

Shrinkable/stretchable bis(calix[4]arenes) comprising photoreactive azobenzene or stilbene linkers

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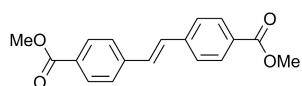
Supplementary Information

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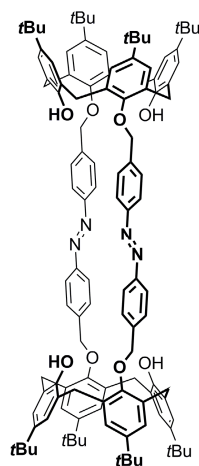
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Synthesis and characterization of novel compounds

General experimental methods: ^1H and ^{13}C NMR spectra were acquired on a Bruker Avance 400 instrument at 20 °C and chemical shifts are reported as ppm referenced to solvent signals. DOSY spectra were acquired on a Bruker Avance 600 instrument at 30 °C. ESI mass spectra were obtained from Sciex TripleTOF 5600+ spectrometers. Chemicals received from commercial sources were used without further purification. Compounds (*E*)-**1**,^[S1] (*E*)-**2**,^[S2] **3**,^[S3] (*E*)-**5**, (*E*)-**6**,^[S4] **7**^[S5] and **8**,^[S6] were prepared according to the published procedures. Photo-induced transformations were studied in NMR sample tubes (5 mm, Norell 506-P-7) or quartz cuvettes (10 mm) using a TLC irradiator (filtered 254, 312 or 365 nm wavelength, 6W mercury lamp light source). Preparative photochemical syntheses were performed in flasks made of quartz or borosilicate glass (Schott Duran) equipped with magnetic stirrer using a 120W high-pressure mercury lamp irradiator equipped with a quartz collimator, IR-filter (deionized water), and a UV-glass filter (max. transmission at 365 nm, ZWB2 or similar).

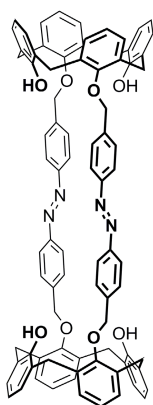


(*E*)-Dimethyl 4,4'-(ethene-1,2-diyl)dibenzoate (*E*)-**4**. A mixture of phosphonate **3** (2.86 g, 10.0 mmol), anhydrous Cs_2CO_3 (4.89 g, 15.0 mmol) and dry DMF (30 mL) was stirred at room temperature for 10 min. Methyl 4-formylbenzoate (2.46 g, 15.0 mmol) was added and the mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the residue was parted between dichloromethane and aqueous HCl (2 M). The organic layer was separated, washed with water, brine, and concentrated to almost dryness. The residue was re-crystallized from methanol. Yield 2.55 g (86%), white solid. Analytical data were the same as previously published.^[S7]

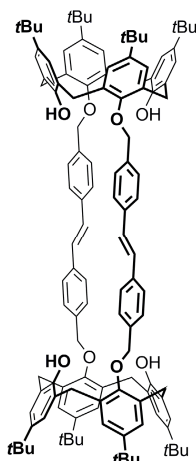


Biscalix[4]arene tetrol (*E,E*)-**9**. A mixture of calixarene **7** (1:1 toluene complex, 3.55 g, 4.80 mmol), anhydrous K_2CO_3 (6.62 g, 48.0 mmol) and dry acetonitrile (400 mL) was stirred at reflux for 1.5 h. After cooling to room temperature, bis(bromomethyl)azobenzene (*E*)-**2** (2.12 g, 5.76 mmol) was added, and the mixture was stirred at reflux for 48 h. After cooling to room temperature, the solvent was removed under reduced pressure, the residue was quenched with aqueous HCl (2 M), and the products were extracted with dichloromethane. The organic solution was washed with water, brine, and dried with Na_2SO_4 . The solvent was evaporated and the residue was subjected to column chromatography (silica, gradient from hexane to hexane/dichloromethane 3:2). The

collected sample was suspended in methanol, refluxed, cooled to room temperature, filtered and dried. Yield 1.26 g (31%), orange solid. M.p. >300 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.94–7.89 (m, 8H; ArH_{azo}), 7.86–7.82 (m, 8H; ArH_{azo}), 7.71 (s, 4H; OH), 7.07 (s, 8H; $\text{ArH}_{\text{calix}}$), 6.89 (s, 8H; $\text{ArH}_{\text{calix}}$), 5.13 (s, 8H; OCH_2), 4.37 (d, 8H, 2J = 12.9 Hz; ArCH_2Ar), 3.38 (d, 8H, 2J = 12.9 Hz; ArCH_2Ar), 1.28 (s, 36H; $\text{C}(\text{CH}_3)_3$), 1.00 (s, 36H; $\text{C}(\text{CH}_3)_3$) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 152.20, 150.83, 149.72, 147.27, 141.39, 139.95, 132.74 (C_{Ar}), 127.44 (CH_{Ar}), 127.34 (C_{Ar}), 125.70, 125.06, 123.23 (CH_{Ar}), 77.54 (OCH_2), 34.01, 33.81 ($\text{C}(\text{CH}_3)_3$), 31.88 (ArCH_2Ar), 31.70, 31.03 ($\text{C}(\text{CH}_3)_3$) ppm. ESI-MS m/z : 1733.0006 $[\text{M}+\text{Na}]^+$ for $\text{C}_{116}\text{H}_{132}\text{NaN}_4\text{O}_8$ (1732.9971).

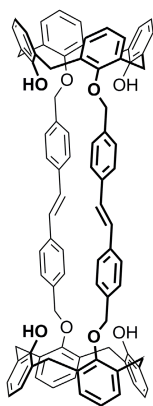


Biscalix[4]arene tetrol (E,E)-10 was prepared as described for compound (*E,E*)-**9** from calixarene **8** (1.06 g, 2.50 mmol), anhydrous K_2CO_3 (3.45 g, 25.0 mmol) and bis(bromomethyl)azobenzene (*E*)-**2** (1.10 g, 3.00 mmol) in dry acetonitrile (230 mL). The product was purified by column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 200:1) followed by recrystallization from dichloromethane/hexane mixture. Yield 0.284 g (18%), orange solid. M.p. 273–275 °C. ^1H NMR (400 MHz, CDCl_3): δ = 8.19 c (4H; OH), 7.97–7.91 (m, 8H; ArH_{azo}), 7.79–7.74 (m, 8H; ArH_{azo}), 7.09 (d, 8H, 3J = 7.5 Hz; $\text{ArH}_{\text{calix}}$), 6.98 (d, 8H, 3J = 7.5 Hz; $\text{ArH}_{\text{calix}}$), 6.85–6.80 (m, 4H; $\text{ArH}_{\text{calix}}$), 6.68 (t, 4H, 3J = 7.5 Hz; $\text{ArH}_{\text{calix}}$), 5.14 (s, 8H; OCH_2), 4.41 (d, 8H, 2J = 13.0 Hz; ArCH_2Ar), 3.46 (d, 8H, 2J = 13.0 Hz; ArCH_2Ar) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 153.38, 152.15, 151.71, 139.68, 133.24 (C_{Ar}), 129.25, 128.55 (CH_{Ar}), 127.66 (C_{Ar}), 127.38, 125.83, 123.32, 119.05 (CH_{Ar}), 77.82 (OCH_2), 31.53 (ArCH_2Ar) ppm. ESI-MS m/z : 1278.5364 $[\text{M}+\text{NH}_4]^+$ for $\text{C}_{84}\text{H}_{72}\text{N}_5\text{O}_8$ (1278.5375).

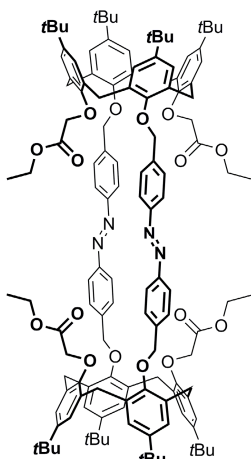


Biscalix[4]arene tetrol (E,E)-11 was prepared as described for compound (*E,E*)-**9** from calixarene **7** (1:1 toluene complex, 3.02 g, 4.08 mmol), anhydrous K_2CO_3 (5.64 g, 40.9 mmol) and bis(bromomethyl)stilbene (*E*)-**6** (1.79 g, 4.89 mmol) in dry acetonitrile (400 mL). Yield 1.15 g (33%), white solid. M.p. 279–281 °C (decomp.). ^1H NMR (400 MHz, CDCl_3): δ = 7.81 (s, 4H; OH), 7.79–7.75 (m, 8H; ArH_{stil}), 7.42–7.37 (m, 8H; ArH_{stil}), 7.07 (s, 8H; $\text{ArH}_{\text{calix}}$), 7.04 (s, 4H; CH), 6.89 (s, 8H; $\text{ArH}_{\text{calix}}$), 5.07 (s, 8H; OCH_2), 4.39 (d, 8H, 2J = 12.9 Hz; ArCH_2Ar), 3.37 (d, 8H, 2J = 12.9 Hz; ArCH_2Ar), 1.29 (s, 36H; $\text{C}(\text{CH}_3)_3$), 1.00 (s, 36H; $\text{C}(\text{CH}_3)_3$) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 150.89, 149.68, 147.15, 141.31, 136.94, 136.56, 132.77 (C_{Ar}), 128.52 (CH_{stil}), 127.39 (C_{Ar}),

126.99, 126.80, 125.62, 125.02 (CH_{Ar}), 77.65 (OCH_2), 34.00, 33.80, ($\text{C}(\text{CH}_3)_3$), 31.82 (ArCH_2Ar), 31.71, 31.02 ($\text{C}(\text{CH}_3)_3$) ppm. ESI-MS m/z : 1744.9897 $[\text{M}+\text{K}]^+$ for $\text{C}_{120}\text{H}_{136}\text{K}\text{O}_8$ (1744.9900).

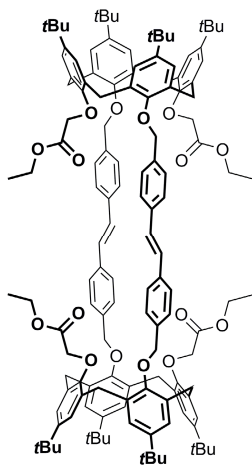


Biscalix[4]arene tetrol (E,E)-12 was prepared as described for compound (*E,E*)-**9** from calixarene **8** (1.06 g, 2.50 mmol), anhydrous K_2CO_3 (3.45 g, 25.0 mmol) and bis(bromomethyl)stilbene (*E*)-**6** (1.10 g, 3.01 mmol) in dry acetonitrile (230 mL). Yield 0.223 g (14%), white solid. M.p. >300 °C. ^1H NMR (400 MHz, CDCl_3): δ = 8.21 (s, 4H; OH), 7.81–7.76 (m, 8H; ArH_{stil}), 7.40–7.35 (m, 8H; ArH_{stil}), 7.09 (d, 8H, $^3J = 7.5$ Hz; $\text{ArH}_{\text{calix}}$), 7.01 (s, 4H; CH), 6.97 (d, 8H, $^3J = 7.5$ Hz; $\text{ArH}_{\text{calix}}$), 6.84–6.78 (m, 4H; $\text{ArH}_{\text{calix}}$), 6.67 (t, 4H, $^3J = 7.5$ Hz; $\text{ArH}_{\text{calix}}$), 5.08 (s, 8H; OCH_2), 4.43 (d, 8H, $^2J = 13.0$ Hz; ArCH_2Ar), 3.45 (d, 8H, $^2J = 13.0$ Hz; ArCH_2Ar) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 153.46, 151.79, 137.04, 136.25, 133.25 (C_{Ar}), 129.18, 128.54 (CH_{Ar} , CH_{stil}), 127.74 (C_{Ar}), 126.94, 126.93, 125.70, 118.98 (CH_{Ar}), 78.01 (OCH_2), 31.50 (ArCH_2Ar) ppm. ESI-MS m/z : 1274.5562 $[\text{M}+\text{NH}_4]^+$ for $\text{C}_{88}\text{H}_{76}\text{NO}_8$ (1274.5565).

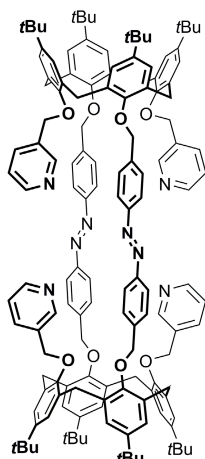


Biscalixarene tetrakis(ester) (E,E)-13. To a stirred suspension of bis(calixarene) (*E,E*)-**9** (0.342 g, 0.20 mmol) in dry THF (20 mL) sodium hydride (60%, 0.096 g, 2.40 mmol) was added followed by dry DMF (6.7 mL), and the mixture was stirred at room temperature for 1 h. Ethyl bromoacetate (0.266 mL, 2.40 mmol) was added and the mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the mixture was quenched with aqueous HCl (2 M) and the products were extracted with dichloromethane. The extract was washed with water and brine, dried and evaporated to almost dryness. The residue was dissolved in a small volume of dichloromethane and methanol was added. The solid formed was collected, washed with methanol and dried. The product was purified by column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 100:1). Yield 0.291 g (71%), orange solid. M.p. >300 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.93–7.88 (m, 8H; ArH_{azo}), 7.79–7.75 (m, 8H; ArH_{azo}), 7.11 (s, 8H; $\text{ArH}_{\text{calix}}$), 6.55 (s, 8H; $\text{ArH}_{\text{calix}}$), 4.82 (s, 8H; OCH_2), 4.82 (d, 8H, $^2J = 12.8$ Hz; ArCH_2Ar), 4.76 (s, 8H; OCH_2), 3.75 (q, 8H, $^3J = 7.1$ Hz; OCH_2CH_3), 3.31 (d, 8H, $^2J = 12.8$ Hz; ArCH_2Ar), 1.32 (s, 36H; $\text{C}(\text{CH}_3)_3$), 1.00 (t, 12H, $^3J = 7.1$ Hz; OCH_2CH_3), 0.88 (s, $\text{C}(\text{CH}_3)_3$) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 170.31 ($\text{C}=\text{O}$), 152.86, 152.19, 152.09, 145.34, 145.01, 141.26, 135.01, 132.08 (C_{Ar}), 129.08, 125.82, 124.87, 122.67 (CH_{Ar}), 77.00 (OCH_2Ar), 69.61 (OCH_2CO), 59.85 (OCH_2CH_3), 34.05, 33.66 ($\text{C}(\text{CH}_3)_3$), 31.84 (ArCH_2Ar), 31.65, 31.13

(C(CH₃)₃), 13.98 (OCH₂CH₃) ppm. ESI-MS *m/z*: 2055.1621 [M+H]⁺ for C₁₃₂H₁₅₇N₄O₁₆ (2055.1623).

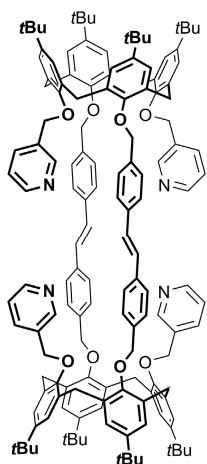


Biscalixarene tetrakis(ester) (E,E)-14 was prepared as described for compound (*E,E*)-**13** from bis(calixarene) (*E,E*)-**11** (0.511 g, 0.30 mmol), sodium hydride (60%, 0.144 g, 3.60 mmol) and ethyl bromoacetate (0.399 mL, 3.60 mmol) in the mixture of dry THF (30 mL) and dry DMF (10 mL). Yield 0.344 g (56%), white solid. M.p. >300 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.63–7.58 (m, 8H; ArH_{stil}), 7.50–7.46 (m, 8H; ArH_{stil}), 7.11 (s, 8H; ArH_{calix}), 7.11 (s, 4H; CH), 6.53 (s, 8H; ArH_{calix}), 4.81 (d, 8H, ²J = 12.8 Hz; ArCH₂Ar), 4.73 (s, 8H; OCH₂), 4.70 (s, 8H; OCH₂), 3.74 (q, 8H, ³J = 7.1 Hz; OCH₂CH₃), 3.30 (d, 8H, ²J = 12.8 Hz; ArCH₂Ar), 1.33 (s, 36H; C(CH₃)₃), 1.01 (t, 12H, ³J = 7.1 Hz; OCH₂CH₃), 0.87 (s, 36H; C(CH₃)₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 170.38 (C=O), 153.00, 152.36, 145.25, 144.86, 137.64, 136.55, 135.09, 132.02 (C_{Ar}), 129.25, 128.30, 126.25, 125.78, 124.78 (CH_{ArH}, CH_{stil}), 77.42 (OCH₂Ar), 69.55 (OCH₂CO), 59.66 (OCH₂CH₃), 34.05, 33.64 (C(CH₃)₃), 31.87 (ArCH₂Ar), 31.67, 31.13 (C(CH₃)₃), 14.06 (OCH₂CH₃) ppm. ESI-MS *m/z*: 1048.0769 [M+2Na]²⁺ for C₁₃₆H₁₆₀Na₂O₁₆ (1048.0762).



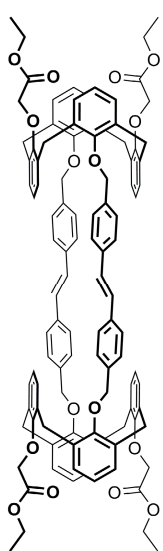
Picolylated bis(calixarene) (E,E)-15. To a stirred suspension of bis(calixarene) (*E,E*)-**9** (0.256 g, 0.15 mmol) in dry THF (27 mL) sodium hydride (60%, 0.180 g, 4.50 mmol) was added followed by dry DMF (3 mL), and the mixture was stirred at room temperature for 1 h. 3-(Chloromethyl)pyridine hydrochloride (0.246 g, 1.50 mmol) was added and the mixture was stirred at 60 °C for 48 h. After cooling to room temperature, the mixture was quenched with ethanol, and the solvents were removed under reduced pressure. The residue was suspended in dichloromethane, and the solution was washed with water, dried, and concentrated to dryness. The product was purified by column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 50:1), the obtained solid was then washed with ether and then crystallized from methanol. Yield 0.106 g (34%), orange solid. M.p. >300 °C. ¹H NMR (400 MHz, CDCl₃+CD₃OD): δ = 8.54–8.50 (m, 4H; ArH_{Py}), 8.36–8.32 (m, 4H; ArH_{Py}), 7.64–7.55 (m, 12H; ArH_{azo}, ArH_{Py}), 7.44–7.38 (m, 8H; ArH_{azo}), 7.05 (s, 8H; ArH_{calix}), 6.94–6.88 (m, 4H; ArH_{Py}), 6.68 (s, 8H; ArH_{calix}), 5.08 (s, 8H; OCH₂), 4.58 (s, 8H; OCH₂), 4.39 (d, 8H, ²J = 12.5 Hz; ArCH₂Ar), 3.13 (d, 8H, ²J = 12.5 Hz; ArCH₂Ar), 1.28 (s, 36H; C(CH₃)₃), 0.94 (36H; C(CH₃)₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ =

151.82, 151.60 (C_{Ar}), 149.43, 148.15 (CH_{Ar}), 145.61, 144.90, 140.59 (C_{Ar}), 137.04 (CH_{Ar}), 134.73, 133.03, 132.48 (C_{Ar}), 129.18, 125.42, 125.10, 122.85, 122.63 (CH_{Ar}), 77.14 (OCH_2Ar), 73.29 (OCH_2Py), 33.90, 33.65 ($C(CH_3)_3$), 31.42, 31.09 ($C(CH_3)_3$), 30.51 ($ArCH_2Ar$) ppm. ESI-MS m/z : 1038.0951 $[M+2H]^{2+}$ for $C_{140}H_{154}N_8O_8$ (1038.0956).



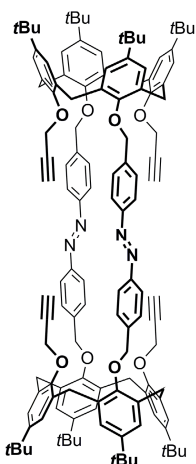
Picolylated bis(calixarene) (E,E)-16 was prepared as described for compound (*E,E*)-**15** from bis(calixarene) (*E,E*)-**11** (0.128 g, 0.075 mmol), sodium hydride (60%, 0.108 g, 2.70 mmol) and 3-(chloromethyl)pyridine hydrochloride (0.148 g, 0.90 mmol) in THF (7.5 mL) and DMF (2.5 mL). The solid obtained after extraction was purified by crystallization from dichloromethane/methanol solvent mixture. Yield 0.118 g (76%), white solid. M.p. >300 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 8.43–8.40 (m, 4H; ArH_{Py}), 8.39–8.36 (m, 4H; ArH_{Py}), 7.69–7.64 (m, 4H; ArH_{Py}), 7.29–7.24 (m, 8H; ArH_{stil}), 7.21–7.16 (m, 8H; ArH_{stil}), 7.10 (s, 8H; ArH_{calix}), 6.98 (s, 4H; CH), 6.79–6.74 (m, 4H; ArH_{Py}),

6.61 (s, 8H; ArH_{calix}), 5.06 (s, 8H; OCH_2), 4.49 (s, 8H; OCH_2), 4.41 (d, 8H, $^2J = 12.5$ Hz; $ArCH_2Ar$), 3.14 (d, 8H, $^2J = 12.5$ Hz; $ArCH_2Ar$), 1.32 (s, 36H; $C(CH_3)_3$), 0.89 (36H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3+CD_3OD$): δ = 151.81, 151.65 (C_{Ar}), 148.90, 147.88 (CH_{Ar}), 145.62, 144.73 (C_{Ar}), 137.31 (CH_{Ar}), 136.82, 136.71, 135.16, 133.33, 132.12 (C_{Ar}), 128.93, 128.11, 126.20, 125.54, 124.90, 122.90 (CH_{Ar} , CH), 77.66 (OCH_2Ar), 72.88 (OCH_2Py), 33.93, 33.58 ($C(CH_3)_3$), 31.48, 31.02 ($C(CH_3)_3$), 30.51 ($ArCH_2Ar$) ppm. ESI-MS m/z : 1036.1044 $[M+2H]^{2+}$ for $C_{144}H_{158}N_4O_8$ (1036.1051).



