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Supporting Information

Transformation of Imine Cages into Hydrocarbon Cages

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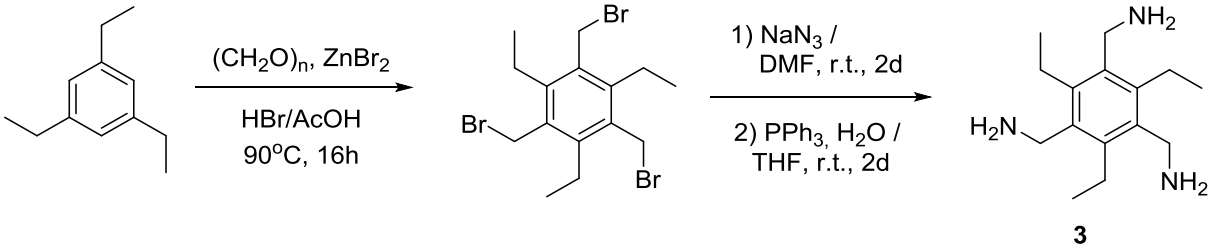
1 General remarks

Analytical Thin Layer Chromatography was performed with POLYGRAM® SIL G/UV$_{254}$ gel plates sold by Macherey-Nagel. Detection was accomplished using UV-light (254 nm). Flash column chromatography was accomplished using Silica gel 60 (40 – 63 µm / 230 – 400 mesh ASTM) purchased from Macherey-Nagel. Recycling high performance liquid chromatography was performed with a Shimadzu LC-20AP preparative pump unit, CBM-20A communication bus module, SPD-M20A diode array detector, FCV-20AH$_2$ valve unit and a Restek ultra silica 5 µm (250 x 21.2 mm) normal phase column. Recycling gel permeation chromatography was performed with a Shimadzu DGU-20A$_{3R}$ degassing unit, LC-20AD pump unit, CTO-20AC column oven, CBM-20A communication bus module, SPD-M20A diode array detector, FRC-10A fraction collector, FCV-20AH$_2$ valve unit, a PSS SDV (20 x 50 mm) precolumn and three SDV 100 Å (20 x 300 mm) columns connected in series. Melting points (not corrected) were measured with a Büchi Melting Point B-545. IR-Spectra were recorded on a Bruker Tensor 27 spectrometer on a ZnSe ATR crystal. NMR spectra were taken on a Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz) and Bruker Avance III 600 (600 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of the non-deuterated solvent in the corresponding deuterated solvent. HRMS experiments were carried out on a Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer solariX (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7.0 T superconducting magnet and interfaced to an Apollo II Dual ESI/MALDI source. MALDI-TOF MS experiments were carried out on a Bruker Daltonik Reflex III, on a Bruker ApexQe or on a Bruker AutoFlex Speed TOF with DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix. Elemental analysis was performed by the Microanalytical Laboratory of the University of Heidelberg using an Elementar Vario EL machine. Crystal structure analysis was accomplished on a STOE Stadivari diffractometer with a copper source (Cu Kα = 1.54178 Å) or a Bruker APEX II Quazar diffractometer with a molybdenum source (Mo Kα = 0.71073 Å). All crystallographic information files (1858590 (**13**), 1858591 (**13**), 1858592 (**11**), 1858593 (**5a**), 1858594 (**8a**), 1858595 (**9**), 1858596 (**8b**), 1858597 (**17**) and 1858598 (**8c**)) have been deposited in the Cambridge Crystallographic Data Centre and can be downloaded free of charge via www.ccdc.camac.uk/data_request/cif.

2 Synthesis and characterization

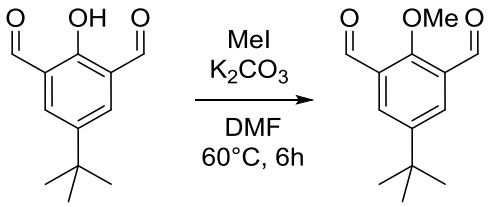
Synthesis of 3



3

1,3,5-Tri(bromomethyl)-2,4,6-triethylbenzene [S1] and (2,4,6-triethylbenzene-1,3,5-triyl)-trimethanamine (**3**)[S2] were obtained following literature known procedures. All obtained analytical data were in accordance with literature.

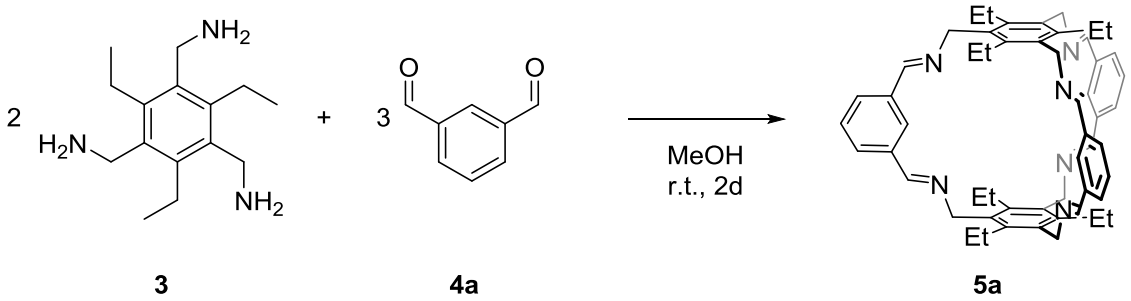
Synthesis of 4c



4c

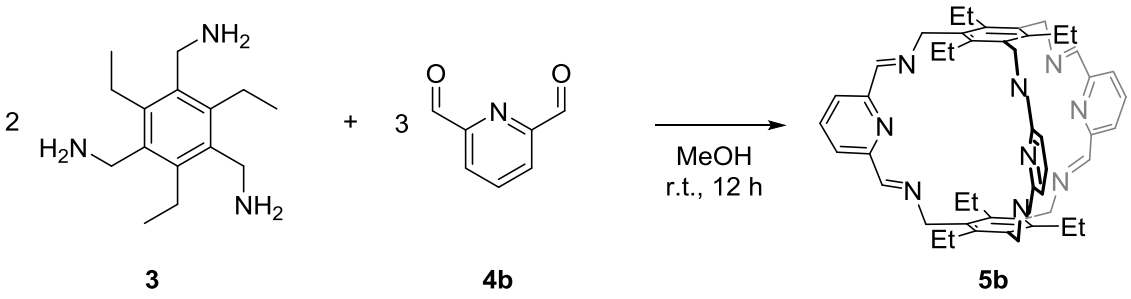
5-(tert-butyl)-2-methoxyisophthalaldehyde (**4c**)[S5] was obtained following a literature known procedure. All obtained analytical data were in accordance with literature.

Synthesis of [2+3] Imine Cage Compound 5a



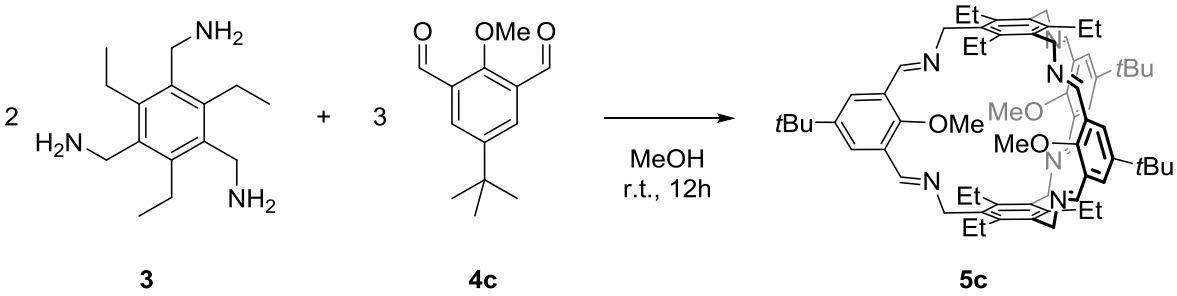
To a solution of isophthalaldehyde **4a** (969 mg, 7.23 mmol) in methanol (267 mL), a solution of triamine **3** (1.20 g, 4.82 mmol) in methanol (266 mL) was added dropwise within 1 hour and stirred 2 days at room temperature. The precipitate was collected by filtration, washed with methanol (50 mL) and dried in vacuum (7 mbar, 40°C) to give cage **5a** as a colourless solid (1.59 g, 83%, Lit.: 90%). Single-crystals could be obtained by slow evaporation of chloroform. **Mp** > 300°C, **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.14 (d, J = 7.8 Hz, 6H, Ar'-4/6-H), 7.78 (s, 6H, C*H*=N), 7.50 (t, J = 7.80 Hz, 3H, Ar'-5-H), 7.03 (s, 3H, Ar'-2-H), 5.09 (s, 12H, Ar-CH_2), 2.30 (q, J = 7.5 Hz, Ar-CH_2CH$_3$), 1.23 (t, J = 7.3 Hz, Ar-CH$_2$CH_3). The analytical data are in accordance with those from literature.[S3]

Synthesis of [2+3] Imine Cage Compound 5b



To a solution of pyridin-2,6-dicarbaldehyde **4b** (1.70 g, 12.6 mmol) in methanol (450 mL) a solution of triamine **3** (2.03 g, 8.39 mmol) in methanol (450 mL) was added dropwise within 1 hour and the reaction mixture was stirred 12 hours at room temperature. The precipitate was collected by filtration, washed with methanol (100 mL) and dried at room temperature overnight to give cage **5b** as colourless solid (2.39 g, 75%). **Mp** = 281°C (dec.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.15 (d, J = 8.6 Hz, 6H, H3, Py-H-3/5), 7.94 (s, 6H, C*H*=N), 7.76 (t, J = 7.8 Hz, 3H, Py-H-4), 5.14 (s, 12H, Ar-CH_2), 2.30 (q, J = 8.1 Hz, 12H, Ar-CH_2CH$_3$), 1.25 (t, J = 8.1 Hz, 12H, Ar-CH$_2$CH_3). The analytical data are in accordance with those from literature.[S4]

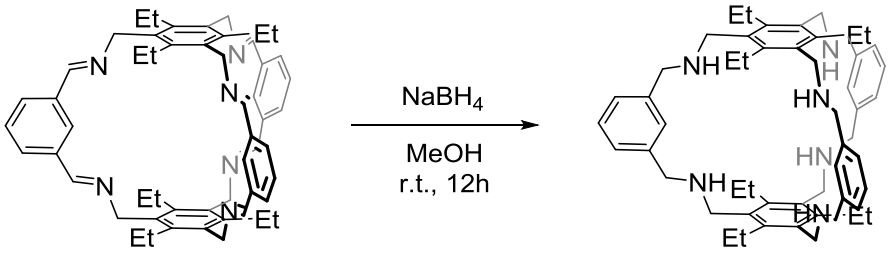
Synthesis of [2+3] Imine Cage Compound 5c



3 **4c** **5c**

To a solution of 5-(*tert*-Butyl)-2-methoxyisophthalaldehyde **4c** (708 mg, 2.89 mmol) in methanol (200 mL) a solution of triamine **3** (481 mg, 1.93 mmol) in methanol (200 mL) was added dropwise within 2 hours and the reaction mixture stirred for 12 hours at room temperature. The solvent was removed under reduced pressure (10 mbar, 50°C). To the remaining yellow residue *n*-pentane (50 mL) was added and the solid was removed by filtration. After removal of the solvent under reduced pressure (6 mbar, 50°C) compound **5c** was obtained as a colorless solid (397 mg, 39%). **Mp** = 294°C (dec.). **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.17 (s, 6H, *H*C=N), 8.05 (s, 6H, Ar'-3/5-H), 5.11 (s, 12H, Ar-C*H*$_2$), 3.03 (s, 9H, OC*H*$_3$), 2.36 (q, *J*=7.5 Hz, 12 H, Ar-C*H*$_2$CH$_3$), 1.36 (s, 27H, *t*Butyl), 1.26 (t, *J*=7.6 Hz, 18H, Ar-CH$_2$C*H*$_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ (ppm) = 158.7 (Ar'*C*-1), 154.9 (H*C*=N), 147.4 (Ar'*C*-4), 144.5 (Ar*C*-1/3/5), 132.1 (Ar'*C*-2/6), 128.9 (Ar*C*-2/4/6), 126.4 (Ar'*C*-3/5), 64.4 (O*C*H$_3$), 55.2 (Ar-*C*H$_2$), 35.0 (*C*(CH$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 23.8 (Ar-*C*H$_2$CH$_3$), 16.0 (Ar-CH$_2$*C*H$_3$). **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 2962 (m), 2872 (m), 1678 (w), 1638 (m), 1476 (m), 1463 (m), 1428 (m), 1394 (m), 1364 (m), 1312 (m), 1246 (m), 1214 (m), 1104 (m), 1044 (w), 1004 (m), 977 (m), 937 (w), 895 (m), 813 (m), 753 (s), 665 (m), 643 (m), 594 (m), 555 (m), 519 (m), 508 (m). **HRMS**-MALDI-TOF MS (DCTB): *m*/*z* $[M+H]^+$ calcd. for $C_{69}H_{91}N_6O_3$, 1051.7147; found, 1051.5563 ($\Delta m/z$ = 150 ppm).

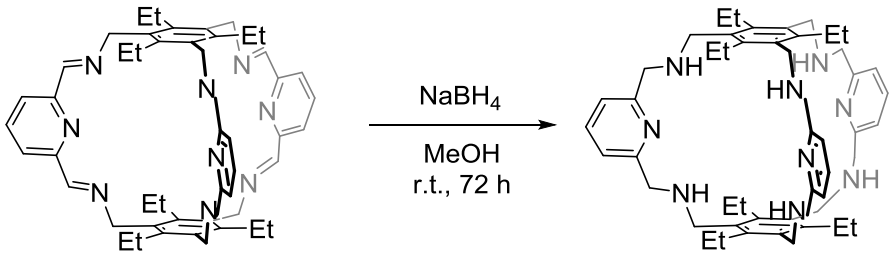
Synthesis of Amine Cage Compound 6a



5a **6a**

To a cooled (0°C) solution of imine cage **5a** (3.50 g, 4.42 mmol) in methanol (500 mL) sodium borohydride (10.1 g, 226 mmol) was added in portions and the reaction was allowed to reach room temperature. After stirring the reaction mixture 12 hours at room temperature the solvent was removed under reduced pressure (7 mbar, 50°C). A saturated solution of sodium hydrogencarbonate (500 mL) was added and extracted with dichloromethane (3 × 100 mL). The combined organic layer was dried over magnesium sulfate and solvent removed in vacuum (10 mbar, 50°C) to give amine cage **6a** as a yellow solid (3.34 g, 93%). **Mp** = 141–142°C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.33 (s, 3H, Ar'-2-H), 7.21 (m, 3H, Ar'-5-H), 7.07 (d, J = 7.6 Hz, 6H, Ar'-4/6-H) 3.96 (s, 12H, Ar-CH_2), 3.83 (s, 12H, Ar-CH_2NH), 2.77 (q, J = 7.6 Hz, 12H, Ar-CH_2CH$_3$), 1.25 (t, J = 7.5 Hz, 12H, Ar-CH$_2$CH_3). The analytical data are in accordance with those from literature.[S3]

Synthesis of Amine Cage Compound 6b

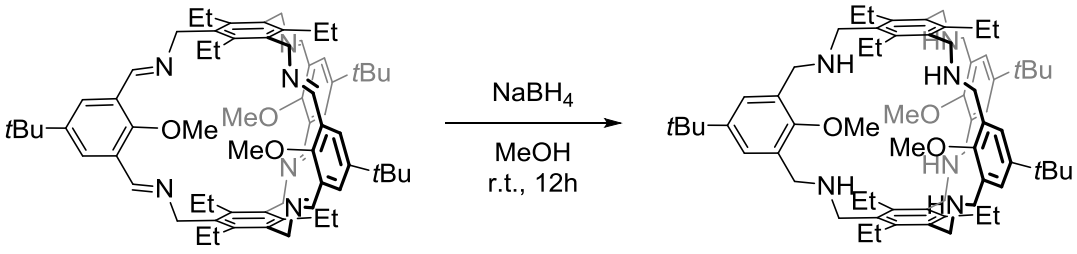


5b **6b**

To a suspension of imine cage **5b** (460 mg, 580 µmol) in methanol (80 mL) sodium borohydride (1.30 g, 78.0 mmol) was added in portions. The reaction mixture was stirred for one hour at room temperature and then refluxed for 72 hours. After 24 and 48 hours addition of sodium borohydride (1.30 g, 78.0 mmol) was repeated. After cooling the reaction mixture to room temperature the solvent was removed in vacuum (8 mbar, 50°C). Water was added (100 mL) and the aqueous suspension was extracted with chloroform (3 × 30 mL). The combined organic layers were washed with water (30 mL) and the solvent removed in vacuum

(2 mbar, 40°C) to give amine cage **6b** as colorless solid (455 mg, 99%). **Mp** > 300°C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.51 (t, J = 7.8 Hz, 3H, Py-4-H), 7.04 (d, J = 7.9 Hz 6H, Py-3/5-H), 3.92 (s, 11H, Py-CH_2), 3.80 (s, 11H, Ar-CH_2), 2.77 (q, J = 7.5 Hz, 12H, Ar-CH_2CH$_3$), 1.10 (t, J = 7.4 Hz, 12H, Ar-CH$_2$CH_3). **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 3514 (w), 2962 (w), 2875 (w), 1644 (m), 1585 (w), 1571 (w), 1484 (w), 1453 (m), 1380 (w), 1346 (w), 1311 (w), 1277 (w), 1234 (w), 1219 (w), 1150 (w), 1077 (w), 1043 (w), 976 (m), 920 (w), 849 (w), 817 (w), 770 (w), 733 (w), 701 (w), 654 (w), 643 (w). The analytical data are in accordance with those from literature.[S4]

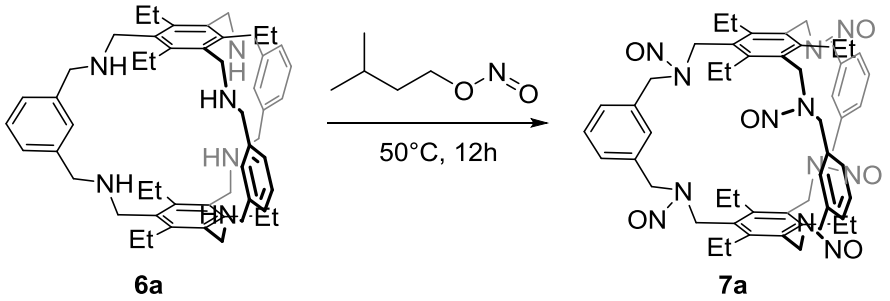
Synthesis of Amine Cage Compound 6c



5c **6c**

To a solution of imine cage **5c** (397 mg, 0.38 mmol) in methanol (40 mL sodium borohydride) was added in portions (2 × 830 mg). After stirring the reaction mixture for 12 hours at room temperature, solvent was evaporated under reduced pressure (10 mbar, 50°C), water was added (40 mL) and the aqueous suspension was extracted with dichloromethane (3 × 20 mL). The organic layers were combined, dried over magnesium sulfate and solvent was removed under reduced pressure (6 mbar, 50°C) to give amine cage **6c** as colorless solid (424 mg, 99%). **Mp** = 162–163°C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 7.23 (s, 6H, Ar'-3/4-H), 3.79 (s, 12H, Ar-CH_2), 3.70 (s, 12H, Ar'-CH_2), 3.24 (s, 9H, OCH$_3$), 2.74 (q, J = 7.5 Hz, 12H, Ar-CH_2CH$_3$), 1.31 (s, 27H, *t*Butyl), 1.08 (t, J = 7.53 Hz, 18H, Ar-CH$_2$CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$) δ (ppm) = 155.0 (Ar'C-1), 147.1 (Ar'C-4), 142.6 (ArC-1/3/5), 133.5 (Ar'C-2/6), 132.4 (ArC-2/4/6), 127.2 (Ar'C-3/5), 60.8 (OCH$_3$), 49.9 (Ar'-CH$_2$), 46.9 (Ar-CH$_2$), 34.5 (C(CH$_3$)$_3$), 31.6 (C(CH$_3$)$_3$), 22.6 (Ar-CH$_2$CH$_3$), 16.9 (Ar-CH$_2$$CH_3$). **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 2958 (s), 2869 (s), 2827 (s), 1632 (w), 1566 (w), 1482 (s), 1451 (s), 1393 (w), 1362 (m), 1299 (m), 1249 (m), 1206 (2), 1175 (m), 1118 (m), 1102 (m), 1077 (m), 1006 (s), 927 (w), 879 (m), 813 (m), 767 (m), 734 (m), 704 (m), 655 (m). **HRMS**-ESI (pos): m/z [M+H]$^+$ calcd. for $C_{69}H_{103}N_6O_3$, 1063.8086; found, 1063.8097 (Δm/z = 1 ppm); m/z [M+2H]$^{2+}$ calcd. for $C_{69}H_{104}N_6O_3$, 532.4085; found, 532.4083 ($\Delta m/z$ = 0.4 ppm). **Elemental Analysis**. calcd. for $C_{69}H_{102}N_6O_3 \cdot CH_2Cl_2$: C 73.20, H 9.13, N 7.32, found: C 73.20, H 9.48, N 7.10.

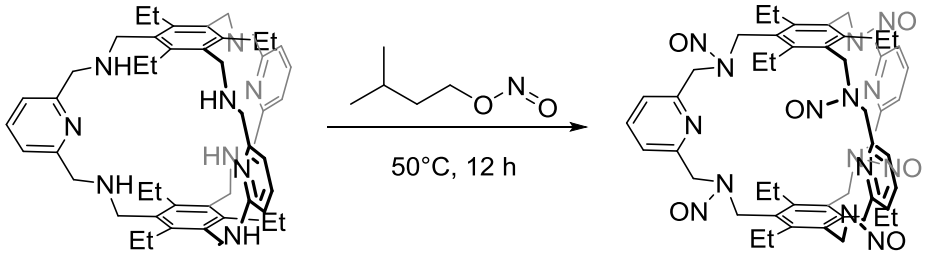
Synthesis of Nitrosamine Cage Compound 7a



6a **7a**

Amine cage **6a** (200 mg, 0.25 mmol) was suspended in isoamylnitrite (4.00 mL, 29.7 mmol) and stirred at 50°C for 12 hours. After cooling the reaction mixture to room temperature, the precipitate was collected by filtration, washed with methanol (20 mL) and dried in vacuum (8 mbar, 60°C) to give cage **7a** as pale yellow solid (164 mg, 68%). **Mp** = 290°C (dec.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.43-6.20 (m, 12H, Ar'-1/3/4/5-H) 5.62-3.60 (m, 24H, C*H*$_2$N(NO)C*H*$_2$) 2.96-1.61 (m, 12H, Ar-C*H*$_2$CH$_3$), 1.29-0.70 (m, 18H, Ar-CH$_2$C*H*$_3$). **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 2956 (m), 2934 (m), 2876 (m), 1693 (m), 1610 (m), 1593 (m), 1566 (m), 1492 (m), 1443 (m), 1376 (m), 1331 (m), 1278 (m), 1178 (m), 1134 (m), 1087 (m), 1068 (m), 1038 (m), 963 (m), 942 (m), 901 (m), 855 (m), 779 (m), 747 (m), 726 (m), 698 m), 662 (m), 629 (w), 587 (w), 561 (w), 530 (w). **HRMS**-ESI (pos): *m/z* [M-NO+H]$^+$ calcd. for $C_{54}H_{68}N_{11}O_5$, 950.5399; found, 950.5410 (Δm/z = 1 ppm); *m/z* [M+Na]$^+$ calcd. for $C_{54}H_{66}N_{12}NaO_6$, 1001.5120; found, 1001.5138 (Δ*m/z* = 2 ppm). **Elemental Analysis** calcd. for $C_{54}H_{66}N_{12}O_6$: C 66.24, H 6.79, N 17.17, found: C 66.03, H 6.67, N 17.07. A ^{13}C NMR spectrum was recorded but signals cannot be assigned due to the large number of isomers. The spectrum is shown in Figure S7.

Synthesis of Nitrosamine Cage Compound 7b

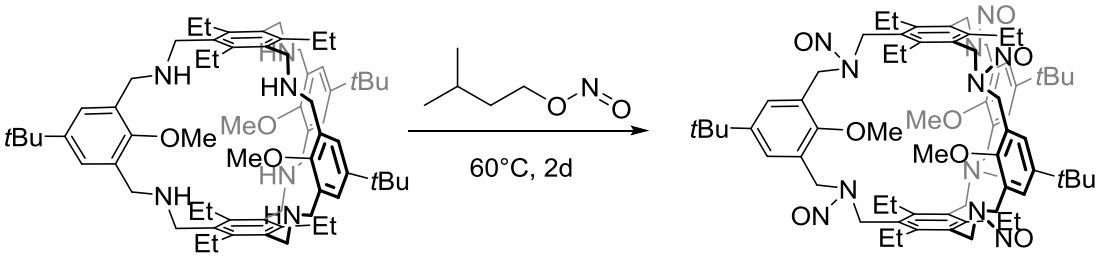


6b **7b**

Amine cage **6b** (500 mg, 0.62 mmol) was suspended in isoamylnitrite (9.00 mL, 66.9 mmol) and stirred at 50°C for 12 hours. After cooling the reaction mixture to room temperature, the

precipitate was collected by filtration, washed with methanol (50 mL) and dried in vacuum (16 mbar, 60°C) to give cage **7b** as colorless solid (360 mg, 60%). **Mp** = 203°C (dec.). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) = 7.50–7.30 (m, 3H, Py-6-H), 7.20–6.59 (m, 6H, Py-2/3-H), 5.49–4.10 (m, 24H, C*H*$_2$N(NO)C*H*$_2$), 2.75–1.75 (m, 12H, Ar-C*H*$_2$CH$_3$), 1.25–0.75 (m, 18H, Ar-CH$_2$C*H*$_3$). **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) = 156.6–155.6, 154.8–153.5, 146.9–145.7, 138.4–137.7, 129.1–127.7, 122.1–119.8, 55.7–54.6, 52.3–47.6, 42.6–39.9, 23.6–22.3, 16.6–15.1. **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 2968 (m), 2932 (m), 2872 (m), 1645 (m), 1593 (m), 1576 (m), 1450 (s), 1380 (m), 1339 (m), 1219 (m), 1180 (m), 1124 (m), 1089 (m), 1070 (m), 1042 (m), 976 (m), 941 (m), 847 (m), 804 (m), 758 (m), 644 (m), 628 (m), 597 (m), 545 (m), 514 (m). **HRMS**-MALDI-TOF (DCTB): *m/z* = 470.3050, 889.4970, 905.5449, 918.5680, 934.5517, 951.5562, 965.6032. **Elemental Analysis** calcd. for $C_{54}H_{66}N_{12}O_6$·MeOH: C 61.58, H 6.66, N 20.72, found: C 61.82, H 6.36, N 20.98.

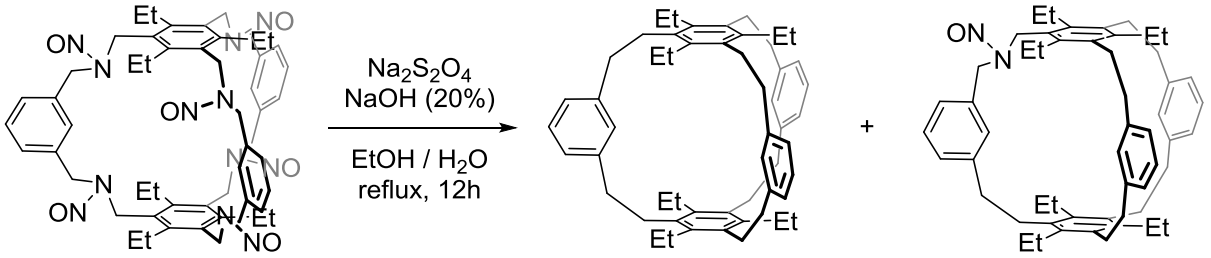
Synthesis of Nitrosamine Cage Compound 7c



6c **7c**

Amine cage **6c** (318 mg, 0.30 mmol) was dissolved in isoamylnitrite (25.0 mL, 36.0 mmol) and stirred at 60°C for 2 days. After the reaction was cooled down to room temperature, *n*-pentane (40 mL) was added to the reaction mixture. The solid was collected by filtration, washed with *n*-pentane (5 mL) and then dried under reduced pressure (7 mbar, 50°C). The product was obtained as colourless solid (312 mg, 83%). **Mp** = 253°C (dec.). **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 2964 (m), 2878 (m), 2834 (m), 1732 (w), 1636 (w), 1556 (w), 1485 (m), 1435 (m), 1394 (m), 1364 (m), 1333 (m), 1278 (m), 1206 (m), 1134 (m), 1109 (m), 1070 (m), 1040 (m), 1001 (m), 949 (m), 887 (m), 852 (m), 811 (m), 756 (m), 700 (m), 644 (m), 596 (m), 555 (m), 532 (m), 508 (m). **HRMS**-MALDI-TOF (DCTB): *m/z* $[M\text{-}NO]^+$ calcd. for $C_{69}H_{96}N_{11}O_8$, 1206.7443; found, 1206.9068 ($\Delta m/z$ = 135 ppm). **Elemental Analysis** calcd. for $C_{69}H_{96}N_{12}O_9$·2 H_2O: C 65.07, H 7.91, N 13.20, found: C 64.72, H 7.37, N 12.95. ^{1}H and ^{13}C NMR spectra were recorded, but signals cannot be assigned due to the large number of isomers. The spectra are shown in Figures S10 and S11.

Synthesis of Carbon Cage 8a and Mononitrosamine Cage 9



7a **8a** **9**

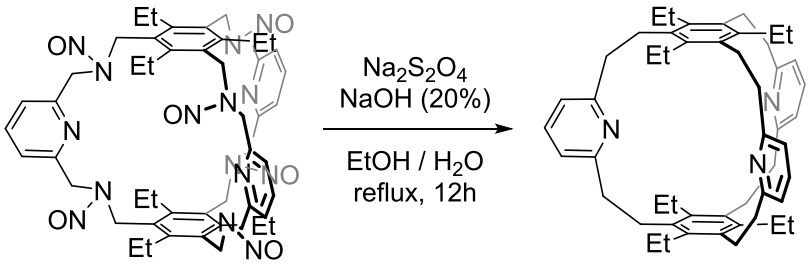
A suspension of nitrosoamine cage **7a** (150 mg, 0.15 mmol) in ethanol (65 mL) and $NaOH_{aq}$ (20 wt%, 65 mL) was heated to reflux and sodium dithionite (3.65 g, 20.9 mmol) was added in one portion. After stirring the reaction mixture 12 hours under reflux it was cooled to room temperature and water was added (100 mL). The aqueous suspension was extracted with dichloromethane (3 × 50 mL), the organic layers were combined and dried over magnesium sulfate. The solvent was removed in vacuum (10 mbar, 50°C) to give 106 mg of a colorless solid. TLC (SiO_2, hexanes:CH_2Cl_2 = 1:2): R_f = 0.4 (**9**); R_f = 0.9 (**8a**). Purification by silica gel flash column chromatography (CH_2Cl_2:*n*-pentane = 1:2) gave after drying in vacuum (6 mbar, 50°C):

Fraction 1 (R_f = 0.9): **8a** as a colorless solid (27 mg, 25%) **Mp** > 300°C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.32 (t, *J* = 7.5 Hz, 3H, Ar'-5-H), 7.10 (d, *J* = 7.3 Hz, Ar'-4/6-H), 5.89 (s, 3H, Ar'-2-H), 2.79–2.48 (m, 24H, Ar'-C*H*$_2$C*H*$_2$-Ar), 1.67–1.54 (m, 12 H, Ar-C*H*$_2$CH$_3$), 0.74 (t, *J* = 7.89 Hz, 18H, Ar-CH$_2$C*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 141.9 (Ar'*C*-1/3), 139.1 (Ar*C*-1/3/5), 135.6 (Ar*C*-2/4/6), 130.0 (Ar'*C*-2), 129.3 (Ar'*C*-5), 127.2 (Ar'*C*-4/6), 39.0 (Ar'-*C*H$_2$), 30.1 (Ar-*C*H$_2$), 22.5 (Ar-*C*H$_2$CH$_3$), 15.3 (Ar-CH$_2$*C*H$_3$). **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 3015 (w), 2961 (m), 2930 (m), 2870 (m), 1603 (w), 1588 (w), 1493 (w), 1439 (m), 1374 (w), 1321 (m), 1250 (w), 1173 (w), 1138 (m), 1097 (w), 1079 (w), 1042 (w), 1001 (w), 949 (w), 930 (w), 908 (m), 883 (w), 851 (w), 791 (m), 742 (w), 727 (s), 706 (s). **HRMS**-MALDI-TOF (DCTB): *m*/*z* [M]$^+$ calcd. for $C_{54}H_{66}$, 714.5165; found, 714.5182 ($\Delta m/z$ = 2 ppm). **Elemental Analysis** calcd. for $C_{54}H_{66}$·CH_2Cl_2: C 89.42, H 9.19 found: C 89.65, H 9.17

Fraction 2 (R_f = 0.4): **9** as a colorless solid (23 mg, 20%). **Mp** = 299–300°C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 7.35 (t, *J*=6.6 Hz, 3H, Ar'-4-H), 7.23–7.19 (m, 2H; Ar'-3/5-H), 7.17–7.13 (m, 4H, Ar''-3/5-H), 5.96 (s, 2H, Ar''-2-H), 5.84 (s, 1H, Ar'-1-H), 4.85–4.36 (m, 2H, C*H*$_2$N(NO)C*H*$_2$), 2.77–2.60 (m, 22H, -C*H*$_2$C*H*$_2$-), 1.79–1.44 (m, 12H,Ar-C*H*$_2$CH$_3$), 0.83–0.62 (m, 18H, Ar-CH$_2$C*H*$_3$). **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) = 142.8, 142.5, 141.7,

140.7, 139.5, 139.3, 136.7, 135.4, 135.1, 134.8, 129.7, 129.7, 129.6, 129.5, 128.4, 127.7, 125.7, 125.4, 53.5, 44.4, 39.0, 38.7, 38.3, 30.2, 30.0, 22.8, 22.6, 22.2, 22.0, 15.4, 15.3, 15.2. **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 3726 (w), 3703 (w), 3628 (w), 3599 (w), 3013 (w), 2965 (w), 2929 (w), 2870 (w), 2360 (m), 2341 (m), 2252 (w), 1701 (w), 1634 (w), 1604 (w), 1588 (w), 1559 (w), 1541 (w), 1490 (w), 1447 (w), 1376 (w), 1326 (w), 1283 (w), 1252 (w), 1204 (w), 1142 (w), 1079 (w), 1040 (w), 1002 (w), 973 (w), 940 (w), 909 (m), 882 (w), 854 (w), 792 (w), 769 (w), 732 (m), 707 (w), 669 (w), 649 (w). **HRMS**-MALDI-TOF (DCTB): *m*/*z* $[M–NO]^+$ calcd. for $C_{54}H_{66}N$, 728.5195; found, 728.5182 ($\Delta m/z$ = 2 ppm). **Anal**. calcd. for $C_{54}H_{66}N_2O \cdot 1.5\ H_2O$: C 84.11, H 8.80, N 3.63 found: C 84.30, H 8.74, N 3.22.

Synthesis of Carbon Cage Compound 8b

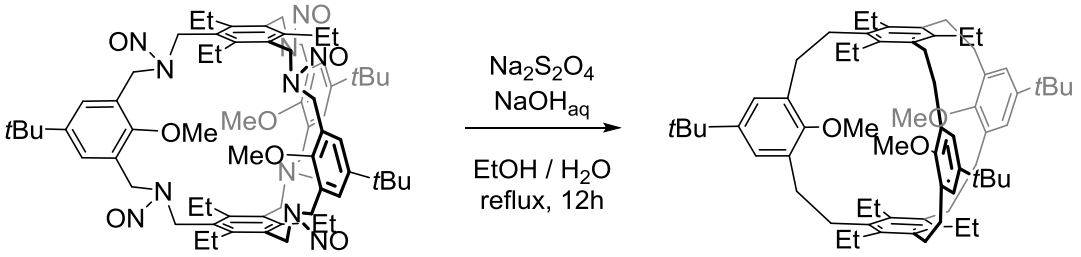


7b **8b**

Cage compound **7b** (500 mg, 0.51 mmol) was suspended in ethanol (190 mL) and $NaOH_{aq}$ (20%, 190 mL). The mixture was heated to reflux, sodium dithionite (7.1 g, 34 mmol) was added and refluxed for another 12 hours. After cooling the reaction mixture to room temperature, water (300 mL) and dichloromethane (300 mL) were added and the two layers were separated. The aqueous layer was extracted with dichloromethane (2 × 100 mL) and the solvent of the combined organic layers was evaporated in vacuo. A silica gel column was prepared by basifying the silica gel first with 100 mL triethylamine and then 1000 mL dichloromethane/NEt_3 99:1. The crude product was purified by chromatography with dichloromethane/NEt_3 99:1 (R_f = 0.18) to give 194 mg (53%) of cage compound **8b** as a colorless solid. **Mp** = 239°C (dec.). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ (ppm) = 7.53 (t, *J* = 7.7 Hz, 3H, Py-3-H), 7.04 (d, *J* = 7.8 Hz, 6H, Py-2/4-H), 2.88 (t, *J* = 7.2 Hz, 12H, Ar-CH_2), 2.51 (t, *J* = 7.2 Hz, 12H, Py-CH_2), 2.31 (q, *J* = 7.5 Hz, 12 H, Ar-C$H_2$$CH_3$), 0.97 (t, *J* = 7.4 Hz, 18H, Ar-CH_2CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 161.6 (Py*C*-1/5), 139.8 (Ar*C*-1/3/5), 136.9 (Py*C*-3), 136.2 (Ar*C*-2/4/6), 119.7 (Py*C*-2/4), 41.2 (Py-*C*H_2), 28.9 (Ar-*C*H_2), 23.0 (Ar-*C*$H_2$$CH_3$), 16.3 (Ar-$CH_2$*C*$H_3$). **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 2963 (m), 2924 (m), 2870 (m), 2390 (w), 2228 (w), 1737 (w), 1587 (m), 1575 (m), 1491 (w), 1456 (m), 1375 (w), 1313 (w), 1250

(w), 1220 (w), 1139 (w), 1090 (w), 1043 (w), 983 (w), 908 (m), 806 (m), 727 (s), 646 (m). **HRMS**-MALDI (DCTB+CsI): *m/z* $[M+H]^+$ calcd. for $C_{51}H_{64}N_3$, 718.5095; found, 718.5109 ($\Delta m/z$ = 2 ppm); $[M+H_2O+H]^+$ calcd. for $C_{51}H_{67}N_4$, 736.5200; found, 736.5217 ($\Delta m/z$ = 2 ppm). **Elemental Analysis** calcd. for $C_{51}H_{63}N_3 \cdot CH_2Cl_2$: C 77.78, H 8.16, N 5.23 found: C 77.85, H 8.36, N 5.66.

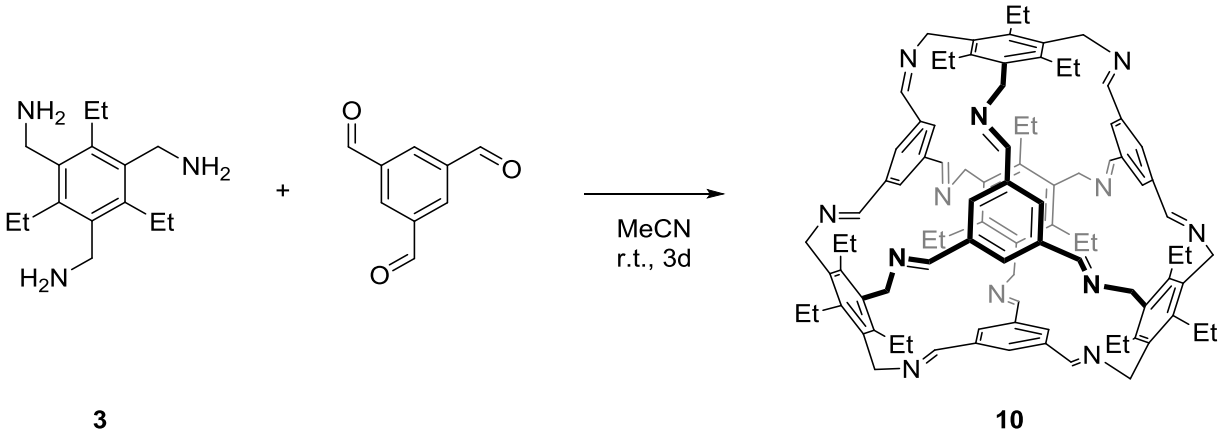
Synthesis of Carbon Cage 8c



7c **8c**

To a suspension of nitrosamine cage **7c** (102 mg, 0.08 mmol) in ethanol (30 mL) and $NaOH_{aq}$ (20 wt%, 30 mL), sodium dithionite (2.19 g, 12.6 mmol) was added under reflux in one portion. After refluxing for another 12 hours, the reaction mixture was cooled to room temperature and water (30 mL) was added. The aqueous suspension was extracted with dichloromethane (3 × 30 mL). The organic layers were combined and dried over magnesium sulfate and the solvent was removed in vacuum (6 mbar, 50°C) to give a colorless solid (81 mg). Purification by silica gel flash column chromatography (*n*-pentane, R_f = 0.88) gave cage **8c** as a colorless solid (16 mg, 20%). **Mp** = 131°C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.08 (s, 6H, Ar'-3/5-H), 2.98 (s, 9H, OCH_3), 2.89 (t, *J* = 6.9 Hz, 12H, Ar-CH_2), 2.63 (t, *J* = 6.8 Hz, 12H, Ar'-CH_2), 2.43 (q, *J* = 7.1 Hz, 12H, Ar-CH_2CH$_3$), 1.33 (s, 27H, *t*Butyl), 1.03 (t, *J* = 6.98 Hz, 18H, Ar-CH$_2$CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) = 155.9 (Ar'*C*-1), 145.4 (Ar'*C*-4), 139.6 (Ar*C*-1/3/5), 135.6 (Ar*C*-2/4/6) 133.4 (Ar'*C*-2/6), 124.7 (Ar'*C*-3/5), 60.2 (O*C*H$_3$), 34.4 (*C*(CH$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 31.2 (Ar'-*C*H$_2$), 28.3 (Ar-*C*H$_2$), 22.8 (Ar-*C*H$_2$CH$_3$), 16.1 (Ar-CH$_2$*C*H$_3$). **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 2959 (s), 2930 (s), 2866 (m), 2823 (w), 1740 (w), 1600 (w), 1479 (s), 1460 (m), 1392 (w), 1373 (m), 1362 (m), 1297 (m), 1257 (m), 1239 (m), 1202 (m), 1170 (m), 1110 (m), 1069 (m), 1018 (s), 955 (w), 872 (m), 809 (m), 773 (m), 737 (m), 710 (m), 653 (m), 581 (w), 555 (w), 542 (w), 532 (w), 520 (w), 509 (w). **HRMS**-MALDI (DCTB): *m/z* $[M]^+$ calcd. for $C_{69}H_{96}O_3$, 972.7359; found, 972.7368 ($\Delta m/z$ = 1 ppm); $[M+Na]^+$ calcd. for $C_{69}H_{96}NaO_3$, 995.7280; found, 995.7257 ($\Delta m/z$ = 2 ppm); $[M+K]^+$ calcd. for $C_{69}H_{96}KO_3$, 1011.7000; found, 1011.6997 ($\Delta m/z$ = 0.3 ppm). **Elemental Analysis** calcd. for $C_{69}H_{96}O_3$: C 85.13, H 9.94, found: C 85.14, H 10.01.

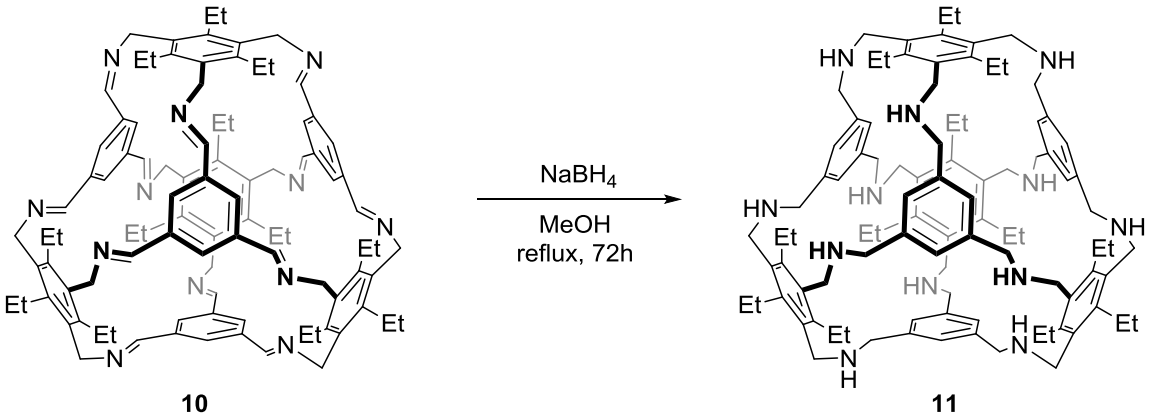
Synthesis of cage compound 10:



3 **10**

Cage compound **10** [S6] was obtained following literature known procedures.

Synthesis of [4+4] Amine Cage Compound 11

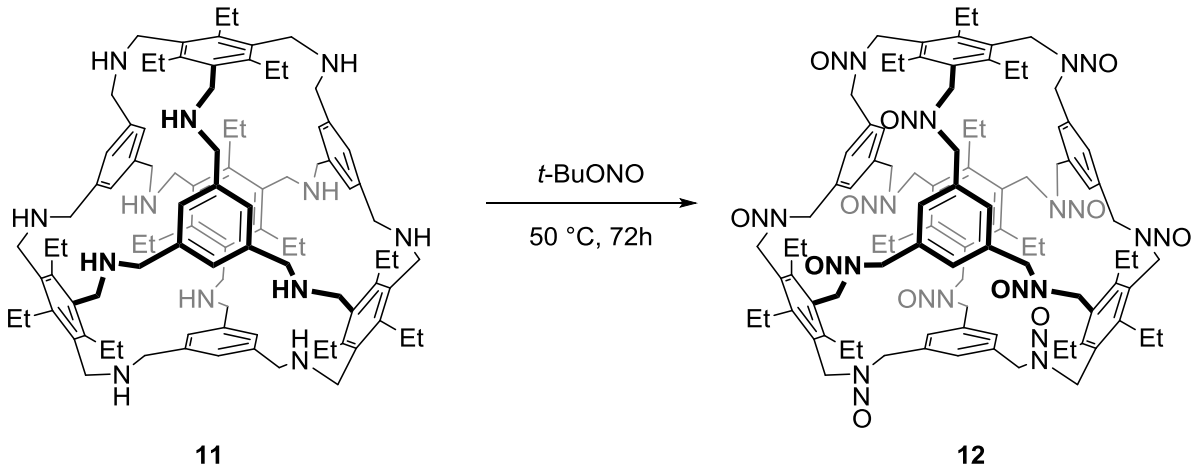


10 **11**

To a stirred solution of cage **10** (300 mg, 200 µmol) in dry methanol (100 mL) atmosphere sodium borohydride (5 g, 130 mmol) was added under argon in small portions. After complete addition, the reaction mixture was stirred at room temperature for 2 hours, followed by heating under reflux for 72 hours. After cooling to room temperature, the solvent was evaporated under vacuum to dryness, HCl_{aq} (1 M, 250 mL) was added and the flask was shaken very well. The solution was made basic with KOH_{aq} (6 M, 100 mL) and extracted with chloroform (3 x 100 mL). The combined organic layer was washed with water (40 mL). The solvent was evaporated and the solid residue dried in vacuo to give compound **11** (320 mg, 99%) as a colourless solid. **Mp** : 300°C (dec.). **^{1}H NMR** (600 MHz, C_6D_6): δ (ppm) = 7.35 (s, 12H, Ar*H*), 3.84 (s, 24H, Ar´C*H*$_2$N-), 3.77 (s, 24H, ArC*H*$_2$N-), 2.95 (q, *J* = 7.3 Hz, 24H, -C*H*$_2$CH$_3$), 1.26 (t, *J* = 7.4 Hz, 36H, -CH$_2$C*H*$_3$), 0.61 (s, 12H, -N*H*). **^{13}C NMR** (150 MHz, C_6D_6): δ (ppm) = 142.5 (-*C*CH$_2$CH$_3$), 140.9 (Ar´*C*CH$_2$N-), 134.4 (Ar*C*CH$_2$N-), 129.2 (-*C*H), 56.4 (Ar´*C*H$_2$N-),

49.6 (Ar*C*H$_2$N-), 23.1 (-*C*H$_2$CH$_3$), 17.2 (-CH$_2$*C*H$_3$) ppm. **FT-IR** (ATR): ṽ (cm^{-1}) = 2954 (m), 2923 (s), 2866 (m), 2854 (m), 2812 (w), 2733 (vw), 1650 (w), 1622 (w), 1610 (w), 1571 (vw), 1502 (w), 1436 (s), 1400 (w), 1386 (w), 1373 (m), 1313 (w), 1259 (m), 1182 (vw), 1159 (vw), 1099 (m), 1080 (m), 1066 (m), 1010 (m), 929 (w), 875 (m), 835 (m), 802 (m), 744 (s), 727 (vs), 692 (s), 675 (s), 646 (m), 603 (m), 595 (m), 586 (m), 559 (m), 541 (s), 518 (w). **HRMS**-ESI (DCM/MeOH, pos): *m/z* [M+H]$^+$ calcd. for $C_{96}H_{133}N_{12}$, 1455.0803; found: 1455.0834 ($\Delta m/z$ = 2 ppm); [M+2H]$^{2+}$ calcd. for $C_{96}H_{134}N_{12}$, 728.0444; found: 728.0448 ($\Delta m/z$ = 0.5 ppm). **Elemental Anal**. calcd. for $C_{96}H_{132}N_{12}\cdot CHCl_3$: C 76.56, H 8.82, N 11.10 found: C 76.86, H 7.98, N 10.05.

