Supporting Information

Singlet Oxygen Stimulus for Switchable Functional Organic Cages

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Synthesis and Characterization of Cages 1a–b and 2a–b

General Procedures. All reagents were purchased at the highest commercial grade and used as supplied. Anhydrous tetrahydrofurane and dichloromethane were distilled from sodium/benzophenone and calcium hydride respectively. Diisopropylethylamine was freshly dried and distilled from sodium hydride. All reactions were carried out under dry glassware and a nitrogen atmosphere. Flash column chromatography was carried out on silica gel 230–400 mesh.

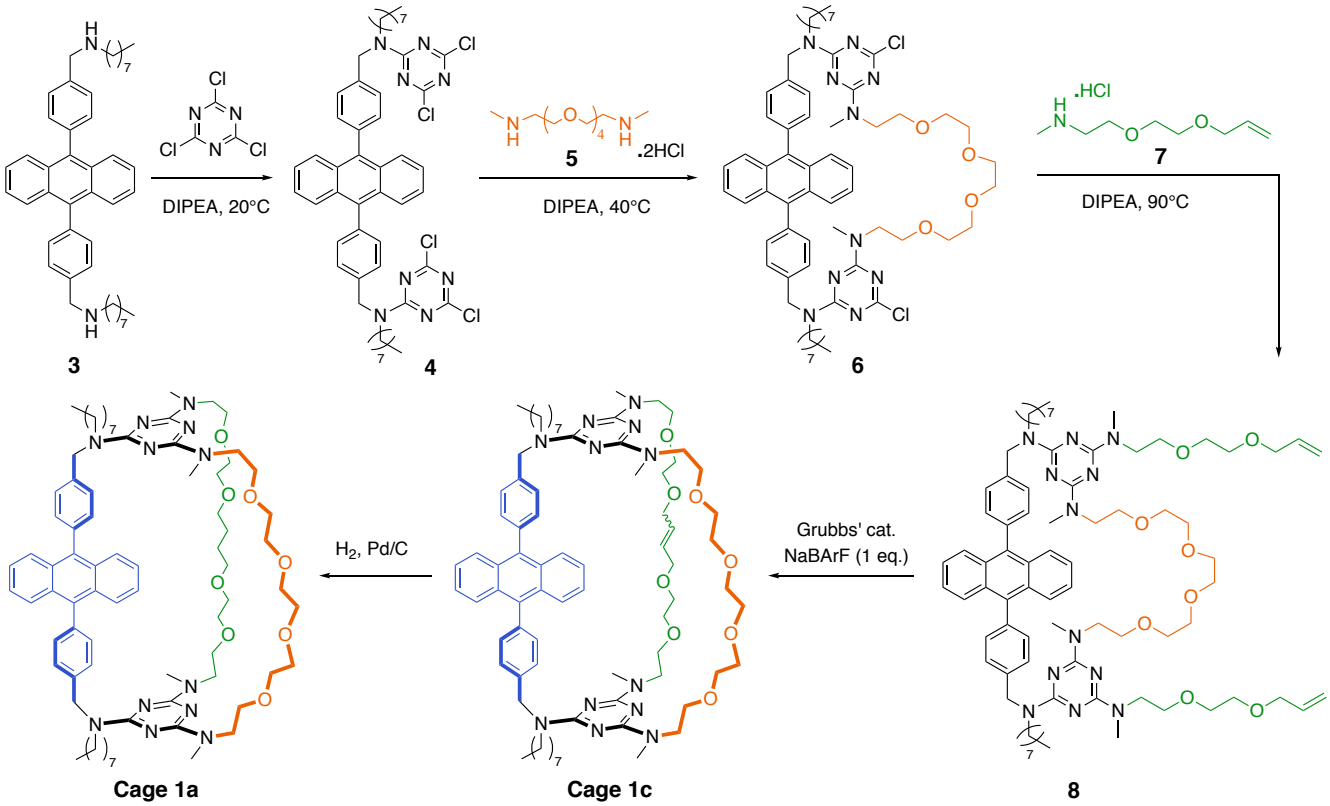
NMR Spectra were recorded on Bruker AvanceIII 200, AvanceII 300, AvanceII 400 or AvanceIII 600 spectrometers and traces of residual solvent were used as internal standard. The following abbreviations were used to describe the signals: s for singlet, d for doublet, t for triplet, q for quadruplet, m for multiplet, br for broad. ESI (electrospray ionization) and FD (field desorption) mass spectrometry were performed using a Qstar Mass Elite (Applied Biosystems). Elemental analysis was measured on a Thermo Fisher Scientific Flash 2000. UV-visible spectra were recorded at room temperature on a Varian Cary 5000 or Hitachi U3300 spectrometers using quartz cells (1 cm). Fluorescence emission spectra were recorded on a HORIBA JOBIN-YVON Fluorolog 3.

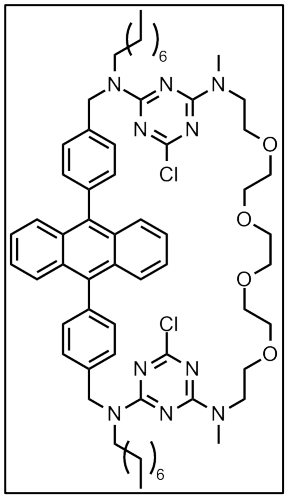
Commercially available 9,10-dibromoanthracene, 4-formylphenyl boronic acid, *n*-octylamine were used as received.

Titration experiments. Solutions of cage **2a** were purified by HPLC and the concentration determined by UV spectroscopy. Aliquots of guest solution in dichloromethane were added to a solution of cage **1a** or **2a** in dichloromethane at 298 K. For endoperoxide titrations, the same procedure was applied to an equimolar solution of cages **1a** + **1b** or **2a** + **2b** to allow a monitoring through fluorescence emission. In all cases, the variations of the maximum emission intensity of 9,10-diphenylanthracene upon addition of the cation were collected. The binding constant was determined either by non-linear square curve-fitting program implemented within MS Excel, or using WinEqNMR[1] software. The (host:guest) stoichiometry model was chosen in function of the cage and cations (1:1 or 1:2) and the contribution of the endoperoxide was taken into account by using a model with 4 complexes (sodium) or 2 complexes (cesium).

[1] Hynes, M. J. *J. Chem. Soc., Dalton Trans*. **1993**, 311-312.

Synthesis of Cages 1a and 1b



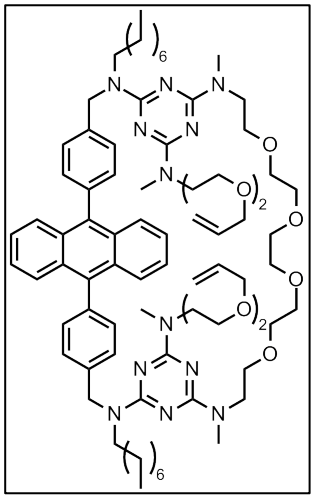


Macrocycle 6: To a cold solution of 1,3,5-trichloro-*s*-triazine (370 mg, 2 mmol) in anhydrous THF (50 mL) was added a solution of **3** (613 mg, 1 mmol) and DIPEA (350 µL, 2 mmol) in anhydrous THF (50 mL). The reaction mixture was stirred 2 hour at room temperature. Then a solution of diamine **5** (338 mg, 1 mmol) and *N,N*-diisopropyl-ethylamine (350 µL, 2mmol) in anhydrous THF (50 mL) was added, followed by cesium carbonate (3.25 g, 10 mmol). The reaction mixture was stirred at 40°C for 24 hours. The solvent was removed under reduced pressure and the residue was suspended in water (150 mL) and extracted with diethyl ether (4×40 mL). The organic phases were collected, dried, and evaporated. The residue was purified by chromatography column on silica gel (toluene/ethyl acetate, 60:40) and compound **6** was isolated as a white solid (660 mg, 60 %).

^{1}H NMR (600MHz, $CDCl_3$): δ (ppm) = 7.60 (d, J = 8.3 Hz, C**H**, 4H), 7.38 (d, J = 8.3 Hz, C**H**, 4H), 7.19 (m, C**H**, 4H), 7.12 (m, C**H**, 4H), 4.79 (s, PhC**H₂**, 4H), 3.87 - 3.48 (m, C**H₂**, 10H), 3.26 - 2.96 (m, C**H₂**, 20H), 1,70 (m, 4H, C**H₂**), 1.42 - 1.21 (m, C**H₂**, 20H) , 0.87 (t, J = 6.6 Hz, C**H₃**, 6H).

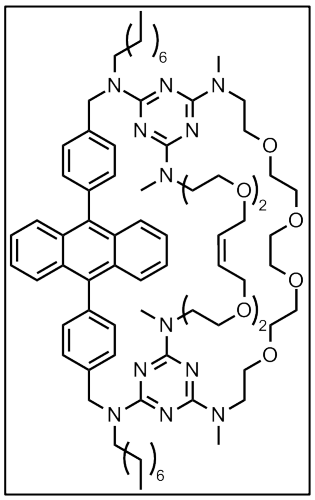
^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 169.4 (Cq), 164.9 (Cq), 164.7 (Cq), 140.3 (Cq), 138.8 (Cq), 131.3 (Cq), 127.6 (CH), 125.9 (CH), 123.3 (CH), 70.2 (CH_2), 70.0 (CH_2), 69.9 (CH_2), 69.3 (CH_2), 68.4 (CH_2), 51.1 (CH_2), 49.1 (CH_2), 48.6 (CH_2), 36.3 (CH_3), 31.9 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.3 (CH_2), 26.9 (CH_2), 22.7 (CH_2), 14.1 (CH_3).

HRMS (FD): calcd for $C_{62}H_{80}Cl_2N_{10}O_4$ m/z = 1098.5741; found m/z = 1098.5737 $[M]^+$.



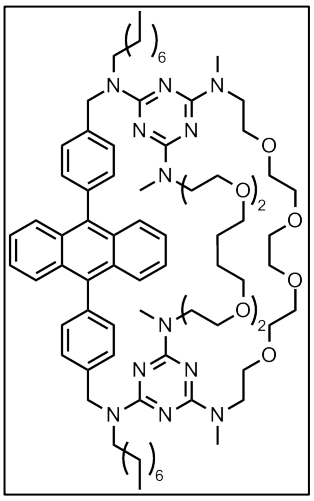
Macrocycle 8: To a solution of **6** (550 mg, 0.5 mmol) in anhydrous THF (5 mL) was added a solution of **7** (600 mg, 3 mmol) and DIPEA (1.74 mL, 10 mmol) in anhydrous THF (5 mL). The reaction mixture was heated to 90°C in a pressure tube for 12 hours. After cooling to room temperature, volatile material was removed under reduced pressure and the residue was purified by chromatography column on silica gel (toluene/ethyl acetate, 40:60). Compound **8** was isolated as a yellow fluorescent oil (610 mg, 92 %).

^{1}H NMR (600MHz, $CDCl_3$): δ (ppm) = 7.68 (m, C**H**, 4H), 7.43 (d, J = 8.0 Hz, C**H**, 4H), 7.35 (d, J = 8.0 Hz, C**H**, 4H), 7.30 (m, C**H**, 4H), 5.89 (m, C=C**H**, 2H), 5.25 (dd, J_1 = 17.4 Hz, J_2 = 1.5 Hz, C=C**H$_2$**, 2H), 5.15 (dd, J_1 = 10.3 Hz, J_2 = 1.5 Hz, C=C**H$_2$**, 2H), 4.81 (s, PhC**H$_2$**, 4H), 4.01 (d, J = 5.5 Hz, C**H$_2$**, 4H), 3.80 - 3.70 (br, C**H$_2$**, 12H), 3.70 - 3.60 (m, C**H$_2$**, 12H), 3.40 - 2.85 (br, C**H$_2$**, 28H), 1,71 (br, 4H, C**H$_2$**), 1.40 - 1.20 (m, C**H$_2$**, 20H), 0.87 (t, J = 6.6 Hz, C**H$_3$**, 6H).
^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 165.7 (Cq), 139.9 (Cq), 137.2 (Cq), 137.0 (Cq), 135.0 (CH), 131.3 (CH), 130.1 (Cq), 127.2 (CH), 127.0 (CH), 125.2 (CH), 117.3 (CH_2), 72.5 (CH_2), 70.0 (CH_2), 70.7 (CH_2), 70.4 - 69.5 (CH_2), 51.0 (CH_2), 49.0 - 48.1 (CH_2), 35.8 (CH_3), 35.7 (CH_3), 32.1 (CH_2), 30.1 - 29.4 (CH_2), 28.6 (CH_2), 27.5 (CH_2), 22.9 (CH_2), 14.3 (CH_3).
HRMS (FD): calcd for $C_{78}H_{112}N_{12}O_8$ m/z = 1344.8726; found m/z = 1344.8731 $[M]^{+\cdot}$.



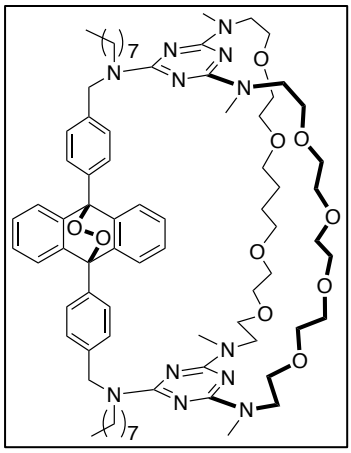
Cage 1c: To a refluxing solution of **8** (300 mg, 0.2 mmol) in anhydrous dichloromethane (150 mL) under argon was added a solution of the Grubbs 2nd generation catalyst (9 mg, 10 µmol) in anhydrous dichloromethane (1 mL). Three additional quantities of Grubbs' catalyst (9 mg, 10 µmol in dry dichloromethane) were introduced every hour. After the last addition the reaction mixture was refluxed for 2 hours. The reaction was cooled to room temperature and hydrogen peroxide (30% in H_2O, 150 mL) was slowly added. The reaction was stirred 3 hours and the solvent was evaporated under reduced pressure. The aqueous residue was extracted with diethyl ether (4×50 mL). The organic phases were collected, dried and concentrated. The crude product was purified by chromatography column on silica gel (toluene/ethyl acetate, 40:60). Molecule **1c** was obtained as a pale yellow solid (253 mg, 95 %).

1H NMR (600MHz, *o*-dichlorobenzene-d_4, 413 K): δ (ppm) = 7.72 (m, C**H**, 4H), 7.45 (d, J = 7.9 Hz, C**H**, 4H), 7.28 (d, J = 7.9 Hz, C**H**, 4H), 7.24 (m, C**H**, 4H), 5.44 (t, J = 2.3 Hz, C**H**=C**H**, 2H), 4.89 (s, PhC**H$_2$**, 4H), 3.86 (t, J = 6.9 Hz, C**H$_2$**, 4H), 3.70 (br, C**H$_2$**, 8H), 3.65 (d, J = 2.3 Hz, C**H$_2$**, 4H), 3.62 (t, J = 5.0 Hz, C**H$_2$**, 4H), 3.46 (t, J = 5.6 Hz, C**H$_2$**, 4H), 3.38 (t, J = 5.6 Hz, C**H$_2$**, 4H), 3.35 (t, J = 5.6 Hz, C**H$_2$**, 4H), 3.31 (t, J = 5.6 Hz, C**H$_2$**, 4H), 3.21 (s, C**H$_2$**, 4H), 3.13 (s, C**H$_3$**, 6H), 3.09 (s, C**H$_3$**, 6H), 1,82 (q, J = 6.9 Hz, 4H, C**H$_2$**), 1.50 - 1.25 (m, C**H$_2$**, 20H), 0.88 (t, J = 6.9 Hz, C**H$_3$**, 6H).
^{13}C NMR (150 MHz, toluene-d_8): δ (ppm) = 166.1 (Cq), 140.3 (Cq), 131.6 (CH), 130.7 (Cq), 72.2 - 68.5 (CH_2), 48.9 (CH_2), 35.9 (CH_3), 32.5 (CH_2), 30.4 - 28.2 (CH_2), 27.8 (CH_2), 23.2 (CH_2), 14.5 (CH_3).
HRMS (FD): calcd for $C_{76}H_{108}N_{12}O_8$ m/z = 1316.8413; found m/z = 1316.8363 $[M]^{+\cdot}$.



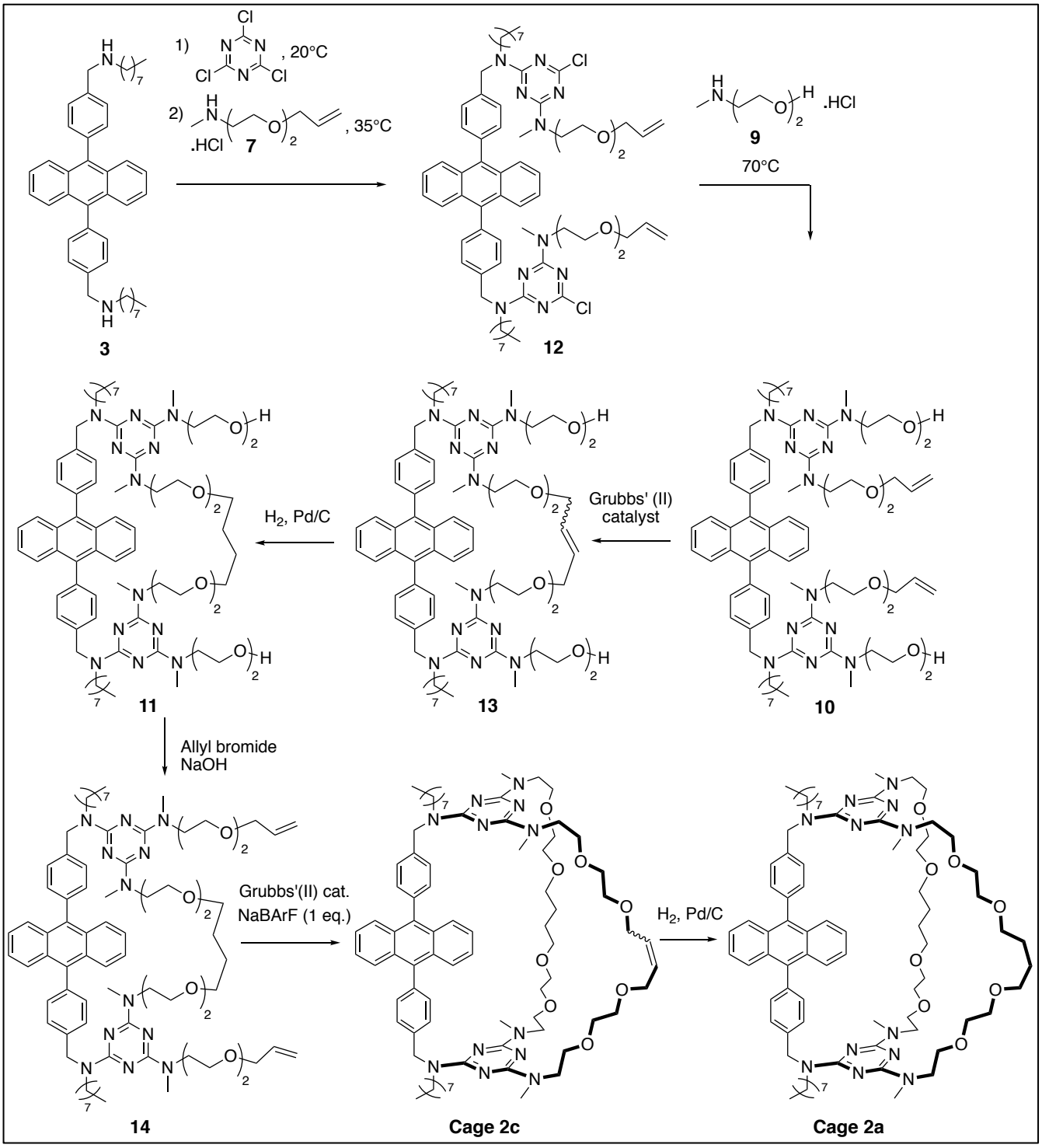
Cage 1a: To a cold suspension of Palladium on Carbon (10% Pd) in methanol (5 mL) was added a solution of **1c** (100 mg, 7.5 µmol) in THF (5 mL). The reaction was flushed out under vacuum and filled in with dihydrogen (3 times). The reaction was stirred under an H_2 atmosphere for 1 hour. The dihydrogen atmosphere was removed under vacuum. The reaction mixture was filtered and the filter cake was washed with THF (3×5 mL). The filtrate was concentrated under reduced pressure and cage **1a** was obtained as a white solid (99 mg, 99%).

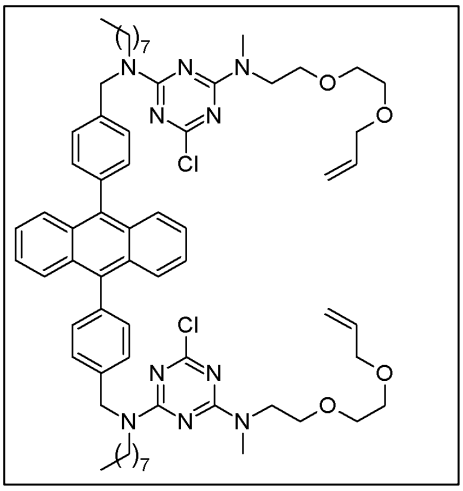
^{1}H NMR (400MHz, toluene-*d*$_8$, 373 K): δ (ppm) = 7.78 (m, C**H**, 4H), 7.38 (d, J = 7.9 Hz, C**H**, 4H), 7.24 (d, J = 7.9 Hz, C**H**, 4H), 7.20 (m, C**H**, 4H), 4.82 (s, PhC**H$_2$**, 4H), 3.82 (t, J = 6.9 Hz, C**H$_2$**, 4H), 3.65 (br, C**H$_2$**, 8H), 3.56 (t, J = 5.3 Hz, C**H$_2$**, 4H), 3.49 (t, J = 5.3 Hz, C**H$_2$**, 4H), 3.41 (t, J = 5.8 Hz, C**H$_2$**, 4H), 3.35 (t, J = 5.8 Hz, C**H$_2$**, 4H), 3.29 (m, C**H$_2$**, 8H), 3.18 (s, C**H$_2$**, 4H), 3.11 (s, C**H$_3$**, 6H), 3.07 (s, C**H$_3$**, 6H), 3.06 (br, C**H$_2$**, 4H), 1,78 (q, J = 7.2 Hz, 4H, C**H$_2$**), 1.48 - 1.21 (m, C**H$_2$**, 20H), 0.88 (t, J = 7.2 Hz, C**H$_3$**, 6H).
^{13}C NMR (100 MHz, toluene-*d*$_8$, 343 K): δ (ppm) = 165.2 (Cq), 164.9 (Cq), 139.3 (Cq), 137.1 (Cq), 136.8 (Cq), 135.0 (CH), 131.3 (CH), 130.1 (Cq), 128.7 (CH), 127.9 (CH), 125.1 (CH), 70.5 - 68.5 (CH_2), 47.8 (CH_2), 35.4 (CH_3), 35.3 (CH_3), 32.1 (CH_2), 30.0 - 28.6 (CH_2), 27.5 (CH_2), 26.6 (CH_2), 22.8 (CH_2), 14.0 (CH_3).
UV/Vis (CH_2Cl_2, λ_{max} (ε in $M^{-1}.cm^{-1}$)): 263 (85460), 342 (3517), 359 (7576), 377 (12200), 398 (11460) nm.
HRMS (FD): calcd for $C_{76}H_{110}N_{12}O_8$ m/z = 1318.8570; found m/z = 1318.8537 $[M]^{+\cdot}$.



Cage 1b: To a solution of **1a** (5 mg, 3.8 µM) in dichloromethane (10 mL) was added methylene blue (1mg, 3.1 µM). The solution was bubbled with O_2 for 15 min and irradiated for 30 min with visible light until complete conversion of the starting material (monitored by UV). The solution was evaporated, dissolved in EtOAc and filtered through celite. The solution was evaporated and further purified by filtration through a silica pad (CH_2Cl_2/MeOH, 9:1).
HRMS (FD): calcd for $C_{76}H_{110}N_{12}O_{10}$ m/z = 1350.8468; found m/z = 1350.8513 $[M]^+$

Synthesis of Cages **2a** and **2b**



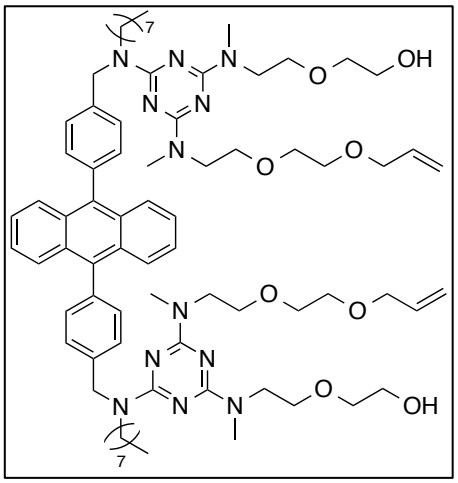


Compound 12: To a solution of cyanuric chloride (595 mg, 3.2 mmol, 1 eq.) at 0 °C in dry THF (25 mL) under nitrogen atmosphere, **3** (1 g, 1.63 mmol) was added DIPEA (0.56 mL, 3.2 mmol, 1 eq.). The solution was stirred at room temperature for 2 h. Then, a solution of **7** (624 mg, 3.2 mmol, 1 eq.) and DIPEA (0.56 mL, 3.2 mmol, 1 eq.) in dry THF (25 mL), was added, followed by the addition of Cs_2CO_3 (4.4 g, 13.5 mmol, 6.7 eq.). The mixture was vigorously stirred overnight at room temperature for 1h and and then at 35 °C for 6 h. The solvent was evaporated. The residue was suspended in water (50 mL) and extracted with Et_2O (3×30 mL). The combined organic layers were dried, filtrated and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether, 1:5), to give compound **12** as slightly yellow oil (860 mg, 46 %). R_f = 0.28 (EtOAc-Petroleum ether 1:5)

^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) = 7.69 (m, 4 H, Ar-H), 7.44 (m, 8 H, Ar-H), 7.33 (m, 4 H, Ar-H), 5.89 (m, 2 H, C**H**=CH_2), 5.29 (m, 4 H, CH=C**H**$_2$), 5.00, 4.93 (2 s, 4 H, $CH_{2,\ bencine}$), 3.97 (m, 4 H, C**H**$_2$CH=CH_2), 3.80-3.50 (m, 20 H, NCH_2, OCH_2), 3.23 (m, 6 H, NCH_3), 1.68 (b, 4 H, C**H**$_2$$(CH_2)_5CH_3$), 1.31 (b, 20 H, (C**H**$_2$$)_5CH_3$), 0.89 (t, 6 H, $J_{H,H}$ = 6.0 Hz, CH_3).

^{13}C NMR (50.4 MHz, $CDCl_3$): 169.5-169.1 ($C_{triazine}$), 165.3-164.9 ($C_{triazine}$), 138-136.9 (C_q), 134.6 (CH=CH_2), 131.51 (CH), 129.94 (C_q), 127.91 (CH), 127.0 (CH), 125.09 (CH), 117.2 (CH=CH_2), 72.1 (OCH_2), 70.5 (OCH_2), 70.3 (OCH_2), 69.3 (OCH_2), 69.0 (OCH_2), 68.8 (OCH_2), 49.8-47.0 (NCH_2, Ar-**C**H_2), 31.9, 29.5, 29.4, 27.3-26.9, 22.7 (CH_2), 14.2 (CH_3).

HRMS (FD): calcd for $C_{66}H_{86}Cl_2N_{10}O_4$ m/z = 1152.6211; found m/z = 1152.6220.

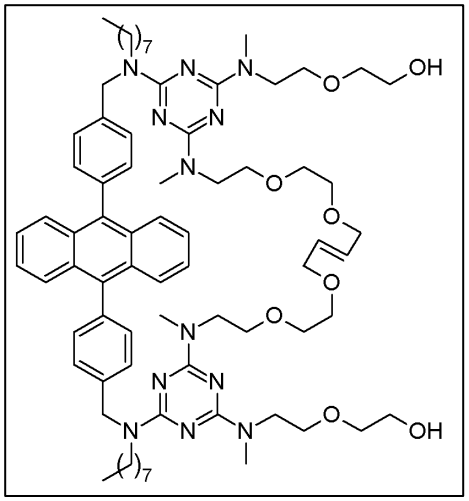


Compound 10: A solution of **12** (400 mg, 0.35 mmol), **9** (360 mg, 2.3 mmol, 3.3 eq) and DIPEA (0.8 mL, 4.6 mmol, 6.6 eq) in a mixture of dry THF/MeOH (3:1, 13 mL) was stirred at 70 °C overnight in a pressure flask. The solvent was concentrated in vacuum and diluted with CH_2Cl_2 (30 mL). The organic phase was washed with water (3×10 mL) and the organic layer was dried, filtrated and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether, 1:5 to 3:2 gradient) to give compound **9** as slightly yellow oil (346 mg, 76%). R_f = 0.22 (EtOAc-Petroleum ether 1:1)

^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 7.72 (m, 4 H, Ar-H), 7.50 (d, 4 H, $J_{H,H}$ = 8.0 Hz, Ar-H), 7.39 (d, 4 H, Ar-H), 7.31 (m, 4 H, Ar-H), 5.89 (m, 2 H, C*H*=CH_2), 5.20 (m, 4 H, CH=CH_2), 4.98, 4.93 (s, 4 H, Ar-C**H$_2$**), 4.00 (m, 4 H, CH_2CH=CH_2), 3.80-3.50 (m, 36 H, NCH_2, OCH_2), 3.19 (s, 12 H, NCH_3), 2.19 (bs, 2 H, OH), 1.67 (b, 4 H, C$H_2$$(CH_2)_5CH_3$), 1.33 (b, 20 H, (C$H_2$$)_5CH_3$), 0.88 (t, 6 H, $J_{H,H}$ = 8.0 Hz, CH_3).

