

Electronic Supplementary Information for

Tuning the conformational flexibility of quinoxaline cavitands for complexation at the gas-solid interface

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Index

1	General experimental methods	S2
2	Synthetic procedures.....	S4
3	NMR and MS spectra	S8
4	X-ray crystallography	S20
5	Thermogravimetric analyses.....	S24

1 General experimental methods

Synthesis

QxCav¹ and QxCav@SiO₂² were prepared following published procedures. Unless stated otherwise, all reactions were carried out under strictly anhydrous conditions under Ar atmosphere. All solvents were dried and distilled using standard procedures. All commercially obtained reagents were used as received unless otherwise specified. Automatic flash column chromatography was performed on Combiflash 300.

NMR spectroscopy

NMR spectra were collected on Bruker Avance 400 (400 MHz) and JEOL ECZ600R (600MHz) spectrometer at 25 °C. ¹H and ¹³C NMR chemical shifts (δ) are given in part per million (ppm) and calibrated to either residual solvent signal. NMR data are reported in the following format: chemical shift (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz), integration).

ATR-IR spectroscopy

Infrared absorption spectroscopy analyses were performed with a Perkin Elmer FT-IR Spectrum Two instrument using powder samples. The background was subtracted from every spectrum recorded.

TGA analysis

TGA analysis were performed on a Perkin Elmer TGA 8000. Heating run: 25° to 900°C at 10°C/min, in air.

Mass spectrometry

Electrospray ionization mass spectrometry (ESI-MS) experiments were performed using a Waters ZMD spectrometer equipped with an electrospray interface.

High-resolution MALDI-TOF was performed using an AB SCIEX MALDI TOF-TOF 4800 Plus (matrix: α-cyano-4-hydroxycinnamic acid).

GC-MS analyses were performed using an Agilent Technologies 6890N Network GC System

1. P. Soncini, S. Bonsignore, E. Dalcanale and F. Ugozzoli *J. Org. Chem.* 1992, **57**, 4608.

2. A. Rozzi, A. Pedrini, R. Pinalli, E. Cozzani, I. Elmi, S. Zampolli and E. Dalcanale submitted for publication

MEMS devices

The preconcentration MEMS cartridge is a 25x14x1.5 mm³ silicon/borosilicate stack containing a 90 mm³ reservoir for the cavitand etched into the silicon wafer by deep reactive ion etching. The geometry of the reservoir consists of 8 parallel channels, 1 mm wide 550 μm deep and 17 mm long, with two common sections connecting them all to the inlet and outlet holes drilled in the borosilicate wafer (Figure S1). The outlet section contains a MEMS filter array designed to retain the mesh during the MEMS packing.

Furthermore, the MEMS devices integrate Platinum thin film metallization on the silicon wafer backside as heater and temperature sensor. The small thermal mass of the MEMS device enables very rapid temperature cycling with heating rates up to 10°C/s and maximum temperature up to 300°C, as necessary for an efficient purge&trap injection.

The following figure shows the geometries of the MEMS device:

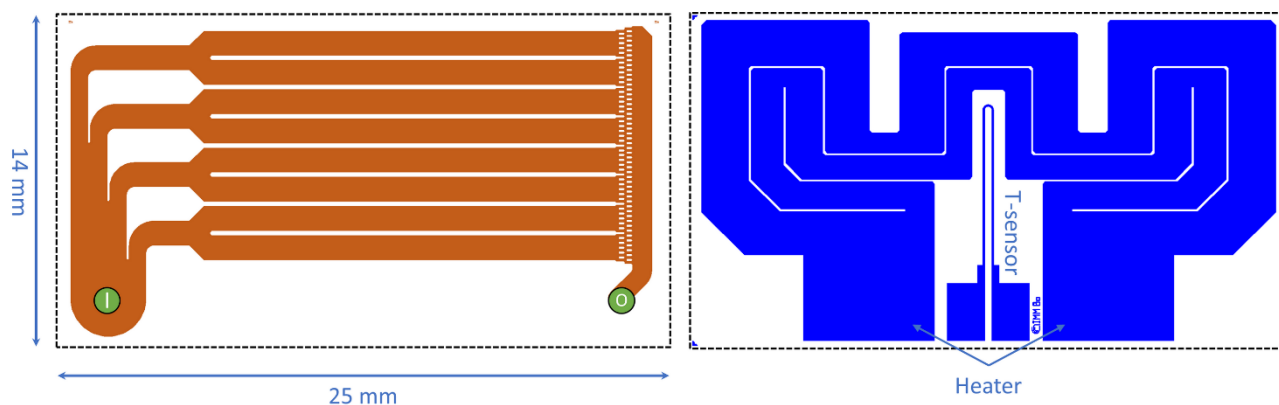
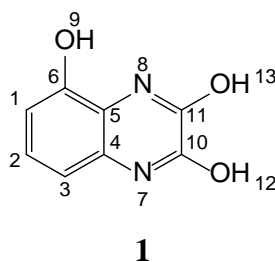


Figure S1. MEMS device layout: geometry of the channels fabricated by deep reactive ion etching (left) and of the Platinum metallization (right) defined on the backside of the silicon die. The green circles represent the inlet (I) and outlet (O) holes laser-drilled through the borosilicate wafer.

2 Synthetic procedures

Synthesis of quinoxaline-2,3,5-triol (1). 400 mg of 2,3-diaminophenol (3.22 mmol, 1 eq) and 348 mg of oxalic acid (3.87 mmol, 1.2 eq) were suspended in 20 mL of HCl 4 M. The suspension was stirred at 100°C overnight. The suspension was cooled to room temperature, filtered on a Büchner funnel and washed with water. The precipitate was dried in oven at 100°C affording 545 mg of grey powder (96% yield).

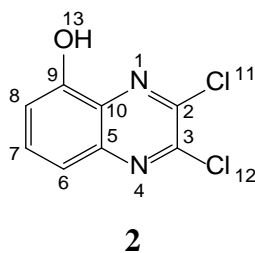


¹H NMR (400 MHz, DMSO-d₆): δ = 11.83 (s, 1H, H₁₂), 11.02 (s, 1H, H₁₃), 10.19 (s, 1H, H₉), 6.89 (t, J_o = 8.0 Hz, 1H, H₂), 6.60 (dd, J_o = 8.0, J_m = 5.5 Hz, 2H, H₁, H₃).

¹³C NMR (101 MHz, DMSO-d₆): δ = 155.8, 155.2, 144.8, 126.9, 123.7, 114.8, 109.5, 106.4.

ESI(+)-MS: m/z = 179.08 [M+H]⁺, 201.08 [M+Na]⁺, 217.07 [M+K]⁺, 379.08 [2M+Na]⁺

Synthesis of 2,3-dichloroquinoxalin-5-ol (2). 1.05 g of compound **1** (5.9 mmol, 1 eq) were dissolved in 20 mL of anhydrous dichloroethane (DCE) and 5 drops of DMF were added. 2.8 mL of phosphorus(V) oxychloride (29.5 mmol, 5 eq) were added to the brownish solution and the reaction was stirred overnight at 80°C. TLC was performed (eluent: DCM/MeOH 95:5, R_f of the product = 0.85, yellow dot) to monitor the reaction evolution. After the completion of the reaction, the mixture was cooled to room temperature and quenched by the addition of 50 mL of MeOH. Volatiles were evaporated under reduced pressure and 50 mL of HCl 1 M were added. The mixture was extracted with AcOEt (3 x 20 mL) and the orange organic phases were collected and dried with Na₂SO₄. After rotary evaporation of the solvent, the crude was loaded on silica and purified by automatic flash column chromatography using a linear gradient from 100% hexane to hexane/AcOEt 1:1 in 15 minutes. 881 mg of product were collected as yellow solid (69% yield).

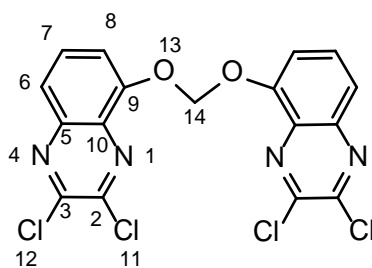


¹H NMR (400 MHz, DMSO-d₆): δ = 10.84 (s, 1H, H₁₃), 7.75 (t, J_o = 8.0 Hz, 1H, H₇), 7.49 (m, 1H, H₈), 7.26 (m, 1H, H₆).

^{13}C NMR (101 MHz, DMSO- d_6): $\delta = 153.7, 145.0, 142.6, 141.7, 133.0, 131.8, 118.0, 114.9$.

GC-MS: $t_R = 10.934$ min, $m/z = 213.990$ $[\text{M}]^+$

Synthesis of bis((2,3-dichloroquinoxalin-5-yl)oxy)methane (3). 530 μL of diiodomethane (6.58 mmol, 20 eq) and 680 mg of potassium carbonate (4.93 mmol, 15 eq) were suspended in 15 mL of anhydrous ACN under inert atmosphere. Temperature was raised to 80°C and 70 mg of compound **2** (329 μmol , 1 eq) dissolved in 10 mL of dry ACN were slowly added during 3h. The reaction turned brownish. TLC in DCM was performed (R_f of the product = 0.20, fluorescent spot) to monitor the reaction evolution. After the completion of the reaction, the mixture was cooled to room temperature, and acidic water was added to quench the reaction. Organic solvent was removed by rotary evaporation, and the suspension of the crude in water was sonicated, filtered and washed with water. The crude was loaded on silica gel and purified by automatic flash column chromatography using DCM as eluent. 20 mg of white product were obtained (28% yield).



^1H NMR (400 MHz, CDCl_3): $\delta = 7.84 - 7.70$ (m, 6H, H6, H7, H8), 6.28 (s, 2H, H14).

^{13}C NMR (101 MHz, CDCl_3): $\delta = 151.4, 146.1, 144.7, 141.6, 133.0, 131.5, 123.4, 116.6, 93.1$.

GC-MS: $t_R = 10.955$ min, $m/z = 213.990$ fragment ion.

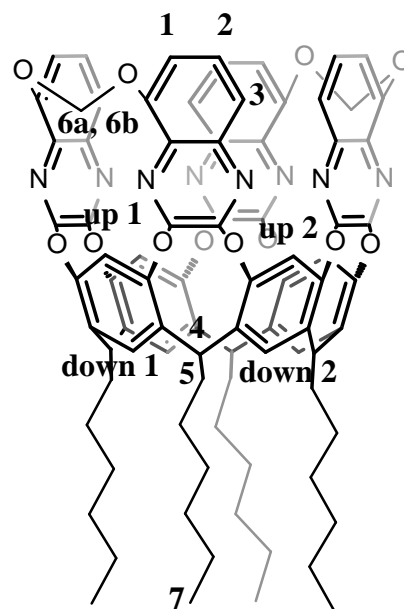
Synthesis of hexyl-footed cavitand (MeQxCleft). 13.4 mg of **Res** [**C₆H₁₃,H**] (16.3 μ mol, 1 eq), 13.5 mg of anhydrous potassium carbonate (97.8 μ mol, 6 eq) and 20 mg of compound **3** (32.5 μ mol, 2 eq) were introduced in a microwave reactor with 25 mL of DMF. The mixture was heated at 80 °C (maximum power = 300 W) for 3h. TLC confirmed the completion of the reaction (eluent: hexane/AcOEt 6:4, R_f of the product = 0.72, blue fluorescent spot).

The solvent was evaporated under reduced pressure. The crude was suspended in water, filtered, and washed repeatedly with water. The residue was purified by automatic flash column chromatography on silica gel with a gradient elution from hexane to hexane/AcOEt 1:1 in 15 minutes. 3.5 mg of product were collected as white solid (15% yield).

¹H NMR (400 MHz, CD₂Cl₂) δ 8.19 (s, 2H, H up 1), 8.13 (s, 2H, H up 2), 7.57 (dd, $J_o = 8.4$, $J_m = 1.5$ Hz, 4H, H1), 7.50 (t, $J_o = 8.1$ Hz, 4H, H2), 7.38 (s, 4H, H down 1,2), 7.32 (dd, $J_o = 7.7$, $J_m = 1.4$ Hz, 4H, H3), 6.76 (d, $J_{vic} = 6.0$ Hz, 2H, H6a), 6.13 (d, $J_{vic} = 6.0$ Hz, 2H, H6b), 5.74 (t, $J = 8.2$ Hz, 4H, H4), 2.37 (m, 8H, H5), 1.40 (m, 32H, -CH₂-), 1.03 – 0.92 (m, 12H, H7).

¹³C NMR (101 MHz, CD₂Cl₂) δ 152.8, 152.7, 152.5, 152.4, 151.0, 141.1, 136.7, 136.3, 131.6, 129.6, 123.8, 123.2, 122.7, 119.5, 119.3, 118.7, 100.5, 34.2, 32.5, 31.9, 29.7, 29.4, 28.0, 22.7, 13.8.

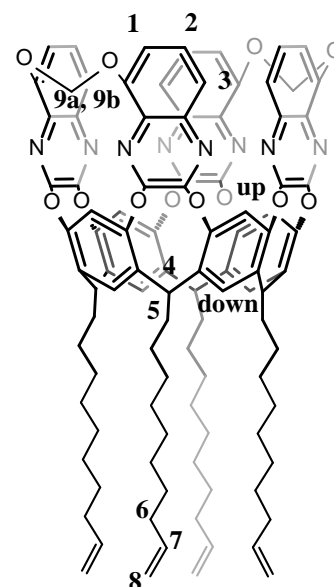
MALDI-TOF: m/z calculated for $[M+H]^+$ C₈₆H₈₁N₈O₁₂ = 1417.5939; found = 1417.59685.