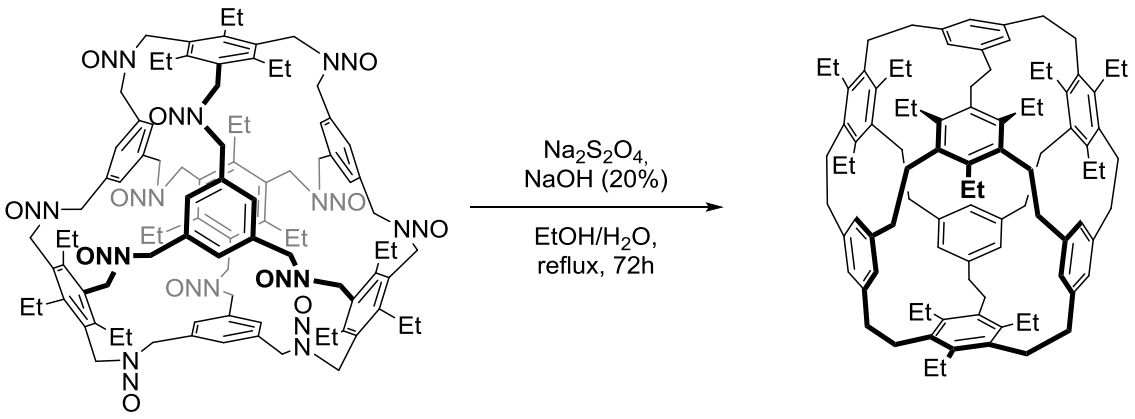
Synthesis of [4+4] Nitrosamine Cage Compound 12:



11 **12**

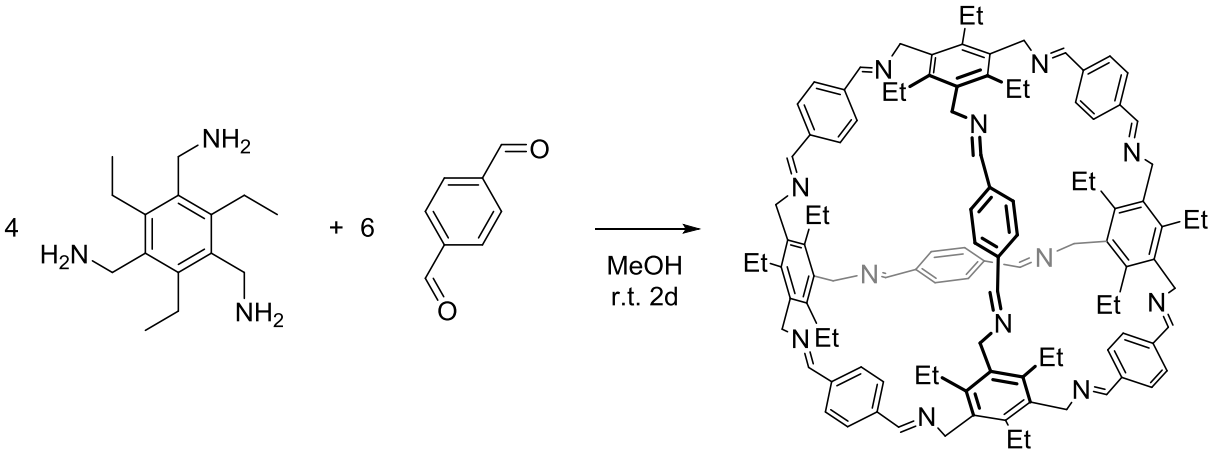
Compound **11** (300 mg, 0.2 mmol) was suspended in *tert*-butyl nitrite (25 mL) and stirred at 50 °C for 72 hours. After cooling to room temperature, the solvent was evaporated to give 370 mg (99%) of crude cage **12** as a yellow powder. The material was used in the next step without further purification. **Mp**: 120°C. **FT-IR** (ATR): ṽ (cm^{-1}) = 2972 (w), 2932 (w), 2874 (w), 1707 (m), 1632 (m), 1607 (w), 1551 (s), 1493 (vw), 1437 (s), 1377 (s), 1333 (s), 1302 (s), 1279 (s), 1221 (m), 1177 (s), 1134 (vs), 1094 (w), 1069 (vw), 1042 (m), 1024 (s), 989 (s), 961 (s), 943 (s), 860 (m), 824 (m), 760 (m), 739 (m), 694 (w), 652 (w), 631 (w). **HRMS**-ESI (MeCN/MeOH, pos): *m/z* [M-NO+H]$^+$ calcd. for $C_{96}H_{122}N_{23}O_{11}$, 1773.9822; found, 1773.9840 ($\Delta m/z$ = 1 ppm). **Elemental Analysis** calcd. for $C_{96}H_{120}N_{24}O_{12}\cdot 4H_2O$: C 61.52, H 6.88, N 17.94, found: C 61.38, H 6.34, N 15.74. ^{1}H and ^{13}C NMR spectra were recorded, but signals cannot be assigned due to the large number of isomers. The spectra are shown in Figures S27 and S28.

Synthesis of Carbon Cage Compound 13:



Compound **12** (370 mg, 0.2 mmol) was suspended in ethanol (180 mL) and $NaOH_{aq}$ (20%, 180 mL). The mixture was heated to reflux, sodium dithionite (5.2 g, 25 mmol) was added and refluxed for another 72 hours. After cooling the reaction mixture to room temperature, water (200 mL) and dichloromethane (200 mL) were added and the two layers were separated. The aqueous layer was extracted with dichloromethane (2 × 100 mL) and the solvent of the combined organic layers was evaporated in vacuo. The crude product was purified by column chromatography (Hexanes/DCM 5:1, R_f = 0.37) to give 10 mg (5%) of cage **13** as a colourless solid. **Mp** : >400°C. **^{1}H NMR** (600 MHz, 253 K, $CDCl_3$): δ (ppm) = 6.95 (s, 4H, Ar*H*), 6.85 (s, 4H, Ar*H*), 5.76 (s, 4H, Ar*H*), 3.40 (q, 7.0 Hz, 4H, -C*H*$_2$-), 3.31 – 3.18 (m, 8H, -C*H*$_2$-), 3.11 – 2.84 (m, 36H, -C*H*$_2$-), 2.51 (t, *J* = 11.8 Hz, 4H, -C*H*$_2$-), 2.33 (q, *J* = 7.2 Hz, 4H, -C*H*$_2$-), 2.15 (t, *J* = 11.8 Hz, 4H, -C*H*$_2$-), 1.74 – 1.68 (m, 4H, -C*H*$_2$-), 1.64 (t, *J* = 7.2 Hz, 4H, -C*H*$_2$-), 1.19 (t, *J* = 7.1 Hz, 12H, -CH_2CH_3), 1.09 (t, *J* = 11.5 Hz, 4H, -C*H*$_2$-), 0.91 (t, *J* = 7.3 Hz, 12H, -CH_2CH_3), 0.86 (t, *J* = 7.2 Hz, 12H, -CH_2CH_3) ppm. **^{13}C NMR** (151 MHz, 253 K, $CDCl_3$): δ (ppm) = 141.7 (-*C*CH_2-), 141.1 (-*C*CH_2-), 139.6 (-*C*CH_2CH_3), 139.5 (-*C*CH_2-), 139.0 (-*C*CH_2CH_3), 137.7 (-*C*CH_2CH_3), 137.6 (-*C*CH_2-), 134.9 (-*C*CH_2-), 133.3 (-*C*CH_2-), 128.8 (-*C*H), 127.5 (-*C*H), 123.6 (-*C*H), 39.2 (-*C*H_2-), 38.3 (-*C*H_2-), 35.2 (-*C*H_2-), 34.7 (-*C*H_2-), 27.3 (-*C*H_2-), 26.3 (-*C*H_2-), 25.4 (-*C*H_2-), 23.0 (-*C*H_2-), 22.7 (-*C*H_2-), 17.2 (-CH_2*C*H_3), 16.3 (-CH_2*C*H_3), 16.2 (-CH_2*C*H_3) ppm. **FT-IR** (ATR): $\tilde{\upsilon}$ (cm^{-1}) = 3003 (w), 2959 (s), 2924 (vs), 2868 (m), 1601 (m), 1493 (m), 1452 (s), 1431 (m), 1373 (m), 1312 (w), 1254 (w), 1223 (w), 1192 (vw), 1080 (w), 1069 (m), 1038 (w), 1022 (w), 1005 (w), 955 (w), 916 (w), 899 (w), 879 (m), 858 (s), 820 (w), 810 (w,) 775 (w), 754 (w), 739 (w), 716 (s), 694 (w), 671 (w), 663 (w), 619 (w), 598 (w), 588 (w), 577 (w), 561 (w), 542 (s), 525 (s), 517 (s). **HRMS**-MALDI-TOF (DCTB): *m/z* $[M]^+$ calcd. for $C_{96}H_{120}$, 1273.9426; found: 1273.9529 ($\Delta m/z$ = 8 ppm).

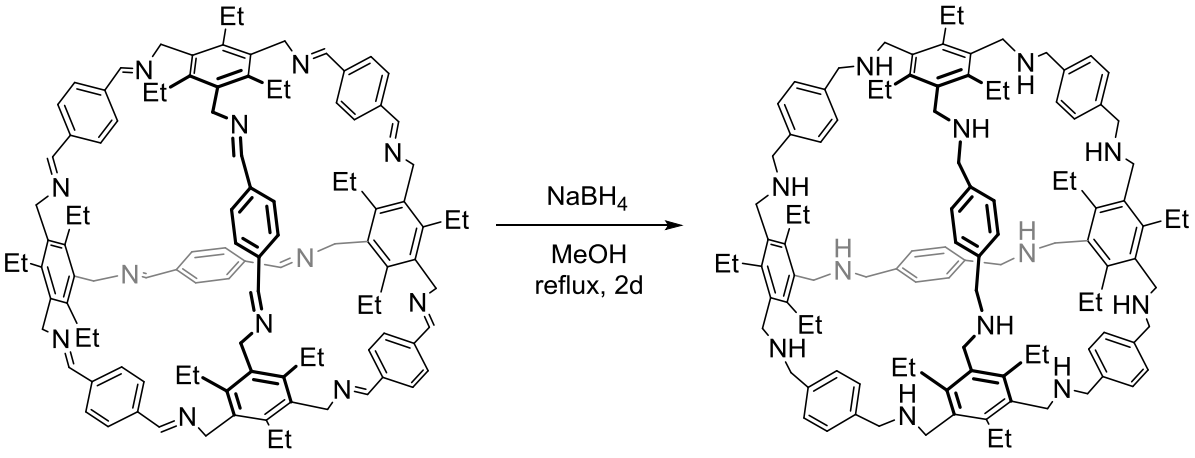
Synthesis of [4+6] Imine Cage Compound 14



3 **14**

To a solution of terephthalaldehyde (339 mg, 2.53 mmol) in methanol (100 mL) a solution of amine **3** (422 mg, 1.69 mmol) in methanol (100 mL) was added dropwise over 2 hours. After stirring the reaction mixture for 2 days at room temperature the precipitate was collected by filtration and washed with methanol (100 mL) and *n*-pentane (100 mL). Extraction of the solid with chloroform (100 mL) and removal of the solvent in vacuum (8 mbar, 50°C) gave imine cage **14** as a colorless solid (288 mg, 42%). **Mp** = 203°C (dec.). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) = 8.30 (s, 12H, *H*C=N), 7.74 (s, 12H, Ar'-2/3/5/6-H), 4.94 (s, 24H, N-C*H*$_2$), 2.74 (q, *J* = 7.3 Hz, 24H, Ar-C*H*$_2$CH$_3$), 1.26 (t, *J* = 7.6 Hz, 36H, Ar-CH$_2$C*H*$_3$). **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) = 160.3 (H*C*=N), 144.0 (Ar*C*-1/3/5), 138.1 (Ar'*C*-1/4), 132.7 (Ar*C*-2/4/6), 128.6 (Ar'*C*-2/3/5/6), 58.0 (Ar-*C*H$_2$), 23.2 (Ar-*C*H$_2$CH$_3$), 15.6 (Ar-CH$_2$*C*H$_3$). **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 2959 (m), 2926 (m), 2872 (m), 2361 (w), 1639 (s), 1566 (w), 1484 (w), 1452 (m), 1415 (m), 1372 (m), 1314 (m), 1298 (m), 1217 (m), 1074 (w), 1043 (w), 1016 (m), 976 (m), 825 (m), 766 (m). **HRMS**-MALDI-TOF (DCTB): *m*/*z* $[M+H]^+$ calcd. for $C_{108}H_{121}N_{12}$, 1586.9856; found, 1587.0971 ($\Delta m/z$ = 70 ppm). **Elemental Anal**. calcd. for $C_{108}H_{120}N_{12}\cdot 7H_2O$: C 75.76, H 7.89, N 9.82 found: C 75.85, H 7.62, N 9.68.

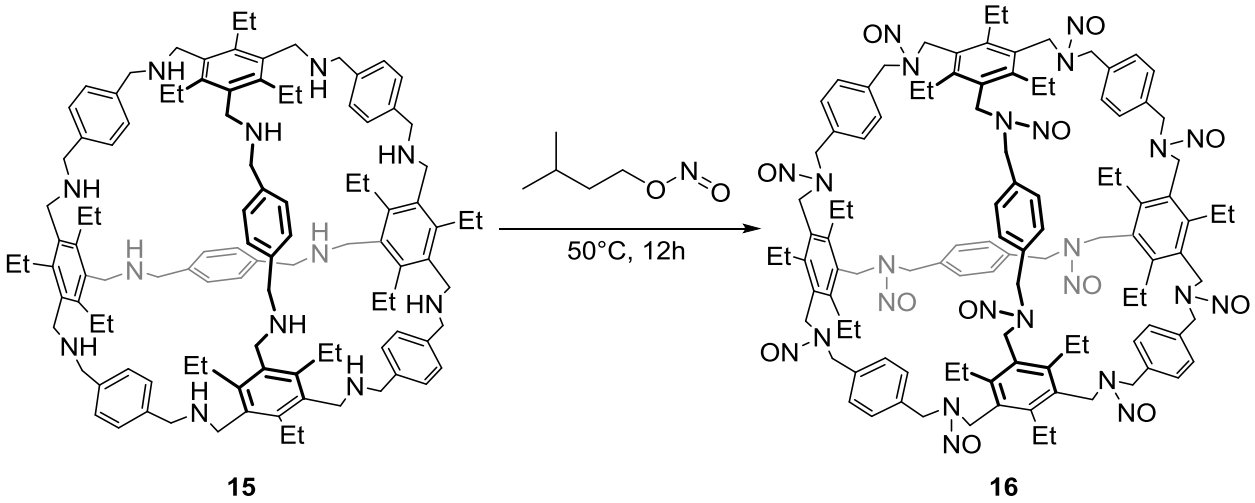
Synthesis of Amine Cage Compound 15



14 **15**

To a suspension of imine cage **14** (1.72 g, 1.08 mmol) in methanol (120 mL) sodium borohydride (4.92 g, 130 mmol) was added in portions. After stirring the reaction mixture at room temperature for one hour it was refluxed for two days. The reaction mixture was cooled to room temperature and the solvent removed in vacuum (46 mbar, 50°C). The residue was suspended in water (200 mL) and extracted with dichloromethane (3 × 50 mL). The organic layers were combined and dried over magnesium sulfate. After removal of the solvent in vacuum (6 mbar, 50°C) amine cage **15** was obtained as colorless solid (505 mg, 29%). **Mp** = 283°C (dec.). **^{1}H NMR** (500 MHz, C_6D_6): δ (ppm) = 7.27 (s, 24H, Ar'-2/3/5/6-H), 3.74 (s, 48H, Ar'-C*H*$_2$, Ar-C*H*$_2$), 2.88 (q, *J* = 7.7 Hz, 24H, Ar-C*H*$_2$CH$_3$), 1.22 (t, *J* = 7.30 Hz, 36H, Ar-CH$_2$C*H*$_3$). **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) = 142.4 (Ar*C*-1/3/5), 139.1 (Ar'*C*-1/4), 134.2 (Ar*C*-2/4/6), 128.2 (Ar'*C*-2/3/5/6), 54.8 (Ar-*C*H$_2$), 47.6 (Ar'-*C*H$_2$), 22.8 (Ar-*C*H$_2$CH$_3$), 17.1 (Ar-CH$_2$*C*H$_3$) **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 2963 (m), 2926 (m), 2866 (m), 2364 (w), 1639 (m), 1567 (w), 1509 (w), 1450 (m), 1372 (m), 1313 (m), 1299 (w), 1265 (w), 1215 (w), 1102 (m), 1072 (m), 1045 (w), 1018 (w), 976 (w), 814 (m), 765 (m), 735 (s), 701 (m), 602 (m), 549 (m), 529 (m), 505 (m). **HRMS**-ESI (pos): *m*/*z* $[M+H]^+$ calcd. for $C_{108}H_{145}N_{12}$, 1611.1748; found, 1611.1819 ($\Delta m/z$ = 4 ppm); $[M+2H]^{2+}$ calcd. for $C_{108}H_{146}N_{12}$, 806.0914; found, 806.0923 ($\Delta m/z$ = 1 ppm). **Elemental Anal**ysis calcd. for $C_{108}H_{144}N_{14}O_{12}\cdot CH_2Cl_2$: C 77.22, H 8.68, N: 9.91 found: C 77.44, H 8.67, N: 9.67.

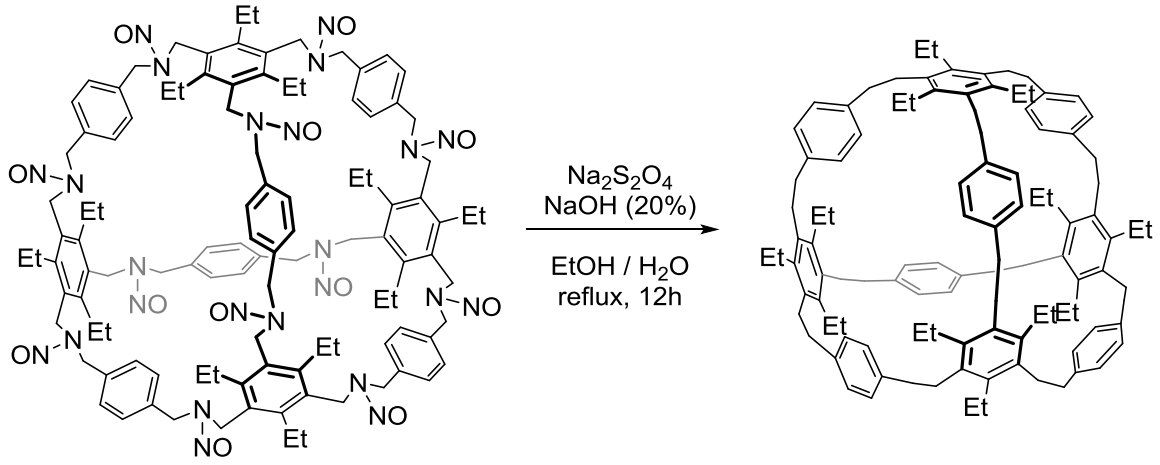
Synthesis of Nitrosamine Cage Compound 16



15 **16**

Amine cage **15** (576 mg, 0.36 mmol) was suspended in isoamylnitrite (10.2 mL, 75.7 mmol) and stirred at 50°C for 12 hours. After cooling the reaction mixture to room temperature, the solid was isolated by filtration, washed with methanol (25 mL) and dried under vacuum (8 mbar, 60°C) to give the cage compound **16** as colorless solid (523 mg, 75%). **Mp** = 218°C (dec.). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) = 7.58–6.32 (m, 24H, Ar'-2/3/5/6-H), 6.22–3.35 (m, 48H, C*H*$_2$N(NO)C*H*$_2$), 2.28–1.40 (m, 24H, Ar-C*H*$_2$CH$_3$), 1.21–0.24 (m, 36H, Ar-CH$_2$C*H*$_3$). **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 2970 (m), 2937 (m), 2874 (m), 1697 (w), 1630 (w), 1567 (w), 1514 (w), 1443 (s), 1333 (s), 1213 (m), 1170 (m), 1132 (s), 1069 (m), 1039 (m), 1021 (m), 937 (m), 734 (m). **HRMS**-ESI (pos): *m*/*z* [M+K+Na]$^{2+}$ calcd. for $C_{108}H_{132}KN_{24}NaO_{12}$, 1010.0003; found, 1010.9912 ($\Delta m/z$ = 98 ppm). **Elemental Analysis** calcd. for $C_{108}H_{136}N_{24}O_{12}$·MeOH: C 65.72, H 6.89, N: 16.89 found: C 65.42, H 6.80, N: 16.78. A ^{13}C NMR spectrum was recorded but signals cannot be assigned due to the large number of isomers. The spectrum is shown in Figure S40.

Synthesis of Carbon Cage Compound 17



16 **17**

A solution of nitrosamine cage **16** (207 mg, 0.11 mmol) in ethanol (90 mL) and aqueous sodium hydroxide (20% (*w*/*w*), 90 mL) was heated to reflux. After the addition of sodium dithionite (5.04 g, 29.0 mmol) in one portion the reaction mixture was kept under reflux for 12 hours. The reaction mixture was cooled to room temperature and water (100 mL) was added. After extraction of the aqueous suspension with dichloromethane (4 × 50 mL) the organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure (10 mbar, 50°C) and gave 143 mg of crude product. Compound **17** was isolated after purification by silica gel column chromatography (CH_2Cl_2 100%, R_f = 0.93) as a colorless solid (19 mg). Further purification via rGPC ($CHCl_3$, 40°C, 5 mL/min) was applied and 5 mg of the product was obtained in 4% yield. **Mp** = 254°C (dec.). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 6.81 (s, 12H, Ar'-2/3/5/6-H), 2.81 (t, *J* = 6.9 Hz 24H, Ar-CH_2), 2.63 (t, *J* = 6.7 Hz, 24H, Ar'-CH_2), 2.05 (q, *J* = 7.6 Hz, 24H, Ar-CH_2CH$_3$), 0.95 (t, *J* = 7.27 Hz, 36H, Ar-CH$_2$CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) = 139.6 (Ar*C*-1/3/5), 139.0 (Ar'*C*-1/4), 134.1 (Ar*C*-2/4/6), 128.4 (Ar'*C*-2/3/5/6), 36.6 (Ar'-*C*H$_2$), 29.0 (Ar-*C*H$_2$), 22.1 (Ar-*C*H$_2$CH$_3$), 15.7 (Ar-CH$_2$*C*H$_3$). **FT-IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 2961 (s), 2928 (s), 2866 (m), 2360 (w), 1893 (w), 1788 (w), 1614 (w), 1572 (w), 1512 (m), 1489 (m), 1447 (m), 1419 (m), 1375 (m), 1315 (w), 1250 (w), 1210 (w), 1155 (w), 1109 (w), 1069 (m), 1041 (m), 1021 (m), 955 (m), 931 (m), 902 (m), 825 (s), 756 (m), 672 (w), 640 (w), 584 (m), 534 (m). **HRMS**-MALDI (DCTB+CsI): *m*/*z* $[M]^+$ calcd. for $C_{108}H_{132}$, 1430.0357; found, 1430.0590 ($\Delta m/z$ = 16 ppm); $[M+Na]^+$ calcd. for $C_{108}H_{132}Na$, 1453.0257; found, 1453.0567 ($\Delta m/z$ = 21 ppm).

3 NMR Analytics

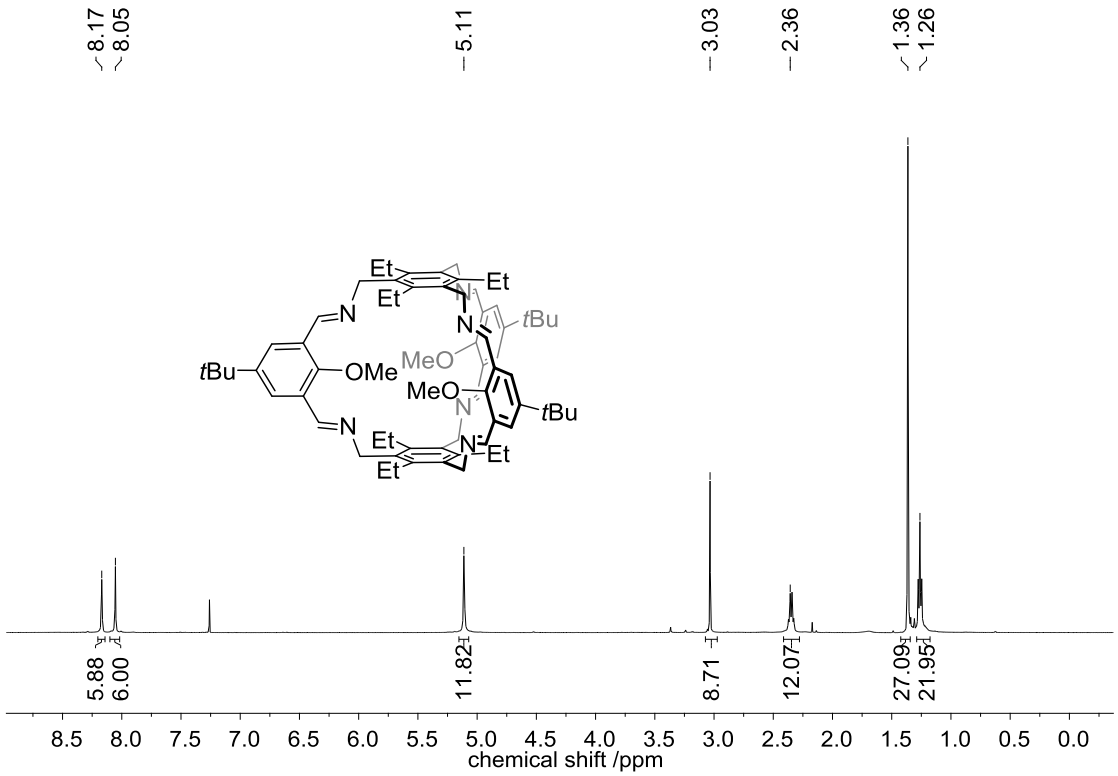


Figure S1: ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **5c**.

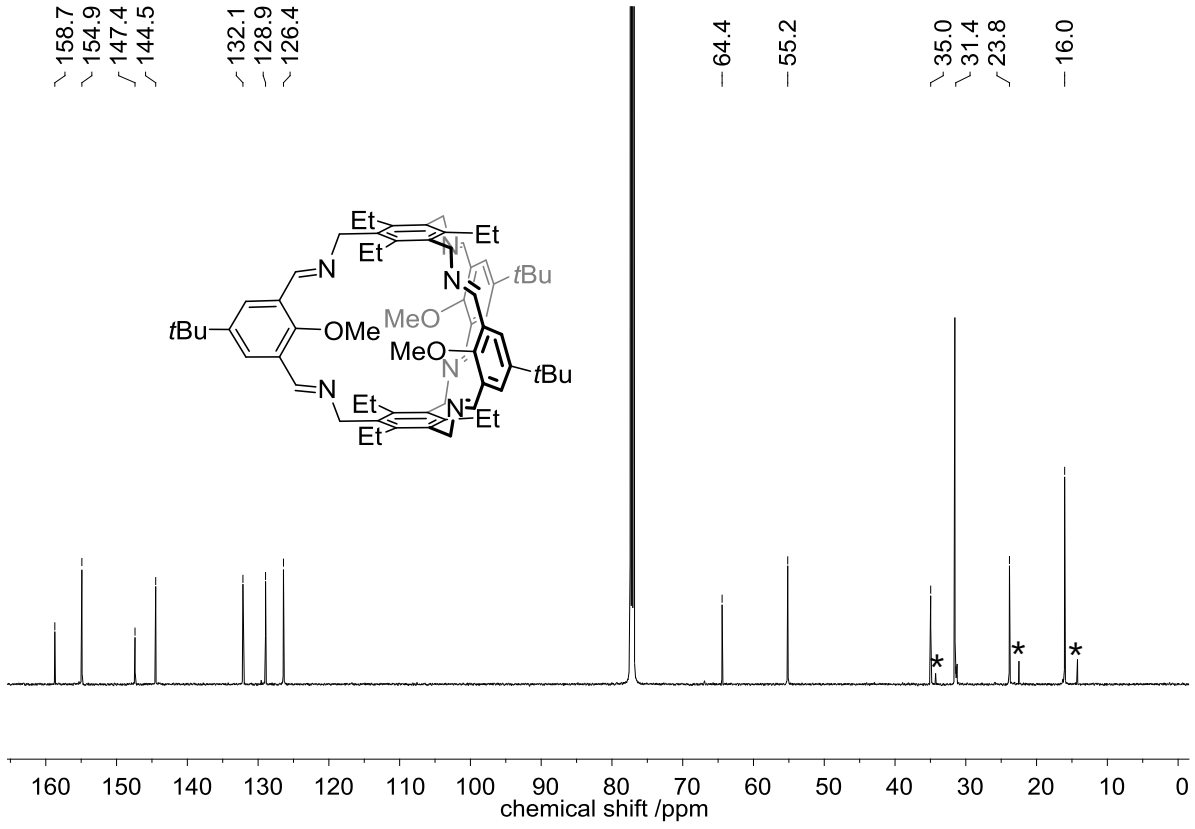


Figure S2: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of compound **5c**.*=residual *n*-pentane.

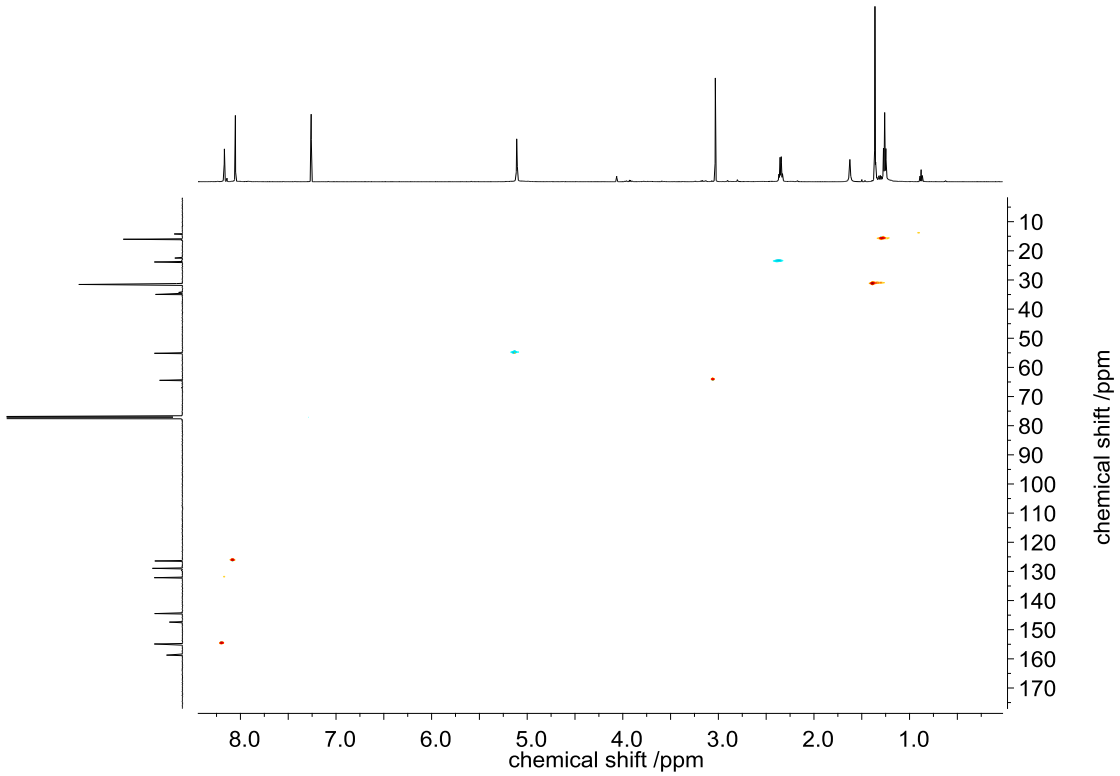


Figure S3: HSQC NMR spectrum ($CDCl_3$, 600 MHz) of compound **5c**.

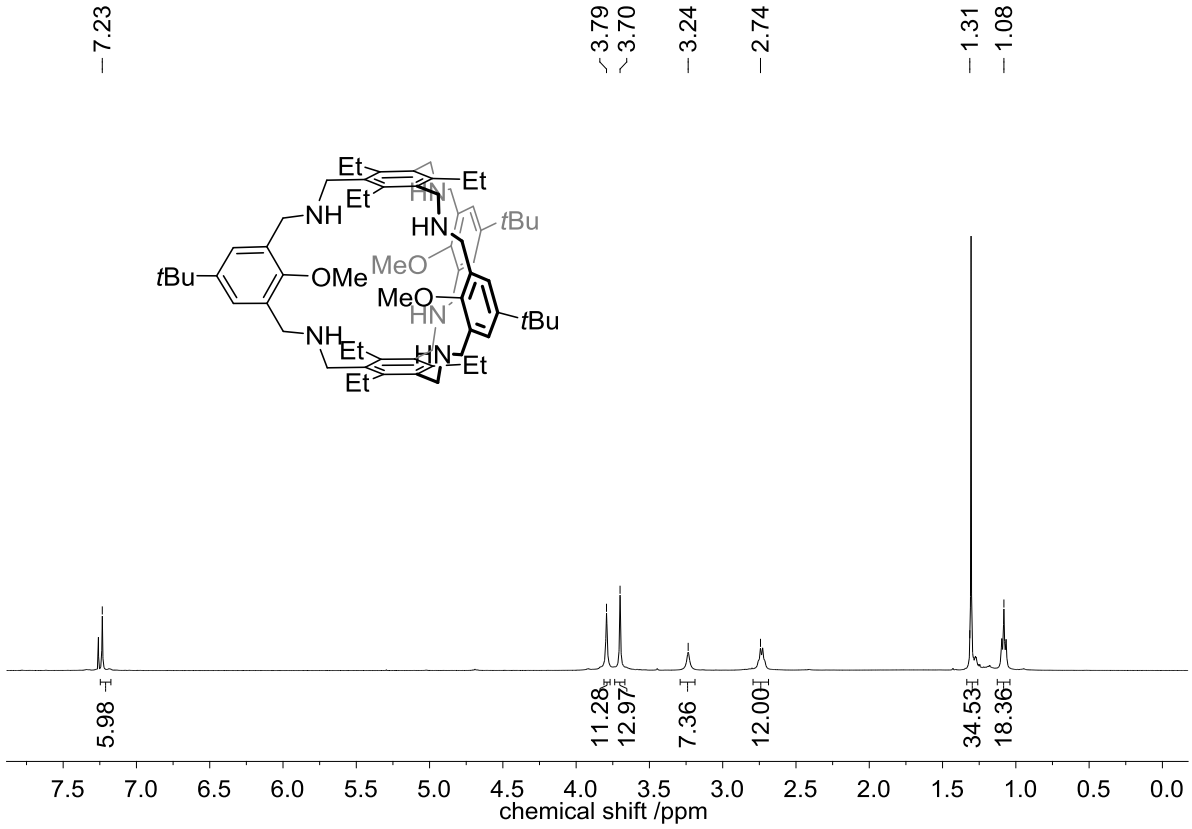


Figure S4: ^1H NMR spectrum ($CDCl_3$, 500 MHz) of compound **6c**.

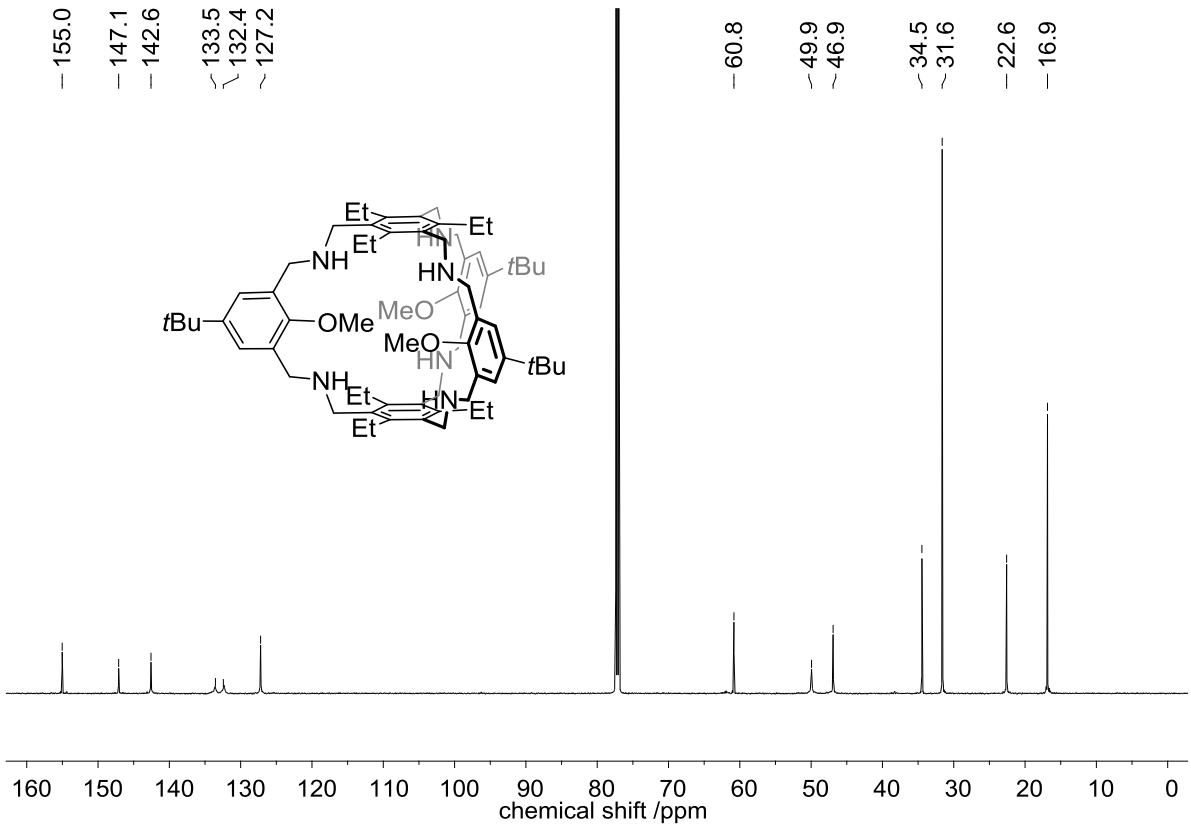


Figure S5: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of compound **6c**.

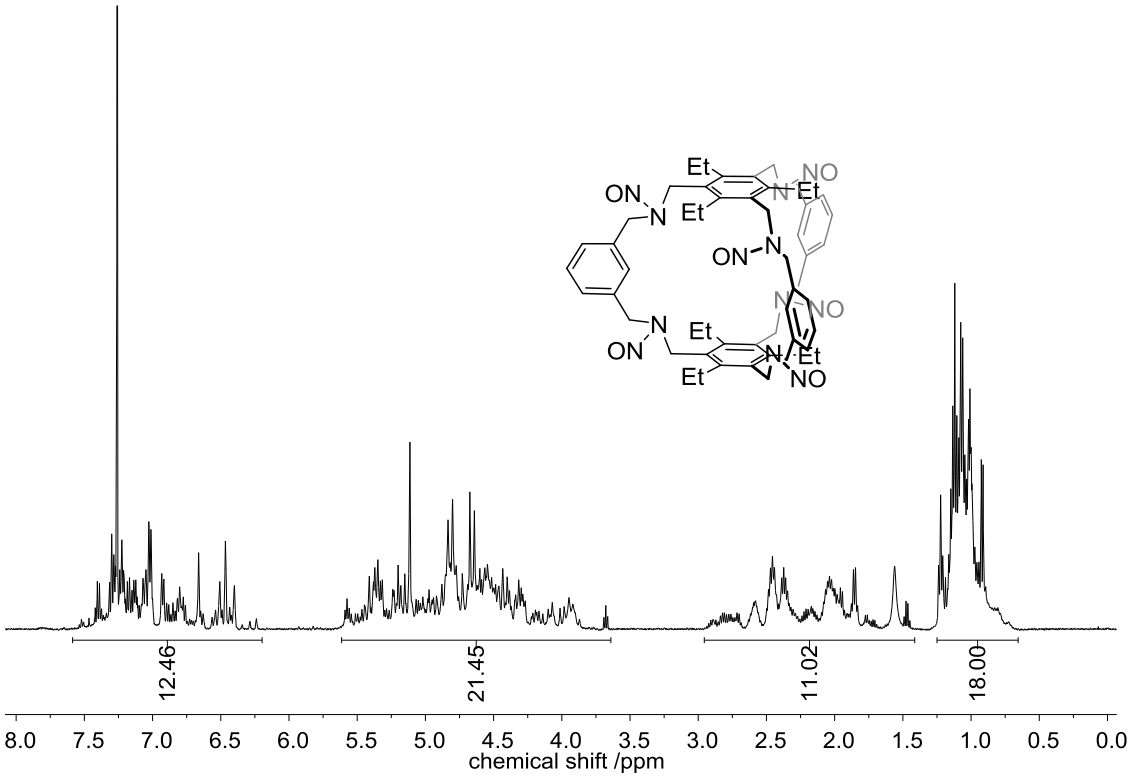


Figure S6: ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **7a**.

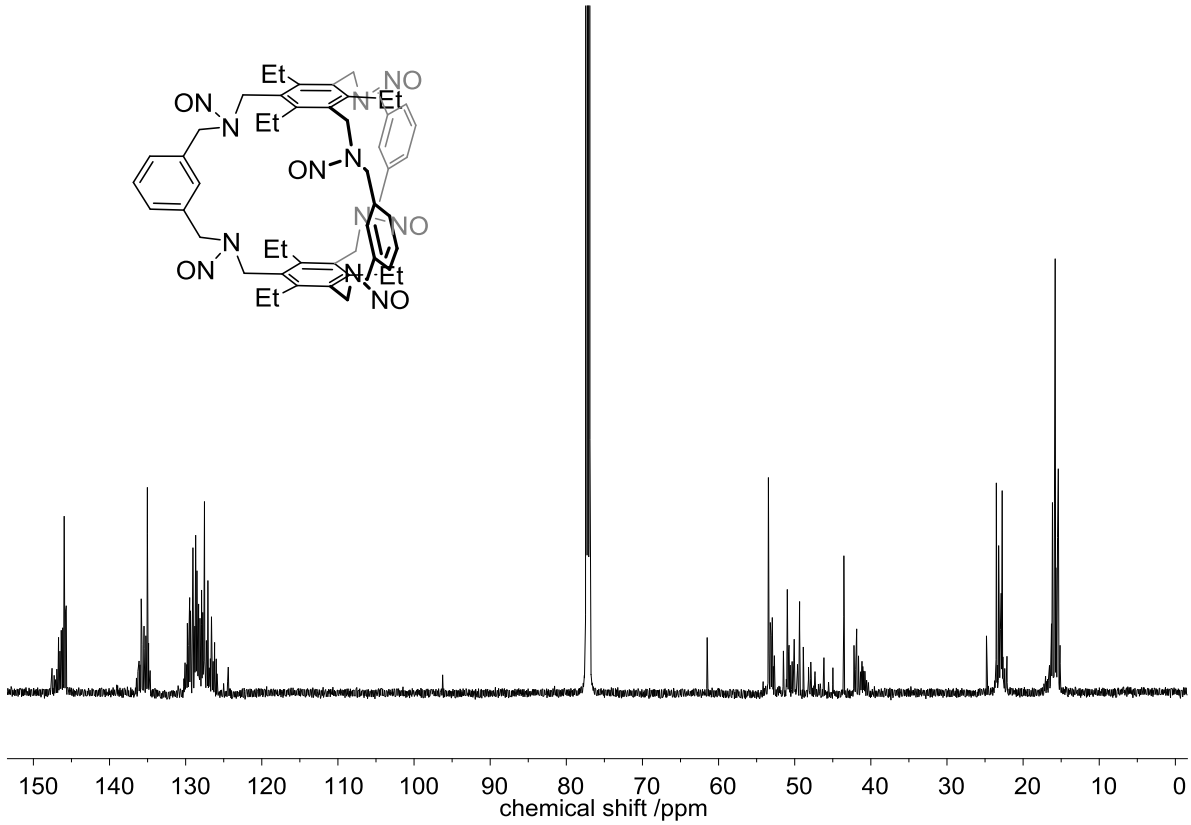


Figure S7: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of compound **7a**.

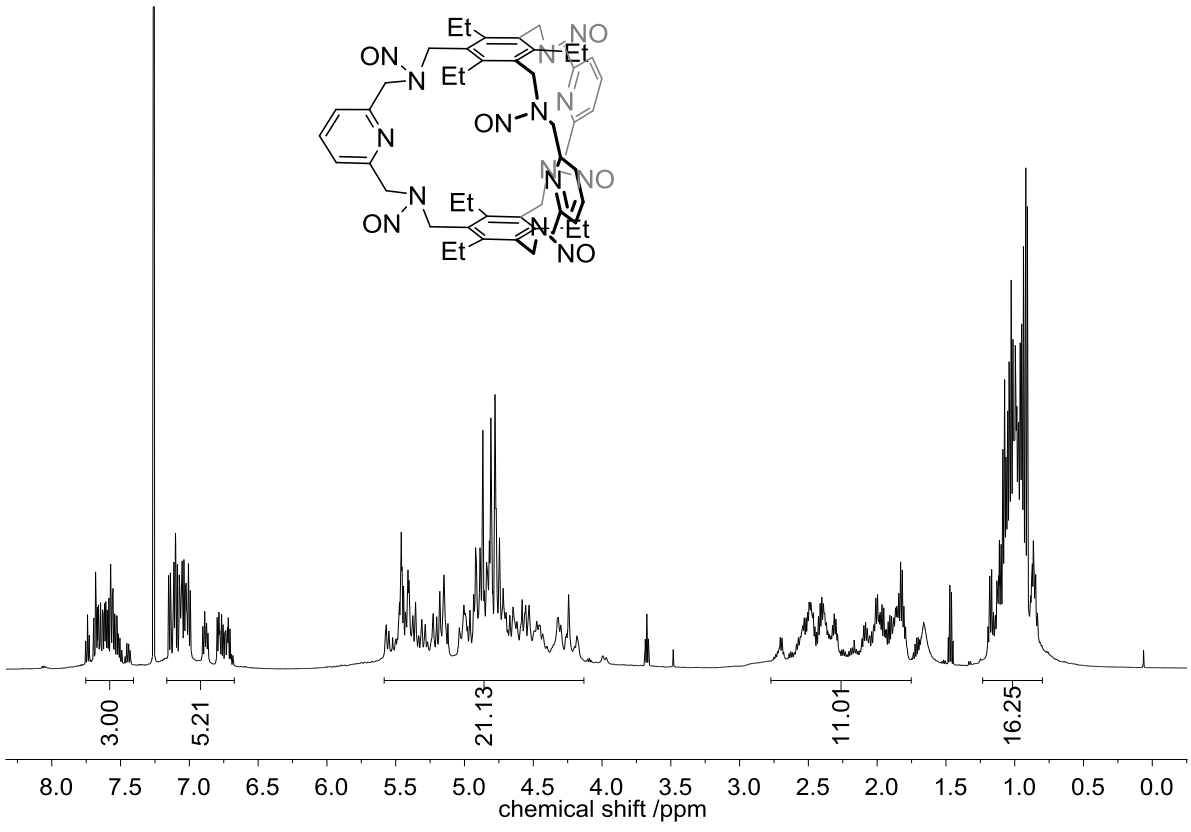


Figure S8: ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **7b**.

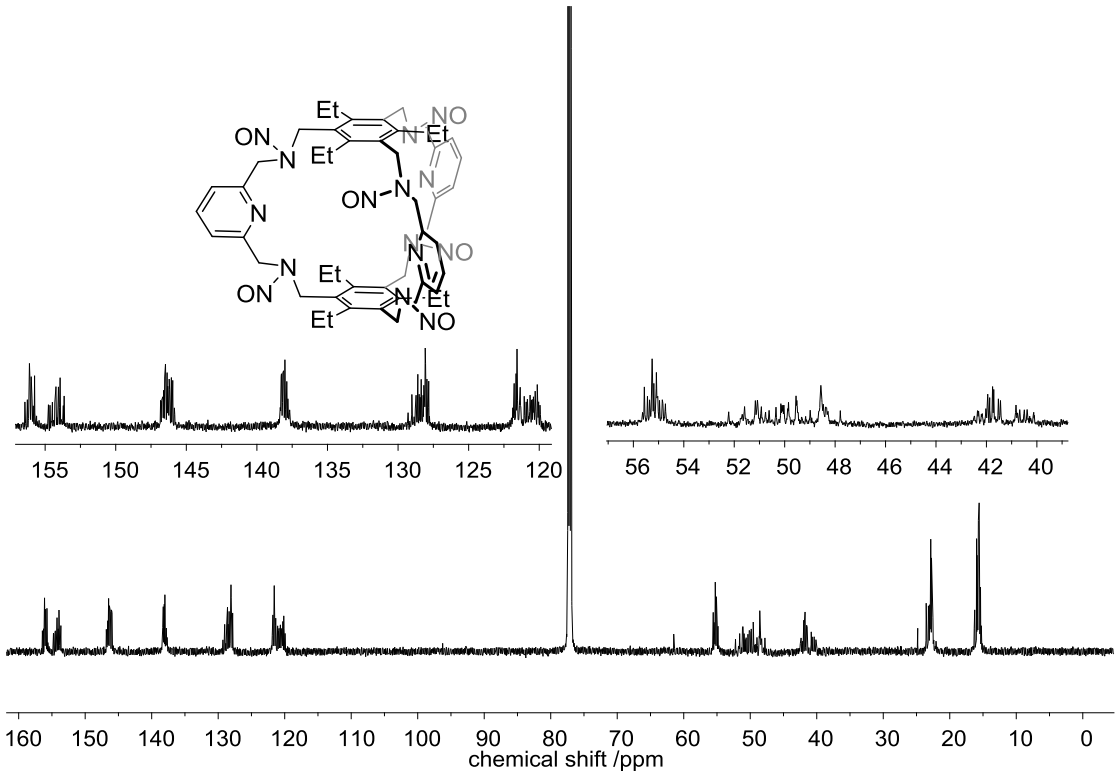


Figure S9: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of compound **7b**.

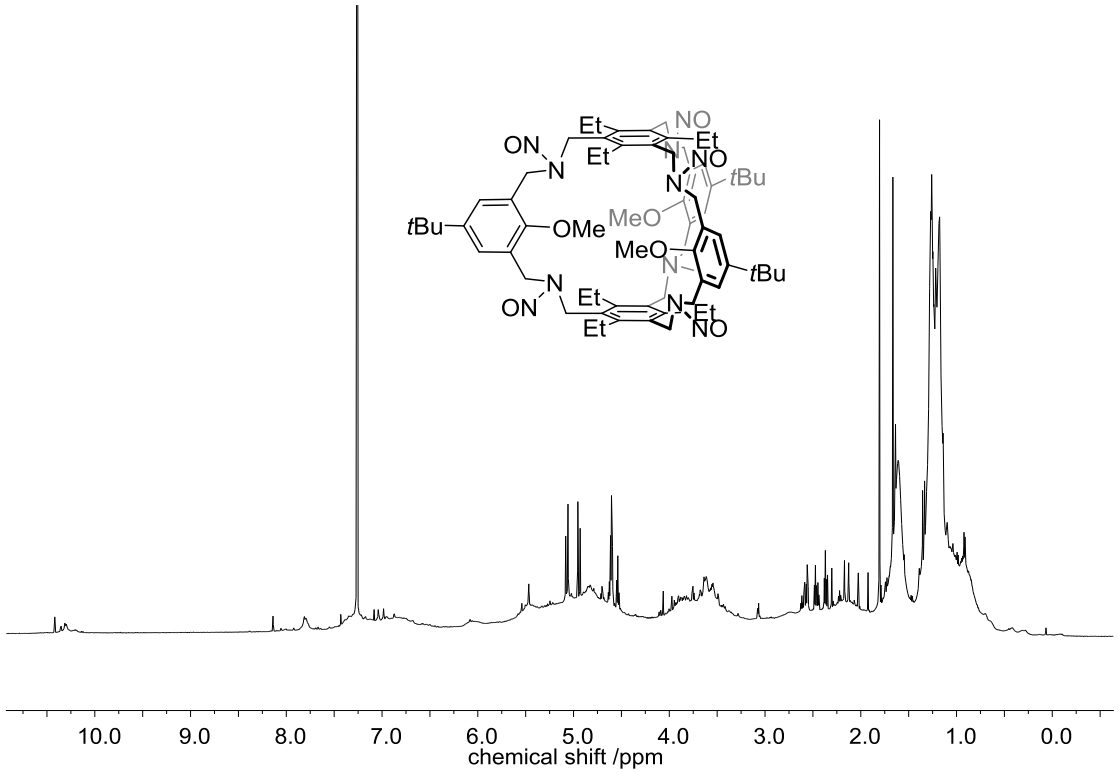


Figure S10: ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **7c**.