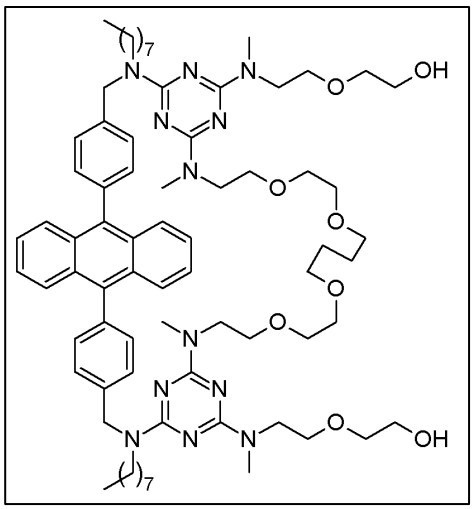
^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 165.6 ($C_{triazine}$), 139.3 (C_q), 137.4 (C_q), 137.1 (C_q), 134.8 (**C**H=CH_2), 131.3 (CH), 130.0 (CH), 127.6 (CH), 127.1 (CH), 125.0 (CH), 117.2 (CH=**C**H_2), 72.3 (OCH_2), 69.8 (OCH_2), 69.5 (OCH_2), 61.9 (COH), 49.7, 48.4, 46.8, 46.7, 35.7 (NCH_3), 32.0 (CH_2), 29.5 (CH_2), 27.4 (CH_2), 22.8 (CH_2), 14.3 (CH_2), 14.2 (CH_3).

HRMS (FD): calcd for $C_{76}H_{110}N_{12}O_8$ m/z = 1318.8570; found m/z = 1318.8579.

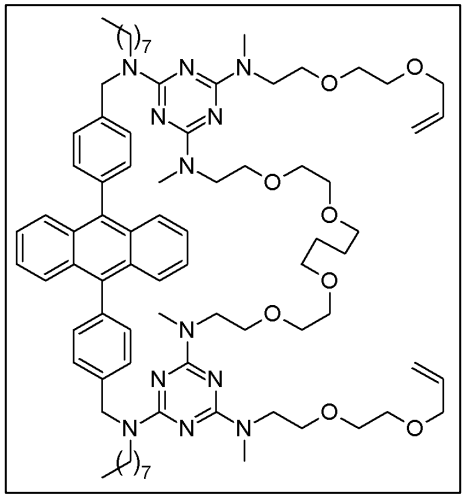


Macrocycle 13: A solution of **10** (210 mg, 0.16 mmol) in dry dichloromethane (159 mL) and Grubbs 2nd generation catalyst (7 mg) was refluxed under N_2. Additional Grubbs 2nd generation catalyst (7 mg) was added every hour for five hours. After the last addition the solution was refluxed for an additional hour. The solution was concentrated and the residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH, 99.5/0.5 to 99/1 gradient). Compound **13** was isolated as a slightly yellow oil (146 mg, 71%).

R_f = 0.31 (EtOAc/Petroleum ether, 2:1).
^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 7.70 (m, 4 H, Ar-H), 7.46 (d, 4 H, Ar-H), 7.37 (d, 4 H, $J_{H,H}$ = 10.2 Hz, Ar-H), 7.4-7.30 (m, 4 H, Ar-H), 5.37 (s, 2 H, C**H**=C**H**), 4.88 (s, 4 H, Ar-C**H$_2$**), 3.79-3.25 (m, 40 H, C**H**$_2$CH=CH, NCH_2, OCH_2), 3.19 (m, 12 H, NCH_3,), 2.15 (bs, 2 H, OH), 1.72 (b, 4 H, C**H**$_2$$(CH_2)_5CH_3$), 1.34 (b, 20 H, (C**H**$_2$$)_5CH_3$), 0.88 (t, 6 H, $J_{H,H}$ = 5.4 Hz, CH_3).
^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 165.5 ($C_{triazine}$), 139.4 (C_q), 136.9 (C_q), 131.1 (CH), 129.8 (C_q), 129.2 (CH=CH), 126.9 (CH), 126.7 (CH), 124.9 (CH), 72.0 (OCH_2), 70.7 (OCH_2), 70.0 (OCH_2), 69.4 (OCH_2), 68.8 (OCH_2), 61.8 (COH), 50.4 ($CH_{2,bencine}$), 48.4, 48.2, 35.6 (NCH_3), 35.5 (CH_2), 31.9 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 28.2 ($CH_2(CH_2)_5CH_3$), 27.2 (CH_2), 22.7 (CH_2), 14.1 (CH_3).
HRMS (FD): calcd for $C_{74}H_{106}N_{12}O_8$ m/z = 1290.8257; found m/z = 1290.8261.

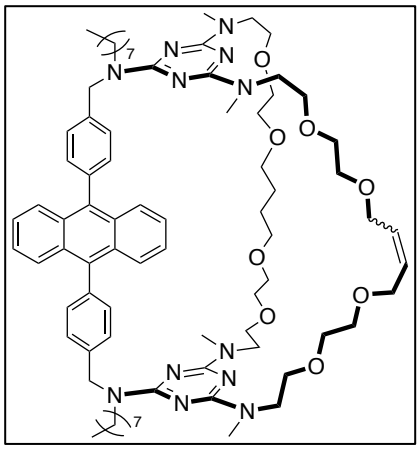


Macrocycle 11: To a solution of **13** (136 mg, 0.11 mmol) in dry THF/MeOH (1:1, 10 mL) under N_2 was added Pd/C (14 mg). The reaction flask was saturated with H_2 by consecutive cycles of vaccum/H_2. The mixture was stirred for 1 h. The suspension was filtered through a celite pad, and eluted with EtOAc/MeOH (1:1, 15 mL). The solvent was evaporated under reduced pressure to give **11** as slightly yellow oil (130 mg, 100%). R_f = 0.57 (EtOAc/Petroleum ether 2:1, 2 elutions)
^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 7.71 (m, 4 H, Ar-H), 7.47 (d, 4 H, $J_{H,H}$ = 10.3 Hz, Ar-H), 7.38 (d, 4 H, Ar-H), 7.34 (m, 4 H, Ar-H), 4.89 (s, 4 H, Ar-C**H$_2$**), 3.88-3.29 (m, 36 H, NCH_2, OCH_2), 3.19 (m, 16 H, NCH_3, OCH_2), 1.73 (b, 4 H, C$H_2$$(CH_2)_5CH_3$), 1.43-1.23 (b, 24H, (C$H_2$$)_5CH_3$, $OCH_2CH_2CH_2$), 0.88 (m, 6 H, CH_3).
^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 165.7, 165.5, 165.4 ($C_{triazine}$), 139.5 (C_q), 137.0 (C_q), 131.2 (CH), 130.0 (C_q), 127.0 (CH), 126.9 (CH), 125.0 (CH), 72.2 (OCH_2), 71.0 (OCH_2), 70.2 (OCH_2), 69.5 (OCH_2), 61.9 (COH), 50.5 ($_{CH2,bencine}$), 48.4 (NCH_2), 47.8 (NCH_2), 35.5 (NCH_3), 32.0 (CH_2), 30.37 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 28.3 (CH_2), 27.3 (CH_2), 26.0 (CH_2), 22.7 (CH_2), 14.2 (CH_3)
HRMS (FD): calcd for $C_{74}H_{108}N_{12}O_8$ m/z = 1292.8413; found m/z = 1292.8410.



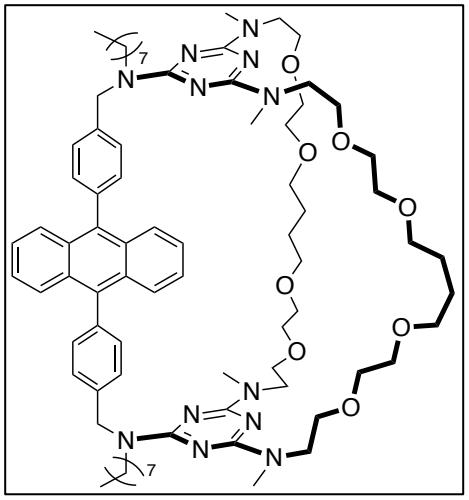
Macrocycle 14: A mixture of **11** (150 mg, 0.12 mmol), allyl bromide (1.6 mL) and grounded NaOH (48 mg, 1.2 mmol, 5 eq.) in dry THF (1.6 mL) was stirred at room temperature under nitrogen atmosphere for 13 h. The solvent was concentrated under vacuum. The residue was dissolved in Et_2O (15 mL), and washed with water (3×5 mL). The organic layer was ried, filtered and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether, 1:1) to give **14** as slightly yellow oil (96 mg, 58%). R_f = 0.75 (EtOAc/Petroleum ether, 1:1)

^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 7.71 (m, 4 H, Ar-H), 7.46 (d, 4 H, $J_{H,H}$ = 10.1 Hz, Ar-H), 7.38 (d, 4 H, Ar-H), 7.34 (m, 4 H, Ar-H), 5.93 (m, 2 H, C**H**=CH_2), 5.25 (2m, 4 H, CH=C**H**$_2$), 4.89 (s, 4 H, Ar-CH_2), 4.05 (dt, 4 H, $^3J_{H,H}$ = 7.5 Hz, C**H**$_2$CH=CH_2), 3.90-3.55 (m, 40 H, NCH_2, OCH_2), 3.20, 3.13 (m, 16 H, NCH_3, OCH_2), 1.73 (b, 4 H, C**H**$_2$$(CH_2)_5CH_3$), 1.43-1.12 (b, 24 H, OCH_2C**H**$_2$C**H**$_2$$CH_2O$,(C**H**$_2$$)_5CH_3$), 0.88 (t, 6 H, $J_{H,H}$ = 9.3 Hz, CH_3).
^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 165.6, 165.5, 165.4 ($C_{triazine}$), 139.6 (C_q), 137.3 (C_q), 134.9 (CH=CH_2), 131.2, (CH) 130.2 (C_q), 127.4 (CH), 127.1 (CH), 125.1 (CH), 117.2 (CH=CH_2), 72.4 (OCH_2), 71.0 (OCH_2), 70.6 (OCH_2), 70.2 (OCH_2), 69.6 (OCH_2), 50.5 (**C**$H_{2\ benzyl}$), 48.4 (NCH_2), 47.8 (NCH_2), 35.9 (NCH_3), 32.0 (CH_2), 29.8 (CH_2), 29.4 (CH_2), 28.5 (CH_2), 27.4 (CH_2), 26.0 (CH_2), 22.8 (CH_2), 14.2 (CH_3)
HRMS (FD): calcd for $C_{80}H_{116}N_{12}O_8$ m/z = 1372.9039; found m/z = 1372.9022.



Cage 2c: A solution of **14** (42 mg, 0.03 mmol) in dry CH_2Cl_2 (49 mL), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (35 mg, 0.04 mmol, 1.3 eq.) and Grubbs 2nd generation catalyst (3 mg) was refluxed under N_2. Additional Grubbs 2nd generation catalyst (7 mg) was added every hour for five hours. After the last addition the solution was refluxed for an additional hour. The solution was concentrated and the residue was purified by preparative TLC (EtOAc/cyclohexane, 1:1) to give **2c** as slightly yellow oil (25 mg, 62%). R_f = 0.56 (EtOAc-cyclohexane 1:1).

^{1}H NMR (600 MHz, toluene-d_8, 373 K): δ (ppm) = 7.84 (m, 4 H, Ar-H), 7.44 (d, 4 H, $J_{H,H}$ = 7.8 Hz, Ar-H), 7.30 (d, 4 H, Ar-H), 7.22 (m, 4 H, Ar-H), 5.43 (s, 2 H, C**H**=C**H**), 4.90 (b, 4 H, $CH_{2,\ bencine}$), 3.90-3.60 (m, 24 H, OCH_2, NCH_2) , 3.44 (m, 8 H, OCH_2), 3.33 (t, 8 H, $J_{H,H}$ = 6 Hz, OCH_2), 3.15 (s, 12 H, NCH_3), 3.07 (bs, 4 H, OCH_2), 1.81 (b, 4 H, $J_{H,H}$ = 7.2 Hz, C**H**$_2$$(CH_2)_5CH_3$), 1.46-1.34 (b, 24 H, OCH_2C**H**$_2$C**H**$_2$$CH_2O$, (C**H**$_2$$)_5CH_3$), 0.88 (t, 6 H, $J_{H,H}$ = 6.6 Hz, CH_3).
^{13}C NMR (151 MHz, toluene-d_8): δ (ppm) = 166.0 ($C_{triazine}$), 140.1 (C_q), 131.7 (CH), 130.7 (C_q), 71.4-70.3 (OCH_2), 50.4, 48.9, 36.0 (NCH_3), 29.9 (CH_2), 29.1 (CH_2), 27.7 (CH_2), 27.0 (CH_2), 23.2 (CH_2), 14.4 (CH_3).
HRMS (FD): calcd for $C_{78}H_{112}N_{12}O_8Na$ m/z = 1367.8624; found m/z = 1367.8591.

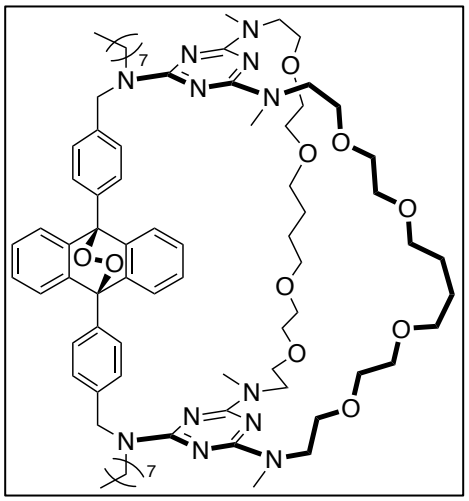


Cage 2a: To a solution of **2c** (25 mg, 0.019 mmol) in dry THF/MeOH (1:1, 2 mL) was added Pd/C (3 mg). The reaction flask was saturated with H_2 by consecutive cycles of vacuum/H_2. The mixture was stirred for 1 h, then filtered through a celite pad and eluted with EtOAc/MeOH (1:1, 5 mL). The solvent was evaporated under reduced pressure. The crude product was purified by preparative TLC (EtOAc/toluene, 1:1) to give **2a** as slightly yellow oil (25 mg, 100%). R_f = 0.64 (EtOAc/toluene, 1:1)

^{1}H NMR (600 MHz, toluene-d_8, 363 K): δ (ppm) = 7.81 (m, 4 H, Ar-H), 7.41 (d, 4 H, $J_{H,H}$ = 12.0 Hz, Ar-H), 7.26 (d, 4 H, Ar-H), 7.20 (m, 4 H, Ar-H), 4.87 (bs, 4 H, $CH_{2,bencine}$), 3.80 (bs, 4H, CH_2), 3.68, (bs, 4 H, CH_2), 3.55 (t, 8 H, J = 7.1 Hz, CH_2), 3.41 (t, 8 H, J = 8.9 Hz, CH_2), 3.30 (t, 8 H, J = 8.9 Hz, CH_2), 3.10 (s, 12 H, NCH_3), 3.04 (b, 8 H, OCH_2), 1.77 (m, 4 H, t, 8 H, J = 10.5 Hz, $NCH_2CH_2CH_2$), 1.30 (m, 28 H, $OCH_2CH_2CH_2CH_2O$, $(CH_2)_5CH_3$), 0.89 (m, 6 H, CH_3)

^{13}C NMR (151 MHz, toluene-d_8): δ (ppm) = 165.7 ($C_{triazine}$), 141.1 (C_q), 139.8 (C_q), 131.3 (CH), 130.3 (C_q), 123.3 (CH) 71.1-70.0 (OCH_2), 52.9, 48.6, 35.7 (NCH_3), 32.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 28.8 (CH_2), 27.4 (CH_2), 27.0 (CH_2), 22.8 (CH_2), 14.4 (CH_3)

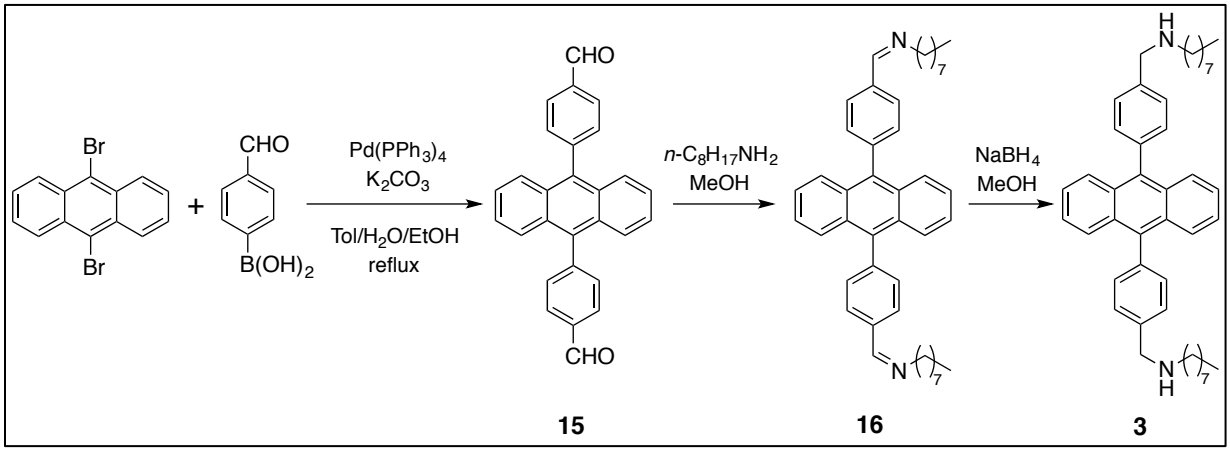
HRMS (FD): calcd for $C_{78}H_{114}N_{12}O_8$ m/z = 1346.8883; found m/z = 1346.8889.

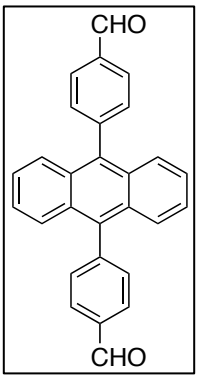


Cage 2b: To a solution of **2a** (1 mg) in dichloromethane (3 mL) was added a crystal of methylene blue. The solution was bubbled with O_2 for 15 min and irradiated for 30 min with visible light until complete conversion of the starting material (monitored by UV). The solution was evaporated, dissolved in EtOAc and filtered through celite. The solution was evaporated and further purified by filtration through a silica pad (CH_2Cl_2/MeOH, 9:1).

MS (FD): m/z = 1382.9 (M^+), 1347.9 ($M^+ - O_2$).

Synthesis of diamine 3



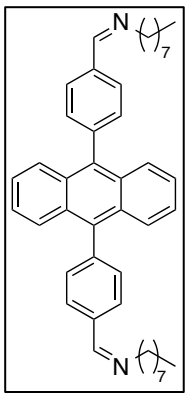


9,10-di(4-formylphenyl)anthracene[2] (**15**): To a solution of 4-formylphenyl boronic acid (10 g, 66.7 mmol) in a mixture of toluene (80 mL), water (40 mL) and ethanol (20 mL) in the dark under argon atmosphere was added 9,10-dibromoanthracene (10 g, 29.8 mmol) and potassium carbonate (20 g, 144.7 mmol). The reaction mixture was degassed using argon bubbling for 1 h. Then solid tetrakis(triphenylphosphine) palladium(0) (689 mg, 0.60 mmol) was added and the reaction mixture was heated to reflux for 24h in the dark. The reaction mixture was allowed to cool at room temperature and filtered. The solid was washed with toluene (10 mL), ethanol (25 mL), water (50 mL), ethanol (50 mL) and dried under vacuum for 24 h. Compound **15** was isolated as a yellow crystalline solid (11.28 g, 98%).

^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 10.20 (s, C**H**O, 2H), 8.13 (d, J = 8.1 Hz, C**H**, 4H), 7.66 (d, J = 8.1 Hz, C**H**, 4H), 7.60 (m, C**H**, 4H), 7.35 (m, C**H**, 4H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 192.2 (CHO), 146.0 (Cq), 136.4 (Cq), 136.0 (Cq), 132.3 (CH), 130.1 (CH), 129.6 (CH), 126.7 (CH), 125.9 (CH).

HRMS (FD): calcd for $C_{28}H_{18}O_2$ m/z = 386.1307; found m/z = 386.1325 $[M]^+$.



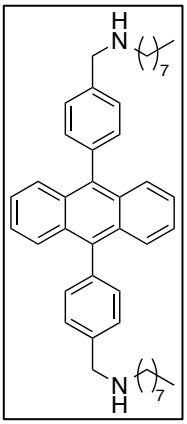
9,10-di(4-(octylimino)methylphenyl)anthracene (**16**): To a suspension of **15** (5 g, 12.9 mmol) in dry methanol (30 mL) was added *n*-octylamine (12.8 mL, 77.4 mmol). The reaction mixture was vigorously stirred at room temperature for 48 hours. Dry methanol (30 mL) was added, the reaction mixture was filtered and the solid was washed with methanol (3×50 mL) to remove the excess of amine. After drying under vacuum for 12 hours, product **16** was isolated as a pale yellow powder (7.75 g, 99%).

^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 8.44 (s, C**H**=N, 2H), 7.96 (d, J = 8.0 Hz, C**H**, 4H), 7.67 (m, C**H**, 4H), 7.52 (d, J = 8.0 Hz, C**H**, 4H), 7.31 (m, C**H**, 4H), 3.69 (t, J = 7.0 Hz, C**H$_2$**N, 4H), 1.76 (m, C**H$_2$**, 4H), 1.50-1.20 (m, C**H$_2$**, 20H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 160.6 (CHN), 141.6 (Cq), 136.9 (Cq), 136.0 (Cq), 131.9 (CH), 129.9 (Cq), 128.3 (CH), 127.0 (CH), 125.4 (CH), 62.2 (CH_2), 32.1 (CH_2), 31.3 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 27.7 (CH_2), 22.9 (CH_2), 14.4 (CH_3).

HRMS (FD): calcd for $C_{44}H_{52}N_2$ m/z = 608.4130; found m/z = 608.4135 $[M]^+$.

[2] (a) Y. Teki, S. Miyamoto, M. Nakatsuji, Y. Miura, *J. Am. Chem. Soc*, **2001**, *123*, 294-305; b) S. Kotha, A. K. Ghosh, *Synlett* **2002**, 451-452.

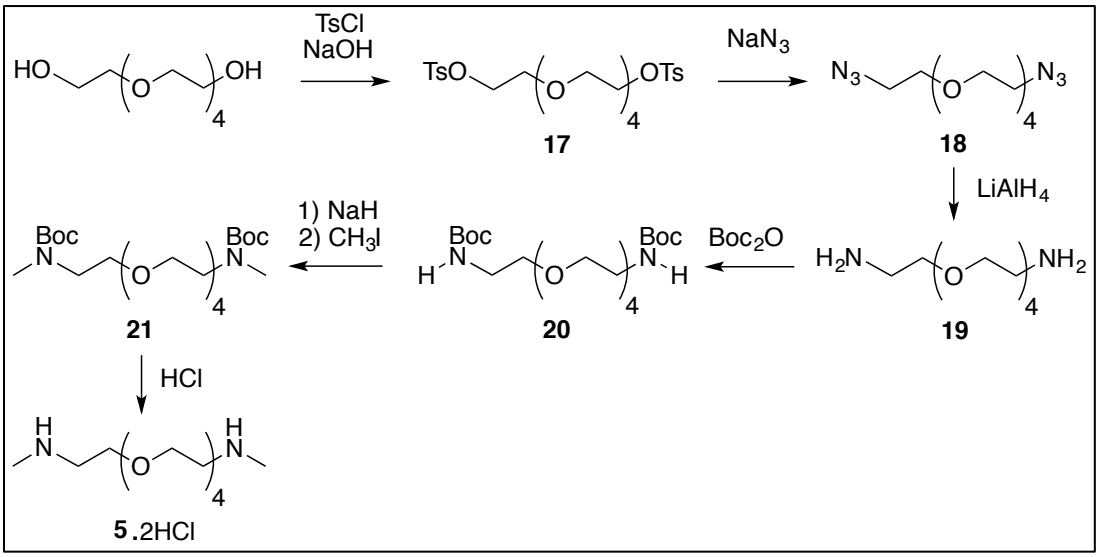


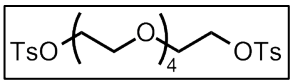
9,10-di(4-(octylamino)methylphenyl)anthracene (**3**): To a cold solution of sodium borohydride (3 g, 79.3 mmol) in dry methanol (100 mL) at 0°C under nitrogen atmosphere was added dropwise a solution of **16** (5 g, 8.2 mmol) in dichloromethane (100 mL) over 2 h. The reaction mixture was allowed to reach room temperature and stirred for 12 h. The reaction was quenched by adding dropwise a aqueous solution of hydrochloric acid (2N, 50 mL) at 0°C. Then, the volatile materials were removed under reduced pressure and the residue was suspended in an aqueous solution of sodium hydroxide (1M, 150 mL). The yellow solid was filtered and washed with an aqueous solution of sodium hydroxide (1 M, 2×50 mL) and water (3×50 mL). After drying under vacuum for 12 h, the yellow solid was recrystallized from boiling ethanol (60 mL) to yield to **3** as yellow crystals (4.85 g, 97%).

^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 7.69 (m, C**H**, 4H), 7.54 (d, J = 8.0 Hz, C**H**, 4H), 7.42 (d, J = 8.0 Hz, C**H**, 4H), 7.30 (m, C**H**, 4H), 3.95 (s, PhC$\mathbf{H}_2$, 4H), 2.77 (t, J = 7.1 Hz, C$\mathbf{H}_2$N, 4H), 1.60 (m, C$\mathbf{H}_2$CH$_2$N, 4H), 1.46-1.24 (m, C$\mathbf{H}_2$, 20H), 0.88 (t, J = 6.8 Hz, C$\mathbf{H}_3$, 6H).
^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 140.1 (Cq), 137.8 (Cq), 137.2 (Cq), 131.5 (CH), 130.1 (Cq), 128.3 (CH), 127.2 (CH), 125.1 (CH), 54.3 (CH_2), 50.1 (CH_2), 32.1 (CH_2), 30.4 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 27.7 (CH_2), 22.9 (CH_2), 14.3 (CH_3).
HRMS (FD): calcd for $C_{44}H_{56}N_2$ m/z = 612.4443; found m/z = 612.4437

Synthesis of diamine 5

The following synthesis of compound **19** (90% yield from pentaethyleneglycol) is adapted from literature[3] (34% yield over three steps).

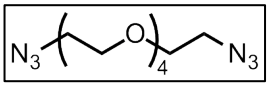




Pentaethyleneglycol-ditosylate [3] (**17**): To a cold solution (0°C) of pentaethyleneglycol (10 g, 42 mmol) in THF (75 mL) was added tosyl chloride (32 g, 170 mmol). The reaction mixture was stirred for 5 minutes at 0°C. A solution of potassium hydroxide (20 g, 340 mmol) in distilled water (50 mL) was added dropwise at 0°C. Then the reaction was was stirred at room temperature for 12 hours. After concentration under reduced pressure, the residue was poured in an ammonium chloride solution (5 M, 100 mL). The aqueous phase was extracted with dichloromethane (5×50 mL). The organic phases were collected, dried and evaporated under reduced pressure. Compound **17** is isolated as a colorless oil (22.5 g, 98%).

^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 7.77 (d, J = 8.3 Hz, C**H**, 4H), 7.31 (d, J = 8.3 Hz, C**H**, 4H), 4.13 (d, J = 4.8 Hz, TsOC**H$_2$**CH$_2$, 4H), 3.66 (d, J = 4,8 Hz, TsOCH$_2$C**H$_2$**, 4H), 3.58-3.55 (m, OC**H$_2$**C**H$_2$**O, 12H), 2.42 (s, C**H$_3$**, 6H).

HRMS (ESI): calcd for $C_{24}H_{34}O_{10}S_2$ m/z = 546.1593; found m/z = 569.1486 $[M + Na]^+$.

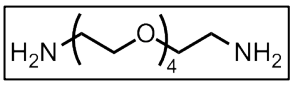


Pentaethyleneglycol-diazide[3] (**18**): To a solution of **17** (11 g, 20 mmol) in dry acetonitrile (50 mL) under argon was added sodium azide (6.5 g, 0.1 mol). The reaction mixture was refluxed for 18 hours. The reaction was cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by chromatography column (silica gel, hexane/ethyl acetate, 25:75). The product is a colorless liquid (5.5 g, 95 %).

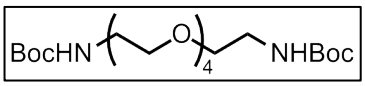
^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 3.68 (t, J = 5.0 Hz, N$_3$CH$_2$C**H$_2$**, 4H), 3.65 (s, OC**H$_2$**C**H$_2$**O, 12H), 3.36 (t, J = 5.0 Hz, N$_3$C**H$_2$**CH$_2$, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 73.5 (CH_2), 71.5 (CH_2), 53.8 (CH_2N_3).

