Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Triazolated calix[4]semitubes: assembling strategies towards long multicalixarene architectures

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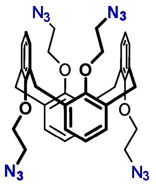
Supplementary Information

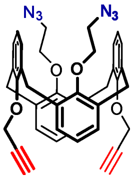
Contents

Synthesis and characterization of novel compounds

General experimental methods: NMR spectra were acquired on Bruker Avance 400 instrument at 20 ºC if not stated otherwise, and chemical shifts are reported as ppm referenced to solvent signals. ESI mass spectra were obtained from Sciex TripleTOF 5600+ spectrometers. Chemicals received from commercial sources were used without further purification. Calixarenes **1**,[S1] **2**–**4**,[S2] **5**,[S3] **6**,[S4] **7**,[S5] **8**,[S2] **9**,[S6] and **10**[S7] were prepared according to the published procedures.

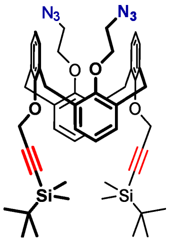


Tetrakis(azide) ***11***. Diisopropyl azodicarboxylate (2.73 ml, 13.87 mmol) was added dropwise at stirring to a cooled (0–5 °C) solution of Ph_3P (2.73 g, 10.4 mmol) in dry THF (30 ml). After a solid formed, the mixture was stirred at cooling for 1 h. A solution of calix[4]arene **10** (1.04 g, 1.73 mmol) and diphenyl phosphoryl azide (2.99 ml, 13.87 mmol) in THF (90 ml) was added dropwise. The reaction mixture was stirred at cooling for 1 h and then allowed to stay at room temperature for 48 h. The solution was concentrated under reduced pressure and the resultant oil was treated with cold methanol. The solid formed was collected, washed with methanol and dried. Yield 0.627 g (52%), white solid. M.p. 97–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (d, 8H, $^3J_{HH} = 7.6$ Hz; ArH), 6.89 (t, 4H, $^3J_{HH} = 7.6$ Hz; ArH), 3.82 (s, 8H; $ArCH_2Ar$), 3.54–3.48 (m, 8H; OCH_2), 2.97–2.91 (m, 8H; CH_2N_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.77, 133.70 (C_{Ar}), 129.48, 123.10 (CH_{Ar}), 68.02 (OCH_2), 50.13 (CH_2N_3), 37.42 ($ArCH_2Ar$) ppm. ESI-MS *m/z*: 718.3314 $[M+NH_4]^+$ for $C_{36}H_{40}N_{13}O_4$ (718.3321).



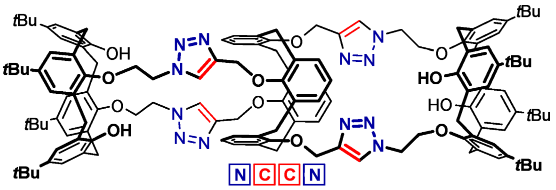
Bis(azide)/bis(alkyne) ***12***. A mixture of bis(azide) **2** (2.81 g, 5.00 mmol) and anhydrous Cs_2CO_3 (6.52 g, 20.0 mmol) in dry DMF (80 ml) was stirred at room temperature for 2 h. Propargyl bromide (80% in toluene, 2.23 ml, 20.0 mmol) was added and stirring was continued for 48 h at room temperature. The solvent was removed under reduced pressure without heating, and the residue was parted between dichloromethane and 2 M HCl. The organic layer was separated, washed with water, dried with $MgSO_4$ and concentrated to dryness. The residue was purified by column chromatography (gradient from hexane to hexane/dichloromethane (1:2)). Yield 1.091 g (34%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 7.08 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.85 (t, 2H, $^3J_{HH} = 7.5$ Hz; ArH), 6.83 (t, 2H, $^3J_{HH} = 7.5$ Hz; ArH), 4.01 (d, 4H, $^4J_{HH} = 2.4$ Hz; $OC\underline{H}_2CCH$), 3.88 (d, 4H, $^2J_{HH} = 15.1$ Hz; $ArCH_2Ar$), 3.70 (d, 4H, $^2J_{HH} = 15.1$ Hz; $ArCH_2Ar$), 3.52–3.47 (m, 4H; OCH_2), 3.19–3.13 (m, 4H; CH_2N_3), 2.39 (t, 2H, $^4J_{HH} = 2.4$ Hz; CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.49, 155.35, 134.52, 133.61

(C_{Ar}), 130.41, 129.75, 123.14, 123.08 (CH_{Ar}), 80.29 ($OCH_2\underline{C}$), 74.56 (CH), 68.87 (OCH_2), 58.62 ($O\underline{C}H_2CCH$), 50.62 (CH_2N_3), 37.16 ($ArCH_2Ar$) ppm. ESI-MS *m*/*z*: 656.2980 $[M+NH_4]^+$ for $C_{38}H_{38}N_7O_4$ (656.2980).

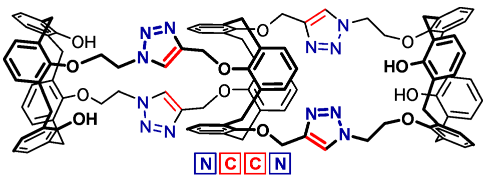


Bis(azide) ***13***. Under argon, *n*BuLi (2.5 M in hexane, 0.442 ml, 1.10 mmol) was added dropwise to a solution of bis(trimethylsilyl)amine (0.308 ml, 1.47 mmol) in dry THF (10 ml) at cooling (–78 °C). The mixture was slowly heated to room temperature, stirred for 1 h, and cooled again (–78 °C). A solution of calixarene **12** (0.235 g, 0.37 mmol) in dry THF (10 ml) was added dropwise with stirring, and the mixture was stirred at cooling for 30 min. A solution of *tert*-butyldimethylsilyl chloride (0.167 g, 1.10 mmol) in dry THF (10 ml) was added, the mixture was heated to room temperature and stirred overnight. Saturated solution of NH_4Cl (30 ml) was added to the reaction mixture, the organic phase was separated, the aqueous phase was washed with dichloromethane (2×20 ml). The combined organic extracts were washed with water, dried with $MgSO_4$ and evaporated to dryness. The residue was purified by flash chromatography on SiO_2 (dichloromethane). Yield 0.220 g (69%), white solid. M.p. 103–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 7.04 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.79 (t, 2H, $^3J_{HH} = 7.5$ Hz; ArH), 6.74 (t, 2H, $^3J_{HH} = 7.5$ Hz; ArH), 4.21 (s, 4H; $OC\underline{H}_2CCH$), 3.82 (d, 4H, $^2J_{HH} = 14.5$ Hz; $ArCH_2Ar$), 3.62 (d, 4H, $^2J_{HH} = 14.5$ Hz; $ArCH_2Ar$), 3.54–3.48 (m, 4H; OCH_2), 3.31–3.25 (m, 4H; CH_2N_3), 0.93 (s, 18H; $C(CH_3)_3$), 0.12 (s, 12H; $SiCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.60, 155.26, 134.47, 133.39 (C_{Ar}), 130.50, 129.66, 122.93, 122.60 (CH_{Ar}), 102.82 ($OCH_2\underline{C}$), 89.83 ($OCH_2C\underline{C}$), 69.23 (OCH_2), 59.48 ($O\underline{C}H_2CC$), 51.00 (CH_2N_3), 36.78 ($ArCH_2Ar$), 26.03 ($C(\underline{C}H_3)_3$), 16.47 ($\underline{C}(CH_3)_3$), –4.75 ($SiCH_3$) ppm. ESI-MS *m*/*z*: 884.4705 $[M+NH_4]^+$ for $C_{50}H_{66}N_7O_4Si_2$ (884.4709).

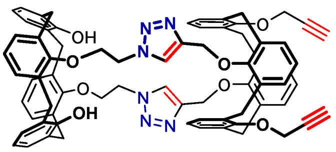
General procedure for the preparation of calix[4]semitubes. To a stirred mixture of calixarene (bis)alkyne and (bis)azide in toluene or THF, Cu(I)-catalyst was added (CuI dissolved in a small portion of toluene by addition of Et_3N, or $CuSO_4\cdot5H_2O$/sodium ascorbate mixture dissolved in water). The mixture was stirred at room temperature or at heating, and then concentrated under reduced pressure. The residue was parted between dichloromethane and 2 M HCl at vigorous stirring for at least 2 h. The organic layer was separated, washed with aqueous Na_2SO_3 (5%, for CuI-catalyzed reactions only), water and dried with $MgSO_4$. The solvent was removed and the residue was subjected to column chromatography. The two-step column separation was applied in several cases: from the first column, a polymeric material was first eluted followed by a semitube-containing fraction, which was then evaporated to dryness and subjected to the second column (with the same or different eluent) for the final purification.



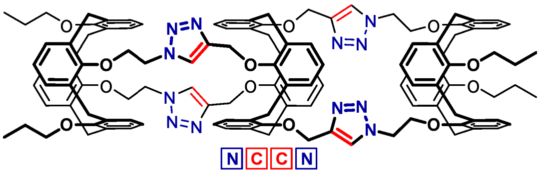
Tris(calix[4]arene) **14** was prepared according to *General procedure* from calixarene **1** (0.524 g, 0.68 mmol), calixarene **9** (0.195 g, 0.34 mmol), CuI (0.038 g, 0.20 mmol) and Et_3N (0.56 ml, 4.0 mmol) in toluene (40 ml). The reaction mixture was stirred at room temperature for 48 h. Column: gradient from dichloromethane to dichloromethane/ethanol (50:1). Yield 0.270 g (38%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.09$ (s, 8H; ArH), 7.05 (s, 4H; OH), 6.77 (s, 8H; ArH), 6.74 (d, 8H, $^3J_{HH} = 7.5$ Hz; ArH), 6.45 (s, 4H; ArH_{Trz}), 6.37 (t, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 4.98–4.93 (m, 8H; NCH_2), 4.87 (s, 8H; OCH_2Trz), 4.40–4.34 (m, 8H; $NCH_2C\underline{H}_2$), 4.00 (d, 8H, $^2J_{HH} = 13.2$ Hz; $ArCH_2Ar$), 3.60 (s, 8H; $ArCH_2Ar$), 3.38 (d, 8H, $^2J_{HH} = 13.2$ Hz; $ArCH_2Ar$), 1.31 (s, 36H; $C(CH_3)_3$), 0.91 (s, 36H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.63$, 149.99, 148.63, 147.80 (C_{Ar}), 144.73 ($C_{Ar\,Trz}$), 142.12, 134.18, 131.92 (C_{Ar}), 129.04 (CH_{Ar}), 127.23 (C_{Ar}), 125.83 (CH_{Ar}), 125.38 ($CH_{Ar\,Trz}$)*, 125.17, 122.67 (CH_{Ar}), 73.57, 63.42 (OCH_2), 49.18 (NCH_2), 37.94 ($ArCH_2Ar$), 33.90, 33.87 ($\underline{C}(CH_3)_3$), 31.66 ($C(\underline{C}H_3)_3$), 31.50 ($ArCH_2Ar$), 30.83 ($C(\underline{C}H_3)_3$) ppm. ESI-MS *m/z*: 1098.0888 $[M+2Na]^{2+}$ for $C_{136}H_{156}Na_2N_{12}O_{12}$ (1098.0892); 2151.2055 $[M+H]^+$ for $C_{136}H_{157}N_{12}O_{12}$ (2151.2072).



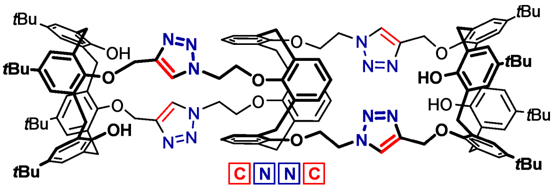
Tris(calix[4]arene) **15** was prepared according to *General procedure* from calixarene **2** (0.101 g, 0.18 mmol), calixarene **9** (0.052 g, 0.09 mmol), CuI (0.011 g, 0.06 mmol) and Et_3N (1.0 ml) in toluene (10 ml). The reaction mixture was stirred at room temperature for 24 h. Column: gradient from dichloromethane to dichloromethane/ethanol (50:1). Yield 0.045 g (29%), white solid. M.p. 264–266 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.11$ (d, 8H, $^3J_{HH} = 7.5$ Hz; ArH), 7.10 (s, 4H; OH), 6.98 (s, 4H; ArH_{Trz}), 6.84 (d, 8H, $^3J_{HH} = 7.5$ Hz; ArH), 6.77–6.70 (m, 12H; ArH), 6.65 (t, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.39 (t, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 5.07–5.01 (m, 8H; NCH_2), 4.87 (s, 8H; OCH_2Trz), 4.42–4.36 (m, 8H; $NCH_2C\underline{H}_2$), 4.05 (d, 8H, $^2J_{HH} = 13.2$ Hz; $ArCH_2Ar$), 3.61 (s, 8H; $ArCH_2Ar$), 3.45 (d, 8H, $^2J_{HH} = 13.2$ Hz; $ArCH_2Ar$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.83$, 152.60, 150.75 (C_{Ar}), 144.80 ($C_{Ar\,Trz}$), 134.12, 132.25 (C_{Ar}), 129.36, 129.03, 128.80 (CH_{Ar}), 127.32 (C_{Ar}), 126.08 (CH_{Ar}), 125.07 ($CH_{Ar\,Trz}$), 122.67, 119.58 (CH_{Ar}), 74.00, 63.57 (OCH_2), 49.12 (NCH_2), 37.93, 31.16 ($ArCH_2Ar$) ppm. ESI-MS *m*/*z*: 1702.7060 $[M+H]^+$ for $C_{104}H_{93}N_{12}O_{12}$ (1702.7062).



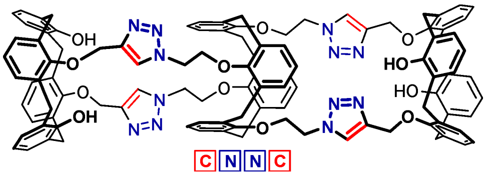
Bis(calix[4]arene) ***16*** was collected during purification of the tris(calixarene) **15** by column chromatography. Yield 0.015 g (15%), white solid. M.p. 219–221 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 7.10 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 7.06 (s, 2H; OH), 6.97 (s, 2H; ArH_{Trz}), 6.96 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.87 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.75 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.72 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.70 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.32 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 5.08–5.02 (m, 4H; NCH_2), 4.86 (s, 4H; OCH_2Trz), 4.43–4.36 (m, 4H; $NCH_2C\underline{H}_2$), 4.05 (d, 4H, $^2J_{HH}$ = 13.2 Hz; $ArCH_2Ar$), 3.92 (d, 4H, $^2J_{HH}$ = 15.8 Hz; $ArCH_2Ar$), 3.62 (d, 4H, $^2J_{HH}$ = 15.8 Hz; $ArCH_2Ar$), 3.60 (d, 4H, $^4J_{HH}$ = 2.4 Hz; OCH_2C), 3.46 (d, 8H, $^2J_{HH}$ = 13.2 Hz; $ArCH_2Ar$), 2.30 (t, 2H, $^4J_{HH}$ = 2.4 Hz; CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.72, 155.30, 152.63, 150.82 (C_{Ar}), 144.80 ($C_{Ar\,Trz}$), 135.17, 134.27, 132.35 (C_{Ar}), 130.19, 129.40, 129.25, 128.79 (CH_{Ar}), 127.38 (C_{Ar}), 126.11 (CH_{Ar}), 125.24 ($CH_{Ar\,Trz}$), 124.22, 122.51, 119.63 (CH_{Ar}), 80.39 ($\underline{C}CH$), 74.42 ($\underline{C}H$), 74.05, 64.09, 58.16 (OCH_2), 49.15 (NCH_2), 38.09, 31.17 ($ArCH_2Ar$) ppm. ESI-MS *m*/*z*: 1139.4706 $[M+H]^+$ for $C_{72}H_{63}N_6O_8$ (1139.4707).



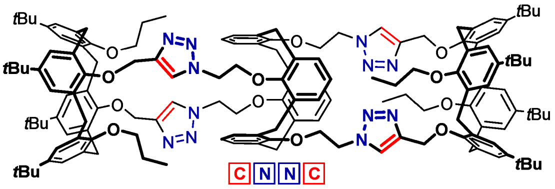
Tris(calix[4]arene) ***17*** was prepared according to *General procedure* from calixarene **4** (0.129 g, 0.20 mmol), calixarene **9** (0.057 g, 0.10 mmol), CuI (0.012 g, 0.06 mmol) and Et_3N (0.148 ml, 1.20 mmol) in toluene (12 ml). The reaction mixture was stirred at 60 °C for 24 h. Column: gradient from dichloromethane to dichloromethane/ethanol (50:1). Yield 0.028 g (15%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (d, 8H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.94 (d, 8H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.89 (t, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.82 (d, 8H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.68 (t, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.49 (t, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.12 (s, 4H; ArH_{Trz}), 4.80 (s, 8H; OCH_2Trz), 4.40–4.31 (m, 8H; NCH_2), 4.08–3.98 (m, 8H; $NCH_2C\underline{H}_2$), 3.91 (d, 8H, $^2J_{HH}$ = 16.4 Hz; $ArCH_2Ar$), 3.82 (d, 8H, $^2J_{HH}$ = 16.4 Hz; $ArCH_2Ar$), 3.58 (s, 8H; $ArCH_2Ar$), 3.42–3.32 (m, 8H; $OC\underline{H}_2CH_2CH_3$), 1.19–1.07 (m, 8H; $C\underline{H}_2CH_3$), 0.69 (t, 12H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.16, 155.63, 155.02 (C_{Ar}), 144.30 ($C_{Ar\,Trz}$), 134.35, 134.22, 133.38 (C_{Ar}), 129.99, 129.07, 128.46 (CH_{Ar}), 123.30 ($CH_{Ar\,Trz}$), 123.26, 122.57, 122.53 (CH_{Ar}), 71.52, 68.70, 63.19 (OCH_2), 48.83 (NCH_2), 38.39, 38.07 ($ArCH_2Ar$), 22.16 ($\underline{C}H_2CH_3$), 9.89 (CH_3) ppm. ESI-MS *m*/*z*: 935.9506 $[M+2H]^{2+}$ for $C_{116}H_{118}N_{12}O_{12}$ (935.9507).



