Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Comparing the anion binding of 4-amido- with 4-amino-1,8-naphthalimides

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Contents

S1 Spectra

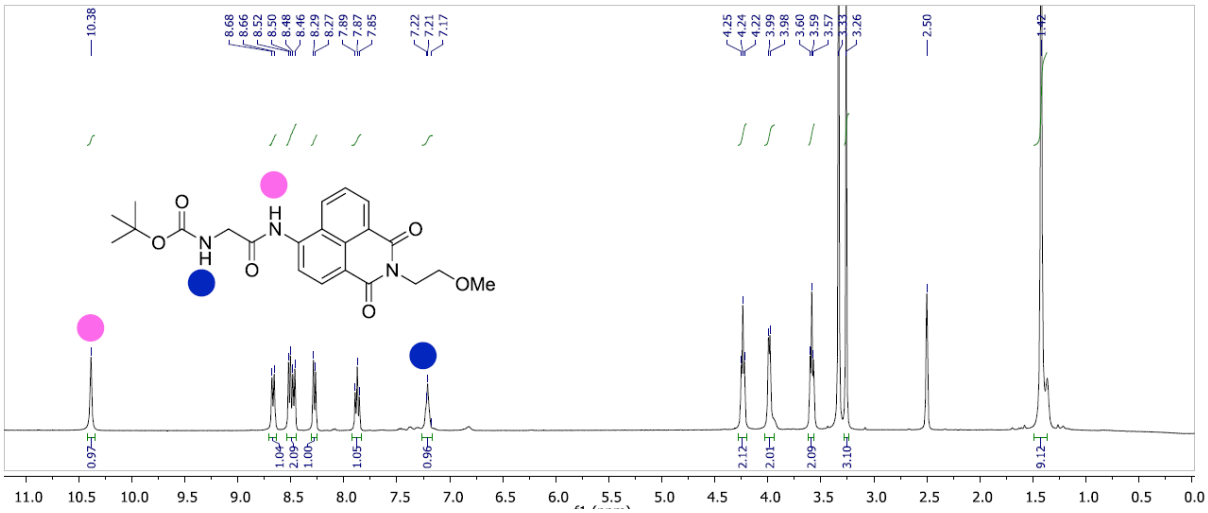


Figure S1.1: ^{1}H NMR spectrum of 4-amidonaphthalimide **5** in DMSO-d_6

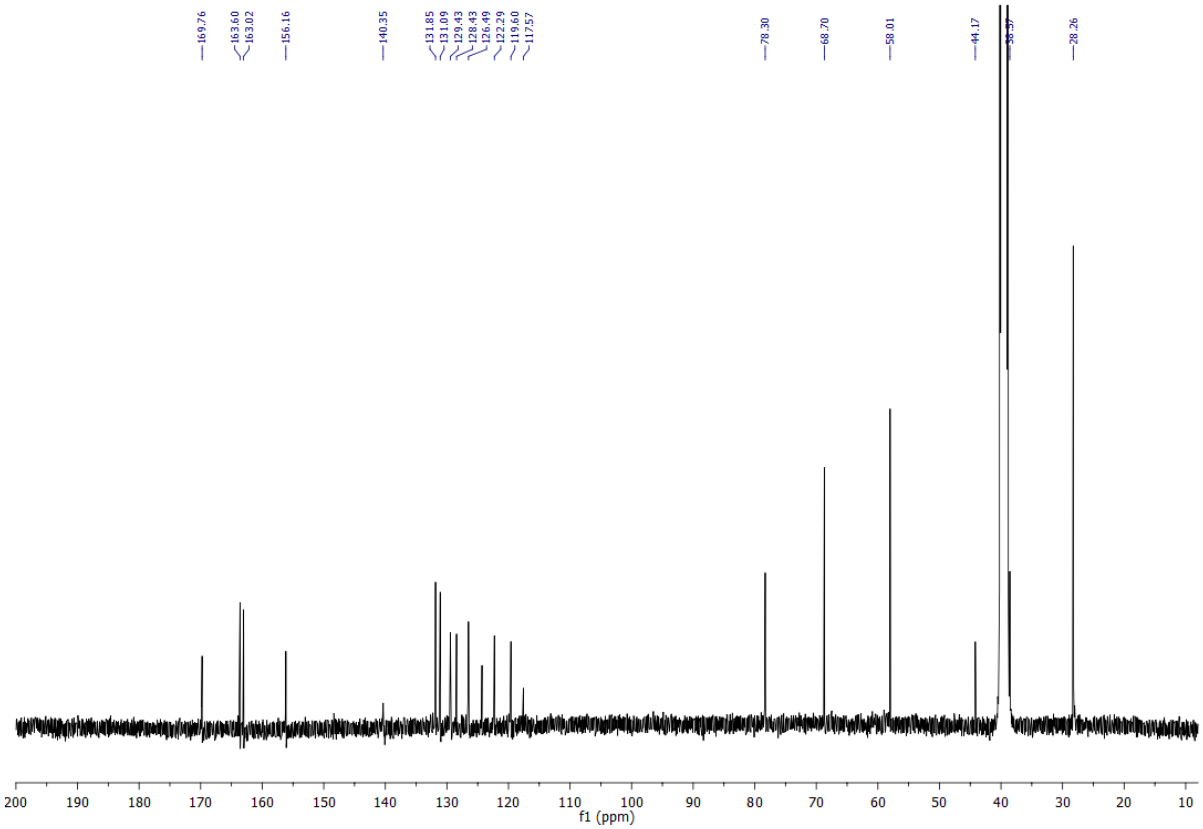