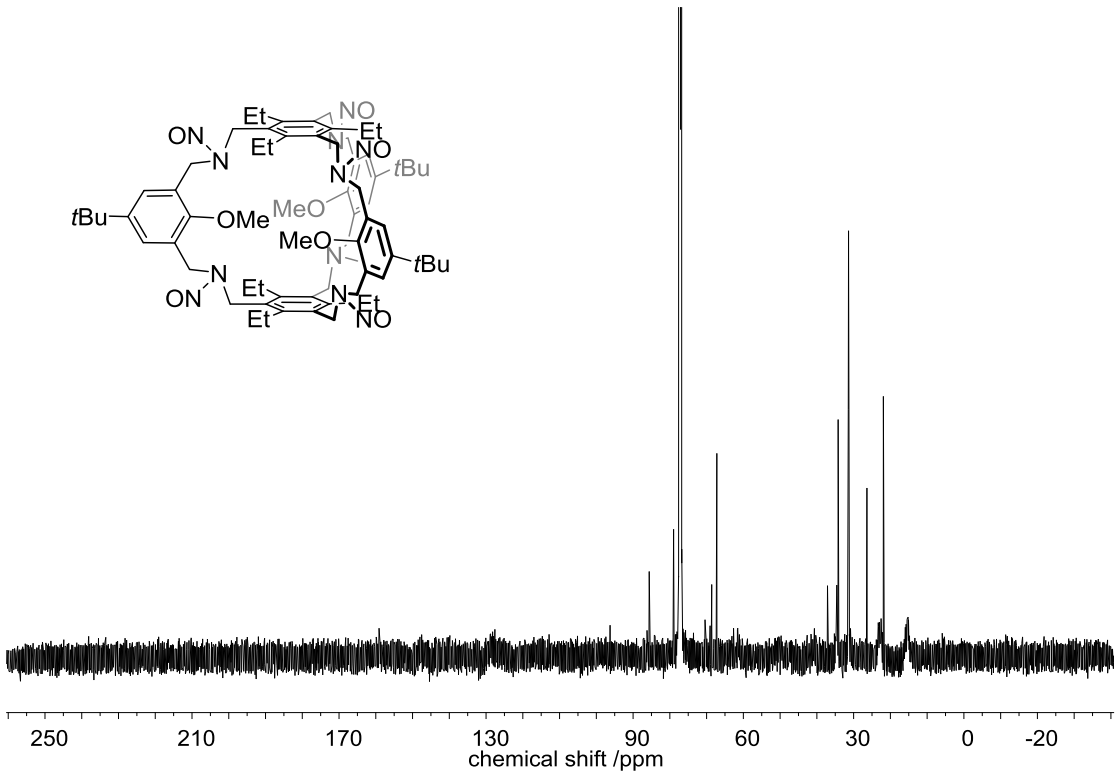


Figure S11: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of compound **7c**.

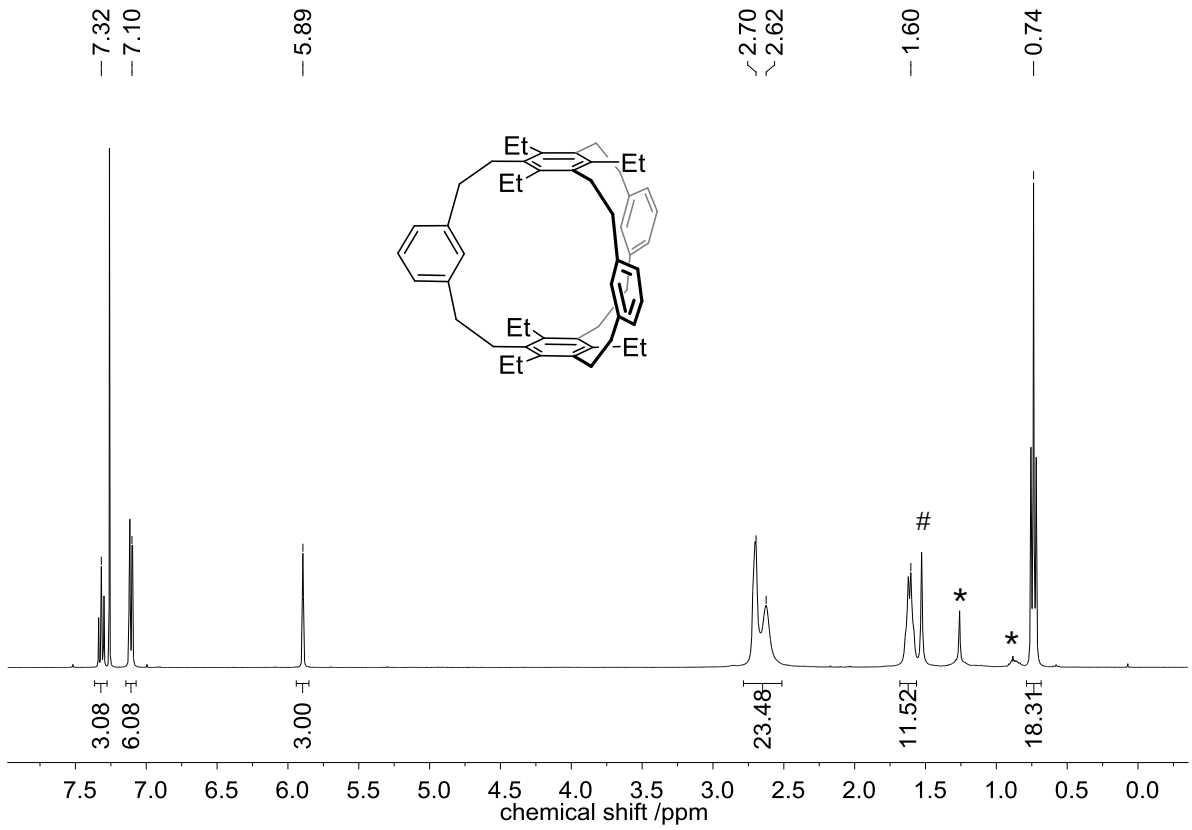


Figure S12: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **8a**, $^{\#}H_2O$, *H-grease.

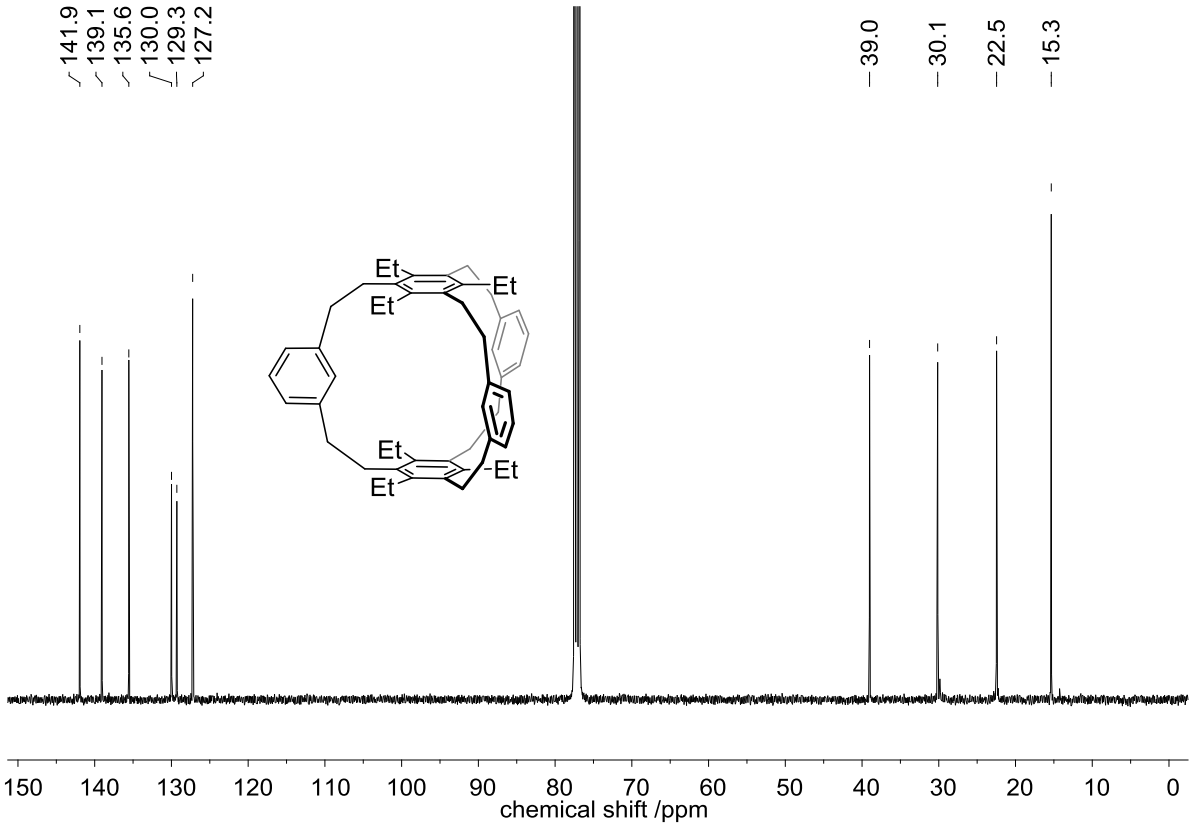


Figure S13: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **8a**.

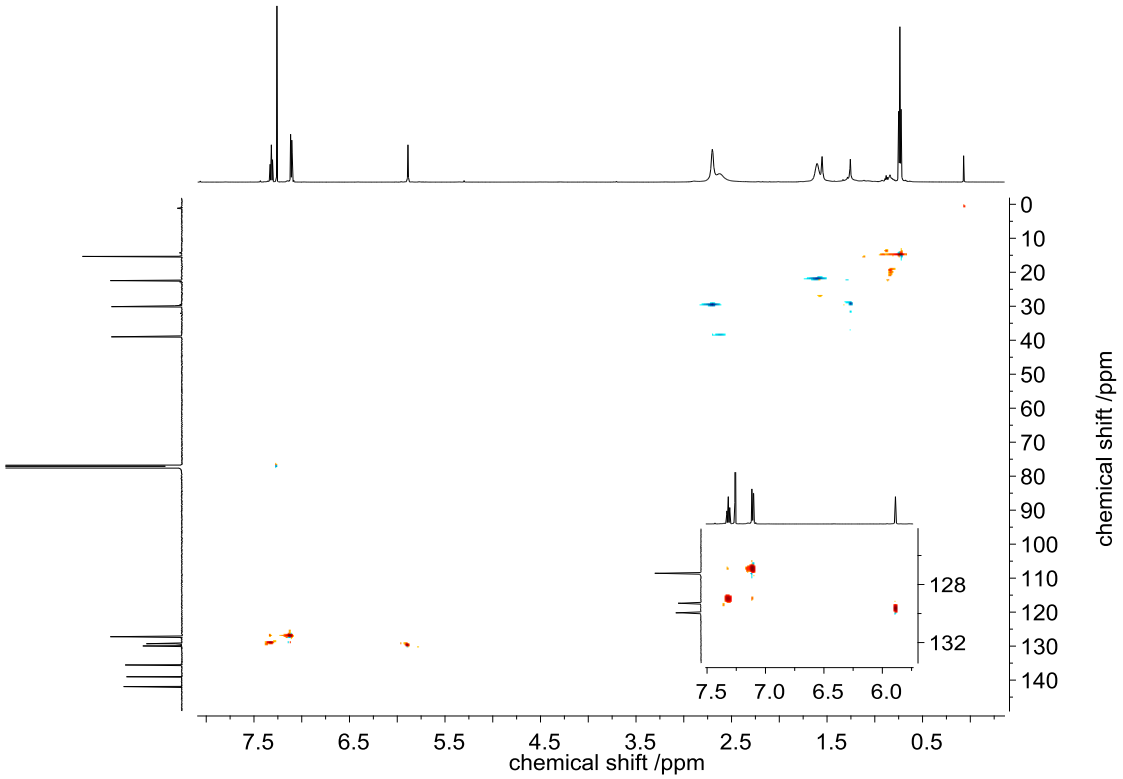


Figure S14: HSQC NMR spectrum ($CDCl_3$, 600 MHz) of compound **8a**.

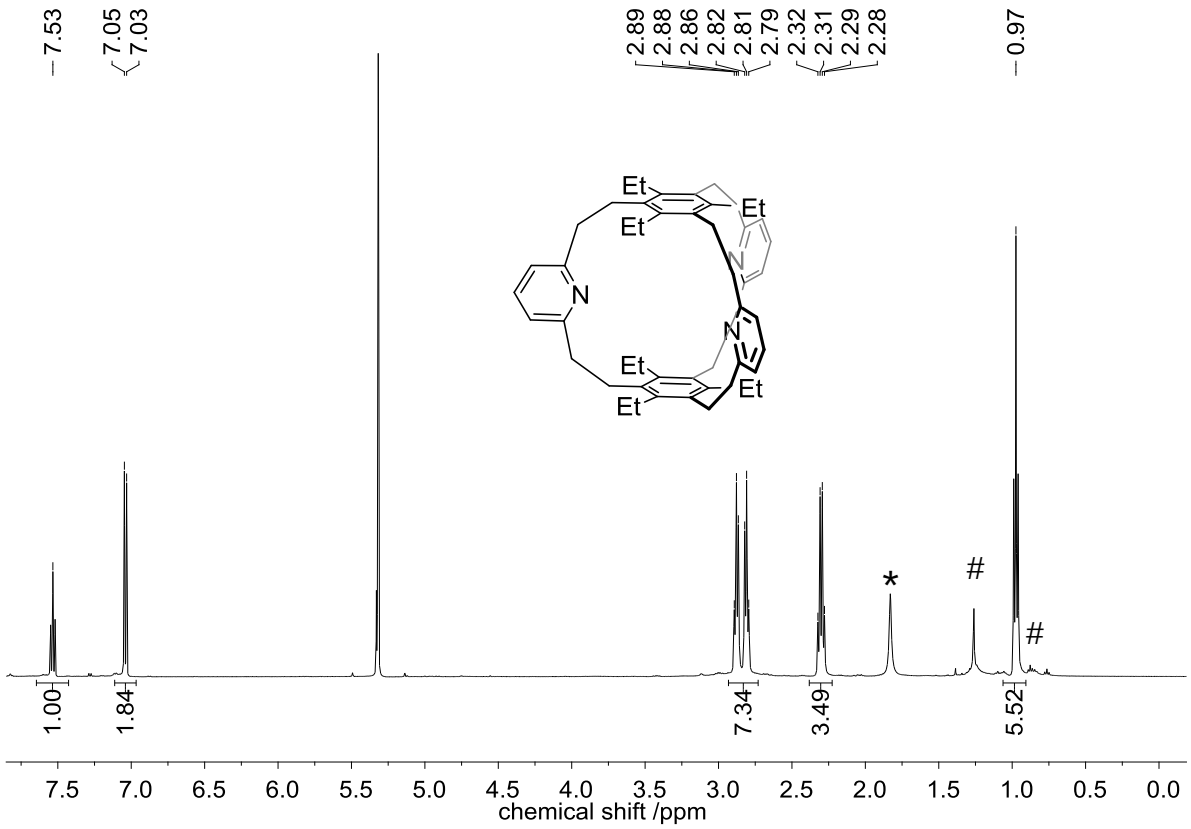


Figure S15: ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of compound **8b**. *H_2O, $^{\#}$H-grease.

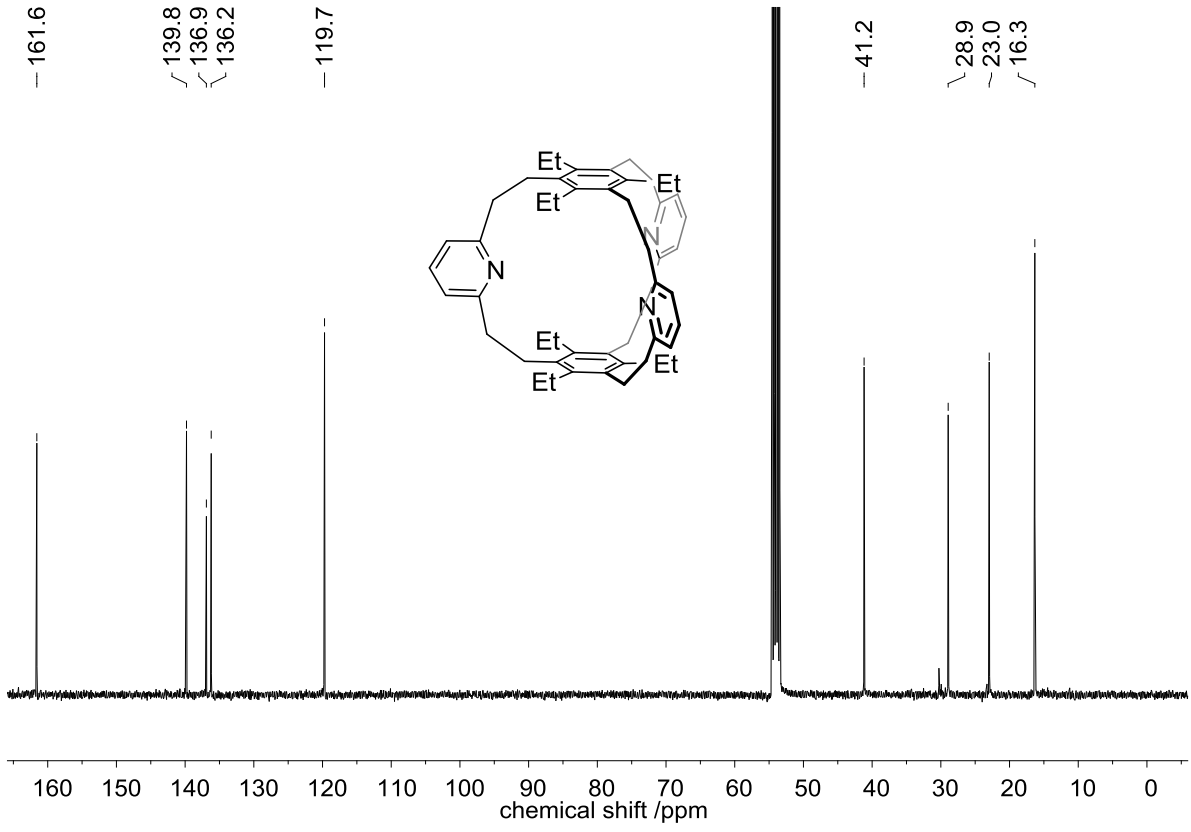


Figure S16: ^{13}C NMR spectrum (CD_2Cl_2, 100 MHz) of compound **8b**.

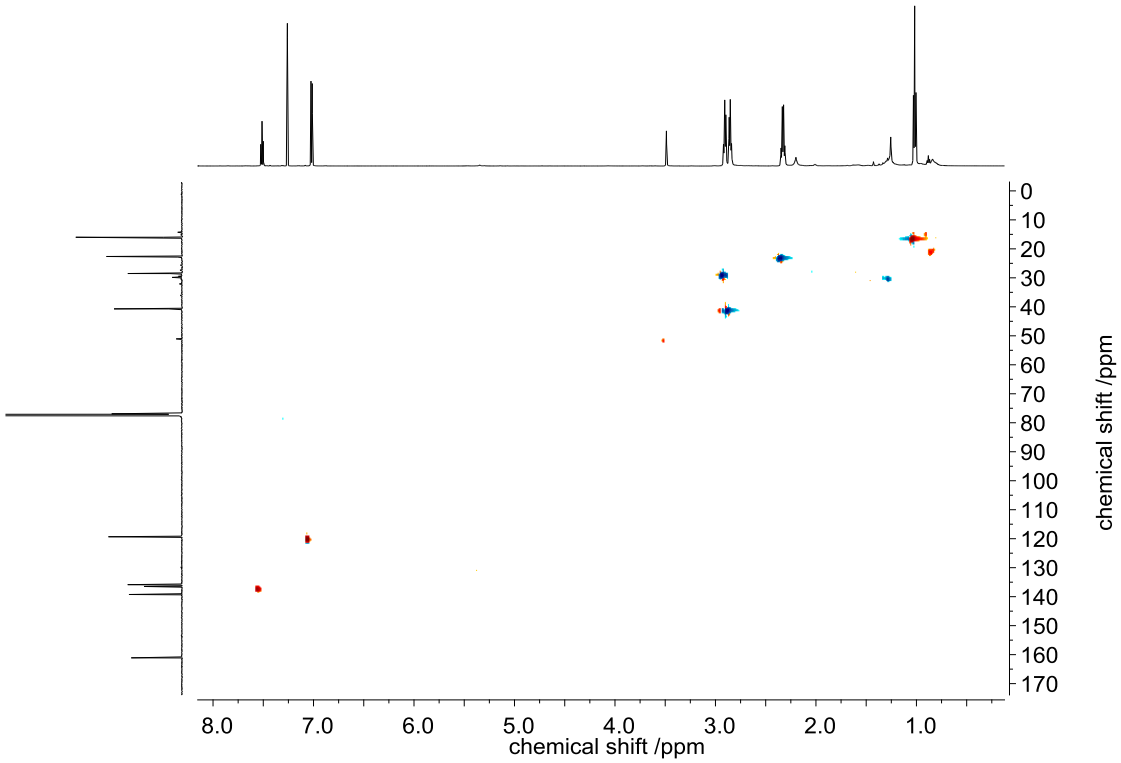


Figure S17: HSQC NMR spectrum ($CDCl_3$, 600 MHz) of compound **8b**.

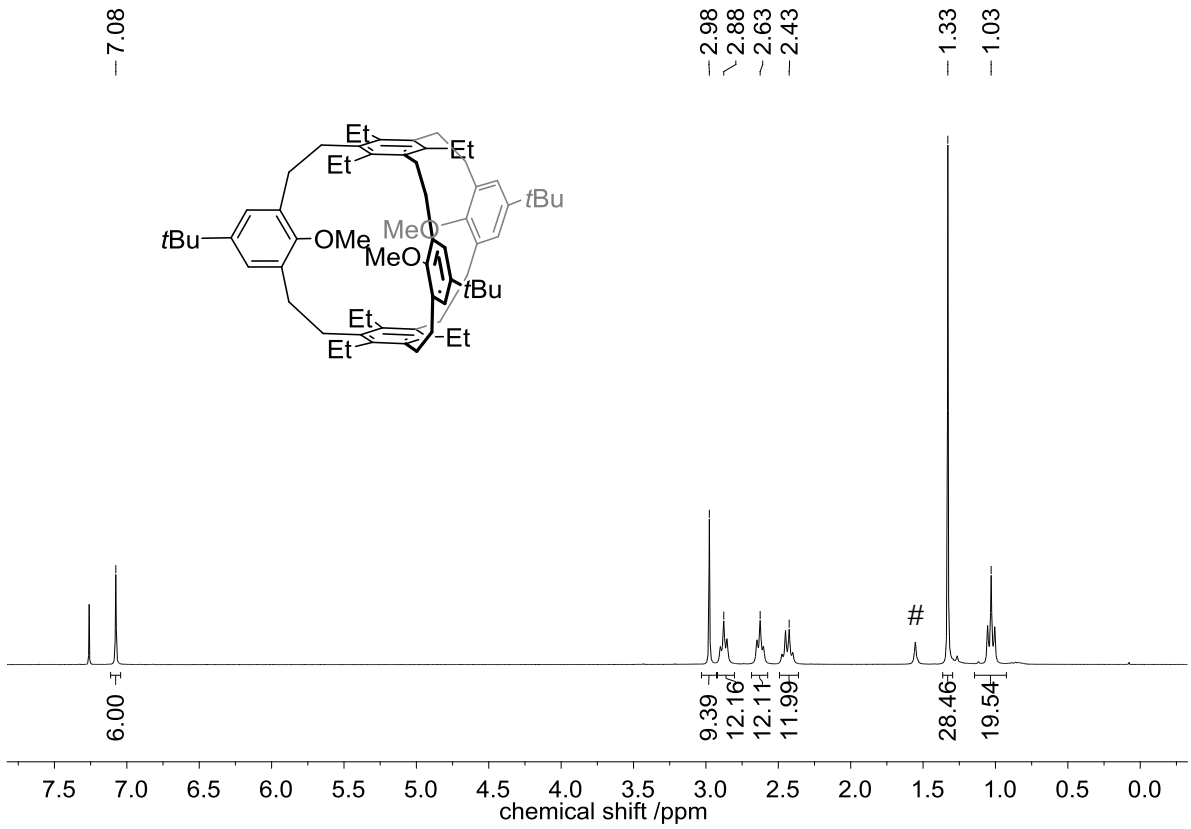


Figure S18: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **8c**. $^{\#}H_2O$.

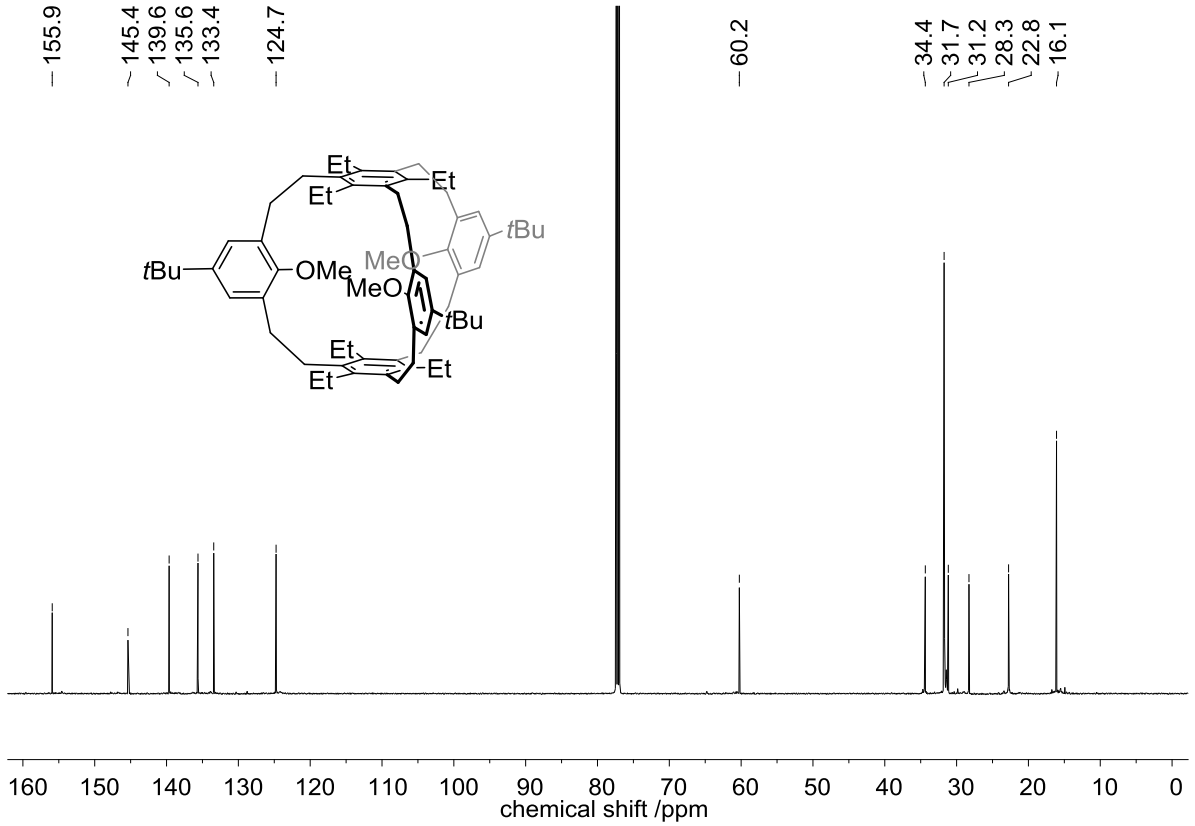


Figure S19: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of compound **8c**.

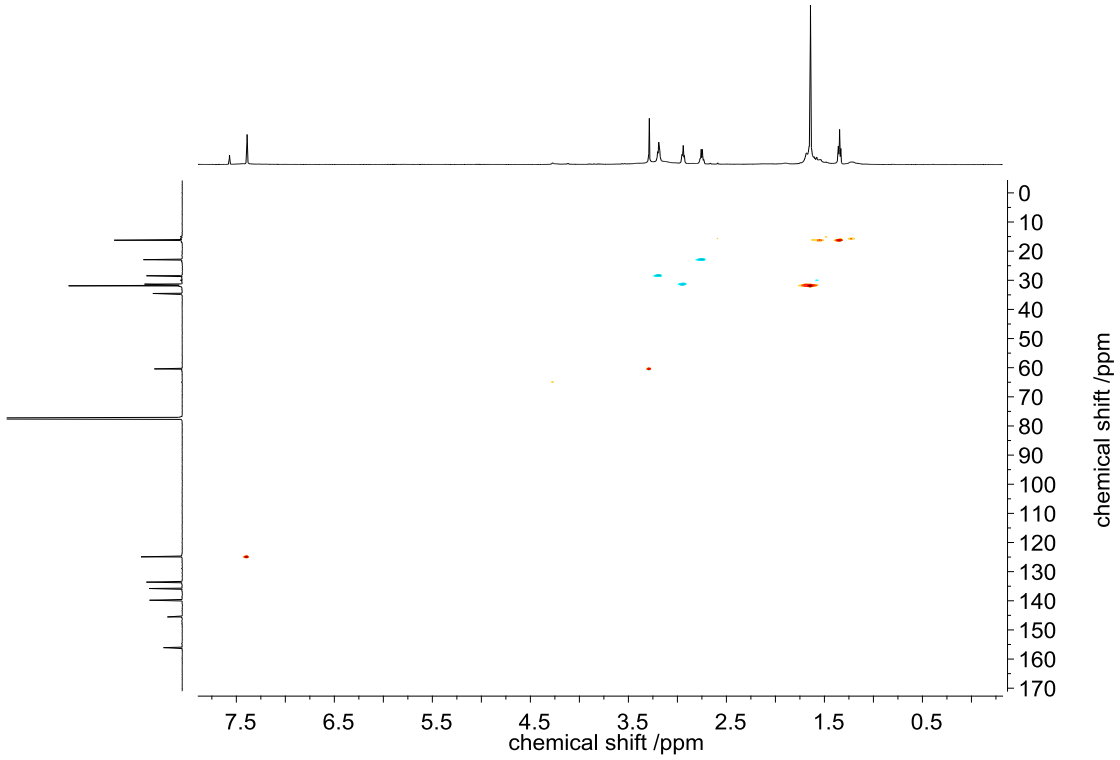


Figure S20: HSQC NMR spectrum ($CDCl_3$, 600 MHz) of compound **8c**.

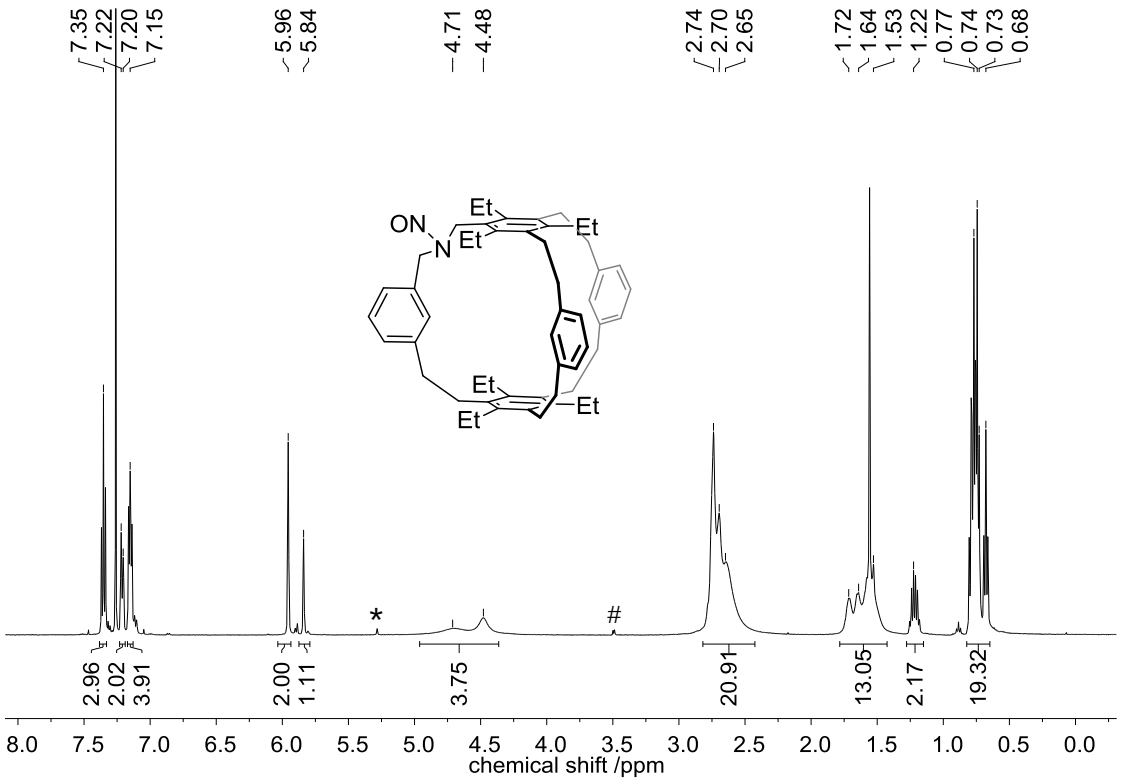


Figure S21: ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **9**. *CH_2Cl_2, #Methanol.

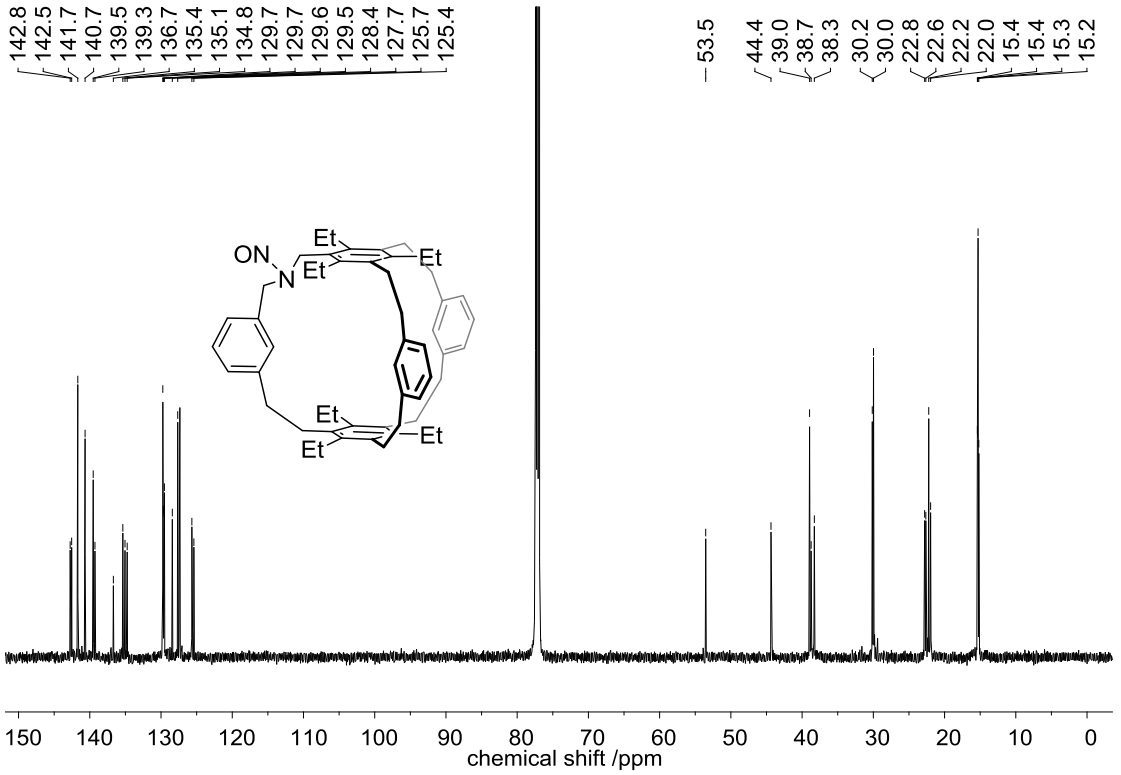


Figure S22: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of compound **9**.

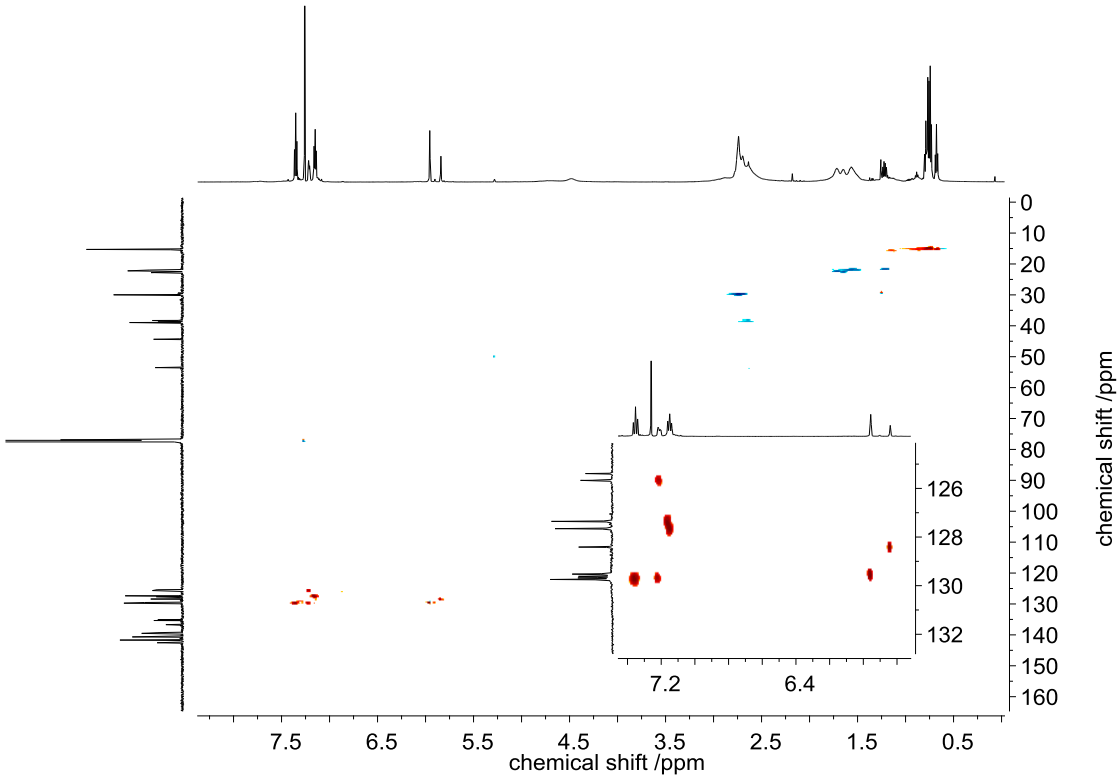


Figure S23: HSQC NMR spectrum ($CDCl_3$, 600 MHz) of compound **9**.

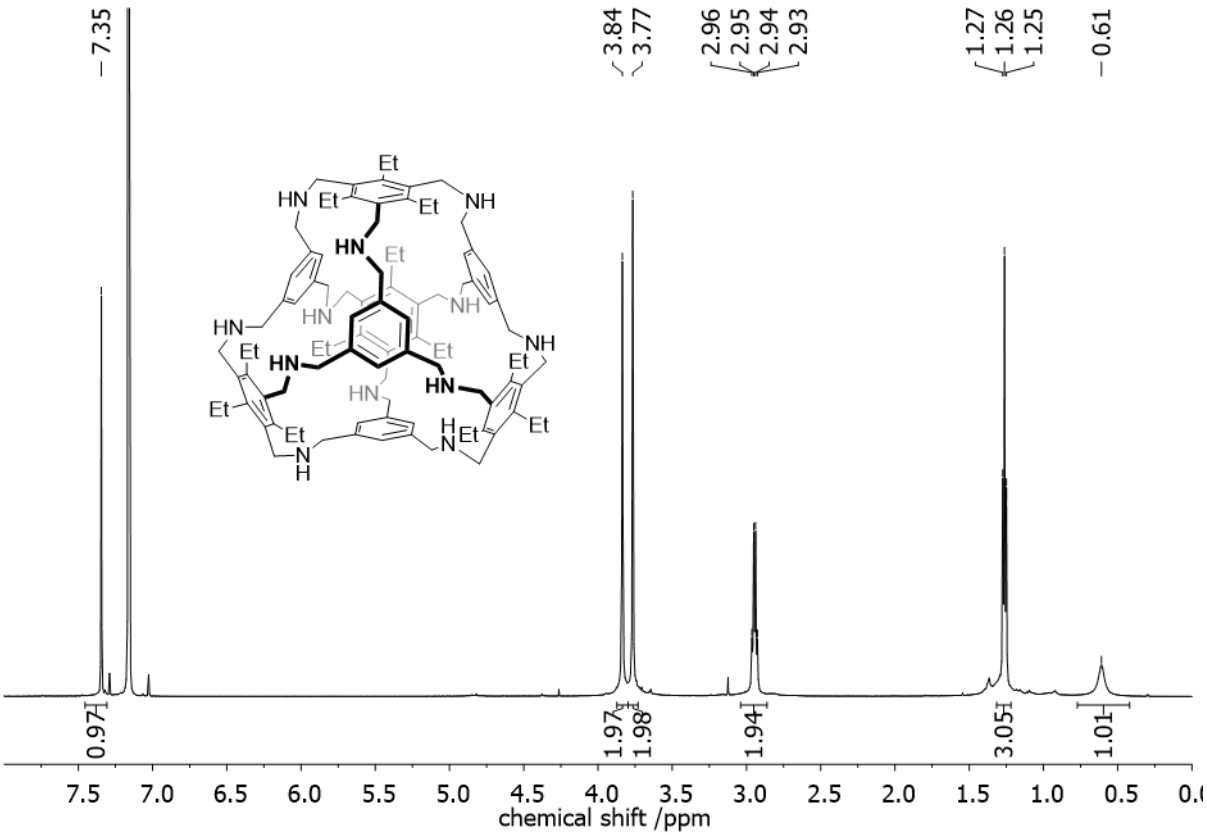


Figure S24: ^1H NMR spectrum (600 MHz, C_6D_6) of cage compound **11**.

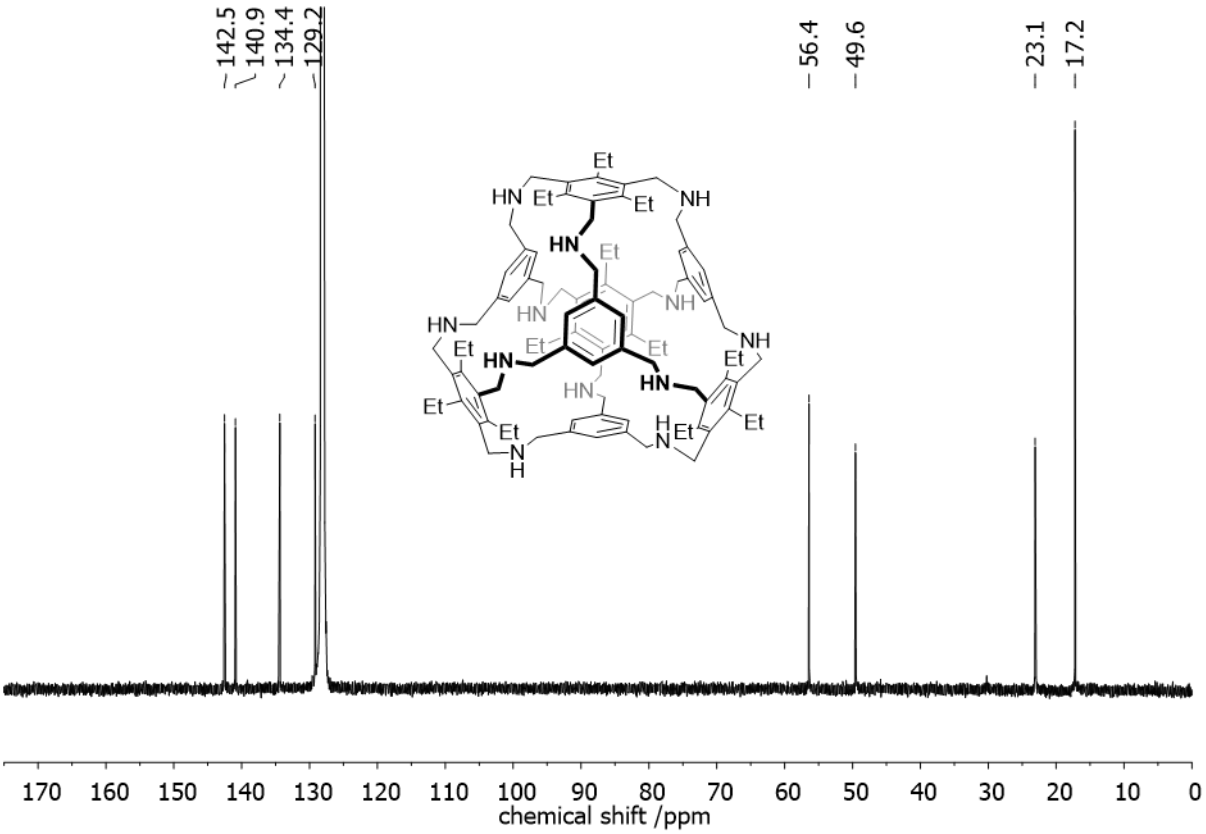


Figure S25: ^{31}C NMR spectrum (150 MHz, C_6D_6) of cage compound **11**.

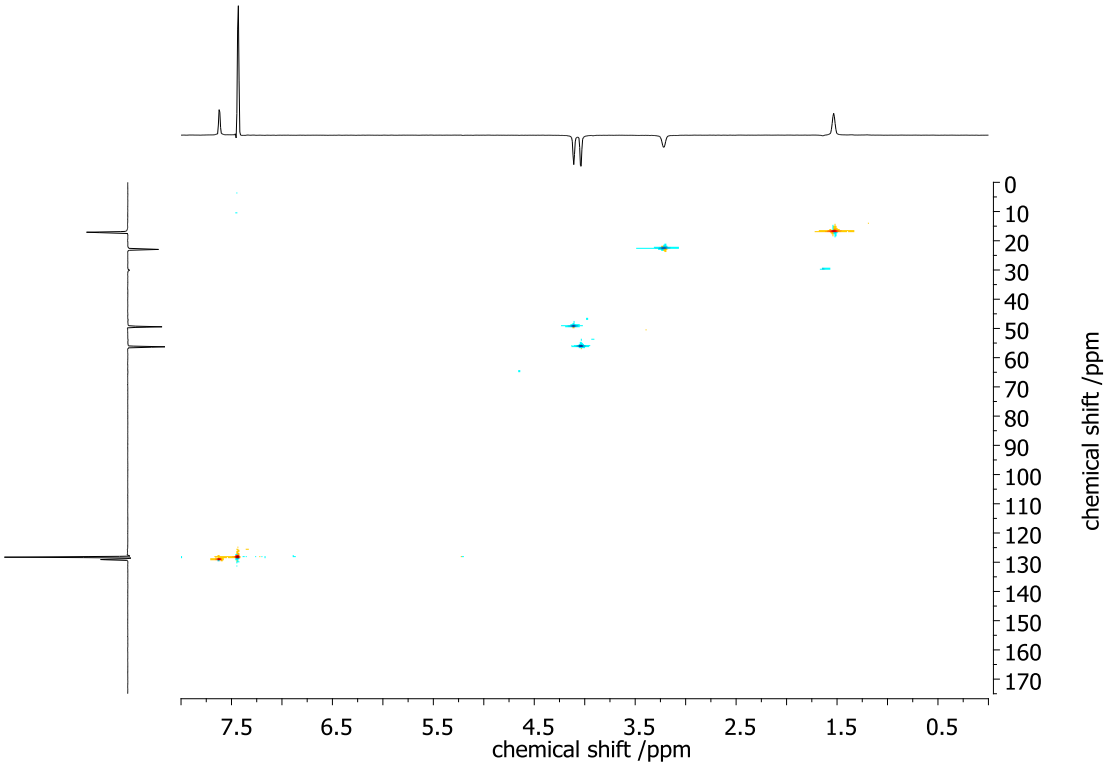


Figure S26: HSQC NMR spectrum (600 MHz, C_6D_6) of cage compound **11**.

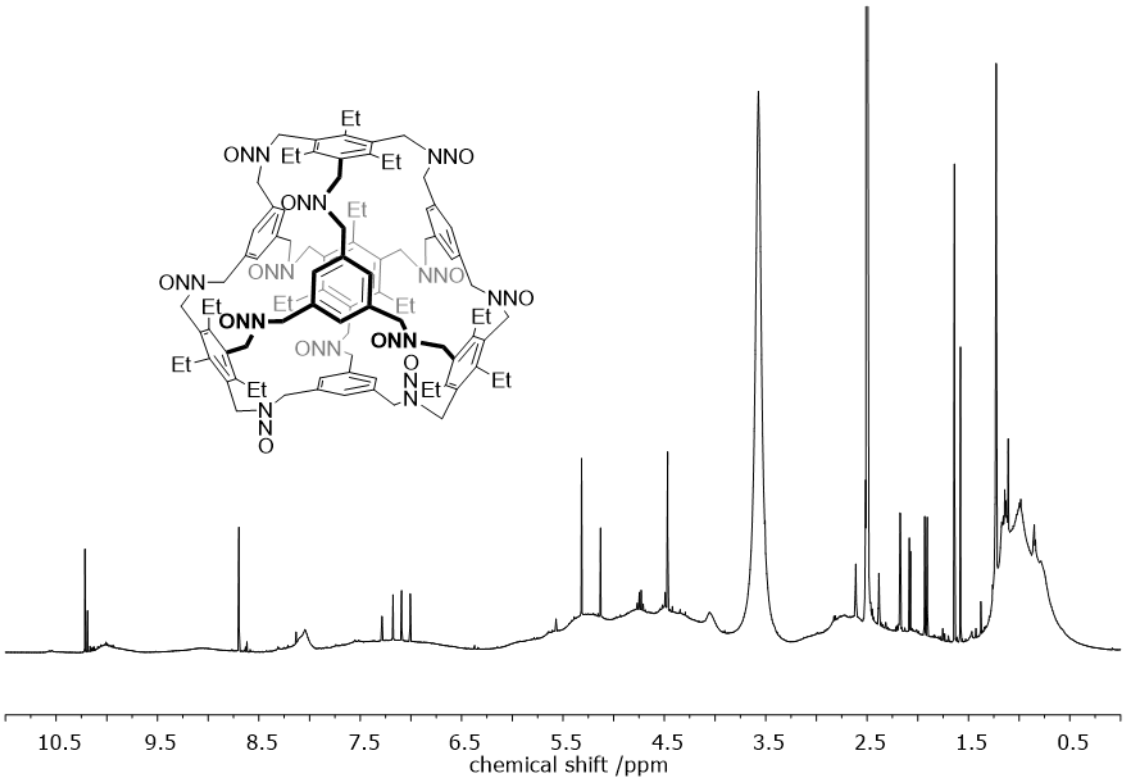


Figure S27: ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of cage compound **12**.

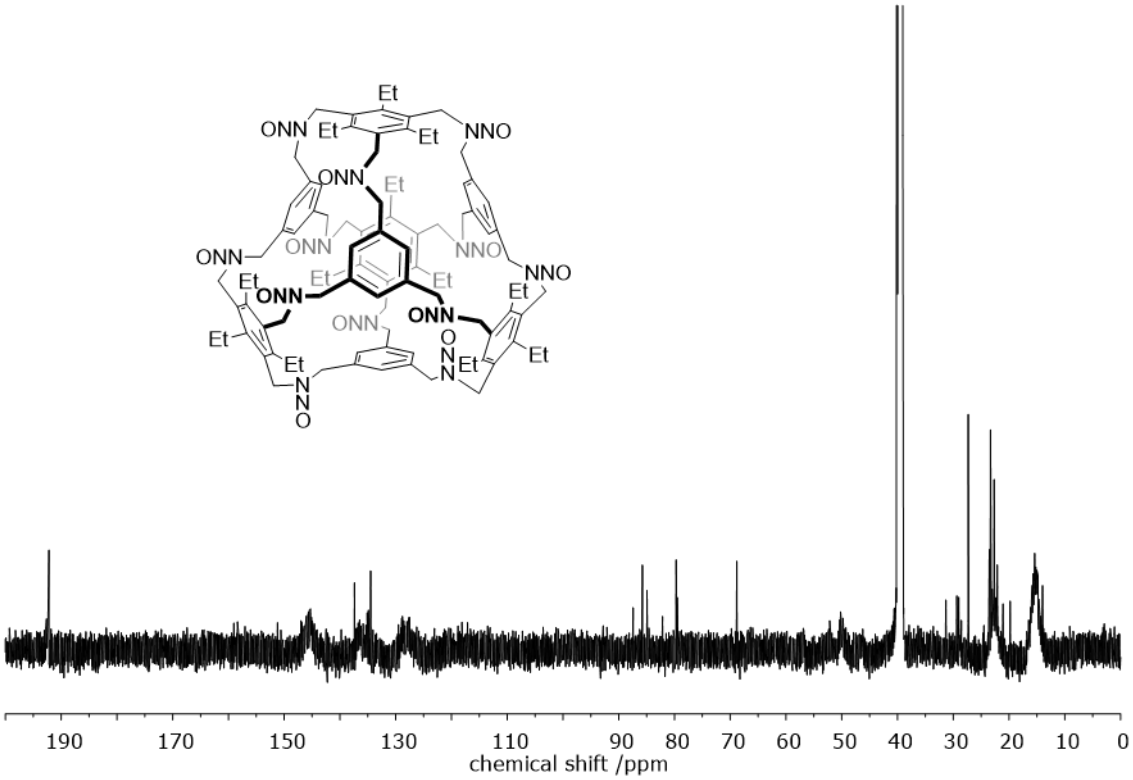


Figure S28: ^{13}C NMR spectrum (150 MHz, DMSO-d_6) of cage compound **12**.

