Hybrid multicyclophanes based on thiacalix[4]arene and pillar[5]arene: synthesis and influence on the formation of polyaniline.

*Dmitriy N. Shurpik [1], Luidmila S. Yakimova [1], Vladimir V. Gorbatchuk [1], Denis A. Sevastyanov[1],. Pavel L. Padnya [1], Vladimir G. Evtugyn [1], Olga B. Bazanova [2], Il'dar Kh. Rizvanov [2] and Ivan I. Stoikov[1]**

1. Kazan Federal University, A.M. Butlerov Chemistry Institute, 420008, Kremlevskaya Street, 18, Kazan, Russian Federation.

2. A.E. Arbuzov' Institute of Organic and Physical Chemistry of KSC RAS, 420088 Kazan, Russian Federation

E-mail: Ivan.Stoikov@mail.ru; Fax: +7-8432-752253; Tel: +7-8432-337463

Electronic Supplementary Information (21 pages)

1. Materials and methods

^{1}H NMR spectra were recorded on the Bruker Avance-400 (400 MHz) spectrometer and ^{13}C and 2D NOESY NMR spectra were obtained on the impulse spectrometer Bruker Avance-400 (with 100 MHz and 400 MHz respectively). Chemical shifts were determined against the signals of residual protons of deuterated solvent (DMSO-d_6, $CDCl_3$). The concentration of sample solutions was 3-5 %.

Attenuated total internal reflectance IR spectra were recorded with Spectrum 400 (Perkin Elmer) Fourier spectrometer.

Elemental analysis was performed with Perkin Elmer 2400 Series II instrument.

Mass spectra (MALDI-TOF) were recorded on Ultraflex III mass spectrometer in the 4-nitroaniline matrix.Melting points were determined using the Boetius Block apparatus.

Additional control of the purity of compounds and monitoring of the reaction were carried out by thin-layer chromatography using Silica G, 200 μm plates, UV 254.

Most chemicals were purchased from Aldrich and used as received without additional purification. Organic solvents were purified in accordance with standard procedures.

^{1}H Diffusion Ordered Spectroscopy (DOSY) The spectra were recorded on a Bruker Avance 400 spectrometer, at 9.4 tesla, at the resonating frequency of 400.17 MHz for ^{1}H, using a BBO Bruker 5 mm gradient probe. The temperature was regulated at 298 K and no spinning was applied to the NMR tube. *DOSY* experiments were performed using the STE bipolar gradient pulse pair (stebpgp1s) pulse sequence. 16 scans of 16 data points were collected. The maximum gradient strength produced in the z direction was 5.35 Gmm^{-1}. The duration of the magnetic field pulse gradients (δ) was optimized for each diffusion time (Δ) in order to obtain a 2% residual signal with the maximum gradient strength. The values of δ and Δ were 1.800 μs and 100 ms, respectively. The pulse gradients were incremented from 2 to 95% of the maximum gradient strength in a linear ramp.[S1]

UV-visible spectra were recorded on the Shimadzu UV-3600 spectrophotometer using a 1cm quartz cuvette at 25 °C. The UV measurements were performed with “Shimadzu UV-3600” instrument. The $2.4\cdot10^{-4}$ M solution of the aniline or p-toluenesulfonic acid (100, 200, 300, 400, 500, 600, 70, 800, 900 and 1000 μl) in water was added to 0.1 ml of the solution of host (multicyclophanes) ($3.4\cdot10^{-3}$ M) in water and diluted to final volume of 3 ml with water. The UV spectra of the solutions were then recorded. The stability constant of complexes were calculated as described below. Three independent experiments were carried out for each series. Student’s *t*-test was applied in statistical data processing. Experiment was carried out according to the literature method.[S2]

Transmission electron microscopy (TEM) analysis of polyaniline was carried out using the Hitachi HT7700 Exalens transmission electron microscope with Oxford Instruments X-Max^{n} 80T EDS detector. For sample preparation, 10 μl of the suspension were placed on the Formvar™/carbon coated 3 mm copper grid, which was then dried at room temperature. After complete drying, the grid was placed into the transmission electron microscope using special holder for microanalysis. Analysis was held at the accelerating voltage of 80 kV in STEM mode using Oxford Instruments X-Max^{n} 80T EDS detector.

Simultaneous thermogravimetry and scanning calorimetry (TG–DSC) was performed on a Netzsch Jupiter STA 449 C Jupiter analyzer in 40-μL platinum crucibles with a cap having a 0.5-mm hole at constant heating rates (10 and 4 deg/min; heating range 303–1173 K) in a

dynamic argon atmosphere, flow rate 20 mL/min, at atmospheric pressure; sample weight 10–20 mg.

Dielectric measurements were performed in the frequency range of 10^6–10^9 Hz and in the temperature range of 0–25 °C on a BDS Concept-80 (Novocontrol) dielectric spectrometer with an automatic temperature control, cryosystem QUATRO with precision ±0.5 °C. The cell was in the form of a plate-parallel capacitor with 10-mm diameter electrodes and a 0.5-mm gap between the electrodes.

2. Synthesis of the compounds 8-14

Pillar[5]arenes **1** and **7** were synthesized according to the literature procedure [S3].
Thiacalix[4]arene **3**, **4** and **11**, **12** were synthesized according to the literature procedure [S3, S4].

4- (bromopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (8).

0.38 g of anhydrous K_2CO_3 (2.75 mmol) was added to a solution of 0.38 g (0.512 mmol) of compound (**7**) in 30 ml of CH_3CN. The reaction mixture was refluxed for 20 minutes. Further, an excess of 1,3-dibromopropane 0.53 g (0.31 ml, 3.10 mmol) was added to the reaction mixture. The reaction mixture was refluxed for 24 hours. After that, the reaction mixture was cooled, the precipitate formed was filtered off, and the filter cake was washed with chloroform. The filtrate was evaporated under reduced pressure. The residue was dissolved in a minimal amount of chloroform and slowly poured into excess methanol. The precipitate which formed was filtered off and dried at room temperature.

Yield: 0.39 g (88%), mp. 114 °C. ^{1}H NMR ($CDCl_3$): 2.28 (2H, m, -CH_2-$\underline{CH_2}$-CH_2-), 3.59 (2H, t, $^3J_{HH}$= 6.6 Hz, -CH_2-CH_2-$\underline{CH_2}$-), 3.66-3.79 (37H, m, -O-CH_3, -CH_2-), 3.99 (t, 2H, $^3J_{HH}$= 6.5 Hz, -$\underline{CH_2}$-CH_2-CH_2-), 6.74 – 6.86 (10H, m, Ar-H). ^{13}C NMR ($CDCl_3$): 150.54, 150.53, 149.43, 128.41, 128.34, 128.28, 128.23, 128.21, 128.16, 128.07, 117.04, 114.76, 114.69, 113.71, 113.68, 113.59, 66.01, 55.69, 55.66, 55.63, 55.60, 33.34, 33.06, 30.43, 30.18, 29.51, 29.45. . IR (ν/см$^{-1}$): 2986 (-CPh-H), 2828 (-CH_2-, -CH_3-CH_2-CH_3), 1497 (-CH_2-), 1208 (CPh-O-CH_2-). MS (MALDI-TOF): calc. [M^+] m/z = 857.82, found [M+H]$^+$ m/z = 858.41, [M+K]$^+$ m/z = 897.39. Found (%):C, 65.81; H, 6.23. Calc. for $C_{47}H_{53}BrO_{10}$. (%):C, 67.06; H, 6.61.

4- (azidopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (9).

To a solution of 1.5 g (1.75 mmol) of compound (**8**) in 50 ml of anhydrous DMF was added 0.34 g of anhydrous NaN_3 (5.24 mmol). The reaction mixture was heated for 24 hours at a temperature of 100°C. After that, the reaction mixture was cooled, slowly poured into an excess of distilled H_2O. The precipitate which formed was filtered off and dried at room temperature.

Yield: 1.29 g (90%), mp. 120 °C with decomposition. ^{1}H NMR ($CDCl_3$): 1.98 (2H, m, -CH_2-$\underline{CH_2}$-CH_2-), 3.44 (2H, t, $^3J_{HH}$= 6.6 Hz, -CH_2-CH_2-$\underline{CH_2}$-), 3.63-3.80 (37H, m, -O-CH_3, -CH_2-), 3.93 (t, 2H, $^3J_{HH}$= 6.5 Hz, -$\underline{CH_2}$-CH_2-CH_2-), 6.71– 6.84 (10H, m, Ar-H). ^{13}C NMR ($CDCl_3$): 150.94, 150.75, 150.59, 128.50, 128.44, 128.42, 128.38, 128.33, 128.29, 128.25, 114.87, 114.06, 113.98, 113.91, 65.20, 55.82, 48.61, 32.91, 30.47, 29.70, 29.63, 29.29. IR (ν/см$^{-1}$): 2929 (-CPh-H), 2864 (-CH_2-, -CH_3-CH_2-CH_3), 2087 (-N_3), 1497 (-CH_2-), 1200(CPh-O-CH_2-). MS

(MALDI-TOF): calc. $[M^+]$ m/z = 819.37, found $[M+Na]^+$ m/z = 819.3. Found (%):C, 68.85; H, 6.52; N, 5.12. Calc. for $C_{47}H_{53}N_3O_{10}$. (%):C, 67.93; H, 6.85; N, 5.44.

4- (aminopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (10).

The macrocycle (**9**) 1 g (1.22 mmol) was dissolved in 50 ml of THF, then triphenylphosphine was added 0.96 g (3.67 mmol). The reaction mixture was refluxed for 1 hour. To the reaction mixture was added 12 ml of aqueous ammonia (15%) and stirred for 72 hours. The reaction mixture was evaporated, the solid precipitate was washed with ethanol, then recrystallized from methanol. It was dried under reduced pressure over phosphoric anhydride.

Yield: 0.72 g (75%), mp. 114- 115°C. ^{1}H NMR (DMSO-d_6): 1.77 (2H, m, -CH_2-$\underline{CH_2}$-CH_2-), 2.72 (2H, t, $^3J_{HH}$= 6.3 Hz, -CH_2-CH_2-$\underline{CH_2}$-), 3.55-3.80 (37H, m, -O-CH_3, -CH_2-), 3.89 (2H, t, $^3J_{HH}$ = 6.2 Hz, $\underline{-CH_2-}CH_2$-CH_2-), 6.64 – 6.90 (10H, m, Ar-H). ^{13}C NMR (DMSO-d_6): 149.91, 149.81, 149.31, 129.00, 128.82, 128.75, 127.47, 127.42, 114.09, 113.61, 113.32, 65.75, 65.68, 55.43, 55.39, 38.62, 33.19, 29.15, 28.98, 28.76. IR (ν/см$^{-1}$): 3340 (-NH_2), 2938 (-CPh-H), 2827 (-CH_2-, -CH_3-CH_2-CH_3), 1498 (-CH_2-), 1208 (CPh-O-CH_2-). MS (MALDI-TOF): calc. $[M^+]$ m/z = 793.4, found $[M+H]^+$ m/z = 794.3, $[M+Na]^+$ m/z = 817.2, $[M+K]^+$ m/z = 832.2. Found (%): C, 71.10; H, 6.98; N, 1.76. Calc. for $C_{47}H_{55}NO_{10}$. (%):C, 71.18; H, 6.96; N, 1.73.

General procedure for the synthesis of hybrid multicyclophanes 13, 14.

The freshly obtained dry residue of chloroanhydride the *p-tert*-butylthiacalix[4]arene (**11** - 1,3-alternate or **12**-cone), 0.12 g (0.124 mmol) was dissolved in dichloromethane (10 ml). The resulting solution was then added over 20 minutes to a mixture of 4-(aminopropyloxy)-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (**10**) 0.34 g (0.5 mmol) and diisopropylethylamine (5 ml, 36 mmol) in 20 ml of dichloromethane. The mixture was stirred at room temperature under argon for 48 hours. The reaction mixture was then washed with a 2M solution of hydrochloric acid (2×30 ml) and distilled water (2×30 ml). The organic phase was separated, dried over molecular sieves (molecular sieves, 3A), then the solvent was removed under reduced pressure. The target compound was isolated by column chromatography (eluent: $CHCl_3$: $CH_3C(O)CH_3$ = 18: 1).

Tetrakispillar[5]thiacalix[4]arene in 1,3-alternate configuration (13).

