Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Selective azide-alkyne cycloaddition reactions of azidoalkylated calixarenes

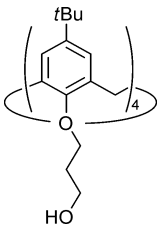
Alexander Gorbunov, Julia Kuznetsova, Ilya Deltsov, Anastasia Molokanova, Dmitry Cheshkov, Stanislav Bezzubov, Vladimir Kovalev and Ivan Vatsouro

Supplementary Information

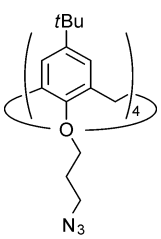
Contents

Synthesis and characterization of novel compounds

General experimental methods: NMR spectra were acquired on Bruker Avance 400 and Avance 600 instruments at 25 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 $\mathbf{1}_2$,[S1] $\mathbf{2}_2$,[S2] $\mathbf{2}_3$,[S3] $\mathbf{2}_4$,[S4] $\mathbf{3}_2$,[S5] $\mathbf{4}_2$,[S5] **5**,[S6] **7**,[S7] **8**,[S8] **10**,[S7] **11**,[S9] $\mathbf{15}_2$,[S5] $\mathbf{16}_2$,[S5] $\mathbf{17}_2$,[S5] $\mathbf{18}_2$,[S5] and complex CuI·P(OEt)$_3$[S10] were prepared according to the published procedures.

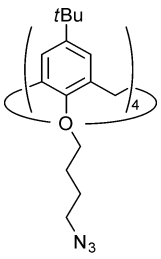


Hydroxypropylated calix[4]arene ***6***. Under Ar, 9-BBN (0.4 M in hexane, 10.0 ml, 4.00 mmol) was added dropwise to a cold (0 °C) solution of allyloxycalixarene **5** (0.404 g, 0.50 mmol) in dry THF (15 ml). The reaction mixture was stirred at 0 °C for 30 min and then stirred at room temperature for 2 h. The mixture was cooled again (0 °C) and aqueous NaOH (5 M, 10.0 ml, 50.0 mmol) and H_2O_2 (30%, 2.5 ml, 20.0 mmol) were subsequently added. The mixture was heated to 40 °C and was stirred at this temperature for 12 h. After cooling, the aqueous phase was separated and washed with THF. The combined organic phases were washed with brine, the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane, 2 M HCl was added, and the mixture was stirred intensively for several hours. The aqueous phase was separated, washed with dichloromethane, the combined organic phase was washed with water and concentrated. The residue dissolved in a minimum amount of dichloromethane, hexane was added, and the solid formed was collected, washed with hexane and dried. Yield 0.35 g (78%), white solid. M. p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.78 (s, 8H; ArH), 4.35 (d, 4H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.00–3.88 (m, 16H; $OC\underline{H}_2CH_2C\underline{H}_2OH$), 3.14 (d, 4H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 2.35–2.24 (m, 8H; $OCH_2C\underline{H}_2$), 1.07 (s, 36H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.03, 144.58, 133.67 (C_{Ar}), 125.04, (CH_{Ar}), 72.14 (OCH_2), 60.08 (CH_2OH), 33.80 ($\underline{C}(CH_3)_3$), 33.23 (CH_2), 31.40 ($C(\underline{C}H_3)_3$), 30.85 ($ArCH_2Ar$) ppm. ESI-MS *m*/*z*: 903.5743 $[M+Na]^+$ for $C_{56}H_{80}NO_8$ (903.5745).

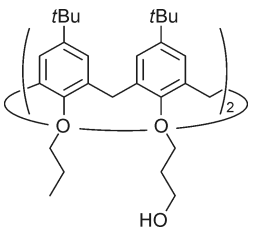


Azidopropylated calix[4]arene $\mathbf{1}_3$.[S11] Diisopropyl azodicarboxylate (DIAD, 0.197 ml, 1.00 mmmol) was added dropwide at stirring to a cooled (0–5 °C) solution of Ph_3P (0.210 g, 0.80 mmol) in dry THF (3 ml). After a solid formed, a solution of calixarene **6** (0.088 g, 0.10 mmol) and diphenyl phosphoryl azide (DPPA, 0.215 ml, 1.00 mmol) in THF (3 ml) was added dropwise. The reaction

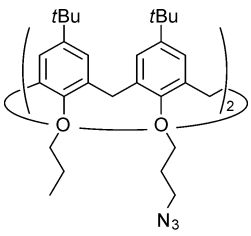
mixture was stirred at 0–5 C for 1 h and then allowed to stay at room temperature for 48 h. The solution was concentrated under reduced pressure and the resultant oil was treated with cold methanol. The solid formed was collected, washed with methanol and dried. Yield 0.066 g (67%), white solid. NMR spectra was in agreement with the published data.[S11]



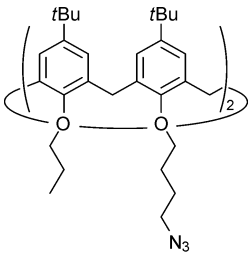
Azidobutylated calix[4]arene ***1₄***. A mixture of bromobutylated calix[4]arene **7** (0.290 g, 0.24 mmol) and NaN_3 (0.130 g, 2.00 mmol) in dry DMF (10 ml) was stirred at 75 °C for 8 h. The solvent was removed under reduced pressure, and the residue was parted between dichloromethane and aqueous HCl (2 M). The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated to dryness. The residue was purified by column chromatography on silica (gradient from hexane to hexane/THF (100:1)). Yield 0.120 g (48%), white solid. M. p. 143–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77 (s, 8H; ArH), 4.34 (d, 4H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 3.91–3.84 (m, 8H; OCH_2), 3.42–3.35 (m, 8H; CH_2N_3), 3.14 (d, 4H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 2.13–2.02 (m, 8H; $CH_2C\underline{H}_2CH_2$), 1.76–1.66 (m, 8H; $CH_2C\underline{H}_2CH_2$), 1.07 (s, 36H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.22, 144.61, 133.58 (C_{Ar}), 125.02, (CH_{Ar}), 74.47 (OCH_2), 51.52 (CH_2N_3), 33.81 ($\underline{C}(CH_3)_3$), 31.40 ($C(\underline{C}H_3)_3$), 31.06 ($ArCH_2Ar$), 27.52, 25.66 (CH_2) ppm. ESI-MS *m*/*z*: 1059.6625 $[M+Na]^+$ for $C_{60}H_{84}NaN_{12}O_4$ (1059.6631).



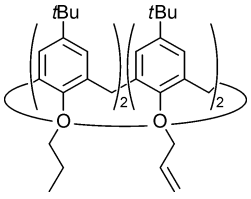
Hydroxypropylated calix[4]arene ***9*** was prepared as described for calixarene **6** from allyloxycalixarene **8** (0.406 g, 0.50 mmol), 9-BBN (0.4 M in hexane, 5.00 ml, 2.00 mmol), aqueous NaOH (5 M, 5.0 ml, 25.0 mmol) and H_2O_2 (30%, 1.25 ml, 10.0 mmol) in THF (15 ml). The product was purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol (20:1)). Yield 0.31 g (74%), white solid. M. p. 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (s, 4H; ArH), 6.54 (s, 4H; ArH), 4.39 (d, 4H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.12 (t, 4H, $^3J_{HH}$ = 6.7 Hz; $HOCH_2CH_2C\underline{H}_2$), 3.98 (t, 4H, $^3J_{HH}$ = 6.1 Hz; $CH_3CH_2C\underline{H}_2$), 3.69 (m, 4H; $HOC\underline{H}_2$), 3.25 (bs, 2H; OH), 3.13 (d, 4H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 2.25–2.17 (m, 4H; $HOCH_2C\underline{H}_2$), 1.96–1.85 (m, 4H; $CH_3C\underline{H}_2$), 1.28 (s, 18H; $C(CH_3)_3$), 0.98 (t, 6H, $^3J_{HH}$ = 7.4 Hz; CH_3), 0.86 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.27, 152.17, 144.75, 144.09, 135.15, 132.27 (C_{Ar}), 125.39, 124.58 (CH_{Ar}), 77.69, 71.92 (OCH_2), 60.01 (CH_2OH), 33.98, 33.61 ($\underline{C}(CH_3)_3$), 32.79 ($\underline{C}H_2CH_2OH$), 31.67, 31.18 ($C(\underline{C}H_3)_3$), 30.81 ($ArCH_2Ar$), 23.16 ($\underline{C}H_2CH_3$), 10.45 (CH_3) ppm. ESI-MS *m*/*z*: 871.5844 $[M+Na]^+$ for $C_{56}H_{80}NaO_6$ (871.5847).



Azidopropylated calix[4]arene ***3₃*** was prepared as described for calixarene **1₃** from calixarene **9** (0.134 g, 0.16 mmol), DIAD (0.157 ml, 0.80 mmol), Ph_3P (0.168 g, 0.64 mmol) and DPPA (0.172 ml, 0.80 mmol) in THF (5 ml). Yield 0.097 g (68%), white solid. M. p. 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93 (s, 4H; ArH), 6.60 (s, 4H; ArH), 4.33 (d, 4H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.00 (t, 4H, $^3J_{HH}$ = 7.5 Hz; $OC\underline{H}_2CH_2CH_2$), 3.73 (t, 4H, $^3J_{HH}$ = 7.6 Hz; $OC\underline{H}_2CH_2CH_3$), 3.51 (t, 4H, $^3J_{HH}$ = 7.0 Hz; CH_2N_3), 3.13 (d, 4H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 2.37–2.28 (m, 4H; $C\underline{H}_2CH_2N_3$), 2.00–1.88 (m, 4H; $C\underline{H}_2CH_3$), 1.19 (s, 18H; $C(CH_3)_3$), 1.00 (t, 6H, $^3J_{HH}$ = 7.5 Hz; CH_3), 0.93 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.61, 152.81, 144.90, 144.20, 134.56, 132.67 (C_{Ar}), 125.29, 124.70 (CH_{Ar}), 77.32, 71.88 (OCH_2), 49.04 (CH_2N_3), 33.94, 33.67 ($\underline{C}(CH_3)_3$), 31.55, 31.26 ($C(\underline{C}H_3)_3$), 30.98 ($ArCH_2Ar$), 29.64 ($\underline{C}H_2CH_2N_3$), 23.46 ($\underline{C}H_2CH_3$), 10.42 (CH_3) ppm. ESI-MS *m*/*z*: 921.5975 $[M+Na]^+$ for $C_{56}H_{78}NaN_6O_4$ (921.5977).

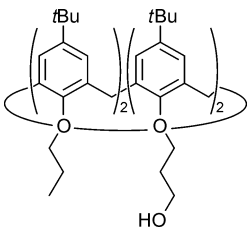


Azidobutylated calix[4]arene ***3₄*** was prepared as described for calixarene **1₄** from calixarene **10** (0.161 g, 0.16 mmol) and NaN_3 (0.042 g, 0.64 mmol) in DMF (10 ml). The product was purified by column chromatography on silica (gradient from hexane to hexane/THF (200:1)). Yield 0.120 g (81%), white solid. M. p. 153–155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (s, 4H; ArH), 6.69 (s, 4H; ArH), 4.36 (d, 4H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 3.93–3.87 (m, 4H; OCH_2), 3.79–3.73 (m, 4H; OCH_2), 3.36 (t, 4H, $^3J_{HH}$ = 6.9 Hz; CH_2N_3), 3.11 (d, 4H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 2.14–2.04 (m, 4H; CH_2), 2.03–1.92 (m, 4H; CH_2), 1.76–1.66 (m, 4H; CH_2), 1.12 (s, 18H; $C(CH_3)_3$), 1.03–0.97 (m, 24H; $C(CH_3)_3$+CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.57, 153.27, 144.55, 144.20, 134.13, 133.24 (C_{Ar}), 125.06, 124.79 (CH_{Ar}), 77.08, 74.29 (OCH_2), 51.59 (CH_2N_3), 33.86, 33.73 ($\underline{C}(CH_3)_3$), 31.49, 31.36 ($C(\underline{C}H_3)_3$), 31.03 ($ArCH_2Ar$), 27.41, 25.66, 23.45 (CH_2), 10.41 (CH_3) ppm. ESI-MS *m*/*z*: 949.6289 $[M+Na]^+$ for $C_{58}H_{82}NaN_6O_4$ (949.6290).

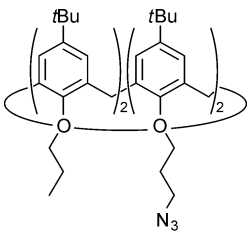


Allylated calix[4]arene ***12***. To a suspension of calixarene **11** (0.732 g, 1.00 mmol) in dry DMF (20 ml) NaH (60% in mineral oil, 0.240 g, 6.00 mmol) was added. The mixture was stirred for 1 h at room temperature and allyl bromide (0.520 ml, 6.00 mmol) was added. The mixture was stirred for 24 h at room temperature and then quenched by a few drops of methanol followed by water (50 ml). The precipitate formed was collected, washed with water, dried and dissolved in dichloromethane (5 ml). Methanol (15 ml) was added and the precipitate formed was collected,

with methanol and dried. Yield 0.710 g (87%), white solid. M. p. 196–198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79 (m, 8H; ArH), 6.41 (ddt, $^3J_{HH}$ = 17.1 Hz, $^3J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 6.5 Hz, 2H; C<u>H</u>=CH_2), 5.28–5.20 (m, 2H; CH=C<u>H</u>$_2$), 5.19–5.13 (m, 2H; CH=C<u>H</u>$_2$), 4.49–4.34 (m, 8H; $ArCH_2Ar$+OC<u>H</u>$_2$CH), 3.80 (t, 4H, $^3J_{HH}$ = 7.8 Hz; OC<u>H</u>$_2CH_2$), 3.14–3.06 (m, 4H; $ArCH_2Ar$), 2.07–1.96 (m, 4H; CH_3C<u>H</u>$_2$), 1.07 (s, 18H; $C(CH_3)_3$), 1.06 (s, 18H; $C(CH_3)_3$), 0.98 (t, 6H, $^3J_{HH}$ = 7.5 Hz, CH_2C<u>H</u>$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.69, 153.16, 144.47, 144.16 (C_{Ar}), 136.52 (<u>C</u>H=CH_2), 134.03, 133.98, 133.84, 133.76 (C_{Ar}), 124.89, 124.81, 124.80 (CH_{Ar}), 116.11, (CH=<u>C</u>H_2), 76.91, 76.06 (OCH_2), 33.81, 33.78 (<u>C</u>$(CH_3)_3$), 31.56 ($ArCH_2Ar$), 31.45, 31.42 ($C($<u>C</u>$H_3)_3$), 31.30, 31.05 ($ArCH_2Ar$), 23.36 (<u>C</u>H_2CH_3), 10.32 (CH_3) ppm. ESI-MS *m*/*z*: 830.6079 $[M+NH_4]^+$ for $C_{56}H_{80}NO_4$ (830.6082).

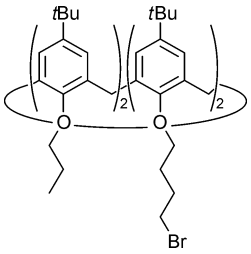


Hydroxypropylated calix[4]arene ***13*** was prepared as described for calixarene **6** from allyloxycalixarene **12** (0.406 g, 0.50 mmol), 9-BBN (0.4 M solution in hexane, 5.00 ml, 2.00 mmol), aqueous NaOH (5 M, 5.0 ml, 25.0 mmol) and H_2O_2 (30%, 1.25 ml 10.0 mmol) in THF (15 ml). The product was purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol (20:1)). Yield 0.17 g (39%), white solid. M. p. 134–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80–6.76 (m, 8H; ArH), 4.43 (d, 1H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.37 (d, 3H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.04–3.87 (m, 8H; OC<u>H</u>$_2CH_2$C<u>H</u>$_2$), 3.83 (t, 4H, $^3J_{HH}$ = 7.8 Hz; C<u>H</u>$_2CH_2CH_3$), 3.14 (d, 1H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 3.13 (d, 2H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 3.12 (d, 1H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 2.88 (bs, 2H; OH), 2.27–2.18 (m, 4H; CH_2C<u>H</u>$_2CH_2$), 2.00–1.85 (m, 4H; CH_2C<u>H</u>$_2CH_3$), 1.07 (s, 18H; $C(CH_3)_3$), 1.06 (s, 18H; $C(CH_3)_3$), 0.95 (t, 6H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.33, 153.20, 144.55, 144.22, 133.73, 133.66, 133.63, 133.59 (C_{Ar}), 125.11, 124.97, 124.87 (CH_{Ar}), 77.05, 72.33 (OCH_2), 60.33, (CH_2OH), 33.80, 33.78 (<u>C</u>$(CH_3)_3$), 33.01 (<u>C</u>H_2CH_2OH), 31.43, 31.41 ($C($<u>C</u>$H_3)_3$), 30.93, 30.81 ($ArCH_2Ar$), 23.15 (<u>C</u>H_2CH_3), 10.25 (CH_3) ppm. ESI-MS *m*/*z*: 871.5842 $[M+Na]^+$ for $C_{56}H_{80}NaO_6$ (871.5847).

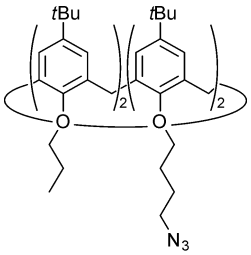


Azidopropylated calix[4]arene ***4$_3$*** was prepared as described for calixarene **1$_3$** from calixarene **13** (0.214 g, 0.25 mmol), DPPA (0.269 ml, 1.25 mmol), Ph_3P (0.262 g, 1.00 mmol) and DIAD (0.246 ml, 1.25 mmol) in THF (7 ml). Yield 0.180 g (79%), white solid. M. p. 166–168 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79–6.77 (m, 8H; ArH), 4.41 (d, 1H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.35 (d, 2H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.29 (d, 1H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 3.99–3.88 (m, 4H; OC<u>H</u>$_2CH_2CH_2$), 3.88–3.75 (m, 4H; OC<u>H</u>$_2CH_2CH_3$), 3.60–3.48 (m, 4H;

CH_2N_3), 3.16 (d, 1H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 3.14 (d, 2H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 3.13 (d, 1H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 2.39–2.23 (m, 4H; $C\underline{H}_2CH_2N_3$), 2.05–1.90 (m, 4H; $C\underline{H}_2CH_3$), 1.08 (s, 18H; $C(CH_3)_3$), 1.07 (s, 18H; $C(CH_3)_3$), 1.00 (t, 6H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.43, 153.05, 144.75, 144.32, 133.76, 133.69, 133.54, 133.47 (C_{Ar}), 125.15, 125.01, 124.85 (CH_{Ar}), 77.03, 72.02 (OCH_2), 48.97 (CH_2N_3), 33.82, 33.79 ($\underline{C}(CH_3)_3$), 31.43, 31.40 ($C(\underline{C}H_3)_3$), 30.97 ($ArCH_2Ar$), 29.66 ($\underline{C}H_2CH_2N_3$), 23.35 ($\underline{C}H_2CH_3$), 10.24 (CH_3) ppm. ESI-MS *m*/*z*: 921.5988 $[M+Na]^+$ for $C_{56}H_{78}NaN_6O_4$ (921.5977).



Bromobutylated calix[4]arene ***14***. To a stirred suspension of calixarene **11** (0.293 g, 0.40 mmol) in dry DMF (15 ml) NaH (60% in mineral oil, 0.160 g, 4.00 mmol) was added. The mixture was stirred for 4 h at room temperature, and 1,4-dibromobutane (0.483 ml, 4.00 mmol) was added. The mixture was stirred for 48 h at 85 °C, cooled and then quenched by methanol (5 ml). The solvent was removed under reduced pressure, and the residue was parted between dichloromethane and aqueous HCl (2 M). The organic layer was separated, washed with water and dried. After removal of the solvent, the resulted yellow oil was dissolved in dichloromethane (5 ml). Methanol (20 ml) was added and the precipitate formed was collected, washed with cold methanol and dried. Yield 0.275 g (68%), white solid. M. p. 186–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85–6.70 (m, 8H; ArH), 4.39 (d, 1H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 4.36 (d, 2H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 4.34 (d, 1H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 3.91–3.84 (m, 4H; OCH_2), 3.84–3.76 (m, 4H; OCH_2), 3.50 (t, 4H, $^3J_{HH}$ = 6.7 Hz; CH_2Br), 3.12 (d, 1H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 3.11 (d, 2H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 3.10 (d, 1H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 2.20–2.10 (m, 4H; $C\underline{H}_2CH_3$), 2.06–1.93 (m, 8H; $C\underline{H}_2C\underline{H}_2CH_2Br$), 1.07 (bs, 36H; $C(CH_3)_3$), 0.99 (t, 6H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.52, 153.37, 144.48, 144.24, 133.82, 133.74, 133.64, 133.58 (C_{Ar}), 125.03, 124.94, 124.91, 124.81 (CH_{Ar}), 76.93, 74.16 (OCH_2), 33.80, 33.79 ($\underline{C}(CH_3)_3$), 33.63 (CH_2Br), 31.44, 31.42 ($C(\underline{C}H_3)_3$), 31.03, 31.00 ($ArCH_2Ar$), 29.70, 29.06 (CH_2), 23.34 ($\underline{C}H_2CH_3$), 10.37 (CH_3) ppm. ESI-MS *m*/*z*: 1003.4638 $[M+H]^+$ for $C_{58}H_{83}Br_2O_4$ (1003.4632).

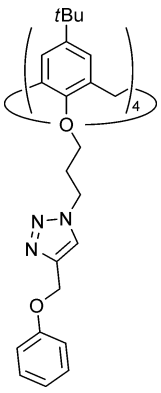


Azidobutylated calix[4]arene ***4₄*** was prepared as described for calixarene $\mathbf{1_4}$ from calixarene **14** (0.260 g, 0.26 mmol) and NaN_3 (0.068 g, 1.00 mmol) in DMF (10 ml). The product was purified by column chromatography on silica (gradient from hexane to hexane/THF (200:1)) followed by re-crystallization from dichloromethane/methanol. Yield 0.130 g (54%), white solid. M. p. 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85–6.70 (m, 8H; ArH), 4.43–4.29

(m, 4H; $ArCH_2Ar$), 3.92–3.83 (m, 4H; OCH_2), 3.83–3.74 (m, 4H; OCH_2), 3.37 (t, 4H, $^3J_{HH}$ = 6.9 Hz; CH_2N_3), 3.15–3.08 (m, 4H; $ArCH_2Ar$), 2.14–1.93 (m, 8H; CH_2), 1.77–1.68 (m, 4H; CH_2), 1.06 (bs, 36H; $C(CH_3)_3$), 0.99 (t, 6H, $^3J_{HH}$ = 7.4 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.52, 153.35, 144.48, 144.26, 133.79, 133.73, 133.62, 133.58 (C_{Ar}), 125.03, 124.94, 124.92, 124.82 (CH_{Ar}), 76.94, 74.43 (OCH_2), 51.54 (CH_2N_3), 33.80, 33.79 ($\underline{C}(CH_3)_3$), 31.43, 31.42 ($C(\underline{C}H_3)_3$), 31.03 ($ArCH_2Ar$), 27.47, 25.70, 23.34 (CH_2), 10.31 (CH_3) ppm. ESI-MS *m*/*z*: 949.6289 $[M+Na]^+$ for $C_{58}H_{82}NaN_6O_4$ (949.6290).

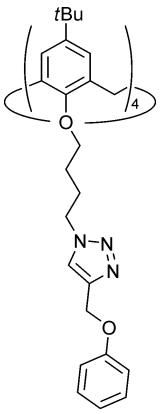
General procedure A (syntheses of triazolated calixarenes using CuI·P(OEt)₃). A mixture of a calixarene azide, phenyl propargyl ether, $CuI{\cdot}P(OEt)_3$, and toluene was stirred at heating (100 °C) in an argon-flushed capped flask for 8 h. The solvent was removed under reduced pressure, and the residue was parted between dichloromethane and aqueous HCl (2 M) at vigorous stirring for 2 h. The organic layer was separated, washed with aqueous Na_2SO_3 (5%) and water, and dried with $MgSO_4$. The solvent was removed and the residue was dissolved in minimum amount of dichloromethane. Hexane was added, and the solid formed was collected, washed with hexane and dried.

General procedure B (syntheses of triazolated calixarenes using CuSO₄·5H₂O/Na ascorbate). To a mixture of a calixarene azide, phenyl propargyl ether, sodium ascorbate and THF a solution of $CuSO_4{\cdot}5H_2O$ in water was added. The reaction mixture was stirred at 60 °C for 8 h in an argon-flushed capped flask. The solvent was removed under reduced pressure, and the residue was treated as described in *General procedure A*.

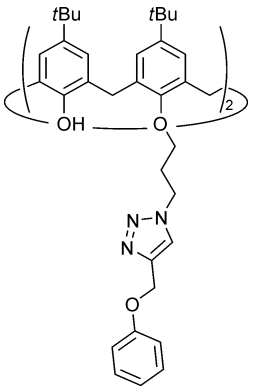


Triazolated calix[4]arene ***15₃*** was prepared according to *General procedure A* from calixarene **1₃** (0.065 g, 0.07 mmol), phenyl propargyl ether (0.042 g, 0.32 mmol) and $CuI{\cdot}P(OEt)_3$ (0.005 g, 0.01 mmol) in toluene (5 ml). Yield 0.086 g (86%), beige solid. M. p. 98–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 4H; ArH_{Trz}), 7.24–7.19 (m, 8H; ArH_{Ph}), 6.95–6.88 (m, 12H; ArH_{Ph}), 6.76 (s, 8H; ArH), 5.09 (s, 8H; OCH_2Trz), 4.47 (t, 8H, ^3J = 7.1 Hz; $OC\underline{H}_2CH_2$), 4.23 (d, 4H, ^2J = 12.6 Hz; $ArCH_2Ar$), 3.89 (t, 8H, ^3J = 7.1 Hz; NCH_2), 3.11 (d, 4H, ^2J = 12.6 Hz; $ArCH_2Ar$), 2.56–2.45 (m, 8H; $OCH_2C\underline{H}_2$), 1.05 (s, 36H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.13 ($C_{Ar\,Ph}$), 152.67, 145.07 (C_{Ar}), 143.93 ($C_{Ar\,Trz}$), 133.30 (C_{Ar}), 129.46 ($CH_{Ar\,Ph}$), 125.19 (CH_{Ar}), 123.46 ($CH_{Ar\,Trz}$), 121.12, 114.60 ($CH_{Ar\,Ph}$), 71.58 (OCH_2Trz), 61.63

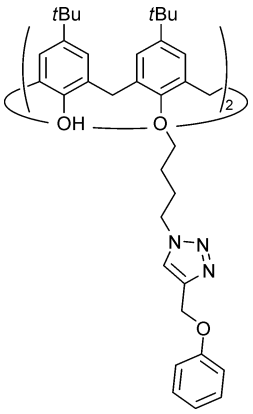
(O<u>C</u>H$_2$CH$_2$), 47.55 (NCH$_2$), 33.79 (<u>C</u>(CH$_3$)$_3$), 31.31 (C(<u>C</u>H$_3$)$_3$), 30.95 (ArCH$_2$Ar), 30.84 (CH$_2$) ppm. ESI-MS *m*/*z*: 1510.8518 [M+H]$^+$ for $C_{92}H_{109}N_{12}O_8$ (1510.8519).



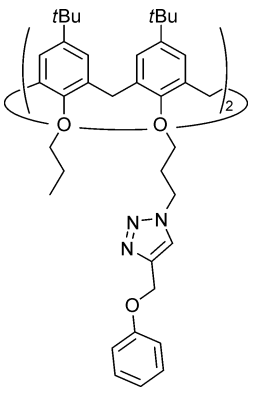
Triazolated calix[4]arene ***15$_4$*** was prepared according to *General procedure A* from calixarene **1$_4$** (0.052 g, 0.05 mmol), phenyl propargyl ether (0.032 g, 0.24 mmol) and CuI·P(OEt)$_3$ (0.004 g, 0.01 mmol) in toluene (5 ml). Yield 0.068 g (87%), beige solid. M. p. 88–90 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.73 (s, 4H; ArH$_{Trz}$), 7.25–7.21 (m, 8H; ArH$_{Ph}$), 6.95–6.90 (m, 12H; ArH$_{Ph}$), 6.75 (s, 8H; ArH), 5.09 (s, 8H; OCH$_2$Trz), 4.45–4.38 (m, 8H; O<u>C</u>H$_2$CH$_2$), 4.24 (d, 4H, ^2J = 12.4 Hz; ArCH$_2$Ar), 3.88–3.78 (m, 8H; NCH$_2$), 3.09 (d, 4H, ^2J = 12.4 Hz; ArCH$_2$Ar), 2.02–1.91 (m, 16H; CH$_2$), 1.06 (s, 36H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.13 (C$_{Ar\ Ph}$), 152.98, 144.62 (C$_{Ar}$), 143.84 (C$_{Ar\ Trz}$), 133.41 (C$_{Ar}$), 129.45 (CH$_{Ar\ Ph}$), 124.97 (CH$_{Ar}$), 123.15 (CH$_{Ar\ Trz}$), 121.10, 114.57 (CH$_{Ar\ Ph}$), 74.09 (OCH$_2$Trz), 61.67 (O<u>C</u>H$_2$CH$_2$), 50.21 (NCH$_2$), 33.74 (<u>C</u>(CH$_3$)$_3$), 31.32 (C(<u>C</u>H$_3$)$_3$), 30.99 (ArCH$_2$Ar), 27.20, 27.00 (CH$_2$) ppm. ESI-MS *m*/*z*: 1588.8989 [M+Na]$^+$ for $C_{96}H_{116}NaN_{12}O_8$ (1588.8965).



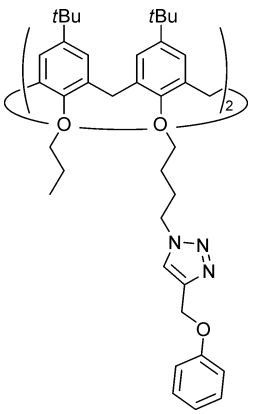
Triazolated calix[4]arene ***16$_3$*** was prepared according to *General procedure B* from calixarene **2$_3$** (0.081 g, 0.10 mmol), phenyl propargyl ether (0.032 g, 0.24 mmol), CuSO$_4$·5H$_2$O (0.010 g, 0.04 mmol) and sodium ascorbate (0.040 g, 0.20 mmol) in the mixture of THF (5 ml) and H$_2$O (1 ml). Yield 0.100 g (92%), beige solid. M. p. 104–106 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.85 (s, 2H; ArH$_{Trz}$), 7.47 (s, 2H; OH), 7.27–7.21 (m, 4H; ArH$_{Ph}$), 7.05 (s, 4H; ArH), 6.96–6.88 (m, 6H; ArH$_{Ph}$), 6.81 (s, 4H; ArH), 5.15 (s, 4H; OCH$_2$Trz), 4.83 (t, 4H, $^3J_{HH}$ = 6.8 Hz; O<u>C</u>H$_2$CH$_2$), 4.16 (d, 4H, $^2J_{HH}$ = 13.1 Hz; ArCH$_2$Ar), 3.98 (t, 4H, $^3J_{HH}$ = 5.7 Hz; NCH$_2$), 3.30 (d, 4H, $^2J_{HH}$ = 13.1 Hz; ArCH$_2$Ar), 2.64–2.54 (m, 4H; CH$_2$), 1.28 (s, 18H; C(CH$_3$)$_3$), 0.96 (s, 18H; C(CH$_3$)$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.13 (C$_{Ar\ Ph}$), 150.22, 149.14, 147.36 (C$_{Ar}$), 144.10 (C$_{Ar\ Trz}$), 141.98, 132.36 (C$_{Ar}$), 129.41 (CH$_{Ar\ Ph}$), 127.54 (C$_{Ar}$), 125.65, 125.21 (CH$_{Ar}$), 123.49 (CH$_{Ar\ Trz}$), 121.04, 114.65 (CH$_{Ar\ Ph}$), 72.19 (OCH$_2$Trz), 61.78 (O<u>C</u>H$_2$CH$_2$), 47.02 (NCH$_2$), 33.91, 33.77 (<u>C</u>(CH$_3$)$_3$), 31.69 (ArCH$_2$Ar), 31.60, 30.90 (C(<u>C</u>H$_3$)$_3$), 30.70 (CH$_2$) ppm. ESI-MS *m*/*z*: 1101.6189 [M+Na]$^+$ for $C_{68}H_{82}NaN_6O_6$ (1101.6188).