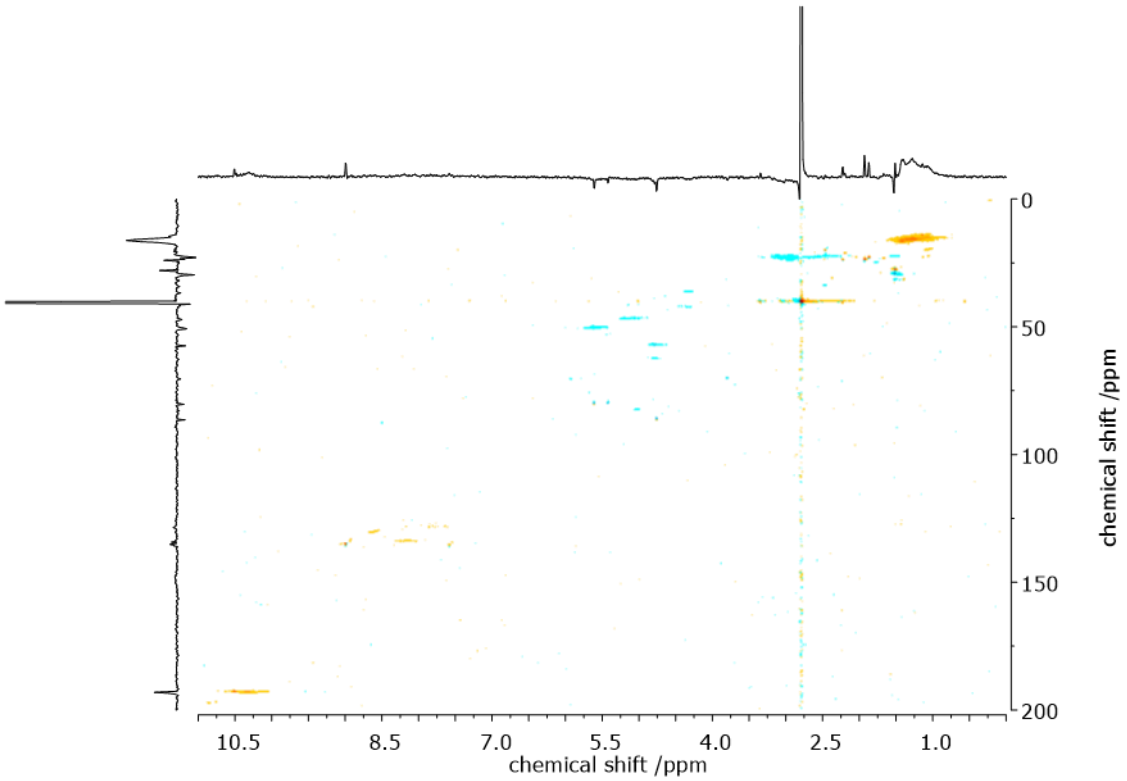


Figure S29: HSQC NMR spectrum (600 MHz, DMSO-d_6) of cage compound **12**.

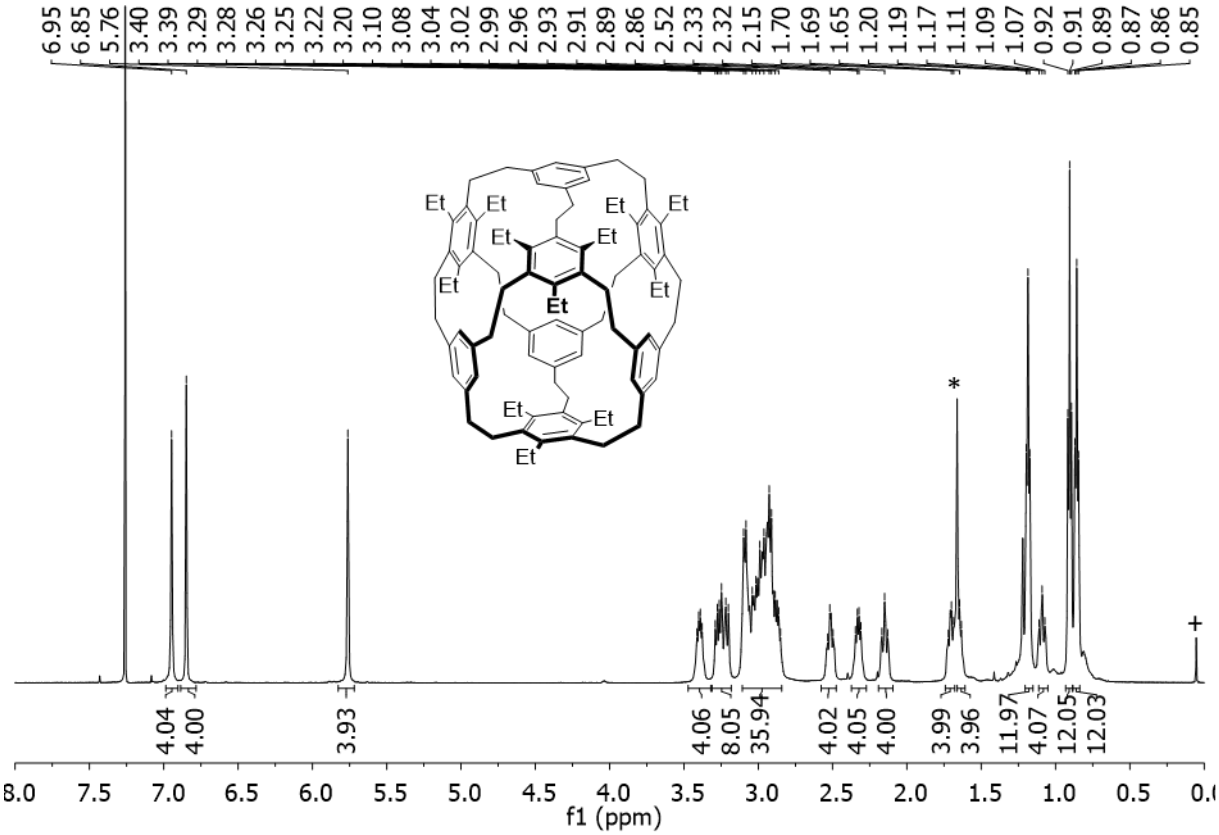


Figure S30: ^{1}H NMR spectrum (600 MHz, 253 K, $CDCl_3$) of compound **13**. *H_2O, $^+$silicone-grease.

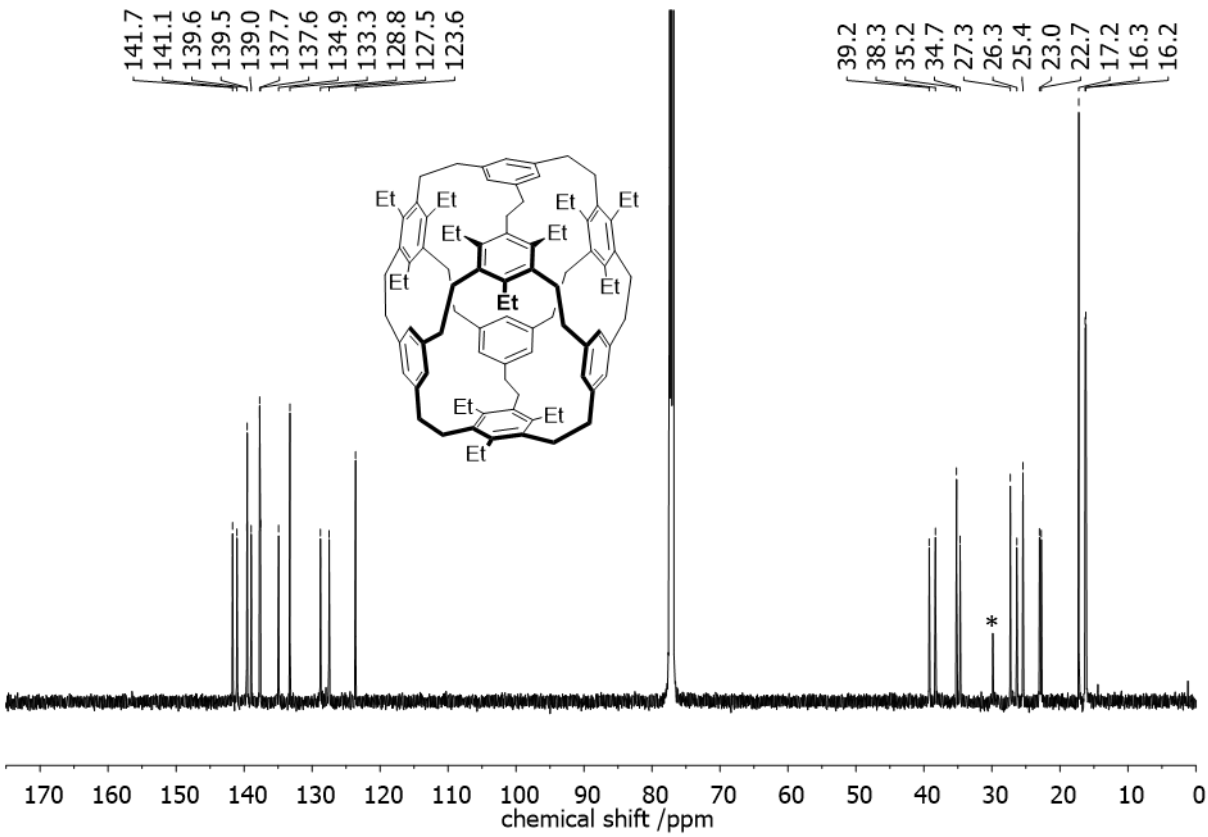


Figure S31: ^{13}C NMR spectrum (151 MHz, 253 K, $CDCl_3$) of compound **13**. *H-Grease.

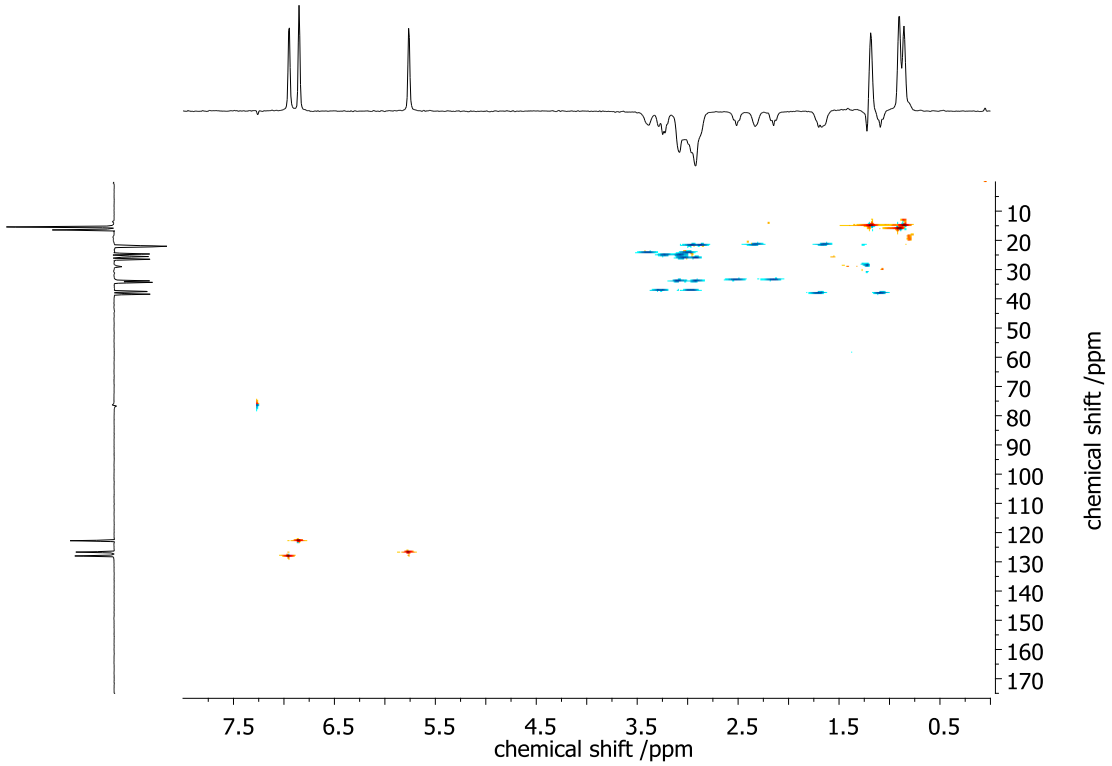


Figure S32: HSQC NMR spectrum (600 MHz, 253 K, $CDCl_3$) of compound **13**.

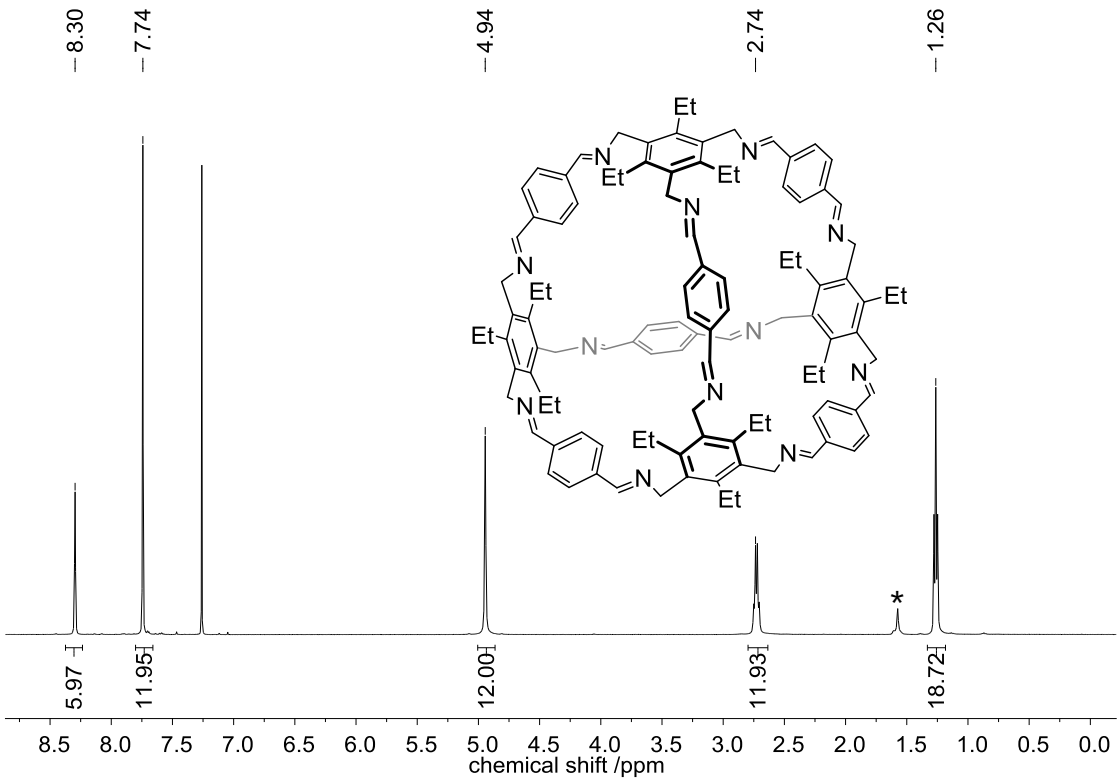


Figure S33: ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of compound **14**.*H_2O.

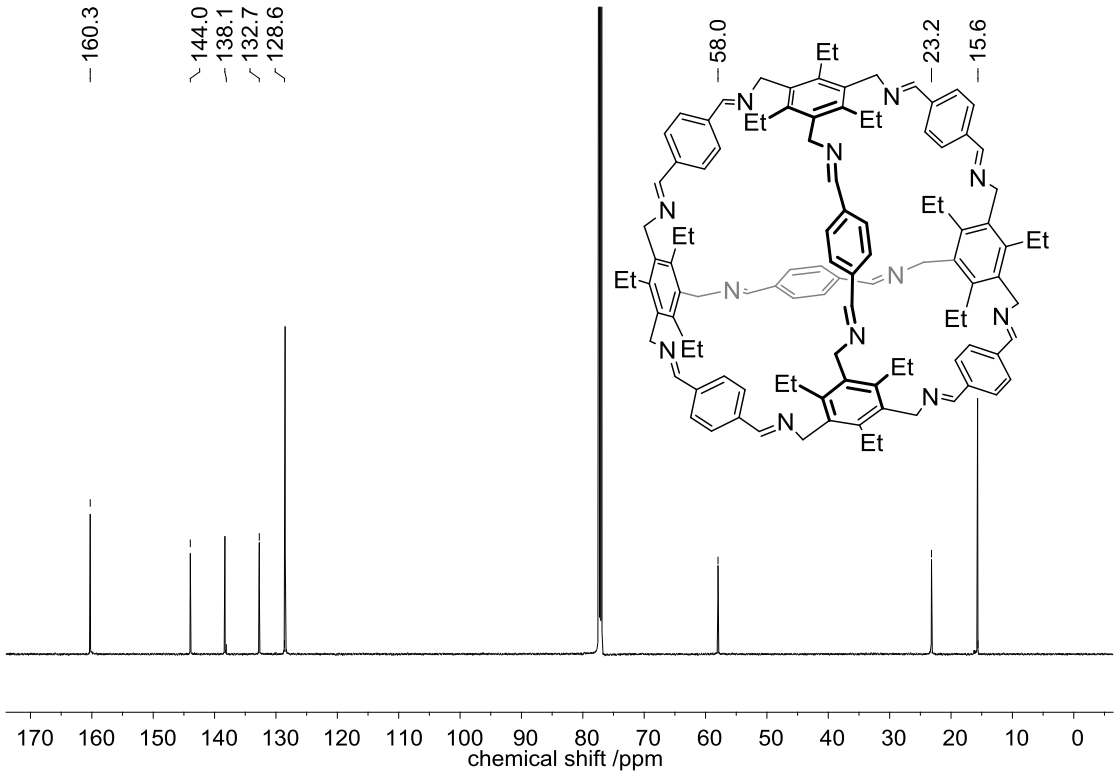


Figure S34: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of compound **14**.

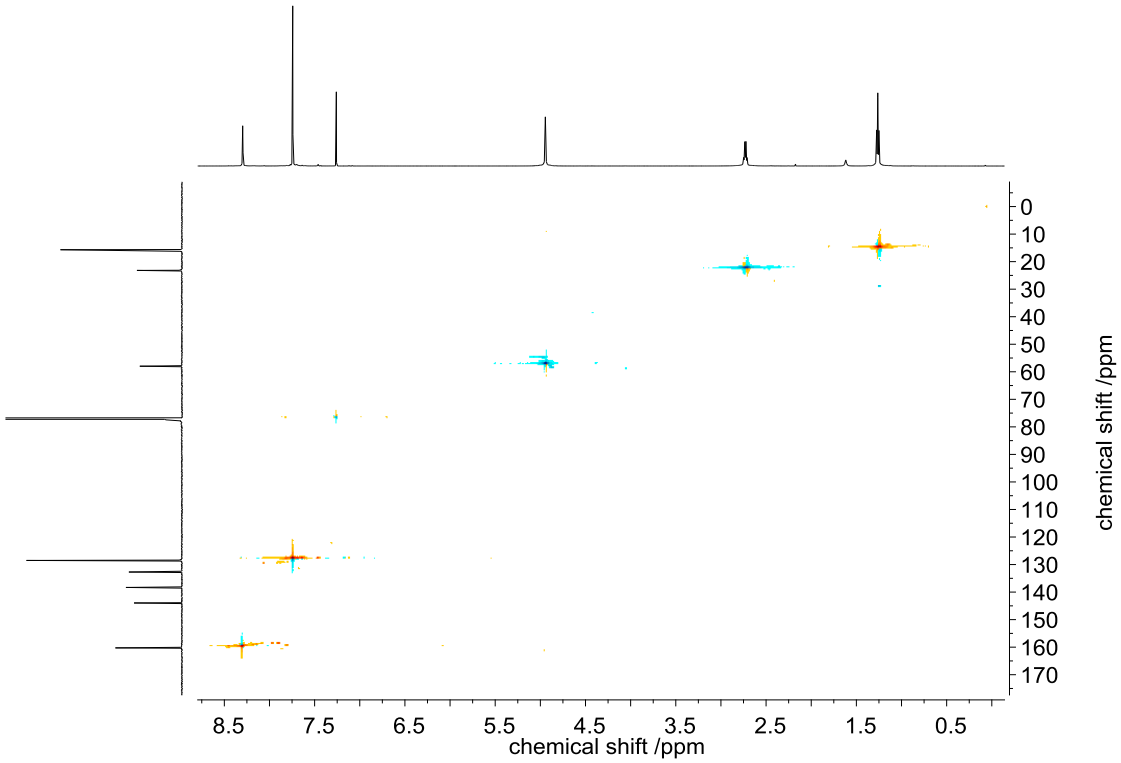


Figure S35: HSQC NMR spectrum ($CDCl_3$, 600 MHz) of compound **14**.

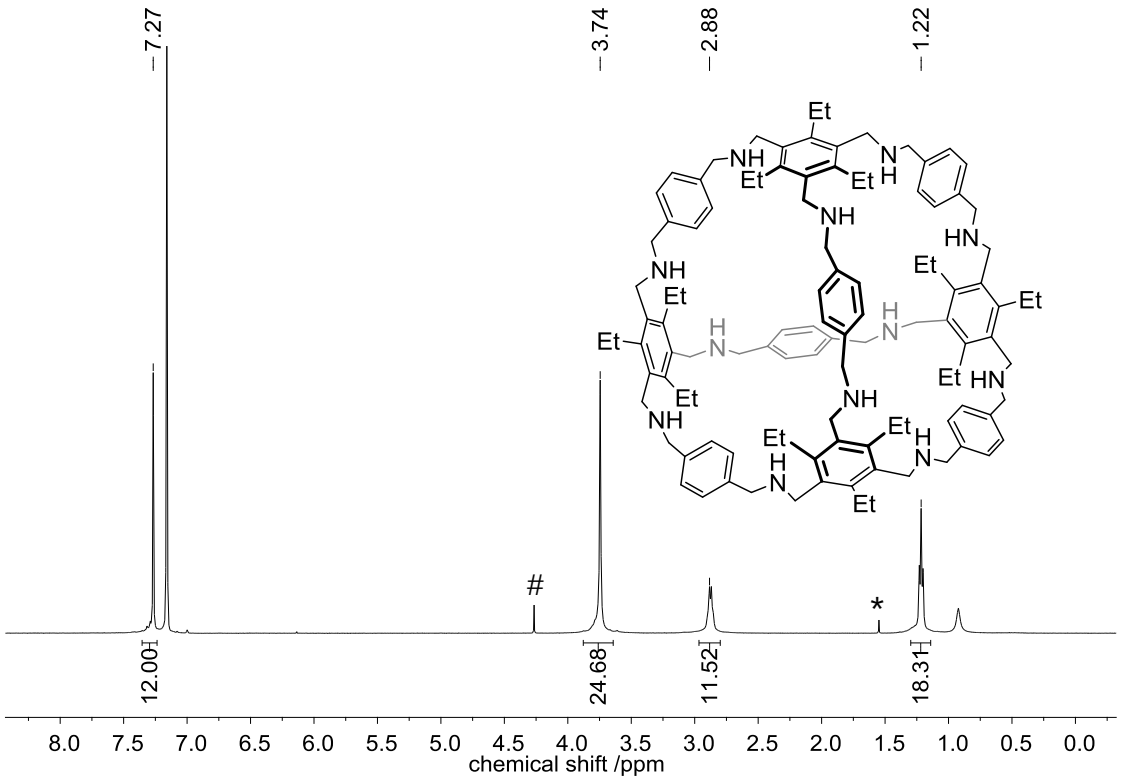


Figure S36: ^1H NMR spectrum (C_6D_6, 500 MHz) of compound **15**. $^{\#}CH_2Cl_2$, $*H_2O$.

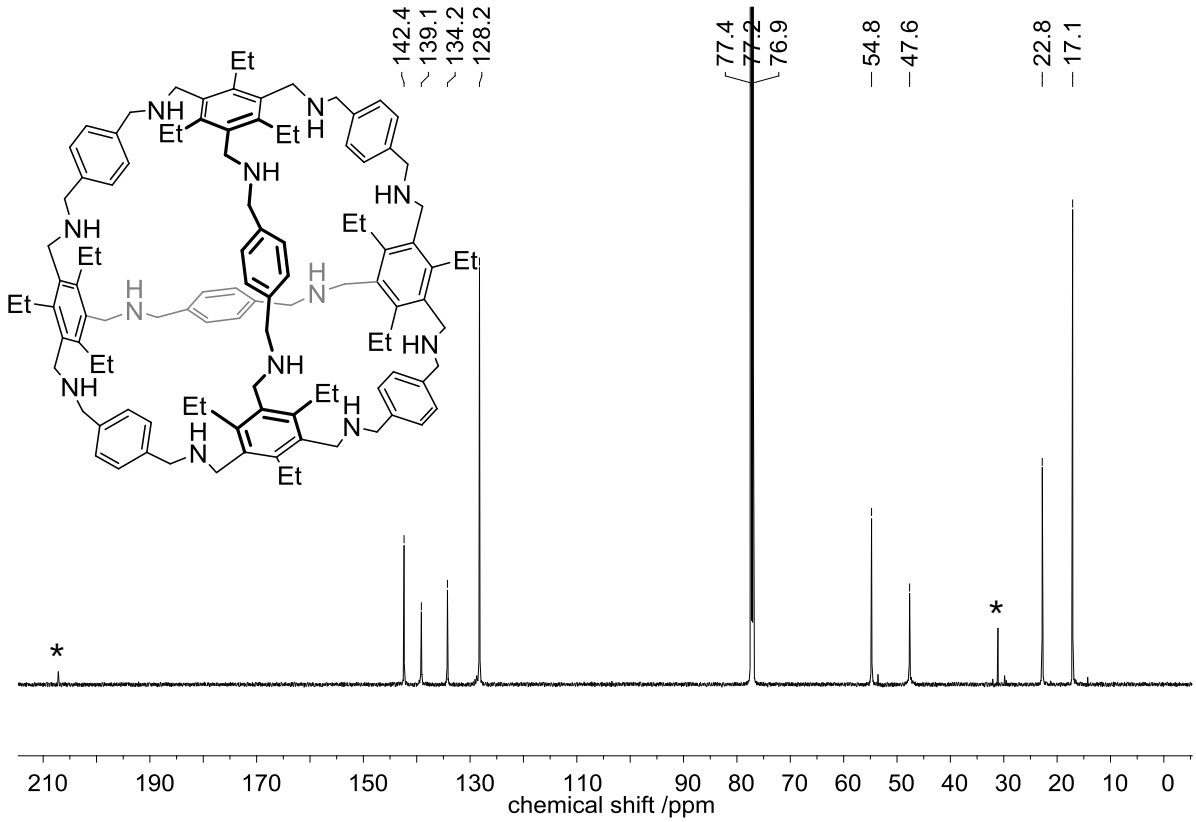


Figure S37: ^{13}C NMR spectrum ($CHCl_3$, 150 MHz) of compound **15**. *Acetone.

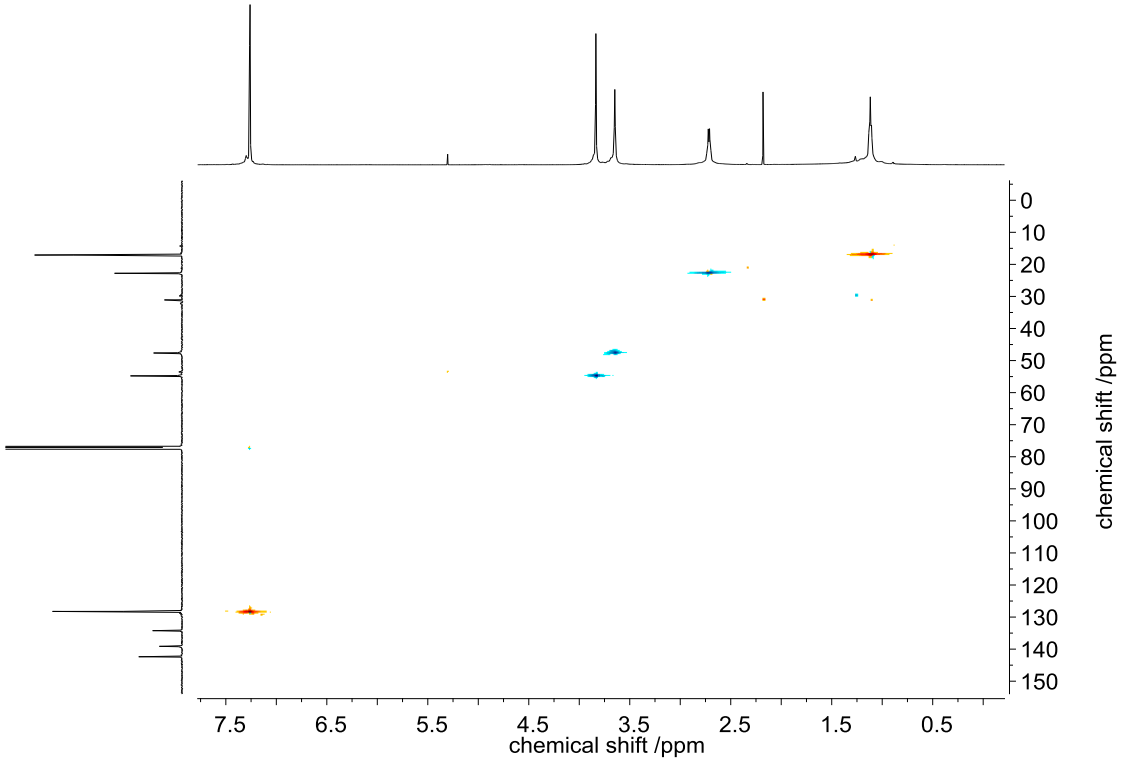


Figure S38: HSQC NMR spectrum ($CHCl_3$, 600 MHz) of compound **15**.

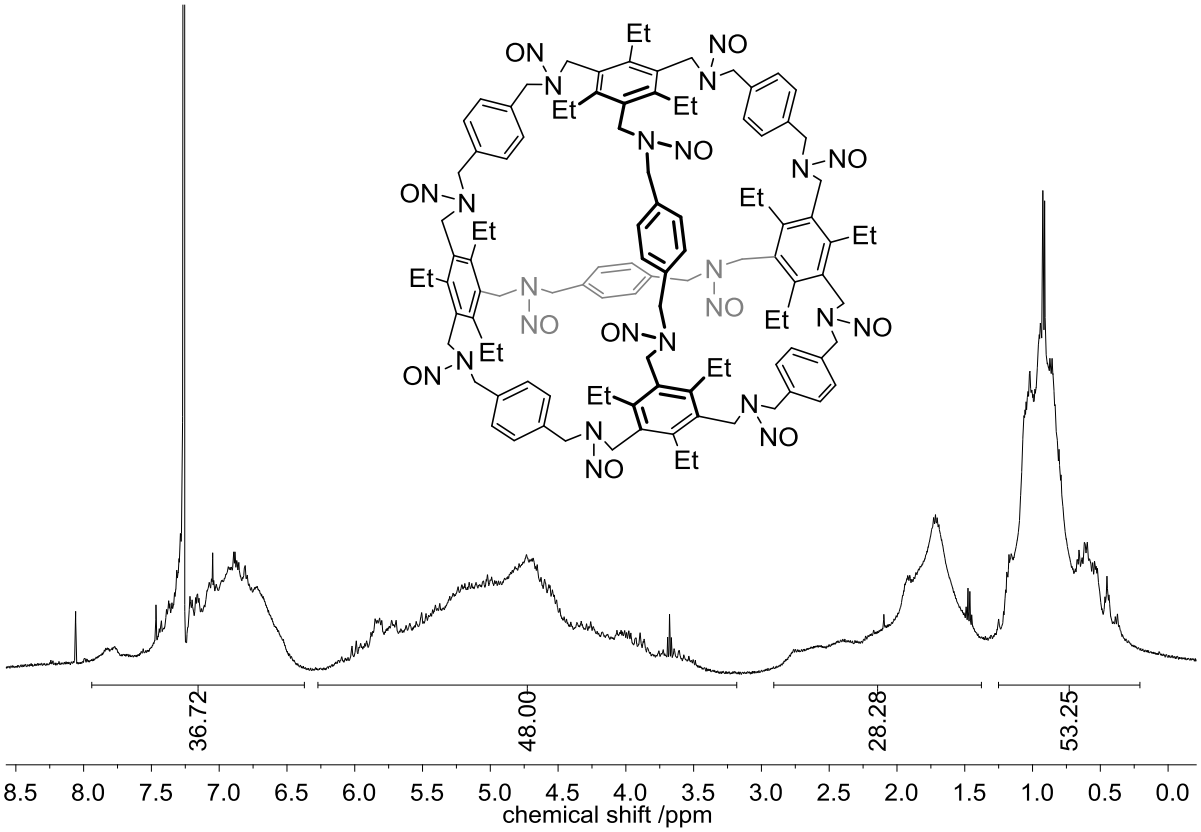


Figure S39: ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **16**.

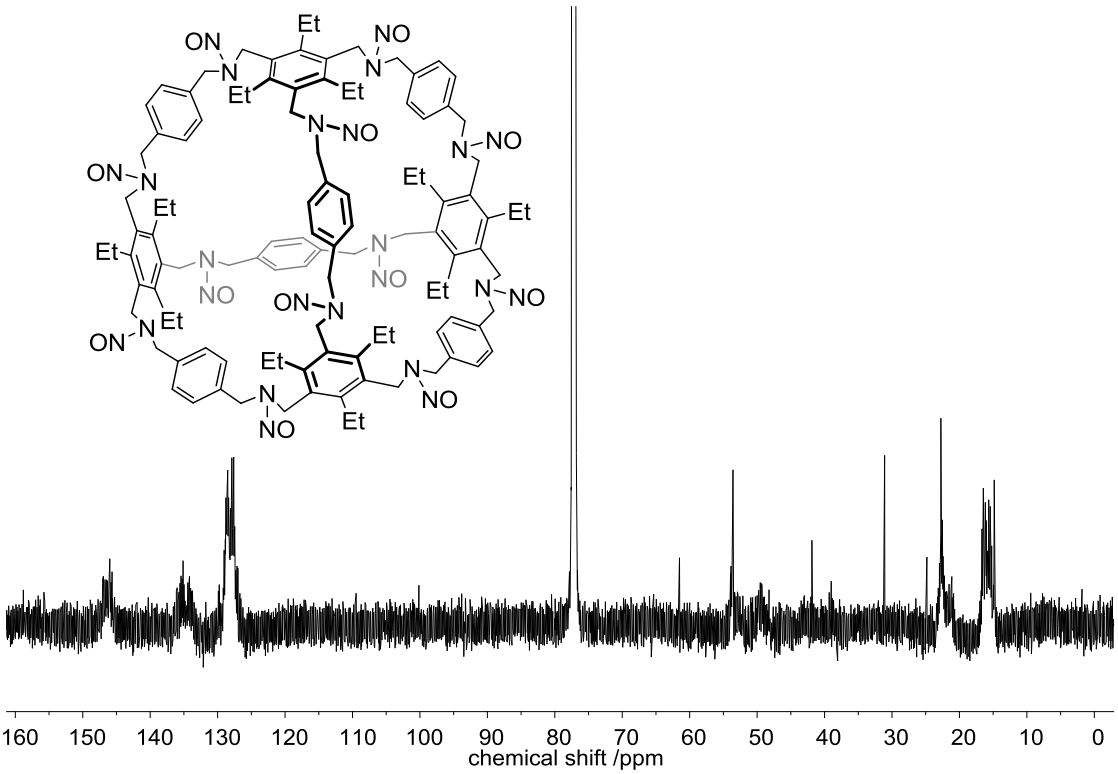


Figure S40: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of compound **16**.

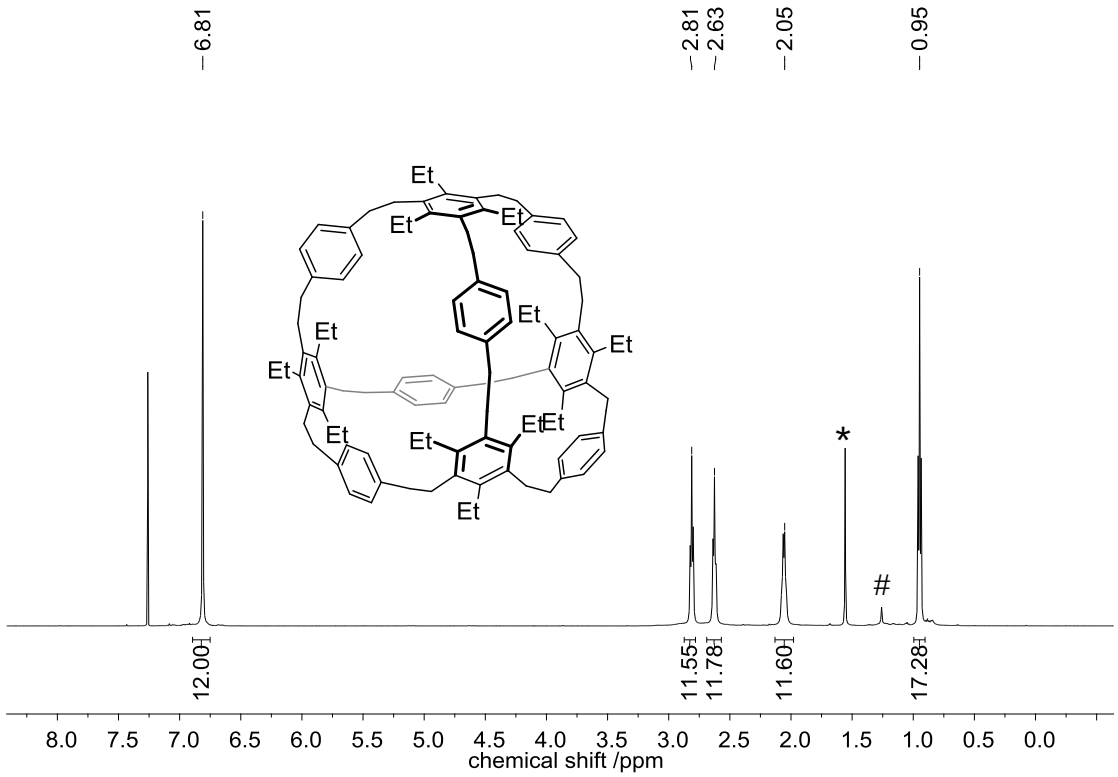


Figure S41: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **17**.*H_2O, $^{\#}$H-grease.

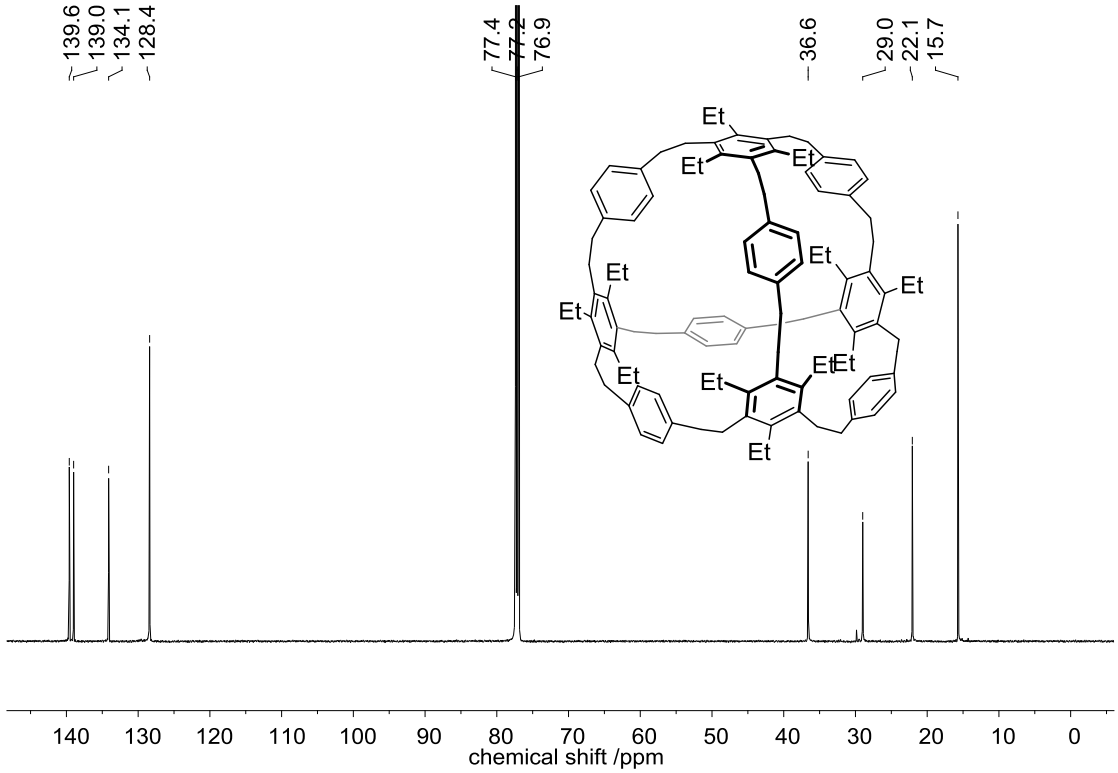


Figure S42: ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of compound **17**.

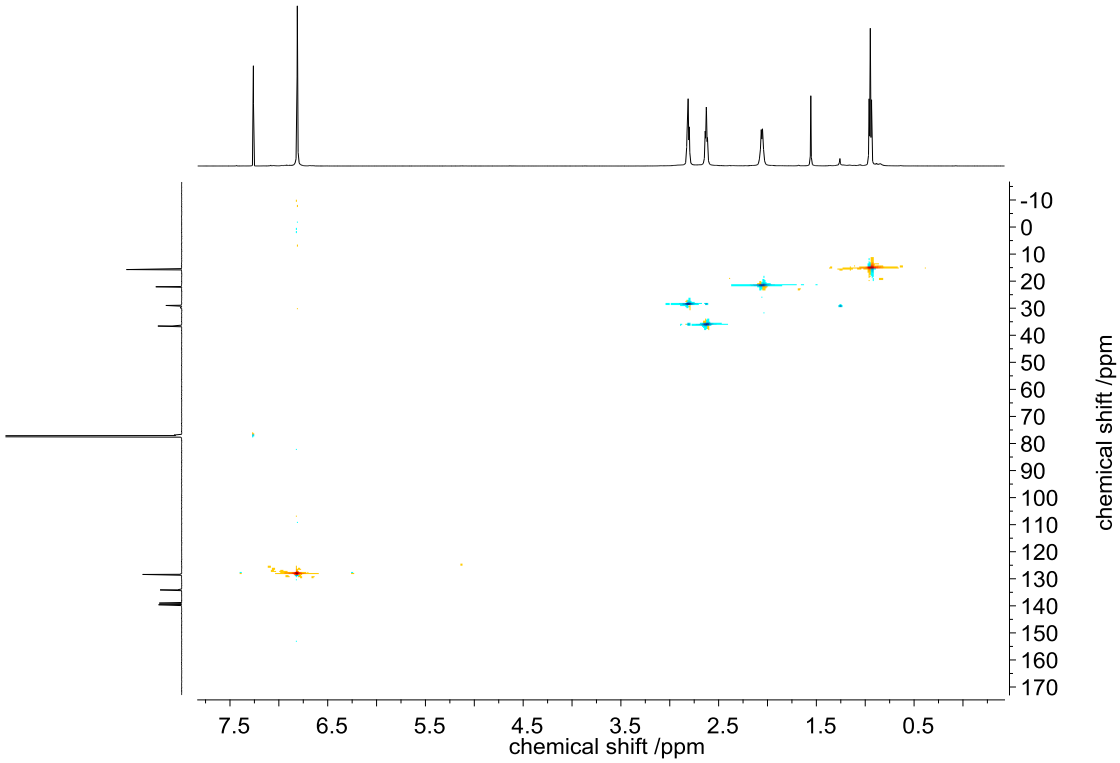


Figure S43: HSQC NMR spectrum ($CDCl_3$, 600 MHz) of compound **17**.

5 Temperature Dependent NMR analytics

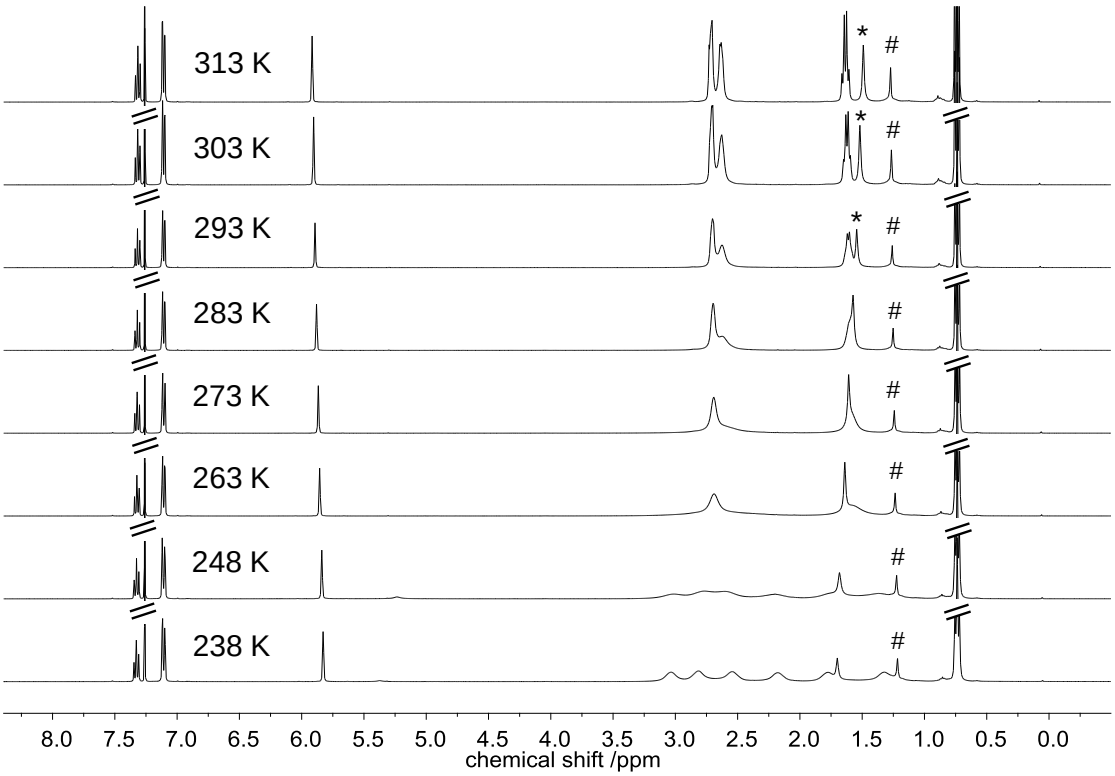


Figure S44: Temperature dependent ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **8a**. *H_2O, $^{\#}$ grease. Coalescence temperature T_c = -10°C (263 K), k_c (hexasubstituted benzene) = 242 Hz, k_c (disubstituted benzene) = 769 Hz, ΔG = 51 kJ·mol^{-1}.

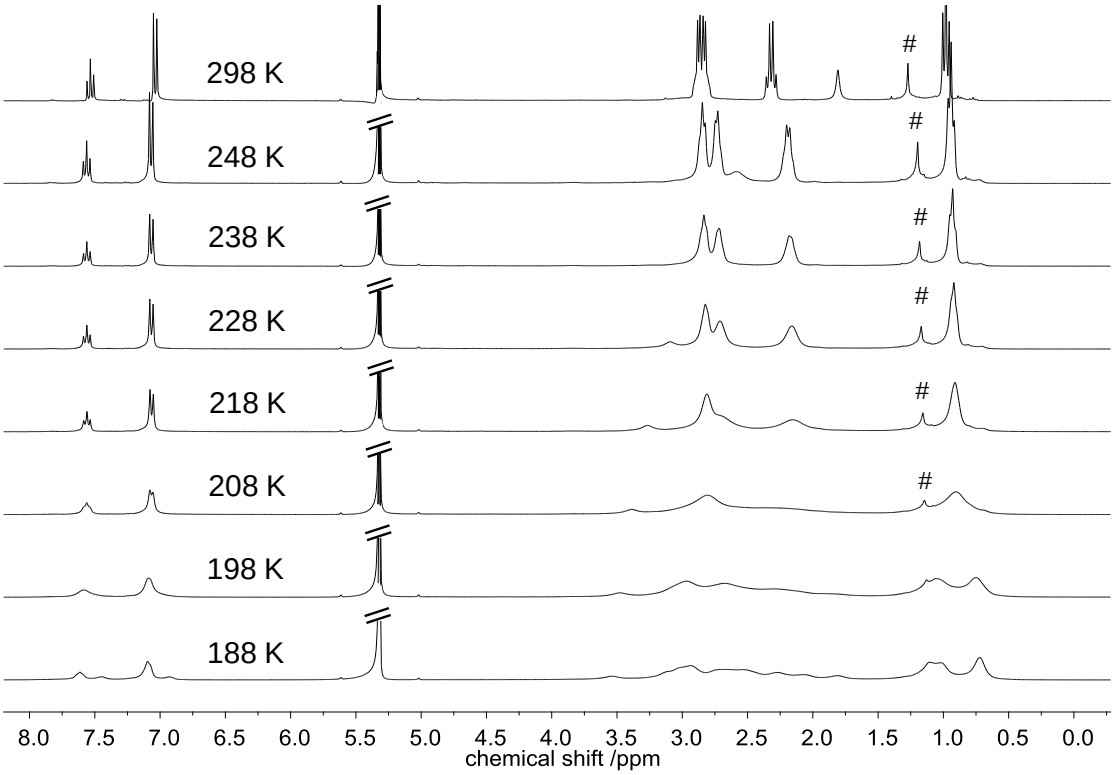


Figure S45: Temperature dependent ^{1}H NMR spectrum (CD_2Cl_2, 300 MHz) of compound **8b**. $^{\#}$grease. Coalescence temperature T_c = -65°C (208 K), k_c (hexasubstituted benzene) = 804 Hz, k_c (disubstituted benzene) = 195 Hz, ΔG = 40 kJmol^{-1}.

