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Supporting Information

# Soluble Congeners of Prior Insoluble Shape-Persistent Imine Cages

Mattes Holsten, Sarah Feierabend, Sven M. Elbert, Frank Rominger, Thomas Oeser, and Michael Mastalerz*

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# 1 General Remarks

## Chemicals and Solvents

All utilised chemicals and solvents were purchased from *abcr*, *Acros Organics*, *Alfa Aesar*, *Carbolution*, *Degussa*, *Fisher Chemical*, *Grüssing*, *Honeywell*, *Merck*, *Sigma Aldrich*, *TCI* or *VWR*. They were used without further purification, if not mentioned otherwise. Dry DCM, THF or toluene were obtained from *Honeywell* and purified by a *Solvent Purification System MB SPS-800*.

## Analytical and Purification Methods

### Elemental analysis

The elemental analyses were performed on a *Vario EL Element Analyzer* by the microanalytical laboratory of University of Heidelberg.

### IR Spectroscopy

Infrared spectroscopical measurements were conducted using a *Bruker Tensor 27 spectrometer* with ZnSe ATR crystal. The used abbreviations for describing the relative intensity of the obtained signals are *vw* (very weak, 0 – 10%), *w* (weak, 10 – 30%), *m* (medium, 30 – 60%), *s* (strong, 60 – 90%) and *vs* (very strong, 90 – 100% ).

### Mass Spectrometry

Mass spectrometric analyses were performed by the mass spectrometry department of University of Heidelberg under the supervision of Dr Jürgen H. Gross. The utilised devices were *Bruker AutoFlex Speed time-of-flight* spectrometer (MALDI-TOF) and *Bruker ApexQe hybrid 9.4T FT-ICR* spectrometer (ESI). For the MALDI analyses DCTB (*trans*-2-[3-(4-tert-Butylphenyl)-2-methylpropenylidene)malononitrile) was used as matrix. High resolution MALDI-TOF spectra were obtained by utilizing an internal polyethylene glycole (PEG) standard.

### Melting Point Measurement

All measured melting points were obtained using a *Büchi Melting Point B-545* device.

## NMR Spectroscopy

Nuclear magnetic resonance spectra were obtained using a *Bruker Avance III 300* (300 MHz), *Bruker Avance DRX 300* (300 MHz), *Bruker Fourier 300* (300 MHz), *Bruker Avance III 400* (400 MHz), *Bruker Avance III 500* (500 MHz) or *Bruker Avance III 600* (600 MHz) spectrometer. The chemical shifts $\delta$ are shown in parts per million (ppm) and the coupling constants $J$ in Hertz (Hz). The spectra were recorded at 298 K, if not mentioned otherwise. The obtained signals of $^1$H, $^2$H and $^{13}$C{1H} NMR spectra were referred to known solvent signals ($CDCl_3$: $^1$H/$^2$H NMR 7.26 ppm, $^{13}$C{1H} NMR 77.2 ppm; THF-$d_8$: $^1$H NMR 3.58 ppm, 1.73 ppm, $^{13}$C{1H} NMR 67.6 ppm, 25.3 ppm).[S1] To obtain a referable solvent signal in $^2$H NMR spectroscopy $CHCl_3$ containing a low amount of $CDCl_3$ or a THF/THF-$d_8$ mixture has been used as solvent. Multiplicities were labelled with *s* (singlet), *d* (doublet), *dd* (doublet of doublet), *t* (triplet), *td* (triplet of doublet), *q* (quartet) and *m* (multiplet).

DOSY spectra were recorded at 298 K using THF-$d_8$ as solvent and referred to its self-diffusion coefficient ($D_{THF}$ = $2.33 \cdot 10^{-9}$ m$^2$ s$^{-1}$).[S2] The solvodynamic radii $r$ of cage molecules were calculated using the Stokes-Einstein equation solved for $r$:

$$r = \frac{\mathrm{k}_B T}{6\pi\eta D} \qquad \text{(eq.1)}$$

$k_B$ is the Boltzmann constant, $T$ the temperature, $\eta$ the viscosity of THF and $D$ the determined diffusion coefficient of the cage molecule.

## Single Crystal X-Ray Diffraction

X-Ray diffraction measurements were proceeded using a *Stoe Stadivari* diffractometer containing a Cu micro source ($\lambda_{K_\alpha}$ = 1.54178 Å) and PILATUS detector or *Bruker APEX II Quazar* with Mo micro source ($\lambda_{K_\alpha}$ = 0.71073 Å). The structures were solved with *SHELXT-2014*[S3] and refined against $F^2$ with a Full-matrix least-squares algorithm using the *SHELXL-2018/3*[S4] software.

## Size Exclusion Chromatography

The synthesised cage compounds were purified using a recycling size exclusion chromatography system from *Shimadzu* containing a control unit (*CBM-20A*), a degassing unit (*DGU-20A*), a pump system (*LC-20AD*), an autosampler (*SIL-20A HT*), a column oven (*CTO-20A*), a high pressure switching valve (*FCV-20AH2*), a photo diode array (PDA) detector (*SPC-M20A*) and a fraction collector (*FRC-10A*). As stationary phase one 20 x 50 mm pre-column and three 20 x 300 mm columns containing *SDV preparative 100 Å* SEC material purchased from *Polymer Standards Service*. THF (chromatography GPC grade) from *Fisher Scientific* was used as mobile phase at a flow rate of 5 mL min$^{-1}$. During the separation the oven temperature was set to 40 °C. The shown chromatograms have been recorded with an absorption wavelength of 254 nm. To remove residual butylated hydroxytoluene (BHT, stabilizer in THF), the product containing fractions were washed with *n*-hexane (3 x 6 mL) and dried *in vacuo*.

## Thin Layer and Flash Chromatography

Analytical thin layer chromatography was conducted using *TLC Silica gel 60* $F_{254}$ plates purchased from *Merck*. The resulted spots were analysed using ultraviolet radiation (254 nm and 366 nm). Flash chromatography was performed using *Silica gel 60 (40–63 µm / 230–400 mesh ASTM)* from *Machery-Nagel*.

## UV/vis Spectroscopy

UV/vis absorption spectra have been recorded using a *Jasco V-730* spectrophotometer. Molar extinction coefficients ($\varepsilon$) were calculated by absorption measurements of five different concentrated solutions prepared by standard addition method. The illustrated absorption spectra have been obtained by normalizing the measured spectra and multiplying with the molar extinction coefficient of the global absorption maximum.

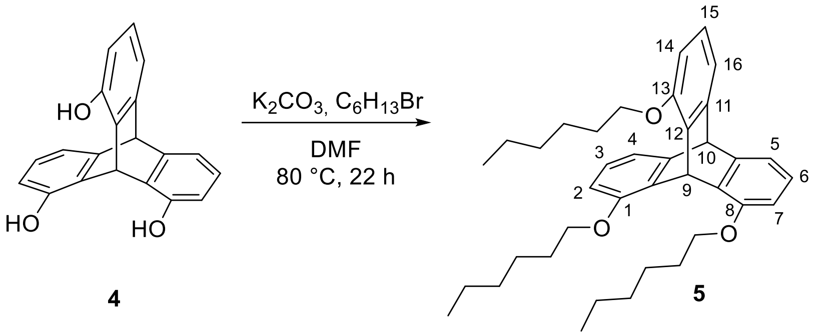
## Synthesis of Literature-Known Starting Materials

1,8,13-Trihydroxytriptycene and 2,7,14-Triflormyl-1,8,13-trihydroxytriptycene have been synthesised by following the synthesis route described from Elbert *et al.*[S5] 3,5-Diformyl-2,6-dihydroxytoluene was synthesised by a Duff formylation of 2,6-dihydroxytoluene.[S6]

# 2 Experimental Procedures

## 2.1 Synthesis of 1,8,13-Trihexyloxy-3,6,15-triaminotriptycene Derivatives

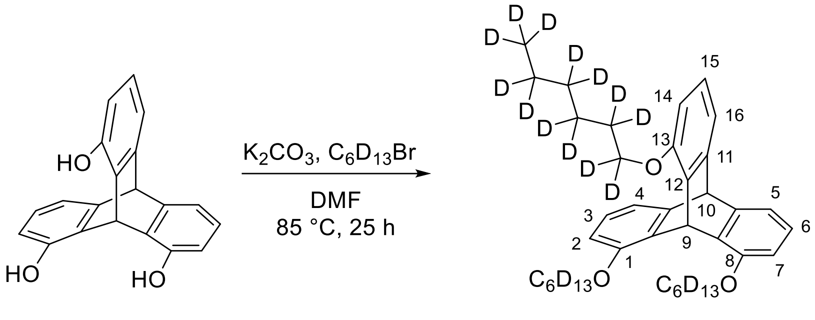
### 2.1.1 1,8,13-Trihexyloxytriptycene 5



According to a modified procedure from Kumano *et al.*,[S7] 1,8,13-trihydroxytriptycene **4** (300 mg, 0.99 mmol), potassium carbonate (823 mg, 5.95 mmol) and *N*,*N*-dimethylformamide (10 mL) were stirred for 1 h at 80 °C. To the emerged brown suspension 1-bromohexane (0.83 mL, 5.95 mmol) was added dropwise and the mixture was stirred for further 21 h at 80 °C. After cooling down to room temperature water (15 mL) was added to the light brown mixture and the precipitate collected by filtration. The solid was washed with water (2 x 30 mL) and methanol (2 x 5 mL) and dried *in vacuo* to give triptycene **5** in 92% yield (506 mg, 0.91 mmol) as off-white solid. **Melting point:** *T* = 226 °C. **$^{1}$H NMR:** (400 MHz, $CDCl_3$) δ (ppm) 7.00 (d, *J* = 7.2 Hz, 3H, Ar*H*-4,5,16), 6.92 (s, 1H, *H*9), 6.88 (dd, *J* = 8.2, 7.3 Hz, 3H, Ar*H*-3,6,15), 6.56 (dd, *J* = 8.3, 0.9 Hz, 3H, Ar*H*-2,7,14), 5.37 (s, 1H, *H*10), 3.97 (t, *J* = 6.4 Hz, 6H, -O-C*H*$_2$-), 1.94 – 1.80 (m, 6H, -O-CH$_2$-C*H*$_2$-), 1.66-1.56 (m, 6H, -O-CH$_2$-CH$_2$-C*H*$_2$-), 1.47-1.33 (m, 12H, -C*H*$_2$-C*H*$_2$-CH$_3$), 1.03-0.88 (m, 9H, -C*H*$_3$). **$^{13}$C{1H} NMR:** (100 MHz, $CDCl_3$) δ (ppm) 154.3 (Ar*C*-1,8,13), 148.7 (Ar*C*-4a,10a,11), 134.0 (Ar*C*-8a,9a,12), 125.6 (Ar*C*-3,6,15), 116.6 (Ar*C*-4,5,16), 110.4 (Ar*C*-2,7,14), 69.0 (-O-*C*H$_2$-), 54.8 (*C*-10), 33.7 (*C*-9), 32.0 (-*C*H$_2$-CH$_2$-CH$_3$), 29.8 (-O-CH$_2$-*C*H$_2$-), 25.9 (-O-CH$_2$-CH$_2$-*C*H$_2$-), 22.8 (-CH$_2$-*C*H$_2$-CH$_3$), 14.3 (-*C*H$_3$). **HRMS (MALDI-TOF+, DCTB):** $[M]^+$: *m/z* calcd. for $C_{38}H_{50}O_3^+$: 554.3760, found: 554.3763. **IR:** (ATR, FT) $\tilde{\nu}$ (cm$^{-1}$) 3047 (w), 3032 (w), 3015 (w), 2949 (m), 2928 (m), 2866 (m), 1597 (s), 1485 (m), 1468 (s), 1439 (m), 1394 (m), 1377 (w), 1346 (w), 1323 (w), 1277 (vs), 1234 (m), 1198 (m), 1161 (w), 1124 (w), 1097 (s), 1065 (m), 1053 (m), 1024 (m), 991 (w), 949 (w), 916 (m), 858 (w), 824 (vw), 789 (s), 773 (m), 735 (vs), 683 (vw), 640 (w), 604 (w). **Elemental Anal.** Calcd. for $C_{38}H_{50}O_3 \cdot 1/5$

$H_2O$: C, 81.60; H, 9.10. Found: C, 81.66; H, 8.98. The analytical data is in accordance with the literature data.[S7]

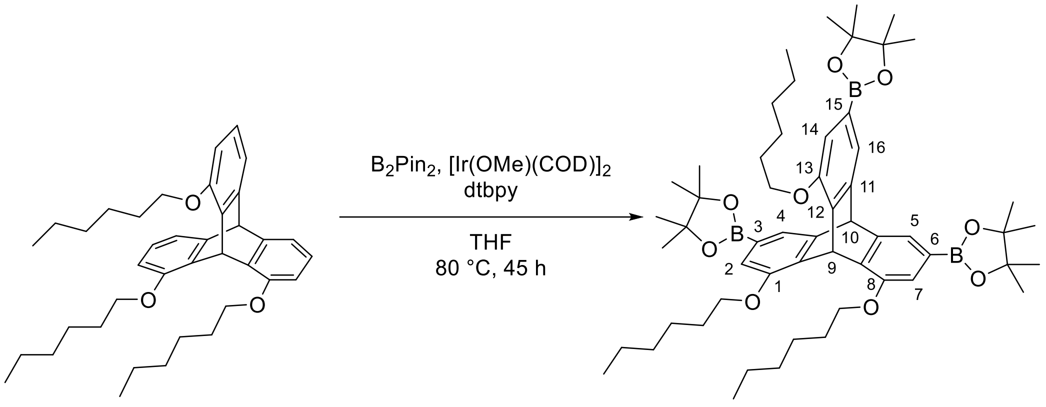
### 2.1.2 1,8,13-Trihexyloxytriptycene-$d_{39}$ 5-$d_{39}$



**4** **5-$d_{39}$**

According to a modified procedure from Kumano *et al.* for the synthesis of 1,8,13-trihexyloxytriptycene,[S7] 1,8,13-trihydroxytriptycene **4** (566 mg, 1.87 mmol), potassium carbonate (1.56 g, 11.2 mmol) and dry *N*,*N*-dimethylformamide (17 mL) were stirred under argon atmosphere for 1 h at 85 °C. 1-Bromohexane-*d13* (1.6 mL, 11.2 mmol) was added dropwise and the reaction mixture was stirred for further 24 h at 85 °C. After cooling down to room temperature water (40 mL) was added to the light brown suspension and the precipitate collected by filtration. The solid was washed with water (2 x 40 mL) and methanol (4 x 8 mL) and dried *in vacuo* to give triptycene **5-$d_{39}$** in 89% yield (987 mg, 1.66 mmol) as off-white solid. **Melting point:** $T$ = 226 °C. **$^1$H NMR:** (400 MHz, $CDCl_3$) δ (ppm) 6.99 (dd, $J$ = 7.2, 0.9 Hz, 3H, Ar*H*-4,5,16), 6.92 (s, 1H, *H*9), 6.87 (dd, $J$ = 8.2, 7.3 Hz, 3H, Ar*H*-3,6,15), 6.55 (dd, $J$ = 8.2, 0.9 Hz, 3H, Ar*H*-2,7,14), 5.37 (s, 1H, *H*10). **$^{13}$C{1H} NMR:** (100 MHz, $CDCl_3$) δ (ppm) 154.3 (Ar-*C*1,8,13), 148.7 (Ar-*C*4a,10a,11), 134.0 (Ar-*C*8a,9a,12), 125.6 (Ar-*C*3,6,15), 116.5 (Ar-*C*4,5,16), 110.4 (Ar-*C*2,7,14), 54.8 (*C*10), 33.7 (*C*9). **$^2$H NMR:** (92 MHz, $CHCl_3/CDCl_3$) δ (ppm) 3.95 (s, 6D, -OC*D*$_2$-), 1.81 (s, 6D, -OCD$_2$-C*D*$_2$-), 1.53 (s, 6D, -OCD$_2$-CD$_2$-C*D*$_2$-), 1.33 (s, 12D, -C*D*$_2$-C*D*$_2$-CD$_3$), 0.89 (s, 9D, -C*D*$_3$). **HRMS (MALDI-TOF+, DCTB):** $[M]^+$: *m/z* calcd. for $C_{38}H_{11}D_{39}O_3^+$:593.6202, found: 593.6219. **IR:** (ATR, FT) $\tilde{\nu}$ ($cm^{-1}$) 2208 (w), 2097 (w), 2070 (vw), 1595 (m), 1479 (s), 1439 (w), 1325 (vw), 1281 (vs), 1248 (w), 1221 (w), 1165 (m), 1105 (s), 1059 (w), 1028 (m), 961 (vw), 922 (w), 856 (w), 824 (vw), 789 (s), 737 (vs), 644 (w). **Elemental Anal.** Calcd. for $C_{38}H_{11}D_{39}O_3$: C, 76.83; H+D, 8.53 (Value was corrected by detection difference of hydrogen and deuterium. Analyzing a compound containing a known deuterium amount resulted in detection of 50.4% of the apparent deuterium.). Found: C, 76.52; H+D, 8.68.

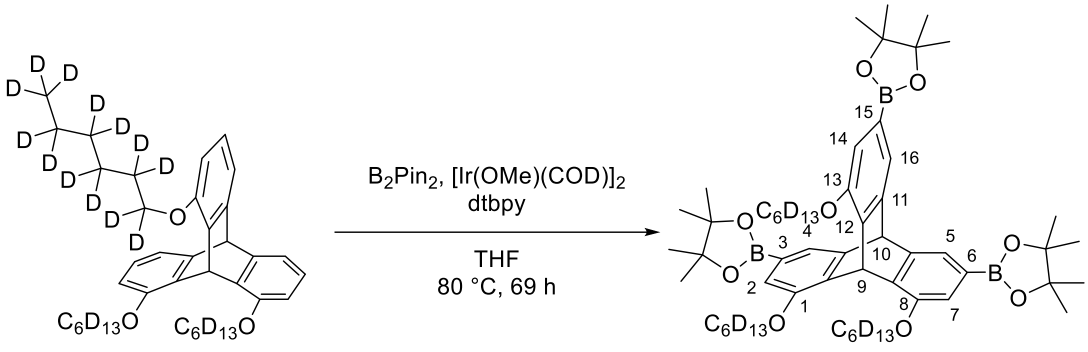
### 2.1.3 1,8,13-Trihexyloxytriptycene-3,6,15-triyltris(4,4,5,5-tetramethyl-1,3,2-dioxa)borolane 6



**5** **6**

In analogy to a literature procedure[S8] 1,8,13-trihexyloxytriptycene **5** (3.42 g, 6.16 mmol) and bis(pinacolato)diboron (9.0 g, 35.44 mmol) were suspended in dry tetrahydrofuran (15 mL) under argon and stirred for 30 min. In another tube bis(pinacolato)diboron (440 mg, 1.73 mmol), 4,4′-di-tert-butyl-2,2′-dipyridine (538 mg, 2.0 mmol) and (1,5-cyclooctadiene)(methoxy)iridium(I) dimer (178 mg, 0.27 mmol) were filled under argon atmosphere and dry tetrahydrofuran (15 mL) was added. The mixture was stirred for 20 min at room temperature and turned dark red. The two solutions were combined and stirred for 41 h at 80 °C. After cooling to room temperature, solvent was evaporated *in vacuo* and methanol (50 mL) was added and the brownish suspension ultrasonicated for 10 min, before it was collected by filtration. Recrystallization using an ethanol-chloroform mixture gave boronic ester **6** in 70% yield (3.98 g, 4.26 mmol) as colourless solid.**Melting point:** *T* = 314 °C. **$^{1}$H NMR:** (400 MHz, $CDCl_3$) δ (ppm) 7.42 (s, 3H, Ar-*H*4,5,16), 6.98 (d, *J* = 0.8 Hz, 3H, Ar-*H*2,7,14), 6.94 (s, 1H, *H*9), 5.44 (s, 1H, *H*10), 3.99 (t, *J* = 6.5 Hz, 6H, -OC$\mathit{H}_2$-), 1.89-1.80 (m, 6H, -OCH$_2$-C$\mathit{H}_2$-), 1.62-1.50 (m, 6H, -OCH$_2$-CH$_2$-C$\mathit{H}_2$-), 1.41-1.34 (m, 12H, -C$\mathit{H}_2$-C$\mathit{H}_2$-CH$_3$), 1.28 (s, 36H, -B-O-C(C$\mathit{H}_3$)$_2$-), 0.98-0.89 (m, 9H, -CH$_2$-C$\mathit{H}_3$). **$^{13}$C{1H} NMR:** (100 MHz, $CDCl_3$) δ (ppm) 154.1 (Ar-*C*1,8,13), 148.0 (Ar-*C*4a,10a,11), 136.8 (Ar-*C*8a,9a,12), 126.6 (Ar-*C*3,6,15), 122.9 (Ar-*C*4,5,16), 116.5 (Ar-*C*2,7,14), 83.6 (-B-O-*C*(CH$_3$)$_2$-), 69.1 (-O*C*H$_2$-), 54.5 (*C*10), 34.5 (*C*9), 32.0 (-*C*H$_2$-CH$_2$-CH$_3$), 29.9 (-OCH$_2$-*C*H$_2$-), 25.9 (-OCH$_2$-CH$_2$-*C*H$_2$-), 24.9 (-B-O-C(*C*H$_3$)$_2$-), 22.8 (-CH$_2$-*C*H$_2$-CH$_3$), 14.3 (-CH$_2$-*C*H$_3$). **HRMS (+ESI):** [M+Na]$^+$: *m/z* calcd. for $C_{56}H_{83}B_3O_9Na^+$: 955.6208, found: 955.6217. **IR:** (ATR, FT) $\tilde{\nu}$ (cm$^{-1}$) 3082 (vw), 3065 (vw), 3045 (vw), 2972 (w), 2930 (w), 2864 (w), 1589 (w), 1574 (w), 1483 (m), 1412 (m), 1356 (vs), 1331 (m), 1298 (m), 1248 (s), 1215 (w), 1140 (s), 1107 (m), 1090 (m), 1001 (w), 964 (m), 937 (w), 916 (m), 856 (m), 831 (m), 768 (m), 714 (w), 696 (m), 667 (m), 648 (w), 609 (vw). **Elemental Anal.** Calcd. for $C_{56}H_{83}B_3O_9$: C, 72.11; H, 8.97. Found: C, 72.11; H, 9.00.

### 2.1.4 1,8,13-Trihexyloxytriptycene-3,6,15-triyltris(4,4,5,5-tetramethyl-1,3,2-dioxa)borolane-d$_{39}$ 6-d$_{39}$

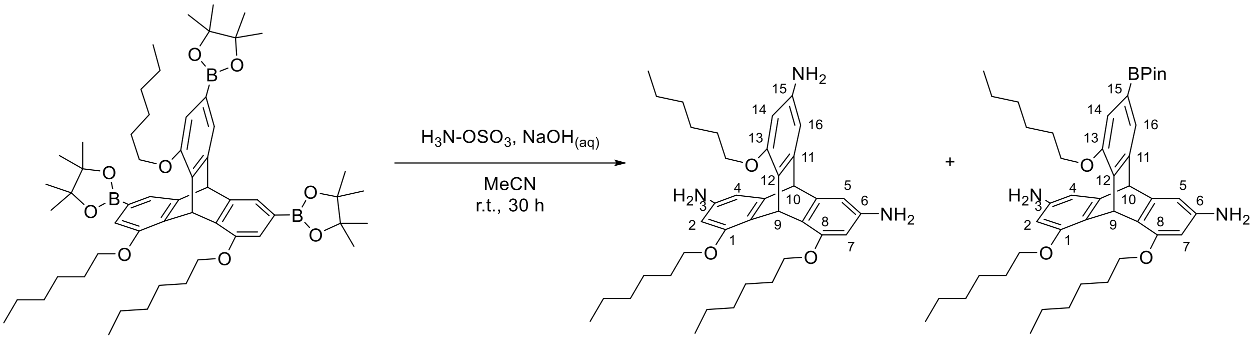


**5-d$_{39}$** **6-d$_{39}$**

In analogy to a literature procedure[S8] 1,8,13-trihexyloxytriptycene-d$_{39}$ **5-d$_{39}$** (901 mg, 1.52 mmol) and bis(pinacolato)diboron (1.62 g, 6.32 mmol) under argon atmosphere were suspended in dry tetrahydrofuran (3.6 mL) and stirred for 25 min. In another Schlenk tube bis(pinacolato)diboron (117 mg, 0.46 mmol), 4,4′-di-tert-butyl-2,2′-dipyridine (41 mg, 0.15 mmol) and (1,5-cyclooctadiene)(methoxy)iridium(I) dimer (51 mg, 0.08 mmol) were filled under argon atmosphere and dry tetrahydrofuran (3.6 mL) was added. The reaction mixture was stirred for 25 min at room temperature. The mixtures were combined and stirred for 69 h at 80 °C. The dark red reaction mixture was allowed to cool to room temperature, solvent was evaporated *in vacuo* and methanol (7 mL) was added. The resulting brown suspension was ultrasonicated for 10 min, before it was collected by filtration. Recrystallization from ethanol-chloroform gave boronic ester **6-d$_{39}$** in 70% yield (1.03 g, 1.05 mmol) as colourless crystals. **Melting point:** $T$ = 315 °C. **$^1$H NMR:** (700 MHz, $CDCl_3$) δ (ppm) 7.41 (s, 3H, Ar-*H*4,5,16), 6.97 (s, 3H, Ar-*H*2,7,14), 6.94 (s, 1H, *H*9), 5.44 (s, 1H, *H*10), 1.27 (s, 36H, -B-O-C(C*H*$_3$)$_2$-). **$^{13}$C{1H} NMR:** (176 MHz, $CDCl_3$) δ (ppm) 154.0 (Ar-*C*1,8,13), 148.0 (Ar-*C*4a,10a,11), 136.7 (Ar-*C*8a,9a,12), 126.5 (Ar-*C*3,6,15), 122.8 (Ar-*C*4,5,16), 116.4 (Ar-*C*2,7,14), 83.6 (-B-O-*C*(CH$_3$)$_2$-), 54.4 (*C*10), 34.4 (*C*9), 24.9 (-B-O-C(*C*H$_3$)$_2$-). **$^2$H NMR:** (92 MHz, $CHCl_3/CDCl_3$) δ (ppm) 3.97 (s, 6D, -OC*D*$_2$-), 1.79 (s, 6D, -OCD$_2$-C*D*$_2$-), 1.51 (s, 6D, -OCD$_2$-CD$_2$-C*D*$_2$-), 1.31 (s, 12D, -C*D*$_2$-C*D*$_2$-CD$_3$), 0.88 (s, 9D, -C*D*$_3$). **HRMS (MALDI-TOF+, DCTB):** $[M]^+$: *m/z* calcd. for $C_{56}H_{44}D_{39}B_3O_9^+$: 971,8759, found:

971,8764. **IR:** (ATR, FT) $\tilde{\nu}$ ($cm^{-1}$) 2976 (w), 2932 (vw), 2208 (w), 2097 (vw), 1587 (w), 1479 (w), 1412 (w), 1362 (vs), 1333 (w), 1296 (m), 1254 (m), 1215 (w), 1140 (s), 1113 (m), 1082 (m), 1040 (w), 1005 (vw), 966 (m), 926 (w), 910 (vw), 856 (m), 831 (w), 766 (w), 716 (w), 696 (m), 667 (w), 646 (w), 617 (vw). **Elemental Anal.** Calcd. for $C_{56}H_{44}D_{39}B_3O_9$: C, 69.20; H+D, 8.64 (Value was corrected by detection difference of hydrogen and deuterium. Analyzing a compound containing a known deuterium amount resulted in detection of 50.4% of the apparent deuterium.). Found: C, 68.93; H+D, 8.72.

### 2.1.5 3,6,15-Triamino-1,8,13-trihexyloxytriptycene 7a and 3,6-Diamino-1,8,13-trihexyloxytriptycene-15-yl(4,4,5,5-tetramethyl-1,3,2-dioxa)borolane 7b



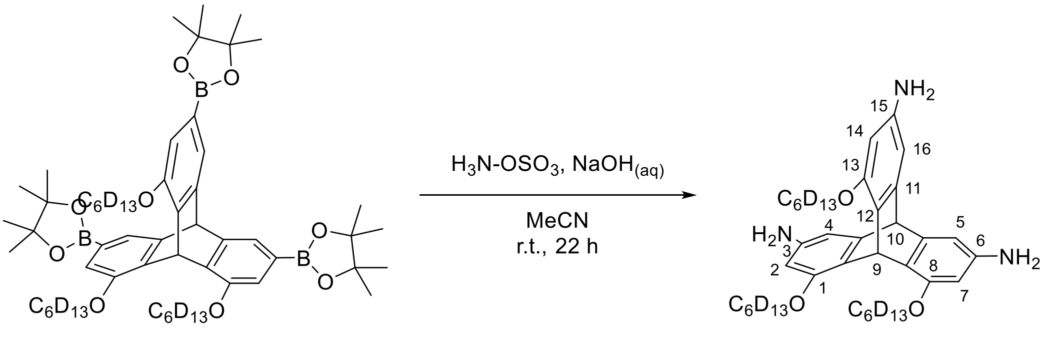
In analogy to a literature procedure[S9] trisboronic ester **6** (1.01 g, 1.1 mmol), hydroxylamine-*O*-sulfonic acid (672 mg, 5.9 mmol), acetonitrile (32 mL) and aqueous sodium hydroxide solution (16 mL, 1 mol $L^{-1}$, 16 mmol) were stirred under argon atmosphere. After 24 h additional amounts of hydroxylamine-*O*-sulfonic acid (336 mg, 2.8 mmol) and aqueous sodium hydroxide solution (8 mL, 1 mol $L^{-1}$, 8 mmol) were added and stirred for additional 6 h at room temperature. Water (40 mL) was added and the mixture extracted with dichloromethane (3 x 60 mL). The combined organic phase was dried over sodium sulphate and solvent removed by rotary evaporation. Purification by silica column chromatography (dichloromethane/methanol 40:1) gave after drying in vacuum triamine **7a** in 62% yield (398 mg, 0.66 mmol) as off-white solid and **7b** in 9% yield (67 mg, 0.09 mmol) as dark brown solid.

Compound **7a**: **Melting point:** $T$ = 253 °C. **Retention factor:** $R_f$ = 0.29 (in dichloromethane/methanol 20:1 v/v). **$^1$H NMR:** (600 MHz, $CDCl_3$) δ (ppm) 6.44 (s, 1H, *H*9), 6.37 (d, $J$ = 1.9 Hz, 3H, Ar-*H*4,5,16), 5.90 (s, $J$ = 1.9 Hz, 3H, Ar-*H*2,7,14), 4.93 (s, 1H, *H*10), 3.88 (t, $J$ = 6.5 Hz, 6H, -OC$H_2$-), 3.23 (br. s, 6H, -N$H_2$), 1.85 – 1.78 (m, 6H,

-OCH$_2$-C*H*$_2$-), 1.59 – 1.51 (m, 6H, -OCH$_2$-CH$_2$-C*H*$_2$-), 1.41 – 1.34 (m, 12H, -C*H*$_2$-C*H*$_2$-CH$_3$), 0.98 – 0.91 (m, 9H, -C*H*$_3$). **$^{13}$C{1H} NMR:** (150 MHz, CDCl$_3$) δ (ppm) 154.0 (Ar-*C*1,8,13), 149.2 (Ar-*C*4a,10a,11), 144.1 (Ar-*C*3,6,15), 126.0 (Ar-*C*8a,9a,12), 104.7 (Ar-*C*4,5,16), 97.9 (Ar-*C*2,7,14), 69.0 (-O*C*H$_2$-), 55.0 (*C*10), 32.2 (*C*9), 31.9 (-*C*H$_2$-CH$_2$-CH$_3$), 29.8 (-OCH$_2$-*C*H$_2$-), 25.9 (-OCH$_2$-CH$_2$-*C*H$_2$-), 22.8 (-CH$_2$-*C*H$_2$-CH$_3$), 14.3 (-*C*H$_3$). **HRMS (+ESI):** [M+H]$^+$: *m/z* calcd. for $C_{38}H_{54}N_3O_3^+$: 600.4160, found: 600.4166. **IR:** (ATR, FT) $\tilde{\nu}$ (cm$^{-1}$) 3396.49 (vw), 3335 (w), 2955 (m), 2930 (m), 2858 (w), 1603 (vs), 1495 (m), 1456 (m), 1394 (vw), 1375 (vw), 1325 (m), 1242 (w), 1196 (m), 1142 (vs), 1103 (m), 1076 (m), 1034 (w), 993 (vw), 976 (w), 914 (w), 816 (m), 766 (m), 725 (w), 681 (w), 635 (w), 619 (vw). **Elemental Anal.** Calcd. for $C_{38}H_{53}N_3O_3$ · 13/10 $CH_3OH$: C, 73.58; H, 9.14; N, 6.55. Found: C, 73.60; H, 9.32; N, 6.33.

Compound **7b**: **Melting point:** *T* = 254 °C. **Retention factor:** $R_f$ = 0.5 (in dichloromethane/methanol 20:1 v/v). **$^1$H NMR:** (500 MHz, CDCl$_3$) δ (ppm) 7.42 (s, 1H, Ar-*H*16), 7.01 (s, 1H, Ar-*H*14), 6.62 (s, 1H, *H*9), 6.38 (d, *J* = 1.8 Hz, 2H, Ar-*H*4,5), 5.90 (d, *J* = 1.9 Hz, 2H, Ar-*H*2,7), 5.10 (s, 1H, *H*10), 3.99 (t, *J* = 6.5 Hz, 2H, PinB-Ar-OC*H*$_2$-), 3.88 (t, *J* = 6.5 Hz, 4H, H$_2$N-Ar-OC*H*$_2$-), 3.54 (br. s, 4H, -N*H*$_2$), 1.88 – 1.77 (m, 6H, -OCH$_2$-C*H*$_2$-), 1.60 – 1.51 (m, 6H, -OCH$_2$-CH$_2$-C*H*$_2$-), 1.42 – 1.34 (m, 12H, -C*H*$_2$-C*H*$_2$-CH$_3$), 1.29 (s, 12H, -B-O-C(C*H*$_3$)$_2$), 0.97 – 0.92 (m, 9H, -C*H*$_3$). **$^{13}$C{$^1$H} NMR:** (126 MHz, CDCl$_3$) δ (ppm) 154.5 (Ar-*C*1,8), 153.2 (Ar-*C*13), 149.3 (Ar-*C*4a,10a), 147.8 (Ar-*C*11), 144.1 (Ar-*C*3,6), 138.8 (Ar-*C*12), 125.0 (Ar-*C*9a,8a), 122.6 (Ar-*C*14), 116.7 (Ar-*C*16), 104.8 (Ar-*C*4,5), 97.9 (Ar-*C*2,7), 83.6 (-B-O-*C*(CH$_3$)$_2$), 69.0 (-O*C*H$_3$-), 68.9 (-O*C*H$_3$-), 54.8 (*C*10), 32.9 (C9), 32.0 (-*C*H$_2$-*C*H$_2$-CH$_3$), 31.9 (-OCH$_2$-*C*H$_2$-), 29.8 (-OCH$_2$-*C*H$_2$-), 29.8 (-OCH$_2$-*C*H$_2$-), 25.9 (-OCH$_2$-CH$_2$-*C*H$_2$-), 25.9 (-OCH$_2$-CH$_2$-*C*H$_2$-), 24.9 (-B-O-C(*C*H$_3$)$_2$), 22.8 (-*C*H$_2$-*C*H$_2$-CH$_3$), 14.3 (-*C*H$_3$). ($^1$H,$^{13}$C HMBC spectrum shows cross peak, which results from a $^2J$ coupling between Ar-*H*16 and Ar-*C*15, at 7.42 ppm/125.8 ppm ($^1$H/$^{13}$C). The signal for Ar-*C*15 is not apparent in $^{13}$C{1H} NMR spectrum due to its low intensity resulting from coupling with bound boron nucleus.) **HRMS (+ESI):** [M+H]$^+$: *m/z* calcd. for $C_{44}H_{64}BN_2O_5^+$: 711.4903, found: 711.4911. **IR:** (ATR, FT) $\tilde{\nu}$ (cm$^{-1}$) 3464 (vw), 3410 (vw), 3337 (w), 2955 (m), 2930 (m), 2860 (m), 1599 (s), 1493 (m), 1468 (m), 1454 (m), 1402 (m), 1358 (vs), 1337 (s), 1296 (w), 1248 (m), 1196 (m), 1159 (m), 1130 (s), 1103 (s), 1084 (m), 966 (m), 932 (w), 916 (w), 854 (m), 839 (m), 824 (m), 814 (m), 768 (m), 725 (w), 698 (w), 673 (w), 629 (w). **Elemental Anal.** Calcd. for $C_{44}H_{63}BN_2O_5$: C, 74.35; H, 8.93; N, 3.94. Found: C, 74.11; H, 9.01; N, 3.65.

### 2.1.6 3,6,15-Triamino-1,8,13-trihexyloxytriptycene-$d_{39}$ 7a-$d_{39}$

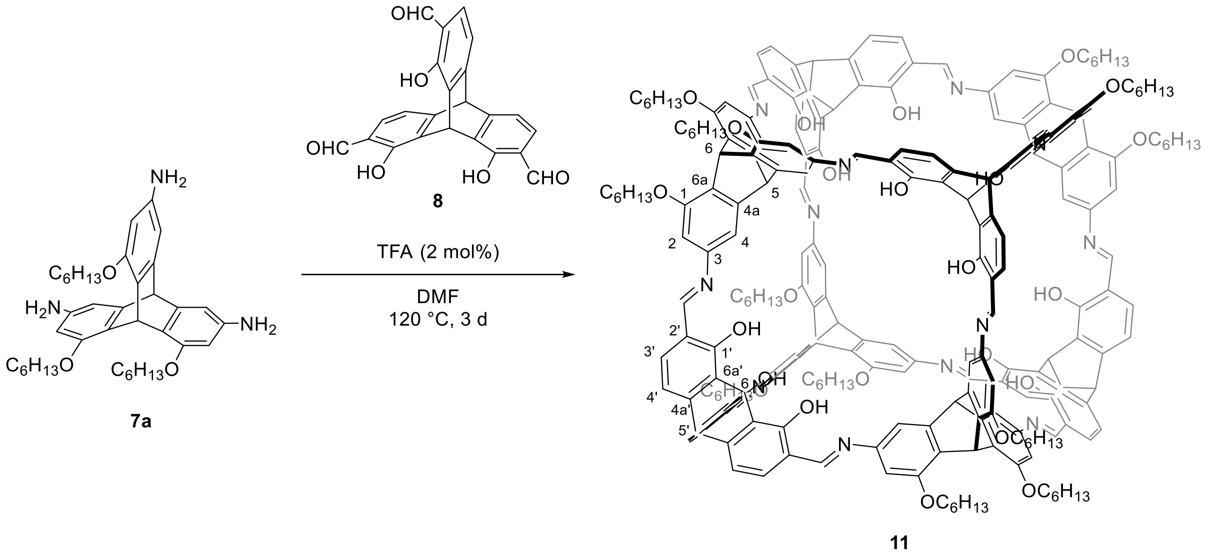


**6-$d_{39}$** **7a-$d_{39}$**

In analogy to a literature procedure[S9] triboronic ester **6-$d_{39}$** (850 mg, 0.9 mmol), hydroxylamine-*O*-sulfonic acid (97 %-wt, 566 mg, 4.9 mmol), acetonitrile (27 mL) and aqueous sodium hydroxide solution (13 mL, 1 mol $L^{-1}$, 13 mmol) were stirred at room temperature under argon atmosphere. After 13 h additional amounts of hydroxylamine-*O*-sulfonic acid (283 mg, 2.4 mmol) and aqueous sodium hydroxide solution (6.5 mL, 1 mol $L^{-1}$, 6.5 mmol) were added and stirred for further 9 h at room temperature. Water (40 mL) was added and the mixture extracted with dichloromethane (3 x 60 mL). The combined organic phase was dried over sodium sulphate. After removal of the solvent byrotary evaporation the residue was purified by silica column chromatography (dichloromethane/methanol = 40:1) to give **7a-$d_{39}$** in 66% yield (370 mg, 0.58 mmol) as an off-white solid. **Melting point:** $T$ = 254 °C. **Retention factor:** $R_f$ = 0.29 (dichloromethane/methanol 20:1). **$^1$H NMR:** (600 MHz, $CDCl_3$) δ (ppm) 6.44 (s, 1H, *H*9), 6.37 (d, $J$ = 1.9 Hz, 3H, Ar-*H*4,5,16), 5.89 (d, $J$ = 2.0 Hz, 3H, Ar-*H*2,7,14), 4.93 (s, 1H, *H*10), 3.42 (br. s, 6H, $-NH_2$). **$^{13}$C{$^1$H} NMR:** (151 MHz, $CDCl_3$) δ (ppm) 154.1 (Ar-*C*1,8,13), 149.3 (Ar-*C*4a,10a,11), 144.2 (Ar-*C*3,6,15), 126.1 (Ar-*C*8a,9a,12), 104.6 (Ar-*C*4,5,16), 97.9 (Ar-*C*2,7,14), 55.1 (*C*10), 32.2(*C*9). **$^2$H NMR:** (92 MHz, $CHCl_3/CDCl_3$) δ (ppm) 3.87 (s, 6D, $-OCD_2-$), 1.75 (s, 6D, $-OCD_2-CD_2-$), 1.48 (s, 6D, $-OCD_2-CD_2-CD_2-$), 1.31 (s, 12D, $-CD_2-CD_2-CD_3$), 0.88 (s, 9D, $-CD_3$). **HRMS (MALDI-TOF+, DCTB):** $[M]^+$: *m/z* calcd. for $C_{38}H_{14}N_3O_3^+$: 638.6529, found: 638.6540. **IR:** (ATR, FT) $\tilde{\nu}$ ($cm^{-1}$) 3605 (vw), 3460 (vw), 3412 (vw), 3371 (vw), 3339 (vw), 3217 (vw), 3020 (vw), 2208 (m), 2095 (w), 1601 (vs), 1493 (m), 1456 (m), 1360 (w), 1331 (m), 1244 (w), 1198 (m), 1169 (w), 1140 (s), 1107 (s), 1036 (m), 993 (w), 970 (vw), 916 (vw), 860 (w), 810 (m), 764 (m), 717 (w), 677 (w), 621 (w). **Elemental Anal.** Calcd. for $C_{38}H_{14}D_{39}N_3O_3 \cdot 6/10\ H_2O$: C, 70.23; H+D, 8.45 (Value was corrected by detection difference of hydrogen and deuterium. Analyzing a compound containing a known deuterium amount resulted in detection of 50.4% of the apparent deuterium.); N, 6.47. Found: C, 70.27; H+D, 8.58; N 6.29.

## 2.2 Syntheses of Soluble Organic Cages

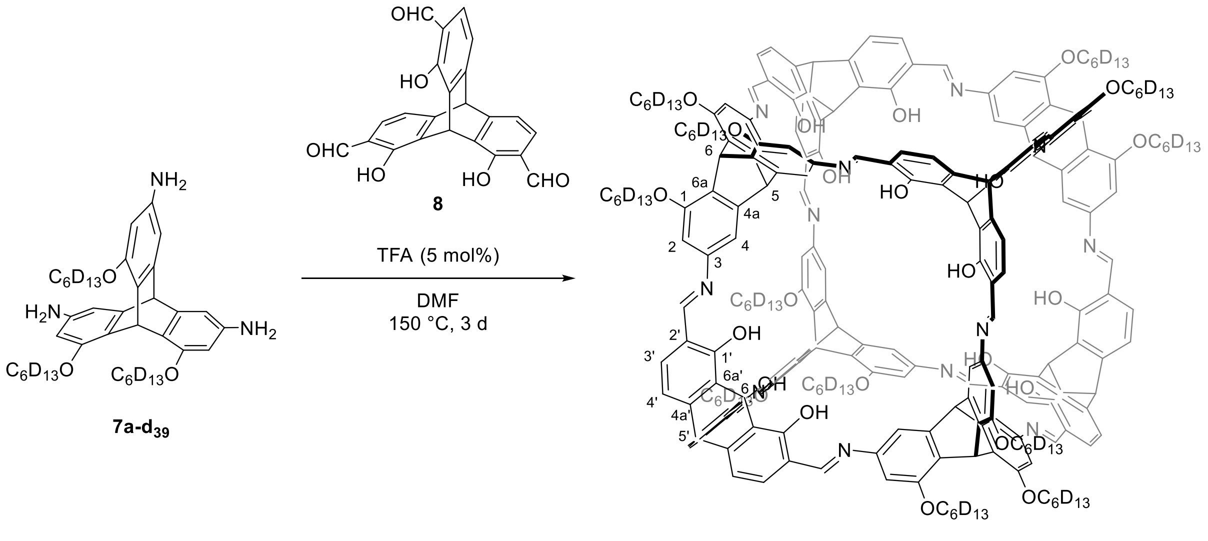
### 2.2.1 [4+4] Cube 11



In a 25 mL screw-capped vial triaminotriptycene **7a** (20.1 mg, 34 µmol) and triformytriptycene **8** (13.0 mg, 34 µmol), DMF (8 mL) and TFA (167 µL, 0.01 mol $L^{-1}$ in dry DMF, 1.67 µmol, 0.2 eq) were heated for 5 days at 150 °C. The orange suspension was cooled toroom temperature molecular sieves (3 Å) added and stirred for additional 20 min. The mixture was filtration through Celite and the solvent was evaporated *in vacuo*. The residue was purified by rGPC (THF) to give **11** as yellow solid in 42% yield (13.0 mg, 3 µmol). **Melting point:** *T* = 352 °C (dec.). **$^1$H NMR:** (600 MHz, THF-$d_8$) δ (ppm) 15.21 (s, 12H, -O*H*), 9.02 (s, 12H, -C*H*N-), 7.51 (d, *J* = 1.6 Hz, 12H, *H*4), 7.45 (s, 4H, *H*6’), 7.07 – 7.02 (m, 24H, *H*2, *H*3’), 6.94 (d, *J* = 7.7 Hz, 12H, *H*4’), 6.89 (s, 4H, *H*6), 5.86 (s, 4H, *H*5), 5.51 (s, 5H, *H*5’), 4.08 (t, *J* = 6.5 Hz, 24H, -OC$H_2$-), 1.97 – 1.87 (m, 24H, -OCH$_2$-C$H_2$-), 1.70 – 1.60 (m, 24H, -OCH$_2$-CH$_2$-C$H_2$-), 1.49 – 1.38 (m, 48H, -C$H_2$-C$H_2$-CH$_3$), 1.01 – 0.91 (m, 36H, -CH$_2$-CH$_2$-C$H_3$). **$^{13}$C{$^1$H} NMR:** (150 MHz, THF-$d_8$) δ (ppm) 158.8 (-*C*HN-), 158.3 (*C*1’), 157.8(*C*1’), 156.0 (*C*1), 152.0 (*C*4a’), 150.4 (*C*4a), 143.8 (*C*3), 134.4 (*C*6a), 134.3 (*C*6a’), 134.3 (*C*6a’), 129.4 (*C*3’), 119.3 (*C*4), 119.0 (*C*2’), 115.1 (*C*4’), 97.1 (*C*2), 69.8 (-O*C*H$_2$-), 56.6 (*C*5’), 55.5 (*C*5), 35.6 (*C*6), 33.5 (*C*6’), 32.9 (-*C*H$_2$-CH$_2$-CH$_3$), 30.8 (-OCH$_2$-*C*H$_2$-), 26.9 (-OCH$_2$-CH$_2$-*C*H$_2$-), 23.8 (-CH$_2$-*C*H$_2$-CH$_3$), 14.7 (-CH$_2$-CH$_2$-*C*H$_3$). **MS (MALDI-TOF+, DCTB):** [M+H]$^+$: *m/z* calcd. for $C_{244}H_{245}N_{12}O_{24}^+$: 3726.832, found: 3726.755. **IR:** (ATR, FT) $\tilde{\nu}$ (cm$^{-1}$) 2955 (w), 2928

(w) 2858 (w), 1620 (m), 1589 (vs), 1566 (m), 1470 (m), 1437 (m), 1364 (w), 1329 (w), 1281 (w), 1234 (m), 1163 (w), 1119 (s), 1099 (m), 1042 (w) 982 (w), 935 (vw), 872 (w), 827 (w), 808 (w), 781 (m), 762 (m), 731 (m), 662 (w). **UV/vis** (THF) $\lambda_{max}$ (lg $\varepsilon$) 363 nm (5.54). **Elemental Anal.** Calcd. for $C_{244}H_{244}N_{12}O_{24}\cdot 4THF$: C, 77.74; H, 6.92; N, 4.18. Found: C, 77.69; H, 7.07; N, 3.99.

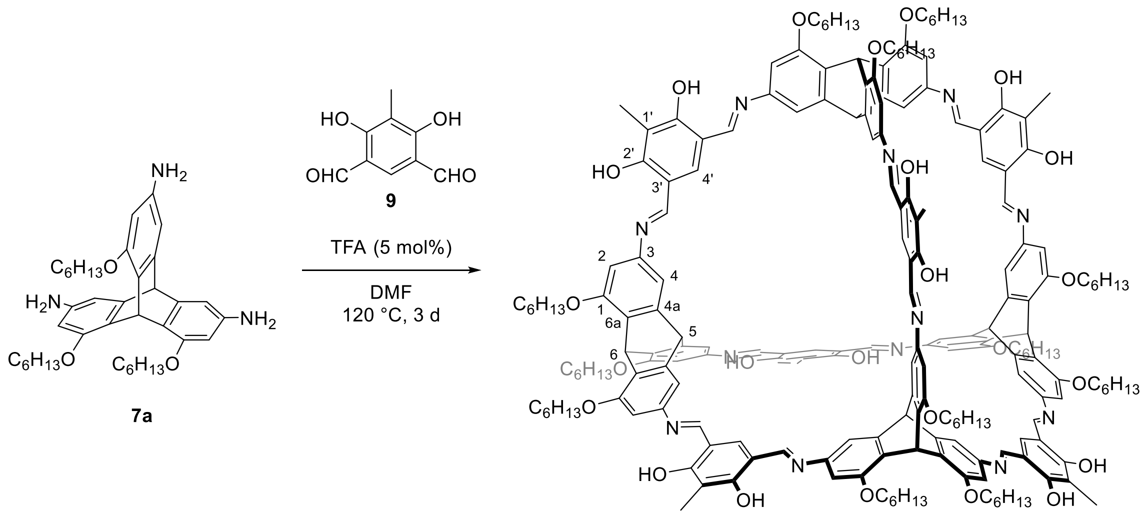
### 2.2.2 [4+4] Cube 11-d$_{156}$



In a 25 mL-screw-capped vial triaminotriptycene **7a-d$_{39}$** (21.3 mg, 34 µmol), triformyltriptycene **8** (13.0 mg, 34 µmol), dry DMF (8 mL) and TFA (167 µL, 0.01 mol L$^{-1}$ in dry DMF, 1.67 µmol) were stirred for 4 days at 150 °C under argon atmosphere. After cooling to room temperature MeCN (2 mL) was added and solids removed by filtration through a polyamide filter (0.45 µm). The solvent of the filtrate was evaporated *in vacuo* and the remaining residue purified by rGPC (THF) to give **11-d$_{156}$** as yellow solid in 31% yield (10.0 mg, 3 µmol). **Melting point:** *T* = 354 °C (dec.). **$^1$H NMR:** (600 MHz, THF-d$_8$) δ (ppm) 15.21 (s, 12H, -O*H*), 9.02 (s, 12H, -C*H*N-), 7.51 (d, *J* = 1.8 Hz, 12H, *H*4), 7.45 (s, 4H, *H*6'), 7.07-7.02 (m, 24H, *H*2, *H*3'), 6.94 (d, *J* = 7.7 Hz, 12H, *H*4'), 6.89 (s, 4H, *H*6), 5.85 (s, 4H, *H*5), 5.51 (s, 4H, *H*5'). **$^{13}$C{$^1$H} NMR:** (150 MHz, THF-d$_8$) δ (ppm) 158.8 (-*C*HN-), 158.3 (*C*1'), 156.0 (*C*1), 152.0 (*C*4a'), 150.4 (*C*4a), 143.8 (*C*3), 134.4 (*C*6a), 134.3 (*C*6a'), 129.3 (*C*3'), 119.3 (*C*4), 119.0 (*C*2'), 115.1 (*C*4'), 97.1 (*C*2), 69.3 – 68.5 (m, -O*C*D$_2$-), 56.6 (*C*5'), 55.5 (*C*5), 35.6 (*C*6), 33.5 (*C*6'), 32.1-31.1 (m, -*C*D$_2$-CD$_2$-CD$_3$), 30.0-29.0 (m, -OCD$_2$-*C*D$_2$-), 22.9 – 22.2 (m, -CD$_2$-*C*D$_2$-CD$_3$), 14.0 – 13.1 (m, -CD$_2$-CD$_2$-*C*D$_3$). **$^2$H NMR:** (92 MHz, THF/THF-d$_8$) δ (ppm) 4.09 (s, 24D, -OC*D*$_2$-), 1.87 (s, 24D, -OCD$_2$-C*D*$_2$-), 1.59 (s, 24D, -OCD$_2$-CD$_2$-C*D*$_2$-), 1.37 (s, 48D, -

$CD_2$-$CD_2$-$CD_3$), 0.90 (s, 36D, -$CD_2$-$CD_2$-$CD_3$). **MS (MALDI-TOF+, DCTB):** $[M]^+$: *m/z* calcd. for $C_{244}H_{88}D_{156}N_{12}O_{24}^+$: 3882.803, found: 3882.182. **IR:** (ATR, FT) $\tilde{\nu}$ ($cm^{-1}$) 2210 (w), 2097 (w), 1620 (m), 1587 (vs), 1566 (s), 1474 (m), 1435 (m), 1364 (m), 1329 (w), 1279 (w), 1232 (m), 1163 (w), 1119 (s), 1086 (m), 1040 (m), 989 (w), 968 (w), 935 (w), 870 (m), 827 (m), 806 (m), 779 (m), 760 (m), 729 (m), 663 (w). **UV/vis** (THF) $\lambda_{max}$ (lg $\varepsilon$) 363 nm (5.54). **Elemental Anal.** Calcd. for $C_{244}H_{88}D_{156}N_{12}O_{24}\cdot H_2O$: C, 75.08; H+D, 6.38 (Value was corrected by detection difference of hydrogen and deuterium. Analyzing a compound containing a known deuterium amount resulted in detection of 50.4% of the apparent deuterium.); N, 4.31. Found: C, 74.90; H+D, 6.24; N, 4.04.

### 2.2.3 [4+6]-*exo* Cage 12



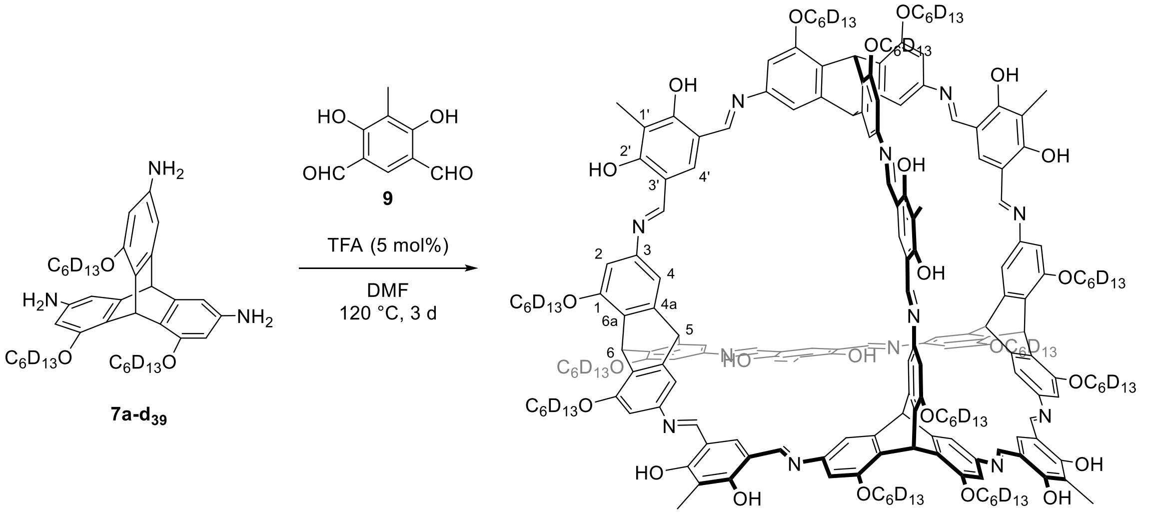
7a

12

A 25 mL screw-capped vial was charged with triaminotriptycene **7a** (20.1 mg, 34 µmol) and 3,5-diformyl-2,6-dihydroxytoluene **9** (9.0 mg, 50 µmol) under argon atmosphere. Dry DMF (6 mL) and TFA (167 µL, 0.01 mol $L^{-1}$ in dry DMF, 1.67 µmol) were added and the orange solution was stirred for 3 days at 120 °C. The red solution was allowed to reach room temperature, the solvent was evaporated *in vacuo* and the residue was mixed with DMSO (2 mL) and ultrasonicated for 10 min. After filtration through a polyamide filter (0.45 µm) the orange residue was washed with DMSO (4 mL) and methanol (6 mL). After further purification by rGPC (THF) exo-cage **12** was obtained as yellow solid in 63% yield (17.3 mg, 5 µmol).**Melting point:** *T* = 338 °C (dec.). **$^1$H NMR:** (600 MHz, THF-$d_8$) δ (ppm) 15.01 (s, 12H, -O*H*), 9.00 (s, 12H, -C*H*N-), 7.46 (s, 6H, *H*4'), 7.36 (d, *J* = 1.7 Hz, 12H, *H*4), 6.97 (s, 4H, *H*6), 6.81 (d, *J* = 1.7 Hz, 12H, *H*2), 5.56 (s, 4H, *H*5), 4.11 (t, *J* = 6.4 Hz, 24H, -O$CH_2$-), 2.12 (s, 18H, -C1'-$CH_3$), 2.01-1.92 (m, 24H, -O$CH_2$-$CH_2$-), 1.76-1.67 (m, 24H, -O$CH_2$-$CH_2$-$CH_2$-), 1.52-1.43 (m, 48H, -

*C*$H_2$-*C*$H_2$-$CH_3$), 1.00 (t, *J* = 6.8 Hz, 36H, -$CH_2$-$CH_2$-*C*$H_3$). **$^{13}$C{$^1$H} NMR:** (150 MHz, THF-$d_8$) δ (ppm) 165.7 (*C*2’), 159.2 (-*C*HN-), 155.8 (*C*1), 149.8 (*C*4a), 145.1 (*C*3), 135.8 (*C*4’), 133.0 (*C*6a), 113.7 (*C*3’), 112.9 (*C*1’), 110.1 (*C*2), 104.1 (*C*4), 69.5 (-O*C*$H_2$-), 57.0 (*C*5), 34.4 (*C*6), 33.0 (-*C*$H_2$-$CH_2$-$CH_3$), 30.7 (-O$CH_2$-*C*$H_2$-), 26.9 (-O$CH_2$-$CH_2$-*C*$H_2$-), 23.8 (-$CH_2$-*C*$H_2$-$CH_3$), 14.8 (-$CH_2$-$CH_2$-*C*$H_3$), 7.6 (C1’-*C*$H_3$). **MS (MALDI-TOF+, DCTB):** $[M+H]^+$: *m/z* calcd. for $C_{206}H_{237}N_{12}O_{24}^+$: 3262.769, found: 3262.884. **IR:** (ATR, FT) $\tilde{\nu}$ ($cm^{-1}$) 2953 (w), 2928 (w), 2858 (w), 1620 (m), 1576 (vs), 1464 (m), 1435 (m), 1393 (m), 1369 (m), 1296 (m), 1225 (w), 1165 (m), 1123 (s), 1099 (m), 1067 (w), 1028 (w), 972 (m), 914 (w), 872 (m), 845 (m), 800 (w), 764 (m), 741 (m); 636 (w), 606 (w), 573 (w). **UV/vis** (THF) $\lambda_{max}$ (lg *ε*) 316.5 nm (5.31), 377.5 nm (5.50). **Elemental Anal.** Calcd. for $C_{206}H_{236}N_{12}O_{24}\cdot10H_2O$: C, 71.84; H, 7.49; N 4.88. Found: C, 71.98; H, 7.26; N, 4.52.

### 2.2.4 [4+6]-*exo* Cage 12-d$_{156}$

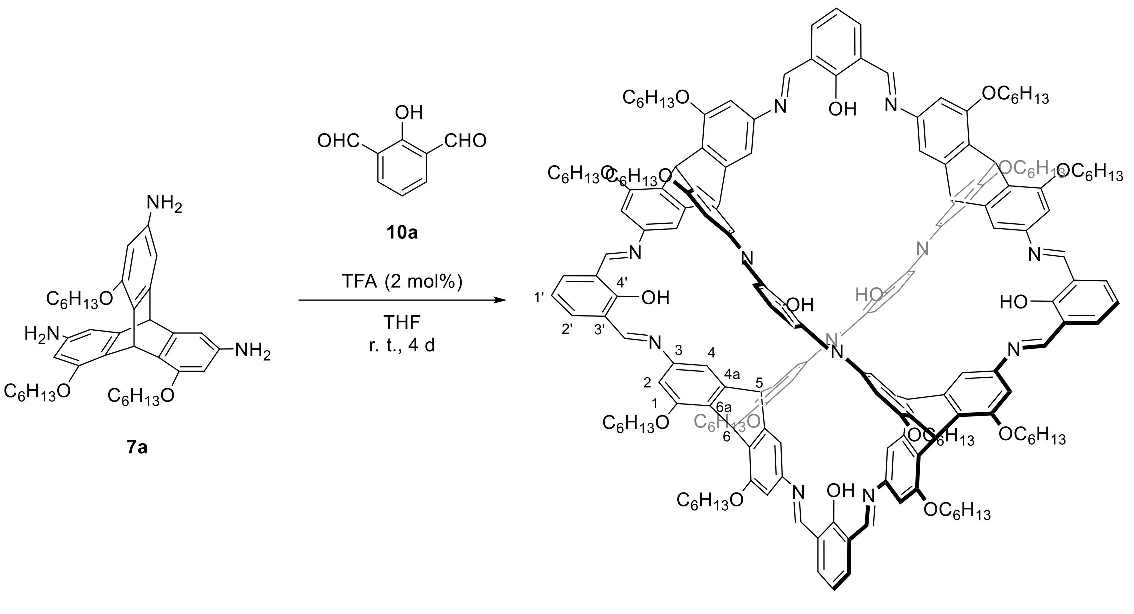


**7a-d$_{39}$**

**12-d$_{39}$**

A 25 mL screw-capped vial was charged with triaminotriptycene **7a-d$_{39}$** (21.3 mg, 33 µmol) and 3,5-diformyl-2,6-dihydroxytoluene **9** (9.1 mg, 51 µmol) under argon atmosphere. Dry DMF (6 mL) and TFA (167 µL, 0.01 mol $L^{-1}$ in dry DMF, 1.67 µmol) were added and the orange solution was stirred for 3 days at 120 °C. The red solution was allowed to reach room temperature, the solvent was evaporated *in vacuo* and the residue was combined with DMSO (4 mL) and ultrasonicated for 10 min. After filtration through a polyamide filter (0.45 µm) the orange residue was washed with DMSO (4 mL) and methanol (6 mL). After further purification by rGPC (THF) cage **12-d$_{156}$** was obtained as yellow solid in 61% yield (17.3 mg, 5 µmol). **Melting point:** *T* = 337 °C (dec.). **$^1$H NMR:** (600MHz, THF-$d_8$) δ (ppm) 15.01 (s, 12H, -O*H*), 8.99 (s, 12H, -C*H*N-), 7.45 (s, 6H, *H*4'), 7.36 (d, *J* = 1.7 Hz, 12H, *H*4), 6.97 (s, 4H, *H*6), 6.80 (d, *J* = 1.7 Hz, 12H, *H*2), 5.55 (s, 4H, *H*5), 2.12 (s, 18H, -C1'-C$H_3$). **$^{13}$C{1H} NMR:** (150 MHz, THF-$d_8$) δ (ppm) 165.7 (*C*2'), 159.1 (-*C*HN-), 155.8 (*C*1), 149.8 (*C*4a), 145.1 (*C*3), 135.8 (*C*4'), 133.0 (*C*6a), 113.7 (*C*3'), 112.9 (*C*1'), 110.1 (*C*2), 104.0 (*C*4), 69.1 – 68.3 (m, -OC$D_2$-), 57.0 (*C*5), 34.4 (*C*6), 32.131.1 (m, -C$D_2$-C$D_2$-C$D_3$), 30.1 – 29.1 (m, -OC$D_2$-C$D_2$-), 23.0-22.0 (m, -C$D_2$-C$D_2$-C$D_3$), 14.0-13.2 (m, -C$D_2$-C$D_2$-C$D_3$), 7.6 (C1'-C$H_3$). **$^2$H NMR:** (92 MHz, THF/THF-$d_8$) δ (ppm) 4.12 (s, 24D, -OC$D_2$-), 1.91 (s, 24D, -OC$D_2$-C$D_2$-), 1.63 (s, 24D, -OC$D_2$-C$D_2$-C$D_2$-), 1.40 (s, 48H, -C$D_2$-C$D_2$-C$D_3$), 0.93 (s, 36H, -C$D_2$-C$D_2$-C$D_3$). **MS (MALDI-TOF+, DCTB):** [M]$^+$: *m/z* calcd. for $C_{206}H_{80}D_{156}N_{12}O_{24}^+$: 3418.741, found: 3418.847. **IR:** (ATR, FT) $\tilde{\nu}$ (cm$^{-1}$) 2210 (vw), 2097 (vw), 1620 (m), 1578 (vs), 1468 (w), 1435 (w), 1391 (w), 1369 (w), 1317 (w), 1296 (w), 1223 (vw), 1165 (m), 1124 (s), 1053 (vw), 993 (w), 970 (w), 874 (w), 849 (w), 798 (vw), 766 (w), 741 (w), 669 (vw), 638 (w). **UV/vis** (THF) $\lambda_{max}$ (lg $\varepsilon$) 318.8 (5.28), 377.8 (5.46). **Elemental Anal.** Calcd. for $C_{206}H_{80}D_{156}N_{12}O_{24}\cdot 2\ H_2O$: C, 71.57; H+D, 7.03 (Value was corrected by detection difference of hydrogen and deuterium. Analyzing a compound containing a known deuterium amount resulted in detection of 50.4% of the apparent deuterium.); N, 4.86. Found: C, 71.41; H+D, 7.20; N, 4.89.

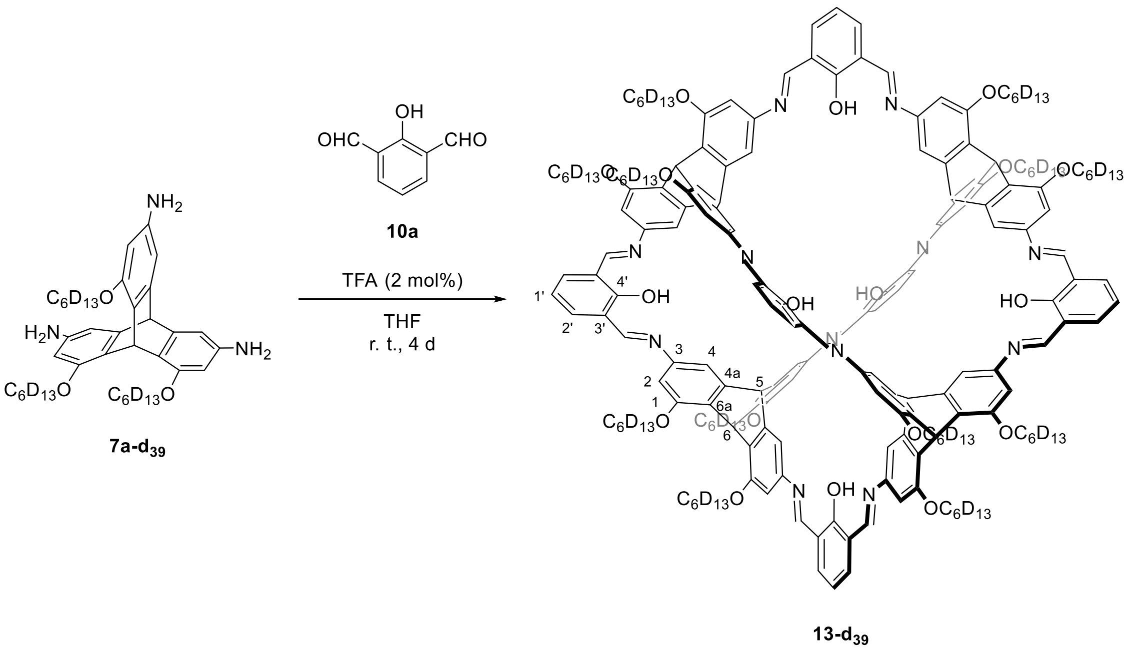
### 2.2.5 [4+6]-*endo* Cage 13



In an 8 mL screw-capped vial triaminotriptycene **7a** (20.1 mg, 34 µmol) and 2,6-diformylphenol **10a** (7.8 mg, 52 µmol) were combined under argon atmosphere. Dry

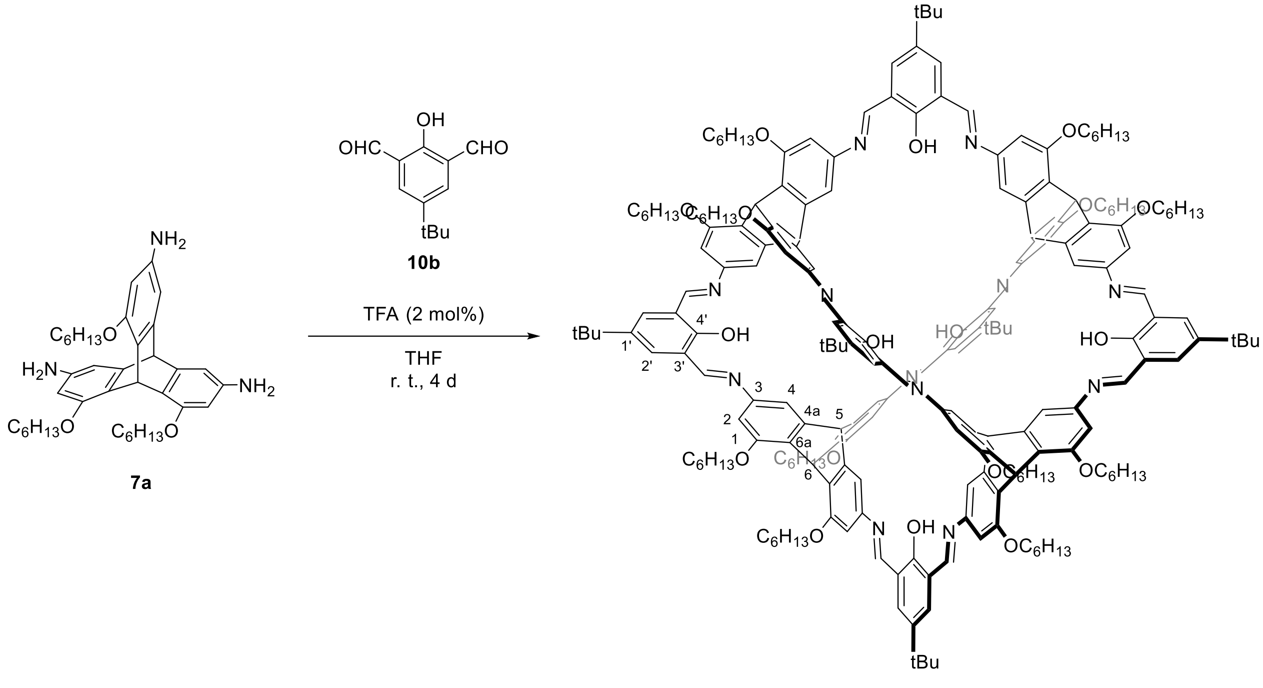
THF (5 mL) and TFA (67 µL, 0.01 mol $L^{-1}$ in dry THF, 0.67 µmol) were added and the red solution was stirred for 4 days at room temperature. Molecular sieves (3 Å, 300 mg) was added and stirred for additional 20 min before the mixture was filtrated through Celite. Purification by rGPC (THF) gave cage **13** as yellow solid in 50% yield (12.9 mg, 4 µmol). **Melting point:** $T$ = 357 °C (dec.). **$^1$H NMR:** (600 MHz, 328 K, THF- $d_8$) δ (ppm) 13.84 (s, 6H, -O*H*), 9.06 (s, 12H, -C*H*N-), 7.91 (s, 12H, *H*2'), 7.29 (s, 12H, *H*4), 6.96 (s, 4H, *H*6), 6.93 (t, $J$ = 7.7 Hz, 6H, *H*1'), 6.81 (s, 12H, *H*2), 5.73 (s, 4H, *H*5), 4.12 (t, $J$ = 6.5 Hz, 24H, -OC$H_2$-), 2.00 – 1.92 (m, 24H, -OC$H_2$-C$H_2$-), 1.73 – 1.66 (m, 24H, -OC$H_2$-C$H_2$-C$H_2$-), 1.53 – 1.42 (m, 48H, -C$H_2$-C$H_2$-C$H_3$), 0.99 (t, $J$ = 6.8 Hz, 36H, -C$H_3$). **$^{13}$C{$^1$H} NMR:** (150 MHz, 328 K, THF-$d_8$) δ (ppm) 162.4 (*C*4'), 155.7 (*C*1), 150.3 (*C*4a), 148.5 (*C*3), 133.8 (*C*6a, *C*2'), 123.7 (*C*3'), 119.7 (*C*1'), 110.8 (*C*4), 105.5 (*C*2), 70.0 (-O*C*$H_2$-), 56.2 (*C*5), 34.9 (*C*6), 33.0 (-*C*$H_2$-C$H_2$-C$H_3$), 30.9 (-OC$H_2$-*C*$H_2$-), 26.9 (-OC$H_2$-C$H_2$-*C*$H_2$-), 23.7 (-C$H_2$-*C*$H_2$-C$H_3$), 14.6 (-*C*$H_3$). **MS (MALDI-TOF+, DCTB):** $[M+H]^+$: *m/z* calcd. for $C_{200}H_{225}N_{12}O_{18}^+$: 3082.705, found: 3083.223. **IR:** (ATR, FT) $\tilde{\nu}$ ($cm^{-1}$) 2953 (w), 2928 (m), 2858 (w), 1620 (m), 1593 (vs), 1576 (vs), 1468 (m), 1435 (m), 1377 (w), 1358 (w), 1321 (m), 1300 (m), 1258 (w), 1229 (w), 1169 (w), 1124 (s), 1099 (s), 1076 (w), 1007 (m), 976 (m), 916 (vw), 858 (m), 793 (w), 750 (s), 723 (m), 640 (w). **UV/vis** (THF) $\lambda_{max}$ (lg $\varepsilon$) 295.8 (5.22), 372.8 (5.35). **Elemental Anal.** Calcd. for $C_{200}H_{224}N_{12}O_{18}\cdot 5\ H_2O$: C, 75.68; H, 7.43; N, 5.30. Found: C, 75.73; H, 7.35; N, 4.99.