Synthesis of decenyl-footed cavitand (MeQxCleft-DB). 229 mg of **Res** [**C₁₀H₁₉, H**] (220 μ mol, 1 eq), 194 mg of compound **3** (440 μ mol, 2 eq) and 213 mg of potassium carbonate (1.54 mmol, 7 eq) were suspended in 30 mL of DMF and inserted in a 250 mL Schlenk tube.

Temperature was set to 80°C and the reaction were stirred overnight. The completion of the reaction was checked by TLC (AcOEt/hexane 1:1, R_f of product = 0.83, blue fluorescent spot). The reaction was cooled to room temperature and poured in 500 mL of 1 M HCl. The obtained orange solid was filtered, loaded on silica gel and purified by automatic flash column chromatography with a gradient elution from 100% hexane to 100% AcOEt in 16 minutes. 98 mg of brownish solid were obtained (27% yield).

¹H NMR (600 MHz, CDCl₃): δ = 8.19 (s, 2H, H up1), 8.05 (s, 2H, H up2), 7.50 (dd, $J = 8.3$, 1.3 Hz, 4H, H1), 7.37 (t, $J = 8.1$ Hz, 4H, H2), 7.26 –



7.20 (m, 8H, H3 and H down), 6.62 (d, J = 6.3 Hz, 2H, H9a), 6.35 (d, J = 6.3 Hz, 2H, H9b), 5.87 – 5.77 (m, 4H, H7), 5.67 (t, J = 8.1 Hz, 4H, H4), 5.03 – 4.87 (m, 8H, H8), 2.26 (q, J = 7.9 Hz, 8H, H5), 2.05 (q, J = 7.1 Hz, 8H, H6), 1.44 – 1.25 (m, 48H, –CH₂-).

¹³C NMR (101 MHz, CDCl₃): δ = 152.8, 152.7, 152.5, 152.5, 151.5, 141.1, 139.2, 136.3, 136.0, 131.8, 129.3, 124.1, 123.1, 122.8, 119.5, 119.1, 118.6, 114.2, 34.0, 33.9, 32.5, 29.7, 29.7, 29.5, 29.2, 29.0, 28.0.

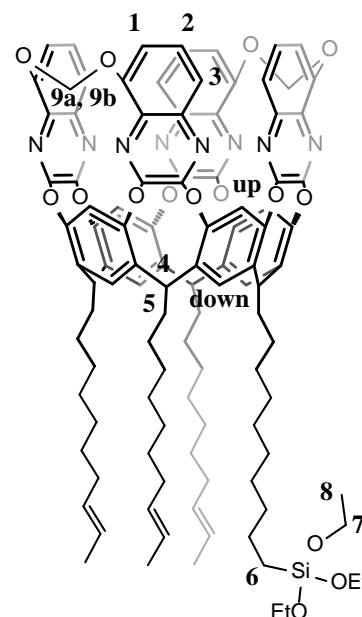
MALDI-TOF: m/z calculated for [M+H]⁺ C₁₀₂H₁₀₅N₈O₁₁ = 1634.7886, found = 1634.7887.

Synthesis of silylated cavitanol (MeQxCleft-Si): 63.8 mg of **MeQxCleft-DB** (39 μmol, 1 eq), were dissolved in 7 mL of anhydrous toluene; four cycles of freeze-pump thaw were performed to degas the solution. 43.2 μL of triethoxysilane 95% (230 μmol, 6 eq) and 16 μL of Karstedt's catalyst were added in a glove-box under nitrogen atmosphere. The reaction was stirred for 48 hours at room temperature. The reaction was poured in a mixture of 200 mL of methanol and 100 mL of water, and the obtained white precipitate was filtered. The residue was dissolved in AcOEt, dried with Na₂SO₄, filtered and the solvent was removed under reduced pressure. The product was obtained as brown powder (31 mg, 37% yield).

¹H NMR (600 MHz, CDCl₃): δ = 8.19 (s, 2H, H up 1), 8.04 (s, 2H, H up 2), 7.49 (d, J = 8.4 Hz, 4H, H1), 7.37 (t, J = 8.1 Hz, 4H, H2), 7.27-7.22 (m, 8H, H down, H3), 6.62 (d, J = 6.3 Hz, 2H, H9a), 6.35 (d, J = 6.3 Hz, 2H, H9b), 5.67 (t, J = 8.2 Hz, 4H, H4), 3.81 (q, J = 7.0 Hz, 18H, H7), 2.26 (m, J = 8.0 Hz, 8H, H6), 2.05 – 1.96 (m, 8H, H5), 1.45-1.23 (m, 64H, –CH₂-), 1.23-1.18 (m, 27 H, H8).

¹³C NMR (101 MHz, CDCl₃): δ = 152.8, 151.5, 141.1, 131.8, 129.3, 123.1, 122.8, 119.5, 119.1, 118.6, 77.3, 77.0, 76.7, 59.0, 58.5, 58.3, 34.0, 33.3, 32.5, 29.7, 28.0, 22.7, 18.4, 18.3, 14.1.

MALDI-TOF: m/z calculated for C₁₂₀H₁₅₃N₈O₂₁Si₃ (four silyl groups) [M+H]⁺ = 2127.0488, found = 1798.8736 (one silyl group, major peak), 1634.7868 (no silyl groups), 1962.9599 (two silyl groups).



3 NMR and MS spectra

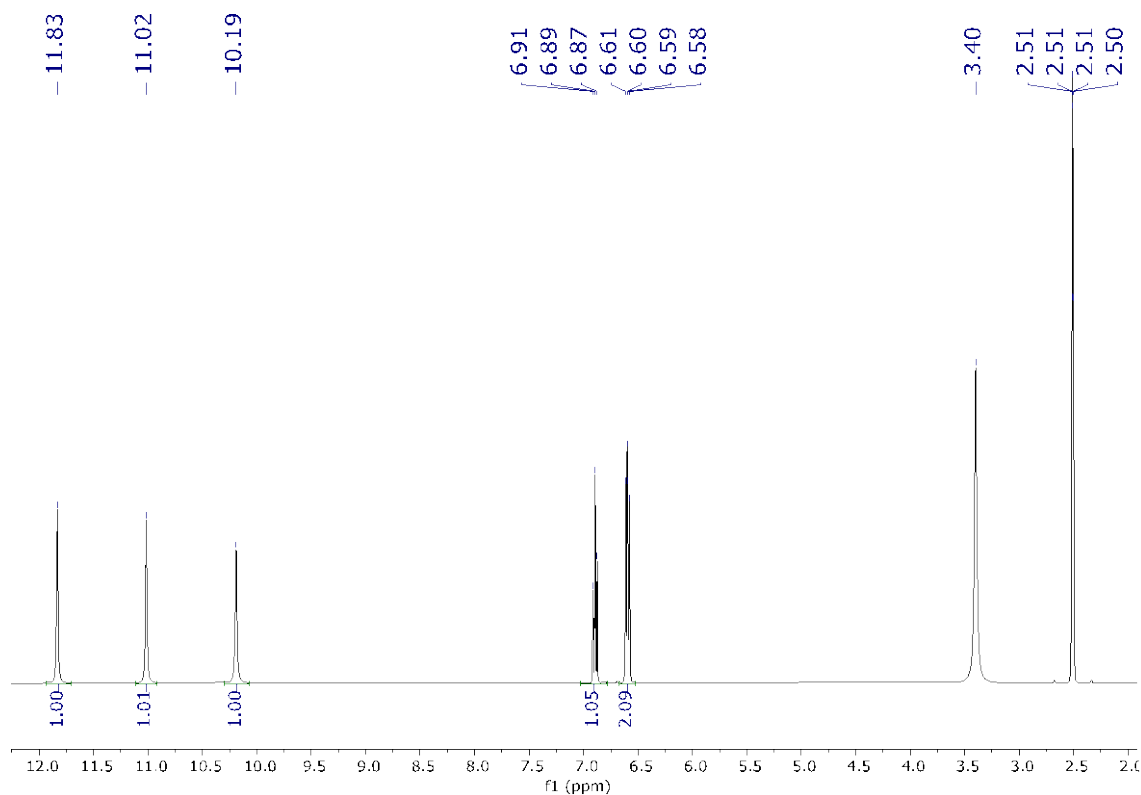


Figure S2. ^1H NMR (400 MHz, DMSO-d_6) spectrum of compound **1**.

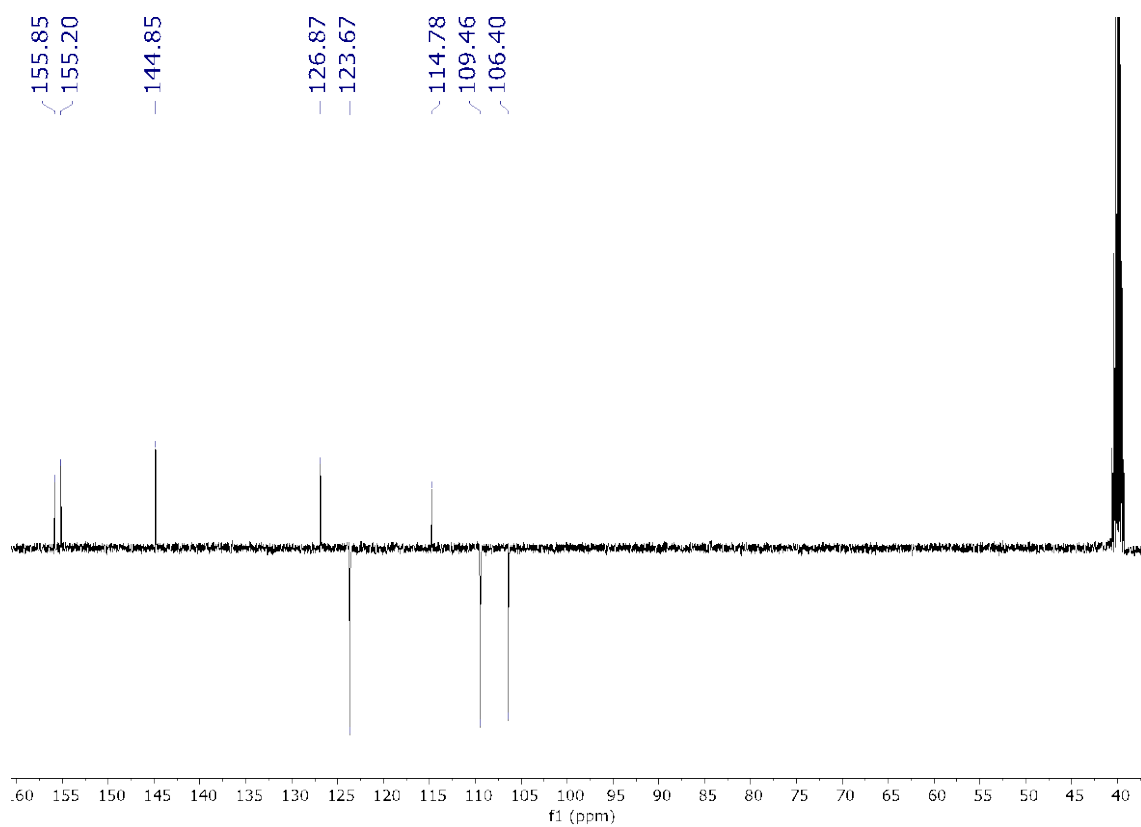


Figure S3. ^{13}C -APT NMR (101 MHz, DMSO-d_6) spectrum of compound **1**.

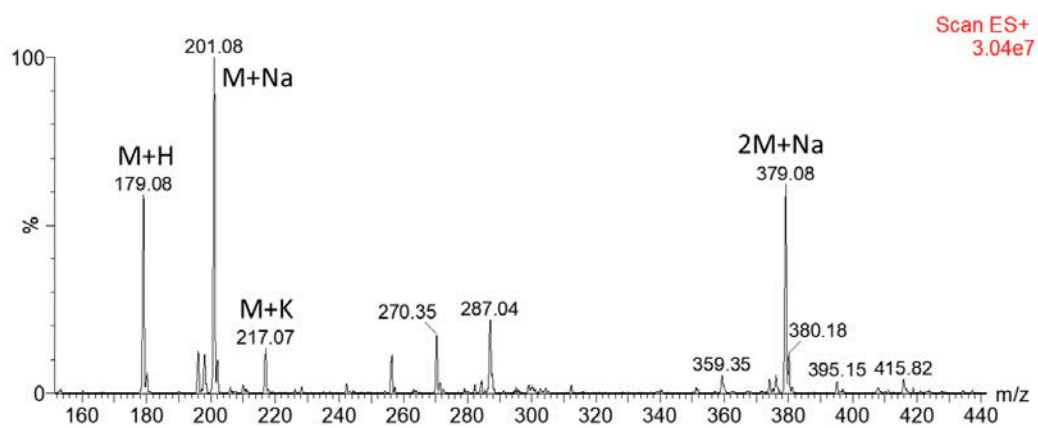


Figure S4. GC-MS spectrum of compound **1**.

