Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Constructing bridged multifunctional calixarenes by intramolecular indole coupling

Boris Bolshchikov, Sergey Volkov, Daria Sokolova, Alexander Gorbunov, Alina Serebryannikova, Igor Gloriozov, Dmitry Cheshkov, Stanislav Bezzubov, Wen-Sheng Chung, Vladimir Kovalev and Ivan Vatsouro

Supplementary Information

Contents

Synthesis and characterization of novel compounds

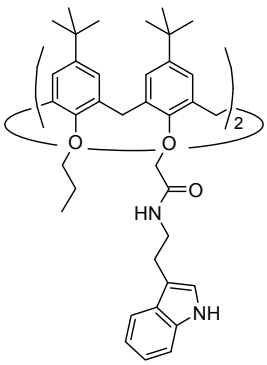
General experimental methods: NMR spectra were acquired on Bruker Avance 400 and Avance 600 instruments at 25 ºC if not stated otherwise, and chemical shifts are reported as ppm referenced to solvent signals. ESI mass spectra were obtained from a Thermo Scientific LTQ Orbitrap spectrometer. Chemicals received from commercial sources were used without further purification. Solvents were purified and dried according to standard procedures.

General procedure A (preparation of amides through activation of acids with $SOCl_2$): A solution of an acid-functionalized calixarene in a mixture of dry benzene and $SOCl_2$ was gently refluxed (oil bath) at stirring for 2 h. The excess $SOCl_2$ was removed *in vacuo*, and the residue was repeatedly re-evaporated with fresh dry benzene. The solid obtained was dissolved in dry THF, and the solution was added to an ice-cooled THF solution of L-tryptophan methyl ester hydrochloride or tryptamine, Et_3N, and water (in several cases) in THF. The stirring at cooling was continued for 1 h, and the mixture was allowed to stay overnight at room temperature. After removal of the solvent, CH_2Cl_2 was added, and the solution was washed with 2 M HCl, water, and dried. After removal of the solvent, the product was purified by column chromatography (CH_2Cl_2/ethanol, gradient) or by re-precipitation from CH_2Cl_2-solution by addition of hexane.

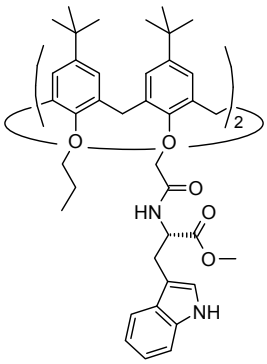
General procedure B (preparation of amides through activation of acids with DCC/HOSu): Dicyclohexylcarbodiimide (DCC) was added to a stirred solution/suspension of an acid-functionalized calixarene and *N*-hydroxysuccinimide (HOSu) in dry CH_2Cl_2. The mixture was allowed to stay overnight at 0–5 °C. The solid formed was separated by filtration and washed twice with small portions of dry CH_2Cl_2. To the clear solution L-tryptophan methyl ester hydrochloride or tryptamine, and Et_3N were added and the mixture was stirred for 48 h at room temperature. The solution was washed with 2 M HCl, water, and dried. After removal of the solvent, the product was purified by column chromatography (CH_2Cl_2/ethanol, gradient).

General procedure C (intramolecular bridging of the indole-containing calixarenes): Trifluoroacetic acid (TFA) was degassed by sonication under argon for 15 min and added to an indole-containing calixarene. The resultant solution was allowed to stay at room temperature in a dark place for 48 h in a tightly closed flask flushed with argon. The red-colored solution was concentrated *in vacuo* at room temperature (in the cases of highly concentrated solutions this step was omitted), the resultant oil was diluted with CH_2Cl_2 and the solution was poured into ice. $NaHCO_3$ was added portion-wise to neutralize the remaining acid, that was accompanied with a change of the solution color from red to yellow. The organic phase was separated, washed with water, and dried by passing through the filtering paper. The solvent was removed *in vacuo* and the resultant solid was dissolved in 1,4-dioxane. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone

(DDQ) was added and the mixture was stirred at room temperature for 4 h. The solvent was removed and the residue was dissolved in CH_2Cl_2. The solution was repeatedly washed with fresh saturated $NaHCO_3$ (aq) until the aqueous phase turned colorless. The organic phase was washed with water and dried. After removal of the solvent, the product was purified by column chromatography (CH_2Cl_2/ethanol, gradient) or by re-crystallization from acetonitrile.

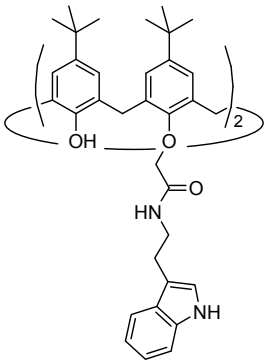


*Calixarene amide **3*** was prepared according to *General procedure A* from acid **1**[S1] (0.35 g, 0.41 mmol), $SOCl_2$ (7 ml), dry benzene (6 ml), tryptamine (0.26 g, 1.64 mmol), Et_3N (0.23 ml, 1.65 mmol), THF (15 ml), and water (0.3 ml); purified by chromatography. Yield 0.37 g (79%), beige solid. M.p. 159–161 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (bs, 2H; NH_{Ind}), 8.49 (t, 2H, $^3J_{HH}$ = 5.9 Hz; C(O)NH), 7.65–7.62 (m, 2H; ArH_{Ind}), 7.34–7.32 (m, 2H; ArH_{Ind}), 7.14–7.10 (m, 2H; ArH_{Ind}), 7.06 (s, 4H; ArH), 7.05–7.02 (m, 2H; ArH_{Ind}), 6.89–6.87 (m, 2H; ArH_{Ind}), 6.48 (s, 4H; ArH), 4.77 (s, 4H; OCH_2CO), 4.32 (d, 4H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 3.75–3.68 (m, 4H; NCH_2), 3.63–3.58 (m, 4H; OCH_2), 3.19 (d, 4H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 3.18–3.13 (m, 4H; $IndCH_2$), 1.56–1.48 (m, 4H; $OCH_2C\underline{H}_2$), 1.31 (s, 18H; $C(CH_3)_3$), 0.85 (s, 18H; $C(CH_3)_3$), 0.64 (6H, $^3J_{HH}$ = 7.4 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.02 (C=O), 154.57, 150.65, 145.70, 145.13 (C_{Ar}), 136.31 ($C_{Ar\ Ind}$), 133.84, 131.64 (C_{Ar}), 127.44 ($C_{Ar\ Ind}$), 126.34, 124.88 (CH_{Ar}), 122.51, 121.39, 118.85, 118.31 ($CH_{Ar\ Ind}$), 112.61 ($C_{Ar\ Ind}$), 111.33 ($CH_{Ar\ Ind}$), 77.91, 74.30 (OCH_2), 41.97 (NCH_2), 34.01, 33.65 ($\underline{C}(CH_3)_3$), 31.94 ($ArCH_2Ar$), 31.58, 31.06 ($C(\underline{C}H_3)_3$), 25.43 ($IndCH_2$), 21.73 ($OCH_2\underline{C}H_2$), 9.60 (CH_3) ppm; ESI-MS *m*/*z*: 1155.6903 $[M+Na]^+$ for $C_{74}H_{92}NaN_4O_6$ (1155.6909).

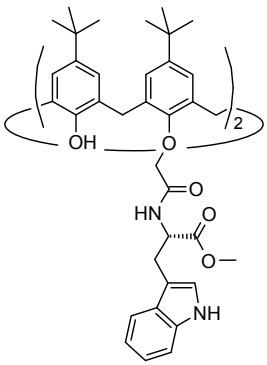


*Calixarene amide **4*** was prepared according to *General procedure A* from acid **1**[S1] (0.20 g, 0.24 mmol), $SOCl_2$ (4 ml), dry benzene (2 ml), L-tryptophan methyl ester hydrochloride (0.24 g, 0.96 mmol), Et_3N (0.40 ml, 2.88 mmol), and THF (15 ml); purified by re-precipitation. Yield 0.21 g (71%), white solid. M.p. 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (bs, 2H; NH_{Ind}), 7.79 (2H, $^3J_{HH}$ = 8.4 Hz, C(O)NH), 7.55–7.51 (m, 2H; ArH_{Ind}), 7.36–7.31 (m, 2H; ArH_{Ind}), 7.20–7.13 (m, 2H; ArH_{Ind}), 7.09–7.03 (m, 2H; ArH_{Ind}), 6.97–6.93 (m, 2H; ArH_{Ind}), 6.81 (d, 2H, $^4J_{HH}$ = 2.5 Hz; ArH), 6.79 (d, 2H, $^4J_{HH}$ = 2.5 Hz; ArH), 6.63 (d, 2H, $^4J_{HH}$ = 2.4 Hz; ArH), 6.61 (d, 2H, $^4J_{HH}$ = 2.4 Hz; ArH), 5.06–4.99 (m, 2H; CHCO), 4.90 (d, 2H, $^2J_{HH}$ = 15.8 Hz; OCH_2CO), 4.71 (d, 2H, $^2J_{HH}$ = 15.8 Hz; OCH_2CO), 4.47 (d, 2H, $^2J_{HH}$ = 12.8 Hz; $ArCH_2Ar$), 4.33 (d, 2H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 3.73–3.67 (m, 4H; OCH_2), 3.49 (s, 6H; OCH_3), 3.44 (dd, 2H, $^2J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 5.7 Hz; $IndCH_2$), 3.37 (dd, 2H, $^2J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 6.4 Hz; $IndCH_2$), 3.15

(d, 2H, $^{2}J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 3.02 (d, 2H, $^{2}J_{HH}$ = 12.8 Hz; $ArCH_2Ar$), 1.71–1.59 (m, 4H; $OCH_2C\underline{H}_2$), 1.13 (s, 18H; $C(CH_3)_3$), 1.00 (18H; $C(CH_3)_3$), 0.67 (t, 6H, $^{3}J_{HH}$ = 7.4 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.21, 170.48 (C=O), 153.21, 152.34, 144.81, 144.60 (C_{Ar}), 135.99 ($C_{Ar\ Ind}$), 133.07, 132.74, 132.33 (C_{Ar}), 127.36 ($C_{Ar\ Ind}$), 125.86, 125.41, 125.01, 124.98 (CH_{Ar}), 123.08, 121.88, 119.37, 118.29, 111.23 ($CH_{Ar\ Ind}$), 110.09 ($C_{Ar\ Ind}$), 76.64, 73.31 (OCH_2), 52.93, 52.20 (NCH, OCH_3), 33.75, 33.69 ($\underline{C}(CH_3)_3$), 31.77, 31.59 ($ArCH_2Ar$), 31.35, 31.27 ($C(\underline{C}H_3)_3$), 27.51 ($IndCH_2$), 22.56 ($OCH_2\underline{C}H_2$), 9.78 (CH_3) ppm; ESI-MS *m*/*z*: 1271.7008 $[M+Na]^+$ for $C_{78}H_{96}NaN_4O_{10}$ (1271.7019).

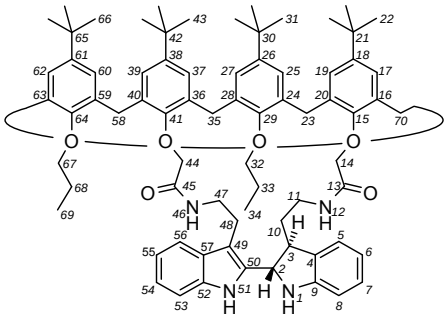


Calixarene amide ***5*** was prepared according to *General procedure A* from acid **2**[S2] (0.16 g, 0.21 mmol), $SOCl_2$ (3 ml), dry benzene (2 ml), tryptamine (0.10 g, 0.63 mmol), Et_3N (0.088 ml, 0.63 mmol), and THF (15 ml); purified by chromatography. Yield 0.12 g (55%), beige solid. Alternatively, it was prepared according to *General procedure B* from acid **2**[S2] (0.420 g, 0.55 mmol), HOSu (0.253 g, 2.20 mmol), DCC (0.283 g, 1.37 mmol), tryptamine (0.220 g, 1.37 mmol), and CH_2Cl_2 (15 ml). Yield 0.42 g (73%), beige solid. M.p. 143–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (t, 2H, $^{3}J_{HH}$ = 5.9 Hz; C(O)NH), 7.63–7.57 (m, 2H; ArH_{Ind}), 7.27 (s, 2H, OH), 7.15–7.07 (m, 4H; ArH_{Ind}), 7.06–6.97 (m, 4H; ArH_{Ind}+NH_{Ind}), 6.94 (s, 4H; ArH), 6.83–6.80 (m, 2H; ArH_{Ind}), 6.78 (s, 4H; ArH), 4.28 (s, 4H; OCH_2CO), 3.88–3.81 (m, 4H; NCH_2), 3.41 (d, 4H, $^{2}J_{HH}$ = 13.2 Hz; $ArCH_2Ar$), 3.07 (d, 4H, $^{2}J_{HH}$ = 13.2 Hz; $ArCH_2Ar$), 3.05 (t, 4H, $^{3}J_{HH}$ = 6.2 Hz; $IndCH_2$), 1.29 (s, 18H; $C(CH_3)_3$), 0.99 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.12 (C=O), 149.40, 148.38, 148.16, 142.61 (C_{Ar}), 136.63 ($C_{Ar\ Ind}$), 132.09 (C_{Ar}), 127.13 ($C_{Ar\ Ind}$), 126.80 (C_{Ar}), 125.98, 125.16 (CH_{Ar}), 122.39, 121.80, 119.15, 118.50 ($CH_{Ar\ Ind}$), 112.73 ($C_{Ar\ Ind}$), 111.47 ($CH_{Ar\ Ind}$), 74.45 (OCH_2), 39.00 (NCH_2), 34.02, 33.85 ($\underline{C}(CH_3)_3$), 31.95 ($ArCH_2Ar$), 31.69, 30.90 ($C(\underline{C}H_3)_3$), 25.67 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1071.5953 $[M+Na]^+$ for $C_{68}H_{80}NaN_4O_6$ (1071.5970).

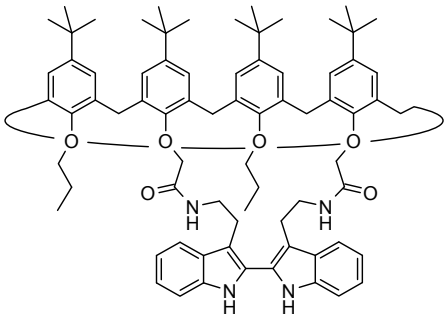


Calixarene amide ***6***[S3] was prepared according to *General procedure A* from acid **2**[S2] (0.22 g, 0.29 mmol), $SOCl_2$ (4 ml), dry benzene (4 ml), L-tryptophan methyl ester hydrochloride (0.29 g, 1.16 mmol), Et_3N (0.48 ml, 3.48 mmol), water (0.3 ml), and THF (15 ml); purified by re-precipitation. Yield 0.11 g (33%), white solid. Alternatively, it was prepared according to *General procedure B* from acid **2**[S2] (0.229 g, 0.30 mmol), HOSu (0.138 g, 1.20 mmol), DCC (0.155 g, 0.75 mmol), L tryptophan methyl ester hydrochloride (0.191 g, 0.75 mmol), Et_3N (0.208 ml, 1.50 mmol), and CH_2Cl_2 (10 ml). Yield 0.24 g (69%), white solid. ^{1}H NMR

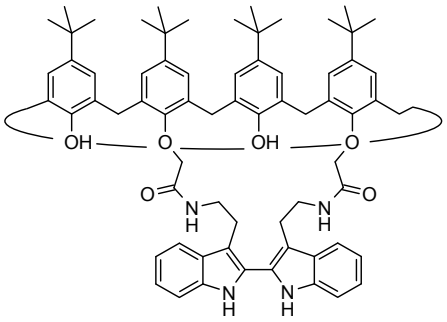
(400 MHz, $CDCl_3$): δ = 9.38 (d, 2H, $^3J_{HH}$ = 7.8 Hz; C(O)NH), 7.55 (s, 2H; OH), 7.42–7.38 (m, 2H; ArH_{Ind}), 7.16 (bs, 2H; NH_{Ind}), 7.19–7.09 (m, 4H; ArH_{Ind}), 7.05–6.98 (m, 2H; ArH_{Ind}), 7.03 (d, 2H, $^4J_{HH}$ = 2.4 Hz; ArH), 6.94 (d, 2H, $^4J_{HH}$ = 2.4 Hz; ArH), 6.82–6.79 (m, 2H; ArH_{Ind}), 6.77 (d, 2H, $^4J_{HH}$ = 2.5 Hz; ArH), 6.75 (d, 2H, $^4J_{HH}$ = 2.5 Hz; ArH), 5.13–5.06 (m, 2H; CHCO), 4.89 (d, 2H, $^2J_{HH}$ = 15.1 Hz; OCH_2CO), 4.09 (d, 2H, $^2J_{HH}$ = 15.1 Hz; OCH_2CO), 3.90 (d, 2H, $^2J_{HH}$ = 13.8 Hz; $ArCH_2Ar$), 3.77 (d, 2H, $^2J_{HH}$ = 12.9 Hz; $ArCH_2Ar$), 3.66 (s, 6H; OCH_3), 3.40–3.32 (m, 4H; $IndCH_2$), 3.35 (d, 2H, $^2J_{HH}$ = 13.8 Hz; $ArCH_2Ar$), 2.76 (d, 2H, $^2J_{HH}$ = 12.9 Hz; $ArCH_2Ar$), 1.32 (s, 18H; $C(CH_3)_3$), 0.96 (s, 18H; $C(CH_3)_3$) ppm.



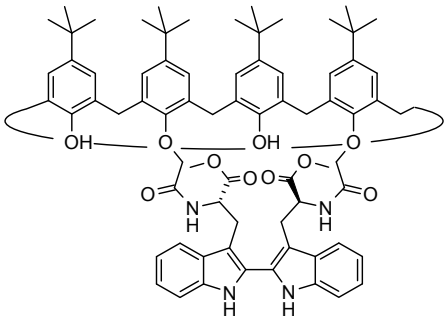
Calixarene indolylindoline ***7***. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.47 (s, 1H; H^{51}), 7.86–7.83 (m, 1H; H^{53}), 7.36–7.33 (m, 1H; H^5), 7.32–7.29 (m, 1H; H^{56}), 7.20–7.17 (m, 1H; H^{55}), 7.17–7.14 (m, 1H; H^{54}), 7.16–7.12 (m, 1H; H^7), 6.98–6.95 (m, 2H; H^{25}+H^{27} or H^{60}+H^{62}), 6.95–6.93 (m, 2H; H^{60}+H^{62} or H^{25}+H^{27}), 6.88–6.85 (m, 1H; H^6), 6.79 (d, 1H, $^4J_{HH}$ = 2.5 Hz; H^{37} or H^{39}), 6.78 (d, 1H, $^4J_{HH}$ = 2.5 Hz; H^{39} or H^{37}), 6.77 (d, 1H, $^4J_{HH}$ = 2.5 Hz; H^{17} or H^{19}), 6.76 (d, 1H, $^4J_{HH}$ = 2.5 Hz; H^{19} or H^{17}), 6.73–6.71 (m, 1H; H^8), 5.04 (d, 1H, $^3J_{HH}$ = 8.5 Hz; H^2), 4.53 (d, 1H, $^2J_{HH}$ = 14.8 Hz; H^{44}), 4.41 (d, 1H, $^2J_{HH}$ = 12.5 Hz; H^{35} or H^{58}), 4.36 (d, 1H, $^2J_{HH}$ = 15.1 Hz; H^{14}), 4.33 (d, 1H, $^2J_{HH}$ = 14.8 Hz; H^{44}), 4.31 (d, 1H, $^2J_{HH}$ = 12.1 Hz; H^{23} or H^{70}), 4.29 (d, 1H, $^2J_{HH}$ = 12.8 Hz; H^{35} or H^{58}), 4.29 (d, 1H, $^2J_{HH}$ = 12.6 Hz; H^{23} or H^{70}), 4.29 (d, 1H, $^2J_{HH}$ = 15.1 Hz; H^{14}), 4.18 (bs, 1H; H^1), 4.15–4.09 (m, 1H; H^{47}), 4.04–3.94 (m, 2H; H^{32} or H^{67}), 3.90–3.79 (m, 2H; H^{67} or H^{32}), 3.68–3.59 (m, 2H; H^{11}), 3.55–3.50 (m, 1H; H^3), 3.48–3.39 (m, 2H; H^{47}+H^{48}), 3.25 (d, 1H, $^2J_{HH}$ = 12.8 Hz; H^{35} or H^{58}), 3.20 (bd, 3H; H^{23}+H^{70}+(H^{35} or H^{58})), 3.12–3.07 (m, 1H; H^{48}), 2.40–2.25 (m, 2H; H^{10}), 1.89–1.79 (m, 2H; H^{33} or H^{68}), 1.69–1.56 (m, 2H; H^{68} or H^{33}), 1.18 (s, 9H; H^{31} or H^{66}), 1.17 (s, 9H; H^{66} or H^{31}), 1.01 (s, 9H; H^{43}), 0.99 (s, 9H; H^{22}), 0.92 (3H, $^3J_{HH}$ = 7.6 Hz; H^{34} or H^{69}), 0.66 (t, 3H, $^3J_{HH}$ = 7.5 Hz; H^{69} or H^{34}) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.09 (*45*), 169.71 (*13*), 151.66, 151.58 (*29*, *64*), 150.24 (*15*), 150.02 (*41*), 149.70 (*9*), 145.90 (*38+18*), 145.62 (*26+61*), 136.54 (*50*), 135.36 (*57*), 134.23, 134.15, 134.08, 132.81, 132.65, 132.62, 132.57 (*16*, *20*, *24*, *28*, *36*, *40*, *59*, *63*), 129.34 (*4*), 128.50 (*52*), 128.20 (*7*), 125.67, 125.60, 125.55, 125.51 (*17*, *19*, *37*, *39*), 125.50, 125.46 (*25*, *27*, *60*, *62*), 124.49 (*5*), 122.24 (*55*), 119.88 (*6*), 119.71 (*54*), 119.16 (*53*), 110.93 (*56*), 109.47 (*8*), 108.78 (*49*), 77.32, 77.30 (*32*, *67*), 74.28 (*14*), 74.27 (*44*), 60.33 (*2*), 48.47 (*3*), 40.88 (*47*), 36.50 (*11*), 33.97, 33.96 (*30, 65*), 33.85, 33.83 (*21*, *42*), 33.08 (*10*), 31.48, 31.47 (*31+66*), 31.21, 31.19 (*22*, *43*), 30.74, 30.56, 30.42, 30.30 (*23*, *35*, *58*, *70*), 25.39 (*48*), 22.39, 22.16 (*33*, *68*), 10.34, 10.00 (*34*, *69*) ppm.



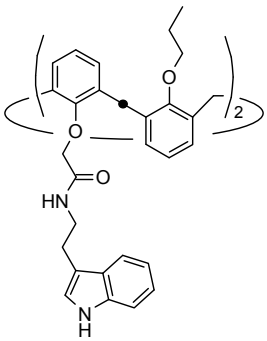
Bisindole-bridged calixarene ***8*** was prepared according to *General procedure C* from calixarene **3** (0.210 g, 0.186 mmol), TFA (18.6 ml), DDQ (0.046 g, 0.205 mmol), and 1,4-dioxane (20 ml); purified by chromatography. Yield 0.16 g (76%), beige solid. M.p. 228–230 °C (decomp.); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.73 (s, 2H; NH_{Ind}), 7.87 (bs, 2H; C(O)NH), 7.73–7.70 (m, 2H; ArH_{Ind}), 7.49–7.45 (m, 2H; ArH_{Ind}), 7.27–7.23 (m, 2H; ArH_{Ind}), 7.18–7.15 (m, 2H; ArH_{Ind}), 6.96 (s, 4H; ArH), 6.47 (s, 4H; ArH), 4.22 (s, 4H; OCH_2CO), 4.13 (d, 4H, $^{2}J_{HH}$ = 12.8 Hz; $ArCH_2Ar$), 3.77–3.72 (m, 4H; NCH_2), 3.46–3.42 (m, 4H; OCH_2), 3.26–3.22 (m, 4H; $IndCH_2$), 3.06 (d, 4H, $^{2}J_{HH}$ = 12.8 Hz; $ArCH_2Ar$), 1.41–1.34 (m, 4H; $OCH_2C\underline{H}_2$), 1.21 (s, 18H; $C(CH_3)_3$), 0.83 (s, 18H; $C(CH_3)_3$), 0.69 (t, 6H, $^{3}J_{HH}$ = 7.4 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.66 (C=O), 150.76, 145.65, 144.84 (C_{Ar}), 136.29 ($C_{Ar\ Ind}$), 133.77, 132.22 (C_{Ar}), 127.92, 127.34 ($C_{Ar\ Ind}$), 126.00, 124.83 (CH_{Ar}), 122.75, 119.83, 118.81 ($CH_{Ar\ Ind}$), 111.82 ($C_{Ar\ Ind}$), 111.42 ($CH_{Ar\ Ind}$), 77.00, 74.07 (OCH_2), 39.78 (NCH_2), 33.91, 33.61 ($\underline{C}(CH_3)_3$), 31.44 ($C(\underline{C}H_3)_3$), 31.27 ($ArCH_2Ar$), 31.09 ($C(\underline{C}H_3)_3$), 24.91 ($IndCH_2$), 21.98 ($OCH_2\underline{C}H_2$), 10.03 (CH_3); ESI-MS *m*/*z*: 1153.6729 $[M+Na]^+$ for $C_{74}H_{90}NaN_4O_6$ (1153.6753).



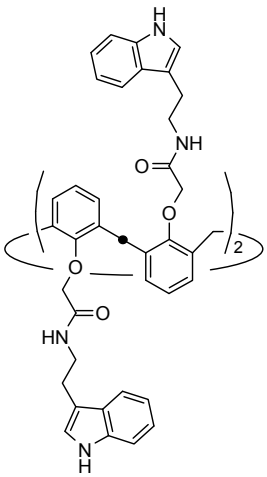
Bisindole-bridged calixarene ***9*** was prepared according to *General procedure C* from calixarene **5** (0.200 g, 0.191 mmol), TFA (19.1 ml), DDQ (0.047 g, 0.210 mmol), and 1,4-dioxane (20 ml); purified by crystallization. Yield 0.13 g (65%), beige solid. M.p. 258–260 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (s, 2H; NH_{Ind}), 7.79 (t, 2H, $^{3}J_{HH}$ = 6.3 Hz; C(O)NH), 7.75–7.71 (m, 2H; ArH_{Ind}), 7.31–7.24 (m, 4H; ArH_{Ind}), 7.19–7.14 (m, 2H; ArH_{Ind}), 7.02 (s, 4H; ArH), 6.60 (s, 4H; ArH), 5.83 (s, 2H; OH), 4.32 (s, 4H; OCH_2CO), 3.75 (d, 4H, $^{2}J_{HH}$ = 13.4 Hz; $ArCH_2Ar$), 3.70–3.62 (m, 4H; NCH_2), 3.20–3.14 (m, 4H; $IndCH_2$), 3.09 (d, 4H, $^{2}J_{HH}$ = 13.4 Hz; $ArCH_2Ar$), 1.32 (s, 18H; $C(CH_3)_3$), 0.83 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.56 (C=O), 149.40, 149.01, 147.68, 142.79 (C_{Ar}), 136.11 ($C_{Ar\ Ind}$), 131.51 (C_{Ar}), 128.50 ($C_{Ar\ Ind}$), 128.26 (C_{Ar}), 126.47 ($C_{Ar\ Ind}$), 125.77, 125.39 (CH_{Ar}), 122.75, 119.97, 119.12 ($CH_{Ar\ Ind}$), 112.85 ($C_{Ar\ Ind}$), 111.36 ($CH_{Ar\ Ind}$), 74.30 (OCH_2), 40.11 (NCH_2), 33.90, 33.80 ($\underline{C}(CH_3)_3$), 31.63 ($C(\underline{C}H_3)_3$), 31.06 ($ArCH_2Ar$), 30.78 ($C(\underline{C}H_3)_3$), 24.78 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1047.5964 $[M+H]^+$ for $C_{68}H_{79}N_4O_6$ (1047.5994).



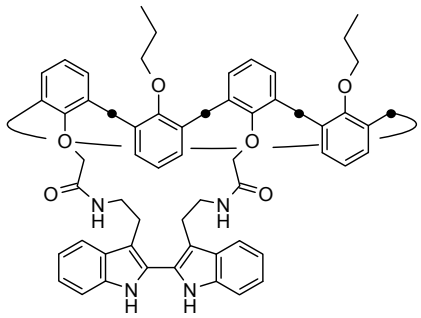
*Bisindole-bridged calixarene **10*** was prepared according to *General procedure C* from calixarene **6**[S3] (0.100 g, 0.086 mmol), TFA (8.6 ml), DDQ (0.021 g, 0.095 mmol), and 1,4-dioxane (10 ml); purified by crystallization. Yield 0.065 g (65%), white solid. M.p. 253–255 °C (decomp.); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.62 (s, 2H; NH_{Ind}), 7.87 (bs, 2H; C(O)NH), 7.72–7.69 (m, 2H; ArH_{Ind}), 7.23–7.15 (m, 6H; ArH_{Ind}), 7.07 (d, 2H, $^4J_{HH}$ = 2.3 Hz; ArH), 6.96 (d, 2H, $^4J_{HH}$ = 2.3 Hz; ArH), 6.62 (d, 2H, $^4J_{HH}$ = 2.3 Hz; ArH), 6.54 (d, 2H, $^4J_{HH}$ = 2.3 Hz; ArH), 5.79 (s, 2H; OH), 5.03–4.96 (m, 2H; CHCO), 4.37 (d, 2H, $^2J_{HH}$ = 14.4 Hz; OCH_2CO), 4.19 (d, 2H, $^2J_{HH}$ = 14.4 Hz; OCH_2CO), 4.02 (d, 2H, $^2J_{HH}$ = 13.3 Hz; $ArCH_2Ar$), 3.65 (d, 2H, $^2J_{HH}$ = 13.6 Hz; $ArCH_2Ar$), 3.64 (dd, 2H, $^2J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 7.5 Hz; $IndCH_2$), 3.48 (dd, 2H, $^2J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 7.5 Hz; $IndCH_2$), 3.42 (s, 6H; OCH_3), 3.17 (d, 2H, $^2J_{HH}$ = 13.3 Hz; $ArCH_2Ar$), 3.03 (d, 2H, $^2J_{HH}$ = 13.6 Hz; $ArCH_2Ar$), 1.34 (s, 18H; $C(CH_3)_3$), 0.82 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.67, 168.08 (C=O), 149.52, 149.23, 147.36, 142.38 (C_{Ar}), 136.21 ($C_{Ar\ Ind}$), 131.43, 131.40, 128.24 (C_{Ar}), 128.07, 127.78 ($C_{Ar\ Ind}$), 127.36 (C_{Ar}), 126.13, 125.51, 125.41, 125.30 (CH_{Ar}), 123.06, 120.18, 118.92, 111.62 ($CH_{Ar\ Ind}$), 109.81 ($C_{Ar\ Ind}$), 74.22 (OCH_2), 52.35 (OCH_3), 52.19 (NCH), 33.86, 33.77 ($\underline{C}(CH_3)_3$), 31.66 ($C(\underline{C}H_3)_3$), 31.15, 31.00 ($ArCH_2Ar$), 30.79 ($C(\underline{C}H_3)_3$), 27.01 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1163.6057 $[M+H]^+$ for $C_{72}H_{83}N_4O_{10}$ (1163.6104).



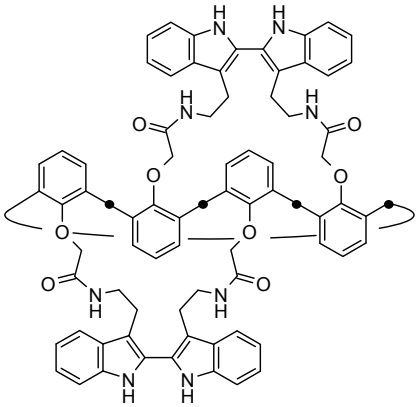
*Calixarene amide **13*** was prepared according to *General procedure A* from acid **11**[S4] (0.187 g, 0.30 mmol), $SOCl_2$ (5 ml), dry benzene (5 ml), tryptamine (0.192 g, 1.20 mmol), Et_3N (0.334 ml, 2.40 mmol), water (0.2 ml), and THF (20 ml); purified by chromatography. Yield 0.215 g (79%), white solid. M.p. 117–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (s, 2H; NH_{Ind}), 7.71–7.64 (m, 2H; ArH_{Ind}), 7.37–7.31 (m, 2H; ArH_{Ind}), 7.23–7.16 (m, 2H; ArH_{Ind}), 7.14–7.08 (m, 2H; ArH_{Ind}), 7.04 (d, 4H, $^3J_{HH}$ = 7.6 Hz; ArH), 6.87–6.84 (m, 2H; ArH_{Ind}), 6.78 (t, 2H, $^3J_{HH}$ = 7.6 Hz; ArH), 6.71 (d, 4H, $^3J_{HH}$ = 7.4 Hz; ArH), 6.67 (t, 2H, $^3J_{HH}$ = 6.0 Hz; C(O)NH), 6.34 (t, 2H, $^3J_{HH}$ = 7.4 Hz; ArH), 3.77 (s, 4H; OCH_2CO), 3.65 (d, 4H, $^2J_{HH}$ = 14.6 Hz; $ArCH_2Ar$), 3.63–3.54 (m, 8H; NCH_2+$OC\underline{H}_2CH_2$), 3.47 (d, 4H, $^2J_{HH}$ = 14.6 Hz; $ArCH_2Ar$), 3.09 (t, 4H, $^3J_{HH}$ = 7.3 Hz; $IndCH_2$), 1.75–1.62 (m, 4H; $OCH_2C\underline{H}_2$), 0.92 (6H, $^3J_{HH}$ = 7.4 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.95 (C=O), 157.24, 153.86 (C_{Ar}), 136.34 ($C_{Ar\ Ind}$), 134.34, 133.14 (C_{Ar}), 131.22, 130.15 (CH_{Ar}), 127.54 ($C_{Ar\ Ind}$), 122.60, 122.10 ($CH_{Ar\ Ind}$), 121.83, 121.36 (CH_{Ar}), 119.43, 118.73 ($CH_{Ar\ Ind}$), 113.08 ($C_{Ar\ Ind}$), 111.28 ($CH_{Ar\ Ind}$), 73.35, 70.20 (OCH_2), 40.12 (NCH_2), 36.81 ($ArCH_2Ar$), 25.36 ($IndCH_2$), 23.32 ($OCH_2\underline{C}H_2$), 10.16 (CH_3) ppm; ESI-MS *m*/*z*: 909.4563 $[M+H]^+$ for $C_{58}H_{61}N_4O_6$ (909.4586).



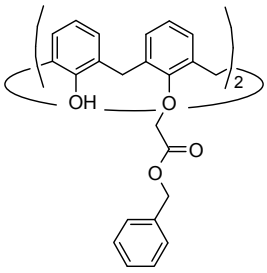
Calixarene amide ***14*** was prepared according to *General procedure A* from acid **12**[S5] (0.164 g, 0.25 mmol), $SOCl_2$ (2.5 ml), dry benzene (2.5 ml), tryptamine (0.320 g, 2.00 mmol), Et_3N (0.556 ml, 4.00 mmol), and THF (10 ml); the solid obtained after concentration of the reaction mixture was washed with washed with 2 M HCl, water, methanol. and dried. Yield 0.241 g (78%), white solid. M.p. 257–259 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.82 (bs, 4H; NH_{Ind}), 7.57–7.54 (m, 4H; ArH_{Ind}), 7.36–7.32 (m, 4H; ArH_{Ind}), 7.1–7.11 (m, 4H; ArH_{Ind}), 7.08–7.04 (m, 4H; ArH_{Ind}), 6.97 (d, 8H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.97–6.94 (m, 4H; ArH_{Ind}), 6.65 (t, 4H, $^3J_{HH}$ = 5.9 Hz; NH), 6.57 (t, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 3.81 (s, 8H; $ArCH_2Ar$), 3.79 (s, 8H; OCH_2), 3.35–3.28 (m, 8H; NCH_2), 2.86–2.81 (m, 8H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.83 (C=O), 154.85 (C_{Ar}), 136.29 ($C_{Ar\ Ind}$), 134.04 (C_{Ar}), 129.92 (CH_{Ar}), 127.25 ($C_{Ar\ Ind}$), 122.78 (CH_{Ar}), 122.62, 120.96, 118.27, 111.77 ($CH_{Ar\ Ind}$), 111.42 ($C_{Ar\ Ind}$), 69.76 (OCH_2), 48.61 (NCH_2), 36.07 ($ArCH_2Ar$), 25.07 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1225.5508 $[M+H]^+$ for $C_{76}H_{73}N_8O_8$ (1225.5546).



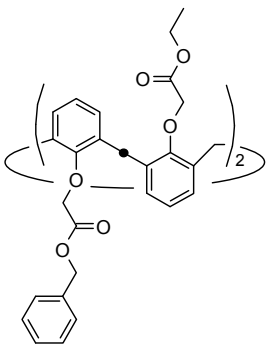
Bisindole-bridged calixarene ***15*** was prepared according to *General procedure C* from calixarene **13** (0.073 g, 0.080 mmol), TFA (8 ml), DDQ (0.020 g, 0.088 mmol), and 1,4-dioxane (10 ml); purified by crystallization. Yield 0.053 g (73%), beige solid. M.p. 234–236 °C (decomp.); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.66 (s, 2H; NH_{Ind}), 7.82–7.76 (m, 2H; ArH_{Ind}), 7.44–7.39 (m, 2H; ArH_{Ind}), 7.29–7.23 (m, 2H; ArH_{Ind}), 7.22–7.16 (m, 2H; ArH_{Ind}), 6.97 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.73 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.30 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.25 (bs, 2H; C(O)NH), 5.99 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 4.11 (s, 4H; OCH_2CO), 3.56–3.50 (m, 4H, $OC\underline{H}_2CH_2$) 3.51 (d, 4H, $^2J_{HH}$ = 14.2 Hz; $ArCH_2Ar$), 3.47–3.39 (m, 4H; NCH_2), 3.26 (d, 4H, $^2J_{HH}$ = 14.2 Hz; $ArCH_2Ar$), 3.14 (t, 4H, $^3J_{HH}$ = 7.1 Hz; $IndCH_2$), 1.77–1.65 (m, 4H; $OCH_2C\underline{H}_2$), 0.91 (6H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.05 (C=O), 156.92, 153.54 (C_{Ar}), 136.17 ($C_{Ar\ Ind}$), 133.94, 133.02 (C_{Ar}), 131.11, 130.50 (CH_{Ar}), 128.73, 125.98 ($C_{Ar\ Ind}$), 123.21, 122.68 ($CH_{Ar\ Ind}$), 120.09 (CH_{Ar}), 119.52 ($CH_{Ar\ Ind}$), 114.71 ($C_{Ar\ Ind}$), 111.56 ($CH_{Ar\ Ind}$), 73.32, 69.82 (OCH_2), 41.21 (NCH_2), 36.51 ($ArCH_2Ar$), 24.53 ($IndCH_2$), 23.57 ($OCH_2\underline{C}H_2$), 10.19 (CH_3) ppm; ESI-MS *m*/*z*: 907.4398 $[M+H]^+$ for $C_{58}H_{59}N_4O_{60}$ (907.4429).



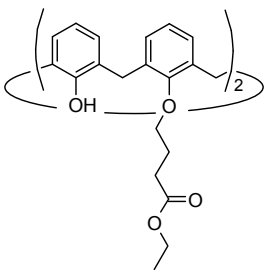
Bisindole-bridged calixarene ***16*** was prepared according to *General procedure C* from calixarene **14** (0.076 g, 0.062 mmol), TFA (6.2 ml), DDQ (0.038 g, 0.167 mmol), and 1,4-dioxane (8 ml); the solid formed at the oxidation step was collected, washed with dioxane, and dried. Yield 0.051 g (67%), beige solid. M.p. > 300 °C; ^{1}H NMR (600 MHz, DMSO-d_6, 85 °C): δ = 11.15 (bs, 4H; NH_{Ind}), 7.72–7.68 (m, 4H; ArH_{Ind}), 7.42–7.38 (m, 4H; ArH_{Ind}), 7.18–7.11 (m, 8H; ArH_{Ind}), 6.43 (d, 8H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.18 (t, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 5.74 (t, 4H, $^{3}J_{HH}$ = 5.8 Hz; NH), 4.05(s, 8H; OCH_2), 3.41 (s, 8H; $ArCH_2Ar$), 3.40–3.35 (m, 8H; NCH_2), 3.09–3.05 (m, 8H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.76 (C=O), 153.63 (C_{Ar}), 136.09 ($C_{Ar\ Ind}$), 133.35 (C_{Ar}), 130.44 (CH_{Ar}), 128.32, 126.96 ($C_{Ar\ Ind}$), 121.94 (CH_{Ar}), 121.25, 119.00, 118.54, 112.53 ($CH_{Ar\ Ind}$), 111.66 ($C_{Ar\ Ind}$), 69.45 (OCH_2), 40.59 (NCH_2), 35.14 ($ArCH_2Ar$), 24.36 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1221.5192 $[M+H]^+$ for $C_{76}H_{69}N_8O_8$ (1221.5233). Crystallographic data: space group C2/c, *a*(Å) = 30.104(3), *b*(Å) = 23.487(2), *c*(Å) = 26.090(4), β(°) = 121.5570(10), *V*(Å^3) 15720(3), *Z* = 8, no. of collected/unique reflections 63317/15461, GOOF 1.034, R1 = 0.1640, wR2 = 0.3643, ρ_{max}/ρ_{min} (e/Å^3) 0.834/–0.598, CCDC 1866294.



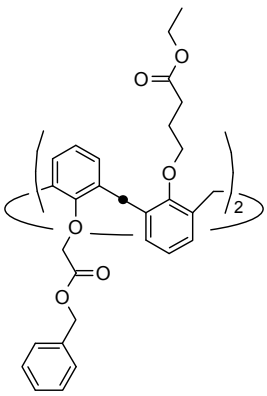
Calixarene dibenzyl ester ***21***. Benzyl alcohol (2.99 ml, 28.9 mmol) was added to a stirred suspension of calixarene **20**[S6] (1.56 g, 2.89 mmol) and *p*-toluenesulfonic acid monohydrate (0.110 g, 0.58 mmol) in toluene (60 ml). The reaction mixture was heated at 50 °C (oil bath) for 15 h. After cooling, the solvent was removed under reduced pressure, and the residue was purified by a short column chromatography (CH_2Cl_2) followed by crystallization from diethyl ether. Yield 1.72 g (83%), white needles. M.p. 135–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 2H; OH), 7.41–7.28 (m, 10H; ArH_{Ph}), 7.02 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.88 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.73 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.64 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 5.26 (s, 4H; CH_2Ph), 4.75 (s, 4H; CH_2CO), 4.45 (d, 4H, $^{2}J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 3.36 (d, 4H, $^{2}J_{HH}$ = 13.1 Hz; $ArCH_2Ar$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.59 (C=O), 152.88, 152.23 (C_{Ar}), 135.06 ($C_{Ar\ Ph}$), 132.92 (C_{Ar}), 129.07 (CH_{Ar}), 128.50, 128.39 ($CH_{Ar\ Ph}$), 128.04 (C_{Ar}), 125.51, 119.03 (CH_{Ar}), 72.31 (OCH_2CO), 66.95 (CH_2Ph), 31.40 ($ArCH_2Ar$) ppm; ESI-MS *m*/*z*: 738.3081 $[M+NH_4]^+$ for $C_{46}H_{44}NO_8$ (738.3067). Crystallographic data: space group $P2_1/n$, *a*(Å) = 10.1647(9), *b*(Å) = 17.2468(15), *c*(Å) = 20.8692(18), β(°) = 101.136(2), *V*(Å^3) = 3589.7(5), *Z* = 4, no. of collected/unique reflections 26578/8662, GOOF 1.020, R1 = 0.0432, wR2 = 0.0905, ρ_{max}/ρ_{min} (e/Å^3) 0.245/–0.219, CCDC 1866292.



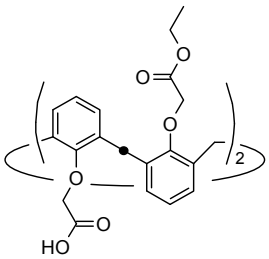
*Calixarene dibenzyl/diethyl ester **22**.* A mixture of calixarene **21** (1.08 g, 1.50 mmol), Cs_2CO_3 (2.45 g, 7.50 mmol) and dry acetone (30 ml) was stirred at room temperature for 24 h. Ethyl bromoacetate (1.00 ml, 9.00 mmol) was added and the mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure, 2 M HCl was added and the products were extracted by CH_2Cl_2. The solution was washed with water, dried and concentrated. The residue was purified by column chromatography (gradient from hexane to hexane/ethyl acetate 3:1), the product-containing fractions were combined, concentrated, and the residue was dissolved in a minimum amount of CH_2Cl_2. Hexane was added and the solid formed was collected, washed with hexane, and dried. Yield 0.320 g (24%), white crystals. M.p. 150–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.30 (m, 10H; ArH_{Ph}), 7.12 (d, 4H, $^3J_{HH}$ = 7.6 Hz; ArH), 7.07 (d, 4H, $^3J_{HH}$ = 7.6 Hz; ArH), 6.70 (t, 2H, $^3J_{HH}$ = 7.6 Hz; ArH), 6.55 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 5.18 (s, 4H; $PhCH_2$), 4.23 (q, 4H, $^3J_{HH}$ = 7.2 Hz; $OC\underline{H}_2CH_3$), 4.03 (s, 4H; OCH_2CO), 3.96 (s, 4H; OCH_2CO), 3.76 (bs, 8H; $ArCH_2Ar$), 1.31 (t, 6H, $^3J_{HH}$ = 7.2 Hz; CH_3) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.54, 169.40 (C=O), 155.51, 155.30 (C_{Ar}), 135.32 ($C_{Ar\ Ph}$), 133.58, 133.52 (C_{Ar}), 130.40, 130.29 (CH_{Ar}), 128.59, 128.48, 128.44 ($CH_{Ar\ Ph}$), 123.00, 122.92 (CH_{Ar}), 69.50, 69.44 ($O\underline{C}H_2CO$), 66.47 ($PhCH_2$), 60.72 ($O\underline{C}H_2CH_3$), 35.65 ($ArCH_2Ar$), 14.14 (CH_3) ppm; ESI-MS *m*/*z*: 910.3799 $[M+NH_4]^+$ for $C_{54}H_{56}NO_{12}$ (910.3803).



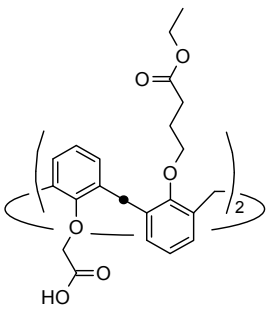
*Calixarene diethyl ester **24**.* A mixture of calixarene **23**[S7] (3.18 g, 7.50 mmol) and K_2CO_3 (2.28 g, 16.52 mmol) in dry acetonitrile (150 ml) was stirred at reflux for 1 h and cooled. Ethyl 4-bromobutyrate (2.36 ml, 16.50 mmol) was added and the reaction mixture was stirred at reflux for 48 h. After cooling, the mixture was filtered, the solid was washed with CH_2Cl_2 and removed. The combined filtrates were concentrated under reduced pressure, and the residue was dissolved in a minimum amount of CH_2Cl_2. Ethanol was added and the solution was heated to reflux shortly. The solid formed at cooling the solution was collected, washed with cold ethanol and dried. Yield 1.91 g (39%), white crystals. M.p. 159–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 2H; OH), 8.95 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.90 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.74 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.65 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 4.25 (d, 4H, $^2J_{HH}$ = 13.0 Hz; $ArCH_2Ar$), 4.17 (q, 4H, $^3J_{HH}$ = 7.1 Hz; $OC\underline{H}_2CH_3$), 4.09–4.03 (m, 4H; $OC\underline{H}_2CH_2$), 3.38 (d, 4H, $^2J_{HH}$ = 13.0 Hz; $ArCH_2Ar$), 2.93–2.86 (m, 4H; CH_2CO), 2.40–2.30 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.25 (t, 6H, $^3J_{HH}$ = 7.1 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.29 (C=O), 153.23, 151.46, 133.23 (C_{Ar}), 128.97, 128.44 (CH_{Ar}), 127.91 (C_{Ar}), 125.46, 119.02 (CH_{Ar}), 75.25 ($O\underline{C}H_2CH_2$), 60.41 ($O\underline{C}H_2CH_3$), 31.34 ($ArCH_2Ar$), 30.60 ($\underline{C}H_2CO$), 25.42 ($CH_2\underline{C}H_2CH_2$), 14.20 (CH_3) ppm; ESI-MS *m*/*z*: 670.3385 $[M+NH_4]^+$ for $C_{40}H_{48}NO_8$ (670.3380).



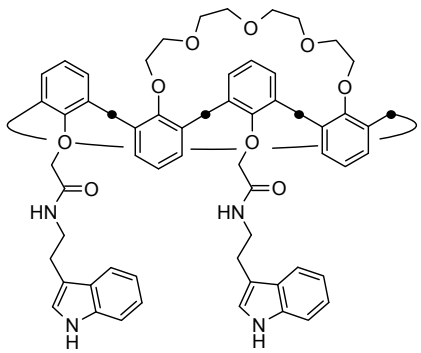
Calixarene dibenzyl/diethyl ester ***25***. A mixture of calixarene **24** (1.56 g, 2.40 mmol), Cs_2CO_3 (3.91 g, 12.00 mmol) and dry acetone (48 ml) was stirred at room temperature for 24 h. Benzyl bromoacetate (2.28 ml, 14.40 mmol) was added and the mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure, 2 M HCl was added and the products were extracted by CH_2Cl_2. The solution was washed with water, dried and concentrated. The product was purified by column chromatography (gradient from CH_2Cl_2 to CH_2Cl_2/ethanol 100:1). Yield 0.460 g (20%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.26 (m, 10H; ArH_{Ph}), 7.05 (d, 8H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.78 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.61 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 5.00 (s, 4H; $PhCH_2$), 4.16 (q, 4H, $^3J_{HH}$ = 7.2 Hz; $OC\underline{H}_2CH_3$), 3.96 (d, 4H, $^2J_{HH}$ = 15.3 Hz; $ArCH_2Ar$), 3.71 (d, 4H, $^2J_{HH}$ = 15.3 Hz; $ArCH_2Ar$), 3.64–3.56 (m, 4H; $OC\underline{H}_2CH_2$), 3.31 (s, 4H; OCH_2CO), 2.24–2.17 (m, 4H; $CH_2C\underline{H}_2CO$), 1.77–1.66 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.29 (t, 6H, $^3J_{HH}$ = 7.2 Hz, CH_3) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.32, 169.75 (C=O), 156.96, 154.97 (C_{Ar}), 135.51 ($C_{Ar\ Ph}$), 134.56, 133.83 (C_{Ar}), 130.35, 130.19 (CH_{Ar}), 128.45, 128.33, 128.25 ($CH_{Ar\ Ph}$), 122.92, 122.49 (CH_{Ar}), 70.04, 68.33 (OCH_2), 65.97 ($PhCH_2$), 60.23 ($O\underline{C}H_2CH_3$), 37.39 ($ArCH_2Ar$), 30.46 ($CH_2\underline{C}H_2CO$), 24.78 ($CH_2\underline{C}H_2CH_2$), 14.26 (CH_3) ppm; ESI-MS *m*/*z*: 966.4448 $[M+NH_4]^+$ for $C_{58}H_{64}NO_{12}$ (966.4429).



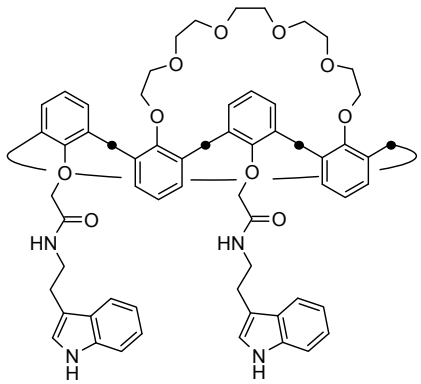
Calixarene ester/acid ***26***. A mixture of calixarene **22** (0.205 g, 0.230 mmol), Pd/C (10%, 0.0245 g, 0.023 mmol), and THF (10 ml) was degassed with a vacuum pump and hydrogenated (1 atm) at vigorous stirring for 24 h. The catalyst was filtered off, and the filtrate was concentrated to dryness. The residue was washed with hexane. Yield 0.159 g (97%), white solid. M.p. 229–231 °C; ^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD): δ = 7.09 (d, 4H, $^3J_{HH}$ = 7.6 Hz; ArH), 7.03 (d, 4H, $^3J_{HH}$ = 7.6 Hz; ArH), 6.84 (t, 2H, $^3J_{HH}$ = 7.6 Hz; ArH), 6.78 (t, 2H, $^3J_{HH}$ = 7.6 Hz; ArH), 4.10 (d, 4H, $^2J_{HH}$ = 16.2 Hz; $ArCH_2Ar$), 3.99 (q, 4H, $^3J_{HH}$ = 7.1 Hz; $OC\underline{H}_2CH_3$), 3.98 (s, 4H; OCH_2CO), 3.87 (d, 4H, $^2J_{HH}$ = 16.2 Hz; $ArCH_2Ar$), 3.41 (s, 4H; OCH_2CO), 1.13 (t, 6H, $^3J_{HH}$ = 7.1 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ = 170.02, 169.83 (C=O), 154.94, 154.26, 134.10, 133.46 (C_{Ar}), 130.31, 129.79, 124.06, 123.90 (CH_{Ar}), 68.05, 67.15 ($O\underline{C}H_2CO$), 60.38 ($O\underline{C}H_2CH_3$), 37.21 ($ArCH_2Ar$), 13.68 (CH_3) ppm; ESI-MS *m*/*z*: 730.2883 $[M+NH_4]^+$ for $C_{40}H_{44}NO_{12}$ (730.2864).