Yield: 0.29 г (58%), mp.181 °C. ^{1}H NMR (DMSO-d_6): 1.22 (36H, br. s, -$C(CH_3)_3$), 1.94-2.08 (m, 8H, -NH-CH_2-$\underline{CH_2}$-CH_2-O-), 3.05 (м, 8H, -NH-$\underline{CH_2}$-CH_2-CH_2-O-), 3.58-3.76 (148H, m, -CH_2-, -OCH_3), 3.78 (8H, br. s, -CH_2-C(O)-), 3.93 (8H, m, -NH-$\underline{CH_2}$-CH_2-$\underline{CH_2}$-O-), 6.68-6.85(40H, m, $ArH_{P[5]A}$), 7.56 (8H, s, $ArH_{TC[4]A}$), 7.85 (4H, br. s, -NH-).^{13}C NMR (ДМСО-d_6):25.41, 29.45, 29.81, 30.09, 30.22, 31.09, 31.19, 31.36, 31.51, 34.37, 37.43, 55.67, 55.90, 66.56, 74.54, 114.02, 114.23, 115.23, 128.21, 134.98, 147.77, 149.98, 150.93, 151.11, 157.87, 157.94, 159.24, 168.89. IR (ν/см$^{-1}$): 2931 (-CPh-H), 2827 (-CH_2-, -CH_3-CH_2-CH_3), 1674 (-NH-C(O)-), 1498 (-CH_2-), 1206(CPh-O-CH_2-). MS (MALDI-TOF): calc. $[M^+]$ m/z = 4055.76, found $[M+H]^+$ m/z = 4057.0, $[M+Na]^+$ m/z = 4081.0 Found (%): C, 69.87; H, 6.66; N, 1.38. Calc. for $C_{236}H_{268}N_4O_{48}S_4$. (%): C, 70.42; H, 6.86; N, 1.54.

Tetrakispillar[5]thiacalix[4]arene in cone configuration (14).

Yield: 0.31 g (65%), mp. 176 °C. ^{1}H NMR (DMSO-d_6): 1.63 (36H, br. s, -C(CH_3)$_3$), 2.60 (m, 8H, -NH-CH_2-$\underline{CH_2}$-CH_2-O-), 3.28 (м, 8H, -NH-$\underline{CH_2}$-CH_2-CH_2-O-), 4.14-4.22 (148H, m, -CH_2-, -OCH_3), 4.38 (8H, m, -NH-$\underline{CH_2}$-CH_2-$\underline{CH_2}$-O-), 7.27-7.35 (40H, m, $ArH_{P[5]A}$), 7.95 (8H, s, $ArH_{TC[4]A}$), 7.85 (4H, br. s, -NH-). ^{13}C NMR ($CDCl_3$): 168.88, 157.80, 151.11, 151.03, 150.93, 150.87, 150.78, 149.92, 147.69, 115.23, 114.23, 114.12, 114.08, 114.02, 113.90, 74.54, 64.54, 55.90, 55.67, 37.39, 34.37, 31.51, 31.36, 31.19, 31.06, 30.22, 29.81, 29.45. IR (ν/см$^{-1}$): 2932 (-CPh-H), 2826 (-CH_2-, -CH_3-CH_2-CH_3), 1675 (-NH-C(O)-), 1500 (-CH_2-), 1207(CPh-O-CH_2-). MS (MALDI-TOF): calc. [M^+] m/z = 4055.76, found $[M]^+$ m/z = 4055.56, $[M+Na]^+$ m/z = 4078.46, $[M+K]^+$ m/z = 4096.26. Found (%):C, 69.87; H, 6.66; N, 1.38. Calc. for $C_{236}H_{268}N_4O_{48}S_4$. (%):C, 70.37; H, 7.01; N, 1.89.

Oxidative polymerization of aniline without supramolecular assistance.

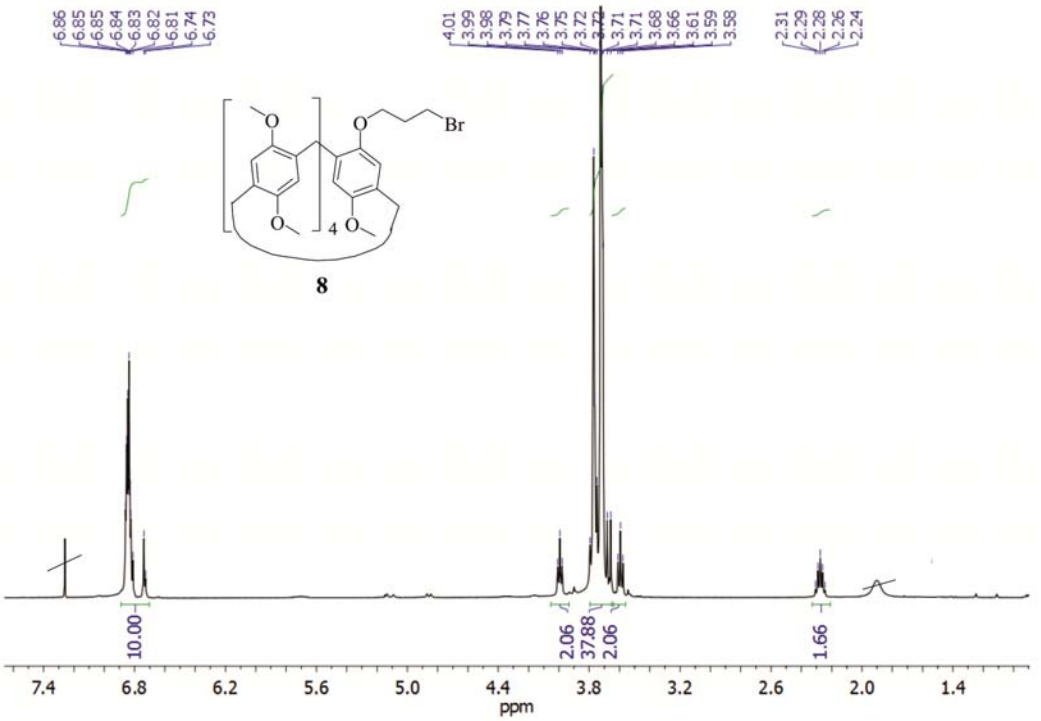
To 0.93 g of aniline (10 mmol) was added p-toluenesulfonic acid monohydrate (1.9 g, 10 mmol), added 5 ml of water, agitated on shaker until white homogeneous paste (at 2700 rpm) then with intensive stirring (800 rpm) using magnetic stirring bar were added to solution of ammonium persulfate (0.57 g, 2.5 mmol) in 45 ml of water. Stirring was stopped after reaction mixture became homogenous (5 minutes). Reaction mixture was left for 24 hours at room temperature, then it was filtered, washed with 0.1% solution of p-toluenesulfonic acid in Type 1 water, then with methanol.

Oxidative polymerization of aniline in presence of tetrakispillar[5]thiacalix[4]arenes **13** and **14** was conducted following similar procedure, with the difference in the first step: to 0.93 g of aniline were added 0.0041 g (1 μmol) of tetrakispillar[5]thiacalix[4]arene (**13** or **14**) and the mixture was agitated until dissolution of tetrakispillar[5]thiacalix[4]arene, then similar further steps were carried out.

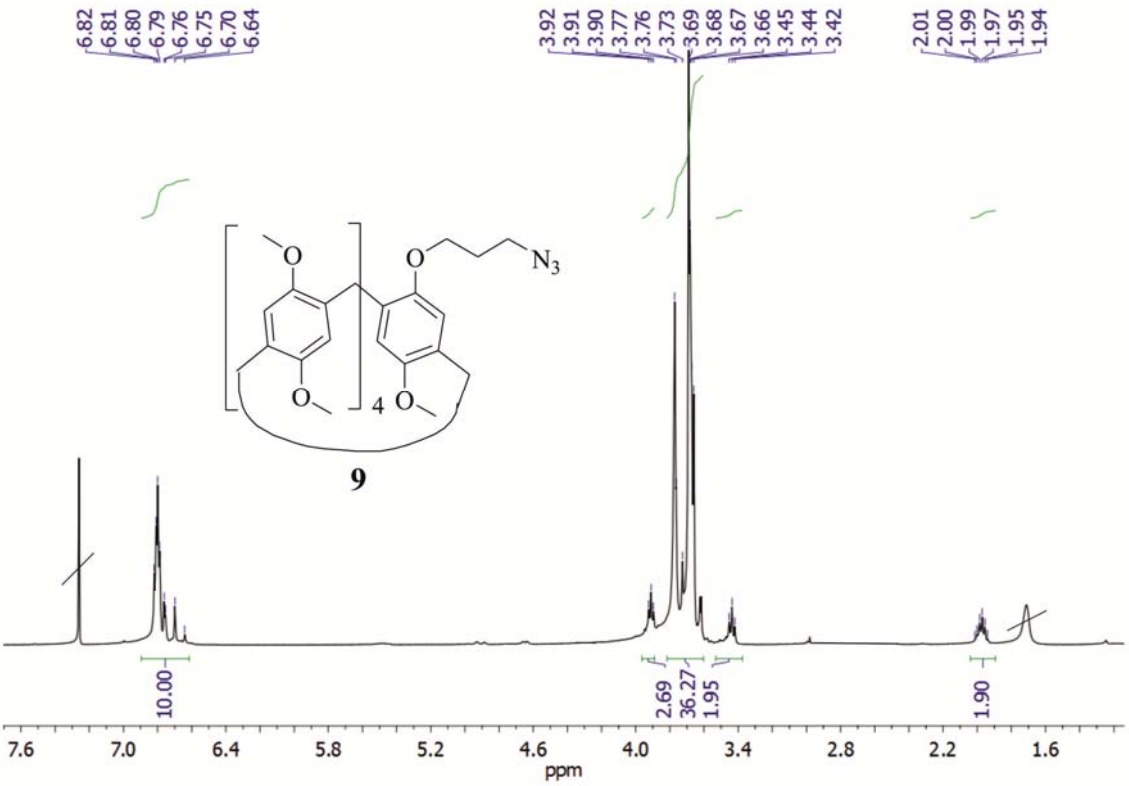
The concentration was definded by UV-spectrophotometry, by comparing to literary [S6] values of absorption for emeraldine. 30 mg of emeraldine was dispersed in 10 ml of acetone, then after leaving unagitated for 2 days, from upper part of mixture, 3 ml of dispersion was carefully taken by syringe and poured into quartz cuvette for UV measurement.

3. NMR, MALDI TOF MS, IR spectra of the compounds 8-14.

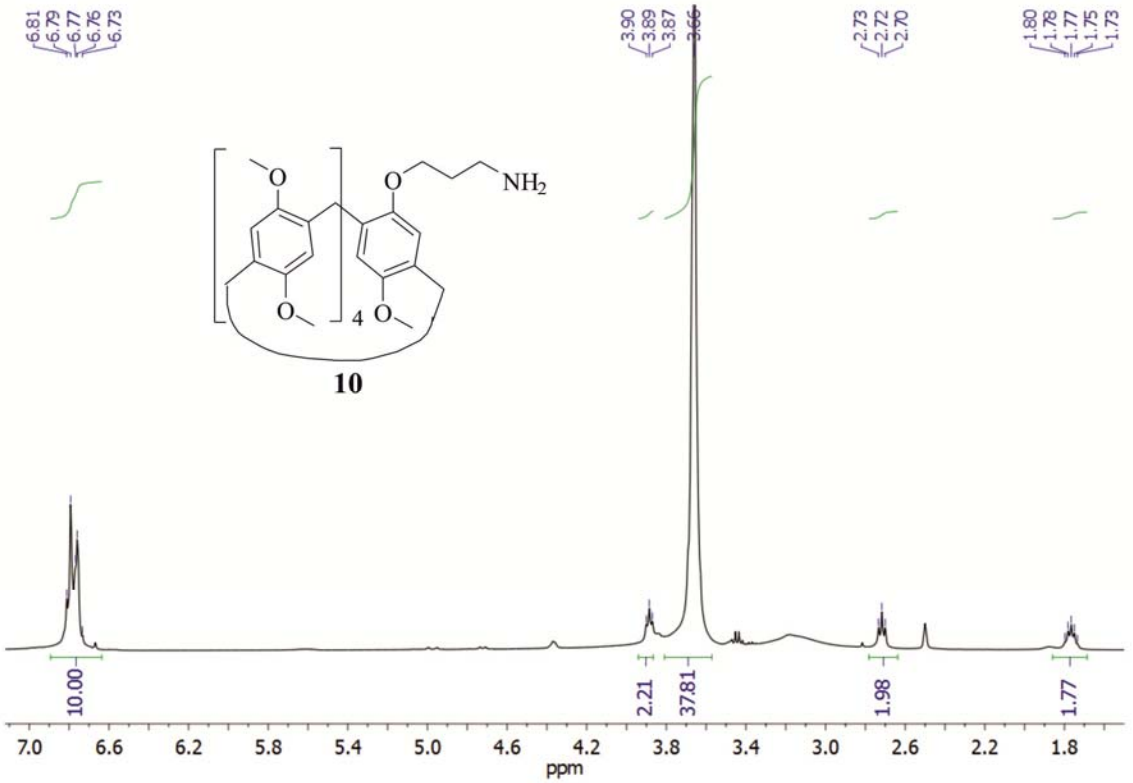
^{1}H NMR spectrum of 4- (bromopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (8), $CDCl_3$, 298 K, 400 MHz



