

Supporting Information for
Shaping of calix[4]arenes via double bridging of the upper rim

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General Experimental Procedures

All chemicals were purchased from commercial sources and used without further purification. Solvents were dried and distilled using conventional methods. Melting points were measured on Heitisch Mikroskop – Polytherm A (Wagner & Munz, Germany). NMR spectra were performed on Varian Gemini 300 (^1H : 300 MHz, ^{13}C : 75 MHz) or Agilent 400-MR DDR2 (^1H : 400 MHz, ^{13}C : 100 MHz). Deuterated solvents used are indicated in each case. Chemical shifts (δ) are expressed in ppm and are referred to the residual peak of the solvent or TMS as an internal standard; coupling constants (J) are in Hz. The mass analyses were performed using ESI technique on Q-TOF (Micromass) spectrometer. Elemental analyses were done on Perkin-Elmer 240, Elementar vario EL (Elementar, Germany) or Mitsubishi TOX-100 instruments. All samples were dried in the desiccator over P_2O_5 under vacuum (1 Torr) at 80 °C for 8 hours. The IR spectra were measured on an FT-IR spectrometer Nicolet 740 or Bruker IFS66 spectrometers equipped with a heatable Golden Gate Diamante ATR-Unit (SPECAC) in KBr. 100 Scans for one spectrum were co-added at a spectral resolution of 4 cm^{-1} . The courses of the reactions were monitored by TLC using TLC aluminium sheets with Silica gel 60 F254 (Merck). The column chromatography was performed using Silica gel 60 (Merck).

General remark:

All organomercury derivatives are considered potentially hazardous and require special consideration!

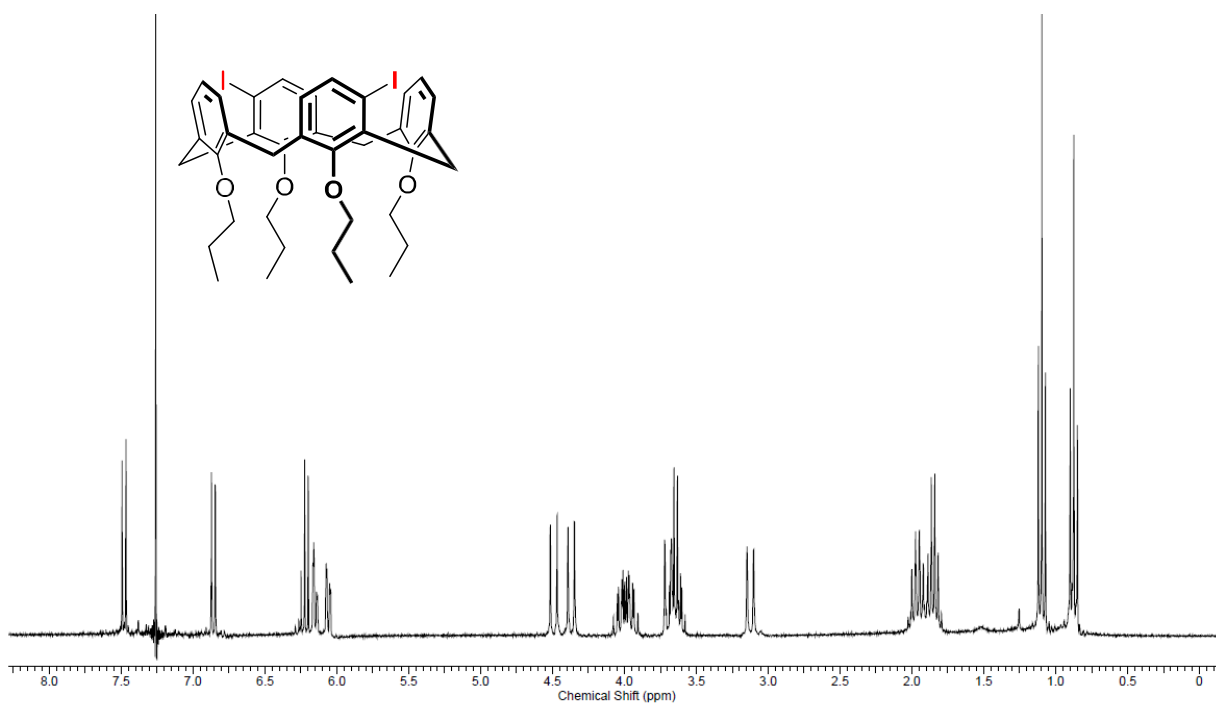


Figure 1. ^1H NMR of compound **8** (CDCl_3 , 300 MHz).

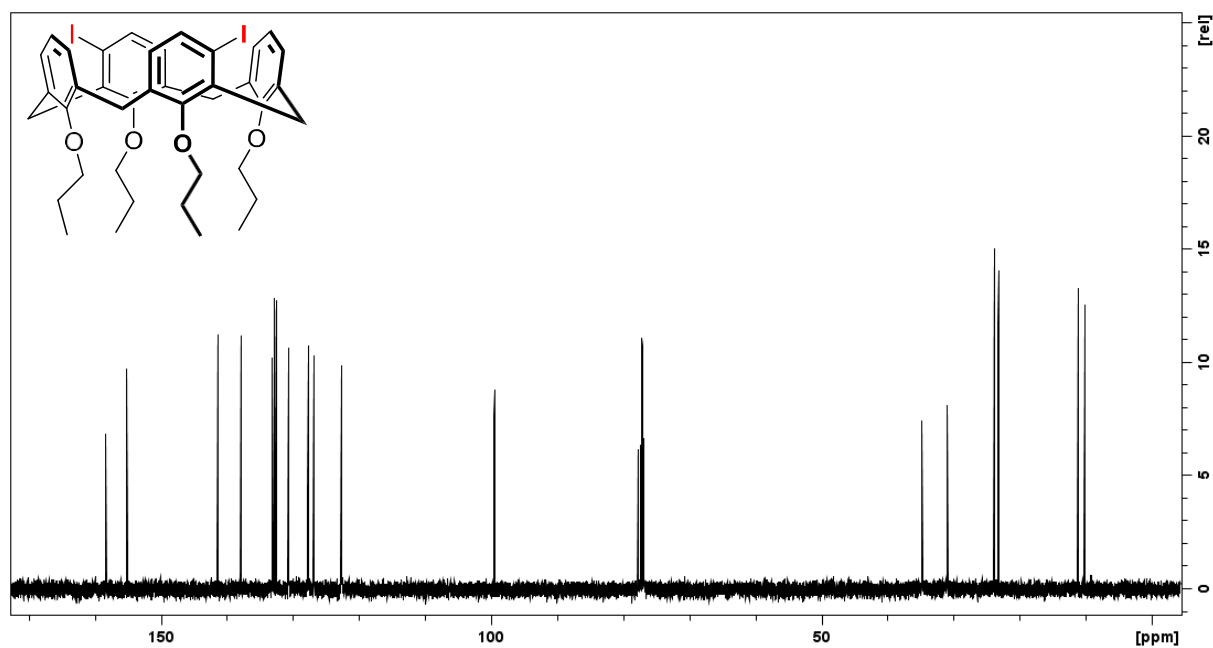


Figure 2. ^{13}C NMR of compound **8** (CDCl_3 , 75 MHz).