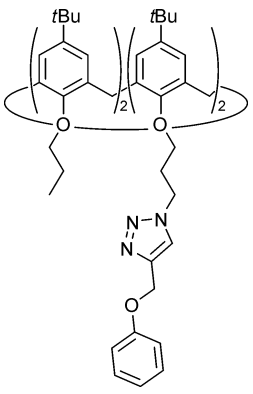
Triazolated calix[4]arene ***16₄*** was prepared according to *General procedure B* from calixarene **2₄** (0.042 g, 0.05 mmol), phenyl propargyl ether (0.016 g, 0.12 mmol), $CuSO_4 \cdot 5H_2O$ (0.050 g, 0.02 mmol) and sodium ascorbate (0.020 g, 0.10 mmol) in the mixture of THF (5 ml) and H_2O (1 ml). Yield 0.038 g (68%), beige solid. M. p. 102–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (s, 2H; ArH_{Trz}), 7.27–7.21 (m, 4H; ArH_{Ph}), 7.07 (bs, 6H; ArH+OH), 6.97–6.90 (m, 6H; ArH_{Ph}), 6.72 (s, 4H; ArH), 5.17 (s, 4H; OCH_2Trz), 4.56–4.49 (m, 4H; $OC\underline{H}_2CH_2$), 4.16 (d, 4H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 3.91–3.85 (m, 4H; NCH_2), 3.30 (d, 4H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 2.23–2.13 (m, 4H; CH_2), 1.78–1.68 (m, 4H; CH_2), 1.30 (s, 18H; $C(CH_3)_3$), 0.89 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.24 ($C_{Ar\ Ph}$), 150.27, 149.44, 147.11 (C_{Ar}), 143.90 ($C_{Ar\ Trz}$), 141.93, 132.05 (C_{Ar}), 129.47 ($CH_{Ar\ Ph}$), 127.71 (C_{Ar}), 125.53, 125.11 (CH_{Ar}), 123.80 ($CH_{Ar\ Trz}$), 121.09, 114.71 ($CH_{Ar\ Ph}$), 76.13 (OCH_2Trz), 61.83 ($O\underline{C}H_2CH_2$), 49.98 (NCH_2), 33.85, 33.84 ($\underline{C}(CH_3)_3$), 31.67 ($C(\underline{C}H_3)_3$), 31.40 ($ArCH_2Ar$), 30.89 ($C(\underline{C}H_3)_3$), 27.70, 26.39 (CH_2) ppm. ESI-MS *m*/*z*: 1129.6507 $[M+Na]^+$ for $C_{70}H_{86}NaN_6O_6$ (1129.6501).



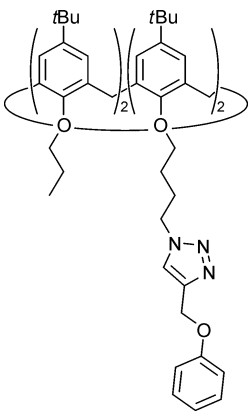
Triazolated calix[4]arene ***17₃*** was prepared according to *General procedure A* from calixarene **3₃** (0.045 g, 0.05 mmol), phenyl propargyl ether (0.016 g, 0.12 mmol) and $CuI \cdot P(OEt)_3$ (0.004 g, 0.01 mmol) in toluene (3 ml). Yield 0.049 g (84%), white solid. M. p. 176–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (s, 2H; ArH_{Trz}), 7.30–7.23 (m, 4H; ArH_{Ph}), 6.99 (s, 4H; ArH), 6.98–6.92 (m, 6H; ArH_{Ph}), 6.53 (s, 4H; ArH), 5.18 (s, 4H; OCH_2Trz), 4.48 (t, 4H, $^3J_{HH}$ = 7.3 Hz; OCH_2), 4.29 (d, 4H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.00 (t, 4H, $^3J_{HH}$ = 7.3 Hz; OCH_2), 3.65 (t, 4H, $^3J_{HH}$ = 7.4 Hz; NCH_2), 3.11 (d, 4H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 2.68–2.57 (m, 4H; CH_2), 1.86–1.74 (m, 4H; CH_2), 1.24 (s, 18H; $C(CH_3)_3$), 0.95 (t, 6H, $^3J_{HH}$ = 7.4 Hz; CH_3), 0.88 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.21 ($C_{Ar\ Ph}$), 153.58, 152.47, 145.24, 144.24 (C_{Ar}), 144.04 ($C_{Ar\ Trz}$), 134.83, 132.20 (C_{Ar}), 129.48 ($CH_{Ar\ Ph}$), 125.46, 124.64 (CH_{Ar}), 122.99 ($CH_{Ar\ Trz}$), 121.14, 114.68 ($CH_{Ar\ Ph}$), 77.39, 71.28, 61.90 (OCH_2), 47.81 (NCH_2), 33.98, 33.61 ($\underline{C}(CH_3)_3$), 31.51, 31.17 ($C(\underline{C}H_3)_3$), 31.00 ($ArCH_2Ar$), 30.93, 23.50 (CH_2), 10.54 (CH_3) ppm. ESI-MS *m*/*z*: 1185.7130 $[M+Na]^+$ for $C_{74}H_{94}NaN_6O_6$ (1185.7127).



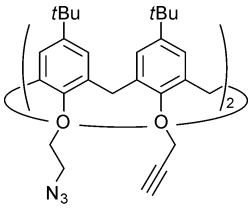
Triazolated calix[4]arene ***17₄*** was prepared according to *General procedure A* from calixarene **3₄** (0.046 g, 0.05 mmol), phenyl propargyl ether (0.016 g, 0.12 mmol) and CuI·P(OEt)$_3$ (0.004 g, 0.01 mmol) in toluene (5 ml). Yield 0.042 g (70%), white solid. M. p. 73–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (s, 2H; ArH_{Trz}), 7.31–7.26 (m, 4H; ArH_{Ph}), 7.00–6.92 (m, 6H; ArH_{Ph}), 6.81 (s, 4H; ArH), 6.70 (s, 4H; ArH), 5.19 (s, 4H; OCH_2Trz), 4.47–4.39 (m, 4H; OCH_2), 4.32 (d, 4H, $^2J_{HH}$ = 12.6 Hz; $ArCH_2Ar$), 3.96–3.86 (m, 4H; OCH_2), 3.76–3.69 (m, 4H; NCH_2), 3.11 (d, 4H, $^2J_{HH}$ = 12.6 Hz; $ArCH_2Ar$), 2.11–1.99 (m, 8H; CH_2), 1.96–1.84 (m, 4H; CH_2), 1.10 (s, 18H; $C(CH_3)_3$), 1.02 (s, 18H; $C(CH_3)_3$), 0.95 (t, 6H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.18 ($C_{Ar\,Ph}$), 153.25, 153.20, 144.65, 144.29 (C_{Ar}), 144.18 ($C_{Ar\,Trz}$), 133.88, 133.25 (C_{Ar}), 129.49 ($CH_{Ar\,Ph}$), 125.06, 124.83 (CH_{Ar}), 122.57 ($CH_{Ar\,Trz}$), 121.14, 114.65 ($CH_{Ar\,Ph}$), 76.92, 73.85, 61.91 (OCH_2), 50.34 (NCH_2), 33.82, 33.72 ($\underline{C}(CH_3)_3$), 31.42, 31.34 ($C(\underline{C}H_3)_3$), 31.01 ($ArCH_2Ar$), 27.15, 27.14, 23.36 (CH_2), 10.40 (CH_3) ppm. ESI-MS *m*/*z*: 1213.7442 $[M+Na]^+$ for $C_{76}H_{98}NaN_6O_6$ (1213.7440).



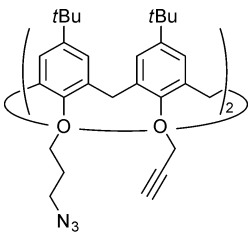
Triazolated calix[4]arene ***18₃*** was prepared according to *General procedure A* from calixarene **4₃** (0.045 g, 0.05 mmol), phenyl propargyl ether (0.016 g, 0.12 mmol) and CuI·P(OEt)$_3$ (0.004 g, 0.01 mmol) in toluene (3 ml). Yield 0.050 g (86%), white solid. M. p. 205–207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (s, 2H; ArH_{Trz}), 7.31–7.26 (m, 4H; ArH_{Ph}), 7.01–6.92 (m, 6H; ArH_{Ph}), 6.79 (bs, 4H; ArH), 6.76 (bs, 4H; ArH), 5.19 (s, 4H; OCH_2Trz), 4.65–4.48 (m, 4H; OCH_2), 4.39 (d, 1H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.33 (d, 2H, $^2J_{HH}$ = 12.3 Hz; $ArCH_2Ar$), 4.24 (d, 1H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 4.00–3.84 (m, 4H; OCH_2), 3.83–3.72 (m, 4H; NCH_2), 3.19–3.07 (m, 4H; $ArCH_2Ar$), 2.67–2.55 (m, 4H; CH_2), 1.99–1.83 (m, 4H; CH_2), 1.08 (s, 18H; $C(CH_3)_3$), 1.07 (s, 18H; $C(CH_3)_3$), 0.95 (t, 6H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.21 ($C_{Ar\,Ph}$), 153.30, 152.90, 144.97, 144.42 (C_{Ar}), 144.17 ($C_{Ar\,Trz}$), 133.70, 133.59, 133.39, 133.31 (C_{Ar}), 129.49 ($CH_{Ar\,Ph}$), 125.24, 125.06, 124.86 (CH_{Ar}), 122.88 ($CH_{Ar\,Trz}$), 121.14, 114.71 ($CH_{Ar\,Ph}$), 77.00, 71.47, 61.91 (OCH_2), 47.85 (NCH_2), 33.82, 33.78 ($\underline{C}(CH_3)_3$), 31.40, 31.36 ($C(\underline{C}H_3)_3$), 31.02, 31.01 ($ArCH_2Ar$), 30.96, 23.36 (CH_2), 10.33 (CH_3) ppm. ESI-MS *m*/*z*: 1185.7137 $[M+Na]^+$ for $C_{74}H_{94}NaN_6O_6$ (1185.7127).



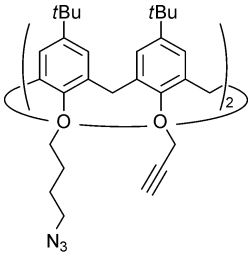
Triazolated calix[4]arene ***18₄*** was prepared according to *General procedure A* from calixarene **4₄** (0.046 g, 0.05 mmol), phenyl propargyl ether (0.016 g, 0.12 mmol) and CuI·P(OEt)$_3$ (0.004 g, 0.01 mmol) in toluene (3 ml). Yield 0.036 g (60%), white solid. M. p. 143–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (s, 2H; ArH_{Trz}), 7.31–7.26 (m, 4H; ArH_{Ph}), 7.01–6.92 (m, 6H; ArH_{Ph}), 6.79 (bs, 4H; ArH), 6.76 (bs, 4H; ArH), 5.19 (s, 4H; OCH_2Trz), 4.65–4.48 (m, 4H; OCH_2), 4.39 (d, 1H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.33 (d, 2H, $^2J_{HH}$ = 12.3 Hz; $ArCH_2Ar$), 4.24 (d, 1H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 4.00–3.84 (m, 4H; OCH_2), 3.83–3.72 (m, 4H; NCH_2), 3.19–3.07 (m, 4H; $ArCH_2Ar$), 2.67–2.55 (m, 4H; CH_2), 1.99–1.83 (m, 4H; CH_2), 1.08 (s, 18H; $C(CH_3)_3$), 1.07 (s, 18H; $C(CH_3)_3$), 0.95 (t, 6H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.20 ($C_{Ar\ Ph}$), 153.42, 153.16, 144.59, 144.32 (C_{Ar}), 144.15 ($C_{Ar\ Trz}$), 133.73, 133.63, 133.51, 133.46 (C_{Ar}), 129.49 ($CH_{Ar\ Ph}$), 125.09, 124.97, 124.91, 124.81 (CH_{Ar}), 122.72 ($CH_{Ar\ Trz}$), 121.15, 114.66 ($CH_{Ar\ Ph}$), 76.87, 74.04, 61.89 (OCH_2), 50.34 (NCH_2), 33.79, 33.77 ($\underline{C}(CH_3)_3$), 31.40, 31.39 ($C(\underline{C}H_3)_3$), 31.03, 30.98 ($ArCH_2Ar$), 27.24, 27.17, 23.34 (CH_2), 10.39 (CH_3) ppm. ESI-MS *m*/*z*: 1213.7446 $[M+Na]^+$ for $C_{76}H_{98}NaN_6O_6$ (1213.7440).



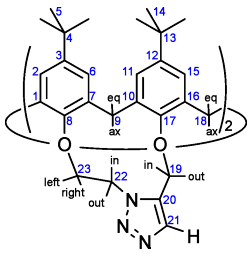
Azidoethylated/propargylated calix[4]arene ***19₂***. To a stirred solution of calixarene **2₂** (0.240 g, 0.30 mmol) in dry DMF (10 ml) NaH (60% in mineral oil, 0.072 g, 1.80 mmol) was added. The mixture was stirred at room temperature for 1 h. Propargyl bromide (80% in toluene, 0.168 ml, 1.50 mmol) was added and the mixture was stirred at room temperature for 48 h. The reaction was quenched with several drops of methanol and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane, the solution was washed with 2 M HCl, water, and dried with $MgSO_4$. The solvent was removed and the residue was purified by column chromatography (gradient from hexane to hexane/ethyl acetate (10:1)). Yield 0.140 g (54%), white solid. M. p. > 300 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94 (s, 4H; ArH), 6.67 (s, 4H; ArH), 4.85 (d, 4H, $^4J_{HH}$ = 2.4 Hz; $OC\underline{H}_2CCH$), 4.49 (d, 4H, $^2J_{HH}$ = 12.7 Hz; $ArCH_2Ar$), 4.05–4.00 (m, 4H; $OC\underline{H}_2CH_2$), 3.95–3.90 (m, 4H; CH_2N_3), 3.18 (d, 4H, $^2J_{HH}$ = 12.7 Hz; $ArCH_2Ar$), 2.51 (t, 2H, $^4J_{HH}$ = 2.4 Hz; CH), 1.18 (s, 18H; $C(CH_3)_3$), 0.98 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.59, 151.75, 145.83, 145.16, 134.96, 132.81 (C_{Ar}), 125.29, 124.90 (CH_{Ar}), 81.19 ($CH_2\underline{C}CH$), 74.60 ($CH_2C\underline{C}H$), 72.16 ($O\underline{C}H_2CH_2$), 60.54 ($O\underline{C}H_2CCH$), 51.08 (CH_2N_3), 33.99, 33.74 ($\underline{C}(CH_3)_3$), 31.49 ($ArCH_2Ar$), 31.44, 31.22 ($C(\underline{C}H_3)_3$) ppm. ESI-MS *m*/*z*: 863.5218 $[M+H]^+$ for $C_{54}H_{67}N_6O_4$ (863.5218).



Azidopropylated/propargylated calix[4]arene ***19₃*** was prepared as descibed for compound **19₂** from calixarene **2₃** (0.463 g, 0.60 mmol), NaH (60% in mineral oil, 0.180 g, 4.50 mmol) and propargyl bromide (80% in toluene, 0.334 ml, 3.00 mmol) in DMF (20 ml). Yield 0.402 g (75%), white solid. M. p. 142–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (s, 4H; ArH), 6.54 (s, 4H; ArH), 4.90 (d, 4H, $^{4}J_{HH}$ = 2.5 Hz; $OC\underline{H}_2CCH$), 4.46 (d, 4H, $^{2}J_{HH}$ = 12.7 Hz; $ArCH_2Ar$), 3.87 (t, 4H, $^{3}J_{HH}$ = 6.7 Hz; OCH_2), 3.67 (t, 4H, $^{3}J_{HH}$ = 6.7 Hz; CH_2N_3), 3.18 (d, 4H, $^{2}J_{HH}$ = 12.7 Hz; $ArCH_2Ar$), 2.49 (t, 2H, $^{4}J_{HH}$ = 2.5 Hz; $OCH_2CC\underline{H}$), 2.28 (m, 4H; $OCH_2C\underline{H}_2$), 1.28 (s, 18H; $C(CH_3)_3$), 0.90 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.79, 151.88, 145.92, 144.65, 135.70, 132.10 (C_{Ar}), 125.44, 124.62 (CH_{Ar}), 81.23 ($CH_2\underline{C}CH$), 74.76 ($CH_2C\underline{C}H$), 72.28, 59.94 (OCH_2), 48.91 (CH_2N_3), 34.07, 33.63 ($\underline{C}(CH_3)_3$), 31.58 ($ArCH_2Ar$), 31.56, 31.14 ($C(\underline{C}H_3)_3$), 29.83 (CH_2) ppm. ESI-MS *m/z*: 891.5532 $[M+H]^+$ for $C_{56}H_{71}N_6O_4$ (891.5531).

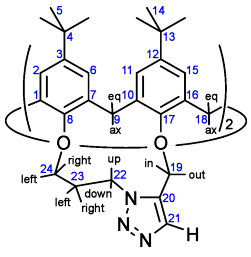


Azidobutylated/propargylated calix[4]arene ***19₄*** was prepared as descibed for compound **19₂** from calixarene **2₄** (0.338 g, 0.42 mmol), NaH (60% in mineral oil, 0.102 g, 2.55 mmol) and propargyl bromide (80% in toluene, 0.237 ml, 2.12 mmol) in DMF (15 ml). The product was purified by column chromatography (dichloromethane) followed by re-crystallization from dichloromethane/methanol. Yield 0.263 g (71%), white solid. M. p. 178–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (s, 4H; ArH), 6.49 (s, 4H; ArH), 4.97 (d, 4H, $^{4}J_{HH}$ = 2.4 Hz; $OC\underline{H}_2CCH$), 4.49 (d, 4H, $^{2}J_{HH}$ = 12.7 Hz; $ArCH_2Ar$), 3.79 (t, 4H, $^{3}J_{HH}$ = 6.9 Hz; OCH_2), 3.40 (t, 4H, $^{3}J_{HH}$ = 6.9 Hz; CH_2N_3), 3.17 (d, 4H, $^{2}J_{HH}$ = 12.7 Hz; $ArCH_2Ar$), 2.44 (t, 2H, $^{4}J_{HH}$ = 2.4 Hz; $OCH_2CC\underline{H}$), 2.07 (m, 4H; CH_2), 1.88 (m, 4H; CH_2), 1.31 (s, 18H; $C(CH_3)_3$), 0.86 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.93, 151.97, 145.86, 144.42, 136.08, 131.95 (C_{Ar}), 125.39, 124.48 (CH_{Ar}), 81.39 ($CH_2\underline{C}CH$), 74.79 ($CH_2C\underline{C}H$), 74.52, 59.86 (OCH_2), 51.48 (CH_2N_3), 34.10, 33.58 ($\underline{C}(CH_3)_3$), 31.72 ($ArCH_2Ar$), 31.62, 31.12 ($C(\underline{C}H_3)_3$), 27.69, 25.93 (CH_2) ppm. ESI-MS *m/z*: 936.6104 $[M+NH_4]^+$ for $C_{58}H_{78}N_7O_4$ (936.6110).

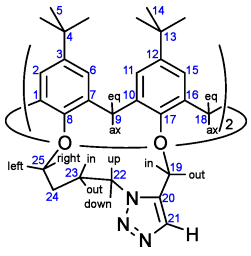


Doubly-bridged calix[4]arene ***20₂***. A solution of calixarene **19₂** (0.020 g, 0.023 mmol) in *o*-xylene (2.3 ml) was heated in an inert atmosphere at 130 °C for 72 h and cooled. The solvent was evaporated under reduced pressure, the residue was dissolved in a minimum volume of dichloromethane and hexane was added. The precipitate formed was collected, washed with hexane and dried. Yield 0.017 g (85%), white solid. M. p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 30 °C): δ = 7.23 (d, 2H, ^{4}J = 2.2 Hz; H^{15}), 7.19 (bs, 2H; H^{21}), 6.89

(d, 2H, ^4J = 2.2 Hz; H^{11}), 6.54 (d, 2H, ^4J = 2.3 Hz; H^{2}), 6.41 (d, 2H, ^4J = 2.3 Hz; H^{6}), 5.49 (bd, 2H; H$^{19\text{in}}$), 5.18–5.13 (m, 2H; H$^{22\text{out}}$), 5.11 (d, 2H, ^2J = 13.1 Hz; H$^{19\text{out}}$), 4.86 (ddd, 2H, ^2J = 14.6 Hz; ^3J = 10.7 Hz, ^3J = 2.0 Hz; H$^{22\text{in}}$), 4.63–4.58 (m, 2H; H$^{23\text{left}}$), 4.46 (d, 2H, ^2J = 12.6 Hz; H$^{18\text{ax}}$), 4.03–3.97 (m, 2H; H$^{23\text{right}}$), 3.31 (d, 2H, ^2J = 12.6 Hz; H$^{18\text{eq}}$), 2.62 (d, 2H, ^2J = 13.0 Hz; H$^{9\text{eq}}$), 2.27 (bs, 2H; H$^{9\text{ax}}$), 1.31 (s, 18H; H^{14}), 0.78 (s, 18H; H^{5}) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 30 °C): δ = 150.52 (*17*), 150.17 (*8*), 147.03 (*12*), 145.71 (*3*), 136.97 (*10*), 136.83 (*21*), 135.31 (*16*), 134.69 (*20*), 132.99 (*1*), 131.74 (*7*), 126.18 (*15*), 125.37 (*6*), 125.07 (*11*), 124.91 (*2*), 72.75 (*23*), 60.95 (*19*), 51.09 (*22*), 34.23 (*13*), 33.61 (*4*), 32.95 (*9*), 31.61 (*14*), 30.87 (*18*+*5*) ppm. ESI-MS *m*/*z*: 863.5226 $[M+H]^+$ for $C_{54}H_{67}N_6O_4$ (863.5218).



Doubly-bridged calix[4]arene ***20$_3$*** was prepared as described for compound **20$_2$** from calixarene **19$_3$** (0.021 g, 0.02 mmol) in *o*-xylene (4 ml). The product was purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol (50:1)). Yield 0.016 g (75%), white solid. M. p. > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 30 °C): δ = 7.35 (s, 2H; H^{21}), 7.21 (d, 2H, ^4J = 2.2 Hz; H^{15}), 6.97 (d, 2H, ^4J = 2.2 Hz; H^{11}), 6.56 (d, 2H, ^4J = 2.3 Hz; H^{2}), 6.45 (d, 2H, ^4J = 2.3 Hz; H^{6}), 5.62–5.54 (m, 2H; H$^{22\text{up}}$), 5.53 (d, 2H, ^2J = 13.8 Hz; H$^{19\text{in}}$), 4.79 (d, 2H, ^2J = 13.8 Hz; H$^{19\text{out}}$), 4.57–4.51 (m, 2H; H$^{22\text{down}}$), 4.38 (d, 2H, ^2J = 12.4 Hz; H$^{18\text{ax}}$), 3.85–3.80 (m, 2H; H$^{24\text{left}}$), 3.76–3.69 (m, 2H; H$^{24\text{right}}$), 3.25 (d, 2H, ^2J = 12.4 Hz; H$^{18\text{eq}}$), 3.11–3.04 (m, 2H; H$^{23\text{left}}$), 2.73–2.64 (m, 2H; H$^{23\text{right}}$), 2.61 (d, 2H, ^2J = 12.9 Hz; H^{9}), 2.60 (d, 2H, ^2J = 12.9 Hz; H^{9}), 1.31 (s, 18H; H^{14}), 0.79 (s, 18H; H^{5}) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.40 (*17*), 149.81 (*8*), 146.87 (*12*), 145.15 (*3*), 136.18 (*10*), 135.00 (*16*), 134.73 (*21*), 134.22 (*20*), 132.24 (*7*), 132.09 (*1*), 126.13 (*15*), 125.15 (*6*), 124.94 (*11*), 124.82 (*2*), 67.84 (*24*), 62.98 (*19*), 42.80 (*22*), 34.18 (*13*), 33.60 (*4*), 31.61 (*14*), 30.95 (*9*), 30.93 (*5*), 30.84 (*18*), 28.12 (*23*) ppm. ESI-MS *m/z* 891.5530 $[M+H]^+$ for $C_{56}H_{71}N_6O_4$ (891.5531).



Doubly-bridged calix[4]arene ***20$_4$*** was prepared as described for compound **20$_2$** from calixarene **19$_4$** (0.092 g, 0.10 mmol) in *o*-xylene (10 ml). The product was purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol (50:1)). Yield 0.066 g (72%), white solid. M. p. 221–223 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 30 °C): δ = 7.67 (s, 2H; H^{21}), 7.14 (d, 2H, ^4J = 2.4 Hz; H^{15}), 7.10 (d, 2H, ^4J = 2.4 Hz; H^{11}), 6.64 (d, 2H, ^4J = 2.4 Hz; H^{2}), 6.61 (d, 2H, ^4J = 2.4 Hz; H^{6}), 4.73 (d, 2H, ^2J = 12.1 Hz; H$^{19\text{in}}$), 4.73–4.69 (m, 2H; H$^{22\text{up}}$), 4.67 (d, 2H, ^2J = 12.1 Hz; H$^{19\text{out}}$), 4.49–4.43 (m, 2H; H$^{22\text{down}}$), 4.29 (d, 2H, ^2J = 12.3 Hz; H$^{18\text{ax}}$), 4.20 (d, 2H, ^2J = 12.3 Hz; H$^{9\text{ax}}$), 3.65–3.59 (m, 2H; H$^{25\text{left}}$), 3.50–3.45 (m, 2H; H$^{25\text{right}}$),

3.25 (d, 2H, ^{2}J = 12.3 Hz; H^{9eq}), 3.24–3.19 (m, 2H; H^{23in}), 3.19 (d, 2H, ^{2}J = 12.3 Hz; H^{18eq}), 1.93–1.83 (m, 2H; H^{23out}), 1.62–1.48 (m, 4H; H^{24}), 1.31 (s, 18H; H^{14}), 0.86 (s, 18H; H^{5}) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 154.55 (*8*), 150.27 (*17*), 145.77 (*12*), 145.46 (*3*), 135.43 (*10*), 134.24 (*21*), 134.01 (*16*), 132.76 (*20*), 132.28 (*7*), 131.99 (*1*), 125.76 (*15*), 125.73 (*2*), 125.49 (*11*), 124.50 (*6*), 73.81 (*25*), 64.56 (*19*), 49.36 (*22*), 34.06 (*13*), 33.76 (*4*), 31.65 (*14*), 31.25 (*9*), 31.06 (*5*), 29.56 (*18*), 28.37 (*23*), 26.14 (*24*) ppm. ESI-MS *m/z* 919.5842 $[M+H]^+$ for $C_{58}H_{75}N_6O_4$ (919.5844).

NMR spectra of novel compounds

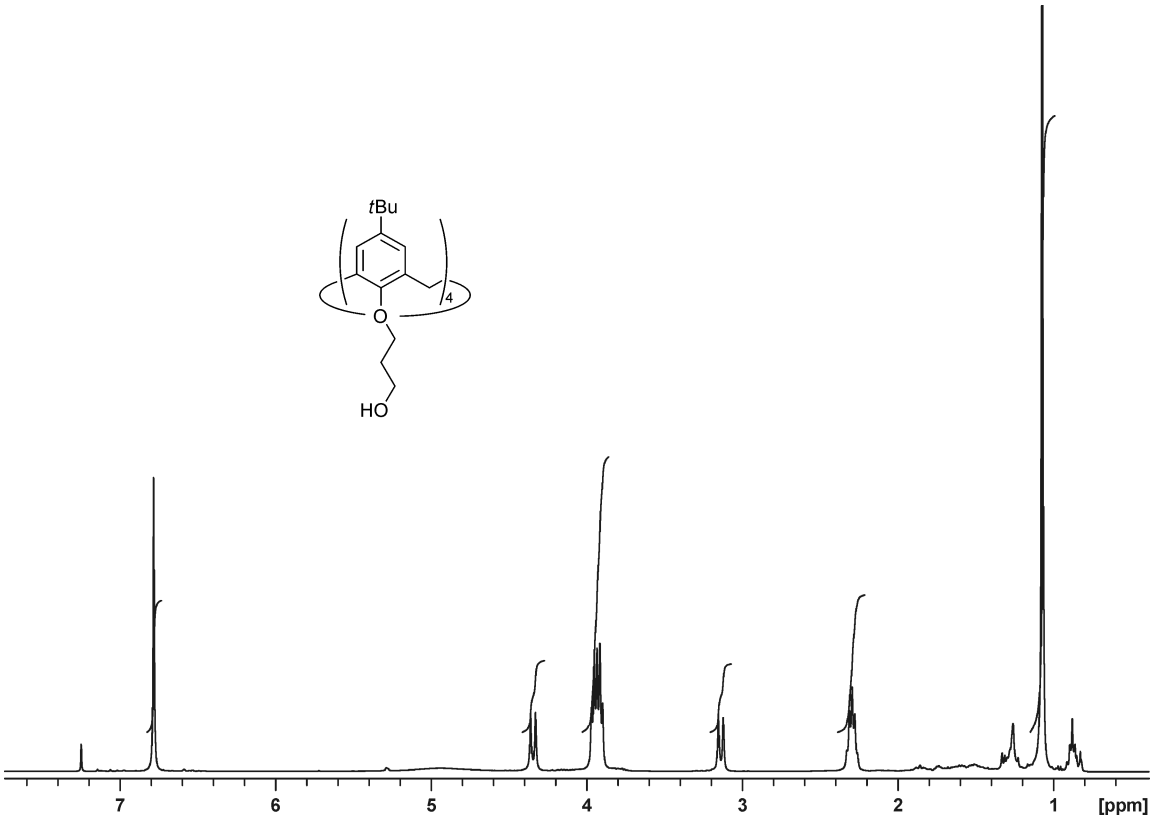


Figure S1. ^{1}H NMR spectrum of calixarene **6** (400 MHz, $CDCl_3$).

