Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cucurbitimines – Imine Cages with Concave Walls

Christine Bourguignon, Dorothee Schindler, Gangxiang Zhou, Frank Rominger, and Michael Mastalerz*

Table of Contents

1. General Remarks

All commercially available reagents and solvents were used without further purification, unless otherwise noted. 2,3,6,7,14,15-Hexamethoxytriptycene **1**[1] and 1,2-diamino-4,5-dihexylbenzene **3**[2] were synthesized according to literature procedures. Thin layer chromatography was performed on fluorescent labeled silica coated aluminium plates (60 F254, Merck), which were examined using UV-light irradiation with λ_{ex} = 254 and 366 nm. For flash column chromatography silicagel with a particle size of 0.040-0.063 mm (Macherey-Nagel & Co. KG, Düren) was used. Recycling gel permeation chromatography (GPC) was performed with a Shimadzu system consisting of a DGU-20A$_{3R}$ degassing unit, LC-20AD pump unit, SIL-20A HT autosampler, CBM-20A communication bus module, CTO-20AC column oven, FCV-20AH$_2$ valve unit, SPD-M20A diode array detector, FRC-10A fraction collector, PSS SDV (20 x 50 mm) precolumn and three SDV 100 Å (20 x 300 mm) columns connected in series. All shown NMR spectra were recorded on the following instruments: Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 600 (600 MHz) or Bruker Avance III 700 (700 MHz). Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants in Hertz (Hz). The spectras were calibrated relative to the traces of $CHCl_3$ (δ_H = 7.26 ppm, δ_C = 77.2 ppm)[3], CD_2Cl_2 (δ_H = 5.32 ppm, δ_C = 53.8 ppm)[3], DMSO-d$_6$ (δ_H = 2.50 ppm, δ_C = 39.5 ppm)[3] and THF-d$_8$ (δ_H = 3.58, 1.72 ppm, δ_C = 67.2, 52.3 ppm).[3] The melting points (not corrected) were determined using a Büchi Melting Point B-545. Open glass capillaries were used for this. Mass spectrometry experiments (MALDI) were carried out on a Bruker AutoFlex Speed time-of-flight spectrometer. DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methylpropylidene)-malononitrile) was used as matrix in MALDI-MS experiments. Mass spectrometry experiments (DART) were carried out on a Bruker ApexQe hybrid 9.4T FT-ICR spectrometer. Mass spectrometry experiments (EI) were carried out on a JEOL AccuTOF GCx time-of-flight spectrometer. All MS measurements were performed by the mass-spectrometry division of Dr. Jürgen H. Gross of the University of Heidelberg. IR spectra were measured on a Bruker Tensor 27 spectrometer equipped with a ZnSe ATR crystal. The absorption intensity was described by the following abbreviations: w (weak), m (medium), s (strong). Elemental analysis was conducted by the microanalytical laboratory of the University of Heidelberg using a Vario EL Element Analyzer. UV/VIS spectra were measured on a

Jasco V-730 spectrometer and fluorescence spectra on a FP-8300 spectrometer. CD spectra were recorded on a Jasco J-1500 CD spectrometer. Crystal structure analysis was performed on a Stoe Stadivari diffractometer using Cu-K_α radiation (λ = 1.54186 Å). Intensity correction for Lorentz and polarization effects were applied. Absorption correction was carried out using Sa-DABD[4, 5] or X-Area LANA 1.70.0.0[6] based on the Laue symmetry of the reciprocal space (μ, T_{min}, T_{max}). Resolving of the structures was performed with SHELXT-2014 (Sheldrick 2014)[7] and they were refined against F2 with a Full-matrix least squares algorithm using SHELXL-2018/1.[8] Geometry optimizations were performed using PM3 semi empirical method[9-12] in Spartan 14. The IUPAC names and enumeration of the synthesized compounds were created using ChemDraw© 17.0. In Figure S1 the structure and numbering of the synthesized compounds is shown. The electron density maps were calculated using the DMol3 module of Material Studios© with DND basis set.

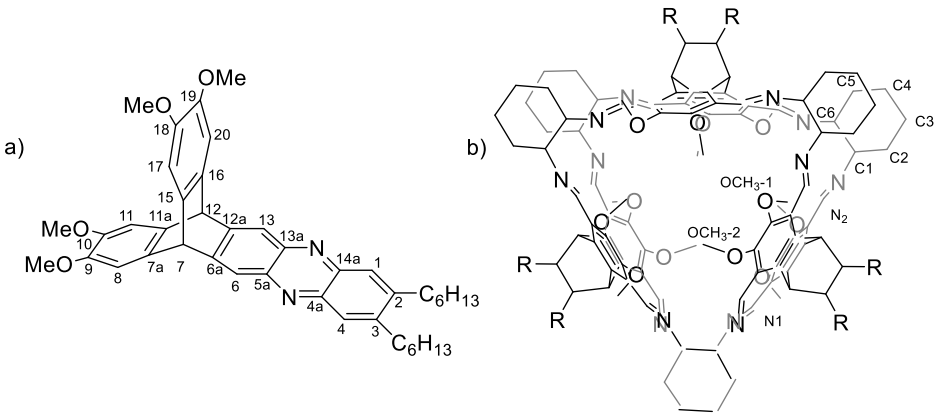
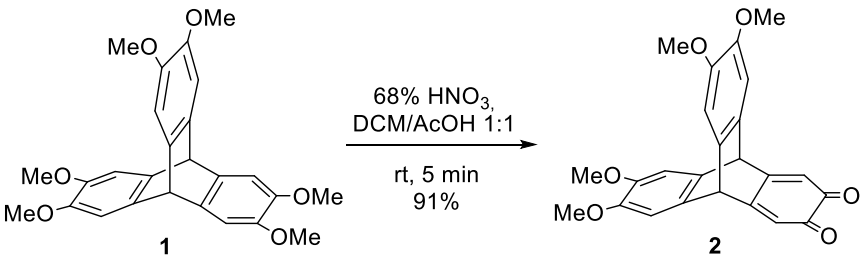


Figure S1: Labeling of a) substituted triptycenes, b) cage compound **9**.

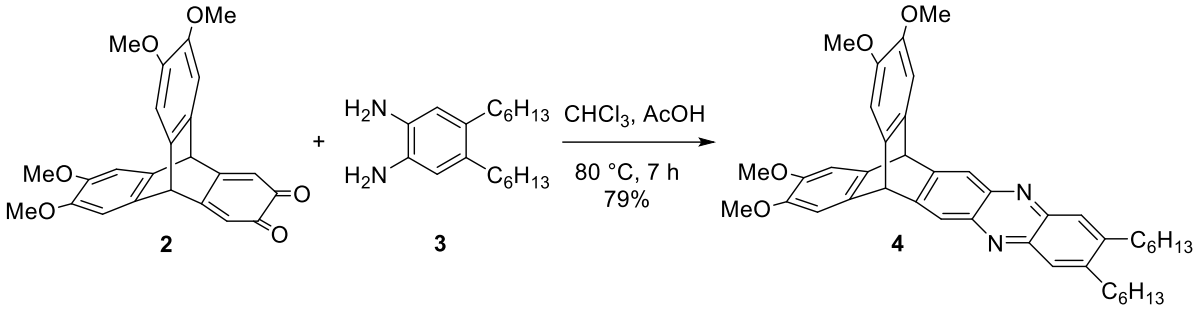
2. Experimental Procedures

2.1. 2,3,6,7-Tetramethoxytriptycene-14,15-dione (2)



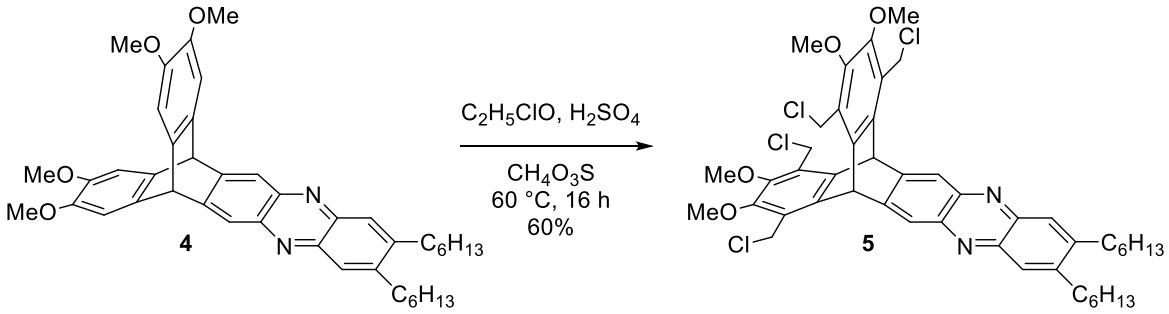
To a solution of **1** (573 mg, 1.32 mmol, 1 eq) in dichloromethane and acetic acid (7.5 mL, 1:1, v:v), nitric acid (485 µL, 68%) was added dropwise. The reaction mixture was stirred for 5 min and then poured on ice-water (50 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 30 mL) and the organic layers combined. The organic layer was washed with sodium bicarbonate solution (30%, 20 mL), dried over anhydrous Na_2SO_4 and the solvent was removed *in vacuo*. After column chromatography (SiO_2, PE/EA 1:1, R_f = 0.21), **2** was obtained as a dark red solid (486 mg, 1.20 mmol, 91%). M.p.: 260 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 6.97 (s, 4H, Ar-*H*-1,4,5,8), 6.28 (s, 2H, Ar-*H*-13,16), 4.97 (s, 2H, bridgehead-*H*-9,10), 3.90 (s, 12H, Ar-OC*H*$_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 180.3 (Ar-*C*-14,15), 152.7 (Ar-*C*-11,12), 149.1 (Ar-*C*-2,3,6,7-OCH_3), 131.2 (Ar-*C*-4a,5a,8a,9a), 120.4 (Ar-*C*-13,16), 108.1 (Ar-*C*-1,4,5,8), 56.3 (Ar-O*C*H_3), 51.3 (bridgehead-*C*-9,10). IR (ATR, FT): $\tilde{\nu}$ (cm^{-1}) = 3054 (w), 2954 (w), 2834 (w), 1732 (w), 1672 (w), 1651 (m), 1593 (m), 1579 (m), 1493 (s), 1467 (m), 1440 (m), 1413 (w), 1365 (m), 1338 (w), 1289 (s), 1259 (m), 1225 (s), 1208 (m), 1197 (m), 1184 (m), 1165 (w), 1153 (m), 1089 (s), 1040 (w), 990 (m), 887 (m), 877 (m), 792 (w), 776 (w), 736 (m), 708 (m), 685 (m), 633 (m), 606 (m). MS (HR-EI): m/z calculated for $[M]^+$: 404.1254, found: 404.1248. Elem. Anal.: calculated for $C_{24}H_{20}O_6$ + DCM: C 61.36%, H 4.53%; found: C 61.45%, H 4.75%.

2.2. (7*s*,12*s*)-2,3-Dihexyl-9,10,18,19-tetramethoxy-7,12-dihydro-7,12-[1,2]benzenonaphto[2,3-*b*]phenazine (4)



A solution of triptycene **2** (997 mg, 2.47 mmol, 1.00 eq) and diamine **3** (1.02 g, 3.70 mmol, 1.50 eq.) in $CHCl_3$ (9 mL) and glacial acetic acid (9 mL) was stirred for 7 h at 80 °C. After cooling to room temperature, DCM (80 mL) was added, the organic phase washed with water (30 mL) and $NaHCO_3$ (30 %, 30 mL) and dried over $MgSO_4$. Column chromatography (SiO_2, PE/EA 1:1, R_f = 0.34) gave **4** (1.25 g, 1.94 mmol, 79%) as a yellow solid. M.p.: 185 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) = 7.95 (s, 2H, Ar-*H*-6,13), 7.90 (s, 2H, Ar-*H*-1,4), 7.10 (s, 4H, Ar-*H*-8,11,17,20), 5.48 (s, 2H, bridgehead-*H*-7,12), 3.82 (s, 12H, Ar-OC*H*$_3$), 2.88 - 2.84 (m, 4H, Ar-C*H*$_2$-$(CH_2)_4$-CH_3), 1.75 (p, $^3J_{H-H}$ = 7.4 Hz, 4H, Ar-CH_2-C*H*$_2$-$(CH_2)_3$-CH_3), 1.48 (p, $^3J_{H-H}$ = 6.3 Hz, 4H, Ar-$(CH_2)_2$-C*H*$_2$-$(CH_2)_2$-CH_3), 1.44 – 1.33 (m, 8H, Ar-$(CH_2)_3$-(C*H*$_2$)$_2$-CH_3), 0.92 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, Ar-$(CH_2)_5$-C*H*$_3$). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ (ppm) = 147.5 (Ar-*C*-9,10,18,19), 146.9 (Ar-*C*-6a,12a), 145.4 (Ar-*C*-2,3), 143.0 (Ar-*C*-5a,13a), 142.8 (Ar-*C*-4a,14a), 137.1 (Ar-*C*-7a,11a,15,16), 127.6 (Ar-*C*-1,4), 121.9 (Ar-*C*-6,13), 109.4 (Ar-*C*-8,11,17,20), 56.7 (Ar-O*C*H_3), 53.1 (bridgehead-*C*-7,12), 33.4 (Ar-*C*H_2-$(CH_2)_4$-CH_3), 32.2 (Ar-$(CH_2)_3$-*C*H_2-CH_2-CH_3), 30.8 (Ar-CH_2-*C*H_2-$(CH_2)_3$-CH_3), 29.8 (Ar-$(CH_2)_2$-*C*H_2-$(CH_2)_2$-CH_3), 23.0 (Ar-$(CH_2)_4$-*C*H_2-CH_3), 14.3 (Ar-$(CH_2)_5$-*C*H_3). IR (ATR, FT): $\tilde{\nu}$ (cm^{-1}) = 2953 (w), 2926 (w), 2856 (w), 1738 (w), 1650 (w), 1610 (w), 1554 (w), 1490 (m), 1462 (m), 1427 (m), 1366 (s), 1287 (s), 1225 (s), 1199 (m), 1183 (m), 1161 (m), 1120 (s), 1037 (w), 990 (m), 980 (m), 880 (m), 738 (m), 652 (w), 622 (w), 609 (s), 571 (w), 550 (w), 536 (w). UV/Vis (DCM): λ (log ε) = 406 nm (4.26), 295 (3.93), 264 (4.96). Fluorescence (DCM): λ_{em} (λ_{ex}) = 559 nm (406). MS (HR-MALDI): m/z calculated for $[M]^+$: 645.3648, found: 645.3697. Elem. Anal.: calculated for $C_{42}H_{48}N_2O_4$ + $\frac{1}{2}$ H_2O: C 77.17%, H 7.55%, N 4.29%; found: C 77.19%, H 7.72%, N 4.06%.

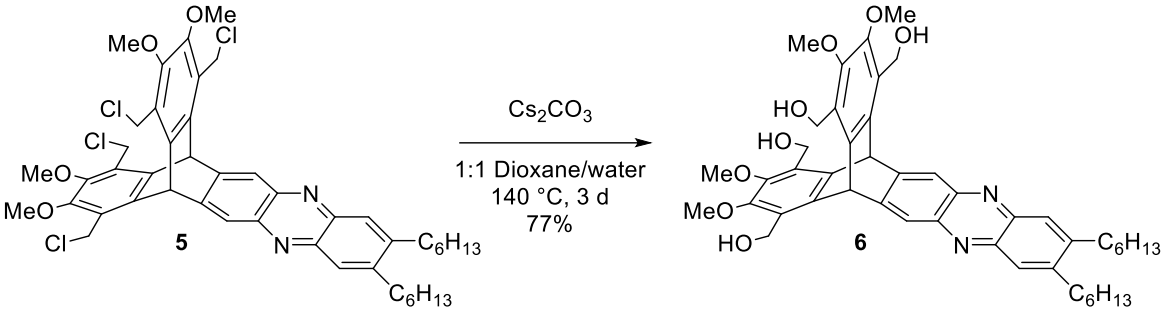
2.3. (7*s*,12*s*)-8,11,17,20-Tetrakis(chloromethyl)-2,3-dihexyl-9,10,18,19-tetramethoxy-7,12-dihydro-7,12-[1,2]benzenonaphtho[2,3-*b*]phenazine (5)



Triptycene **4** (200 mg, 0.31 mmol, 1.00 eq.) was dissolved in chloromethyl methyl ether (1.07 mL, 13.6 mmol, 44.0 eq.) and methanesulfonic acid (0.90 mL, 13.6 mmol, 44.0 eq.) and conc. H_2SO_4 (0.08 mL, 1.55 mmol, 5.00 eq.) were added dropwise. The dark green solution was stirred for 16 h at 60 °C. After cooling to room temperature, solvent was removed by reduced pressure and collected into a cooling trap. The residue was taken up in DCM (50 mL), washed with water (20 mL), sat. $NaHCO_3$ (20 mL) and brine (20 mL) and dried over $MgSO_4$. After column chromatography (SiO_2, DCM, R_f = 0.23) triptycene **5** (157 mg, 0.19 mmol, 60%) was obtained as a yellow solid. M.p.: 224 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) = 8.14 (s, 2H, Ar-*H*-6,13), 7.91 (s, 2H, Ar-*H*-1,4), 6.28 (s, 2H, bridgehead-*H*-7,12), 5.14 (d, $^3J_{H\text{-}H}$ = 11.0 Hz, 4H, Ar-C*H*$_2$-Cl), 5.03 (d, $^3J_{H\text{-}H}$ = 11.0 Hz, 4H, Ar-C*H*$_2$-Cl), 3.85 (s, 12H, Ar-OC*H*$_3$), 2.88 - 2.84 (m, 4H, Ar-C*H*$_2$-$(CH_2)_4$-CH_3), 1.75 (p, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, Ar-CH_2-C*H*$_2$-$(CH_2)_3$-CH_3), 1.48 (p, $^3J_{H\text{-}H}$ = 6.7 Hz, 4H, Ar-$(CH_2)_2$-C*H*$_2$-$(CH_2)_2$-CH_3), 1.39 – 1.34 (m, 8H, Ar-$(CH_2)_3$-(C*H*$_2$)$_2$-CH_3), 0.91 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 6H, Ar-$(CH_2)_5$-C*H*$_3$). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ (ppm) = 149.6 (Ar-*C*-9,10,18,19), 146.0 (Ar-*C*-2,3), 144.3 (Ar-*C*-6a,12a), 143.0 (Ar-*C*-5a,13a), 142.8 (Ar-*C*-4a,14a), 139.5 (Ar-*C*-7a,11a,15,16), 128.7 (Ar-*C*-8,11,17,20), 127.6 (Ar-*C*-1,4), 123.6 (Ar-*C*-6,13), 61.7 (Ar-O*C*H_3), 46.6 (bridgehead-*C*-7,12), 37.3 (Ar-*C*H_2-Cl), 33.4 (Ar-*C*H_2-$(CH_2)_4$-CH_3), 32.2 (Ar-$(CH_2)_3$-*C*H_2-CH_2-CH_3), 30.8 (Ar-CH_2-*C*H_2-$(CH_2)_3$-CH_3), 29.8 (Ar-$(CH_2)_2$-*C*H_2-$(CH_2)_2$-CH_3), 23.0 (Ar-$(CH_2)_4$-*C*H_2-CH_3), 14.3 (Ar-$(CH_2)_5$-*C*H_3). IR (ATR, FT): $\tilde{\nu}$ (cm^{-1}) = 2953 (w), 2925 (w), 2855 (w), 1710 (w), 1650 (w), 1591 (w), 1554 (w), 1512 (w), 1453 (s), 1407 (s), 1358 (w), 1318 (s), 1281 (m), 1210 (w), 1258 (w), 1087 (s), 1050 (m), 1013 (s), 983 (m), 954 (w), 888 (w), 803 (w), 738 (m), 647 (s). UV/Vis (DCM): λ (log ε) = 393 nm (4.25), 383 (sh., 4.14), 309

(3.80), 267 (4.84). MS (HR-DART): m/z calculated for $[M+H]^+$: 839.2730, found: 839.2737. Elem. Anal.: calculated for $C_{46}H_{52}Cl_4N_2O_4$: C 75.87%, H 6.25%, N 3.34%; found: C 75.72%, H 6.52%, N 3.07%.

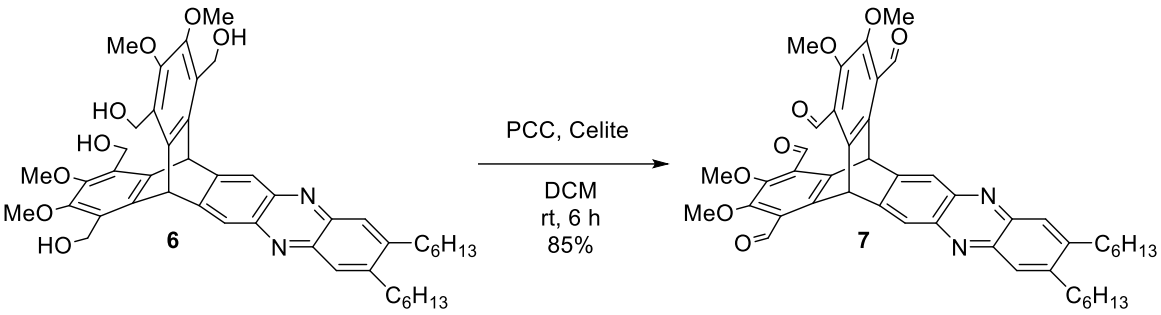
2.4. ((7*s*,12*s*)-2,3-Dihexyl-9,10,18,19-tetramethoxy-7,12-dihydro-7,12-[1,2]benzenonaphtho[2,3-*b*]phenazine-8,11,17,20-tetrayl)tetramethanol (6)



A reaction tube with magnetic rotating lid was charged with triptycene **5** (1.61 g, 1.92 mmol, 1.00 eq.) and Cs_2CO_3 (20.0 g, 61.40 mmol, 32.0 eq.). A dioxane/water mixture (38 mL, 1:1, v:v) was added and the reaction mixture was stirred vigorously for 3 d at 140 °C. After cooling down to room temperature, aqueous HCl (6 M, 30 mL) was added and the solution was extracted with ethyl acetate (3 x 75 mL). The combined extract was washed with water (20 mL) and dried over $MgSO_4$. After column chromatography (SiO_2, DCM/MeOH 20:1, R_f = 0.11) triptycene **6** was obtained as a yellow solid (1.14 g, 1.49 mmol, 77%). M.p: 279 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ (ppm) = 8.10 (s, 2H, Ar-*H*-6,13), 7.88 (s, 2H, Ar-*H*-1,4), 6.54 (s, 2H, bridgehead-*H*-7,12), 5.23 (t, $^3J_{H\text{-}H}$ = 5.6 Hz, 4H, Ar-CH$_2$-O*H*), 4.82 (qd, $^3J_{H\text{-}H}$ = 11.2 Hz, $^3J_{H\text{-}H}$ = 5.7 Hz, 8H, Ar-C*H*$_2$-OH), 3.68 (s, 12H, Ar-OC*H*$_3$), 2.80 (t, $^3J_{H\text{-}H}$ = 7.9 Hz, 4H, Ar-C*H*$_2$-(CH$_2$)$_4$-CH$_3$), 1.66 (p, $^3J_{H\text{-}H}$ = 7.9 Hz, 4H, Ar-CH$_2$-C*H*$_2$-(CH$_2$)$_3$-CH$_3$), 1.41 (p, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H, Ar-(CH$_2$)$_2$-C*H*$_2$-(CH$_2$)$_2$-CH$_3$), 1.33 – 1.26 (m, 8H, Ar-(CH$_2$)$_3$-(C*H*$_2$)$_2$-CH$_3$), 0.85 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 6H, Ar-(CH$_2$)$_5$-C*H*$_3$). ^{13}C NMR (DMSO-d_6, 151 MHz): δ (ppm) = 148.2 (Ar-*C*-9,10,18,19), 146.7 (Ar-*C*-2,3), 144.6 (Ar-*C*-6a,12a), 142.0 (Ar-*C*-5a,13a), 141.5 (Ar-*C*-4a,14a), 139.6 (Ar-*C*-7a,11a,15,16), 130.5 (Ar-*C*-8,11,17,20), 126.9 (Ar-*C*-1,4), 121.9 (Ar-*C*-6,13), 61.3 (Ar-OCH$_3$), 54.1 (Ar-*C*H$_2$-OH), 45.3 (bridgehead-*C*-7,12), 32.1 (Ar-*C*H$_2$-(CH$_2$)$_4$-CH$_3$), 31.1 (Ar-(CH$_2$)$_3$-*C*H$_2$-CH$_2$-CH$_3$), 29.9 (Ar-CH$_2$-*C*H$_2$-(CH$_2$)$_3$-CH$_3$), 28.8 (Ar-(CH$_2$)$_2$-*C*H$_2$-(CH$_2$)$_2$-CH$_3$), 22.1 (Ar-(CH$_2$)$_4$-*C*H$_2$-CH$_3$), 14.0 (Ar-(CH$_2$)$_5$-*C*H$_3$). IR (ATR, FT): $\tilde{\nu}$ (cm^{-1}) = 3322 (w), 2955 (m), 2927 (m), 2854 (m), 1683 (w), 1589 (w),

1514 (s), 1441 (s), 1406 (m) 1360 (m), 1312 (m), 1257 (m), 1219 (w), 1191 (w), 1164 (w), 1082 (s), 1027 (s), 999 (s), 936 (w), 880 (w), 803 (w), 758 (w), 727 (w), 702 (w), 686 (w), 632 (w). UV/Vis (DCM): λ (log ε) = 395 nm (4.45), 384 (sh., 4.35), 310 (3.64), 266 (5.08). MS (HR-MALDI): m/z calculated for $[M+H]^+$: 765.4115, found: 765.4117. Elem. Anal.: calculated for $C_{46}H_{56}N_2O_8 + \frac{1}{2} H_2O$: C 71.45%, H 7.42%, N 3.54%; found: C 71.38%, H 7.50%, N 3.67%.

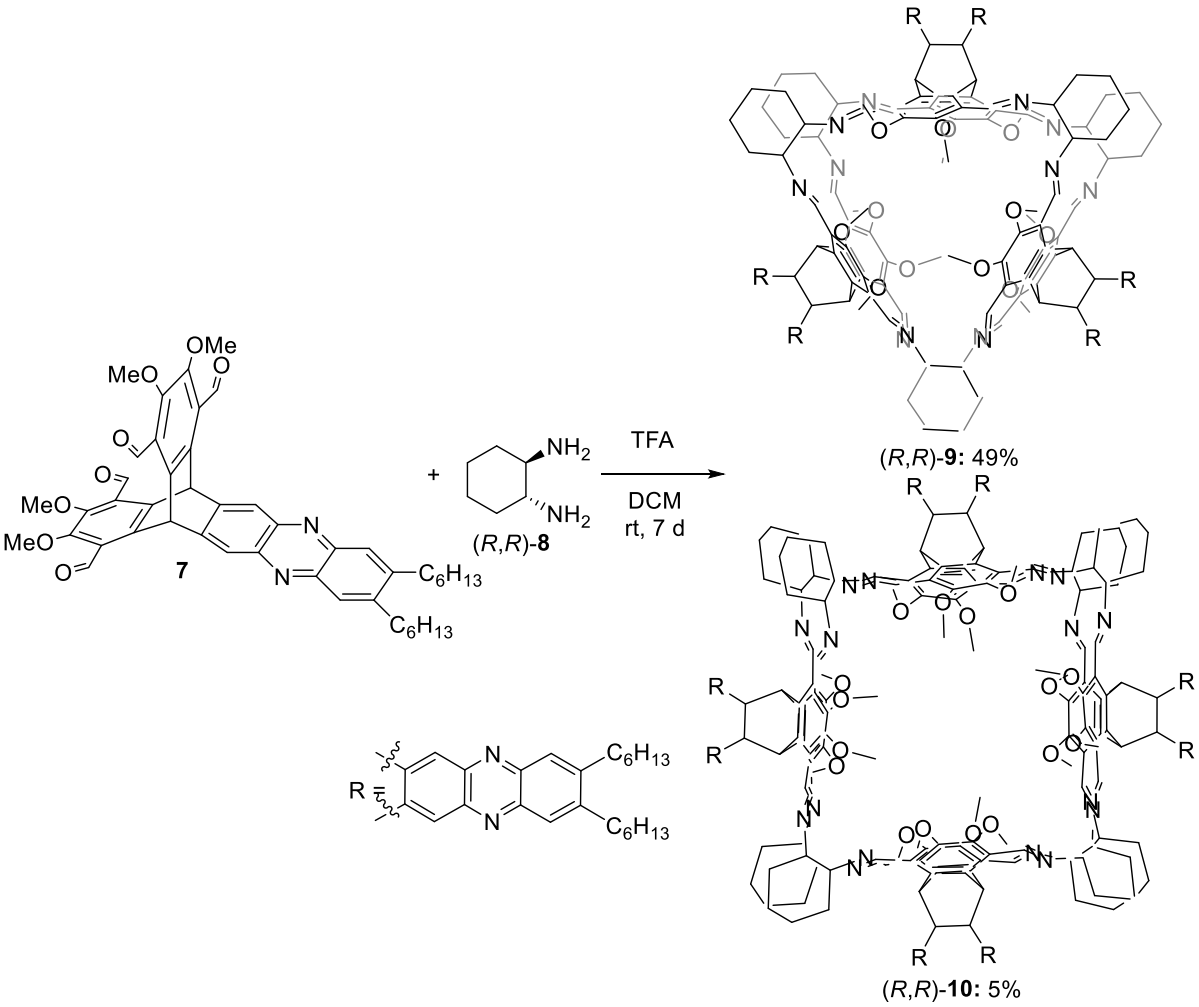
2.5. (7*s*,12*s*)-2,3-Dihexyl-9,10,18,19-tetramethoxy-7,12-dihydro-7,12-[1,2]benzenonaphtho[2,3-*b*]phenazine-8,11,17,20-tetracarbaldehyde (7)



Diatomaceous earth (33 mg) and triptycene **6** (28.6 mg, 37.4 µmol, 1.00 eq.) were suspended in DCM (4 mL) and PCC (136 mg, 0.63 mmol, 16.8 eq.) was added in portions. The suspension was stirred for 6 h at room temperature. After a short filtration over silica gel (eluent: EA), triptycene **7** was obtained as a yellow solid (24.1 mg, 31.9 µmol, 85%). M.p: 123 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) = 10.63 (s, 4H, Ar-C*H*=O), 8.20 (s, 2H, Ar-*H*-6,13), 8.10 (s, 2H, bridgehead-*H*-7,12), 7.92 (s, 2H, Ar-*H*-1,4), 3.92 (s, 12H, Ar-OC*H*$_3$), 2.84 – 2.82 (m, 4H, Ar-C*H*$_2$-$(CH_2)_4$-CH_3), 1.78 – 1.72 (m, 4H, Ar-CH_2-C*H*$_2$-$(CH_2)_3$-CH_3), 1.49 – 1.44 (m, 4H, Ar-$(CH_2)_2$-C*H*$_2$-$(CH_2)_2$-CH_3), 1.37 – 1.33 (m, 8H, Ar-$(CH_2)_3$-$(CH_2)_2$-CH_3), 0.90 (t, $^3J_{H-H}$ = 6.8 Hz, 6H, Ar-$(CH_2)_5$-C*H*$_3$). ^{13}C NMR ($CDCl_3$, 151 MHz): δ (ppm) = 190.8 (Ar-*C*H=O), 153.7 (Ar-*C*-9,10,18,19), 145.4 (Ar-*C*-2,3), 143.4 (Ar-*C*-6a,12a), 142.4 (Ar-*C*-5a,13a), 142.4 (Ar-*C*-4a,14a), 141.0 (Ar-*C*-7a,11a,15,16), 130.0 (Ar-*C*-8,11,17,20), 127.1 (Ar-*C*-1,4), 124.2 (Ar-*C*-6,13), 62.2 (Ar-O*C*H_3), 41.7 (bridgehead-*C*-7,12), 32.9 (Ar-*C*H_2-$(CH_2)_4$-CH_3), 31.7 (Ar-$(CH_2)_3$-*C*H_2-CH_2-CH_3), 30.1 (Ar-CH_2-*C*H_2-$(CH_2)_3$-CH_3), 29.3 (Ar-$(CH_2)_2$-*C*H_2-$(CH_2)_2$-CH_3), 22.5 (Ar-$(CH_2)_4$-*C*H_2-CH_3), 14.0 (Ar-$(CH_2)_5$-*C*H_3). IR (ATR, FT): $\tilde{\nu}$ (cm^{-1}) = 3030 (w), 2930 (m), 2954 (m), 2749 (w), 1695 (s), 1572 (m), 1513 (w), 1448 (m), 1441 (m)

1419 (s), 1379 (s), 1295 (m), 1264 (m), 1195 (m), 1159 (w), 1080 (s), 1067 (s), 1022 (s), 977 (w), 945 (m), 894 (w), 872 (w), 794 (w), 777 (w), 743 (s), 691 (w), 615 (w). UV/Vis (DCM): λ (log ε) = 396 nm (4.41), 382 (sh., 4.32), 268 (4.91). MS (HR-MALDI): m/z calculated for $[M+H]^+$: 757.3489, found: 757.3502. Elem. Anal.: calculated for $C_{46}H_{48}N_2O_8$: C 73.00%, H 6.93%, N 3.70%; found: C 72.86%, H 6.64%, N 3.45%.

