SUPPORTING INFORMATION

"CLICKABLE" THIACALIX[4]ARENE DERIVATIVES BEARING POLYMERIZABLE 1,3-BUTADIYNE FRAGMENTS: SYNTHESIS AND INCORPORATION INTO PDA VESICLES.

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Materials and methods

All reagents were purchased from either Acros or Sigma-Aldrich and used without further purification. Solvents were purified by standard methods [1]. Parent p-tert-butylthiacalix[4]arene[2], 5-phenylpenta-2,4-diyn-1-ol[3] and 3-azido-1-propanol[4] were synthesized according to literature methods.

TLC was done using "Silufol UV 254" with UV lamp VL-6.LC (6W –254 nm tube). Column chromatography was performed on silica gel (70–230 mesh) from Merck. Elemental analysis was performed with automated CHNS/O analyzer «Perkin Elmer PE 2400 series 2». NMR experiments were recorded at Bruker Avance 400 Nanobay with $CDCl_3$ (δ:H 7.26 ppm) as internal standard. MALDI mass-spectra were recorded at UltraFlex III TOF/TOF with PNA matrix, laser Nd:YAG, λ=355 nm.

UV–VIS absorption spectra were recorded using a spectrophotometer LAMBDA 35 (Perkin Elmer production, USA) using 10 mm quarts cuvettes.

Colorimetric response was calculated using equation (**1**)

$$\mathbf{CR} = [(PB_0 - PB_1)/PB_0] \times 100 \quad (1)$$

Where $PB = A_{blue}/(A_{blue} + A_{red})$; A_{blue} = absorbance at 670 nm, A_{red} = absorbance at 550 nm.

Dynamic light scattering measurements were performed by Malvern Zetasizer equipment at 25 °C using 1 cm disposable polystyrene fluorescence cuvettes (VWR). 4 MW He–Ne laser with 633 nm wavelength acted as radiation source. The analysis of the obtained signal was performed on the basis of frequency and phase analysis of scattered light using software supplied with the device.

TEM was performed on Hitachi HT7700 (Japan). The images were acquired at an accelerating voltage of 80 kV. Samples were ultrasonicated in vater for 10 min, dispersed on 200 mesh copper grids with continuous formvar support films and then dried at 65 oC during 3 hours.

Vesicle preparation and polymerization procedure

Concentrated dichloromethane solutions of 10,12 pentacosadiynoic acid (PCDA) and calixarene amounts were mixed together and the organic solvent was removed by purging with N_2 at room temperature to give a thin lipid film on the glass surface, which was dried under reduced pressure for a minimum of 2 h to remove all traces of organic solvent. Then a buffer solution (TRIS, 10 mM, pH

7.4) was added to yield a total PCDA -calixarene lipid concentration of 0.22 mM. The samples were then sonicated for 15 min at room temperature. The resulting solution was filtered through a 0.8 μm filter and kept at 4 °C for 12 h. Polymerization was carried out at room temperature by irradiating the solutions with 254 nm UV light (1 mW/cm^2) for 15 minutes under vigorous stirring in 10 mm quarts cuvettes.

X-ray Structure Determination (XRD)

Data set for single crystal of **1** was collected on a Bruker AXS Kappa APEX Duo diffractometer with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). Programs used: data collection APEX2[5], data reduction SAINT[6], structure solution SHELXS[7], structure refinement by full-matrix least-squares against F^2 using SHELXL[7]. Hydrogen atoms were placed into calculated positions and refined as riding atoms, except the atoms in the hydroxyl groups, which were revealed from a difference Fourier map and refined with constraints. The figures were generated using Mercury program[8].

The crystal exhibits solvent disorder: the chloroform molecule is disordered over two positions, the refinement with constraints gave the population ratio 85:15. In the vicinity of the solvent molecule there is a peak of the rest electron density, which cannot be reliably modelled with any solvent. The disorder results in the decrease of the reflections intensity, thus the weighted R-factor is relatively high. However the structure of the calixarene molecule is determined reliably.

Crystal data for 1: formula $C_{62}H_{60}O_4S_4 \cdot CHCl_3$, M = 1116.70, a = 12.3272(11), b = 12.9232(11), c = 19.3080(16) Å, α== 86.148(3)^0, β = 81.088(3)^0, γ=80.140(3)^0, V = 2991.3(4)Å^3, ρ_{calc} = 1.240 g cm^{-3}, μ= 0.338 mm^{-1}, empirical absorption correction, Z = 2, triclinic, space group *P-1* (No. 2), T = 198(2) K, 74874 reflections collected (±h, ±k, ±l), θ range = 1.60 to 29.23^0, 16172 independent (R_{int} = 0.0289) and 11598 observed reflections [$I \geq 2\ \sigma(I)$], 690 refined parameters, R = 0.0779, wR^2 = 0.2278, max. residual electron density near the solvent 1.790 (-1.381) e Å^{-3}.

CCDC 1463902 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Synthesis.

5,11,17,23-tetra-tert-butyl-25,27-bis((5-phenylpenta-2,4-dyin-1-yl)oxy)-26,28-dihydroxythiacalix[4]arene **1**: *p-tert*-butylthiacalix[4]arene (1 g, 1.38 mmol), diethyl azodicarboxylate (0.52 ml, 3.18 mmol), triphenylphosphine (0.92 g, 3.46 mmol), and 5-phenylpenta-2,4-diyn-1-ol (0.47 g, 3.05 mmol) were dissolved in 40 ml of dry toluene under inert atmosphere. The reaction mixture was stirred at room temperature for 3 h, and then solvent was evaporated in *vacuo*. The crude product was washed twice with methanol to give **1** as light yellow powder. m= 0.94 g (68 %).

R_f= 0.67 (eluent: hexane–EtOAc=4:1). Mp: 125°C.

MALDI TOF(*m/z*): 997 $[M]^+$, 1036 $[M+K]^+$, 1020 $[M+Na]^+$, 1130 $[M+Cs]^+$.

IR (KBr) ν_{max} cm^{-1}: 3387 (OH), 2246 (C≡C).

^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 0.82 (s, 18H, CMe_3), 1.34 (s, 18H, CMe_3), 5.42 (s, 4H, -OCH_2-), 7.00 (s, 4H, H_{Ar}), 7.29-7.34 (m, 6H, H_{Ar}), 7.49-7.52 (m, 4H, H_{Ar}), 7.56 (s, 2H, OH), 7.68 (s, 4H, H_{Ar}); ^{13}C NMR: δ 155.57, 154.7, 148.65, 142.84, 134.46, 132.8, 129.43, 129.26, 128.34, 121.91, 73.03, 63.08, 50.89, 34.21, 34.1, 31.47, 30.75.

Found (%): C, 75.8; H, 6.4; S, 12.74. $C_{62}H_{60}O_4S_4$.

Calculated (%): C, 74.66; H, 6.06; S, 12.86.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(3-azidopropoxy)-26,28-dihydroxythiacalix[4]arene **2**: p-tert-butylthiacalix[4]arene (0.2 g, 0.277 mmol), diethyl azodicarboxylate (0.104 ml, 0.638 mmol), triphenylphosphine (0.184 g, 0.694 mmol), and 3-azidopropan-1-ol (0.056 ml, 0.61 mmol) were dissolved in 10 ml of dry toluene under inert atmosphere. The reaction mixture was stirred at room temperature for 14 h, and then solvent was evaporated in vacuo. The crude product was washed twice with methanol to give **2** as white powder. m= 0.38 g (60 %).

R_f= 0.61 (eluent: hexane–EtOAc=6:1). Mp: 212°C.

MALDI TOF(*m/z*): 858 $[M - N_2]^+$.

IR (KBr) ν_{max} cm^{-1}: 2096 (N_3), 3382 (OH).

^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 0.82 (s, 18H, CMe_3), 1.33 (s, 18H, CMe_3), 2.24-2.32 (m, 4H, CH_2), 3.73-3.78 (t, 4H, OCH_2), 4.52-4.58 (t, 4H, CH_2N_3), 6.99 (s, 4H, H_{Ar}), 7.66 (s, 4H, H_{Ar}), 7.80 (s, 2H, OH); ^{13}C NMR: δ 156.12, 155.90,

148.33, 142.96, 134.61, 133.21, 128.91, 122.03, 72.75, 48.54, 34.32, 31.61, 30.89, 29.75.

Found (%):C, 62.33; H, 6.7; N, 9.42; S, 14.3.$C_{46}H_{58}N_6O_4S_4$.

Calculated (%): C, 62.27; H, 6.59; N, 9.47; S, 14.45.