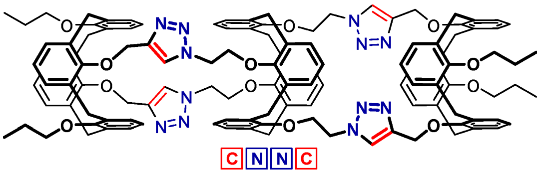
Tris(calix[4]arene) **18** was prepared according to *General procedure* from calixarene **5** (0.290 g, 0.40 mmol), calixarene **11** (0.140 g, 0.20 mmol), CuI (0.023 g, 0.12 mmol) and Et_3N (0.360 ml, 2.40 mmol) in toluene (20 ml). The reaction mixture was stirred at 60 °C for 12 h. Column: gradient from dichloromethane to dichloromethane/ethanol (70:1). Yield 0.025 g (6%), white solid. M.p. >300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 4H; ArH_{Trz}), 7.11 (s, 12H; ArH), 7.10 (s, 8H; ArH), 6.77 (s, 8H; ArH), 6.75 (s, 4H; OH), 5.18 (s, 8H; OCH_2Trz), 4.31 (d, 8H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 4.10–4.04 (m, 8H; NCH_2), 4.01 (s, 8H; $ArCH_2Ar$), 3.62–3.54 (m, 8H; $NCH_2C\underline{H}_2$), 3.39 (d, 8H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 1.31 (s, 36H; $C(CH_3)_3$), 0.92 (s, 36H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.82, 150.32, 149.51, 147.49 (C_{Ar}), 144.81 ($C_{Ar\ Trz}$), 141.97, 133.61, 132.18 (C_{Ar}), 128.93 (CH_{Ar}), 127.81 (C_{Ar}), 125.64, 125.16 (CH_{Ar}), 123.98 ($CH_{Ar\ Trz}$)*, 122.68 (CH_{Ar}), 70.40, 66.59 (OCH_2), 48.68 (NCH_2), 37.97 ($ArCH_2Ar$), 33.91, 33.85 ($\underline{C}(CH_3)_3$), 31.67 ($C(\underline{C}H_3)_3$), 31.45 ($ArCH_2Ar$), 30.92 ($C(\underline{C}H_3)_3$) ppm; ESI-MS *m/z*: 1098.0884 $[M+2Na]^{2+}$ for $C_{136}H_{156}Na_2N_{12}O_{12}$ (1098.0892); 2173.1874 $[M+Na]^+$ for $C_{136}H_{156}NaN_{12}O_{12}$ (2173.1891).



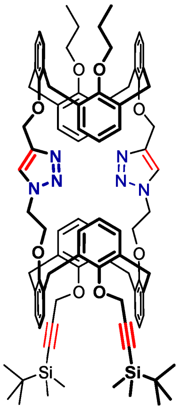
Tris(calix[4]arene) **19** was prepared according to *General procedure* from calixarene **6** (0.100 g, 0.20 mmol), calixarene **11** (0.070 g, 0.10 mmol), CuI (0.011 g, 0.06 mmol) and Et_3N (0.15 ml) in toluene (15 ml). The reaction mixture was stirred at 60 °C for 12 h. Column: gradient from dichloromethane to dichloromethane/ethanol (50:1). Yield 0.025 g (14%), white solid. M.p. >300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (s, 4H; ArH_{Trz}), 7.44 (s, 4H; OH), 7.13–7.08 (m, 20H; ArH), 6.88 (d, 8H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.75 (t, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.71 (t, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 5.19 (s, 8H; OCH_2Trz), 4.36 (d, 8H, $^2J_{HH}$ = 13.2 Hz; $ArCH_2Ar$), 4.09–4.03 (m, 8H; NCH_2), 4.01 (s, 8H; $ArCH_2Ar$), 3.69–3.63 (m, 8H; $NCH_2C\underline{H}_2$), 3.46 (d, 8H, $^2J_{HH}$ = 13.2 Hz; $ArCH_2Ar$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.81, 153.02, 151.75 (C_{Ar}), 144.22 ($C_{Ar\ Trz}$), 133.57, 132.80 (C_{Ar}), 129.16, 129.01, 128.66 (CH_{Ar}), 127.88 (C_{Ar}), 125.79 (CH_{Ar}), 124.04 ($CH_{Ar\ Trz}$), 122.64, 119.33 (CH_{Ar}), 70.42, 66.97 (OCH_2), 48.81 (NCH_2), 37.96, 31.29 ($ArCH_2Ar$) ppm. ESI-MS *m/z*: 1724.6871 $[M+Na]^+$ for $C_{104}H_{92}NaN_{12}O_{12}$ (1724.6883).



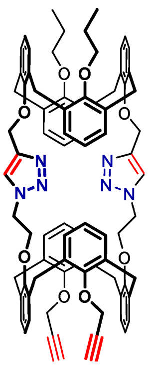
Tris(calix[4]arene) **20** was prepared according to *General procedure* from calixarene **7** (0.194 g, 0.24 mmol), calixarene **11** (0.084 g, 0.12 mmol), CuI (0.046 g, 0.24 mmol) and Et_3N (4 ml) in toluene (15 ml). The reaction mixture was stirred at 70 °C for 9 h. Column: gradient from dichloromethane to dichloromethane/ethanol (40:1), the product separated from the column was additionally washed with methanol. Yield 0.060 g (22%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 4H; ArH_{Trz}), 7.08 (s, 8H; ArH), 6.90–6.81 (m, 12H; ArH), 6.43 (s, 8H; ArH), 5.28 (s, 8H; OCH_2Trz), 4.26 (d, 8H, $^2J_{HH}$ = 12.8 Hz; $ArCH_2Ar$), 4.07–4.01 (m, 8H; NCH_2), 3.90–3.84 (m, 8H; $NCH_2C\underline{H}_2$), 3.82 (s, 8H; $ArCH_2Ar$), 3.71–3.65 (m, 8H; $OC\underline{H}_2CH_2CH_3$), 3.09 (d, 8H, $^2J_{HH}$ = 12.8 Hz; $ArCH_2Ar$), 1.82–1.71 (m, 8H; $C\underline{H}_2CH_3$), 1.31 (s, 36H; $C(CH_3)_3$), 1.05 (t, 12H, $^3J_{HH}$ = 7.5 Hz; CH_3), 0.81 (s, 36H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ = 155.77, 153.33, 152.24, 145.27, 145.12 (C_{Ar}), 144.03 $(C_{Ar\ Trz})^*$, 135.39, 133.36, 131.53 (C_{Ar}), 129.41, 125.69, 125.16, 124.31 (CH_{Ar}), 122.51 $(CH_{Ar\ Trz})^*$, 76.96, 68.35, 65.52 (OCH_2), 49.62 (NCH_2), 36.92 ($ArCH_2Ar$), 33.89, 33.40 ($\underline{C}(CH_3)_3$), 31.48 ($C(\underline{C}H_3)_3$), 31.05 ($ArCH_2Ar$), 30.92 ($C(\underline{C}H_3)_3$), 23.17 ($\underline{C}H_2CH_3$), 10.50 (CH_3) ppm. ESI-MS *m*/*z*: 1171.1915 $[M+H+Na]^{2+}$ for $C_{148}H_{181}NaN_{12}O_{12}$ (1171.1921); 1182.1825 $[M+2Na]^{2+}$ for $C_{148}H_{180}Na_2N_{12}O_{12}$ (1182.1831).



Tris(calix[4]arene) **21** was prepared according to *General procedure* from calixarene **8** (0.234 g, 0.40 mmol), calixarene **11** (0.140 g, 0.20 mmol), CuI (0.076 g, 0.40 mmol) and Et_3N (1.12 ml, 8.0 mmol) in a mixture of toluene (10 ml) and 1,2-dichloroethane (10 ml). The reaction mixture was stirred at room temperature for 48 h. Column: gradient from dichloromethane to dichloromethane/ethanol (50:1). Yield 0.041 g (11%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 (d, 8H, $^3J_{HH}$ = 7.5 Hz; ArH), 7.06 (d, 8H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.89 (t, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.86 (t, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.78 (d, 8H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.43 (s, 4H; ArH_{Trz}), 6.36 (t, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 4.85 (s, 8H; OCH_2Trz), 4.15 (s, 16H; $NC\underline{H}_2C\underline{H}_2$), 4.01 (s, 8H; $ArCH_2Ar$), 3.77 (d, 8H, $^2J_{HH}$ = 15.5 Hz; $ArCH_2Ar$), 3.62 (d, 8H, $^2J_{HH}$ = 15.5 Hz; $ArCH_2Ar$), 3.43–3.37 (m, 8H; $OC\underline{H}_2CH_2CH_3$), 1.48–1.37 (m, 8H; $C\underline{H}_2CH_3$), 0.75 (t, 12H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ = 156.89, 155.93, 154.79 (C_{Ar}), 144.52 ($C_{Ar\ Trz}$), 134.28, 133.82 (C_{Ar}), 129.88, 129.28, 129.07 (CH_{Ar}), 123.95 $(CH_{Ar\ Trz})^*$, 123.64, 122.92, 120.69 (CH_{Ar}), 71.96, 67.88, 63.41 (OCH_2), 48.41 (NCH_2), 38.09, 37.68 ($ArCH_2Ar$), 22.87 ($\underline{C}H_2CH_3$), 9.90 (CH_3) ppm. ESI-MS *m*/*z*: 957.9321 $[M+2Na]^{2+}$ for $C_{116}H_{116}Na_2N_{12}O_{12}$ (957.9327); 1892.8754 $[M+Na]^+$ for $C_{116}H_{116}NaN_{12}O_{12}$ (1892.8761).

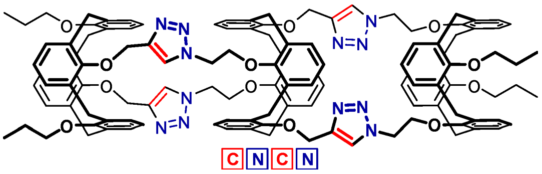


Bis(calix[4]arene) ***22*** was prepared according to *General procedure* from calixarene **13** (0.554 g, 0.64 mmol), calixarene **8** (0.373 g, 0.64 mmol), $CuSO_4 \cdot 5H_2O$ (0.160 g, 0.64 mmol) and sodium ascorbate (0.253 g, 1.28 mmol) in a mixture of THF (76 ml) and water (15 ml). The reaction mixture was stirred at 60 °C for 24 h. Column 1: gradient from dichloromethane to dichloromethane/ethanol (50:1). Column 2: gradient from hexane to hexane/ethyl acetate (5:1). Yield 0.420 g (45%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 7.04 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.92 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.90 (t, 2H, $^3J_{HH} = 7.5$ Hz; ArH), 6.87 (t, 2H, $^3J = 7.5$ Hz; ArH), 6.82 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.67 (t, 2H, $^3J_{HH} = 7.5$ Hz; ArH), 6.39 (t, 2H, $^3J_{HH} = 7.5$ Hz; ArH), 6.17 (s, 2H; ArH_{Trz}), 4.80 (s, 4H; OCH_2Trz), 4.45–4.39 (m, 4H; NCH_2), 4.13–4.08 (m, 4H; $NCH_2C\underline{H}_2$), 4.04 (d, 4H, $^2J_{HH} = 15.8$ Hz; $ArCH_2Ar$), 4.02 (s, 4H; OCH_2CC), 3.80 (d, 4H, $^2J_{HH} = 15.2$ Hz; $ArCH_2Ar$), 3.76 (d, 4H, $^2J_{HH} = 15.2$ Hz; $ArCH_2Ar$), 3.62 (d, 4H, $^2J_{HH} = 15.8$ Hz; $ArCH_2Ar$), 3.35–3.28 (m, 4H; $OC\underline{H}_2CH_2CH_3$), 1.36–1.26 (m, 4H; $C\underline{H}_2CH_3$), 0.87 (s, 18H; $C(CH_3)_3$), 0.68 (t, 6H, $^3J_{HH} = 7.5$ Hz; CH_3), 0.08 (s, 12H; $SiCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.94, 155.63, 155.55, 154.74 (C_{Ar}), 144.26 ($C_{Ar\,Trz}$), 135.23, 134.44, 134.06, 133.51 (C_{Ar}), 130.25, 129.75, 129.03, 128.44 (CH_{Ar}), 124.41 ($CH_{Ar\,Trz}$),* 123.69, 123.08, 121.39 (CH_{Ar}), 102.57 ($OCH_2\underline{C}$), 89.94 ($OCH_2C\underline{C}$), 71.79, 68.67, 63.21 (OCH_2), 58.33 ($O\underline{C}H_2CC$), 49.04 (NCH_2), 38.25, 38.13 ($ArCH_2Ar$), 25.95 ($C(\underline{C}H_3)_3$), 22.89 ($\underline{C}H_2CH_3$), 16.38 ($\underline{C}(CH_3)_3$), 10.07 ($CH_2\underline{C}H_3$), –4.84 ($SiCH_3$) ppm. ESI-MS *m*/*z*: 1452.7400 $[M+H]^+$ for $C_{90}H_{103}N_6O_8Si_2$ (1452.7400).

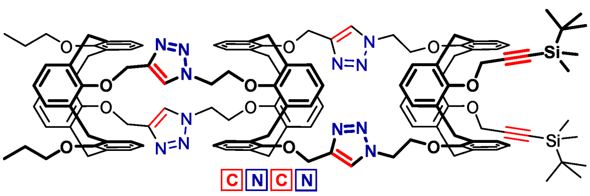


Bis(calix[4]arene) ***23***. To a suspension of bis(calix[4]arene) **22** (0.420 g, 0.29 mmol) in THF (1.7 ml) a solution of $n\mathrm{Bu}_4NF \cdot 3H_2O$ (0.018 g, 0.058 mmol) in THF (1.7 ml) and water (0.034 ml) was added. The mixture was stirred at 50 °C for 12 h and cooled to room temperature. The solvent was removed and the residue was dissolved in dichloromethane. The solid formed was collected and dissolved in dichloromethane. Methanol was added, and the solid formed was collected and dried. Yield 0.250 g (70%), white solid. M.p. 294–296 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 7.05 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.97 (d, 4H,

$^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.95 (t, 2H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.87 (t, 2H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.82 (d, 4H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.73 (t, 2H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.38 (t, 2H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.21 (s, 2H; $\mathrm{ArH_{Trz}}$), 4.81 (s, 4H; $\mathrm{OCH_2Trz}$), 4.39–4.32 (m, 4H; $\mathrm{NCH_2}$), 4.14–4.07 (m, 4H; $\mathrm{NCH_2C\underline{H}_2}$), 4.05 (d, 4H, $^2J_{\mathrm{HH}}$ = 16.1 Hz; $\mathrm{ArCH_2Ar}$), 3.84 (d, 4H, $^4J_{\mathrm{HH}}$ = 2.4 Hz; $\mathrm{OCH_2CC}$), 3.81 (d, 4H, $^2J_{\mathrm{HH}}$ = 16.1 Hz; $\mathrm{ArCH_2Ar}$), 3.79 (d, 4H, $^2J_{\mathrm{HH}}$ = 15.8 Hz; $\mathrm{ArCH_2Ar}$), 3.63 (d, 4H, $^2J_{\mathrm{HH}}$ = 15.8 Hz; $\mathrm{ArCH_2Ar}$), 3.37–3.30 (m, 4H; $\mathrm{OC\underline{H}_2CH_2CH_3}$), 2.33 (t, 2H, $^4J_{\mathrm{HH}}$ = 2.4 Hz; CH), 1.38–1.26 (m, 4H; $\mathrm{C\underline{H}_2CH_3}$), 0.68 (t, 6H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; $\mathrm{CH_3}$) ppm; ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 156.92, 155.56, 155.50, 154.74 ($\mathrm{C_{Ar}}$), 144.30 ($\mathrm{C_{Ar\,Trz}}$), 135.17, 134.41, 134.02, 133.52 ($\mathrm{C_{Ar}}$), 130.43, 129.79, 129.09, 128.68 ($\mathrm{CH_{Ar}}$), 124.28 ($\mathrm{CH_{Ar\,Trz}}$), 124.00, 123.28, 123.07, 121.25 ($\mathrm{CH_{Ar}}$), 80.10 ($\mathrm{OCH_2\underline{C}CH}$), 74.72 ($\mathrm{OCH_2C\underline{C}H}$), 71.85, 68.70, 63.24 ($\mathrm{OCH_2}$), 57.83 ($\mathrm{O\underline{C}H_2CCH}$), 48.88 ($\mathrm{NCH_2}$), 38.24, 38.07 ($\mathrm{ArCH_2Ar}$), 22.89 ($\mathrm{\underline{C}H_2CH_3}$), 10.06 ($\mathrm{CH_2\underline{C}H_3}$) ppm. ESI-MS *m*/*z*: 1223.5637 $[\mathrm{M+H}]^+$ for $\mathrm{C_{78}H_{75}N_6O_8}$ (1223.5641).



