Synthesis of Cavity Extended Cyclotriveratrylenes

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General Remarks: All reactions were carried out under nitrogen; all solvents were freshly distilled under nitrogen and stored over molecular sieves for at least 3 h prior to use. All other reagents were of reagent grade quality as obtained from commercial suppliers and were used without further purification. Column chromatography were performed on silica gel 63-200 mesh. NMR spectra were recorded at 300 K unless otherwise indicated. Mass spectra were determined in the CI mode (CH_4) as appropriate. Melting point are uncorrected.

*General procedure for the synthesis of CTV derivatives **3a-d:*** (±)2,7,12-trihydroxy-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[adg]cyclononene **1** (0.40 g, 0.98 mmol), K_2CO_3 (0.67g, 4.90 mmol) and the appropriate 4-fluorobenzene derivative **2a-d** (5.88 mmol) were dissolved in DMF (30 mL). The resulting heterogeneous mixture was poured into a small glass autoclave and after a few nitrogen-vacuum cycles, was refluxed with stirring overnight. The solvent was then evaporated under vacuum and the residue taken up with a solution of HCl (10%) and dichloromethane. The separated organic phase was washed with water until the aqueous washing were neutral, dried over anhydrous Na_2SO_4, filtered and evaporated to dryness.

(±)2,7,12-Tris-(4-formyl-phenoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (3a): Purification of the solid residue by column chromatography (CH_2Cl_2 : ethyl acetate = 95 : 5) afforded 0.49 g (70%) of **3a** as a white solid: mp 204-206 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.54 and 4.71 (2d, AX system, 6H, J = 14 Hz), 3.55 (s, 9H), 6.79 (s, 3H), 6.84 and 7.67 (2dd, 6H, J_1 = 9 Hz, J_2 =2 Hz), 7.00 (s, 3H), 9.72 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 36.3, 56.0, 114.5, 115.4, 115.7, 116.2, 123.5, 131.7, 132.0, 132.6, 132.7, 150.2, 190.7. MS-CI(+) *m/z*: 721 [MH^+]; Anal. Calcd. for $C_{45}H_{36}O_9$: C, 74.99; H, 5.03; Found: C, 75.10; H, 5.20.

(±)2,7,12-Tris-(4-acetyl-phenoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (3b): Purification of the solid residue by column chromatography (*n*-hexane : CH_2Cl_2 : ethyl acetate = 15 : 60 : 25) afforded 0.41 g (55%) of **3b** as a white solid: mp: 294-296 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.55 (s, 9H), 3.63 and 4.81 (2d, 6H, AX system, J = 14 Hz), 3.69 (s, 9H), 6.86 (s, 3H), 6.92 and 7.89 (2dd, 6H, J_1 =9, J_2 =2 Hz), 7.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 25 MHz) δ: 26.6, 36.7, 56.4, 115.0, 116.3, 122.5, 130.7, 131.9, 132.3, 137.3, 142.5, 150.7, 162.6, 196.8. MS-CI(+) *m/z*: 763 [MH^+]. Anal. Calcd. for $C_{48}H_{42}O_9$: C, 75.58; H, 5.55; Found: C, 75.70; H, 5.62.

(±)2,7,12-Tris-(4-cyanophenoxy)-3,8,13-tri-methoxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (3c): Trituration of the solid residue with hot methanol gave 0.5 g (70%) of **3c** as a white solid: mp 227-230 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.65 and 4.82 (2d, 6H, AX system, J = 14 Hz), 3.69 (s, 9H), 6.88 (s, 3H), 6.91 (d, 6H, J = 7 Hz), 7.08 (s, 3H), 7.55 (d, 6H, J = 7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 36.3, 56.0, 105.3, 114.5, 116.5, 118.8, 123.6, 132.0, 133.8, 137.5, 141.3, 150.3, 161.7. MS-CI(+) m/z: 712 [MH^+]; Anal. Calcd. for $C_{45}H_{33}N_3O_6$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.90; H, 4.80; N, 5.90.

