Electronic Supplementary Information

A pyridine-*N*-oxide catenane for cation recognition

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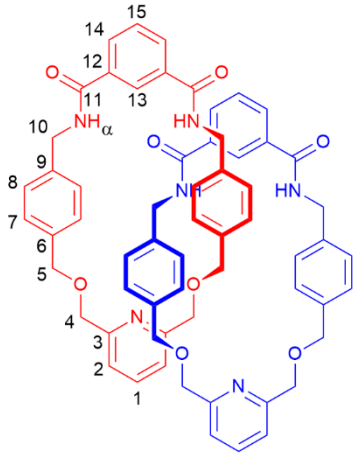
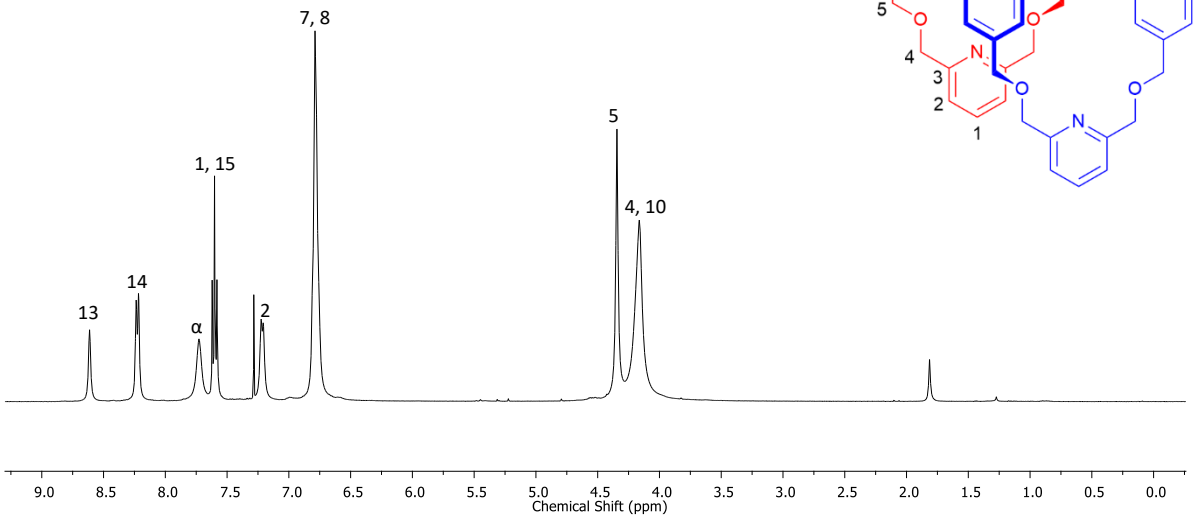
Contents:

Part 1: Spectral Data for Main Article

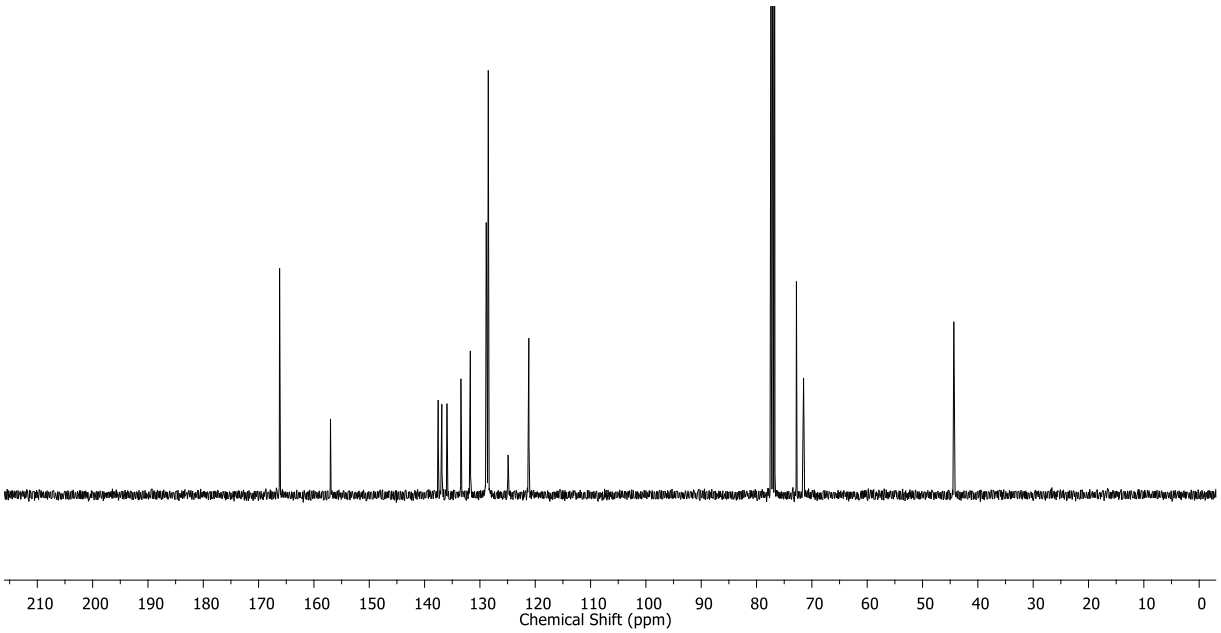
Pyridyl [2]Catenane 2



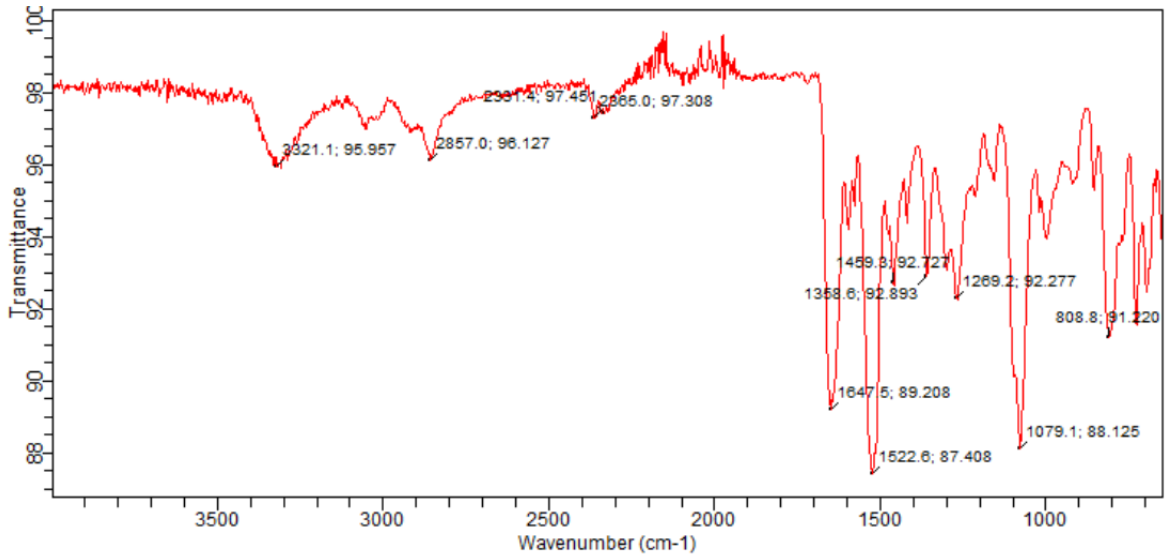
^{1}H NMR (400 MHz, $CDCl_3$)



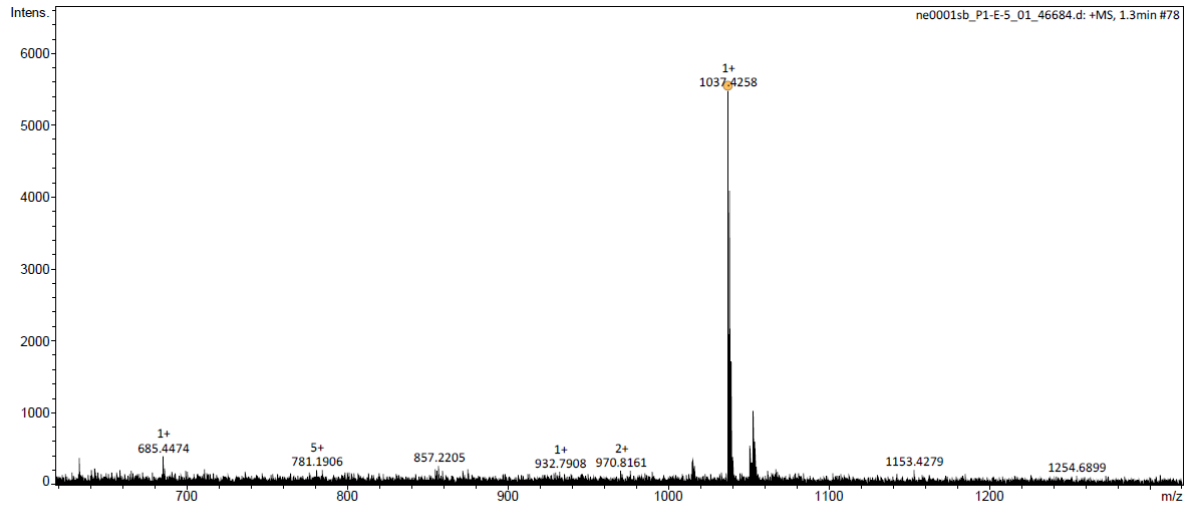
^{13}C NMR (100 MHz, $CDCl_3$)



