Coumarin[4]arene: A Fluorescent Macrocycle

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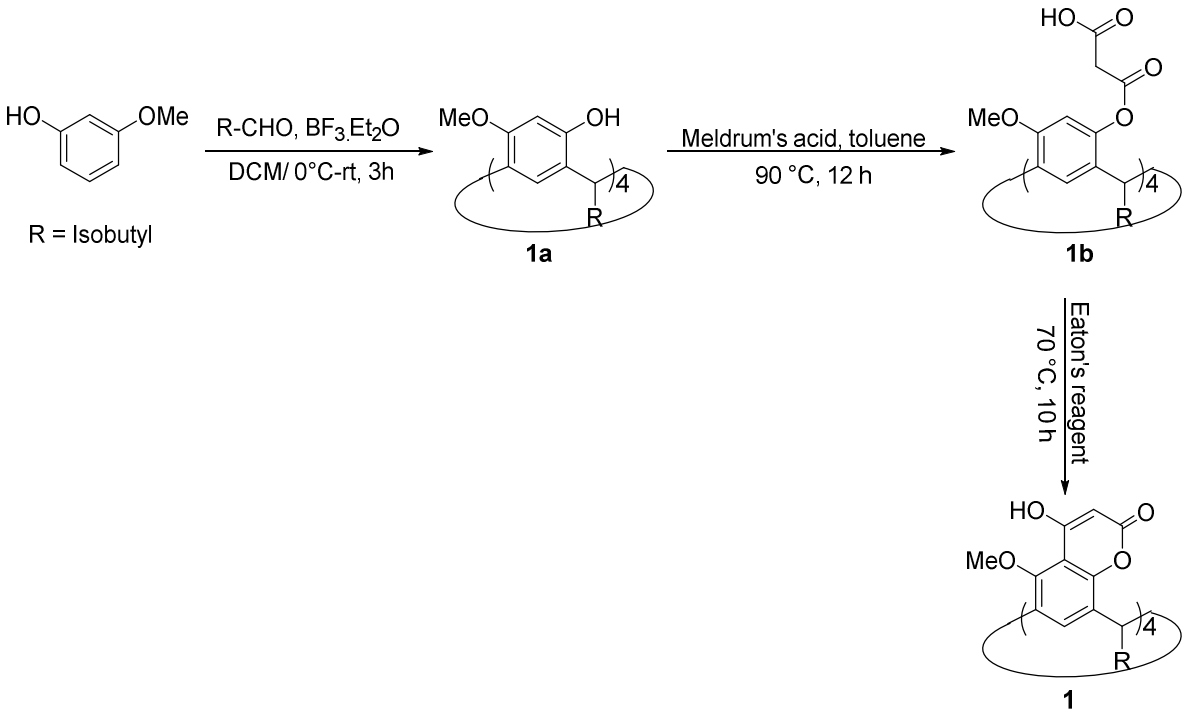
Supporting Information

1. General methods and materials

Reactions were performed in oven dried round bottom flask under N_2 gas atmosphere. Solvents were dried by standard procedures unless otherwise mentioned.[1] Solvents used for extraction and purification were technical grade and distilled prior to use. All other chemicals were obtained from Aldrich, Avra, Alfa-Aesar and used as received, unless otherwise mentioned. The reactions were monitored by thin-layer chromatography (TLC) analysis using silica-gel (60 F254) plates and compounds were visualized under UV chamber. Column chromatography was performed on silica gel (100-200 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 400 and 500 FT-NMR spectrometer with BBFO, 5 mm probes, operating at a frequency of 400/500 MHz for ^{1}H NMR and 101/126 MHz for ^{13}C NMR respectively, with the probe temperature maintained at 298 K, unless otherwise stated. NMR spectra were recorded at 298 K and samples were dissolved in the stated solvents and chemical shifts were referenced internally to residual solvent resonances; $CDCl_3$, ^{1}H = 7.26 ppm; $(CD_3)_2CO$, ^{1}H = 2.05 ppm; $(CD_3)_2SO$, ^{1}H = 2.50 ppm; $CDCl_3$, ^{13}C = 77.16 ppm; $(CD_3)_2CO$, ^{13}C = 29.84 ppm; $(CD_3)_2SO$, ^{13}C = 39.52 ppm. Signals are recorded in chemical shift (δ in ppm from residual solvent resonances referenced to tetramethylsilane, TMS), multiplicity, coupling constants (J in Hz), relative integral, and assignments in that order. Multiplicity abbreviations used are: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; dt, doublet of triplets; br s, broad singlet; br d, broad doublet; br t, broad triplet. Uncertainties in chemical shifts at 298 K are typically ±0.01 ppm for ^{1}H and ±0.05 ppm for ^{13}C. Coupling constants (J) have an uncertainty of ±0.1 Hz for ^{1}H–^{1}H coupling. For new compounds, two-dimensional NMR methods were used to assign ^{1}H and ^{13}C resonances; Heteronuclear correlation through Single Quantum Coherence (HSQC), Heteronuclear Multiple Bond Correlation (HMBC) and ^{1}H–^{1}H Correlation Spectroscopy (COSY). NMR data were processed using TopSpin and MestReNova softwares. The infrared spectra of compounds were recorded on a JASCO FT/IR–4100, Fourier transform infra-red spectrometer. The wave numbers of recorded IR signals are quoted in cm^{-1}. For high resolution mass spectrometry, samples were analyzed using Agilent Technologies 6545 Q-TOF LC/MS and Q-Tof Micro mass spectrometer equipped with a Time of Flight (TOF) analyzer. Melting points (mp) were determined on a BMQR melting point apparatus, and are corrected.

2. Synthesis and characterization



Scheme S1. Synthesis of *C*-Isobutylcoumarin[4]arene.

2.1 General procedure for the preparation of *C*-isobutyl-tetramethoxyresorcinarene 1a.

Macrocycle **1a** was prepared by the literature[2] modified procedure as described below.

To a solution of 3-methoxyphenol (10.0 g, 80.6 mmol) and the isobutyraldehyde (5.81 g, 80.6 mmol) in anhydrous dichloromethane (200 mL) under N_2 gas atmosphere, boron trifluoride–diethyl etherate (24.0 g, 169.3 mmol) was added at 0°C dropwise with a flow rate of 1 mL/min to the reaction mixture, while maintaining temperature below 10 °C throughout the addition. The mixture was then warmed to room temperature and stirred for 2 h. After 2h, the reaction was quenched by adding deionized water (100 mL). The organic layers were separated and washed once with brine. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure to give dark red oil which was then dissolved in a minimum amount of hot methanol (25 mL) and sonicated to afford a white precipitate. The solids obtained were filtered at room temperature and then washed with cold methanol to give pure **1a** (12.07 g, 1.57 mmol) yields in 78%.

2,8,14,20-Tetraisobutyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxycalix[4]arene 1a.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.55 (s, 4H, O*H*), 7.23 (s, 4H, C*Hmeta* to COH), 6.37(s, 4H, C*Hortho* to COH), 4.43 (t, ^{3}J = 8.0 Hz, 4H, ArC*H*(R)Ar), 3.85 (s, 12H, OCH_3), 2.09 (t, ^{2}J = 7.6, Hz, 8H, CH_2), 1.46 (m, 4H, Me_2C*H*), 0.99 (d, ^{3}J = 6.8 Hz, 12H, CH_3CH) and 0.98 (d, ^{3}J = 6.4 Hz, 12H, CH_3CH) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 153.69, 153.04, 124.77, 124.65, 124.11, 100.10, 56.00, 43.05, 30.70, 26.15, 22.96 and 22.92 ppm.

FT-IR (neat): 3630, 2953, 2867, 1618, 1589, 1497, 1467, 1428, 1366, 1328, 1293, 1229, 1196, 1168, 1088, 1039, 1003, 837, 737, 523 cm^{-1}.

HRMS (ESI+) *m/z* calcd. for $[C_{48}H_{64}O_8H]^+$ = 768.4679, found 768.4694.
Mp. 305 °C.

2.2 General procedure for the preparation of *C*-alkyl-coumarin[4]arene, 1.

Preparation of the tetraacid intermediate 1b

To a solution of **1a** (0.768 g, 1.0 mmol) in toluene (10 mL) under N_2 atmosphere at 90 °C, Meldrum acid (0.583 g, 4.05 mmol) was added portion-wise over a period of 2 h, and the reaction mixture was heated for 12 h with stirring. The mixture was then cooled to room temperature, the resultant precipitates were filtered off, washed with toluene (3 × 10 mL) and dried to yield **1b** as a crude white solid (1.079 g, 0.97 mmol, 97%). The crude solid obtained was taken to the next step without further purification.

HRMS(ESI+) *m/z* calcd. for $[C_{60}H_{72}O_{20}Na]^+$ = 1135.4515, found 1135.4509.
Mp. 218–220 °C.

Preparation of coumarin[4]arene, 1

To a freshly prepared solution of Eaton's reagent 10 mL, **1b** (1.079 g, 0.970 mmol) was added at 70 °C under N_2 atmosphere and heated with stirring for 10 h. The mixture was then cooled to room temperature and poured into crushed ice (100 g). The resultant off white precipitates were filtered and dried. Crude product (0.891 g, 0.8567 mmol) was recrystallized

from ^{t}Butylbenzene and DCM/$CHCl_3$ in 1:1 ratio to afford **1** as a pure white solid, (0.853 g, 0.8202 mmol, 84%).

The overall yield for both the steps (**1a→1**) is calculated to be 82%.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.83 (bs, 4H, O*H*), 6.87 (s, 4H, C*H meta* to C-OMe), 5.70 (s, 4H, C*H ortho* to COH), 4.85 (t, J = 7.3 Hz, 4H, ArC*H*(R)Ar), 3.97 (s, 12H, OCH_3), 1.94–1.75 (m, 8H, CH_2), 1.56–1.50 (m, 4H, Me_2C*H*), 1.03 (d, ^3J = 6.5 Hz, 12H, CH_3CH) and 0.99 (d, ^3J = 6.5 Hz, 12H, CH_3CH).

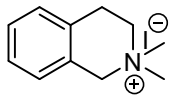
^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.3 (*C*=O), 161.2 (*C*OH), 152.7 and 150.3 (2*C*O), 131.9 and 129.0 (2 *C*quat., arom.), 128.4 (*C*H *meta* to COMe), 108.5 (*C*quat., arom. *ortho* to COMe), 93.8 (*C*H *ortho* to COH), 64.2 (O*C*H_3), 43.9 (*C*H_2), 34.3 (*C*HCH_2), 26.1 (CH_3*C*H), 22.7 (*C*H_3CH) and 22.6 (*C*H_3CH).

FT-IR (neat): 3275, 2956, 2926, 2869, 1719, 1654, 1617, 1586, 1459, 1424, 1387, 1303, 1265, 1167, 1093, 989, 834, 736, 702 cm^{-1}.

HRMS(ESI+): *m/z* calcd. for $[C_{60}H_{64}O_{16}Na]^+$ = 1063.4092, found 1063.4100.
Mp. 235–238 °C.

2.3 General procedure for the preparation of neutral and cationic guest

Organic cationic guests **2-3**, and neutral guests **5-6** were purchased commercially and were used as received. The cationic guest **4** was prepared using the literature modified procedure.[3]



4

***N*-Methyl-1,2,3,4-tetrahydroisoquinoline**

1,2,3,4-Tetrahydroisoquinoline (0.66 g, 1.0 eq, 5.0 mmol) was dissolved in ethanol (10 mL) and potassium hydroxide (0.279 g, 1.1 eq, 5.5 mmol) was added followed by methyl iodide (1.06 g, 1.5 eq, 7.5 mmol). The mixture was stirred overnight at room temperature. After completion of the reaction (monitored by TLC), solvent was removed at reduced pressure and crude was extracted with $CHCl_3$ (3 × 25 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent:

98:2 v/v, *n*-hexane/EtOAc gradually changing to 90:10 v/v, *n*-hexane/EtOAc) to afford **15**, as a light brown oil (0.670 g, 4.55 mmol, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.10 – 7.06 (m, 1H), 6.96 (d, J = 7.2 Hz, 1H), 6.63–6.59 (m, 2H), 3.22 (t, J = 5.6 Hz, 2H), 2.89 (s, 3H), 2.78 (t, J = 6.7 Hz, 2H), 1.99 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 146.88, 128.94, 127.17, 122.99, 116.32, 111.09, 51.41, 39.26, 27.92 and 22.58.

HRMS (ESI+): *m/z* calcd. for $[C_{10}H_{13}NH]^+$ = 148.1126, found 148.1115.

***N,N*-Dimethyl-1,2,3,4-tetrahydroisoquinolinium iodide, 4.**[3]

A solution of a mixture of 2-methyl-1,2,3,4-tetrahydroisoquinoline (0.294 g, 1.0 eq, 2.0 mmol) and methyl iodide (0.426 g, 1.5 eq, 3.0 mmol) in THF (5 mL) was heated at reflux for 4 h under a N_2 gas atmosphere. The precipitate formed was filtered off, washed with diethyl ether (2 × 10 mL), and dried to afford **12**, as an off–white solid (0.548 g, 1.89 mmol, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.13 (d, J = 8.0 Hz, 1H), 7.45–7.35 (m, 2H), 7.24 (m, 1H), 4.29 (t, J = 5.6 Hz, 2H), 3.95 (s, 6H), 3.04 (t, J = 6.7 Hz, 2H), 2.32 (m,2H).

^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 142.91, 131.47, 130.33, 129.78, 129.16, 121.90, 65.09, 58.27, 25.92 and 17.90.

HRMS(ESI+): *m/z* calcd. for $[C_{11}H_{16}N]^+$ = 162.1283, found 162.1266.

3. ^{1}H, ^{13}C NMR, ESI-HRMS spectra and XRD data of 1a

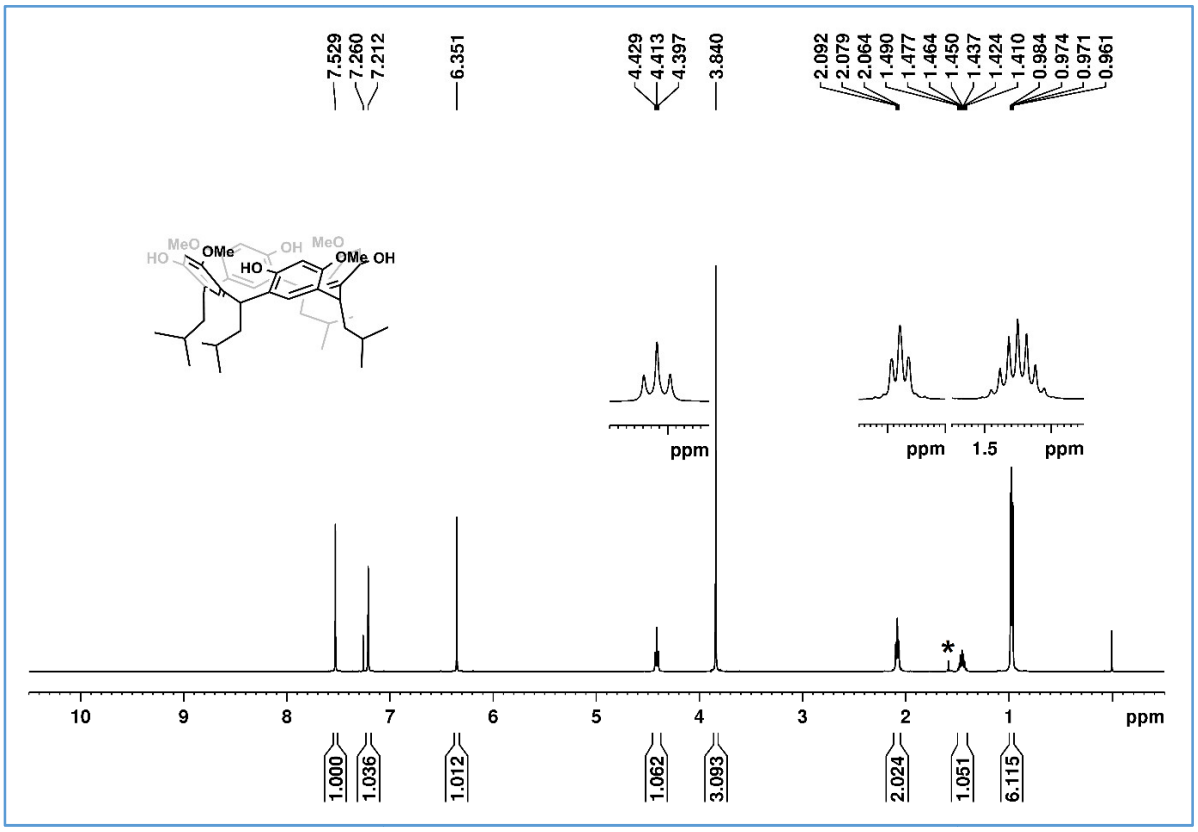


Figure S1: ^{1}H NMR spectrum (500 MHz, 298 K) of **1a** in $CDCl_3$."*" = H_2O in $CDCl_3$.