_Figure S1.2: ^{13}C NMR spectrum of 4-amidonaphthalimide **5** in DMSO-d_6

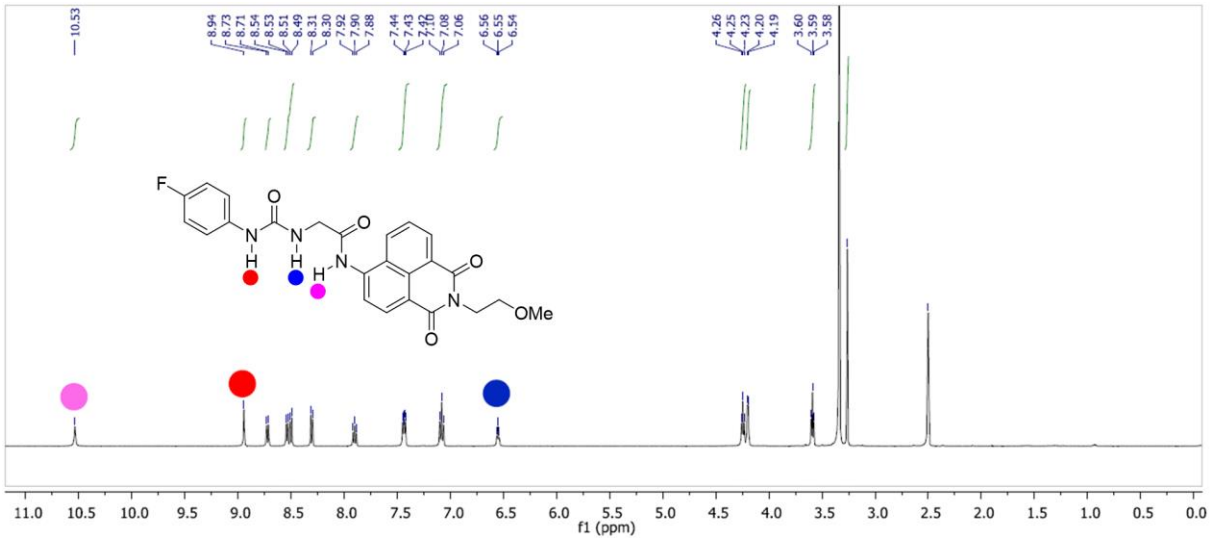


Figure S1.3: ^{1}H NMR spectrum of Host **3** in DMSO-d_6

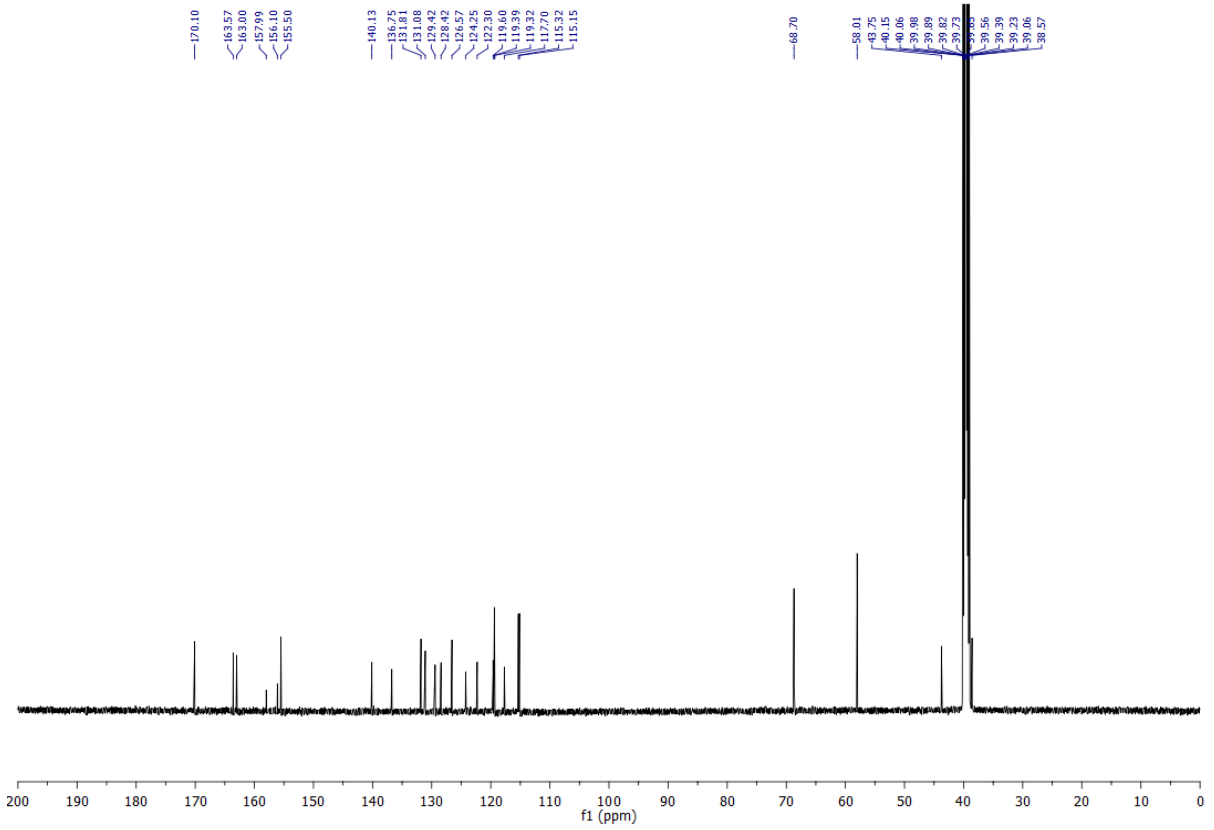


Figure S1.4: ^{13}C NMR spectrum of Host **3** in DMSO-d_6

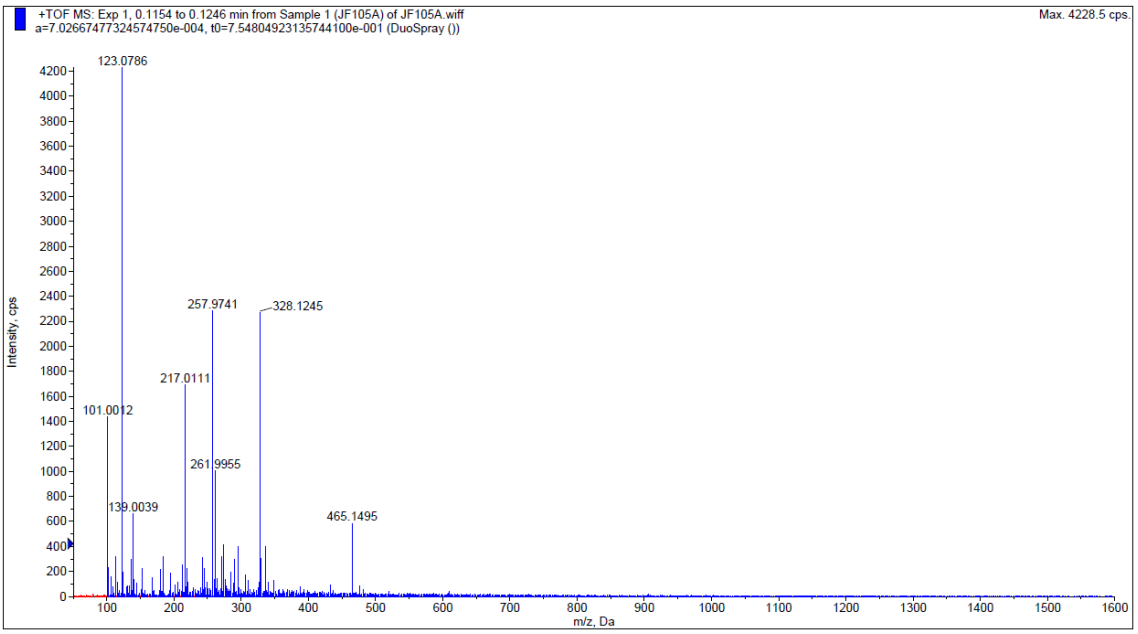


Figure S1.5: HRMS spectrum of Host **3**

S2 Anion titration studies

All titrations were performed in DMSO-d_6. The chemical shift data was plotted as a titration isotherm and the data fitted using bindfit{Brynn Hibbert, 2016 #158;Thordarson, 2011 #284} fitting program to determine binding constants. A number of fitting protocols were trialled using the Bindfit software but reliable fitting was only seen when the 1:1 model was used.