2.6. *R*,*R*-Cyclohexane Cages ((*R*,*R*)-9 and (*R*,*R*)-10)



Triptycene **7** (91.2 mg, 120 µmol, 3.00 eq.) was dissolved in DCM (1.8 mL) and a solution of TFA in DCM (0.1 M, 72.0 µL, 2 mol%) was added. A solution of (1*R*,2*R*)-(-)-1,2-Diaminocyclohexane (*R*,*R*)-**8** (27.6 mg, 240 µmol, 6.00 eq.) in DCM (1.8 mL) was layered onto this. The reaction mixture was left standing at room temperature without stirring for 7 d. The solvent was evaporated and the residue suspended in methanol (8 mL), filtered and washed with methanol (2 x 3 mL). The crude product was subjected to GPC (SDV column, THF, 5 mL/min, fraction 1: 368 min, fraction 2:

380 min) and two fractions could be collected in which the first fraction is the [4+8]-cage ((*R*,*R*)-**10**) and the second fraction is the [3+6]-cage ((*R*,*R*)-**9**). Each fraction was afterwards again suspended in methanol (6 mL), filtered and washed with methanol (2 x 4 mL). (*R*,*R*)-**9** was obtained as a light yellow solid (54.7 mg, 20.0 µmol, 49%) and (*R*,*R*)-**10** was obtained as a light yellow solid (6.50 mg, 1.78 mol, 5%, not pure). (*R*,*R*)-**9**) M.p: <350 °C (decomposition). ^{1}H NMR (CD_2Cl_2, 700 MHz): δ (ppm) = 9.20 (s, 6H, Ar-C*H*=N), 8.61 (s, 6H, Ar-C*H*=N), 7.84 (s, 6H, Ar-*H*-1,4), 7.74 (s, 6H, bridgehead-*H*-7,12), 7.71 (s, 6H, Ar-*H*-6,13), 4.34 – 4.31 (m, 6H, Ar-*H*-C1), 3.61 (s, 24H, Ar-OC*H*$_3$, Ar-*H*-C6), 3.56 (s, 18H, Ar-OC*H*$_3$), 2.84 – 2.82 (m, 12H, Ar-C*H*$_2$-(CH$_2$)$_4$-CH$_3$), 2.21 – 2.17 (m, 12H, cyclohexane-*H*), 2.13 – 2.11 (m, 20H, cyclohexane-*H*), 2.05 – 2.00 (m, 8H, cyclohexane-*H*), 1.95 – 1.90 (m, 8H, cyclohexane-*H*), 1.74 – 2.72 (m, 12H, Ar-CH$_2$-C*H*$_2$-(CH$_2$)$_3$-CH$_3$), 1.47 – 1.45 (m, 12H, Ar-(CH$_2$)$_2$-C*H*$_2$-(CH$_2$)$_2$-CH$_3$), 1.37 – 1.33 (m, 24H, Ar-(CH$_2$)$_3$-(C*H*$_2$)$_2$-CH$_3$), 0.90 (*t*, $^{3}J_{H-H}$ = 6.9 Hz, 18H, Ar-(CH$_2$)$_5$-C*H*$_3$). *Because of the lack of resolution in 2D NMR the* cyclohexane-*H signals could not be further assigned.* ^{13}C NMR (CD_2Cl_2, 176 MHz): δ (ppm) = 158.2 (Ar-*C*H=N1), 156.7 (Ar-*C*H=N2), 152.9 (Ar-*C*-9,18), 150.0 (Ar-*C*-10,19), 146.9 (Ar-*C*-6a,12a), 145.5 (Ar-*C*-2,3), 142.8 (Ar-*C*-5a,13a), 142.6 (Ar-*C*-4a,14a), 140.9 (Ar-*C*-11a,16), 138.2 (Ar-*C*-7a,15), 128.6 (Ar-*C*-11,20), 127.5 (Ar-*C*-1,4), 126.3 (Ar-*C*-8,17), 122.4 (Ar-*C*-6,13), 78.1 (Ar-*C*6), 76.6 (Ar-*C*1), 61.9 (Ar-OCH$_3$), 61.9 (Ar-OCH$_3$), 44.5 (bridgehead-*C*-7,12), 34.7 (cyclohexane-*C*-5), 33.8 (cyclohexane-*C*-2), 33.3 (Ar-*C*H$_2$-(CH$_2$)$_4$-CH$_3$), 32.1 (Ar-(CH$_2$)$_3$-*C*H$_2$-CH$_2$-CH$_3$), 30.7 (Ar-CH$_2$-*C*H$_2$-(CH$_2$)$_3$-CH$_3$), 29.7 (Ar-(CH$_2$)$_2$-*C*H$_2$-(CH$_2$)$_2$-CH$_3$), 25.5 (cyclohexane-*C*), 25.1 (cyclohexane-*C*), 23.0 (Ar-(CH$_2$)$_4$-*C*H$_2$-CH$_3$), 14.3 (Ar-(CH$_2$)$_5$-*C*H$_3$). *Because of the lack of resolution in 2D NMR the* cyclohexane-*C signals could not be further assigned*. IR (ATR, FT): ṽ (cm^{-1}) = 2926 (m), 2855 (m), 1634 (m), 1448 (m), 1373 (s), 1298 (m), 1265 (w), 1199 (w), 1160 (w), 1146 (w), 1109 (w), 1083 (m), 1031 (m), 1015 (m), 994 (m), 956 (m), 936 (w), 899 (w), 877 (w), 747 (w), 681 (w), 669 (w), 650 (w). UV/Vis (DCM): λ (log ε) = 402 nm (5.07), 385 (sh., 4.87), 269 (5.68). Fluorescence (DCM): λ_{em} (λ_{ex}) = 537 nm (402), 492 (402). MS (MALDI): m/z calculated for [M+H]$^{+}$: 2739.6018, found: 2739.8755. Elem. Anal.: calculated for $C_{174}H_{204}N_{18}O_{12}$ + 2DCM: C 72.66%, H 7.21%, N 8.67%; found: C 72.74%, H 7.30%, N 8.34%. $\Delta\varepsilon$ (M^{-1}cm^{-1}) = 354 nm (-22.7), 329 nm (20.4), 281 nm (-98.2), 261 nm (209.0). (R,R)-**10**) ^{1}H NMR (THF-d$_8$, 600 MHz): δ (ppm) = 9.25 (s, 8H, Ar-C*H*=N), 8.71 (s, 8H, Ar-C*H*=N), 8.46 (s, 8H, bridgehead-*H*-7,12), 7.91 (s, 8H, Ar-*H*-1,4), 7.86 (s, 8H, Ar-*H*-6,13), 4.34 (s, 8H, Ar-*H*-C1), 3.88 (s, 20H, Ar-OC*H*$_3$), 2.88 (s, 16H,

Ar-C*H*$_2$-(CH$_2$)$_4$-CH$_3$), 2.16 – 1.93 (m, 64H, Ar-*H*-C2,C3,C4,C5), 1.80 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 16H, Ar-CH$_2$-C*H*$_2$-(CH$_2$)$_3$-CH$_3$), 1.54 – 1.51 (m, 16H, Ar-(CH$_2$)$_2$-C*H*$_2$-(CH$_2$)$_2$-CH$_3$), 1.43 – 1.38 (m, 32H, Ar-(CH$_2$)$_3$-(C*H*$_2$)$_2$-CH$_3$), 0.93 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 24H, Ar-(CH$_2$)$_5$-C*H*$_3$). *The signals for* Ar-*H*-C6 and Ar-OC*H*$_3$-1 *are located under the THF peak at 3.58 ppm.* ^{13}C NMR (THF-d$_8$, 151 MHz): δ (ppm) = 158.1 (Ar-*C*H=N), 156.2 (Ar-*C*H=N), 154.3 (Ar-*C*-9,18), 150.3 (Ar-*C*-10,19), 147.0 (Ar-*C*-6a,12a), 145.5 (Ar-*C*-2,3), 143.9 (Ar-*C*-5a,13a), 143.4 (Ar-*C*-4a,14a), 141.2 (Ar-*C*-11a,16), 140.6 (Ar-*C*-7a,15), 131.6 (Ar-*C*-11,20), 128.3 (Ar-*C*-1,4), 127.2 (Ar-*C*-8,17), 123.5 (Ar-*C*-6,13), 77.3 (Ar-*C*1), 76.6 (Ar-*C*6), 62.2 (Ar-O*C*H$_3$), 44.2 (bridgehead-*C*-7,12), 36.3 (cyclohexane-*C*), 34.6 (cyclohexane-*C*), 33.8 (Ar-*C*H$_2$-(CH$_2$)$_4$-CH$_3$), 32.9 (Ar-(CH$_2$)$_3$-*C*H$_2$-CH$_2$-CH$_3$), 31.3 (Ar-CH$_2$-*C*H$_2$-(CH$_2$)$_3$-CH$_3$), 30.5 (CH$_2$)$_2$-*C*H$_2$-(CH$_2$)$_2$-CH$_3$), 26.2 (cyclohexane-*C*), 26.0 (cyclohexane-*C*), 23.7 (Ar-(CH$_2$)$_4$-*C*H$_2$-CH$_3$), 14.6 (Ar-(CH$_2$)$_5$-*C*H$_3$). *Because of the lack of resolution in 2D NMR the* cyclohexane-*C signals could not be further assigned*. MS (MALDI): m/z calculated for [M+H]$^+$: 3653.1348, found: 3653.7070. Δε (M^{-1}cm^{-1}) = 352 nm (-17.2), 320 nm (35.0), 277 nm (-163.1), 256 nm (170.7).

***S*,*S*-Cyclohexane Cages ((*S*,*S*)-9** and **(*S*,*S*)-10)** were synthesized by the same procedure using (1*S*,2*S*)-(+)-1,2-diaminocyclohexane (*S*,*S*)-**8** instead of (1*R*,2*R*)-(-)-1,2-diaminocyclohexane (*R*,*R*)-**8**. (*S*,*S*)-**9** was obtained as a light yellow solid (60.1 mg, 21.9 µmol, 54%) and (*S*,*S*)-**10** was obtained as a light yellow solid (5.90 mg, 1.62 mol, 5%, not pure). *S*,*S*)-**9)** The analytical data of NMR, IR, UV/Vis, Fluorescence and MS are identical to (*R*,*R*)-**9**. Elem. Anal.: calculated for C$_{174}$H$_{204}$N$_{18}$O$_{12}$ + 3H$_2$O: C 74.81%, H 7.58%, N 9.02%; found: C 74.92%, H 7.65%, N 9.00%. Δε (M^{-1}cm^{-1}) = 354 nm (26.3), 329 nm (-13.1), 281 nm (118.9), 261 nm (-198.8). (S,S)-**10**: The analytical data of NMR, MS, UV/Vis and Fluorescence are identical to (*R*,*R*)-**10**. Δε (M^{-1}cm^{-1}) = 352 nm (15.4), 320 nm (-32.5), 277 nm (150.0), 256 nm (-155.8).

3. NMR Spectra

3.1. ^{1}H NMR Spectra

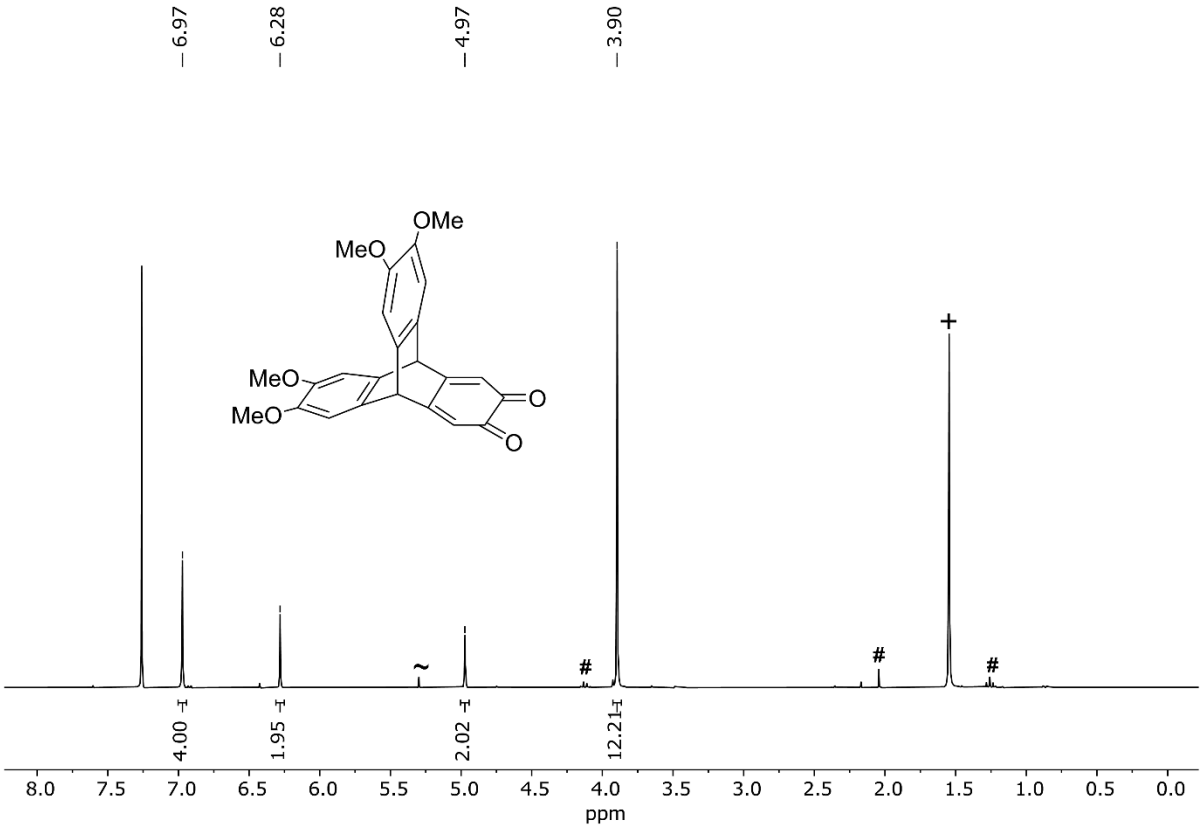


Figure S2: ^{1}H NMR Spectrum ($CDCl_3$, 300 MHz) of **2**. Solvent residues: +: H_2O, #: EA, ~: DCM.

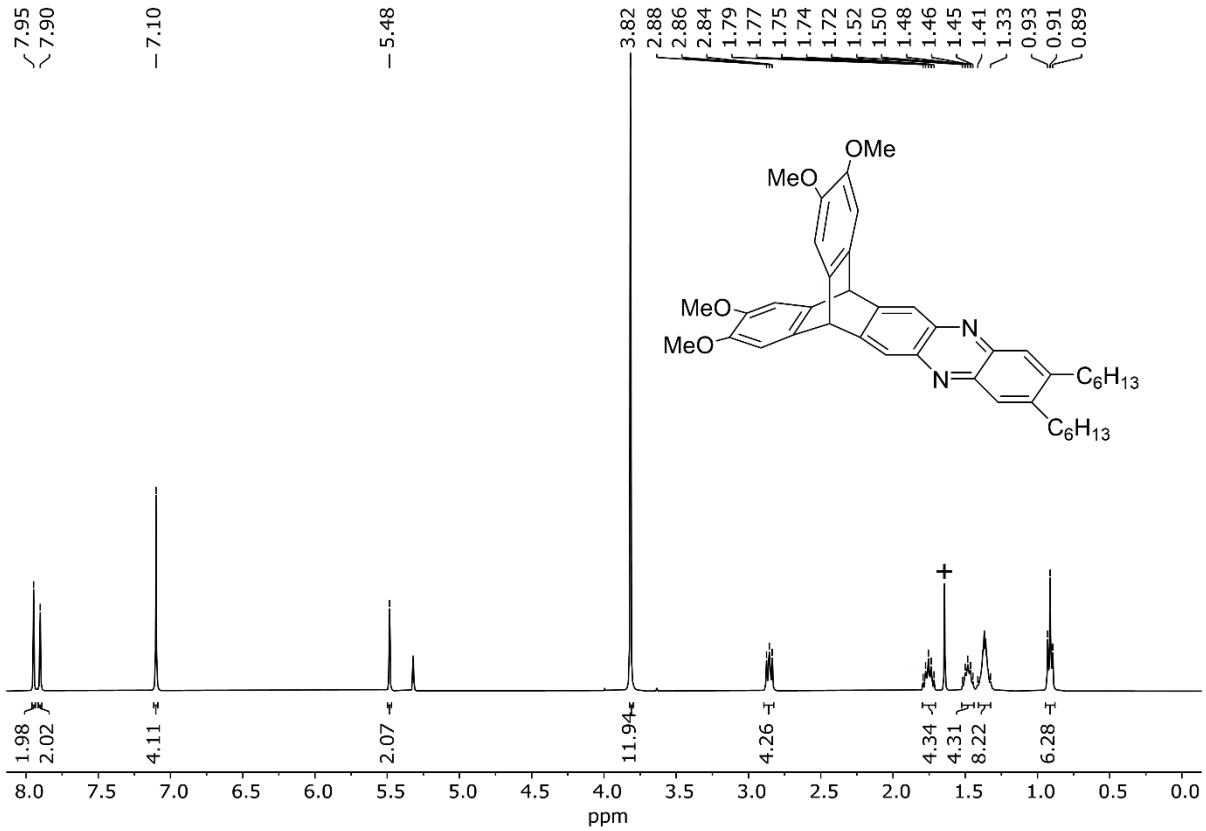


Figure S3: ^{1}H NMR Spectrum (CD_2Cl_2, 400 MHz) of **4**. Solvent residues: +: H_2O.

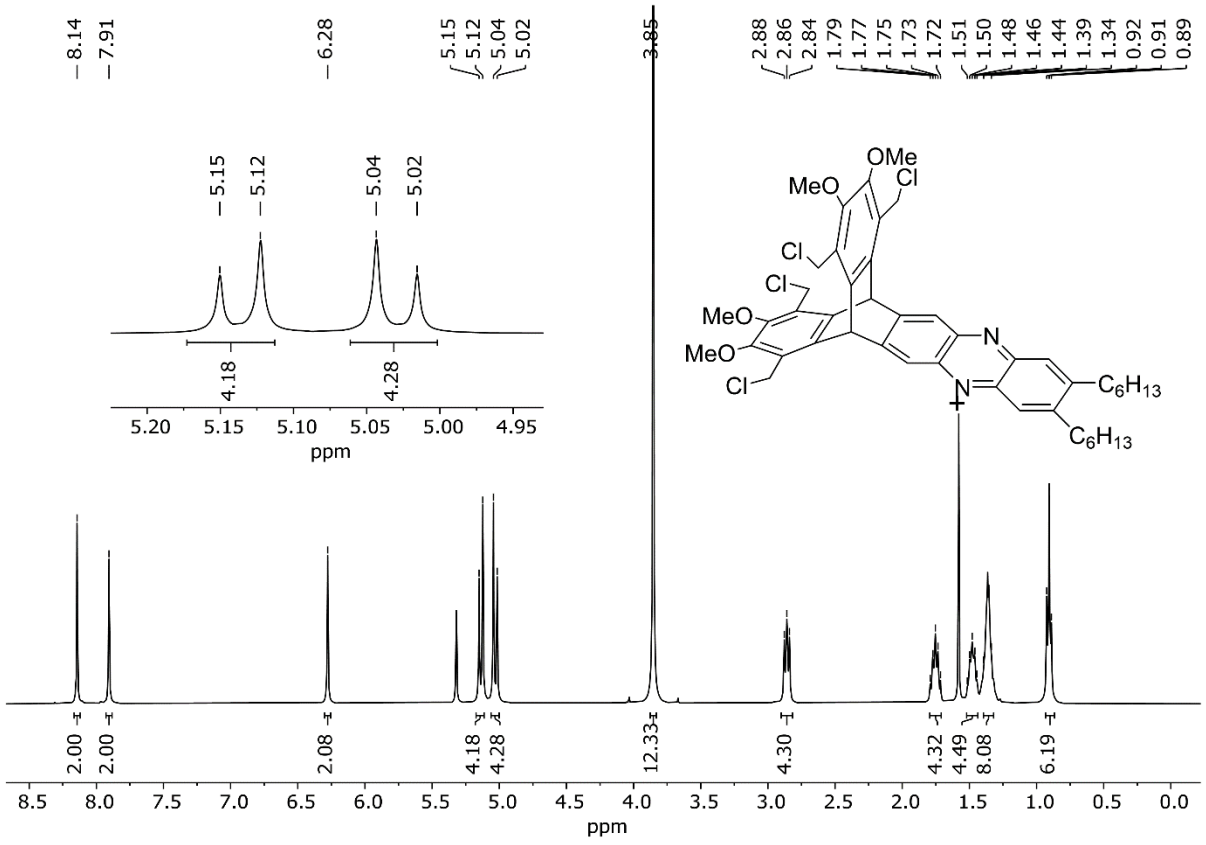


Figure S4: ^{1}H NMR Spectrum (CD_2Cl_2, 400 MHz) of **5**. Solvent residues: +: H_2O.

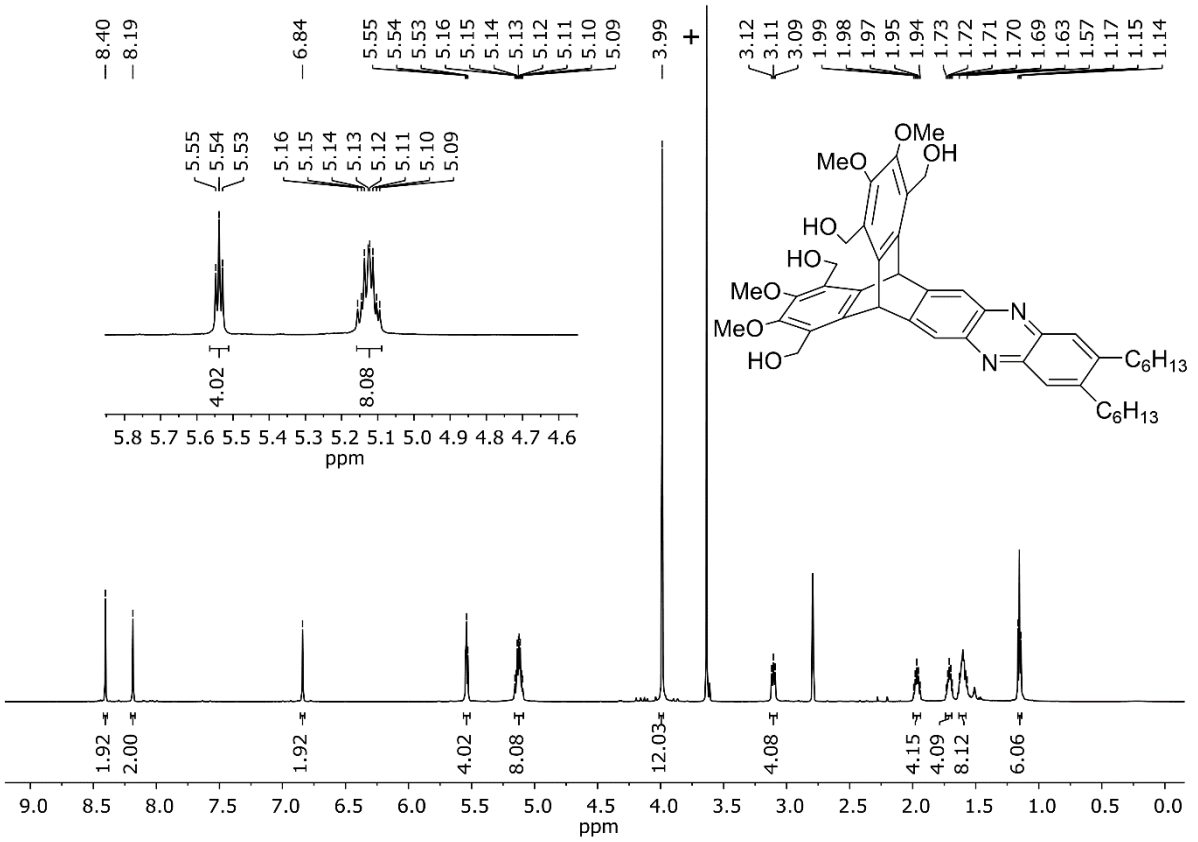


Figure S5: ^{1}H NMR Spectrum (DMSO-d_6, 600 MHz) of **6**. Solvent residues: +: H_2O.

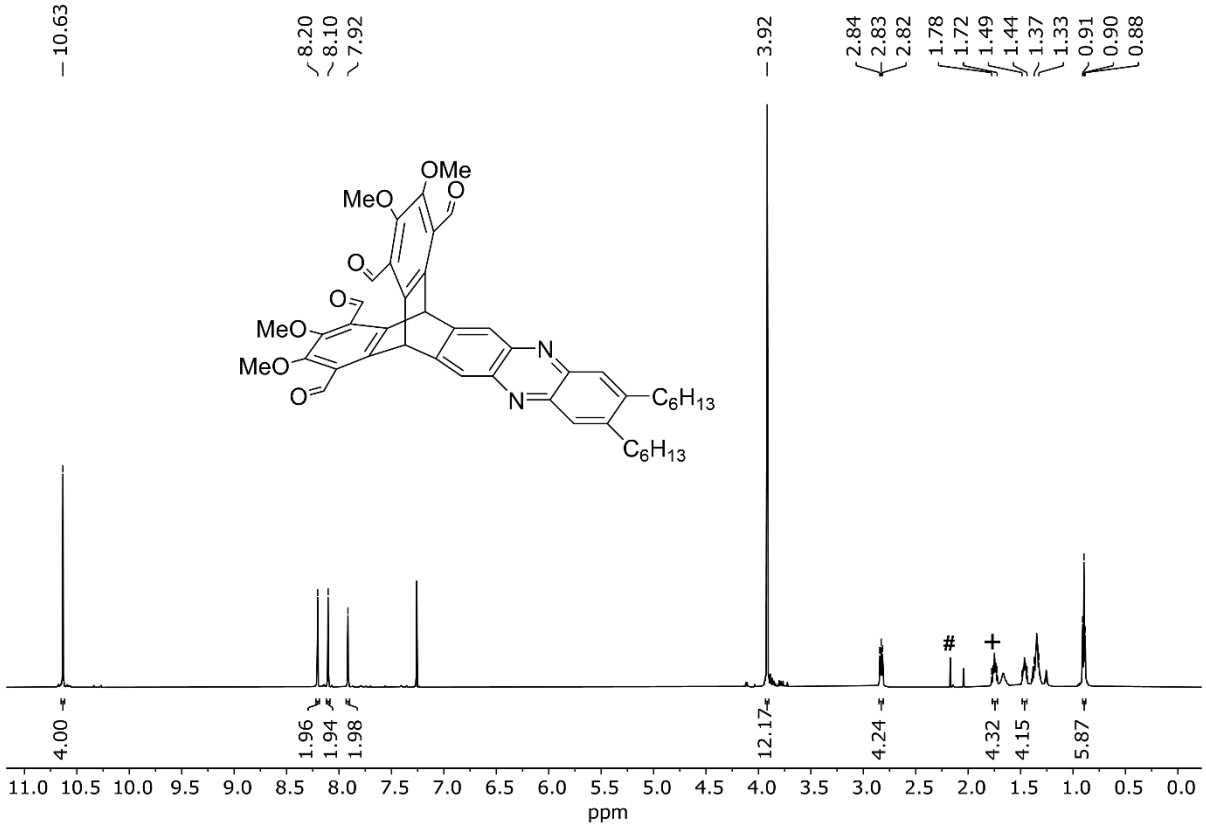


Figure S6: ^{1}H NMR Spectrum ($CDCl_3$, 600 MHz) of **7**. Solvent residues: +: H_2O, #: Acetone.

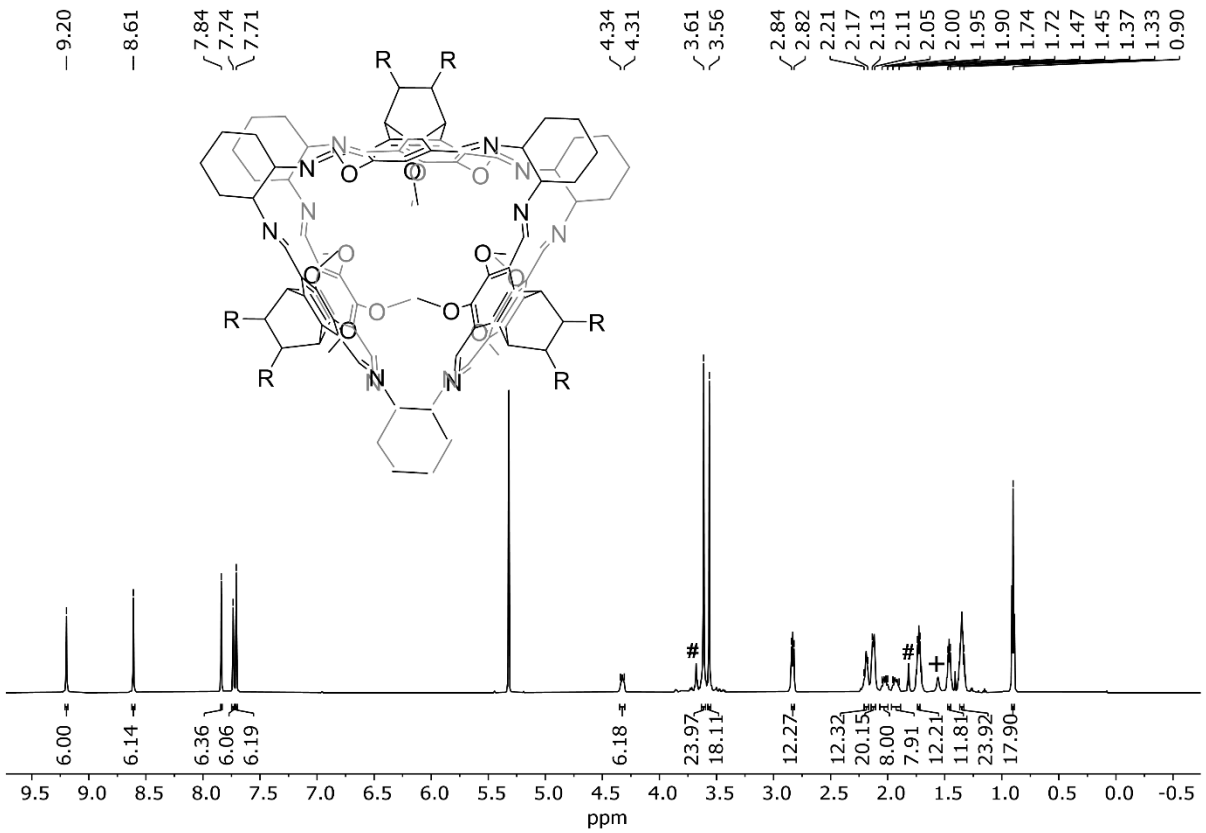


Figure S7: ^{1}H NMR Spectrum (CD_2Cl_2, 700 MHz) of **9**. Solvent residues: +: H_2O, #: THF.

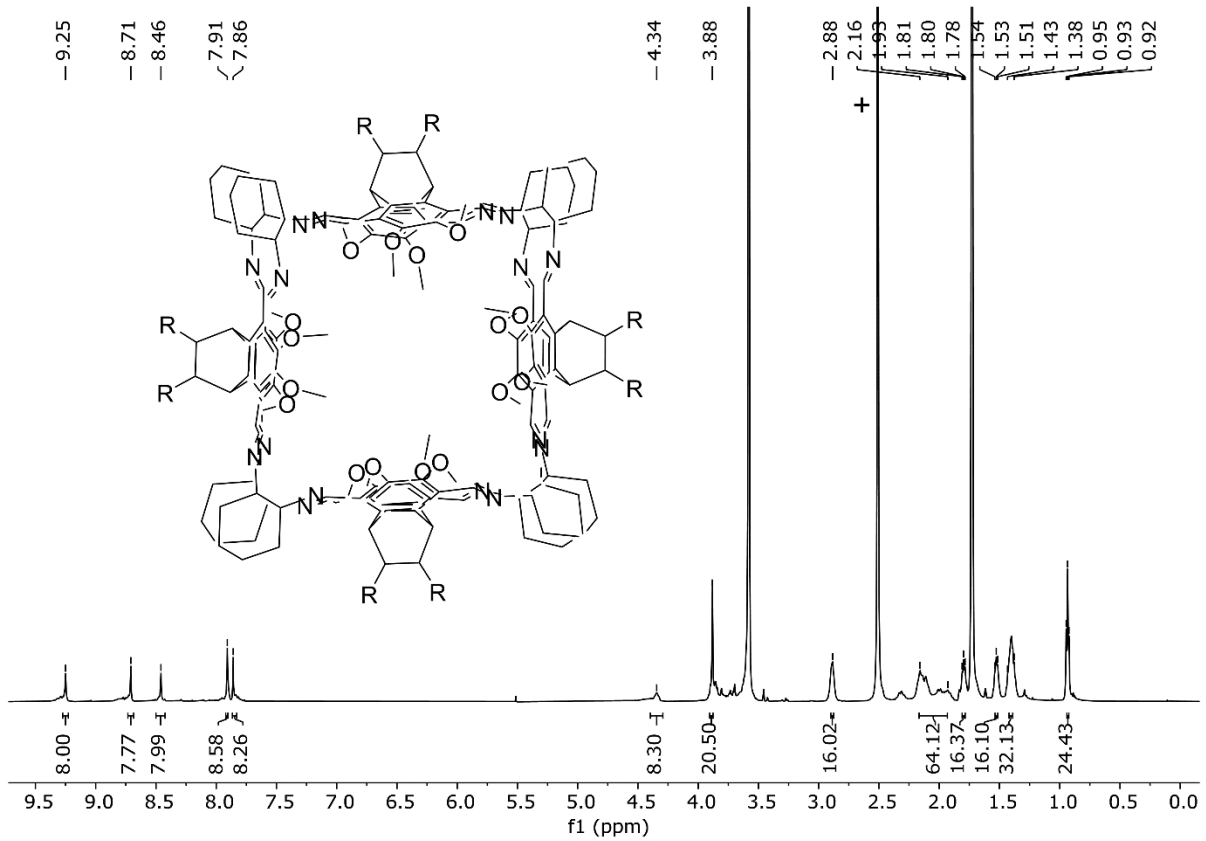


Figure S8: ^{1}H NMR Spectrum (THF-d_8, 600 MHz) of **10**. Solvent residues: +: H_2O.

3.2. ^{13}C NMR Spectra

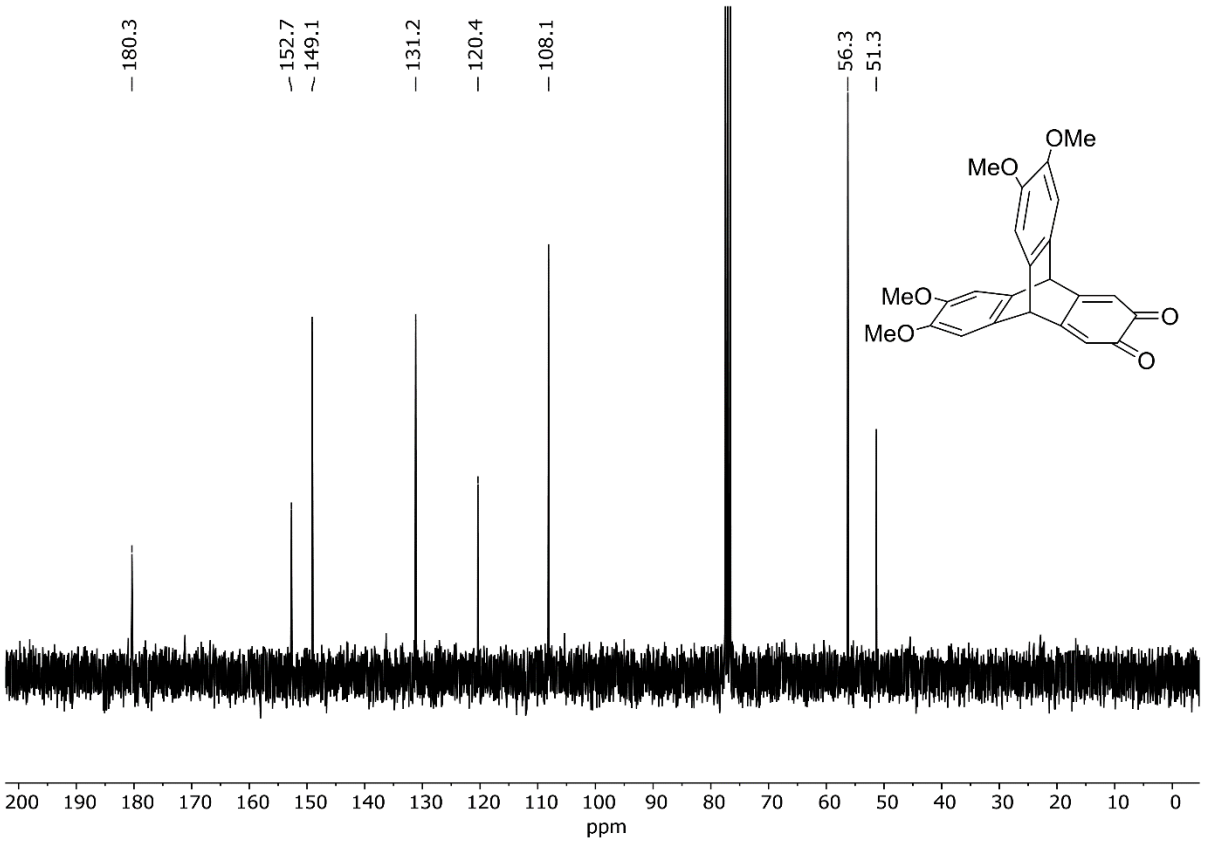


Figure S9: ^{13}C NMR Spectrum ($CDCl_3$, 75 MHz) of **2**.

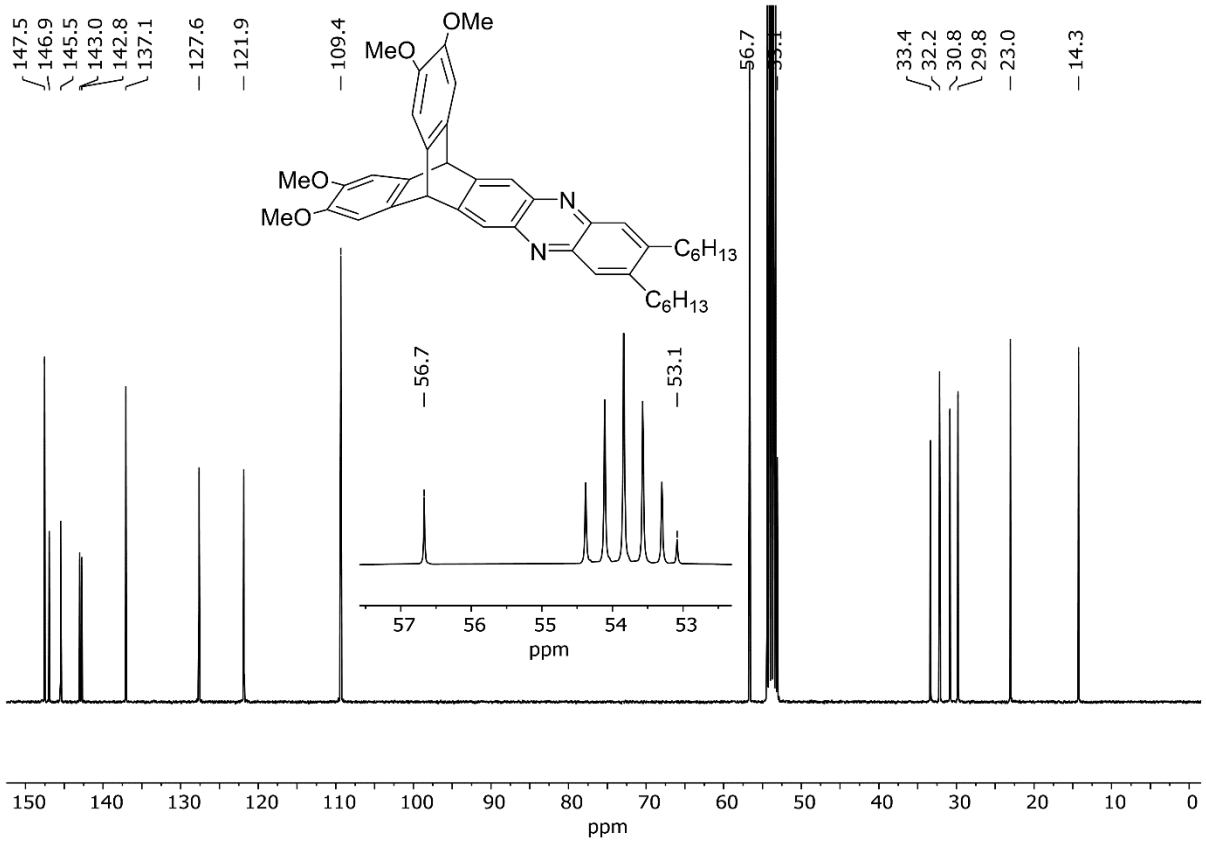


Figure S10: ^{13}C NMR Spectrum (CD_2Cl_2, 101 MHz) of **4**.