### 2.2.6 [4+6]-*endo* Cage 13-d$_{156}$



In an 8 mL screw-capped vial 3,6,15-triamino-1,8,13-trihexyloxytriptycene-$d_{39}$ **7a-$d_{39}$** (21.3 mg, 33 µmol) and 2,6-diformylphenol **10a** (7.8 mg, 52 µmol) were combined under argon atmosphere. Dry THF (5 mL) and TFA (67 µL, 0.01 mol $L^{-1}$ in dry THF, 0.67 µmol) were added and the red solution was stirred for 4 days at room temperature. The red solution was stirred with molecular sieves (3 Å, 300 mg) and the mixture was filtrated through Celite. The resulted red solution was purified by rGPC (THF) to give cage **13-$d_{156}$** as yellow solid in 56% yield (15.2 mg, 5 µmol). **Melting point:** $T$ = 357 °C (dec.). **$^1$H NMR:** (700 MHz, THF- $d_8$) δ (ppm) 13.95 (s, 6H, -O*H*), 9.09 (s, 12H, -C*H*N-), 7.93 (s, 12H, *H*2'), 7.31 (s, 12H, *H*4), 6.97 (s, 4H, *H*6), 6.95 (t, $J$ = 7.7 Hz, 6H, *H*1'), 6.83 (s, 12H, *H*2), 5.77 (s, 4H, *H*5). **$^{13}$C{$^1$H} NMR**: (176 MHz, THF-$d_8$) 162.3 (-*C*HN-), 155.6 (*C*1), 150.3 (*C*4a), 133.6 (*C*6a, *C*2'), 123.6 (*C*3'), 119.7 (*C*1'), 69.1 – 68.3 (m, -O$CD_2$-), 55.9 (*C*5), 34.6 (*C*6), 32.0 – 31.3 (m, -$CD_2$-$CD_2$-$CD_3$), 30.0 – 29.3 (m, -O$CD_2$-$CD_2$-), 22.8 – 22.1 (m, -$CD_2$-$CD_2$-$CD_3$), 14.1 – 13.2 (m, -$CD_3$). **$^2$H NMR:** (92 MHz, THF/THF- $d_8$) δ (ppm) 4.11 (s, 24D, -O$CD_2$-), 1.91 (s, 24D, -O$CD_2$-$CD_2$-), 1.64 (s, 24D, -O$CD_2$-$CD_2$-$CD_2$-), 1.40 (s, 48H, -$CD_2$-$CD_2$-$CD_3$), 0.93 (s, 36D, -$CD_3$). **MS (MALDI-TOF+, DCTB):** $[M]^+$: *m/z* calcd. for $C_{200}H_{68}D_{156}N_{12}O_{18}^+$: 3238.677, found: 3238.642. **IR:** (ATR, FT) ṽ ($cm^{-1}$) 2210 (w), 2098 (w), 1620 (m), 1593 (vs), 1576 (vs), 1474 (m), 1437 (m), 1360 (w), 1323 (m), 1302 (m), 1256 (w), 1231 (w), 1167 (w), 1124 (vs), 1105 (m), 1088 (m), 1053 (w), 1040 (w), 1005 (w), 982 (m), 918 (vw), 858 (m), 793 (w), 750 (s), 721 (w), 642 (w). **UV/vis** (THF) $\lambda_{max}$ (lg $\varepsilon$) 295.8 (5.20), 372.8 (5.32). **Elemental Anal.** Calcd. for $C_{200}H_{68}D_{156}N_{12}O_{18}\cdot H_2O$: C, 73.71; H+D, 7.02 (Value was corrected by detection difference of hydrogen and deuterium. Analyzing a compound containing a known deuterium amount resulted in detection of 50.4% of the apparent deuterium.); N, 5.16. Found: C, 73.62; H+D, 7.07; N, 4.87.

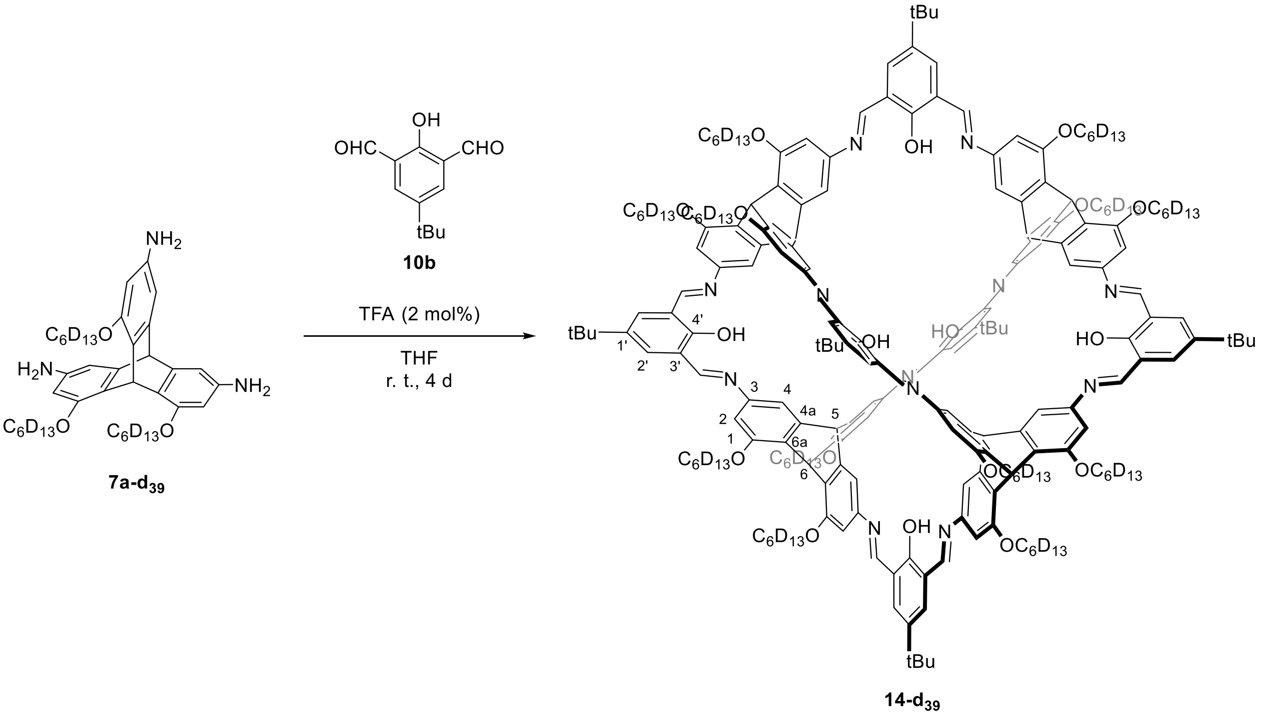
### 2.2.7 [4+6]-*endo* Cage 14



In an 8 mL screw-capped triaminotriptycene **7a** (20.0 mg, 33 µmol) and 2,6-diformyl-4-*tert*-butylphenol **10b** (10.3 mg, 50 µmol) were combined under argon atmosphere. Dry THF (5 mL) and TFA (67 µL, 0.01 mol L$^{-1}$ in dry THF, 0.67 µmol) were added and the red solution was stirred for 4 days at room temperature. Afterwards the solution was stirred with molecular sieves (3 Å, 300 mg) for 20 min and filtrated through Celite. The product was further purified by rGPC (THF) to give cage **14** as orange solid in 62% yield (17.6 mg, 5 µmol).

**Melting point:** *T* = 380 °C (dec.). **$^1$H NMR:** (700 MHz, THF- d$_8$) δ (ppm) 13.71 (s, 6H, -O*H*), 9.12 (s, 12H, -C*H*N-), 8.02 (s, 12H, *H*2'), 7.33 (s, 12H, *H*4), 6.98 (s, 4H, *H*6), 6.86 (s, 12H, *H*2), 5.79 (s, 4H, *H*5), 4.12 (t, *J* = 6.5 Hz, 24H, -OC*H*$_2$-), 2.04 – 1.92 (m, 24H, -OCH$_2$-C*H*$_2$-), 1.78 – 1.67 (m, 24H, -OCH$_2$-CH$_2$-C*H*$_2$-), 1.55 – 1.43 (m, 48H, -C*H*$_2$-C*H*$_2$-CH$_3$), 1.35 (s, 54H, -C(C*H*$_3$)$_3$), 1.06 – 0.95 (m, 36H, -CH$_2$-CH$_2$-C*H*$_3$). **$^{13}$C{$^1$H} NMR:** (176 MHz, THF- d$_8$) δ (ppm) 160.3 ppm(-*C*HN-), 159.9 (*C*4'), 155.5 (*C*1), 150.3 (*C*4a), 148.4 (*C*3), 142.4 (*C*1'), 142.3 (*C*1'), 133.5 (*C*6a), 130.9 (*C*2'), 122.9 (*C*3'), 69.5 (-OCH$_2$-), 55.9 (C5), 35.0 (C1'-*C*(CH$_3$)$_3$), 34.6 (*C*6), 33.0 (-*C*H$_2$-CH$_2$-CH$_3$), 31.9 (-C1'-C(*C*H$_3$)$_3$), 30.9 (-OCH$_2$-*C*H$_2$-), 27.0 (-OCH$_2$-CH$_2$-*C*H$_2$-), 23.9 (-CH$_2$-*C*H$_2$-CH$_3$), 14.8 (-CH$_2$-CH$_2$-*C*H$_3$). **MS (MALDI-TOF+, DCTB):** [M+H]$^+$: *m/z* calcd. for $C_{224}H_{273}N_{12}O_{18}^+$: 3419.081, found: 3419.723. **IR:** (ATR, FT) $\tilde{\nu}$ (cm$^{-1}$) 2955 (m), 2930 (w), 2870 (w), 1624 (m), 1582 (vs), 1468 (s), 1433 (m), 1394 (w), 1377 (w), 1362 (w), 1300 (m), 1263 (m), 1227 (m), 1178 (w), 1124 (s), 1099 (s), 1065 (w), 1038 (w), 1015 (m), 976 (m), 918 (w), 887 (w), 858 (m), 825 (w), 762 (m), 744 (m), 729 (w), 650 (vw), 631 (w). **UV/vis** (THF) $\lambda_{max}$ (lg $\varepsilon$) 298.4 nm (5.16), 377.8 nm (5.26). **Elemental Anal.** Calcd. for $C_{224}H_{272}N_{12}O_{18}\cdot 3THF$: C, 77.94; H, 8.20; N, 4.62. Found: C, 77.78; H, 8.40; N, 4.96.

### 2.2.8 [4+6]-*endo* Cage 14-d₁₅₆



In an 8 mL screw-capped vial triaminotriptycene **7a-d₃₉** (21.3 mg, 33 µmol) and 2,6-diformyl-4-*tert*-butylphenol **10b** (10.5 mg, 51 µmol) were combined under argon atmosphere. Dry THF (5 mL) and TFA (67 µL, 0.01 mol $L^{-1}$ in dry THF, 0.67 µmol) were added and the red solution was stirred for 4 days at room temperature. Afterwards the solution was stirred with molecular sieves (3 Å, 300 mg) for 20 min and filtrated through Celite. Further purification by GPC (THF) gave cage **14-d₁₅₆** as orange solid in 66% yield (19.6 mg, 5 µmol). **Melting point:** $T$ = 380 °C (dec.) **$^1$H NMR:** (700 MHz, THF-$d_8$) δ (ppm) 13.69 (s, 6H, -O*H*), 9.11 (s, 12H, -C*H*N-), 8.01 (s, 12H, *H*2'), 7.31 (s, 12H, *H*4), 6.97 (s, 4H, *H*6), 6.84 (s, 12H, *H*2), 5.77 (s, 4H, *H*5), 1.34 (s, 54H, -C(C$H_3$)$_3$). **$^{13}$C{$^1$H} NMR:** (176 MHz, THF- $d_8$) δ (ppm) 160.3 (-*C*HN-), 155.5 (*C*1), 150.3 (*C*4a), 148.4 (*C*3), 142.3 (*C*1'), 133.5 (*C*6a), 123.0 (C3'), 69.0 – 68.3 (m, -O*C*$D_2$-), 55.9 (*C*5), 35.0 (C1'-*C*($CH_3$)$_3$), 34.6 (*C*6), 31.9 (-C1'-C(*C*$H_3$)$_3$) 31.8 – 31.3 (m, -*C*$D_2$-$CD_2$-$CD_3$), 30.0 – 29.3 (m, -O$CD_2$-*C*$D_2$-), 22.9 – 22.1 (m, -$CD_2$-*C*$D_2$-$CD_3$), 14.0 – 13.2 (m, (-$CD_2$-$CD_2$-*C*$D_3$). **$^2$H NMR:** (92 MHz, THF/THF- $d_8$) δ (ppm) 4.13 (s, 24D, -OC*D*$_2$-), 1.92 (s, 24D, -O$CD_2$-

$\mathrm{C}\mathit{D}_2$-), 1.65 (s, 24D, -$\mathrm{OCD_2}$-$\mathrm{CD_2}$-$\mathrm{C}\mathit{D}_2$-), 1.41 (s, 48D, -$\mathrm{C}\mathit{D}_2$-$\mathrm{C}\mathit{D}_2$-$\mathrm{CD_3}$), 0.93 (s, 36D, -$\mathrm{CD_2}$-$\mathrm{CD_2}$-$\mathrm{C}\mathit{D}_3$). **MS (MALDI-TOF+, DCTB):** $[\mathrm{M}]^+$: *m/z* calcd. for $\mathrm{C_{224}H_{116}D_{156}N_{12}O_{18}}^+$: 3575.053, found: 3575.511. **IR:** (ATR, FT) $\tilde{\nu}$ ($\mathrm{cm^{-1}}$) 2961 (w), 2907 (vw), 2874 (vw), 2212 (w), 2098 (w), 1624 (m), 1583 (vs), 1474 (m), 1433 (m), 1362 (w), 1323 (w), 1304 (m), 1285 (w), 1229 (m), 1167 (w), 1126 (s), 1109 (m), 1040 (w), 1007 (w), 991 (w), 976 (w), 885 (w), 858 (w), 827 (w), 760 (w), 744 (w), 712 (vw), 652 (vw), 629 (w). **UV/vis** (THF) $\lambda_{max}$ (lg $\varepsilon$) 298.2 (5.15), 376.8 (5.26). **Elemental Anal.** Calcd. for $\mathrm{C_{224}H_{116}D_{156}N_{12}O_{18}\cdot 4H_2O}$: C, 73.72; H+D, 7.76 (Value was corrected by detection difference of hydrogen and deuterium. Analyzing a compound containing a known deuterium amount resulted in detection of 50.4% of the apparent deuterium.); N, 4.61. Found: C, 73.56; H+D, 7.66; N, 4.38.

# 3 NMR Spectra

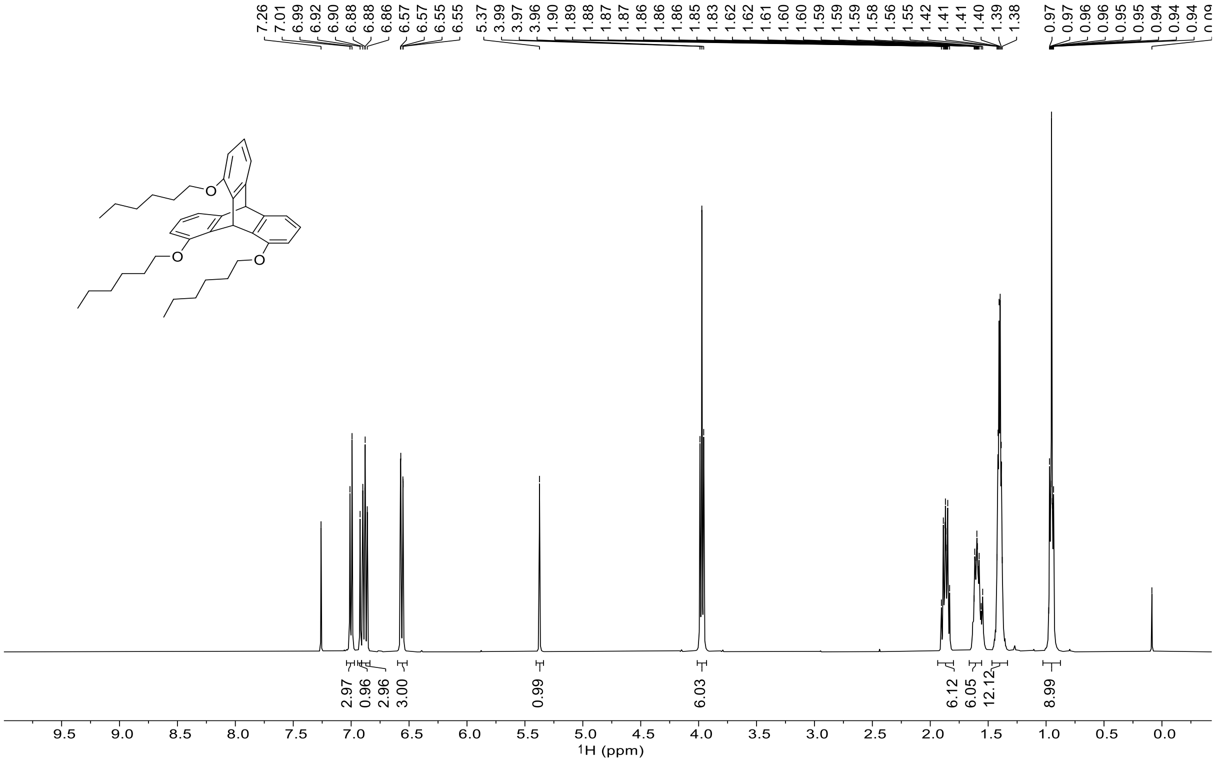


**Figure S1.** ${}^{1}$H NMR spectrum of compound **5** (400 MHz, $CDCl_3$).

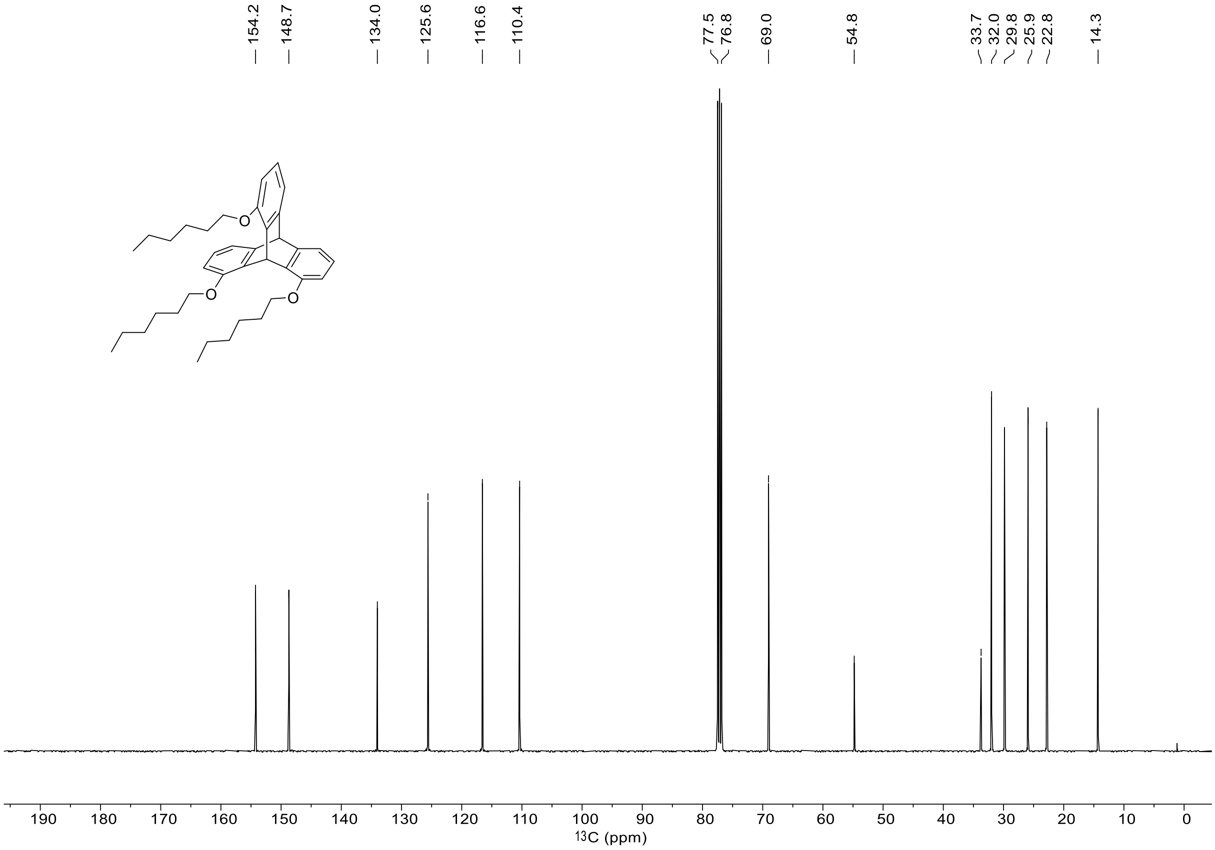


**Figure S2.** ${}^{13}C\{{}^{1}H\}$ NMR spectrum of compound **5** (100 MHz, $CDCl_3$).

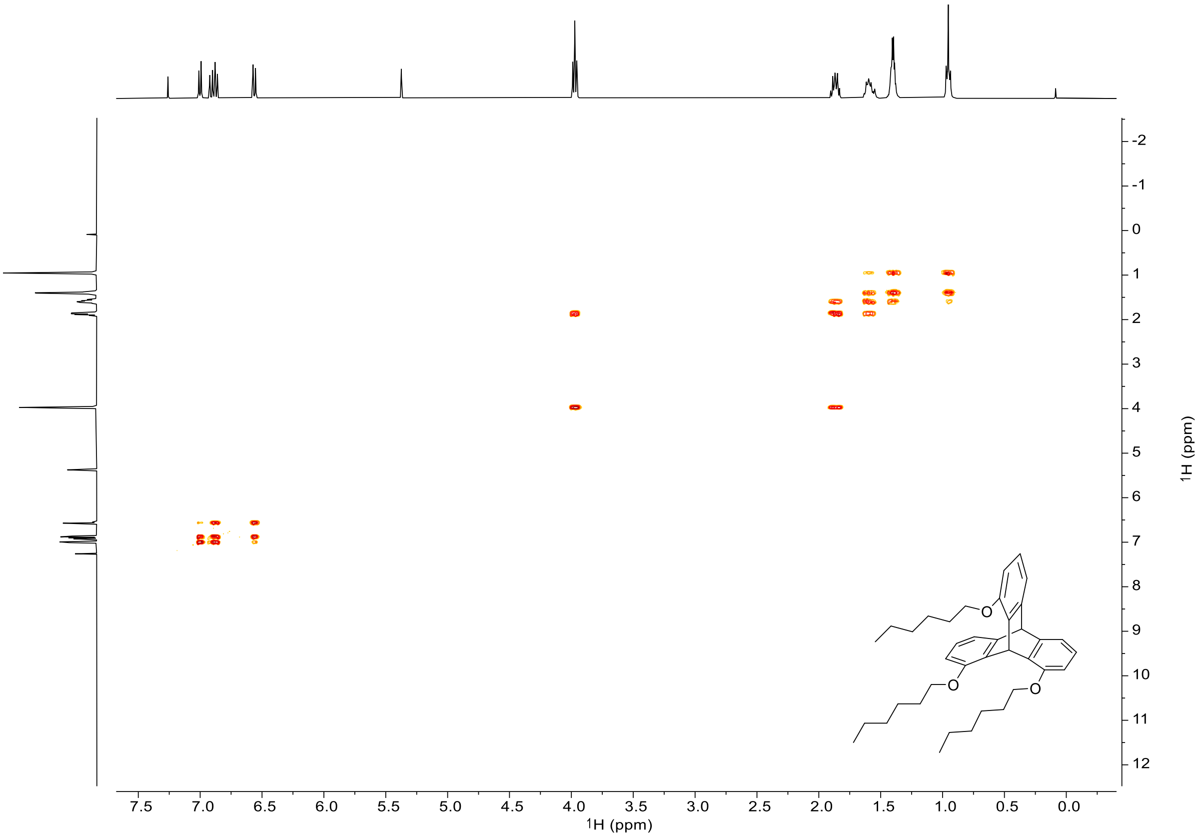


**Figure S3.** $^1$H,$^1$H-COSY spectrum of compound **5** (400 MHz, CDCl$_3$).

**Table S1.** Cross-peak assignment of $^1$H,$^1$H-COSY spectrum of compound **5**.

| **$^1$H nucleus** | **$\delta_{1H}$ [ppm]** | **COSY** |
|---|---|---|
| *a* | 7.00 | *c, d* |
| *b* | 6.92 | - |
| *c* | 6.88 | *a, d* |
| *d* | 6.56 | *a, c* |
| *e* | 5.37 | - |
| *f* | 3.97 | *g* |
| *g* | 1.94 – 1.80 | *f, h* |
| *h* | 1.66 – 1.56 | *g, i, j* |
| *i* | 1.47 – 1.33 | *h, j* |
| *j* | 1.03 – 0.88 | *h, i* |

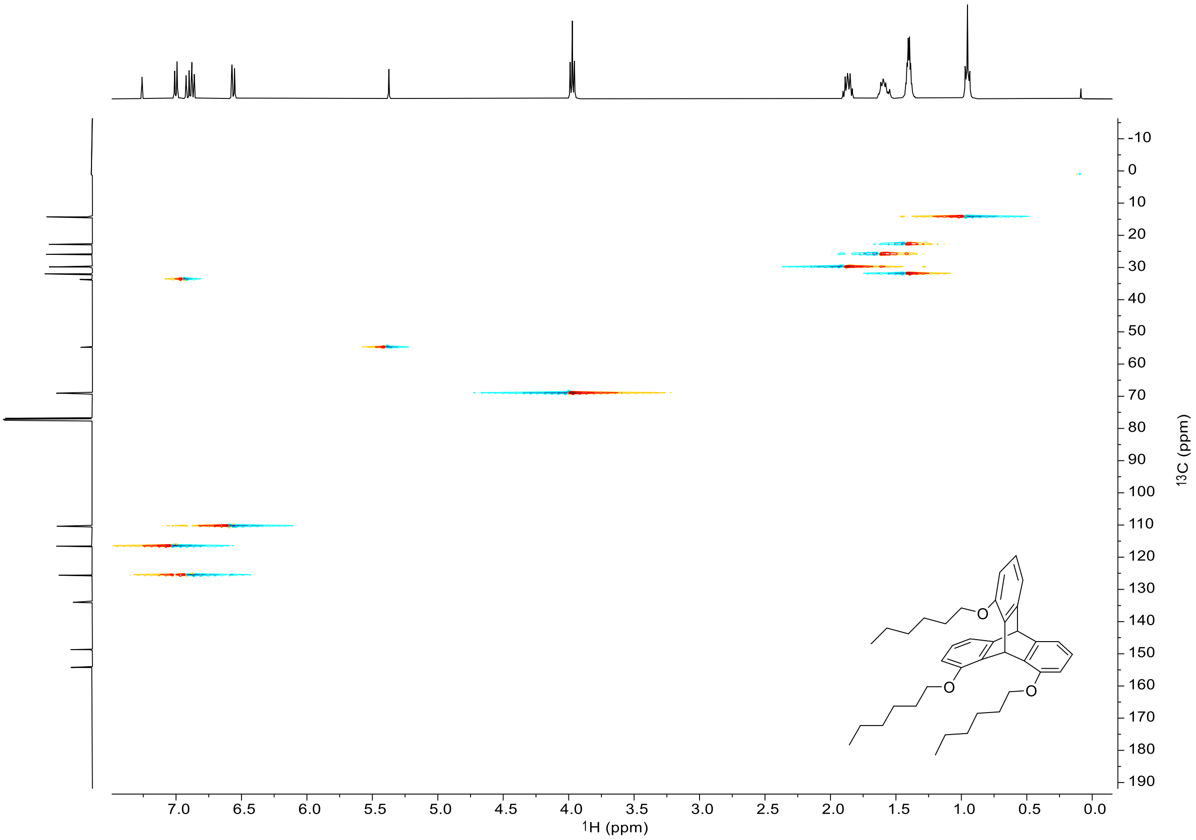


**Figure S4.** $^{1}$H,$^{13}$C-HSQC spectrum of compound **5** (400 MHz, 100 MHz, CDCl$_3$).

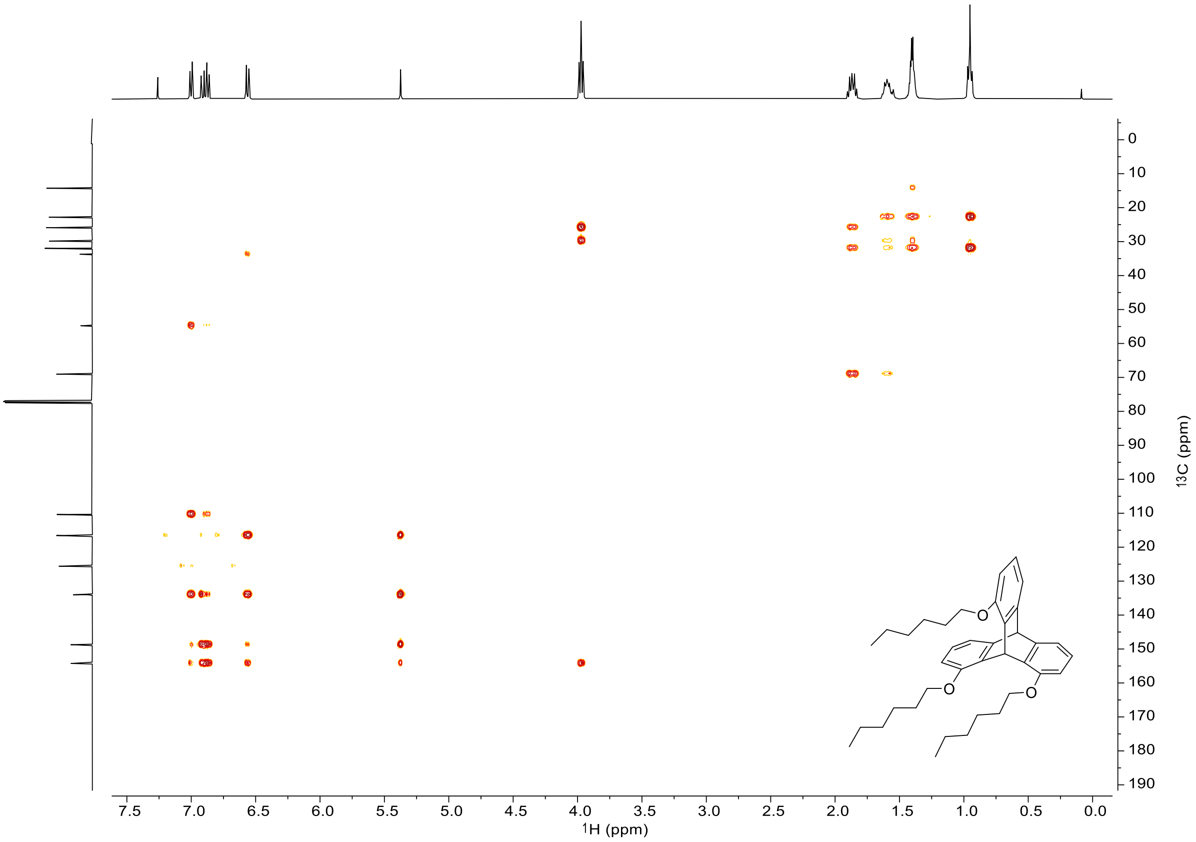


**Figure S5.** $^{1}$H,$^{13}$C-HMBC spectrum of compound **5** (400 MHz, 100 MHz, CDCl$_3$).

**Table S2.** Correlations of $^1$H,$^{13}$C-HSQC and $^1$H,$^{13}$C-HMBC spectra of compound **5**.

| **$^{13}$C nucleus** | **$\delta_{13C}$ [ppm]** | **$^1$H nucleus** | | |
|---|---|---|---|---|
| | | **HSQC** | **$\delta_{1H}$ [ppm]** | **HMBC** |
| *A* | 154.3 | - | - | *a, b, c, d, e, f* |
| *B* | 148.7 | - | - | *a, b, c, d, e* |
| *C* | 134.0 | - | - | *a, b, c, d, e* |
| *D* | 125.6 | *c* | 6.88 | - |
| *E* | 116.6 | *a* | 7.00 | *d, e* |
| *F* | 110.4 | *d* | 6.56 | *a, c* |
| *G* | 69.0 | *f* | 3.97 | *g, h* |
| *H* | 54.8 | *e* | 5.37 | *a, c* |
| *I* | 33.7 | *b* | 6.92 | *d* |
| *J* | 32.0 | *i* | 1.47 – 1.33 | *g, h, i, j* |
| *K* | 29.8 | *g* | 1.94 – 1.80 | *f, h, i* |
| *L* | 25.9 | *h* | 1.66 – 1.56 | *f, g* |
| *M* | 22.8 | *i* | 1.47 – 1.33 | *h, i, j* |
| *N* | 14.3 | *j* | 1.03 – 0.88 | *i* |

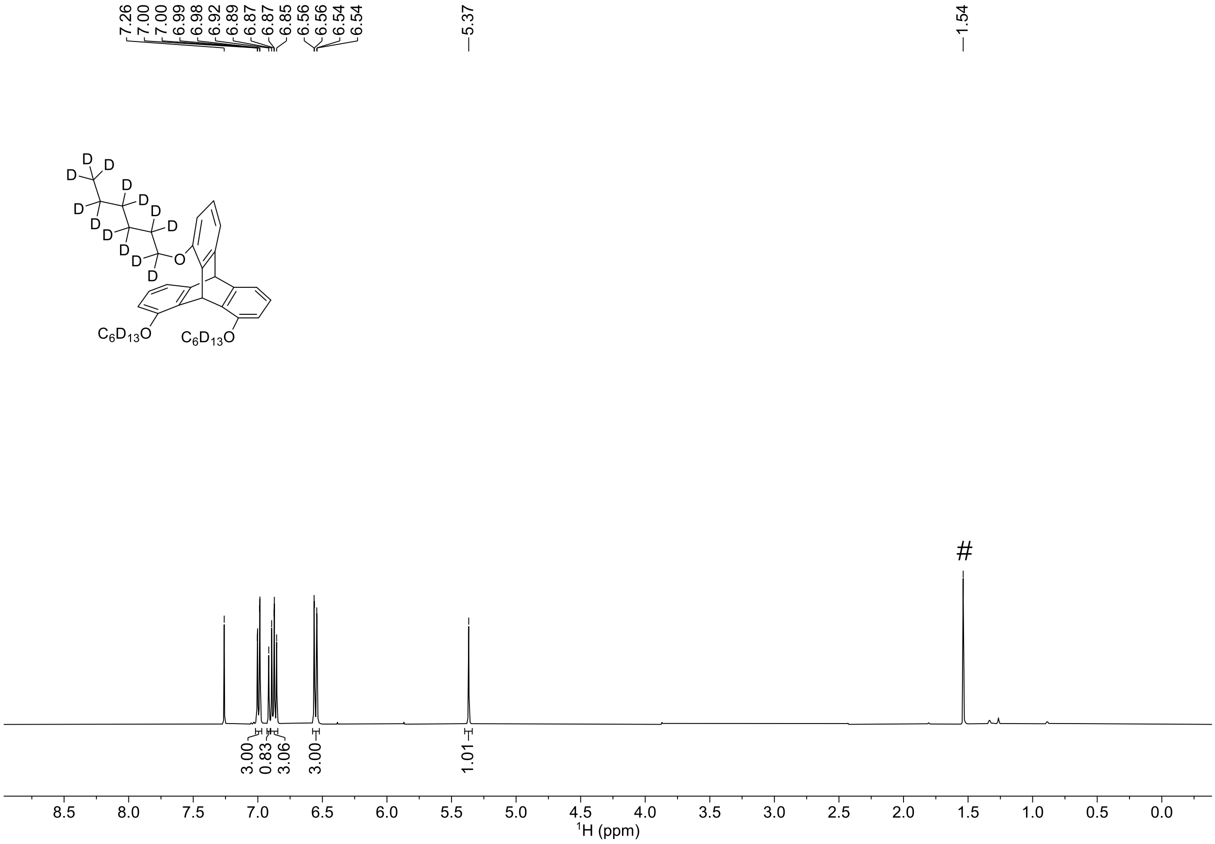


**Figure S6.** $^1$H NMR spectrum of compound **5-d$_{39}$** (400 MHz, CDCl$_3$). #: H$_2$O.

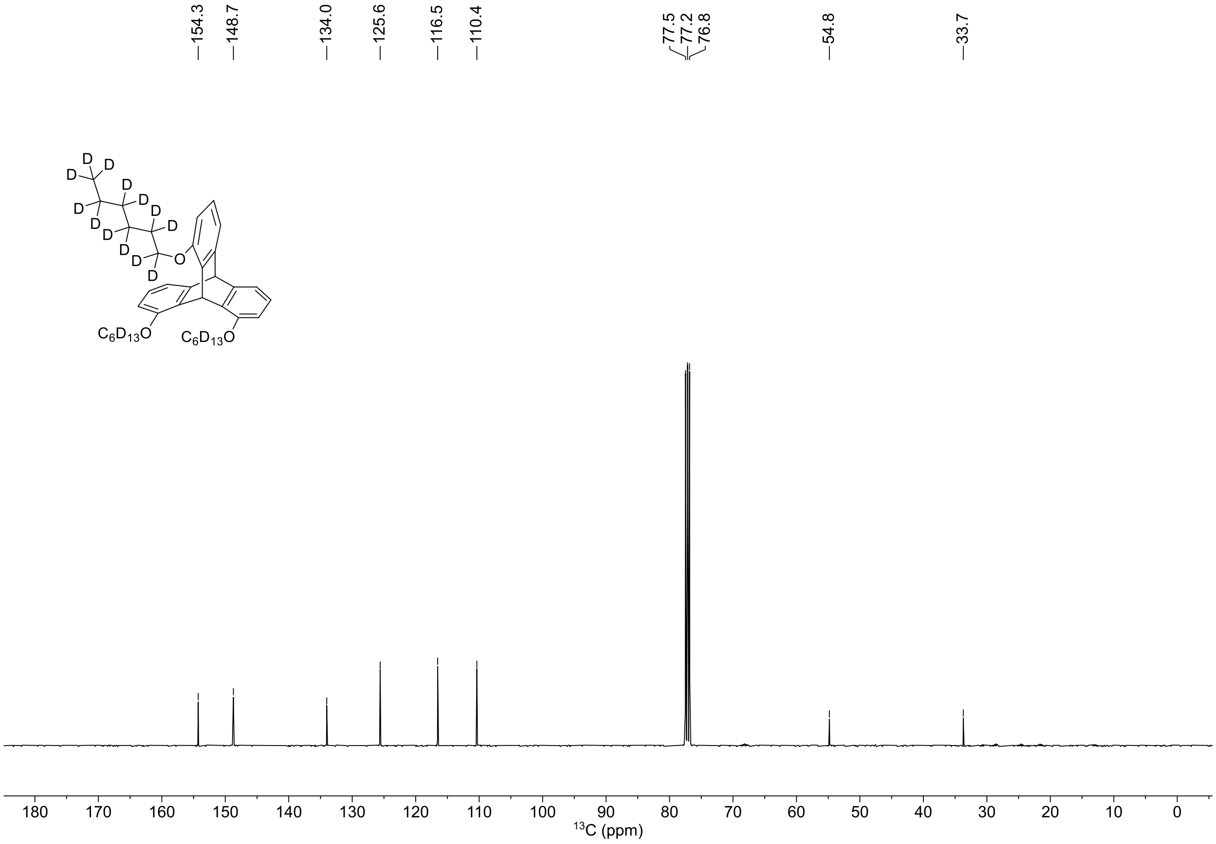


**Figure S7.** $^{13}$C{$^1$H} NMR spectrum of compound **5-d$_{39}$** (100 MHz, CDCl$_3$).

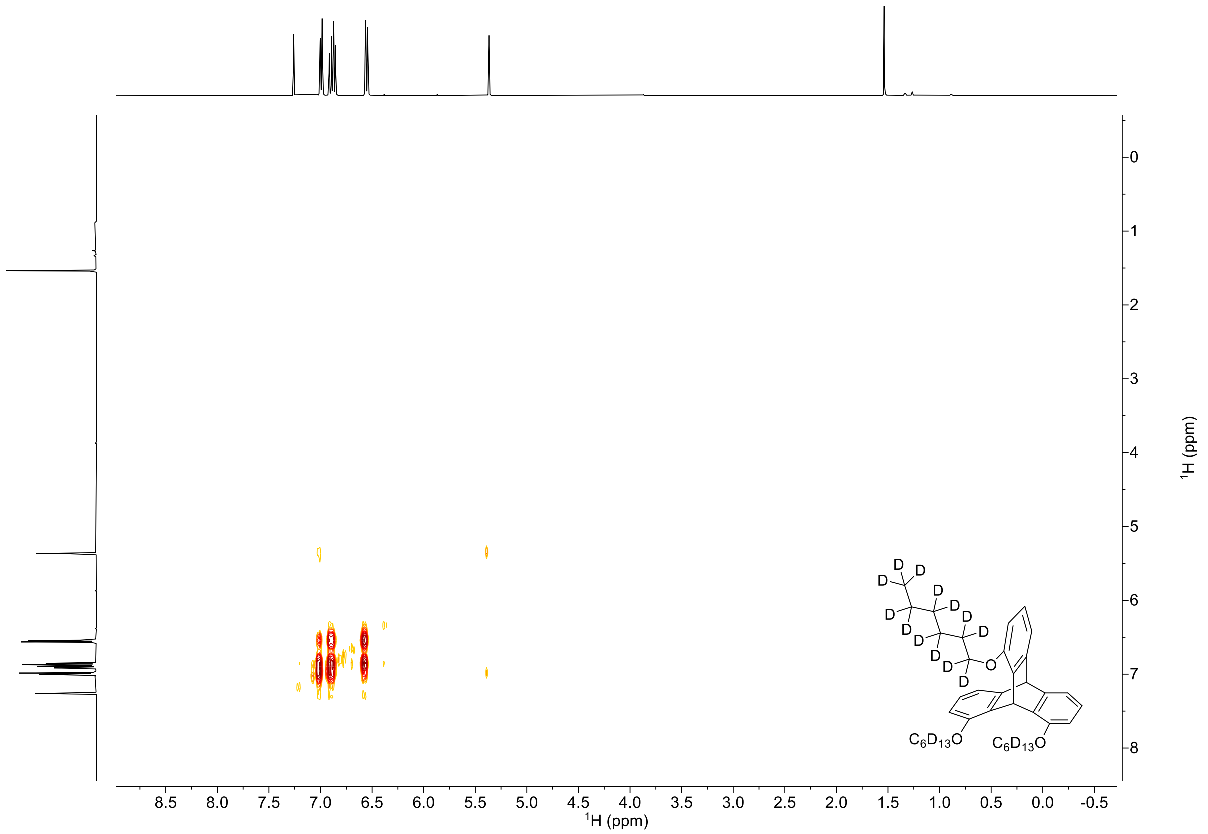


**Figure S8.** $^1$H,$^1$H-COSY spectrum of compound **5-d$_{39}$** (400 MHz, $CDCl_3$).

**Table S3.** Cross-peak assignment of $^1$H,$^1$H-COSY spectrum of compound **5-d$_{39}$**.

| **$^1$H nucleus** | **$\delta_{1H}$ [ppm]** | **COSY** |
|---|---|---|
| *a* | 6.99 | *b, d, e* |
| *b* | 6.92 | - |
| *c* | 6.87 | *a, d* |
| *d* | 6.55 | *c* |
| *e* | 5.37 | *a* |

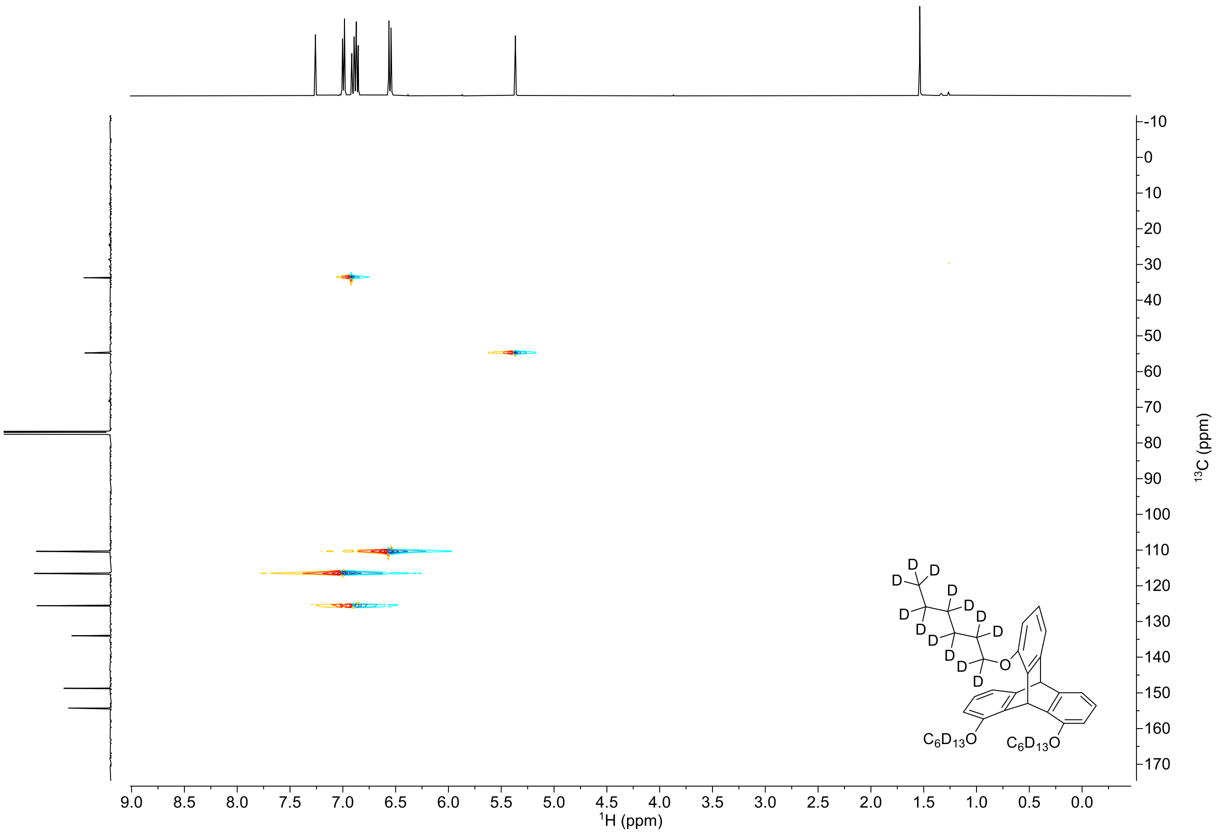


**Figure S9.** $^1$H,$^{13}$C-HSQC spectrum of compound **5-d₃₉** (400 MHz, 100 MHz, $CDCl_3$).

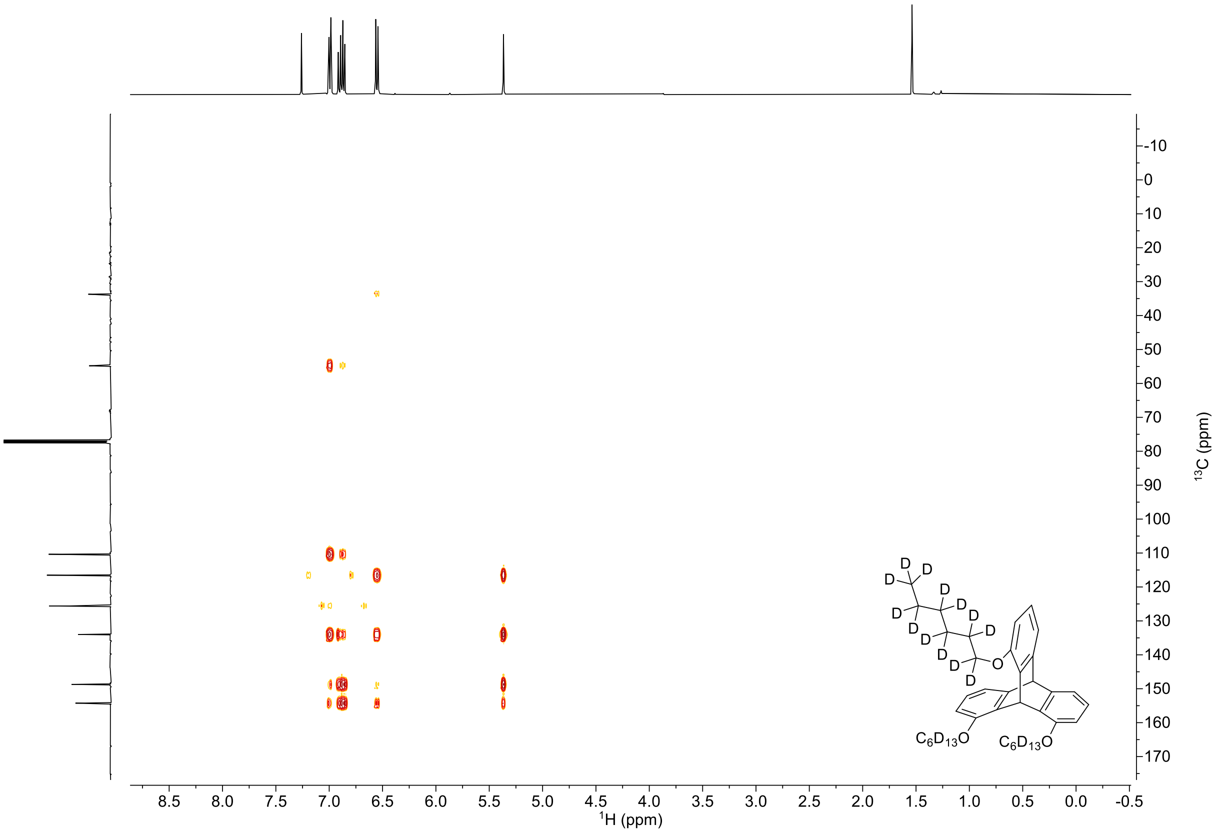


**Figure S10.** $^1$H,$^{13}$C-HMBC spectrum of compound **5-d₃₉** (400 MHz, 100 MHz, $CDCl_3$).

**Table S4.** Correlations of $^{1}H,^{13}C$-HSQC and $^{1}H,^{13}C$-HMBC spectra of compound **5-d$_{39}$**.

| $^{13}C$ nucleus | $\delta_{13C}$ [ppm] | $^{1}H$ nucleus | | |
|---|---|---|---|---|
| | | HSQC | $\delta_{1H}$ [ppm] | HMBC |
| *A* | 154.3 | - | - | *a, b, c, d, e* |
| *B* | 148.7 | - | - | *a, b, c, e* |
| *C* | 134.0 | - | - | *a, b, d, e* |
| *D* | 125.6 | *c* | 6.87 | *a* |
| *E* | 115.5 | *a* | 6.99 | *d, e* |
| *F* | 110.4 | *d* | 6.55 | *a, c* |
| *G* | 54.8 | *e* | 5.37 | *a* |
| *H* | 33.7 | *b* | 6.92 | *d* |

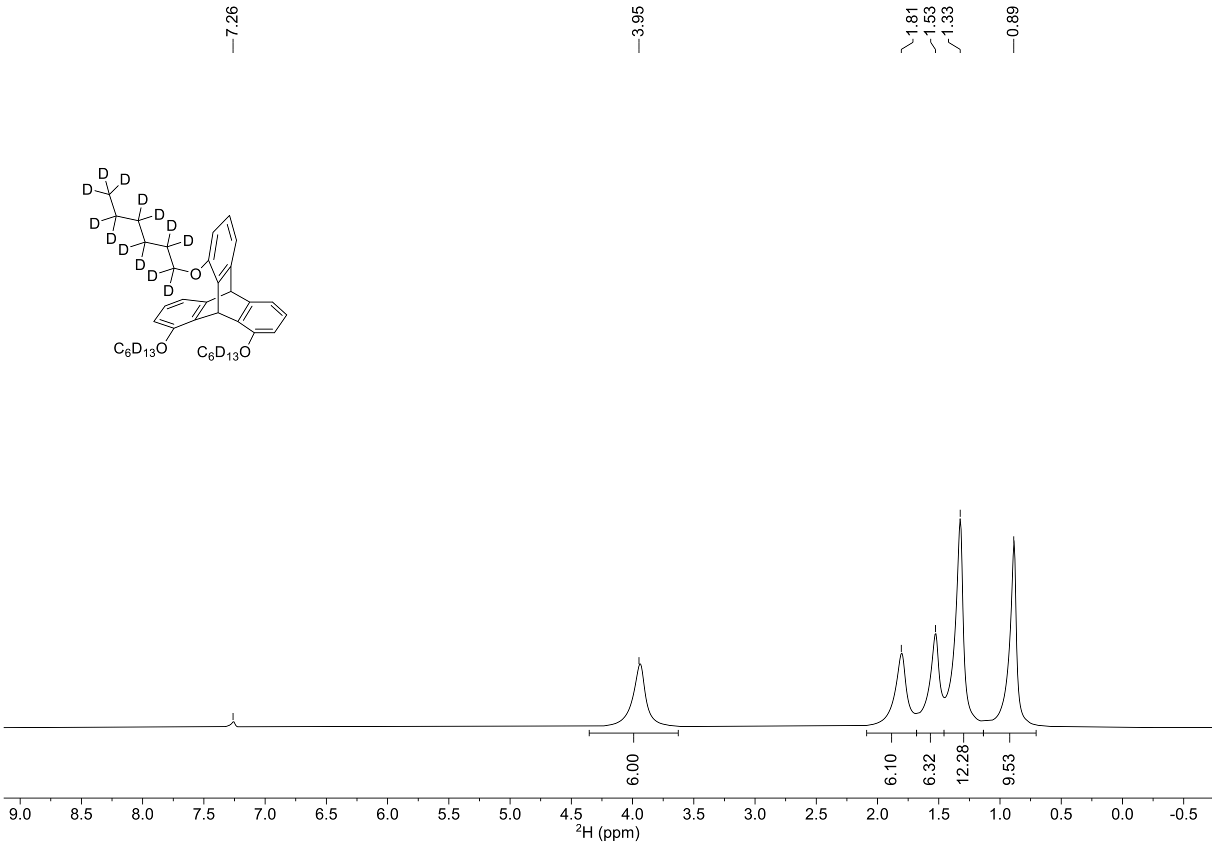


**Figure S11.** $^{2}H$ NMR spectrum of compound **5-d$_{39}$** (92 MHz, $CHCl_3$).

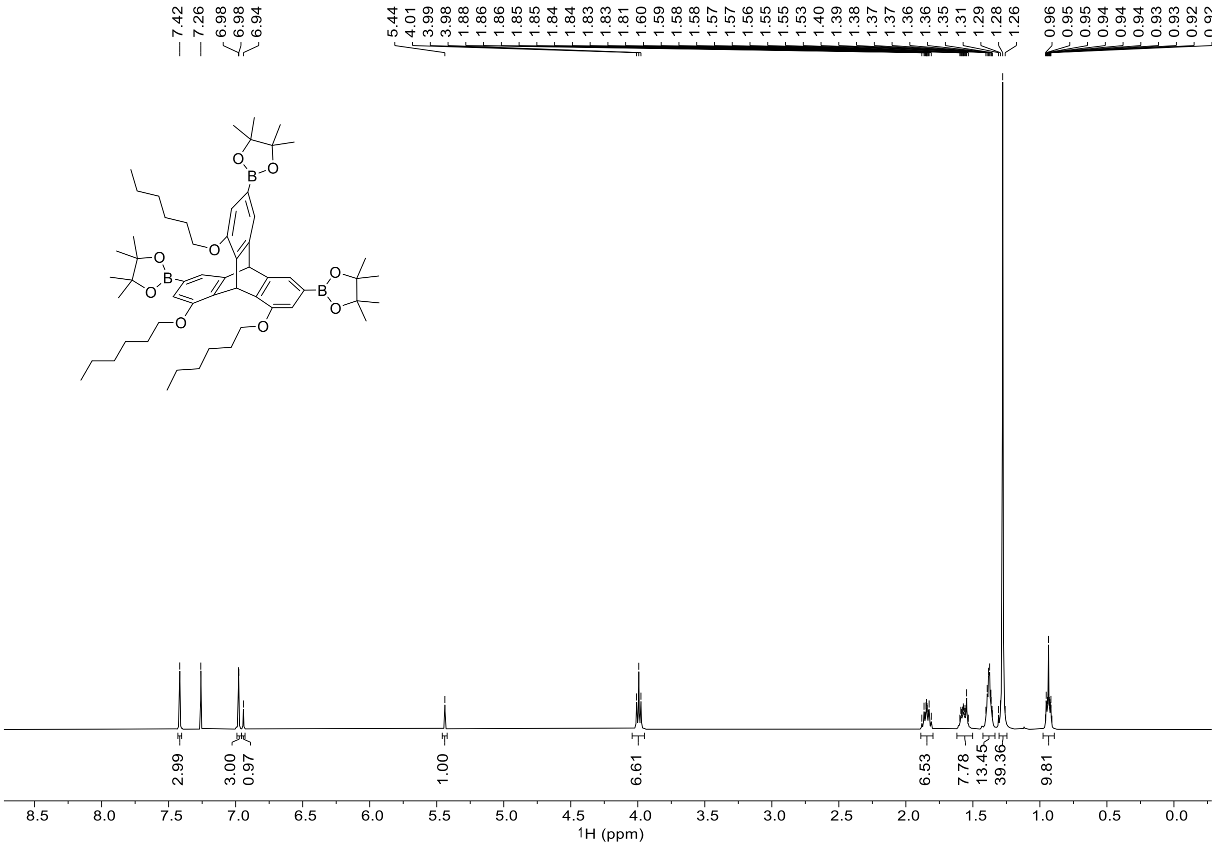


**Figure S12.** $^{1}$H NMR spectrum of compound **6** (400 MHz, CDCl$_3$).

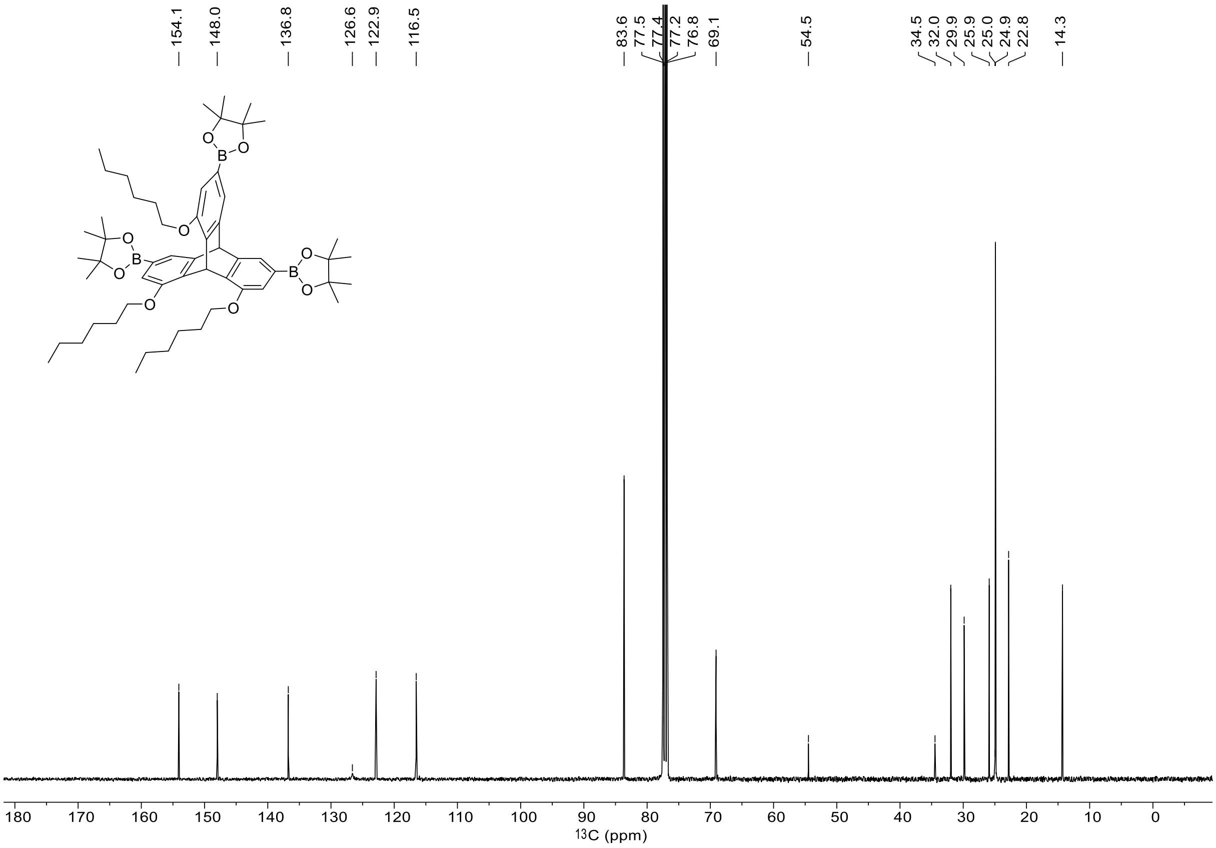


**Figure S13.** $^{13}$C{$^{1}$H} NMR spectrum of compound **6** (100 MHz, CDCl$_3$).

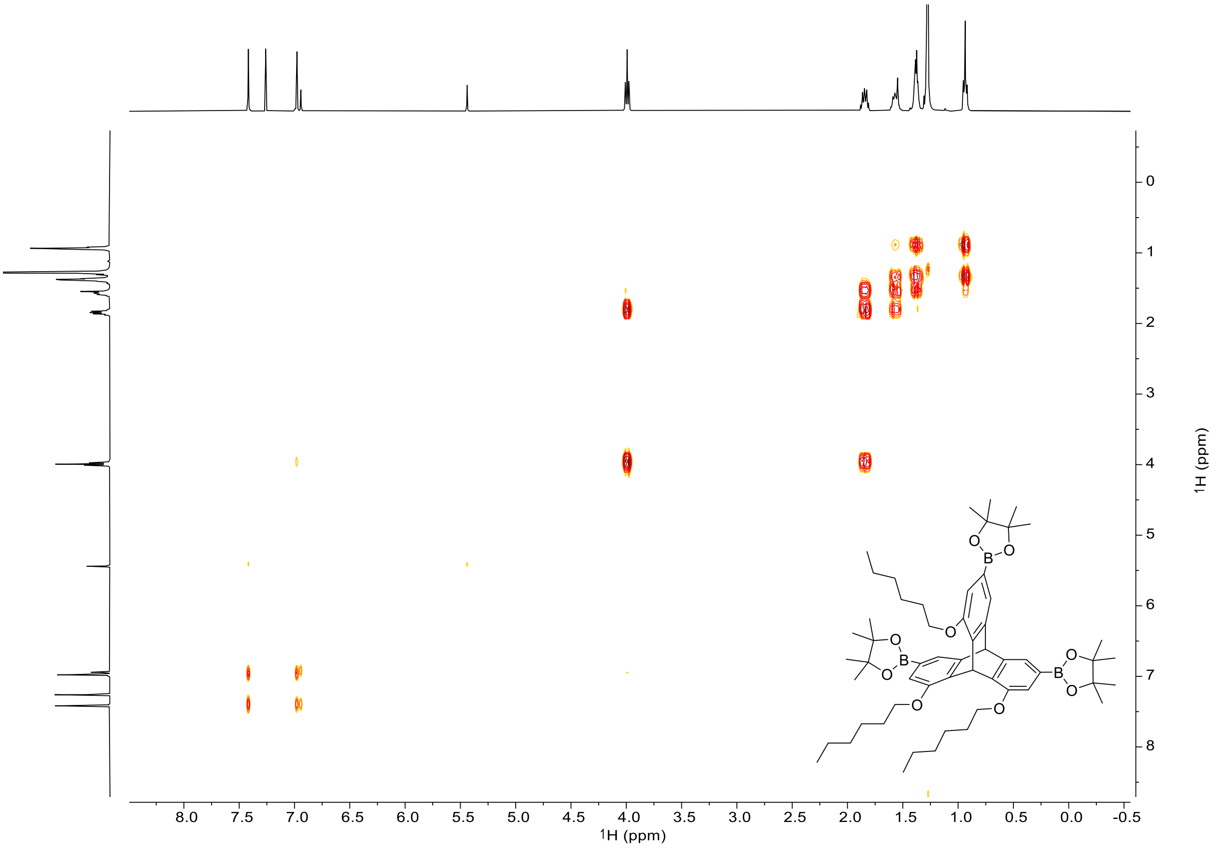


**Figure S14.** $^1$H,$^1$H-COSY spectrum of compound **6** (400 MHz, CDCl$_3$).

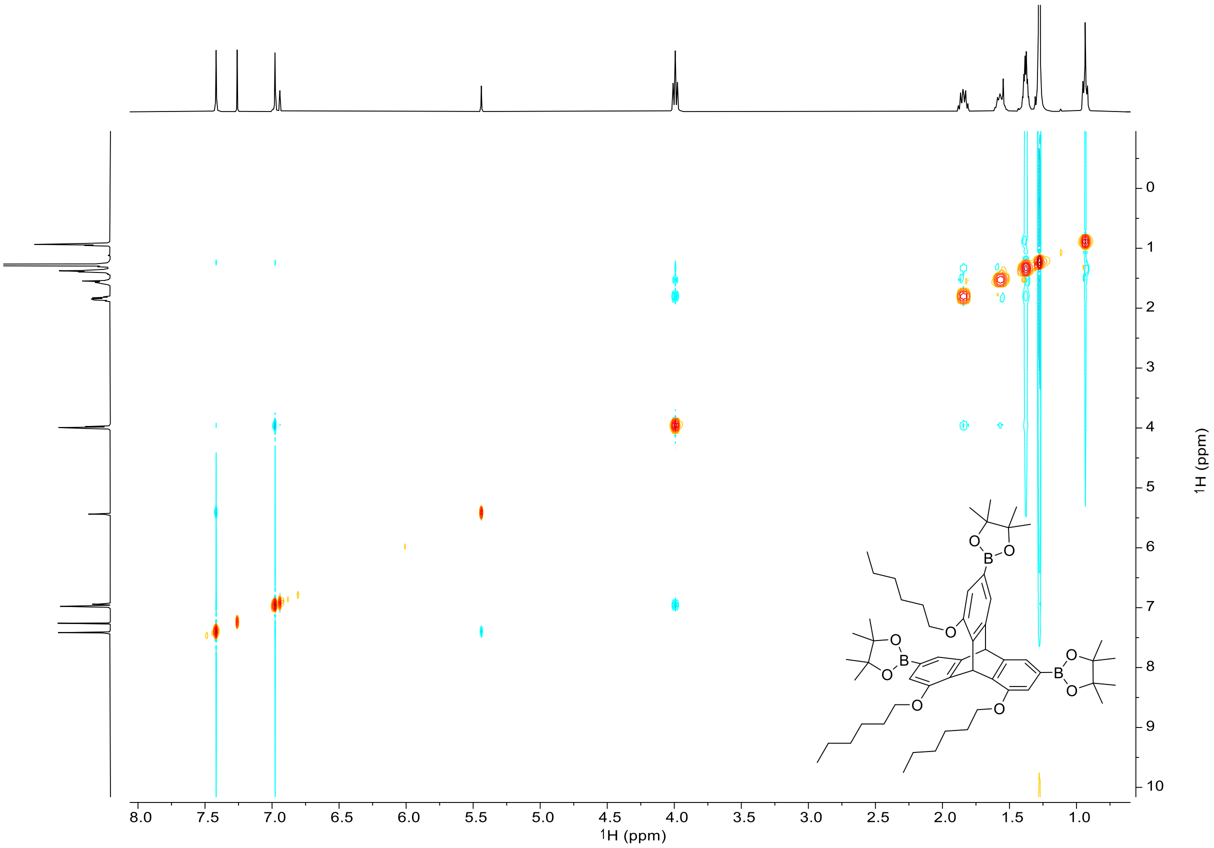


**Figure S15.** $^1$H,$^1$H-NOESY spectrum of compound **6** (400 MHz, CDCl$_3$).

**Table S5.** Cross-peak assignment of $^1H$,$^1H$-COSY and $^1H$,$^1H$-NOESY spectra of compound **6**.

| **$^1H$ nucleus** | **$\delta_{1H}$ [ppm]** | **COSY** | **NOESY** |
|---|---|---|---|
| *a* | 7.42 | *b, d* | *d, i* |
| *b* | 6.98 | *a, e* | *e, f, g, h* |
| *c* | 6.94 | *a* | *e, f, g* |
| *d* | 5.44 | *a* | *a* |
| *e* | 3.99 | *f* | *b, c, f, g, h* |
| *f* | 1.89 – 1.80 | *e, g* | *b, c, e, h* |
| *g* | 1.62 – 1.50 | *f, h, j* | *b, c, e, h* |
| *h* | 1.41 – 1.34 | *g, j* | *b, e, f, g, j* |
| *i* | 1.28 | - | *a* |
| *j* | 0.98 – 0.89 | *g, h* | *h* |

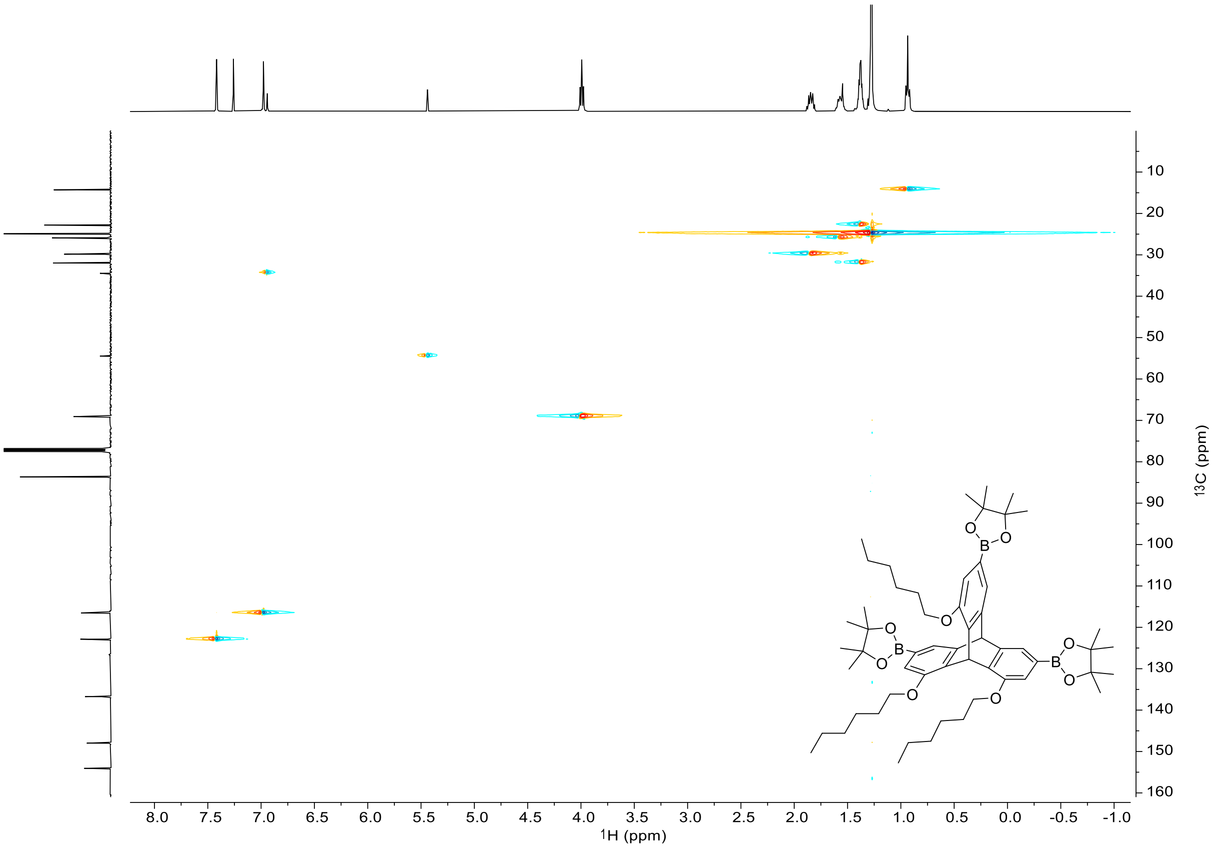


**Figure S16.** $^1$H,$^{13}$C-HSQC spectrum of compound **6** (400 MHz, 100 MHz, CDCl$_3$).

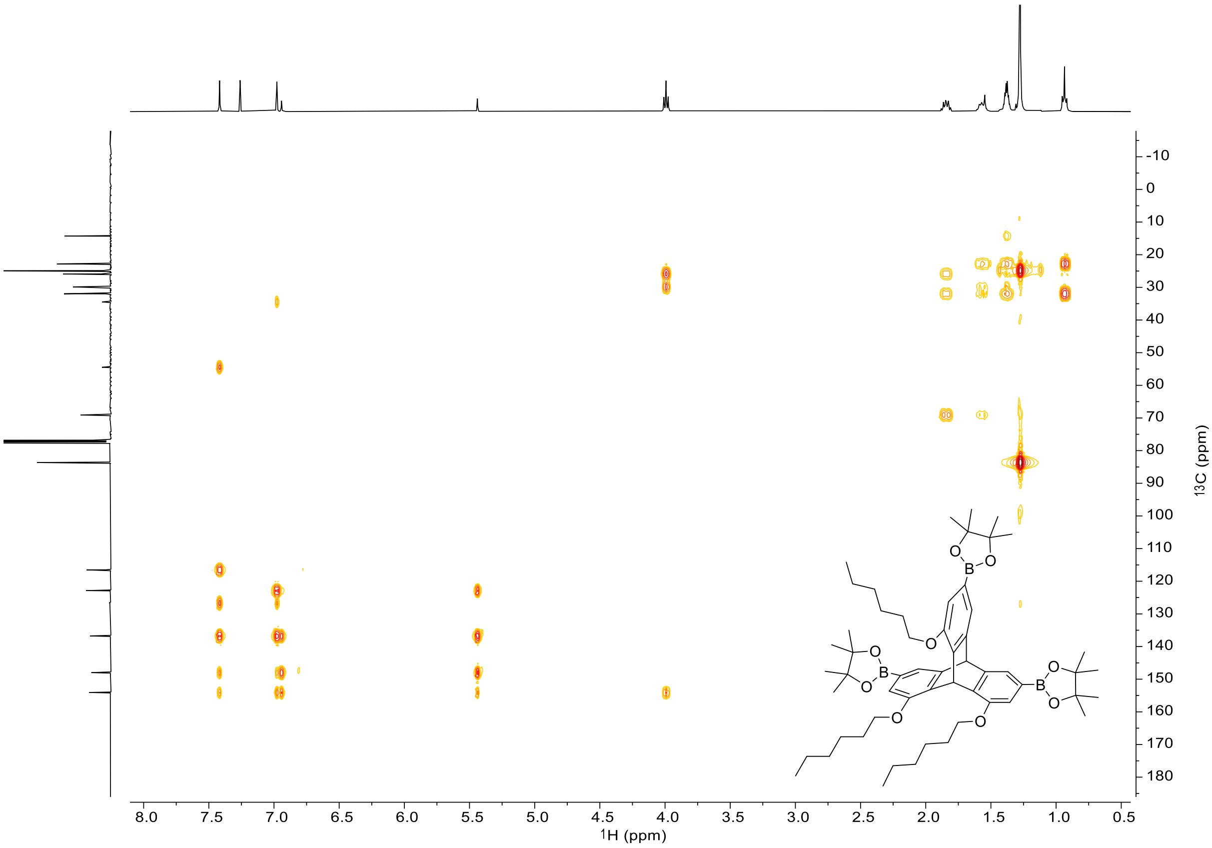


**Figure S17.** $^1$H,$^{13}$C-HMBC spectrum of compound **6** (400 MHz, 100 MHz, CDCl$_3$).

**Table S6.** Correlations of $^{1}H$,$^{13}C$-HSQC and $^{1}H$,$^{13}C$-HMBC spectra of compound **6**.

| **$^{13}C$ nucleus** | **$\delta_{13C}$ [ppm]** | **$^{1}H$ nucleus** | | |
|---|---|---|---|---|
| | | **HSQC** | **$\delta_{1H}$ [ppm]** | **HMBC** |
| *A* | 154.1 | - | - | *a, b, c, d, e* |
| *B* | 148.0 | - | - | *a, b, c, d* |
| *C* | 136.8 | - | - | *a, b, c, d* |
| *D* | 126.6 | - | - | *a, b, i* |
| *E* | 122.9 | *a* | 7.42 | *b, c, d* |
| *F* | 116.5 | *b* | 6.98 | *a* |
| *G* | 83.6 | - | - | *i* |
| *H* | 69.1 | *e* | 3.99 | *f, g* |
| *I* | 54.5 | *d* | 5.44 | *a* |
| *J* | 34.5 | *c* | 6.94 | *a, b* |
| *K* | 32.0 | *h* | 1.41 – 1.34 | *f, g, h, j* |
| *L* | 29.9 | *f* | 1.89 – 1.80 | *e, g, h* |
| *M* | 25.9 | *g* | 1.62 – 1.50 | *e, g* |
| *N* | 24.9 | *i* | 1.28 | *i* |
| *O* | 22.8 | *h* | 1.41 – 1.34 | *g, h, j* |
| *P* | 14.3 | *j* | 0.98 – 0.89 | *h* |