5,11,17,23-tetra-tert-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis(3-azidopropoxy)thiacalix[4]arene **3**: Compound **1** (0.48 g, 0.48 mmol), diethyl azodicarboxylate (0.63 ml, 1.35 mmol), triphenylphosphine (1.02 g, 3.85 mmol), and 3-azido-1-propanol (0.355 ml, 3.85 mmol) were dissolved in 20 ml of dry toluene under inert atmosphere. The reaction mixture was stirred at 70 Cº for 20 h, and then solvent was evaporated in *vacuo*. The crude product was washed twice with methanol to give **3** as light yellow powder. m= 0.29 g (52 %)

R_f= 0.63, (eluent: hexane–EtOAc=5:1). Mp: 140° C.

MALDI TOF(*m/z*): 1162 $[M]^+$.

IR (KBr) ν_{max} cm^{-1}: 2096 (N_3).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 1.29 (s, 18H, CMe_3), 1.37 (s, 18H, CMe_3), 1.61-1.66 (m, 4H, CH_2), 3.08 (t, 4H, OCH_2, *J*=7.09), 4.04 (t, 4H, CH_2N_3, *J*=6.68), 4.64 (s, 4H, OCH_2), 7.29 (d, 6H, H_{Ar}, *J*=7.62), 7.35 (s, 4H, H_{Ar}), 7.44 (d, 4H, H_{Ar}, *J*=7.04), 7.56 (s, 4H, H_{Ar}). ^{13}C NMR: δ 157.21, 155.38, 146.67, 132.52, 131.0, 129.46, 129.13, 128.39, 128.26, 127.29, 79.03, 78.24, 70.72, 67.10, 57.36, 48.39, 34.39, 31.26, 29.18.

Found (%):C, 70.4 ; H, 6.31; N, 7.17; S, 10.95.$C_{68}H_{70}N_6O_4S_4$.

Calculated (%): C, 70.19; H, 6.06; N, 7.22; S, 11.02.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis[3-(4-phenyl-1,2,3-triazol-1-yl)propoxy]thiacalix[4]arene **4**: Compound **3** (0.1 g, 0.086 mmol), phenylacetylene (0.024 ml, 0.214 mmol, 0.93 g/ml), triethylamine (2 ml, 14 mmol), and CuI (0.0016 g, 8,38*10^{-3} mmol) were dissolved in 5 ml of dry toluene. The reaction mixture was stirred at 55 Cº for 6 h. Product was extracted with chloroform, the organic phase washed with ammonia and dried over $MgSO_4$ and then solvent was evaporated in *vacuo*. The crude product was washed

twice with ethanol to give **4** as white powder, which was purified using column chromatography on silica gel (hexane:ethylacetate 2:1). m= 0.11 g (85 %).

R_f= 0.53 (eluent: hexane–EtOAc=2:1). Mp: 125°C.

MALDI TOF(*m/z*): 1366 $[M]^+$.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 1.07 (s, 18H, CMe_3), 1.38 (s, 18H, CMe_3), 1.97-2.01 (m, 4H, CH_2), 4.12 (t, 4H, OCH_2, *J*=6.44), 4.26 (t, 4H, CH_2Trz, *J*=7.36), 4.64 (s, 4H, OCH_2), 7.30 (s, 4H, H_{Ar}), 7.33-7.42 (m, 10H, H_{Ar}), 7.44-7.47 (m, 5H, H_{Ar}), 7.59 (s, 4H, H_{Ar}), 7.83 (m, 5H, H_{Ar}, *J*=7.23), 7.92 (s, 2H, TrzH). ^{13}C NMR: δ 157.23, 155.13, 147.77, 147.04, 132.68, 131.29, 131.05, 130.87, 129.77, 129.34, 128.98, 128.94, 128.55, 128.17, 127.68, 127.18, 125.81, 121.73, 120.01, 79.06, 78.45, 74.23, 70.9, 68.28, 67.42, 57.34, 47.92, 38.82, 34.53, 34.38, 31.15, 30.47, 29.85, 29.05, 23.85, 23.13, 14.22, 11.1.

Found (%):C, 73.80; H, 6.14; N, 6.10; S, 9.34. $C_{84}H_{82}N_6O_4S_4$.

Calculated (%): C, 73.76; H, 6.04; N, 6.14; S, 9.38.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis [3-(4-(1,3-dioxoisoindolin-2-yl)methyl)-1,2,3-triazol-1-yl)propoxy] thiacalix[4]arene **5**: Compound **3** (0.1 g, 0.086 mmol), N-propargylphthalimide (0.041 g, 0.214 mmol), triethylamine (0.62 ml, 4.4 mmol), and CuI (0.0008 g, $4.3*10^{-6}$ mmol) were dissolved in 20 ml of dry toluene under inert atmosphere. The reaction mixture was stirred at room temperature for 18 h. Product was extracted with chloroform, the organic phase washed with ammonia and dried over $MgSO_4$, filtered and then solvent was evaporated in *vacuo*. The crude product was washed twice with hexane to give **5** as white powder. m= 0.091 g (70 %).

R_f= 0.88 (eluent: EtOAc). Mp: 120°C.

MALDI TOF(*m/z*): 1532 $[M]^+$.

IR (KBr) ν_{max} cm^{-1}: 1718 (CO).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 1.02 (s, 18H, CMe_3), 1.36 (s, 18H, CMe_3), 1.88-1.96 (m, 4H, CH_2), 4.04 (t, 4H, OCH_2), 4.20 (t, 4H, CH_2Trz), 4.62 (s, 4H, OCH_2), 3.60 (s, 4H, NCH_2Trz), 7.265 (s, 4H, H_{Ar}), 7.28-7.31 (m, 5H, H_{Ar}), 7.43-7.465 (m, 5H, H_{Ar}), 7.54 (s, 4H, H_{Ar}), 7.67 (s, 2H, TrzH), 7.69-7.718 (m, 4H, H_{Ar}), 7.83-7.856 (m, 4H, H_{Ar}). ^{13}C NMR: δ 167.61, 157.01, 155.24, 146.81, 142.71, 134.05, 132.53, 132.12, 131.24, 129.55, 129.18, 128.41, 127.99, 127.14, 123.60,

123.44, 122.90, 121.64, 78.96, 78.30, 74.13, 71.50, 70.77, 67.11, 57.35, 47.67, 34.35, 34.16, 33.08, 31.24, 30.99, 27.00.

Found (%): C, 70.55; H, 5.60; N, 7.28; S, 8.31.$C_{90}H_{84}N_8O_8S_4$.

Calculated (%): C, 70.47; H, 5.52; N, 7.31; S, 8.36.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis[3-(4-aminomethyl-1,2,3-triazol-1-yl)propoxy])thiacalix[4]arene **6**: Compound **4** (0.074 g, 0.048 mmol) and hydrazine monohydrate (0.697 ml, 14.3 mmol) were dissolved in 20 ml of dry ethanol. The reaction mixture was stirred at room temperature for 4 h. Product was extracted with dichloromethane, the organic phase dried over $MgSO_4$, filtered and solvent was evaporated in vacuo. The crude product was washed twice with hexane to give **6** as white powder. m= 0.04 g (75 %).

Mp: 115°C.

MALDI TOF(*m/z*): 1272 $[M]^+$, 1410 $[M+PNA]^+$

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 1.10 (s, 18H, CMe_3), 1.37 (s, 18H, CMe_3), 1.94-2.00 (m, 4H, CH_2-CH_2N), 2.025-2.15 (broad s., 4H, NH_2), 3.99 (s, 4H, CH_2NH_2), 4.05-4.09 (t, 4H, OCH_2), 4.19-4.25 (t, 4H, CH_2Trz), 4.66 (s, 4H, OCH_2), 7.28-7.31 (m, 5H, H_{Ar}), 7.30 (s, 4H, H_{Ar}), 7.44-7.47 (m, 5H, H_{Ar}), 7.55 (s, 2H, TrzH), 7.60 (s, 4H, H_{Ar}). ^{13}C NMR: δ 157.15, 155.25, 146.91, 132.54, 131.50, 129.76, 129.21, 128.42, 127.91, 127.37, 121.61, 120.88, 78.91, 78.38, 74.08, 70.91, 67.37, 57.38, 47.81, 37.56, 34.38, 34.26, 31.24, 31.09.

Found (%): C, C, 69.85; H, 6.39; N, 8.76; S, 10.01. $C_{74}H_{80}N_8O_4S_4$.

Calculated (%): C, 69.78; H, 6.33; N, 8.80; S, 10.07.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis[3-(4,5-dicarboxy-1,2,3-triazol-1-yl)propoxy]thiacalix[4]arene **7**: Compound **3** (0.1 g, 0.086 mmol) and acetylenedicarboxylic acid (0.196 g, 1.72 mmol) were dissolved in 20 ml of dry acetone under inert atmosphere. The reaction mixture was stirred at 65 Cº for 40 h. Solvent was evaporated in *vacuo*. The crude product was washed twice with diethyl ether to give **7** as white powder. m= 0.089 g (75 %).

Mp: 165°C.