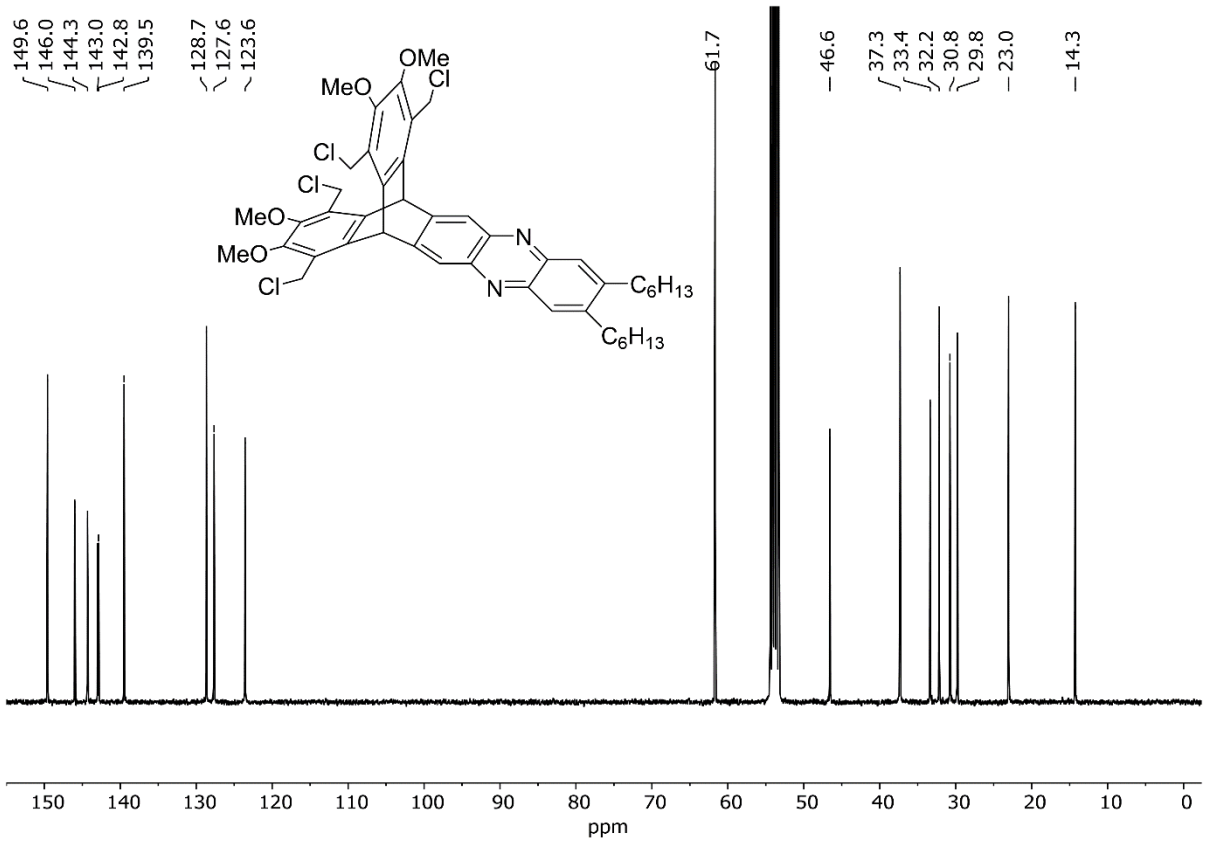


Figure S11: ^{13}C NMR Spectrum (CD_2Cl_2, 101 MHz) of **5**.

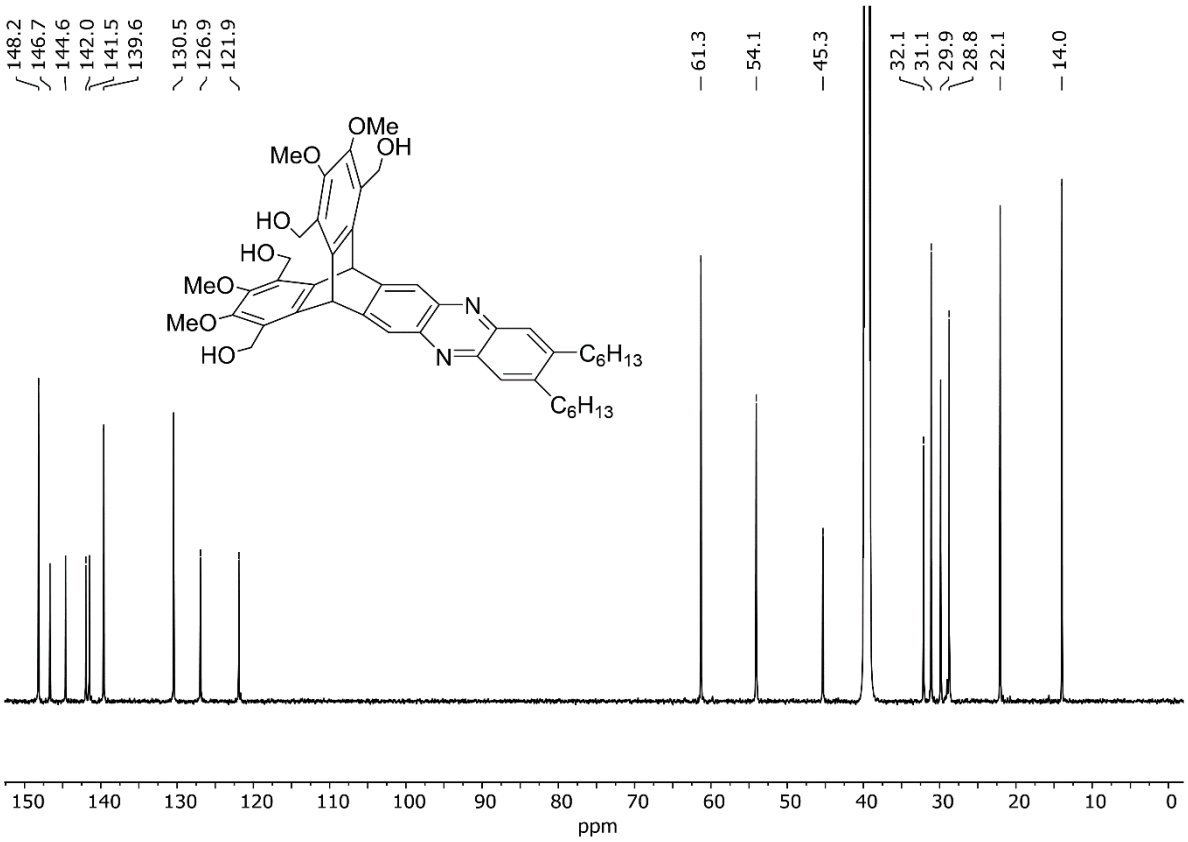


Figure S12: ^{13}C NMR Spectrum (DMSO-d_6, 151 MHz) of **6**.

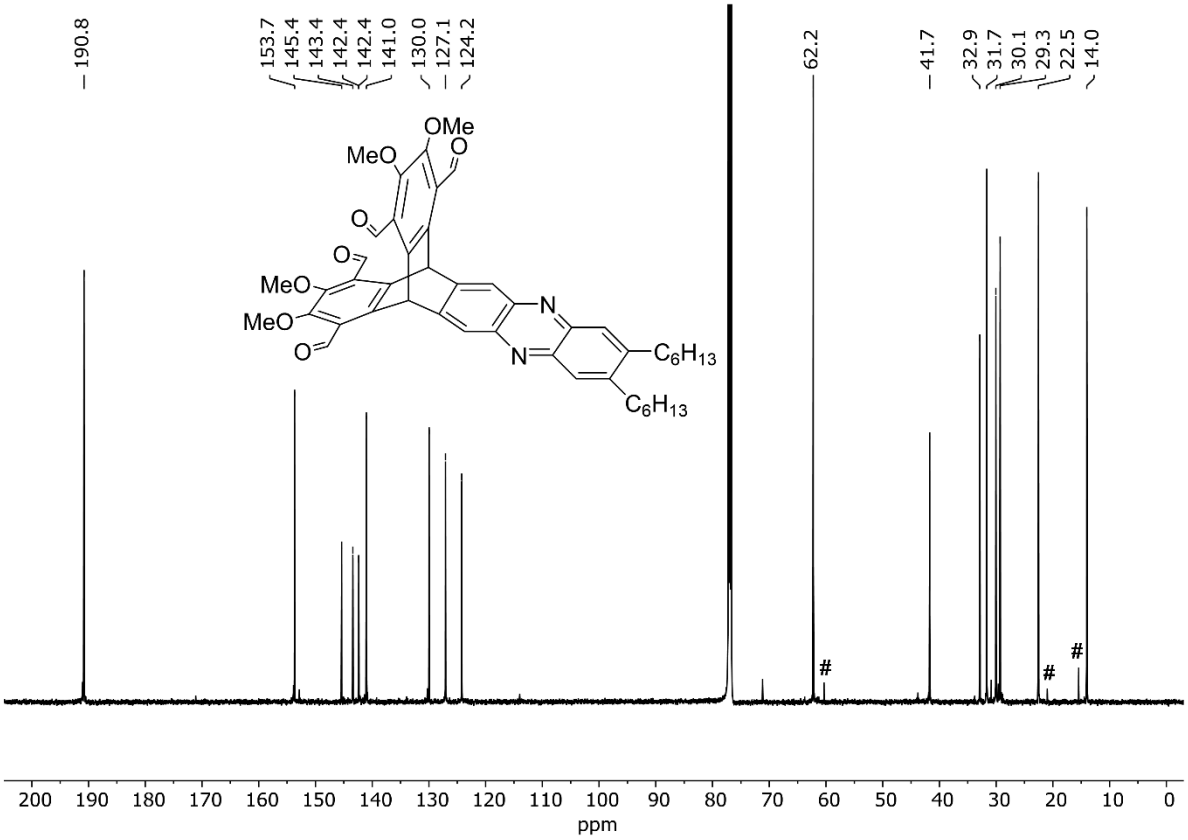


Figure S13: ^{13}C NMR Spectrum ($CDCl_3$, 151 MHz) of **7**. Solvent residues: #: EA.

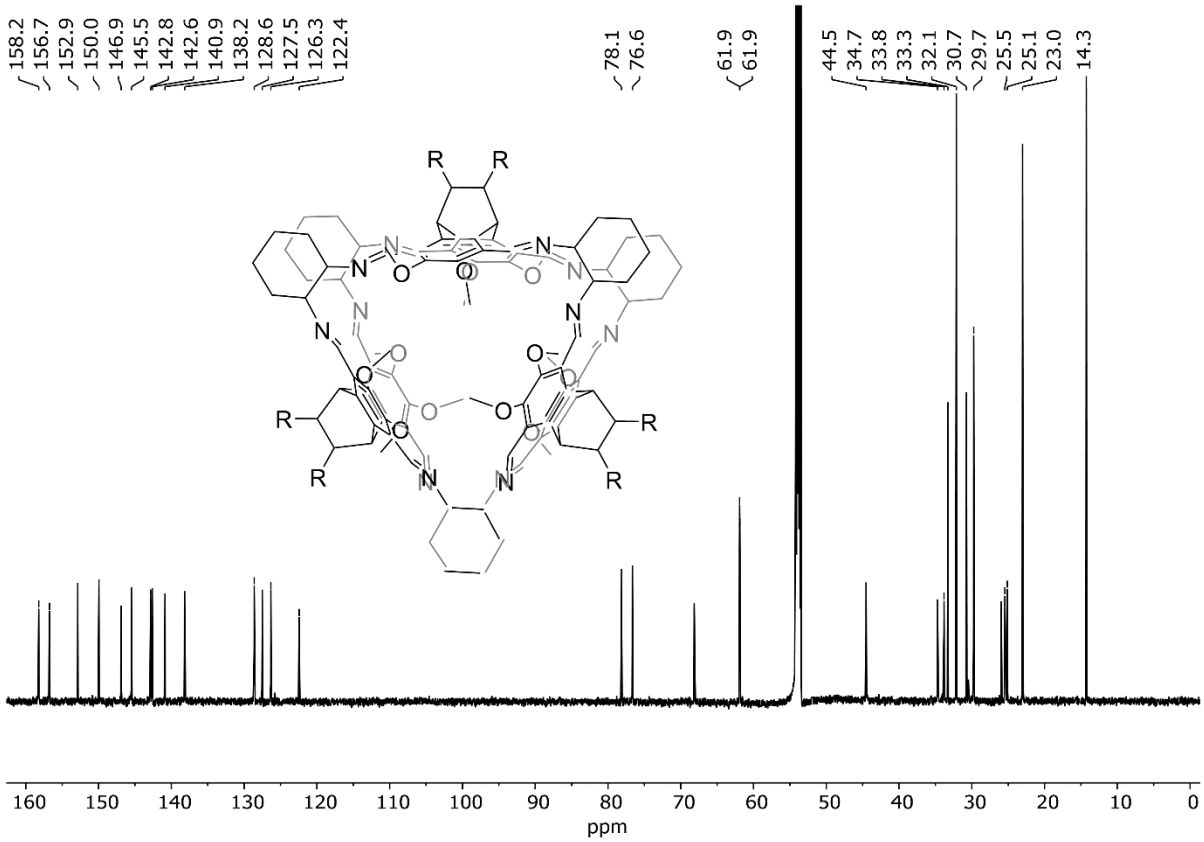


Figure S14: ^{13}C NMR Spectrum (CD_2Cl_2, 176 MHz) of **9**.

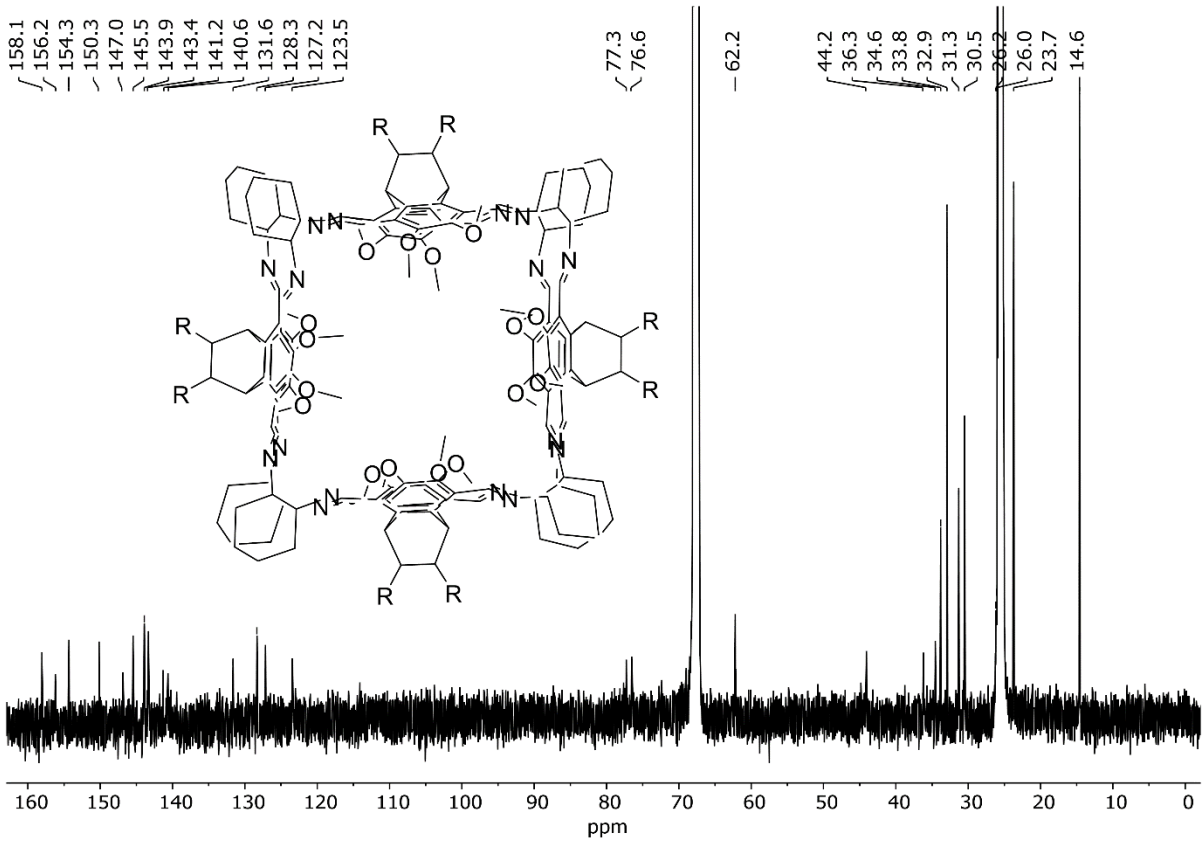


Figure S15: ^{13}C NMR Spectrum (THF-d_8, 151 MHz) of **10** (not pure).

3.3. 2D NMR Spectra

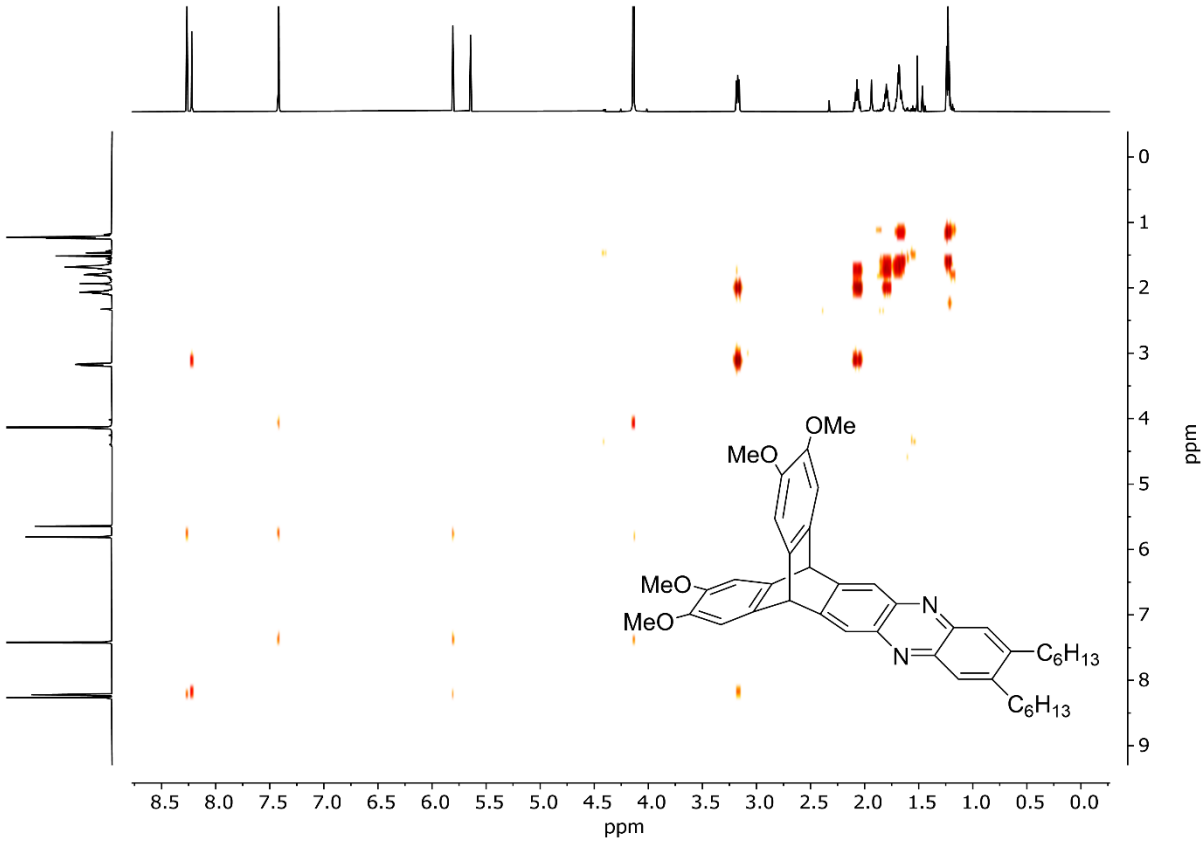


Figure S16: ^{1}H,^{1}H-COSY Spectrum (CD_2Cl_2, 600MHz) of **4**.

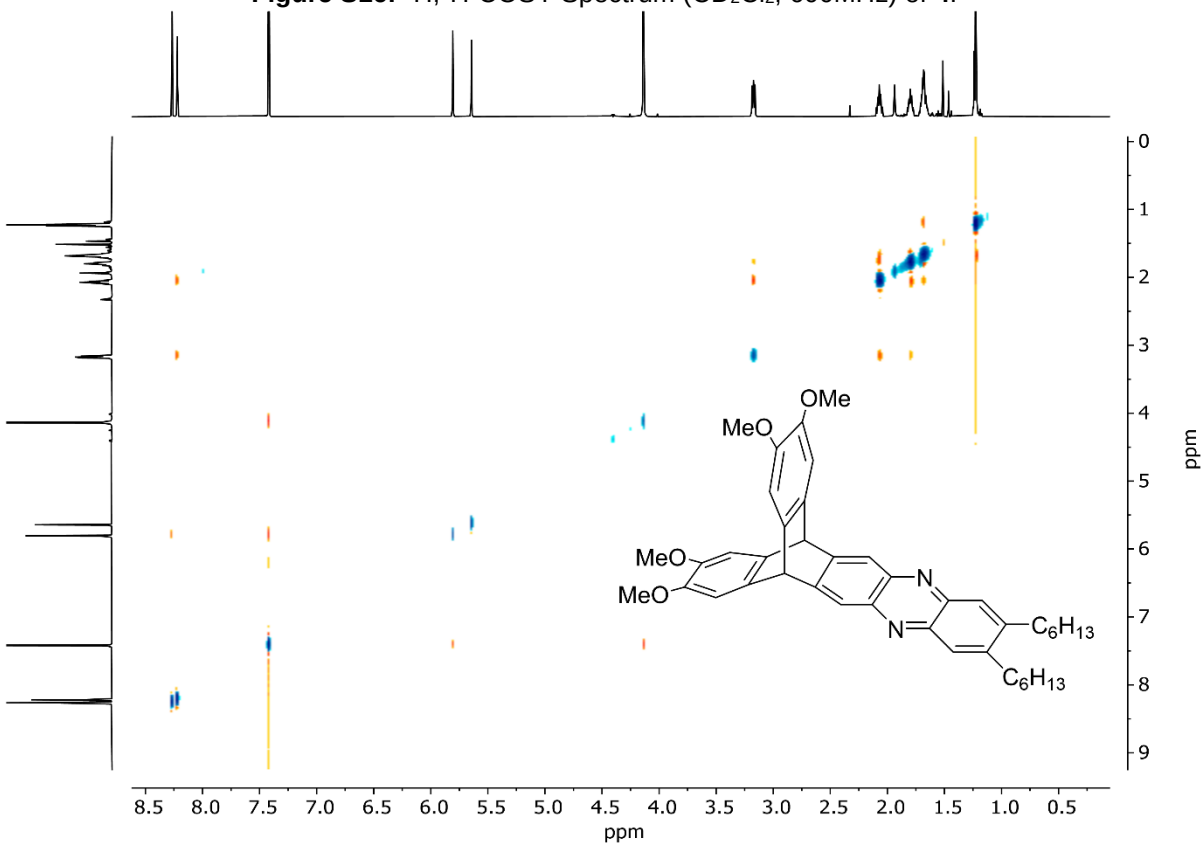


Figure S17: ^{1}H,^{1}H-ROESY Spectrum (CD_2Cl_2, 600MHz) of **4**.

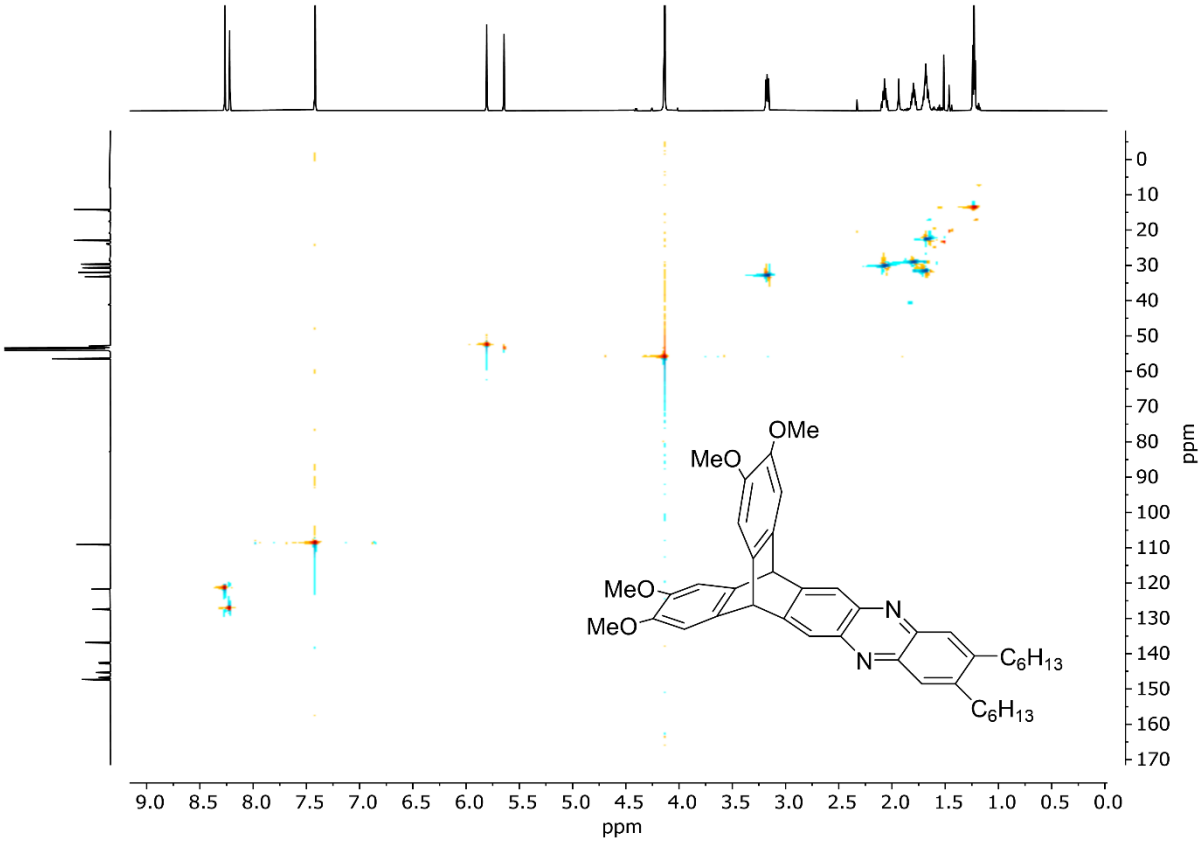


Figure S18: $^{1}H,^{13}C$-HSQC Spectrum (CD_2Cl_2, 600MHz, 151 MHz) of **4**.

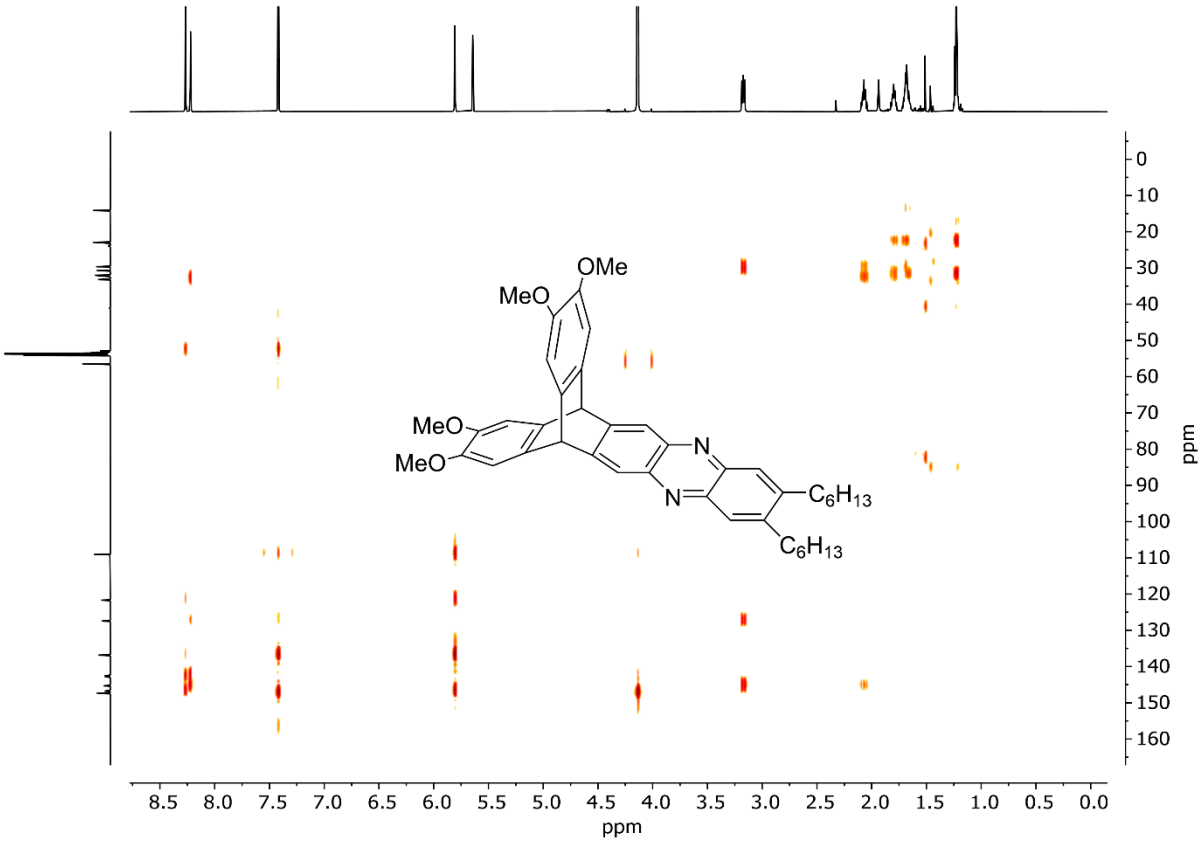


Figure S19: $^{1}H,^{13}C$-HMBC Spectrum (CD_2Cl_2, 600MHz, 151 MHz) of **4**.

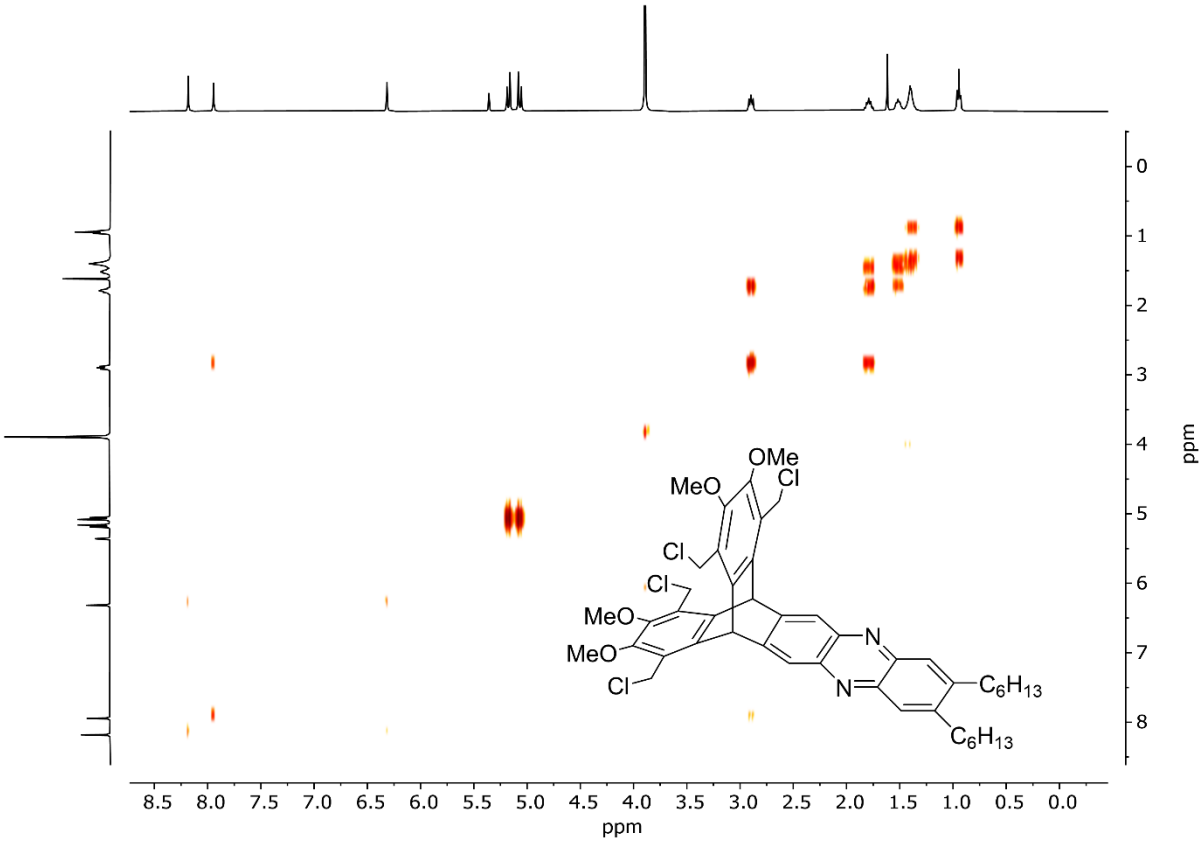


Figure S20: $^{1}H,^{1}H$-COSY Spectrum (CD_2Cl_2, 400MHz) of **5**.

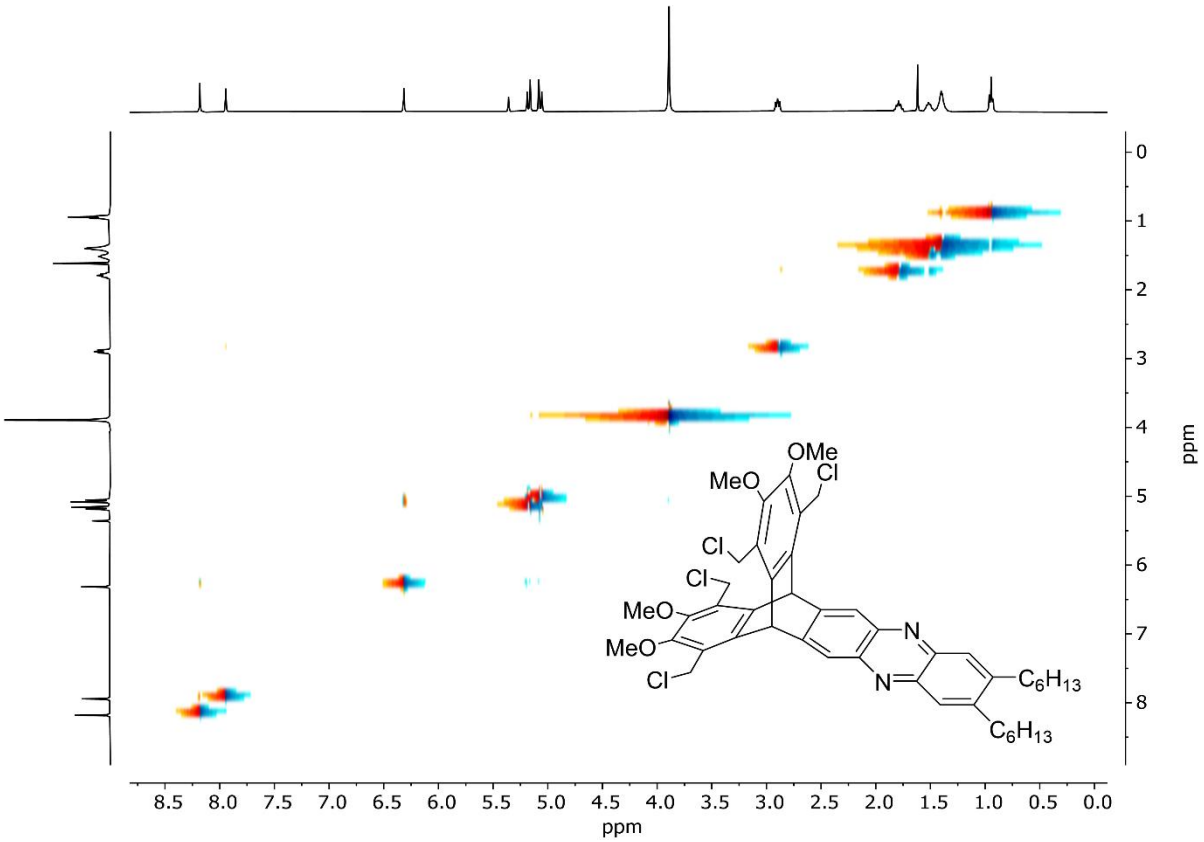


Figure S21: $^{1}H,^{1}H$-ROESY Spectrum (CD_2Cl_2, 400MHz) of **5**.