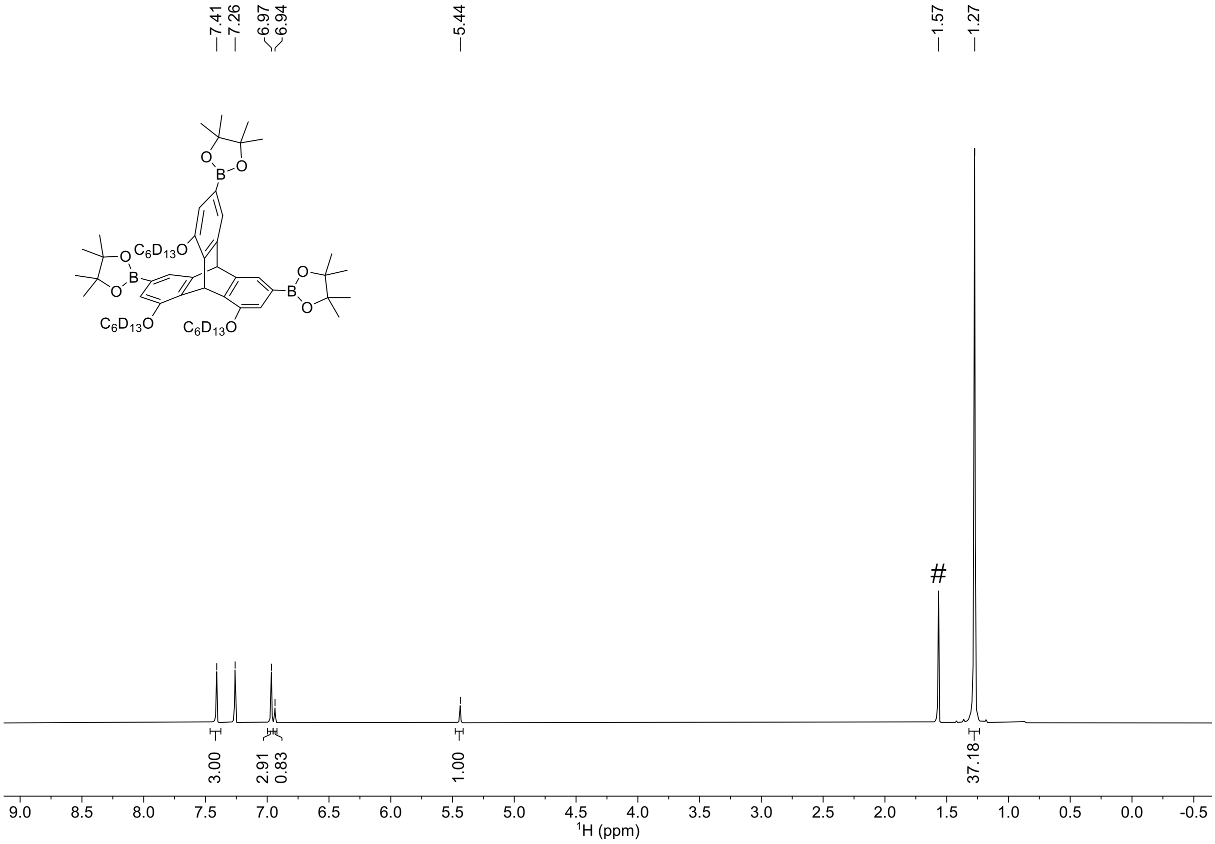


**Figure S18.** $^1$H NMR spectrum of compound **6-d$_{39}$** (700 MHz, CDCl$_3$). #: H$_2$O.

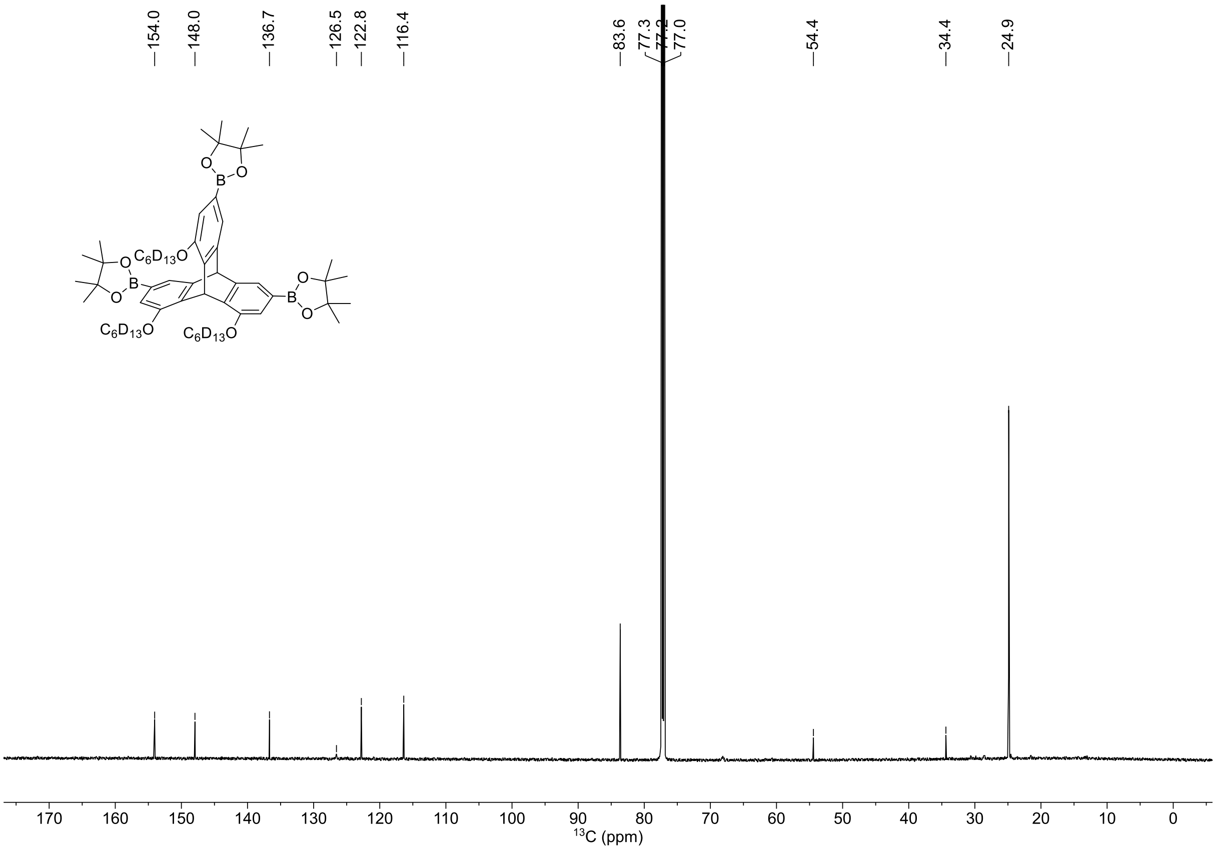


**Figure S19.** $^{13}$C{$^1$H} NMR spectrum of compound **6-d$_{39}$** (176 MHz, CDCl$_3$).

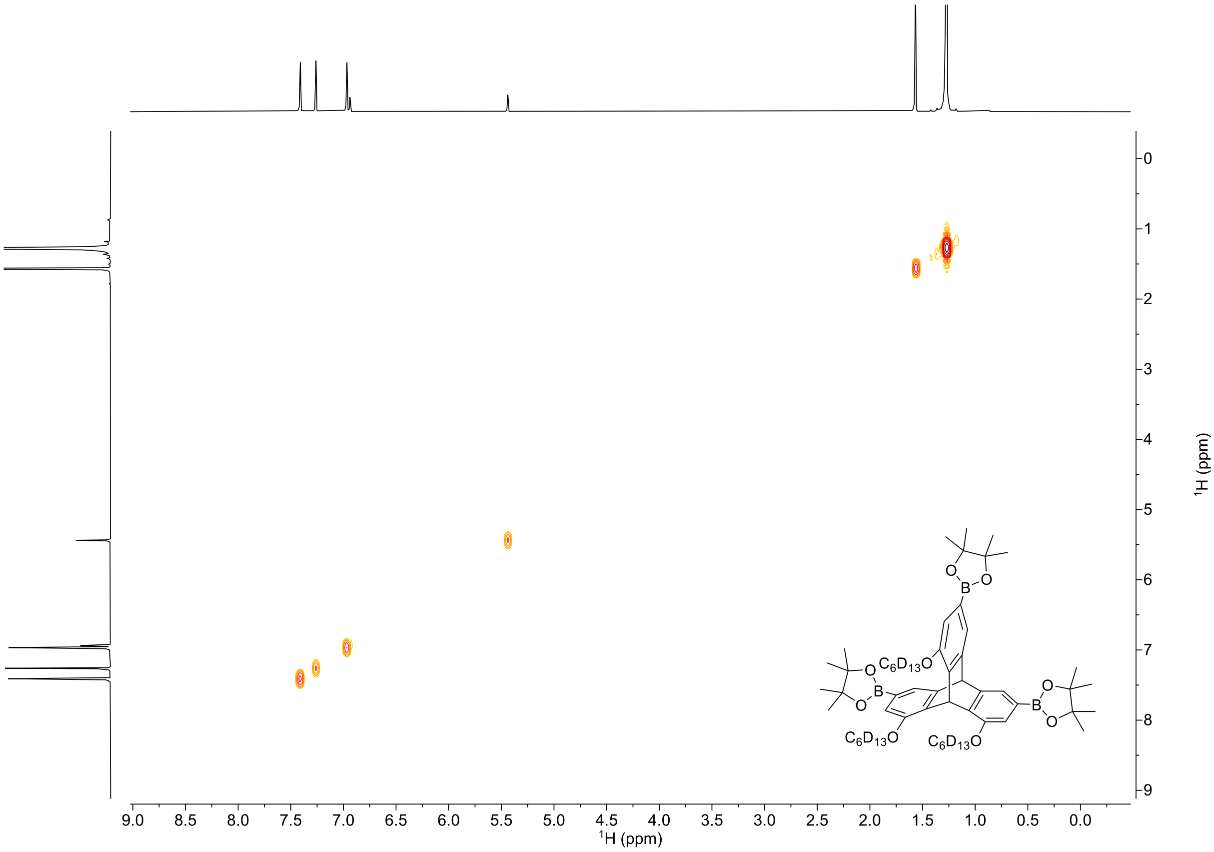


**Figure S20.** $^1$H,$^1$H-COSY spectrum of compound **6-d$_{39}$** (700 MHz, CDCl$_3$).

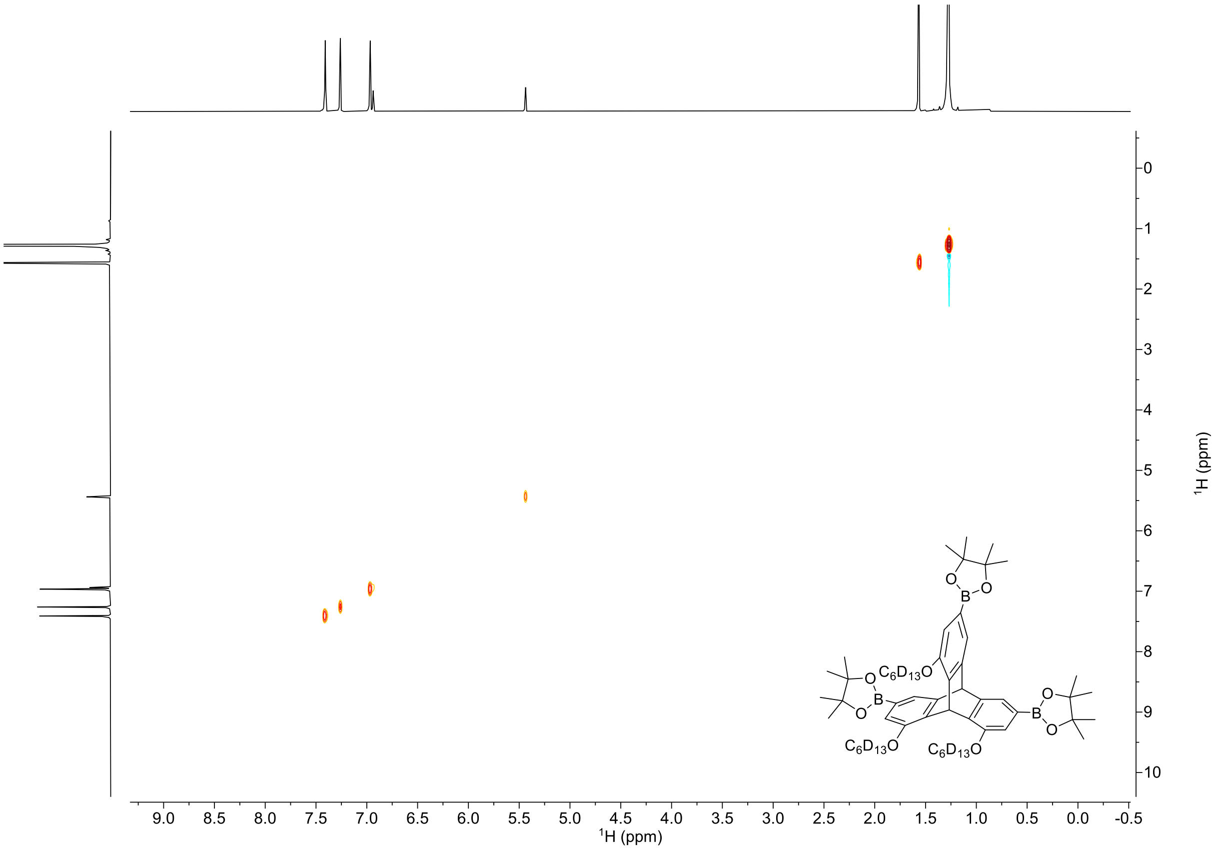


**Figure S21.** $^1$H,$^1$H-NOESY spectrum of compound **6-d$_{39}$** (700 MHz, CDCl$_3$).

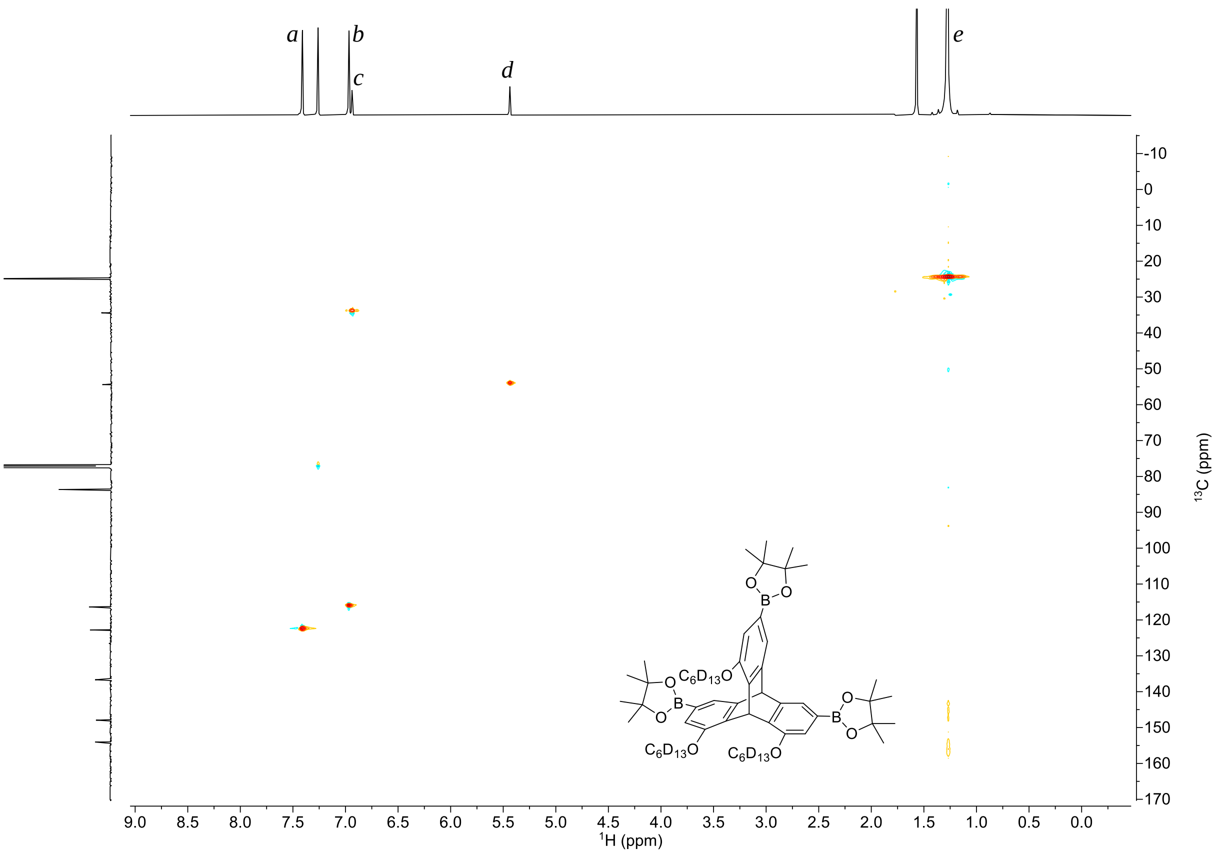


**Figure S22.** $^1$H,$^{13}$C-HSQC spectrum of compound **6-d$_{39}$** (700 MHz, 176 MHz, CDCl$_3$).

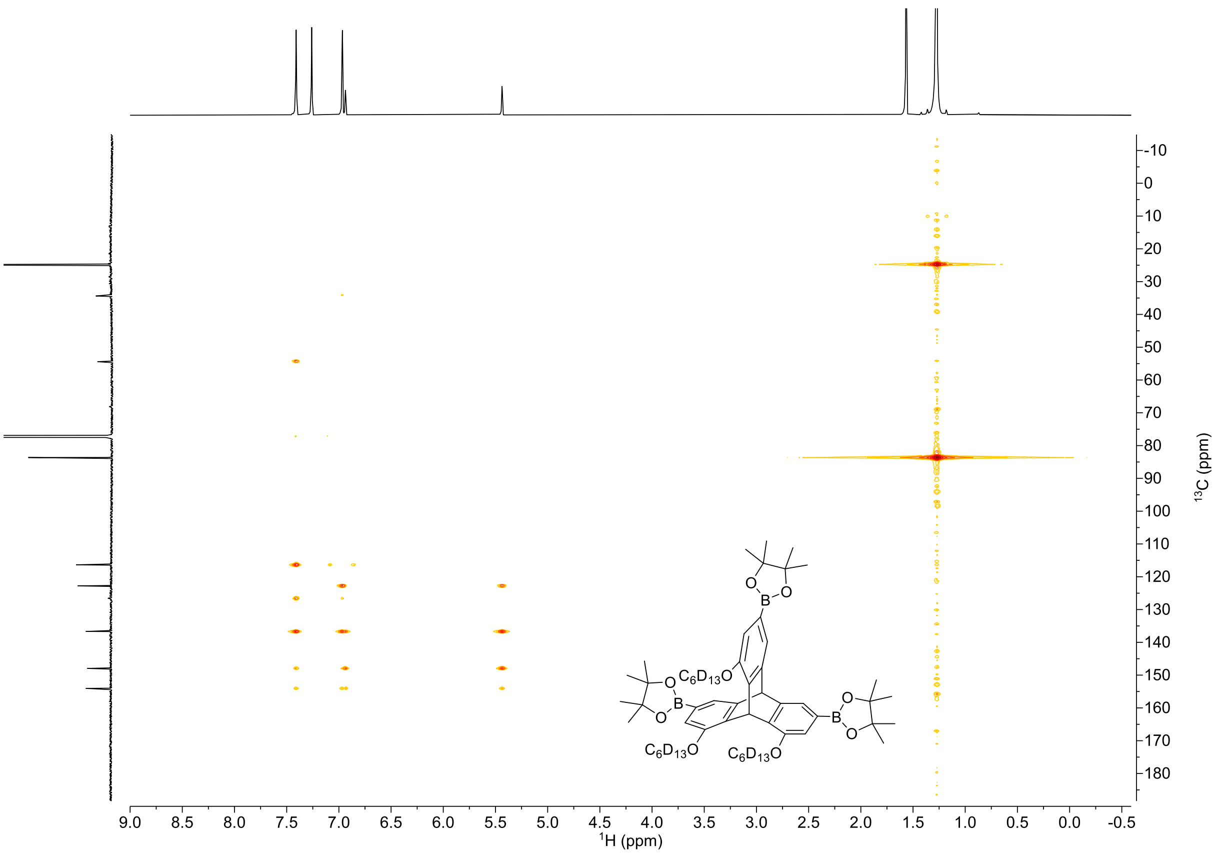


**Figure S23.** $^1$H,$^{13}$C-HMBC spectrum of compound **6-d$_{39}$** (700 MHz, 176 MHz, CDCl$_3$).

**Table S7.** Correlations of $^{1}H$,$^{13}C$-HSQC and $^{1}H$,$^{13}C$-HMBC spectra of compound **6-d₃₉**.

| **$^{13}C$ nucleus** | **$\delta_{13C}$ [ppm]** | **$^{1}H$ nucleus** | | |
|---|---|---|---|---|
| | | **HSQC** | **$\delta_{1H}$ [ppm]** | **HMBC** |
| *A* | 154.0 | - | - | *a, b, c, d* |
| *B* | 148.0 | - | - | *a, c, d* |
| *C* | 136.7 | - | - | *a, b, c, d* |
| *D* | 126.5 | - | - | *a, b* |
| *E* | 122.8 | *a* | 7.41 | *b, d* |
| *F* | 116.4 | *b* | 6.97 | *a* |
| *G* | 83.6 | - | - | *e* |
| *H* | 54.4 | *d* | 5.44 | *a* |
| *I* | 34.4 | *c* | 6.94 | *b* |
| *J* | 24.9 | *e* | 1.27 | *e* |

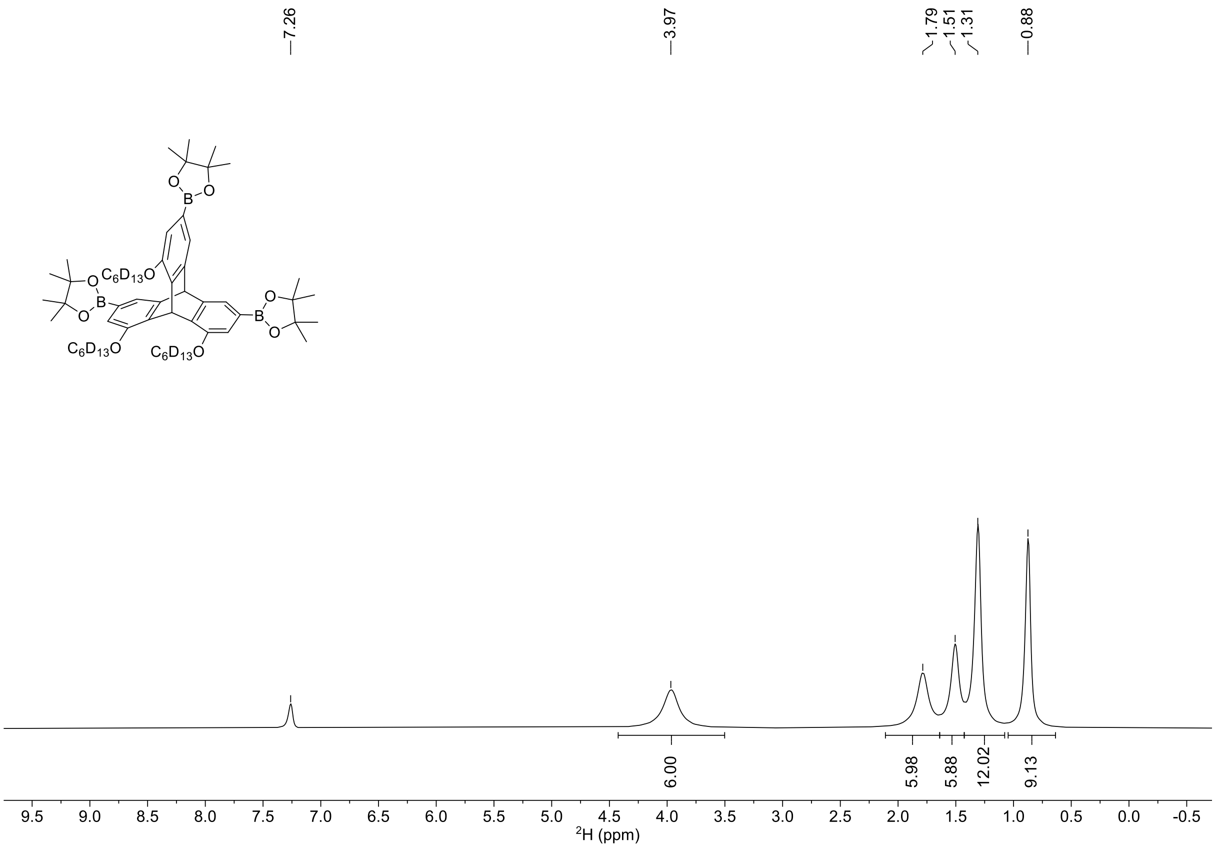


**Figure S24.** $^{2}H$ NMR spectrum of compound **6-d₃₉** (92 MHz, $CHCl_3$).

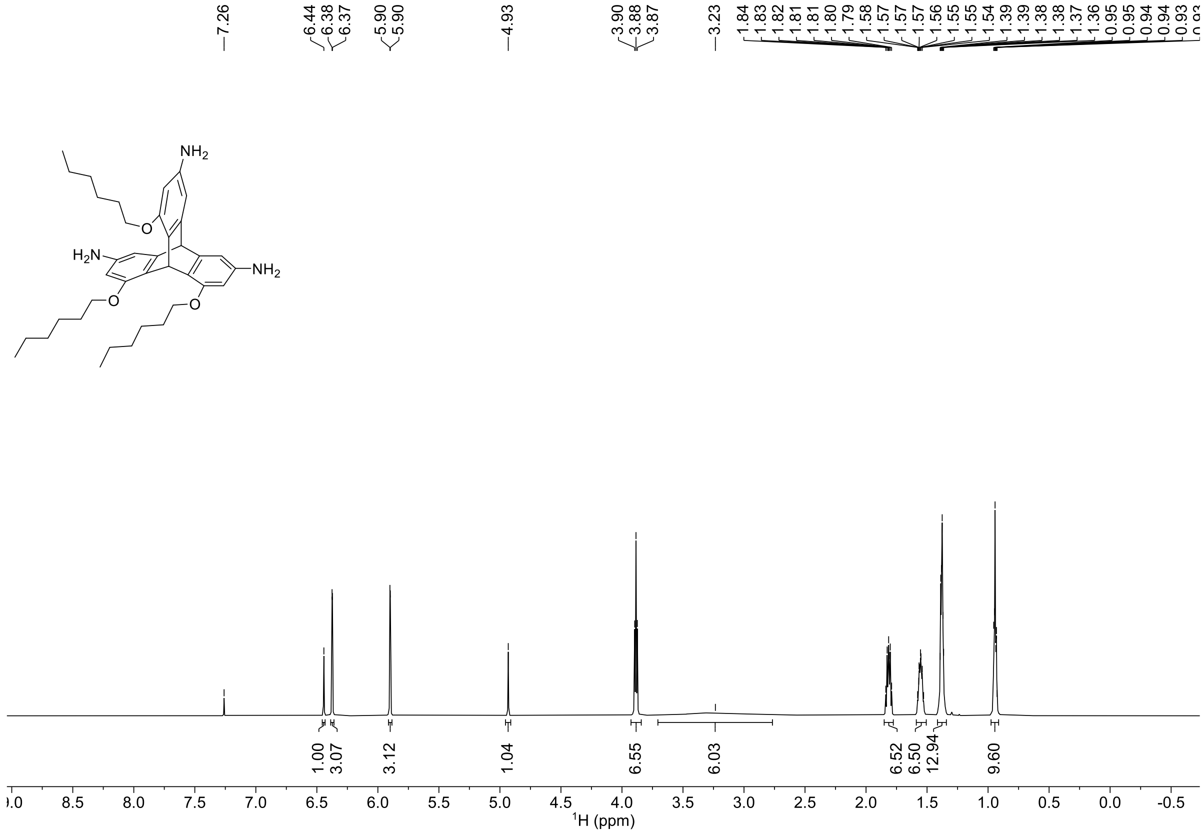


**Figure S25.** $^1$H NMR spectrum of compound **7a** (600 MHz, CDCl$_3$).

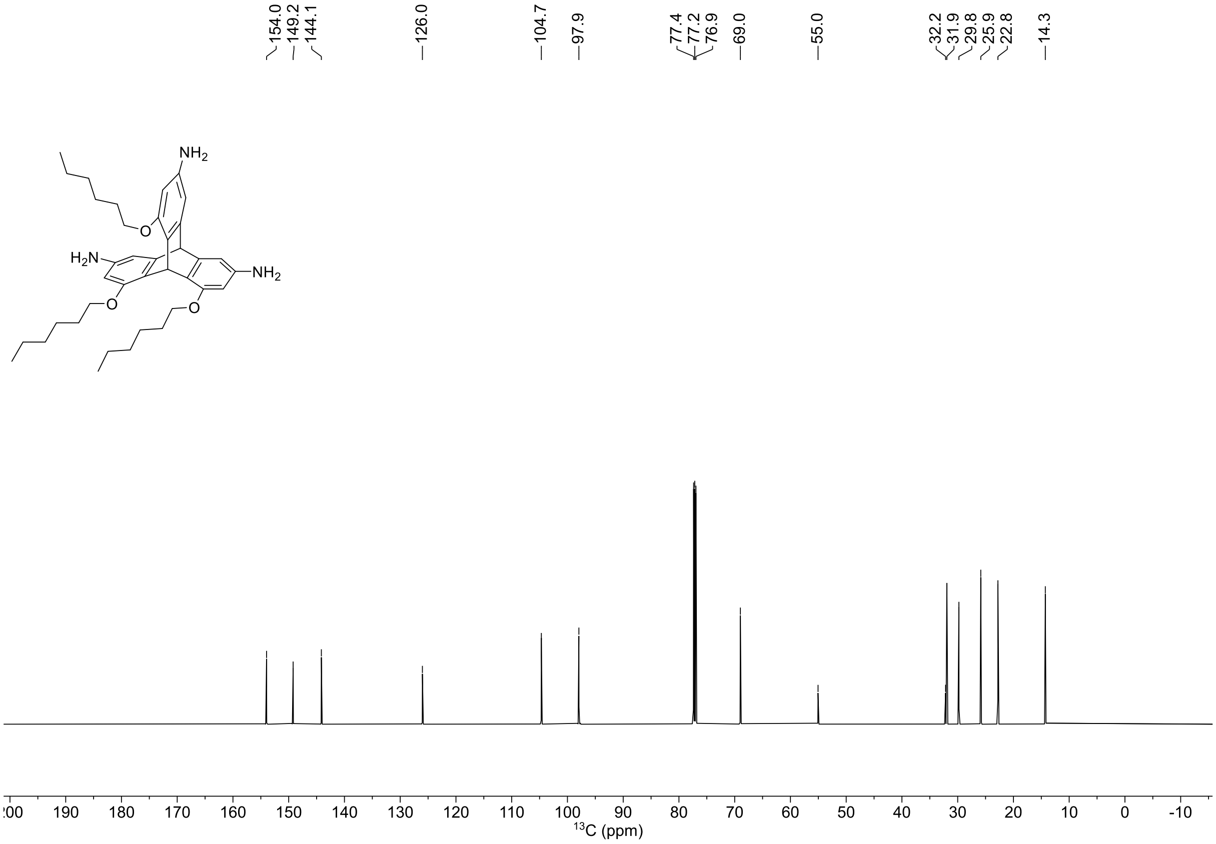


**Figure S26.** $^{13}$C{$^1$H} NMR spectrum of compound **7a** (150 MHz, CDCl$_3$).

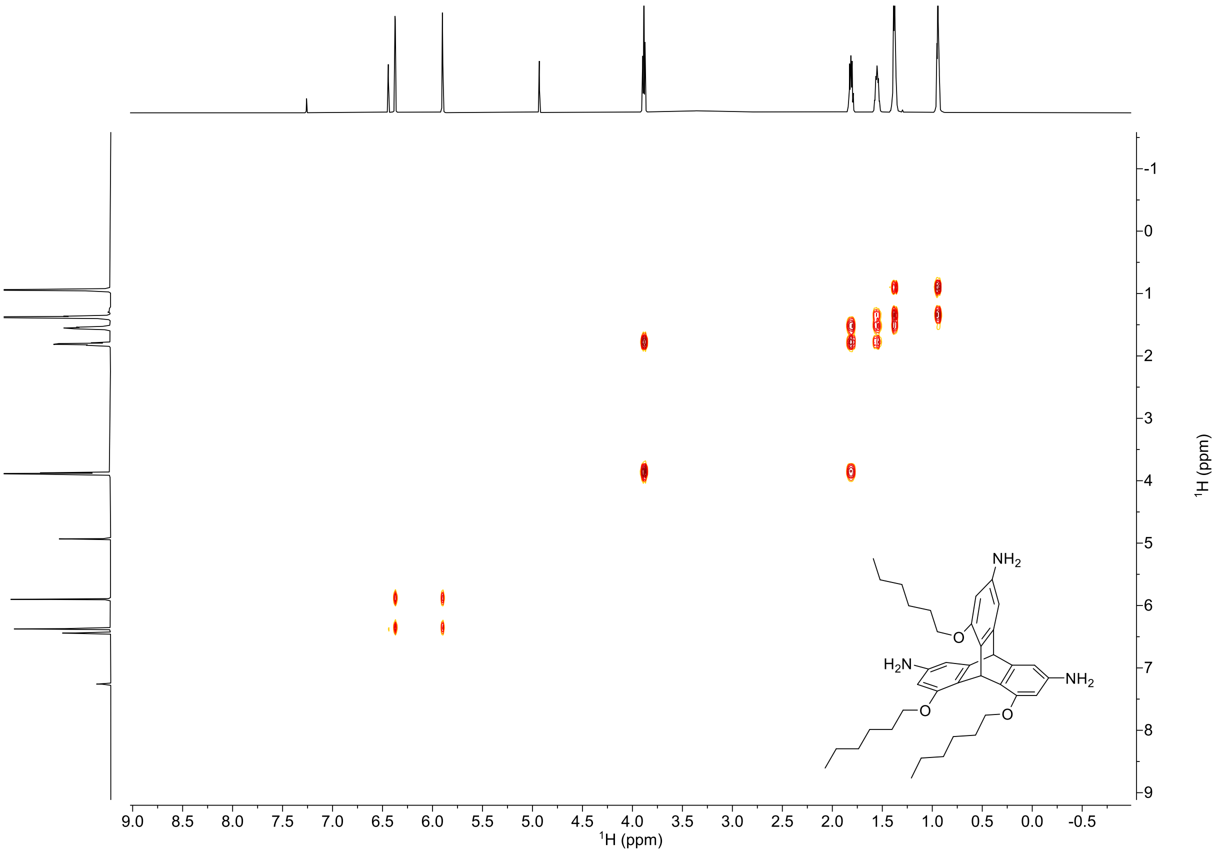


**Figure S27.** $^1$H,$^1$H-COSY spectrum of compound **7a** (600 MHz, CDCl$_3$).

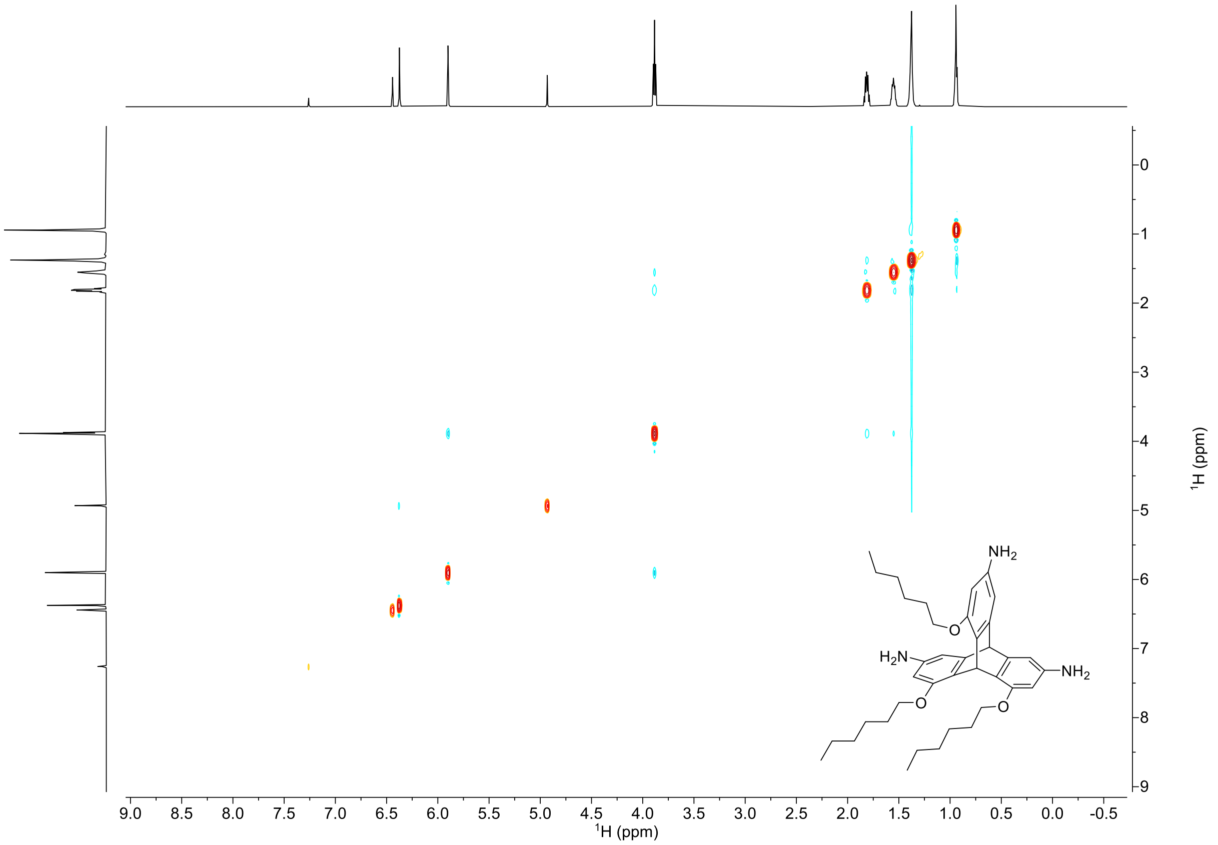


**Figure S28.** $^1$H,$^1$H-NOESY spectrum of compound **7a** (600 MHz, CDCl$_3$).

**Table S8.** Cross-peak assignment of $^{1}H,^{1}H$-COSY spectrum of compound **7a**.

| $^{1}$H nucleus | $\delta_{1H}$ [ppm] | COSY |
|---|---|---|
| *a* | 6.45 | - |
| *b* | 6.38 | *c, d* |
| *c* | 5.90 | *b, d* |
| *d* | 4.94 | - |
| *e* | 3.88 | *g* |
| *f* | 3.40 | - |
| *g* | 1.86 – 1.74 | *e, h, i* |
| *h* | 1.60 – 1.47 | *g, i* |
| *i* | 1.42 – 1.30 | *g, h, j* |
| *j* | 0.97 – 0.88 | *i* |

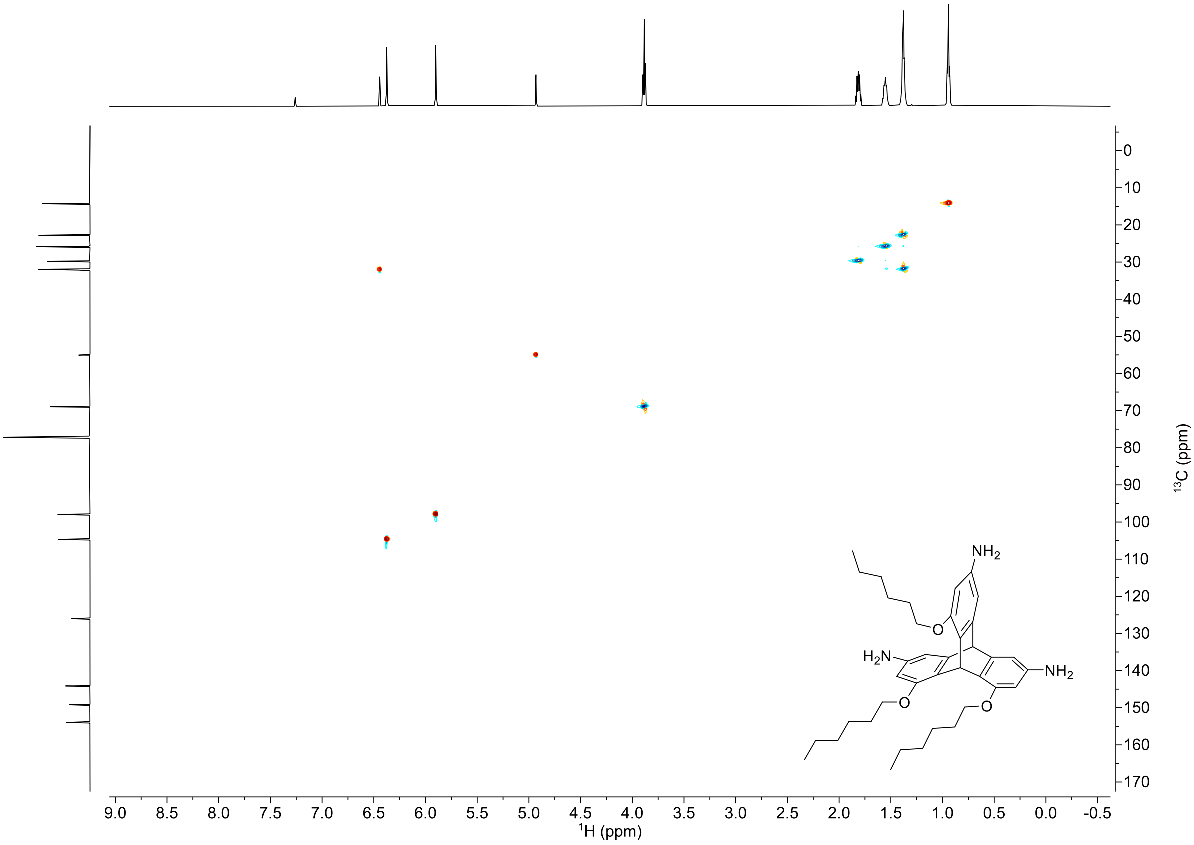


**Figure S29.** $^{1}H,^{13}C$-HSQC spectrum of compound **7a** (600 MHz, 150 MHz, $CDCl_3$).

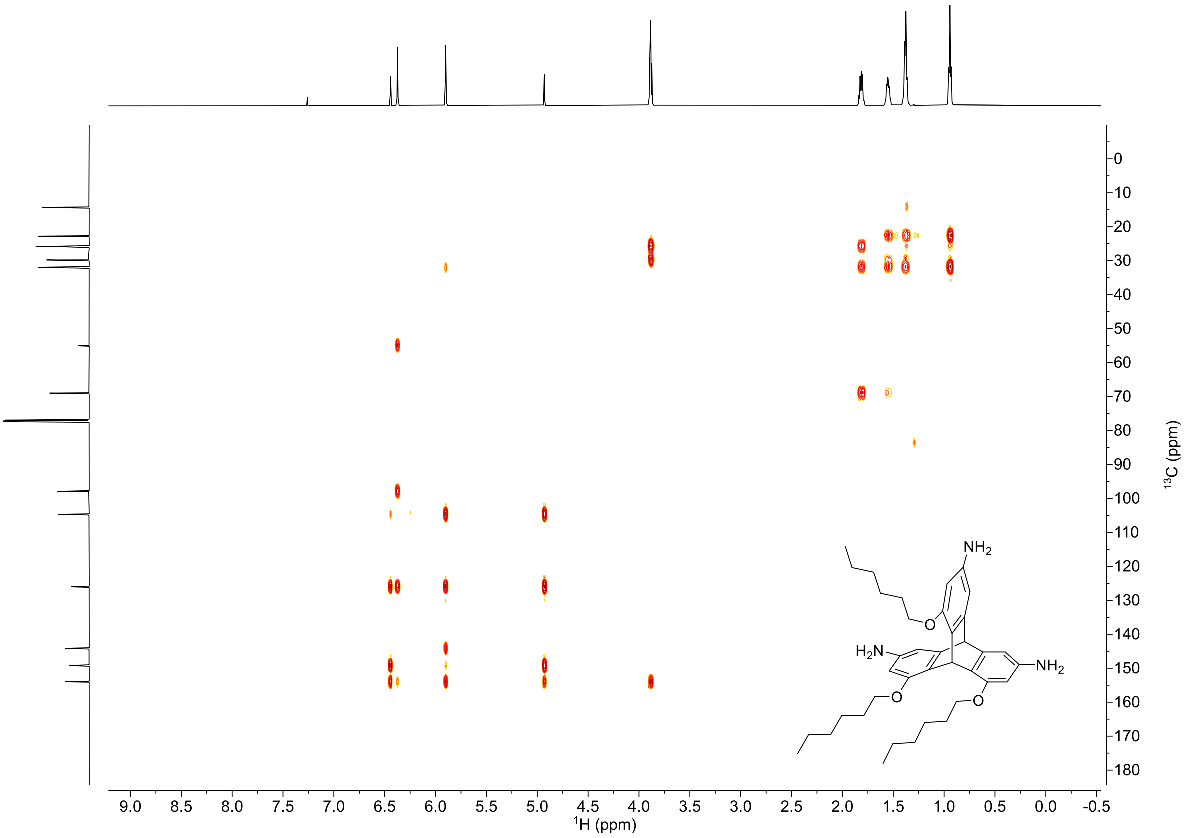


**Figure S30.** $^{1}H,^{13}C$-HMBC spectrum of compound **7a** (600 MHz, 150 MHz, $CDCl_3$).

**Table S9.** Correlations of $^1$H,$^{13}$C-HSQC and $^1$H,$^{13}$C-HMBC spectra of compound **7a**.

| **$^{13}$C nucleus** | **$\delta_{13C}$ [ppm]** | **$^1$H nucleus** | | |
|---|---|---|---|---|
| | | **HSQC** | **$\delta_{1H}$ [ppm]** | **HMBC** |
| *A* | 154.0 | - | - | *a, c, e* |
| *B* | 149.2 | - | - | *a, d* |
| *C* | 144.1 | - | - | *c* |
| *D* | 126.1 | - | - | *a, b, c, d* |
| *E* | 104.7 | *b* | 6.38 | *c, d* |
| *F* | 98.0 | *c* | 5.90 | *b* |
| *G* | 69.0 | *e* | 3.88 | *g, h* |
| *H* | 55.1 | *d* | 4.94 | *b* |
| *I* | 32.2 | *a* | 6.45 | - |
| *J* | 32.0 | *i* | 1.42 – 1.30 | *g, i, j* |
| *K* | 29.8 | *g* | 1.86 – 1.74 | *e* |
| *L* | 25.9 | *h* | 1.60 – 1.47 | *e, g* |
| *M* | 22.8 | *i* | 1.42 – 1.30 | *h, i, j* |
| *O* | 14.3 | *j* | 0.97 – 0.88 | - |

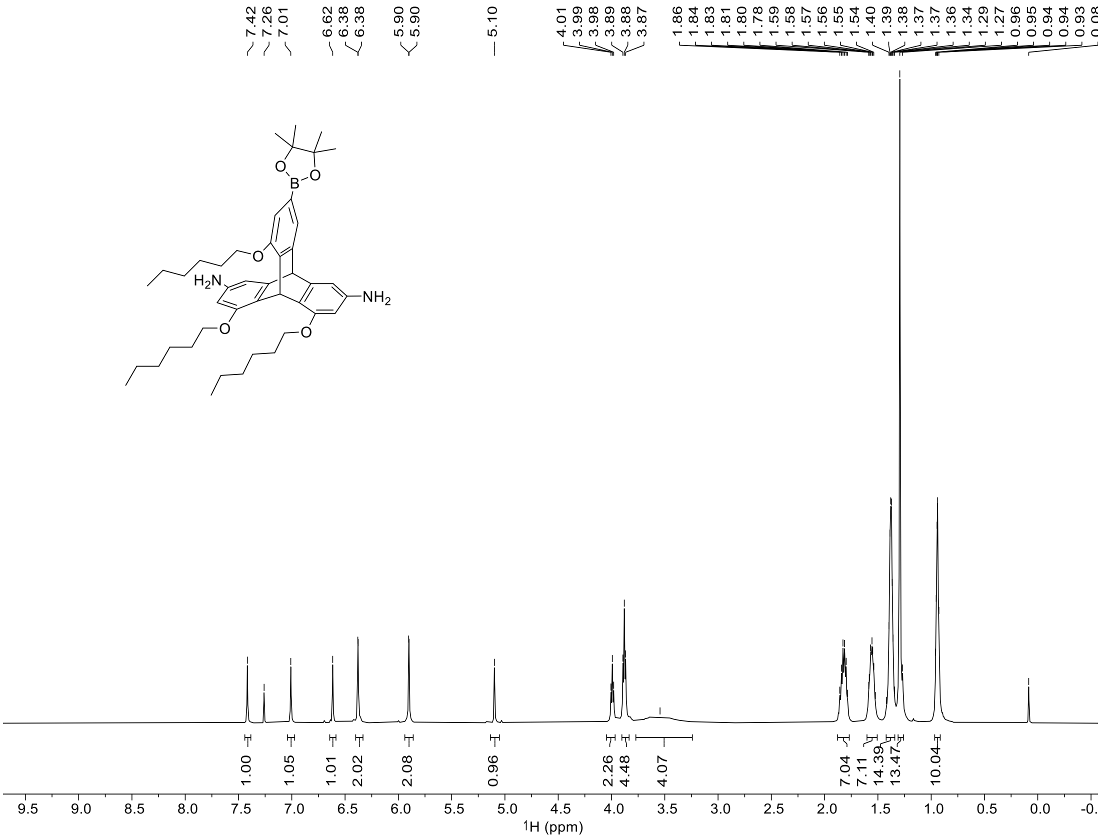


**Figure S31.** $^{1}$H NMR spectrum of compound **7b** (500 MHz, CDCl$_3$).

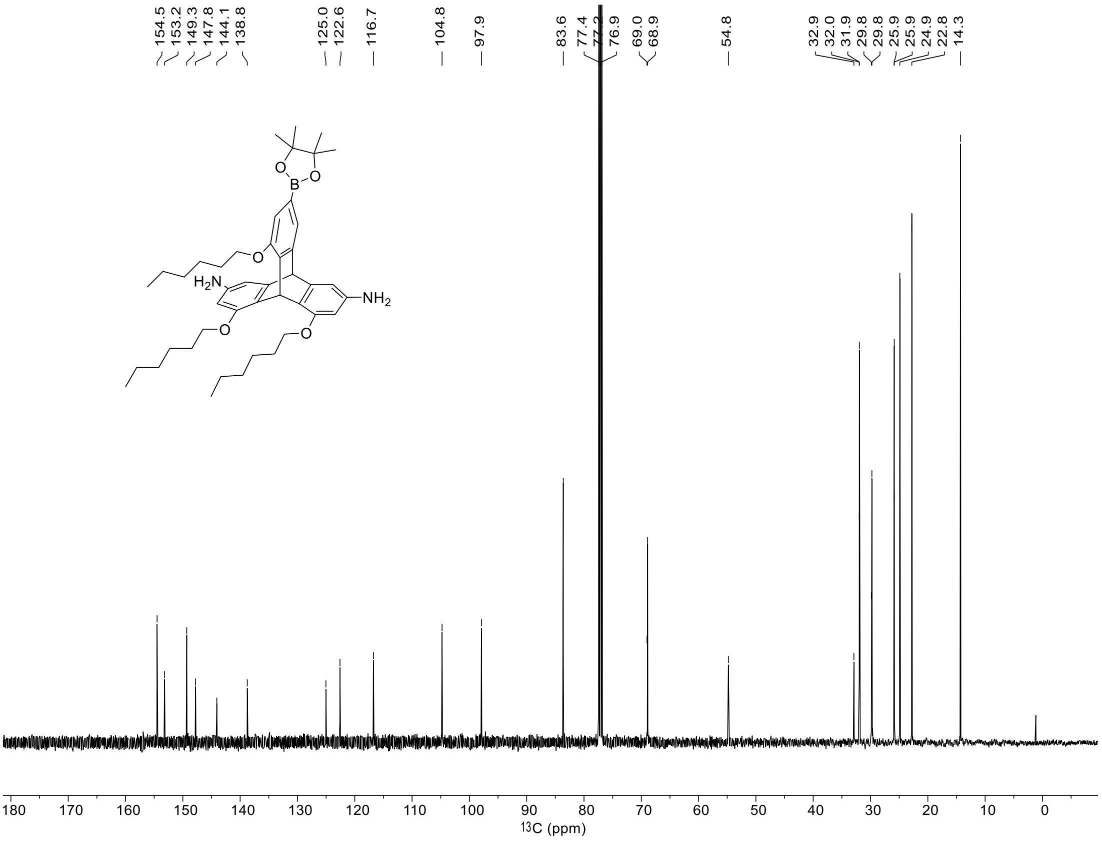


**Figure S32.** $^{13}$C{$^{1}$H} NMR spectrum of compound **7b** (125 MHz, CDCl$_3$).

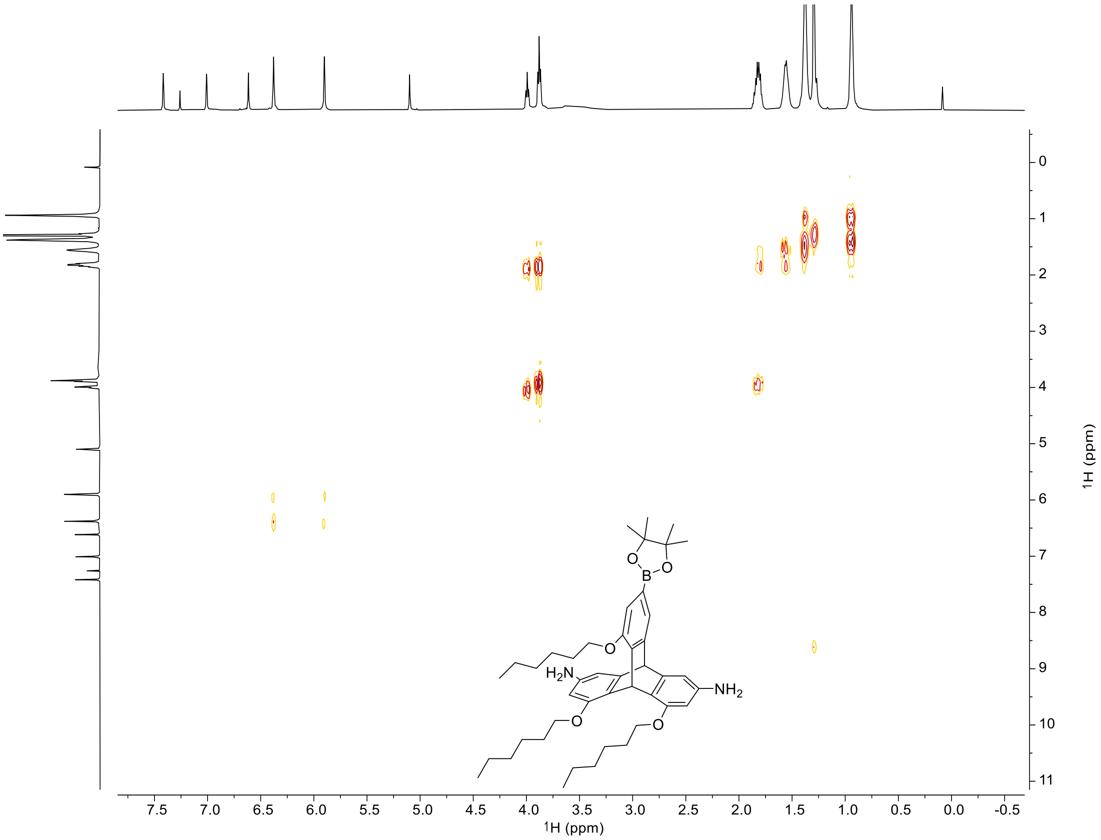


**Figure S33.** $^1$H,$^1$H-COSY spectrum of compound **7b** (500 MHz, 125 MHz, $CDCl_3$).

**Table S10.** Cross-peak assignment of $^1$H,$^1$H-COSY spectrum of compound **7b**.

| $^1$H nucleus | $\delta_{1H}$ [ppm] | COSY |
|---|---|---|
| *a* | 7.42 | - |
| *b* | 7.01 | - |
| *c* | 6.62 | - |
| *d* | 6.38 | *e* |
| *e* | 5.90 | *d* |
| *f* | 5.10 | - |
| *g* | 3.99 | *j* |
| *h* | 3.88 | *j* |
| *i* | 3.54 | - |
| *j* | 1.88 – 1.77 | *g, h, k, l, n* |
| *k* | 1.60 – 1.51 | *j, l, n* |
| *l* | 1.42 – 1.34 | *j, k, n* |
| *m* | 1.29 | - |
| *n* | 0.97 – 0.92 | *j, k, l* |

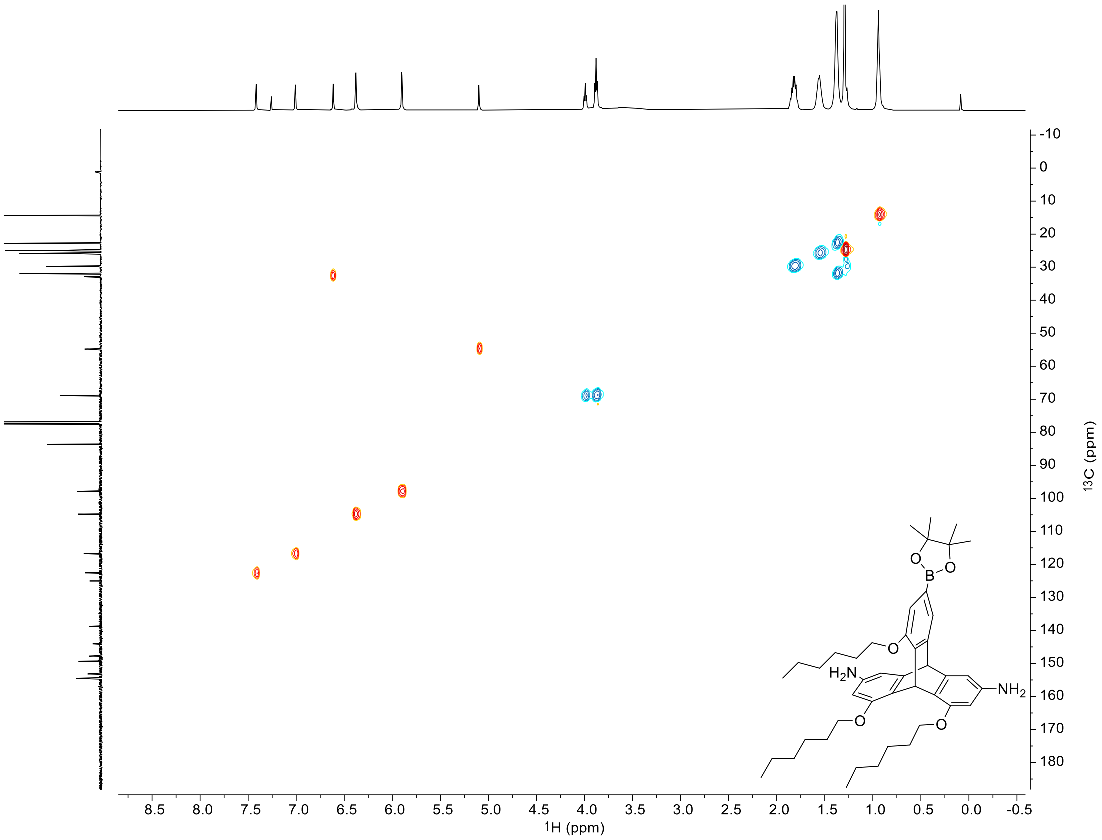


**Figure S34.** $^{1}$H,$^{13}$C-HSQC spectrum of compound **7b** (500 MHz, 125 MHz, CDCl$_3$).

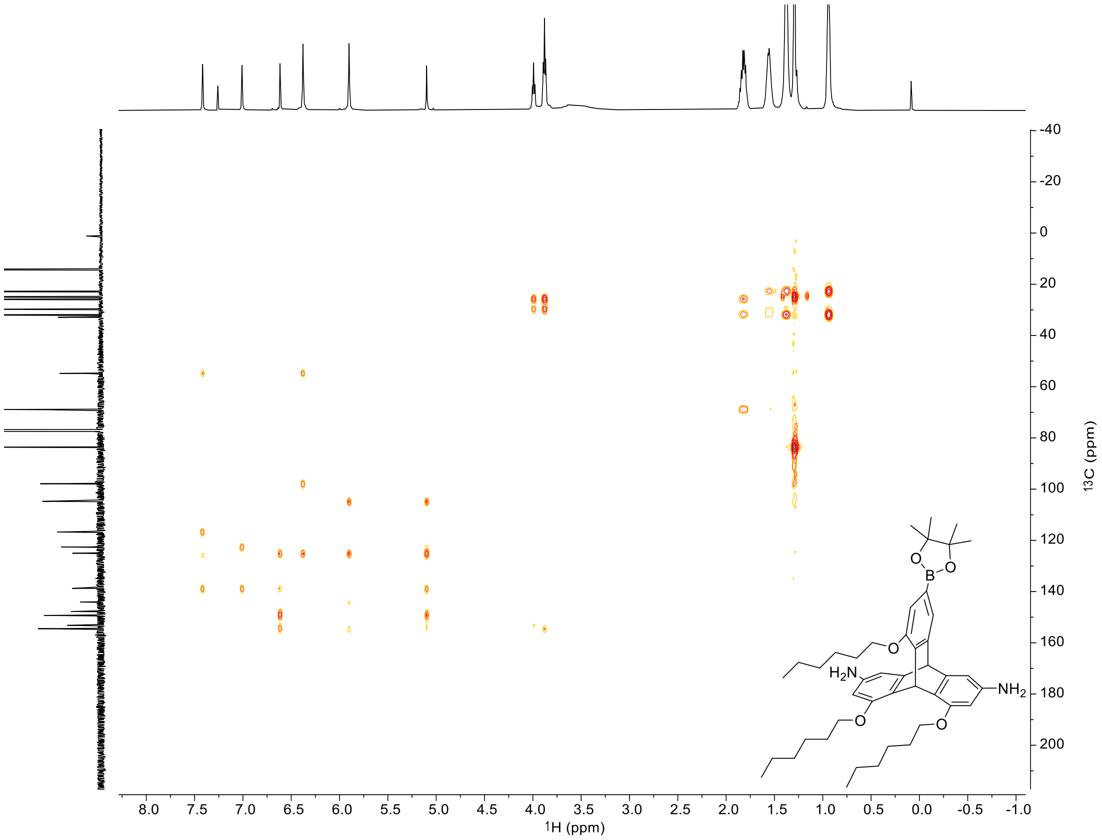


**Figure S35.** $^{1}$H,$^{13}$C-HMBC spectrum of compound **7b** (500 MHz, 125 MHz, CDCl$_3$).

**Table S11.** Correlations of $^1$H,$^{13}$C-HSQC and $^1$H,$^{13}$C-HMBC spectra of compound **7b**.

| **$^{13}$C nucleus** | **$\delta_{13C}$ [ppm]** | **$^1$H nucleus** | | |
|---|---|---|---|---|
| | | **HSQC** | **$\delta_{1H}$ [ppm]** | **HMBC** |
| *A* | 154.5 | - | - | *c, e, f, h* |
| *B* | 153.2 | - | - | *b, f, g* |
| *C* | 149.3 | - | - | *c, f* |
| *D* | 147.8 | - | - | *c, f* |
| *E* | 144.1 | - | - | *e* |
| *F* | 138.8 | - | - | *a, b, c, f* |
| *G* | 125.0 | - | - | *c, d, e, f* |
| *H* | 122.6 | *a* | 7.42 | *b* |
| *I* | 116.7 | *b* | 7.01 | *a* |
| *J* | 104.8 | *d* | 6.38 | *e, f* |
| *K* | 97.9 | *e* | 5.90 | *d* |
| *L* | 83.6 | - | - | *m* |
| *M* | 69.0 | *g* | 3.99 | *j, k* |
| *O* | 68.9 | *h* | 3.88 | *j, k* |
| *P* | 54.8 | *f* | 5.10 | *a, d* |
| *Q* | 32.9 | *c* | 6.62 | - |
| *R* | 32.0 | *l* | 1.42 – 1.34 | *j, k, l, n* |
| *S* | 31.9 | *l* | 1.42 – 1.34 | *j, k, l, n* |
| *T* | 29.8 | *j* | 1.88 – 1.77 | *g, h, k* |
| *U* | 29.8 | *j* | 1.88 – 1.77 | *g, h, k* |
| *V* | 25.9 | *k* | 1.60 – 1.51 | *g, h, j* |
| *W* | 25.9 | *k* | 1.60 – 1.51 | *g, h, j* |
| *X* | 24.9 | *m* | 1.29 | *m* |
| *Y* | 22.8 | *l* | 1.42 – 1.34 | *k, l, n* |
| *Z* | 14.3 | *n* | 0.97 – 0.92 | - |

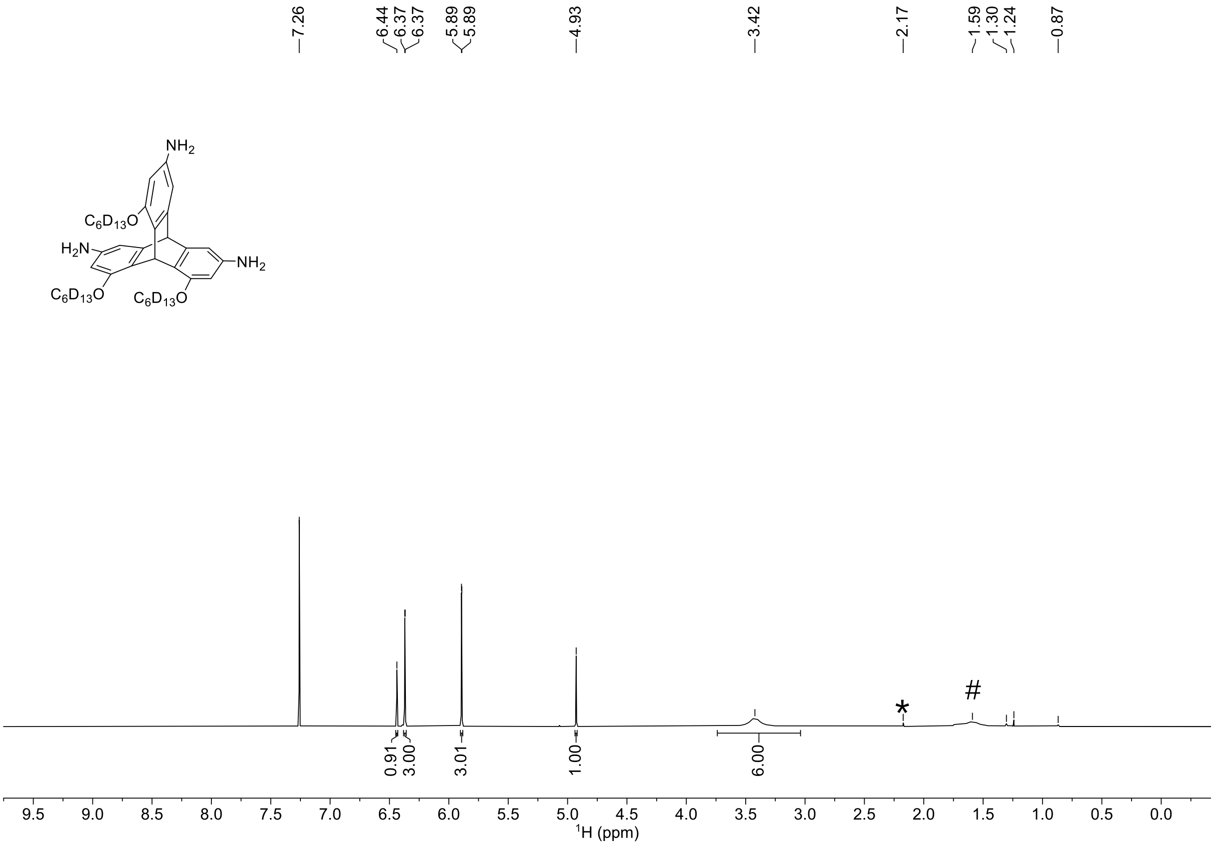


**Figure S36.** $^1$H NMR spectrum of compound **7a-d$_{39}$** (600 MHz, $CDCl_3$). #: $H_2O$. *: Acetone.

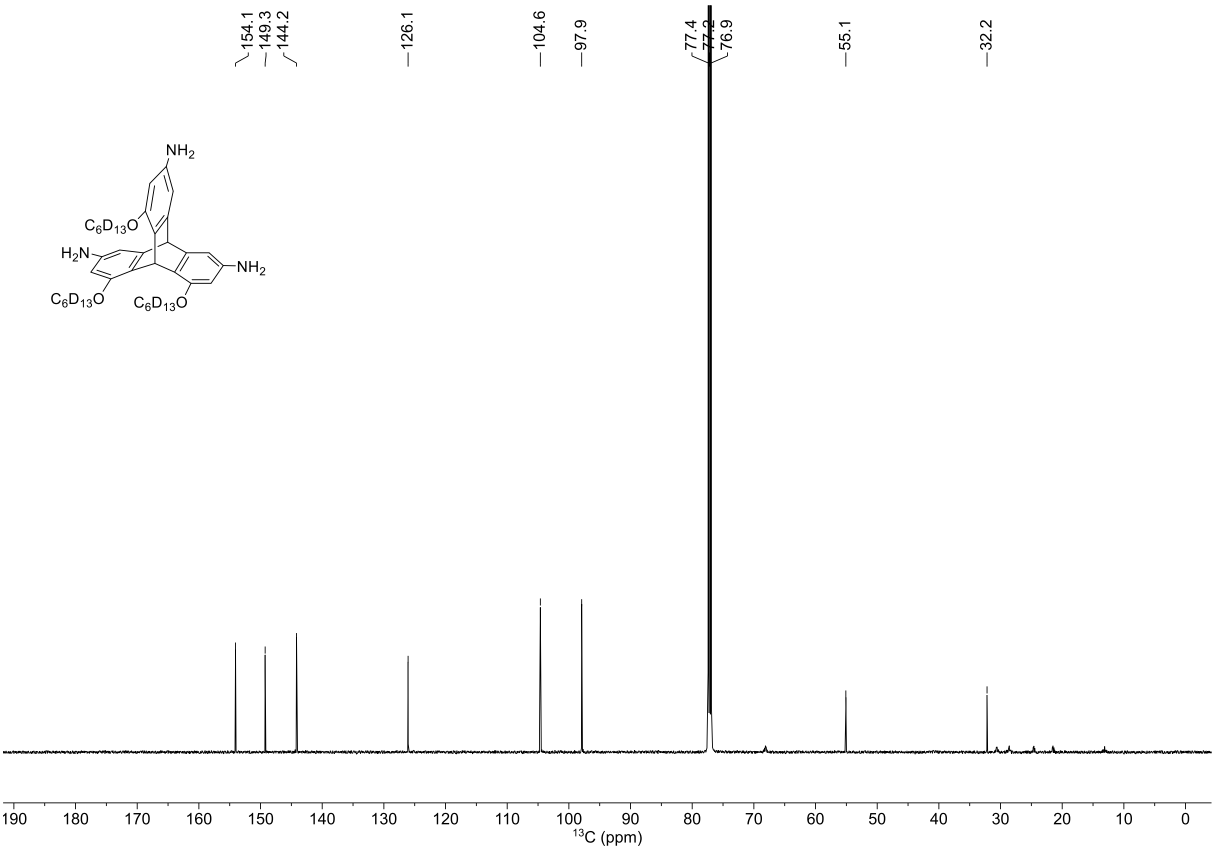


**Figure S37.** $^{13}C\{^1H\}$ NMR spectrum of compound **7a-d$_{39}$** (150 MHz, $CDCl_3$).

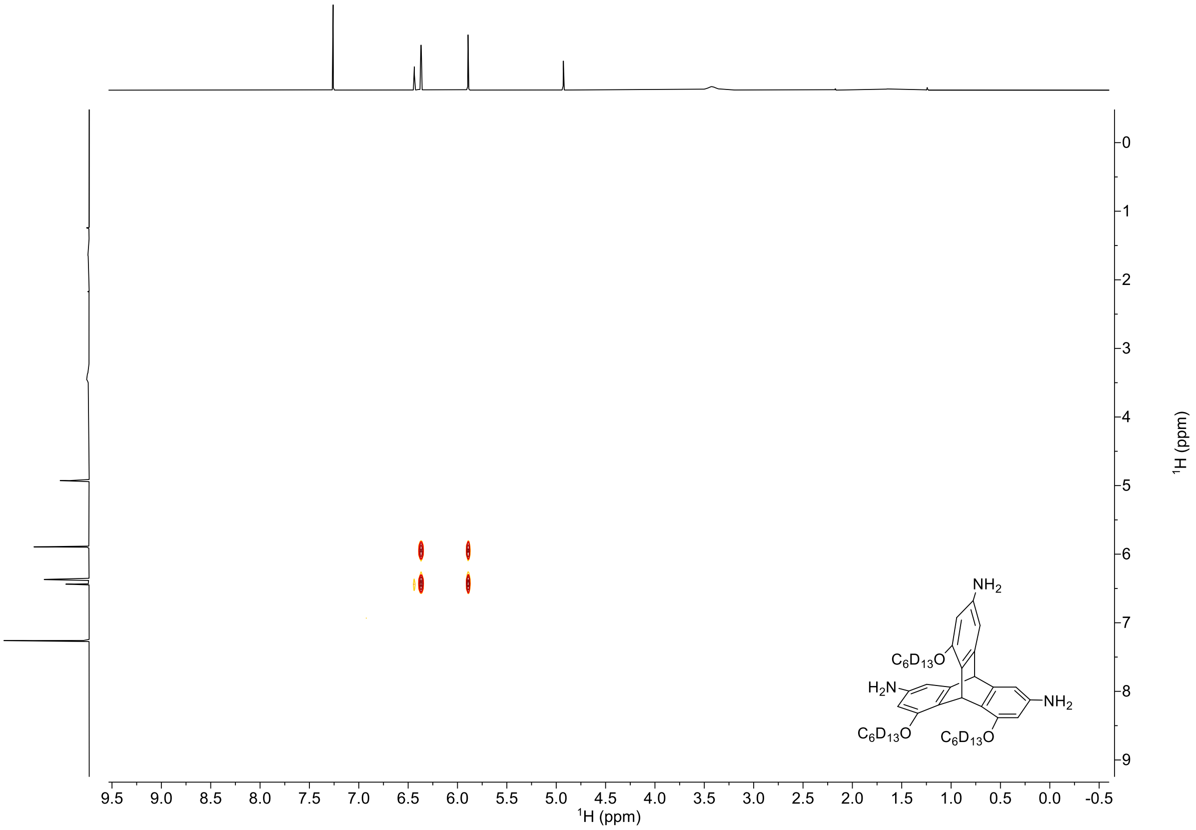


**Figure S38.** $^1$H,$^1$H-COSY spectrum of compound **7a-d$_{39}$** (600 MHz, CDCl$_3$).

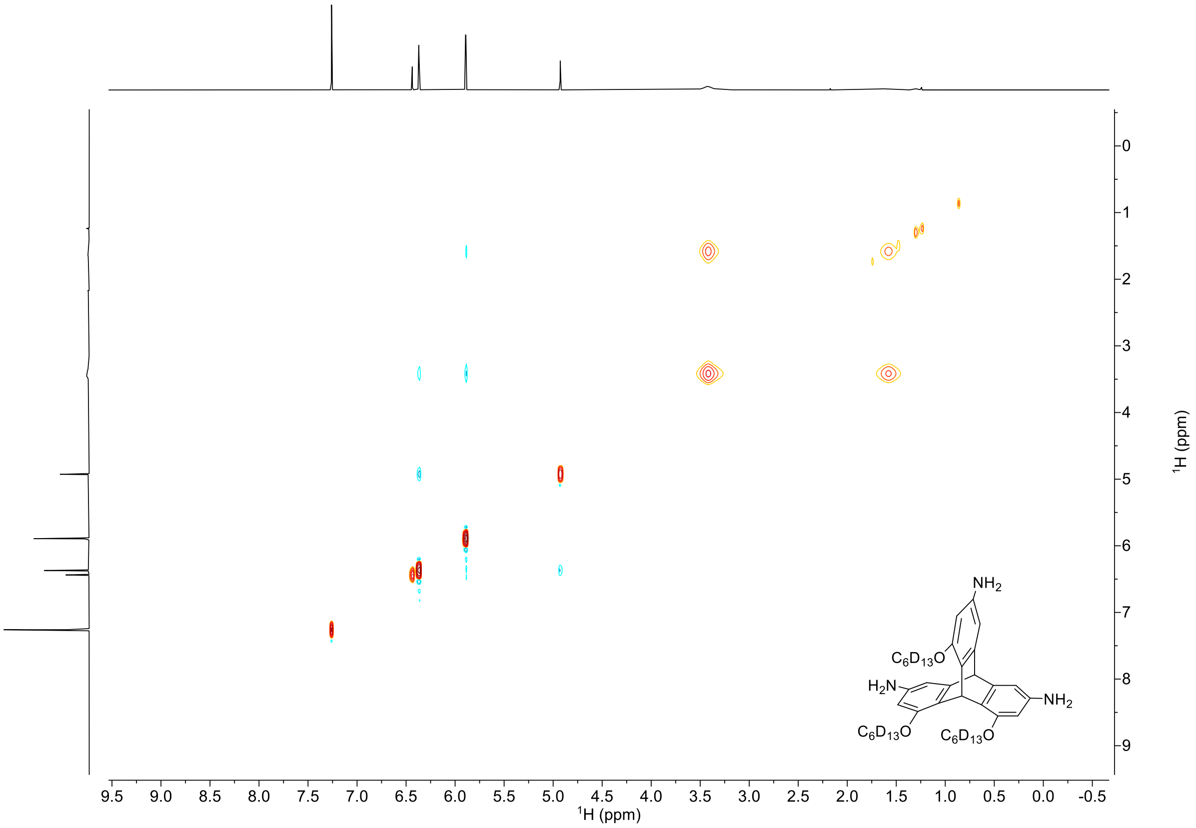


**Figure S39.** $^1$H,$^1$H-NOESY spectrum of compound **7a-d$_{39}$** (600 MHz, CDCl$_3$).

**Table S12.** Cross-peak assignment of $^1$H,$^1$H-COSY and $^1$H,$^1$H-NOESY spectrum of compound **7a-d$_{39}$**.

| $^1$H nucleus | $\delta_{1H}$ [ppm] | COSY | NOESY |
|---|---|---|---|
| *a* | 6.44 | - | - |
| *b* | 6.37 | *c* | *d, e* |
| *c* | 5.89 | *b* | *e,* $H_2O$ |
| *d* | 4.93 | - | *b* |
| *e* | 3.42 | - | $H_2O$ |