MALDI TOF(*m/z*): 1372[M-H_2O]$^+$, 1346[M-CO_2]$^+$, 1302[M-2CO_2]$^+$

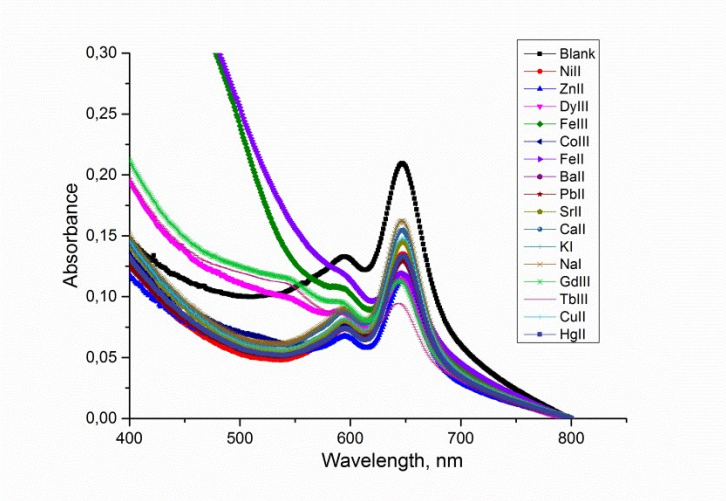
IR (KBr) ν_{max} cm^{-1}: 1726 (CO).

^{1}H NMR (400 MHz, DMSO-d6, 25 °C) δ: 1.14 (s, 18H, CMe_3), 1.30 (s, 18H, CMe_3), 2.05-2.10 (m, 4H, CH_2), 3.85-3.90 (t, 4H, OCH_2), 4.60 (s, 4H, OCH_2), 4.84-4.88 (t, 4H, CH_2Trz), 7.38 (s, 4H, H_{Ar}), 7.44-7.49 (m, 5H, H_{Ar}), 7.52 (s, 4H, H_{Ar}).

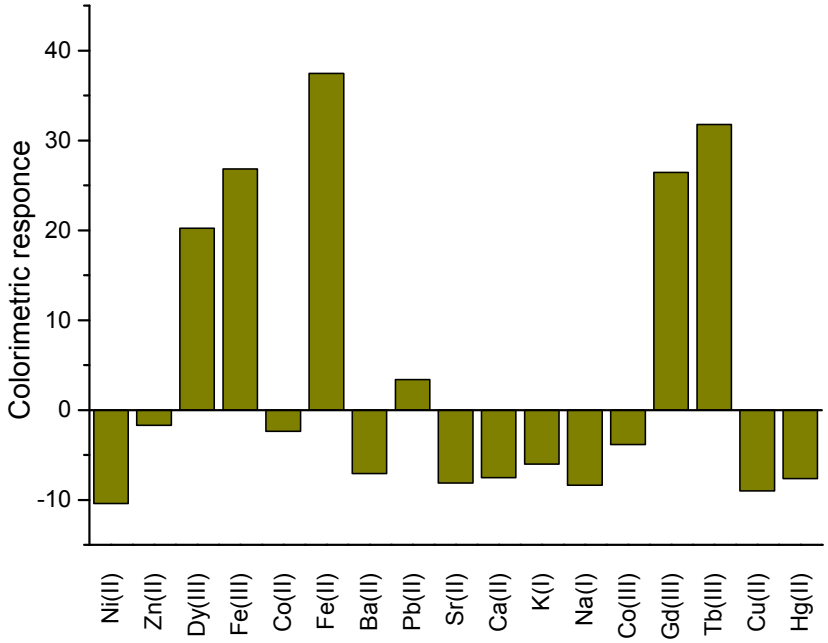
Found (%):C, 65.66; H, 5.42; N, 6.0 ; S, 9.17.$C_{76}H_{74}N_6O_{12}S_4$.

Calculated (%): C, 65.59; H, 5.36; N, 6.04; S, 9.21.

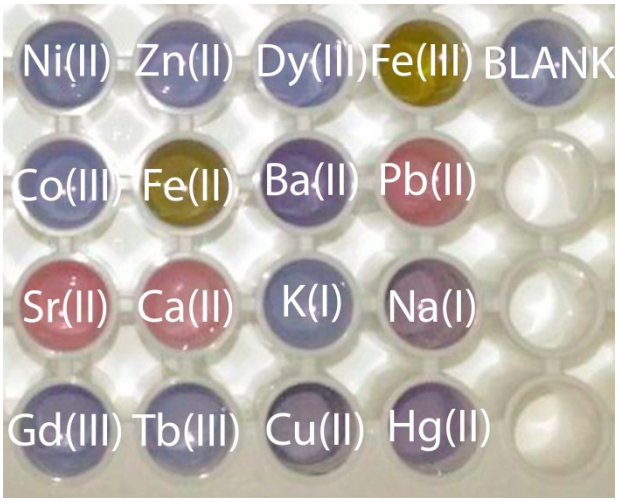
UV-VIS spectra



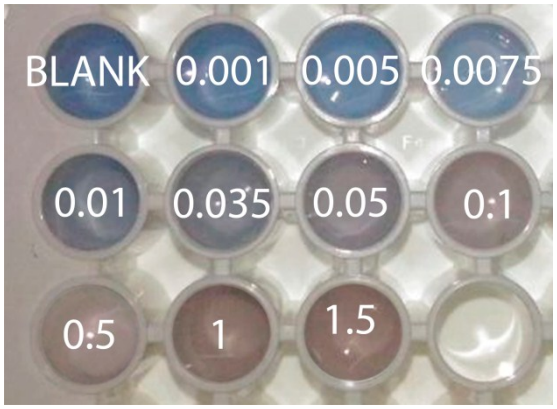
Graph 1. UV-vis spectra of PDA-calixarene 7 nanoparticles solution (C(PCDA) = 0.2 mM, C (Calix)= 0.02mM 0.04mM) in 10 mM Tris Buffer, pH = 7.4 in the presence of 1 mM of different metal ions chloride salts (except Dy^{3+}, Ba^{2+}, Pd^{2+}, Gd^{3+}, Tb^{3+} and Hg^{2+} were nitrates).



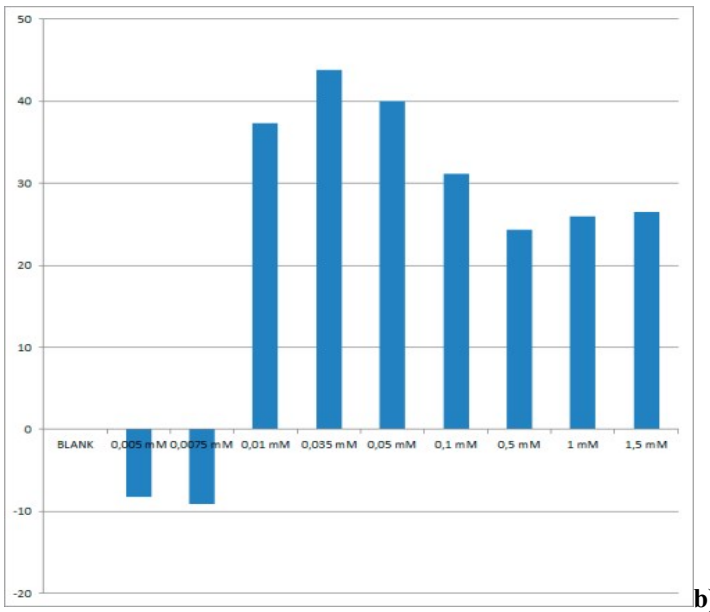
Graph 2. Colorimetric response of PDA-calixarene **7** nanoparticles solution (C(PCDA) = 0.2 mM, C (Calix)= 0.02mM) in 10 mM Tris Buffer, pH = 7.4 in the presence of 1 mM of different metal ions chloride salts (except Dy^{3+}, Ba^{2+}, Pd^{2+}, Gd^{3+}, Tb^{3+} and Hg^{2+} were nitrates).