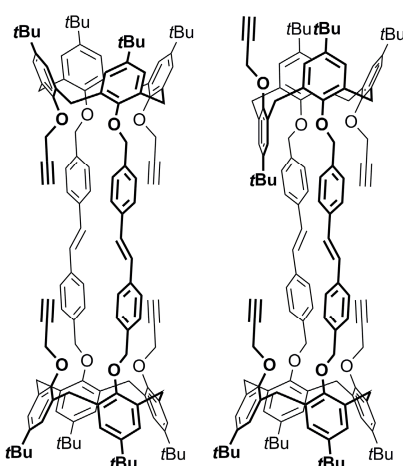
Biscalixarene tetrakis(ester) (E,E)-17. A mixture of bis(calixarene) (*E,E*)-**12** (0.207 g, 0.165 mmol), CS_2CO_3 (0.431 g, 1.32 mmol) and ethyl bromoacetate (0.220 mL, 1.98 mmol) in dry DMF (15 mL) was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the residue was quenched with aqueous HCl (2 M). The products were extracted by dichloromethane, the solution was washed with water and brine, and dried. The solvent was evaporated and the residue was crystallized twice from ethanol. Yield 0.165 g (63%), white solid. M.p. >300 °C. 1H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.69 (m, 8H; ArH_{stil}), 7.40 (s, 4H; CH), 7.26–7.19 (m, 16H; $ArH_{stil,calix}$), 6.82 (t, 4H, $^3J = 7.5$ Hz; ArH_{calix}), 6.73 (d, 8H, $^3J = 7.5$ Hz; ArH_{calix}), 6.51 (t, 8H, $^3J = 7.5$ Hz; ArH_{calix}), 4.93 (s, 8H; OCH_2Ar), 4.18 (q, 8H, $^3J = 7.2$ Hz; OCH_2CH_3), 3.96 (d, 8H, $^2J = 14.7$ Hz; $ArCH_2Ar$), 3.71 (d, 8H, $^2J = 14.7$ Hz; $ArCH_2Ar$), 3.56 (s, 8H; OCH_2CO), 1.27 (t, 12H; $^3J = 7.2$ Hz; OCH_2CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.87

(C=O), 157.01, 155.23, 137.48, 135.98, 134.72, 133.39 (C_{Ar}), 131.98, 130.60, 128.19, 126.91, 125.95, 123.10, 122.26 (CH_{Ar} , CH), 71.96 (OCH_2Ar), 68.95 (OCH_2CO), 60.42 (OCH_2CH_3), 37.25 ($ArCH_2Ar$), 14.18 (OCH_2CH_3) ppm. ESI-MS m/z : 1602.6795 $[M+H]^+$ for $C_{104}H_{97}O_{16}$ (1602.6805).



Propargylated bis(calixarene) (E,E)-18 was prepared as described for compound (*E,E*)-**13** from bis(calixarene) (*E,E*)-**9** (0.409 g, 0.239 mmol), sodium hydride (60%, 0.115 g, 2.88 mmol) and propargyl bromide (80% in toluene, 0.321 mL, 2.88 mmol) in THF (18 mL) and DMF (2 mL). The solid obtained after extraction was purified by column chromatography (silica, gradient from hexane to hexane/dichloromethane 1:3). Yield 0.254 g (57%, contains traces of bis(calixarene) (*E,E*)-**19**), orange solid. M.p. 295–297 °C.

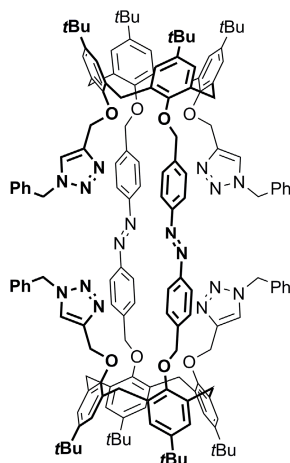
1H NMR (400 MHz, $CDCl_3$): δ = 8.01–7.97 (m, 8H; ArH_{azo}), 7.88–7.83 (m, 8H; ArH_{azo}), 7.17 (s, 8H; ArH_{calix}), 6.50 (s, 8H; ArH_{calix}), 4.76 (d, 8H, 4J = 2.4 Hz; $OCH_2C\equiv CH$), 4.72 (s, 8H; OCH_2Ar), 4.63 (d, 8H, 2J = 12.7 Hz; $ArCH_2Ar$), 3.27 (d, 8H, 2J = 12.7 Hz; $ArCH_2Ar$), 2.08 (t, 4H, 4J = 2.4 Hz; $OCH_2C\equiv CH$), 1.37 (s, 36H; $C(CH_3)_3$), 0.84 (s, 36H; $C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.32, 152.12, 151.98, 145.94, 144.87, 141.04, 136.50, 131.79 (C_{Ar}), 129.28, 125.49, 124.58, 123.01 (CH_{Ar}), 80.68 ($OCH_2C\equiv CH$), 77.37 (OCH_2Ar), 75.08 ($OCH_2C\equiv CH$), 59.26 ($OCH_2C\equiv CH$), 34.19, 33.68 ($C(CH_3)_3$), 31.71 ($C(CH_3)_3$), 31.66 ($ArCH_2Ar$), 31.10 ($C(CH_3)_3$) ppm. ESI-MS m/z : 1863.0761 $[M+H]^+$ for $C_{128}H_{141}N_4O_8$ (1863.0777).



Propargylated bis(calixarenes) (E,E)-20 and (E,E)-21 were prepared as described for compound (*E,E*)-**18** from bis(calixarene) (*E,E*)-**11** (0.445 g, 0.261 mmol), sodium hydride (60%, 0.125 g, 3.13 mmol) and propargyl bromide (80% in toluene, 0.349 mL, 3.13 mmol) in THF (10.8 mL) and DMF (1.2 mL). During the chromatographic purification a fraction containing a mixture of compounds (*E,E*)-**20** and (*E,E*)-**21** (~3:2, 0.192 g) was separated followed by a fraction containing pure compound (*E,E*)-**20** (0.169 g). Yield 0.362 g (75%).

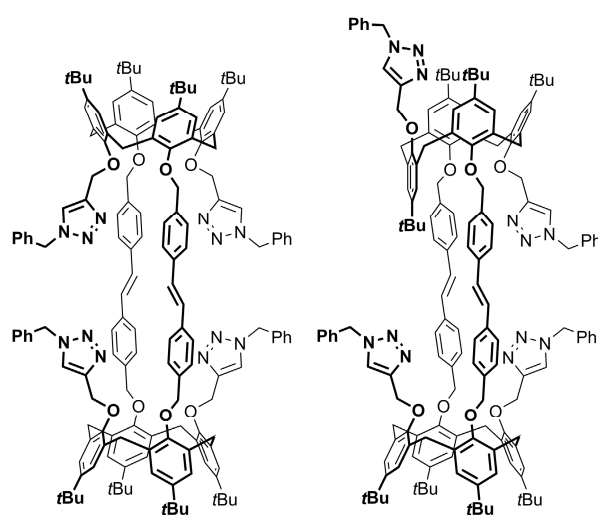
Compound (*E,E*)-**20**: white solid. M.p. 289–291 °C (decomp.). 1H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.66 (m, 8H; ArH_{stil}), 7.60–7.55 (m, 8H; ArH_{stil}), 7.21 (s, 4H; CH), 7.16 (s, 8H; ArH_{calix}), 6.47 (s, 8H; ArH_{calix}), 4.74 (d, 8H, 4J = 2.4 Hz; $OCH_2C\equiv CH$), 4.64 (s, 8H; OCH_2Ar), 4.62 (d, 8H, 2J = 12.8 Hz; $ArCH_2Ar$), 3.25 (d, 8H, 2J = 12.8 Hz; $ArCH_2Ar$), 2.03 (t,

4H, $^4J = 2.4$ Hz; $\text{OCH}_2\text{C}\equiv\text{CH}$), 1.36 (s, 36H; $\text{C}(\text{CH}_3)_3$), 0.83 (s, 36H; $\text{C}(\text{CH}_3)_3$) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 152.49, 152.10, 145.83, 144.69, 137.53, 136.69, 136.53, 131.80$ (C_{Ar}), 129.08, 128.39, 126.49, 125.42, 124.49 (CH_{Ar} , CH), 80.80 ($\text{OCH}_2\text{C}\equiv\text{CH}$), 77.63 (OCH_2Ar), 74.83 ($\text{OCH}_2\text{C}\equiv\text{CH}$), 59.22 ($\text{OCH}_2\text{C}\equiv\text{CH}$), 34.17, 33.61 ($\text{C}(\text{CH}_3)_3$), 31.71 ($\text{C}(\text{CH}_3)_3$), 31.66 (ArCH_2Ar), 31.10 ($\text{C}(\text{CH}_3)_3$) ppm. ESI-MS m/z : 947.0787 $[\text{M}+2\text{NH}_4]^{2+}$ for $\text{C}_{132}\text{H}_{152}\text{N}_2\text{O}_8$ (947.0786). Compound (*E,E*)-**21** (data extracted from the spectra of the (*E,E*)-**20** + (*E,E*)-**21** mixture): ^1H NMR (400 MHz, CDCl_3): $\delta = 7.70\text{--}7.66$ (m, 4H; ArH_{stil}), 7.64–7.61 (m, 4H; ArH_{stil}), 7.60–7.56 (s, 4H; ArH_{stil}), 7.55–7.52 (s, 4H; ArH_{stil}), 7.19–7.15 (m, 6H; $\text{CH}+\text{ArH}_{\text{calix}}$), 7.13 (s, 2H; $\text{ArH}_{\text{calix}}$), 7.03 (d, 2H, $^4J = 2.5$ Hz; $\text{ArH}_{\text{calix}}$), 6.92 (s, 2H; $\text{ArH}_{\text{calix}}$), 6.57 (d, 2H, $^4J = 2.5$ Hz; $\text{ArH}_{\text{calix}}$), 6.50–6.47 (m, 4H; $\text{ArH}_{\text{calix}}$), 4.83 (d, 2H, $^4J = 2.5$ Hz; $\text{OCH}_2\text{C}\equiv\text{CH}$), 4.71 (d, 2H, $^4J = 2.5$ Hz; $\text{OCH}_2\text{C}\equiv\text{CH}$), 4.66 (d, 2H, $^2J = 12.6$ Hz; ArCH_2Ar), 4.65–4.59 (m, 10H; $\text{OCH}_2\text{Ar}+\text{ArCH}_2\text{Ar}$), 4.46 (d, 2H, $^4J = 2.5$ Hz; $\text{OCH}_2\text{C}\equiv\text{CH}$), 4.39 (d, 2H, $^2J = 13.1$ Hz; ArCH_2Ar), 4.21 (d, 2H, $^4J = 2.5$ Hz; $\text{OCH}_2\text{C}\equiv\text{CH}$), 3.77 (d, 2H, $^2J = 14.2$ Hz; ArCH_2Ar), 3.75 (d, 2H, $^2J = 14.2$ Hz; ArCH_2Ar), 3.28 (d, 2H, $^2J = 12.6$ Hz; ArCH_2Ar), 3.26 (d, 2H, $^2J = 12.8$ Hz; ArCH_2Ar), 3.24 (2H, $^2J = 12.6$ Hz; ArCH_2Ar), 2.48 (t, 2H, $^4J = 2.5$ Hz; $\text{OCH}_2\text{C}\equiv\text{CH}$), 2.22 (t, 2H, $^4J = 2.5$ Hz; $\text{OCH}_2\text{C}\equiv\text{CH}$), 2.21 (t, 2H, $^4J = 2.5$ Hz; $\text{OCH}_2\text{C}\equiv\text{CH}$), 2.09 (t, 2H, $^4J = 2.5$ Hz; $\text{OCH}_2\text{C}\equiv\text{CH}$), 1.38 (s, 9H; $\text{C}(\text{CH}_3)_3$), 1.37 (s, 18H; $\text{C}(\text{CH}_3)_3$), 1.07 (s, 18H; $\text{C}(\text{CH}_3)_3$), 0.84 (s, 18H; $\text{C}(\text{CH}_3)_3$), 0.64 (s, 9H; $\text{C}(\text{CH}_3)_3$) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.94, 153.42, 152.54, 151.75, 151.16, 145.92, 145.90, 145.54, 144.74, 144.55, 144.31, 137.45, 137.15, 137.08, 136.82, 136.66, 136.62, 132.77, 132.03, 131.74, 131.39$ (C_{Ar}), 129.45, 129.17, 128.67, 128.42, 128.34, 126.78, 126.62, 126.07, 125.28, 124.56 (CH_{Ar} , CH), 81.07, 80.99, 80.86, 80.71 ($\text{OCH}_2\text{C}\equiv\text{CH}$), 77.74, 76.43 (OCH_2Ar), 75.29, 75.27, 74.88, 74.36 ($\text{OCH}_2\text{C}\equiv\text{CH}$), 59.18, 59.06, 59.00, 57.41 ($\text{OCH}_2\text{C}\equiv\text{CH}$), 37.60 (ArCH_2Ar), 34.19, 33.77, 33.28 ($\text{C}(\text{CH}_3)_3$), 31.91, 31.69, 31.45, 30.42. (ArCH_2Ar , $\text{C}(\text{CH}_3)_3$) ppm.



Biscalixarene tetrakis(triazole) (E,E)-22. To a stirred suspension of copper(I) iodide (0.015 g, 0.079 mmol) in toluene (20 mL) triethylamine (0.216 mL, 1.55 mmol) was added, and the mixture was stirred at room temperature until a clear solution formed. A solution of bis(calixarene) (*E,E*)-**18** (containing traces of bis(calixarene) (*E,E*)-**19**, 0.241 g, 0.130 mmol) in dichloromethane (20 mL) was added followed by benzylazide (0.083 g, 0.624 mmol), and the mixture was stirred at room temperature under inert atmosphere for 24 h. The solvents were removed under reduced pressure, the residue was dissolved in dichloromethane and washed continuously (for 2 h) with aqueous HCl (2 M) at vigorous stirring. The organic

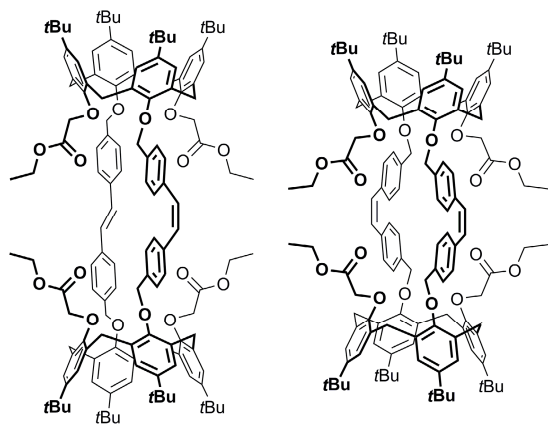
phase was separated, washed with aqueous Na₂SO₃ (5%) and water, dried, and the solvent was evaporated. The product was purified by column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 100:1) followed by crystallization from hexane. Yield 0.131 g (42%, orange solid). M.p. >300 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.78–7.74 (m, 8H; ArH_{azo}), 7.69–7.65 (m, 8H; ArH_{azo}), 7.27–7.23 (m, 12H; ArH_{Ph}), 7.06–7.00 (m, 8H; ArH_{Ph}), 6.78 (s, 4H; ArH_{Trz}), 6.70 (s, 8H; ArH_{calix}), 6.67 (s, 8H; ArH_{calix}), 5.30 (s, 8H; NCH₂), 5.20 (s, 8H; OCH₂Trz), 4.70 (s, 8H; OCH₂Ar), 4.31 (d, 8H, ²J = 12.6 Hz; ArCH₂Ar), 2.92 (d, 8H, ²J = 12.6 Hz; ArCH₂Ar), 1.07 (s, 36H; C(CH₃)₃), 1.04 (s, 36H; C(CH₃)₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 152.98, 151.95, 150.81, 144.86, 144.71 (C_{Ar}), 144.26 (C_{Ar,Trz}), 141.27, 135.01, 134.50, 133.32 (C_{Ar}), 129.85, 128.87, 128.40, 127.62, 125.05, 124.88 (CH_{Ar}), 123.64 (CH_{Ar,Trz}), 122.80 (CH_{Ar}), 76.56 (OCH₂Ar), 65.27 (OCH₂Trz), 53.64 (NCH₂), 33.80, 33.77 (C(CH₃)₃), 31.47 (ArCH₂Ar), 31.41, 31.35 (C(CH₃)₃) ppm. ESI-MS *m/z*: 1198.1695 [M+2H]²⁺ for C₁₅₆H₁₇₀N₁₆O₈ (1198.1705).



Biscalixarene tetrakis(triazoles) (E,E)-23 and (E,E)-24 were prepared as described for compound *(E,E)-22* from the mixture of bis(calixarenes) *(E,E)-20* and *(E,E)-21* (~3:2, 0.192 g, 0.104 mmol), copper(I) iodide (0.012 g, 0.062 mmol), triethylamine (0.173 mL, 1.24 mmol) and benzylazide (0.066 g, 0.498 mmol) in toluene (17.5 mL) and dichloromethane (17.5 mL). After the extraction step, the product mixture was separated by the

column chromatography (silica, gradient from dichloromethane to dichloromethane/ethanol 100:1), and each of the products was additionally purified by crystallization from hexane. Compound *(E,E)-23*: Yield 0.079 g (32%, white solid). M.p. >300 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.57–7.53 (m, 8H; ArH_{stil}), 7.36–7.31 (m, 8H; ArH_{stil}), 7.20–7.15 (m, 12H; ArH_{Ph}), 6.96–6.91 (m, 8H; ArH_{Ph}), 6.88 (s, 8H; ArH_{calix}), 6.84 (s, 4H; CH or ArH_{Trz}), 6.83 (s, 4H; CH or ArH_{Trz}), 6.56 (s, 8H; ArH_{calix}), 5.28 (s, 8H; NCH₂), 5.19 (s, 8H; OCH₂Trz), 4.63 (s, 8H; OCH₂Ar), 4.37 (d, 8H, ²J = 12.6 Hz; ArCH₂Ar), 3.02 (d, 8H, ²J = 12.6 Hz; ArCH₂Ar), 1.20 (s, 36H; C(CH₃)₃), 0.93 (s, 36H; C(CH₃)₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 152.79, 151.27, 145.01, 144.58 (C_{Ar}), 144.47 (C_{Ar,Trz}), 137.61, 136.72, 135.40, 135.16, 132.42 (C_{Ar}), 129.17, 128.76, 128.32, 128.25, 127.33, 126.61, 125.18, 124.78 (CH_{Ar}, CH), 123.92 (CH_{Ar,Trz}), 77.32 (OCH₂Ar), 64.87 (OCH₂Trz), 53.42 (NCH₂), 33.93, 33.68 (C(CH₃)₃), 31.57 (C(CH₃)₃), 31.51

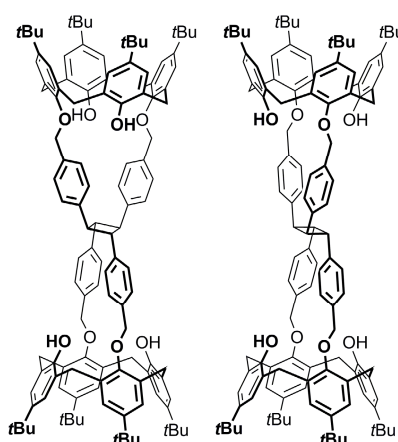
(ArCH₂Ar), 31.23 (C(CH₃)₃) ppm. ESI-MS *m/z*: 2391.3503 [M+H]⁺ for C₁₆₀H₁₇₃N₁₂O₈ (2391.3527). Compound (*E,E*)-**24**: Yield 0.054 g (22%, white solid). M.p. 279–281 °C (decomp.). ¹H NMR (400 MHz, CDCl₃): δ = 7.68–7.63 (m, 4H; ArH_{stil}), 7.63–7.58 (m, 4H; ArH_{stil}), 7.48–7.44 (m, 4H; ArH_{stil}), 7.44–7.40 (m, 4H; ArH_{stil}), 7.40–7.37 (m), 7.33–7.20 (m), 7.15–7.06 (m), 7.04–6.96 (m), 6.92 (s), 6.89–6.85 (m), 6.79–6.74 (m), 6.70 (s), 6.53 (s), 6.49 (s, ²*J* = 2.3 Hz), 6.48 (s), 6.49–6.46 (m) (44H, ArH_{Ph}+ArH_{calix}+ArH_{Trz}+CH), 5.51 (s, 2H; NCH₂), 5.40 (s, 2H; NCH₂), 5.25 (s, 2H; NCH₂), 5.24 (s, 2H; NCH₂), 5.23 (s, 2H; OCH₂Trz), 5.14 (s, 2H; OCH₂Trz), 4.91 (s, 2H; OCH₂Trz), 4.79 (s, 2H; OCH₂Trz), 4.70 (d, 2H, ²*J* = 10.5 Hz; OCH₂Ar), 4.59 (s, 4H, OCH₂Ar), 4.54 (d, 2H, ²*J* = 10.5 Hz; OCH₂Ar), 4.47 (d, 2H, ²*J* = 12.5 Hz; ArCH₂Ar), 4.34 (d, 2H, ²*J* = 12.5 Hz; ArCH₂Ar), 4.20 (d, 2H, ²*J* = 12.9 Hz; ArCH₂Ar), 3.72 (d, 2H, ²*J* = 13.5 Hz; ArCH₂Ar), 3.58 (d, 2H, ²*J* = 13.5 Hz; ArCH₂Ar), 3.12 (d, 2H, ²*J* = 12.7 Hz; ArCH₂Ar), 3.07 (d, 2H, ²*J* = 12.7 Hz; ArCH₂Ar), 3.04 (d, 2H, ²*J* = 12.9 Hz; ArCH₂Ar), 1.30 (s, 9H; C(CH₃)₃), 1.29 (s, 9H; C(CH₃)₃), 1.28 (s, 9H; C(CH₃)₃), 0.95 (s, 18H; C(CH₃)₃), 0.86 (s, 18H; C(CH₃)₃), 0.74 (s, 9H; C(CH₃)₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 153.83, 153.53, 152.48, 151.39, 151.20, 150.43, 145.22, 145.19, 144.71, 144.65, 144.59, 144.51, 144.47, 144.08, 143.93, 143.78, 137.49, 137.41, 136.90, 136.87, 136.30, 136.05, 136.03, 135.41, 135.23, 135.15, 134.55, 133.04, 131.99, 131.82, 131.47 (C_{Ar}) 129.37, 129.09, 129.07, 128.76, 128.74, 128.73, 128.62, 128.58, 128.48, 128.23, 128.20, 128.17, 128.08, 128.01, 127.25, 127.02, 126.76, 126.74, 125.93, 125.37, 125.34, 124.91, 124.66, 124.61, 124.11, 124.06, 123.66, 123.24 (CH_{Ar}, CH), 77.68, 76.35 (OCH₂Ar), 64.71, 64.65, 64.11, 61.09 (OCH₂Trz), 54.05, 53.33, 53.21, 53.14 (NCH₂), 37.46 (ArCH₂Ar), 34.00, 33.94, 33.62, 33.60, 33.40 (C(CH₃)₃), 32.05 (ArCH₂Ar), 31.66, 31.65 (C(CH₃)₃), 31.53, 31.42 (ArCH₂Ar), 31.30, 31.12, 30.76 (C(CH₃)₃) ppm. ESI-MS *m/z*: 2391.3513 [M+H]⁺ for C₁₆₀H₁₇₃N₁₂O₈ (2391.3527).