Tris(calix[4]arene) **24** was prepared according to *General procedure* from bis(calix[4]arene) **23** (0.122 g, 0.10 mmol), calixarene **4** (0.065 g, 0.10 mmol), $\mathrm{CuSO_4{\cdot}5H_2O}$ (0.025 g, 0.10 mmol) and sodium ascorbate (0.040 g, 0.20 mmol) in a mixture of THF (12 ml) and water (2.4 ml). The reaction mixture was stirred at 60 °C for 24 h. Column: gradient from dichloromethane to dichloromethane/ethanol (40:1). Yield 0.048 g (26%), white solid. M.p. >300 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 7.09 (d, 4H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 7.05 (d, 4H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.99 (d, 4H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.96–6.85 (m, 12H; ArH), 6.81 (d, 4H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.77 (t, 2H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.65 (t, 2H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.50 (t, 2H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.37 (t, 2H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; ArH), 6.13 (s, 2H; $\mathrm{ArH_{Trz}}$), 6.11 (s, 2H; $\mathrm{ArH_{Trz}}$), 4.79 (s, 4H; $\mathrm{OCH_2Trz}$), 4.78 (s, 4H; $\mathrm{OCH_2Trz}$), 4.51–4.40 (m, 8H; $\mathrm{NCH_2}$), 4.14–4.07 (m, 4H; $\mathrm{NCH_2C\underline{H}_2}$), 4.07–4.01 (m, 4H; $\mathrm{NCH_2C\underline{H}_2}$), 3.91 (d, 4H, $^2J_{\mathrm{HH}}$ = 16.4 Hz; $\mathrm{ArCH_2Ar}$), 3.84 (s, 4H; $\mathrm{ArCH_2Ar}$), 3.80 (d, 4H, $^2J_{\mathrm{HH}}$ = 15.8 Hz; $\mathrm{ArCH_2Ar}$), 3.79 (s, 4H; $\mathrm{ArCH_2Ar}$), 3.69 (d, 4H, $^2J_{\mathrm{HH}}$ = 16.4 Hz; $\mathrm{ArCH_2Ar}$), 3.60 (d, 4H, $^2J_{\mathrm{HH}}$ = 15.8 Hz; $\mathrm{ArCH_2Ar}$), 3.43–3.36 (m, 4H; $\mathrm{OC\underline{H}_2CH_2CH_3}$), 3.36–3.29 (m, 4H; $\mathrm{OC\underline{H}_2CH_2CH_3}$), 1.38–1.26 (m, 4H; $\mathrm{C\underline{H}_2CH_3}$), 1.21–1.08 (m, 4H; $\mathrm{C\underline{H}_2CH_3}$), 0.71 (t, 6H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; $\mathrm{CH_3}$), 0.68 (t, 6H, $^3J_{\mathrm{HH}}$ = 7.5 Hz; $\mathrm{CH_3}$) ppm; ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 157.08, 156.94, 155.80, 155.61, 154.96, 154.63 ($\mathrm{C_{Ar}}$), 144.30, 143.75 ($\mathrm{C_{Ar\,Trz}}$), 134.42, 134.39, 134.30, 134.00, 133.81, 133.30 ($\mathrm{C_{Ar}}$), 130.05, 129.74, 129.45, 128.93, 128.70, 128.37 ($\mathrm{CH_{Ar}}$), 124.25, 124.16 ($\mathrm{CH_{Ar\,Trz}}$), 123.61, 123.24, 123.09, 122.92, 122.44, 121.36 ($\mathrm{CH_{Ar}}$), 71.71, 71.43, 68.89, 68.64, 63.18, 63.06 (OCH_2), 48.96, 48.85 (NCH_2), 38.34, 38.25, 38.11 ($ArCH_2Ar$), 22.84, 22.08 ($\underline{C}H_2CH_3$), 10.05, 9.82 ($CH_2\underline{C}H_3$) ppm. ESI-MS *m/z*: 1870.8942 $[M+H]^+$ for $C_{116}H_{117}N_{12}O_{12}$ (1870.8942).



Tris(calix[4]arene) **25** was prepared according to *General procedure* from bis(calix[4]arene) **23** (0.122 g, 0.10 mmol), calixarene **13** (0.087 g, 0.10 mmol), $CuSO_4{\cdot}5H_2O$ (0.025 g, 0.10 mmol) and sodium ascorbate (0.040 g, 0.20 mmol) in a mixture of THF (12 ml) and water (2.4 ml). The reaction mixture was stirred at 60 °C for 24 h. Column 1: gradient from dichloromethane to dichloromethane/ethanol (20:1). Column 2: gradient from hexane to hexane/ethyl acetate (1:1). Yield 0.052 g (25%), white solid. M.p. >300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 7.05 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.99 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.92 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.91 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.88 (t, 2H, $^3J_{HH} = 7.5$ Hz; ArH), 6.81 (d, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.77 (t, 4H, $^3J_{HH} = 7.5$ Hz; ArH), 6.66 (t, 2H, $^3J_{HH} = 7.5$ Hz; ArH), 6.52 (t, 2H, $^3J_{HH} = 7.5$ Hz; ArH), 6.36 (t, 2H, $^3J_{HH} = 7.5$ Hz; ArH), 6.14 (s, 2H; ArH_{Trz}), 6.10 (s, 2H; ArH_{Trz}), 4.79 (s, 8H; OCH_2Trz), 4.55–4.48 (m, 4H; NCH_2), 4.47–4.40 (m, 4H; NCH_2), 4.14–4.07 (m, 8H; $NCH_2C\underline{H}_2$), 4.05 (d, 4H, $^2J_{HH} = 16.0$ Hz; $ArCH_2Ar$), 4.04 (s, 4H; OCH_2CC), 3.83 (d, 4H, $^2J_{HH} = 16.3$ Hz; $ArCH_2Ar$), 3.79 (d, 4H, $^2J_{HH} = 16.0$ Hz; $ArCH_2Ar$), 3.75 (d, 4H, $^2J_{HH} = 16.0$ Hz; $ArCH_2Ar$), 3.72 (d, 4H, $^2J_{HH} = 16.3$ Hz; $ArCH_2Ar$), 3.60 (d, 4H, $^2J_{HH} = 16.0$ Hz; $ArCH_2Ar$), 3.38–3.27 (m, 4H; $OC\underline{H}_2CH_2CH_3$), 1.36–1.25 (m, 4H; $C\underline{H}_2CH_3$), 0.87 (s, 18H; $C(CH_3)_3$), 0.67 (t, 6H, $^3J_{HH} = 7.5$ Hz; CH_3), 0.08 (s, 12H; $Si(CH_3)_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.00, 155.86, 155.66, 155.56, 154.88, 154.68 (C_{Ar}), 144.37, 143.75 ($C_{Ar\ Trz}$), 135.34, 134.47, 134.31, 134.03, 133.88, 133.44 (C_{Ar}), 130.36, 129.77, 129.44, 128.97, 128.70, 128.38 (CH_{Ar}), 124.37, 124.26 ($CH_{Ar\ Trz}$), 123.74, 123.66, 123.11, 123.07, 123.00, 121.37 (CH_{Ar}), 102.51 ($OCH_2\underline{C}$), 90.05 ($OCH_2C\underline{C}$), 71.71, 68.97, 68.70, 63.25, 62.92 (OCH_2), 58.32 ($O\underline{C}H_2CC$), 49.25, 48.86 (NCH_2), 38.37, 38.28, 38.15 ($ArCH_2Ar$), 25.96 ($C(\underline{C}H_3)_3$), 22.88 ($\underline{C}H_2CH_3$), 16.40 ($\underline{C}(CH_3)_3$), 10.09 ($CH_2\underline{C}H_3$), –4.84 ($Si(CH_3)_2$) ppm. ESI-MS *m/z*: 1046.0055 $[M+2H]^{+2}$ for $C_{128}H_{138}N_{12}O_{12}Si_2$ (1046.0059).

Tuning the conditions for the preparation of calix[4]semitubes

Table S1 Different catalytic systems used in the CuAAC reactions between calixarenes **3** and **9**

Entry	Catalyst (equiv per bis(azide))	External ligand (equiv per Cu)	Solvent	Temp., °C	Time, h	Reaction outcome			
						3 or **9**	Semitube	Polymer	Other products
1	$CuI\cdot P(OEt)_3$ (0.3)	–	THF	50	24	+	–	+	–
2	$CuSO_4$/Na asc. (0.3)	–	THF/H_2O (5:1)	50	24	+	–	–	+
3	CuI (0.3)	Et_3N (20)	toluene	rt	48	+	+	++	–
4	CuI (0.3)	Et_3N (20)	THF	50	24	+	–	+	+
4	CuI (0.3)	Et_3N (20)	toluene	75	24	–	+	++	–
6	CuI (0.3)	Et_3N (20)	toluene/1,2-dichloroethane	60	9	+	+	+	+

Table S2 Different catalytic systems tested in the CuAAC reactions between calixarenes **4** and **9**

Entry	Catalyst (equiv per bis(azide))	External ligand (equiv per Cu)	Solvent	Temp., °C	Time, h	Reaction outcome			
						4 or **9**	**17**	Polymer	Other products
1	$CuSO_4$/Na asc. (0.1)	–	THF/H_2O (5:1)	60	36	+	–	+	+
2	$CuSO_4$/Na asc. (0.3)	–	THF/H_2O (5:1)	60	24	+	–	+	+
3	$CuSO_4$/Na asc. (1.0)	–	THF/H_2O (5:1)	60	24	–	–	+	+
4	$CuSO_4$/Na asc. (1.0)[*]	–	THF/H_2O (5:1)	60	24	+	+	+	–
5	$CuSO_4$/Na asc. (1.0)[**]	–	THF/H_2O (5:1)	60	24	+	–	–	+
6	CuI (0.3)	Et_3N (20)	toluene	rt	48	+	+	+	–
7	CuI (0.3)	Et_3N (20)	toluene	rt	60	+	–	++	+
8	CuI (1.0)	Et_3N (20)	toluene	rt	48	+	–	+	+
9	CuI (0.1)	Et_3N (20)	toluene	60	36	–	+	++	–
10	CuI (0.3)	Et_3N (20)	toluene	60	24	–	+	+	–
11	CuI (0.3)	Et_3N (400)	toluene	60	24	–	+	+	–
12	CuI (1.0)	Et_3N (20)	toluene	60	24	–	+	+	+
13	CuI (1.0)	Et_3N (20)	toluene/1,2-dichloroethane	60	24	–	+	+	+

[*] – the reaction was conducted in a diluted solution (2 volumes of the solvent were used);
[**] – the reaction was conducted in a diluted solution (10 volumes of the solvent were used).

Table S3 Different catalytic systems used in the CuAAC reactions between calixarenes **5** and **11**

Entry	Catalyst (equiv per bis(alkyne))	External ligand (equiv per Cu)	Solvent	Temp., °C	Time, h	Reaction outcome			
						5 or **11**	**18**	Polymer	Other products
1	$CuI\cdot P(OEt)_3$ (1.0)	–	toluene	rt	48	+	–	–	+
2	$CuI\cdot P(OEt)_3$ (1.0)	–	toluene	60	5	+	+	+	–
3	$CuI\cdot P(OEt)_3$ (1.0)	$i\text{Pr}_2\text{EtN}$ (20)	toluene	rt	48	+	+	+	–
4	$CuI\cdot P(OEt)_3$ (1.0)	$i\text{Pr}_2\text{EtN}$ (20)	toluene	60	5	–	+	+	–
5	CuI (1.0)	–	toluene	rt	48	+	–	–	–
6	CuI (1.0)	Et_3N (2)	toluene	rt	48	+	–	++	–
7	CuI (1.0)	Et_3N (4)	toluene	rt	48	+	+	+	–
8	CuI (1.0)	Et_3N (10)	toluene	rt	48	–	+	+	–
9	CuI (0.3)	Et_3N (20)	toluene	rt	48	–	+	+	–
10	CuI (1.0)	Et_3N (20)	toluene	rt	48	–	+	+	–
11	CuI (2.0)	Et_3N (20)	toluene	rt	48	–	+	+	–
12	CuI (0.3)	Et_3N (20)	toluene	60	12	–	+	+	–
13	CuI (1.0)	Et_3N (20)	toluene	60	5	–	+	+	–

Table S4 Tuning the CuI/Et_3N/toluene catalytic system in the CuAAC between calixarenes **7** and **11**

Entry	Catalyst (equiv per bis(alkyne))	External ligand (equiv per Cu)	Solvent	Temp., °C	Time, h	Reaction outcome			
						7 or **11**	**20**	Polymer	Other products
1	CuI (1.0)	–	toluene	rt	48	+	–	–	–
2	CuI (0.3)	Et_3N (20)	toluene	rt	48	+	+	+	+
3	CuI (1.0)	Et_3N (20)	toluene	rt	48	+	+	+	–
4	CuI (2.0)	Et_3N (20)	toluene	rt	48	–	+	++	–
5	CuI (1.0)	Et_3N (400)	toluene	70	9	–	+	+	–

Table S5 Different catalytic systems tested in the CuAAC reactions between calixarenes **8** and **11**

Entry	Catalyst (equiv per bis(alkyne))	External ligand (equiv per Cu)	Solvent	Temp., °C	Time, h	Reaction outcome			
						8 or **11**	**21**	Polymer	Other products
1	$CuSO_4$/Na asc. (0.1)	–	THF/H_2O (5:1)	rt	60	++	–	–	+
2	$CuSO_4$/Na asc. (0.3)	–	THF/H_2O (5:1)	60	24	–	–	+	+
3	$CuSO_4$/Na asc. (1.0)	–	THF/H_2O (5:1)	60	24	–	–	+	+
4	CuI (1.0)	–	toluene/dichloromethane	rt	48	++	–	–	–
5	CuI (0.3)	Et_3N (20)	toluene	rt	48	++	+	–	+
6	CuI (1.0)	Et_3N (20)	toluene	rt	48	+	+	+	–
7	CuI (2.0)	Et_3N (20)	toluene	rt	48	+	+	+	–
8	CuI (0.3)	Et_3N (20)	toluene/1,2-dichloroethane	rt	48	–	+	++	–
9	CuI (1.0)	Et_3N (20)	toluene/1,2-dichloroethane	rt	48	–	+	+	–
10	CuI (0.3)	Et_3N (20)	toluene/1,2-dichloroethane	60	24	+	+	++	+
11	CuI (1.0)	Et_3N (20)	toluene/1,2-dichloroethane	60	24	+	+	+	+

NMR spectra of novel compounds

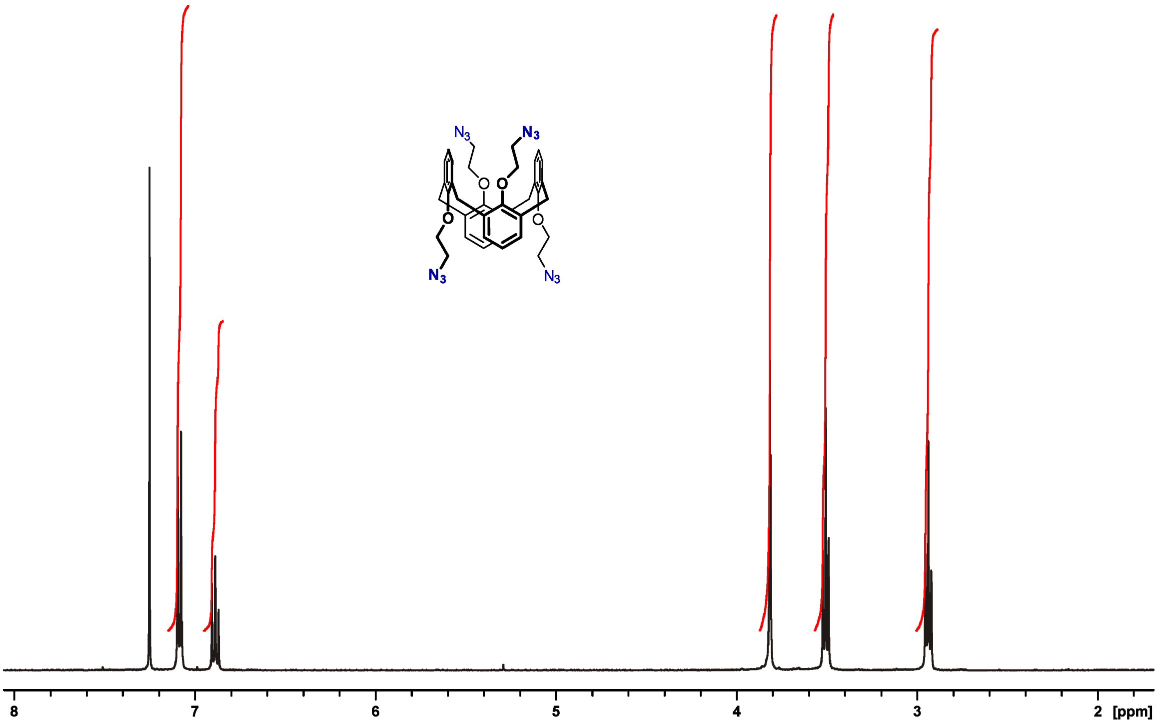


Figure S1. ^{1}H NMR spectrum of calix[4]arene **11** (400 MHz, $CDCl_3$).