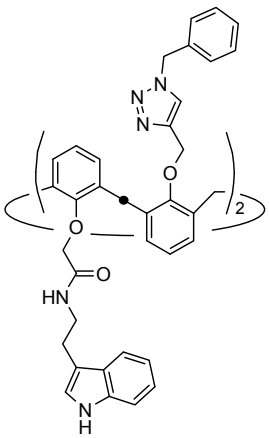
*Calixarene ester/acid **27*** was prepared as described for calixarene **26** from calixarene **26** (0.273 g, 0.288 mmol), Pd/C (10%, 0.0305 g, 0.0288 mmol), and THF (10 ml). Yield 0.212 g (96%), white solid. M.p. 196–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD): δ = 7.08 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 7.02 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.91 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.83 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 4.12 (q, 4H, $^{3}J_{HH}$ = 7.1 Hz; $OC\underline{H}_2CH_3$), 4.01 (s, 4H; OCH_2CO), 3.89 (d, 4H, $^{2}J_{HH}$ = 16.5 Hz; $ArCH_2Ar$), 3.84 (d, 4H, $^{2}J_{HH}$ = 16.5 Hz; $ArCH_2Ar$), 3.58–3.52 (m, 4H; $OC\underline{H}_2CH_2$), 2.01–1.94 (m, 4H; $CH_2C\underline{H}_2CO$), 1.59–1.49 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.27 (t, 6H, $^{3}J_{HH}$ = 7.1 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ = 173.64, 170.12 (C=O), 156.29, 153.78, 133.44, 133.41 (C_{Ar}), 129.58, 129.14, 123.60, 123.54 (CH_{Ar}), 68.89, 66.67 (OCH_2), 60.17 ($O\underline{C}H_2CH_3$), 37.57 ($ArCH_2Ar$), 30.13 ($CH_2\underline{C}H_2CO$), 24.68 ($CH_2\underline{C}H_2CH_2$), 14.05 (CH_3) ppm; ESI-MS *m*/*z*: 786.3509 $[M+NH_4]^+$ for $C_{44}H_{52}NO_{12}$ (786.3490).



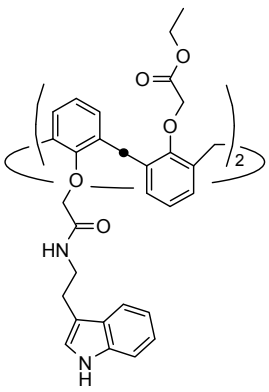
*Calixcrown amide **28*** was prepared according to *General procedure A* from acid **17**[S4] (0.105 g, 0.15 mmol), $SOCl_2$ (2.5 ml), dry benzene (2.5 ml), tryptamine (0.096 g, 0.60 mmol), Et_3N (0.167 ml, 1.20 mmol), water (0.2 ml), and THF (10 ml); purified by re-precipitation. Yield 0.123 g (83%), white solid. M.p. 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (bs, 2H; NH_{Ind}), 7.69–7.65 (m, 2H; ArH_{Ind}), 7.37–7.32 (m, 2H; ArH_{Ind}), 7.22–7.16 (m, 2H; ArH_{Ind}), 7.13 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 7.13–7.09 (m, 2H; ArH_{Ind}), 6.91 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.90 (bs, 2H; ArH_{Ind}), 6.74 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.50 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.26 (t, 2H, $^{3}J_{HH}$ = 6.1 Hz; C(O)NH), 3.74 (d, 4H, $^{2}J_{HH}$ = 15.8 Hz; $ArCH_2Ar$), 3.72 (s, 4H; CH_2CO), 3.64 (d, 4H, $^{2}J_{HH}$ = 15.8 Hz; $ArCH_2Ar$), 3.58 (bs, 8H; OCH_2CH_2O), 3.54–3.49 (m, 4H; OCH_2CH_2O), 3.42–3.34 (m, 4H; NCH_2), 3.32–3.28 (m, 4H; OCH_2CH_2O), 3.00–2.94 (m, 4H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.96 (C=O), 156.22, 154.86 (C_{Ar}), 136.30 ($C_{Ar\ Ind}$), 134.41, 133.48 (C_{Ar}), 130.43, 129.69 (CH_{Ar}), 127.51 ($C_{Ar\ Ind}$), 123.44, 122.85 (CH_{Ar}), 122.07, 121.85, 119.40, 118.79 ($CH_{Ar\ Ind}$), 113.15 ($C_{Ar\ Ind}$), 111.27 ($CH_{Ar\ Ind}$), 72.20, 70.71, 70.27, 69.94, 68.97 (OCH_2), 40.07 (NCH_2), 37.55 ($ArCH_2Ar$), 25.11 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1021.4123 $[M+K]^+$ for $C_{60}H_{62}KN_4O_9$ (1021.4148).



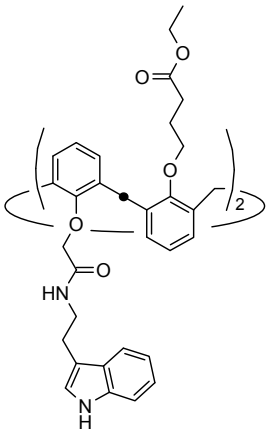
Calixcrown amide ***29*** was prepared according to *General procedure A* from acid **18**[S8] (0.111 g, 0.15 mmol), $SOCl_2$ (2.5 ml), dry benzene (2.5 ml), tryptamine (0.096 g, 0.60 mmol), Et_3N (0.167 ml, 1.20 mmol), water (0.2 ml), and THF (10 ml); purified by re-precipitation. Yield 0.129 g (84%), white solid. M.p. 119–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (bs, 2H; NH_{Ind}), 7.69–7.64 (m, 2H; ArH_{Ind}), 7.37–7.33 (m, 2H; ArH_{Ind}), 7.23–7.17 (m, 2H; ArH_{Ind}), 7.14 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 7.13–7.08 (m, 2H; ArH_{Ind}), 6.90–6.88 (m, 2H; ArH_{Ind}), 6.86 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.69 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.42 (t, 2H, $^3J_{HH}$ = 5.7 Hz; C(O)NH), 6.32 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 3.79 (s, 4H; CH_2CO), 3.75–3.70 (m, 12H; OCH_2CH_2O), 3.65 (d, 4H, $^2J_{HH}$ = 15.5 Hz; $ArCH_2Ar$), 3.65–3.63 (m, 4H; OCH_2CH_2O), 3.63–3.59 (m, 4H; OCH_2CH_2O), 3.57–3.52 (m, 4H; NCH_2), 3.50 (d, 4H, $^2J_{HH}$ = 15.5 Hz; $ArCH_2Ar$), 3.10–3.04 (m, 4H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.87 (C=O), 156.84, 154.04 (C_{Ar}), 136.31 ($C_{Ar\ Ind}$), 134.27, 133.19 (C_{Ar}), 131.19, 130.31 (CH_{Ar}), 127.50 ($C_{Ar\ Ind}$), 123.14 (CH_{Ar}), 122.09, 121.84, 119.41, 118.70 ($CH_{Ar\ Ind}$), 113.01 ($C_{Ar\ Ind}$), 111.30 ($CH_{Ar\ Ind}$), 71.45, 71.26, 71.00, 70.90, 70.17, 70.11 (OCH_2), 40.21 (NCH_2), 36.93 ($ArCH_2Ar$), 25.23 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1044.5095 $[M+NH_4]^+$ for $C_{62}H_{70}N_5O_{10}$ (1044.5117).



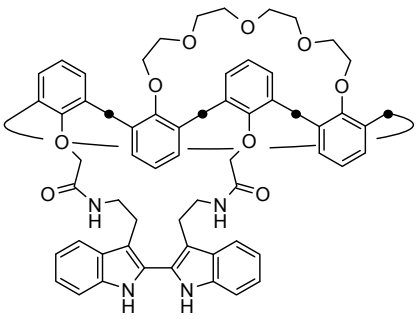
Triazolated calixarene amide ***30*** was prepared according to *General procedure A* from acid **19**[S9] (0.063 g, 0.071 mmol), $SOCl_2$ (1 ml), dry benzene (1 ml), tryptamine (0.045 g, 0.281 mmol), Et_3N (0.078 ml, 0.561 mmol), and THF (3 ml); purified by chromatography. Yield 0.035 g (42%), white solid. M.p. 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 2H; NH_{Ind}), 7.69–7.65 (m, 2H; ArH_{Ind}), 7.45–7.36 (m, 6H; ArH_{Ph}), 7.36–7.27 (m, 6H; ArH_{Ph}+ArH_{Ind}), 7.21–7.15 (m, 2H; ArH_{Ind}), 7.12–7.07 (m, 2H; ArH_{Ind}), 6.89–6.87 (m, 2H; ArH_{Ind}), 6.68 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.65 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.61 (s, 2H; ArH_{Trz}), 6.59 (t, 2H, $^3J_{HH}$ = 5.9 Hz; C(O)NH), 6.45 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.04 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 5.55 (s, 4H; NCH_2), 4.79 (s, 4H; OCH_2Trz), 3.55–3.47 (m, 4H; $NC\underline{H}_2CH_2$), 3.43 (s, 4H, OCH_2CO), 3.42 (d, 4H, $^2J_{HH}$ = 15.0 Hz; $ArCH_2Ar$), 3.37 (d, 4H, $^2J_{HH}$ = 15.0 Hz; $ArCH_2Ar$), 3.04–2.98 (m, 4H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.82 (C=O), 155.51, 154.02 (C_{Ar}), 144.29 ($C_{Ar\ Trz}$), 136.30 ($C_{Ar\ Ind}$), 134.94 ($C_{Ar\ Ph}$), 134.23, 133.23 (C_{Ar}), 130.83, 129.92 (CH_{Ar}), 129.06, 128.75, 127.95 ($CH_{Ar\ Ph}$), 127.47 ($C_{Ar\ Ind}$), 123.43 ($CH_{Ar\ Trz}$), 123.14, 122.71 (CH_{Ar}), 122.05, 121.85, 119.35, 118.73 ($CH_{Ar\ Ind}$), 113.07 ($C_{Ar\ Ind}$), 111.28 ($CH_{Ar\ Ind}$), 70.18 ($O\underline{C}H_2CO$), 64.24 (OCH_2Trz), 53.93 (NCH_2Ph), 39.86 ($N\underline{C}H_2CH_2$), 37.01 ($ArCH_2Ar$), 25.24 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1167.5271 $[M+H]^+$ for $C_{72}H_{67}N_{10}O_6$ (1167.5245).



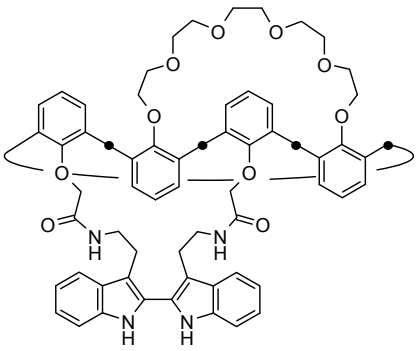
*Calixarene ester/amide **31*** was prepared according to *General procedure A* from acid **26** (0.110 g, 0.154 mmol), $SOCl_2$ (2 ml), dry benzene (2 ml), tryptamine (0.099 g, 0.616 mmol), Et_3N (0.171 ml, 1.232 mmol), and THF (10 ml); purified by chromatography. Yield 0.080 g (52%), white solid. M.p. 111–113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 2H; NH_{Ind}), 7.68–7.64 (m, 2H; ArH_{Ind}), 7.36–7.61 (m, 2H; ArH_{Ind}), 7.21–7.16 (m, 2H; ArH_{Ind}), 7.14 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 7.13–7.08 (m, 2H; ArH_{Ind}), 6.88–6.86 (m, 2H; ArH_{Ind}), 6.77 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.69 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.52 (t, 2H, $^3J_{HH}$ = 5.9 Hz; C(O)NH), 6.31 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 4.20 (q, 4H, $^3J_{HH}$ = 7.2 Hz; $OC\underline{H}_2CH_3$), 3.93 (s, 4H; OCH_2CO), 3.85 (d, 4H, $^2J_{HH}$ = 14.7 Hz; $ArCH_2Ar$), 3.75 (s, 4H; OCH_2CO), 3.63–3.55 (m, 4H; NCH_2), 3.47 (d, 4H, $^2J_{HH}$ = 14.7 Hz; $ArCH_2Ar$), 3.12–3.16 (m, 4H; $IndCH_2$), 1.32 (t, 6H, $^3J_{HH}$ = 7.2 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.26, 168.75 (C=O), 156.20, 154.13 (C_{Ar}), 136.33 ($C_{Ar\ Ind}$), 134.04, 133.23 (C_{Ar}), 131.17, 130.49 (CH_{Ar}), 127.48 ($C_{Ar\ Ind}$), 123.30 (CH_{Ar}), 122.09 ($CH_{Ar\ Ind}$), 121.87 (CH_{Ar}), 119.41, 118.64 ($CH_{Ar\ Ind}$), 112.94 ($C_{Ar\ Ind}$), 111.34 ($CH_{Ar\ Ind}$), 70.25, 69.20 ($O\underline{C}H_2CO$), 60.79 ($O\underline{C}H_2CH_3$), 40.17 (NCH_2), 36.45 ($ArCH_2Ar$), 25.24 ($IndCH_2$), 14.12 (CH_3) ppm; ESI-MS *m*/*z*: 1019.4218 $[M+Na]^+$ for $C_{60}H_{60}NaN_4O_{10}$ (1019.4207).



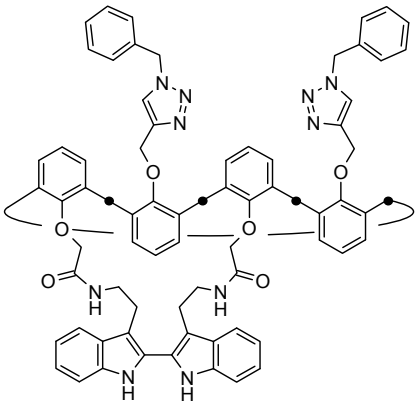
*Calixarene ester/amide **32*** was prepared according to *General procedure A* from acid **27** (0.104 g, 0.135 mmol), $SOCl_2$ (2 ml), dry benzene (2 ml), tryptamine (0.086 g, 0.540 mmol), Et_3N (0.150 ml, 1.080 mmol), and THF (10 ml); purified by chromatography. Yield 0.074 g (52%), white solid. M.p. 90–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 2H; NH_{Ind}), 7.69–7.65 (m, 2H; ArH_{Ind}), 7.36–7.32 (m, 2H; ArH_{Ind}), 7.21–7.16 (m, 2H; ArH_{Ind}), 7.13–7.08 (m, 2H; ArH_{Ind}), 7.07 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.87–6.84 (m, 2H; ArH_{Ind}), 6.81 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.70 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.51 (t, 2H, $^3J_{HH}$ = 5.9 Hz; C(O)NH), 6.36 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 4.20 (q, 4H, $^3J_{HH}$ = 7.1 Hz; $OC\underline{H}_2CH_3$), 3.73 (s, 4H; OCH_2CO), 3.66–3.60 (m, 4H; $OC\underline{H}_2CH_2$), 3.64 (d, 4H, $^2J_{HH}$ = 15.2 Hz; $ArCH_2Ar$), 3.59–3.52 (m, 4H; NCH_2), 3.50 (d, 4H, $^3J_{HH}$ = 15.2 Hz; $ArCH_2Ar$), 3.10–3.04 (m, 4H; $IndCH_2$), 2.33–2.27 (m, 4H; $CH_2C\underline{H}_2CO$), 1.99–1.89 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.32 (t, 6H, $^3J_{HH}$ = 7.1 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.29, 168.88 (C=O), 156.84, 154.00 (C_{Ar}), 136.29 ($C_{Ar\ Ind}$), 134.20, 133.27 (C_{Ar}), 130.95, 130.08 (CH_{Ar}), 127.45 ($C_{Ar\ Ind}$), 122.71 (CH_{Ar}), 122.01, 121.85 ($CH_{Ar\ Ind}$), 121.76 (CH_{Ar}), 119.33, 118.65 ($CH_{Ar\ Ind}$), 112.90 ($C_{Ar\ Ind}$), 111.28 ($CH_{Ar\ Ind}$), 70.08, 70.03 (OCH_2), 60.38 ($O\underline{C}H_2CH_3$), 40.14 (NCH_2), 36.90 ($ArCH_2Ar$), 30.27 ($CH_2\underline{C}H_2CO$), 25.22, 25.15 ($CH_2\underline{C}H_2CH_2$, $IndCH_2$), 14.24 (CH_3) ppm; ESI-MS *m*/*z*: 1053.5033 $[M+H]^+$ for $C_{64}H_{69}N_4O_{10}$ (1053.5014).



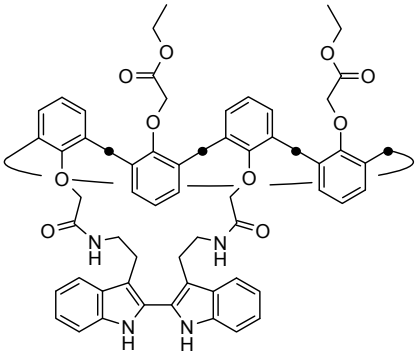
Bisindole-bridged calixcrown ***33*** was prepared according to *General procedure C* from calixarene **28** (0.059 g, 0.060 mmol), TFA (6 ml), DDQ (0.015 g, 0.066 mmol), and 1,4-dioxane (4 ml); purified by crystallization. Yield 0.036 g (60%), beige solid. M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (bs, 2H; NH_{Ind}), 7.89–7.84 (m, 2H; ArH_{Ind}), 7.46–7.41 (m, 2H; ArH_{Ind}), 7.32–7.27 (m, 2H; ArH_{Ind}), 7.27–7.22 (m, 2H; ArH_{Ind}), 7.12 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.87 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.44 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.13 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 5.87 (t, 2H, $^{3}J_{HH}$ = 5.6 Hz; C(O)NH), 4.11 (s, 4H; CH_2CO), 3.63 (d, 4H, $^{2}J_{HH}$ = 15.1 Hz; $ArCH_2Ar$), 3.58–3.52 (m, 8H; OCH_2CH_2O), 3.50–3.46 (m, 8H; OCH_2CH_2O), 3.48 (d, 4H, $^{2}J_{HH}$ = 15.1 Hz; $ArCH_2Ar$), 3.46–3.40 (m, 4H; NCH_2), 3.20–3.14 (m, 4H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.01 (C=O), 156.05, 154.38 (C_{Ar}), 136.26 ($C_{Ar\ Ind}$), 134.20, 133.35 (C_{Ar}), 130.87, 130.59 (CH_{Ar}), 128.61, 126.23 ($C_{Ar\ Ind}$), 123.49, 123.12 (CH_{Ar}), 121.03, 120.05, 119.49 ($CH_{Ar\ Ind}$), 114.15 ($C_{Ar\ Ind}$), 111.53 ($CH_{Ar\ Ind}$), 70.93, 70.73, 70.50, 70.28, 70.17 (OCH_2), 41.05 (NCH_2), 37.02 ($ArCH_2Ar$), 24.44 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1019.3962 $[M+K]^+$ for $C_{60}H_{60}KN_4O_9$ (1019.3992).



Bisindole-bridged calixcrown ***34*** was prepared according to *General procedure C* from calixarene **29** (0.061 g, 0.060 mmol), TFA (6 ml), DDQ (0.015 g, 0.066 mmol), and 1,4-dioxane (5 ml); purified by crystallization. Yield 0.036 g (60%), beige solid. M.p. 223–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (bs, 2H; NH_{Ind}), 7.86–7.82 (m, 2H; ArH_{Ind}), 7.44–7.40 (m, 2H; ArH_{Ind}), 7.31–7.25 (m, 2H; ArH_{Ind}), 7.26–7.21 (m, 2H; ArH_{Ind}), 7.10 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.82 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.35 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.04 (bs, 2H; C(O)NH), 6.01 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 4.14 (s, 4H; CH_2CO), 3.76–3.61 (m, 20H; OCH_2CH_2O), 3.54 (d, 4H, $^{2}J_{HH}$ = 14.5 Hz; $ArCH_2Ar$), 3.51–3.43 (m, 4H; NCH_2), 3.34 (d, 4H, $^{2}J_{HH}$ = 14.5 Hz; $ArCH_2Ar$), 3.23–3.16 (m, 4H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.01 (C=O), 156.57, 153.63 (C_{Ar}), 136.19 ($C_{Ar\ Ind}$), 133.87, 133.01 (C_{Ar}), 131.17, 130.71 (CH_{Ar}), 128.67, 126.08 ($C_{Ar\ Ind}$), 123.15 (CH_{Ar}), 120.40, 120.04, 119.45 ($CH_{Ar\ Ind}$), 114.42 ($C_{Ar\ Ind}$), 111.60 ($CH_{Ar\ Ind}$), 71.70, 71.36, 71.34, 70.70, 70.35, 69.83 (OCH_2), 41.25 (NCH_2), 36.51 ($ArCH_2Ar$), 24.50 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1042.4927 $[M+NH_4]^+$ for $C_{62}H_{68}N_5O_{10}$ (1042.4961).

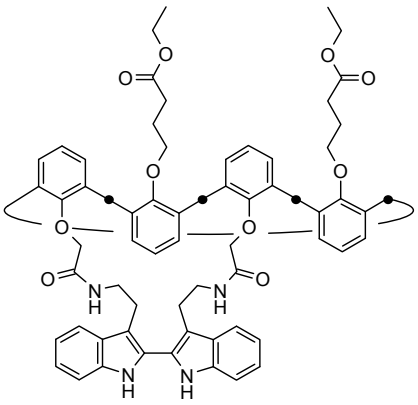


Bisindole-bridged triazolated calixarene ***35*** was prepared according to *General procedure C* from calixarene **30** (0.035 g, 0.030 mmol), TFA (3 ml), DDQ (0.008 g, 0.035 mmol), and 1,4-dioxane (5 ml); purified by chromatography. Yield 0.029 g (84%), beige solid. M.p. 189–191 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (s, 2H; NH_{Ind}), 7.78–7.35 (m, 2H; ArH_{Ind}), 7.45–7.36 (m, 8H; ArH_{Ph}+ArH_{Ind}), 7.31–7.27 (m, 4H; ArH_{Ph}), 7.27–7.22 (m, 2H; ArH_{Ind}), 7.19–7.13 (m, 2H; ArH_{Ind}), 6.79 (s, 2H; ArH_{Trz}), 6.59 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.27 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.08 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 5.97 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 5.95 (bs, 2H; C(O)NH), 5.51 (s, 4H; NCH_2), 4.75 (s, 4H; OCH_2Trz), 4.00 (s, 4H; OCH_2CO), 3.39–3.31 (m, 4H; $NC\underline{H}_2CH_2$), 3.28 (d, 4H, $^{2}J_{HH}$ = 14.8 Hz; $ArCH_2Ar$), 3.16 (d, 4H, $^{2}J_{HH}$ = 14.8 Hz; $ArCH_2Ar$), 3.10–3.04 (m, 4H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.88 (C=O), 155.26, 153.54 (C_{Ar}), 144.60 ($C_{Ar\ Trz}$), 136.16 ($C_{Ar\ Ind}$), 134.87 ($C_{Ar\ Ph}$), 134.27, 132.86 (C_{Ar}), 130.83, 130.33 (CH_{Ar}), 129.16, 128.85 ($CH_{Ar\ Ph}$), 128.62 ($C_{Ar\ Ind}$), 128.05 ($CH_{Ar\ Ph}$), 126.08 ($C_{Ar\ Ind}$), 123.24 ($CH_{Ar\ Trz}$), 123.16, 122.51 (CH_{Ar}), 121.21, 120.05, 119.45 ($CH_{Ar\ Ind}$), 114.28 ($C_{Ar\ Ind}$), 111.55 ($CH_{Ar\ Ind}$), 69.75 ($O\underline{C}H_2CO$), 64.25 (OCH_2Trz), 54.03 (NCH_2Ph), 41.06 ($N\underline{C}H_2CH_2$), 36.41 ($ArCH_2Ar$), 24.46 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1165.5103 $[M+H]^+$ for $C_{72}H_{65}N_{10}O_6$ (1165.5089). Crystallographic data: space group $P2_1/c$, *a*(Å) = 16.5782(11), *b*(Å) = 28.2895(19), *c*(Å) = 17.3002(11), β(°) = 93.414(2), *V*(Å^3) = 8099.2(9), *Z* = 4, no. of collected/unique reflections 69052/14960, GOOF 1.472, R1 = 0.1582, wR2 = 0.4204, ρ_{max}/ρ_{min} (e/Å^3) 1.591/–0.780, CCDC 1866293.

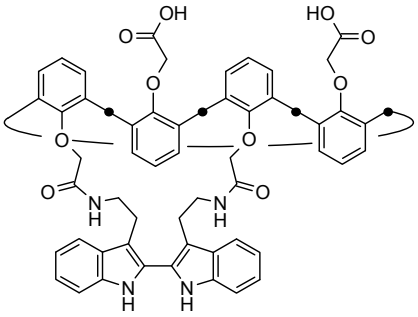


Bisindole-bridged calixarene ester ***36*** was prepared according to *General procedure C* from calixarene **31** (0.080 g, 0.080 mmol), TFA (8 ml), DDQ (0.020 g, 0.088 mmol), and 1,4-dioxane (8 ml); purified by chromatography. Yield 0.055 g (69%), beige solid. M.p. 190–192 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.16 (s, 2H; NH_{Ind}), 7.74–7.69 (m, 2H; ArH_{Ind}), 7.43–7.39 (m, 2H; ArH_{Ind}), 7.26–7.20 (m, 2H; ArH_{Ind}), 7.15–7.10 (m, 2H; ArH_{Ind}), 7.05 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.71 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.26 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 6.00 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz; ArH), 5.95 (bs, 2H; C(O)NH), 4.18 (q, 4H, $^{3}J_{HH}$ = 7.2 Hz; $OC\underline{H}_2CH_3$), 4.05 (s, 4H; OCH_2CONH), 3.72 (s, 4H; OCH_2CO_2), 3.65 (d, 4H, $^{2}J_{HH}$ = 14.6 Hz; $ArCH_2Ar$), 3.40–3.32 (m, 4H; NCH_2), 3.19 (d, 4H, $^{2}J_{HH}$ = 14.6 Hz; $ArCH_2Ar$), 3.12–3.05 (m, 4H; $IndCH_2$), 1.28 (t, 6H, $^{3}J_{HH}$ = 7.2 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.21, 168.89 (C=O), 155.75, 153.91 (C_{Ar}), 136.18 ($C_{Ar\ Ind}$), 133.53, 133.16 (C_{Ar}), 130.88 (CH_{Ar}), 128.54, 126.16 ($C_{Ar\ Ind}$), 123.46, 123.01 (CH_{Ar}), 120.67, 119.92, 119.27 ($CH_{Ar\ Ind}$),

114.07 ($C_{Ar\ Ind}$), 111.70 ($CH_{Ar\ Ind}$), 69.77, 69.13 (OCH_2), 60.72 ($O\underline{C}H_2CH_3$), 41.25 (NCH_2), 36.08 ($ArCH_2Ar$), 24.39 ($IndCH_2$), 14.12 (CH_3) ppm; ESI-MS *m*/*z*: 1012.4519 $[M+NH_4]^+$ for $C_{60}H_{62}N_5O_{10}$ (1012.4497).

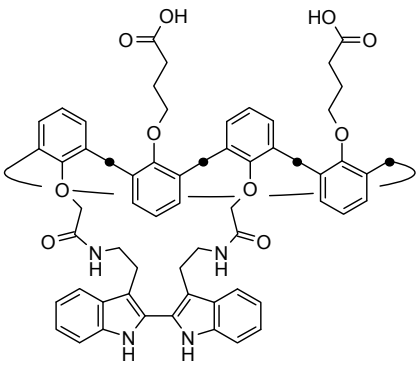


*Bisindole-bridged calixarene ester **37*** was prepared according to *General procedure C* from calixarene **32** (0.074 g, 0.070 mmol), TFA (7 ml), DDQ (0.018 g, 0.077 mmol), and 1,4-dioxane (10 ml); purified by chromatography. Yield 0.056 g (76%), beige solid. M.p. 132–134 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.05 (s, 2H; NH_{Ind}), 7.75–7.71 (m, 2H; ArH_{Ind}), 7.43–7.39 (m, 2H; ArH_{Ind}), 7.26–7.20 (m, 2H; ArH_{Ind}), 7.16–7.10 (m, 2H; ArH_{Ind}), 6.97 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.74 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.26 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.04 (bs, 2H; C(O)NH), 5.99 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 4.19 (q, 4H, $^3J_{HH}$ = 7.2 Hz; $OC\underline{H}_2CH_3$), 4.06 (s, 4H; OCH_2CO), 3.61–3.55 (m, 4H; $OC\underline{H}_2CH_2$), 3.45 (d, 4H, $^2J_{HH}$ = 14.5 Hz; $ArCH_2Ar$), 3.41–3.33 (m, 4H; NCH_2), 3.21 (d, 4H, $^2J_{HH}$ = 14.5 Hz; $ArCH_2Ar$), 3.13–3.06 (m, 4H; $IndCH_2$), 2.34–2.27 (m, 4H; $CH_2C\underline{H}_2CO$), 2.04–1.94 (m, 4H; $CH_2C\underline{H}_2CH_2$), 1.30 (t, 6H, $^3J_{HH}$ = 7.2 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.31, 168.97 (C=O), 156.49, 153.57 (C_{Ar}), 136.19 ($C_{Ar\ Ind}$), 133.73, 133.09 (C_{Ar}), 130.87, 130.50 (CH_{Ar}), 128.60, 126.14 ($C_{Ar\ Ind}$), 122.99, 122.70 (CH_{Ar}), 120.27, 119.91, 119.34 ($CH_{Ar\ Ind}$), 114.18 ($C_{Ar\ Ind}$), 111.63 ($CH_{Ar\ Ind}$), 70.11, 69.70 (OCH_2), 60.44 ($O\underline{C}H_2CH_3$), 41.19 (NCH_2), 36.40 ($ArCH_2Ar$), 30.27 ($CH_2\underline{C}H_2CO$), 25.48, 24.40 ($CH_2\underline{C}H_2CH_2$, $IndCH_2$), 14.25 (CH_3) ppm; ESI-MS *m*/*z*: 1051.4866 $[M+H]^+$ for $C_{64}H_{67}N_4O_{10}$ (1051.4857).

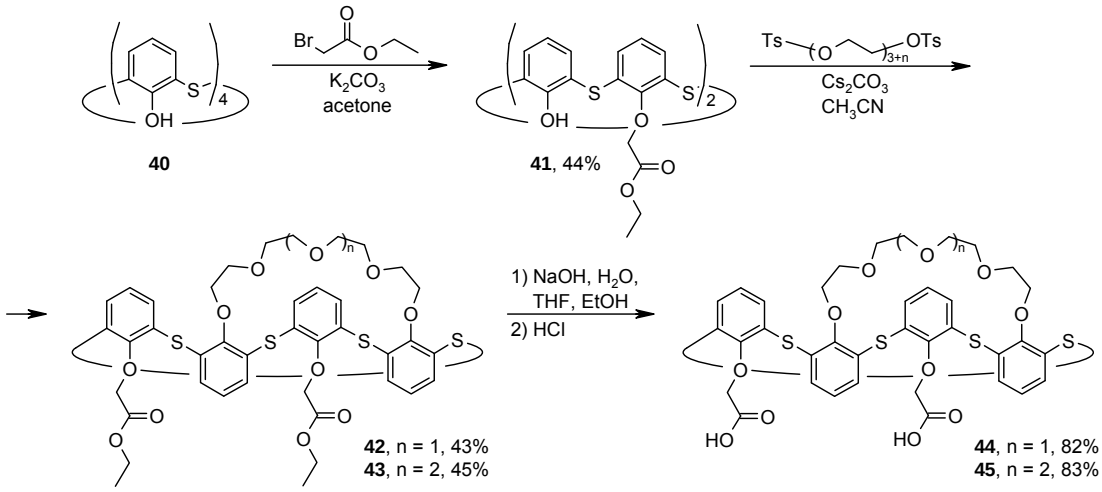


*Bisindole-bridged calixarene acid **38***. To a stirred solution of calixarene **36** (0.055 g, 0.055 mmol) in THF (1 ml) and methanol (5 ml) a solution of K_2CO_3 (0.091 g, 0.66 mmol) in water (0.5 ml) was added. The mixture was stirred at reflux for 6 h, cooled, and the solvents evaporated. The residue was treated with 2 M HCl overnight. The solid formed was collected, washed with water and dried. Yield 0.048 g (93%), yellow solid. M.p. > 300 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.4 (bs, 2H; OH), 11.4 (bs, 2H; NH_{Ind}), 7.74–7.67 (m, 2H; ArH_{Ind}), 7.40–7.33 (m, 2H; ArH_{Ind}), 7.20–7.10 (m, 4H; ArH_{Ind}), 7.07 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.69 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.42 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.17 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 5.94 (bs, 2H; C(O)NH), 4.08 (s, 4H; OCH_2CO), 3.98 (s, 4H; OCH_2CO), 3.79 (d, 4H, $^2J_{HH}$ = 14.5 Hz; $ArCH_2Ar$), 3.46 (d, 4H, $^2J_{HH}$ = 14.6 Hz; $ArCH_2Ar$), 3.41–3.34 (m, 4H; NCH_2), 3.11–3.02 (m, 4H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.76, 167.84 (C=O), 156.01, 154.21 (C_{Ar}), 136.16 ($C_{Ar\ Ind}$), 133.28, 133.11 (C_{Ar}), 130.40, 130.22 (CH_{Ar}),

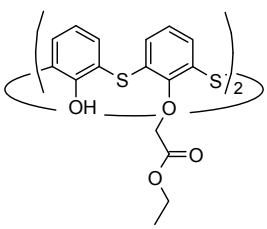
128.32, 127.13 ($C_{Ar\ Ind}$), 122.95, 121.85 (CH_{Ar}), 120.58, 118.93, 118.60 ($CH_{Ar\ Ind}$), 112.37 ($C_{Ar\ Ind}$), 111.61 ($CH_{Ar\ Ind}$), 69.52, 69.12 (OCH_2), 40.33 (NCH_2), 35.53 ($ArCH_2Ar$), 24.48 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 961.3433 $[M+Na]^+$ for $C_{56}H_{50}NaN_4O_{10}$ (961.3419).



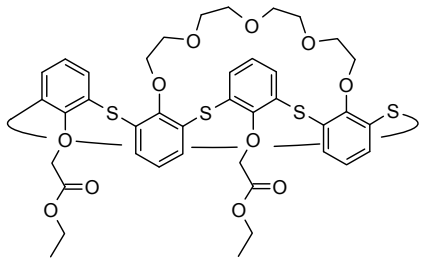
Bisindole-bridged calixarene acid ***39*** was prepared as described for compound **38** from calixarene **37** (0.062 g, 0.059 mmol), K_2CO_3 (0.098 g, 0.71 mmol), THF (1 ml), methanol (5 ml), and water (0.5 ml). Yield 0.047 g (80%), beige solid. M.p. 228–230 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.10 (bs, 2H; OH) 11.40 (bs, 2H; NH_{Ind}), 7.73–7.67 (m, 2H; ArH_{Ind}), 7.40–7.35 (m, 2H; ArH_{Ind}), 7.19–7.10 (m, 4H; ArH_{Ind}), 7.00 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.70 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.39 (d, 4H, $^3J_{HH}$ = 7.5 Hz; ArH), 6.12 (t, 2H, $^3J_{HH}$ = 7.5 Hz; ArH), 5.88 (bs, 2H; C(O)NH), 4.08 (s, 4H; OCH_2CO), 3.51 (d, 4H, $^2J_{HH}$ = 14.1 Hz; $ArCH_2Ar$), 3.50–3.44 (m, 4H; $OC\underline{H}_2CH_2$), 3.46 (d, 4H, $^2J_{HH}$ = 14.1 Hz; $ArCH_2Ar$), 3.40–3.31 (m, 4H; NCH_2), 3.09–3.03 (m, 4H; $IndCH_2$), 2.24–2.17 (m, 4H; $CH_2C\underline{H}_2CO$), 1.85–1.75 (4H; $CH_2C\underline{H}_2CH_2$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 174.47, 167.91 (C=O), 156.29, 153.94 (C_{Ar}), 136.14 ($C_{Ar\ Ind}$), 133.39, 133.26 (C_{Ar}), 130.38, 130.19 (CH_{Ar}), 128.32, 127.06 ($C_{Ar\ Ind}$), 122.21 (CH_{Ar}), 121.87 ($CH_{Ar\ Ind}$), 120.17 (CH_{Ar}). 118.94, 118.58 ($CH_{Ar\ Ind}$), 112.43 ($C_{Ar\ Ind}$), 111.63 ($CH_{Ar\ Ind}$), 70.12, 69.53 (OCH_2), 40.44 (NCH_2), 35.83 ($ArCH_2Ar$), 29.65 ($CH_2\underline{C}H_2CO$), 25.19, 24.42 ($CH_2\underline{C}H_2CH_2$, $IndCH_2$) ppm; ESI-MS *m*/*z*: 995.4244 $[M+H]^+$ for $C_{60}H_{59}N_4O_{10}$ (995.4226).



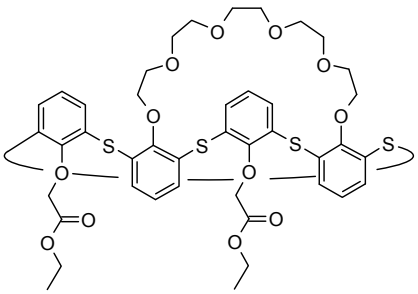
Scheme S1. Preparation of carboxymethylated thiacalix[4]crown-ethers **44**, **45**.



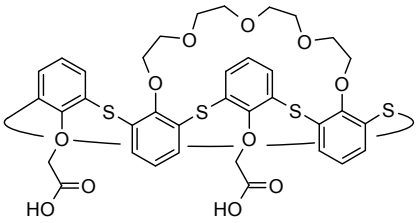
Thiacalix[4]arene ester ***41***. A mixture of thiacalix[4]arene **40**[S10] (1.80 g, 3.63 mmol), K_2CO_3 (0.55 g, 4.00 mmol), and dry acetone (60 ml)) was stirred at room temperature for 15 h. Ethyl bromoacetate (4.80 ml, 43.29 mmol) was added, the mixture was stirred at reflux for 24 h and then cooled down to –18 °C. The solid was collected, washed with cold acetone, and the acetone filtrates were removed. The solid was washed thoroughly with CH_2Cl_2, and the filtrate evaporated under reduced pressure. The residue was re-crystallized from acetone. Yield 1.06 g (44%), white crystals. M.p. 203–205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 7.56 (s, 2H; OH), 6.79 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.78 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.49 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 5.23 (s, 4H; CH_2CO), 4.35 (q, 4H, $^3J_{HH}$ = 7.1 Hz; $OC\underline{H}_2CH_3$), 1.34 (t, 6H, $^3J_{HH}$ = 7.1 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.95 (C=O), 157.28, 156.77 (C_{Ar}), 136.65, 134.30 (CH_{Ar}), 129.89 (C_{Ar}), 125.52 (CH_{Ar}), 122.81 (C_{Ar}), 119.65 (CH_{Ar}), 70.28 ($ArOCH_2$), 61.31 ($O\underline{C}H_2CH_3$), 14.19 (CH_3) ppm; ESI-MS *m*/*z*: 707.0288 $[M+K]^+$ for $C_{32}H_{28}KO_8S_4$ (707.0299).



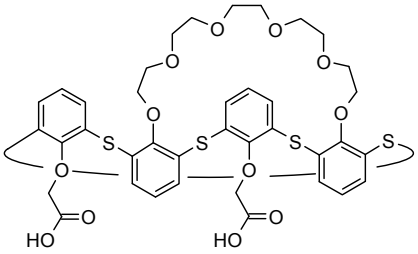
Thiacalixcrown ester ***42***. A mixture of calixarene **41** (1.34 g, 2.00 mmol), tetraethylene glycol di(*p*-toluenesulfonate) (1.10 g, 2.20 mmol), Cs_2CO_3 (1.96 g, 6.00 mmol), and dry acetonitrile (115 ml) was stirred at 70 °C for 24 h and then cooled. The solid was filtered off, washed with acetonitrile and removed. The filtrate was concentrated under reduced pressure, The residue was dissolved in CH_2Cl_2, washed with 2 M HCl, water, dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography (gradient from CH_2Cl_2 to CH_2Cl_2/ethanol 100:0.7) followed by re-crystallization from CH_2Cl_2/methanol. Yield 0.71 g (43%), white solid. M.p. 208–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 7.40 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.95 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.81 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 4.53 (s, 4H; CH_2CO), 4.11 (q, 4H, $^3J_{HH}$ = 7.2 Hz; $OC\underline{H}_2CH_3$), 4.10–4.06 (m, 4H; $OC\underline{H}_2CH_2O$), 3.52–3.41 (m, 12H; OCH_2CH_2O), 1.20 (t, 6H, $^3J_{HH}$ = 7.2 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.32 (C=O), 159.94, 158.34 (C_{Ar}), 133.91, 133.29 (CH_{Ar}), 129.05, 128.67 (C_{Ar}), 123.72, 123.48 (CH_{Ar}), 71.08, 70.64, 70.18, 69.41, 66.70 (OCH_2), 60.62 ($O\underline{C}H_2CH_3$), 14.08 (CH_3) ppm; ESI-MS *m*/*z*: 865.1231 $[M+K]^+$ for $C_{40}H_{42}KO_{11}S_4$ (865.1242).



Thiacalixcrown ester ***43*** was prepared as described for calixarene **42** from calixarene **41** (0.39 g, 0.58 mmol), pentaethylene glycol di(*p*-toluenesulfonate) (0.35 g, 0.64 mmol), Cs_2CO_3 (0.57 g, 1.75 mmol), and dry acetonitrile (25 ml). The sample collected after the column chromatography was re-crystallized from acetonitrile. Yield 0.23 g (45%), white solid. M.p. 116–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 7.47 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.93 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.80 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 4.60 (s, 4H; CH_2CO), 4.20 (q, 4H, $^3J_{HH}$ = 7.2 Hz; O$\underline{C}H_2CH_3$), 4.19–4.15 (m, 4H; O$\underline{C}H_2CH_2O$), 3.74–3.69 (m, 4H; O$\underline{C}H_2CH_2O$), 3.69–3.65 (m, 8H; OCH_2CH_2O), 3.52–3.47 (m, 4H; O$\underline{C}H_2CH_2O$), 1.28 (t, 6H, $^3J_{HH}$ = 7.2 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.32 (C=O), 160.97, 158.93 (C_{Ar}), 136.00, 134.74 (CH_{Ar}), 129.26, 128.39 (C_{Ar}), 123.75, 123.15 (CH_{Ar}), 71.36, 71.26, 71.20, 70.97, 70.45, 67.44 (OCH_2), 60.69 (O$\underline{C}H_2CH_3$), 14.15 (CH_3) ppm; ESI-MS *m*/*z*: 888.2201 $[M+NH_4]^+$ for $C_{42}H_{50}NO_{12}S_4$ (888.2210).

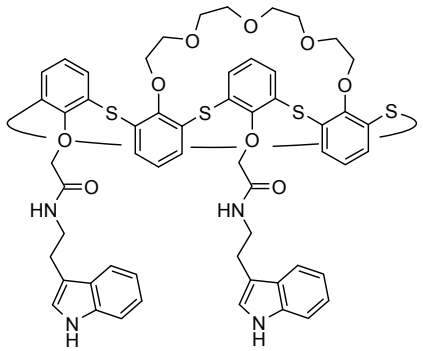


Thiacalixcrown acid ***44***. A mixture of calixarene **42** (0.50 g, 0.61 mmol), NaOH (0.25 g, 6.25 mmol), THF (5 ml), ethanol (10 ml), and water (5 ml) was stirred at reflux for 24 h and then cooled. The solvents were removed under reduced pressure, the residue was dissolved in CH_2Cl_2. The solution was washed with 2 M HCl, water, dried, and the solvent was evaporated. Yield 0.38 g (82%), white solid. M.p. 284–286 °C; ^{1}H NMR (400 MHz, $CDCl_3$+CF_3CO_2D): δ = 7.50 (d, 4H, $^3J_{HH}$ = 7.8 Hz; ArH), 7.46 (d, 4H, $^3J_{HH}$ = 7.8 Hz; ArH), 7.10 (t 2H, $^3J_{HH}$ = 7.8 Hz; ArH), 6.96 (t, 2H, $^3J_{HH}$ = 7.8 Hz; ArH), 4.75 (s, 4H; CH_2CO), 4.31–4.27 (m, 4H; O$\underline{C}H_2CH_2O$), 3.76–3.72 (m, 4H; O$\underline{C}H_2CH_2O$), 3.72–3.69 (m, 4H; OCH_2CH_2O), 3.49–3.45 (m, 4H; OCH_2CH_2O) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+CF_3CO_2D): δ = 172.58 (C=O), 159.26, 155.74 (C_{Ar}), 134.10, 132.13 (CH_{Ar}), 130.08, 128.80 (C_{Ar}), 125.99, 125.86 (CH_{Ar}), 71.33, 70.15, 70.07, 69.58, 64.29 (OCH_2) ppm; ESI-MS *m*/*z*: 788.1319 $[M+NH_4]^+$ for $C_{36}H_{38}NO_{11}S_4$ (788.1322).

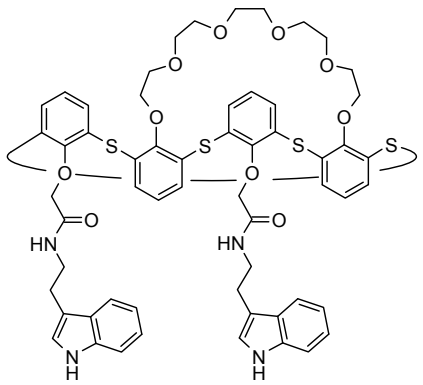


Thiacalixcrown acid ***45*** was prepared as described for calixarene **44** from calixarene **43** (0.22 g, 0.25 mmol), NaOH (0.10 g, 2.50 mmol), THF (2 ml), ethanol (4 ml), and water (2 ml). Yield 0.17 g (83%), white solid. M.p. 207–209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 7.42 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 7.07 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.94 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 4.65 (s, 4H; CH_2CO), 4.18–1.12 (m, 4H; O$\underline{C}H_2CH_2O$), 3.67 (s, 4H; OCH_2CH_2O), 3.61–3.54 (m, 8H; OCH_2CH_2O), 3.31–3.26 (m, 4H;

OCH_2CH_2O) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.35 (C=O), 159.99, 156.09 (C_{Ar}), 133.59, 132.44 (CH_{Ar}), 129.19, 128.52 (C_{Ar}), 125.34, 124.94 (CH_{Ar}), 71.31, 71.06, 70.95, 70.79, 69.93, 65.08 (OCH_2) ppm; ESI-MS *m*/*z*: 832.1581 $[M+NH_4]^+$ for $C_{38}H_{42}NO_{12}S_4$ (832.1584).

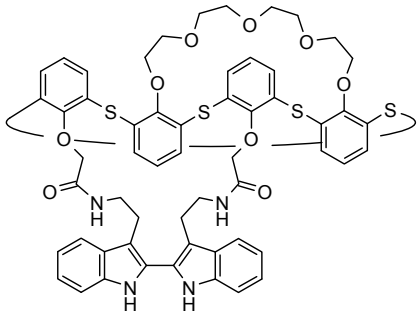


Thiacalixcrown amide ***46*** was prepared according to *General procedure A* from acid **44** (0.116 g, 0.15 mmol), $SOCl_2$ (2.5 ml), dry benzene (2.5 ml), tryptamine (0.096 g, 0.60 mmol), Et_3N (0.167 ml, 1.20 mmol), water (0.2 ml), and THF (10 ml); purified by re-precipitation. Yield 0.122 g (77%), white solid. M.p. 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.64 (m, 2H; ArH_{Ind}), 7.49 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 7.47 (bs, 2H; NH_{Ind}), 7.26–7.22 (m, 2H; ArH_{Ind}), 7.20–7.15 (m, 2H; ArH_{Ind}), 7.14–7.09 (m, 2H; ArH_{Ind}), 7.06 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.99 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.71–6.68 (m, 2H; ArH_{Ind}), 6.57 (t, 2H, $^3J_{HH}$ = 5.5 Hz; C(O)NH), 6.26 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 4.70 (s, 4H; CH_2CO), 4.07–4.02 (m, 4H; OCH_2CH_2O), 3.57–3.47 (m, 8H; OCH_2CH_2O), 3.25–3.20 (m, 4H; $OC\underline{H}_2CH_2O$), 3.21–3.15 (m, 4H; NCH_2), 2.87–2.81 (m, 4H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.40 (C=O), 159.37, 157.26 (C_{Ar}), 136.20 ($C_{Ar\ Ind}$), 133.21, 132.00 (CH_{Ar}), 128.13, 127.22 (C_{Ar}), 127.21 ($C_{Ar\ Ind}$), 124.36, 124.19 (CH_{Ar}), 122.20, 122.13, 119.45, 118.90 ($CH_{Ar\ Ind}$), 112.45 ($C_{Ar\ Ind}$), 111.31 ($CH_{Ar\ Ind}$), 72.04, 70.84, 69.60, 68.39, 67.65 (OCH_2), 39.49 (NCH_2), 25.32 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1055.2809 $[M+H]^+$ for $C_{56}H_{55}N_4O_9S_4$ (1055.2846).

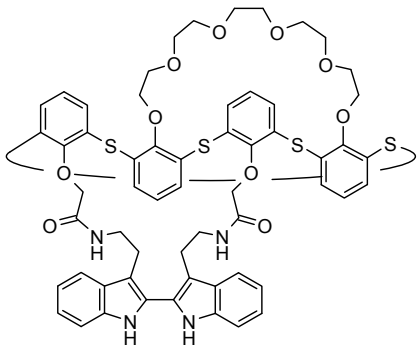


Thiacalixcrown amide ***47*** was prepared according to *General procedure A* from acid **45** (0.122 g, 0.15 mmol), $SOCl_2$ (2.5 ml), dry benzene (2.5 ml), tryptamine (0.096 g, 0.60 mmol), Et_3N (0.167 ml, 1.20 mmol), water (0.2 ml), and THF (10 ml); purified by re-precipitation. Yield 0.100 g (62%), white solid. M.p. 123–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.62 (m, 2H; ArH_{Ind}), 7.59 (bs, 2H; NH_{Ind}), 7.51 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 7.27–7.24 (m, 2H; ArH_{Ind}), 7.20–7.15 (m, 2H; ArH_{Ind}), 7.14–7.09 (m, 2H; ArH_{Ind}), 7.10 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.99 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.78–6.76 (m, 2H; ArH_{Ind}), 6.55 (t, 2H, $^3J_{HH}$ = 5.4 Hz; C(O)NH), 6.24 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 4.68 (s, 4H; CH_2CO), 4.11–4.06 (m, 4H; OCH_2CH_2O), 3.68 (bs, 4H; OCH_2CH_2O), 3.64–3.60 (m, 4H; OCH_2CH_2O), 3.53–3.49 (m, 4H; OCH_2CH_2O), 3.42–3.39 (m, 4H; OCH_2CH_2O), 3.32–3.25 (m, 4H; NCH_2), 2.94–2.88 (m, 4H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.42 (C=O), 160.46, 157.60 (C_{Ar}), 136.25 ($C_{Ar\ Ind}$), 134.19, 133.40 (CH_{Ar}), 128.40, 127.65 (C_{Ar}), 127.22 ($C_{Ar\ Ind}$), 124.26, 123.99 (CH_{Ar}), 122.17, 122.11, 119.44,

118.78 ($CH_{Ar\ Ind}$), 112.45 ($C_{Ar\ Ind}$), 111.34 ($CH_{Ar\ Ind}$), 71.03, 70.98, 70.97, 70.05, 69.82, 68.79 (OCH_2), 39.66 (NCH_2), 25.31 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1099.3077 $[M+H]^+$ for $C_{58}H_{59}N_4O_{10}S_4$ (1099.3109).

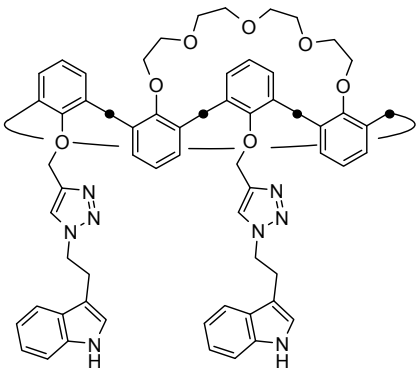


Bisindole-bridged thiacalixcrown ***48*** was prepared according to *General procedure C* from calixarene **46** (0.075 g, 0.071 mmol), TFA (7 ml), DDQ (0.018 g, 0.078 mmol), and 1,4-dioxane (6 ml); purified by crystallization. Yield 0.041 g (55%), beige solid. M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (bs, 2H; NH_{Ind}), 7.77–7.72 (m, 2H; ArH_{Ind}), 7.50 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 7.46–7.42 (m, 2H; ArH_{Ind}), 7.31–7.26 (m, 2H; ArH_{Ind}), 7.27–7.21 (m, 2H; ArH_{Ind}), 6.95 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.91 (bd, 4H; ArH), 6.67 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.30 (bs, 2H; C(O)NH), 4.49 (s, 4H; CH_2CO), 4.08–4.02 (m, 4H; OCH_2CH_2O), 3.50 (bs, 8H; OCH_2CH_2O), 3.39–3.32 (m, 4H; NCH_2), 3.35–3.30 (m, 4H; $OC\underline{H}_2CH_2O$), 2.92–2.85 (m, 4H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$+CD_3OD): δ = 168.67 (C=O), 159.76, 157.59 (C_{Ar}), 136.16 ($C_{Ar\ Ind}$), 134.09, 132.58 (CH_{Ar}), 128.58, 127.64 (C_{Ar}), 127.48, 127.21 ($C_{Ar\ Ind}$), 124.16, 123.89 (CH_{Ar}), 122.31, 119.47, 118.20 ($CH_{Ar\ Ind}$), 111.98 ($C_{Ar\ Ind}$), 111.45 ($CH_{Ar\ Ind}$), 71.47, 70.61, 69.66, 68.50, 67.91 (OCH_2), 39.71 (NCH_2), 23.68 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1091.2213 $[M+K]^+$ for $C_{56}H_{52}KN_4O_9S_4$ (1091.2249).

