Electronic Supplementary Material (ESI) for RSC Advances.

Aromatic *N*-oxides template open inclusion and dimeric capsular assemblies with methylresorcinarene

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Supporting Information

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I General Information

C_2-2-methylresorcinarene **1** was synthesized according to reported procedures.[1] The pyridine N-oxide **2** and quinoline N-oxide **3** were commercially available.

II Solid state analyses

(a) X-ray experimental

Single crystal X-ray data for **1**+**2** were collected at 170 K using Agilent SuperNova single-source diffractometer with an Atlas EoS CCD detector using mirror-monochromated Mo-*K*α (λ = 0.71073 Å) radiation and the data for **1**+**3** was measured at 170 K on Bruker-Nonius Kappa CCD diffractometer with an APEX-II detector and graphite monochromatized Mo-Kα (λ = 0.71073 Å) radiation. The data collection and reduction for **1**+**2** were performed using the program *CrysAlisPro*[2] and for **1**+**3** were performed using the program *COLLECT*[3] and *HKL DENZO AND SCALEPACK*[4], respectively. Gaussian face index absorption correction method[2] was used for **1**+**2**, and for **1**+**3**, the intensities were corrected for absorption using *SADABS*[5] with multi-scan absorption correction type method. All the structures were solved with direct methods (*SHELXS*[6]) and refined by full-matrix least squares on F^2 using the *OLEX2*[7], which utilizes the *SHELXL*-2013 module[6]. No attempt was made to locate the hydrogens for disordered solvent molecules, and for some hydrogen atoms involved in hydrogen bonds were introduced from difference Fourier maps. Constraints and restraints are used where appropriate for disordered models.

Table 1. Crystal data and X-Ray experimental details for $\mathbf{2}_3@\mathbf{1}_2(CH_3OH)_2$ and $\mathbf{3}_2@\mathbf{1}_2(CH_3OH)_6$.

Complex	$\mathbf{2}_3@\mathbf{1}_2(CH_3OH)_2$	$\mathbf{3}_2@\mathbf{1}_2(CH_3OH)_6$
Empirical formula	$C_{97}H_{122}N_3O_{23.70}$	$C_{52}H_{67}NO_{12}$
Formula weight	640.87	898.06
Temperature (K)	170.0	170.0
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
Unit cell dimensions: a (Å)	12.490(9)	12.143(2)
b (Å)	12.536(10)	12.791(3)
c (Å)	16.586(13)	18.158(4)
α (°)	72.84(7)	95.58(3)
β (°)	74.13(7)	106.88(3)
γ (°)	65.72(7)	113.40(3)
Volume / $Å^3$	2227.3(3)	2403.1(10)
Z	1	2
Density (calculated) mg/m^3	1.272	1.241
Absorption Coefficient mm^{-1}	0.091	0.087
F(000)	912	964
Crystal size (mm^3)	0.31 x 0.10 x 0.07	0.28 x 0.23 x 0.08
θ range for data collection (°)	3.00 to 25.0	2.00 to 25.3
Reflections collected [R(int)]	15198 [0.0430]	22981 [0.0708]
Independent reflections	7818	8696
Data completeness (%)	99.8	99.8
Data/ restraints/ parameters	7818/51/627	8696/1/641
Goodness-of-fit on F^2	1.067	1.021
Final R_1 indices [I>2sigma(I)]	$R_1 = 0.0628$, $wR_2 = 0.1564$	$R_1 = 0.0724$, $wR_2 = 0.1222$
Final R indices [all data]	$R_1 = 0.0902$, $wR_2 = 0.1775$	$R_1 = 0.1494$, $wR_2 = 0.1485$
Largest diff. peak/hole ($e.Å^{-3}$)	0.588/ -0.436	0.264/ -0.233