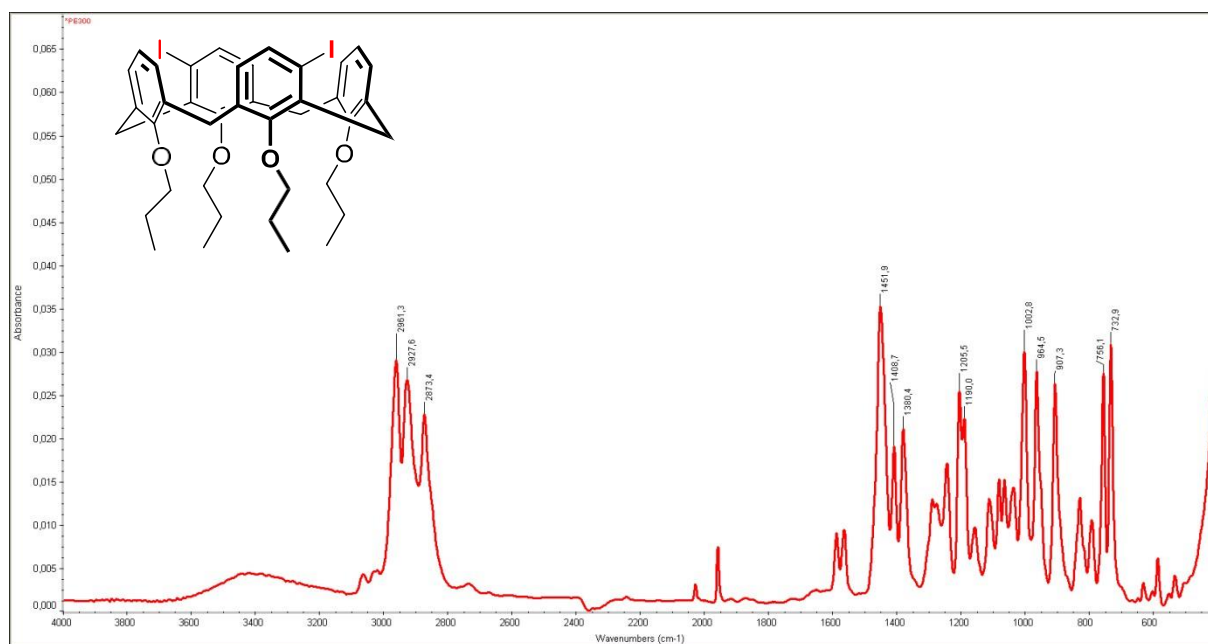


Figure 3. IR of compound 8 (KBr).

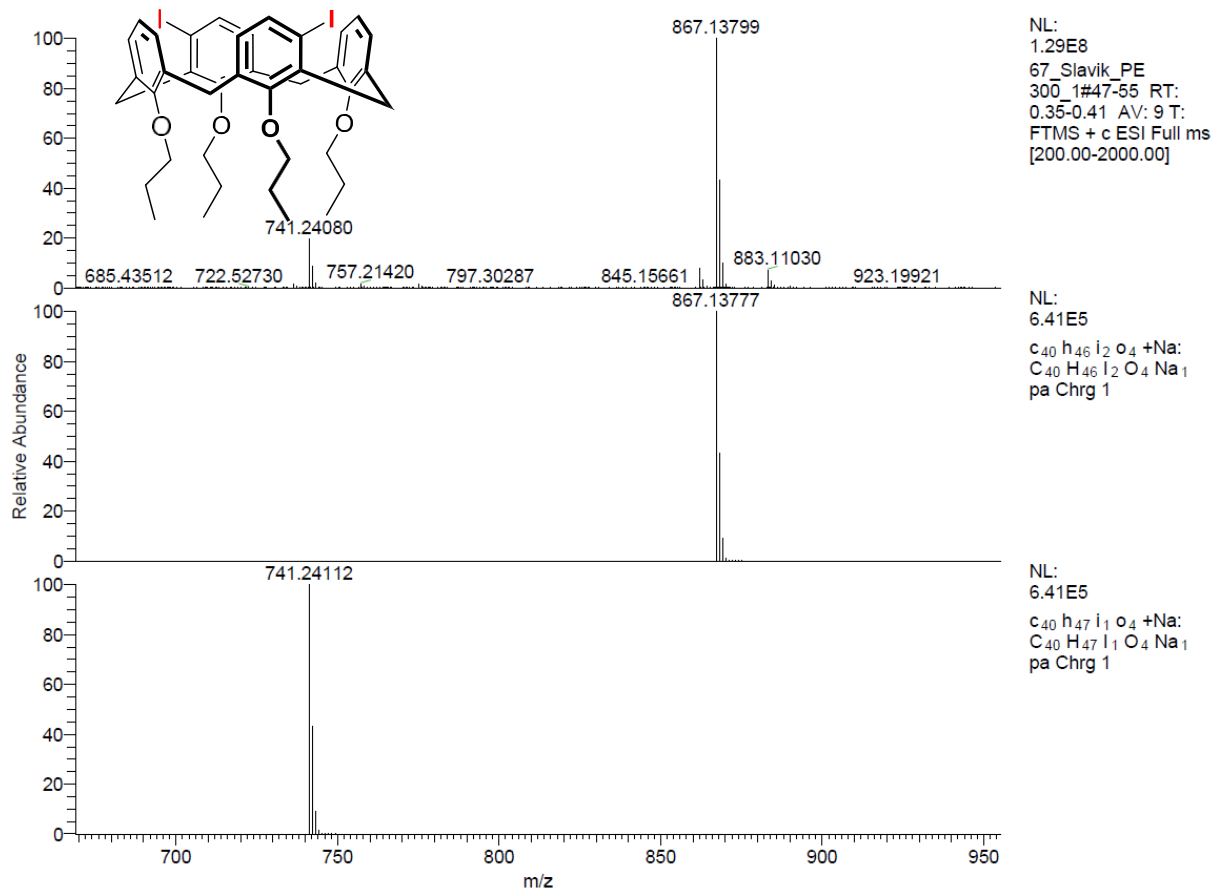


Figure 4. HRMS of compound 8 (ESI⁺).