IR (neat)



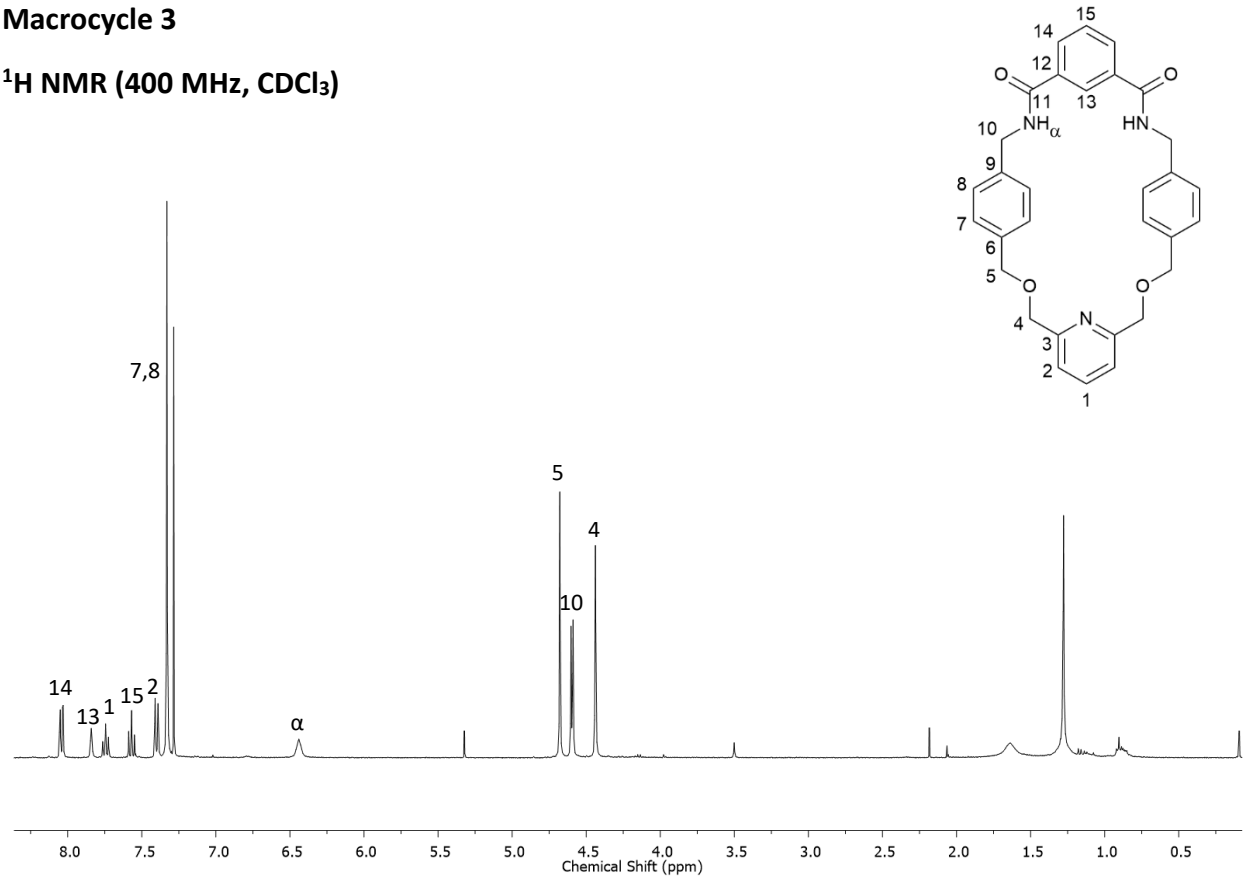
MS (ES +ve)



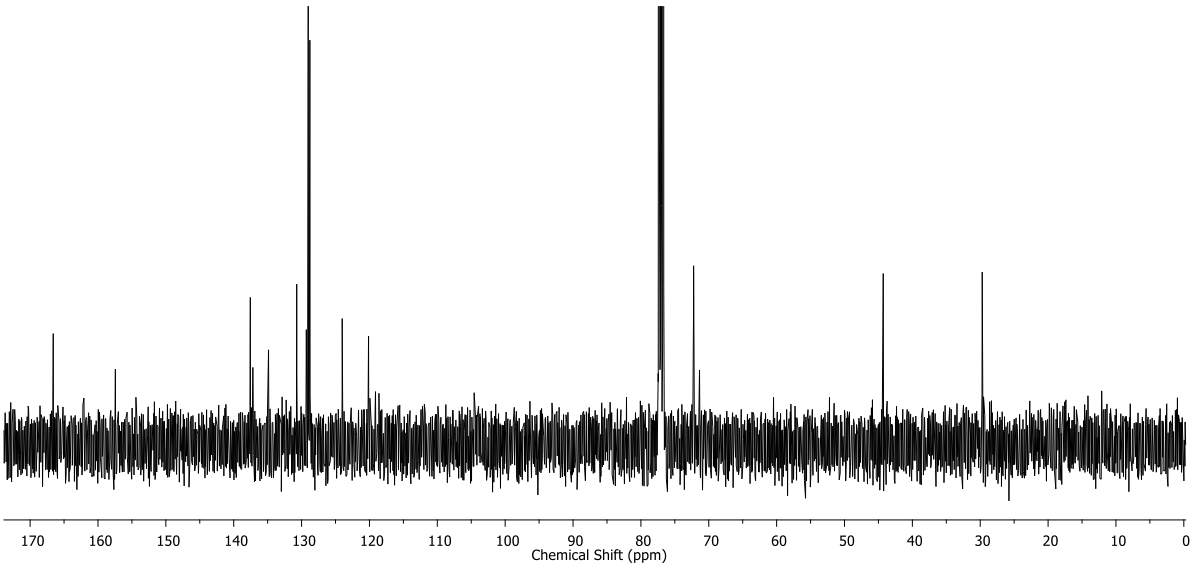
Meas. m/z	#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
1037.4258	1	C62H58N6NaO8	1037.4208	-4.8	-5.0	31.5	-4.3

Macrocycle 3

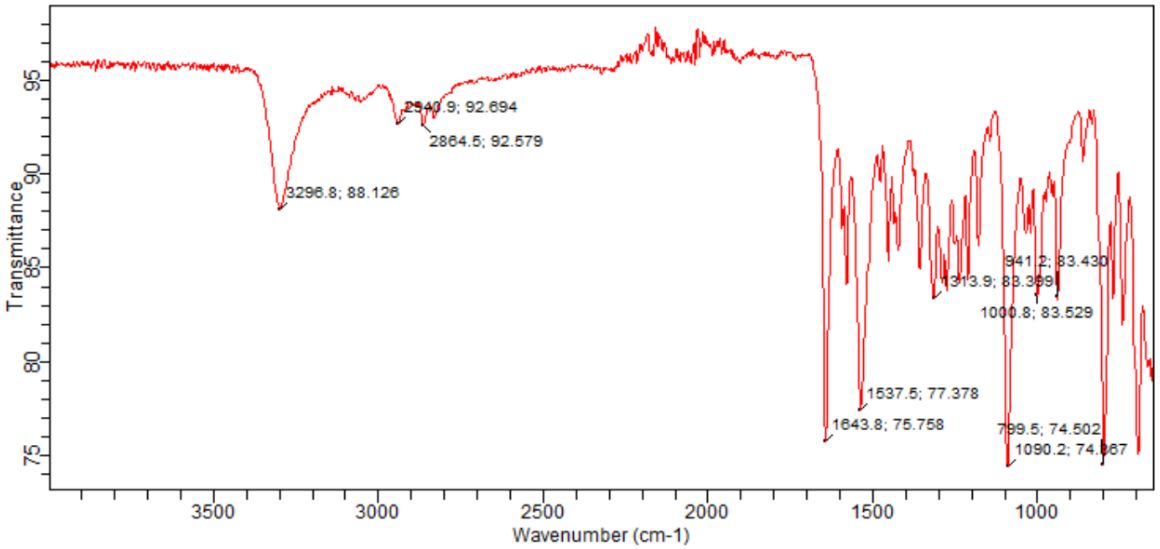
^{1}H NMR (400 MHz, $CDCl_3$)