Biscalixarene tetrakis(esters) (E,Z)-14 and (Z,Z)-14.

A stirred solution of tetrakis(ester) (*E,E*)-**14** (0.123 g, 0.06 mmol) and 1,2-benzanthracene (0.055 g, 0.24 mmol) in benzene/methanol (9:1 v/v) solvent mixture (15 mL) was irradiated at 365 nm (120W lamp) for 10 h. The solvents were removed under reduced pressure and the residue was dissolved in dichloromethane. Hexane was added and the precipitated tetrakis(ester) (*E,E*)-**14** (0.025 g) was filtered-off. The filtrate was evaporated under reduced pressure and the residue was subjected to column chromatography (silica, gradient from dichloromethane/benzene 50:150 to dichloromethane/benzene/methanol

50:150:3) to obtain pure compounds (*E,Z*)-**14**, (*Z,Z*)-**14** and a mixed fraction. Compound (*E,Z*)-**14**: Yield 0.010 g (8%, white solid). M.p. >300 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.83–7.77 (m, 4H; ArH_{stil}), 7.57–7.52 (m, 4H; ArH_{stil}), 7.25–7.20 (m, 4H; ArH_{stil}), 7.15–7.10 (m, 4H; ArH_{stil}), 7.11 (s, 2H; CH_{stil,trans}), 6.88 (d, 4H, ⁴J = 2.5 Hz; ArH_{calix}), 6.79 (s, 4H; ArH_{calix}), 6.79 (d, 4H, ⁴J = 2.5 Hz; ArH_{calix}), 6.63 (s, 4H; ArH_{calix}), 6.53 (s, 2H; CH_{stil,cis}), 4.80 (s, 4H; OCH₂Ar), 4.79 (d, 4H, ²J = 12.8 Hz; ArCH₂Ar), 4.74 (s, 4H; OCH₂Ar), 4.40 (s, 8H; OCH₂CO), 4.38 (d, 4H, ²J = 12.8 Hz; ArCH₂Ar), 3.99 (dq, 4H, ²J = 10.7 Hz, ³J = 7.1 Hz; OCH₂CH₃), 3.92 (dq, 4H, ²J = 10.7 Hz, ³J = 7.1 Hz; OCH₂CH₃), 3.28 (d, 4H, ²J = 12.8 Hz; ArCH₂Ar), 3.02 (d, 4H, ²J = 12.8 Hz; ArCH₂Ar), 1.11 (t, 12H, ³J = 7.2 Hz; OCH₂CH₃), 1.10 (s, 36H; C(CH₃)₃), 1.06 (s, 18H; C(CH₃)₃), 0.98 (s, 18H; C(CH₃)₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 170.44 (C=O), 153.27, 152.77, 145.01, 144.90, 144.70, 138.03, 137.48, 136.68, 136.27, 133.88, 133.76, 133.52, 133.48 (C_{Ar}), 129.78, 129.73, 129.73, 129.29, 128.36, 128.30, 126.26, 125.47, 125.24, 125.14, 124.93 (CH_{Ar}, CH), 72.03 (OCH₂Ar), 70.42 (OCH₂CO), 68.14 (OCH₂Ar), 60.15 (OCH₂CH₃), 33.85, 33.83, 33.72 (C(CH₃)₃), 31.83 (ArCH₂Ar), 31.42, 31.36, 31.33 (C(CH₃)₃), 29.69 (ArCH₂Ar), 14.15 (OCH₂CH₃) ppm. Compound (*Z,Z*)-**14**: Yield 0.045 g (37%, white solid). M.p. >300 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.17–7.11 (m, 8H; ArH_{stil}), 7.00 (s, 8H; ArH_{calix}), 6.62 (s, 4H; CH_{stil,cis}), 6.38 (s, 8H; ArH_{calix}), 5.38 (s, 8H; OCH₂Ar), 4.20 (d, 8H, ²J = 12.8 Hz; ArCH₂Ar), 4.02 (s, 8H; OCH₂CO), 3.95 (q, 8H, ³J = 7.2 Hz; OCH₂CH₃), 2.93 (d, 8H, ²J = 12.8 Hz; ArCH₂Ar), 1.29 (s, 36H; C(CH₃)₃), 1.12 (t, 12H, ³J = 7.2 Hz; OCH₂CH₃), 0.80 (s, 36H; C(CH₃)₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 169.92 (C=O), 153.74, 152.83, 144.70, 144.55, 138.04, 136.30, 135.44, 131.66 (C_{Ar}), 130.43, 130.08, 128.45, 125.56, 124.62 (CH_{Ar}), 76.56 (OCH₂Ar), 71.53 (OCH₂CO), 60.63 (OCH₂CH₃), 34.01, 33.54 (C(CH₃)₃), 31.80 (ArCH₂Ar), 31.69, 31.08 (C(CH₃)₃), 14.11 (OCH₂CH₃) ppm.



Biscalixarene cyclobutanes 25 and 26. A stirred solution of bis(calix[4]arene) (*E,E*)-**11** (0.511 g, 0.30 mmol) in dichloromethane (20 mL) was irradiated at 365 nm (120W lamp) for 2 h. The solvents were removed under reduced pressure and the residue was subjected to column chromatography (silica, gradient from hexane/dichloromethane 3:1 to hexane/dichloromethane 1:2) to obtain pure compounds **25**, **26** and a mixed fraction in total yield of 0.419 g (82%). Compound **25**: Yield 0.192 g (38%, white solid). M.p.

>300 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.75–7.70 (m, 8H; ArH_{cb}), 7.66 (s, 4H; OH), 7.37–7.32 (m, 8H; ArH_{cb}), 7.07 (s, 8H; ArH_{calix}), 6.91 (s, 8H; ArH_{calix}), 4.92 (s, 8H; OCH₂Ar), 4.44 (d,

8H, $^2J = 12.8$ Hz; ArCH₂Ar), 4.30 (s, 4H; CH), 3.40 (d, 8H, $^2J = 12.8$ Hz; ArCH₂Ar), 1.29 (s, 36H; C(CH₃)₃), 1.02 (s, 36H; C(CH₃)₃) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 150.96, 149.23, 147.13, 143.91, 141.27, 134.19, 132.95$ (C_{Ar}), 128.55, 127.36 (CH_{Ar}), 127.33 (C_{Ar}), 125.55, 125.12 (CH_{Ar}), 78.11 (OCH₂Ar), 49.43 (CH), 34.04, 33.79 (C(CH₃)₃), 31.86 (ArCH₂Ar), 31.71, 31.05 (C(CH₃)₃) ppm. ESI-MS m/z : 1707.0371 [M+H]⁺ for C₁₂₀H₁₃₇O₈ (1707.0342). Compound **26**: Yield 0.086 g (17%, white solid). M.p. 259–261 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.81$ (s, 2H; OH), 7.80 (s, 2H; OH), 7.56–7.51 (m, 8H; ArH_{cb}), 7.19–7.14 (m, 8H; ArH_{cb}), 7.05 (s, 4H; ArH_{calix}), 7.04 (s, 4H; ArH_{calix}), 6.96 (bs, 8H; ArH_{calix}), 4.75 (s, 8H; OCH₂Ar), 4.64 (s, 4H; CH), 4.44 (d, 4H, $^2J = 12.7$ Hz; ArCH₂Ar), 4.43 (d, 4H, $^2J = 12.7$ Hz; ArCH₂Ar), 3.40 (d, 8H, $^2J = 12.7$ Hz; ArCH₂Ar), 1.26 (s, 18H; C(CH₃)₃), 1.26 (s, 18H; C(CH₃)₃), 1.08 (s, 36H; C(CH₃)₃) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 151.04, 151.00, 149.34, 147.13, 141.28, 140.84, 133.85, 133.19, 133.13$ (C_{Ar}), 129.31, 128.32 (CH_{Ar}), 127.29, 127.26 (C_{Ar}), 125.64, 125.64, 125.21, 125.17 (CH_{Ar}), 78.54 (OCH₂Ar), 46.89 (CH_{cb}), 34.11, 33.77 (C(CH₃)₃), 32.19, 32.16 (ArCH₂Ar), 31.69, 31.13 (C(CH₃)₃) ppm. ESI-MS m/z : 1707.0343 [M+H]⁺ for C₁₂₀H₁₃₇O₈ (1707.0342).

NMR spectra of novel compounds

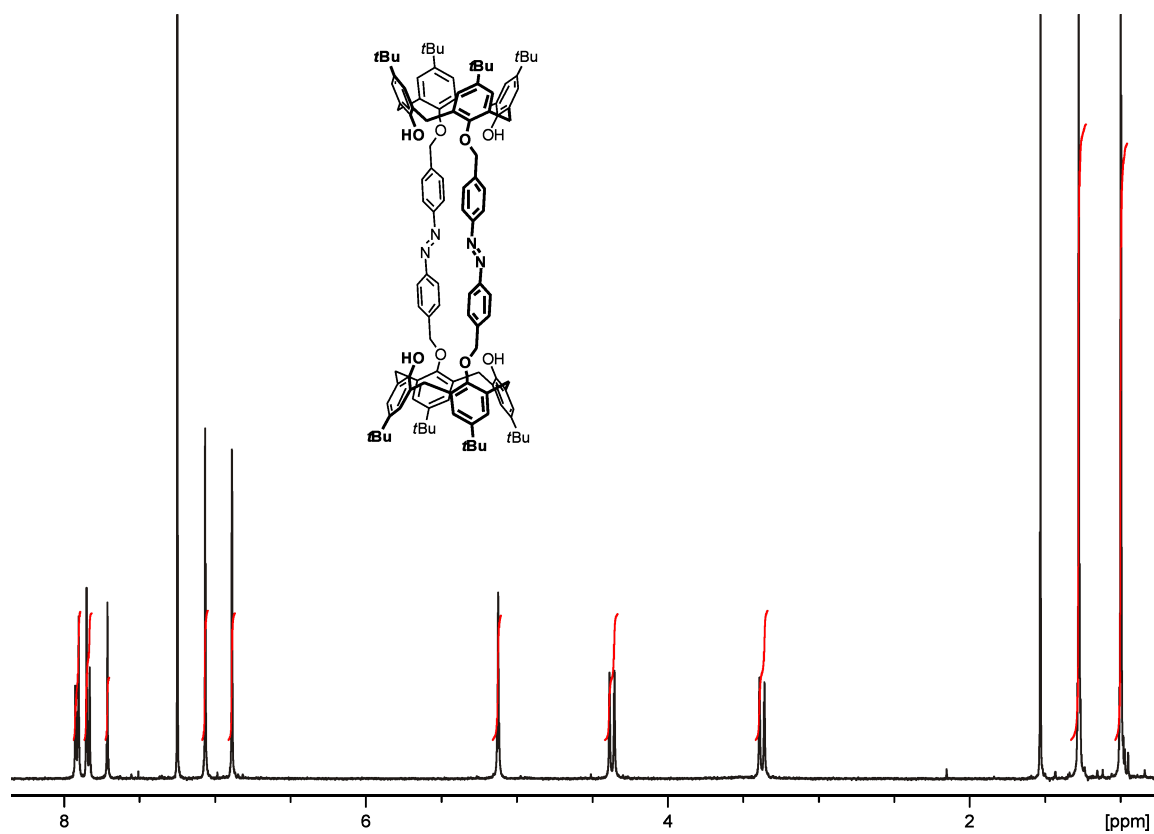


Figure S1. ^1H NMR spectrum of bis(calix[4]arene) (*E,E*)-**9** (400 MHz, CDCl_3).

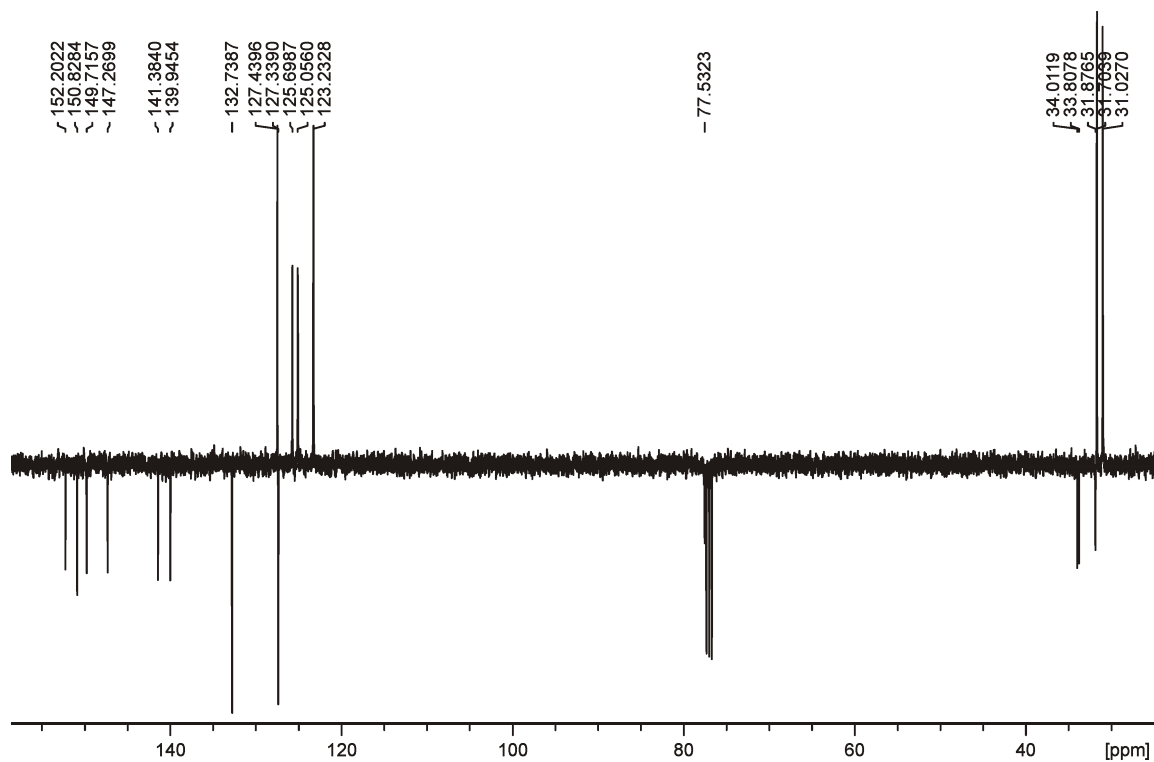


Figure S2. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**9** (100 MHz, CDCl_3).

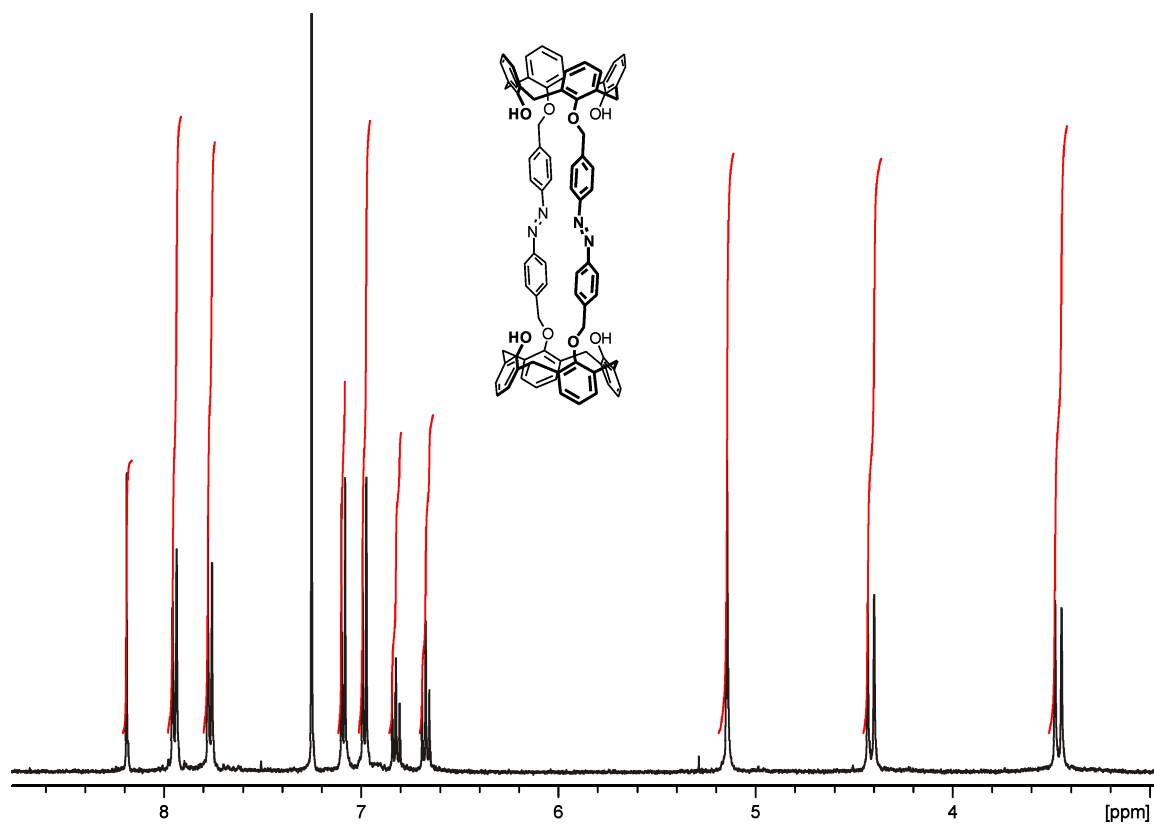


Figure S3. ¹H NMR spectrum of bis(calix[4]arene) (*E,E*)-**10** (400 MHz, CDCl₃).

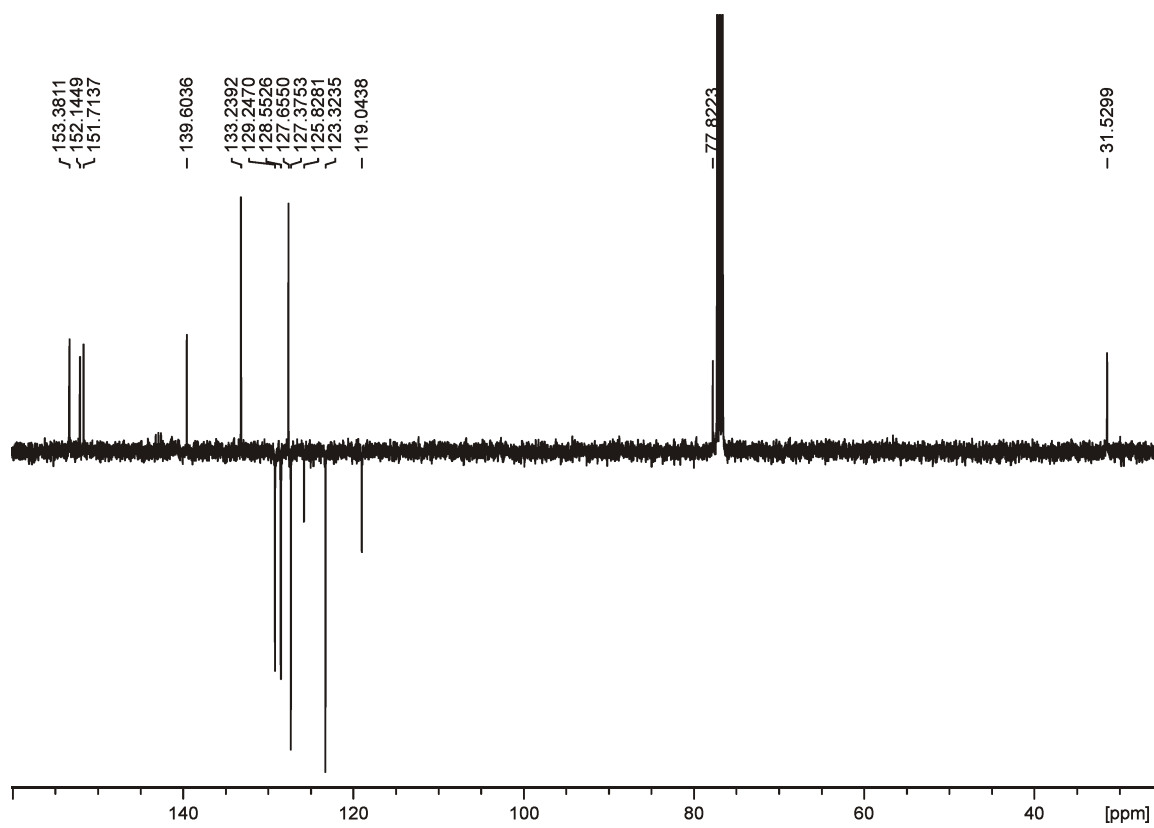


Figure S4. ¹³C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**10** (100 MHz, CDCl₃).

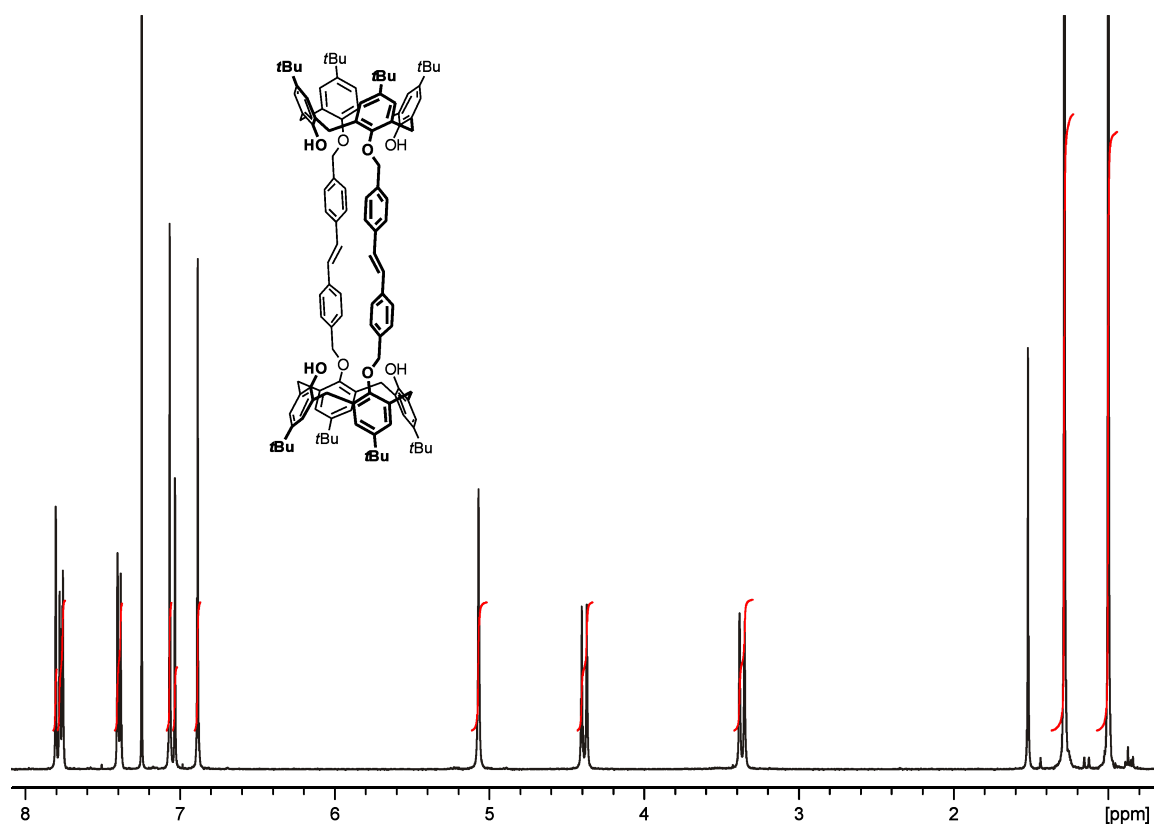


Figure S5. ^1H NMR spectrum of bis(calix[4]arene) (*E,E*)-**11** (400 MHz, CDCl_3).