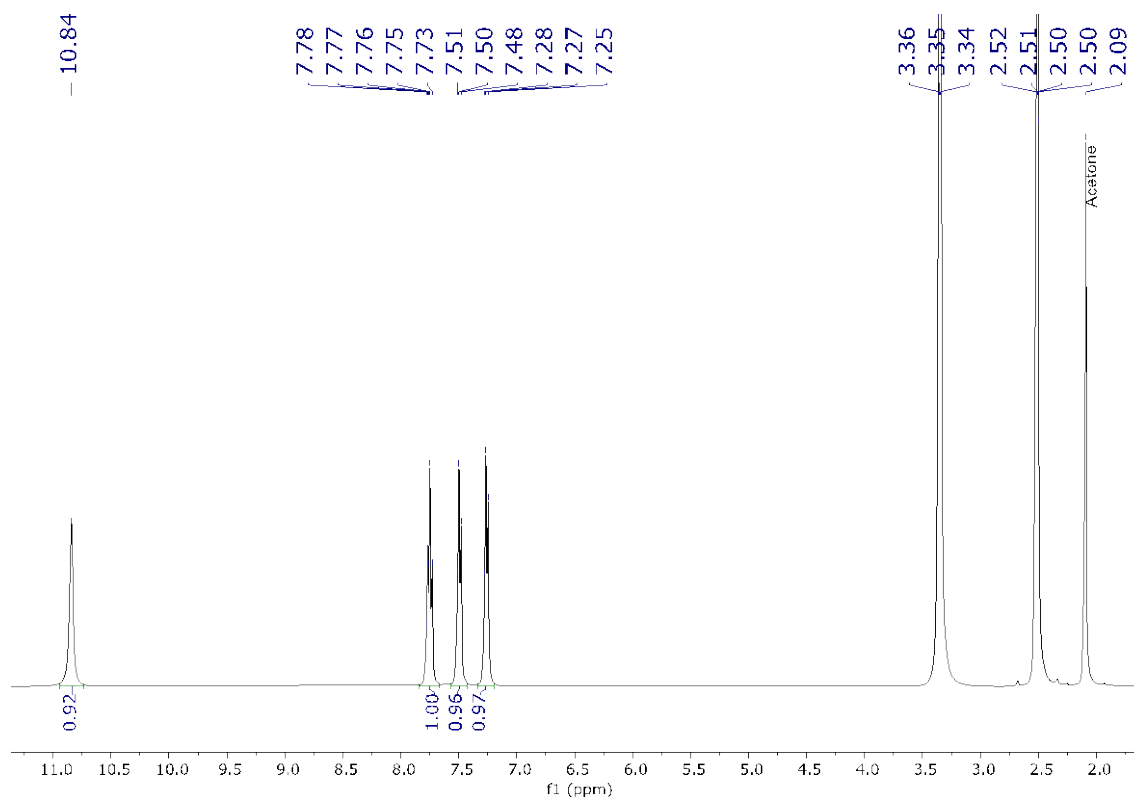


Figure S5. ^1H NMR (400 MHz, DMSO-d_6) spectrum of compound **2**.

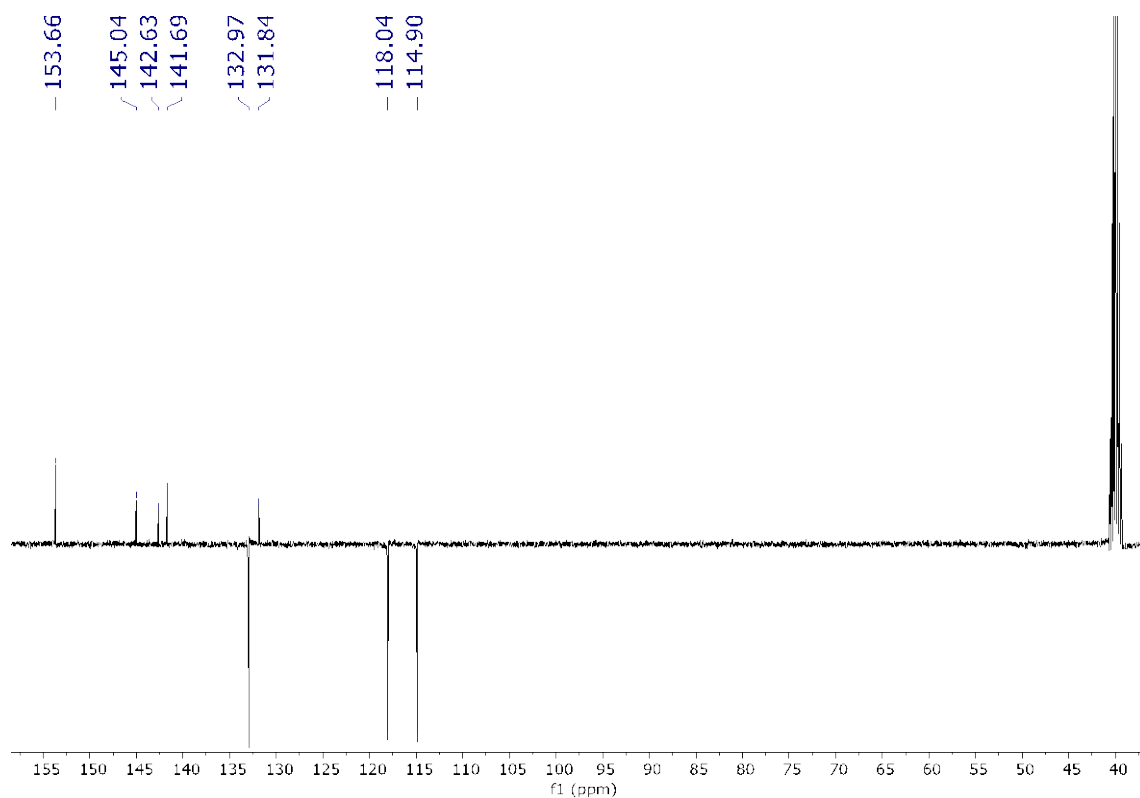


Figure S6. ^{13}C -APT NMR (101 MHz, DMSO-d_6) spectrum of compound **2**.

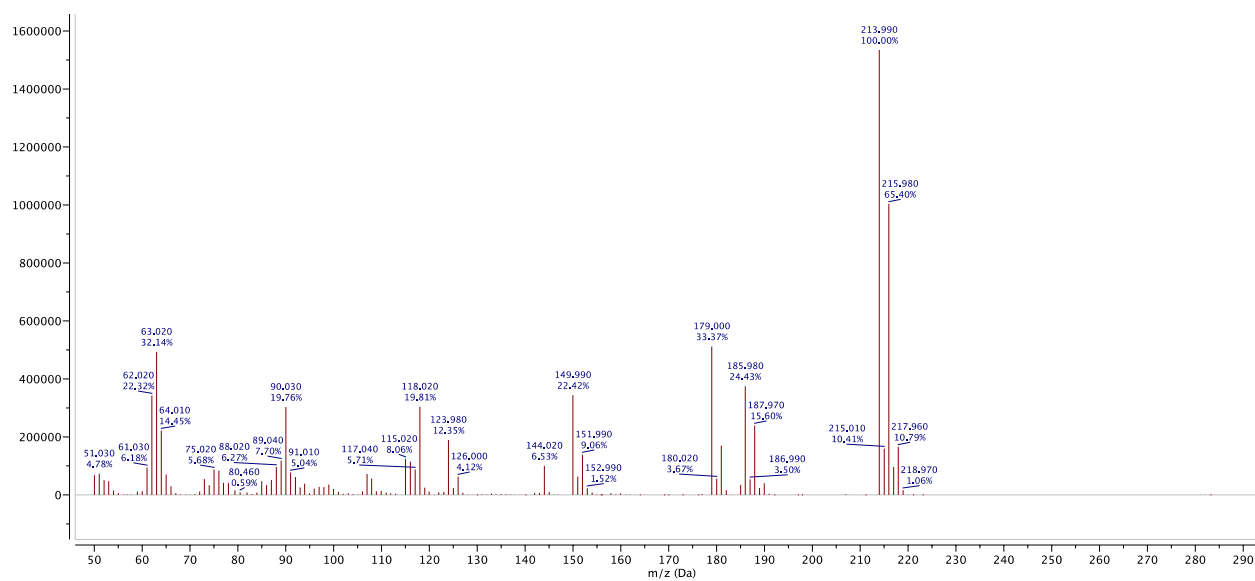


Figure S7. GC-MS spectrum of compound **2**.

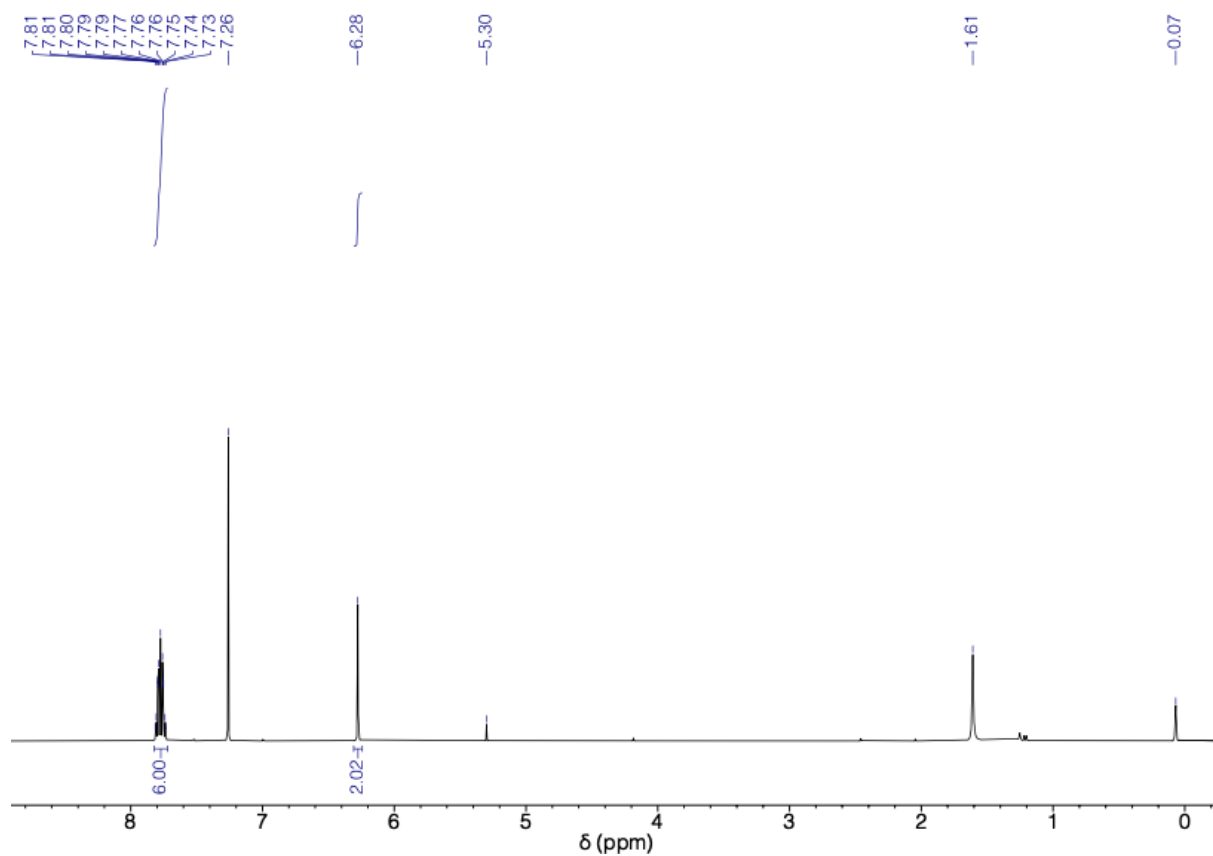


Figure S8. ^1H NMR (400 MHz, CDCl_3) spectrum of compound **3**.