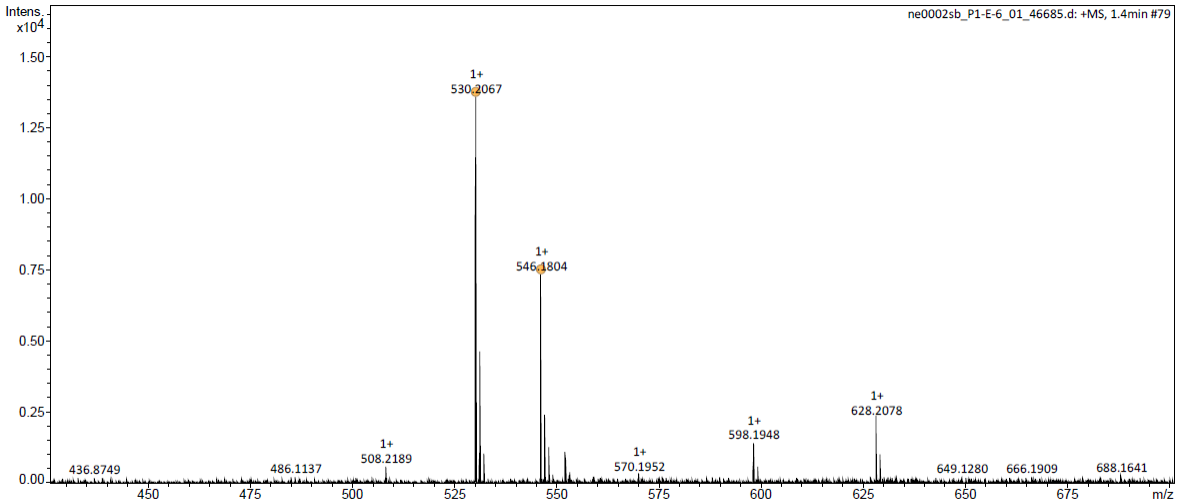
^{13}C NMR (400 MHz, $CDCl_3$)



IR (neat)



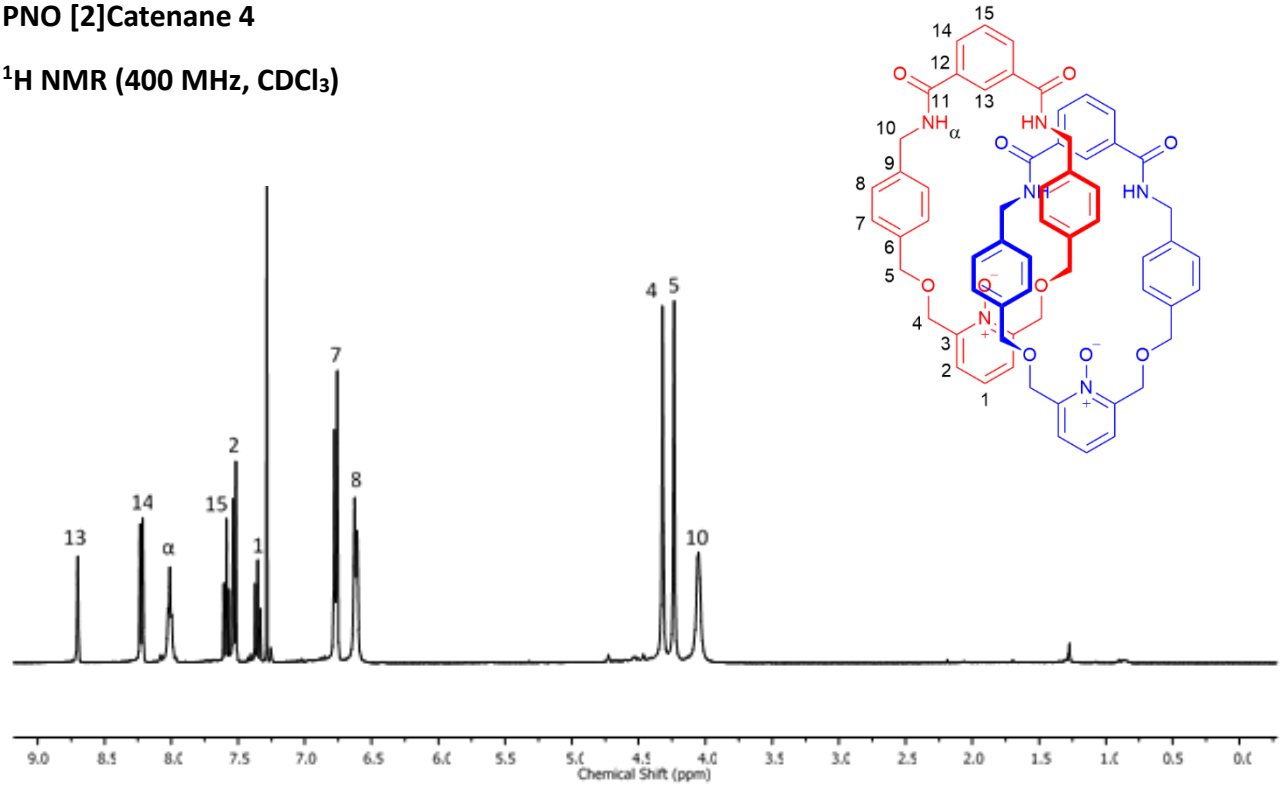
MS (ES +ve)



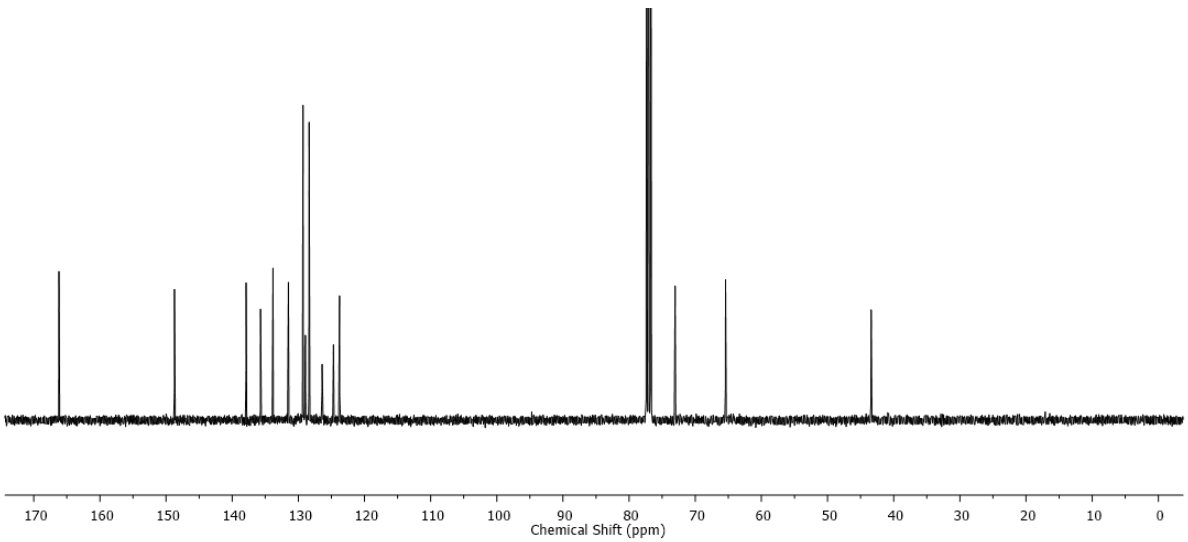
Meas. m/z	#	Ion Formula	m/z	err [ppm]	err [mDa]	mSigma	Mean err [ppm]
530.2067	1	C31H29N3NaO4	530.2050	-3.1	-1.7	7.1	-3.7

