Xanthene[n]arenes: Exceptionally Large, Bowl-shaped Macrocylic Building Blocks Suitable for Self-Assembly

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1 General Information

Experimental: All reactions involving air- or moisture sensitive substances were carried out under an atmosphere of argon, and the glassware was heated out under vacuum unless otherwise stated.

Analytical methods and instruments: For analytical thin-layer chromatography (TLC), MERCK silica gel 60 F_{254} glass-baked plates were used and analyzed under UV light (λ = 254 nm [UV]) or by immersion in a cerium ammonium molybdate solution (CAM) and subsequent heat treatment.

For flash column chromatography separation, a CombiFlash® NextGen 300+ system with silica gel (RediSep® Rf Normal-phase Silica Flash Columns 4 g/12 g/24 g/40 g/80 g) cartridges was used.

For gel permeation chromatography Bio-Beads® S-X1 purchased from Bio-Rad were used. 50 g of the resin was swollen in the eluting solvent prior to packing the chromatographic column. The column was loaded with a maximum of 200 mg of crude material and washed with the eluting solvent prior to each chromatographic run.

^{1}H NMR spectra were recorded at 500 MHz or 600 MHz, using a BRUKER UltraShield 500 or a 600 MHz BRUKER Avance III NMR spectrometer. ^{13}C NMR spectra were recorded at 126 MHz or 151 MHz, using a BRUKER UltraShield 500 or a 600 MHz BRUKER Avance III NMR spectrometer equipped with a cryogenic QCI-F probe. ^{19}F NMR spectra were recorded at 565 MHz on a 600 MHz BRUKER Avance III NMR spectrometer. The experiments were performed at 298 K unless stated otherwise and the temperature was calibrated using a methanol standard showing accuracy within +/– 0.2 K. The chemical shift is given in ppm (parts per million). The ^{1}H-NMR spectra were calibrated on the signals of the residual protons of the respective solvents: $CDCl_3$ $\delta(^{1}H)$ = 7.26 ppm, acetone-d6 $\delta(^{1}H)$ = 2.05 ppm, toluene-d8 $\delta(^{1}H)$ = 2.08 ppm, DMSO-d6 $\delta(^{1}H)$ = 2.50 ppm. In ^{13}C NMR spectra the signal of the deuterium coupled multiplets of the solvents are used as reference: $CDCl_3$ $\delta(^{13}C)$ = 77.16 ppm, acetone-d6 $\delta(^{13}C)$ = 29.84 ppm, toluene-d8 $\delta(^{13}C)$ = 20.43 ppm DMSO-d6 $\delta(^{13}C)$ = 39.52 ppm.[1] The coupling constants *J* are reported in hertz (Hz). Multiplicity is described as: s (singlet), br s (broad singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet). Apparent multiplicity of magnetically non-equivalent protons is marked as virtual multiplets (*virt*). For characterization of compounds unknown in the literature, two-dimensional NMR experiments (HMQC, HMBC, COSY, NOESY) were conducted.

All DOSY-NMR experiments were performed on a Bruker Avance III HD four-channel NMR spectrometer operating at 600.13 MHz proton frequency. The instrument was equipped with a cryogenic 5 mm four-channel QCI probe (H/C/N/F) with self-shielded z-gradient. The experiments were performed at 298 K and the temperature was calibrated using a methanol standard showing accuracy within +/- 0.2 K. For the PFGSE (pulsed field gradient spin echo) diffusion experiment, the sample was placed in a 3 mm outer diameter tube and the 3 mm tube was then inserted in a standard 5 mm round bottom tube and securely kept in place by a simple home-made device. This setup ensured a negligible temperature gradient on the sample even inside a cryogenic probe. The PFGSE experiments were performed using a bipolar gradient pulse sequence.[2] The sigmoidal intensity decrease was fitted with a two-parameter fit (I_0 and diffusion coefficient D) with the DOSY routine implemented in topspin 3.6.2 [Bruker Biospin GmbH].

Infrared spectra were measured on a BRUKER ALPHA IR spectrometer (ATR, attenuated total reflection). Abbreviations indicating intensity were used as follows: vs (very strong), s (strong), m (medium), w (weak).

MALDI-TOF mass spectra were recorded on a Bruker MicroFlex LRF spectrometer using *trans*-2[3-(4-*tert*-butylphenyl)-2-methylpropenylidene]malonitrile (DCTB) as a matrix.

High-resolution mass spectra were obtained using the electrospray ionization (ESI) technique on a BRUKER maXis 4G mass spectrometer.

HPLC was performed on a LC Prominence Liquid Chromatograph system by SHIMADZU equipped with an UV–Vis detector and an ELSD detection unit. For analytical analysis a Shim-pack GIS CN 5 μm column (250 × 4.6 mm) by Shimadzu was used. The analytical separation was achieved by using the following gradient program with *n*-heptane in combination with isopropanol (flow rate: 1.0 mL/min). 0.5 minutes: 99 – 90% *n*-heptane, 15 minutes: 90 – 20% *n*-heptane, 10 minutes: 99% *n*-heptane.

For preparative separation a Shim-pack GIS CN 5 μm column (250 × 30 mm) by SHIMADZU was used. The preparative separation was achieved by using the following gradient program with *n*-heptane in combination with isopropanol (flow rate: 25 mL/min). 0.5 minutes: 99 - 90% *n*-heptane, 30 minutes: 90 – 30% *n*-heptane, 5 minutes: 50 – 5% n-heptane, 5 minutes: 5% *n*-heptane, 1 minute: 5 – 99% *n*-heptane, 4 minutes: 99% *n*-heptane.

Optical Spectroscopy: All optical spectroscopic experiments were carried out at 293 K. Steady-state absorption and luminescence spectra were recorded using a Cary 5000 spectrophotometer (Varian) and a Fluorolog-3-22 instrument (Horiba Jobin-Yvon), respectively. Luminescence lifetime and quenching measurements were performed on a

LifeSpec II spectrometer (time-correlated single photon counting technique) from Edinburgh Instruments using picosecond pulsed diode lasers for excitation at 313 nm. Unless otherwise indicated, the solutions were purged with argon (4.8, PanGas) for at least two minutes before the experiments and sealed under argon (1 atm) using cuvettes with septum caps.

Electrochemistry: Cyclic voltammetry was performed in an MBraun Glovebox under an Ar-atmosphere. A glassy carbon disk electrode served as working electrode and two silver wires were used as counter electrode and (pseudo)-reference electrode. To apply and control the voltage, a Versastat3-200 potentiostat from Princeton Applied Research was used.

Solvents: Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were processed by an INERT solvent purification system prior to use. Anhydrous acetone was purchased from VWR. Anhydrous *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were purchased from ACROS ORGANICS.

For work-up, column chromatography and reactions under non-anhydrous conditions acetonitrile (MeCN), cyclohexane (CH), ethyl acetate (EA), tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), dichloroethane (DCE), heptane (Hep), hexafluroisopropanol (HFIP), methanol (MeOH), ethanol (EtOH), isopropanol (*i*-PrOH), methyl *tert*-butyl ether (MTBE) and tetrachloroethane (TCE) were purchased from VWR in HPLC-grade quality, while for *n*-pentane (P) and diethyl ether (Et_2O) technical grade was used and distilled prior to use.

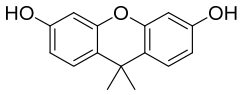
Solvents for NMR spectroscopy were purchased from CAMBRIDGE ISOTOPE LABORATORIES [$CDCl_3$ (99.8%), acetone-d6 (99.8%), DMSO-d6 (99.9%)] or ACROS ORGANICS [toluene-d8 (99.5%)].

Chemicals: All reagents used were purchased from commercial distributers and used without further purification unless otherwise stated.

N-Bromosuccinimide (NBS) used for the aromatic bromination reaction was recrystallized from commercially available material according to a literature procedure and stored under an argon atmosphere at −20 °C.[3]

2 Synthetic Procedures and Analytical Data

9,9-Dimethyl-9H-xanthene-3,6-diol (9)

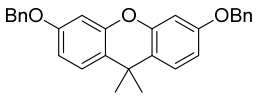


$C_{15}H_{14}O_3$
M = 242.27

Following a modified procedure by Hanousek *et al.*,[4] a suspension of resorcinol (50.0 g, 454 mmol, 1.0 eq.) and anhydrous $ZnCl_2$ (50.0 g, 367 mmol, 0.81 eq.) in anhydrous acetone (18.4 mL, 14.5 g, 250 mmol, 0.55 eq.) was stirred at 140 °C for 6 h. Subsequently, the mixture was cooled down to 60 °C, treated with EtOH (100 mL), water (50 mL) and sonicated to give a homogenous suspension. The suspension was filtered and the residue was washed with a mixture of EtOH:water (1:2, 200 mL), followed by CH_2Cl_2 (100 mL). The residue was dried under high vacuum to give **9** (28.8 g, 119 mmol, 52%) as a yellow powder.

TLC R_f = 0.28 (P:EA = 2:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3277 (s), 2966 (m), 2942 (w), 2361 (w), 1618 (s), 1507 (m), 1442 (vs), 1355 (w), 1322 (w), 1303 (m), 1167 (vs), 1121 (s), 1079 (w), 996 (s), 851 (s), 811 (s).
^{1}H NMR (500 MHz, DMSO-d6) δ [ppm] = 9.44 (s, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.51 (dd, *J* = 8.5, 2.5 Hz, 2H), 6.36 (d, *J* = 2.5 Hz, 2H), 1.47 (s, 6H).
^{13}C{^{1}H} NMR (126 MHz, DMSO-d6) δ [ppm] = 156.5, 150.1, 127.3, 120.5, 110.9, 102.0, 32.9, 32.4.
HR-MS (ESI-): m/z (%) [$C_{15}H_{14}O_3$] = calc.: 241.0870 [M-H]$^-$, meas.: 241.0867 [M-H]$^-$.

