Supplementary Material

Solvent-free synthesis of (poly)thiacalix[*n*]arenes: the evaluation of possible mechanism based on semi-preparative HPLC separation and mass-spectrometric investigation of the reaction products

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Method of analysis

The qualitative composition of the mixture of TCAs from **Methods 1-2** was determined by HPLC analysis on Agilent 1200 chromatograph equipped with columns Zorbax SB-C18 2.1×150 mm (5 µm) and Zorbax SB-C18 9.4 ×150 mm (5 µm), detection wavelength 254 nm.

Analysis of the crude mixture of TCAs (Method 2)

Sample preparation

To the 50 mg of TCAs in the 1.5 mL vial was added 700 µL DMSO. Vial was sonicated on ultrasonic bath for 5 minutes. The suspension in vial was centrifuged and clear fugate was transferred to clear 1.5 mL vial.

The selection of a mobile phase

For the optimal condition for HPLC analysis was carried out separation of the TCAs mixture in isocratic mode in the following systems of solvents:

I) 0.005 M solution of trisodium citrate 5,5-hydrate (channel A) – acetonitrile (channel B) (Table S1)

Table S1

<table>
<tr><th>A</th><th>B</th><th>column</th><th>Flow rate (mL/min)</th><th>comment</th></tr>
<tr><td>50</td><td>50</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td><td>No separation (see. Fig. 1)</td></tr>
<tr><td>25</td><td>75</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td><td rowspan="2">Partial separation (see. Fig. 2)</td></tr>
<tr><td>25</td><td>75</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.3</td></tr>
<tr><td>40</td><td>60</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td><td>No separation (see. Fig. 3)</td></tr>
<tr><td>30</td><td>70</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td><td>Total separation (see. Fig. 4)</td></tr>
<tr><td>30</td><td>70</td><td>Zorbax SB-C18 9.4 ×150 mm</td><td>1.5</td><td rowspan="4">No separation</td></tr>
<tr><td>25</td><td>75</td><td>Zorbax SB-C18 9.4 ×150 mm</td><td>1.5</td></tr>
<tr><td>30</td><td>70</td><td>Zorbax SB-C18 9.4 ×150 mm</td><td>2.5</td></tr>
<tr><td>30</td><td>70</td><td>Zorbax SB-C18 9.4 ×150 mm</td><td>4</td></tr>
<tr><td>30</td><td>70</td><td>Zorbax SB-C18 9.4 ×150 mm</td><td>5</td><td rowspan="2">Total separation</td></tr>
<tr><td>30</td><td>70</td><td>Zorbax SB-C18 9.4 ×150 mm</td><td>4</td></tr>
</table>

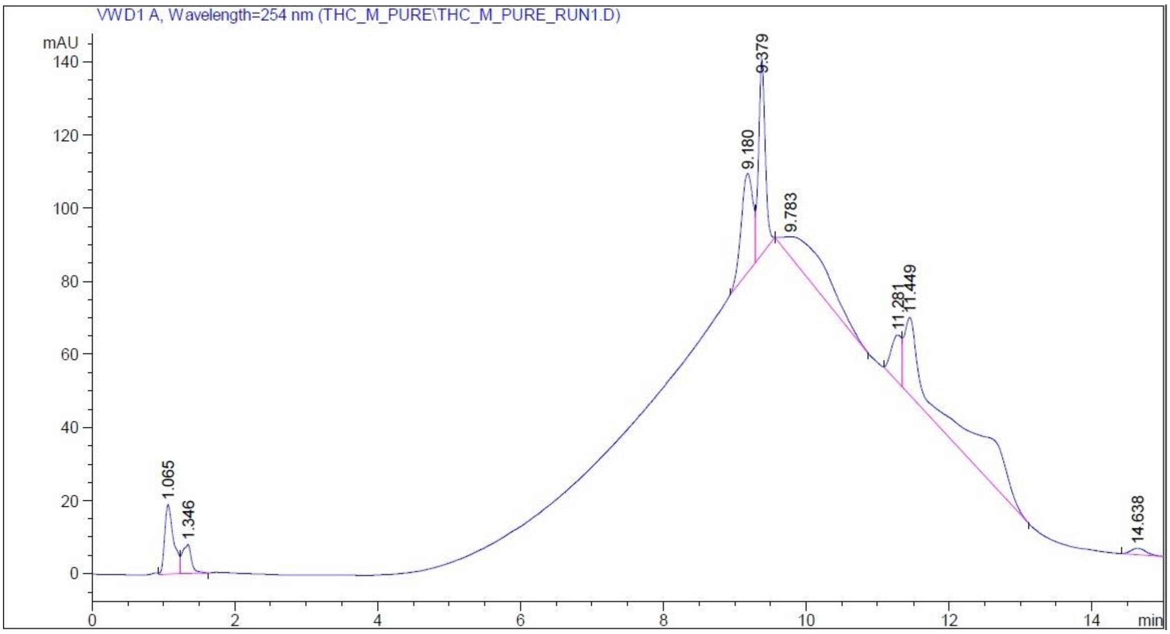

Figure S1.

0.1% water solution of formic acid (channel A) – acetonitrile (channel B) (Table S2)

Table S2

A	B	column	Flow rate (mL/min)	comment
30	70	Zorbax SB-C18 2.1×150 mm	0.5	Irreversible sorbtion of analites (see. Fig. 5)
5	95	Zorbax SB-C18 2.1×150 mm	0.5	
50	50	Zorbax SB-C18 2.1×150 mm	0.5	
40	60	Zorbax SB-C18 2.1×150 mm	0.5	
70	30	Zorbax SB-C18 2.1×150 mm	0.5	
65	35	Zorbax SB-C18 2.1×150 mm	0.5	
20	80	Zorbax SB-C18 2.1×150 mm	0.5	

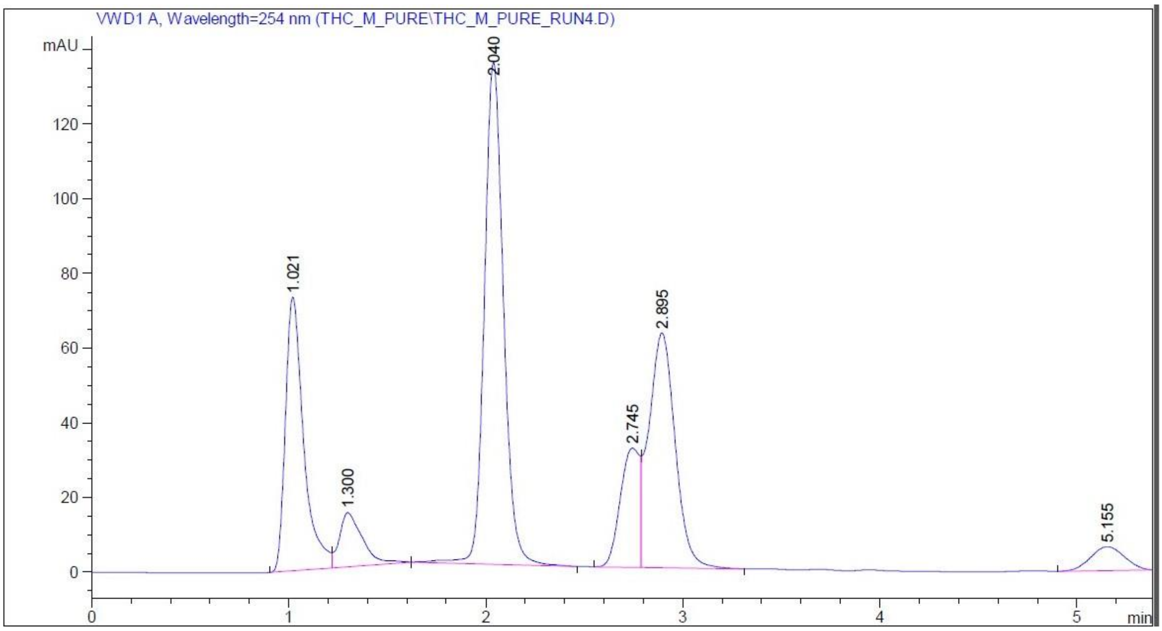

Figure S2.

0.05 M solution of ammonium acetate (channel A) – acetonitrile (channel B) (Table S3)

Table S3

A	B	column	Flow rate (mL/min)	comment
50	50	Zorbax SB-C18 2.1×150 mm	0.5	Irreversible sorbtion of analites
5	95	Zorbax SB-C18 2.1×150 mm	0.5	
30	70	Zorbax SB-C18 2.1×150 mm	0.5	Partial separation
20	80	Zorbax SB-C18 2.1×150 mm	0.5	
15	85	Zorbax SB-C18 2.1×150 mm	0.5	

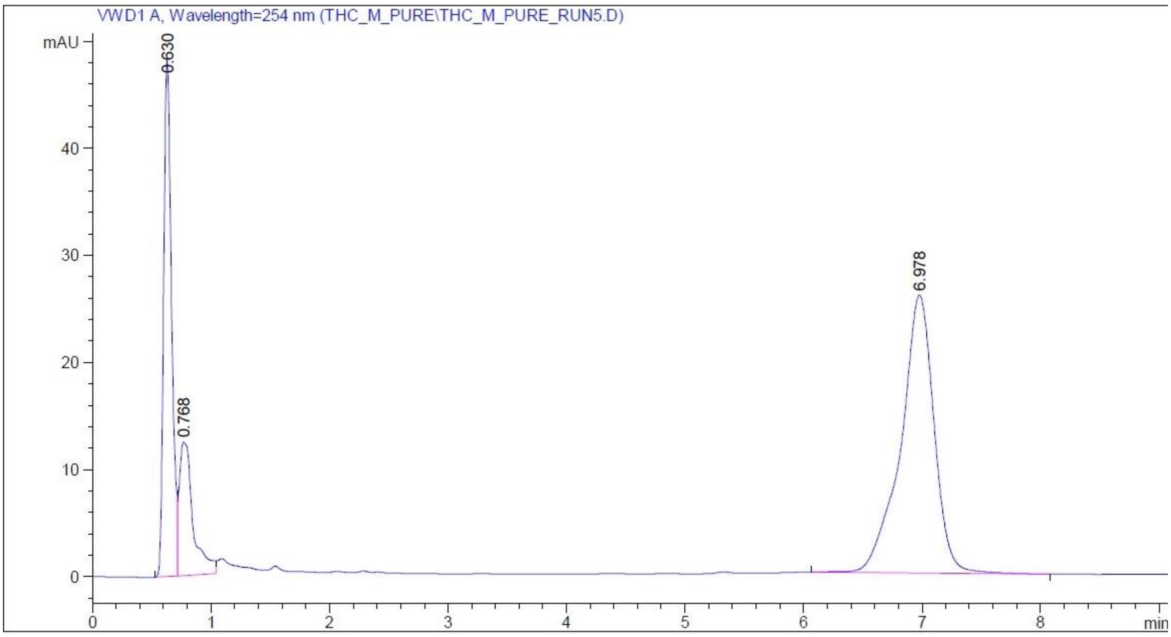

Figure S3.