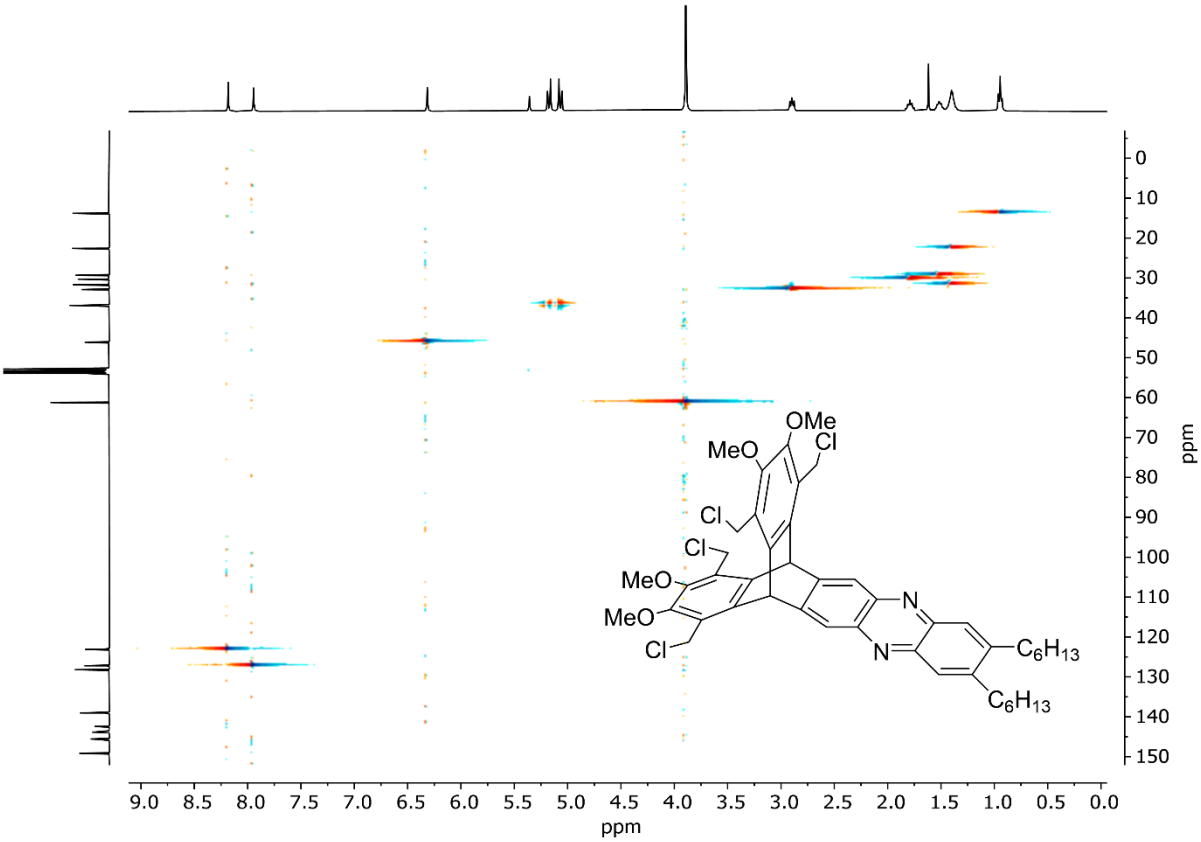


Figure S22: $^{1}H,^{13}C$-HSQC Spectrum (CD_2Cl_2, 400MHz, 101MHz) of **5**.

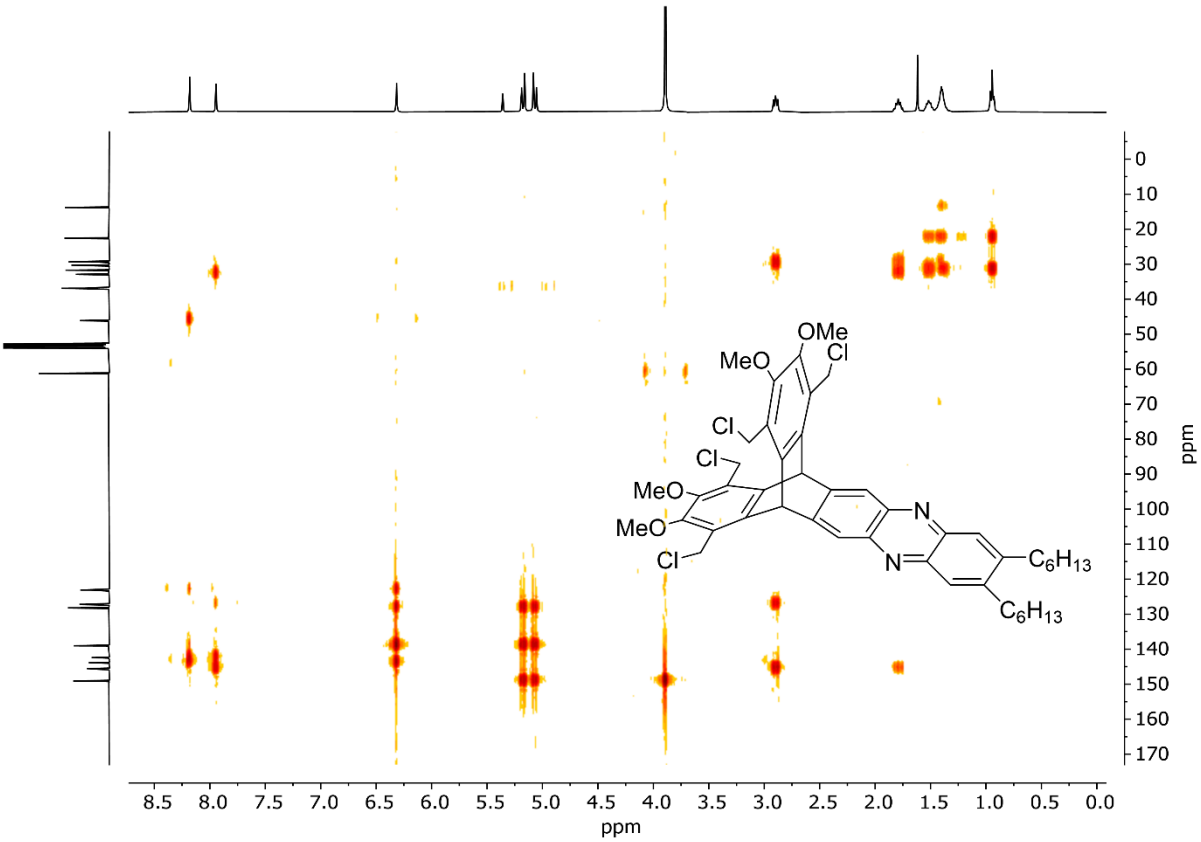


Figure S23: $^{1}H,^{13}C$-HMBC Spectrum (CD_2Cl_2, 400MHz, 101MHz) of **5**.

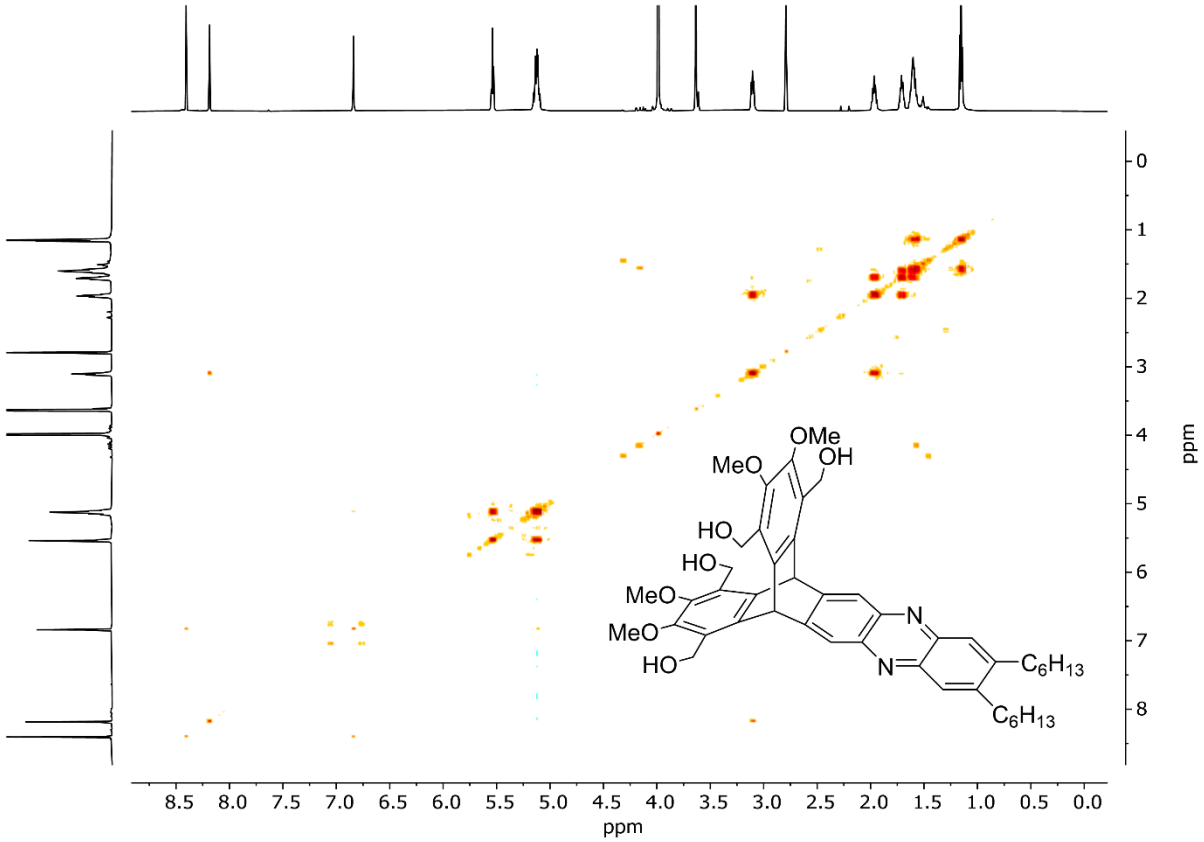


Figure S24: ^{1}H,^{1}H-COSY Spectrum (DMSO-d_6, 600MHz) of **6**.

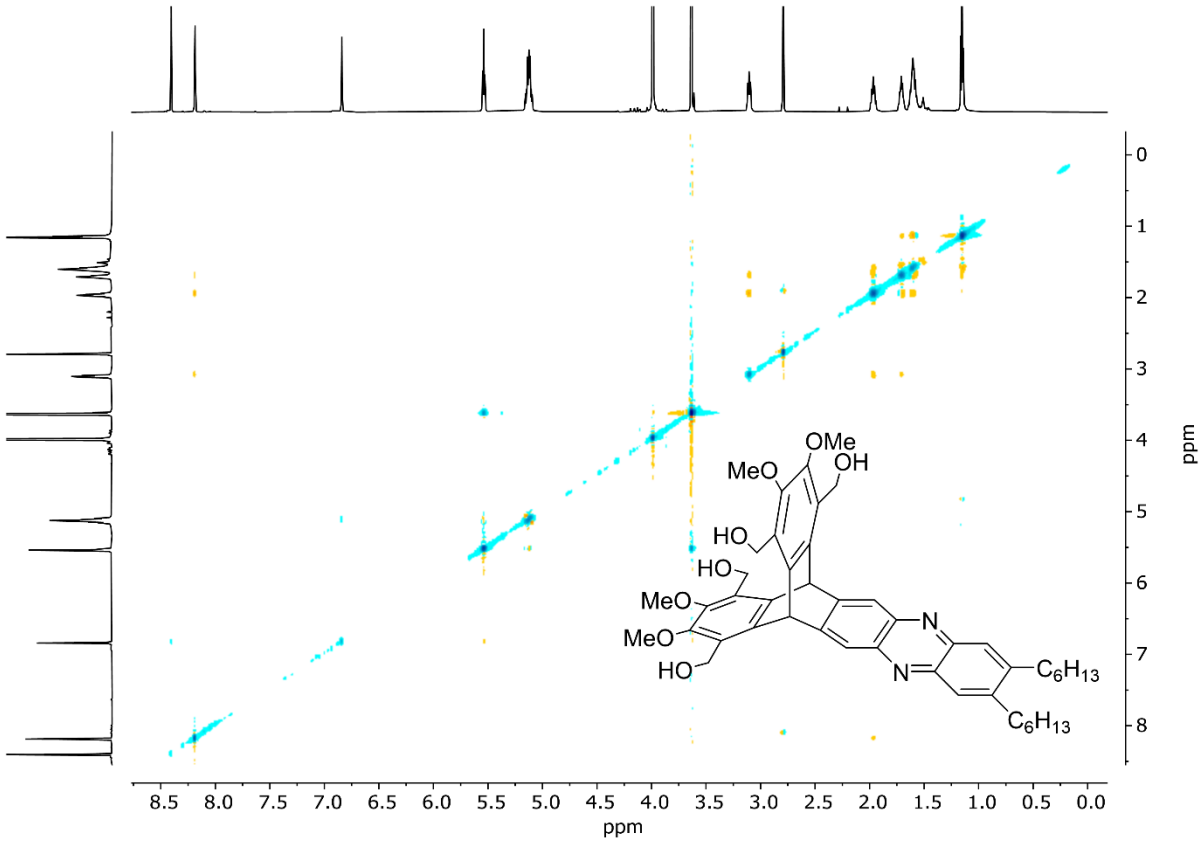


Figure S25: ^{1}H,^{1}H-ROESY Spectrum (DMSO-d_6, 600MHz) of **6**.

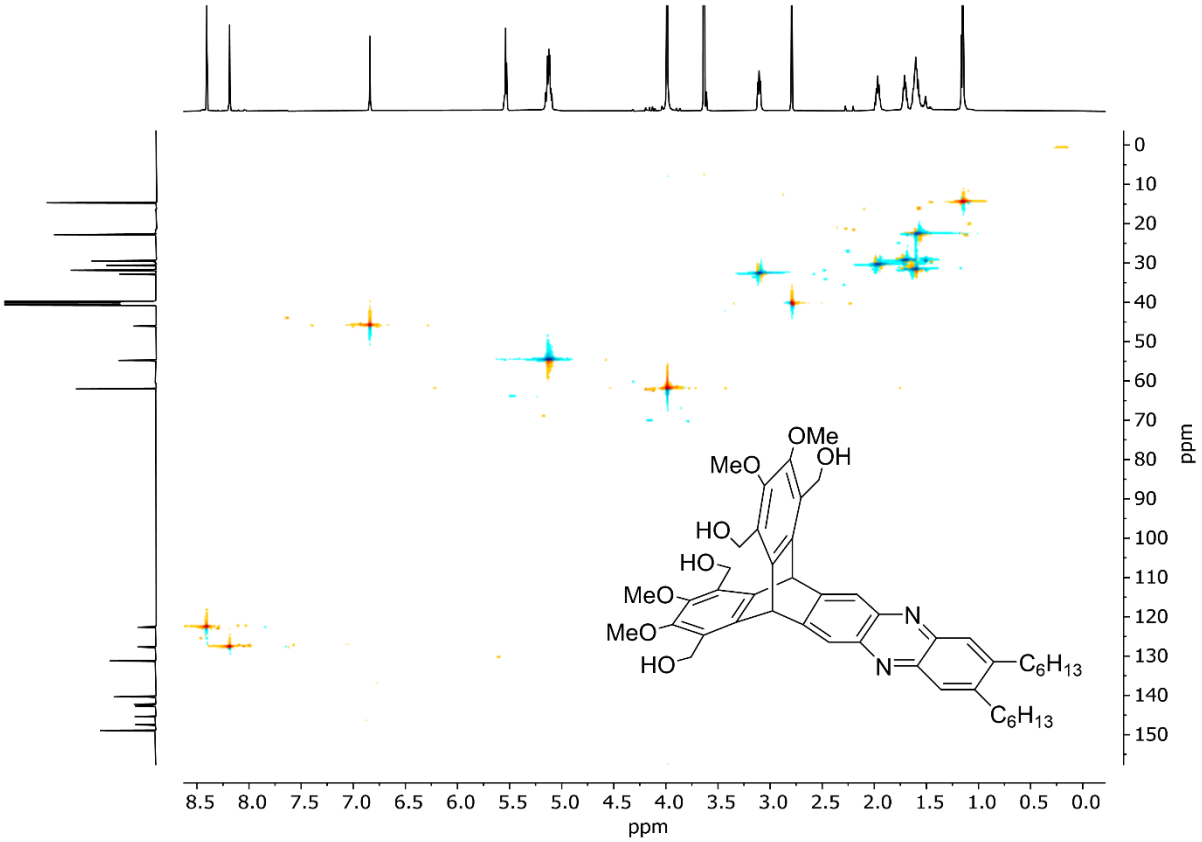


Figure S26: $^{1}H,^{13}C$-HSQC Spectrum (DMSO-d_6, 600MHz, 151MHz) of **6**.

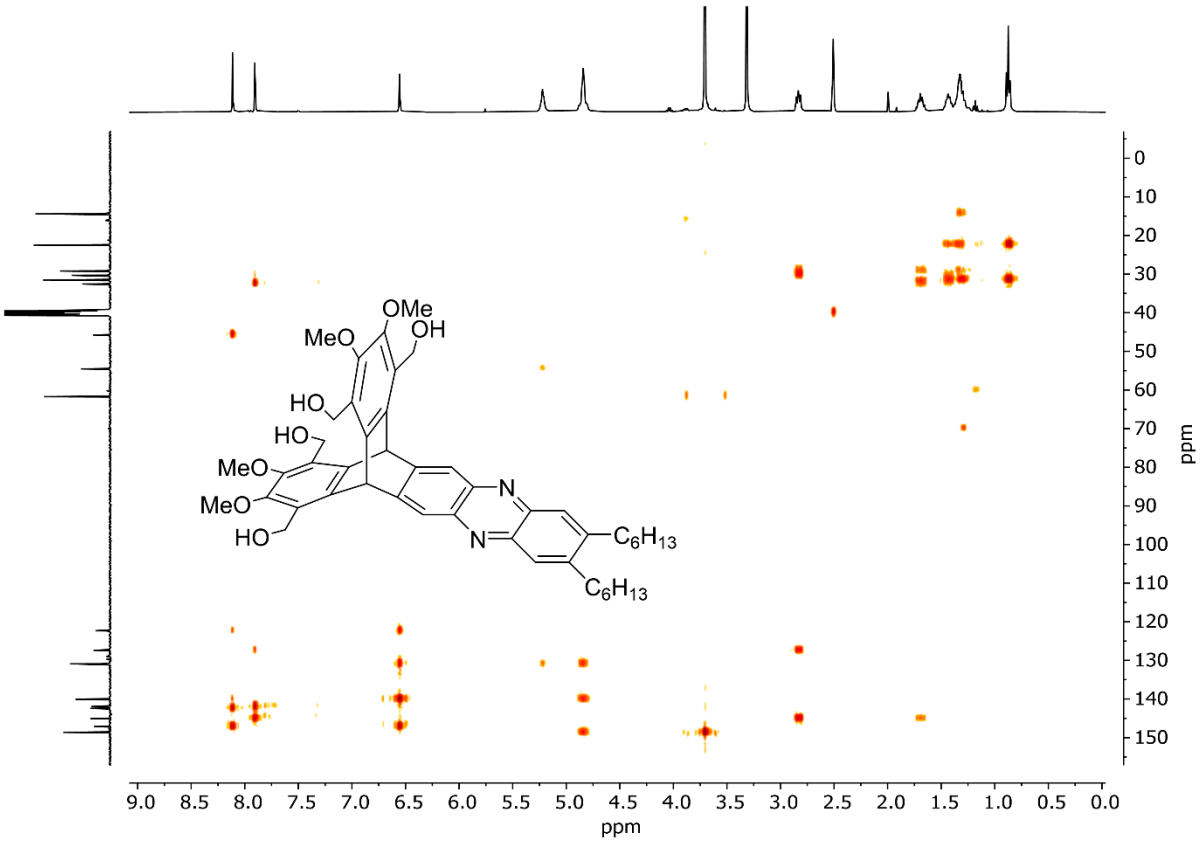


Figure S27: $^{1}H,^{13}C$-HMBC Spectrum (DMSO-d_6, 400MHz, 101MHz) of **6**.

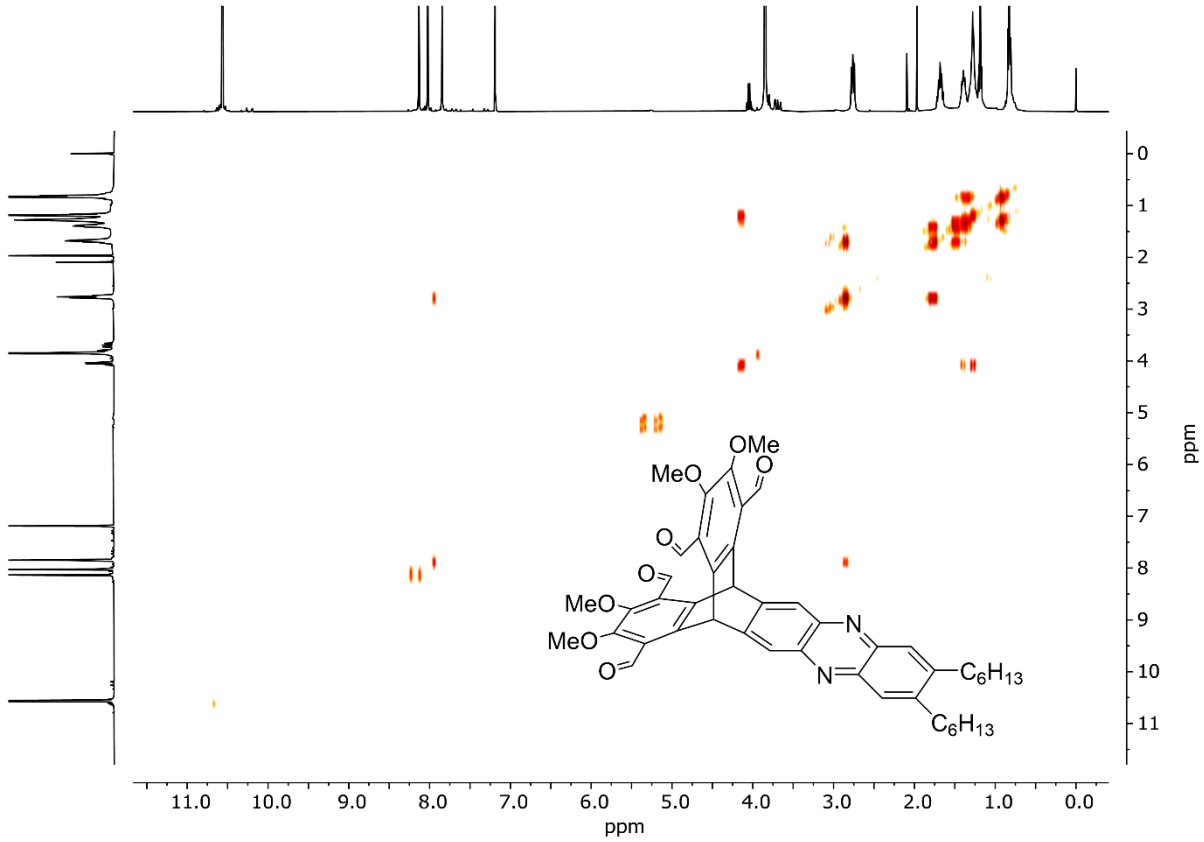


Figure S28: $^{1}H,^{1}H$-COSY Spectrum ($CDCl_3$, 600MHz) of 7.

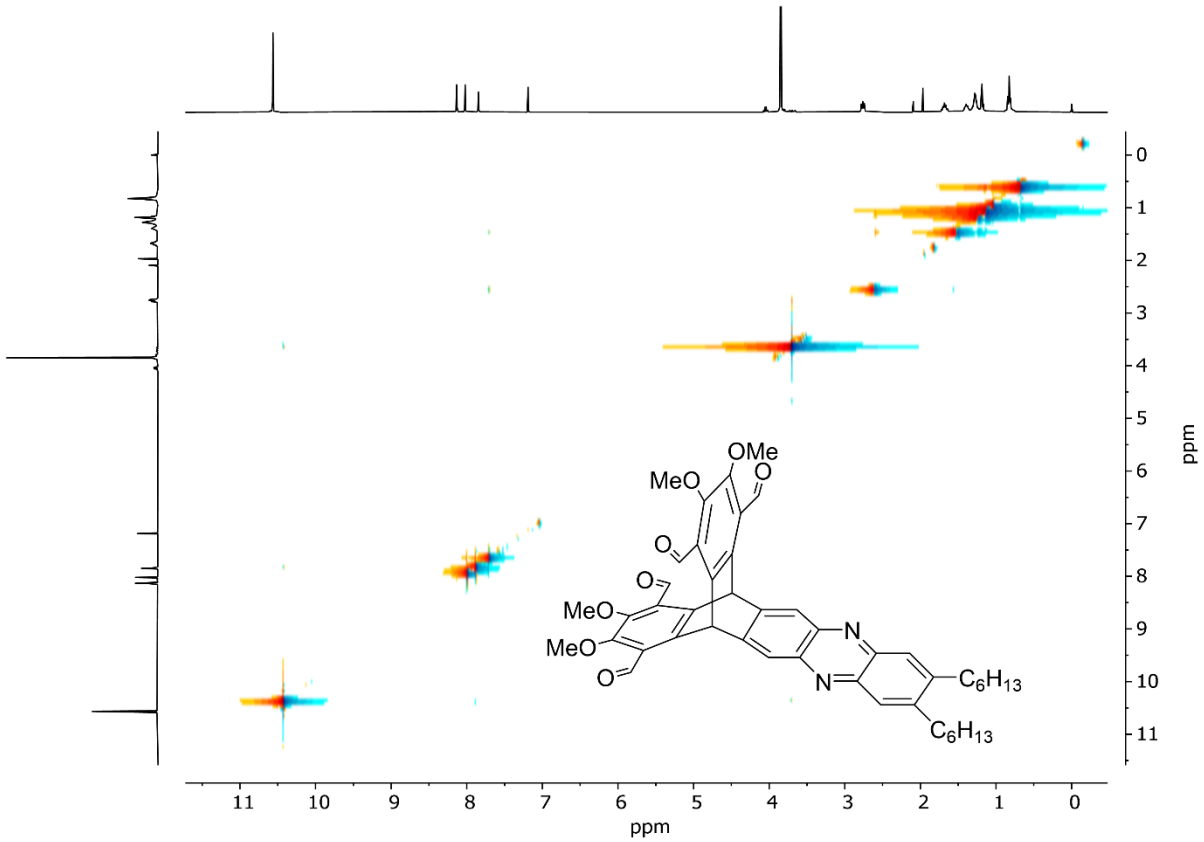


Figure S29: $^{1}H,^{1}H$-ROESY Spectrum ($CDCl_3$, 400MHz) of **7**.

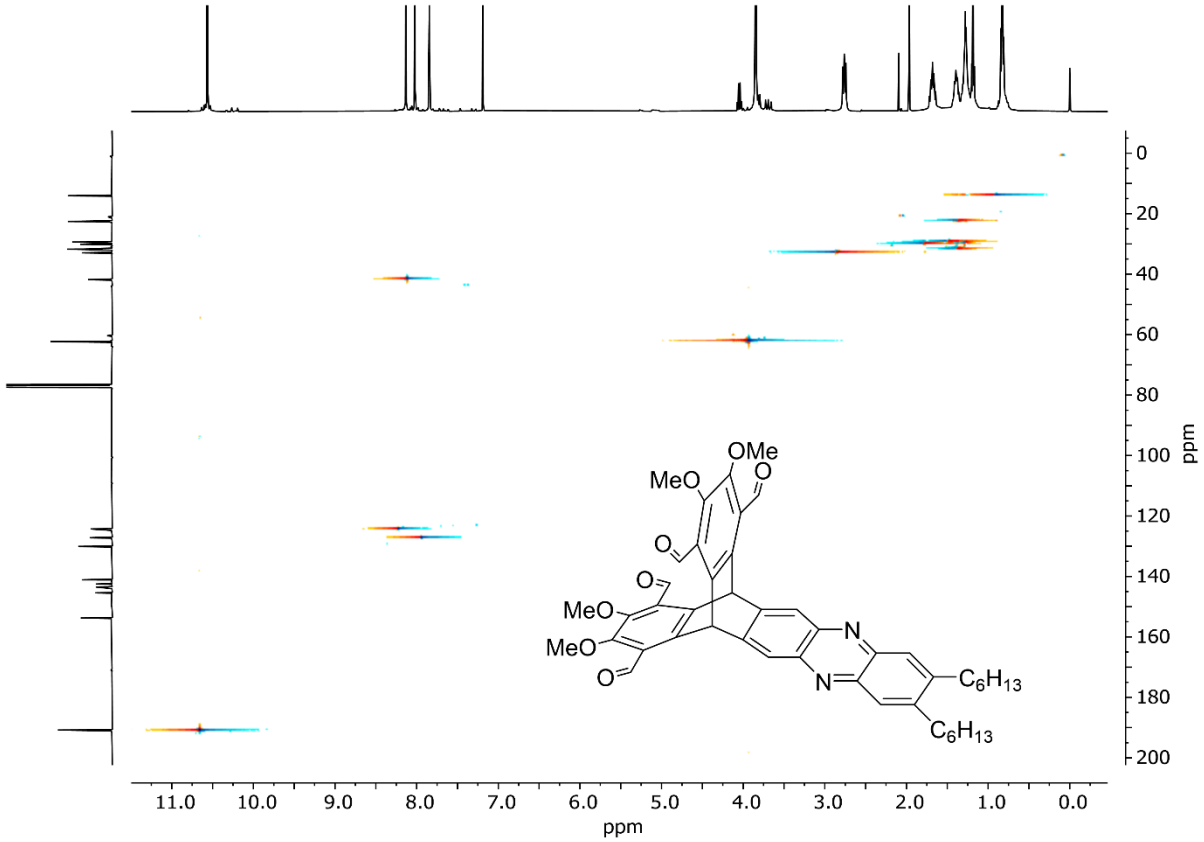


Figure S30: $^{1}H,^{13}C$-HSQC Spectrum ($CDCl_3$, 400MHz, 101MHz) of 7.

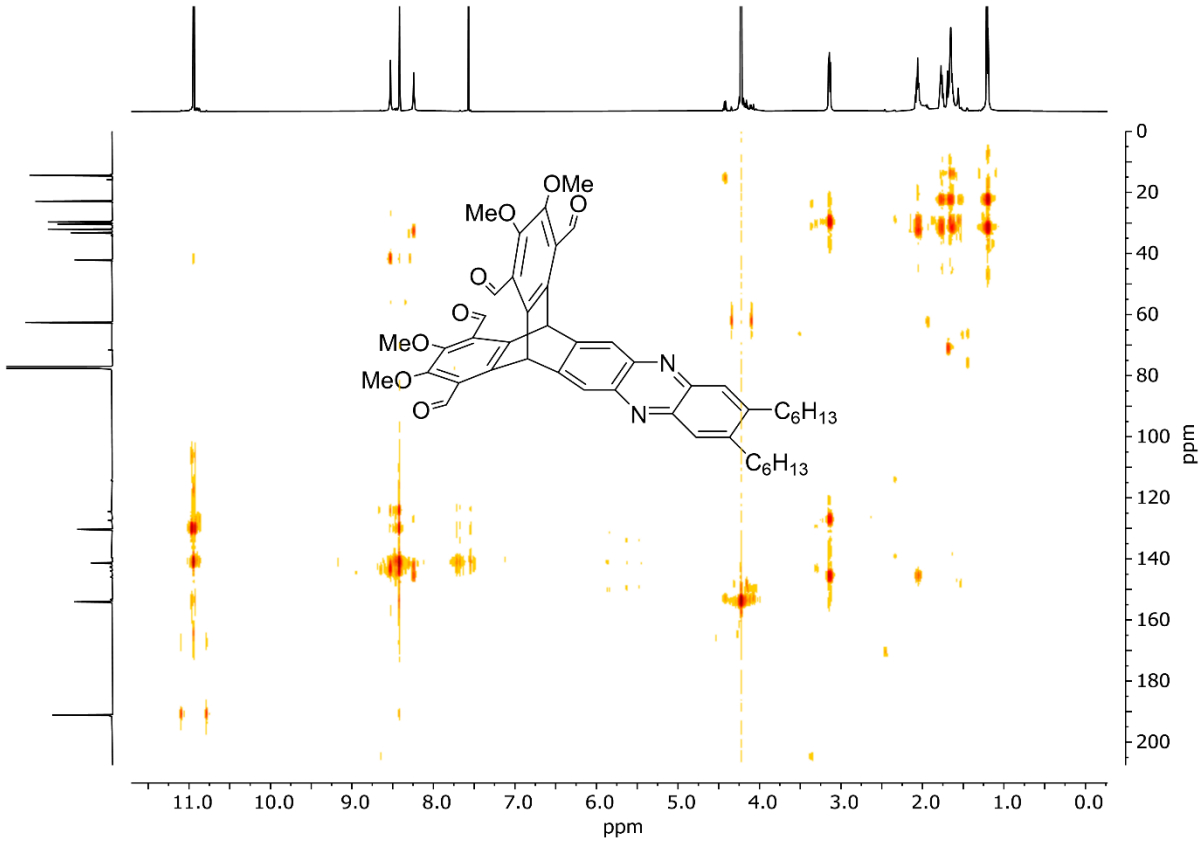


Figure S31: $^{1}H,^{13}C$-HMBC Spectrum ($CDCl_3$, 400MHz, 101MHz) of **7**.

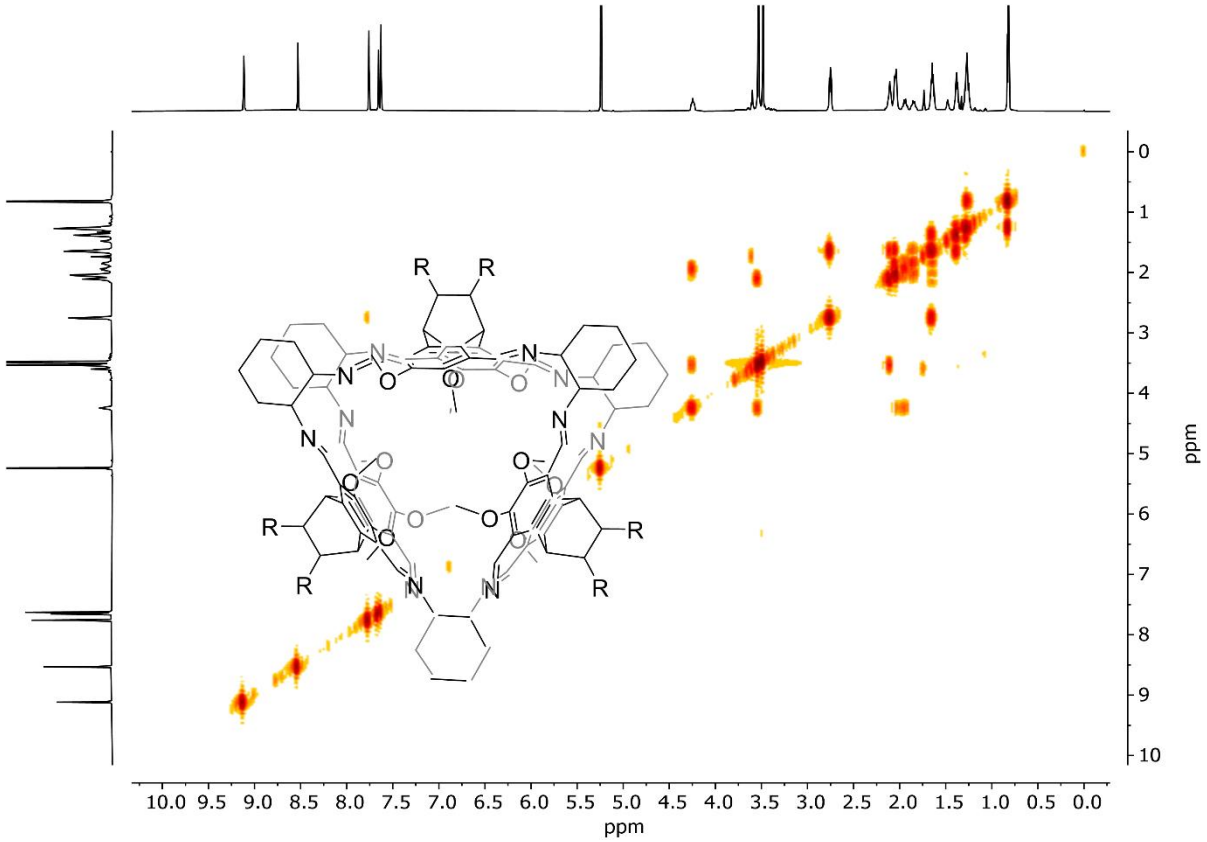


Figure S32: $^{1}H,^{1}H$-COSY Spectrum (CD_2Cl_2, 700MHz) of **9**.