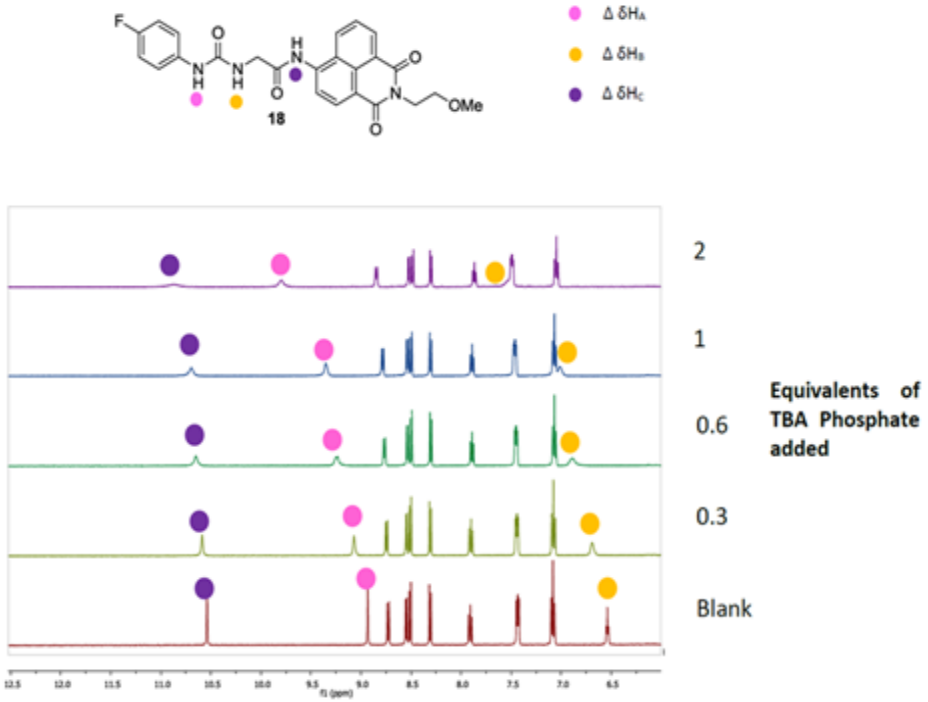


Figure S2.1: ^{1}H NMR titration stack plot for **3** against $TBAH_2PO_4$

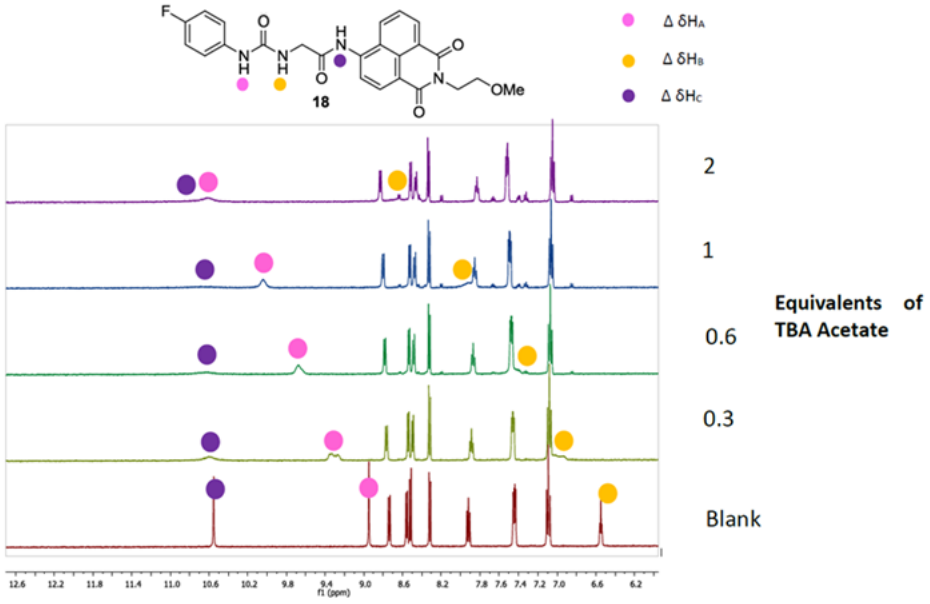


Figure S2.2: ^{1}H NMR titration stack plot for **3** against TBAOAc

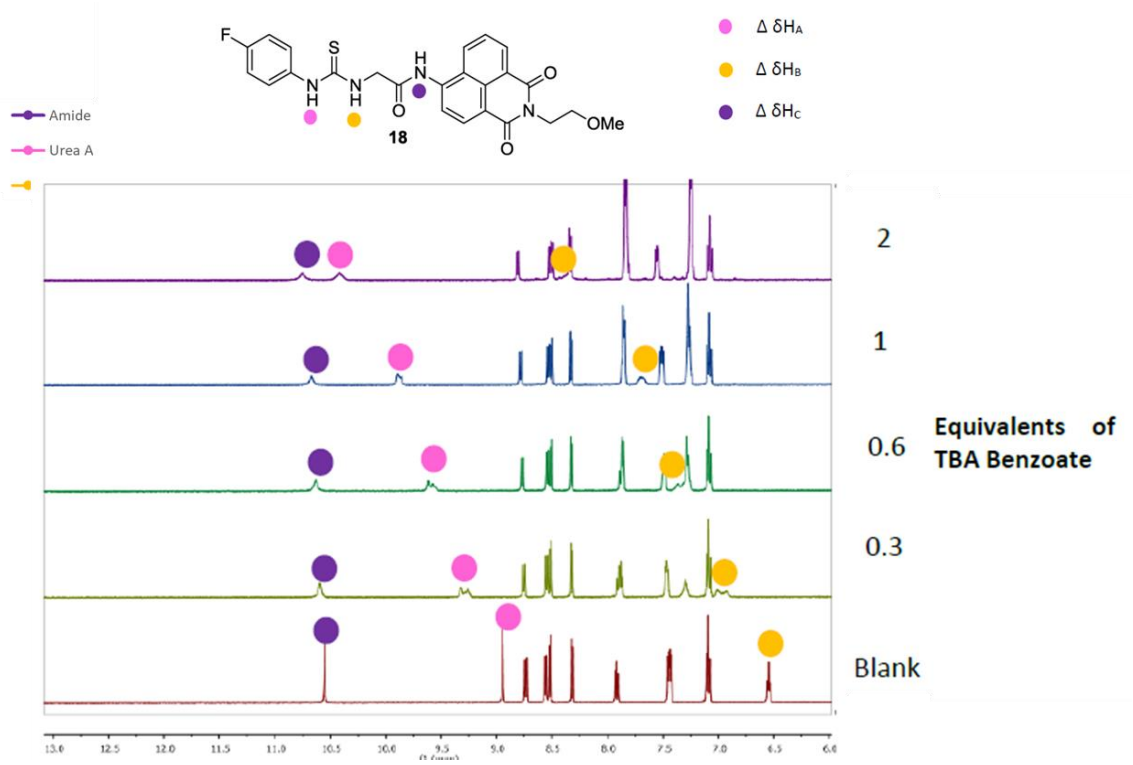


Figure S2.3: ^{1}H NMR titration stack plot for **3** against TBAOBz

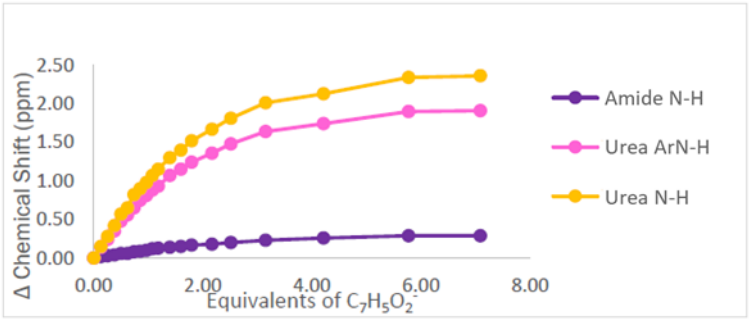


Figure S2.4: Binding isotherm for **3** against TBAOBz

The binding constant for benzoate is provided as an estimate only—log K ~ 2.7—as it is clear from the stack plot that the individual resonances assigned to both urea protons do not remain as singlets during the titration. This artefact likely indicates more than one H:G species in solution.