0.05 M solution of ammonium acetate doped with ammonium hydroxyde (channel A) - acetonitrile (channel B) (Table S4)

Table S4

A	B	column	Flow rate (mL/min)	comment
20	80	Zorbax SB-C18 2.1×150 mm	0.5	Partial separation

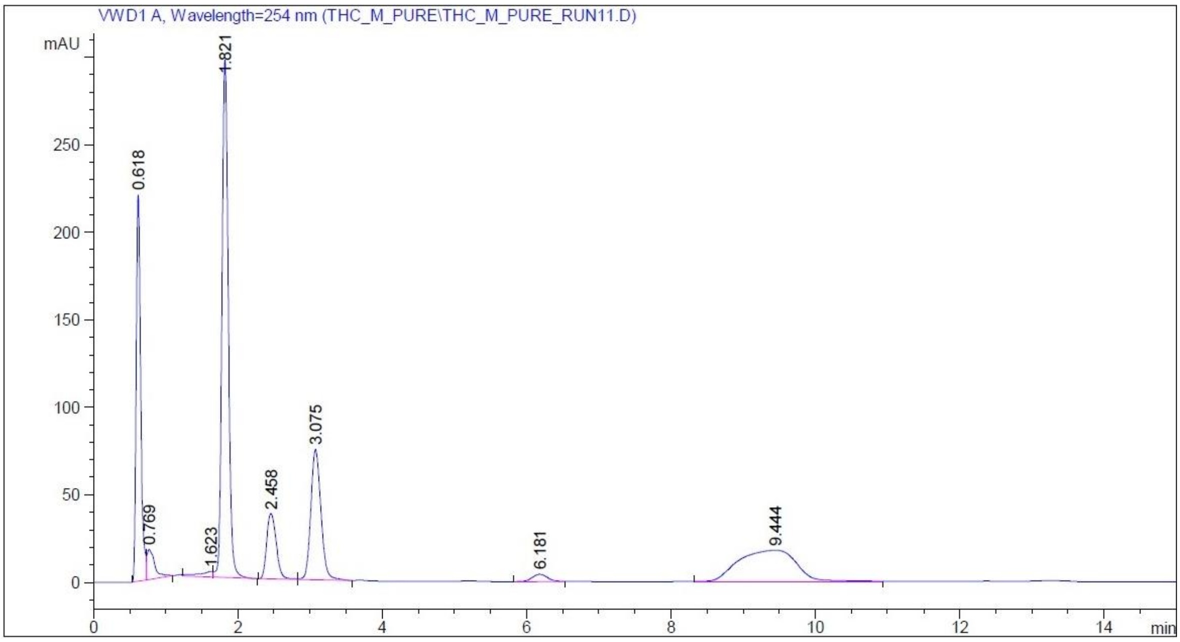

Figure S4.

0.32 M solution of ammonium acetate (channel A) – acetonitrile (channel B) (Table 5)

Table S5

A	B	column	Flow rate (mL/min)	comment
31	69	Zorbax SB-C18 2.1×150 mm	0.5	Total separation
33	67	Zorbax SB-C18 2.1×150 mm	0.5	
33	67	Zorbax SB-C18 9.4 ×150 mm	5	

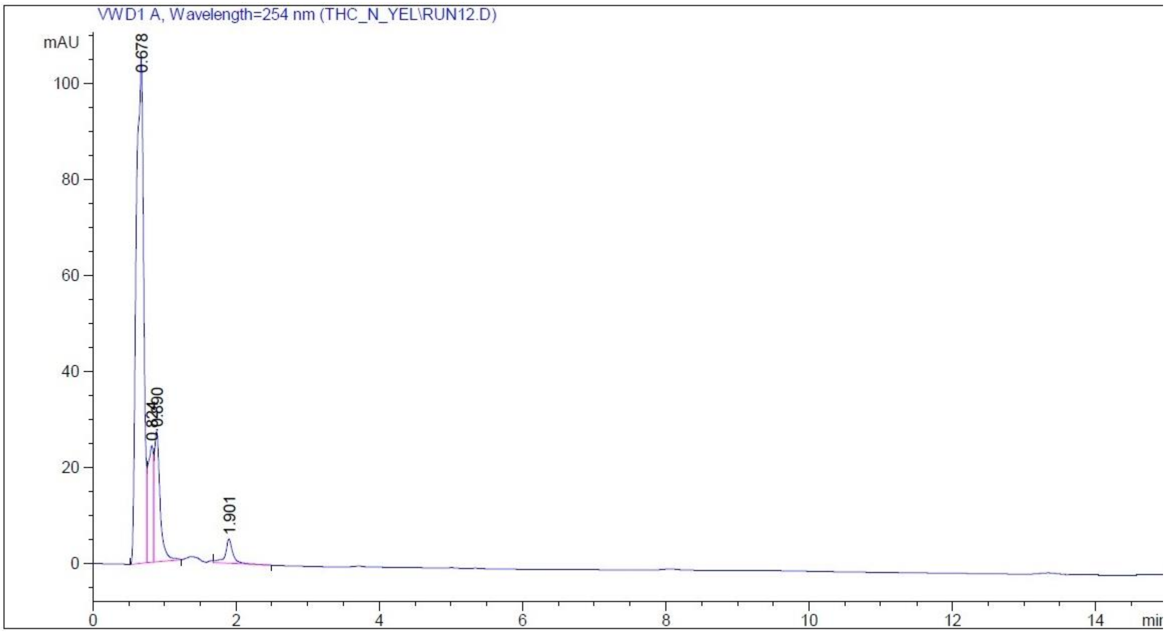

Figure S5.

Analysis of mixture of TCAs (Method 2) triturated with hydrochloric acid

Sample preparation

To the 50 mg of TCAs in the 6 mL vial was added 1 mL DMSO and 20 µL conc. HCl. Vial was sonicated on ultrasonic bath for 5 minutes. To the solution was added 1 mL of DCM and vial was shaked well. After separation of layers the lower layer was taken off and transferred to clear 1.5 mL vial.

The choice of mobile phase

For the optimal condition for HPLC analysis was carried out separation of the TCAs mixture in isocratic mode in the following systems of solvents:

Deionized water (channel A) – acetonitrile (channel B) (Table S6)

Table S6

<table>
<tr><th>A</th><th>B</th><th>column</th><th>Flow rate (mL/min)</th><th>comment</th></tr>
<tr><td>30</td><td>70</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td><td rowspan="4">Irreversible sorbtion of analites</td></tr>
<tr><td>50</td><td>50</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td></tr>
<tr><td>35</td><td>65</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td></tr>
<tr><td>25</td><td>75</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td></tr>
</table>

0.005 M solution of trisodium citrate 5.5-hydrate (channel A) – acetonitrile (channel B) (Table S7)

Table S7

<table>
<tr><th>A</th><th>B</th><th>column</th><th>Flow rate (mL/min)</th><th>comment</th></tr>
<tr><td>30</td><td>70</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td><td rowspan="4">Irreversible sorbtion of analites</td></tr>
<tr><td>60</td><td>40</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td></tr>
<tr><td colspan="2">60:40 (3 min.) then gradient to 50:50</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td></tr>
<tr><td colspan="2">60:40 (3 min.) then gradient to 25:75</td><td>Zorbax SB-C18 2.1×150 mm</td><td>0.5</td></tr>
</table>

After completion of all seven methods it was found that the most clear separation of TCAs mixture was observed using the eluent system I with the phase relation A:B = 30:70.

Semi-preparative separation of TCAs

For the obtaining of TCAs enriched fractions was carried out semi-preparative separation in manual mode on the semi-preparative column Zorbax SB-C18 9.4 ×150 mm. Elution was accomplished in isocratic mode by using system consisting of 30% 0.005 M solution of trisodium citrate 5.5-hydrate (channel A) – 70% acetonitrile (channel B) (see. Fig. S6).

Fractions which were obtained after separation were analyzed by direct input mass-spectrometry with ESI ionization in negative mode.

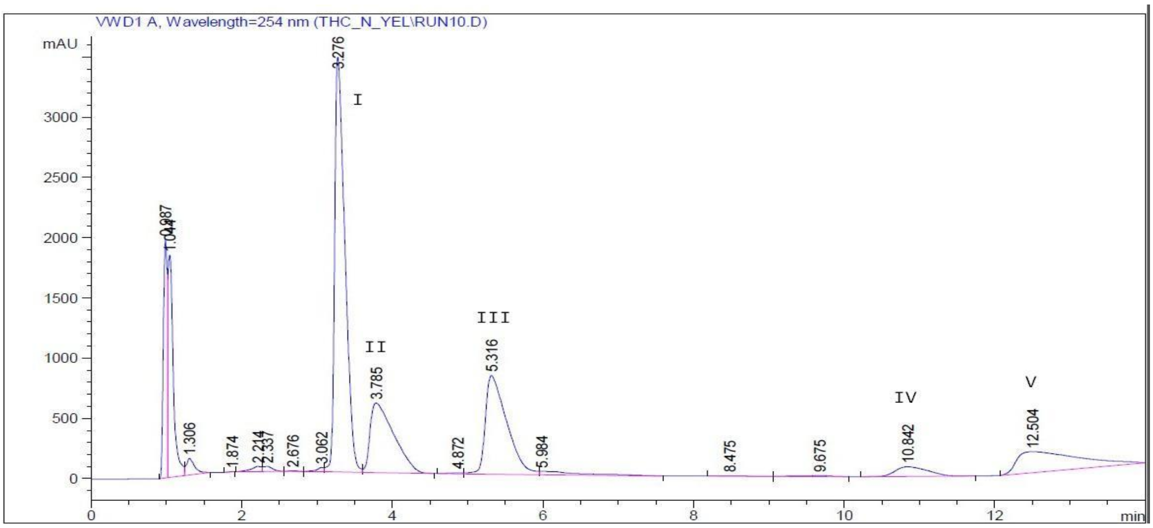

Figure S6. HPLC-analysis for the reaction mixture obtained according to Method 2 (way ii).