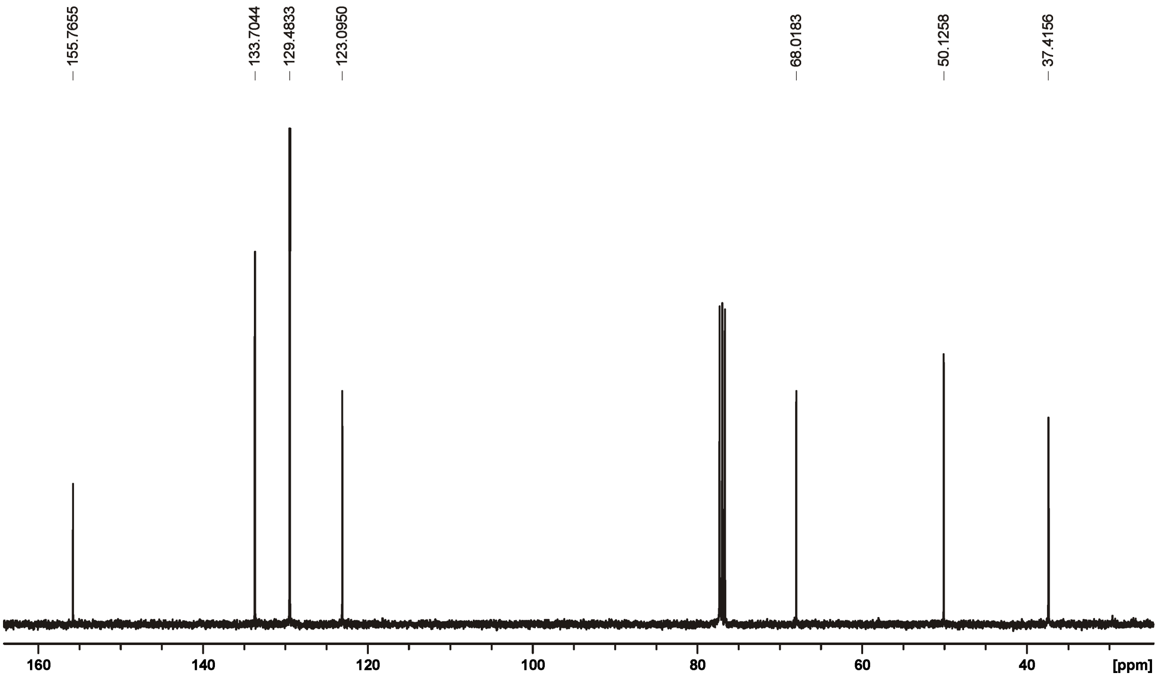


Figure S2. ^{13}C NMR spectrum of calix[4]arene **11** (100 MHz, $CDCl_3$).

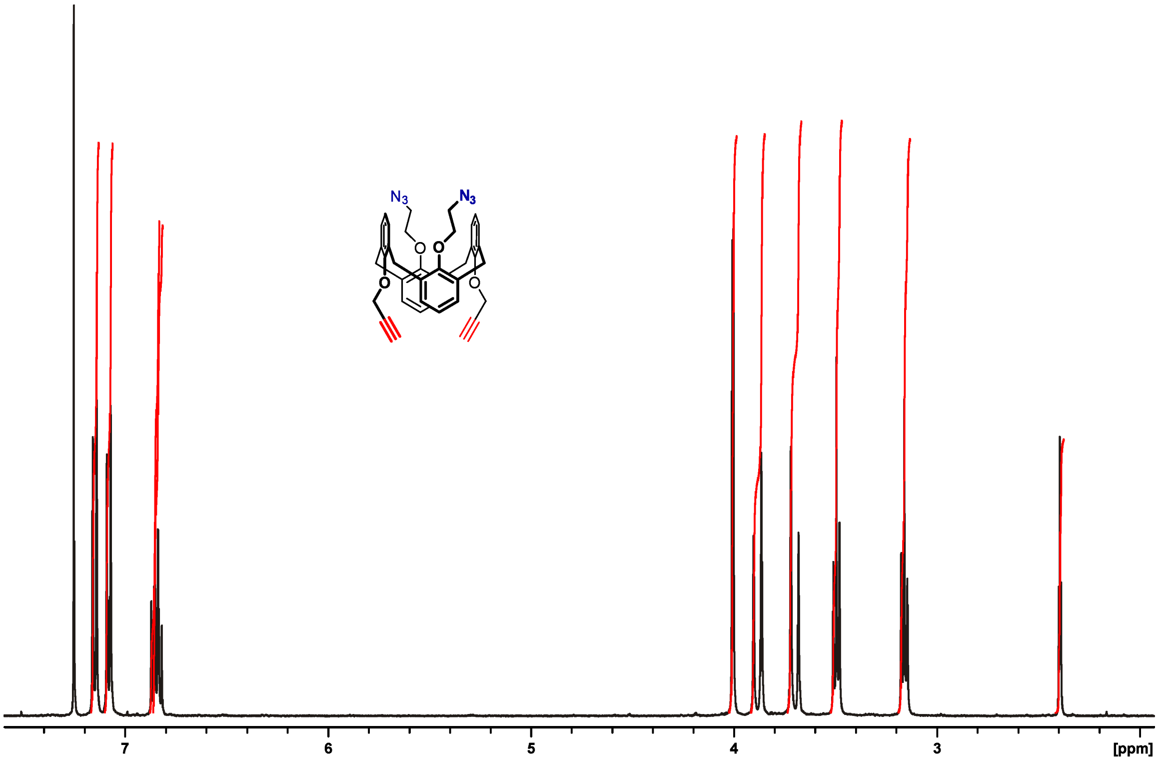


Figure S3. ^{1}H NMR spectrum of calix[4]arene **12** (400 MHz, CDCl$_3$).

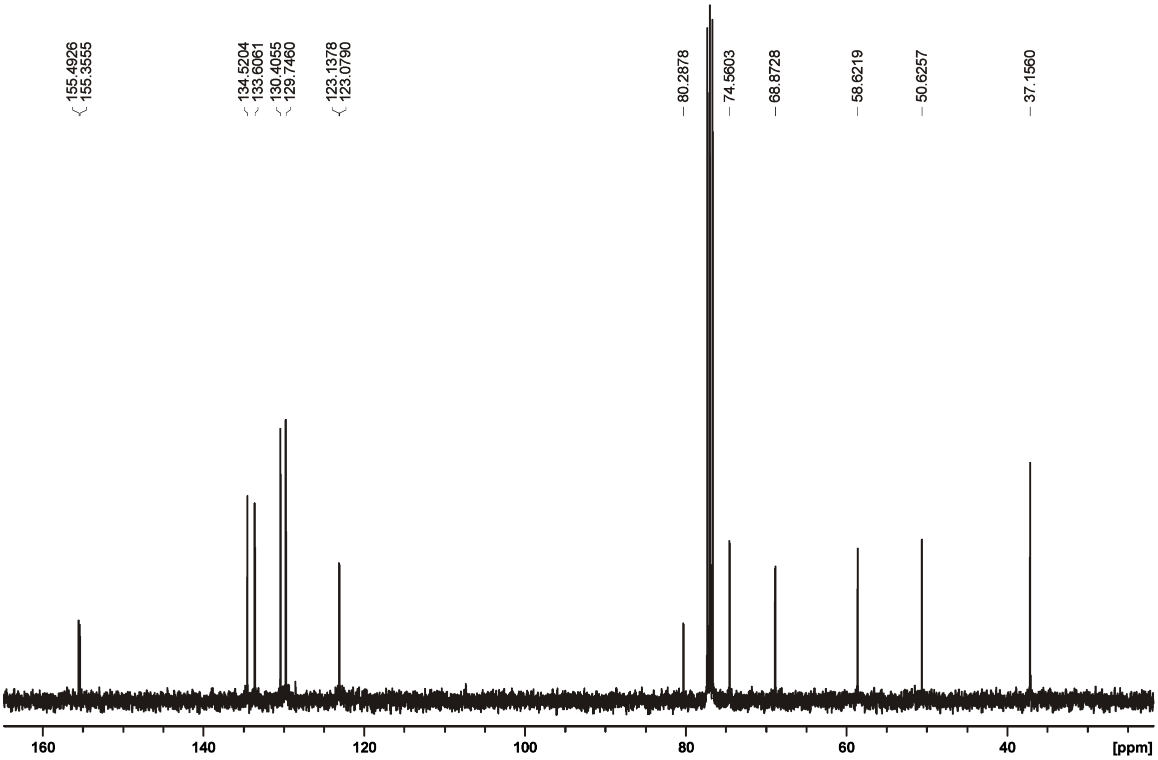


Figure S4. ^{13}C NMR spectrum of calix[4]arene **12** (100 MHz, CDCl$_3$).

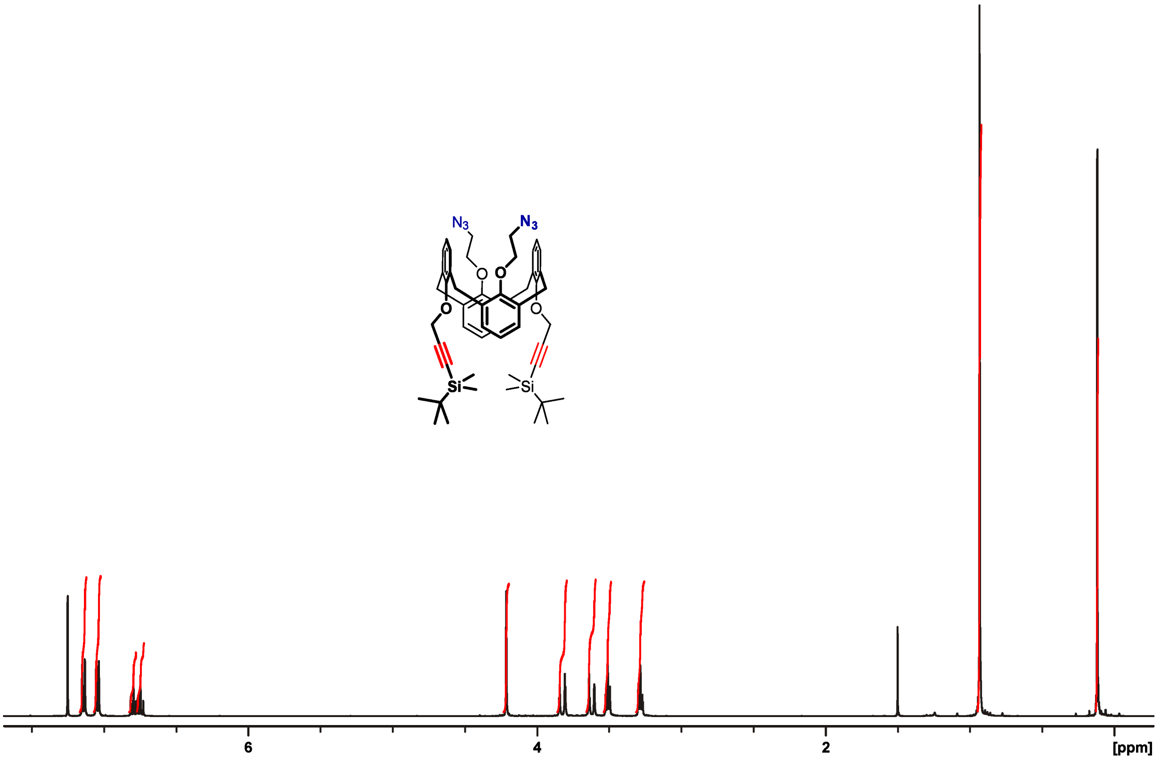


Figure S5. ^{1}H NMR spectrum of calix[4]arene **13** (400 MHz, $CDCl_3$).

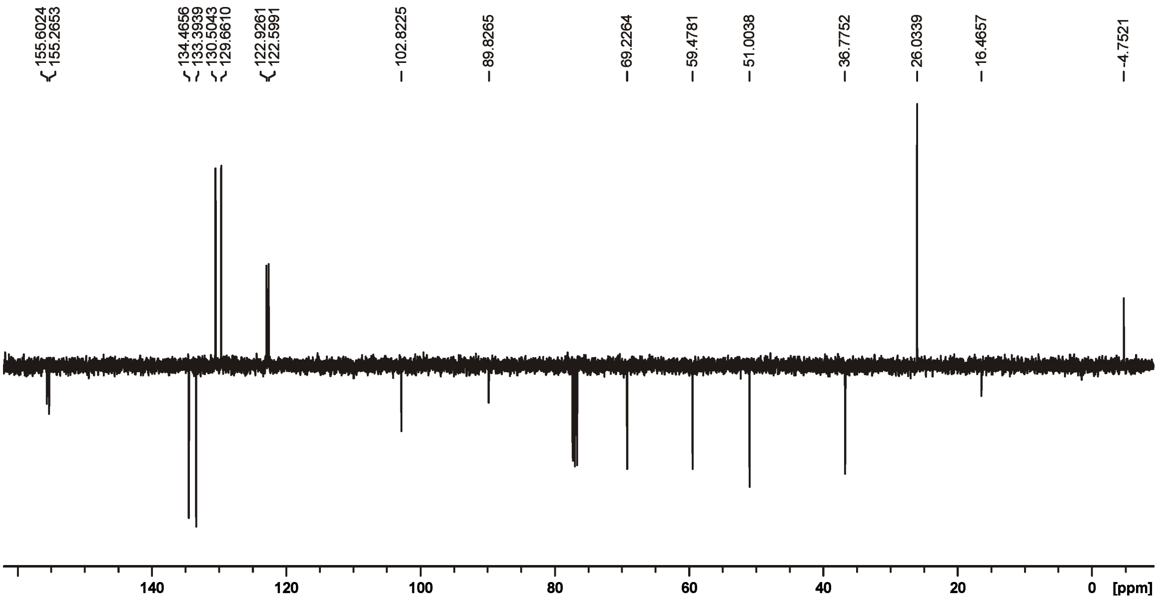


Figure S6. ^{13}C NMR spectrum (APT) of calix[4]arene **13** (100 MHz, $CDCl_3$).

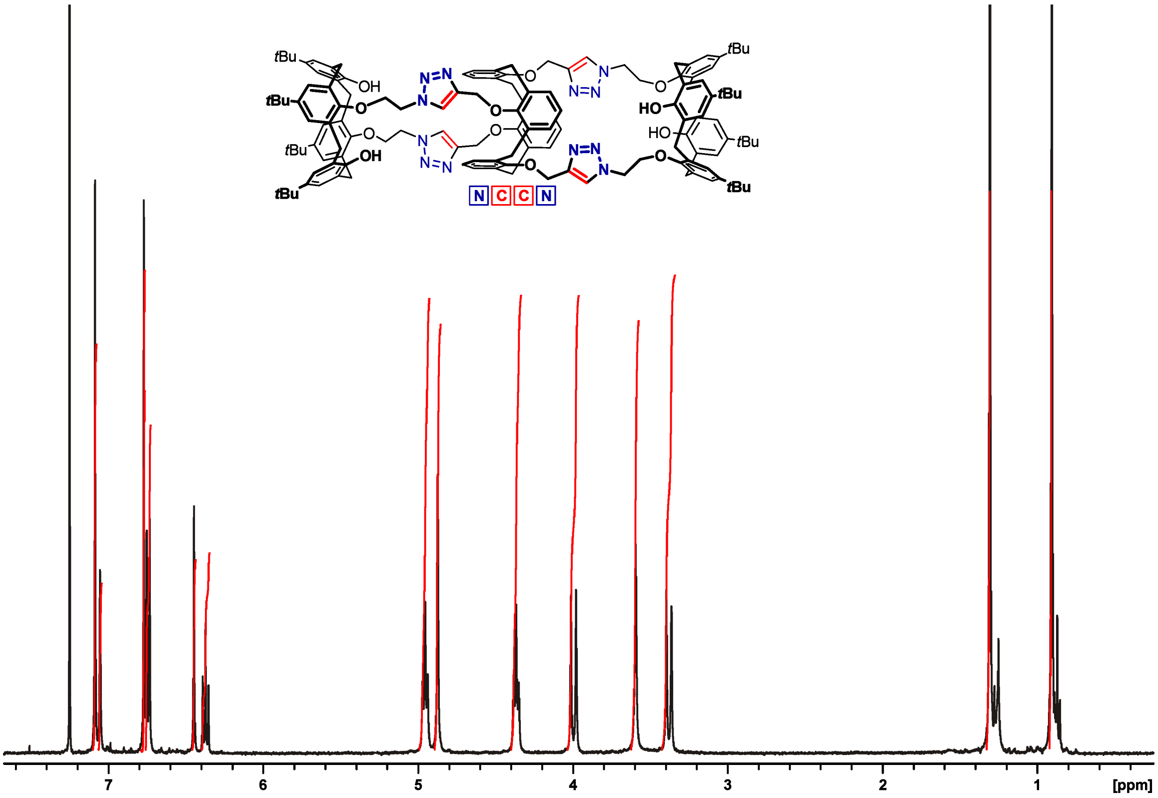


Figure S7. ^{1}H NMR spectrum of tris(calix[4]arene) **14** (400 MHz, CDCl$_3$).