S3 Molecular modelling

*S3.1 Host **1**: Analysis of conformers*

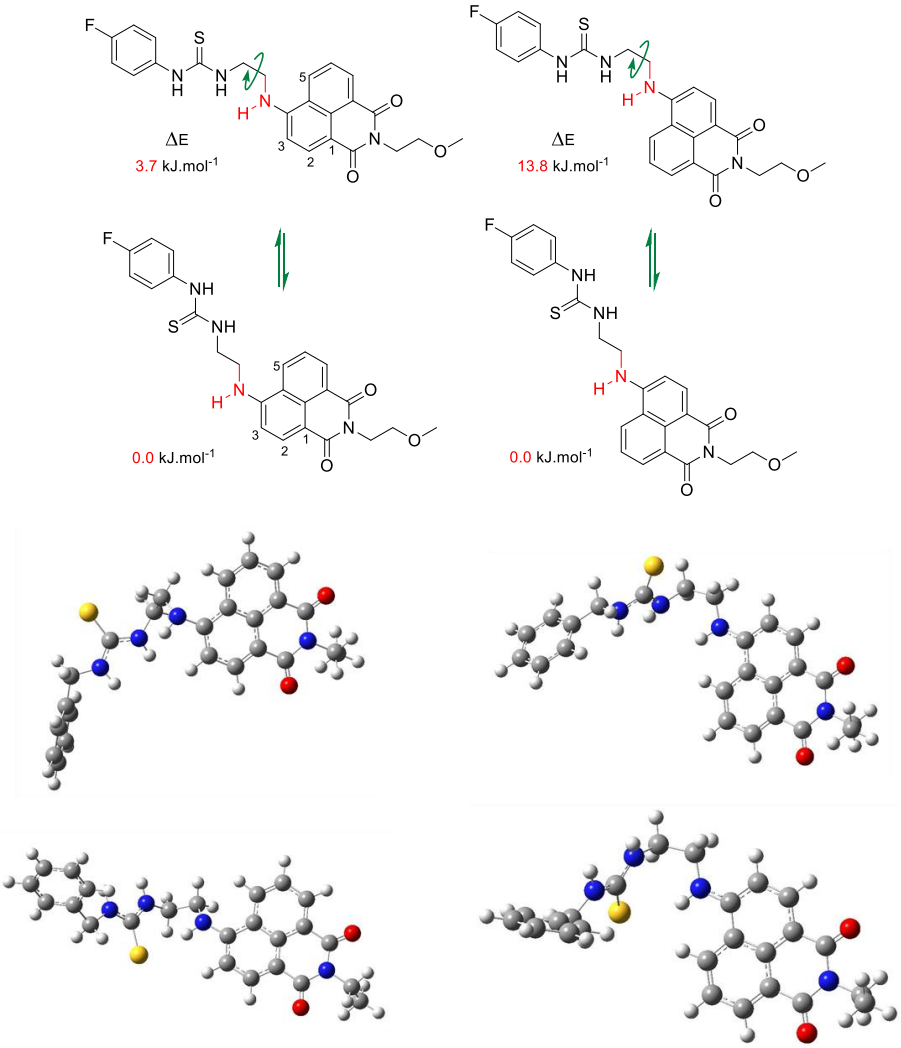
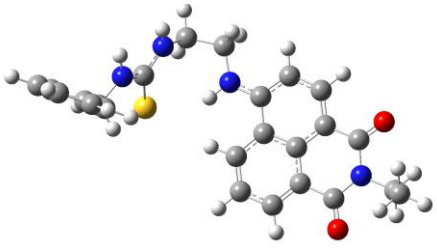


Figure S3.1: Structures and relative energies for previously synthesised host **1**