Peak number	Compound number
I	**1**
II	**2**
III	**3**
IV	**4**
V	**5**

Summary from HPLC report are presented below:

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Structure
1	0.987	BV	0.0538	6918.50537	1976.63367	7.4215	
2	1.044	VV	0.0738	9140.85742	1844.36731	9.8054	
3	1.306	VB	0.1141	1088.99829	137.91559	1.1682	
4	1.874	BB	0.0644	9.02060	2.12894	9.676e-3	
5	2.214	BV	0.1368	413.54599	41.65092	0.4436	
6	2.337	VB	0.1216	351.53564	41.60085	0.3771	
7	2.676	BB	0.1353	40.40646	5.00056	0.0433	
8	3.062	BV	0.0916	227.94693	35.19339	0.2445	
9	3.276	VV	0.1448	3.27034e4	3442.47095	35.0809	I
10	3.785	VB	0.3361	1.26682e4	577.17328	13.5891	II
11	4.872	BV	0.1638	96.47369	8.67368	0.1035	
12	5.316	VV	0.2953	1.61569e4	818.35370	17.3315	III
13	5.984	VB	0.4400	1017.34076	28.46395	1.0913	
14	8.475	BV	0.3008	55.37892	2.61743	0.0594	
15	9.675	VB	0.3691	203.21167	7.92698	0.2180	
16	10.842	BB	0.5092	2420.69141	79.74023	2.5967	IV
17	12.504	BBA	0.8030	9710.39648	173.75133	10.4163	V

Totals : 9.32228e4 9223.66275

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*** End of Report ***

Mass-spectrometric investigation of fractions I-V was disturbed by high background signal from mobile phase due to peaks of clusters of trisodium citrate (see Fig. S7). But none of the fraction with TCAs had targeted peaks overlapped with background peaks.

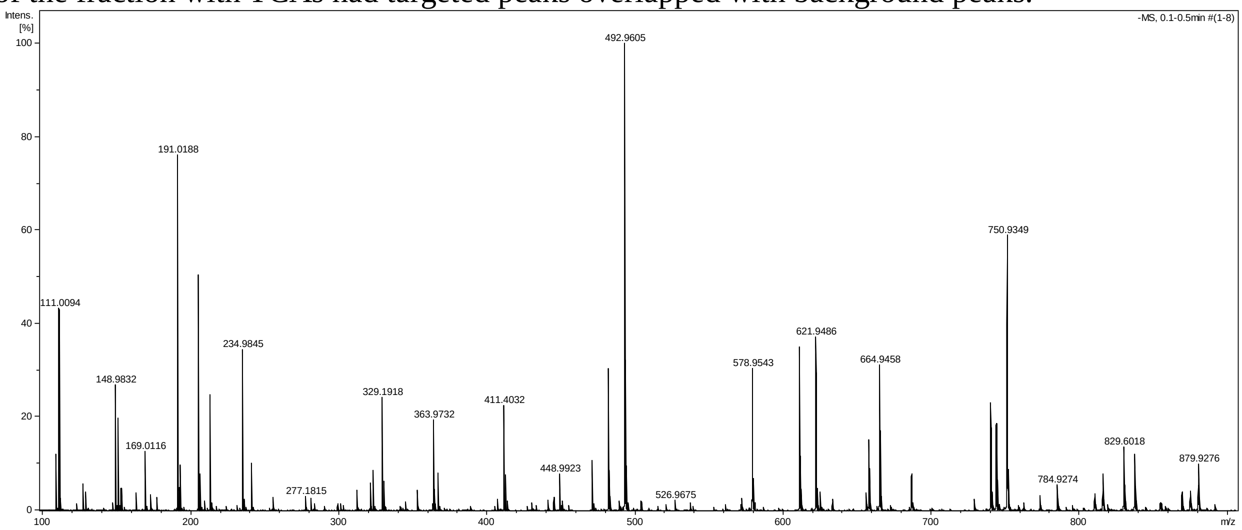


Figure S7

Fraction I contained peak of ion $[M-H]^-$ = 635.09 Da (Fig. S8):

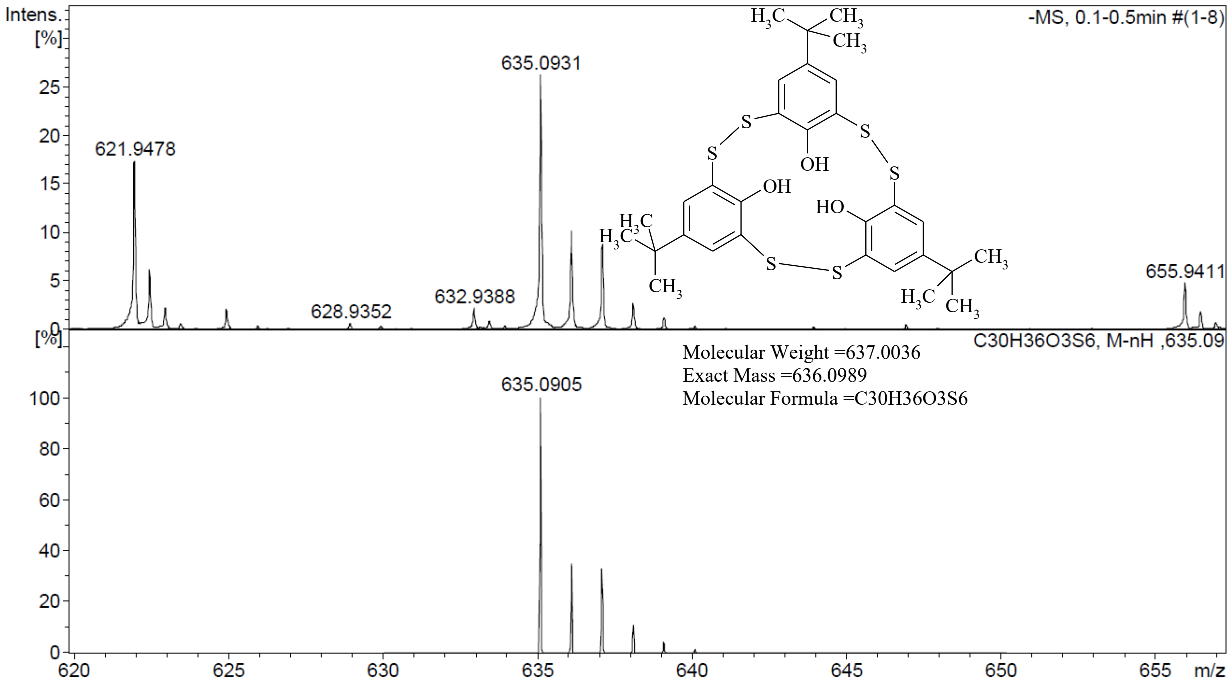
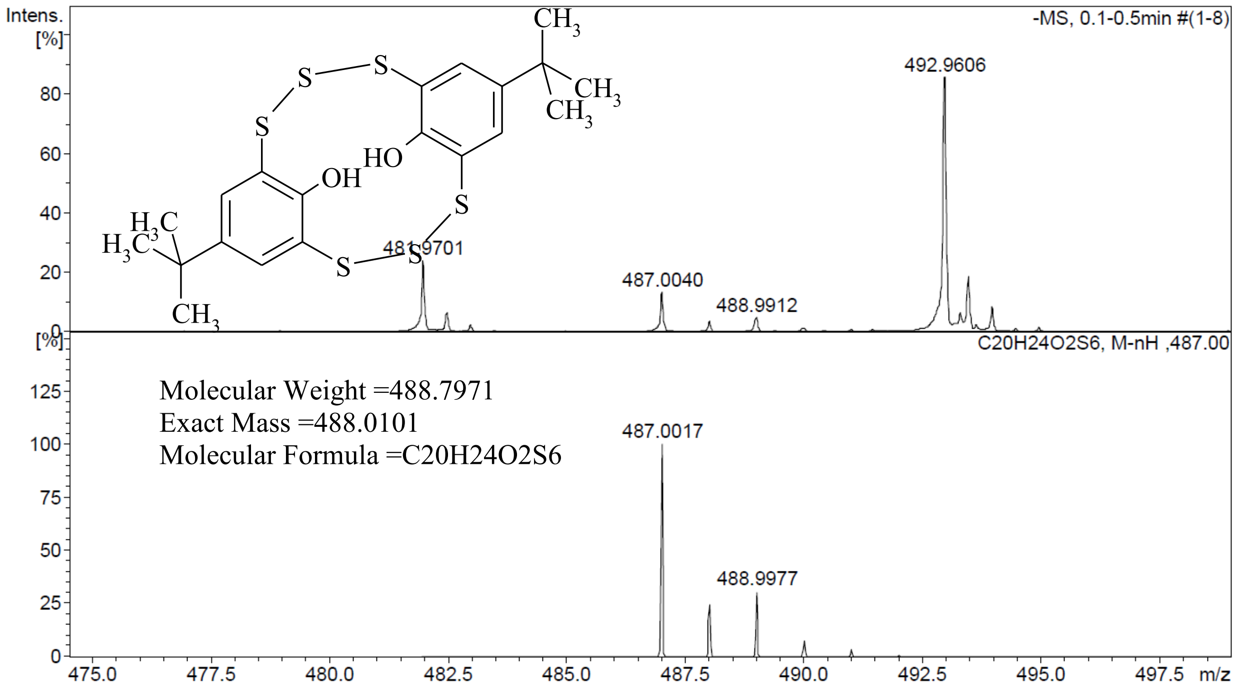


Figure S8

Fraction II contained peak of ion $[M-H]^-$ = 487.00 (Fig. S9):



Fraction III contained peak of ion $[M-H]^-$ = 667.06 (Fig. S10):