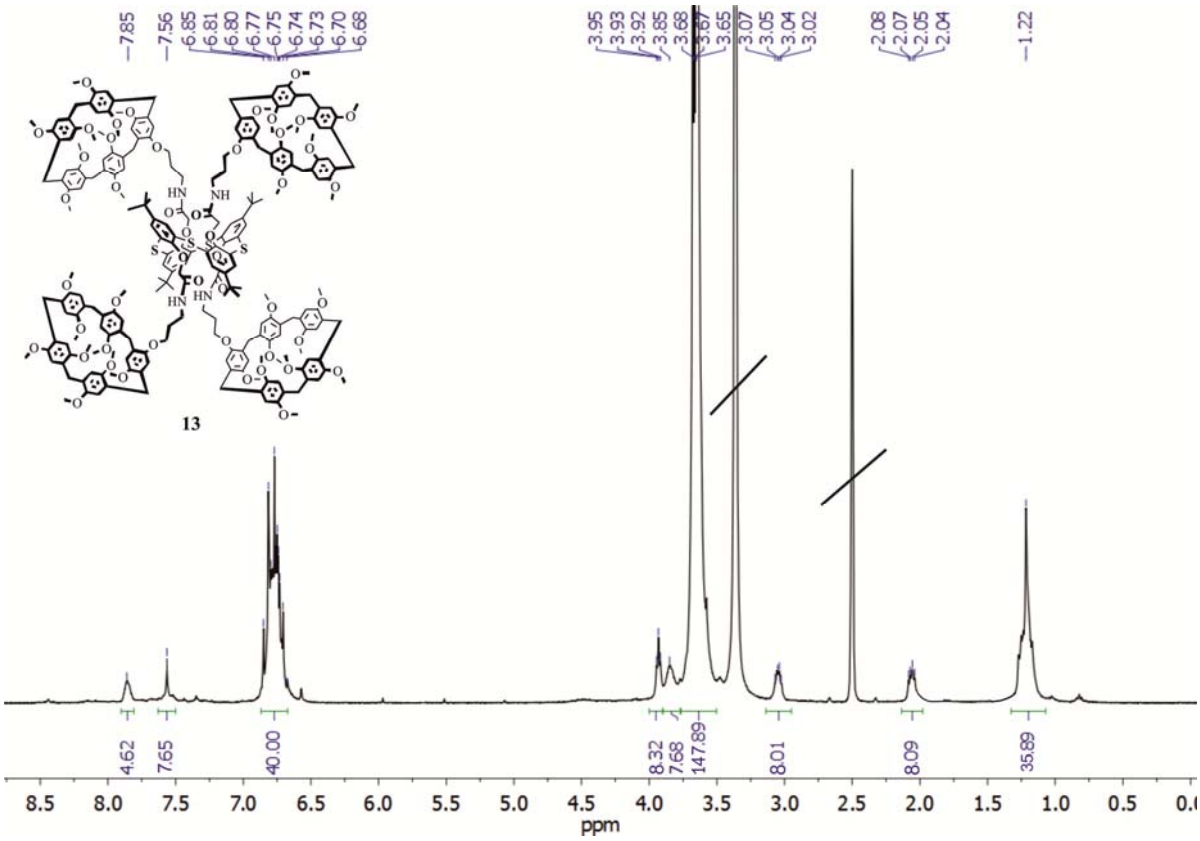
^{1}H NMR spectrum of 4-(azidopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (9), $CDCl_3$, 298 K, 400 MHz



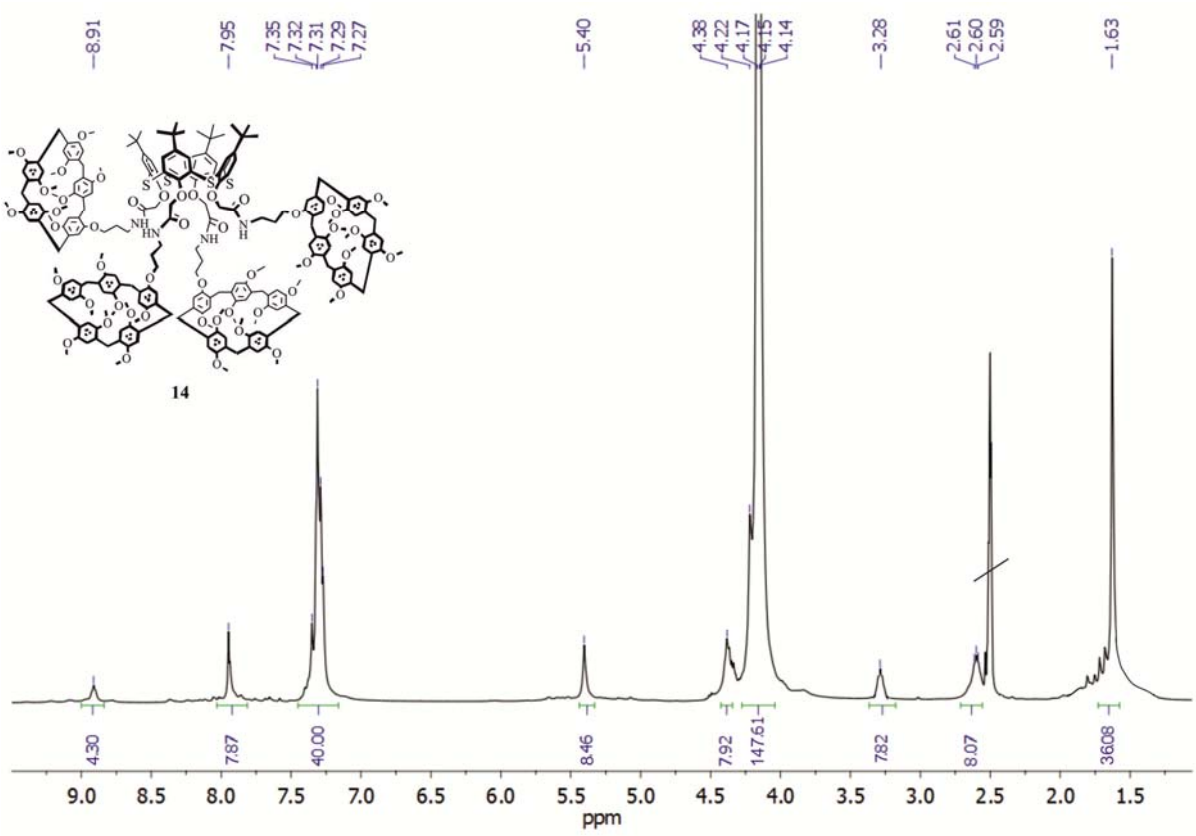
^{1}H NMR spectrum of 4-(aminopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (10), $CDCl_3$, 298 K, 400 MHz



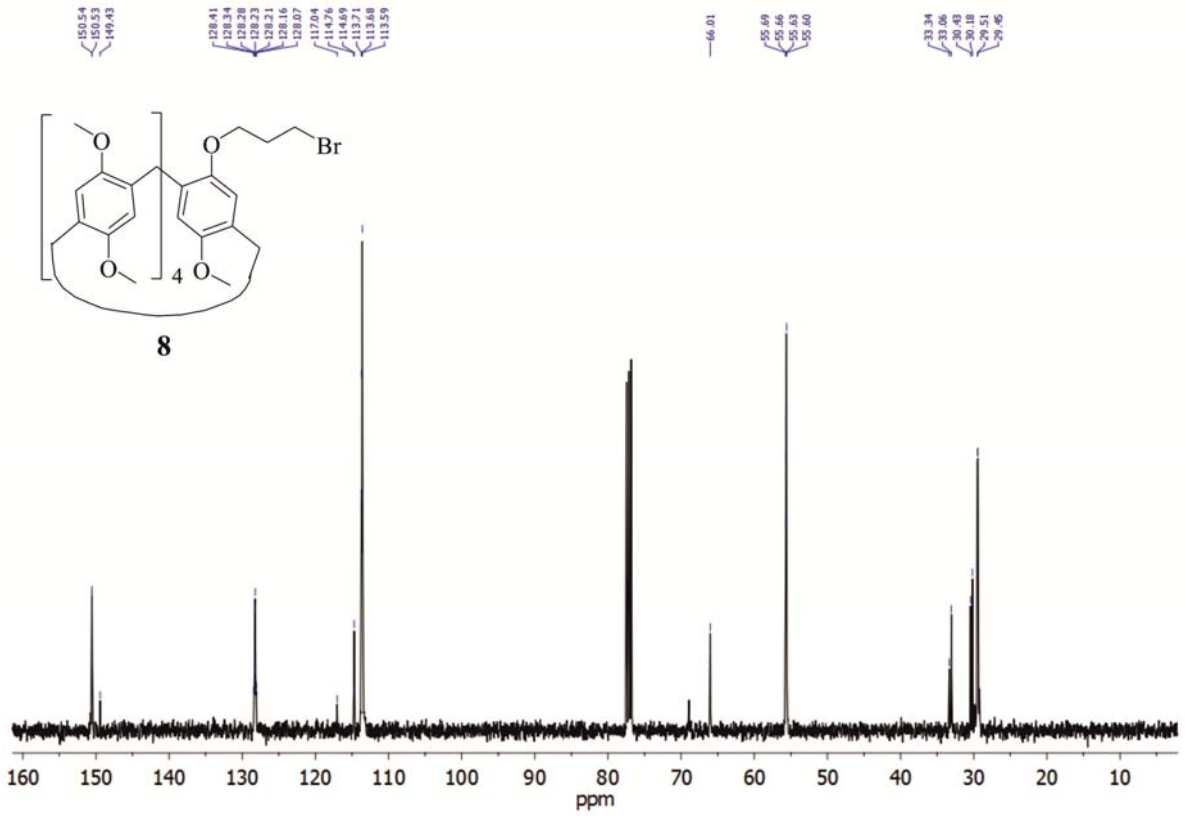
^{1}H NMR spectrum of Tetrakispillar[5]thiacalix[4]arene in 1,3-alternate configuration (13), DMSO-d_6, 298 K, 400 MHz



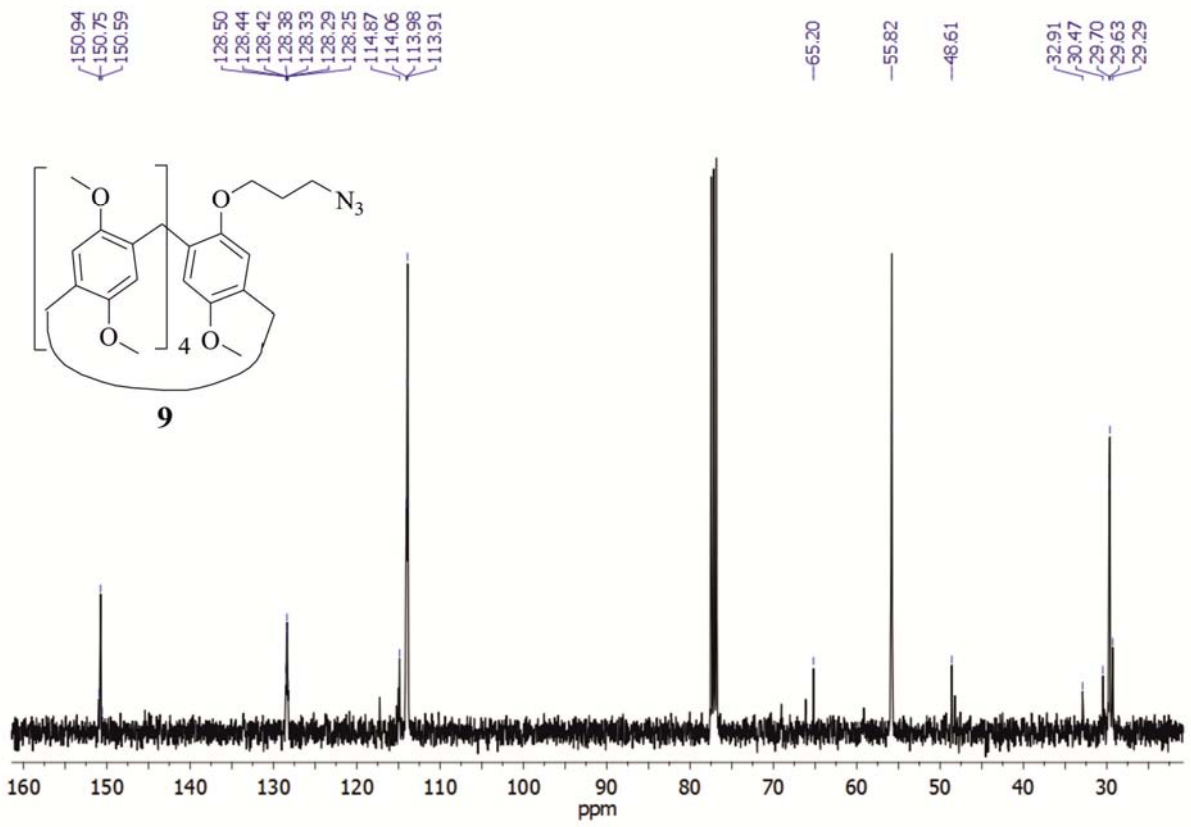
^{1}H NMR spectrum of Tetrakispillar[5]thiacalix[4]arene in cone configuration (14), DMSO-d_6, 298 K, 400 MHz