PNO [2]Catenane 4

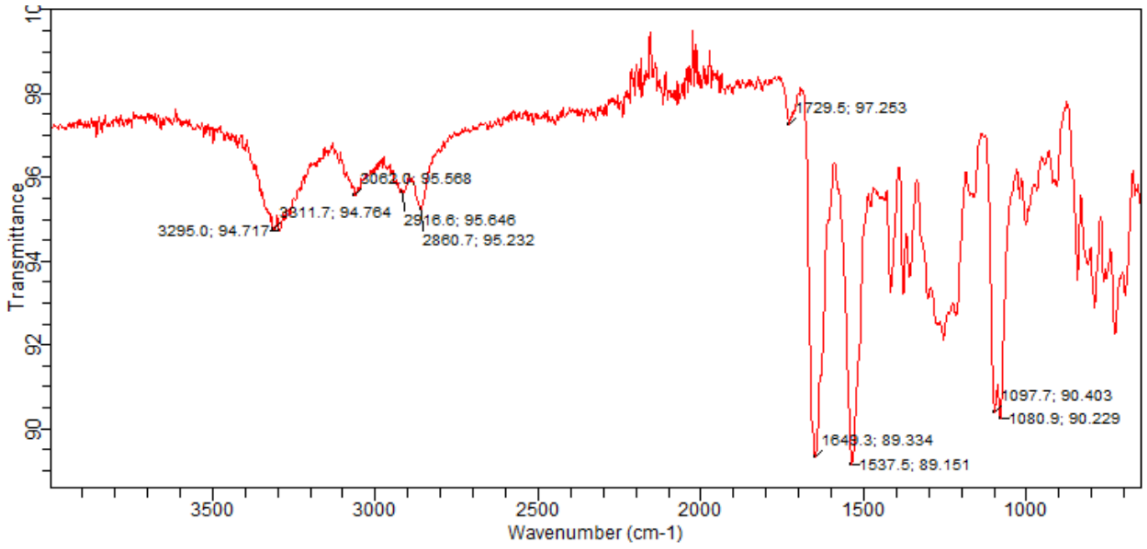
^{1}H NMR (400 MHz, $CDCl_3$)



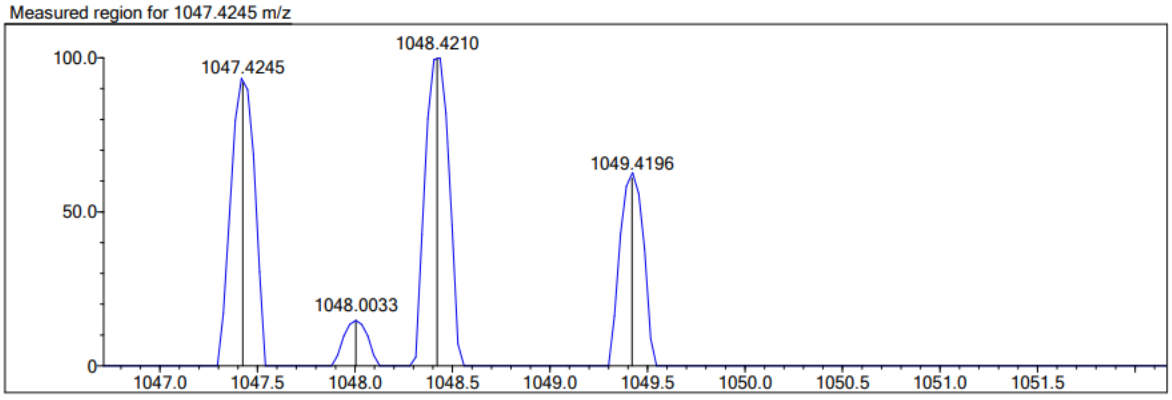
^{13}C NMR (400 MHz, $CDCl_3$)



IR (neat)

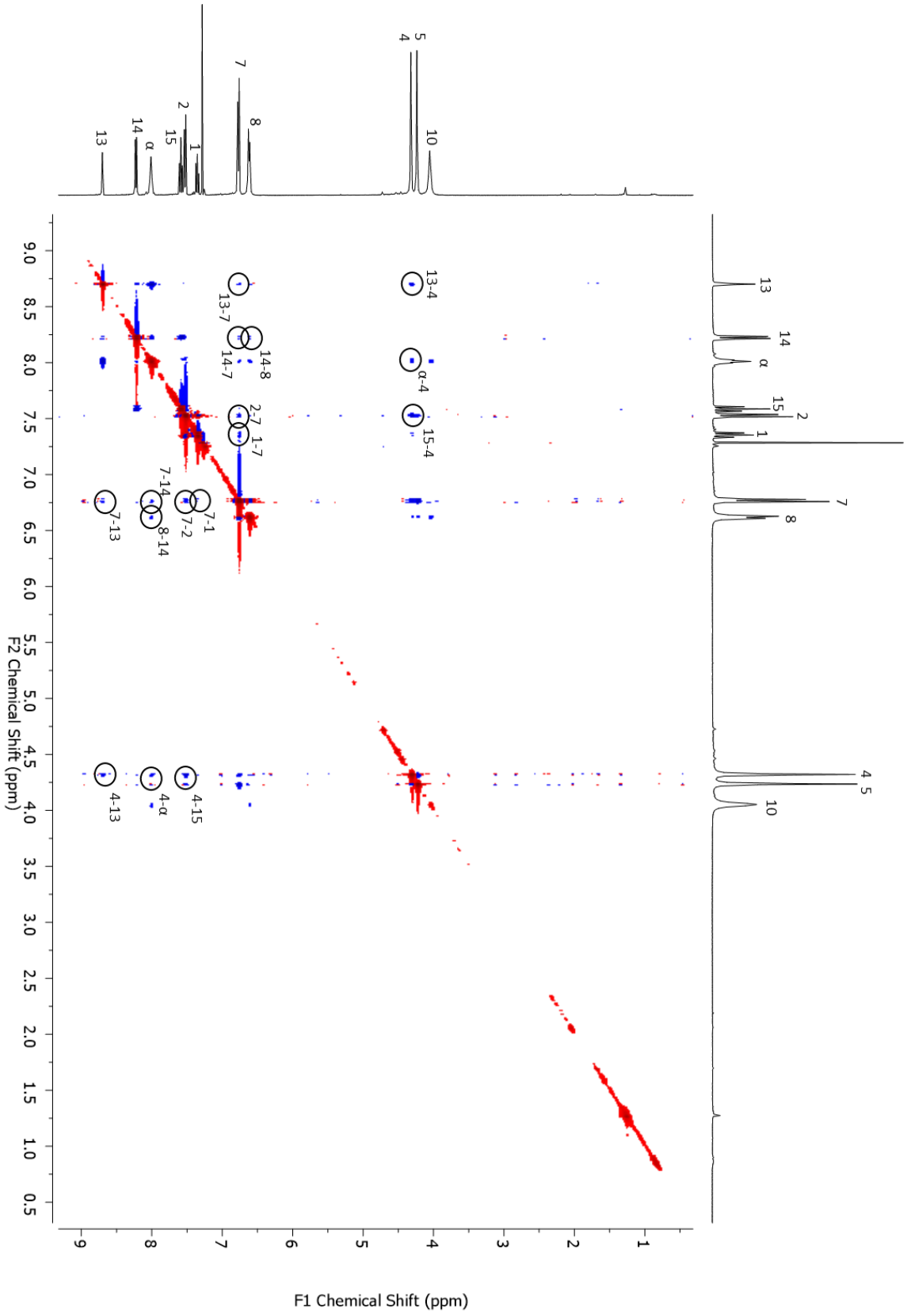


MS (ES +ve)



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	0.00	C62 H58 N6 O10	[M+H]+	1047.4245	1047.4287	-4.2	-4.01	0.00	37.0

^{1}H-^{1}H ROESY NMR of [2]catenane 4 (400 MHz, $CDCl_3$, 298 K).



Inter-component through-space cross-peaks are circled.

Part 2: ^{1}H NMR Binding Studies

General Procedures

(a) Trifluoroacetic Acid Titration Procedure

A 0.25 M solution of TFA was added to 500 µL of a 2.50 mM $CDCl_3$ solution of PNO [2]catenane **4** at 298 K. The volumes added were 5, 5, 15, 25, 50, 50, 50 & 50 µL (i.e. in total 50 equivalents of TFA). A ^{1}H NMR spectrum was acquired after each addition. Then 50 equivalents of base (d_5-pyridine, dissolved in 125 µL of $CDCl_3$) was added and a final ^{1}H NMR spectrum acquired.

On BindFit,[1] attempts were made at fitting to both 1:1[2] and 1:2[3] binding models using the chemical shift values (and thus $\Delta\delta_H$) for protons *1* and *13* of PNO [2]catenane **4**. However, the data did not reasonably fit either model (see below).