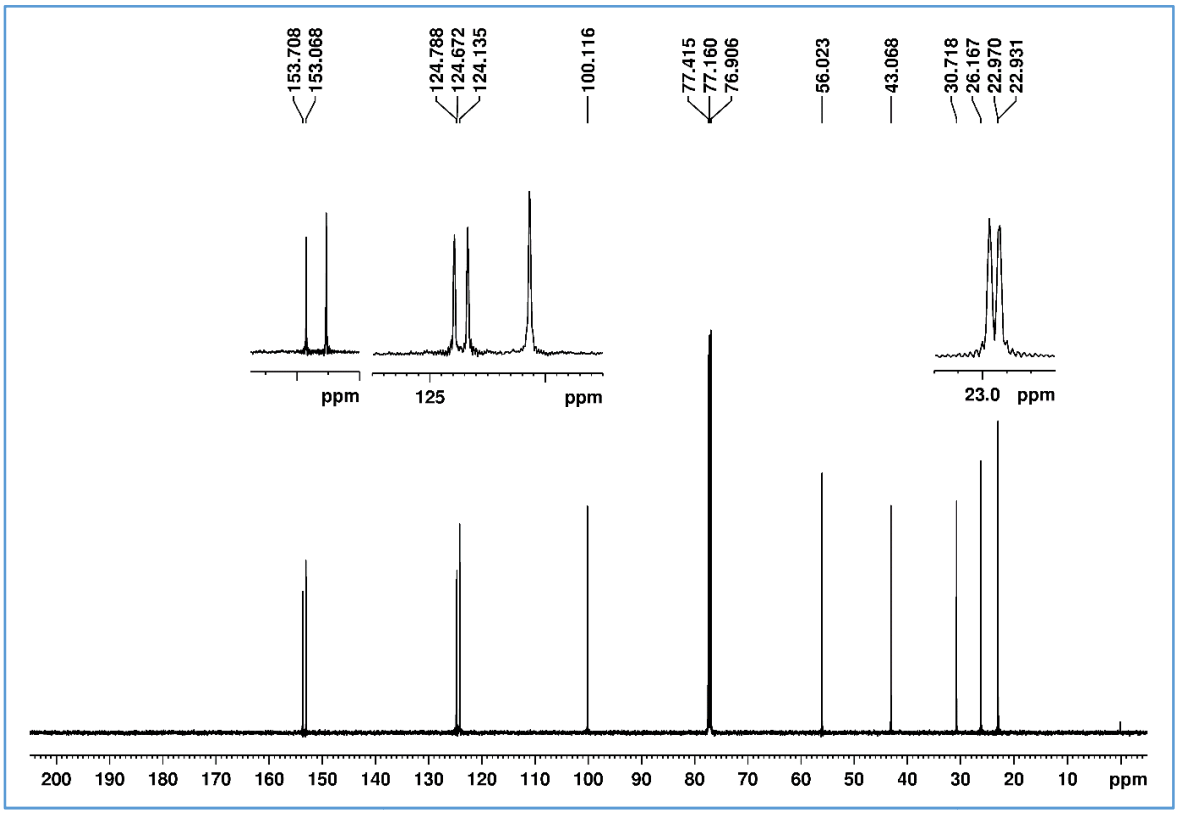


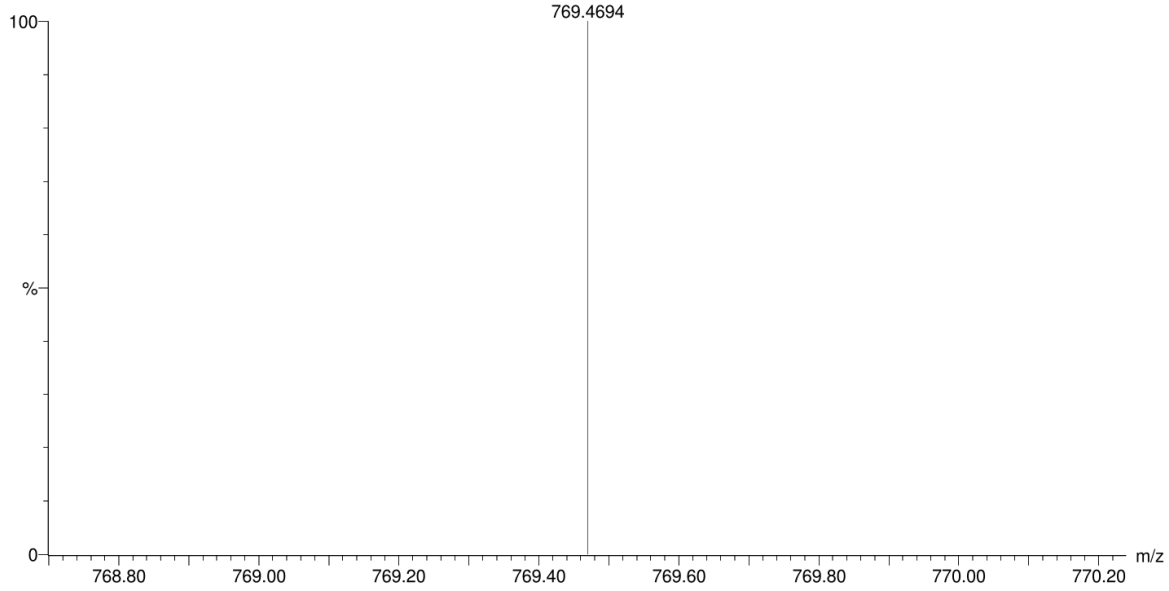
Figure S2: ^{13}C NMR spectrum (125 MHz, 298 K) of **1a** in $CDCl_3$.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-48 H: 0-65 O: 0-8

C-Isobutyl tetramethoxy resorcinarene 3 (0.075) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x0.00); Cm (1:3) TOF MS ES+ 8.10e+000



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
769.4694	769.4679	1.5	1.9	16.5	n/a	C48 H65 O8

Figure S3: HR-ESI mass spectrum of C-Isobutyl tetramethoxyresorcinarene **1a**.

Table S1. X-Ray single crystal data and structure refinement details for **1a** (C-isobutyl tetramethoxyresorcinarene).[4]

Identification code	**1a (CCDC 1813285)**	
Empirical formula	C48 H64 O8	
Formula weight	768.99	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.6068(7) Å	$\alpha = 90°$.
	b = 32.743(3) Å	$\beta = 111.659(2)°$.
	c = 12.6904(9) Å	$\gamma = 90°$.
Volume	4482.3(5) $Å^3$	
Z	4	
Density (calculated)	1.140 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	1664	
Crystal size	0.200 x 0.150 x 0.100 mm^3	
Theta range for data collection	1.835 to 21.831°.	
Index ranges	-12<=h<=10, -34<=k<=29, -13<=l<=13	
Reflections collected	21263	
Independent reflections	5371 [R(int) = 0.0707]	
Completeness to theta = 21.831°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7447 and 0.6548	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5371 / 70 / 566	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0531, wR2 = 0.1179	
R indices (all data)	R1 = 0.1091, wR2 = 0.1488	
Extinction coefficient	0.0022(4)	
Largest diff. peak and hole	0.181 and -0.181 $e.Å^{-3}$	

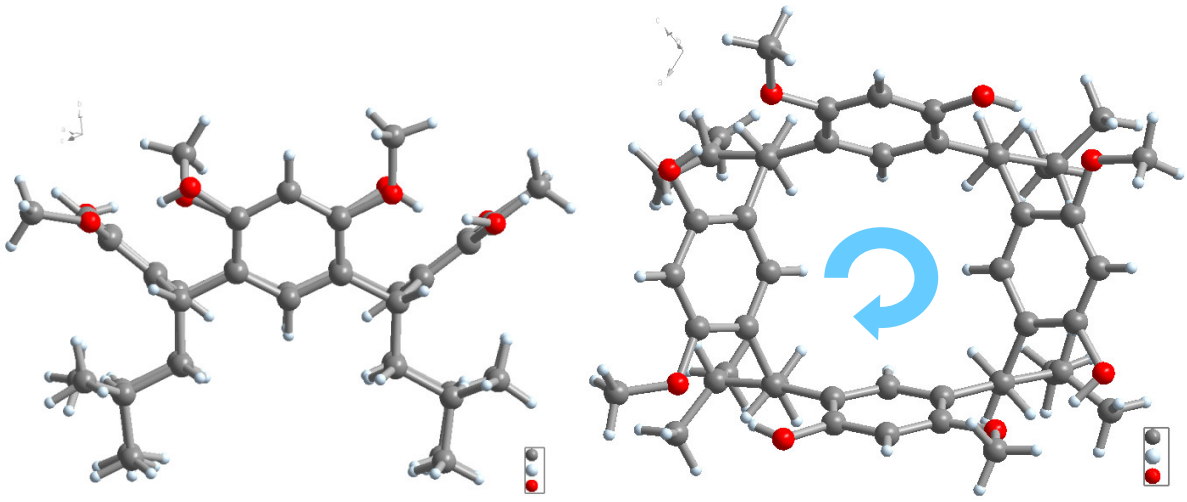


Figure S4: X-ray molecular structure of **1a** showing crown conformation; side view, left and top view, showing the (*P,S)*-enantiomer (right). (*M*,*R*)-enantiomer is also noticed in the crystal lattice.

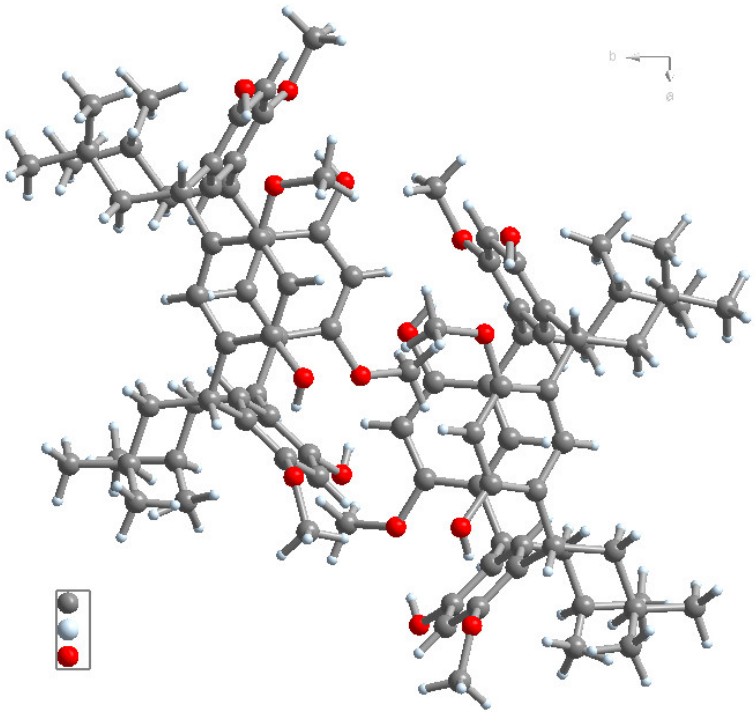


Figure S5: Molecular packing arrangement of **1a** viewed along axis '*c*'.

4. ^{1}H NMR spectrum of product from standard reaction conditions

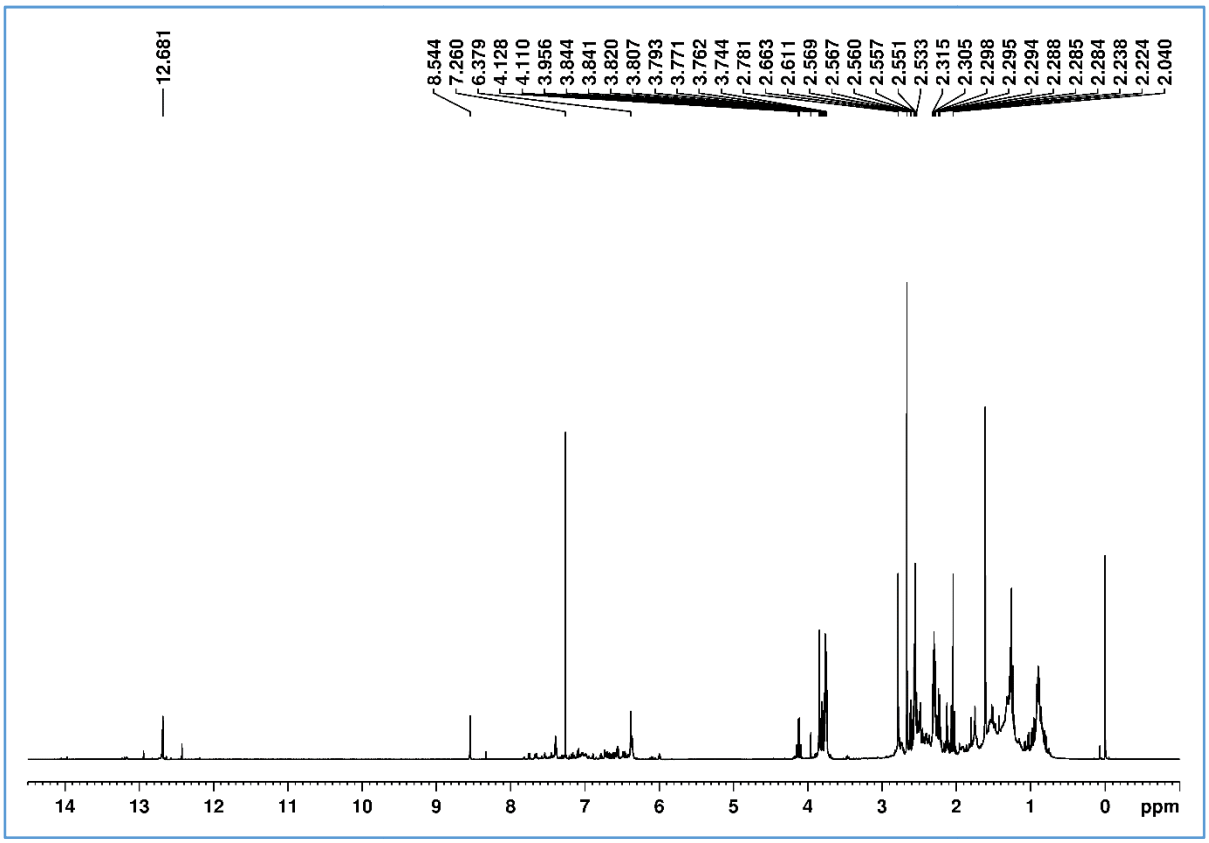


Figure S6: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) obtained for the mass (unidentified) isolated after the reaction of **1a** → **1** under standard conditions.

5. ESI-HRMS spectrum of 1b

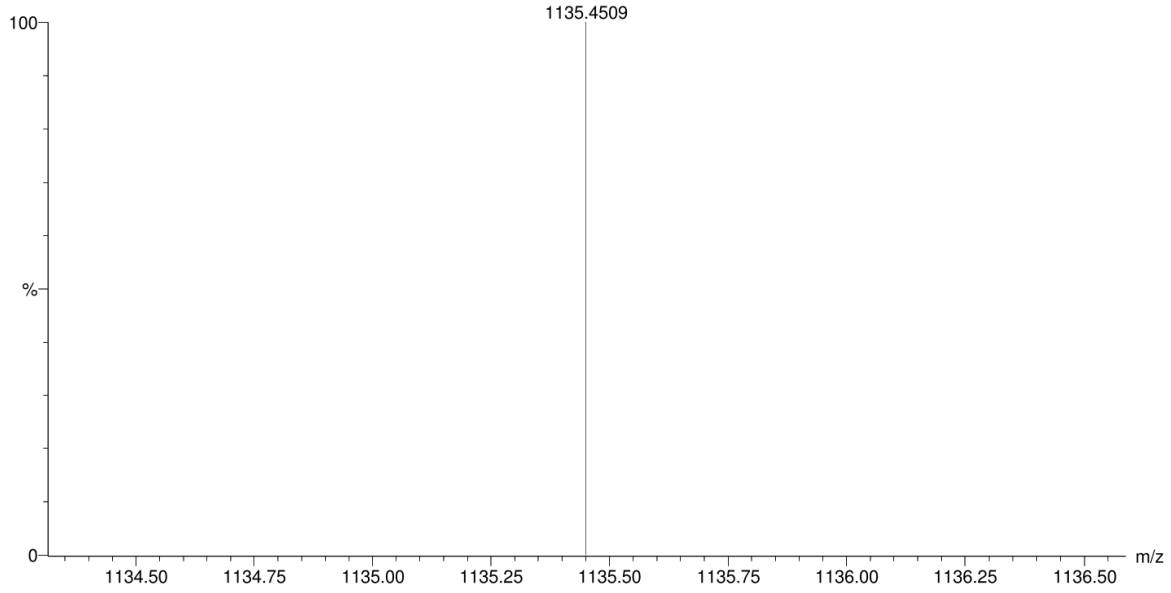
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
36 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-60 H: 0-72 O: 0-20 Na: 0-1

C-Isobutyl tetra acid **1b**

1.96e+003
21 (0.543) AM (Cen,4, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x4.00); Sm (Mn, 1x4.00); Cm (21:2



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
1135.4509	1135.4515	-0.6	-0.5	24.5	n/a	C60 H72 O20 Na

Figure S7: HR-ESI mass spectrum of C-Isobutyl tetraacid intermediate **1b**.

6. ^{1}H, ^{13}C, 2D NMR, ESI-HRMS spectra and XRD data of 1

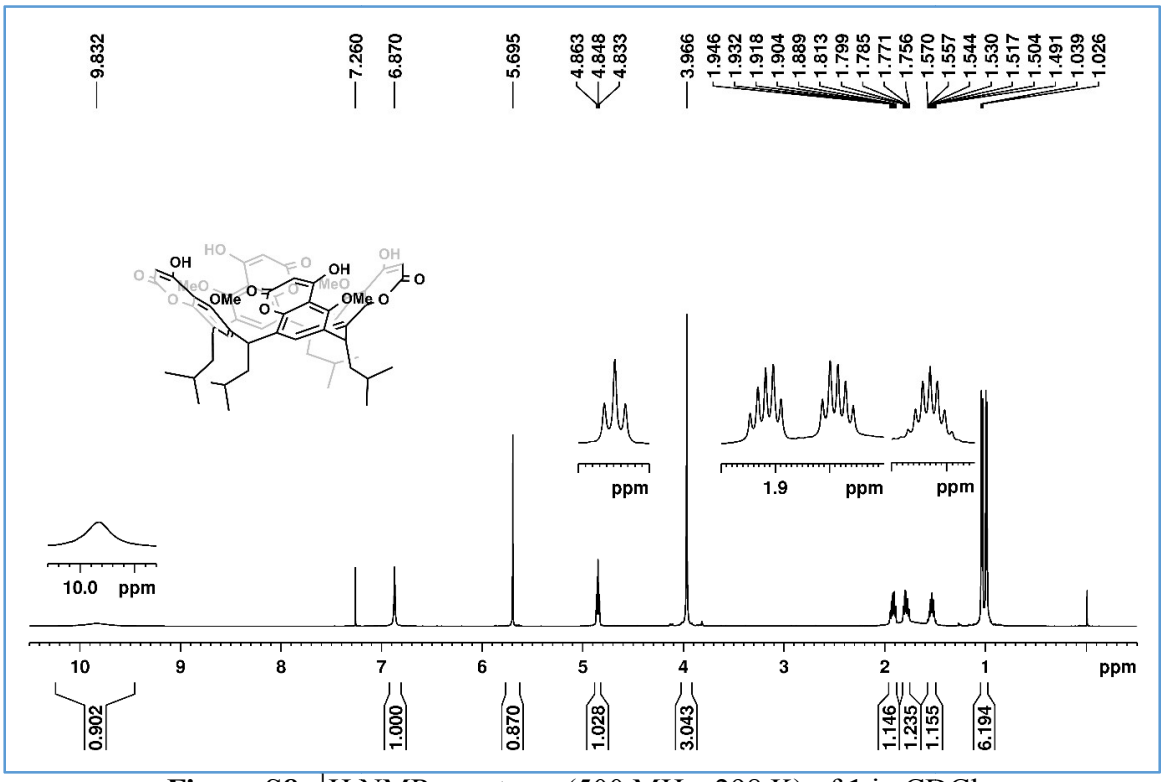


Figure S8: ^{1}H NMR spectrum (500 MHz, 298 K) of **1** in $CDCl_3$.