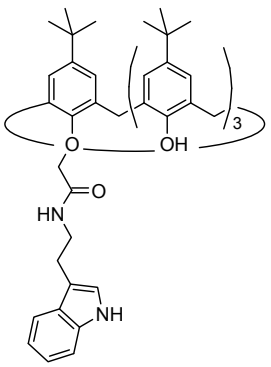


Bisindole-bridged thiacalixcrown ***49*** was prepared according to *General procedure C* from calixarene **47** (0.066 g, 0.06 mmol), TFA (6 ml), DDQ (0.015 g, 0.066 mmol), and 1,4-dioxane (5 ml); purified by crystallization. Yield 0.044 g (67%), beige solid. M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (bs, 2H; NH_{Ind}), 7.80–7.74 (m, 2H; ArH_{Ind}), 7.52 (d, 4H, $^3J_{HH}$ = 7.7 Hz; ArH), 7.45–7.40 (m, 2H; ArH_{Ind}), 7.31–7.25 (m, 2H; ArH_{Ind}), 7.27–7.20 (m, 2H; ArH_{Ind}), 6.96 (t, 2H, $^3J_{HH}$ = 7.7 Hz; ArH), 6.89 (d, 4H, $^3J_{HH}$ = 7.6 Hz; ArH), 6.51 (t, 2H, $^3J_{HH}$ = 7.6 Hz; ArH), 6.11 (bs, 2H; C(O)NH), 4.50 (s, 4H; CH_2CO), 4.11–4.05 (m, 4H; OCH_2CH_2O), 3.68–3.61 (m, 8H; OCH_2CH_2O), 3.61–3.57 (m, 4H; OCH_2CH_2O), 3.47–3.43 (m, 4H; OCH_2CH_2O), 3.41–3.34 (m, 4H; NCH_2), 3.00–2.94 (m, 4H; $IndCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.46 (C=O), 160.97, 158.02 (C_{Ar}), 136.22 ($C_{Ar\ Ind}$), 135.13, 134.36 (CH_{Ar}), 129.08, 128.11 (C_{Ar}), 128.04, 126.99 ($C_{Ar\ Ind}$), 124.32, 123.14 (CH_{Ar}), 122.97, 120.14, 118.94 ($CH_{Ar\ Ind}$), 113.52 ($C_{Ar\ Ind}$), 111.60 ($CH_{Ar\ Ind}$), 71.16, 71.07, 70.52,

70.13, 69.10 (OCH_2), 40.40 (NCH_2), 24.15 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1114.3184 $[M+NH_4]^+$ for $C_{58}H_{60}N_5O_{10}S_4$ (1114.3218).

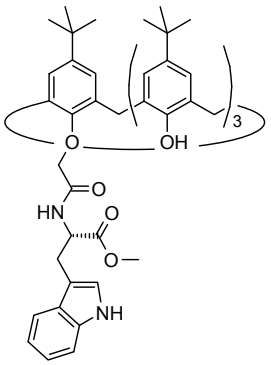


Triazolated calixcrown ***51***. A mixture of propargylated calixcrown **50**[S11] (0.069 g, 0.105 mmol), 3-(2-azidoethyl)indole[S12] (0.045 g, 0.242 mmol), $CuI{\cdot}P(OEt)_3$[S13] (0.011 g, 0.031 mmol), and toluene (5 ml) was stirred at 75 °C for 7 h. After cooling, the solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2. The solution was continuously (approx. 2 h) washed with 2 M HCl, water, then dried and concentrated to almost dryness. Hexane was added and the solid formed was separated, washed with hexane and dried. Yield 0.097 g (90%), brownish solid. M.p. 127–129 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.10 (bs, 2H; NH_{Ind}), 7.62–7.59 (m, 2H; ArH_{Ind}), 7.38–7.35 (m, 2H; ArH_{Ind}), 7.23–7.18 (m, 2H; ArH_{Ind}), 7.14–7.09 (m, 2H; ArH_{Ind}), 7.03 (d, 4H, $^3J_{HH}$ = 7.3 Hz; ArH), 6.95–6.93 (m, 2H; ArH_{Ind}), 6.88 (t, 2H, $^3J_{HH}$ = 7.3 Hz; ArH), 6.67 (d, 4H, $^3J_{HH}$ = 7.4 Hz; ArH), 6.30 (s, 2H; ArH_{Trz}), 6.13 (t, 2H, $^3J_{HH}$ = 7.4 Hz; ArH), 4.67 (s, 4H; OCH_2Trz), 4.67–4.64 (m, 4H; NCH_2), 3.65 (d, 4H, $^2J_{HH}$ = 16.0 Hz; $ArCH_2Ar$), 3.55–3.50 (m, 8H; OCH_2), 3.48 (d, 4H, $^2J_{HH}$ = 16.0 Hz; $ArCH_2Ar$), 3.41–3.37 (m, 4H; $IndCH_2$), 3.26–3.22 (m, 4H; OCH_2), 3.20–3.16 (m, 4H; OCH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.70, 155.41 (C_{Ar}), 143.69 ($C_{Ar\ Trz}$), 136.23 ($C_{Ar\ Ind}$), 134.61, 133.72 (C_{Ar}), 129.50, 129.38 (CH_{Ar}), 126.94 ($C_{Ar\ Ind}$), 123.67 ($CH_{Ar\ Trz}$), 123.11, 122.75 (CH_{Ar}), 122.24, 122.09 ($CH_{Ar\ Ind}$), 119.42, 118.32, 111.38 ($CH_{Ar\ Ind}$), 110.99 ($C_{Ar\ Ind}$), 72.19, 70.25, 70.11, 68.84 (OCH_2), 63.74 (OCH_2Trz), 50.25 (NCH_2), 37.70 ($ArCH_2Ar$), 26.46 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1048.5100 $[M+NH_4]^+$ for $C_{62}H_{66}N_9O_7$ (1048.5085).

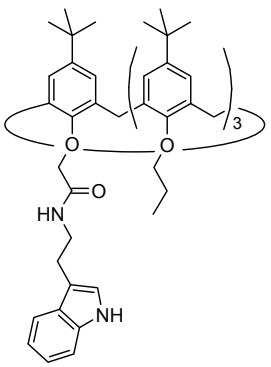


Calixarene amide ***55*** was prepared according to *General procedure B* from acid **52**[S14] (0.425 g, 0.60 mmol), HOSu (0.138 g, 1.20 mmol), DCC (0.154 g, 0.75 mmol), tryptamine (0.120 g, 0.75 mmol), and CH_2Cl_2 (15 ml). Yield 0.440 g (86%), white solid. M.p. 134–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.97 (s, 1H; OH), 9.33 (t, 1H, $^3J_{HH}$ = 5.8 Hz; C(O)NH), 9.32 (s, 2H, OH), 7.83 (bs, 1H; NH_{Ind}), 7.73–7.68 (m, 1H; ArH_{Ind}), 7.29–7.25 (m, 1H; ArH_{Ind}), 7.18–7.13 (m, 1H; ArH_{Ind}), 7.14–7.12 (m, 1H; ArH_{Ind}), 7.12–7.07 (m, 1H; ArH_{Ind}), 7.05 (d, 2H, $^4J_{HH}$ = 2.4 Hz; ArH), 7.05 (s, 2H; ArH), 7.04 (s, 2H; ArH), 7.00 (d, 2H, $^4J_{HH}$ = 2.4 Hz; ArH), 4.56 (s, 2H; OCH_2CO), 4.12 (d, 2H, $^2J_{HH}$ = 13.9 Hz; $ArCH_2Ar$), 4.11 (d, 2H, $^2J_{HH}$ = 13.2 Hz; $ArCH_2Ar$), 3.92–3.85 (m, 2H; NCH_2), 3.44 (d, 2H, $^2J_{HH}$ = 13.9 Hz; $ArCH_2Ar$), 3.40 (d, 2H, $^2J_{HH}$ = 13.2 Hz;

$ArCH_2Ar$), 3.26–3.20 (m, 2H; $IndCH_2$), 1.21 (s, 27H; $C(CH_3)_3$), 1.15 (s, 9H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.89 (C=O), 149.05, 148.67, 147.99, 146.79, 144.12, 143.70 (C_{Ar}), 136.35 (C_{Ind}), 132.70, 128.16 (C_{Ar}), 127.53 (C_{Ind}), 127.24, 126.96 (C_{Ar}), 126.81, 125.99, 125.80, 125.77 (CH_{Ar}), 121.89, 121.86, 119.25, 118.79 (CH_{Ind}), 113.17 (C_{Ind}), 111.07 (CH_{Ind}), 75.49 (OCH_2), 39.76 (NCH_2), 34.24, 34.05, 33.91 ($\underline{C}(CH_3)_3$), 32.82, 32.04 ($ArCH_2Ar$), 31.47, 31.38, 31.06 ($C(\underline{C}H_3)_3$), 25.40 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 849.5170 $[M+H]^+$ for $C_{56}H_{69}N_2O_5$ (849.5201).

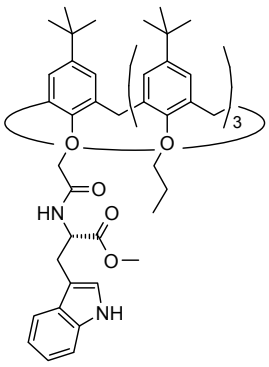


Calixarene amide ***56***[S15] was prepared according to *General procedure B* from acid **52**[S14] (0.212 g, 0.30 mmol), HOSu (0.069 g, 0.60 mmol), DCC (0.077 g, 0.375 mmol), L-tryptophan methyl ester hydrochloride (0.095 g, 0.375 mmol), Et_3N (0.104 ml, 0.75 mmol), and CH_2Cl_2 (10 ml). Yield 0.180 g (66%), white solid. ^1H NMR (600 MHz, $CDCl_3$): δ = 9.95 (s, 1H; OH), 9.47 (s, 1H; OH), 9.42 (d, 1H, $^3J_{HH}$ = 8.5 Hz; C(O)NH), 9.06 (s, 1H; OH), 7.89 (bs, 1H; NH_{Ind}), 7.66–7.63 (m, 1H; ArH_{Ind}), 7.26–7.24 (m, 1H; ArH_{Ind}), 7.16–7.13 (m, 1H; ArH_{Ind}), 7.15 (d, 1H, $^4J_{HH}$ = 2.4 Hz; ArH), 7.08–7.05 (m, 4H; ArH+ArH_{Ind}), 7.05 (d, 2H, $^4J_{HH}$ = 2.5 Hz; ArH), 7.03 (d, 1H, $^4J_{HH}$ = 2.5 Hz; ArH), 7.02 (d, 1H, $^4J_{HH}$ = 2.6 Hz; ArH), 7.01 (d, 1H, $^4J_{HH}$ = 2.5 Hz; ArH), 5.31–5.26 (m, 1H; CHCO), 4.64 (d, 1H, $^2J_{HH}$ = 14.7 Hz; OCH_2CO), 4.40 (d, 1H, $^2J_{HH}$ = 14.7 Hz; OCH_2CO), 4.20 (d, 1H, $^2J_{HH}$ = 13.8 Hz; $ArCH_2Ar$), 4.18 (d, 1H, $^2J_{HH}$ = 13.4 Hz; $ArCH_2Ar$), 4.11 (d, 1H, $^2J_{HH}$ = 13.8 Hz; $ArCH_2Ar$), 4.01 (d, 1H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 3.83 (s, 3H; OCH_3), 3.60–3.55 (m, 1H; $IndCH_2$), 3.52–3.47 (m, 2H; $IndCH_2$+$ArCH_2Ar$), 3.47 (d, 1H, $^2J_{HH}$ = 13.4 Hz; $ArCH_2Ar$), 3.44 (d, 1H, $^2J_{HH}$ = 13.8 Hz; $ArCH_2Ar$), 3.20 (d, 1H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 1.26 (s, 9H; $C(CH_3)_3$), 1.24 (s, 9H; $C(CH_3)_3$), 1.23 (s, 9H; $C(CH_3)_3$), 1.17 (s, 9H; $C(CH_3)_3$) ppm.

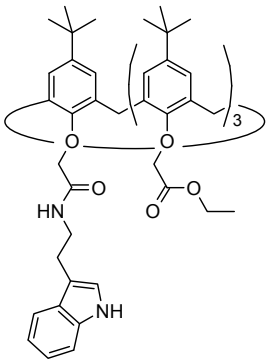


Calixarene amide ***57*** was prepared according to *General procedure A* from acid **53**[S16] (0.291 g, 0.35 mmol), $SOCl_2$ (3.5 ml), dry benzene (3.5 ml), tryptamine (0.112 g, 0.70 mmol), Et_3N (0.195 ml, 1.40 mmol), and THF (20 ml); purified by chromatography. Yield 0.290 g (85%), white solid. M.p. 123–125 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.70 (t, 1H, $^3J_{HH}$ = 6.0 Hz; C(O)NH), 8.11 (bs, 1H; NH_{Ind}), 7.76–7.72 (m, 1H; ArH_{Ind}), 7.39–7.34 (m, 1H; ArH_{Ind}), 7.22–7.16 (m, 1H; ArH_{Ind}), 7.13–7.08 (m, 1H; ArH_{Ind}), 7.10–7.08 (m, 1H; ArH_{Ind}), 7.02 (s, 2H; ArH), 7.01 (s, 2H; ArH), 6.55 (s, 4H; ArH), 4.84 (s, 2H; OCH_2CO), 4.37 (d, 2H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.36 (d, 2H, $^2J_{HH}$ = 13.0 Hz; $ArCH_2Ar$), 3.93–3.86 (m, 2H; OCH_2), 3.83–3.75 (m, 2H; NCH_2), 3.76–3.70 (m, 4H; OCH_2), 3.25–3.19 (m, 2H; $IndCH_2$), 3.19 (d, 2H, $^2J_{HH}$ = 13.0 Hz; $ArCH_2Ar$), 3.13 (d, 2H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 2.01–1.90 (m, 2H; $OCH_2C\underline{H}_2$), 1.85–1.73 (m, 4H; $OCH_2C\underline{H}_2$), 1.27 (s,

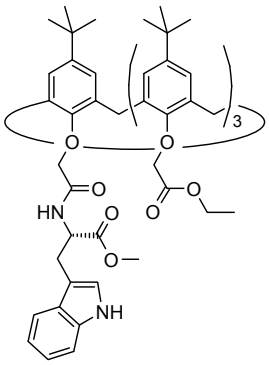
9H; $C(CH_3)_3$), 1.26 (s, 9H; $C(CH_3)_3$), 0.90 (s, 18H; $C(CH_3)_3$), 0.88 (t, 6H, $^3J_{HH}$ = 7.5 Hz; CH_3), 0.87 (t, 3H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.25 (C=O), 154.31, 153.76, 152.02, 145.11, 144.81, 144.52 (C_{Ar}), 136.25 (C_{Ind}), 135.11, 133.50, 132.51, 131.93 (C_{Ar}), 127.57 (C_{Ind}), 126.09, 125.35, 125.00, 124.48 (CH_{Ar}), 122.03, 121.75, 119.43, 118.99 (CH_{Ind}), 113.67 (C_{Ind}), 111.07 (CH_{Ind}), 77.53, 76.21, 74.30 (OCH_2), 40.74 (NCH_2), 33.98, 33.93, 33.66 ($\underline{C}(CH_3)_3$), 31.68 ($ArCH_2Ar$), 31.62, 31.56 ($C(\underline{C}H_3)_3$), 31.37 ($ArCH_2Ar$), 31.19 ($C(\underline{C}H_3)_3$), 25.86 ($IndCH_2$), 23.04, 22.80 ($OCH_2\underline{C}H_2$), 10.12, 10.02 (CH_3) ppm; ESI-MS *m*/*z*: 997.6408 $[M+Na]^+$ for $C_{65}H_{86}NaN_2O_5$ (997.6429).



Calixarene amide ***58*** was prepared according to *General procedure A* from acid **53**[S16] (0.35 g, 0.42 mmol), $SOCl_2$ (4.2 ml), dry benzene (4.2 ml), L-tryptophan methyl ester hydrochloride (0.214 g, 0.84 mmol), Et_3N (0.35 ml, 2.52 mmol), water (0.2 ml), and THF (24 ml); purified by chromatography. Yield 0.29 g (67%), white solid. M.p. 125–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (bs, 1H; NH_{Ind}), 7.64 (d, 1H, $^3J_{HH}$ = 7.9 Hz; C(O)NH), 7.58–7.54 (m, 1H; ArH_{Ind}), 7.36–7.32 (m, 1H; ArH_{Ind}), 7.21–7.15 (m, 1H; ArH_{Ind}), 7.10–7.04 (m, 1H; ArH_{Ind}), 6.96–6.94 (m, 1H; ArH_{Ind}), 6.89 (d, 2H, $^4J_{HH}$ = 2.6 Hz; ArH), 6.86 (d, 1H, $^4J_{HH}$ = 2.5 Hz; ArH), 6.80 (d, 1H, $^4J_{HH}$ = 2.5 Hz; ArH), 6.67 (bs, 2H; ArH), 6.59 (d, 1H, $^4J_{HH}$ = 2.5 Hz; ArH), 6.54 (d, 1H, $^4J_{HH}$ = 2.5 Hz; ArH), 5.05–4.99 (m, 1H; CHCO), 4.58 (d, 1H, $^2J_{HH}$ = 15.7 Hz; OCH_2CO), 4.57 (d, 1H, $^2J_{HH}$ = 15.7 Hz; OCH_2CO), 4.37 (d, 1H, $^2J_{HH}$ = 12.5 Hz; $ArCH_2Ar$), 4.37 (d, 1H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 4.27 (d, 1H, $^2J_{HH}$ = 12.8 Hz; $ArCH_2Ar$), 4.26 (d, 1H, $^2J_{HH}$ = 12.7 Hz; $ArCH_2Ar$), 3.94–3.76 (m, 4H; OCH_2), 3.73–3.67 (m, 2H; OCH_2), 3.67 (s, 3H; OCH_3), 3.50–3.34 (m, 2H; $IndCH_2$), 3.11 (d, 2H, $^2J_{HH}$ = 12.4 Hz; $ArCH_2Ar$), 3.09 (d, 1H, $^2J_{HH}$ = 12.8 Hz; $ArCH_2Ar$), 2.90 (d, 1H, $^2J_{HH}$ = 12.7 Hz; $ArCH_2Ar$), 1.99–1.82 (m, 6H; $OCH_2C\underline{H}_2$), 1.18 (s, 9H; $C(CH_3)_3$), 1.17 (s, 9H; $C(CH_3)_3$), 1.00 (s, 9H; $C(CH_3)_3$), 0.99 (t, 3H, $^3J_{HH}$ = 7.4 Hz; CH_3), 0.96 (s, 9H; $C(CH_3)_3$), 0.87 (t, 3H, $^3J_{HH}$ = 7.5 Hz; CH_3), 0.83 (t, 3H, $^3J_{HH}$ = 7.5 Hz; CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.85, 170.08 (C=O), 153.59, 153.56, 153.12, 152.90, 144.54, 144.53, 144.49, 144.20 (C_{Ar}), 136.07 (C_{Ind}), 134.51, 134.49, 133.98, 133.90, 133.04, 133.02, 131.56, 131.47 (C_{Ar}), 127.54 (C_{Ind}), 125.48, 125.42, 125.33, 125.04, 125.03, 124.65, 124.64 (CH_{Ar}), 122.68, 122.16, 119.70, 118.60, 111.10 (CH_{Ind}), 110.69 (C_{Ind}), 77.07, 76.61, 76.53, 74.33 (OCH_2), 53.04 (NCH), 52.24 (OCH_3), 33.90, 33.89, 33.72, 33.67 ($\underline{C}(CH_3)_3$), 31.54, 31.53 ($C(\underline{C}H_3)_3$), 31.39 ($ArCH_2Ar$), 31.31, 31.29 ($C(\underline{C}H_3)_3$), 31.22, 31.21 ($ArCH_2Ar$), 27.91 ($IndCH_2$), 23.35, 23.13, 23.07 ($OCH_2\underline{C}H_2$), 10.48, 10.01 (CH_3) ppm; ESI-MS *m*/*z*: 1055.6466 $[M+Na]^+$ for $C_{67}H_{88}NaN_2O_7$ (1055.6484).

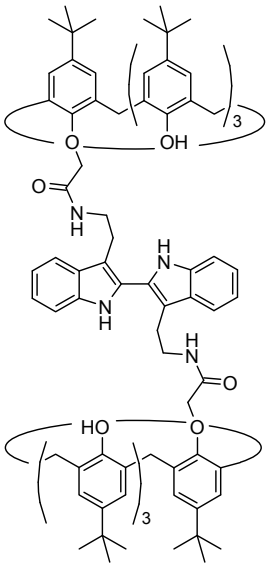


*Calixarene amide **59*** was prepared according to *General procedure A* from acid **54**[S17] (1.00 g, 1.04 mmol), $SOCl_2$ (15 ml), dry benzene (5 ml), tryptamine (0.48 g, 3.00 mmol), Et_3N (0.50 ml, 3.60 mmol), and THF (28 ml); purified by chromatography. Yield 0.75 g (65%), white solid. M.p. 100–105 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (t, 1H, $^3J_{HH}$ = 6.1 Hz; C(O)NH), 8.45 (bs, 1H; NH_{Ind}), 7.70–7.66 (m, 1H; ArH_{Ind}), 7.36–7.32 (m, 1H; ArH_{Ind}), 7.18–7.13 (m, 2H; ArH_{Ind}), 7.10–7.06 (m, 1H; ArH_{Ind}), 6.85 (s, 4H; ArH), 6.73 (s, 2H; ArH), 6.60 (s, 2H; ArH), 4.85 (d, 2H, $^2J_{HH}$ = 15.8 Hz; $OC\underline{H}_2CO_2CH_2$), 4.71 (d, 2H, $^2J_{HH}$ = 12.8 Hz; $ArCH_2Ar$), 4.69 (d, 2H, $^2J_{HH}$ = 15.8 Hz; $OC\underline{H}_2CO_2CH_2$), 4.65 (s, 2H; OCH_2CO), 4.63 (d, 2H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 4.51 (s, 2H; OCH_2CO), 4.19 (q, 2H, $^3J_{HH}$ = 7.1 Hz; $OC\underline{H}_2CH_3$), 4.05–3.85 (m, 4H; $OC\underline{H}_2CH_3$), 3.76–3.69 (m, 2H; NCH_2), 3.21 (d, 2H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 3.20 (d, 2H, $^2J_{HH}$ = 13.1 Hz; $ArCH_2Ar$), 3.14–3.09 (2H; $IndCH_2$), 1.23 (t, 3H, $^3J_{HH}$ = 7.1 Hz; $OCH_2C\underline{H}_3$), 1.13 (s, 18H; $C(CH_3)_3$), 1.07 (t, 6H, $^3J_{HH}$ = 7.1 Hz; $OCH_2C\underline{H}_3$), 1.04 (s, 9H; $C(CH_3)_3$), 0.95 (s, 9H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.45, 170.33, 170.08 (C=O), 152.86, 152.68, 152.32, 145.53, 145.50, 145.22 (C_{Ar}), 136.29 (C_{Ind}), 133.68, 133.51, 132.88, 132.25 (C_{Ar}). 127.50 (C_{Ind}), 125.68, 125.58, 125.47, 125.40 (CH_{Ar}), 121.92, 121.73, 119.07, 118.80 (CH_{Ind}), 113.59 (C_{Ind}), 111.06 (CH_{Ind}), 74.58, 71.35 (OCH_2), 60.62, 60.60 ($O\underline{C}H_2CH_3$), 39.96 (NCH_2), 33.87, 33.80, 33.69 ($\underline{C}(CH_3)_3$), 31.96, 31.42 ($ArCH_2Ar$), 31.37, 31.26, 31.23 ($C(\underline{C}H_3)_3$), 25.56 ($IndCH_2$), 14.06, 13.94 (CH_3) ppm; ESI-MS *m*/*z*: 1129.6109 $[M+Na]^+$ for $C_{68}H_{86}NaN_2O_{11}$ (1129.6124).

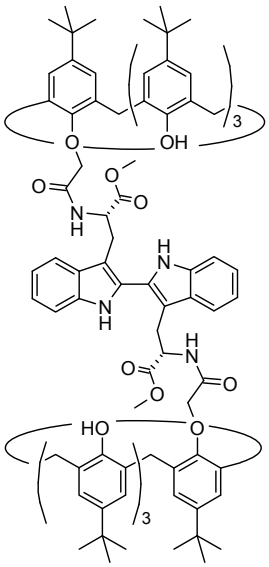


*Calixarene amide **60*** was prepared according to *General procedure A* from acid **54**[S17] (0.20 g, 0.21 mmol), $SOCl_2$ (2 ml), dry benzene (2 ml), L-tryptophan methyl ester hydrochloride (0.11 g, 0.42 mmol), Et_3N (0.175 ml, 1.26 mmol), water (0.3 ml), and THF (15 ml); purified by re-precipitation. Yield 0.21 g (87%), white solid. M.p. 98–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (bs, 1H; NH_{Ind}), 8.17 (d, 1H, $^3J_{HH}$ = 8.1 Hz; C(O)NH), 7.65–7.61 (m, 1H; ArH_{Ind}), 7.33–7.29 (m, 1H; ArH_{Ind}), 7.21–7.19 (m, 1H; ArH_{Ind}), 7.17–7.12 (m, 1H; ArH_{Ind}), 7.10–7.05 (m, 1H; ArH_{Ind}), 6.98–6.94 (m, 4H; ArH), 6.62–6.59 (m, 2H; ArH), 6.43 (d, 1H, $^4J_{HH}$ = 2.6 Hz; ArH), 6.42 (d, 1H, $^4J_{HH}$ = 2.6 Hz; ArH), 5.04–4.98 (m, 1H; CHCO), 4.95 (d, 1H, $^2J_{HH}$ = 16.0 Hz; $OC\underline{H}_2CO_2CH_2$), 4.91 (d, 1H, $^2J_{HH}$ = 15.7 Hz; $OC\underline{H}_2CO_2CH_2$), 4.84 (d, 1H, $^2J_{HH}$ = 16.0 Hz; $OC\underline{H}_2CO_2CH_2$), 4.73 (d, 1H, $^2J_{HH}$ = 15.7 Hz; $OC\underline{H}_2CO_2CH_2$), 4.71 (d, 1H, $^2J_{HH}$ = 12.9 Hz; $ArCH_2Ar$), 4.70 (d, 1H, $^2J_{HH}$ = 12.6 Hz; $ArCH_2Ar$), 4.66 (d, 1H, $^2J_{HH}$ = 12.9 Hz; $ArCH_2Ar$), 4.63 (d, 1H, $^2J_{HH}$ = 13.4 Hz; $ArCH_2Ar$), 4.55 (s, 2H; OCH_2CO), 4.47 (s, 2H; OCH_2CO), 4.26 (q, 2H, $^3J_{HH}$ = 7.2 Hz; $OC\underline{H}_2CH_3$), 4.02–3.78 (m, 4H; $OC\underline{H}_2CH_3$), 3.67 (s, 3H; OCH_3), 3.49–3.44 (d, 2H; $IndCH_2$), 3.19 (d, 1H, $^2J_{HH}$ = 12.9 Hz; $ArCH_2Ar$), 3.18 (d, 1H, $^2J_{HH}$ = 12.6 Hz; $ArCH_2Ar$), 3.16 (d, 1H, $^2J_{HH}$ = 12.9 Hz;

$ArCH_2Ar$), 3.12 (d, 1H, $^2J_{HH}$ = 13.4 Hz; $ArCH_2Ar$), 1.30 (t, 3H, $^3J_{HH}$ = 7.1 Hz; $OCH_2C\underline{H}_3$), 1.23 (s, 9H, $C(CH_3)_3$), 1.22 (s, 9H; $C(CH_3)_3$), 1.06 (t, 3H, $^3J_{HH}$ = 7.2 Hz; $OCH_2C\underline{H}_3$), 1.03 (t, 3H, $^3J_{HH}$ = 7.2 Hz; $OCH_2C\underline{H}_3$), 0.95 (s, 9H; $C(CH_3)_3$), 0.82 (s, 9H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.13, 170.92, 170.63, 170.12, 169.68 (C=O), 153.08, 153.00, 152.46, 152.03, 145.49, 145.47, 145.31, 144.92 (C_{Ar}), 136.09 (C_{Ind}), 134.50, 134.39, 134.33, 132.33, 132.16, 131.51 (C_{Ar}), 127.57 (C_{Ind}), 125.87, 125.83, 125.79, 125.72, 125.18, 125.10, 125.07 (CH_{Ar}), 122.99, 121.81, 119.27, 118.65 (CH_{Ind}), 111.09 (C_{Ind}), 111.03 (CH_{Ind}), 74.50, 71.62, 70.77, 70.73 (OCH_2), 60.65, 60.37, 60.35 ($O\underline{C}H_2CH_3$), 52.82, 52.10 (NCH, OCH_3), 33.95, 33.71, 33.57 ($\underline{C}(CH_3)_3$), 32.06, 31.98 ($ArCH_2Ar$), 31.51 ($C(\underline{C}H_3)_3$), 31.42, 31.35 ($ArCH_2Ar$), 31.15, 31.11 ($C(\underline{C}H_3)_3$), 27.27 ($IndCH_2$), 14.17, 13.92 (CH_3) ppm; ESI-MS *m*/*z*: 602.2966 $[M+H+K]^{2+}$ for $C_{70}H_{89}KN_2O_{13}$ (602.2995).

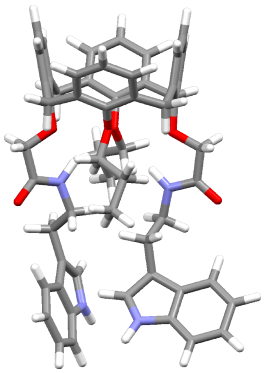


Biscalixarene ***61*** was prepared according to *General procedure C* from calixarene **55** (0.200 g, 0.236 mmol), TFA (0.24 ml), DDQ (0.030 g, 0.130 mmol), and 1,4-dioxane (14 ml); purified by chromatography. Yield 0.025 g (13%), white solid. M.p. 173–175 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.53 (bs, 2H; NH_{Ind}), 10.10 (s, 2H; OH), 9.87 (t, 2H, $^3J_{HH}$ = 6.4 Hz; C(O)NH), 9.43 (s, 4H; OH), 7.70–7.67 (m, 2H; ArH_{Ind}), 7.63–7.59 (m, 2H; ArH_{Ind}), 7.17–7.12 (m, 2H; ArH_{Ind}), 7.13–7.08 (m, 2H; ArH_{Ind}), 7.08 (s, 4H; ArH), 7.07 (d, 4H, $^4J_{HH}$ = 2.5 Hz; ArH), 7.07 (s, 4H; ArH), 7.02 (d, 4H, $^4J_{HH}$ = 2.5 Hz; ArH), 4.68 (s, 4H; OCH_2CO), 4.24 (d, 4H, $^2J_{HH}$ = 13.9 Hz; $ArCH_2Ar$), 4.15 (d, 4H, $^2J_{HH}$ = 13.4 Hz; $ArCH_2Ar$), 3.93–3.85 (m, 4H; NCH_2), 3.51–3.45 (m, 4H; $IndCH_2$), 3.47 (d, 4H, $^2J_{HH}$ = 13.9 Hz; $ArCH_2Ar$), 3.45 (d, 4H, $^2J_{HH}$ = 13.4 Hz; $ArCH_2Ar$), 1.24 (s, 18H; $C(CH_3)_3$), 1.22 (s, 36H; $C(CH_3)_3$), 1.17 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.44 (C=O), 149.22, 148.72, 147.94, 146.81, 144.24, 143.84 (C_{Ar}), 136.93 (C_{Ind}), 132.79 (C_{Ar}), 128.42 (C_{Ind}), 128.25 (C_{Ar}), 127.72 (C_{Ind}), 127.25, 127.12 (C_{Ar}), 126.88, 126.06, 125.90, 125.89 (CH_{Ar}), 122.18, 119.37, 118.06, 111.75 (CH_{Ind}), 110.11 (C_{Ind}), 75.45 (OCH_2), 41.17 (NCH_2), 34.29, 34.09, 33.94 ($\underline{C}(CH_3)_3$), 32.88, 32.12 ($ArCH_2Ar$), 31.48, 31.42, 31.09 ($C(\underline{C}H_3)_3$), 25.42 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1718.9957 $[M+Na]^+$ for $C_{112}H_{134}NaN_4O_{10}$ (1719.0026).

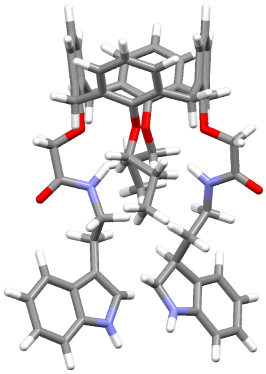


Biscalixarene ***62*** was prepared according to *General procedure C* from calixarene **56**[S15] (0.200 g, 0.221 mmol), TFA (0.22 ml), DDQ (0.028 g, 0.122 mmol), and 1,4-dioxane (14 ml); purified by chromatography. Yield 0.095 g (48%), white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.47 (bs, 2H; NH_{Ind}), 9.94 (s, 2H; OH), 9.58 (d, 2H, $^{3}J_{HH}$ = 8.9 Hz; C(O)NH), 9.37 (s, 2H; OH), 9.00 (s, 2H; OH), 7.75–7.72 (m, 2H; ArH_{Ind}), 7.29–7.25 (m, 2H; ArH_{Ind}), 7.07–6.99 (m, 18H; ArH_{Ind}+ArH), 6.94 (d, 2H, $^{4}J_{HH}$ = 2.4 Hz; ArH), 5.50–5.45 (m, 2H; CHCO), 4.61 (d, 2H, $^{2}J_{HH}$ = 14.7 Hz; OCH_2CO), 4.37 (d, 2H, $^{2}J_{HH}$ = 14.7 Hz; OCH_2CO), 4.16 (d, 2H, $^{2}J_{HH}$ = 14.0 Hz; $ArCH_2Ar$), 4.14 (d, 2H, $^{2}J_{HH}$ = 14.0 Hz; $ArCH_2Ar$), 4.09 (d, 2H, $^{2}J_{HH}$ = 13.3 Hz; $ArCH_2Ar$), 3.92 (d, 2H, $^{2}J_{HH}$ = 13.3 Hz; $ArCH_2Ar$), 3.77–3.72 (m, 2H; $IndCH_2$), 3.63 (s, 6H; OCH_3), 3.48–3.44 (m, 2H; $IndCH_2$), 3.47 (d, 2H, $^{2}J_{HH}$ = 13.3 Hz; $ArCH_2Ar$), 3.39 (d, 2H, $^{2}J_{HH}$ = 14.0 Hz; $ArCH_2Ar$), 3.26 (d, 2H, $^{2}J_{HH}$ = 14.0 Hz; $ArCH_2Ar$), 3.19 (d, 2H, $^{2}J_{HH}$ = 13.3 Hz; $ArCH_2Ar$), 1.26 (s, 18H; $C(CH_3)_3$), 1.23 (s, 18H; $C(CH_3)_3$), 1.22 (s, 18H; $C(CH_3)_3$), 1.15 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.71, 168.14 (C=O), 149.07, 148.26, 148.25, 147.82, 146.95, 144.00, 143.72, 143.32 (C_{Ar}), 136.30 (C_{Ind}), 133.09, 132.28, 128.93, 128.73, 128.17 (C_{Ar}), 127.87 (C_{Ind}), 127.61 (C_{Ar}), 127.14 (CH_{Ar}), 126.88, 126.87 (C_{Ar}), 126.66 (C_{Ind}), 126.38, 126.22, 125.82, 125.81, 125.76, 125.75, 125.64 (CH_{Ar}), 122.07, 119.54, 118.77, 111.56 (CH_{Ind}), 108.89 (C_{Ind}), 75.05 (OCH_2), 52.77 (NCH), 52.75 (OCH_3), 34.25, 34.10, 33.92, 33.89 ($\underline{C}(CH_3)_3$), 32.86, 32.69, 32.11, 31.97 ($ArCH_2Ar$), 31.50, 31.49, 31.45, 31.07 ($C(\underline{C}H_3)_3$), 27.48 ($IndCH_2$) ppm; ESI-MS *m*/*z*: 1850.9814 $[M+K]^+$ for $C_{116}H_{138}KN_4O_{14}$ (1850.9875).

Calculated energy profiles of the cyclization steps at bridging calixarenes 3–6, 13

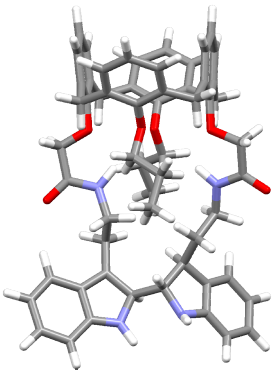


ΔH	–2912.035993 E_h
$T\cdot\Delta S$	0.145655 E_h
ΔG_{298}	–2912.181648 E_h



ΔH	–2912.016119 E_h
$T\cdot\Delta S$	0.143137 E_h
ΔG_{298}	–2912.159256 E_h

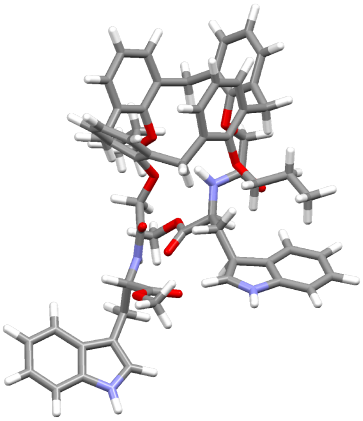
$\Delta\Delta G$ **+14.1** kcal·mol^{-1}



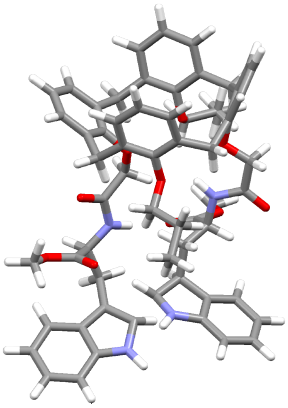
ΔH	–2912.023235 E_h
$T\cdot\Delta S$	0.143376 E_h
ΔG_{298}	–2912.166611 E_h

$\Delta\Delta G$ **–4.7** kcal·mol^{-1}

Figure S1. Calculated structures, energies and energy differences for: **3**·H$^+$ (left), the transition state (middle), and the respective protonated indolylindoline (right); *tert*-butyl groups are omitted to facilitate calculations.

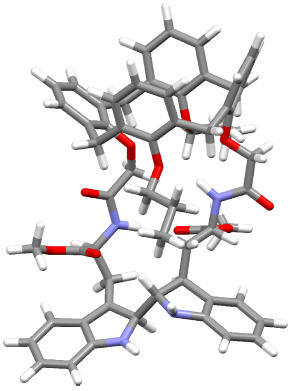


ΔH	–3367.127568 E_h
$T\cdot\Delta S$	0.165145 E_h
ΔG_{298}	–3367.292713 E_h



ΔH	–3367.101383 E_h
$T\cdot\Delta S$	0.160986 E_h
ΔG_{298}	–3367.262369 E_h

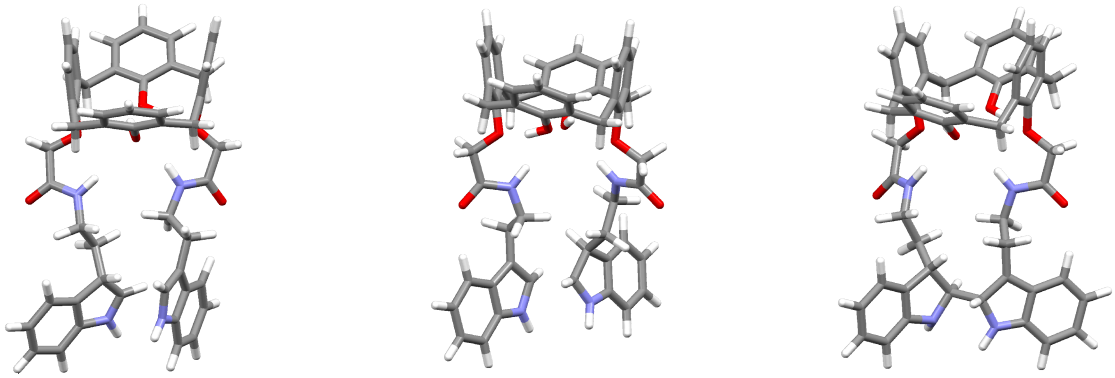
$\Delta\Delta G$ **+19.0** kcal·mol^{-1}



ΔH	–3367.105279 E_h
$T\cdot\Delta S$	0.161336 E_h
ΔG_{298}	–3367.266615 E_h

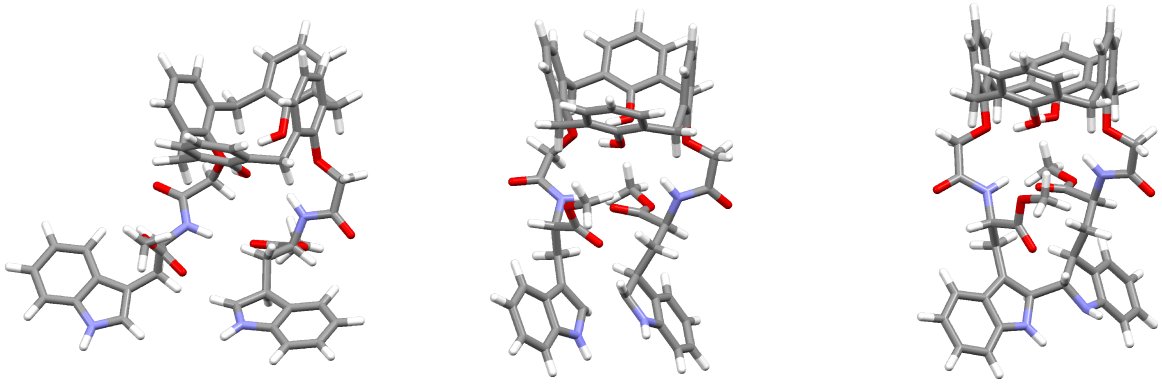
$\Delta\Delta G$ **–2.6** kcal·mol^{-1}

Figure S2. Calculated structures, energies and energy differences for: **4**·H$^+$ (left), the transition state (middle), and the respective protonated indolylindoline (right); *tert*-butyl groups are omitted to facilitate calculations.



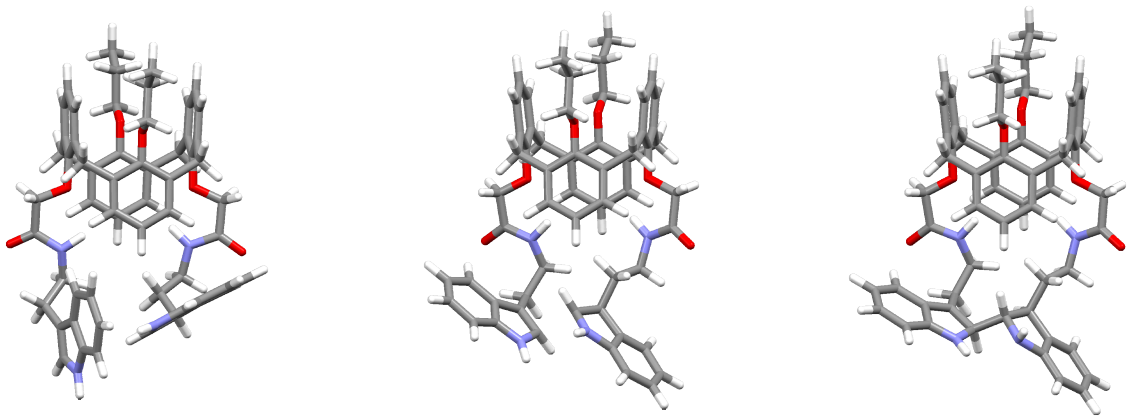
ΔH	–2676.735252 E_h	ΔH	–2676.715061 E_h	ΔH	–2676.721892 E_h
$T\cdot\Delta S$	0.128683 E_h	$T\cdot\Delta S$	0.126134 E_h	$T\cdot\Delta S$	0.126580 E_h
ΔG_{298}	–2676.863935 E_h	ΔG_{298}	–2676.841195 E_h	ΔG_{298}	–2676.848472 E_h
		$\Delta\Delta G$ **+14.3** kcal·mol^{-1}		$\Delta\Delta G$ **–4.6** kcal·mol^{-1}	

Figure S3. Calculated structures, energies and energy differences for: **5**·H$^+$ (left), the transition state (middle), and the respective protonated indolylindoline (right); *tert*-butyl groups are omitted to facilitate calculations.



ΔH	–3131.825398 E_h	ΔH	–3131.806876 E_h	ΔH	–3131.814774 E_h
$T\cdot\Delta S$	0.147520 E_h	$T\cdot\Delta S$	0.142914 E_h	$T\cdot\Delta S$	0.144061 E_h
ΔG_{298}	–3131.972918 E_h	ΔG_{298}	–3131.949790 E_h	ΔG_{298}	–3131.958835 E_h
		$\Delta\Delta G$ **+14.5** kcal·mol^{-1}		$\Delta\Delta G$ **–5.7** kcal·mol^{-1}	

Figure S4. Calculated structures, energies and energy differences for: **6**·H$^+$ (left), the transition state (middle), and the respective protonated indolylindoline (right); *tert*-butyl groups are omitted to facilitate calculations.



ΔH	–2912.040802 E_h	ΔH	–2912.021410 E_h	ΔH	–2912.029124 E_h
$T\cdot\Delta S$	0.146627 E_h	$T\cdot\Delta S$	0.144412 E_h	$T\cdot\Delta S$	0.144046 E_h
ΔG_{298}	–2912.187429 E_h	ΔG_{298}	–2912.165822 E_h	ΔG_{298}	–2912.173170 E_h
		$\Delta\Delta G$ **+13.6** kcal·mol^{-1}		$\Delta\Delta G$ **–4.7** kcal·mol^{-1}	

Figure S5. Calculated structures, energies and energy differences for: **13**·H$^+$ (left), the transition state (middle), and the respective protonated indolylindoline (right).

Calculated energy profile for the mutual rotation of indole parts in 3,3'-dimethyl-2,2'-bisindole

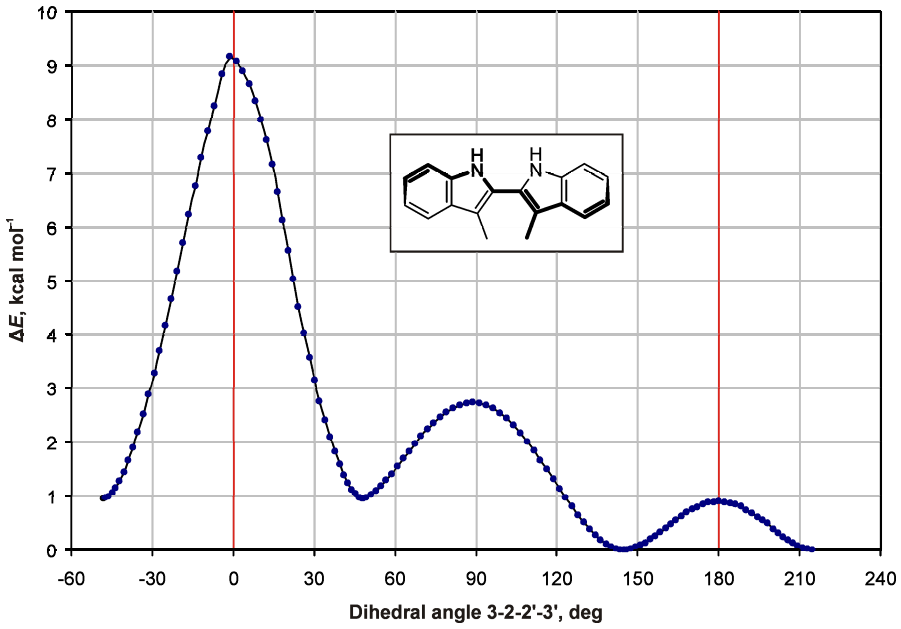


Figure S6. Relative energies for the mutual rotation of indole parts of 3,3'-dimethyl-2,2'-bisindole plotted against the dihedral angle between the two indole planes; the combined plot of six intrinsic reaction coordinate computations for the three transition states of the rotation; DFT B3LYP/def2-SVP.

Details of fluorescence titrations

All fluorescence measurements were carried out at 25 °C in acetonitrile (HPLC grade) in a quartz cell (path length 10 mm, $c_L = 1 \times 10^{-5}$ M) by using Fluorat-02-Panorama spectrofluorometer. Commercially available tetrabutylammonium chloride, bromide, iodide, hydrogen sulfate, nitrate, dihydrogen phosphate, acetate and benzoate were used at the titrations of the hosts with the anions, while sodium, potassium, rubidium and cesium tetraphenylborates were used at the titrations of the hosts with cations. Calixarenes containing non-bridged indole units were excited at 286 nm, and the bridged hosts were excited at 308 nm. The titrant solution was gradually added to the host solution to obtain 20–30 fluorescence spectra in each case. For qualitative purposes, the fluorescence intensity was recalculated according to dilution, while for quantitative purposes, the raw data were analyzed by nonlinear regression modeling using least-squares method.

NMR spectra of novel compounds

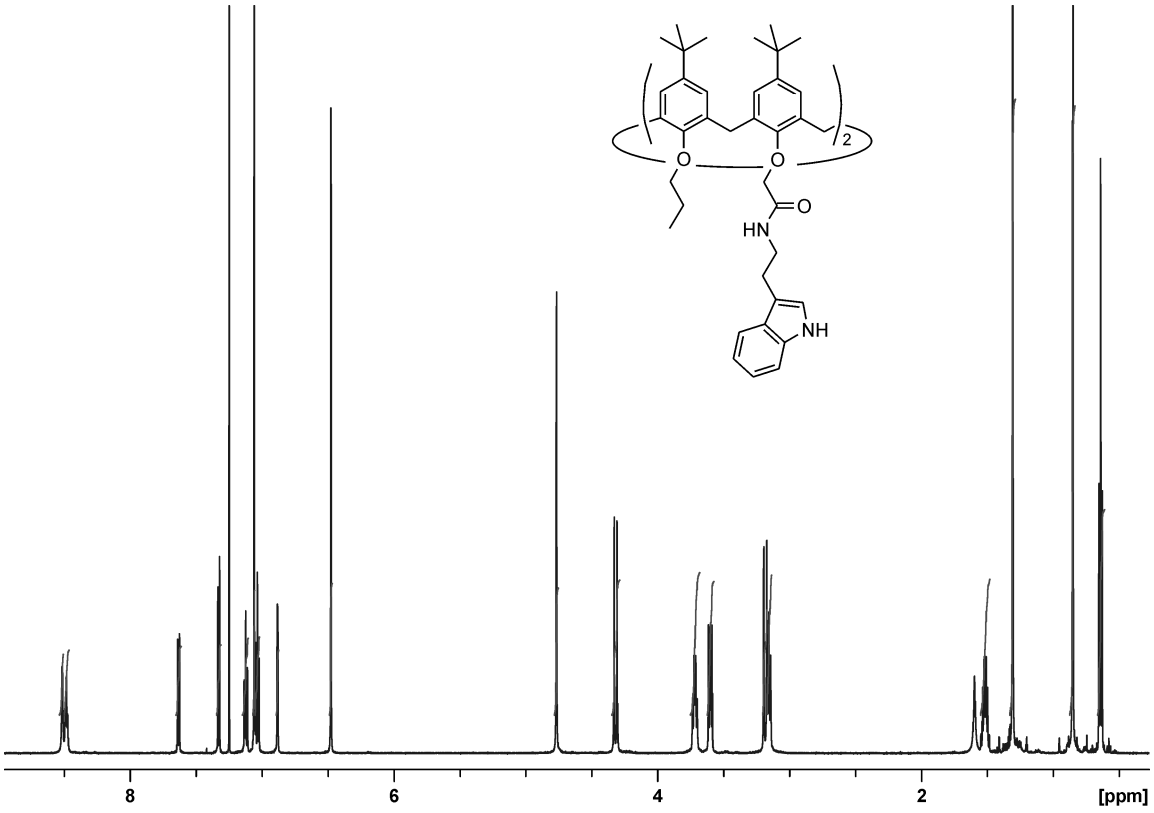


Figure S7. ^{1}H NMR spectrum of calixarene **3** (600 MHz, $CDCl_3$).

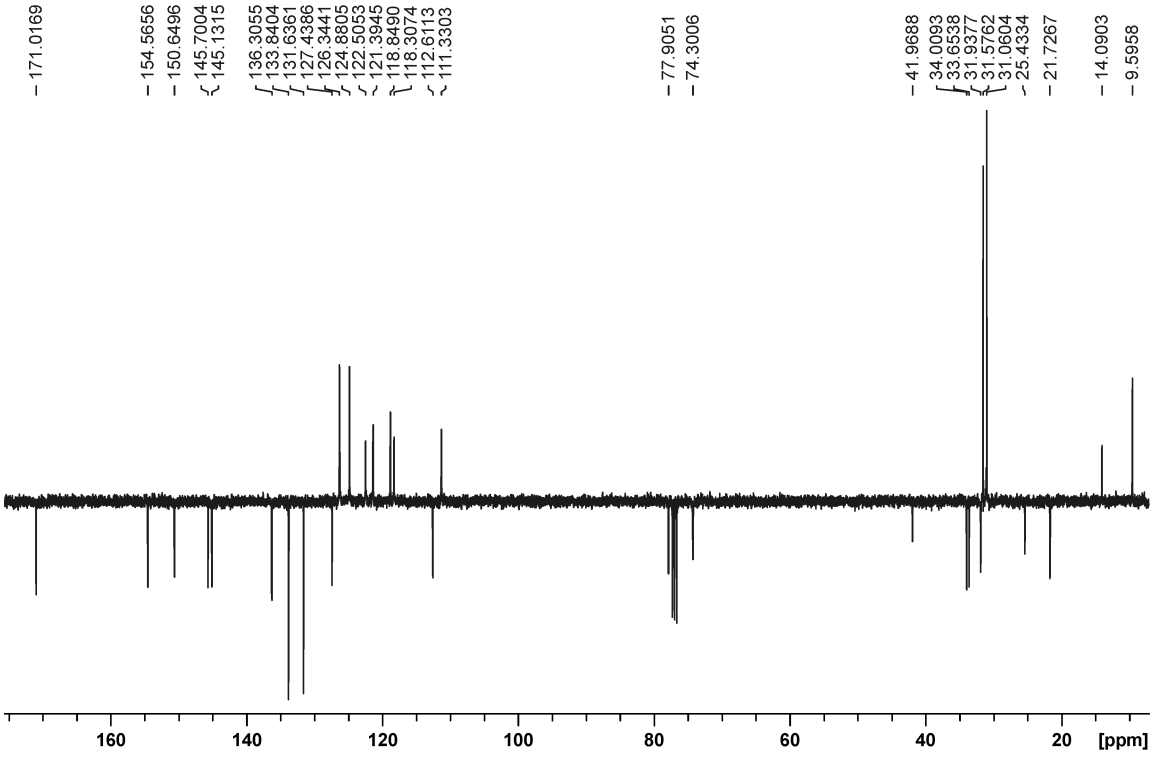


Figure S8. ^{13}C NMR spectrum (APT) of calixarene **3** (100 MHz, $CDCl_3$).