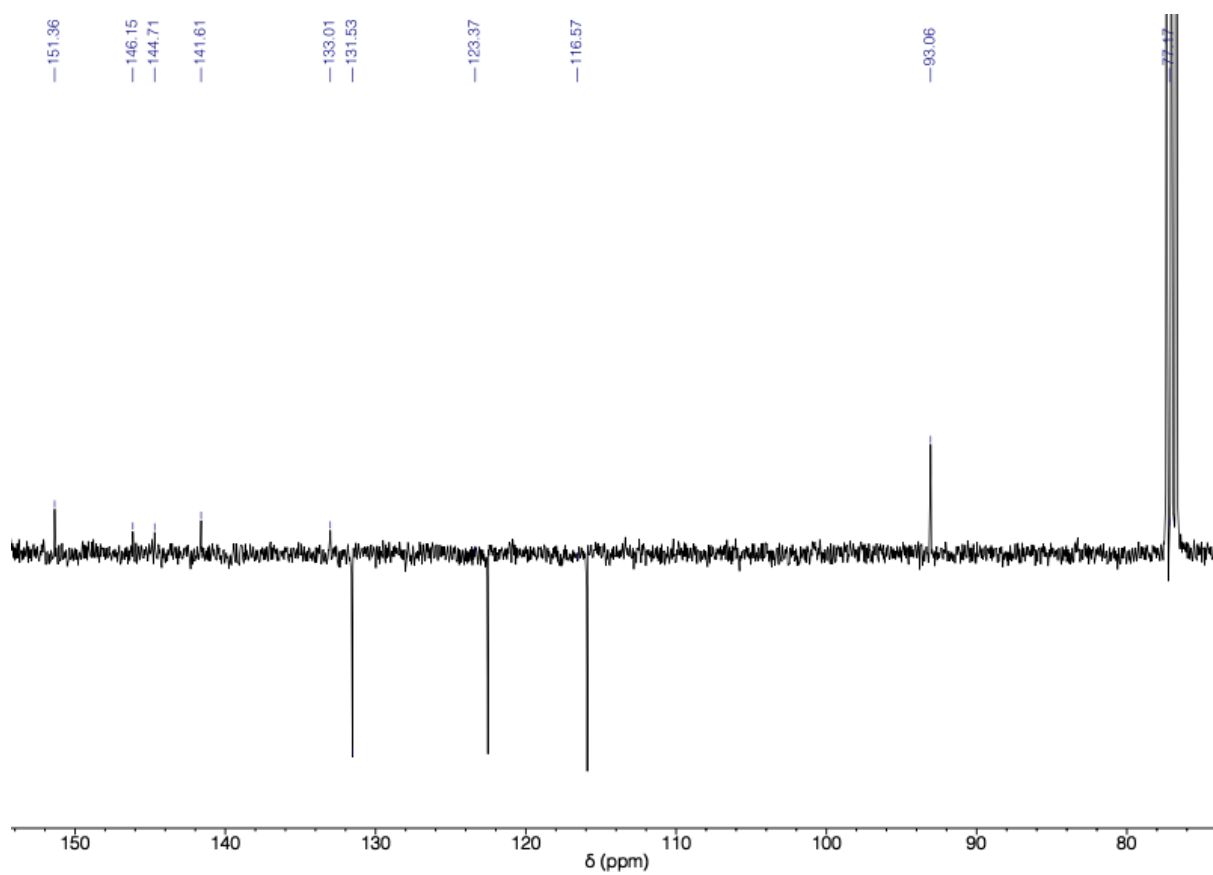


Figure S9. ^{13}C -APT NMR (101 MHz, CDCl_3) spectrum of compound **3**.

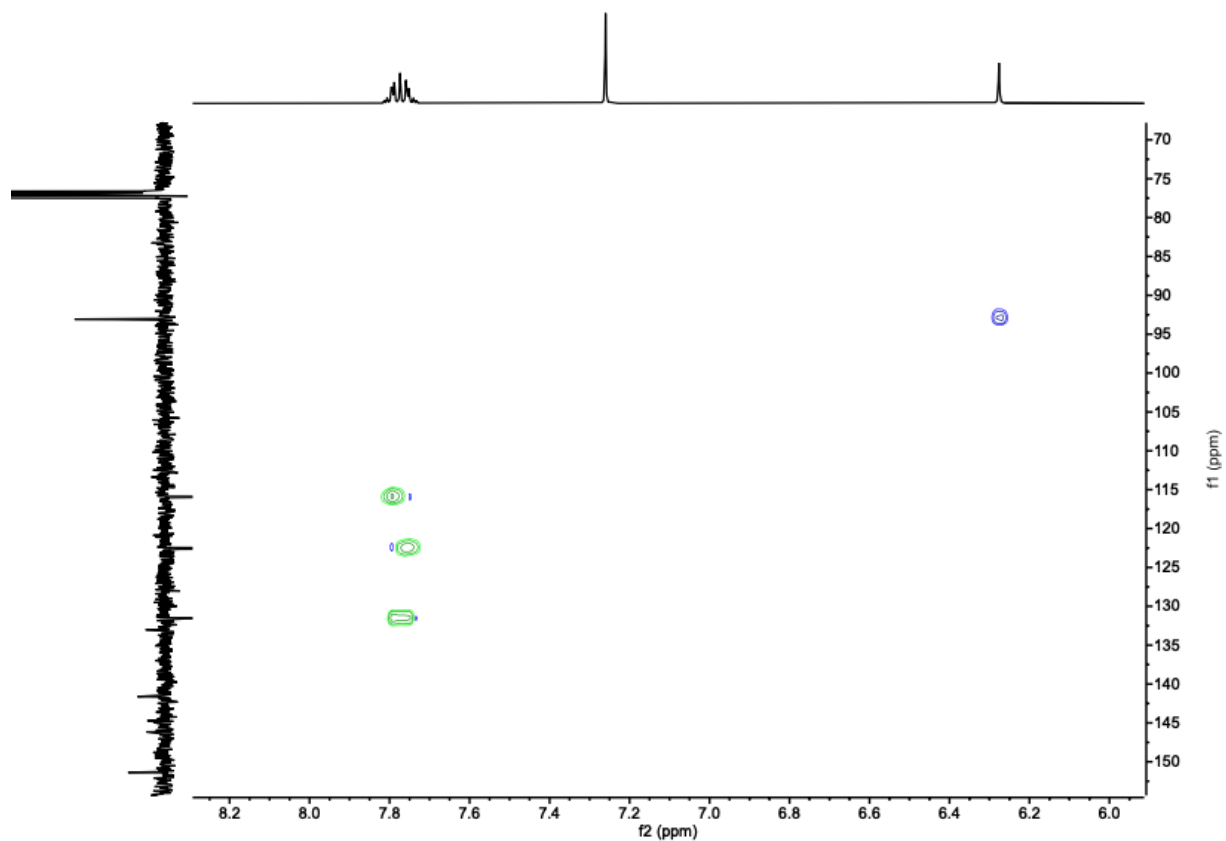


Figure S10. ^1H - ^{13}C HSQC spectrum of compound **3**.

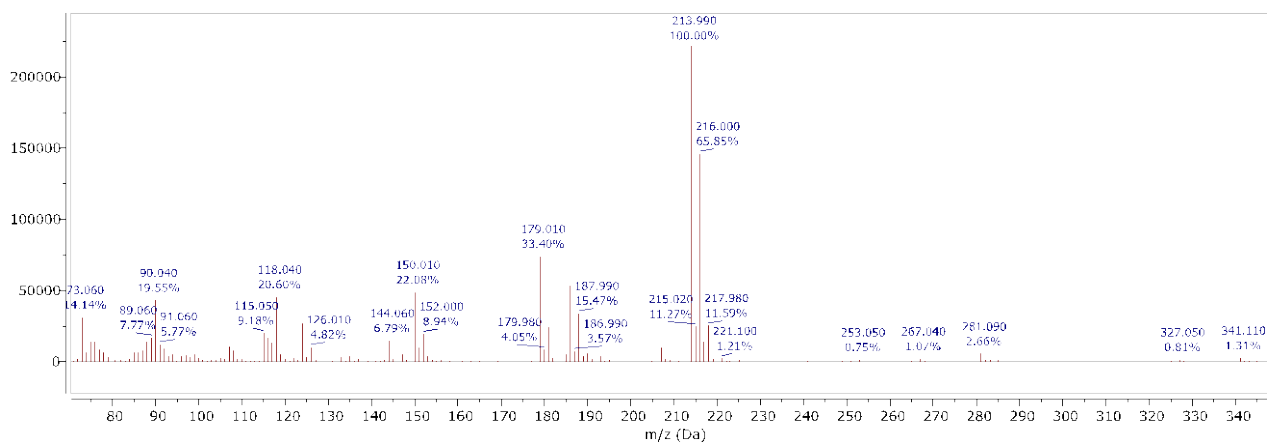


Figure S11. GC-MS spectrum of compound **3**.

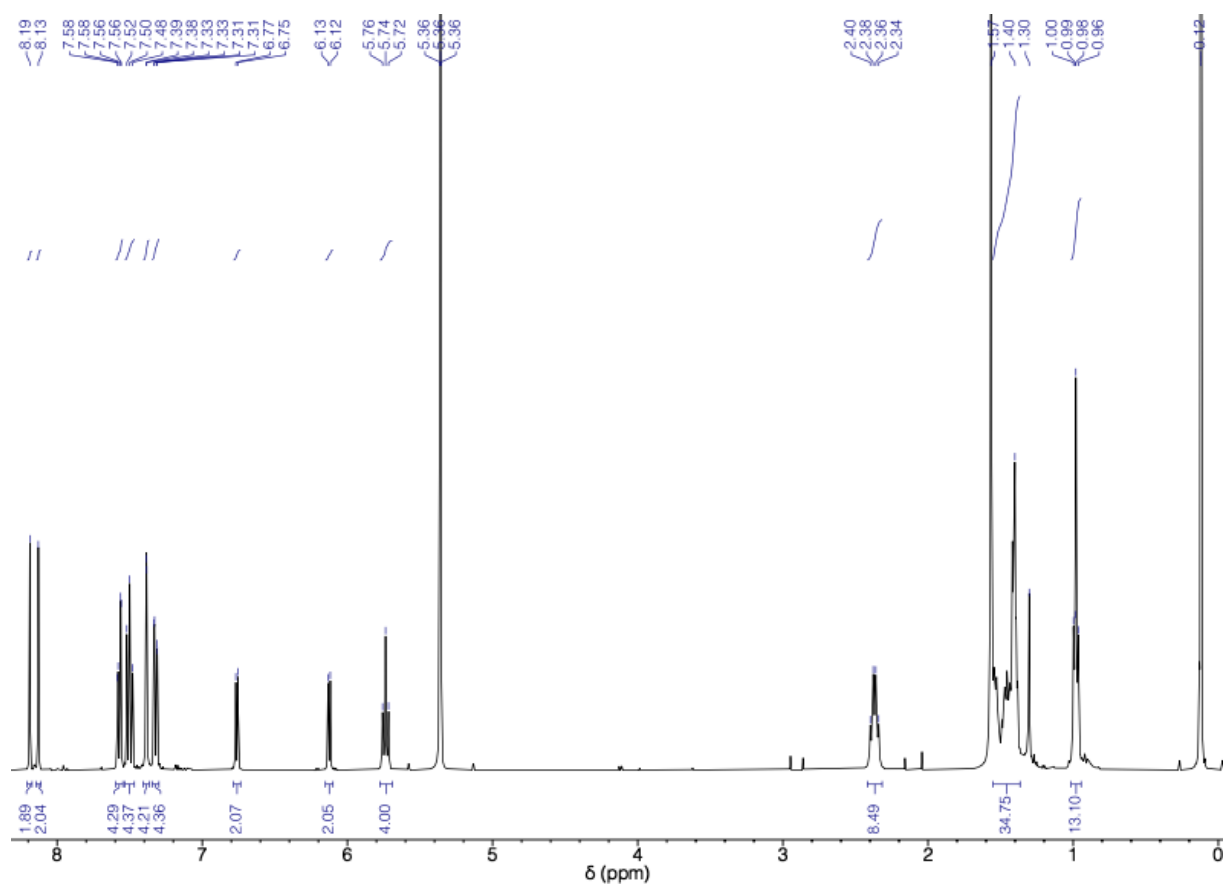


Figure S12. ^1H NMR (600 MHz, CD_2Cl_2) spectrum of MeQxCleft.

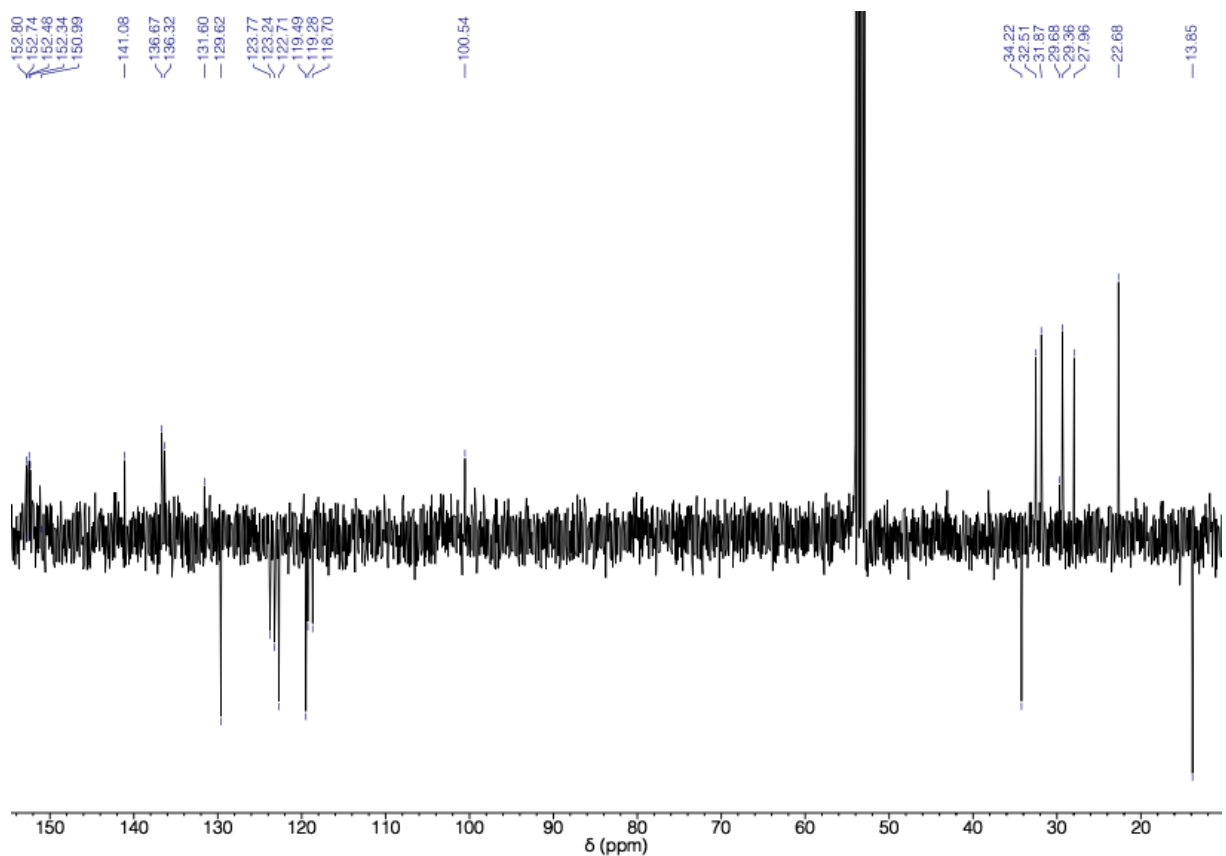


Figure S13. ^{13}C -APT NMR (101 MHz, CD_2Cl_2) spectrum of MeQxCleft.