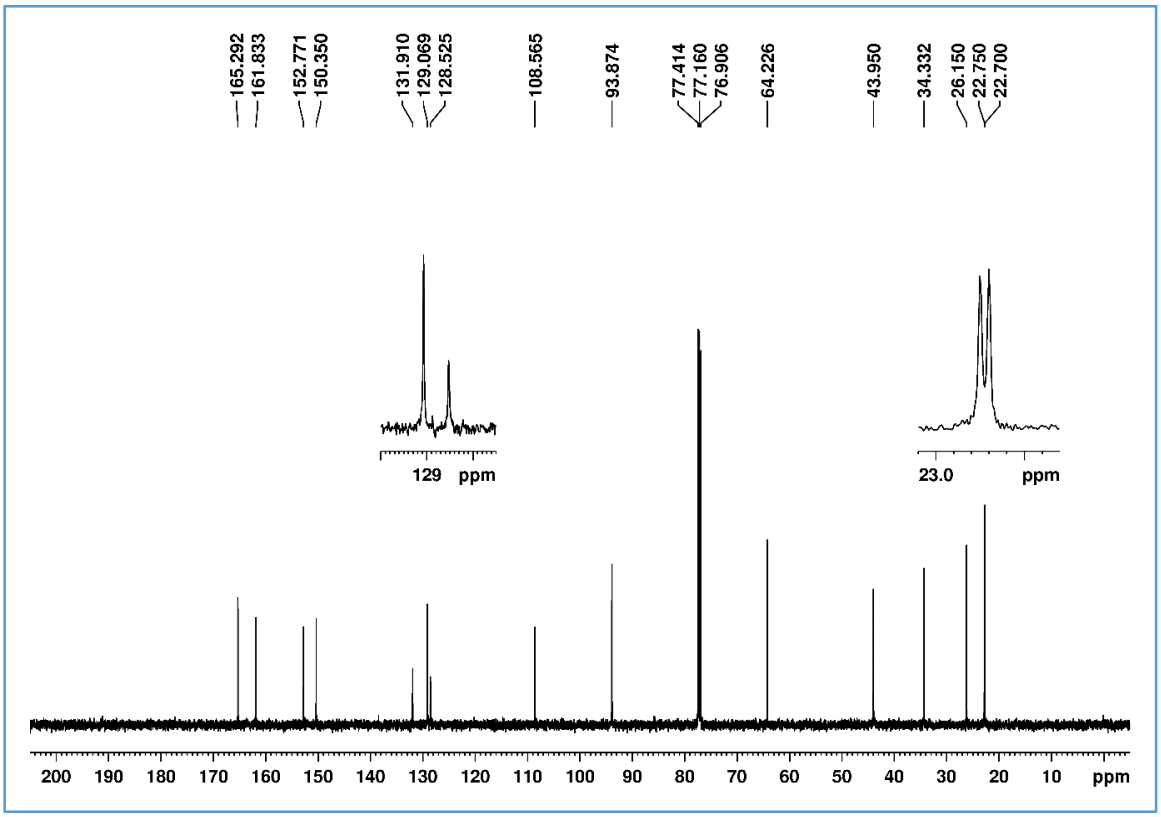


Figure S9: ^{13}C-NMR spectrum (125 MHz, 298 K) of **1** in $CDCl_3$.

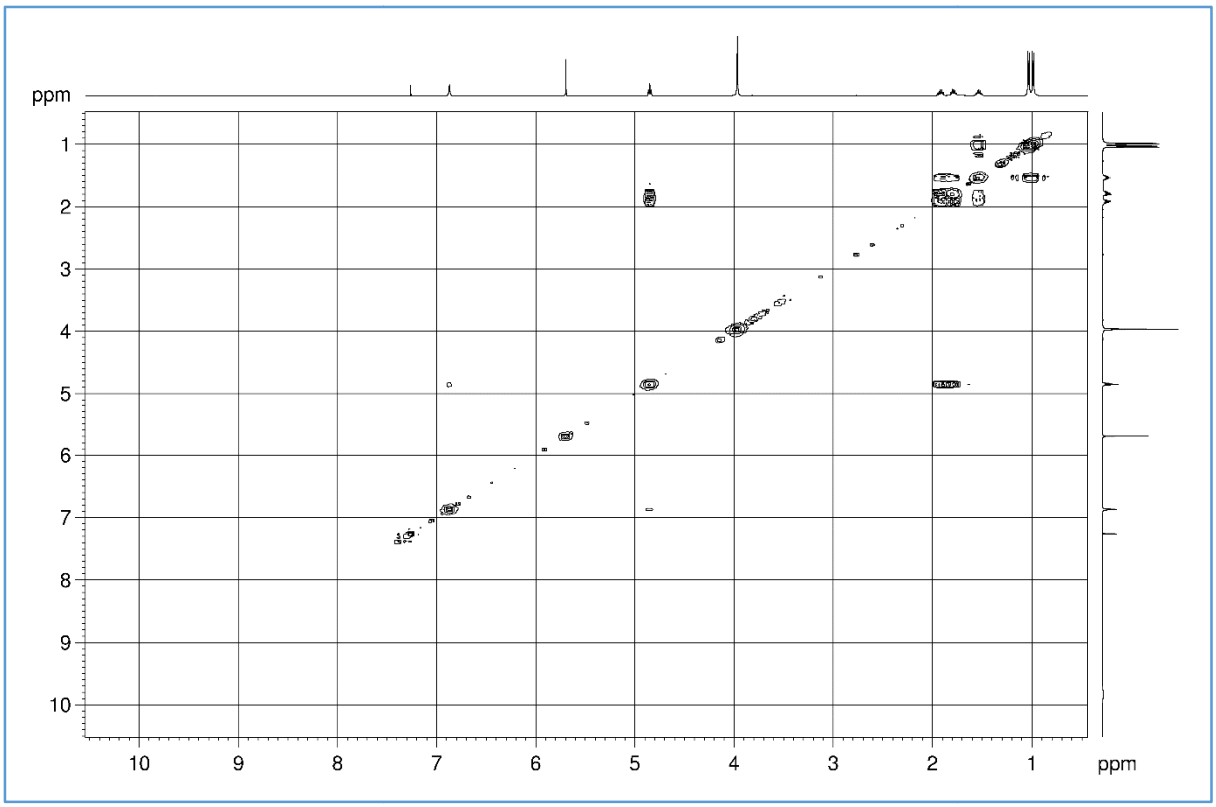


Figure S10: ^{1}H-^{1}H COSY spectrum (400 MHz, 298 K) of **1** in $CDCl_3$.

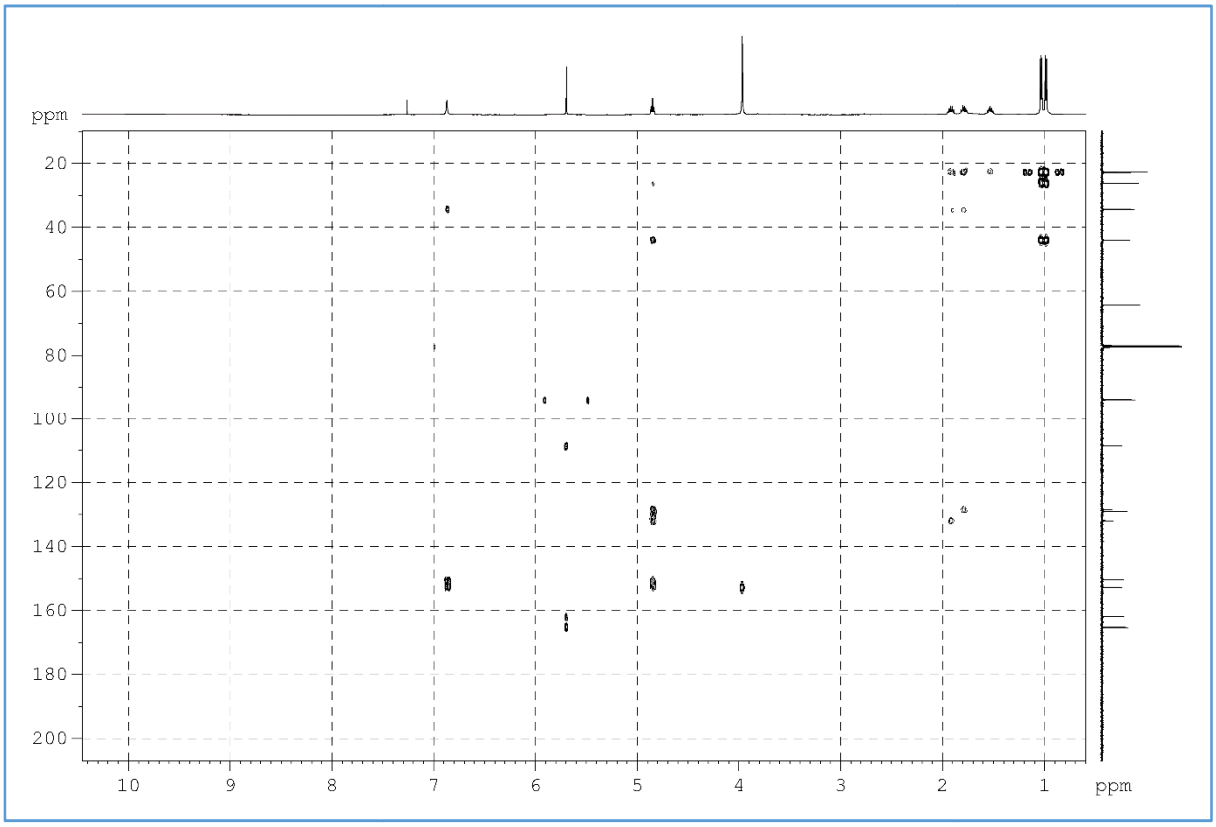


Figure S11: ^{1}H-^{13}C HMBC spectrum (400 MHz, 298 K) of **1** in $CDCl_3$.

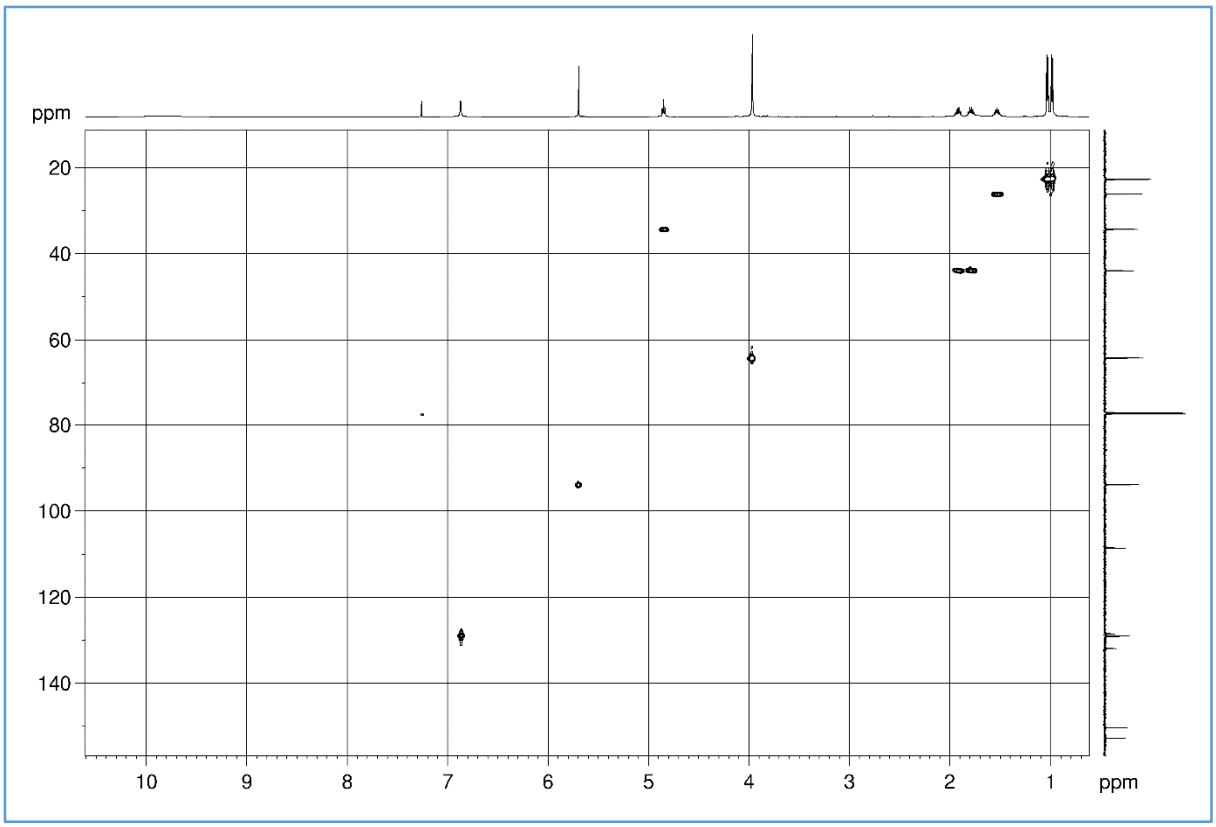


Figure S12: ^{1}H-^{13}C HSQC spectrum (400 MHz, 298 K) of **1** in $CDCl_3$.

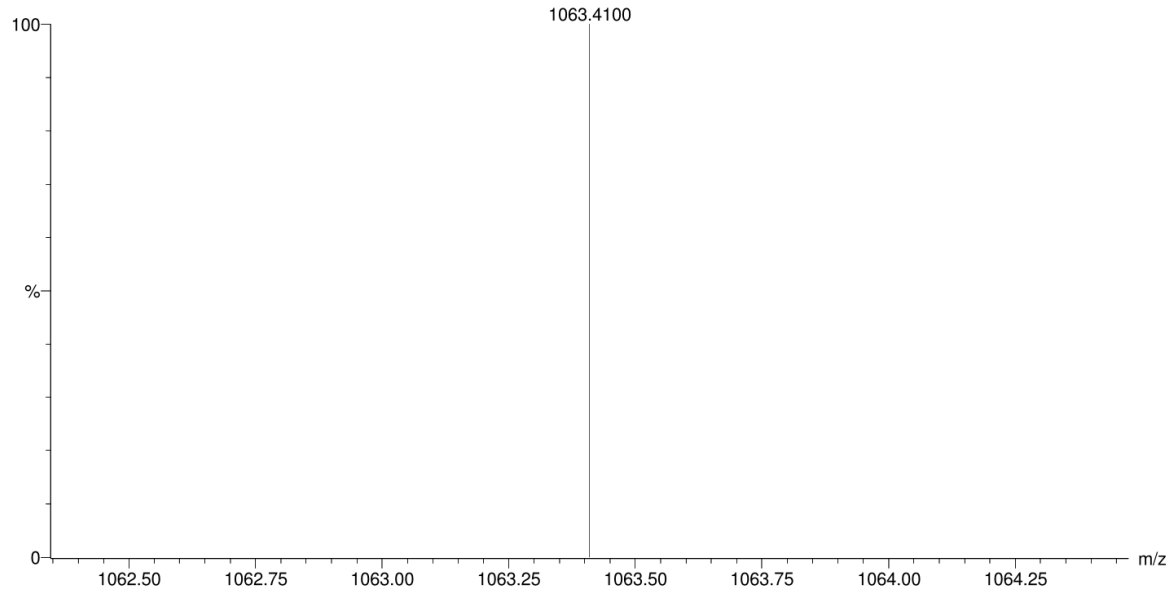
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
27 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-60 H: 0-64 O: 0-16 Na: 0-1

1.55e+004

C-Isobutyl coumarin[4]arene 113 (2.850) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x1.00); Cm (108:119)



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
1063.4100	1063.4092	0.8	0.8	28.5	n/a	C60 H64 O16 Na

Figure S13: HR-ESI mass spectrum of C-Isobutyl coumarin[4]arene **1**.

Table S2. X-ray single crystal data and structure refinement details for **1** (C-isobutyl coumarin[4]arene).