3,6-Bis(benzyloxy)-9,9-dimethyl-9H-xanthene (S1)



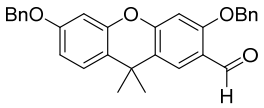
$C_{29}H_{26}O_3$
M = 422.52

A solution of **9** (7.50 g, 31.0 mmol, 1.0 eq.) in anhydrous DMF (100 mL) was cooled to 0 °C and treated portionwise with NaH (60% dispersion in mineral oil, 3.10 g, 77.5 mmol, 2.5 eq.). The mixture was warmed up to room temperature and stirred for 1 h. After gas evolution stopped, the reaction mixture was cooled to 0 °C, treated with BnBr (7.35 mL, 10.6 g, 62.0 mmol, 2.0 eq.), warmed up to room temperature and stirred for 18 h. The reaction mixture was treated with water (5 mL), concentrated *in vacuo*, triturated with water (200 mL) and filtered. The residue was washed with water (100 mL), recrystallized from chloroform and dried under high vacuum to give **S1** (12.1 g, 28.6 mmol, 92%) as a white powder.

TLC: R_f = 0.28 (P:EA = 19:1, [UV/CAM]).

IR (ATR): ν (cm^{-1}) = 3056 (w), 3034 (w), 2974 (w), 2931 (w), 2871 (w), 2360 (w), 2342 (w), 2331 (w), 1627 (w), 1611 (m), 1566 (m), 1500 (s), 1453 (m), 1413 (m), 1379 (m), 1329 (m), 1259 (m), 1177 (s), 1112 (m), 1079 (m), 1013 (s), 994 (w), 833 (s).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.48 – 7.31 (m, 10H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.74 (dd, *J* = 8.6, 2.6 Hz, 2H), 6.65 (d, *J* = 2.6 Hz, 2H), 5.07 (s, 4H), 1.59 (s, 6H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 158.2 (s), 151.1, 137.1, 128.8, 128.1, 127.7, 127.1, 122.8, 110.8, 102.1, 70.3, 33.2, 33.1.
HR-MS (ESI+): m/z (%) [$C_{29}H_{26}O_3$] = calc.: 445.1774 $[M+Na]^+$, meas.: 445.1772 $[M+Na]^+$.

3,6-Bis(benzyloxy)-9,9-dimethyl-9H-xanthene-2-carbaldehyde (S2)

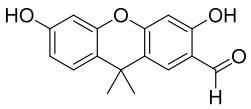


$C_{30}H_{26}O_4$
M = 450.53

A suspension of **S1** (34.9 g, 82.6 mmol, 1.0 eq.) in anhydrous CH_2Cl_2 (500 mL) was treated with DMF (38.3 mL, 36.2 g, 496 mmol, 6.0 eq.) and $POCl_3$ (45.2 mL, 76.0 g, 496 mmol, 6.0 eq.) with the flask being placed in a water bath at room temperature. The mixture was then stirred at reflux for 7 days. After that, water (300 mL) was carefully added under cooling to 0 °C and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL), combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (200 mL), dried (Na_2SO_4), filtered and the solvent was removed *in vacuo* to give **S2** (35.7 g, 79.3 mmol, 96%) as a brown solid. The crude product was sufficiently pure to be used in the next step without further purification.

TLC: R_f = 0.32 (P:EA = 4:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3064 (w), 3034 (w), 2967 (w), 2865 (w), 2358 (w), 1677 (s), 1608 (s), 1567 (m), 1488 (s), 1454 (m), 1420 (m), 1381 (m), 1306 (m), 1289 (m), 1260 (m), 1200 (vs), 1134, (w), 1086 (m), 1071 (m), 1021 (m), 914 (w), 833 (w).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.44 (s, 1H), 7.97 (s, 1H), 7.48 – 7.33 (m, 10H), 7.31 (d, *J* = 8.7 Hz, 1H), 6.78 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.67 (s, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 5.19 (s, 2H), 5.07 (s, 2H), 1.60 (s, 6H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 188.4, 160.8, 158.3, 156.4, 150.2, 136.9, 136.1, 128.9, 128.8, 128.5, 128.2, 127.6, 127.6, 127.5, 127.3, 123.7, 122.4, 121.4, 111.5, 102.4, 100.7, 70.8, 70.4, 33.2, 33.2.
HR-MS (ESI+): m/z (%) [$C_{30}H_{26}O_4$] = calc.: 473.1723 $[M+Na]^+$, meas.: 473.1720 $[M+Na]^+$.

3,6-Dihydroxy-9,9-dimethyl-9H-xanthene-2-carbaldehyde (12)



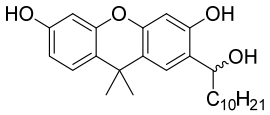
$C_{16}H_{14}O_4$
M = 270.28

Aldehyde **S2** (8.00 g, 17.8 mmol, 1.0 eq.) and thioanisole (8.35 mL, 8.82 g, 71.0 mmol, 4.0 eq.) were dissolved in toluene (250 mL) and cooled to 0 °C. TFA (200 mL) was added, the mixture was warmed up to room temperature and stirred for 72 h. After removing the solvent *in vacuo*, the crude product was purified *via* flash column chromatography (160 g silica gel, P:CH_2Cl_2 = 2:3 → 0:1) to give **12** (2.98 g, 11.0 mmol, 62%) as a white solid.

Note: The reaction gave yields up to 80% when run more dilute at a concentration of 10 mM.

TLC: R_f = 0.21 (CH_2Cl_2, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3466 (m), 2975 (w), 2854 (w), 2359 (w), 2343 (w), 1645 (m), 1624 (s), 1508 (m), 1494 (m), 1423 (s), 1388 (m), 1327 (m), 1293 (s), 1253 (s), 1191 (s), 1169 (s), 1085 (m), 972 (w), 908 (w), 833 (s), 800 (s).
^{1}H NMR (500 MHz, acetone-d6) δ [ppm] =11.12 (s, 1H), 9.94 (s, 1H), 8.53 (s, 1H), 8.00 (s, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 6.68 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.55 (d, *J* = 2.5 Hz, 1H), 6.54 (s, 1H), 1.62 (s, 6H).
^{13}C{^{1}H} NMR (126 MHz, acetone-d6) δ [ppm] =196.5, 162.2, 157.9, 157.8, 150.8, 134.5, 128.2, 124.4, 121.5, 118.9, 112.9, 104.0, 103.5, 33.7, 33.3.
HR-MS (ESI-): m/z (%) [$C_{16}H_{14}O_4$] = calc.: 269.0819 [M-H]$^-$, meas.: 269.0814 [M-H]$^-$.

2-(1-Hydroxyundecyl)-9,9-dimethyl-9H-xanthene-3,6-diol (15)



$C_{26}H_{36}O_4$
M = 412.57

A two-neck round bottom flask equipped with condenser was filled with Mg-turnings (899 mg, 37.0 mmol, 10 eq.) and a crystal of iodine and gently heated with a heatgun. Anhydrous THF (15 mL) was added, followed by the slow addition of 1-bromodecane (3.58 mL, 3.80 g, 16.7 mmol, 4.5 eq.) and the reaction mixture was subsequently heated to 70 °C under reflux for 2 h. Upon cooling to room temperature, the Grignard reagent was transferred into a dropping funnel and used for the following reaction.

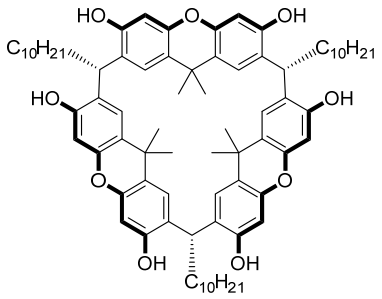
Aldehyde **12** (1.00 g, 3.70 mmol, 1.0 eq.) was dissolved in anhydrous THF (30 mL), cooled to 0 °C and treated dropwise with the Grignard reagent. The reaction mixture was stirred at room temperature for 20 h, then water (5 mL) was added and the solvent concentrated at room

temperature *in vacuo* to 10 mL. The mixture was diluted with CH_2Cl_2 (100 mL) and filtered through celite. After removing the solvent at room temperature *in vacuo*, the crude product was purified *via* flash column chromatography (40 g silica gel, CH_2Cl_2:MeOH = 100:0 → 67:1) to give **15** (1.38 g, 3.34 mmol, 90%) as a colorless oil and used immediately in the next reaction.

Note: The product was unstable under high vacuum and when stored in the freezer at - 20 °C for 16 h. Therefore, it was preferentially used immediately in the next step, or stored at – 80 °C for up to 72 h.

TLC: R_f = 0.12 (CH_2Cl_2:MeOH = 49:1, [UV/CAM]).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.90 (s, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.93 (s, 1H), 6.56 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.52 (s, 1H), 6.47 (d, *J* = 2.6 Hz, 1H), 5.21 (s, 1H), 4.82 (t, *J* = 6.7 Hz, 1H), 2.66 (s, 1H), 1.96 – 1.86 (m, 1H), 1.86 – 1.76 (m, 1H), 1.53 (d, *J* = 3.2 Hz, 6H), 1.49 – 1.25 (m, 15H), 0.87 (t, *J* = 6.9 Hz, 3H).

(2r,4r,6r)-2,4,6-Tris(decyl)-19,19,39,39,59,59-hexamethyl-19H,39H,59H-1,3,5(2,7)-trixanthenacyclohexaphane-13,16,33,36,53,56-hexaol (19)

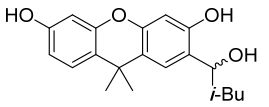


$C_{78}H_{102}O_9$
M = 1183.67

A solution of **15** (1.35 g, 3.27 mmol, 1.0 eq.) in CH_2Cl_2 (115 mL) was cooled to 0 °C, treated with TFA (20 mL), let warm up to room temperature and stirred for 20 h. After removing the solvent *in vacuo*, purification *via* flash column chromatography (24 g silica gel, CH_2Cl_2:MeOH = 99:1 → 39:1) yielded crude **19**. Further purification by gel permeation chromatography (BioBeads® S-X1, toluene) afforded **19** (272 mg, 230 µmol, 21%) as a white solid.