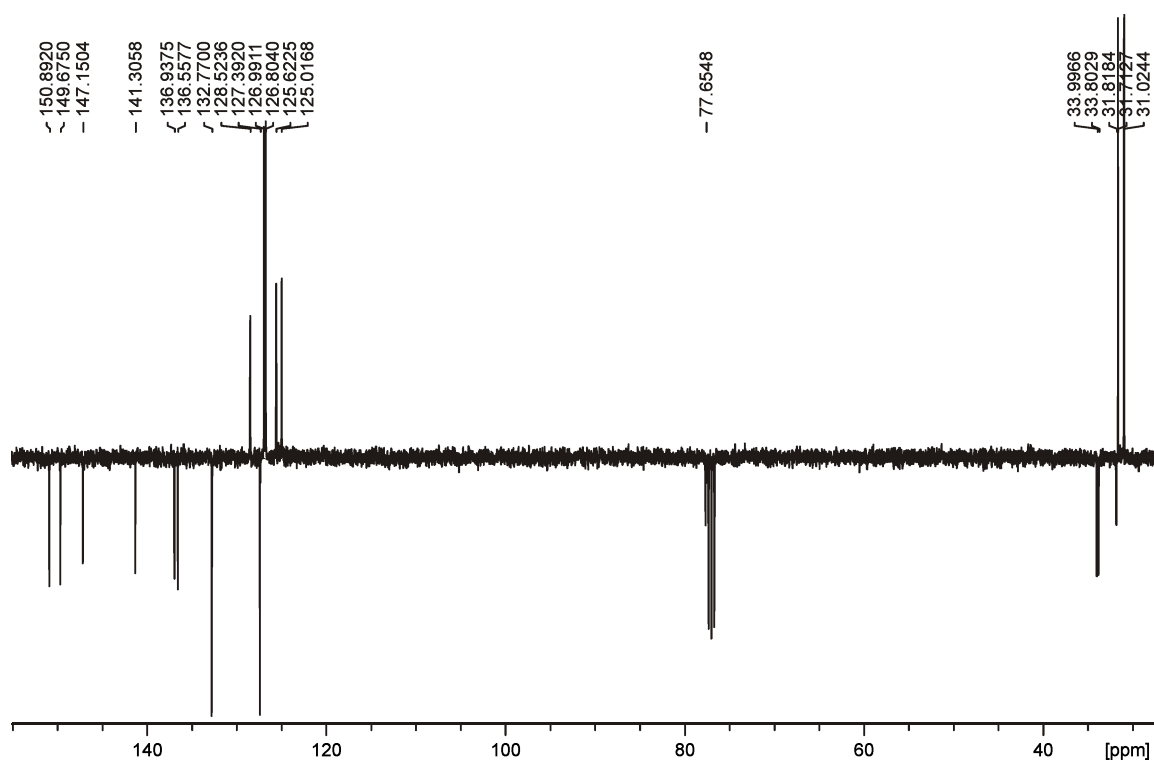


Figure S6. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**11** (100 MHz, CDCl_3).

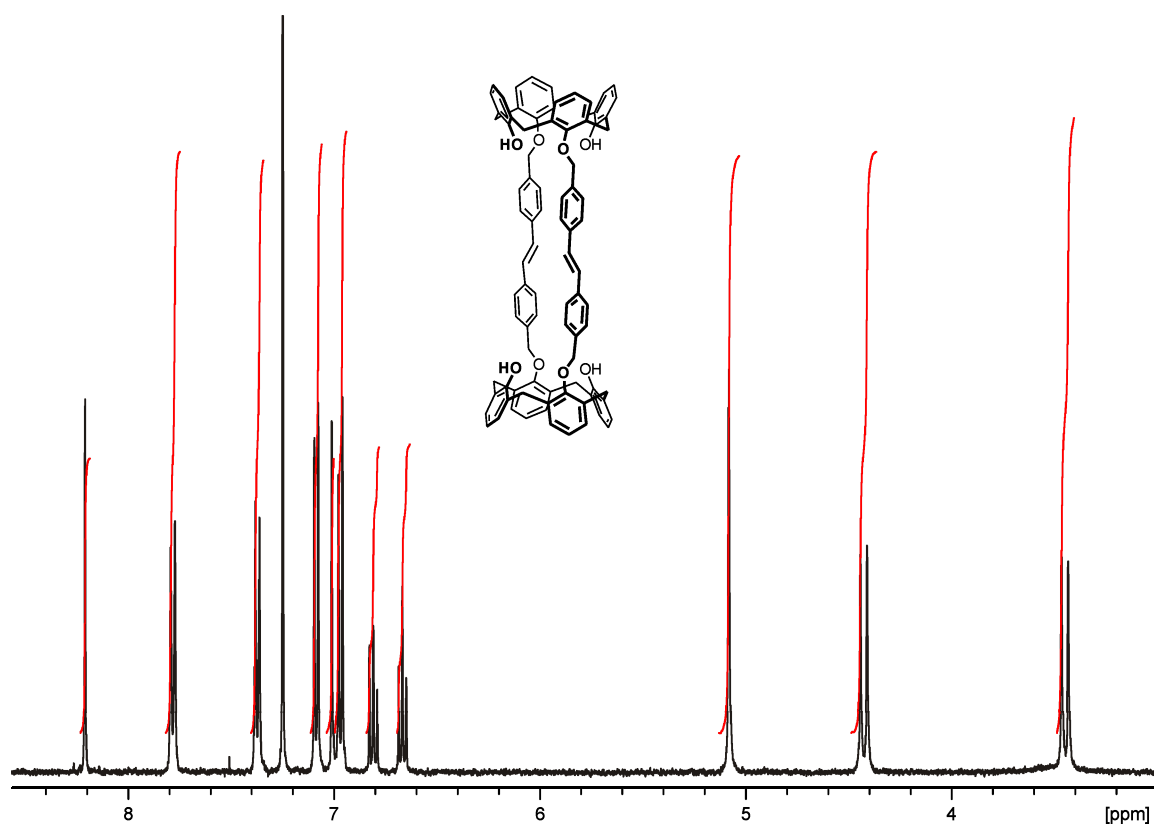


Figure S7. ^1H NMR spectrum of bis(calix[4]arene) (*E,E*)-12 (400 MHz, CDCl_3).

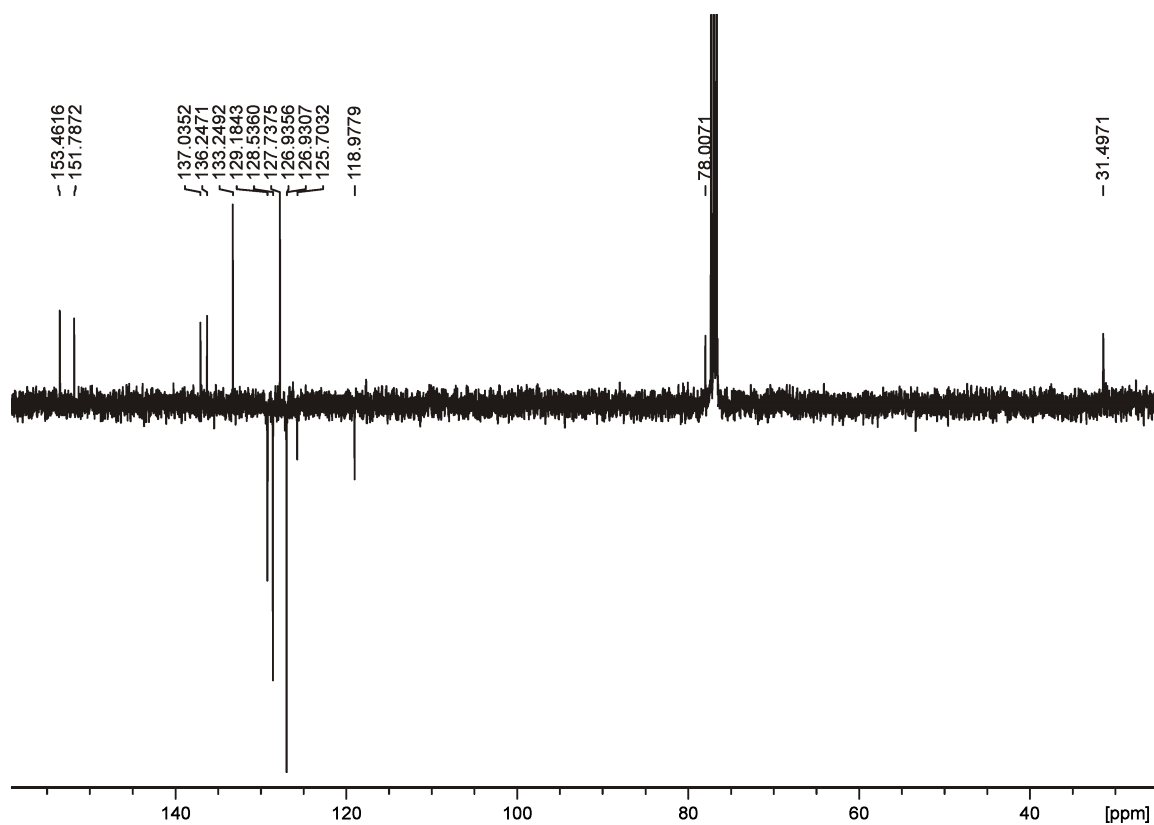


Figure S8. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-12 (100 MHz, CDCl_3).

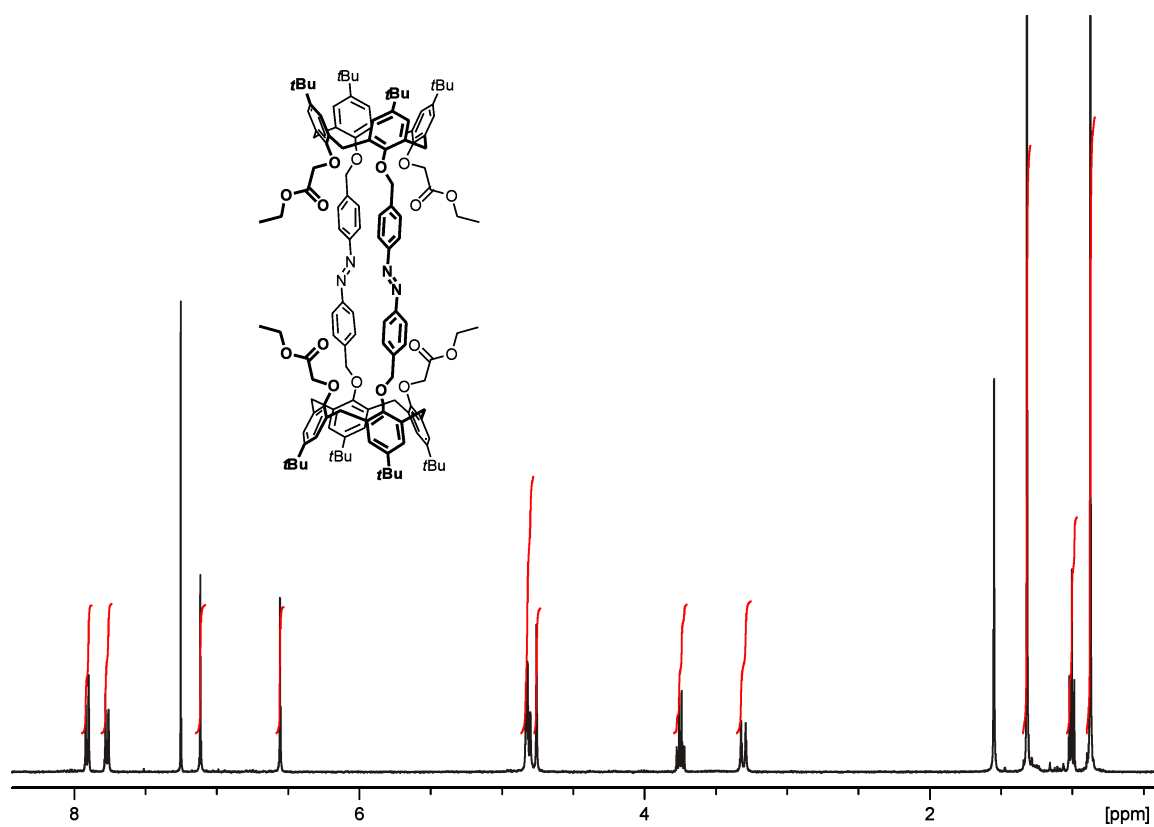


Figure S9. ¹H NMR spectrum of bis(calix[4]arene) (*E,E*)-**13** (400 MHz, CDCl₃).

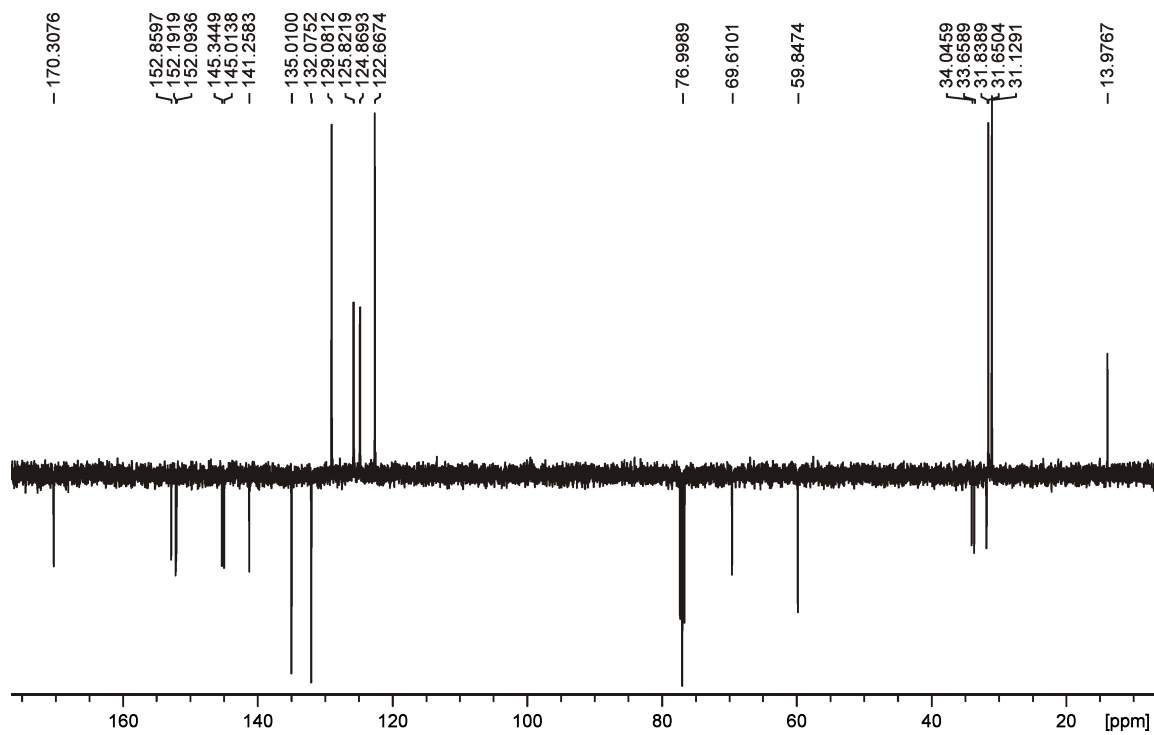


Figure S10. ¹³C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**13** (100 MHz, CDCl₃).

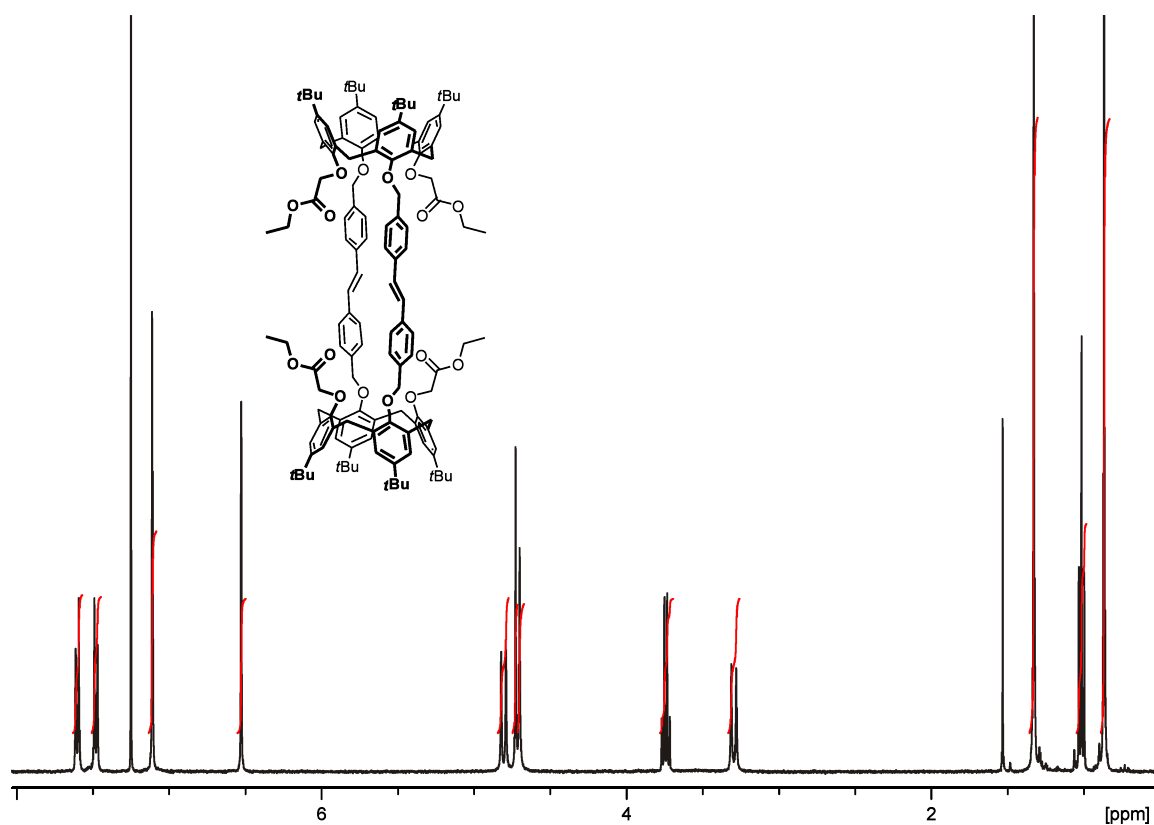


Figure S11. ^1H NMR spectrum of bis(calix[4]arene) (*E,E*)-**14** (400 MHz, CDCl_3).

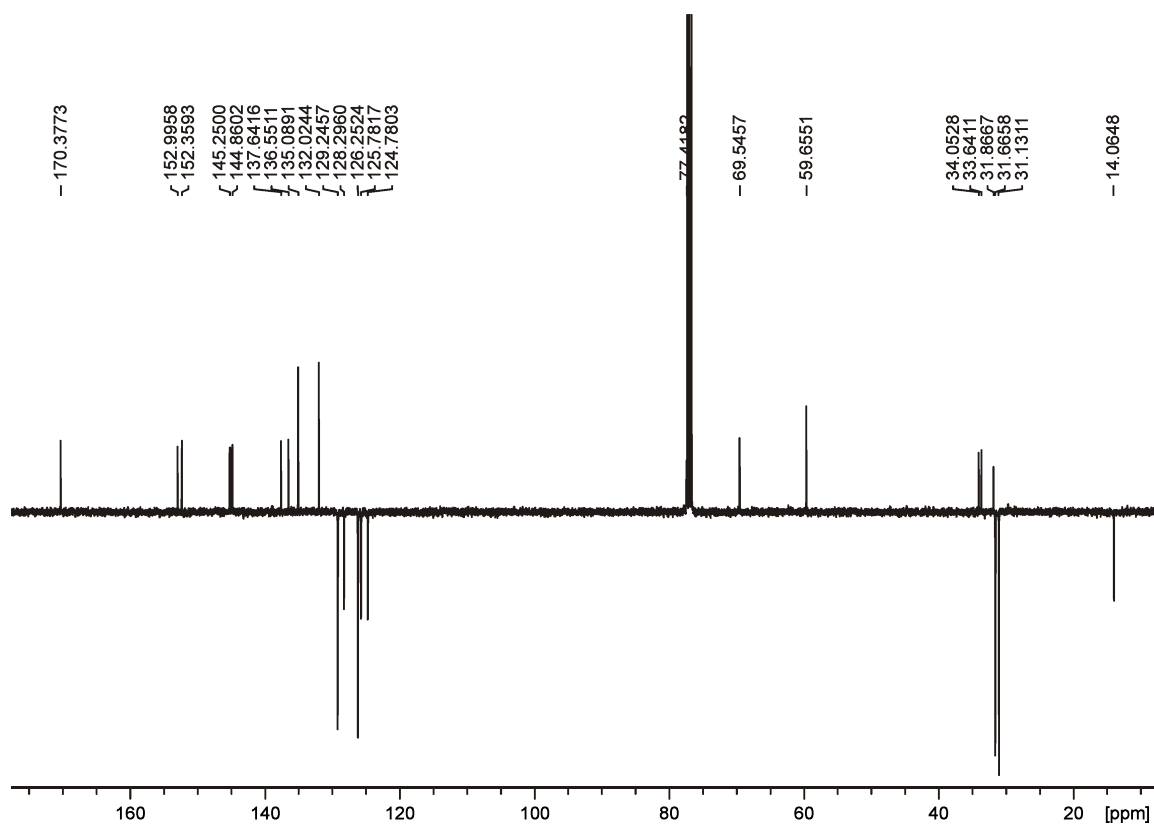


Figure S12. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**14** (100 MHz, CDCl_3).