Identification code	**1 (CCDC 1813284)**	
Empirical formula	C60 H64 O16	
Formula weight	1041.11	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 27.203(8) Å	α = 90°.
	b = 25.845(8) Å	β = 104.720(9)°.
	c = 24.600(10) Å	γ = 90°.
Volume	16727(10) $Å^3$	
Z	8	
Density (calculated)	0.827 Mg/m^3	
Absorption coefficient	0.060 mm^{-1}	
F(000)	4416	
Crystal size	0.400 x 0.300 x 0.300 mm^3	
Theta range for data collection	1.104 to 25.000°.	
Index ranges	-32<=h<=32, -30<=k<=30, -29<=l<=29	
Reflections collected	94660	
Independent reflections	14725 [R(int) = 0.2153]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.5814	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14725 / 212 / 699	
Goodness-of-fit on F^2	0.824	
Final R indices [I>2sigma(I)]	R1 = 0.0893, wR2 = 0.2122	
R indices (all data)	R1 = 0.2651, wR2 = 0.2597	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.359 and -0.229 $e.Å^{-3}$	

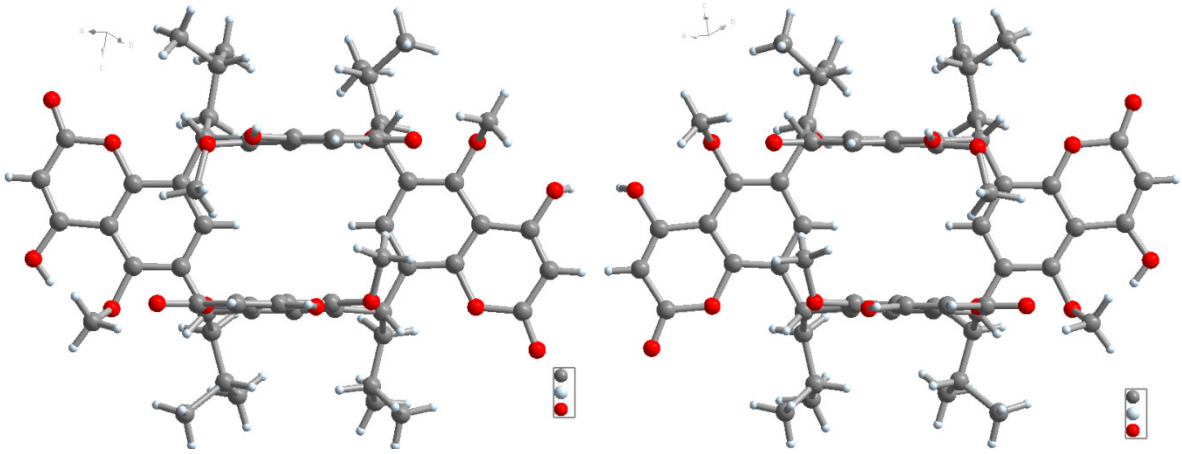


Figure S14: Presence of both the enantiomers of **1** in the crystal lattice.

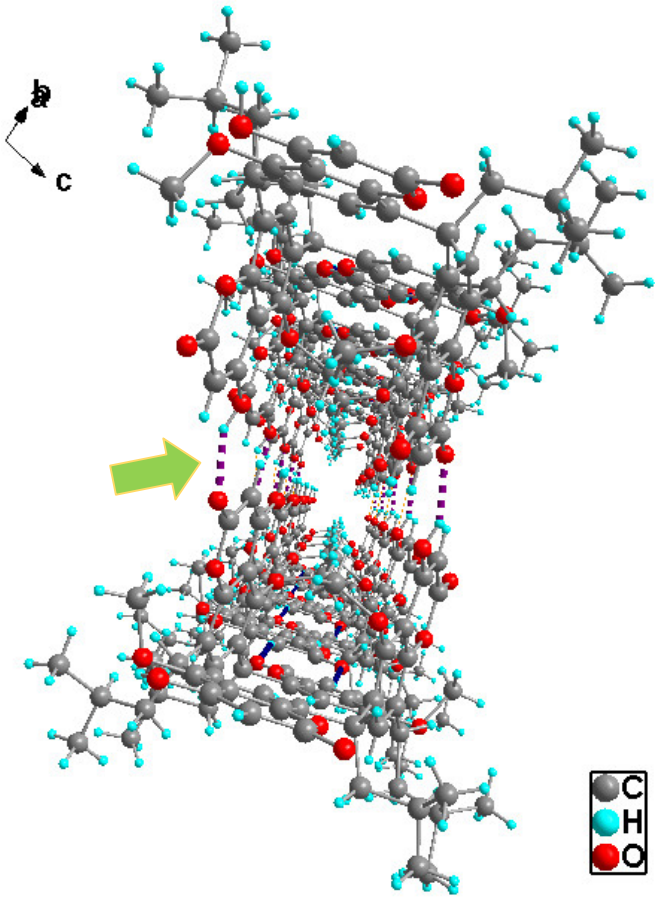


Figure S15: Molecular packing diagram of **1** viewing along the diagonal of the unit cell revealing tubular assembly mediated by edge-edge O-H···O and C-H···O interactions.

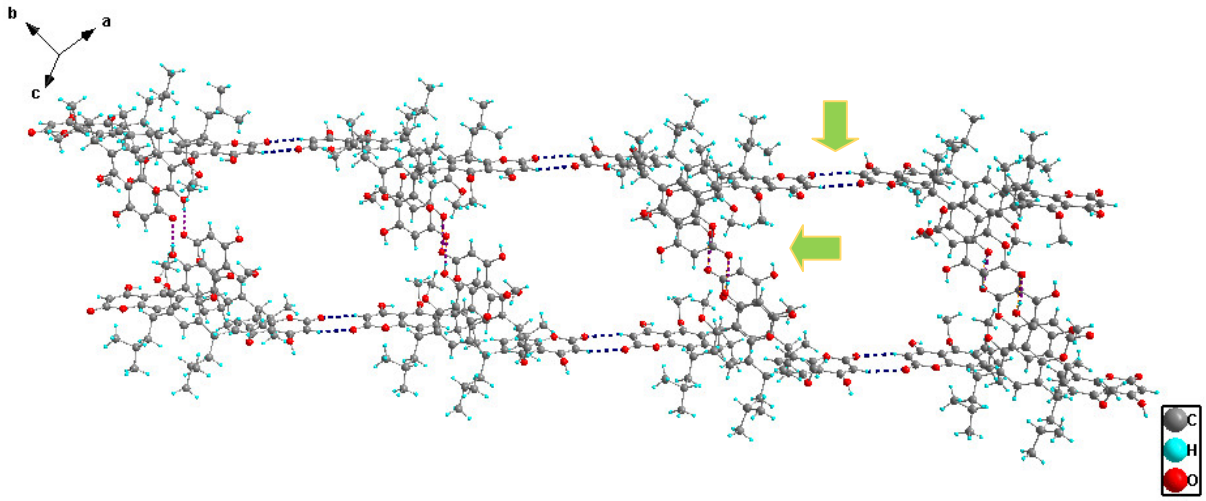


Figure S16: Molecular packing diagram of **1** showing the linear centrosymmetric dimeric assembly by C-H···O interaction as well as the pillared dimeric assembly by O-H···O interaction.

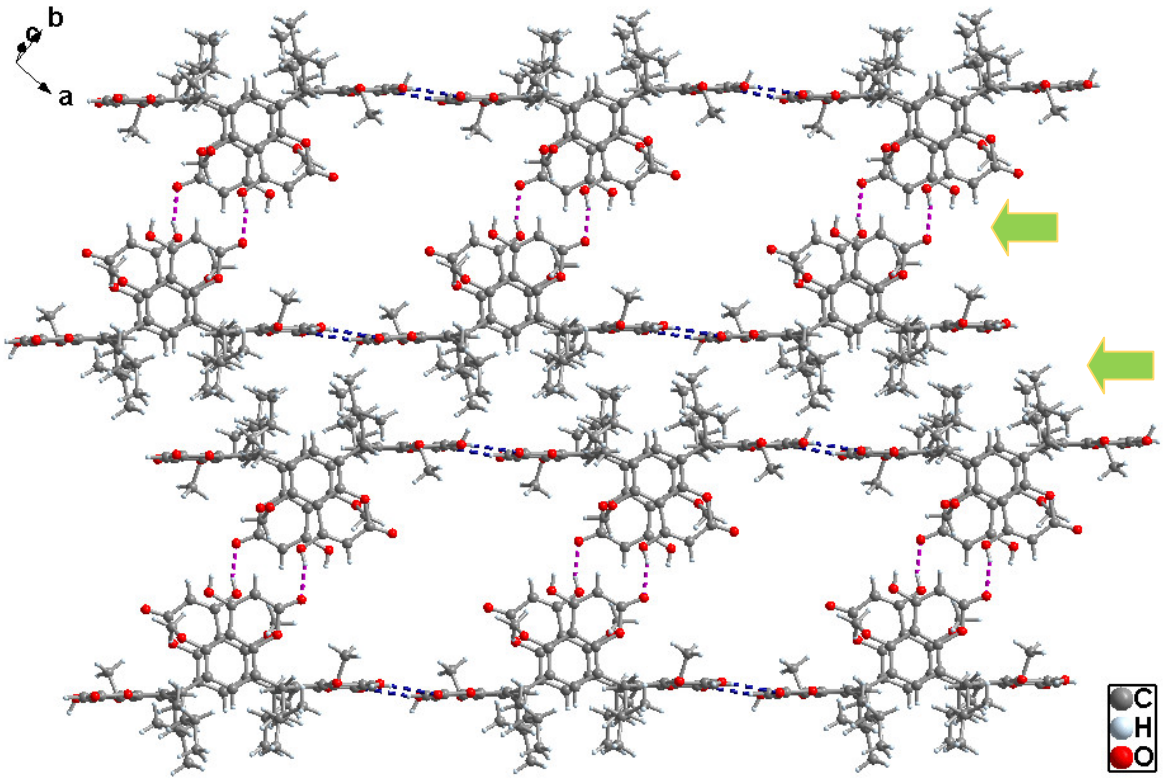


Figure S17: X-ray crystal packing diagram of **1** showing the layers of zipper-like assembly. Notice the hydrophobic alkyl groups are gathered together due to van der Waals interactions.

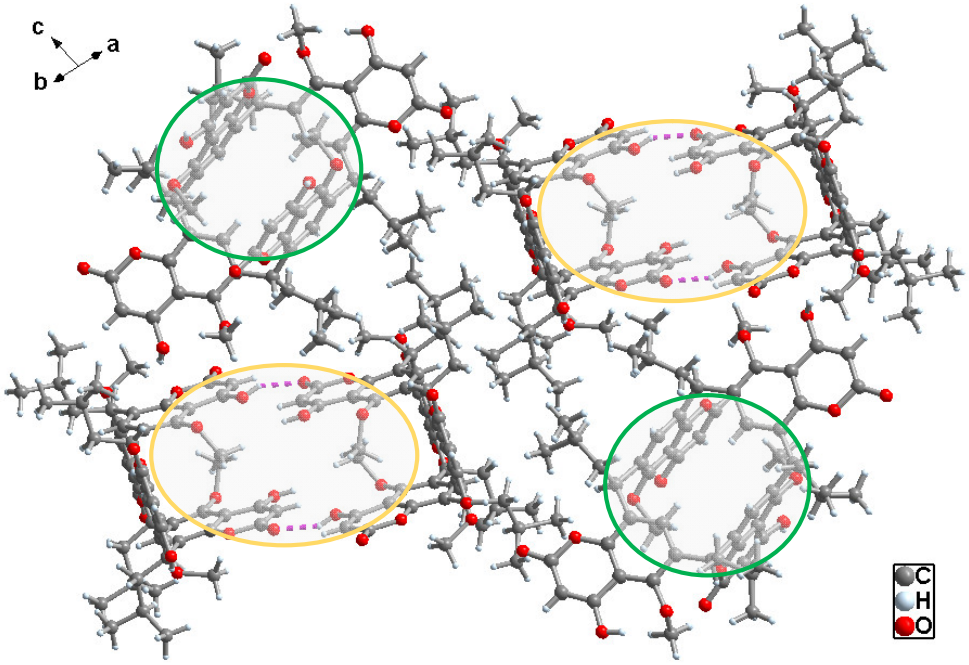


Figure S18: X-ray molecular packing diagram of **1** showing the 3D tubular channels (circled) formed by intermolecular hydrogen bonding and C–H···O interactions.

7. ^{1}H NMR spectrum of 1 in different solvents

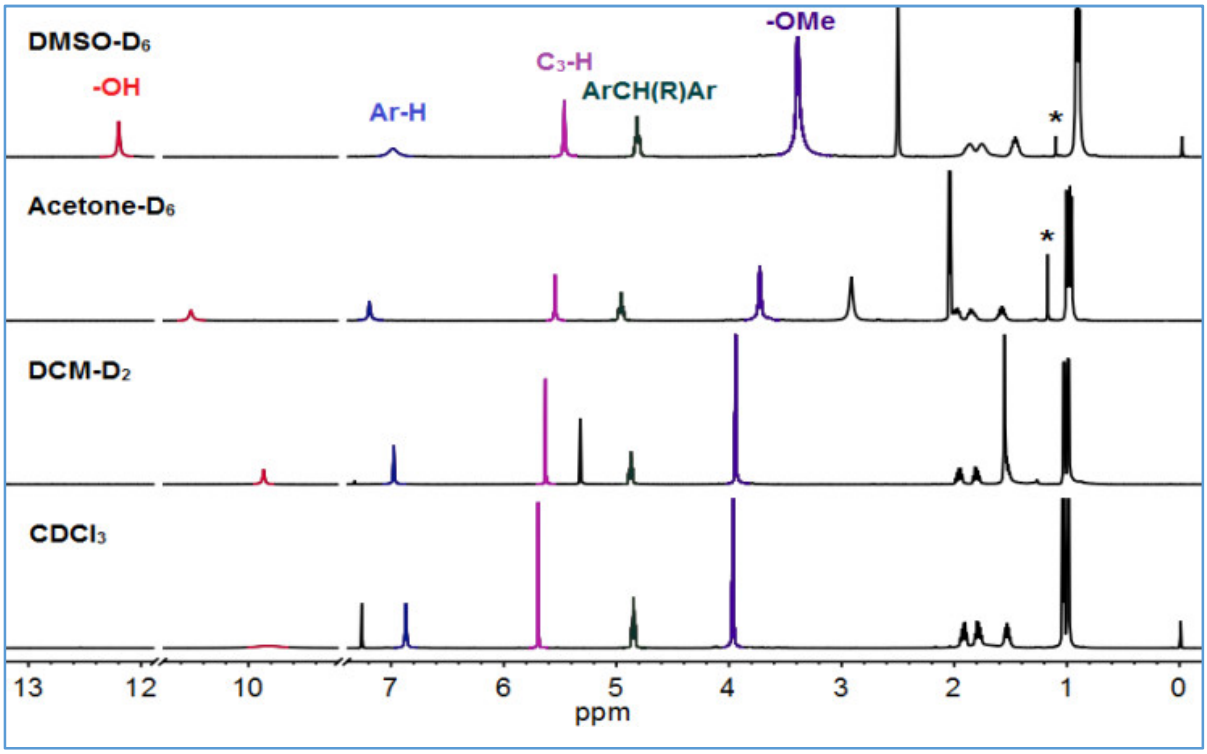


Figure S19: Comparison of ^{1}H NMR spectra of coumarinarene **1** in different solvents; *denotes residual crystallization solvent.

Quantitative Assessment of Intramolecular Hydrogen Bonding Using Abraham's Solute H-Bond Acidity Parameter[5]

Chemical shift value of –C_4OH (**1**) in DMSO-d_6 = 12.1984 ppm

Chemical shift value of – C_4OH (**1**) in $CDCl_3$ = 9.8317 ppm

Calc. A = 0.0065 + 0.133 (12.1984 – 9.8317) = 0.3212

As this value is lesser then 0.5, this indicates a weak intramolecular H-bonding in **1**.

8. ^{1}H VT-NMR spectrum of 1 in DMSO-d_6

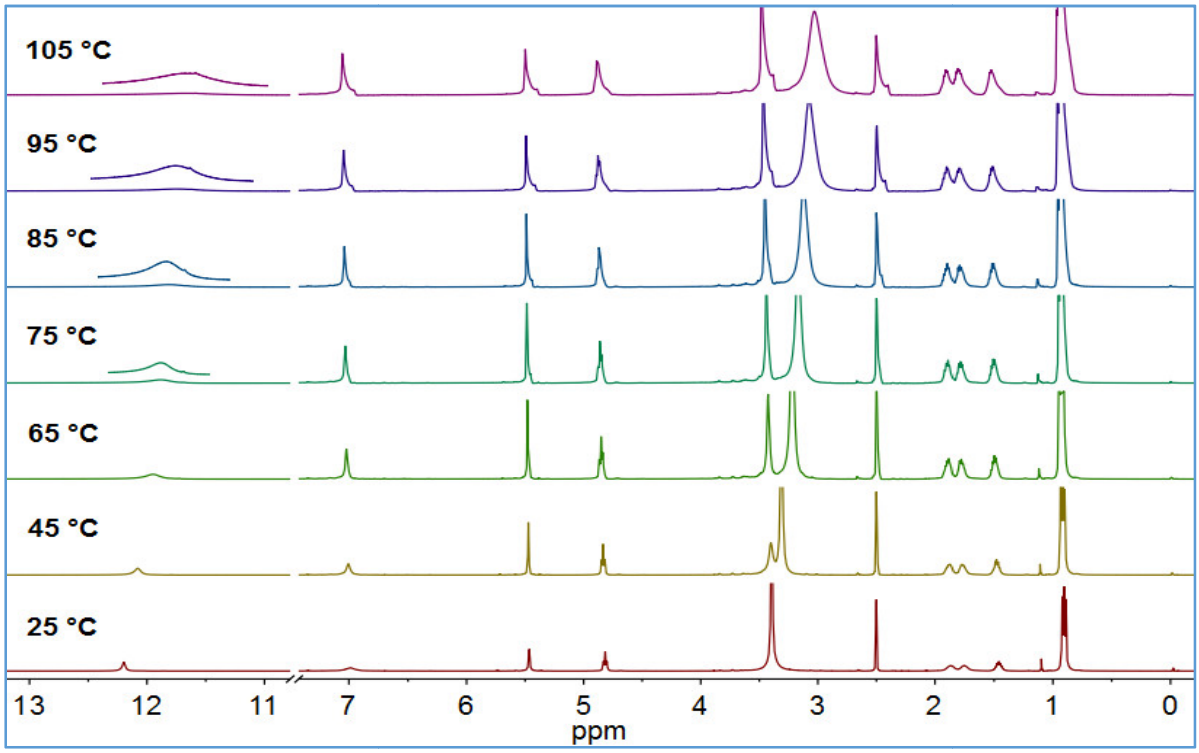


Figure S20: VT-^{1}H NMR spectrum (500 MHz) of coumarin[4]arene **1** in DMSO-D_6. Very minor shifts in the proton signals and in –OH signal are due to temperature effects.