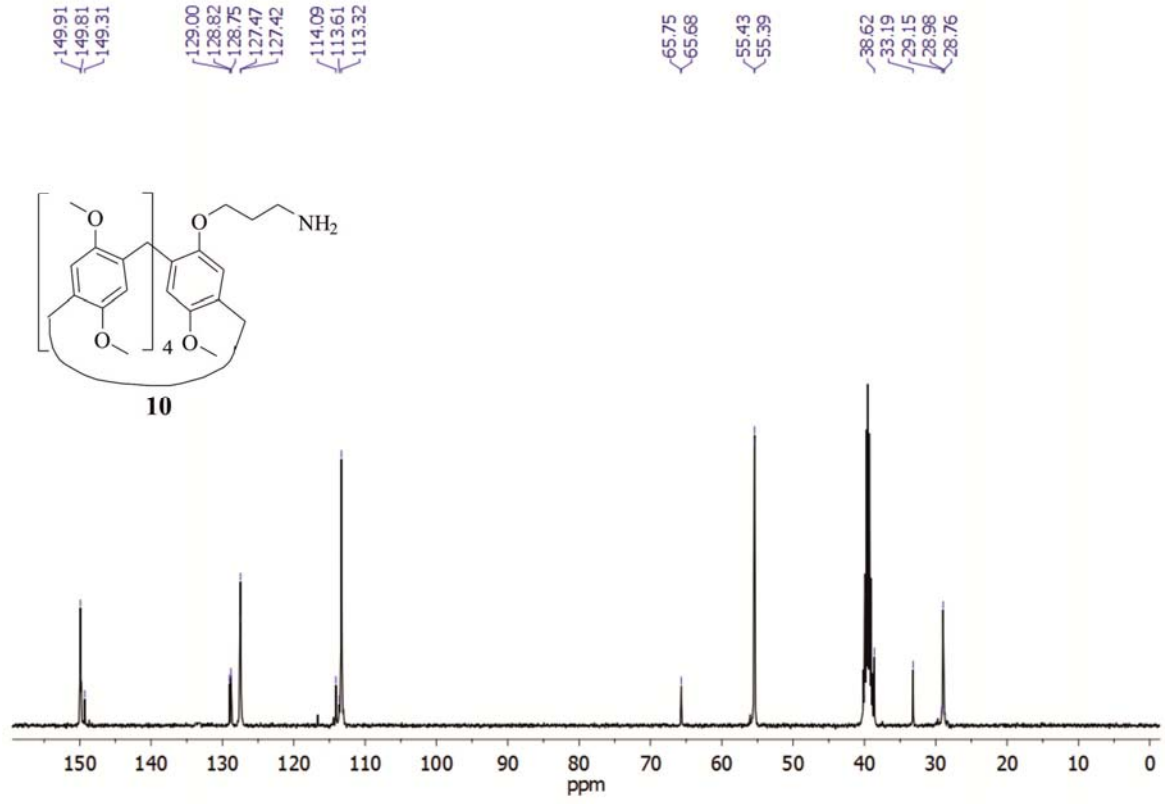
^{13}C NMR spectrum of 4- (bromopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (8), $CDCl_3$, 298 K, 400 MHz



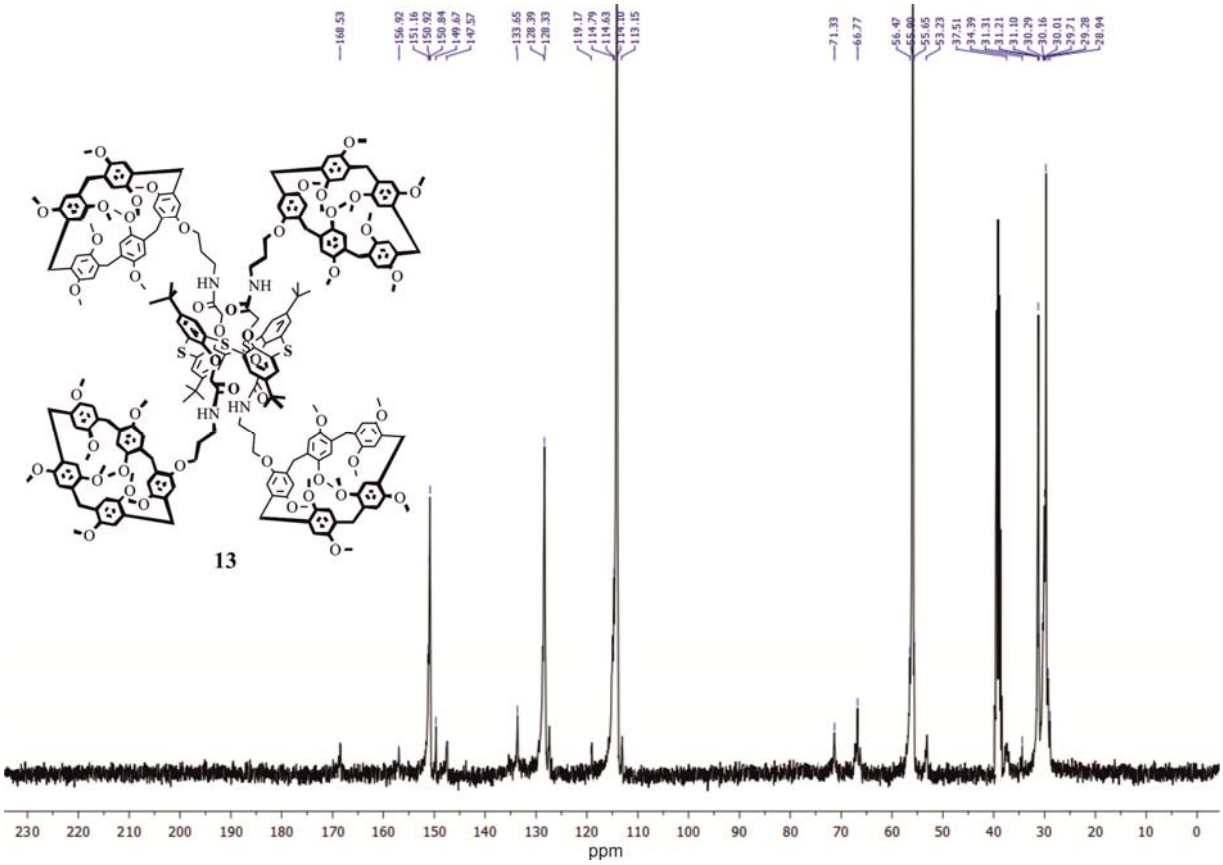
^{13}C NMR spectrum of 4-(azidopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (9), CDCl3, 298 K, 400 MHz



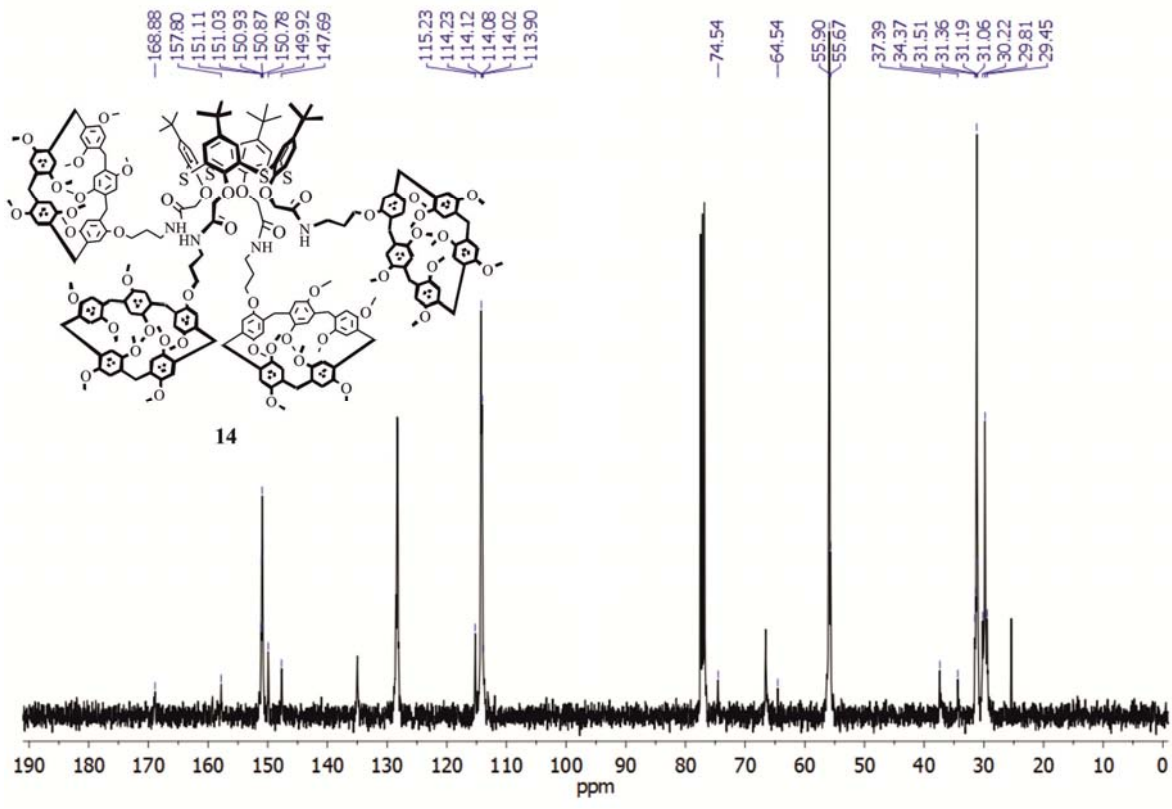
^{13}C NMR spectrum of 4-(aminopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (10), $CDCl_3$, 298 K, 400 MHz



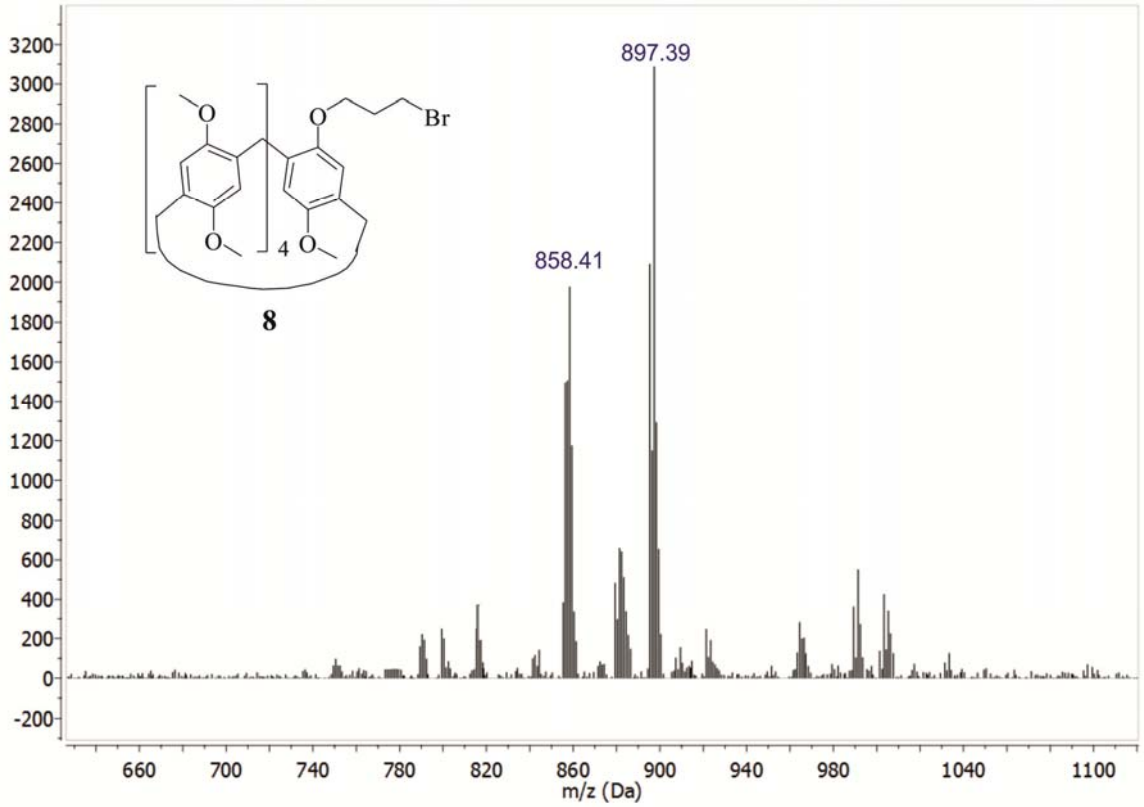
^{13}C NMR spectrum of Tetrakispillar[5]thiacalix[4]arene in 1,3-alternate configuration (13), DMSO-d6, 298 K, 400 MHz