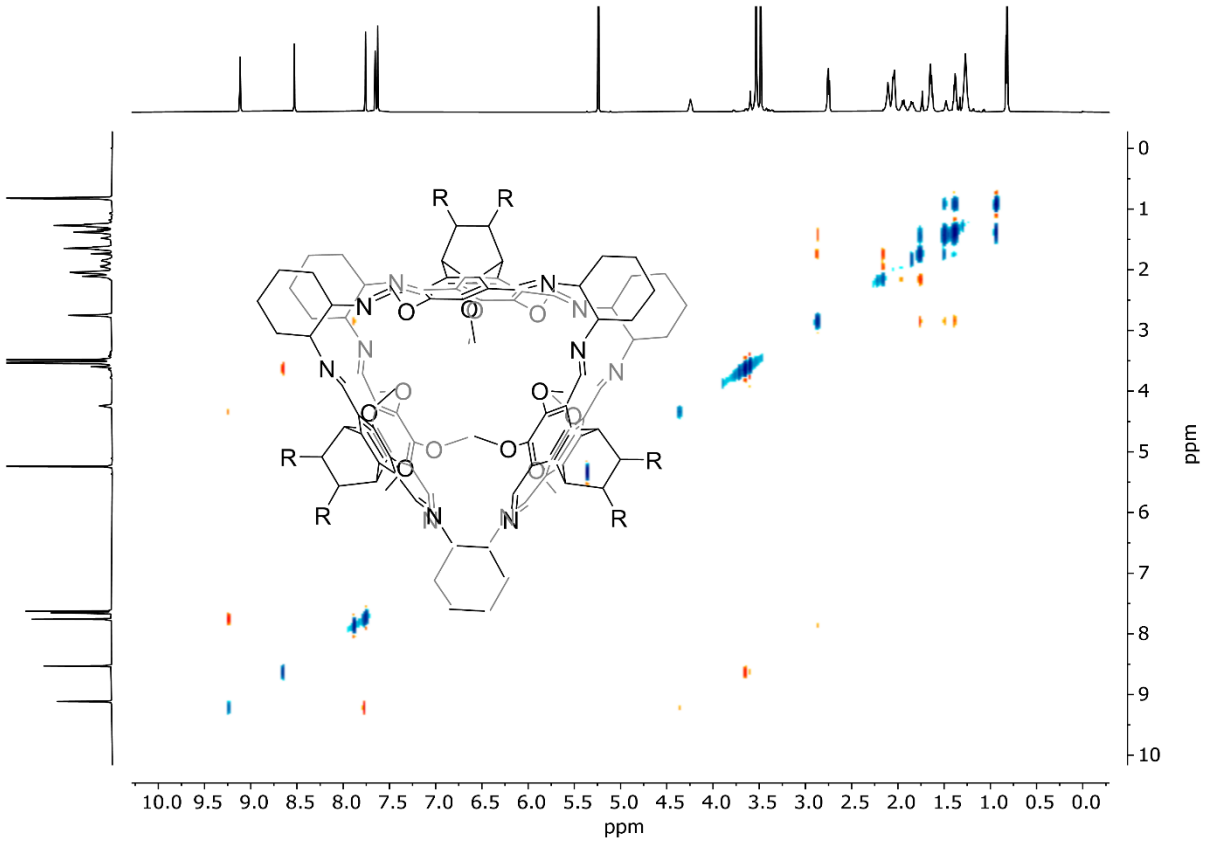


Figure S33: $^{1}H,^{1}H$-ROESY Spectrum (CD_2Cl_2, 700MHz) of **9**.

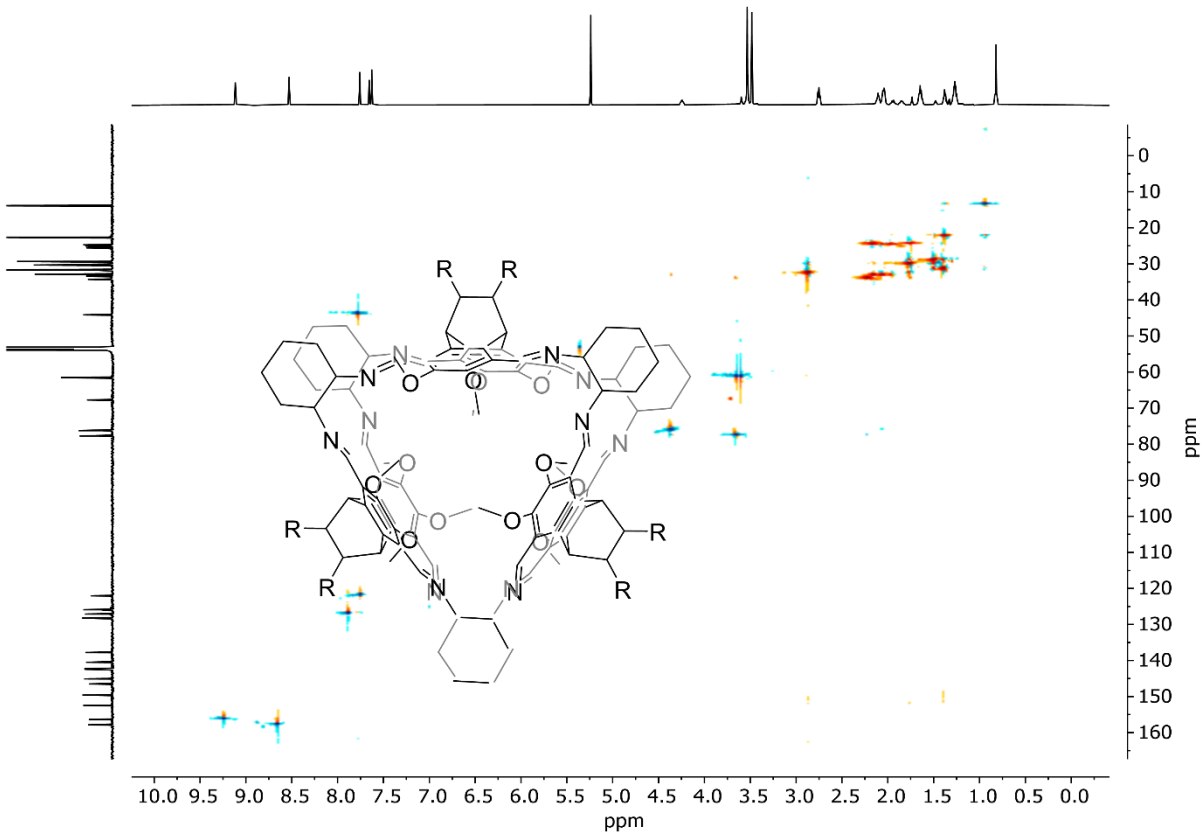


Figure S34: $^{1}H,^{13}C$-HSQC Spectrum (CD_2Cl_2, 700MHz, 176MHz) of **9**.

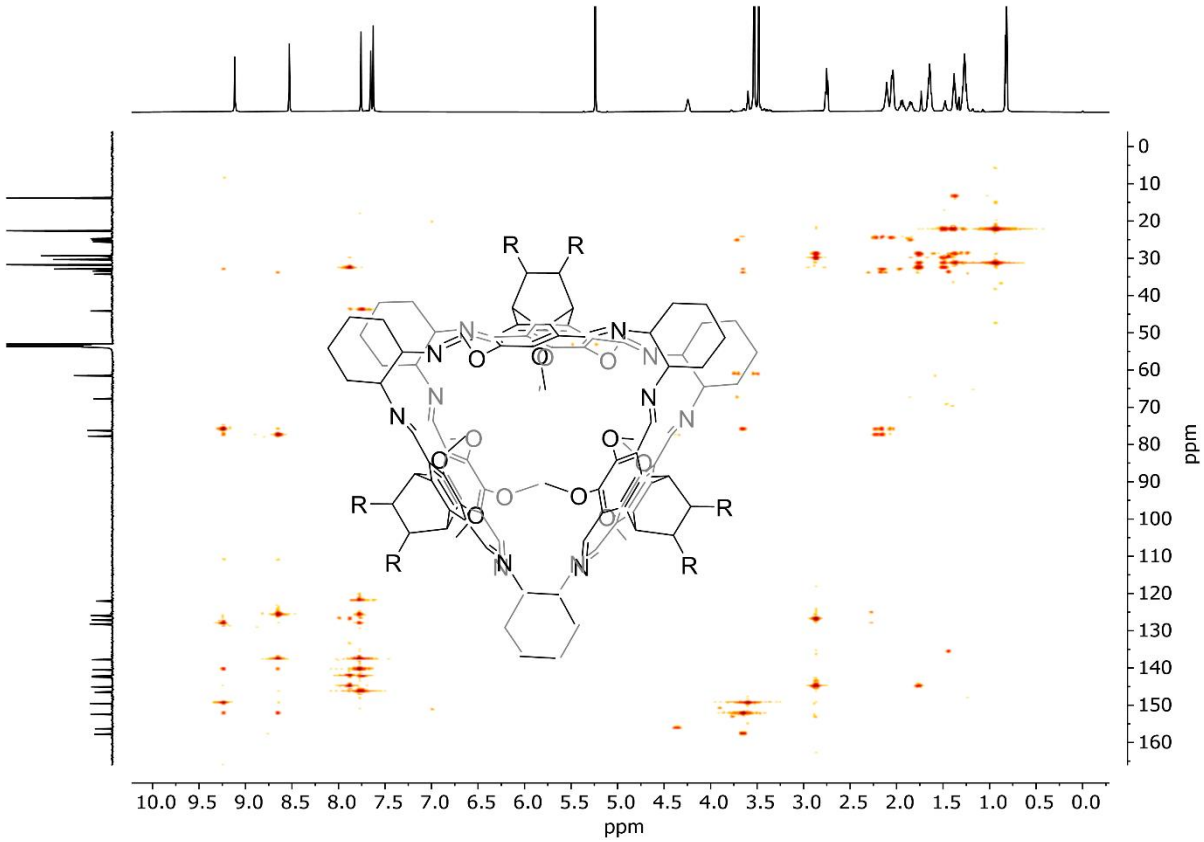


Figure S35: $^{1}H,^{13}C$-HMBC Spectrum (CD_2Cl_2, 700MHz, 176MHz) of **9**.

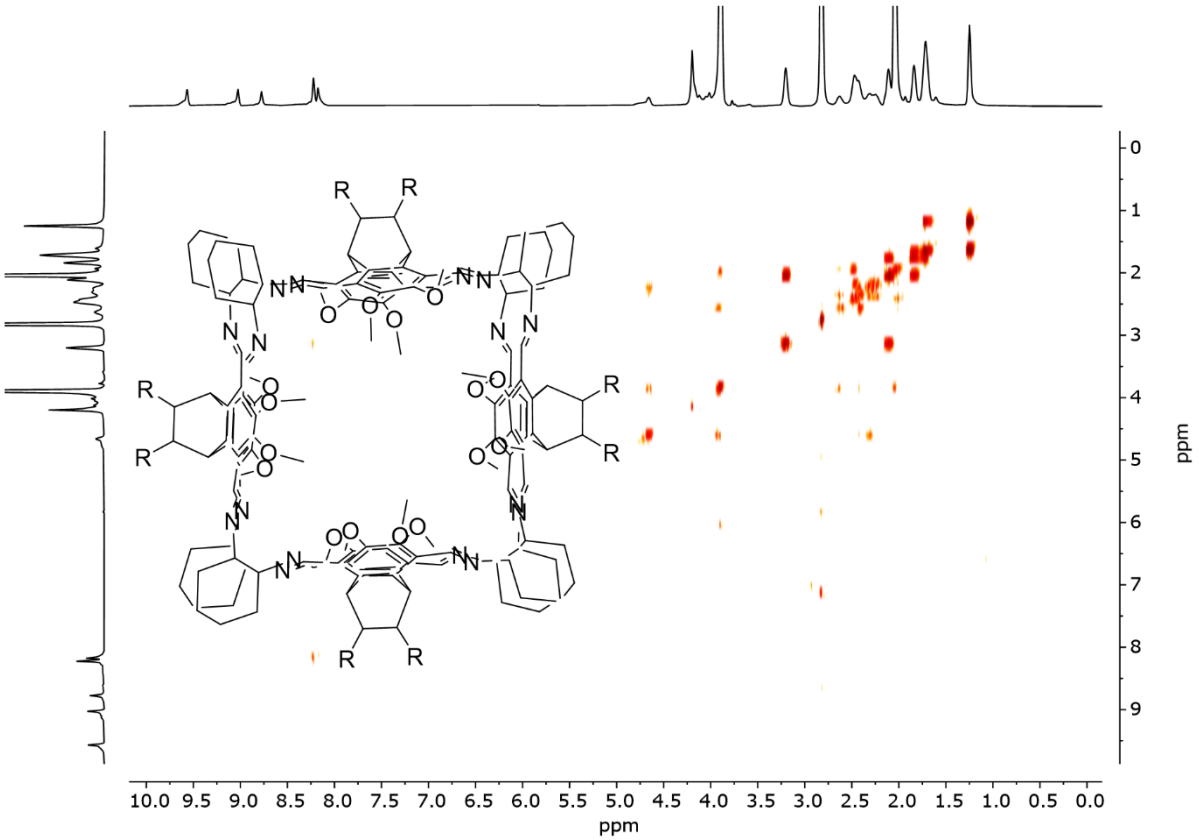


Figure S36: $^{1}H,^{1}H$-COSY Spectrum (THF-d_8, 600MHz) of **10**.

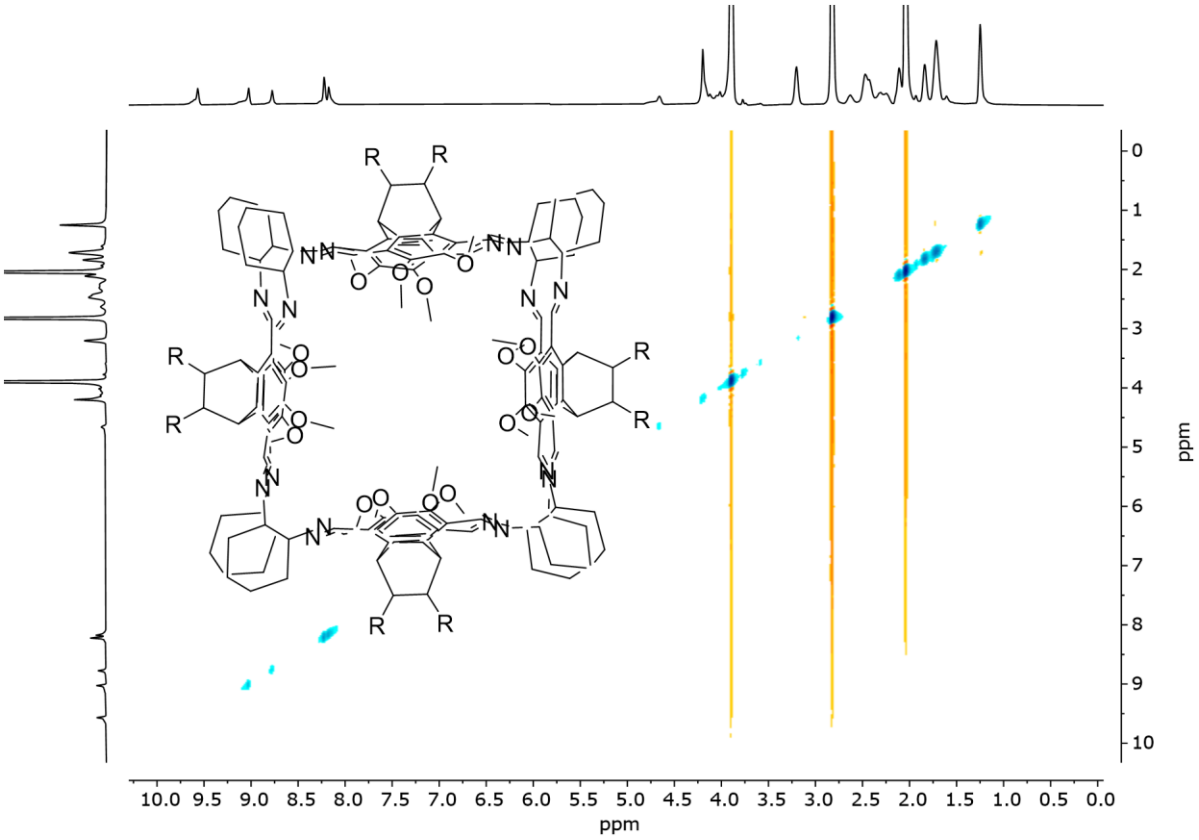


Figure S37: $^{1}H,^{1}H$-ROESY Spectrum (THF-d_8, 600MHz) of **10**.

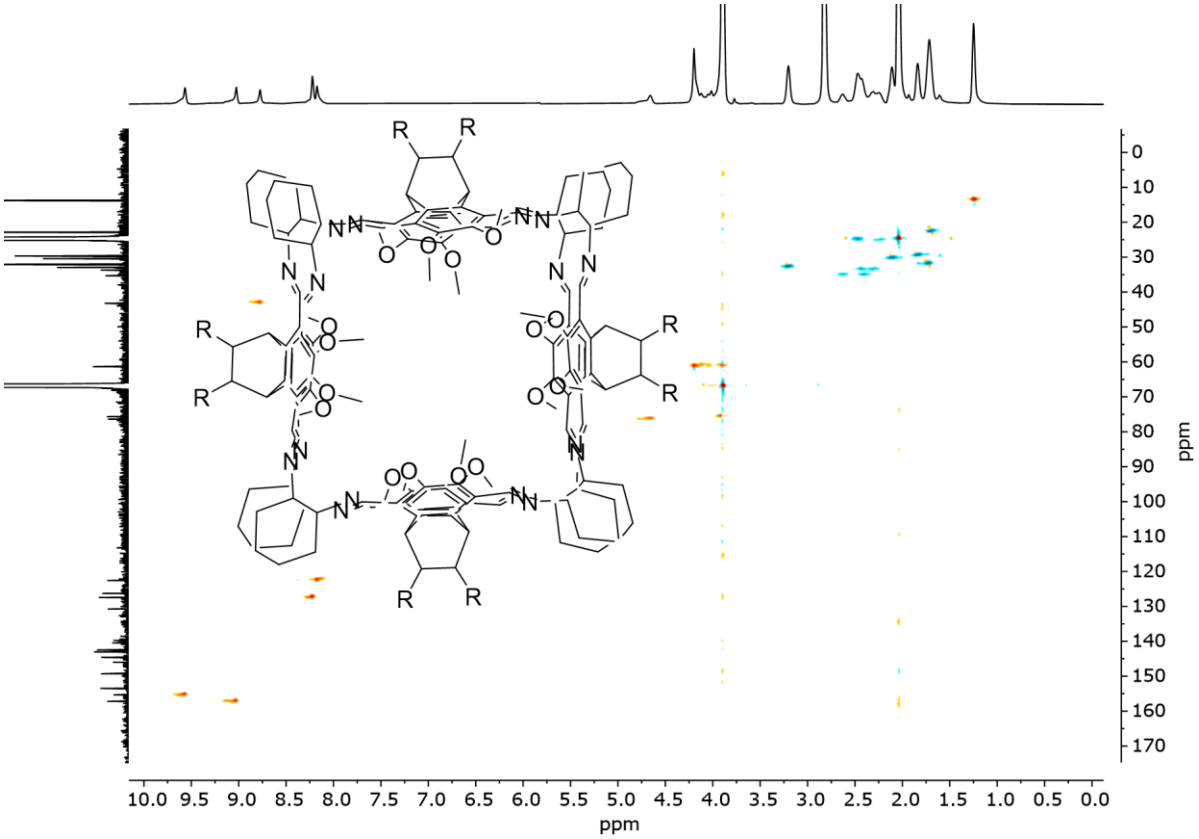


Figure S38: $^{1}H,^{13}C$-HSQC Spectrum (THF-d_8, 600MHz, 151MHz) of **10**.

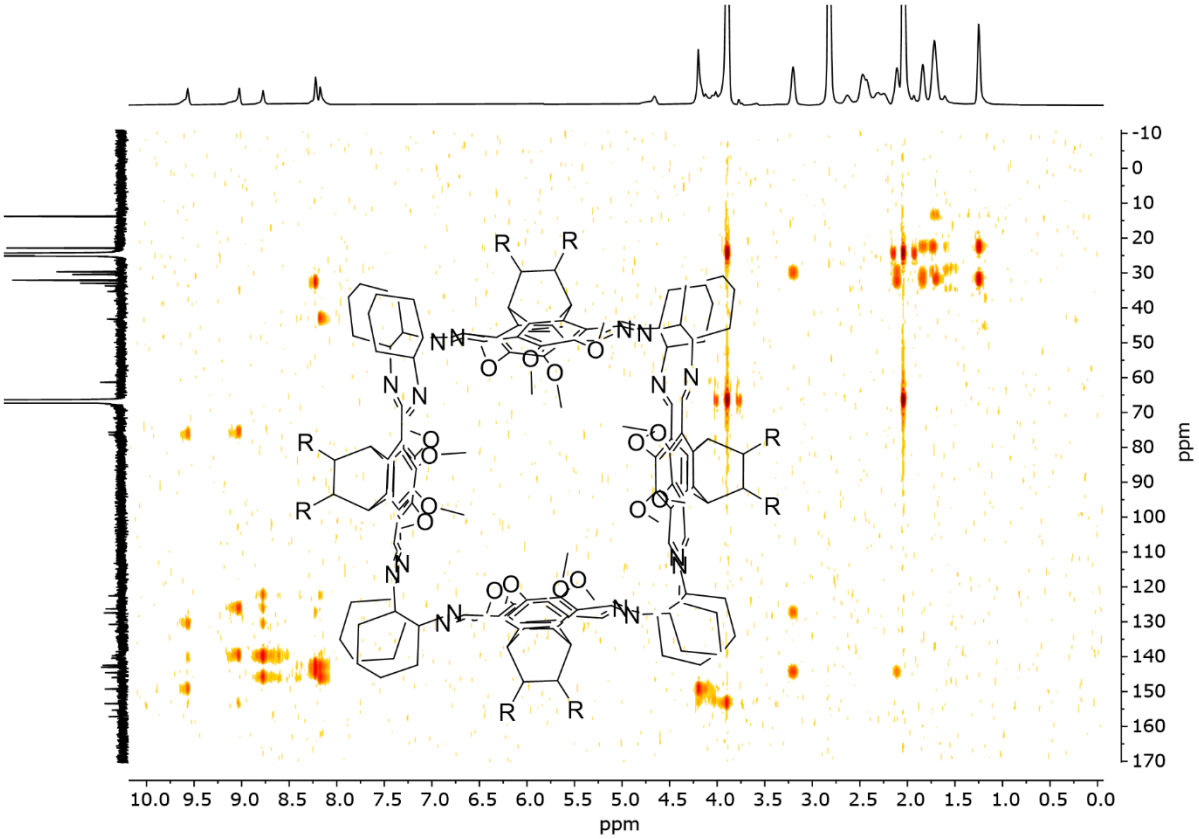


Figure S39: $^{1}H,^{13}C$-HMBC Spectrum (THF-d_8, 600MHz, 151MHz) of **10**.

4. DOSY Experiments

The recordings of the DOSY NMR experiments were carried out at 298 K and calibrated using the known self-diffusion value for the solvent (D_{solv}).[13] The solvodynamic radii were estimated using Stokes-Einstein equation. The equation was solved for r_s using values from literature.[14]

$$D = \frac{k_B T}{6\pi\eta r_s}$$

in which D is the measured diffusion coefficient ($m^2 \cdot s^{-1}$); k_B is the Boltzmann constant ($1.3806485 \cdot 10\ m^2 \cdot kg \cdot s^{-2} \cdot K^{-1}$), T is the temperature (K), r_s is the hydrodynamic radius of the analyte (m) and η is the viscosity of the solvent at temperature T ($kg \cdot m^{-1} \cdot s^{-1}$).

Table S1: Estimation of the solvodynamic radii (r_s) in THF-d_8 for the cage compounds **9** and **10** using parameters from literature and diffusion coefficients measured by DOSY NMR.

Compound	Solvent	T [K]	$D_{solv} \cdot 10^{-9}$ [$m^2 \cdot s^{-1}$]	$\eta \cdot 10^{-3}$ [$kg \cdot m^{-1} \cdot s^{-1}$]	$D \cdot 10^{-10}$ [$m^2 \cdot s^{-1}$]	r_s [nm]
9	THF-d_8	298	2.33	0.47	4.29	1.08
10	THF-d_8	298	2.33	0.47	3.38	1.37

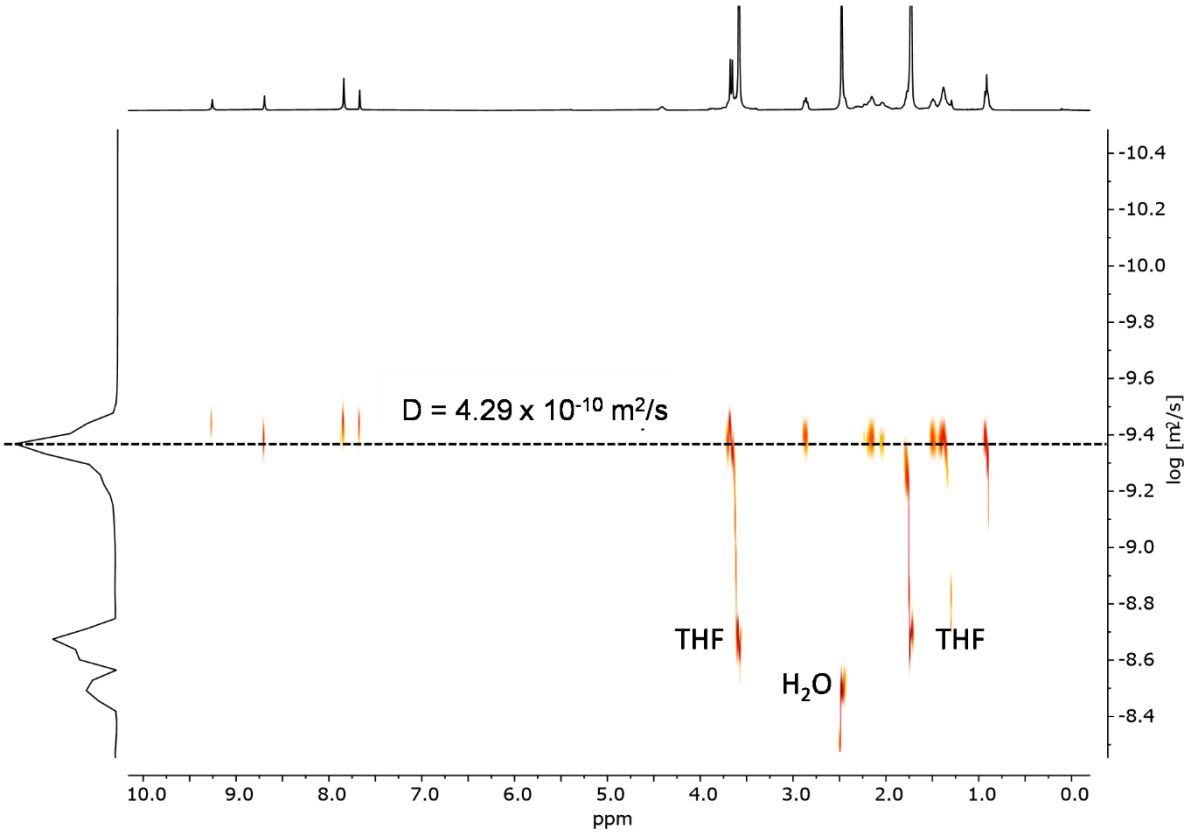


Figure S40: ^{1}H-DOSY Spectrum (THF-d_8, 400MHz) of **9**.

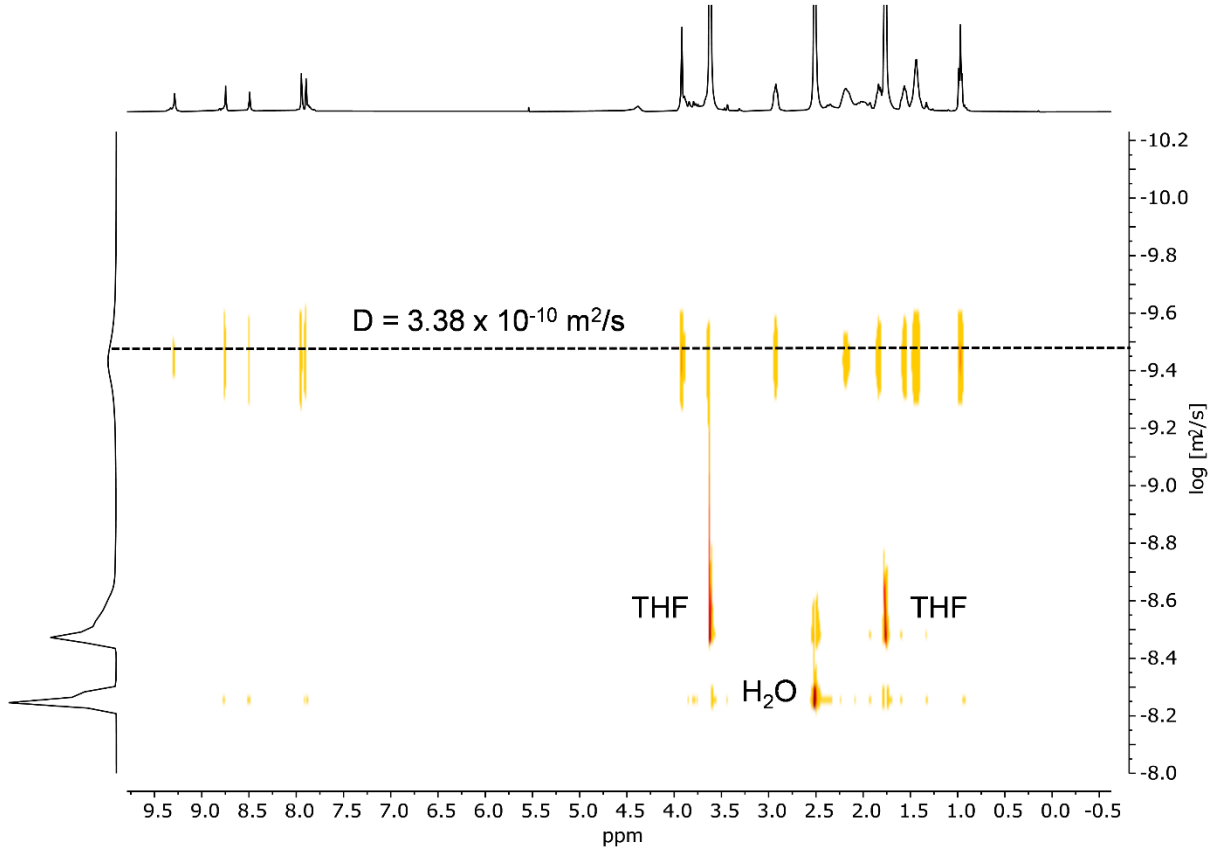


Figure S41: ^{1}H-DOSY Spectrum (THF-d_8, 400MHz) of **10**.

5. Mass Spectra

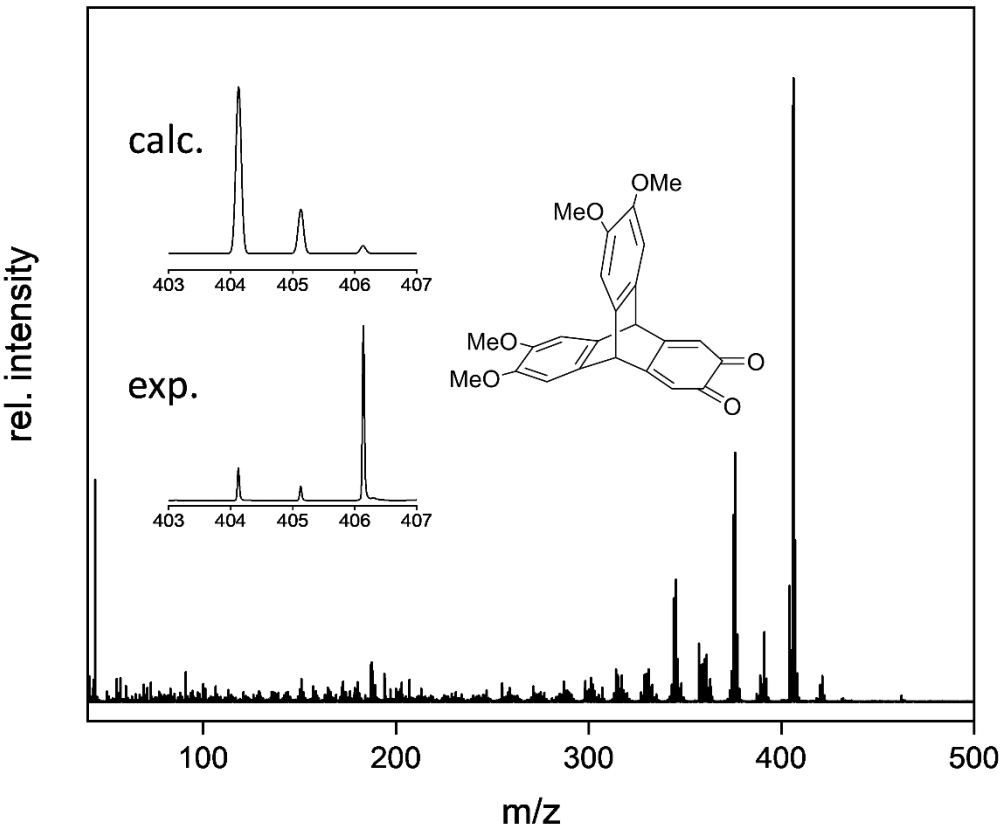


Figure S42: EI-MS of compound **2**.

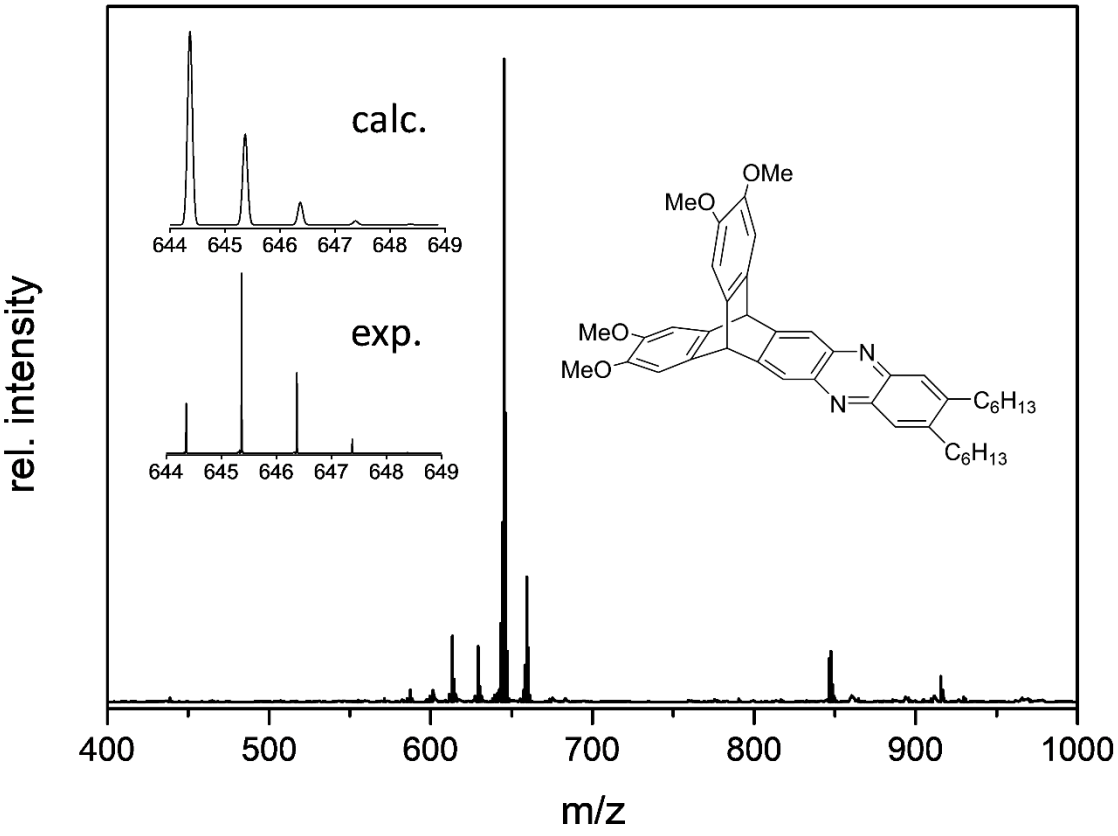


Figure S43: MALDI-TOF-MS of compound **4**.