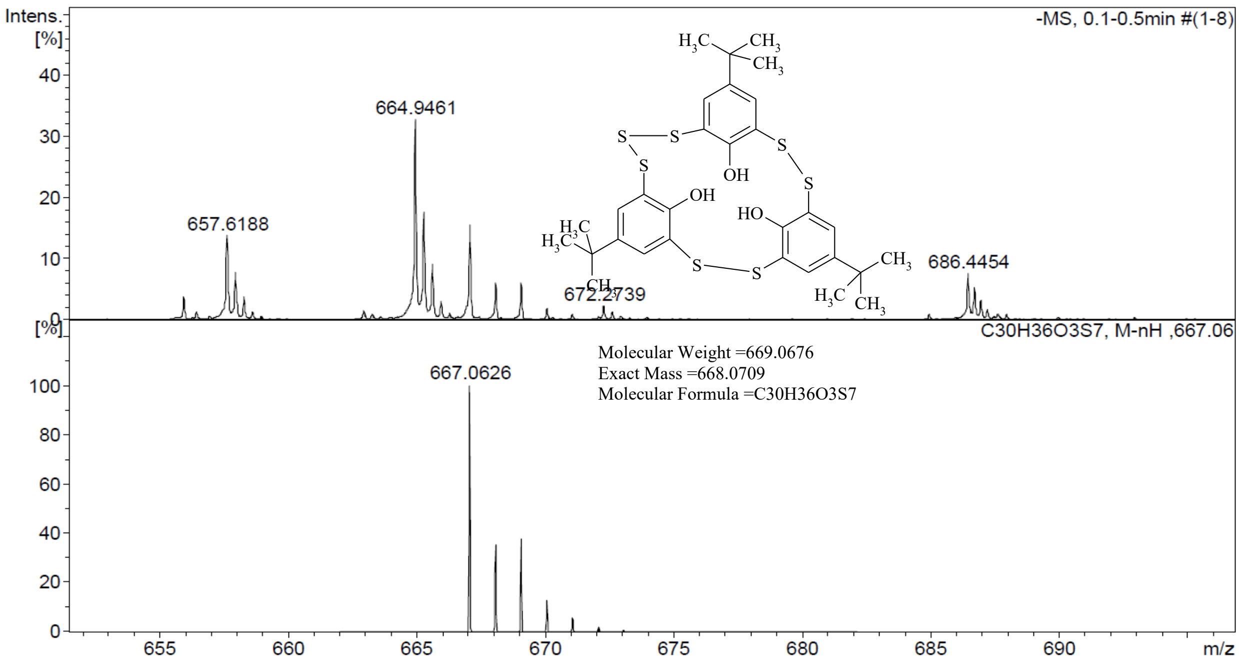


Figure S10

Fraction IV contained peak of ion $[M-H]^-$ = 731.00 (Fig. S11):

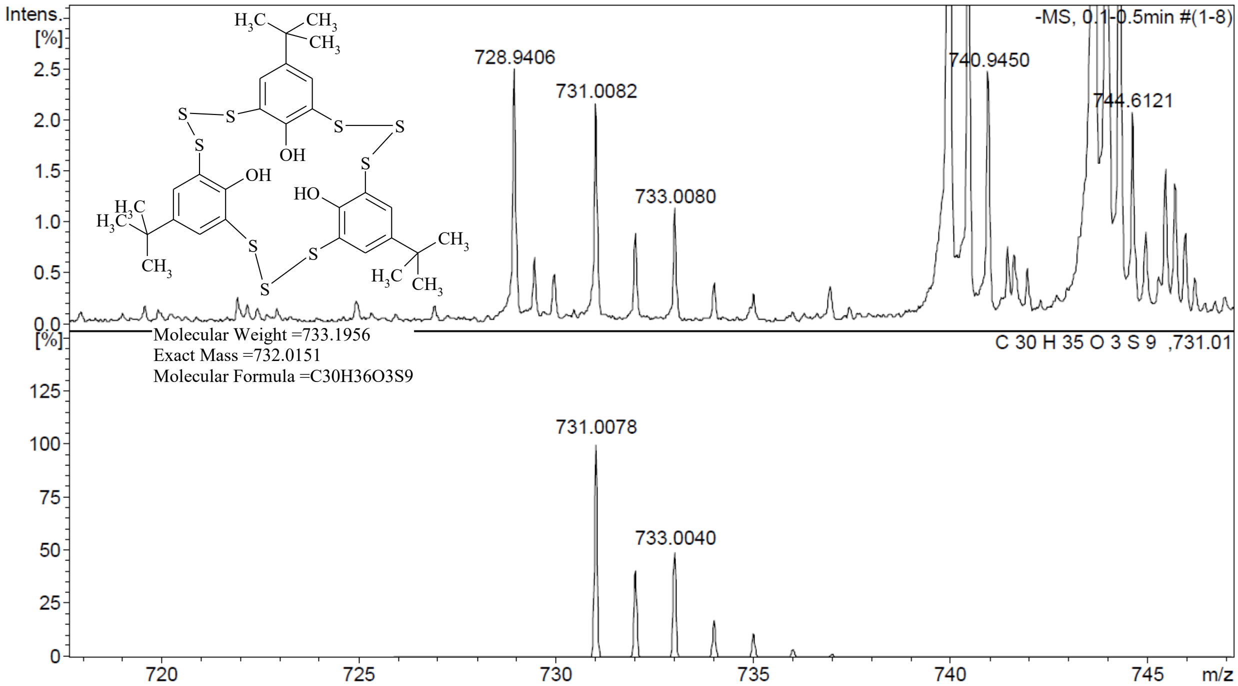


Figure S11

Fraction V contained peak of ion $[M-H]^-$ = 719.23 (Fig. S12):

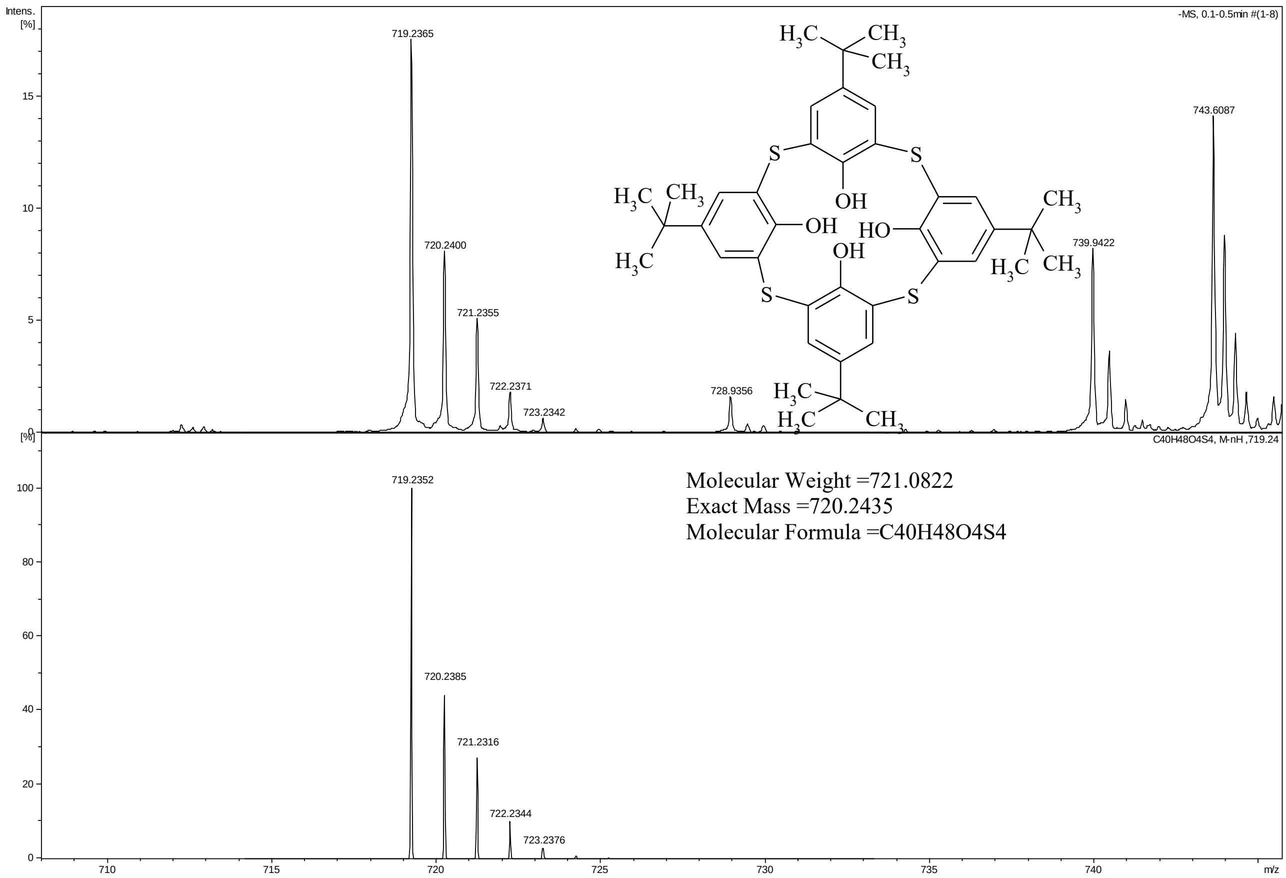
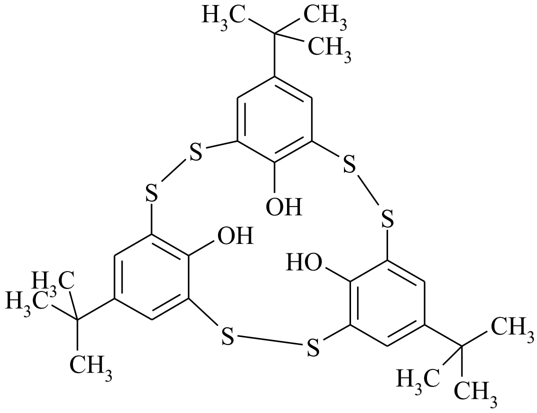
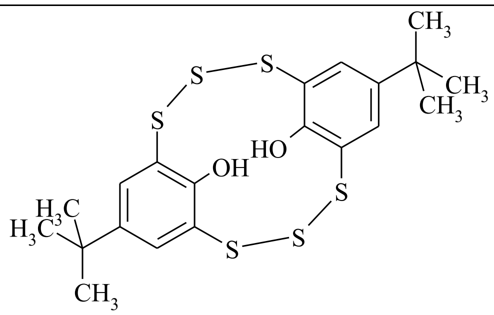
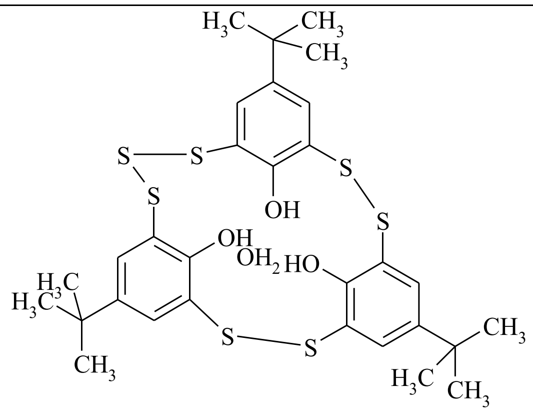
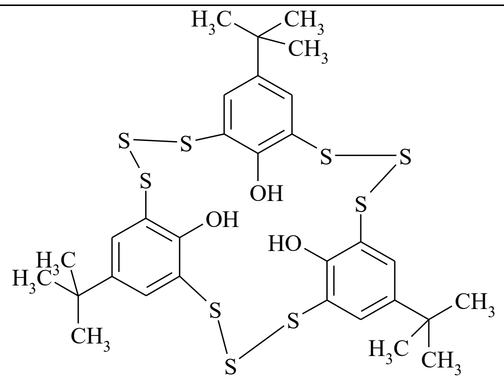
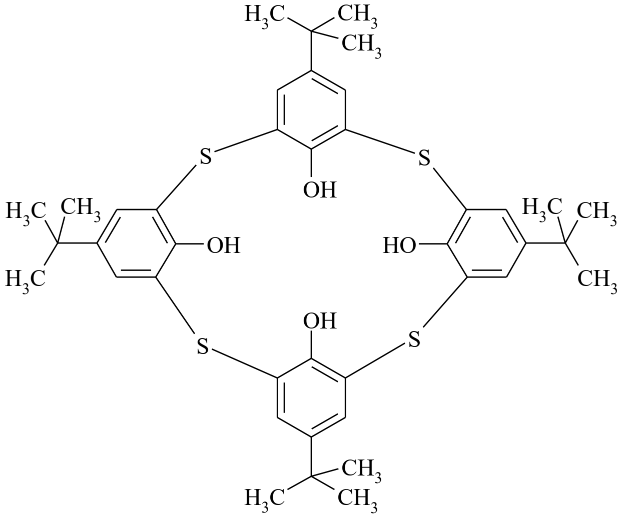