HRMS (ESI): calcd for $C_{10}H_{20}N_6O_4$ m/z = 288.1546; found m/z = 311.1437 $[M + Na]^+$.

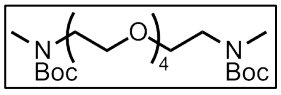
[3] Dorweiler, J. D.; Nemykin, V. N.; Ley, A. N.; Pike, R. D.; Berry, S. M. *Inorg. Chem.* **2009**, *48*, 9365–76.



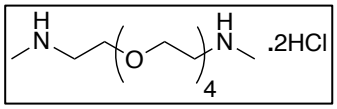
Pentaethyleneglycol-diamine[3] (**19**): To a cold suspension (-20°C) of $LiAlH_4$ (2.3 g, 60 mmol) in dry THF (200 mL) under argon was added dropwise a solution of **18** (12 g, 40 mmol) in dry THF (100 mL). Then reaction mixture was allowed to warm to room temperature and stirred for 12 hours. The reaction mixture was cooled to 0°C and a solution of sodium hydrogenocarbonate (10 %, 10 mL) was dropwise added. The mixture was stirred until the gray suspension turn white and filtered. The solid was washed with dry THF (2×50 mL) and the filtrate was evaporated under reduced pressure. Compound **19** was isolated as a pale yellow oil (9.1 g, 96 %).
^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 3.60 - 3.55 (m, OC**H₂**C**H₂**O, 12H), 3.44 (t, J = 5.2 Hz, $NH_2CH_2C\mathbf{H_2}$, 4H), 2.79 (t, J = 5.2 Hz, $NH_2C\mathbf{H_2}CH_2$, 4H), 1.50 (s, N**H₂**CH_2CH_2, 4H).
MS (ESI): calcd for $C_{10}H_{24}N_2O_4$ m/z = 236.2; found m/z = 222.2 $[M - NH_2 + H]^+$.



Pentaethyleneglycol-di-*tert*-butylcarbamate (**20**): To a cold solution (0°C) of di-*tert*-butyldicarbonate (11 g, 50 mmol) in THF (75 mL) was added a solution of **19** (5 g, 21 mmol) in THF (25 mL) and sodium hydrogenocarbonate (8.4 g, 100 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 4 hours. The reaction mixture was concentrated under reduced pressure. The residue was suspended in diethyl ether (50 mL) and washed with distilled water (100 mL) and brine (100 mL). The organic phases were collected and concentrated under reduced pressure. The crude product was purified by chromatography column (silica gel, hexane/ethyl acetate/methanol, 50:40:10). Compound **20** was isolated as a colorless oil (8.8 g, 96 %).
^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 5.05 (br, N**H**, 2H), 3.70 - 3.57 (m, OC**H₂**C**H₂**O, 12H), 3.52 (t, J = 5.1 Hz, $NCH_2C\mathbf{H_2}$, 4H), 3.30 (m, NC**H₂**CH_2, 4H), 1.42 (s, C**H₃**, 18H).
HRMS (ESI): calcd for $C_{20}H_{40}N_2O_8$ m/z = 436.5402; found m/z = 459.2684 $[M + Na]^+$.

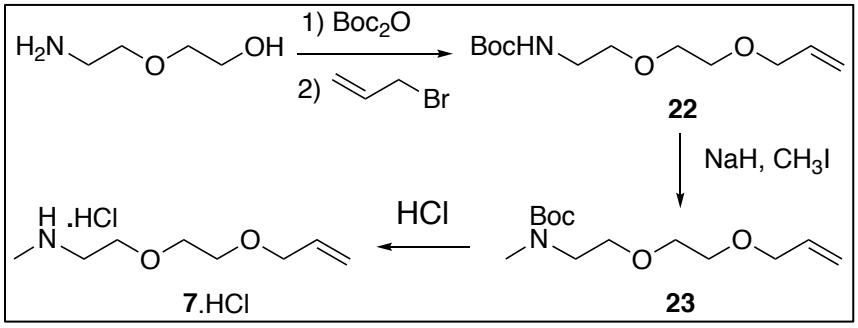


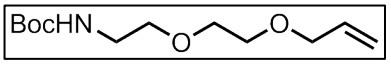
Pentaethyleneglycol-di-*tert*-butyl-*N*-methylcarbamate (**21**): To a suspension of sodium hydride (60% in mineral oil, 5 g, 120 mmol) in anhydrous THF (200 mL) under nitrogen at 0°C was added dropwise to a solution of **20** (13 g, 30 mmol) in anhydrous THF (50 mL). The reaction mixture was allowed to warm to room temperature and stirred for 2 hours. The reaction mixture was cooled to about 10°C and iodomethane (15 mL, 240 mmol) was added dropwise. After stirring at room temperature for 4 hours, the reaction was cooled at 0°C and quenched by the addition of an aqueous mixture of ammonium chloride and sodium thiosulfate (saturated solution, 1:1, 200 mL). After removing THF under reduced pressure, the aqueous solution was extracted with diethyl ether (4×50 mL). The combined organic phases were dried over magnesium sulfate and concentrated in vacuum. The colorless oil was purified by chromatography column (silica gel, hexane/ethyl acetate, 50:40). Compound **21** was isolated as a colorless oil (13.7 g, 98%).
^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 3.70 - 3.57 (m, OC**H₂**C**H₂**O, 12H), 3.56 (t, J = 5.7 Hz, $NCH_2C\mathbf{H_2}$, 4H), 3.36 (m, NC**H₂**CH_2, 4H), 2.88 (s, NC**H₃**, 6H), 1.43 (s, C**H₃**, 18H).
HRMS (ESI): calcd for $C_{22}H_{44}N_2O_8$ m/z = 464.5934; found m/z = 487.2982 $[M + Na]^+$, 365.2652 [M - Boc +Na]$^+$.



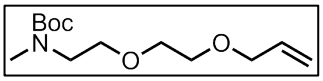
Pentaethyleneglycol-diammonium dichloride (**5**.2HCl)**:** To a solution of **21** (10 g, 21.5 mmol) in anhydrous diethyl ether (10 mL) was added a solution of hydrogen chloride in 1,4-dioxane (4 M, 50 mL). The reaction mixture was stirred for 24 hours. After concentration in vacuum, the product was dried for 12 hours under reduced pressure. Compound **5.**2HCl was isolated as a white hygroscopic solid (7.2 g, 99%).
^{1}H NMR (300MHz, D_2O): δ (ppm) = 3.82 (t, J = 4.9 Hz, C**H₂**CH_2N, 4H), 3.77 – 3.69 (m, C**H₂**O, 12H) 3.29 (t, J = 4.9 Hz, C**H₂**N, 4H), 2,78 (s, C**H₃**, 6H). ^{13}C NMR (75MHz, D_2O): δ (ppm) = 69.6 (CH_2), 65.3 (CH_2), 48.4 (CH_2), 32.7 (CH_3).

Synthesis of allyl amine 7

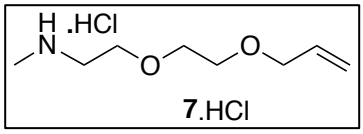




***tert*-butyl (2-(2-(allyloxy)ethoxy)ethyl)carbamate** (**22**): To a solution of 2-(2-aminoethoxy)ethanol (20 mL, 0.2 mol) in THF (50 mL) at 0°C was added dropwise a solution of di-tert-butyl-dicarbonate (43 g, 0.2 mol) in THF (50 mL) over 1 hour. The reaction mixture was then allowed to stir at room temperature for 2 hours. Allyl bromide (52 mL, 0.6 mol) was added. The reaction mixture was cooled to 0°C and a solution of sodium hydroxide (16 g, 0.4 mmol) in deionized water (50 mL) was added dropwise over 2 hours. The reaction mixture was stirred at room temperature for 12 hours. A saturated aqueous solution of ammonium chloride (100 mL) was added and the biphasic mixture was concentrated under reduced pressure to remove THF. The aqueous residue was extracted with diethyl ether (5×50 mL), dried over magnesium sulfate, and evaporated to yield a pale yellow oil which was purified by chromatography column (SiO_2, hexane/AcOEt, 80:20). Compound **22** was isolated as a colorless oil (40.2 g, 81 %).
^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 5.93-5.78 (m, H_2C=C**H**-C, 1H), 5.25-5.09 (m, **H₂**C=CH, 2H), 5.01 (br, N**H**, 1H), 3.96 (dt, J_d= 5.6 Hz, J_t= 1.3 Hz, C**H₂**-CH, 2H), 3.59-3.50 (m, C**H₂**O, 4H), 3.48 (t, J = 5.2Hz, NCH_2C**H₂**, 2H), 3.25 (m, NC**H₂**, 2H), 1.37 (s, C**H₃**, 9H).
^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 156.1 (C_q), 134.7, 117.3, 72.3, 70.4, 70.3, 69.4, 40.5, 28.5.
HRMS (ESI): calcd for $C_{12}H_{23}NO_4$ m/z = 245.1627; found m/z = 212.0923 $[M - tBu + Na]^+$, 268.1517 $[M + Na]^+$.

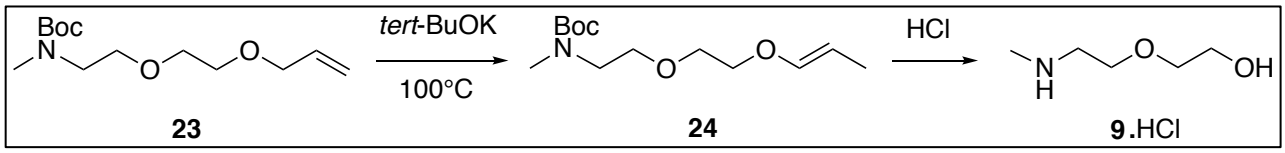


***tert*-butyl (2-(2-(allyloxy)ethoxy)ethyl)(*N*-methyl)carbamate** (**23**): To a suspension of sodium hydride (60% in mineral oil, 4g, 100 mmol) in anhydrous THF (250 mL) under nitrogen at 0°C was added dropwise a solution of **22** (12.5 g, 50 mmol) in anhydrous THF (50 mL). The reaction mixture was allowed to warm to room temperature and stirred for 1 hour. The reaction mixture was cooled to about 10°C and iodomethane (12.5 mL, 200 mmol) was added dropwise. The reaction stirred at room temperature for 2 hours. The reaction was quenched by dropwise addition at 0°C of an aqueous mixture of ammonium chloride and sodium thiosulfate (saturated solution, 1:1, 200 mL). After concentration under reduced pressure, the residue was extracted with diethyl ether (3×50 mL), dried over magnesium sulfate and concentrated under vacuum. The colorless oil was purified by chromatography column (silica gel, hexane/ethyl acetate, 80:20) to remove the mineral oil. Compound **23** was isolated as a colorless oil (12.58 g, 97%).
^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) = 5.97-5.76 (m, H_2C=C**H**-C, 1H), 5.31-5.08 (m, **H₂**C=CH, 2H), 3.99 (dt, J_d= 5.8 Hz, J_t= 1.3 Hz, C**H₂**-CH, 2H), 3.62-3.50 (m, C**H₂**-O, 6H), 3.36 (t, J = 5.7 Hz, C**H₂**-N, 2H), 2.88 (s, N-C**H₃**, 3H), 1.42 (s, C**H₃**, 9H).
^{13}C NMR (75MHz, $CDCl_3$): δ (ppm) = 155.5 (CO), 134.5 (**C**H=CH_2), 116.9 (CH=**C**H_2), 79.1 (C_q), 72.0, 70.3, 69.4, 69.3, 48.4, 35.4, 28.3.
HRMS (ESI): calcd for $C_{13}H_{25}NO_4$ m/z = 259.1784; found m/z = 226.1065 $[M - tBu + Na]^+$, 282.1668 $[M + Na]^+$.



2-(2-(allyloxy)ethoxy)-*N*-methylethane ammonium chloride (7.HCl**):** To a solution of **23** (10 g, 39 mmol) in anhydrous diethyl ether (10 mL) was added a solution of hydrogen chloride (4 M in 1,4-dioxane, 40 mL). The reaction mixture was stirred for 12 hours, then the volatile materials were evaporated. After drying for 12 hours under reduced pressure, amine **7**.HCl was obtained as a viscous oil (7.4 g, 98%).
^{1}H NMR (300 MHz, D_2O): δ (ppm) = 6.01-5.82 (m, H_2C=C**H**-C, 1H), 5.42-5.11 (m, **H_2**C=CH, 2H), 4.01 (dt, J_d= 5.7 Hz, J_t= 1.4 Hz, C**H_2**-CH, 2H), 3.82 (t, J = 5.0 Hz, C**H_2**CH_2N, 2H), 3.74 – 3.65 (m, C**H_2**O, 4H) 3.31 (t, J = 4.9 Hz, C**H_2**N, 2H), 2,78 (s, C**H_3**, 3H).
^{13}C NMR (75 MHz, D_2O): δ (ppm) =133.6, 118.8, 71.8, 69.6, 68.8, 65.2, 48.4, 32.7.
LRMS (FD): calc. for $C_8H_{18}NO_2^+$ m/z = 160.1; found m/z = 160.1 $[M]^+$; 182.1 $[M – H + Na]^+$

Synthesis of amino-alcohol 9



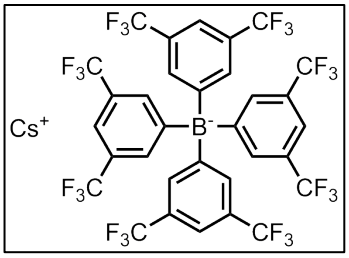
The isomerization of allylether in ether **23** was achieved according a procedure[4] from literature.

***tert*-butyl (2-(2-(2-methylvinyloxy)ethoxy)ethyl)(*N*-methyl)carbamate** (**24**): to a solution of *t*-BuOK (370 mg, 3 mmol) in dry dimethylsulfoxide (16 mL) under nitrogen was added compound **23** (0.778 g, 3 mmol). The reaction mixture was rapidly heated to 100°C and stirred 15 min at this temperature. After cooling at room temperature, the reaction mixture was poured on distilled water (100 mL). The aqueous solution was extracted with diethyl ether (4×25 mL). The combined organic phases were washed with brine (100 mL), dried over magnesium sulfate and concentrated under vacuum. Compound **24** was isolated as a colourless oil (370 mg, 50%) and used without purification.
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 5.67 (m, C**H**(vinyl), 1H) ; 4.09 (m, C**H**(vinyl), 1H) ; 3.55 (t, J=4.8Hz, C**H_2**, 2H) ; 3.25-3.35 (m, C**H_2**, 4H) ; 3.09 (br, C**H_2**, 2H) ; 2.61 (s, C**H_3**-N, 3H) ; 1.28 (dd, J_1=1.8Hz, J_2=6.9Hz, C**H_3**-CH=CH, 3H) ; 1.15 (s, **tBu**, 9H).

2-(2-hydroxyethoxy)-*N*-methylethane ammonium chloride (9.HCl**)**: To a solution of **24** (343 mg, 1.3 mmol) in dry dioxane (2 mL) was added a solution of hydrogen chloride in dioxane (4M, 2 mL) under nitrogen. The reaction mixture was stirred at room temperature for 48 h and concentrated in vacuum. After drying under reduced pressure for 6h, the crude solid was washed with diethylether (3×5 mL) and dried under reduced pressure. Compound **9**.HCl was isolated as a beige solid (150 mg, 72%).
^{1}H NMR (D_2O, 300 MHz): δ (ppm) 3.80 (t, J=4.2Hz, C**H_2**, 2H) ; 3.75 (t, J=3.3Hz, C**H_2**, 2H) ; 3.66 (br, C**H_2**, 2H) ; 2.76 (s, C**H_3**, 3H).
^{13}C NMR (D_2O, 200 MHz): δ (ppm) 71.8, 65.2, 60.5, 48.4, 32.7.
LRMS (TOF): calc. for $C_5H_{14}NO_2^+$ m/z = 120.1; found m/z = 120.1 [M, 100%]$^+$

[4] J. Cunningham, R. Gigg, G. D. Warren, *Tet. Lett*. **1964**, *5*, 1191-1196.

Synthesis of $CsBAr_F$



Cesium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[5]: A solution of $NaBAr_F$ (200 mg, 0.23 mmol) was heated in milliQ water (90 mL) to 90°C. Then, a solution of cesium nitrate (220 mg, 1.1 mmol) in milliQ water (10 mL) was added. A white precipitate was formed instantly. The solution was heated at 90°C for 30 minutes and then cooled slowly to room temperature. The reaction mixture was filtered and the solid was washed with milliQ water (3×20 mL) and dried under vacuum for 48 h. $CsBAr_F$ was isolated as a white solid (216 mg, 94%).

^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 7.70 (m, C**H**, 8H), 7.67 (s, C**H**, 4H).
^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 162.3 (Cq, $^1J_{C\text{-}B}$ = 50 Hz), 135.4 (CH), 129.6 (Cq, $^2J_{CF}$ = 31 Hz), 125.2 (C_q, $^1J_{C\text{-}F}$ = 273 Hz), 118.0 (CH).
^{19}F NMR (376 MHz, CD_3CN): δ (ppm) = - 64.46 (s).
^{11}B NMR (128 MHz, CD_3CN): δ (ppm) = - 6.70 (s).
^{133}Cs NMR (52 MHz, CD_3CN): δ (ppm) = 22.31 (s).

Optimization of Ring-closure Metathesis and use of $NaBAr_F$ template

Table S1. Optimization of Ring-closure metathesis to prepare cage **1c** from macrocycle **8**.[a]

Entry	*Catalyst (10 mol%)*	*Solvent*	*Conc. (mM)*	*Temperature (°C)*	*Yield (%)* [b]
1	Grubbs (II)	CH_2Cl_2	10	R.T.	0 (5)
2	Grubbs (II)	CH_2Cl_2	10	40	0 (100)
3	Grubbs (II)	CH_2Cl_2	5	40	5 (100)
4	Grubbs (II)	Toluene	5	80	0 (50)
5	Grubbs 1st Gen.	CH_2Cl_2	5	40	0 (40)
6	Grubbs (II) + $NaBAr_F$ (1eq)	CH_2Cl_2	5	40	**98 (100)** [c]

[a] Reactions were conducted under argon and in the dark, for 24h. [b] % conversion is indicated into bracket. [c] reaction conducted in 4h.

[5] A. Vidal-Ferran, I. Mon, A. Bauza, A. Frontera, L. Rovira, *Chem. Eur. J.* **2015**, *21*, 11417-11426.

Table S2. Optimization of Ring-closure metathesis to prepare macrocycle **13** from **10**.[a]

Entry	*Catalyst (10 mol%)*	*Solvent*	*Conc. (mM)*	*Temp. (°C)*	*Yield (%)*[b]
1	Grubbs (II)	CH_2Cl_2	10	R.T.	5 (5)
2	Grubbs (II)	Toluene	10	R.T.	0 (2)
3	Grubbs (II)	CH_2Cl_2	10	40	30 (100)
4	Grubbs (II)	Toluène	10	80	0 (60)
5	Grubbs (II)	CH_2Cl_2	5	40	**94 (100)** [c]
6	Grubbs (II)	Toluene	5	80	20 (50)
7	Grubbs 1st Gen.	CH_2Cl_2	5	40	46 (50)

[a] Reactions were conducted under argon and in the dark, for 24h. [b] % conversion is indicated into bracket. [c] reaction conducted in 4h.

Table S3. Optimization of Ring-closure metathesis to prepare cage **2c** from macrocycle **14**.[a]

Entry	*Catalyst (10 mol%)*	*Solvent*	*Conc. (mM)*	*Temp. (°C)*	*Yield (%)*
1	Grubbs (II) + NaBARF	CH_2Cl_2	5	40	95 (6h)
2	Grubbs (II)	CH_2Cl_2	5	40	3 (24h)
3	Grubbs 1st Gen. + NaBARF	CH_2Cl_2	5	40	45 (12h)

[a] Reactions were conducted under argon and in the dark. Reaction time is indicated into bracket.

Crystallographic Data

Crystal data and structure refinement for 9,10-di(4-(octylamino)methylphenyl)anthracene (3).

CCDC Number	1541525
Empirical formula	$C_{22}H_{28}N$
Formula weight	306.45
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 5.899(2) A alpha = 83.465(9)° b = 7.547(3) A beta = 84.681(10)° c = 20.535(8) A gamma = 82.512(8)°
Volume	897.7(6) A^3
Z, Calculated density	2, 1.134 Mg/m^3
Absorption coefficient	0.065 mm^{-1}
F(000)	334
Crystal size	0.25 x 0.20 x 0.02 mm
Theta range for data collection	2.00 to 25.72 deg.
Limiting indices	-7<=h<=6, -9<=k<=9, -24<=l<=24
Reflections collected / unique	10626 / 3361 [R(int) = 0.0553]
Completeness to theta = 25.72	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9987 and 0.9840
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3361 / 0 / 262
Goodness-of-fit on F^2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1117
R indices (all data)	R1 = 0.0942, wR2 = 0.1293
Extinction coefficient	0.023(4)
Largest diff. peak and hole	0.207 and -0.203 $e.A^{-3}$

Table S4A. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	9442(4)	23006(3)	4476(1)	49(1)
C(17)	4545(3)	6230(2)	491(1)	20(1)
C(11)	3420(3)	10000(2)	1966(1)	22(1)
C(20)	6429(3)	4883(2)	522(1)	20(1)
C(18)	3102(3)	6358(2)	-28(1)	20(1)
C(7)	5728(3)	15224(3)	2897(1)	30(1)
N(9)	4597(3)	12591(2)	2448(1)	30(1)
C(5)	6974(3)	17829(3)	3411(1)	30(1)
C(10)	2965(3)	11283(2)	2493(1)	27(1)
C(4)	6577(3)	19022(3)	3972(1)	31(1)
C(14)	4121(3)	7544(2)	999(1)	20(1)
C(6)	5262(4)	16474(3)	3441(1)	31(1)
C(3)	8237(4)	20413(3)	3942(1)	33(1)
C(13)	2229(3)	7546(3)	1462(1)	24(1)
C(8)	4018(4)	13870(3)	2940(1)	31(1)
C(22)	9783(3)	3398(2)	1070(1)	24(1)
C(23)	10261(3)	2203(3)	576(1)	23(1)
C(12)	1880(3)	8762(2)	1931(1)	26(1)
C(16)	5297(3)	10002(2)	1506(1)	24(1)
C(21)	7923(3)	4672(2)	1045(1)	22(1)
C(2)	7767(4)	21619(3)	4496(1)	37(1)
C(15)	5633(3)	8800(2)	1030(1)	23(1)
C(19)	1144(3)	7695(2)	-84(1)	22(1)

Table S4B. Bond lengths [A] and angles [deg] for **3**.

C(1)-C(2)	1.525(3)
C(17)-C(20)	1.406(2)
C(17)-C(18)	1.412(3)
C(17)-C(14)	1.503(2)
C(11)-C(16)	1.387(2)
C(11)-C(12)	1.397(3)
C(11)-C(10)	1.515(2)
C(20)-C(21)	1.434(3)
C(20)-C(18)#1	1.441(2)
C(18)-C(19)	1.436(3)
C(18)-C(20)#1	1.441(2)
C(7)-C(8)	1.517(3)
C(7)-C(6)	1.526(3)
N(9)-C(10)	1.456(2)
N(9)-C(8)	1.464(2)
C(5)-C(6)	1.521(3)
C(5)-C(4)	1.524(3)
C(4)-C(3)	1.519(3)
C(14)-C(15)	1.393(3)
C(14)-C(13)	1.397(2)
C(3)-C(2)	1.520(3)
C(13)-C(12)	1.388(3)
C(22)-C(21)	1.362(3)
C(22)-C(23)	1.418(3)
C(23)-C(19)#1	1.354(3)
C(16)-C(15)	1.392(3)
C(19)-C(23)#1	1.354(3)
C(20)-C(17)-C(18)	119.44(16)
C(20)-C(17)-C(14)	119.81(18)
C(18)-C(17)-C(14)	120.74(17)
C(16)-C(11)-C(12)	117.73(16)
C(16)-C(11)-C(10)	123.08(16)
C(12)-C(11)-C(10)	119.19(15)
C(17)-C(20)-C(21)	121.71(16)
C(17)-C(20)-C(18)#1	120.57(18)
C(21)-C(20)-C(18)#1	117.72(17)
C(17)-C(18)-C(19)	122.06(16)
C(17)-C(18)-C(20)#1	120.00(17)
C(19)-C(18)-C(20)#1	117.94(19)
C(8)-C(7)-C(6)	112.95(16)
C(10)-N(9)-C(8)	112.25(15)
C(6)-C(5)-C(4)	113.88(16)
N(9)-C(10)-C(11)	113.97(14)
C(3)-C(4)-C(5)	114.61(16)
C(15)-C(14)-C(13)	117.43(16)
C(15)-C(14)-C(17)	120.77(15)
C(13)-C(14)-C(17)	121.79(16)
C(5)-C(6)-C(7)	113.80(16)
C(4)-C(3)-C(2)	113.62(16)
C(12)-C(13)-C(14)	120.83(17)
N(9)-C(8)-C(7)	112.21(16)
C(21)-C(22)-C(23)	120.0(2)
C(19)#1-C(23)-C(22)	120.24(19)
C(13)-C(12)-C(11)	121.49(16)
C(11)-C(16)-C(15)	120.83(17)

C(22)-C(21)-C(20)	122.03(18)
C(3)-C(2)-C(1)	114.15(17)
C(16)-C(15)-C(14)	121.66(16)
C(23)#1-C(19)-C(18)	122.03(18)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

Table S4C. Anisotropic displacement parameters (A^2 x 10^3) for **3**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	58(2)	41(1)	53(2)	-12(1)	-10(1)	-14(1)
C(17)	17(1)	16(1)	27(1)	-2(1)	1(1)	-6(1)
C(11)	22(1)	18(1)	25(1)	-2(1)	-4(1)	0(1)
C(20)	17(1)	17(1)	27(1)	-2(1)	-1(1)	-7(1)
C(18)	17(1)	15(1)	29(1)	-1(1)	0(1)	-6(1)
C(7)	34(1)	26(1)	32(1)	-8(1)	-3(1)	-4(1)
N(9)	35(1)	26(1)	30(1)	-11(1)	0(1)	-7(1)
C(5)	32(1)	27(1)	31(1)	-7(1)	-1(1)	-2(1)
C(10)	26(1)	24(1)	29(1)	-4(1)	-1(1)	-2(1)
C(4)	34(1)	28(1)	31(1)	-6(1)	-1(1)	-6(1)
C(14)	19(1)	16(1)	25(1)	-2(1)	-5(1)	-1(1)
C(6)	35(1)	28(1)	33(1)	-10(1)	1(1)	-4(1)
C(3)	36(1)	30(1)	34(1)	-6(1)	-2(1)	-6(1)
C(13)	20(1)	22(1)	32(1)	-2(1)	-2(1)	-7(1)
C(8)	35(1)	27(1)	33(1)	-11(1)	0(1)	-3(1)
C(22)	22(1)	19(1)	31(1)	-2(1)	-7(1)	-4(1)
C(23)	18(1)	17(1)	35(1)	0(1)	-4(1)	-1(1)
C(12)	23(1)	26(1)	28(1)	-4(1)	3(1)	-3(1)
C(16)	18(1)	18(1)	36(1)	-4(1)	-4(1)	-5(1)
C(21)	22(1)	18(1)	28(1)	-4(1)	-1(1)	-6(1)
C(2)	45(1)	31(1)	36(1)	-10(1)	-5(1)	-7(1)
C(15)	20(1)	20(1)	30(1)	-5(1)	1(1)	-4(1)
C(19)	18(1)	15(1)	32(1)	-3(1)	0(1)	-3(1)

Table S4D. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3**.

	x	y	z	U(eq)
H(1A)	10998	22390	4517	73
H(1B)	9012	23748	4840	73
H(1C)	9391	23773	4058	73
H(15)	6900(30)	8850(20)	686(9)	26(5)
H(16)	6370(30)	10760(30)	1517(9)	25(5)
H(8B)	2410(30)	14540(30)	2899(10)	30(5)
H(8A)	3980(30)	13150(30)	3415(10)	34(6)
H(6A)	3640(30)	17100(30)	3424(9)	30(5)
H(6B)	5240(40)	15760(30)	3870(12)	44(7)
H(12)	550(30)	8760(30)	2254(10)	32(5)
H(13)	1130(30)	6690(30)	1446(9)	27(5)
H(21)	7600(30)	5440(20)	1390(9)	21(5)
H(23)	11560(30)	1300(30)	600(9)	25(5)
H(19)	780(30)	8510(30)	261(10)	27(5)
H(22)	10810(30)	3310(30)	1425(10)	28(6)
H(9)	4620(40)	13150(30)	2034(11)	39(7)
H(7A)	5678	15954	2465	36
H(7B)	7291	14572	2923	36
H(5A)	6892	18601	2989	36
H(5B)	8540	17174	3419	36
H(10A)	1403	11933	2461	32
H(10B)	3003	10577	2929	32
H(4A)	4996	19652	3971	37
H(4B)	6692	18249	4394	37
H(3A)	8154	21171	3516	39
H(3B)	9817	19786	3957	39
H(2A)	7828	20858	4921	44
H(2B)	6194	22255	4476	44

Crystal data and structure refinement for 9,10-di(4-formylphenyl)anthracene (15).