(±)2,7,12-Tris-(4-nitrophenoxy)-3,8,13-tri-methoxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (3d): Trituration of the solid residue with hot methanol/water mixture gave 0.53 g (70%) of **3d** as a yellow solid: mp 256-257 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.67 and 4.84 (2d, 6H, AX system, J =14 Hz), 3.69 (s, 9H), 6.90 (s, 3H), 6.92 and 8.16 (2dd, 6H, J_1 = 9 Hz, J_2 = 2 Hz), 7.12 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): 29.6, 36.4, 56.0, 114.5, 115.8, 123.6, 125.7, 132.0, 137.7, 141.3, 142.4, 163.3. MS-CI(+) *m/z*: 772 [MH^+]; Anal. Calcd. for $C_{42}H_{33}N_3O_{12}$: C, 65.37; H, 4.31; N, 5.44. Found: C, 64.47; H, 4.09; N, 5.18 (+1 H_2O).

(±)2,7,12-Tris-(4-hydroxymethyl-phenoxy)-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[adg]cyclononene (4): Compound **3a** (1.00 g, 1.40 mmol) and $NaBH_4$ (0.20 g, 14.00 mmol) were dissolved in ethanol (50 mL) and the resulting mixture was stirred at room temperature for 24 h. Solvent was then evaporated under vacuum and the solid residue was taken up with an aqueous solution of HCl (10%) and CH_2Cl_2. The separated organic phase was washed with water until the aqueous washings were neutral, dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. Purification of the residue by column chromatography (CH_2Cl_2 : MeOH = 9 : 1) afforded 0.71 g (70%) of **4** as a yellowish solid: mp 250-252 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.45 and 4.68 (2d, 6H, AX system, *J* =14 Hz), 3.67 (s, 9H), 4.53 (s, 6H), 6.70 (s, 3H), 6.87 and 7.22 (2d, 6H, *J* = 9 Hz), 6.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz):36.3, 56.0, 64.8, 114.1, 116.3, 117.5, 128.5, 131.8, 135.7, 143.9, 149.8, 155.3; MS-CI(+) *m/z*: 727 [MH^+]. Anal. Calcd. for $C_{45}H_{42}O_9$: C, 74.36; H, 5.8; Found: C, 74.4; H, 5.9.

(±)2,7,12-Tris-(4-hydroxy-phenoxy)-3,8,13-tri-methoxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (5): A solution of *m*-chloroperbenzoic acid (2.00 g, 11.40 mmol) and compound **3a** (1.00 g, 1.40 mmol) in 1,2-dichloroethane (50 mL) was stirred at room temperature for 24 hours, then the solvent was completely evaporated under vacuum. The solid residue was then suspended in methanol (100 mL) and an aqueous solution of HCl (37%, 20 mL) was added. The resulting solution was stirred for further 16 hours, then ethyl acetate (30 mL) was added. The organic layer was separated, washed with water until the aqueous washings were neutral and concentrated under vacuum. The desired product **5** was then obtained by precipitation from methanol as a white solid (0.67g, 70%): mp 243-245 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.44 and 4.65 (2d, 6H, AX system, *J*=14 Hz), 3.70 (s, 9H), 6.69-6.84 (m, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 35.8, 55.5, 113.4, 115.7, 118.6, 120.2, 131.6, 133.9, 145.8, 148.3, 149.2, 152.8. MS-CI(+) *m/z*: 685 [MH^+]. Anal. Calcd. for $C_{42}H_{36}O_9$: C, 73.67; H, 5.30; Found: C, 73.82; H, 5.85.

(±)2,7,12-Tris-(4-aminomethyl-phenoxy)-3,8,13-tri-methoxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (6): To a solution of compound **3c** (0.50 g, 0.70 mmol) in dry THF (50 mL), a 1M solution of B_2H_6 in THF (2.6 mL, 26.0 mmol) was added. The resulting mixture was refluxed overnight, cooled to room temperature, quenched with small portions of water (CAUTION!) and finally extracted with CH_2Cl_2 (50 mL). The separated organic layer was then washed with brine until the aqueous washings were neutral, dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. Purification of the solid residue by column chromatography (*n*-hexane : ethyl acetate : CH_2Cl_2 = 2 : 2 : 6) afford 0.25 g (50%) of **6** as a pale pink solid: mp 295-297 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.53 and 4.74 (2d, 6H, AX system, *J* = 14 Hz), 3.69 (s, 9H), 4.63 (s, 6H), 6.75 (s, 3H), 6.92 (d, 6H, *J* = 9 Hz), 6.94 (s, 3H), 7.27 (d, 6H, *J* = 9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 34.8, 50.9, 55.8, 114.8, 116.0, 122.4, 128.3, 129.4, 132.3, 136.6, 142.5, 149.5, 156.3. MS-CI(+) *m/z*: 724 [MH^+]. Anal. Calcd. for $C_{45}H_{45}N_3O_6$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.80; H, 6.40; N, 5.80.