*S3.2 Coordinates of minimised structures for host **1**.*

Optimized coordinates (B3LYP/6-311++G(d,p). Total energy -1697.107944 a.u



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C	7.87199400	-2.20709200	-0.76672400
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H	8.95553100	-2.17083900	-0.76550700
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H	0.11397200	4.19677400	-0.83422600
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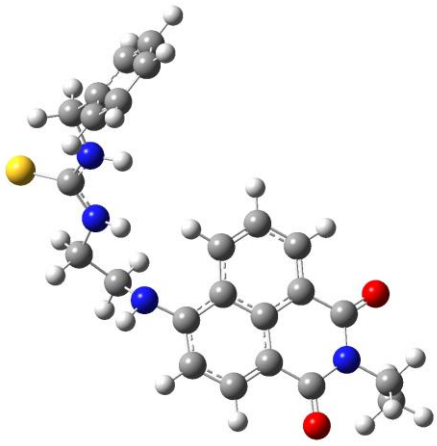
H	2.14173900	3.85329900	0.60683500

H	2.49082600	4.40728800	-1.03271500
H	0.04649100	0.50252100	1.89394400

Optimized coordinates (B3LYP/6-311++G(d,p). Total energy -1697.098002 a.u



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C	-2.27309700	1.96925000	1.79901600
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H	-4.26571600	1.81088000	2.62684900
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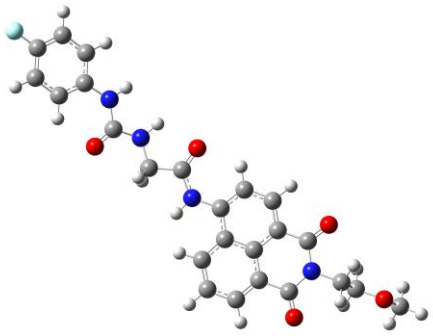
H	-8.13574600	0.29522600	-0.34085200
H	-7.79345700	-0.79869100	-1.70214800
H	0.16302500	0.18549900	-1.00781300
S	4.83136000	2.96348800	-1.22274400

Host 1	E_{tot} (B3LYP/6-311++G(d,p), a.u)	ΔE (Kcal.mol^{-1})	ΔE (KJ.mol^{-1})
NH-C5	-1697.1079440	0.00	0.00
NH-C4	-1697.0980020	6.24	26.10

*S3.3 Coordinates of minimised structures for host **3**.*

Optimized coordinates (B3LYP/6-311++G(d,p). Total energy -1622.700926 a.u



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C	5.75657400	-1.18462000	0.42265500

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O	5.27016000	2.34993100	0.70759200
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O	6.67981700	-1.97883000	0.44575900
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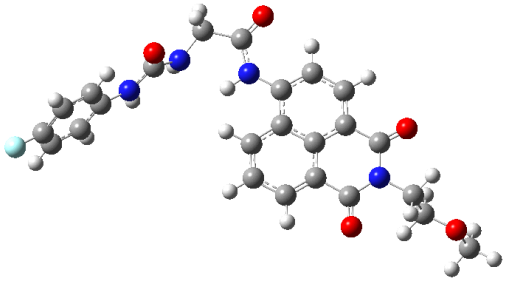
Optimized coordinates (B3LYP/6-311++G(d,p). Total energy -1622.700648 a.u



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C	0.92509300	-0.42345000	-0.17718200
C	1.57355300	-2.78111700	-0.07308000
C	2.30686800	-0.07849500	-0.29283200
C	2.91977700	-2.41292600	-0.20294100
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H	-1.08755600	0.41935400	-0.17444300
C	0.36619300	1.94562300	-0.32883400
H	-0.38222400	2.72840500	-0.36125600
C	1.72765500	2.27896600	-0.41703900
H	2.04892200	3.30924300	-0.50526000
C	4.11721900	1.66310000	-0.51556000
O	4.47710900	2.82532300	-0.58459100
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H	6.96162300	0.16187000	-1.22888100
H	6.65302200	2.01397700	1.19096300
H	7.10109900	0.28624100	1.25152900
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C	9.25865300	1.77483300	1.54602500
H	8.84743500	2.60988000	2.13038300
H	9.29498500	0.88128800	2.18478100
H	10.27088900	2.02697100	1.22907100
N	-3.43492500	-2.10350700	0.86870200
H	-3.50909000	-2.09057900	1.87625200
C	-4.39495100	-1.37481200	0.15353800

N	-5.01897400	-0.40931300	0.91447700
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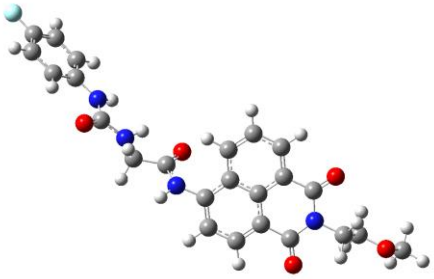
H	-7.73552500	3.12067100	1.89992700
F	-8.83479600	3.37629100	-0.44014400