Figure S12

Summary table of results of investigation of fractions by direct input mass-spectrometry (Table S8):

Table S8

Fraction number	Proposed molecular formula
I	**1** 
II	**2** 
III	**3** 
IV	**4** 

V	**5**	

Mass-spectrometric study of reaction mass from Method 2 by direct input

The sample of solid sediment from Method 2 was dissolved in 100 µL of DMSO and then it was diluted by 1 mL of acetonitrile. This solution was injected into mass-spectrometer by means of direct input. The results are presented on Fig. 13-16 and Table 9 below.

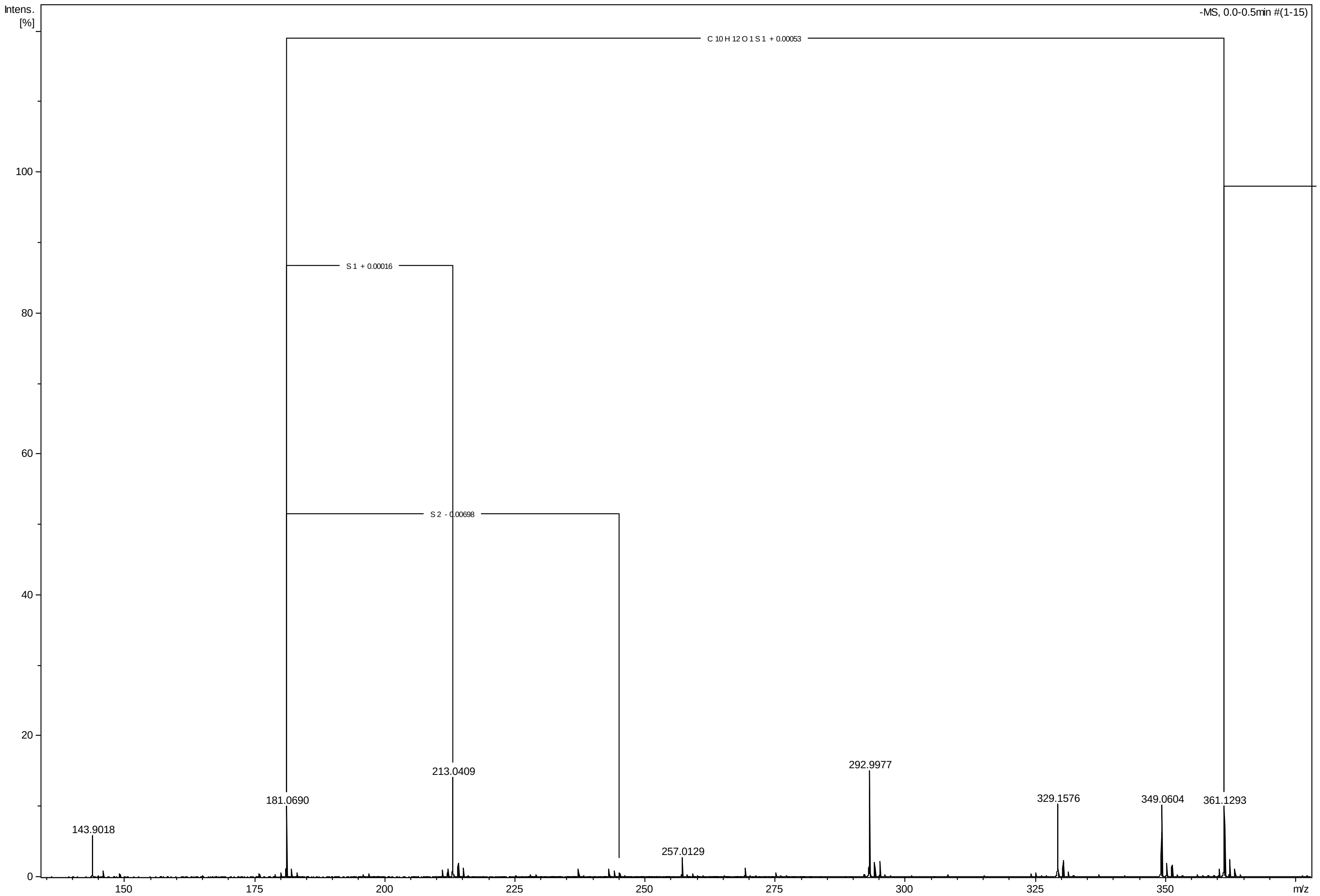


Figure S13. Survey mass-spectra of reaction mass from Method 2, mass range 145-360 Da.

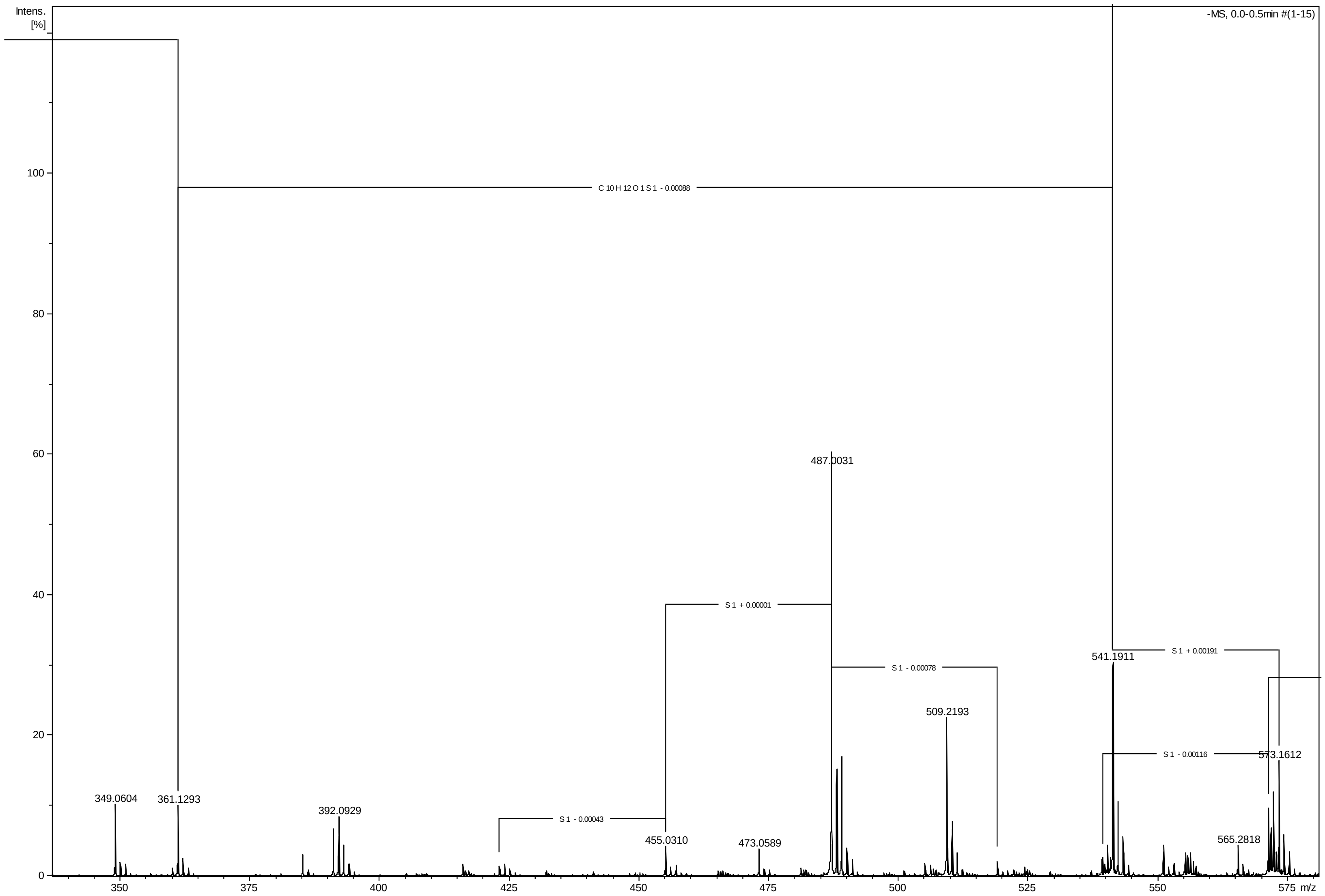


Figure. S14 Survey mass-spectra of reaction mass from Method 2, mass range 340-580 Da.