Pic 1. Photograph of a portion of a 96-well plate containing 1 mM of different metal ions chloride salts (except Dy^{3+}, Ba^{2+}, Pd^{2+}, Gd^{3+}, Tb^{3+} and Hg^{2+} were nitrates) and PDA vesicles (C(PCDA) = 0.2 mM in 10 mM Tris Buffer, pH = 7.4)

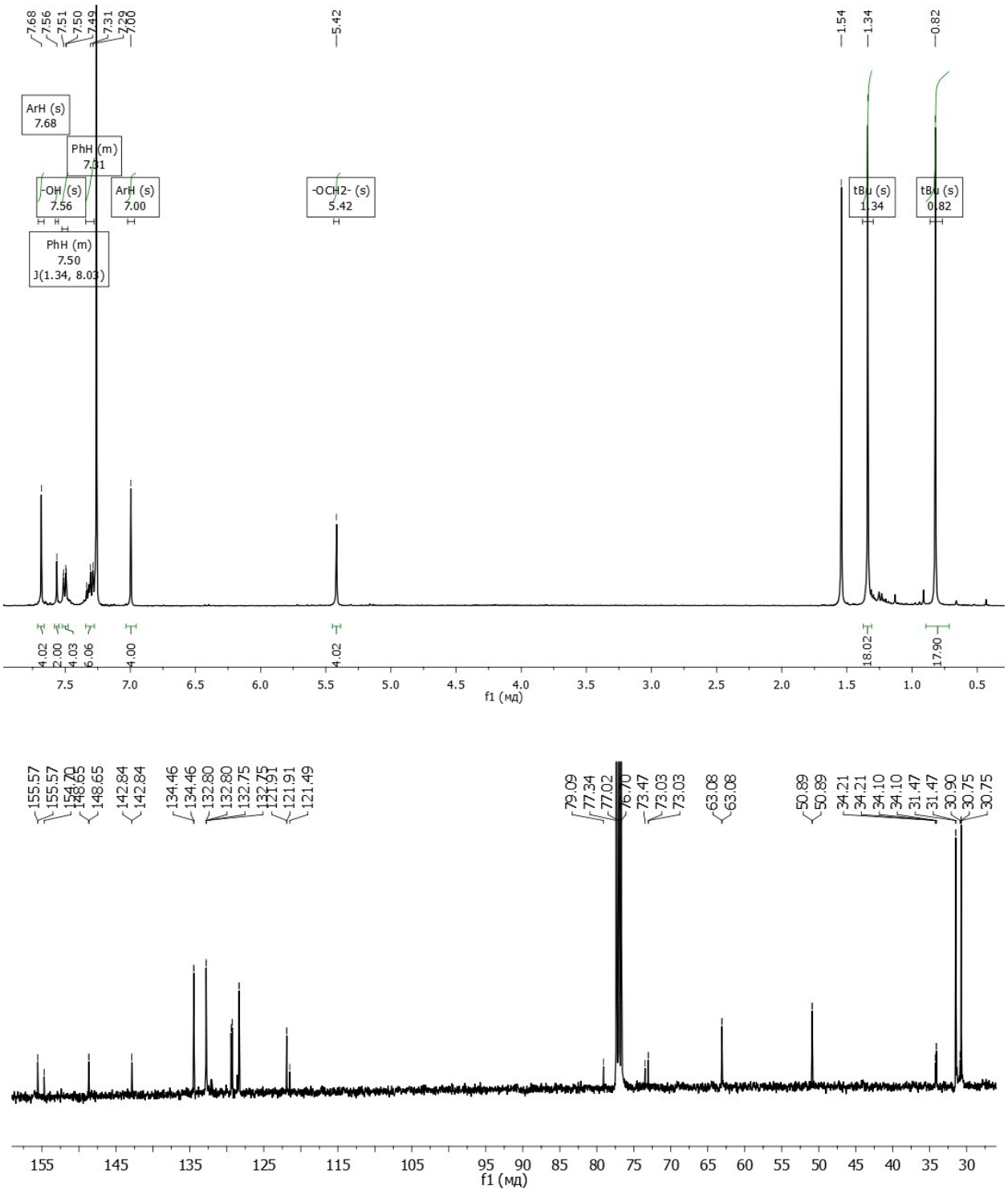


a)

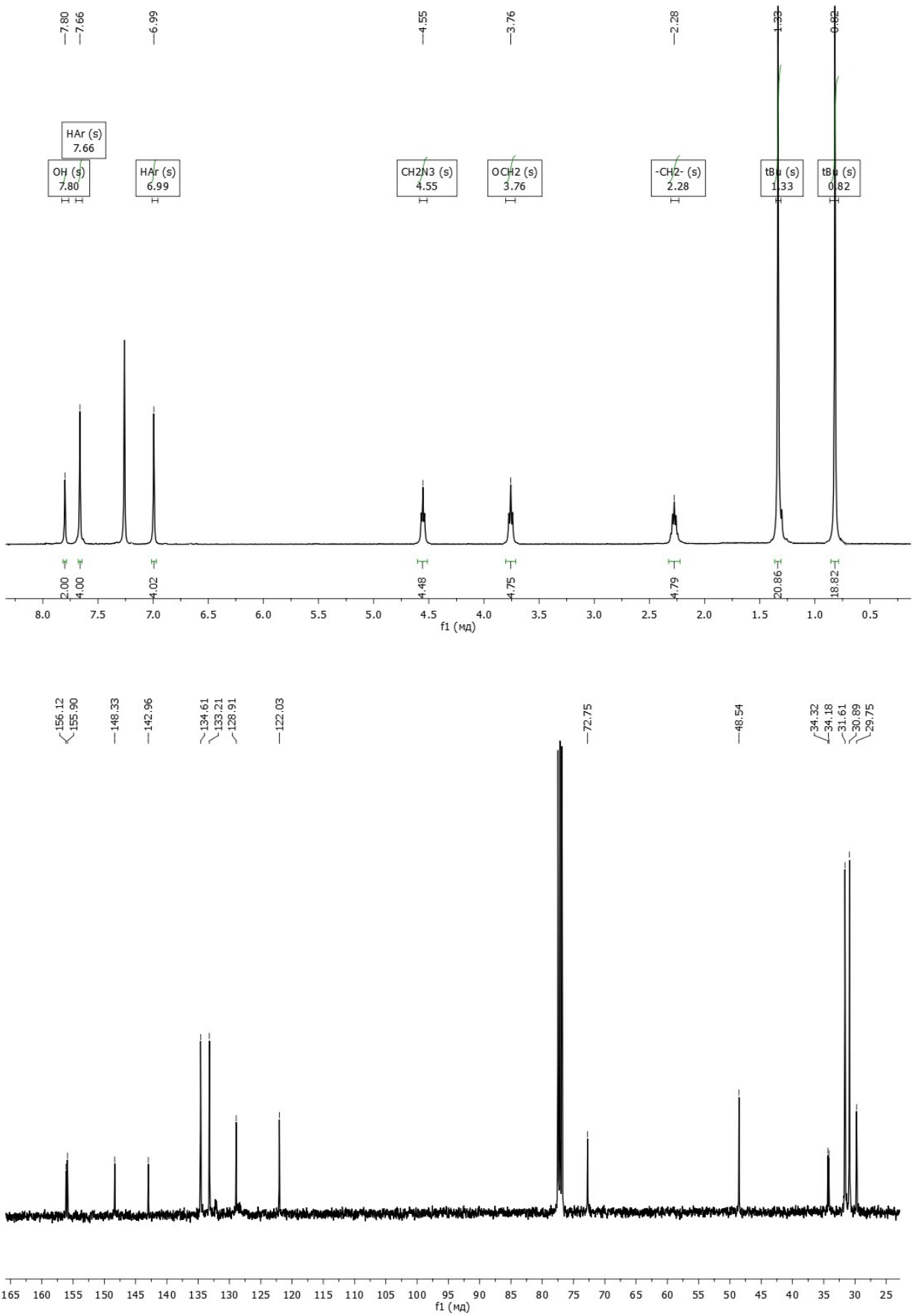


b)