(b) Alkali Metal Titration Procedure

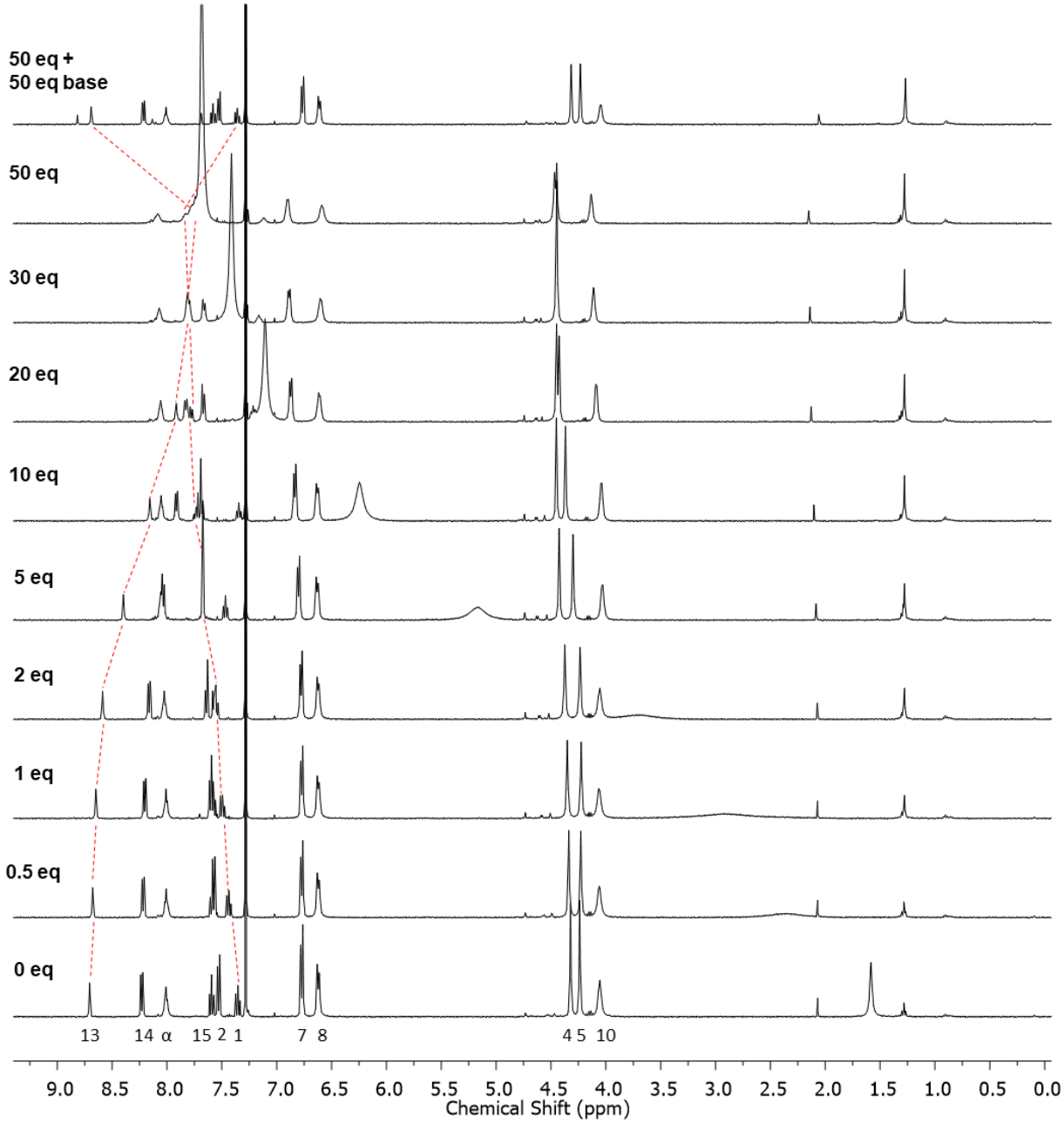
A 0.15 M solution of alkali metal salt ($LiClO_4$ or NaBArF) was added to 500 µL of a 2.50 mM solution of PNO [2]catenane **4** in 4:1 $CDCl_3/CD_3CN$ at 298 K. A ^{1}H NMR spectrum was acquired after each addition. The volumes added were 2, 2, 2, 2, 2, 5, 10, 20, 50, 100, 100, 100 and 100 µL (i.e. in total 50 equivalents of M^+).

In both cases, the data was fitted globally on BindFit[1] using the chemical shift values (and thus $\Delta\delta_H$) for protons *2*, *4*, *7*, *13* and *14* of PNO [2]catenane **4.** The models fitted to were:

- 1:2 binding model for $LiClO_4$.[4]
- 1:1 binding model for NaBArF.[5]

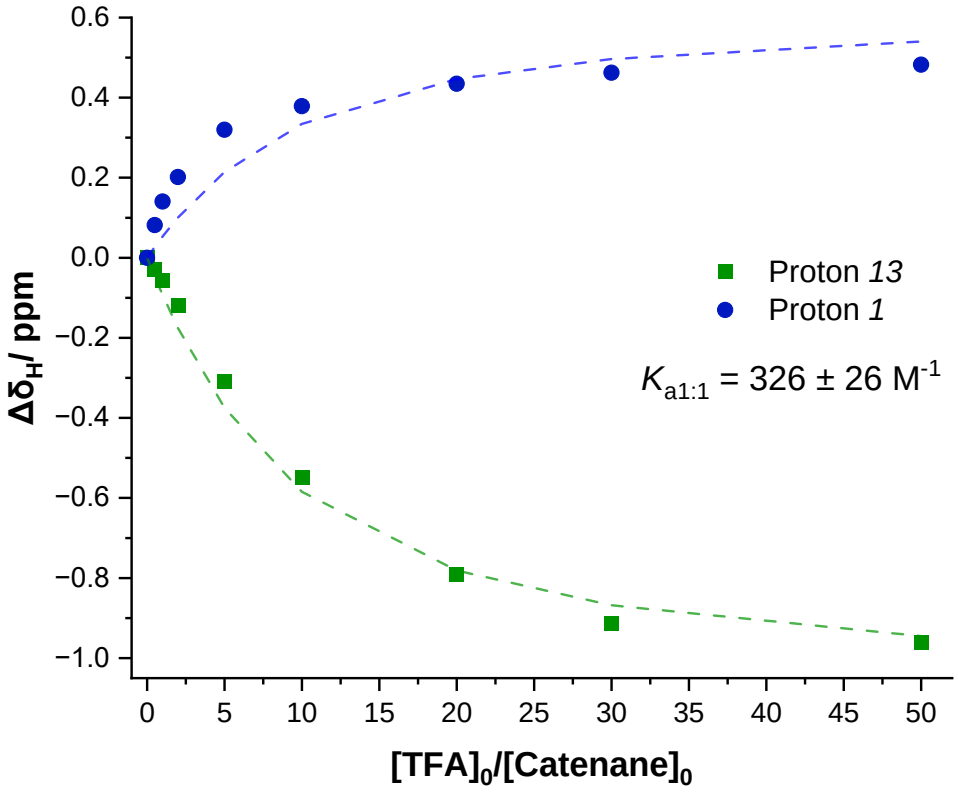
Ion Binding ^{1}H NMR Titration Experimental Data

PNO [2]catenane **4** + TFA

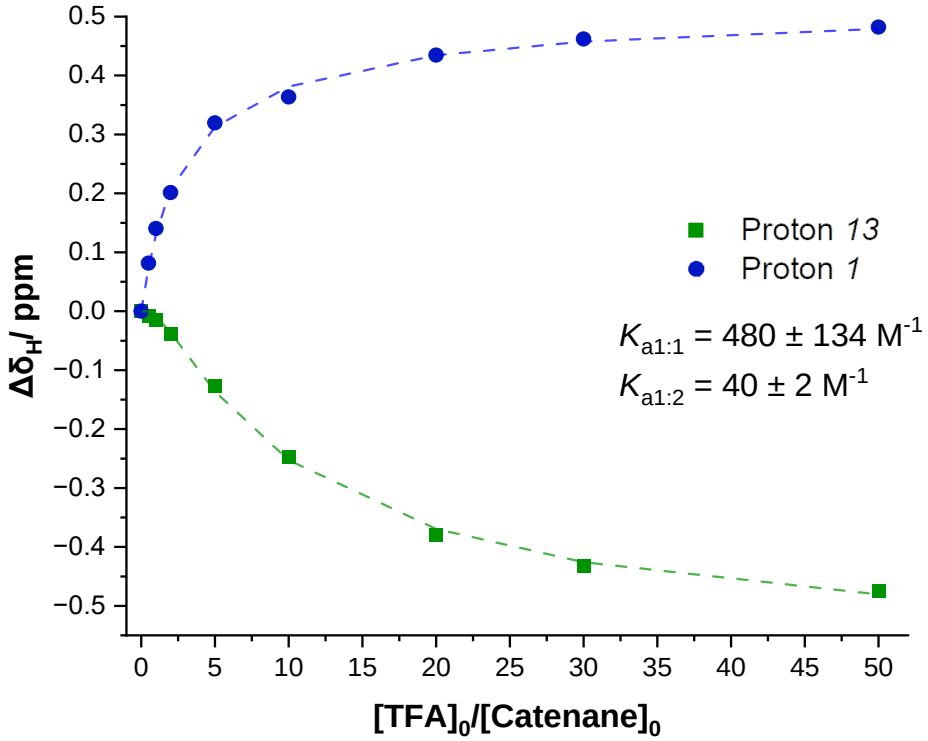


Stacked NMR spectra (400 MHz, $CDCl_3$, 298 K) of PNO [2]catenane **4** upon addition of increasing equivalents of TFA followed by a single addition of 50 equivalents of d_5-pyridine.