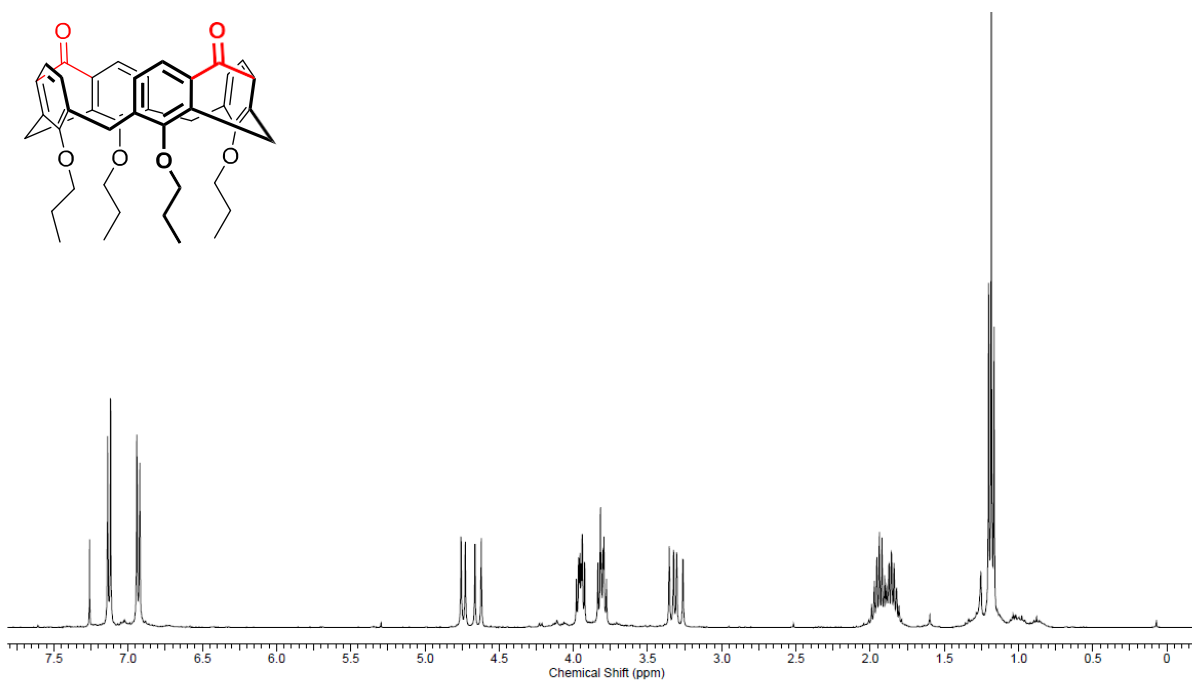


Figure 5. ^1H NMR of compound **10** (CDCl_3 , 400 MHz).

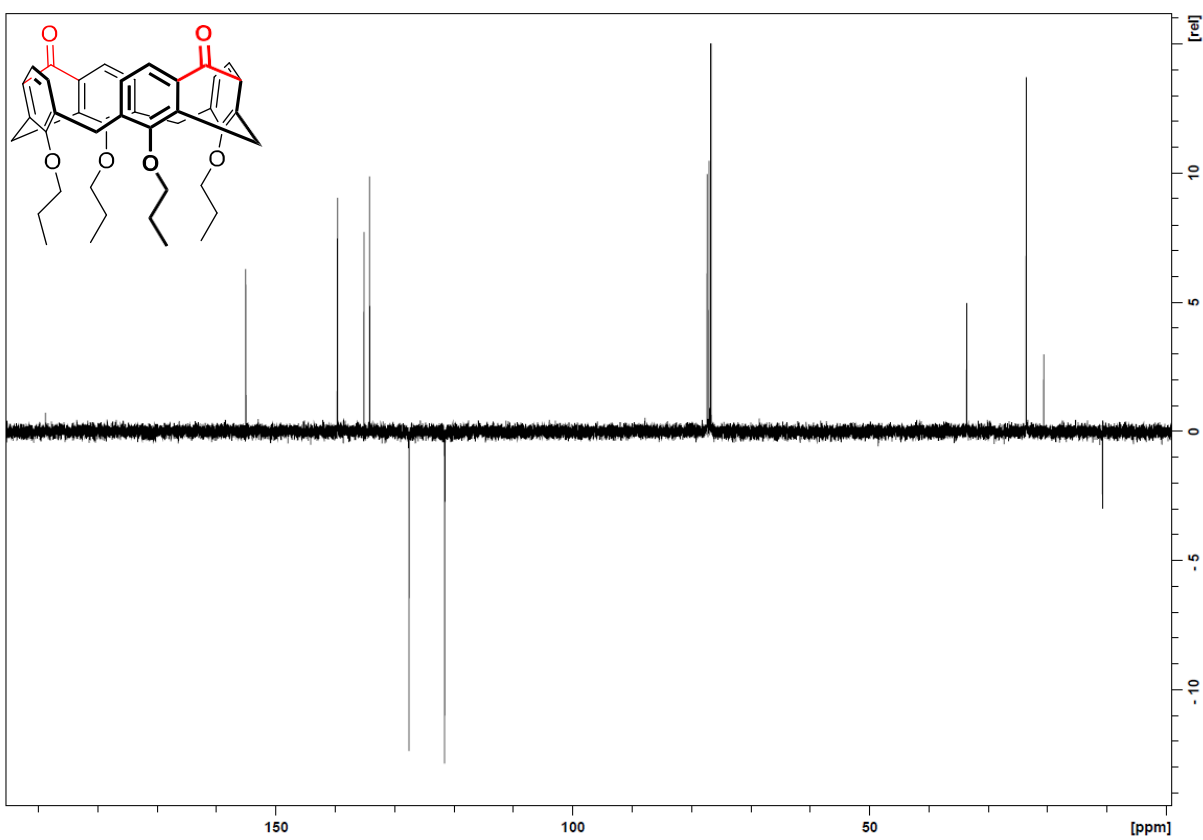


Figure 6. ^{13}C (APT) NMR of compound **10** (CDCl_3 , 100 MHz).