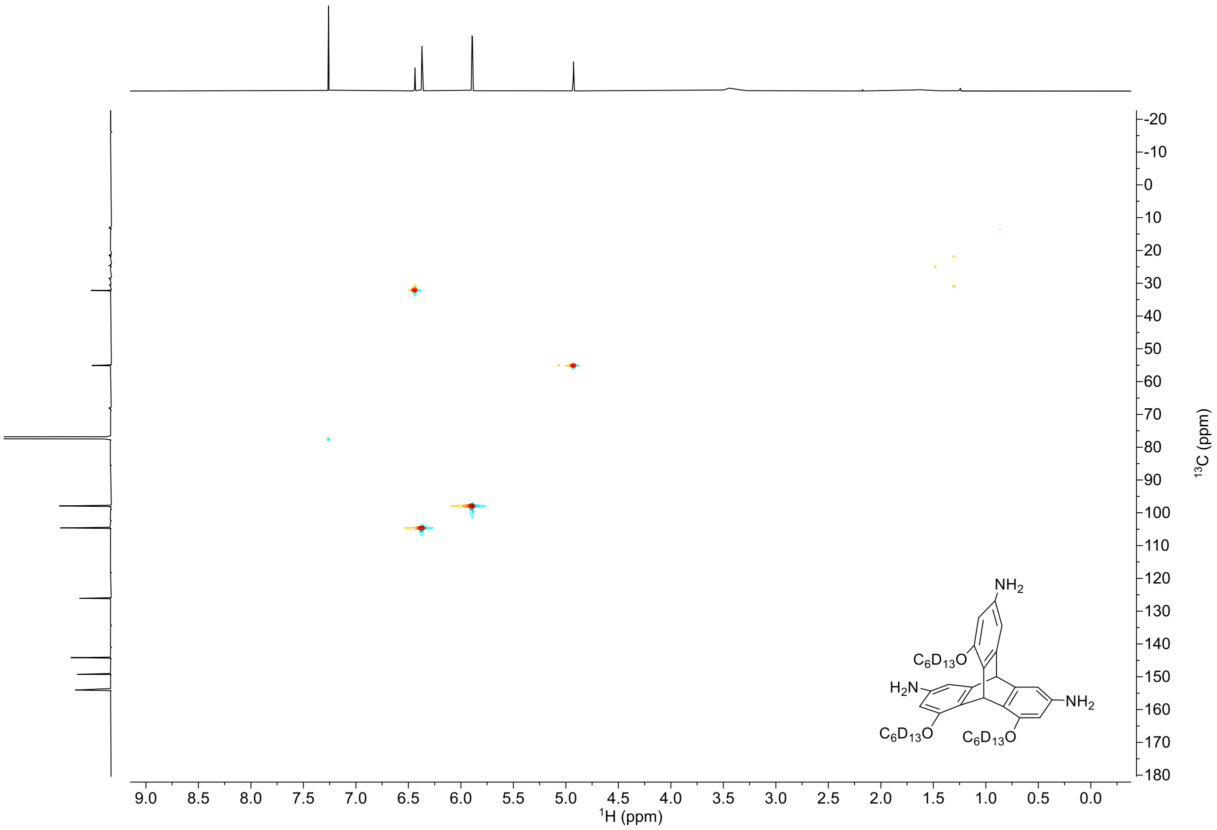


**Figure S40.** $^1$H,$^{13}$C-HSQC spectrum of compound **7a-d$_{39}$** (600 MHz, 150 MHz, CDCl$_3$).

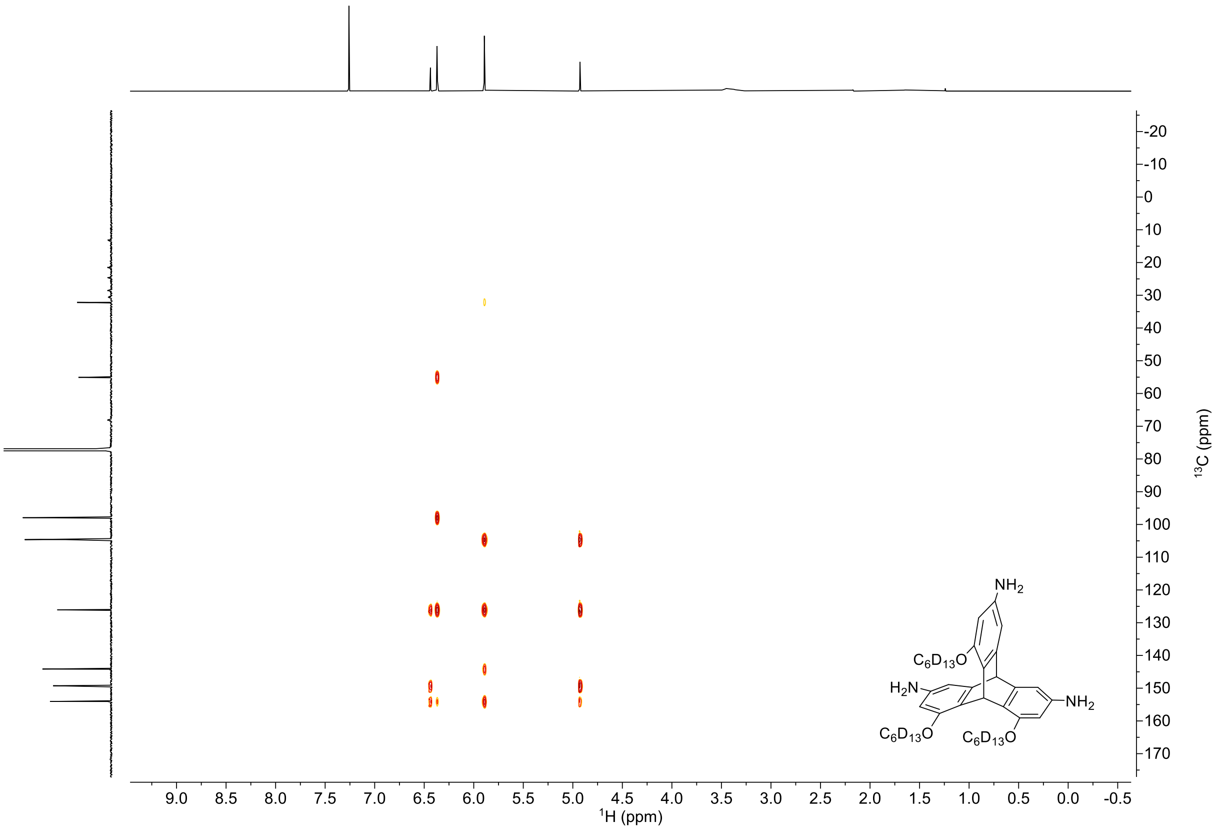


**Figure S41.** $^1$H,$^{13}$C-HMBC spectrum of compound **7a-d$_{39}$** (600 MHz, 150 MHz, CDCl$_3$).

**Table S13.** Correlations of $^{1}H,^{13}C$-HSQC and $^{1}H,^{13}C$-HMBC spectra of compound **7a-d39**.

| $^{13}C$ nucleus | $\delta_{13C}$ [ppm] | $^{1}H$ nucleus | | |
|---|---|---|---|---|
| | | HSQC | $\delta_{1H}$ [ppm] | HMBC |
| *A* | 154.1 | - | - | *a, b, c, d* |
| *B* | 149.3 | - | - | *a, d* |
| *C* | 144.2 | - | - | *c* |
| *D* | 126.1 | - | - | *a, b, c, d* |
| *E* | 104.6 | *b* | 6.37 | *c, d* |
| *F* | 97.9 | *c* | 5.89 | *b* |
| *G* | 55.1 | *d* | 4.93 | *b* |
| *H* | 32.2 | *a* | 6.44 | *c* |

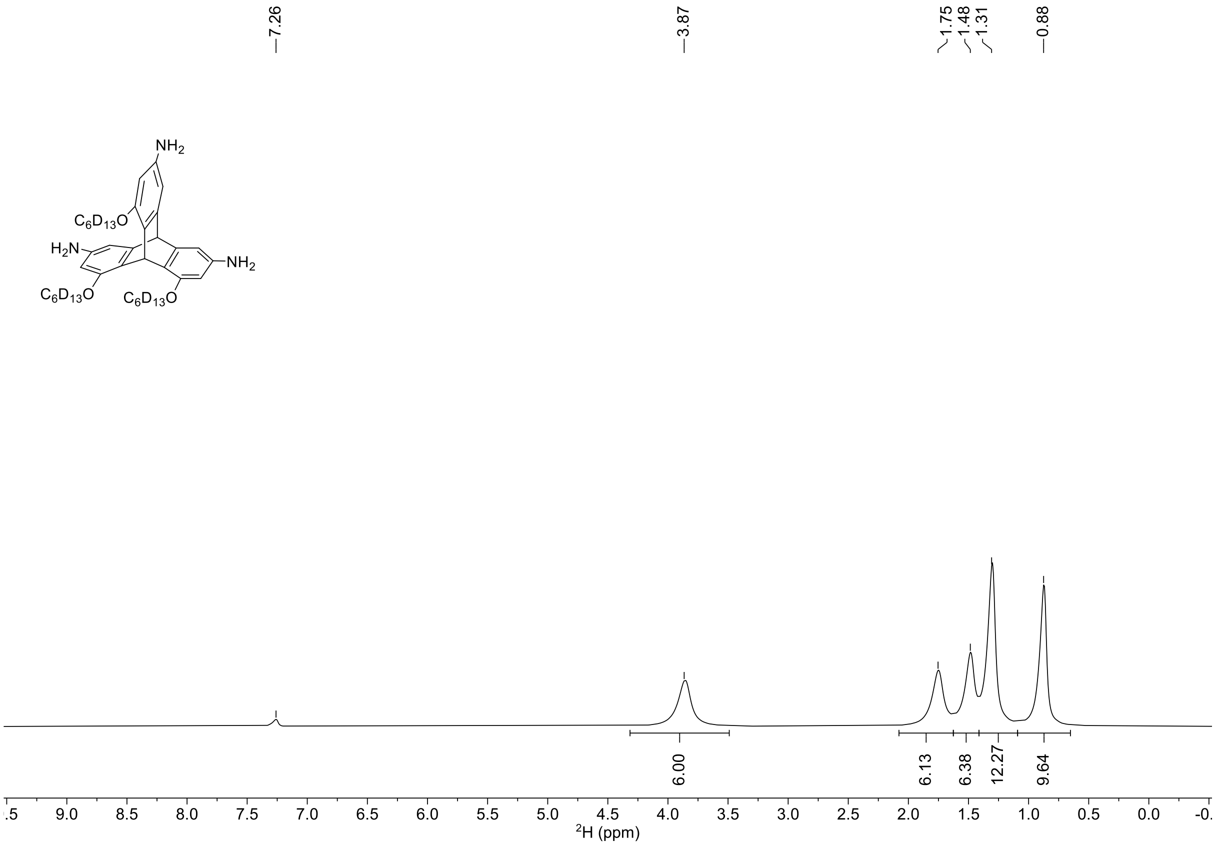


**Figure S42.** $^{2}H$ NMR spectrum of compound **7a-d39** (92 MHz, $CHCl_3$).

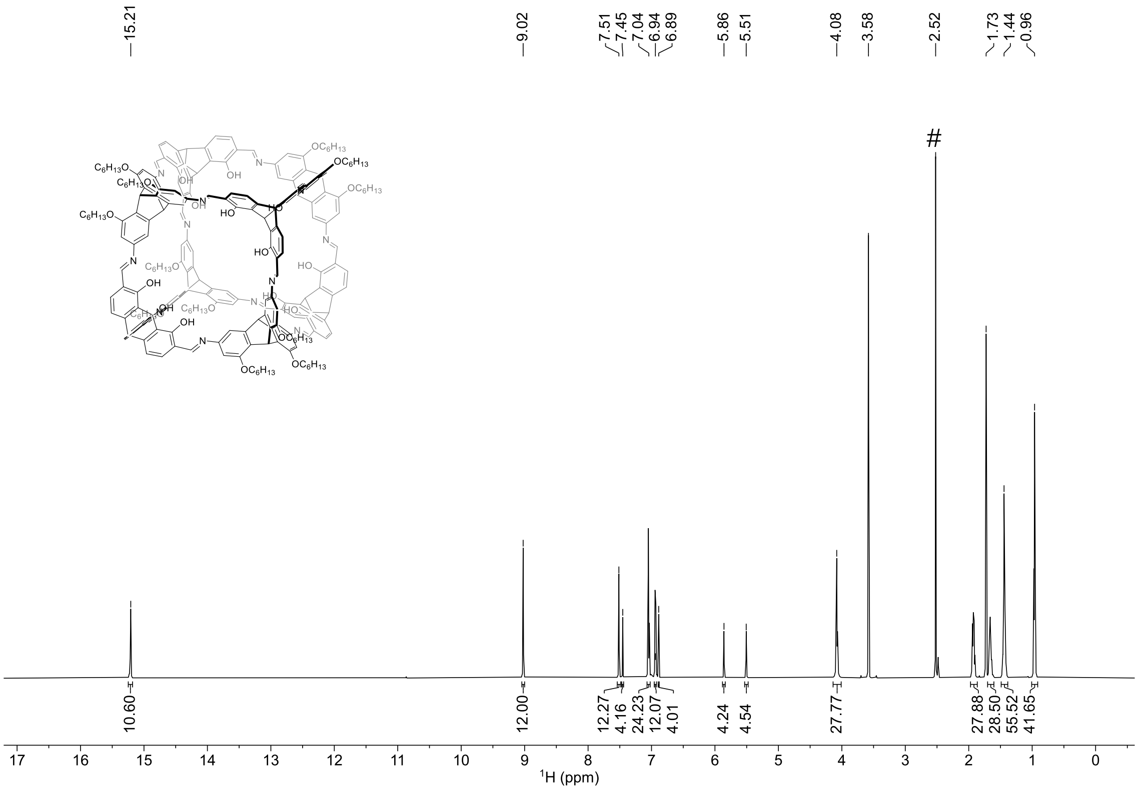


**Figure S43.** $^1H$ NMR spectrum (600 MHz, THF-$d_8$) of [4+4] cube **11**. #: $H_2O$.

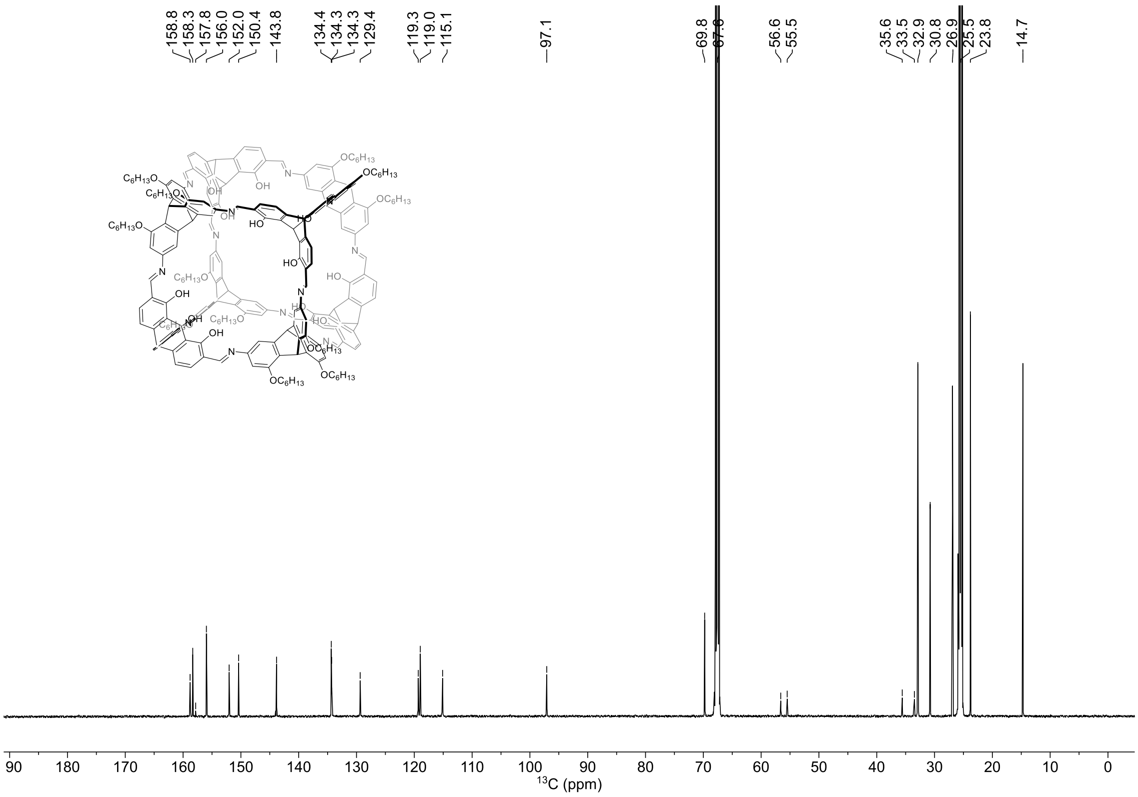


**Figure S44.** $^{13}C\{^1H\}$ NMR spectrum (150 MHz, THF-$d_8$) of [4+4] cube **11**.

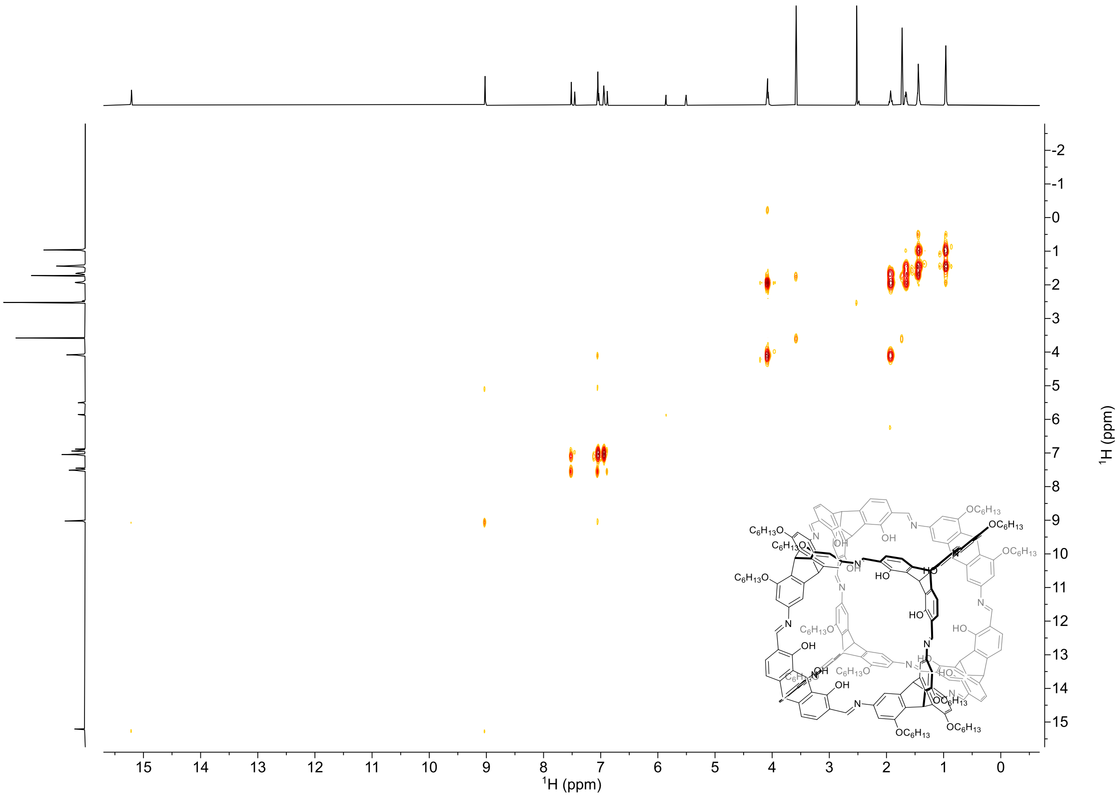


**Figure S45.** $^1$H,$^1$H COSY spectrum (600 MHz, THF-$d_8$) of [4+4] cube **11**.

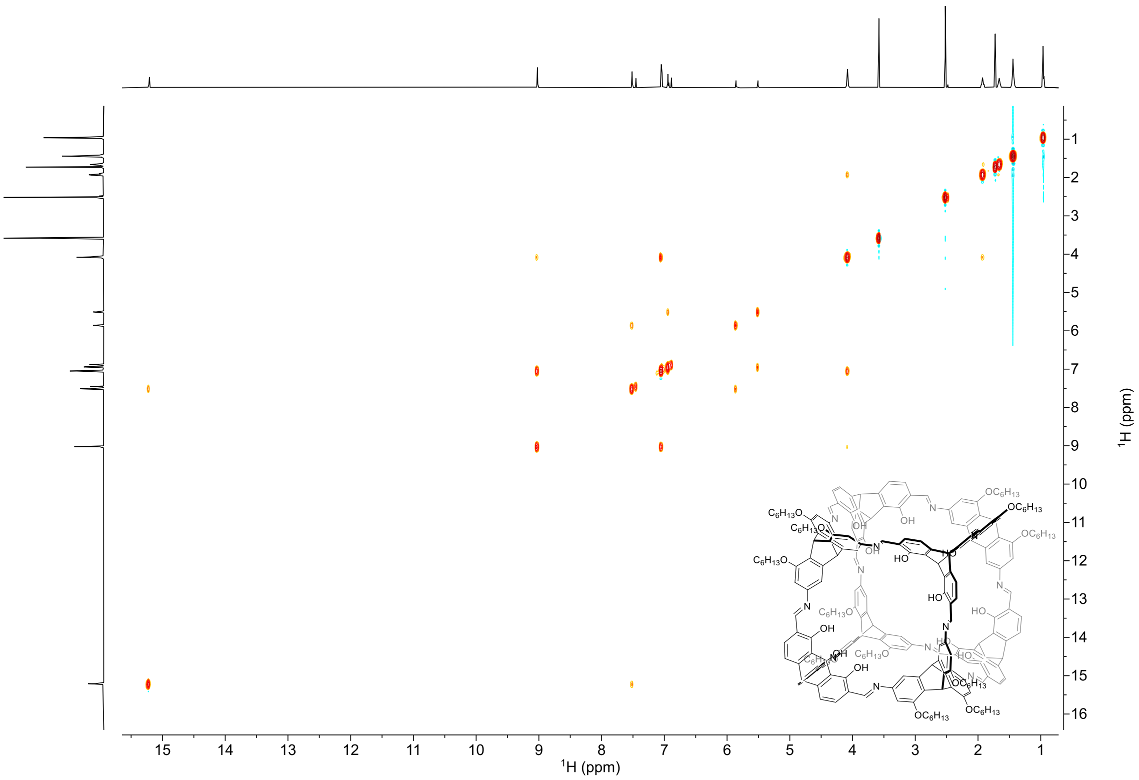


**Figure S46.** $^1$H,$^1$H NOESY spectrum (600 MHz, THF-$d_8$) of [4+4] cube **11**.

**Table S14.** Cross-peak assignment of $^1$H,$^1$H-COSY and $^1$H,$^1$H-NOESY spectra of [4+4] cube **11**.

| **$^1$H nucleus** | **$\delta_{1H}$ [ppm]** | **COSY** | **NOESY** |
|---|---|---|---|
| *a* | 15.25 – 15.18 | - | *c* |
| *b* | 9.02 | - | *e, j* |
| *c* | 7.51 | *e* | *a, h* |
| *d* | 7.45 | - | - |
| *e* | 7.07 – 7.02 | *c* | *b, j* |
| *f* | 6.94 | - | *i* |
| *g* | 6.89 | - | - |
| *h* | 5.86 | - | *c* |
| *i* | 5.51 | - | *f* |
| *j* | 4.08 | *k* | *b, e, k* |
| *k* | 1.97 – 1.87 | *j, l* | *j, l* |
| *l* | 1.70 – 1.60 | *k, m* | - |
| *m* | 1.49 – 1.38 | *l, n* | - |
| *n* | 1.01 – 0.91 | *m* | - |

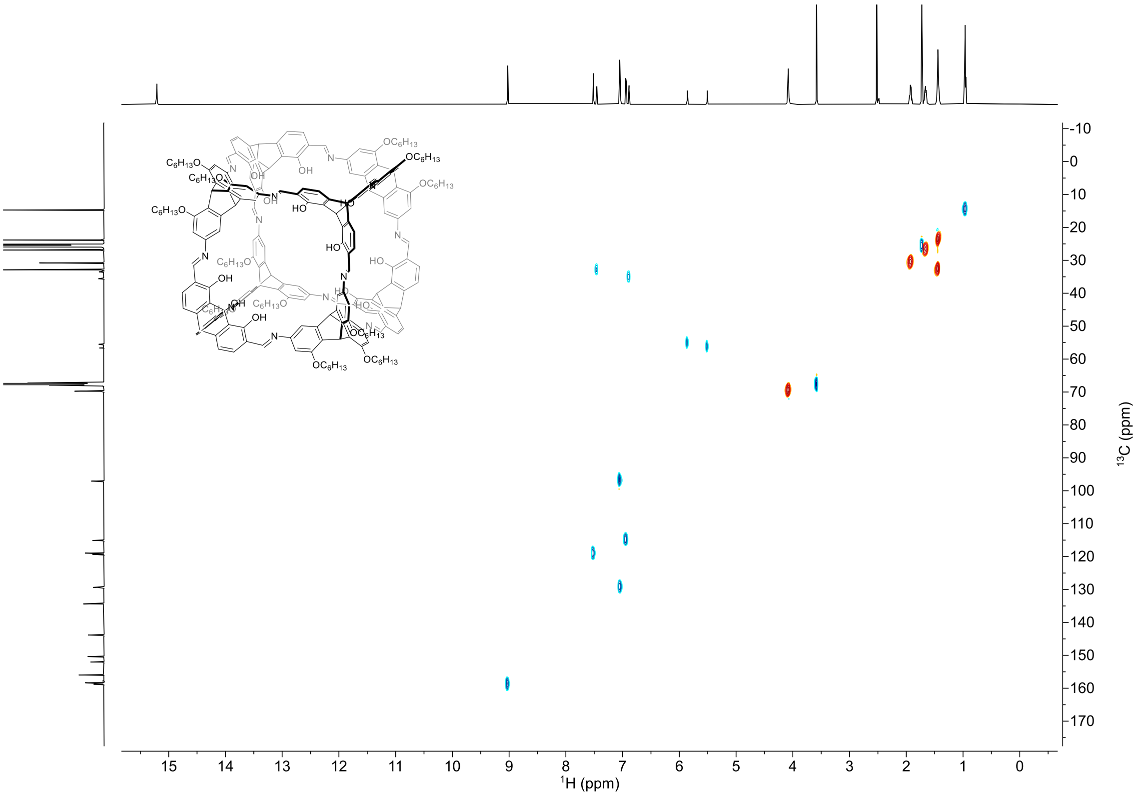


**Figure S47.** $^1H,^{13}C$ HSQC spectrum (600 MHz, 150 MHz, THF-$d_8$) of [4+4] cube **11**.

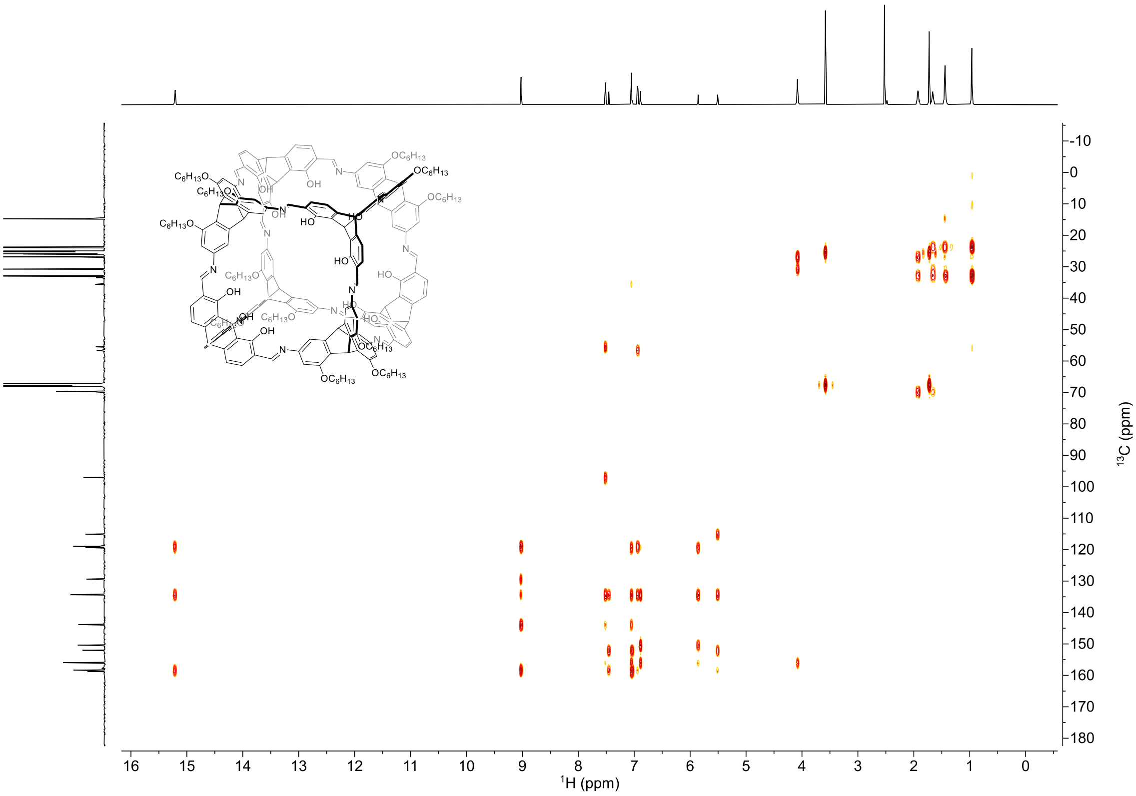


**Figure S48.** $^1H,^{13}C$ HMBC spectrum (600 MHz, 150 MHz, THF-$d_8$) of [4+4] cube **11**.

**Table S15.** Correlations of $^1$H,$^{13}$C-HSQC and $^1$H,$^{13}$C-HMBC spectra of [4+4] cube **11**.

| **$^{13}$C nucleus** | **$\delta_{13C}$ [ppm]** | **$^1$H nucleus** | | |
|---|---|---|---|---|
| | | **HSQC** | **$\delta_{1H}$ [ppm]** | **HMBC** |
| *A* | 158.8 | *b* | 9.02 | *e* |
| *B* | 158.3 | - | - | *a, b, d, e* |
| *C* | 157.8 | - | - | - |
| *D* | 156.0 | - | - | *c, e, g, h, j* |
| *E* | 152.0 | - | - | *d, e, i* |
| *F* | 150.4 | - | - | *g, h* |
| *G* | 143.8 | - | - | *b, c, e* |
| *H* | 134.4 | - | - | *a, b, c, d, e, f, g, h, i* |
| *I* | 134.3 | - | - | *a, b, c, d, e, f, g, h, i* |
| *J* | 134.3 | - | - | *a, b, c, d, e, f, g, h, i* |
| *K* | 129.4 | *e* | 7.07 – 7.02 | *b* |
| *L* | 119.3 | *c* | 7.51 | *e, h* |
| *M* | 119.0 | - | - | *a, b, f* |
| *O* | 115.1 | *f* | 6.94 | *i* |
| *P* | 97.1 | *e* | 7.07 – 7.02 | *c* |
| *Q* | 69.8 | *j* | 4.08 | *k* |
| *R* | 56.6 | *i* | 5.51 | *f* |
| *S* | 55.5 | *h* | 5.86 | *c* |
| *T* | 35.6 | *g* | 6.89 | *e* |
| *U* | 33.5 | *d* | 7.45 | - |
| *V* | 32.9 | *m* | 1.49 – 1.38 | *k, l, m, n* |
| *W* | 30.8 | *k* | 1.97 – 1.87 | *j* |
| *X* | 26.9 | *l* | 1.70 – 1.60 | *j, k* |
| *Y* | 23.8 | *m* | 1.49 – 1.38 | *l, m, n* |
| *Z* | 14.7 | *n* | 1.01 – 0.91 | *m* |

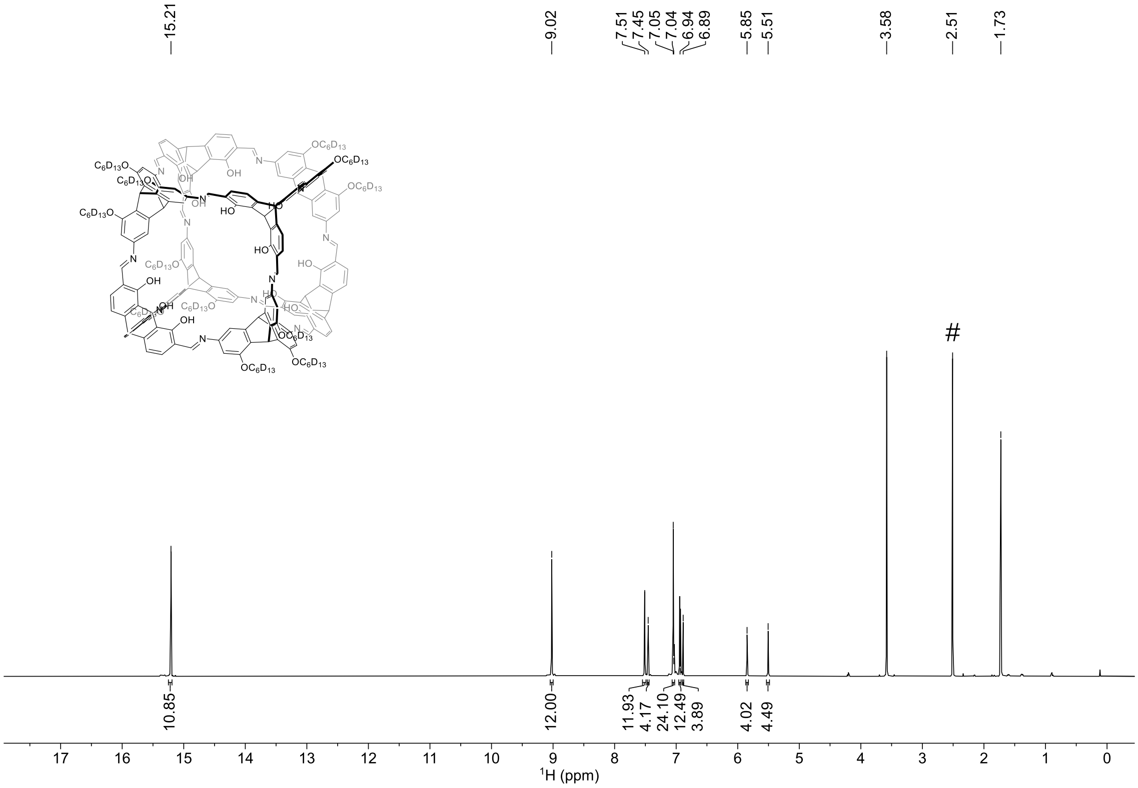


**Figure S49.** $^1$H NMR spectrum (600 MHz, THF-$d_8$) of [4+4] cube **11-d156**. #: $H_2O$.

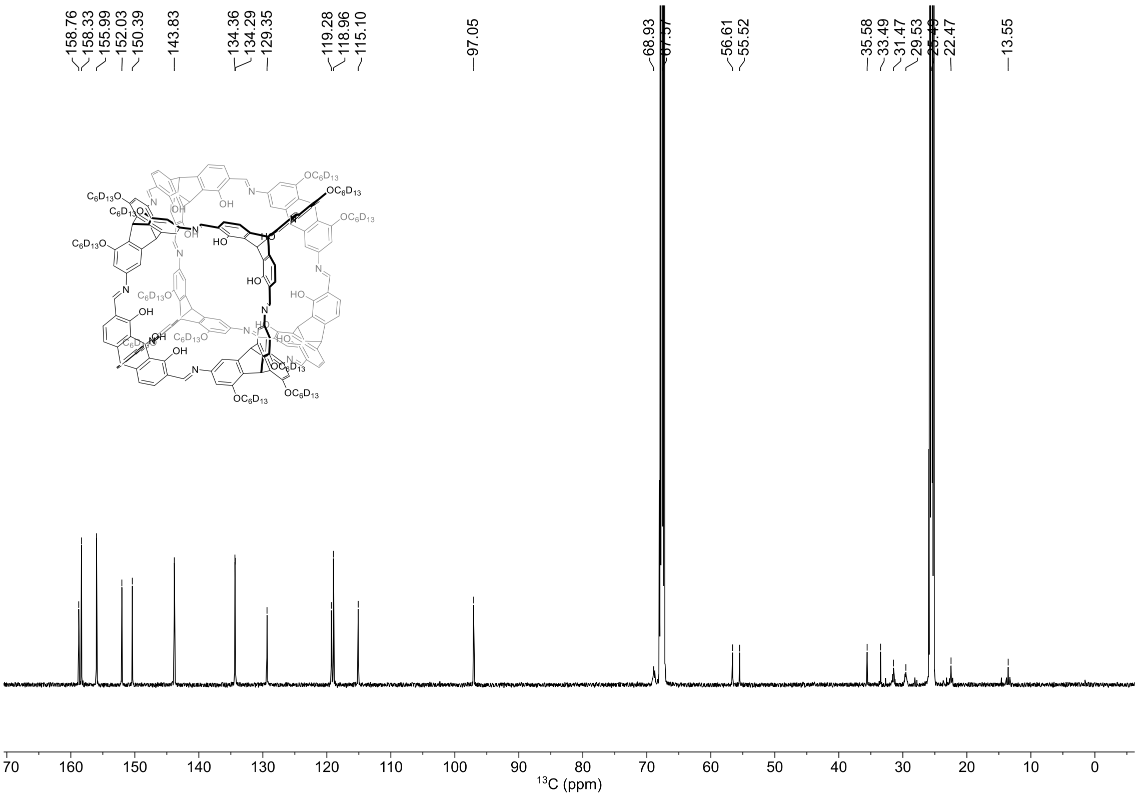


**Figure S50.** $^{13}$C{$^1$H} NMR spectrum (150 MHz, THF-$d_8$) of [4+4] cube **11-d156**.

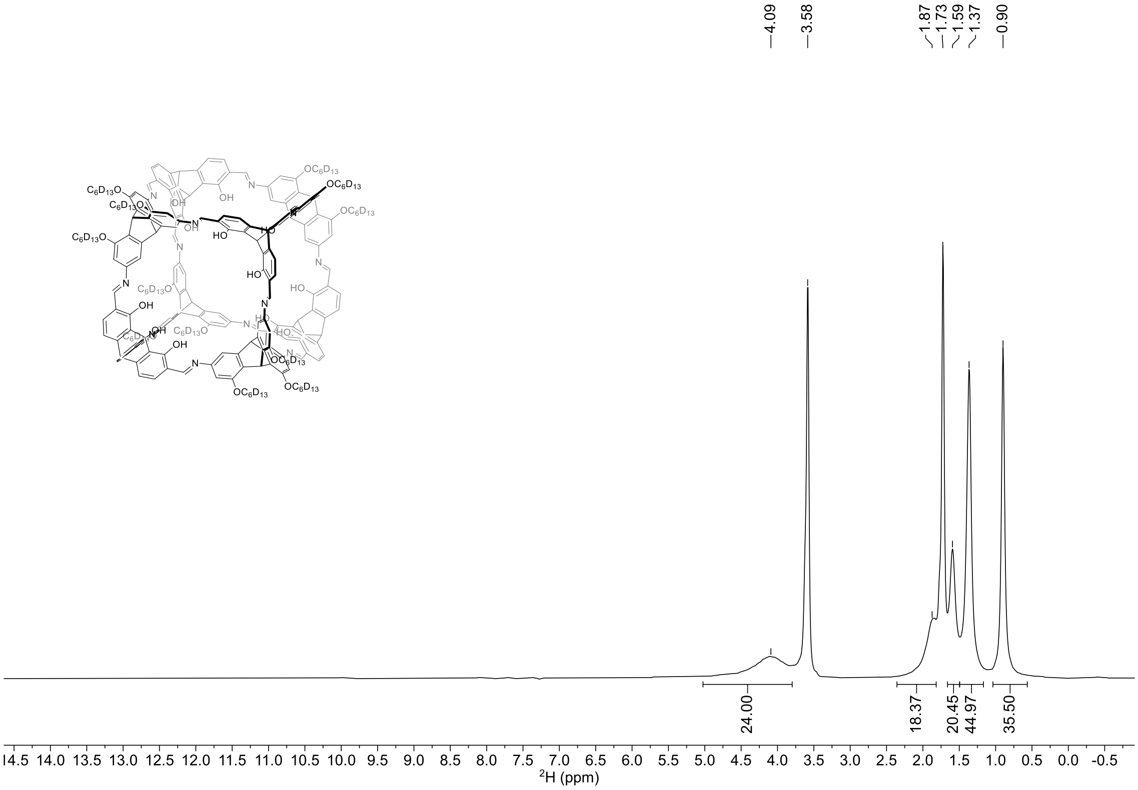


**Figure S51.** $^2$H NMR spectrum (92 MHz, THF/THF-$d_8$) of [4+4] cube **11-d$_{156}$**.

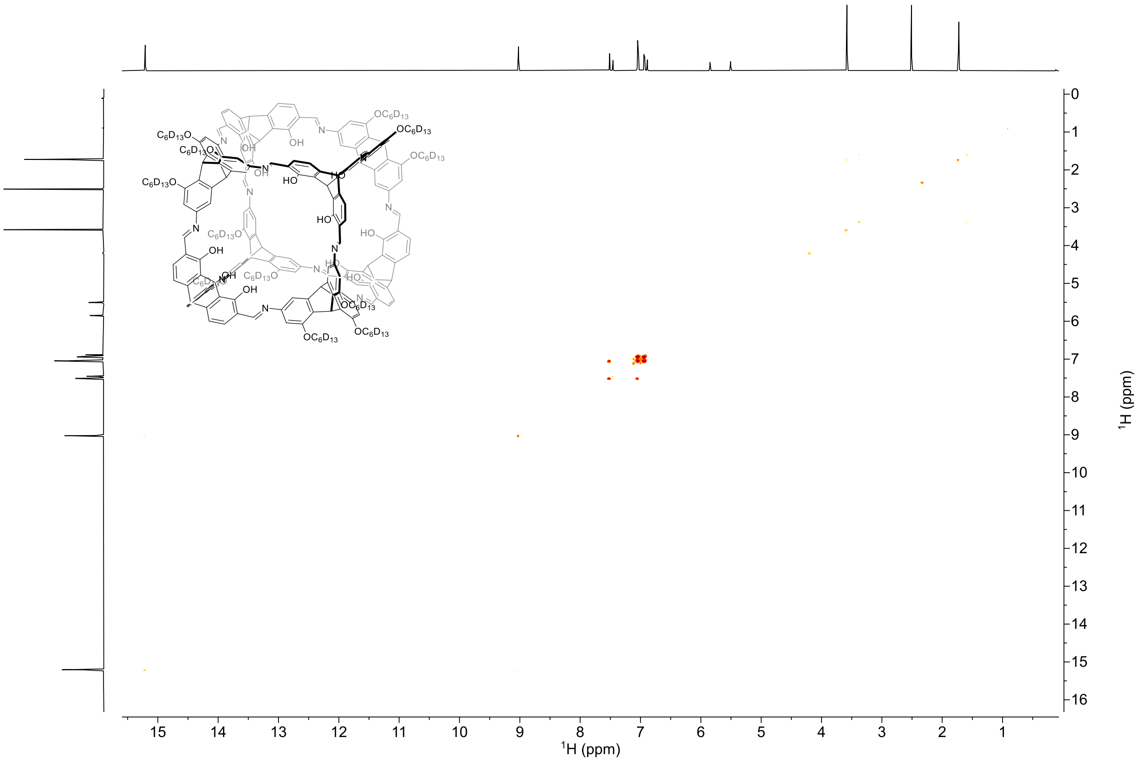


**Figure S52.** $^1$H,$^1$H COSY spectrum (600 MHz, THF-$d_8$) of [4+4] cube **11-d$_{156}$**.

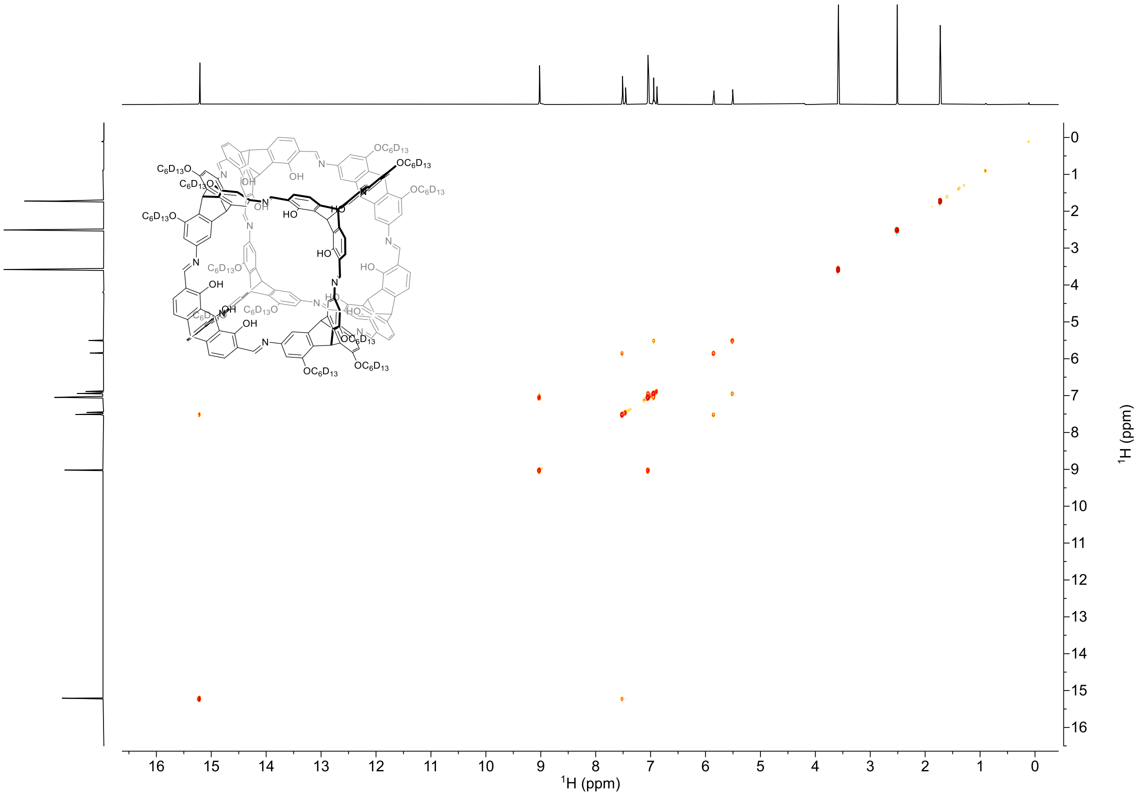


**Figure S53.** $^1$H,$^1$H NOESY spectrum (600 MHz, THF-$d_8$) of [4+4] cube **11-d$_{156}$**.

**Table S16.** Cross-peak assignment of $^1$H,$^1$H-COSY and $^1$H,$^1$H-NOESY spectra of [4+4] cube **11-d$_{156}$**.

| $^1$H nucleus | $\delta_{1H}$ [ppm] | COSY | NOESY |
|---|---|---|---|
| *a* | 15.21 | - | *c* |
| *b* | 9.02 | - | *f* |
| *c* | 7.51 | *e* | *h* |
| *d* | 7.45 | - | - |
| *e* | 7.07 – 7.02 | *c, f* | *b, f* |
| *f* | 6.94 | *e* | *e, i* |
| *g* | 6.89 | - | - |
| *h* | 5.85 | - | *c* |
| *i* | 5.51 | - | *f* |

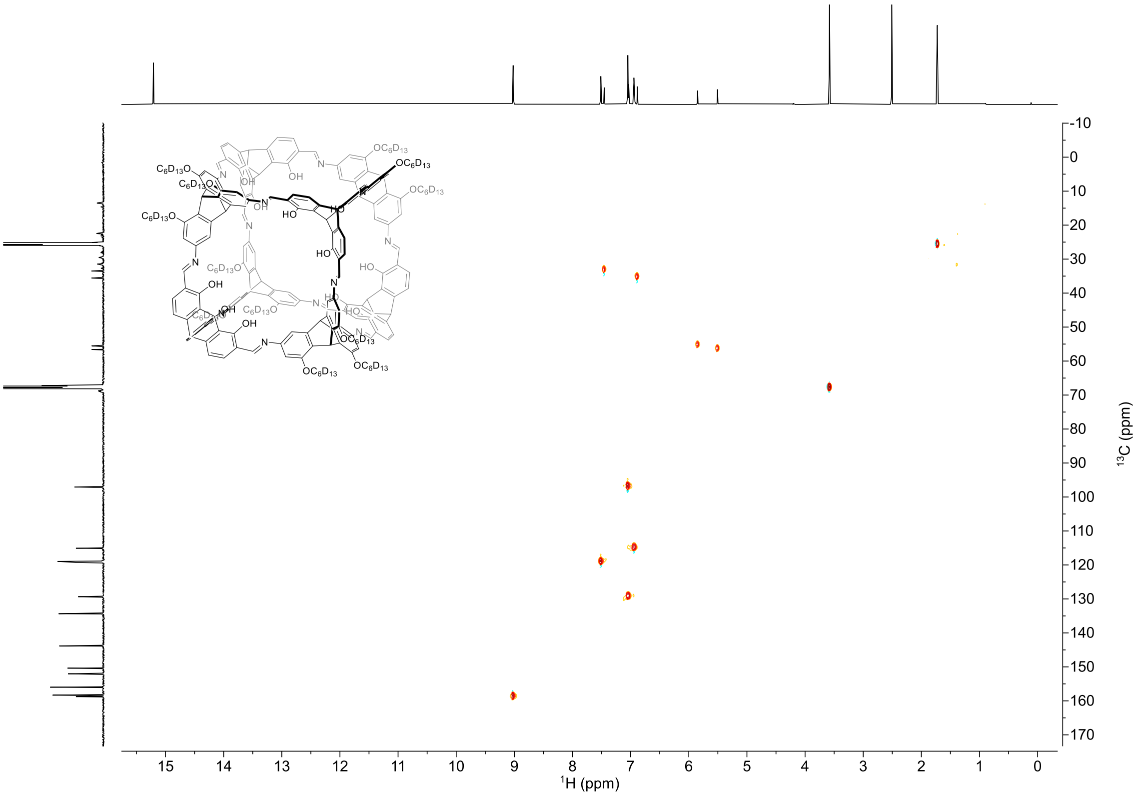


**Figure S54.** $^{1}$H,$^{13}$C HSQC spectrum (600 MHz, 150 MHz, THF-$d_8$) of [4+4] cube **11-d$_{156}$**.

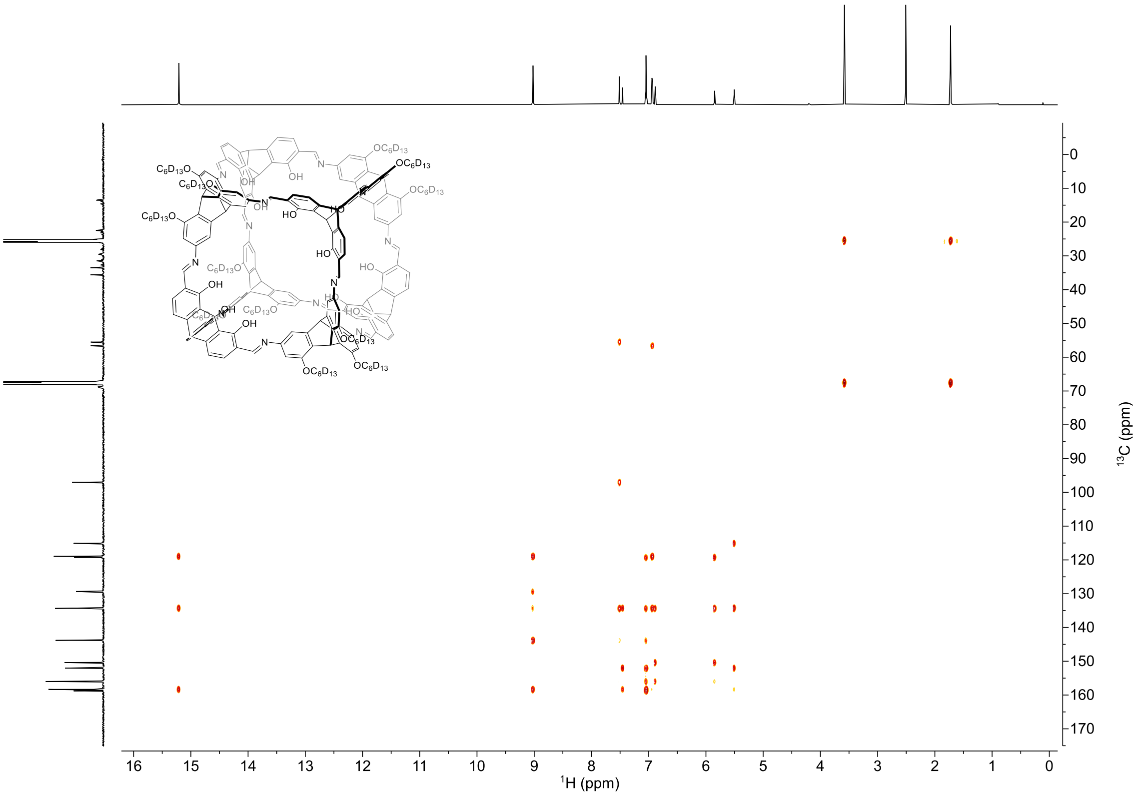


**Figure S55.** $^{1}$H,$^{13}$C HMBC spectrum (600 MHz, 150 MHz, THF-$d_8$) of [4+4] cube **11-d$_{156}$**.

**Table S17.** Correlations of $^{1}$H,$^{13}$C-HSQC and $^{1}$H,$^{13}$C-HMBC spectra of [4+4] cube **11-d$_{156}$**.

| **$^{13}$C nucleus** | **$\delta_{13C}$ [ppm]** | **$^{1}$H nucleus** | | |
|---|---|---|---|---|
| | | **HSQC** | **$\delta_{1H}$ [ppm]** | **HMBC** |
| *A* | 158.8 | *b* | 9.02 | *a, b, d, e* |
| *B* | 158.3 | - | - | *a, b, d, e, i* |
| *C* | 156.0 | - | - | *e, g, h* |
| *D* | 152.0 | - | - | *d, e, i* |
| *E* | 150.4 | - | - | *g, h* |
| *F* | 143.8 | - | - | *b, c, e* |
| *G* | 134.4 | - | - | *a, b, c, d, e, f, g, h, i* |
| *H* | 134.3 | - | - | *a, b, c, d, e, f, g, h, i* |
| *I* | 129.3 | *e* | 7.07 – 7.02 | *b* |
| *J* | 119.3 | - | - | *e, h* |
| *K* | 119.0 | *c* | 7.51 | *a, b, f* |
| *L* | 115.1 | *f* | 6.94 | *i* |
| *M* | 97.1 | *e* | 7.07 – 7.02 | *c* |
| *O* | 69.3 – 68.5 | - | - | - |
| *P* | 56.6 | *i* | 5.51 | *f* |
| *Q* | 55.5 | *h* | 5.85 | *c* |
| *R* | 35.6 | *g* | 6.89 | - |
| *S* | 33.5 | *d* | 7.45 | - |
| *T* | 32.1 – 31.1 | - | - | - |
| *U* | 30 0 – 29.0 | - | - | - |
| *V* | 22.9 – 22.2 | - | - | - |
| *W* | 14.0 – 13.1 | - | - | - |

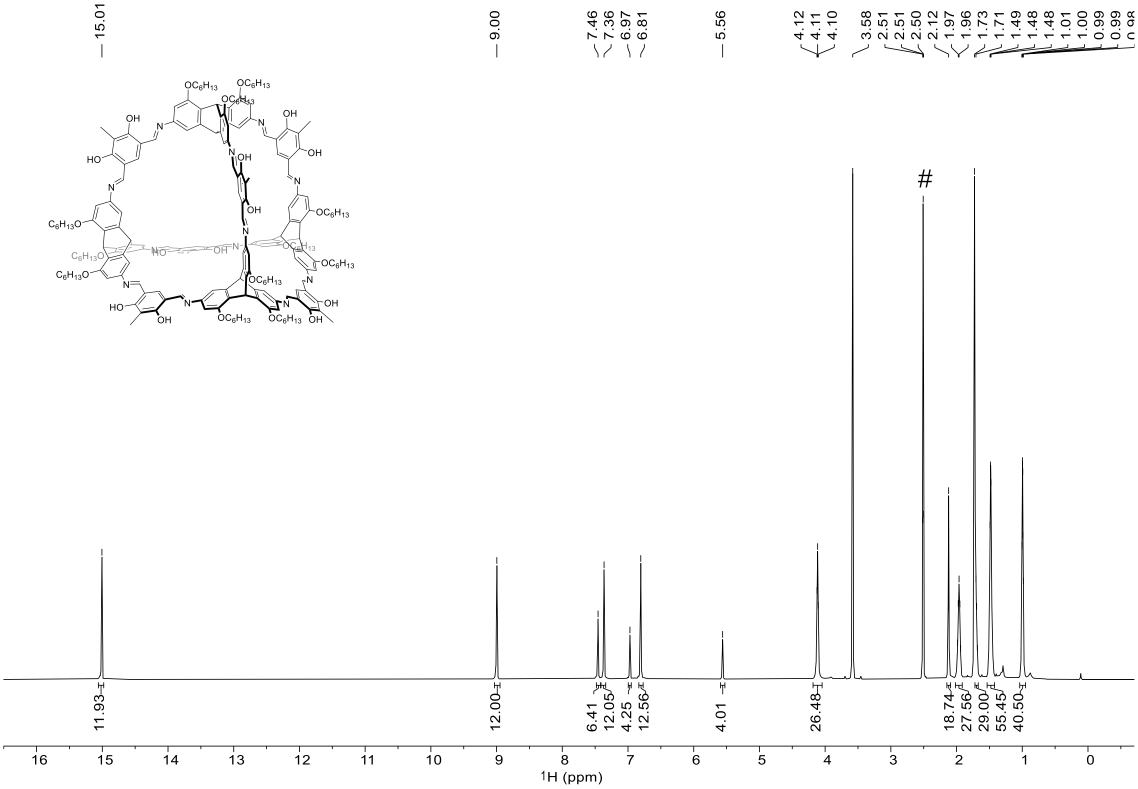


**Figure S56.** $^1$H NMR spectrum (600 MHz, THF-d$_8$) of [4+6]-*exo* cage **12**. #: $H_2O$.

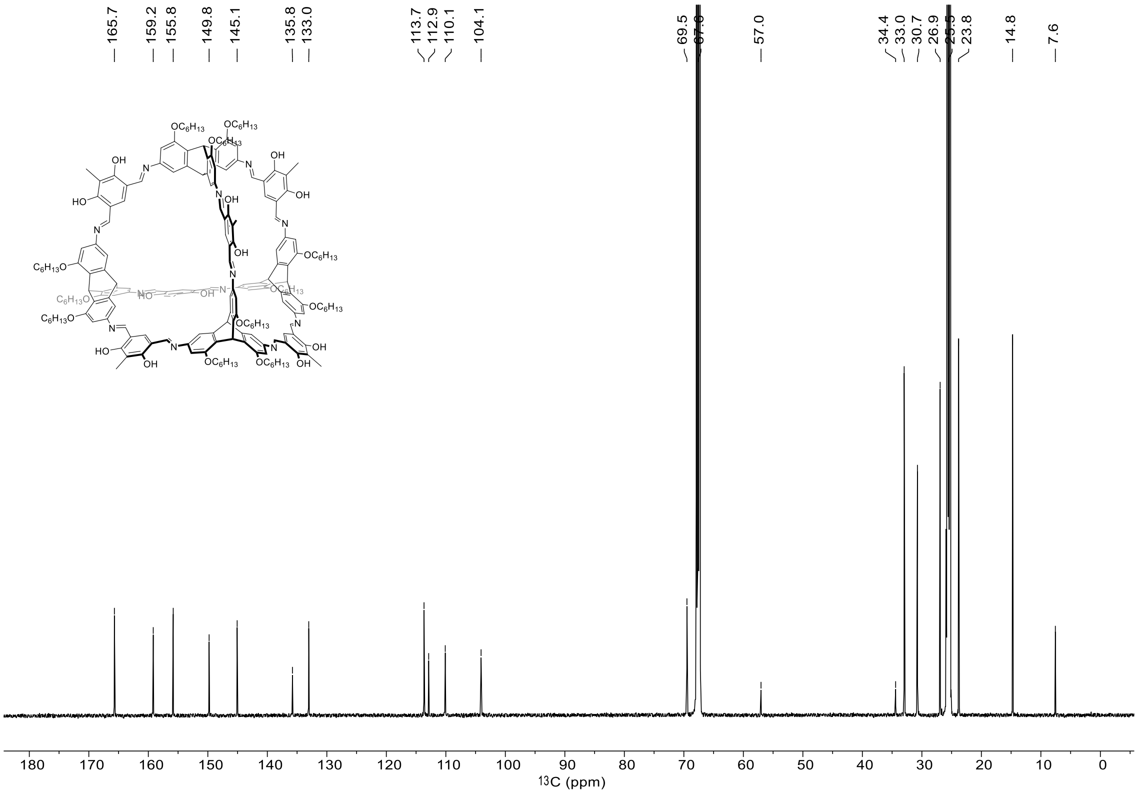


**Figure S57.** $^{13}$C{$^1$H} NMR spectrum (150 MHz, THF-d$_8$) of [4+6]-*exo* cage **12**.

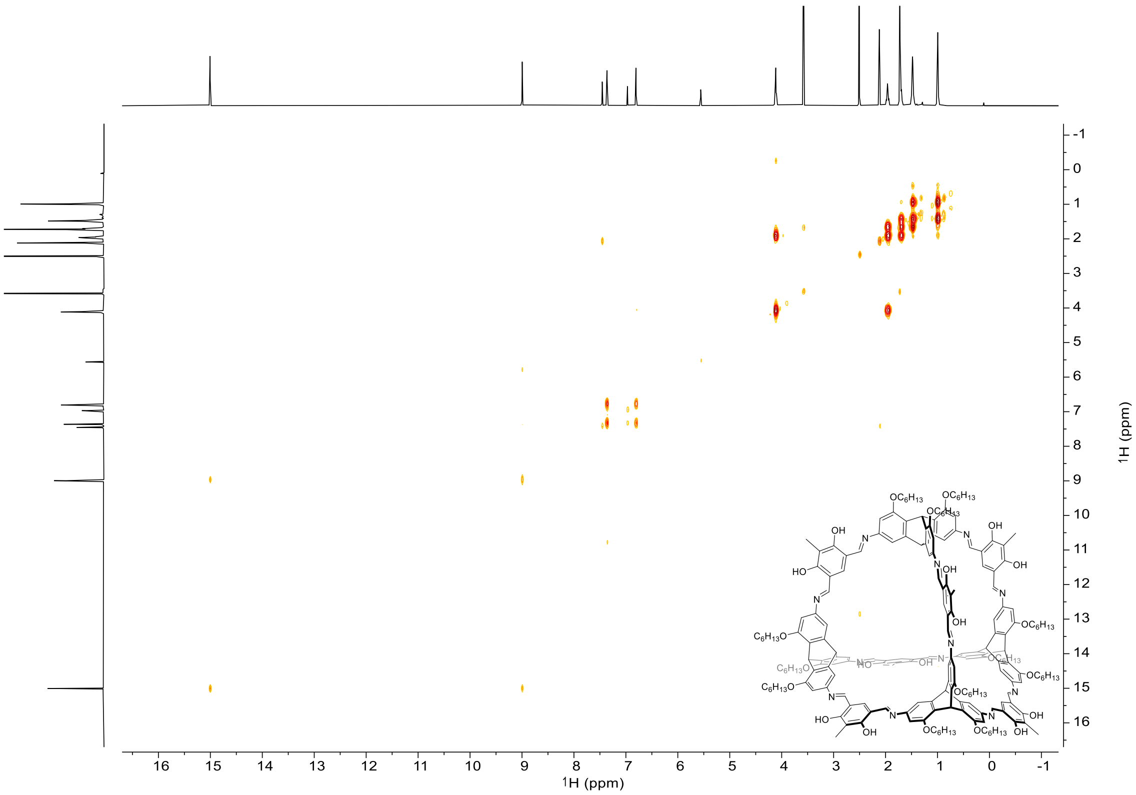


**Figure S58.** $^1$H,$^1$H COSY spectrum (600 MHz, THF-d$_8$) of [4+6]-*exo* cage **12**.

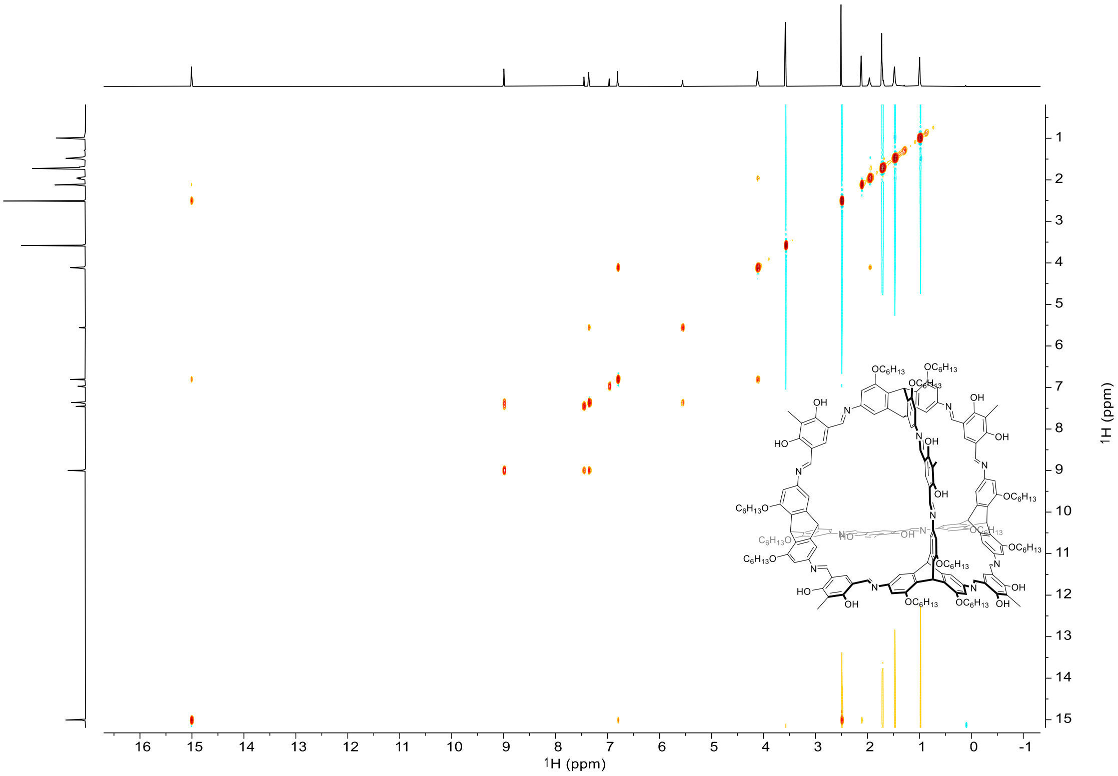


**Figure S59.** $^1$H,$^1$H NOESY spectrum (600 MHz, THF-d$_8$) of [4+6]-*exo* cage **12**.

**Table S18.** Cross-peak assignment of $^1H,^1H$-COSY and $^1H,^1H$-NOESY spectra of [4+6]-*exo* cage **12**.

| $^1H$ nucleus | $\delta_{1H}$ [ppm] | COSY | NOESY |
|---|---|---|---|
| *a* | 15.01 | *b* | *f, i,* $H_2O$ |
| *b* | 9.00 | *a* | *c, d* |
| *c* | 7.46 | - | *b* |
| *d* | 7.36 | *f* | *b, g* |
| *e* | 6.97 | - | - |
| *f* | 6.81 | *d* | *h* |
| *g* | 5.56 | - | *d* |
| *h* | 4.11 | *j* | *f, j* |
| *i* | 2.12 | - | *a* |
| *j* | 2.01 – 1.92 | *h, k* | *h* |
| *k* | 1.76 – 1.67 | *j, l* | - |
| *l* | 1.52 – 1.43 | *k, m* | - |
| *m* | 1.00 | *l* | - |

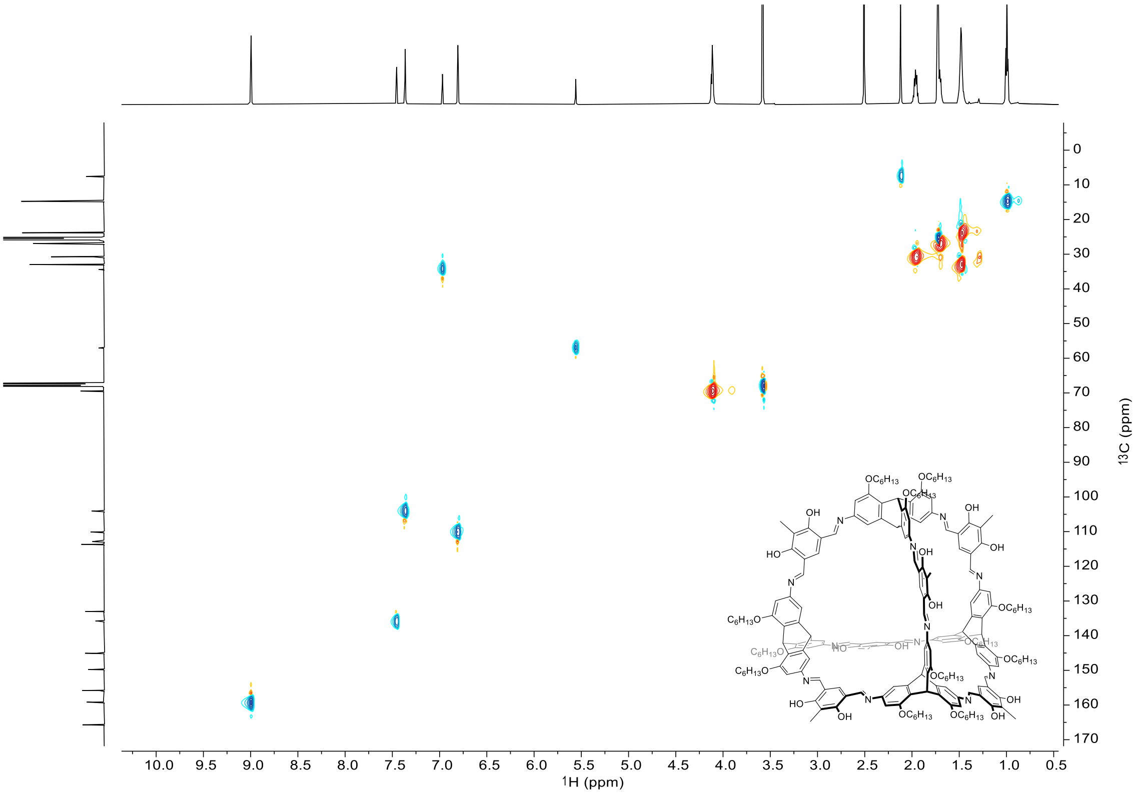


**Figure S60.** $^1$H,$^{13}$C HSQC spectrum (600 MHz, 150 MHz, THF-d$_8$) of [4+6]-exo cage **12**.

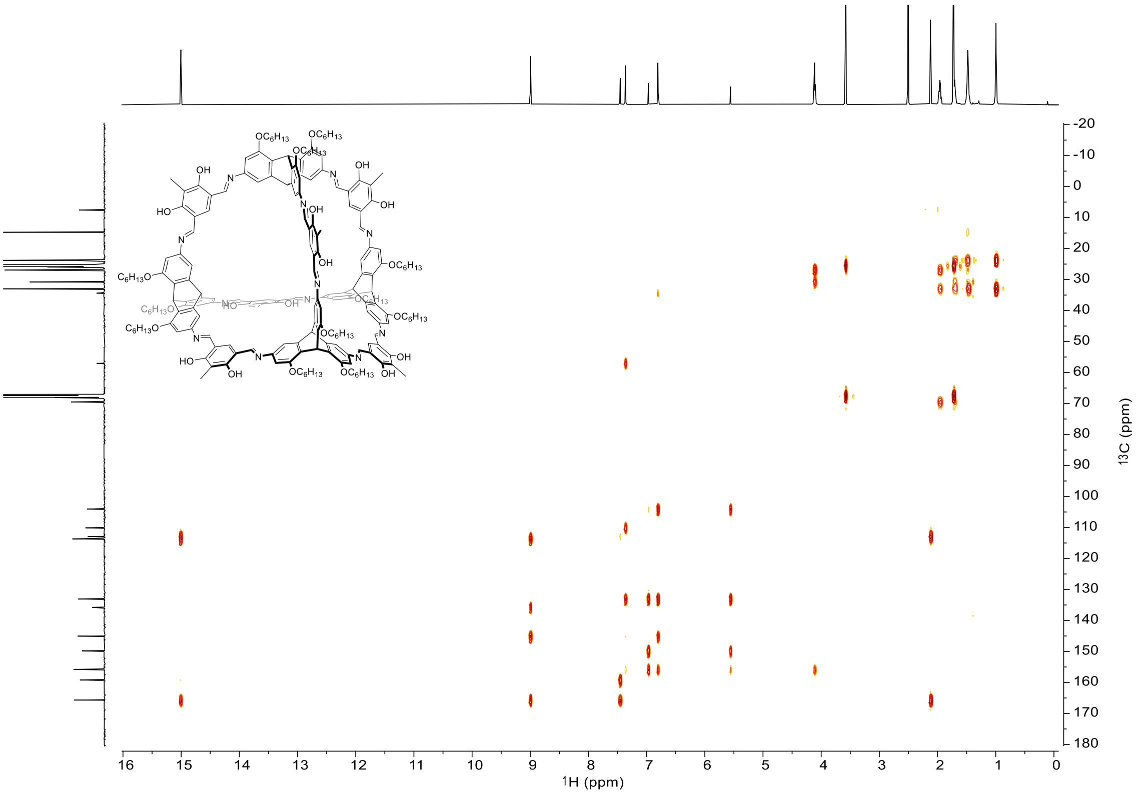


**Figure S61.** $^1$H,$^{13}$C HMBC spectrum (600 MHz, 150 MHz, THF-d$_8$) of [4+6]-exo cage **12**.

**Table S19.** Correlations of $^{1}$H,$^{13}$C-HSQC and $^{1}$H,$^{13}$C-HMBC spectra of [4+6]-*exo* cage **12**.

| **$^{13}$C nucleus** | **$\delta_{13C}$ [ppm]** | **$^{1}$H nucleus** | | |
|---|---|---|---|---|
| | | **HSQC** | **$\delta_{1H}$ [ppm]** | **HMBC** |
| *A* | 165.7 | - | - | *a, b, c, i* |
| *B* | 159.2 | *b* | 9.00 | *c* |
| *C* | 155.8 | - | - | *e, f, h* |
| *D* | 149.8 | - | - | *e, g* |
| *E* | 145.1 | - | - | *b, f* |
| *F* | 135.8 | *c* | 7.46 | *b* |
| *G* | 133.0 | - | - | *d, e, f, g* |
| *H* | 113.7 | - | - | *a, b, i* |
| *I* | 112.9 | - | - | *a, b, i* |
| *J* | 110.1 | *f* | 6.81 | *d* |
| *K* | 104.1 | *d* | 7.36 | *f, g* |
| *L* | 69.5 | *h* | 4.11 | *j* |
| *M* | 57.0 | *g* | 5.51 | *d* |
| *O* | 34.4 | *e* | 6.97 | - |
| *P* | 33.0 | *l* | 1.52 – 1.43 | *j, k, l, m* |
| *Q* | 30.7 | *j* | 2.01 – 1.92 | *h* |
| *R* | 26.9 | *k* | 1.76 – 1.67 | *h, j* |
| *S* | 23.8 | *l* | 1.52 – 1.43 | *k, l, m* |
| *T* | 14.8 | *m* | 1.00 | *l* |
| *U* | 7.6 | *i* | 2.12 | - |