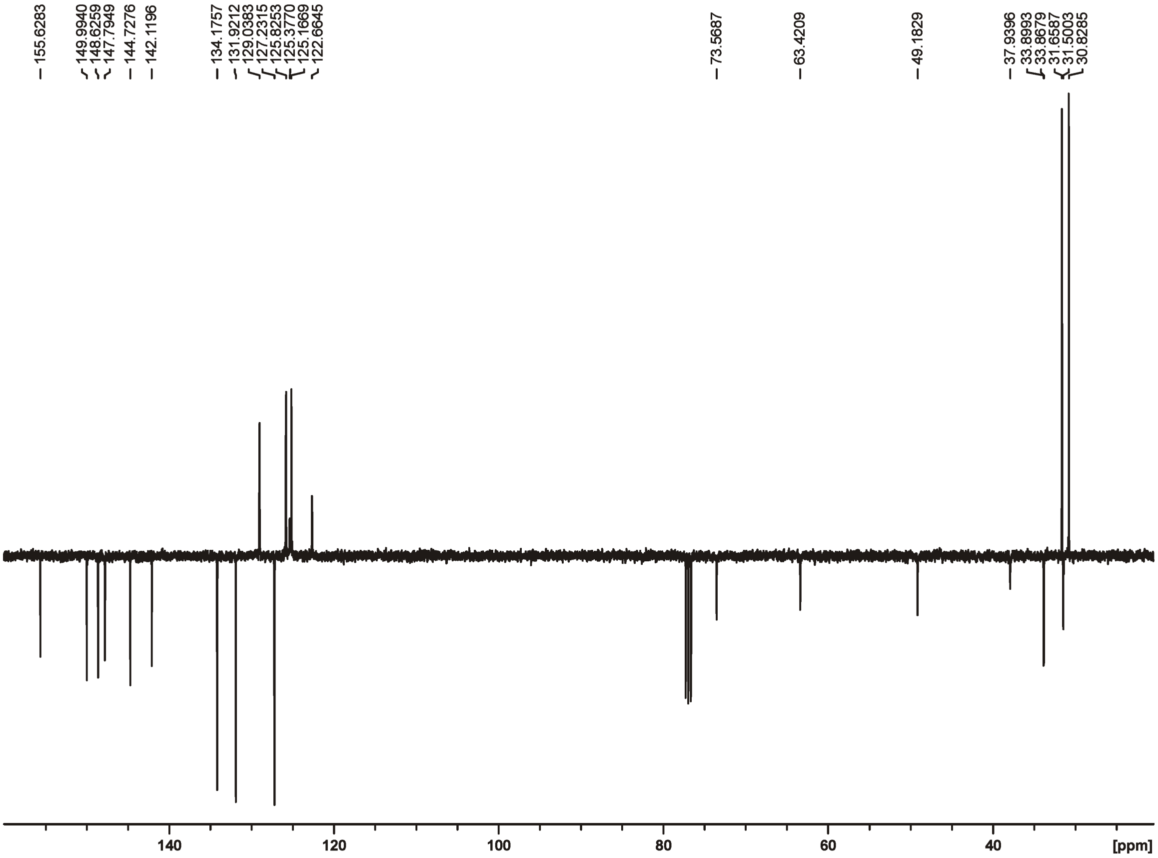


Figure S8. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **14** (100 MHz, CDCl$_3$).

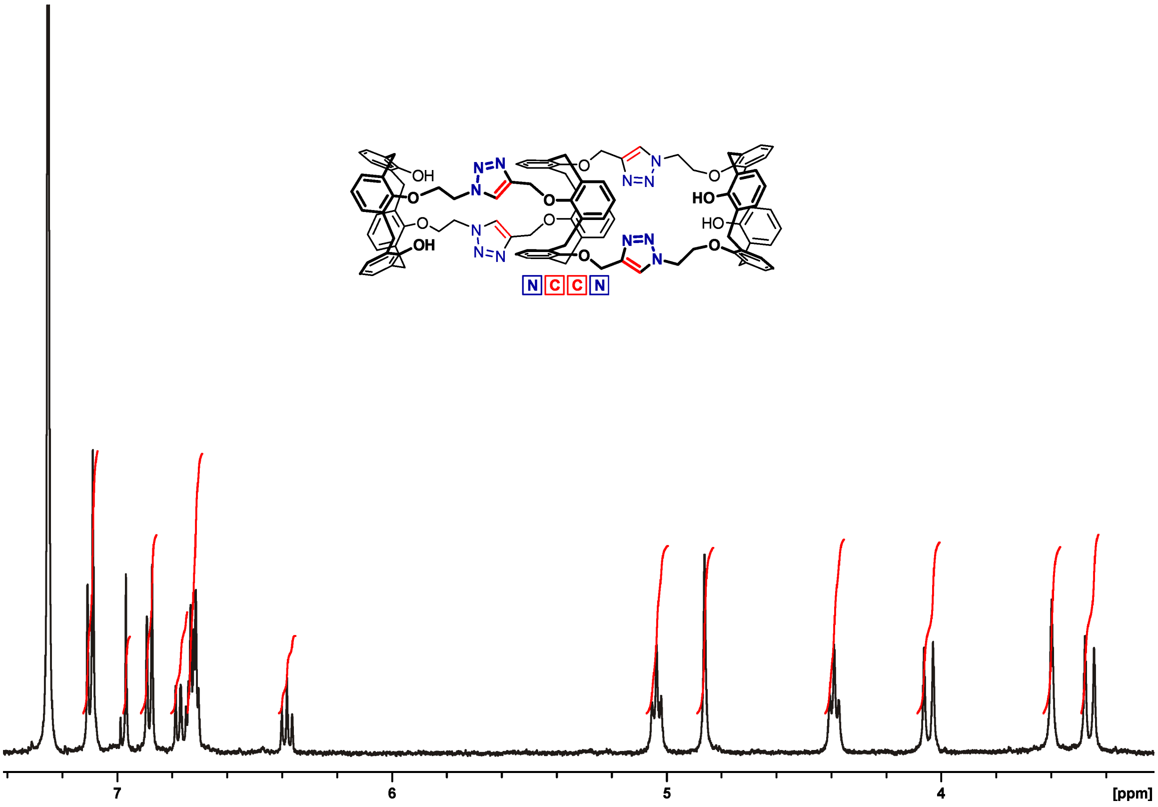


Figure S9. ^{1}H NMR spectrum of tris(calix[4]arene) **15** (400 MHz, $CDCl_3$).

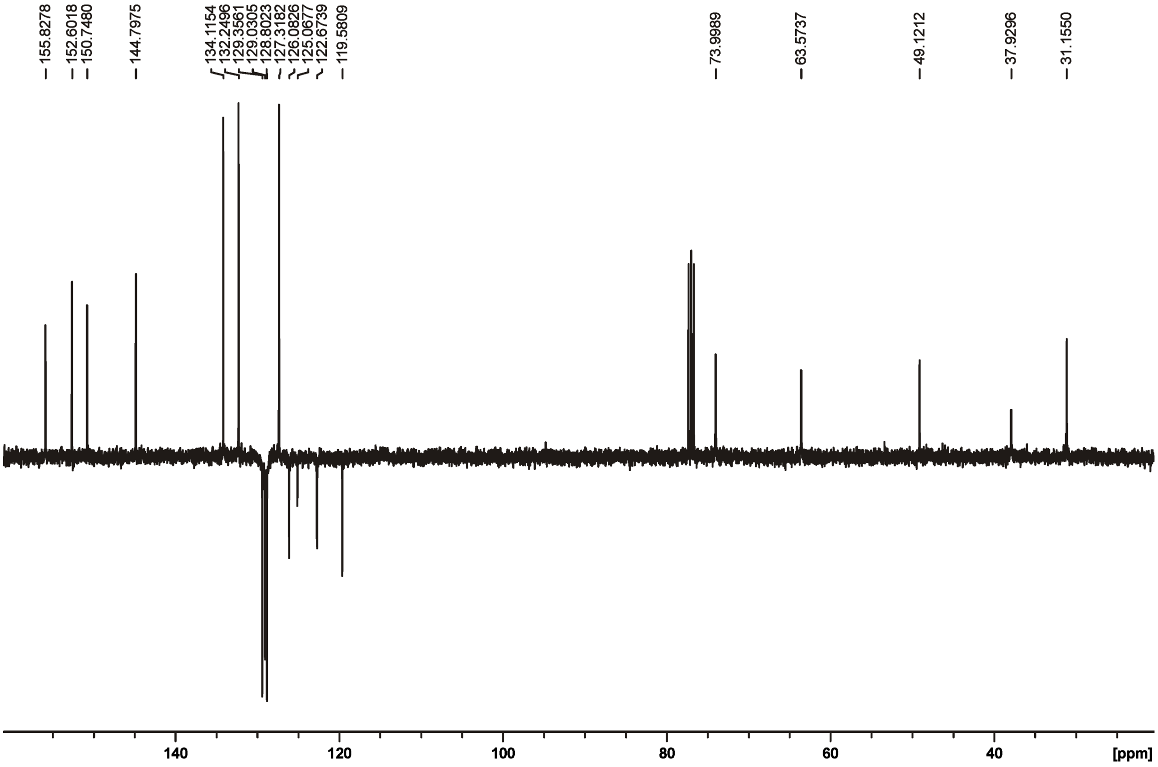


Figure S10. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **15** (100 MHz, $CDCl_3$).

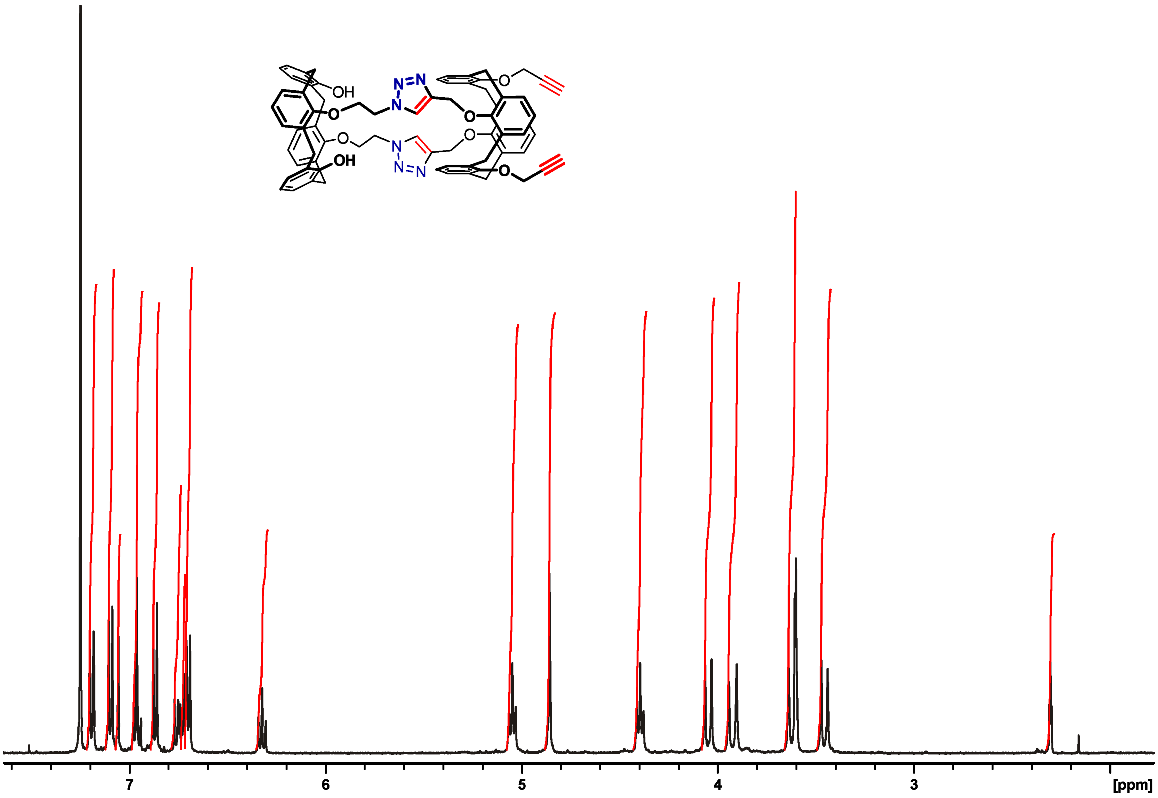


Figure S11. ^{1}H NMR spectrum of bis(calix[4]arene) **16** (400 MHz, CDCl$_3$).

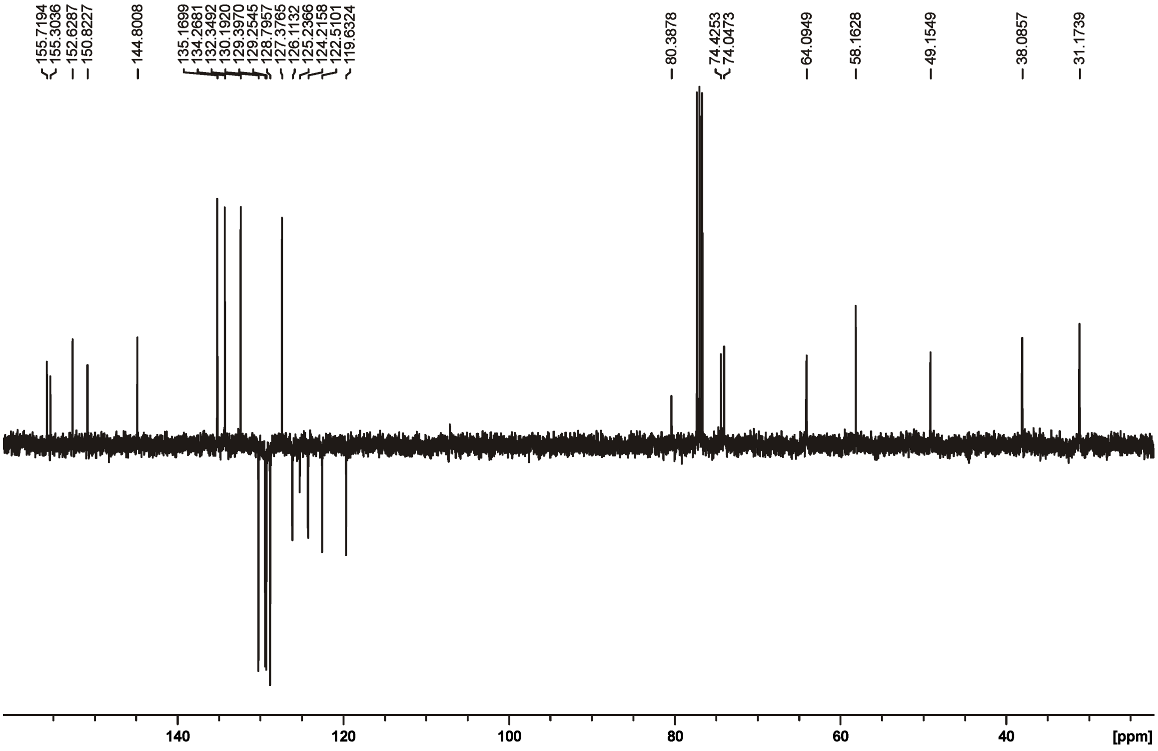


Figure S12. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) **16** (100 MHz, CDCl$_3$).

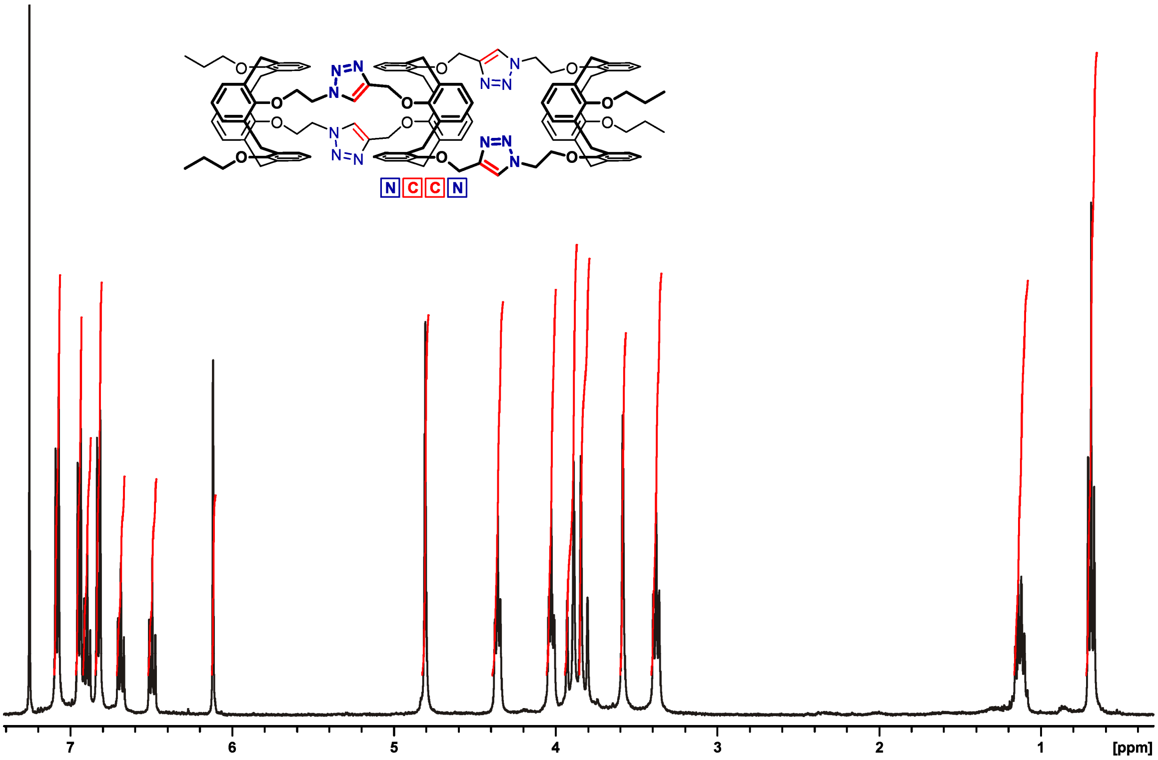


Figure S13. ^{1}H NMR spectrum of tris(calix[4]arene) **17** (400 MHz, $CDCl_3$).