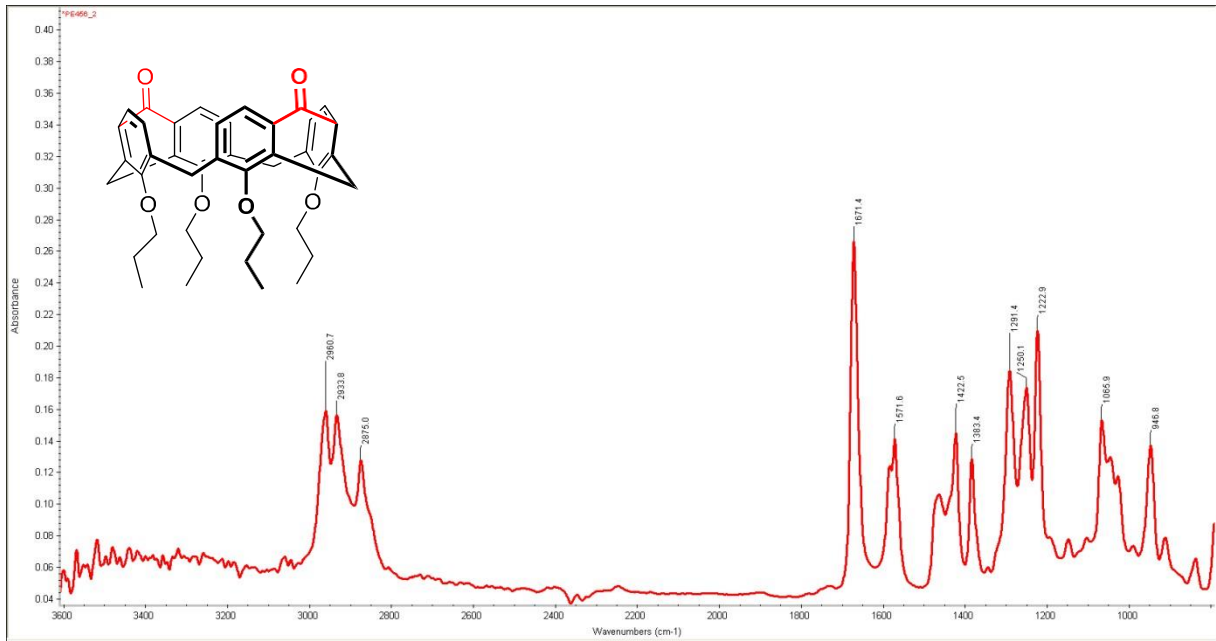


Figure 7. IR of compound **10** (KBr).

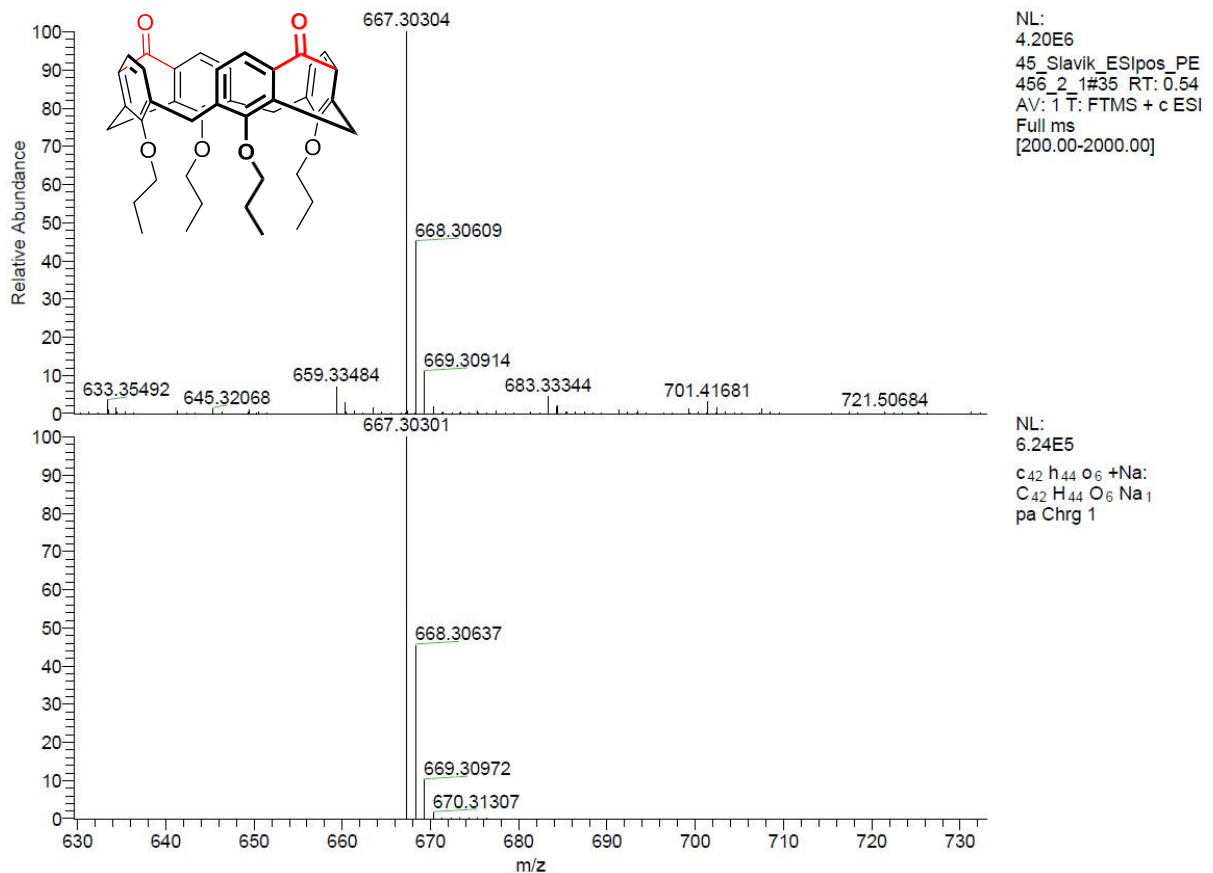


Figure 8. HRMS of compound **10** (ESI⁺).

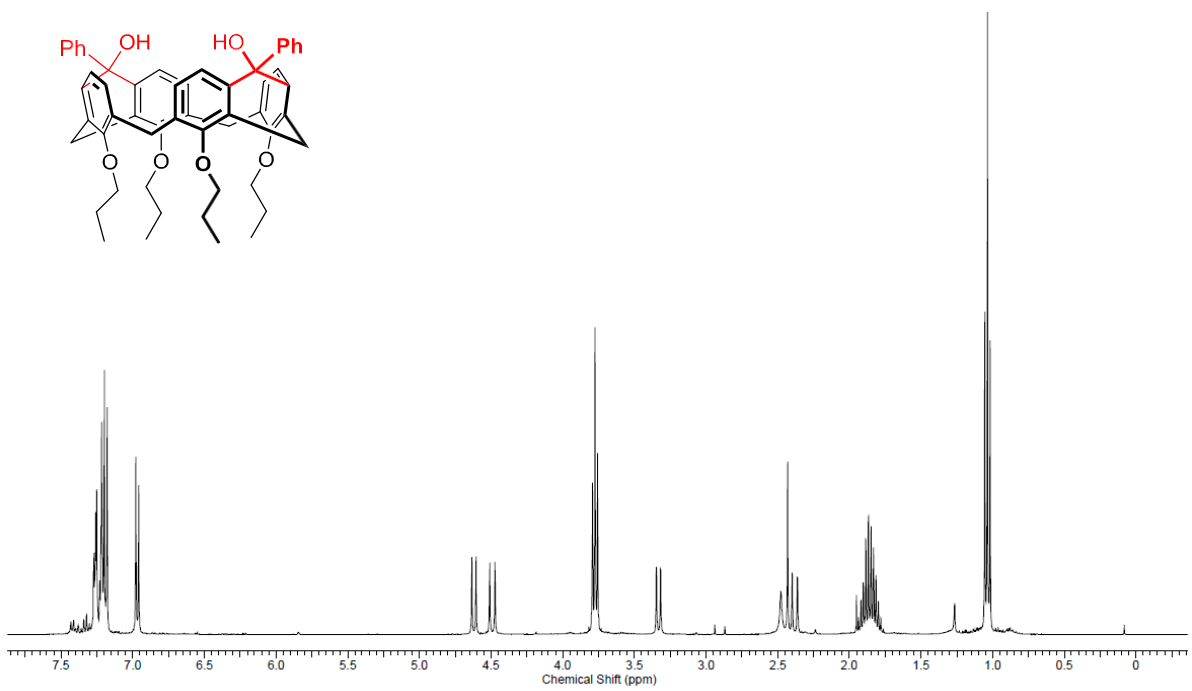


Figure 9. ^1H NMR of compound **11** (CDCl_3 , 400 MHz).

