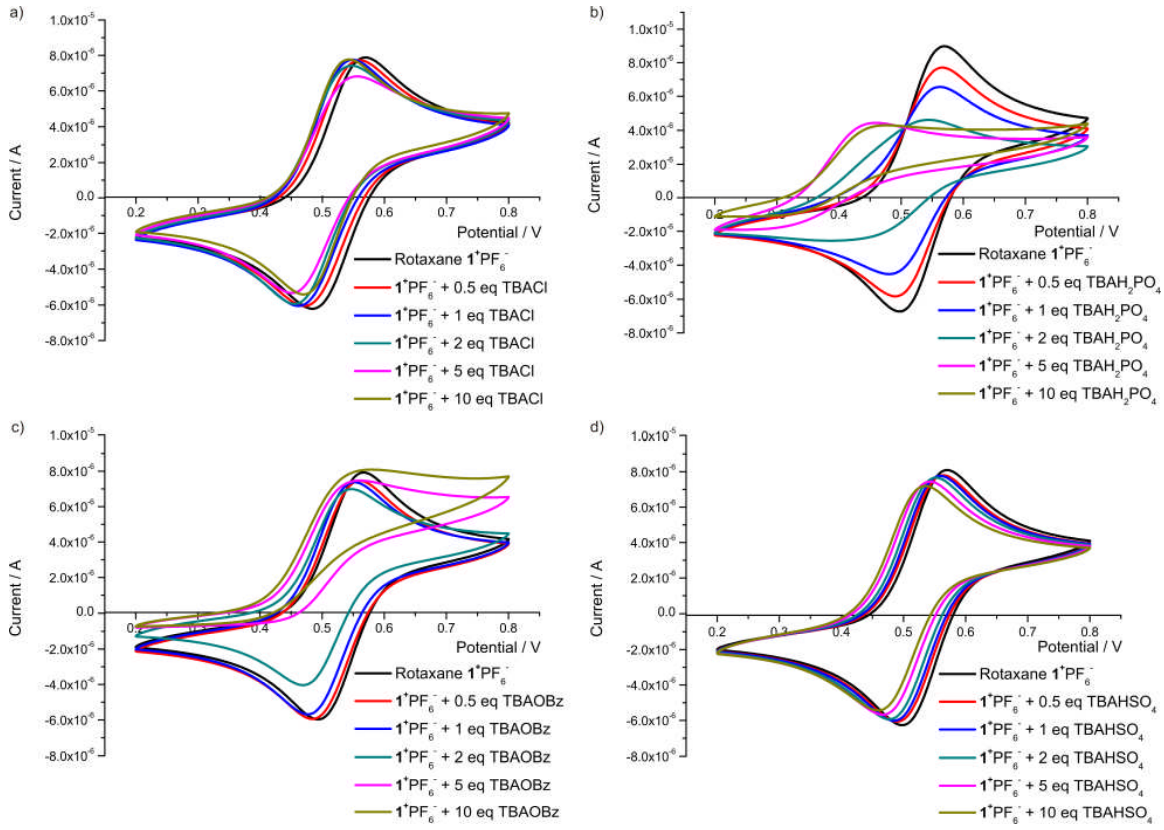
Selected SWVs



Supplementary Fig. 15 SWVs of Model **3** in 0.1 M $TBAPF_6/CH_3CN$ upon the addition of aliquots of (a) TBACl and (b) $TBAHSO_4$ (Potential compared to Ag/AgCl reference).

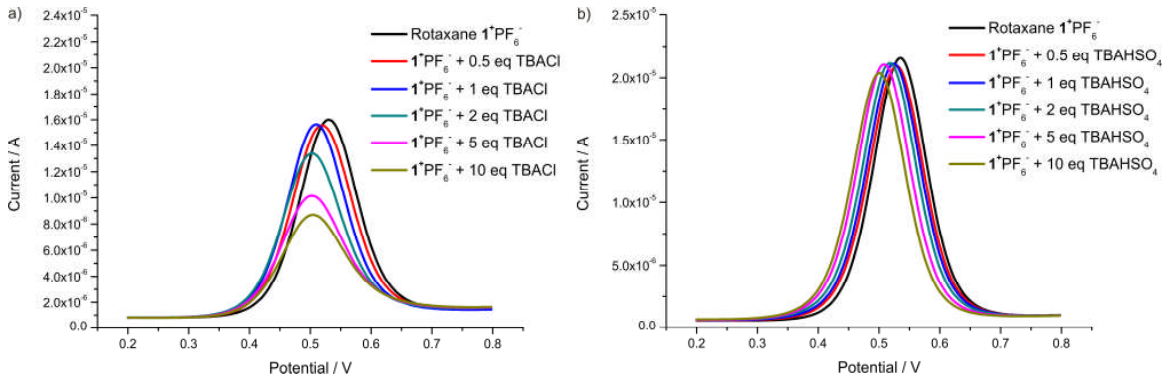
Rotaxane $\mathbf{1}^{+}PF_6^{-}$ ($E_{1/2}$ = + 115 mV relative to $E_{1/2(ferrocene)}$ = 0 V)

CVs



Supplementary Fig. 16 CVs of Rotaxane $\mathbf{1}^{+}PF_6^{-}$ in 0.1 M $TBAPF_6/CH_3CN$ upon the addition of aliquots of (a) TBACl, (b) $TBAH_2PO_4$, (c) TBAOBz and (d) $TBAHSO_4$ (Potential compared to Ag/AgCl reference).

Selected SWVs



Supplementary Fig. 17 SWVs of Rotaxane $\mathbf{1}^{+}PF_6^{-}$ in 0.1 M $TBAPF_6/CH_3CN$ upon the addition of aliquots of (a) TBACl and (b) $TBAHSO_4$ (Potential compared to Ag/AgCl reference).