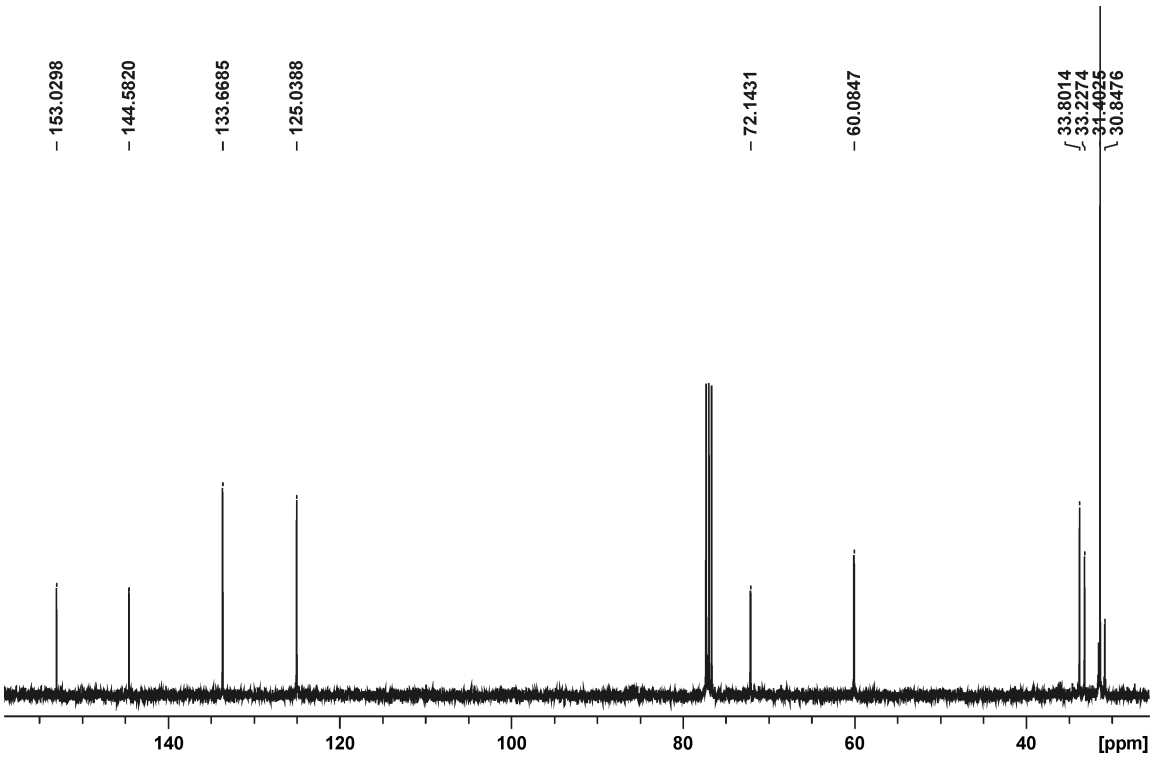


Figure S2. ^{13}C NMR spectrum of calixarene **6** (100 MHz, $CDCl_3$).

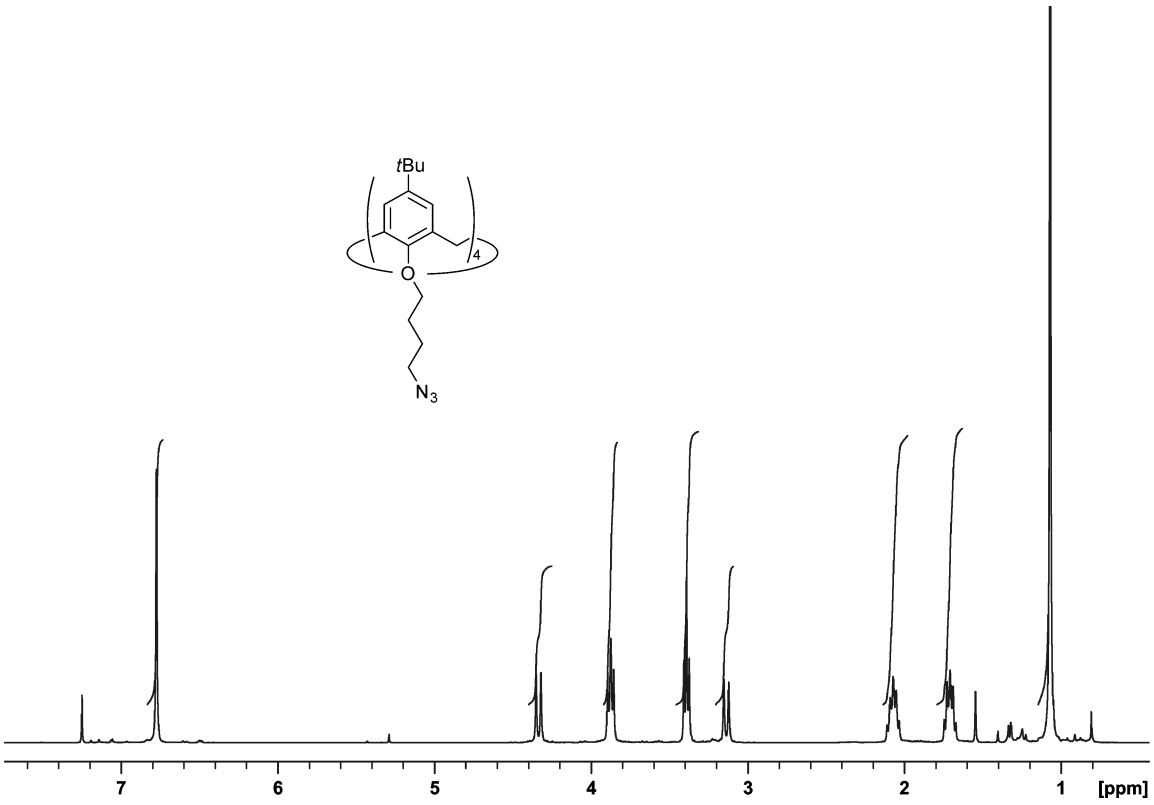


Figure S3. ^{1}H NMR spectrum of calixarene $\mathbf{1_4}$ (400 MHz, $CDCl_3$).

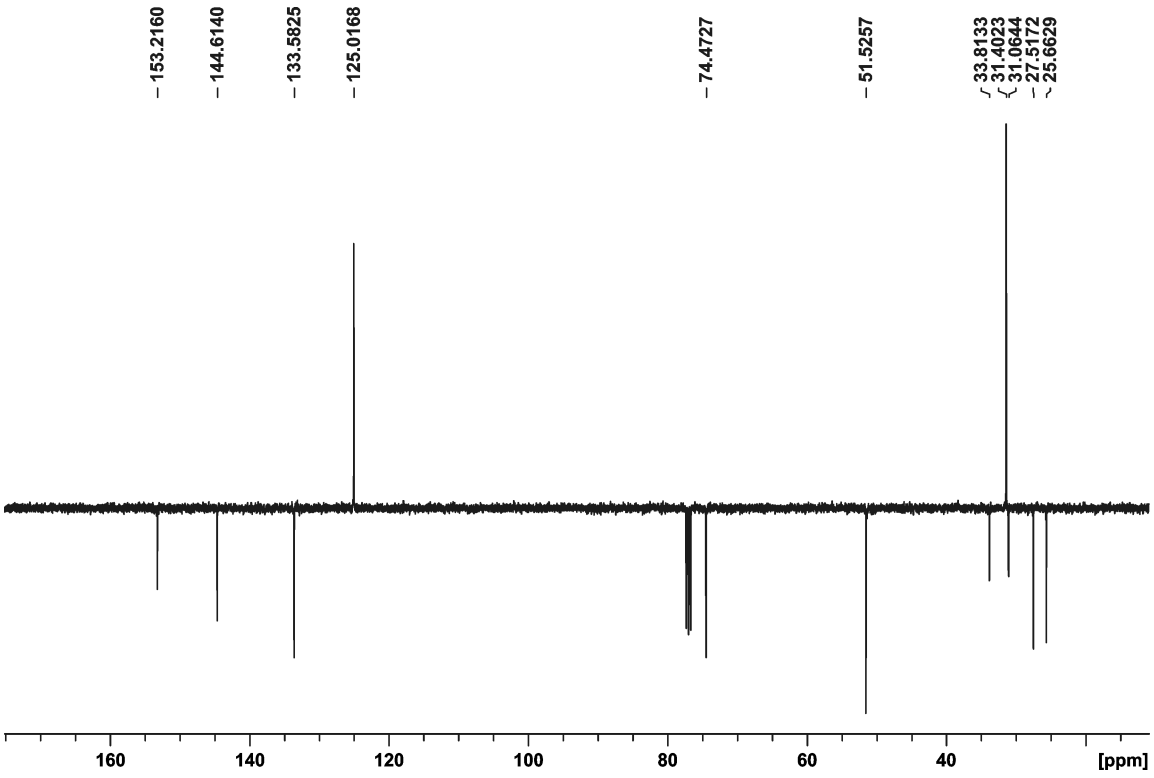


Figure S4. ^{13}C NMR spectrum (APT) of calixarene $\mathbf{1_4}$ (100 MHz, $CDCl_3$).

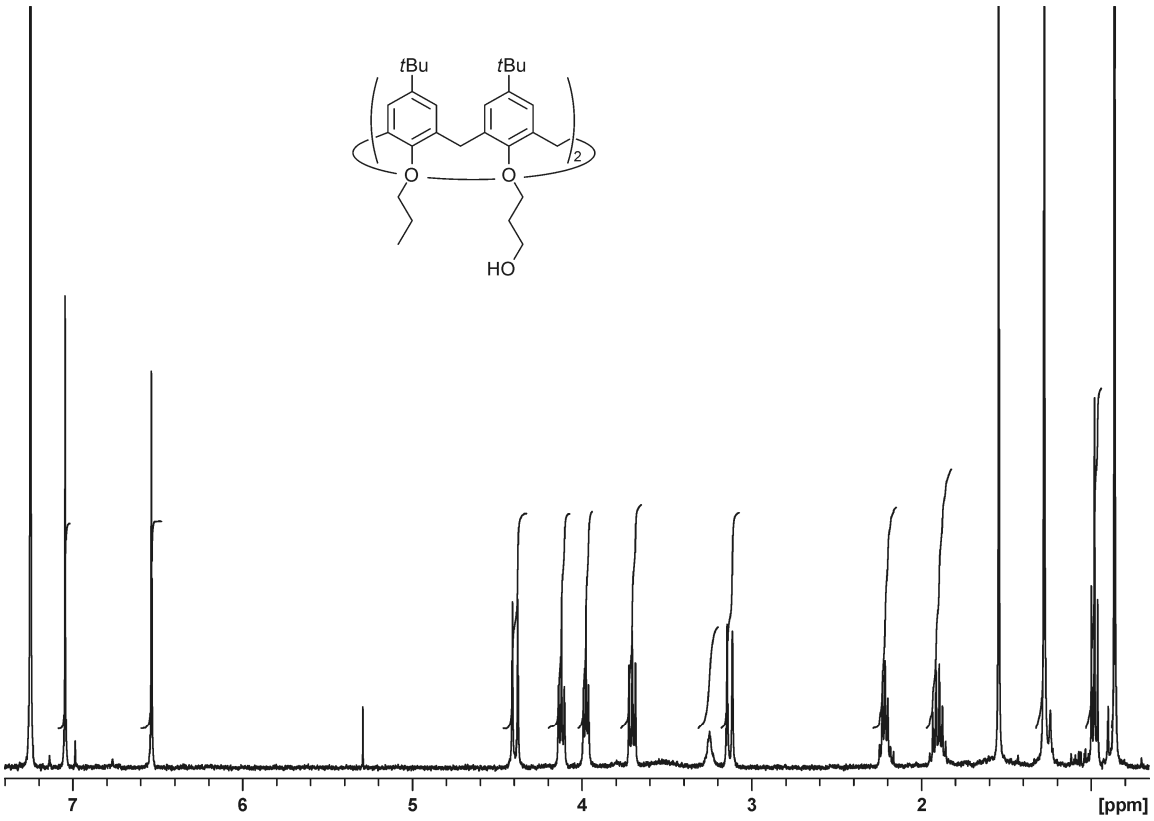


Figure S5. ^{1}H NMR spectrum of calixarene **9** (400 MHz, $CDCl_3$).

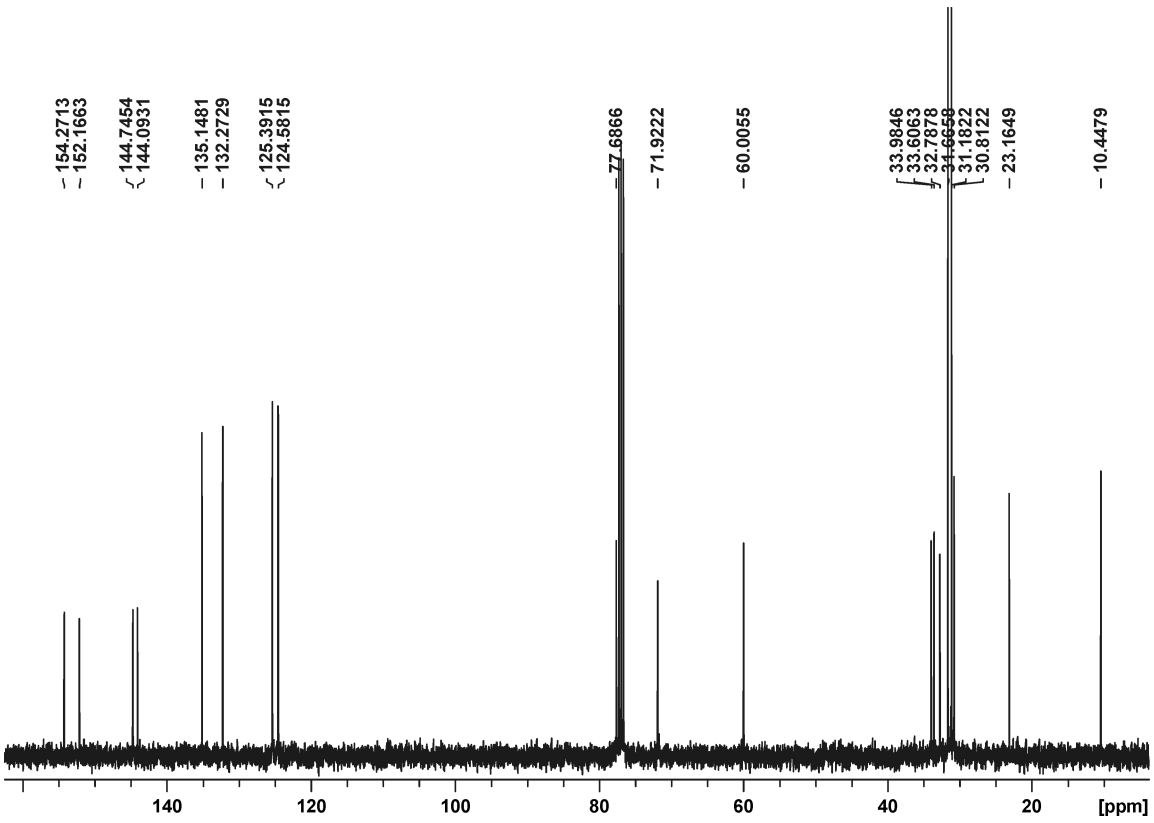


Figure S6. ^{13}C NMR spectrum of calixarene **9** (100 MHz, $CDCl_3$).

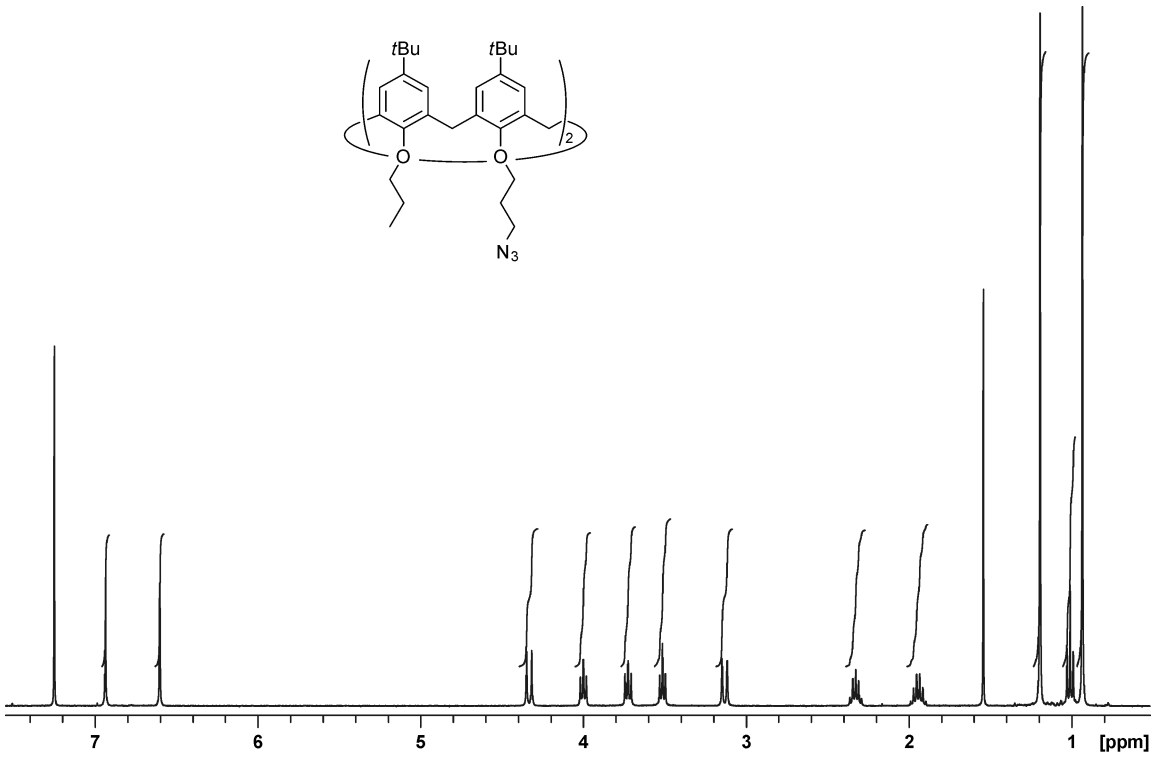


Figure S7. ^{1}H NMR spectrum of calixarene $\mathbf{3_3}$ (400 MHz, $CDCl_3$).

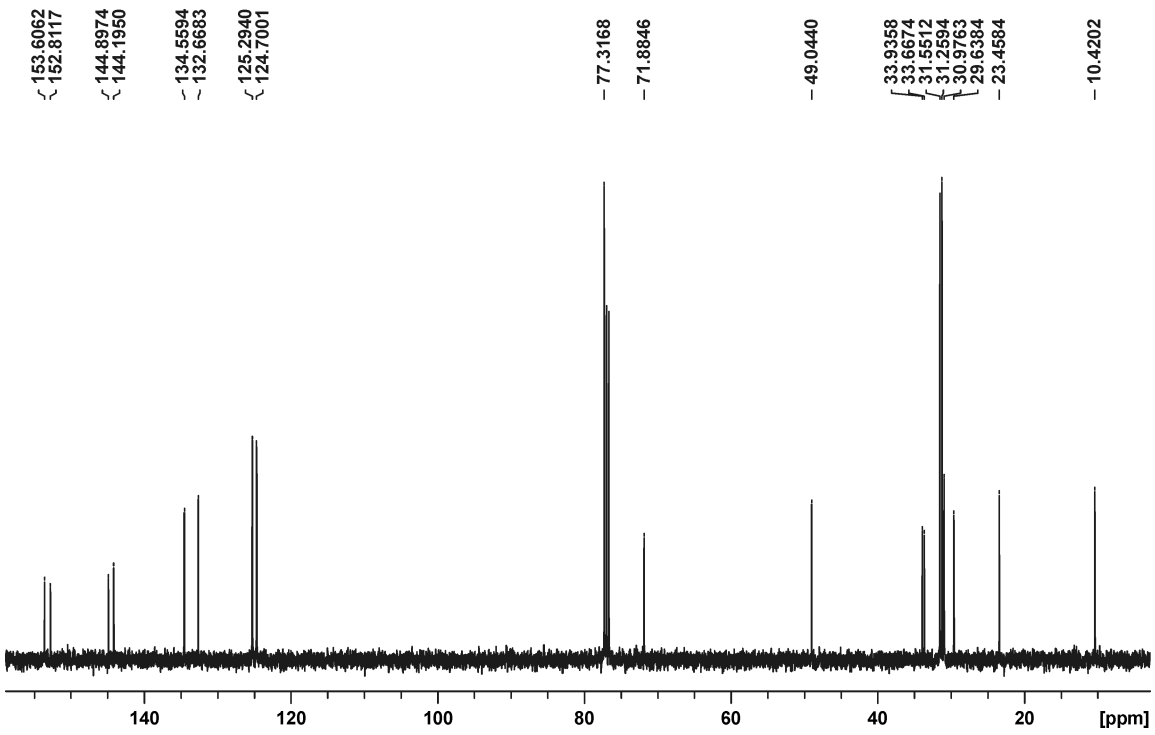


Figure S8. ^{13}C NMR spectrum of calixarene $\mathbf{3_3}$ (100 MHz, $CDCl_3$).

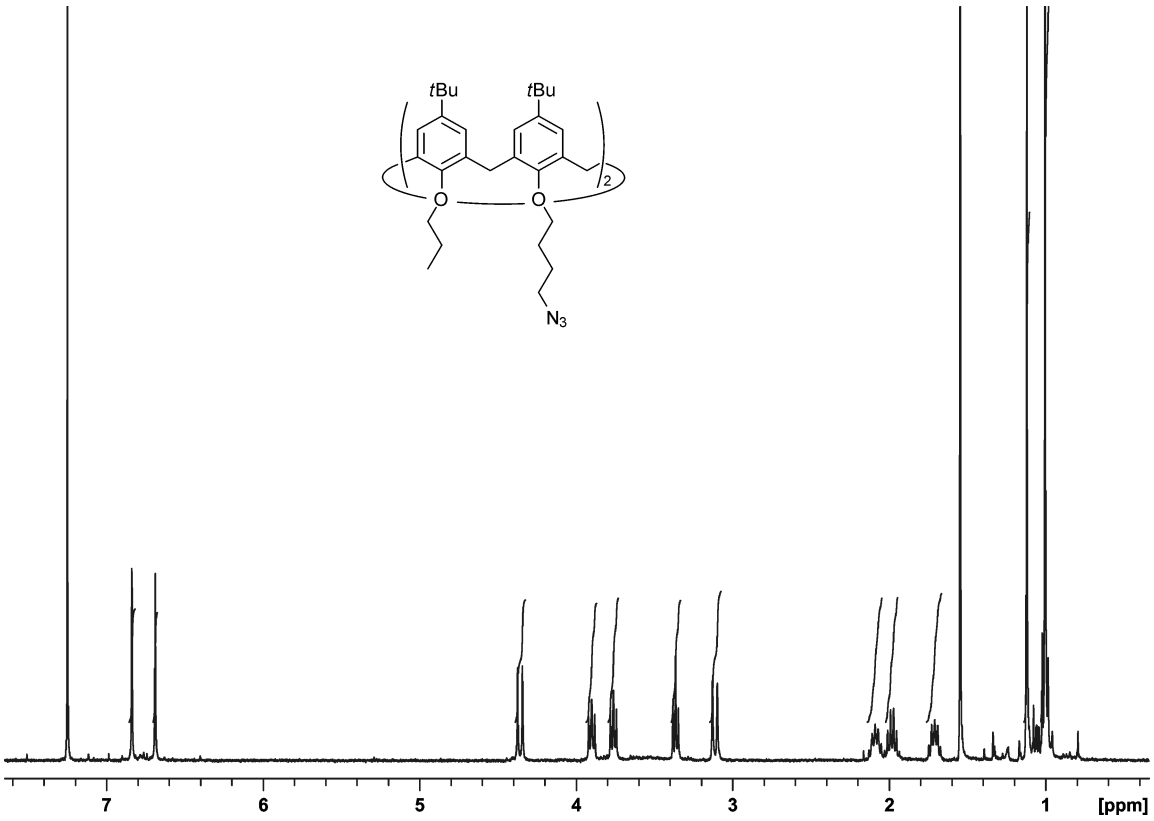


Figure S9. ^{1}H NMR spectrum of calixarene $\mathbf{3_4}$ (400 MHz, $CDCl_3$).

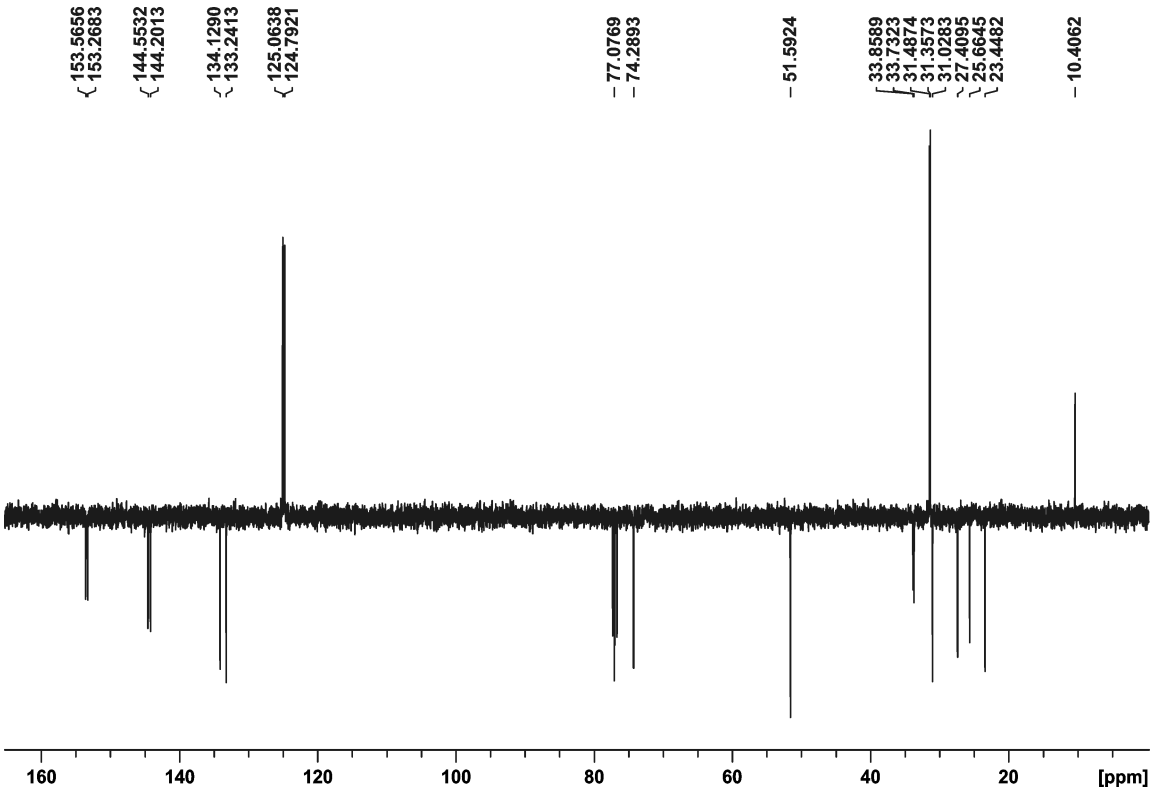


Figure S10. ^{13}C NMR spectrum (APT) of calixarene $\mathbf{3_4}$ (100 MHz, $CDCl_3$).

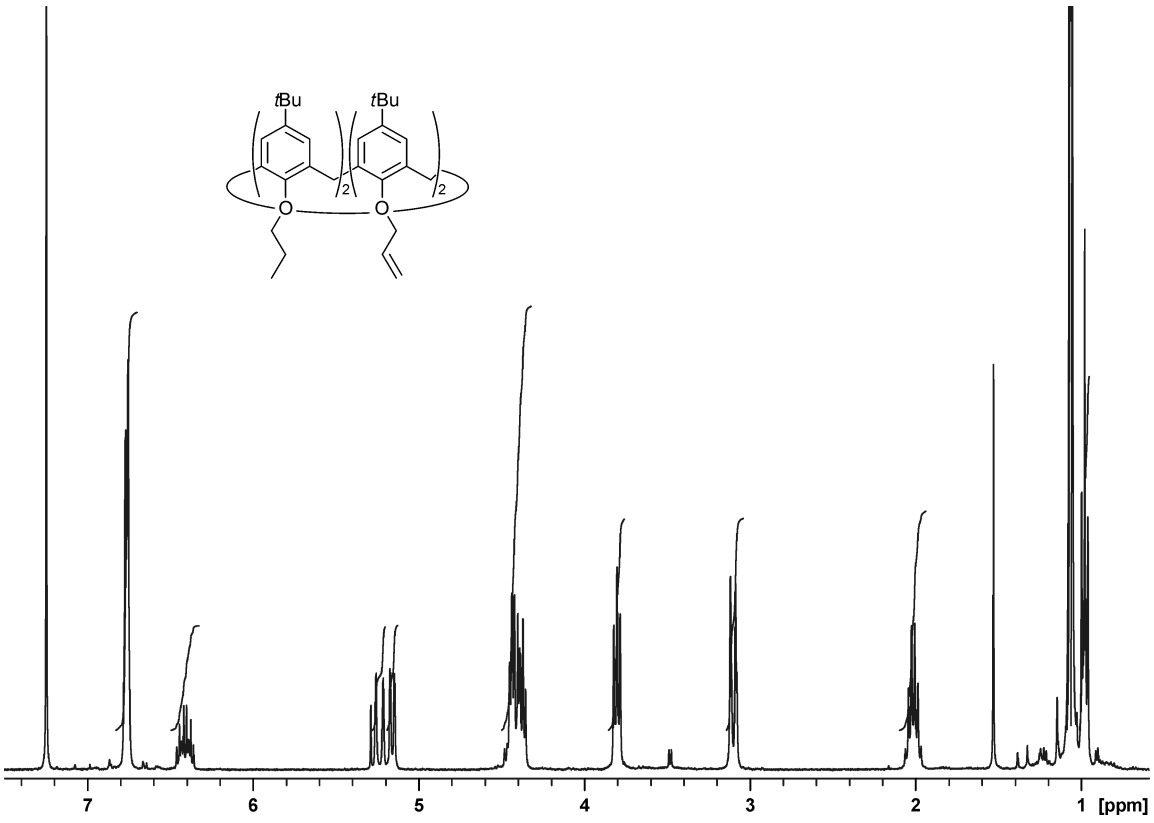


Figure S11. ^{1}H NMR spectrum of calixarene **12** (400 MHz, $CDCl_3$).