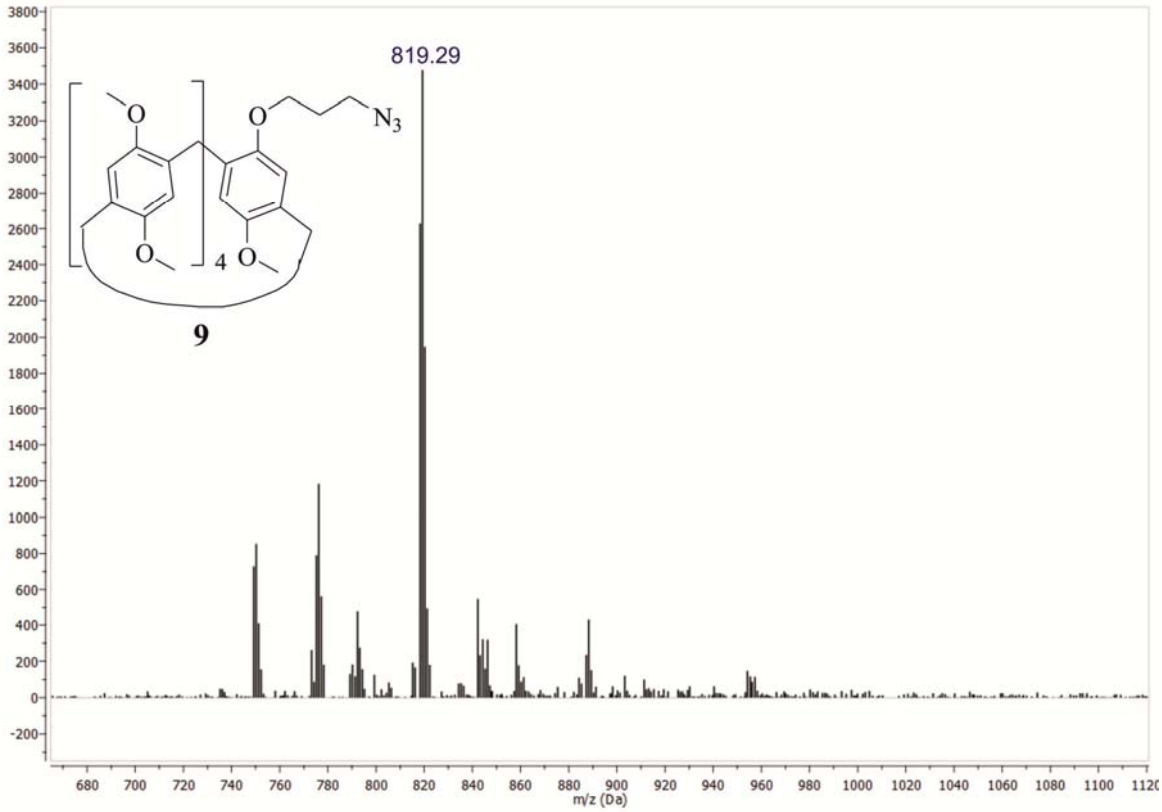
^{13}C NMR spectrum of Tetrakispillar[5]thiacalix[4]arene in cone configuration (14), $CDCl_3$, 298 K, 400 MHz



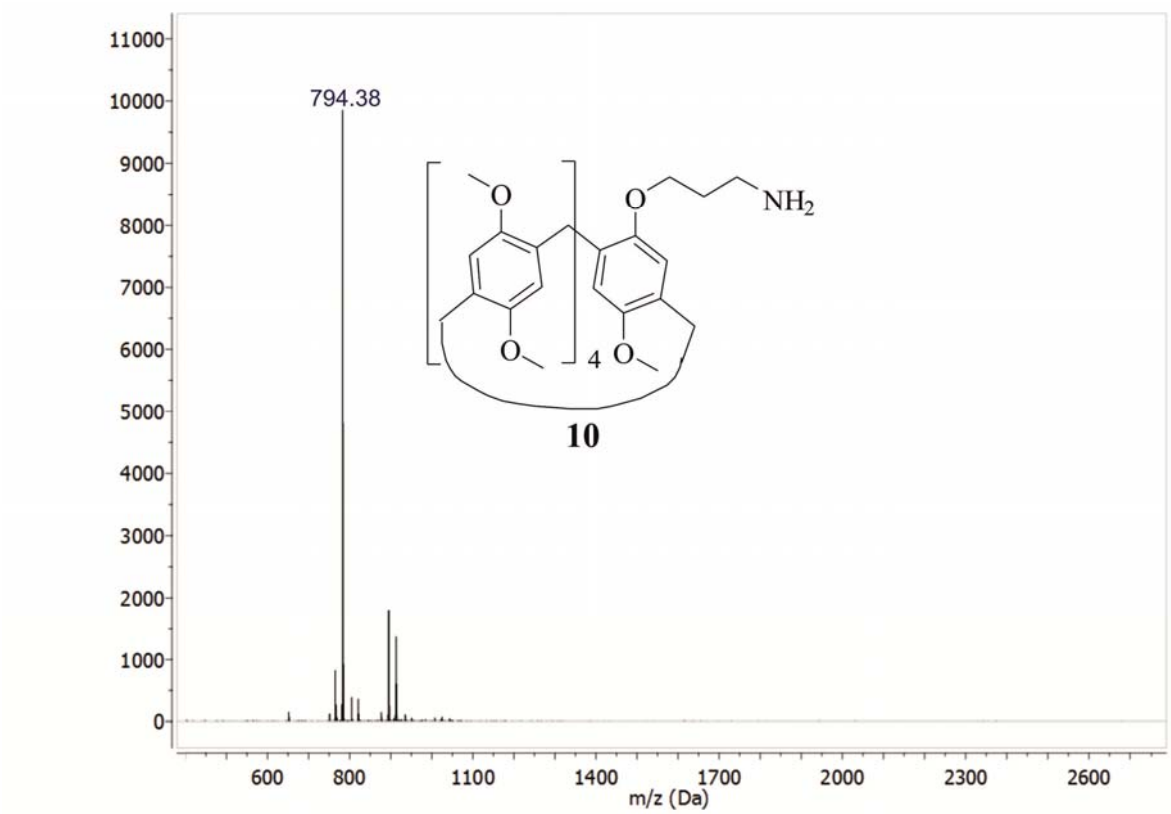
Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 4- (bromopropyloxy) - 8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (8).



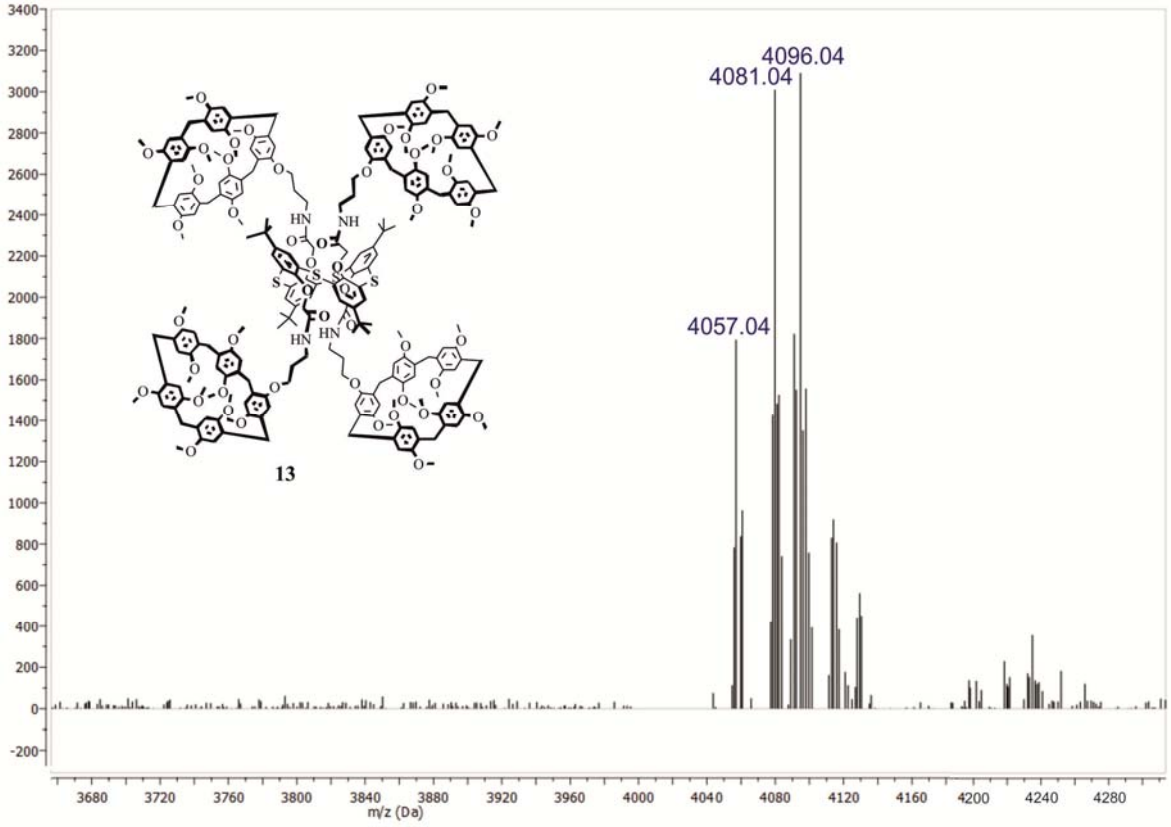
Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 4-(azidopropyloxy) - 8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (9).



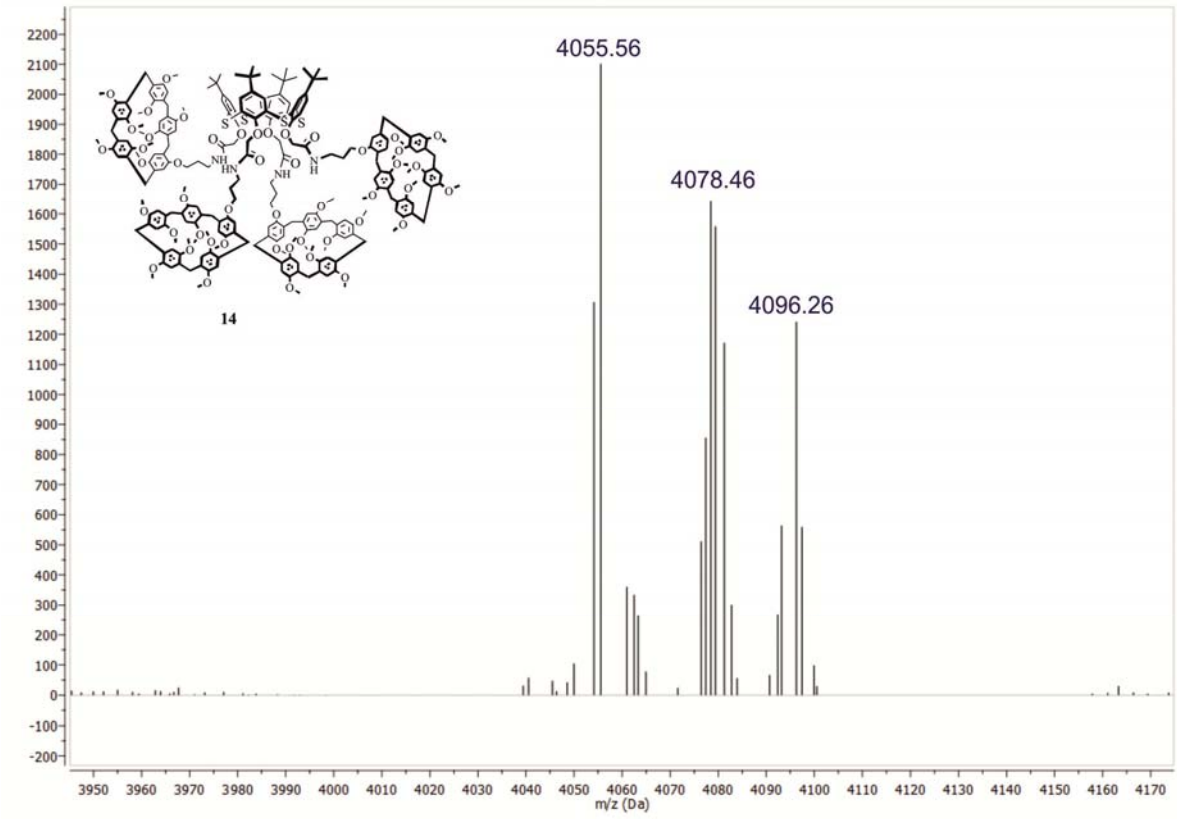
Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 4-(aminopropyloxy) - 8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (10).