(±)2,7,12-Tris-(4-amino-phenoxy)-3,8,13-tri-methoxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (9): Compound **3d** (0.70 g, 0.90 mmol), a catalytic amount of palladium on activated charcoal and hydrazine mono hydrate (0.18g, 3.6mmol) were dissolved in 40 mL of ethanol. The resulting mixture was refluxed with stirring overnight, then Pd catalyst was filtered off over a sintered septum under nitrogen atmosphere. The filtrate was concentrated under vacuum and the resulting oily residue was dissolved in CH_2Cl_2 and washed with water to eliminate hydrazine residues. Pure product **9** was obtained as a white solid (0.6 g, 90%) by precipitation from a CH_2Cl_2/*n*-hexane (1:9) solvent mixture: mp 284-287 °C. ^{1}H NMR (CD_3OD, 300 MHz) δ: 3.33 and 4.55 (2d, 6H, AX system, *J* = 14 Hz), 3.41 (bs, 6H), 3.62 (s, 9H), 6.53 (s, 3H), 6.58 (d, 6H, *J* = 9 Hz), 6.63 (s, 3H), 6.73 (d, 6H, *J* = 9 Hz). ^{13}C NMR (CD_3OD, 75 MHz) δ: 36.1, 55.8, 113.6, 116.0, 118.8, 118.9, 120.4, 131.6, 133.9, 134.0, 142.3, 146.0. MS-CI(+) *m/z*: 682 [MH^+]. Anal. Calcd. for $C_{42}H_{39}N_3O_6$: C, 73.99; H, 5.76; N, 6.16. Found: C, 73.84; H, 5.91; N, 6.27.

*General procedure for the synthesis of N-acetilamino derivatives **7** and **10**:* To a solution of the amino derivative **6** or **9** (0.3 mmol) in CH_2Cl_2 (100 mL), triethyl amine (0.17 g, 0.9 mmol) and acetic anhydride (excess) were added. The resulting mixture was stirred overnight, then the solvent was completely evaporated under vacuum.

(±)2,7,12-Tris-(4-acetylaminomethyl-phenoxy)-3,8,13-tri-methoxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (7): The analytically pure **7** (0.18 g, 70%) was obtained by precipitation from methanol as a pink solid: mp >300 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.97 (s, 9H), 3.53 and 4.73 (2d, 6H, AX system, *J* = 14 Hz), 3.67 (s, 9H), 4.33-4.37 (m, 6H), 5.92 (bs, 3H), 6.76 (s, 3H), 6.85 and 7.15 (2d, 6H, *J* = 9 Hz), 6.94 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 33.4, 36.3, 44.2, 56.5, 113.6, 118.8, 111.4, 126.7, 127.8, 134.1, 142.5, 141.4, 161.2, 174.5. MS-CI(+) *m/z*: 850 [MH^+]. Anal. Calcd. for $C_{51}H_{51}N_3O_9$: C, 72.07; N, 4.94; H, 6.05; Found: C, 72.38; N, 5.04, H, 6.13.

(±)2,7,12-Tris-(4-acetylamino-phenoxy)-3,8,13-tri-methoxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (10): The analytically pure **10** (0.17 g, 70%) was obtained by precipitation from methanol as yellow-pink solid: mp > 300 °C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 2.01 (s, 9H), 3.55 and 4.73 (2d, 6H, AX system, *J* = 14 Hz), 3.69 (s, 9H), 6.01 (bs, 3H), 6.72 (s, 3H), 6.81 (d, 6H, *J* = 9 Hz), 6.95 (s, 3H), 7.10 (d, 6H, *J* = 9 Hz). ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 32.4, 36.2, 55.5, 113.6, 118.8, 121.4, 126.7, 127.8, 133.9, 142.5, 146.4, 168.2. MS-CI(+) *m/z*: 808 [MH^+]. Anal. Calcd. for $C_{48}H_{45}N_3O_9$: C, 71.36; N, 5.20; H, 5.61; Found: C, 71.50; N, 5.30, H, 5.84.