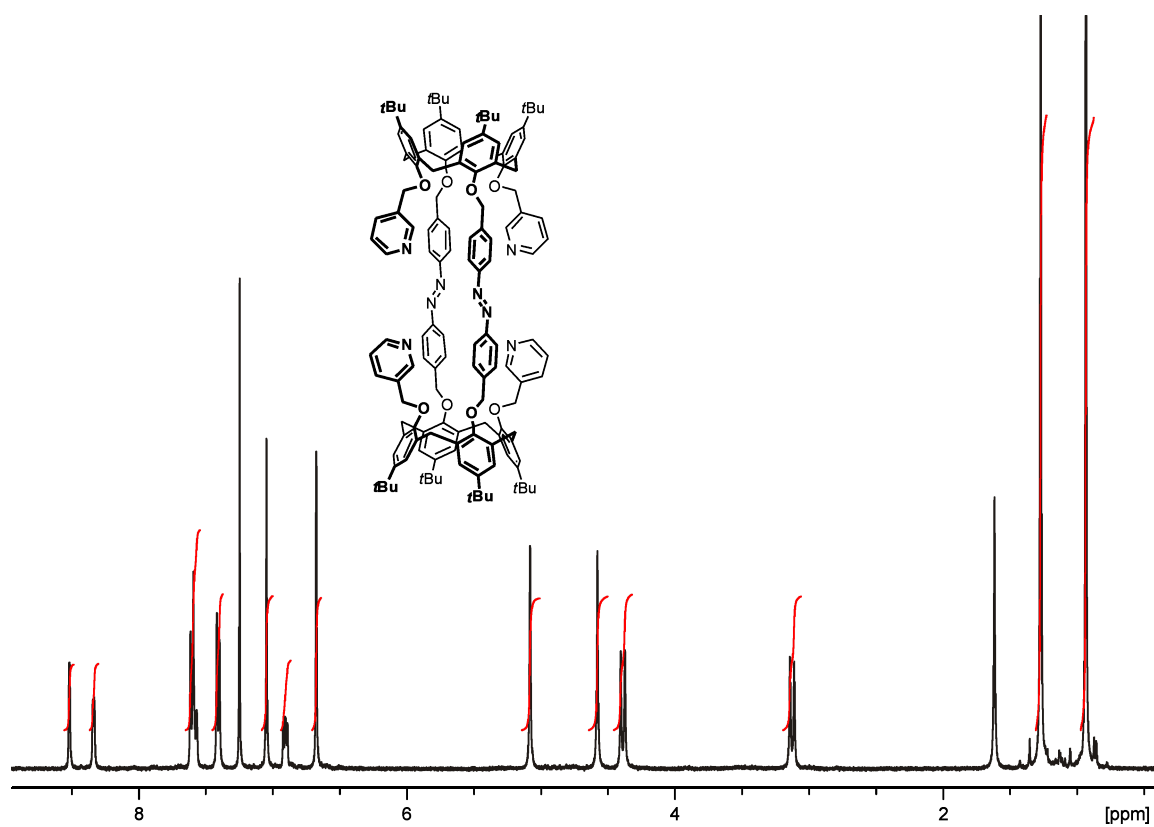


Figure S13. ¹H NMR spectrum of bis(calix[4]arene) (*E,E*)-**15** (400 MHz, CDCl₃).

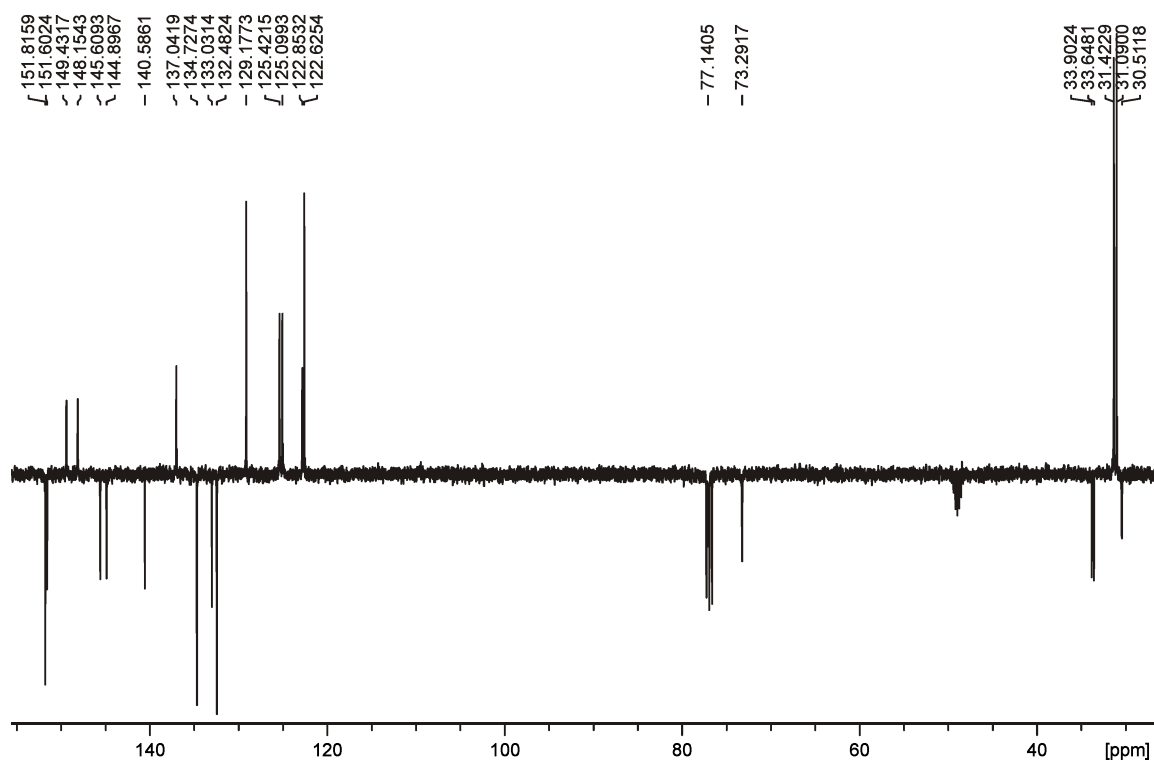


Figure S14. ¹³C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**15** (100 MHz, CDCl₃+CD₃OD).

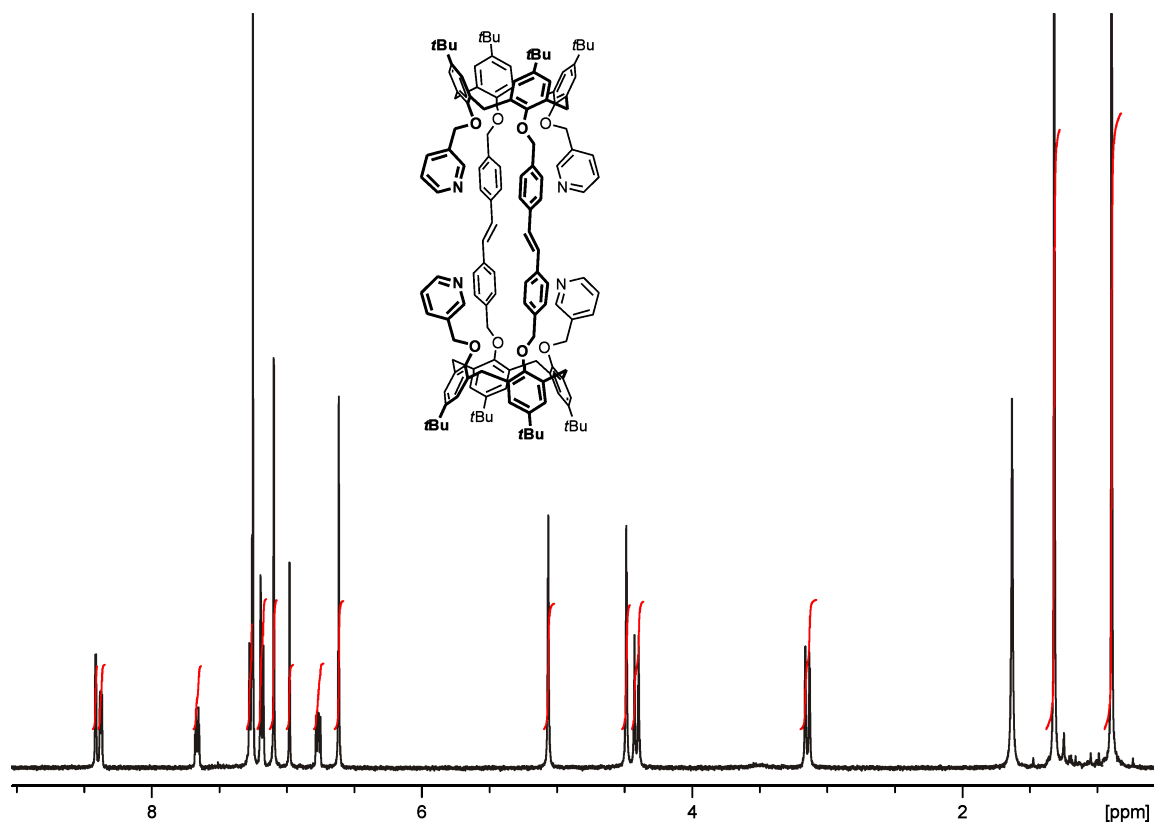


Figure S15. ¹H NMR spectrum of bis(calix[4]arene) (*E,E*)-**16** (400 MHz, CDCl₃).

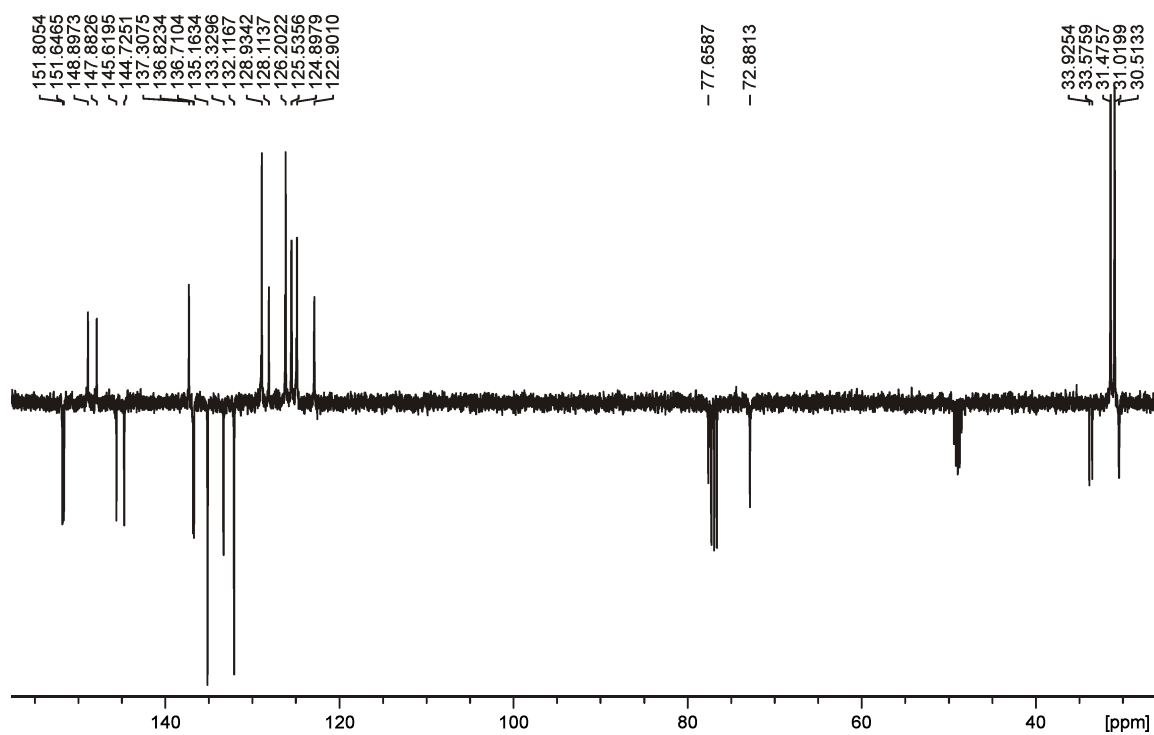


Figure S16. ¹³C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**16** (100 MHz, CDCl₃+CD₃OD).

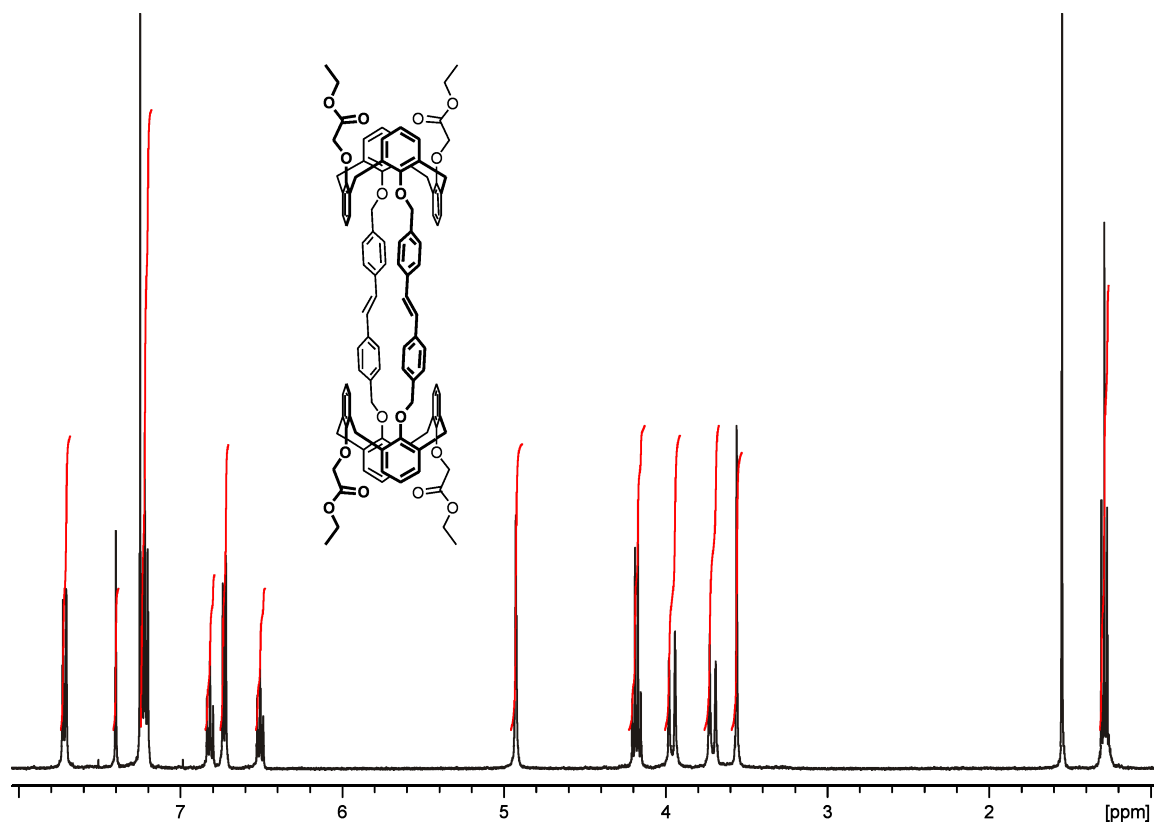


Figure S17. ^1H NMR spectrum of bis(calix[4]arene) (*E,E*)-17 (400 MHz, CDCl₃).

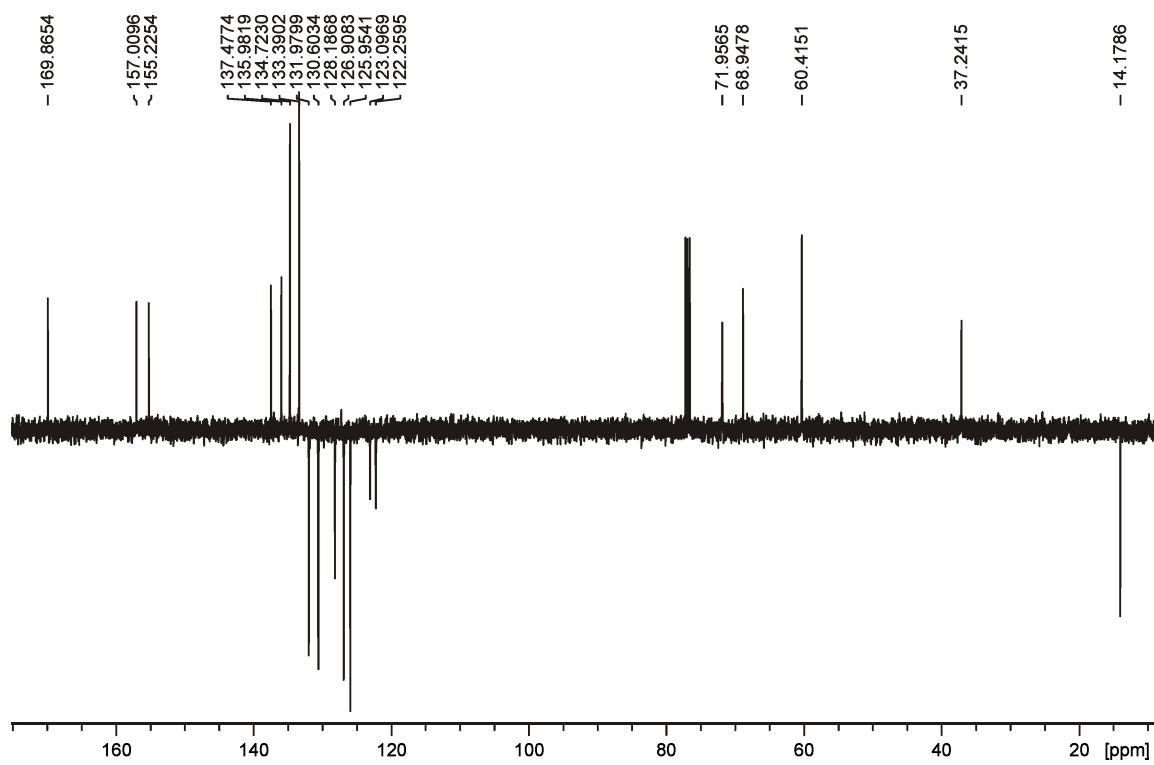


Figure S18. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-17 (100 MHz, CDCl₃).

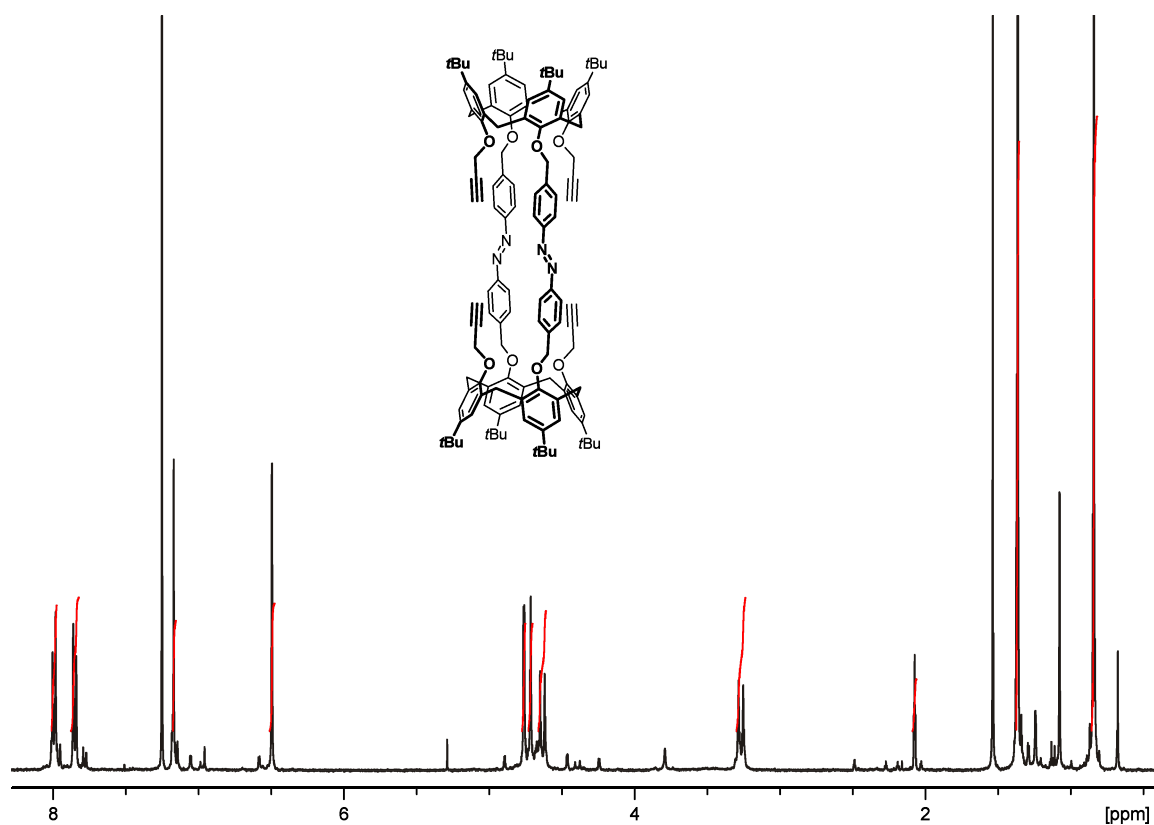


Figure S19. ^1H NMR spectrum of bis(calix[4]arene) (*E,E*)-**18** (400 MHz, CDCl_3 , contains trace signals from bis(calixarene) (*E,E*)-**19**).