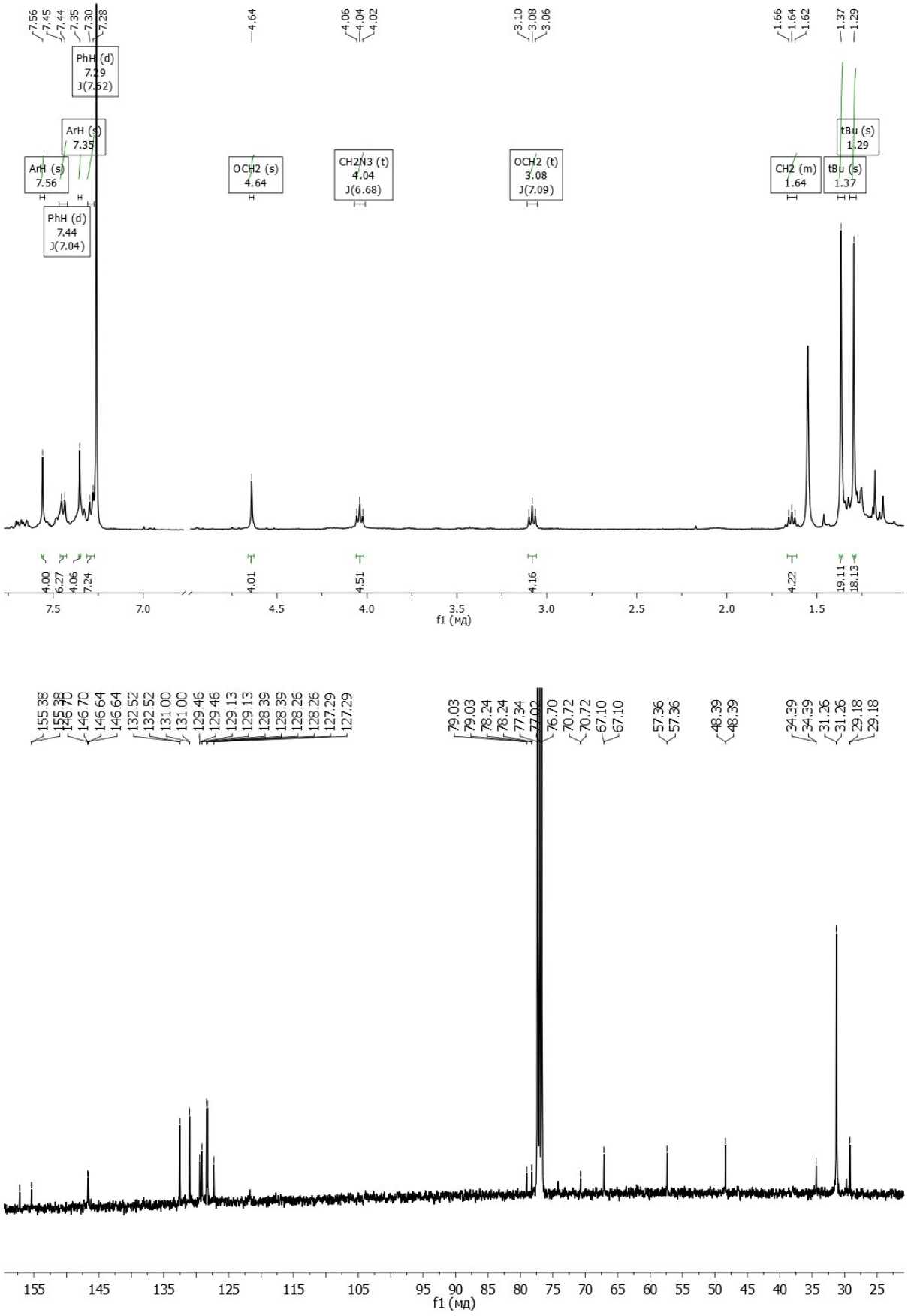
Pic 2. (a) Photograph of a portion of a 96-well plate containing different concentrations (mM) of $Tb(NO_3)_3$ and PDA - calixarene **7** vesicles (C(PCDA) = 0.2 mM, C (Calix)= 0.04 mM in 10 mM Tris Buffer, pH = 7.4); **(b)** Dependence of colorimetric response of PDA-calixarene 7 nanoparticles solution (C(PCDA) = 0.2 mM, C (Calix)= 0.04mM in 10 mM Tris Buffer, pH = 7.4) *vs* concentration of $Tb(NO_3)_3$ (from 0.001 то 1.5 mM).



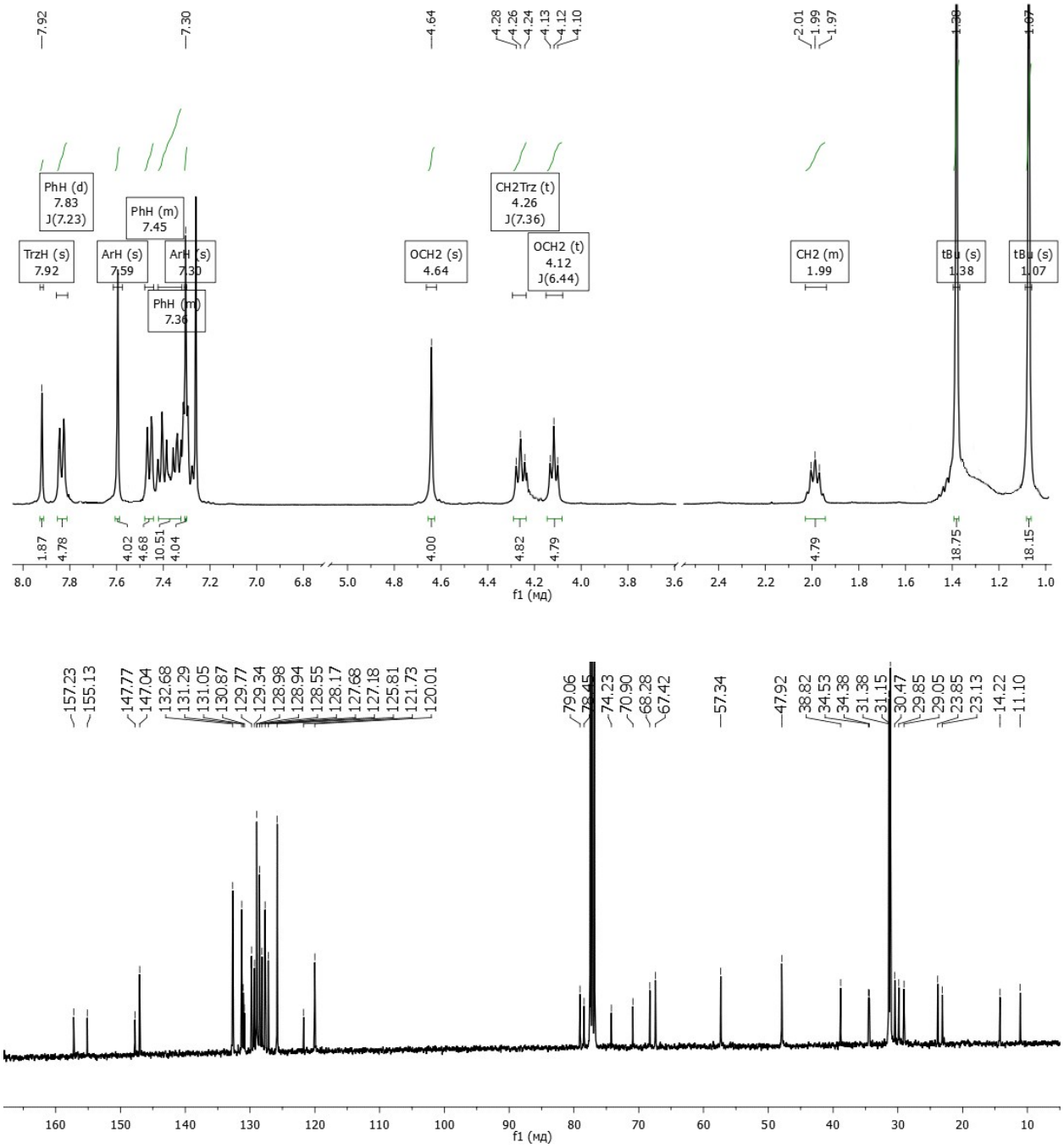
Pic. 2 NMR ^{1}H and ^{13}C (400 MHz, $CDCl_3$, 25 °C) spectra of 5,11,17,23-tetra-tert-butyl-25,27-bis((5-phenylpenta-2,4-dyin-1-yl)oxy)-26,28-dihydroxythiacalix[4]arene **1**



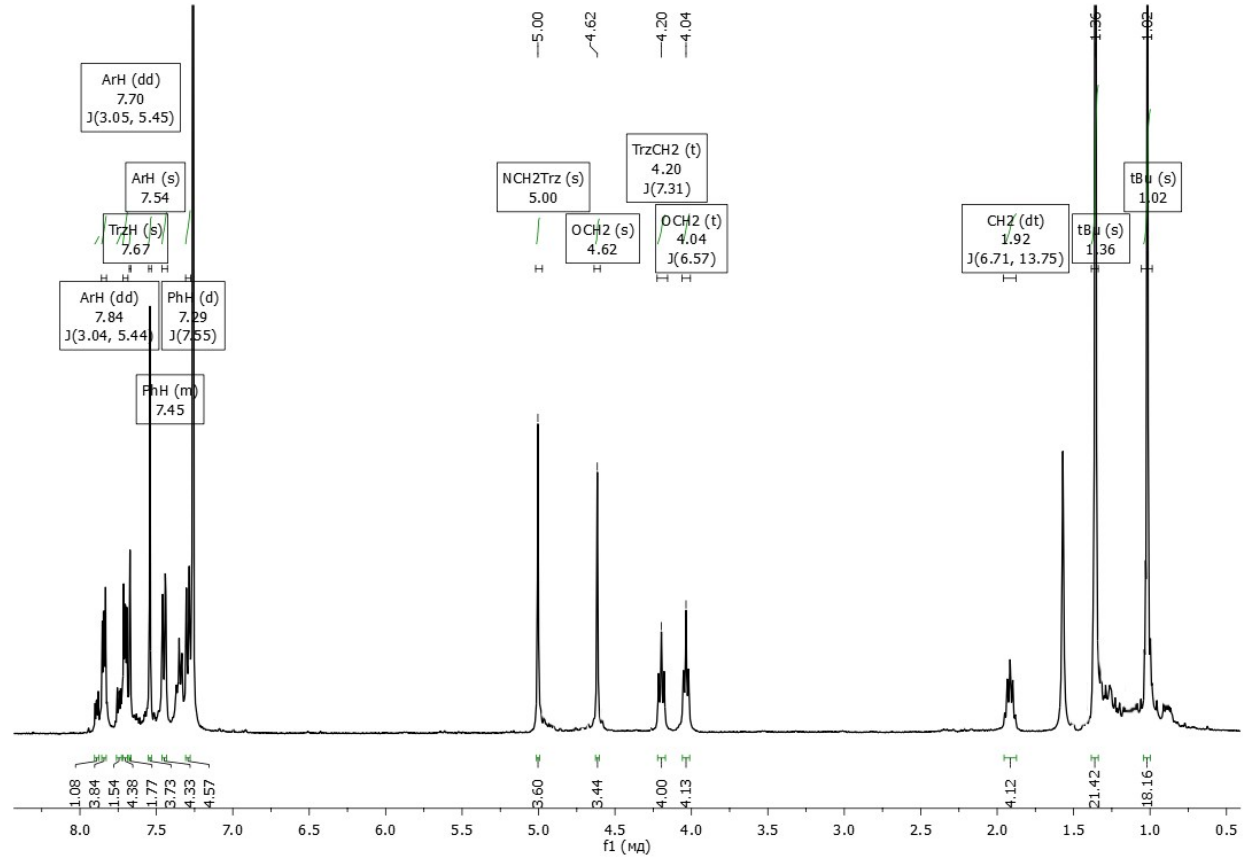
Pic. 3 NMR ^{1}H and ^{13}C (400 MHz, $CDCl_3$, 25 °C) spectra of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis(3-azidopropoxy)-26,28-dihydroxythiacalix[4]arene **2.**