TLC: R_f = 0.44 (CH_2Cl_2:MeOH = 9:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3318 (m), 2953 (w), 2922 (s), 2853 (m), 2360 (w), 2341 (w), 1613 (m), 1487 (s), 1464 (w), 1429 (m), 1384 (w), 1361 (w), 1282 (m), 1218 (m), 1165 (s), 1062 (m), 873 (w), 848 (m).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.48 (s, 6H), 7.18 (s, 6H), 6.56 (s, 6H), 4.35 (t, *J* = 7.5 Hz, 3H), 2.19 (dt, *J* = 7.5 Hz, 6H), 1.58 (s, 9H), 1.42 – 1.17 (m, 57H), 0.89 (t, *J* = 6.9 Hz, 9H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 150.8, 150.5, 126.6, 125.5, 121.9, 104.0, 35.3, 34.1, 33.5, 33.0, 32.1, 29.8, 29.7, 29.6, 29.6, 29.5, 28.0, 24.7, 22.9, 14.3.
HR-MS (ESI-): m/z (%) [$C_{78}H_{102}O_9$] = calc.: 1181.7451 [M-H]$^-$, meas.: 1181.7435 [M-H]$^-$.

2-(1-Hydroxy-3-methylbutyl)-9,9-dimethyl-9H-xanthene-3,6-diol (16)



$C_{20}H_{24}O_4$
M = 328.41

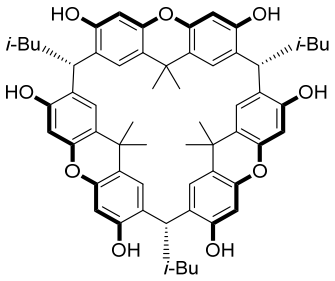
Aldehyde **12** (990 mg, 3.66 mmol, 1.0 eq.) was dissolved in anhydrous THF (60 mL), cooled to 0 °C and treated dropwise with *i*-BuMgBr (2.0 M in Et2O, 7.32 mL, 14.6 mmol, 4.0 eq.). The reaction mixture was stirred at room temperature for 40 h, then water (2 mL) was added and the solvent concentrated at room temperature *in vacuo* to 10 mL. The mixture was diluted with CH_2Cl_2 (100 mL) and filtered through celite. After removing the solvent at room temperature *in vacuo*, the crude product was purified *via* flash column chromatography (24 g silica gel, CH_2Cl_2:MeOH = 100:0 → 67:1) to give **16** (1.20 g, 3.65 mmol, quant.) as a colorless oil that was used immediately in the next reaction.

Note: The product was unstable under high vacuum and when stored in the freezer at - 20 °C for 16 h. Therefore, it was preferentially used immediately in the next step, or stored at – 80 °C for up to 72 h.

TLC: R_f = 0.11 (CH_2Cl_2:MeOH = 49:1, [UV/CAM]).

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.79 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 6.93 (s, 1H), 6.57 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.55 (s, 1H), 6.50 (d, *J* = 2.6 Hz, 1H), 4.91 (dt, *J* = 6.7 Hz, 1H), 4.75 (s, 1H), 2.37 (s, 1H), 1.92 - 1.86 (m, 1H), 1.76 - 169 (m, 1H), 1.62 – 1.50 (m, 7H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.96 (d, *J* = 6.5 Hz, 3H).

(2r,4r,6r)-2,4,6-Triisobutyl-19,19,39,39,59,59-hexamethyl-19H,39H,59H-1,3,5(2,7)-trixanthenacyclohexaphane-13,16,33,36,53,56-hexaol (20)

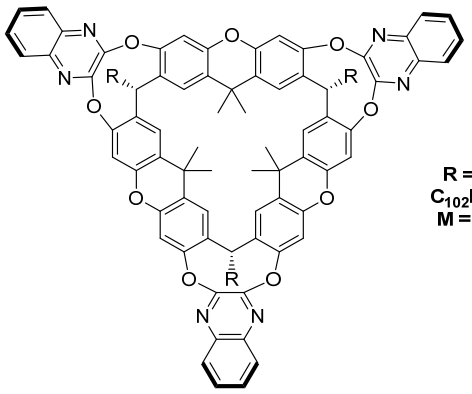


$C_{60}H_{66}O_9$
M = 931.18

A solution of **16** (1.20 g, 3.65 mmol, 1.0 eq.) in CH_2Cl_2 (135 mL) was cooled to 0 °C, treated with TFA (15 mL), let warm up to room temperature and stirred for 20 h. After removing the solvent *in vacuo*, purification *via* flash column chromatography (24 g silica gel, CH_2Cl_2:MeOH = 99:1 → 39:1) yielded crude **20**. Further purification by gel permeation chromatography (BioBeads® S-X1, THF) afforded **20** (193 mg, 17%) as a white, crystalline solid.

TLC: R_f = 0.37 (CH_2Cl_2:MeOH = 9:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3343 (m), 2954 (m), 2929 (w), 2868 (w), 2361 (m), 2339 (w), 1691 (m), 1641 (m), 1499 (s), 1434 (m), 1362 (w), 1285 (m), 1241 (m), 1169 (s), 1065 (m), 875 (w), 852 (w).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.45 (s, 6H), 7.53 (s, 6H), 6.40 (s, 6H), 4.81 (t, *J* = 8.0 Hz, 3H), 2.15 (dd, *J* = 8.0 Hz, 6H), 1.76 (s, 9H), 1.62 – 1.55 (m, 3H), 1.31 (s, 9H), 0.97 (d, *J* = 6.6 Hz, 18H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 153.2, 151.2, 128.3, 124.8, 124.3, 104.0, 43.2, 35.4, 34.5, 32.1, 27.2, 26.7, 23.1.
HR-MS (ESI-): m/z (%) [$C_{60}H_{66}O_9$] = calc.: 929.4634 $[M-H]^-$, meas.: 929.4627 $[M-H]^-$.

Cavitand 23



Xanthene[3]arene **19** (46.0 mg, 38.9 µmol, 1.0 eq.) and 2,3-dichloroquinoxaline (24.0 mg, 120 µmol, 3.1 eq.) were dissolved in anhydrous DMSO (5 mL). Cs_2CO3 (41.8 mg, 128 µmol, 3.3 eq.) was added and the suspension was stirred at room temperature for 96 h. Subsequently water (50 mL) was added and the mixture was extracted with CH_2Cl_2 (5 × 20 mL). The combined organic layers were washed with brine (2 × 50 mL), dried (Na_2SO_4) and filtered. The solvent was removed *in vacuo* and the crude product was purified *via* flash column chromatography (4 g silica gel, P:EA = 1:0 → 4:1) to obtain cavitand **23** (29.3 mg, 18.8 µmol, 48 %) as a white solid.

TLC: R_f = 0.26 (P:EA = 4:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 2954 (w), 2925 (s), 2854 (m), 2361 (m), 2342 (m), 1605 (w), 1478 (s), 1406 (s), 1332 (s), 1272 (w), 1233 (w), 1163 (m), 1138 (w), 1127 (w), 1052 (w), 760 (m).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.93 (dd, *J* = 6.3, 3.5 Hz, 6H), 7.60 (dd, *J* = 6.3, 3.5 Hz, 6H), 7.23 (s, 12H), 5.74 (t, *J* = 8.1 Hz, 3H), 2.36 – 2.20 (m, 6H), 1.55 (s, 9H), 1.51 – 1.42 (m, 9H), 1.39 (s, 9H), 1.37 – 1.19 (m, 39H), 0.88 (t, *J* = 6.9 Hz, 9H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 152.9, 152.1, 149.9, 139.9, 134.2, 129.5, 128.6, 128.4, 122.3, 110.1, 35.8, 34.4, 34.3, 32.1, 31.1, 29.8, 29.8, 29.7, 29.5, 28.1, 26.2, 22.8, 14.3 (The number of signals deviates from the theoretical value due to signal overlap with the residual solvent peak).
HR-MS (ESI-): m/z (%) [$C_{102}H_{108}N_6O_9$] = calc.: 1595.7872 $[M+Cl]^-$, meas.: 1595.7880 $[M+Cl]^-$

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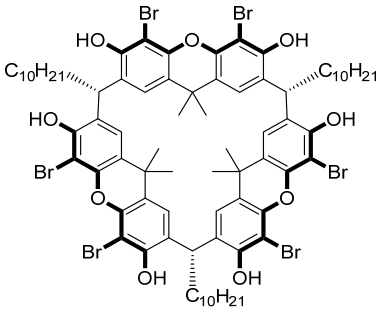
(2r,4r,6r)-14,15,34,35,54,55-Hexabromo-2,4,6-tris(decyl)-19,19,39,39,59,59-hexamethyl-19H,39H,59H-1,3,5(2,7)-trixanthenacyclohexaphane-13,16,33,36,53,56-hexaol (S3)

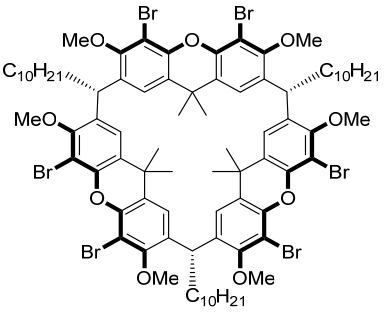


$C_{78}H_{96}Br_6O_9$
M = 1657.04

Xanthene[3]arene **19** (115 mg, 97.2 µmol, 1.0 eq.) was dissolved in anhydrous THF (5 mL) and the flask was wrapped in aluminium foil. NBS (105 mg, 593 µmol, 6.1 eq.) was added and the mixture was subsequently stirred for 18 h at room temperature. After removing the solvent *in vacuo*, the crude product was purified *via* flash column chromatography (4 g silica gel, P:EA = 1:0 → 2:1) to give **S3** (143 mg, 86.3 µmol, 89%) as a yellow solid.