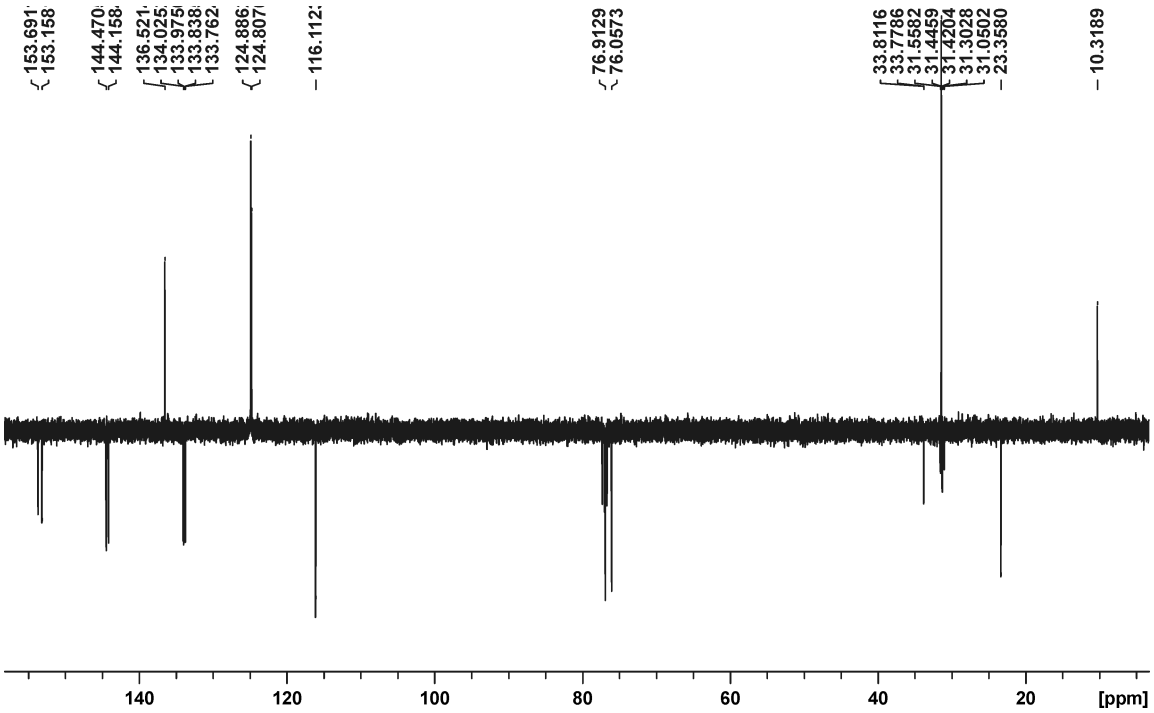


Figure S12. ^{13}C NMR spectrum (APT) of calixarene **12** (100 MHz, $CDCl_3$).

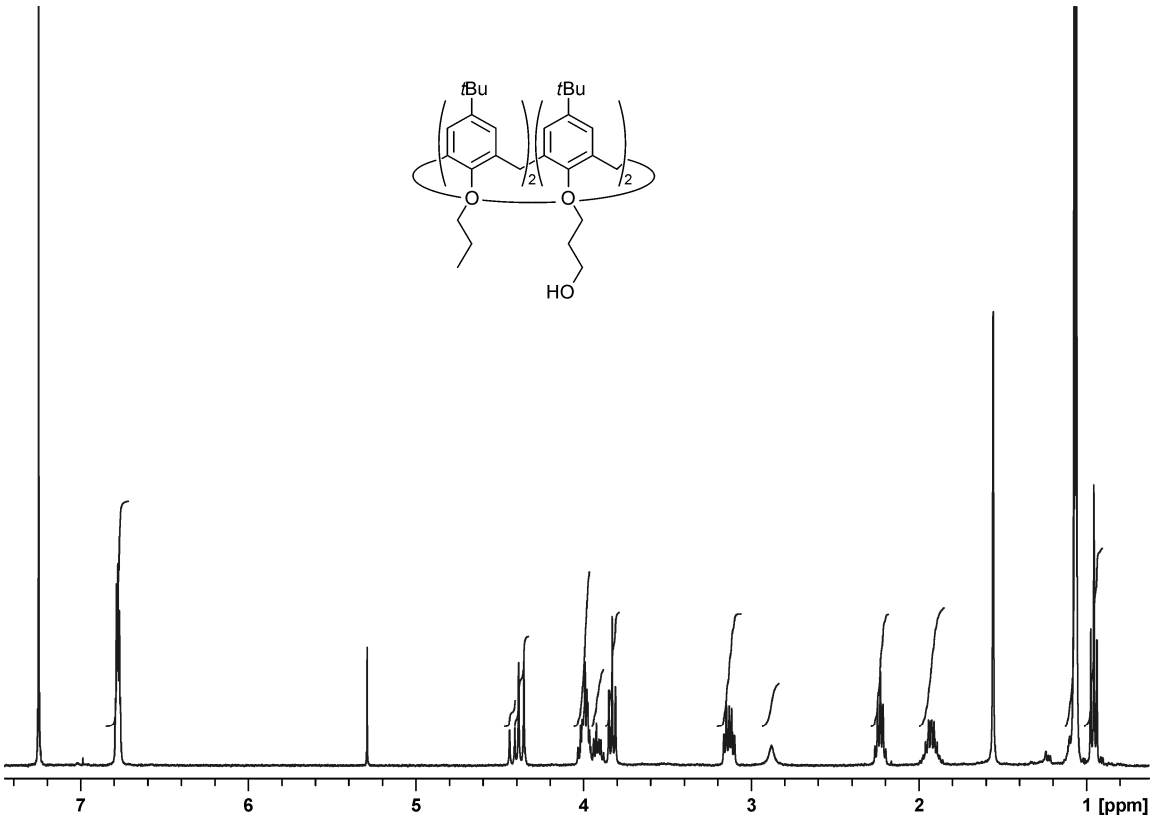


Figure S13. ^{1}H NMR spectrum of calixarene **13** (400 MHz, $CDCl_3$).

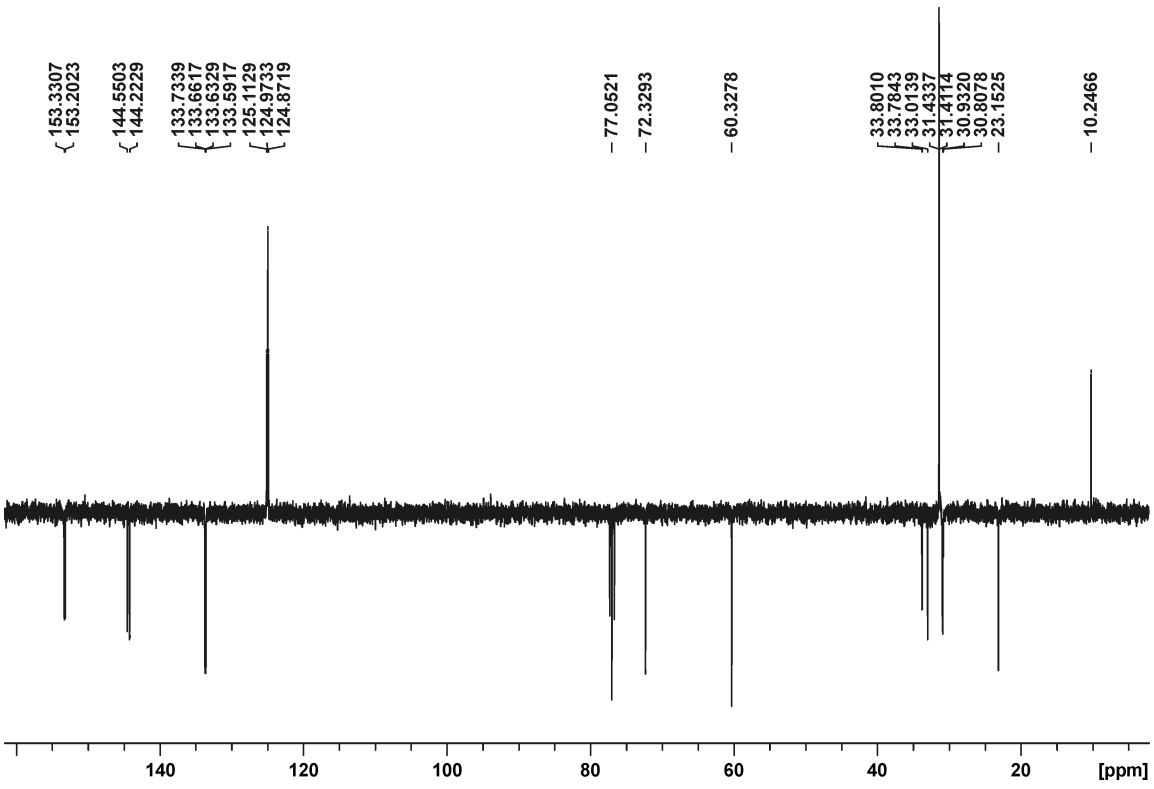


Figure S14. ^{13}C NMR spectrum (APT) of calixarene **13** (100 MHz, $CDCl_3$).

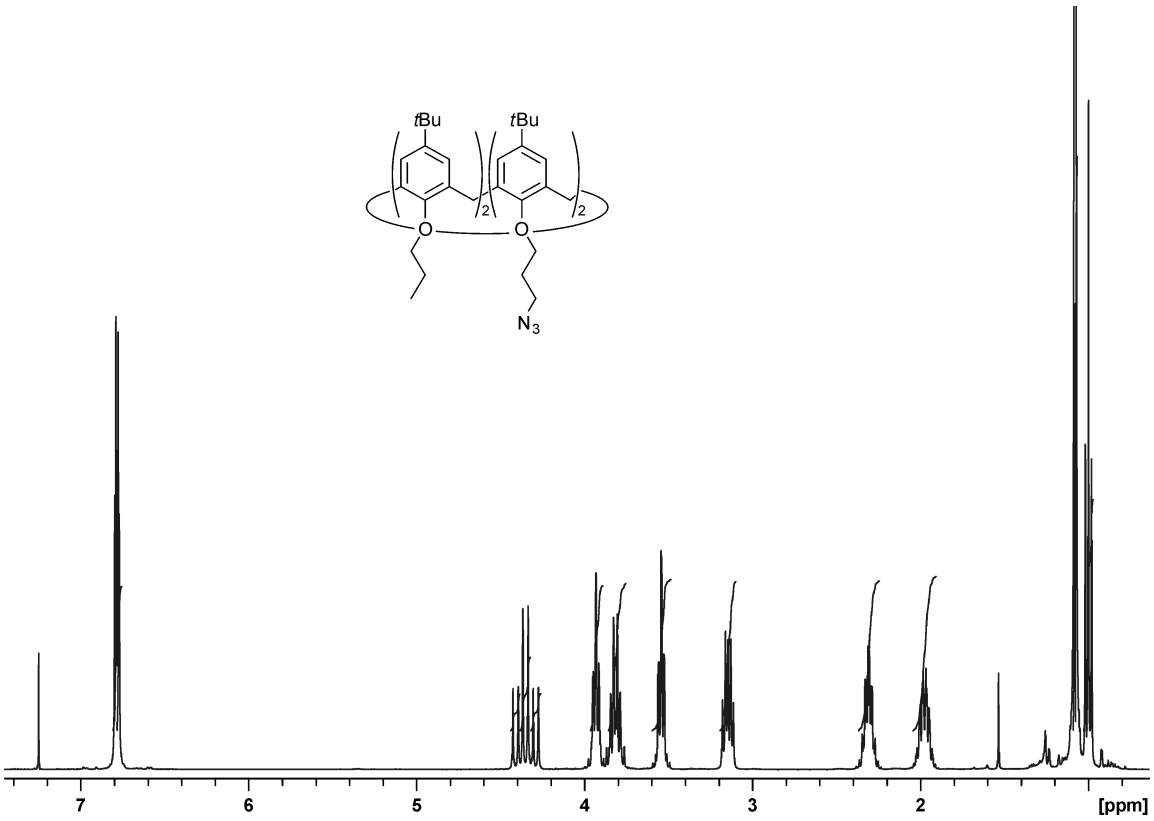


Figure S15. ^{1}H NMR spectrum of calixarene **4$_3$** (400 MHz, $CDCl_3$).

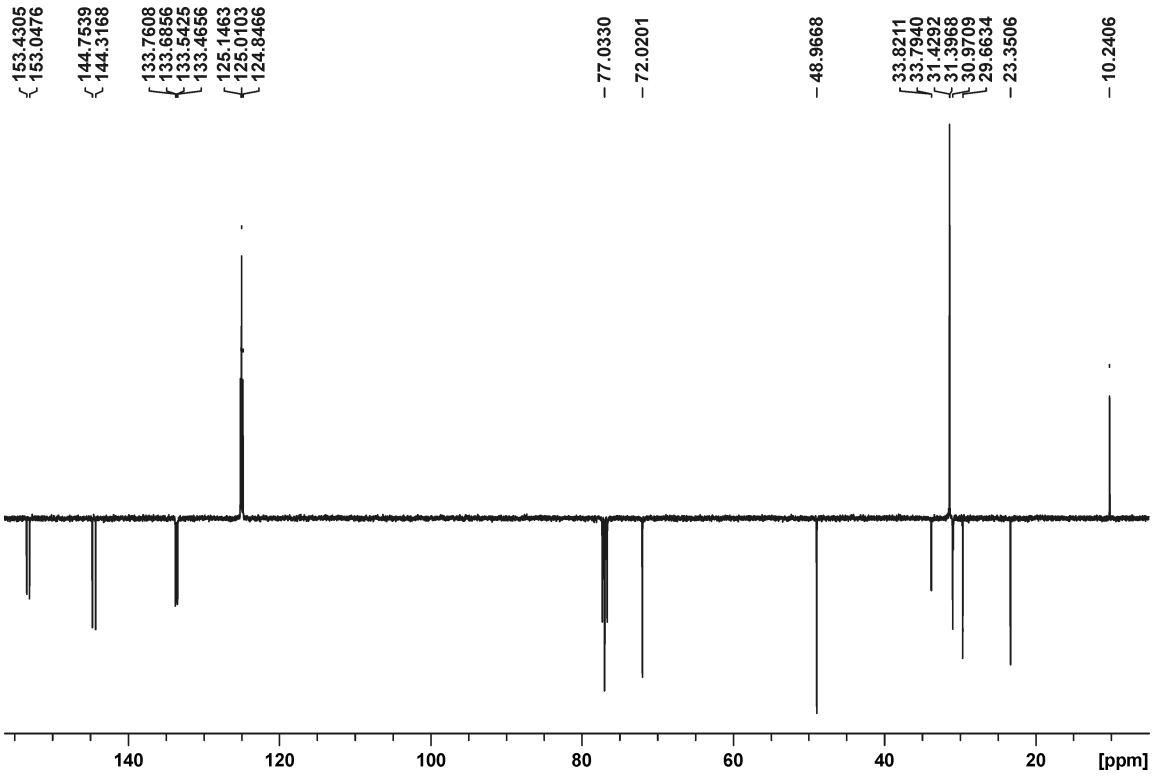


Figure S16. ^{13}C NMR spectrum (APT) of calixarene **4$_3$** (100 MHz, $CDCl_3$).

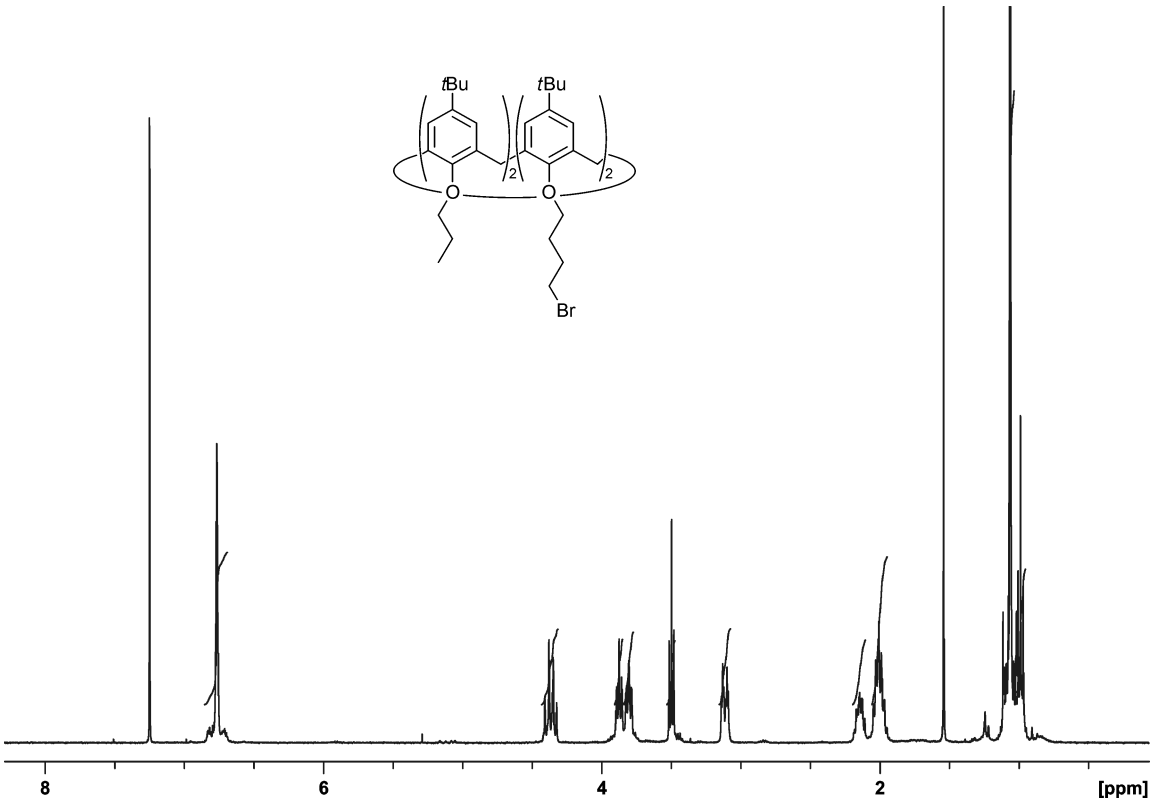


Figure S17. ^{1}H NMR spectrum of calixarene **14** (400 MHz, $CDCl_3$).

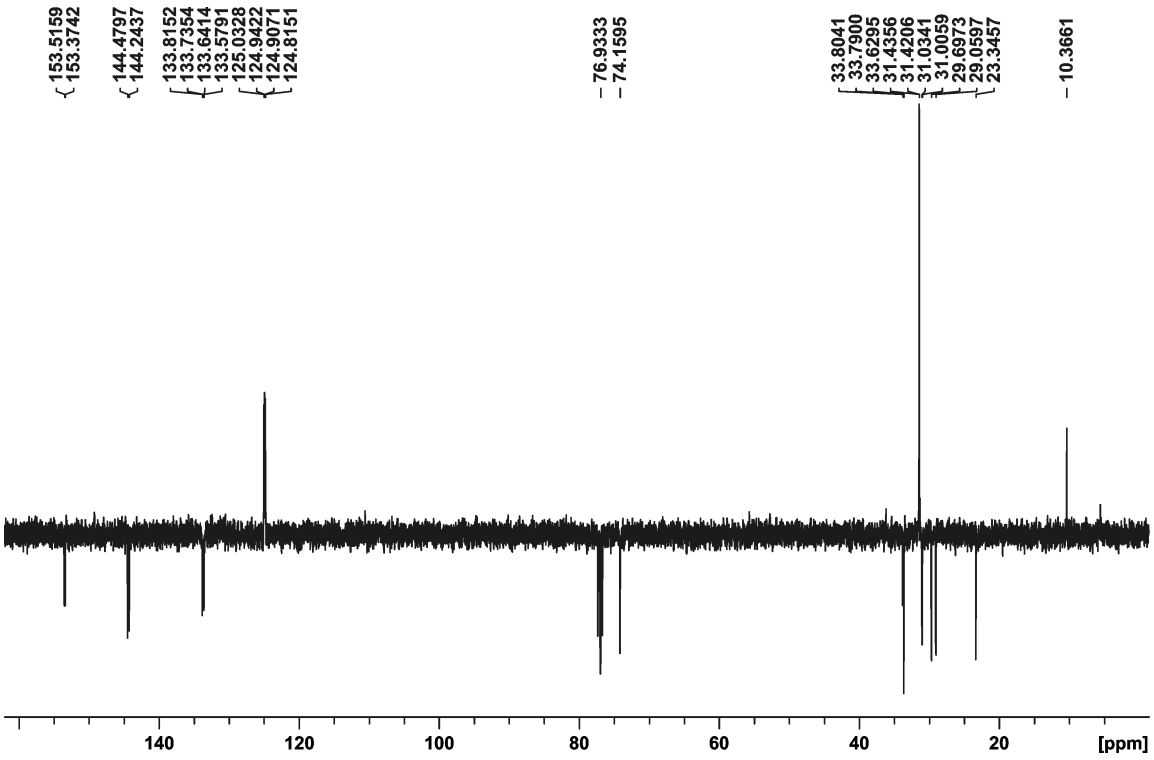


Figure S18. ^{13}C NMR spectrum (APT) of calixarene **14** (100 MHz, $CDCl_3$).

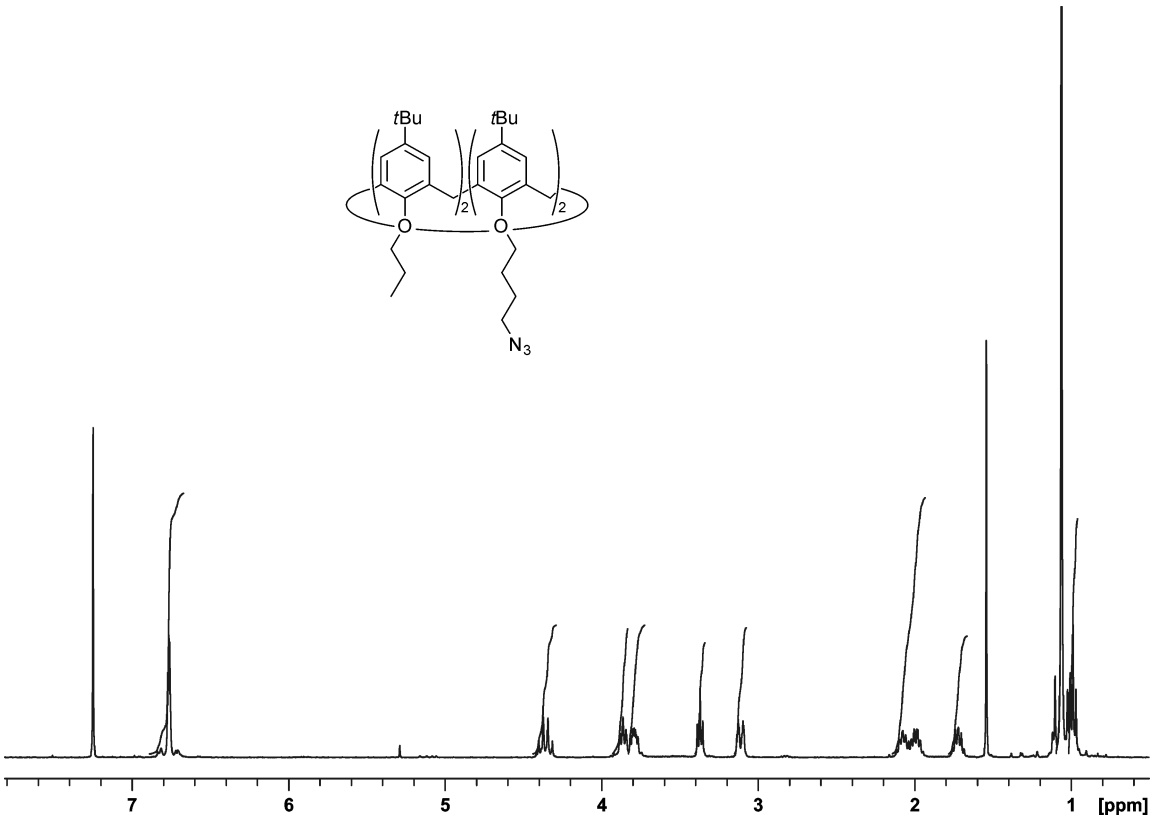


Figure S19. ^{1}H NMR spectrum of calixarene $\mathbf{4_4}$ (400 MHz, $CDCl_3$).

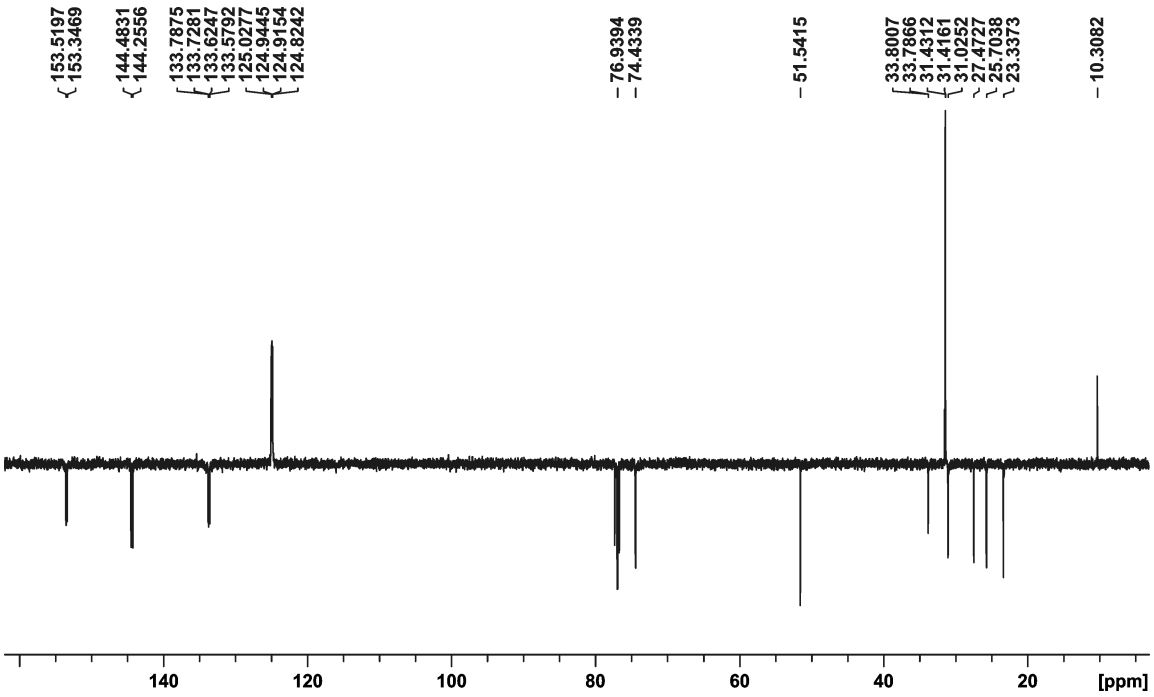


Figure S20. ^{13}C NMR spectrum (APT) of calixarene $\mathbf{4_4}$ (100 MHz, $CDCl_3$).

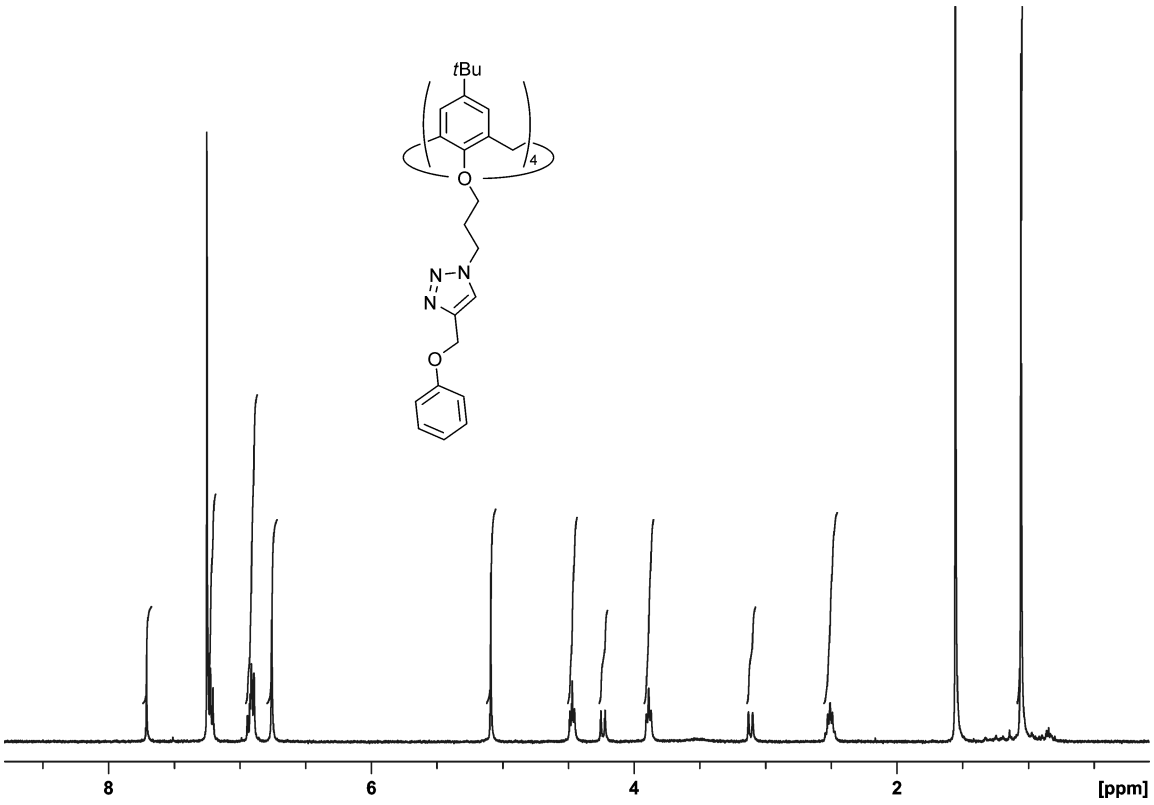


Figure S21. ^{1}H NMR spectrum of calixarene **15$_3$** (400 MHz, $CDCl_3$).

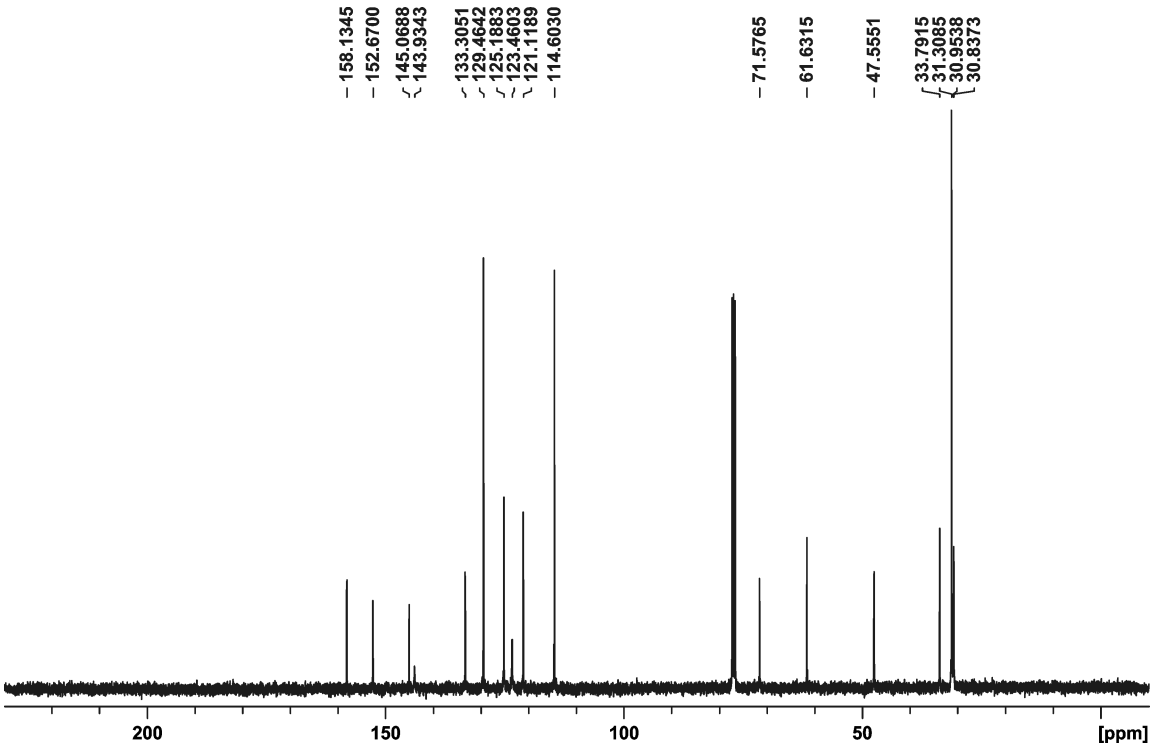


Figure S22. ^{13}C NMR spectrum of calixarene **15$_3$** (100 MHz, $CDCl_3$).