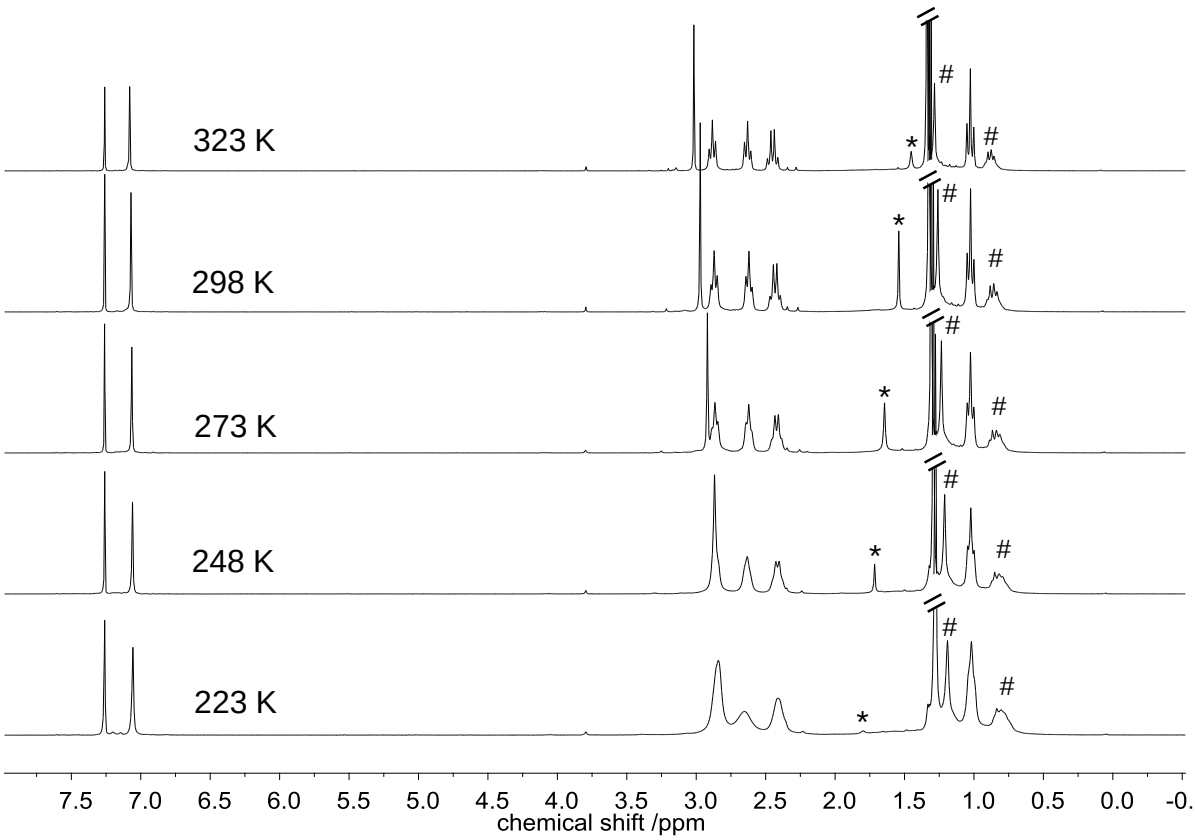


Figure S46: Temperature dependent ^{1}H NMR spectrum ($CDCl_3$, 300MHz) of compound **8c** *H_2O, #grease.

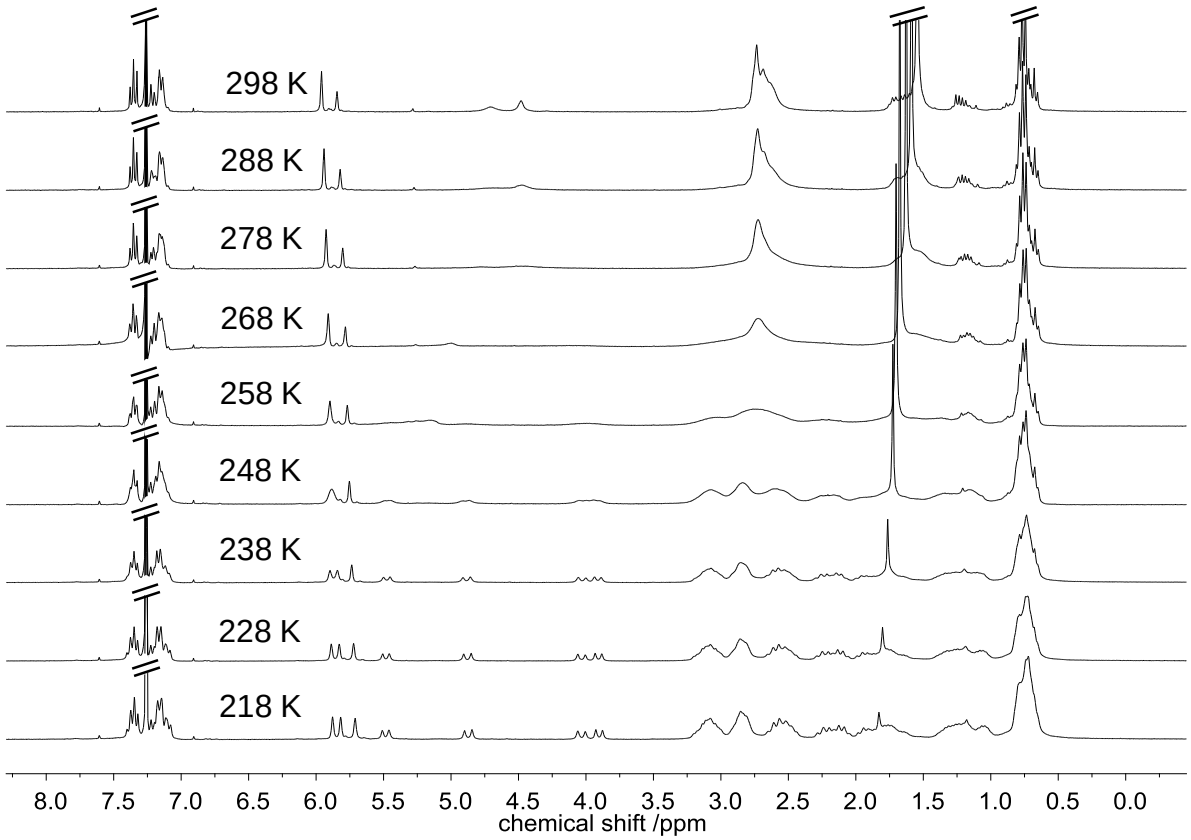


Figure S47: Temperature dependent ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **9**. Coalescence temperature T_{c1} = -5°C (278 K), T_{c2} = -25°C (248 K), k_{c1} (hexasubstituted benzene) = 560 Hz, k_{c1} (disubstituted benzene) = 1055 Hz, ΔG_1 = 50 kJ·mol^{-1}; k_{c2} (disubstituted benzene) = 38 Hz, ΔG_2 = 53 kJ·mol^{-1}

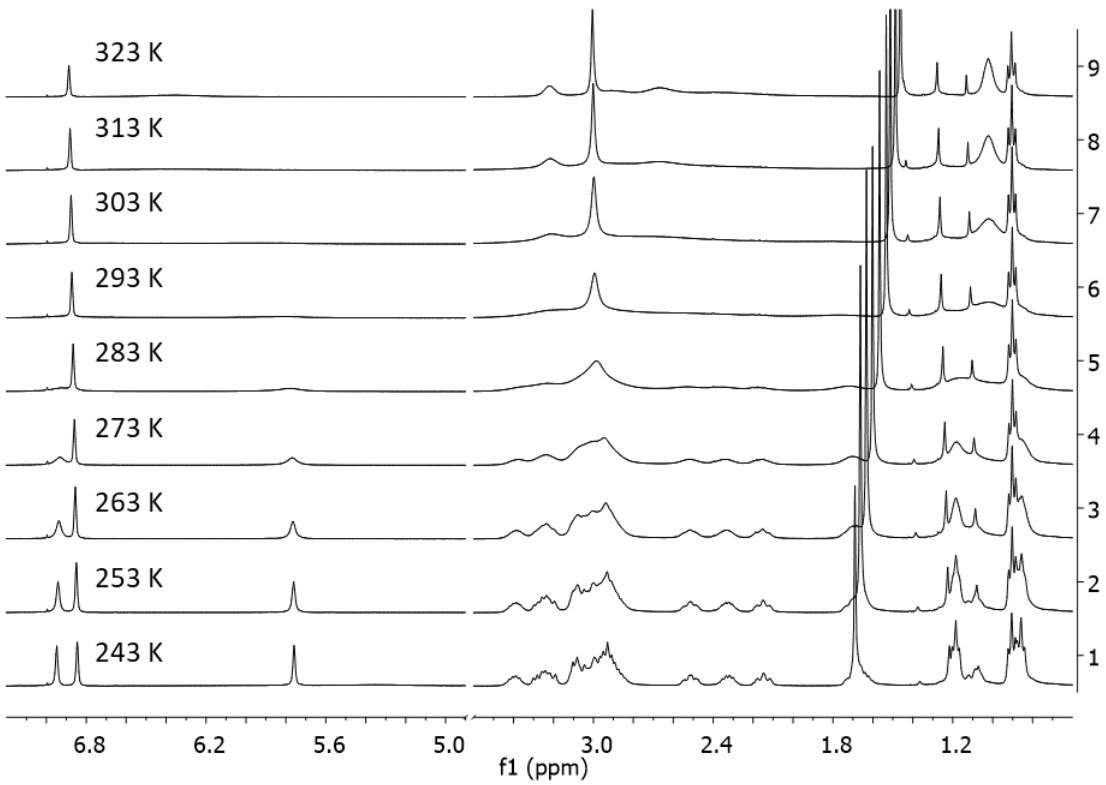


Figure S48: Temperature dependent ^{1}H NMR spectra (400 MHz, $CDCl_3$) of cage compound **13**. Coalescence temperature T_c = 30°C (303 K), k_c (hexasubstituted benzene) = 293 Hz, k_c (trisubstituted benzene) = 1057 Hz, ΔG = 57 kJ·mol^{-1}.

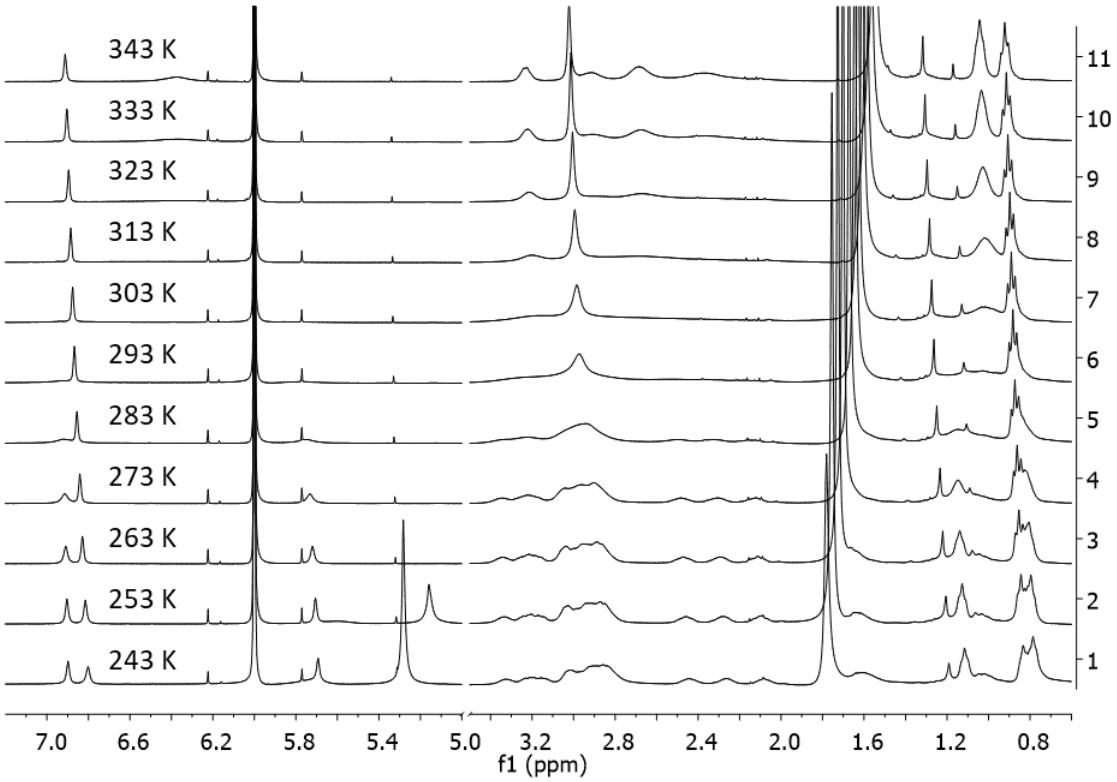


Figure S49: Temperature dependent ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$) of cage compound **13**. Coalescence temperature T_c = 30°C (303 K), k_c (hexasubstituted benzene) = 293 Hz, k_c (trisubstituted benzene) = 1057 Hz, ΔG = 57 kJ·mol^{-1}.

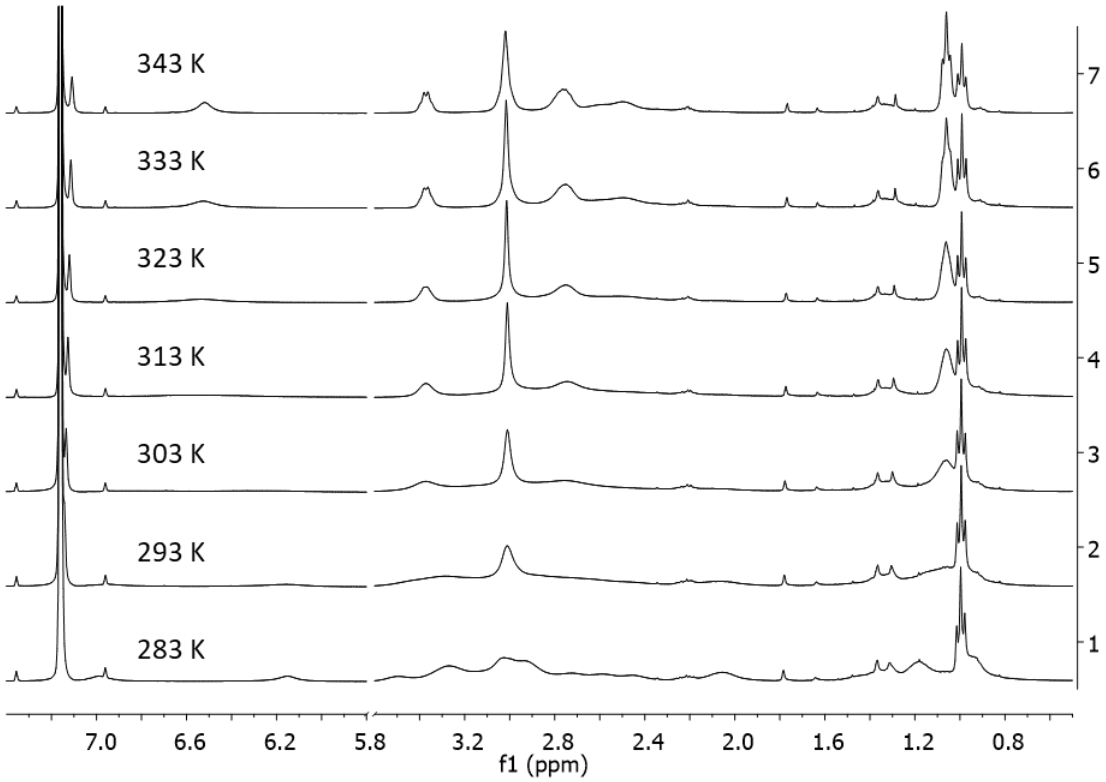


Figure S50: Temperature dependent ^{1}H NMR spectra (400 MHz, C_6D_6) of cage compound **13**. Coalescence temperature T_c = 30°C (303 K), k_c (hexasubstituted benzene) = 293 Hz, k_c (trisubstituted benzene) = 1057 Hz, ΔG = 57 kJ·mol^{-1}.

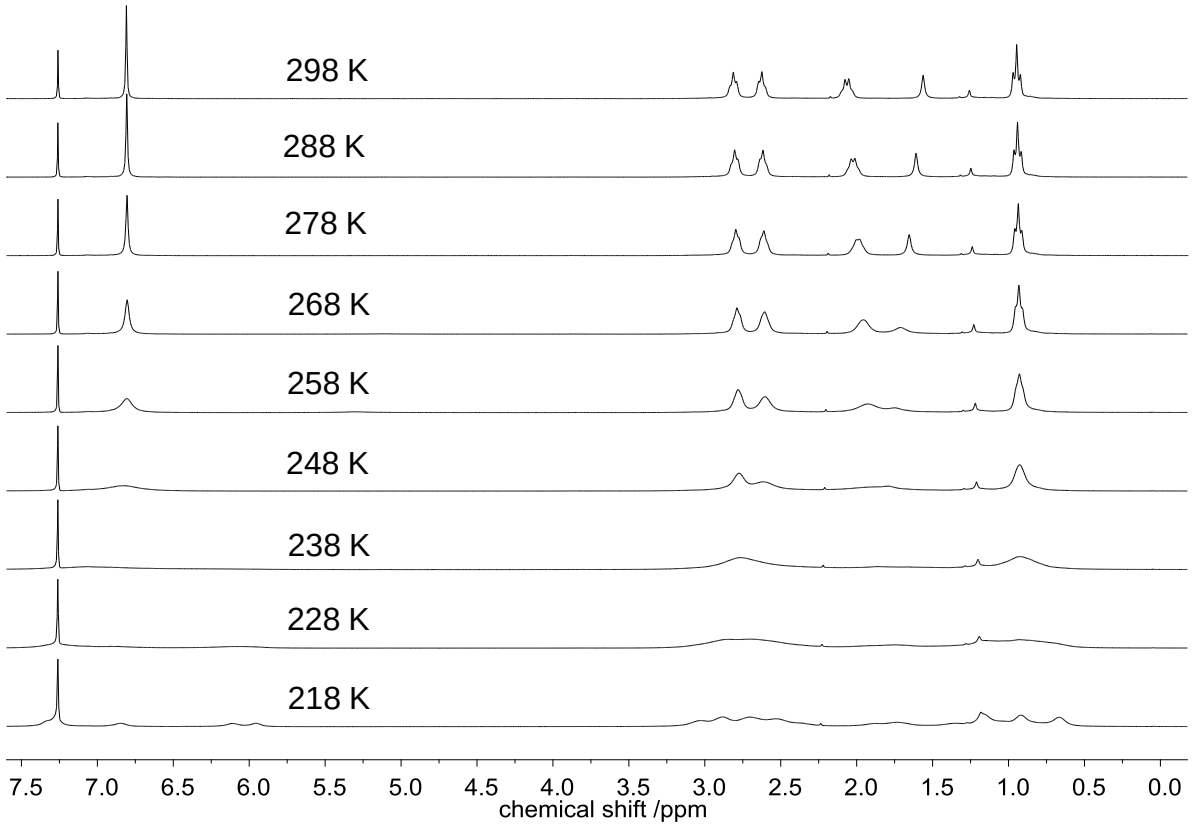


Figure S51: Temperature dependent ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **17**. Coalescence temperature T_c = -35°C (238 K), k_c = 120 Hz, ΔG = 48 kJ·mol^{-1}.

5 DOSY experiments

DOSY NMR experiments were calibrated using known self-diffusion values for the solvents used (D_{solv}).[S7] The solvodynamic radii were estimated using the semi-empirical modification of the Stokes-Einstein equation proposed by Chen and Chen.[S8] This equation was solved for r_s using values of r_{solv} and η from the literature.[S9]

$$D = \frac{k_B T}{\left(\frac{6}{1 + 0.695 \left(\frac{r_{solv}}{r_s} \right)^{2.234}} \right) \pi \eta r_s}$$

D is the measured diffusion coefficient ($m^2 \cdot s^{-1}$)

k_B is Boltzmann constant ($1.3806485 \cdot 10\ m^2 \cdot kg \cdot s^{-2} \cdot K^{-1}$)

T is the temperature (K)

r_{solv} is the hydrodynamic radius of the solvent (m)

r_s is the hydrodynamic radius of the analyte (m)

η is the viscosity of the solvent at temperature T ($kg \cdot m^{-1} \cdot s^{-1}$)

Table S1: Estimation of the hydrodynamic radius of cage compounds (r_h) in the corresponding solvents using parameters from literature and diffusion coefficients measured by DOSY NMR.

Compound	T [K]	Solvent	$D_{solv} \cdot 10^{-9}$ [$m^2 \cdot s^{-1}$]	r_{solv} [nm]	$\eta \cdot 10^{-3}$ [$kg \cdot m^{-1} \cdot s^{-1}$]	$D \cdot 10^{-10}$ [$m^2 \cdot s^{-1}$]	r_h [nm]
5c	298	$CDCl_3$	2.45	0.260	0.542	6.03	0.66
7a	298	$CDCl_3$	2.45	0.260	0.542	6.17	0.65
7b	298	$CDCl_3$	2.45	0.260	0.542	6.76	0.59
7c	298	$CDCl_3$	2.45	0.260	0.542	5.50	0.72
8a	298	$CDCl_3$	2.45	0.260	0.542	6.92	0.59
8b	298	$CDCl_3$	2.45	0.260	0.542	7.56	0.51
8c	298	$CDCl_3$	2.45	0.260	0.542	7.76	0.54
9	298	$CDCl_3$	2.45	0.260	0.542	6.61	0.59
11	298	C_6D_6	2.18	0.270	0.603	4.14	0.87
12	298	DMSO	0.74	0.263	1.99	0.83	1.32
13	298	$CDCl_3$	2.45	0.260	0.542	6.17	0.65
14	298	$CDCl_3$	2.45	0.260	0.542	5.01	0.80
16	298	$CDCl_3$	2.45	0.260	0.542	4.90	0.81
17	298	$CDCl_3$	2.45	0.260	0.542	5.89	0.68

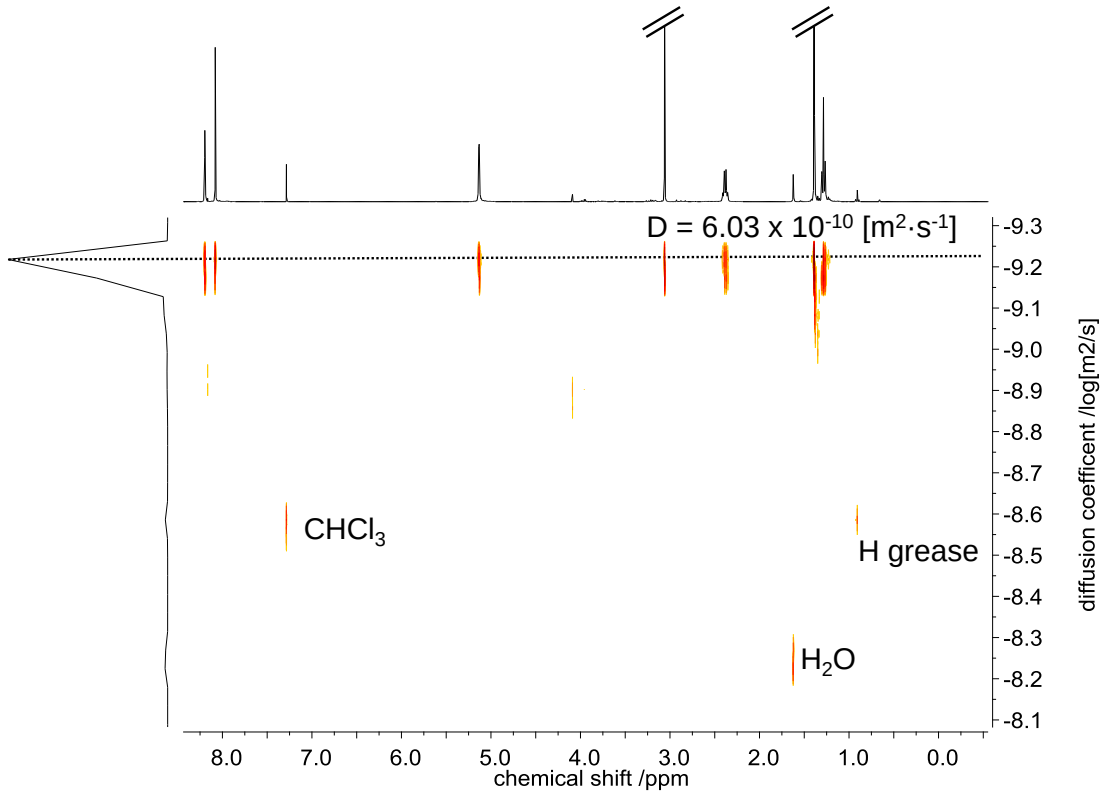


Figure S52: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **5c**.

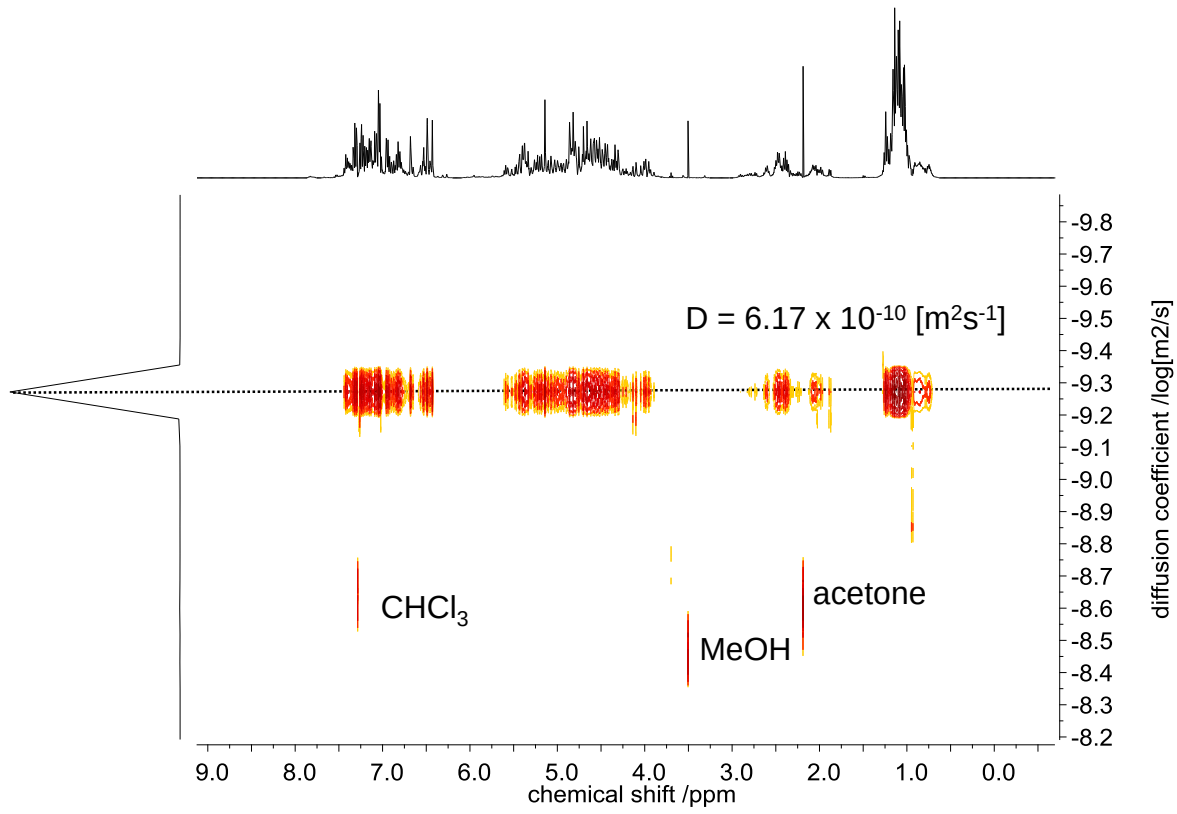


Figure S53: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **7a**.

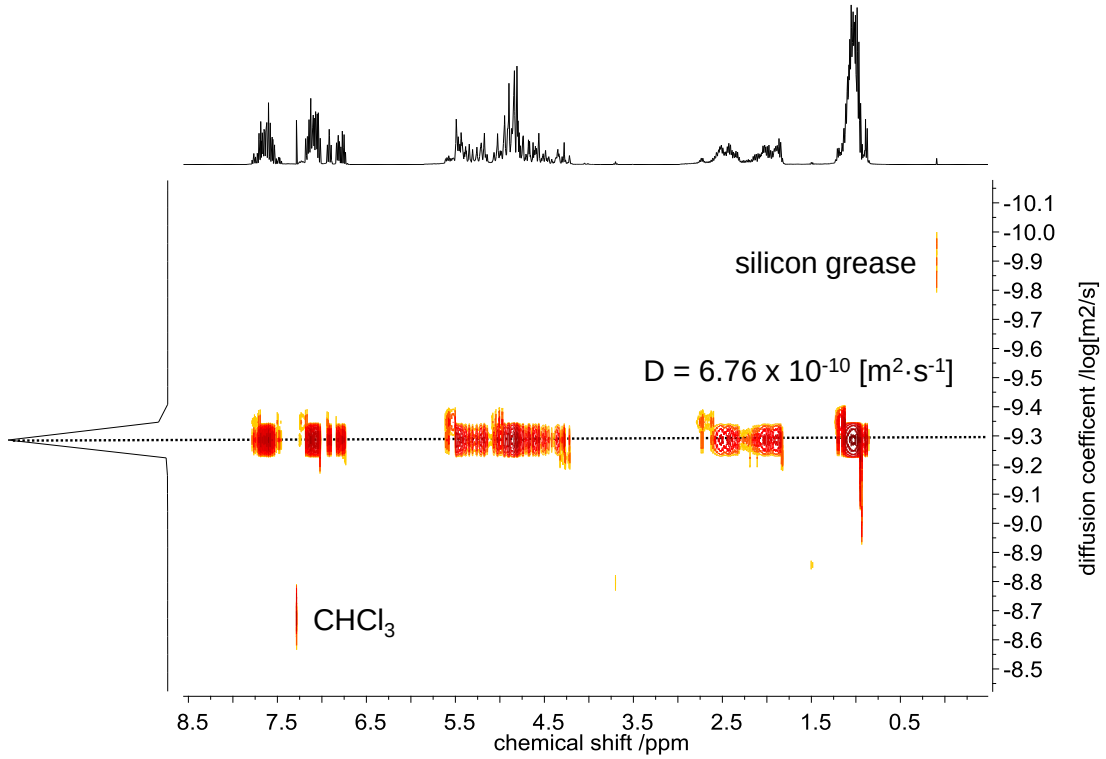


Figure S54: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **7b**.

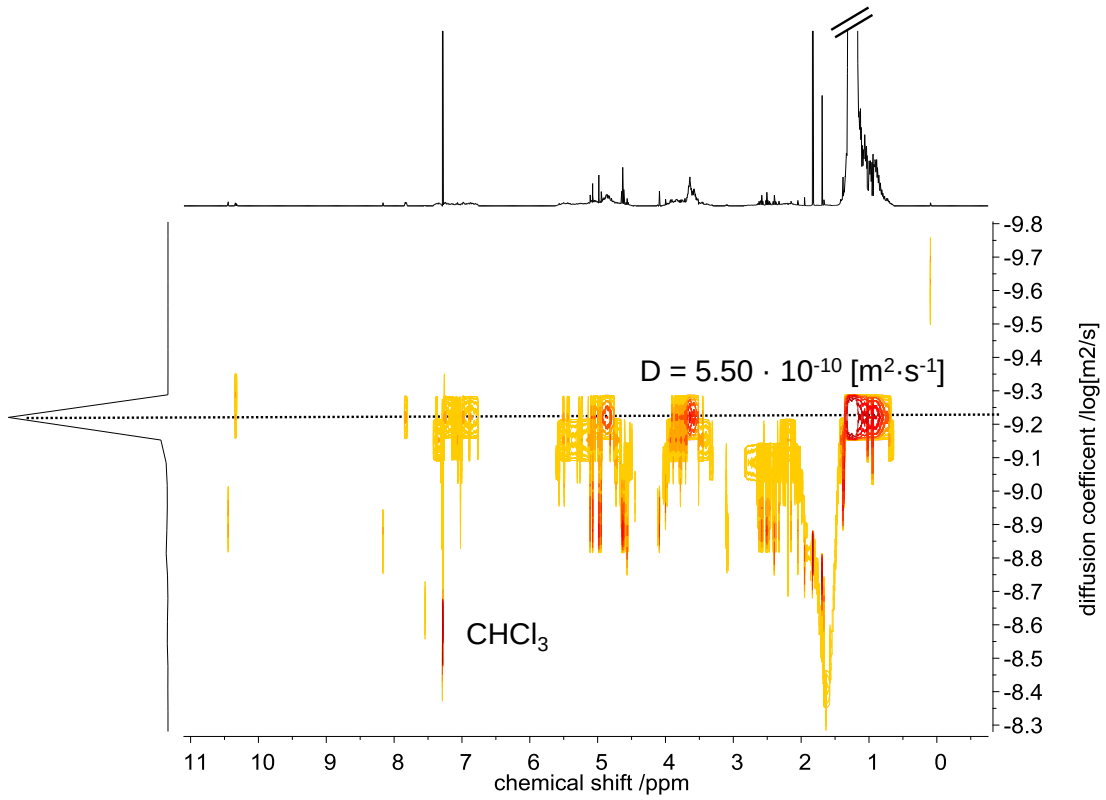


Figure S55: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **7c**.

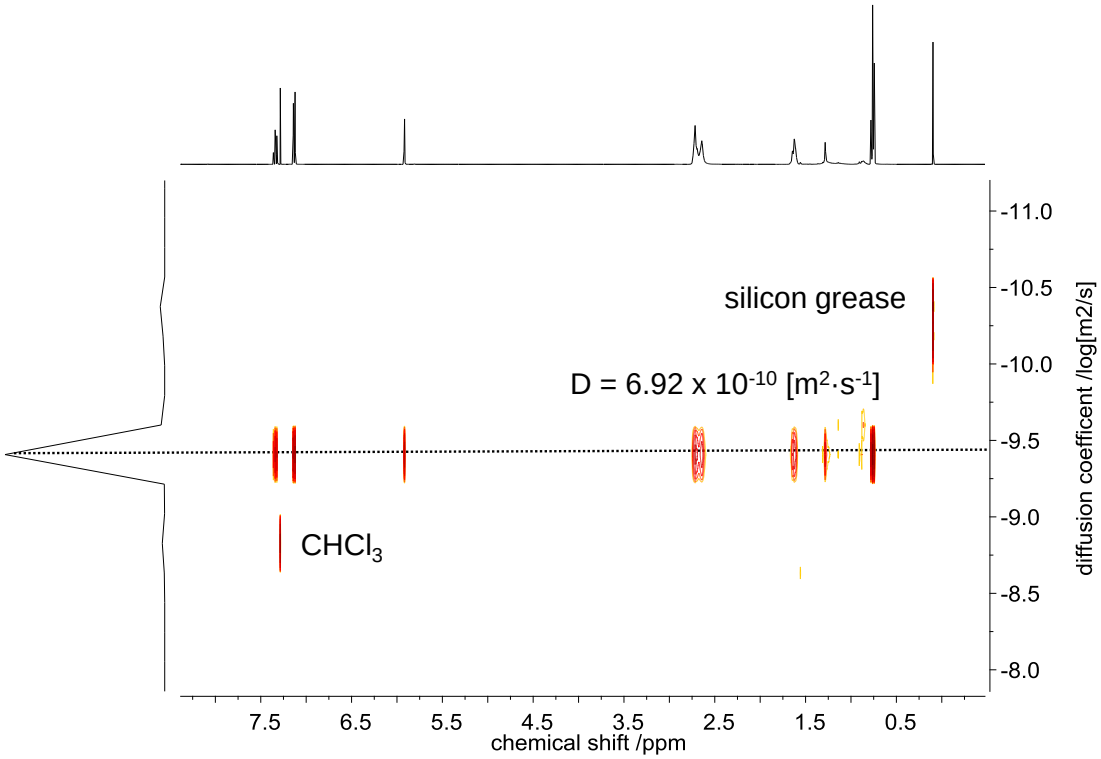


Figure S56: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **8a**.

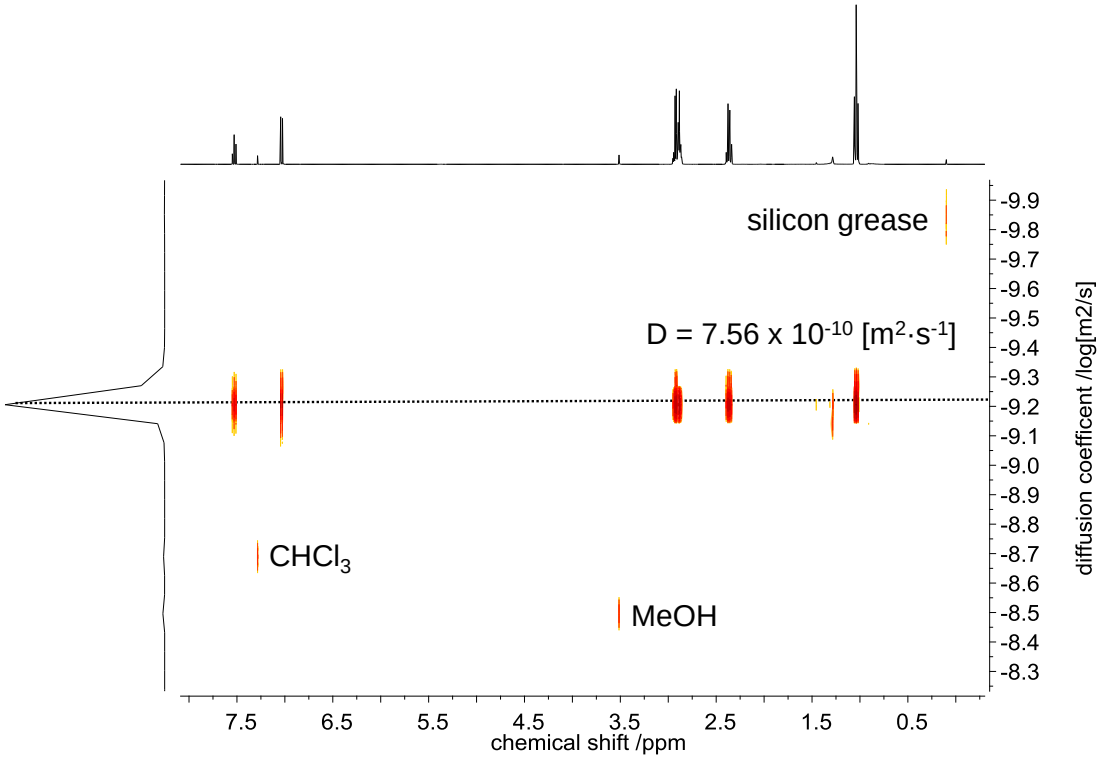


Figure S57: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **8b**.

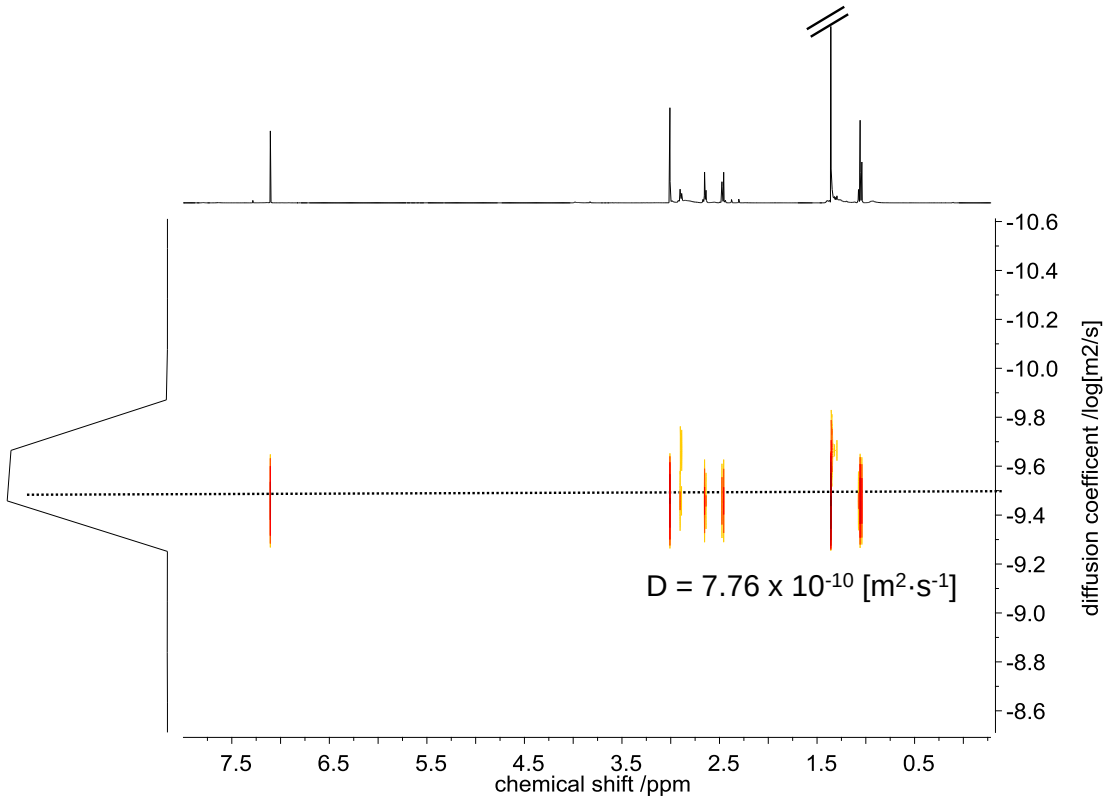


Figure S58: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **8c**.

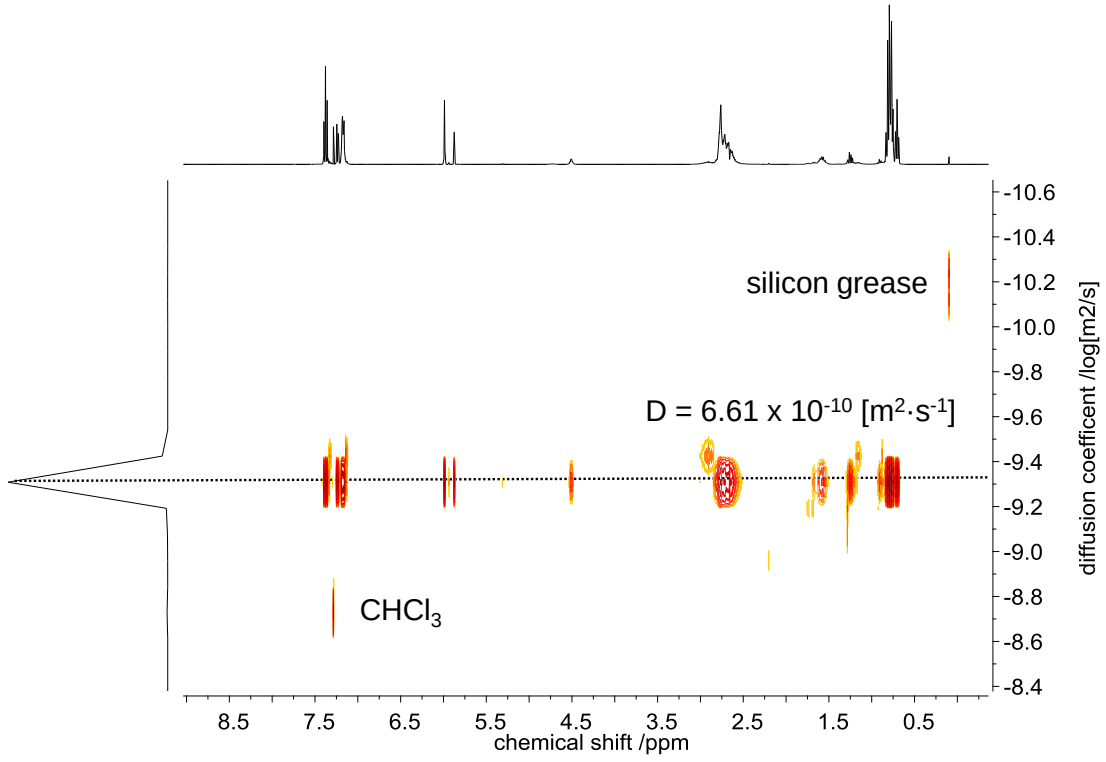


Figure S59: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **9**.

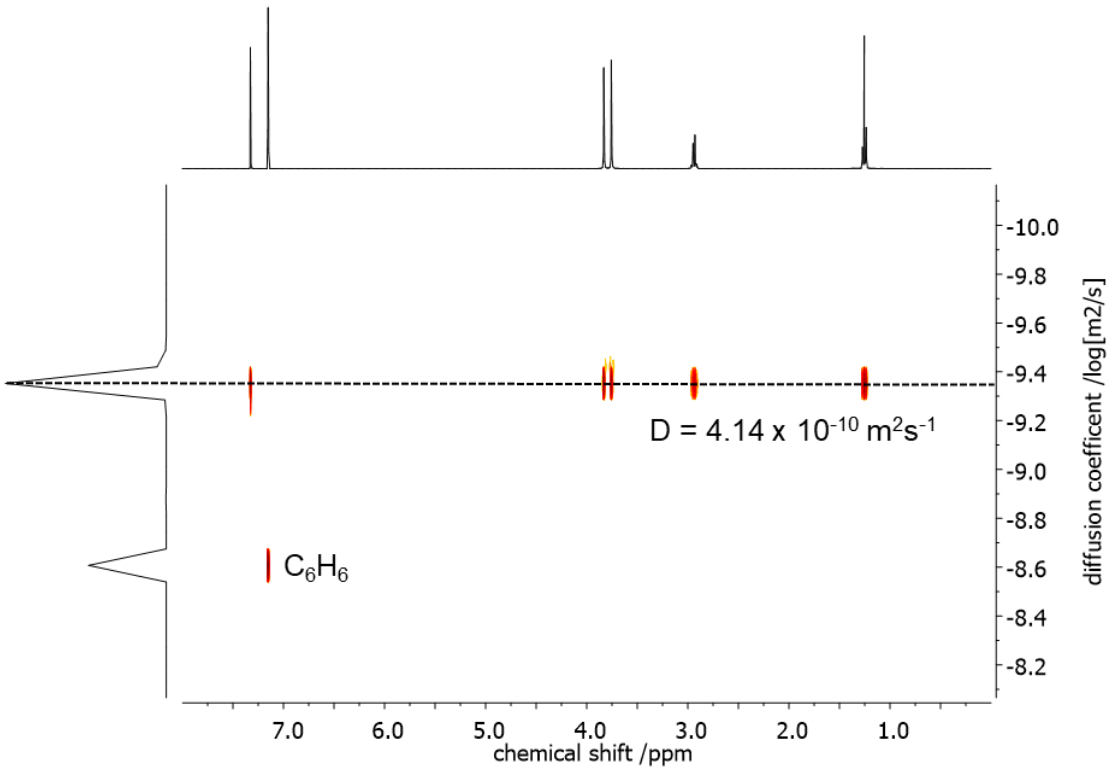


Figure S60: DOSY NMR spectrum (400 MHz, 298 K, C_6D_6) of cage compound **11**.

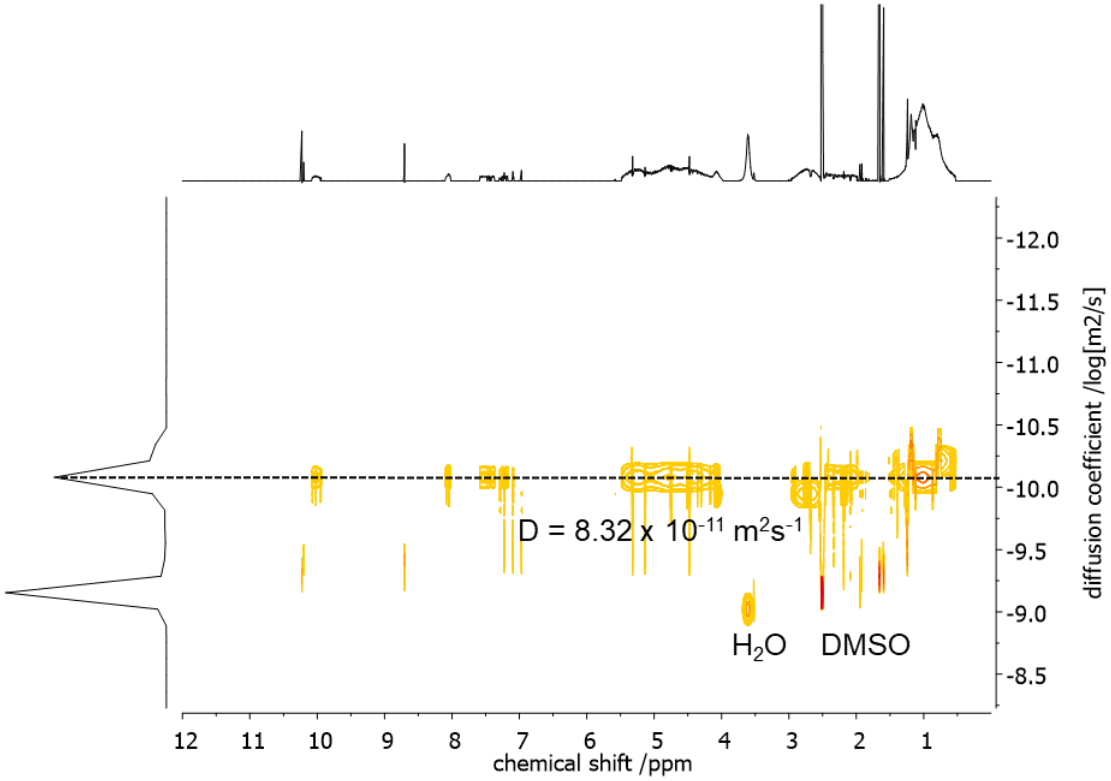


Figure S61: DOSY NMR spectrum (400 MHz, 298 K, DMSO-d_6) of cage compound **12**.

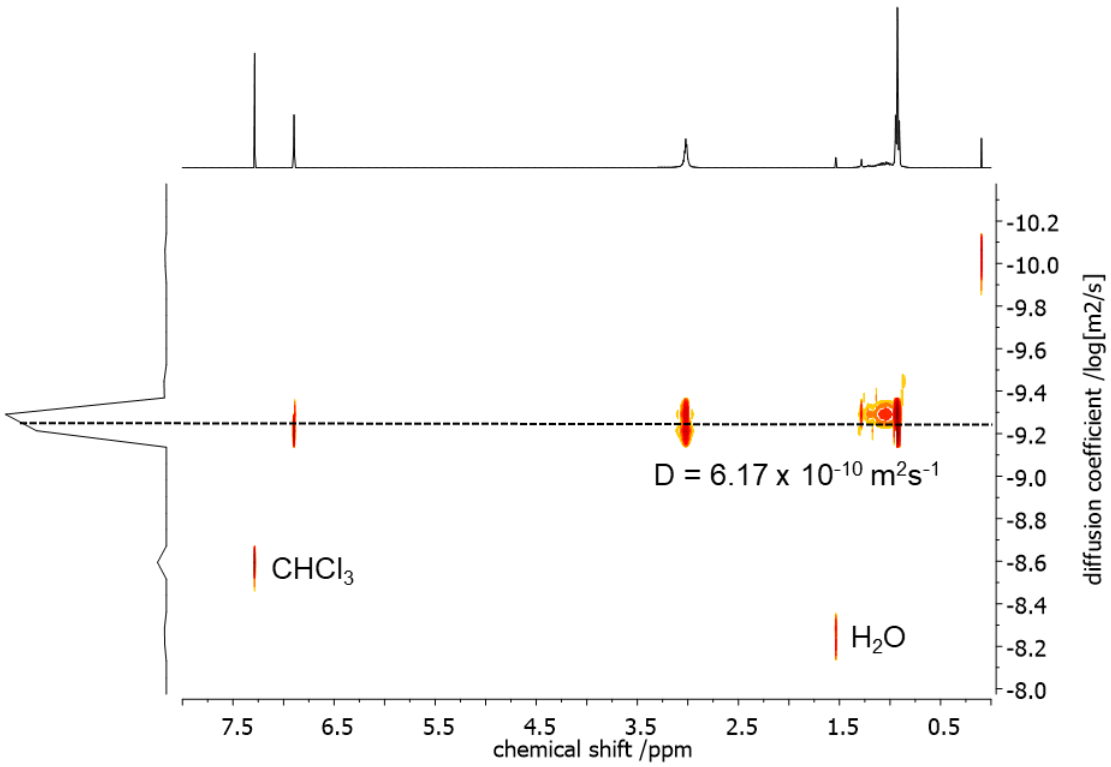


Figure S62: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of cage compound **13**.