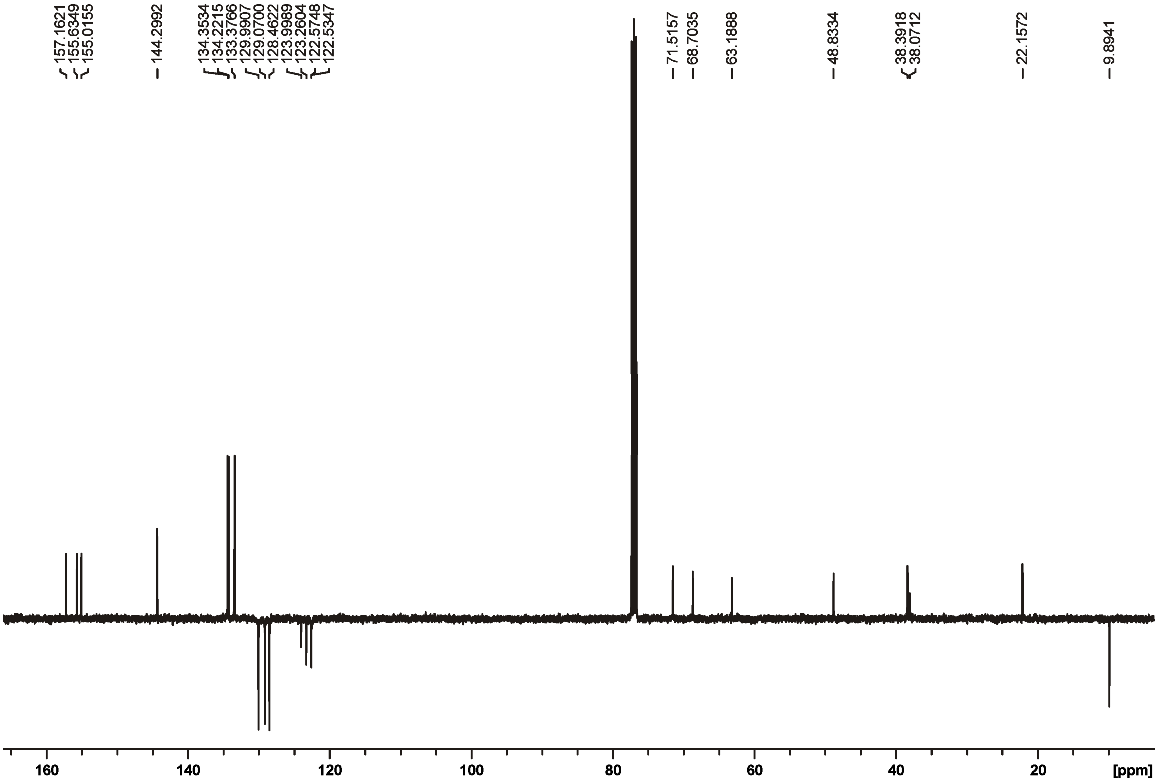


Figure S14. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **17** (100 MHz, $CDCl_3$).

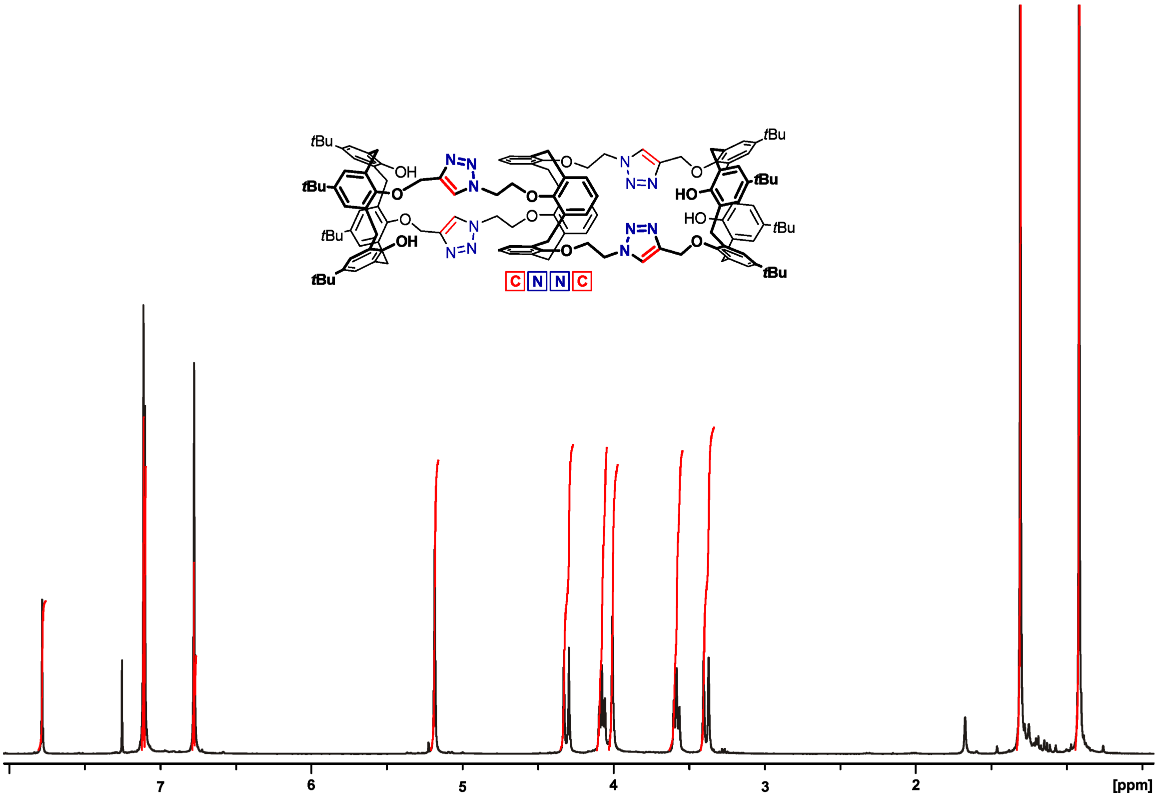


Figure S15. ^{1}H NMR spectrum of tris(calix[4]arene) **18** (400 MHz, CDCl$_3$).

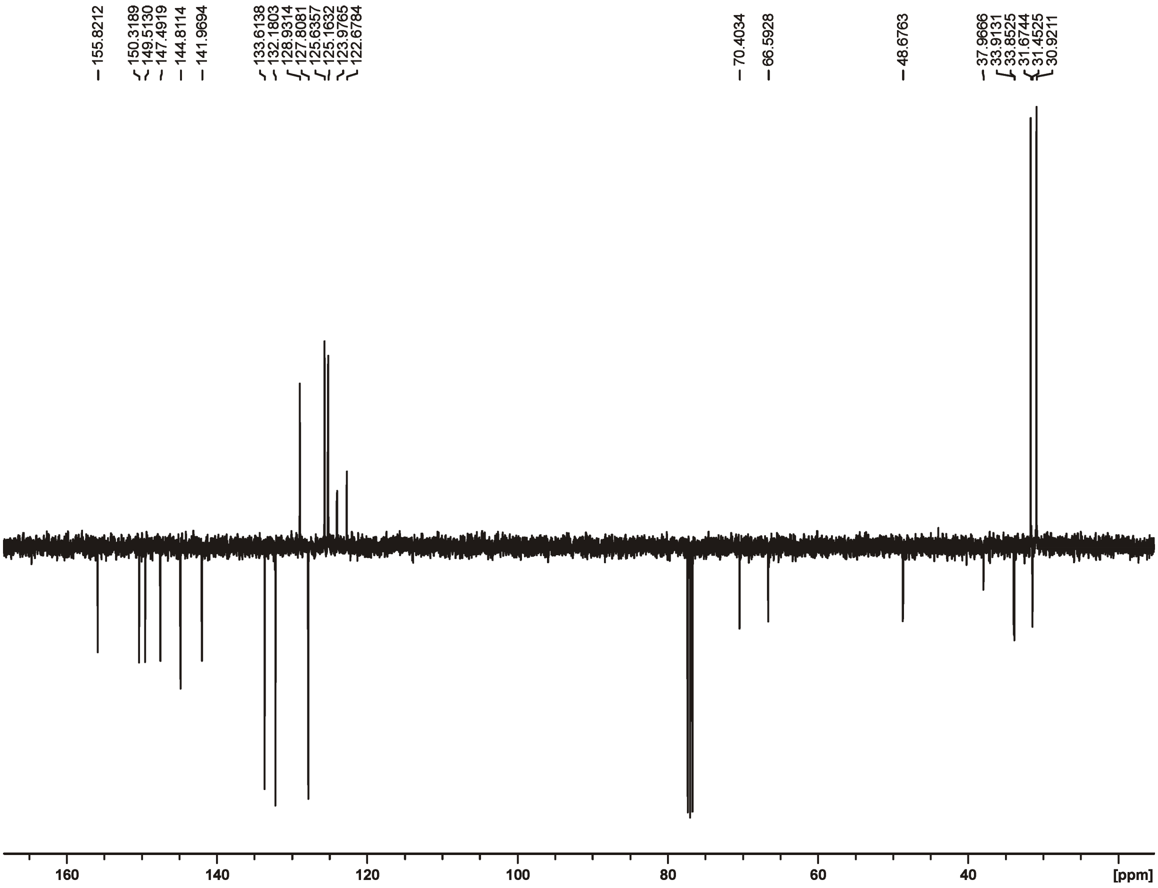


Figure S16. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **18** (100 MHz, CDCl$_3$).

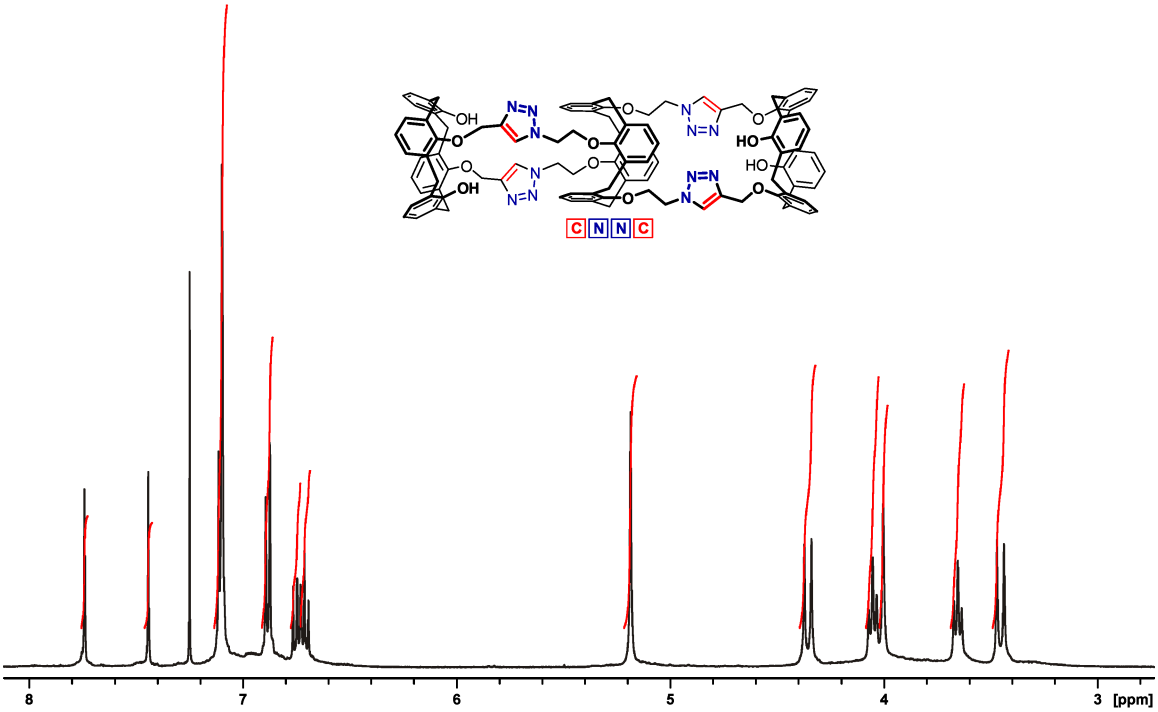


Figure S17. ^{1}H NMR spectrum of tris(calix[4]arene) **19** (400 MHz, CDCl$_3$).

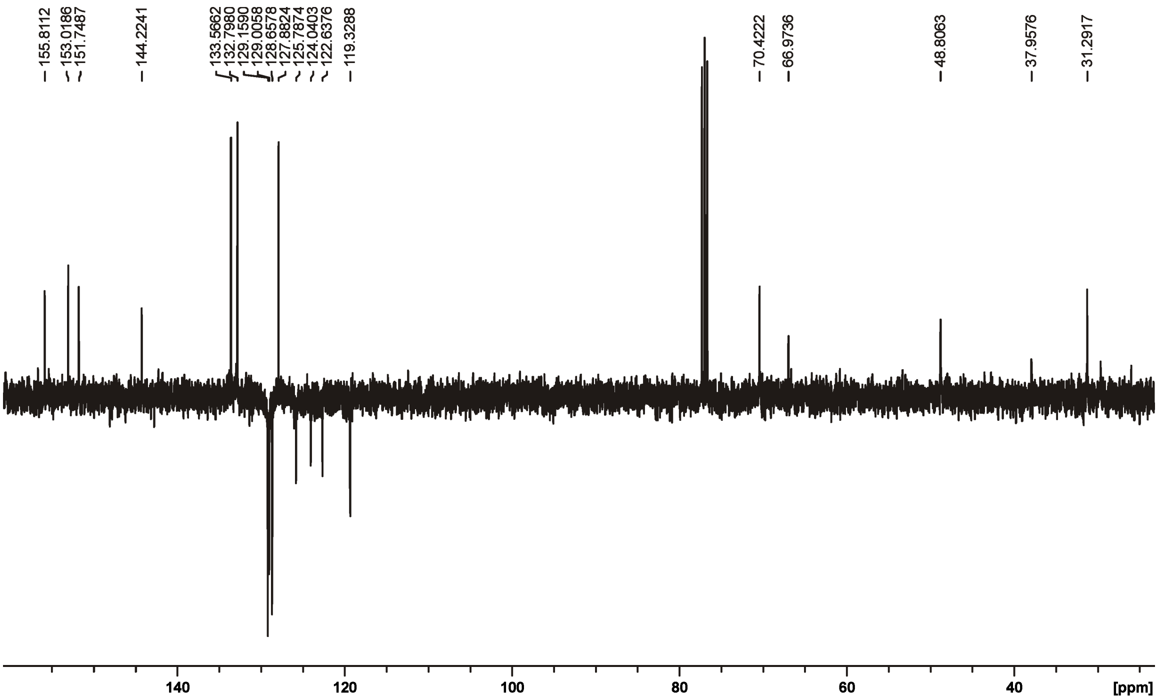


Figure S18. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **19** (100 MHz, CDCl$_3$).

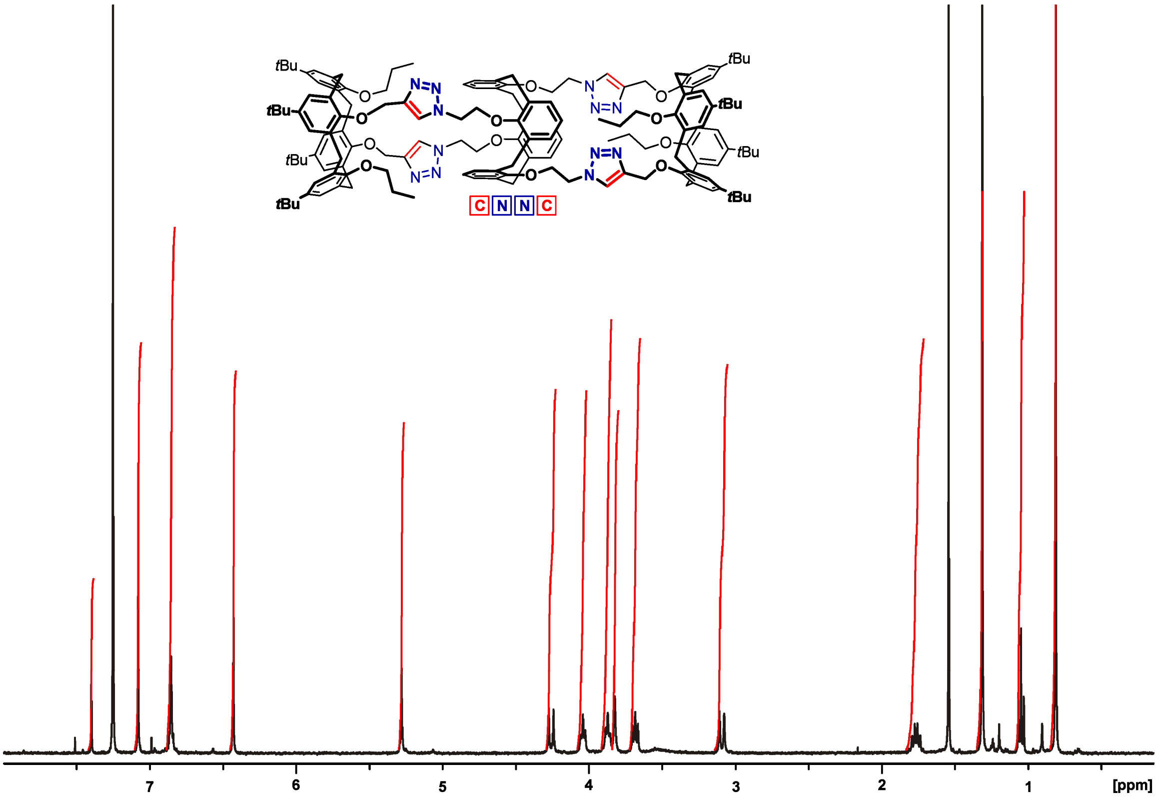


Figure S19. ^{1}H NMR spectrum of tris(calix[4]arene) **20** (400 MHz, $CDCl_3$).