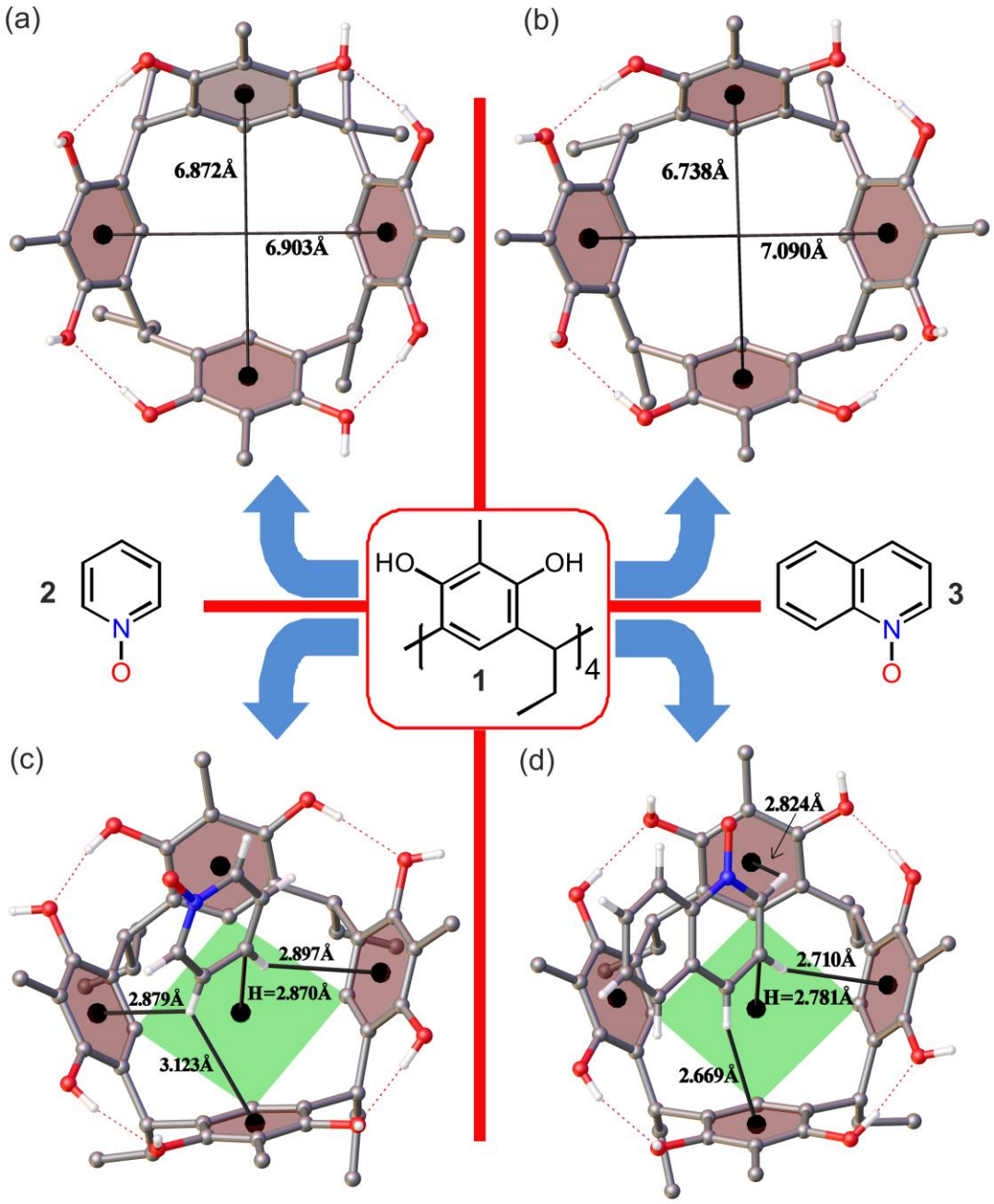


Fig. S1 Breathing behavior of C_2-2-methylresorcinarene **1** with (a) pyridine N-oxide **2,** and (b) quinoline N-oxide **3**. (c & d) Height (H) of the guest molecules calculated from centroid of bottom ring carbon atoms in host **1**; and the proximal C-H···π interactions with host aromatic rings are shown accordingly.

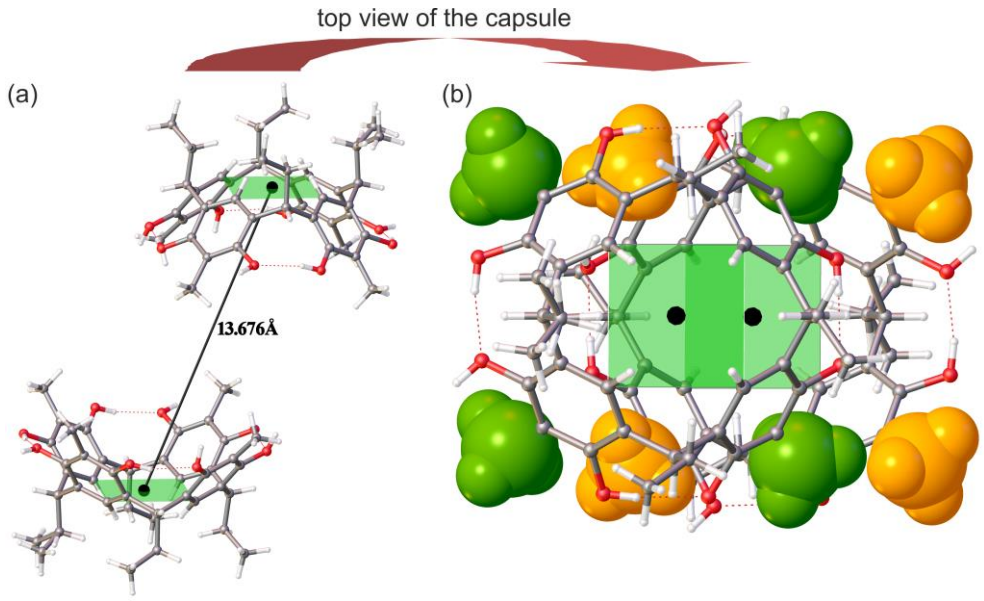


Fig. S2 (a) Side view to show the length of the capsule $\mathbf{2}_3@\mathbf{1}_2(CH_3OH)_2$. Distances are calculated from centroid-to-centroid of bottom ring carbons. (b) Top view of the capsule to show the near eclipsed conformation using colour coded methyl (green top and orange down) groups of host **1**. In both the figures, solvent and guest molecules are omitted for clarity.

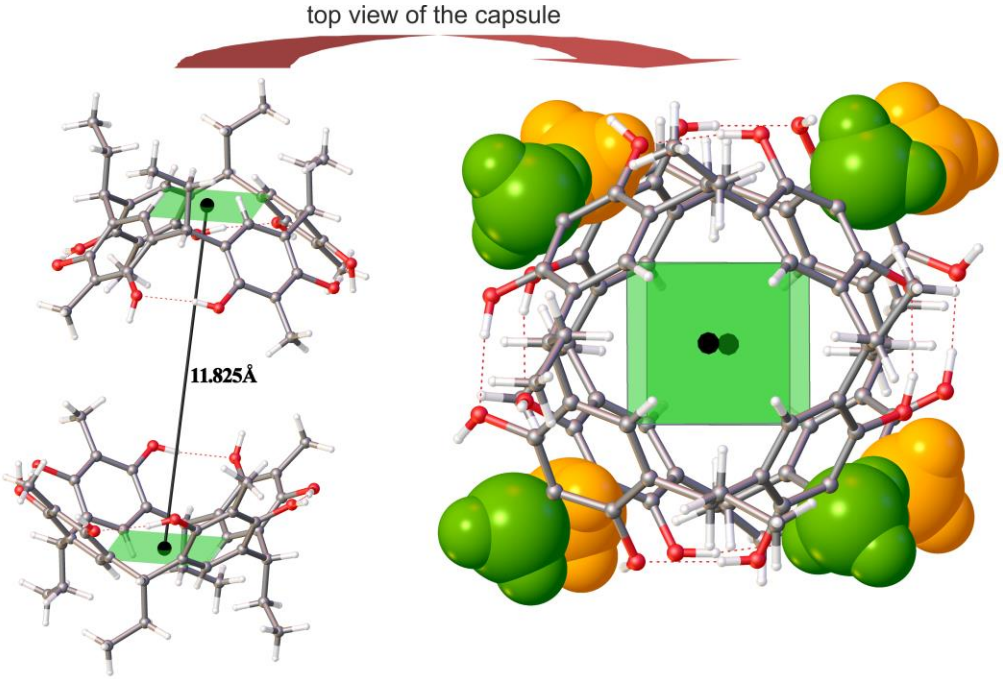


Fig. S3 (a) Side view to show the length of the capsule $\mathbf{3}_2@\mathbf{1}_2(CH_3OH)_6$. Distances are calculated from centroid-to-centroid of bottom ring carbons. (b) Top view of the capsule to show the near eclipsed conformation using colour coded methyl (green top and orange down) groups of host **1**. In both the figures, solvent and guest molecules are omitted for clarity.