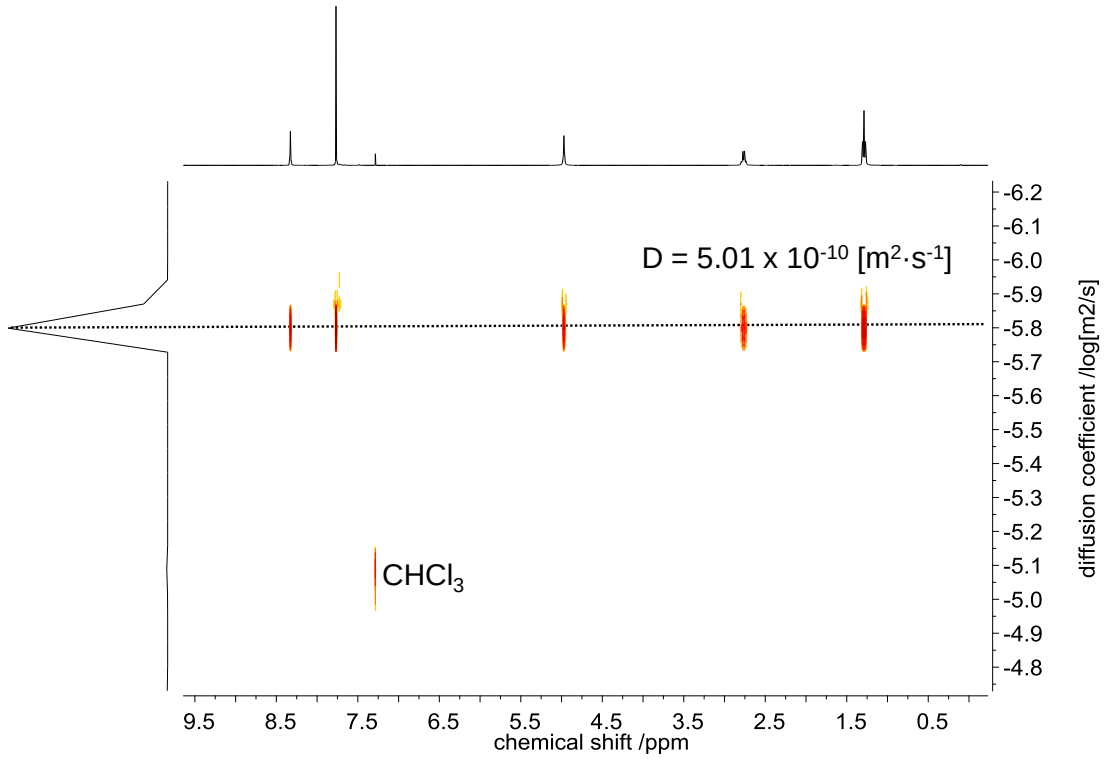


Figure S63: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **14**.

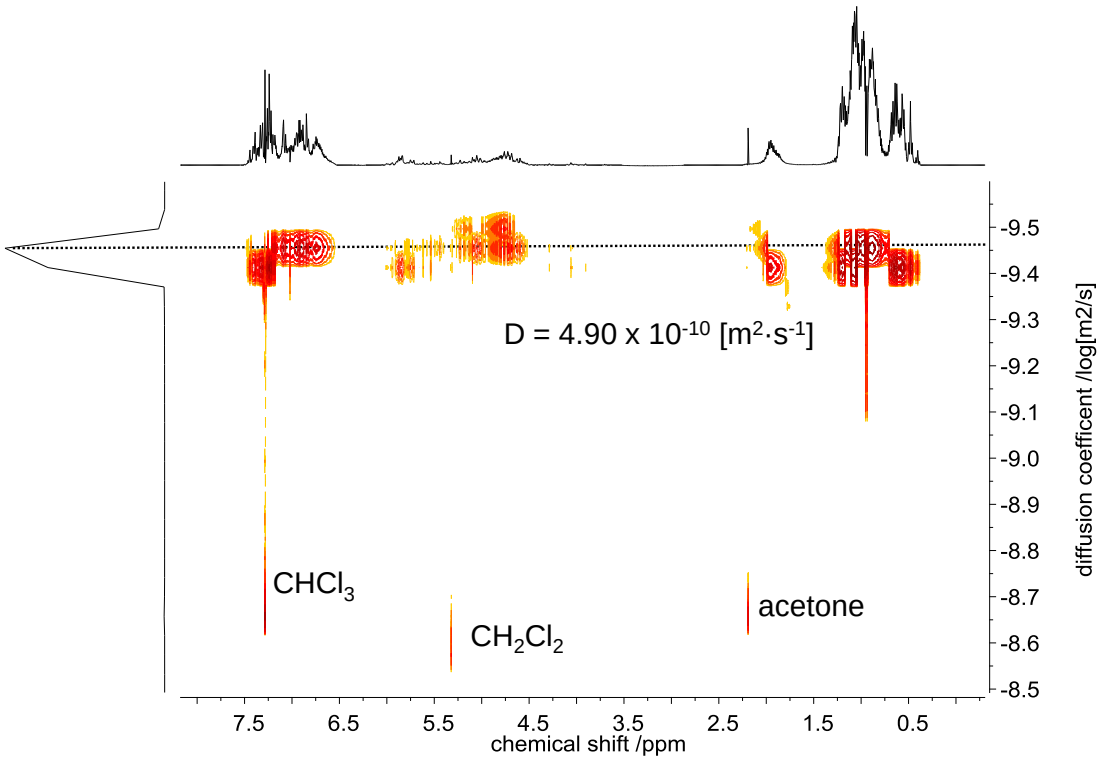


Figure S64: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **16**.

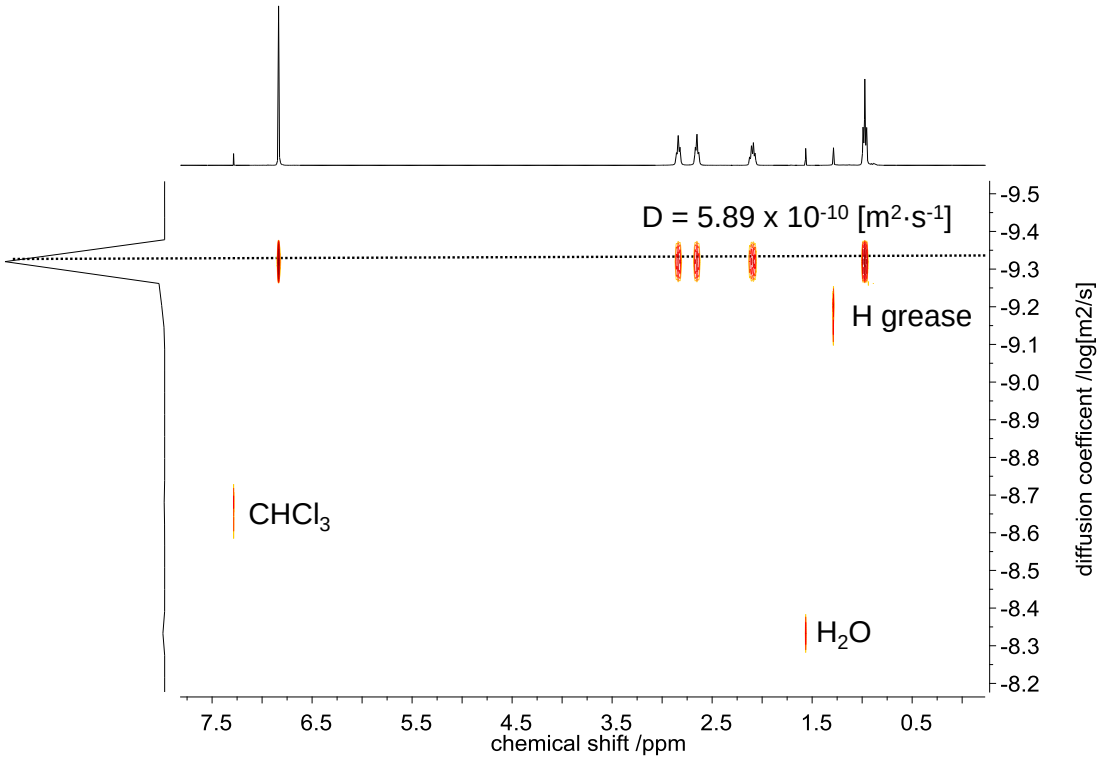


Figure S65: DOSY NMR spectrum (400 MHz, 298 K, $CDCl_3$) of **17**.

6 Mass Spectra

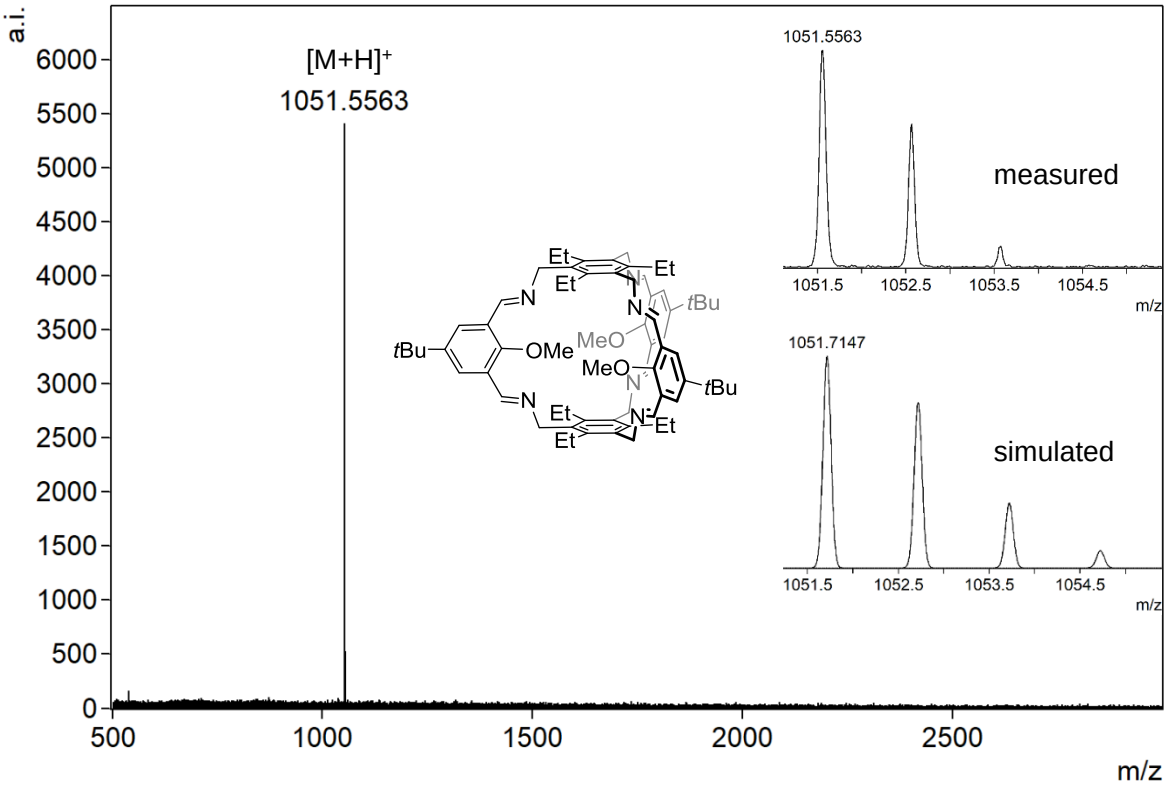


Figure S66: MALDI-TOF (DCTB) of compound **5c**.

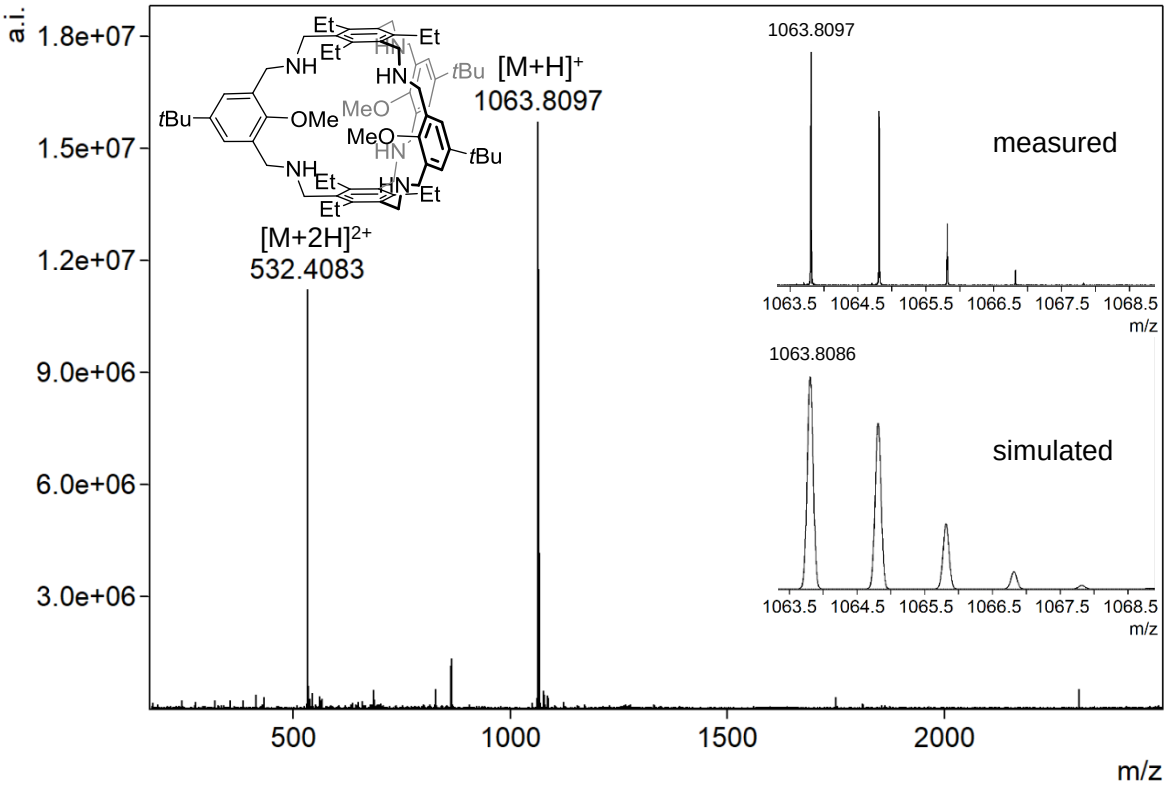


Figure S67: ESI (pos) of compound **6c**.

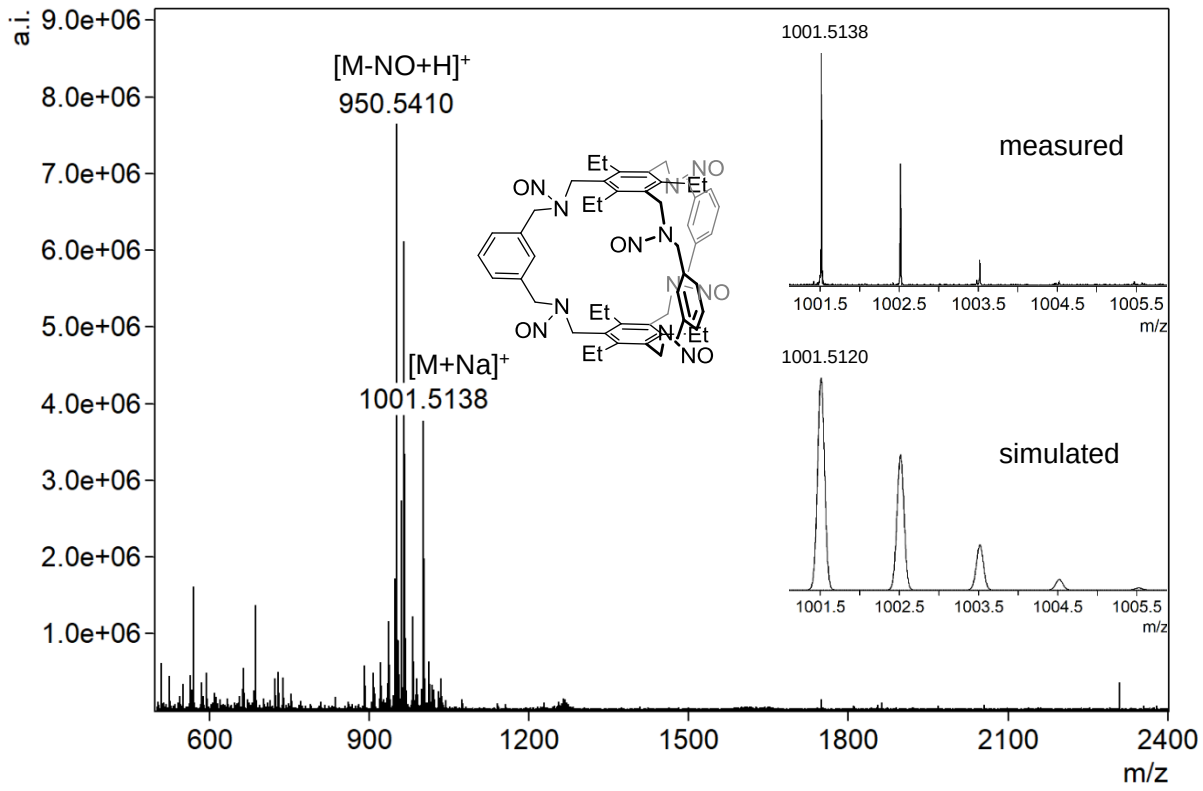


Figure S68: ESI (pos) of compound **7a**.

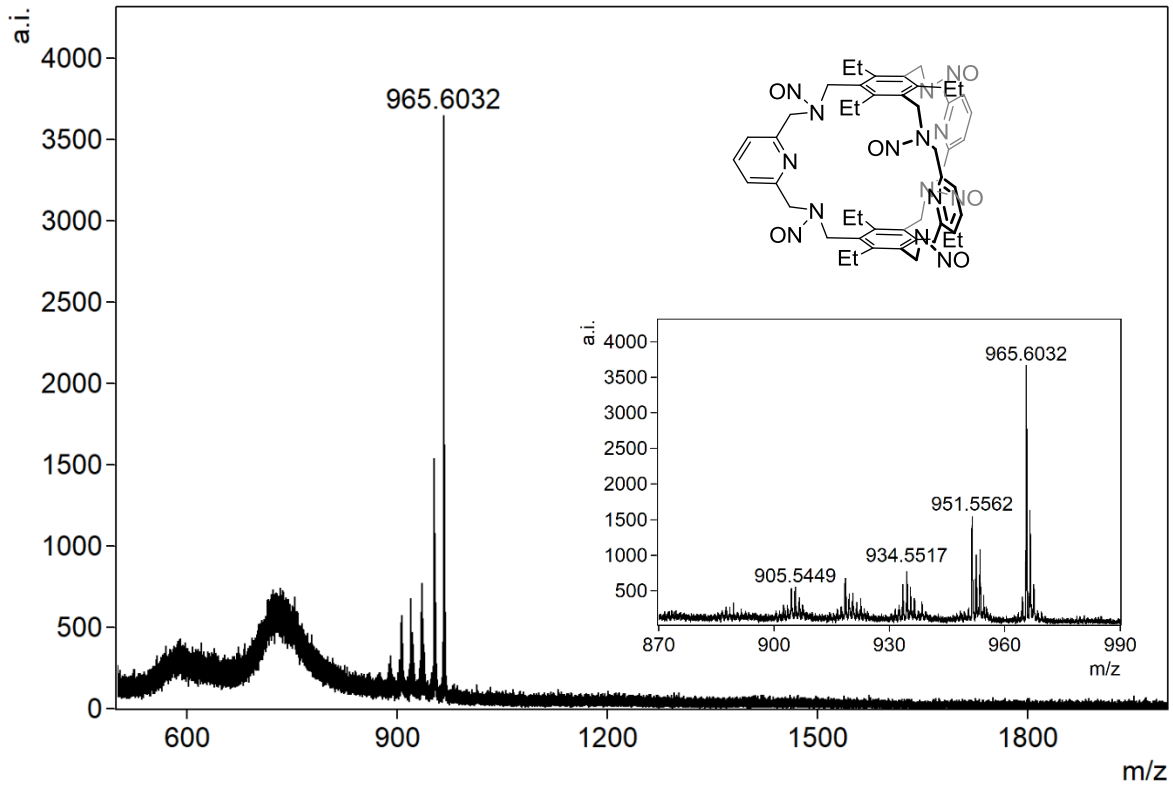


Figure S69: MALDI-TOF (DCTB) of compound **7b**.

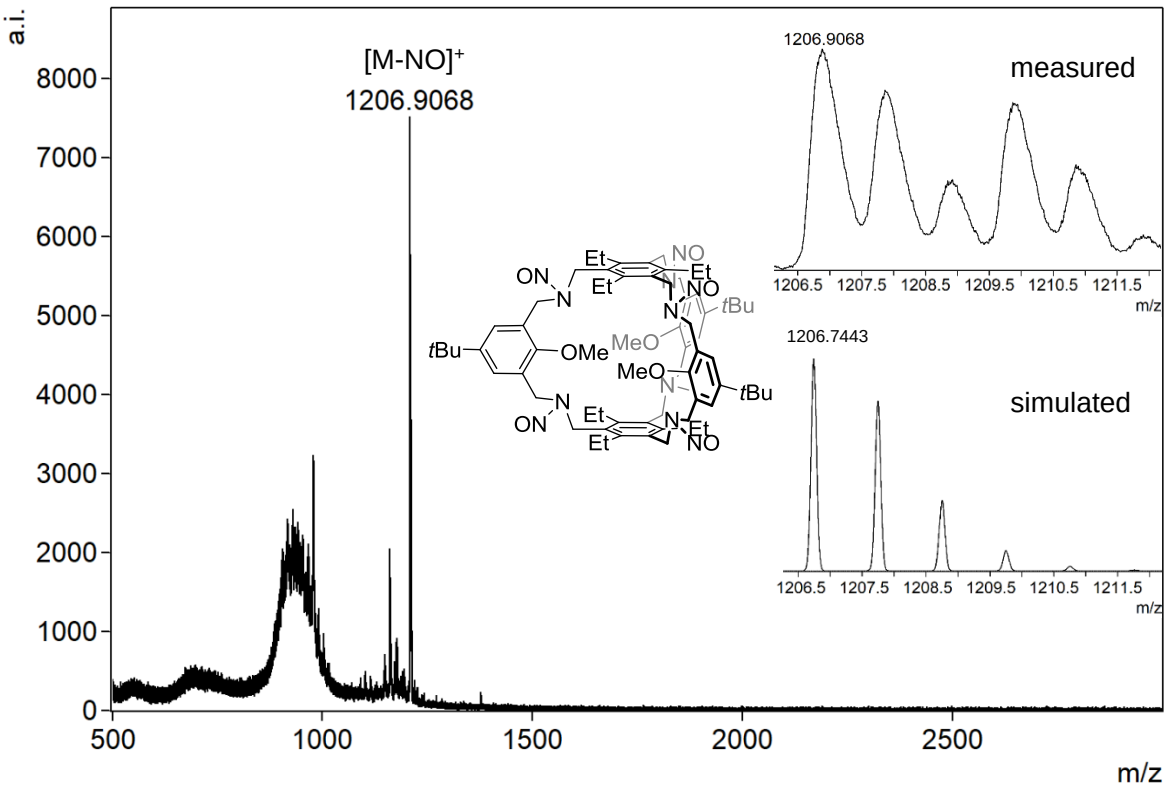


Figure S70: MALDI-TOF (DCTB) of compound **7c**.

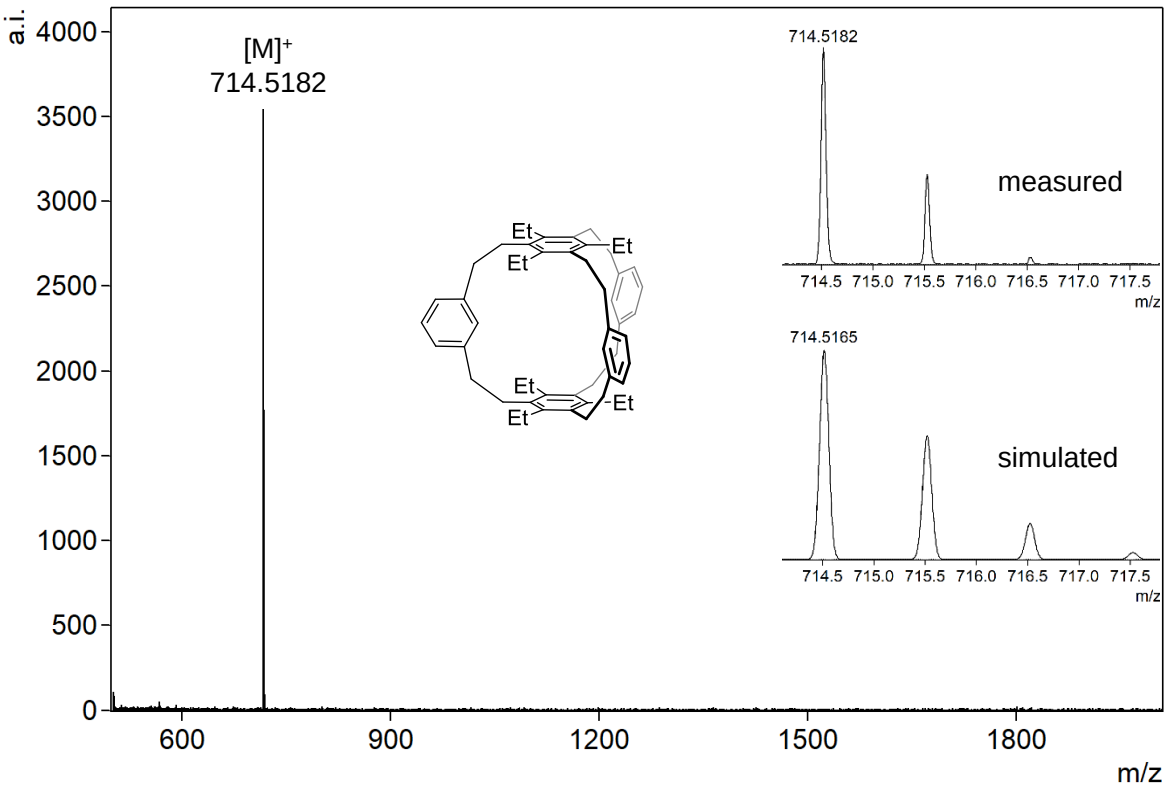


Figure S71: MALDI-TOF (DCTB) of compound **8a**.

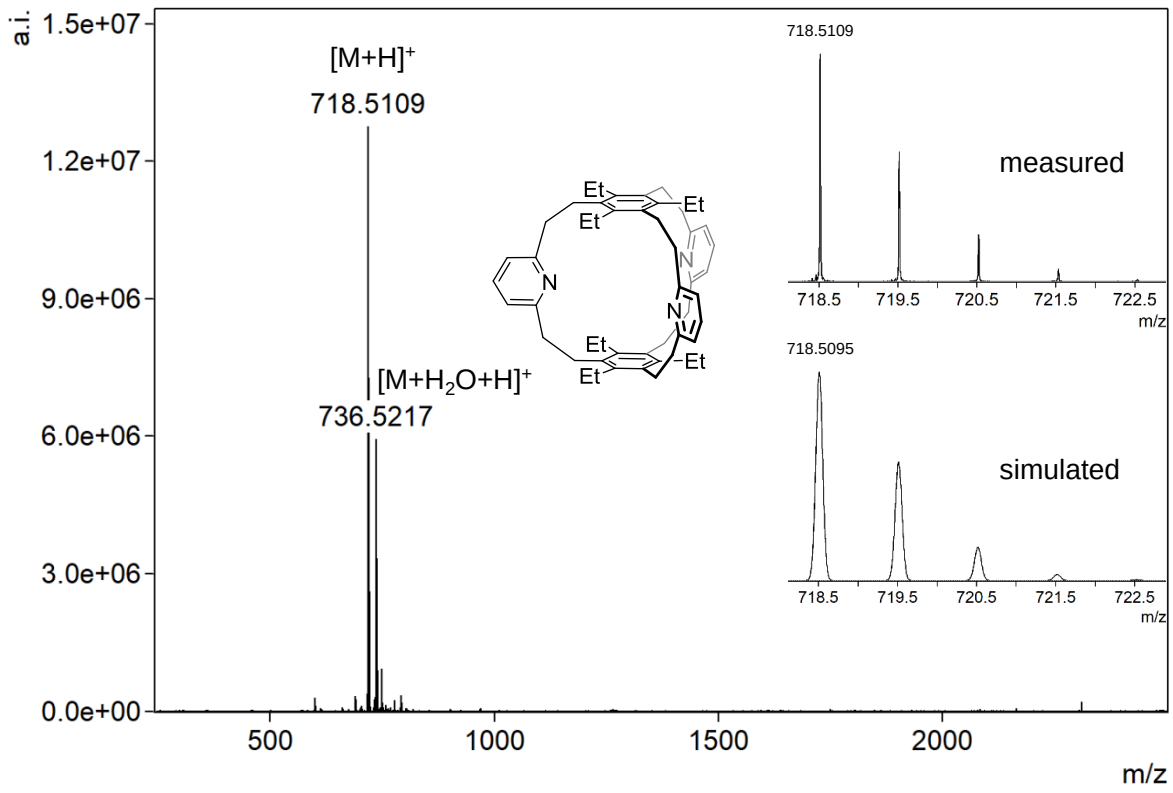


Figure S72: MALDI (DCTB+CsI) of compound **8b**.

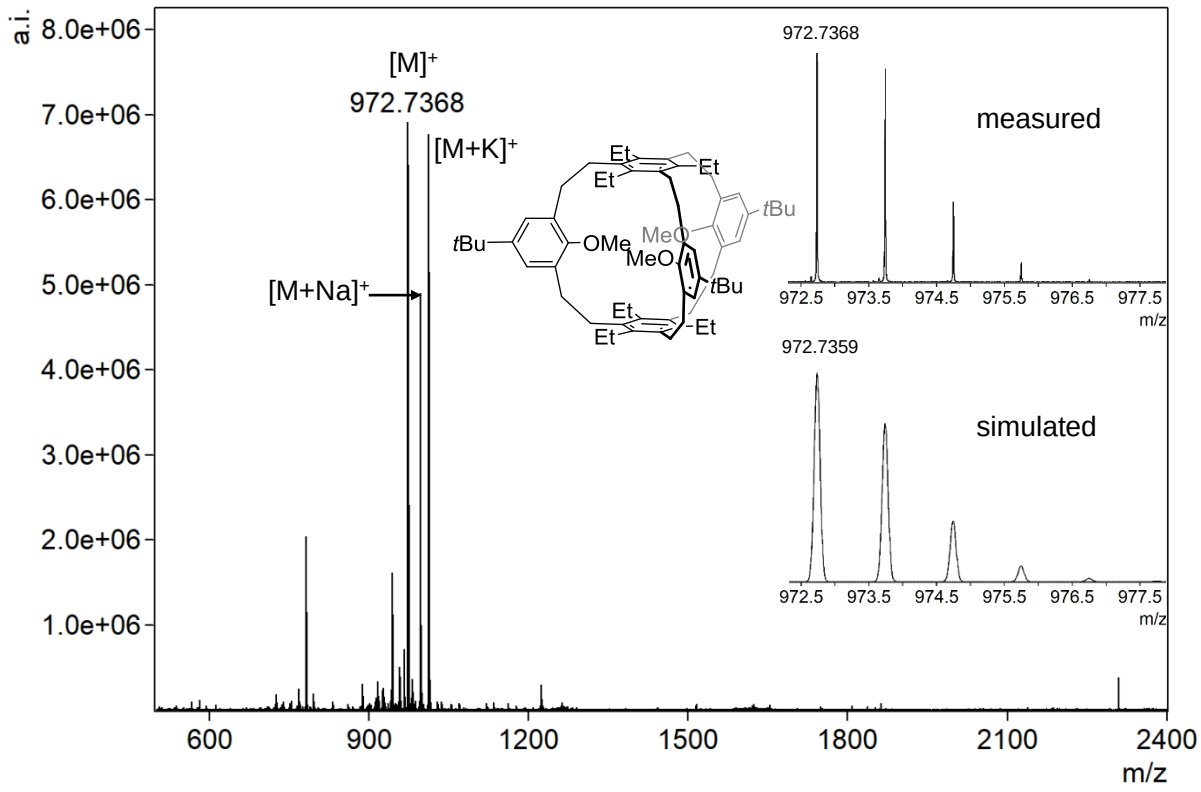


Figure S73: MALDI (DCTB) of compound **8c**.

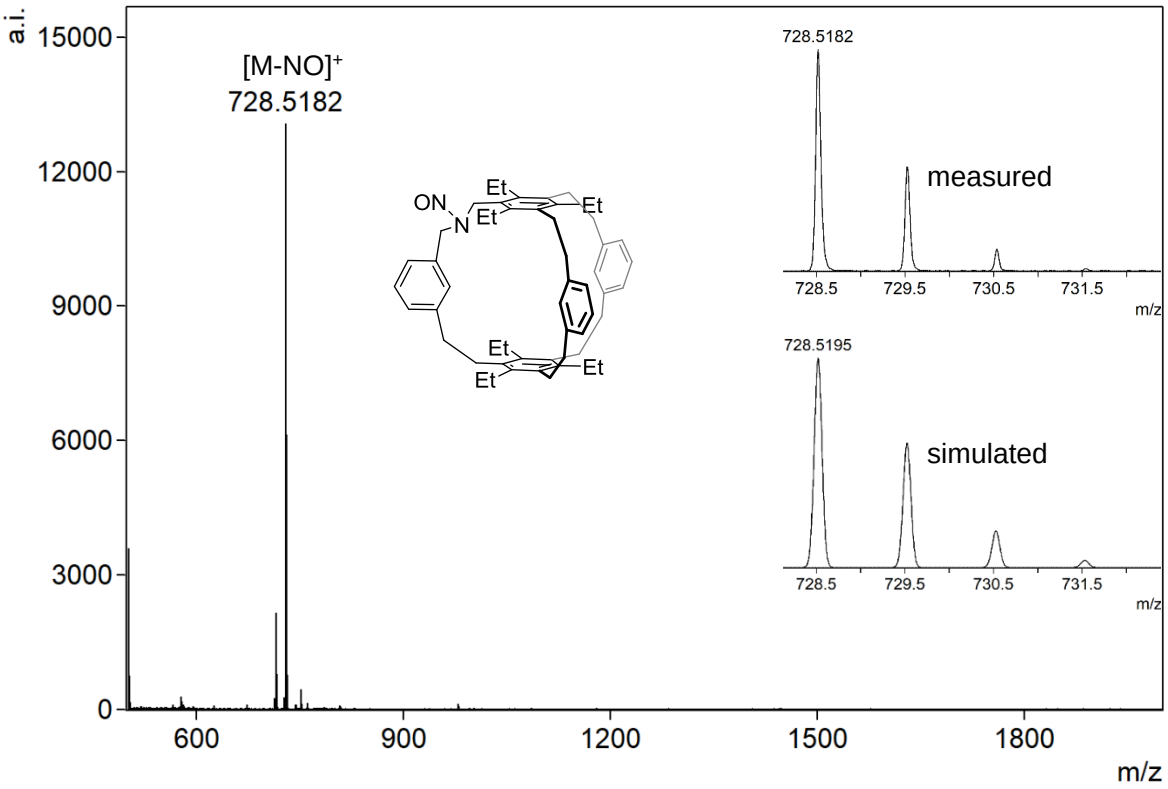


Figure S74: MALDI-TOF (DCTB) of compound **9**.

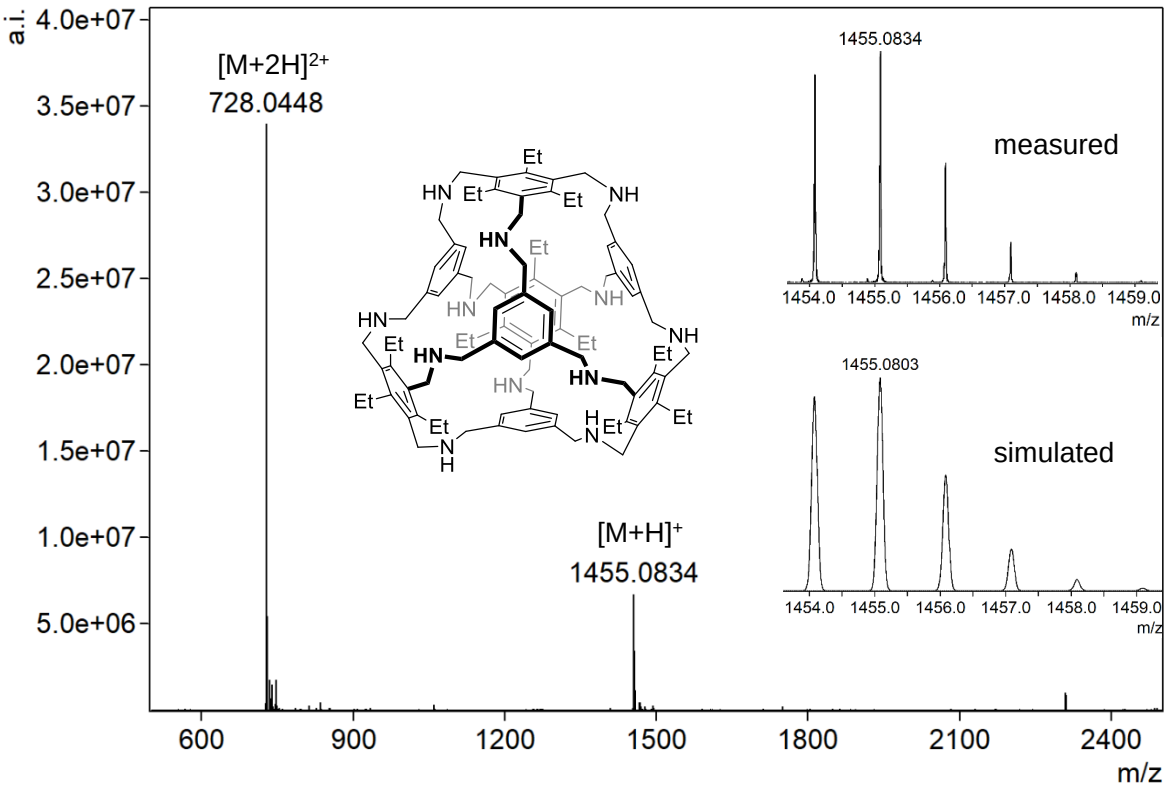


Figure S75: ESI (pos) of cage compound **11** in DCM/MeOH.

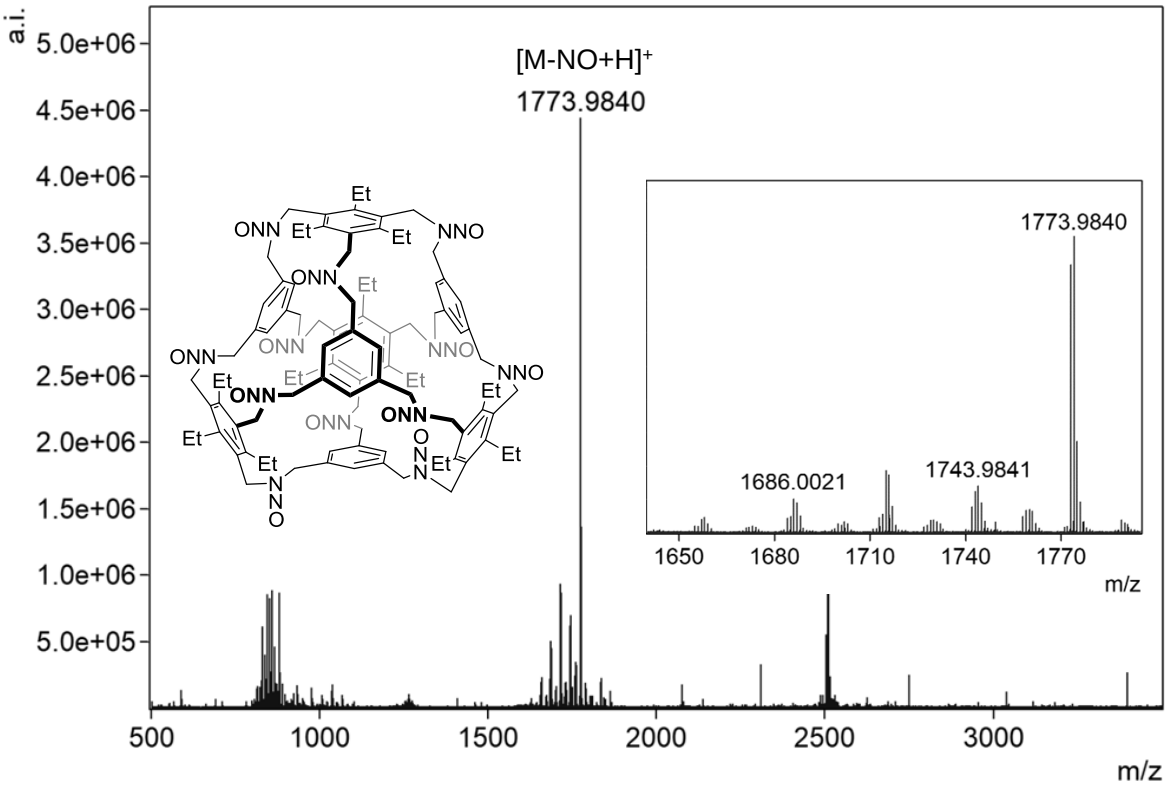


Figure S76: MALDI (DCTB) of cage compound **12**.

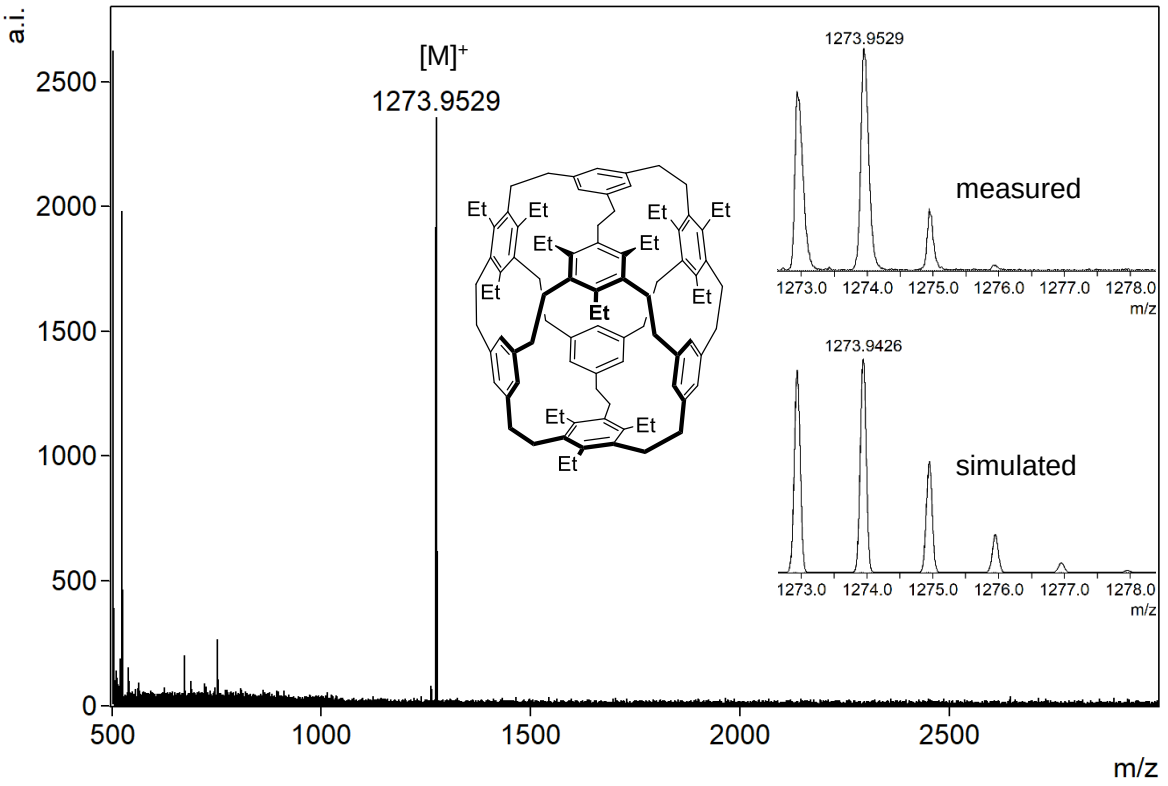


Figure S77: MALDI-TOF (DCTB) of cage compound **13**.

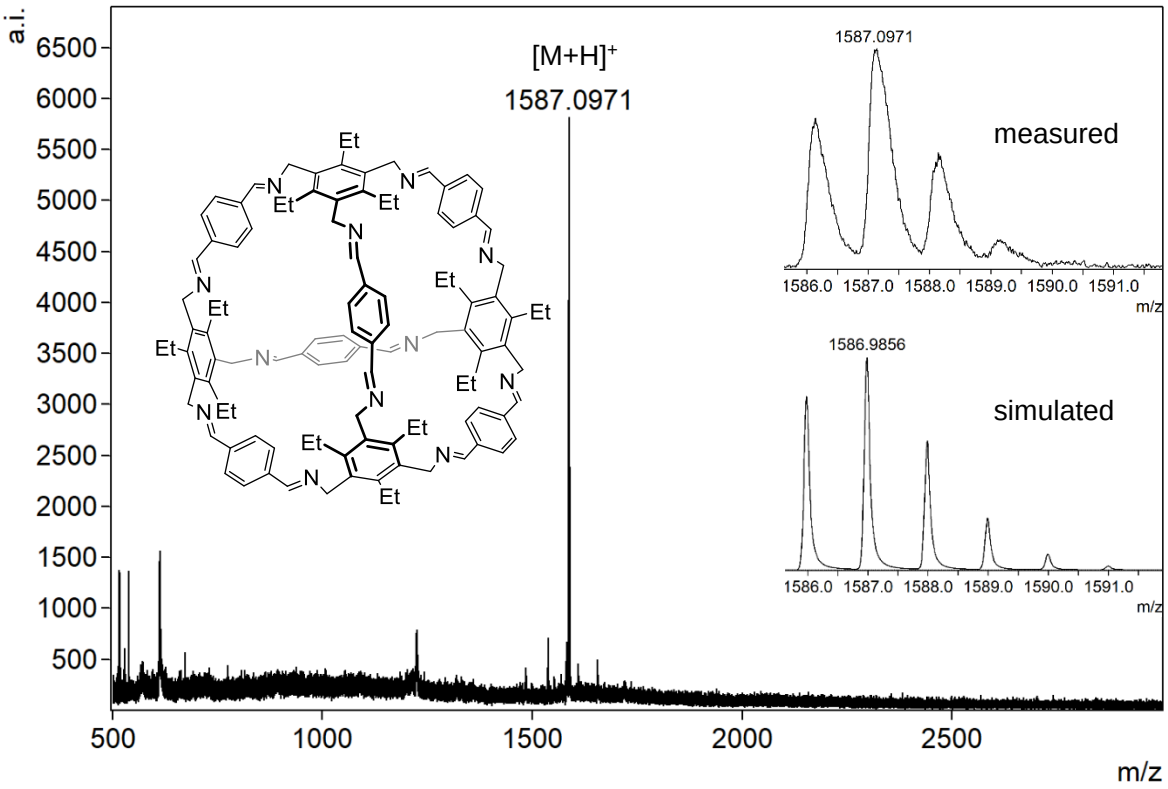


Figure S78: MALDI-TOF (DCTB) of compound **14**.

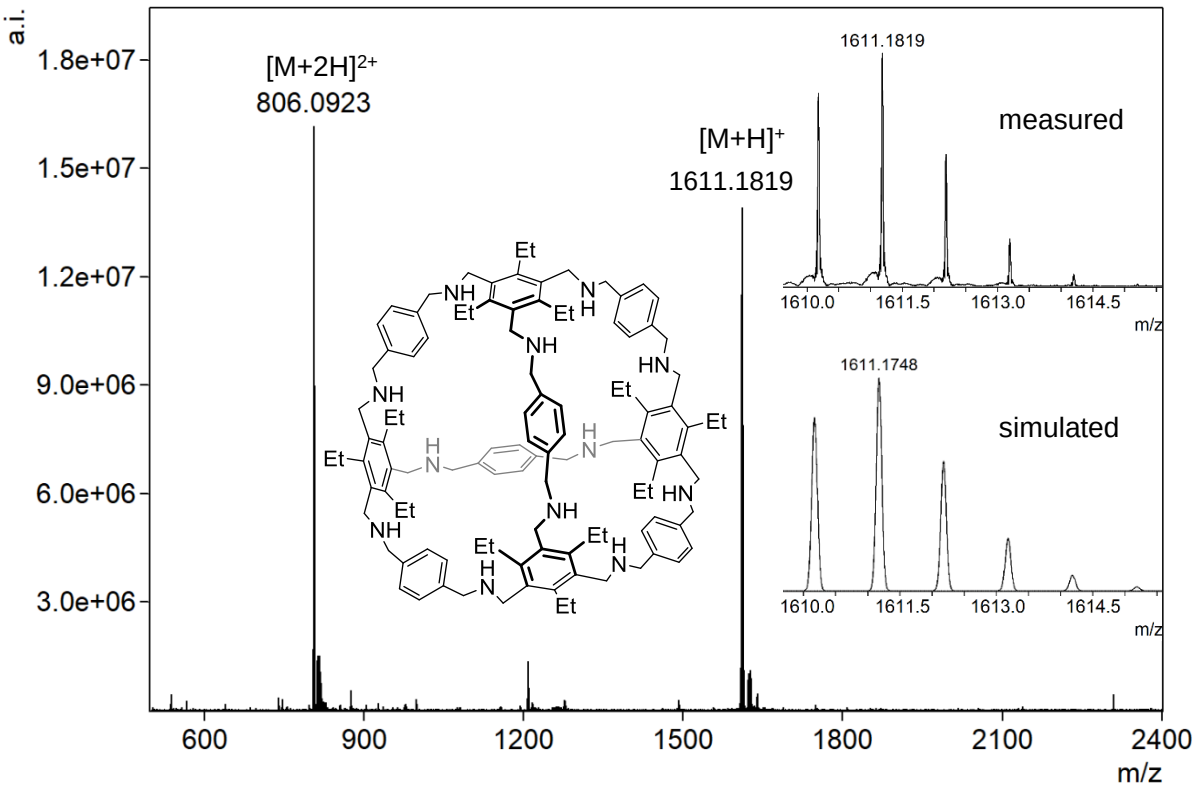


Figure S79: ESI (pos) of compound **15**.

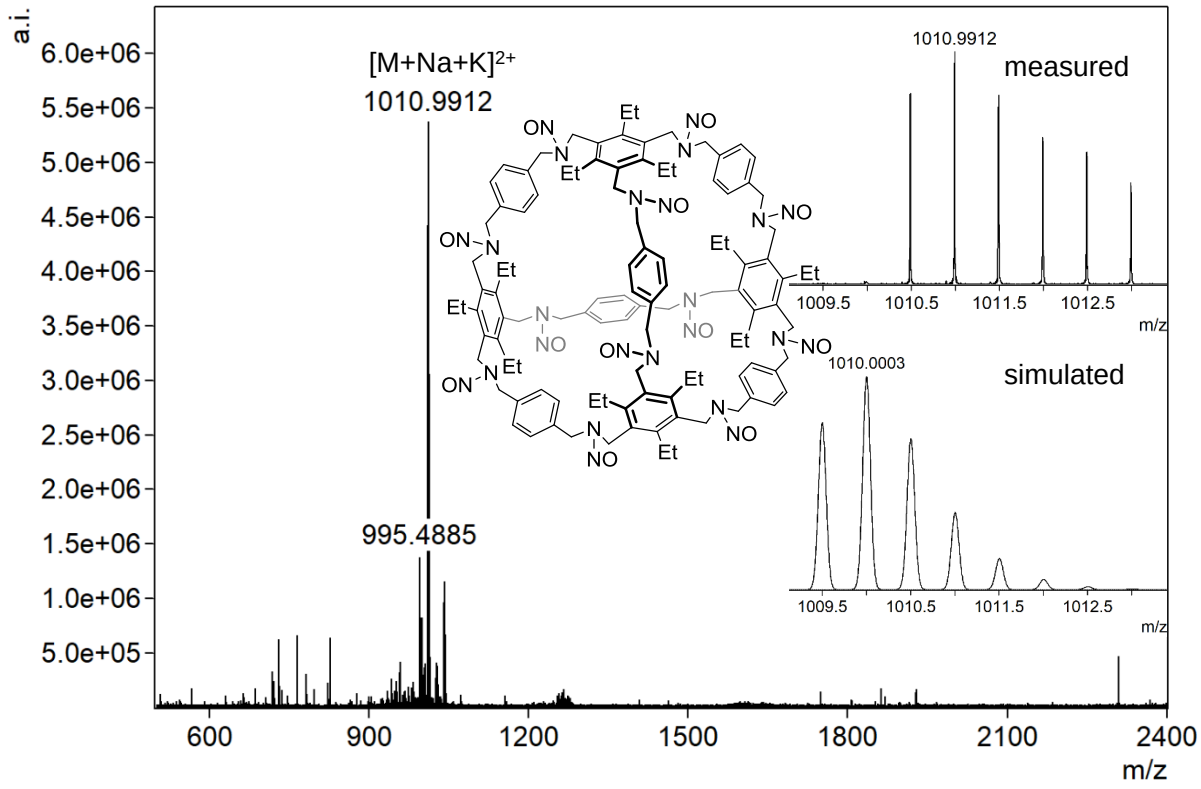


Figure S80: ESI (pos) of compound **16**.