CCDC Number	1541528
Empirical formula	$C_{28}H_{18}O_2$
Formula weight	386.42
Temperature	120(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 13.0175(5) A alpha = 90° b = 9.3290(3) A beta = 106.370(2)° c = 8.3512(3) A gamma = 90°
Volume	973.06(6) A^3
Z, Calculated density	2, 1.319 Mg/m^3
Absorption coefficient	0.645 mm^{-1}
F(000)	404
Crystal size	0.19 x 0.17 x 0.02 mm
Theta range for data collection	3.54 to 65.86 deg.
Limiting indices	-15<=h<=15, -11<=k<=7, -9<=l<=8
Reflections collected / unique	10846 / 1662 [R(int) = 0.0320]
Completeness to theta = 65.86	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9872 and 0.8873
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1662 / 0 / 136
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0922
R indices (all data)	R1 = 0.0382, wR2 = 0.0952
Largest diff. peak and hole	0.142 and -0.160 $e.A^{-3}$

Table S5A. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **15.**

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(10)	4975(1)	611(1)	1539(1)	29(1)
C(9)	4015(1)	406(1)	278(2)	29(1)
C(6)	2968(1)	825(1)	567(1)	30(1)
C(15)	5979(1)	204(1)	1259(1)	29(1)
C(12)	5935(1)	1427(1)	4329(2)	35(1)
O(1)	-449(1)	3149(1)	1010(1)	59(1)
C(11)	5000(1)	1226(1)	3120(2)	33(1)
C(14)	6942(1)	466(1)	2557(2)	32(1)
C(13)	6924(1)	1054(1)	4039(2)	35(1)
C(5)	2536(1)	2182(1)	106(2)	35(1)
C(8)	1447(1)	255(1)	1558(2)	36(1)
C(7)	2417(1)	-133(1)	1299(2)	33(1)
C(3)	1017(1)	1605(1)	1083(2)	35(1)
C(2)	-9(1)	2008(2)	1391(2)	45(1)
C(4)	1567(1)	2570(1)	364(2)	36(1)

Table S5B. Bond lengths [A] and angles [deg] for **15**.

C(10)-C(9)	1.4025(17)
C(10)-C(11)	1.4313(17)
C(10)-C(15)	1.4424(16)
C(9)-C(15)#1	1.4058(17)
C(9)-C(6)	1.5004(15)
C(6)-C(7)	1.3917(17)
C(6)-C(5)	1.3941(18)
C(15)-C(9)#1	1.4058(17)
C(15)-C(14)	1.4286(17)
C(12)-C(11)	1.3584(18)
C(12)-C(13)	1.4184(17)
O(1)-C(2)	1.208(2)
C(14)-C(13)	1.3597(18)
C(5)-C(4)	1.3857(17)
C(8)-C(7)	1.3873(17)
C(8)-C(3)	1.3901(19)
C(3)-C(4)	1.3875(19)
C(3)-C(2)	1.4782(17)
C(9)-C(10)-C(11)	122.08(10)
C(9)-C(10)-C(15)	119.92(11)
C(11)-C(10)-C(15)	117.99(11)
C(10)-C(9)-C(15)#1	120.51(10)
C(10)-C(9)-C(6)	120.06(10)
C(15)#1-C(9)-C(6)	119.43(10)
C(7)-C(6)-C(5)	119.07(11)
C(7)-C(6)-C(9)	120.49(10)
C(5)-C(6)-C(9)	120.45(10)
C(9)#1-C(15)-C(14)	122.16(10)
C(9)#1-C(15)-C(10)	119.57(11)
C(14)-C(15)-C(10)	118.27(10)
C(11)-C(12)-C(13)	120.38(11)
C(12)-C(11)-C(10)	121.55(11)
C(13)-C(14)-C(15)	121.51(11)
C(14)-C(13)-C(12)	120.28(11)
C(4)-C(5)-C(6)	120.58(11)
C(7)-C(8)-C(3)	120.14(11)
C(8)-C(7)-C(6)	120.41(11)
C(4)-C(3)-C(8)	119.75(11)
C(4)-C(3)-C(2)	120.79(12)
C(8)-C(3)-C(2)	119.44(12)
O(1)-C(2)-C(3)	124.27(14)
C(5)-C(4)-C(3)	120.05(12)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z

Table S5C. Anisotropic displacement parameters (A^2 x 10^3) for **15**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(10)	32(1)	24(1)	34(1)	2(1)	15(1)	0(1)
C(9)	30(1)	25(1)	35(1)	3(1)	15(1)	1(1)
C(6)	28(1)	32(1)	30(1)	-3(1)	11(1)	0(1)
C(15)	30(1)	24(1)	34(1)	2(1)	13(1)	0(1)
C(12)	41(1)	32(1)	34(1)	-5(1)	14(1)	-2(1)
O(1)	38(1)	75(1)	66(1)	-15(1)	15(1)	16(1)
C(11)	34(1)	30(1)	38(1)	-2(1)	17(1)	1(1)
C(14)	30(1)	31(1)	38(1)	2(1)	13(1)	1(1)
C(13)	35(1)	33(1)	37(1)	-1(1)	8(1)	-2(1)
C(5)	35(1)	34(1)	41(1)	3(1)	18(1)	2(1)
C(8)	33(1)	42(1)	37(1)	-4(1)	16(1)	-7(1)
C(7)	34(1)	31(1)	37(1)	0(1)	14(1)	-1(1)
C(3)	28(1)	46(1)	31(1)	-9(1)	9(1)	0(1)
C(2)	32(1)	63(1)	42(1)	-15(1)	11(1)	1(1)
C(4)	34(1)	38(1)	37(1)	0(1)	11(1)	8(1)

Table S5D. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **15**.

	x	y	z	U(eq)
H(2)	-357	1262	1969	50
H(12)	5928	1819	5375	42
H(11)	4346	1499	3329	39
H(14)	7611	223	2381	39
H(13)	7576	1215	4883	42
H(5)	2909	2846	-388	42
H(8)	1076	-405	2061	43
H(7)	2706	-1058	1623	40
H(4)	1280	3497	48	43

Photophysical and Photochemical properties of Cages 1–2

1) Cages 1a–b

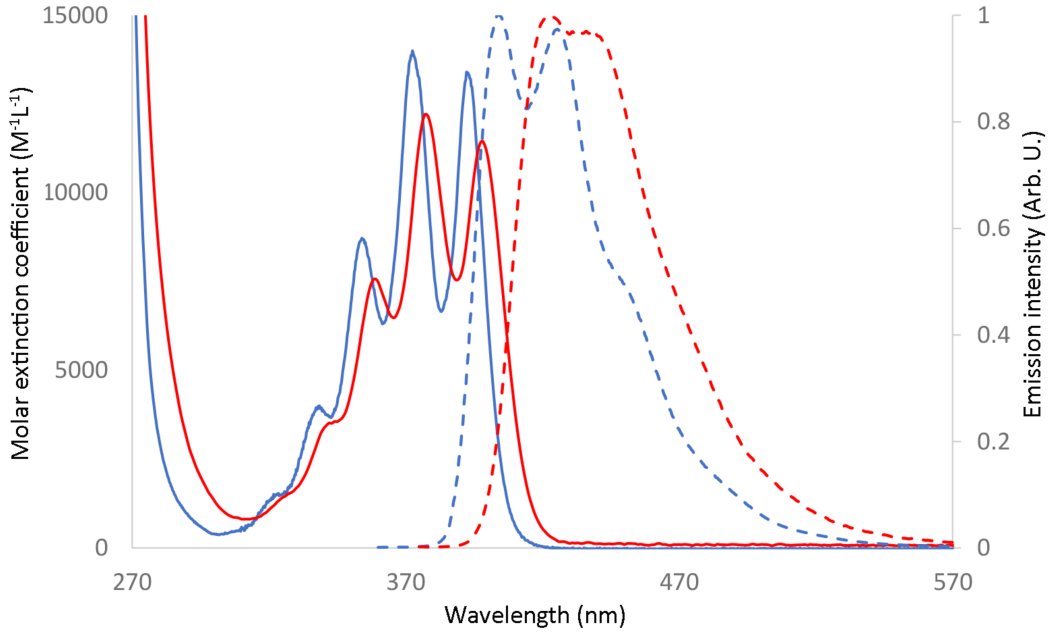


Figure S1. UV-Visible (solid line) and normalized fluorescence emission (dashed lines, λ_{exc} = 365 nm) spectra of 9,10-diphenylanthracene (blue) and cage **1a** (red) in dichloromethane at 298 K.

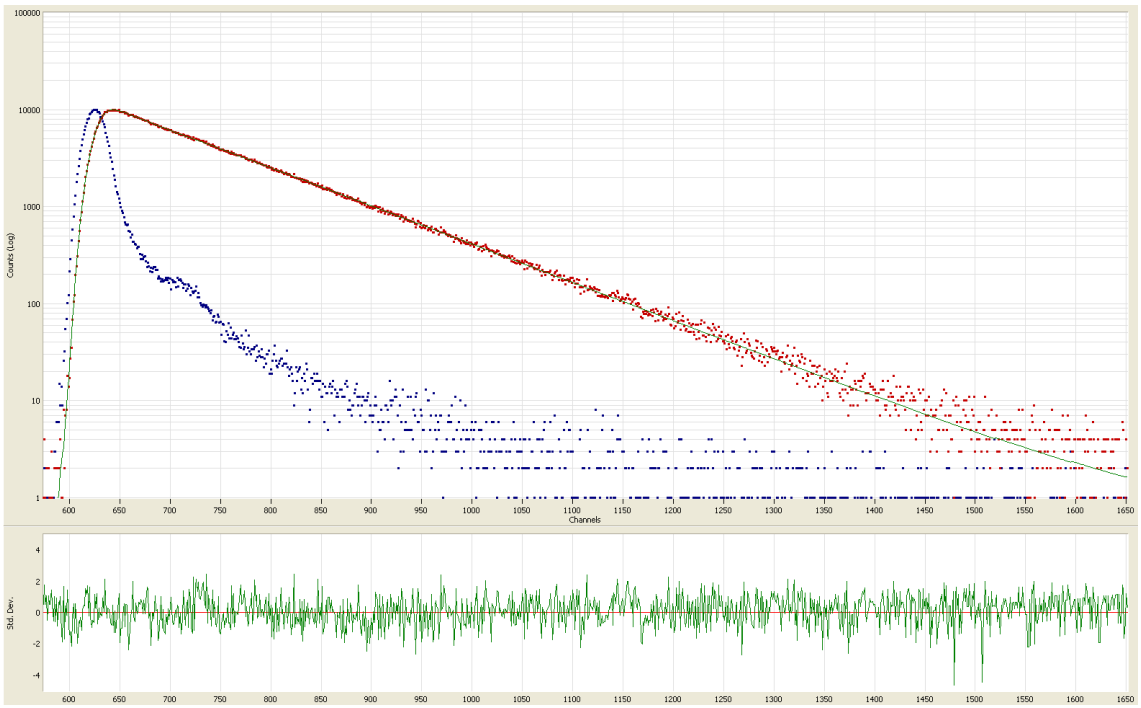


Figure S2. Fluorescence intensity decay of cage **1a** in dichloromethane solution (λ_{ex} = 371 nm, λ_{em} = 425 nm). Red points and green line denote experimental points and fit (τ = 6.1 ns, χ2 = 1.02), respectively.

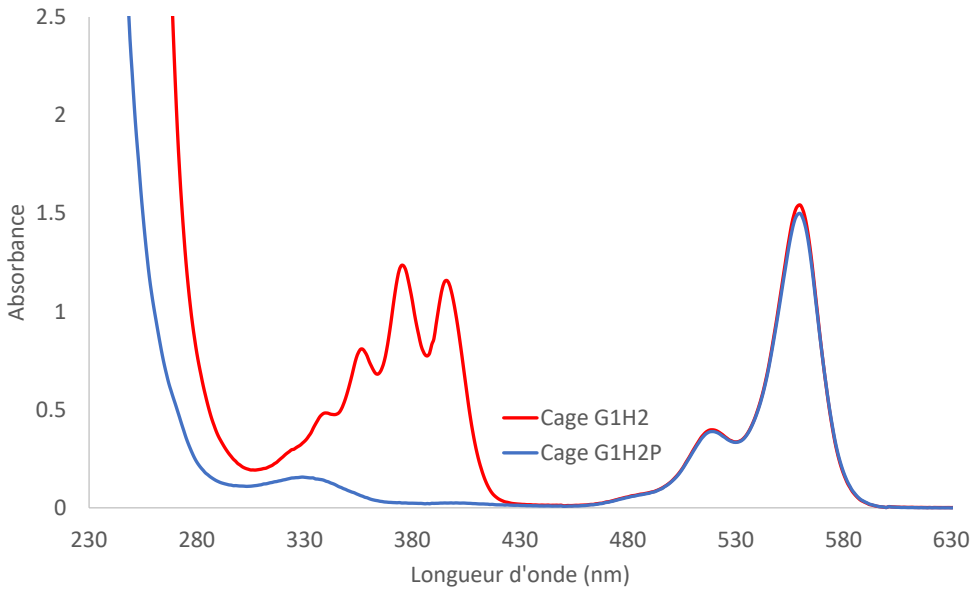


Figure S3. UV-visible spectra of cages **1a** (15 µM, red) et **1b** (15 µM, blue) in the presence of methylene blue, in propylene carbonate at 298K.

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Fatigue Cycles:

The experiment was achieved in a fluorescence cell equipped with a glass tube connected to a Schlenk flask. To an aerated solution of **1a** (0.1 mM, 3 mL) in propylene carbonate was added methylene blue (1% mol). Irradiation was conducted with a Tungsten lamp (60 W) to transform **1a** into cage **1b** at room temperature. After about 1h30, the reaction is complete. Cycloreversion towards **1a** was conducted by stirring at 140°C under argon for about 2h. All reactions were monitored by UV-Visible spectrophotometry, at 359, 377 and 397 nm wavelength.

Table S6. UV-Vis. monitoring of **1a** at 375 nm, along addition/cycloreversion cycles of dioxygen in propylene carbonate.[a]

Cycle Number	0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7
Abs. (375 nm)	1,235	0,025	1,066	0,040	0,924	0,038	0,831	0,047	0,727	0,059	0,640	0,05	0,575	0,075	0,518
% **1a**	100	2	86	3	75	3	67	4	59	5	52	5	47	6	42

[a] Entire cycle number corresponds to the formation of cage **1a** (through cycloreversion from **1b**) meanwhile half-number is the formation of cage **1b** (through $^1O_2$ addition on from **1a**)

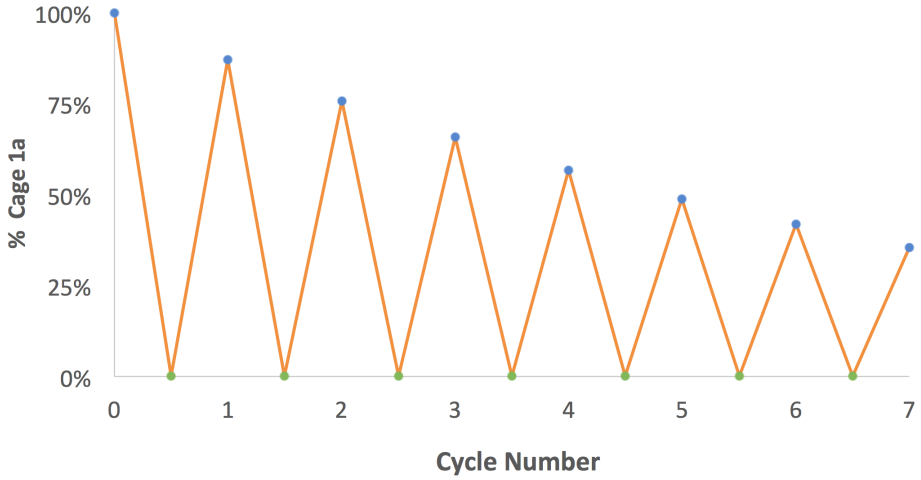

Figure S4. Fatigue cycles for the **1a**/**1b** switch in propylene carbonate in the presence of methylene blue.

2) Cages 2a–b

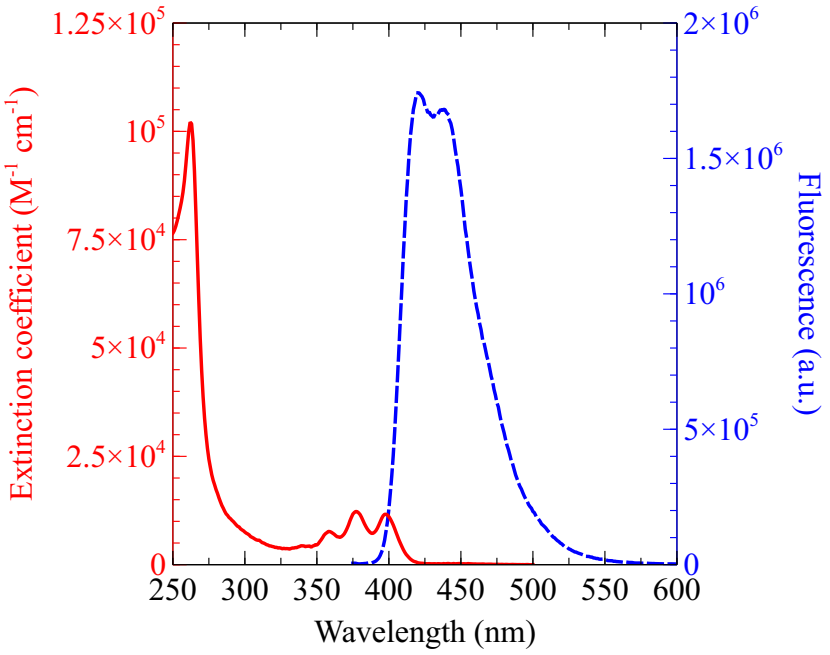

Figure S5. UV-Visible (red full line) and Fluorescence Emission (blue dotted line, λ_{exc} = 365 nm) spectra of cage **2a** (conc.) in dichloromethane at 298 K.

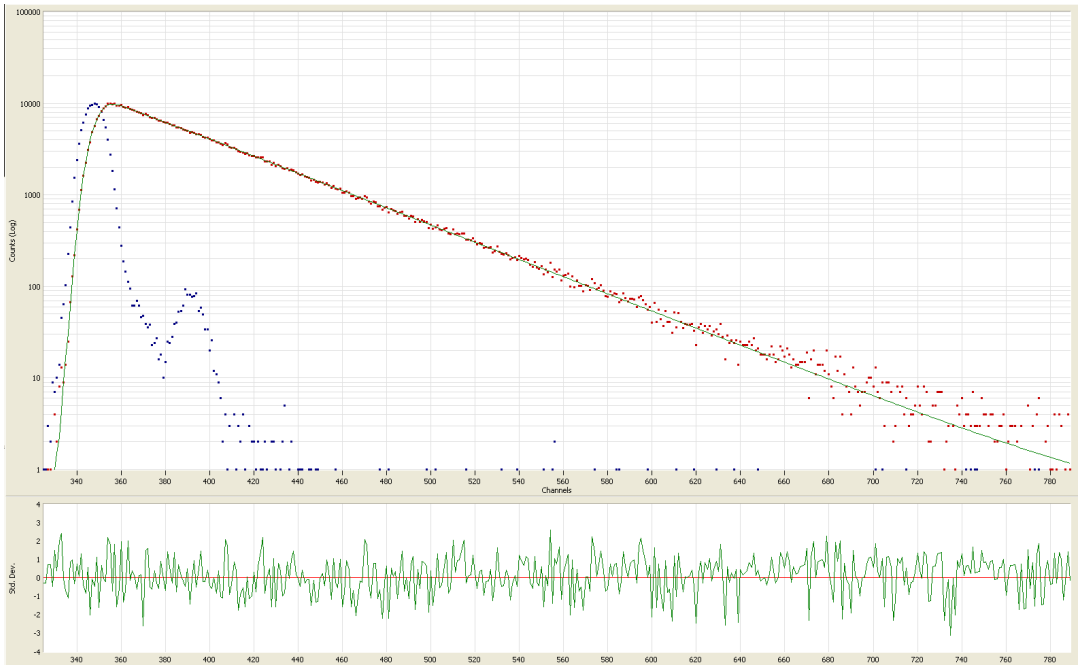

Figure S6. Fluorescence intensity decay of cage **2a** in aerated dichloromethane solution (λ_{ex} = 371 nm, λ_{em} = 425 nm). Red points and green line denote experimental points and fit (τ = 5.0 ns, χ2 = 1.09), respectively.

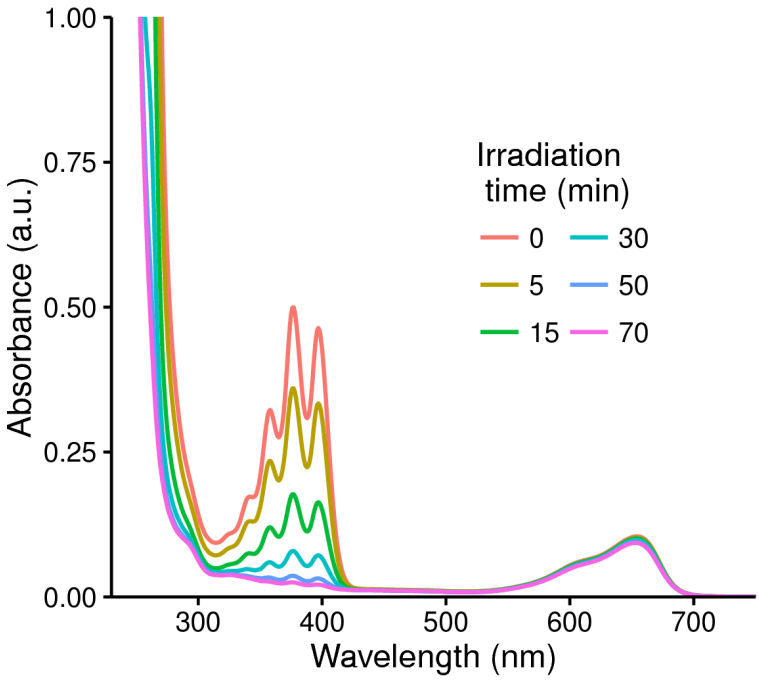

Figure S7. Formation of the endoperoxide **2b** in propylene carbonate by visible light irradiation of **2a** (15μM) in the presence of methylene blue as a photosensitizer.

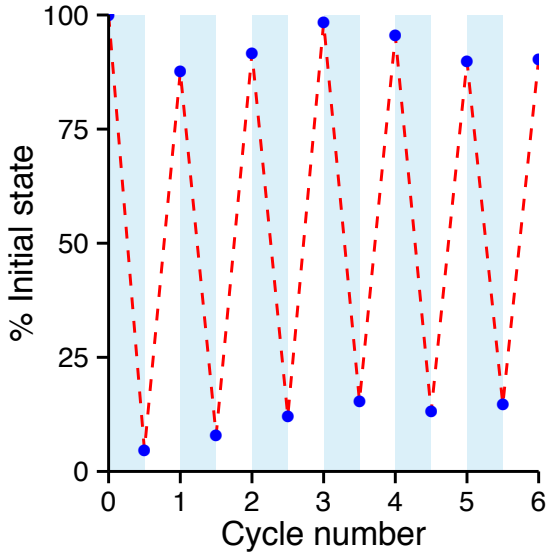

Figure S8. Fatigue cycles for the **2a**/**2b** switch in propylene carbonate in the presence of methylene blue as a photosensitizer. Cycloreversion is conducted by heating to 120°C for 80 – 120 min.

(Host:Guest) Titrations monitored by absorption and emission spectroscopy

1) Cages 1a, 1b

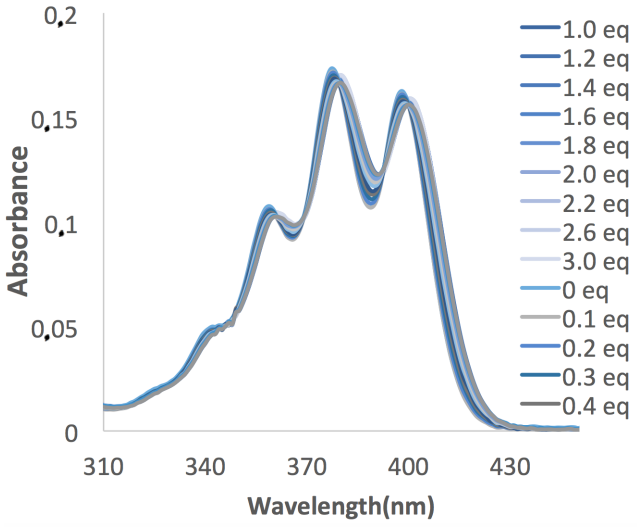

Figure S9. Titration of cage **1a** (15 μM) in CH_2Cl_2 in the presence of $NaBAr_F$ (0-3 eq.) monitored by absorption spectroscopy.

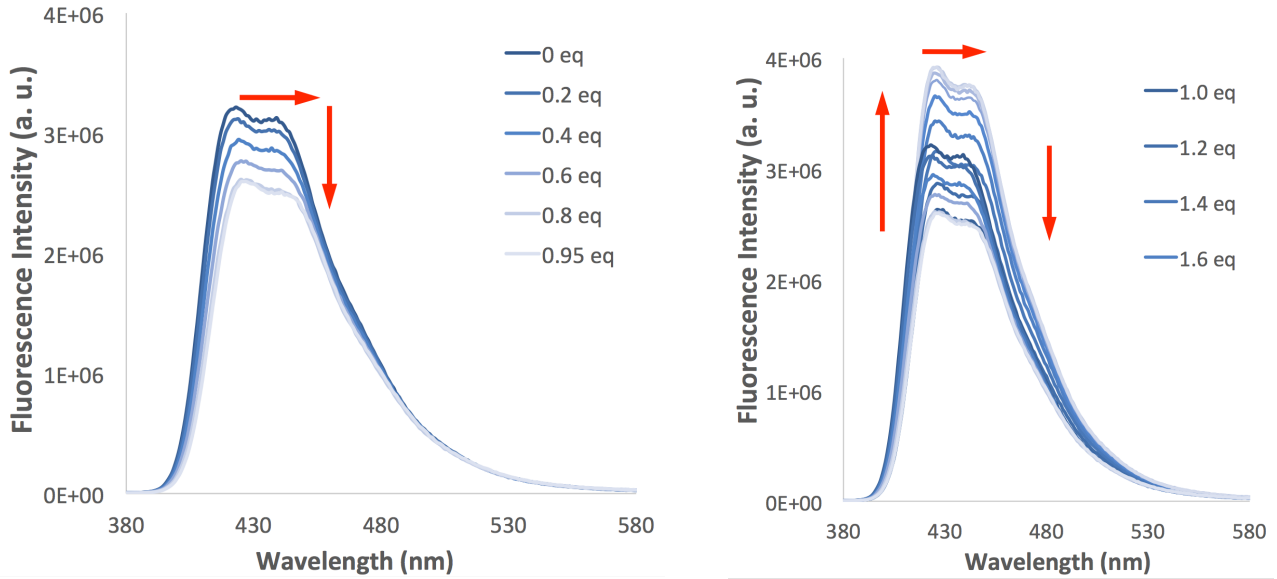

Figure S10. Titration of cage **1a** (15 μM) in CH_2Cl_2 in the presence $NaBAr_F$ monitored by fluorescence emission (λ_{ex} = 365 nm): a) 0–1 equivalent of $NaBAr_F$; b) 0–3 equivalents of $NaBAr_F$.

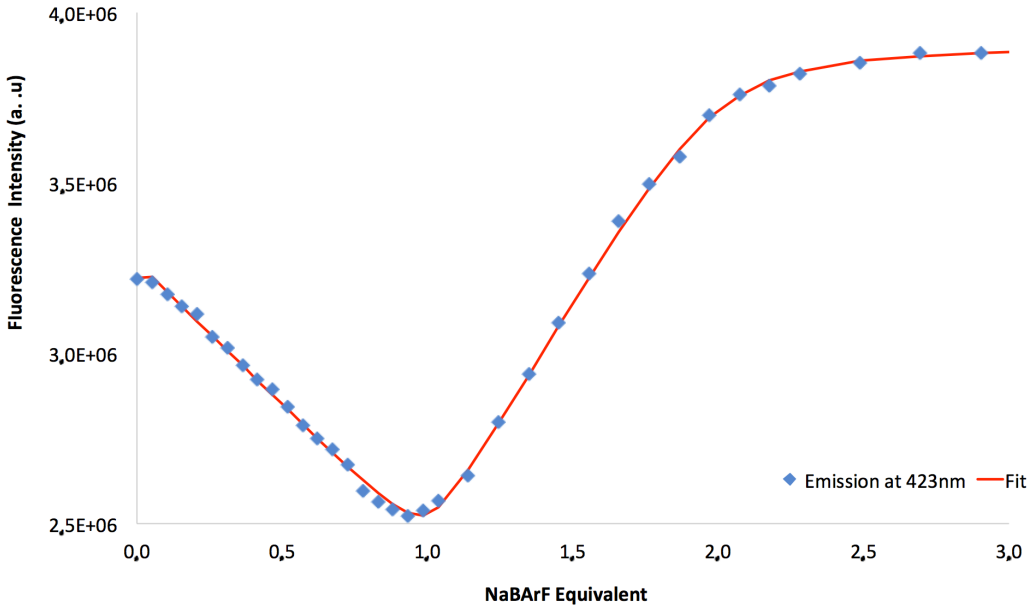

Figure S11. (Host:guest) Titration experiments in CH_2Cl_2 monitored by fluorescence emission spectroscopy (λ_{ex} = 365 nm, λ_{em} = 423 nm) between **1a** (15 μM) and $NaBAr_F$ (0–3.0 eq.) fitted to a (1:2) host-guest model. Blue dots represent experimental points and red line is the fit to the model.