NB: Extra aromatic peaks in top spectrum attributed to trace quantities of protic pyridine.

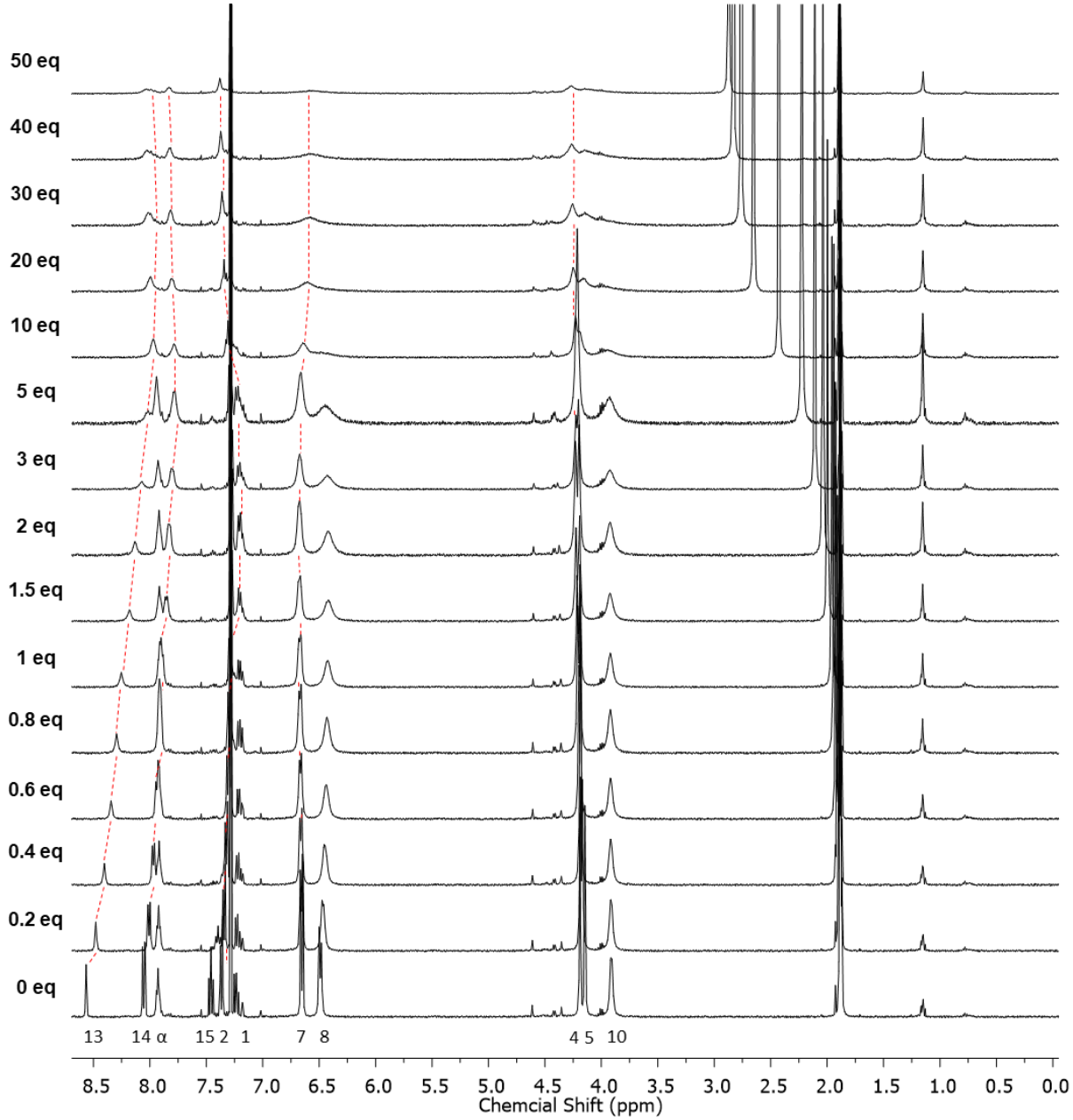


Globally fitted data (by Bindfit) for a 1:1 binding isotherm using change in peak positions against a ratio of initial TFA and catenane concentration.

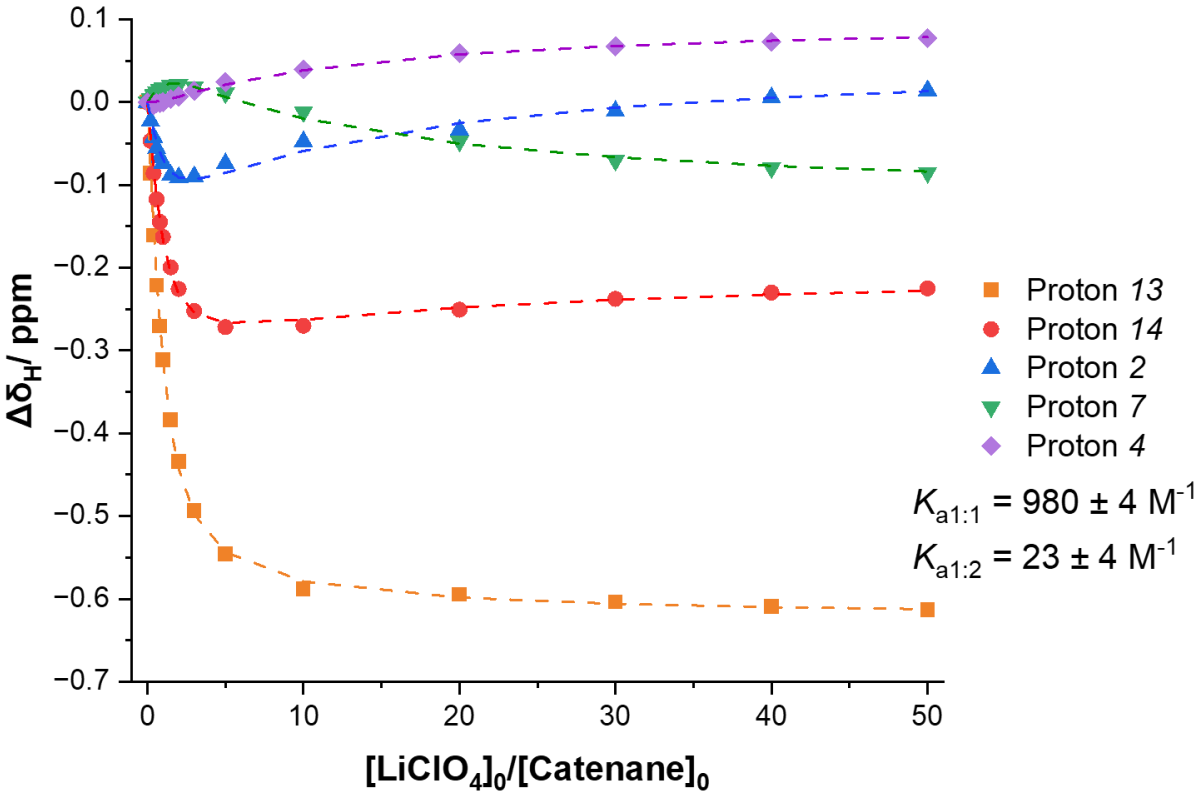


Globally fitted data (by Bindfit) for a 1:2 binding isotherm using change in peak positions against a ratio of initial TFA and catenane concentration.