III Solution studies

Job Plots

The y-axis is the chemical shift change of the guest multiply by the final concentration of the guest. Y= δ*[G] where δ=(δ_o-δ_f) chemical shift change of the guest and [G] final concentration of the guest. The x-axis, X is the mole fraction.[8]

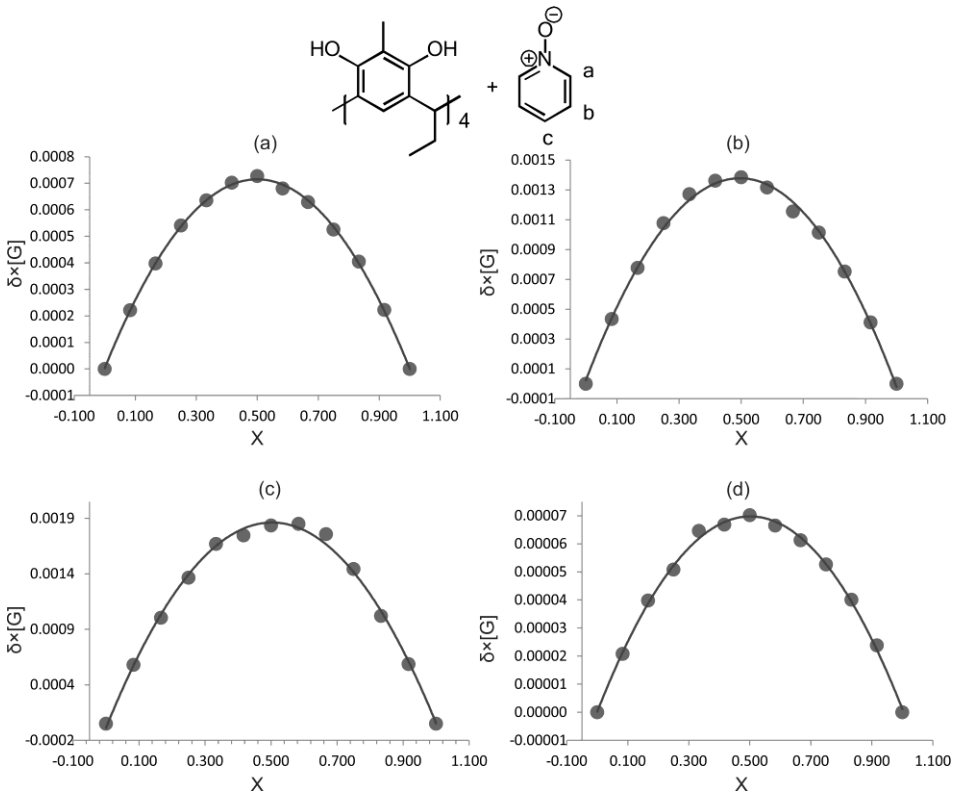


Fig. S4 Job plots (CD_3OD, 298 K) from the combination of resorcinarene **1** and pyridine N-oxide **2**. Following (a) guest a; (b) guest b; (c) guest c, (d) host CH_3 signals.

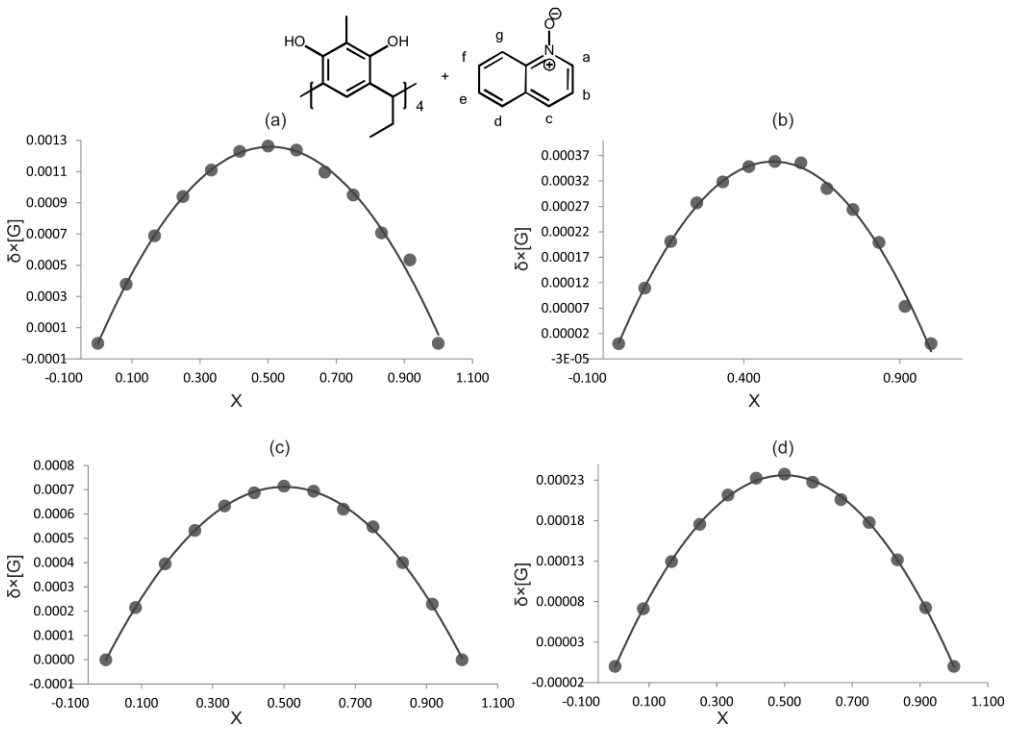
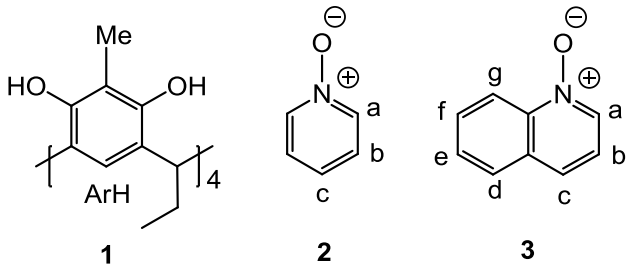