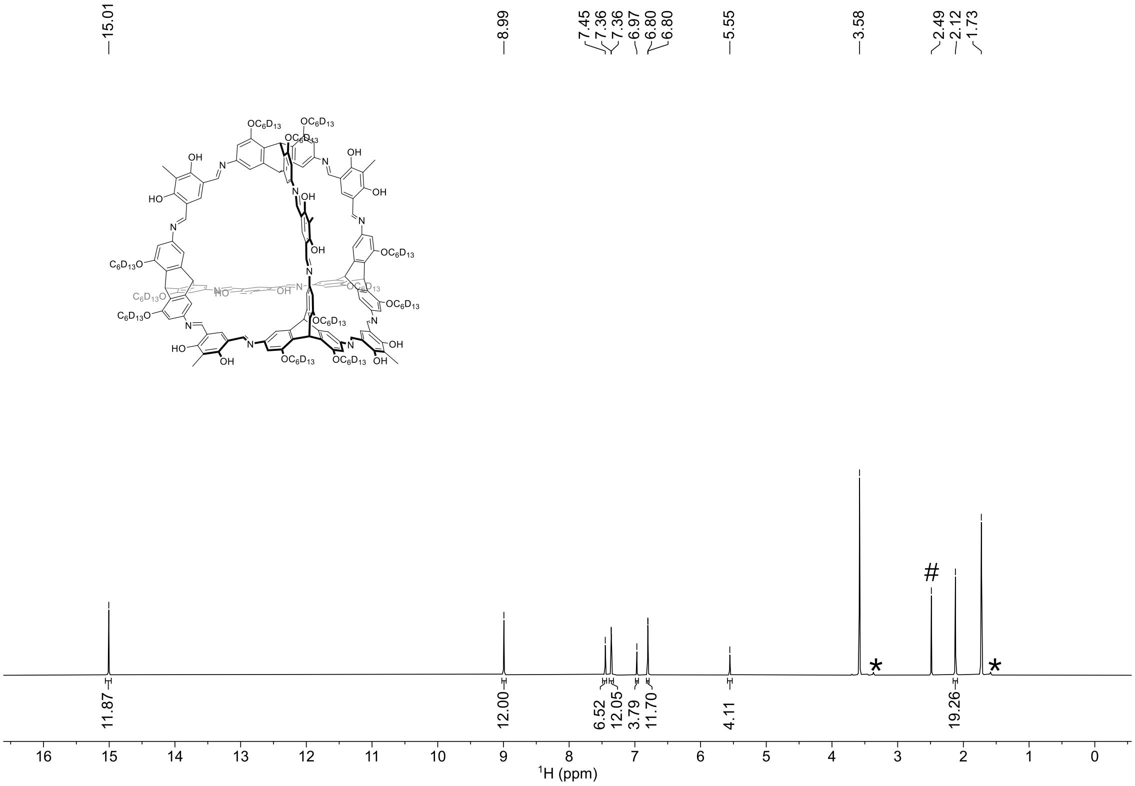


**Figure S62.** $^1$H NMR spectrum (600 MHz, THF-$d_8$) of [4+6]-*exo* cage **12-$d_{156}$**. #: $H_2O$, *: THF.

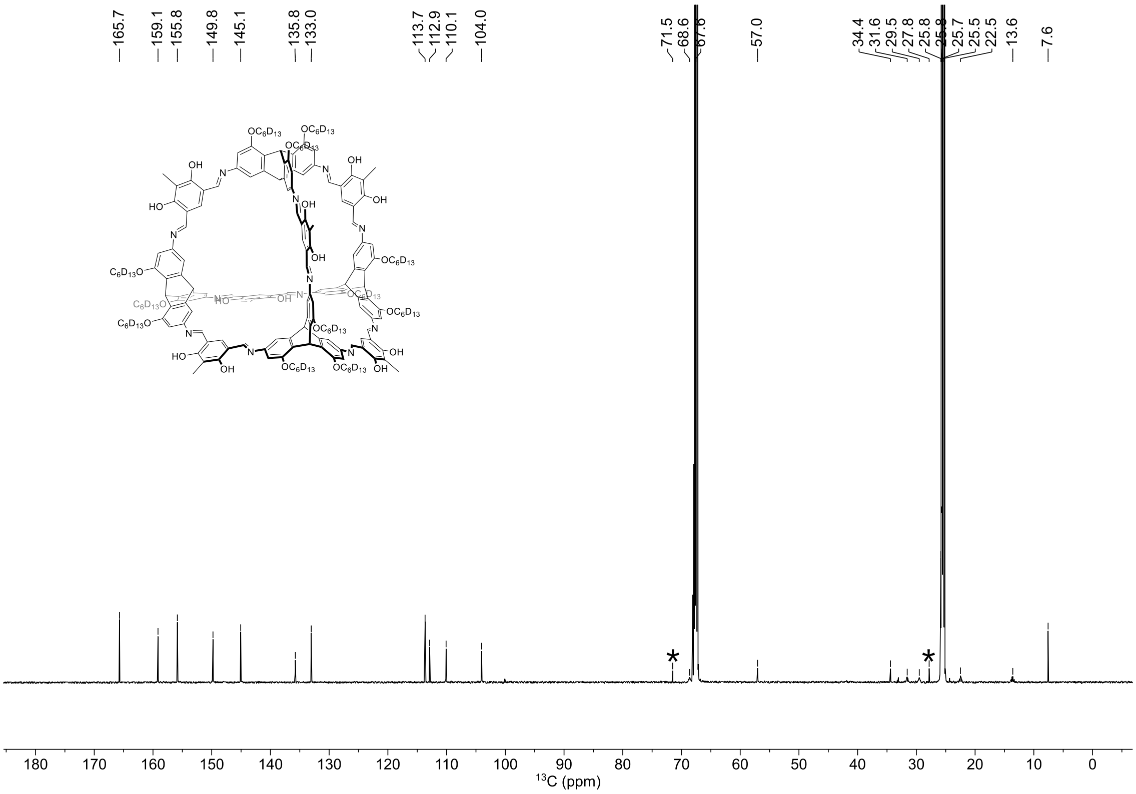


**Figure S63.** $^{13}$C{$^1$H} NMR spectrum (150 MHz, THF-$d_8$) of [4+6]-*exo* cage **12-$d_{156}$**. *: THF.

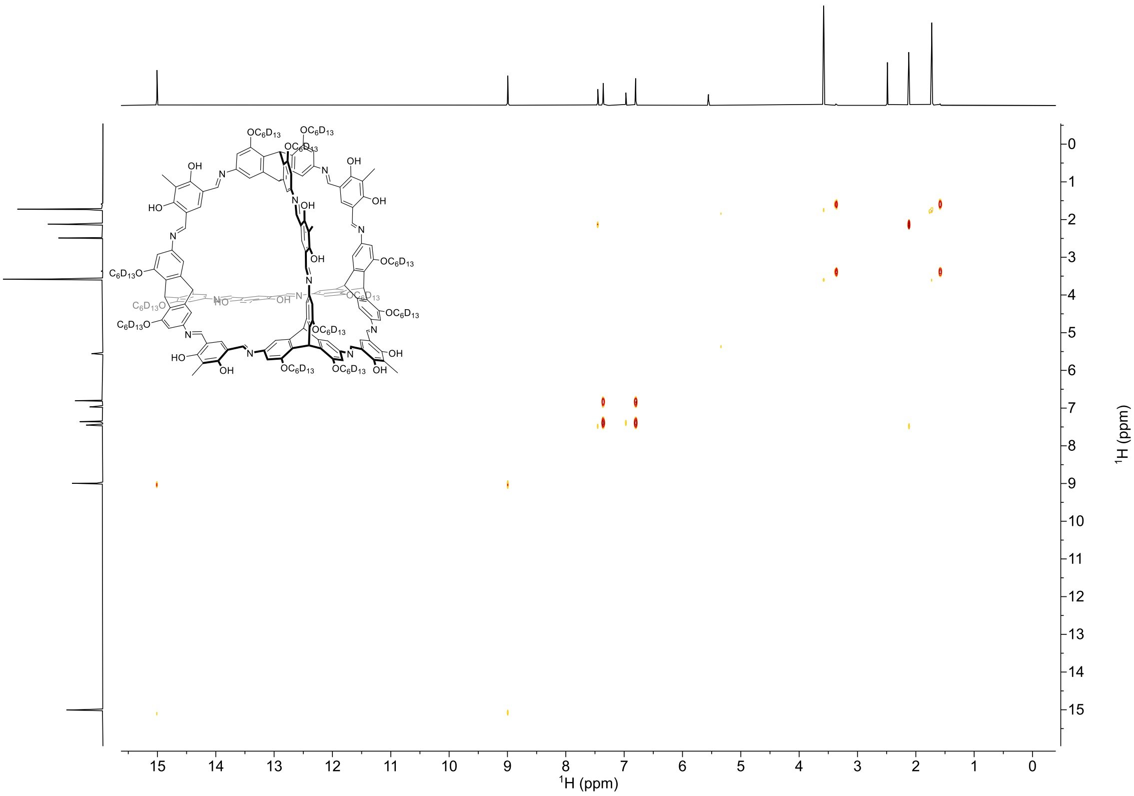


**Figure S64.** $^1$H,$^1$H COSY spectrum (600 MHz, THF-$d_8$) of [4+6]-*exo* cage **12-d$_{156}$**.

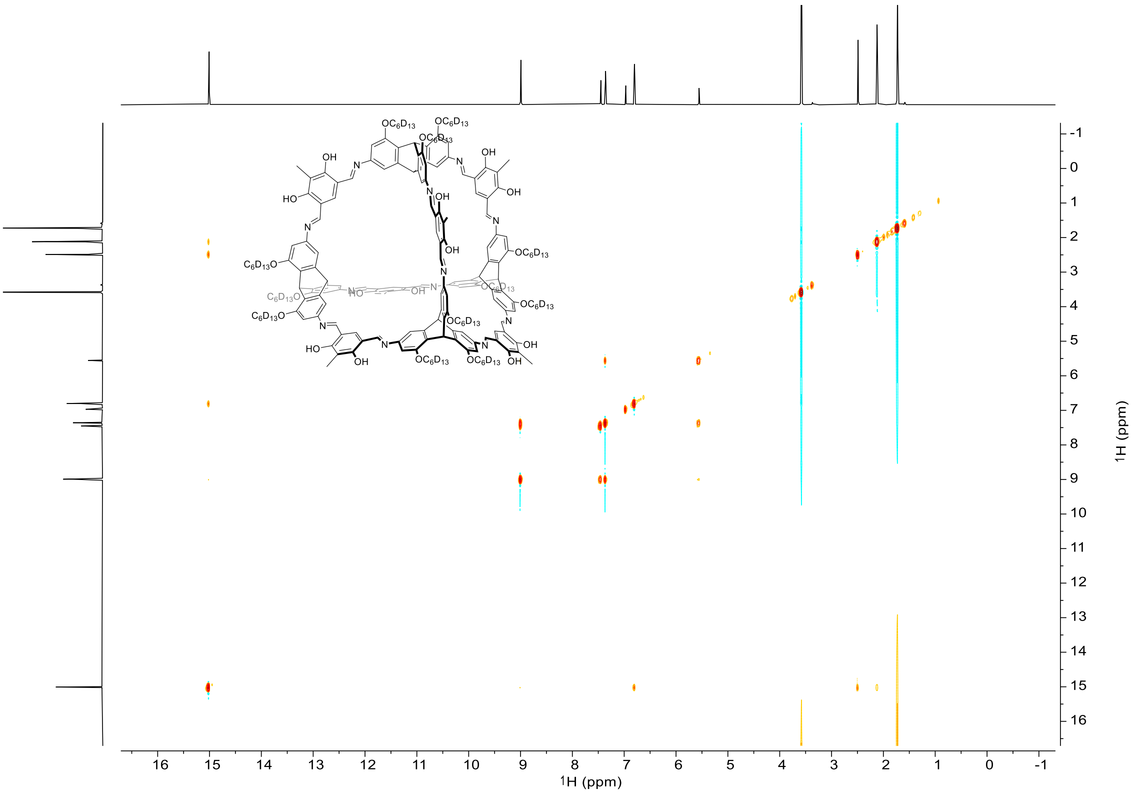


**Figure S65.** $^1$H,$^1$H NOESY spectrum (600 MHz, THF-$d_8$) of [4+6]-*exo* cage **12-d$_{156}$**.

**Table S20.** Cross-peak assignment of $^1H,^1H$-COSY and $^1H,^1H$-NOESY spectra of [4+6]-*exo* cage **12-d$_{156}$**.

| **$^1H$ nucleus** | **$\delta_{1H}$ [ppm]** | **COSY** | **NOESY** |
|---|---|---|---|
| *a* | 15.01 | - | *f*, $H_2O$, *h* |
| *b* | 8.99 | - | *c*, *d* |
| *c* | 7.45 | - | *b* |
| *d* | 7.36 | *f* | *b*, *g* |
| *e* | 6.97 | - | - |
| *f* | 6.80 | *d* | - |
| *g* | 5.55 | - | *d* |
| *h* | 2.12 | - | *a* |

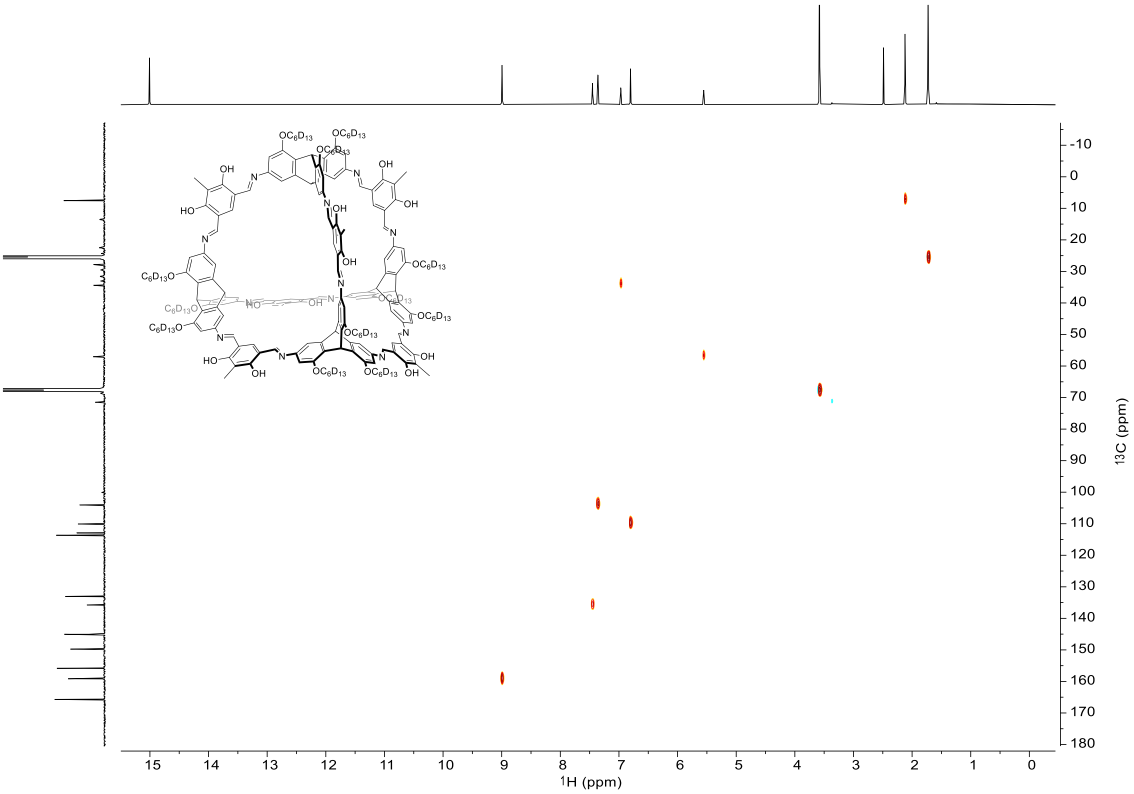


**Figure S66.** $^1$H,$^{13}$C HSQC spectrum (600 MHz, 150 MHz, THF-$d_8$) of [4+6]-*exo* cage **12-d$_{156}$**.

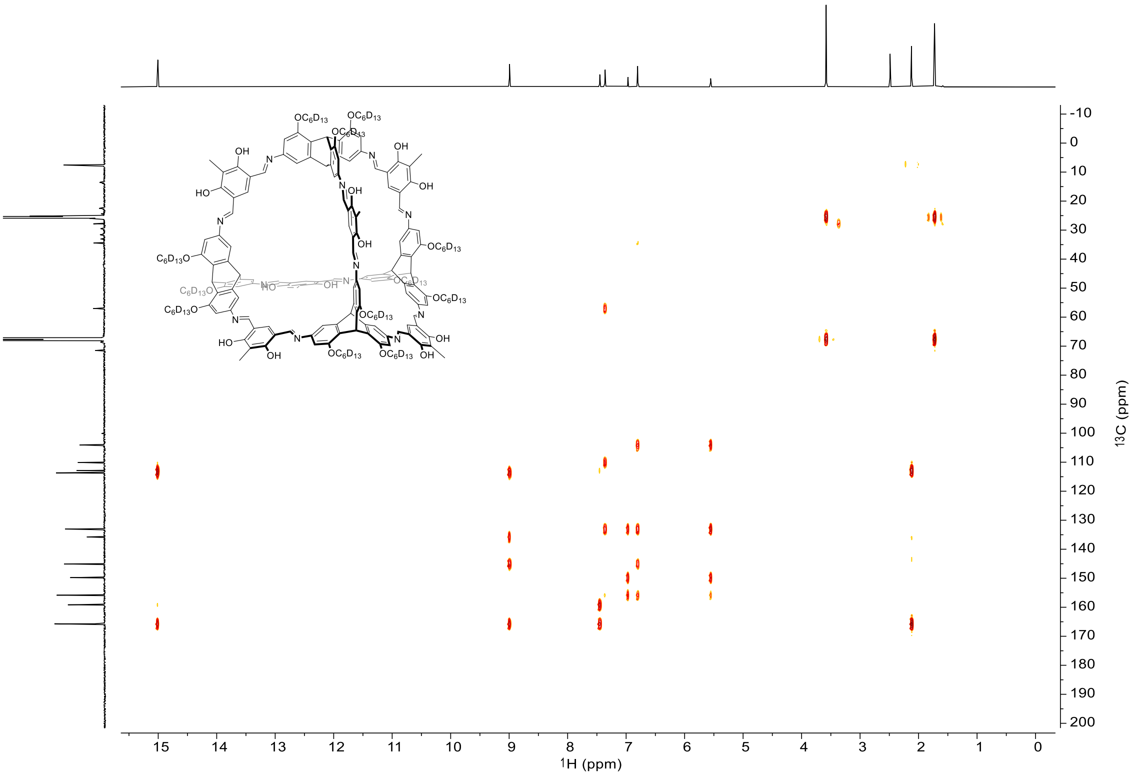


**Figure S67.** $^1$H,$^{13}$C HMBC spectrum (600 MHz, 150 MHz, THF-$d_8$) of [4+6]-*exo* cage **12-d$_{156}$**.

**Table S21.** Correlations of $^{1}H$,$^{13}C$-HSQC and $^{1}H$,$^{13}C$-HMBC spectra of [4+6]-*exo* cage **12-d$_{156}$**.

| **$^{13}C$ nucleus** | **$\delta_{13C}$ [ppm]** | **$^{1}H$ nucleus** | | |
|---|---|---|---|---|
| | | **HSQC** | **$\delta_{1H}$ [ppm]** | **HMBC** |
| *A* | 165.7 | *b* | 8.99 | *a, b, c, h* |
| *B* | 159.1 | - | - | *c* |
| *C* | 155.8 | - | - | *d, e, f, g* |
| *D* | 149.8 | - | - | *e, g* |
| *E* | 145.1 | - | - | *b, f* |
| *F* | 135.8 | *c* | 7.45 | *b* |
| *G* | 133.0 | - | - | *d, e, f, g* |
| *H* | 113.7 | - | - | *a, b, h* |
| *I* | 112.9 | - | - | *a, b, h* |
| *J* | 110.1 | *f* | 6.80 | *d* |
| *K* | 104.0 | *d* | 7.36 | *f, g* |
| *L* | 69.1 – 68.3 | - | - | - |
| *M* | 57.0 | *g* | 5.55 | *d* |
| *O* | 34.4 | *e* | 6.97 | - |
| *P* | 32.1 – 31.1 | - | - | - |
| *Q* | 30.1 – 29.1 | - | - | - |
| *R* | 23.0 – 22.0 | - | - | - |
| *S* | 14.0 – 13.2 | - | - | - |
| *T* | 7.6 | *h* | 2.12 | - |

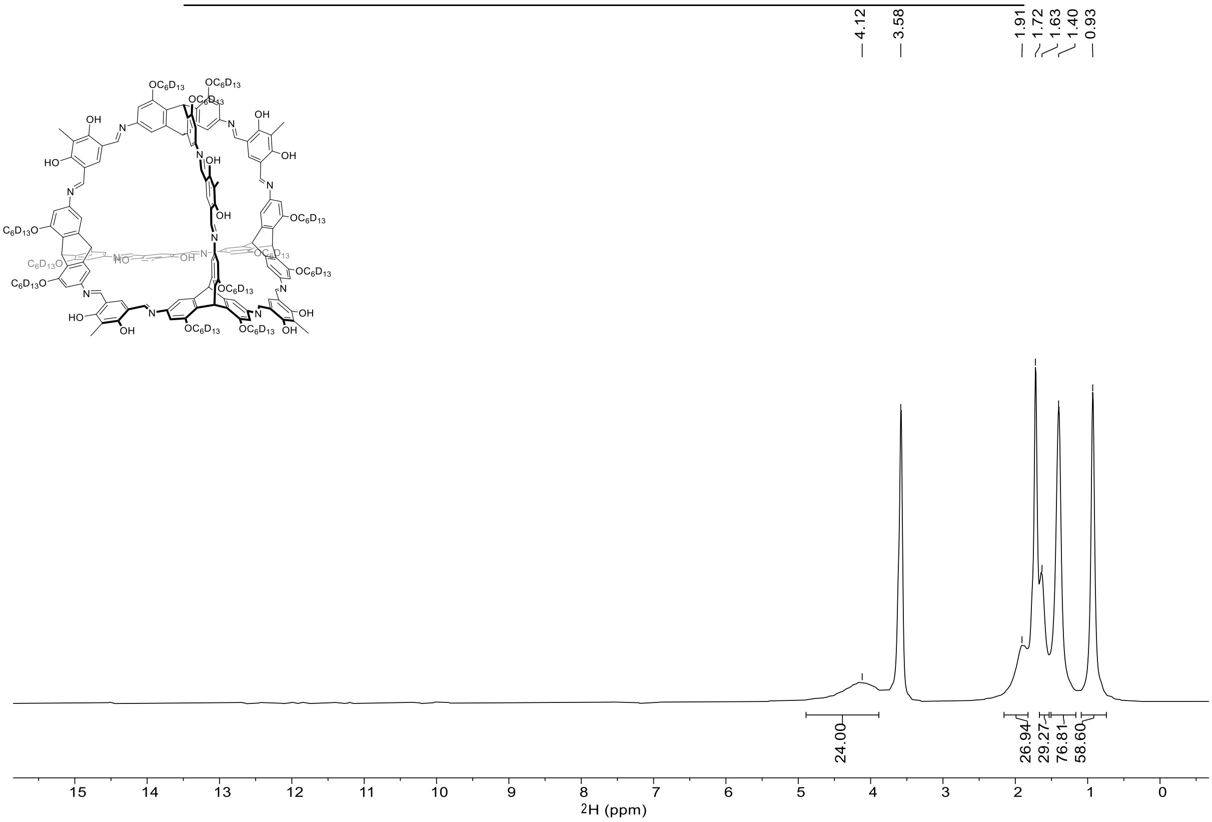


**Figure S68.** $^{2}H$ NMR spectrum (92 MHz, THF/THF-d$_{8}$) of [4+6]-*exo* cage **12-d$_{156}$**

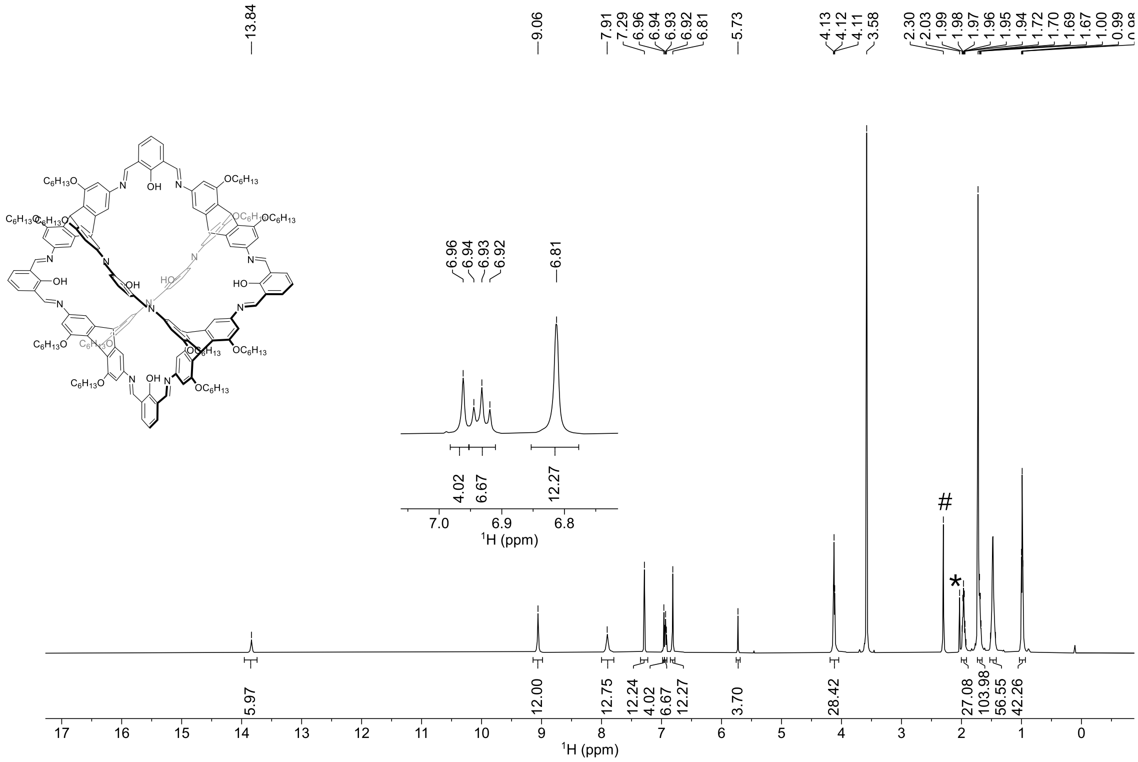


**Figure S69.** $^1$H NMR spectrum (600 MHz, 328 K, THF-$d_8$) of [4+6]-*endo* cage **13**. #: $H_2O$, *: Acetone.

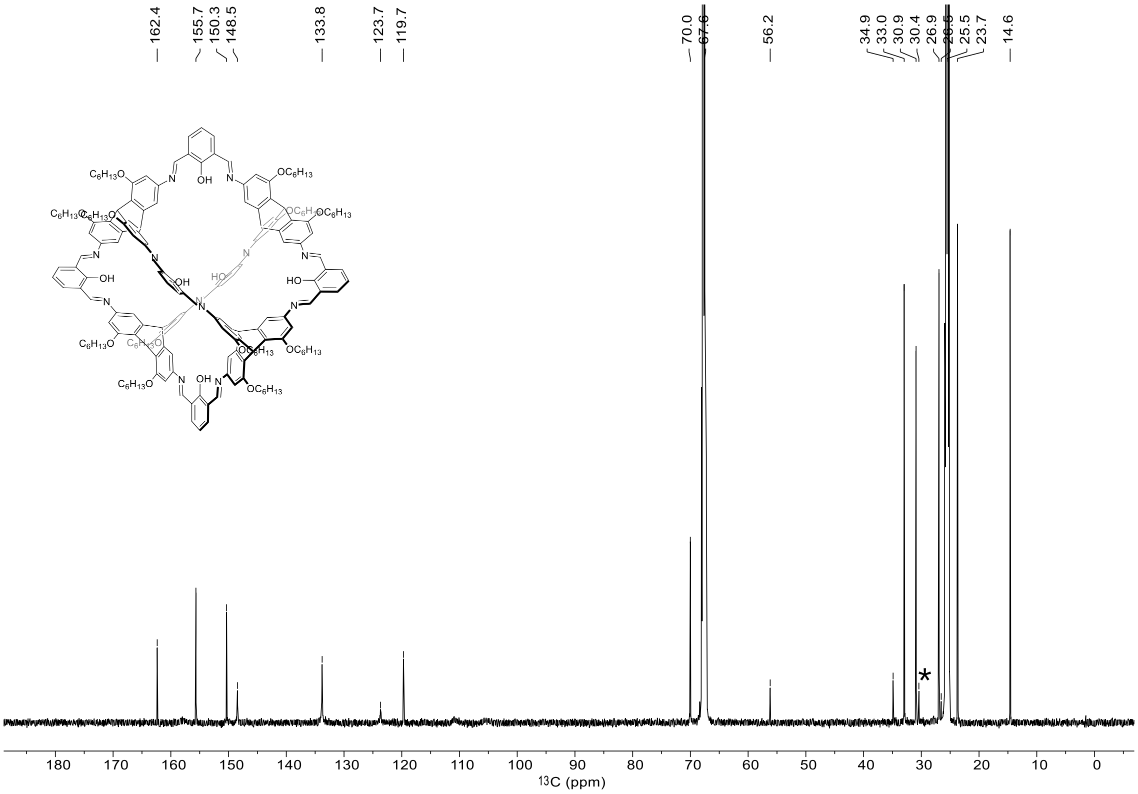


**Figure S70.** $^{13}C\{^1H\}$ NMR spectrum (150 MHz, 328 K, THF-$d_8$) of [4+6]-*endo* cage **13**. *: Acetone

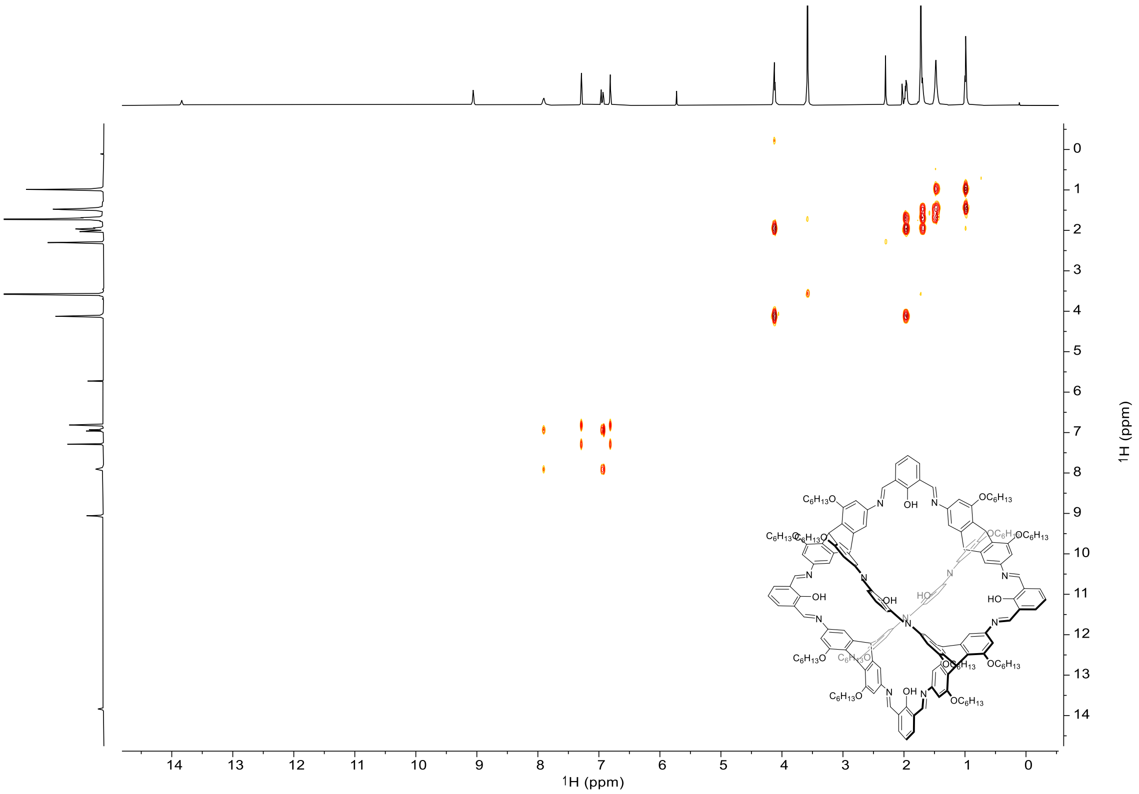


**Figure S71.** $^1$H,$^1$H COSY spectrum (600 MHz, 328 K, THF-d$_8$) of [4+6]-*endo* cage **13**.

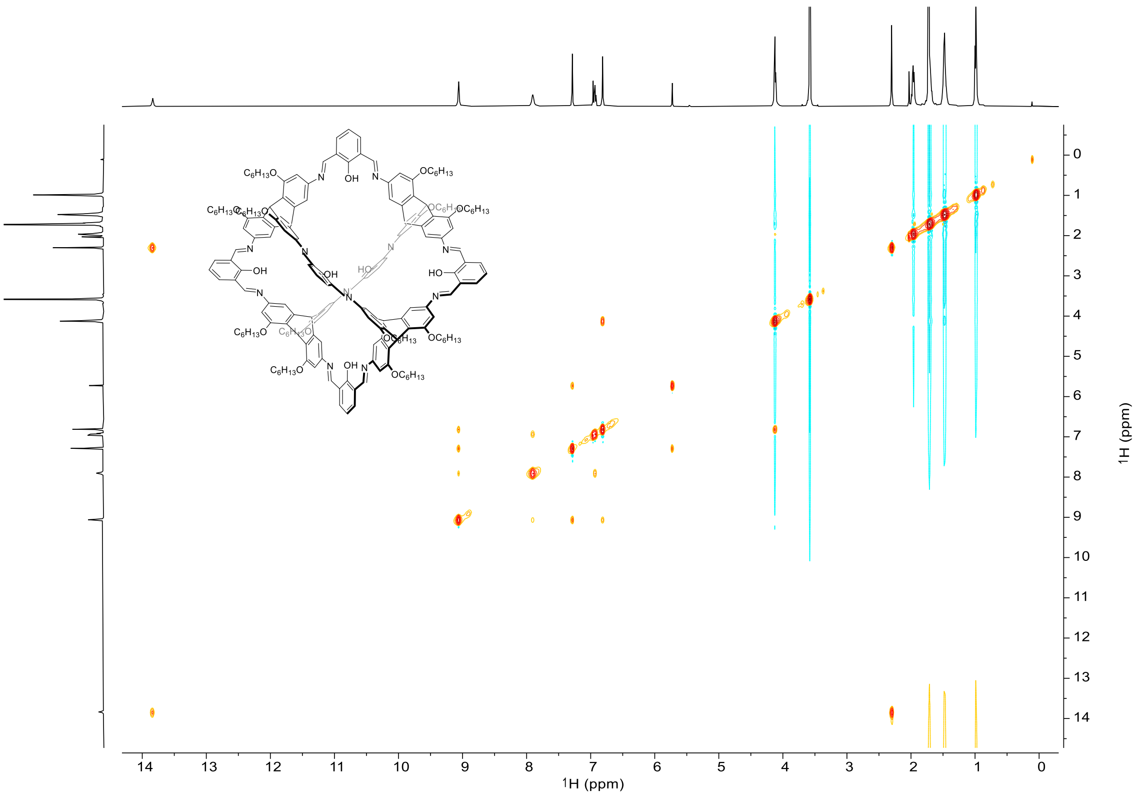


**Figure S72.** $^1$H,$^1$H NOESY spectrum (600 MHz, 328 K, THF-d$_8$) of [4+6]-*endo* cage **13**.

**Table S22.** Cross-peak assignment of $^1H,^1H$-COSY and $^1H,^1H$-NOESY spectra of [4+6]-*endo* cage **13**.

| **$^1H$ nucleus** | **$\delta_{1H}$ [ppm]** | **COSY** | **NOESY** |
|---|---|---|---|
| *a* | 13.84 | - | $H_2O$ |
| *b* | 9.06 | - | *c, d, g* |
| *c* | 7.91 | *f* | *b, f* |
| *d* | 7.29 | *g* | *b, h* |
| *e* | 6.96 | - | - |
| *f* | 6.93 | *c* | *c* |
| *g* | 6.81 | *d* | *b, i* |
| *h* | 5.73 | - | *d* |
| *i* | 4.12 | *j* | *g* |
| *j* | 2.00 – 1.92 | *i, k* | - |
| *k* | 1.73 – 1.66 | *j, l* | - |
| *l* | 1.53 – 1.42 | *k, m* | - |
| *m* | 0.99 | *l* | - |

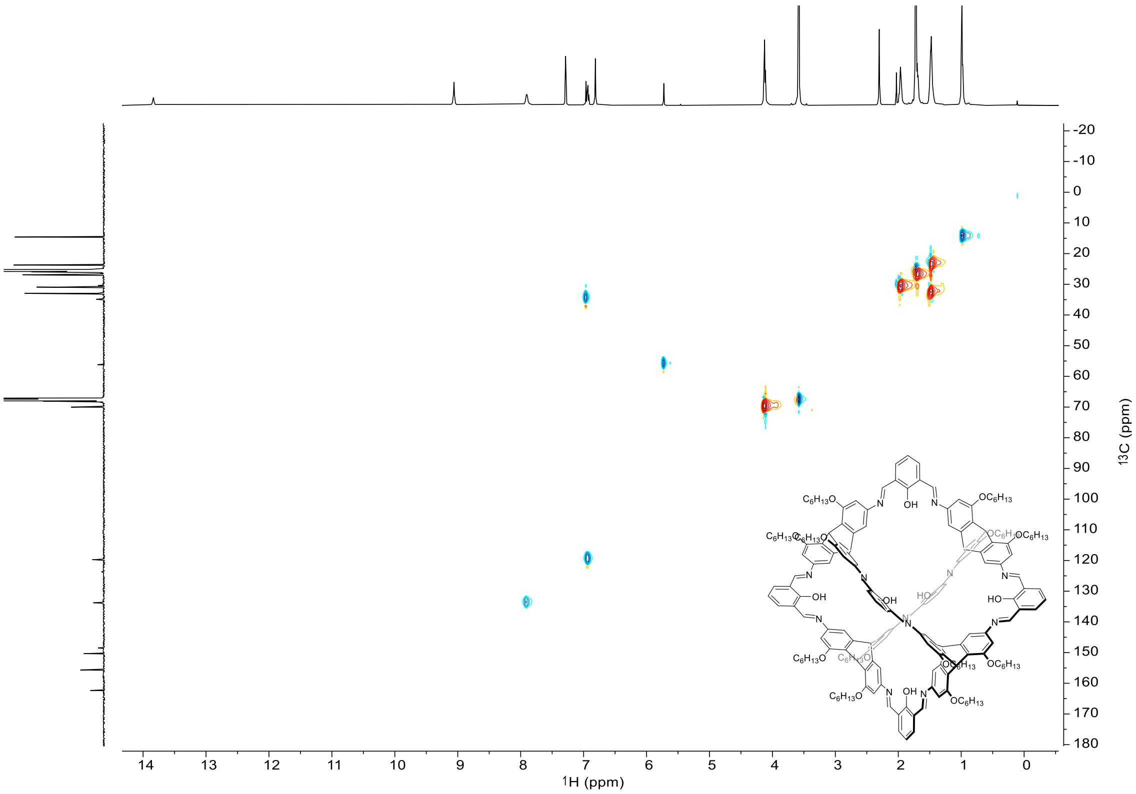


**Figure S73.** $^{1}$H,$^{13}$C HSQC spectrum (600 MHz, 150 MHz, 328 K, THF-$d_8$) of [4+6]-*endo* cage **13**.

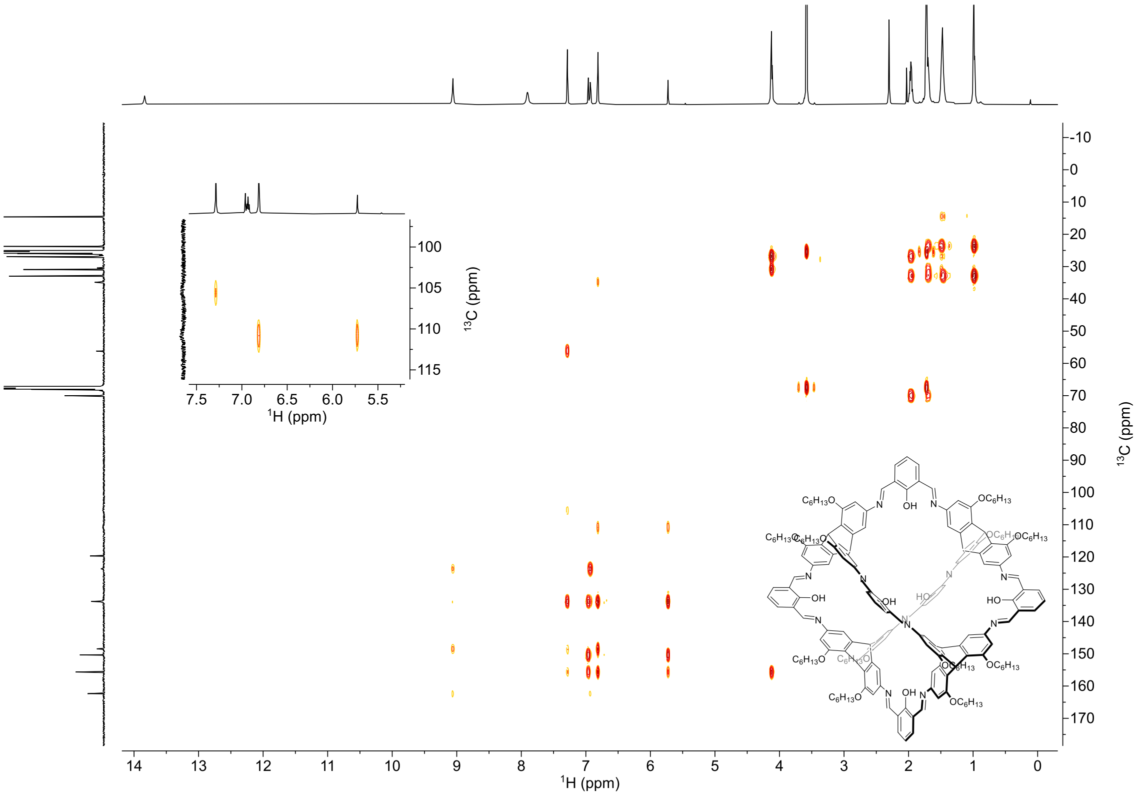


**Figure S74.** $^{1}$H,$^{13}$C HMBC spectrum (600 MHz, 150 MHz, 328 K, THF-$d_8$) of [4+6]-*endo* cage **13**. Also, a zoom into the region of 7.5 – 5.5 ppm ($^{1}$H) and 115 – 100 ppm ($^{13}$C) is illustrated to show the chemical shifts of the hydrogen bound aromatic carbon nuclei of the triptycene building block.

**Table S23.** Correlations of $^{1}H,^{13}C$-HSQC and $^{1}H,^{13}C$-HMBC spectra of [4+6]-*endo* cage **13**.

| **$^{13}C$ nucleus** | **$\delta_{13C}$ [ppm]** | **$^{1}H$ nucleus** | | |
|---|---|---|---|---|
| | | **HSQC** | **$\delta_{1H}$ [ppm]** | **HMBC** |
| *A* | 162.4 | - | - | *b, f* |
| *B* | 155.7 | - | - | *d, e, g, h, i* |
| *C* | 150.3 | - | - | *e, h* |
| *D* | 148.5 | - | - | *b, d, g* |
| *E* | 133.8 | *c* | 7.91 | *b, d, e, f, g, h* |
| *F* | 123.7 | - | - | *b, f* |
| *G* | 119.7 | *f* | 6.93 | - |
| *H* | 110.8 | - | - | *g, h* |
| *I* | 105.5 | - | - | *d* |
| *J* | 70.0 | *i* | 4.12 | *j, k* |
| *K* | 56.2 | *h* | 5.73 | *d* |
| *L* | 34.9 | *e* | 6.96 | *g* |
| *M* | 33.0 | *l* | 1.53 -.1.42 | *j, k, l, m* |
| *O* | 30.9 | *j* | 2.00 – 1.92 | *i, k* |
| *P* | 26.9 | *k* | 1.73 – 1.66 | *i, j, l* |
| *Q* | 23.7 | *l* | 1.53 – 1.42 | *k, l, m* |
| *R* | 14.6 | *m* | 0.99 | *l* |

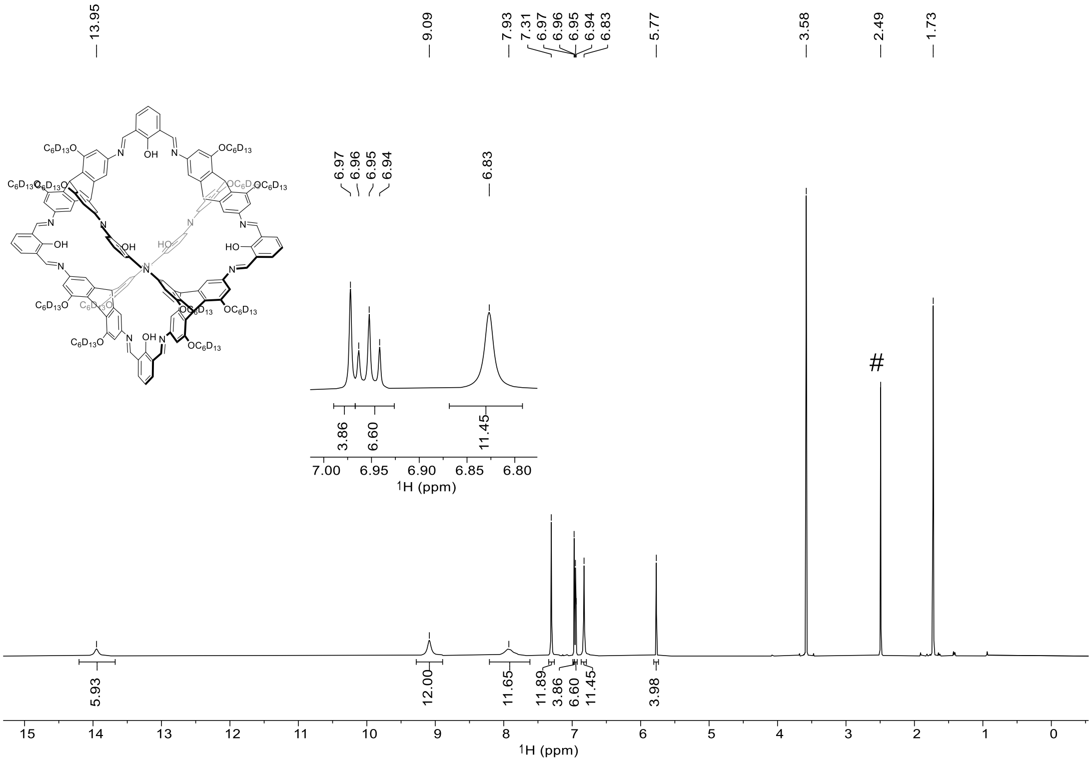


**Figure S75.** $^1$H NMR spectrum (700 MHz, THF-$d_8$) of [4+6]-*endo* cage **13-d$_{156}$**. #: $H_2O$.

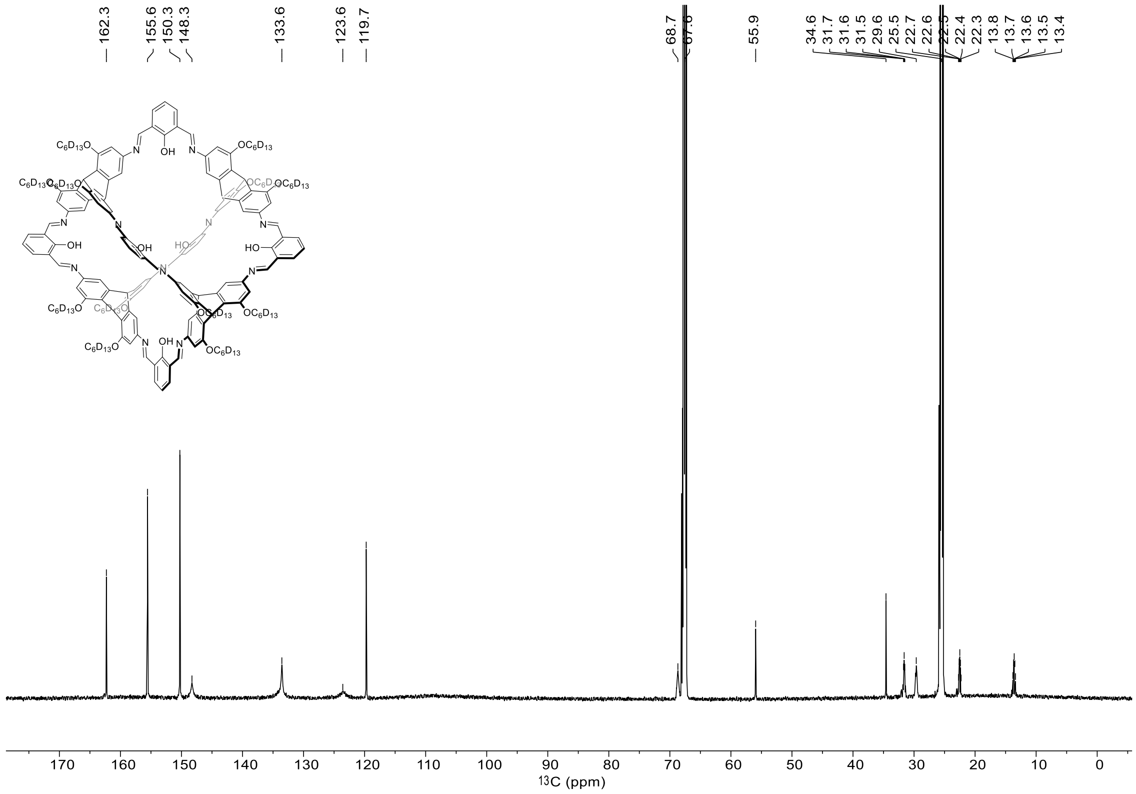


**Figure S76.** $^{13}C\{^1H\}$ NMR spectrum (176 MHz, THF-$d_8$) of [4+6]-*endo* cage **13-d$_{156}$**.

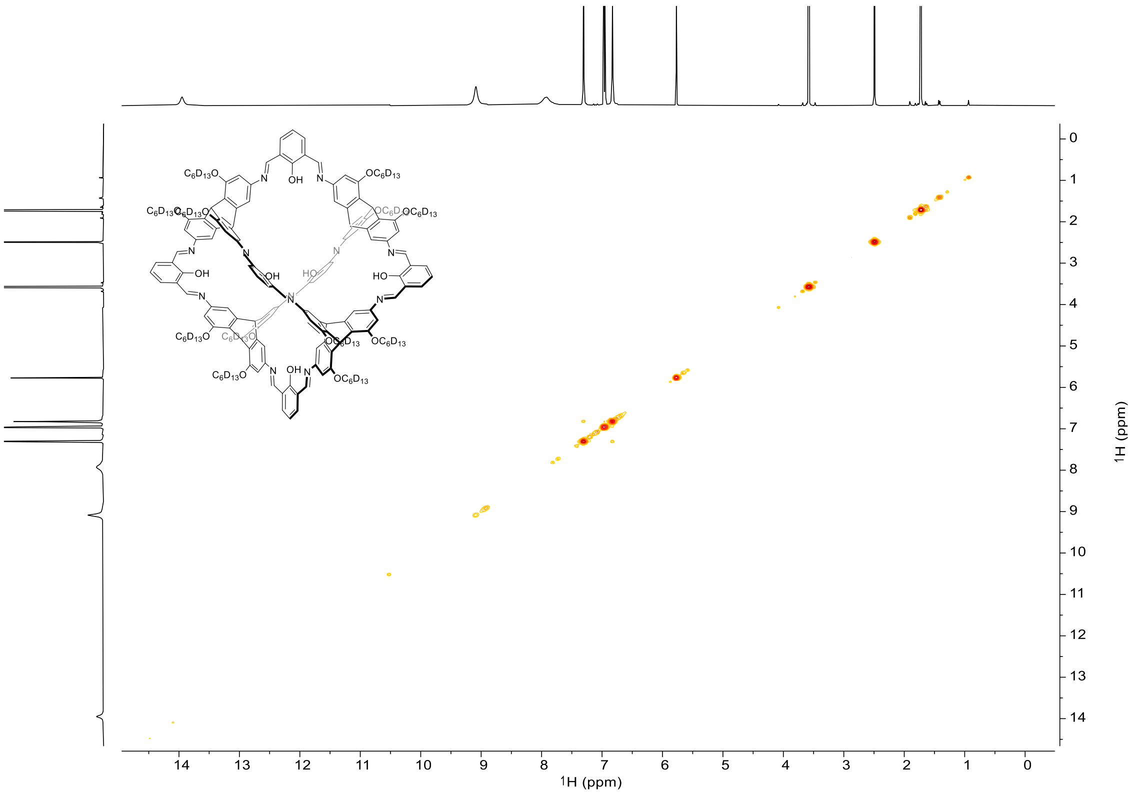


**Figure S77.** $^1H,^1H$ COSY spectrum (700 MHz, THF-$d_8$) of [4+6]-*endo* cage **13-d156**.

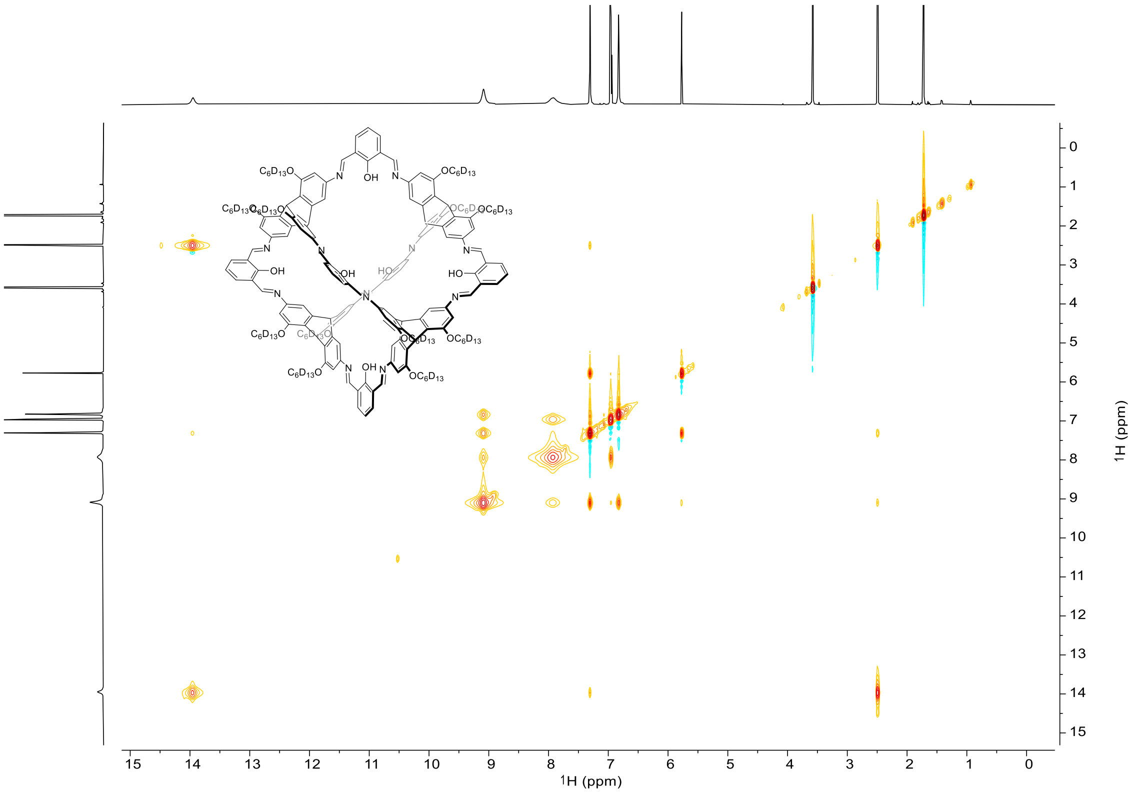


**Figure S78.** $^1H,^1H$ NOESY spectrum (700 MHz, THF-$d_8$) of [4+6]-*endo* cage **13-d156**.

**Table S24.** Cross-peak assignment of $^1$H,$^1$H-COSY and $^1$H,$^1$H-NOESY spectra of [4+6]-*endo* cage **13-d$_{156}$**.

| $^1$H nucleus | $\delta_{1H}$ [ppm] | COSY | NOESY |
|---|---|---|---|
| *a* | 13.95 | - | *d,* $H_2O$ |
| *b* | 9.09 | - | *c, d, g* |
| *c* | 7.93 | - | *b, f* |
| *d* | 7.31 | *g* | *b, h* |
| *e* | 6.97 | - | - |
| *f* | 6.95 | - | *c* |
| *g* | 6.83 | *d* | *b* |
| *h* | 5.77 | - | *d* |

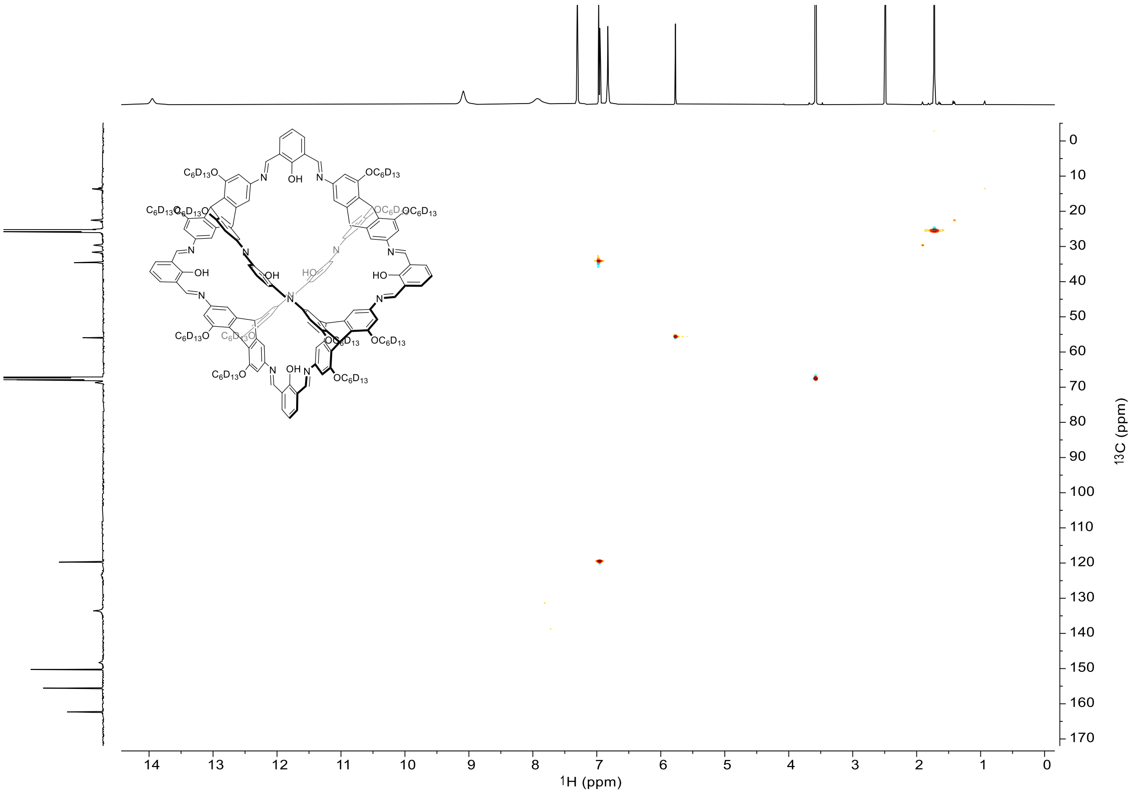


**Figure S79.** $^1$H,$^{13}$C HSQC spectrum (700 MHz, 176 MHz, THF-d$_8$) of [4+6]-*endo* cage **13-d$_{156}$**.

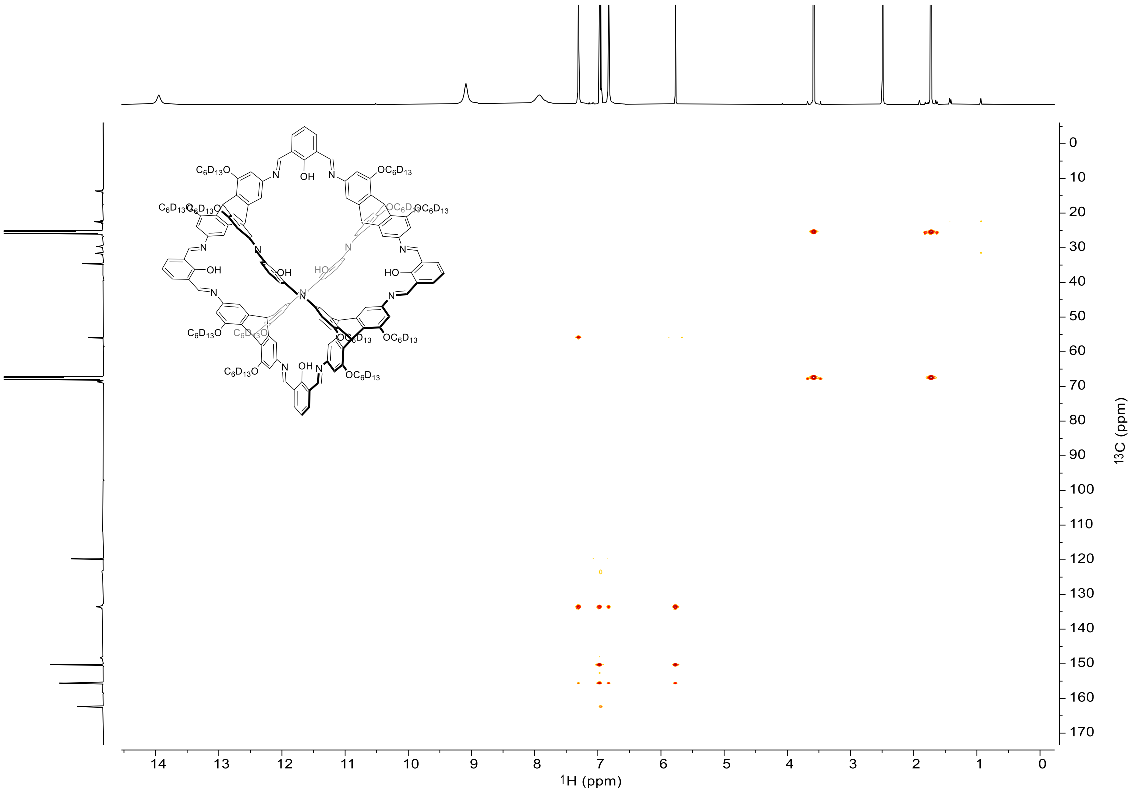


**Figure S80.** $^1$H,$^{13}$C HMBC spectrum (700 MHz, 176 MHz, THF-d$_8$) of [4+6]-*endo* cage **13-d$_{156}$**.

**Table S25.** Correlations of $^{1}H,^{13}C$-HSQC and $^{1}H,^{13}C$-HMBC spectra of [4+6]-*endo* cage **13-d$_{156}$**.

| $^{13}C$ nucleus | $\delta_{13C}$ [ppm] | $^{1}H$ nucleus | | |
|---|---|---|---|---|
| | | HSQC | $\delta_{1H}$ [ppm] | HMBC |
| *A* | 162.3 | - | - | *f* |
| *B* | 155.6 | - | - | *d, e, g, h* |
| *C* | 150.3 | - | - | *e, h* |
| *D* | 133.6 | - | - | - |
| *E* | 123.6 | - | - | *d, e, g, h* |
| *F* | 119.7 | *f* | 6.83 | - |
| *G* | 69.1 – 68.3 | - | - | - |
| *H* | 55.9 | *h* | 5.77 | *d* |
| *I* | 34.6 | *e* | 6.95 | - |
| *J* | 32.0 – 31.3 | - | - | - |
| *K* | 30.0 – 29.3 | - | - | - |
| *L* | 22.8 – 22.1 | - | - | - |
| *M* | 14.1 – 13.2 | - | - | - |

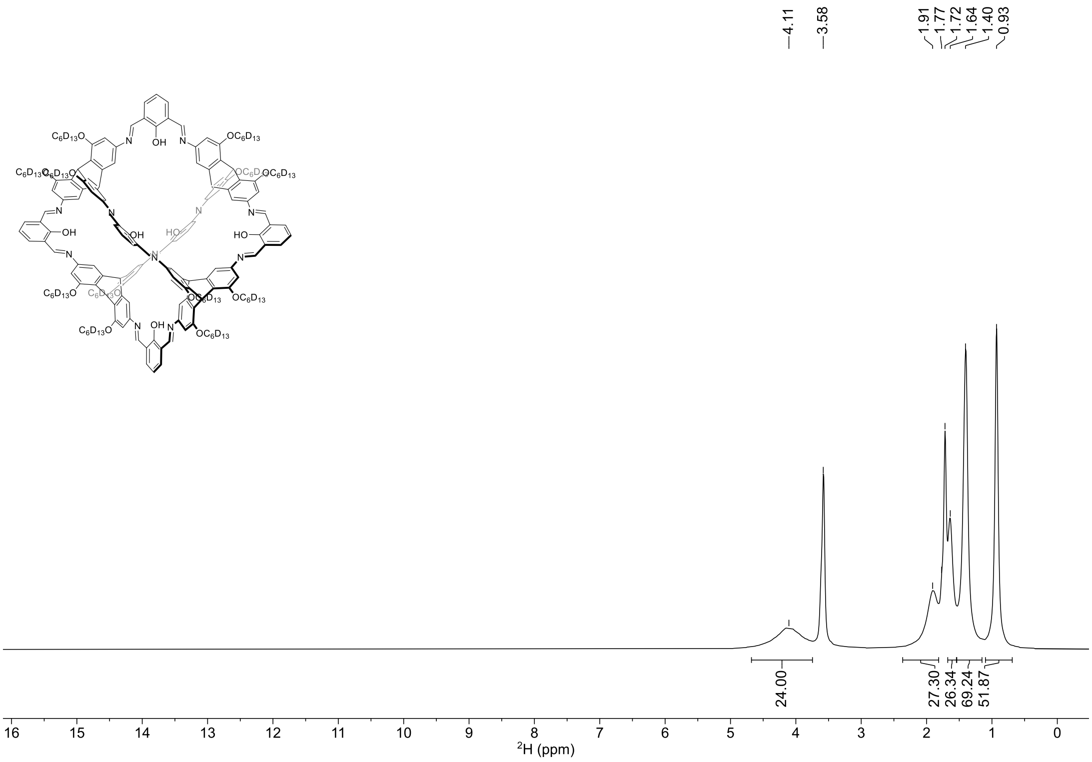


**Figure S81.** $^{2}H$ NMR spectrum (92 MHz, THF/THF-d$_8$) of [4+6]-*endo* cage **13-d$_{156}$**.

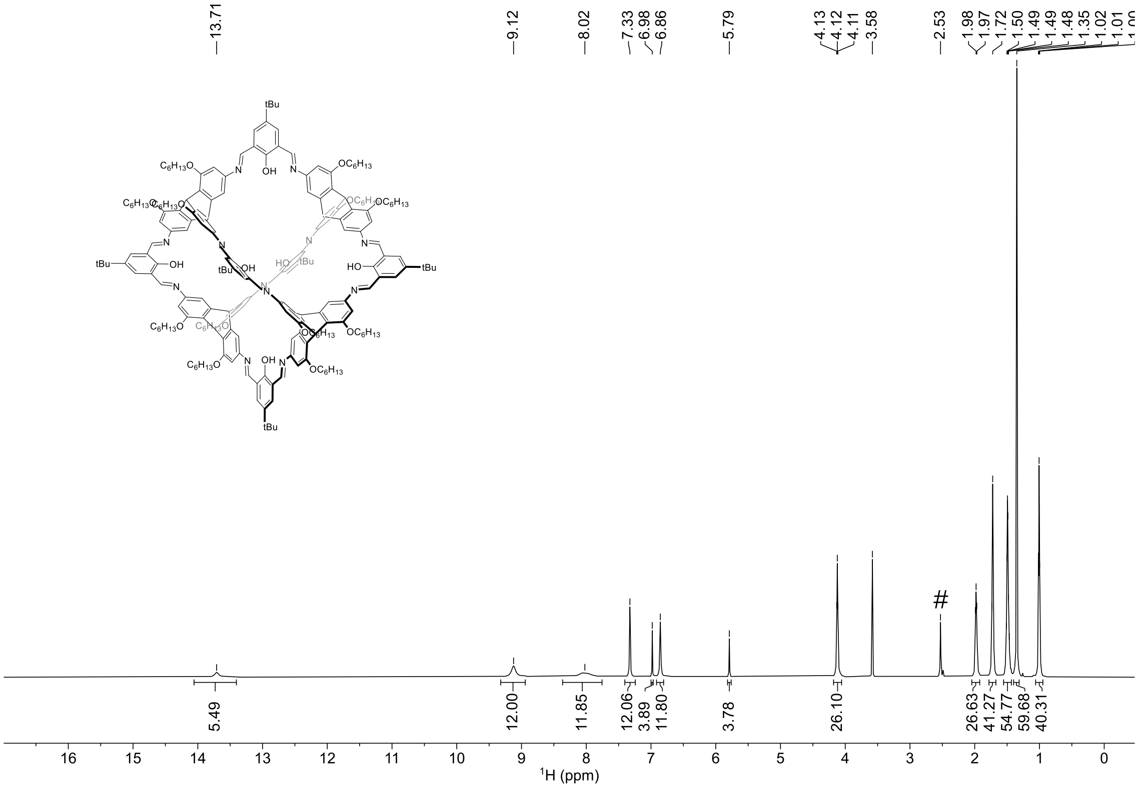


**Figure S82.** $^1$H NMR spectrum (700 MHz, THF-$d_8$) of *tert*-butylated [4+6]-*endo* cage **14**. #: $H_2O$.

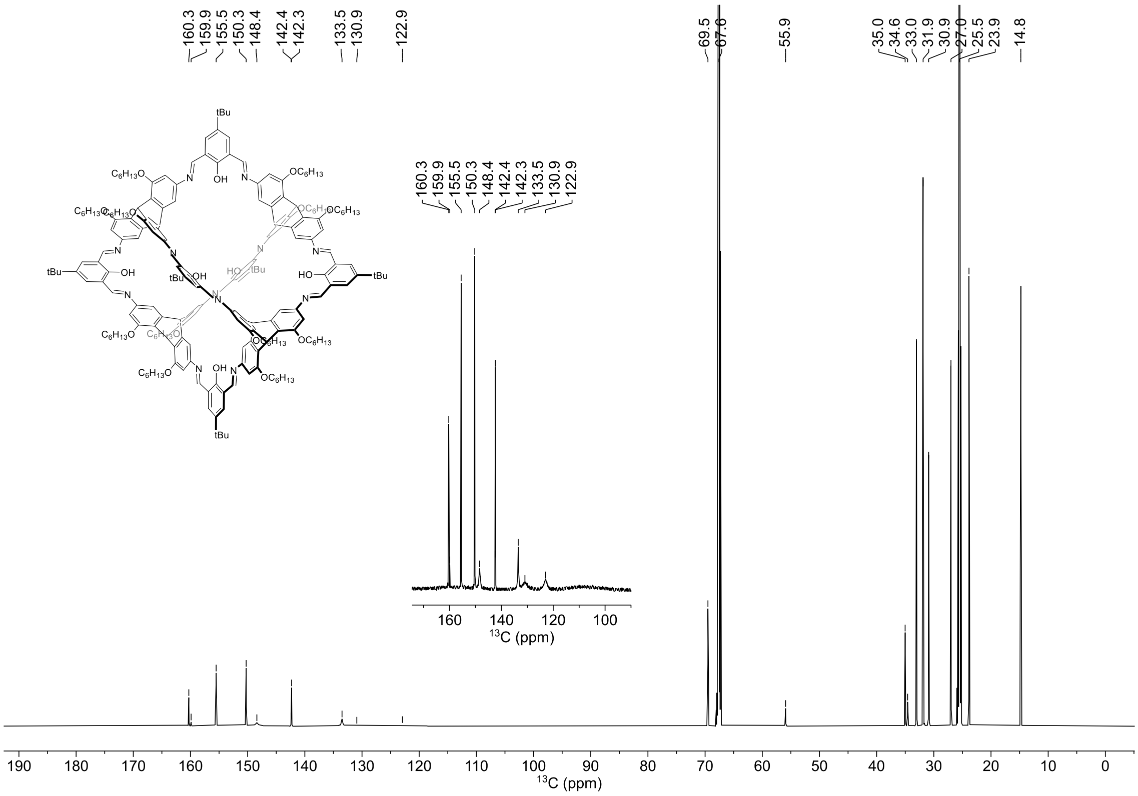


**Figure S83.** $^{13}$C{$^1$H} NMR spectrum (176 MHz, THF-$d_8$) of *tert*-butylated [4+6]-*endo* cage **14**.

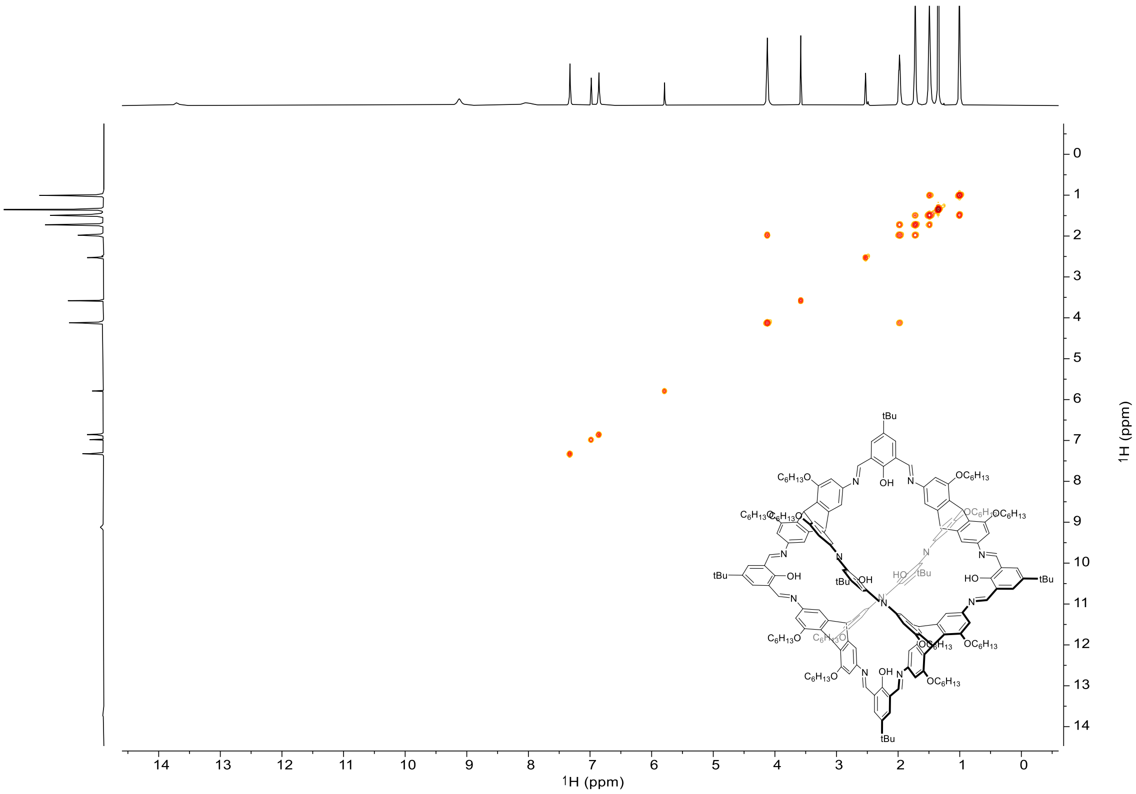


**Figure S84.** $^1$H,$^1$H COSY spectrum (700 MHz, THF-d$_8$) of *tert*-butylated [4+6]-*endo* cage **14**.

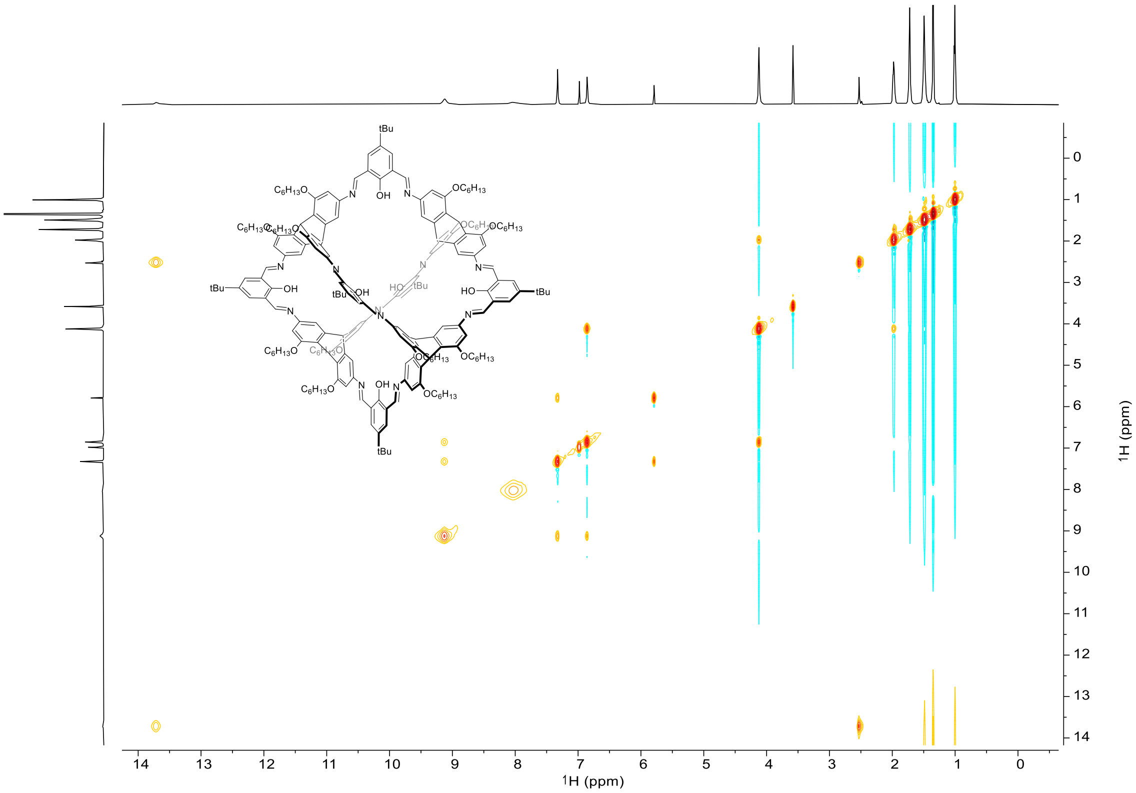


**Figure S85.** $^1$H,$^1$H NOESY spectrum (700 MHz, THF-d$_8$) of *tert*-butylated [4+6]-*endo* cage **14**.

**Table S26.** Cross-peak assignment of $^1H,^1H$-COSY and $^1H,^1H$-NOESY spectra of *tert*-butylated [4+6]-*endo* cage **14**.