PNO [2]catenane **4** + $LiClO_4$

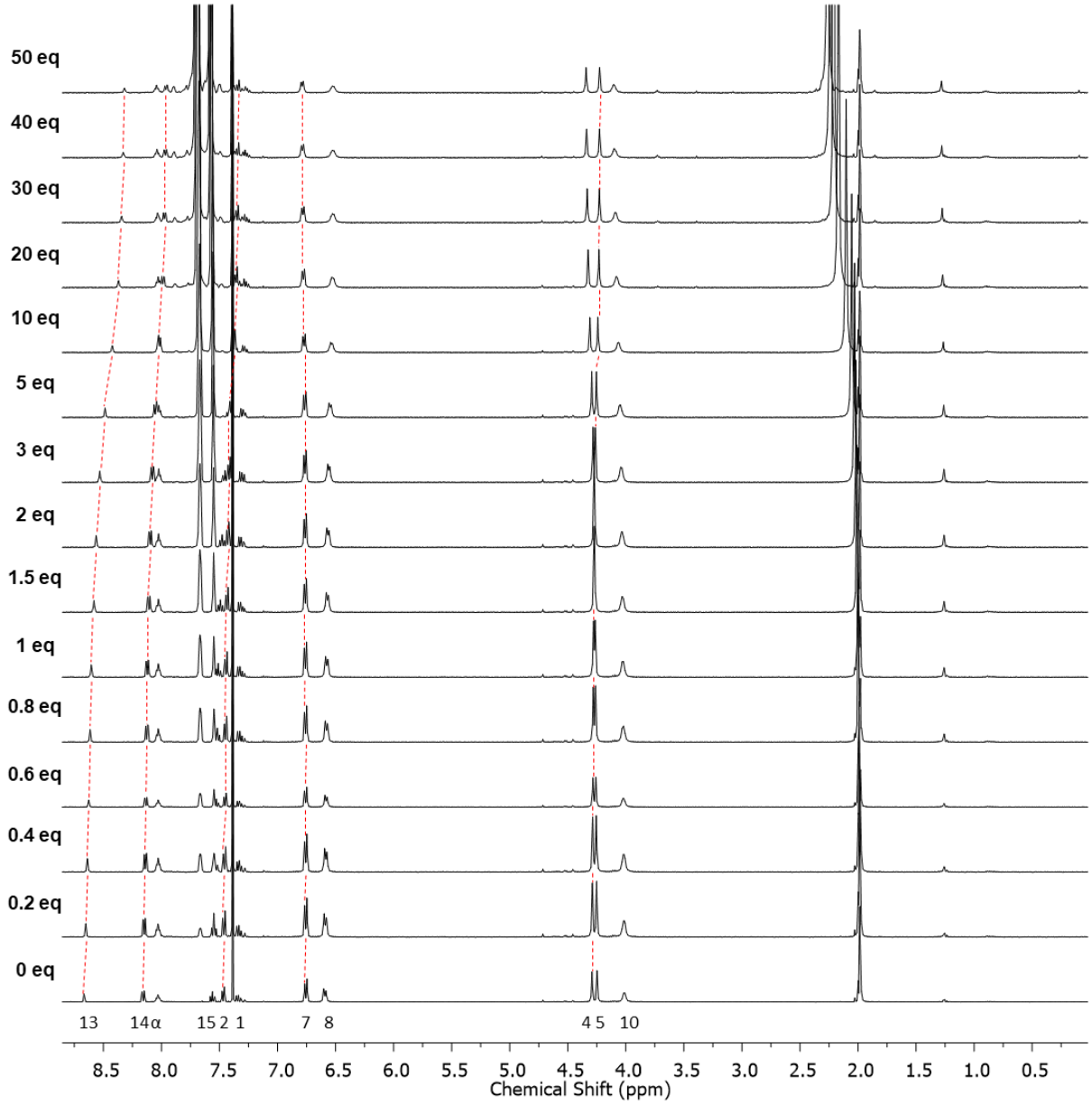


Stacked NMR spectra (400 MHz, 4:1 $CDCl_3$:CD_3CN, 298 K) of PNO [2]catenane **4** upon addition of increasing equivalents of $LiClO_4$.

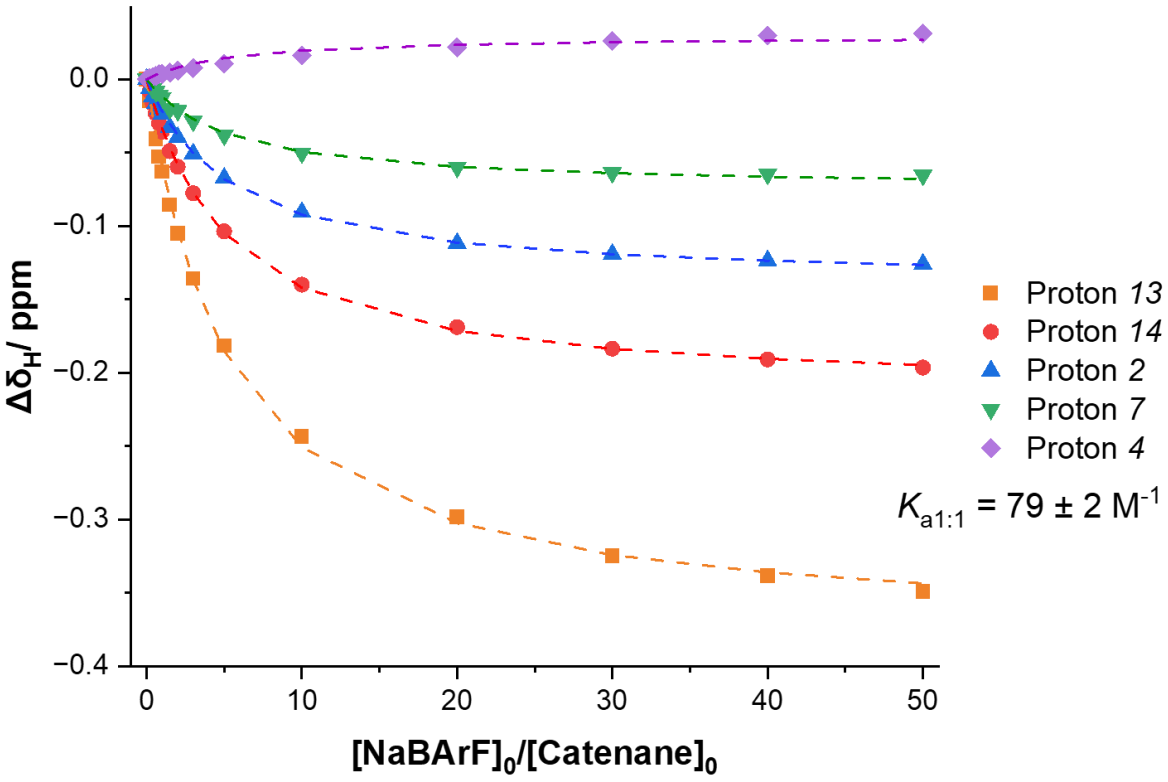


Globally fitted data (by Bindfit) for a 1:2 binding isotherm using change in peak positions against a ratio of initial $LiClO_4$ and catenane concentration.

PNO [2]catenane **4** + NaBArF



Stacked NMR spectra (400 MHz, 4:1 $CDCl_3$:CD_3CN, 298 K) of PNO [2]catenane **4** upon addition of increasing equivalents of NaBArF.