Fig. S5 Job plots (CD_3OD, 298 K) from the combination of resorcinarene **1** and quinoline N-oxide **3**. Following (a) guest a; (b) guest b; (c) guest f, (d) host CH_3 signals.

^{1}H Titration experiments

Titration experiments were carried out in CD_3OD at 298 K on a Bruker Avance 400 MHz spectrometer. Stock solution of the host **1** (10 mM) and guest **2**-**3** (200 mM) were prepared. After obtaining free-host spectrum of **1**, aliquots of corresponding guest solution (containing **2** or **3**) were added to the respective NMR tubes. Spectra were obtained after each addition.



H + G ⇌ HG, K1 = [HG]/[H][G] (1)

HG + G ⇌ HG2, K2 = [HG2]/[HG][G] (2)

Job plots had revealed a 1:1 binding stoichiometry. Therefore a simple 1:1 model was used for calculating the binding constant. HypNMR 2008[9] was used to refine the isothermal fits of multiple signals (**1**+**2**: **1**=Me and ArH, **2**=Ha, Hb, Hc; **1**+**3**: **1**=Me and ArH, **2**=Ha, Hb, Hc, Hd, He, Hf, Hg) simultaneously.

The Spectra Changes

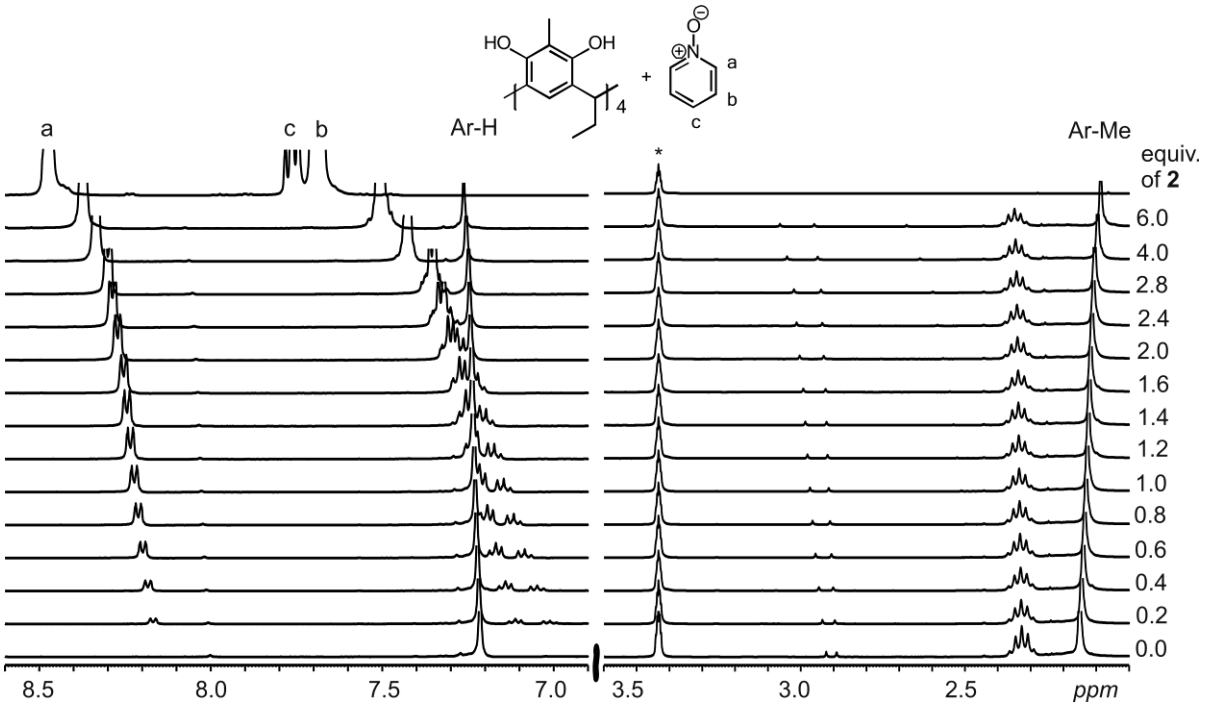


Fig. S6 ^{1}H NMR spectral changes observed upon the titration of resorcinarene **1** with pyridine N-oxide **2** in CD_3OD at 298 K.