*General procedure for the synthesis of CTV derivatives **8c-d:*** To a solution of compound **3c** or **3d** (0.35 mmol) in toluene (50 mL) maintained under argon atmosphere, BBr_3 (0.4 g, 1.57 mmol) was added (CAUTION!). The resulting mixture was stirred at 90°C for 12 h, then cooled with an external ice bath

and quenched by dropwise adding of water (50 mL, CAUTION!). The organic phase was separated, the remaining water phase was first diluted with a aqueous solution of Na_2CO_3 (5%) and then extracted with dichloromethane (2 x 100 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness under vacuum.

(±)3,8,13-Tris-(4-cyanophenoxy)-2,7,12-trihydroxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (8c): Purification of the residue by chromatography (*n*-hexane : CH_2Cl_2 : ethyl acetate = 1 : 7 : 2) afforded 0.14 g (60%) of **8c** as a white solid: mp 247-249 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.58 and 4.74 (2d, AX system, J = 14 Hz, 3H), 6.92 (d, 6H, J = 9 Hz), 7.02 (s, 3H), 7.12 (s, 3H), 7.73 (d, 6H, J = 9 Hz), 9.50 (s, 3H); ^{13}C NMR (75 MHz, [D_6]DMSO, 298 K) δ: 34.5, 103.7, 116.1, 118.4, 118.7, 123.4, 131.2, 134.1, 138.4, 138.9, 147.5, 161.4; MS, CI(+) m/z: 669 [M^+]. Anal. Calcd. for $C_{42}H_{27}N_3O_6$: C, 75.33; H, 4.06; N, 6.27. Found: C, 72.38; H, 4.36; N, 5.98.

(±)2,7,12-Trihydroxy-3,8,13-tri-(4-nitrofenoxy)-10,15-dihydro-5H-tribenzo[adg]-cyclononene (8d): Purification of the residue by chromatography (*n*-hexane : CH_2Cl_2 : ethyl acetate = 1 : 7 : 2) afforded 0.15 g (60%) of **8d** as a white solid: mp 255-259 °C ^{1}H NMR (300 MHz, CD_3CN) δ: 3.59 and 4.72 (2d, 6H, J = 14 Hz), 6.94 (d, 6H, J = 7.2 Hz), 7.00 (s, 3H), 7.16 (s, 3H), 8.16 (d, 6H, J = 7 Hz); ^{13}C NMR (75 MHz, CD_3CN, 298 K) δ: 35.6, 116.6, 117.8, 119.2, 124.0, 126.4, 132.8, 139.3, 140.5, 143.2, 147.9; MS, (ESI, CH_3OH) m/z: 752.5 [M^++Na^+], 768.3 [M^++K^+]; Anal. Calcd. for $C_{39}H_{27}N_3O_{12}$: C, 64.20; H, 3.73; N, 5.76. Found: C, 64.12; H, 3.89; N, 5.55.

(±)3,8,13-Tris-(4-phtalimmido-phenoxy)-2,7,12-trimethoxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (11): Compound **9** (0.40 g, 0.59 mmol) was dissolved in a 1:1 CH_3CN\toluene solvent mixture (50 ml), then acetic acid (10 mL) and phthalic anhydride (0.30 g, 3.60 mmol) were added. The

resulting mixture was refluxed with stirring overnight, then quenched with a aqueous solution of $NaHCO_3$ (10%) and extracted with dichloromethane. The separated organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness under vacuum. Purification of the residue by crystallization from ethyl acetate afforded 0.44g (70%) of pure compound **11**: mp 182-185 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 3.60 and 4.78 (2d, 6H, AX system. *J* = 14 Hz), 3.77 (s, 9H), 6.85 (s, 3H), 7.04 (s, 3H), 7.05 (d, 6H, *J* = 7 Hz), 7.32 (d, 6H, *J* = 7 Hz), 7.8-7.9 (m, 6H), 7.9–8.0 (m, 6H,); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ: 36.3, 56.2, 114.2, 117.5, 122.3, 123.6, 125.8, 127.9, 131.7, 131.8, 134.2, 136.3, 143.1, 150.1, 157.6, 167.3,; MS- CI(+) *m/z*: 1072 [MH^+]; Anal. Calcd. for $C_{66}H_{45}N_3O_{12}$: C, 73.94; H, 4.23; N, 3.92. Found: C, 74.03; H, 4.27; N, 3.99.