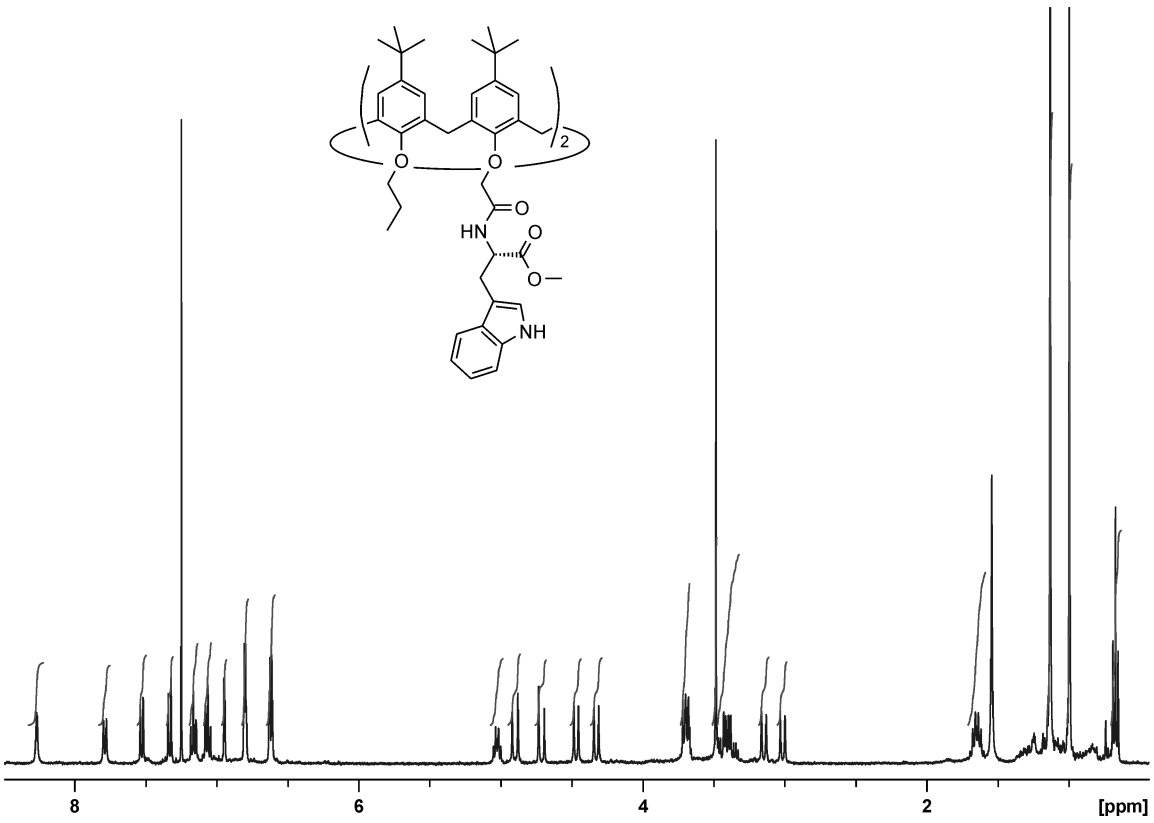


Figure S9. ^{1}H NMR spectrum of calixarene **4** (400 MHz, $CDCl_3$).

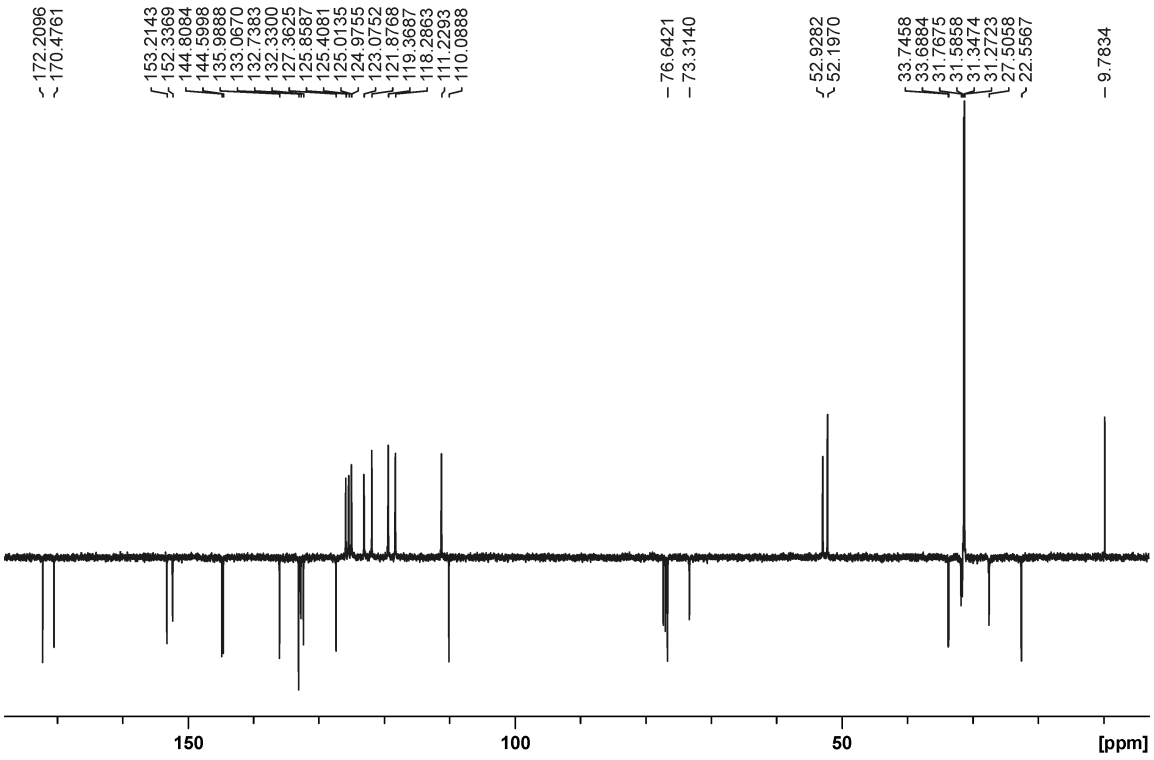


Figure S10. ^{13}C NMR spectrum (APT) of calixarene **4** (100 MHz, $CDCl_3$).

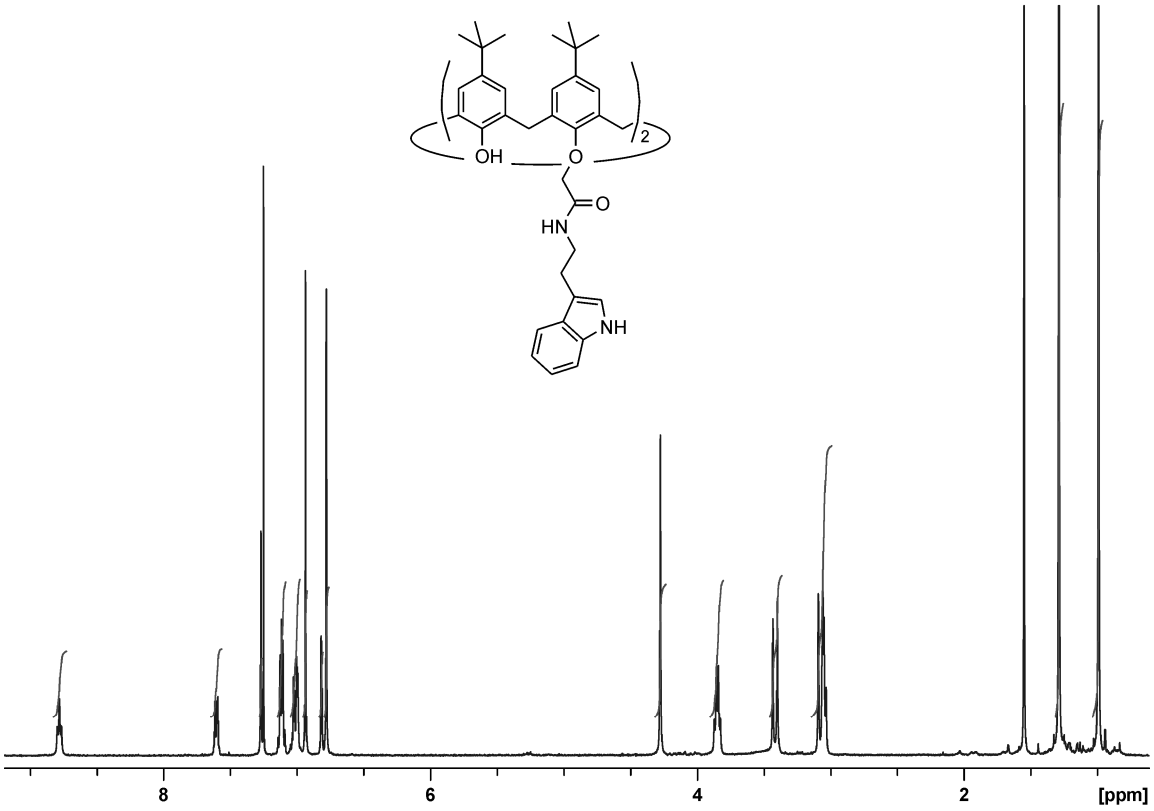


Figure S11. ^{1}H NMR spectrum of calixarene **5** (400 MHz, $CDCl_3$).

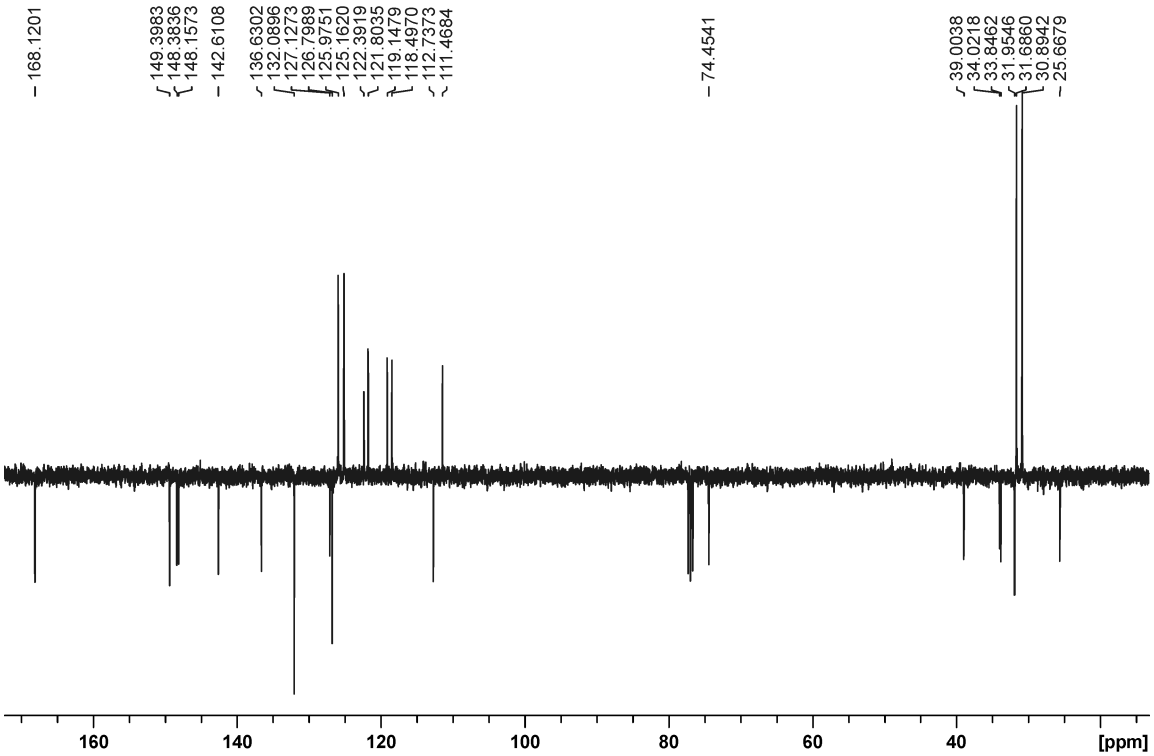


Figure S12. ^{13}C NMR spectrum (APT) of calixarene **5** (100 MHz, $CDCl_3$).

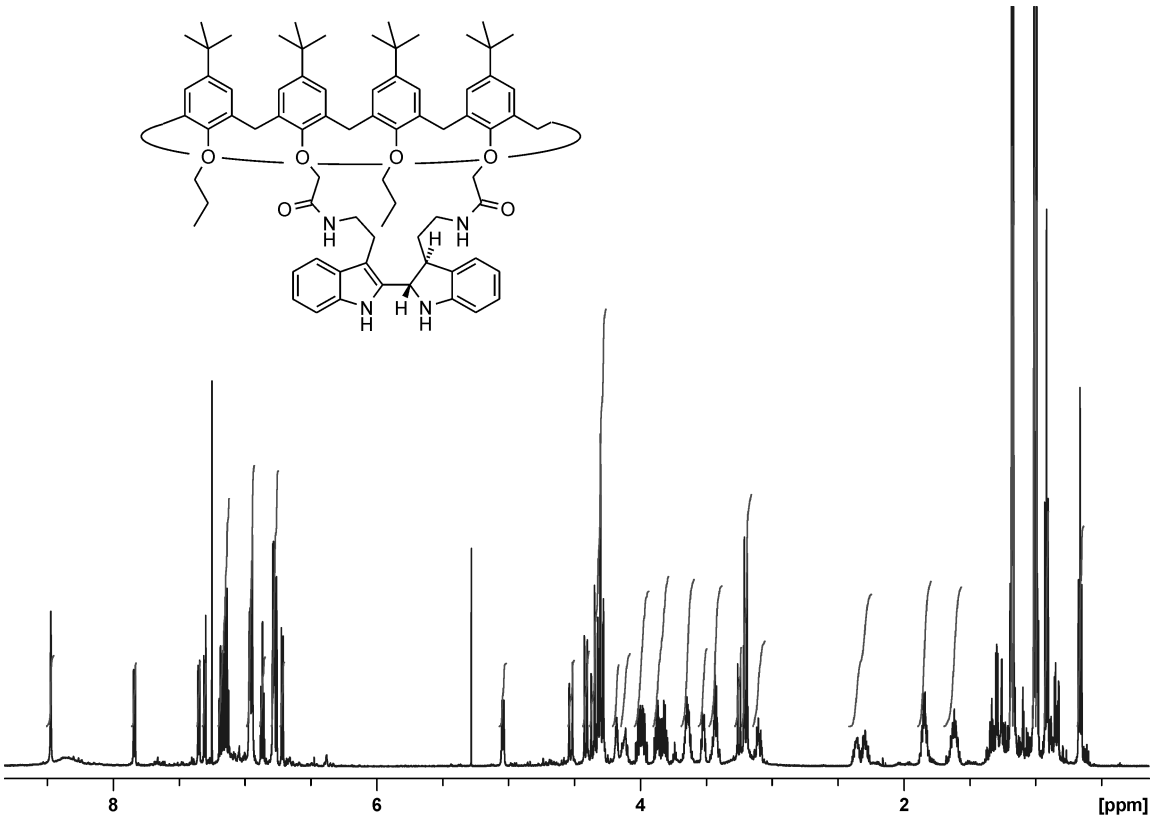


Figure S13. ^{1}H NMR spectrum of calixarene **7** (600 MHz, $CDCl_3$).

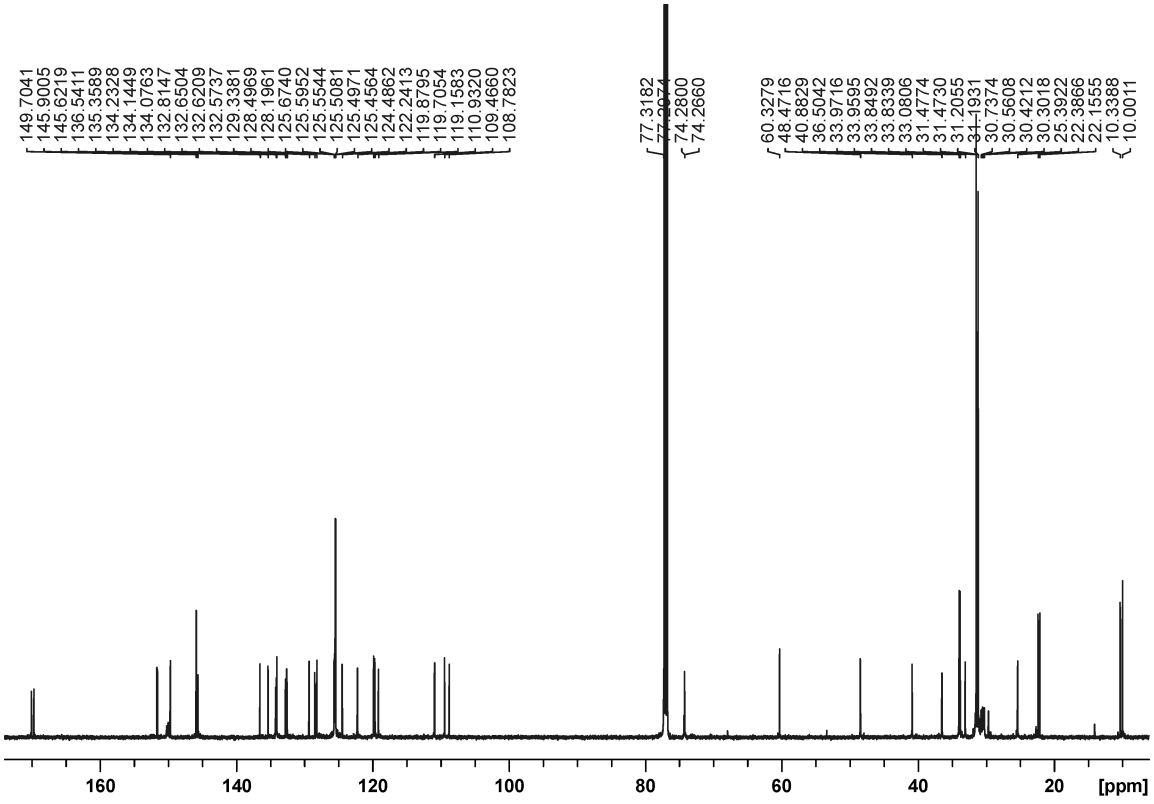


Figure S14. ^{13}C NMR spectrum of calixarene **7** (150 MHz, $CDCl_3$).

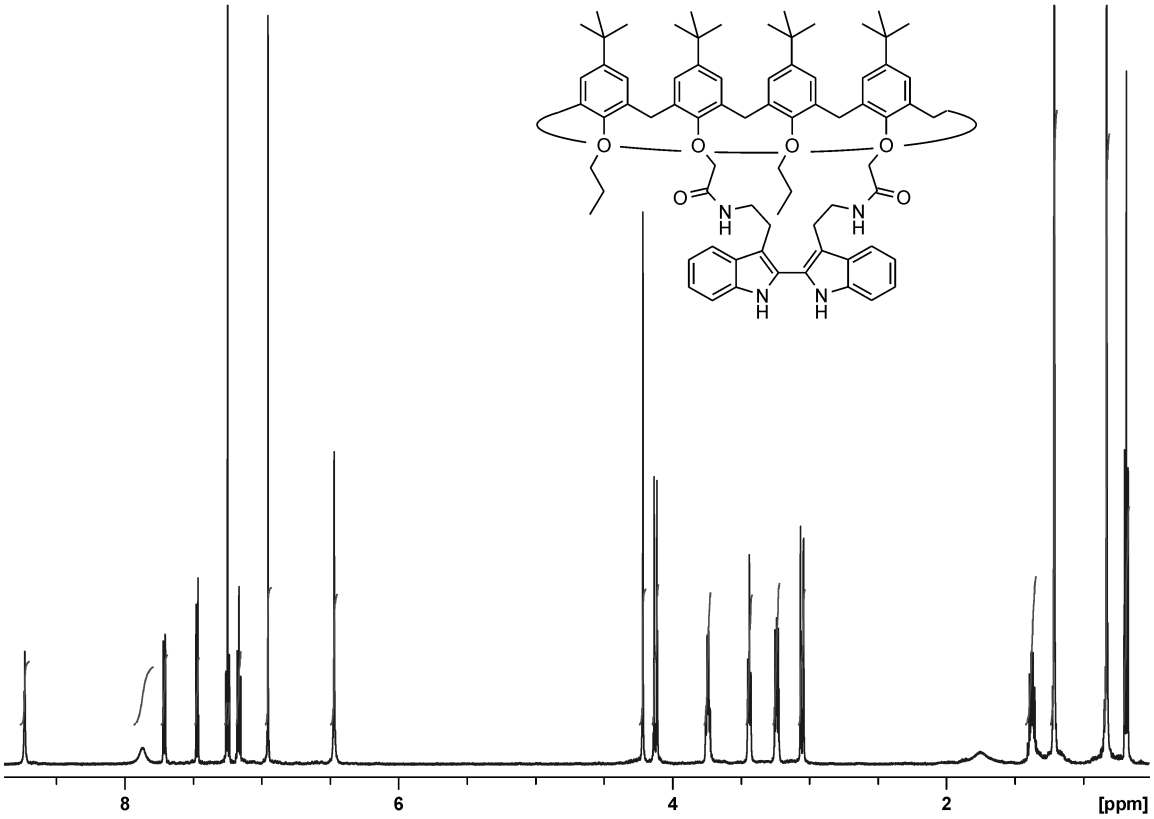


Figure S15. ^{1}H NMR spectrum of calixarene **8** (600 MHz, $CDCl_3$).

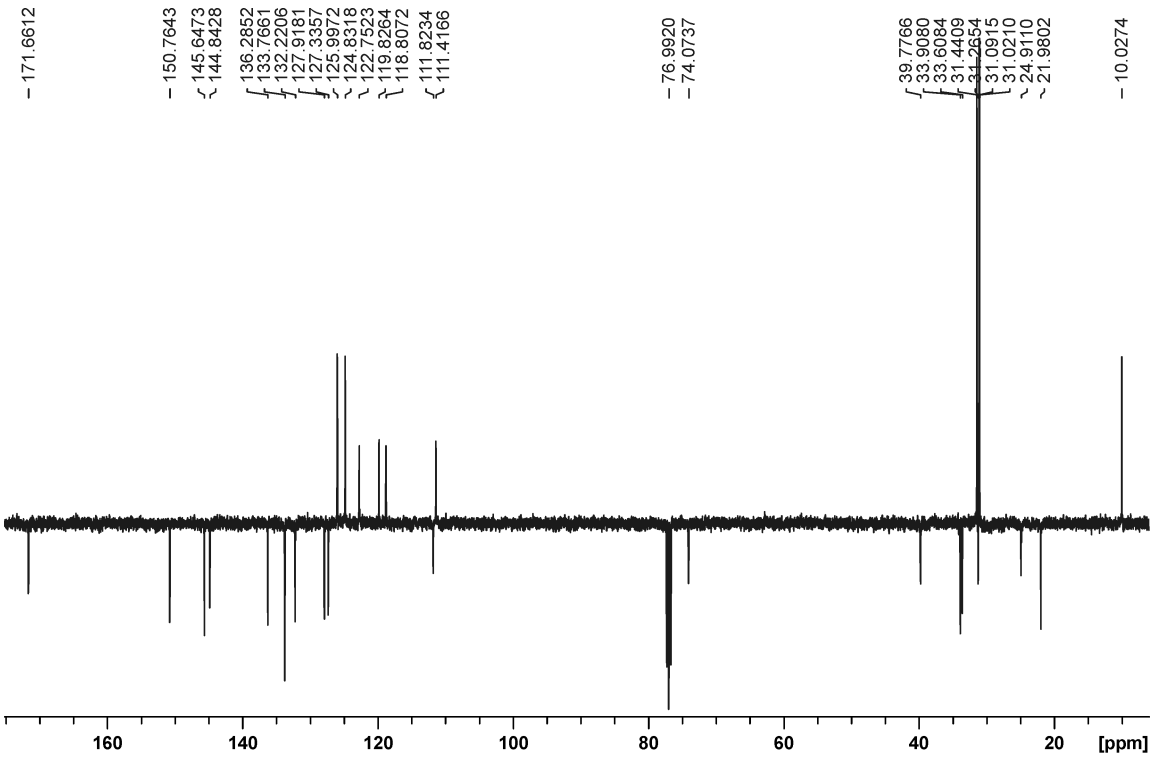


Figure S16. ^{13}C NMR spectrum (APT) of calixarene **8** (100 MHz, $CDCl_3$).

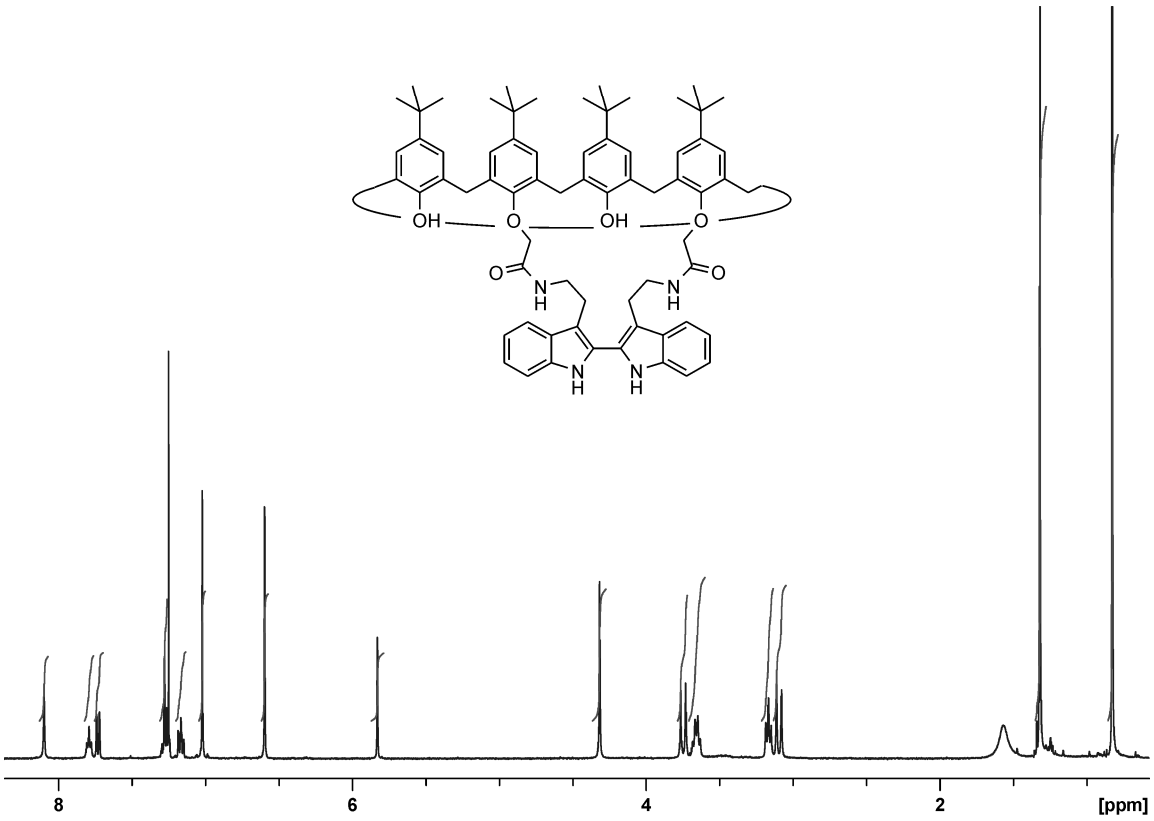


Figure S17. ^{1}H NMR spectrum of calixarene **9** (400 MHz, $CDCl_3$).

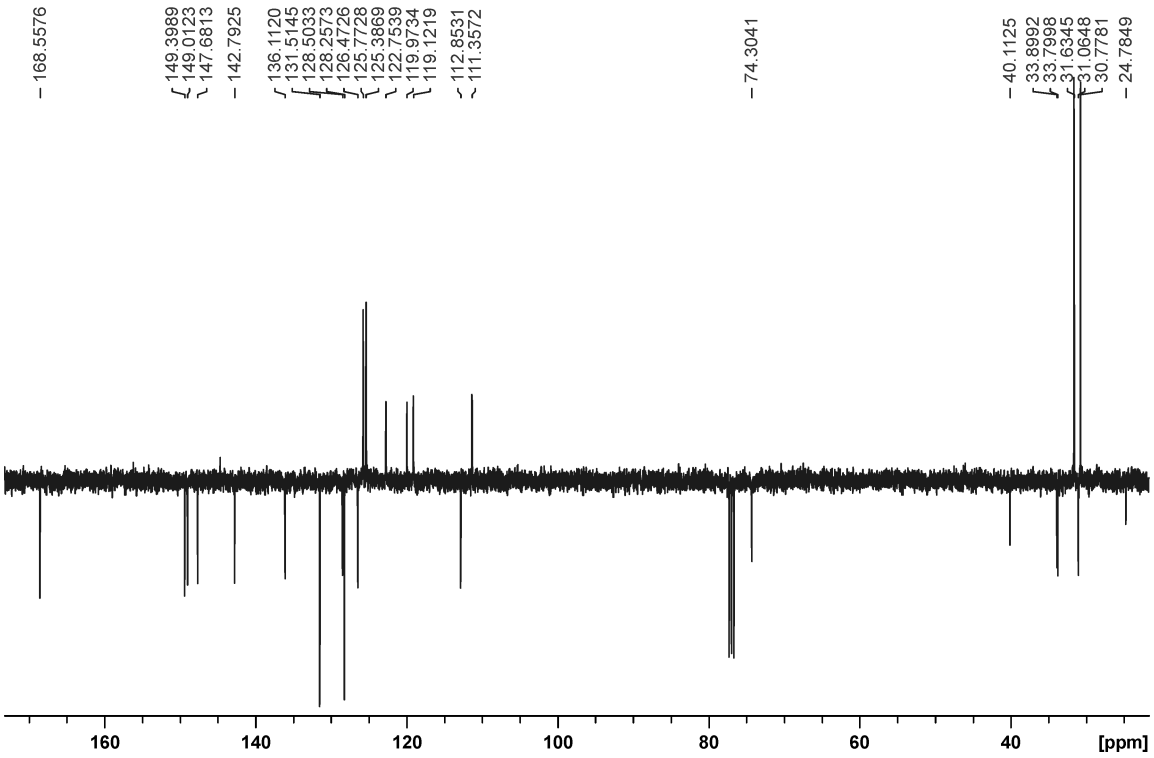


Figure S18. ^{13}C NMR spectrum (APT) of calixarene **9** (100 MHz, $CDCl_3$).

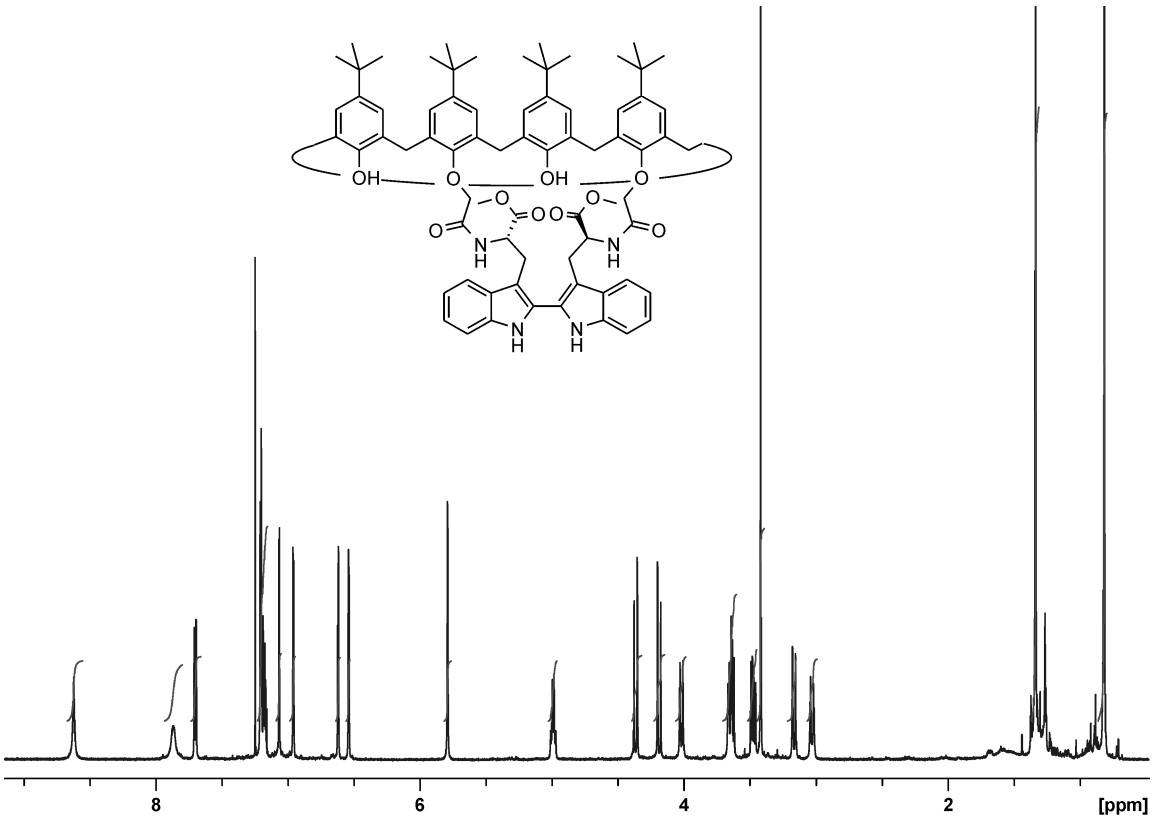


Figure S19. ^{1}H NMR spectrum of calixarene **10** (600 MHz, $CDCl_3$).

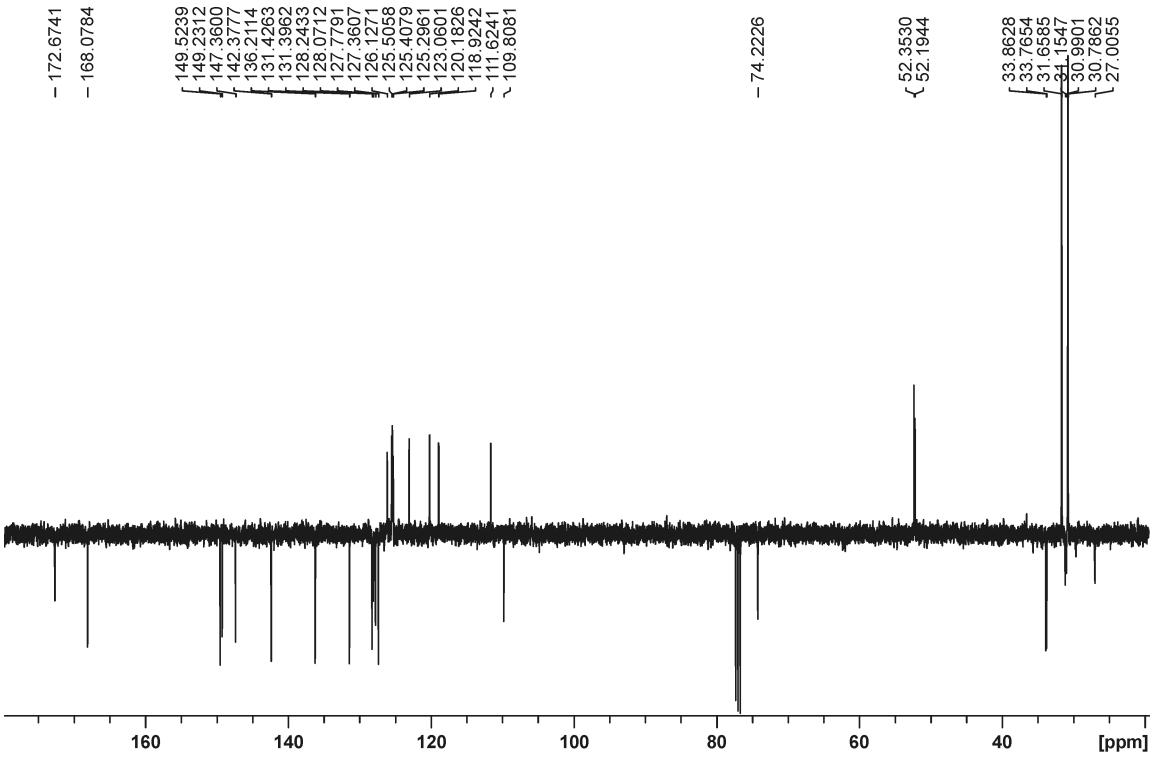


Figure S20. ^{13}C NMR spectrum (APT) of calixarene **10** (100 MHz, $CDCl_3$).

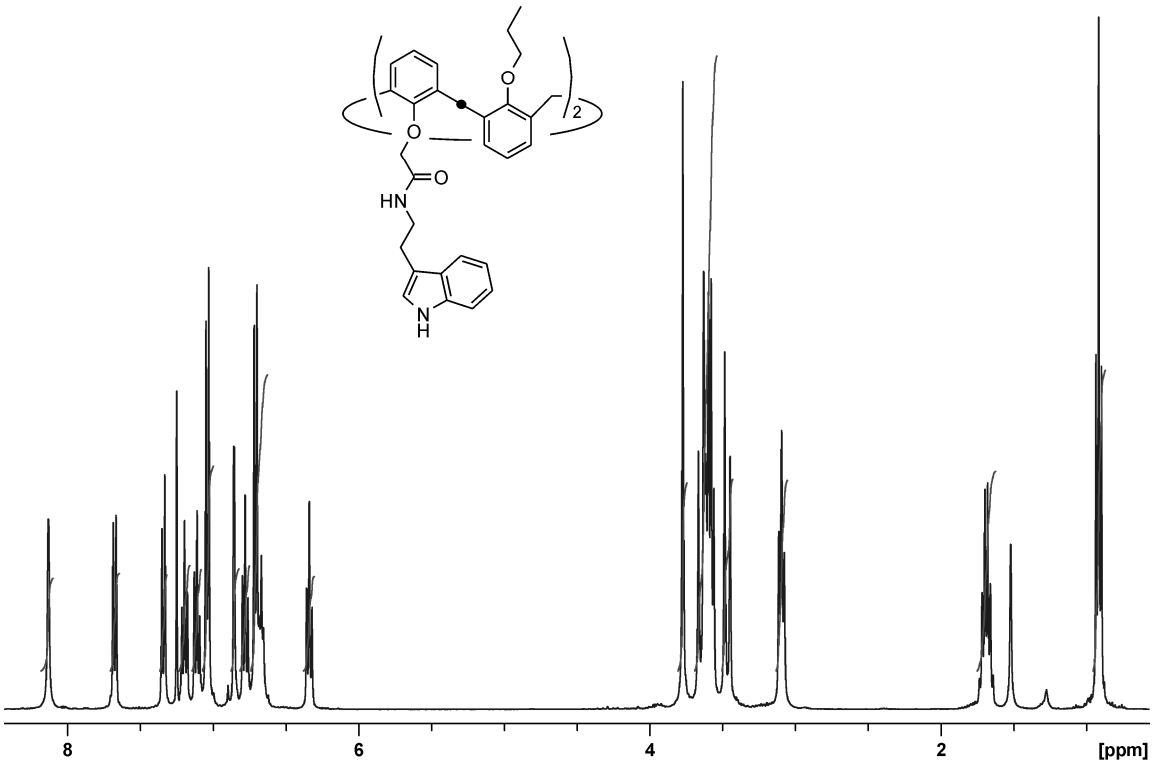


Figure S21. ^{1}H NMR spectrum of calixarene **13** (400 MHz, $CDCl_3$).

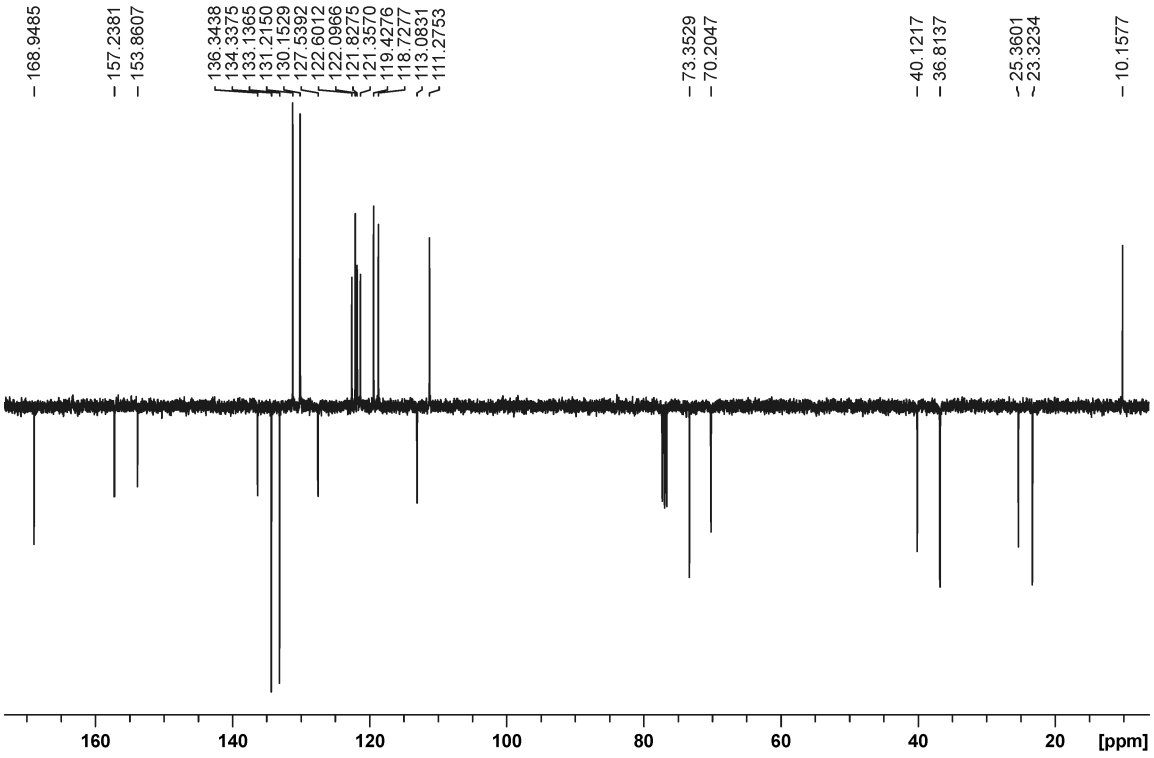


Figure S22. ^{13}C NMR spectrum (APT) of calixarene **13** (100 MHz, $CDCl_3$).

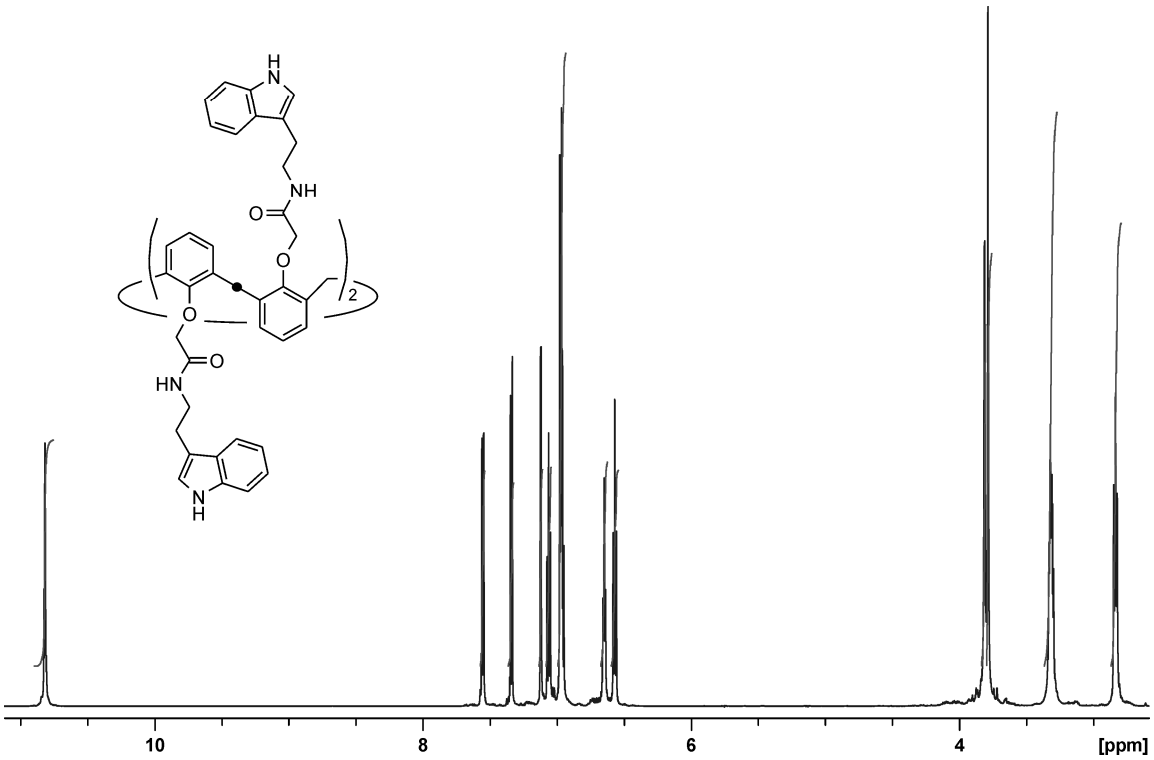


Figure S23. ^{1}H NMR spectrum of calixarene **14** (600 MHz, DMSO-d_6).

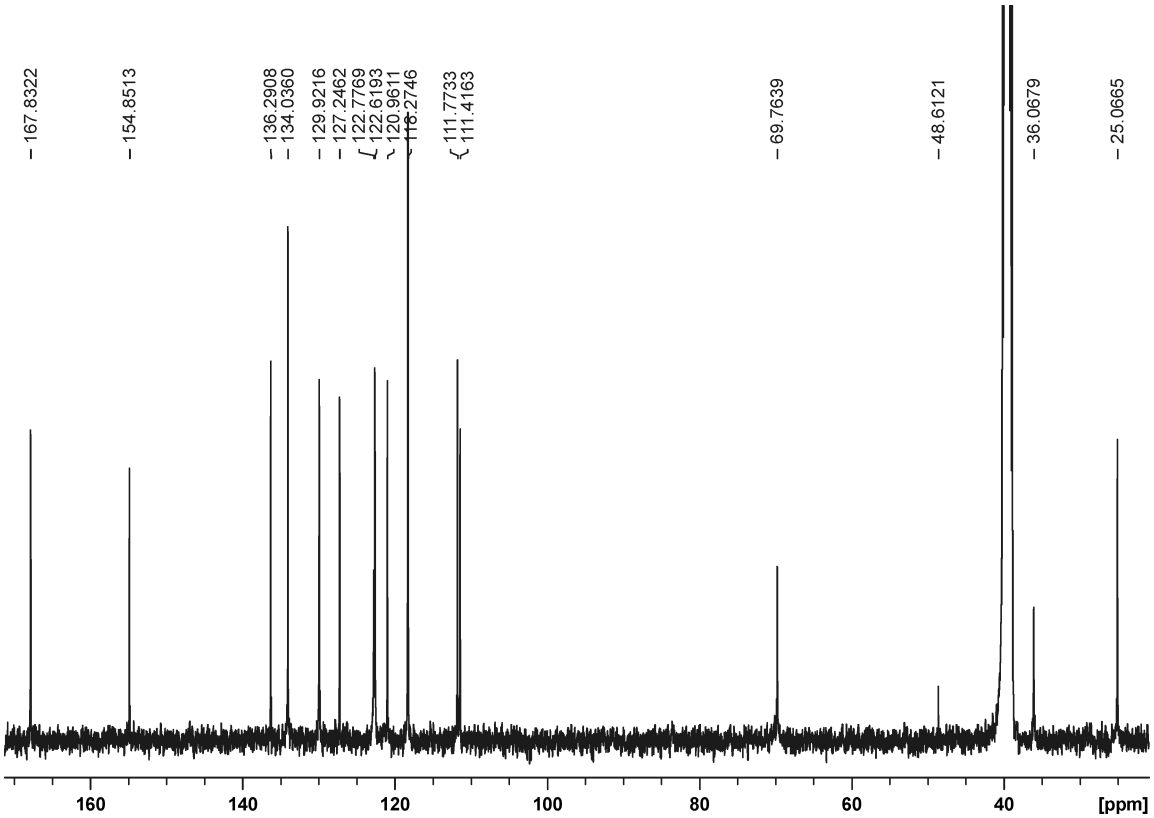


Figure S24. ^{13}C NMR spectrum of calixarene **14** (100 MHz, DMSO-d_6).

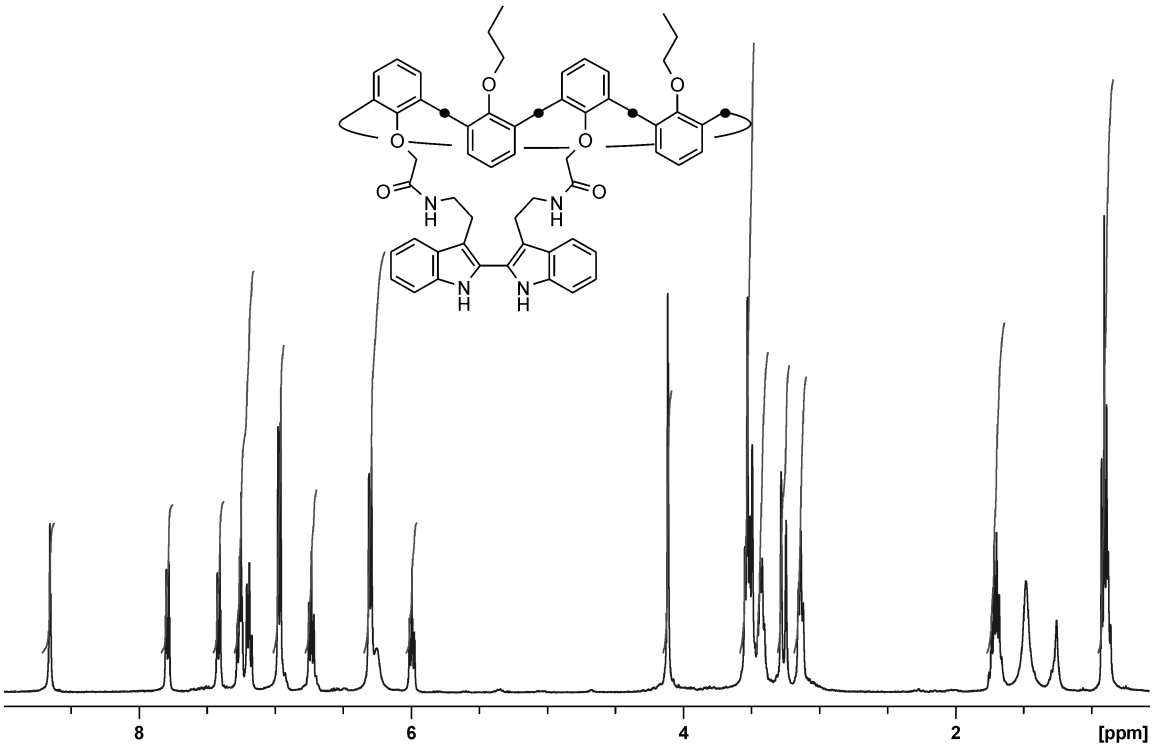


Figure S25. ^{1}H NMR spectrum of calixarene **15** (400 MHz, $CDCl_3$).

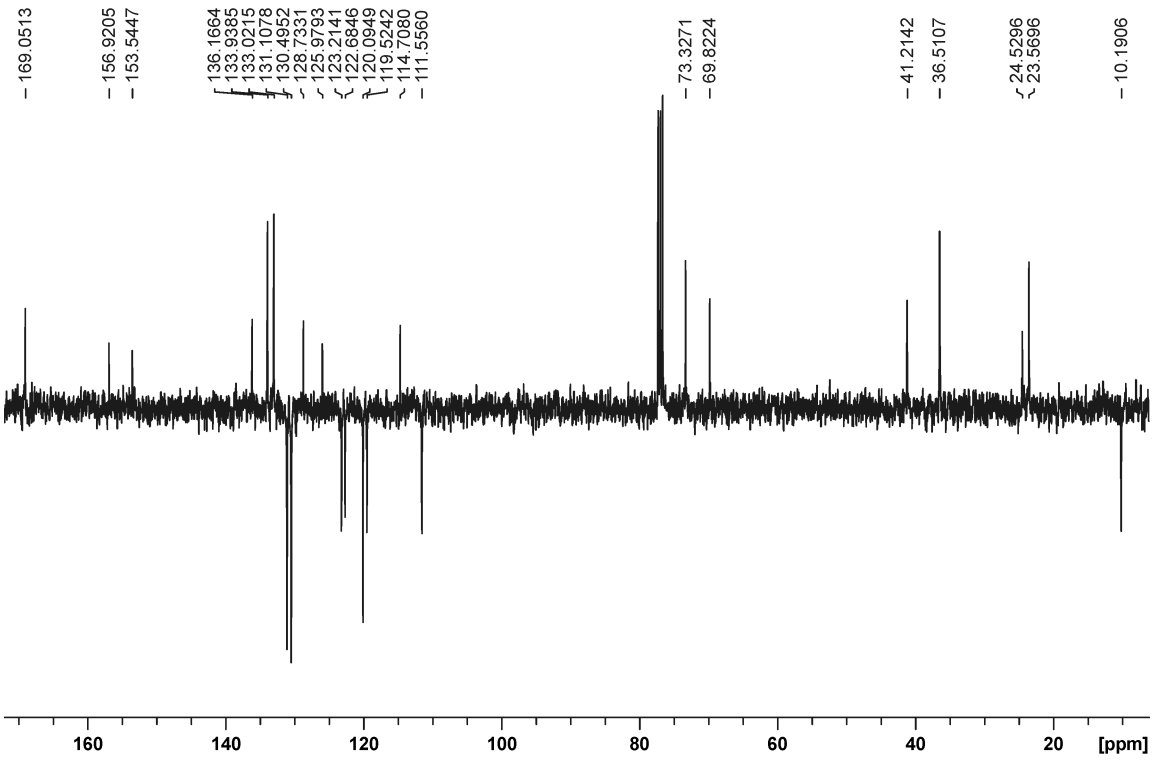


Figure S26. ^{13}C NMR spectrum (APT) of calixarene **15** (100 MHz, $CDCl_3$).