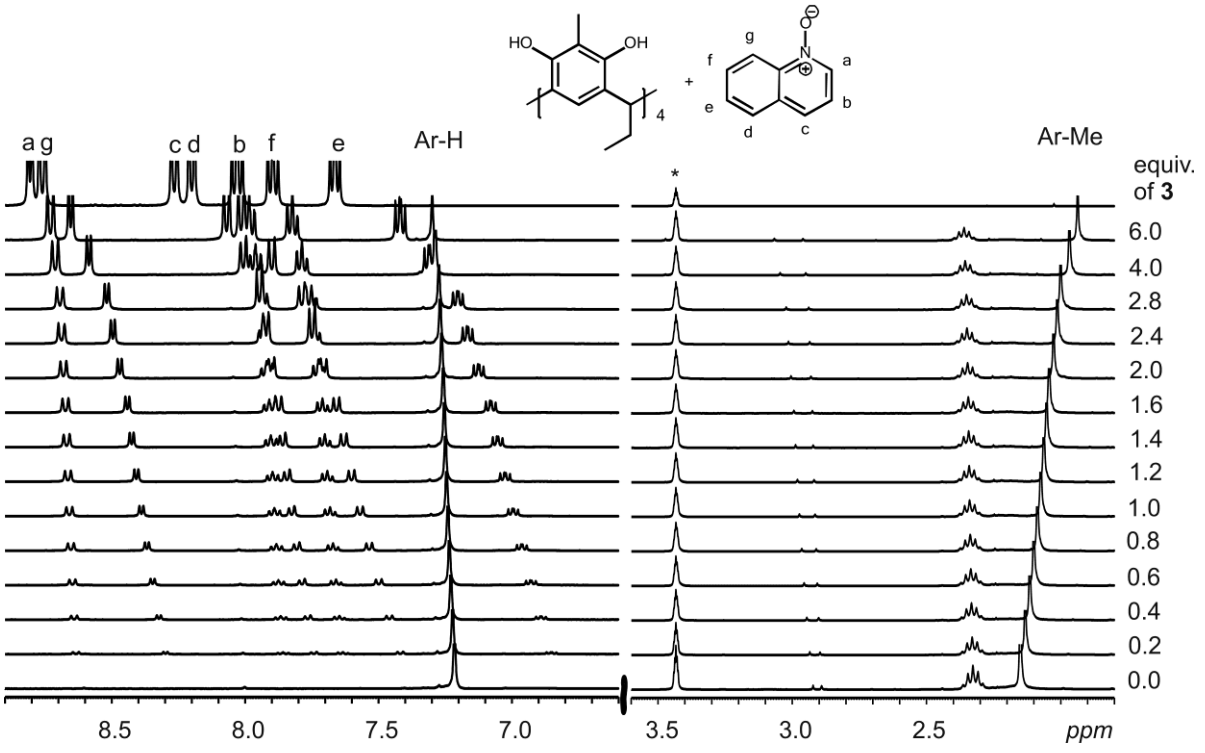


Fig. S7 ^{1}H NMR spectral changes observed upon the titration of resorcinarene **1** with quinoline N-oxide **3** in CD_3OD at 298 K.

1 + 2 experiment

Species	Log beta	Guest	Host	
1	1,7527	1	1	refine

Species concentrations/mol dm-3

Point	T(Guest)	T(Host)	F(Guest)	F(Host)	species 1
1	1,98E-03	9,90E-03	1,30E-03	9,22E-03	6,79E-04
2	3,92E-03	9,80E-03	2,65E-03	8,53E-03	1,28E-03
3	5,83E-03	9,71E-03	4,02E-03	7,91E-03	1,80E-03
4	7,69E-03	9,62E-03	5,43E-03	7,35E-03	2,26E-03
5	9,52E-03	9,52E-03	6,86E-03	6,86E-03	2,66E-03
6	1,13E-02	9,43E-03	8,30E-03	6,42E-03	3,02E-03
7	1,31E-02	9,35E-03	9,76E-03	6,02E-03	3,32E-03
8	1,48E-02	9,26E-03	1,12E-02	5,66E-03	3,60E-03
9	1,65E-02	9,17E-03	1,27E-02	5,34E-03	3,83E-03
10	1,82E-02	9,09E-03	1,41E-02	5,05E-03	4,04E-03
11	1,98E-02	9,01E-03	1,56E-02	4,79E-03	4,22E-03
12	2,14E-02	8,93E-03	1,70E-02	4,55E-03	4,38E-03
13	2,30E-02	8,85E-03	1,85E-02	4,33E-03	4,52E-03
14	2,46E-02	8,77E-03	1,99E-02	4,12E-03	4,65E-03
15	2,61E-02	8,70E-03	2,13E-02	3,94E-03	4,76E-03
16	3,33E-02	8,33E-03	2,82E-02	3,21E-03	5,12E-03
17	4,00E-02	8,00E-03	3,47E-02	2,70E-03	5,30E-03
18	4,62E-02	7,69E-03	4,08E-02	2,33E-03	5,37E-03

Measured chemical shifts

Point	a	b	c	Ar-H	Me
1	8,17E+00	7,11E+00	7,01E+00	7,22E+00	2,15E+00
2	8,18E+00	7,14E+00	7,05E+00	7,22E+00	2,14E+00
3	8,20E+00	7,17E+00	7,08E+00	7,23E+00	2,14E+00
4	8,21E+00	7,19E+00	7,12E+00	7,23E+00	2,13E+00
5	8,22E+00	7,22E+00	7,15E+00	7,23E+00	2,13E+00
6	8,23E+00	7,23E+00	7,17E+00	7,23E+00	2,12E+00
7	8,24E+00	7,26E+00	7,20E+00	7,24E+00	2,12E+00
8	8,25E+00	7,28E+00	7,24E+00	7,24E+00	2,12E+00
9	8,26E+00	7,29E+00	7,26E+00	7,24E+00	2,12E+00
10	8,27E+00	7,31E+00	7,28E+00	7,24E+00	2,11E+00
11	8,28E+00	7,31E+00	7,32E+00	7,24E+00	2,11E+00
12	8,29E+00	7,32E+00	7,34E+00	7,25E+00	2,11E+00
13	8,29E+00	7,34E+00	7,35E+00	7,25E+00	2,11E+00

14	8,30E+00	7,35E+00	7,36E+00	7,25E+00	2,10E+00
15	8,31E+00	7,36E+00	7,37E+00	7,25E+00	2,10E+00
16	8,33E+00	7,42E+00	7,43E+00	7,26E+00	2,10E+00
17	8,36E+00	7,47E+00	7,48E+00	7,26E+00	2,09E+00
18	8,37E+00	7,50E+00	7,51E+00	7,26E+00	2,09E+00