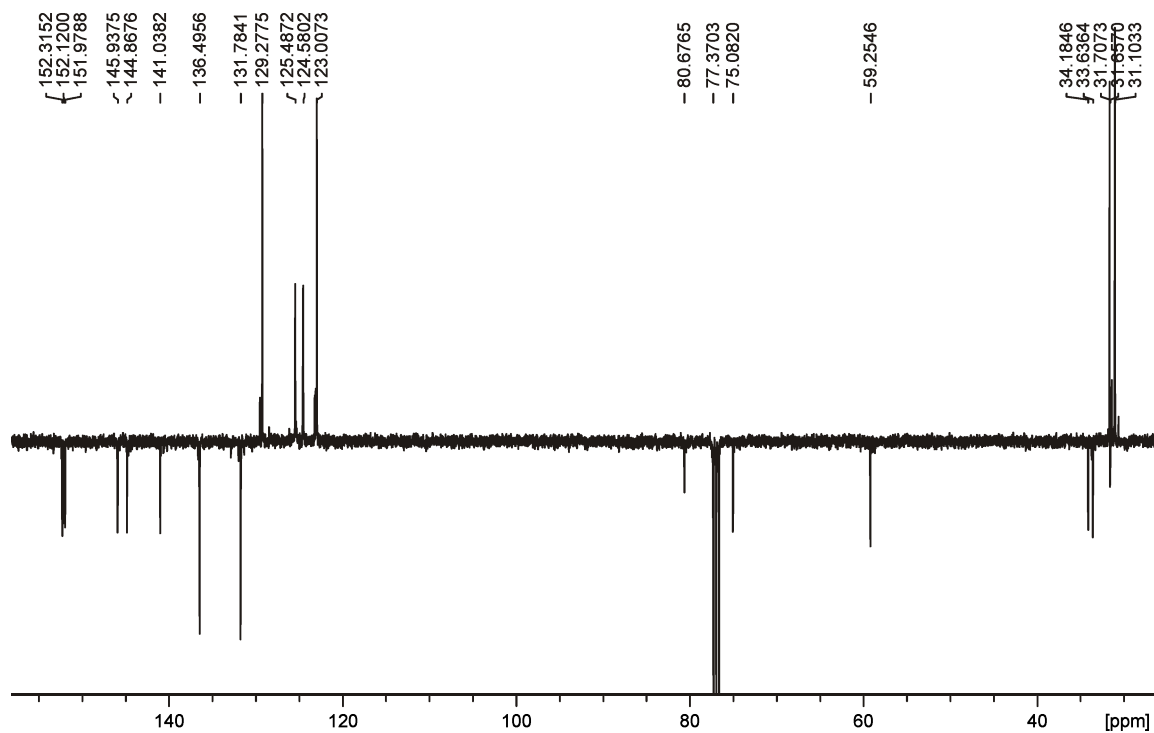


Figure S20. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**18** (100 MHz, CDCl_3 , contains trace signals from bis(calixarene) (*E,E*)-**19**).

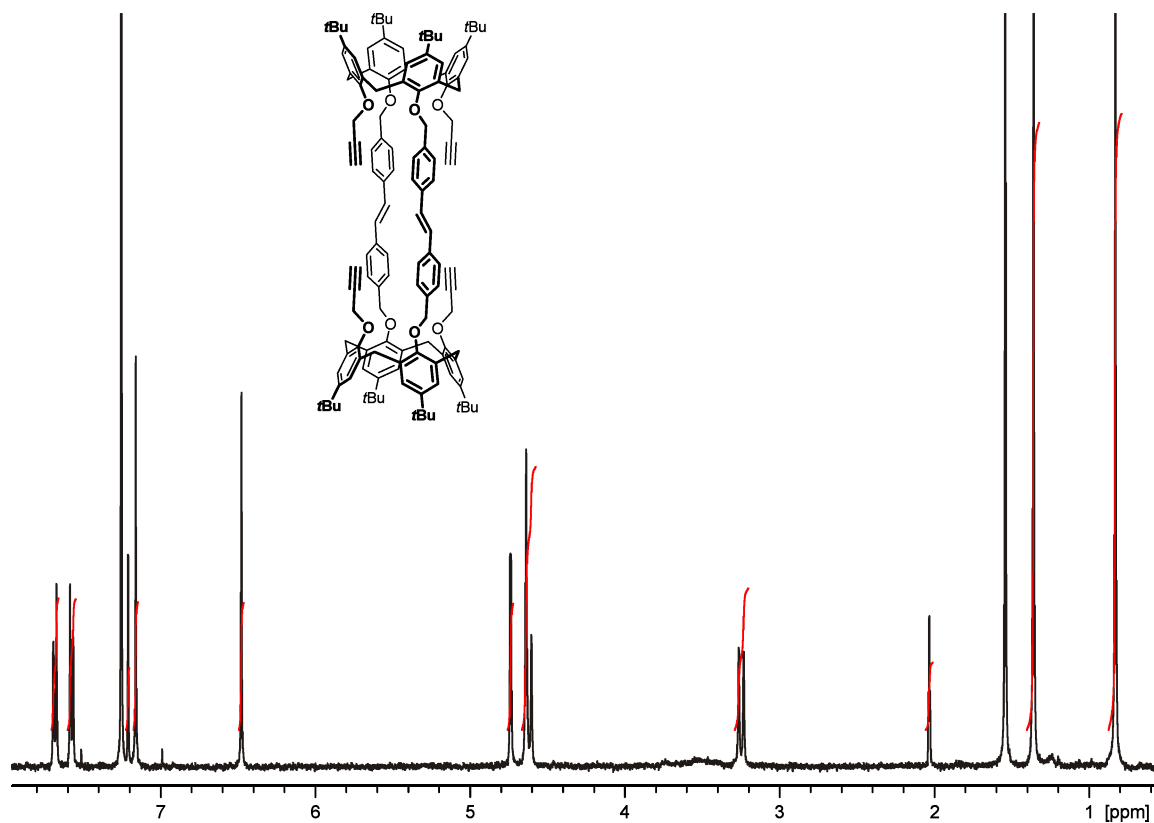


Figure S21. ^1H NMR spectrum of bis(calix[4]arene) (*E,E*)-**20** (400 MHz, CDCl_3).

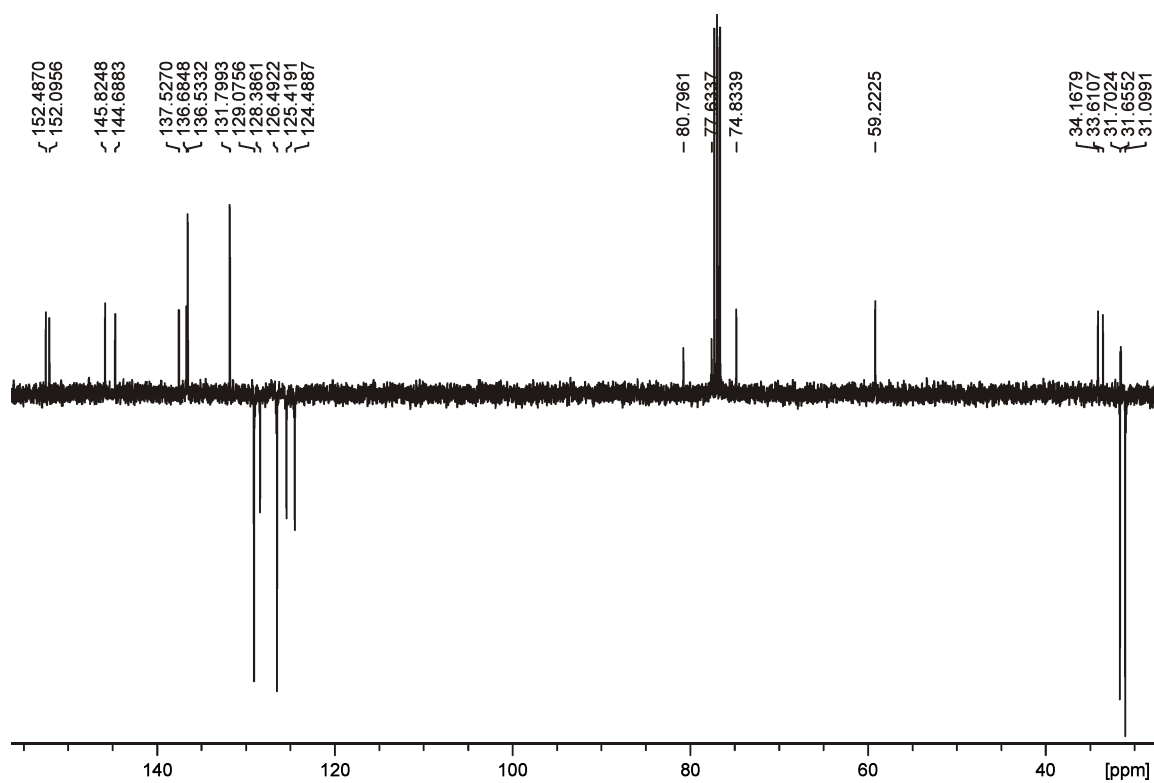


Figure S22. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**20** (100 MHz, CDCl_3).

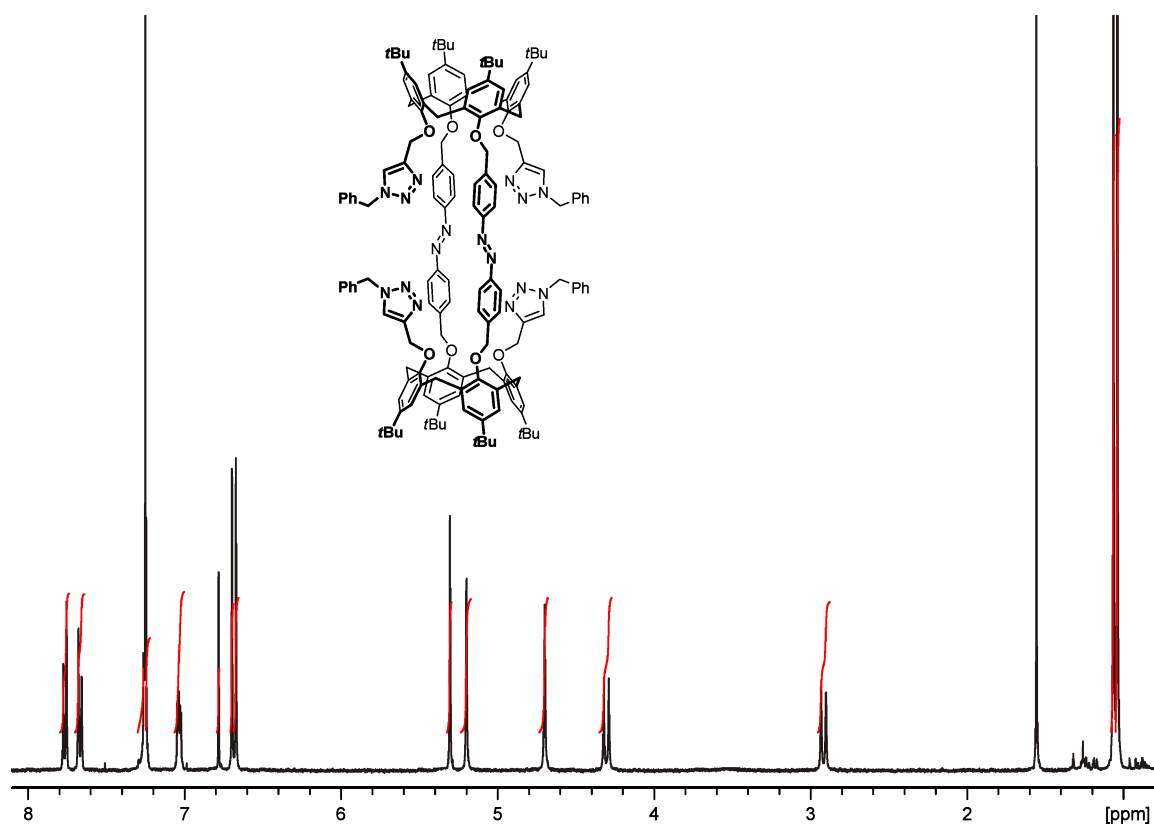


Figure S23. ^1H NMR spectrum of bis(calix[4]arene) (*E,E*)-**22** (400 MHz, CDCl_3).

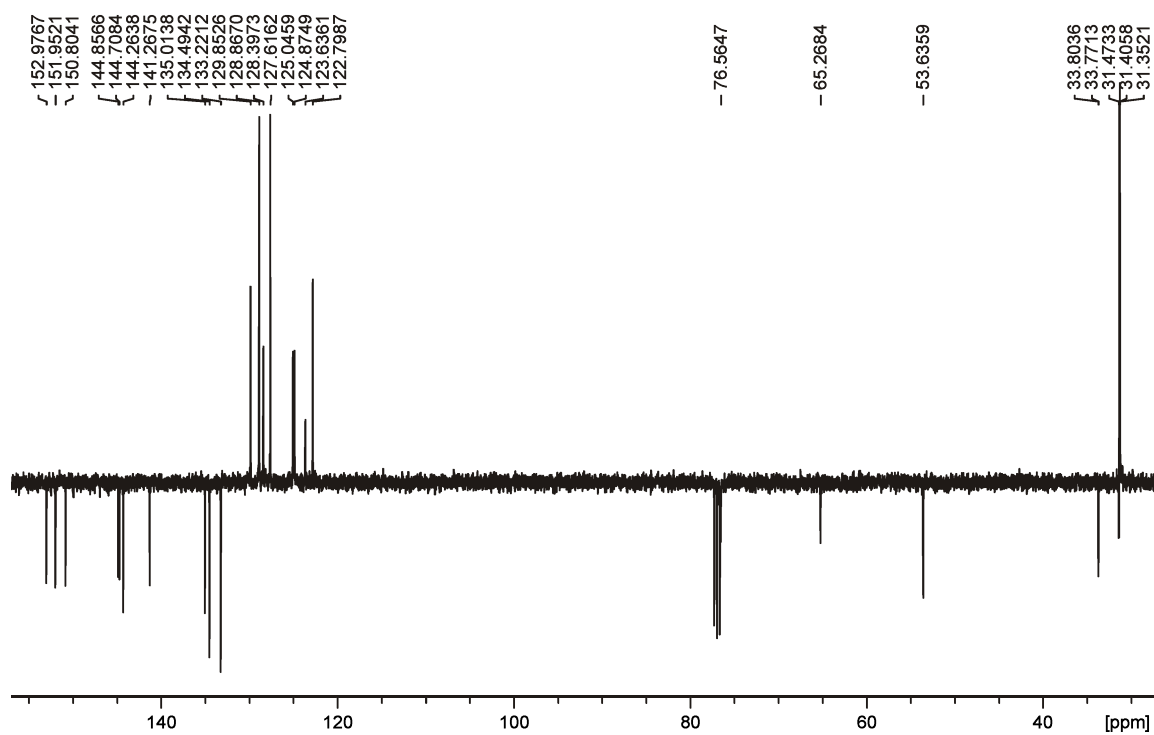


Figure S24. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**22** (100 MHz, CDCl_3).

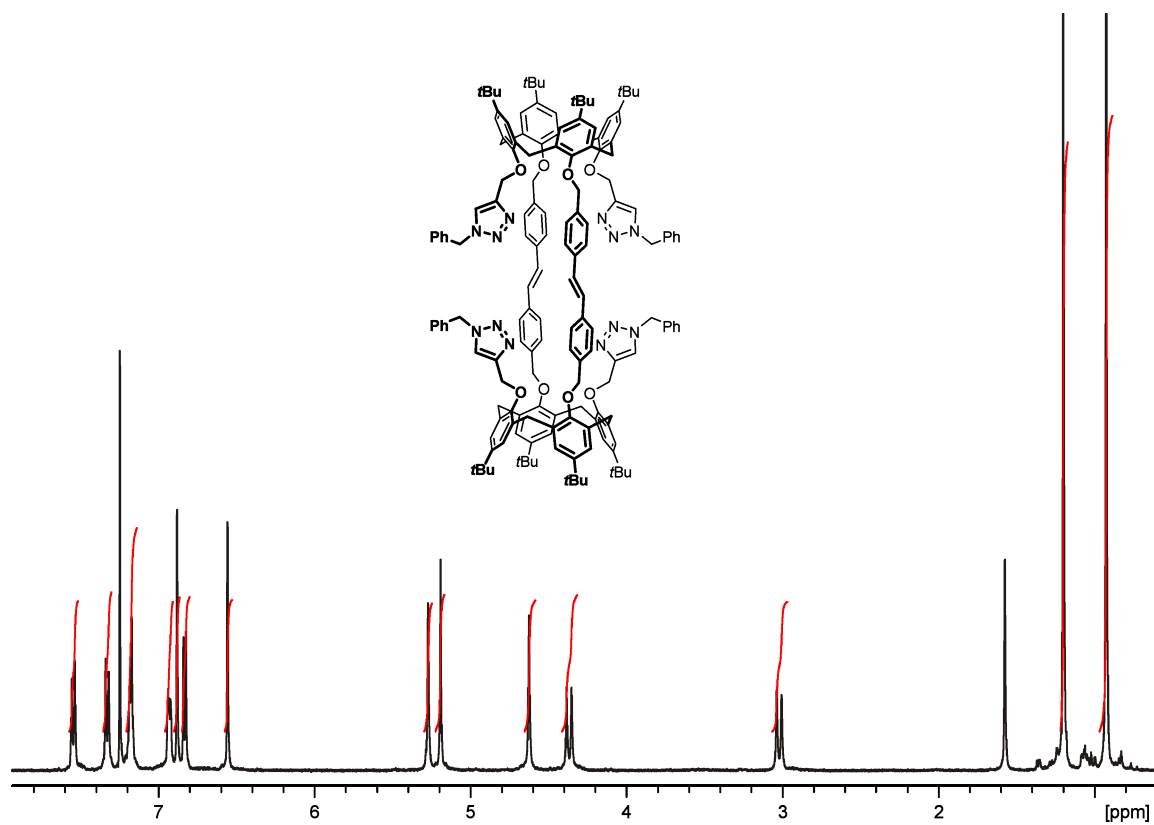


Figure S25. ¹H NMR spectrum of bis(calix[4]arene) (*E,E*)-**23** (400 MHz, CDCl₃).

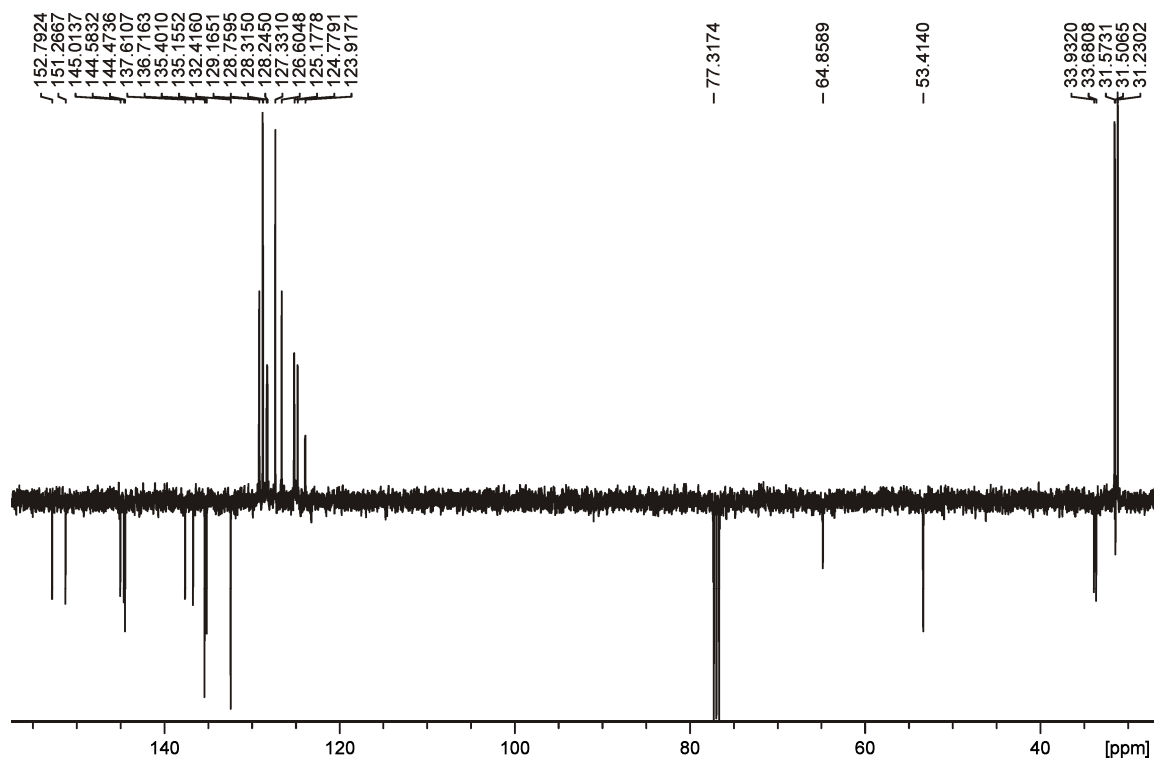


Figure S26. ¹³C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**23** (100 MHz, CDCl₃).

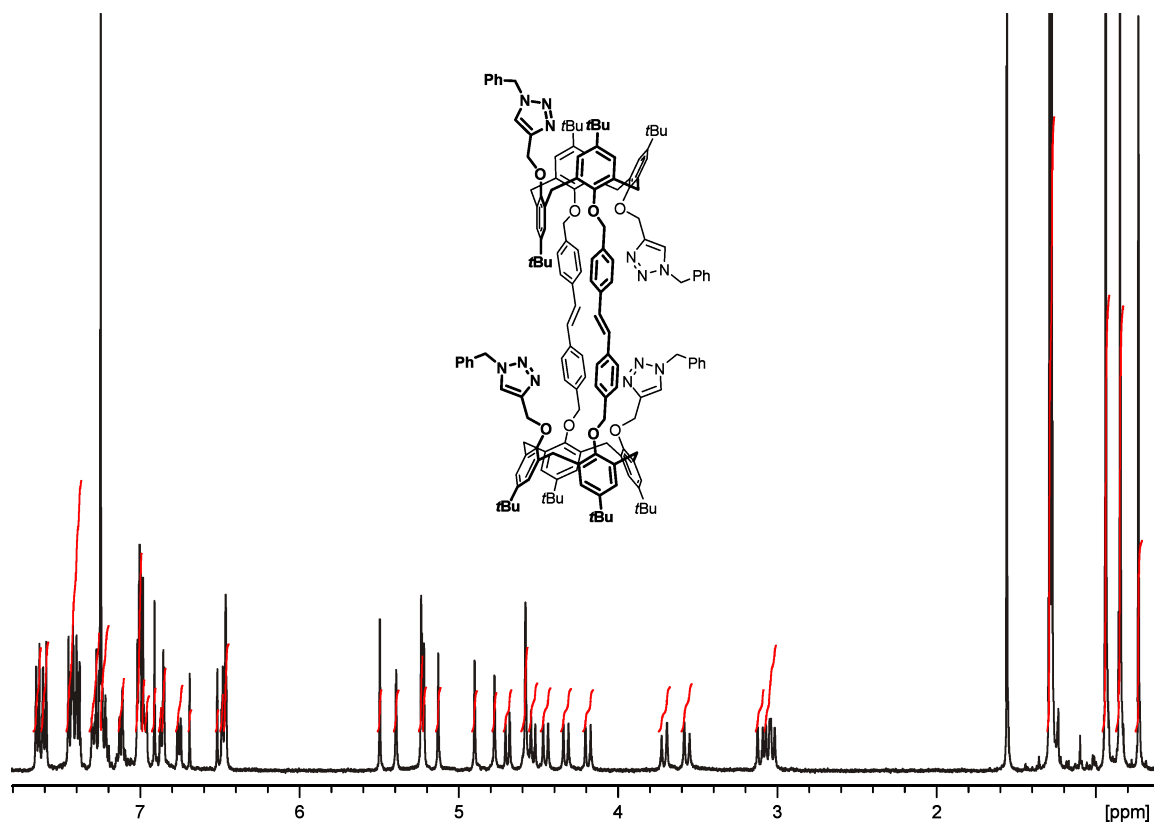


Figure S27. ^1H NMR spectrum of bis(calix[4]arene) (*E,E*)-**24** (400 MHz, CDCl_3).

