Макрогетероциклы
http://macroheterocycles.isuct.ru

DOI: 10.6060/mhc170304m

Azide–Akyne *Click* Approach to the Preparation of Dendrimer–Type Multi(thia)calix[4]arenes with Triazole Linkers

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The design of polymacrocyclic structures is of high importance for the improvement of recognition ability to various guests. We present a convenient approach towards two types of dendrimer-shaped pentakis-thiacalix[4]arenes with triazolyl linkers using the click reaction of tetraazidoalkoxycalixarenes with monoalkynyloxy derivatives, as well as tetraalkynyloxycalixarenes with monoazidoalkoxy derivatives. Mitsunobu alkylation of hydroxyl groups has been employed to afford tetrasubstituted derivatives in 1,3-alternate configuration. A facile procedure for the synthesis of monosubstituted cone precursors in high yields by the hydrolysis of one ether fragment in disubstituted counterparts under basic conditions (n-BuNH$_2$ or NaN$_3$ in DMF) has been suggested and optimized. CuAAC reaction has been conducted in microwave reactor and on a hot plate. It has been found that microwave irradiation promotes the reaction and the yields of products are as high as 40–80 %.

Keywords: Multicalixarenes, azide-alkyne cycloaddition, triazoles, microwave irradiation.

Азид–алкинильный *клик*–подход к синтезу мульти(тиа)–каликс[4]аренов дендримерного типа с триазольными мостиками

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Дизайн полимакроциклических структур является важным для улучшения способности распознавания различных "молекул-гостей". Предложен удобный подход к синтезу двух типов дендримерных структур на основе пентакистиакаликс[4]аренов с триазольными мостиками при использовании клик-реакции тетраазидоалкоксикаликсаренов с моноалкинилокси-производными, а также тетраалкинилоксикаликсаренов с моноазидоалкокси-производными. Для получения тетразамещенных производных в конфигурации 1,3-альтернат было использовано алкилирование в условиях реакции Мицунобу. Предложена и оптимизирована удобная методика синтеза монозамещенных прекурсоров в стереоизомерной форме конус с высокими выходами путем гидролиза одного эфирного фрагмента в дизамещенных аналогах в щелочной среде (н-BuNH$_2$ или NaN$_3$ в ДМФА). Реакция CuAAC была проведена в микроволновом реакторе и в условиях обычного нагревания. Было установлено, что микроволновое облучение ускоряет реакции, и выходы продуктов составляют 40–80 %.

Ключевые слова: Мультикаликсарены, азид–алкиновое циклоприсоединение, триазолы, микроволновое облучение.

Introduction

Recently, dendritic structures based on organic molecules attract increasing attention of researchers due to the high concentration of functional groups within a molecule, which may lead to a synergetic effect in molecular recognition phenomena.[1] These nanosized objects take advantage of their monodisperse character (in contrast with hyperbranched polymers) and provide topological encapsulation of specific guests. A promising scaffold for the design of dendrimer structures is represented by macrocycles, in particular, thiacalixarenes, which offer conformational diversity (that can be frozen in case bulky substituents are introduced), variety of reaction centers and their relatively facile modification giving almost unlimited possibilities towards the design of a specific receptor.[2]

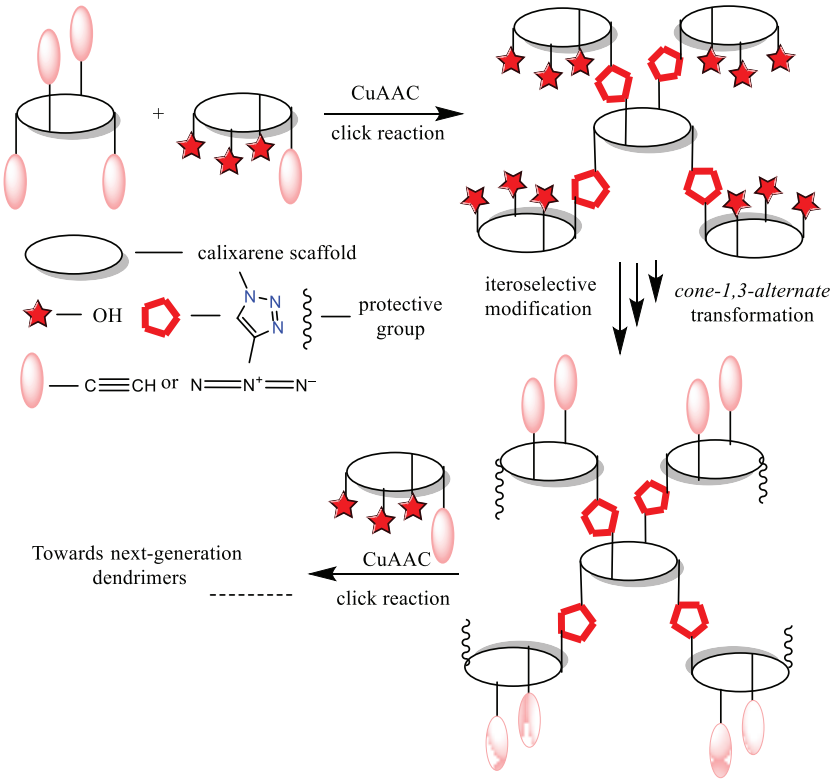
According to published data, multicalixarenes are capable of self-association,[3] they are promising supramolecular drugs,[4] and they can bind large biological objects such as DNA.[5] The complexation of multicalixarenes with metal ions was also studied.[6] There are several structural types of multicalixarenes: spirocycles,[6a,7] tubes,[8] linear polymers,[9] in the synthesis of which polyfunctional reagents are employed and whose preparation may result in a large number of side products involving intramolecular crosslink and/or open-chain compounds. In contrast with these approaches, the formation of calixdendrimers gives less ambiguous synthetic result.[10] The most common synthetic pathway towards dendrimer-shaped multicalixarenes is aminolysis reaction between acid chlorides and amines,[3,10c,10g] which is widely employed because of the valuable recognition properties of the bridging amide functionality towards metal ions and anions. To extend the choice of functional spacer groups, *click* reactions are of particular interest for the synthesis of multicalixarenes such as 1,3-dipolar azide-alkyne cycloaddition due to high rate and regioselectivity of the process.[11] These reactions afford triazole heterocycles, which possess improved complexation properties towards transition metal ions and biological substrates due to pre-organization.[12] However, there are still no reports, where *click* approach was applied to the synthesis of dendrimer multicalixarenes.

The aim of this work was to synthesize dendrimer-shaped multicalixarenes with triazole fragments on the lower rim (Scheme 1). The proposed strategy is focused on the conjugation of tetrasubstituted thiacalix[4]arene in *1,3-alternate* stereoisomeric form as a core with *cone*-shaped monosubstituted thiacalix[4]arenes as a monodendron by CuAAC reaction. In this case, azido or ethynyl groups can be located on the core or dendron. Remaining hydroxyl groups, firstly, may assist binding during polynuclear complex formation and, secondly, serve the points of omnidirectional growth upon modification leading to next-generation dendrimer, when *cone*-to-*1,3-alternate* transition occurs.

Experimental

General

Solvents were purified by known procedures;[13] CuI, NaN_3, TPP, DEAD, and *n*-butylamine were used as received. All reactions were carried out in argon atmosphere in anhydrous solvents. Thiacalixarenes **2**,[14,15a] **4**,[15b] **5**,[15b] **7**[15a,16] were prepared by previously reported procedures. Microwave irradiation was performed in a CEM MARS Xtraction reactor in thick-wall glass



Scheme 1. General pathway towards the synthesis of dendrimer-shaped multicalixarenes by azide–alkyne *click* reaction.

reactors under atmospheric pressure; temperature was controlled using a built-in fiber optic sensor.

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance spectrometers with the working frequencies of 400 and 500 (^{1}H) and 100 (^{13}C) MHz, chemical shifts were determined relative to the signals of residual protons of deuterated solvents ($CDCl_3$). MALDI-TOF mass spectra of molecules were recorded on a Bruker Ultraflex III TOF/TOF mass spectrometer on 4-nitroaniline (10 mg·mL^{-1}, CH_3CN) or 2,5-dihydroxybenzoic acid (10 mg·mL^{-1}, CH_3CN) matrix. Exact masses for all compounds were recorded in high-resolution mode (the most intense peak of isotope cluster). For this purpose, the calibration mixture of PEG-4000 (0.1 mg·mL^{-1}, CH_3CN) with CsCl (1 mg·mL^{-1}, water) was applied along with the analyzed compound (1 mg·mL^{-1}, $CHCl_3$). This composition provided the relative error of mass measurement of less than 5 ppm. Melting points of substances were identified on a Boetius compact heating table with an RNMK 05 visual instrument. The purity of substances was controlled by TLC analysis on Silufol UV 254 plates or MALDI TOF mass-spectrometry. IR spectra were recorded on a Bruker Vector-22 spectrometer; KBr pellet was used as a matrix.

*Synthesis of Compounds **3***

General procedure. A suspension of thiacalix[4]arene **5** (1 eq.) and NaN_3 (10 eq.) was stirred at 90–110 °C in DMF for 30 hours. The solvent was removed and the residue was washed with methanol to give a desired product.

*5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra(2-azidoethoxy)-2,8,14,20-tetrathiacalix[4]arene **(3a)***. (700 mg, 84 %). R_f =0.58 (hexane/ethylacetate 4:1). mp 246 °C (decomp.). *m/z* (HRMS MALDI) (%): 1129.2764 (100) [(M+Cs)$^+$]. Calcd for $C_{48}H_{60}N_{12}O_4S_4$+Cs$^+$: 1129.2792 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1441 s, 1536 s, 1574 s (C_{Ar}–C_{Ar}), 2091 s (N≡N), 2875 s ($C_{t\text{-}Bu}$–$C_{t\text{-}Bu}$), 2964 s (C_{Ar}–H). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 7.40 (8H, s, ArH), 4.01 (8H, t *J*=7 Hz, OCH_2), 2.86 (8H, t *J*=7 Hz, CH_2N), 1.32 (36 H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 31.4 (CH_3), 34.6 ($C_{i,t\text{-}Bu}$), 49.3 (CH_2N), 66.1 (CH_2O), 128.2 (CH_{Ar}), 128.2 ($C_{i,Ar\text{–}t\text{-}Bu}$), 147.1 ($C_{i,Ar\text{–}S}$), 156.2 ($C_{i,Ar\text{–}O}$).

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra(3-azidopropoxy)-2,8,14,20-tetrathiacalix[4]arene (***3b***). (450 mg, 89 %). R_f=0.58 (hexane/ethylacetate 4:1). mp 234 °C (decomp.). *m/z* (HRMS MALDI) (%): 1185.3390 (100) [(M+Cs)$^+$]. Calcd for $C_{52}H_{68}N_{12}O_4S_4$+Cs$^+$: 1185.3418 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1444 s, 1548 s, 1575 s (C_{Ar}-C_{Ar}), 2096 s (N≡N), 2871 s ($C_{t\text{-}Bu}$-$C_{t\text{-}Bu}$), 2963 s (C_{Ar}-H). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 7.34 (8H, s, ArH), 3.93 (8H, t *J*=7 Hz, OCH_2), 2.99 (8H, t *J*=7 Hz, CH_2N), 1.40 (8H, m, OCH_2CH_2), 1.30 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 28.7 (OCH_2CH_2), 31.6 (CH_3), 34.5 ($C_{i,t\text{-}Bu}$), 48.6 (CH_2N), 66.0 (CH_2O), 127.6 (CH_{Ar}), 128.3 ($C_{i,Ar\text{–}t\text{-}Bu}$), 146.4 ($C_{i,Ar\text{–}S}$), 156.6 ($C_{i,Ar\text{–}O}$).

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra(4-azidobutoxy)-2,8,14,20-tetrathiacalix[4]arene (***3c***). (550 mg, 89 %). R_f = 0.56 (hexane/ethylacetate 4:1). mp 247 °C (decomp.). *m/z* (HRMS MALDI) (%): 1241.4046 (100) [(M+Cs)$^+$]. Calcd for $C_{56}H_{76}N_{12}O_4S_4$+Cs$^+$: 1241.4044 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1442 s, 1537 s, 1575 s (C_{Ar}–C_{Ar}), 2092 s (N≡N), 2871 s ($C_{t\text{-}Bu}$–$C_{t\text{-}Bu}$), 2963 s (C_{Ar}–H). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 7.33 (8H, s, ArH), 3.86 (8H, t *J*=8 Hz, OCH_2), 3.17 (8H, t *J*=7 Hz, CH_2N), 1.42 (8H, m, CH_2CH_2O), 1.29 (36H, s, *t*-Bu), 1.18 (8H, m, CH_2CH_2N). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 25.5 (NCH_2CH_2), 26.4 (OCH_2CH_2), 31.4 (CH_3), 34.4 ($C_{i,t\text{-}Bu}$), 51.4 (CH_2N), 68.5 (CH_2O), 128.0 (CH_{Ar}), 128.4 ($C_{i,Ar\text{–}t\text{-}Bu}$), 145.9 ($C_{i,Ar\text{–}S}$), 157.2 ($C_{i,Ar\text{–}O}$).

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra(5-azidopentoxy)-2,8,14,20-tetrathiacalix[4]arene (***3d***). (560 mg, 91 %). R_f =0.59 (hexane/ethylacetate 4:1). mp 250 °C (decomp.). *m/z* (HRMS MALDI) (%): 1187.5542 (100) [(M+Na)$^+$]. Calcd for $C_{60}H_{84}N_{12}O_4S_4$+Na$^+$: 1187.5514 [(M+Na)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1452 s, 1542 s, 1574 s (C_{Ar}–C_{Ar}), 2095 s (N≡N), 2868 s ($C_{t\text{-}Bu}$–H), 2948 s (C_{Ar}–H). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 7.32 (8H, s, ArH), 3.85 (8H, t *J*=8 Hz, OCH_2), 3.22 (8H, t *J*=7 Hz, CH_2N), 1.49 (8H, m, CH_2CH_2O), 1.28 (36H, s, *t*-Bu), 1.23 (8H, m, CH_2CH_2N), 1.09 (8H, m, $CH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 23.1 (CH_2), 28.6 (NCH_2CH_2), 29.1 (OCH_2CH_2), 31.5 (CH_3), 34.4 ($C_{i,t\text{-}Bu}$), 51.6 (CH_2N), 68.5 (CH_2O), 127.8 (CH_{Ar}), 128.3 ($C_{i,Ar\text{–}t\text{-}Bu}$), 145.7 ($C_{i,Ar\text{–}S}$), 157.1 ($C_{i,Ar\text{–}O}$).