TLC: R_f = 0.29 (P:EA = 4:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3448 (m), 2953 (w), 2923 (s), 2853 (m), 2361 (w), 2340 (w), 1606 (w), 1456 (s), 1426 (s), 1325 (w), 1294 (w), 1209 (s), 1144 (w), 1085 (m), 907 (w), 778 (w), 833 (m).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.25 (s, 6H), 6.41 (s, 6H), 4.68 (t, *J* = 7.8 Hz, 3H), 2.20 – 2.10 (m, 6H), 1.67 (s, 9H), 1.40 – 1.18 (m, 57H), 0.88 (t, *J* = 6.9 Hz, 9H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 148.7, 147.5, 127.0, 125.4, 121.2, 100.2, 35.4, 35.1, 35.0, 34.4, 32.1, 29.7, 29.7, 29.6, 29.5, 29.5, 27.9, 25.5, 22.8, 14.3.
HR-MS (ESI-): m/z (%) [$C_{78}H_{96}Br_6O_9$] = calc.: 1649.2082 [M-H]$^-$, meas.: 1649.2055 [M-H]$^-$.

(2r,4r,6r)-14,15,34,35,54,55-Hexabromo-2,4,6-tris(decyl)-13,16,33,36,53,56-hexamethoxy-19,19,39,39,59,59-hexamethyl-19H,39H,59H-1,3,5(2,7)-trixanthenacyclohexaphane (S4)

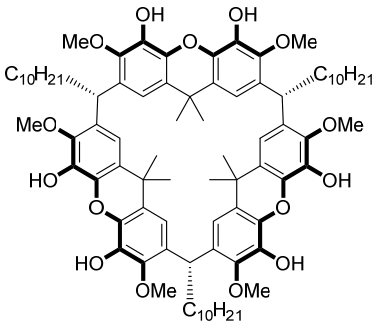


$C_{84}H_{108}Br_6O_9$
M = 1741.20

To a solution of hexa-bromide **S3** (320 mg, 193 µmol, 1.0 eq.) in anhydrous acetone (10 mL) was added potassium carbonate (801 mg, 5.79 mmol, 30 eq.) and the resulting suspension was stirred for 30 min at room temperature before adding MeI (0.60 mL, 1.37 g, 9.66 mmol, 50 eq.). The suspension was subsequently refluxed for 72 h. After cooling to room temperature, the solvent was removed *in vacuo*. The residue was taken up in CH_2Cl_2 (25 mL) and water (50 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL), the combined organic layers were dried (Na_2SO_4), filtered and the solvent was removed *in vacuo*. The crude product was purified *via* flash column chromatography (4 g silica gel, P:EA = 1:0 → 5:1) to give **S4** (295 mg, 169 µmol, 88%) as a slightly yellow solid.

TLC: R_f = 0.32 (P:EA = 9:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 2923 (s), 2853 (m), 2360 (w), 1595 (w), 1459 (s), 1425 (vs), 1287 (m), 1249 (m), 1202 (m), 1144 (w), 1085 (s), 985 (m), 777 (m).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.24 (s, 6H), 4.89 (t, *J* = 7.9 Hz, 3H), 3.87 (s, 18H), 2.02 – 1.93 (m, 6H), 1.62 (s, 9H), 1.39 – 1.15 (m, 57H), 0.88 (t, *J* = 7.0 Hz, 9H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 154.7, 148.6, 134.1, 128.5, 122.3, 107.1, 61.5, 36.9, 36.6, 35.6, 32.6, 32.1, 29.7, 29.7, 29.5, 29.5, 28.5, 26.7, 22.8, 22.5, 14.3.
HR-MS (ESI-): m/z (%) [$C_{84}H_{108}Br_6O_9$] = calc.: 1769.2788 $[M+Cl]^-$, meas1769.2754 $[M+Cl]^-$.

(2r,4r,6r)-2,4,6-Tris(decyl)-13,16,33,36,53,56-hexamethoxy-19,19,39,39,59,59-hexamethyl-19H,39H,59H-1,3,5(2,7)-trixanthenacyclohexaphane-14,15,34,35,54,55-hexaol (25)

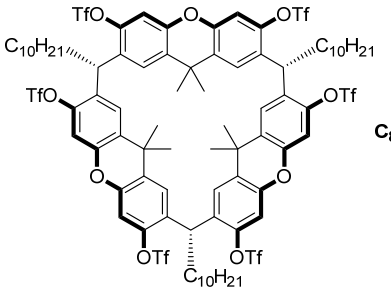


$C_{84}H_{114}O_{15}$
M = 1363.82

A solution of **S4** (100 mg, 57.4 µmol, 1.0 eq.) in anhydrous THF (5 mL) was cooled to –78 °C. *n*-BuLi (2.5 M in hexane, 0.20 mL, 500 µmol, 8.7 eq.) was added and stirred for 60 min. At the temperature of -78 °C, $B(OMe)_3$ (0.20 mL, 186 mg, 1.79 mmol, 31 eq.) was added, stirred for 30 min and then warmed to room temperature and stirred for 18 h. Subsequently, the solution was cooled to -78 °C and a mixture of hydrogen peroxide (30%) and 1 M aq. NaOH (1:4, 0.5 mL) was added. The mixture was warmed to room temperature and stirred for 40 h before adding sodium bisulfate (50 mg) and water (50 mL). The aqueous layer was extracted with CH_2Cl_2 (5 × 30 mL), combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (50 mL), dried (Na_2SO_4), filtered and the solvent was removed *in vacuo.* Flash column chromatography (4 g silica gel, CH_2Cl_2:MeOH = 99:1 → 19:1) gave **25** (20.8 mg, 15.3 µmol, 27%) as a colorless solid.

TLC: R_f = 0.34 (CH_2Cl_2:MeOH = 9:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3541 (w), 3485 (w), 3295 (m), 2954 (w), 2922 (s), 2853 (m), 2360 (w), 2342 (w), 1604 (m), 1487 (m), 1462 (s), 1377 (w), 1359 (w), 1310 (s), 1232 (m), 1198 (m), 1118 (w), 1081 (s), 1026 (w), 990 (w), 902 (w), 838 (w).
^{1}H NMR (500 MHz, acetone-d6) δ [ppm] = 8.06 (s, 6H), 6.98 (s, 6H), 4.86 (t, *J* = 8.0 Hz, 3H), 3.71 (s, 18H), 1.97 – 1.91 (m, 6H), 1.61 (s, 9H), 1.31 – 1.09 (m, 57H), 0.74 (t, *J* = 7.1 Hz, 9H).
^{13}C{^{1}H} NMR (126 MHz, acetone-d6) δ [ppm] = 145.4, 139.6, 138.8, 134.4, 128.0, 114.1, 60.6, 36.9, 35.5, 35.2, 33.8, 32.7, 30.3, 30.2, 30.1, 30.1, 29.1, 27.2, 23.3, 14.4 (The number of signals deviates from the theoretical value due to signal overlap with the residual solvent peak).
HR-MS (ESI-): m/z (%) [$C_{84}H_{114}O_{15}$] = calc.: 1397.7852 $[M+Cl]^-$, meas.: 1397.7853 $[M+Cl]^-$.

(2r,4r,6r)-2,4,6-tris(decyl)-19,19,39,39,59,59-hexamethyl-19H,39H,59H-1,3,5(2,7)-trixanthenacyclohexaphane-13,16,33,36,53,56-hexayl hexakis(trifluoromethanesulfonate) (S5)

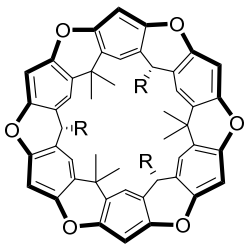


$C_{84}H_{96}F_{18}O_{21}S_6$
M = 1976.00

A solution of **19** (150 mg, 127 µmol, 1.0 eq.) in anhydrous CH_2Cl_2 (10 mL) was cooled to 0 °C. Pyridine (0.16 mL, 157 mg, 1.99 mmol, 15.6 eq.) was added followed by the dropwise addition of Tf_2O (0.26 mL, 437 mg, 1.55 mmol, 12.2 eq.). The mixture was warmed to room temperature and stirred for 20 h before adding water (20 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (50 mL), dried (Na_2SO_4), filtered and the solvent was removed *in vacuo.* Flash column chromatography (4 g silica gel, CH:EA = 1:0 → 4:1) gave **S5** (248 mg, 126 µmol, 99%) as a colorless solid.

TLC: R_f = 0.54 (CH:EA = 4:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 2927 (m), 2856 (w), 1605 (m), 1479 (s), 1406 (s), 1206 (vs), 1138 (s), 1110 (m), 865 (s), 690 (w).
^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 7.46 (s, 6H), 7.00 (s, 6H), 4.73 (t, *J* = 7.9 Hz, 3H), 2.18 – 2.07 (m, 6H), 1.78 (s, 9H), 1.45 – 1.19 (m, 57H), 0.88 (t, *J* = 7.0 Hz, 9H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ [ppm] = 150.3, 145.9, 131.6, 130.7, 124.5, 118.6 (q, *J* = 320 Hz), 110.2, 35.8, 35.6, 35.0, 34.7, 32.0, 29.7, 29.6, 29.5, 29.5, 29.5, 27.8, 26.5, 22.8, 14.3.
^{19}F NMR (565 MHz, $CDCl_3$) δ [ppm] = -73.3.
HR-MS (ESI-): m/z (%) [$C_{84}H_{96}F_{18}O_{21}S_6$] = calc.: 2019.4463 [M+$HCO_2$]$^-$, meas.: 2019.4504 [M+$HCO_2$]$^-$.

O_6-Belt[12]arene (26)

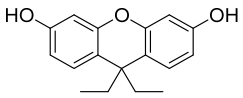


R = $C_{10}H_{21}$
$C_{78}H_{96}O_6$
M = 1129.62

A solution of **S5** (80.0 mg, 40.5 µmol, 1.0 eq.) in anhydrous DMF (1.4 mL) was treated with K_3PO_4 (77.4 mg, 365 µmol, 9.0 eq.) and heated at 140 °C for 18 h. Subsequently water (20 mL) was added, followed by extraction of the aqueous layer with CH_2Cl_2 (4 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. Flash column chromatography (4 g silica gel, CH:EA = 1:0 → 9:1 gave **26** (34.9 mg, 30.9 µmol, 76%) as a colorless solid.