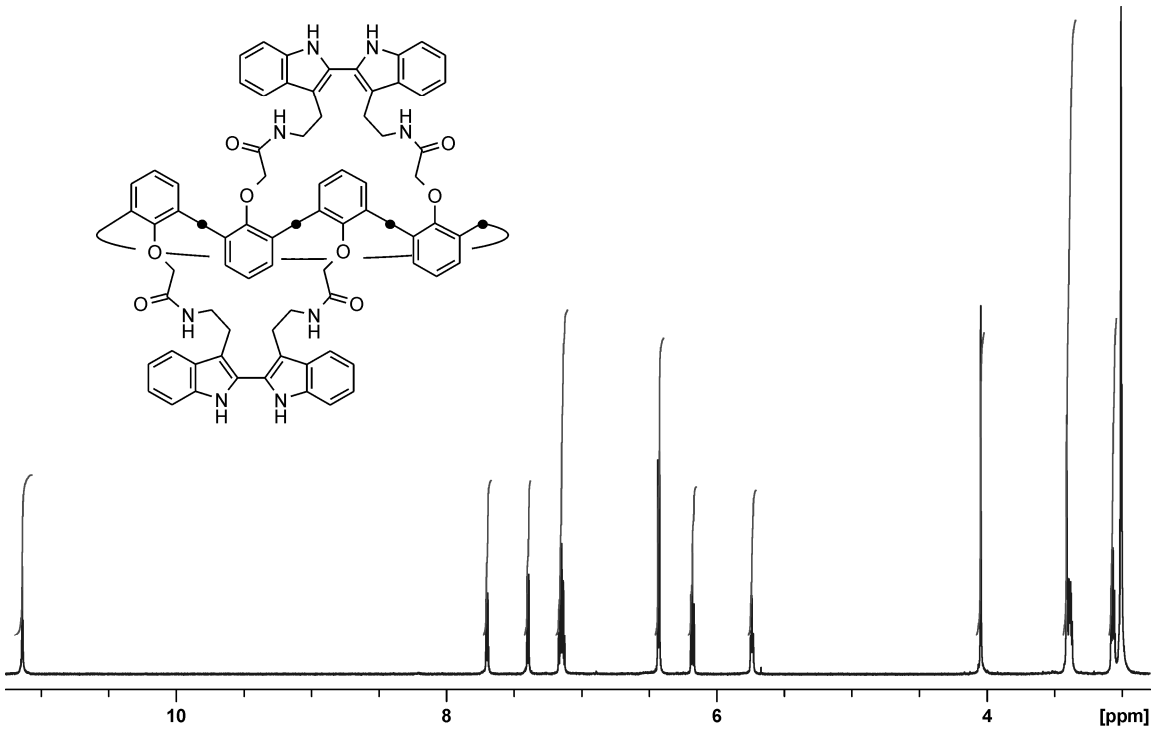


Figure S27. ^{1}H NMR spectrum of calixarene **16** (600 MHz, DMSO-d_6, 85 °C).

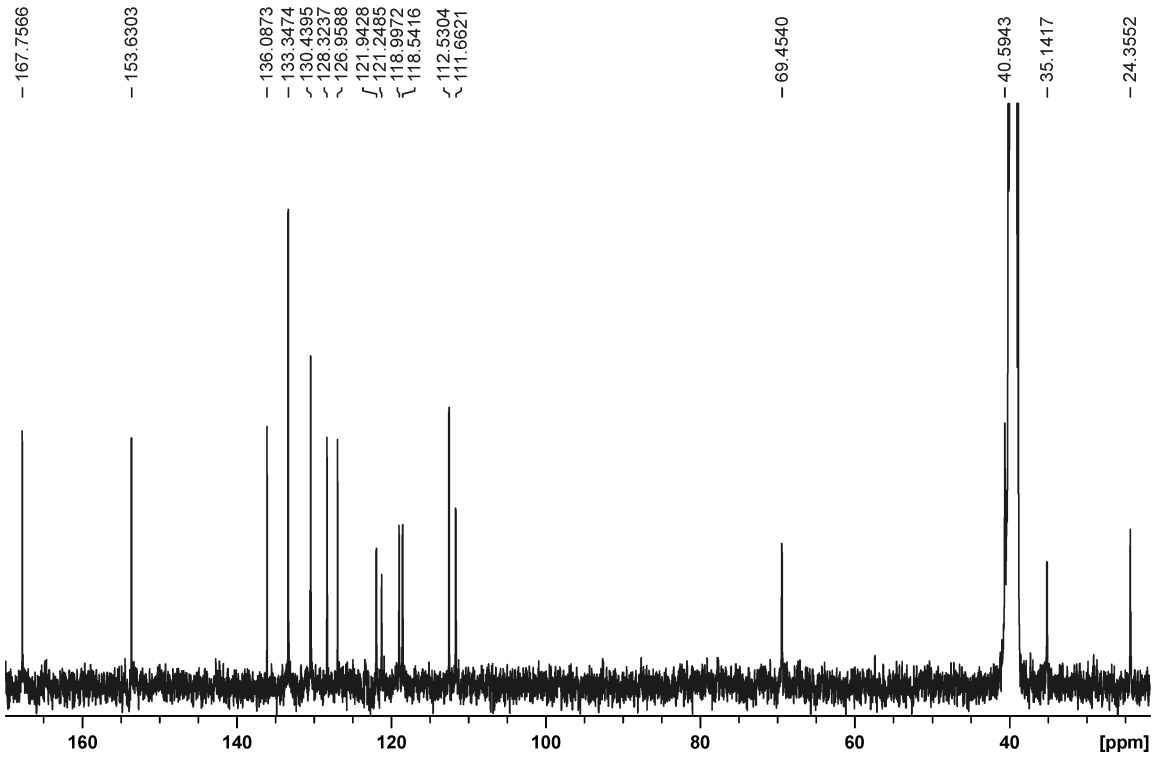


Figure S28. ^{13}C NMR spectrum of calixarene **16** (100 MHz, DMSO-d_6).

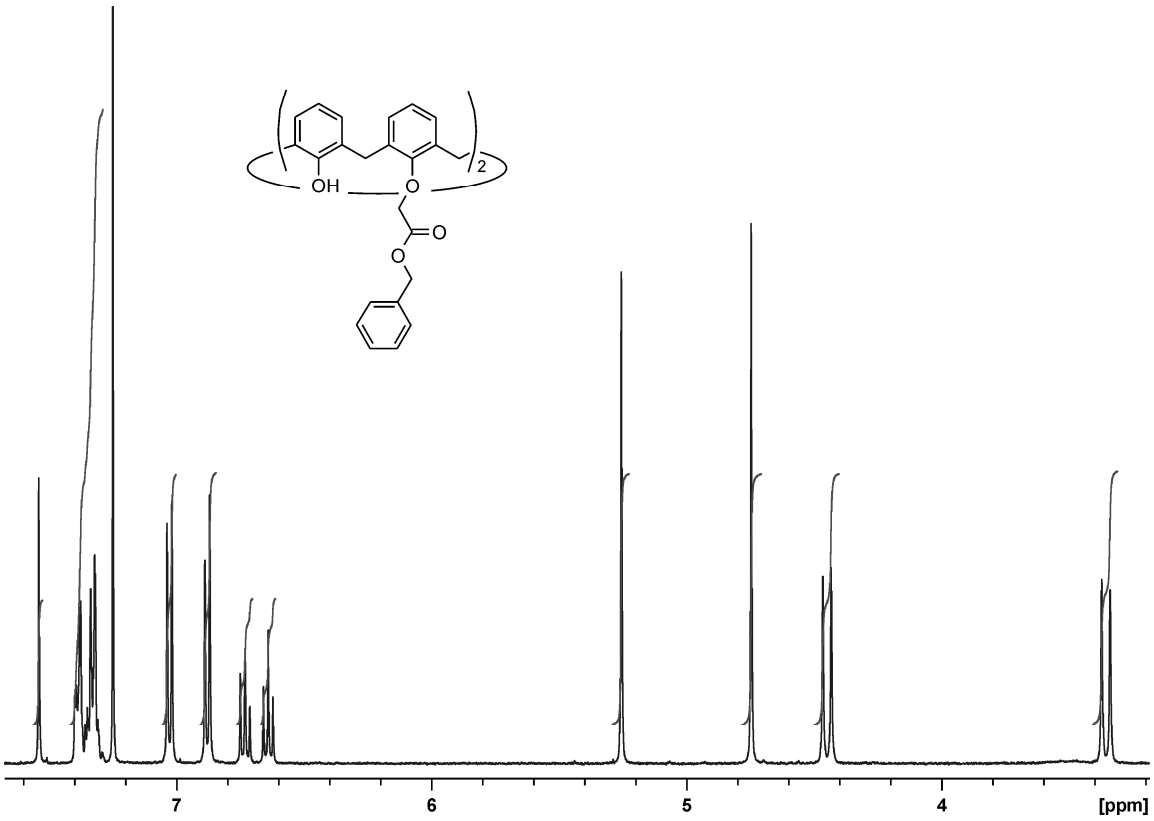


Figure S29. ^{1}H NMR spectrum of calixarene **21** (400 MHz, $CDCl_3$).

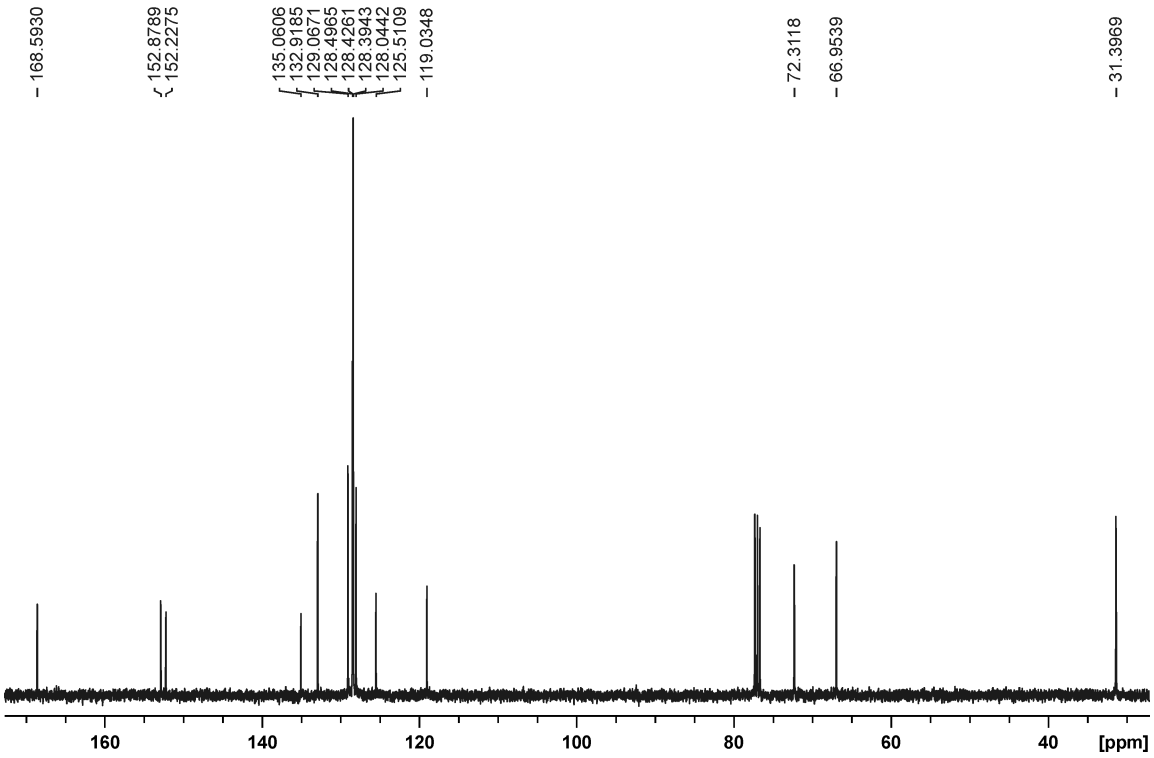


Figure S30. ^{13}C NMR spectrum of calixarene **21** (100 MHz, $CDCl_3$).

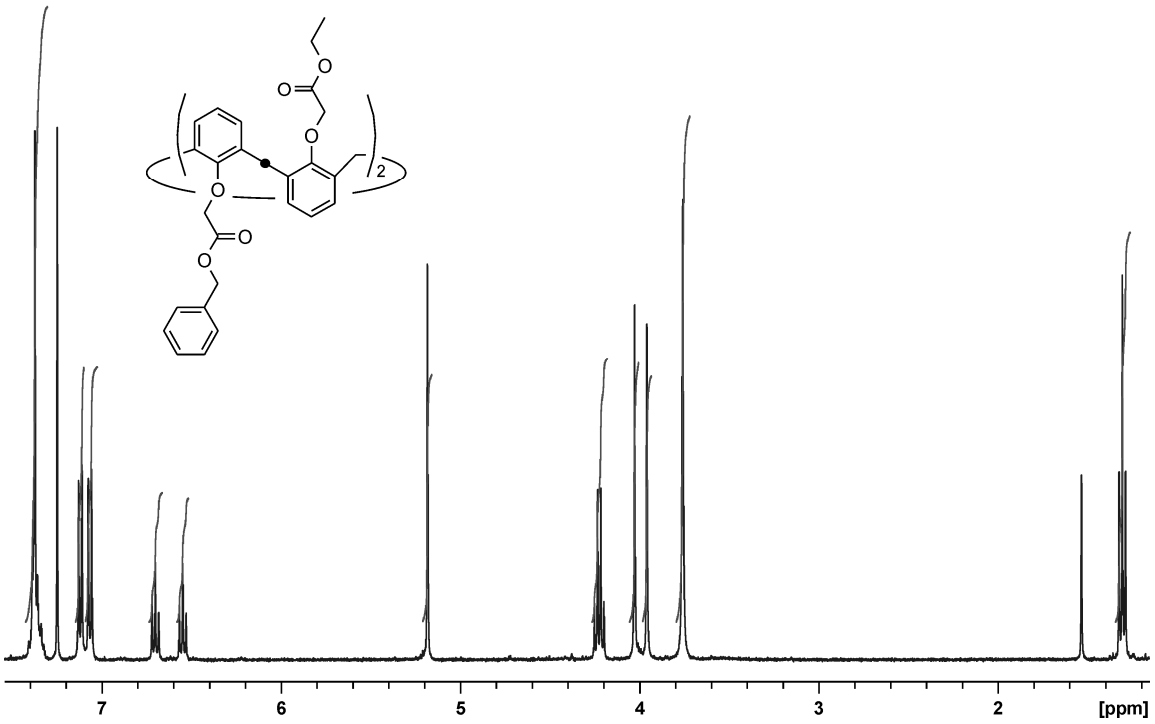


Figure S31. ^{1}H NMR spectrum of calixarene **22** (400 MHz, $CDCl_3$).

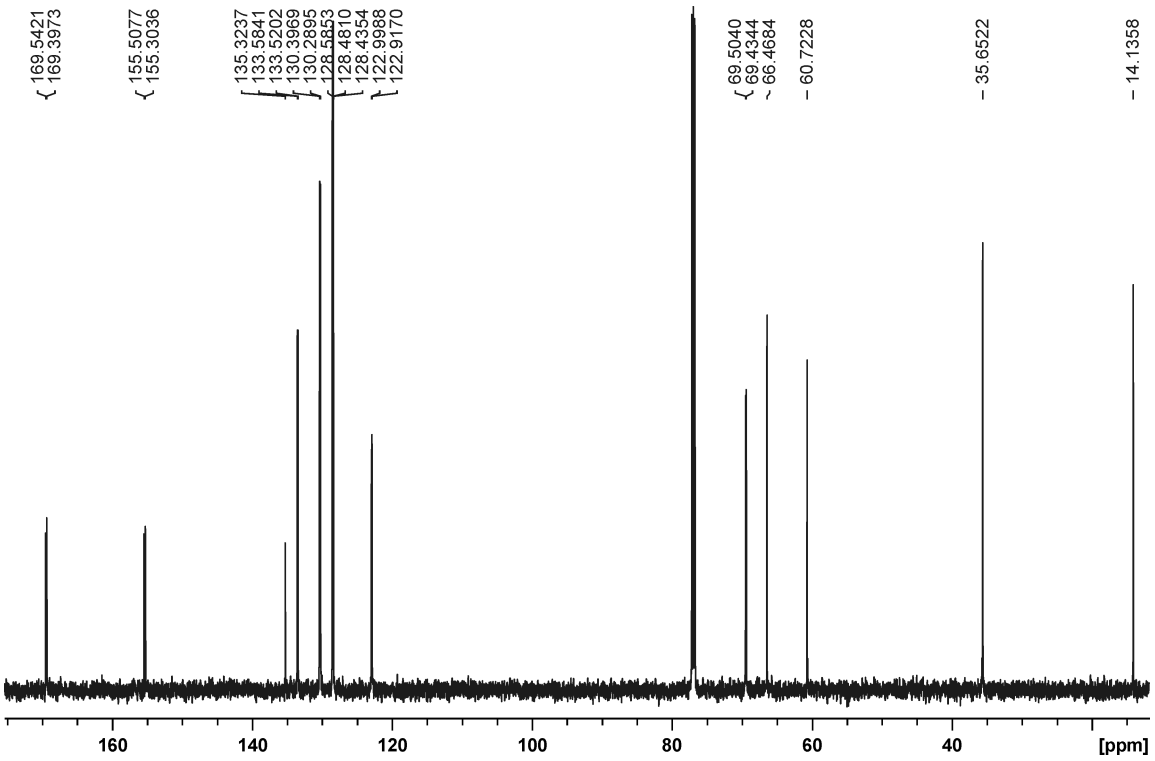


Figure S32. ^{13}C NMR spectrum of calixarene **22** (150 MHz, $CDCl_3$).

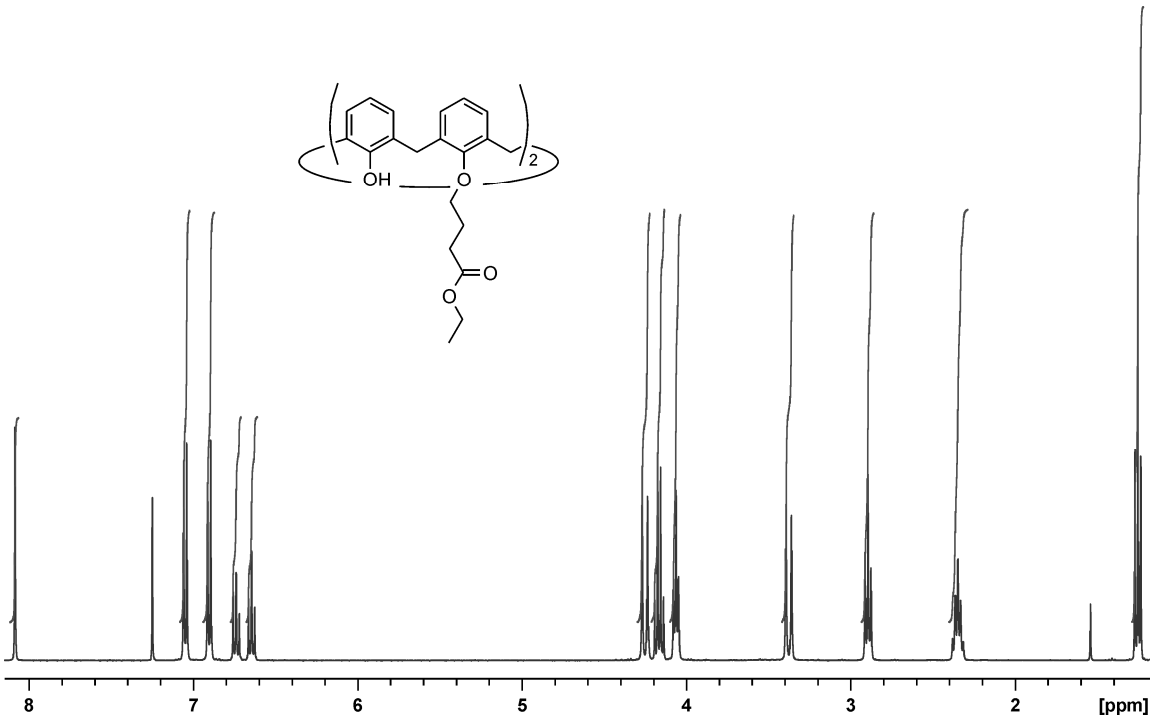


Figure S33. ^{1}H NMR spectrum of calixarene **24** (400 MHz, $CDCl_3$).

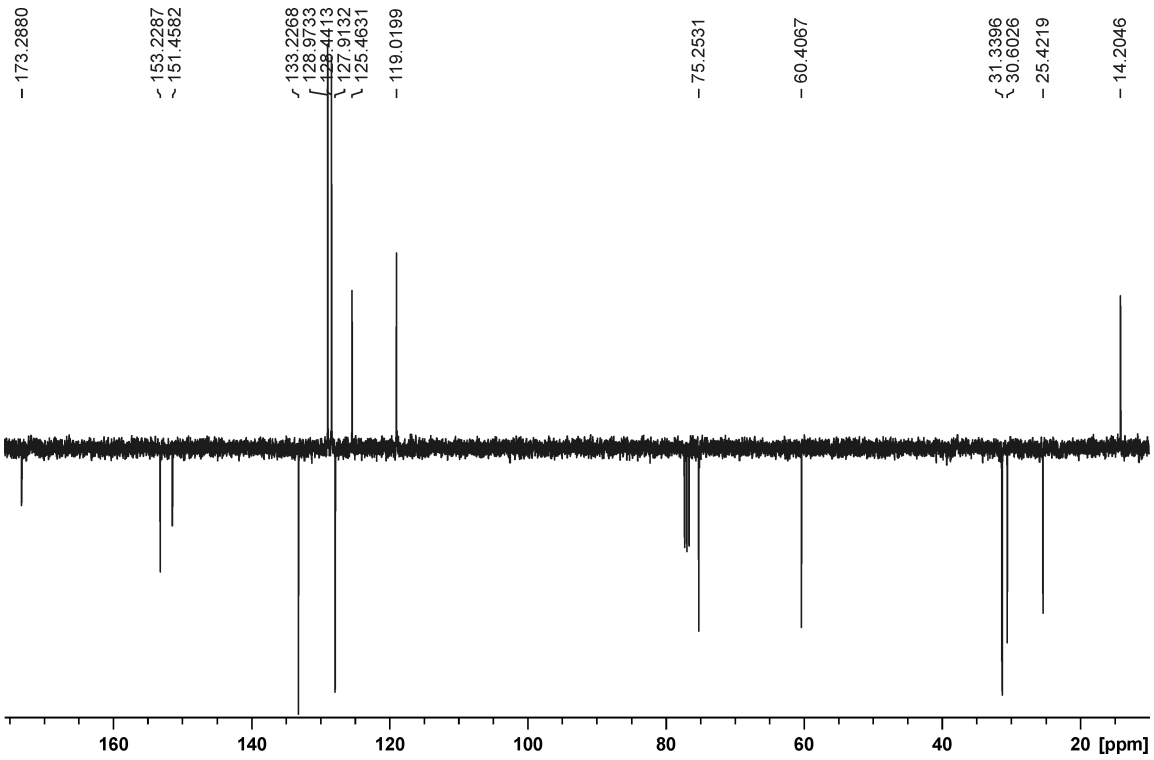


Figure S34. ^{13}C NMR spectrum (APT) of calixarene **24** (100 MHz, $CDCl_3$).

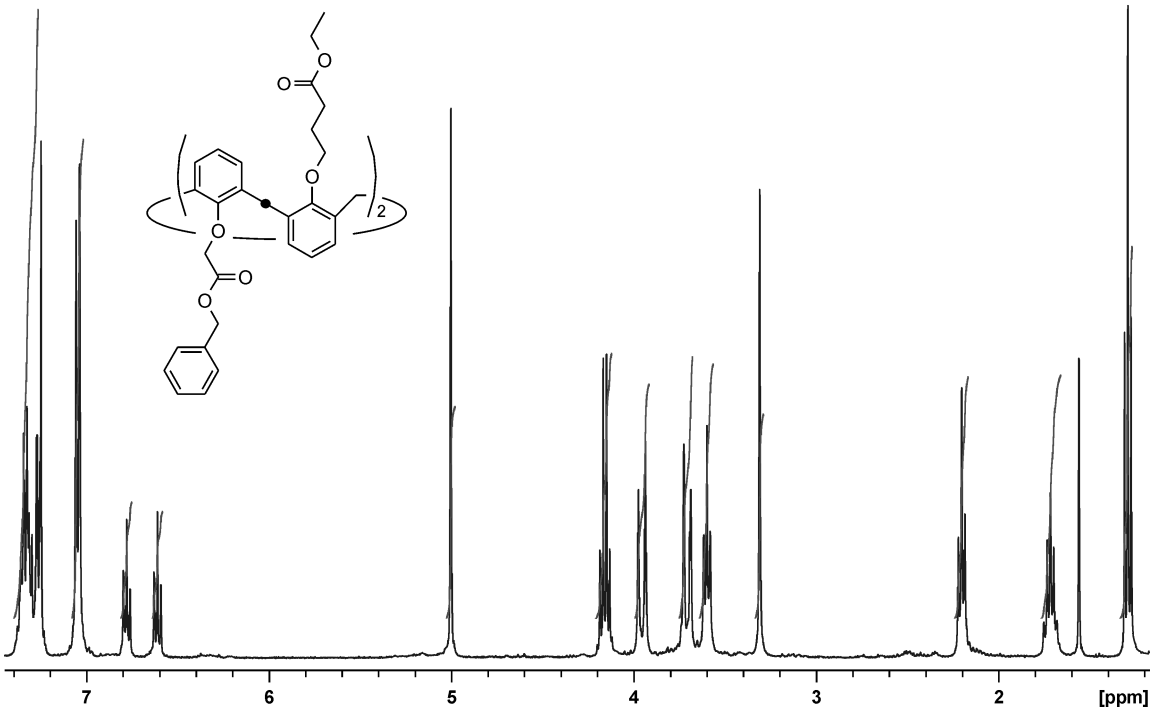


Figure S35. ^{1}H NMR spectrum of calixarene **25** (400 MHz, $CDCl_3$).

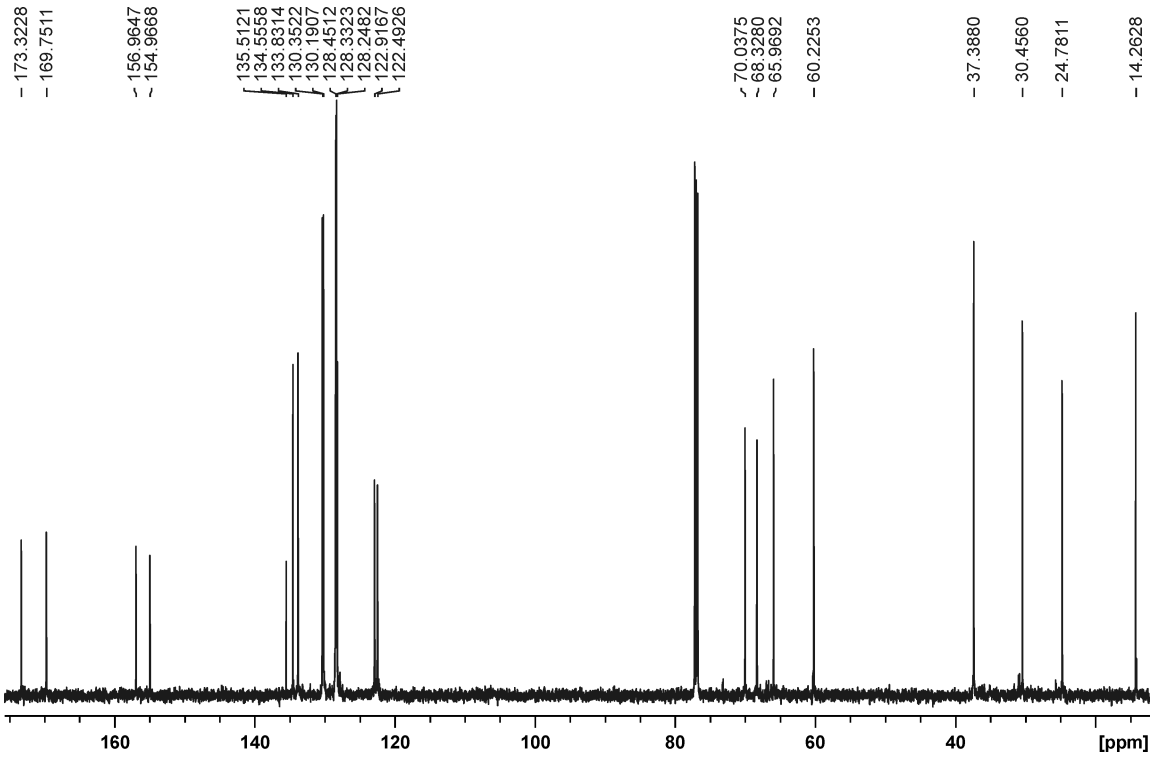


Figure S36. ^{13}C NMR spectrum of calixarene **25** (150 MHz, $CDCl_3$).

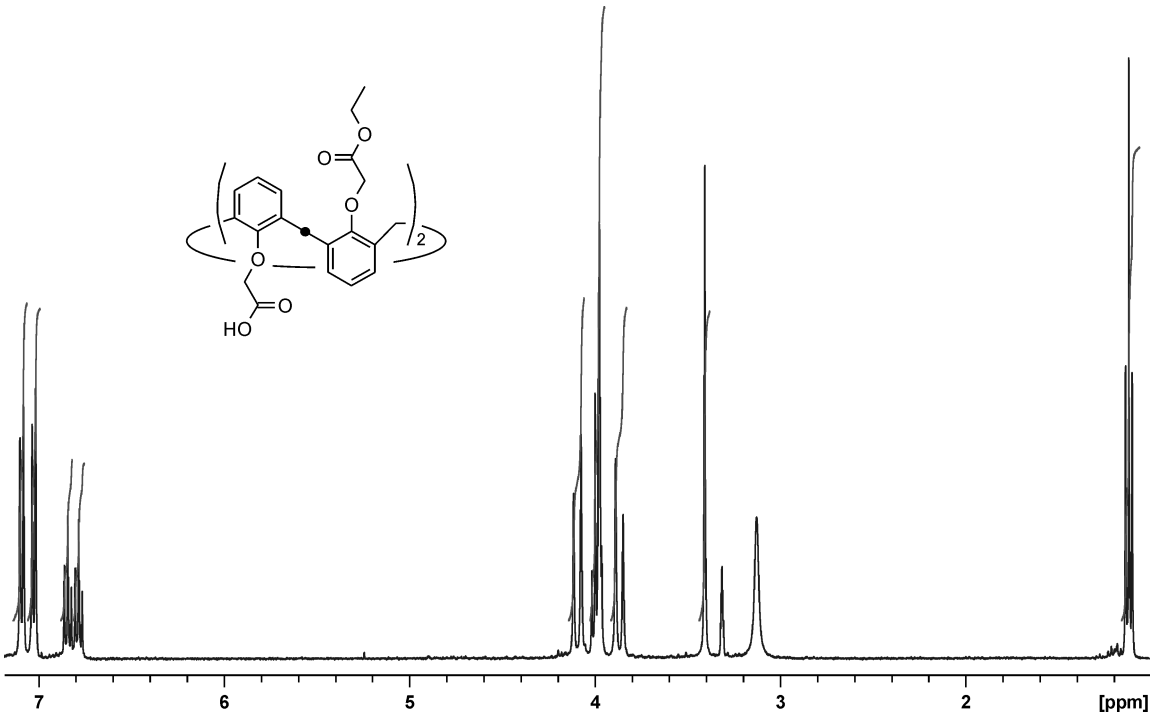


Figure S37. ^{1}H NMR spectrum of calixarene **26** (400 MHz, $CDCl_3$+CD_3OD).

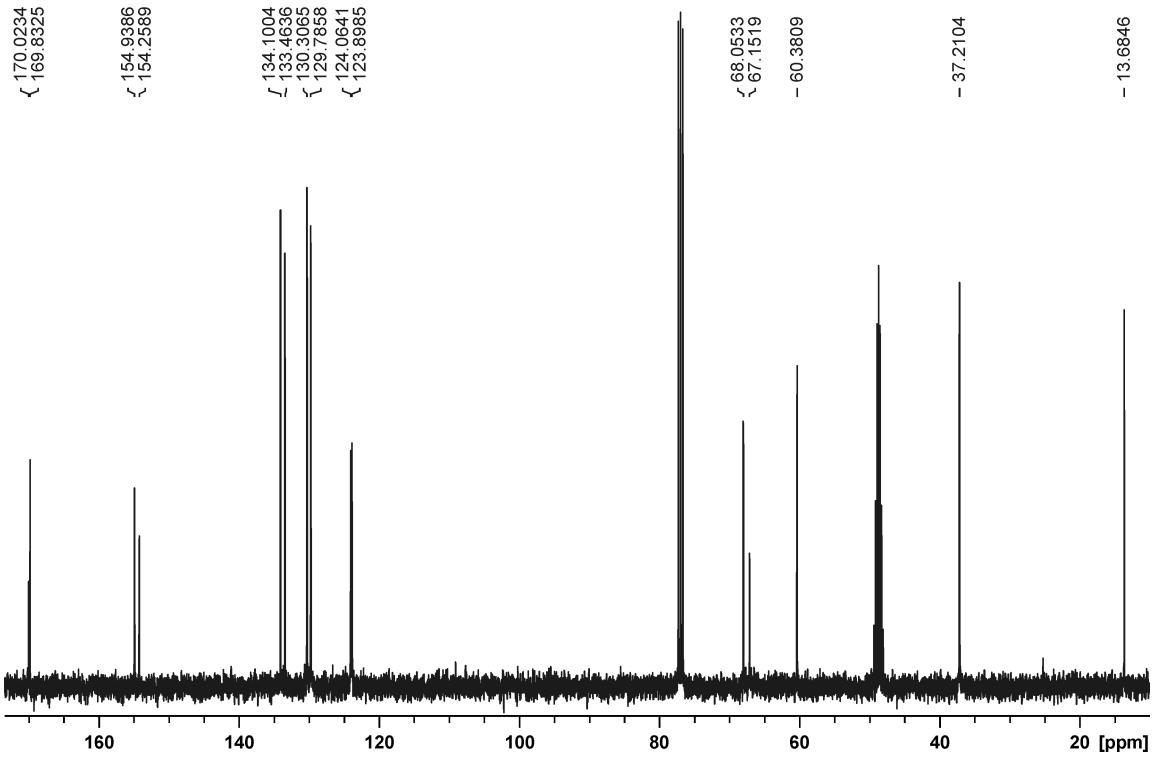


Figure S38. ^{13}C NMR spectrum of calixarene **26** (100 MHz, $CDCl_3$+CD_3OD).

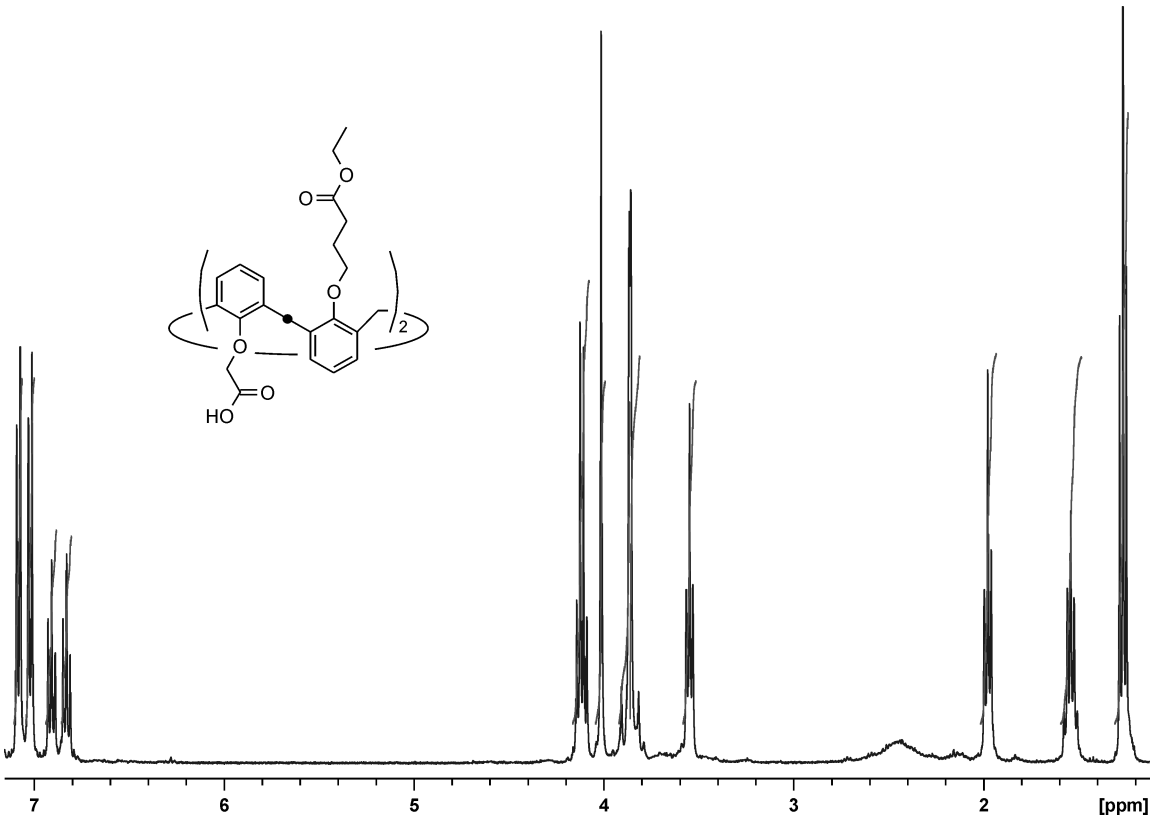


Figure S39. ^{1}H NMR spectrum of calixarene **27** (400 MHz, $CDCl_3$+CD_3OD).

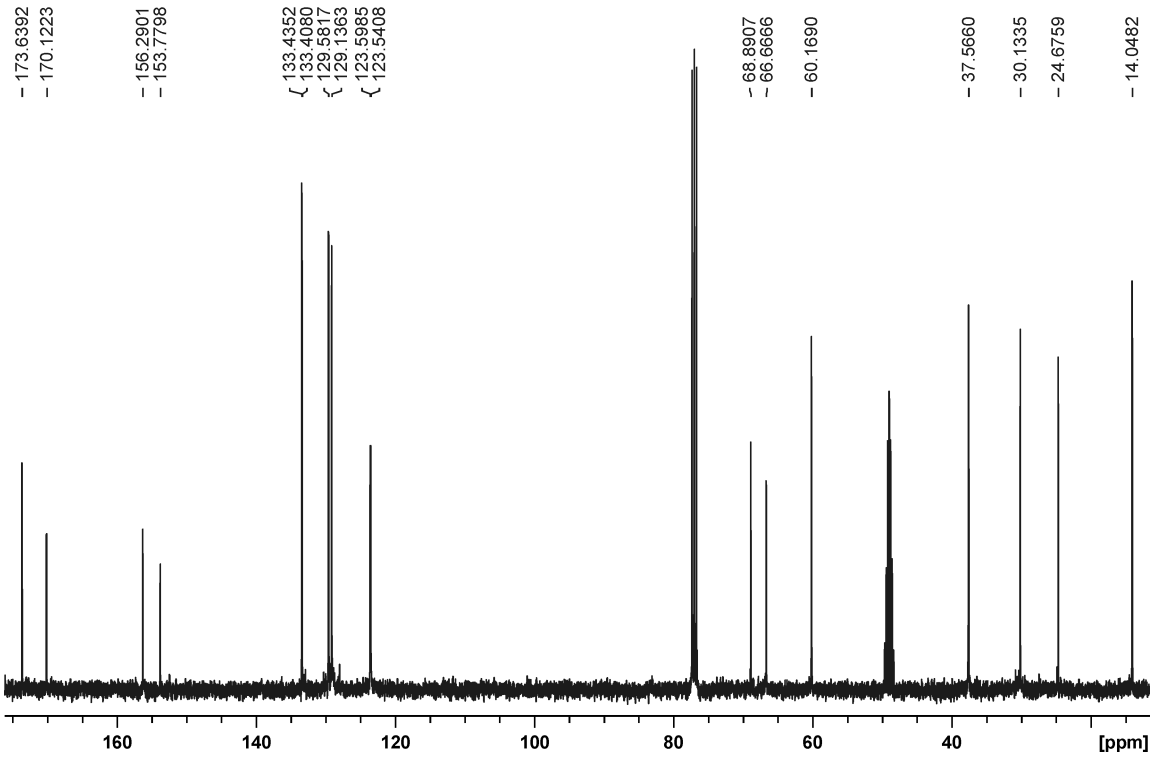


Figure S40. ^{13}C NMR spectrum of calixarene **27** (100 MHz, $CDCl_3$+CD_3OD).

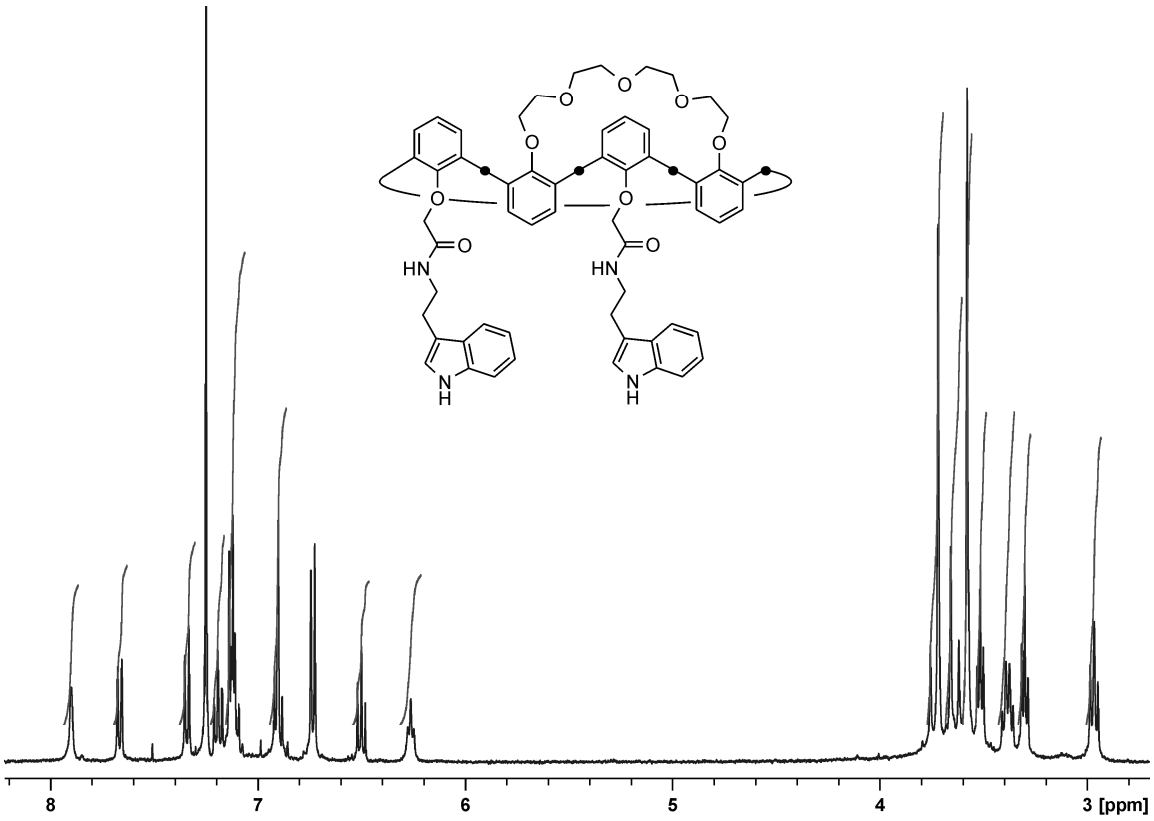


Figure S41. ^{1}H NMR spectrum of calixarene **28** (400 MHz, $CDCl_3$).

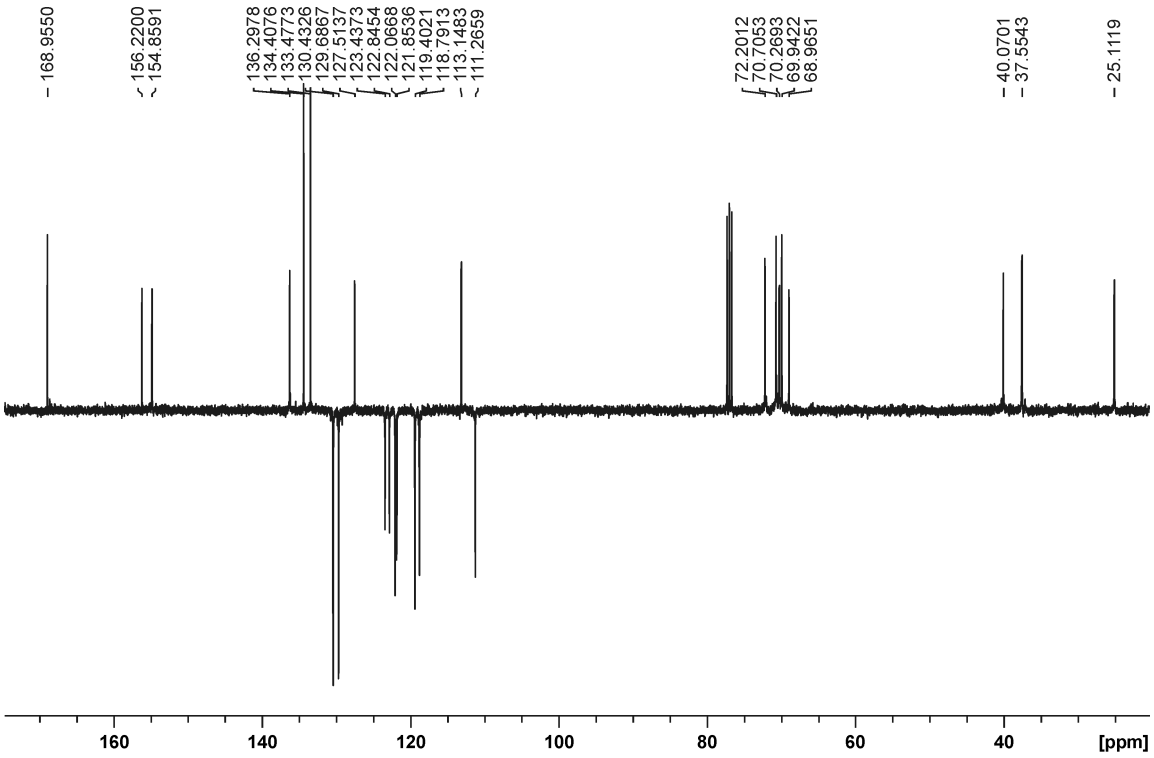


Figure S42. ^{13}C NMR spectrum (APT) of calixarene **28** (100 MHz, $CDCl_3$).

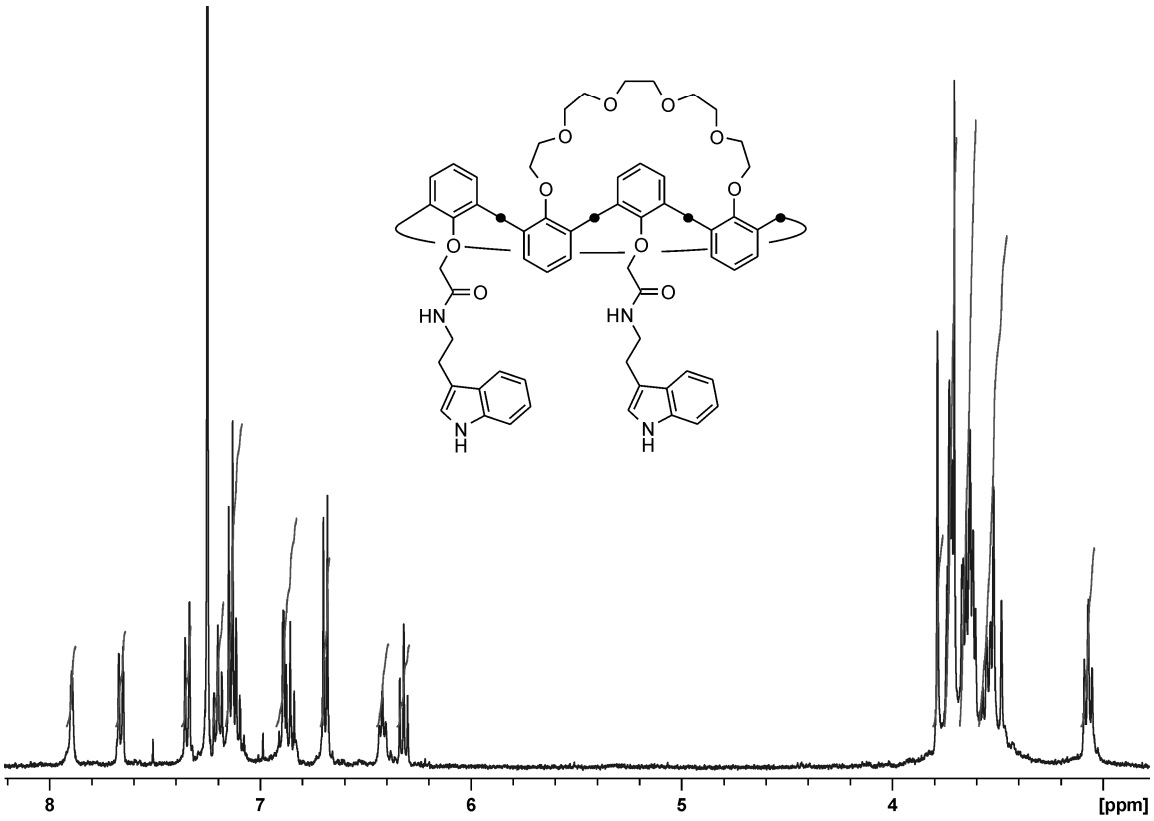


Figure S43. ^{1}H NMR spectrum of calixarene **29** (400 MHz, $CDCl_3$).

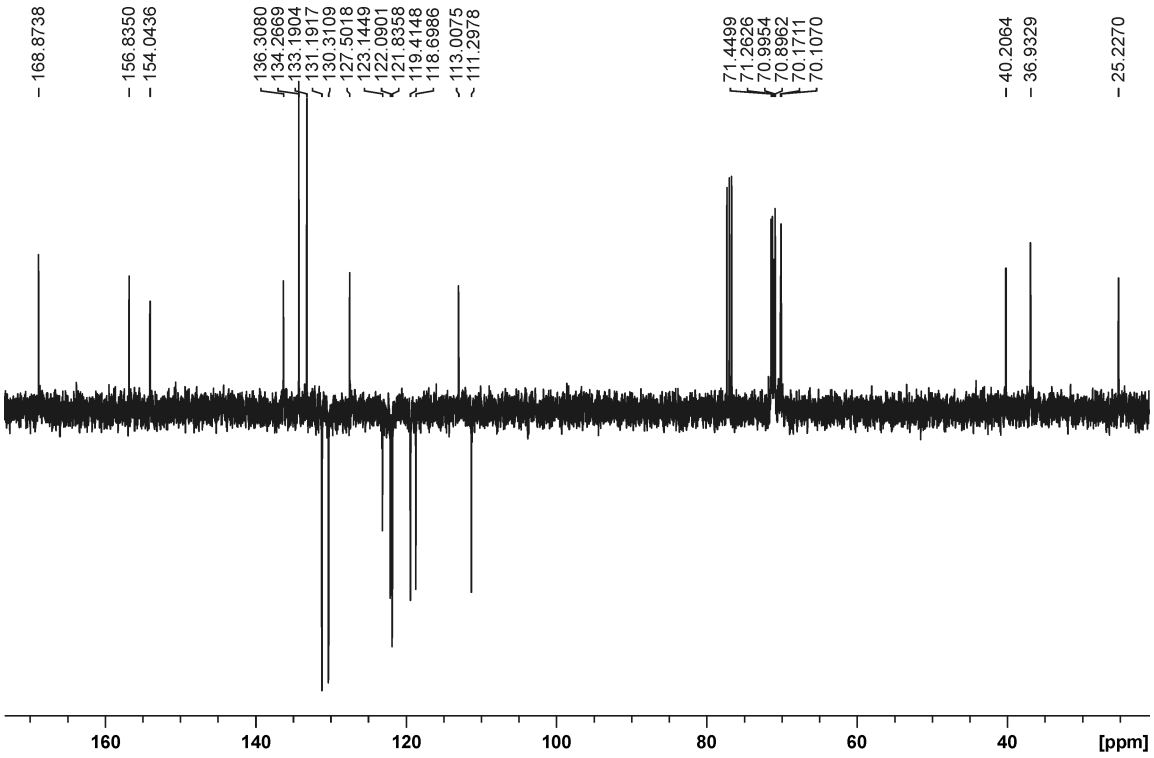


Figure S44. ^{13}C NMR spectrum (APT) of calixarene **29** (100 MHz, $CDCl_3$).