9. ^{1}H, ^{13}C NMR and ESI-HRMS spectra of 4

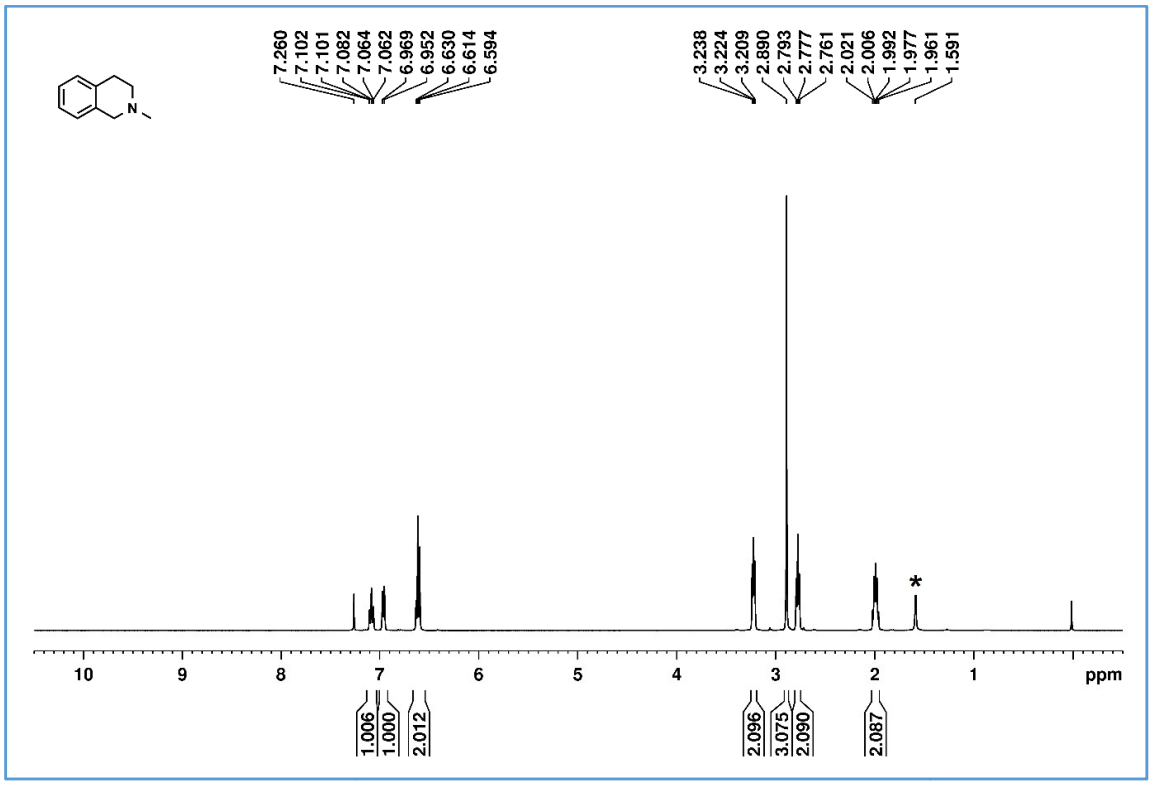


Figure S21: ^{1}H NMR spectrum(400 MHz, 298 K) in $CDCl_3$."*" = H_2O in $CDCl_3$.

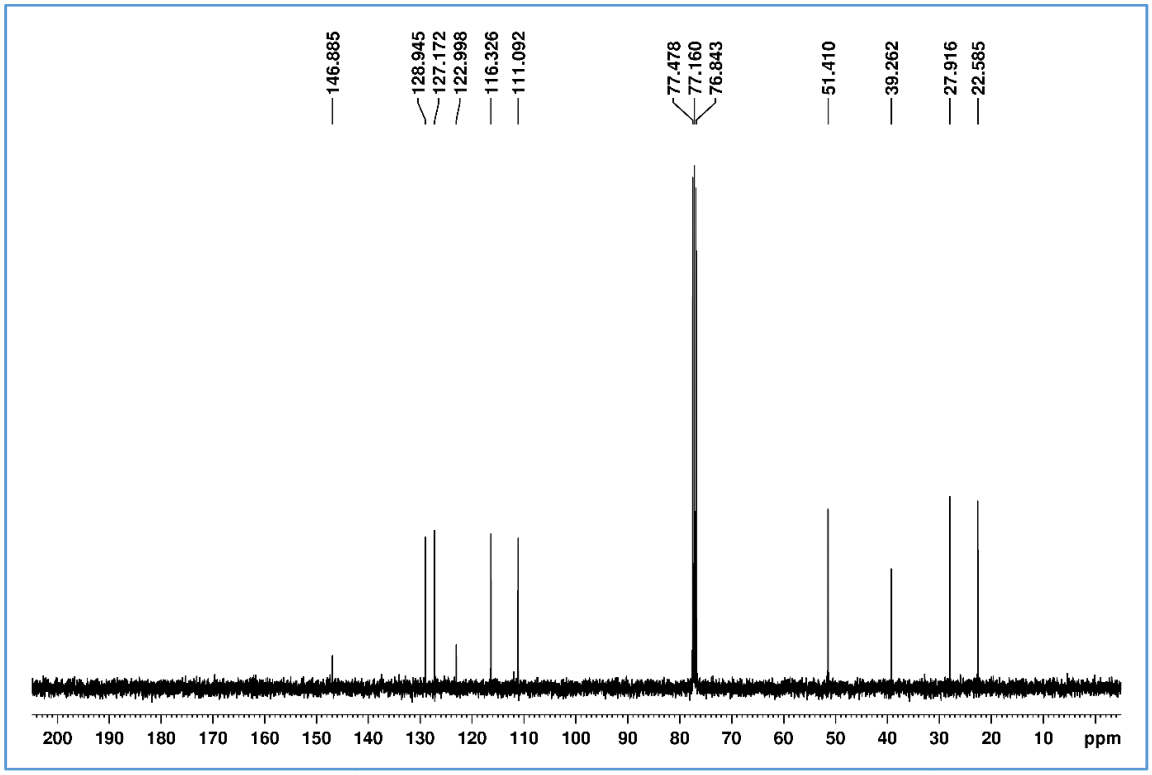


Figure S22: ^{13}C NMR spectrum (100 MHz, 298 K) in $CDCl_3$.

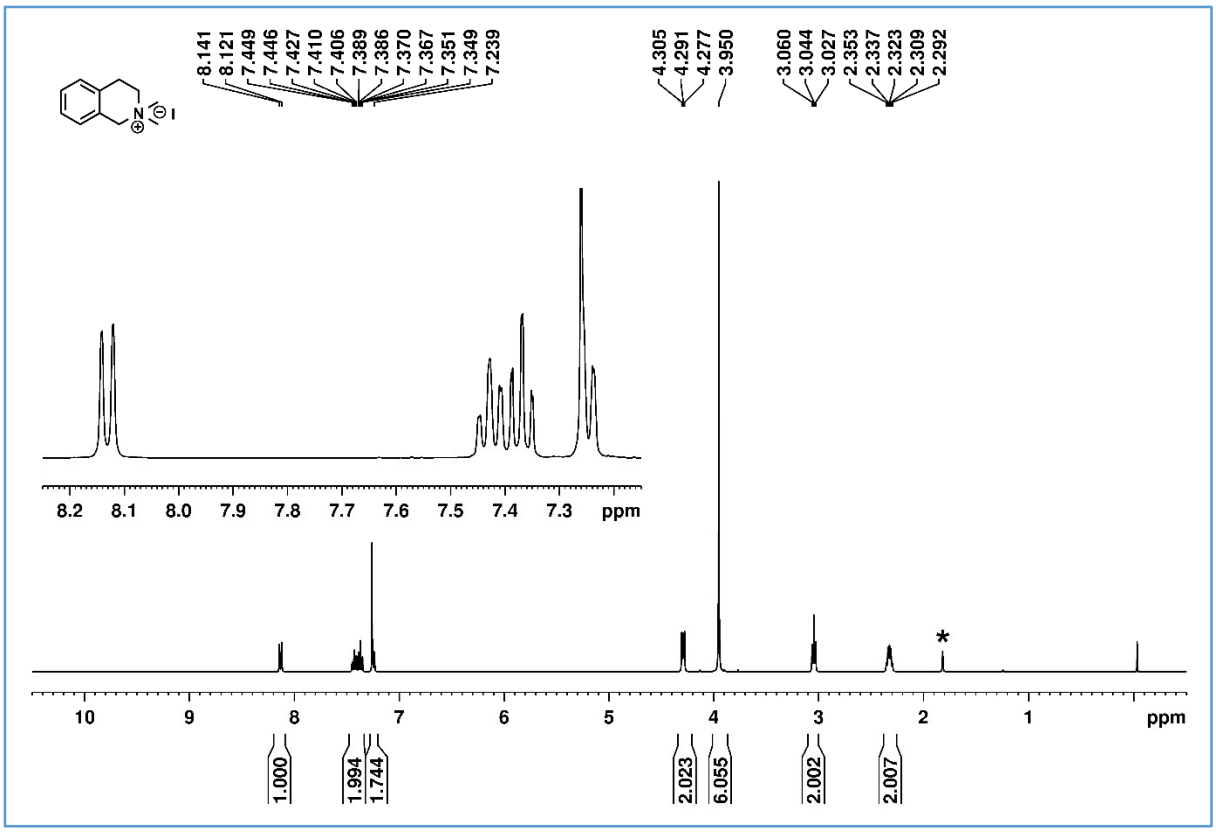


Figure S23: ^{1}H NMR spectrum (400 MHz, 298 K) of **4** in $CDCl_3$."*" = H_2O in $CDCl_3$.

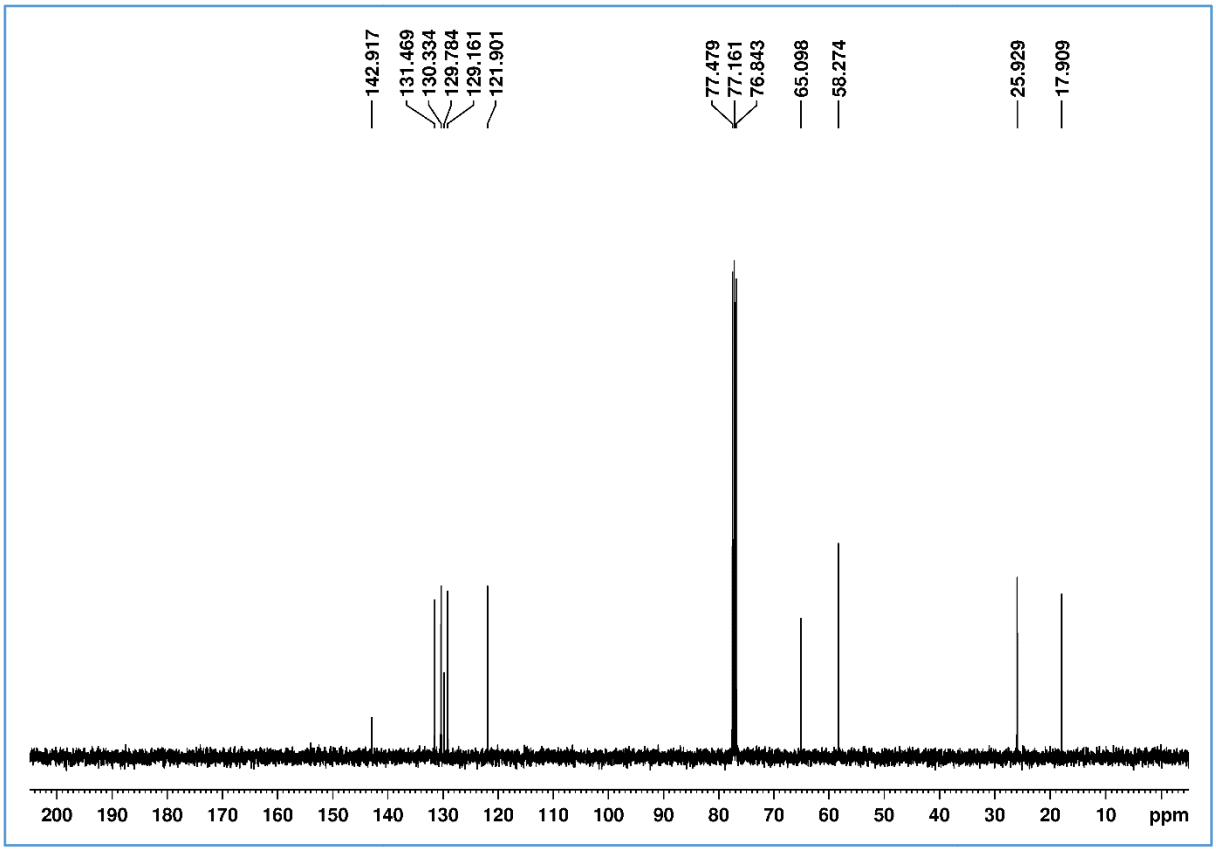
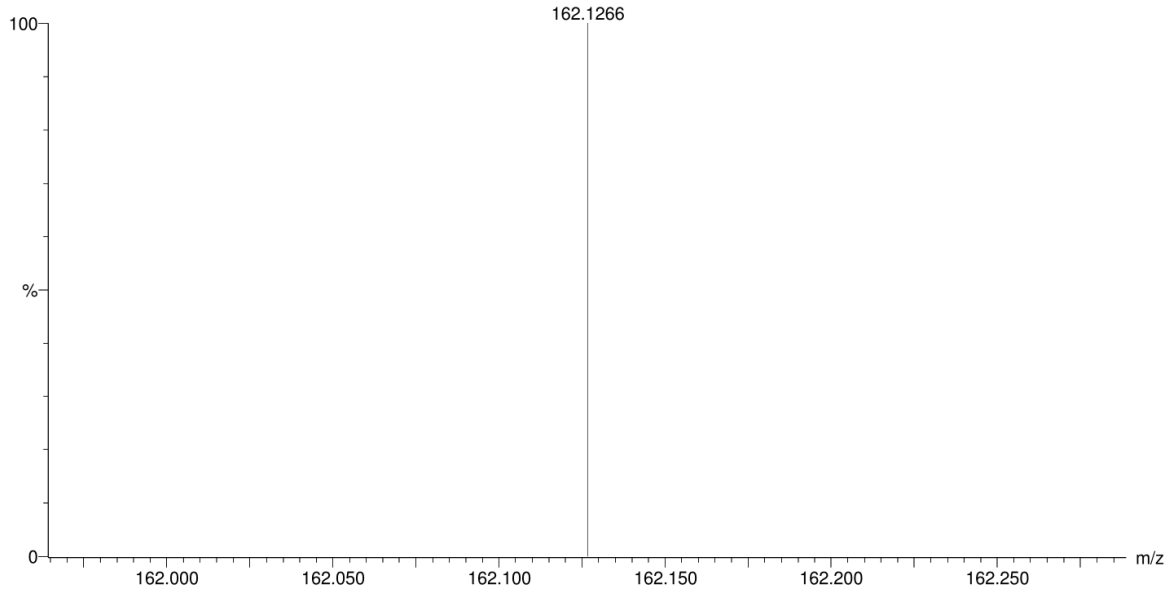


Figure S24: ^{13}C-NMR spectrum (100 MHz, 298 K) of **4** in $CDCl_3$.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-19 H: 0-17 N: 0-2 O: 0-2
N,N-dimethyl
tetrahydroisoquinoline iodide 100 (2.516) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x0.00); Cm (95:105) TOF MS ES+
1.76e+005



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
162.1266	162.1283	-1.7	-10.5	4.5	n/a	C11 H16 N

Figure S25: HR-ESI mass spectrum of *N,N*-dimethyltetrahydroisoquinolinium iodide **4**.

10. DOSY NMR spectra of 1 with guests 2 and 3

DOSY NMR experiment[6] was conducted on a Bruker 500 MHz Avance-III FT-NMR spectrometer. For diffusion measurements, echo pulse sequence ledgp2s using bipolar gradient pulses and 1 spoil gradient was used. The machine was calibrated against the $CHCl_3$ peak in a $CDCl_3$ reference at 25 ˚C, and the 5 mM samples were not spun during measurement. A typical experiment involved 16 scans over 8 steps up to a maximum gradient of 95 G cm^{-1}. Diffusion coefficients were then evaluated using Topspin's T_1/T_2 relaxation module, where a vargrad fitting was applied to the sigmoidal plots of I/I_0 vs. G.