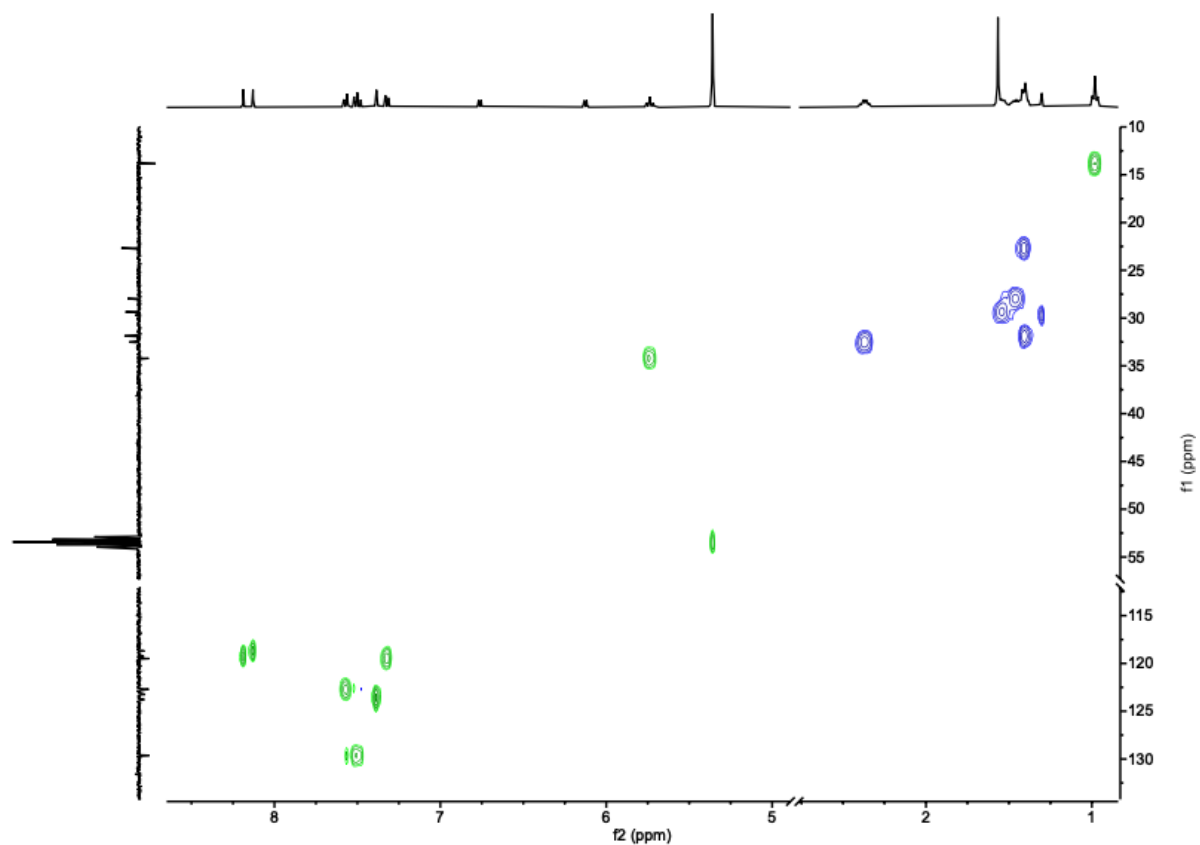


Figure S14. ^1H - ^{13}C HSQC spectrum of MeQxCleft.

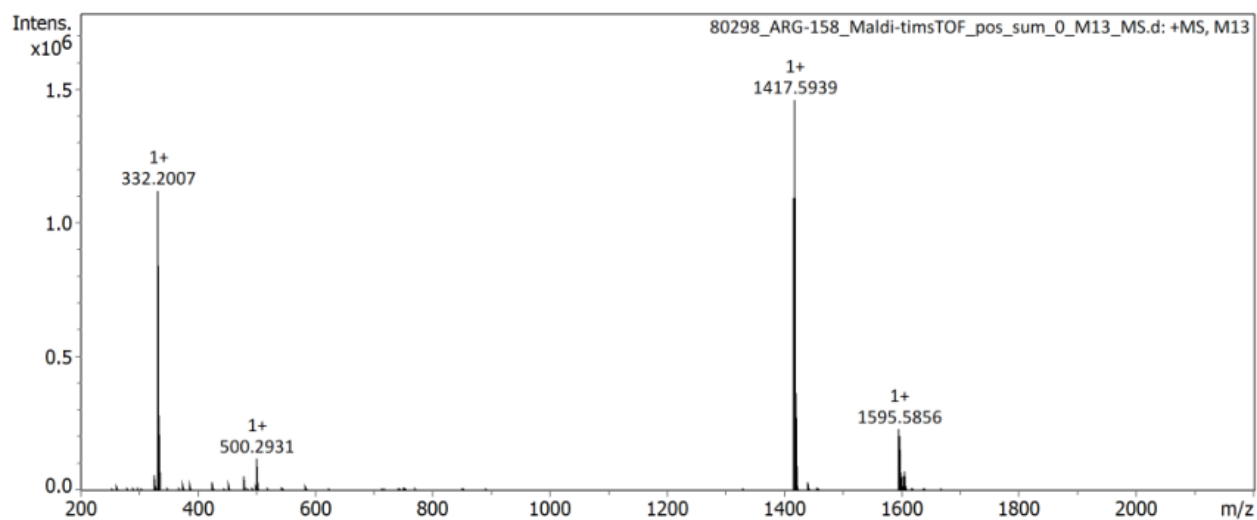


Figure S15. MALDI-TOF spectrum of MeQxCleft.

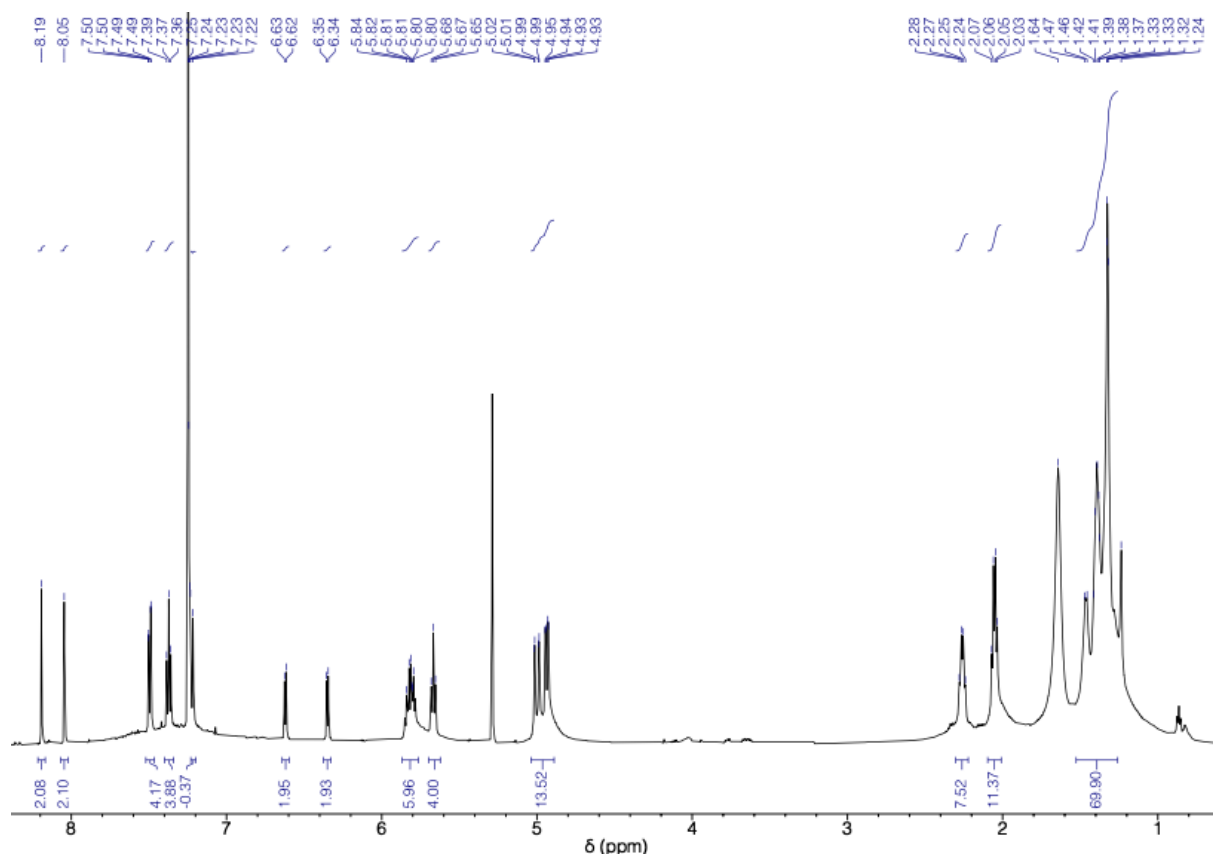


Figure S16. ^1H NMR (600 MHz, CDCl_3) spectrum of MeQxCleft-DB.

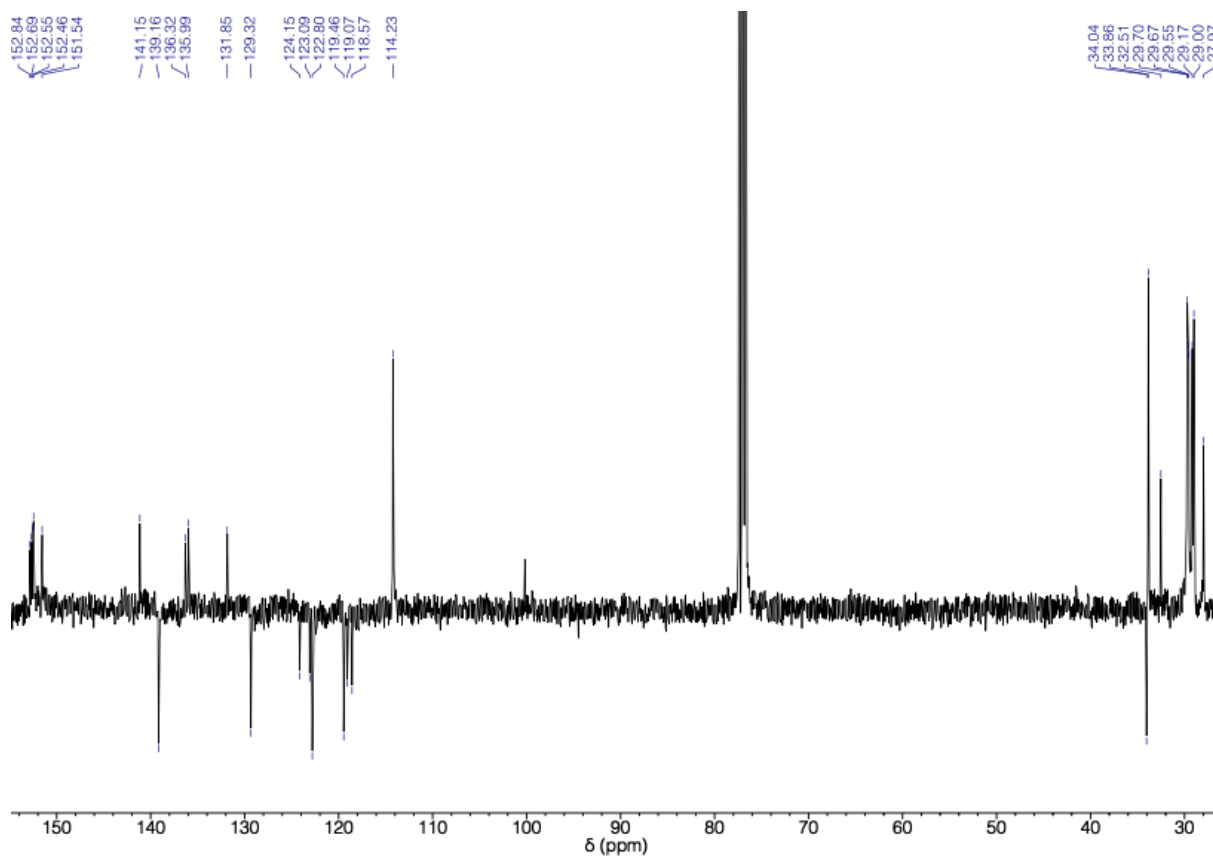


Figure S17. ^{13}C -APT NMR (101 MHz, CDCl_3) spectrum of MeQxCleft-DB.