| $^1H$ nucleus | $\delta_{1H}$ [ppm] | COSY | NOESY |
|---|---|---|---|
| *a* | 13.71 | - | $H_2O$ |
| *b* | 9.12 | - | *d, f* |
| *c* | 8.02 | - | - |
| *d* | 7.33 | - | *b, g* |
| *e* | 6.98 | - | - |
| *f* | 6.86 | - | *b, h* |
| *g* | 5.79 | - | *d* |
| *h* | 4.12 | *i* | *f, i* |
| *i* | 2.04 – 1.92 | *h, j* | *h* |
| *j* | 1.78 – 1.67 | *i, k* | - |
| *k* | 1.55 – 1.43 | *j, m* | - |
| *l* | 1.35 | - | - |
| *m* | 1.06 – 0.95 | *k* | - |

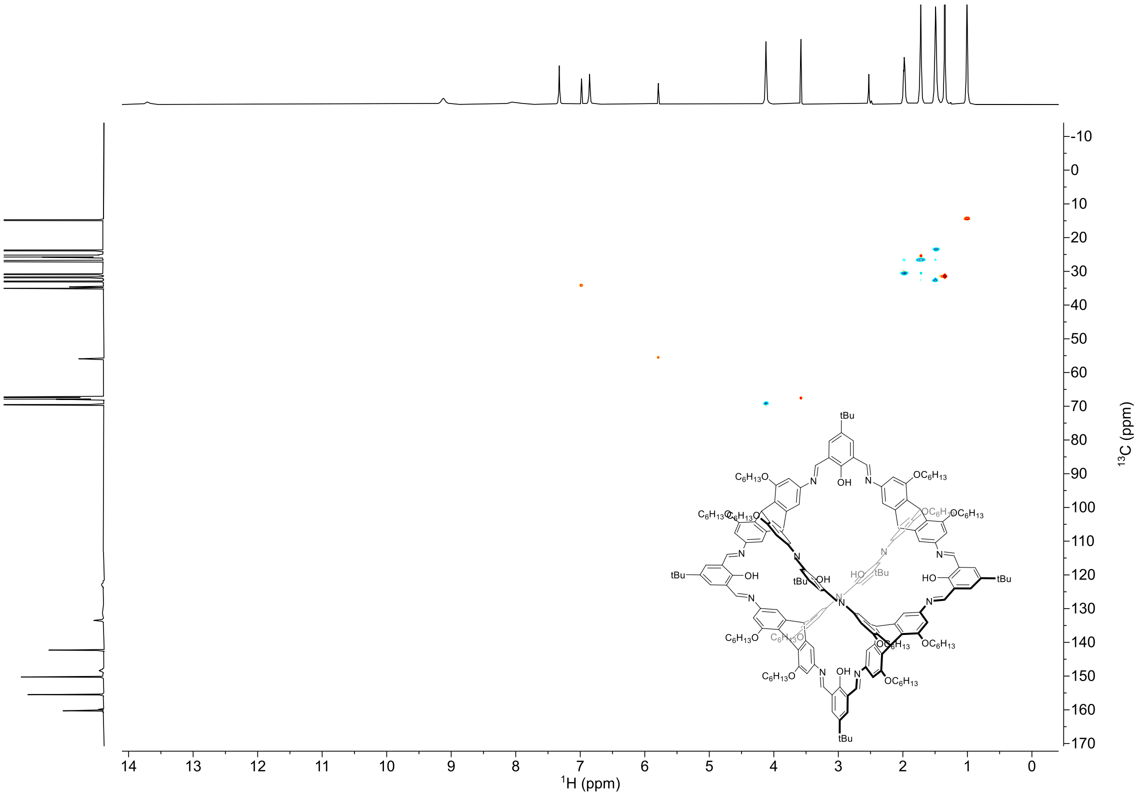


**Figure S86.** $^1$H,$^{13}$C HSQC spectrum (700 MHz, 176 MHz, THF-$d_8$) of *tert*-butylated [4+6]-*endo* cage **14**.

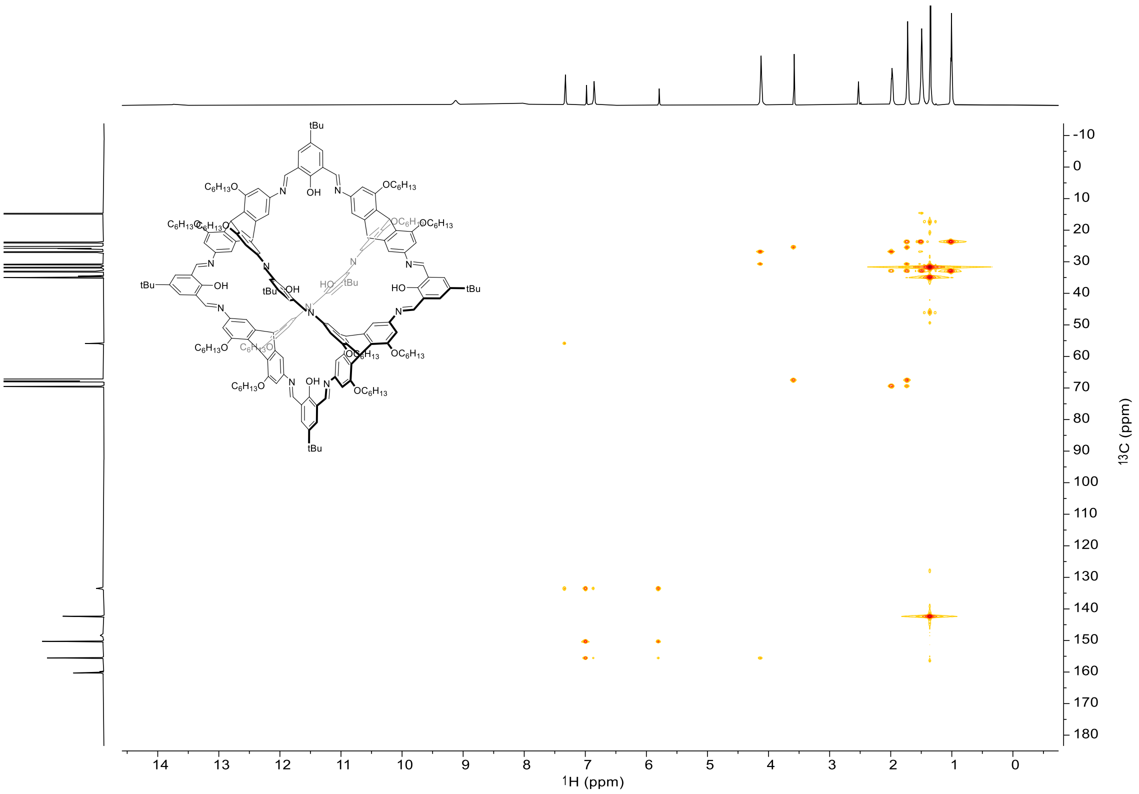


**Figure S87.** $^1$H,$^{13}$C HMBC spectrum (700 MHz, 176 MHz, THF-$d_8$) of *tert*-butylated [4+6]-*endo* cage **14**.

**Table S27.** Correlations of $^1$H,$^{13}$C-HSQC and $^1$H,$^{13}$C-HMBC spectra of *tert*-butylated [4+6]-*endo* cage **14**.

| **$^{13}$C nucleus** | **$\delta_{13C}$ [ppm]** | **$^1$H nucleus** | | |
|---|---|---|---|---|
| | | **HSQC** | **$\delta_{1H}$ [ppm]** | **HMBC** |
| *A* | 160.3 | - | - | - |
| *B* | 159.9 | - | - | - |
| *C* | 155.5 | - | - | *d, e, g, h* |
| *D* | 150.3 | - | - | *e, g* |
| *E* | 148.4 | - | - | - |
| *F* | 142.4 | - | - | *l* |
| *G* | 142.3 | - | - | *l* |
| *H* | 133.5 | - | - | *d, e, f, g* |
| *I* | 130.9 | - | - | |
| *J* | 122.9 | - | - | |
| *K* | 69.5 | *h* | 4.12 | *i, j* |
| *L* | 55.9 | *g* | 5.79 | *d* |
| *M* | 35.0 | *e* | 6.98 | *l* |
| *O* | 34.6 | - | - | - |
| *P* | 33.0 | *k* | 1.55 – 1.43 | *i, j, k, m* |
| *Q* | 31.9 | *l* | 1.35 | *l* |
| *R* | 30.9 | *i* | 2.04 – 1.92 | *h, j* |
| *S* | 27.0 | *j* | 1.78 – 1.67 | *h, i, k* |
| *T* | 23.9 | *k* | 1.55 – 1.43 | *j, k, m* |
| *U* | 14.8 | *m* | 1.06 – 0.95 | *k* |

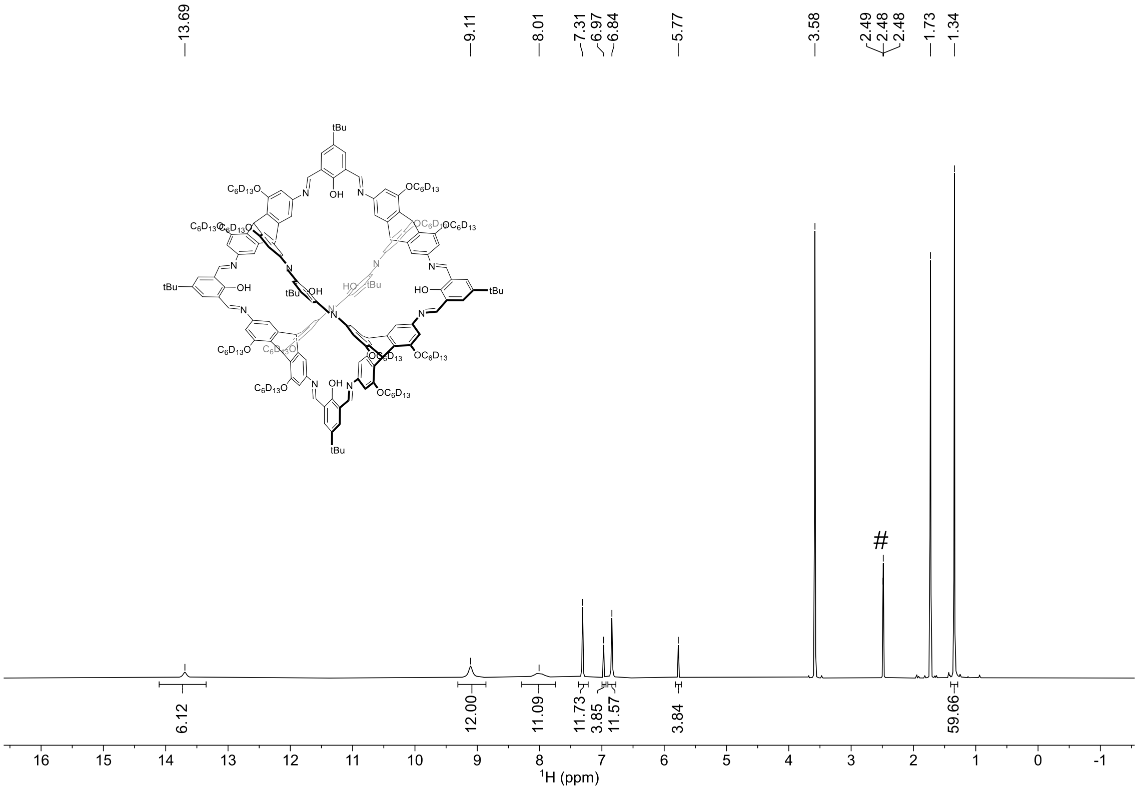


**Figure S88.** $^1$H NMR spectrum (700 MHz, THF-$d_8$) of *tert*-butylated [4+6]-*endo* cage **14-d$_{156}$**. #: $H_2O$.

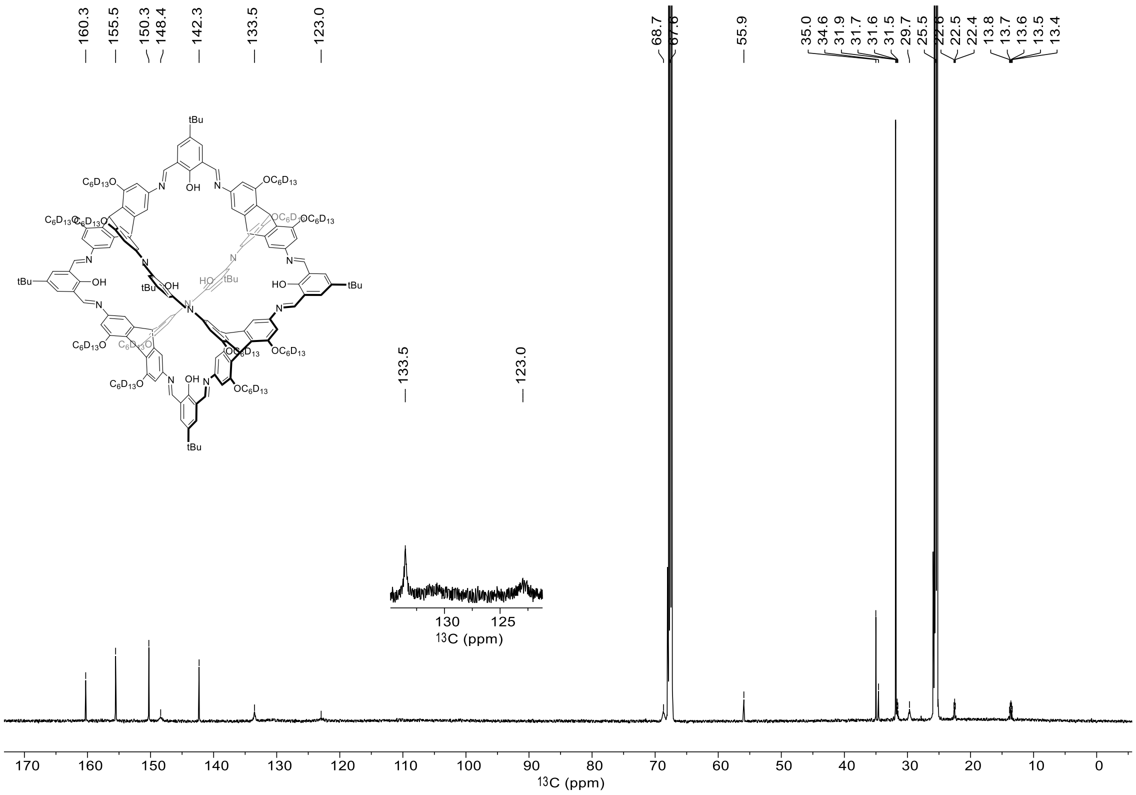


**Figure S89.** $^{13}C\{^1H\}$ NMR spectrum (176 MHz, THF-$d_8$) of *tert*-butylated [4+6]-*endo* cage **14-d$_{156}$**.

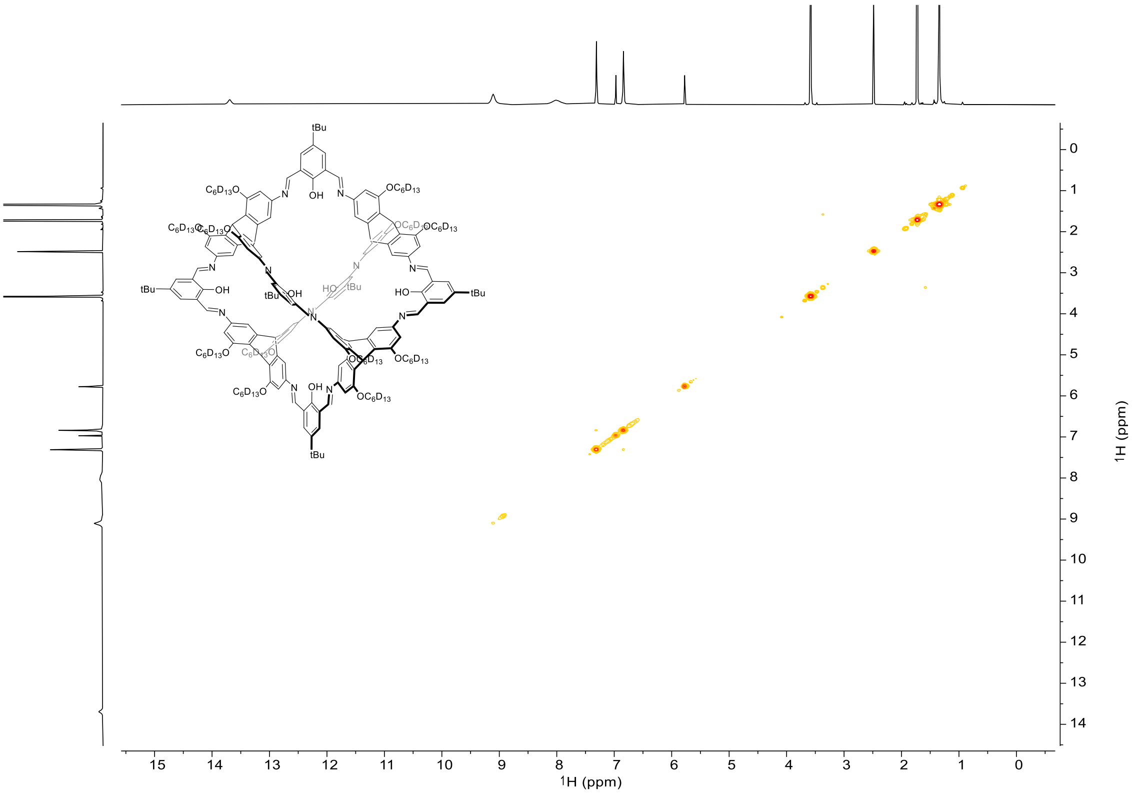


**Figure S90.** $^1$H,$^1$H COSY spectrum (700 MHz, THF-d$_8$) of *tert*-butylated [4+6]-*endo* cage **14-d$_{156}$**.

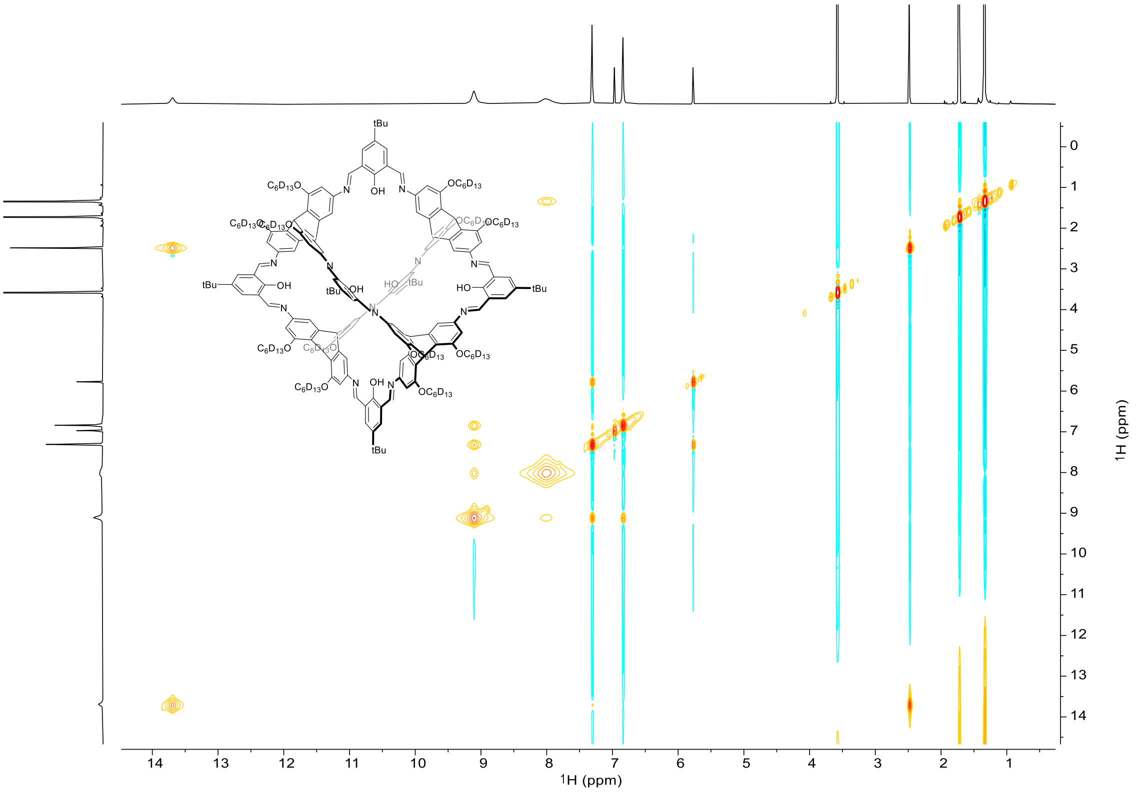


**Figure S91.** $^1$H,$^1$H NOESY spectrum (700 MHz, THF-d$_8$) of *tert*-butylated [4+6]-*endo* cage **14-d$_{156}$**.

**Table S28.** Cross-peak assignment of $^{1}$H,$^{1}$H-COSY and $^{1}$H,$^{1}$H-NOESY spectra of *tert*-butylated [4+6]-*endo* cage **14-d$_{156}$**.

| $^{1}$H nucleus | $\delta_{1H}$ [ppm] | COSY | NOESY |
|---|---|---|---|
| *a* | 13.69 | - | $H_2O$ |
| *b* | 9.11 | - | *c, d, f* |
| *c* | 8.01 | - | *h* |
| *d* | 7.31 | - | *b, g* |
| *e* | 6.97 | - | - |
| *f* | 6.84 | - | *b* |
| *g* | 5.77 | - | *d* |
| *h* | 1.34 | - | *c* |

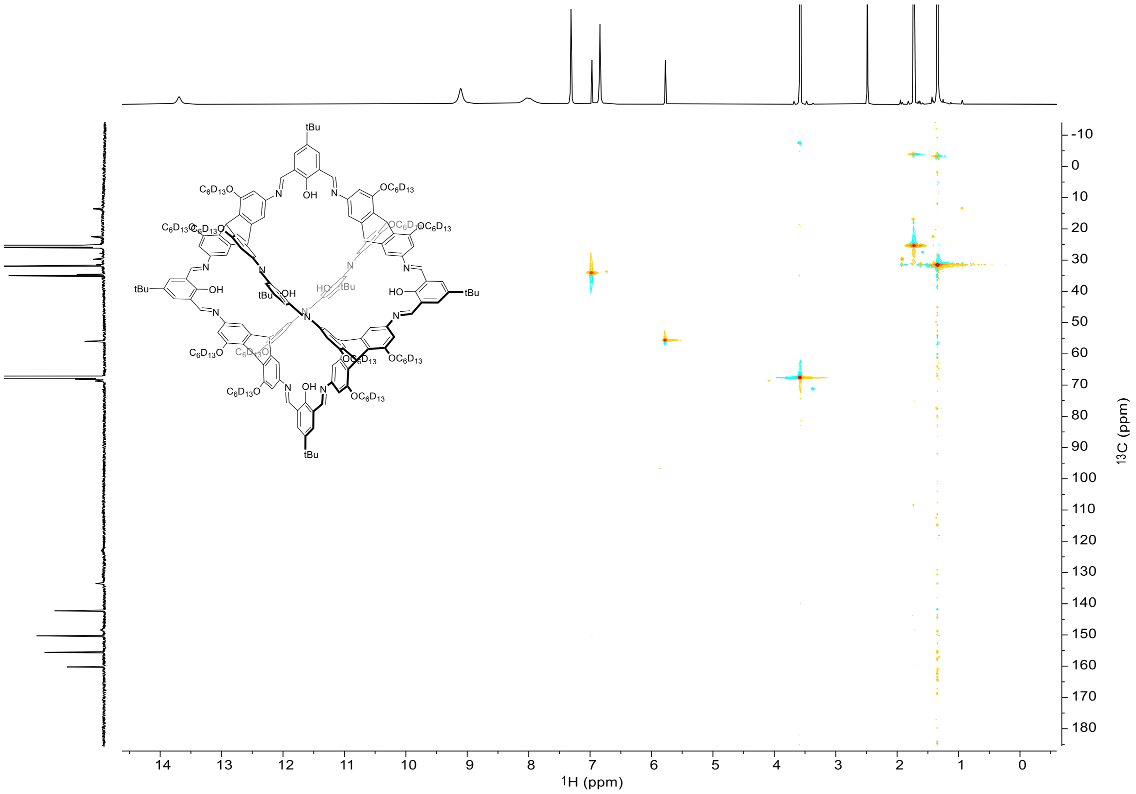


**Figure S92.** $^1$H,$^{13}$C HSQC spectrum (700 MHz, 176 MHz, THF-d$_8$) of *tert*-butylated [4+6]-*endo* cage **14-d$_{156}$**.

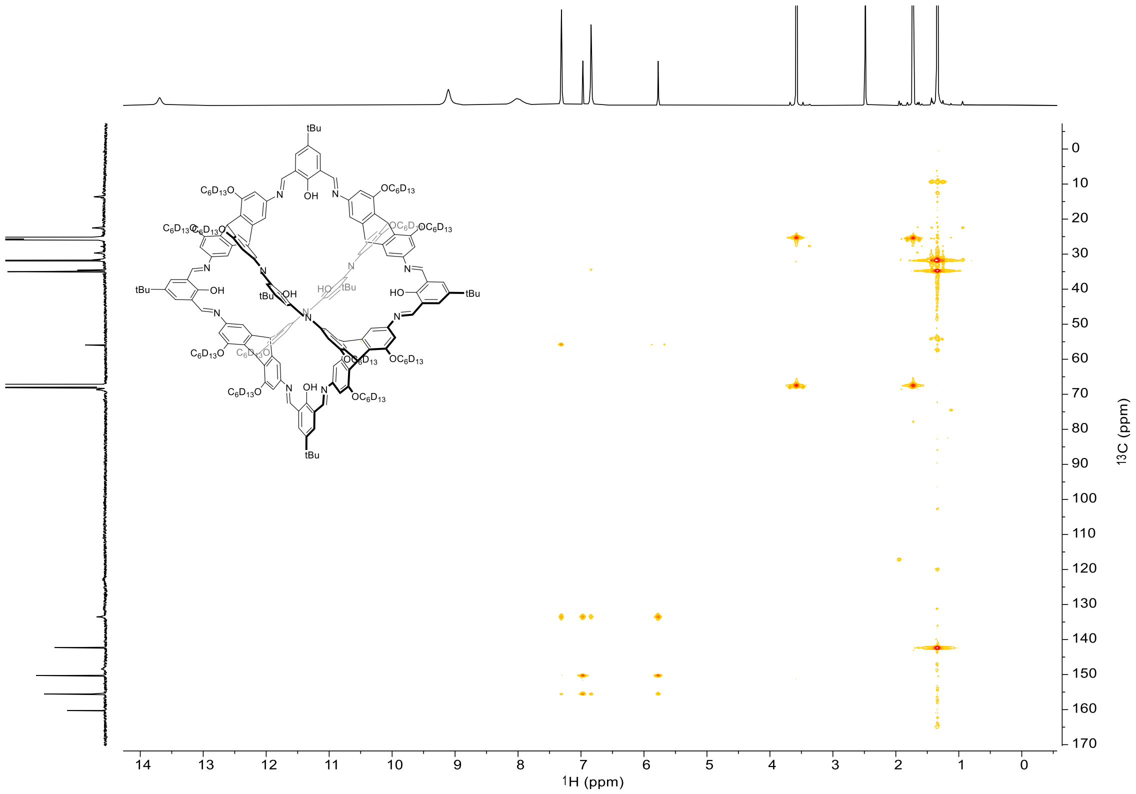


**Figure S93.** $^1$H,$^{13}$C HMBC spectrum (700 MHz, 176 MHz, THF-d$_8$) of *tert*-butylated [4+6]-*endo* cage **14-d$_{156}$**.

**Table S29.** Correlations of $^{1}$H,$^{13}$C-HSQC and $^{1}$H,$^{13}$C-HMBC spectra of *tert*-butylated [4+6]-*endo* cage **14-d$_{156}$**.

| $^{13}$C nucleus | $\delta_{13C}$ [ppm] | $^{1}$H nucleus | | |
|---|---|---|---|---|
| | | HSQC | $\delta_{1H}$ [ppm] | HMBC |
| *A* | 160.3 | - | - | - |
| *B* | 155.5 | - | - | *d, e, f, g* |
| *C* | 150.3 | - | - | *e, g* |
| *D* | 148.4 | - | - | - |
| *E* | 142.3 | - | - | *h* |
| *F* | 133.5 | - | - | *d, e, f, g* |
| *G* | 123.0 | - | - | - |
| *H* | 69.0 – 68.3 | - | - | - |
| *I* | 55.9 | *g* | 5.77 | *d* |
| *J* | 35.0 | - | - | *h* |
| *K* | 34.6 | *e* | 6.97 | *f* |
| *L* | 31.9 | *h* | 1.34 | *h* |
| *M* | 31.8 – 31.3 | - | - | - |
| *N* | 30.0 – 29.3 | - | - | - |
| *O* | 22.9 – 22.05 | - | - | - |
| *P* | 14.01 – 13.2 | - | - | - |

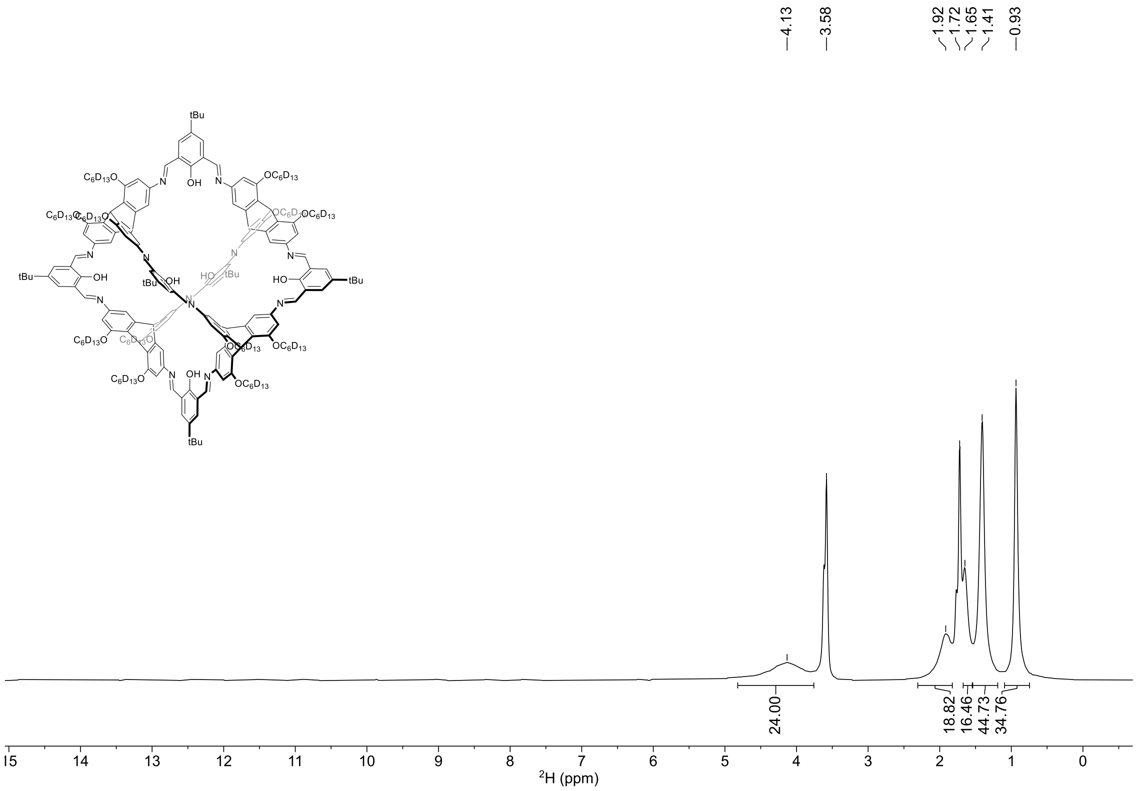


**Figure S94.** $^{2}$H NMR spectrum (92 MHz, THF/THF-d$_{8}$) of *tert*-butylated [4+6]-*endo* cage **14-d$_{156}$**.

# 4 DOSY Spectra

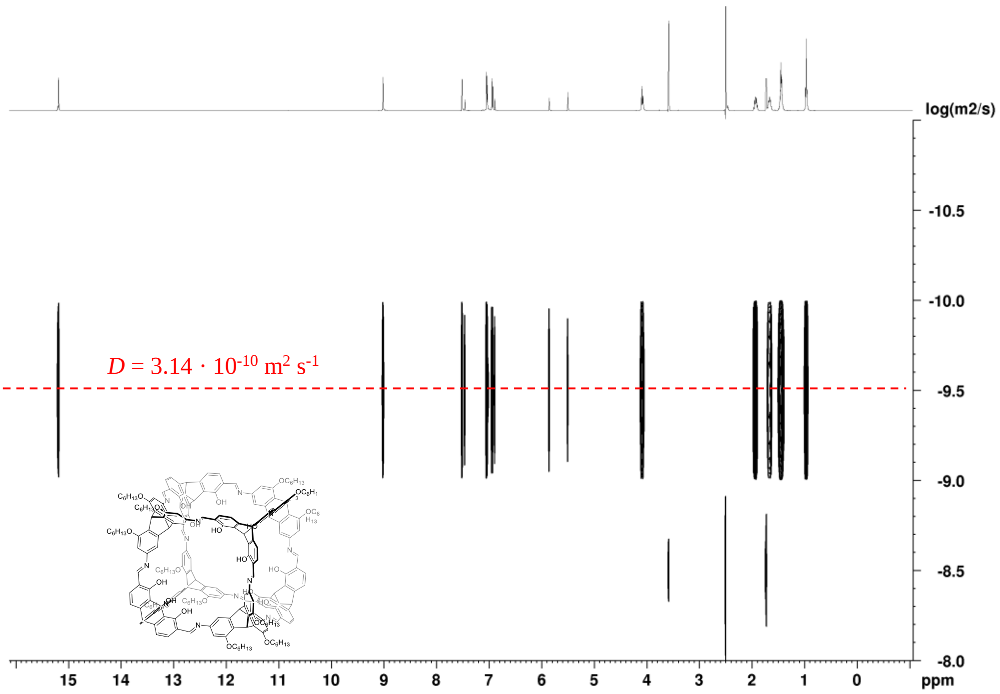


**Figure S95.** $^1$H-DOSY spectrum (400 MHz, THF-$d_8$) of [4+4] cube **11**.

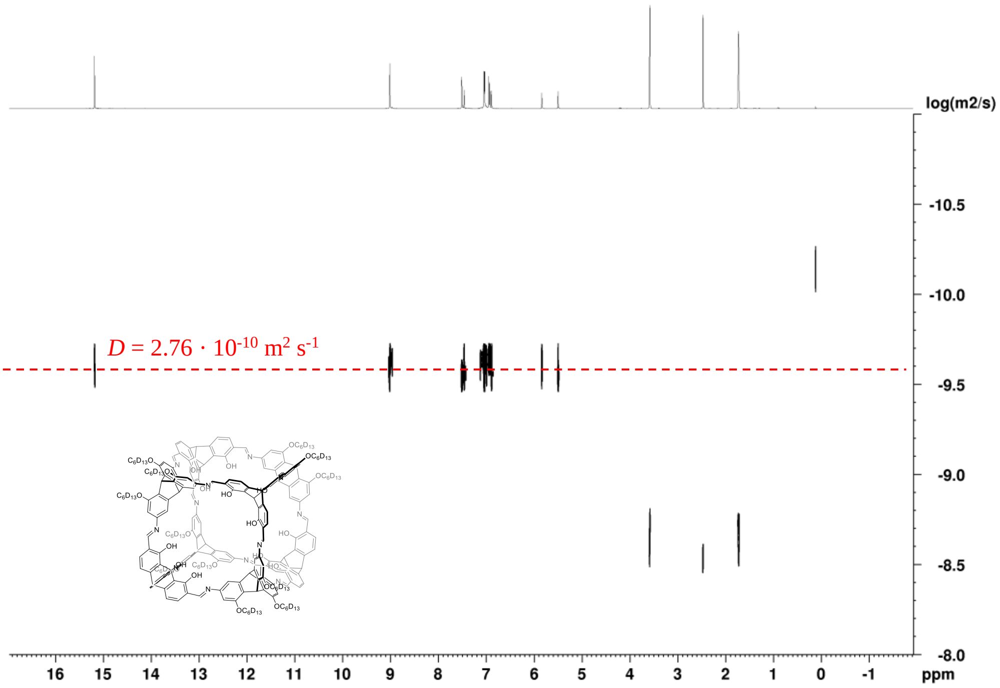


**Figure S96.** $^1$H-DOSY spectrum (400 MHz, THF-$d_8$) of [4+4] cube **11-d$_{156}$**.

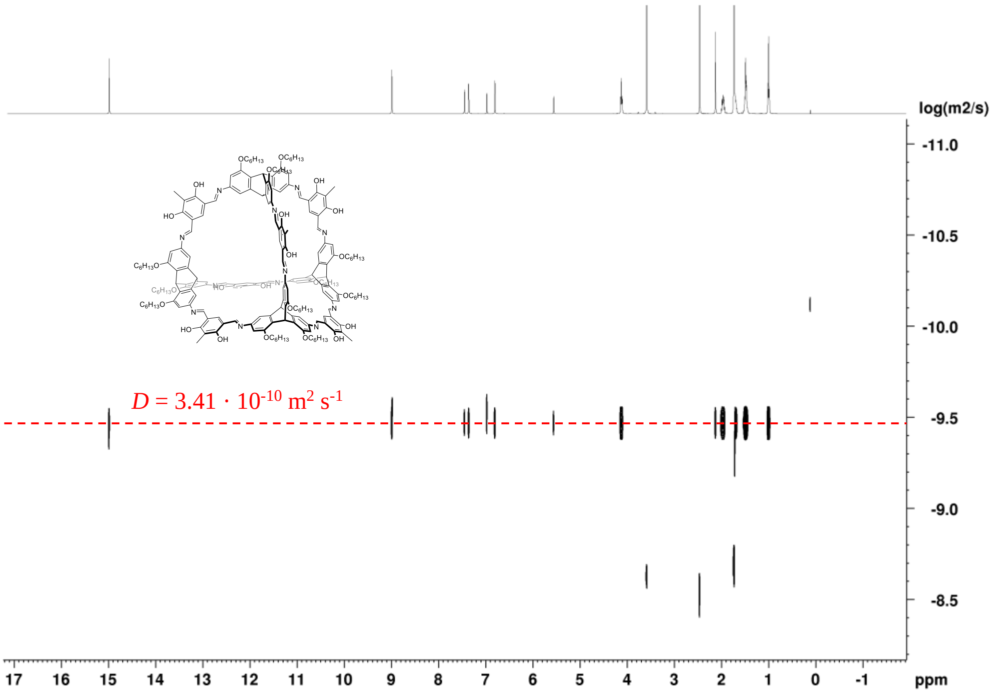


**Figure S97.** $^1$H-DOSY spectrum (400 MHz, THF-$d_8$) of [4+6]-*exo* cage **12**.

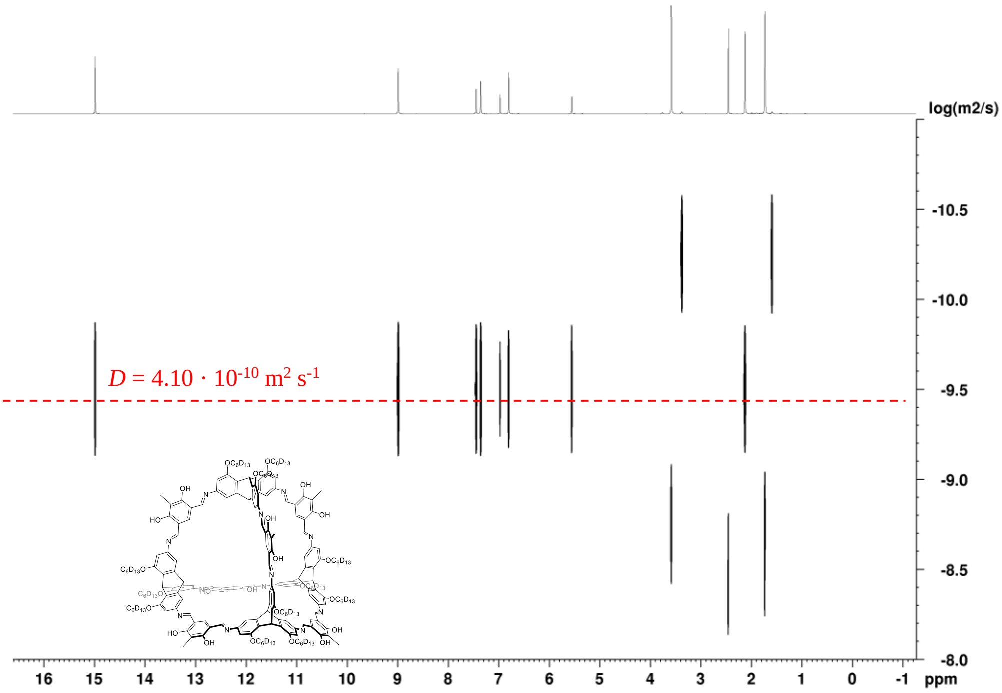


**Figure S98.** $^1$H-DOSY spectrum (400 MHz, THF-$d_8$) of [4+6]-*exo* cage **12-d$_{156}$**.

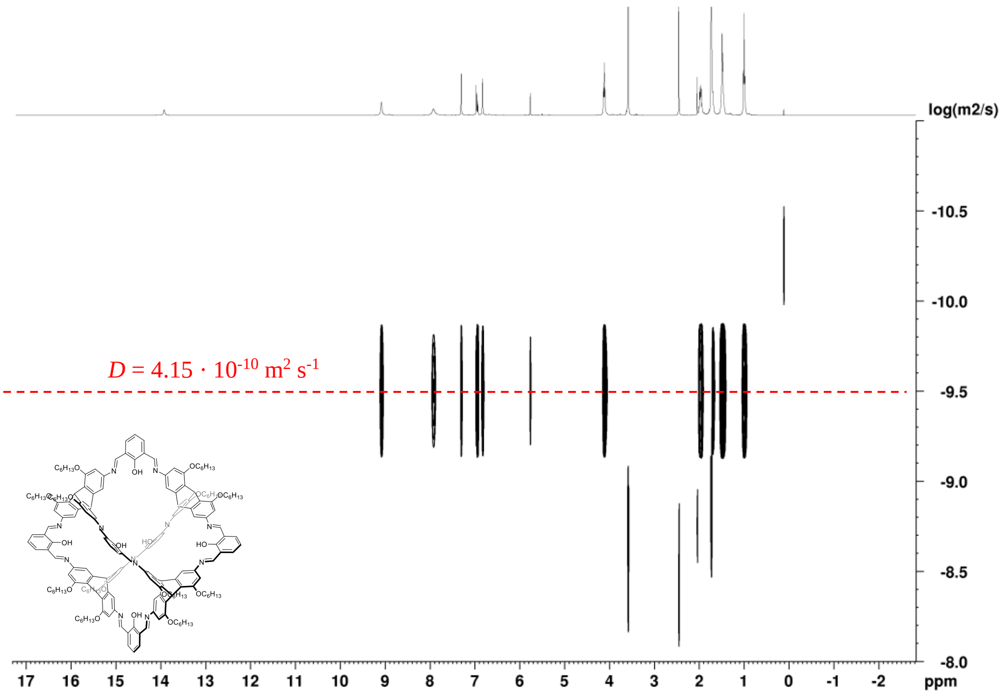


**Figure S99.** ${}^1$H-DOSY spectrum (400 MHz, THF-$d_8$) of [4+6]-*endo* cage **13**.

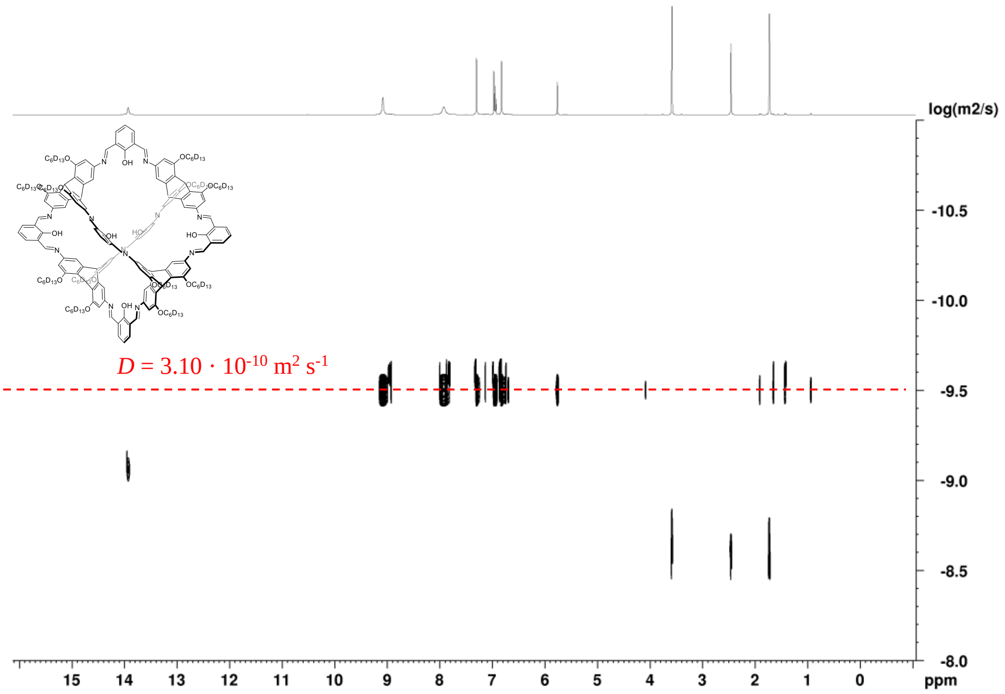


**Figure S100.** ${}^1$H-DOSY spectrum (400 MHz, THF-$d_8$) of [4+6]-*endo* cage **13-d$_{156}$**.

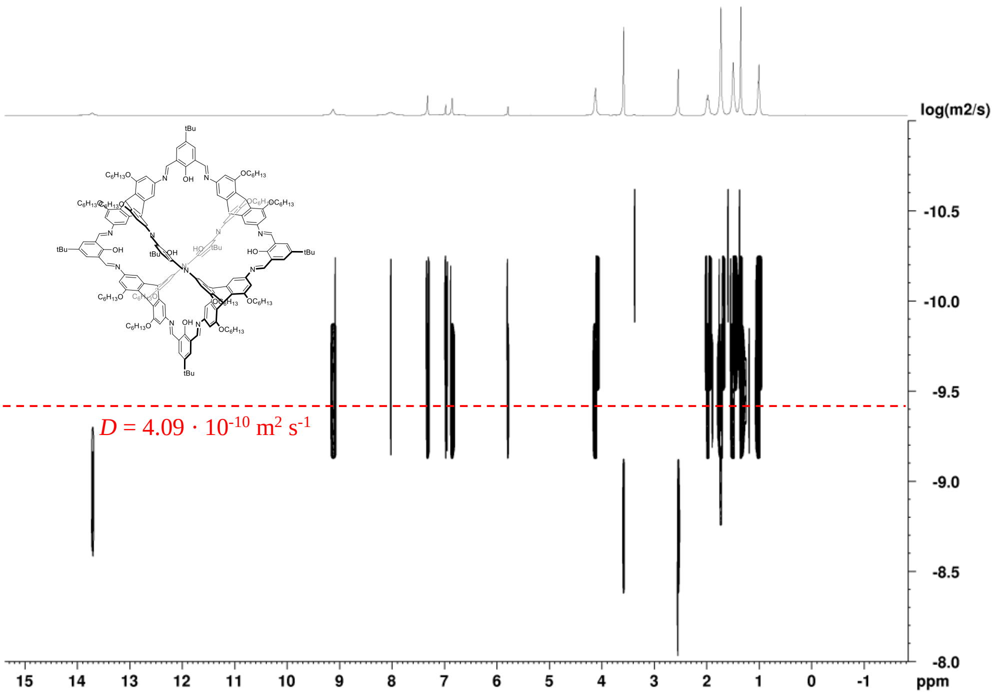


**Figure S101.** $^1$H-DOSY spectrum (400 MHz, THF-$d_8$) of *tert*-butylated [4+6]-*endo* cage **14**.

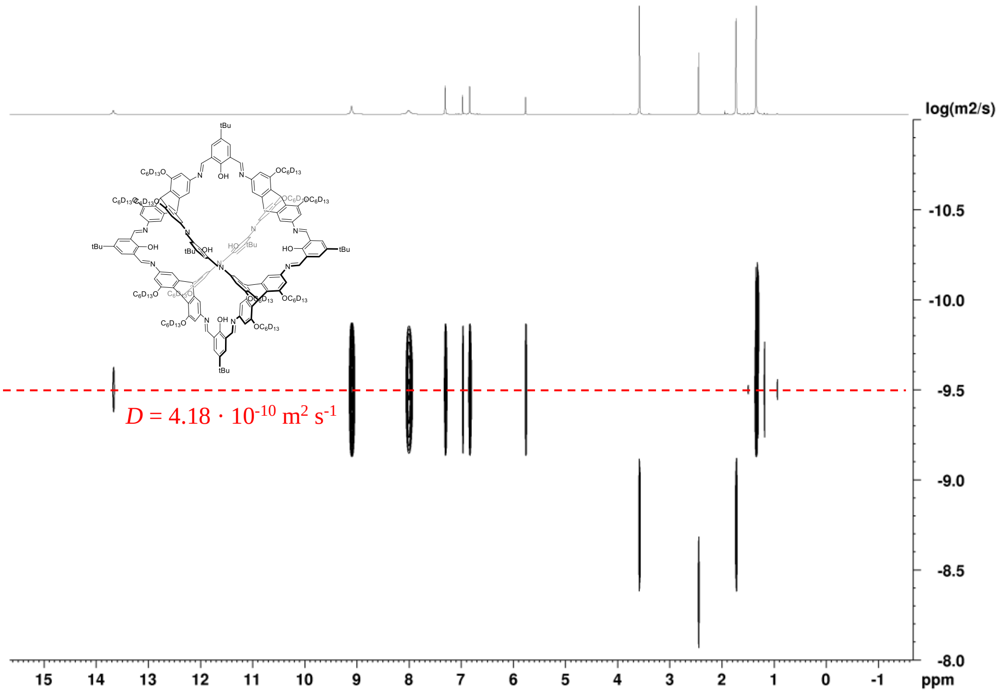


**Figure S102.** $^1$H-DOSY spectrum (400 MHz, THF-$d_8$) of *tert*-butylated [4+6]-*endo* cage **14-d$_{156}$**.

# 5 Mass Spectra of Cage Compounds

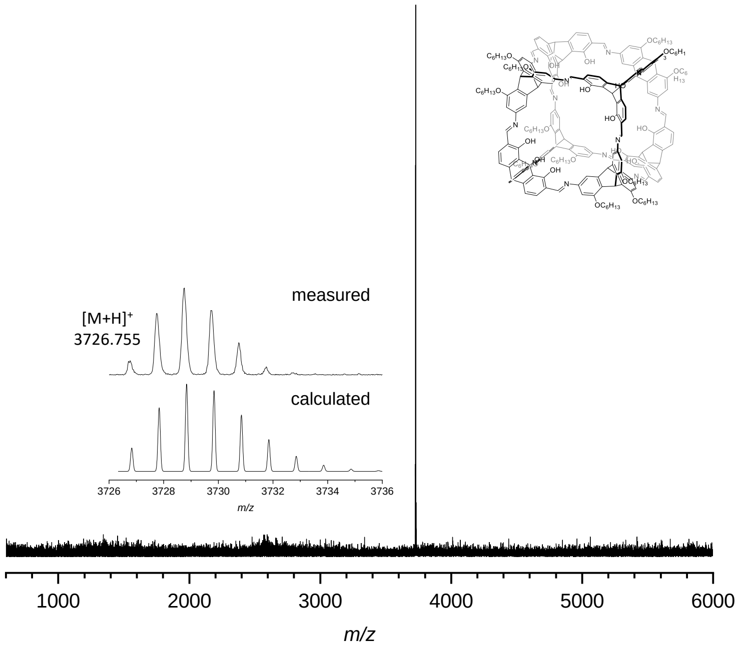


**Figure S103.** MALDI-TOF mass spectrum of the [4+4] cube **11** (DCTB matrix, reflector mode, positive polarisation).

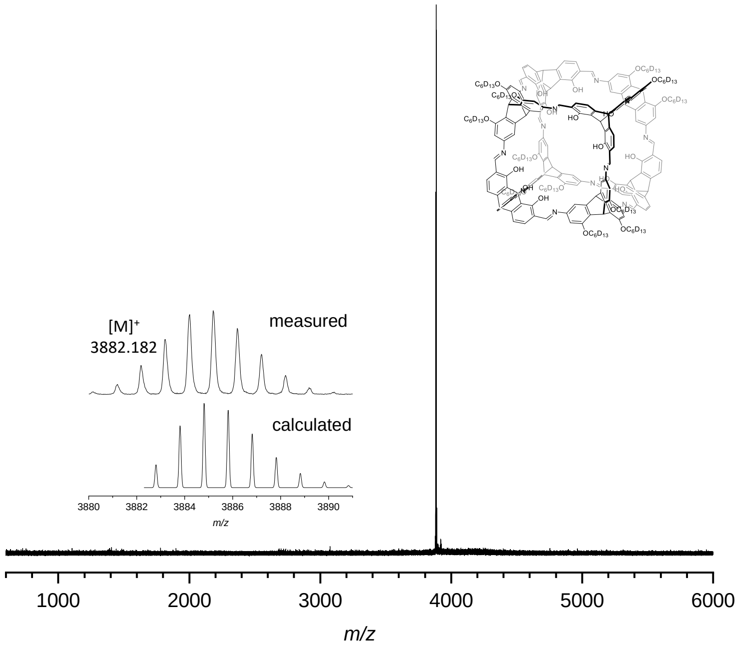


**Figure S104.** MALDI-TOF mass spectrum of the [4+4] cube **11-d$_{156}$** (DCTB matrix, reflector mode, positive polarisation).

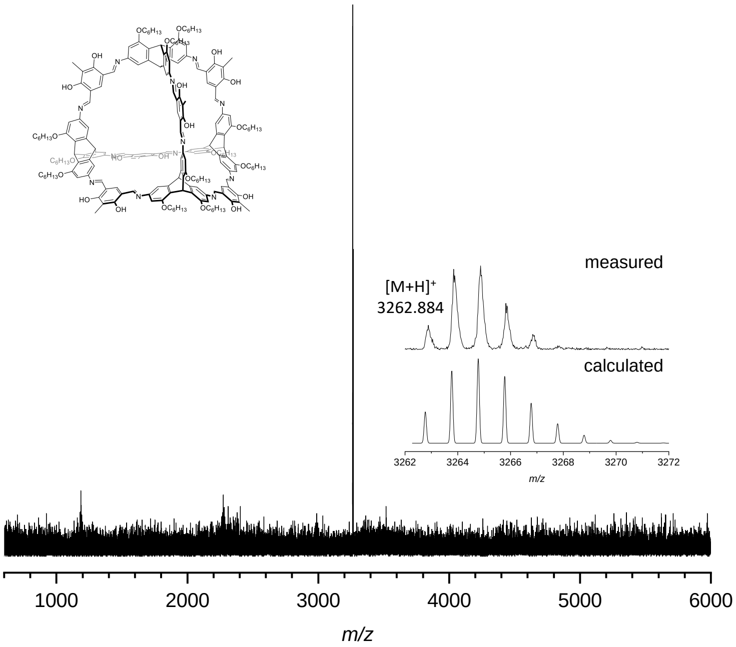


**Figure S105.** MALDI-TOF mass spectrum of the [4+6]-*exo* cage **12** (DCTB matrix, reflector mode, positive polarisation).

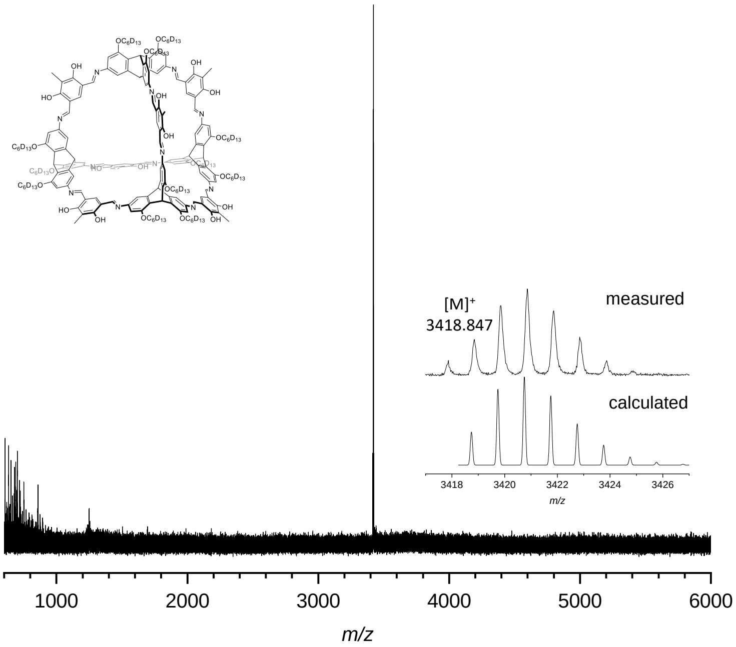


**Figure S106.** MALDI-TOF mass spectrum of the [4+6]-*exo* cage **12-d$_{156}$** (DCTB matrix, reflector mode, positive polarisation).

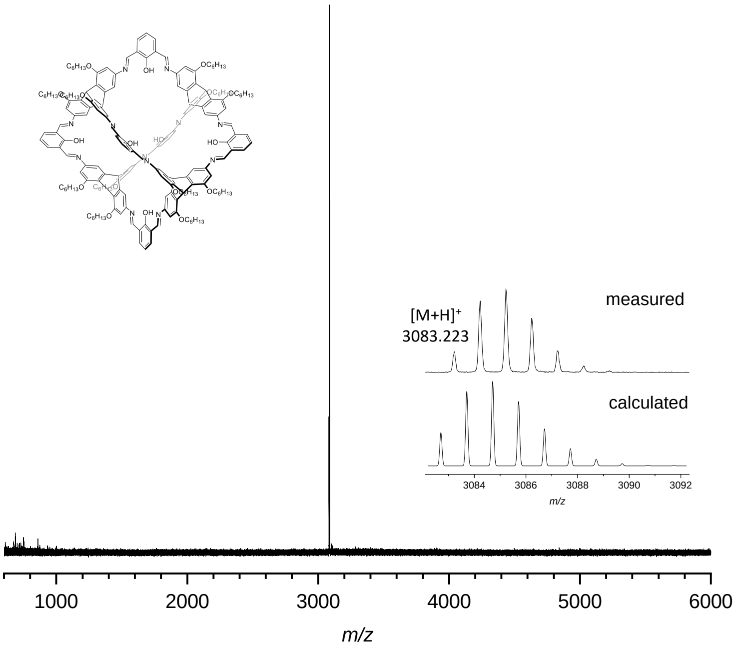


**Figure S107.** MALDI-TOF mass spectrum of the [4+6]-*endo* cage **13** (DCTB matrix, reflector mode, positive polarisation).

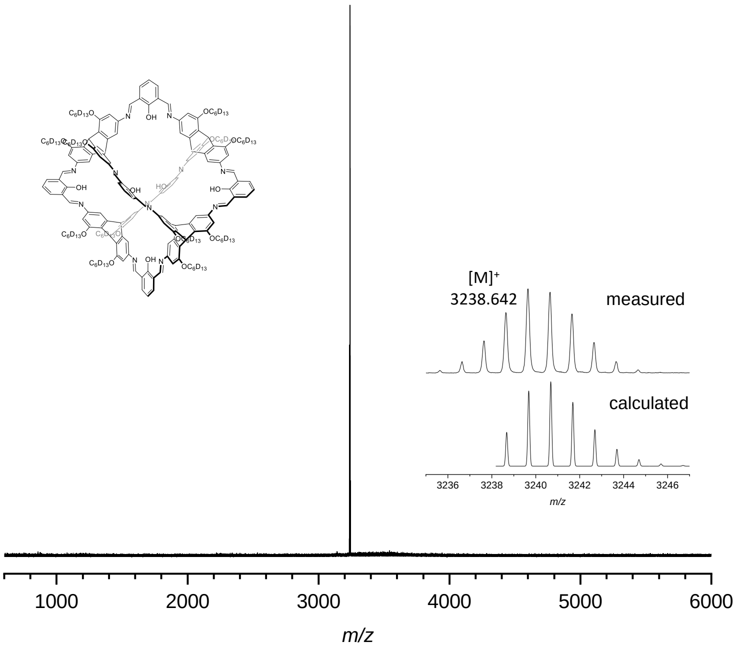


**Figure S108.** MALDI-TOF mass spectrum of the [4+6]-*endo* cage **13-d$_{156}$** (DCTB matrix, reflector mode, positive polarisation).

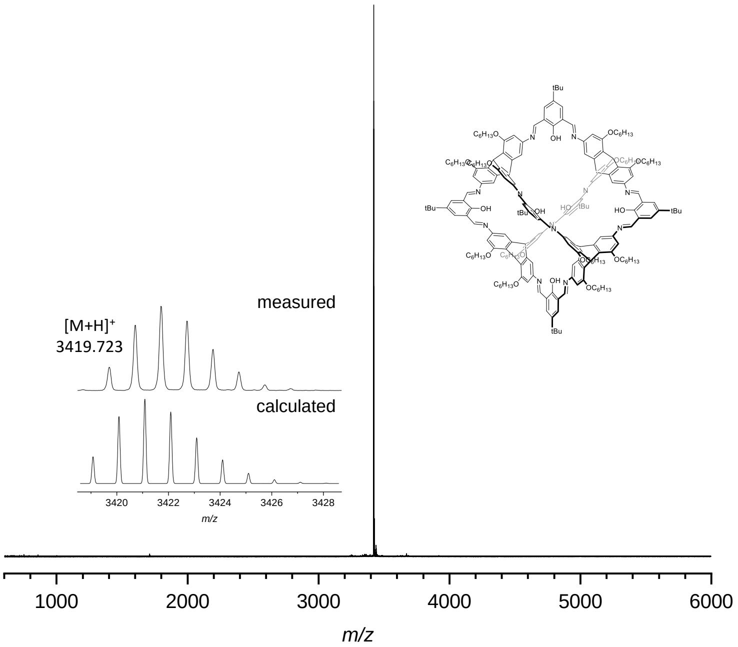


**Figure S109.** MALDI-TOF mass spectrum of the *tert*-butyl substituted [4+6]-*endo* cage **14** (DCTB matrix, reflector mode, positive polarisation).

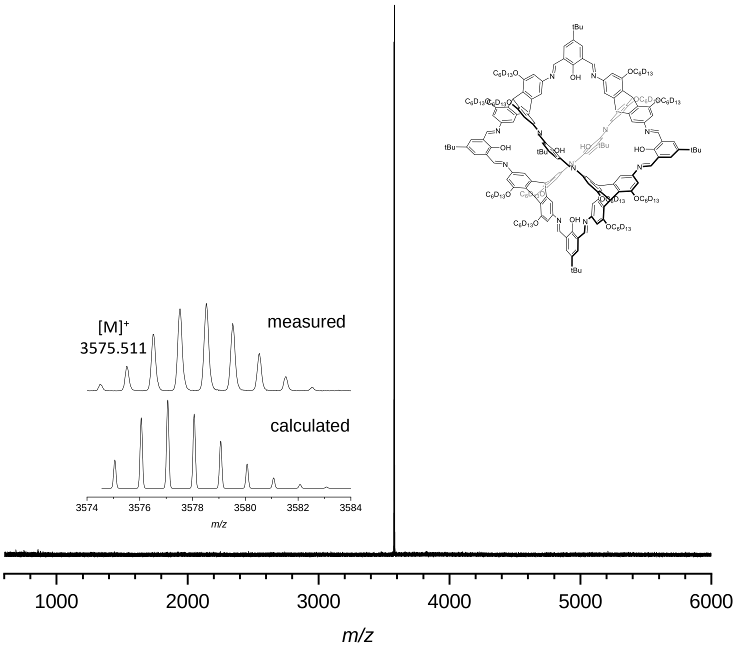


**Figure S110.** MALDI-TOF mass spectrum of the *tert*-butyl substituted [4+6]-*endo* cage **14-d$_{156}$** (DCTB matrix, reflector mode, positive polarisation).