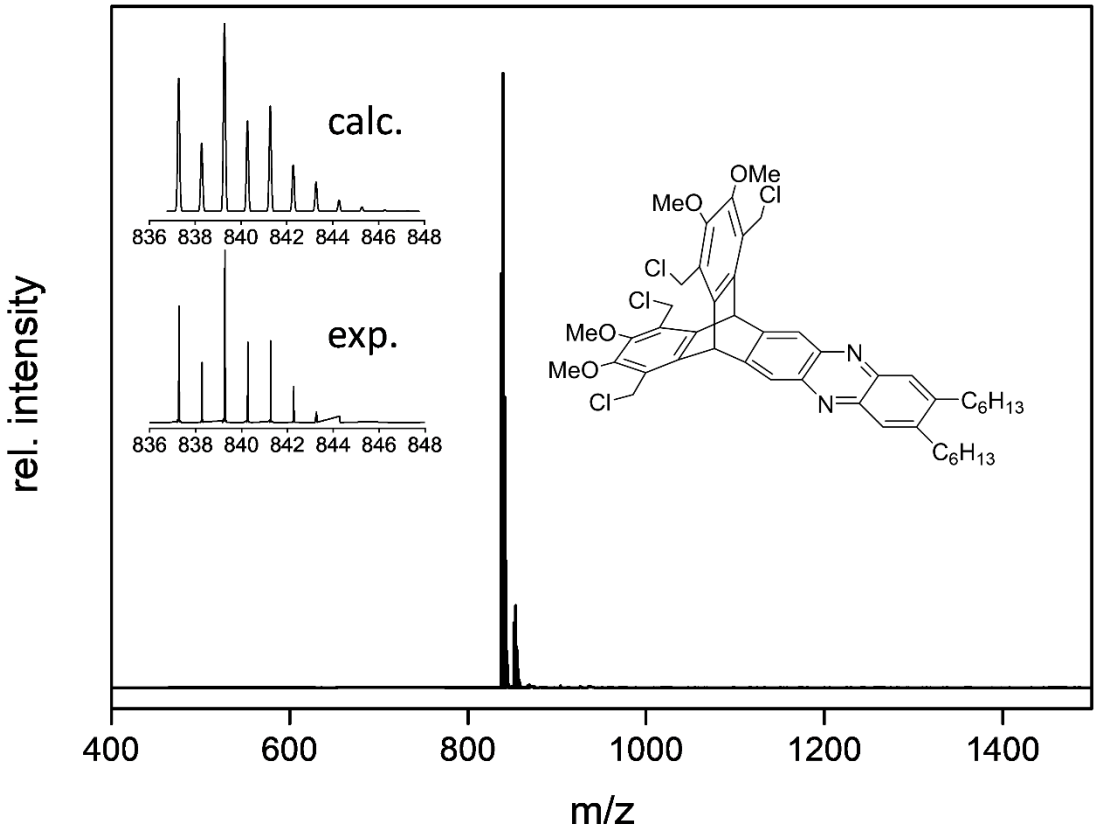


Figure S44: MALDI-TOF-MS of compound **5**.

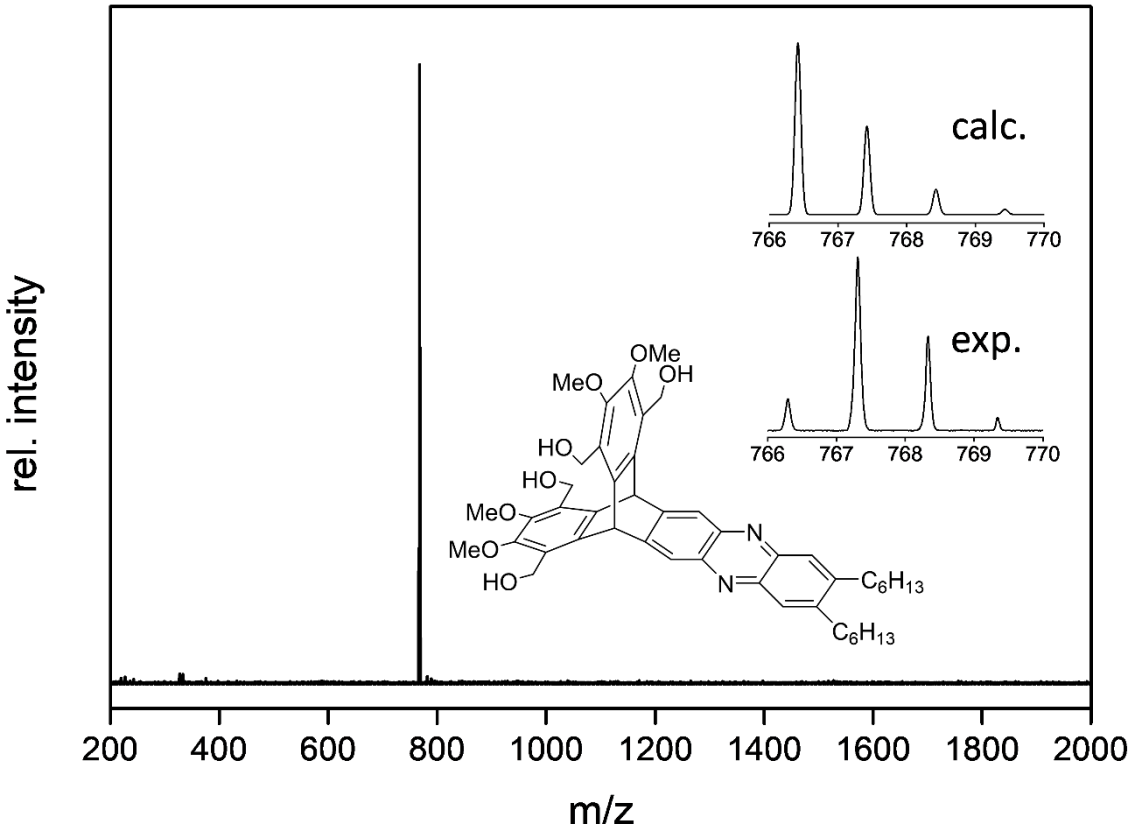


Figure S45: MALDI-TOF-MS of compound **6**.

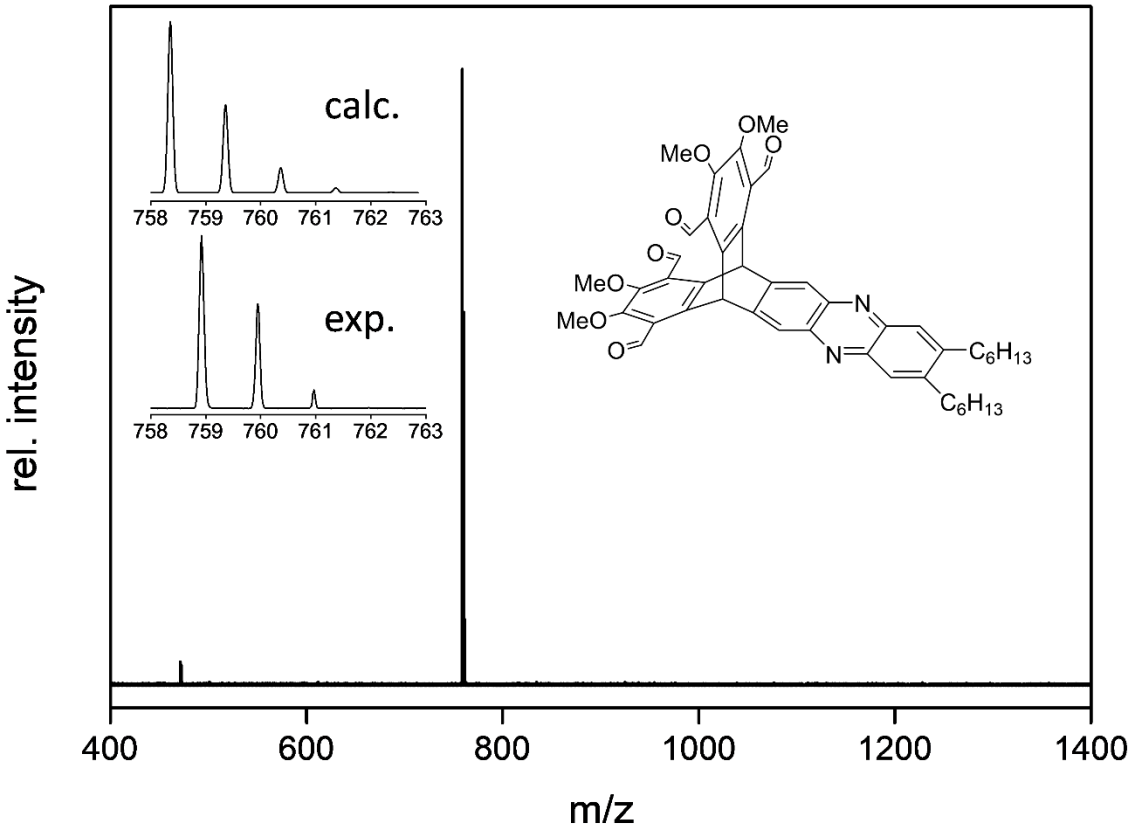


Figure S46: MALDI-TOF-MS of compound **7**.

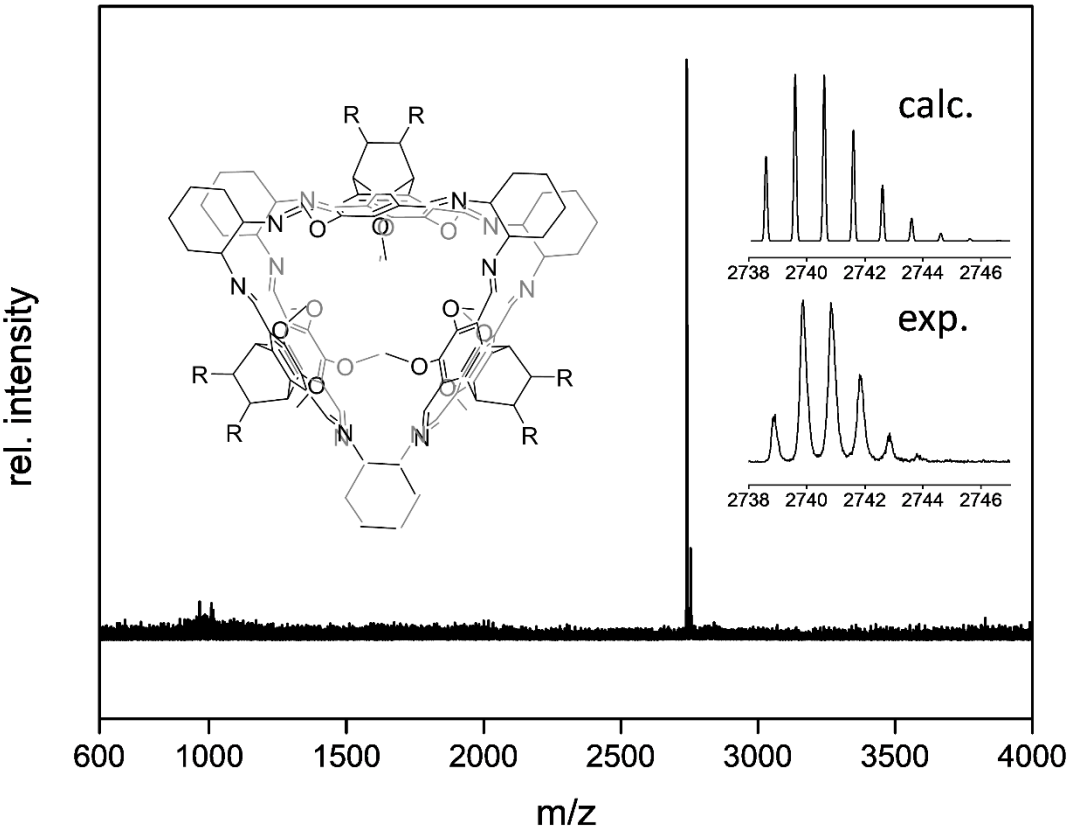


Figure S47: MALDI-TOF-MS of compound **9**.

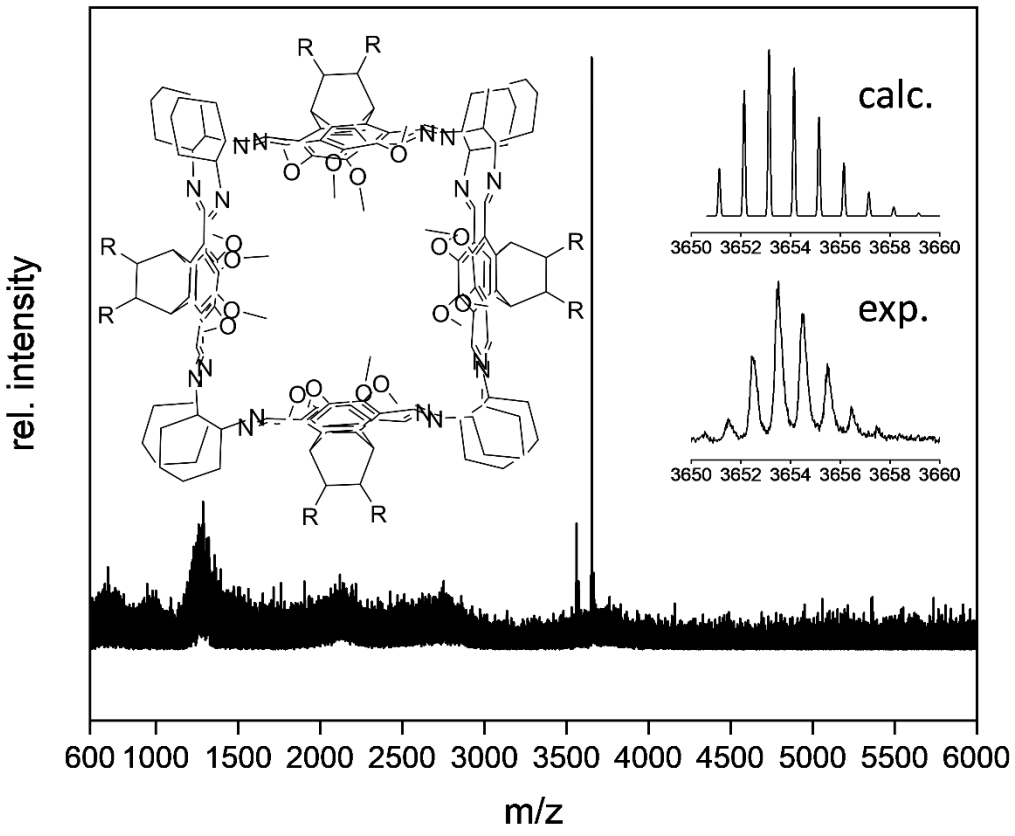


Figure S48: MALDI-TOF-MS of compound **10**.

6. IR Spectra

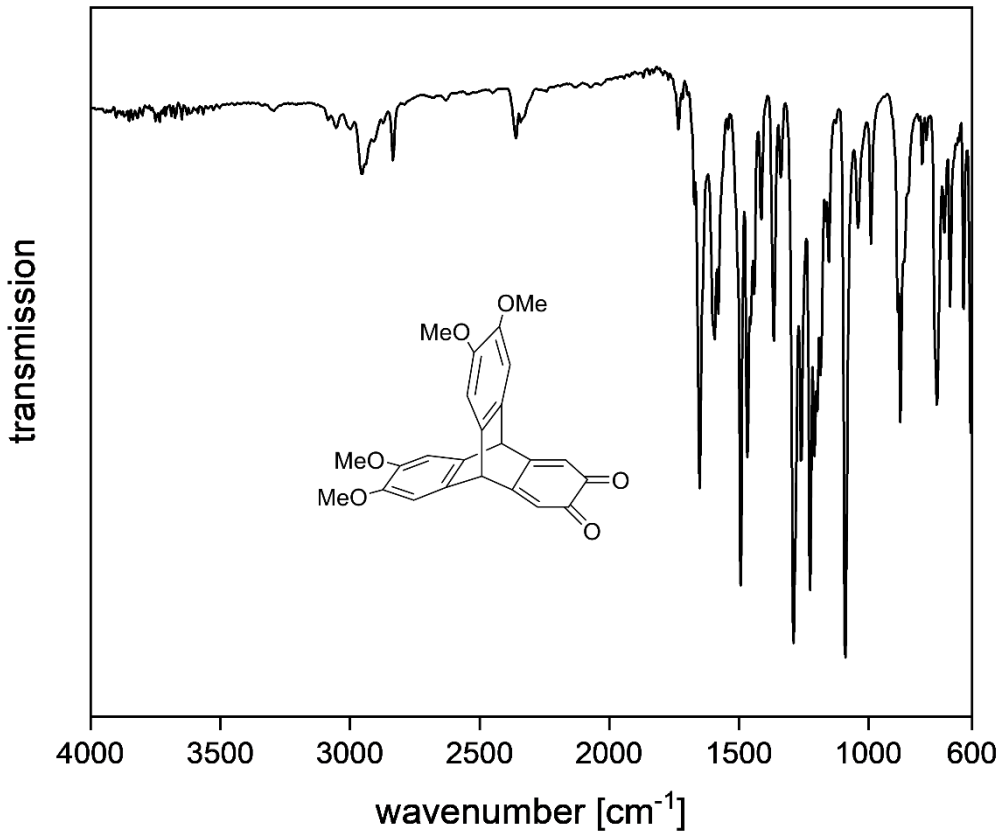


Figure S49: IR Spectrum (ATR, ZnSe) of **2**.

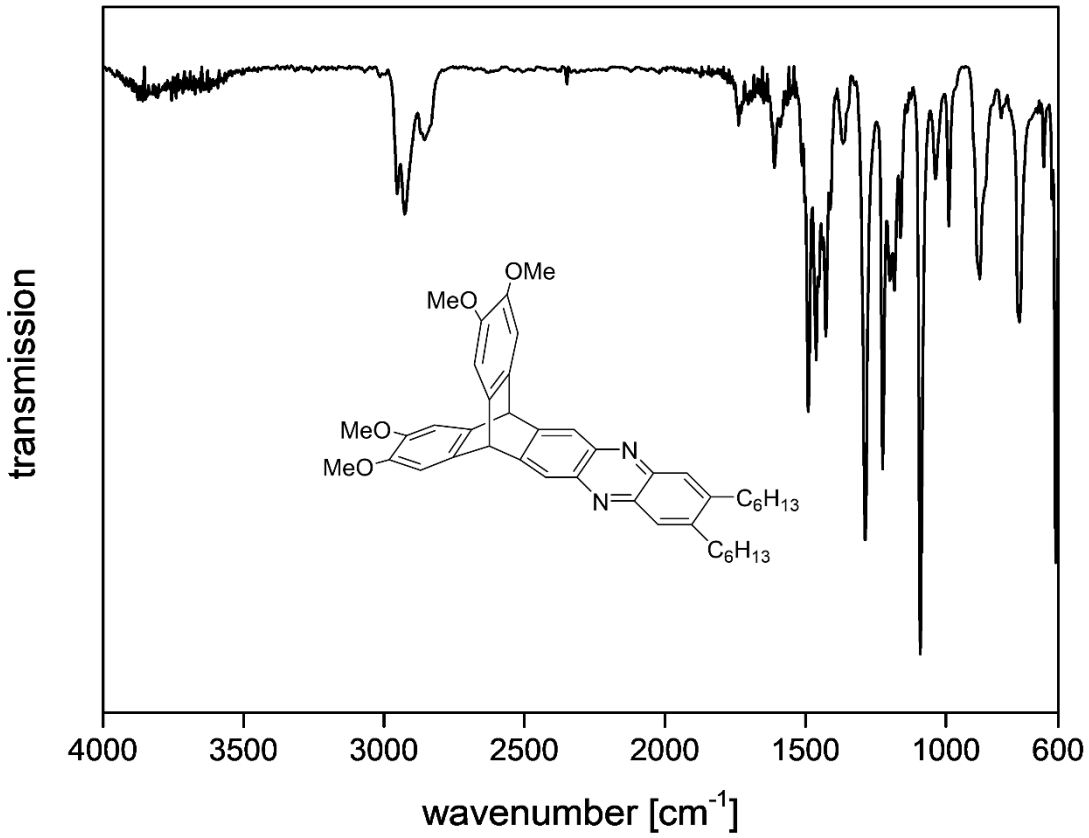


Figure S50: IR Spectrum (ATR, ZnSe) of **4**.

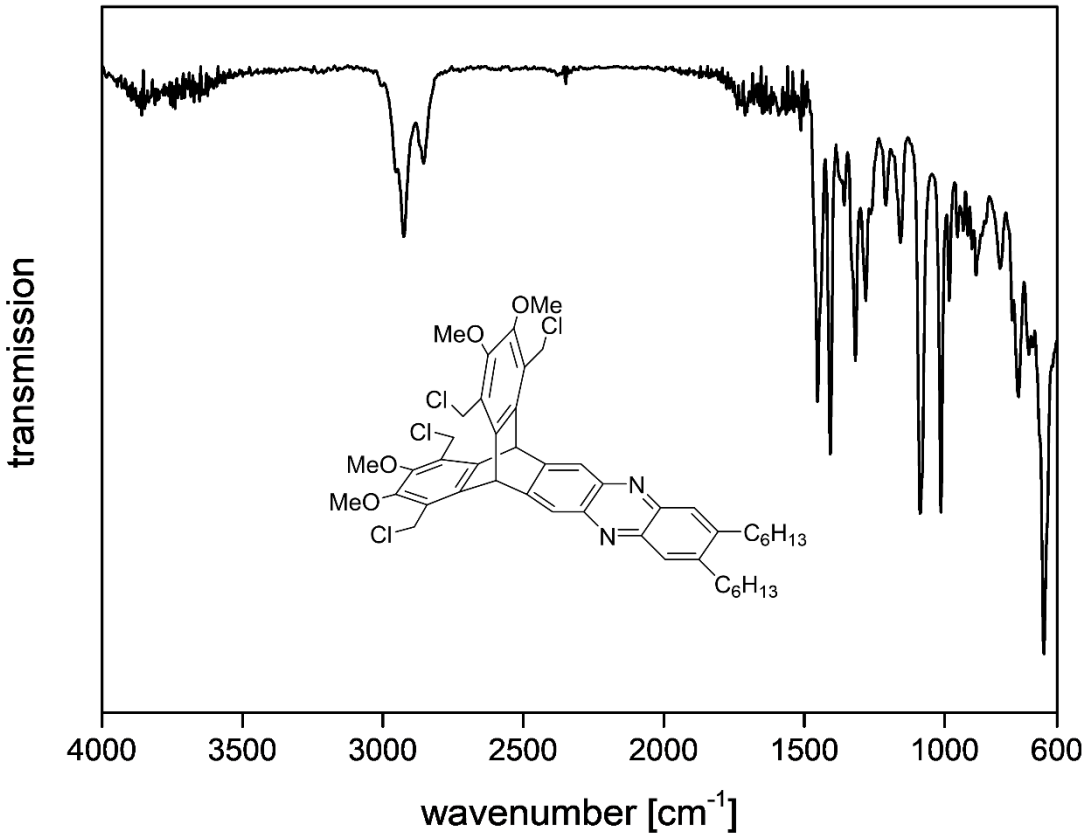


Figure S51: IR Spectrum (ATR, ZnSe) of **5**.

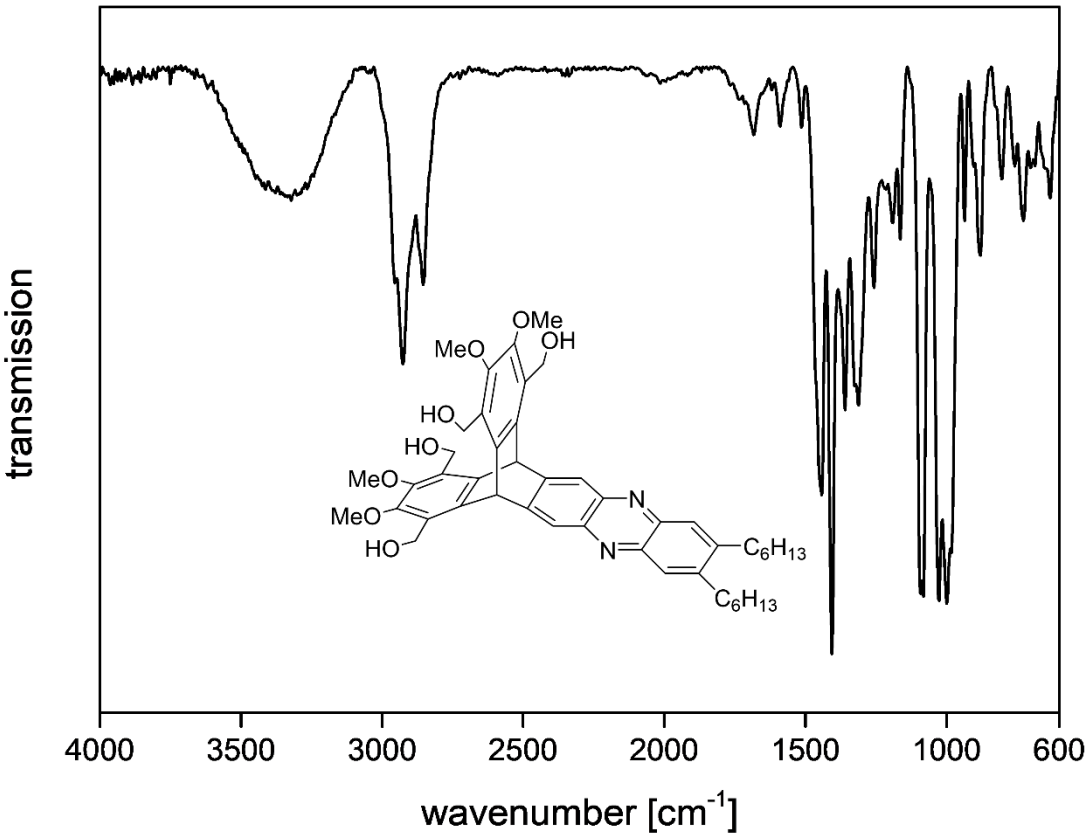


Figure S52: IR Spectrum (ATR, ZnSe) of **6**.

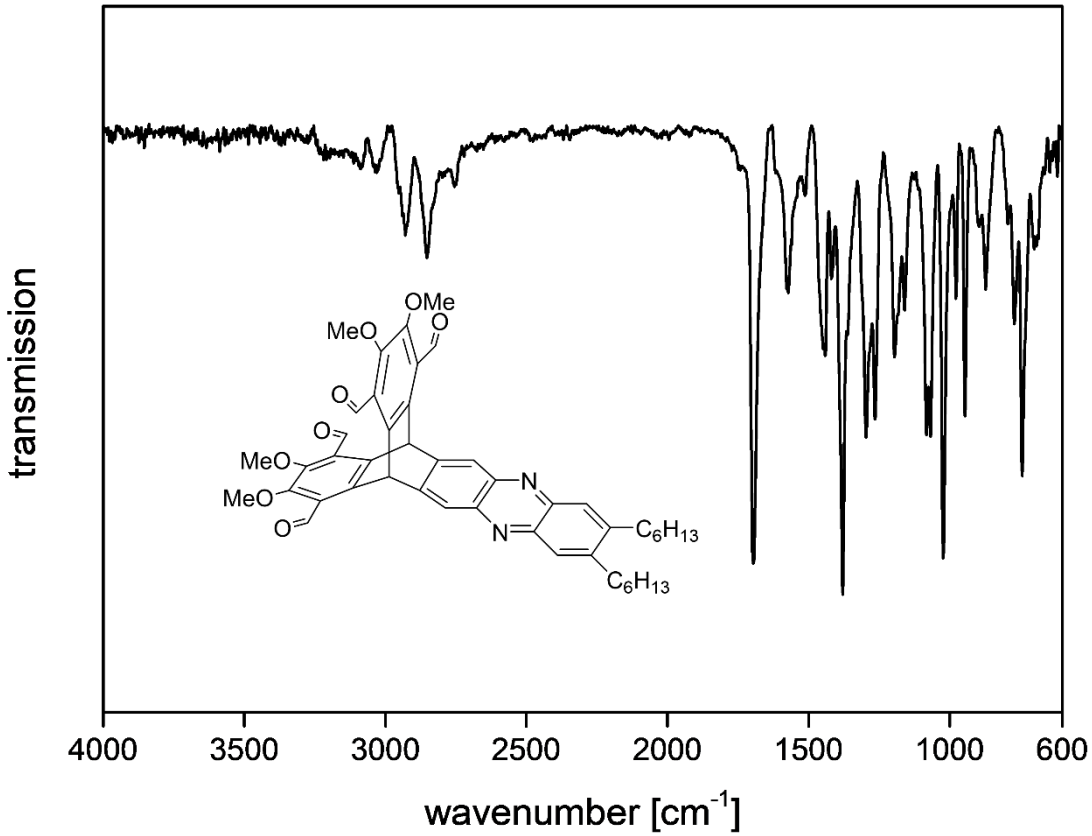


Figure S53: IR Spectrum (ATR, ZnSe) of 7.

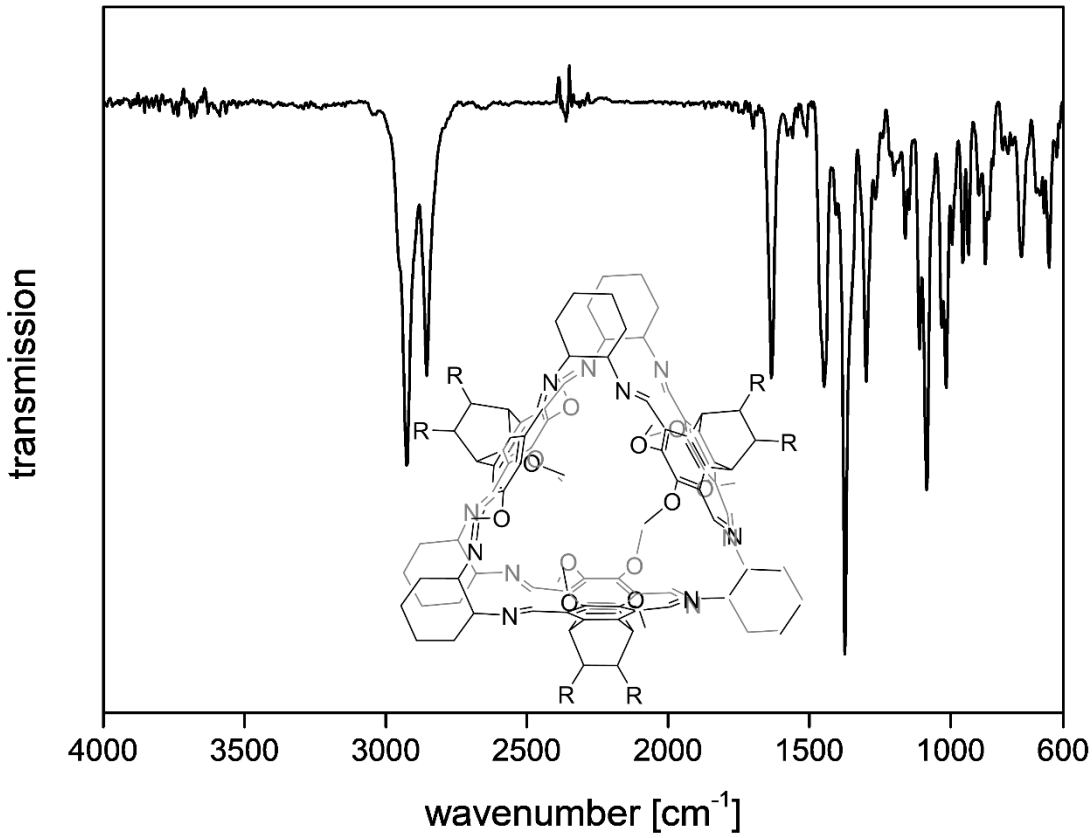


Figure S54: IR Spectrum (ATR, ZnSe) of **9**.

7. UV-Vis/Fluorescence Spectra

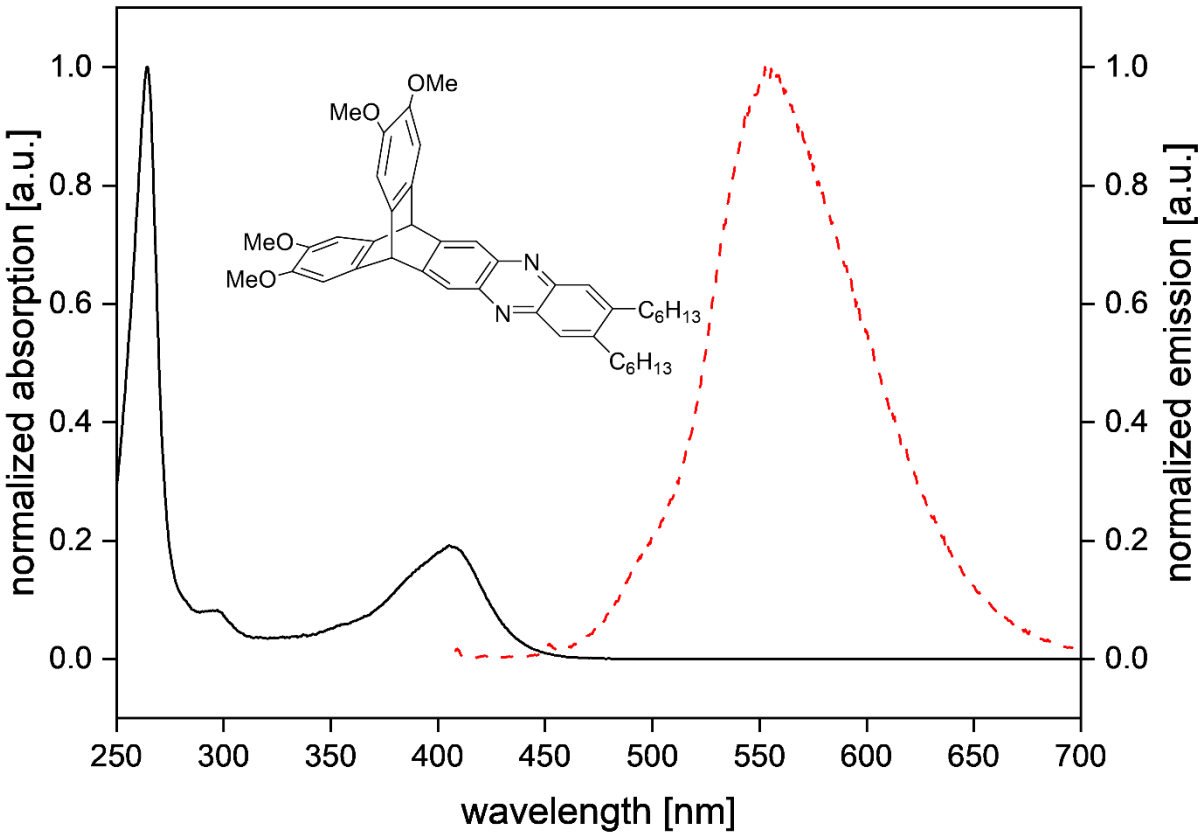


Figure S55: UV/vis (black solid line) and fluorescence (red dotted line) spectrum of **4** in dichlormethane. The excication energy for the fluorescence is 406 nm.