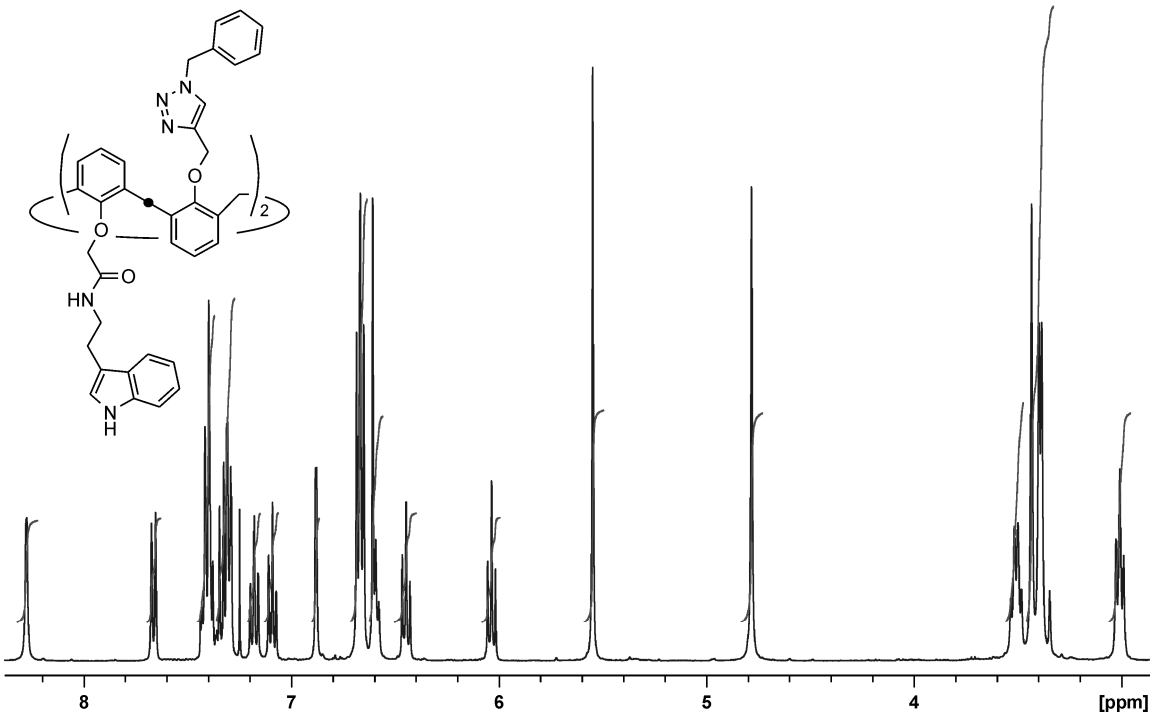


Figure S45. ^{1}H NMR spectrum of calixarene **30** (400 MHz, $CDCl_3$).

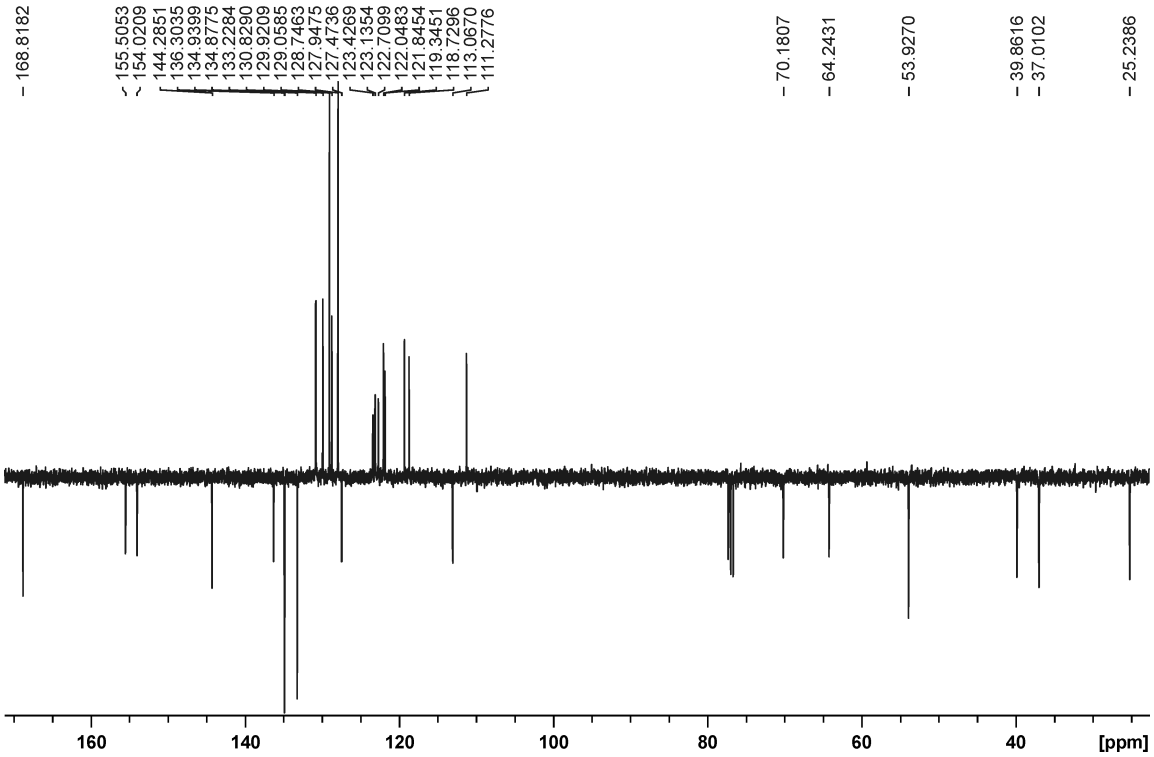


Figure S46. ^{13}C NMR spectrum (APT) of calixarene **30** (100 MHz, $CDCl_3$).

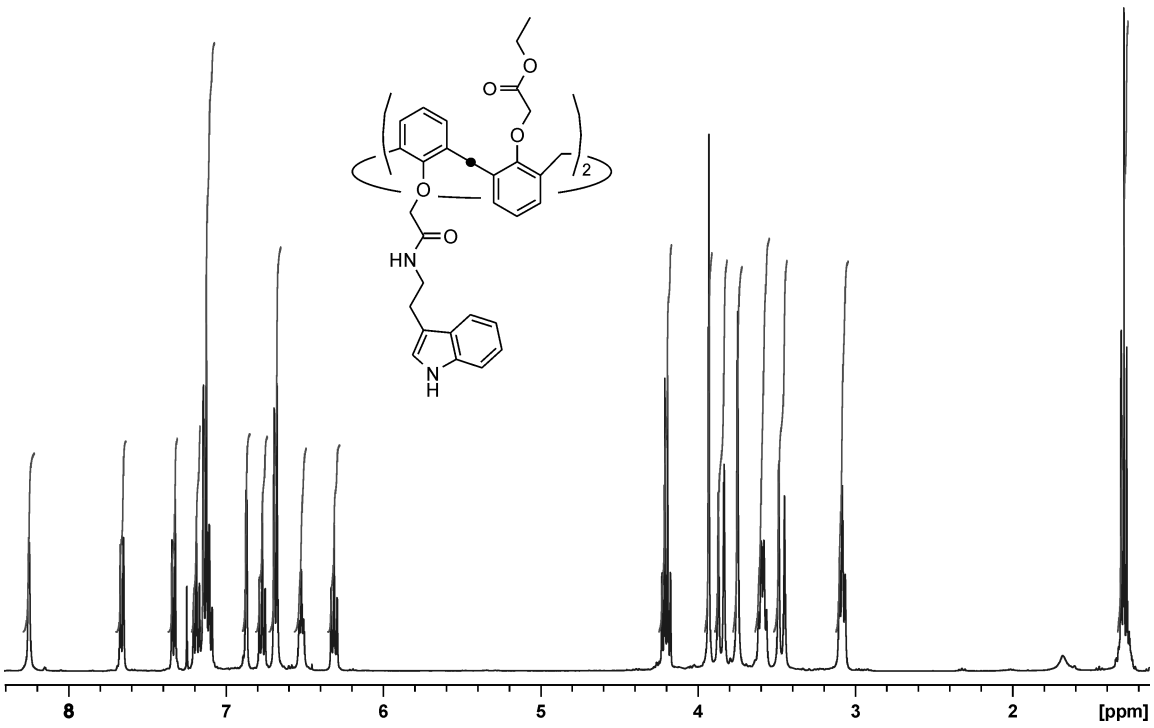


Figure S47. ^{1}H NMR spectrum of calixarene **31** (400 MHz, $CDCl_3$).

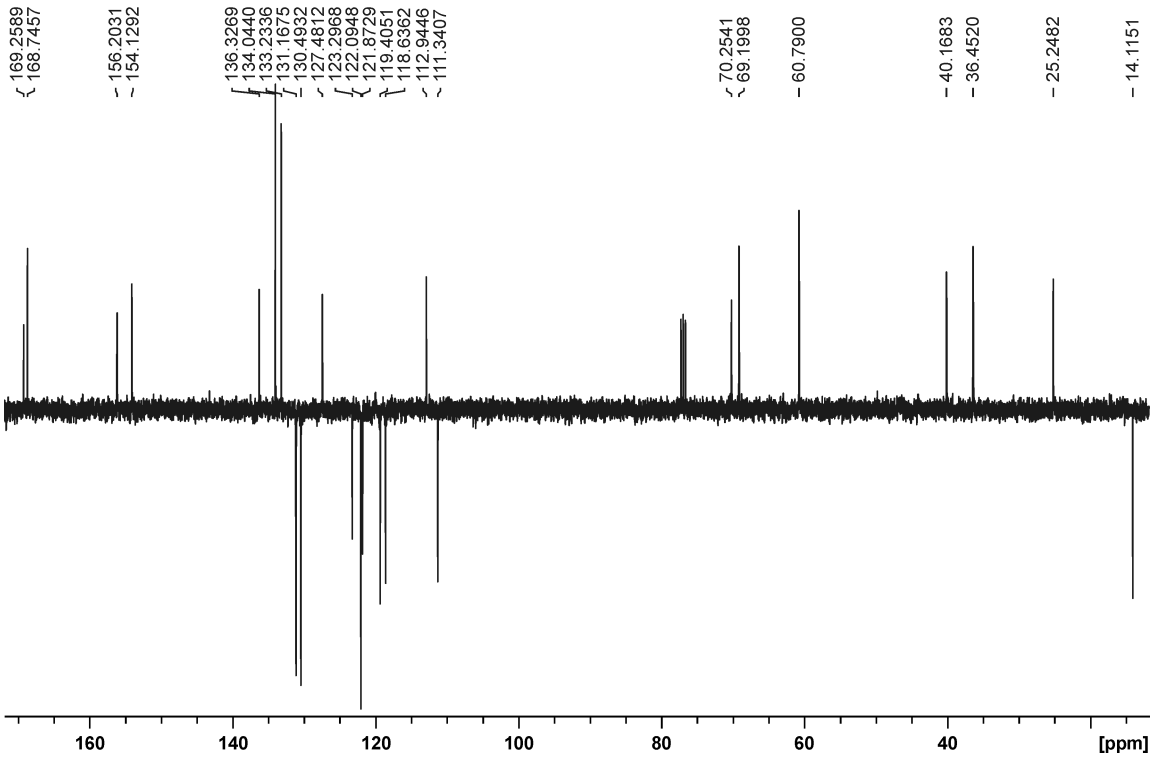


Figure S48. ^{13}C NMR spectrum (APT) of calixarene **31** (100 MHz, $CDCl_3$).

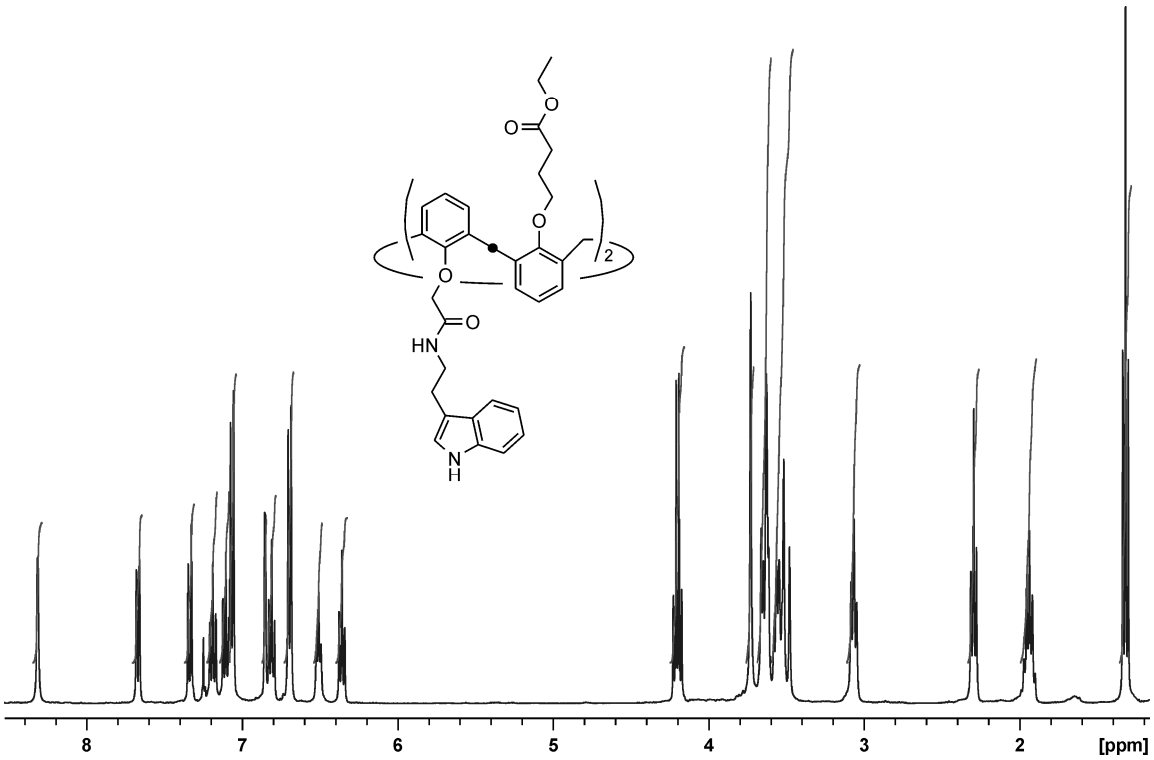


Figure S49. ^{1}H NMR spectrum of calixarene **32** (400 MHz, $CDCl_3$).

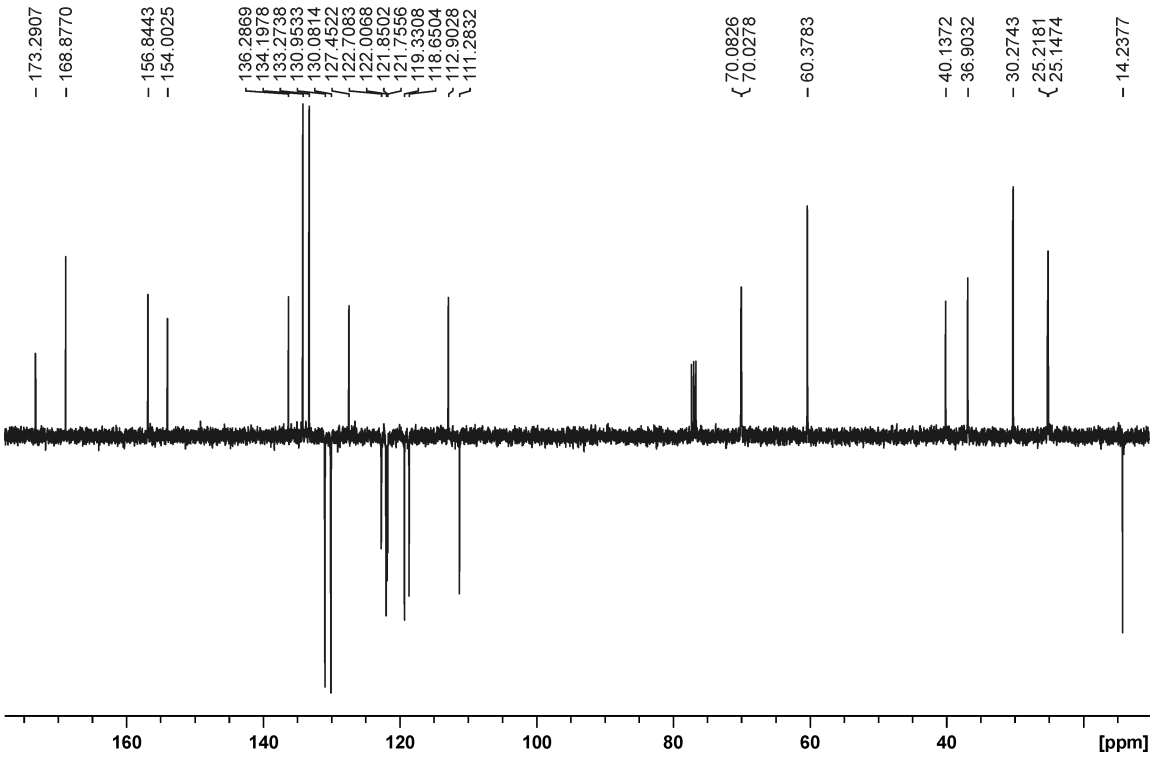


Figure S50. ^{13}C NMR spectrum (APT) of calixarene **32** (100 MHz, $CDCl_3$).

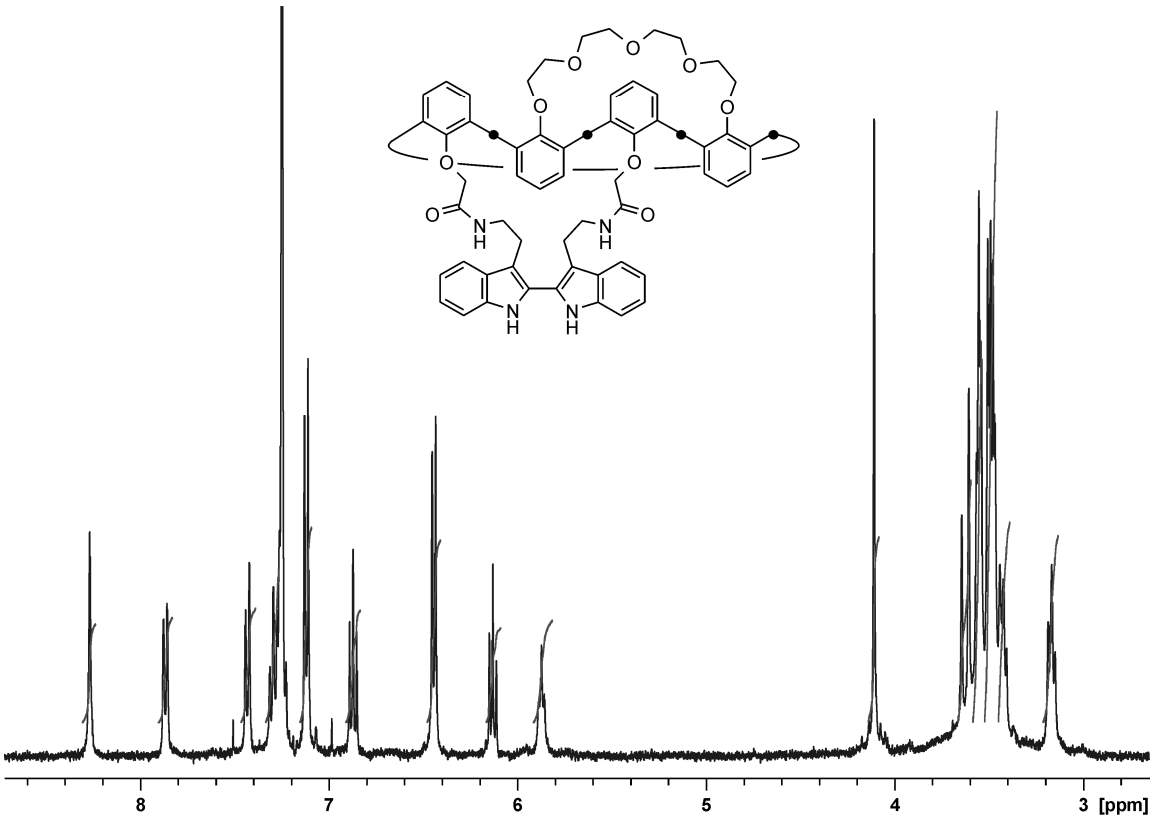


Figure S51. ^{1}H NMR spectrum of calixarene **33** (400 MHz, $CDCl_3$).

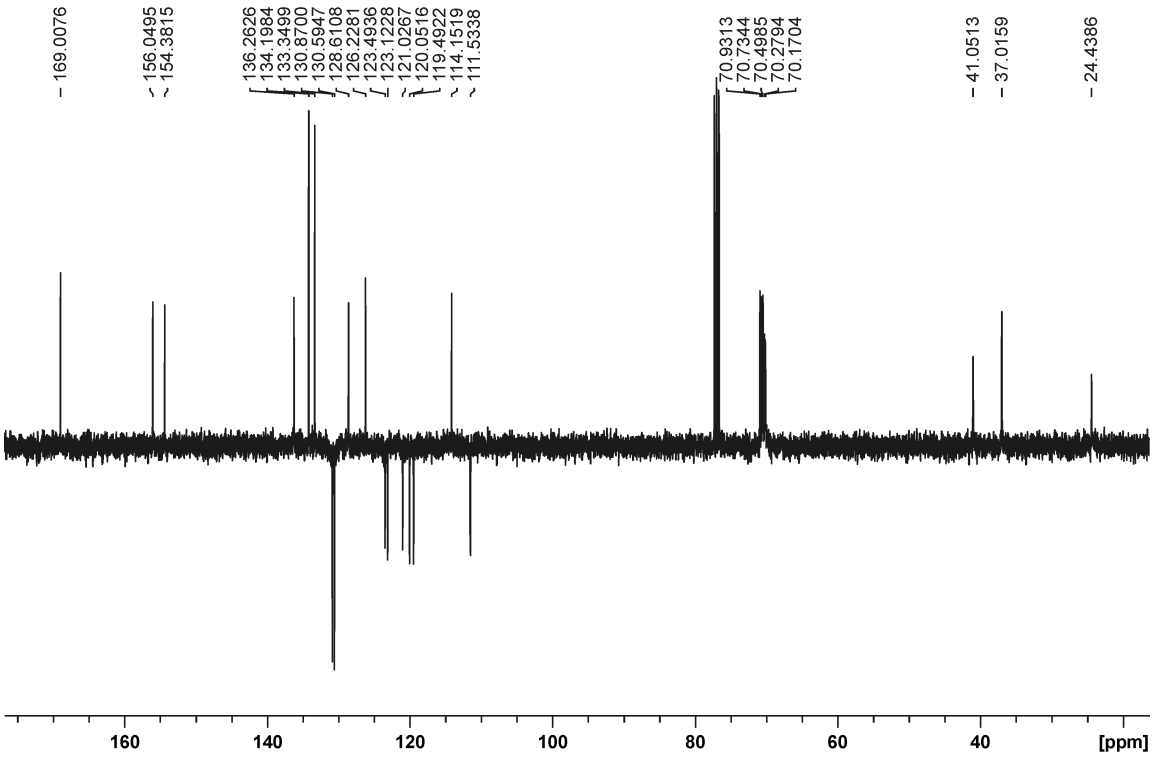


Figure S52. ^{13}C NMR spectrum (APT) of calixarene **33** (100 MHz, $CDCl_3$).

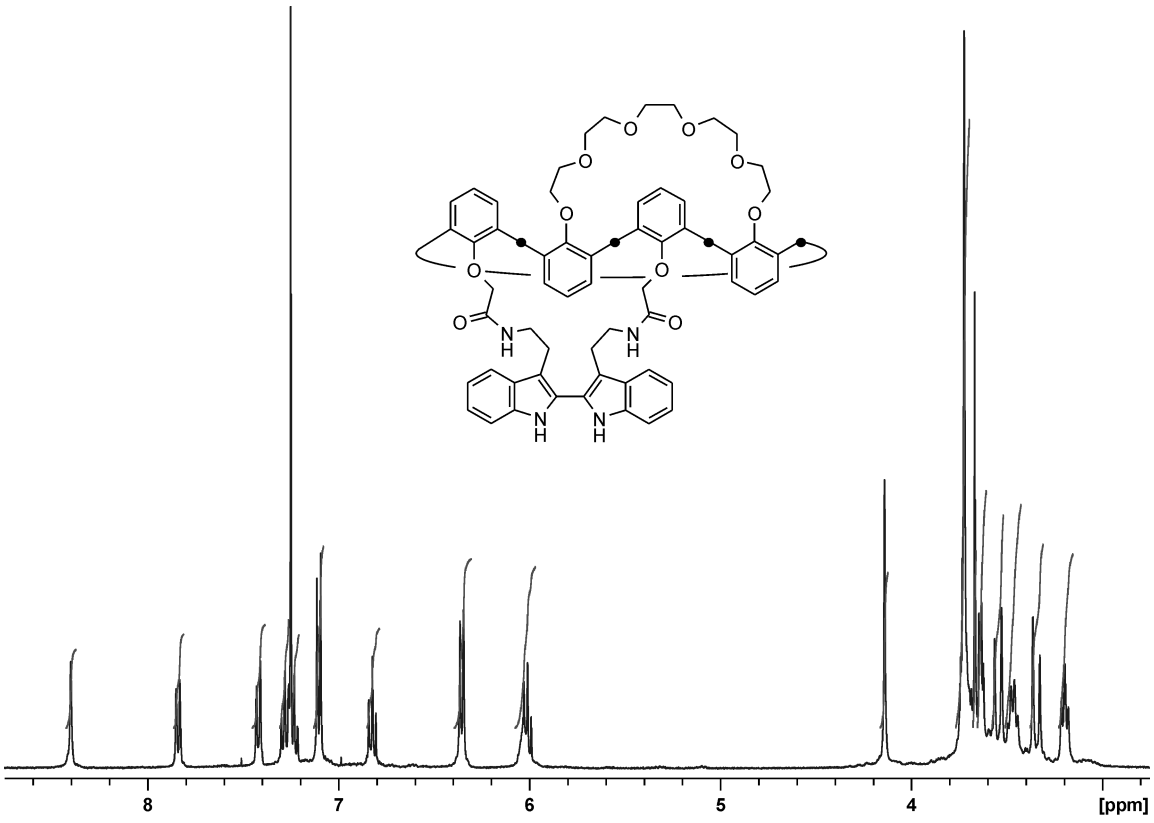


Figure S53. ^{1}H NMR spectrum of calixarene **34** (400 MHz, $CDCl_3$).

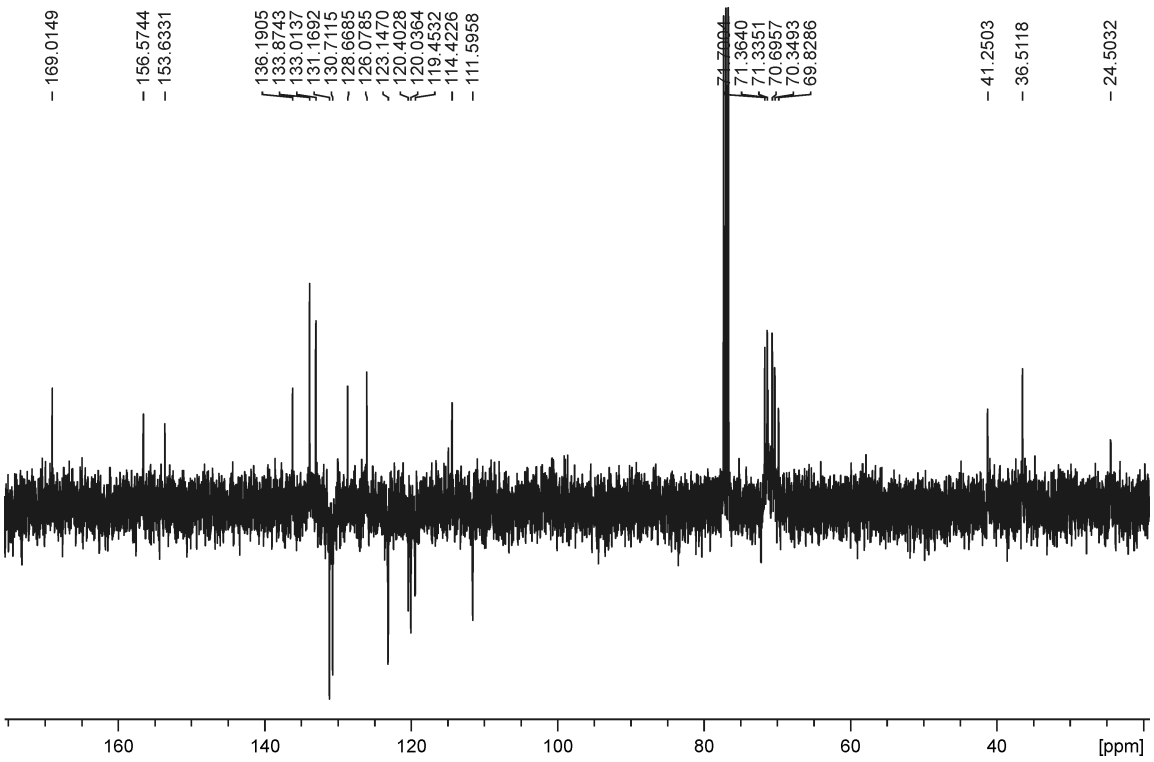


Figure S54. ^{13}C NMR spectrum (APT) of calixarene **34** (100 MHz, $CDCl_3$).

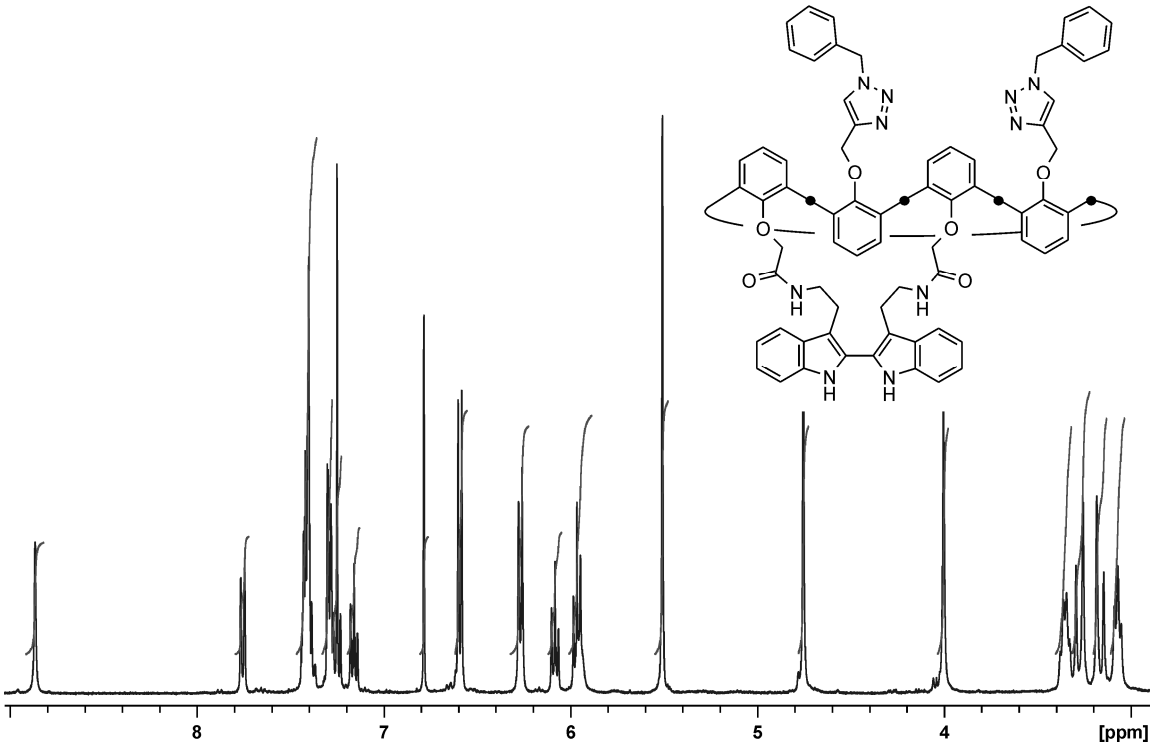


Figure S55. ^{1}H NMR spectrum of calixarene **35** (400 MHz, $CDCl_3$).

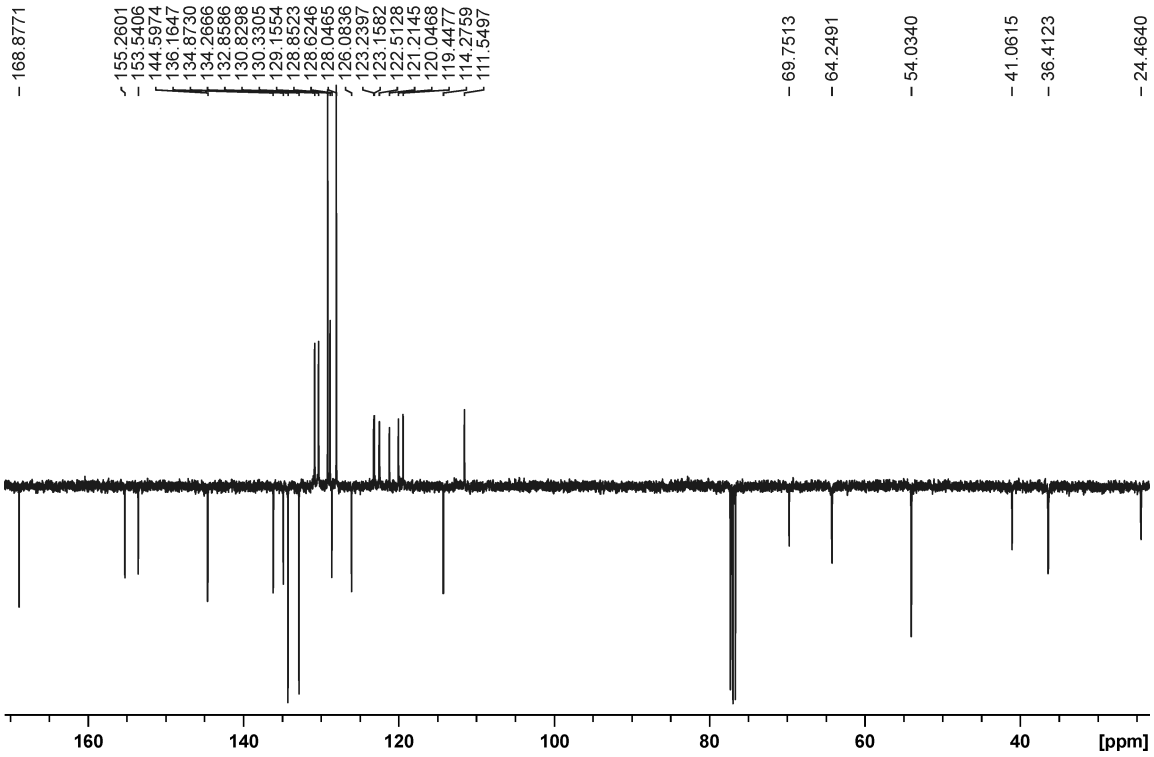


Figure S56. ^{13}C NMR spectrum (APT) of calixarene **35** (100 MHz, $CDCl_3$).

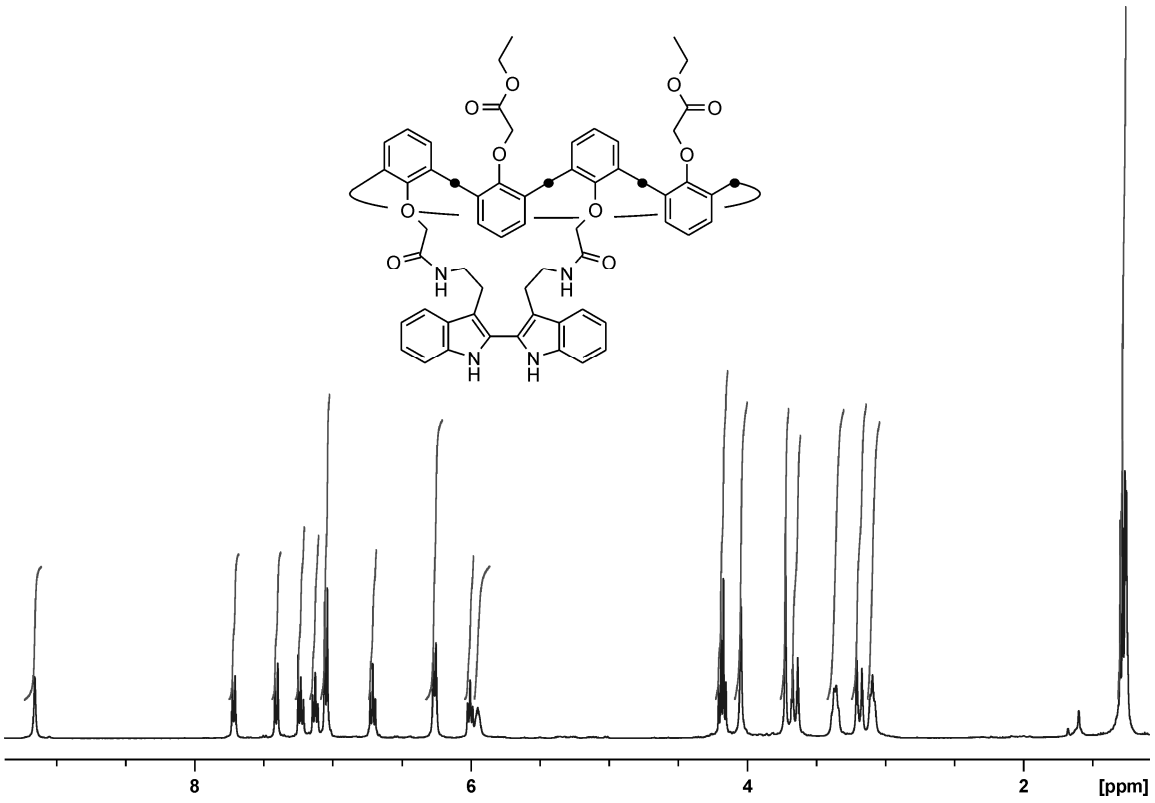


Figure S57. ^{1}H NMR spectrum of calixarene **36** (400 MHz, $CDCl_3$).

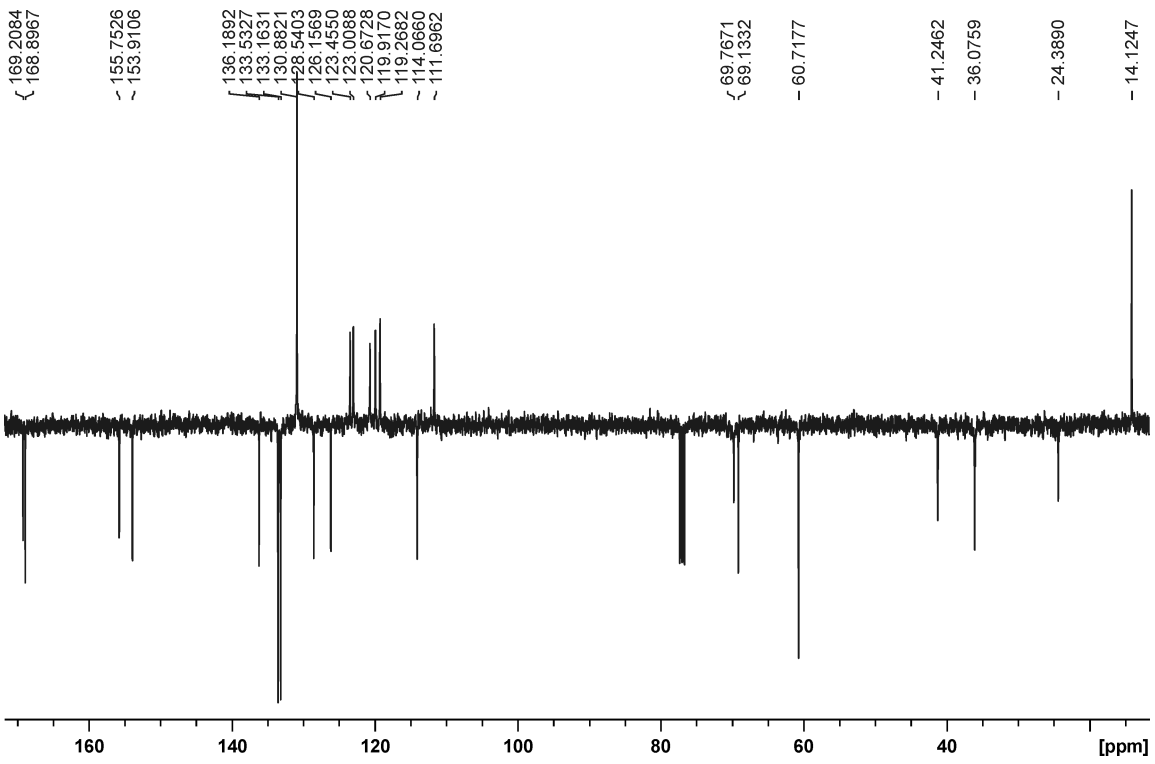


Figure S58. ^{13}C NMR spectrum (APT) of calixarene **36** (100 MHz, $CDCl_3$).

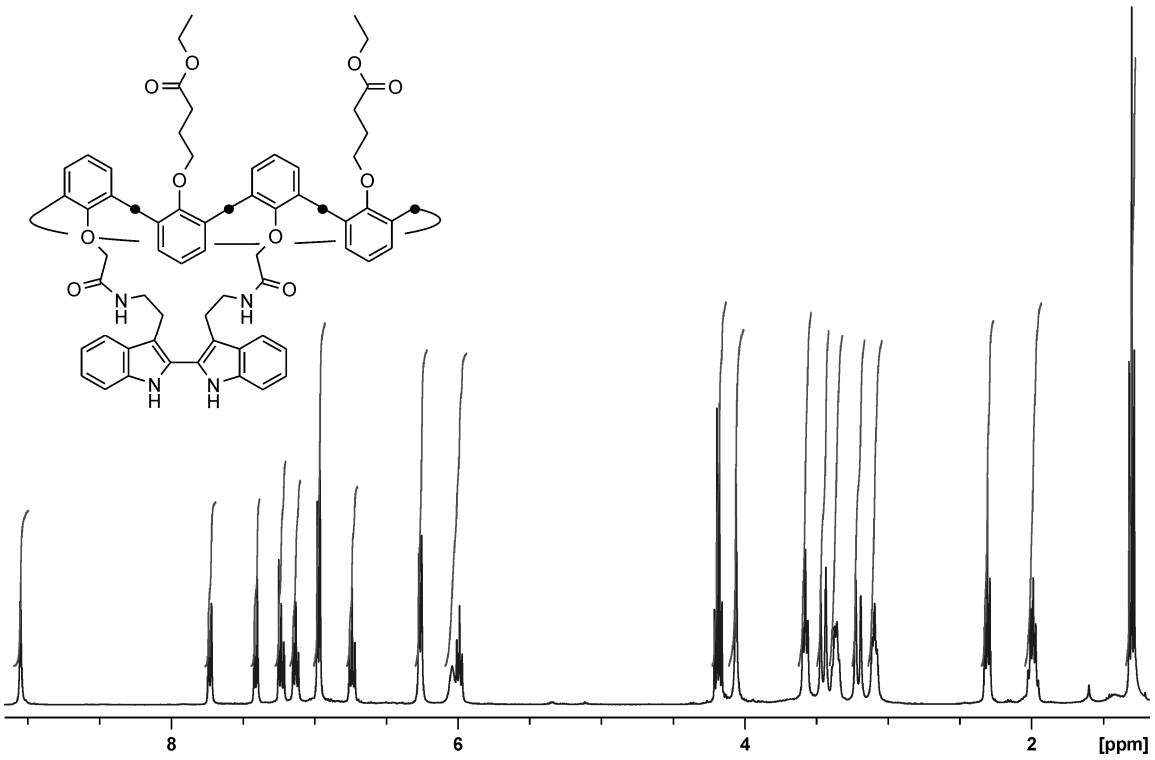


Figure S59. ^{1}H NMR spectrum of calixarene **37** (400 MHz, $CDCl_3$).

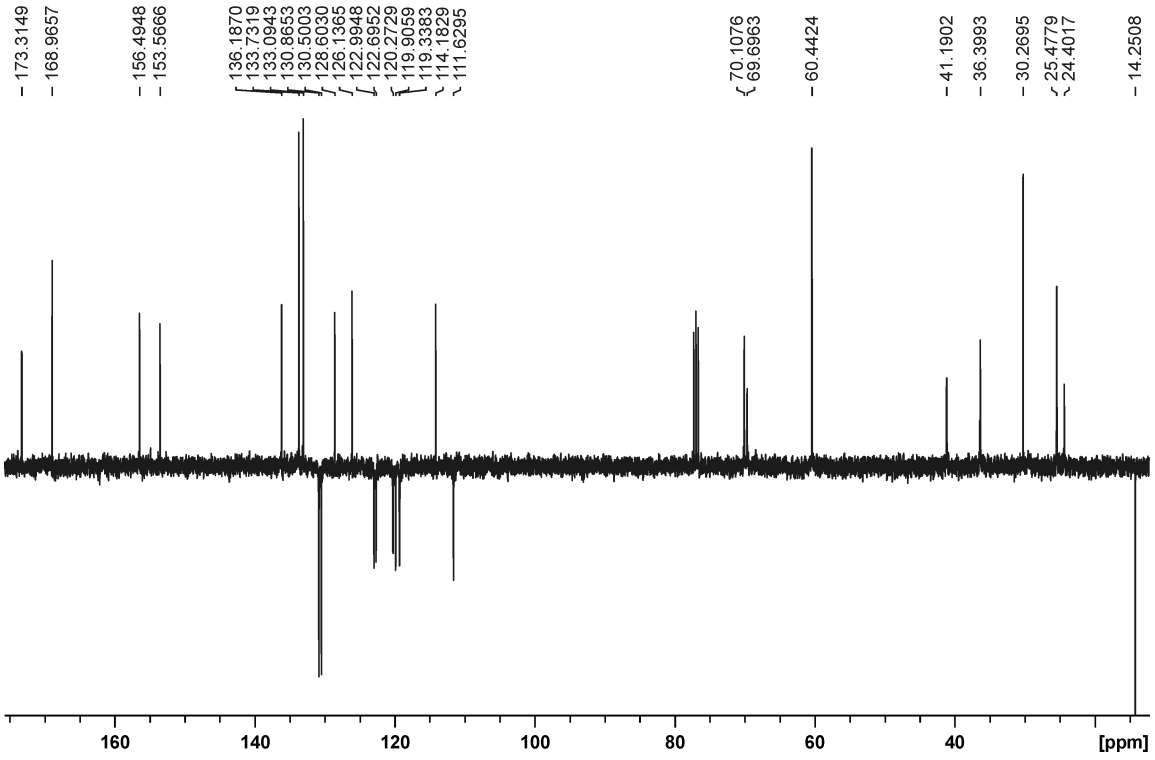


Figure S60. ^{13}C NMR spectrum (APT) of calixarene **37** (100 MHz, $CDCl_3$).

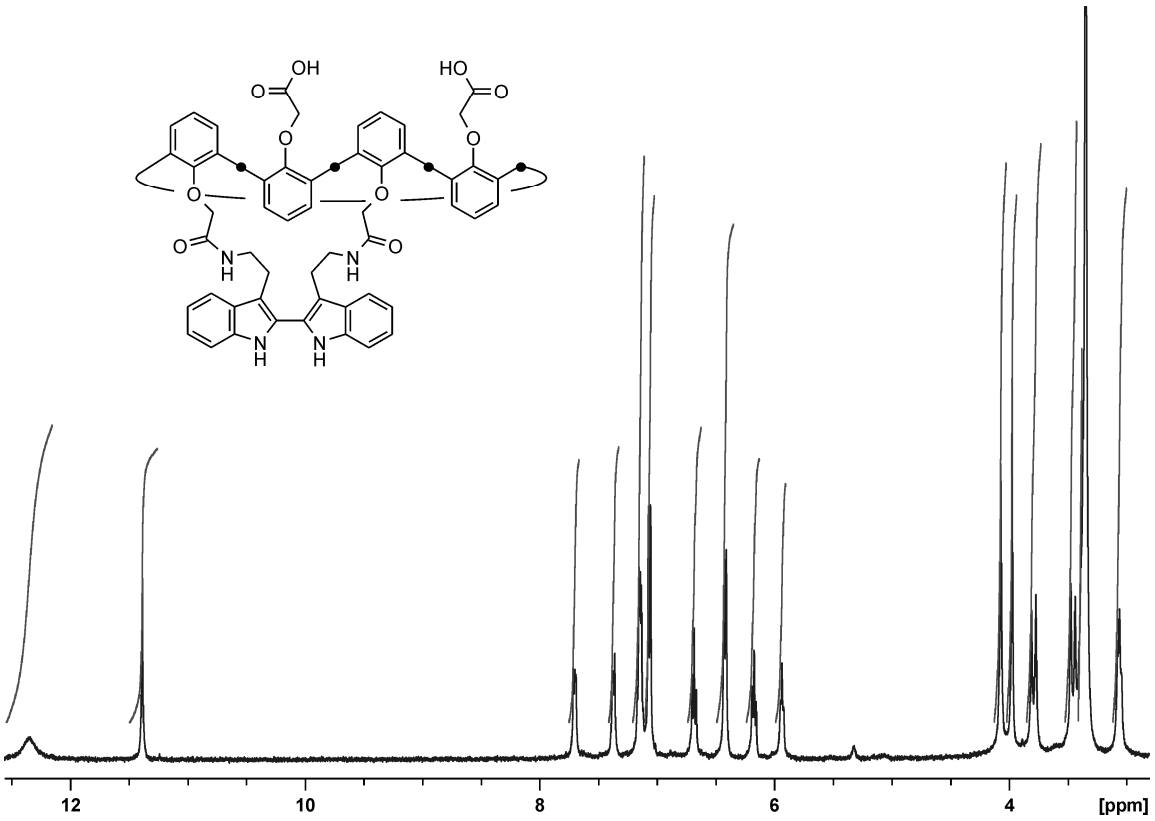


Figure S61. ^{1}H NMR spectrum of calixarene **38** (400 MHz, DMSO-d_6).

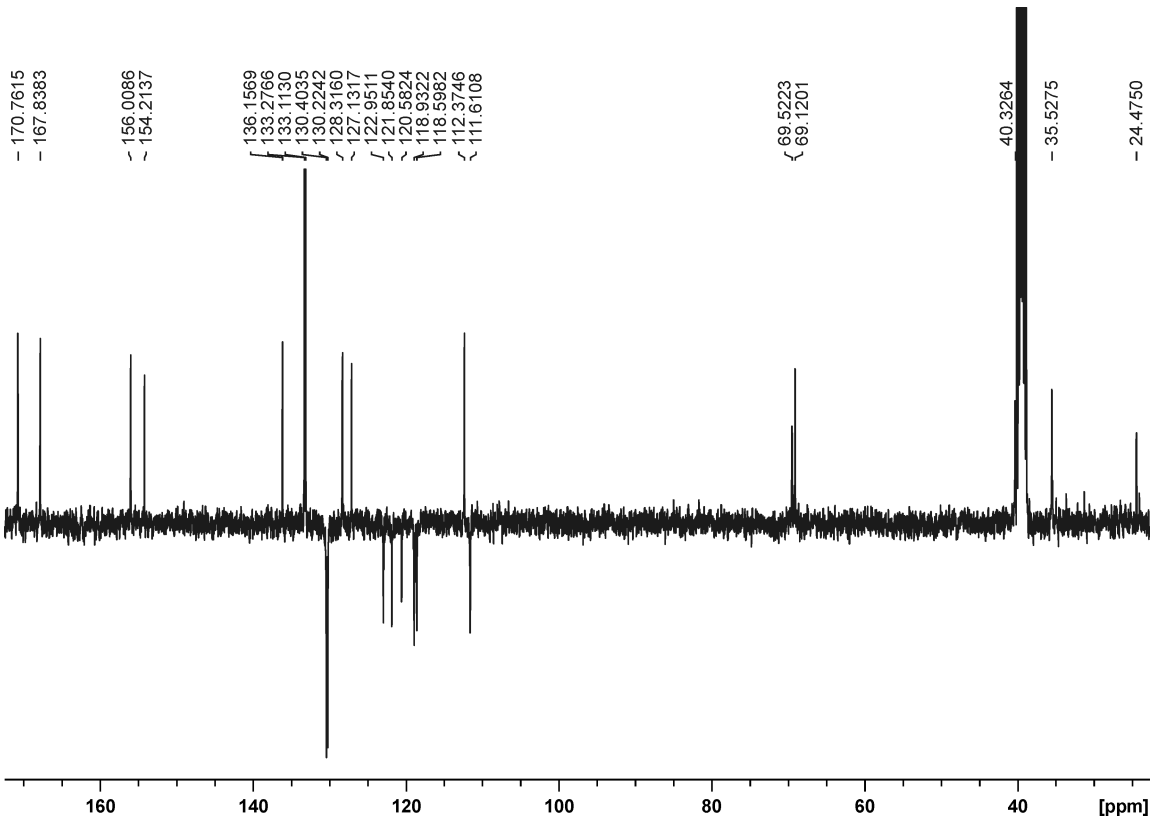


Figure S62. ^{13}C NMR spectrum (APT) of calixarene **38** (100 MHz, DMSO-d_6).