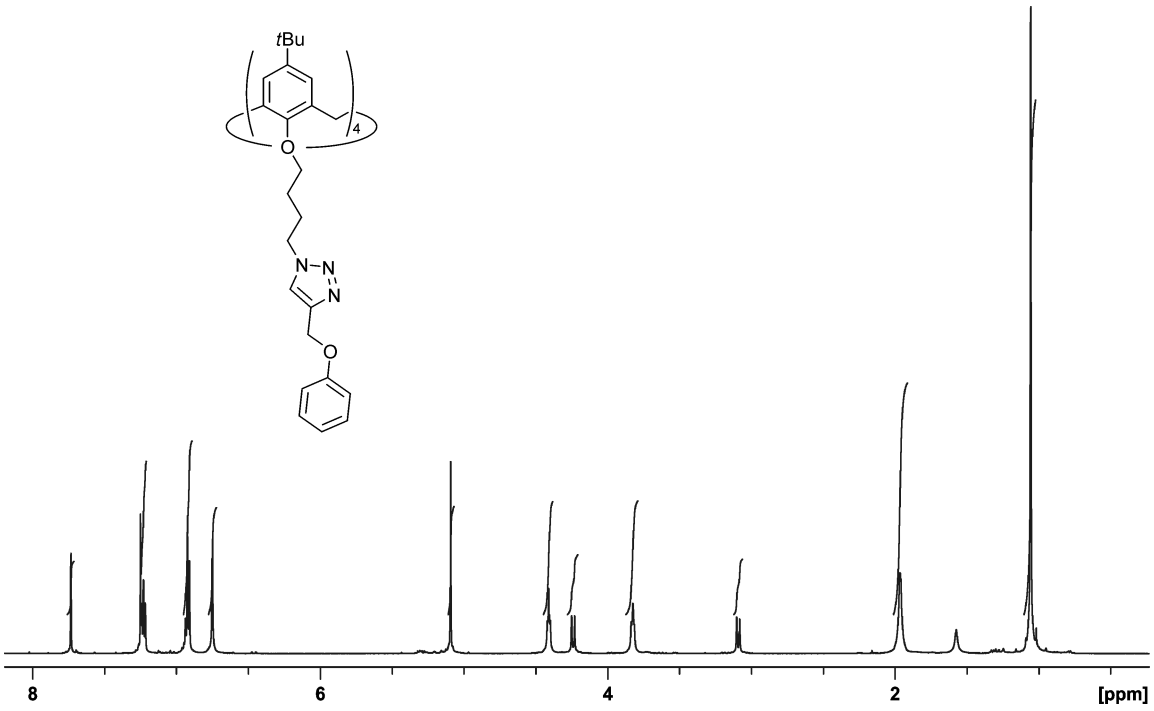


Figure S23. ^{1}H NMR spectrum of calixarene **15$_4$** (400 MHz, $CDCl_3$).

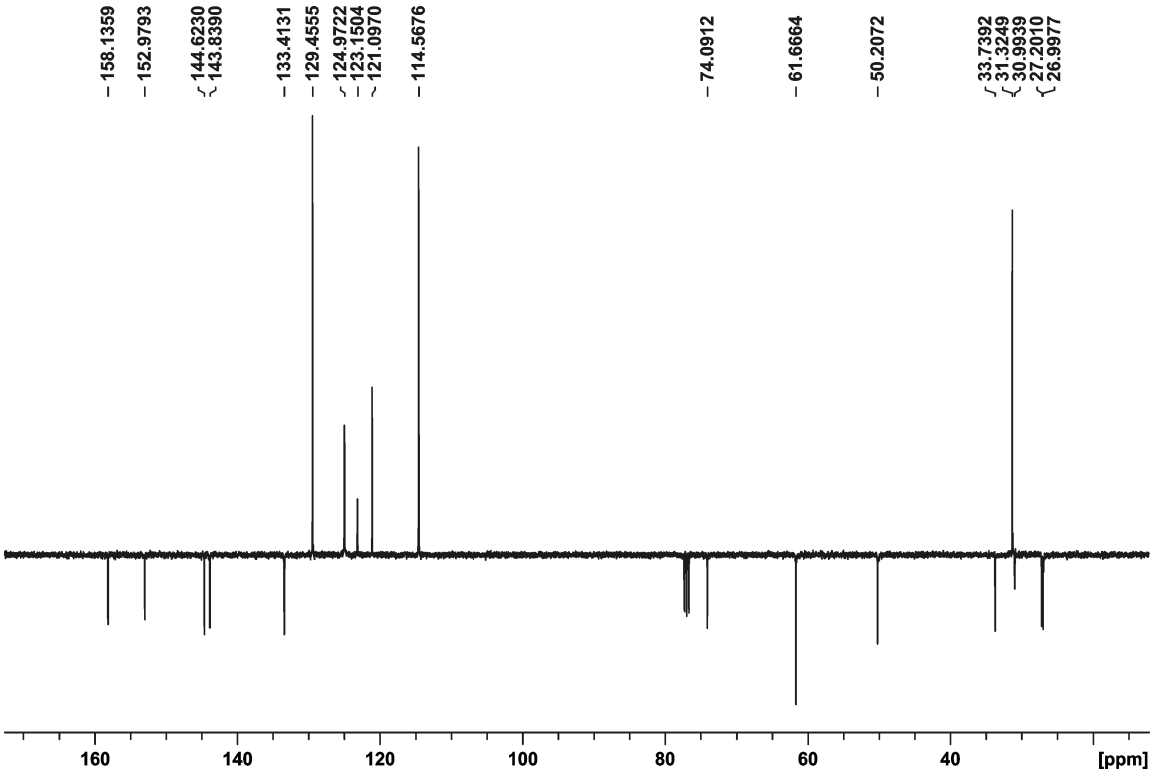


Figure S24. ^{13}C NMR spectrum (APT) of calixarene **15$_4$** (100 MHz, $CDCl_3$).

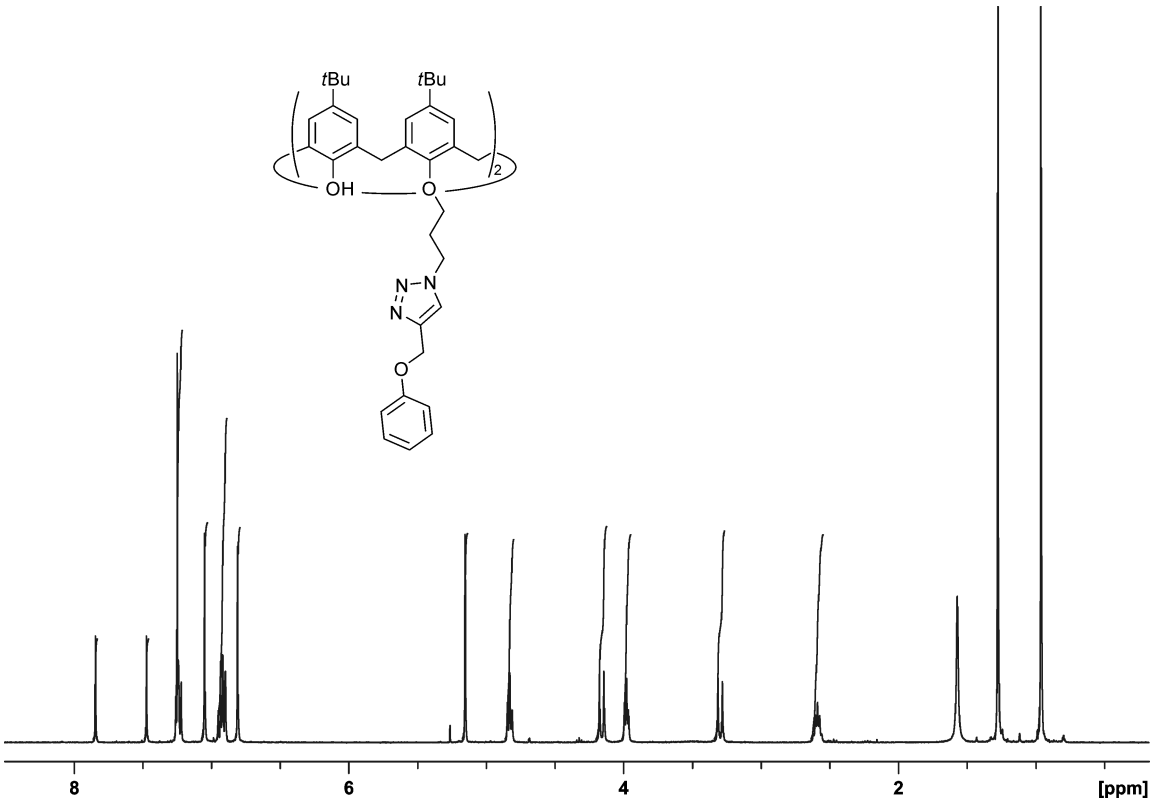


Figure S25. ^{1}H NMR spectrum of calixarene **16$_3$** (400 MHz, $CDCl_3$).

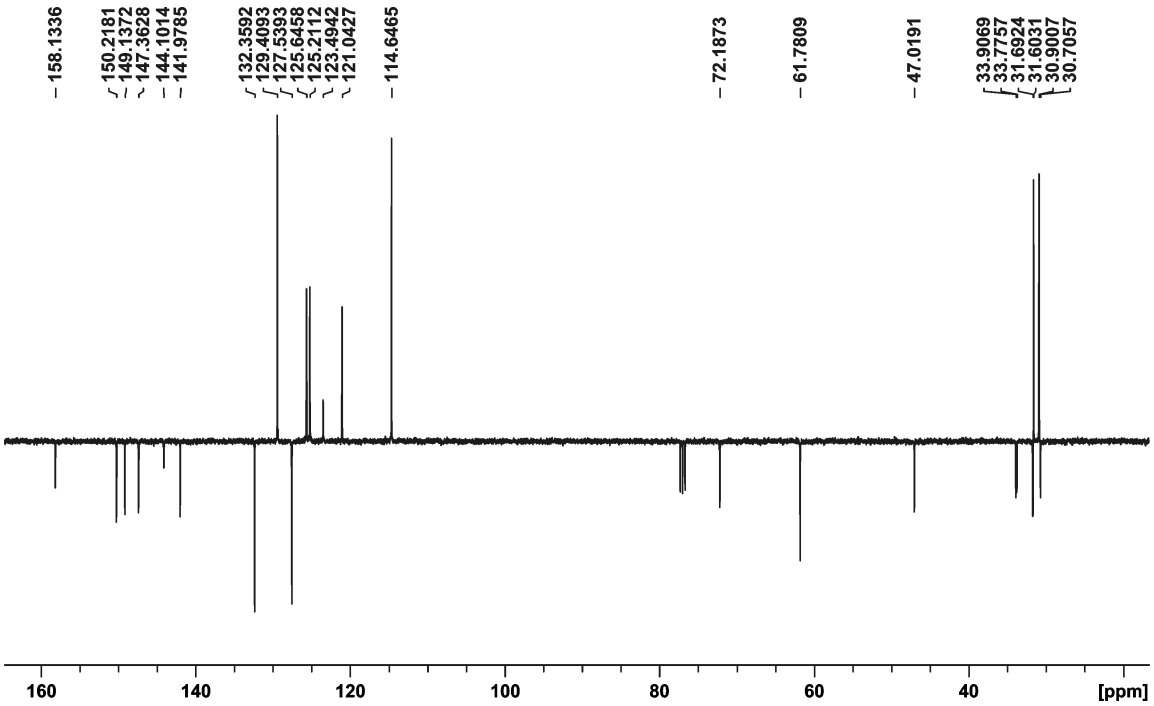


Figure S26. ^{13}C NMR spectrum (APT) of calixarene **16$_3$** (100 MHz, $CDCl_3$).

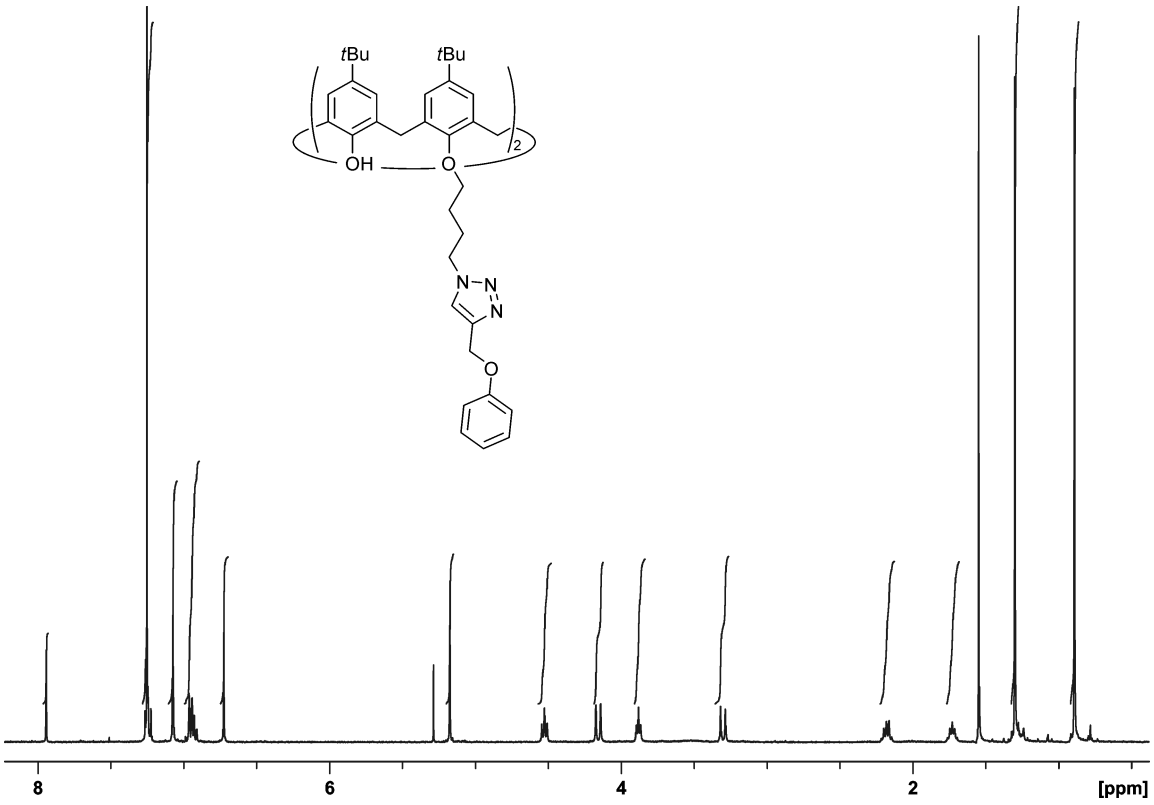


Figure S27. ^{1}H NMR spectrum of calixarene **16$_4$** (400 MHz, $CDCl_3$).

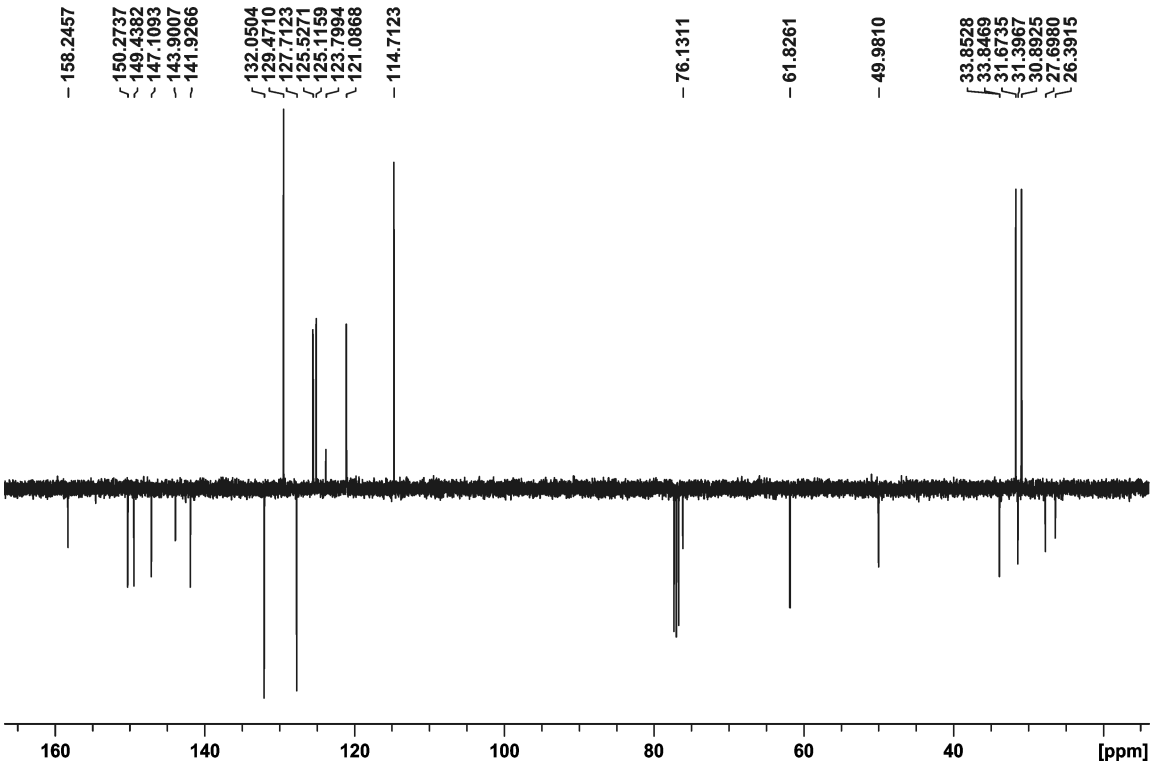


Figure S28. ^{13}C NMR spectrum (APT) of calixarene **16$_4$** (100 MHz, $CDCl_3$).

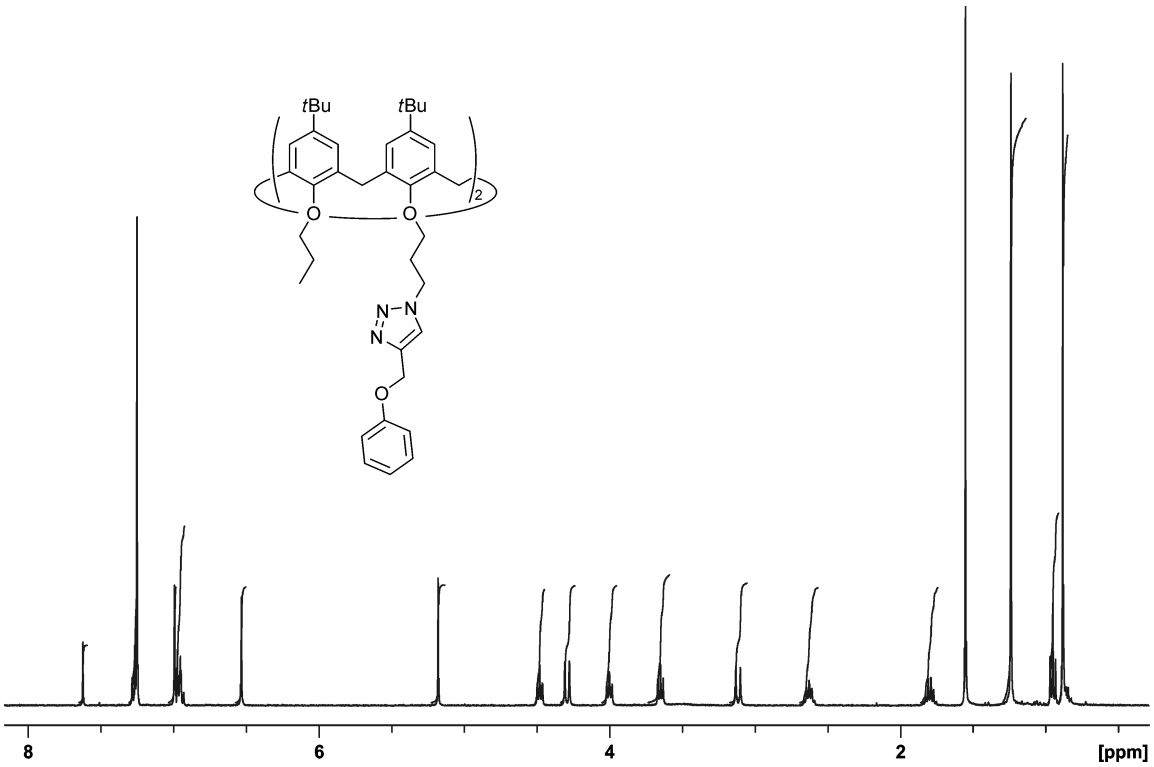


Figure S29. ^{1}H NMR spectrum of calixarene **17$_3$** (400 MHz, $CDCl_3$).

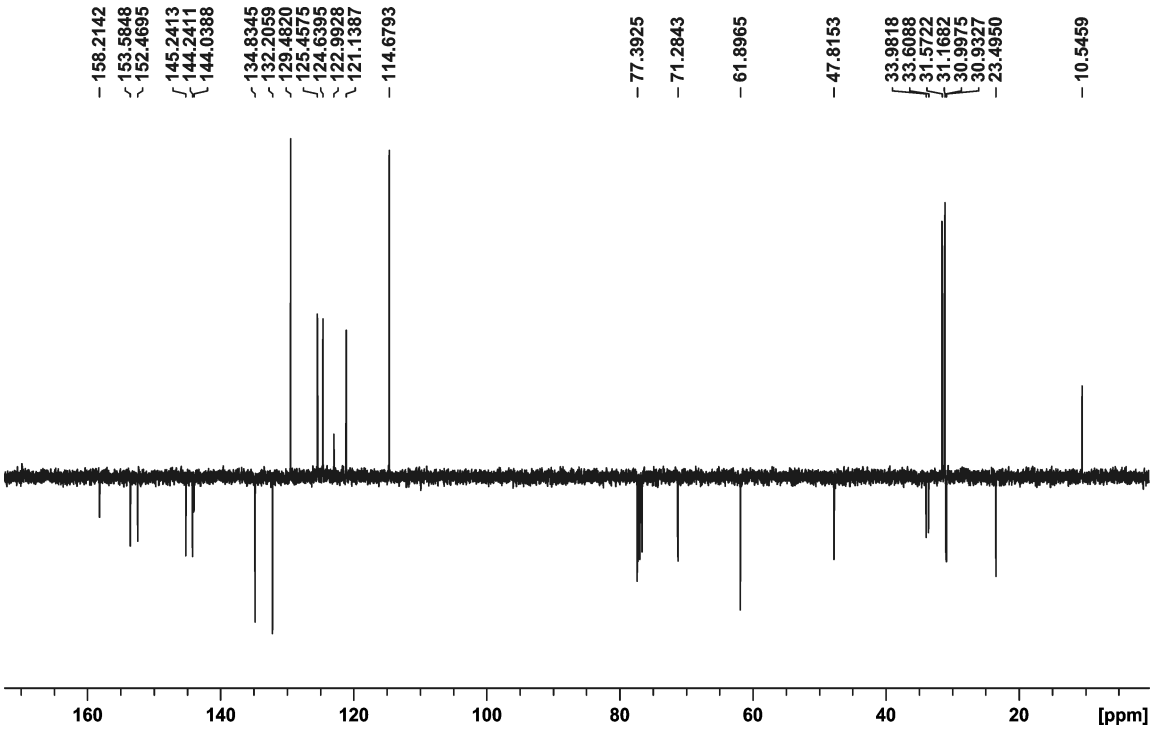


Figure S30. ^{13}C NMR spectrum (APT) of calixarene **17$_3$** (100 MHz, $CDCl_3$).

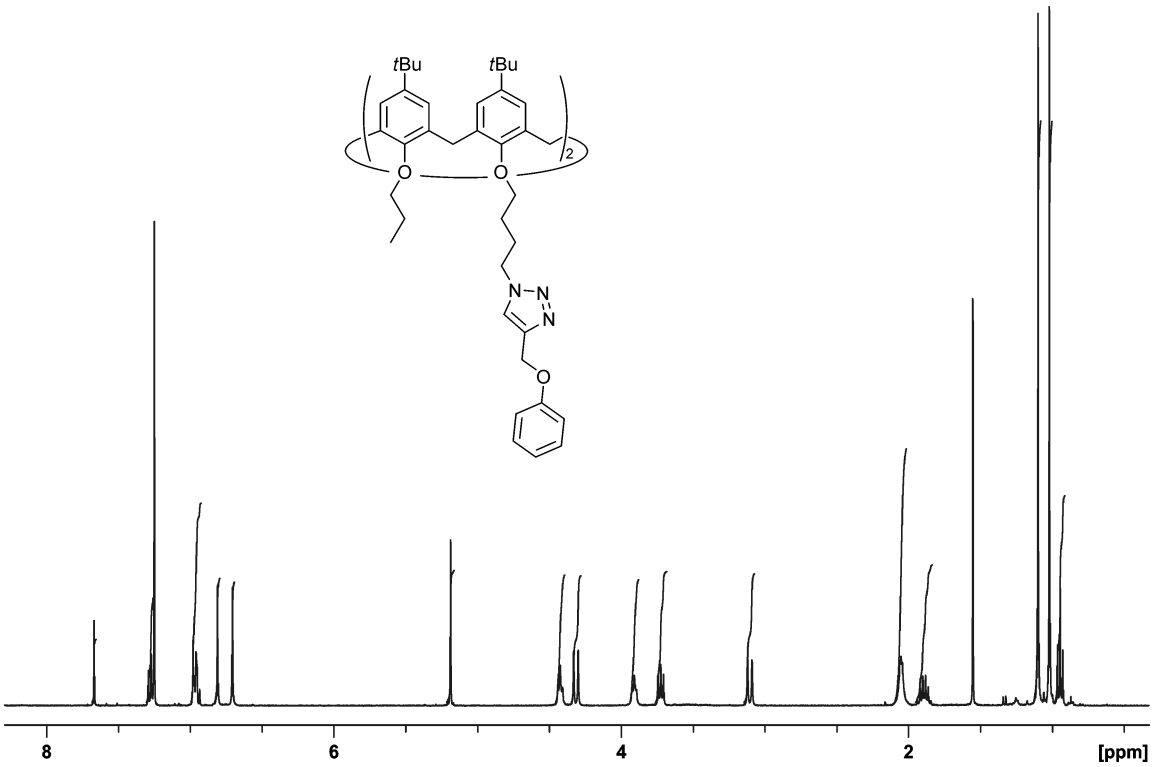


Figure S31. ^{1}H NMR spectrum of calixarene **17$_4$** (400 MHz, $CDCl_3$).

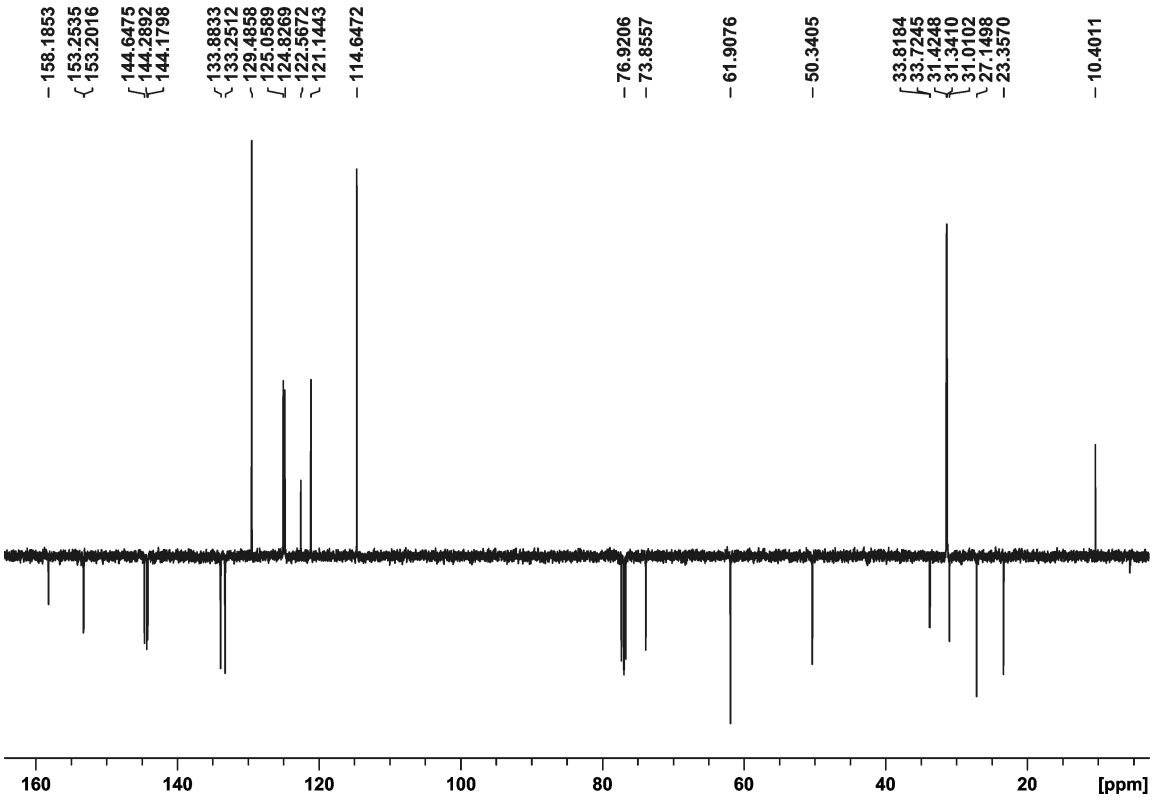


Figure S32. ^{13}C NMR spectrum (APT) of calixarene **17$_4$** (100 MHz, $CDCl_3$).