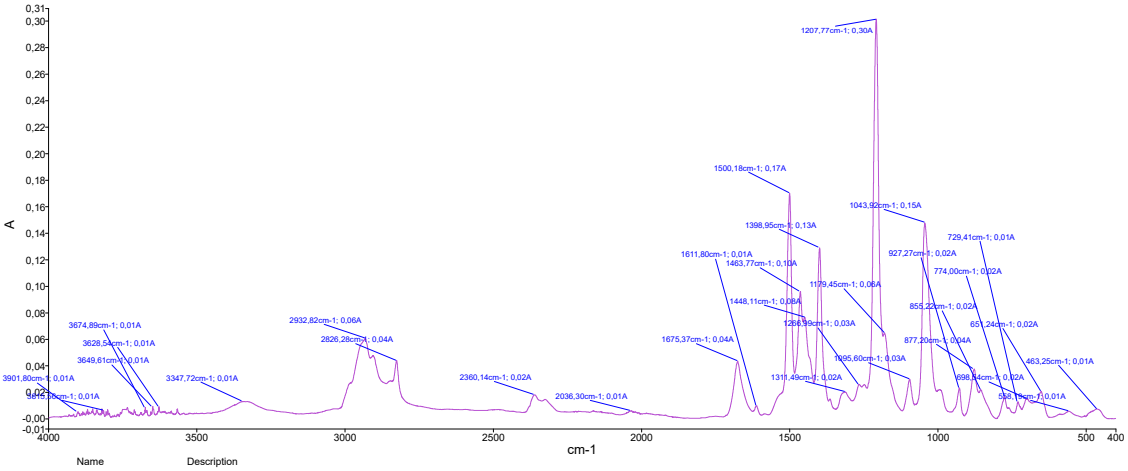
Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of Tetrakispillar[5]thiacalix[4]arene in 1,3-alternate configuration (13).



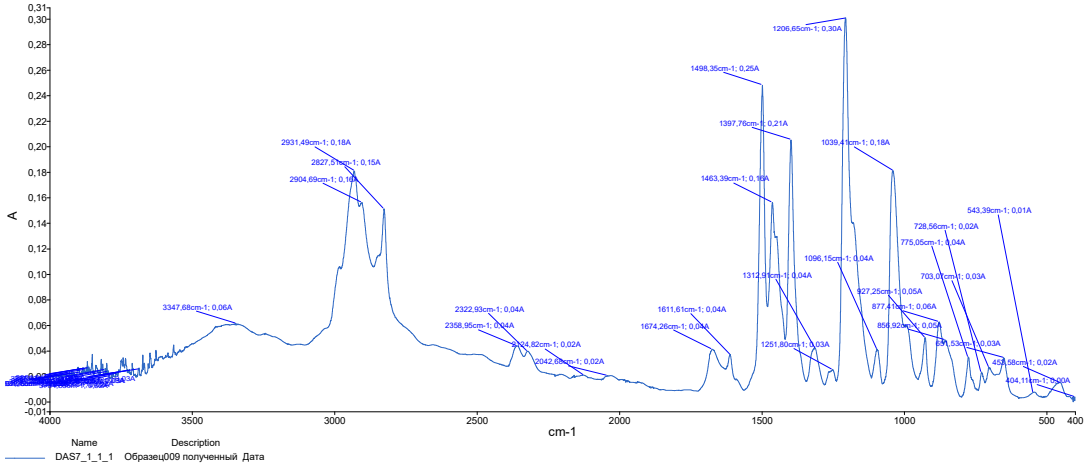
Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of Tetrakispillar[5]thiacalix[4]arene in cone configuration (14).



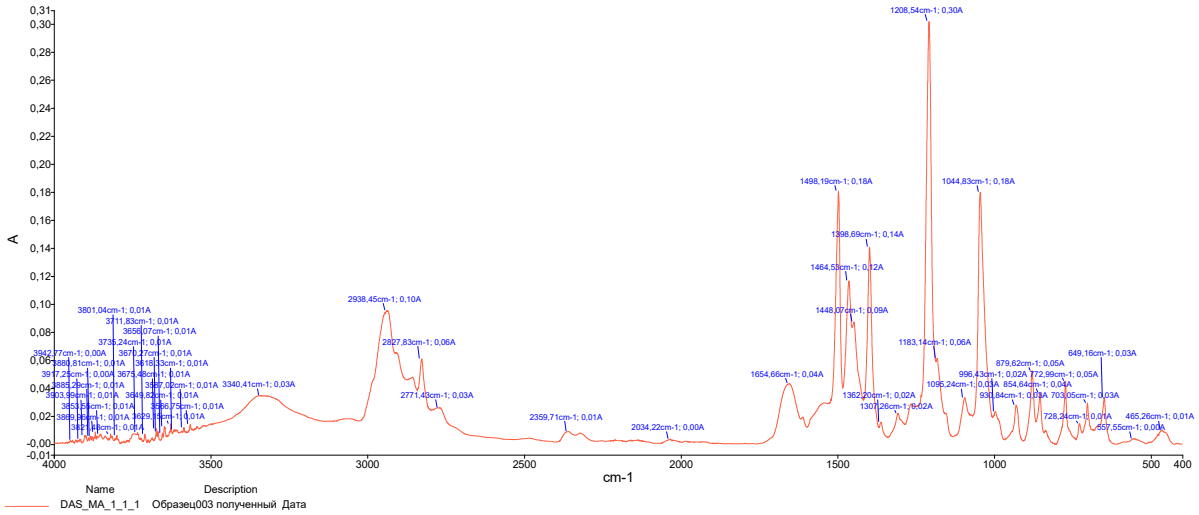
IR spectrum of Tetrakispillar[5]thiacalix[4]arene in cone configuration (14).



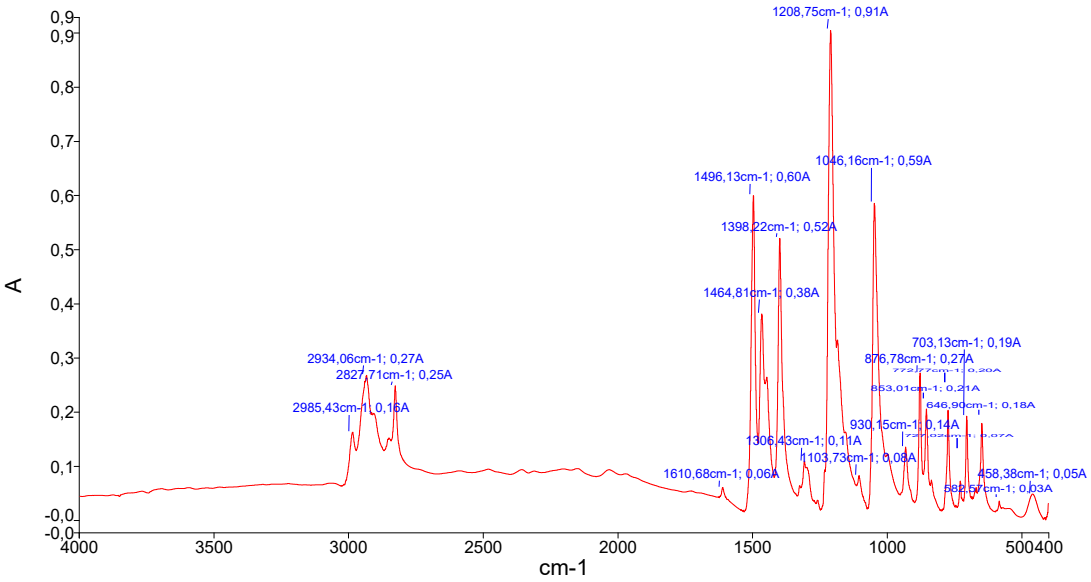
IR spectrum of Tetrakispillar[5]thiacalix[4]arene in 1,3-alternate configuration (13).



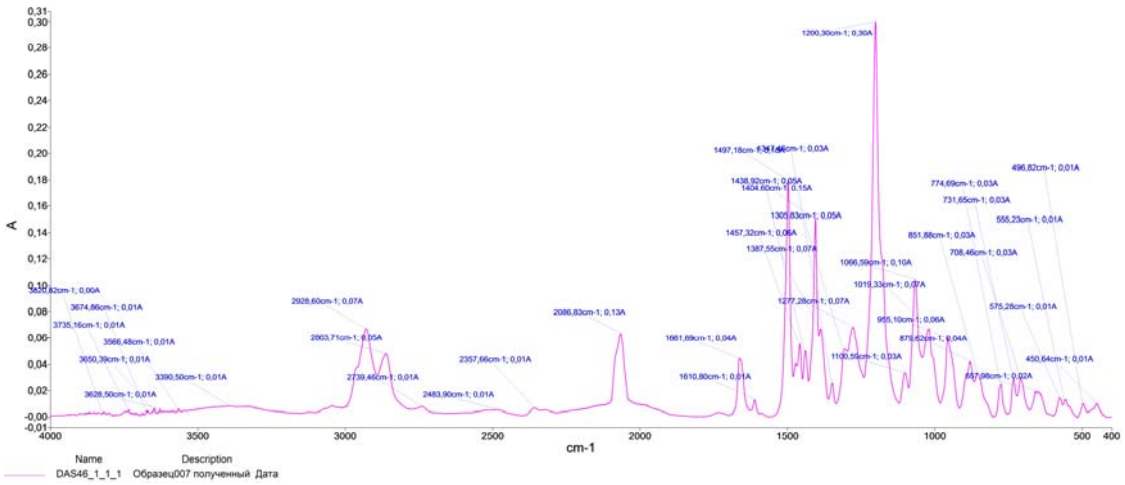
IR spectrum of 4-(aminopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (10).



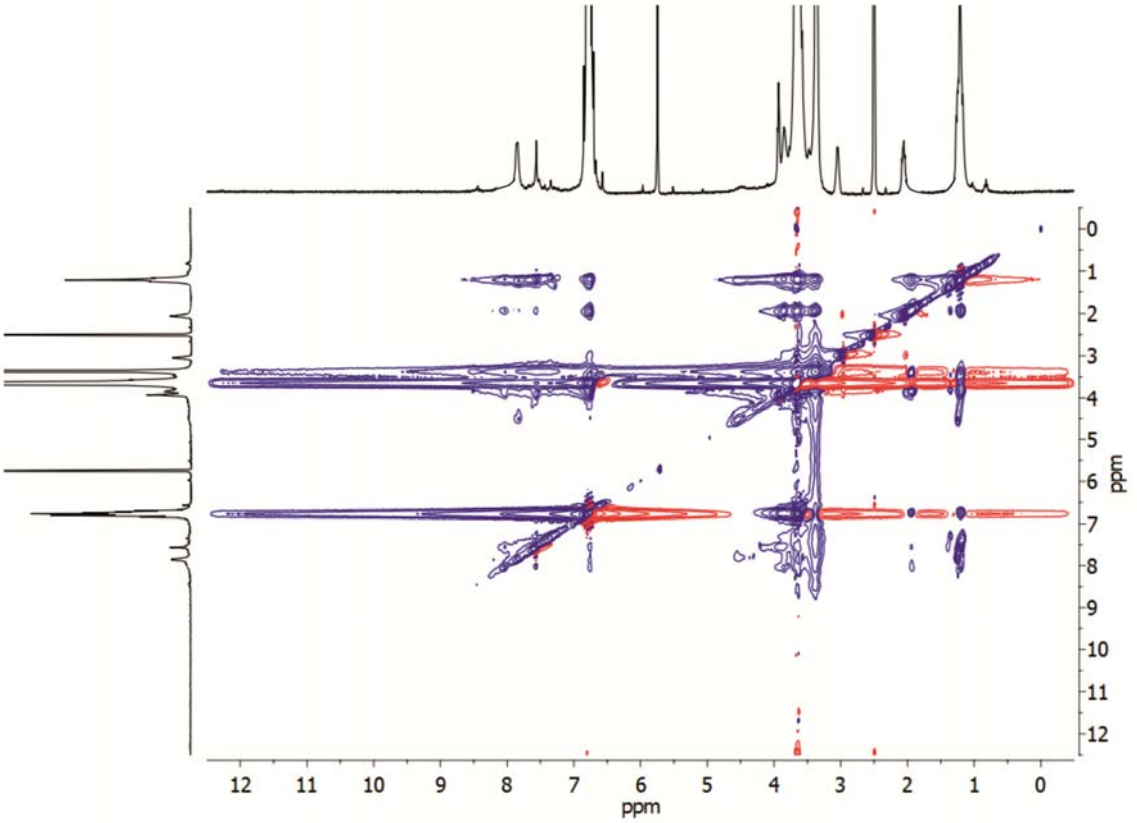
IR spectrum of 4- (bromopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (8).