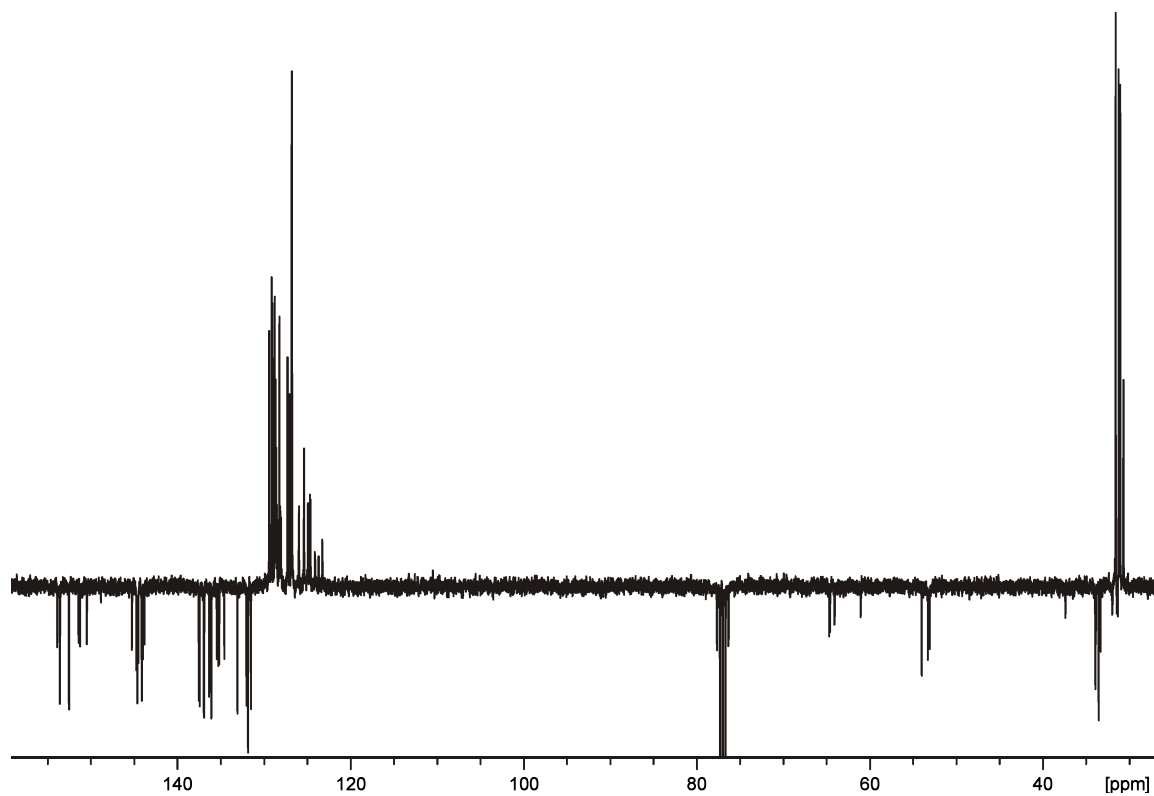


Figure S28. ^{13}C NMR spectrum (APT) of bis(calix[4]arene) (*E,E*)-**24** (100 MHz, CDCl_3).

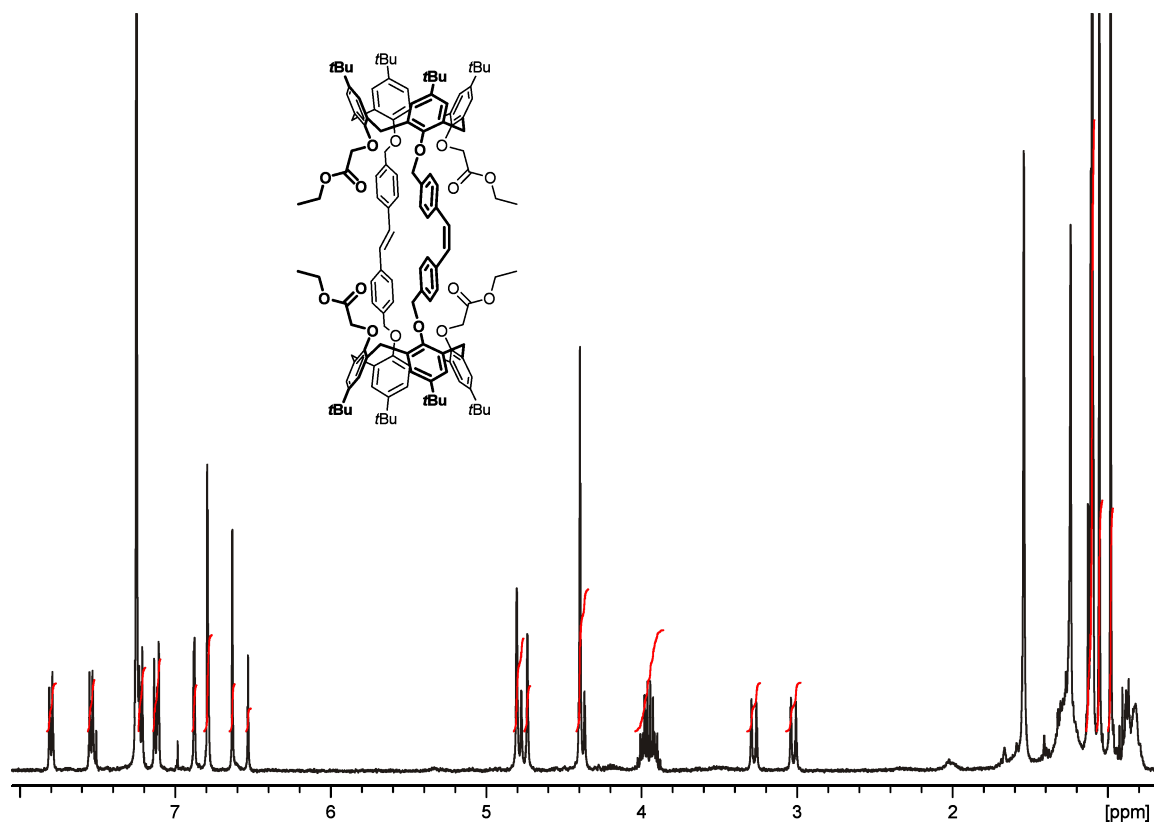


Figure S29. ¹H NMR spectrum of bis(calix[4]arene) (*E,Z*)-**14** (400 MHz, CDCl₃).

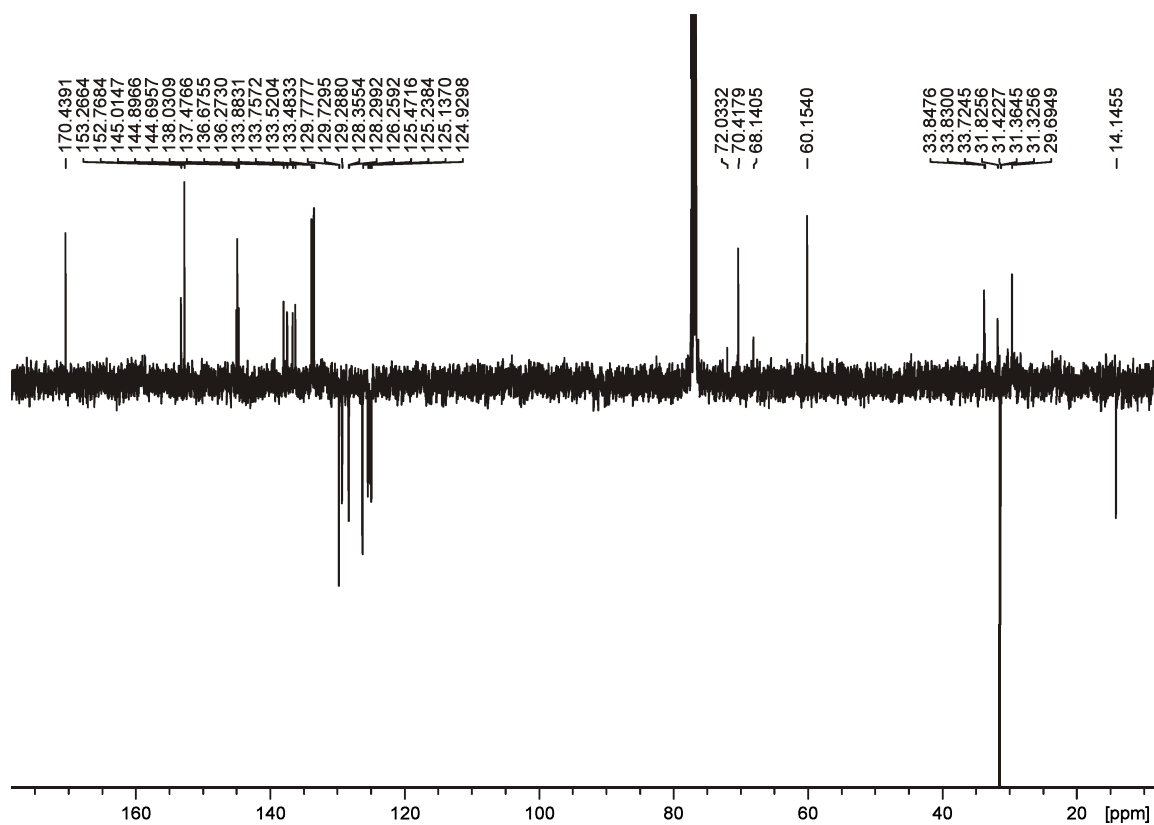


Figure S30. ¹³C NMR spectrum (APT) of bis(calix[4]arene) (*E,Z*)-**14** (100 MHz, CDCl₃).

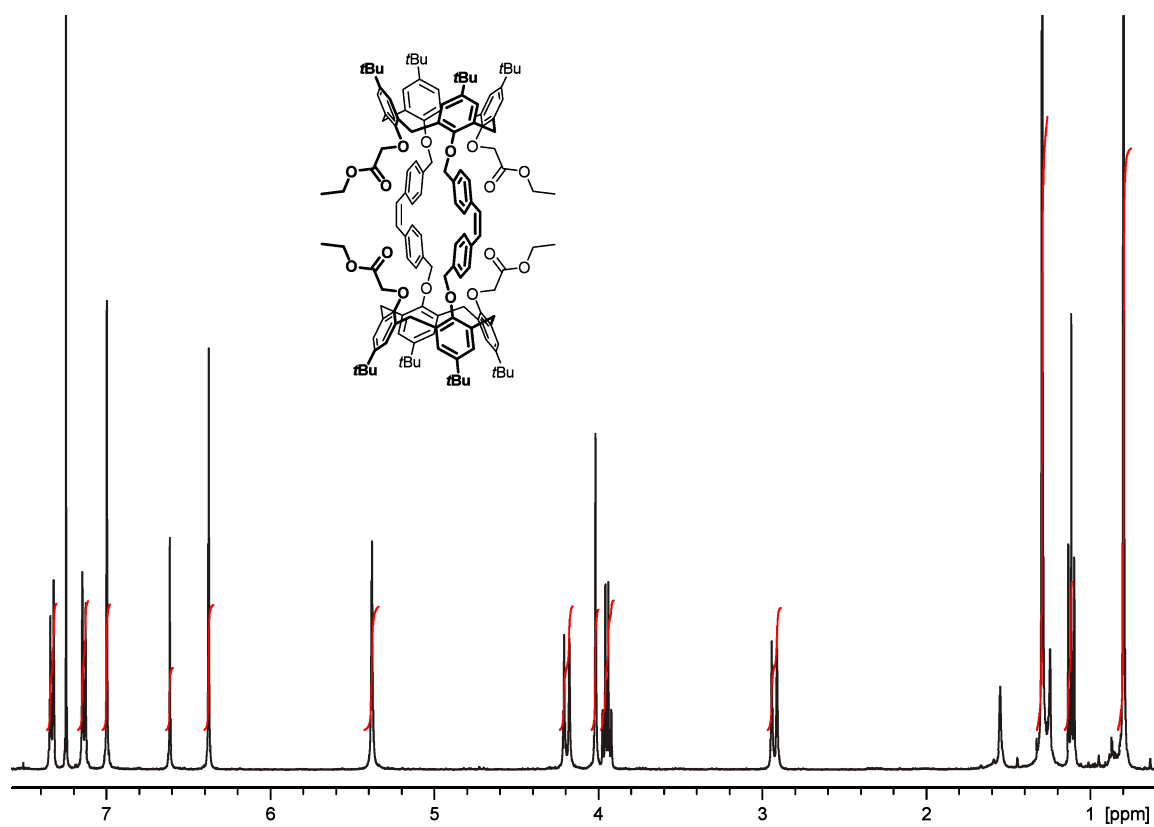


Figure S31. ¹H NMR spectrum of bis(calix[4]arene) (Z,Z)-14 (400 MHz, CDCl₃).

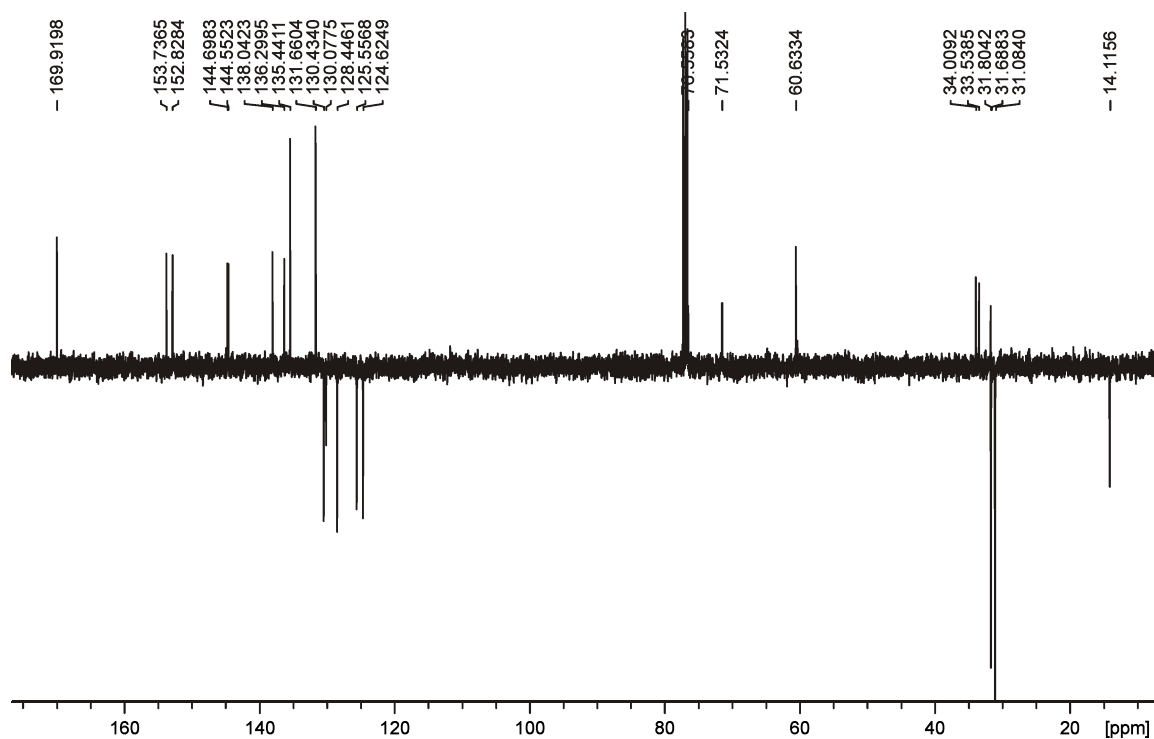


Figure S32. ¹³C NMR spectrum (APT) of bis(calix[4]arene) (Z,Z)-14 (100 MHz, CDCl₃).

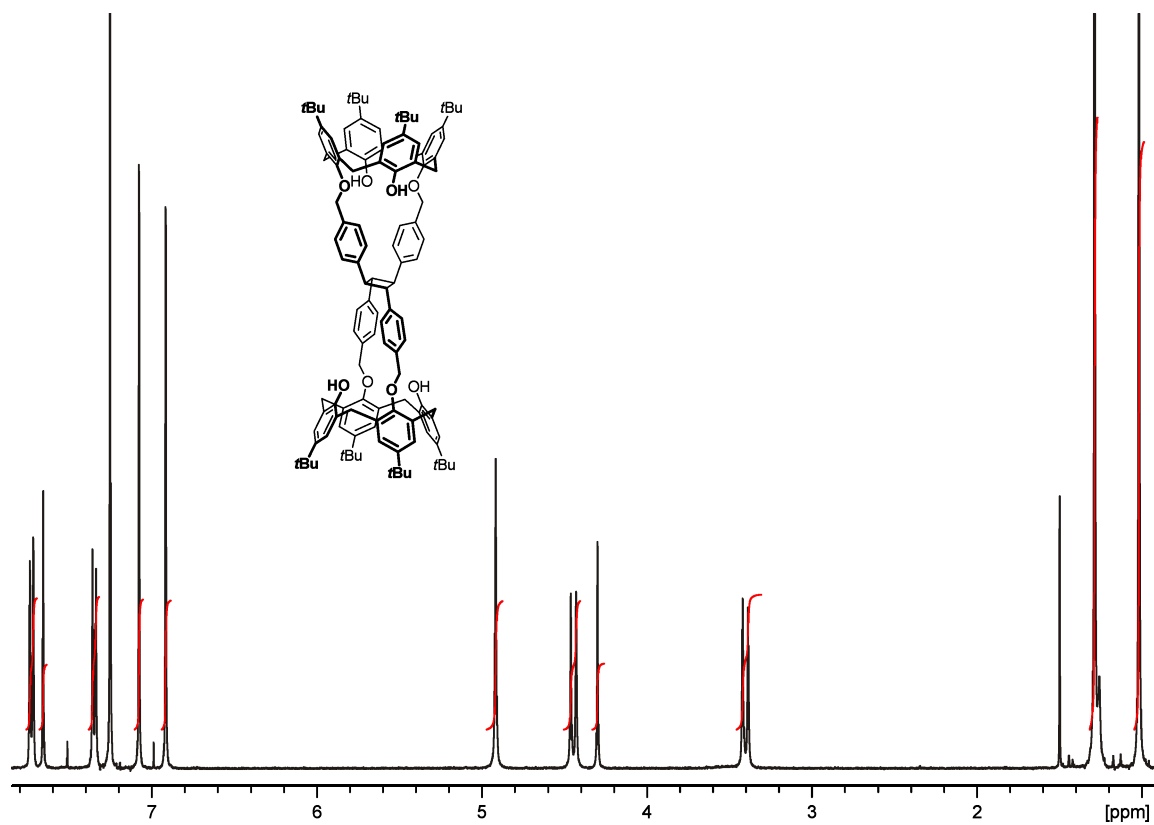


Figure S33. ¹H NMR spectrum of bis(calix[4]arene) **25** (400 MHz, CDCl₃).

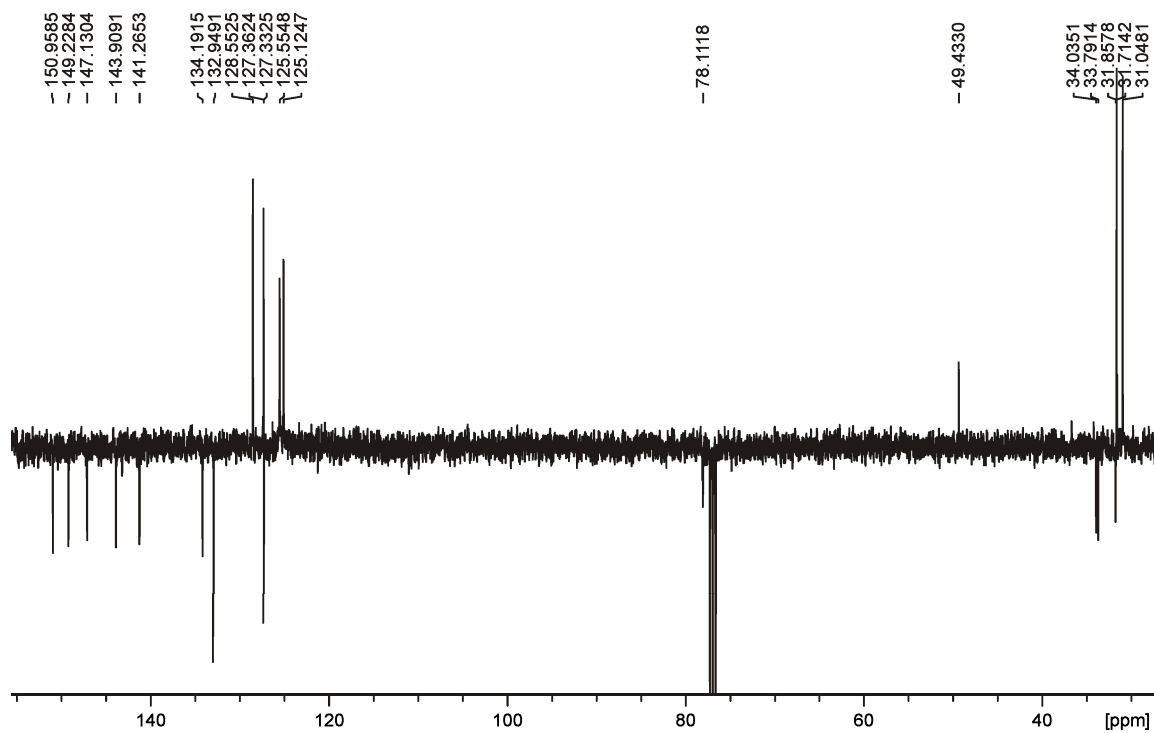


Figure S34. ¹³C NMR spectrum (APT) of bis(calix[4]arene) **25** (100 MHz, CDCl₃).