*Synthesis of Compounds **6***

General procedure. A suspension of thiacalix[4]arene **3** (1 eq.) and *n*-butylamine (3 eq.) was stirred at 100–125°C in DMF for 7–27 hours. The solvent was removed and the residue was washed with methanol and filtered. Target product was precipitated with HCl (0.1 M) from filtrate.

5,11,17,23-Tetra-tert-butyl–25,26,27-trihydroxy-28-(prop-2-yn-1-yloxy)-2,8,14,20-tetrathiacalix[4]arene (***6a***). (510 mg, 76 %). R_f =0.45 (hexane/ethylacetate 4:1). mp 230 °C (decomp.). *m/z* (HRMS MALDI) (%): 891.1611 (100) [(M+Cs)$^+$]. Calcd for $C_{43}H_{50}O_4S_4$+Cs$^+$: 891.1641 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1364 s, 1394 s ($C_{t\text{-}Bu}$–$C_{t\text{-}Bu}$), 1454 s, 1564 s (C_{Ar}–C_{Ar}), 2963 s (C_{Ar}–H), 3298 s (≡C–H), 3389 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.23 (1H, s, OH), 8.80 (2H, s, OH), 7.64 (2H, AB-d *J*=3 Hz, ArH), 7.61 (2H, AB-d *J*=3 Hz, ArH), 7.59 (2H, s, ArH), 7.55 (2H, s, ArH), 5.29 (2H, d *J*=2 Hz, CH_2), 2.70 (2H, t *J*=2 Hz, ≡CH), 1.25 (18H, s, *t*-Bu), 1.21 (9H, s, *t*-Bu), 1.14 (9H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 31.1 (CH_3), 31.4 (CH_3), 31.5 (CH_3), 34.3 ($C_{i,t\text{-}Bu}$), 34.3 ($C_{i,t\text{-}Bu}$), 34.5 ($C_{i,t\text{-}Bu}$), 63.9 (CH_2), 77.5 (≡CH), 78.2 ($C_{i,\equiv}$), 120.7 ($C_{i,Ar\text{–}S}$), 120.8 ($C_{i,Ar\text{–}S}$), 121.1 ($C_{i,Ar\text{–}S}$), 129.1 ($C_{i,Ar\text{–}S}$), 135.9 (CH_{Ar}), 136.0 (CH_{Ar}), 136.0 (CH_{Ar}), 136.1 (CH_{Ar}), 143.8 ($C_{i,Ar\text{–}t\text{-}Bu}$), 144.1 ($C_{i,Ar\text{–}t\text{-}Bu}$), 149.4 ($C_{i,Ar\text{–}t\text{-}Bu}$), 156.2 ($C_{i,Ar\text{–}O}$), 156.5 ($C_{i,Ar\text{–}O}$), 156.6 ($C_{i,Ar\text{–}O}$).

5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-(but-3-yn-1-yloxy)-2,8,14,20-tetrathiacalix[4]arene (***6b***). (630 mg, 93 %). R_f =0.48 (hexane/ethylacetate 4:1). mp 271 °C (decomp.). *m/z* (HRMS MALDI) (%): 1037.0781 (100) [(M+2Cs-H)$^+$]. Calcd for $C_{44}H_{52}O_4S_4$+2Cs$^+$-H$^+$: 1037.0774 [(M+2Cs-H)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1366 s, 1395 s ($C_{t\text{-}Bu}$–$C_{t\text{-}Bu}$), 1456 s, 1562 s (C_{Ar}–C_{Ar}), 2963 s (C_{Ar}–H), 3296 s (≡C–H), 3389 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.38 (1H, s, OH), 9.06 (2H, s, OH), 7.66 (2H, AB-d *J*=3 Hz, ArH), 7.63 (2H, s, ArH), 7.61 (2H, s, ArH), 7.60 (2H, AB-d *J*=3 Hz, ArH), 4.53 (2H, t *J*=7 Hz, OCH_2), 3.15 (2H, m, $CH_2C\equiv$), 2.17 (2H, t *J*=3 Hz, ≡CH), 1.25 (18H, s, *t*-Bu), 1.23 (9H, s, *t*-Bu), 1.19 (9H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 20.1 (CH_2), 31.2 (CH_3), 31.4 (CH_3), 31.5 (CH_3), 34.3 ($C_{i,t\text{-}Bu}$), 34.3 ($C_{i,t\text{-}Bu}$), 34.6 ($C_{i,t\text{-}Bu}$), 70.6 (≡CH), 75.2 (OCH_2), 80.3 ($C_{i,\equiv}$), 120.6 ($C_{i,Ar\text{–}S}$), 120.9 ($C_{i,Ar\text{–}S}$), 120.9 ($C_{i,Ar\text{–}S}$), 128.6 ($C_{i,Ar\text{–}S}$), 136.0 (CH_{Ar}), 136.1 (CH_{Ar}), 136.1 (CH_{Ar}), 136.7 (CH_{Ar}), 143.8 ($C_{i,Ar\text{–}t\text{-}Bu}$), 144.1 ($C_{i,Ar\text{–}t\text{-}Bu}$), 149.4 ($C_{i,Ar\text{–}t\text{-}Bu}$), 156.3 ($C_{i,Ar\text{–}O}$), 156.8 ($C_{i,Ar\text{–}O}$), 157.8 ($C_{i,Ar\text{–}O}$).

5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-(pent-4-yn-1-yloxy)-2,8,14,20-tetrathiacalix[4]arene (***6c***). (770 mg, 87 %). R_f =0.50 (hexane/ethylacetate 4:1). mp 238 °C. *m/z* (HRMS MALDI) (%): 1051.0928 (100) [(M+2Cs-H)$^+$]. Calcd for $C_{45}H_{54}O_4S_4$+2Cs$^+$-H$^+$: 1051.0930 [(M+2Cs-H)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1365 s, 1394 s ($C_{t\text{-}Bu}$–$C_{t\text{-}Bu}$), 1456 s, 1561 s (C_{Ar}–C_{Ar}), 2118 s (C≡C), 2963 s (C_{Ar}–H), 3301 s (≡C–H), 3385 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.31 (1H, s, OH), 9.09 (2H, s, OH), 7.66 (2H, AB-d *J*=2 Hz, ArH), 7.62 (2H, s, ArH), 7.61 (2H, AB-d *J*=2 Hz, ArH), 7.60 (2H, s, ArH), 4.50 (2H, t *J*=6 Hz, OCH_2), 2.75 (2H, m, $CH_2C\equiv$), 2.40 (2H, m, CH_2), 2.05 (1H, t *J*=3 Hz, ≡CH), 1.25 (18H, s, *t*-Bu), 1.22 (9H, s, *t*-Bu), 1.18 (9H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 15.4 (CH_2), 28.7 (CH_2), 30.9 (CH_3), 31.1 (CH_3), 31.2 (CH_3), 33.9 ($C_{i,t\text{-}Bu}$), 34.0 ($C_{i,t\text{-}Bu}$), 34.3 ($C_{i,t\text{-}Bu}$), 68.8 (≡CH), 77.2 (OCH_2), 83.6 ($C_{i,\equiv}$), 120.1 ($C_{i,Ar\text{–}S}$), 120.6 ($C_{i,Ar\text{–}S}$), 120.8 ($C_{i,Ar\text{–}S}$), 128.3 ($C_{i,Ar\text{–}S}$), 135.7 (CH_{Ar}), 135.7 (CH_{Ar}), 135.7

(CH_{Ar}), 136.5 (CH_{Ar}), 143.5 ($C_{i,Ar–t-Bu}$), 143.8 ($C_{i,Ar–t-Bu}$), 148.9 ($C_{i,Ar–t-Bu}$), 155.9 ($C_{i,Ar–O}$), 156.5 ($C_{i,Ar–O}$), 157.6 ($C_{i,Ar–O}$).

5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-(hex-5-yn-1-yloxy)-2,8,14,20-tetrathiacalix[4]arene (***6d***). (1460 mg, 91 %). R_f = .49 (hexane/ethylacetate 4:1). mp 182 °C (decomp.). *m/z* (HRMS MALDI) (%): 933.2081 (100) [(M+Cs)$^+$]. Calcd for $C_{46}H_{56}O_4S$+Cs^+: 933.2110 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1364 s, 1394 s (C_{t-Bu}–H), 1455 s, 1563 s (C_{Ar}-C_{Ar}), 2118 s (C≡C), 2962 s (C_{Ar}–H), 3313 s (≡C–H), 3383 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.33 (1H, s, OH), 9.16 (2H, s, OH), 7.66 (2H, AB-d *J*=2 Hz, ArH), 7.63 (2H, s, ArH), 7.61 (2H, AB-d *J*=2 Hz, ArH), 7.60 (2H, s, ArH), 4.42 (2H, t *J*=7 Hz, OCH_2), 2.49 (2H, m, CH_2C≡), 2.32 (2H, m, CH_2), 2.04 (1H, t *J*=2 Hz, ≡CH), 2.02 (2H, m, CH_2), 1.25 (18H, s, *t*-Bu), 1.22 (9H, s, *t*-Bu), 1.19 (9H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 18.0 (CH_2), 24.6 (CH_2), 28.5 (CH_2), 30.9 (CH_3), 31.1 (CH_3), 31.2 (CH_3), 33.9 ($C_{i,t-Bu}$), 34.0 ($C_{i,t-Bu}$), 34.3 ($C_{i,t-Bu}$), 68.6(≡CH), 77.5 (OCH_2), 84.1 ($C_{i,≡}$), 120.2 ($C_{i,Ar–S}$), 120.6 ($C_{i,Ar–S}$), 120.8 ($C_{i,Ar–S}$), 128.3 ($C_{i,Ar–S}$), 135.7 (CH_{Ar}), 135.7 (CH_{Ar}), 135.8 (CH_{Ar}), 136.5 (CH_{Ar}), 143.4 ($C_{i,Ar–t-Bu}$), 143.8 ($C_{i,Ar–t-Bu}$), 148.9 ($C_{i,Ar–t-Bu}$), 156.0 ($C_{i,Ar–O}$), 156.5 ($C_{i,Ar–O}$), 157.8 ($C_{i,Ar–O}$).

*Synthesis of Compounds **8***

General procedure. A suspension of thiacalix[4]arene **7** (1 eq.) and NaN_3 (10 eq.) was stirred at 90 °C in DMF for 12–17 hours. The solvent was removed and the residue was washed with methanol and filtered. Target product was precipitated with HCl (0.1 M) from filtrate.

5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-(2-azidoethoxy)-2,8,14,20-tetrathiacalix[4]arene (***8a***). (890 mg, 86 %). R_f =0.40 (hexane/ethylacetate 4:1). mp 241 °C. *m/z* (HRMS MALDI) (%): 1054.0766 (100) [(M+2Cs-H)$^+$]. Calcd for $C_{42}H_{51}N_3O_4S_4$+2Cs^+-H^+: 1054.0788 [(M+2Cs-H)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1246 s (C_{t-Bu}–C_{t-Bu}), 1459 s, 1564 s (C_{Ar}–C_{Ar}), 2106 s (N≡N), 2869 s (C_{t-Bu}–H), 2963 s (C_{Ar}–H), 3381 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.36 (1H, s, OH), 9.03 (2H, s, OH), 7.65 (2H, AB-d *J*=3 Hz, ArH), 7.62 (2H, s, ArH), 7.62 (2H, s, ArH), 7.60 (2H, AB-d *J*=3 Hz, ArH), 4.54 (2H, t *J*=5 Hz, OCH_2), 4.10 (2H, t *J*=5 Hz, CH_2N), 1.24 (18H, s, *t*-Bu), 1.23 (9H, s, *t*-Bu), 1.18 (9H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 31.2 (CH_3), 31.4 (CH_3), 31.4 (CH_3), 34.3 ($C_{i,t-Bu}$), 34.3 ($C_{i,t-Bu}$), 34.6 ($C_{i,t-Bu}$), 51.3 (NCH_2), 75.1 (OCH_2), 120.6 ($C_{i,Ar–S}$), 120.8 ($C_{i,Ar–S}$), 120.9 ($C_{i,Ar–S}$), 128.5 ($C_{i,Ar–S}$), 136.1 (CH_{Ar}), 136.1 (CH_{Ar}), 136.2 (CH_{Ar}), 136.7 (CH_{Ar}), 143.8 ($C_{i,Ar–t-Bu}$), 144.1 ($C_{i,Ar–t-Bu}$), 149.4 ($C_{i,Ar–t-Bu}$), 156.3 ($C_{i,Ar–O}$), 156.8 ($C_{i,Ar–O}$), 157.8 ($C_{i,Ar–O}$).

5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-(3-azidopropoxy)-2,8,14,20-tetrathiacalix[4]arene (***8b***). (360 mg, 82 %). R_f =0.44 (hexane/ethylacetate 4:1). mp 255 °C. *m/z* (HRMS MALDI) (%): 1068.0920 (100) [(M+2Cs-H)$^+$]. Calcd for $C_{43}H_{53}N_3O_4S_4$+2Cs^+-H^+: 1068.0944 [(M+2Cs-H)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1245 s (C_{t-Bu}–C_{t-Bu}), 1457 s, 1565 s (C_{Ar}–C_{Ar}), 2096 s (N≡N), 2863 s (C_{t-Bu}–H), 2963 s (C_{Ar}–H), 3381 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.20 (2H, s, OH), 7.67 (2H, AB-d *J*=3 Hz, ArH), 7.61 (2H, s, ArH), 7.60 (2H, s, ArH), 7.60 (2H, br, ArH), 7.58 (1H, br, OH), 4.43 (2H, t *J*=6 Hz, OCH_2), 3.95 (2H, t *J*=7 Hz, CH_2N), 2.39 (2H, m, CH_2), 1.25 (18H, s, *t*-Bu), 1.22 (9H, s, *t*-Bu), 1.14 (9H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 29.7 (CH_2), 31.1 (CH_3), 31.4 (CH_3), 31.5 (CH_3), 34.3 ($C_{i,t-Bu}$), 34.3 ($C_{i,t-Bu}$), 34.6 ($C_{i,t-Bu}$), 48.5 (NCH_2), 75.2 (OCH_2), 120.7 ($C_{i,Ar–S}$), 121.0 ($C_{i,Ar–S}$), 121.2 ($C_{i,Ar–S}$), 128.7 ($C_{i,Ar–S}$), 136.0 (CH_{Ar}), 136.1 (CH_{Ar}), 143.8 ($C_{i,Ar–t-Bu}$), 149.4 ($C_{i,Ar–t-Bu}$), 156.7 ($C_{i,Ar–O}$).