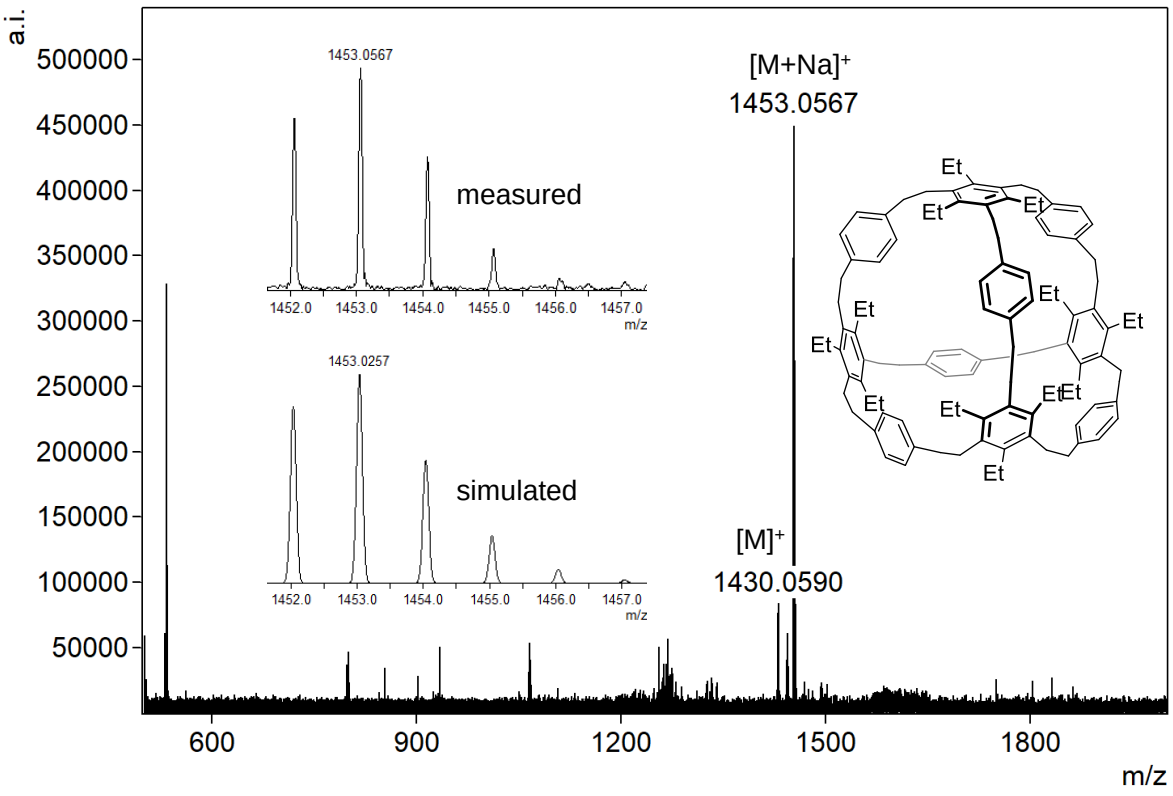


Figure S81: MALDI (DCTB+CsI) of compound **17**.

7 Infrared spectra

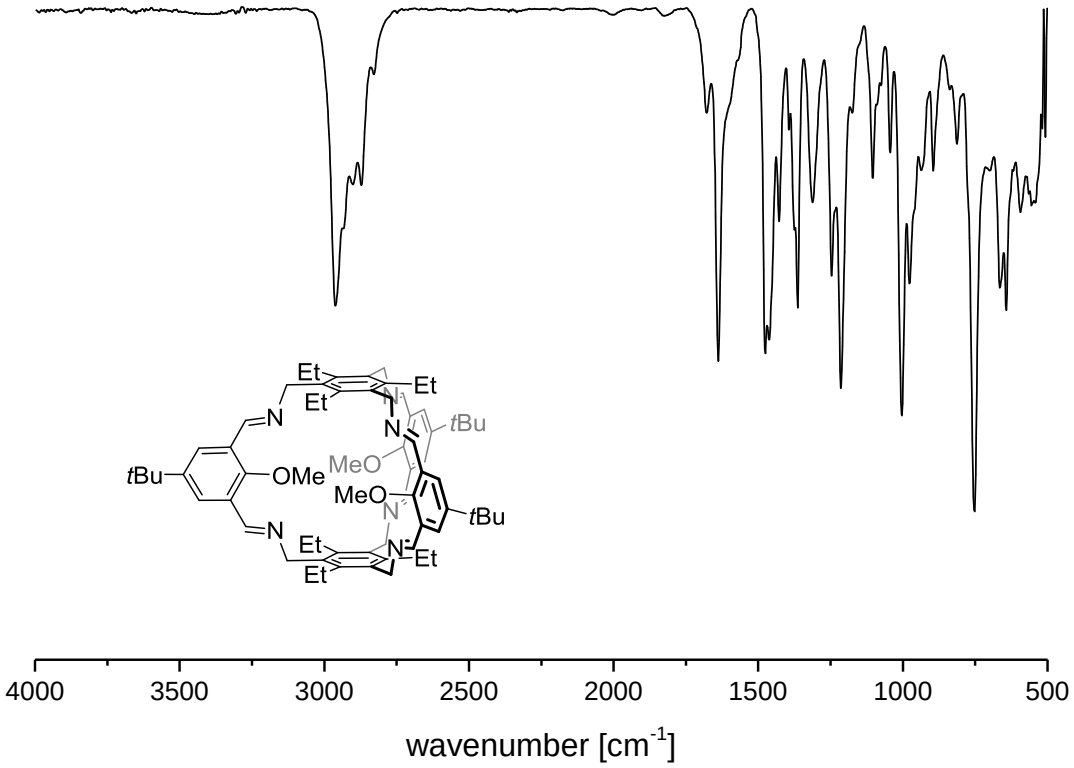


Figure S82: FTIR spectrum (ZnSe-ATR) of compound **5c**.

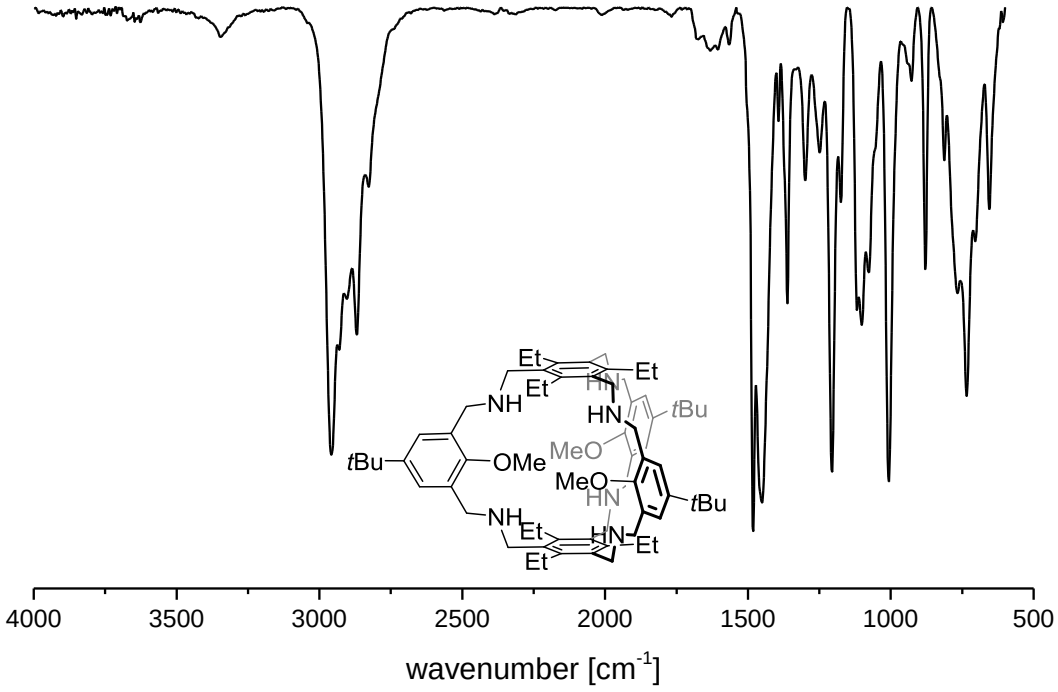


Figure S83: FTIR spectrum (ZnSe-ATR) of compound **6c**.

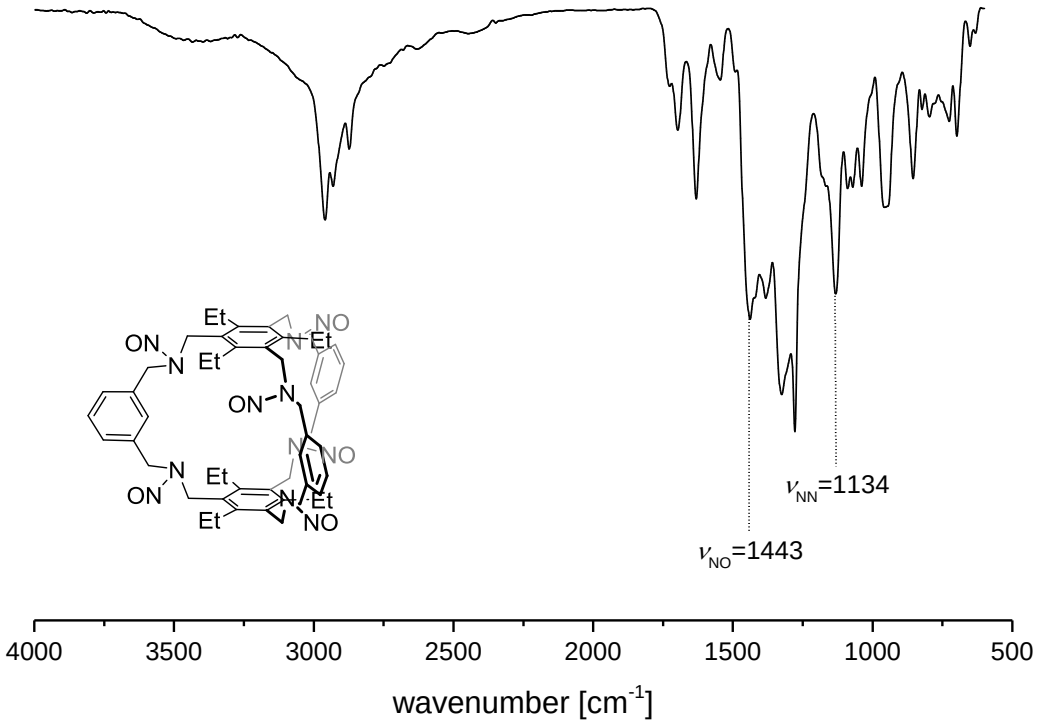


Figure S84: FTIR spectrum (ZnSe-ATR) of compound **7a.**

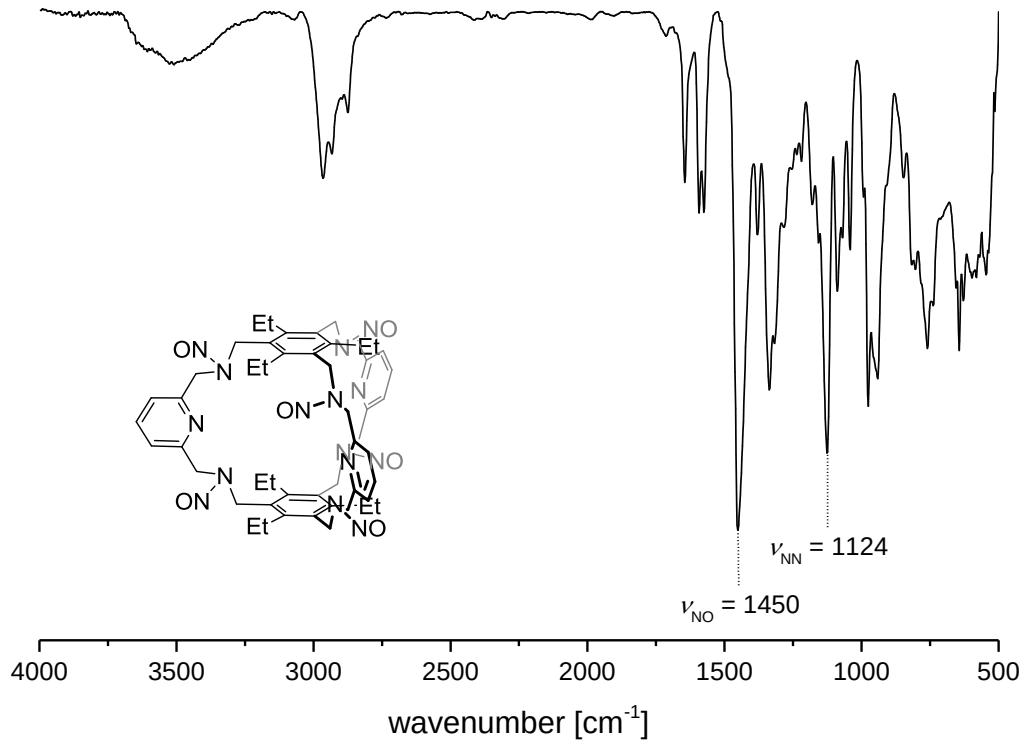


Figure S85: FTIR spectrum (ZnSe-ATR) of compound **7b**.

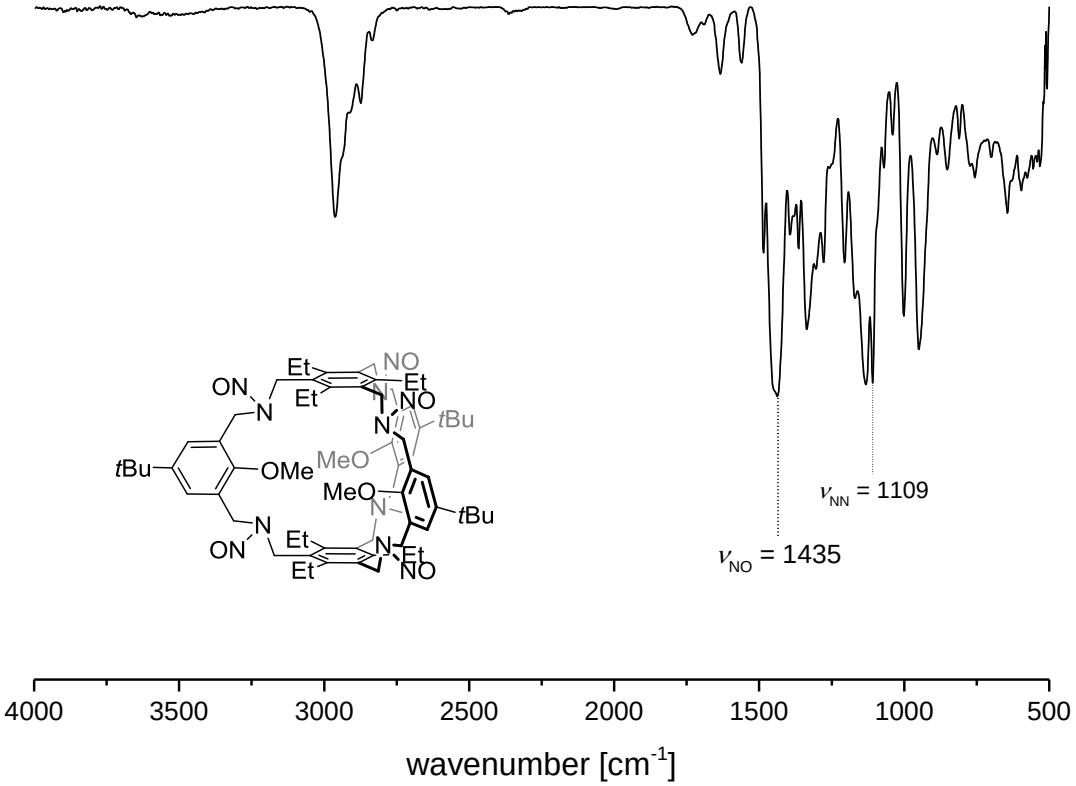


Figure S86: FTIR spectrum (ZnSe-ATR) of compound **7c**.

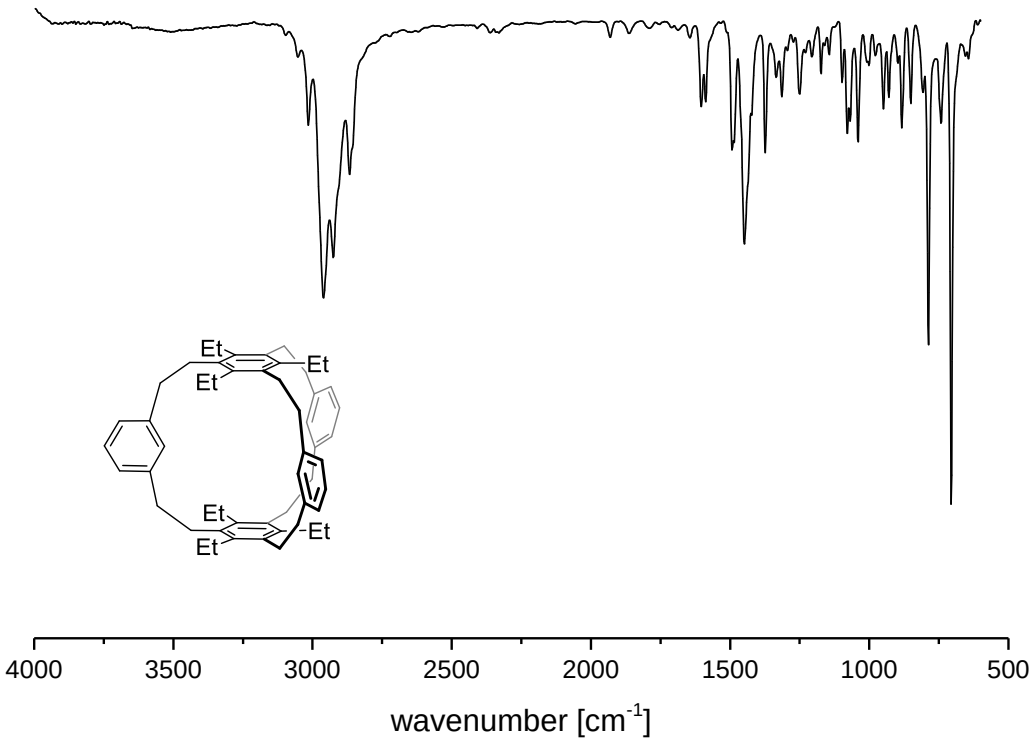


Figure S87: FTIR spectrum (ZnSe-ATR) of compound **8a**.

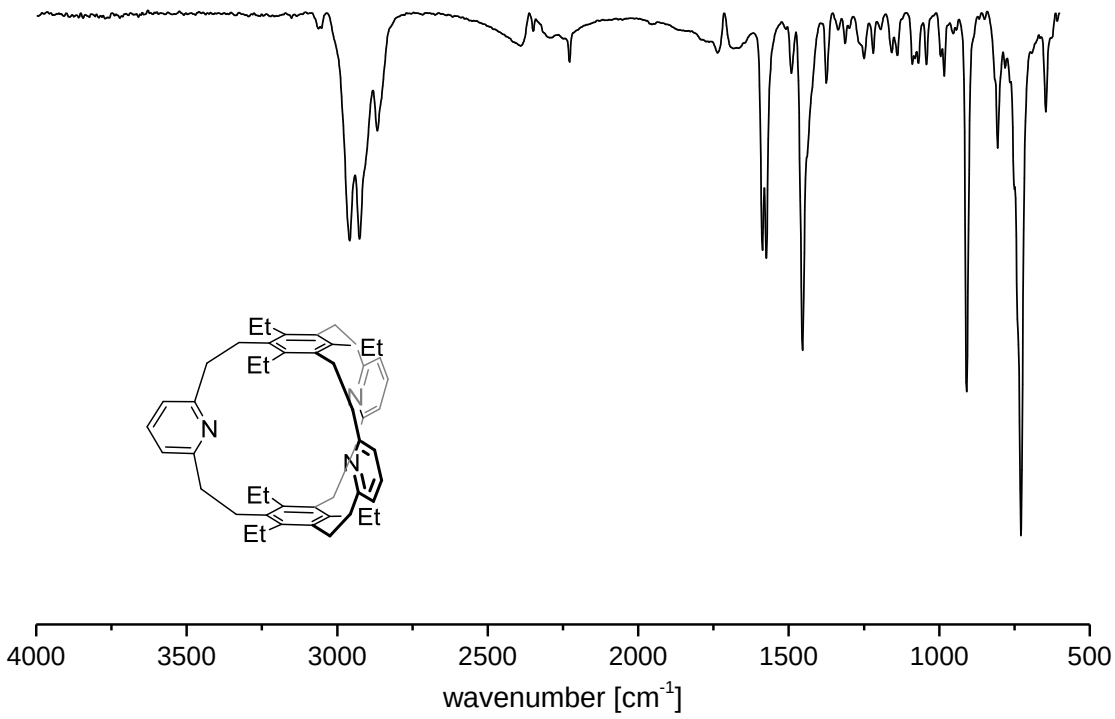


Figure S88: FTIR spectrum (ZnSe-ATR) of compound **8b.**

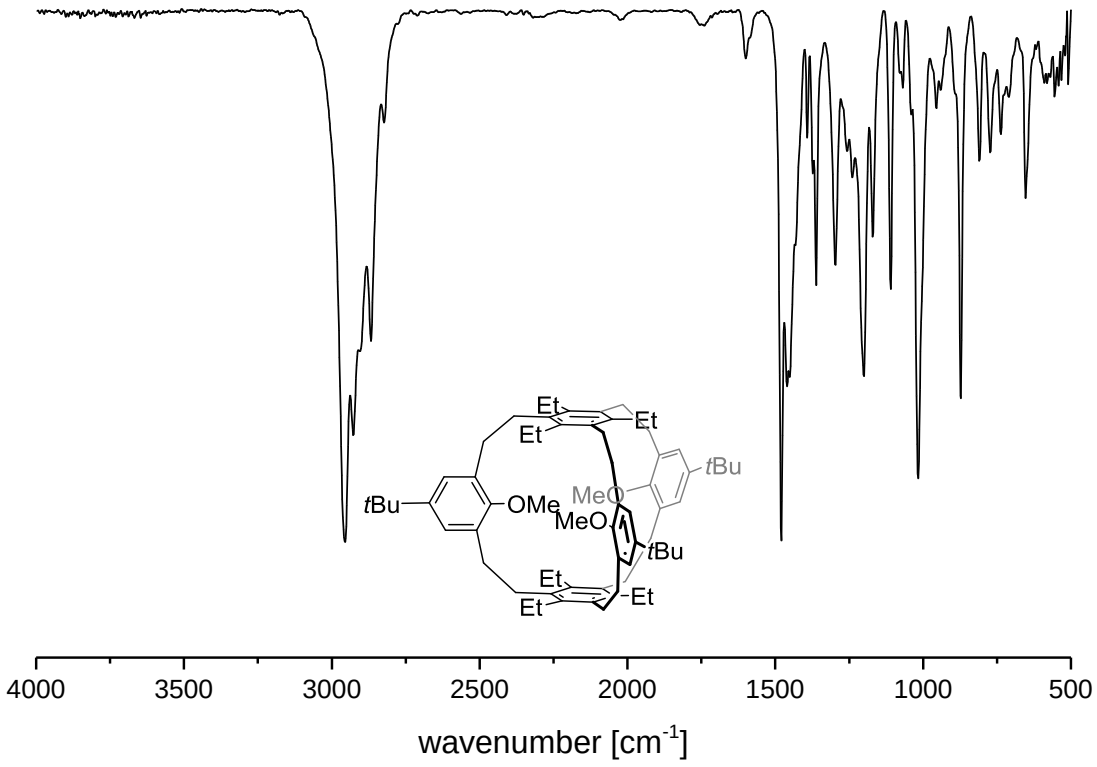


Figure S89: FTIR spectrum (ZnSe-ATR) of compound **8c**.

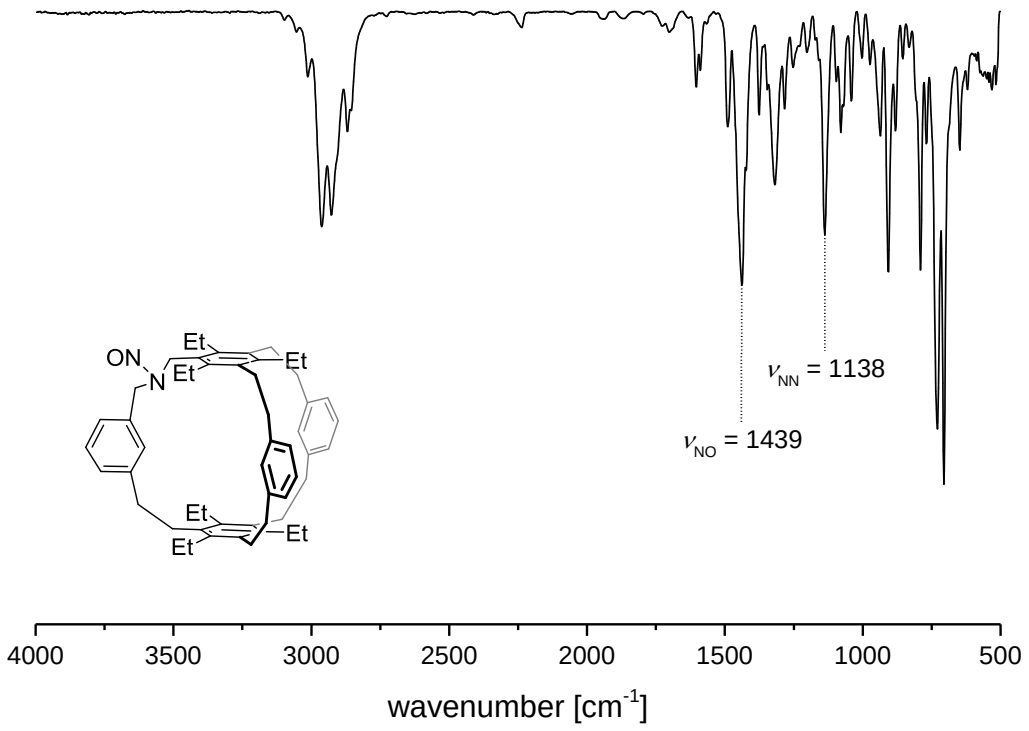


Figure S90: FTIR spectrum (ZnSe-ATR) of compound **9**.

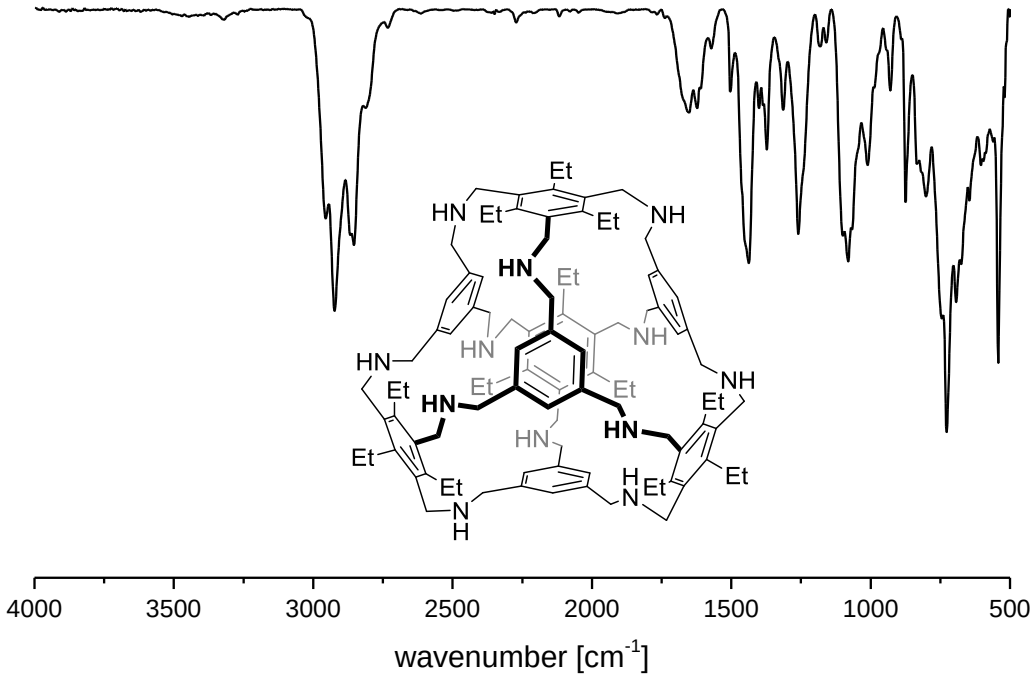


Figure S91: IR spectrum (ATR) of cage compound **11**.

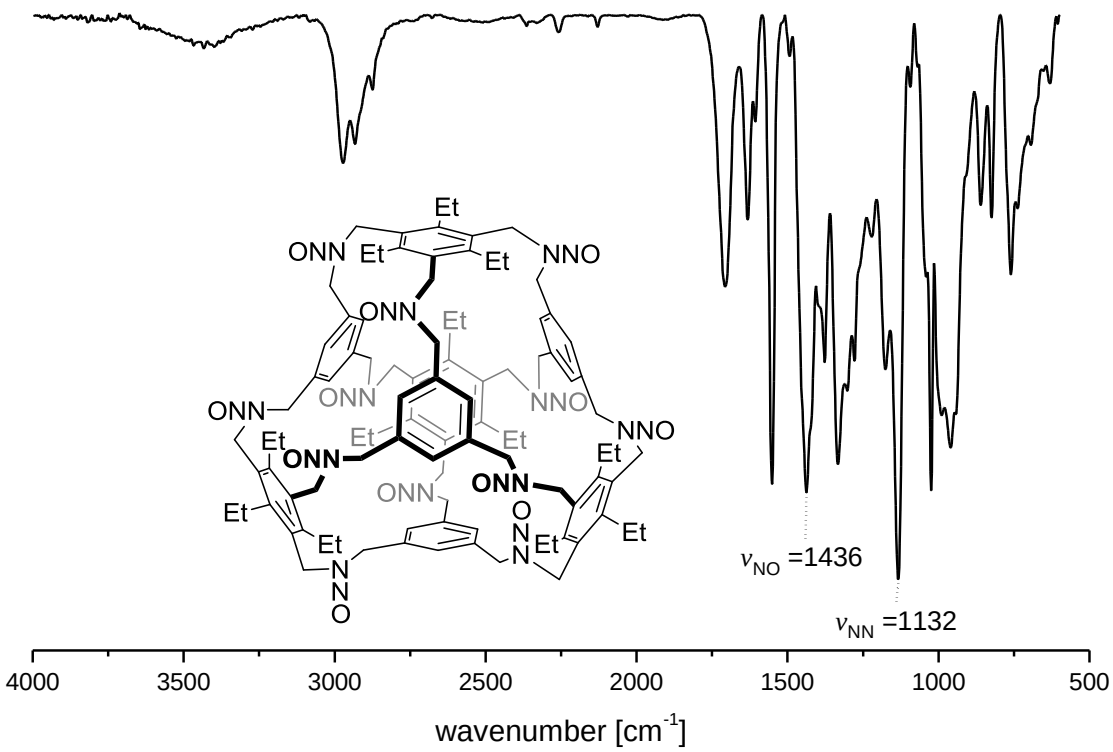


Figure S92: IR spectrum (ATR) of cage compound **12**.

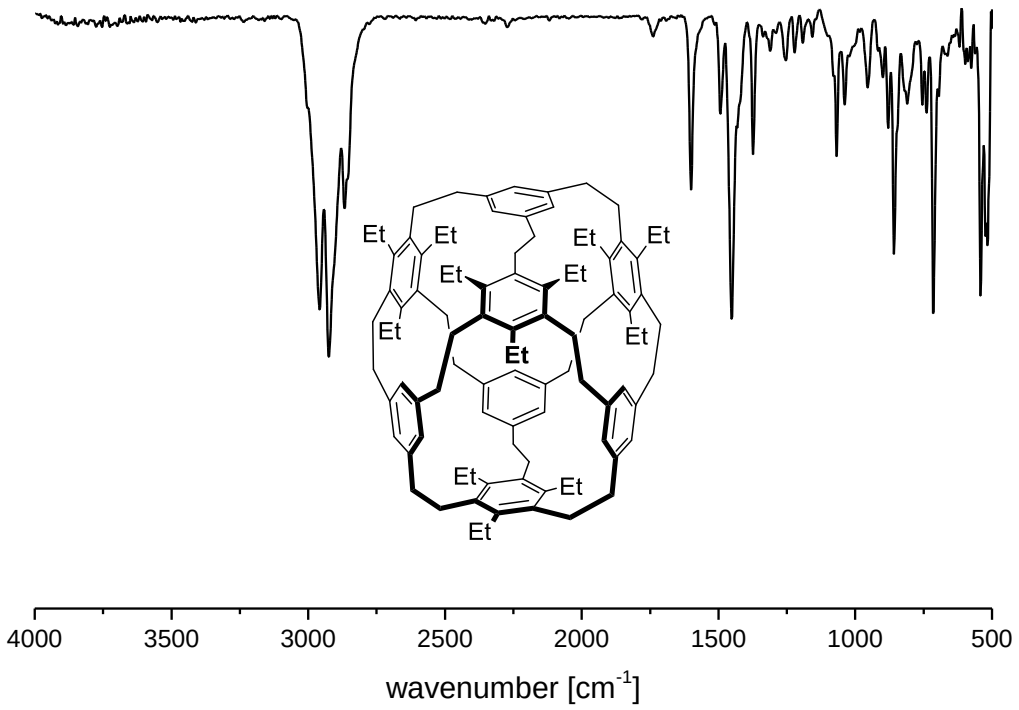


Figure S93: IR spectrum (ATR) of cage compound **13**.

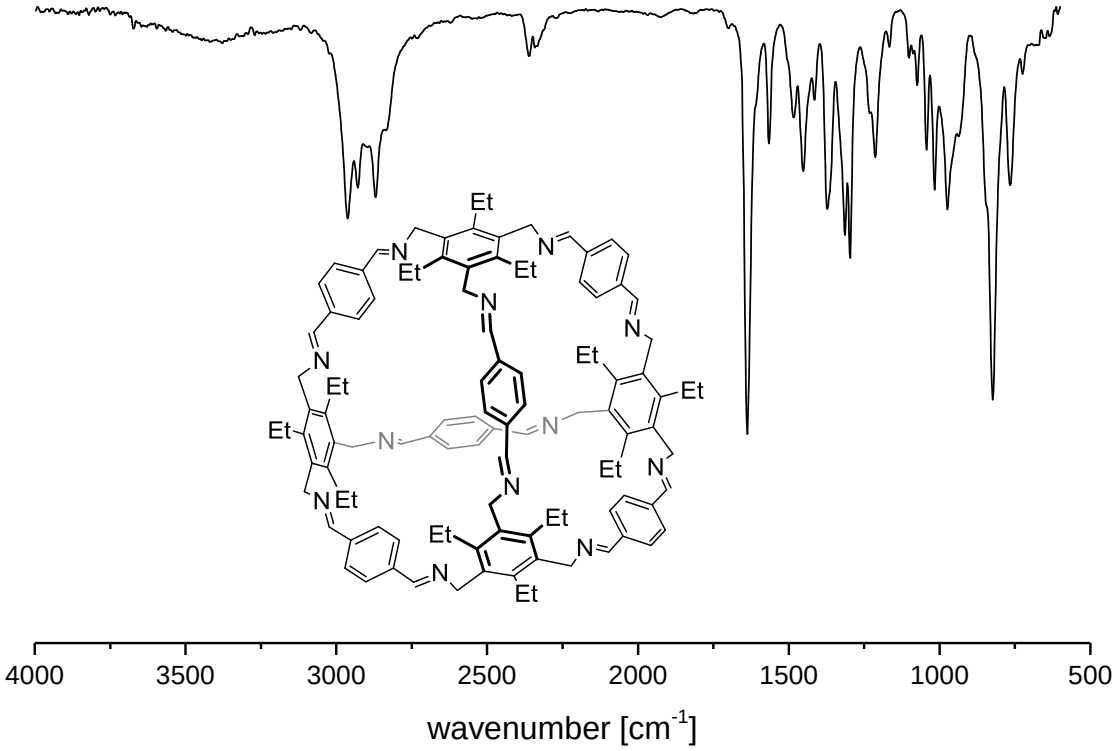


Figure S94: FTIR spectrum (ZnSe-ATR) of compound **14**.

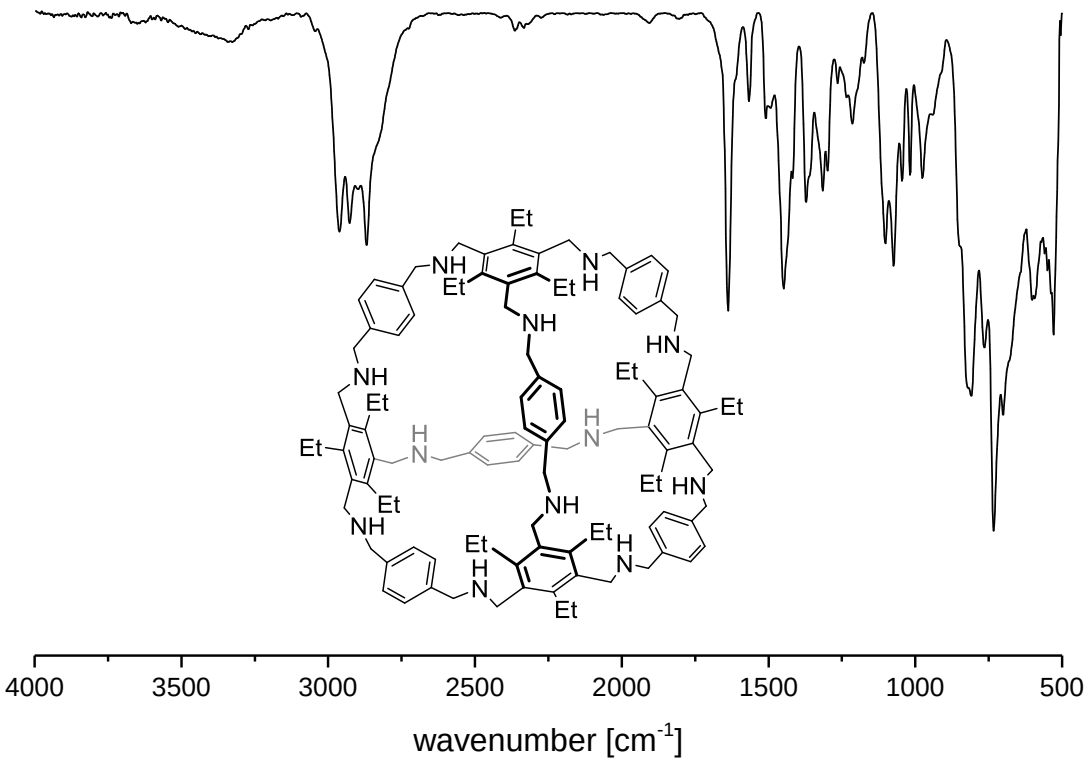


Figure S95: FTIR spectrum (ZnSe-ATR) of compound **15**.

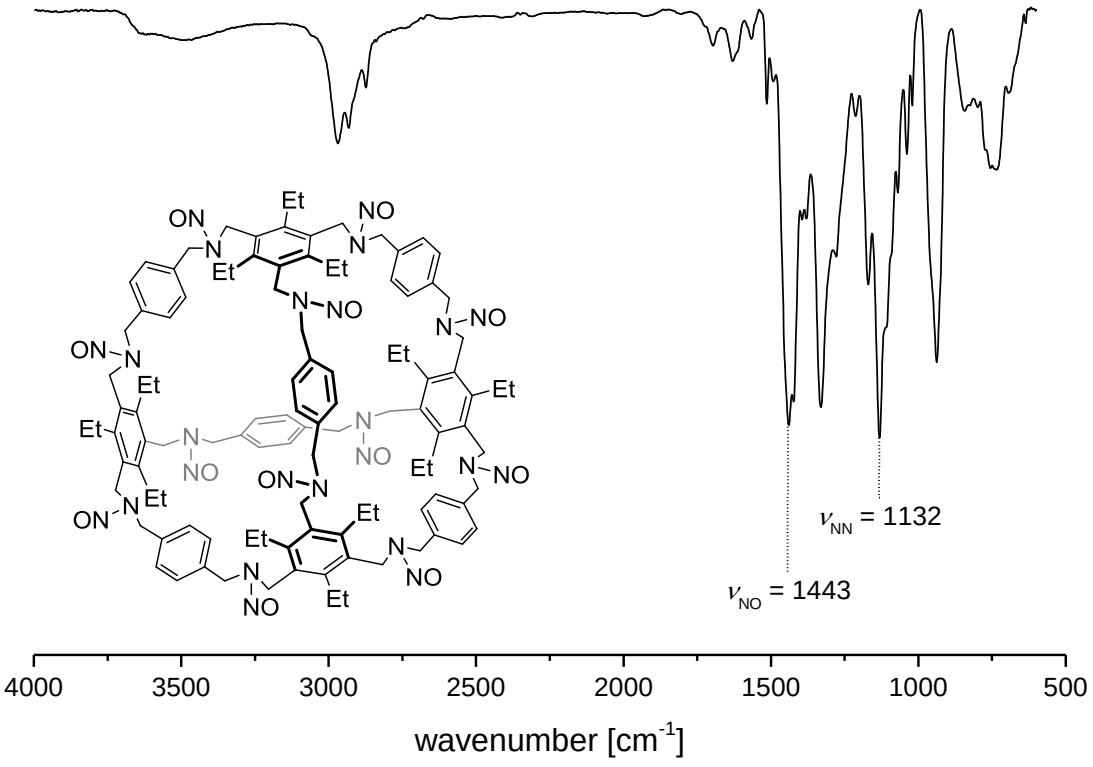


Figure S96: FTIR spectrum (ZnSe-ATR) of compound **16**.

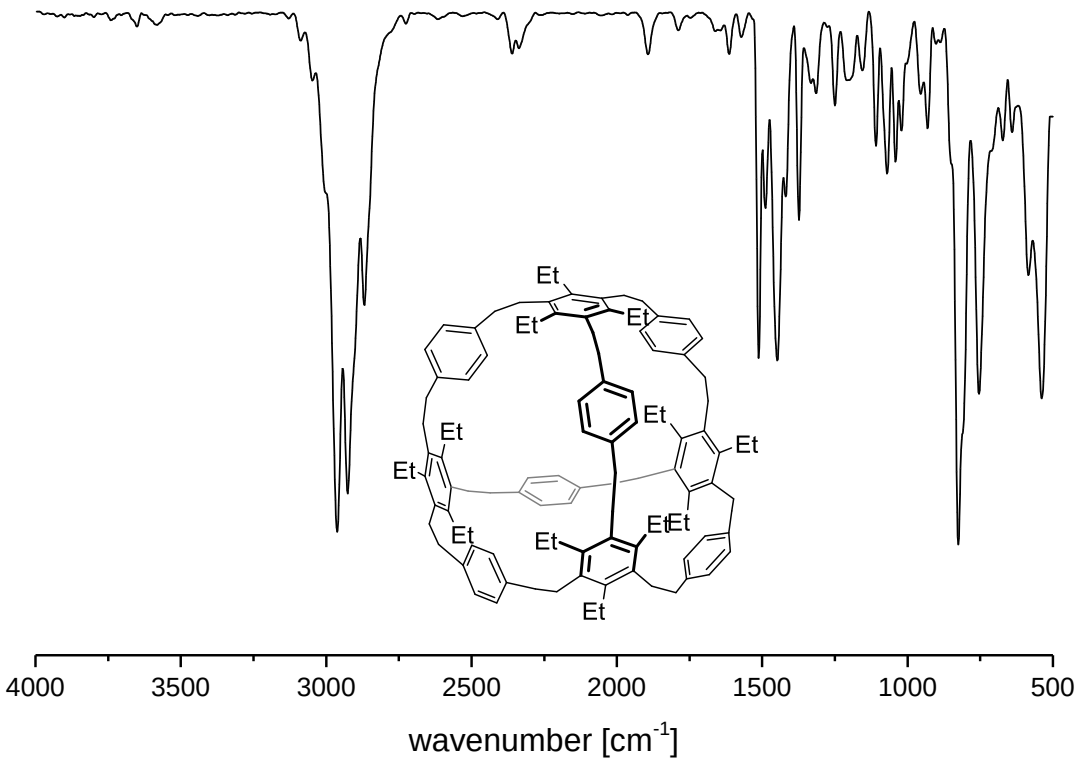


Figure S97: FTIR spectrum (ZnSe-ATR) of compound **17**.

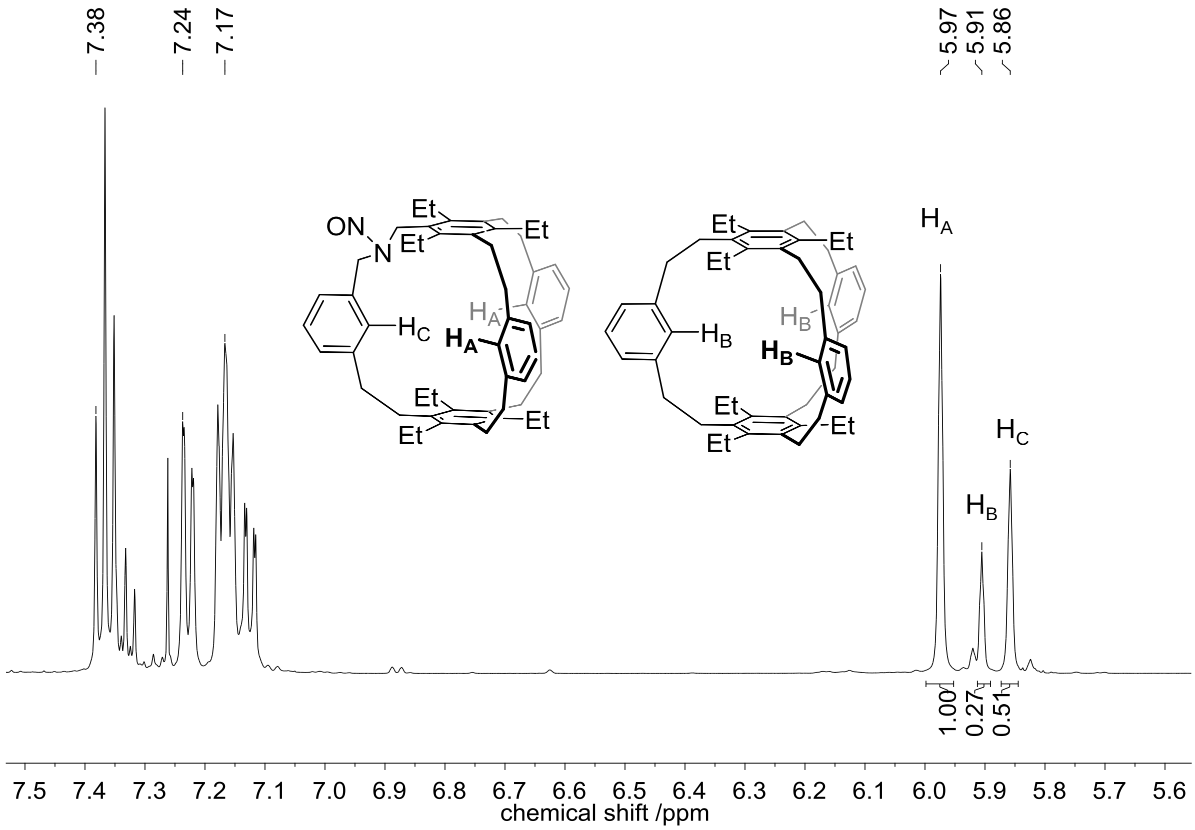


Figure S98: zoomed in section of the [1]H NMR spectrum (500 MHz, $CDCl_3$) of the crude product of the reaction of cage **9** under Overberger conditions. The estimated ratio of **8a**:**9** is 22:78)

8 Single-Crystal X-ray Diffraction Data

Crystal structure of cage compound 5a

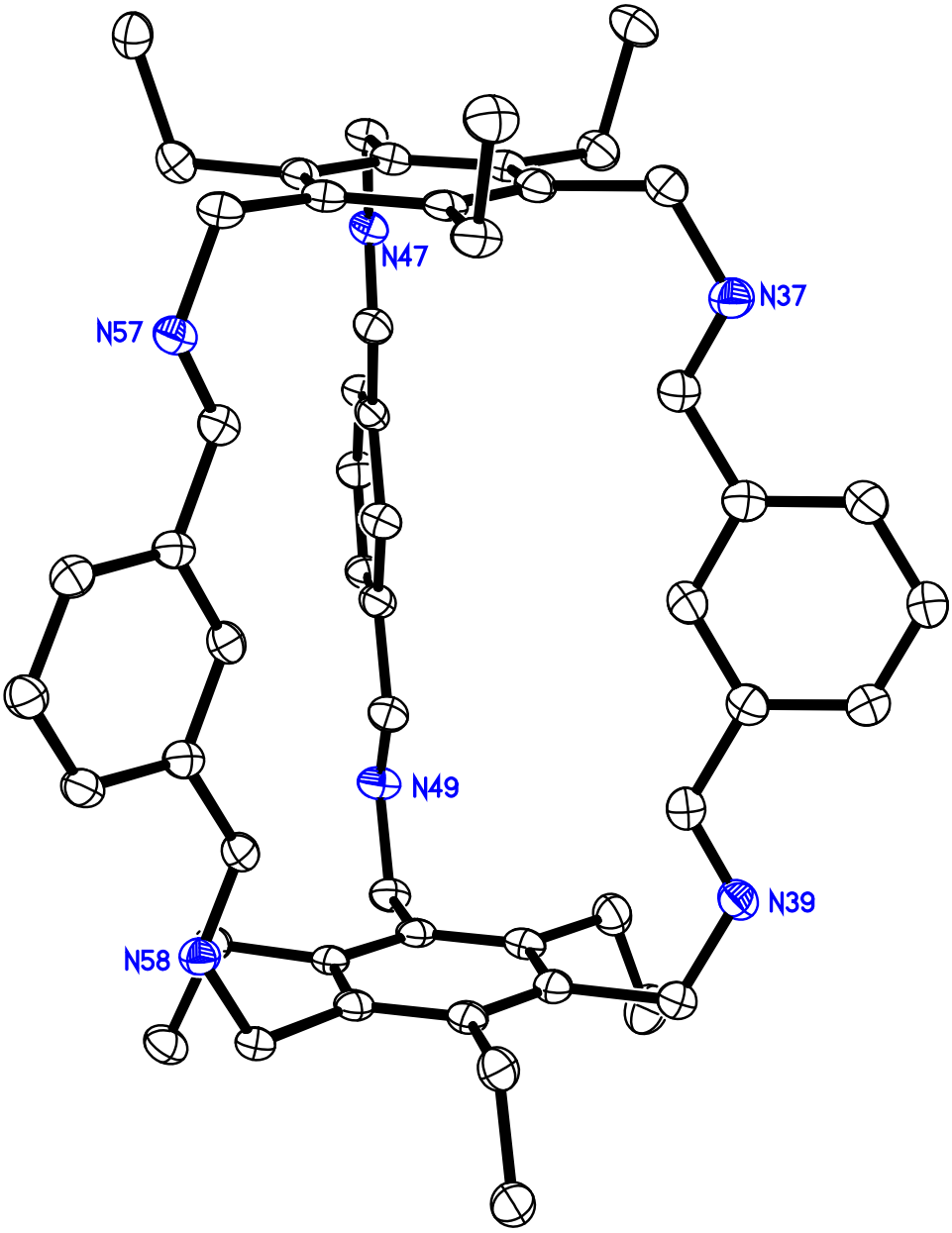


Figure S98: Crystal structure of compound **5a**. Atoms of carbon are depicted in white and nitrogen in blue.