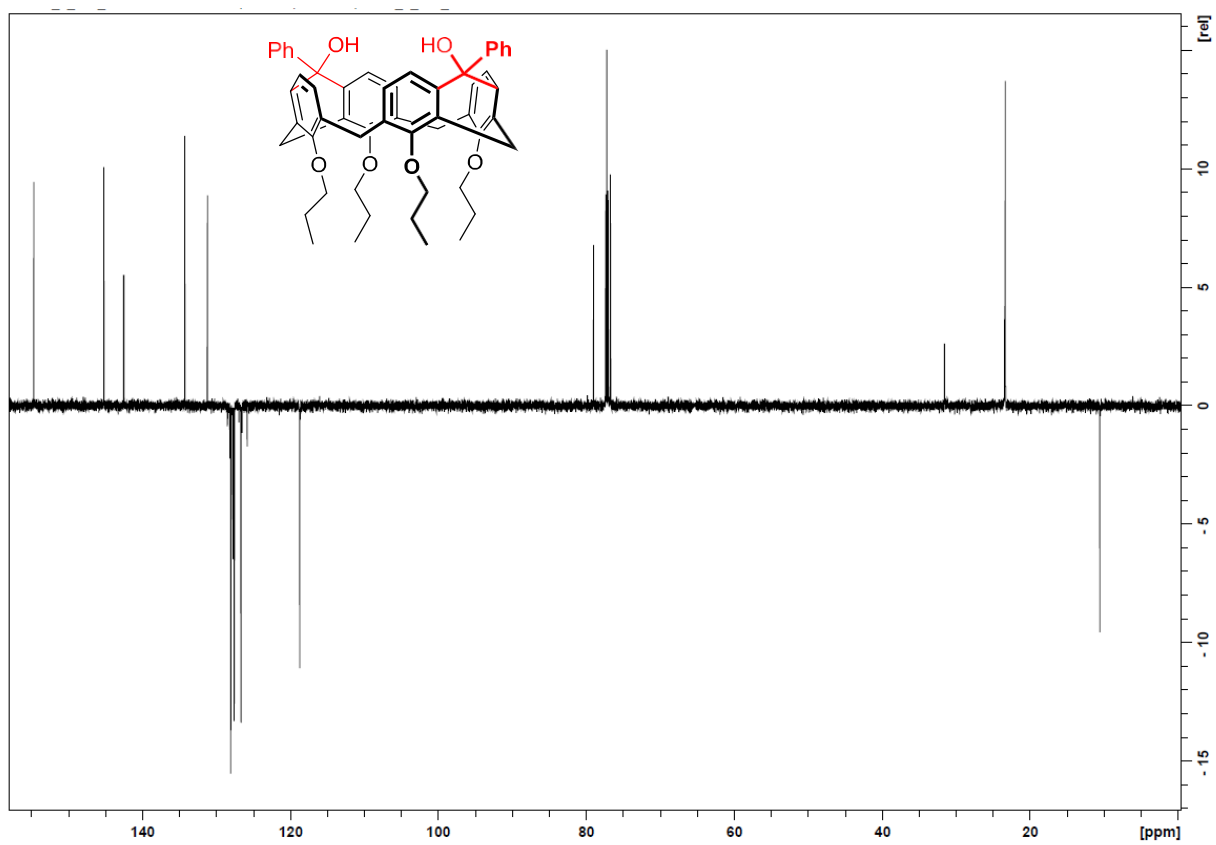


Figure 10. ^{13}C (APT) NMR of compound **11** (CDCl_3 , 100 MHz).

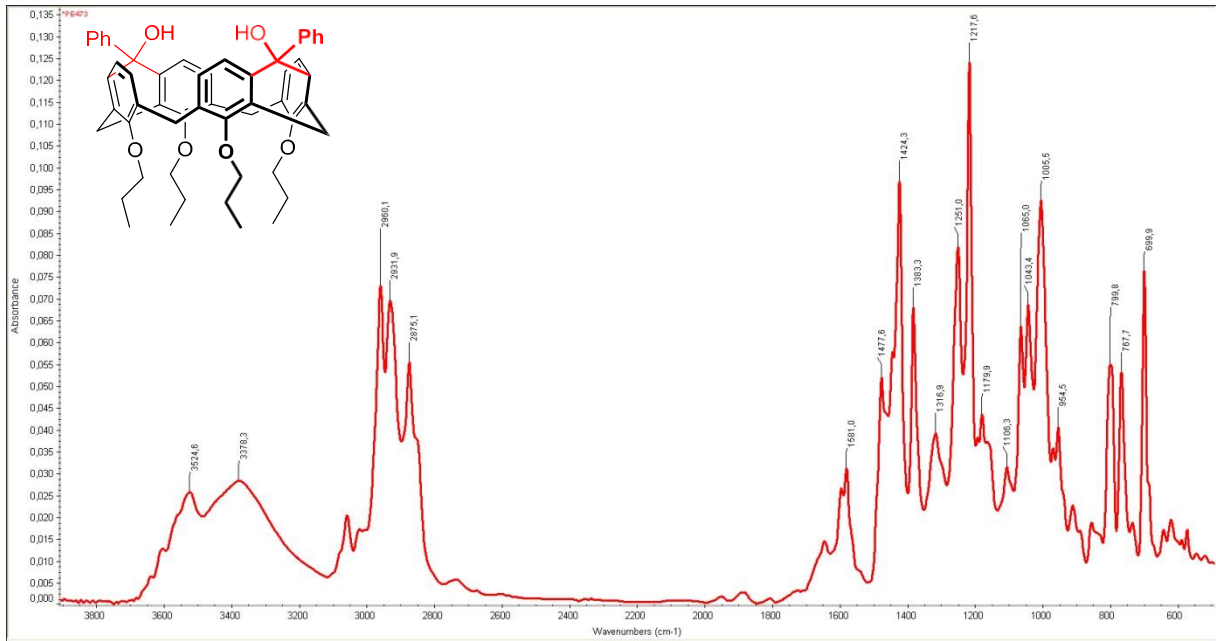


Figure 11. IR of compound 11 (KBr).