*Synthesis of Compounds **9–14***

General procedure. A suspension of thiacalix[4]arenes **2**, **6** (1 eq.), thiacalix[4]arenes **4**, **8** (4-6 eq.) and CuI (6 eq.) in toluene–Et_3N (2:1 v/v) was stirred at 70 °C for 12 h (400 W, 24 cycles 30 min each). The solvent was evaporated; a residue was transferred into dichloromethane and washed with water containing trilon-B until aqueous phase became colorless. Organic phase was dried over Na_2SO_4, the solvent was evaporated under vacuum, and a target product was precipitated with methanol from residue. The product was purified by column chromatography on silica gel (eluent: hexane/ethylacetate (4:1 to 1:1 gradient)).

*Compound **9a***. (190 mg, 77 %). R_f=0.18 ($CHCl_3$/MeOH 40:1). mp 208 °C (decomp.). *m/z* (HRMS MALDI) (%): 4166.3101 (100) [(M+Cs)$^+$]. Calcd for $C_{220}H_{260}N_{12}O_{20}S_{20}$+$Cs^+$: 4166.3209 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1267 s (C_{t-Bu}–C_{t-Bu}), 1453 s (C_{Ar}–C_{Ar}), 1627 s (C=C), 2869 s (C_{t-Bu}–H), 2962 s (C_{Ar}–H), 3380 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.29 (4H, br, OH), 8.88 (8H, br, OH), 7.78 (4H, br, CH_{triaz}), 7.60 (8H, br, ArH), 7.59 (8H, AB-d *J*=3 Hz, ArH), 7.57 (8H; AB-d *J*=3 Hz, ArH), 7.55 (8H, br, ArH), 7.37 (8H, s, ArH), 5.26 (8H, br, CH_2), 4.81 (8H, br, CH_2), 1.32 (8H, br, CH_2), 1.22 (72H, br, *t*-Bu), 1.20 (36H, br, *t*-Bu), 1.14 (36H, br, *t*-Bu), 1.08 (36H, br, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 29.8 (CH_2), 31.0 (CH_3), 31.2 (CH_3), 31.3 (CH_3), 31.4 (CH_3), 34.2 ($C_{i,t-Bu}$), 34.4 ($C_{i,t-Bu}$), 34.4 ($C_{i,t-Bu}$), 34.5 ($C_{i,t-Bu}$), 50.0 (CH_2), 75.2 (OCH_2), 120.4 ($C_{i,Ar–S}$), 120.5 ($C_{i,Ar–S}$), 120.8 ($C_{i,Ar–S}$), 123.1 (CH_{triaz}), 128.4 ($C_{i,Ar–S}$), 128.5 ($C_{i,Ar–S}$), 129.8 (CH_{Ar}), 136.0 (CH_{Ar}), 136.2 (CH_{Ar}), 136.2 (CH_{Ar}), 136.4 (CH_{Ar}), 143.1 ($C_{i,Ar–t-Bu}$), 143.5 ($C_{i,Ar–t-Bu}$), 143.7 ($C_{i,Ar–t-Bu}$), 146.2 ($C_{i,Ar–t-Bu}$), 149.3 ($C_{i,triaz}$), 155.8 ($C_{i,Ar–O}$), 156.3 ($C_{i,Ar–O}$), 156.5 ($C_{i,Ar–O}$), 156.6 ($C_{i,Ar–O}$).

*Compound **9b***. (110 mg, 78 %). R_f=0.25 ($CHCl_3$/MeOH 40:1). mp 217 °C (decomp.). *m/z* (HRMS MALDI) (%): 4222.3720 (100) [(M+Cs)$^+$]. Calcd for $C_{224}H_{268}N_{12}O_{20}S_{20}$+$Cs^+$: 4222.3837 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1267 s (C_{t-Bu}–C_{t-Bu}), 1451 s (C_{Ar}–C_{Ar}), 1625 s (C=C), 2870 s (C_{t-Bu}–H), 2962 s (C_{Ar}–H), 3381 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.28 (4H, br, OH), 8.83 (8H, br, OH), 7.98 (4H, br, CH_{triaz}), 7.65 (8H, br, ArH), 7.57 (8H, br, ArH), 7.54 (8H, br, ArH), 7.51 (8H, br, ArH), 7.36 (8H, br, ArH), 5.12 (8H, br, CH_2), 4.84 (8H, br, CH_2), 4.32 (8H, br, CH_2), 2.55 (8H, br, CH_2), 1.27 (36H, s, *t*-Bu), 1.23 (72H, s, *t*-Bu), 1.21 (36H, s, *t*-Bu), 1.12 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 25.4 (CH_2), 29.6 (CH_2), 30.9 (CH_3), 31.3 (CH_3), 31.3 (CH_3), 31.3 (CH_3), 34.1 ($C_{i,t-Bu}$), 34.1 ($C_{i,t-Bu}$), 34.3 ($C_{i,t-Bu}$), 34.3 ($C_{i,t-Bu}$), 50.0 (CH_2), 66.5 (OCH_2), 120.3 ($C_{i,Ar–S}$), 120.7 ($C_{i,Ar–S}$), 120.8 ($C_{i,Ar–S}$), 122.4 (CH_{triaz}), 128.0 ($C_{i,Ar–S}$), 128.1 ($C_{i,Ar–S}$), 128.2 (CH_{Ar}), 135.9 (CH_{Ar}), 136.0 (CH_{Ar}), 136.0 (CH_{Ar}), 136.4 (CH_{Ar}), 143.7 ($C_{i,Ar–t-Bu}$), 143.8 ($C_{i,Ar–t-Bu}$), 144.0 ($C_{i,Ar–t-Bu}$), 146.3 ($C_{i,Ar–t-Bu}$), 149.4 ($C_{i,triaz}$), 155.9 ($C_{i,Ar–O}$), 156.4 ($C_{i,Ar–O}$), 156.4 ($C_{i,Ar–O}$), 157.3 ($C_{i,Ar–O}$).

*Compound **9c***. (160 mg, 73 %). R_f=0.24 ($CHCl_3$/MeOH 40:1). mp 193 °C (decomp.). *m/z* (HRMS MALDI) (%): 4278.4259 (100) [(M+Cs)$^+$]. Calcd for $C_{228}H_{276}N_{12}O_{20}S_{20}$+$Cs^+$: 4278.4464 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s (C_{t-Bu}–C_{t-Bu}), 1452 s (C_{Ar}–C_{Ar}), 1628 s (C=C); 2869 s (C_{t-Bu}–H), 2962 s (C_{Ar}–H), 3381 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.25 (4H, br, OH), 8.84 (8H, br, OH), 8.06 (4H, br, CH_{triaz}), 7.63 (8H, AB-d *J*=2 Hz, ArH), 7.59 (8H, br, ArH), 7.58 (8H, AB-d *J*=2 Hz, ArH), 7.54 (8H, br, ArH), 7.31 (8H; br, ArH), 5.25 (8H, t *J*=5 Hz, CH_2), 4.85 (8H, t *J*=5 Hz, CH_2), 4.01 (8H, t *J*=7 Hz, CH_2), 2.73 (8H, t *J*=8 Hz, CH_2), 1.69 (8H, t *J*=7 Hz, CH_2), 1.22 (72H, s, *t*-Bu), 1.21 (36H, s, *t*-Bu), 1.13 (36H, s, *t*-Bu), 1.09 (36H, br, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 22.4 (CH_2), 28.5 (CH_2), 30.8 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 31.1 (CH_3), 33.9 ($C_{i,t-Bu}$), 33.9 ($C_{i,t-Bu}$), 34.0 ($C_{i,t-Bu}$), 34.2 ($C_{i,t-Bu}$), 49.6 (CH_2), 68.9 (CH_2), 75.5 (OCH_2), 120.0 ($C_{i,Ar–S}$), 120.6 ($C_{i,Ar–S}$), 120.8 ($C_{i,Ar–S}$), 122.5 (CH_{triaz}), 127.8 ($C_{i,Ar–S}$), 128.0 ($C_{i,Ar–S}$), 128.4 (CH_{Ar}), 135.8 (CH_{Ar}), 135.9 (CH_{Ar}), 136.3 (CH_{Ar}), 136.4 (CH_{Ar}), 143.5 ($C_{i,Ar–t-Bu}$), 143.5 ($C_{i,Ar–t-Bu}$), 143.8 ($C_{i,Ar–t-Bu}$), 147.5 ($C_{i,Ar–t-Bu}$), 149.1 ($C_{i,triaz}$), 155.9 ($C_{i,Ar–O}$), 156.3 ($C_{i,Ar–O}$), 157.1 ($C_{i,Ar–O}$), 157.5 ($C_{i,Ar–O}$).

*Compound **9d***. (260 mg, 65 %). R_f=0.18 ($CHCl_3$/MeOH 40:1). mp 127 °C (decomp.). *m/z* (HRMS MALDI) (%): 4334.4991 (100) [(M+Cs)$^+$]. Calcd for $C_{232}H_{284}N_{12}O_{20}S_{20}$+$Cs^+$: 4334.5091 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s (C_{t-Bu}–C_{t-Bu}), 1453 s (C_{Ar}–C_{Ar}), 1628 s (C=C), 2869 s (C_{t-Bu}–H), 2962 s (C_{Ar}–H), 3376 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.34 (4H, br, OH), 8.97 (8H, br, OH), 8.07 (4H, br, CH_{triaz}), 7.67 (8H, AB-d *J*=1 Hz, ArH), 7.65 (8H, br, ArH),

7.64 (8H, AB-d *J*=1 Hz, ArH), 7.57 (8H, br, ArH), 7.34 (8H, br, ArH), 5.16 (8H, m, CH_2), 4.80 (8H, m, CH_2), 3.85 (8H, m, CH_2), 2.82 (8H, t *J*=8 Hz, CH_2), 1.73 (8H, m, CH_2), 1.39 (8H, m, CH_2), 1.23 (144H, s, *t*-Bu), 1.15 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 22.6 (CH_2), 28.7 (CH_2), 29.7 (CH_2), 30.8 (CH_3), 31.0 (CH_3), 31.0 (CH_3), 31.3 (CH_3), 34.1 ($C_{i,t\text{-Bu}}$),34.1 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 34.4 ($C_{i,t\text{-Bu}}$), 49.8 (CH_2), 69.0 (CH_2), 75.7 (OCH_2), 120.2 ($C_{i,Ar\text{–}S}$), 120.7 ($C_{i,Ar\text{–}S}$), 121.0 ($C_{i,Ar\text{–}S}$), 122.7 (CH_{triaz}), 128.2 ($C_{i,Ar\text{–}S}$), 128.3 ($C_{i,Ar\text{–}S}$), 128.3 (CH_{Ar}), 136.0 (CH_{Ar}), 136.0 (CH_{Ar}), 136.1 (CH_{Ar}), 136.5 (CH_{Ar}), 143.7 ($C_{i,Ar\text{–}t\text{-Bu}}$), 144.1 ($C_{i,Ar\text{–}t\text{-Bu}}$), 145.6 ($C_{i,Ar\text{–}t\text{-Bu}}$), 147.7 ($C_{i,Ar\text{–}t\text{-Bu}}$), 149.3 ($C_{i,triaz}$), 156.1 ($C_{i,Ar\text{–}O}$), 156.5 ($C_{i,Ar\text{–}O}$), 157.3 ($C_{i,Ar\text{–}O}$), 157.6 ($C_{i,Ar\text{–}O}$).

Compound ***10a***. (230 mg, 48 %). R_f =0.68 ($CHCl_3$/MeOH 40:1). mp 157 °C (decomp.). *m/z* (HRMS MALDI) (%): 4222.3740 (100) [(M+Cs)$^+$]. Calcd for $C_{224}H_{268}N_{12}O_{20}S_{20}$+Cs$^+$: 4222.3837 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1269 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1453 s (C_{Ar}–C_{Ar}), 2870 s ($C_{t\text{-Bu}}$–H), 2962 s (C_{Ar}–H), 3378 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.40 (4H, br, OH), 9.19 (8H, s, OH), 7.64 (8H, AB-d *J*=2 Hz, ArH), 7.60 (16H, s, ArH), 7.58 (8H, AB-d *J*=2 Hz, ArH), 7.49 (4H, br, CH_{triaz}), 7.29 (8H, s, ArH), 5.10 (8H, br, CH_2), 5.09 (8H, m, CH_2), 4.44 (8H, t *J*=5 Hz, CH_2), 2.79 (8H, t *J*=5 Hz, CH_2), 1.23 (72H, s, *t*-Bu), 1.21 (36H, s, *t*-Bu), 1.16 (36H, s, *t*-Bu), 1.09 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 30.8 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 31.1 (CH_3), 33.9 ($C_{i,t\text{-Bu}}$), 33.9 ($C_{i,t\text{-Bu}}$), 34.0 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 47.0 (CH_2), 63.7 (CH_2), 74.8 (OCH_2), 120.1 ($C_{i,Ar\text{–}S}$), 120.5 ($C_{i,Ar\text{–}S}$), 120.8 ($C_{i,Ar\text{–}S}$), 123.9 (CH_{triaz}), 128.3 ($C_{i,Ar\text{–}S}$), 128.4 ($C_{i,Ar\text{–}S}$), 129.8 (CH_{Ar}), 135.8 (CH_{Ar}), 135.8 (CH_{Ar}), 135.8 (CH_{Ar}), 136.6 (CH_{Ar}), 143.5 ($C_{i,Ar\text{–}t\text{-Bu}}$), 143.8 ($C_{i,Ar\text{–}t\text{-Bu}}$), 143.9 ($C_{i,Ar\text{–}t\text{-Bu}}$), 146.3 ($C_{i,Ar\text{–}t\text{-Bu}}$), 149.1 ($C_{i,triaz}$), 155.9 ($C_{i,Ar\text{–}O}$), 156.2 ($C_{i,Ar\text{–}O}$), 156.4 ($C_{i,Ar\text{–}O}$), 157.4 ($C_{i,Ar\text{–}O}$).