(±)3,8,13-Tris-(4-phtalimmido-phenoxy)-2,7,12-trihydroxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (12): To a solution of compound **11** (0.20 g, 0.19 mmol) in CH_2Cl_2 (50 mL) maintained under argon atmosphere, BBr_3 (0.40 g, 1.6 mmol) was added (CAUTION!). The resulting mixture was stirred at room temperature for 12 h, then cooled with an external ice bath and quenched by dropwise adding of water 50 mL (CAUTION!). The organic phase was separated and the remaining water phase was extracted with dichloromethane (2 x 100 mL). The combined organic phases were dried over Na_2SO_4 and evaporated to dryness under vacuum. Purification of the residue by chromatography (CH_2Cl_2 : ethyl acetate = 8 : 2) afforded 0.08 g (40%) of pure **12**: mp 182-185 °C (dec). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ: 3.60 and 4.76 (2d, 6H, AX system, *J* = 13 Hz), 6.9 (d, 6H, *J* = 9 Hz, 6H), 7.05 (s, 3H), 7.15 (s, 3H), 7.33 (d, 6H, *J* = 9 Hz), 7.9-8.0 (m, 12H),9.43 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6, 298 K) δ: 34.7, 115.2, 118.3, 123.2, 123.7, 125.1, 128.7, 131.1, 131.4, 134.5, 137.9, 139.7, 147.9, 157.7, 167.1; MS, CI(+) m/z: 1029 [M^+]; Anal. Calcd. for $C_{63}H_{39}N_3O_{12}$: C, 73.46; H, 3.82; N, 4.08. Found: C, 72.91; H, 4.03; N, 4.13.

*General procedure for the alkylation of CTV derivatives **8c,d:*** To a solution of compound **8c** or **8d** (0.60 mmol) in CH_3CN (50 mL), K_2CO_3 (0.51g, 3.90 mmol) and 1-iodooctane (0.48 g ml, 2.70 mmol) were added. The mixture was stirred overnight at 80 °C, then the solvent was evaporated under reduce pressure The solid residue was taken up with an aqueous solution of HCl (10%, 10 mL) and extracted twice with ethyl acetate (2 x 50 mL). The separated organic phase was dried over anhydrous Na_2SO_4, filtered and then evaporated to dryness under vacuum.

(±)2,7,12-Tris-(4-cyano-phenoxy)-3,8,13-triottiloxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (13c) and **(±)2,7,13-Tris-(4-cyano-phenoxy)-3,8,12-triottiloxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (14c)**: Purification of the residue by column chromatography (*n*-hexane : CH_2Cl_2 = 2 : 8) afforded 0.18 g (30%) of **13c** (rf = 0.4) and 0.34 g (60%) of **14c** (rf = 0.36).

13c mp: 212-214 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 0.87 (t, 9H, *J* = 7 Hz), 1.14 (bs, 18H), 1.20-1.28 (m, 12H), 1.46-1.52 (m, 6H), 3.63 and 4.80 (2d, 6H, AX system, *J* = 14 Hz), 3.78-3.84 (m, 6H), 6.88 (s, 3H), 6.91 (d, 6H, *J* = 9 Hz), 7.10 (s, 3H), 7.53 (d, 6H, *J* = 9 Hz); ^{13}C NMR (75 MHz,$CDCl_3$) δ: 14.0, 22.5, 25.6, 28.9, 29.1, 31.6, 36.3, 36.8, 68.8, 105.1, 115.6, 116.4, 118.8, 1237.7, 131.9, 133.7, 137.5, 141.4, 149.7, 162.0; MS-CI(+) *m/z*: 1006 [MH^+]; MS-ESI (+) *m/z*: 1028.4 [M^++Na^+] Anal. Calcd. for $C_{66}H_{75}N_3O_6$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.71; H, 7.65; N, 4.11.

14c mp 211-214°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, j=6.9 Hz, 3H), 1.14 (bs,18H), 1.20-1.28 (m, 12H), 1.4-1.5 (m, 6H), 3.57 (d, 1H, *J* = 14 Hz), 3.63 (d, 1H, *J* = 14 Hz), 3.68 (d, 1H, *J* =14 Hz), 3.78-3.84 (m, 6H), 4.75 (d, 1H, *J* = 14 Hz), 4.80 (d, 1H, *J* = 14 Hz), 4.85 (d, 1H, J = 14 Hz), 6.85 (d, 2H, *J* = 9 Hz), 6.87 (d, 2H, *J* = 9 Hz), 6.88 (s, 1H), 6.92 (d, 2H, *J* = 9 Hz), 6.98 (s, 1H), 6.99 (s, 1H), 7.00 (s, 1H), 7.02 (s, 1H), 7.12 (s, 1H), 7.48 (d, 2H, *J* = 9 Hz), 7.49 (d, 2H, *J* = 9 Hz), 7.54 (d, 2H, *J* = 9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ: 13.9, 22.5, 25.6, 25.6, 25.7, 25.9, 28.8, 28.9, 29.0, 29.3, 31.6, 31.7, 32.7,