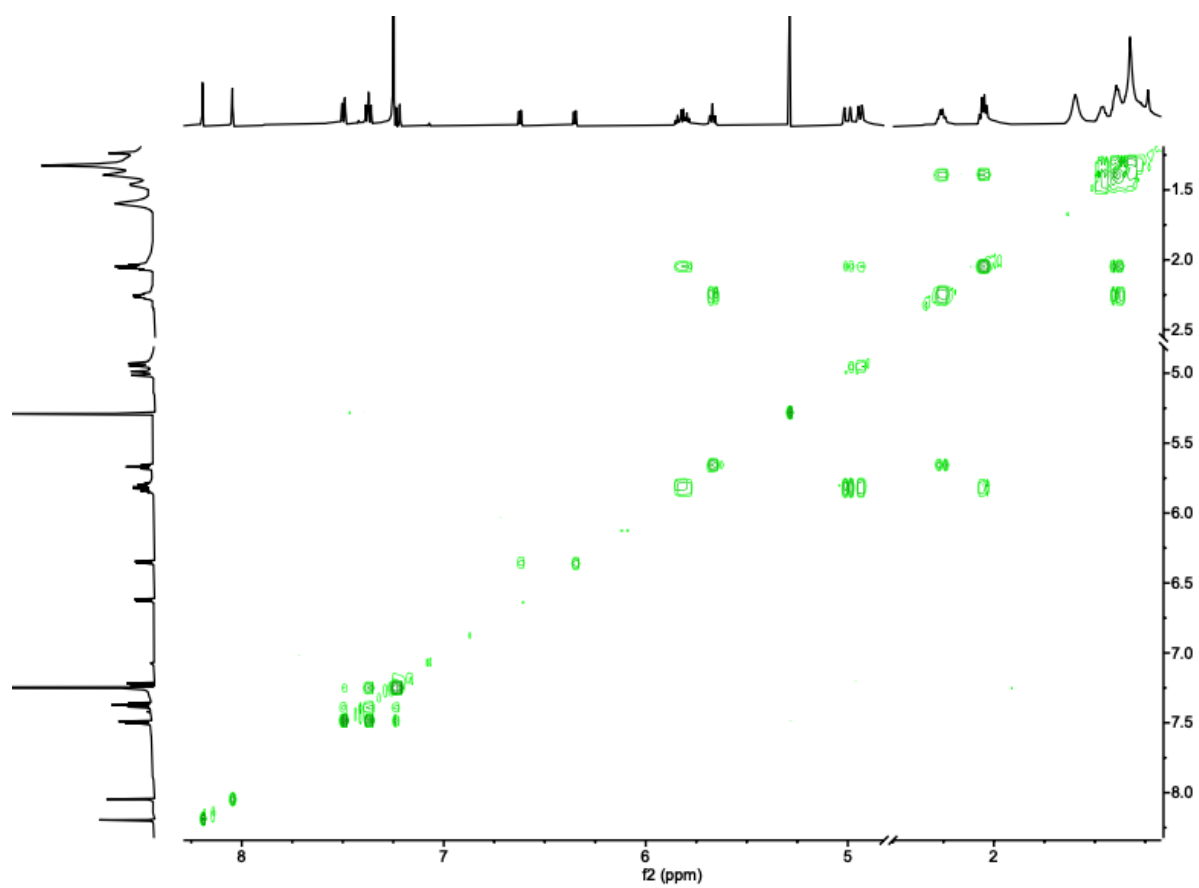


Figure S18. ^1H - ^1H COSY spectrum of MeQxCleft-DB.

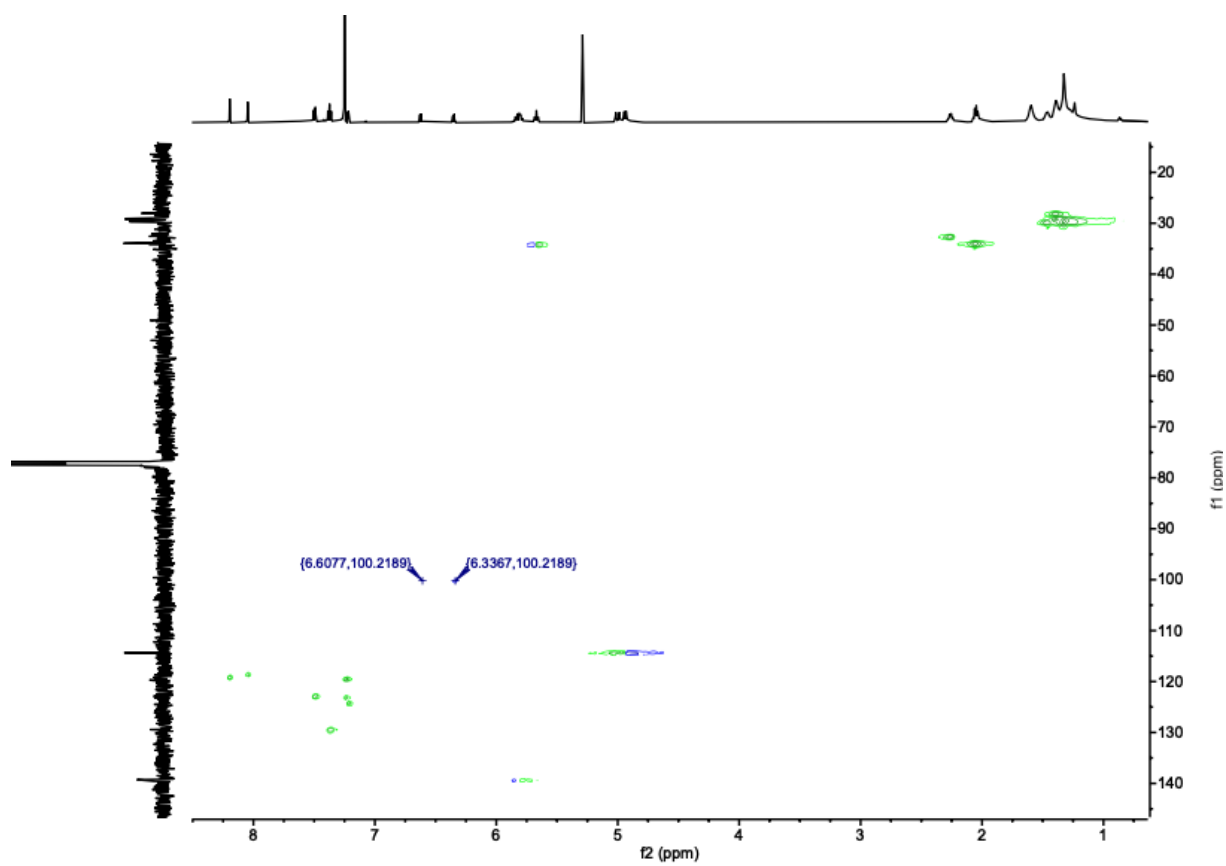


Figure S19. ^1H - ^{13}C HSQC spectrum of MeQxCleft-DB.

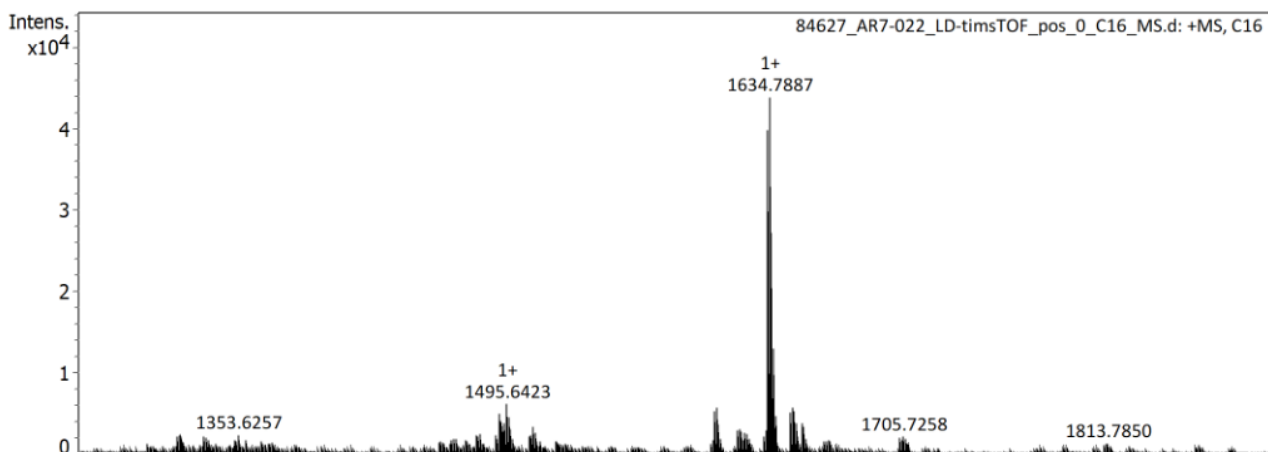


Figure S20. MALDI-TOF spectrum of MeQxCleft-DB.

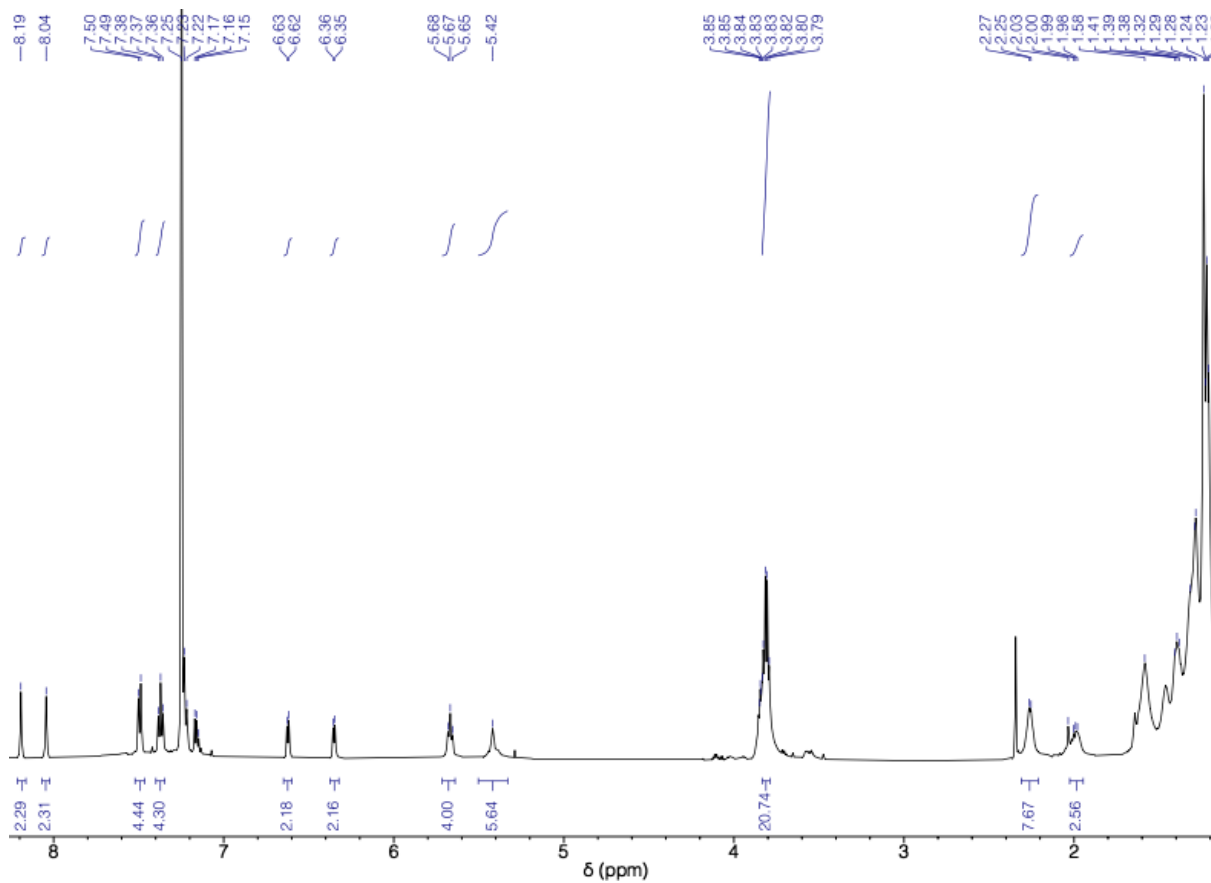


Figure S21. ^1H NMR (600 MHz, CDCl_3) spectrum of MeQxCleft-Si.