Compound ***10b***. (270 mg, 60 %). R_f =0.65 ($CHCl_3$/MeOH 40:1). mp 144 °C (decomp.). *m/z* (HRMS MALDI) (%): 4278.4368 (100) [(M+Cs)$^+$]. Calcd for $C_{228}H_{276}N_{12}O_{20}S_{20}$+Cs$^+$: 4278.4464 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1451 (C_{Ar}–C_{Ar}), 1627 s (C=C), 2869 s ($C_{t\text{-Bu}}$–H), 2962 s (C_{Ar}–H), 3380 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.47 (4H, br, OH), 9.29 (8H, br, OH), 7.94 (4H, br, CH_{triaz}), 7.71 (8H, AB-d *J*=2 Hz, ArH), 7.64 (8H, br, ArH), 7.64 (8H, s, ArH), 7.62 (8H, AB-d *J*=2 Hz, ArH), 7.43 (8H, br, ArH), 5.04 (8H, br, CH_2), 4.30 (8H, br, CH_2), 4.27 (8H, br, CH_2), 2.78 (8H, br, CH_2), 2.53 (8H, br, CH_2), 1.24 (72H, s, *t*-Bu), 1.23 (72H, s, *t*-Bu), 1.18 (36H, s, *t*-Bu), 1.13 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 25.4 (CH_2), 30.6 (CH_2), 30.8 (CH_3), 31.0 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 33.9 ($C_{i,t\text{-Bu}}$), 34.0 ($C_{i,t\text{-Bu}}$), 34.0 ($C_{i,t\text{-Bu}}$), 34.3 ($C_{i,t\text{-Bu}}$), 46.3 (CH_2), 66.5 (CH_2), 74.3 (OCH_2), 120.0 ($C_{i,Ar\text{–}S}$), 120.6 ($C_{i,Ar\text{–}S}$), 120.7 ($C_{i,Ar\text{–}S}$), 122.6 (CH_{triaz}), 127.6 ($C_{i,Ar\text{–}S}$), 128.0 ($C_{i,Ar\text{–}S}$), 128.3 (CH_{Ar}), 135.9 (CH_{Ar}), 135.9 (CH_{Ar}), 136.0 (CH_{Ar}), 136.8 (CH_{Ar}), 143.2 ($C_{i,Ar\text{–}t\text{-Bu}}$), 143.7 ($C_{i,Ar\text{–}t\text{-Bu}}$), 144.0 ($C_{i,Ar\text{–}t\text{-Bu}}$), 146.0 ($C_{i,Ar\text{–}t\text{-Bu}}$), 149.4 ($C_{i,triaz}$), 155.8 ($C_{i,Ar\text{–}O}$), 156.2 ($C_{i,Ar\text{–}O}$), 156.4 ($C_{i,Ar\text{–}O}$), 157.3 ($C_{i,Ar\text{–}O}$).

Compound ***10c***. (280 mg, 66 %). R_f =0.67 ($CHCl_3$/MeOH 40:1). mp 139 °C (decomp.). *m/z* (HRMS MALDI) (%): 4334.4952 (100) [(M+Cs)$^+$]. Calcd for $C_{232}H_{284}N_{12}O_{20}S_{20}$+Cs$^+$: 4334.5091 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1451 s (C_{Ar}–C_{Ar}), 1627 s (C=C), 2869 s ($C_{t\text{-Bu}}$–H), 2961 s (C_{Ar}–H), 3364 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.45 (4H, br, OH), 9.25 (8H, br, OH), 8.08 (4H, br, CH_{triaz}), 7.66 (8H, AB-d *J*=2 Hz, ArH), 7.62 (8H, br, ArH), 7.61 (8H, br, ArH), 7.60 (8H, AB-d *J*=2 Hz, ArH), 7.31 (8H, s, ArH), 5.14 (8H, br, CH_2), 4.37 (8H, br, CH_2), 3.95 (8H, br, CH_2), 2.84 (8H, br, CH_2), 2.66 (8H, br, CH_2), 1.66 (8H, br, CH_2), 1.22 (72H, s, *t*-Bu), 1.21 (36H, s, *t*-Bu), 1.17 (36H, s, *t*-Bu), 1.08 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 22.2 (CH_2), 28.5 (CH_2), 30.8 (CH_3), 31.0 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 33.9 ($C_{i,t\text{-Bu}}$), 33.9 ($C_{i,t\text{-Bu}}$), 33.9 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 46.6 (CH_2), 68.7 (CH_2), 74.7 (OCH_2), 120.1 ($C_{i,Ar\text{–}S}$), 120.5 ($C_{i,Ar\text{–}S}$), 120.7 ($C_{i,Ar\text{–}S}$), 122.0 (CH_{triaz}), 128.1 ($C_{i,Ar\text{–}S}$), 128.2 ($C_{i,Ar\text{–}S}$), 128.3 (CH_{Ar}), 135.8 (CH_{Ar}), 135.8 (CH_{Ar}), 136.2 (CH_{Ar}), 136.2 (CH_{Ar}), 143.6 ($C_{i,Ar\text{–}t\text{-Bu}}$), 143.9 ($C_{i,Ar\text{–}t\text{-Bu}}$), 145.4 ($C_{i,Ar\text{–}t\text{-Bu}}$), 146.9 ($C_{i,Ar\text{–}t\text{-Bu}}$), 149.2 ($C_{i,triaz}$), 155.8 ($C_{i,Ar\text{–}O}$), 156.4 ($C_{i,Ar\text{–}O}$), 157.0 ($C_{i,Ar\text{–}O}$), 157.4 ($C_{i,Ar\text{–}O}$).

Compound ***10d***. (270 mg, 67 %). R_f= 0.53 (MeOH). mp 160 °C (decomp.). *m/z* (HRMS MALDI) (%): 4334.4952 (100) [(M+Cs)$^+$]. Calcd for $C_{232}H_{284}N_{12}O_{20}S_{20}$+Cs$^+$: 4334.5091 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1267 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1451 s (C_{Ar}–C_{Ar}), 2868 s ($C_{t\text{-Bu}}$–H), 2961 s (C_{Ar}–H), 3379 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.44 (4H, br, OH), 9.29 (8H, br, OH), 7.97 (4H, s, CH_{triaz}), 7.68 (8H, AB-d *J*=1 Hz, ArH), 7.64 (8H, br, ArH), 7.63 (8H, br, ArH), 7.61 (8H, AB-d *J*=1 Hz, ArH), 7.32 (8H, br, ArH), 5.04 (8H, br, CH_2), 4.24 (8H, br, CH_2), 3.88 (8H, br, CH_2), 2.75 (8H, br, CH_2), 2.67 (8H, br, CH_2), 1.59 (16H, br, CH_2), 1.26 (36H, br, *t*-Bu), 1.22 (108H, br, *t*-Bu), 1.17 (36H, br, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 25.9 (CH_2), 28.7 (CH_2), 29.5 (CH_2), 30.6 (CH_3), 30.9 (CH_3), 31.2 (CH_3), 31.2 (CH_3), 34.0 ($C_{i,t\text{-Bu}}$), 34.1 ($C_{i,t\text{-Bu}}$), 34.1 ($C_{i,t\text{-Bu}}$), 34.3 ($C_{i,t\text{-Bu}}$), 46.4 (CH_2), 68.5 (CH_2), 74.4 (OCH_2), 120.1 ($C_{i,Ar\text{–}S}$), 120.6 ($C_{i,Ar\text{–}S}$), 120.7 ($C_{i,Ar\text{–}S}$), 122.5 (CH_{triaz}), 128.1 ($C_{i,Ar\text{–}S}$), 128.2 ($C_{i,Ar\text{–}S}$), 128.3 (CH_{Ar}), 136.0 (CH_{Ar}), 136.0 (CH_{Ar}), 136.2 (CH_{Ar}), 136.9 (CH_{Ar}), 143.8 ($C_{i,Ar\text{–}t\text{-Bu}}$), 144.1 ($C_{i,Ar\text{–}t\text{-Bu}}$), 145.3 ($C_{i,Ar\text{–}t\text{-Bu}}$), 147.5 ($C_{i,Ar\text{–}t\text{-Bu}}$), 149.6 ($C_{i,triaz}$), 155.8 ($C_{i,Ar\text{–}O}$), 156.5 ($C_{i,Ar\text{–}O}$), 156.5 ($C_{i,Ar\text{–}O}$), 157.4 ($C_{i,Ar\text{–}O}$).

Compound ***11a***. (220 mg, 58 %). R_f=0.57 ($CHCl_3$/MeOH 40:1). mp 181 °C (decomp.). *m/z* (HRMS MALDI) (%): 4166.3150 (100) [(M+Cs)$^+$]. Calcd for $C_{220}H_{260}N_{12}O_{20}S_{20}$+Cs$^+$: 4166.3209 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1453 s (C_{Ar}–C_{Ar}), 2869 s ($C_{t\text{-Bu}}$–H), 2962 s (C_{Ar}–H), 3354 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.25 (4H, br, OH), 9.10 (8H, br, OH), 8.32 (4H, br, CH_{triaz}), 7.64 (8H, AB-d *J*=3 Hz, ArH), 7.58 (8H, br, ArH), 7.57 (8H, AB-d *J*=3 Hz, ArH), 7.56 (8H, br, ArH), 7.53 (8H, br, ArH), 5.55 (8H, br, CH_2), 4.56 (8H, t *J*=8 Hz, CH_2), 4.12 (8H, t *J*=8 Hz, CH_2), 1.24 (36H, s, *t*-Bu), 1.23 (36H, s, *t*-Bu), 1.22 (36H, s, *t*-Bu), 1.19 (36H, s, *t*-Bu), 1.11 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 31.1 (CH_3), 31.4 (CH_3), 31.4 (CH_3), 31.4 (CH_3), 34.2 ($C_{i,t\text{-Bu}}$), 34.3 ($C_{i,t\text{-Bu}}$), 34.5 ($C_{i,t\text{-Bu}}$), 34.6 ($C_{i,t\text{-Bu}}$), 48.1 (CH_2), 65.8 (CH_2), 70.6 (OCH_2), 120.7 ($C_{i,Ar\text{–}S}$), 120.8 ($C_{i,Ar\text{–}S}$), 121.2 ($C_{i,Ar\text{–}S}$), 124.8 (CH_{triaz}), 127.9 ($C_{i,Ar\text{–}S}$), 128.7 ($C_{i,Ar\text{–}S}$), 129.0 (CH_{Ar}), 136.0 (CH_{Ar}), 136.1 (CH_{Ar}), 136.2 (CH_{Ar}), 136.2 (CH_{Ar}), 143.8 ($C_{i,Ar\text{–}t\text{-Bu}}$), 144.0 ($C_{i,Ar\text{–}t\text{-Bu}}$), 144.8 ($C_{i,Ar\text{–}t\text{-Bu}}$), 148.2 ($C_{i,Ar\text{–}t\text{-Bu}}$), 149.3 ($C_{i,triaz}$),155.8 ($C_{i,Ar\text{–}O}$), 156.1 ($C_{i,Ar\text{–}O}$), 156.6 ($C_{i,Ar\text{–}O}$), 157.4 ($C_{i,Ar\text{–}O}$).

Compound ***11b***. (250 mg, 61 %). R_f =0.37 ($CHCl_3$/MeOH 40:1). mp 184 °C (decomp.). *m/z* (HRMS MALDI) (%): 4222.3643 (100) [(M+Cs)$^+$]. Calcd for $C_{224}H_{268}N_{12}O_{20}S_{20}$+Cs$^+$: 4222.3837 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1267 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1452 s (C_{Ar}–C_{Ar}), 2870 s ($C_{t\text{-Bu}}$–H), 2962 s (C_{Ar}–H), 3376 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.04 (12H, br, OH), 8.00 (4H, s, CH_{triaz}), 7.66 (8H, AB-d *J*=2 Hz, ArH), 7.59 (8H, s, ArH), 7.55 (16H, br, ArH), 7.42 (8H, s, ArH), 4.66 (8H, t *J*=5 Hz, CH_2), 4.46 (8H, t *J*=8 Hz, CH_2), 3.92 (8H, t *J*=8 Hz, CH_2), 3.61 (8H, t *J*=5 Hz, CH_2), 1.25 (36H, s, *t*-Bu), 1.23 (72H, s, *t*-Bu), 1.20 (36H, s, *t*-Bu), 1.15 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 26.5 (CH_2), 30.8 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 31.1 (CH_3), 33.9 ($C_{i,t\text{-Bu}}$), 33.9 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 34.3 ($C_{i,t\text{-Bu}}$), 47.7 (CH_2), 65.2 (CH_2), 76.8 (OCH_2), 120.1 ($C_{i,Ar\text{–}S}$), 120.7 ($C_{i,Ar\text{–}S}$), 120.9 ($C_{i,Ar\text{–}S}$), 122.4 (CH_{triaz}), 127.3 ($C_{i,Ar\text{–}S}$), 128.1 ($C_{i,Ar\text{–}S}$), 128.2 (CH_{Ar}), 135.7 (CH_{Ar}), 135.7 (CH_{Ar}), 135.7 (CH_{Ar}), 136.3 (CH_{Ar}), 143.4 ($C_{i,Ar\text{–}t\text{-Bu}}$), 143.7 ($C_{i,Ar\text{–}t\text{-Bu}}$), 144.0 ($C_{i,Ar\text{–}t\text{-Bu}}$), 147.5 ($C_{i,Ar\text{–}t\text{-Bu}}$), 148.9 ($C_{i,triaz}$), 155.3 ($C_{i,Ar\text{–}O}$), 155.9 ($C_{i,Ar\text{–}O}$), 156.4 ($C_{i,Ar\text{–}O}$), 157.7 ($C_{i,Ar\text{–}O}$).

Compound ***11c***. (180 mg, 69 %). R_f =0.48 ($CHCl_3$/MeOH 40:1). mp 138 °C (decomp.). *m/z* (HRMS MALDI) (%): 4278.4306 (100) [(M+Cs)$^+$]. Calcd for $C_{228}H_{276}N_{12}O_{20}S_{20}$+Cs$^+$: 4278.4464 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1269 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1452 s (C_{Ar}–C_{Ar}), 2870 s ($C_{t\text{-Bu}}$–H), 2962 s (C_{Ar}–H), 3391 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.47 (4H, br, OH), 9.32 (8H, br, OH), 7.76 (4H, s, CH_{triaz}), 7.67 (8H, AB-d *J*=2 Hz, ArH), 7.63 (8H, s, ArH), 7.61 (8H, br, ArH), 7.60 (8H, AB-d *J*=2 Hz, ArH), 7.46 (8H, s, ArH), 4.41 (8H, t *J*=7 Hz, CH_2), 4.33 (8H, t *J*=5 Hz, CH_2), 3.91 (8H, t *J*=7 Hz, CH_2), 3.31 (8H, t *J*=5 Hz, CH_2), 2.60 (8H, br, CH_2), 1.23 (72H, s, *t*-Bu), 1.22 (36H, s, *t*-Bu), 1.19 (36H, s, *t*-Bu), 1.18 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 21.6 (CH_2), 29.6 (CH_2), 31.2 (CH_3), 31.2 (CH_3), 31.5 (CH_3), 31.5 (CH_3), 34.3 ($C_{i,t\text{-Bu}}$), 34.3 ($C_{i,t\text{-Bu}}$), 34.6 ($C_{i,t\text{-Bu}}$), 34.6 ($C_{i,t\text{-Bu}}$), 48.3 (CH_2), 65.6 (CH_2), 76.9

(OCH_2), 120.5 ($C_{i,Ar–S}$), 121.0 ($C_{i,Ar–S}$), 121.1 ($C_{i,Ar–S}$), 127.9 (CH_{triaz}), 128.4 ($C_{i,Ar–S}$), 128.6 ($C_{i,Ar–S}$), 128.6 (CH_{Ar}), 136.0 (CH_{Ar}), 136.2 (CH_{Ar}), 136.3 (CH_{Ar}), 137.1 (CH_{Ar}), 143.8 ($C_{i,Ar–t-Bu}$), 144.0 ($C_{i,Ar–t-Bu}$), 144.3 ($C_{i,Ar–t-Bu}$), 148.3 ($C_{i,Ar–t-Bu}$), 149.5 ($C_{i,triaz}$), 155.6 ($C_{i,Ar–O}$), 156.2 ($C_{i,Ar–O}$), 156.8 ($C_{i,Ar–O}$), 158.0 ($C_{i,Ar–O}$).