Optimized coordinate of **3...** (B3LYP/6-311++G(d,p).
Total energy -1622.697684 a.u



C	0.96978800	0.55910000	1.61318400
C	1.67219800	-0.43076700	0.88102000
C	1.62049200	1.66938300	2.10177200
C	3.07741700	-0.26149800	0.68496400
C	2.99881400	1.84810700	1.88128400
H	1.06761800	2.41571700	2.65964900
C	3.72038100	0.89679200	1.18848400
H	3.51585000	2.72311400	2.25521000
C	3.83038700	-1.25224600	0.01045900
C	5.17743100	1.09982400	0.98593000
C	1.06239100	-1.60575000	0.35057700
C	1.82513800	-2.56218000	-0.29137900
H	1.34289400	-3.44821200	-0.68892000
C	3.20814900	-2.39115700	-0.45866800
H	3.80085000	-3.13955300	-0.96954800
C	5.29063600	-1.08635200	-0.19833800
O	5.96301300	-1.91407400	-0.78678200
N	5.87588500	0.07915700	0.31887200
O	5.75885500	2.09520400	1.37741500
C	7.33042400	0.24532000	0.15030600
C	7.67092200	0.96760500	-1.15054000
H	7.78021600	-0.74503000	0.14769400
H	7.69964000	0.82099700	0.99607700
H	7.28909400	0.39818100	-2.00986500

H	7.21161900	1.96623400	-1.15932900
O	9.08103300	1.06901300	-1.20934800
C	9.54187400	1.72561400	-2.37471000
H	9.23990400	1.18728300	-3.28388100
H	9.16201400	2.75518800	-2.43127300
H	10.63043300	1.75026000	-2.32060800
H	-0.09037500	0.44009300	1.78589700
N	-0.33339800	-1.84774900	0.51366200
H	-0.58704600	-2.78026500	0.80975500
C	-1.33839900	-1.08388500	-0.03044200
O	-1.15247400	-0.02394200	-0.59820700
C	-2.73612800	-1.67311400	0.15799000
H	-2.75286000	-2.70350100	-0.21843100
H	-2.97552600	-1.72561500	1.22619300
N	-3.69157900	-0.84479400	-0.53877100
H	-3.27622700	-0.02988800	-0.97556100
C	-5.00191600	-0.81554500	-0.10198100
O	-5.42009400	-1.57993400	0.75426200
N	-5.76934700	0.13696900	-0.74818100
H	-5.32320500	0.64031400	-1.49986900
C	-7.13807000	0.42896900	-0.56827900
C	-7.69852000	1.40997600	-1.39894300
C	-7.94659700	-0.19778000	0.38922900
C	-9.03782700	1.76501700	-1.28507500
H	-7.08241100	1.90414300	-2.14369600
C	-9.28909700	0.15809000	0.50390200
H	-7.52497700	-0.95682900	1.02934500
C	-9.81422300	1.12950600	-0.33005300
H	-9.47472200	2.52158600	-1.92452800
H	-9.92511900	-0.31936400	1.23900000
F	-11.12391500	1.47019500	-0.21169500

Host 3	E_{tot} (B3LYP/6-311++G(d,p), a.u)	ΔE (Kcal.mol^{-1})	ΔE (KJ.mol^{-1})
NH-C5(Z)	-1622.7006480	0.17	0.73
NH-C5(E)	-1622.7009260	0.00	0.00
NH-C4(E)	-1622.6976840	2.03	8.51

*S3.4 Evaluation of intramolecular H-bonding for **3**.*

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j) -E(i) a.u.	F(i,j) a.u.
within unit 1				
110. LP (1) O 26	/840. BD*(2) C 11 - C 12	0.95	0.51	0.021
110. LP (1) O 26	/842. BD*(1) C 12 - H 13	0.65	1.18	0.025

111. LP (2) O 26	**/860. BD*(1) N 30 - H 31**	**0.74**	**0.66**	**0.020**
111. LP (2) O 26	/861. BD*(1) N 30 - C 32	0.75	0.69	0.021
111. LP (2) O 26	/862. BD*(1) C 32 - O 33	1.11	0.77	0.027
111. LP (2) O 26	/868. BD*(2) C 36 - C 38	0.96	0.29	0.016
111. LP (2) O 26	/869. BD*(1) C 37 - C 39	2.79	0.64	0.039