# 6 IR Spectra

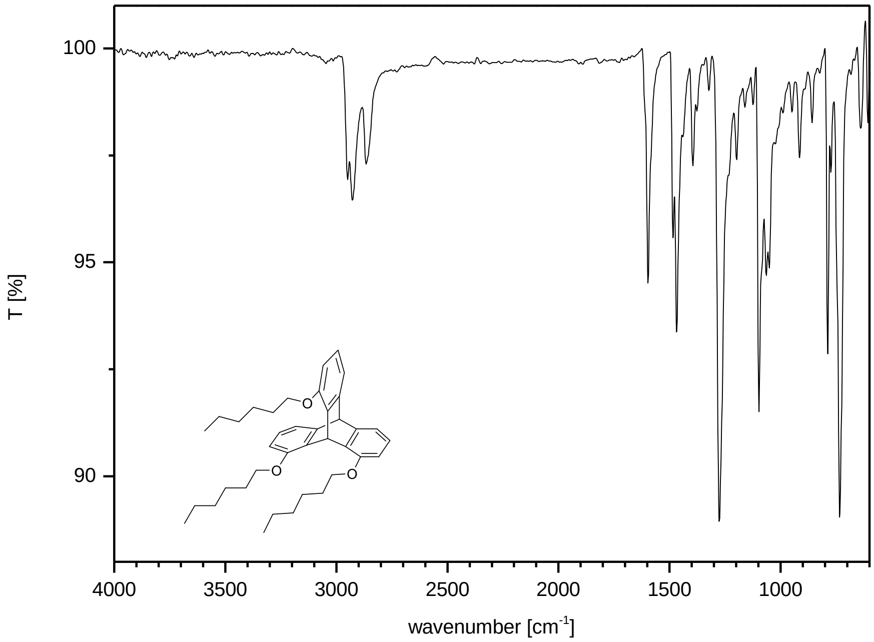


**Figure S111.** FT-IR spectrum of compound **5** (ATR, ZnSe).

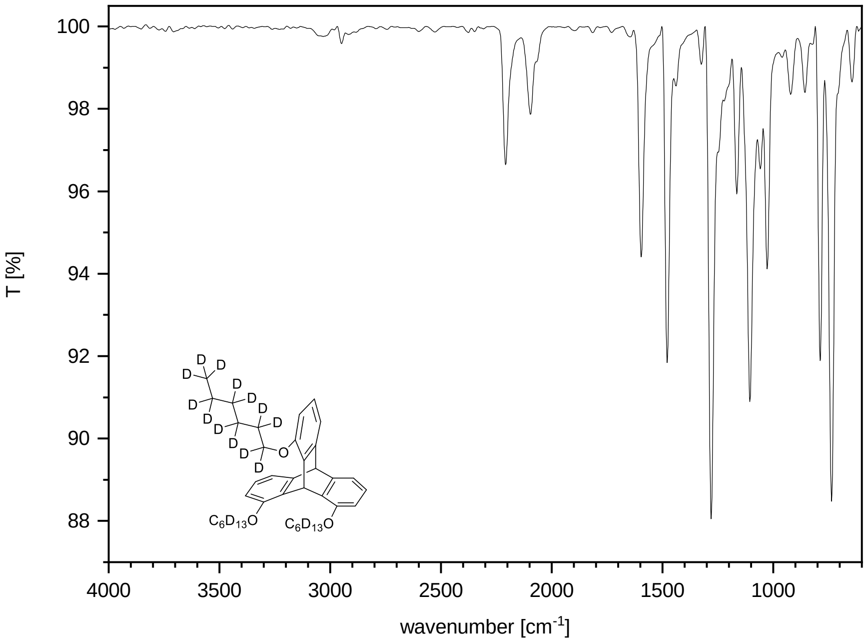


**Figure S112.** FT-IR spectrum of compound **5-d<sub>39</sub>** (ATR, ZnSe).

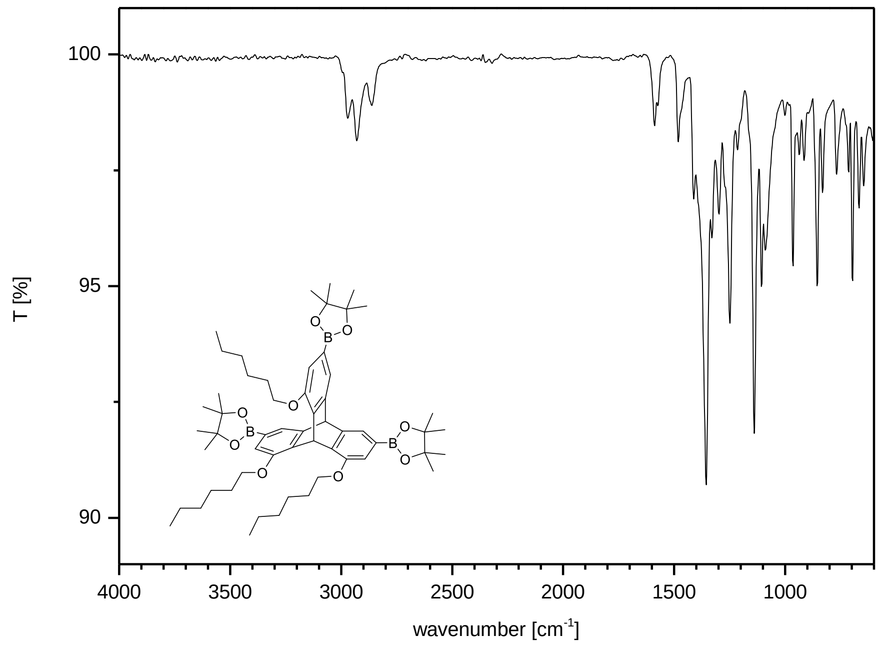


**Figure S113.** FT-IR spectrum of compound **6** (ATR, ZnSe).

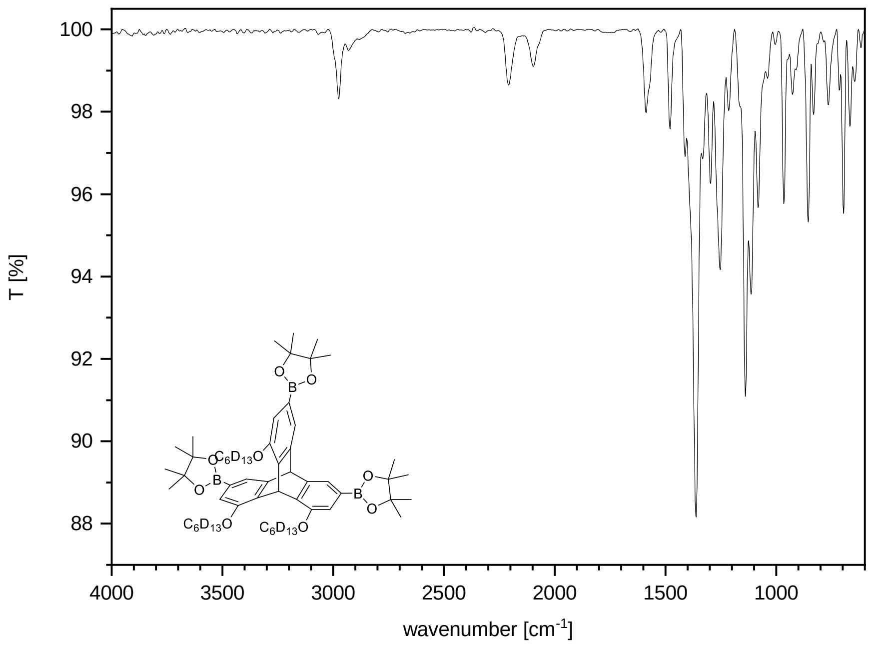


**Figure S114.** FT-IR spectrum of compound **6-d$_{39}$** (ATR, ZnSe).

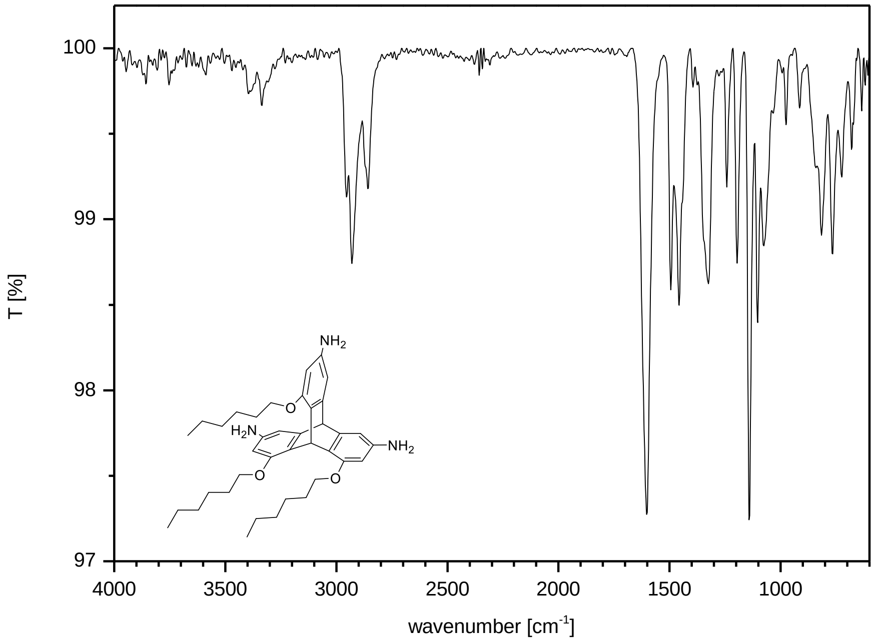


**Figure S115.** FT-IR spectrum of compound **7a** (ATR, ZnSe).

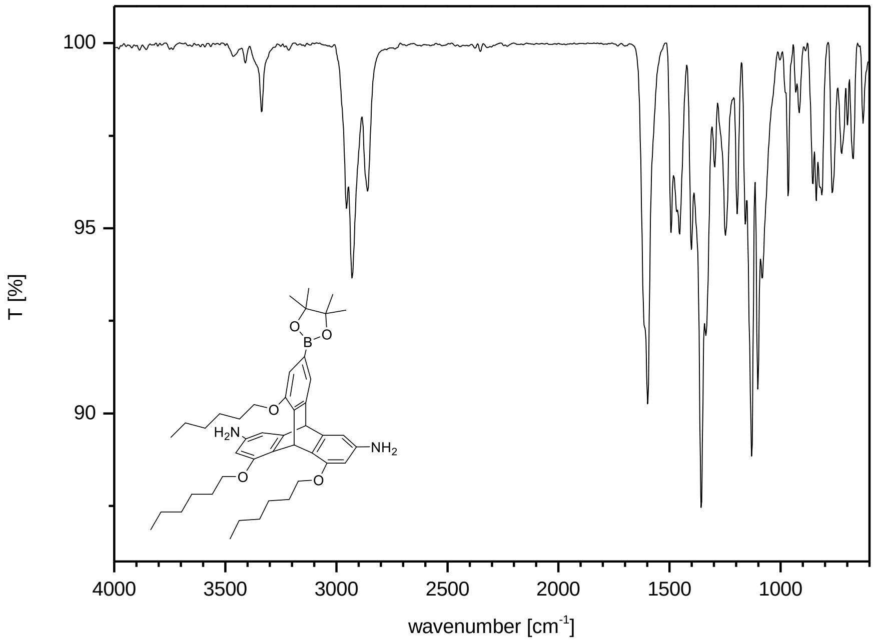


**Figure S116.** FT-IR spectrum of compound **7b** (ATR, ZnSe).

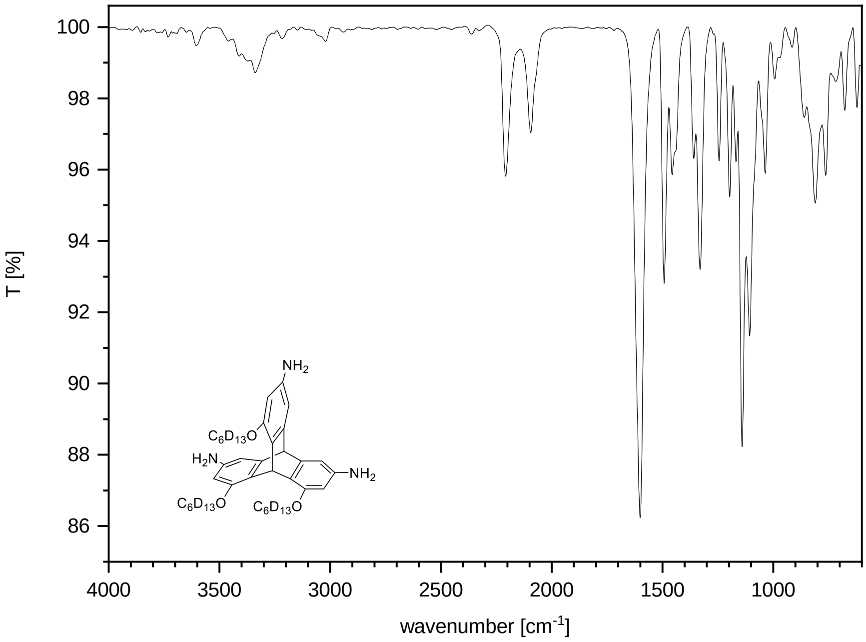


**Figure S117.** FT-IR spectrum of compound **7a-d39** (ATR, ZnSe).

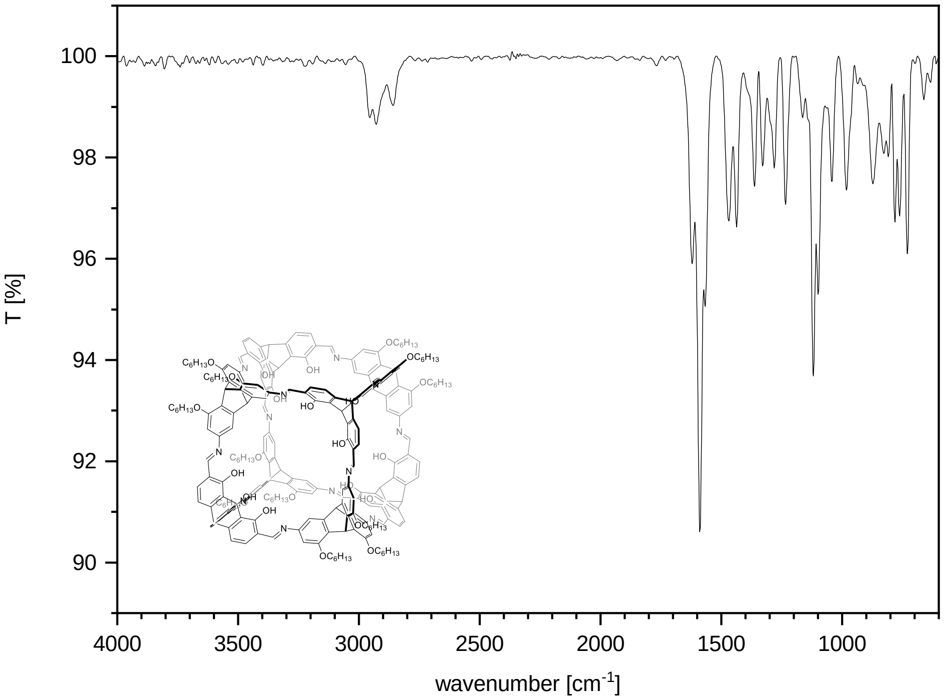


**Figure S118.** FT-IR spectrum of [4+4] cube **11** (ATR, ZnSe).

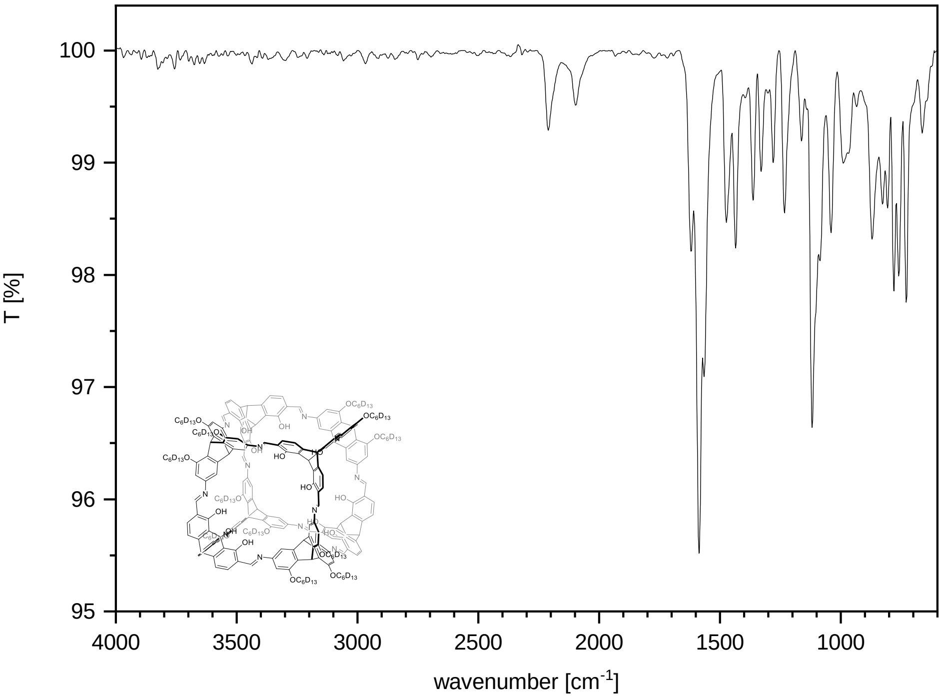


**Figure S119.** FT-IR spectrum of [4+4] cube **11-d$_{156}$** (ATR, ZnSe).

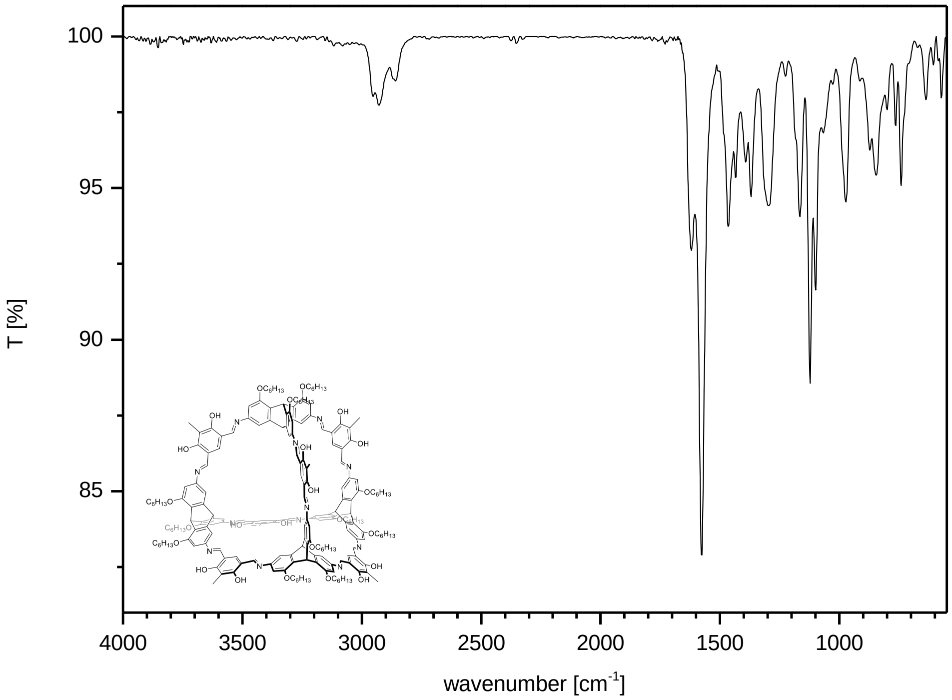


**Figure S120.** FT-IR spectrum of [4+6]-*exo* cage **12** (ATR, ZnSe).

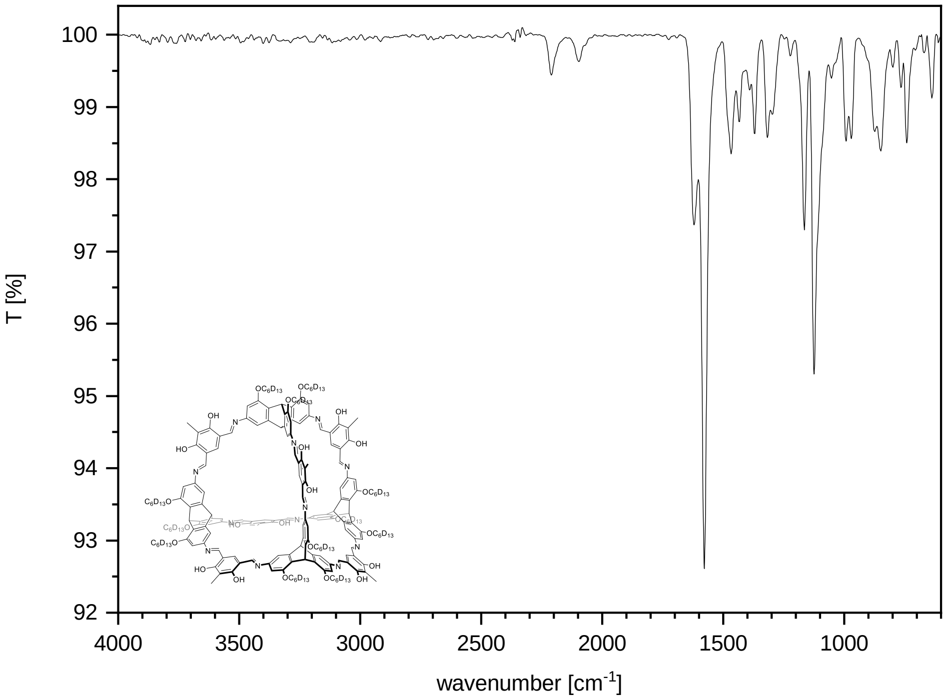


**Figure S121.** FT-IR spectrum of [4+6]-*exo* cage **12-d$_{156}$** (ATR, ZnSe).

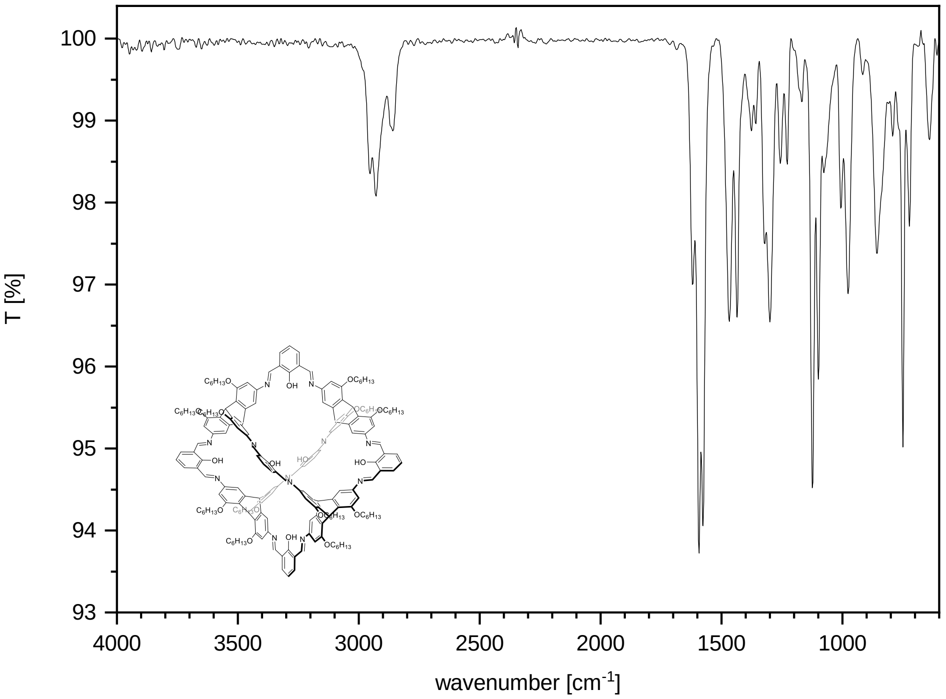


**Figure S122.** FT-IR spectrum of [4+6]-*endo* cage **13** (ATR, ZnSe).

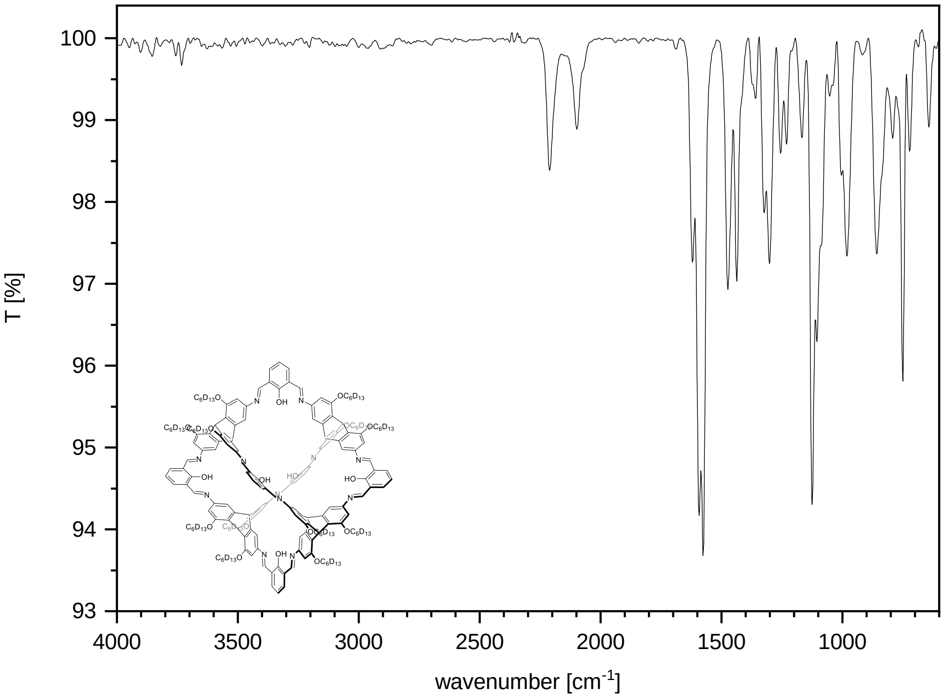


**Figure S123.** FT-IR spectrum of [4+6]-*endo* cage **13-d$_{156}$** (ATR, ZnSe).

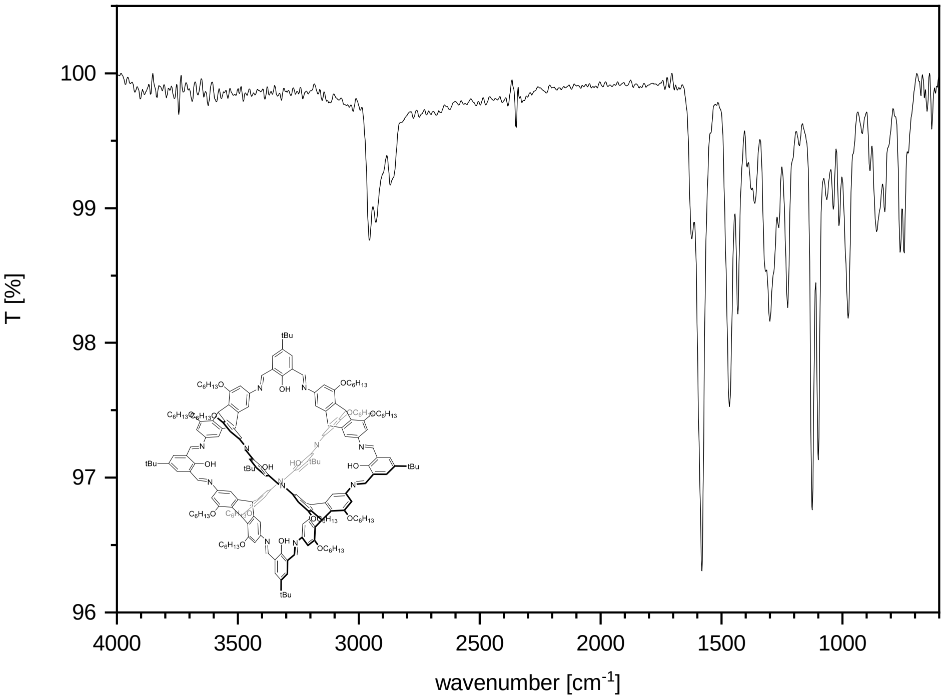


**Figure S124.** FT-IR spectrum of *tert*-butylated [4+6]-*endo* cage **14** (ATR, ZnSe).

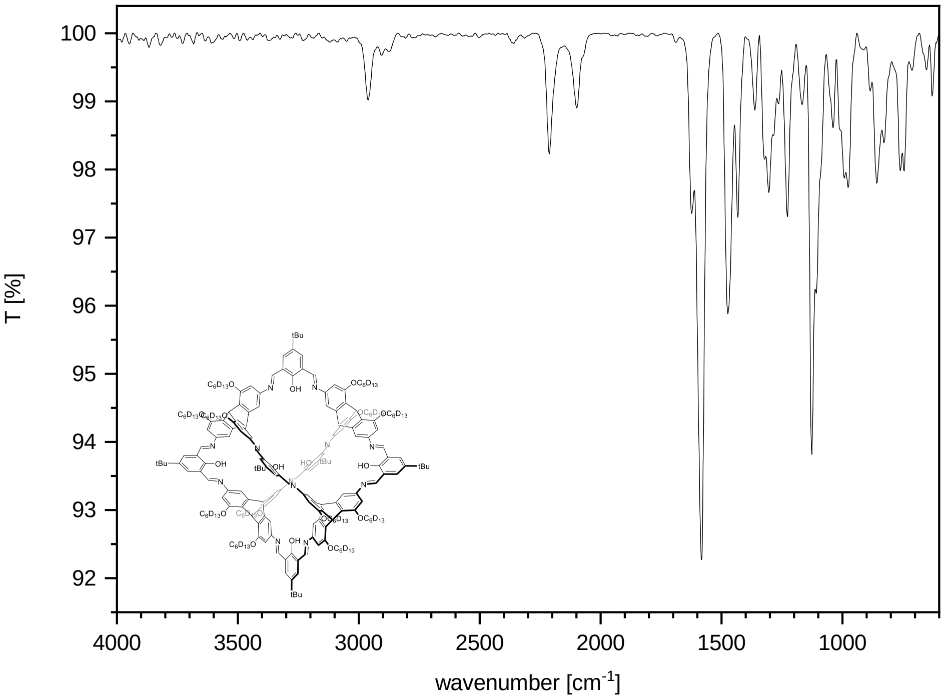


**Figure S125.** FT-IR spectrum of *tert*-butylated [4+6]-*endo* cage **14-d₁₅₆** (ATR, ZnSe).

# 7 UV/vis spectra

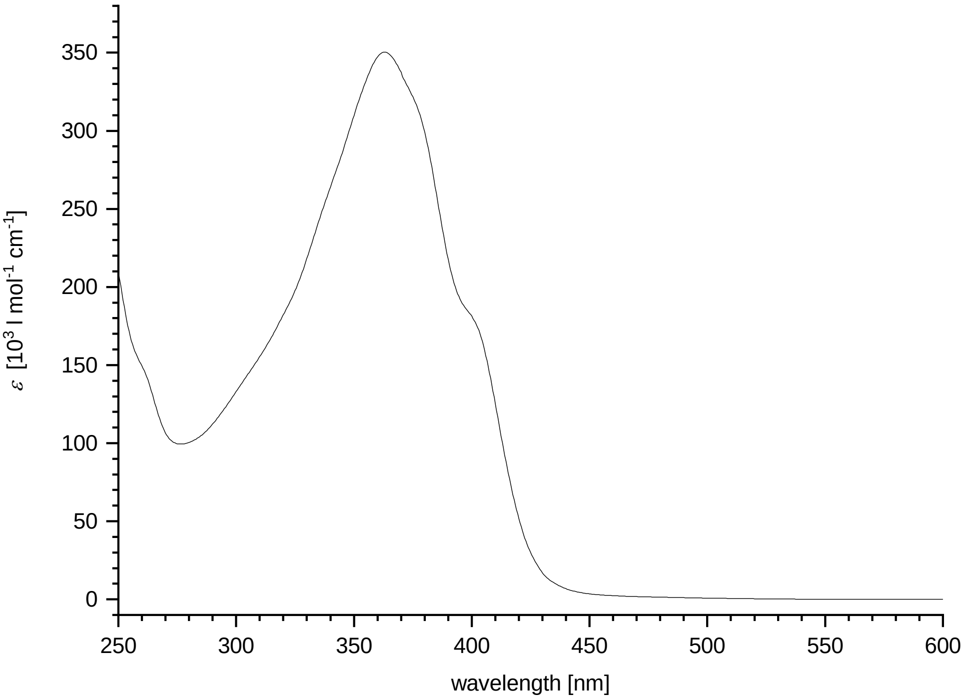


**Figure S126.** UV/vis spectrum of [4+4] cube **11** in THF.

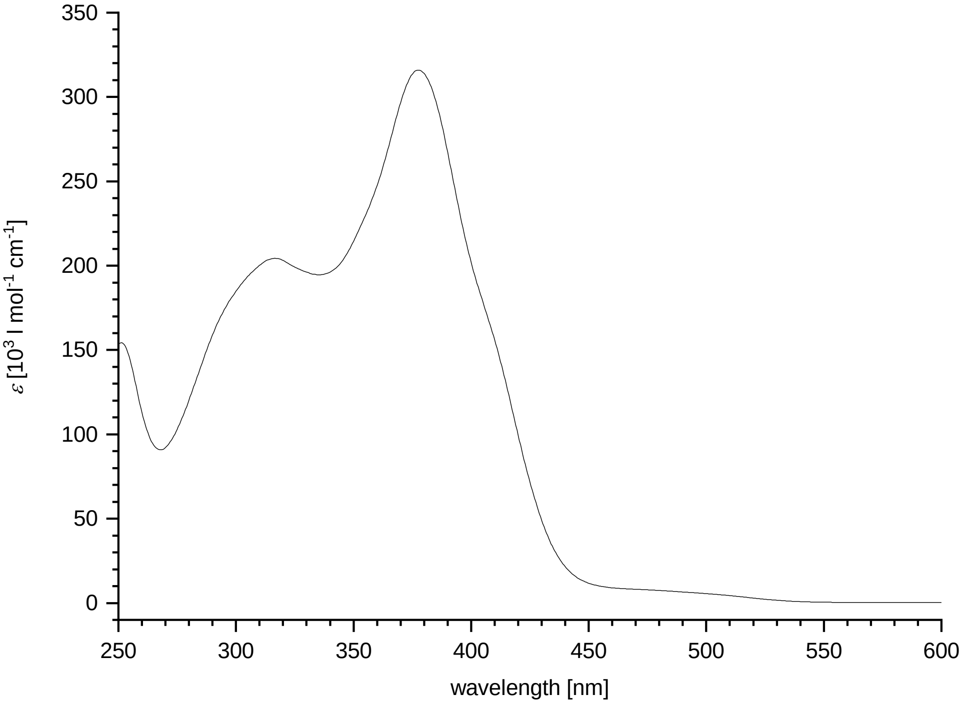


**Figure S127**. UV/vis spectrum of [4+6]-*exo* cage **12** in THF.

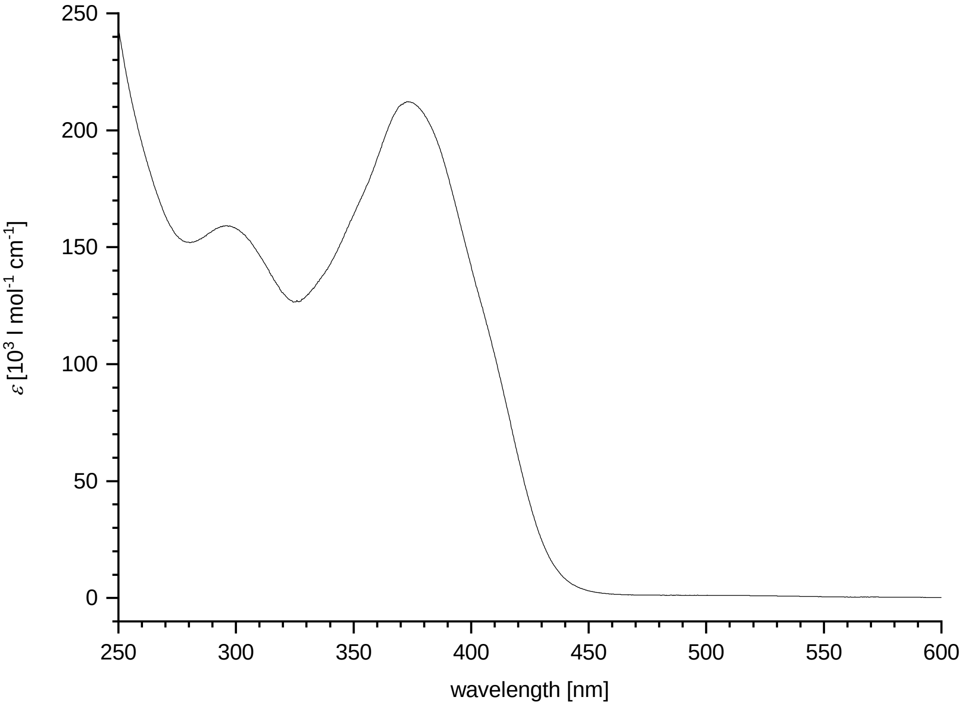


**Figure S128.** UV/vis spectrum of [4+6]-*endo* cage **13** in THF.

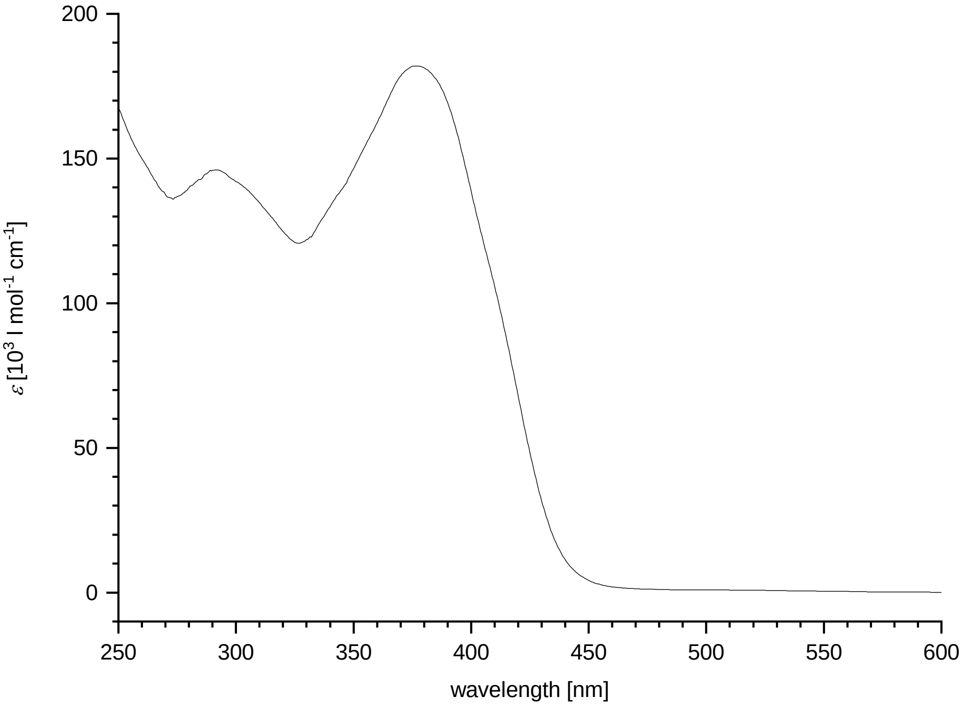


**Figure S129.** UV/vis spectrum of *tert*-butylated [4+6]-*endo* cage **14** in THF.

# 8 GPC Chromatograms

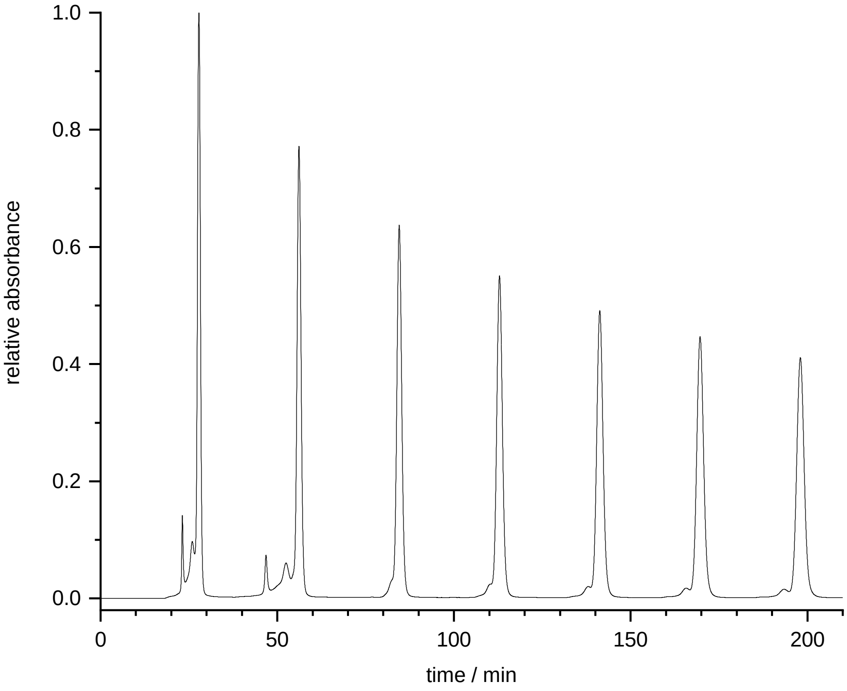


**Figure S130.** GPC chromatogram of crude [4+4] cube **11** using THF as mobile phase.

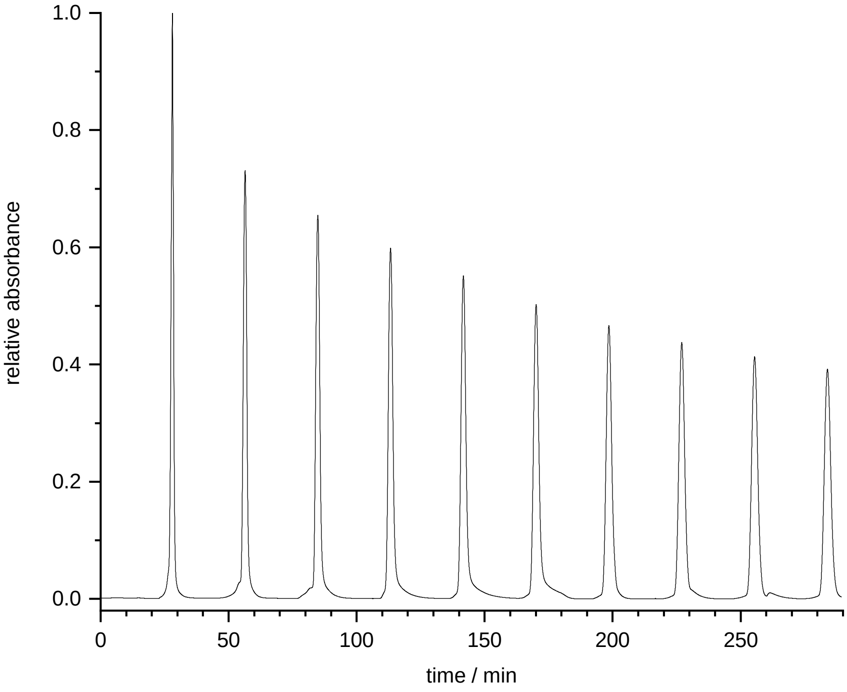


**Figure S131.** GPC chromatogram of [4+6]-*exo* cage **12** after washing with DMSO and methanol using THF as mobile phase.

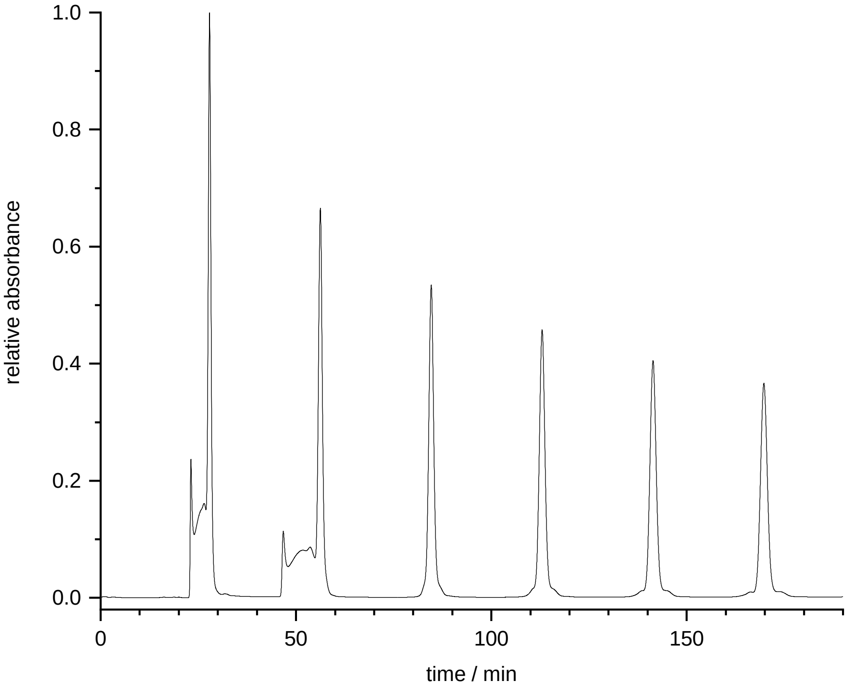


**Figure S132.** GPC chromatogram of crude [4+6]-*endo* cage **13** after stirring with molecular sieves (3 Å) and filtration through diatomaceous earth powder using THF as mobile phase.

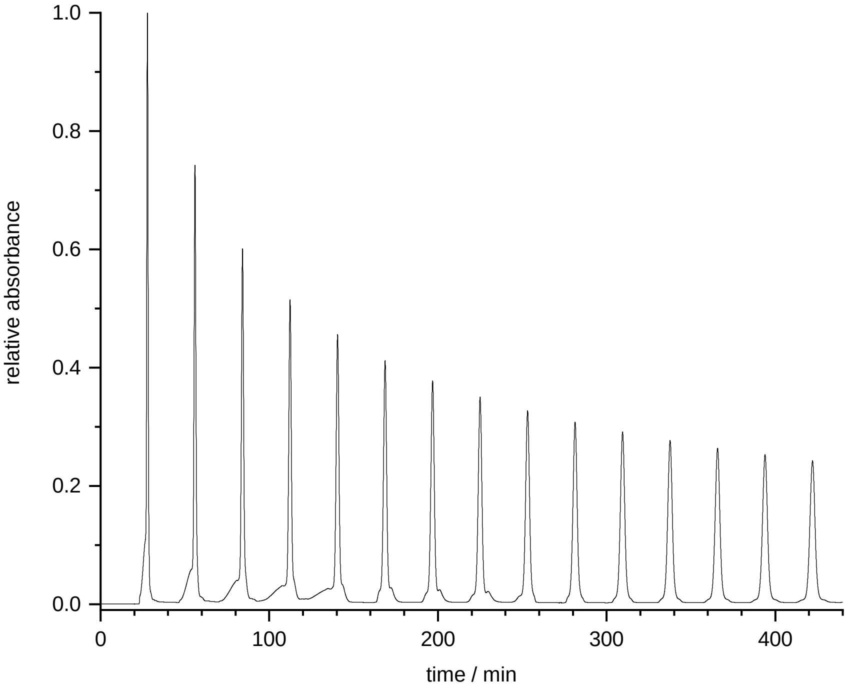


**Figure S133.** GPC chromatogram of *tert*-butylated [4+6]-*endo* cage **14** after stirring with molecular sieves (3 Å) and filtration through Celite.

# 9 Crystallographic Data

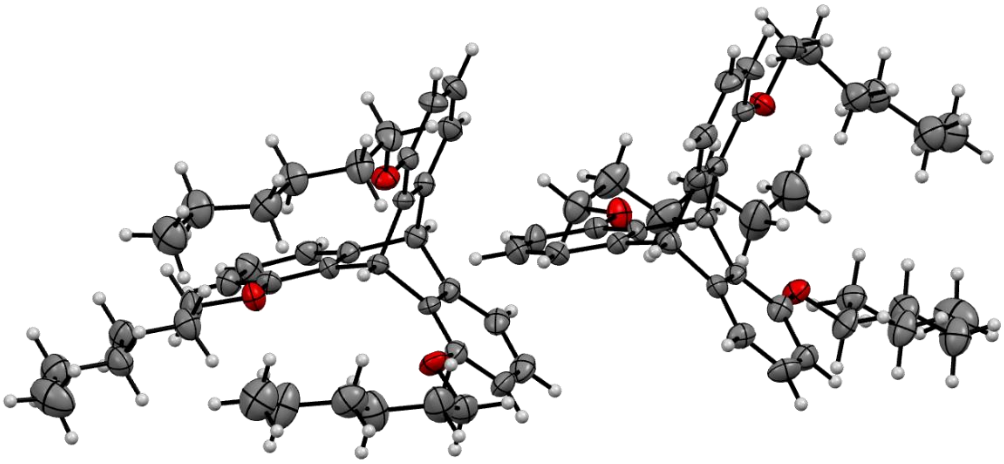


**Figure S134.** X-ray crystal structure of compound **5**. Atoms are illustrated as thermal ellipsoids with 50% probability. Grey: carbon, white: hydrogen, red: oxygen. Crystals were obtained via slow evaporation of a **5** containing $CDCl_3$ solution in an NMR tube at room temperature.

| | |
|---|---|
| CCDC | 2060523 |
| Empirical formula | $C_{38}H_{50}O_3$ |
| Formula weight | 554.78 |
| Temperature [K] | 200(2) |
| $\lambda(Cu_{K\alpha})$ [Å] | 1.54178 |
| Crystal system | monoclinic |
| Space group | $P2_1$ |
| *Z* | 2 |
| *a* [Å] | 13.9339(12) |
| *b* [Å] | 8.0969(6) |
| *c* [Å] | 14.6140(13) |
| *α* [°] | 90 |
| *β* [°] | 100.695(7) |
| *γ* [°] | 90 |
| Volume [Å$^3$] | 1620.1(2) |
| *ρ* (calculated) [mg mm$^{-3}$] | 1.14 |
| *μ* [mm$^{-1}$] | 0.54 |
| Crystal shape | plate |
| Crystal size [mm$^3$] | 0.057 x 0.041 x 0.012 |
| Crystal colour | colourless |
| *Θ* range for data collection [°] | 3.1 to 69.5 |
| Index ranges | $-16 \le h \le 10$, $-9 \le k \le 8$, $-16 \le l \le 17$ |
| Reflections collected | 11486 |
| Independent reflections | 4884 ($R_{int}$ = 0.1139) |
| Observed reflections | 2824 ($I > 2\sigma(I)$) |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.41 and 0.73 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 4884 / 1 / 373 |
| Goodness-of-fit on $F^2$ | 1.07 |
| Final R indices ($I > 2\sigma(I)$) | $R_1$ = 0.073, $wR_2$ = 0.122 |
| Largest diff. peak and hole [e Å$^{-3}$] | 0.24 and -0.25 |
| Resolution [Å] | 0.82 |

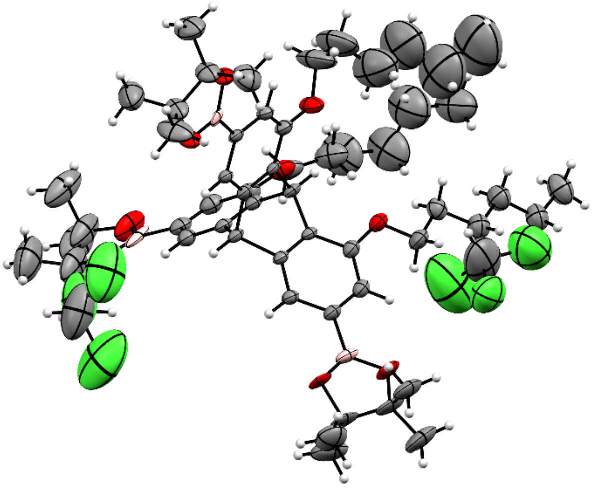


**Figure S135.** X-ray crystal structure of compound **6** co-crystallised with two chloroform molecules. Atoms are illustrated as thermal ellipsoids with 50% probability. Grey: carbon, white: hydrogen, red: oxygen, pink: boron, green: chlorine. Crystals were obtained via thermal recrystallization of **6** in ethanol by adding chloroform under reflux conditions.

| | |
|---|---|
| CCDC | 2060524 |
| Empirical formula | $C_{58}H_{85}B_3Cl_6O_9$ |
| Formula weight | 1171.39 |
| Temperature [K] | 200(2) |
| $\lambda(\mathrm{Mo}_{K\alpha})$ [Å] | 0.71073 Å |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| *Z* | 2 |
| *a* [Å] | 12.652(4) |
| *b* [Å] | 12.778(4) |
| *c* [Å] | 22.927(7) |
| *α* [°] | 77.132(8) |
| *β* [°] | 79.236(8) |
| *γ* [°] | 60.982(7) |
| Volume [Å$^3$] | 3146.4(17) |
| *ρ* (calculated) [mg mm$^{-3}$] | 1.24 |
| *μ* [mm$^{-1}$] | 0.32 |
| Crystal shape | polyhedron |
| Crystal size [mm$^3$] | 0.200 x 0.110 x 0.080 |
| Crystal colour | colourless |
| *Θ* range for data collection [°] | 0.9 to 19.4 |
| Index ranges | $-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-21 \leq l \leq 21$ |
| Reflections collected | 17297 |
| Independent reflections | 5362 ($R_{int}$ = 0.1292) |
| Observed reflections | 3063 ($I > 2\sigma(I)$) |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.96 and 0.66 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 5362 / 1644 / 685 |
| Goodness-of-fit on $F^2$ | 1.75 |
| Final R indices ($I > 2\sigma(I)$) | $R_1$ = 0.202, $wR_2$ = 0.491 |
| Largest diff. peak and hole [e Å$^{-3}$] | 0.91 and -0.92 |
| Resolution [Å] | 1.07 |

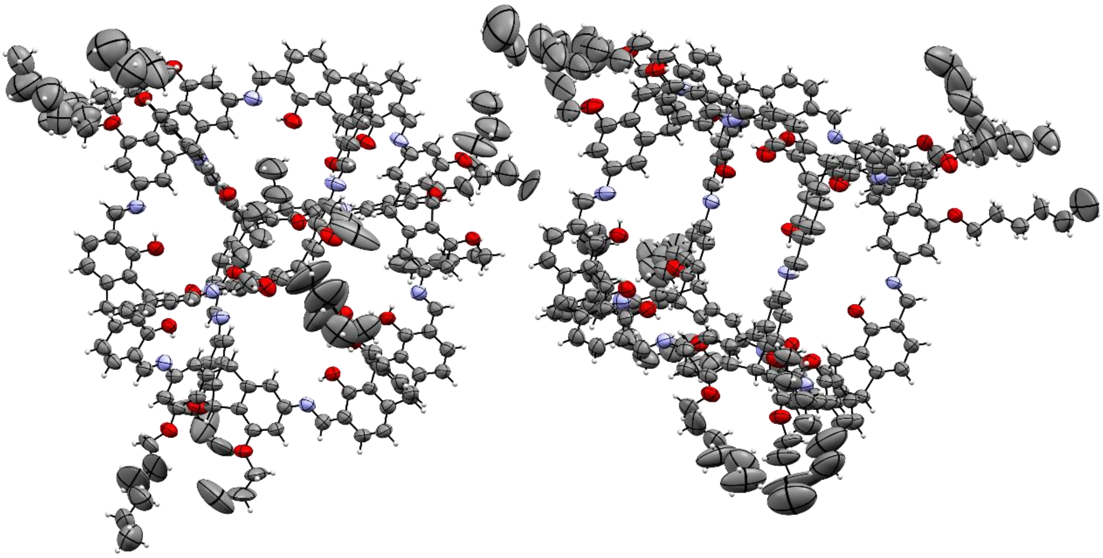


**Figure S136:** X-ray crystal structure of [4+4] cube **11**. Atoms are illustrated as thermal ellipsoids with 50% probability. Grey: carbon, white: hydrogen, blue: nitrogen, red: oxygen. Crystals were obtained via gas phase diffusion of methanol in a solution of [4+4] cube in ethyl acetate at room temperature.

| | |
|---|---|
| CCDC | 2060526 |
| Empirical formula | $C_{488}H_{488}N_{24}O_{48}$ |
| Formula weight | 7457.00 |
| Temperature [K] | 200(2) |
| $\lambda(Cu_{K\alpha})$ [Å] | 1.54178 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| $Z$ | 2 |
| $a$ [Å] | 25.1707(5) |
| $b$ [Å] | 32.4180(6) |
| $c$ [Å] | 40.0124(8) |
| $\alpha$ [°] | 85.230(2) |
| $\beta$ [°] | 85.835(2) |
| $\gamma$ [°] | 71.082(1) |
| Volume [Å$^3$] | 30742.8(11) |
| $\rho$ (calculated) [mg mm$^{-3}$] | 0.81 |
| $\mu$ [mm$^{-1}$] | 0.41 |
| Crystal shape | brick |
| Crystal size [mm$^3$] | 0.158 x 0.133 x 0.068 |
| Crystal colour | orange |
| $\Theta$ range for data collection [°] | 2.2 to 49.1 |
| Index ranges | $-24 \leq h \leq 24$, $-31 \leq k \leq 24$, $-39 \leq l \leq 39$ |
| Reflections collected | 154010 |
| Independent reflections | 59090 ($R_{int}$ = 0.0799) |
| Observed reflections | 26500 ($I > 2\sigma(I)$) |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.44 and 0.66 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 59090 / 26804 / 4870 |
| Goodness-of-fit on $F^2$ | 1.45 |
| Final R indices ($I > 2\sigma(I)$) | $R_1$ = 0.099, $wR_2$ = 0.281 |
| Largest diff. peak and hole [e Å$^{-3}$] | 0.60 and -0.26 |
| Resolution [Å] | 1.02 |

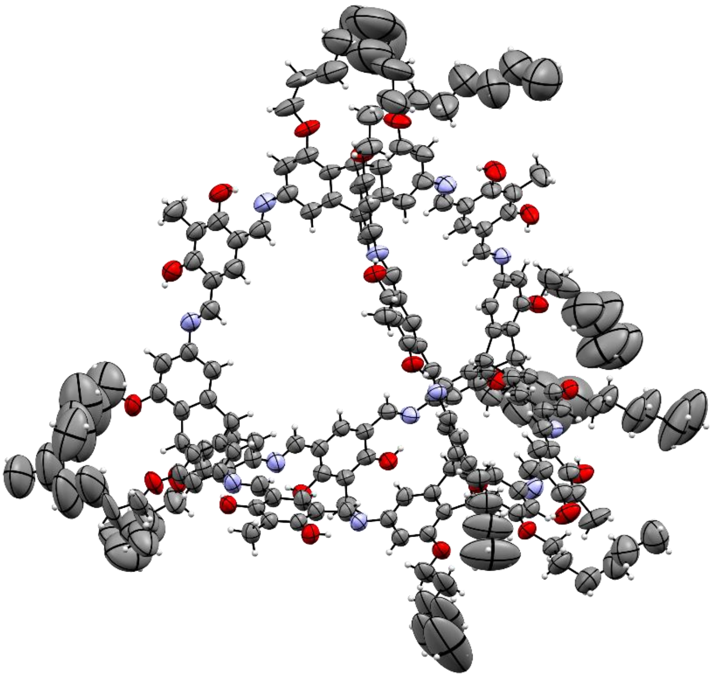


**Figure S137.** X-ray crystal structure of [4+6]-*exo*-cage **12**. Atoms are illustrated as thermal ellipsoids with 50% probability. Grey: carbon, white: hydrogen, blue: nitrogen, red: oxygen. Crystals were obtained via slow solvent evaporation of a solution of **12** in DCM at room temperature.

| | |
|---|---|
| CCDC | 2060525 |
| Empirical formula | $C_{210}H_{236}N_{12}O_{24}$ |
| Formula weight | 3312.09 |
| Temperature [K] | 200(2) |
| $\lambda(Cu_{K\alpha})$ [Å] | 1.54178 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| $Z$ | 2 |
| $a$ [Å] | 23.9115(7) |
| $b$ [Å] | 26.0674(8) |
| $c$ [Å] | 27.8715(8) |
| $\alpha$ [°] | 63.665(2) |
| $\beta$ [°] | 74.083(2) |
| $\gamma$ [°] | 84.127(2) |
| Volume [Å$^3$] | 14968.9(8) |
| $\rho$ (calculated) [mg mm$^{-3}$] | 0.74 |
| $\mu$ [mm$^{-1}$] | 0.38 |
| Crystal shape | brick |
| Crystal size [mm$^3$] | 0.136 x 0.106 x 0.100 |
| Crystal colour | orange |
| $\Theta$ range for data collection [°] | 2.4 to 52.6 |
| Index ranges | $-24 \leq h \leq 22$, $-26 \leq k \leq 19$, $-28 \leq l \leq 27$ |
| Reflections collected | 95908 |
| Independent reflections | 33955 ($R_{int}$ = 0.0498) |
| Observed reflections | 21587 ($I > 2\sigma(I)$) |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.56 and 0.58 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 33955 / 9312 / 2257 |
| Goodness-of-fit on $F^2$ | 1.37 |
| Final R indices ($I > 2\sigma(I)$) | $R_1$ = 0.112, $wR_2$ = 0.333 |
| Largest diff. peak and hole [e Å$^{-3}$] | 0.72 and -0.36 |
| Resolution [Å] | 0.97 |

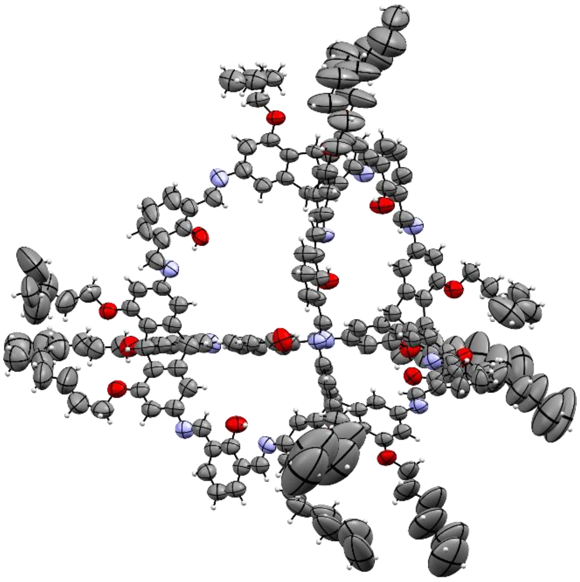


**Figure S138:** X-ray crystal structure of [4+6]-*endo* cage **13**. Atoms are illustrated as thermal ellipsoids with 50% probability. Grey: carbon, white: hydrogen, blue: nitrogen, red: oxygen. Crystals were obtained via gas phase diffusion of acetonitrile in a solution of [4+6]-*endo* cage in DMF at room temperature.

| | |
|---|---|
| CCDC | 2060527 |
| Empirical formula | $C_{200}H_{224}N_{12}O_{18}$ |
| Formula weight | 3083.90 |
| Temperature [K] | 200(2) |
| $\lambda(Cu_{K\alpha})$ [Å] | 1.54178 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| $Z$ | 2 |
| $a$ [Å] | 21.9869(7) |
| $b$ [Å] | 23.7687(6) |
| $c$ [Å] | 29.5082(8) |
| $\alpha$ [°] | 78.767(2) |
| $\beta$ [°] | 76.553(2) |
| $\gamma$ [°] | 63.044(2) |
| Volume [Å$^3$] | 13297.5(7) |
| $\rho$ (calculated) [mg mm$^{-3}$] | 0.77 |
| $\mu$ [mm$^{-1}$] | 0.39 |
| Crystal shape | brick |
| Crystal size [mm$^3$] | 0.280 x 0.210 x 0.130 |
| Crystal colour | orange |
| $\Theta$ range for data collection [°] | 2.1 to 51.1 |
| Index ranges | $-21 \leq h \leq 22$, $-24 \leq k \leq 22$, $-27 \leq l \leq 29$ |
| Reflections collected | 76777 |
| Independent reflections | 28074 ($R_{int}$ = 0.0464) |
| Observed reflections | 17341 ($I > 2\sigma(I)$) |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.30 and 0.78 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 28074 / 9681 / 2255 |
| Goodness-of-fit on $F^2$ | 2.37 |
| Final R indices ($I > 2\sigma(I)$) | $R_1$ = 0.135, $wR_2$ = 0.358 |
| Largest diff. peak and hole [e Å$^{-3}$] | 0.55 and -0.43 |
| Resolution [Å] | 0.99 |

# 10 Exchange Experiments

### Exchange between [4+4] cubes 11 and 11-d<sub>156</sub>

In an 8 mL screw-capped vial cage **11** (1.0 mg, 0.3 µmol, 1 eq) and cage **11-d$_{156}$** (1.0 mg, 0.3 µmol, 1 eq) were combined under argon atmosphere with 0.49 mL dry DMF and TFA, p-toluidine or water (each 10.29 µL, 0.01 mol L$^{-1}$ in dry DMF, 0.4 eq). In an additional experiment TFA (10.29 µL, 0.01 mol L$^{-1}$ in dry DMF, 0.4 eq) and water (61.8 µL, 0.1 mol L$^{-1}$ in dry DMF, 24 eq) were used. The orange solutions were stirred at 150 °C. After 3 and 7 days aliquots were analysed by mass spectrometry.

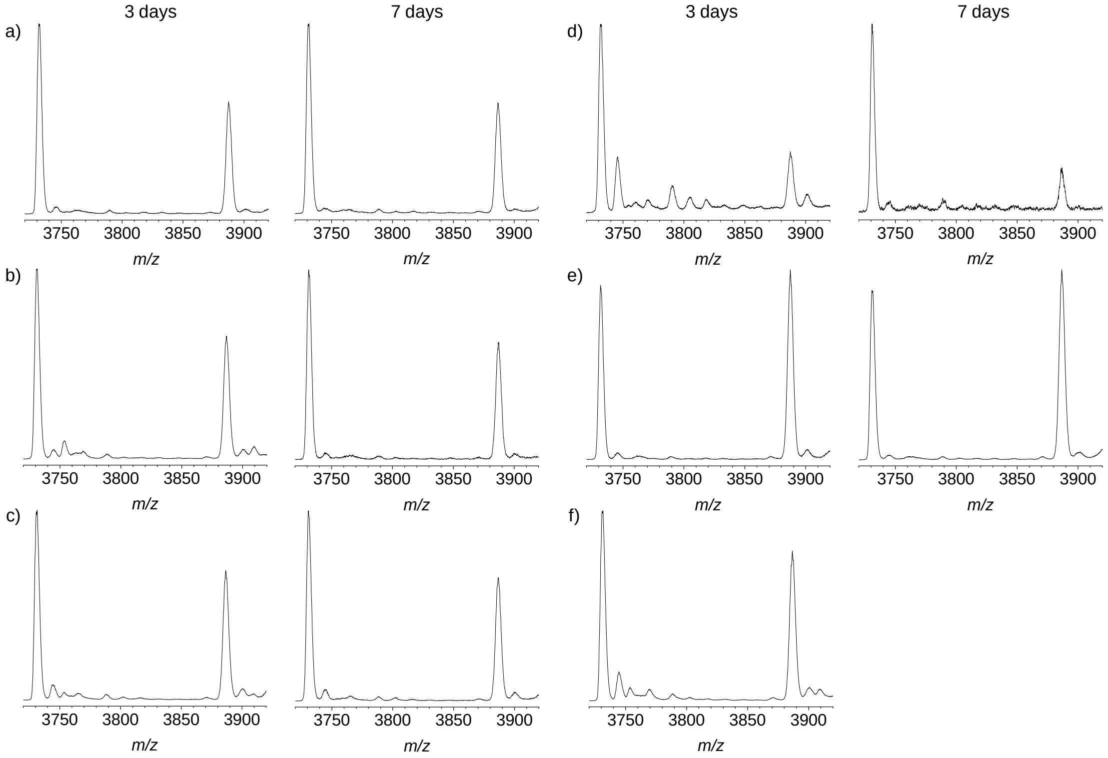


**Figure S139.** MALDI-TOF mass spectra of building block exchange between [4+4] cubes **11** and **11-d$_{156}$** after 3 and 7 days (DCTB matrix, linear mode, positive polarisation) using a) TFA, b) TFA and water (0.4 eq), c) TFA and p-toluidine, d) p-toluidine and water, e) p-toluidine and f) TFA and water (24 eq) as additives.

### Exchange between [4+6]-*exo* cages 12 and 12-d<sub>156</sub>

In an 8 mL screw-capped vial cage **12** (1.1 mg, 0.3 µmol, 1 eq) and cage **12-d$_{156}$** (1.1 mg, 0.3 µmol, 1 eq) were combined under argon atmosphere with 0.48 mL dry DMF and TFA, p-toluidine or water (each 13.48 µL, 0.01 mol L$^{-1}$ in dry DMF, 0.4 eq). The orange solutions were stirred at 120 °C. After 3 and 7 days aliquots were analysed by mass spectrometry.

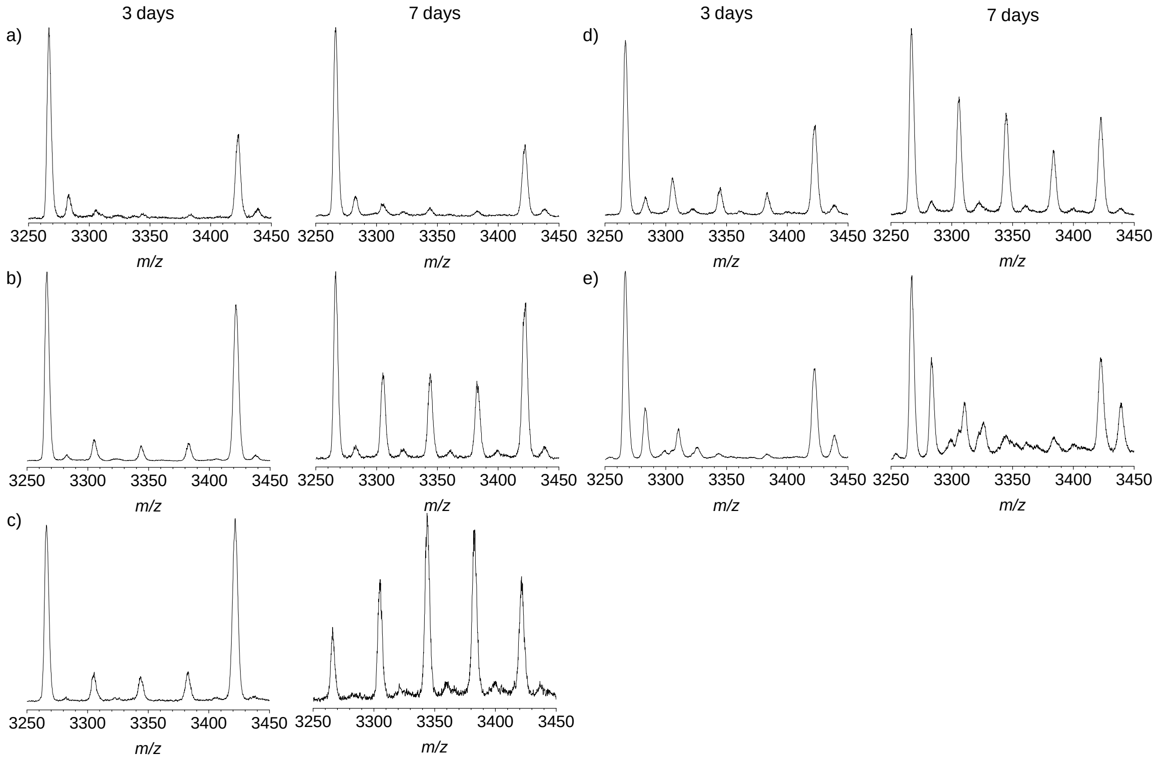


**Figure S140.** MALDI-TOF mass spectra of building block exchange between [4+6]-*exo* cages **12** and **12-d$_{156}$** after 3 and 7 days (DCTB matrix, linear mode, positive polarisation) using a) TFA, b) TFA and water, c) TFA and p-toluidine, d) p-toluidine and water and e) p-toluidine as additives.

## Exchange between [4+6]-*endo* cages 14 and 14-d$_{156}$

In an 8 mL screw-capped vial cage **14** (1.0 mg, 0.3 µmol, 1 eq) and cage **14-d$_{156}$** (1.0 mg, 0.3 µmol, 1 eq) were combined under argon atmosphere with 0.35 mL dry THF and TFA, p-toluidine or water (each 4.68 µL, 0.01 mol L$^{-1}$ in dry THF, 0.16 eq). In an additional experiment TFA (4.68 µL, 0.01 mol L$^{-1}$ in dry THF, 0.16 eq) and water (70.2 µL, 0.1 mol L$^{-1}$ in dry THF, 24 eq) were used. The orange solutions were stirred at room temperature. After 3 and 7 days aliquots were analysed by mass spectrometry.

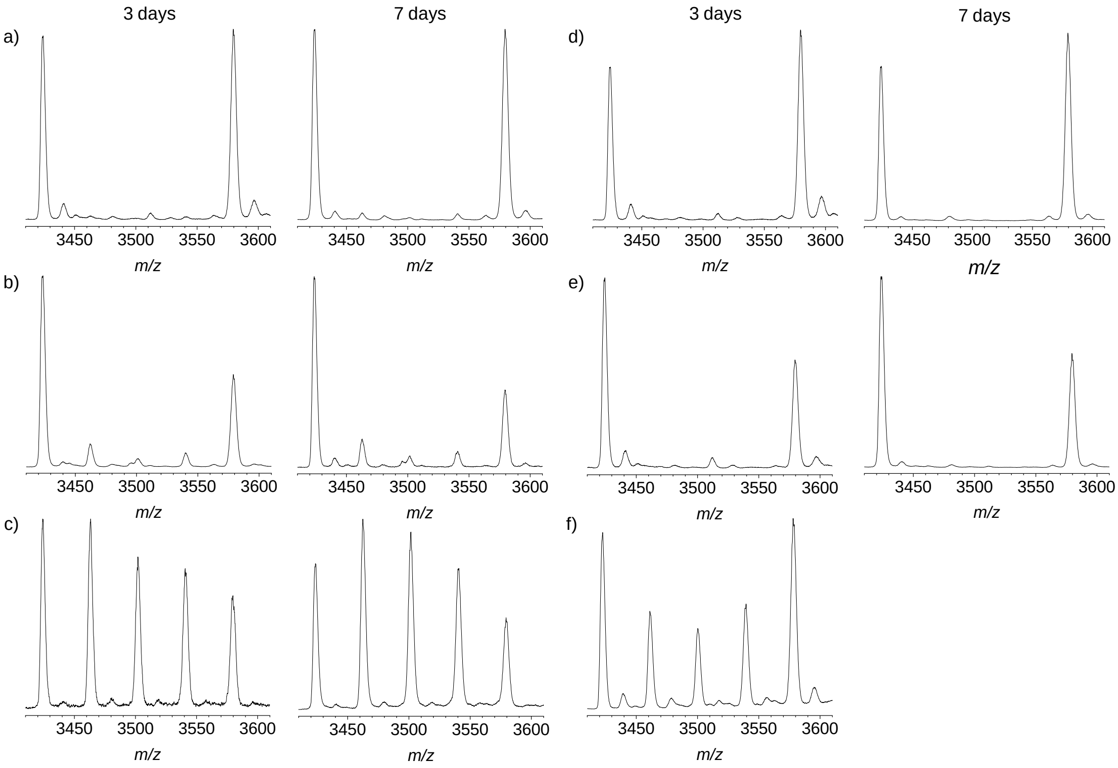


**Figure S141.** MALDI-TOF mass spectra of building block exchange between *tert*-butylated [4+6]-*endo* cages **14** and **14-d**$_{156}$ after 3 and 7 days (DCTB matrix, linear mode, positive polarisation) using a) TFA, b) TFA and water (0.16 eq), c) TFA and p-toluidine, d) p-toluidine and water, e) p-toluidine and f) TFA and water (24 eq) as additives.

# 11 Monitoring of Cage Formation in Deuterated Solvents

## Formation of [4+4] cube 11

A 25 mL screw-capped vial was charged with triaminotriptycene **7a** (20.1 mg, 34 µmol), triformyltriptycene **8** (13.0 mg, 34 µmol) and 1,3,5-trimethoxybenzene (1.6 mg, 9.51 µmol) as internal standard. Under argon atmosphere DMF-d$_7$ (8 mL) and TFA (167 µL, 0.01 mol L$^{-1}$ in CDCl$_3$, 1.67 µmol) were added and the orange solution was stirred at 150 °C. After 1h, 2 h, 4h, 8 h, 24 h, 48 h, 72 h and 96 h aliquots of 0.5 mL were taken and analyse by GPC and $^1$H NMR spectroscopy.

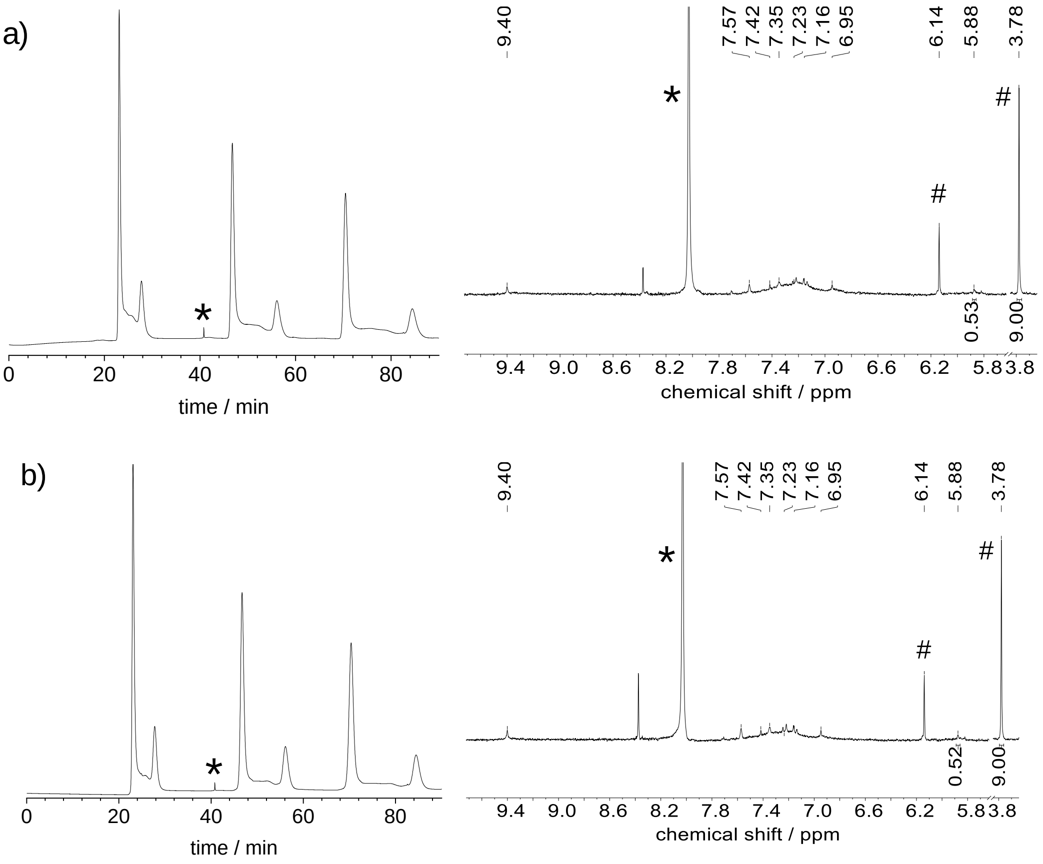


**Figure S142.** GPC chromatograms and $^1$H-NMR spectra (300 MHz, DMF-d$_7$) of samples from reaction mixtures for synthesis of cage **11** after a) 1 h and b) 2 h. *: DMF-d$_7$. #: 1,3,5-Trimethoxybenzene. $^1$H NMR spectra show a range from 9.72 to 3.64 ppm with a cut out from 5.70 to 3.80 ppm.