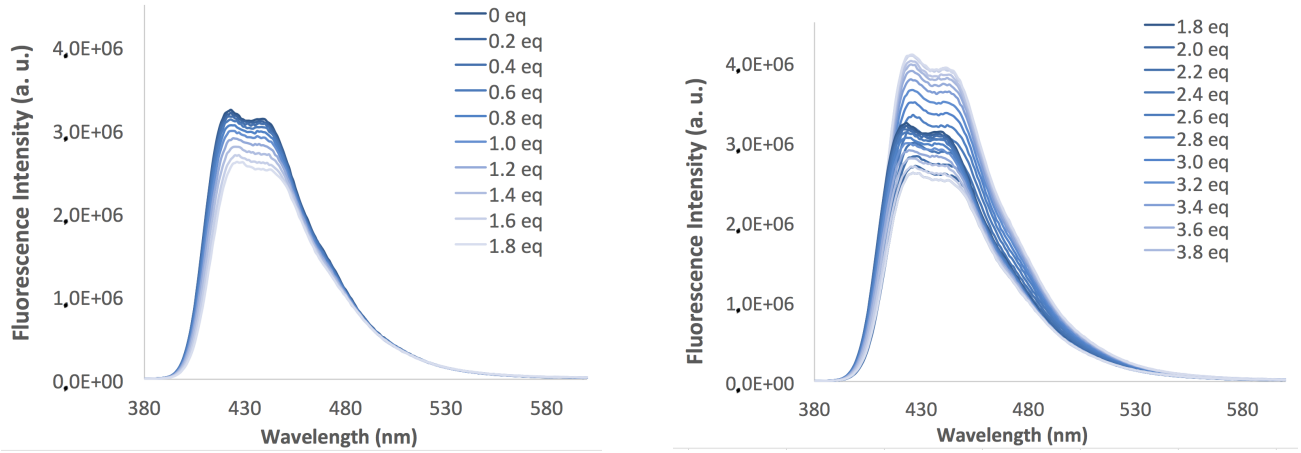

Figure S12. Titration of cage **1b** (15 μM) in the presence of **1a** (15 μM) and $NaBAr_F$ (0–6 eq.) monitored by Fluorescence Emission (λ_{ex} = 365 nm, λ_{em} = 423 nm): a) 0–2 equiv. of $NaBAr_F$; b) 0–4 equiv. of $NaBAr_F$.

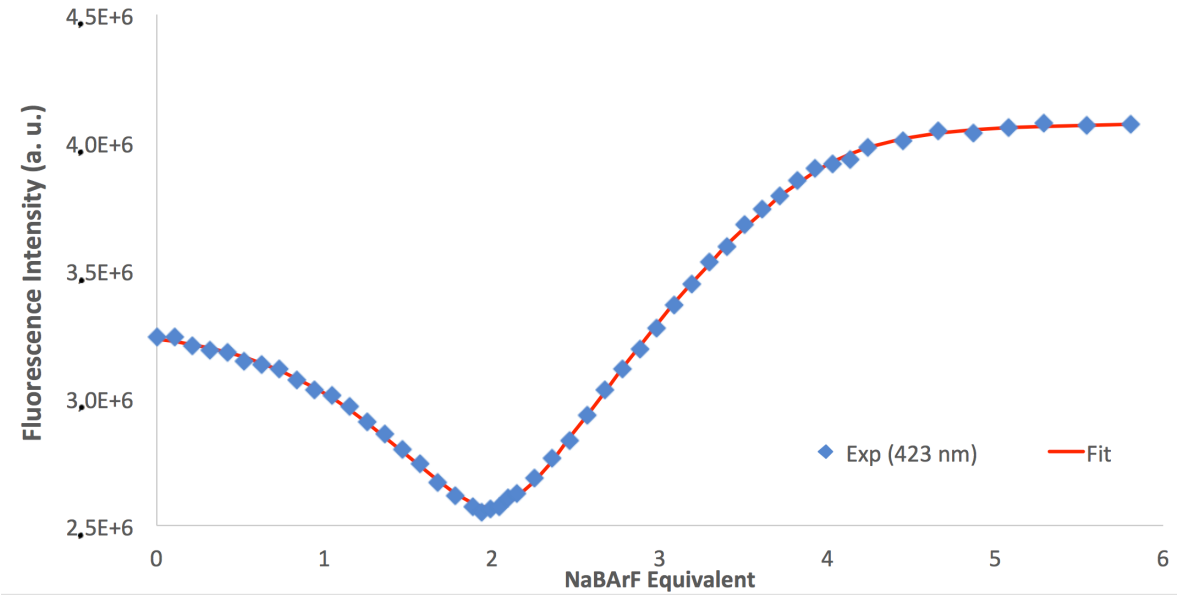

Figure S13. Competitive (Host:guest) Titration experiment in CH_2Cl_2 monitored by fluorescence emission spectroscopy (λ_{ex} = 365 nm, λ_{em} = 423 nm) between **1b** (15 μM) and $NaBAr_F$ (0–6.0 eq.) in the presence of **1b** (15 μM), fitted to a (1:2) host-guest model. Blue dots represent experimental points and red line is the fit to the model.

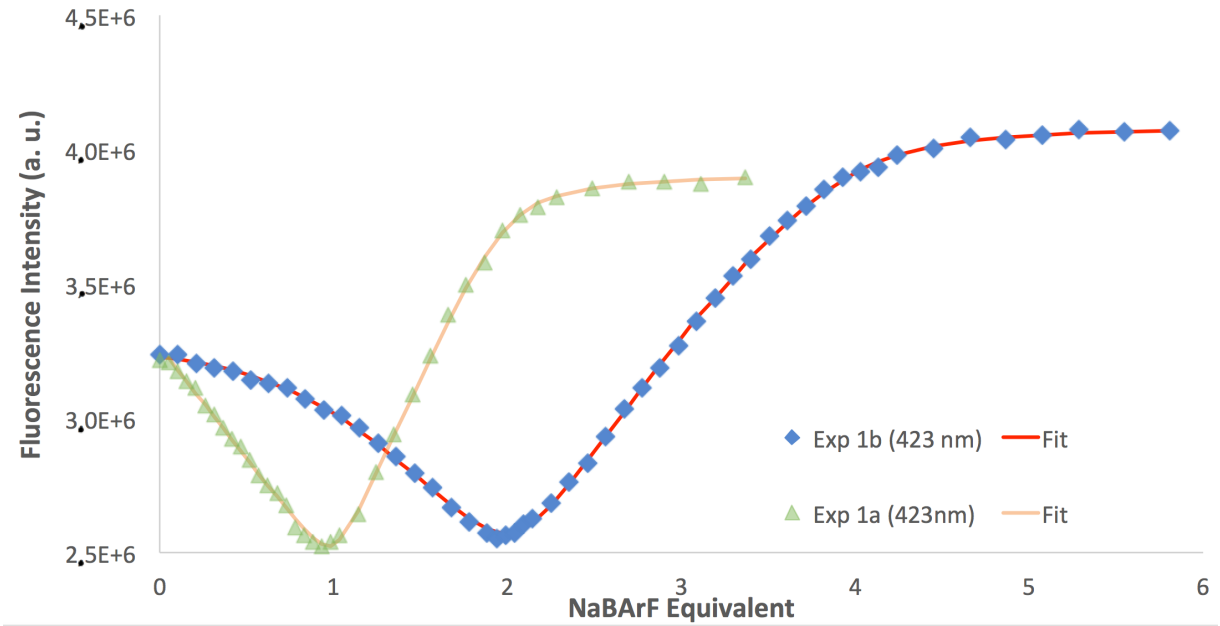

Figure S14. Comparison between (Host:Guest) Titration experiments in CH_2Cl_2 monitored by fluorescence emission spectroscopy (λ_{ex} = 365 nm, λ_{em} = 423 nm) between cage **1a** alone (15 μM, green dots) and the competitive experiment **1a** *versus* **1b** (15 μM, 1:1 ratio, blue dots) in the presence of $NaBAr_F$.

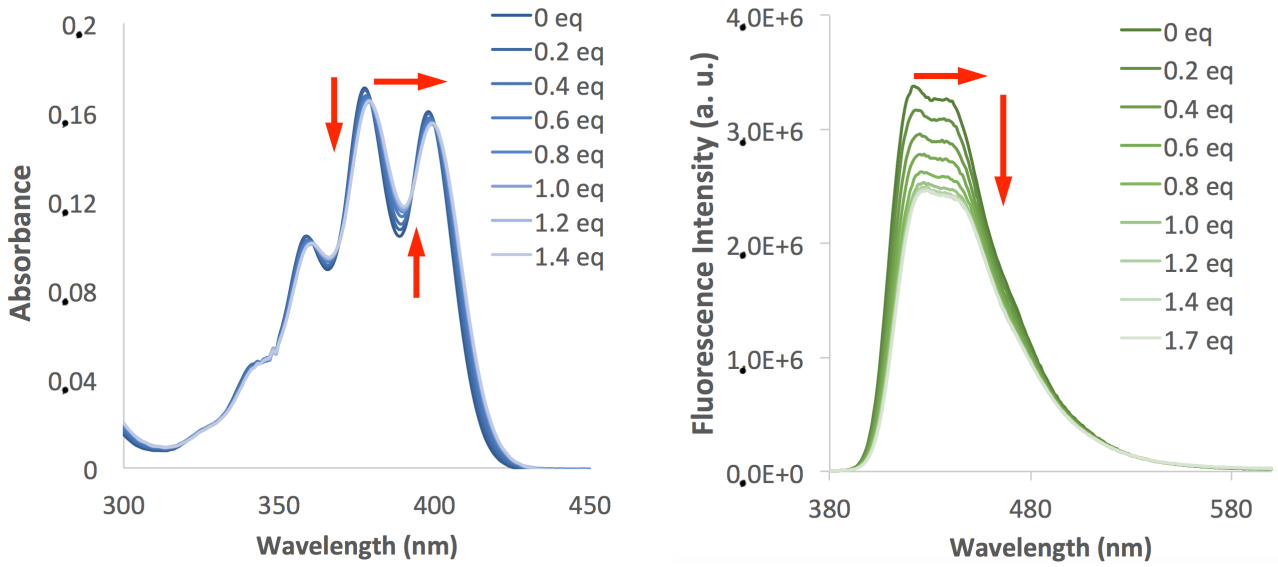

Figure S15. Titration of cage **1a** (15 μM) in CH_2Cl_2 in the presence of $CsBAr_F$ (0–2 eq.) monitored by UV–Visible (left) and Fluorescence emission (right).

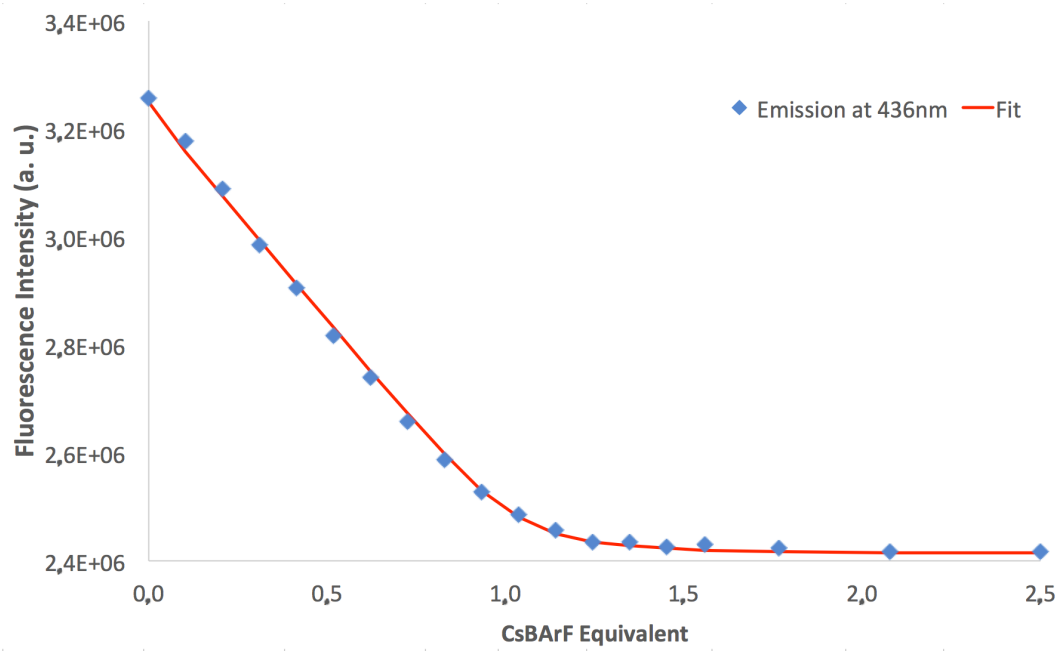

Figure S16. (Host:guest) Titration experiment in CH_2Cl_2 monitored by fluorescence emission spectroscopy (λ_{ex} = 365 nm, λ_{em} = 436 nm) between **1a** (15 μM) and $CsBAr_F$ (0–2.5 eq.) fitted to a (1:1) host-guest model. Blue dots represent experimental points and red line is the fit to the model.

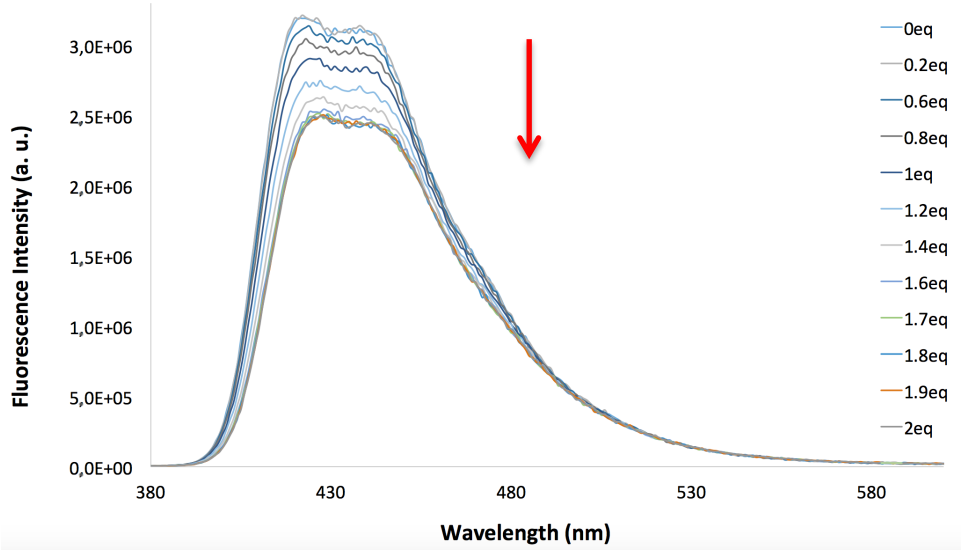

Figure S17. Titration of cage **1b** (15 μM) in the presence of **1a** (15 μM) and $CsBAr_F$ (0–2.2 eq.) monitored by Fluorescence Emission (λ_{ex} = 365 nm, λ_{em} = 423 nm).

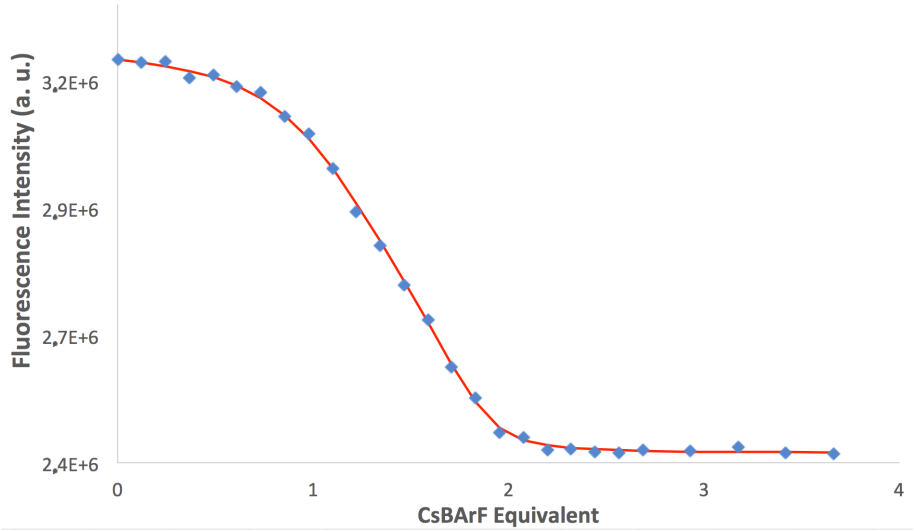

Figure S18. Competitive (Host:guest) Titration experiment in CH_2Cl_2 monitored by fluorescence emission spectroscopy (λ_{ex} = 365 nm, λ_{em} = 423 nm) between **1b** (15 μM) and $CsBAr_F$ (0–3.5 eq.) in the presence of **1a** (15 μM), fitted to a (1:1) host-guest model. Blue dots represent experimental points and red line is the fit to the (1:1) model.

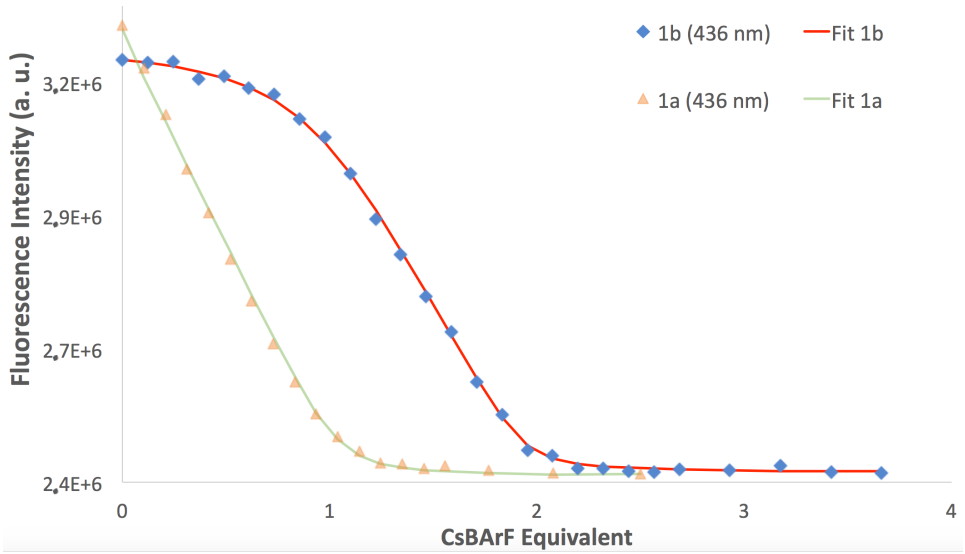

Figure S19. Comparison between (Host:guest) Titration experiments in CH_2Cl_2 monitored by fluorescence emission spectroscopy (λ_{ex} = 365 nm, λ_{em} = 436 nm) between cage **1a** alone (15 μM, yellow dots) and the competitive experiment **1a** *versus* **1b** (15 μM, 1:1 ratio, blue dots) in the presence of $CsBAr_F$.

2) Cages 2a, 2b

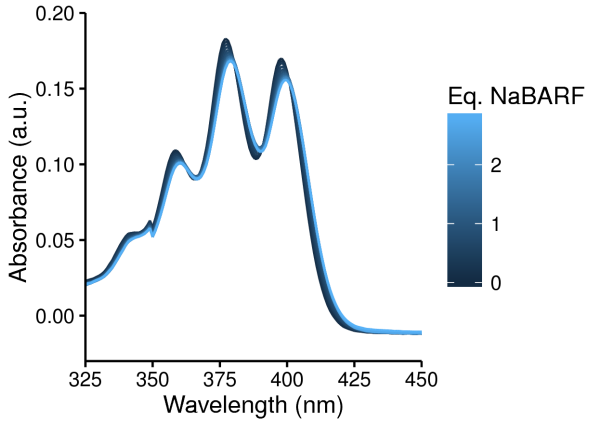

Figure S20. Titration of cage **2a** (14.6 μM) in CH_2Cl_2 in the presence of $NaBAr_F$ (0-3 eq.) monitored by UV-visible.

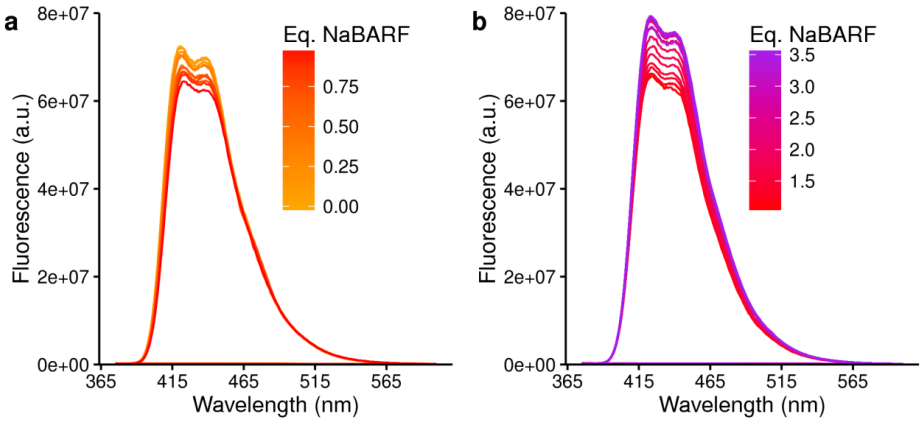

Figure S21. Titration of cage **2a** (3 μM) in the presence $NaBAr_F$ monitored by Fluorescence Emission (λ_{ex} = 365 nm): a) 0–1 equivalent of $NaBAr_F$; b) addition of more than 1 eq of $NaBAr_F$.

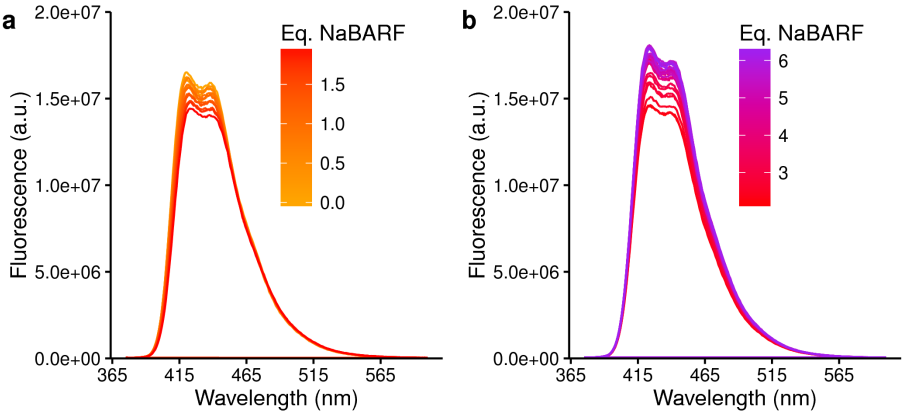

Figure S22. Competitive titration of cage **2b** (10.5 μM) in the presence of **2a** (10.5 μM) and $NaBAr_F$ (0–6 eq.) monitored by Fluorescence Emission (λ_{ex} = 365 nm): a) 0–2 equiv. of $NaBAr_F$; b) 2–6 equiv. of $NaBAr_F$.

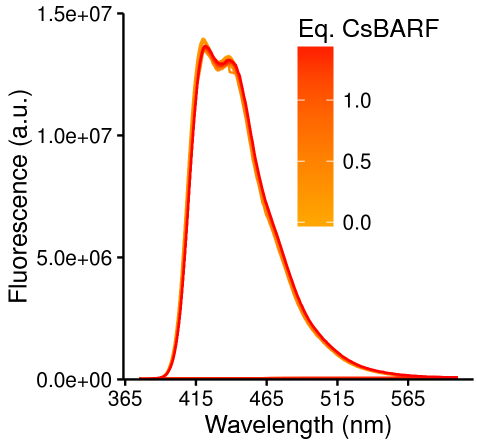

Figure S23. Titration of cage **2a** (10.5 μM) in the presence $CsBAr_F$ monitored by Fluorescence Emission (λ_{ex} = 365 nm).

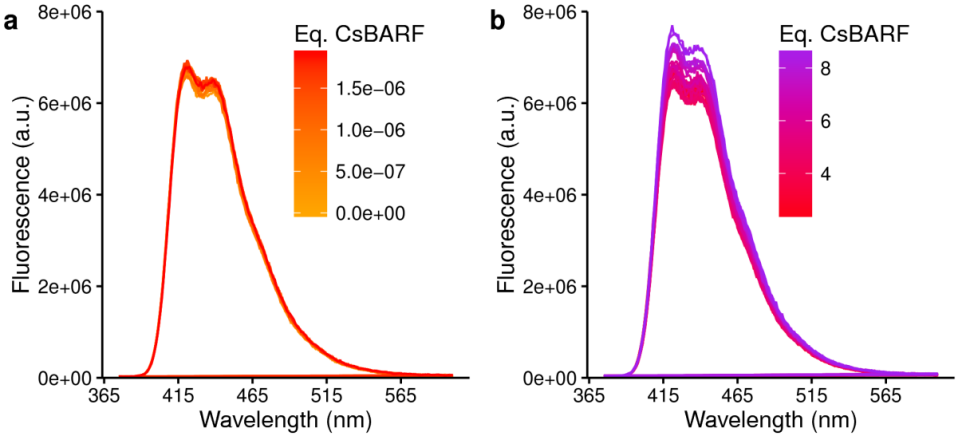

Figure 24. Competitive titration of cage **2b** (10.5 μM) in the presence of **2a** (10.5 μM) and $CsBAr_F$ (0–8 eq.) monitored by Fluorescence Emission (λ_{ex} = 365 nm): a) 0–2 equiv. of $CsBAr_F$; b) 2–8 equiv. of $CsBAr_F$.

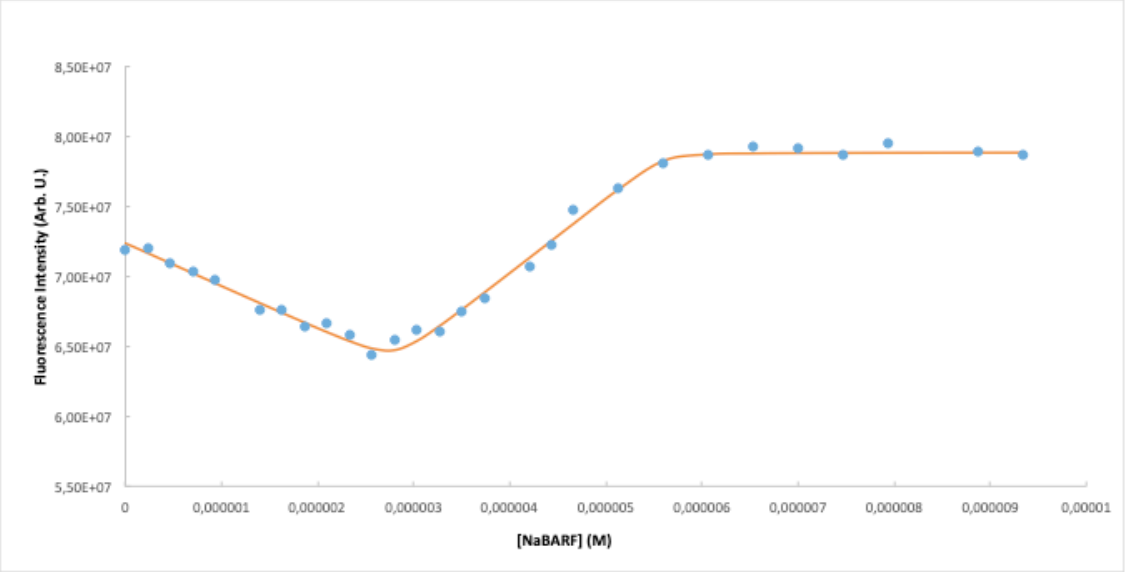

Figure S25. (Host:guest) Titration experiment in CH_2Cl_2 monitored by fluorescence emission spectroscopy (λ_{ex} = 350 nm, λ_{em} = 423 nm) between **2a** (2.8 μM) and $NaBAr_F$ (0–3.0 eq.) fitted to a (1:2) host-guest model. Blue dots represent experimental points and red line is the fit to the model.