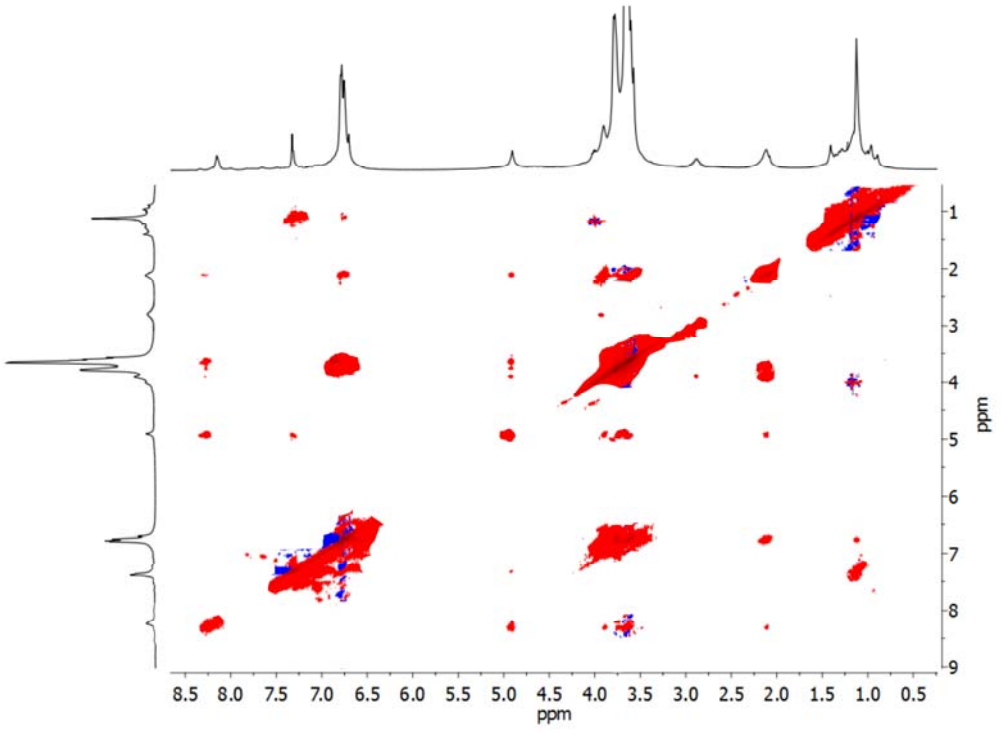
IR spectrum of 4-(azidopropyloxy) -8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (9).



^{1}H-^{1}H NOESY NMR spectrum of Tetrakispillar[5]thiacalix[4]arene in 1,3-alternate configuration (13), DMSO-d_6, 298 K, 400 MHz

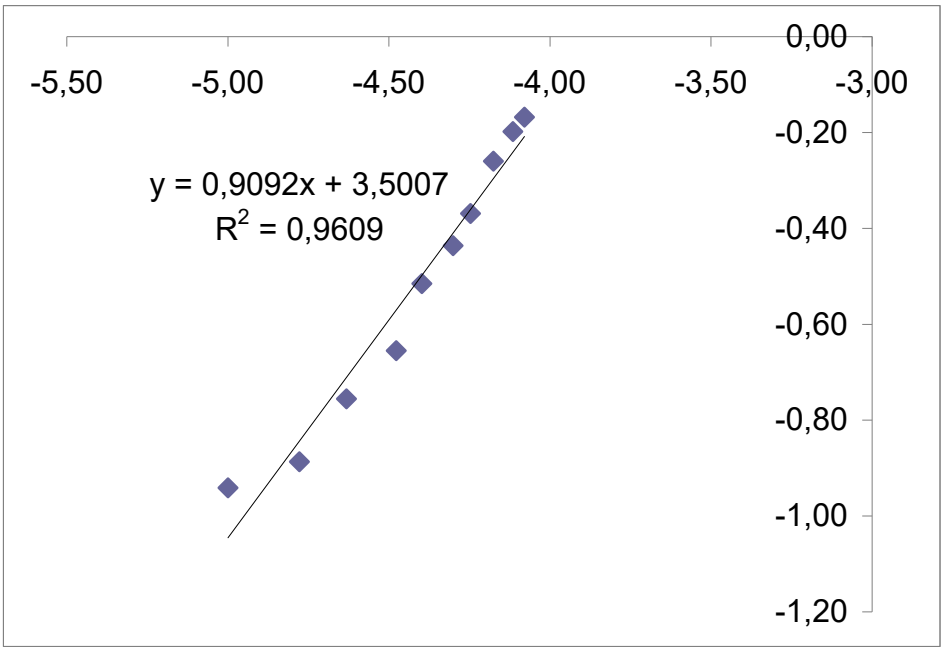


^{1}H-^{1}H NOESY NMR spectrum of Tetrakispillar[5]thiacalix[4]arene in cone configuration (14), DMSO-d_6, 298 K, 400 MHz

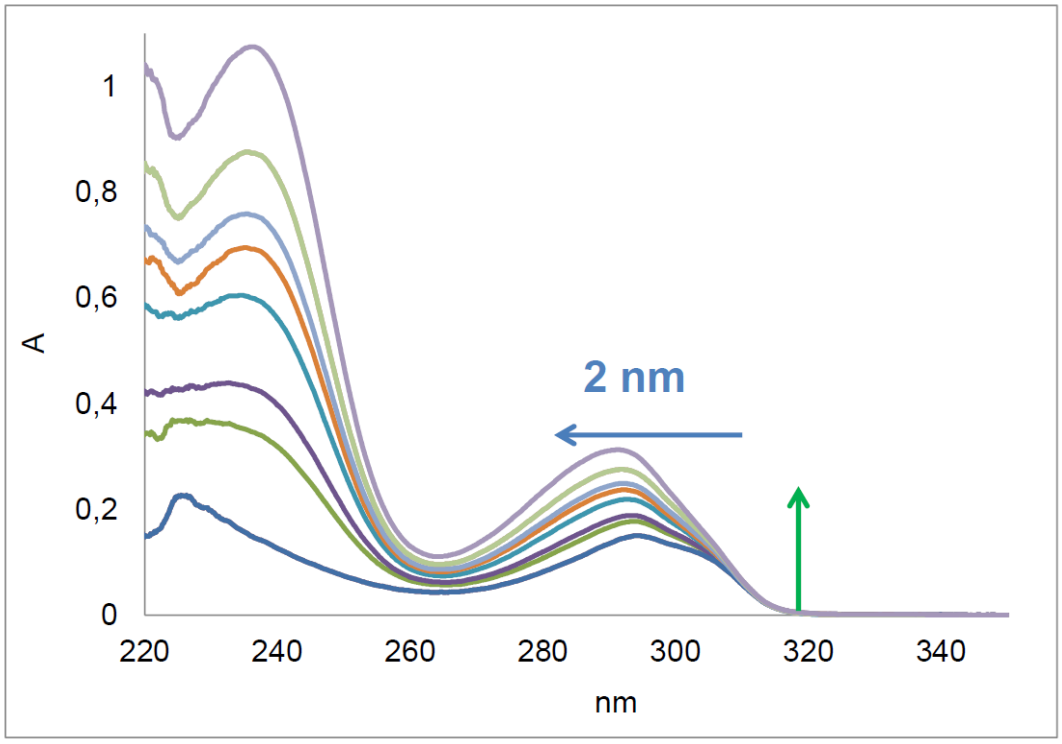


4. UV spectra

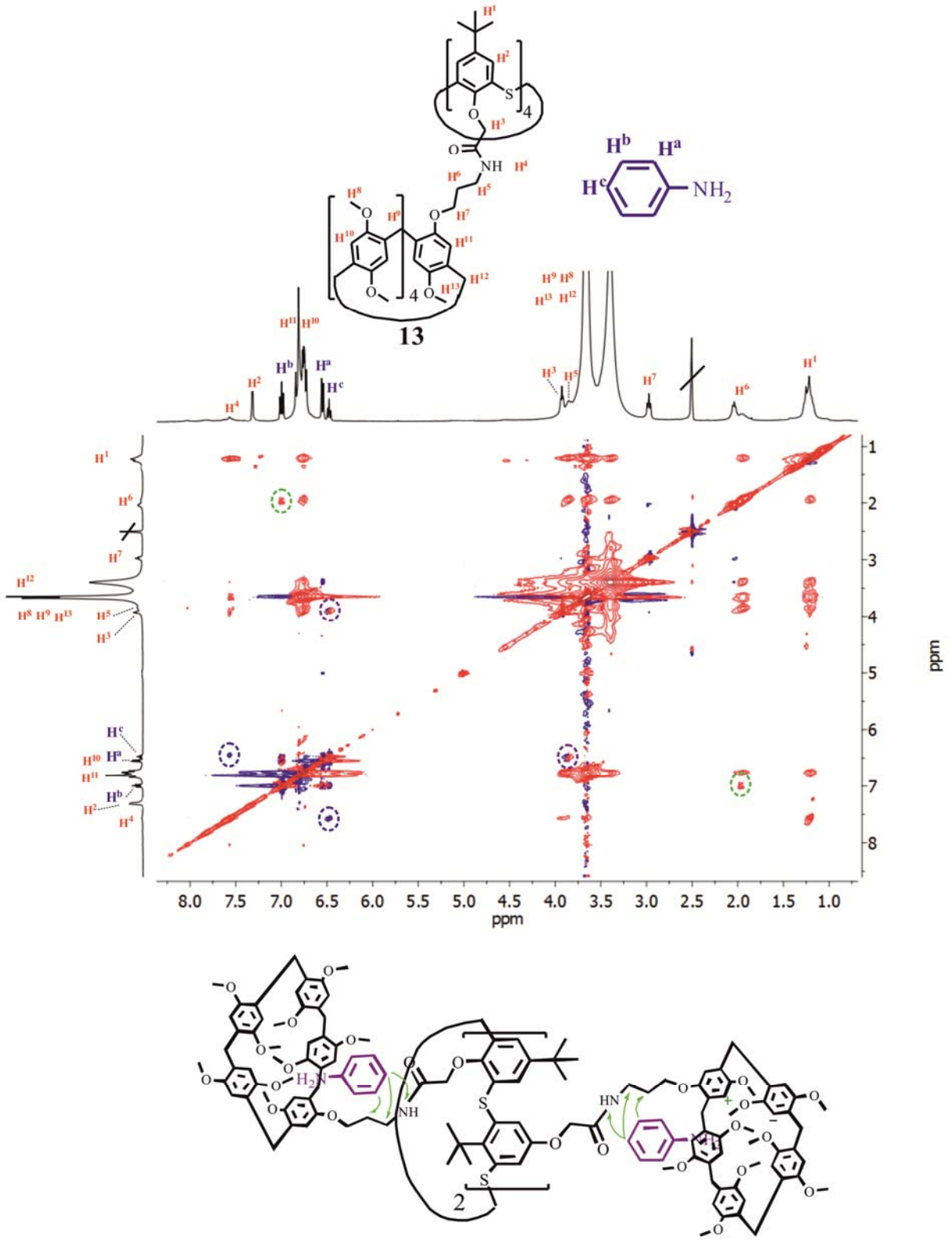
Titration curvefor the system Tetrakispillar[5]thiacalix[4]arene in 1,3-alternate configuration (13)/ aniline



UV titration spectra for the system Tetrakispillar[5]thiacalix[4]arene in 1,3-alternate configuration (13)/ aniline



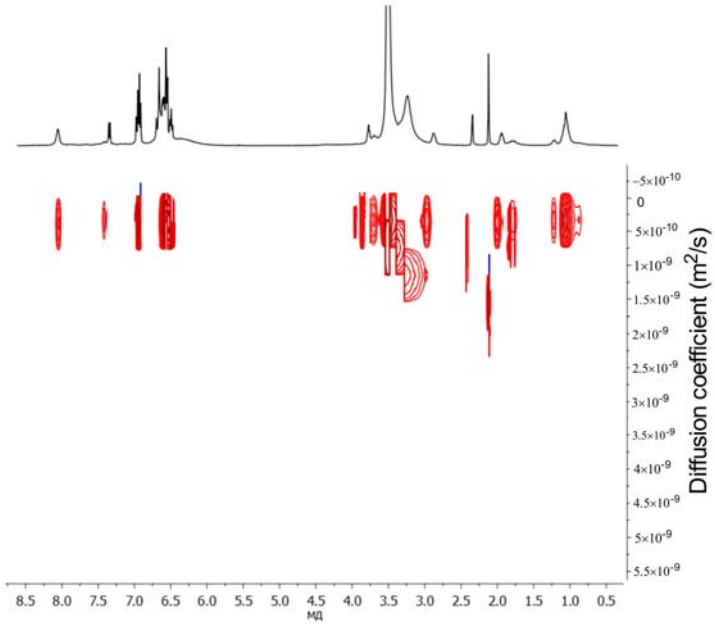
5. 2D ^{1}H-^{1}H NOESY NMR spectrum of the complex 13 with aniline (10^{-2}M)DMSO-d_6, 298 K, 400 MHz and the proposed structure of the complex.