TLC: R_f = 0.92 (CH:EA = 9:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 2924 (s), 2853 (m), 1608 (m), 1468 (vs), 1446 (w), 1417 (m), 1279 (m), 1239 (w), 1197 (w), 1144 (m), 1130 (s), 1117 (w), 1045 (m), 872 (m).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 6.88 (s, 6H), 6.85 (s, 6H), 3.62 (t, *J* = 6.5 Hz, 3H), 2.09 – 2.01 (m, 6H), 1.77 – 1.66 (m, 6H), 1.63 (s, 9H), 1.56 – 1.48 (m, 6H), 1.47 – 1.21 (m, 45H), 0.90 (t, *J* = 7.1 Hz, 9H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 156.6, 154.7, 131.4, 128.2, 118.2, 108.5, 37.0, 36.4, 32.1, 30.3, 29.9, 29.8, 29.6, 29.5, 28.1, 26.0, 23.0, 22.9, 14.3.
HR-MS (ESI-): m/z (%) [$C_{78}H_{96}O_6$] = calc.: 1145.7240 $[M+OH]^-$, meas.: 1145.7258 $[M+OH]^-$.

9,9-Diethyl-9H-xanthene-3,6-diol (10)

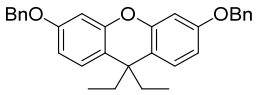


$C_{17}H_{18}O_3$
M = 270.33

A suspension of resorcinol (9.40 g, 85.3 mmol, 8.0 eq.), 3-pentanone (1.13 mL, 919 mg, 10.7 mmol, 1.0 eq.) and 1-dodecanethiol (102 µL, 86.4 mg, 427 µmol, 0.04 eq.) in water (1.54 mL) was heated to 50 °C and treated dropwise with conc. HCl (2.26 mL). The mixture was then stirred at 50 °C for 96 h. Subsequently water (200 mL) and aq. NaOH (2 M, 14 mL) was added, followed by extraction of the aqueous layer with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. Flash column chromatography (80 g silica gel, P:EA = 9:1 → 5:1) gave **10** (1.87 g, 6.92 mmol, 65%) as an off-white solid.

TLC: R_f = 0.26 (P:EA = 4:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3343 (s), 2962 (m), 2930 (m), 2873 (w), 2362 (w), 2339 (w), 1610 (s), 1502 (s), 1443 (s), 1303 (m), 1262 (m), 1229 (m), 1170 (s), 1117 (m), 1095 (m), 996 (m), 973 (w), 846 (m), 803 (w).
^{1}H NMR (500 MHz, acetone-d6) δ [ppm] = 8.43 (s, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.61 (dd, *J* = 8.6, 2.5 Hz, 2H), 6.46 (d, *J* = 2.5 Hz, 2H), 1.92 (q, *J* = 7.3 Hz, 4H), 0.48 (t, *J* = 7.3 Hz, 6H).
^{13}C{^{1}H} NMR (126 MHz, acetone-d6) δ [ppm] = 157.3, 153.9, 128.1, 116.5, 111.9, 102.7, 43.2, 38.0, 9.6.
HR-MS (ESI-): m/z (%) [$C_{17}H_{18}O_3$] = calc.: 269.1183 $[M-H]^-$, meas.: 269.1185 $[M-H]^-$.

3,6-Bis(benzyloxy)-9,9-diethyl-9H-xanthene (S6)

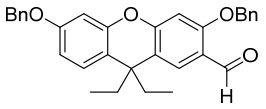


$C_{31}H_{30}O_3$
M = 450.58

A solution of **10** (1.71 g, 6.33 mmol, 1.0 eq.) in anhydrous DMF (50 mL) was cooled to 0 °C and treated portionwise with NaH (60% dispersion in mineral oil, 633 mg, 15.8 mmol, 2.5 eq.). The mixture was warmed up to room temperature and stirred for 1 h. After gas evolution stopped, the reaction mixture was cooled to 0 °C, treated with BnBr (1.52 mL, 2.19 g, 12.8 mmol, 2.0 eq.), warmed up to room temperature and stirred for 18 h. The reaction mixture was treated with water (5 mL), concentrated *in vacuo*, triturated with water (100 mL) and Et_2O (100 mL) and filtered. The residue was washed with water (100 mL) and Et_2O (100 mL) and dried under high vacuum to give **S6** (2.21 g, 4.90 mmol, 77%) as a white powder.

TLC: R_f = 0.32 (P:EA = 19:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3032 (w), 2959 (w), 2930 (w), 2874 (w), 2362 (m), 2339 (m), 1610 (m), 1568 (m), 1500 (m), 1455 (m), 1417 (m), 1376 (m), 1328 (m), 1253 (m), 1188 (m), 1178 (m), 1117 (w), 1095 (m), 1008 (s), 831 (s), 778 (w), 754 (m), 734 (w), 701 (s).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.50 – 7.29 (m, 10H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.74 (dd, *J* = 8.7, 2.6 Hz, 2H), 6.62 (d, *J* = 2.6 Hz, 2H), 5.06 (s, 4H), 1.90 (q, *J* = 7.3 Hz, 4H), 0.52 (t, *J* = 7.3 Hz, 6H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 158.1, 153.1, 137.1, 128.8, 128.2, 127.8, 127.2, 117.4, 111.1, 101.5, 70.3, 42.8, 37.7, 9.5.
HR-MS (ESI+): m/z (%) [$C_{31}H_{30}O_3$] = calc.: 473.2087 [M+Na]$^+$, meas.: 473.2078 [M+Na]$^+$.

3,6-Bis(benzyloxy)-9,9-diethyl-9H-xanthene-2-carbaldehyde (S7)

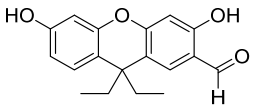


$C_{32}H_{30}O_4$
M = 478.59

A suspension of **S6** (2.21 g, 4.90 mmol, 1.0 eq.) in anhydrous CH_2Cl_2 (150 mL) was treated with DMF (4.00 mL, 3.78 g, 51.7 mmol, 10.5 eq.) and $POCl_3$ (4.00 mL, 6.58 g, 42.9 mmol, 8.75 eq.) with the flask being placed in a water bath at room temperature. The mixture was then stirred at reflux for 9 days. After that, water (100 mL) was carefully added under cooling to 0 °C and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (100 mL), dried (Na_2SO_4) and filtered. After removing the solvent *in vacuo*, the crude material was purified *via* flash column chromatography (40 g silica gel, P:CH_2Cl_2 = 4:1 → 0:1) to give recovered starting material **S6** (408 mg, 905 µmol) and aldehyde **S7** (1.58 g, 3.30 mmol, 83% based on recovered starting material) as a white solid.

TLC: R_f = 0.33 (P:EA = 4:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) =2963 (m), 2931 (m), 2872 (m), 2363 (w), 2342 (w), 1679 (m), 1609 (s), 1568 (m), 1500 (s), 1455 (m), 1421 (m), 1376 (m), 1328 (w), 1307 (w), 1274 (m), 1253 (w), 1179 (vs), 1096 (m), 1010 (m), 832 (m), 754 (w), 735 (w), 700 (w).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.43 (s, 1H), 7.81 (s, 1H), 7.56 – 7.32 (m, 10H), 7.16 (d, *J* = 8.7 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.65 (s, 2H), 6.64 (d, *J* = 2.6 Hz, 2H), 5.18 (s, 2H), 5.07 (s, 2H), 2.05 – 1.88 (m, 4H), 0.50 (t, *J* = 7.3 Hz, 6H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ [ppm] = 188.3, 160.8, 158.2, 158.2, 152.2, 136.9, 136.1, 128.9, 128.8, 128.8, 128.5, 128.3, 127.8, 127.8, 127.5, 127.3, 121.5, 118.6, 117.1, 111.8, 101.8, 100.2, 70.7, 70.3, 42.9, 37.9, 9.4.
HR-MS (ESI+): m/z (%) [$C_{32}H_{30}O_4$] = calc.: 501.2036 [M+Na]$^+$, meas.: 501.2031 [M+Na]$^+$.

9,9-Diethyl-3,6-dihydroxy-9H-xanthene-2-carbaldehyde (13)

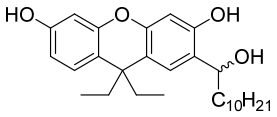


$C_{18}H_{18}O_4$
M = 298.34

Aldehyde **S7** (1.56 g, 3.26 mmol, 1.0 eq.) and thioanisole (2.31 mL, 2.43 g, 19.6 mmol, 6.0 eq.) were dissolved in toluene (250 mL) and cooled to 0 °C. TFA (250 mL) was added, the mixture was warmed up to room temperature and stirred for 40 h. After removing the solvent *in vacuo*, the crude product was purified *via* flash column chromatography (40 g silica gel, P:CH_2Cl_2 = 2:3 → 0:1) to give **13** (688 mg, 2.31 mmol, 71%) as a colorless oil.

TLC: R_f = 0.27 (CH_2Cl_2, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3360 (m), 2964 (m), 2931 (w), 2874 (w), 2360 (w), 2333 (w), 1656 (s), 1624 (s), 1508 (w), 1488 (m), 1431 (s), 1310 (m), 1280 (s), 1235 (m), 1178 (vs), 1094 (s), 972 (w), 851 (w), 822 (w), 758 (m), 731 (m).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 11.08 (s, 1H), 9.79 (s, 1H), 7.43 (s, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.65 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.57 (s, 1H), 6.54 (d, *J* = 2.6 Hz, 1H), 5.11 (br s, 1H), 2.00 – 1.86 (m, 4H), 0.53 (t, *J* = 7.3 Hz, 6H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 195.0, 161.5, 159.0, 155.0, 152.2, 133.3, 127.4, 118.7, 118.0, 116.8, 112.1, 103.8, 103.1, 42.8, 38.1, 9.3.
HR-MS (ESI-): m/z (%) [$C_{18}H_{18}O_4$] = calc.: 297.1132 $[M-H]^-$, meas.: 297.1133 $[M-H]^-$.