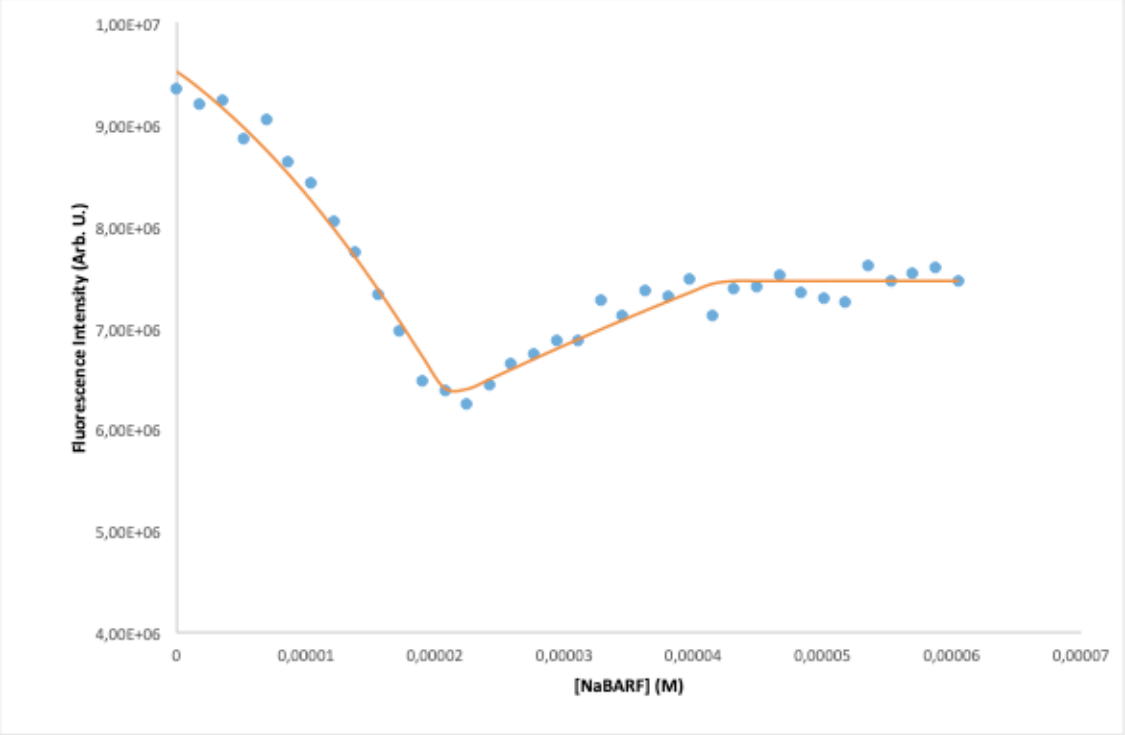

Figure S26. Competitive (Host:guest) Titration experiment in CH_2Cl_2 monitored by fluorescence emission spectroscopy (λ_{ex} = 365 nm, λ_{em} = 409 nm) between **2b** (10.1 μM) and $NaBAr_F$ (0–3.5 eq.) in the presence of **2a** (10.1 μM), fitted to a (1:2) host-guest model. Blue dots represent experimental points and red line is the fit to the (1:2) model.

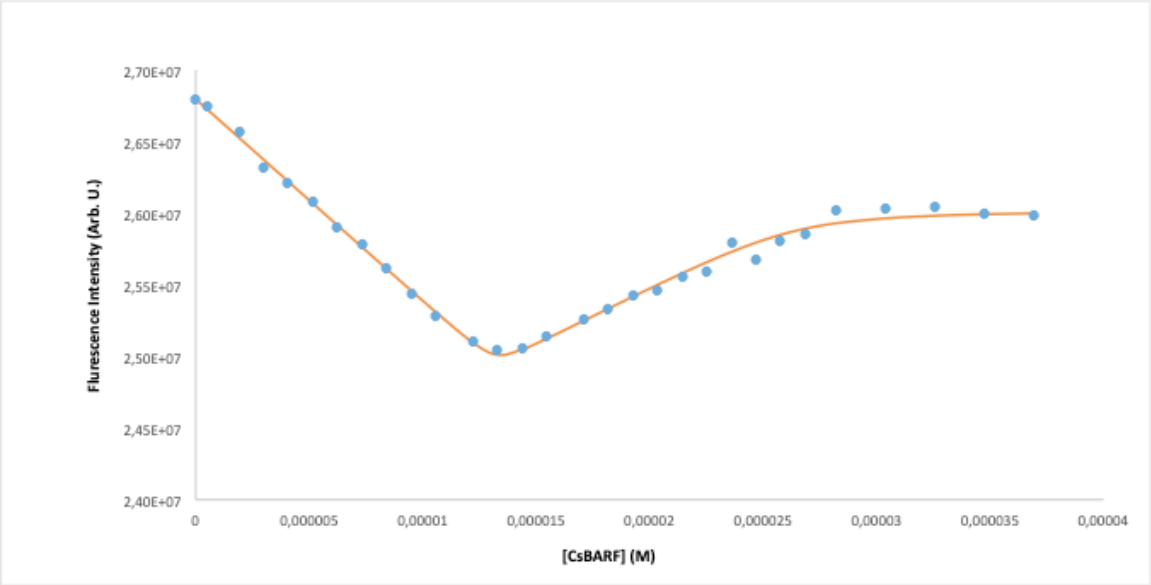

Figure S27. (Host:guest) Titration experiment in CH_2Cl_2 monitored by fluorescence emission spectroscopy (λ_{ex} = 350 nm, λ_{em} = 420 nm) between **2a** (13.2 μM) and $CsBAr_F$ (0–3.0 eq.) fitted to a (1:2) host-guest model. Blue dots represent experimental points and red line is the fit to the model.

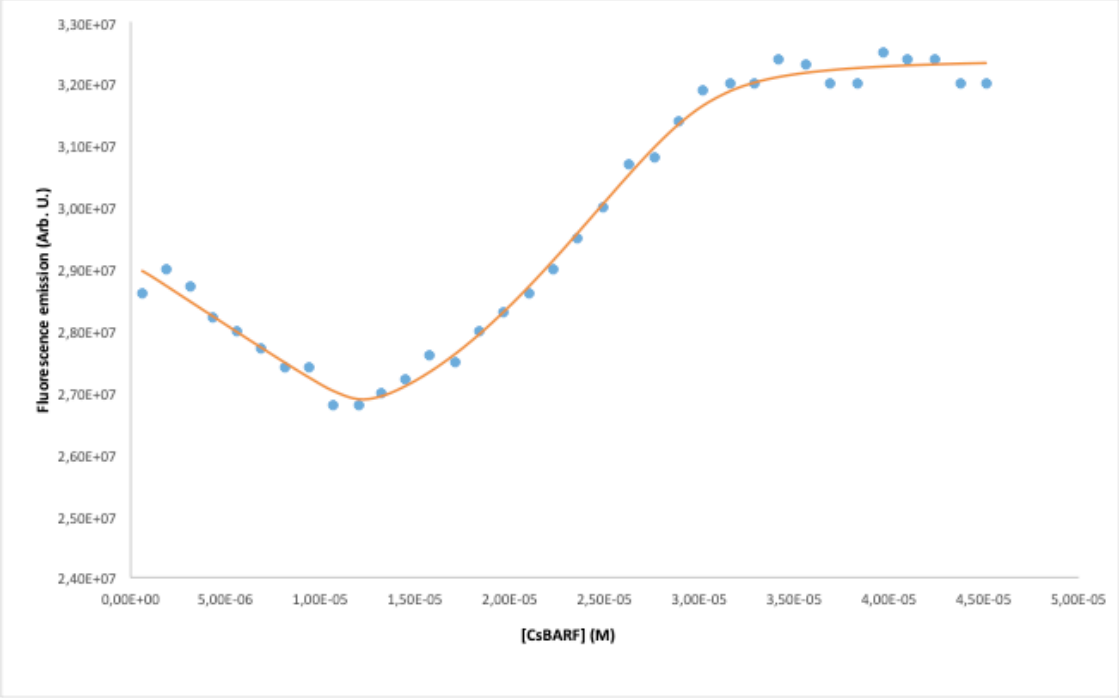

Figure S28. Competitive (Host:guest) Titration experiment in CH_2Cl_2 monitored by fluorescence emission spectroscopy (λ_{ex} = 350 nm, λ_{em} = 420 nm) between **2b** (6.2 μM) and $CsBAr_F$ (0–3.5 eq.) in the presence of **2a** (12.0 μM), fitted to a (1:2) host-guest model. Blue dots represent experimental points and red line is the fit to the (1:2) model.

Fluorescence quenching studies

The quenching of 9,10-diphenylanthracene fluorescence by NaBArF (BArF = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) was investigated by monitoring the fluorescence emission of an aerated solution of 9,10-diphenylanthracene (ca. 20 µM in THF) upon addition of NaBArF (0 – 40 mg).

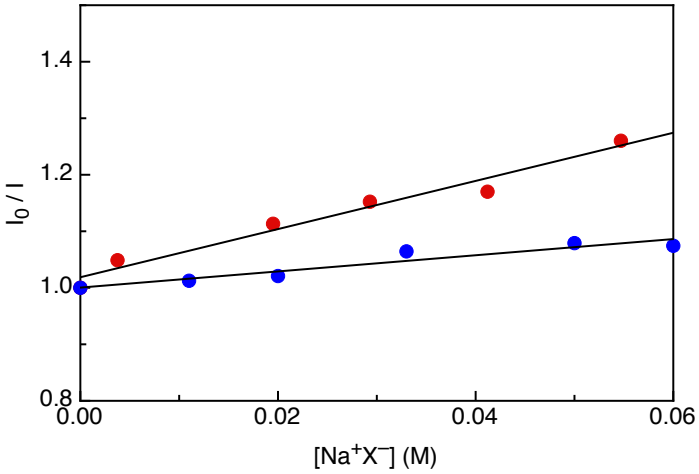

Figure S29. Stern-Volmer plot of the quenching of 9,10-diphenylanthracene fluorescence by NaBArF (red filled circles) or $NaPF_6$ (blue filled circles) in aerated THF solution (λ_{ex} = 365 nm, λ_{em} = 385 nm). Black lines are best fit with K_{SV} = 4.3 M^{-1} (r = 0.983) and 1.3 M^{-1} (r = 0.953). In the case of quenching by $NaPF_6$, 1.1 equiv. of benzo-15C5 crown ether was added to the salt solution to improve solubility.

Computational Details

All quantum chemical calculations were performed with the Gaussian 16 package.[6] The hybrid density functional B3LYP[7] together with the Def2svp basis set[8] were used for the geometry optimisations. Vibrational frequency calculations were performed at the same level of theory to verify that a local minimum has no imaginary frequency. Single point energy calculations were then conducted on every species at the post HF MP2(full)/Def2svp level of theory and Gibbs free energies were derived from this energy by adding the zero-point energy and the thermal corrections to Gibbs free energy obtained at the B3LYP Def2svp level. B3LYP and MP2[9] calculations were performed using the Polarisable Continuum Model (PCM) in its integral equation formalism variant (IEFPCM) to simulate the dichloromethane environnement.

Table 7. Gibbs free energy ΔG (kcal/mol) for the association [Cage + Ion] of guest stoichiometry (1:1) or (1:2) calculated at the MP2/Def2svp//B3LYP/ Def2svp.

		Na^+		**Cs^+**
		ΔG_{11}	ΔG_{12}	ΔG_{11}
1a	(side)[a] (center)[b]	[c]	[c]	-17.6 -16.3
1b	*(side)* *(center)*	*[c]*	*[c]*	*-19.1* *-24.9*
2a	*(side)* *(center)*	*-25.3* *-19.7*	*-29.1*	*-20.2* *-16.3*
2b	*(side)* *(center)*	*-18.6* *-27.3*	*-33.9*	*-22.3* *-26.7*

[a]: side refers to the position of the ion in the cage ie near the anthracene ring (see Figure 4a)
[b]: center refers to the position of the ion in the cage i.e. near the triazine moieties (see Figure 4b)
[c]: Not calculated.

$\Delta G = G(Cage+n.Ion) - [G(Cage) + n.G(Ion)]$ *with n=1 or 2*

[6] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[7] (a) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988,** *37*, 785-789. (c) Vosko, S.H.; Wilk, L.; Nusair, M. *Can. J. Phys*. **1980**, *58*, 1200-1211. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem*. **1994,** *98*, 11623-11627.

[8] (a) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-305. (b) Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.

[9] Moller, C.; Plesset, M. S. *Phys. Rev*. **1934**, *46*, 618 -622.

NMR Spectra

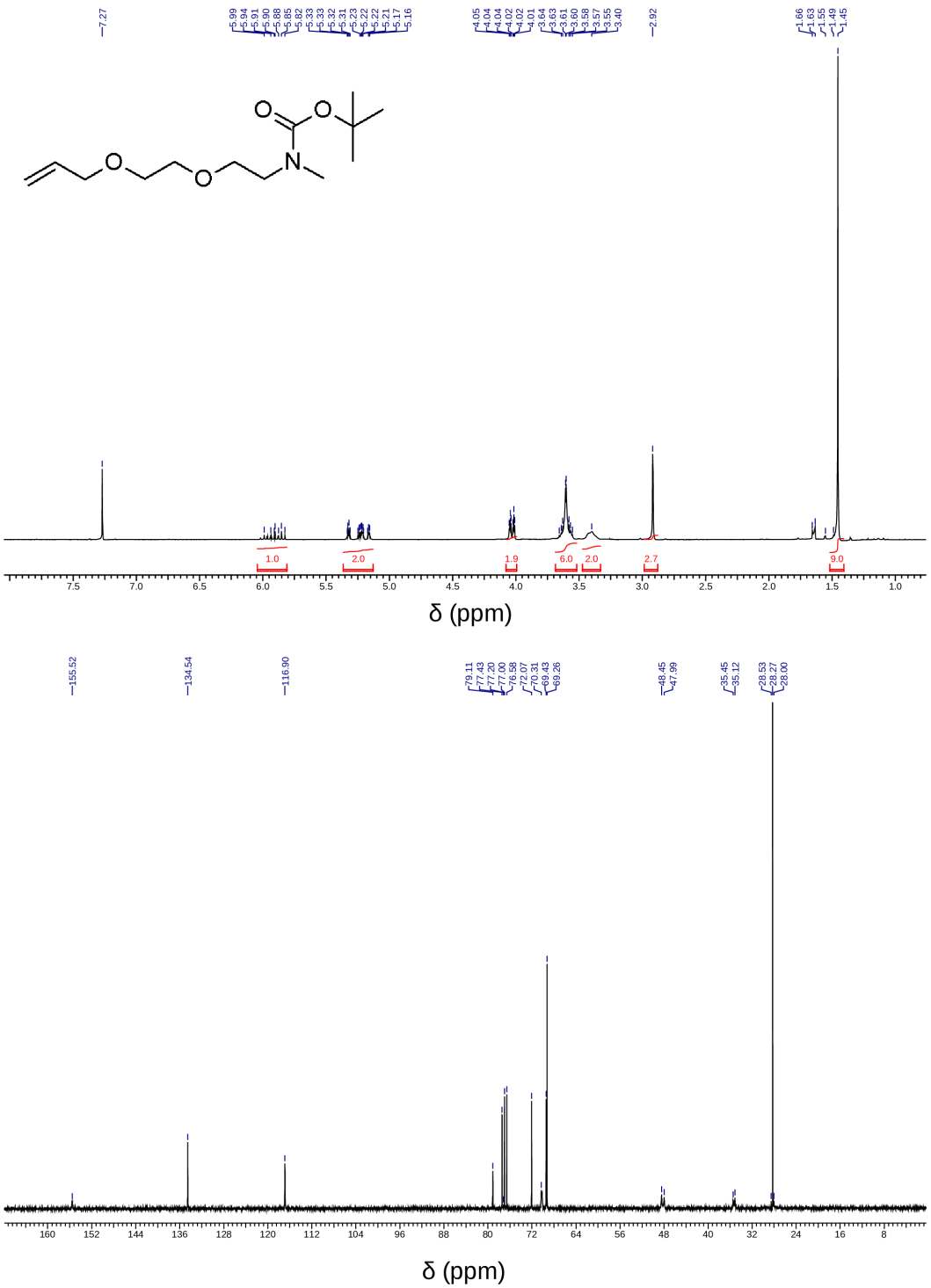

Figure S30. ^{1}H and ^{13}C (300 MHz and 75.5 MHz, $CDCl_3$) spectra of compound **23**.

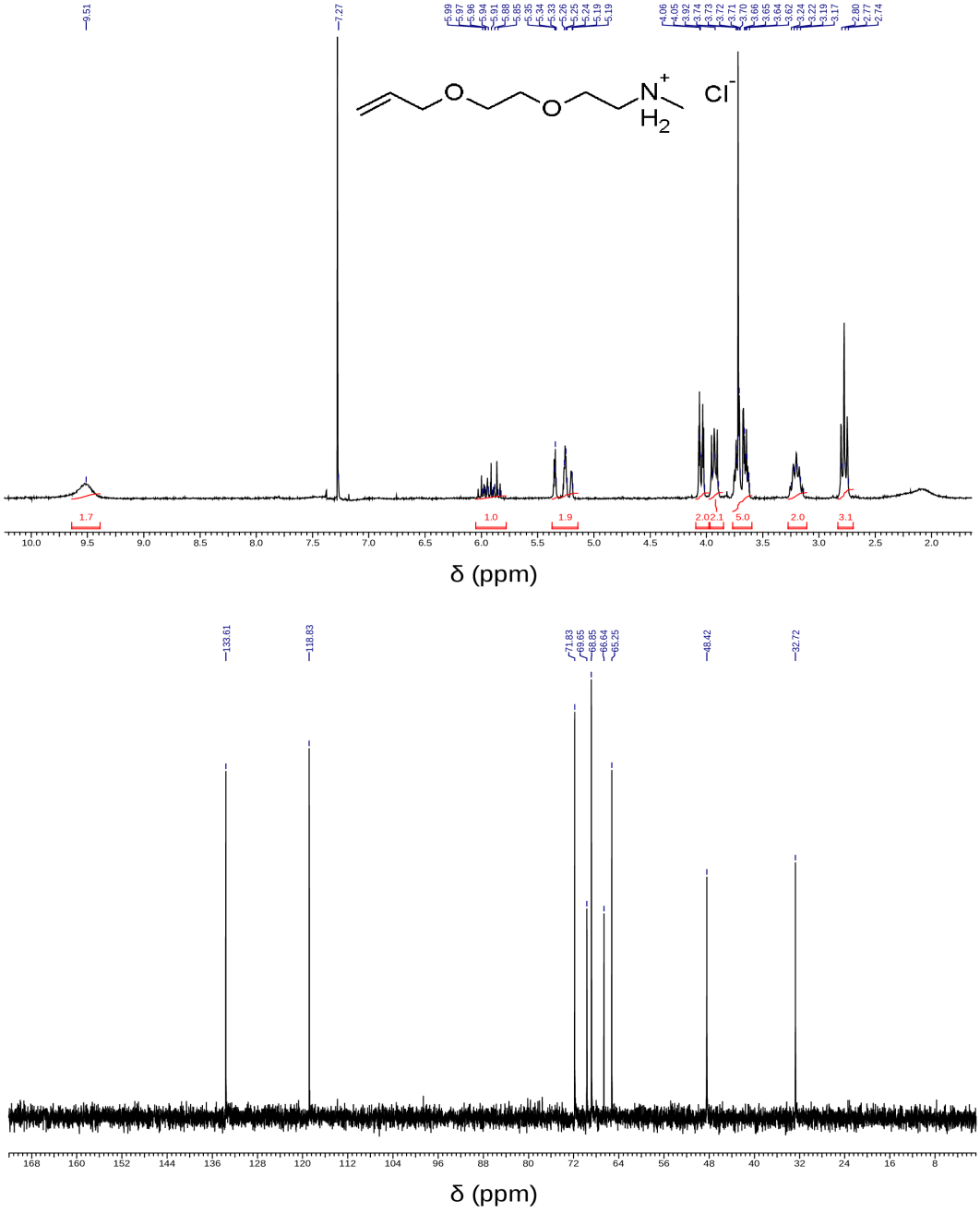

Figure S31. ^{1}H and ^{13}C (300 MHz and 75.5 MHz, $CDCl_3$) spectra of compound **7.**HCl.

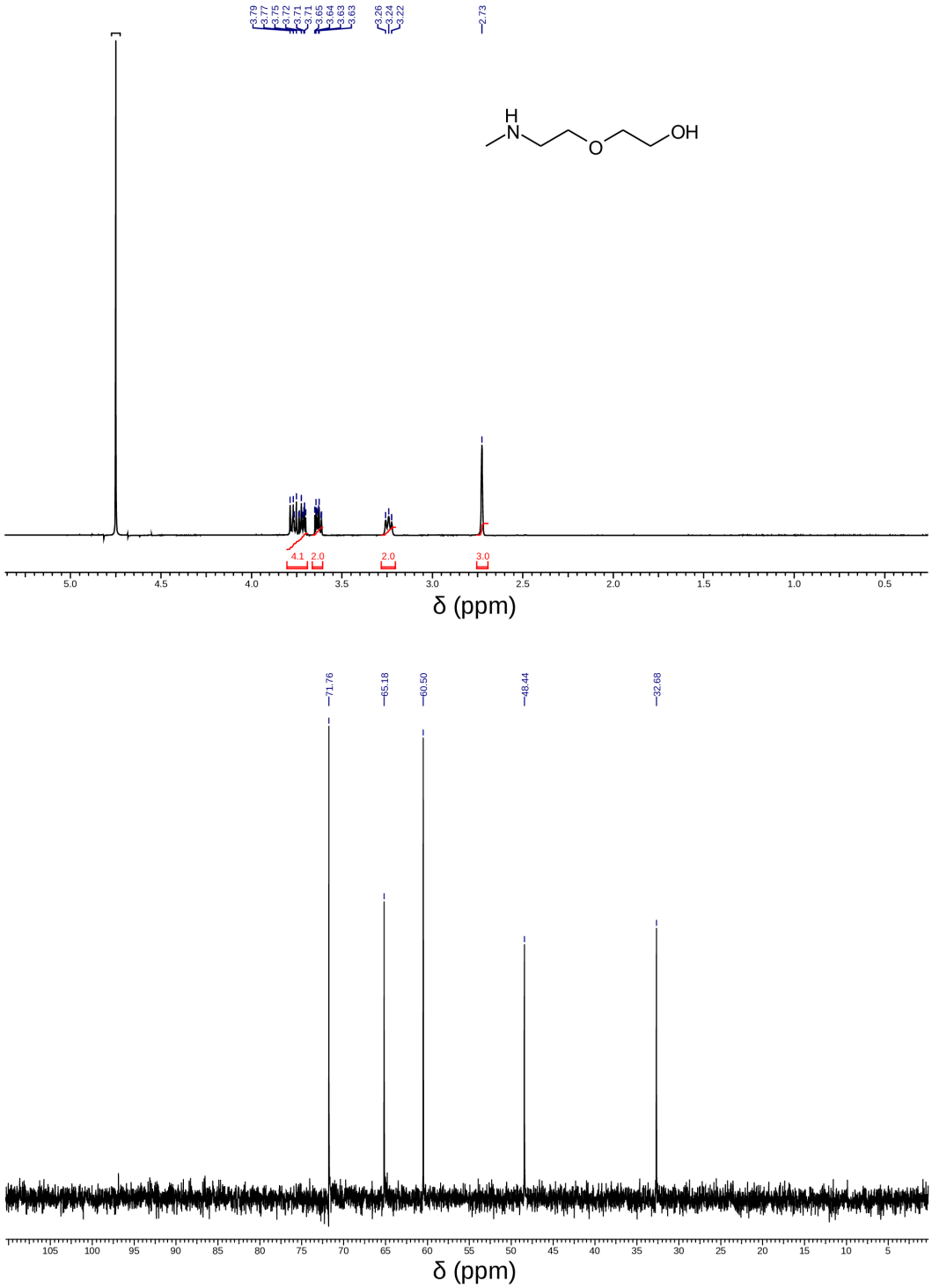

Figure S32. ^{1}H and ^{13}C (200 MHz and 50.4 MHz, $CDCl_3$ and D_2O) spectra of compound **9.**HCl.

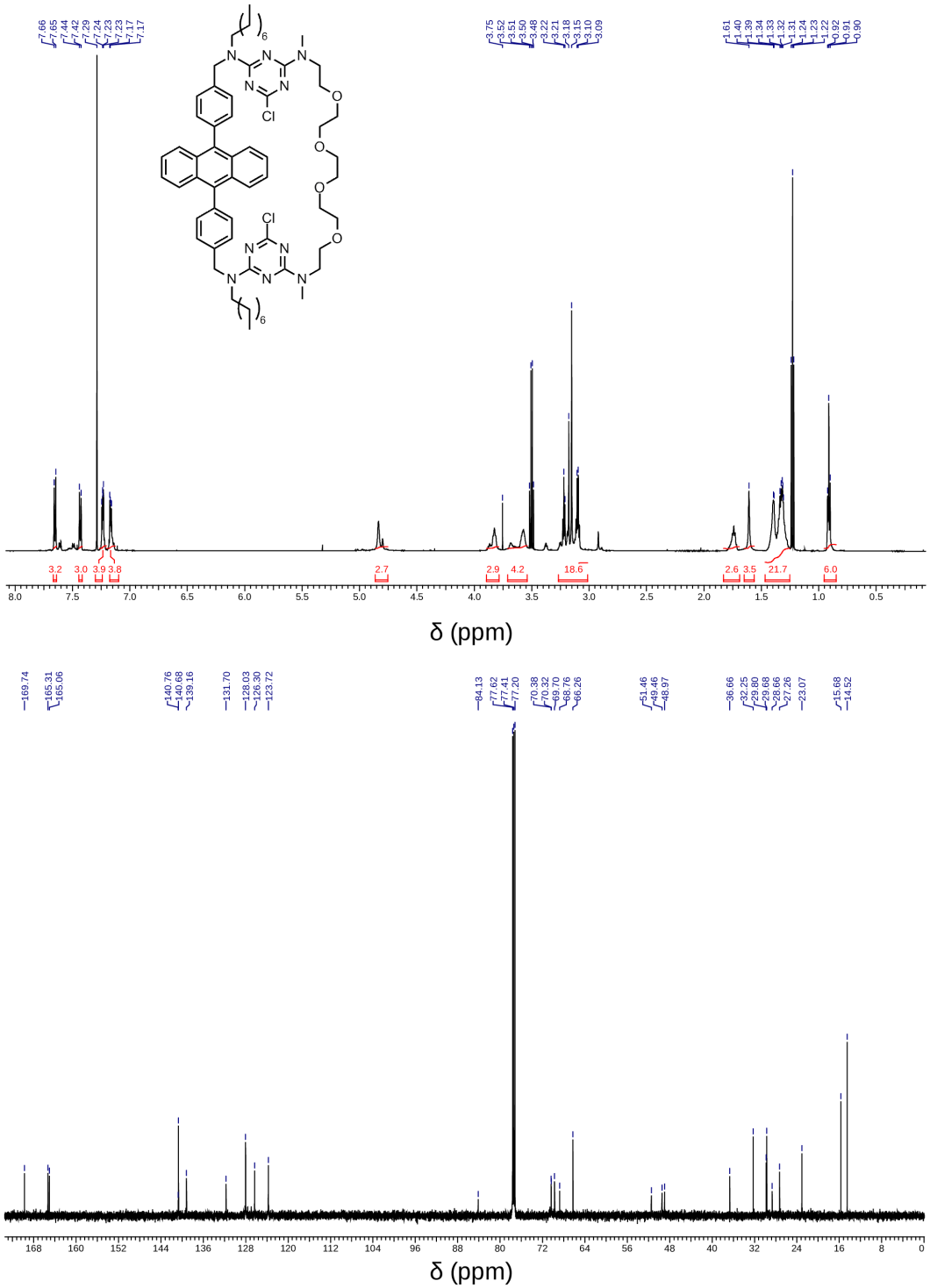

Figure S33. ^{1}H and ^{13}C (600 MHz and 151 MHz, $CDCl_3$) spectra of compound **6**.