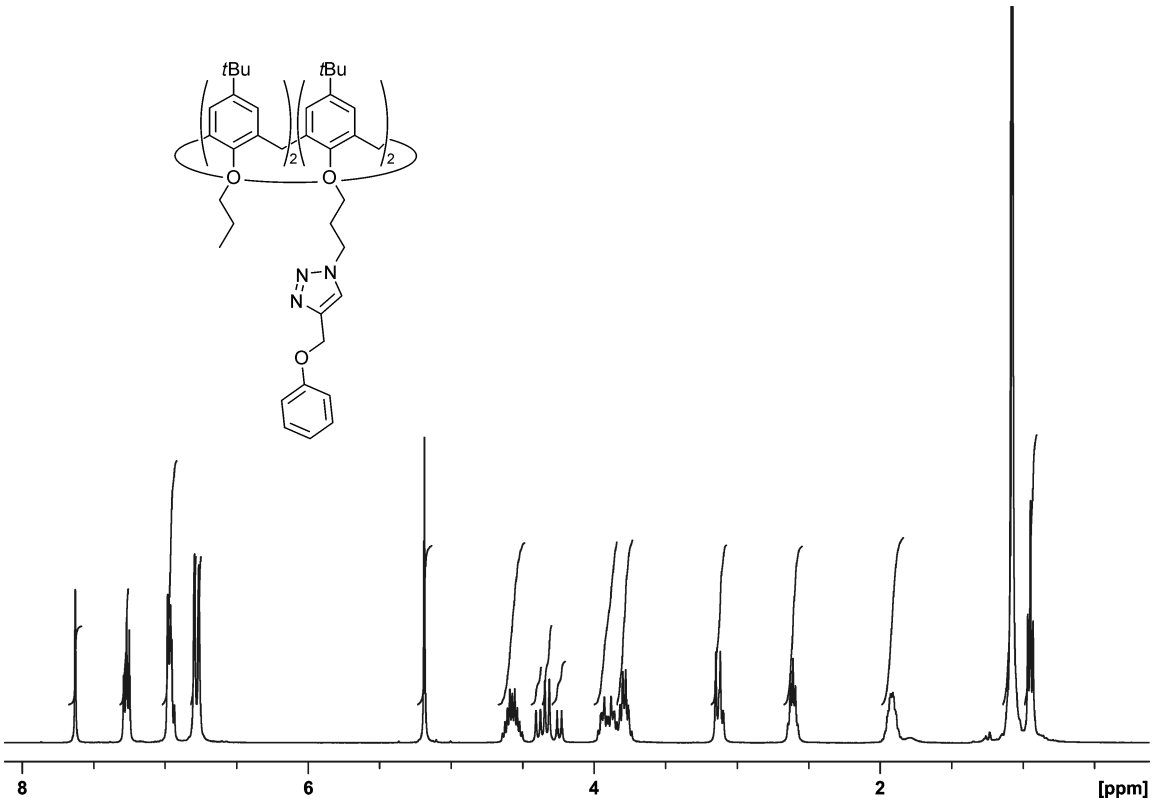


Figure S33. ^{1}H NMR spectrum of calixarene **18$_3$** (400 MHz, $CDCl_3$).

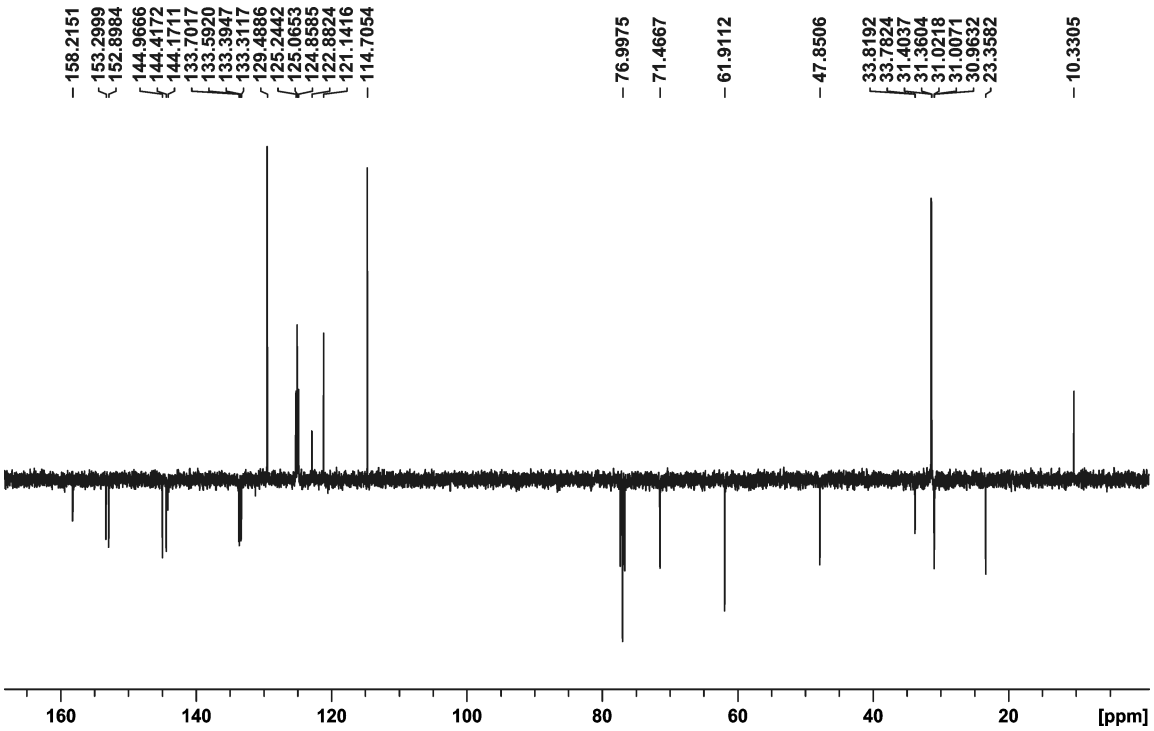


Figure S34. ^{13}C NMR spectrum (APT) of calixarene **18$_3$** (100 MHz, $CDCl_3$).

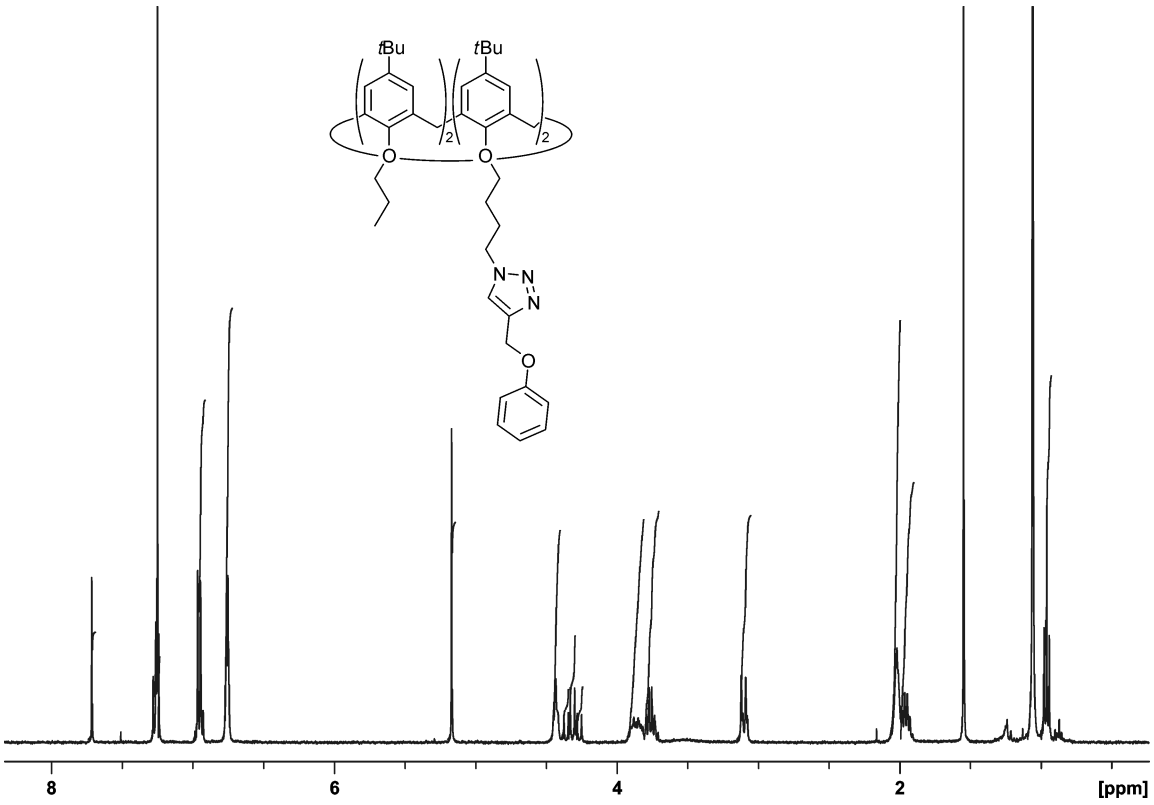


Figure S35. ^{1}H NMR spectrum of calixarene **18$_4$** (400 MHz, $CDCl_3$).

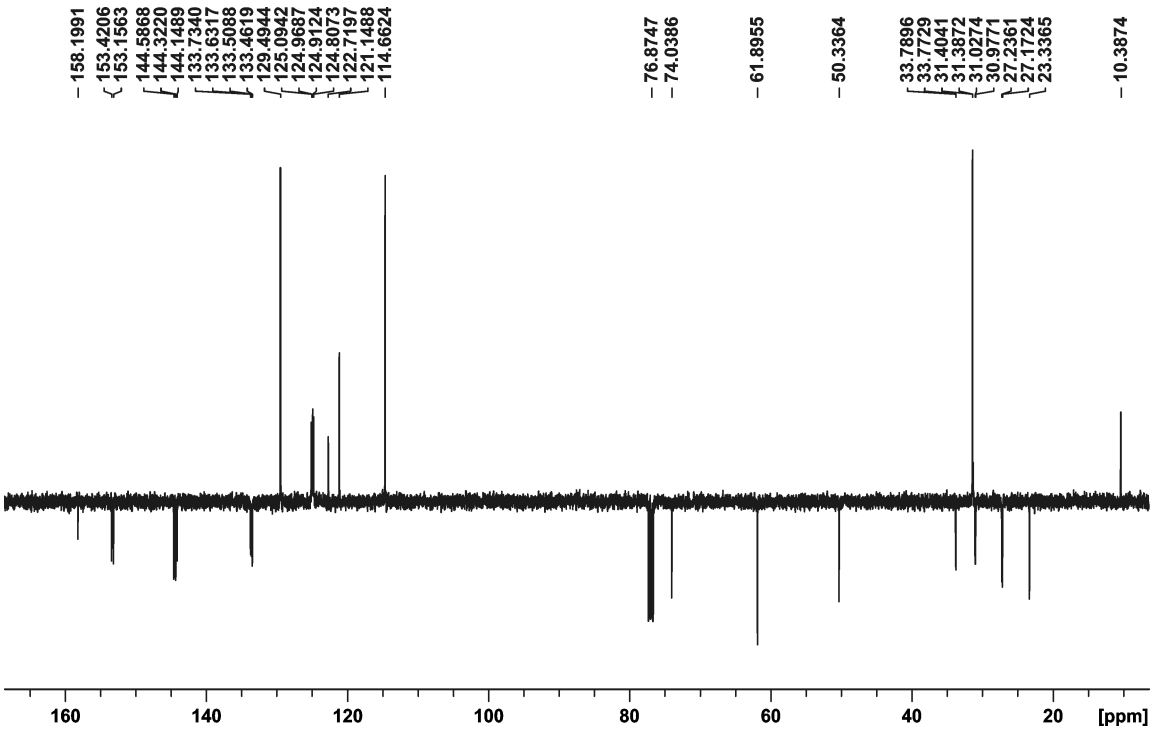


Figure S36. ^{13}C NMR spectrum (APT) of calixarene **18$_4$** (100 MHz, $CDCl_3$).

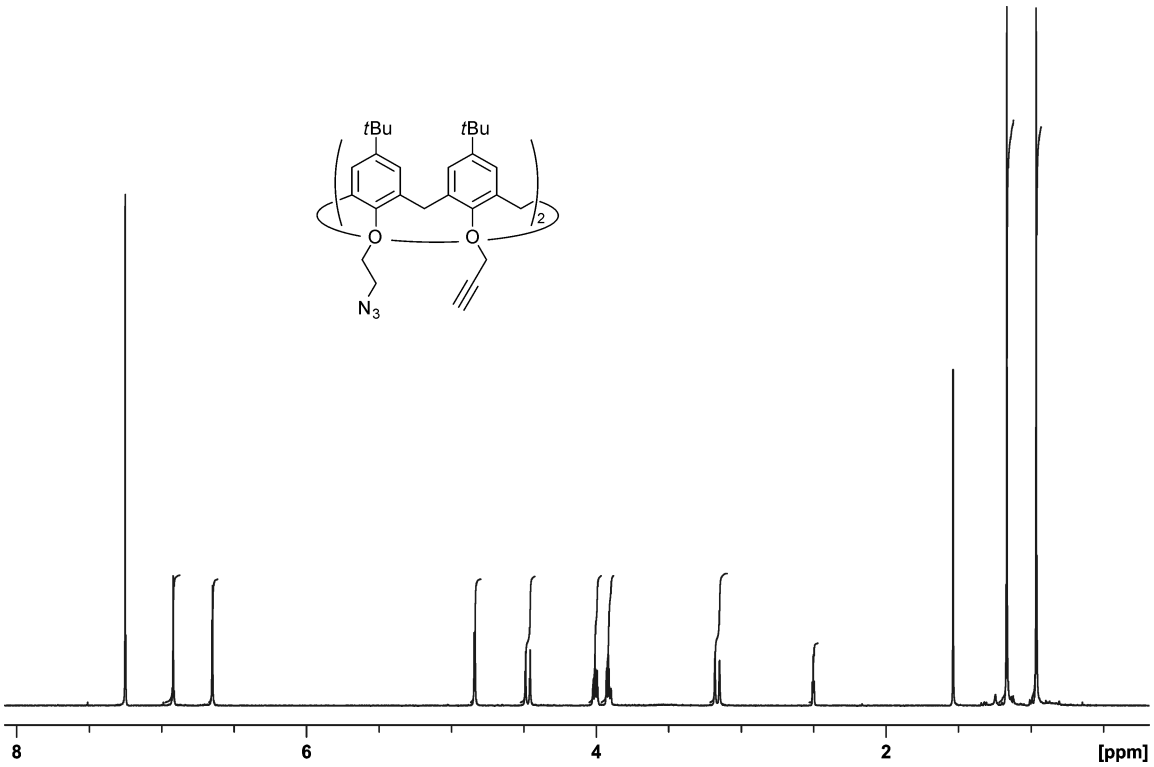


Figure S37. ^{1}H NMR spectrum of calixarene **19$_2$** (400 MHz, $CDCl_3$).

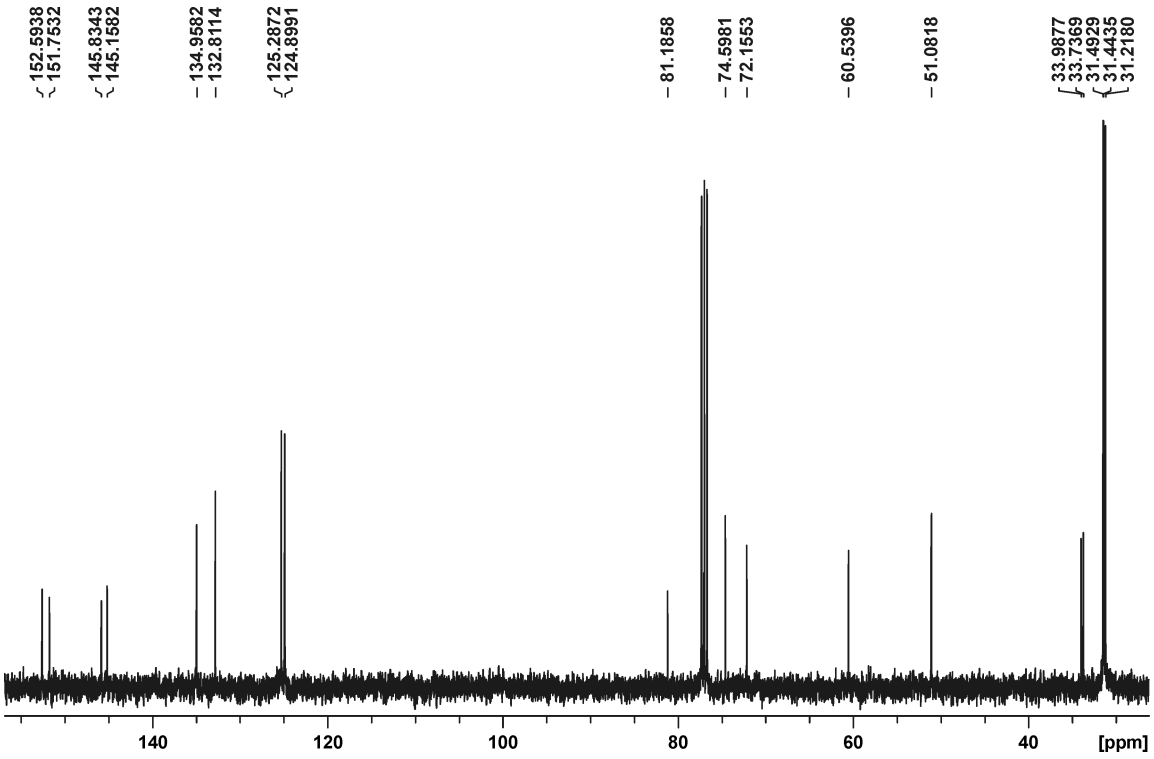


Figure S38. ^{13}C NMR spectrum of calixarene **19$_2$** (100 MHz, $CDCl_3$).

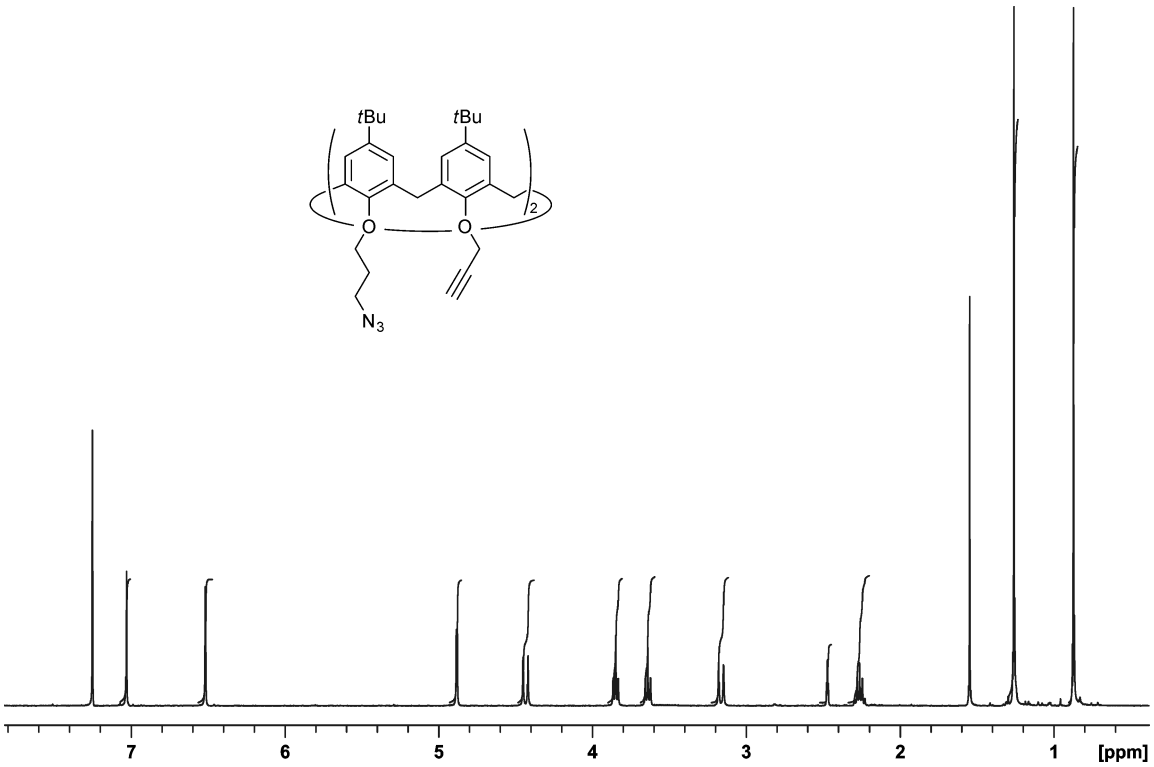


Figure S39. ^{1}H NMR spectrum of calixarene **19$_3$** (400 MHz, $CDCl_3$).

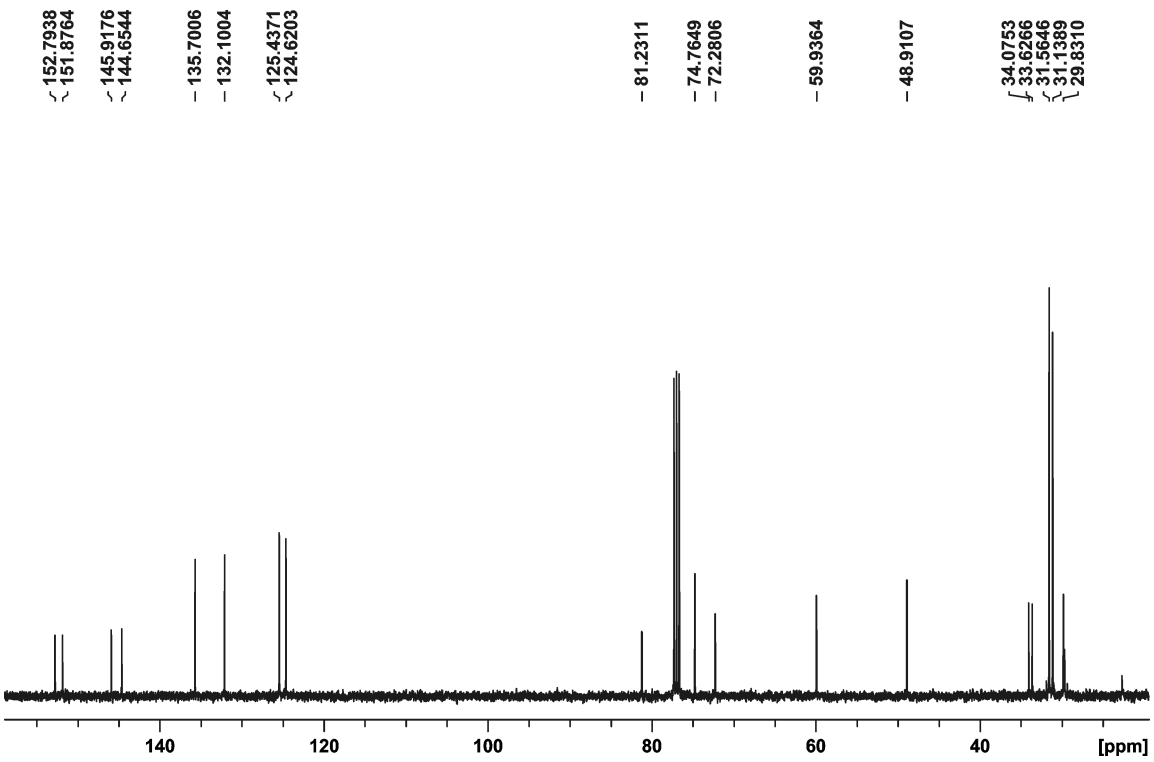


Figure S40. ^{13}C NMR spectrum of calixarene **19$_3$** (100 MHz, $CDCl_3$).

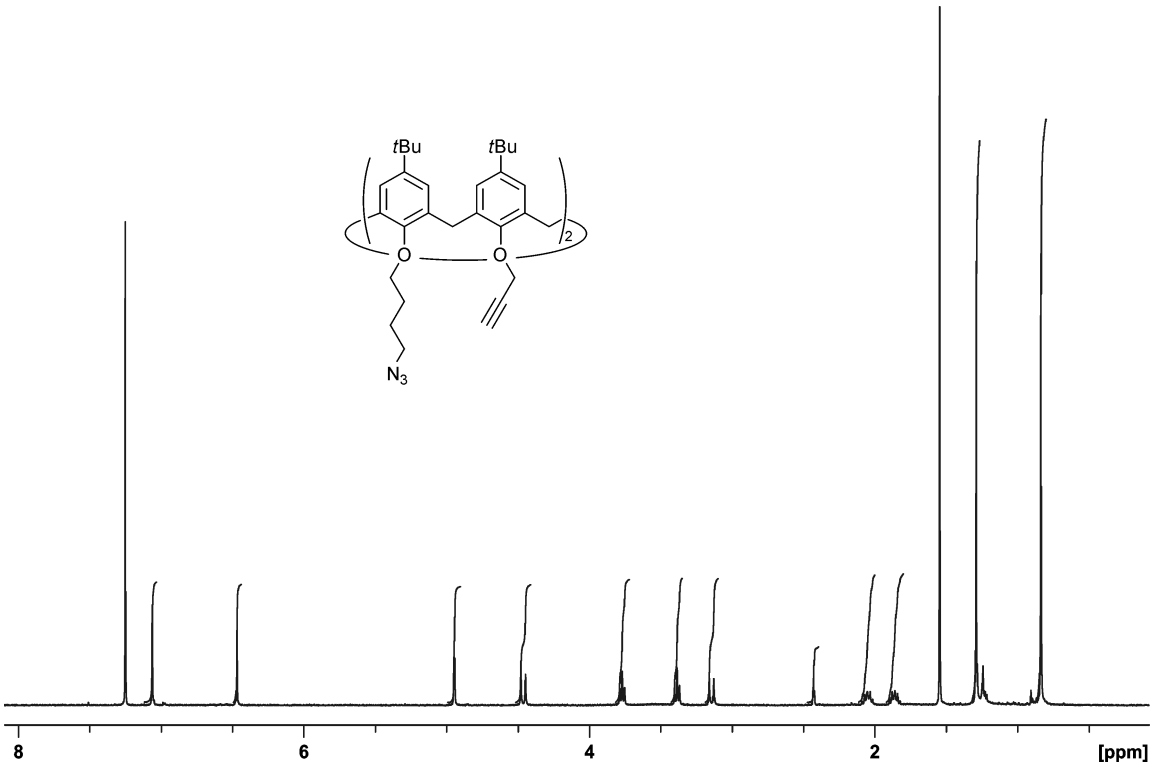


Figure S41. ^{1}H NMR spectrum of calixarene **19$_4$** (400 MHz, $CDCl_3$).

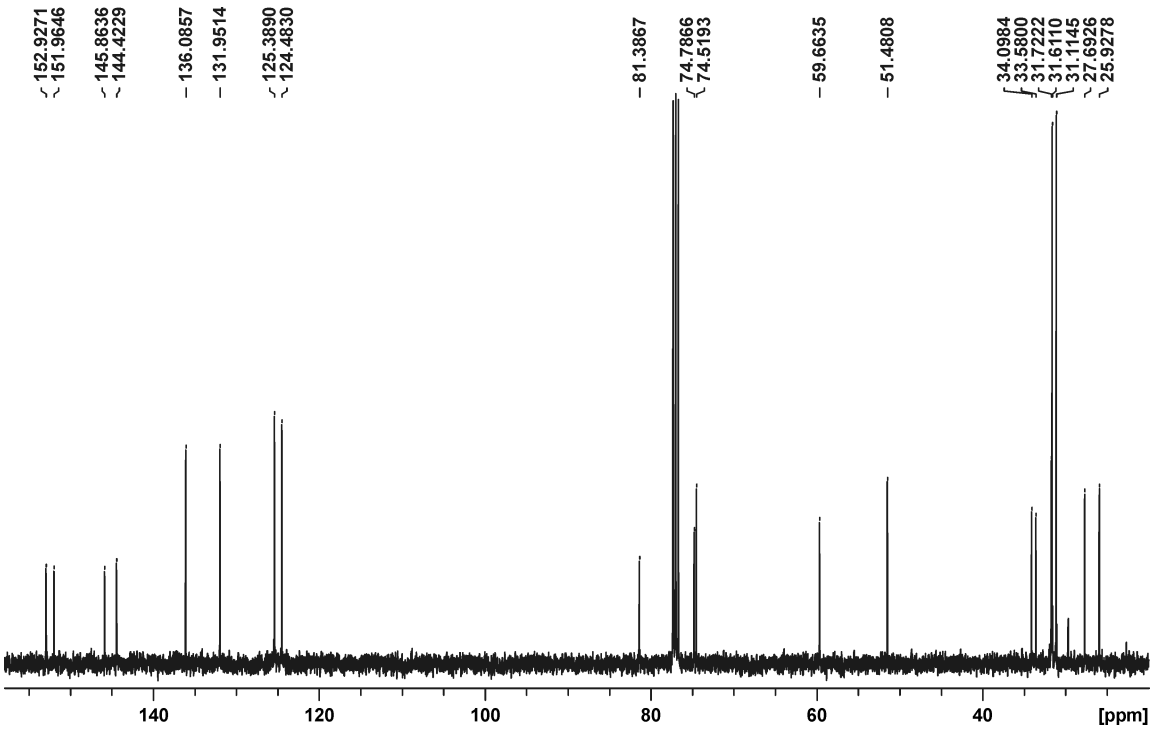


Figure S42. ^{13}C NMR spectrum of calixarene **19$_4$** (100 MHz, $CDCl_3$).

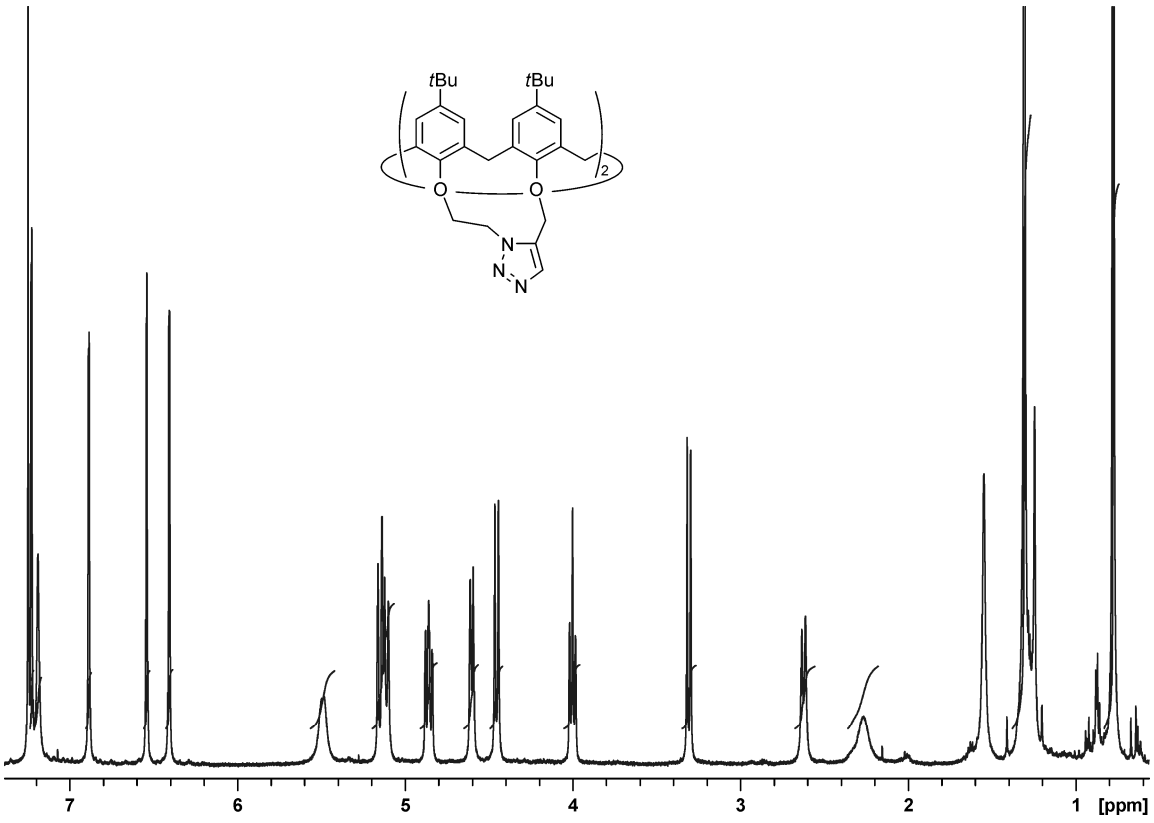


Figure S43. ^{1}H NMR spectrum of calixarene **20$_2$** (600 MHz, $CDCl_3$, 30 °C).