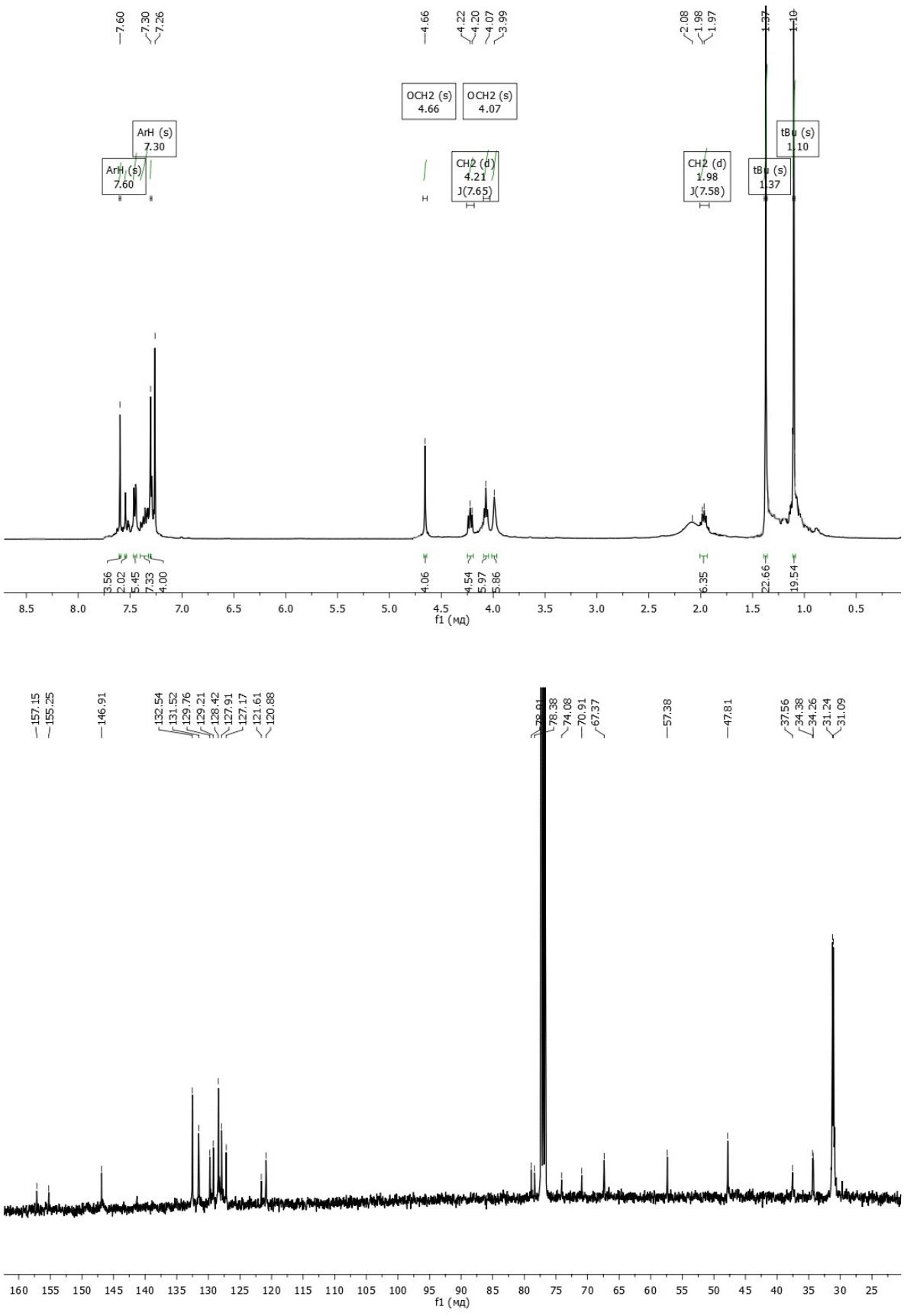
Pic. 4 NMR ^{1}H and ^{13}C (400 MHz, $CDCl_3$, 25 °C) spectra of 5,11,17,23-tetra-tert-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis(3-azidopropoxy)thiacalix[4]arene **3.**



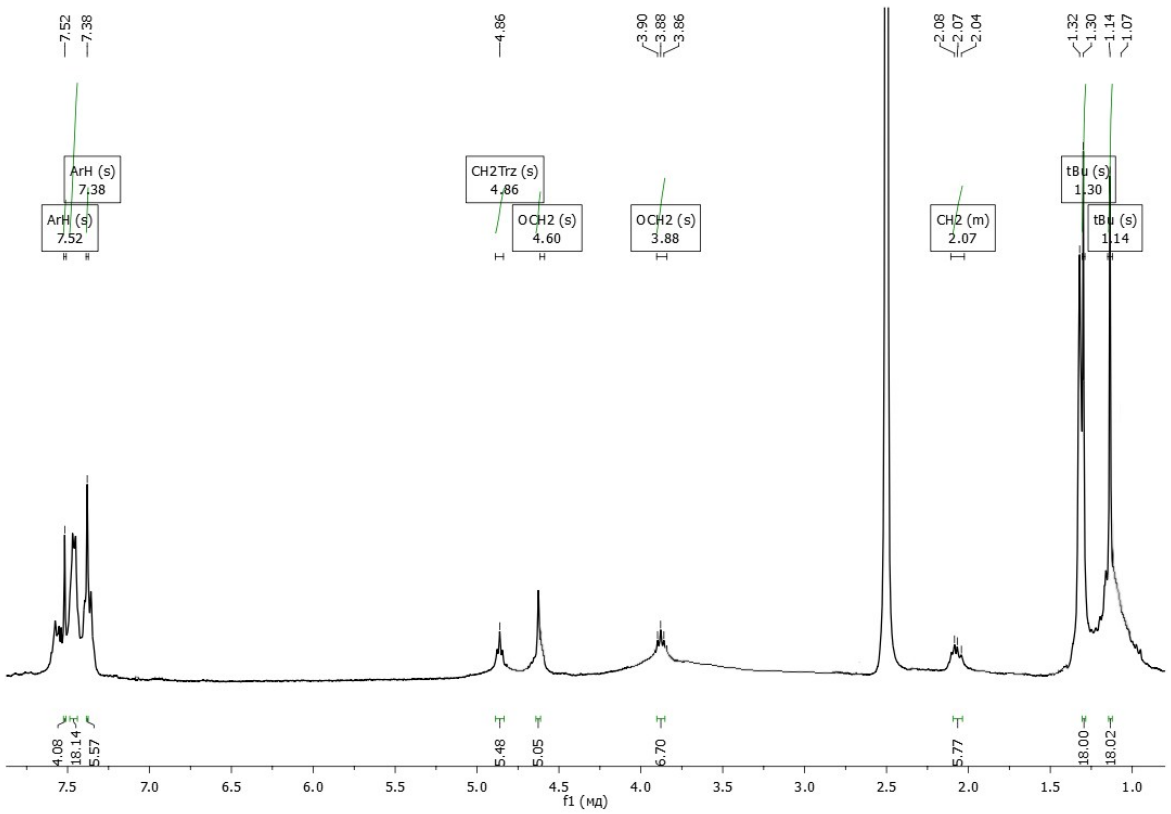
Pic. 5 NMR ^{1}H and ^{13}C (400 MHz, $CDCl_3$, 25 °C) spectra of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis[3-(4-phenyl-1,2,3-triazol-1-yl)propoxy]thiacalix[4]arene **4.**