Compound ***11d***. (280 mg, 66 %). R_f=0.30 ($CHCl_3$/MeOH 40:1). mp 166 °C (decomp.). *m/z* (HRMS MALDI) (%): 4334.4992 (100) [(M+Cs)$^+$]. Calcd for $C_{232}H_{284}N_{12}O_{20}S_{20}$+$Cs^+$: 4334.5091 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s (C_{t-Bu}–C_{t-Bu}), 1452 s (C_{Ar}–C_{Ar}), 2869 s (C_{t-Bu}–H), 2962 s (C_{Ar}–H), 3379 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.22 (12H, br, OH), 7.65 (8H, AB-d *J*=2 Hz, ArH), 7.63 (8H, s, ArH), 7.61 (4H, br, CH_{triaz}), 7.59 (8H, AB-d *J*=2 Hz, ArH), 7.57 (8H, s, ArH), 7.39 (8H, s, ArH), 4.41 (8H, m, CH_2), 4.40 (8H, m, CH_2), 3.88 (8H, t *J*=7 Hz, CH_2), 3.03 (8H, t *J*=8 Hz, CH_2), 2.27 (8H, br, CH_2), 2.20 (8H, br, CH_2), 1.22 (72H, s, *t*-Bu), 1.20 (36H, s, *t*-Bu), 1.18 (72H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 25.2 (CH_2), 25.6 (CH_2), 29.2 (CH_2), 30.9 (CH_3), 30.9 (CH_3), 31.1 (CH_3), 31.2 (CH_3), 33.9 ($C_{i,t-Bu}$), 34.0 ($C_{i,t-Bu}$), 34.0 ($C_{i,t-Bu}$), 34.3 ($C_{i,t-Bu}$), 47.6 (CH_2), 65.4 (CH_2), 77.7 (OCH_2), 120.3 ($C_{i,Ar–S}$), 120.7 ($C_{i,Ar–S}$), 120.7 ($C_{i,Ar–S}$), 120.8 (CH_{triaz}), 127.4 ($C_{i,Ar–S}$), 128.0 ($C_{i,Ar–S}$), 128.3 (CH_{Ar}), 135.7 (CH_{Ar}), 135.8 (CH_{Ar}), 135.8 (CH_{Ar}), 136.6 (CH_{Ar}), 143.5 ($C_{i,Ar–t-Bu}$), 143.9 ($C_{i,Ar–t-Bu}$), 147.7 ($C_{i,Ar–t-Bu}$), 148.0 ($C_{i,Ar–t-Bu}$), 148.9 ($C_{i,triaz}$), 155.4 ($C_{i,Ar–O}$), 155.9 ($C_{i,Ar–O}$), 156.5 ($C_{i,Ar–O}$), 157.8 ($C_{i,Ar–O}$).

Compound ***12a***. (210 mg, 44 %). R_f=0.22 ($CHCl_3$/MeOH 40:1). mp 173 °C (decomp.). *m/z* (HRMS MALDI) (%): 4222.3671 (100) [(M+Cs)$^+$]. Calcd for $C_{224}H_{268}N_{12}O_{20}S_{20}$+$Cs^+$: 4222.3837 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s (C_{t-Bu}–C_{t-Bu}), 1452 s (C_{Ar}–C_{Ar}), 2869 s (C_{t-Bu}–H), 2962 s (C_{Ar}–H), 3382 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.20 (12H, br, OH), 8.28 (4H, br, CH_{triaz}), 7.64 (8H, br, ArH), 7.60 (8H, AB-d *J*=2 Hz, ArH), 7.56 (8H, br, ArH), 7.51 (8H, AB-d *J*=2 Hz, ArH), 7.43 (8H, s, ArH), 5.66 (8H, br, CH_2), 4.33 (8H, br, CH_2), 4.12 (8H, br, CH_2), 1.85 (8H, br, CH_2), 1.23 (108H, s, *t*-Bu), 1.19 (36H, s, *t*-Bu), 1.05 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 29.5 (CH_2), 30.8 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 31.1 (CH_3), 33.9 ($C_{i,t-Bu}$), 34.0 ($C_{i,t-Bu}$), 34.1 ($C_{i,t-Bu}$), 34.2 ($C_{i,t-Bu}$), 48.1 (CH_2), 66.0 (CH_2), 69.9 (OCH_2), 120.4 ($C_{i,Ar–S}$), 120.6 ($C_{i,Ar–S}$), 121.4 ($C_{i,Ar–S}$), 124.2 (CH_{triaz}), 127.5($C_{i,Ar–S}$), 128.0 ($C_{i,Ar–S}$), 128.7 (CH_{Ar}), 135.4 (CH_{Ar}), 135.8 (CH_{Ar}), 136.2 (CH_{Ar}), 136.7 (CH_{Ar}), 143.3 ($C_{i,Ar–t-Bu}$), 143.6 ($C_{i,Ar–t-Bu}$), 143.7 ($C_{i,Ar–t-Bu}$), 146.3 ($C_{i,Ar–t-Bu}$), 148.5 ($C_{i,triaz}$), 155.4 ($C_{i,Ar–O}$), 155.8 ($C_{i,Ar–O}$), 156.3 ($C_{i,Ar–O}$), 157.2 ($C_{i,Ar–O}$).

Compound ***12b***. (220 mg, 48 %). R_f =0.20 ($CHCl_3$/MeOH 40:1). mp 141 °C (decomp.). *m/z* (HRMS MALDI) (%): 4278.4366 (100) [(M+Cs)$^+$]. Calcd for $C_{228}H_{276}N_{12}O_{20}S_{20}$+$Cs^+$: 4278.4464 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s (C_{t-Bu}–C_{t-Bu}), 1451 s (C_{Ar}–C_{Ar}), 2870 s (C_{t-Bu}–H), 2962 (C_{Ar}–H), 3376 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.17 (12H, br, OH), 8.05 (4H, s, CH_{triaz}), 7.64 (8H, AB-d *J*=3 Hz, ArH), 7.59 (8H, br, ArH), 7.58 (8H, br, ArH), 7.58 (8H, AB-d *J*=3 Hz, ArH), 7.29 (8H, s, ArH), 4.64 (8H, t *J*=8 Hz, CH_2), 4.29 (8H, t *J*=8 Hz, CH_2), 4.04 (8H, t *J*=8 Hz, CH_2), 3.63 (8H, t *J*=8 Hz, CH_2), 1.80 (8H, t *J*=8 Hz, CH_2), 1.23 (72H, s, *t*-Bu), 1.19 (36H, s, *t*-Bu), 1.15 (36H, s, *t*-Bu), 1.07 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 26.4 (CH_2), 29.8 (CH_2), 30.8 (CH_3), 30.9 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 33.9 ($C_{i,t-Bu}$), 33.9 ($C_{i,t-Bu}$), 34.1 ($C_{i,t-Bu}$), 47.7 (CH_2), 66.2 (CH_2), 76.8 (OCH_2), 120.1 ($C_{i,Ar–S}$), 120.7 ($C_{i,Ar–S}$), 120.9 ($C_{i,Ar–S}$), 122.8 (CH_{triaz}), 127.3 ($C_{i,Ar–S}$), 128.0 ($C_{i,Ar–S}$), 128.3 (CH_{Ar}), 135.6 (CH_{Ar}), 135.8 (CH_{Ar}), 135.9 (CH_{Ar}), 136.1 (CH_{Ar}), 143.3 ($C_{i,Ar–t-Bu}$), 143.5 ($C_{i,Ar–t-Bu}$), 143.7 ($C_{i,Ar–t-Bu}$), 146.1 ($C_{i,Ar–t-Bu}$), 148.8 ($C_{i,triaz}$), 156.0 ($C_{i,Ar–O}$), 156.3 ($C_{i,Ar–O}$), 156.5 ($C_{i,Ar–O}$), 157.6 ($C_{i,Ar–O}$).

Compound ***12c***. (240 mg, 65 %). R_f =0.19 ($CHCl_3$/MeOH 40:1). mp 143 °C (decomp.). *m/z* (HRMS MALDI) (%): 4334.4896 (100) [(M+Cs)$^+$]. Calcd for $C_{232}H_{284}N_{12}O_{20}S_{20}$+$Cs^+$: 4334.5091 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1267 s (C_{t-Bu}–C_{t-Bu}), 1451 s (C_{Ar}–C_{Ar}), 2870 s (C_{t-Bu}–H), 2962 s (C_{Ar}–H), 3377 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.35 (12H, br, OH), 7.81 (4H, br, CH_{triaz}), 7.65 (8H, AB-d *J*=2 Hz, ArH), 7.61 (8H, s, ArH), 7.59 (16H, br, ArH), 7.31 (8H, s, ArH), 4.41 (8H, br, CH_2), 4.17 (8H, br, CH_2), 4.01 (8H, br, CH_2), 3.24 (8H, br, CH_2), 2.59 (8H, br, CH_2), 1.76 (8H, br, CH_2), 1.23 (72H, s, *t*-Bu), 1.21 (36H, s, *t*-Bu), 1.17 (36H, s, *t*-Bu), 1.08 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 22.0 (CH_2), 29.8 (CH_2), 30.3 (CH_2), 31.2 (CH_3), 31.3 (CH_3), 31.4 (CH_3), 31.5 (CH_3), 34.2 ($C_{i,t-Bu}$), 34.3 ($C_{i,t-Bu}$), 34.3 ($C_{i,t-Bu}$), 34.6 ($C_{i,t-Bu}$), 48.2 (CH_2), 66.5 (CH_2), 77.5 (OCH_2), 120.5 ($C_{i,Ar–S}$), 120.9 ($C_{i,Ar–S}$), 121.2 ($C_{i,Ar–S}$), 127.7 (CH_{triaz}), 128.3 ($C_{i,Ar–S}$), 128.6 ($C_{i,Ar–S}$), 128.6 (CH_{Ar}), 136.1 (CH_{Ar}), 136.1 (CH_{Ar}), 136.9 (CH_{Ar}), 136.9 (CH_{Ar}), 143.8 ($C_{i,Ar–t-Bu}$), 144.1 ($C_{i,Ar–t-Bu}$), 146.6 ($C_{i,Ar–t-Bu}$), 146.9 ($C_{i,Ar–t-Bu}$), 149.2 ($C_{i,triaz}$), 156.2 ($C_{i,Ar–O}$), 156.6 ($C_{i,Ar–O}$), 156.8 ($C_{i,Ar–O}$), 158.1 ($C_{i,Ar–O}$).

Compound ***12d***. (180 mg, 67 %). R_f =0.22 ($CHCl_3$/MeOH 40:1). mp 149 °C (decomp.). *m/z* (HRMS MALDI) (%): 4390.5510 (100) [(M+Cs)$^+$]. Calcd for $C_{236}H_{292}N_{12}O_{20}S_{20}$+$Cs^+$: 4390.5718 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s (C_{t-Bu}–C_{t-Bu}), 1452 s (C_{Ar}–C_{Ar}), 2869 s (C_{t-Bu}–H), 2962 s (C_{Ar}–H), 3376 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.19 (12H, br, OH), 7.95 (4H, br, CH_{triaz}), 7.65 (8H, AB-d *J*=2 Hz, ArH), 7.63 (8H, s, ArH), 7.61 (8H, AB-d *J*=2 Hz, ArH), 7.59 (8H, s, ArH), 7.27 (8H, s, ArH), 4.42 (8H, t *J*=3 Hz, CH_2), 4.18 (8H, br, CH_2), 3.95 (8H, t *J*=5 Hz, CH_2), 3.05 (8H, br, CH_2), 2.28 (8H, br, CH_2), 2.21 (8H, br, CH_2), 1.74 (8H, br, CH_2), 1.23 (72H, s, *t*-Bu), 1.19 (36H, s, *t*-Bu), 1.18 (36 H, s, *t*-Bu), 1.05 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 25.2 (CH_2), 25.5 (CH_2), 29.0 (CH_2), 30.0 (CH_2), 30.8 (CH_3), 30.9 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 33.9 ($C_{i,t-Bu}$), 33.9 ($C_{i,t-Bu}$), 33.9 ($C_{i,t-Bu}$), 34.2 ($C_{i,t-Bu}$), 47.6 (CH_2), 66.2 (CH_2), 77.9 (OCH_2), 120.2 ($C_{i,Ar–S}$), 120.6 ($C_{i,Ar–S}$), 120.8 ($C_{i,Ar–S}$), 121.2 (CH_{triaz}), 127.2 ($C_{i,Ar–S}$), 128.0 ($C_{i,Ar–S}$), 128.2 (CH_{Ar}), 135.6 (CH_{Ar}), 135.6 (CH_{Ar}), 135.7 (CH_{Ar}), 136.5 (CH_{Ar}), 143.4 ($C_{i,Ar–t-Bu}$), 143.8 ($C_{i,Ar–t-Bu}$), 146.1 ($C_{i,Ar–t-Bu}$), 147.4 ($C_{i,Ar–t-Bu}$), 148.9 ($C_{i,triaz}$), 155.9 ($C_{i,Ar–O}$), 156.3 ($C_{i,Ar–O}$), 156.4 ($C_{i,Ar–O}$), 157.7 ($C_{i,Ar–O}$).