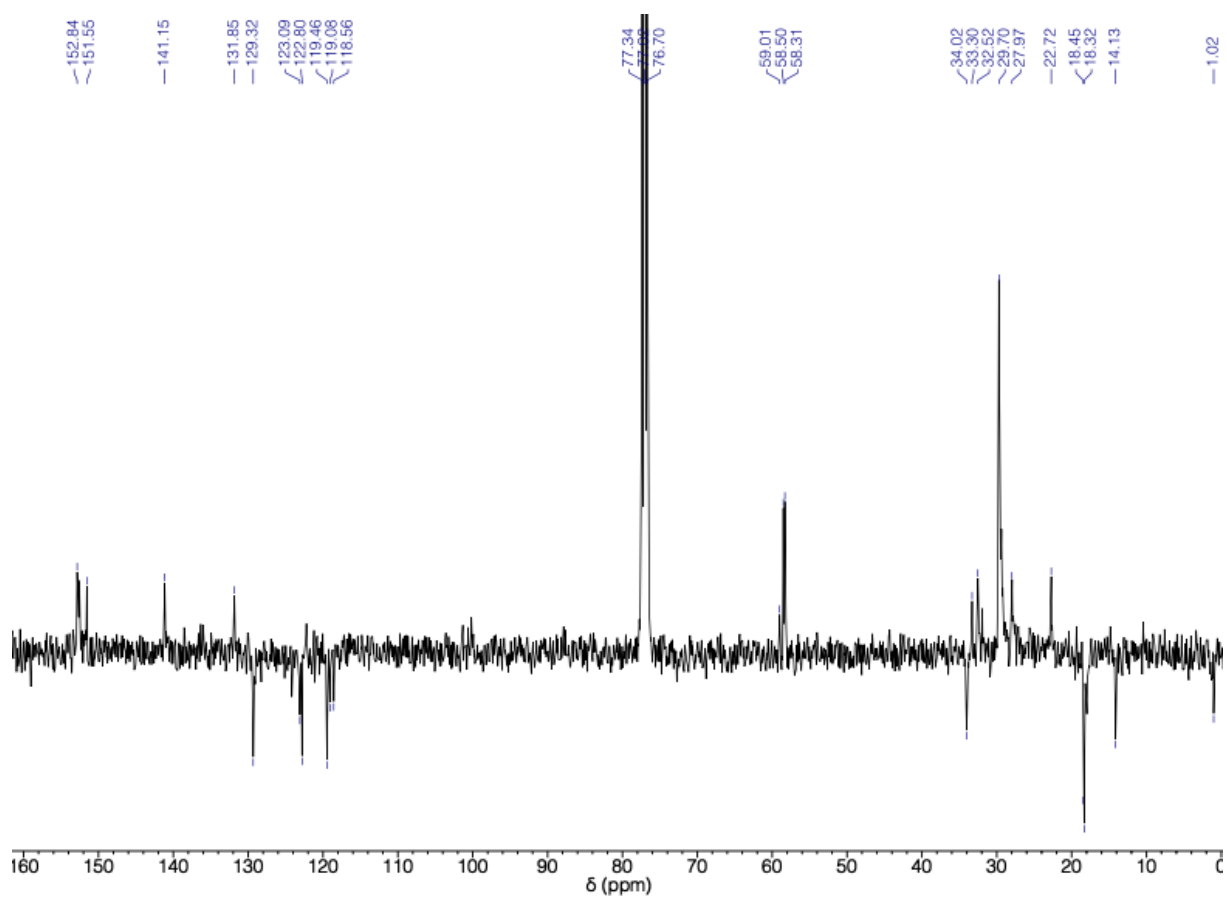


Figure S22. ^{13}C -APT NMR (101 MHz, CDCl_3) spectrum of MeQxCleft-Si.

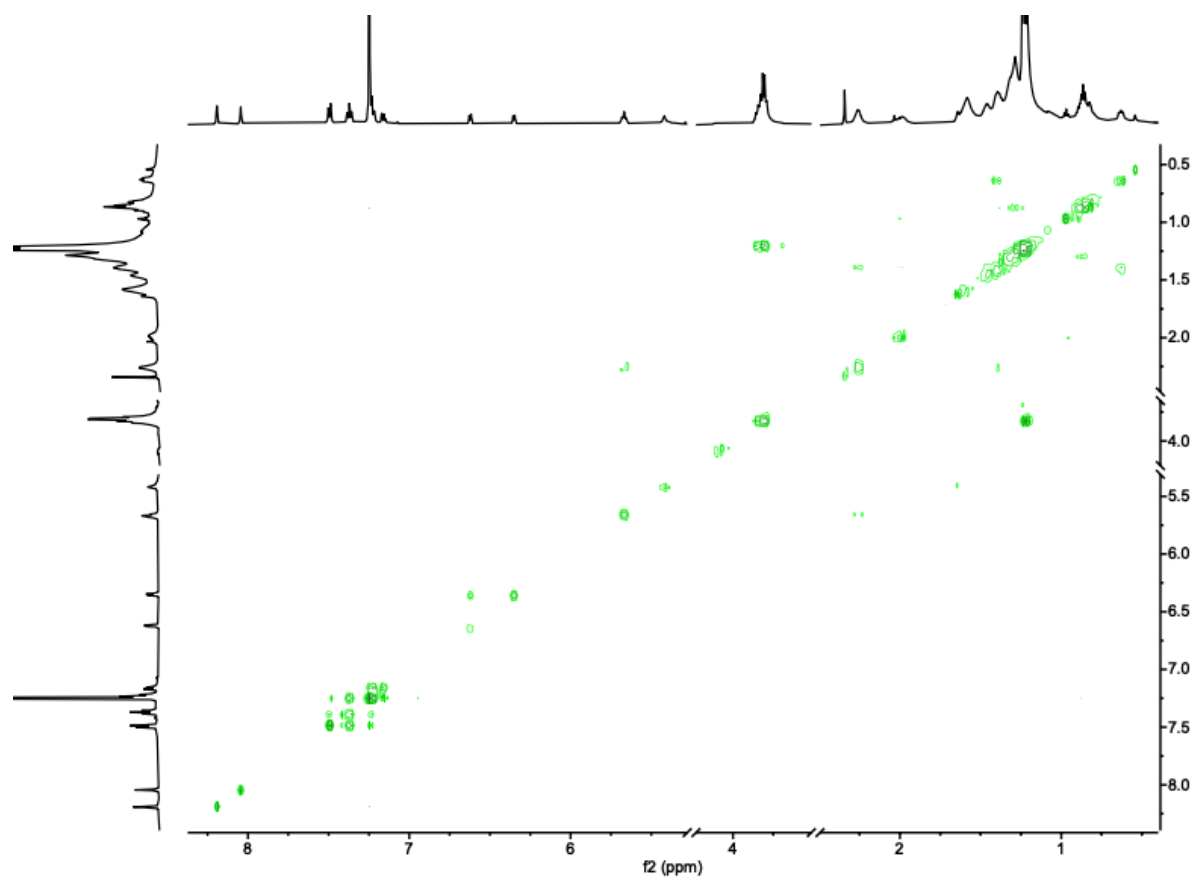


Figure S23. ^1H - ^1H COSY spectrum of MeQxCleft-Si.

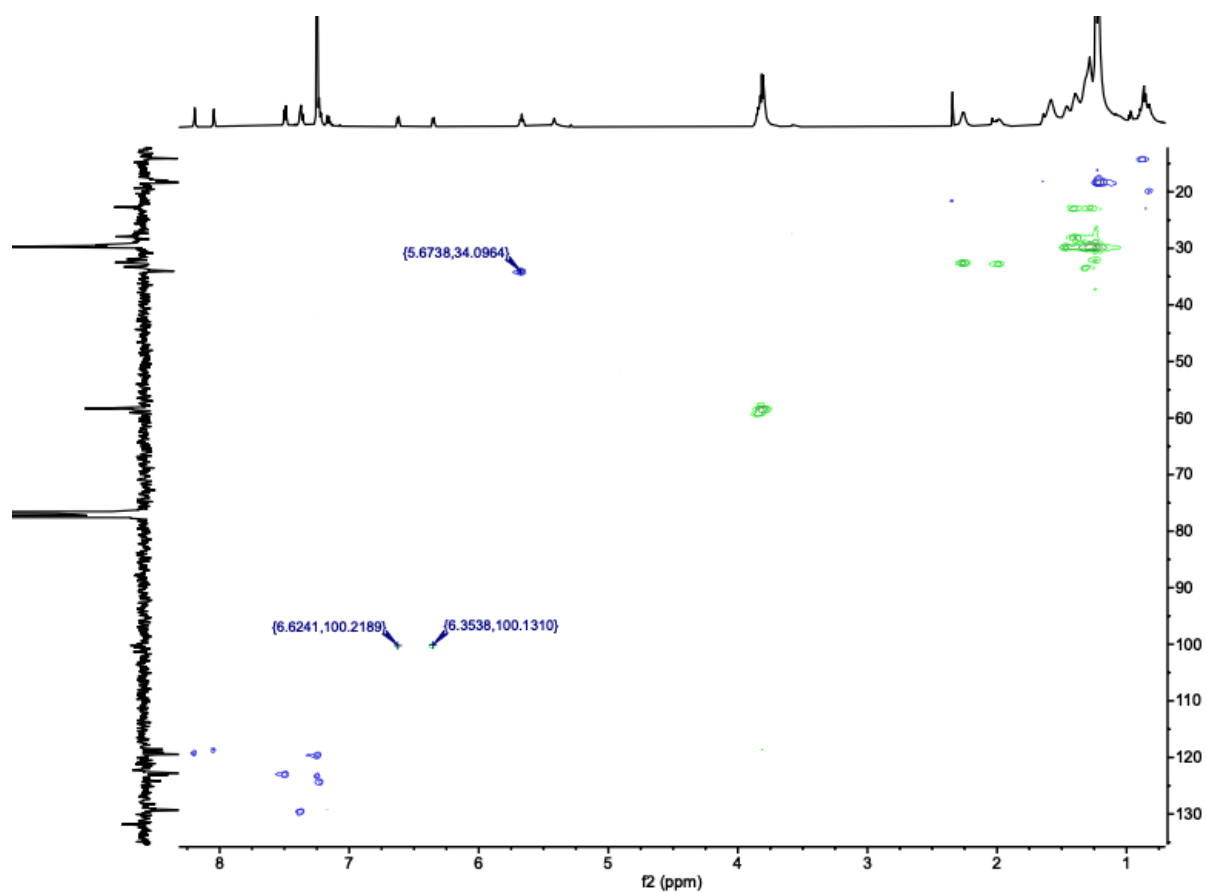


Figure S24. ^1H - ^{13}C HSQC spectrum of MeQxCleft-Si.

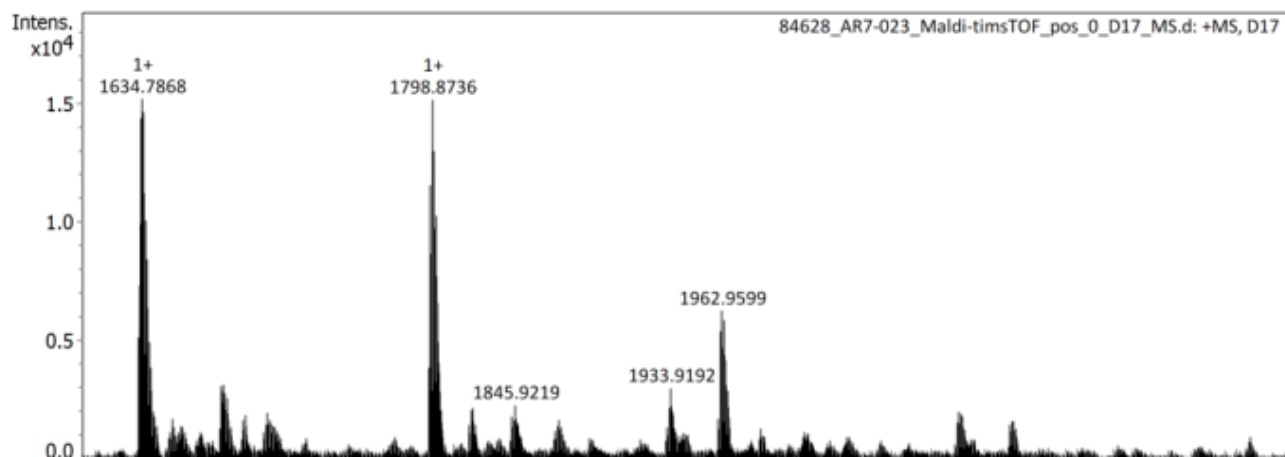


Figure S25. MALDI-TOF spectrum of MeQxCleft-Si.

4 X-ray crystallography

The crystal structures of compounds benzene@MeQxCleft and toluene@MeQxCleft were determined by X-ray diffraction methods. Intensity data and cell parameters were recorded at 200(2) K on a Bruker D8 Venture PhotonII diffractometer with CuK α radiation. The raw frame data were processed using the programs SAINT and SADABS to yield the reflection data files.³ All the structures were solved by dual space methods implemented in the software SHELXT⁴ and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-2014/7 program⁵ in the WinGX suite v.2014.1.⁶ All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were included in the refinement at idealized geometry (C-H 0.93, 0.97 and 0.98 Å for aromatic, methyl/methylenic and methine H atoms, respectively) and refined “riding” on the corresponding parent atoms. The weighting schemes used in the last cycle of refinement were $w = 1/[\sigma^2 F_o^2 + (0.0908P)^2 + 2.3749P]$ and $w = 1/[\sigma^2 F_o^2 + (0.1397P)^2 + 5.7476P]$, where $P = (F_o^2 + 2F_c^2)/3$, benzene@MeQxCleft and toluene@MeQxCleft, respectively. Crystal data and experimental details for data collection and structure refinement are reported in Table S1.