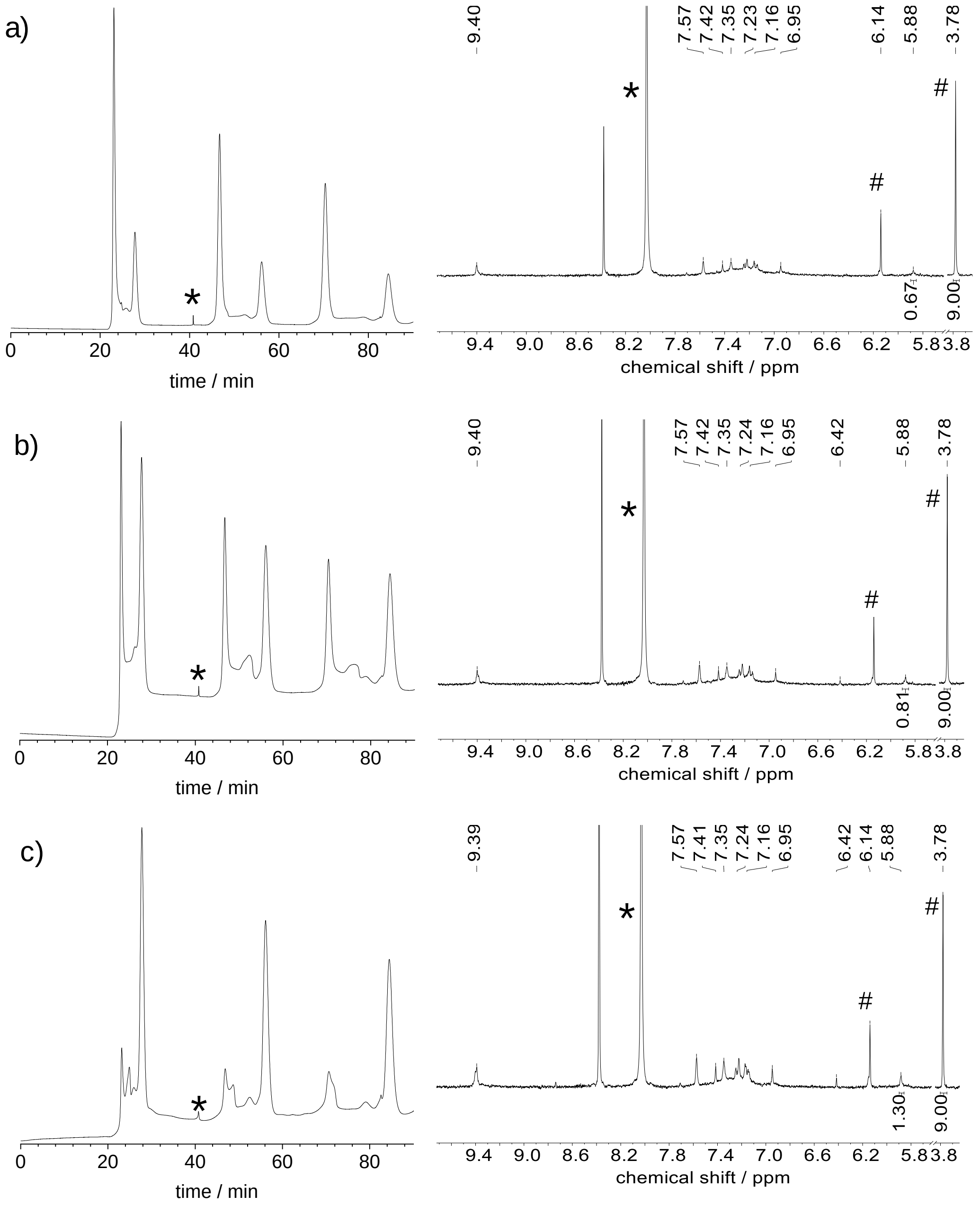


**Figure S143.** GPC chromatograms and $^1$H-NMR spectra (300 MHz, DMF-$d_7$) of samples from reaction mixtures for synthesis of cage **11** after a) 4 h, b) 8 h and c) 24 h. *: DMF-$d_7$. #: 1,3,5-Trimethoxybenzene. $^1$H NMR spectra show a range from 9.72 to 3.64 ppm with a cut out from 5.70 to 3.80 ppm.

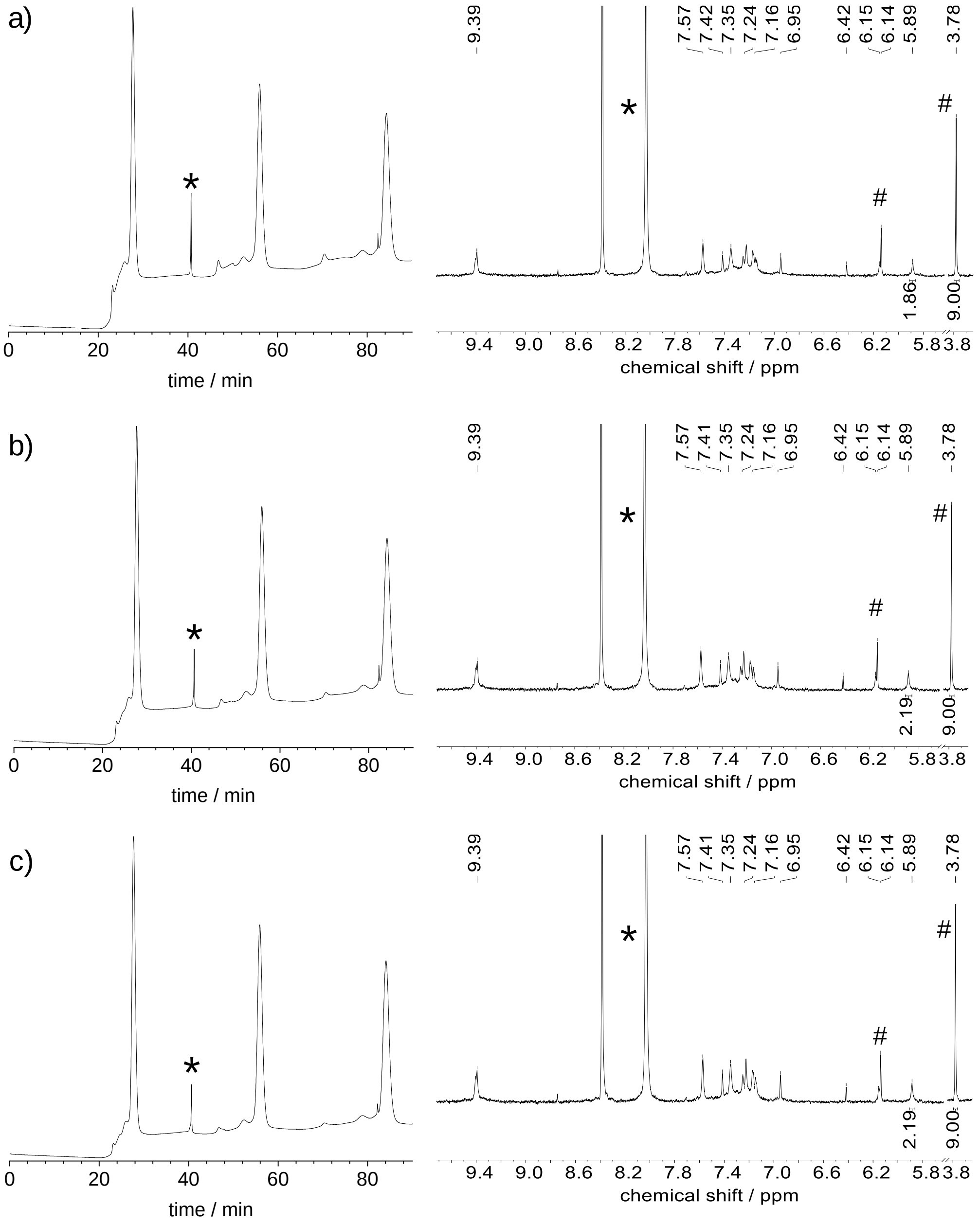


**Figure S144.** GPC chromatograms and $^1$H-NMR spectra (300 MHz, DMF-$d_7$) of samples from reaction mixtures for synthesis of cage **11** after a) 48 h, b) 72 h and c) 96 h. *: DMF-$d_7$. #: 1,3,5-Trimethoxybenzene. $^1$H NMR spectra show a range from 9.72 to 3.64 ppm with a cut out from 5.70 to 3.80 ppm.

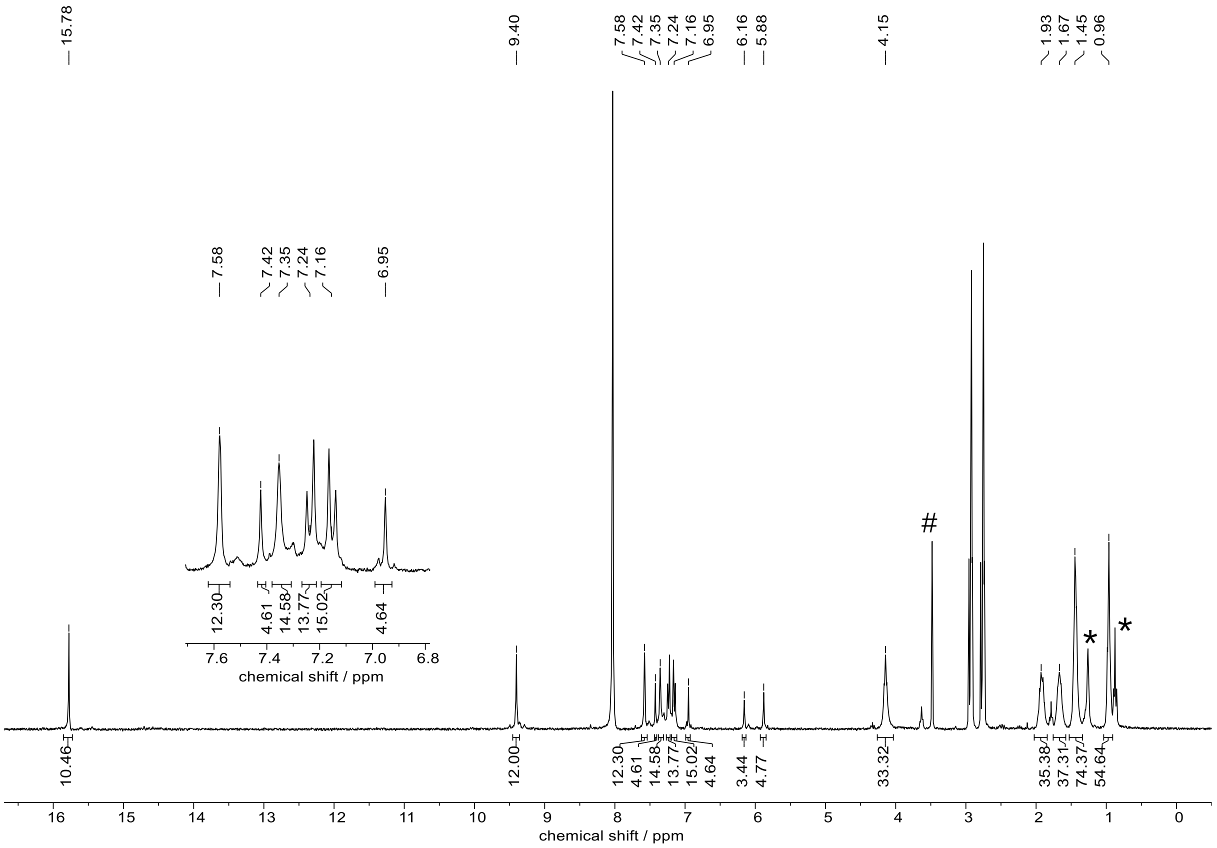


**Figure S145.** $^1H$ NMR spectrum (300 MHz, DMF-$d_7$) of [4+4] cube **11**. #: $H_2O$. *: *n*-hexane.

## Formation of [4+6] exo cage 12

An 8 mL screw-capped vial was charged with triaminotriptycene **7a** (20.0 mg, 33 µmol), 3,5-diformyl-2,6-dihydroxytoluene **9** (9.0 mg, 50 µmol) and 1,3,5-trimethoxybenzene (1.8 mg, 10.7 µmol) as internal standard. Under argon atmosphere DMF-$d_7$ (6 mL) and TFA (167 µL, 0.01 mol L$^{-1}$ in $CDCl_3$, 1.67 µmol) were added and the orange solution was stirred at 120 °C. After 1h, 2 h, 4h, 8 h, 24 h, 48 h, 72 h and 96 h aliquots of 0.5 mL were taken and analysed by GPC and $^1H$ NMR spectroscopy.

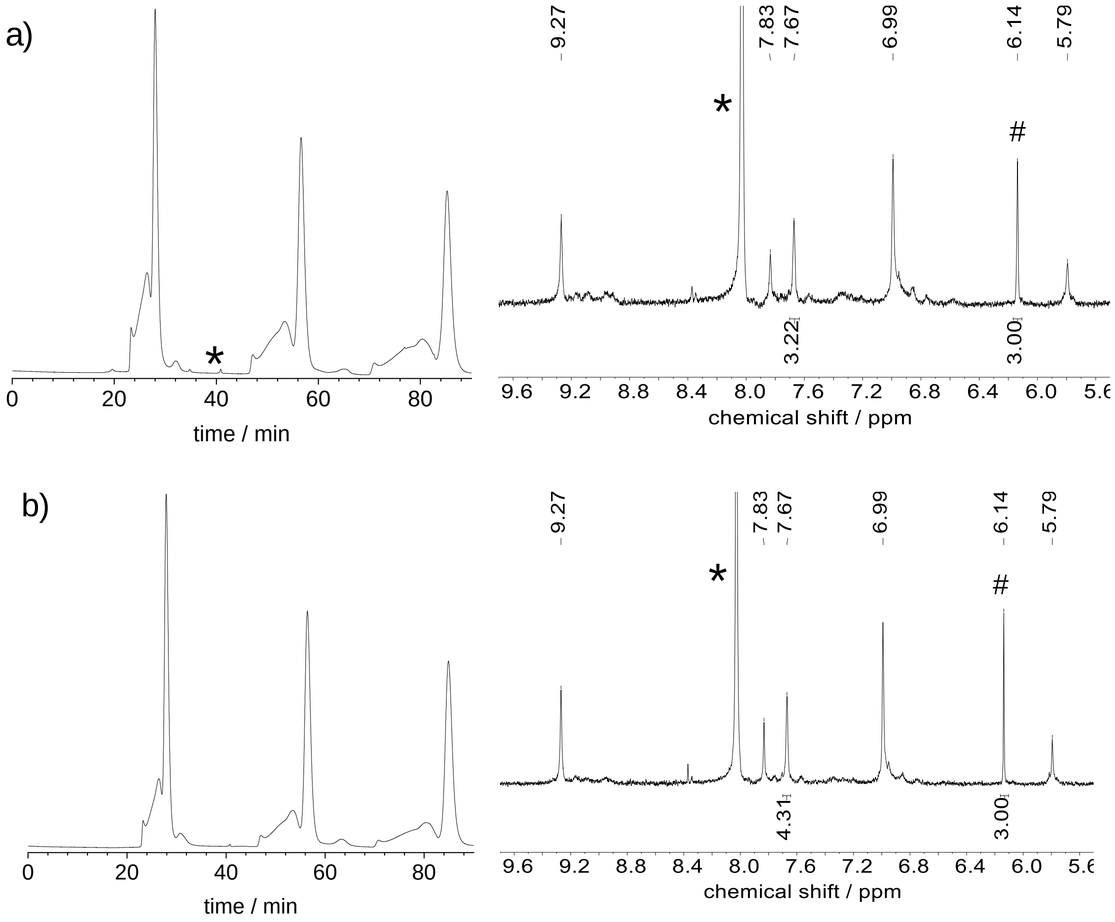


**Figure S146.** GPC chromatograms and $^1H$-NMR spectra (300 MHz, DMF-$d_7$) of samples from reaction mixtures for synthesis of [4+6]-*exo* cage **12** after a) 1 h and b) 2 h. *: DMF-$d_7$. #: 1,3,5-Trimethoxybenzene. $^1H$ NMR spectra show a range from 9.70 to 5.50 ppm.

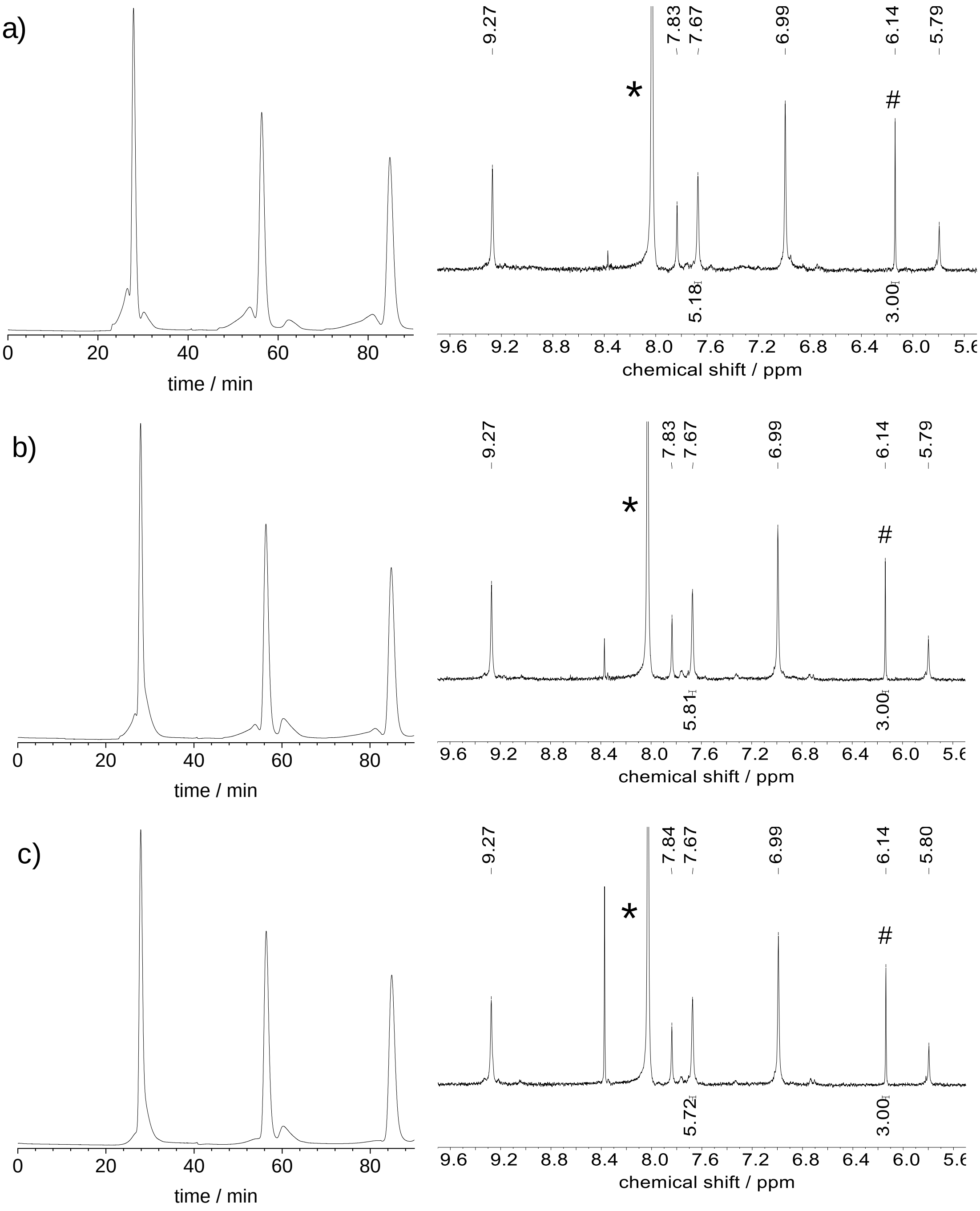


**Figure S147.** GPC chromatograms and $^1$H-NMR spectra (300 MHz, DMF-$d_7$) of samples from reaction mixtures for synthesis of [4+6]-*exo* cage **12** after a) 4 h, b) 8 h and c) 24 h. *: DMF-$d_7$. #: 1,3,5-Trimethoxybenzene. $^1$H NMR spectra show a range from 9.70 to 5.50 ppm.

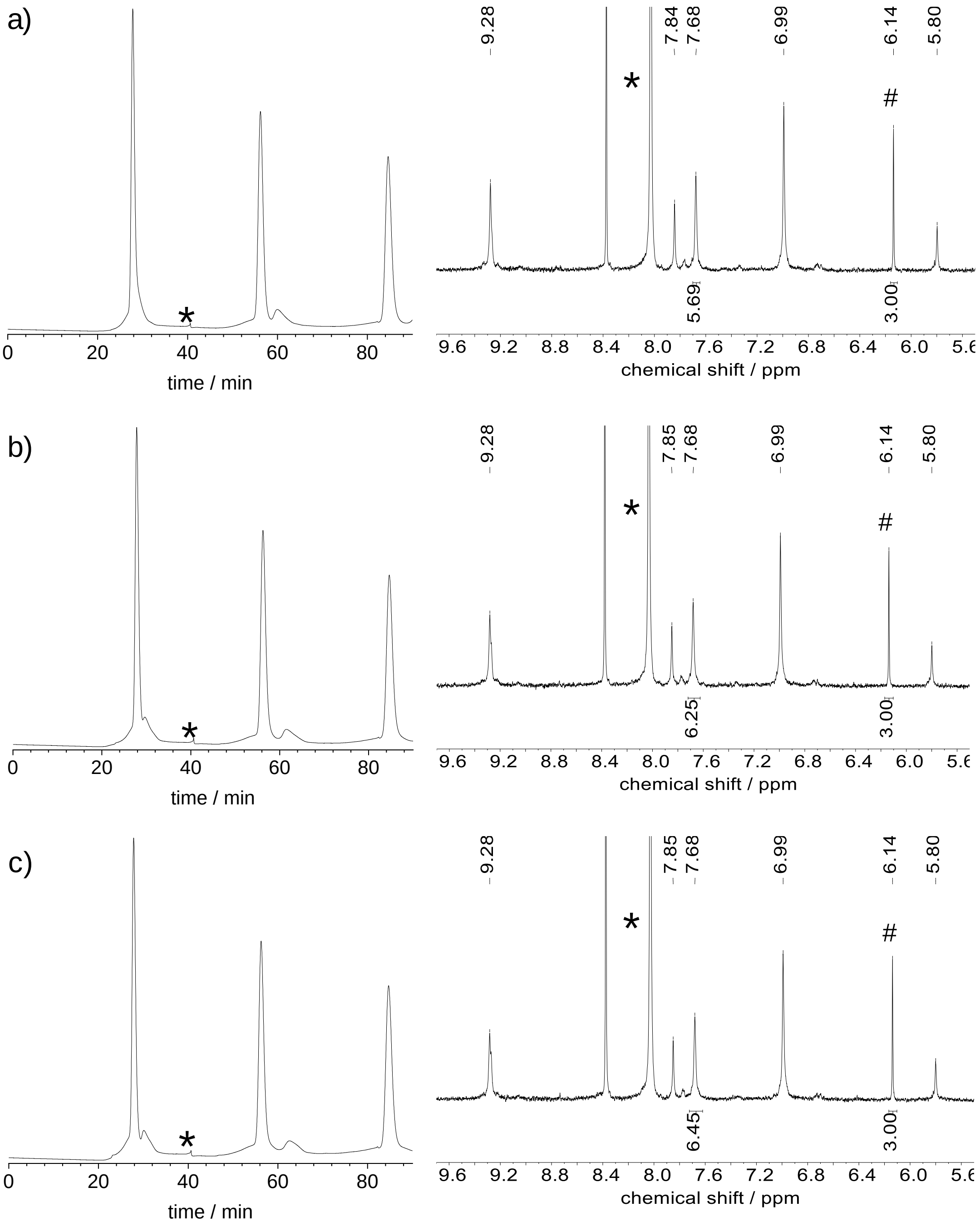


**Figure S148.** GPC chromatograms and $^1$H-NMR spectra (300 MHz, DMF-$d_7$) of samples from reaction mixtures for synthesis of [4+6]-*exo* cage **12** after a) 48 h, b) 72 h and c) 96 h. *: DMF-$d_7$. #: 1,3,5-Trimethoxybenzene. $^1$H NMR spectra show a range from 9.70 to 5.50 ppm.

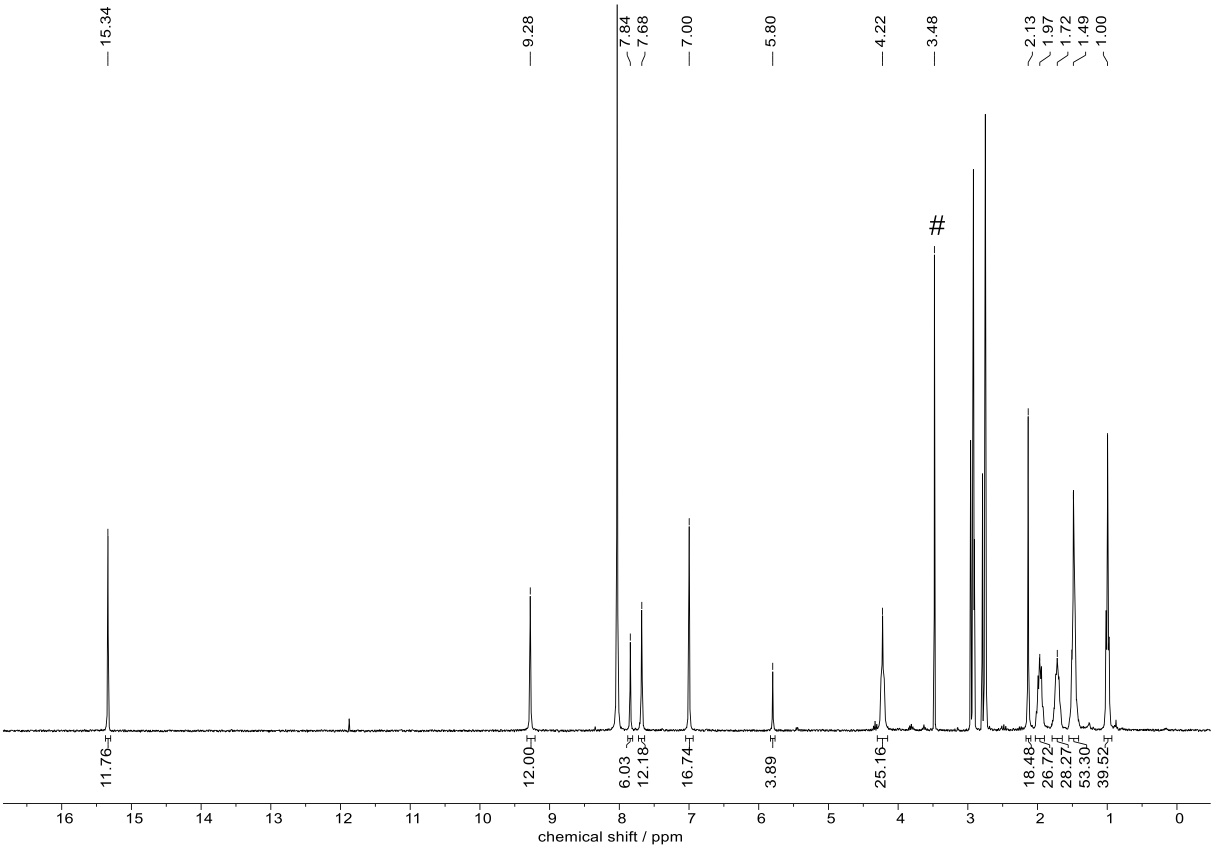


**Figure S149.** $^1$H NMR spectrum (300 MHz, DMF-$d_7$) of [4+6]-*exo* cage **12**. #: $H_2O$.

## Formation of [4+6] *endo* cage 13

An 8 mL screw-capped vial was charged with triaminotriptycene **7a** (20.1 mg, 34 µmol), 2,6-diformylphenol **10a** (7.8 mg, 52 µmol) and 1,3,5-trimethoxybenzene (1.7 mg, 10.11 µmol) as internal standard. Under argon atmosphere THF-$d_8$ (5 mL) and TFA (67 µL, 0.01 mol $L^{-1}$ in $CDCl_3$, 0.67 µmol) were added and the orange solution was stirred at room temperature. After 1h, 2 h, 4h, 8 h, 24 h, 48 h, 72 h and 96 h aliquots of 0.5 mL were taken and analysed by GPC and $^1H$ NMR spectroscopy.

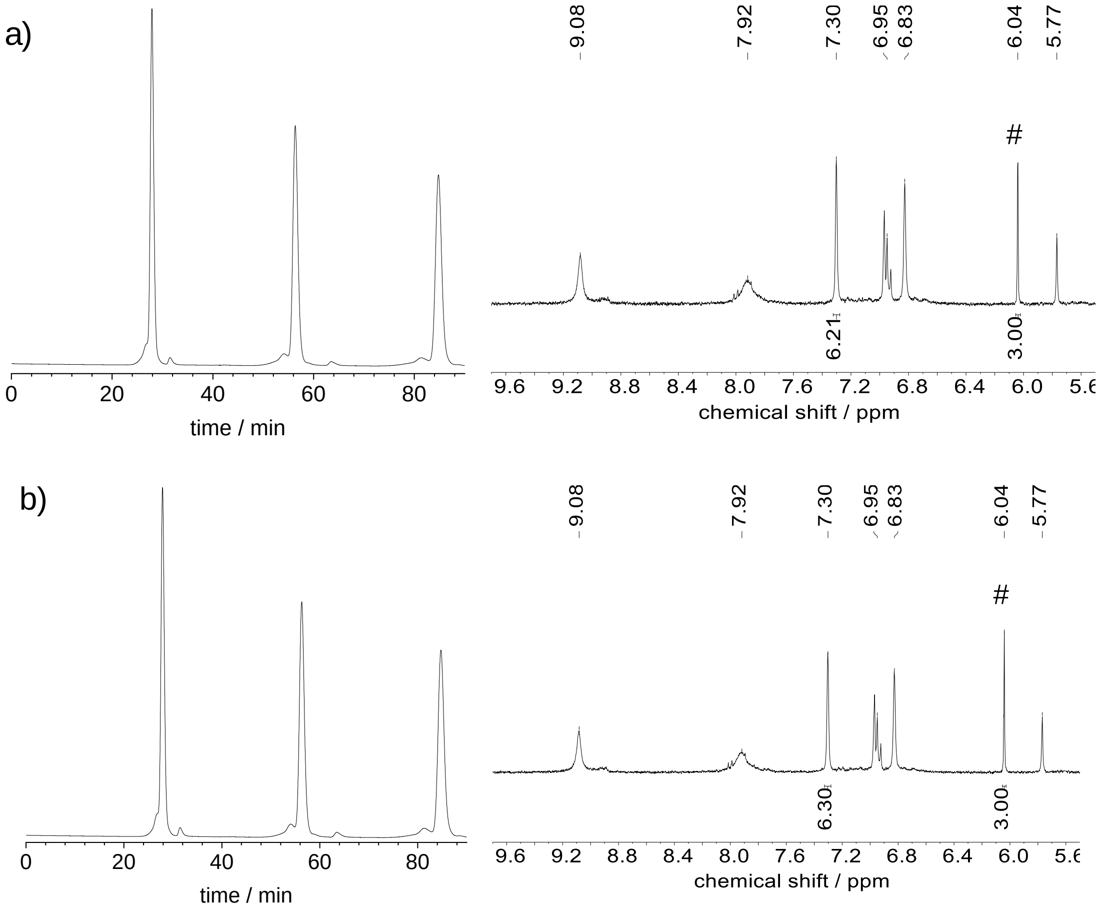


**Figure S150.** GPC chromatograms and $^1H$-NMR spectra (300 MHz, THF-$d_8$) of samples from reaction mixtures for synthesis of [4+6]-*endo* cage **13** after a) 1 h and b) 2 h. #: 1,3,5-Trimethoxybenzene. $^1H$ NMR spectra show a range from 9.70 to 5.50 ppm.

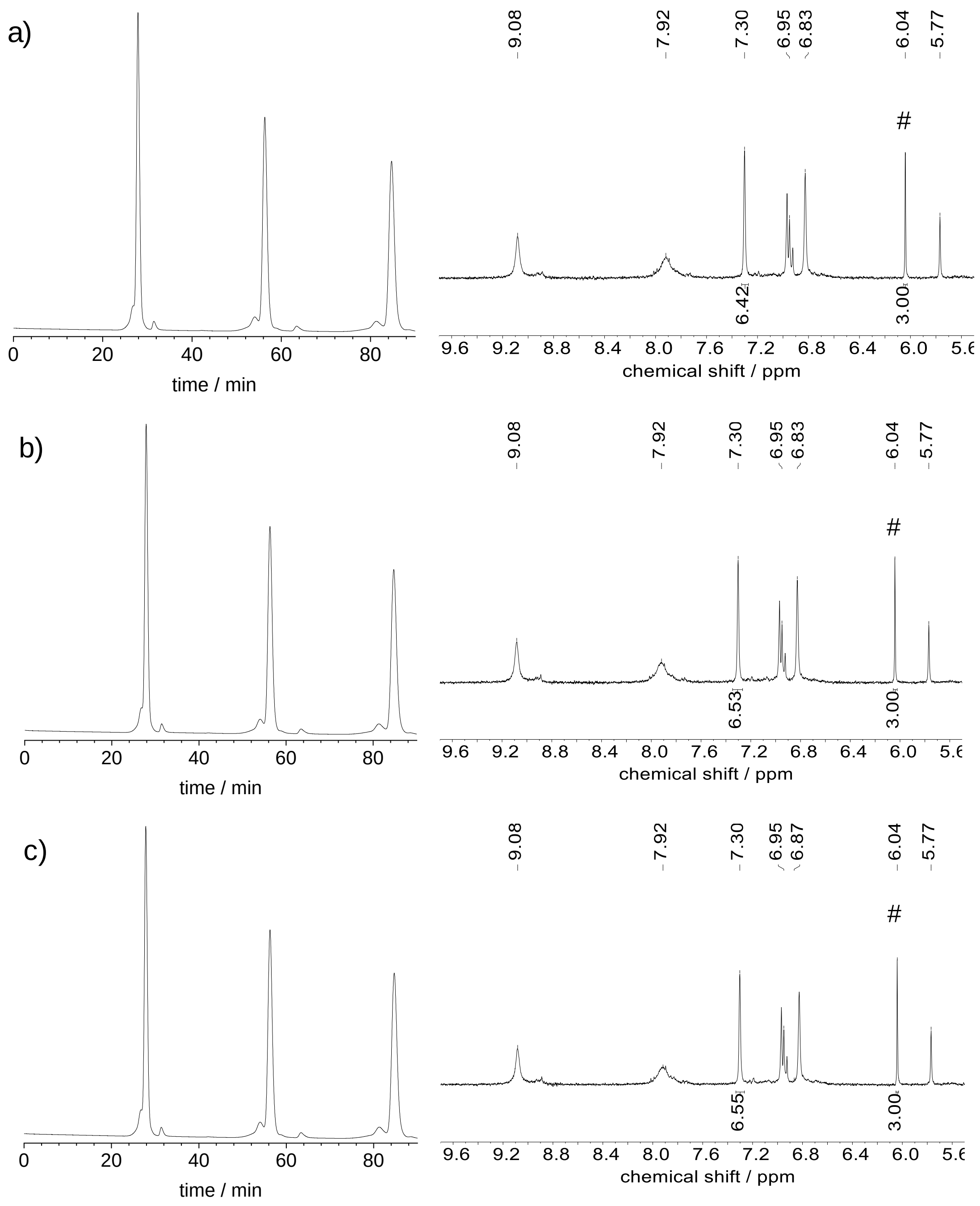


**Figure S151.** GPC chromatograms and $^1$H-NMR spectra (300 MHz, THF-d$_8$) of samples from reaction mixtures for synthesis of [4+6]-*endo* cage **13** after a) 4 h, b) 8 h and c) 24 h. *: #: 1,3,5-Trimethoxybenzene. $^1$H NMR spectra show a range from 9.70 to 5.50 ppm.

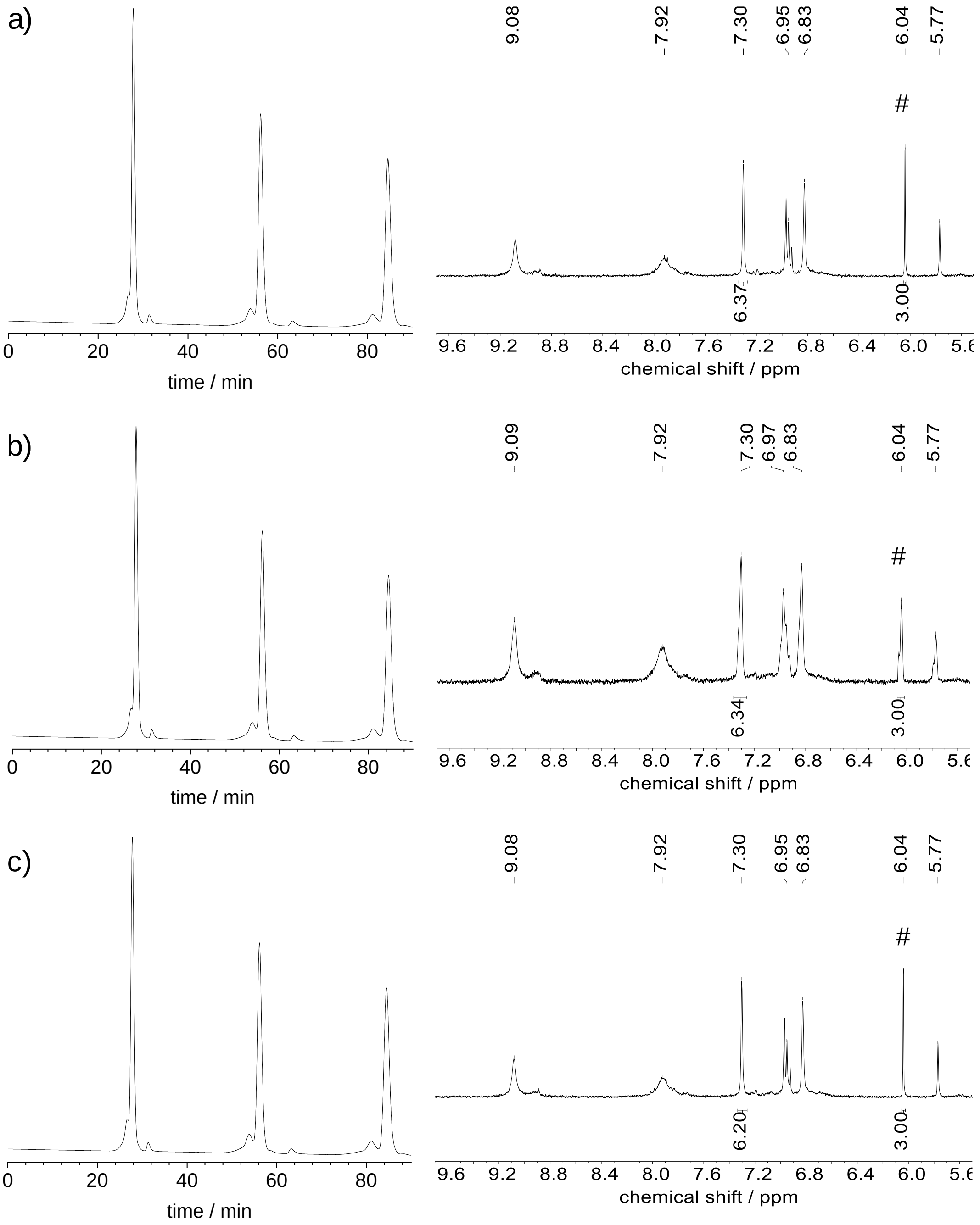


**Figure S152.** GPC chromatograms and $^{1}$H-NMR spectra (300 MHz, THF-$d_8$) of samples from reaction mixtures for synthesis of [4+6]-*endo* cage **13** after a) 48 h, b) 72 h and c) 96 h. #: 1,3,5-Trimethoxybenzene. $^{1}$H NMR spectra show a range from 9.70 to 5.50 ppm.

## Formation of [4+6] *endo* cage 14

An 8 mL screw-capped vial was charged with triaminotriptycene **7a** (20.0 mg, 33 µmol), 2,6-diformyl-4-*tert*-butylphenol **10b** (10.3 mg, 50 µmol) and 1,3,5-trimethoxybenzene (1.8 mg, 10.7 µmol) as internal standard. Under argon atmosphere THF-$d_8$ (5 mL) and TFA (67 µL, 0.01 mol $L^{-1}$ in $CDCl_3$, 0.67 µmol) were added and the orange solution was stirred at room temperature. After 1h, 2 h, 4h, 8 h, 24 h, 48 h, 72 h and 96 h aliquots of 0.5 mL were taken and analysed by GPC and $^1$H NMR spectroscopy.

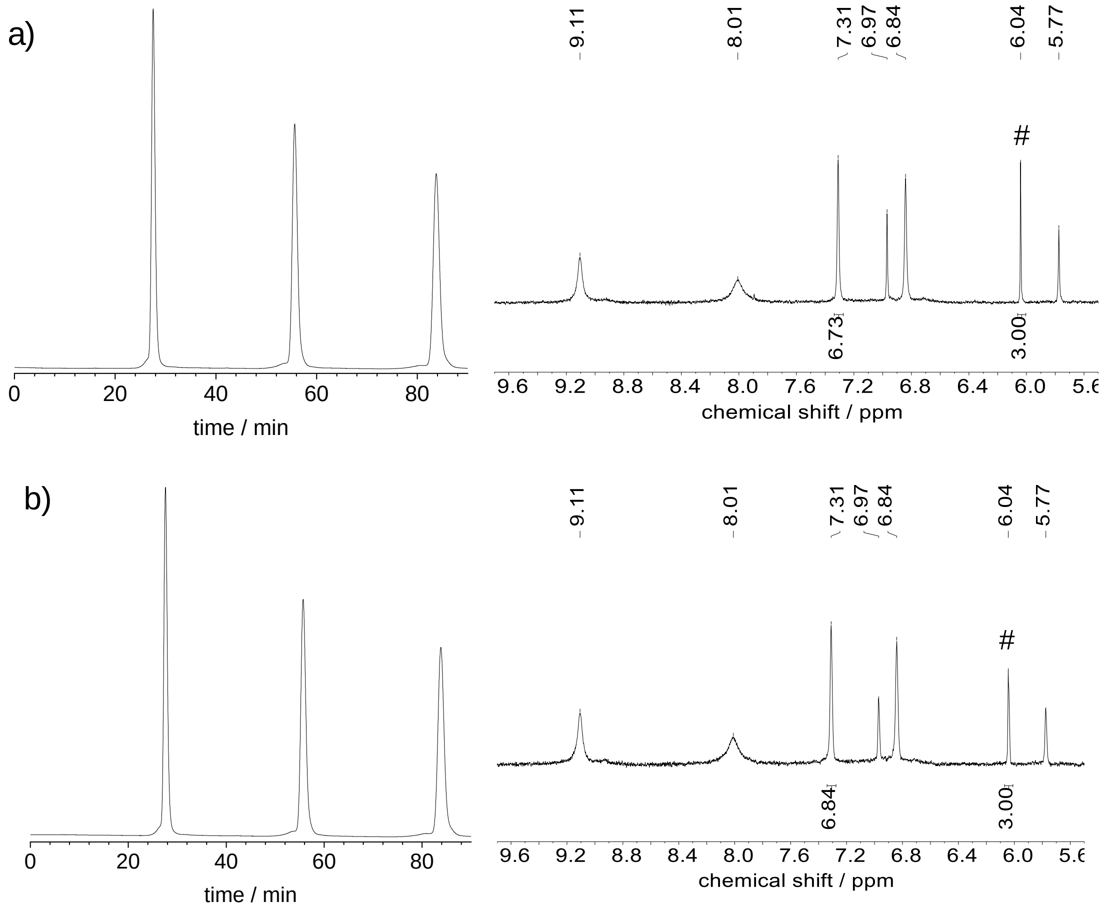


**Figure S153.** GPC chromatograms and $^1$H-NMR spectra (300 MHz, THF-$d_8$) of samples from reaction mixtures for synthesis of [4+6]-*endo* cage **14** after a) 1 h and b) 2 h. #: 1,3,5-Trimethoxybenzene. $^1$H NMR spectra show a range from 9.70 to 5.50 ppm.

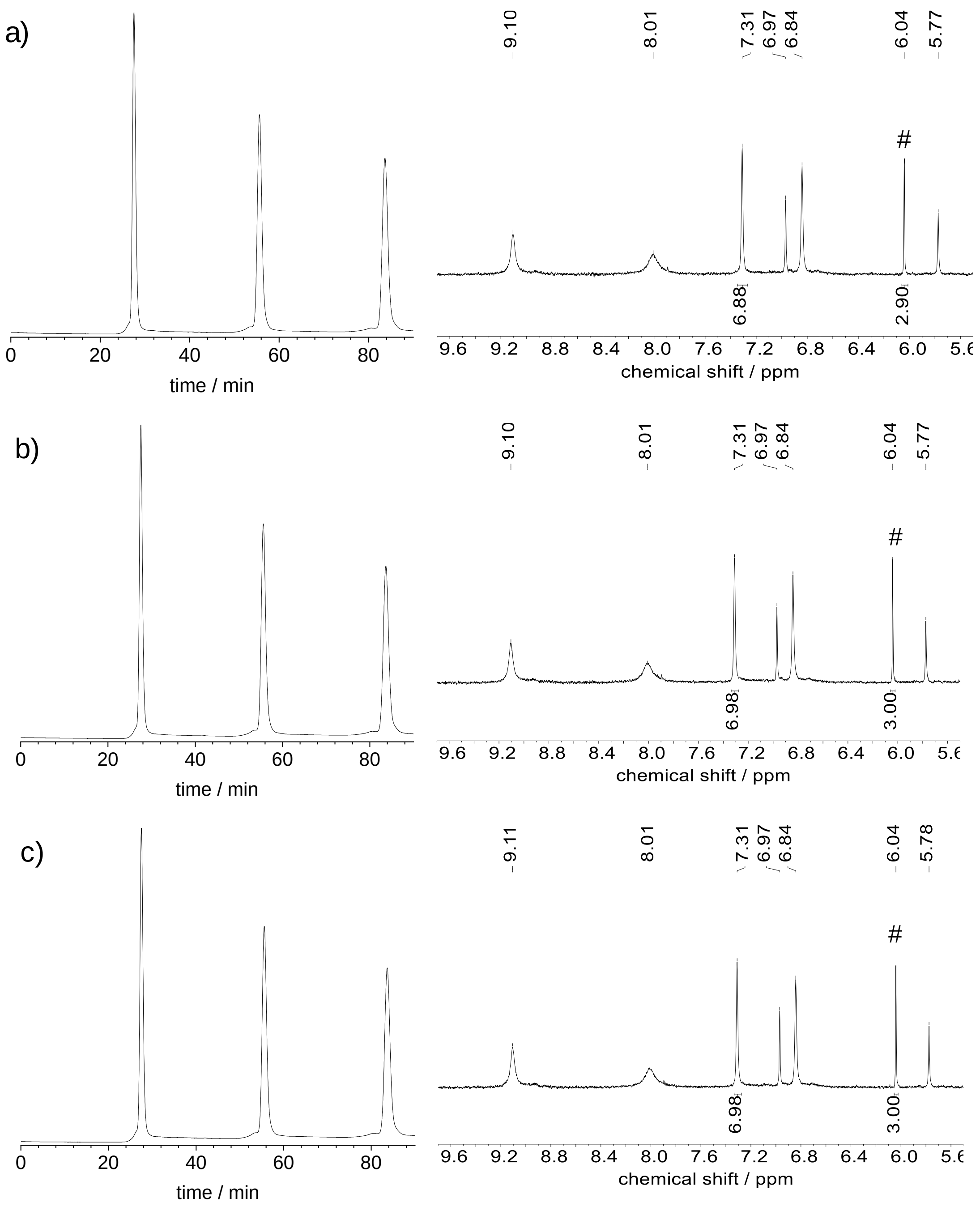


**Figure S154.** GPC chromatograms and $^1$H-NMR spectra (300 MHz, THF-$d_8$) of samples from reaction mixtures for synthesis of [4+6]-*endo* cage **14** after a) 4 h, b) 8 h and c) 24 h. *: #: 1,3,5-Trimethoxybenzene. $^1$H NMR spectra show a range from 9.70 to 5.50 ppm.

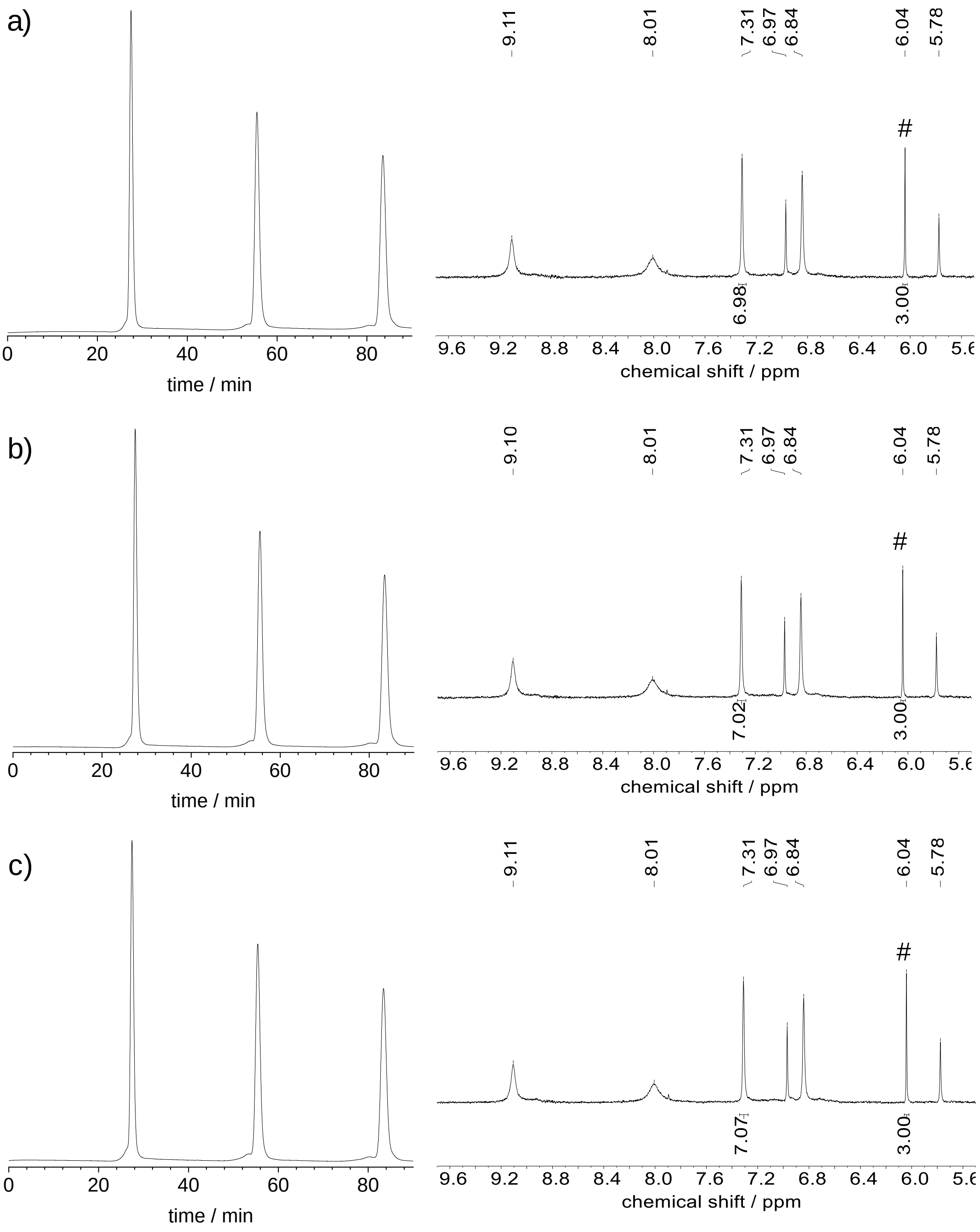


**Figure S155.** GPC chromatograms and $^1$H-NMR spectra (300 MHz, THF-$d_8$) of samples from reaction mixtures for synthesis of [4+6]-*endo* cage **14** after a) 48 h, b) 72 h and c) 96 h. #: 1,3,5-Trimethoxybenzene. $^1$H NMR spectra show a range from 9.70 to 5.50 ppm.

## Determination of Yields by Using an Internal Standard

Yields have been calculated from measured $^1$H NMR spectra of cages **11** – **14** using the following formula

$$\eta = \frac{I_1 n_{standard}}{I_0 n_{theor.}} * 100\%. \tag{2}$$

$\eta$ is the yield, $I_1$ describes the measured integral of a cage signal in $^1$H NMR spectrum, $I_0$ is the integral of the same signal, if the cage and the standard would have a 1:1 stoichiometry, $n_{standard}$ is the amount of added standard and $n_{theor.}$ resembles the amount of cage molecules at 100% yield. Uncertainties were calculated applying propagation of uncertainty by using the error of weighing. Since the amount of standard has been calculated by its mass and the 100% yield amount of cage has been calculated by the amount of added 3,6,15-triamino-1,8,13-trihexyloxytriptycene divided by 4 the variables $n_{standard}$ and $n_{theor.}$ can be exchanged using $n = m\,M^{-1}$:

$$\eta = \frac{I_1 m_{standard} 4 M_{amine}}{I_0 M_{standard} m_{amine}} * 100\% = 400\% * \frac{I_1 M_{amine}}{I_0 M_{standard}} \frac{m_{standard}}{m_{amine}}. \tag{3}$$

$m_{standard}$ and $m_{amine}$ are the added masses of 1,3,5-trimethoxybenzen and 3,6,15-triamino-1,8,13-trihexyloxytriptycene, respectively, as well as $M_{standard}$ and $M_{amine}$ are their molecular masses. The error of the yield $\Delta\eta$ can be calculated using propagation of uncertainty:

$$\Delta\eta = \frac{\delta\eta}{\delta m_{standard}} \Delta m_{standard} + \frac{\delta\eta}{\delta m_{amine}} \Delta m_{amine}. \tag{4}$$

Since the errors of the weighing is for both compounds the same value ($\Delta m$ = 0.0001 g), equation (4) can be changed to:

$$\Delta\eta = \Delta m \frac{\delta\eta}{\delta m_{standard}} + \frac{\delta\eta}{\delta m_{amine}}. \tag{5}$$

From equation (5) results equation (6).

$$\Delta\eta = 400\% * \frac{I_1 M_{amine} \Delta m}{I_0 M_{standard}} \left( \frac{1}{m_{amine}} - \frac{m_{standard}}{m_{amine}^2} \right) \tag{6}$$

**Table S30.** Calculated yields and errors of cages **11** - **14** by $^1$H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. Yields and errors were calculated applying equations (2) and (6). log t is the logarithm of time.

| **Cage** | | **11** | | **12** | | **13** | | **14** | |
|---|---|---|---|---|---|---|---|---|---|
| **time / h** | **log t** | ***η* / %** | ***Δη* / %** | ***η* / %** | ***Δη* / %** | ***η* / %** | ***Δη* / %** | ***η* / %** | ***Δη* / %** |
| 1 | 0.00 | 15 | 1 | 34 | 2 | 63 | 3 | 72 | 4 |
| 2 | 0.30 | 15 | 1 | 46 | 2 | 63 | 3 | 73 | 4 |
| 4 | 0.60 | 19 | 1 | 55 | 3 | 65 | 3 | 74 | 4 |
| 8 | 0.90 | 23 | 1 | 62 | 3 | 66 | 4 | 75 | 4 |
| 24 | 1.38 | 37 | 2 | 61 | 3 | 66 | 4 | 75 | 4 |
| 48 | 1.68 | 53 | 3 | 61 | 3 | 64 | 3 | 75 | 4 |
| 72 | 1.86 | 62 | 4 | 67 | 3 | 64 | 3 | 75 | 4 |
| 96 | 1.98 | 62 | 4 | 69 | 3 | 62 | 3 | 76 | 4 |

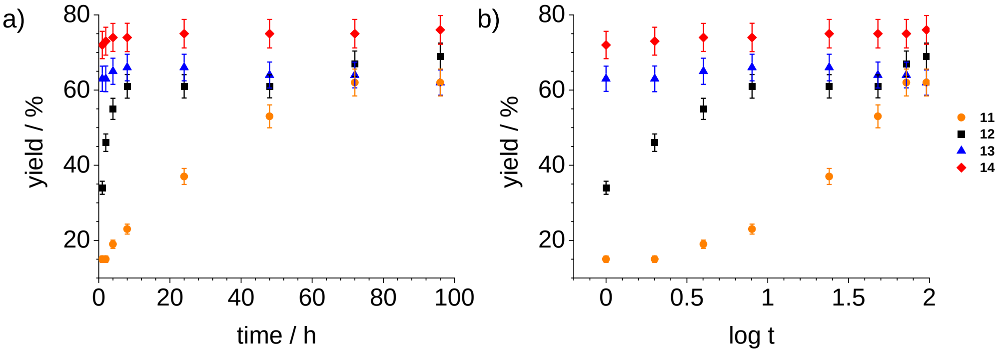


**Figure S156.** Diagram of yields of cages **11** – **14** determined by $^1$H NMR spectroscopy in a) linear and b) logarithmic time axis. 1,3,5-Trimethoxybenzene has been used as internal standard. For every obtained yield an error bar has been illustrated.

# 12 VT NMR Spectra of [4+6]-*endo* cages 13 and 14

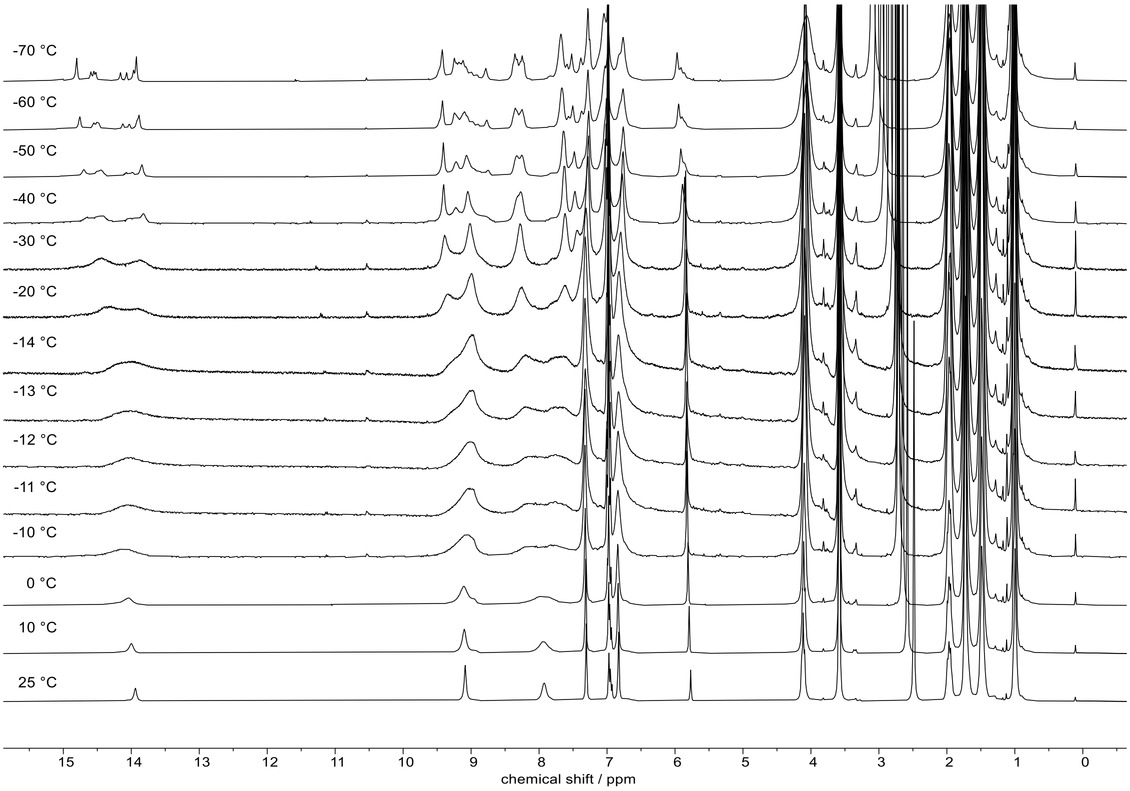


**Figure S157.** $^1$H NMR spectra (300 MHz, THF-d$_8$) of [4+6]-*endo* cage **13** at different temperatures.

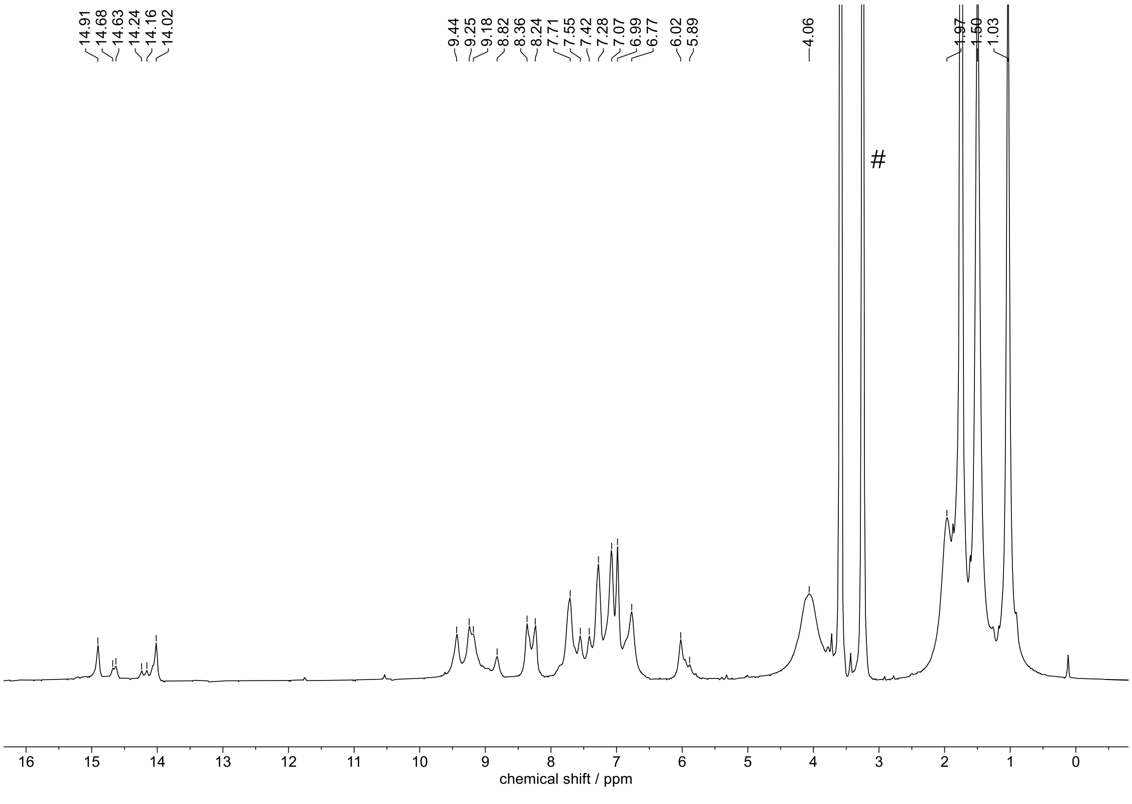


**Figure S158.** $^1$H NMR spectrum (500 MHz, 203K, THF-d$_8$) of [4+6]-*endo* cage **13** at -70 °C. #: $H_2O$.

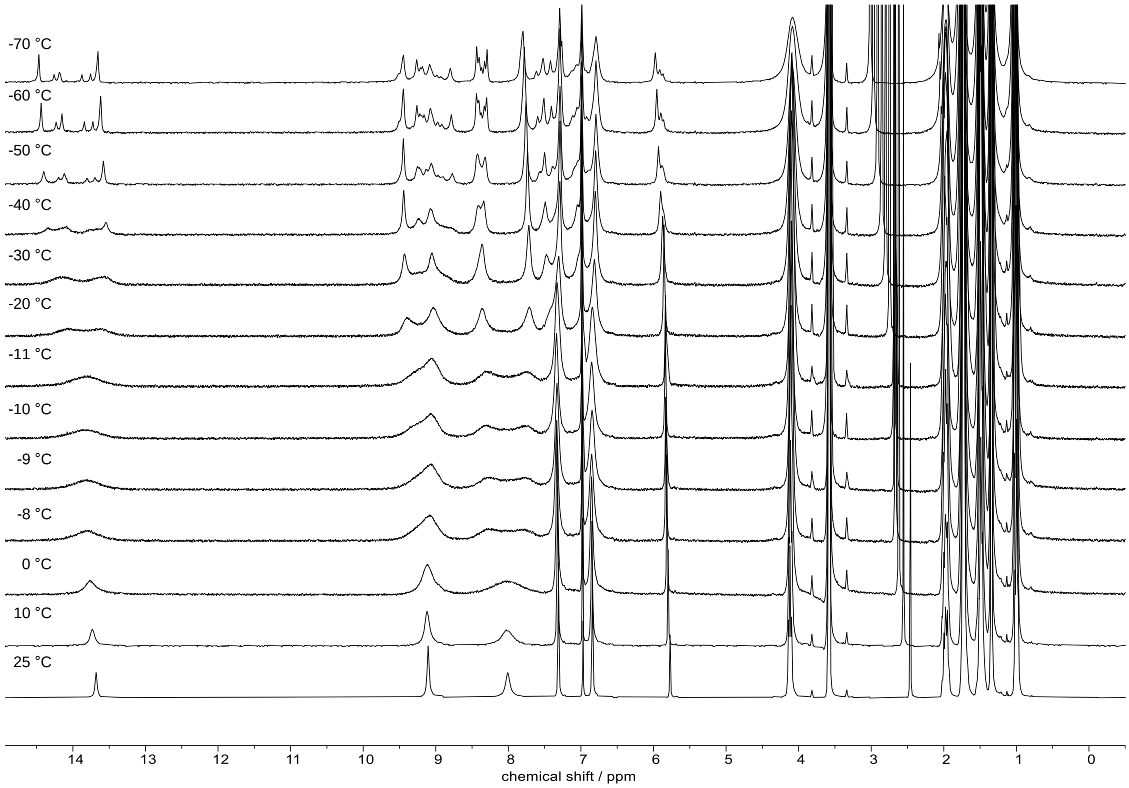


**Figure S159.** $^1$H NMR spectra (300 MHz, THF-d$_8$) of *tert*-butylated [4+6]-*endo* cage **14** at different temperatures.

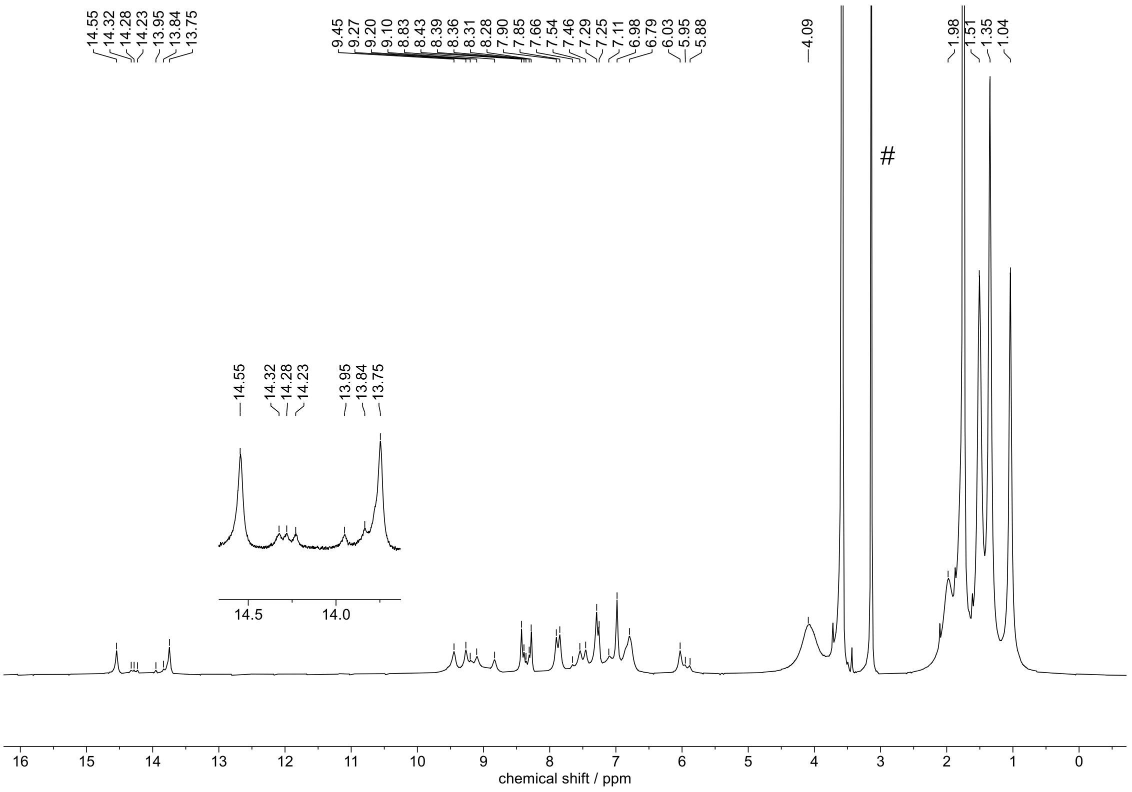


**Figure S160.** $^1$H NMR spectrum (500 MHz, 203 K, THF-d$_8$) of *tert*-butylated [4+6]-*endo* cage **14** at -70 °C. #: $H_2O$.

# 13 Screening of Reaction Conditions

## Synthesis of [4+4] cube 11

**Table S31.** Screening conditions for synthesis of [4+4] cube **11**. $eq_{TFA}$ is the used equivalents of TFA, $V$ is the volume of used solvent, $T$ is the reaction temperature, $t$ is the reaction duration and $\eta$ is the obtained yield after GPC purification.

| **No.**[a] | $eq_{TFA}$ | **Solvent**[b] | $V$ **/ mL** | $T$ **/ °C** | $t$ **/ d** | $\eta$ **/ %** |
|---|---|---|---|---|---|---|
| 1 | 0.08 | DMF | 3 | 100 | 3 | 11 |
| 2 | 0.08 | DMF | 3 | 100 | 4 | 5 |
| 3 | 0.08 | DMF | 3 | 120 | 4 | 6 |
| 4 | 0.08 | DMF | 3 | 120 | 2 | 3 |
| 5 | 0.08 | DCM | 3 | 80 | 2 | 4 |
| 6 | 0.08 | DCM | 3 | 50 | 1 | 8 |
| 7 | 0.08 | DMF | 4 | 120 | 3 | 31 |
| 8 | 0.00 | DMF | 4 | 120 | 3 | 17 |
| 9 | 0.20 | DMF | 4 | 120 | 3 | 19 |
| 10 | 0.20 | DMF | 4.5 | 120 | 3 | 3 |
| 11 | 0.08 | THF | 5 | 80 | 2 | 6 |
| 12 | 0.20 | DMF | 5 | 120 | 3 | 8 |
| 13 | 0.20 | THF | 7 | r. t. | 11 | 1 |
| 14 | 0.20 | THF | 7 | 80 | 12 | 2 |
| 15 | 0.20 | $CHCl_3$ | 7 | 80 | 3 | 5 |
| 16 | 0.20 | toluene | 7 | 120 | 3 | 4 |
| 17 | 0.20 | DMSO | 7 | 120 | 3 | 8 |
| 18 | 0.00 | DMF | 7 | 120 | 3 | 6 |
| 19 | 0.08 | DMF | 7 | 120 | 3 | 17 |
| 20 | 0.20 | DMF | 7 | 120 | 4 | 6 |
| 21 | 0.20 | DMF | 7 | 120 | 12 | 14 |
| 22 | 0.28 | DMF | 7 | 120 | 3 | 5 |
| 23 | 0.20 | DMF | 7 | 140 | 3 | 3 |
| 24 | 0.20 | DMF | 7.5 | 120 | 3 | 4 |
| 25 | 0.20 | 1.4-dioxane | 8 | 120 | 3 | 7 |
| 26 | 0.08 | DMF | 8 | 120 | 3 | 6 |
| 27 | 0.20 | DMF | 8 | 120 | 3 | 34 |
| 28 | 0.20 | DMF | 8 | 150 | 3 | 37 |
| 29 | 0.20 | DMF | 8 | 150 | 5 | 42 |
| 30 | 0.20 | DMF | 8 | 180 | 3 | 20 |
| 31 | 0.20 | DMF | 9 | 120 | 3 | 13 |
| 32 | 0.20 | DMF | 15 | 120 | 3 | 17 |
| 33 | 0.20 | DMF | 20 | 120 | 3 | 2 |

a) General conditions: 3,6,15-triamino-1,8,13-trihexyloxytriptycene (20.0 mg, 33 µmol, 4.0 eq), 2,7,14-triformyl-1,8,13-trihydroxytriptycene (13.0 mg, 34 µmol, 4.0 eq), TFA (0.01 mol $L^{-1}$ in dry DMF).

b) Dry solvents have been used.

## Synthesis of [4+6]-exo cage 12

**Table S32.** Screening conditions for synthesis of [4+6]-*exo* cage **12**. $eq_{TFA}$ is the used equivalents of TFA, $V$ is the volume of used dry DMF, $T$ is the reaction temperature, $t$ is the reaction duration and $\eta$ is the obtained yield after GPC purification.

| No.[a] | $eq_{TFA}$ | $V$ / mL | $T$ / °C | $t$ / d | $\eta$ / % |
|---|---|---|---|---|---|
| 1 | 0.08 | 3 | 100 | 3 | 36 |
| 2 | 0.20 | 4 | 120 | 3 | 55 |
| 3 | 0.08 | 5 | 120 | 3 | 47 |
| 4 | 0.20 | 5 | 120 | 3 | 51 |
| 5 | 0.20 | 5 | 120 | 4 | 53 |
| 6 | 0.20 | 5 | 120 | 5 | 55 |
| 7 | 0.28 | 5 | 120 | 3 | 47 |
| 8 | 0.40 | 5 | 120 | 3 | 45 |
| 9 | 0.20 | 6 | 120 | 3 | 63 |
| 10 | 0.20 | 6 | 120 | 4 | 54 |
| 11 | 0.20 | 6 | 120 | 6 | 57 |
| 12 | 0.20 | 7 | 120 | 3 | 48 |

a) General conditions: 3,6,15-triamino-1,8,13-trihexyloxytriptycene (20.0 mg, 33 µmol, 4.0 eq), 3,5-diformyl-2,6-dihydroxytoluene (9.0 mg, 50 µmol, 6.0 eq), TFA (0.01 mol $L^{-1}$ in dry DMF), dry DMF.

## Synthesis of [4+6]-endo cage 13

**Table S33.** Screening conditions for synthesis of [4+6]-*endo* cage **13**. $eq_{Aldehyde}$ is the used equivalents of 2,6-diformylphenol, V is the volume of used dry THF, $t$ is the reaction duration and $\eta$ is the obtained yield after SEC purification.

| No.[a] | $eq_{Aldehyde}$ | $V$ / mL | $t$ / d | $\eta$ / % |
|---|---|---|---|---|
| 1 | 6.1 | 2 | 4 | 25 |
| 2 | 6.1 | 3 | 4 | 29 |
| 3 | 6.2 | 5 | 4 | 50 |
| 4 | 6.0 | 6 | 4 | 21 |

a) General conditions: 3,6,15-triamino-1,8,13-trihexyloxytriptycene (20.0 mg, 33 µmol, 4.0 eq), 2,6-diformylphenol, TFA (67 µL, 0.01 mol $L^{-1}$ in dry THF, 0.08 eq), dry THF, r. t.

## Synthesis of [4+6]-endo cage 14

**Table S34.** Screening conditions for synthesis of [4+6]-*endo* cage **14**. *V* is the volume of used dry THF, *t* is the reaction duration and *η* is the obtained yield after SEC purification.

| **No.**[a] | ***V* / mL** | ***t* / d** | ***η* / %** |
|---|---|---|---|
| 1 | 3.0 | 3 | 41 |
| 2 | 4.5 | 4 | 46 |
| 3 | 5.0 | 4 | 62 |
| 4 | 7.0 | 4 | 47 |

a) General conditions: 3,6,15-triamino-1,8,13-trihexyloxytriptycene (20.0 mg, 33 µmol, 4.0 eq), 2,6-diformyl-4-*tert*-butylphenol (10.3 mg, 50 µmol, 6.0 eq), TFA (67 µL, 0.01 mol $L^{-1}$ in dry THF, 0.08 eq), dry THF, r. t.

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