Compound ***13a***. (210 mg, 61 %). R_f=0.18 ($CHCl_3$/MeOH 40:1). mp 167 °C (decomp.). *m/z* (HRMS MALDI) (%): 4278.4395 (100) [(M+Cs)$^+$]. Calcd for $C_{228}H_{276}N_{12}O_{20}S_{20}$+$Cs^+$: 4278.4464 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s (C_{t-Bu}–C_{t-Bu}), 1453 s (C_{Ar}–C_{Ar}), 2869 s (C_{t-Bu}–H), 2962 s (C_{Ar}–H), 3363 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.28 (4H, br, OH), 9.11 (8H, br, OH), 8.34 (4H, br, CH_{triaz}), 7.65 (8H, AB-d *J*=3 Hz, ArH), 7.58 (8H, br, ArH), 7.58 (8H, AB-d *J*=3 Hz, ArH), 7.55 (8H, s, ArH), 7.36 (8H, s, ArH), 5.61 (8H, br, CH_2), 4.43 (8H, t *J*=7 Hz, CH_2), 3.97 (8H, t *J*=7 Hz, CH_2), 1.98 (8H, t *J*=7 Hz, CH_2), 1.42 (8H, t *J*=6 Hz, CH_2), 1.25 (36H, s, *t*-Bu), 1.22 (72H, s, *t*-Bu), 1.20 (36H, s, *t*-Bu), 1.13 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 26.1 (CH_2), 26.9 (CH_2), 30.8 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 31.2 (CH_3), 33.9 ($C_{i,t-Bu}$), 34.0 ($C_{i,t-Bu}$), 34.1 ($C_{i,t-Bu}$), 34.2 ($C_{i,t-Bu}$), 50.0 (CH_2), 68.2 (CH_2), 70.4 (OCH_2), 120.3 ($C_{i,Ar–S}$), 120.5 ($C_{i,Ar–S}$), 120.9 ($C_{i,Ar–S}$), 124.6 (CH_{triaz}), 128.3 ($C_{i,Ar–S}$), 128.5 ($C_{i,Ar–S}$), 128.6 (CH_{Ar}), 135.6 (CH_{Ar}), 135.8 (CH_{Ar}), 136.0 (CH_{Ar}), 136.2 (CH_{Ar}), 143.5 ($C_{i,Ar–t-Bu}$), 143.8 ($C_{i,Ar–t-Bu}$), 144.6 ($C_{i,Ar–t-Bu}$), 145.5 ($C_{i,Ar–t-Bu}$), 149.0 ($C_{i,triaz}$), 155.7 ($C_{i,Ar–O}$), 156.3 ($C_{i,Ar–O}$), 157.0 ($C_{i,Ar–O}$), 157.1 ($C_{i,Ar–O}$).

Compound ***13b***. (230 mg, 70 %). R_f =0.08 ($CHCl_3$/MeOH 40:1). mp 164 °C (decomp.). *m/z* (HRMS MALDI) (%): 4334.5076 (100) [(M+Cs)$^+$]. Calcd for $C_{232}H_{284}N_{12}O_{20}S_{20}$+$Cs^+$: 4334.5091 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s (C_{t-Bu}–C_{t-Bu}), 1452 s (C_{Ar}–C_{Ar}), 1629 s (C=C), 2870 s (C_{t-Bu}–H), 2962 s (C_{Ar}–H), 3376 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.19 (4H, br, OH), 9.00 (8H, br, OH), 8.14 (4H, br, CH_{triaz}), 7.64 (8H, AB-d *J*=2 Hz, ArH), 7.59 (8H, AB-d *J*=2 Hz, ArH), 7.58 (16H, s, ArH), 7.32 (8H, s, ArH), 4.64 (8H, t *J*=6 Hz, CH_2), 4.39 (8H, t *J*=7 Hz, CH_2), 3.84 (8H, t *J*=7 Hz, CH_2), 3.61 (8H, t *J*=5 Hz, CH_2), 1.94 (8H, m, CH_2), 1.35 (8H, m, CH_2), 1.21 (108H, s, *t*-Bu), 1.19 (36H, s, *t*-Bu), 1.15 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 26.8 (CH_2), 27.2 (CH_2), 27.3 (CH_2), 31.4 (CH_3), 31.6 (CH_3), 31.7 (CH_3), 32.3 (CH_3), 34.5 ($C_{i,t-Bu}$), 34.6 ($C_{i,t-Bu}$), 34.6 ($C_{i,t-Bu}$), 34.8 ($C_{i,t-Bu}$), 50.5 (CH_2), 68.9 (CH_2), 77.8 (OCH_2), 120.6 ($C_{i,Ar–S}$), 121.3 ($C_{i,Ar–S}$), 121.4 ($C_{i,Ar–S}$), 123.3 (CH_{triaz}), 128.8 ($C_{i,Ar–S}$), 128.9 ($C_{i,Ar–S}$), 129.4 (CH_{Ar}), 136.2 (CH_{Ar}), 136.3 (CH_{Ar}), 136.4 (CH_{Ar}), 136.9 (CH_{Ar}), 144.1 ($C_{i,Ar–t-Bu}$), 144.5 ($C_{i,Ar–t-Bu}$), 144.6 ($C_{i,Ar–t-Bu}$), 146.0 ($C_{i,Ar–t-Bu}$), 149.6 ($C_{i,triaz}$), 156.4 ($C_{i,Ar–O}$), 156.9 ($C_{i,Ar–O}$), 157.6 ($C_{i,Ar–O}$), 158.3 ($C_{i,Ar–O}$).

Compound ***13c***. (250 mg, 67 %). R_f=0.11 ($CHCl_3$/MeOH 40:1). mp 169 °C (decomp.). *m/z* (HRMS MALDI) (%): 4334.5076 (100)

[(M+Cs)$^+$]. Calcd for $C_{232}H_{284}N_{12}O_{20}S_{20}$+Cs$^+$: 4334.5091 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1451 s (C_{Ar}–C_{Ar}), 1626 s (C=C), 2869 s ($C_{t\text{-Bu}}$–H), 2962 s (C_{Ar}–H), 3375 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.33 (12H, br, OH), 7.83 (4H, br, CH_{triaz}), 7.66 (8H, AB-d *J*=3 Hz, ArH), 7.63 (8H, s, ArH), 7.61 (8H, br s, ArH), 7.60 (8H, AB-d *J*=3 Hz, ArH), 7.32 (8H, s, ArH), 4.32 (8H, br, CH_2), 4.27 (8H, br, CH_2), 3.85 (8H, t *J*=8 Hz, CH_2), 3.28 (8H, br, CH_2), 2.58 (8H, br, CH_2), 1.84 (8H, t *J*=6 Hz, CH_2), 1.33 (8H, br, CH_2), 1.22 (108H, s, *t*-Bu), 1.21 (36H, s, *t*-Bu), 1.18 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 21.5 (CH_2), 26.0 (CH_2), 26.8 (CH_2), 29.3 (CH_2), 30.8 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 31.2 (CH_3), 33.9 ($C_{i,t\text{-Bu}}$), 33.9 ($C_{i,t\text{-Bu}}$), 34.0 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 49.6 (CH_2), 68.0 (CH_2), 76.8 (OCH_2), 120.1 ($C_{i,Ar–S}$), 120.6 ($C_{i,Ar–S}$), 120.8 ($C_{i,Ar–S}$), 121.7 (CH_{triaz}), 128.1 ($C_{i,Ar–S}$), 128.1 ($C_{i,Ar–S}$), 128.3 (CH_{Ar}), 135.8 (CH_{Ar}), 135.9 (CH_{Ar}), 136.6 (CH_{Ar}), 143.5 ($C_{i,Ar–t\text{-Bu}}$), 143.8 ($C_{i,Ar–t\text{-Bu}}$), 145.5 ($C_{i,Ar–t\text{-Bu}}$), 146.9 ($C_{i,Ar–t\text{-Bu}}$), 149.0 ($C_{i,triaz}$), 155.9 ($C_{i,Ar–O}$), 156.5 ($C_{i,Ar–O}$), 156.8 ($C_{i,Ar–O}$), 157.7 ($C_{i,Ar–O}$).

Compound ***13d***. (250 mg, 80 %). R_f=0.18 ($CHCl_3$/MeOH 40:1). mp 149 °C (decomp.). *m/z* (HRMS MALDI) (%): 4446.6123 (100) [(M+Cs)$^+$]. Calcd for $C_{240}H_{300}N_{12}O_{20}S_{20}$+Cs$^+$: 4446.6346 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1452 s (C_{Ar}–C_{Ar}), 2869 s ($C_{t\text{-Bu}}$–H), 2961 s (C_{Ar}–H), 3380 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.27 (12H, br, OH), 7.66 (4H, br, CH_{triaz}), 7.65 (8H, AB-d *J*=2 Hz, ArH), 7.63 (8H, s, ArH), 7.60 (16H, AB-d *J*=2 Hz, ArH), 7.34 (8H, s, ArH), 4.41 (8H, t *J*=6 Hz, CH_2), 4.28 (8H, t *J*=7 Hz, CH_2), 3.86 (8H, t *J*=7 Hz, CH_2), 3.01 (8H, br, CH_2), 2.28 (8H, m, CH_2), 2.19 (8H, m, CH_2), 1.87 (8H, m, CH_2), 1.33 (8H, m, CH_2), 1.22 (108H, s, *t*-Bu), 1.19 (36H, s, *t*-Bu), 1.18 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 25.2 (CH_2), 25.5 (CH_2), 26.1 (CH_2), 26.7 (CH_2), 29.1 (CH_2), 30.8 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 31.1 (CH_3), 33.8 ($C_{i,t\text{-Bu}}$), 33.9 ($C_{i,t\text{-Bu}}$), 33.9 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 49.6 (CH_2), 68.3 (CH_2), 77.7 (OCH_2), 120.1 ($C_{i,Ar–S}$), 120.6 ($C_{i,Ar–S}$), 120.7 ($C_{i,Ar–S}$), 120.8 (CH_{triaz}), 128.1 ($C_{i,Ar–S}$), 128.2 ($C_{i,Ar–S}$), 128.7 (CH_{Ar}), 135.7 (CH_{Ar}), 135.8 (CH_{Ar}), 136.2 (CH_{Ar}), 136.6 (CH_{Ar}), 143.4 ($C_{i,Ar–t\text{-Bu}}$), 143.8 ($C_{i,Ar–t\text{-Bu}}$), 145.4 ($C_{i,Ar–t\text{-Bu}}$), 147.8 ($C_{i,Ar–t\text{-Bu}}$), 148.9 ($C_{i,triaz}$), 155.9 ($C_{i,Ar–O}$), 156.4 ($C_{i,Ar–O}$), 157.0 ($C_{i,Ar–O}$), 157.7 ($C_{i,Ar–O}$).

Compound ***14a***. (210 mg, 73 %). R_f= 0.46 ($CHCl_3$/MeOH 40:1). mp 182 °C (decomp.). *m/z* (HRMS MALDI) (%): 4334.4890 (100) [(M+Cs)$^+$]. Calcd for $C_{232}H_{284}N_{12}O_{20}S_{20}$+Cs$^+$: 4334.5091 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1453 s (C_{Ar}–C_{Ar}), 1626 s (C=C), 2869 s ($C_{t\text{-Bu}}$–H), 2962 s (C_{Ar}–H), 3374 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.32 (4H, br, OH), 9.17 (8H, br, OH), 8.29 (4H, br, CH_{triaz}), 7.65 (8H, br, ArH), 7.57 (8H, br, ArH), 7.57 (8H, AB-d *J*=3 Hz, ArH), 7.52 (8H, s, ArH), 7.27 (8H, br, ArH), 5.64 (8H, br, CH_2), 4.45 (8H, br, CH_2), 3.84 (8H, t *J*=6 Hz, CH_2), 1.93 (8H, br, CH_2), 1.29 (16H, br, CH_2), 1.22 (108H, s, *t*-Bu), 1.20 (36H, s, *t*-Bu), 1.10 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 26.5 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 31.1 (CH_3), 31.3 (CH_3), 31.4 (CH_3), 31.5 (CH_3), 34.2 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 34.5 ($C_{i,t\text{-Bu}}$), 50.1 (CH_2), 68.5 (CH_2), 77.5 (OCH_2), 120.2 ($C_{i,Ar–S}$), 120.9 ($C_{i,Ar–S}$), 121.2 ($C_{i,Ar–S}$), 123.0 (CH_{triaz}), 128.5 ($C_{i,Ar–S}$), 128.5 ($C_{i,Ar–S}$), 129.0 (CH_{Ar}), 135.9 (CH_{Ar}), 136.0 (CH_{Ar}), 136.1 (CH_{Ar}), 136.6 (CH_{Ar}), 143.8 ($C_{i,Ar–t\text{-Bu}}$), 144.2 ($C_{i,Ar–t\text{-Bu}}$), 144.3 ($C_{i,Ar–t\text{-Bu}}$), 145.6 ($C_{i,Ar–t\text{-Bu}}$), 149.3 ($C_{i,triaz}$), 156.1 ($C_{i,Ar–O}$), 156.6 ($C_{i,Ar–O}$), 157.2 ($C_{i,Ar–O}$), 157.9 ($C_{i,Ar–O}$).

Compound ***14b***. (230 mg, 55 %). R_f =0.22 ($CHCl_3$/MeOH 40:1). mp 160 °C (decomp.). *m/z* (HRMS MALDI) (%): 4390.5584 (100) [(M+Cs)$^+$]. Calcd for $C_{236}H_{292}N_{12}O_{20}S_{20}$+Cs$^+$: 4390.5718 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1451 s (C_{Ar}–C_{Ar}), 1629 s (C=C), 2868 s ($C_{t\text{-Bu}}$–H), 2961 s (C_{Ar}–H), 3375 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.10 (12H, br, OH), 8.10 (4H, br, CH_{triaz}), 7.65 (8H, AB-d *J*=2 Hz, ArH), 7.59 (16H, AB-d *J*=2 Hz, ArH), 7.59 (8H, br, ArH), 7.58 (8H, br, ArH), 7.27 (8H, s, ArH), 4.65 (8H, br, CH_2), 4.43 (8H, br, CH_2), 3.81 (8H, t *J*=8 Hz, CH_2), 3.64 (8H, br, CH_2), 1.88 (8H, br, CH_2), 1.26 (16H, br, CH_2), 1.22 (108H, s, *t*-Bu), 1.20 (36H, s, *t*-Bu), 1.16 (36H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 22.8 (CH_2), 26.5 (CH_2), 28.4 (CH_2), 29.4 (CH_2), 30.2 (CH_2), 30.8 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 31.1 (CH_3), 33.8 ($C_{i,t\text{-Bu}}$), 34.0 ($C_{i,t\text{-Bu}}$), 34.0 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 50.2 (CH_2), 68.3 (CH_2), 76.8 (OCH_2), 119.9 ($C_{i,Ar–S}$), 120.6 ($C_{i,Ar–S}$), 120.8 ($C_{i,Ar–S}$), 122.8 (CH_{triaz}), 127.9 ($C_{i,Ar–S}$), 128.0 ($C_{i,Ar–S}$), 128.2 (CH_{Ar}), 135.7 (CH_{Ar}), 135.8 (CH_{Ar}), 135.8 (CH_{Ar}), 136.4 (CH_{Ar}), 143.4 ($C_{i,Ar–t\text{-Bu}}$), 143.7 ($C_{i,Ar–t\text{-Bu}}$), 143.9 ($C_{i,Ar–t\text{-Bu}}$), 145.1 ($C_{i,Ar–t\text{-Bu}}$), 149.0 ($C_{i,triaz}$), 155.8 ($C_{i,Ar–O}$), 156.3 ($C_{i,Ar–O}$), 156.8 ($C_{i,Ar–O}$), 157.7 ($C_{i,Ar–O}$).