3. SADABS Bruker AXS; Madison, Wisconsin, USA, 2004; SAINT, Software Users Guide, Version 6.0; Bruker Analytical X-ray Systems, Madison, WI (1999). Sheldrick, G. M. SADABS v2.03: Area-Detector Absorption Correction. University of Göttingen, Germany, 1999.
4. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, **A71**, 3.
5. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **A64**, 112.
6. L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849.

Table S1. Crystal data and structure refinement information for benzene@MeQxCleft and toluene@MeQxCleft

Compound	benzene@MeQxCleft	toluene@MeQxCleft
empirical formula	C ₈₆ H ₈₀ N ₈ O ₁₂ ·3C ₆ H ₆	C ₈₆ H ₈₀ N ₈ O ₁₂ ·2C ₇ H ₈
<i>M</i>	1651.90	1601.84
crys syst	Triclinic	Monoclinic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	13.945(3)	17.4000(9)
<i>b</i> /Å	17.044(4)	19.810(1)
<i>c</i> /Å	19.700(5)	25.4310(1)
<i>α</i> [°]	76.945(8)	
<i>β</i> [°]	71.585(7)	107.655(3)
<i>γ</i> [°]	85.672(8)	
<i>V</i> /Å ³	4327(2)	8353.1(7)
<i>Z</i>	2	4
<i>ρ</i> /g cm ⁻³	1.268	1.274
<i>μ</i> /mm ⁻¹	0.668	0.674
<i>F</i> (000)	1748	3392
total reflections	145822	243643
unique reflections (<i>R</i> _{int})	16269 (0.0382)	17076 (0.0575)
observed reflections	14932	14199
GOF on <i>F</i> ^{2a}	1.017	1.026
<i>R</i> indices [<i>F</i> _o >4σ(<i>F</i> _o)] ^b <i>R</i> ₁ , <i>wR</i> ₂	0.0617, 0.1711	0.0722, 0.2222
largest diff. peak and hole (eÅ ⁻³)	0.953, -0.627	0.639, -1.195

^aGoodness-of-fit $S = [\sum w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters. ^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

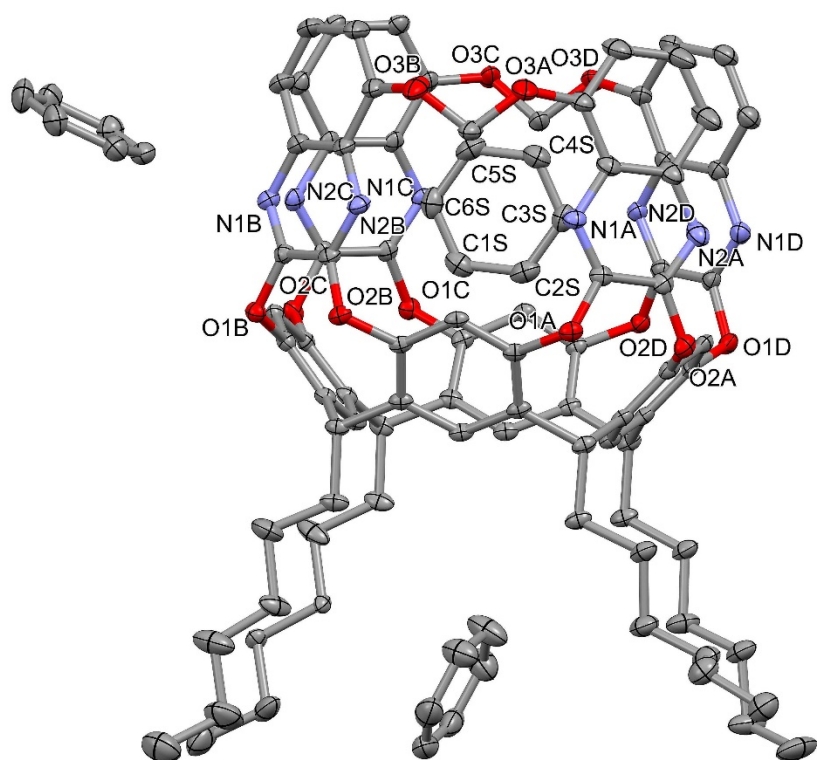


Figure S26. Ortep view of benzene@MeQxCleft with partial labelling scheme. Hydrogen atoms and the disorder in the alkyl chains have been omitted for clarity

Benzene is stabilized inside the cavity by two C–H \cdots π interactions with the lower aromatic rings of the cavitand [C1S \cdots Cg1, 3.679(5) Å and C1S–H1S \cdots Cg1 155.4(2) $^\circ$; C2S \cdots Cg2, 3.694(4) Å and C2S–H2S \cdots Cg2 145.0(2) $^\circ$; Cg1 and Cg2 are the centroids C1C–C6C and C1A–C6A, respectively] and by two bifurcated weak C–H \cdots N interactions involving the nitrogen atoms of non-bridged, adjacent quinoxaline moieties (Figure S25. [C3S \cdots N2A, 3.812(4) Å and C3S–H3S \cdots N2A, 137.8(5) $^\circ$; C3S \cdots N1D, 3.984(3) Å and C3S–H3S \cdots N1D, 136.0(5) $^\circ$; C6S \cdots N1B, 3.695(3) Å and C6S–H6S \cdots N1B, 133.3(2) $^\circ$; C6S \cdots N2C, 3.914(4) Å and C6S–H6S \cdots N2C, 137.5(6) $^\circ$].

The distance of the atoms C1S and C2S from the mean plane passing through the eight oxygen atoms of the resorcinol-based cavity is of 1.176(3) and 1.123(4) Å, respectively.

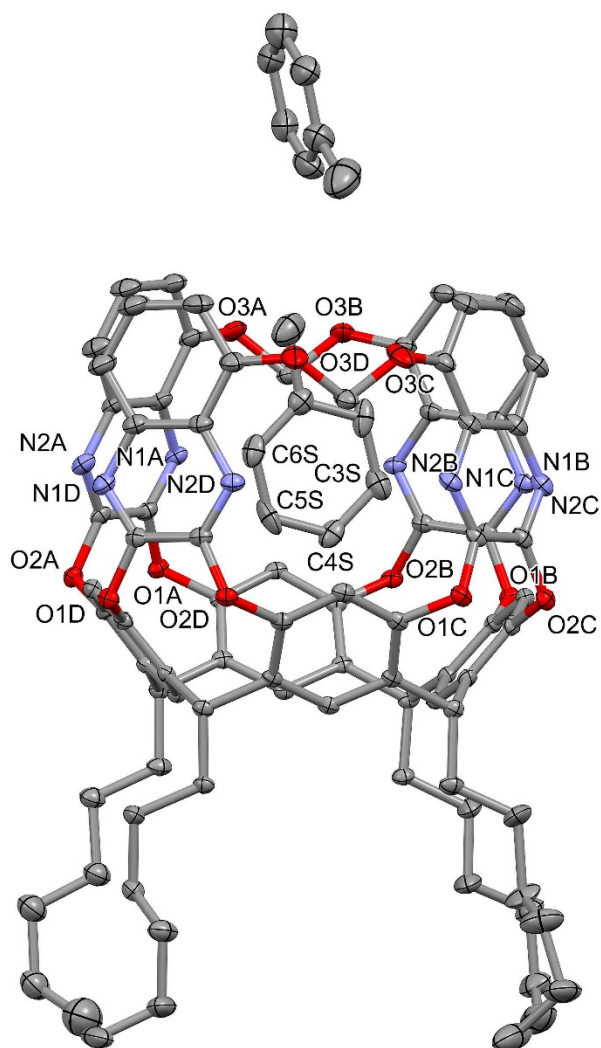


Figure S27. Ortep view of toluene@MeQxCleft with partial labelling scheme. The hydrogen atoms and the disorder of the alkyl chains and of the solvent have been omitted for clarity

As in the case of the benzene complex, the interactions stabilizing the inclusion of toluene inside the cavity comprise C–H \cdots π interactions with the lower aromatic rings of the cavitand and weak C–H \cdots N interactions involving the nitrogen atoms of non-bridged, adjacent quinoxaline moieties. Some weak C–H \cdots π interactions are also present between the methyl group of toluene and the upper aromatic rings of the cavitand. [C5S \cdots Cg1, 3.691(4) Å and C1S–H5S \cdots Cg1 171.6(4) $^\circ$; C5V \cdots Cg2, 3.666(6) Å and C5V–H5V \cdots Cg2 168.3(3) $^\circ$; Cg1 and Cg2 are the centroids C1A–C6A and C1C–C6C, respectively. C3S \cdots N1B, 3.939(5) Å and C3S–H3S \cdots N1B, 148.2(6) $^\circ$; C3V \cdots N1D, 3.982(3) Å and C3V–H3V \cdots N1D, 140.8(4) $^\circ$]. The shortest distance between toluene and the mean plane passing through the eight oxygen atoms of the resorcinol-based cavity is of 1.113(5) Å from C4S and 1.062(3) Å from C4V, respectively.

5 Thermogravimetric analyses

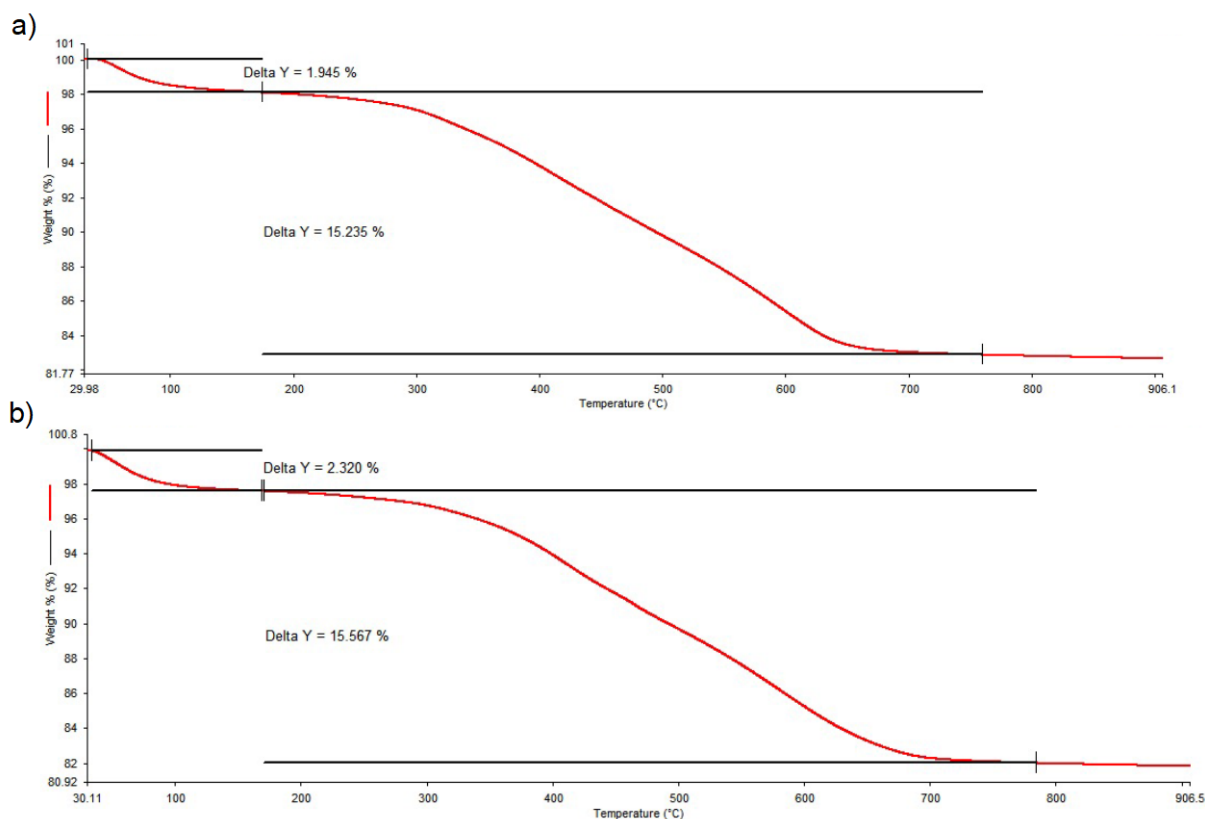


Figure S28. TGA graph of QxCav@SiO₂ (a) and MeQxCleft@SiO₂ (b) from 25 to 900°C at 10°C/min, in air.

Table S2. Desorption areas and temperatures for the four BTEX analytes

	Pure QxCav	QxCav@SiO ₂	MeQxCleft@SiO ₂
Benzene area (mVs/ppb)	1708	2189	6122
Toluene area (mVs/ppb)	1192	1476	5351
Ethylbenzene area (mVs/ppb)	341	1414	1408
Xylene area (mVs/ppb)	1150	1180	725
Benzene maximum T (°C)	155	142	> 170
Toluene maximum T (°C)	155	141	> 170
Ethylbenzene maximum T (°C)	155	145	> 170
Xylene maximum T (°C)	165	144 & 160	> 170