9,9-Diethyl-2-(1-hydroxyundecyl)-9H-xanthene-3,6-diol (17)



$C_{28}H_{40}O_4$
M = 440.62

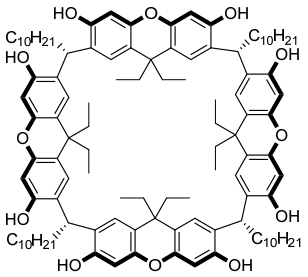
A two-neck round bottom flask equipped with condenser was filled with Mg-turnings (652 mg, 26.8 mmol, 10 eq.) and a crystal of iodine and gently heated with a heatgun. Anhydrous THF (50 mL) was added, followed by the slow addition of 1-bromodecane (2.31 mL, 2.44 g, 10.7 mmol, 4.0 eq.) and the reaction mixture was subsequently heated to 70 °C under reflux for 2 h. Upon cooling to room temperature, the Grignard reagent was transferred into a dropping funnel and used for the following reaction.

Aldehyde **13** (800 mg, 2.68 mol, 1.0 eq.) was dissolved in anhydrous THF (50 mL), cooled to 0 °C and treated dropwise with the Grignard reagent. The reaction mixture was stirred at room temperature for 20 h, then water (2 mL) was added and the solvent concentrated at room temperature *in vacuo* to 10 mL. The mixture was diluted with CH_2Cl_2 (100 mL) and filtered

through celite. After removing the solvent at room temperature *in vacuo*, the crude product was purified *via* flash column chromatography (40 g silica gel, CH_2Cl_2:MeOH = 100:0 → 99:1) to give **17** (1.13 g, 2.56 mmol, 96%) as a colorless oil.

TLC: R_f = 0.16 (CH_2Cl_2:MeOH = 49:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3346 (m), 2961 (m), 2925 (s), 2854 (m), 2360 (m), 2344 (m), 1618 (s), 1497 (s), 1452 (s), 1375 (m), 1318 (m), 1268 (w), 1237 (w), 1174 (s), 1137 (w), 1095 (m), 1080 (w), 821 (m).
^{1}H NMR (500 MHz, acetone-d6) δ [ppm] = 8.65 (br s, 1H), 8.38 (br s, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.12 (s, 1H), 6.61 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.45 (d, *J* = 2.5 Hz, 1H), 6.40 (s, 1H), 4.93 (t, *J* = 6.6 Hz, 2H), 1.92 (*virt* qd, *J* = 7.3, 2.7 Hz, 4H), 1.83 – 1.72 (m, 2H), 1.47 – 1.20 (m, 16H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.48 (*virt* td, *J* = 7.3, 2.0 Hz, 6H).
^{13}C{^{1}H} NMR (126 MHz, acetone-d6) δ [ppm] = 156.5, 154.3, 153.0, 151.7, 127.2, 125.6, 124.7, 115.7, 115.1, 111.0, 102.4, 101.9, 72.2, 42.3, 38.0, 37.2, 37.0, 31.7, 29.5, 29.5, 29.4, 29.4, 29.2, 25.5, 22.4, 13.5, 8.8.
HR-MS (ESI-): m/z (%) [$C_{28}H_{40}O_4$] = calc.: 439.2854 [M-H]$^-$, meas.: 439.2856 [M-H]$^-$.

(2r,4r,6r,8r)-2,4,6,8-Tetrakis(decyl)-19,19,39,39,59,59,79,79-octaethyl-19H,39H,59H,79H-1,3,5,7(2,7)-tetraxanthenacyclooctaphan-13,16,33,36,53,56,73,76-octaol (21)



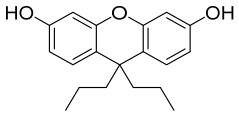
$C_{112}H_{152}O_{12}$
M = 1690.44

A solution of **17** (1.12 g, 2.54 mmol, 1.0 eq.) in DCE (30 mL) was cooled to 0 °C, treated with TFA (3 mL) and stirred at 0 °C for 90 min. After removing the solvent at 0 °C *in vacuo*, purification *via* flash column chromatography (12 g silica gel, CH_2Cl_2:MeOH = 99:1 → 39:1) yielded crude **21**. Further purification by gel permeation chromatography (BioBeads® S-X1, THF) and subsequent preparative HPLC (see general Information for details) afforded **21** (77.3 mg, 45.7 µmol, 7%) as a white solid.

TLC: R_f = 0.36 (CH_2Cl_2:MeOH = 9:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3314 (m), 2962 (m), 2925 (s), 2854 (m), 2360 (m), 2343 (m), 1694 (w), 1615 (m), 1490 (s), 1464 (m), 1436 (m), 1375 (w), 1275 (w), 1234 (w), 1209 (w), 1172 (m), 1083 (m).

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.44 (s, 8H), 7.26 (s, 8H), 6.42 (s, 8H), 4.67 (t, *J* = 7.9 Hz, 4H), 2.09 (q, *J* = 7.5 Hz, 8H), 1.88 (q, *J* = 7.2 Hz, 8H), 1.38 – 1.20 (m, 72H), 0.87 (t, *J* = 6.8 Hz, 12H), 0.58 (t, *J* = 7.2 Hz, 12H), 0.23 (t, *J* = 7.2 Hz, 12H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 153.9, 151.6, 128.0, 125.7, 116.7, 102.8, 43.5, 38.7, 37.9, 35.3, 34.8, 32.6, 30.4, 30.4, 30.3, 30.1, 23.4, 14.4, 10.1, 9.8.
HR-MS (ESI-): m/z (%) [$C_{112}H_{152}O_{12}$] = calc.: 1688.1211 [M-H]$^-$, meas.: 1688.1178 [M-H]$^-$.

9,9-Dipropyl-9H-xanthene-3,6-diol (11)

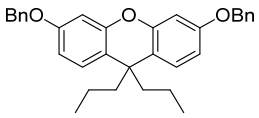


$C_{19}H_{22}O_3$
M = 298.38

A suspension of resorcinol (4.66 g, 42.4 mmol, 8.0 eq.), 4-heptanone (0.74 mL, 605 mg, 5.29 mmol, 1.0 eq.) and 1-dodecanethiol (50.7 µL, 42.8 mg, 212 µmol, 0.04 eq.) in water (0.77 mL) was heated to 50 °C and treated dropwise with conc. HCl (1.13 mL). The mixture was then stirred at 50 °C for 96 h. Subsequently water (100 mL) and aq. NaOH (2 M, 7 mL) was added, followed by extraction of the aqueous layer with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. Flash column chromatography (40 g silica gel, P:EA = 9:1 → 6:1) gave **11** (1.04 g, 3.49 mmol, 66%) as a colorless oil.

TLC: R_f = 0.32 (P:EA = 4:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3362 (m), 2956 (m), 2929 (m), 2871 (w), 2360 (m), 2342 (w), 1610 (m), 1502 (s), 1440 (s), 1388 (w), 1311 (w), 1262 (w), 1228 (w), 1171 (s), 1121 (w), 1100 (m), 996 (m), 847 (w).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.12 (d, *J* = 8.5 Hz, 2H), 6.57 (dd, *J* = 8.5, 2.6 Hz, 2H), 6.46 (d, *J* = 2.6 Hz, 2H), 4.75 (s, 2H), 1.85 – 1.77 (m, 4H), 0.92 – 0.82 (m, 4H), 0.71 (t, *J* = 7.3 Hz, 6H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 154.5, 152.5, 127.4, 118.5, 111.0, 102.7, 47.9, 41.6, 18.2, 14.5.
HR-MS (ESI-): m/z (%) [$C_{19}H_{22}O_3$] = calc.: 297.1496 [M-H]$^-$, meas.: 297.1497 [M-H]$^-$.

3,6-Bis(benzyloxy)-9,9-dipropyl-9H-xanthene (S8)



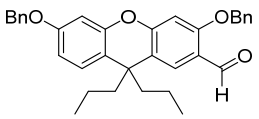
$C_{33}H_{34}O_3$
M = 478.63

A solution of **11** (2.39 g, 8.01 mmol, 1.0 eq.) in anhydrous DMF (100 mL) was cooled to 0 °C and treated portionwise with NaH (60% dispersion in mineral oil, 801 mg, 20.0 mmol, 2.5 eq.). The mixture was warmed up to room temperature and stirred for 1 h. After gas evolution stopped, the reaction mixture was cooled to 0 °C, treated with BnBr (2.10 mL, 3.01 g, 17.6 mmol, 2.2 eq.), warmed up to room temperature and stirred for 18 h. The reaction mixture was treated with water (5 mL) and concentrated *in vacuo*. Then water (100 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 100 mL), dried (Na_2SO_4) and filtered. After removing the solvent *in vacuo*, the crude material was purified *via* flash column chromatography (40 g silica gel, P:EA = 1:0 → 1:1) to give **S8** (3.48 g, 7.27 mmol, 91%) as an off-white solid.

Note: The crude material can alternatively be purified by trituration with MeOH and subsequent filtration. On a 20 mmol scale 73% product was isolated.

TLC: R_f = 0.37 (P:EA = 19:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3066 (w), 3032 (w), 2954 (m), 2929 (m), 2870 (m), 2359 (m), 2339 (m), 1613 (m), 1570 (w), 1499 (s), 1454 (m), 1420 (m), 1379 (w), 1330 (w) 1286 (w), 1256 (m), 1176 (s), 1102 (m), 1024 (m), 832 (w), 735 (m), 696 (m).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.50 – 7.31 (m, 10H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.74 (dd, *J* = 8.6, 2.6 Hz, 2H), 6.61 (d, *J* = 2.6 Hz, 2H), 5.06 (s, 4H), 1.89 – 1.77 (m, 4H), 0.96 – 0.81 (m, 4H), 0.72 (t, *J* = 7.3 Hz, 6H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 158.0, 152.6, 137.1, 128.8, 128.2, 127.8, 127.2, 118.4, 111.0, 101.5, 70.3, 47.9, 41.6, 18.3, 14.6.
HR-MS (ESI+): m/z (%) [$C_{33}H_{34}O_3$] = calc.: 501.2400 $[M+Na]^+$, meas.: 501.2395 $[M+Na]^+$.