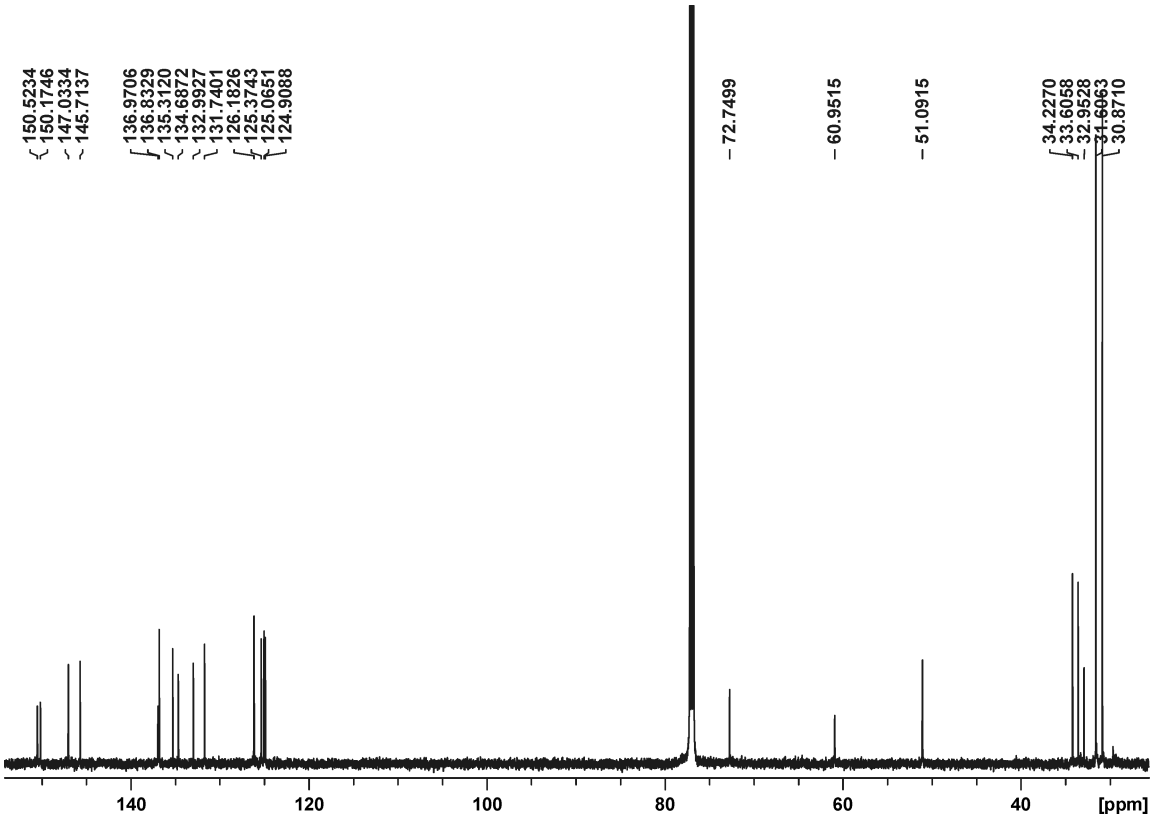


Figure S44. ^{13}C NMR spectrum of calixarene **20$_2$** (150 MHz, $CDCl_3$, 30 °C).

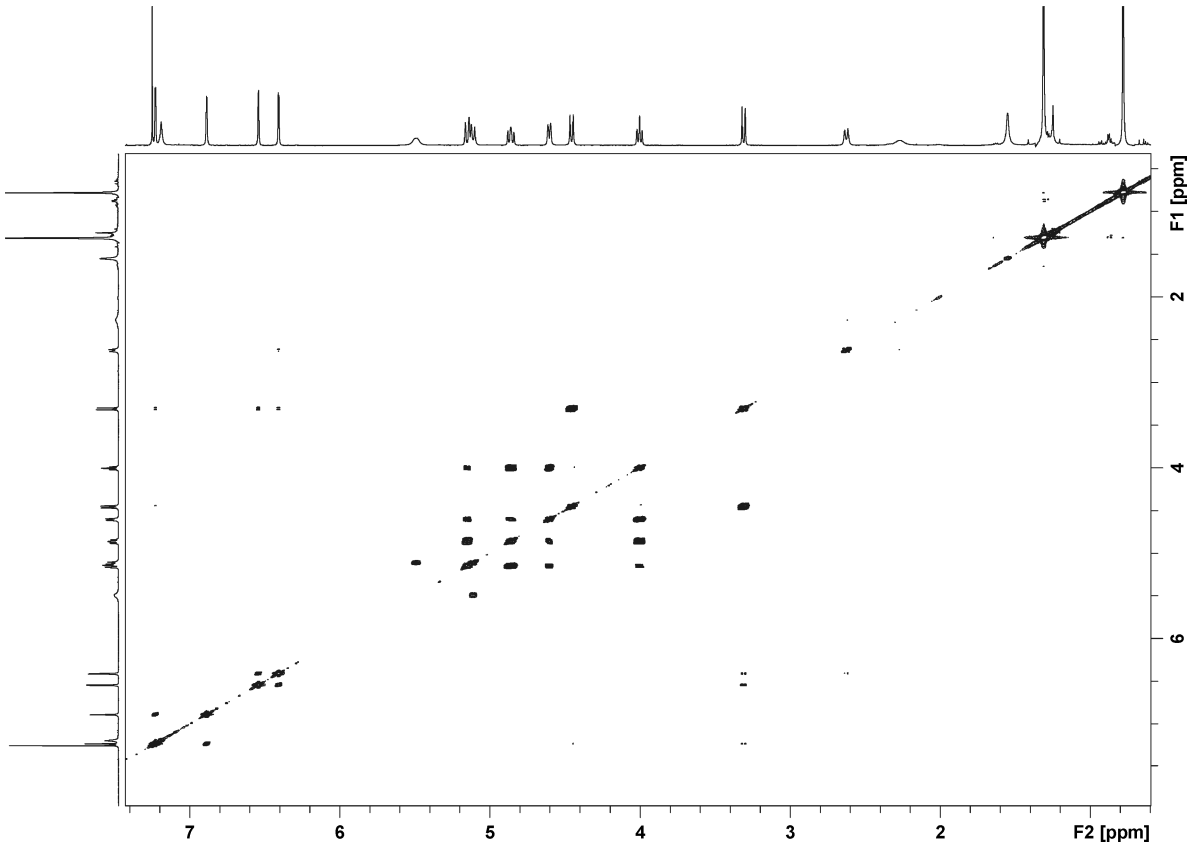


Figure S45. $^{1}H–^{1}H$ COSY spectrum of calixarene $\mathbf{20_2}$ (600 MHz, $CDCl_3$, 30 °C).

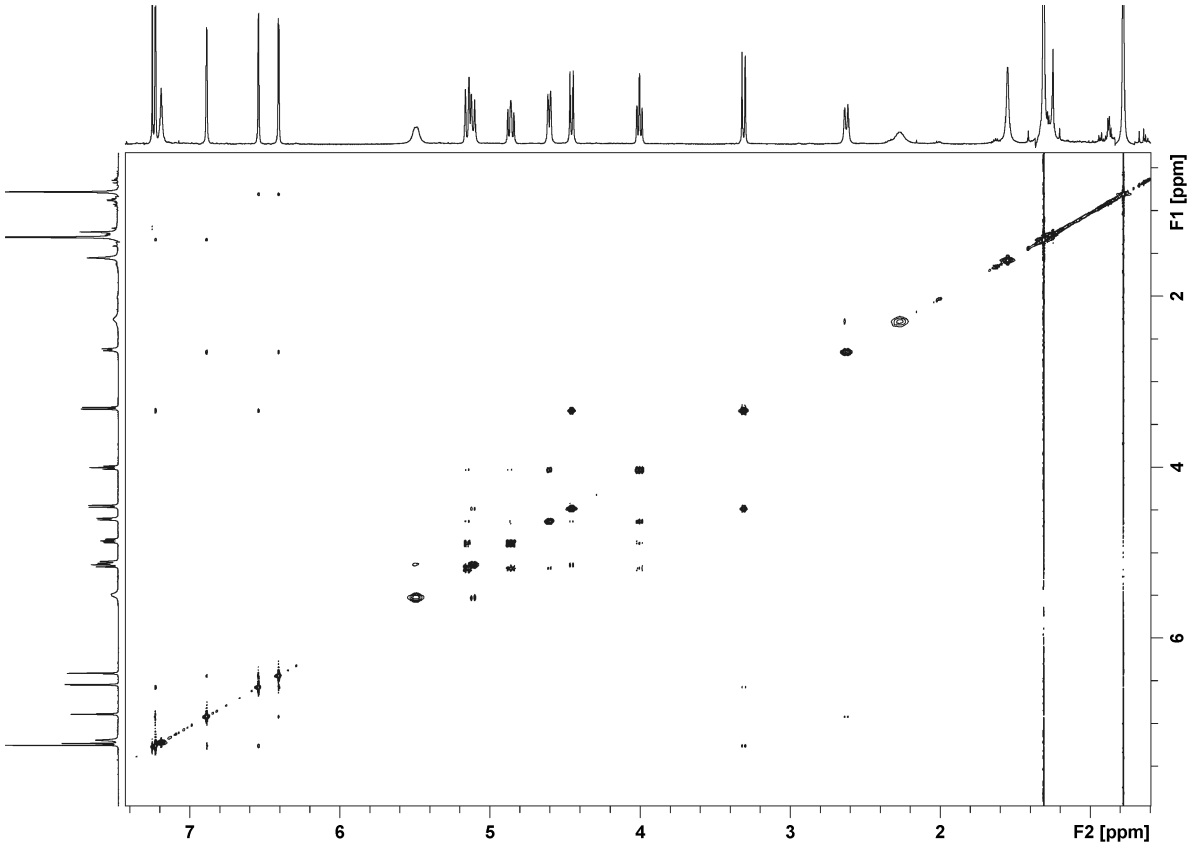


Figure S46. $^{1}H–^{1}H$ NOESY spectrum of calixarene $\mathbf{20_2}$ (600 MHz, $CDCl_3$, 30 °C).

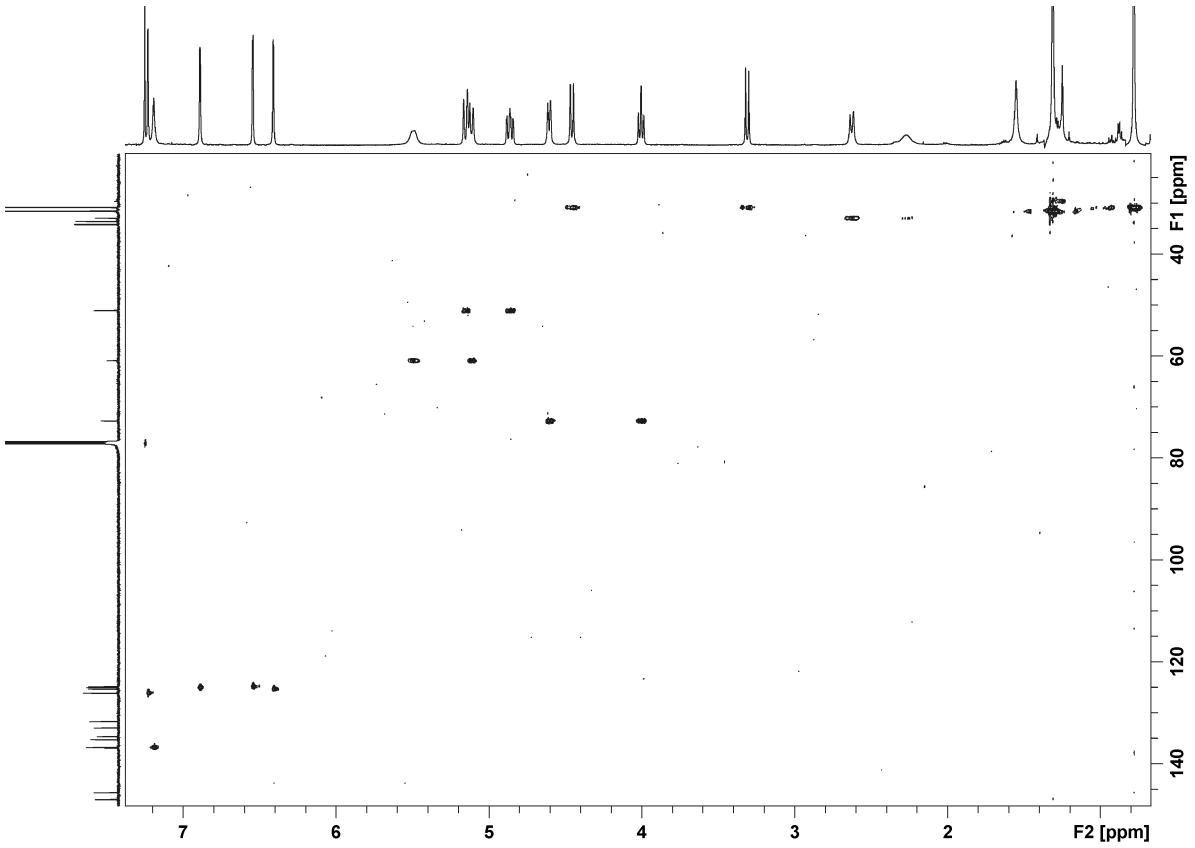


Figure S47. $^{1}H–^{13}C$ HSQC spectrum of calixarene $\mathbf{20_2}$ (600 MHz, $CDCl_3$, 30 °C).

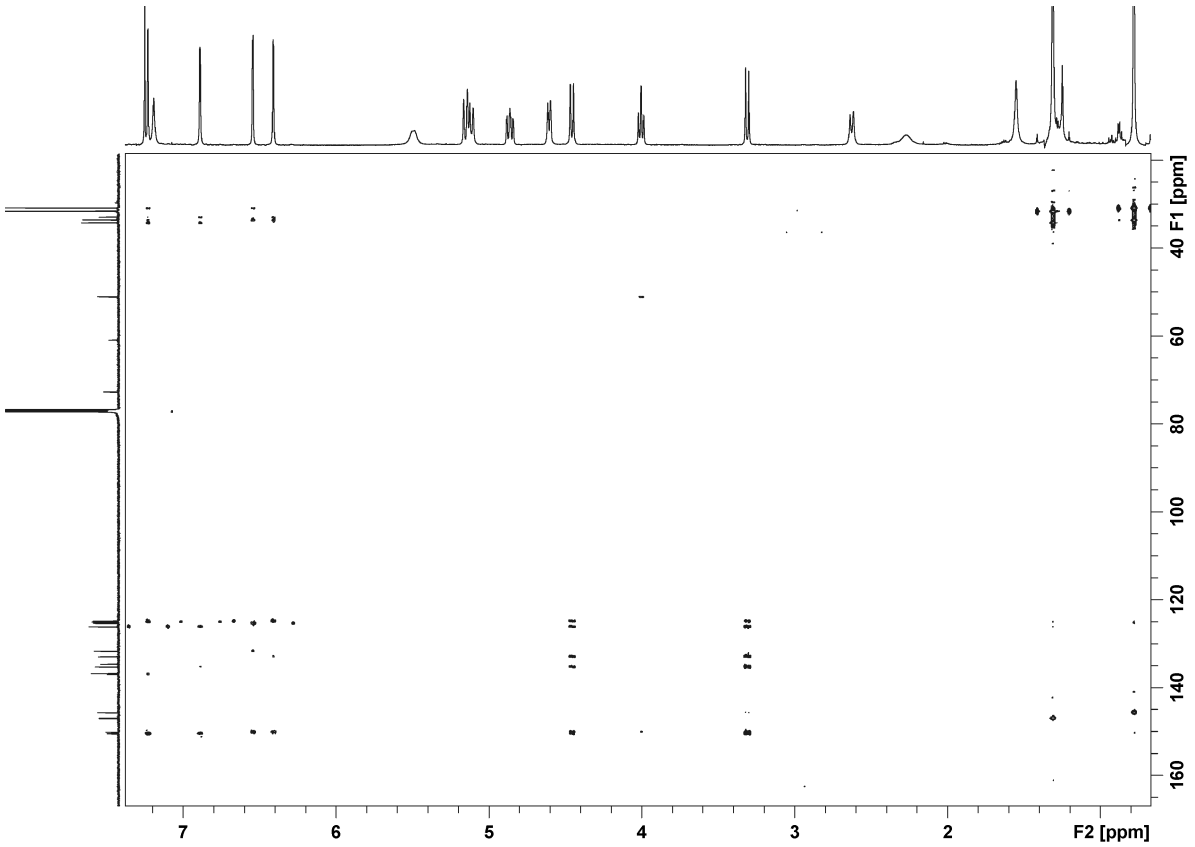


Figure S48. $^{1}H–^{13}C$ HMBC spectrum of calixarene $\mathbf{20_2}$ (600 MHz, $CDCl_3$, 30 °C).

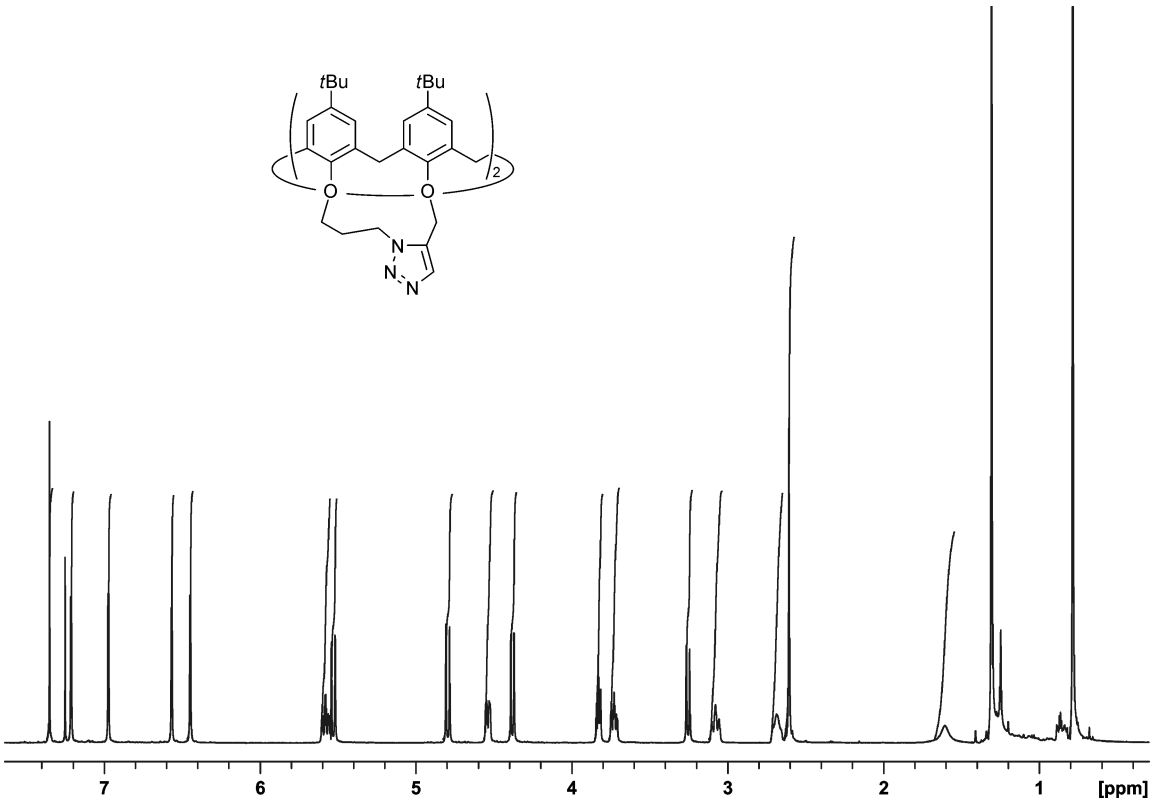


Figure S49. ^{1}H NMR spectrum of calixarene **20$_3$** (600 MHz, $CDCl_3$, 30 °C).

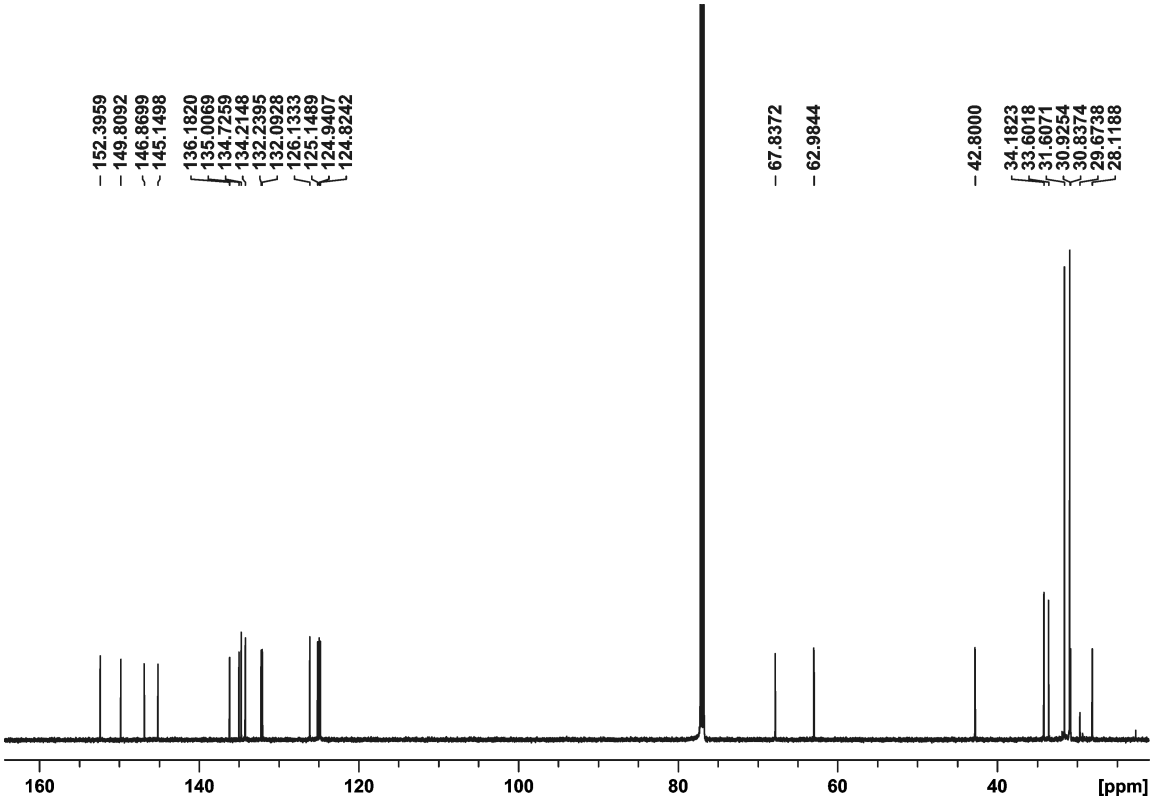


Figure S50. ^{13}C NMR spectrum of calixarene **20$_3$** (150 MHz, $CDCl_3$, 30 °C).

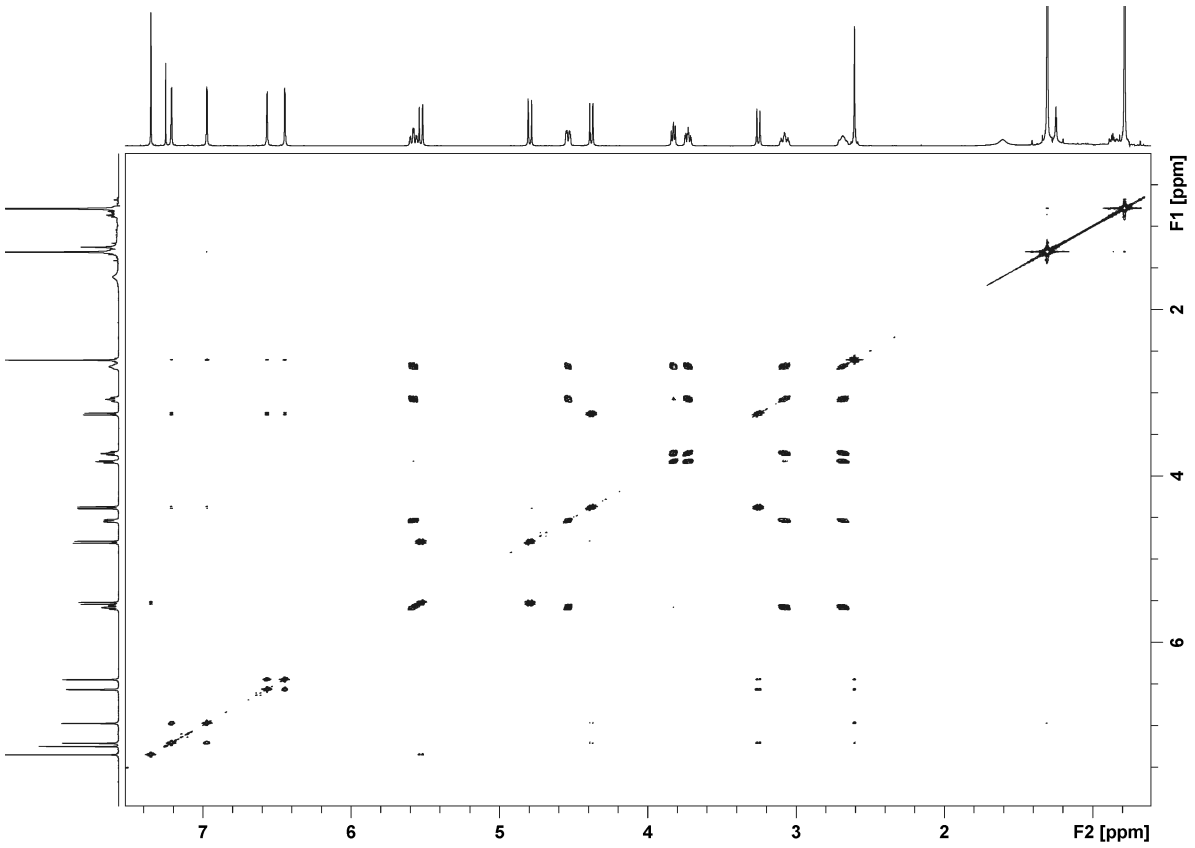


Figure S51. $^{1}H–^{1}H$ COSY spectrum of calixarene **20$_3$** (600 MHz, $CDCl_3$, 30 °C).

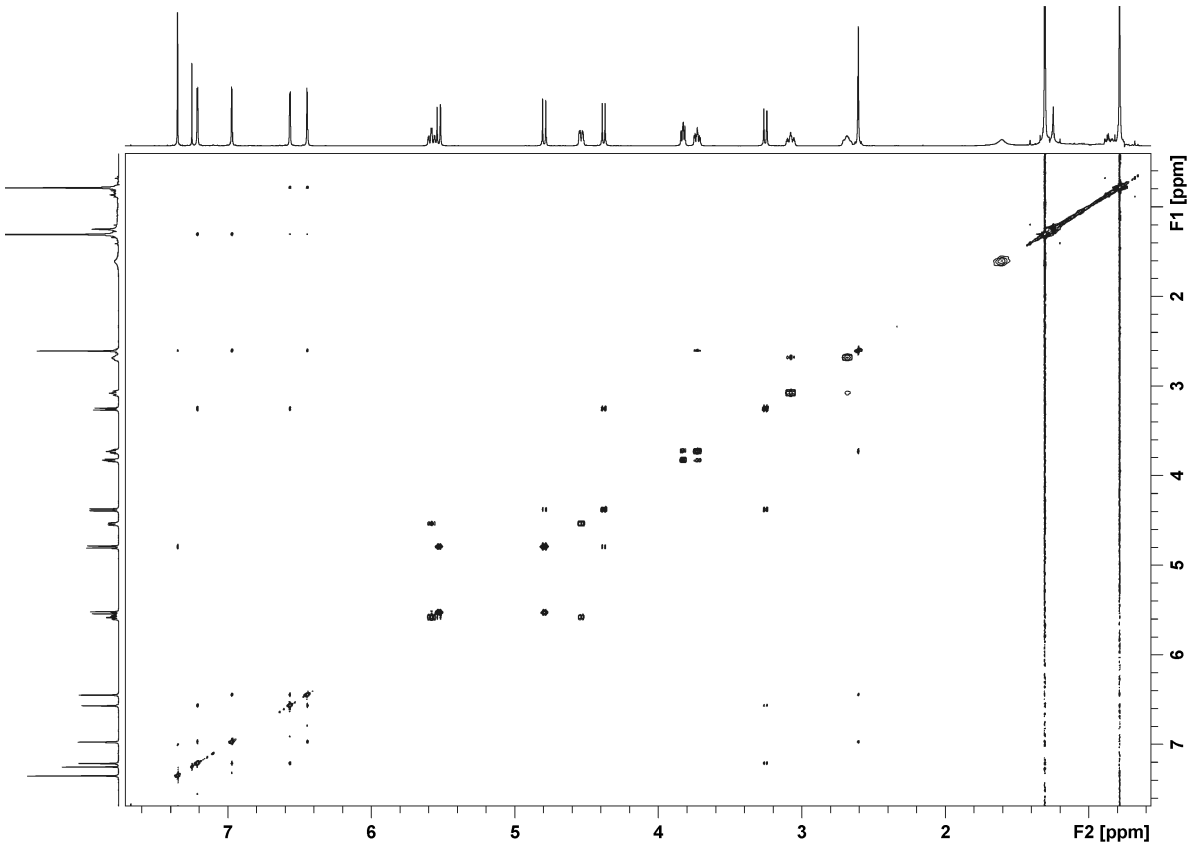


Figure S52. $^{1}H–^{1}H$ NOESY spectrum of calixarene **20$_3$** (600 MHz, $CDCl_3$, 30 °C).