Compound ***14c***. (250 mg, 76 %). R_f=0.22 ($CHCl_3$/MeOH 40:1). mp 164 °C (decomp.). *m/z* (HRMS MALDI) (%): 4446.6210 (100) [(M+Cs)$^+$]. Calcd for $C_{240}H_{300}N_{12}O_{20}S_{20}$+Cs$^+$: 4446.6346 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1451 s (C_{Ar}–C_{Ar}), 1634 s (C=C), 2868 s ($C_{t\text{-Bu}}$–H), 2961 s (C_{Ar}–H), 3383 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.35 (12H, br, OH), 7.90 (4H, br, CH_{triaz}), 7.65 (8H, AB-d *J*=3 Hz, ArH), 7.63 (8H, s, ArH), 7.60 (8H, br, ArH), 7.59 (8H, AB-d *J*=3Hz, ArH), 7.27 (8H, br, ArH), 4.35 (16H, br, CH_2), 3.81 (8H, t *J*=7 Hz, CH_2), 3.33 (8H, br, CH_2), 2.62 (8H, br, CH_2), 1.81 (8H, br, CH_2), 1.31 (8H, br, CH_2), 1.26 (8H, br, CH_2), 1.21 (108H, s, *t*-Bu), 1.16 (72H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 21.6 (CH_2), 22.7 (CH_2), 28.3 (CH_2), 29.3 (CH_2), 30.3 (CH_2), 30.8 (CH_3), 31.0 (CH_3), 31.0 (CH_3), 31.2 (CH_3), 33.8 ($C_{i,t\text{-Bu}}$), 33.9 ($C_{i,t\text{-Bu}}$), 34.0 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 50.0 (CH_2), 68.0 (CH_2), 76.8 (OCH_2), 120.1 ($C_{i,Ar–S}$), 120.6 ($C_{i,Ar–S}$), 120.7 ($C_{i,Ar–S}$), 121.8 (CH_{triaz}), 127.5 ($C_{i,Ar–S}$), 127.8 ($C_{i,Ar–S}$), 128.2 (CH_{Ar}), 135.7 (CH_{Ar}), 135.8 (CH_{Ar}), 135.8 (CH_{Ar}), 136.6 (CH_{Ar}), 143.5 ($C_{i,Ar–t\text{-Bu}}$), 143.8 ($C_{i,Ar–t\text{-Bu}}$), 145.2 ($C_{i,Ar–t\text{-Bu}}$), 146.8 ($C_{i,Ar–t\text{-Bu}}$), 149.0 ($C_{i,Ar–t\text{-Bu}}$+$C_{i,triaz}$), 155.8 ($C_{i,Ar–O}$), 156.4 ($C_{i,Ar–O}$), 156.7 ($C_{i,Ar–O}$), 157.7 ($C_{i,Ar–O}$).

Compound ***14d***. (250 mg, 76 %). R_f =0.18 ($CHCl_3$/MeOH 40:1). mp 147 °C (decomp.). *m/z* (HRMS MALDI) (%): 4502.6828 (100) [(M+Cs)$^+$]. Calcd for $C_{244}H_{308}N_{12}O_{20}S_{20}$+Cs$^+$: 4502.6973 [(M+Cs)]$^+$. IR (KBr) ν_{max} cm^{-1}: 1268 s ($C_{t\text{-Bu}}$–$C_{t\text{-Bu}}$), 1452 s (C_{Ar}–C_{Ar}), 1632 s (C=C), 2868 s ($C_{t\text{-Bu}}$–H), 2961 s (C_{Ar}–H), 3378 br (OH). ^{1}H NMR ($CDCl_3$, 293 K) δ_H ppm: 9.20 (12H, br, OH), 7.85 (4H, br, CH_{triaz}), 7.64 (8H, AB-d *J*=2 Hz, ArH), 7.63 (8H, s, ArH), 7.60 (8H, AB-d *J*=2 Hz, ArH), 7.58 (8H, s, ArH), 7.24 (8H, s, ArH), 4.41 (8H, t *J*=5 Hz, CH_2), 4.35 (8H, t *J*=7 Hz, CH_2), 3.74 (8H, t *J*=7 Hz, CH_2), 3.07 (8H, t *J*=7 Hz, CH_2), 2.26 (16H, m, CH_2), 1.80 (8H, m, CH_2), 1.31 (8H, m, CH_2), 1.26 (8H, m, CH_2), 1.22 (72H, s, *t*-Bu), 1.18 (108H, s, *t*-Bu). ^{13}C NMR ($CDCl_3$, 293 K) δ_C ppm: 23.0 (CH_2), 25.6 (CH_2), 25.9 (CH_2), 28.7 (CH_2), 29.4 (CH_2), 30.6 (CH_2), 31.2 (CH_3), 31.3 (CH_3), 31.4 (CH_3), 31.6 (CH_3), 34.2 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 34.2 ($C_{i,t\text{-Bu}}$), 34.5 ($C_{i,t\text{-Bu}}$), 50.4 (CH_2), 68.5 (CH_2), 78.1 (OCH_2), 120.5 ($C_{i,Ar–S}$), 120.9 ($C_{i,Ar–S}$), 121.1 ($C_{i,Ar–S}$), 121.3 (CH_{triaz}), 128.1 ($C_{i,Ar–S}$), 128.2 ($C_{i,Ar–S}$), 128.5 (CH_{Ar}), 136.0 (CH_{Ar}), 136.0 (CH_{Ar}), 136.1 (CH_{Ar}), 136.9 (CH_{Ar}), 143.8 (CH_{Ar}), 144.1 ($C_{i,Ar–t\text{-Bu}}$), 145.5 ($C_{i,Ar–t\text{-Bu}}$), 148.0 ($C_{i,Ar–t\text{-Bu}}$), 149.2 ($C_{i,triaz}$), 156.2 ($C_{i,Ar–O}$), 156.8 ($C_{i,Ar–O}$), 157.1 ($C_{i,Ar–O}$), 158.1 ($C_{i,Ar–O}$).

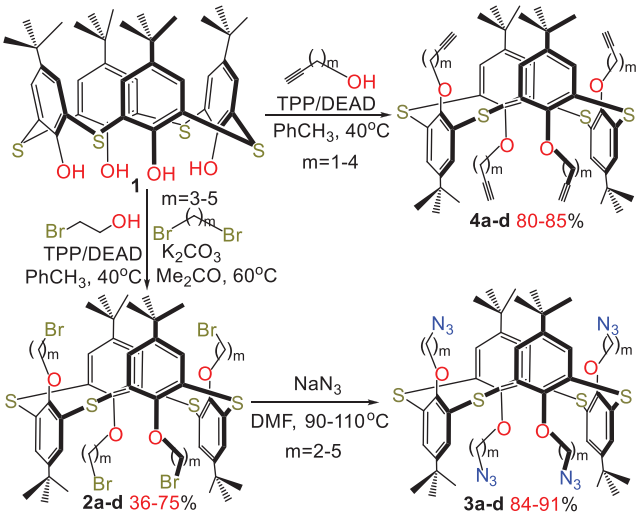
Results and Discussion

Synthesis of Azide and Alkyne-Containing Precursors

At the first step, we replaced lower-rim hydroxyl groups in thiacalixarene **1** by the groups containing terminal bromide and alkyne fragments using the 10–40-fold excess of appropriate reagents (Scheme 2). In the former case, we employed potassium carbonate as a base for the deprotonation of hydroxyl groups and the reaction of phenolate salt with commercially available dibromoalkanes to afford tetrasubstituted products **2b-d** without any products of partial substitution. Rather, bifunctional dibromoalkanes may lead to the products of intramolecular and intermolecular crosslink (in the case of 1,2-dibromoethane[17] or 1,6-dibromohexane)[14] and give lower yields of target products **2**. For this reason, the substitution of Mitsunobu protocol (triphenylphosphine (TPP) / diethylazodicarboxylate (DEAD) system) for

alkali salt-mediated nucleophilic substitution in the case of 2-bromoethanol seems more convenient and affords bromoethoxy-substituted thiacalix[4]arene **2a** in 75 % yield. Analogously, alkynyloxy derivatives **4** were synthesized in higher yields (80–85 %) using available acetylenic alcohols.[15] Note that propynyloxy derivative **4a** exists as the mixture of *1,3-alternate* and *partial cone* stereoisomers due to the rotation of propynyloxy fragments through the annulus of calixarene and may at first sight restrict the synthetic applicability of this compound in the synthesis of multicalixarenes. Thermal isomerization is also possible in the case of tetrapropoxythiacalix[4]arene.[18] However, Burilov *et al.*[19] showed that the *partial cone*-to-*1,3-alternate* transition occurs upon azide–alkyne coupling with copper catalyst and exclusively *1,3-alternate* atropoisomer of triazole product is formed.

To convert bromine-substituted thiacalixarenes **2** into corresponding azide derivatives **4**, we employed sodium azide in DMF; this approach proved effective for the synthesis of ethoxy to pentoxy substituents at 90–110 °C, though it took longer time to obtain azidoethoxy derivatives probably due to the steric hindrance of carbon–bromine bond by neighboring *tert*-butyl groups for azide nucleophile. In the latter case, we avoided the mixture of *partial cone* and *1,3-alternate* atropoisomers of **3a** as in the case of analogous azidoethoxy derivatives of amphiphilic thiacalixarenes,[20] which underwent the rotation of substituents at much higher temperatures (150–160 °C) possibly due to the dissociation of C–Br bond according to S_N1 mechanism and through-the-annulus rotation of resulting ethoxy carbocation.

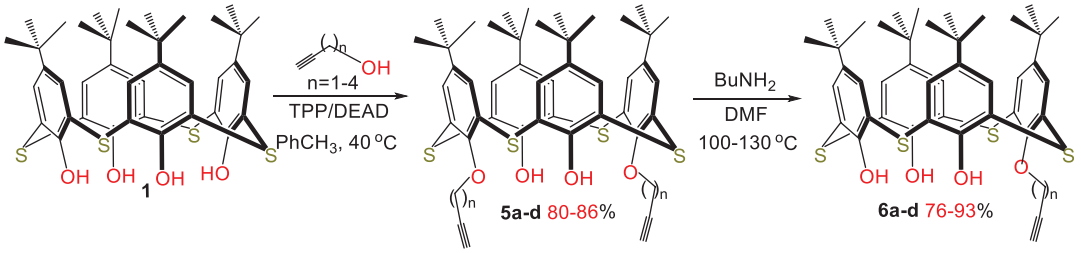


Scheme 2. Synthesis of tetrasubstituted thiacalixarenes by Mitsunobu protocol[15] (**2a**, **4**) and K_2CO_3-medaited alkylation of **1**[14] followed by the reaction of **2** with NaN_3 (**3**).

The next component for CuAAC *click* reaction, monosubstituted thiacalix[4]arenes, highlights challenges to the substitution of a particular number of hydroxyl groups. In contrast to calixarene platform, where iteroselective modification[21] of the lower and upper rims is more straightforward due to large differences in stepwise deprotonation constants of hydroxyl groups,[22] thiacalixarenes have less distinguishable stepwise deprotonation constants.[23] A natural result of this behavior is a very small number of papers, which concern the direct alkylation of thiacalix[4]arene by small excess of alkylating reagent, according to which the products are obtained as the mixtures of iteromers in generally low yields.[24] We also noticed the formation of the mixture of various products when reacting TCA **1** with equimolar amounts of TPP/DEAD and acetylenic alcohols, among which no monosubstituted product was detected (Scheme 3).

However, recent research of distally disubstituted thiacalixarene derivatives, which are accessible by Mitsunobu reaction,[25] provides some useful procedures (though not so wide in scope) towards monosubstituted thiacalixarenes. One of them is base-mediated cleavage of one ether group on the lower rim using TBAB.[26] However, when applied to distally disubstituted alkynyloxythiacalixrenes **5**, which were prepared using 3-fold excess of TPP/DEAD system, these conditions resulted in a 4:1 mixture of target product **6** and parent thiacalix[4]arene **1** in low overall yield. On the one hand, the reason for such instability of monosubstituted derivatives may arise from the anchimeric effect of the terminal triple bond of substituent. On the other hand, tuning the basicity of medium and other environmental conditions such as temperature and time of reaction may afford the target product in higher yields.

As a weaker base, we focused on *n*-butylamine, which was effective in the preparation of monopropyloxy/monoacetophenyloxy derivatives of thiacalix[4]arene[27] (Scheme 3). Optimization of reaction conditions is summarized in Table 1. In the case of butynyloxy to hexynyloxy derivatives, optimal temperature and reaction time were 115–125 °C and 20–27 h, respectively, while an increase in the reaction time or rise of temperature assisted the increase in the rate of elimination of remaining alkoxy group to give thiacalixarene **1**. In contrast to longer-chain monoalkoxy derivatives **6b–d**, propynyloxy derivative **6a** requires significantly milder conditions, more specifically, 100 °C and 7 h, otherwise the fraction of thiacalixarene would



Scheme 3. Synthesis of monosubstituted products **6** by butylamine-assisted elimination of disubstituted intermediates **5**.

be too large and even exceed the content of monoderivative in the reaction mixture (after heating at 130 °C). An interesting point here is that propynyloxy derivative **6a** is represented in solution by a single *cone* conformer (SI, Fig. S17) in contrast with analogous distally disubstituted derivative **5a**,[15b] which was found to exist in *partial cone–1,2-alternate* conformational equilibrium. The rationalization of peculiar stability of *cone* conformation in **6a** requires detailed quantum-chemical investigation and will be discussed elsewhere.

Table 1. Optimization of reaction conditions towards monoalkynyloxythiacalix[4]arenes **6a–d** (temperature, time of reaction).