Calculated chemical shifts

Point	a	b	c	Ar-H	Me
1	8,16E+00	7,10E+00	7,02E+00	7,22E+00	2,15E+00
2	8,18E+00	7,13E+00	7,05E+00	7,22E+00	2,14E+00
3	8,20E+00	7,16E+00	7,09E+00	7,23E+00	2,14E+00
4	8,21E+00	7,19E+00	7,12E+00	7,23E+00	2,13E+00
5	8,22E+00	7,21E+00	7,15E+00	7,23E+00	2,13E+00
6	8,23E+00	7,23E+00	7,18E+00	7,23E+00	2,12E+00
7	8,24E+00	7,25E+00	7,21E+00	7,24E+00	2,12E+00
8	8,26E+00	7,27E+00	7,24E+00	7,24E+00	2,12E+00
9	8,26E+00	7,29E+00	7,26E+00	7,24E+00	2,11E+00
10	8,27E+00	7,31E+00	7,28E+00	7,24E+00	2,11E+00
11	8,28E+00	7,32E+00	7,30E+00	7,24E+00	2,11E+00
12	8,29E+00	7,34E+00	7,32E+00	7,25E+00	2,11E+00
13	8,30E+00	7,35E+00	7,34E+00	7,25E+00	2,11E+00
14	8,30E+00	7,37E+00	7,35E+00	7,25E+00	2,10E+00
15	8,31E+00	7,38E+00	7,37E+00	7,25E+00	2,10E+00
16	8,34E+00	7,43E+00	7,43E+00	7,25E+00	2,10E+00
17	8,35E+00	7,46E+00	7,48E+00	7,26E+00	2,09E+00
18	8,37E+00	7,49E+00	7,51E+00	7,26E+00	2,09E+00

Chemical shifts for each nucleus

species	a	b	c	Ar-H	Me
Guest	8,47E+00	7,69E+00	7,76E+00	0,00E+00	0,00E+00
Host	0,00E+00	0,00E+00	0,00E+00	7,21E+00	2,15E+00
GuestHost	7,57E+00	5,97E+00	5,59E+00	7,28E+00	2,06E+00

Converged in 3 iterations with sigma = 6,845463

	value	standard deviation	Comments
1 log beta(GuestHost)	1.7527	0.0125	1.75(1)

Correlation coefficients between stability constants. Numbering as above

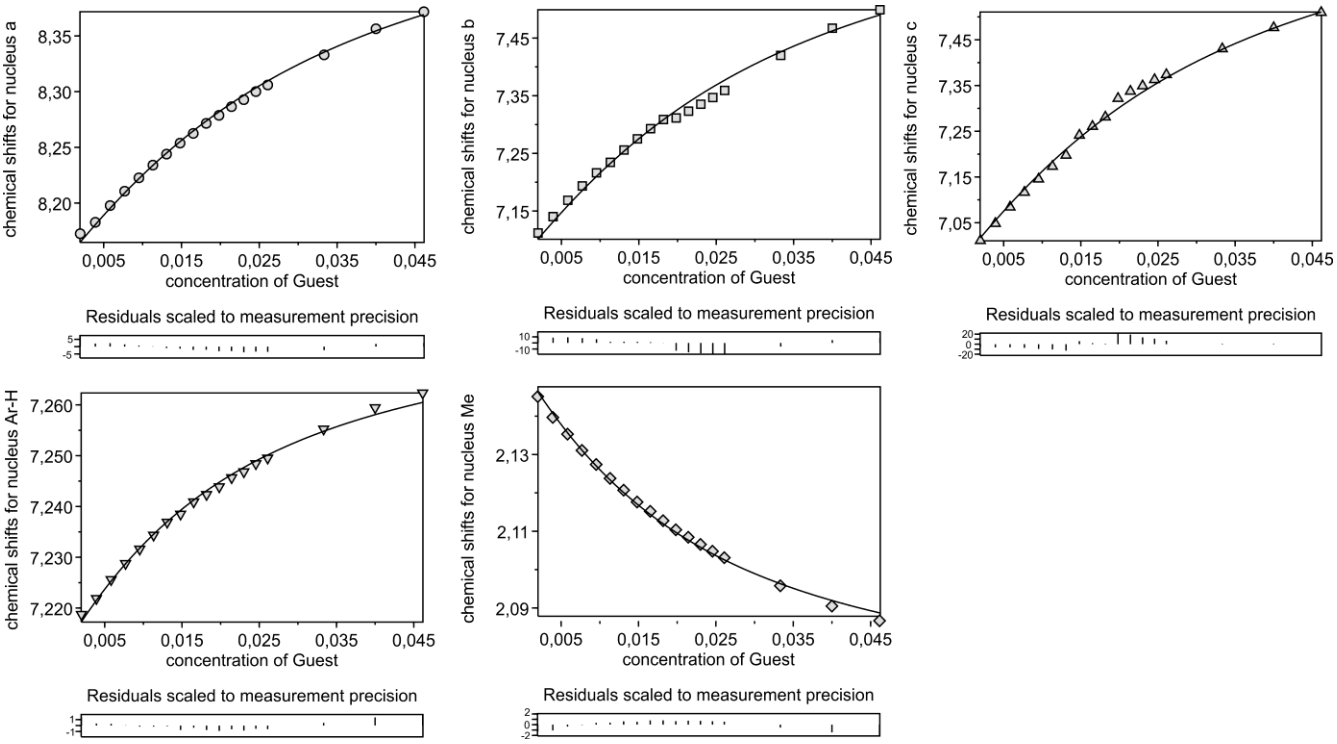


Fig. S8 ^{1}H NMR fittings of resorcinarene **1** and pyridine N-oxide **2** signals.