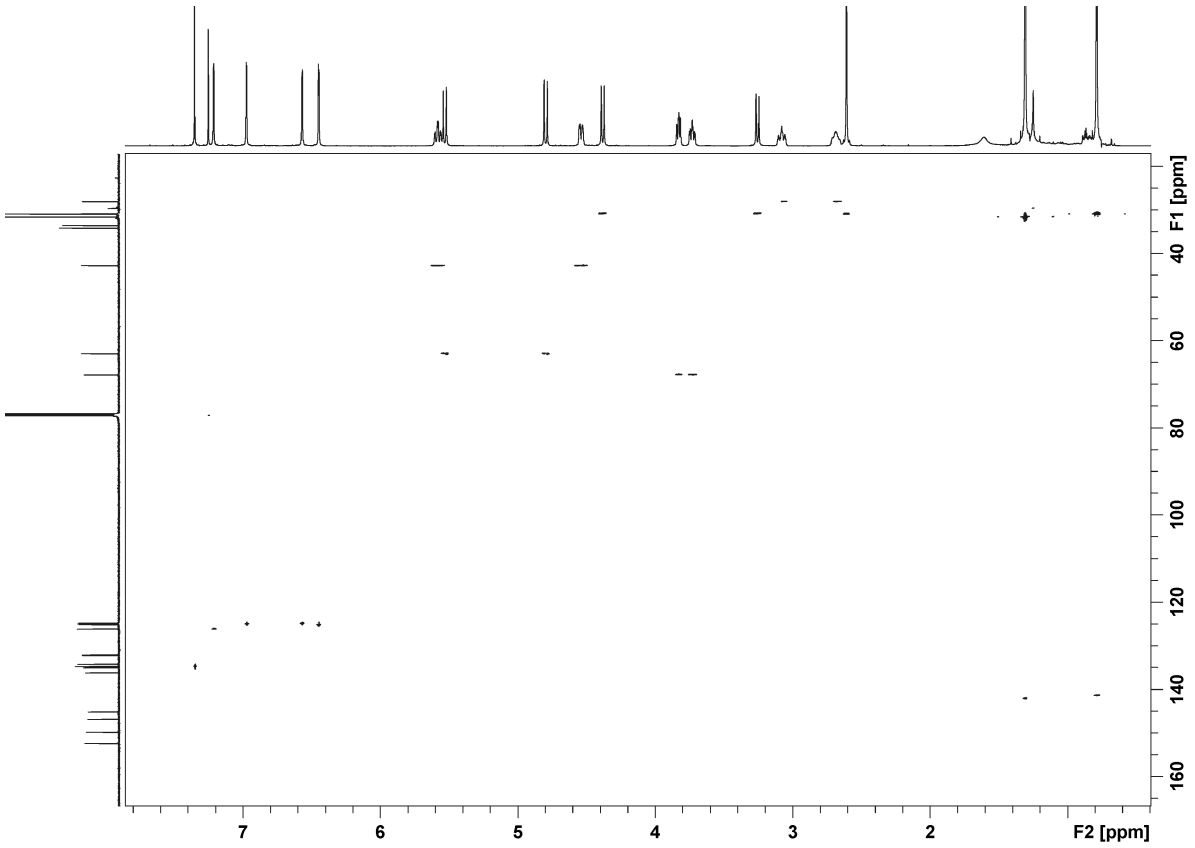


Figure S53. $^{1}H–^{13}C$ HSQC spectrum of calixarene **20$_3$** (600 MHz, $CDCl_3$, 30 °C).

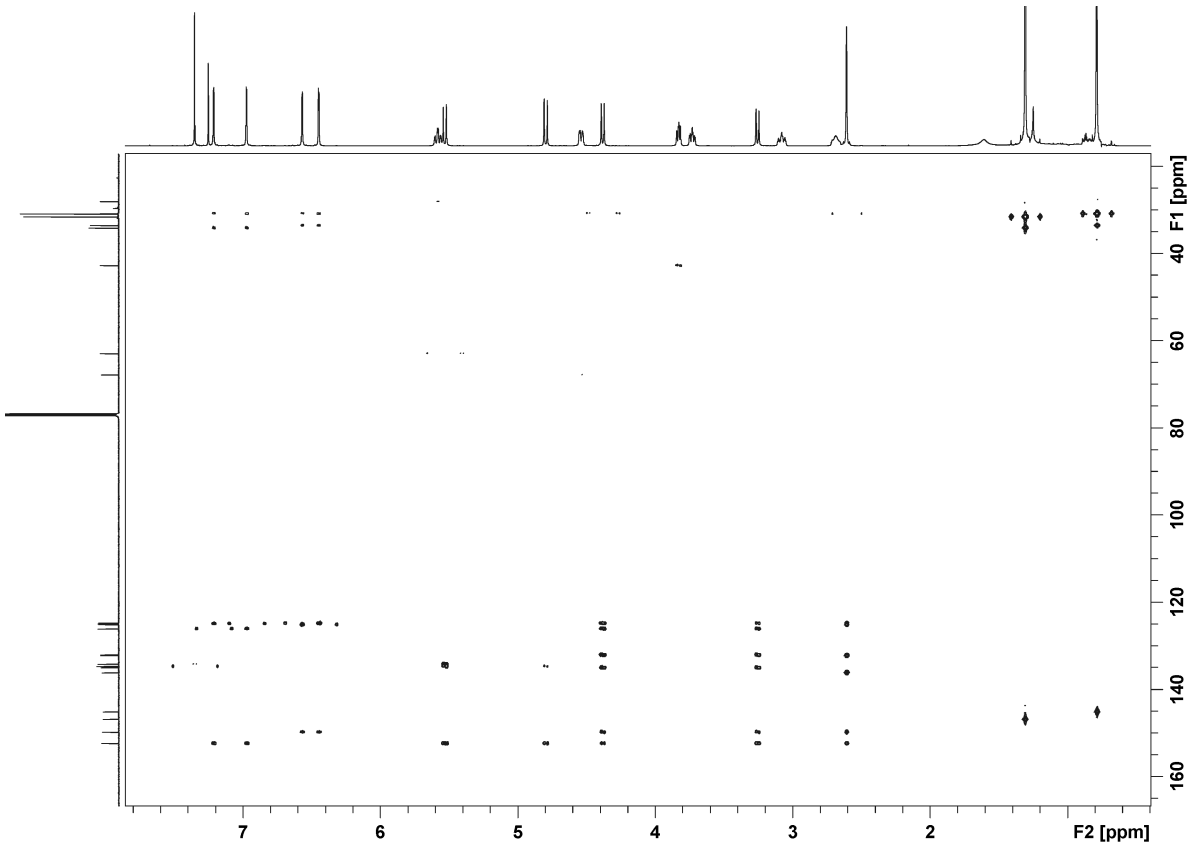


Figure S54. $^{1}H–^{13}C$ HMBC spectrum of calixarene **20$_3$** (600 MHz, $CDCl_3$, 30 °C).

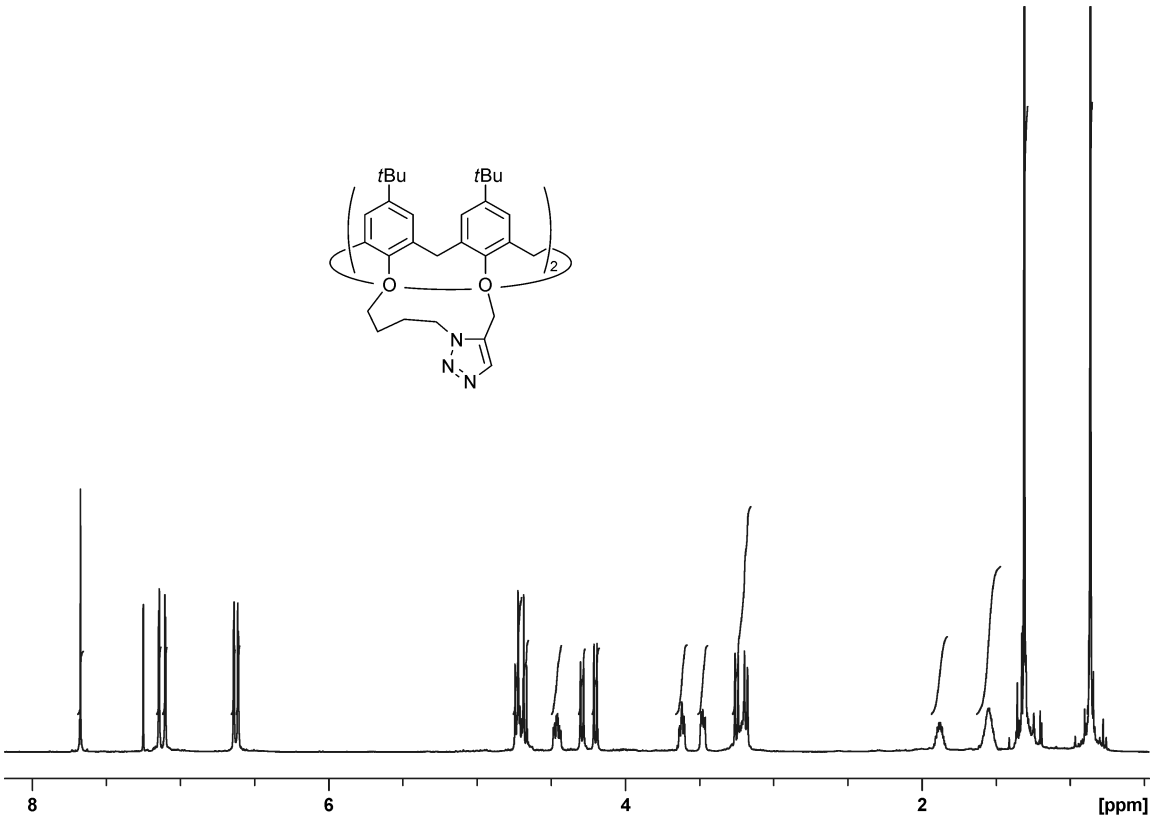


Figure S55. ^{1}H NMR spectrum of calixarene **20$_4$** (600 MHz, $CDCl_3$, 30 °C).

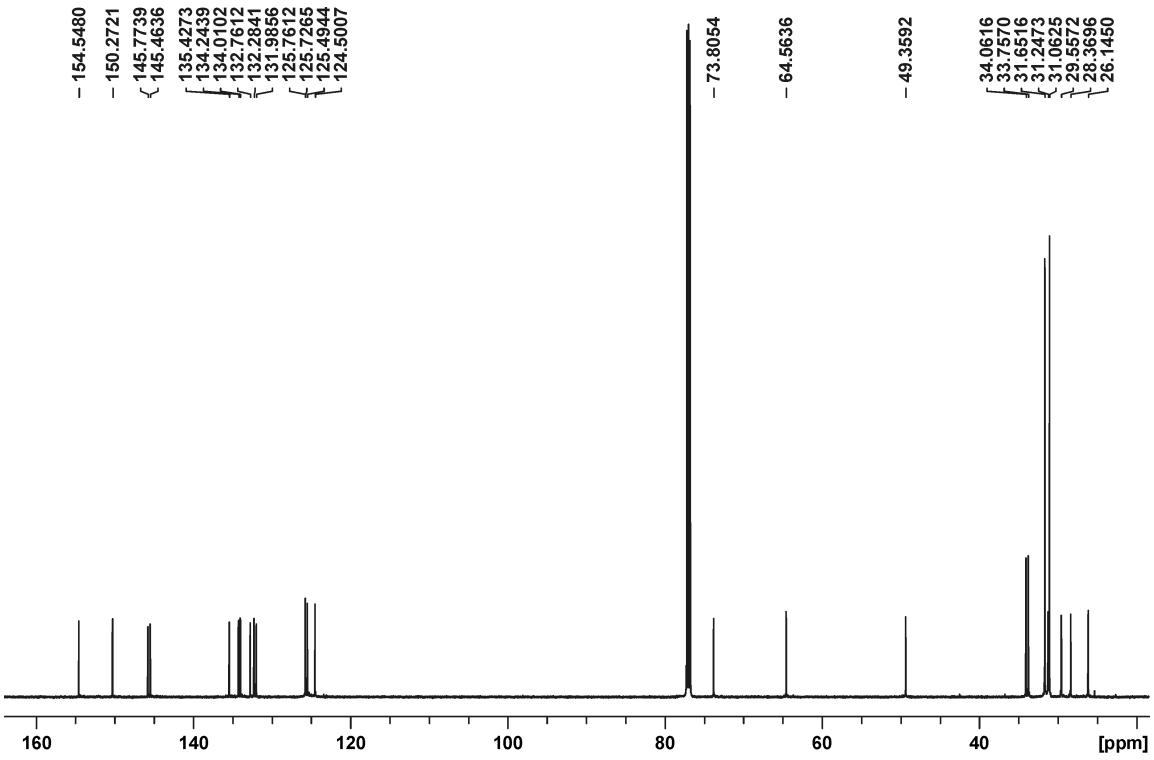


Figure S56. ^{13}C NMR spectrum of calixarene **20$_4$** (150 MHz, $CDCl_3$, 30 °C).

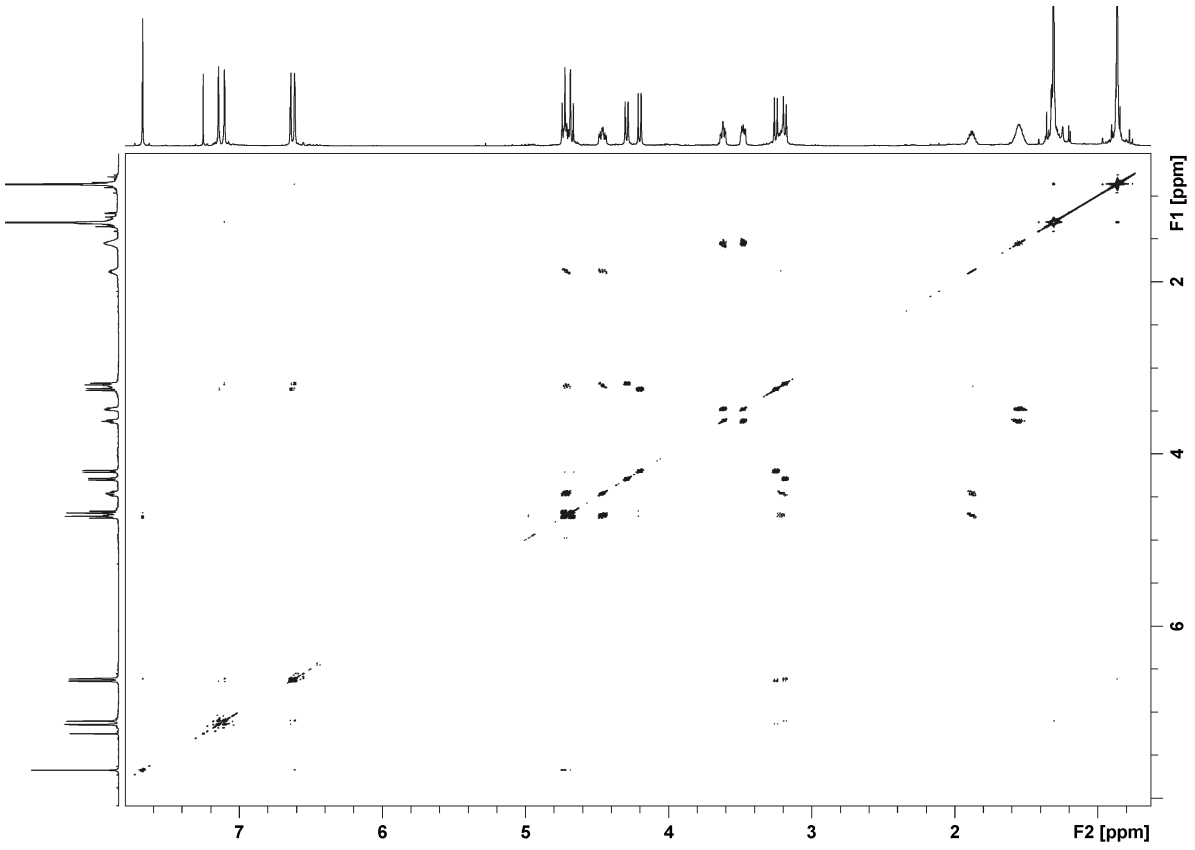


Figure S57. ^{1}H–^{1}H COSY spectrum of calixarene **20_4** (600 MHz, $CDCl_3$, 30 °C).

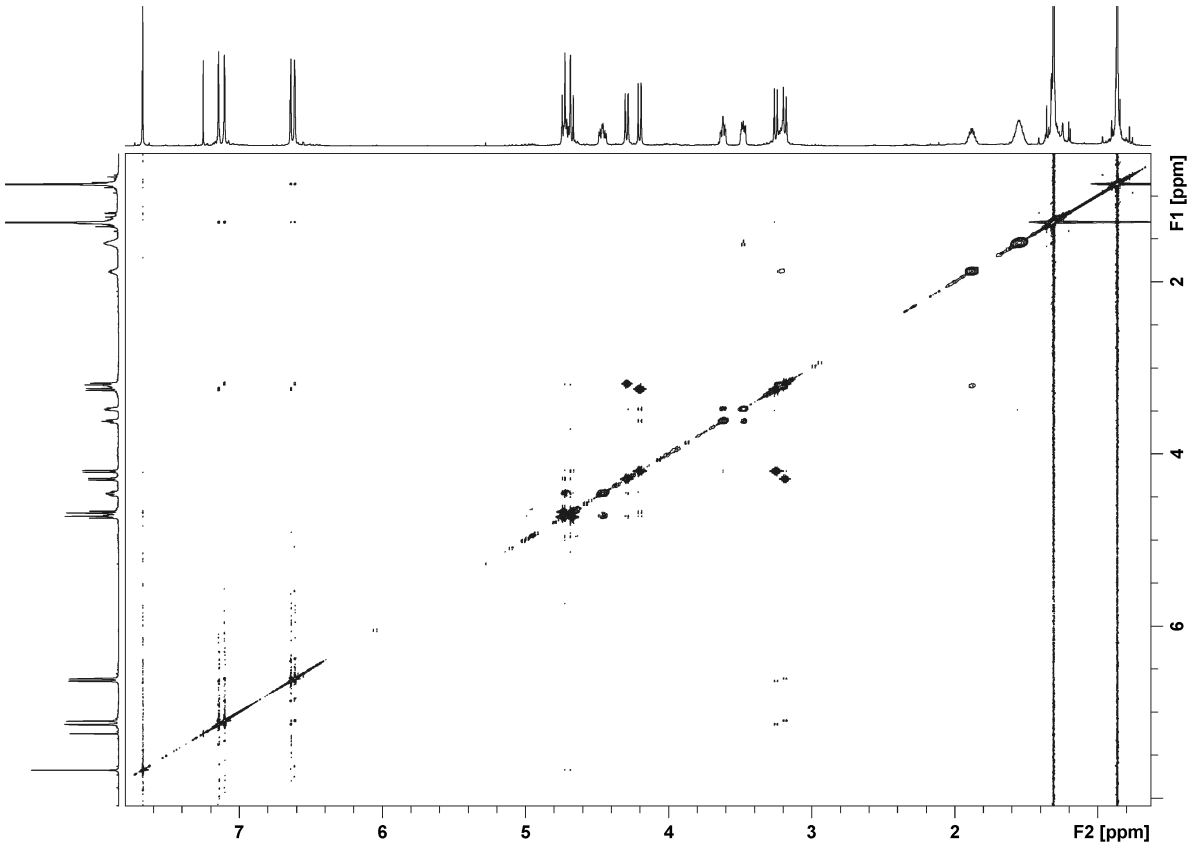


Figure S58. ^{1}H–^{1}H NOESY spectrum of calixarene **20_4** (600 MHz, $CDCl_3$, 30 °C).

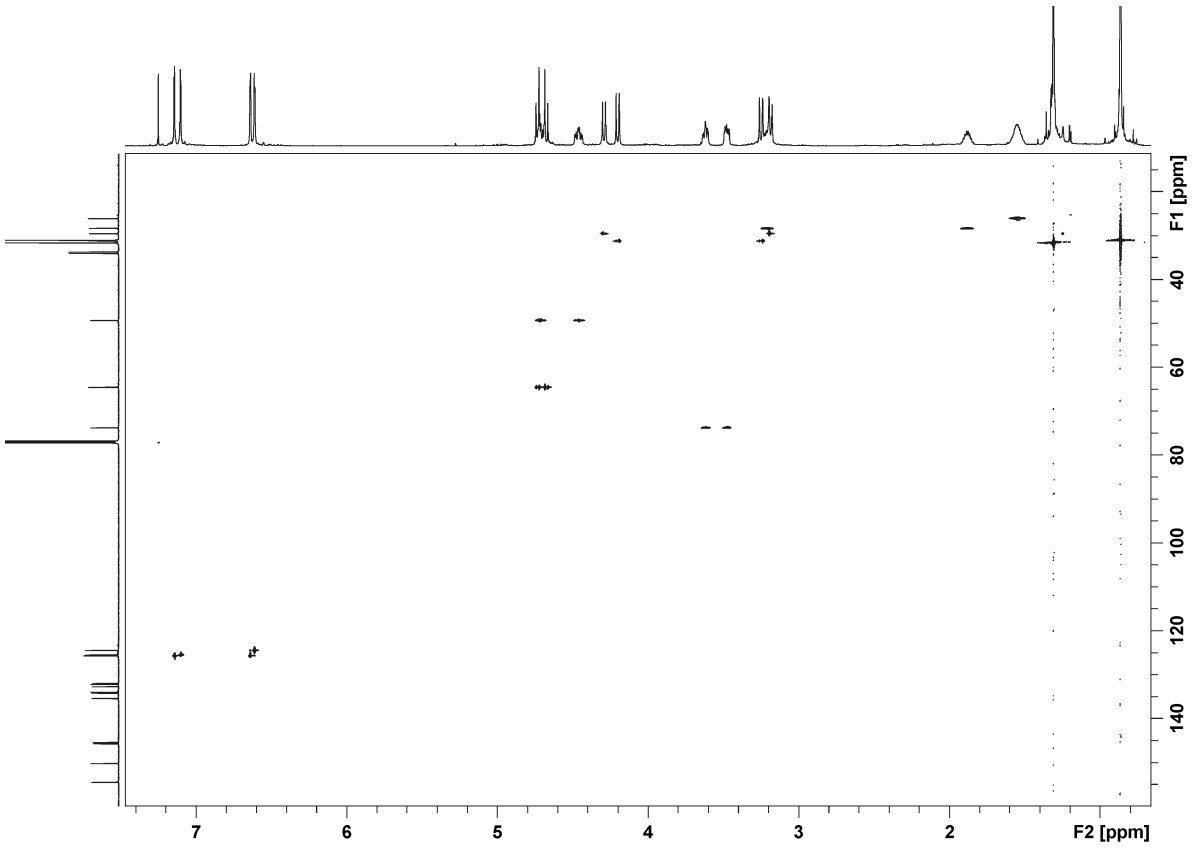


Figure S59. $^{1}H–^{13}C$ HSQC spectrum of calixarene **20$_4$** (600 MHz, $CDCl_3$, 30 °C).

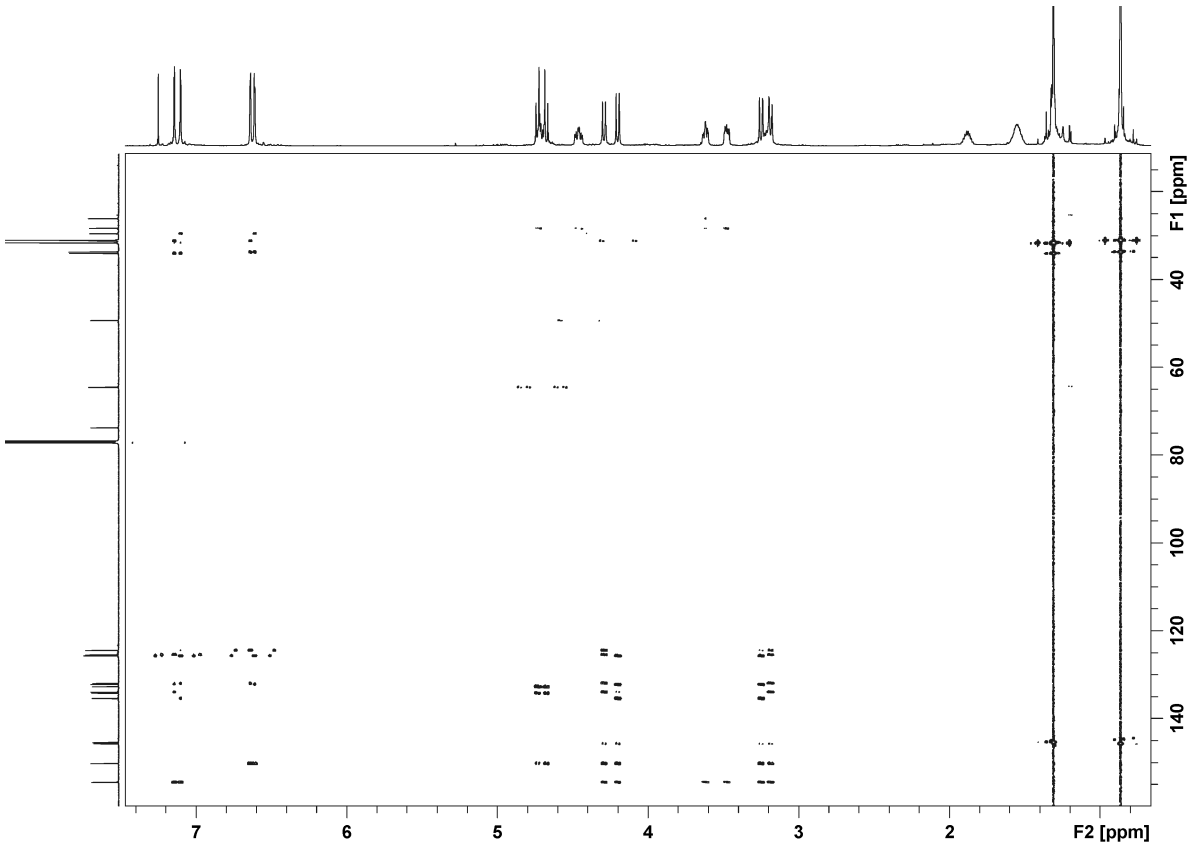


Figure S60. $^{1}H–^{13}C$ HMBC spectrum of calixarene **20$_4$** (600 MHz, $CDCl_3$, 30 °C).

Details of X-ray diffraction measurements

Crystallographic data were collected at 100 and 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.[S12] The structures were 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.[S13] Hydrogen atoms were placed in calculated positions and refined using a riding model. Crystallographic details are presented in the table below.

Compound	**2_4**	**20_2**	**20_3**	**20_4**
Formula	$C_{52}H_{70}N_6O_4$	$C_{54}H_{66}N_6O_4 \cdot 2CH_3OH$	$C_{56}H_{70}N_6O_4 \cdot 0.25CH_3OH \cdot 0.65H_2O$	$C_{58}H_{74}N_6O_4 \cdot 2C_7H_8$
M_w	843.14	927.21	914.40	1103.50
Temperature (K)	150(2)	150(2)	150(2)	100(2)
Size (mm)	0.41 × 0.33 × 0.20	0.32 × 0.24 × 0.08	0.21 × 0.17 × 0.13	0.90 × 0.40 × 0.04
Cryst. system	triclinic	monoclinic	triclinic	triclinic
Space group	P–1	$P2_1/n$	P–1	P–1
a (Å)	12.8923(3)	11.0508(3)	12.9522(10)	10.4623(12)
b (Å)	14.3755(3)	35.7303(11)	18.5010(13)	24.710(3)
c (Å)	15.8793(3)	12.8339(4)	23.7564(15)	24.745(2)
α (°)	91.9790(10)	90	75.737(2)	97.703(4)
β (°)	110.3990(10)	91.2770(10)	83.236(2)	90.024(4)
γ (°)	111.0270(10)	90	87.838(3)	93.981(4)
V (Å^3)	2531.52(10)	5066.2(3)	5478.6(7)	6323.7(12)
Z	2	4	4	4
ρ_{cald} (g·cm^{-3})	1.106	1.216	1.109	1.159
Abs coeff (mm^{-1})	0.070	0.079	0.071	0.072
F(000)	912	2000	1972	2384
θ range (deg)	1.82 < *θ* < 25.05	2.17 < *θ* < 25.03	1.73 < *θ* < 25.05	1.66 < *θ* < 25.03
no. of collected/ /unique rflns	38488 / 8892	42339 / 8934	54607 / 19314	63769 / 21438
Completeness to *θ* (%)	99.2	99.8	99.5	95.7
no. of data/ /restraints/ /params	8892/ /68/ /579	8934/ /32/ /624	19314/ /33/ /1250	21438/ /0/ /1425
Goodness of fit on F^2	1.062	1.027	1.037	1.063
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0871, wR2 = 0.2339	R1 = 0.0631, wR2 = 0.1403	R1 = 0.0708, wR2 = 0.1760	R1 = 0.1649, wR2 = 0.3513
R indices (all data)	R1 = 0.0999, wR2 = 0.2467	R1 = 0.0902, wR2 = 0.1546	R1 = 0.0985, wR2 = 0.1921	R1 = 0.2715, wR2 = 0.3931
Largest diff peak/hole (e/Å^3)	1.19 / −1.02	0.65 / −0.57	0.72 / −0.69	0.61 / −0.43

References

S1. S. Barboso, A. G. Carrera, S. E. Matthews, F. Arnaud-Neu, V. Böhmer, J.-F. Dozol, H. Rouquette and M.-J. Schwing-Weill, Calix[4]arenes with CMPO functions at the narrow rim. Synthesis and extraction properties, *J. Chem. Soc., Perkin Trans. 2*, 1999, 719–723.

S2. Z.-G. Luo, Y. Zhao, F. Xu, C. Ma, X.-M. Xu and X.-M. Zhang, Synthesis and thermal properties of novel calix[4]arene derivatives containing 1,2,3-triazole moiety *via* K_2CO_3-catalyzed 1,3-dipolar cycloaddition reaction, *Chinese Chem. Lett.*, 2014, **25**, 1346–1348.

S3. R. Hosseinzadeh, E. Domehri, M. Tajbakhsh and A. Bekhradnia, New fluorescent sensor based on a calix[4]arene bearing two triazole–coumarin units for copper ions: application for Cu^{2+} detection in human blood serum, *J. Incl. Phenom. Macrocyclic Chem.*, 2019, **93**, 245–252.

S4. D. Tian, H. Yan and H. Li, A selective fluorescent probe of Hg^{2+} based on triazole-linked 8-oxyquinoline calix[4]arene by click chemistry, *Supramol. Chem.*, 2010, **22**, 249–255.

S5. A. Gorbunov, J. Kuznetsova, K. Puchnin, V. Kovalev and I. Vatsouro, Triazolated calix[4]arenes from 2-azidoethylated precursors: is there a difference in the way the triazoles are attached to narrow rims? *New J. Chem.*, 2019, **43**, 4562–4580.

S6. C. D. Gutsche, B. Dhawan, J. A. Levine, K. H. No and L. J. Bauer, Calixarenes. 9. Conformational isomers of the ethers and esters of calix[4]arenes, *Tetrahedron*, 1983, **39**, 409–426.

S7. R. Pomecko, Z. Asfari, V. Hubscher-Bruder, M. Bochenska and F. Arnaud-Neu, Anion recognition by phosphonium calix[4]arenes: synthesis and physico-chemical studies, *Supramol. Chem.*, 2010, **22**, 275–288.

S8. I. Bitter, A. Grün, B. Ágai and L. Tôke, An easy access to tetra-O-alkylated calix[4]arenes of cone conformation, *Tetrahedron*, 1995, **51**, 7835–7840.

S9. V. I. Boyko, A. A. Podoprigorina, A. V. Yakovenko, V. V. Pirozhenko and V. I. Kalchenko, Alkylation of narrow rim calix[4]arenes in a DMSO-NaOH medium, *J. Incl. Phenom. Macrocyclic Chem.*, 2004, **50**, 193–197.

S10. Y. Nishizawa, Studies on organophosphorus compounds. II. On phosphite cuprous halide complex compounds, *Bull. Chem. Soc. Jpn.* 1961, **34**, 1170–1178.

S11. A. Tikad, H. Fu, C. M. Sevrain, S. Laurent, J.-F. Nierengarten and S. P. Vincent, Mechanistic insight into heptosyltransferase inhibition by using Kdo multivalent glycoclusters, *Chem. – Eur. J.*, 2016, **22**, 13147–13155.

S12. G. M. Sheldrick, A short history of *SHELX*, *Acta Crystallogr.*, 2008, **A64**, 112–122.

S13. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *OLEX2*: a complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, 2009, **42**, 339–341.