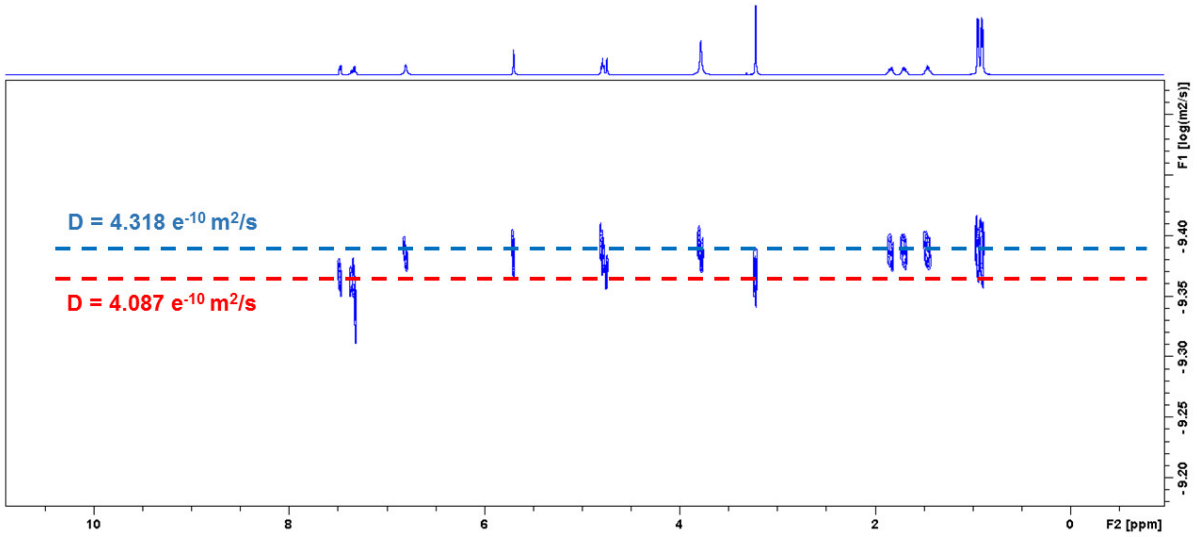


Figure 26: DOSY NMR spectrum for the host-guest complex between **1** and **2**.

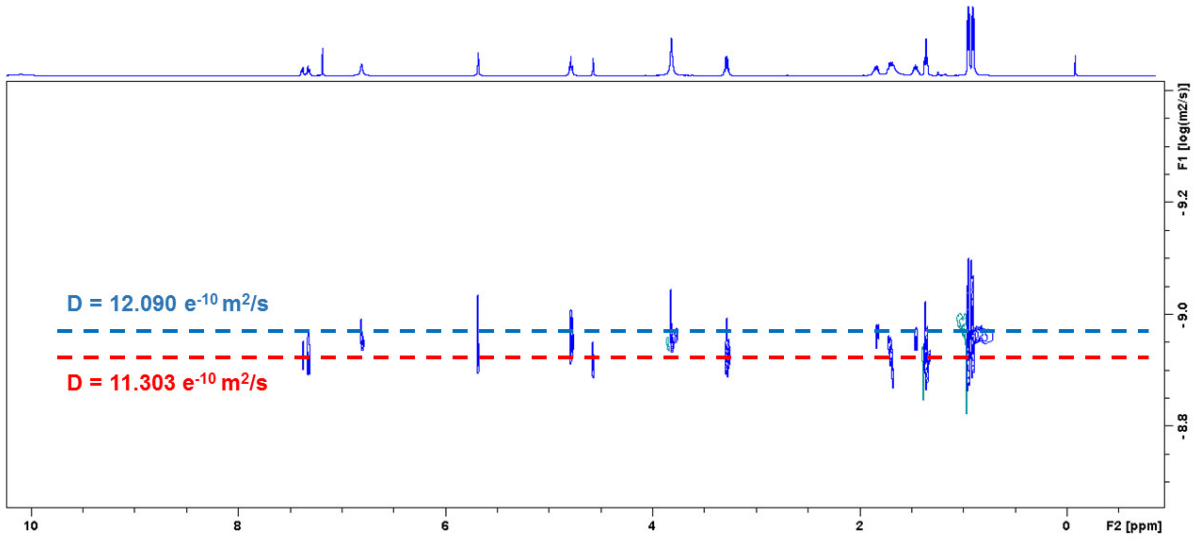


Figure 27: DOSY NMR spectrum for the host-guest complex between **1** and **3**.

11. ^{1}H NMR titration binding studies

11.1 Equipment and Sample Preparation

^{1}H NMR titrations were conducted on a Bruker Avance III 400 and 500 FT-NMR spectrometer with BBFO, 5 mm probes, operating at a frequency of 400 and 500 MHz for ^{1}H NMR with the probe temperature maintained at 298 K unless otherwise stated. In all cases, NMR titrations were performed while maintaining a constant host concentration (usually around 2.0 mM) by dissolving the guest in the same host solution to make up the guest solution. Aliquots of the guest solution were added accurately to the NMR sample of the host solution using the appropriate Gilson's Pipetman **P200** (20-200 Microlitre) pipette. All salts were dried under high vacuum (< 1.0 mmHg) before use. Stock solutions of host (~2.0 mM) were prepared in $CDCl_3$. For better concentration accuracy, the volumes of deuterated solvents were determined by Gilson's Pipetman **P1000** (100-1000 Microlitre) pipette. The stock solutions (~500 μL) were transferred into air-tight capped NMR sample tubes using Gilson's Pipetman **P1000** pipette. The same host stock solutions were then used for the preparation of standard titrant solutions containing approximately 10 mM of the various salts, hence maintaining the concentration of the host constant (~2.0 mM) throughout the entire titration experiment.

11.2 Titration Protocol

Typically, to approximately 500 μL of a stock solution of host (~2.0 mM), were added small aliquots (20–100 μL) of a standard solution. For each titration, 8–10 data points were collected, and approximately 2.5 equivalents of the ionic salt guest was present at the end of the titration. After each aliquot addition of the standard guest solution, the samples were shaken thoroughly within the capped NMR sample tube and then allowed to equilibrate inside the NMR probe for 1-2 min before the spectra were recorded. All parameters of the NMR spectrometer were kept constant throughout each titration experiment.

11.3 Titration Data Fitting Analysis

In all cases of ^{1}H NMR titration binding studies, all proton resonances were monitored to study the trends of the change in chemical shifts. The association constant (K_a) were determined by global fitting analysis to the 2:1 binding model using the supramolecular.org

web applet.[7] It should be emphasized that the global analysis approach of fitting all data sets simultaneously, greatly enhances the quality of the nonlinear curve fitting analysis. Here, we define the NMR resonance for the host as δ_H, the guest as δ_G and the host–guest complex as δ_{HG}. From this, we can also define the change in resonance for the host–guest complexation as $\delta_{\Delta HG} = \delta_{HG} - \delta_H$; and the change in observed resonance as $\Delta\delta = \delta - \delta_H$. We can now write the NMR version of the simple 2:1 equilibria according to equation:[7]

$$\delta = \frac{\delta_{HG}[G]_0 K_1[H] + 2\delta_{H_2G}[G]_0 K_1 K_2[H]^2}{[H]_0(1 + K_1[H] + K_1 K_2[H]^2)}$$

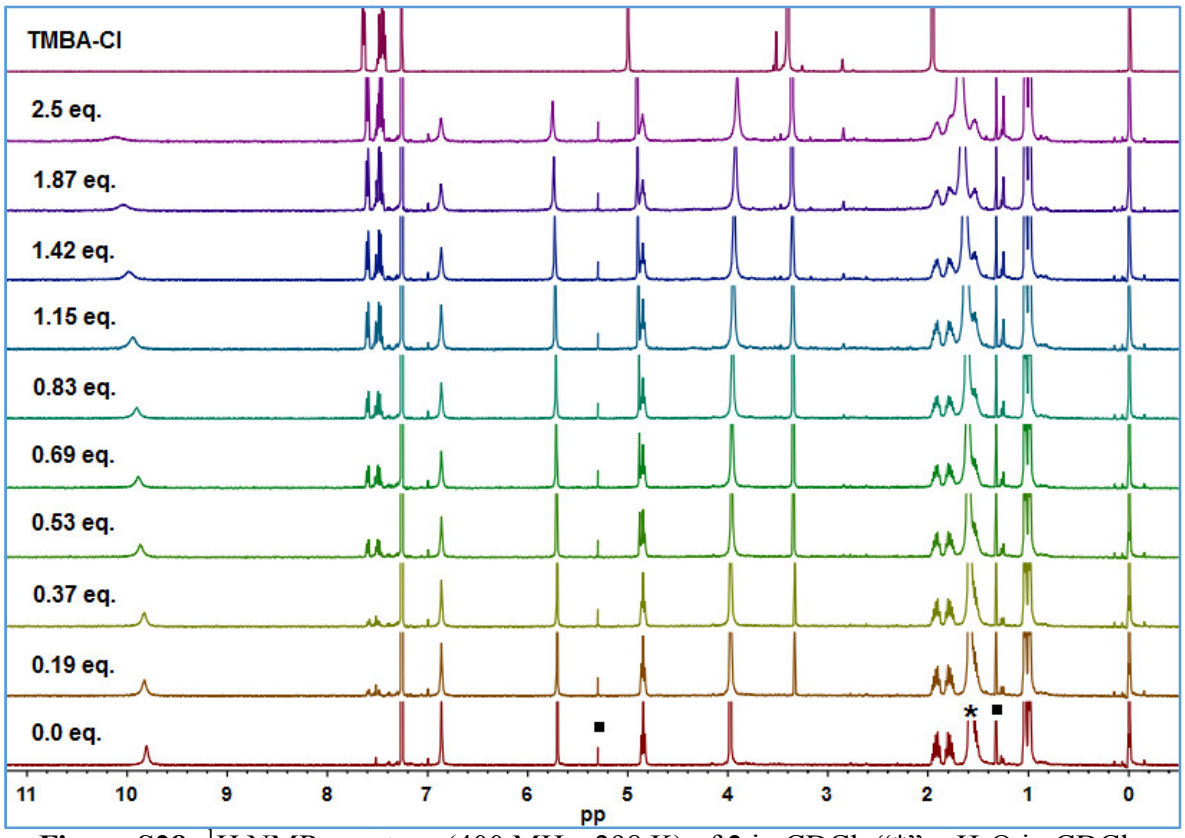


Figure S28: ^{1}H NMR spectrum(400 MHz, 298 K) of **2** in $CDCl_3$."*" = H_2O in $CDCl_3$, "■" = Crystallization solvents residue (DCM/^{t}Butylbenzene).

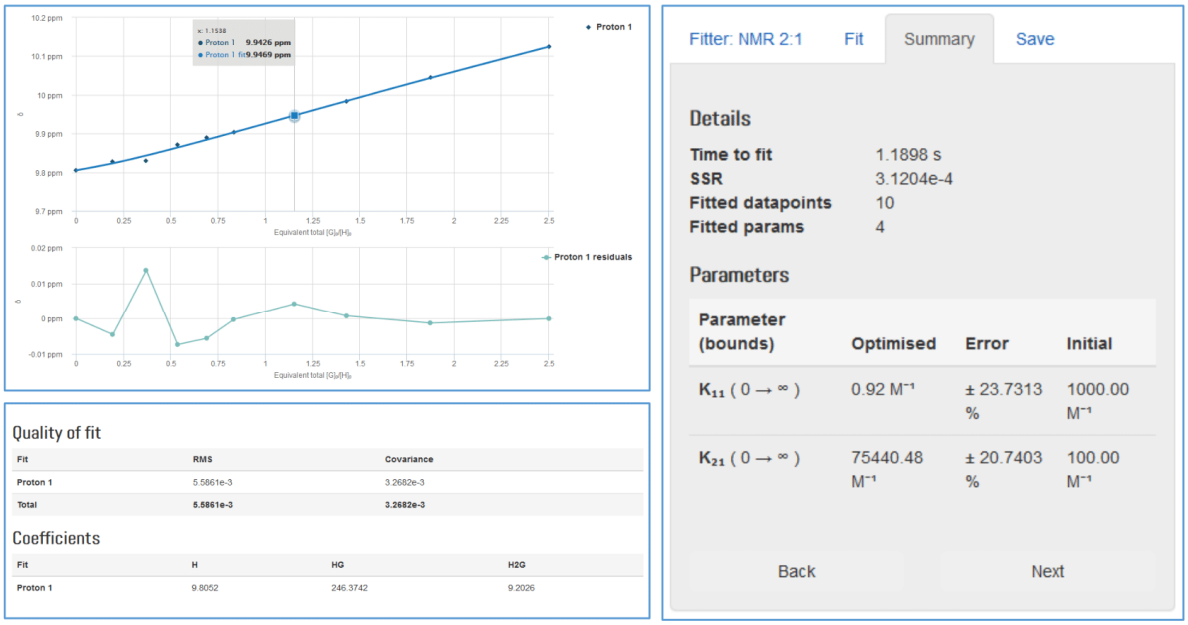


Figure S29. Screen captured output[7b] showing 2:1 NMR binding model of **1** for various concentrations of **2** at 298 K by the Thordarson's global fit analysis. The association constant (K_a) was based on the chemical shift changes of the –OH proton only.

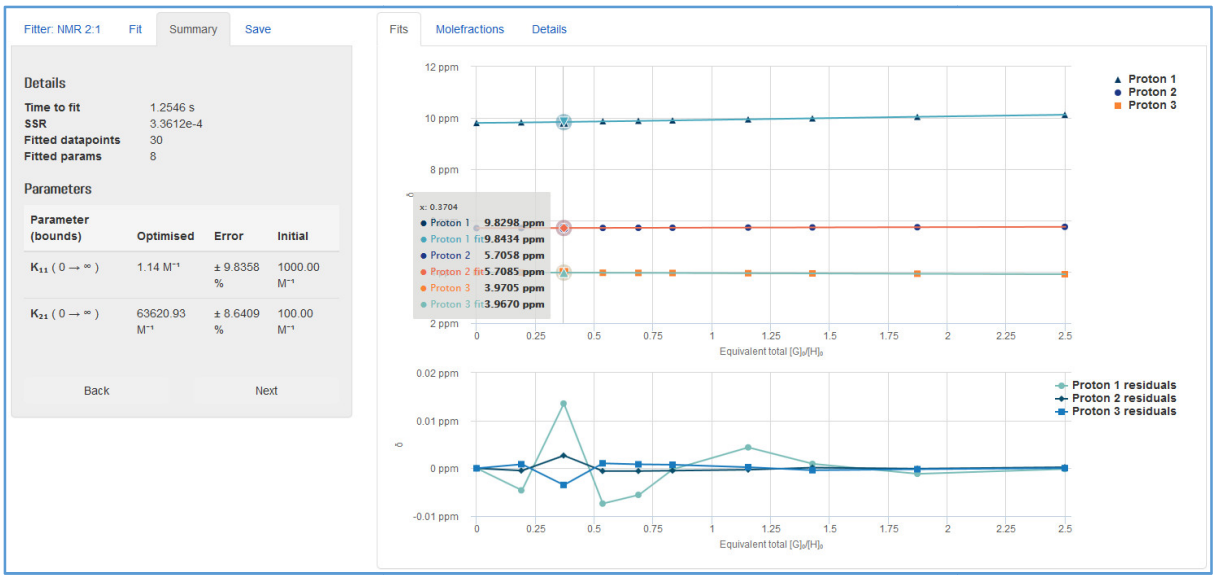


Figure S30. Screen captured output[7b] showing 2:1 NMR binding model of **1** for various concentrations of trimethylbenzylammonium chloride **2** at 298 K by the Thordarson's global fit analysis. The association constant (K_a) was based on the chemical shift changes of the –OMe, –C_3H and –OH protons.

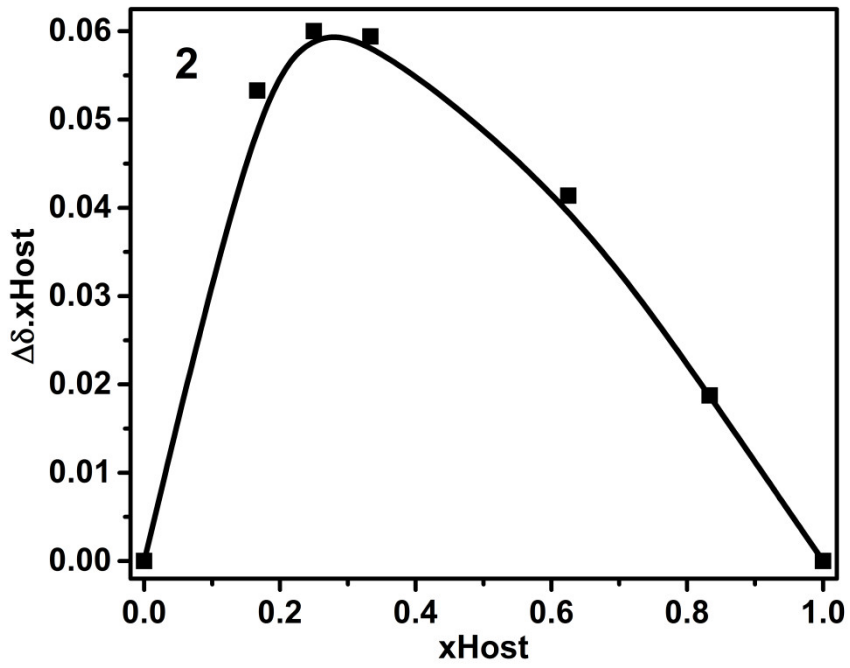


Figure S31: Job's plot showing the 2:1 stoichiometry of the complexes of host **1** and guest **2** from ^{1}H NMR titrations.