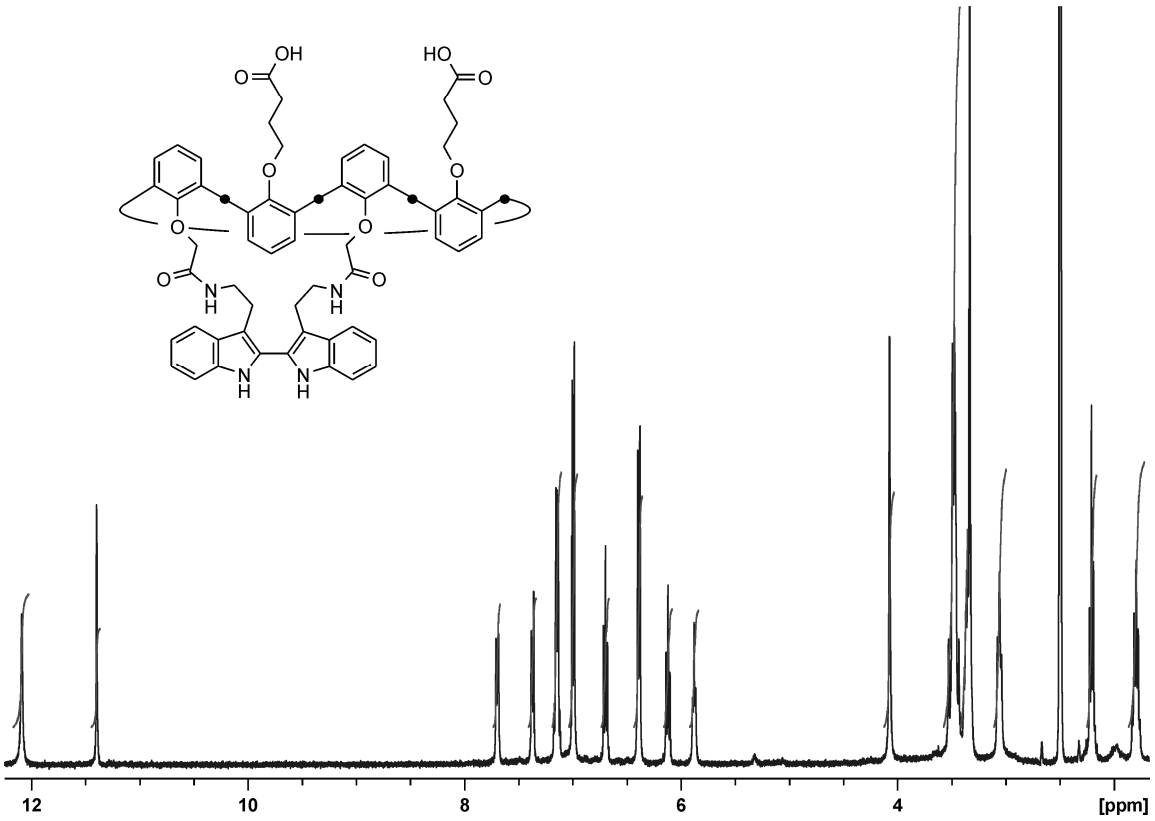


Figure S63. ^{1}H NMR spectrum of calixarene **39** (400 MHz, DMSO-d_6).

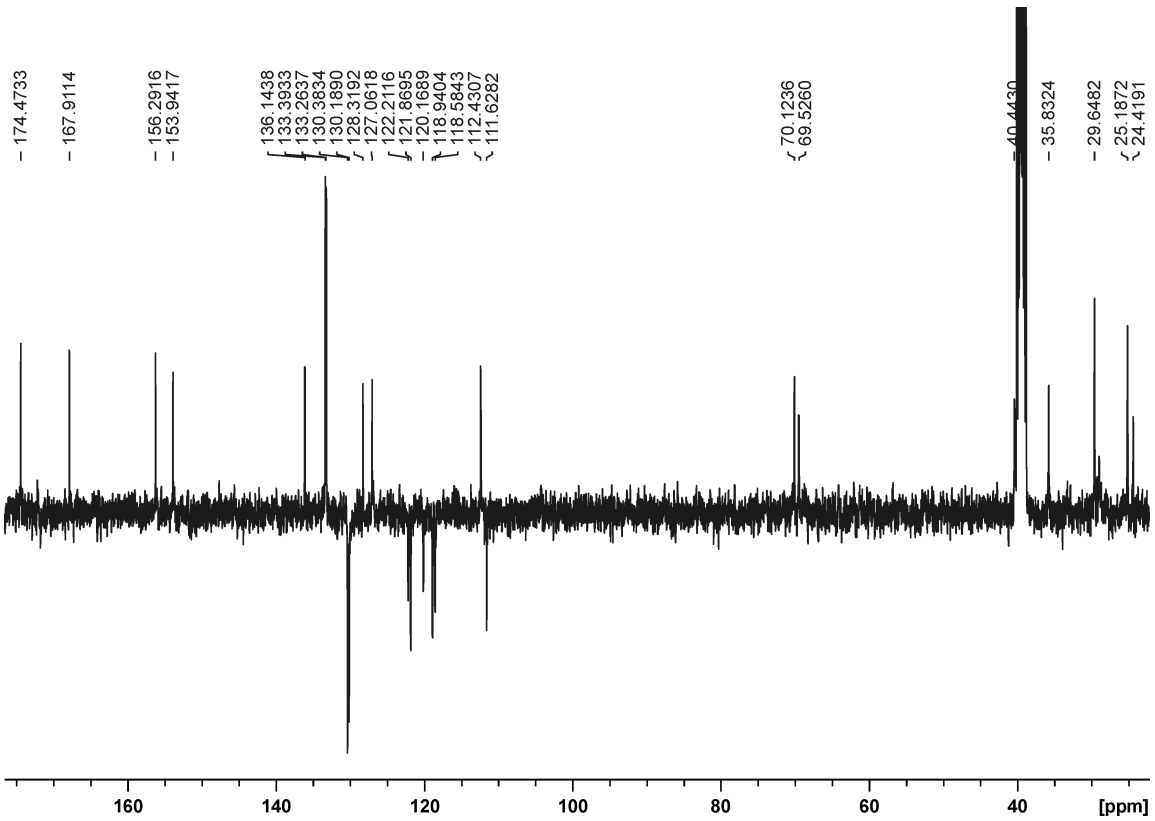


Figure S64. ^{13}C NMR spectrum (APT) of calixarene **39** (100 MHz, DMSO-d_6).

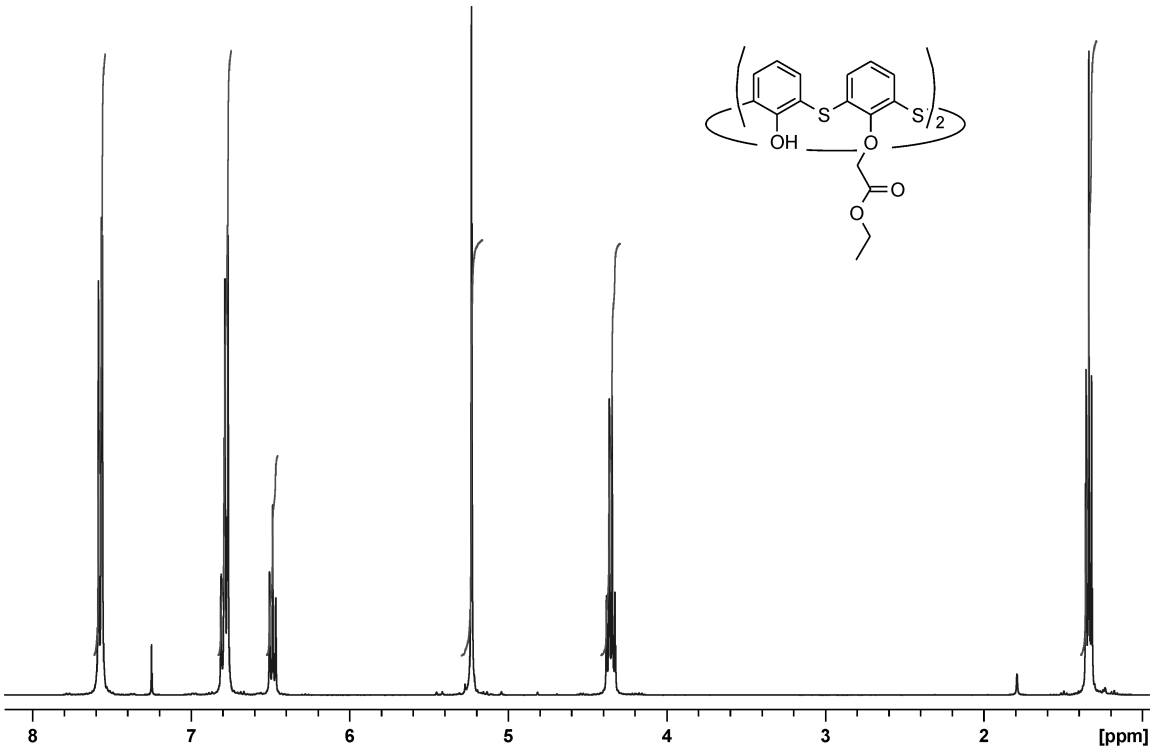


Figure S65. ^{1}H NMR spectrum of calixarene **41** (400 MHz, $CDCl_3$).

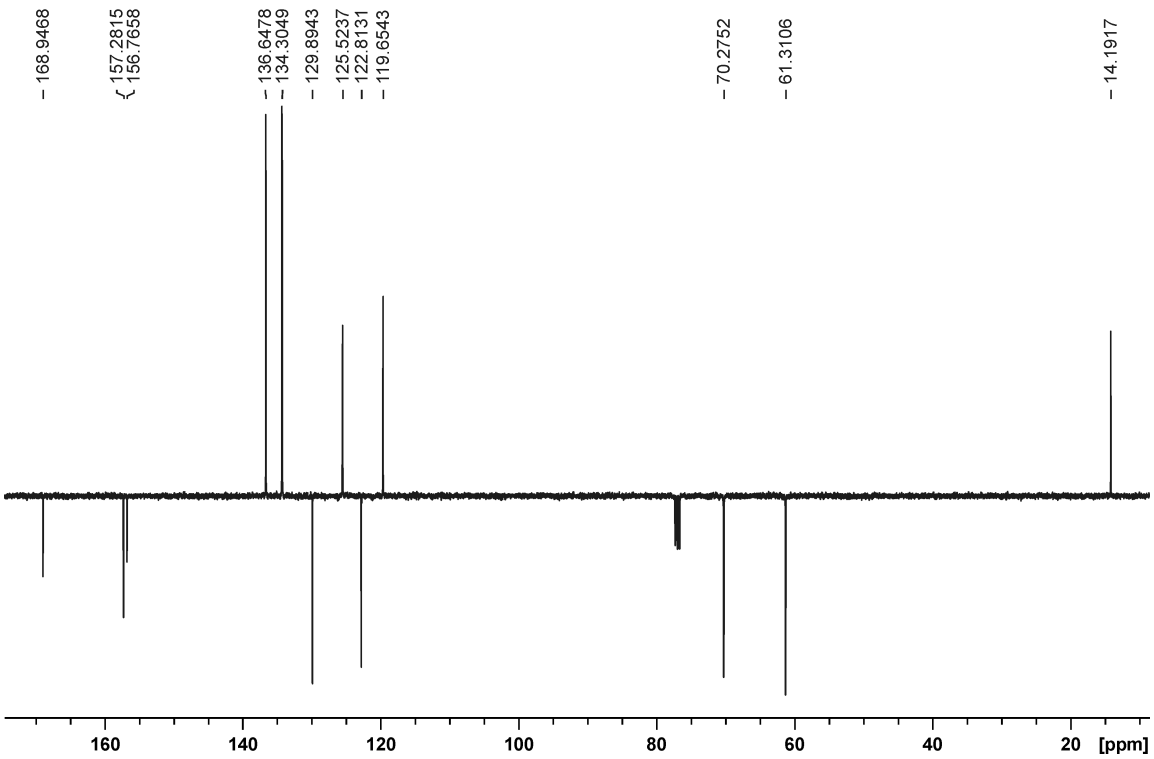


Figure S66. ^{13}C NMR spectrum (APT) of calixarene **41** (100 MHz, $CDCl_3$).

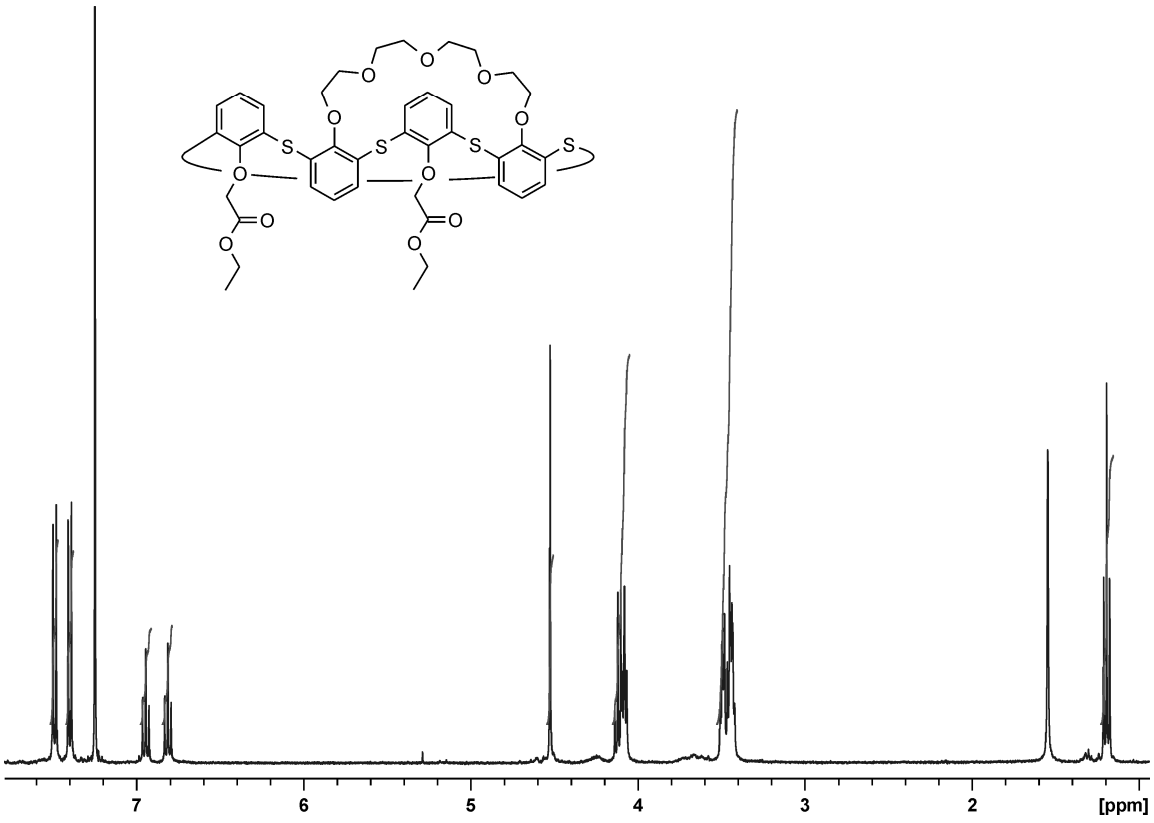


Figure S67. ^{1}H NMR spectrum of calixarene **42** (400 MHz, $CDCl_3$).

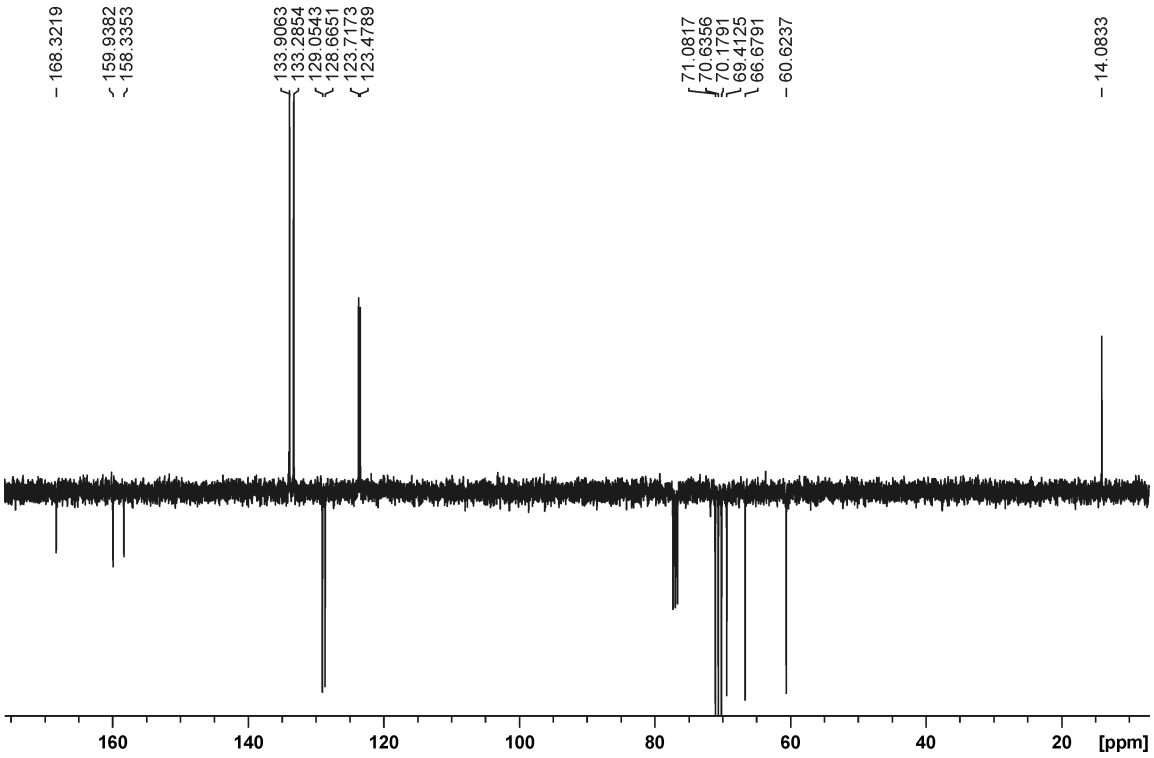


Figure S68. ^{13}C NMR spectrum (APT) of calixarene **42** (100 MHz, $CDCl_3$).

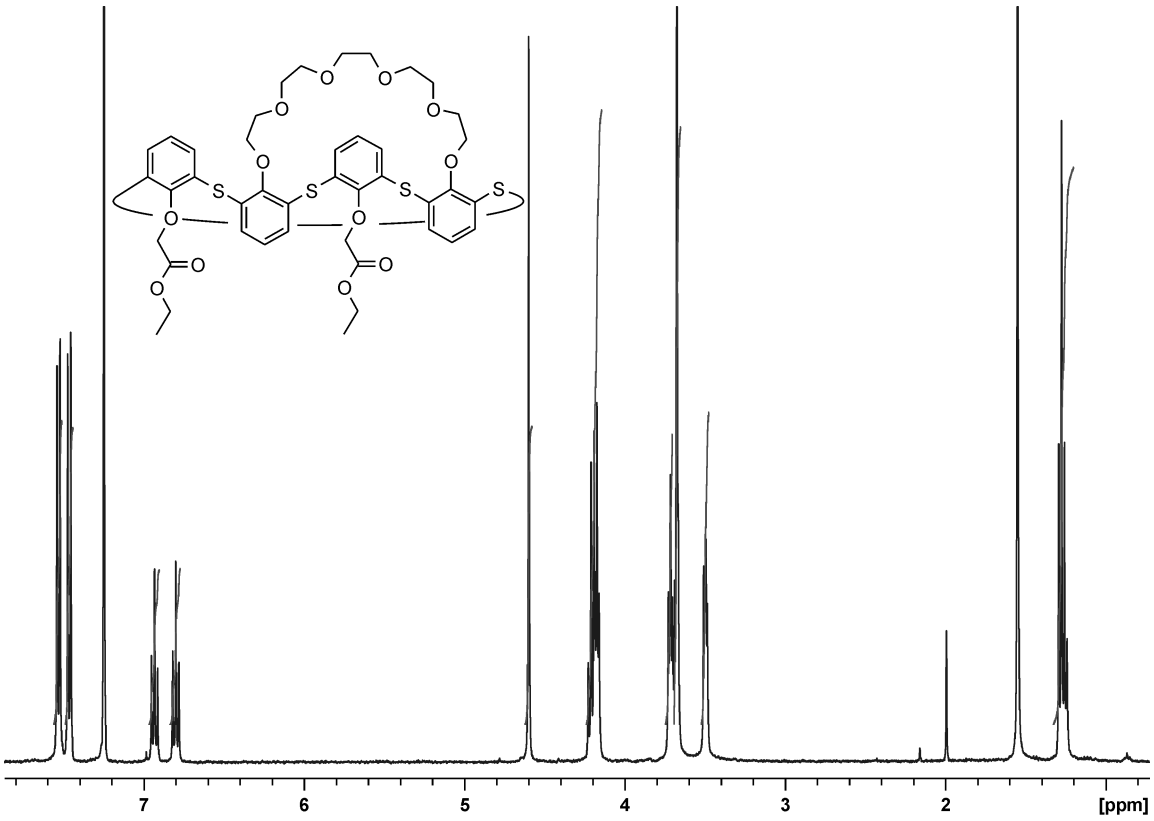


Figure S69. ^{1}H NMR spectrum of calixarene **43** (400 MHz, $CDCl_3$).

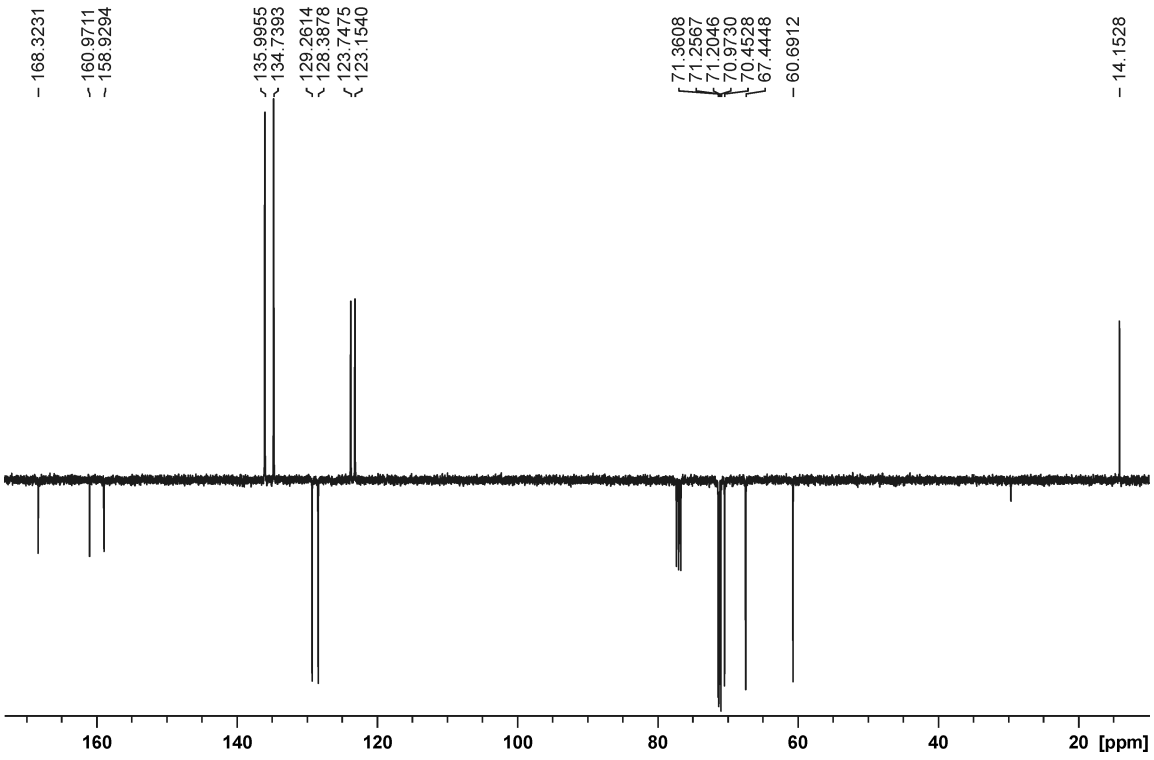


Figure S70. ^{13}C NMR spectrum (APT) of calixarene **43** (100 MHz, $CDCl_3$).

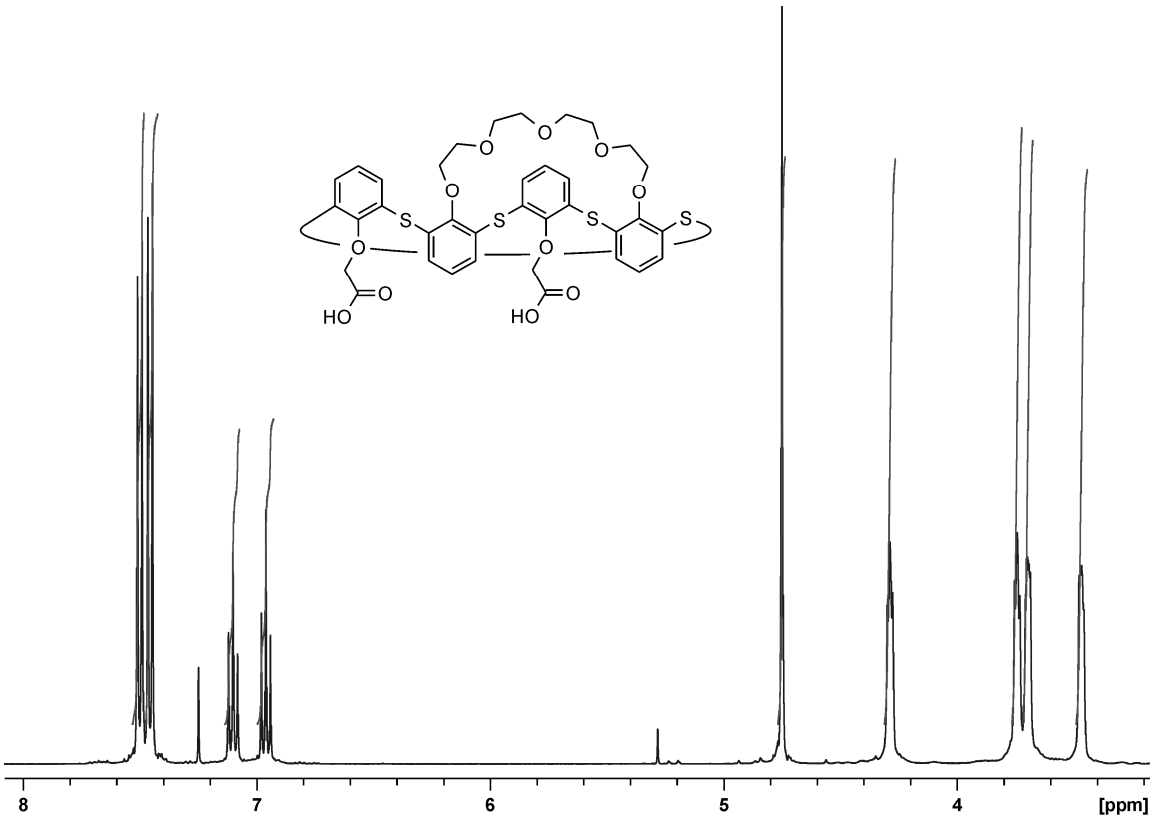


Figure S71. ^{1}H NMR spectrum of calixarene **44** (400 MHz, $CDCl_3$+CF_3CO_2D).

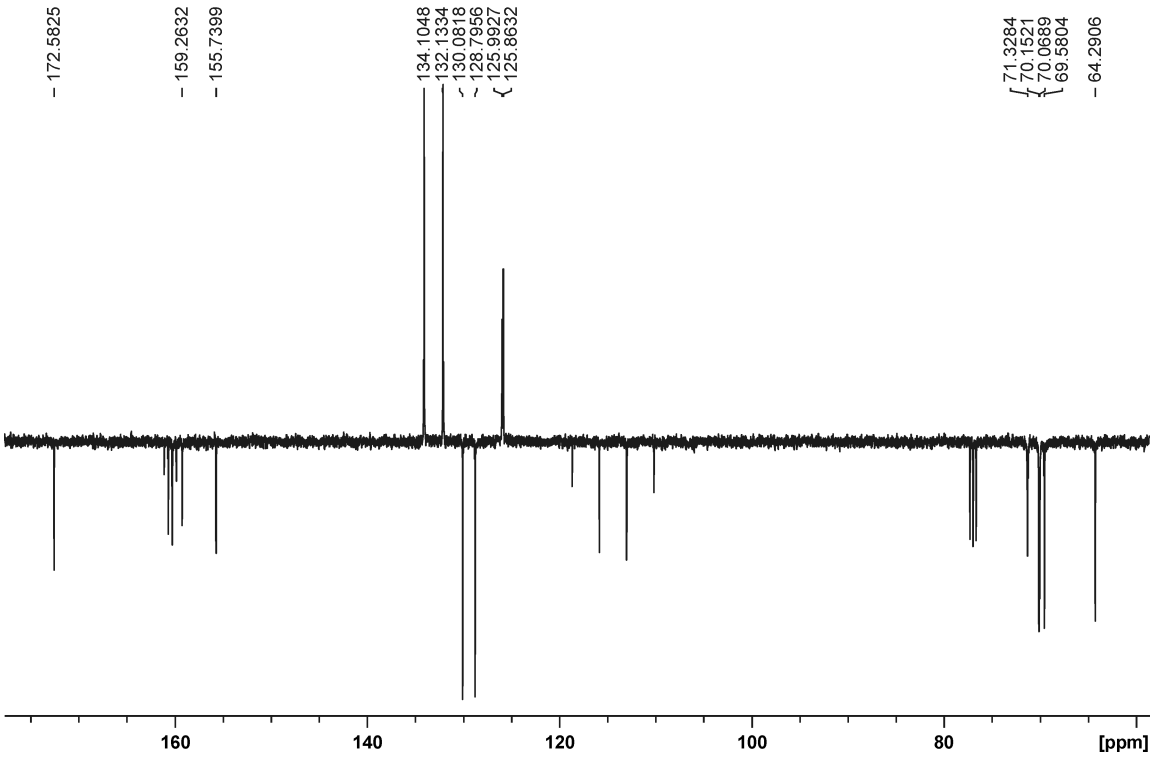


Figure S72. ^{13}C NMR spectrum (APT) of calixarene **44** (100 MHz, $CDCl_3$+CF_3CO_2D).

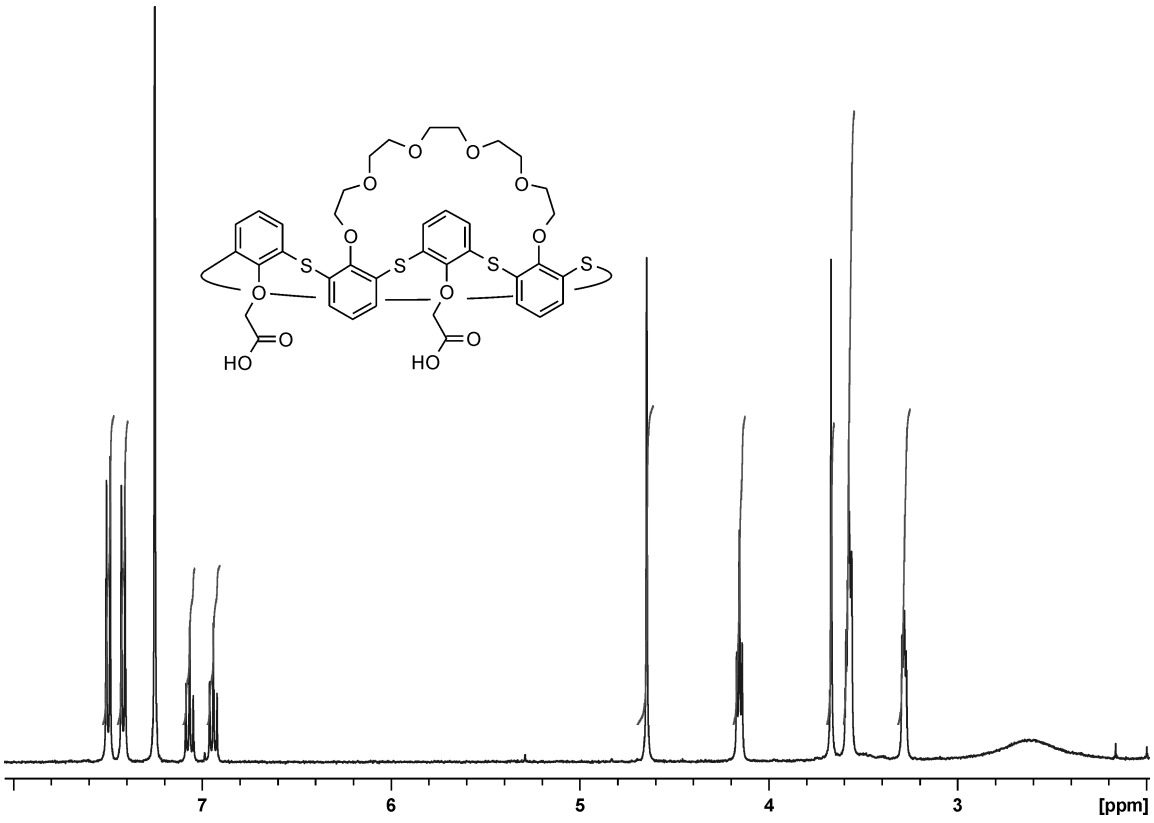


Figure S73. ^{1}H NMR spectrum of calixarene **45** (400 MHz, $CDCl_3$).

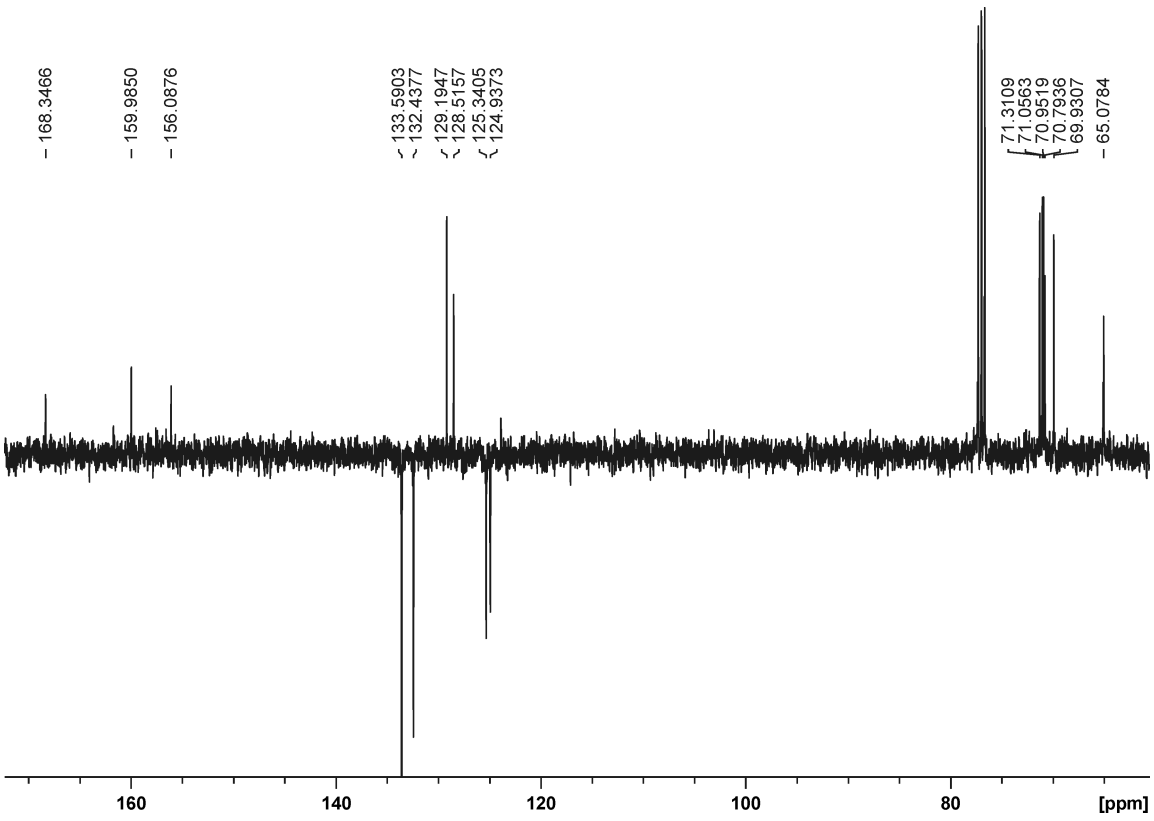


Figure S74. ^{13}C NMR spectrum (APT) of calixarene **45** (100 MHz, $CDCl_3$).

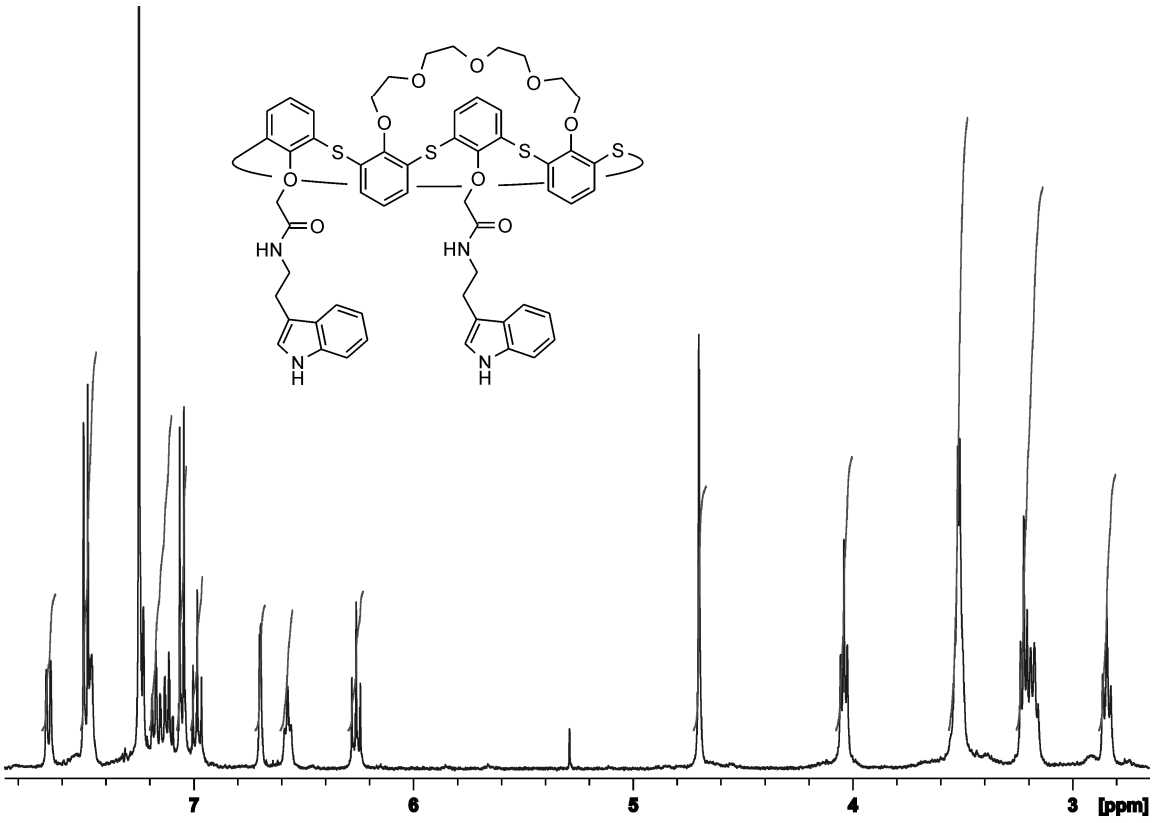


Figure S75. ^{1}H NMR spectrum of calixarene **46** (400 MHz, $CDCl_3$).

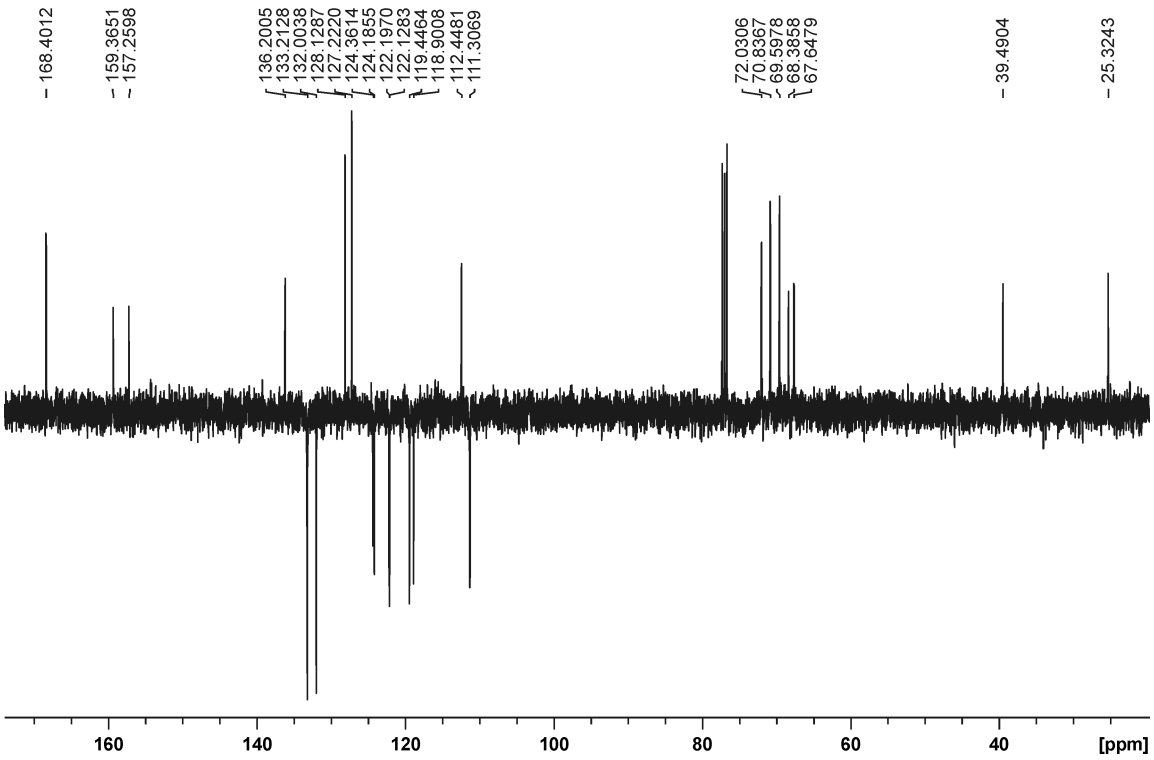


Figure S76. ^{13}C NMR spectrum (APT) of calixarene **46** (100 MHz, $CDCl_3$).

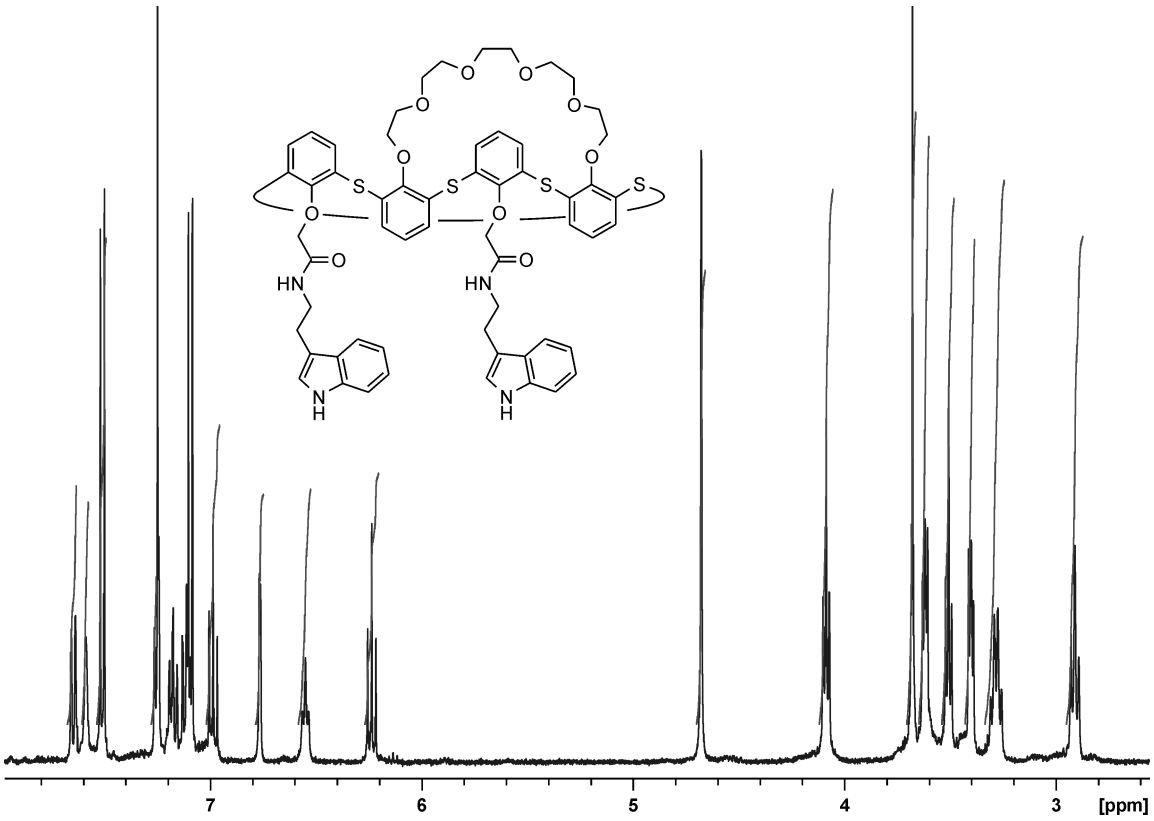


Figure S77. ^{1}H NMR spectrum of calixarene **47** (400 MHz, $CDCl_3$).

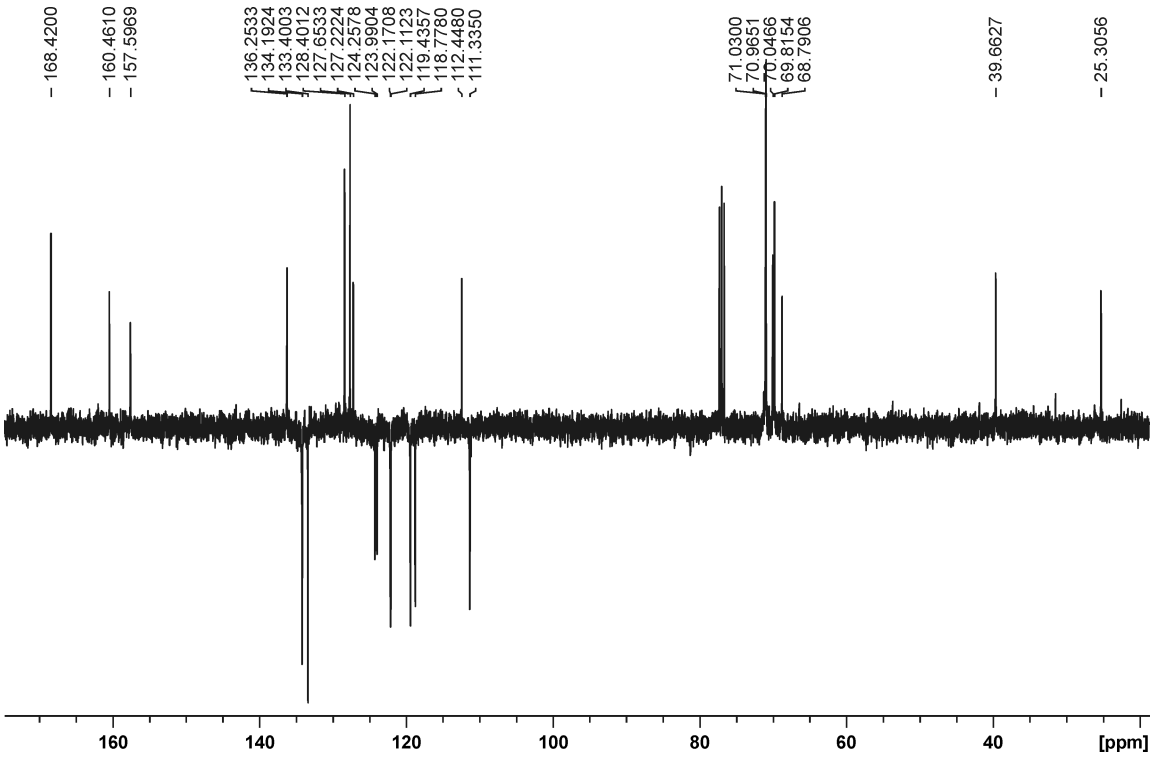


Figure S78. ^{13}C NMR spectrum (APT) of calixarene **47** (100 MHz, $CDCl_3$).

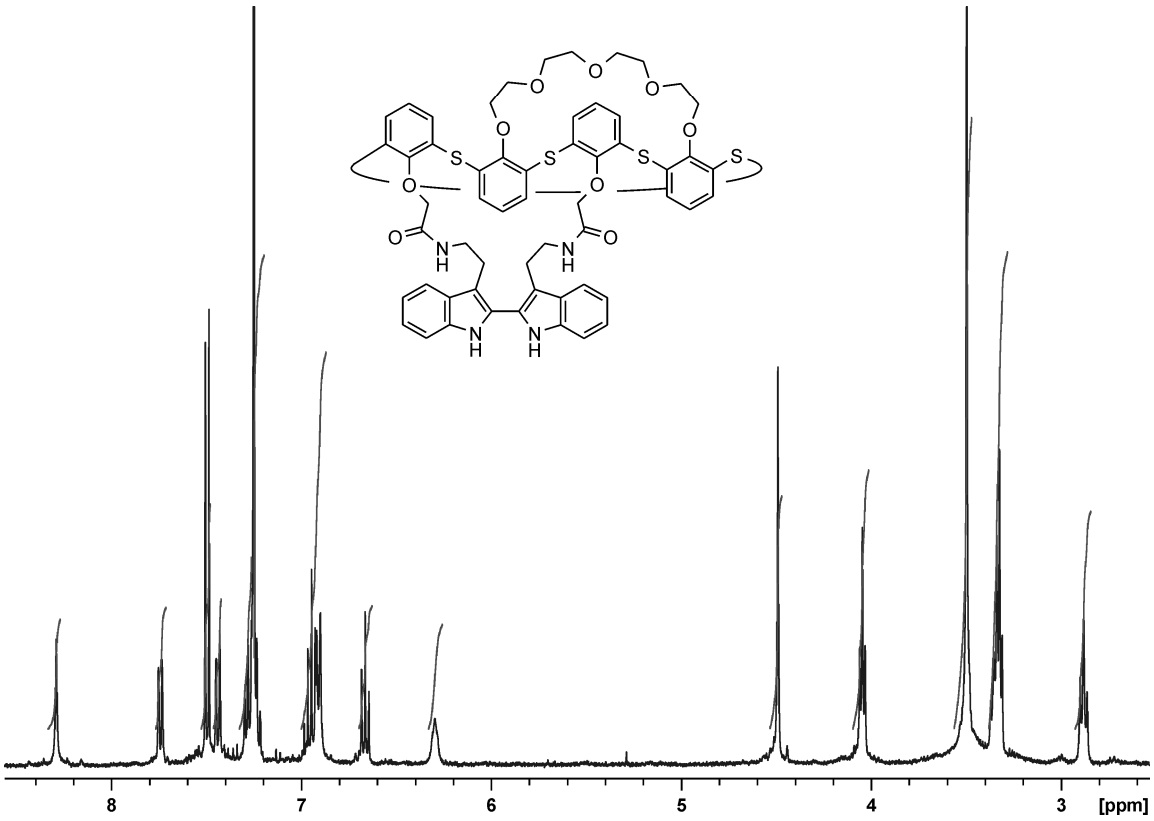


Figure S79. ^{1}H NMR spectrum of calixarene **48** (400 MHz, $CDCl_3$).

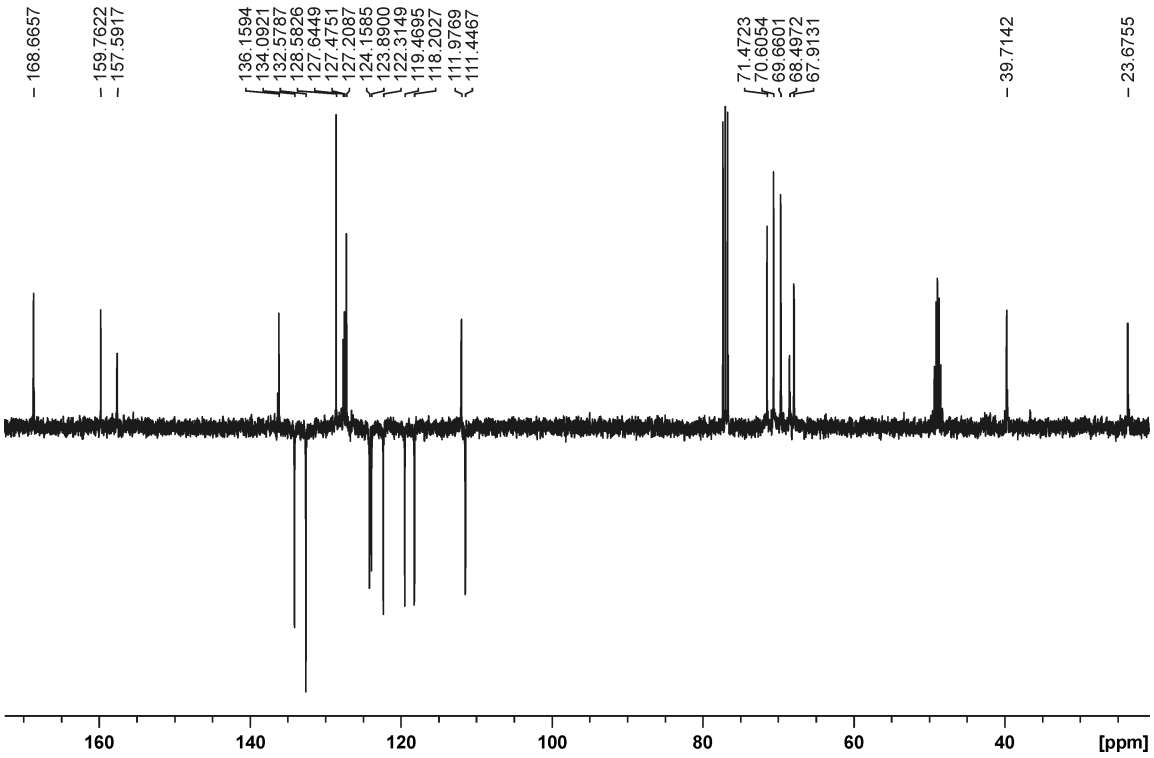


Figure S80. ^{13}C NMR spectrum (APT) of calixarene **48** (100 MHz, $CDCl_3$+CD_3OD).