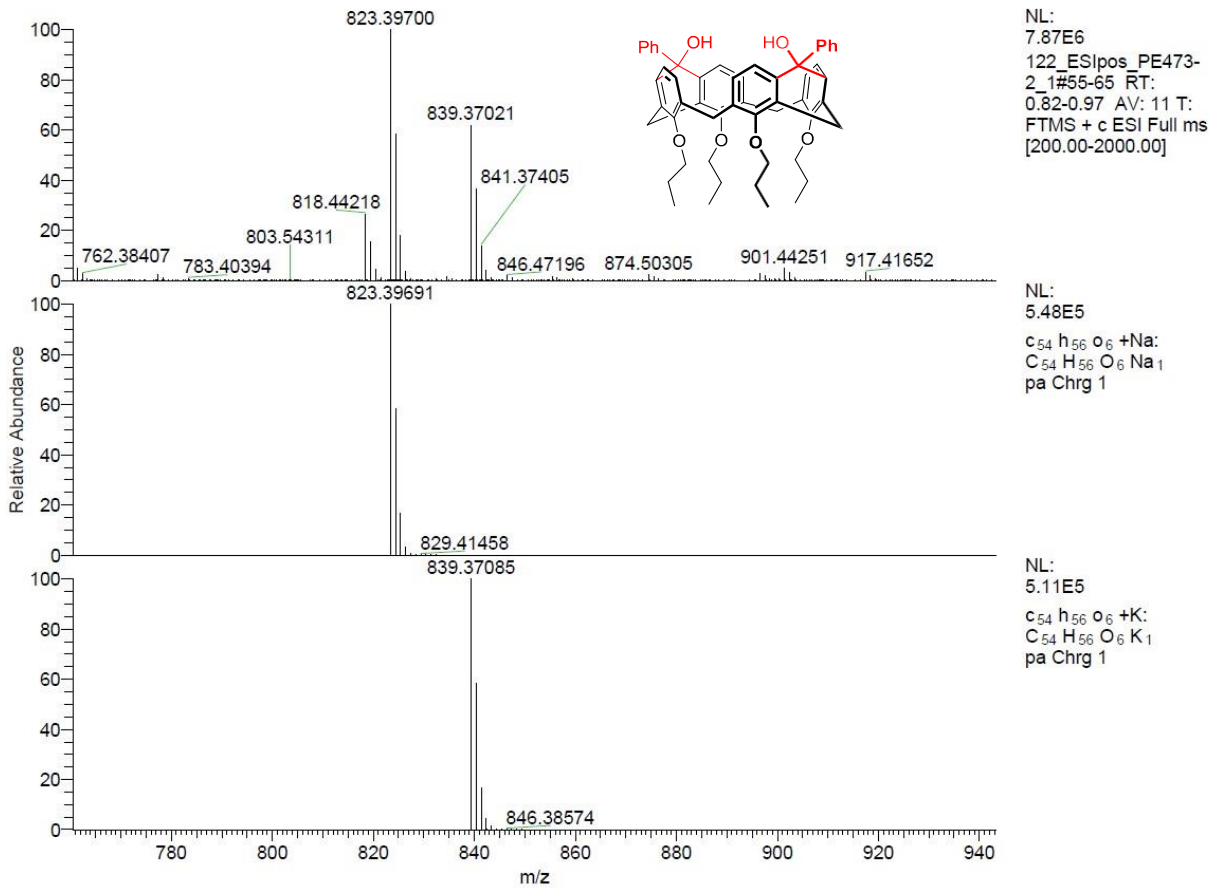


Figure 12. HRMS of compound 11 (ESI⁺).

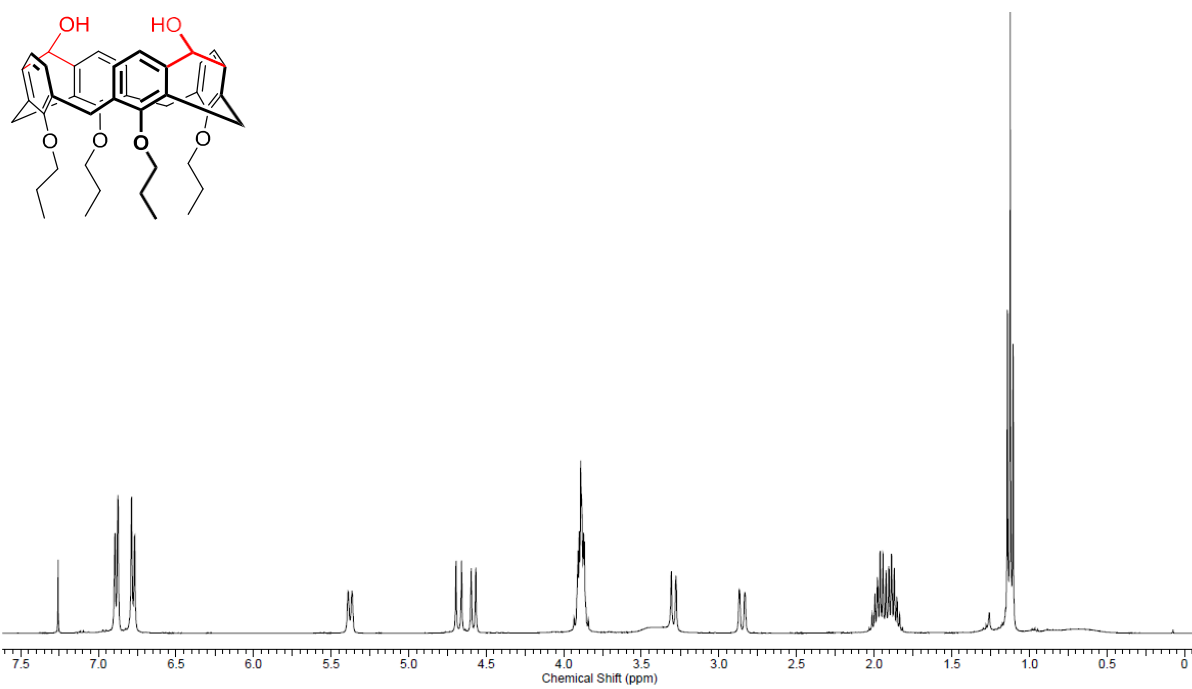


Figure 13. ¹H NMR of compound **12** (CDCl₃, 400 MHz).