1 + 3 experiment

Species	Log beta	Guest	Host	
1	1,4	1	1	refine

Species concentrations/mol dm-3

Point	T(Guest)	T(Host)	F(Guest)	F(Host)	species 1
1	1,98E-03	9,90E-03	1,60E-03	9,52E-03	3,82E-04
2	3,92E-03	9,80E-03	3,19E-03	9,08E-03	7,28E-04
3	5,83E-03	9,71E-03	4,78E-03	8,67E-03	1,04E-03
4	7,69E-03	9,62E-03	6,37E-03	8,29E-03	1,33E-03
5	9,52E-03	9,52E-03	7,94E-03	7,94E-03	1,58E-03
6	1,13E-02	9,43E-03	9,50E-03	7,62E-03	1,82E-03
7	1,31E-02	9,35E-03	1,11E-02	7,31E-03	2,03E-03
8	1,48E-02	9,26E-03	1,26E-02	7,03E-03	2,22E-03
9	1,65E-02	9,17E-03	1,41E-02	6,77E-03	2,40E-03
10	1,82E-02	9,09E-03	1,56E-02	6,53E-03	2,56E-03
11	1,98E-02	9,01E-03	1,71E-02	6,30E-03	2,71E-03
12	2,14E-02	8,93E-03	1,86E-02	6,09E-03	2,84E-03

13	2,30E-02	8,85E-03	2,00E-02	5,89E-03	2,96E-03
14	2,46E-02	8,77E-03	2,15E-02	5,70E-03	3,07E-03
15	2,61E-02	8,70E-03	2,29E-02	5,52E-03	3,18E-03
16	3,33E-02	8,33E-03	2,98E-02	4,77E-03	3,57E-03
17	4,00E-02	8,00E-03	3,62E-02	4,19E-03	3,81E-03
18	4,62E-02	7,69E-03	4,22E-02	3,73E-03	3,96E-03

Measured chemical shifts

Point	a	b	c	d	e	f	g	Ar-H	Me
1	8,63E+00	8,30E+00	7,74E+00	7,42E+00	7,86E+00	7,63E+00	6,85E+00	7,22E+00	2,13E+00
2	8,64E+00	8,32E+00	7,77E+00	7,46E+00	7,87E+00	7,65E+00	6,89E+00	7,23E+00	2,12E+00
3	8,65E+00	8,35E+00	7,79E+00	7,50E+00	7,88E+00	7,66E+00	6,93E+00	7,23E+00	2,10E+00
4	8,65E+00	8,37E+00	7,81E+00	7,54E+00	7,88E+00	7,67E+00	6,96E+00	7,24E+00	2,09E+00
5	8,66E+00	8,39E+00	7,83E+00	7,57E+00	7,89E+00	7,68E+00	6,99E+00	7,24E+00	2,07E+00
6	8,66E+00	8,41E+00	7,84E+00	7,60E+00	7,90E+00	7,69E+00	7,03E+00	7,25E+00	2,06E+00
7	8,67E+00	8,43E+00	7,86E+00	7,63E+00	7,90E+00	7,70E+00	7,05E+00	7,25E+00	2,05E+00
8	8,67E+00	8,44E+00	7,87E+00	7,66E+00	7,91E+00	7,71E+00	7,08E+00	7,26E+00	2,04E+00
9	8,68E+00	8,46E+00	7,89E+00	7,68E+00	7,91E+00	7,72E+00	7,10E+00	7,26E+00	2,03E+00
10	8,68E+00	8,47E+00	7,90E+00	7,71E+00	7,92E+00	7,73E+00	7,12E+00	7,26E+00	2,03E+00
11	8,69E+00	8,48E+00	7,91E+00	7,73E+00	7,92E+00	7,73E+00	7,15E+00	7,27E+00	2,02E+00
12	8,69E+00	8,50E+00	7,92E+00	7,75E+00	7,93E+00	7,74E+00	7,17E+00	7,27E+00	2,01E+00
13	8,69E+00	8,51E+00	7,93E+00	7,77E+00	7,93E+00	7,75E+00	7,18E+00	7,27E+00	2,01E+00
14	8,69E+00	8,52E+00	7,95E+00	7,79E+00	7,94E+00	7,75E+00	7,20E+00	7,27E+00	2,00E+00
15	8,70E+00	8,53E+00	7,95E+00	7,81E+00	7,94E+00	7,76E+00	7,22E+00	7,28E+00	2,00E+00
16	8,71E+00	8,59E+00	8,01E+00	7,90E+00	7,96E+00	7,79E+00	7,31E+00	7,29E+00	1,97E+00
17	8,72E+00	8,62E+00	8,04E+00	7,96E+00	7,98E+00	7,81E+00	7,37E+00	7,29E+00	2,00E+00
18	8,73E+00	8,65E+00	8,09E+00	8,02E+00	7,99E+00	7,82E+00	7,42E+00	7,30E+00	1,94E+00

Calculated chemical shifts

Point	a	b	c	d	e	f	g	Ar-H	Me
1	8,63E+00	8,35E+00	7,76E+00	7,50E+00	7,87E+00	7,66E+00	6,91E+00	7,22E+00	2,12E+00
2	8,64E+00	8,37E+00	7,78E+00	7,53E+00	7,88E+00	7,67E+00	6,94E+00	7,23E+00	2,11E+00
3	8,65E+00	8,38E+00	7,80E+00	7,55E+00	7,89E+00	7,67E+00	6,97E+00	7,23E+00	2,10E+00
4	8,65E+00	8,39E+00	7,82E+00	7,58E+00	7,89E+00	7,68E+00	6,99E+00	7,24E+00	2,09E+00
5	8,66E+00	8,41E+00	7,83E+00	7,60E+00	7,90E+00	7,69E+00	7,02E+00	7,24E+00	2,08E+00
6	8,66E+00	8,42E+00	7,85E+00	7,62E+00	7,90E+00	7,70E+00	7,04E+00	7,25E+00	2,07E+00
7	8,67E+00	8,43E+00	7,86E+00	7,64E+00	7,91E+00	7,70E+00	7,06E+00	7,25E+00	2,06E+00
8	8,67E+00	8,44E+00	7,87E+00	7,66E+00	7,91E+00	7,71E+00	7,08E+00	7,26E+00	2,05E+00
9	8,68E+00	8,45E+00	7,89E+00	7,67E+00	7,91E+00	7,72E+00	7,10E+00	7,26E+00	2,04E+00
10	8,68E+00	8,46E+00	7,90E+00	7,69E+00	7,92E+00	7,72E+00	7,11E+00	7,26E+00	2,03E+00
11	8,68E+00	8,47E+00	7,91E+00	7,71E+00	7,92E+00	7,73E+00	7,13E+00	7,27E+00	2,02E+00