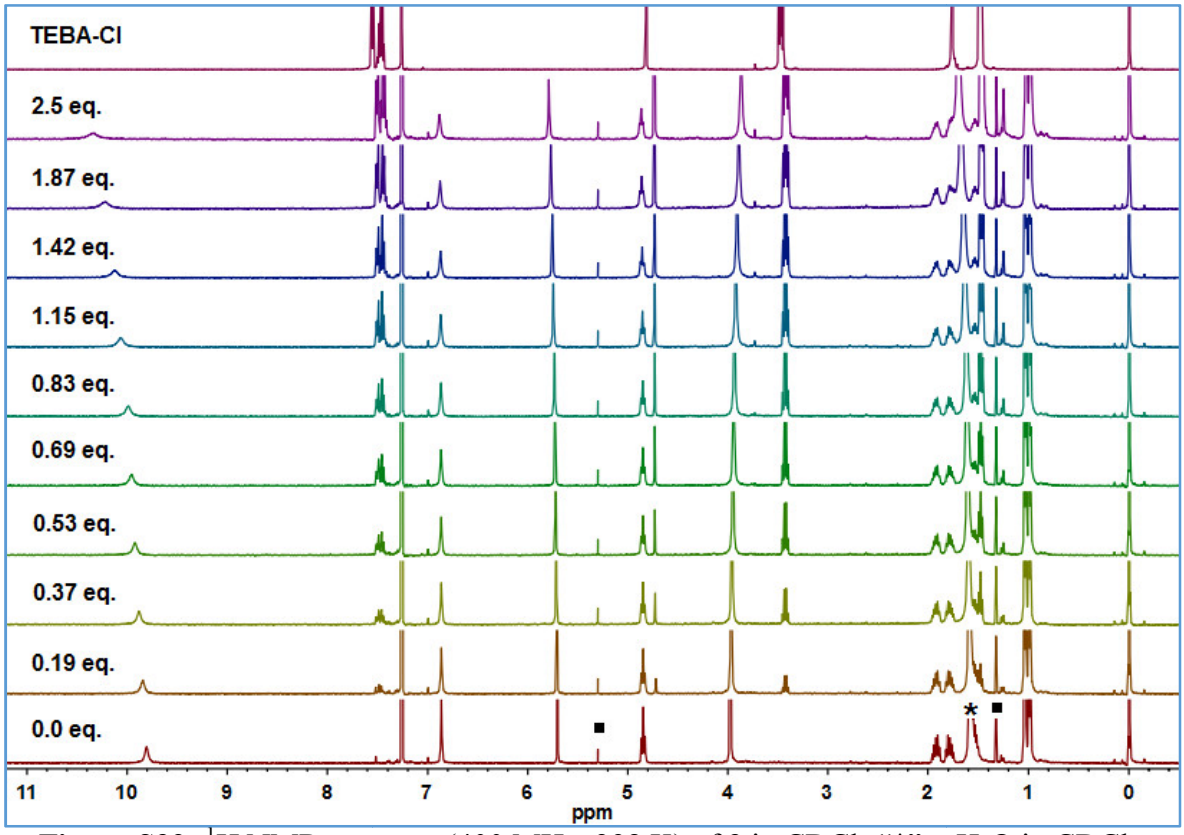


Figure S32: ^{1}H NMR spectrum(400 MHz, 298 K) of **3** in $CDCl_3$."*" = H_2O in $CDCl_3$, "■" = Crystallization solvents residue (DCM/^{t}Butylbenzene).

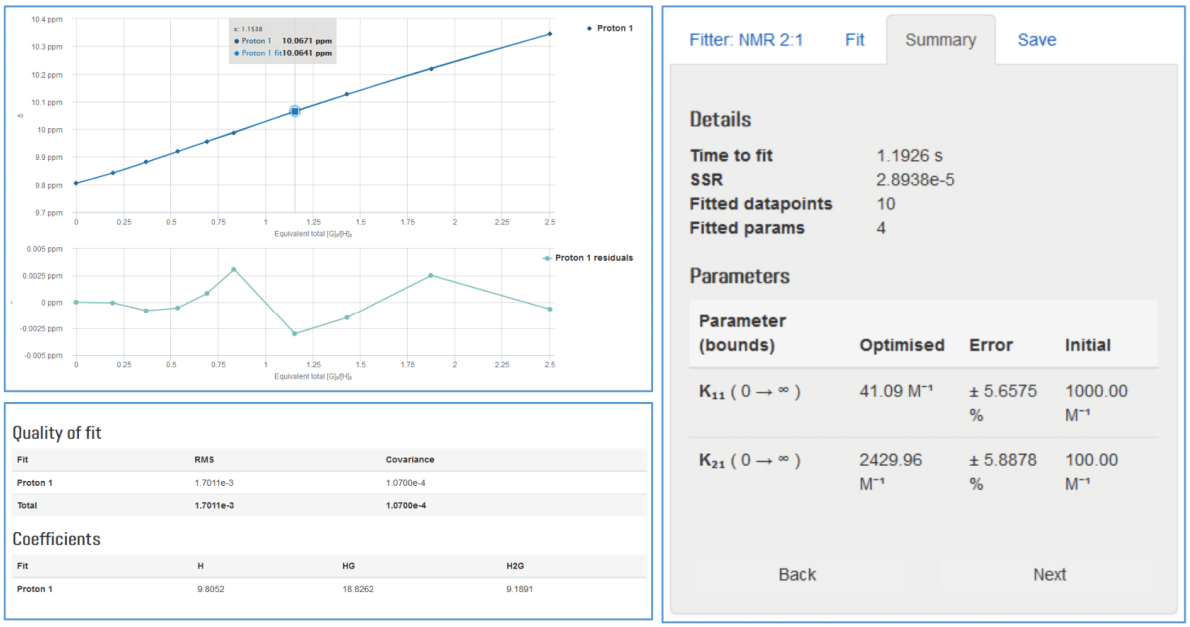


Figure S33. Screen captured output[7b] showing 2:1 NMR binding model of **1** for various concentrations of **3** at 298 K by the Thordarson's global fit analysis. The association constant (K_a) was based on the chemical shift changes of the –OH proton only.

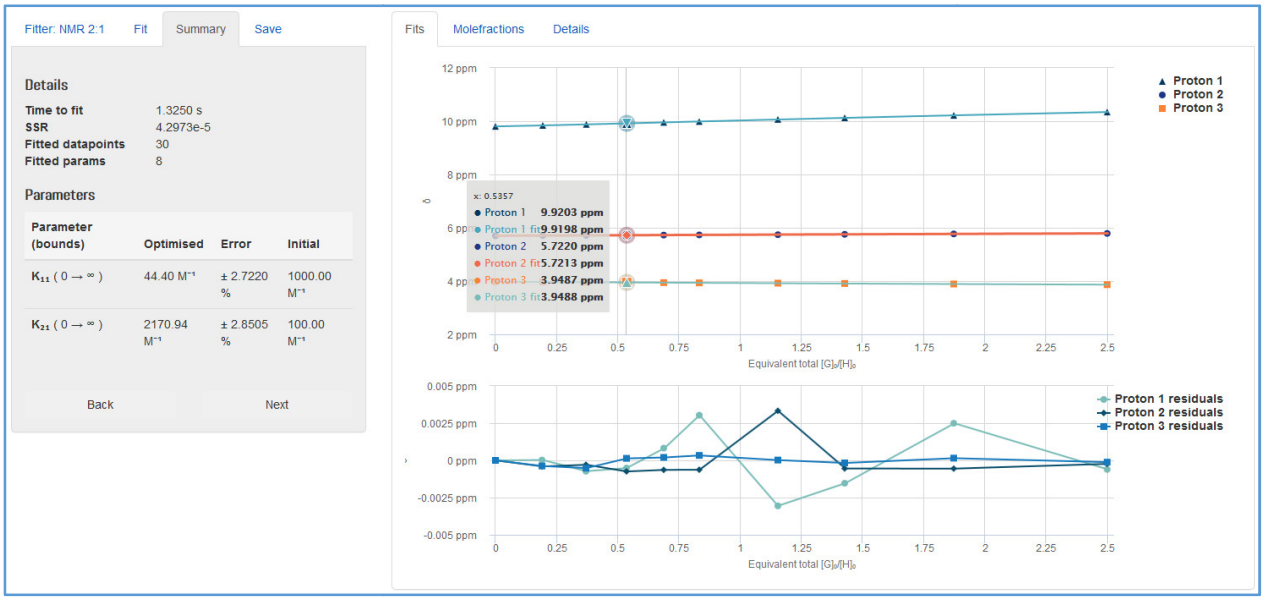


Figure S34. Screen captured output[7b] showing 2:1 NMR binding model of **1** for various concentrations of triethylbenzylammonium chloride **3** at 298 K by the Thordarson's global fit analysis. The association constant (K_a) was based on the chemical shift changes of the –OMe, –C_3H and –OH protons.

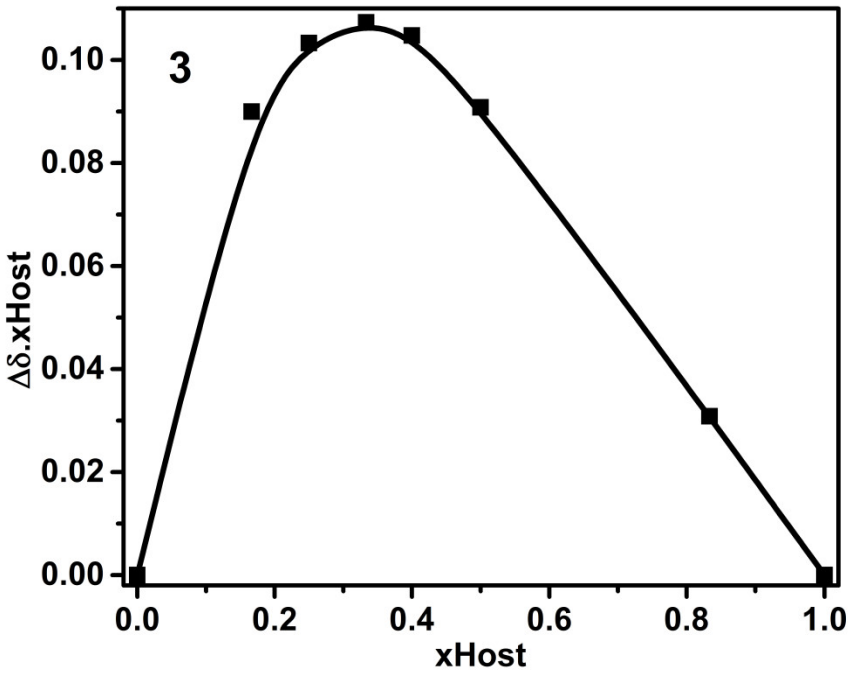


Figure S35: Job's plot showing the 2:1 stoichiometry of the complexes of host **1** and guest **3** from ^{1}H NMR titrations.

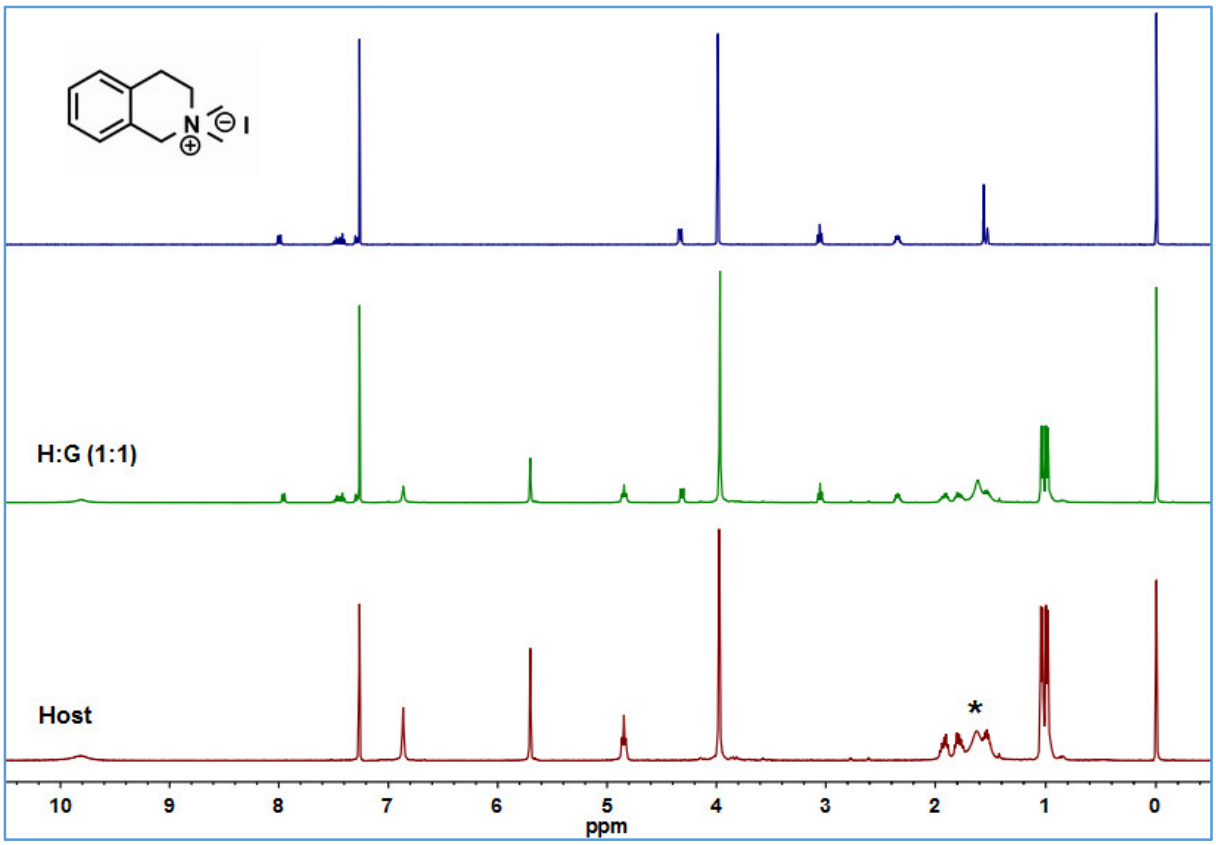


Figure S36: ^{1}H NMR spectrum (400 MHz, 298 K) of **4** in $CDCl_3$."*" = H_2O in $CDCl_3$.

No obvious changes in chemical shift were observed for the host and guest proton signals upon addition of 1.0 equiv. of the guest, indicating that **1** did not form inclusion complex with **4** or at least had very weak interactions.

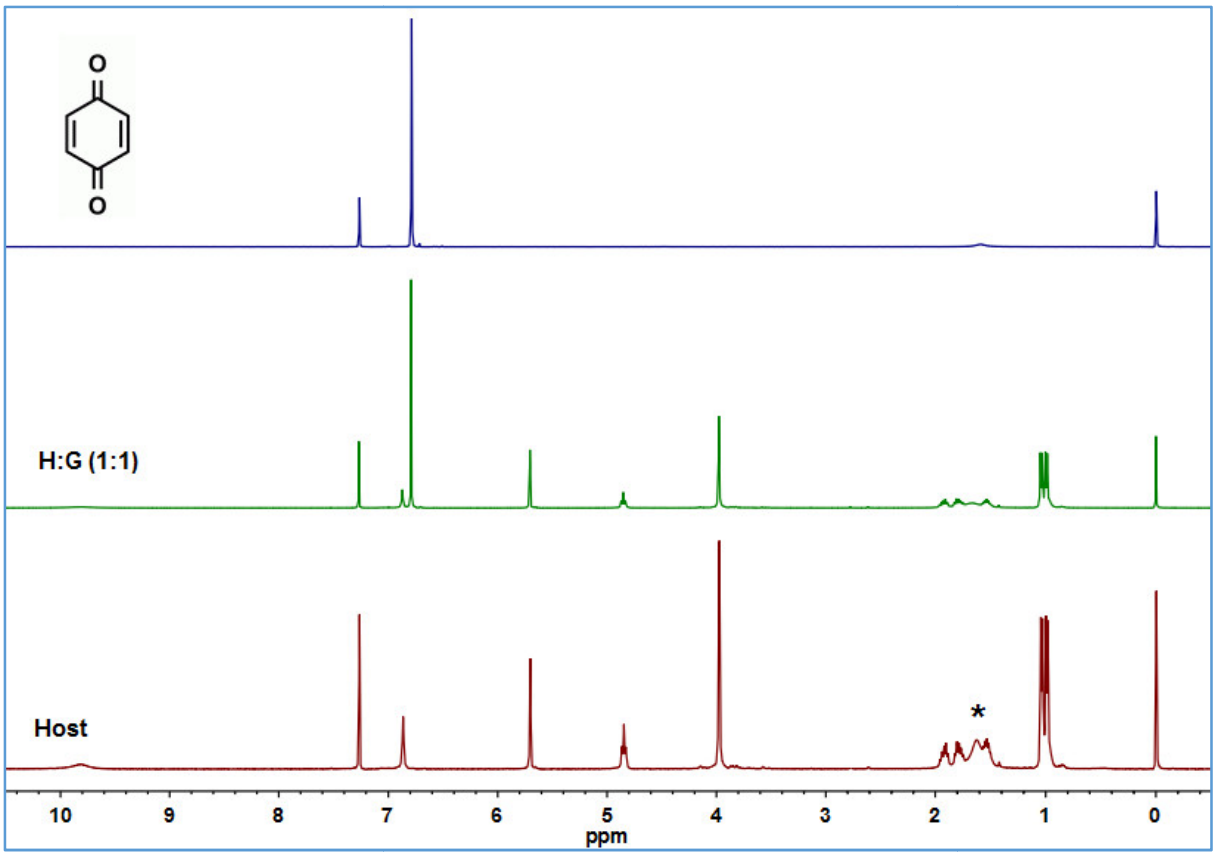


Figure S37: ^{1}H NMR spectrum (400 MHz, 298 K) of **5** in $CDCl_3$."*" = H_2O in $CDCl_3$.

No obvious changes in chemical shift were observed for the host and guest proton signals upon addition of 1.0 equiv. of the guest, indicating that **1** did not form inclusion complex with **5** or at least had very weak interactions.