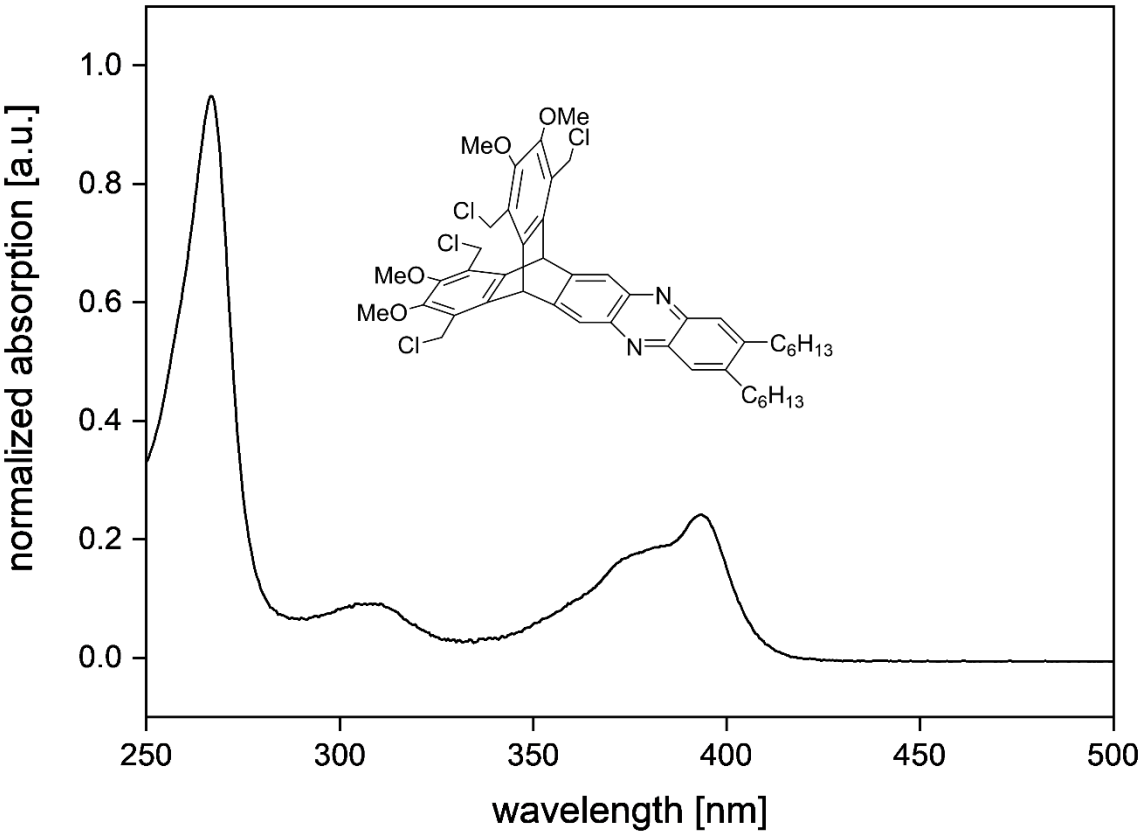


Figure S56: UV/vis spectrum of **5** in dichlormethane.

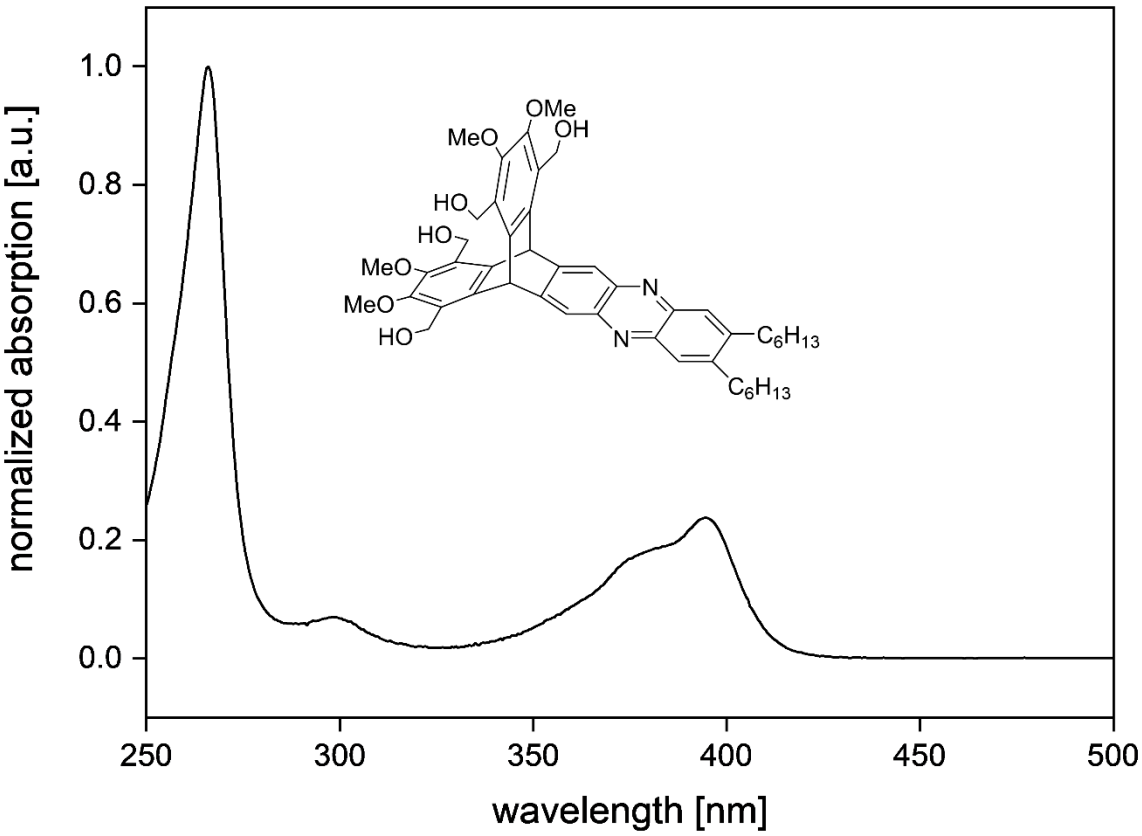


Figure S57: UV/vis spectrum of **6** in dichlormethane.

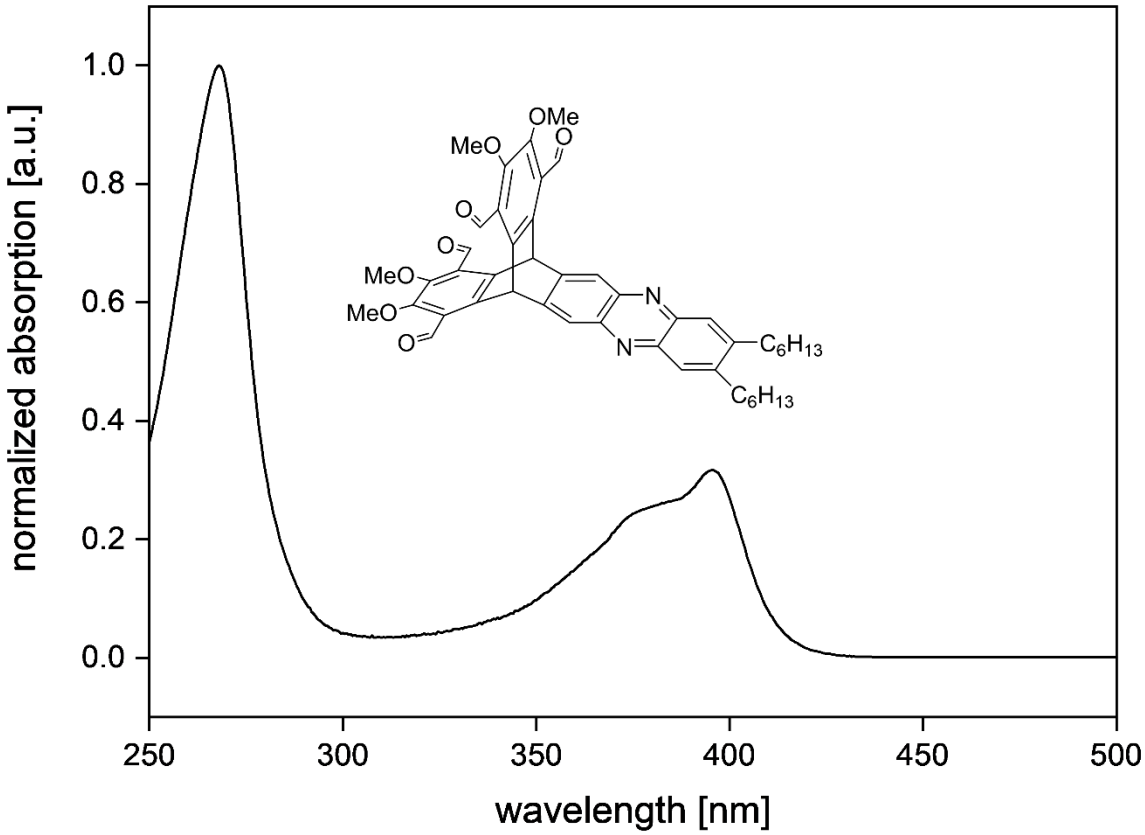


Figure S58: UV/vis spectrum of **7** in dichlormethane.

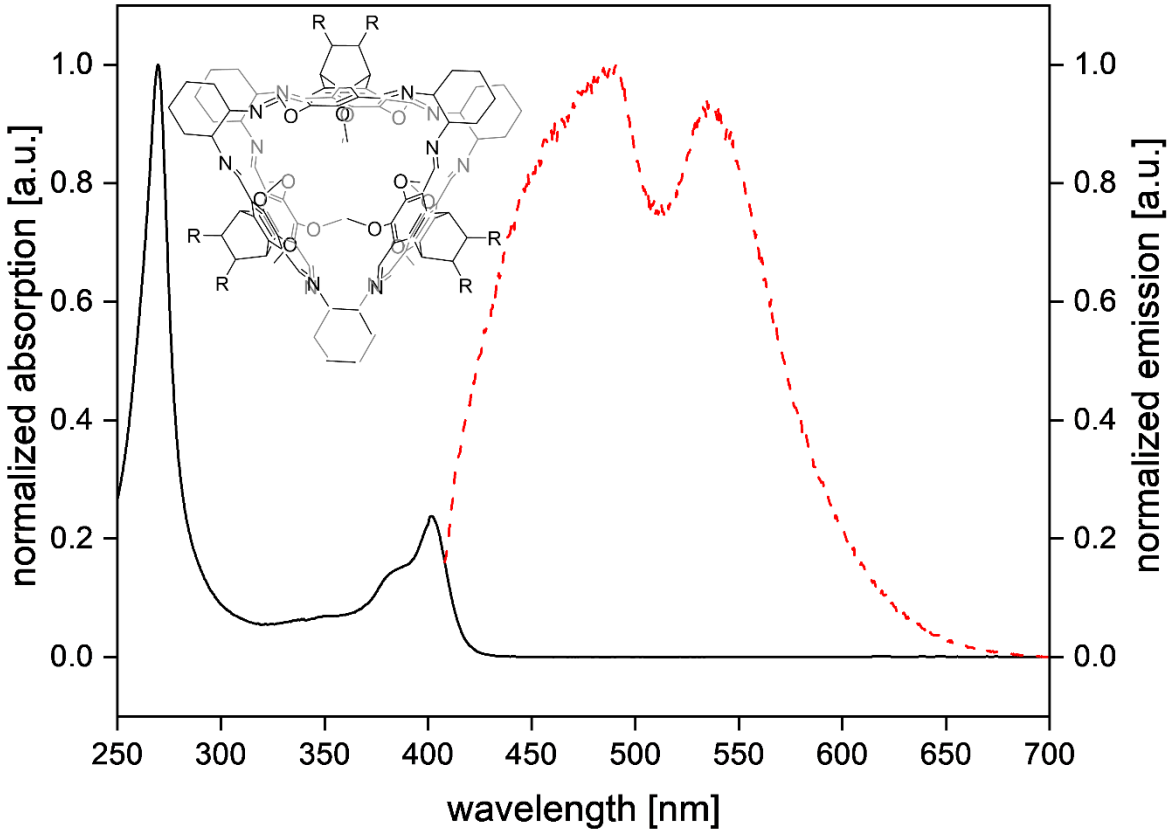


Figure S59: UV/vis (black solid line) and fluorescence (red dotted line) spectrum of 9 in dichlormethane. The excication energy for the fluorescence is 402 nm.

8. CD Spectra

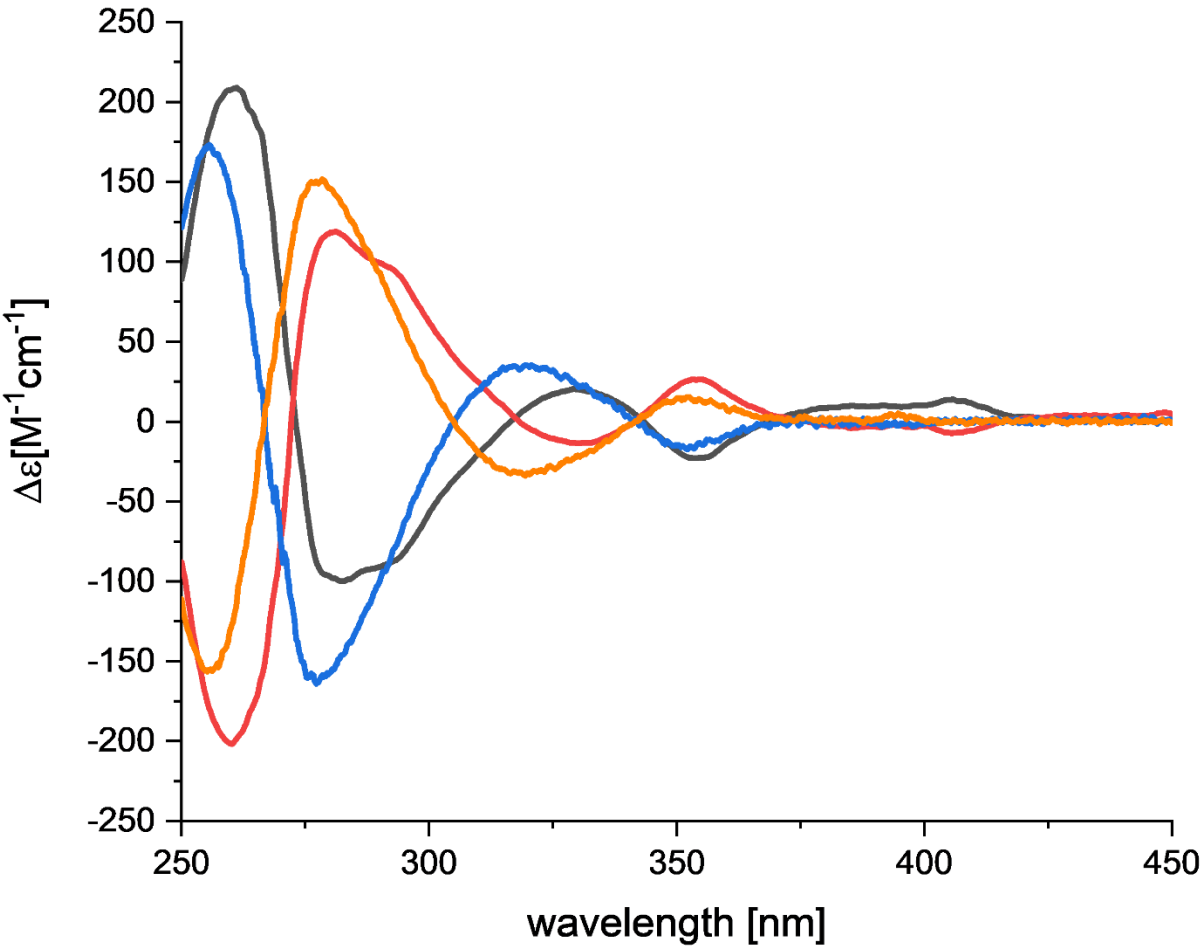


Figure S60: CD spectra of (*R*,*R*)-**9** (black line, c = 6.09·10^{-6}mol/L), (*S*,*S*)-**9** (red line, c = 5.98·10^{-6}mol/L), (*R*,*R*)-**10** (blue line, c = 6.00·10^{-6}mol/L), (*S*,*S*)-**10** (orange line, c = 6.00·10^{-6}mol/L), in DCM at 20 °C.

9. Determination of the Cavity Volume

The molecular model for the [3+6]-Cage **9** is based on single-crystal diffraction data of **9** which were imported in the Chem3D Pro 17.0 software in order to remove the hexyl substituents to simplify later calculations. The molecular model for the [4+8]-Cage **10** was modeled with Chem3D Pro 17.0 software. Further optimization of the models was conducted in the Spartan 14 software using the PM3 semi empirical method.[9-12]

The determination of the cavity volume was carried out using SwissPdbViewer[15] 4.1.0 at the highest quality level (Surface Preferences: Quality 6). Two dummy atoms were added to the cage models and positioned in front of the larger windows of the cage to prevent the 1.4 Å radius measuring probe from “falling out” of the cavity of the cage.

This lead to a calculated volume of 177 Å^3 for **9** and 368 Å^3 for **10**. For **CB6** two dummy atoms and for **CB8** two rings of 8 dummy atoms were positioned in front of the windows to prevent the 1.4 Å radius measuring probe from “falling out” of the cavity leading to a volume of 115 Å^3 for **CB6** and 351 Å^3 for **CB8**.

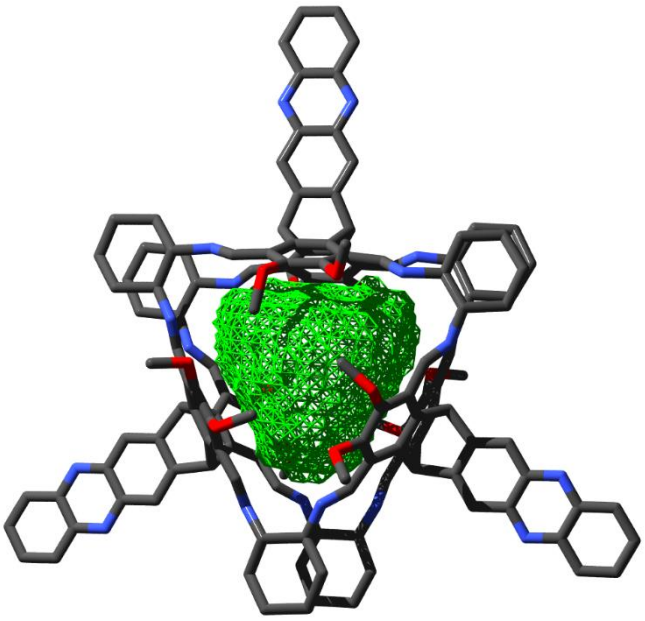


Figure S61: Representation of the cavity volume (177 Å^3) of **9** determined by using SwissPdbViewer 4.0.1 software.

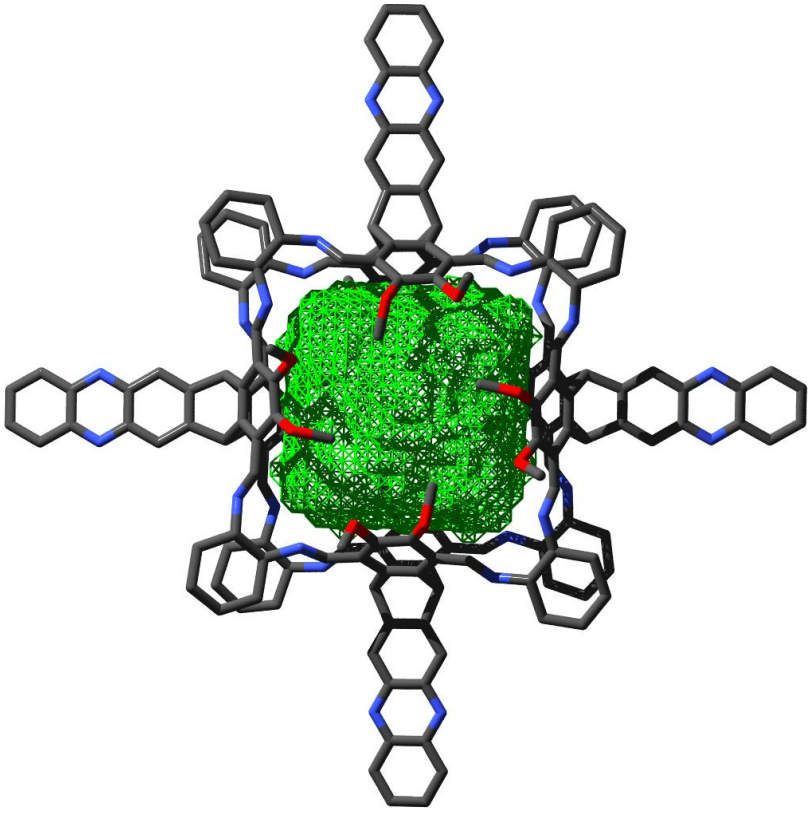


Figure S62: Representation of the cavity volume (368 Å^3) of **10** determined by using SwissPdbViewer 4.0.1 software.

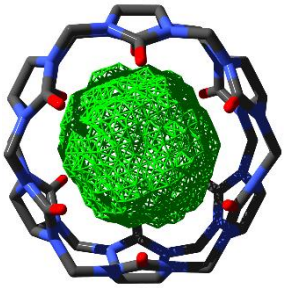


Figure S63: Representation of the cavity volume (115 Å^3) of **CB6** determined by using SwissPdbViewer 4.0.1 software.

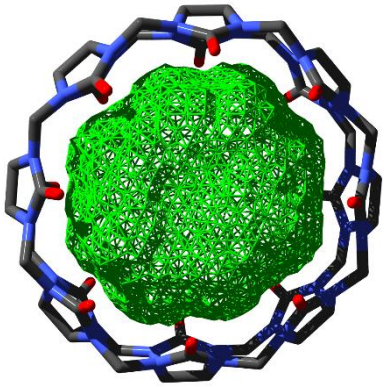


Figure S64: Representation of the cavity volume (351 Å^3) of **CB8** determined by using SwissPdbViewer 4.0.1 software.

10. GPC Chromatograms

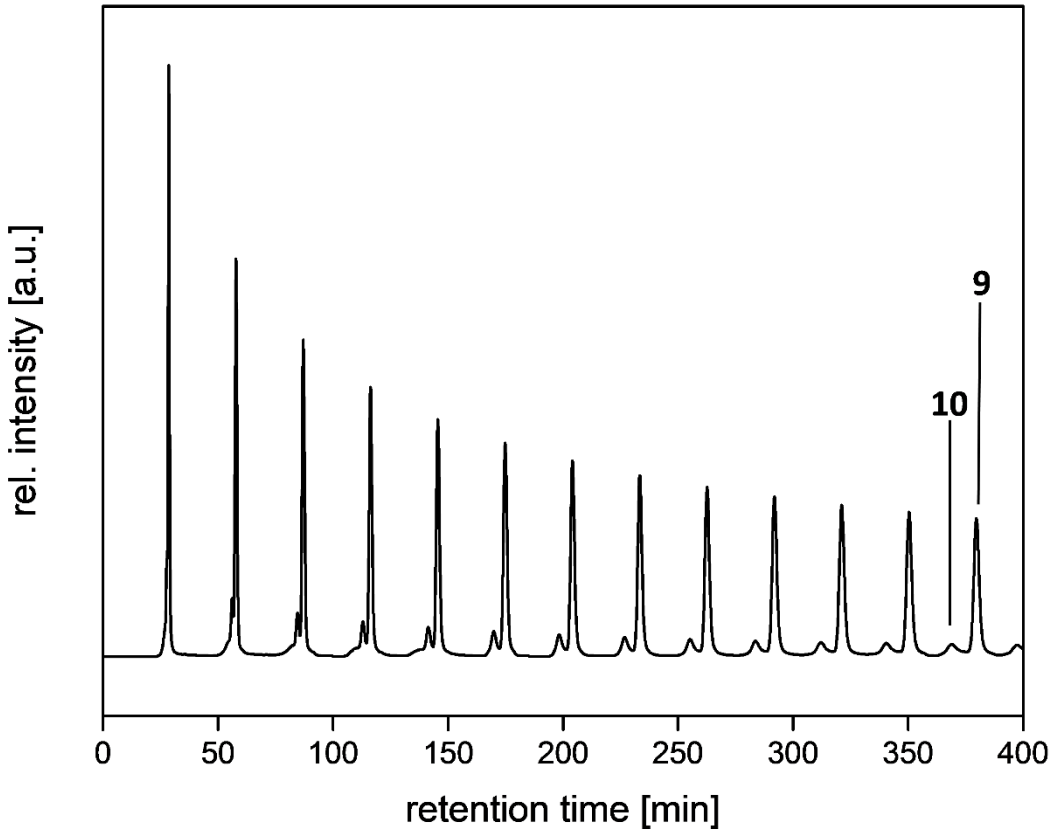


Figure S65: Chromatogram of the crude mixture of **9** and **10** (SDV column, THF, 5 mL/min, R_t = 28.65 min, 254 nm).

11. Crystallographic Data

Crystals of **4** suitable for X-ray diffraction were obtained by heating a solution of **4** in methanol, letting it cool to room temperature and subsequent evaporation of the solvent.

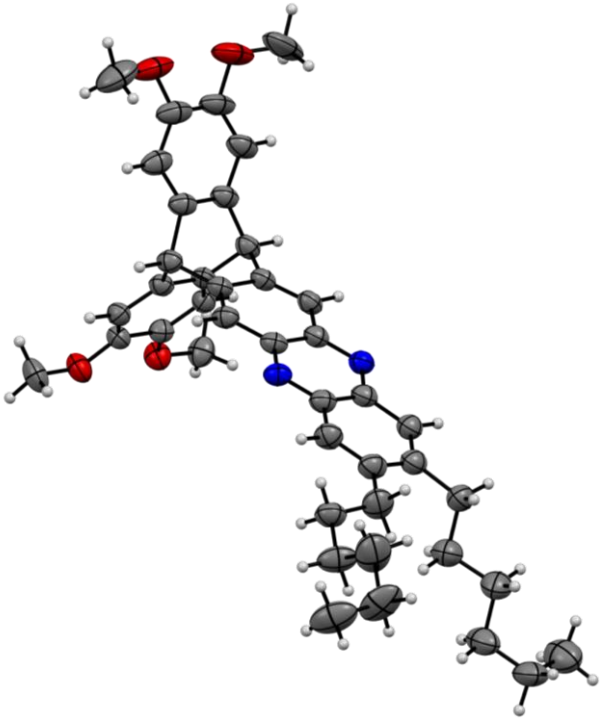


Figure S66: ORTEP representation of the structure of **4** with thermal ellipsoid drawn at 50% probability. Carbon atoms are depicted in grey, oxygen in red, nitrogen in blue and hydrogen in white.

Empirical formular	$C_{42}H_{48}N_2O_4+H_2O$	
Formula weight	671.27	
Temperature	2110(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Z	7	
Unit cell dimensions	a = 35.1098(13) Å	α = 90°
	b = 10.3315(3) Å	β = 90°
	c = 20.2989(8) Å	γ = 90°
Volume	7363.2(5) $Å^3$	
Density (calculated)	1.211 g/cm^3	
Absorption coefficient μ	0.623 mm^{-1}	
Crystal shape	Plank	
Crystal size	0.262 x 0.202 x 0.028 mm^3	
Crystal colour	Orange	
Theta range for data collection	4.461 to 62.378°	
Index ranges	-39≤h≤22, -10≤k≤11, -22≤l≤19	
Reflections collected	24471	

Independent reflections	5624 (R(int) = 0.0202)
Observed reflections	4505 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max/min transmission	1.51 and 0.60
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5624 / 537 / 566
Goodness-of-fit on F^2	1.05
Final R indices (I>2σ(I))	R1 = 0.060, wR2 = 0.162
Largest diff. peak and hole	0.38 and -0.33 $eÅ^{-3}$

Crystals of **5** suitable for X-ray diffraction were obtained by heating a solution of **5** in methanol, letting it cool to room temperature and diffusing hexane into this solution.

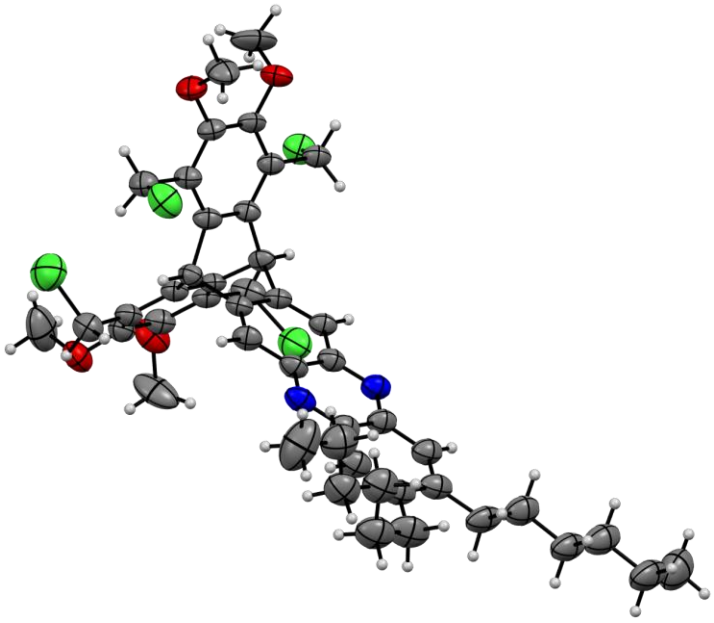


Figure S67: ORTEP representation of the structure of **5** with thermal ellipsoid drawn at 50% probability. Carbon atoms are depicted in grey, oxygen in red, nitrogen in blue, chlorine in green and hydrogen in white.

Empirical formular	$C_{46}H_{52}Cl_4N_2O_4+H_2O$
Formula weight	838.69
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	2

Unit cell dimensions	a = 10.0510(6) Å	α = 98°
	b = 12.6954(7) Å	β = 103°
	c = 17.8371(10) Å	γ = 99°
Volume	2155.8(2) $Å^3$	
Density (calculated)	1.29 g/cm^3	
Absorption coefficient μ	2.85 mm^{-1}	
Crystal shape	Plate	
Crystal size	0.150 x 0.060 x 0.016 mm^3	
Crystal colour	Colourless	
Theta range for data collection	3.6 to 60.0°	
Index ranges	-11≤h≤9, -10≤k≤14, -20≤l≤20	
Reflections collected	17852	
Independent reflections	6371 (R(int) = 0.0673)	
Observed reflections	3723 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max/min transmission	1.69 and 0.51	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	6371 / 0 / 511	
Goodness-of-fit on F^2	1.01	
Final R indices (I>2σ(I))	R1 = 0.073, wR2 = 0.171	
Largest diff. peak and hole	0.65 and -0.36 $eÅ^{-3}$	

Crystals of **9** suitable for X-ray diffraction were obtained by diffusion of Pentane into a solution of **9** dissolved in DCM.

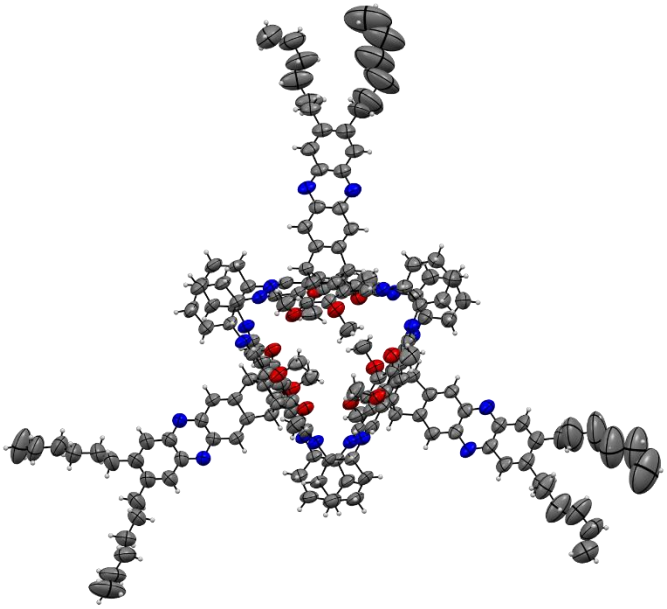


Figure S68: ORTEP representation of the structure of **9** with thermal ellipsoid drawn at 50% probability. Carbon atoms are depicted in grey, oxygen in red, nitrogen in blue, and hydrogen in white.