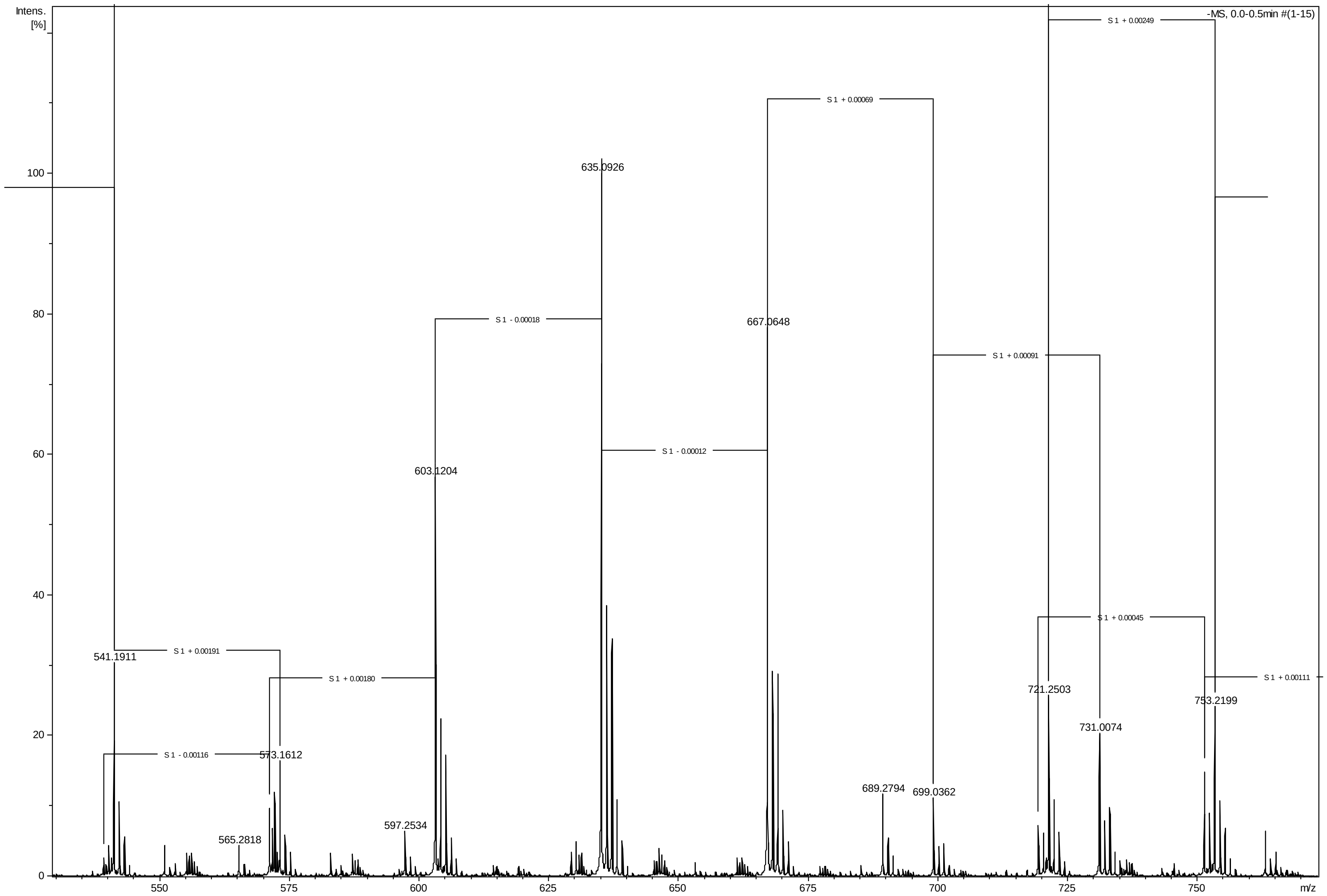


Figure S15 Survey mass-spectra of reaction mass from Method 2, mass range 545-770 Da.

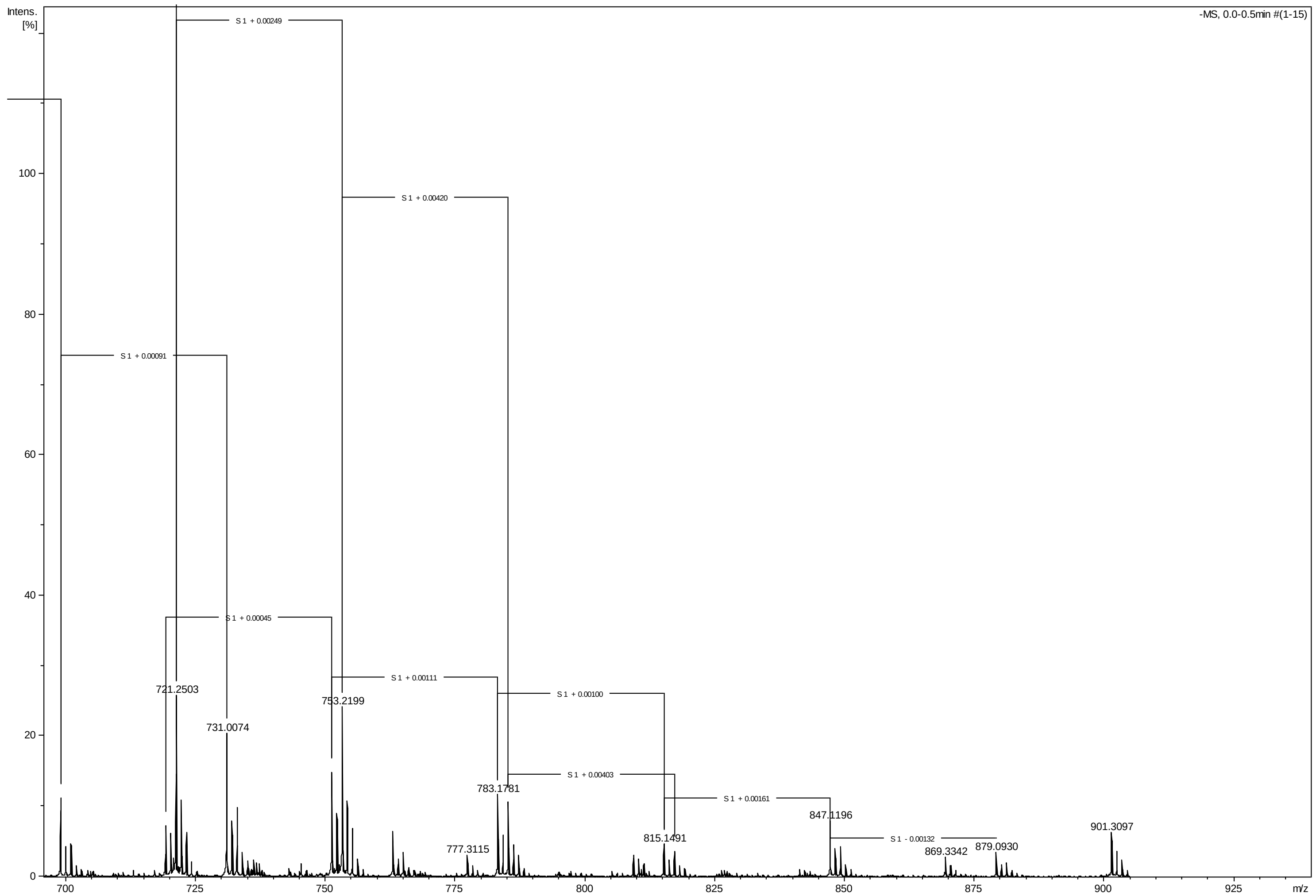


Figure S16 Survey mass-spectra of reaction mass from Method 2, mass range 700-925 Da.

Table S9 mass-list of mass-spectra of probe from Method 2

#	*m/z*	Res.	S/N	I	FWHM
1	112.94	4804	275.9	5654	0.0235
2	114.93	4735	23.5	623	0.0243
3	143.9	5062	792.6	18200	0.0284
4	144.9	4991	23.9	719	0.029
5	145.9	5111	113.2	2776	0.0285
6	149.1	5078	60.2	1583	0.0294
7	165.04	5545	23.9	789	0.0298
8	175.87	5738	58.4	1756	0.0306
9	178.91	6012	35.6	1157	0.0298
10	180.06	5343	73	2188	0.0337
11	181.07	5916	1119.5	31034	0.0306
12	182.07	5798	130	3786	0.0314
13	183.06	5662	60.5	1870	0.0323
14	195.86	6036	41.1	1365	0.0324
15	196.87	5960	53.7	1725	0.033
16	197.86	5503	13.3	575	0.036
17	198.86	5708	12.3	545	0.0348
18	211.03	6118	106	3234	0.0345
19	212.03	6308	122.4	3706	0.0336
20	212.4	2393	14	602	0.0888
21	213.04	6081	1504.4	43286	0.035
22	214.04	6342	205.7	6093	0.0337
23	215.04	5912	135.1	4072	0.0364
24	216.04	6117	17.4	701	0.0353
25	225.04	6298	15.4	648	0.0357
26	227.02	5692	12.2	557	0.0399
27	227.83	6671	39.7	1349	0.0342
28	229.05	4931	38.8	1324	0.0465
29	237.13	6653	126	3840	0.0356
30	238.13	7015	21.6	836	0.0339
31	243	6579	126.2	3854	0.0369
32	244	6255	98.2	3048	0.039
33	245.02	3974	66	2121	0.0617

34	246.01	4357	17	711	0.0565
35	257.01	6966	271.3	8595	0.0369
36	258.02	6883	39	1438	0.0375
37	259.01	6664	39.4	1457	0.0389
38	260.02	6008	12.5	622	0.0433
39	261.02	6708	17.3	778	0.0389
40	265.15	7091	13.7	676	0.0374
41	269.1	7047	118.4	4140	0.0382
42	270.11	6636	19.7	892	0.0407
43	271.1	6637	11.5	622	0.0408
44	274.97	7035	47.9	1871	0.0391
45	275.98	4982	20.5	945	0.0554
46	276.98	5125	15	761	0.054
47	291.99	6919	22	1072	0.0422
48	292.11	3413	11.5	683	0.0856
49	293	7074	1240.2	46343	0.0414
50	294	6920	165.7	6448	0.0425
51	295	6930	182.9	7122	0.0426
52	296	6781	21.1	1058	0.0436
53	296.99	7040	11	679	0.0422
54	301.09	7637	11.1	696	0.0394
55	307.97	6693	20.9	1103	0.046
56	314.98	8204	10.4	705	0.0384
57	323.96	7283	33.9	1711	0.0445
58	324.97	7412	41	2019	0.0438
59	325.96	5547	10.8	746	0.0588
60	326.06	6519	15.9	965	0.05
61	329.16	7565	735	31704	0.0435
62	330.16	7357	167.1	7461	0.0449
63	331.16	7137	51.5	2512	0.0464
64	336.97	7760	22.7	1296	0.0434
65	349.06	7265	680.3	31367	0.048
66	350.06	7496	127	6130	0.0467
67	351.06	7656	111.6	5440	0.0459
68	352.06	8061	16.5	1075	0.0437