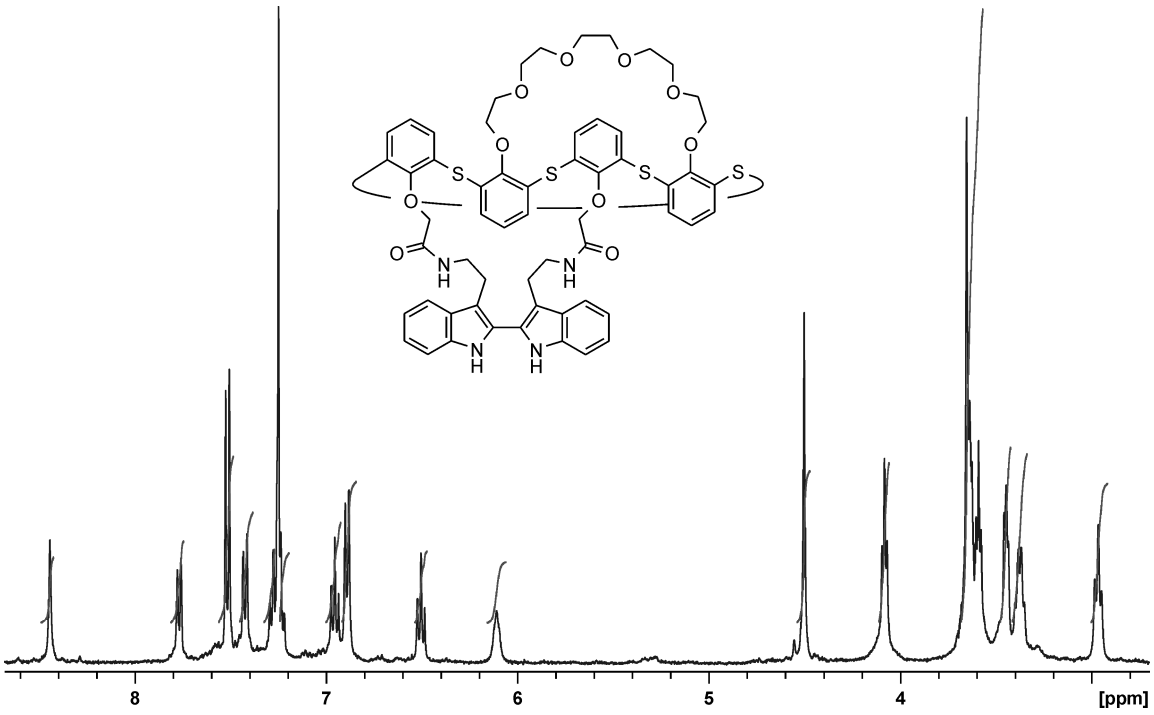


Figure S81. ^{1}H NMR spectrum of calixarene **49** (400 MHz, $CDCl_3$).

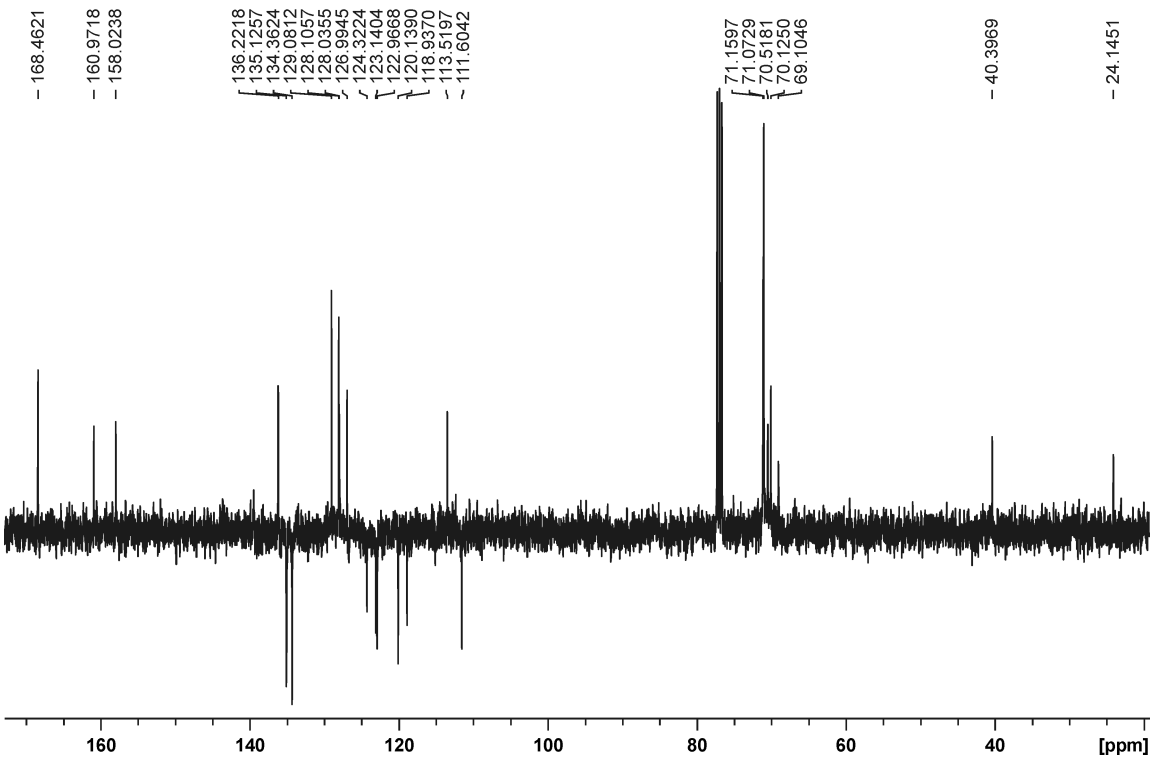


Figure S82. ^{13}C NMR spectrum (APT) of calixarene **49** (100 MHz, $CDCl_3$).

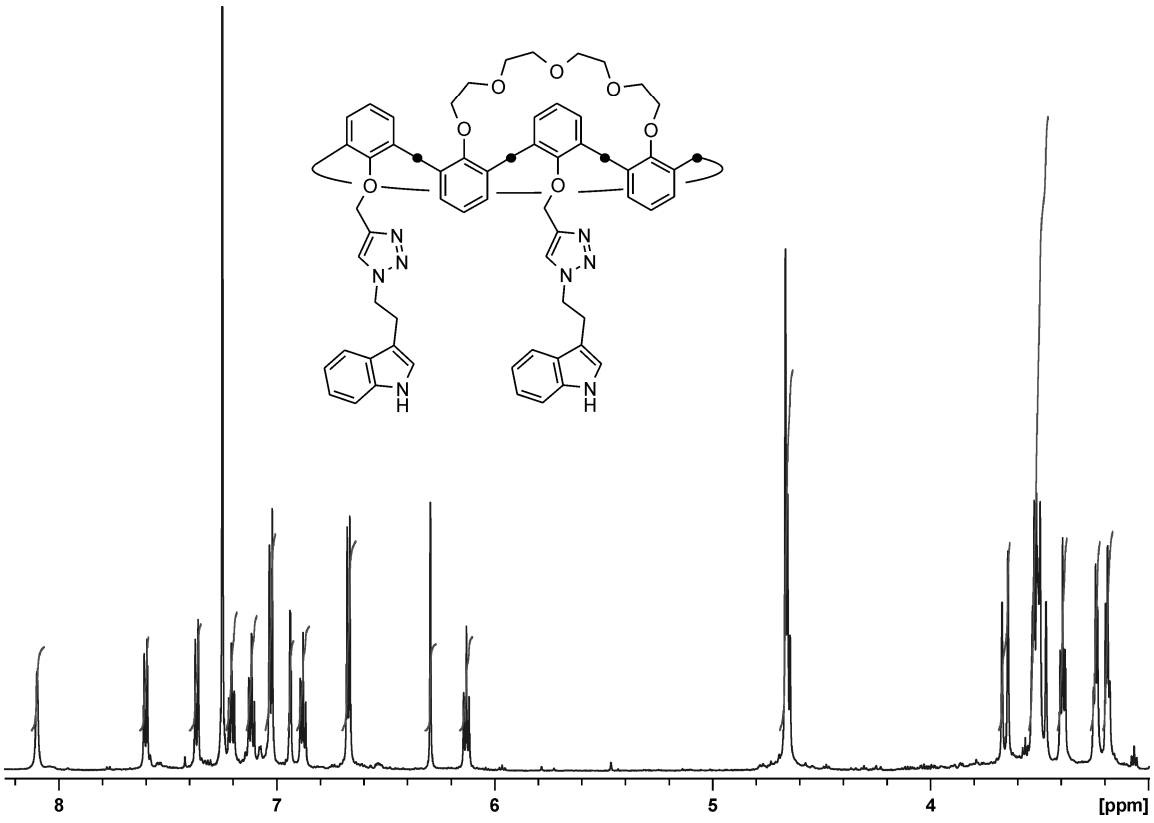


Figure S83. ^{1}H NMR spectrum of calixarene **51** (600 MHz, $CDCl_3$).

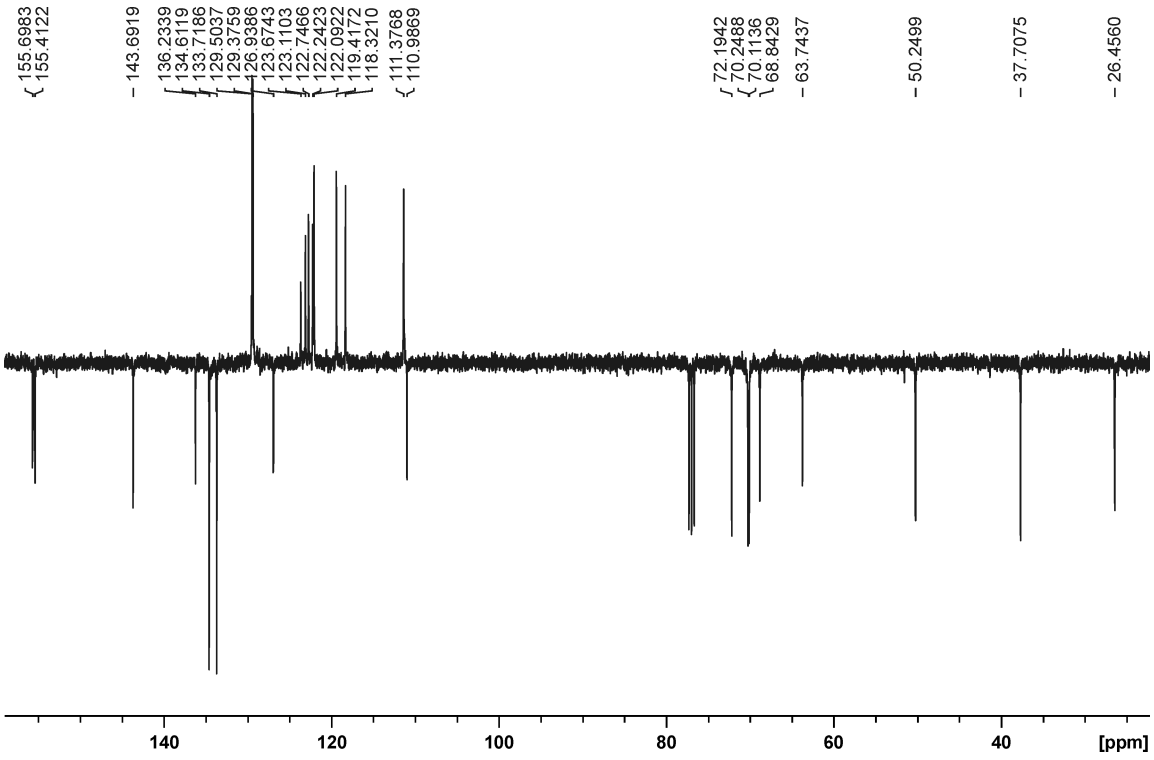


Figure S84. ^{13}C NMR spectrum (APT) of calixarene **51** (100 MHz, $CDCl_3$).

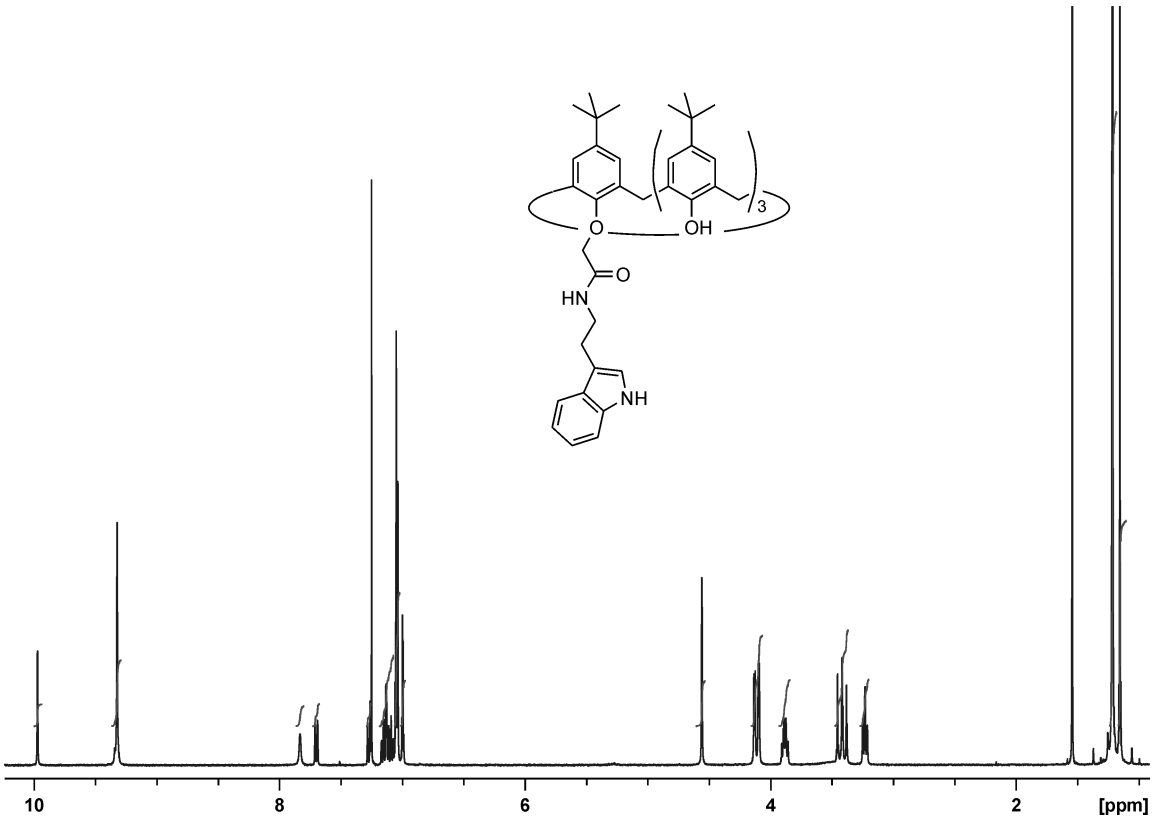


Figure S85. ^{1}H NMR spectrum of calixarene **55** (400 MHz, $CDCl_3$).

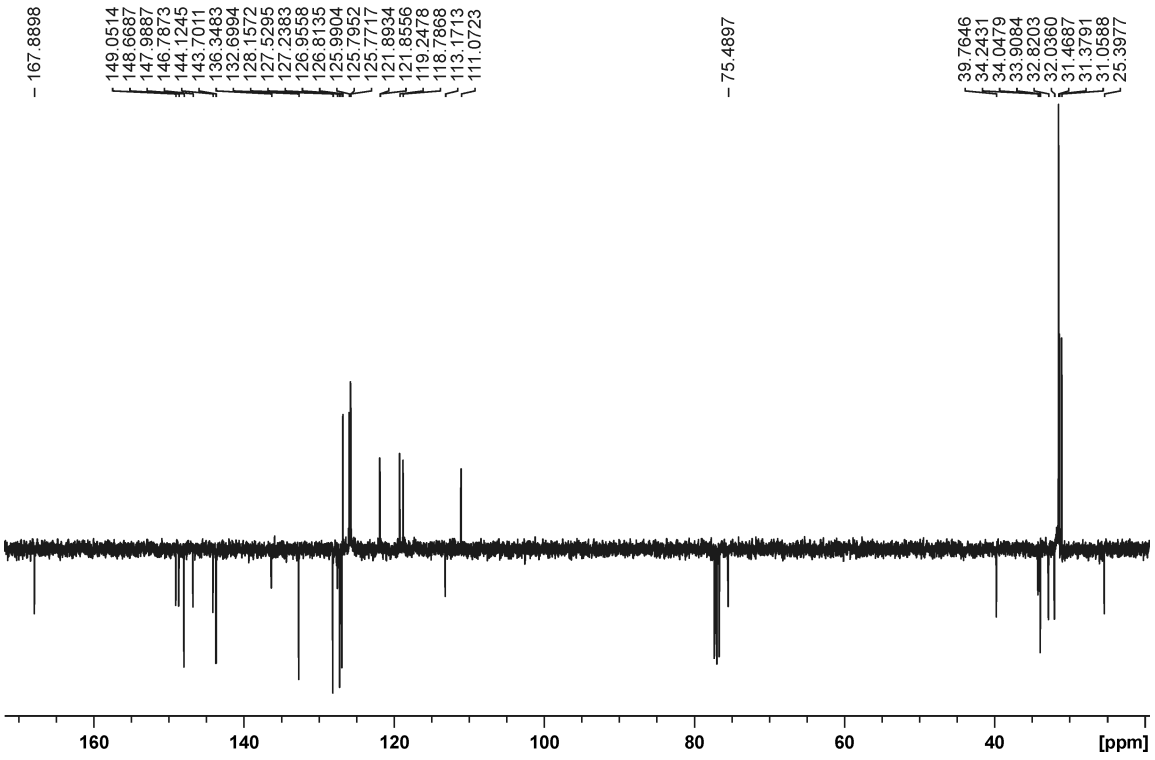


Figure S86. ^{13}C NMR spectrum (APT) of calixarene **55** (100 MHz, $CDCl_3$).

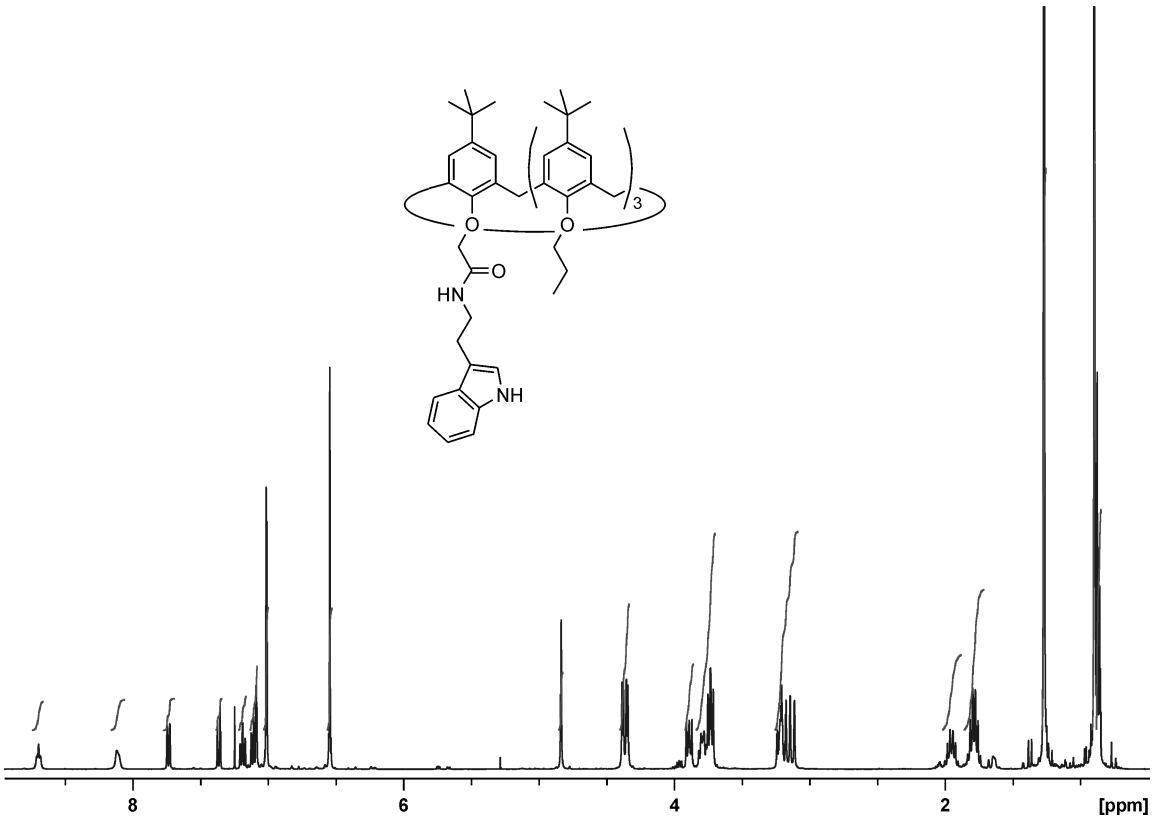


Figure S87. ^{1}H NMR spectrum of calixarene **57** (400 MHz, $CDCl_3$).

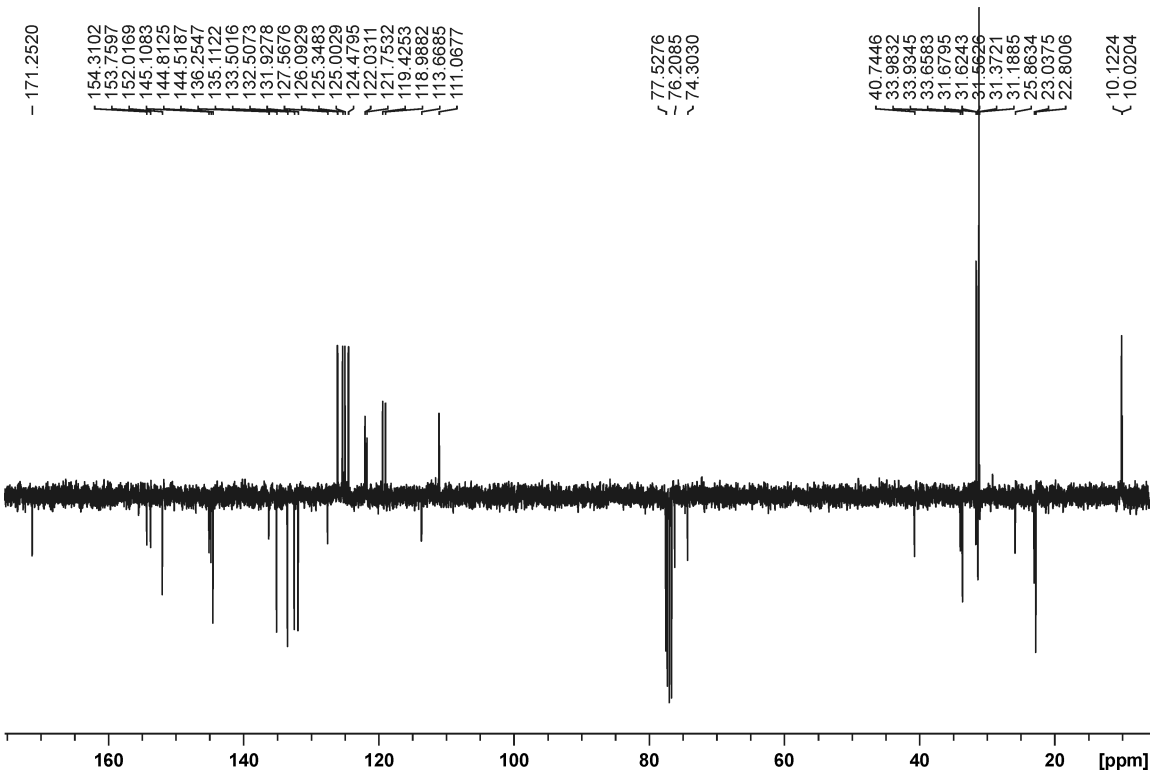


Figure S88. ^{13}C NMR spectrum (APT) of calixarene **57** (100 MHz, $CDCl_3$).

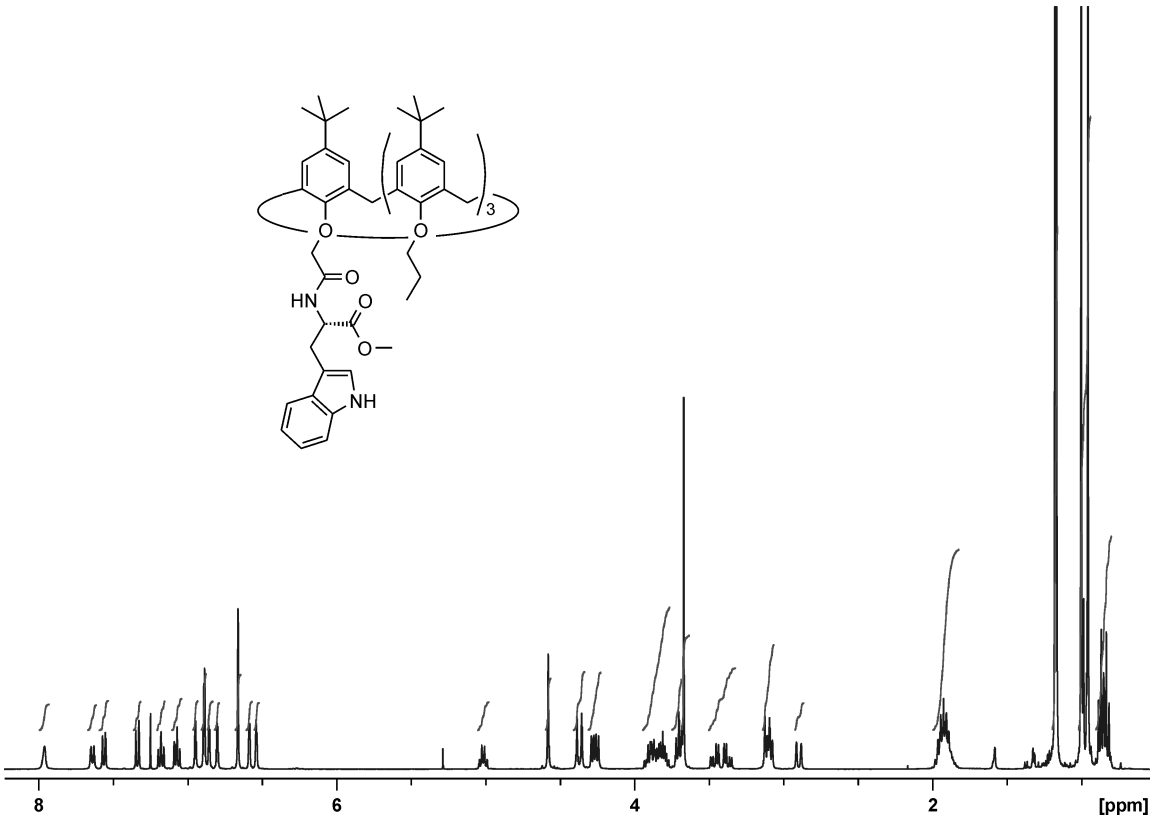


Figure S89. ^{1}H NMR spectrum of calixarene **58** (400 MHz, $CDCl_3$).

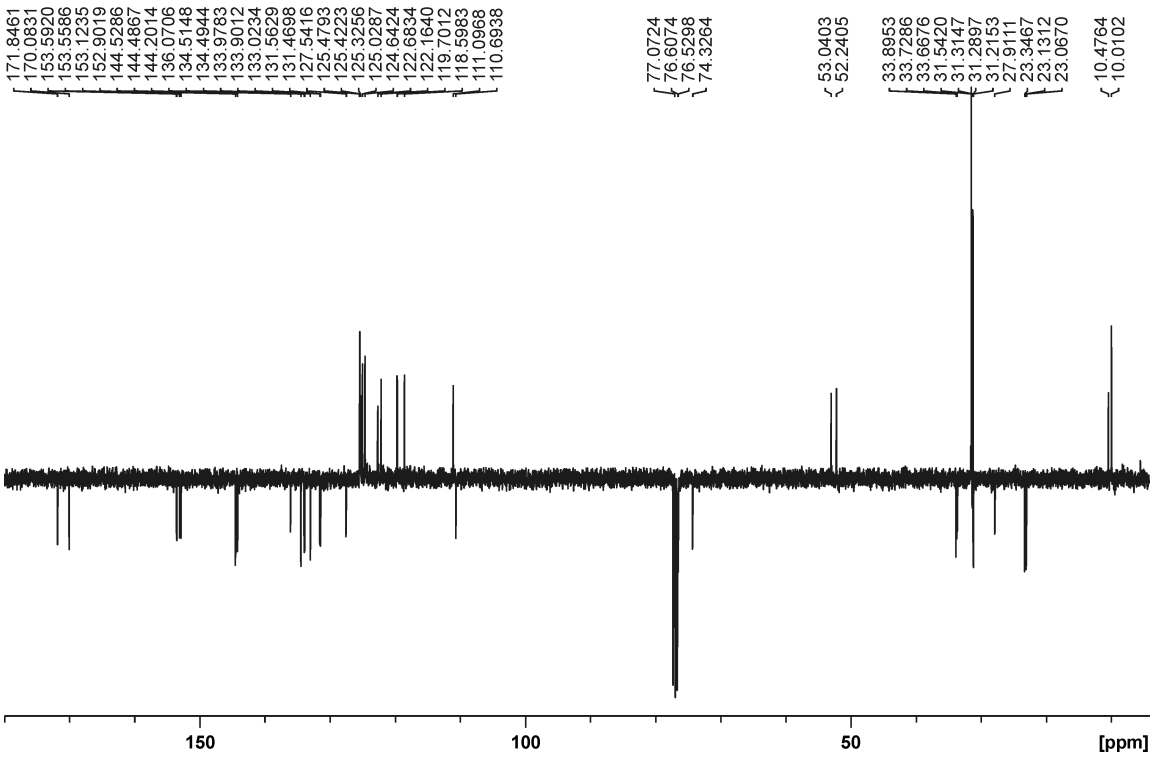


Figure S90. ^{13}C NMR spectrum (APT) of calixarene **58** (100 MHz, $CDCl_3$).

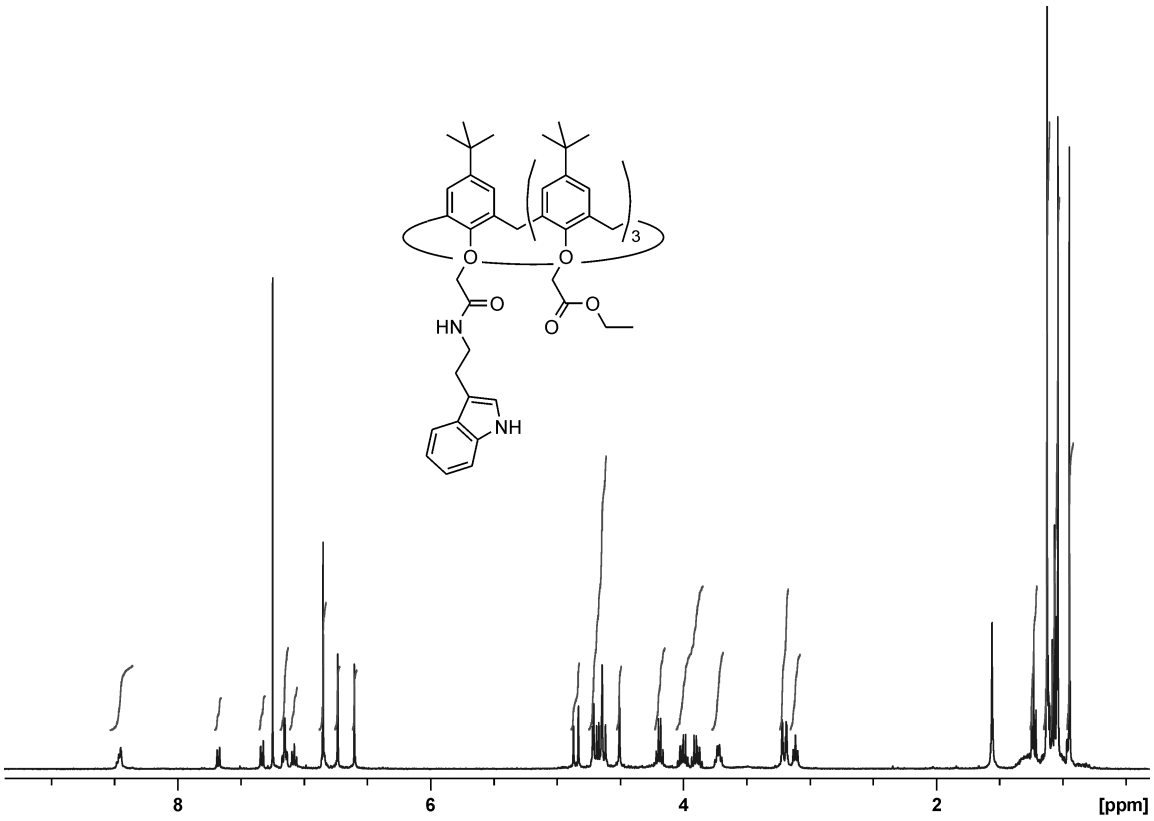


Figure S91. ^{1}H NMR spectrum of calixarene **59** (400 MHz, $CDCl_3$).

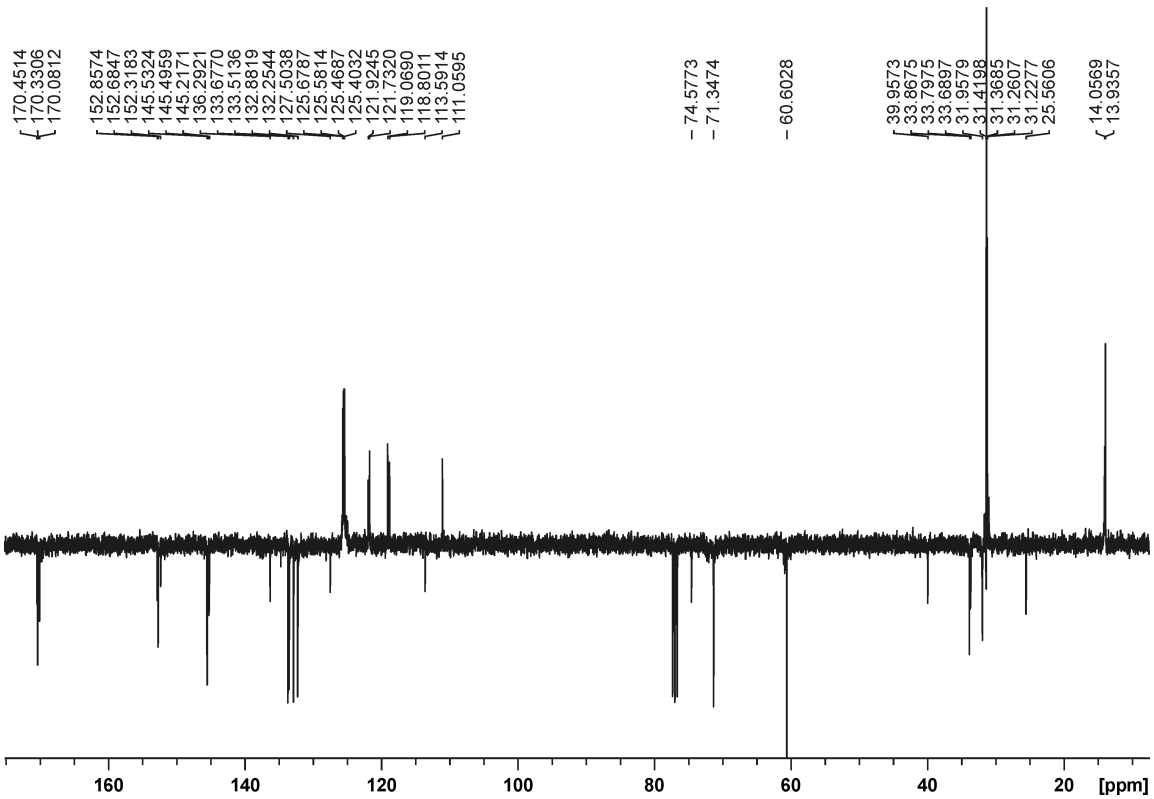


Figure S92. ^{13}C NMR spectrum (APT) of calixarene **59** (100 MHz, $CDCl_3$).

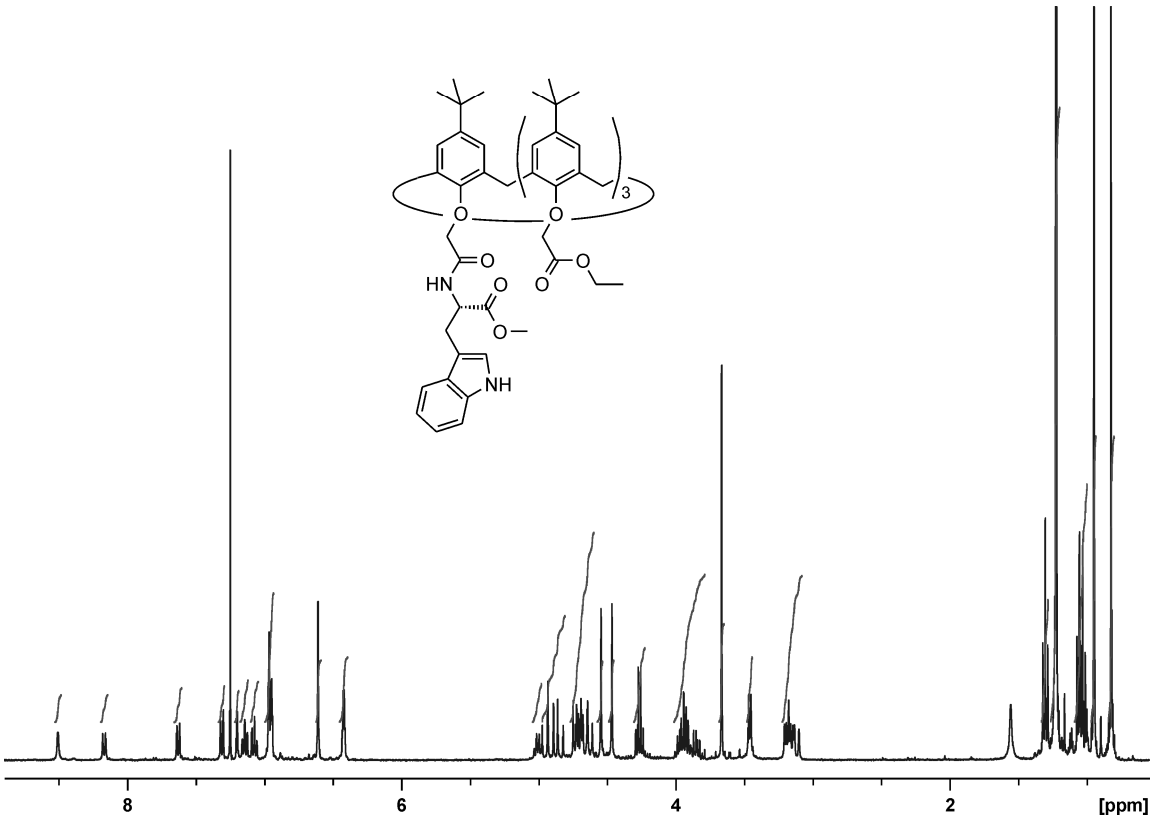


Figure S93. ^{1}H NMR spectrum of calixarene **60** (400 MHz, $CDCl_3$).

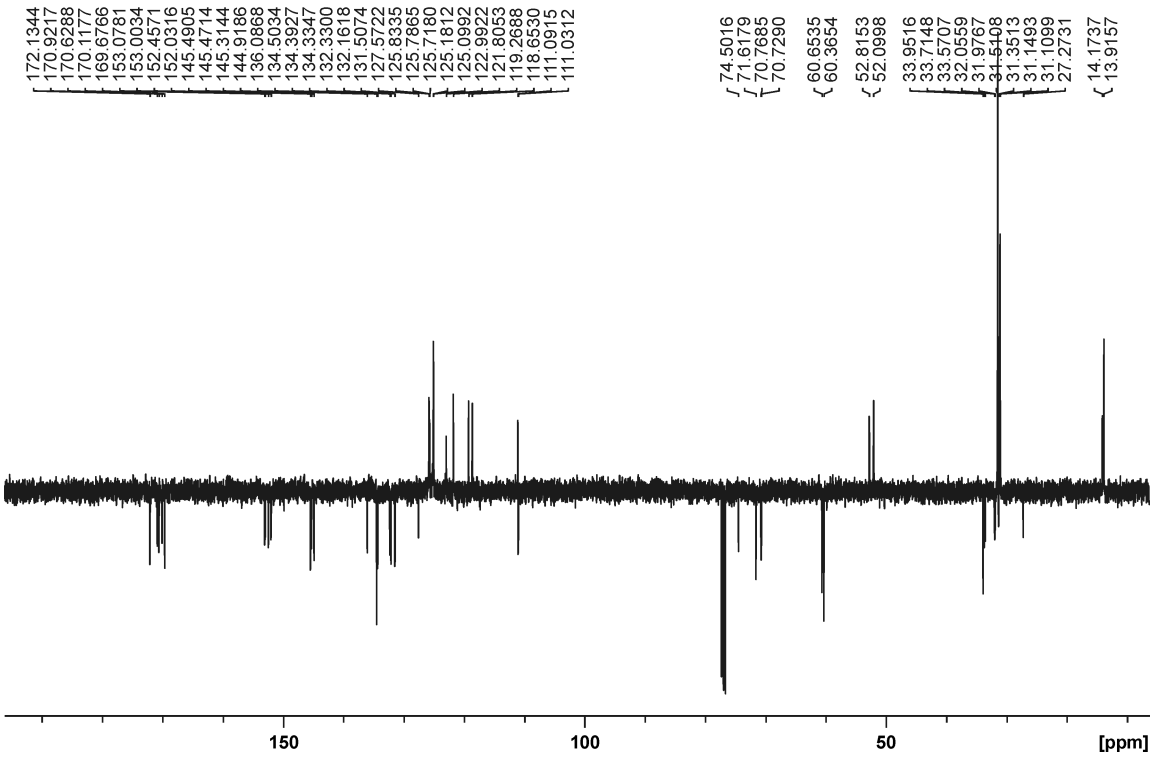


Figure S94. ^{13}C NMR spectrum (APT) of calixarene **60** (100 MHz, $CDCl_3$).

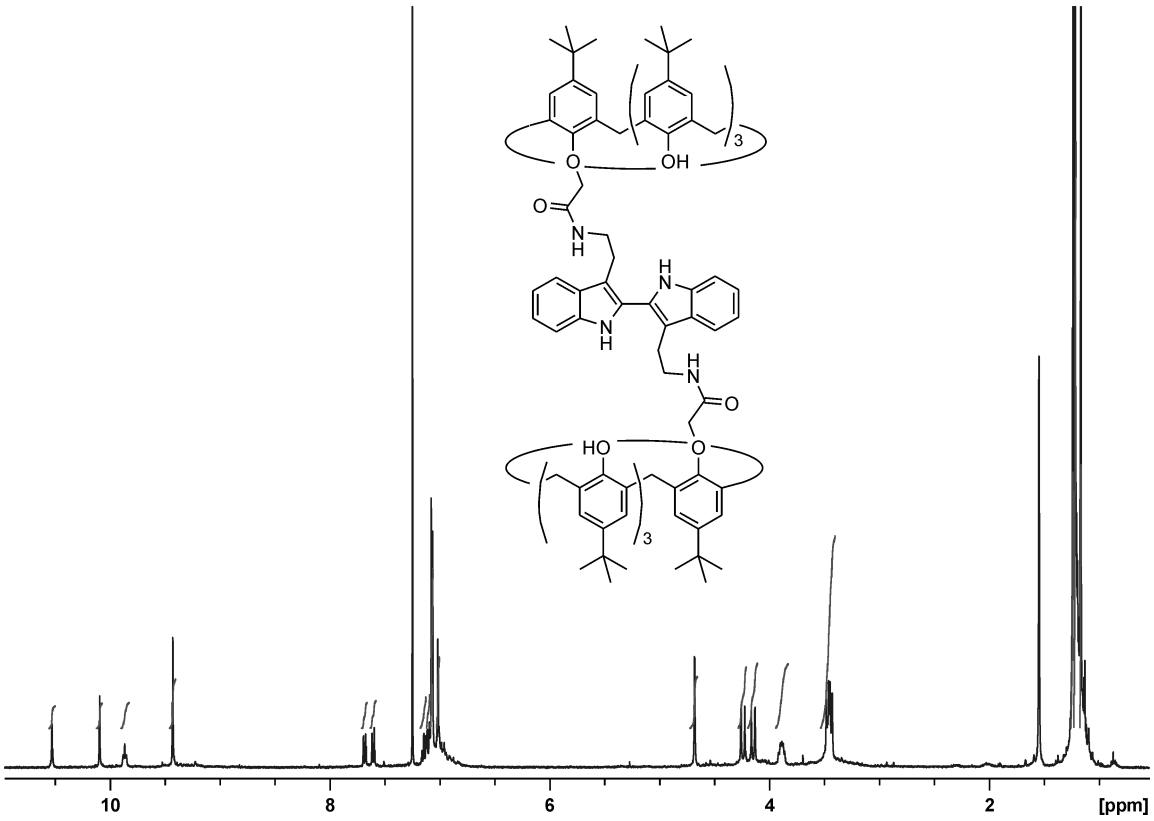


Figure S95. ^{1}H NMR spectrum of calixarene **61** (400 MHz, $CDCl_3$).

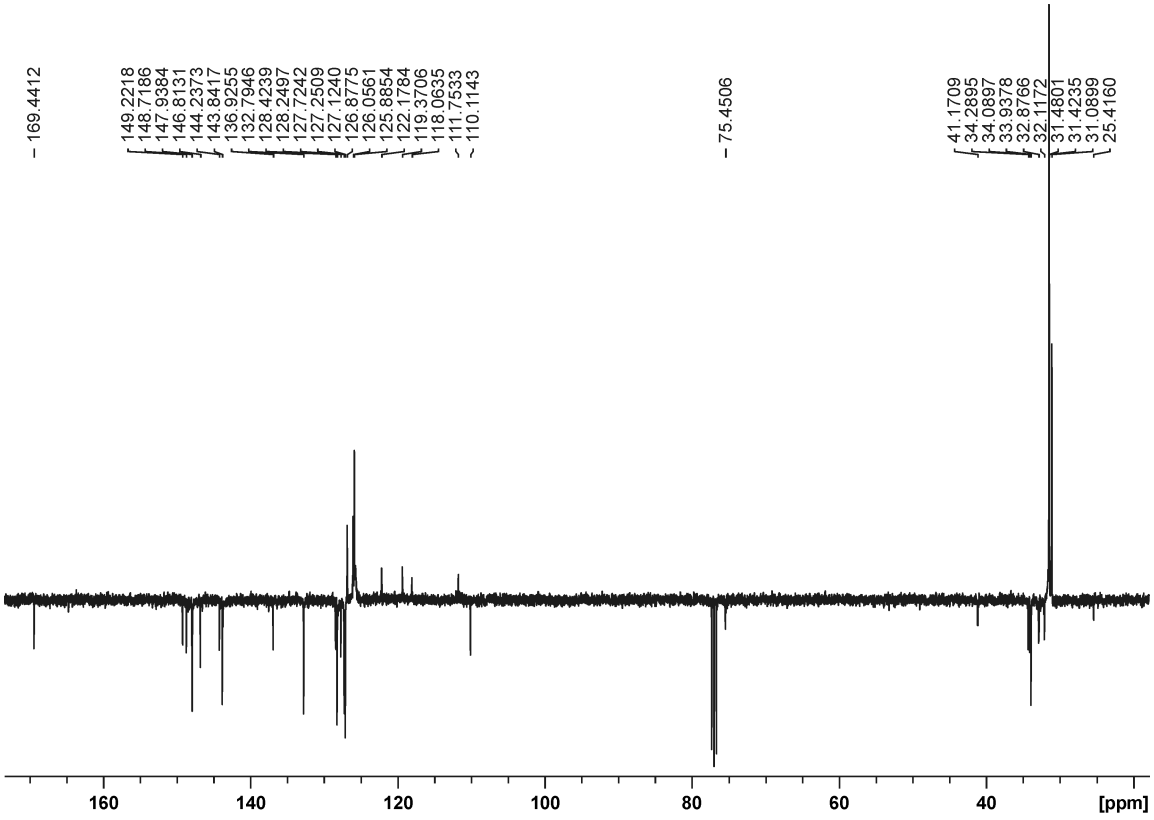


Figure S96. ^{13}C NMR spectrum (APT) of calixarene **61** (100 MHz, $CDCl_3$).

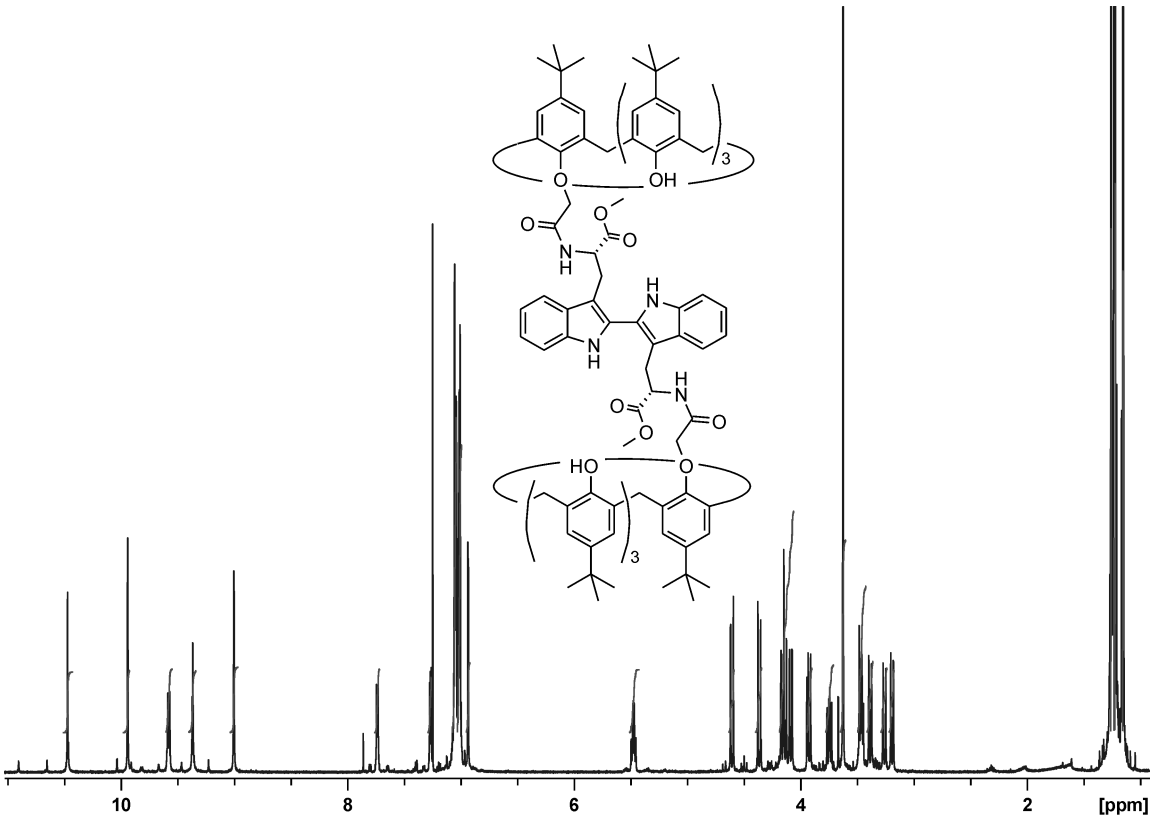


Figure S97. ^{1}H NMR spectrum of calixarene **62** (600 MHz, $CDCl_3$).

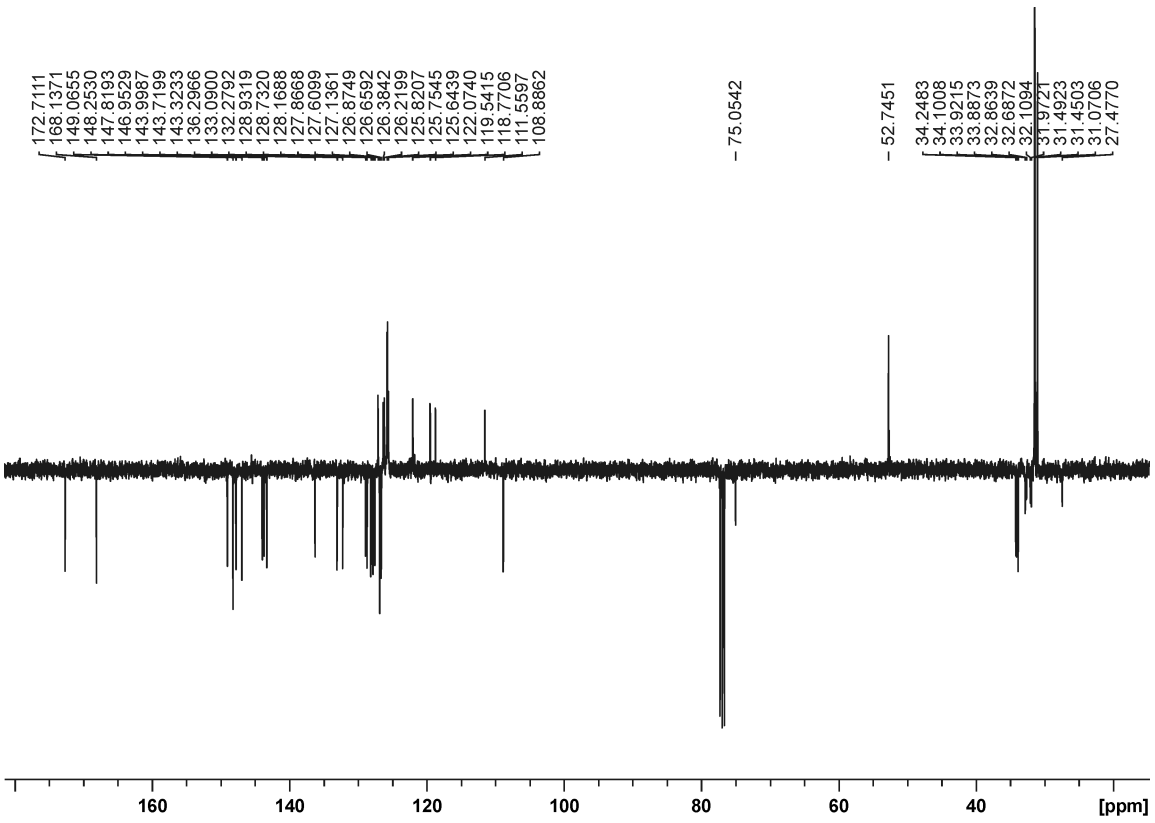


Figure S98. ^{13}C NMR spectrum (APT) of calixarene **62** (100 MHz, $CDCl_3$).

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