Product	t (°C)	Time, h	Yield of **6** (%)	Yield of **1** (%)
6a; n=1	130	36	18	58
	110	30	42	26
	100	24	47	36
	100	7.5	64	18
	100	7	76	8
6b; n=2	120	35	28	36
	120	12	85	8
	115	27	93	-
6c; n=3	125	23	85	3
	125	19	87	<1
6d; n=4	130	22	70	21
	125	27	91	2

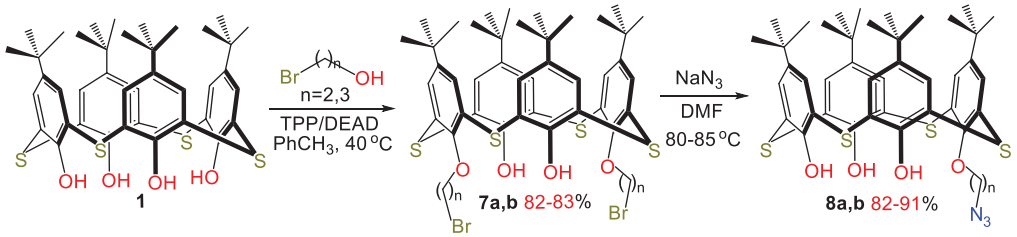
The introduction of one azide group in thiacalixarene appears not to differ significantly from that for alkyne group; however, the reactivity of azide group does not allow Mitsunobu conditions, because it can participate in Staudinger ligation and formation of amino derivatives. This limitation forced us to add one more step including bromide groups (compounds **7**, Scheme 4), which may further be converted into azide derivatives by nucleophilic substitution with sodium azide in DMF followed by base-mediated cleavage of a single ether group. We firstly aimed at the synthesis of corresponding disubstituted derivatives using 8-fold excess of sodium azide; surprisingly, we detected only monosubstituted azidoalkoxy derivatives **8**, which were obtained in high yields (Scheme 4).

This unusual behavior can be interpreted either by the enhanced anchimeric assistance of azide group in disubstituted derivative towards the cleavage of one ether group on the lower rim of thiacalix[4]arene or nucleophilic attack of azide anion or primary dealkylation of bromoalkyl fragment in **7** followed by nucleophilic substitution by sodium azide. To eliminate the latter two possibilities, we reduced the excess of sodium azide to 2.2-fold and observed only distally disubstituted azide derivatives of thiacalix[4]arene.

In summary, we obtained necessary precursors represented by tetra- and monosubstituted thiacalix[4]arenes containing terminal azide and ethynyl functional groups in *1,3-alternate* and *cone* configurations, respectively, and optimized the dealkylation protocol for distally disubstituted thiacalixarenes by varying the reaction time and temperature (in the case of alkynes), as well as excess of reagent (in the case of azides). We recently suggested a common explanation towards high reactivity of only one ether group towards elimination pathway in distally disubstituted derivatives and will describe it in detail elsewhere.

Synthesis of Multicalixarenes

Our successful attempts to prepare mono- and tetrasubstituted azide and alkyne derivatives of thiacalixarene allowed us to carry out the final step of the synthetic chain towards multithiacalixarenes. Having previously discussed the instability of monosubstituted derivatives at high temperatures and basic conditions, it was particularly important to maintain as low temperature as possible, avoid air oxygen in order to prevent alkyne homocoupling, and optimize the amount of copper ions, which is taken at excess due to the possible complexation with sulfur and oxygen atoms of thiacalixarene molecules. Unfortunately, assumption of these conditions still did not give satisfactory yields of target multicalixarenes and we looked into the way how the reagent ratio, time of reaction, and heating conditions affect the yields of the products by the example of multicalixarene **9c** (Table 2). We discovered that stoichiometric **4c**-to-**8a** reagent ratio gives the mixture of the products of partial cycloaddition according to MALDI TOF mass spectrometry, while an increase in the excess of monosubstituted derivative increases the yield by 1.5 times along with that for thiacalixarene **1** (from <1 % (entry 1) to 11 % (entry 2)), which is presumably caused by the copper-assisted cleavage of one ether group in monosubstituted derivative.[28] The most important factor towards the optimization of the yield of target multi(thia)calixarenes was the employment of microwave irradiation, which provided a remarkable decrease in the reaction time by one order (from 105 h (entry 3) to 11 h (entry 4)) and improved the yield of multicalixarene from



Scheme 4. Synthesis of azidoalkoxythiacalix[4]arenes **8** by the reaction of bromoderivatives **7** with sodium azide.

42 % to 73 %. The most probable explanation to this behavior is a selective heating of copper catalyst, on the surface of which the cycloaddition reaction proceeds much faster, and a small effect on competitive elimination to give thiacalixarene **1**.

Table 2. Optimization of CuAAC reaction conditions for compound **9c** (mode of heating, reagent ratio, time of reaction) in toluene–triethylamine.

Entry	**4c**-to-**8a** Reagent ratio	Heating element	t, h	Yield of **9c** (%)	Yield of **1** (%)
1	1:4	Hot plate	82	25	<1
2	1:6	Hot plate	84	39	11
3	1:5	Hot plate	105	42	6
4	1:5	MW (400 W)	11	73	3

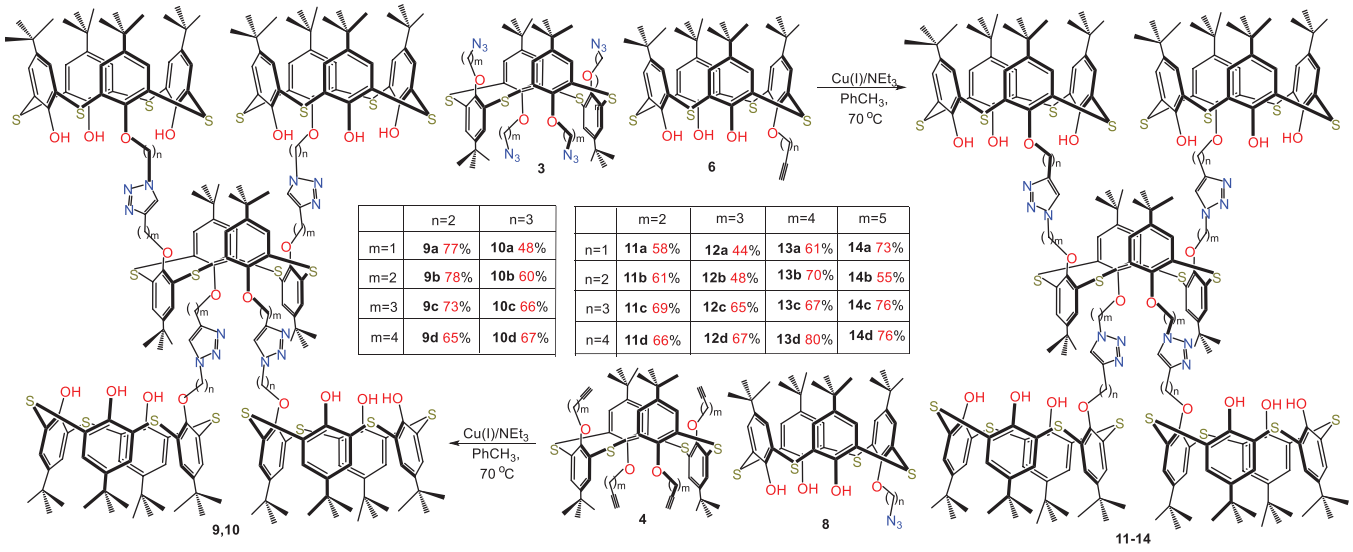
Given the optimized reaction conditions, we obtained dendrimer-shaped multicalixarenes **9**–**14** in moderate to high yields (Scheme 5), which were much higher than those for previously reported amide derivatives of pentakis-thiacalixarenes[24e] and comparable to those of calixarene dendrimers.[3,10d,10e] Following aspects should be emphasized in this reaction. Firstly, in spite of large size of macrocycles, the yields were satisfactory even in the case of short alkyl chain length (m,n=1–2), which links ethynyl and azide functional groups with calixarene (from 44 % for **12a** to 78 % for **9b**), and gradually increased with an increase in the alkyl chain length up to 80 % for **13d**. This dependence is almost not influenced upon the exchange of azide and alkyne groups between tetra- and monosubstituted derivatives (from **9**, **10** to **11**–**14**).

The structure of the synthesized compounds was determined by a series of physical methods such as high-resolution MALDI TOF mass spectrometry and NMR spectroscopy (see SI, Fig. S98). A clear indication of the 1,4-regioisomer formation is the difference of chemical shifts of C1 (149.2 ppm) and C5 (127.7 ppm) atoms of triazole ring in ^{13}C NMR spectrum (21.5 ppm), which is similar to that of theoretically calculated by DFT method (~27 ppm).[29] Proton NMR spectrum of **12c** (Figure 1) shows a broad signal of hydroxyl groups at 9.35 ppm and a singlet of CH-triazole proton at 7.81 ppm, which suggests the symmetric orientation of calixarene pendant groups around the core calixarene molecule and triazole linker, respectively, as well as the retention of the conformation of monosubstituted azide derivative due to similar chemical shifts of hydroxyl groups (Fig. S97). However, no clear information can be deduced about the shape that pendant groups acquire around the core molecule and, consequently, the accessibility of the "binding pocket", which consists of three hydroxyl groups and triazole ring. Broad peaks of hydroxyl groups and methylene units (from 4.4. to 1.8 ppm) indicate the high conformational mobility of calixarene units around alkyl chain at the temperature of experiment (293 K).

Structural investigations of multicalixarene dendrimers are of certain interest, because varying the length of alkyl chain, we not only attempt to assess the synthetic availability of the given dendrimers, but also look into the gold standard, at which the binding domain would be most efficient towards particular guest ion/molecule at the given alkyl chain length. Our further research will follow this principle by theoretical modeling of the binding behavior of multicalixarenes and experimental study of their receptor activity (by solution-state NMR and on the solid phase as an ultrathin film).

Conclusions

Synthesis of tetra- and disubstituted thiacalix[4]arenes by nucleophilic substitution on the lower rim has been optimized. New method for the preparation of monosubstituted thiacalix[4]arene derivatives has been suggested and optimized, which is based on the instability of disubstituted derivatives in alkaline medium. A series of dendrimer-shaped multicalixarenes with bridging triazole units has been synthesized in 44–80 % yields. The effect of MW irradiation on the acceleration of 1,3-dipolar azide–alkyne



	n=2	n=3
m=1	**9a** 77%	**10a** 48%
m=2	**9b** 78%	**10b** 60%
m=3	**9c** 73%	**10c** 66%
m=4	**9d** 65%	**10d** 67%

	m=2	m=3	m=4	m=5
n=1	**11a** 58%	**12a** 44%	**13a** 61%	**14a** 73%
n=2	**11b** 61%	**12b** 48%	**13b** 70%	**14b** 55%
n=3	**11c** 69%	**12c** 65%	**13c** 67%	**14c** 76%
n=4	**11d** 66%	**12d** 67%	**13d** 80%	**14d** 76%

Scheme 5. Synthesis of multi(thia)calixarenes **9**–**14** using CuAAC reaction.

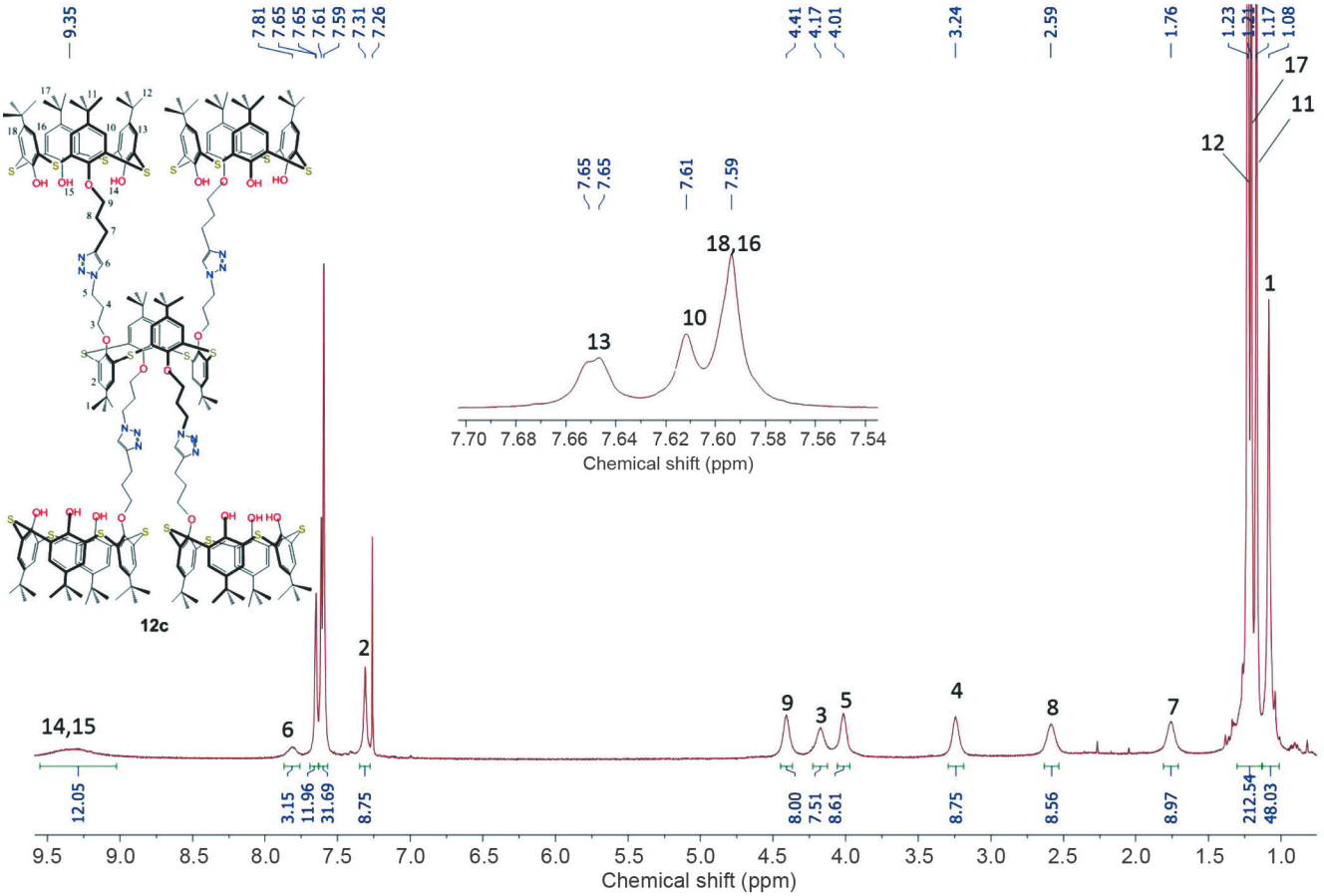


Figure 1. ^{1}H NMR spectrum of pentakis-thiacalix[4]arene **12c** ($CDCl_3$, 400 MHz, 293 K).

cycloaddition and increase in the yield of pentakisthiacalix[4]arenes has been established.

Acknowledgements. The work was funded by the Russian Foundation for Basic Research (project No. 15-53-61021-Egypt-a) and the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities.

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Received 31.03.2017
Accepted 15.05.2017