69	355.93	7717	21.1	1306	0.0461
70	359.11	7503	11.5	866	0.0479
71	360.12	7222	74.2	3832	0.0499
72	361.13	7560	648.5	31118	0.0478
73	362.13	7649	154	7674	0.0473
74	363.13	7446	71.7	3762	0.0488
75	364.13	7258	15.4	1067	0.0502
76	376.12	7012	11	900	0.0536
77	376.93	7931	11.8	943	0.0475
78	381.03	8203	19.2	1342	0.0464
79	385.22	8123	174.5	9610	0.0474
80	386.22	8210	49.3	2975	0.047
81	387.22	8274	13	1041	0.0468
82	391.09	7925	372.8	20656	0.0494
83	392.09	7665	467.7	25935	0.0512
84	393.1	7567	243.7	13737	0.0519
85	394.09	7270	94.4	5560	0.0542
86	395.1	7681	32.2	2141	0.0514
87	400.1	7660	11.3	996	0.0522
88	405.11	7113	12.2	1068	0.057
89	407.08	6619	15.3	1256	0.0615
90	408.08	7324	15.4	1266	0.0557
91	409.11	7064	16	1305	0.0579
92	416.09	7792	85.5	5529	0.0534
93	416.59	7299	35.5	2520	0.0571
94	417.09	7093	36.8	2605	0.0588
95	417.19	7754	31.5	2284	0.0538
96	417.59	8131	11.9	1098	0.0514
97	422.05	8374	12.1	1173	0.0504
98	423.06	7856	65.1	4685	0.0539
99	424.06	8122	72	5212	0.0522
100	425.07	6527	45.5	3481	0.0651
101	426.07	7093	17.9	1624	0.0601
102	432.07	8053	27.5	2457	0.0537
103	432.57	8097	13.1	1388	0.0534

104	433.07	7684	10.8	1220	0.0564
105	441.09	8414	20.4	2119	0.0524
106	448.16	8468	10.6	1382	0.0529
107	449.16	7493	14.3	1736	0.0599
108	450.16	7569	15.3	1843	0.0595
109	455.03	8689	131.6	13288	0.0524
110	456.03	8214	37	4076	0.0555
111	457.04	5909	43.5	4768	0.0773
112	458.04	5995	10.6	1498	0.0764
113	465.13	7565	20.2	2616	0.0615
114	465.63	8169	14	1952	0.057
115	466.14	7856	19	2504	0.0593
116	473.06	8928	100.7	12085	0.053
117	474.06	8707	25.2	3394	0.0544
118	475.06	8393	21.4	2970	0.0566
119	481.12	7679	26.8	3808	0.0627
120	481.62	8149	18.3	2760	0.0591
121	482.12	8076	19.8	2967	0.0597
122	482.63	8412	10.5	1795	0.0574
123	485.52	2839	10.3	1815	0.171
124	487	8280	1345.7	178295	0.0588
125	488.01	8663	345.8	46598	0.0563
126	489	8311	382.7	51985	0.0588
127	490	8247	87	12296	0.0594
128	491	8583	50.7	7425	0.0572
129	492	8960	10.2	1887	0.0549
130	501.02	8800	12.7	2383	0.0569
131	505.03	8899	35.4	5956	0.0567
132	506.12	7892	29.3	5052	0.0641
133	506.62	8013	17.4	3211	0.0632
134	507.03	6633	12	2373	0.0764
135	507.12	7561	15.6	2939	0.0671
136	509.22	8541	430.9	69113	0.0596
137	510.22	9126	147	24093	0.0559
138	511.22	8762	62.1	10540	0.0583

139	512.22	8790	14.5	2865	0.0583
140	518.98	9001	34.5	6426	0.0577
141	520.97	8977	12	2604	0.058
142	522.11	8699	13.2	2831	0.06
143	524.2	8165	20	4069	0.0642
144	524.7	8656	13.9	3008	0.0606
145	525.2	8442	11.8	2627	0.0622
146	539.18	8380	39.1	8390	0.0643
147	539.68	7720	24.7	5526	0.0699
148	540.18	8108	65.7	13851	0.0666
149	540.69	6794	37.3	8136	0.0796
150	541.19	8582	452.3	93081	0.0631
151	541.69	6845	12.1	3037	0.0791
152	542.19	8961	154.8	32515	0.0605
153	543.19	8807	81.4	17515	0.0617
154	544.19	9004	21.3	5028	0.0604
155	550.95	9046	58.9	13719	0.0609
156	551.95	9529	16.6	4295	0.0579
157	552.94	9038	22.8	5751	0.0612
158	555.16	8406	42.2	10329	0.066
159	555.67	8442	36.8	9112	0.0658
160	556.17	8562	42	10378	0.065
161	556.67	8573	25.7	6591	0.0649
162	557.17	8322	17	4582	0.0669
163	565.28	9205	52.8	13839	0.0614
164	566.28	9176	19.7	5564	0.0617
165	571.15	8548	111.9	29943	0.0668
166	571.65	8517	77.7	21046	0.0671
167	572.15	8881	137.1	36837	0.0644
168	572.65	7921	38.8	10888	0.0723
169	573.16	8969	187.7	50571	0.0639
170	574.16	8802	65.3	18105	0.0652
171	575.16	9291	38.2	10914	0.0619
172	576.16	9260	10.5	3447	0.0622
173	582.92	9285	34.4	10426	0.0628

174	584.92	9839	15.7	5167	0.0595
175	587.14	8658	31.3	9805	0.0678
176	587.64	8939	21.6	6995	0.0657
177	588.14	8499	22.5	7279	0.0692
178	588.64	9444	12	4175	0.0623
179	597.25	9006	60.9	20048	0.0663
180	598.26	9706	24.4	8498	0.0616
181	599.25	9459	12.3	4632	0.0633
182	603.12	9034	519.2	173937	0.0668
183	603.62	6970	21.5	7885	0.0866
184	604.12	9331	201.9	68590	0.0647
185	604.63	6312	11.5	4570	0.0958
186	605.12	8793	153.8	52825	0.0688
187	606.12	9080	47.3	16856	0.0668
188	607.12	9257	20.6	7799	0.0656
189	614.23	9365	11.6	4913	0.0656
190	614.89	10227	10.5	4549	0.0601
191	619.11	9371	10.2	4574	0.0661
192	629.22	9457	25.1	10850	0.0665
193	630.22	9027	36.3	15473	0.0698
194	630.72	9292	21.8	9619	0.0679
195	631.22	9180	23.4	10297	0.0688
196	635.09	8650	729.8	305817	0.0734
197	636.1	9342	278.7	117991	0.0681
198	637.09	8987	242.8	103521	0.0709
199	638.09	9668	76.7	33425	0.066
200	639.09	9545	34.7	15616	0.067
201	645.19	9063	13.9	6943	0.0712
202	645.7	9035	13.3	6696	0.0715
203	646.2	8907	26.2	12458	0.0726
204	646.7	9039	19.3	9424	0.0715
205	647.2	9383	14.3	7132	0.069
206	653.12	9927	12.8	6230	0.0658
207	661.18	9074	18.8	8251	0.0729
208	661.68	9270	13.6	6154	0.0714

209	662.18	9100	19.1	8322	0.0728
210	662.68	9405	11.6	5284	0.0705
211	667.06	9083	621.4	238744	0.0734
212	668.07	9509	233.2	89247	0.0703
213	669.06	9444	231.9	88004	0.0708
214	670.06	9767	75.9	29011	0.0686
215	671.06	9860	39.3	15182	0.0681
216	672.06	10215	10.5	4501	0.0658
217	677.17	9502	11.2	4552	0.0713
218	678.17	9340	11.7	4684	0.0726
219	685.09	9740	13.5	4966	0.0703
220	689.28	9580	114.6	36175	0.0719
221	690.28	9878	53.9	17140	0.0699
222	691.28	9768	27.5	8938	0.0708
223	699.04	9963	120.7	34227	0.0702
224	700.04	9847	45.8	13166	0.0711
225	701.03	9881	51.9	14670	0.0709
226	702.04	9924	17.2	5166	0.0707
227	703.03	9814	10.2	3230	0.0716
228	719.24	10023	78.5	22479	0.0718
229	720.24	9627	65.6	18954	0.0748
230	720.75	7258	27.1	8165	0.0993
231	721.25	9562	279.4	79272	0.0754
232	721.75	7455	14.7	4672	0.0968
233	722.25	9586	116.8	33572	0.0753
234	723.25	9501	66.2	19331	0.0761
235	724.25	10147	21.8	6761	0.0714
236	731.01	9561	211.4	62432	0.0765
237	732.01	9902	81.4	24474	0.0739
238	733	9961	100.3	30135	0.0736
239	734.01	10152	33.8	10570	0.0723
240	735	9974	22.2	7163	0.0737
241	735.23	9002	10.9	3815	0.0817
242	736.23	9464	23.3	7513	0.0778
243	736.73	9386	19	6252	0.0785

244	737.23	9545	17.1	5697	0.0772
245	743.01	10370	11	3933	0.0717
246	745.34	10355	17	5823	0.072
247	751.21	9732	142.8	45633	0.0772
248	752.21	9797	86	27804	0.0768
249	752.72	4878	14.6	5213	0.1543
250	753.22	9388	231.4	74084	0.0802
251	754.22	9779	102.3	33208	0.0771
252	755.22	9931	64.7	21290	0.076
253	756.22	10377	22.1	7687	0.0729
254	762.98	10181	59.4	19696	0.0749
255	763.98	10355	23.3	7993	0.0738
256	764.98	10351	31.9	10642	0.0739
257	765.98	10872	10.8	3943	0.0705
258	777.31	10466	32.8	9529	0.0743
259	778.31	10744	15.9	4820	0.0724
260	783.18	9840	139.7	36013	0.0796
261	784.18	10069	71	18312	0.0779
262	785.19	9663	130.6	32812	0.0813
263	786.19	9789	55	13907	0.0803
264	787.19	9982	38.2	9668	0.0789
265	788.19	11056	13.8	3751	0.0713
266	797.19	10618	10.9	2687	0.0751
267	805.16	10554	12.8	2676	0.0763
268	809.28	10153	55.1	9533	0.0797
269	810.28	9986	44.8	7661	0.0811
270	810.78	9677	17.1	3112	0.0838
271	811.28	9918	34.9	5926	0.0818
272	812.28	10199	13.4	2430	0.0796
273	815.15	10249	97.7	14696	0.0795
274	816.15	10421	50.6	7592	0.0783
275	817.16	9617	77.5	11191	0.085
276	818.16	9648	35.2	5131	0.0848
277	819.16	9890	23.9	3520	0.0828
278	826.26	9746	19.6	2813	0.0848