3,6-Bis(benzyloxy)-9,9-dipropyl-9H-xanthene-2-carbaldehyde (S9)



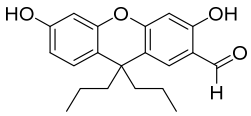
$C_{34}H_{34}O_4$
M = 506.64

A solution of **S8** (3.38 g, 7.06 mmol, 1.0 eq.) in anhydrous CH_2Cl_2 (150 mL) was treated with DMF (5.47 mL, 5.16 g, 70.6 mmol, 10 eq.) and $POCl_3$ (5.92 mL, 9.74 g, 63.5 mmol, 9.0 eq.) with the flask being placed in a water bath at room temperature. The mixture was then stirred

at reflux for 8 days. After that, water (200 mL) was carefully added under cooling to 0 °C and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL), combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (100 mL), dried (Na_2SO_4) and filtered. After removing the solvent *in vacuo*, the crude material was purified *via* flash column chromatography (40 g silica gel, P:EA = 1:0 → 9:1) to give **S9** (2.76 g, 5.45 mmol, 77%) as a white solid.

TLC: R_f = 0.41 (P:EA = 4:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3065 (w), 3034 (w), 2955 (m), 2929 (m), 2869 (m), 2357 (w), 2342 (w), 1688 (s), 1607 (s), 1566 (m), 1488 (s), 1424 (m), 1379 (m), 1287 (m), 1265 (m), 1238 (s), 1177 (vs), 1094 (s), 1020 (m), 910 (m), 833 (m), 733 (s), 696 (s).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.45 (s, 1H), 7.85 (s, 1H), 7.55 – 7.30 (m, 10H), 7.20 (d, *J* = 8.7 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.68 – 6.59 (m, 2H), 5.17 (s, 2H), 5.06 (s, 2H), 1.99 – 1.78 (m, 4H), 0.92 – 0.79 (m, 4H), 0.72 (t, *J* = 7.2 Hz, 6H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] =188.4, 160.7, 158.1, 157.7, 151.7, 136.9, 136.1, 128.9, 128.8, 128.5, 128.2, 127.7, 127.7, 127.5, 127.2, 121.5, 119.6, 118.1, 111.8, 101.8, 100.2, 70.8, 70.3, 47.9, 41.7, 18.3, 14.4.
HR-MS (ESI+): m/z (%) [$C_{34}H_{34}O_4$] = calc.: 529.2349 $[M+Na]^+$, meas.: 529.2353 $[M+Na]^+$.

3,6-Dihydroxy-9,9-dipropyl-9H-xanthene-2-carbaldehyde (14)

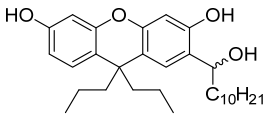


$C_{20}H_{22}O_4$
M = 326.39

Aldehyde **S9** (730 mg, 1.44 mmol, 1.0 eq.) and thioanisole (1.02 mL, 1.07 g, 8.65 mmol, 6.0 eq.) were dissolved in toluene (150 mL) and cooled to 0 °C. TFA (100 mL) was added, the mixture was warmed up to room temperature and stirred for 72 h. After removing the solvent *in vacuo*, the crude product was purified *via* flash column chromatography (24 g silica gel, P:CH_2Cl_2 = 1:1 → 0:1) to give **14** (423 mg, 1.30 mmol, 90%) as a white solid.

TLC: R_f = 0.31 (CH_2Cl_2, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3375 (bs), 2956 (m), 2930 (m), 2871 (m), 1651 (s), 1624 (s), 1488 (m), 1431 (s), 1291 (m), 1273 (m), 1246 (m), 1233 (m), 1218 (m), 1174 (vs), 1097 (m), 737 (m).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 11.08 (s, 1H), 9.80 (s, 1H), 7.44 (s, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.64 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.58 – 6.47 (m, 2H), 4.98 (s, 1H), 2.01 – 1.77 (m, 4H), 0.97 – 0.80 (m, 4H), 0.73 (t, *J* = 7.2 Hz, 6H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 195.0, 161.5, 158.5, 154.9, 151.7, 133.1, 127.3, 119.5, 118.0, 117.8, 112.1, 103.8, 103.1, 48.2, 41.6, 18.2, 14.5.
HR-MS (ESI+): m/z (%) [$C_{20}H_{22}O_4$] = calc.: 349.1410 $[M+Na]^+$, meas.: 349.1404 $[M+Na]^+$.

2-(1-Hydroxyundecyl)-9,9-dipropyl-9H-xanthene-3,6-diol (18)



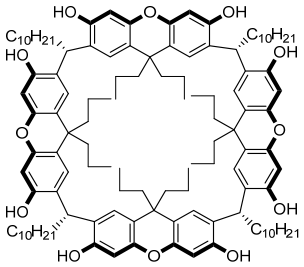
$C_{30}H_{44}O_4$
M = 468.68

A two-neck round bottom flask equipped with condenser was filled with Mg-turnings (899 mg, 37.0 mmol, 10 eq.) and a crystal of iodine and gently heated with a heatgun. Anhydrous THF (15 mL) was added, followed by the slow addition of 1-bromodecane (3.58 mL, 3.80 g, 16.7 mmol, 4.5 eq.) and the reaction mixture was subsequently heated to 70 °C under reflux for 2 h. Upon cooling to room temperature, the Grignard reagent was transferred into a dropping funnel and used for the following reaction.

Aldehyde **14** (1.21 g, 3.70 mmol, 1.0 eq.) was dissolved in anhydrous THF (30 mL), cooled to 0 °C and treated dropwise with the Grignard reagent. The reaction mixture was stirred at room temperature for 20 h, then water (5 mL) was added and the solvent concentrated at room temperature *in vacuo* to 5 mL. The mixture was diluted with CH_2Cl_2 (100 mL) and filtered through celite. After removing the solvent at room temperature *in vacuo*, the crude product was purified *via* flash column chromatography (40 g silica gel, CH_2Cl_2:MeOH = 100:0 → 99:1) to give **18** (1.57 g, 3.35 mmol, 91%) as a colorless oil.

TLC: R_f = 0.22 (CH_2Cl_2:MeOH = 49:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3347 (m), 2954 (m), 2925 (s), 2854 (m), 2360 (w), 2342 (w), 1616 (m), 1497 (s), 1455 (s), 1377 (w), 1317 (m), 1265 (m), 1236 (w), 1173 (s), 1138 (m), 1092 (m), 848 (m).
^{1}H NMR (500 MHz, acetone-d6) δ [ppm] = 8.70 (s, 1H), 8.39 (s, 1H), 7.19 (d, *J* = 8.6 Hz, 1H), 7.14 (s, 1H), 6.59 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.43 (d, *J* = 2.5 Hz, 1H), 6.38 (s, 1H), 4.96 – 4.89 (m, 2H), 1.91 – 1.83 (m, 4H), 1.83 – 1.71 (m, 2H), 1.45 – 1.36 (m, 1H), 1.36 – 1.20 (m, 15H), 0.95 – 0.78 (m, 7H), 0.70 (t, *J* = 7.3 Hz, 6H).
^{13}C{^{1}H} NMR (126 MHz, acetone-d6) δ [ppm] = 157.3, 155.2, 153.4, 152.1, 128.0, 126.2, 125.6, 117.5, 117.0, 111.9, 103.3, 102.8, 73.2, 48.4, 48.2, 42.0, 38.8, 32.6, 30.5, 30.3, 30.0, 26.4, 23.3, 18.9, 14.7, 14.7, 14.4..
HR-MS (ESI-): m/z (%) [$C_{30}H_{44}O_4$] = calc.: 467.3167 [M-H]$^-$, meas.: 467.3163 [M-H]$^-$.

(2r,4r,6r,8r)-2,4,6,8-Tetrakis(decyl)-19,19,39,39,59,59,79,79-octapropyl-19H,39H,59H,79H-1,3,5,7(2,7)-tetraxanthenacyclooctaphan-13,16,33,36,53,56,73,76-octaol (22)



$C_{120}H_{168}O_{12}$
M = 1802.65

A solution of **18** (1.57 g, 3.35 mmol, 1.0 eq.) in DCE (45 mL) was cooled to 0 °C, treated with TFA (5.0 mL) and stirred at 0 °C for 60 min. The reaction mixture was poured into an ice-$NaHCO_3$ suspension under vigorous stirring. The aqueous layer was extracted with $CHCl_3$:*i*PrOH (3:1, 3 × 100 mL), combined organic layers were washed with water (100 mL), dried ($MgSO_4$) and filtered. After removing the solvent *in vacuo*, purification *via* flash column chromatography (24 g silica gel, CH_2Cl_2:MeOH = 99:1 → 33:1) yielded crude **22**. Further purification by gel permeation chromatography (BioBeads® S-X1, THF) and subsequent preparative HPLC (see general Information for details) afforded **22** (57.7 mg, 32.0 µmol, 4%) as a white solid.

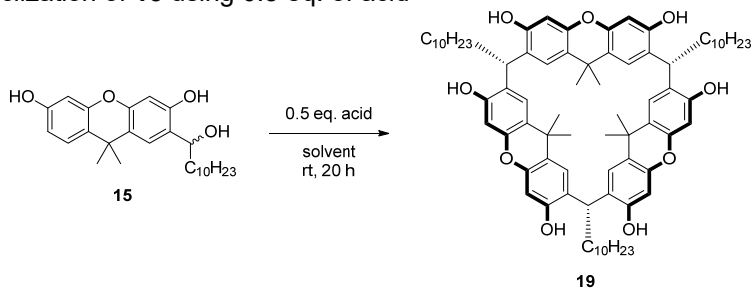
TLC: R_f = 0.27 (CH_2Cl_2:MeOH = 9:1, [UV/CAM]).
IR (ATR): ν (cm^{-1}) = 3406 (m), 2952 (m), 2925 (s), 2854 (m) 2360 (m), 2342 (m), 1615 (m), 1497 (s), 1465 (w), 1426 (m), 1377 (w), 1329 (w), 1309 (w), 1269 (w), 1249 (w), 1216 (m), 1178 (m), 1089 (m).
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.18 (s, 8H), 6.99 (s, 8H), 6.43 (s, 8H), 4.70 (t, *J* = 7.5 Hz, 4H), 2.03 – 1.93 (m, 8H), 1.86 – 1.68 (m, 16H), 1.44 – 1.21 (m, 64H), 1.00 – 0.80 (m, 28H), 0.75 (t, *J* = 7.3 Hz, 12H), 0.61 (t, *J* = 7.3 Hz, 12H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ [ppm] = 154.6, 151.2, 127.5, 126.2, 116.6, 102.5, 49.8, 47.7, 42.0, 36.6, 35.0, 32.7, 30.6, 30.6, 30.4, 30.4, 30.1, 29.2, 23.3, 19.0, 18.9, 15.5, 15.0, 14.4.
HR-MS (ESI-): m/z (%) [$C_{120}H_{168}O_{12}$] = calc.: 1800.2463 $[M-H]^-$, meas.: 1800.2437 $[M-H]^-$.