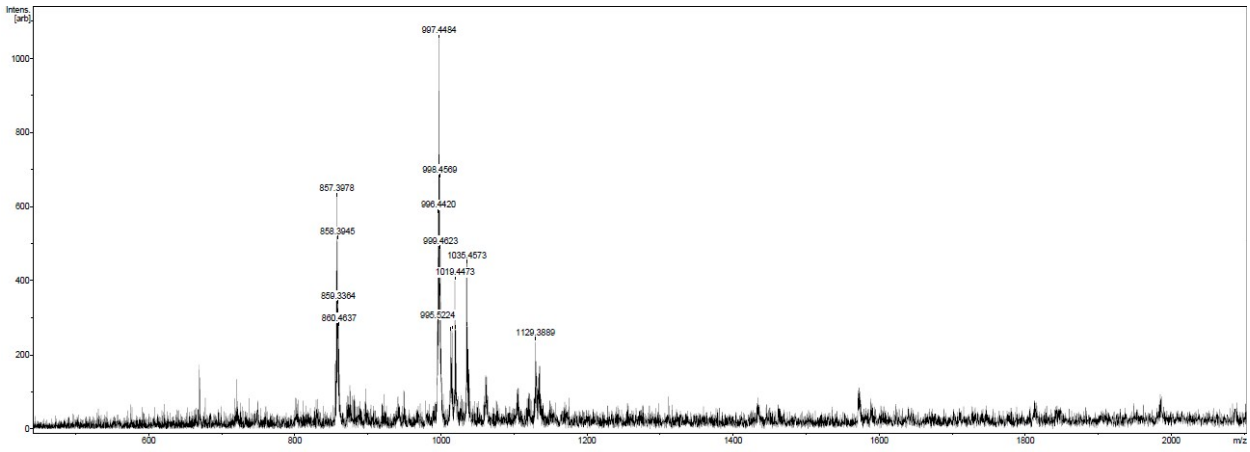
Pic. 6 NMR ^{1}H and ^{13}C (400 MHz, $CDCl_3$, 25 °C) spectra of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis [3-(4-(1,3-dioxoisoindolin-2-yl)methyl)-1,2,3-triazol-1-yl)propoxy] thiacalix[4]arene **5.**



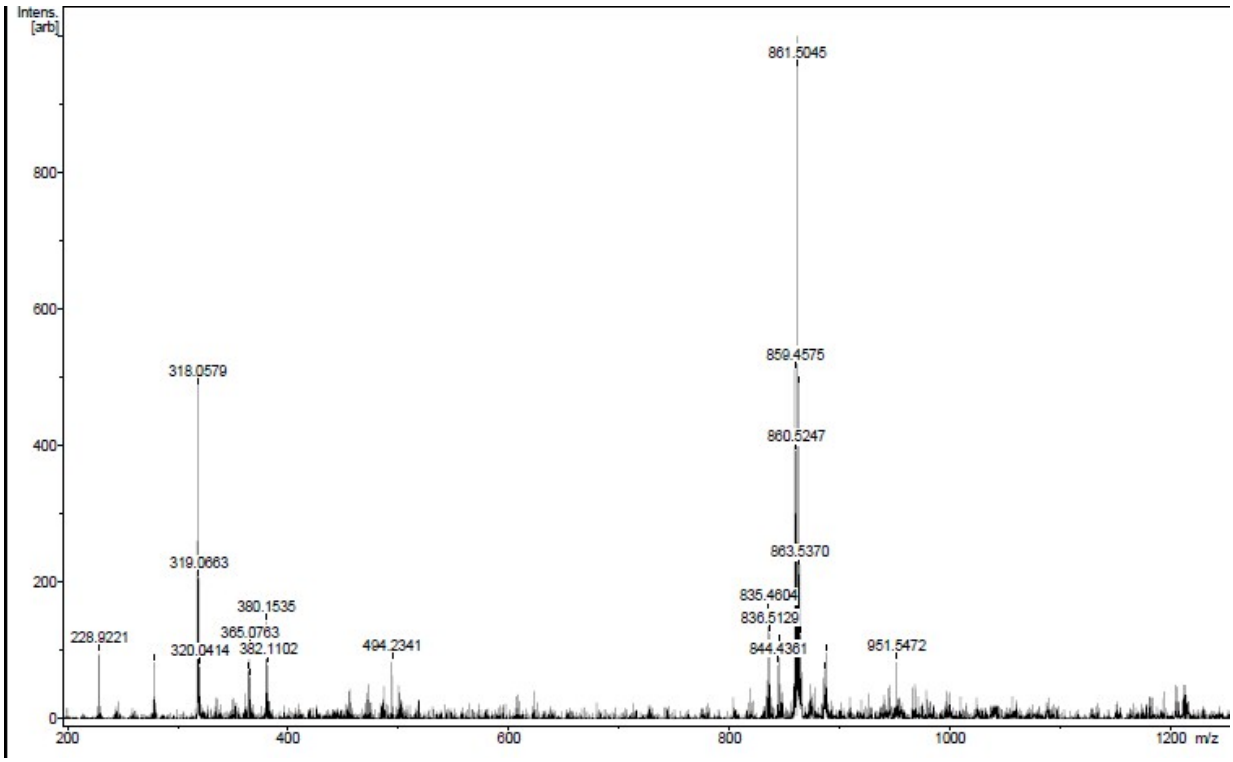
Pic. 7 NMR ^{1}H and ^{13}C (400 MHz, $CDCl_3$, 25 °C) spectra of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis[3-(4-aminomethyl-1,2,3-triazol-1-yl)propoxy])thiacalix[4]arene **6**.



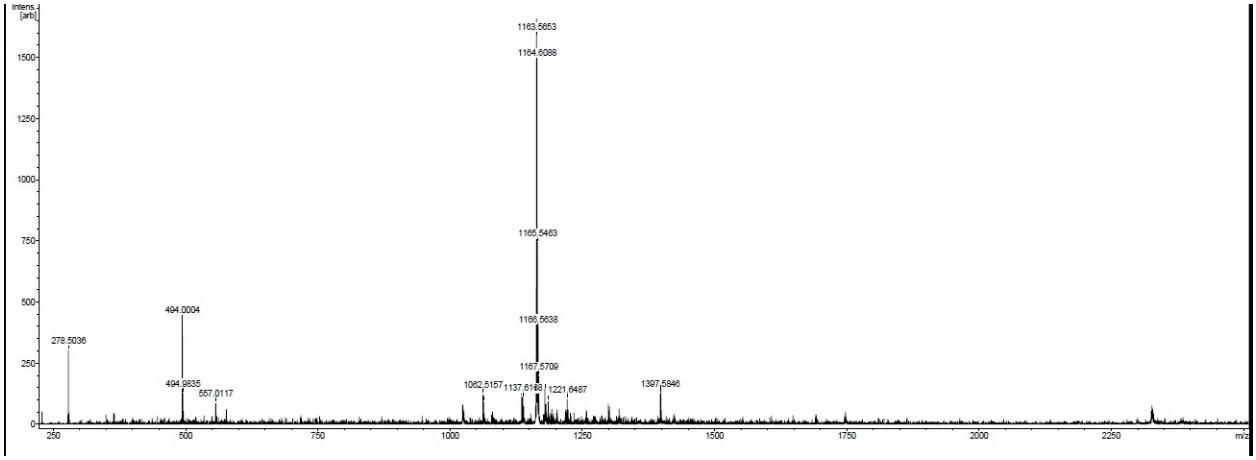
Pic. 8 NMR ^{1}H (400 MHz, DMSO-D6, 25 °C) spectra of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis[3-(4,5-dicarboxy-1,2,3-triazol-1-yl)propoxy]thiacalix[4]arene **7.**