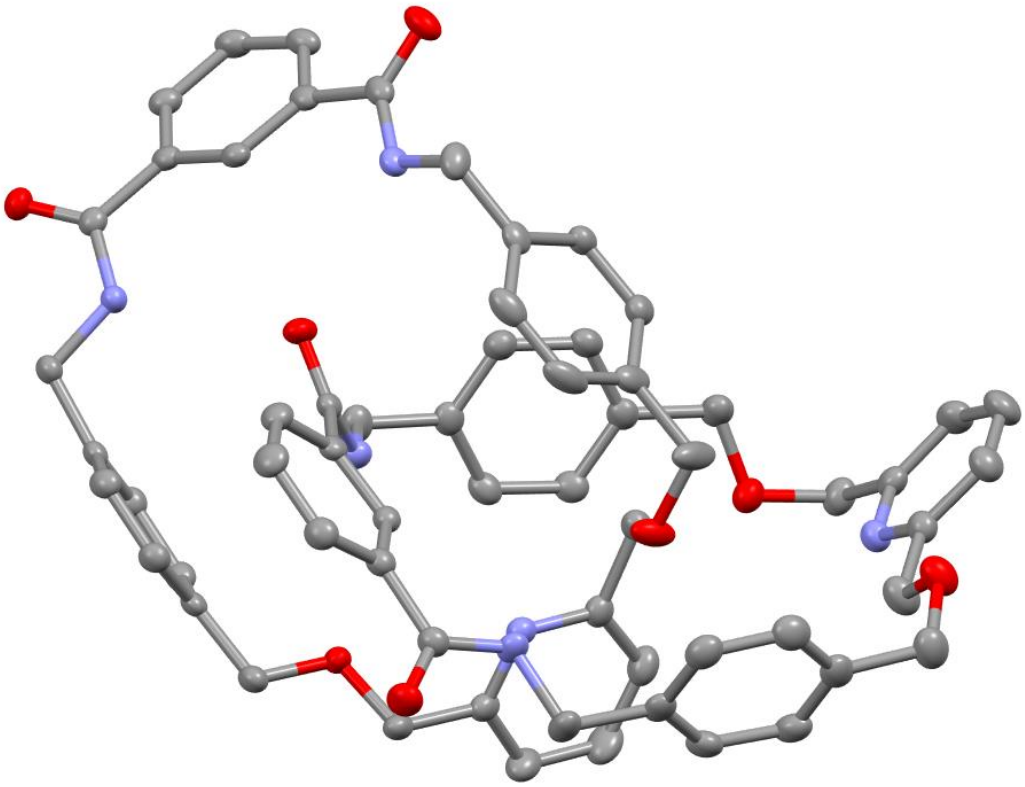


Globally fitted data (by Bindfit) for a 1:1 binding isotherm using change in peak positions against a ratio of initial NaBArF and catenane concentration.

Part 3: Crystallographic Data

Pyridyl [2]catenane **2**

Single crystals of pyridyl [2]catenane **2** were grown by slow evaporation of a chloroform solution. A suitable crystal was selected and studied using an Agilent SuperNova AtlasS2 diffractometer. Using Olex2[6] the structure was solved with the ShelXS[7] structure solution program using Direct Methods and refined with the ShelXL[8] refinement package using Least Squares minimisation.



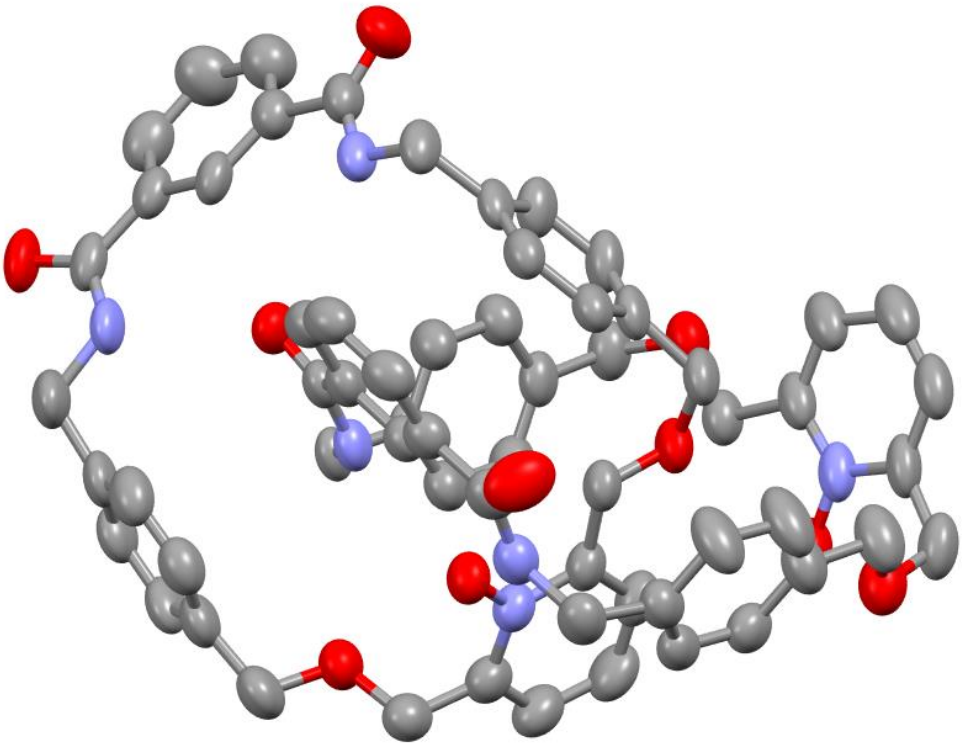
X-ray crystal structure of [2]catenane **2**. Thermal ellipsoids are displayed at 50% probability.

Crystal data and structural refinement for pyridyl [2]catenane **2**:

CCDC Number	23052568
Empirical formula	$C_{31}H_{29}N_3O_4$
Formula weight	507.57
Temperature/K	99.93(16)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	21.5269(2)
b/Å	11.10560(10)
c/Å	21.8729(2)
α/°	90
β/°	99.4400(10)
γ/°	90
Volume/Å^3	5158.32(8)
Z	8
ρ_{calc}g/cm^3	1.307
μ/mm^{-1}	0.704
F(000)	2144.0
Crystal size/mm^3	0.09 × 0.07 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.196 to 148.694
Index ranges	-26 ≤ h ≤ 25, -12 ≤ k ≤ 13, -19 ≤ l ≤ 27
Reflections collected	32736
Independent reflections	10318 [R_{int} = 0.0224, R_{sigma} = 0.0230]
Data/restraints/parameters	10318/0/701
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0372, wR_2 = 0.0907
Final R indexes [all data]	R_1 = 0.0439, wR_2 = 0.0948
Largest diff. peak/hole / e Å^{-3}	0.54/-0.21

PNO [2]catenane **4**

Single crystals of PNO [2]catenane **4** were grown by slow evaporation of a chloroform solution. A suitable crystal was selected and studied using an Agilent SuperNova AtlasS2 diffractometer. Using Olex2[6] the structure was solved with the ShelXT[7] structure solution program using Direct Methods and refined with the olex2.refine[9] refinement package using Gauss-Newton minimisation.



X-ray crystal structure of [2]catenane **4**. Thermal ellipsoids are displayed at 50% probability.

Crystal data and structural refinement for PNO [2]catenane **4**:

CCDC Number	2305367
Empirical formula	$C_{31}H_{29}N_3O_6$
Formula weight	523.57
Temperature/K	139.9(4)
Crystal system	Triclinic
Space group	P-1
a/Å	14.6339(5)
b/Å	15.1689(5)
c/Å	16.0492(3)
α/°	102.718(2)
β/°	111.425(3)
γ/°	105.578(3)
Volume/Å^3	2986.62(17)
Z	4
ρ_{calc}g/cm^3	1.164
μ/mm^{-1}	0.649
F(000)	1104.0
Crystal size/mm^3	0.08 × 0.06 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.02 to 154.532
Index ranges	-18 ≤ h ≤ 17, -17 ≤ k ≤ 18, -20 ≤ l ≤ 19
Reflections collected	48309
Independent reflections	12420 [R_{int} = 0.0811, R_{sigma} = 0.0660]
Data/restraints/parameters	12420/0/712
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0664, wR_2 = 0.1880
Final R indexes [all data]	R_1 = 0.0876, wR_2 = 0.2122
Largest diff. peak/hole / e Å^{-3}	0.31/-0.22

Part 4: References

1 (a) "Supramolecular.org – Binding Constant Calculators" can be found under http://supramolecular.org (accessed 15th July 2023); (b) D. B. Hibbert and P. Thordarson, *Chem. Commun.*, 2016, **52**, 12792-12805; (c) P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305-1323.

2 Attempt to fit titration data for **4** with TFA for a 1:1 binding isotherm can be found under http://app.supramolecular.org/bindfit/view/57e295c3-57ca-410e-8d49-72bcf343dada (accessed 22nd June 2023).

3 Attempt to fit titration data for **4** with TFA for a 2:1 binding isotherm can be found under http://app.supramolecular.org/bindfit/view/034b92d0-c048-4fa1-87e1-1601c5fe91c1 (accessed 15th July 2023).

4 Fitted titration data for **4** with $LiClO_4$ can be found under http://app.supramolecular.org/bindfit/view/29ae08eb-c98c-4e4a-8538-d83822d473a7 (accessed 22nd June 2023).

5 Fitted titration data for **4** with NaBArF can be found under http://app.supramolecular.org/bindfit/view/e26fdd6b-e548-42a4-80fa-da019c6239f5 (accessed 22nd June 2023).

6 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

7 G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3-8.

8 G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3-8.

9 L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst. A*, 2015, **71**, 59-75.