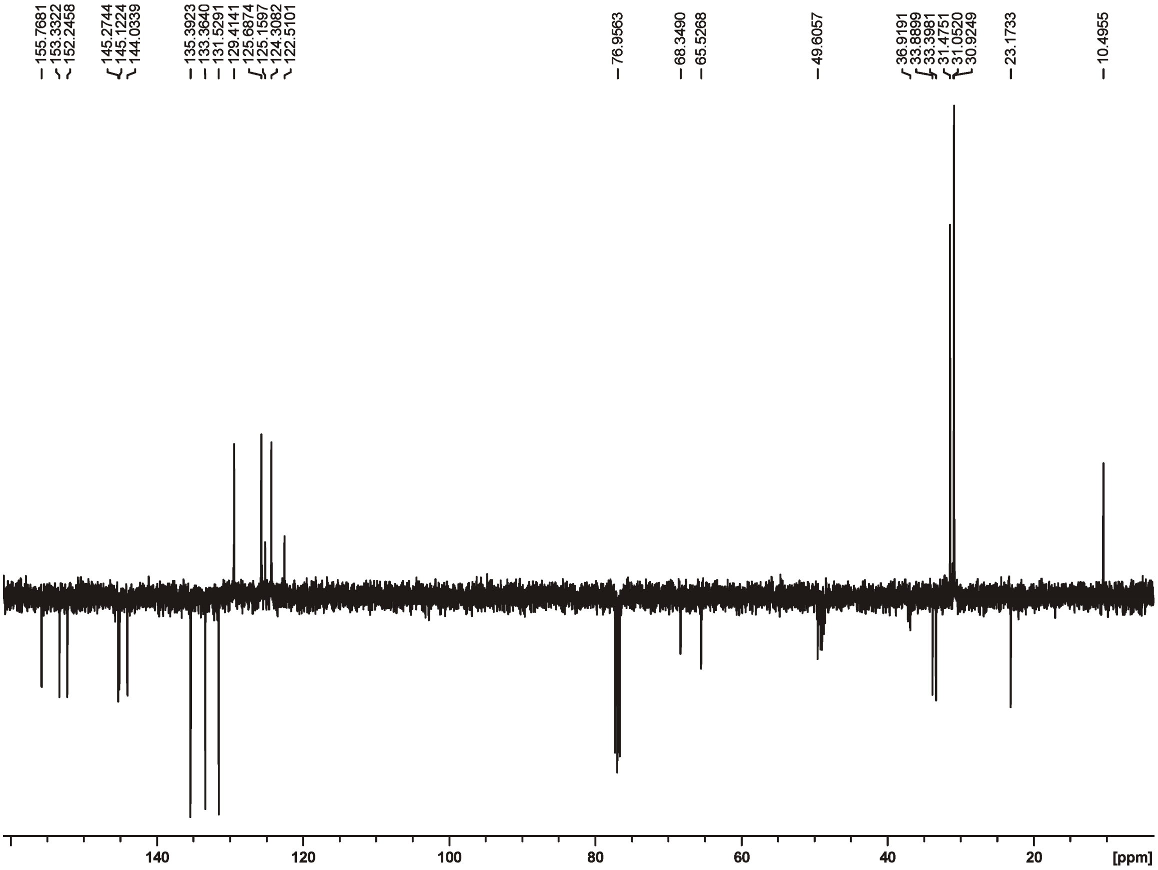


Figure S20. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **20** (100 MHz, $CDCl_3$+CD_3OD).

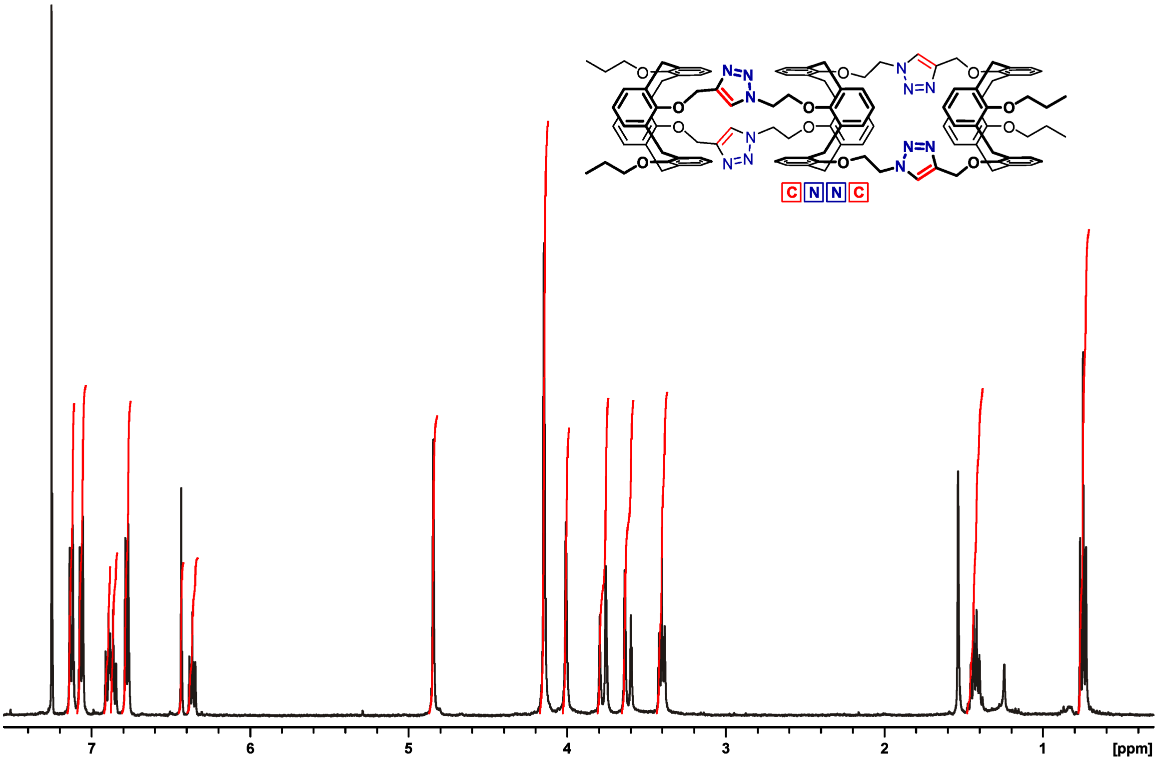


Figure S21. ^{1}H NMR spectrum of tris(calix[4]arene) **21** (400 MHz, $CDCl_3$).

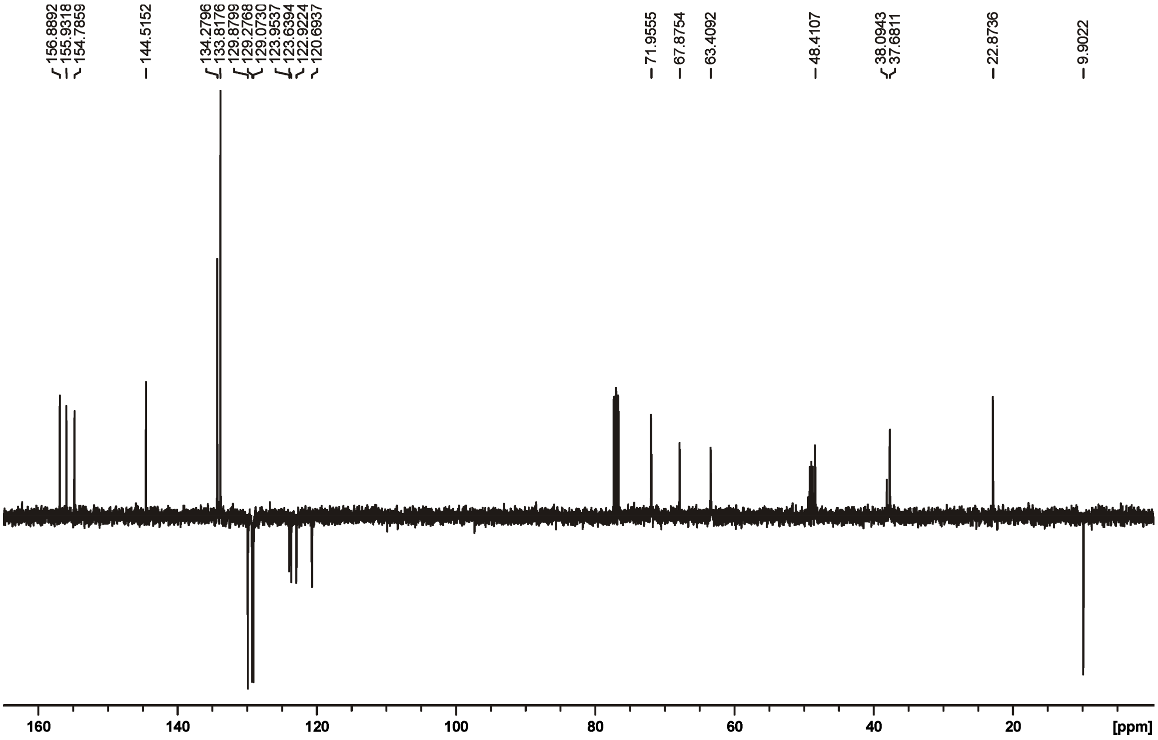


Figure S22. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **21** (100 MHz, $CDCl_3$+CD_3OD).

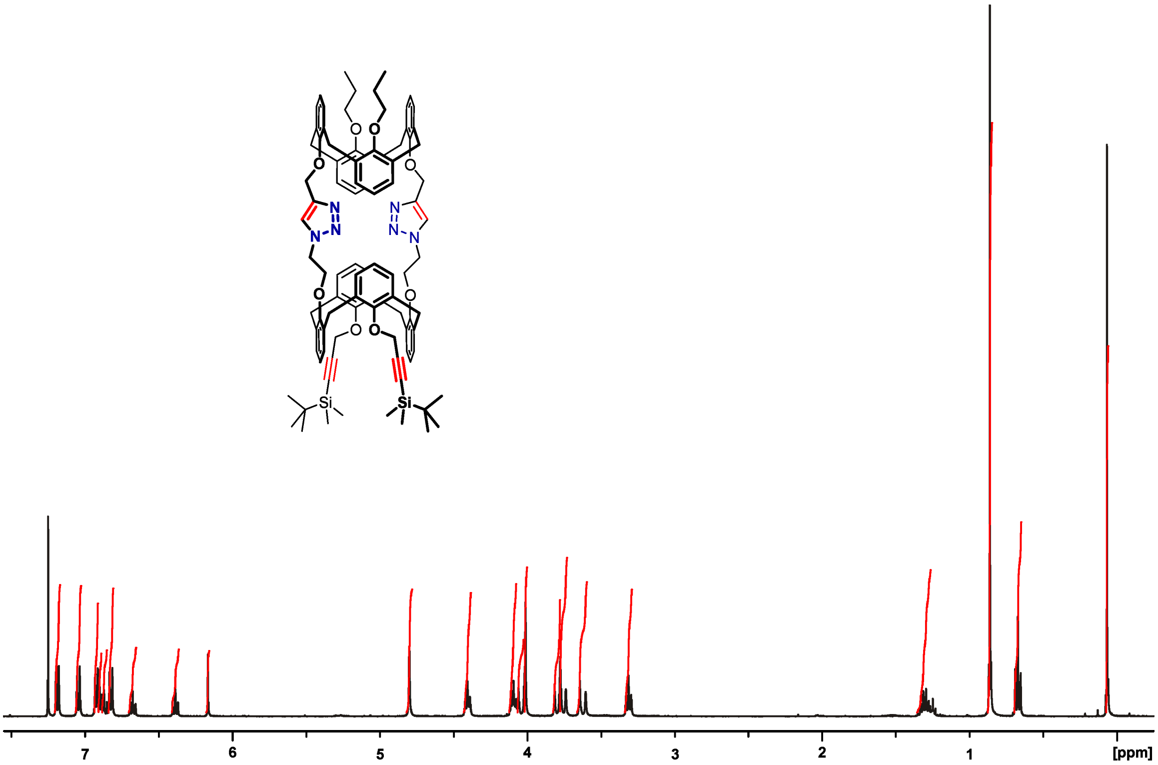


Figure S23. ^{1}H NMR spectrum of bis(calix[4]arene) **22** (400 MHz, $CDCl_3$).

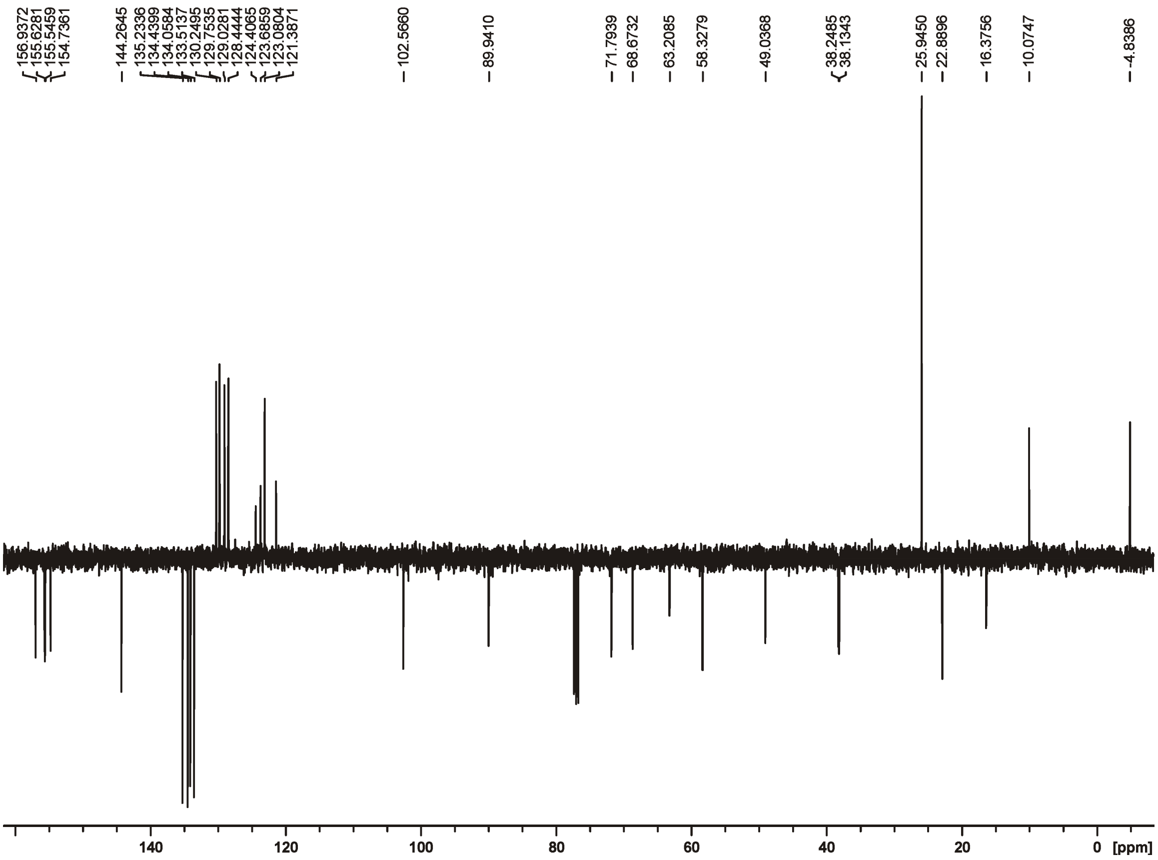


Figure S24. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) **22** (100 MHz, $CDCl_3$).

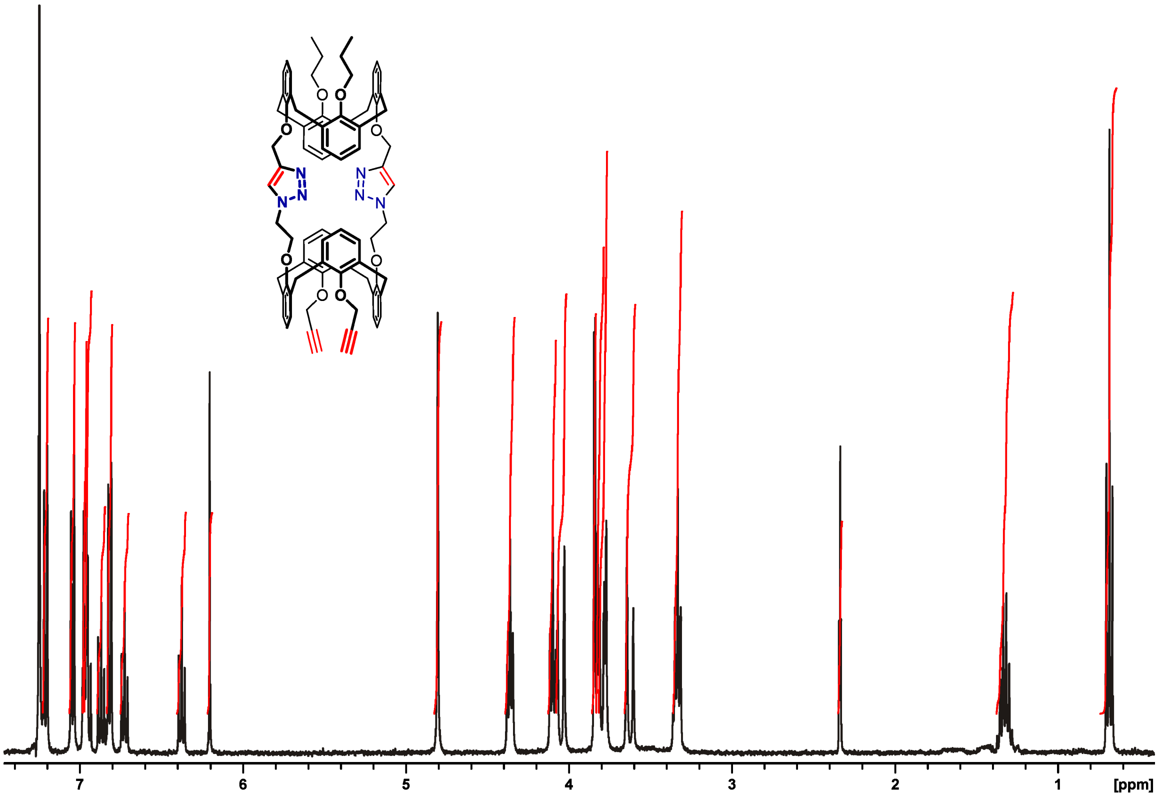


Figure S25. ^{1}H NMR spectrum of bis(calix[4]arene) **23** (400 MHz, $CDCl_3$).