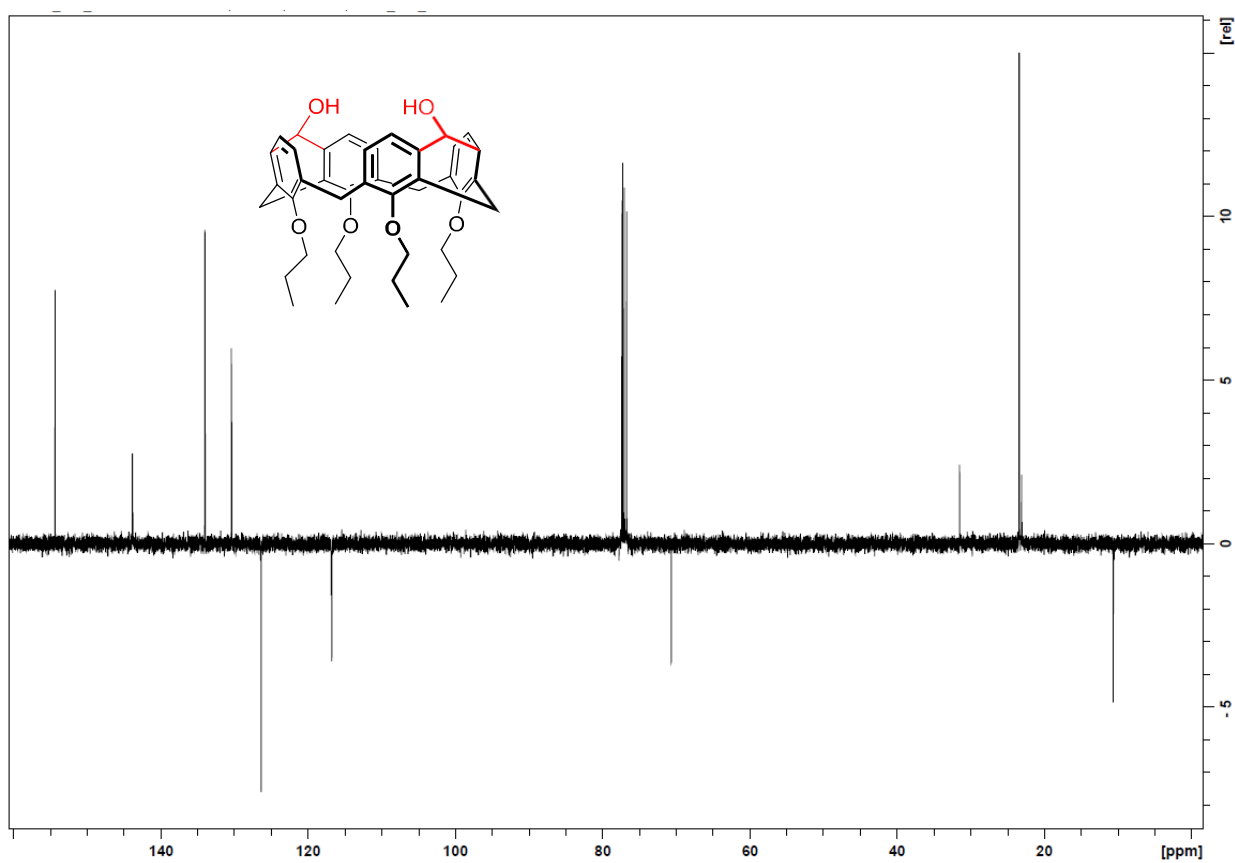


Figure 14. ¹³C(APT) NMR of compound **12** (CDCl₃, 100 MHz).

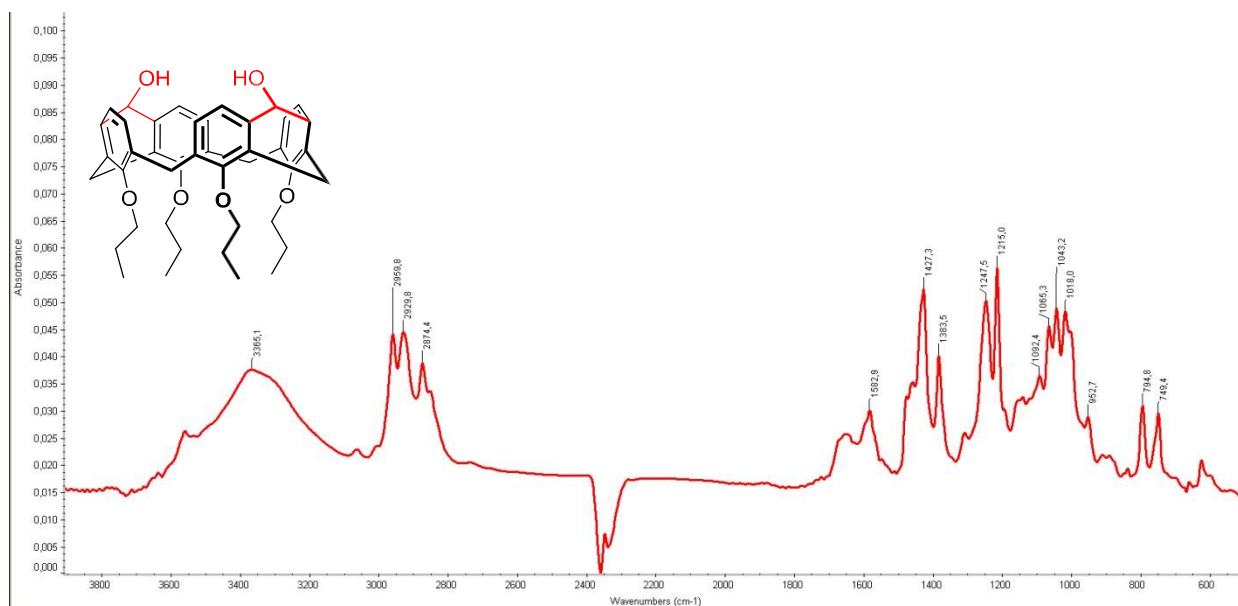


Figure 15. IR of compound 12 (KBr).