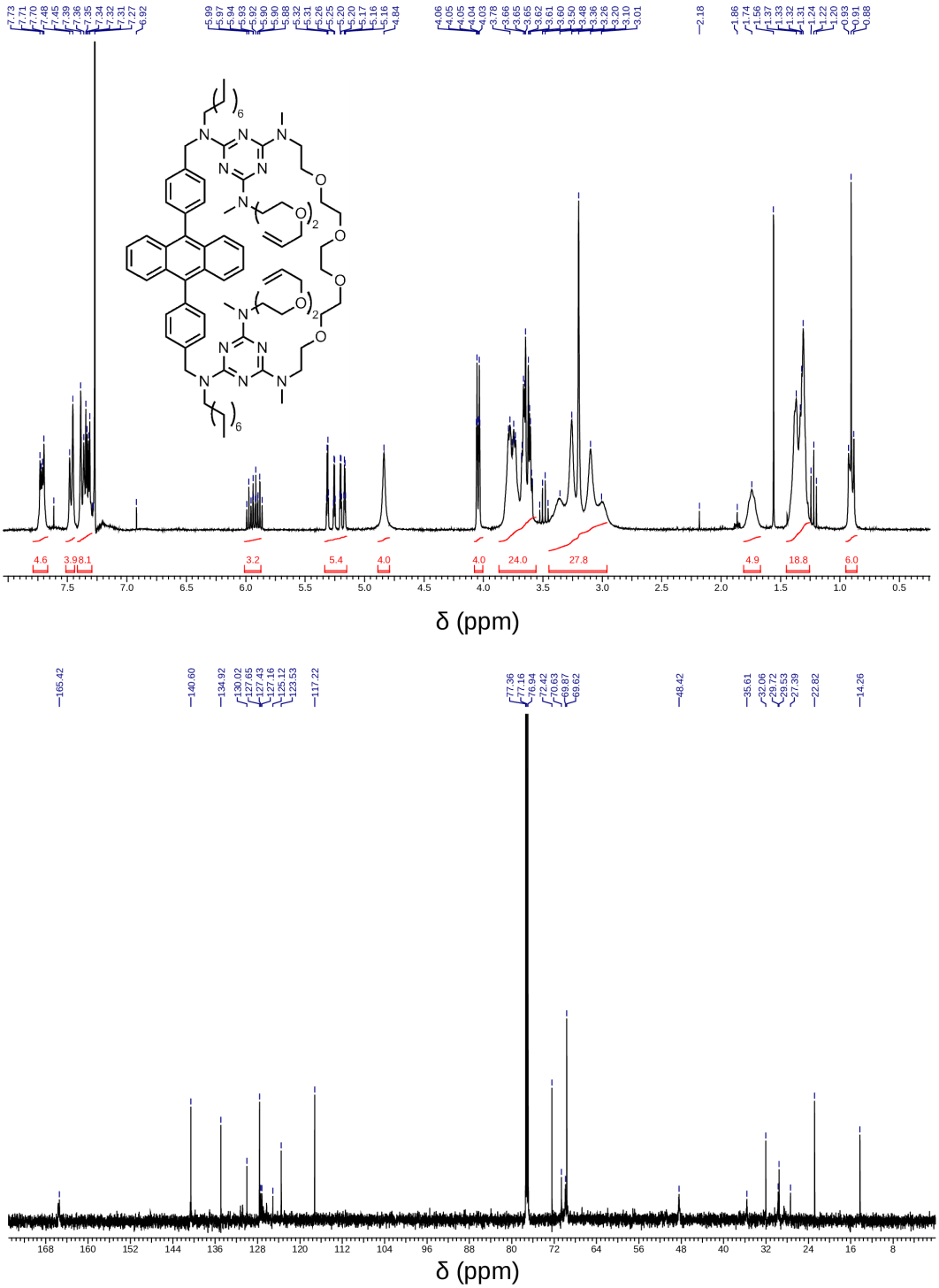

Figure S34. ^{1}H and ^{13}C (600 MHz and 151 MHz, $CDCl_3$) spectra of compound **8**.

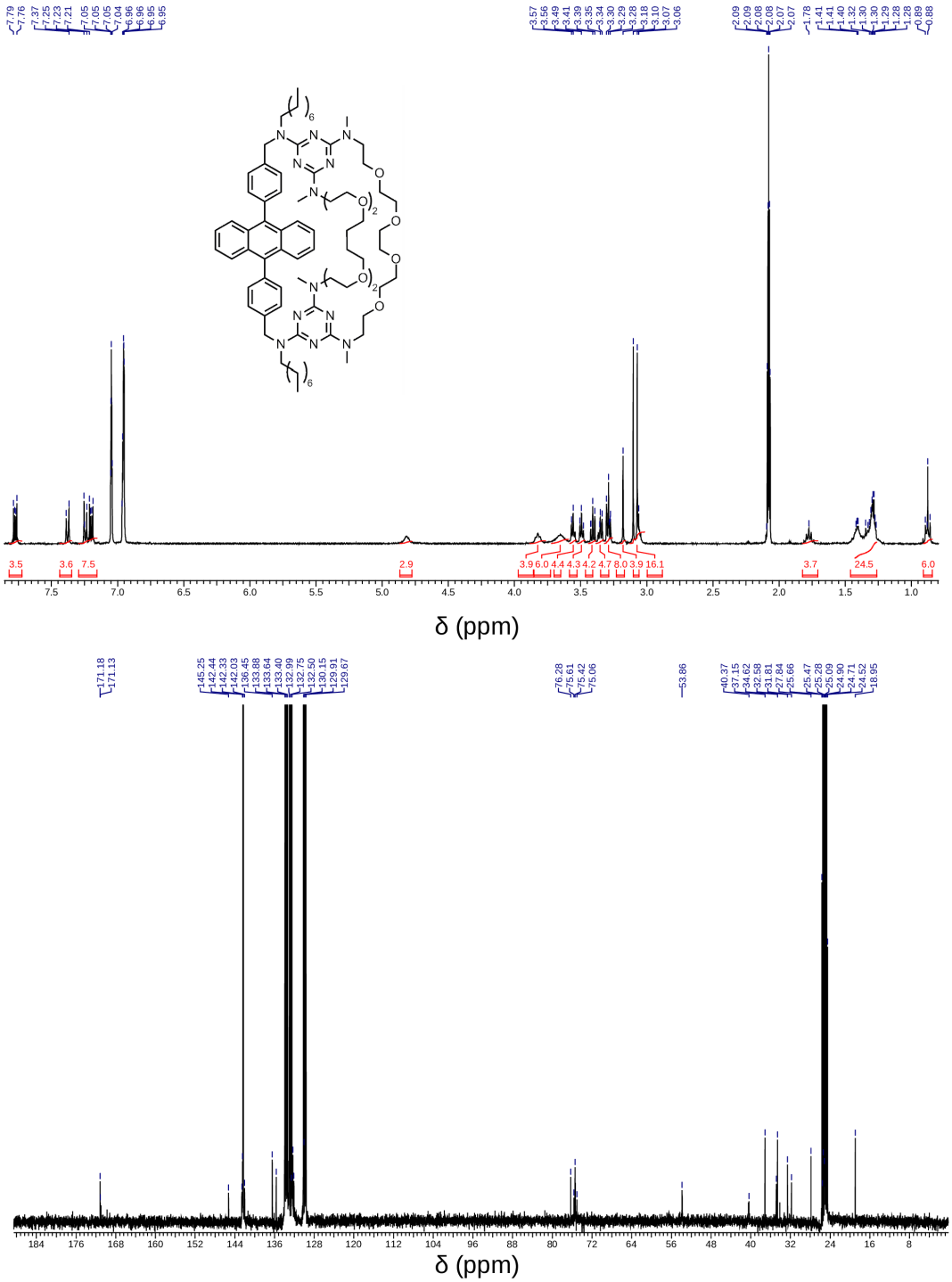

Figure S35. ^{1}H and ^{13}C (400 MHz and 100 MHz, toluene-d_8) spectra of cage **1a**.

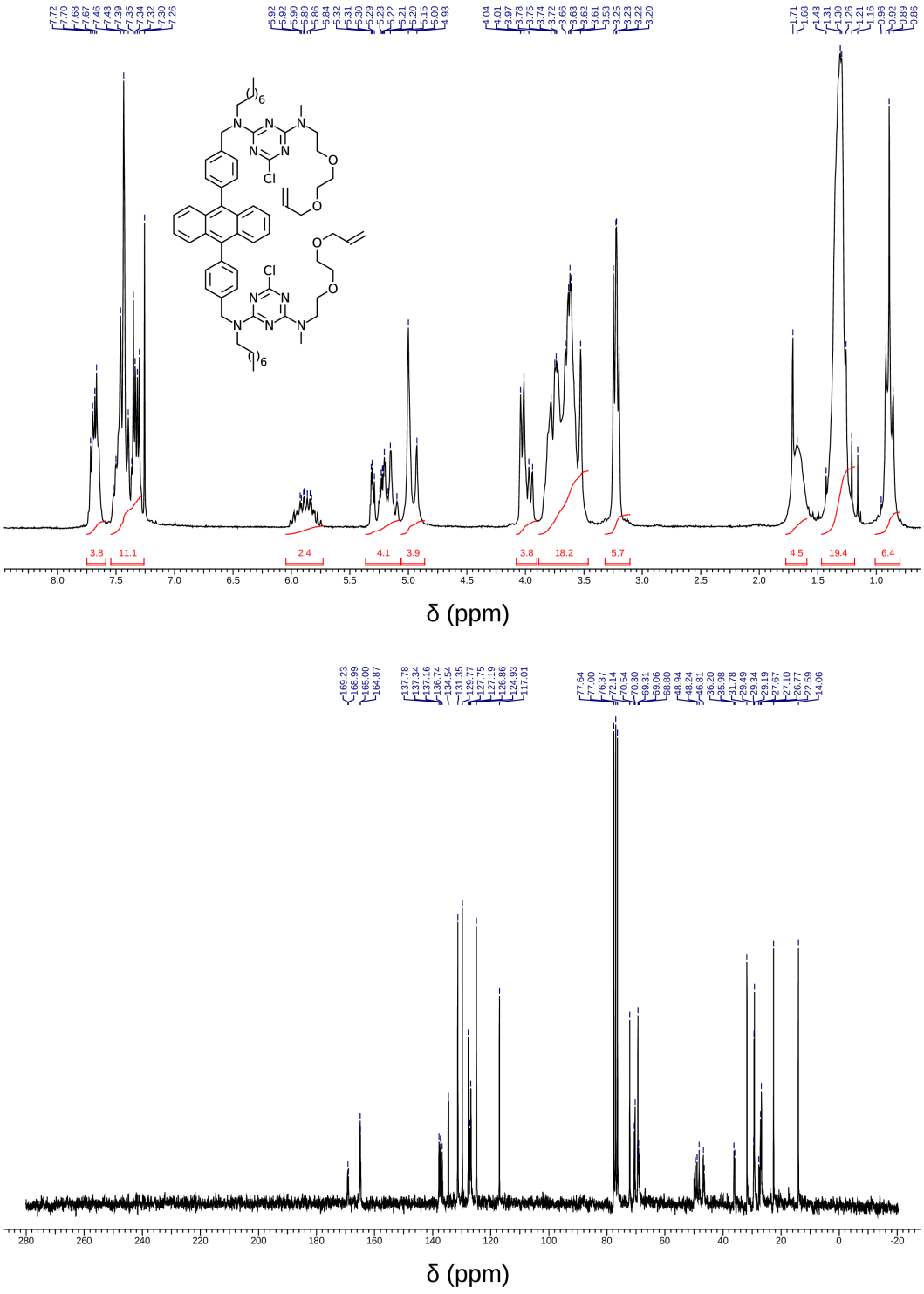

Figure S36. ^{1}H and ^{13}C (200 MHz and 50.4 MHz, $CDCl_3$) spectra of compound **12**.

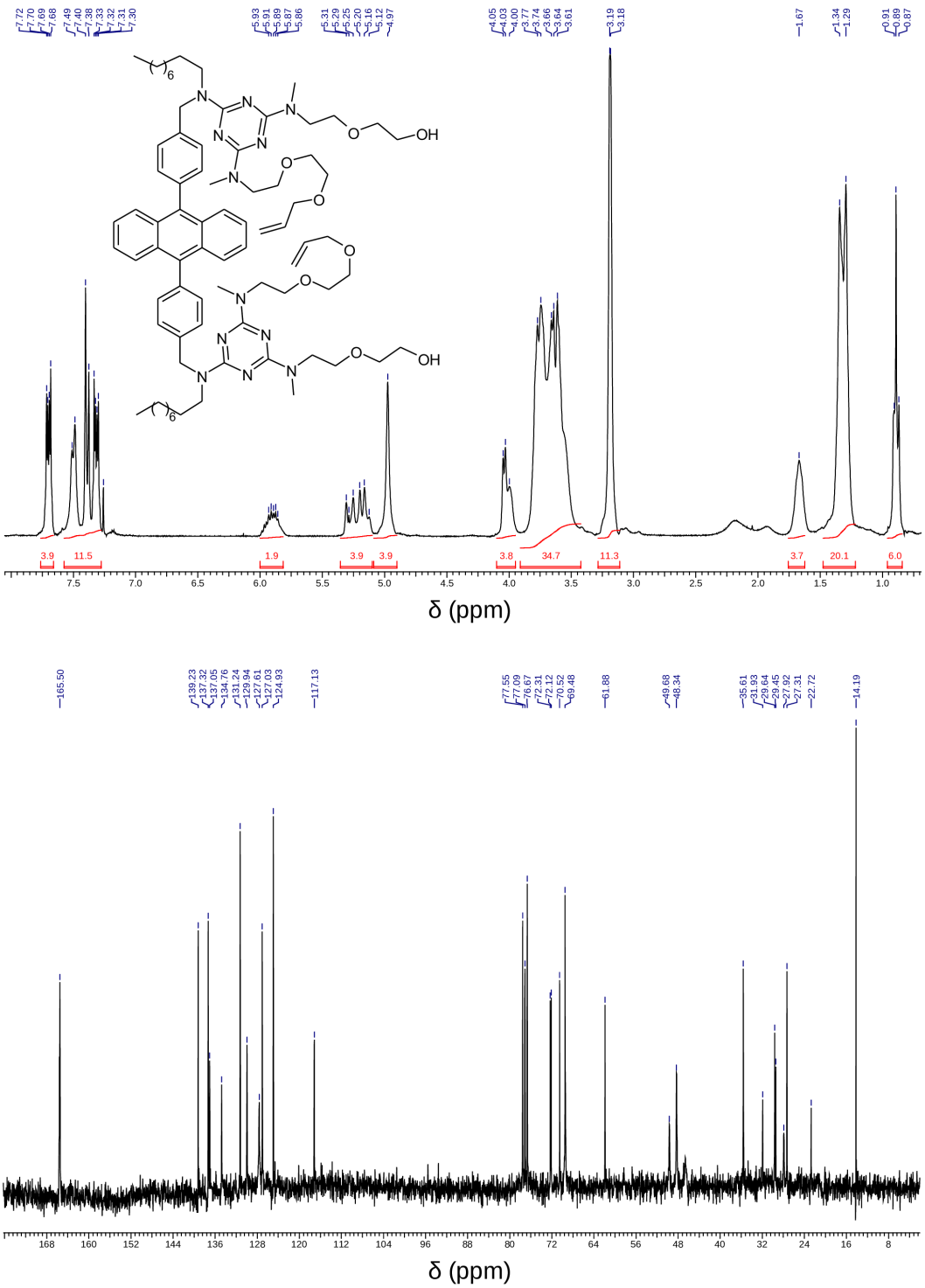

Figure S37. ^{1}H and ^{13}C (300 MHz and 75.5 MHz, $CDCl_3$) spectra of compound **10**.

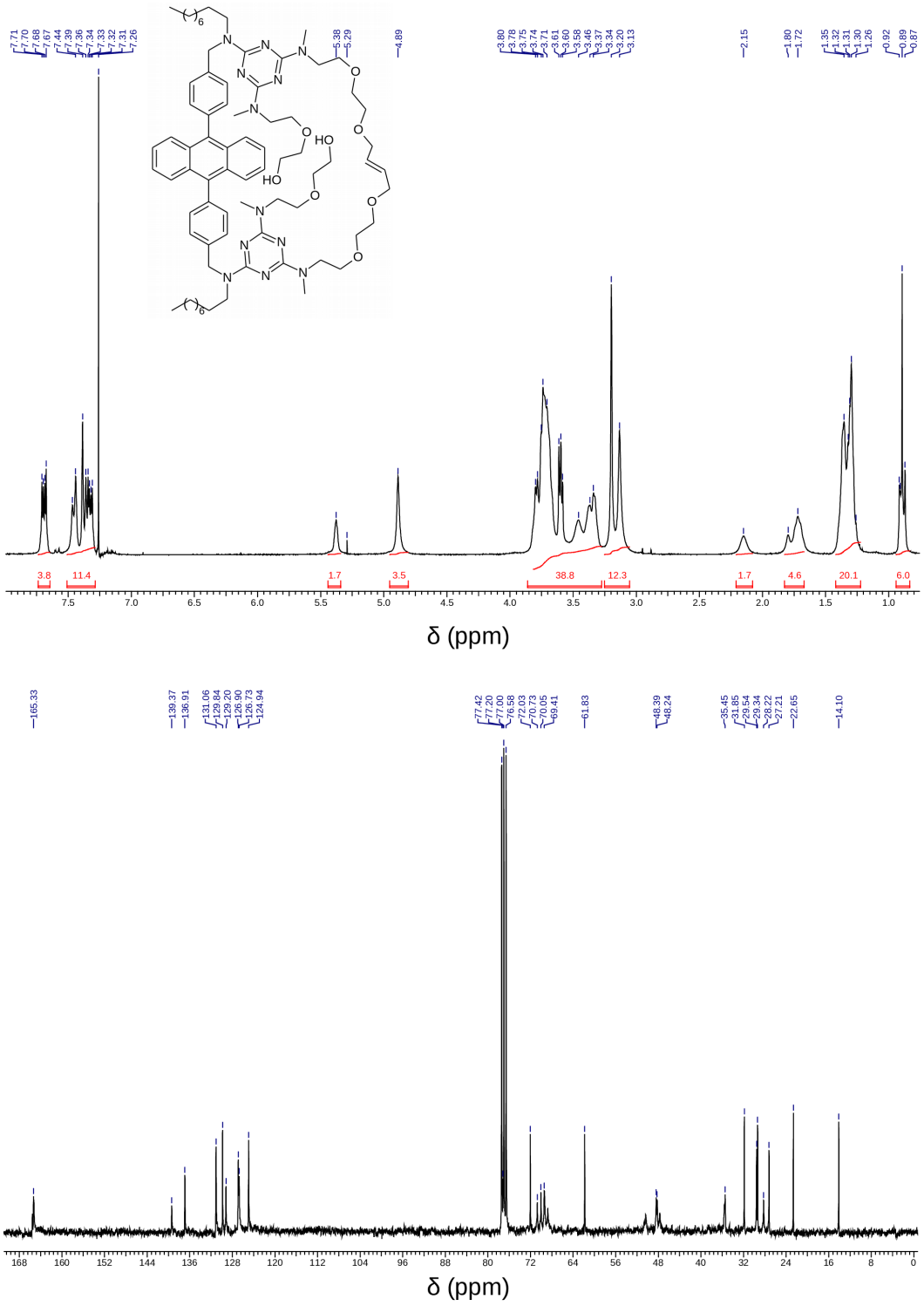

Figure S38. ^{1}H and ^{13}C (300 MHz and 75.5 MHz, $CDCl_3$) spectra of compound **13**.

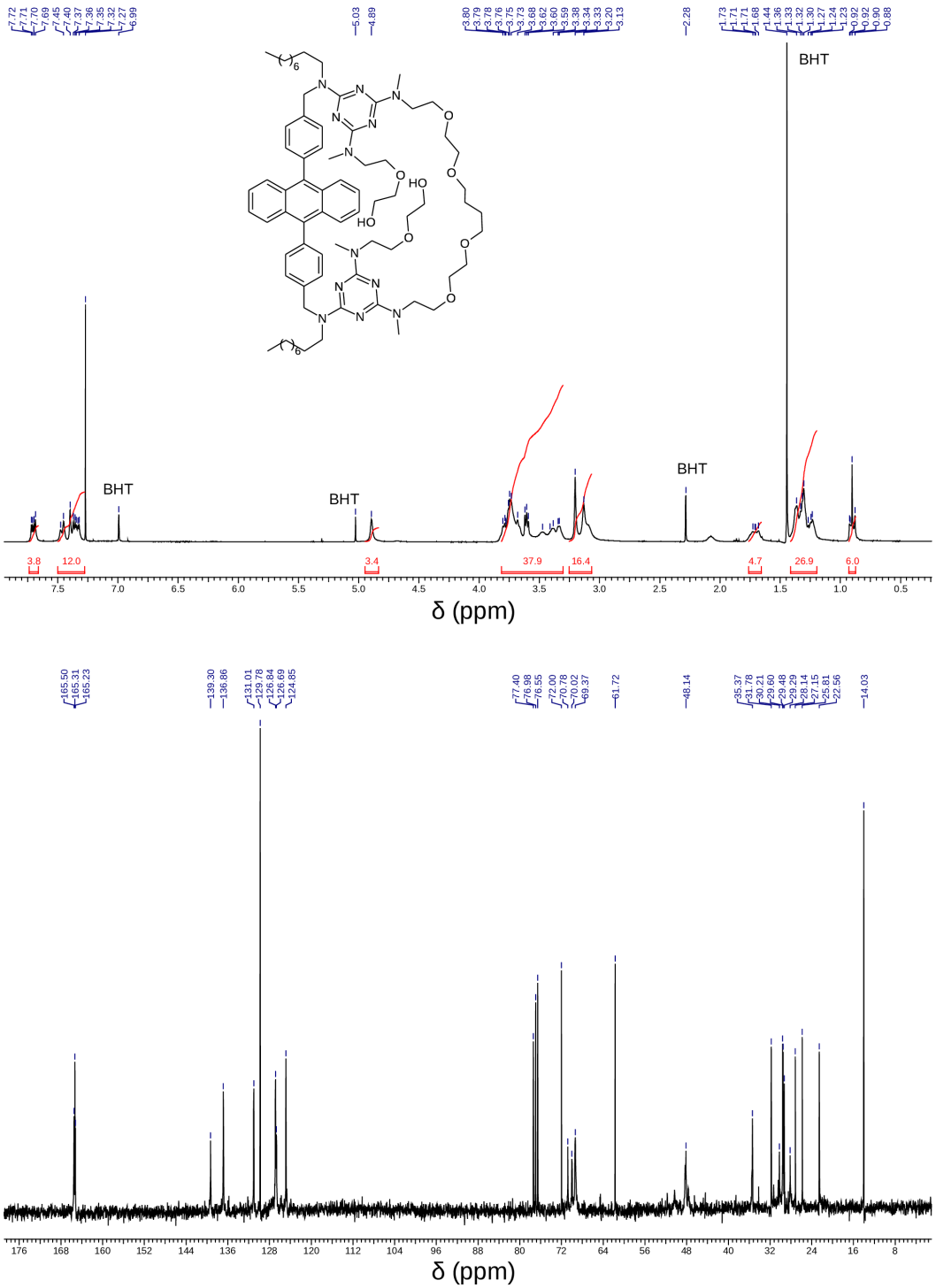

Figure S39. ^{1}H and ^{13}C (300 MHz and 75.5 MHz, $CDCl_3$) spectra of compound **11**.

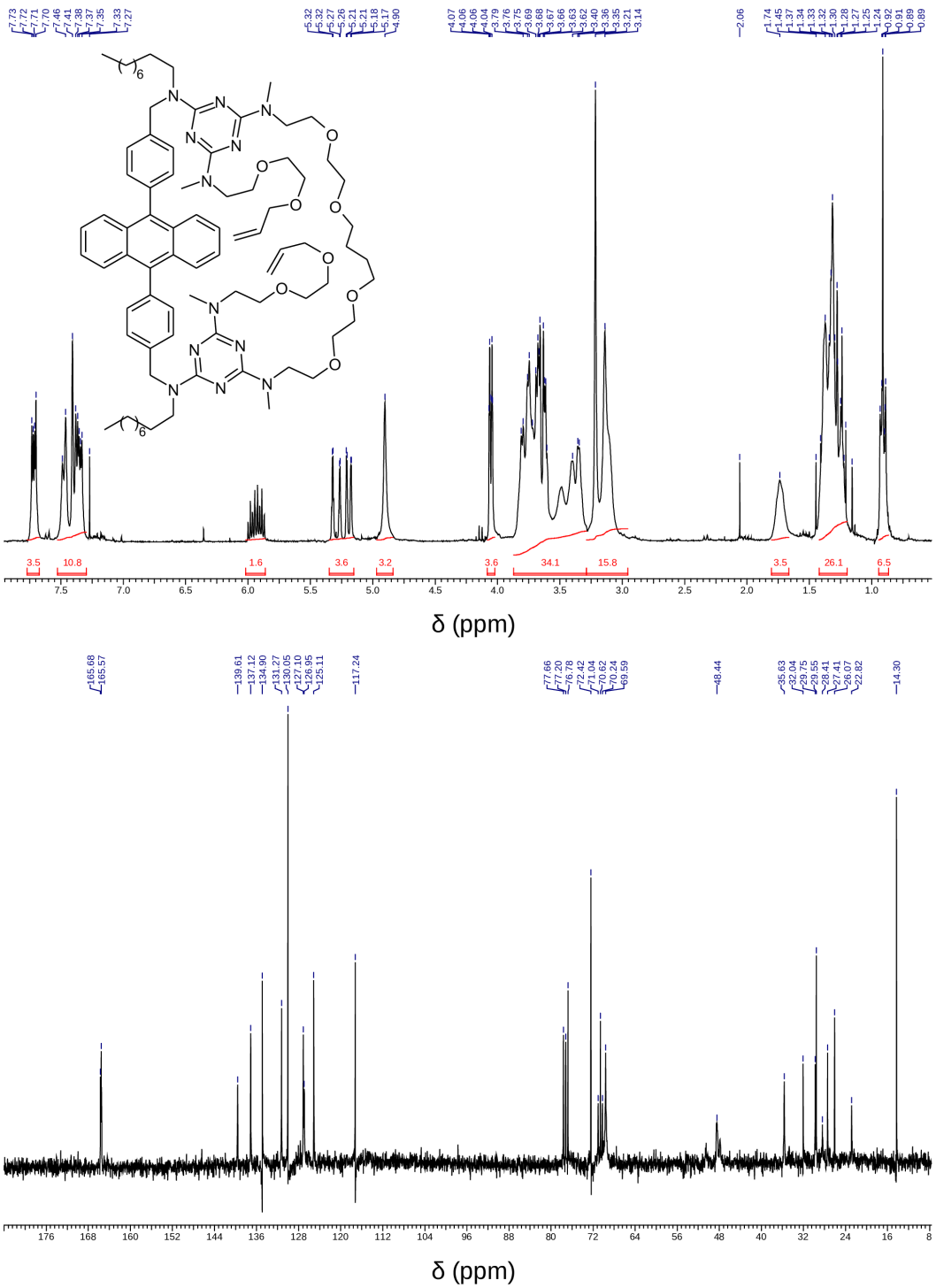

Figure S40. ^{1}H and ^{13}C (300 MHz and 75.5 MHz, $CDCl_3$) spectra of compound **14**.

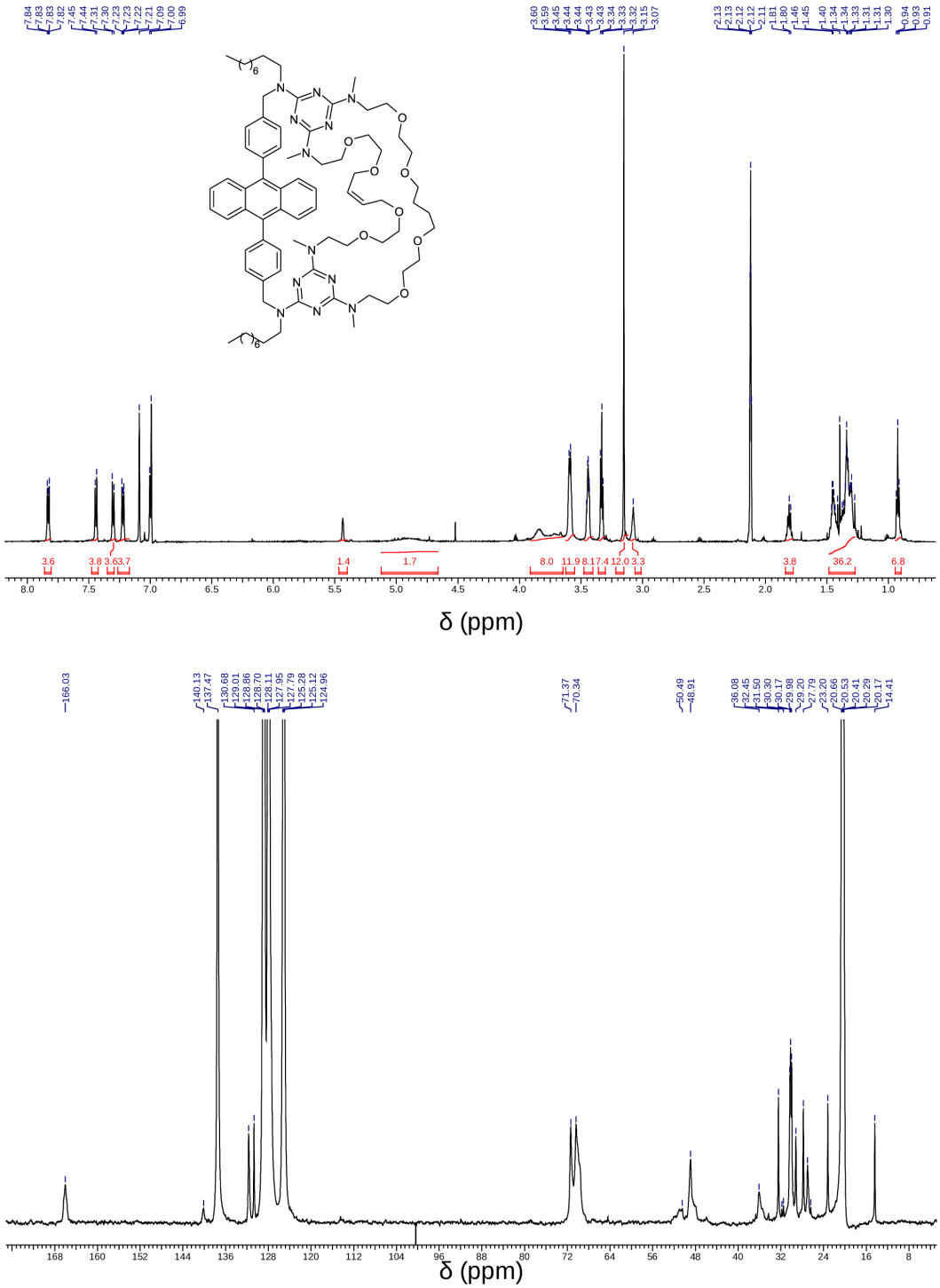

Figure S41. ^{1}H and ^{13}C (373 K, toluene-*d8,* 600 MHz and 151 MHz,) spectra of cage **2c**.