Crystals were obtained by slow evaporation of chloroform.

CCDC-number : 1858593

Table S2: Crystal data and structure refinement for **5a**.

Empirical formula	$C_{29.50}H_{32.50}Cl_{7.50}N_3$	
Formula weight	694.96	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	triklin	
Space group	P $\bar{1}$	
Z	4	
Unit cell dimensions	a = 14.929(2) Å	α =69.451(11) °
	b = 15.988(2) Å	β =77.315(11) °
	c = 16.204(2) Å	γ =65.317(11) °
Volume	3278.4(9) $Å^3$	
Density (calculated)	1.408 g/cm^3	
Absorption coefficient μ	6.100 mm^{-1}	
Crystal shape	plate	
Crystal size	0.195 x 0.099 x 0.072 mm^3	
Crystal colour	colourless	
Theta range for data collection	2.923 bis 68.353 °	
Index ranges	-17≤h≤17, -10≤k≤19, -19≤l≤19	
Reflections collected	38982	
Independent reflections	11585 (R(int) = 0.0421)	
Observed reflections	9624 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	2.46 and 0.47	
Refinement method	Full-matrix least-squares an F^2	
Daten/Restraints/Parameter	11585 / 954 / 818	
Goodness-of-fit on F^2	1.02	
Final R indices (I>2sigma(I))	R1 = 0.053, wR2 = 0.132	
Largest diff. peak and hole	1.66 und -0.63 $eÅ^{-3}$	

IUCr's Checkcif provided no level A error and one level B error

Alert level B

PLAT221_ALERT_2_B

Problem: Solv./Anion Resd 9 Cl Ueq(max)/Ueq(min) Range 10.0 Ratio

Author Response: This structure contains large amounts of mostly disordered solvent $CHCl_3$. It has been refined using rigid bon restraints (SHELX RIGU command) and similarity restraints (SHELX SIMU command). If such a disorder model covers not every possible position, orientation and motion of the solvent molecule (and this will be the rule, not the exception), the deviation between truth and model will be soaked up by the adps, leading to sometimes unrealistic adp patterns. Nevertheless such an imperfect model features much more information than the only alternative of squeezing all the solvent.

Crystal structure of cage compound 8a

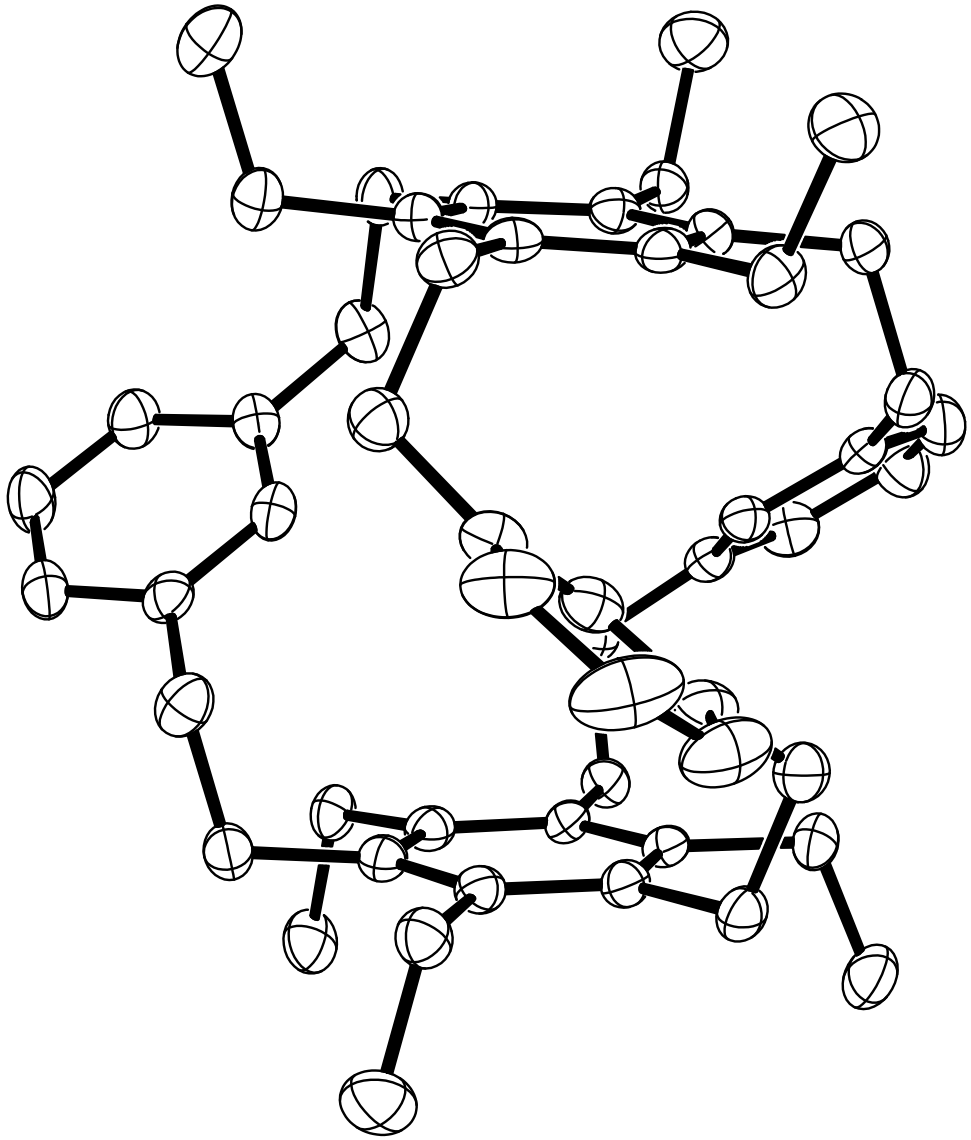


Figure S99: Molecular structure of cage compound **8a** as determined by X-ray diffraction. Atoms of carbon are depicted in white.

Crystals were obtained by slow diffusion of methanol in a chloroform solution of the compound (MeOH:$CHCl_3$ = 1:1).

CCDC-number : 1858594

Table S3: Crystal data and structure refinement for **8a**.

Empirical formula	$C_{55}H_{67}Cl_3$	
Formula weight	834.43	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	triklin	
Space group	P $\bar{1}$	
Z	2	
Unit cell dimensions	a = 12.6309(7) Å	α =72.1893(14) °
	b = 12.6358(7) Å	β =73.8971(14) °
	c = 16.3835(9) Å	γ =72.0826(15) °
Volume	2319.8(2) $Å^3$	
Density (calculated)	1.195 g/cm^3	
Absorption coefficient μ	0.233 mm^{-1}	
Crystal shape	little	
Crystal size	0.183 x 0.133 x 0.119 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.730 bis 25.059 °	
Index ranges	-15≤h≤15, -15≤k≤15, -19≤l≤19	
Reflections collected	29551	
Independent reflections	8193 (R(int) = 0.0644)	
Observed reflections	4711 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.90	
Refinement method	Full-matrix least-squares an F^2	
Data/restraints/parameters	8193 / 0 / 529	
Goodness-of-fit on F^2	1.01	
Final R indices (I>2sigma(I))	R1 = 0.054, wR2 = 0.108	
Largest diff. peak and hole	0.26 und -0.43 $eÅ^{-3}$	

IUCr's Checkcif provided no level A error and no level B error

Crystal structure of cage compound 8b

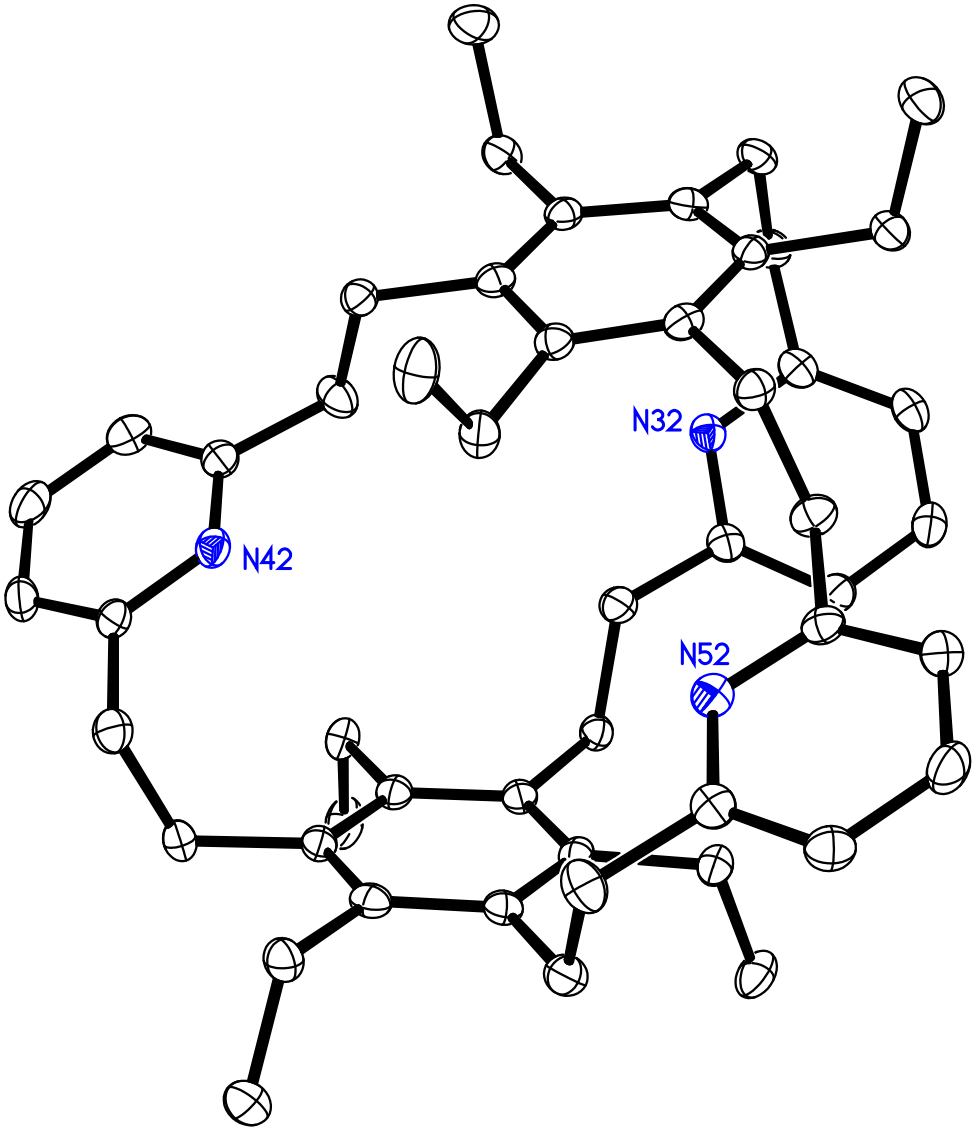


Figure S100: Molecular structure of cage compound **8b** as determined by X-ray diffraction. Atoms of carbon are depicted in white, nitrogen in blue.

Crystals were obtained by slow evaporation of chloroform.

CCDC-number : 1858596

Table S4: Crystal data and structure refinement for **8b**.

Empirical formula	$C_{52}H_{64}Cl_3N_3$	
Formula weight	296.96	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	orthorhombisch	
Space group	$P2_12_12_1$	
Z	4	
Unit cell dimensions	a =8.4676(10) Å	α = 90 °
	b = 21.994(3) Å	β = 90 °
	c = 24.053(4) Å	γ = 90 °
Volume	4479.5(11) $Å^3$	
Density (calculated)	0.440 g/cm^3	
Absorption coefficient μ	1.778 mm^{-1}	
Crystal shape	plank	
Crystal size	0.149 x 0.088 x 0.054 mm^3	
Crystal colour	colourless	
Theta range for data collection	2.722 bis 76.523 °	
Index ranges	-10≤h≤8, -25≤k≤27, -17≤l≤30	
Reflections collected	21810	
Independent reflections	8401 (R(int) = 0.0283)	
Observed reflections	7626 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.44 and 0.64	
Refinement method	Full-matrix least-squares an F^2	
Data/restraints/parameters	8401 / 0 / 530	
Goodness-of-fit on F^2	1.07	
Final R indices (I>2sigma(I))	R1 = 0.038, wR2 = 0.090	
Flack-parameter	0.143(16)	
Largest diff. peak and hole	0.46 und -0.41 $eÅ^{-3}$	

IUCr's Checkcif provided no level A error and no level B error

Crystal structure of cage compound 8c

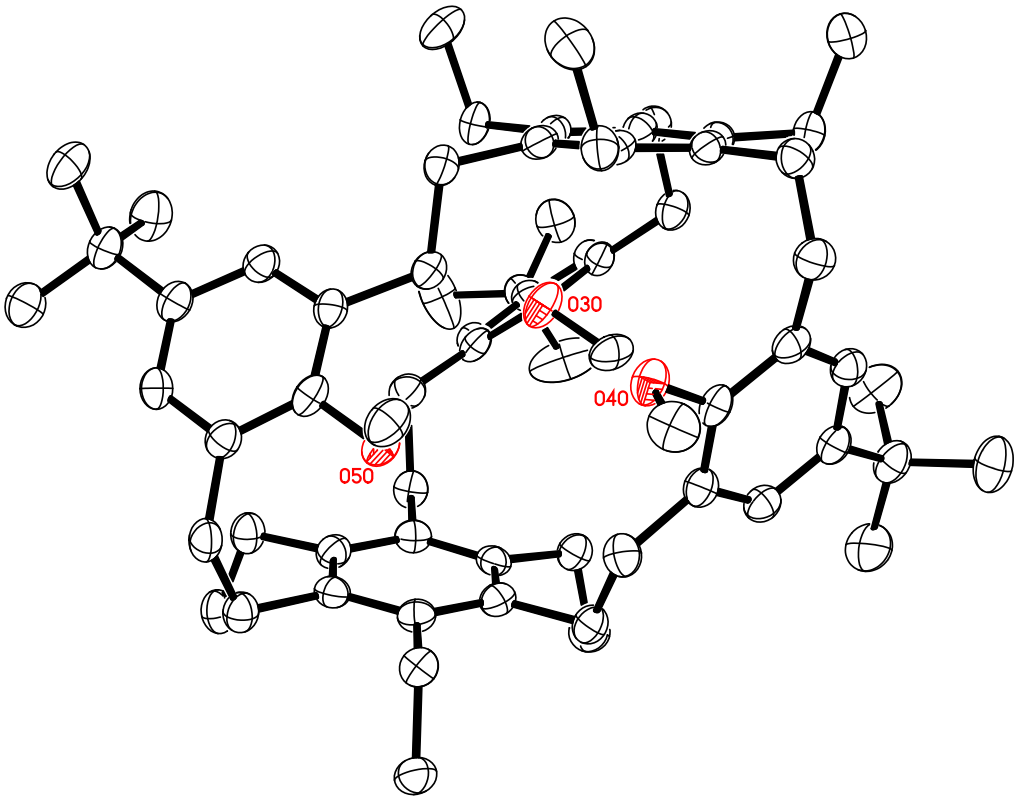


Figure S101: Molecular structure of cage compound **8c** as determined by X-ray diffraction. Atoms of carbon are depicted in white, oxygen in red.

Crystals were obtained by slow diffusion of methanol in a chloroform solution of the compound (MeOH:$CHCl_3$ = 5:1).

CCDC-number : 1858598

Table S5: Crystal data and structure refinement for **8c**.

Empirical formula	$C_{70}H_{97}Cl_3O_3$	
Formula weight	1092.82	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	monoklin	
Space group	P21/c	
Z	4	
Unit cell dimensions	a = 12.4459(4) Å	α = 90 °
	b = 13.5193(4) Å	β =93.333(3) °
	c = 37.1516(13) Å	γ = 90 °
Volume	6240.5(3) Å3	
Density (calculated)	1.163 g/cm3	
Absorption coefficient μ	1.666 mm-1	
Crystal shape	brick	
Crystal size	0.115 x 0.108 x 0.067 mm3	
Crystal colour	colourless	
Theta range for data collection	3.480 bis 68.309 °	
Index ranges	-14≤h≤13, -16≤k≤10, -40≤λ≤44	
Reflections collected	31200	
Independent reflections	10773 (R(int) = 0.0815)	
Absorption correction reflections	7085 (I > 2σ(I))	
Max. and min. transmission	Semi-empirical from equivalents	
Max. and min. transmission	1.90 and 0.52	
Refinement method	Full-matrix least-squares an F2	
Data/restraints/parameters	10773 / 60 / 740	
Goodness-of-fit on F2	1.08	
R Final R indices (I>2sigma(I))	R1 = 0.080, wR2 = 0.166	
Largest diff. peak and hole	0.31 und -0.27 eÅ-3	

IUCr's Checkcif provided no level A error and one level B error

Alert level B

PLAT029_ALERT_3_B

Problem: _diffrn_measured_fraction_theta_full value Low . 0.952 Why?

Author Response: This is the result of a well-planned data collection strategy with 100% completeness and fourfold redundancy. However, with copper radiation, due to the wide spread diffraction pattern, depending on the crystal orientation, the goniometer type and the detector characteristics, sometimes full completeness in outer shells is difficult to reach. Furthermore, there is always a small percentage of the reflections that are indeed measured, but do not fulfil the criteria for a successful integration or have to be omitted in the scaling process. These missing few percent are not critical, neither for the data to parameter ratio nor the reliability or correctness or accuracy of the structure model.

Crystal structure of cage compound 9

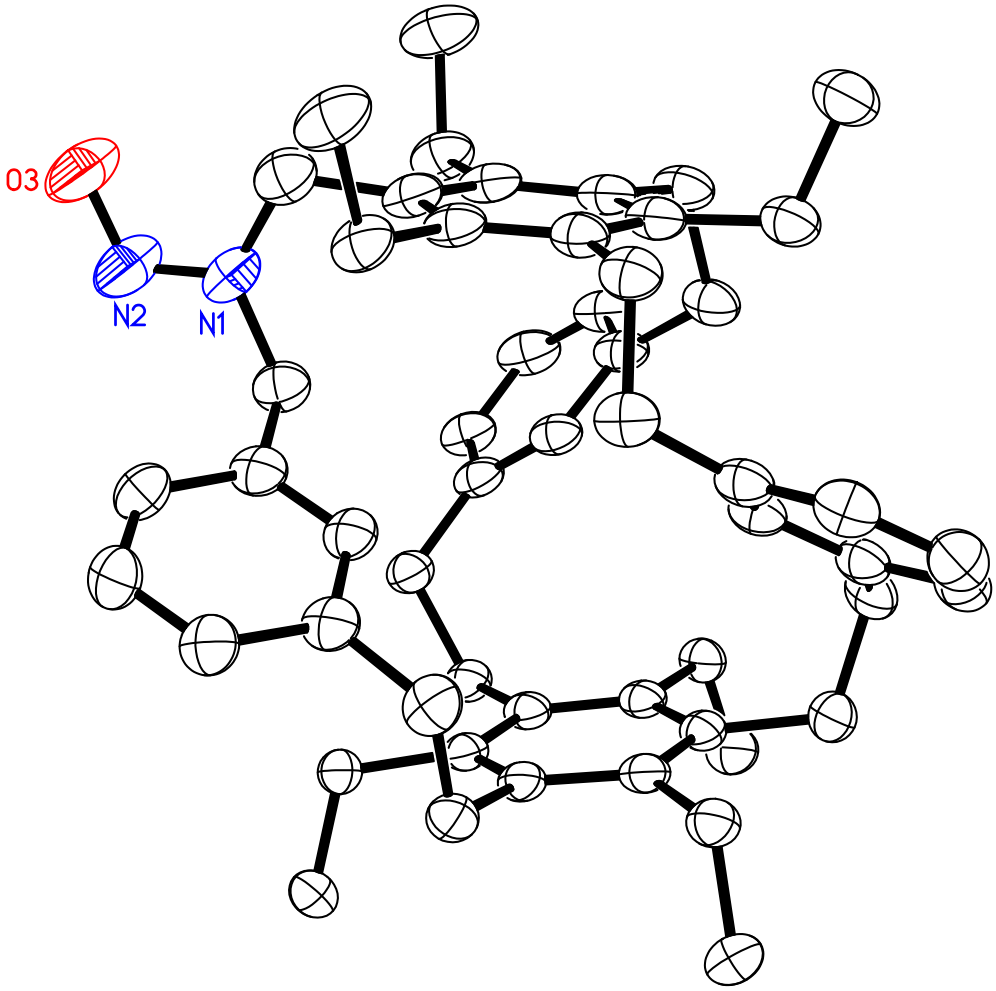


Figure S102: Molecular structure of cage compound **9** as determined by X-ray diffraction. Atoms of carbon are depicted in white, oxygen in red, nitrogen in blue.

Crystals were obtained by slow diffusion of methanol in a chloroform solution of the compound (MeOH:$CHCl_3$ = 1:1).

CCDC-number : 1858595

Table S6:Crystal data and structure refinement for **9**.

Empirical formula	$C_{55}H_{67}Cl_3N_2O$	
Formula weight	878.45	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	monoklin	
Space group	$P2_1/n$	
Z	4	
Unit cell dimensions	a = 13.9522(5) Å	α = 90 °
	b = 16.1430(7) Å	β =102.015(3) °
	c = 21.6831(7) Å	γ = 90 °
Volume	4776.7(3) $Å^3$	
Density (calculated)	1.222 g/cm^3	
Absorption coefficient μ	2.040 mm^{-1}	
Crystal shape	brick	
Crystal size	0.102 x 0.070 x 0.066 mm^3	
Crystal colour	colourless	
Theta range for data collection	3.441 bis 68.402 °	
Index ranges	-11≤h≤16, -19≤k≤17, -25≤l≤25	
Reflections collected	32750	
Independent reflections	8492 (R(int) = 0.0499)	
Observed reflections	6145 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.70 and 0.56	
Refinement method	Full-matrix least-squares an F^2	
Data/restraints/parameters	8492 / 60 / 593	
Goodness-of-fit on F^2	1.05	
Final R indices (I>2sigma(I))	R1 = 0.059, wR2 = 0.137	
Largest diff. peak and hole	0.46 und -0.38 $eÅ^{-3}$	

IUCr's Checkcif provided no level A error and no level B error

Crystal structure of cage compound 11

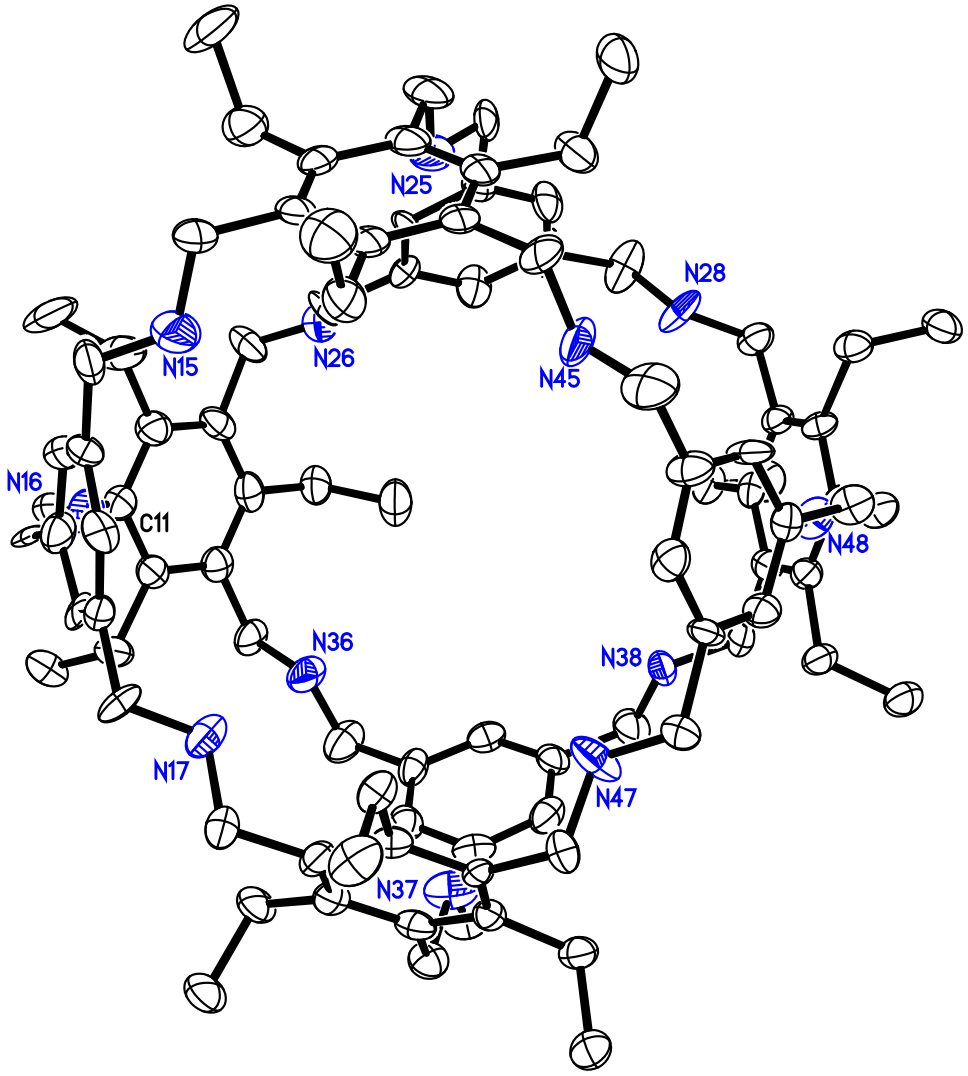


Figure S103: Molecular structure of cage compound **11** as determined by X-ray diffraction. Atoms of carbon are depicted in white, nitogen in blue.

Crystals were obtained by slow evaporation of toluene.

CCDC-number : 1858592

Table S7: Crystal data and structure refinement for **11**.

Empirical formula	$C_{124}H_{164}N_{12}$	
Formula weight	1822.66	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Z	2	
Unit cell dimensions	a = 16.291(2) Å	α =83.595(9) deg.
	b = 18.913(2) Å	β =87.435(10) deg.
	c = 19.263(2) Å	γ =66.625(9) deg.
Volume	5413.8(12) $Å^3$	
Density (calculated)	1.12 g/cm^3	
Absorption coefficient	0.49 mm^{-1}	
Crystal shape	plate	
Crystal size	0.106 x 0.072 x 0.056 mm^3	
Crystal colour	colourless	
Theta range for data collection	3.6 to 57.2 deg.	
Index ranges	-17≤h≤16, -20≤k≤20, -20≤l≤20	
Reflections collected	106868	
Independent reflections	14315 (R(int) = 0.1739)	
Observed reflections	2809 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.63 and 0.52	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	106868 / 5850 / 1452	
Goodness-of-fit on F^2	0.71	
Final R indices (I>2sigma(I))	R1 = 0.074, wR2 = 0.129	
Largest diff. peak and hole	0.66 and -0.49 $eÅ^{-3}$	

IUCr's Checkcif provided four level A errors and four level B errors

Alert level A

THETM01_ALERT_3_A

Problem: The value of sine(theta_max)/wavelength is less than 0.550 Calculated sin(theta_max)/wavelength = 0.5452

Author Response: We have cut the dataset at a resolution of 0.98 due to I/sigma and R(int) criteria. Despite of using a high intensity source and long irradiation times this was the best achievable resolution. The data to parameter ratio is still acceptable. In order to compensate for the lack of information we used all possible local symmetry restraints (SHELX SAME command) and rigid bond restraints (SHELX RIGU command) for all atoms.

PLAT026_ALERT_3_A

Problem: Ratio Observed / Unique Reflections (too) Low. 20% Check.

Author Response: The calculation of this ratio maybe somewhat biased, as the crystal is a fourfold twin. There is one dominating domain (50%) and three smaller domains (10%, 20% and 20%), that have to be considered for overlapping reasons, but add a lot to the "unobserved reflections".

PLAT414_ALERT_2_A

Problem: Short Intra D-H..H-X H15A ..H19C 0.95 Ang. x,y,z = 1_555 Check

Author Response: These hydrogen atoms belong to different PARTs of a disordered model. This was not sensible to declare completely consistently for all atoms.

PLAT414_ALERT_2_A

Problem: Short Intra D-H..H-X H15A ..H19D 1.54 Ang. x,y,z = 1_555 Check

Author Response: These hydrogen atoms belong to different PARTs of a disordered model. This was not sensible to declare completely consistently for all atoms.

Alert level B

PLAT216_ALERT_3_B

Problem: Disordered C114 (An/Solv) ADP max/min Ratio 8.4 Note

Author Response: This is a disordered solvent molecule. It has been refined with rigid bond restraints (SHELX RIGU command) as well as similarity restraints (SHELX SIMU command). The remaining ADP ratio may either be just real for a disordered solvent molecule or artificial due to incomplete disorder modelling. Anyway the only realistic modelling alternative would be squeezing the solvent, which might improve the R-values, but on the other side we would lose structural information.

PLAT216_ALERT_3_B

Problem: Disordered C136 (An/Solv) ADP max/min Ratio 7.5 Note

Author Response: This is a disordered solvent molecule. It has been refined with rigid bond restraints (SHELX RIGU command) as well as similarity restraints (SHELX SIMU command). The remaining ADP ratio may either be just real for a disordered solvent molecule or artificial due to incomplete disorder modelling. Anyway the only realistic modelling alternative would be squeezing the solvent, which might improve the R-values, but on the other side we would lose structural information.

PLAT234_ALERT_4_B

Problem: Large Hirshfeld Difference N26 --C27 . 0.29 Ang.

Author Response: N26 is an atom between an ordered part of the molecule and a disordered one (C27 ...). The structure model can never fulfill the requirements for both parts, so in the transition zone occurs some "friction".

PLAT340_ALERT_3_B

Problem: Low Bond Precision on C-C Bonds ..... 0.01391 Ang.

Author Response: These kind of cage molecules have challenging structures with large unit cells, many parameters, and low resolution weak intensity data. Whether this bond precision is considered as low or sufficient is a question of purpose of the structure determination. We are interested mainly in the overall constitution, shape, and packing than in individual atom geometry, so this precision is by far sufficient for our discussion.

Crystal structure of cage compound 13

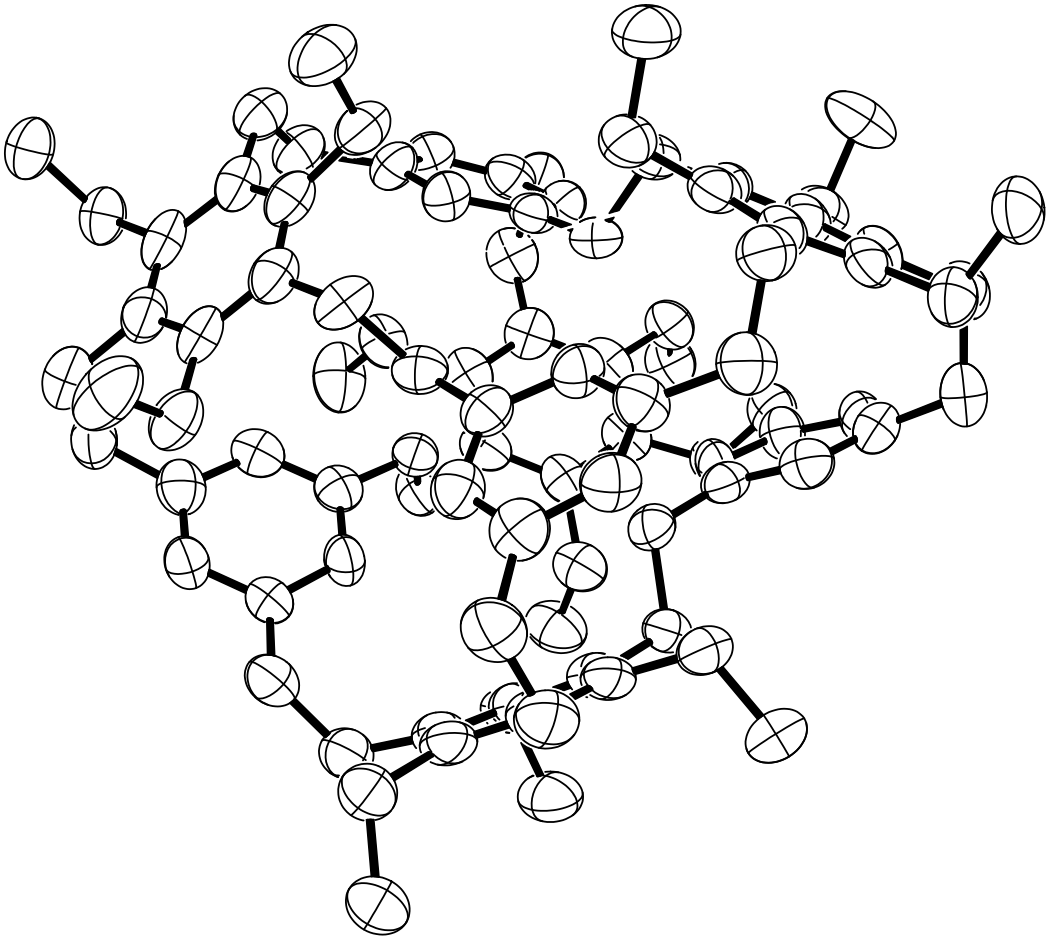


Figure S104: Molecular structure of cage compound **13** as determined by X-ray diffraction. Atoms of carbon are depicted in white.

Crystals were obtained by slow evaporation of $CHCl_3$/*n*-Hexanes.

CCDC-number : 1858590

Table S8: Crystal data and structure refinement for **13**.

Empirical formula	$C_{96}H_{120}$	
Formula weight	1273.91	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	tetragonal	
Space group	$I\bar{4}$	
Z	2	
Unit cell dimensions	a = 16.8191(18) Å	α = 90 deg.
	b = 16.8191(18) Å	β = 90 deg.
	c = 19.299(4) Å	γ = 90 deg.
Volume	5459.4(16) $Å^3$	
Density (calculated)	0.77 g/cm^3	
Absorption coefficient	0.32 mm^{-1}	
Crystal shape	brick	
Crystal size	0.094 x 0.056 x 0.042 mm^3	
Crystal colour	colourless	
Theta range for data collection	3.5 to 53.4 deg.	
Index ranges	$-17\leq h\leq 13$, $-14\leq k\leq 17$, $-20\leq l\leq 13$	
Reflections collected	6951	
Independent reflections	2957 (R(int) = 0.0910)	
Observed reflections	2088 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.47 and 0.63	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2957 / 0 / 220	
Goodness-of-fit on F^2	1.05	
Final R indices (I>2sigma(I))	R1 = 0.053, wR2 = 0.106	
Absolute structure parameter	1.4(8)	
Largest diff. peak and hole	0.10 and -0.12 $eÅ^{-3}$	

IUCr's Checkcif provided one level A error and one level B error

Alert level A

THETM01_ALERT_3_A

Problem: The value of sine(theta_max)/wavelength is less than 0.550 Calculated sin(theta_max)/wavelength = 0.5205

Author Response: We have cut the dataset at a resolution of 0.96 due to I/sigma and R(int) criteria. Despite of using a high intensity source and long irradiation times this was the best achievable resolution. The data to parameter ratio is still acceptable.

Alert level B

PLAT410_ALERT_2_B

Problem: Short Intra H...H Contact H17A ..H31A . 1.85 Ang. x,y,z = 1_555 Check

Author Response: These hydrogen atoms are not at refined positions but on assumed positions based on the geometry of the carbon skeleton. These positions maybe slightly off, as sterical evasion shifts are not considered. Nevertheless, calculating hydrogen atom positions is the best modelling option if refinement is not possible or to parameter demanding.

Crystal structure of cage compound 13

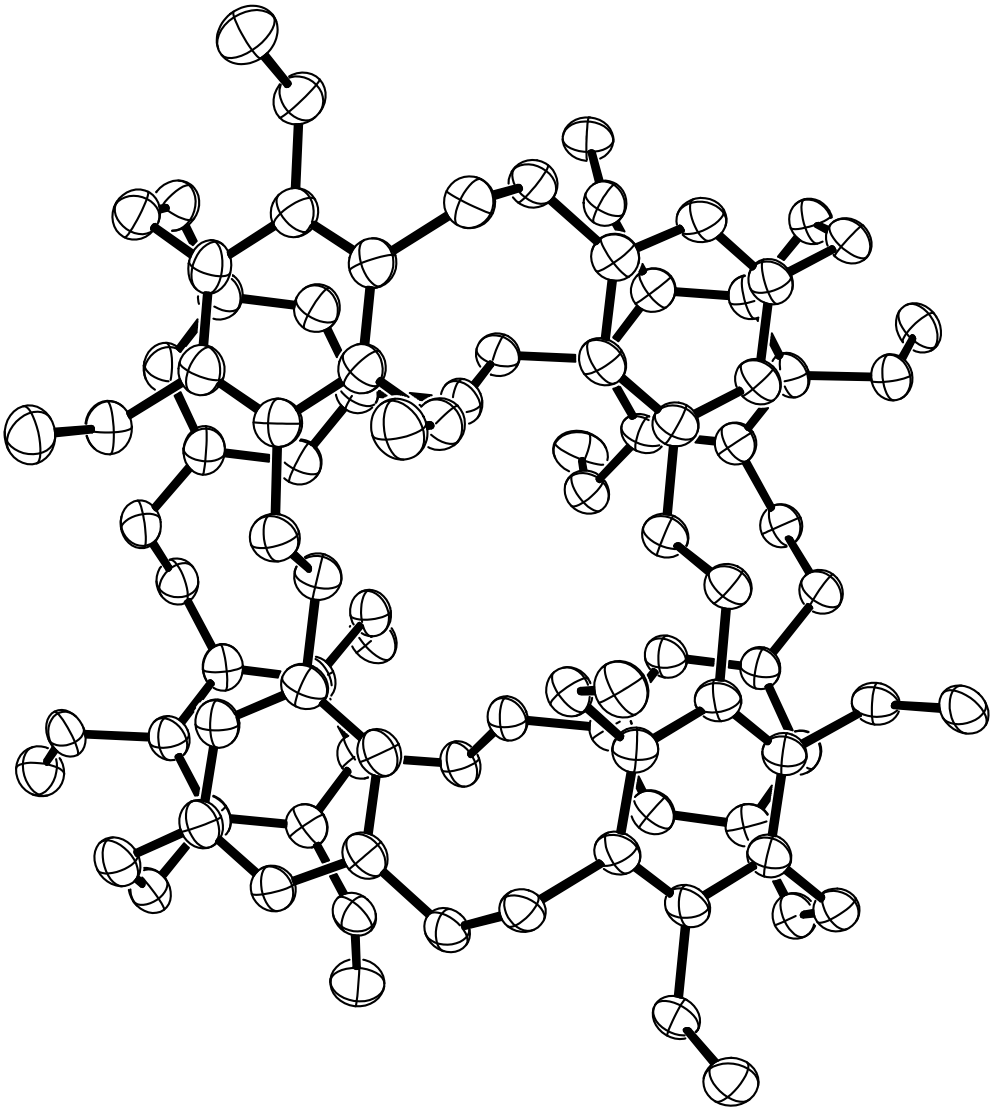


Figure S105: Molecular structure of cage compound **13** as determined by X-ray diffraction. Atoms of carbon are depicted in white.

Crystals were obtained by slow evaporation of acetone.

CCDC-number : 1858591

Table S9: Crystal data and structure refinement for **13**.

Empirical formula	$C_{108}H_{144}O_4$	
Formula weight	1506.22	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	8	
Unit cell dimensions	a = 22.5768(5) Å	α = 90 deg.
	b = 46.3736(11) Å	β = 106.864(2) deg.
	c = 18.3646(4) Å	γ = 90 deg.
Volume	18400.3(7) $Å^3$	
Density (calculated)	1.09 g/cm^3	
Absorption coefficient	0.48 mm^{-1}	
Crystal shape	stick	
Crystal size	0.199 x 0.059 x 0.049 mm^3	
Crystal colour	colourless	
Theta range for data collection	2.7 to 63.7 deg.	
Index ranges	$-26\leq h\leq 24$, $-49\leq k\leq 53$, $-14\leq l\leq 21$	
Reflections collected	88930	
Independent reflections	28520 (R(int) = 0.1316)	
Observed reflections	15797 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	2.47 and 0.37	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	28520 / 2208 / 2098	
Goodness-of-fit on F^2	1.06	
Final R indices (I>2sigma(I))	R1 = 0.086, wR2 = 0.184	
Largest diff. peak and hole	0.44 and -0.34 $eÅ^{-3}$	

IUCr's Checkcif provided no level A error and ten level B errors

Alert level B

PLAT029_ALERT_3_B

Problem: _diffrn_measured_fraction_theta_full value Low . 0.942 Why?

Author Response: This is the result of a well planned data collection strategy with 100% completeness and fourfold redundancy. However, with copper radiation, due to the wide spread diffraction pattern, depending on the crystal orientation, the goniometer type and the detector characteristics, sometimes full completeness in outer shells is difficult to reach. Furthermore there is always a small percentage of the reflections that are indeed measured, but do not fulfill the criteria for a successful integration or have to be omitted in the scaling process. These missing few percent are not critical, neither for the data to parameter ratio nor the reliability or correctness or accuracy of the structure model.

PLAT043_ALERT_1_B

Problem: Calculated and Reported Mol. Weight Differ by .. 17.23 Check

Author Response: We found eight positions occupied by crystal solvent acetone in the asymmetric unit, but not all of them seem to be fully occupied. As it is not very precise to refine occupation factors of rather loose solvent molecules, we decided not to adapt the given unit cell contents to the determined partial occupation of these solvent molecules.

PLAT260_ALERT_2_B

Problem: Large Average Ueq of Residue Including O7 0.153 Check

Author Response: This is a partially occupied and rather loose solvent acetone. It has been refined using rigid bon restraints (SHELX RIGU command) and similarity restraints (SHELX SIMU command). However, large Ueq is exactly what one expects for such a molecule.

PLAT260_ALERT_2_B

Problem: Large Average Ueq of Residue Including O8 0.155 Check

Author Response: This is a partially occupied and rather loose solvent acetone. It has been refined using rigid bon restraints (SHELX RIGU command) and similarity restraints (SHELX SIMU command). However, large Ueq is exactly what one expects for such a molecule.

PLAT410_ALERT_2_B

Problem: Short Intra H...H Contact H17A_1 ..H91A_1 . 1.86 Ang. x,y,z = 1_555 Check

Author Response: These hydrogen atoms are not at refined positions but on assumed positions based on the geometry of the carbon skeleton. These positions maybe slightly off, as sterical evasion shifts are not considered. Nevertheless, calculating hydrogen atom positions is the best modelling option if refinement is not possible or to parameter demanding.

PLAT410_ALERT_2_B

Problem: Short Intra H...H Contact H39A_1 ..H97A_1 . 1.88 Ang. x,y,z = 1_555 Check

Author Response: These hydrogen atoms are not at refined positions but on assumed positions based on the geometry of the carbon skeleton. These positions maybe slightly off, as sterical evasion shifts are not considered. Nevertheless, calculating hydrogen atom positions is the best modelling option if refinement is not possible or to parameter demanding.

PLAT410_ALERT_2_B

Problem: Short Intra H...H Contact H59B_1 ..H10J_1 . 1.89 Ang. x,y,z = 1_555 Check

Author Response: These hydrogen atoms are not at refined positions but on assumed positions based on the geometry of the carbon skeleton. These positions maybe slightly off, as sterical evasion shifts are not considered. Nevertheless, calculating hydrogen atom positions is the best modelling option if refinement is not possible or to parameter demanding.

PLAT410_ALERT_2_B

Problem: Short Intra H...H Contact H17A_2 ..H91A_2 . 1.87 Ang. x,y,z = 1_555 Check

Author Response: These hydrogen atoms are not at refined positions but on assumed positions based on the geometry of the carbon skeleton. These positions maybe slightly off, as sterical evasion shifts are not considered. Nevertheless, calculating hydrogen atom positions is the best modelling option if refinement is not possible or to parameter demanding.

PLAT410_ALERT_2_B

Problem: Short Intra H...H Contact H59B_2 ..H10I_2 . 1.87 Ang. x,y,z = 1_555 Check

Author Response: These hydrogen atoms are not at refined positions but on assumed positions based on the geometry of the carbon skeleton. These positions maybe slightly off, as sterical

evasion shifts are not considered. Nevertheless, calculating hydrogen atom positions is the best modelling option if refinement is not possible or to parameter demanding.

PLAT410_ALERT_2_B

Problem: Short Intra H...H Contact H77B_2 ..H10Y_2 . 1.87 Ang. x,y,z = 1_555 Check

Author Response: These hydrogen atoms are not at refined positions but on assumed positions based on the geometry of the carbon skeleton. These positions maybe slightly off, as sterical evasion shifts are not considered. Nevertheless, calculating hydrogen atom positions is the best modelling option if refinement is not possible or to parameter demanding.

Crystal structure of cage compound 17

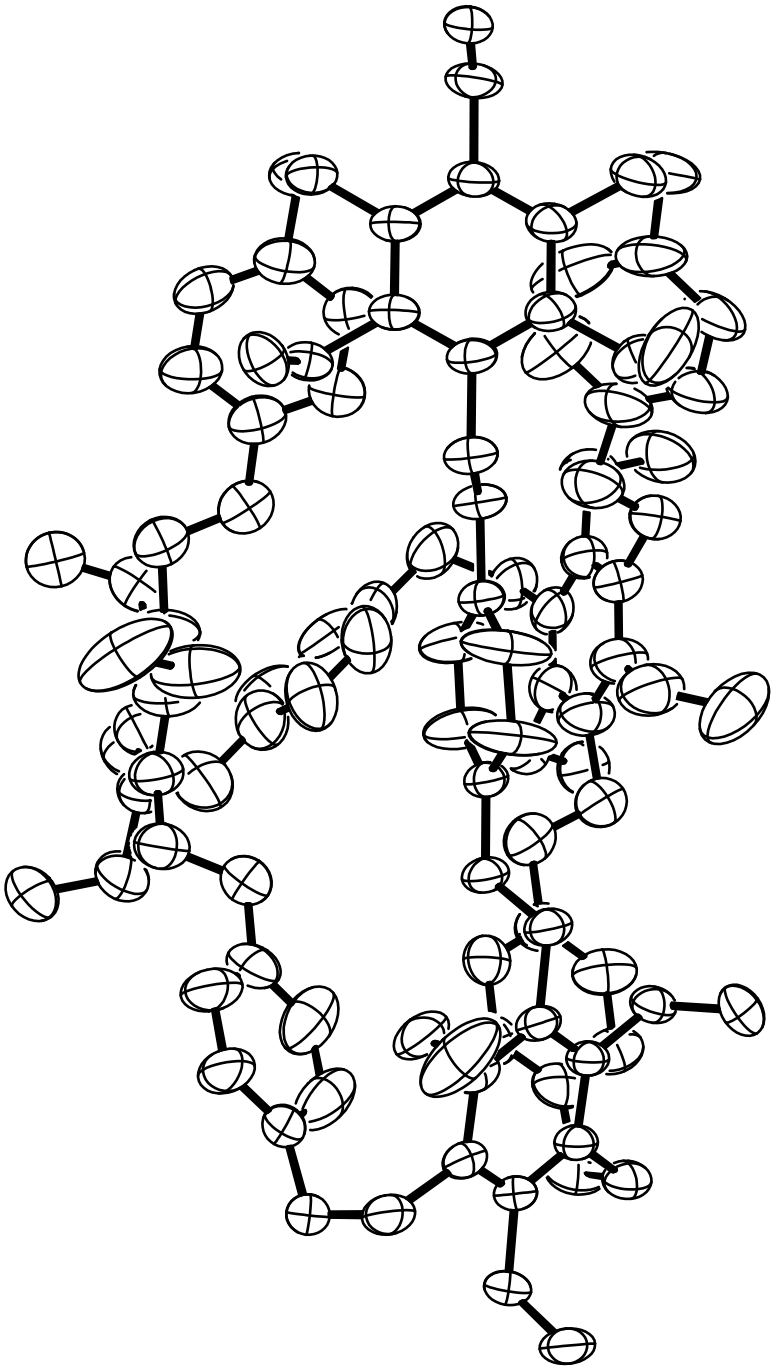


Figure S106: Molecular structure of cage compound **17** as determined by X-ray diffraction. Atoms of carbon are depicted in white.

Crystals were obtained by slow diffusion of methanol in a chloroform solution of the compound (MeOH:$CHCl_3$ = 12:1).

CCDC-number : 1858597

Table S10: Crystal data and structure refinement for **17**.

Empirical formula	$C_{108}H_{132}$	
Formula weight	1430.13	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	monoklin	
Space group	C2/c	
Z	4	
Unit cell dimensions	a = 20.1267(9) Å	α = 90 °
	b = 25.0475(8) Å	β =97.788(4) °
	c = 17.8372(9) Å	γ = 90 °
Volume	8909.2(7) $Å^3$	
Density (calculated)	1.066 g/cm^3	
Absorption coefficient μ	0.440 mm^{-1}	
Crystal shape	brick	
Crystal size	0.260 x 0.087 x 0.039 mm^3	
Crystal colour	colourless	
Theta range for data collection	2.832 bis 68.349 °	
Index ranges	-22≤h≤24, -30≤k≤25, -21≤l≤18	
Reflections collected	33983	
Independent reflections	7966 (R(int) = 0.0655)	
Observed reflections	5034 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.92 and 0.52	
Refinement method	Full-matrix least-squares an F^2	
Data/restraints/parameters	7966 / 475 / 479	
Goodness-of-fit on F^2	1.05	
Final R indices (I>2sigma(I))	R1 = 0.108, wR2 = 0.296	
Largest diff. peak and hole	0.65 und -0.38 $eÅ^{-3}$	

IUCr's Checkcif provided two level A errors and one level B error

Alert level A

PLAT410_ALERT_2_A

Problem: Short Intra H...H Contact H85B ..H27C . 1.64 Ang. x,y,z = 1_555 Check

Author Response: Parts of the structure were modelled as split model, however separation of alternative atom position was not possible for all regions affected by disorder, so that the calculated positions of some hydrogen atoms interfer.

PLAT413_ALERT_2_A

Problem: Short Inter XH3 .. XHn H76A ..H36B . 1.63 Ang. 1-x,1-y,2-z = 5_667 Check

Author Response: Parts of the structure were modelled as split model, however separation of alternative atom position was not possible for all regions affected by disorder, so that the calculated positions of some hydrogen atoms interfer.

Alert level B

PLAT097_ALERT_2_B

Problem: Large Reported Max. (Positive) Residual Density 0.63 eA-3

Author Response: Large parts of this structure had to be modelled disordered, and this "looseness" or "unresolved disorder" holds also for the rest of the molecule. The residual density is very likely owing to this fact. However, the possibility of resolving disorder in crystal structures is limited. Disorder models require lots of parameters, worsing the parameter ratio and the precision of the results, and furthermore assume an evenly distribution of the alternative positions over all unit cells, which is basically impossible. A disordered "crystal" is not a crystal and cannot be described exactly by methods of crystal structure analysis.

9 Literature

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