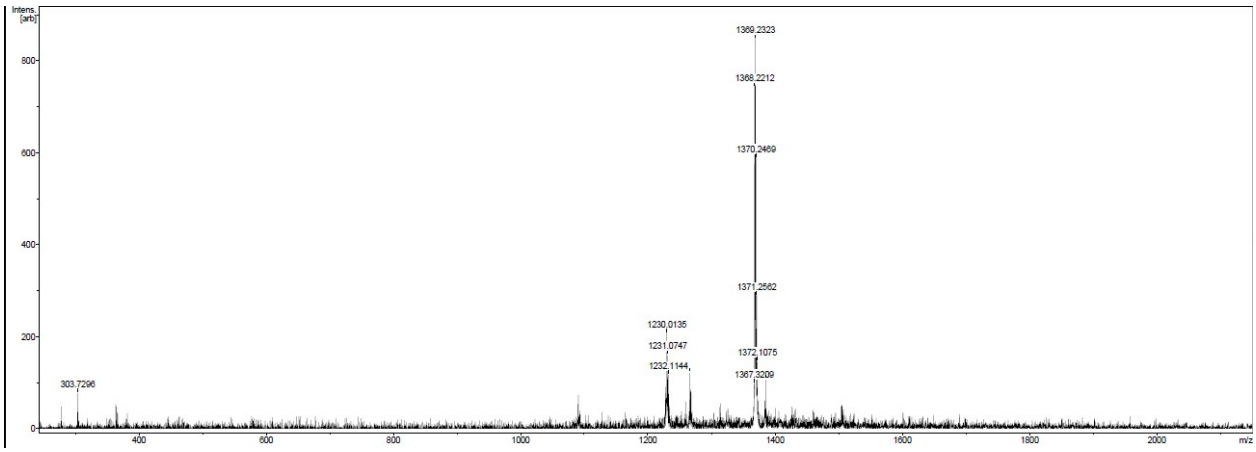
Pic. 9 MALDI-TOF spectra of 5,11,17,23-tetra-tert-butyl-25,27-bis((5-phenylpenta-2,4-dyin-1-yl)oxy)-26,28-dihydroxythiacalix[4]arene **1**



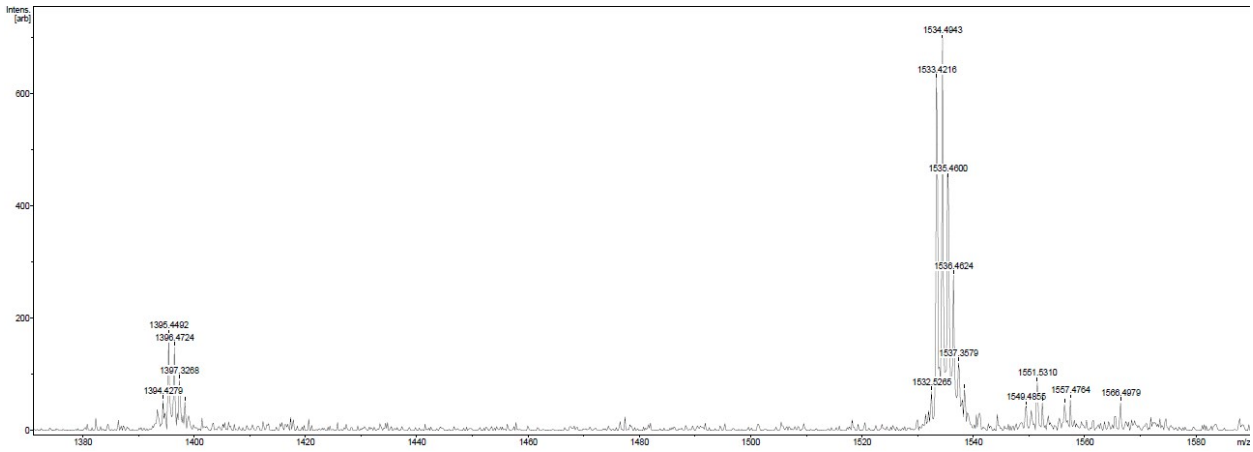
Pic. 10 MALDI-TOF spectra of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis(3-azidopropoxy)-26,28-dihydroxythiacalix[4]arene **2.**



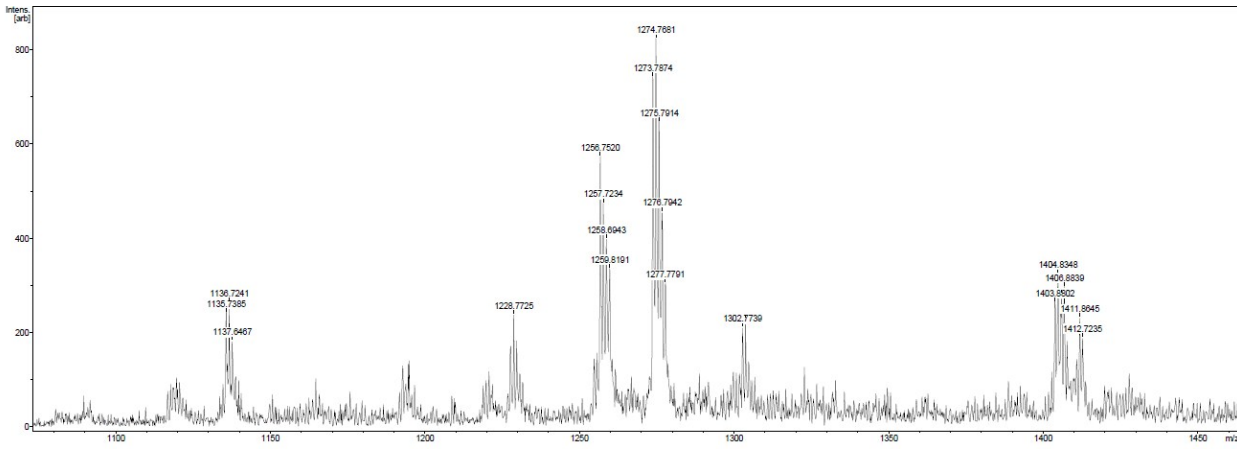
Pic. 11 MALDI-TOF spectra of 5,11,17,23-tetra-tert-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis(3-azidopropoxy)thiacalix[4]arene **3.**



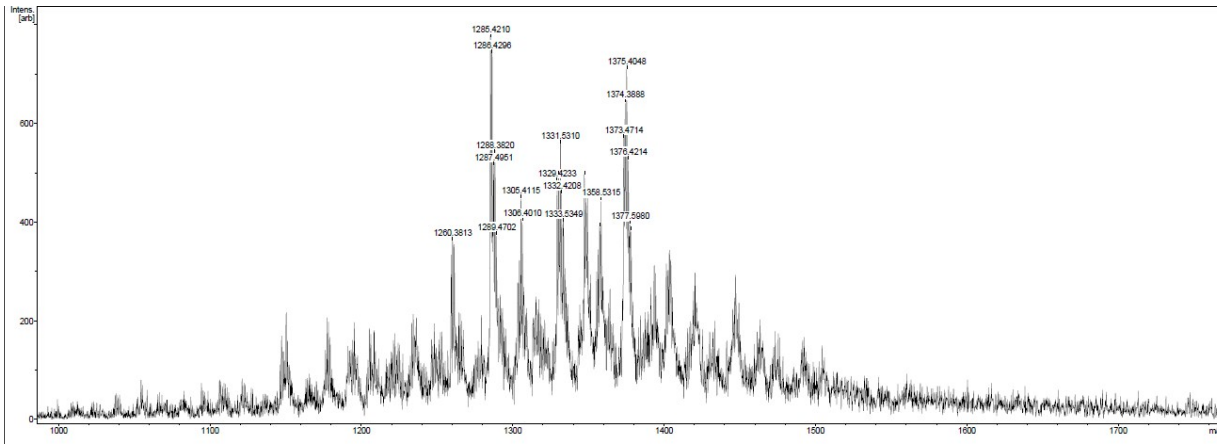
Pic. 12 MALDI-TOF spectra of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis[3-(4-phenyl-1,2,3-triazol-1-yl)propoxy]thiacalix[4]arene **4.**



Pic. 13 MALDI-TOF spectra of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis [3-(4-(1,3-dioxoisoindolin-2-yl)methyl)-1,2,3-triazol-1-yl)propoxy] thiacalix[4]arene **5.**



Pic. 14 MALDI-TOF spectra of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis[3-(4-aminomethyl-1,2,3-triazol-1-yl)propoxy])thiacalix[4]arene **6**.



Pic. 15 MALDI-TOF spectra of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis[(5-phenylpenta-2,4-dyin-1-yl)oxy]-26,28-bis[3-(4,5-dicarboxy-1,2,3-triazol-1-yl)propoxy]thiacalix[4]arene **7.**

References

1 N. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H. Takeya, S. Miyanari, T. Miyashi and S. Miyano, *Tetrahedron*, 2000, **56**, 1437–1443.

2 N. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H. Takeya, S. Miyanari, T. Miyashi and S. Miyano, *Tetrahedron*, 2000, **56**, 1437–1443.

3 N. Bowling, N. Burrmann, R. Halter, J. Hodges, R.McMahon, *J. Org Chem.*,2010, **75**,6382-6390.

4 V. Hong, S.I. Presolski, C. Ma, M. G. Finn, *Angew Chem Int Ed Engl.*, 2009, **48**, 9879-9883.

5 Bruker. APEX2 Software Suite for Crystallographic Programs, Bruker AXS, Inc., Madison, WI, USA, 2009.

6 Bruker. Area detector control and integration software. Version 5.x. In: SMART and SAINT. Madison, Wisconsin (USA): Bruker Analytical X-ray Instruments Inc.; 1996.

7 G.M. Sheldrick., *Acta Crystallogr.*, 2008, **64**, 112-122.

8 C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr*. 2006, **39**, 453-457.