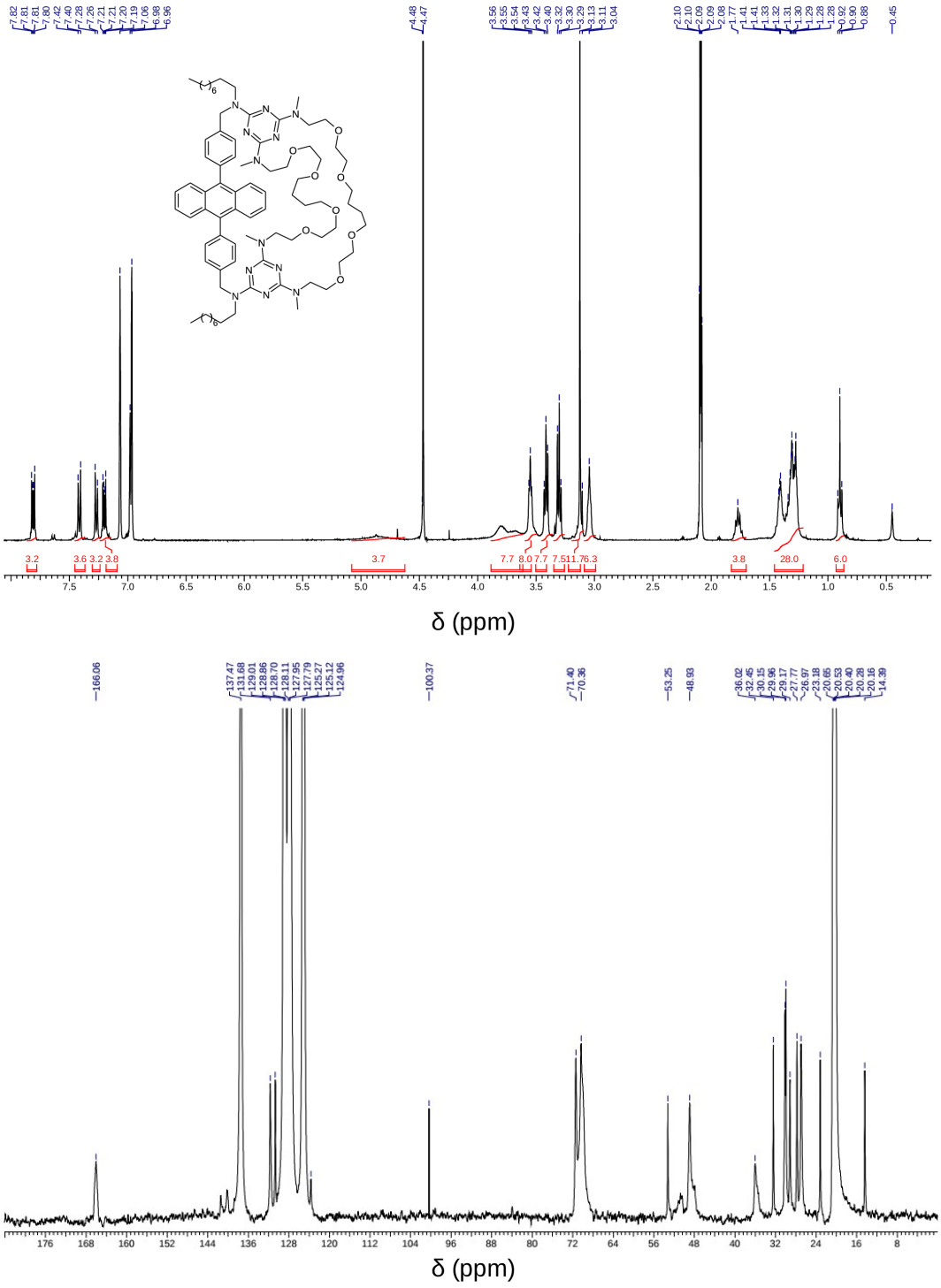

Figure S42. ^{1}H and ^{13}C (600 MHz, 363 K and 151 MHz, toluene-d_8) spectra of cage **2a**.

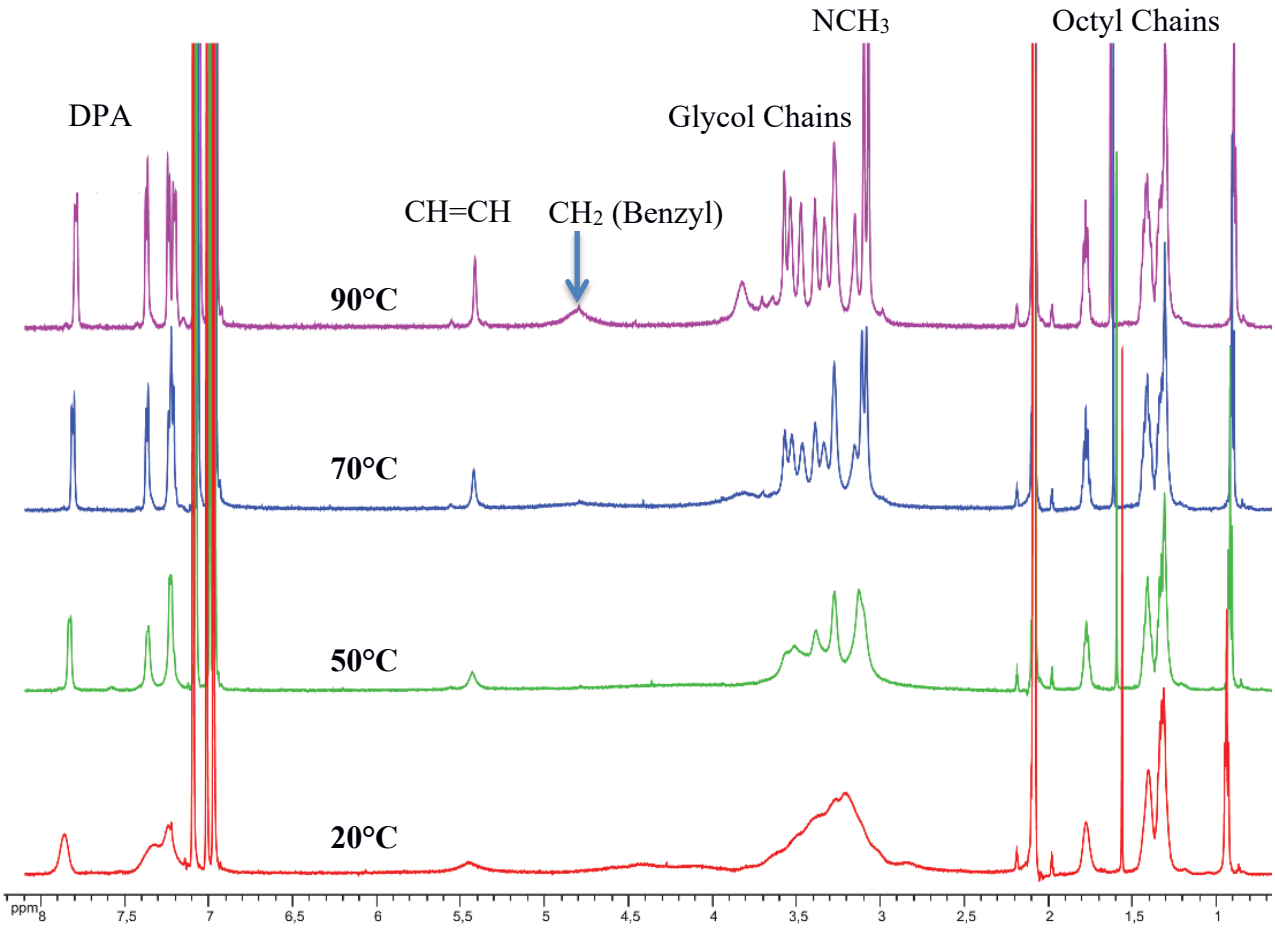

Figure S43. ^{1}H NMR (600 MHz, toluene-d_8) spectra of compound **1c** at variable temperature

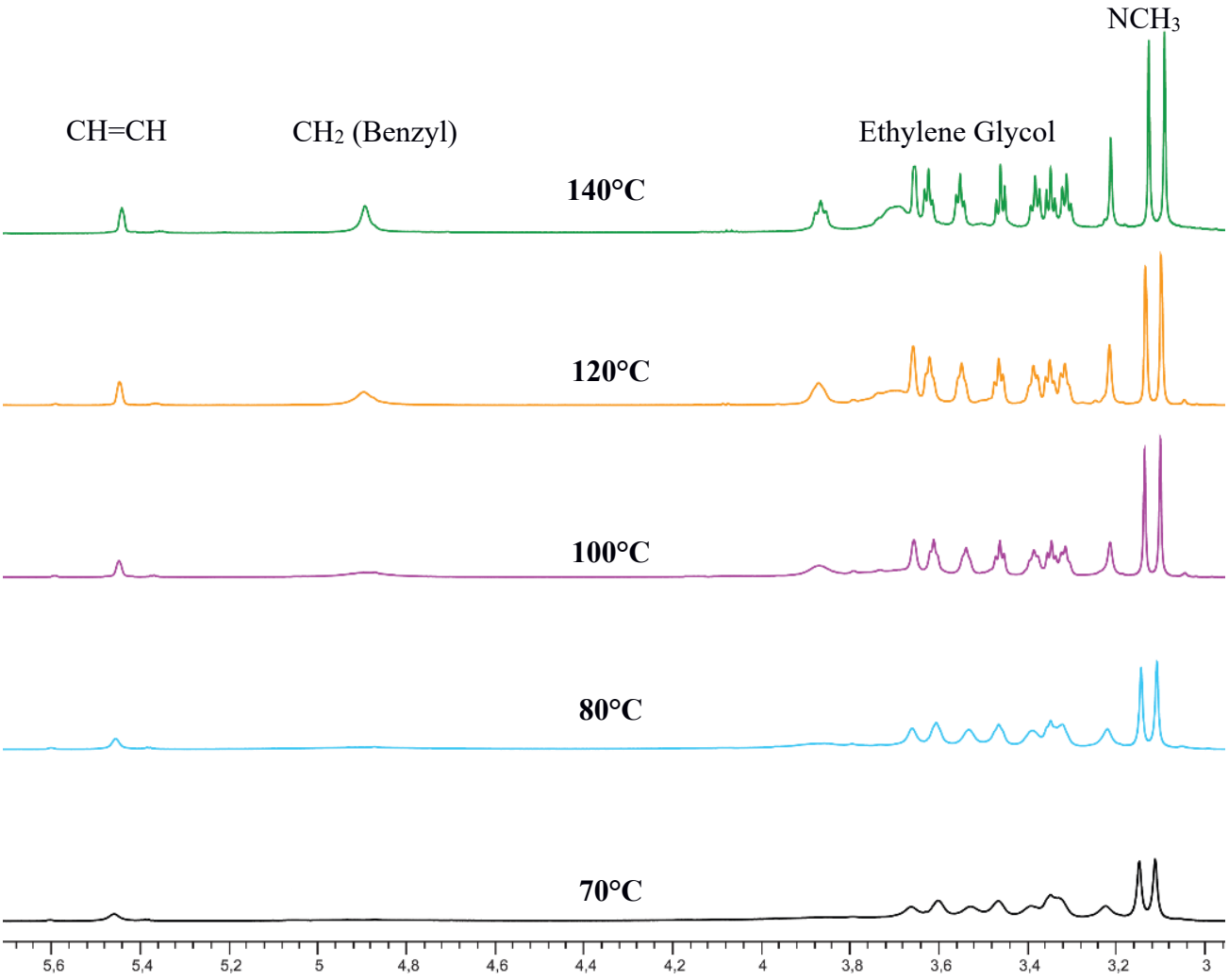

Figure S44. ^{1}H NMR (600 MHz, 1,2-dichlorobenzene-d_4) spectra of compound **1c** at variable temperature in the 0-6 ppm region

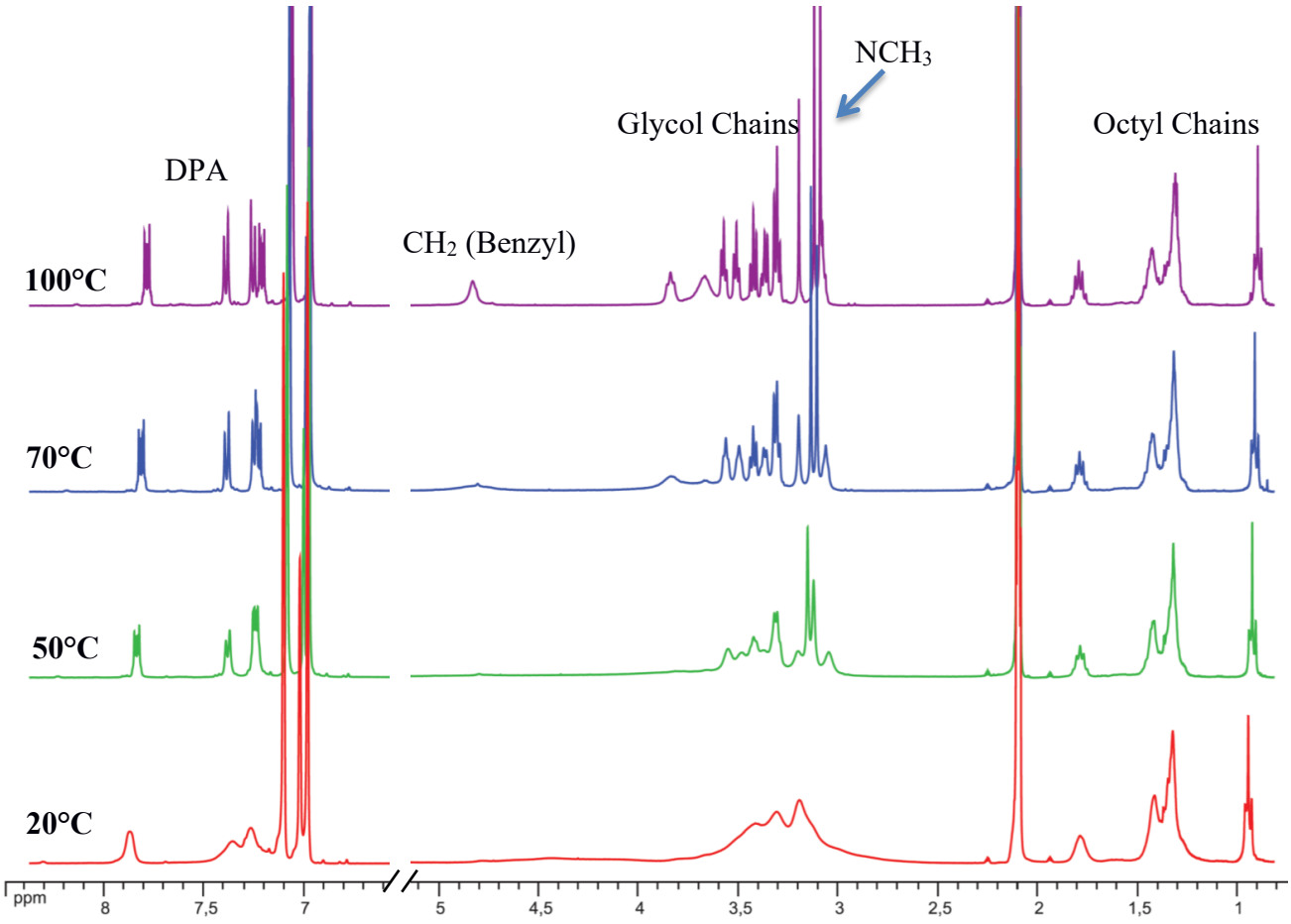

Figure S45. ^{1}H NMR (400 MHz, toluene-d_8) spectra of compound **1a** at variable temperature

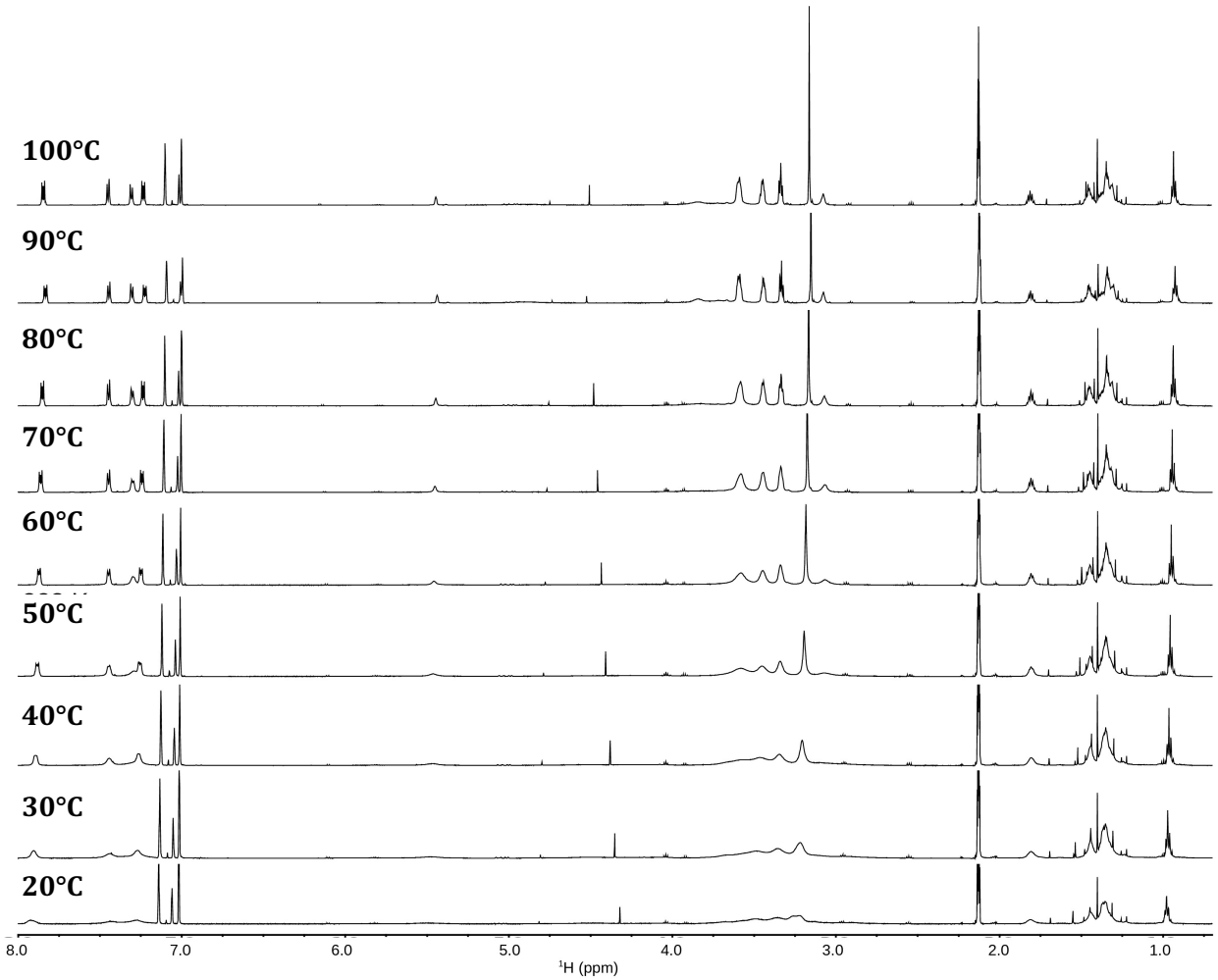

Figure S46. ^{1}H (600 MHz, toluene-d_8) spectra of compound **2c** at variable temperature.

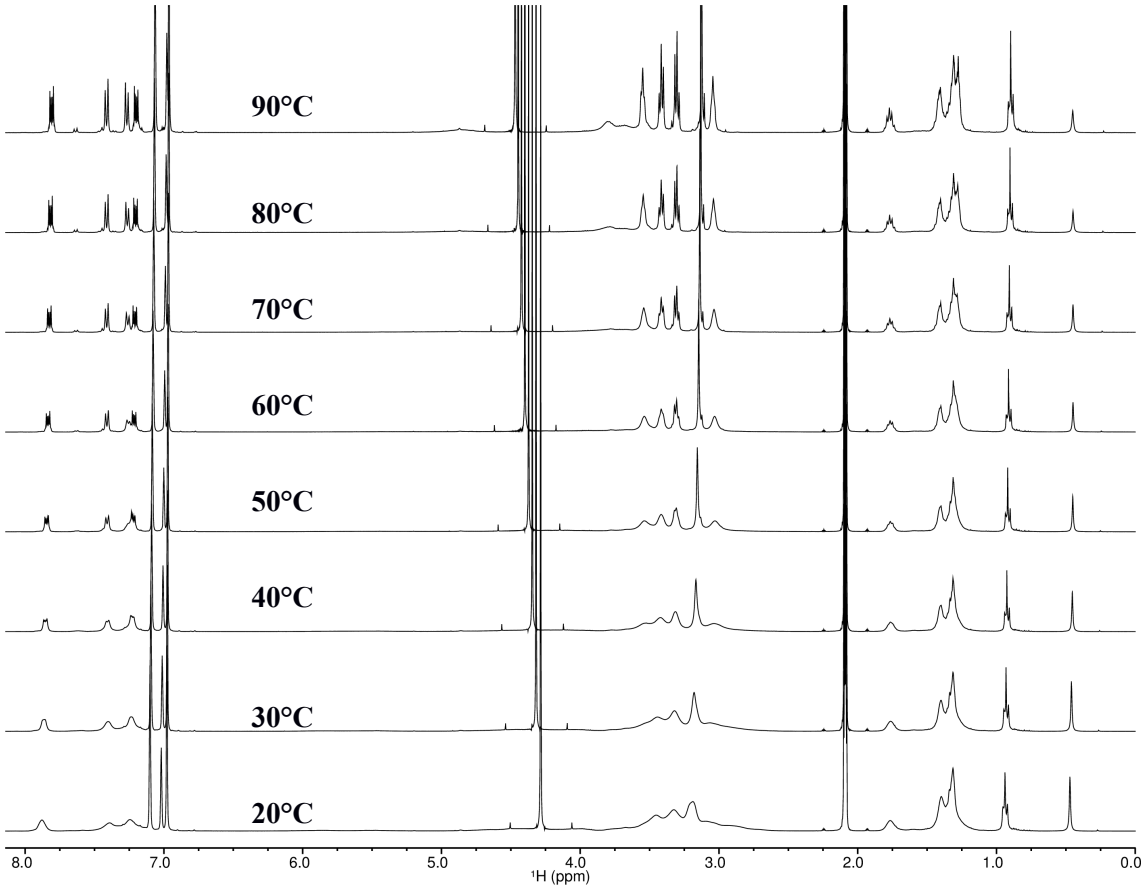

Figure S47. ^{1}H (600 MHz, toluene-d_8) spectra of compound **2a** at variable temperature.

Mass Spectra

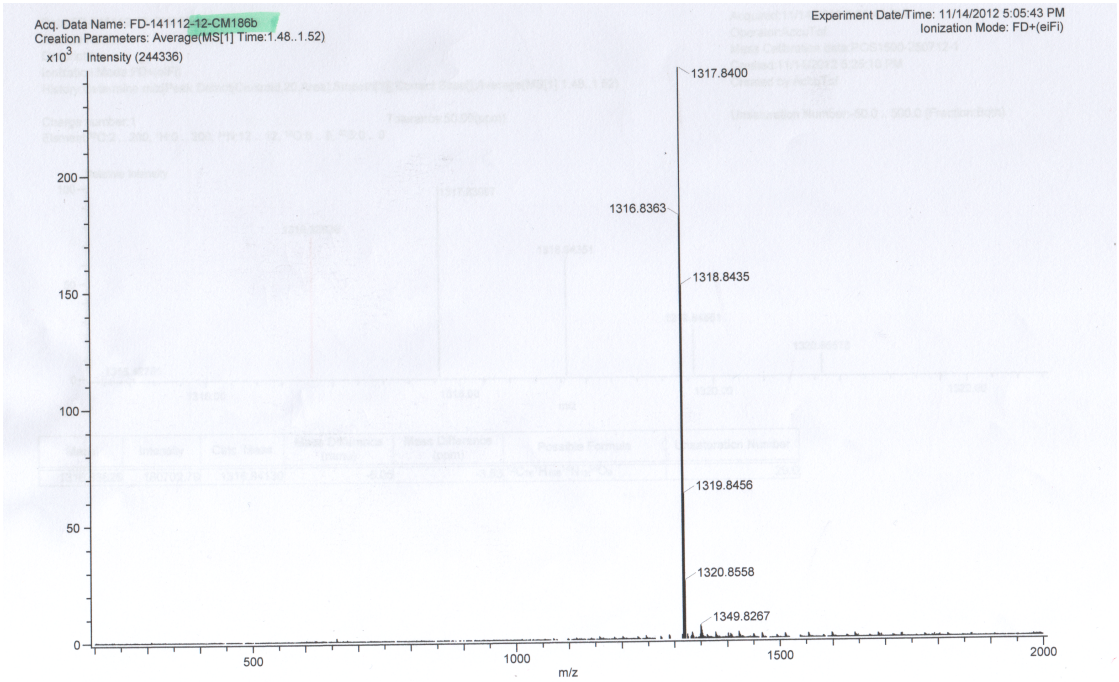

Figure S48. Mass spectrum of cage **1c** (calcd for $C_{76}H_{108}N_{12}O_8$ m/z = 1316.8413).

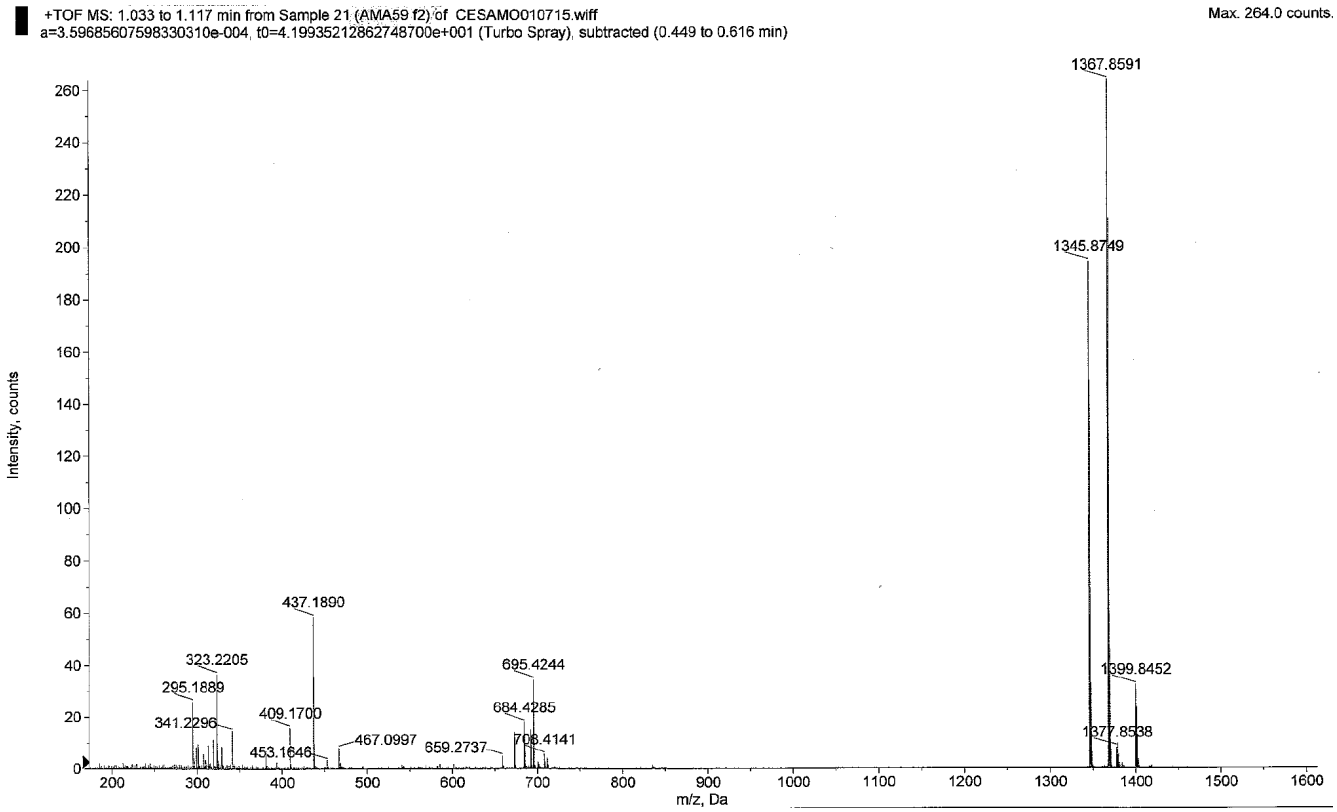

Figure S49. Mass spectrum of cage **2c** (calcd for $C_{78}H_{112}N_{12}O_8Na$ m/z = 1367.8624).