12	8,69E+00	8,48E+00	7,92E+00	7,72E+00	7,92E+00	7,73E+00	7,15E+00	7,27E+00	2,02E+00
13	8,69E+00	8,49E+00	7,93E+00	7,73E+00	7,93E+00	7,74E+00	7,16E+00	7,27E+00	2,01E+00
14	8,70E+00	8,49E+00	7,94E+00	7,75E+00	7,93E+00	7,74E+00	7,18E+00	7,27E+00	2,01E+00
15	8,70E+00	8,50E+00	7,95E+00	7,76E+00	7,93E+00	7,74E+00	7,19E+00	7,28E+00	2,00E+00
16	8,71E+00	8,53E+00	7,99E+00	7,81E+00	7,94E+00	7,76E+00	7,25E+00	7,29E+00	1,98E+00
17	8,72E+00	8,56E+00	8,02E+00	7,86E+00	7,95E+00	7,78E+00	7,29E+00	7,29E+00	1,96E+00
18	8,73E+00	8,58E+00	8,04E+00	7,89E+00	7,96E+00	7,79E+00	7,33E+00	7,30E+00	1,94E+00

Chemical shifts for each nucleus

species	a	b	c	d	e	f	g	Ar-H	Me
Guest	8,81E+00	8,76E+00	8,27E+00	8,20E+00	8,03E+00	7,90E+00	7,66E+00	0,00E+00	0,00E+00
Host	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	7,22E+00	2,14E+00
GuestHost	7,92E+00	6,63E+00	5,65E+00	4,59E+00	7,22E+00	6,66E+00	3,76E+00	7,38E+00	1,76E+00

Converged in 5 iterations with sigma = 12,791699

	value	standard deviation	Comments
1 log beta(GuestHost)	1.8157	0.0171	1.82(2)

Correlation coefficients between stability constants. Numbering as above

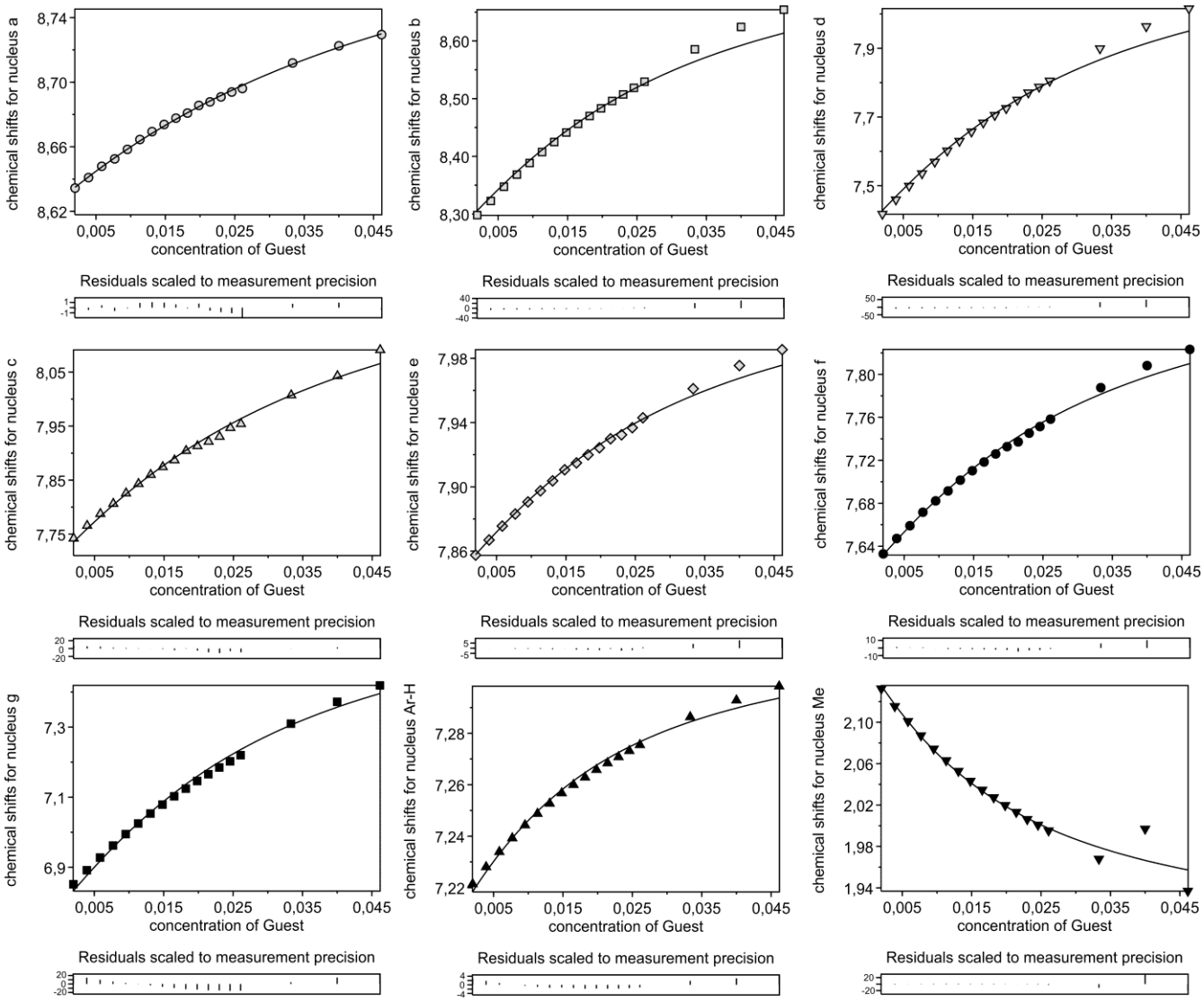


Fig. S9 ^{1}H NMR fittings of resorcinarene **1** and quinoline N-oxide **3** signals.

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