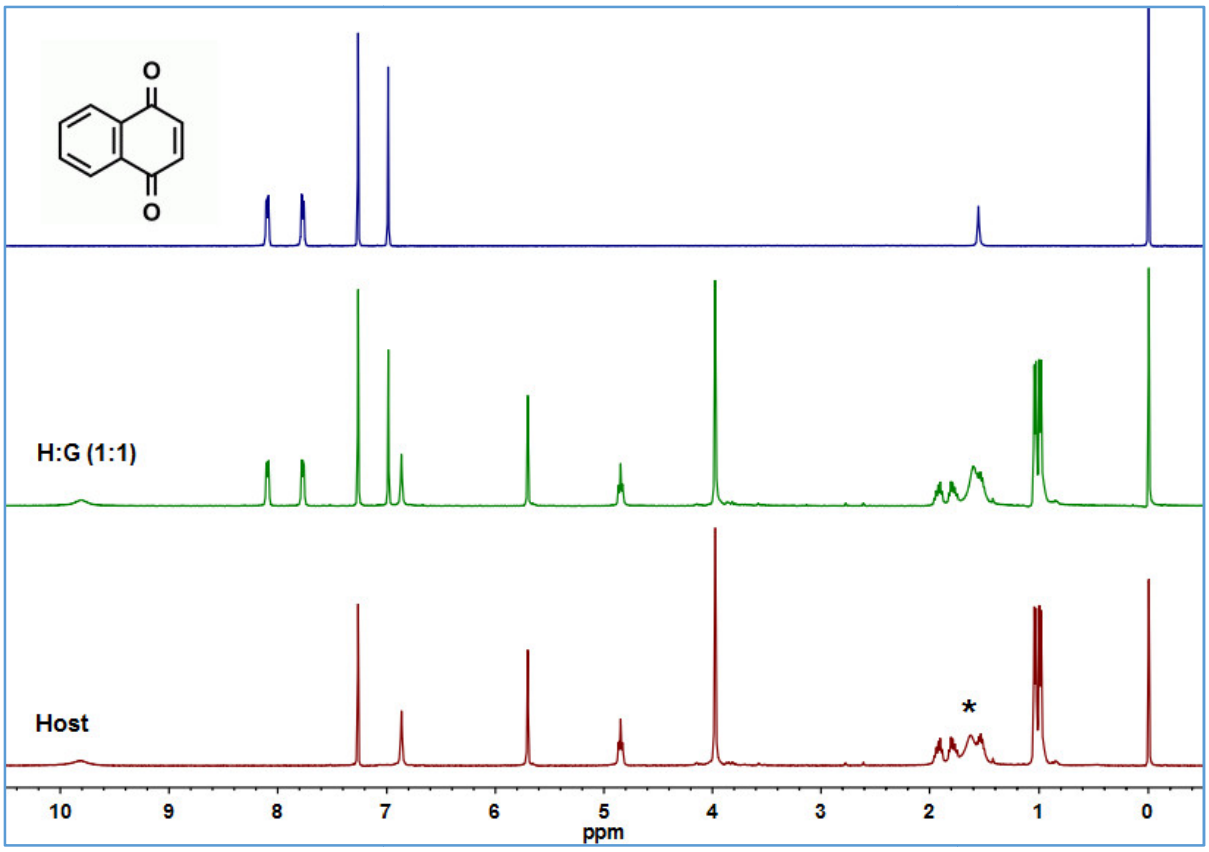


Figure S38: ^{1}H NMR spectrum (400 MHz, 298 K) of **6** in $CDCl_3$."*" = H_2O in $CDCl_3$.

No obvious changes in chemical shift were observed for the host and guest proton signals upon addition of 1.0 equiv. of the guest, indicating that **1** did not form inclusion complex with **6** or at least had very weak interactions.

12. ESI-HRMS spectra of 1 with guests 2 and 3

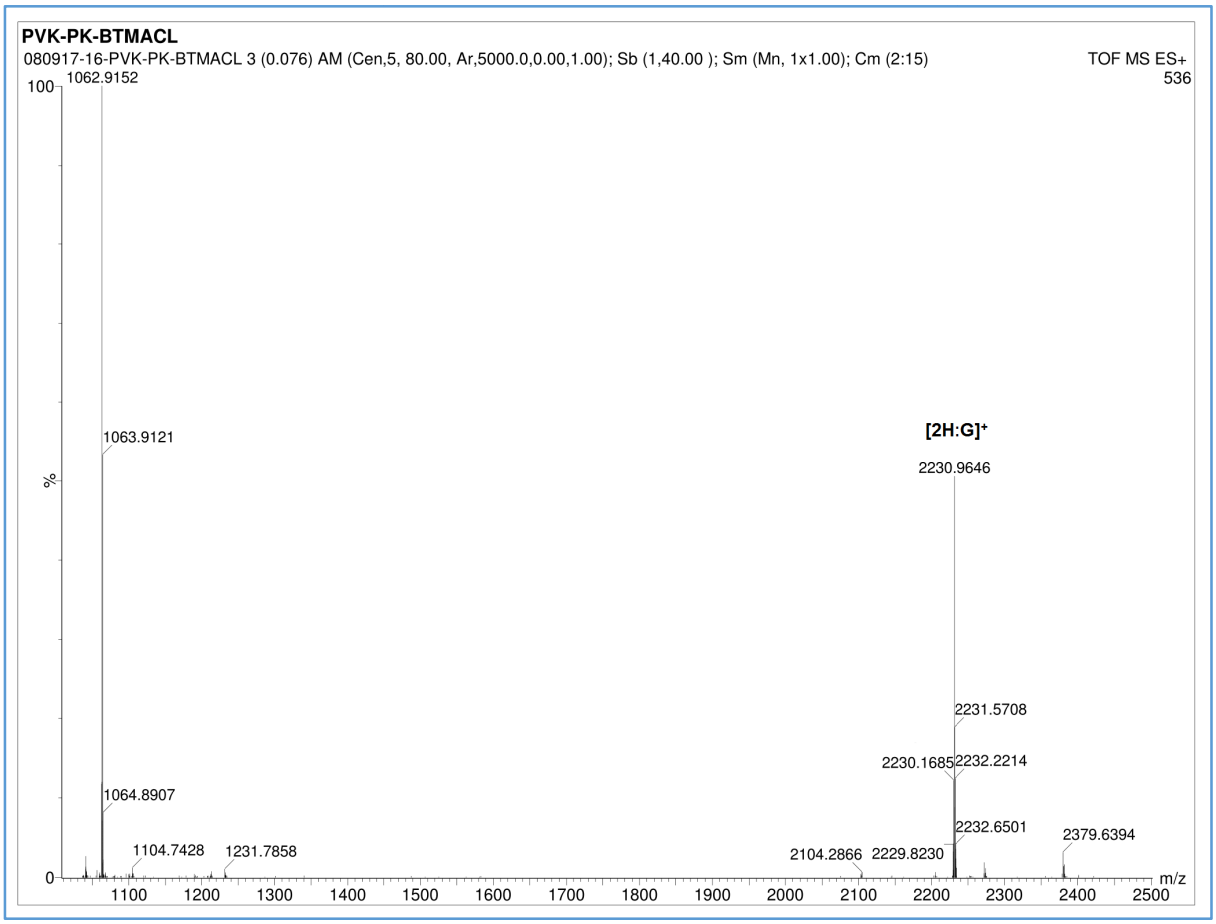


Figure S39: HR-ESI mass spectrum of **H_2:G** complex **2⊂1**.

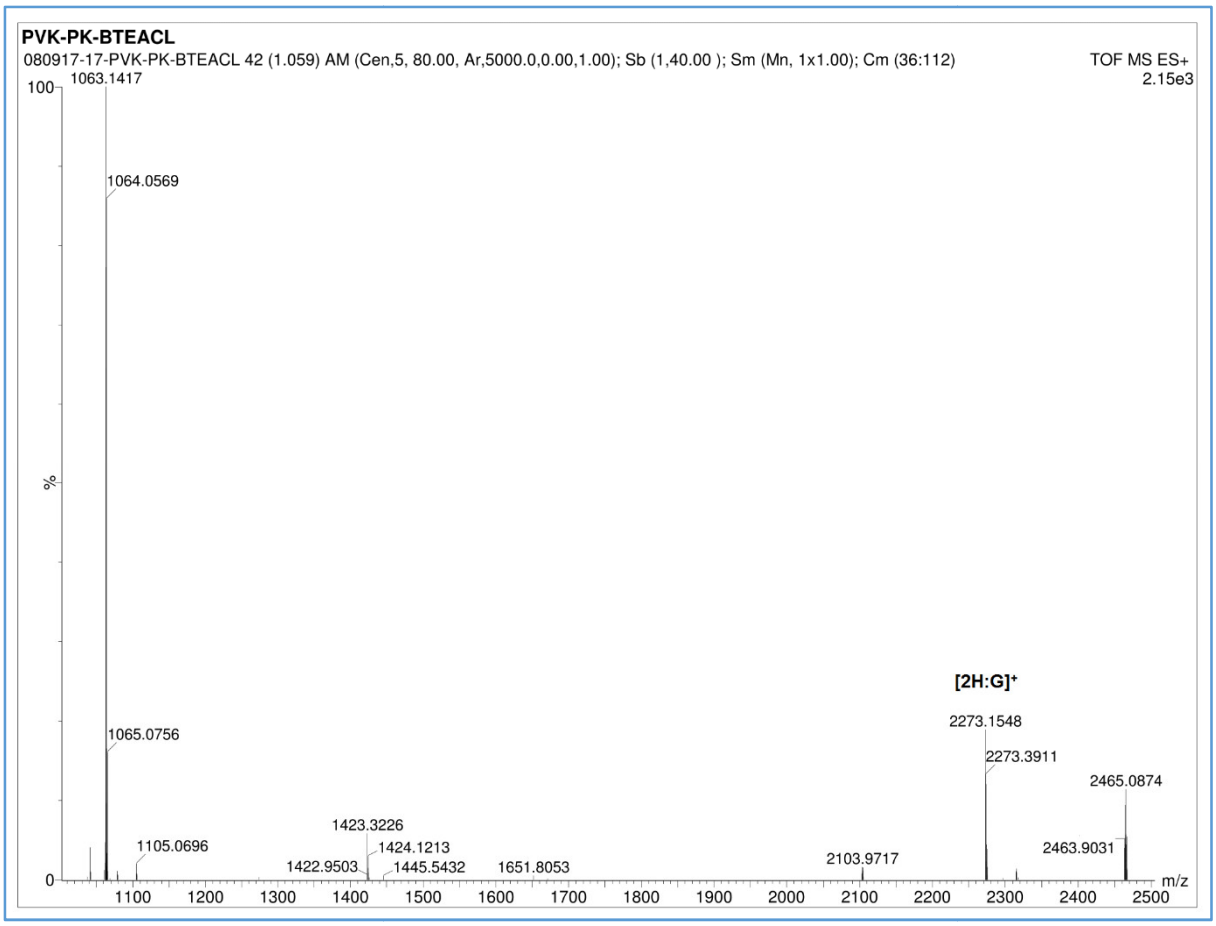


Figure S40: HR-ESI mass spectrum of **H_2:G** complex **3⊂1.**

13. Photophysical characterization details

13.1 UV-vis and PL spectra

UV-visible absorption and photoluminescence spectra were recorded on a JASCO V-650 and JASCO FP-6300 spectrophotometer, respectively. Spectroscopic measurements were done in $CHCl_3$ and DMSO (ca. 10^{-5} M) solutions at room temperature in cuvettes of 1.0 cm pathlength. Molar extinction coefficients obtained were verified for its consistency using Beer-Lambert's law.

13.2 PL quantum yield measurements in solution

For the determination of PLQEs, $CHCl_3$ solutions of **1** were made in such a way that their absorbance at λ = 285 nm was ca. 0.05–0.06. All the samples were excited at λ_{ex} = 310 nm. The quantum yield for the above solutions was calculated using the following relationship:

$$\phi_u = \phi_s (A_s/A_u)\times(I_u/I_s)\times(\eta_u/\eta_s)^2 \quad \text{..... (1)}$$

where the subscripts "s" and "u" refer to standard and unknown samples, A_u and A_s to absorbance of the sample and the standard at the excitation wavelength, I_u and I_s to the integrated emission intensities of the sample and the standard, and η_u and η_s to the refractive indexes of the corresponding solutions, respectively. 9,10-Diphenylanthracene (DPA) in cyclohexane (ϕ = 0.90) was chosen as the reference for measuring PL quantum yield.[8] The PLQE values reported here correspond to the average value of three independent determinations.

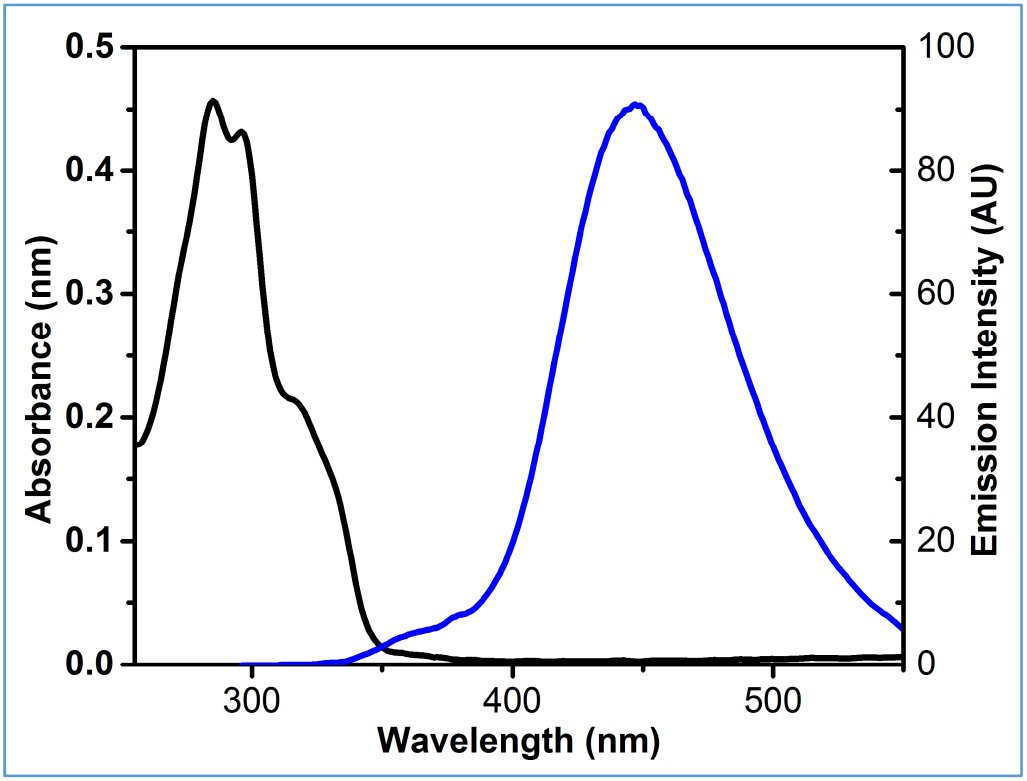


Figure S41: UV-vis absorption (black) and photoluminescence (blue) spectrum of **1** in (ca. 10^{-5} M) $CHCl_3$.

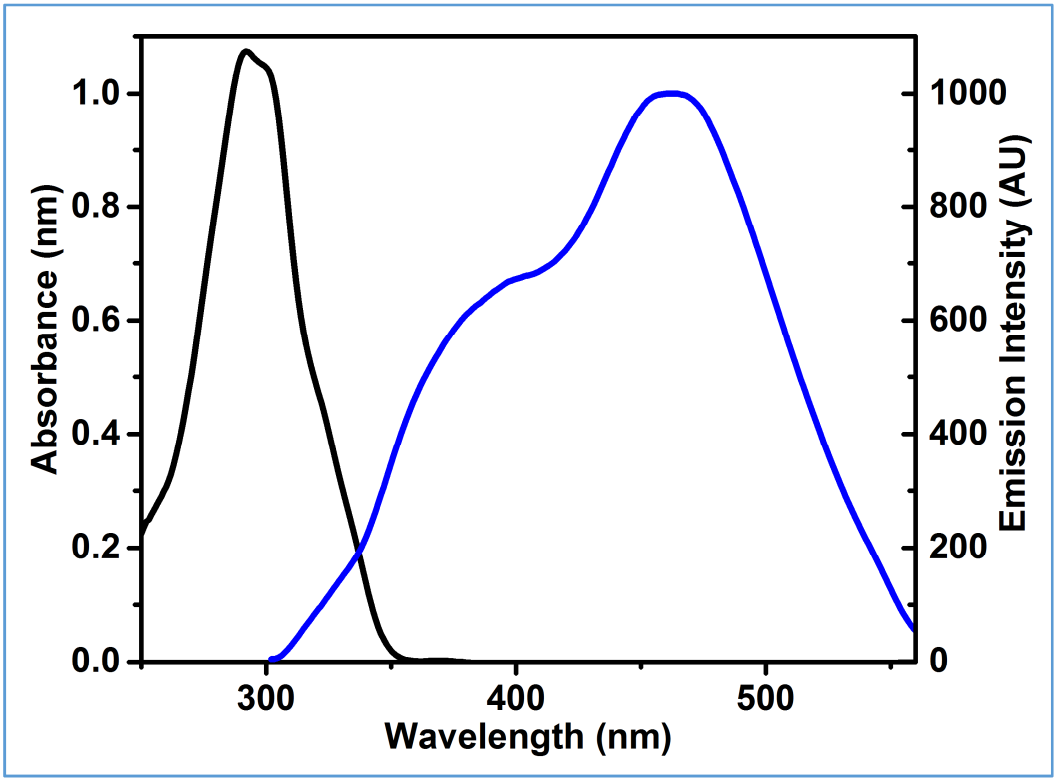


Figure S42: UV-vis absorption (black) and photoluminescence (blue) spectrum of **1** in (ca. 10^{-5} M) DMSO.

9. References

1. Perrin, D. D.; Armarego, W. L.; Willfred, L. F. *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1988.
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3. (a) Soldatenkov, A. T.; Soldatova, S. A.; Mamyrbekova-Bekro, J. A.; Gimranova, G. S.; Malkova, A. V.; Polyanskii, K. B.; Kolyadina, N. M.; Khrustalev, V. N. *Chem. Heterocycl. Compd.* **2012,** *48,* 1332. (b) Kalaska, B.; Piotrowski, L.; Leszczynska, A.; Michalowski, B.; Kramkowski, K.; Kaminski, T.; Adamus, J.; Marcinek, A.; Gebicki, J.; Mogielnicki, A.; Buczko, W. *J. Agric. Food Chem.* **2014**, *62,* 2853.
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