35.7, 36.3, 36.9, 62.9, 65.4, 68.9, 93.2, 104.9, 105.0, 115.5, 115.6, 115.7, 116.3, 116.4, 118.8, 118.8, 123.6, 123.7, 123.9, 132.3, 132.7, 133.7, 136.8, 141.5, 141.5, 141.6, 149.5, 149.6, 161.8, 162.0; MS-CI(+) *m/z*: 1006 [MH^+]; MS-ESI(+) *m/z*: 1028.4 [M^++Na^+]; Anal. Calcd. for $C_{66}H_{75}N_3O_6$: C, 78.77; H, 7.51; N, 4.18. Found: C, 77.39; H, 7.74; N, 4.08 .

(±)2,7,12-Tri-(4-nitro-phenoxy)-3,8,13-triottiloxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (13d) and (±)2,7,13-Tri-(4-nitro-phenoxy)-3,8,12-triottiloxy-10,15-dihydro-5H-tribenzo[adg]-cyclononene (14d): Purification of the residue by column chromatography (*n*-hexane : CH_2Cl_2 = 2 : 8) afforded 0.99 g (30%) of 11d (rf = 0.64) and 0.38 g (60%) of 12d (rf = 0.55).

13d: mp 212-214 °C.^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 0.85 (t, 9H, *J* = 7 Hz), 1.1-1.2 (m, 30H), 1.4-1.5 (m, 6H), 3.66 and 4.83 (2d, 6H, AX system, *J* =14 Hz), 3.8-3.9 (m, 6H), 6.95 (s, 3H), 6.96 (d, 6H, *J* = 9 Hz), 7.13 (s, 3H), 8.14 (d, 6H, *J* = 9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.5, 25.6, 25.7, 28.8, 29.0, 29.6, 31.6, 36.4, 68.9, 115.7, 123.7, 125.5, 131.9, 137.7, 142.3, 149.7, 162.0, 139. MS-CI(+) *m/z*: 1066 [MH^+]; Anal. Calcd. for $C_{63}H_{75}N_3O_{12}$: C, 70.96; H, 7.09; N, 3.94. Found: C, 70.55; H, 7.04; N, 5.13.

14d: mp 211-214°C (dec) ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 0.87 (t, j=6.9 Hz), 1.14 (bs, 18H), 1.20-1.28 (m, 12H), 1.4-1.5 (m, 6H), 3.60 (d, 1H, *J* = 14 Hz), 3.66 (d, 1H, *J* = 14 Hz), 3.71 (d, 1H, *J* = 14 Hz), 3.8-3.9 (m, 6H), 4.78 (d, 1H, *J* = 14 Hz), 4.83 (d, 1H, *J* = 14 Hz), 4.88 (d, 1H, *J* = 14 Hz), 6.87 (d, 2H, *J* = 9 Hz), 6.89 (d, 2H, *J* = 9 Hz), 6.89 (s, 1H) 6.93 (d, 2H, *J* = 9 Hz), 6.98 (s, 1H), 7.0 (s, 1H), 7.04 (s, 1H), 7.05 (s, 1H), 7.15 (s, 1H), 8.11 (d, 2H, *J* = 9 Hz), 8.12 (d, 2H, *J* = 9 Hz), 8.16 (d, 2H, *J* = 9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ: 13.9, 22.5, 25.6, 25.7, 28.7, 28.8, 28.9, 29.0, 29.0, 31.6, 31.6, 35.7, 36.3, 36.9, 68.8, 68.9, 115.5, 115.6, 115.7, 115.7, 123.6, 123.7, 123.9, 125.5, 132.3, 132.7, 137.0, 137.2, 137.4, 141.5, 141.7, 142.3, 149.5, 149.6, 163.4, 163.6; MS-CI(+) *m/z*: 1066 [MH^+]; Anal. Calcd. for $C_{63}H_{75}N_3O_{12}$: C, 70.96; H, 7.09; N, 3.94. Found: C, 69.78; H, 7.21; N, 3.76.