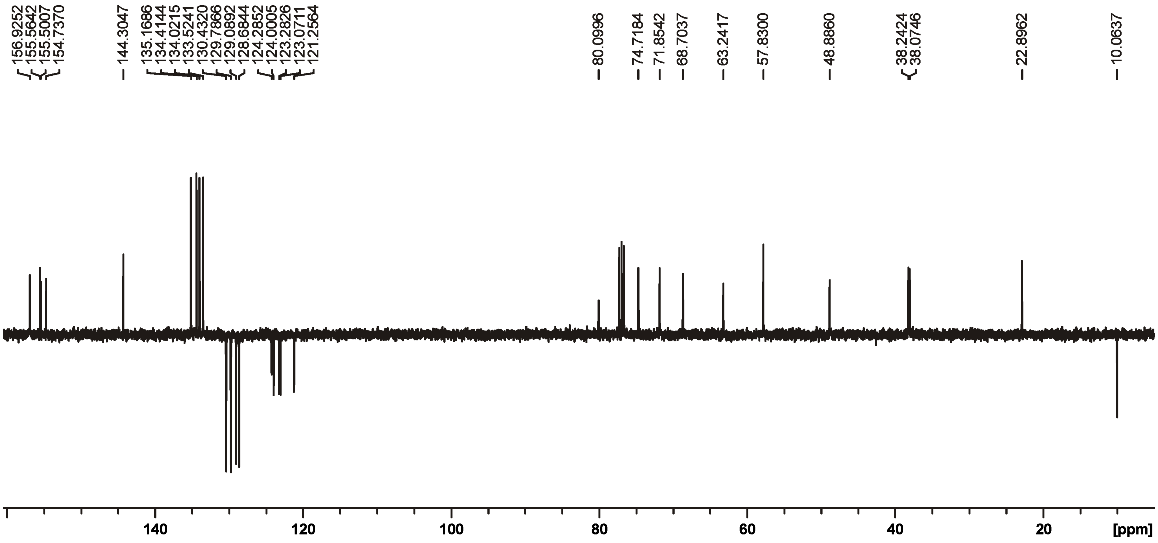


Figure S26. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) **23** (100 MHz, $CDCl_3$).

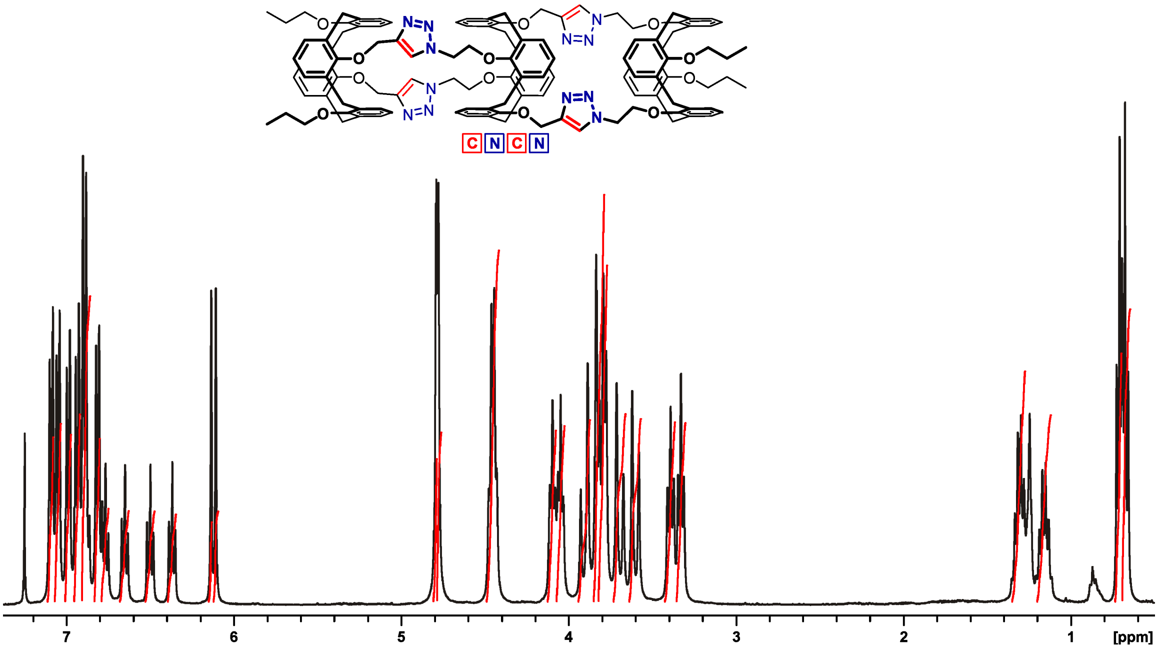


Figure S27. ^{1}H NMR spectrum of tris(calix[4]arene) **24** (400 MHz, CDCl$_3$).

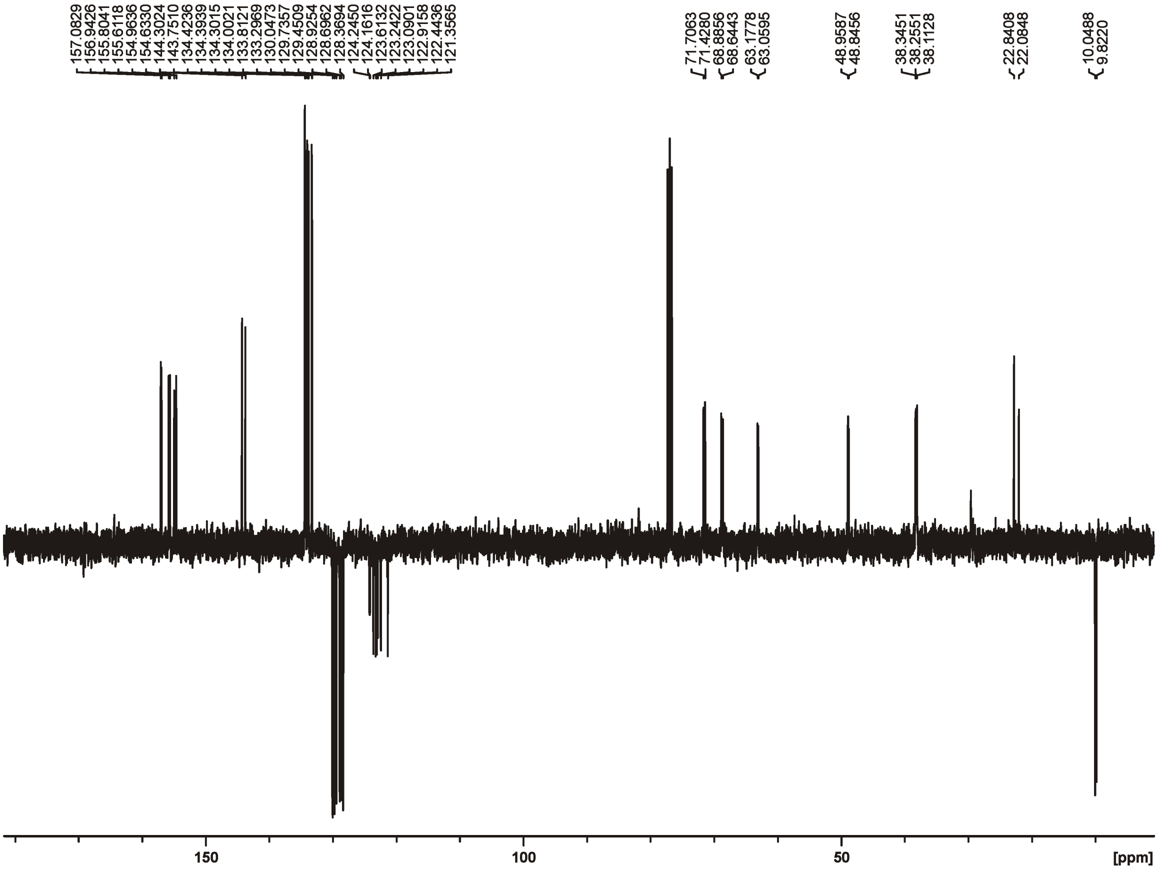


Figure S28. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **24** (100 MHz, CDCl$_3$).

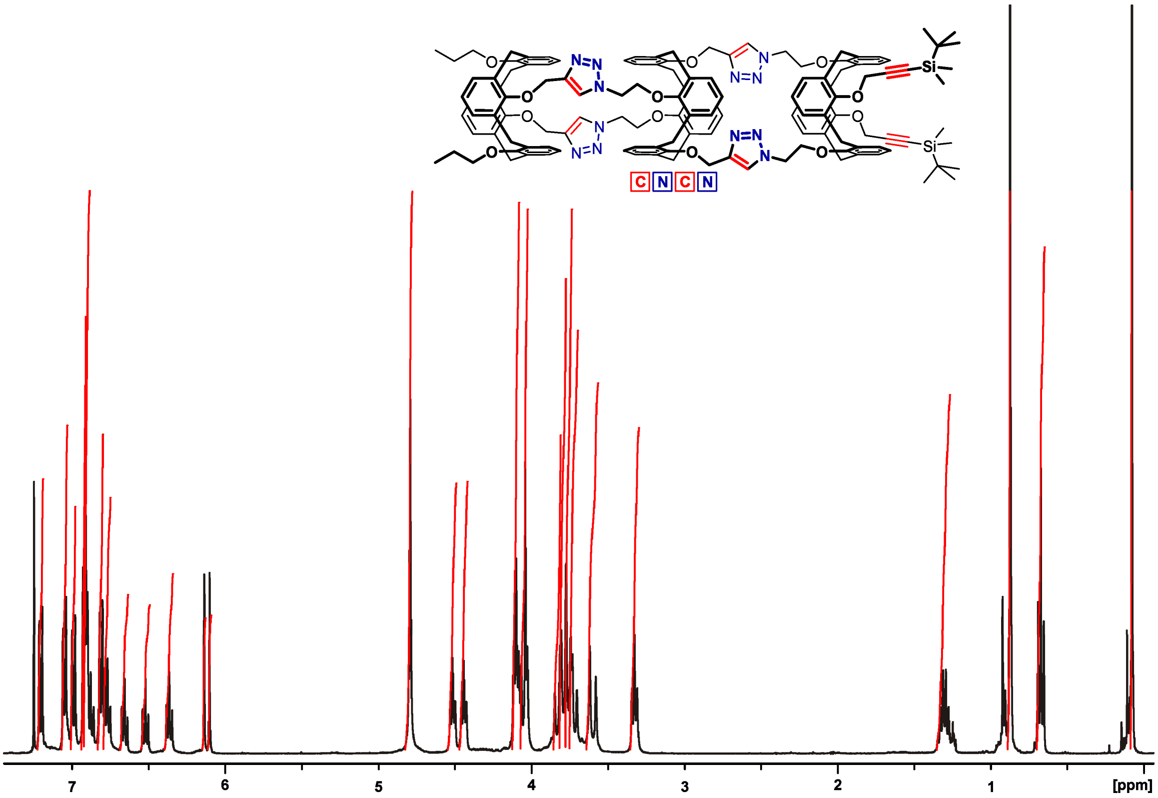


Figure S29. ^{1}H NMR spectrum of tris(calix[4]arene) **25** (400 MHz, CDCl$_3$).

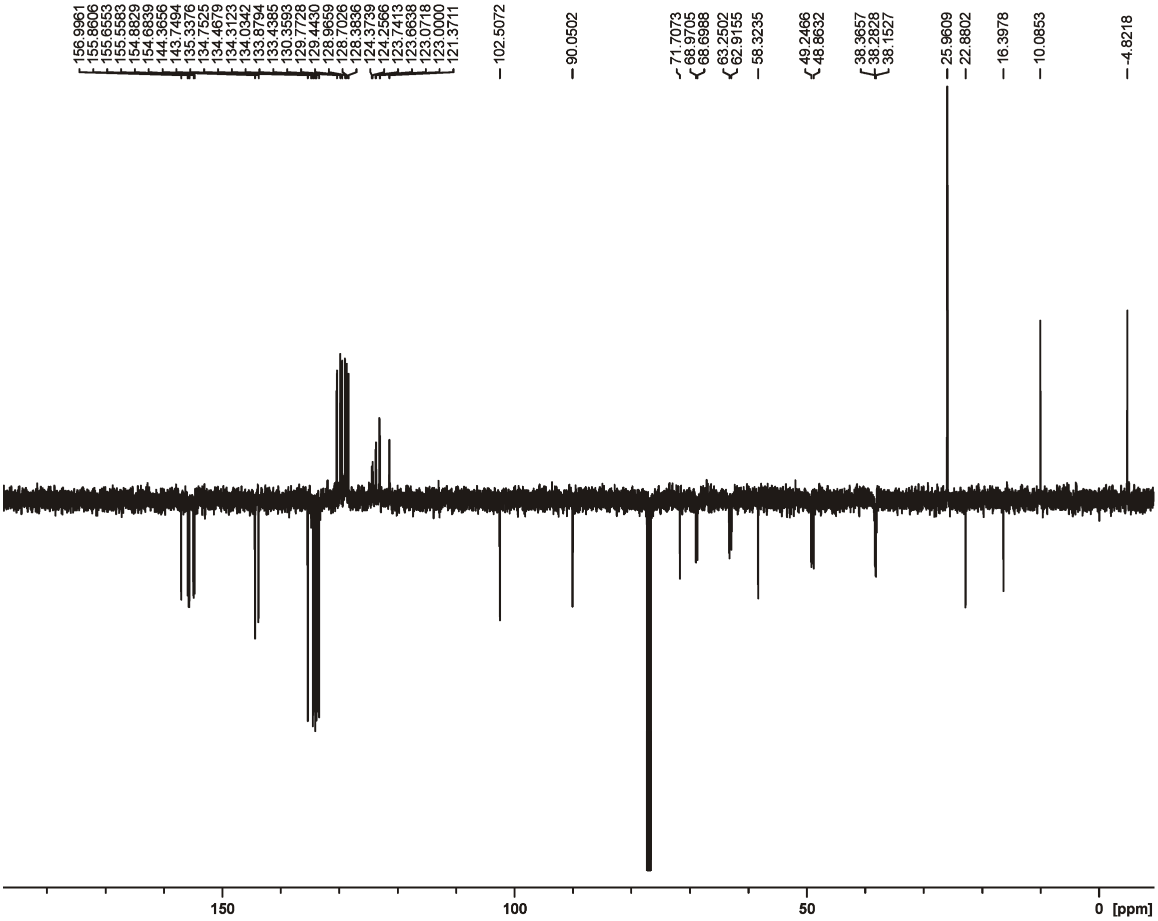


Figure S30. ^{13}C NMR spectrum (APT) of tris(calix[4]arene) **25** (100 MHz, CDCl$_3$).

Details of X-ray diffraction measurements

Crystallographic data were collected at 150 K on a Bruker SMART APEX II diffractometer equipped with a PHOTON II CMOS detector using graphite monochromatized Mo–Kα radiation (λ = 0.71073 Å) using a ω-scan mode. Absorption correction based on measurements of equivalent reflections was applied.[S8] The structure was solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using Olex2 package.[S9] Hydrogen atoms were placed in calculated positions and refined using a riding model. Crystallographic details are presented in Table S6. CCDC 2157422 contains the supplementary crystallographic data for the structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S6. Details of the X-ray crystal data collection and structure refinement for compound **14**

Empirical formula	$C_{136}H_{156}N_{12}O_{12}\cdot 1.75CH_3OH\cdot 3.44CH_2Cl_2$
M_w	2489.94
Temperature (K)	150(2)
Size (mm)	0.35 × 0.28 × 0.17
Cryst. system	triclinic
Space group	P–1
a (Å)	12.9900(8)
b (Å)	23.3144(17)
c (Å)	24.9990(15)
α (deg)	94.717(3)
β (deg)	99.611(2)
γ (deg)	101.122(2)
V (Å^3)	7273.2(8)
Z	2
ρ_{cald} (g·cm^{-3})	1.141
Abs coeff (mm^{-1})	0.195
F(000)	2656
θ range (deg)	$1.63 < \theta < 25.03$
no. of collected/unique rflns	90200 / 25299
Completeness to θ (%)	98.5
no. of data/restraints/params	25299/167/1564
Goodness of fit on F^2	1.569
Final R indices ($I > 2\sigma(I)$)	R1 = 0.1466, wR2 = 0.4014
R indices (all data)	R1 = 0.2255, wR2 = 0.4423
Largest diff peak/hole (e/Å^3)	2.83 / −1.08

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