279	826.76	9683	19.4	2790	0.0854
280	827.26	9284	15.8	2306	0.0891
281	833.17	10548	12.1	1769	0.079
282	841.25	9680	24.7	3200	0.0869
283	842.25	9729	21.4	2784	0.0866
284	842.75	9409	10.4	1468	0.0896
285	843.25	9586	17.8	2342	0.088
286	847.12	10325	209.7	24516	0.082
287	848.12	10312	104.1	12218	0.0822
288	849.12	10155	113.6	13228	0.0836
289	850.12	9929	46	5464	0.0856
290	851.12	9826	25.7	3131	0.0866
291	869.11	5975	20	2245	0.1455
292	869.33	10536	85.4	8825	0.0825
293	870.34	10127	47.1	4935	0.0859
294	871.33	10278	28.9	3099	0.0848
295	872.33	10766	10.3	1241	0.081
296	879.09	9948	107.9	10597	0.0884
297	880.1	10331	53.9	5406	0.0852
298	881.09	10614	61.5	6135	0.083
299	882.1	10813	25.7	2694	0.0816
300	883.09	10658	14.5	1622	0.0829
301	900.3	9820	11.6	1346	0.0917
302	900.82	5548	11.4	1322	0.1624
303	901.31	10238	198.8	19329	0.088
304	901.8	4143	10	1194	0.2177
305	902.31	10440	113.8	11166	0.0864
306	903.31	10298	76.5	7579	0.0877
307	904.31	10606	28.8	3001	0.0853

Mass-spectrometric study of reaction mass from Method 3 by direct input

The sample of solid sediment from Method 3 was dissolved in 100 µL of DMSO and then it was diluted by 1 mL of acetonitrile. This solution was injected into mass-spectrometer by means of direct input. The results are presented on Fig. S17 and Table S10 below.

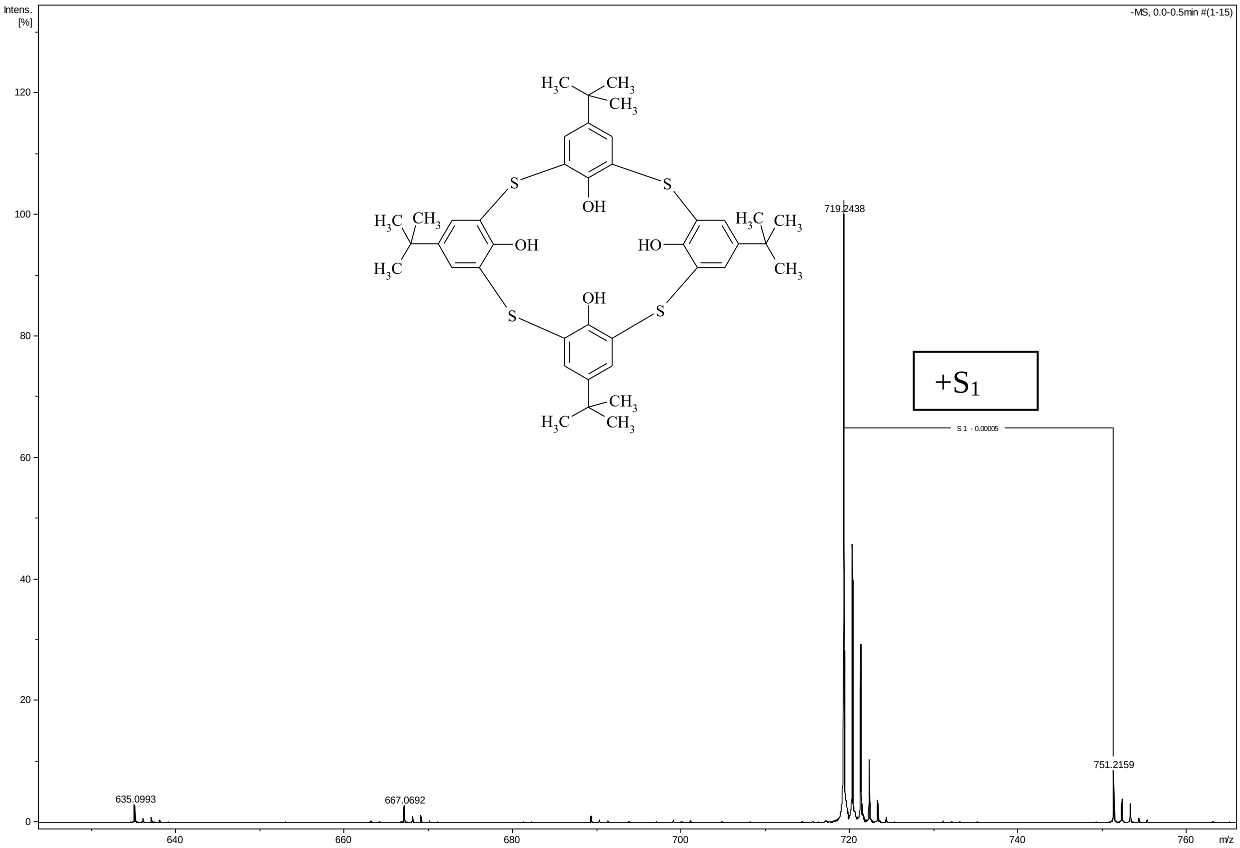


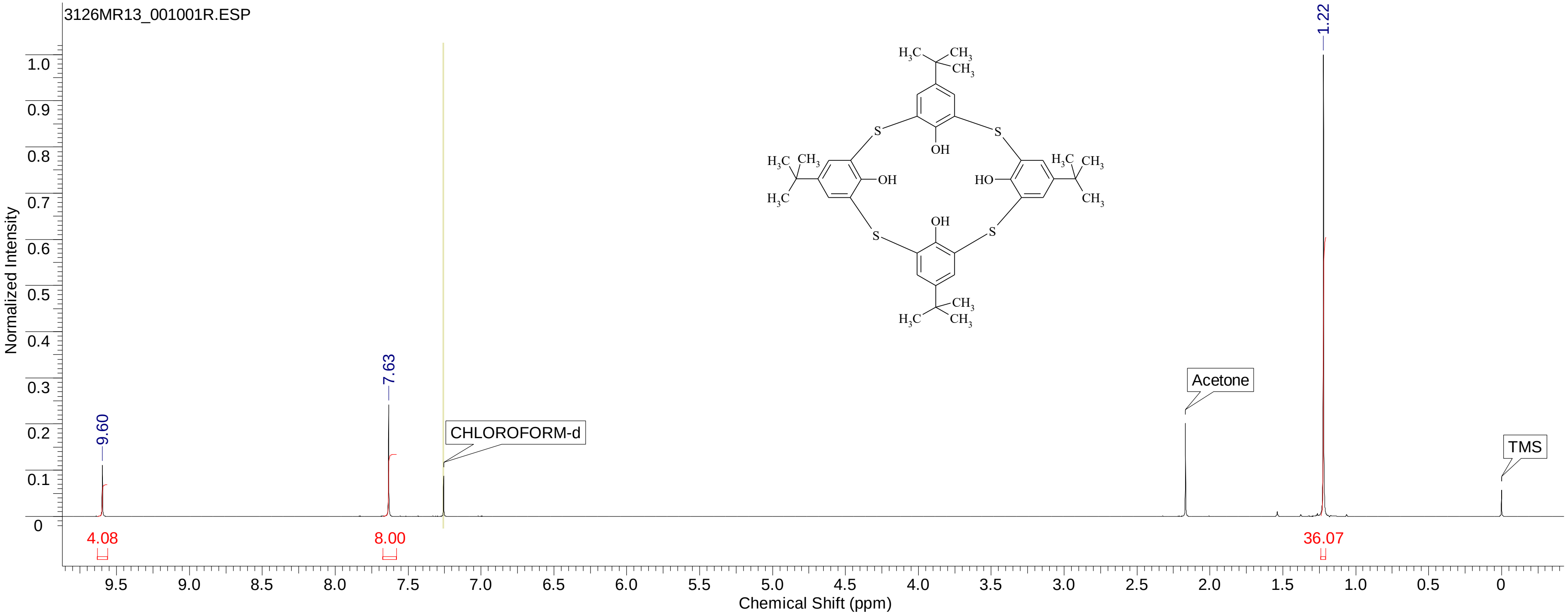
Figure S17

Table S10 List of observed peaks in mass-spectra of sample from **Method 3**

#	*m/z*	Res.	S/N	I	FWHM
1	99.9243	4394	201.9	284	0.0227
2	115.9221	4811	131.6	201	0.0241
3	116.9281	4830	88.4	136	0.0242
4	134.8942	5381	667.3	1101	0.0251
5	136.8915	5037	191.2	316	0.0272
6	146.3091	5659	73.5	123	0.0259
7	162.9966	4841	85.7	144	0.0337
8	171.0117	6164	299.2	506	0.0277
9	194.9773	5785	75.4	131	0.0337
10	255.2326	6597	72.0	140	0.0387
11	265.1490	7215	186.5	374	0.0367
12	281.0302	7141	293.3	617	0.0394
13	282.0355	6396	49.3	105	0.0441
14	293.1800	7871	74.9	164	0.0372
15	309.1754	7021	54.7	119	0.0440
16	311.1715	7400	142.9	305	0.0420
17	325.1845	7579	251.9	492	0.0429
18	326.1916	7442	54.1	106	0.0438

19	339.2009	8074	300.3	533	0.0420
20	487.0070	9578	130.8	172	0.0508
21	635.0993	9583	167.2	293	0.0663
22	667.0692	10106	107.8	284	0.0660
23	668.0762	10101	40.6	109	0.0661
24	669.0698	11030	45.9	125	0.0607
25	689.2809	9507	28.8	101	0.0725
26	719.2438	9646	2841.1	9905	0.0746
27	720.2468	9727	1316.2	4538	0.0740
28	720.5361	4048	55.0	190	0.1780
29	721.2431	9795	853.2	2909	0.0736
30	722.2431	9612	306.7	1034	0.0751
31	723.2448	10196	110.9	370	0.0709
32	751.2159	10264	382.0	859	0.0732
33	752.2208	9531	174.9	387	0.0789
34	753.2137	10603	142.2	309	0.0710

^{1}H NMR spectra of thiacalix[4]arene (5):



^{13}C NMR spectra of thiacalix[4]arene (5):