6. Diffusion experiments

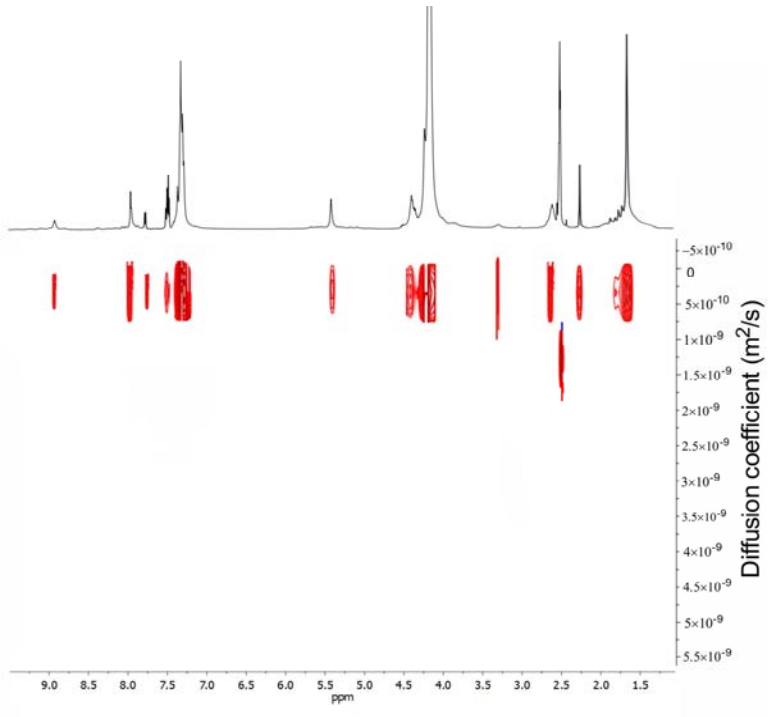
Diffusion coefficients of pure **13**, aniline/p-toluenesulfonic, **13**/p-toluenesulfonic acid/aniline (400 MHz, 298 K).

Compounds	**D (10^{-10} m^2 s^{-1})**
13	2.44
aniline/p-toluenesulfonic	3.22
13/aniline/p-toluenesulfonic	1.92

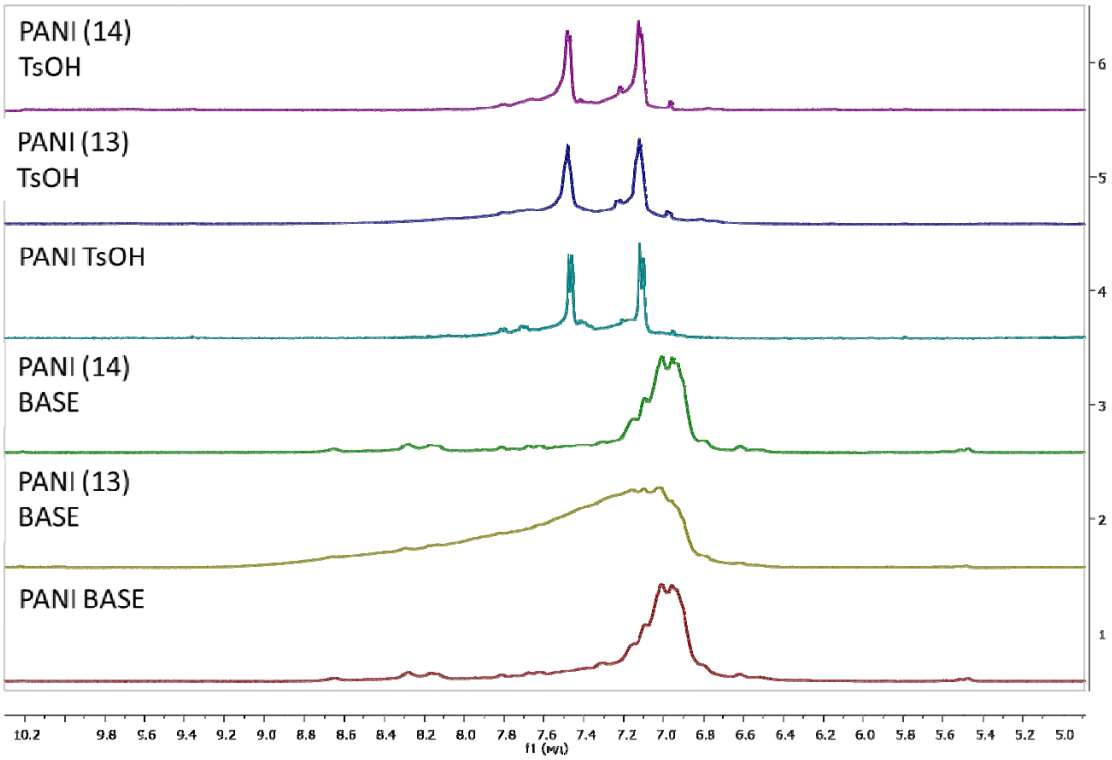


Diffusion coefficients of pure **14**, aniline/p-toluenesulfonic, **14**/p-toluenesulfonic acid/aniline (400 MHz, 298 K).

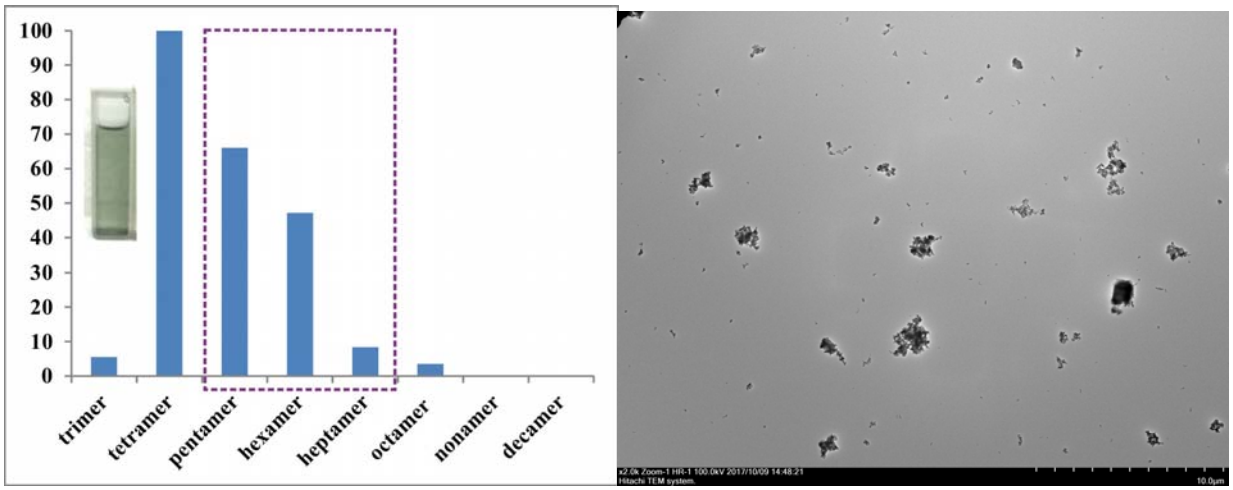
Compounds	**D (10^{-10} m^2 s^{-1})**
14	2.56
aniline/p-toluenesulfonic	3.22
14/aniline/p-toluenesulfonic	1.97



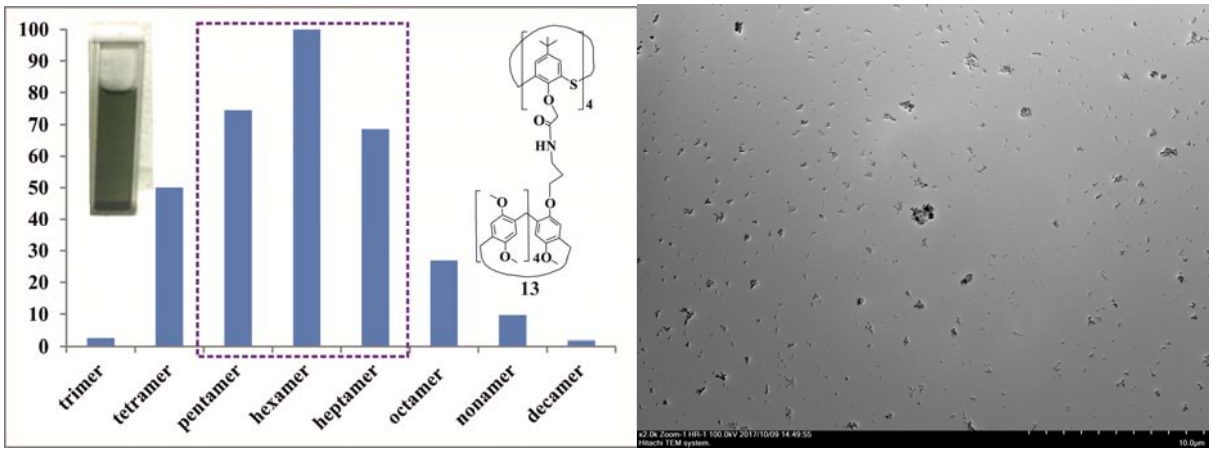
7. ^{1}H NMR spectra of polyaniline p-toluenesulfonates and base samples.



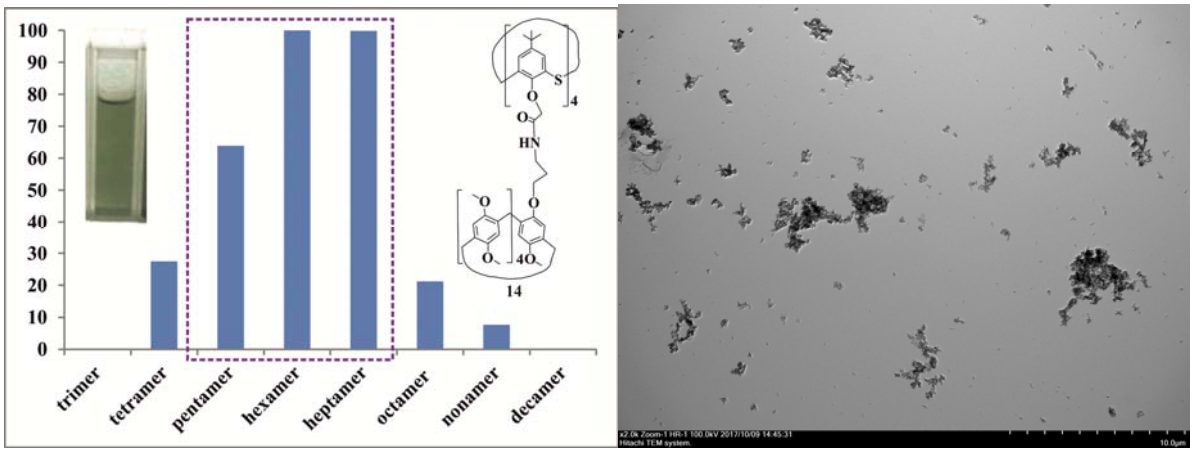
8. Mass distribution of polyaniline synthesized in the presence and absence of multicyclophanes.



Left: a photograph of the dispersion of emeraldine in acetone, the ratio of oligomers, according to the MALDI data of mass spectrometry (HCCA matrix). Right: an image of emeraldine particles obtained without the addition of multycyclophanes, deposited from the dispersion in acetone

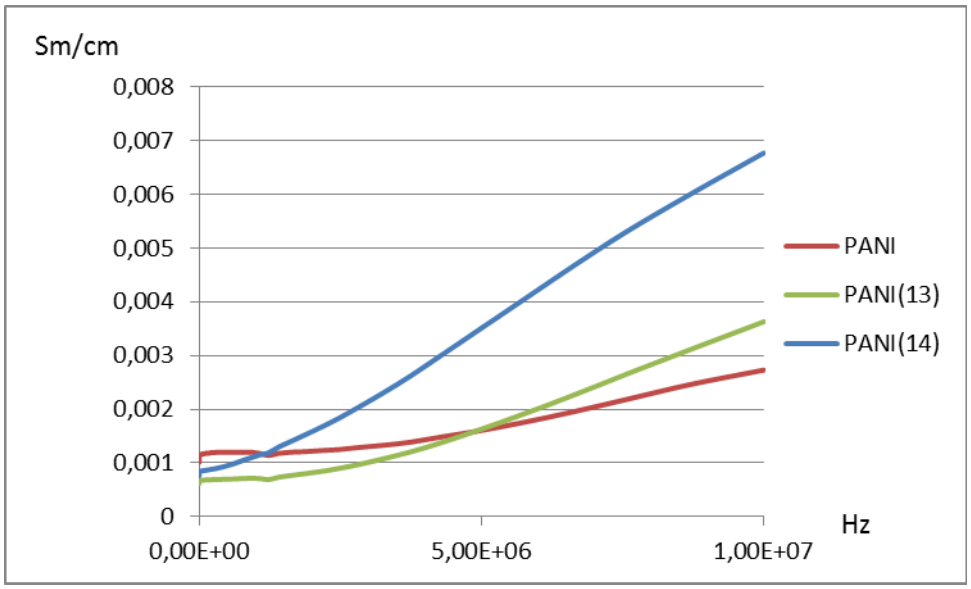


Left: a photograph of the dispersion of emeraldine obtained in the presence of compound **13** in acetone, the ratio of oligomers, according to the MALDI mass spectrometry data (HCCA matrix). Right: an image of emeraldine particles obtained in the presence of Compound **13** applied from a dispersion in acetone.



Left: a photograph of the dispersion of emeraldine obtained in the presence of compound **14** in acetone, the ratio of oligomers, according to the MALDI mass spectrometry data (HCCA matrix). Right: an image of emeraldine particles obtained in the presence of compound **14**, applied from a dispersion in acetone.

9. Conductivity dependence on conditions of emeraldine synthesis: red-emeraldine without additives, green-in presence of cone 14, blue-in presence of 1,3-alternate 13.



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