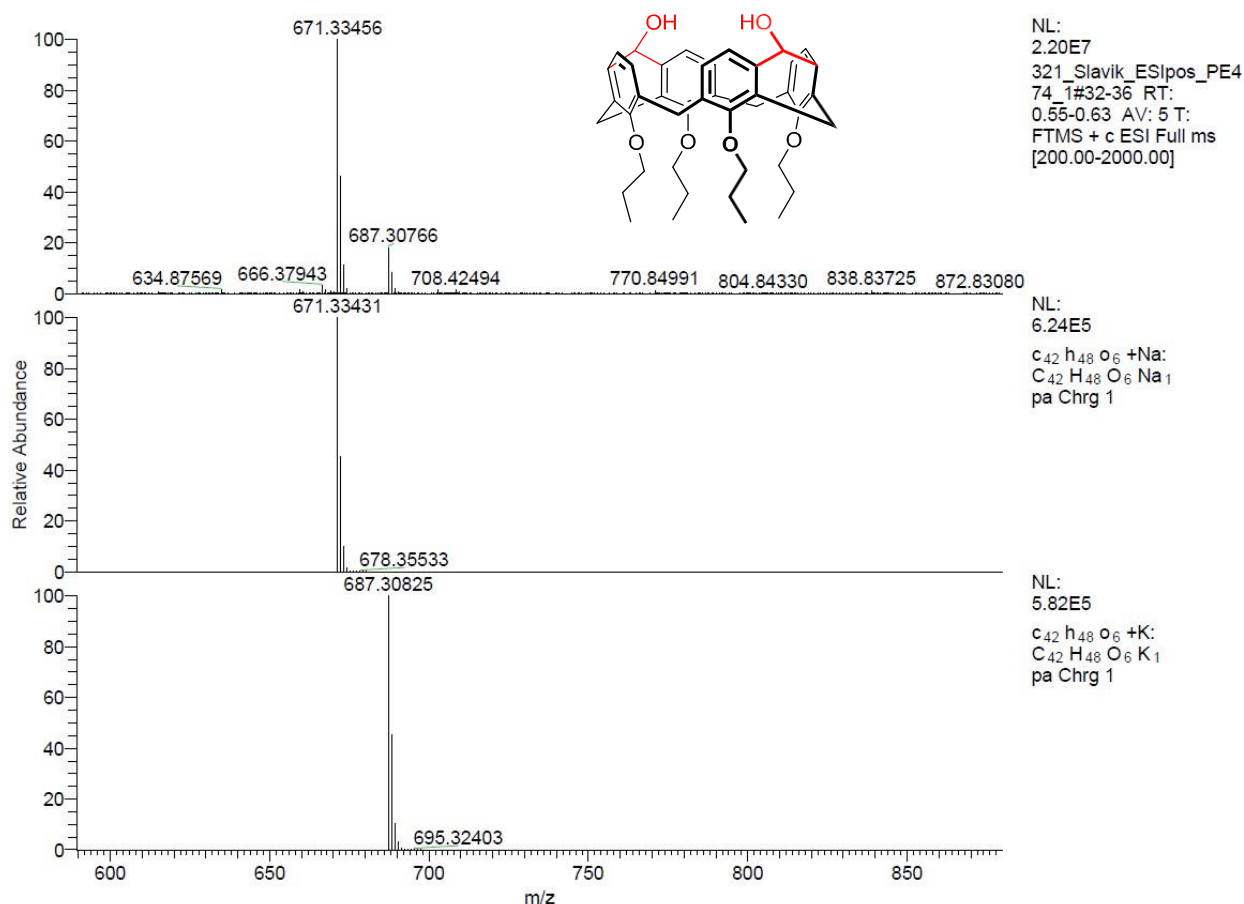


Figure 16. HRMS of compound 12 (ESI⁺).

Crystallographic Data

Table 1 The list of hydrogen bonds

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
Compound 9				
O49–H491···O46 ⁱ	0.71	1.94	2.626 (5)	165
O47–H471···O50 ⁱⁱ	0.80	1.88	2.600 (5)	167
Compound 10				
C5–H51···O10 ⁱⁱⁱ	0.97	2.48	3.409 (7)	160
C13–H131···C1902	0.99	2.66	3.602 (7)	159
C113–H1132···C1902	0.98	2.82	3.692 (12)	148
C901–H9011···O11 ^{iv}	0.95	2.56	3.378 (7)	145
C901–H9011···O11 ^v	0.95	2.56	3.378 (7)	145
Compound 11				
O704–H7041···O130	0.82	1.90	2.705 (10)	169
O804–H8041···O138	0.82	1.96	2.737 (10)	158
O706–H7061···O238	0.82	2.05	2.866 (10)	174
O806–H8061···O230	0.81	2.06	2.795 (10)	152
O904–H9041···O149	0.82	2.41	3.045 (10)	135
O904–H9041···O153	0.82	2.42	3.144 (10)	148
O38–H381···O908	0.83	2.02	2.761 (4)	149
O904–H9042···O145	0.83	2.34	3.036 (4)	142
O904–H9042···O157	0.83	2.34	3.007 (10)	137
O30–H301···O904	0.82	1.92	2.731 (4)	169
O130–H1301···O710 ^{vi}	0.82	1.94	2.738 (10)	164
O130–H1301···O710 ^{vi}	0.82	2.00	2.803 (10)	169
O908–H9082···O245	0.83	2.49	3.099 (10)	131
O908–H9082···O257	0.83	2.33	3.092 (10)	154
O138–H1381···O915 ^{vi}	0.80	1.93	2.687 (10)	158
O908–H9081···O249	0.83	2.41	3.039 (10)	134
O908–H9081···O253	0.83	2.25	2.995 (10)	150

O230–H2301…O806	0.95	1.85	2.795 (10)	173
O810–H8101…O230	0.95	1.51	2.437 (10)	166
O710–H7101…O230	0.95	1.81	2.764 (10)	177
O708–H7081…O710	0.95	1.79	2.736 (10)	179
O708–H7081…O810	0.95	2.60	3.546 (10)	176
O808–H8081…O710	0.95	1.90	2.815 (10)	163
O808–H8081…O810	0.95	2.59	3.502 (10)	161
O915–H9151…O238	0.95	1.98	2.733 (10)	135
O238–H2381…O708 ^{vii}	0.95	1.89	2.812 (10)	164
O238–H2381…O808 ^{vii}	0.95	2.21	3.049 (10)	147
O702–H7021…O30	0.95	2.00	2.948 (10)	175
O802–H8021…O38	0.95	1.99	2.937 (10)	171
C901–H9011…O49	0.95	2.46	3.304 (10)	148
C901–H9011…O53	0.95	2.50	3.224 (10)	134
C901–H9012…O45 [*]	0.95	2.84	3.559 (6)	133
C901–H9012…O57	0.95	2.39	3.270 (10)	154
C911–H9111…O49	0.95	2.29	3.177 (10)	155
C911–H9111…O53 [*]	0.95	2.92	3.63 (2)	133
C911–H9112…O45	0.95	2.44	3.179 (10)	135
C911–H9112…O57	0.95	2.59	3.433 (10)	148

Symmetry codes: (i) $x+1/2, -y+1, z$ (ii) $x-1/2, -y+1, z$ (iii) $-y+1, x, -z-1$ (iv) $y-1/2, x+1/2, z$ (v) $-x, -y+1, z$ (vi) $x+1/2, -y+1/2, z+1/2$ (vii) $x-1, y, z$

* Outside of sum of Van der Waals radii, the contact is listed for the sake of consistency.

Table 2 The list of dihedral angles and planes definition

List of atoms	The angle to reference plane (°)
Compound 8	
C2, C8, C14, C20	Reference plane
C3, C4, C5, C6, C7, C25, O29	138.6 (2)
C9, C10, C11, C12, C13, C26, O33	80.2 (2)
C15, C16, C17, C18, C19, C27, O37	139.7 (2)
C1, C21, C22, C23, C24, C28, O41	81.6 (2)
Compound 9	
C2, C8, C14, C20	Reference plane
C3, C4, C5, C6, C7, C25, O29	140.15 (8)
C9, C10, C11, C12, C13, C26, O33	83.64 (8)
C15, C16, C17, C18, C19, C27, O37	135.15 (8)
C1, C21, C22, C23, C24, C28, O41	83.64 (8)

Table 3 The cavity distortions in compound 11

Cx...Cy	Cx...Cy (Å)
C2...C14	7.864 (6)
C8...C20	6.132 (6)
C102...C114	7.984 (6)
C108...C120	5.998 (6)
C202...C214	7.978 (6)
C208...C220	5.949 (6)