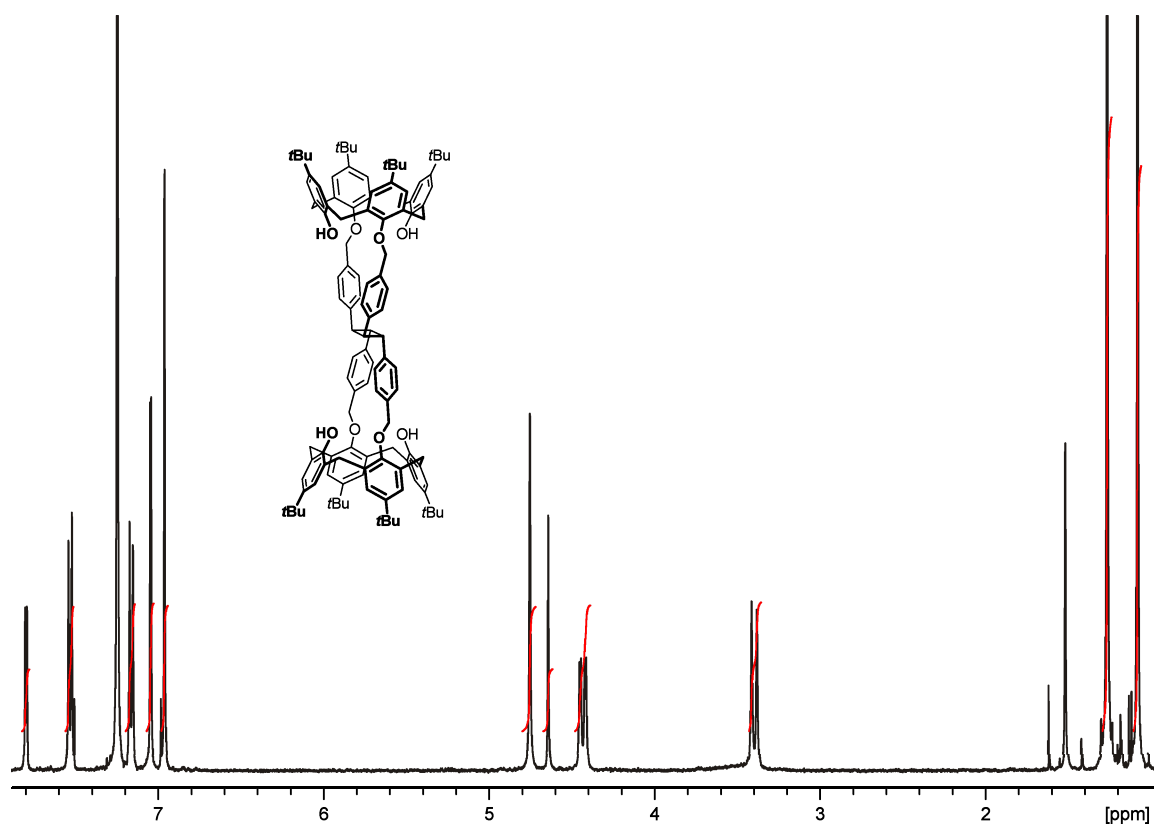


Figure S35. ¹H NMR spectrum of bis(calix[4]arene) **26** (400 MHz, CDCl₃).

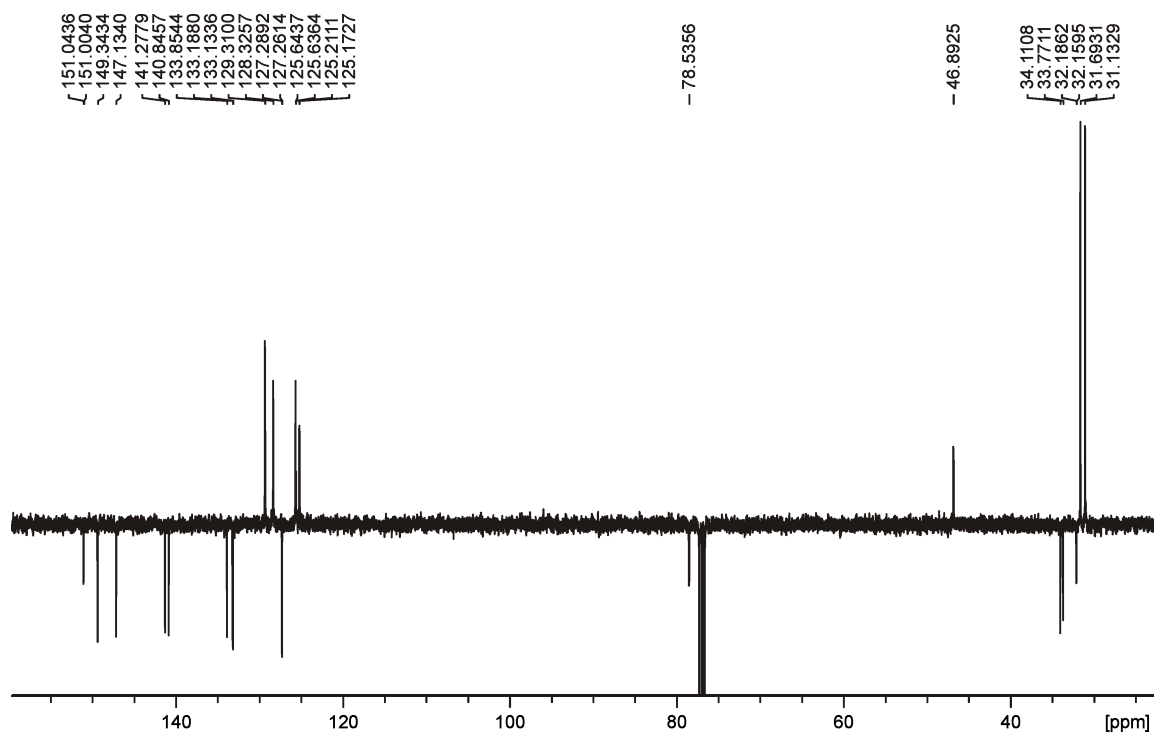


Figure S36. ¹³C NMR spectrum (APT) of bis(calix[4]arene) **26** (100 MHz, CDCl₃).

DOSY spectra of bis(calixarene) tetrakis(esters)

2D DOSY experiments were performed in accordance with the gradient strength $G = 53.5$ G/cm using standard pulse program ledbpgp2s, that is, stimulated echo sequence and LED (longitudinal eddy current delay) using bipolar gradient pulse pair and two spoiling gradients. The gradient strength was changed from 2 to 95% with linear type of ramp. Diffusion time (big delta, $\Delta = 40$ ms), sine shaped gradient pulse length (little delta, $\delta = 2$ ms) and relaxation delay ($D1 = 2$ s) were employed.

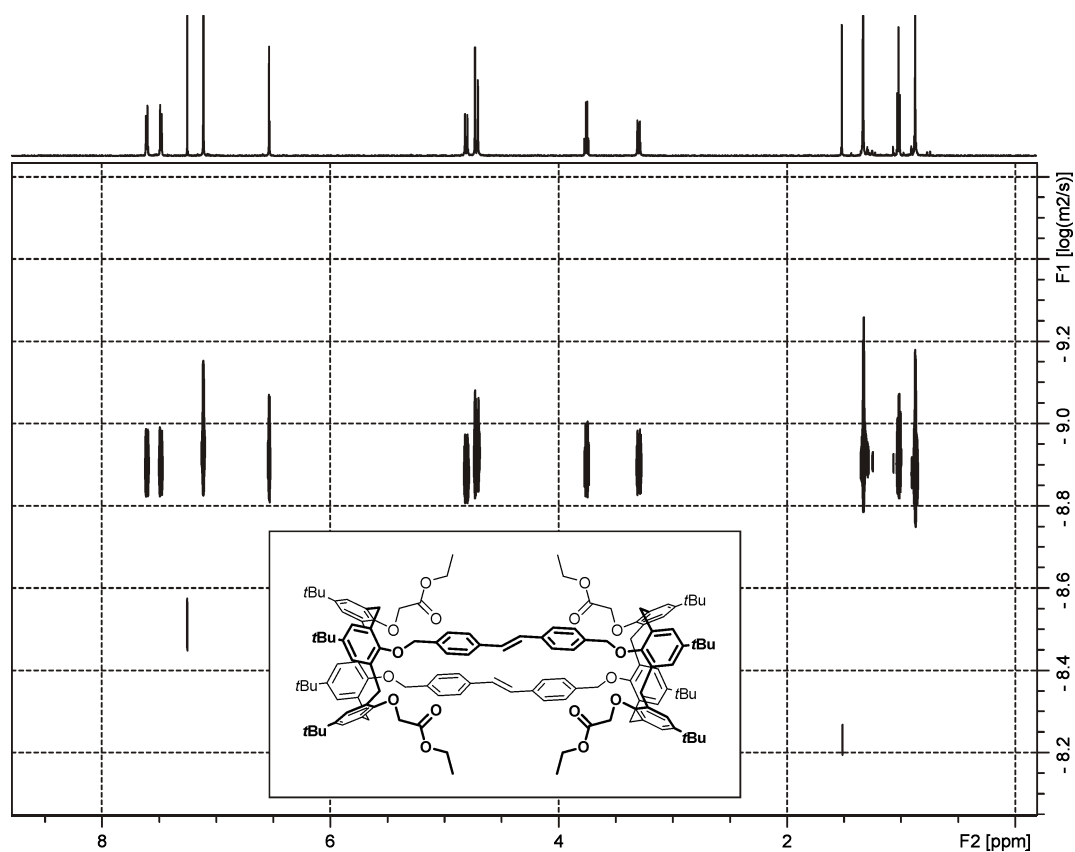


Figure S37. 2D DOSY spectrum of bis(calix[4]arene) (*E,E*)-**14** (600 MHz, CDCl_3 , 30 °C).

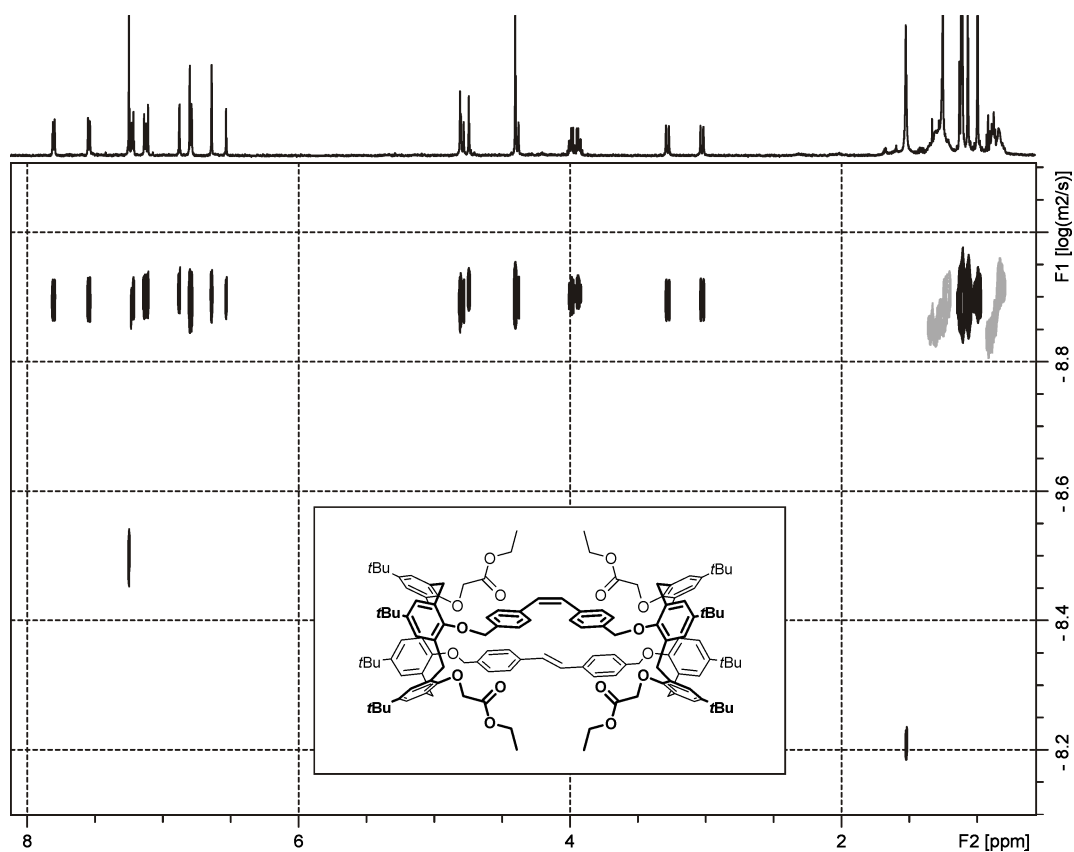


Figure S38. 2D DOSY spectrum of bis(calix[4]arene) (*E,Z*)-**14** (600 MHz, CDCl₃, 30 °C).

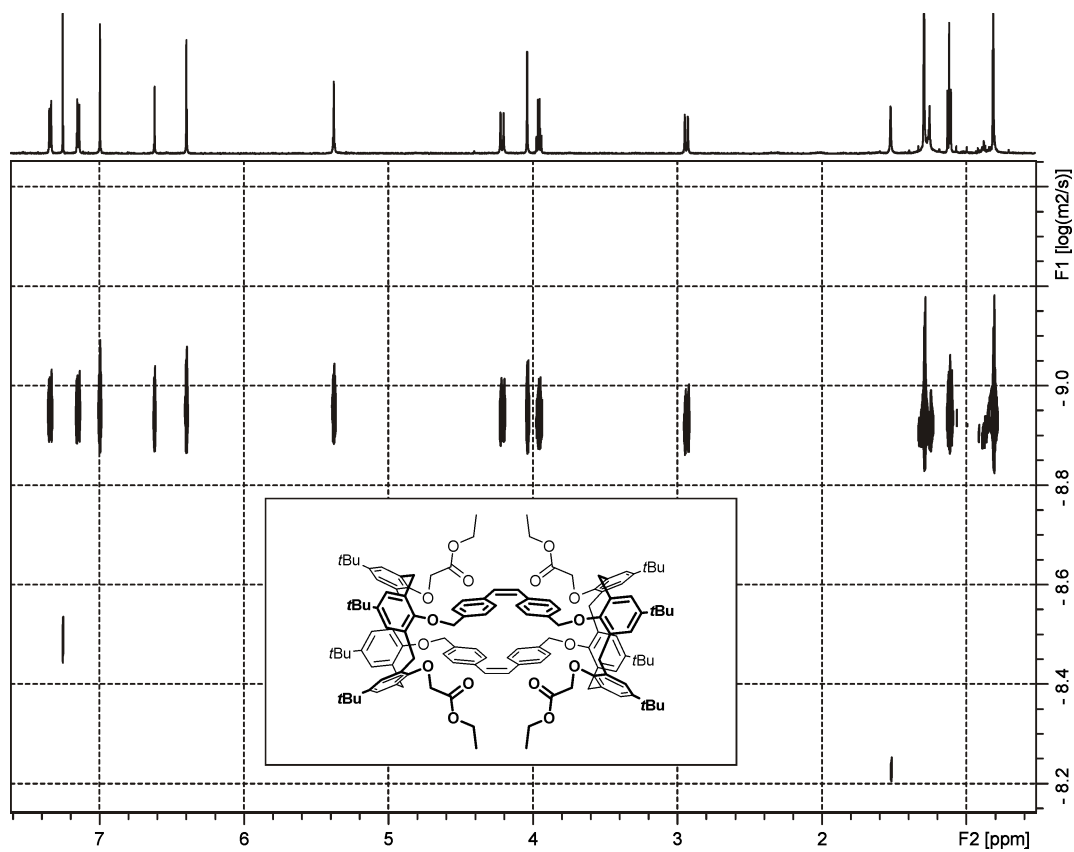


Figure S39. 2D DOSY spectrum of bis(calix[4]arene) (*Z,Z*)-**14** (600 MHz, CDCl₃, 30 °C).

Details of X-ray diffraction measurements

Crystallographic data were collected on a Bruker D8 Venture diffractometer using graphite monochromatized Mo–K α radiation ($\lambda = 0.71073 \text{ \AA}$) using a ω -scan mode. Temperatures above 100 K were used because of destruction of the crystals at lower temperatures. Absorption correction based on measurements of equivalent reflections was applied.^[S8] The structure was solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using Olex2 package.^[S9] For **25**, an attempt to refine the structure in the Cc space group (subgroup of C2/c) with two crystallographically independent cyclobutane molecules was done, but the refinement, although provided slightly smaller R-factor, was unstable because of poor data collected from the only very thin needle. Minor components (occupancy 0.4) of the disordered O–CH₂–COOEt fragment in (*E,E*)-**14** and (*Z,Z*)-**14**, a minor component (occupancy 0.25) of the –CH=CH– unit in (*E,E*)-**11** and minor components (occupancies 0.25–0.5) of four *tert*-butyl groups in **26** were refined isotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model. In all the structures, part or all of highly disordered solvent chloroform, dichloromethane, methanol and/or ether molecules were not located and their contribution was suppressed by the SQUEEZE procedure.^[S10] In all the structures, some *tert*-butyl-groups were disordered over two positions with occupancies in the range from 0.75/0.25 to 0.5/0.5. In (*E,E*)-**14** and (*E,E*)-**11**, probably due to a pedal motion,^[S11] the stilbene moieties were orientationally disordered with occupancies 0.55/0.45, 0.65/0.35 and 0.75/0.25. Crystallographic details are presented in Table S1, S2.

Table S1. Details of the X-ray crystal data collection and structure refinement for compounds (*E,E*)-**11**, (*E,E*)-**13**, (*E,E*)-**14** and (*E,E*)-**22**.

Compound	(<i>E,E</i>)- 11	(<i>E,E</i>)- 13	(<i>E,E</i>)- 14	(<i>E,E</i>)- 22
Formula	C ₁₂₀ H ₁₃₆ O ₈ ·0.16CH ₂ Cl ₂	C ₁₃₂ H ₁₅₆ N ₄ O ₁₆	C ₁₃₆ H ₁₆₀ O ₁₆ · ·CH ₃ CN·0.55CHCl ₃	C ₁₅₆ H ₁₆₈ N ₁₆ O ₈ ·4CH ₃ OH
M _w	1719.87	2054.61	2157.34	2523.24
Temperature (K)	150(2)	100(2)	150(2)	100(2)
Size (mm)	0.20 x 0.13 x 0.02	0.10 x 0.02 x 0.01	0.40 x 0.38 x 0.35	0.22 x 0.16 x 0.04
Cryst. system	monoclinic	triclinic	monoclinic	triclinic
Space group	C2/c	P-1	P2 ₁ /c	P-1
<i>a</i> (Å)	23.5379(9)	11.2996(7)	29.0349(14)	10.8722(6)
<i>b</i> (Å)	27.0914(10)	12.7069(8)	20.9050(9)	12.1396(7)
<i>c</i> (Å)	20.4914(8)	26.6933(16)	27.5569(12)	27.5768(16)
α (°)	90	82.782(2)	90	82.805(2)
β (°)	118.2510(10)	84.101(2)	116.270(2)	83.520(2)
γ (°)	90	69.056(2)	90	77.440(2)
V (Å ³)	11510.4(8)	3544.2(4)	14998.8(12)	3510.8(3)
Z	4	1	4	1
θ range (deg)	1.96 < θ < 25.05	1.40 < θ < 25.05	1.25 < θ < 26.40	1.93 < θ < 26.05
collected/ /unique rflns	113899 / 10168	58552 / 12556	364981 / 30763	57615 / 13851
Completeness to θ (%)	99.8	99.8	99.9	100.0
data/ /restraints/ /params	10168 / 17 / 563	12556 / 77 / 609	30763 / 132 / 1468	13851 / 15 / 863
Goodness of fit on F^2	1.062	1.057	1.041	1.046
Final <i>R</i> indices ($I > 2\sigma(I)$)	R1 = 0.0779 wR2 = 0.2105	R1 = 0.1176 wR2 = 0.3130	R1 = 0.1026 wR2 = 0.3095	R1 = 0.0606 wR2 = 0.1629
Largest diff peak/hole (e/Å ³)	0.94 / -0.98	0.81 / -0.58	1.49 / -1.15	0.67 / -0.62

Table S2. Details of the X-ray crystal data collection and structure refinement for compounds (*E,E*)-**23**, (*Z,Z*)-**14**, **25** and **26**.

Compound	(<i>E,E</i>)- 23	(<i>Z,Z</i>)- 14	25	26
Formula	C ₁₆₀ H ₁₇₂ N ₁₂ O ₈	C ₁₃₆ H ₁₆₀ O ₁₆ · ·C ₄ H ₁₀ O	C ₁₂₀ H ₁₃₆ O ₈	C ₁₂₀ H ₁₃₆ O ₈ ·1.5CH ₃ CN
M _w	2391.09	2124.75	1738.32	1767.56
Temperature (K)	100(2)	120(2)	100(2)	100(2)
Size (mm)	0.30 x 0.18 x 0.10	0.15 x 0.02 x 0.02	0.10 x 0.02 x 0.01	0.12 x 0.02 x 0.01
Cryst. system	monoclinic	monoclinic	monoclinic	triclinic
Space group	P2 ₁ /c	C2/c	C2/c	P-1
<i>a</i> (Å)	29.4689(11)	50.315(9)	59.363(3)	24.1545(11)
<i>b</i> (Å)	24.4754(9)	10.1088(15)	16.5023(10)	24.3029(11)
<i>c</i> (Å)	20.8841(8)	24.881(4)	27.4781(17)	24.3840(11)
α (°)	90	90	90	71.5030(10)
β (°)	93.4950(10)	103.860(4)	102.084(2)	80.835(2)
γ (°)	90	90	90	89.852(2)
V (Å ³)	15034.9(10)	12286(3)	26322(3)	13383.7(11)
Z	4	4	8	4
θ range (deg)	1.80 < θ < 25.05	1.69 < θ < 25.00	1.40 < θ < 25.11	1.41 < θ < 25.11
collected/ /unique rflns	222364 / 26610	43874 / 10667	100401 / 23195	133009 / 47140
Completeness to θ (%)	99.9	98.6	98.8	98.8
data/ /restraints/ /params	26610 / 63 / 1600	10667 / 33 / 712	23195 / 150 / 1064	47140 / 282 / 2072
Goodness of fit on F^2	1.025	1.008	2.496	1.021
Final <i>R</i> indices ($I > 2\sigma(I)$)	R1 = 0.0762 wR2 = 0.2092	R1 = 0.1185 wR2 = 0.3140	R1 = 0.2469 wR2 = 0.6036	R1 = 0.1393 wR2 = 0.4071
Largest diff peak/hole (e/Å ³)	0.60 / -0.44	0.40 / -0.15	1.46 / -1.13	0.76 / -0.67

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