Empirical formular	$C_{174}H_{204}N_{18}O_{12}$	
Formula weight	2739.54	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12$	
Z	2	
Unit cell dimensions	a = 29.2978(13) Å	α = 90°
	b = 13.2859(10) Å	β = 90°
	c = 26.8063(12) Å	γ = 90°
Volume	10434.3(10) $Å^3$	
Density (calculated)	0.87 g/cm^3	
Absorption coefficient μ	0.43 mm^{-1}	
Crystal shape	Brick	
Crystal size	0.160 x 0.110 x 0.110 mm^3	
Crystal colour	Pale Yellow	
Theta range for data collection	2.2 to 50.4°	
Index ranges	-28≤h≤29, -12≤k≤13, -26≤l≤21	
Reflections collected	18963	

Independent reflections	9675 (R(int) = 0.0582)
Observed reflections	5545 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max/min transmission	1.83 and 0.56
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9675 / 1432 / 919
Goodness-of-fit on F^2	0.92
Final R indices (I>2σ(I))	R1 = 0.062, wR2 = 0.155
Largest diff. peak and hole	0.19 and -0.14 $eÅ^{-3}$

12. Xyz coodinates of computed geometries

[3+6] Cyclohexane cage **9**

atom	x	y	z	atom	x	y	z
N1	-0.22162	3.16774	-5.16518	N35	4.3117	-2.20463	2.79337
N2	-2.87087	2.41237	-4.20581	N36	-3.08905	-2.87991	3.7517
C3	-3.70781	2.92663	-3.37053	C37	-4.82471	0.08914	-2.74822
C4	-4.66545	1.0512	2.03286	C38	-4.41437	1.12965	-1.72936
C5	0.71879	2.3623	-4.80288	C39	-4.67037	0.72964	-0.40277
C6	-1.63726	2.15264	5.21828	C40	-5.29822	-0.64687	-0.3004
N7	-2.6343	1.40497	4.88594	C41	-4.14588	-1.21652	-2.37431
C8	4.75497	3.34891	-0.75413	C42	-4.42434	-1.62454	-1.0573
N9	5.13494	2.47932	0.11965	C43	-6.56387	-0.55396	-1.12587
N10	4.62504	2.36735	3.0027	C44	-6.30085	-0.14891	-2.48842
C11	3.80358	1.43185	3.33954	C45	-7.29962	-0.00954	-3.39448
C12	2.4349	-0.68228	4.88664	C46	-8.6514	-0.27567	-2.97203
C13	1.79371	0.64201	4.51117	C47	-8.9116	-0.67929	-1.61954
C14	0.44593	0.74085	4.90686	C48	-7.82005	-0.81697	-0.68885
C15	-0.06719	-0.52607	5.55755	C49	-4.43485	1.58054	0.68054
C16	1.59201	-1.77527	4.26424	C50	-3.95096	2.87536	0.39968
C17	0.22665	-1.66989	4.59997	C51	-3.67157	3.26377	-0.92476
C18	0.83741	-0.75246	6.7511	C52	-3.91123	2.39508	-2.01032
C20	2.2303	-0.82747	6.37917	C53	-3.38447	-2.00793	-3.23789
C21	3.20585	-1.01758	7.30167	C54	-3.02649	-3.29672	-2.78965
C22	2.82503	-1.14717	8.6852	C55	-3.3169	-3.70991	-1.47446
C23	1.44088	-1.07387	9.05491	C56	-3.99243	-2.85834	-0.56981
C24	0.43735	-0.86957	8.0415	C57	-4.24691	-3.33774	0.79824
C25	-0.26476	1.924	4.73152	C58	-3.00554	-1.44145	-4.54084
C26	0.40722	3.00877	4.12775	N59	-1.94424	-1.82055	-5.1674
C27	1.74973	2.90363	3.71399	N60	-5.06031	-2.71762	1.59055
C28	2.4562	1.69267	3.86961	C61	4.85885	0.90724	-2.69502
C29	2.06262	-2.82612	3.4819	C62	3.7964	1.98508	-2.66549
C30	1.11477	-3.75467	3.00061	C63	2.85038	1.84383	-3.69852
C31	-0.25094	-3.64489	3.3226	C64	3.16555	0.70135	-4.64999
C32	-0.72117	-2.57468	4.11374	C65	4.14502	-0.43368	-2.73569
C33	-2.13741	-2.34902	4.4411	C66	3.25933	-0.56357	-3.82337
C34	3.48803	-3.09971	3.22167	C67	4.57782	0.95493	-5.13524

atom	x	y	z
C68	5.52312	1.05368	-4.04784
C69	6.84402	1.26623	-4.26798
C70	7.29994	1.39609	-5.62859
C71	6.3607	1.30054	-6.70895
C72	4.9657	1.0728	-6.42919
C73	1.76448	2.7162	-3.83074
C74	1.72085	3.82717	-2.96252
C75	2.68982	3.988	-1.95236
C76	3.73891	3.05984	-1.78235
C77	4.35194	-1.47152	-1.82169
C78	3.72547	-2.70596	-2.09319
C79	2.87671	-2.84812	-3.20772
C80	2.61624	-1.77116	-4.08349
C81	1.73574	-2.03777	-5.23419
C82	5.13624	-1.1757	-0.61318
N83	5.59869	-2.09231	0.16716
N84	0.82737	-1.21142	-5.62869
O85	1.56508	-4.85972	2.27989
C86	1.4107	-4.70847	0.88248
O87	-0.25702	4.23123	4.04431
C88	-0.74486	4.52239	2.74915
O89	2.32405	3.97857	3.04507
C90	2.88943	4.94901	3.90216
O91	-1.13379	-4.5684	2.76999
C92	-1.2949	-5.73288	3.55248
O93	-2.31809	-4.16508	-3.61687
C94	-3.15161	-4.99348	-4.4
O95	-3.63153	3.74704	1.43428
C96	-4.62327	4.71859	1.69609
O97	-3.26267	4.56739	-1.20147
C98	-1.88446	4.78427	-0.97386
O99	-3.07779	-5.02676	-1.08979
C100	-1.73256	-5.31954	-0.7789
O101	3.83571	-3.77574	-1.21147
C102	4.84338	-4.70211	-1.56121
O103	0.66436	4.72998	-3.00809
C104	0.92744	5.87582	-3.79107
O105	2.68503	5.13918	-1.16596
C106	1.80057	5.06542	-0.06573
O107	2.36661	-4.11096	-3.50777
C108	1.12145	-4.37629	-2.89471
N109	-4.8734	1.80381	3.05985
N110	6.77382	1.4217	-7.99446
C111	8.09746	1.63577	-8.24344
C112	9.03195	1.73091	-7.16836
N113	8.61582	1.60915	-5.87537
C114	8.56239	1.76774	-9.5934
C115	9.88656	1.98161	-9.82745
C116	10.81943	2.07658	-8.75413
C117	10.41779	1.95671	-7.45869
N118	-10.17787	-0.93346	-1.20825
C119	-11.2002	-0.79924	-2.1012
C120	-10.94117	-0.39779	-3.44618
N121	-9.66672	-0.14208	-3.85997
C122	-12.54923	-1.06187	-1.69294
C123	-13.56043	-0.92396	-2.59438
C124	-13.30178	-0.5229	-3.9372
C125	-12.03475	-0.26441	-4.36369
N126	3.78109	-1.33902	9.62717
C127	3.40478	-1.46099	10.93215
C128	2.02712	-1.38788	11.30002
N129	1.06594	-1.1951	10.35216
C130	4.39469	-1.66457	11.94932
C131	4.00474	-1.78462	13.24828
C132	2.62951	-1.71153	13.61548
C133	1.65941	-1.51925	12.67967
C134	-5.60526	1.4178	7.27608
C135	-6.68486	0.98705	6.2966
C136	-6.45594	1.5958	4.92208
C137	-5.06545	1.21106	4.39632
C138	-3.99075	1.73537	5.38002
C139	-4.21915	1.07946	6.7511
C140	-6.40254	-2.84709	5.66418
C141	-7.27027	-3.45681	4.57646
C142	-6.85891	-2.94918	3.20475
C143	-5.37889	-3.25858	2.93077
C144	-4.50661	-2.60245	4.03097
C145	-4.93193	-3.12962	5.40897
C146	-1.97721	-0.86594	-8.86882
C147	-0.5271	-1.1948	-9.18338
C148	0.38003	-0.83315	-8.01819
C149	-0.06675	-1.5745	-6.74944
C150	-1.52149	-1.16157	-6.41479
C151	-2.43448	-1.54534	-7.58883
C152	-3.56306	3.25191	-7.86031
C153	-2.174	3	-8.42296
C154	-1.09247	3.42354	-7.44246
C155	-1.27383	2.71112	-6.09338
C156	-2.67219	3.05611	-5.52448
C157	-3.74011	2.56686	-6.51504
C158	8.6347	2.85519	1.56932
C159	8.41389	2.11606	2.87834
C160	7.03277	2.40274	3.44395
C161	5.94211	2.03553	2.42652
C162	6.16249	2.84126	1.1226
C163	7.55348	2.50769	0.55971
C164	8.5778	-1.76964	2.50341
C165	7.99455	-2.51393	3.6927
C166	6.51947	-2.19229	3.8655
C167	5.73797	-2.54637	2.58996
C168	6.31737	-1.7359	1.40446
C169	7.80499	-2.07643	1.23143
H170	-4.29279	3.83632	-3.59692
H171	-4.65868	-0.05878	2.09237
H172	0.7855	1.32019	-5.1871
H173	-1.75338	3.04476	5.8599
H174	5.14766	4.38182	-0.77102
H175	4.05589	0.35308	3.23854
H176	3.50963	-0.72397	4.58607
H177	-1.14585	-0.47374	5.84107
H178	4.26428	-1.0747	7.02055
H179	-0.61958	-0.81159	8.32726
H180	-2.32755	-1.64895	5.28143
H181	3.79571	-4.14446	3.40864

atom	x	y	z
H182	-4.61234	0.39295	-3.80162
H183	-5.45905	-1.00855	0.76326
H184	-7.10458	0.29762	-4.42857
H185	-8.01608	-1.13269	0.34363
H186	-3.71157	-4.25273	1.11153
H187	-3.64975	-0.61209	-4.90172
H188	5.57734	0.97155	-1.84276
H189	2.42285	0.6357	-5.48076
H190	7.56308	1.34141	-3.44365
H191	4.25002	0.99846	-7.25653
H192	1.87977	-3.02332	-5.71402
H193	5.28304	-0.09163	-0.4121
H194	1.90714	-3.80617	0.50651
H195	1.90263	-5.60207	0.48904
H196	0.3486	-4.69572	0.58337
H197	-1.43424	5.35162	2.93111
H198	-1.27961	3.67735	2.30006
H199	0.06205	4.84137	2.07538
H200	3.70177	4.54096	4.51311
H201	3.28139	5.68148	3.19134
H202	2.13731	5.41267	4.55039
H203	-1.70507	-5.51171	4.54413
H204	-2.0155	-6.30953	2.96664
H205	-0.35812	-6.29109	3.66008
H206	-2.42977	-5.58563	-4.96799
H207	-3.77934	-5.64738	-3.78428
H208	-3.7848	-4.41484	-5.08189
H209	-4.17624	5.28322	2.51906
H210	-4.79634	5.37424	0.83532
H211	-5.57005	4.26906	2.01391
H212	-1.72066	5.7731	-1.41108
H213	-1.25558	4.03964	-1.47585
H214	-1.64668	4.80061	0.09873
H215	-1.79331	-6.36037	-0.44965
H216	-1.3262	-4.69358	0.03265
H217	-1.07493	-5.23864	-1.65471
H218	5.83924	-4.24654	-1.58279
H219	4.77898	-5.43072	-0.74882
H220	4.6392	-5.18602	-2.52299
H221	-0.00851	6.43388	-3.70259
H222	1.76073	6.46403	-3.39036
H223	1.12292	5.62721	-4.83981
H224	2.05572	5.95971	0.50932
H225	1.96312	4.16646	0.54031
H226	0.75007	5.10707	-0.38428
H227	0.88499	-5.37878	-3.2613
H228	0.34688	-3.66572	-3.20784
H229	1.19733	-4.38352	-1.79843
H230	7.84154	1.694	-10.41618
H231	10.25909	2.08494	-10.85238
H232	11.87414	2.24944	-8.99416
H233	11.13219	2.02925	-6.63021
H234	-12.74391	-1.37017	-0.65899
H235	-14.59693	-1.1206	-2.29965
H236	-14.14911	-0.42596	-4.6246
H237	-11.83152	0.04445	-5.39579
H238	5.45148	-1.72004	11.66273
H239	4.74746	-1.94041	14.03826
H240	2.36664	-1.81372	14.67399
H241	0.60051	-1.46216	12.95808
H242	-5.76544	0.92927	8.25646
H243	-5.68125	2.50746	7.46518
H244	-6.7064	-0.12466	6.21906
H245	-7.68133	1.28058	6.67826
H246	-7.24022	1.24479	4.22268
H247	-6.56367	2.69831	4.96935
H248	-5.00321	0.08624	4.35867
H249	-4.10687	2.84742	5.48032
H250	-4.09748	-0.0227	6.67688
H251	-3.45047	1.421	7.47257
H252	-6.69565	-3.24619	6.65411
H253	-6.57301	-1.74658	5.7201
H254	-7.19736	-4.5624	4.6103
H256	-8.3351	-3.21857	4.763
H257	-7.04329	-1.8567	3.13265
H258	-7.49716	-3.4117	2.42627
H259	-5.22537	-4.36967	2.95774
H260	-4.66197	-1.4892	4.00003
H261	-4.73739	-4.2186	5.48307
H266	-4.31963	-2.65362	6.20268
H267	-2.62713	-1.17282	-9.71047
H268	-2.10287	0.23717	-8.77566
H269	-0.42682	-2.27277	-9.42156
H270	-0.20541	-0.6532	-10.09369
H271	1.42936	-1.08748	-8.26531
H272	0.36438	0.26497	-7.8498
H273	-0.039	-2.68049	-6.94426
H274	-1.55976	-0.04422	-6.2696
H275	-2.44697	-2.64536	-7.7272
H276	-3.48086	-1.2534	-7.36515
H277	-4.33119	2.89092	-8.57106
H278	-3.73644	4.34172	-7.75521
H279	-2.05767	1.9203	-8.67086
H280	-2.04864	3.54277	-9.3793
H281	-0.09553	3.18824	-7.8653
H282	-1.11315	4.52386	-7.30644
H283	-1.21341	1.59667	-6.2645
H284	-2.75099	4.17115	-5.42059
H285	-3.67801	1.46356	-6.6367
H286	-4.7545	2.77159	-6.11861
H287	9.63067	2.6058	1.15533
H288	8.6471	3.94883	1.7499
H289	8.53968	1.01995	2.72218
H290	9.18946	2.40533	3.61307
H291	6.88736	1.82712	4.37978
H292	6.95416	3.47164	3.72849
H293	6.0233	0.93391	2.19174
H294	6.11429	3.93704	1.36129
H295	7.61267	1.43032	0.2952
H296	7.7282	3.0617	-0.384
H297	9.64288	-2.04019	2.37162
H298	8.56673	-0.67262	2.69854
H299	8.13119	-3.60591	3.55958
H300	8.54785	-2.25016	4.6145

atom	x	y	z
H301	6.11238	-2.74921	4.73264
H302	6.39108	-1.11587	4.10854
H303	5.85999	-3.64153	2.37485

atom	x	y	z
H304	6.22267	-0.63433	1.634
H305	7.92986	-3.14443	0.96027
H306	8.23063	-1.49649	0.38841

[4+8] Cyclohexane cage **10**

atom	x	y	z
N1	6.24889	-2.66654	-2.52187
N2	4.48417	-4.98268	-3.13376
C3	3.60658	-5.8175	-2.68871
C4	-5.46682	2.80247	-2.31114
C5	5.5965	-1.72974	-3.12819
C6	-3.57485	5.80461	-0.72623
N7	-4.54574	5.94744	-1.56353
C8	5.12886	3.57248	-0.85708
N9	5.18796	4.63043	-1.59209
N10	2.93753	6.55701	-1.17221
C11	2.05503	6.21277	-2.05326
C12	0.97215	6.64236	0.80583
C13	0.1448	6.25147	-0.40198
C14	-1.23378	6.19213	-0.13021
C15	-1.57627	6.56333	1.30048
C16	0.60459	5.67415	1.91556
C17	-0.77464	5.63485	2.18892
C18	-0.98773	7.93854	1.52006
C19	0.42992	7.98357	1.24425
C20	1.14639	9.12733	1.37449
C21	0.46063	10.31791	1.80906
C22	-0.94608	10.27082	2.09253
C23	-1.66928	9.03415	1.93704
C24	-2.15971	5.84949	-1.11789
C25	-1.6624	5.54197	-2.40164
C26	-0.28029	5.60646	-2.67105
C27	0.64706	6.00171	-1.67942
C28	1.51102	4.90323	2.64196
C29	0.99685	4.02937	3.62375
C30	-0.38487	4.00266	3.9032
C31	-1.29464	4.83303	3.20465
C32	-2.71382	4.85511	3.60091
C33	2.93444	5.0688	2.30943
N34	3.85414	5.07943	3.21303
N35	-3.53854	5.68154	3.04651
C36	1.634	-6.80665	-0.74812
C37	1.26375	-6.2184	-2.09721
C38	-0.12501	-6.19516	-2.33812
C39	-0.93224	-6.67705	-1.1473
C40	0.92184	-5.95688	0.28086
C41	-0.46243	-5.86176	0.04406
C42	-0.45794	-8.09111	-0.89273
C43	0.9693	-8.16327	-0.68814
C44	1.59525	-9.3427	-0.45035
C45	0.80098	-10.54402	-0.40835
C46	-0.61883	-10.47041	-0.6055

atom	x	y	z
C47	-1.24404	-9.19524	-0.8483
C48	-0.62204	-5.81613	-3.58207
C49	0.29978	-5.36928	-4.55448
C50	1.68037	-5.30841	-4.2824
C51	2.18101	-5.75366	-3.04093
C52	1.51964	-5.34059	1.37919
C53	0.70744	-4.48683	2.16443
C54	-0.67133	-4.36181	1.90809
C55	-1.27629	-5.09703	0.8709
C56	-6.3045	2.74161	2.15479
C57	2.90339	-5.62167	1.79489
N58	3.72836	-6.22764	1.00291
N59	-5.67522	3.60375	2.88009
C60	6.57799	1.44239	0.55111
C61	5.82237	1.23323	-0.74809
C62	5.93178	-0.07431	-1.25427
C63	6.77154	-0.97713	-0.37525
C64	6.06739	0.39432	1.51867
C65	6.15865	-0.91425	1.01168
C66	8.11499	-0.29349	-0.26059
C67	8.0081	1.05204	0.25553
C68	9.09996	1.83459	0.43966
C69	10.3925	1.29654	0.09843
C70	10.49769	-0.03678	-0.42366
C71	9.31096	-0.83485	-0.60005
C72	5.34101	-0.44019	-2.46416
C73	4.53623	0.52906	-3.10599
C74	4.42663	1.84173	-2.6045
C75	5.10908	2.21877	-1.42977
C76	5.57801	0.64659	2.80053
C77	5.10492	-0.46203	3.54011
C78	5.19613	-1.77547	3.03639
C79	5.74	-2.0178	1.75763
C80	5.87308	-3.33932	1.12952
C81	5.61364	1.97453	3.43417
N82	5.98993	3.02233	2.77517
N83	6.00427	-4.43177	1.80267
O84	1.83597	3.08479	4.20256
C85	2.34677	3.43276	5.4717
O86	-2.52116	5.04933	-3.37782
C87	-2.91626	6.00553	-4.34002
O88	0.17626	5.38707	-3.96963
C89	0.33974	4.01847	-4.28836
O90	-0.8733	3.05071	4.79588
C91	-1.06105	3.52559	6.11293
O92	1.31607	-3.6797	3.11855

atom	x	y	z
C93	1.16272	-4.12034	4.45059
O94	-0.20467	-4.8967	-5.76533
C95	-0.0666	-5.80493	-6.83867
O96	2.5716	-4.9672	-5.29345
C97	2.68329	-3.57842	-5.52272
O98	-1.45626	-3.59102	2.76159
C99	-1.7344	-2.30251	2.25269
O100	4.64198	-0.25568	4.83855
C101	3.23087	-0.20939	4.9334
O102	3.92382	0.23099	-4.32232
C103	2.64275	-0.34975	-4.17811
O104	3.54269	2.73639	-3.19541
C105	4.03843	3.37015	-4.35745
O106	4.62991	-2.82115	3.75679
C107	5.45435	-3.32734	4.78663
N108	-6.20676	3.46143	-1.47969
N109	11.70623	-0.55485	-0.75248
C110	12.82118	0.21151	-0.57776
C111	12.71676	1.53635	-0.05751
N112	11.50025	2.05792	0.2726
C113	14.11234	-0.31123	-0.91712
C114	15.21706	0.4643	-0.73749
C115	15.11279	1.78709	-0.21779
C116	13.90498	2.31958	0.11629
N117	-1.37949	-11.59182	-0.56738
C118	-0.77284	-12.79151	-0.33713
C119	0.63911	-12.86481	-0.14075
N120	1.40421	-11.73642	-0.18015
C121	-1.55279	-13.99373	-0.29107
C122	-0.93425	-15.18473	-0.06116
C123	0.47552	-15.25793	0.13465
C124	1.25091	-14.13928	0.09866
N125	1.15334	11.47464	1.94803
C126	0.49156	12.59328	2.36224
C127	-0.90651	12.54622	2.6451
N128	-1.60357	11.38198	2.50512
C129	1.19947	13.83035	2.51726
C130	0.52683	14.93936	2.93162
C131	-0.86915	14.89237	3.21414
C132	-1.57683	13.73692	3.07915
C133	-8.02556	7.30273	-0.90531
C134	-8.82651	6.19374	-1.56687
C135	-8.19382	4.83527	-1.31499
C136	-6.73523	4.80532	-1.80453
C137	-5.94219	5.92368	-1.08764
C138	-6.58429	7.28556	-1.38712
C139	-6.64985	7.7055	3.74716
C140	-7.63919	6.88245	2.94094
C141	-7.36897	5.39952	3.12219
C142	-5.93515	5.04597	2.6963
C143	-4.92368	5.87334	3.52409
C144	-5.22179	7.37431	3.35225
C145	6.66592	-8.61195	1.11718
C146	7.77763	-7.62678	0.79763
C147	7.54193	-6.30527	1.50976
C148	6.18614	-5.715	1.09681
C149	5.05262	-6.70221	1.46327

atom	x	y	z
C150	5.30668	-8.04156	0.74878
C151	7.96104	-6.55361	-2.9355
C152	8.7619	-5.34926	-3.39871
C153	8.1865	-4.06496	-2.82901
C154	6.70448	-3.89242	-3.21101
C155	5.89928	-5.12479	-2.73663
C156	6.50352	-6.40561	-3.33355
C157	6.981	7.84143	-0.67015
C158	5.97029	8.82213	-1.23923
C159	4.54916	8.35292	-0.9795
C160	4.31009	6.94903	-1.56265
C161	5.34199	5.96173	-0.97109
C162	6.76868	6.45551	-1.25421
C163	7.97412	6.10485	3.72002
C164	7.02984	7.14657	3.14569
C165	5.58598	6.77628	3.43656
C166	5.25325	5.39258	2.85803
C167	6.20478	4.32455	3.44479
C168	7.66444	4.72485	3.16636
N169	-3.01951	-5.53371	-3.28707
N170	-5.24085	-3.58585	-2.85834
C171	-4.61919	-2.90315	-1.96037
C172	-2.02989	-5.97816	-3.98314
C173	-6.57259	-1.52103	-0.18701
C174	-5.65087	-0.81278	-1.1643
C175	-5.8282	0.583	-1.19216
C176	-6.85956	1.06237	-0.19427
C177	-6.30901	-0.89423	1.16903
C178	-6.41394	0.51128	1.14866
C179	-8.13831	0.33724	-0.54501
C180	-7.97623	-1.09689	-0.5582
C181	-8.99808	-1.92979	-0.87656
C182	-10.27867	-1.35053	-1.19349
C183	-10.44233	0.07514	-1.17501
C184	-9.32518	0.92213	-0.84294
C185	-5.11617	1.39248	-2.07558
C186	-4.09237	0.77721	-2.83662
C187	-3.90809	-0.61926	-2.80691
C188	-4.71965	-1.43068	-1.99087
C189	-6.038	-1.56824	2.3569
C190	-5.74729	-0.79416	3.50145
C191	-5.75008	0.61393	3.45527
C192	-6.12972	1.28733	2.27491
C193	-6.15753	-3.02738	2.51873
N194	-5.59907	-3.87656	1.72595
C195	-2.73266	-5.08383	0.63123
N196	-3.47031	-5.92143	1.27294
O197	-5.35266	-1.46277	4.65902
C198	-6.35502	-1.53649	5.65152
O199	-3.16314	1.55354	-3.52106
C200	-3.56217	1.95622	-4.81204
O201	-2.84668	-1.2032	-3.4916
C202	-3.13366	-1.5097	-4.83952
O203	-5.51301	1.33491	4.62089
C204	-4.13736	1.48748	4.91376
N205	-11.64118	0.63525	-1.47031
C206	-12.68896	-0.17901	-1.78497

atom	x	y	z
C207	-12.52615	-1.59717	-1.80279
N208	-11.32017	-2.1603	-1.50562
C209	-13.96812	0.38626	-2.10144
C210	-15.00564	-0.43829	-2.41368
C211	-14.84312	-1.85414	-2.43151
C212	-13.64486	-2.42959	-2.13679
C213	-7.54956	-7.16114	1.66051
C214	-6.62843	-7.91962	0.72101
C215	-5.17573	-7.61835	1.04509
C216	-4.8972	-6.10968	0.95031
C217	-5.82786	-5.32879	1.90594
C218	-7.29278	-5.66721	1.57363
C219	-4.41342	-5.798	-3.71158
C220	-5.37697	-5.05214	-2.76071
C221	-6.83868	-5.37937	-3.10641
C222	-7.08887	-6.87547	-3.0391
C223	-6.15321	-7.61152	-3.9818
C224	-4.70464	-7.30858	-3.6433
H225	3.86098	-6.6206	-1.96255
H226	-5.10999	3.23956	-3.26714
H227	5.24904	-1.83607	-4.17143
H228	-3.7444	5.67319	0.36475
H229	5.1757	3.59897	0.25294
H230	2.31186	6.1003	-3.12233
H231	2.07533	6.64783	0.53915
H232	-2.68033	6.49356	1.55516
H233	2.22144	9.1624	1.15369
H234	-2.74405	8.99356	2.15971
H235	-3.03525	4.1602	4.3988
H236	3.1342	5.27165	1.23552
H237	2.75057	-6.83717	-0.54231
H238	-2.03249	-6.61683	-1.29851
H239	2.6794	-9.3967	-0.28398
H240	-2.33177	-9.13566	-0.9833
H241	-7.00895	3.04958	1.35082
H242	3.18059	-5.33208	2.82503
H243	6.45668	2.47974	0.99535
H244	6.81811	-2.0212	-0.81923
H245	9.01782	2.85323	0.84109
H246	9.38799	-1.85271	-1.00582
H247	5.896	-3.31819	0.0178
H248	5.34089	2.02596	4.5039
H249	3.04368	2.61062	5.66807
H250	2.87701	4.39142	5.47395
H251	1.55854	3.44985	6.23883
H252	-3.60894	5.4292	-4.96007
H253	-3.43165	6.86194	-3.89206
H254	-2.07095	6.35724	-4.94198
H255	0.81433	4.06326	-5.27265
H256	0.99416	3.5019	-3.57637
H257	-0.62299	3.49727	-4.35342
H258	-1.66415	2.7343	6.56757
H259	-0.09938	3.6224	6.63773
H260	-1.59646	4.48137	6.15832
H261	1.70362	-3.35035	5.00951
H262	0.11416	-4.15639	4.76521
H263	1.62772	-5.09998	4.61171

atom	x	y	z
H264	-0.50863	-5.25406	-7.67274
H265	0.98045	-6.04395	-7.05488
H266	-0.62364	-6.73264	-6.66187
H267	3.52473	-3.52295	-6.21824
H268	1.77841	-3.17178	-5.98906
H269	2.91005	-3.00065	-4.6114
H270	-2.34998	-1.86315	3.04189
H271	-0.82319	-1.71251	2.10623
H272	-2.2987	-2.35027	1.31342
H273	3.07649	0.08014	5.97653
H274	2.79541	0.54217	4.26436
H275	2.77681	-1.18859	4.7389
H276	2.22491	-0.26537	-5.18494
H277	2.72749	-1.41306	-3.90014
H278	2.00791	0.17815	-3.45861
H279	3.23196	4.0735	-4.59209
H280	4.97303	3.91133	-4.17408
H281	4.1768	2.66357	-5.18309
H282	4.85712	-4.15989	5.16858
H283	6.41653	-3.69279	4.41155
H284	5.62375	-2.5881	5.57745
H285	14.18829	-1.32939	-1.31647
H286	16.21119	0.081	-0.99153
H287	16.03066	2.37133	-0.0916
H288	13.82048	3.33676	0.51642
H289	-2.63706	-13.93307	-0.44134
H290	-1.51456	-16.11288	-0.02242
H291	0.92619	-16.23968	0.31634
H292	2.33561	-14.19121	0.24932
H293	2.2733	13.86227	2.29867
H294	1.05183	15.89271	3.05527
H295	-1.36527	15.81141	3.54441
H296	-2.65086	13.69667	3.29518
H297	-8.48533	8.2857	-1.12221
H298	-8.0554	7.19329	0.20446
H299	-8.89932	6.38078	-2.65702
H300	-9.86712	6.1987	-1.18935
H301	-8.23858	4.59007	-0.23103
H302	-8.78516	4.04629	-1.82273
H303	-6.71195	4.99094	-2.91082
H304	-5.99697	5.7477	0.02518
H305	-6.54144	7.5064	-2.47289
H306	-6.0129	8.09444	-0.89018
H307	-6.84085	8.78545	3.59678
H308	-6.7981	7.51977	4.82987
H309	-7.58367	7.15083	1.8594
H310	-8.6748	7.11754	3.25322
H311	-8.09725	4.81425	2.52329
H312	-7.53935	5.11068	4.17905
H313	-5.80416	5.30356	1.60873
H314	-5.01755	5.59509	4.60598
H315	-5.04057	7.68154	2.2997
H316	-4.51589	7.97508	3.96024
H317	6.83291	-9.56315	0.57607
H318	6.68895	-8.86908	2.1952
H319	7.84296	-7.45772	-0.30323
H320	8.7569	-8.04779	1.09489

atom	x	y	z
H321	8.35738	-5.59632	1.26453
H322	7.58545	-6.45001	2.6082
H323	6.19247	-5.57306	-0.02225
H324	5.05374	-6.86732	2.57262
H325	5.23901	-7.90568	-0.35299
H326	4.51157	-8.77017	1.00767
H327	8.37902	-7.4806	-3.37274
H328	8.04341	-6.6797	-1.82988
H329	8.7695	-5.30433	-4.50629
H330	9.82063	-5.45482	-3.09307
H331	8.29911	-4.06103	-1.72315
H332	8.77643	-3.19815	-3.18913
H333	6.61357	-3.79822	-4.32488
H334	5.95876	-5.18249	-1.61423
H335	6.41242	-6.39659	-4.43854
H336	5.93198	-7.29112	-2.98617
H337	8.01008	8.18749	-0.88524
H338	6.90349	7.80165	0.44181
H339	6.13645	8.94508	-2.32831
H340	6.12101	9.82495	-0.79527
H341	3.83174	9.07419	-1.41871
H342	4.34461	8.3561	0.11297
H343	4.43171	6.98465	-2.67786
H344	5.1962	5.91748	0.14739
H345	6.9651	6.46997	-2.34546
H346	7.5063	5.75054	-0.82057
H347	9.02319	6.37393	3.49078
H348	7.89845	6.09633	4.82594
H349	7.18257	7.24884	2.04556
H350	7.25667	8.14253	3.57196
H351	4.91013	7.54024	3.00199
H352	5.4038	6.79377	4.53026
H353	5.40016	5.42994	1.73961
H354	6.04316	4.25629	4.55339
H355	7.86781	4.70282	2.07386
H356	8.3537	3.98068	3.61248
H357	-4.04751	-3.34222	-1.11668
H358	-2.1745	-6.51675	-4.93801
H359	-6.44397	-2.6259	-0.20224
H360	-6.95432	2.19311	-0.22576

atom	x	y	z
H361	-8.86805	-3.01955	-0.90333
H362	-9.44627	2.0136	-0.84242
H363	-6.7709	-3.34295	3.3829
H364	-3.10484	-4.37033	-0.13267
H365	-5.85033	-2.07758	6.45595
H366	-6.67489	-0.54873	6.00104
H367	-7.2288	-2.10205	5.30666
H368	-2.69482	2.5264	-5.15834
H369	-3.74709	1.09507	-5.47148
H370	-4.44969	2.60583	-4.77782
H371	-2.19452	-1.94685	-5.18764
H372	-3.95028	-2.2338	-4.93622
H373	-3.37316	-0.6074	-5.42401
H374	-4.14577	2.18615	5.75544
H375	-3.68174	0.53736	5.21497
H376	-3.57278	1.91733	4.07757
H377	-14.08906	1.47582	-2.08664
H378	-15.98955	-0.0236	-2.65828
H379	-15.70819	-2.47482	-2.68915
H380	-13.51566	-3.51823	-2.14964
H381	-8.60755	-7.37512	1.41491
H382	-7.40237	-7.51292	2.70132
H383	-6.8497	-7.6489	-0.33793
H384	-6.81626	-9.00743	0.79808
H385	-4.51304	-8.16981	0.34633
H386	-4.92679	-7.99504	2.05794
H387	-5.11017	-5.77487	-0.10374
H388	-5.60473	-5.62078	2.96398
H389	-7.54825	-5.30267	0.55554
H390	-7.97341	-5.13148	2.26575
H391	-4.56387	-5.43125	-4.75888
H392	-5.17307	-5.39984	-1.70896
H393	-7.09259	-4.99824	-4.11629
H394	-7.51937	-4.85411	-2.4047
H395	-8.14218	-7.09529	-3.29781
H396	-6.95153	-7.24174	-1.99467
H397	-6.36777	-7.32399	-5.03056
H398	-6.33191	-8.70246	-3.92397
H399	-4.0381	-7.85741	-4.33901
H400	-4.46918	-7.697	-2.6292

13. Electron density maps

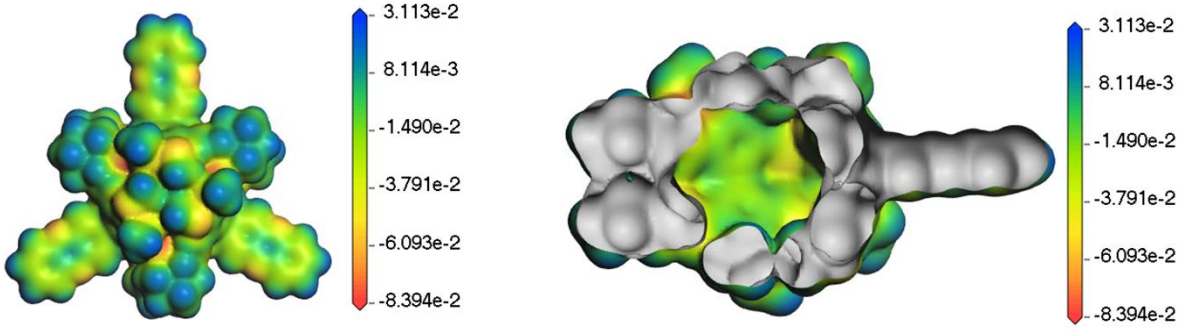


Figure S69: Electron density map top view and cut out of side view of **9**.

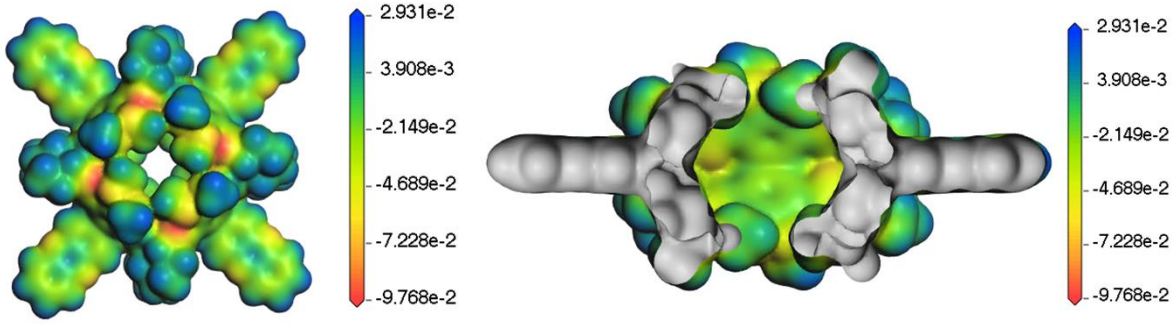


Figure S70: Electron density map top view and cut out of side view of **10**.

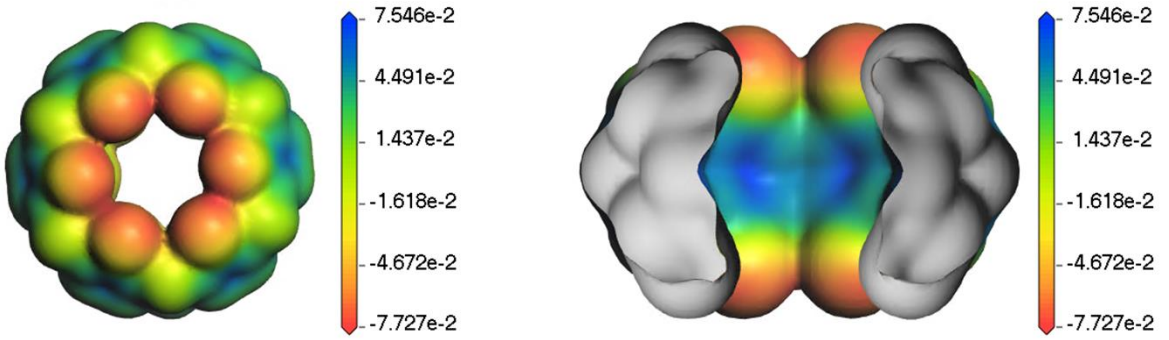


Figure S71: Electron density map top view and cut out of side view of **CB6**.

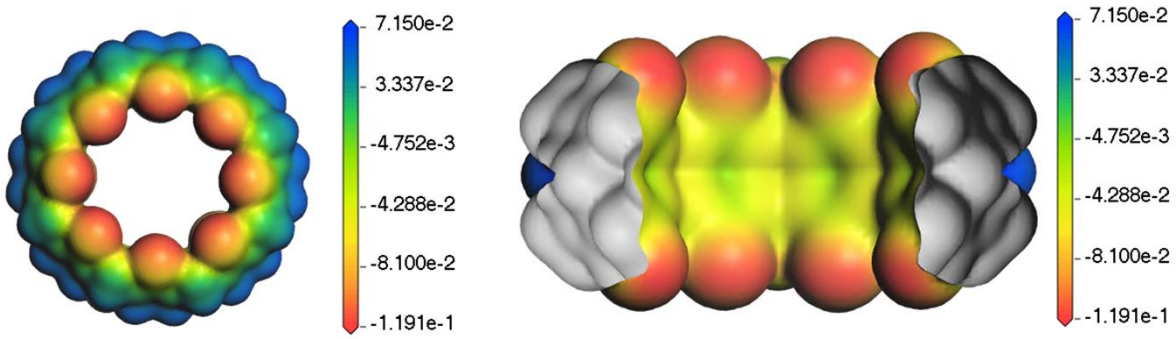


Figure S72: Electron density map top view and cut out of side view of **CB8**.

14. References

1. B. S. Ghanem, M. Hashem, K. D. M. Harris, K. J. Msayib, M. Xu, P. M. Budd, N. Chaukura, D. Book, S. Tedds, A. Walton and N. B. McKeown, *Macromolecules*, 2010, **43**, 5287-5294.
2. F. Zhang, S. Bai, G. P. A. Yap, V. Tarwade and J. M. Fox, *J. Am. Chem. Soc.*, 2005, **127**, 10590-10599.
3. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
4. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3-10.
5. L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *SADABS 2016/2. Bruker AXS area detector scaling and absorption correction*, Bruker Analytical X-ray Division, Madison, Wisconsin, **2016**.
6. *X-Area LANA 1.70.0.0,* Stoe & Cie GmbH, Darmstadt, **2017**.
7. G. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3-8.
8. G. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3-8.
9. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209-220.
10. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 221-264.
11. J. J. P. Stewart, *J. Comput. Chem.*, 1991, **12**, 320-341.
12. J. J. P. Stewart, *J. Mol. Model.*, 2004, **10**, 155-164.
13. S. Viel, F. Ziarelli, G. Pagès, C. Carrara and S. Caldarelli, *J. Magn. Reson.*, 2008, **190**, 113-123.
14. Y. H. Zhao, M. H. Abraham and A. M. Zissimos, *J. Org. Chem.*, 2003, **68**, 7368-7373.
15. N. Guex and M. C. Peitsch, *ELECTROPHORESIS*, 1997, **18**, 2714-2723.