3 Screening for the Macrocyclization of 15

In a test tube, **15** (3.00 mg, 7.27 µmol) was dissolved in the solvent and treated with a stock solution of the acid (as described in tables S1-S3). After stirring for 20 h, the solvent was removed *in vacuo* and the crude dissolved in $CDCl_3$ (1.00 mL). Yields were calculated *via* ^{1}H-NMR analysis, based on the isolated yield of entry 83 using the residual chloroform signal as an internal standard.

While the initial screening (table S1 and S2) showed that the desired cyclization product **19** was detectable in traces for several acid/solvent combinations, only few conditions gave yields >1%. The best results were obtained with TFA in CH_2Cl_2. As higher TFA concentration gave a slightly better yield (cf. entry 7 and entry 43), higher acid amounts of up to 50 vol% were explored (table S3). The optimal conditions (15 vol% TFA, entry 83) resulted in an isolated yield of 21%.

Table S1: Macrocyclization of **15** using 0.5 eq. of acid

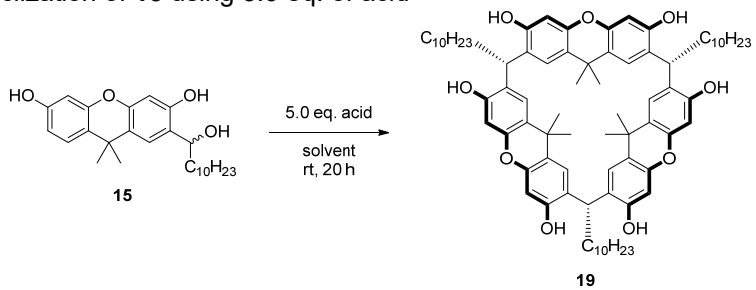


#	Acid	Solvent	Volume [mL]	Yield [%]
1	MsOH	CH_2Cl_2	0.30	5[a]
2	MsOH	CH_2Cl_2	3.0	trace
3	MsOH	CH_2Cl_2	12.0	-
4	TfOH	CH_2Cl_2	0.30	trace
5	TfOH	CH_2Cl_2	3.0	-
6	TfOH	CH_2Cl_2	12.0	-
7	TFA	CH_2Cl_2	0.30	7[a]
8	TFA	CH_2Cl_2	3.0	trace
9	TFA	CH_2Cl_2	12.0	-
10	$BF_3{\cdot}Et_2O$	CH_2Cl_2	0.30	trace
11	$BF_3{\cdot}Et_2O$	CH_2Cl_2	3.0	trace
12	$BF_3{\cdot}Et_2O$	CH_2Cl_2	12.0	-
13	$Sc(OTf)_3$	CH_2Cl_2	0.30	5[a]
14	$Sc(OTf)_3$	CH_2Cl_2	3.0	trace

#	Acid	Solvent	Volume [mL]	Yield [%]
15	$Sc(OTf)_3$	CH_2Cl_2	12.0	-
16	MsOH	MeCN	0.30	-
17	MsOH	MeCN	3.0	-
18	MsOH	MeCN	12.0	-
18	TFA	MeCN	0.30	-
20	TFA	MeCN	3.0	-
21	TFA	MeCN	12.0	trace
22	TsOH	MeCN	0.30	-
23	TsOH	MeCN	3.0	trace
24	TsOH	MeCN	12.0	-
25	$Sc(OTf)_3$	MeCN	0.30	-
26	$Sc(OTf)_3$	MeCN	3.0	-
27	$Sc(OTf)_3$	MeCN	12.0	-
28	HCl	EtOH	0.30	-
29	HCl	EtOH	3.0	-
30	HCl	EtOH	12.0	-
31	TsOH	TCE	0.30	7[a]
32	TsOH	TCE	3.0	trace
33	TsOH	TCE	12.0	-
34	TfOH	HFIP	0.30	trace
35	TfOH	HFIP	3.0	-
36	TfOH	HFIP	12.0	-

[a]NMR yield. Based on the isolated yield of entry 83 using the residual chloroform signal as an internal standard.

Table S2: Macrocyclization of **15** using 5.0 eq. of acid

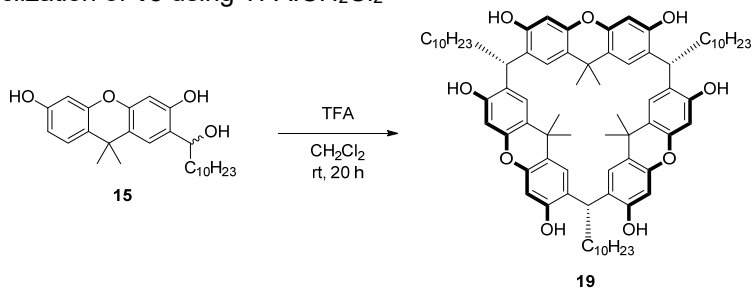


#	Acid	Solvent	Volume [mL]	Yield [%]
37	MsOH	CH_2Cl_2	0.30	-
38	MsOH	CH_2Cl_2	3.0	trace
39	MsOH	CH_2Cl_2	12.0	-
40	TfOH	CH_2Cl_2	0.30	-
41	TfOH	CH_2Cl_2	3.0	-
42	TfOH	CH_2Cl_2	12.0	-
43	TFA	CH_2Cl_2	0.30	9[a]
44	TFA	CH_2Cl_2	3.0	7[a]
45	TFA	CH_2Cl_2	12.0	-
46	$BF_3 \cdot Et_2O$	CH_2Cl_2	0.30	-
47	$BF_3 \cdot Et_2O$	CH_2Cl_2	3.0	-
48	$BF_3 \cdot Et_2O$	CH_2Cl_2	12.0	-
49	$Sc(OTf)_3$	CH_2Cl_2	0.30	trace
50	$Sc(OTf)_3$	CH_2Cl_2	3.0	-
51	$Sc(OTf)_3$	CH_2Cl_2	12.0	-
52	MsOH	MeCN	0.30	-
53	MsOH	MeCN	3.0	-
54	MsOH	MeCN	12.0	-
55	TFA	MeCN	0.30	-
56	TFA	MeCN	3.0	-
57	TFA	MeCN	12.0	-
58	TsOH	MeCN	0.30	-
59	TsOH	MeCN	3.0	-
60	TsOH	MeCN	12.0	-
61	$Sc(OTf)_3$	MeCN	0.30	-
62	$Sc(OTf)_3$	MeCN	3.0	-
63	$Sc(OTf)_3$	MeCN	12.0	-
64	HCl	EtOH	0.30	-

#	Acid	Solvent	Volume [mL]	Yield [%]
65	HCl	EtOH	3.0	-
66	HCl	EtOH	12.0	-
67	TsOH	TCE	0.30	-
68	TsOH	TCE	3.0	-
69	TsOH	TCE	12.0	-
70	TfOH	HFIP	0.30	-
71	TfOH	HFIP	3.0	-
72	TfOH	HFIP	12.0	-

[a]NMR yield. Based on the isolated yield of entry 83 using the residual chloroform signal as an internal standard.

Table S3: Macrocyclization of **15** using TFA:CH_2Cl_2



#	TFA [vol%]	Volume [mL]	Yield [%]
73	1	0.1	10[a]
74	1	0.3	11[a]
75	1	0.9	9[a]
76	5	0.1	13[a]
77	5	0.3	17[a]
78	5	0.9	15[a]
79	10	0.1	15[a]
80	10	0.3	18[a]
81	10	0.9	17[a]
82	15	0.1	15[a]
83	**15**	**0.3**	**21[b]**
84	15	0.9	20[a]
85	20	0.1	15[a]
86	20	0.3	21[a]
87	20	0.9	20[a]

#	TFA [vol%]	Volume [mL]	Yield [%]
88	30	0.1	14[a]
89	30	0.3	20[a]
90	30	0.9	17[a]
91	50	0.1	7[a]
92	50	0.3	16[a]
93	50	0.9	17[a]

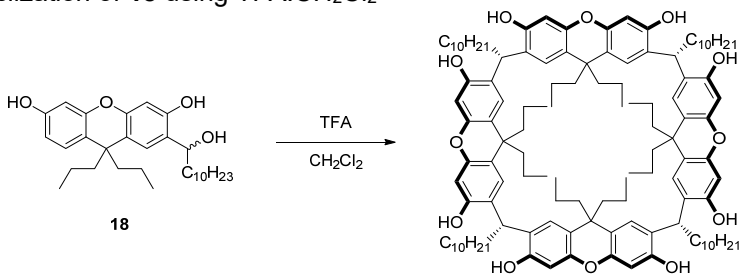
[a]NMR yield. Based on the isolated yield of entry 83 using the residual chloroform signal as an internal standard. [b]isolated yield.

4 Screening for the Macrocyclization of 18

In a test tube, **18** (3.00 mg, 6.40 µmol) was dissolved in the solvent and treated with TFA (as described in tables S4-S5). After stirring for the specified time (T1-T4, 1-24h), the solvent was removed *in vacuo* and the crude dissolved in acetone-*d6* (0.60 mL). Yields were calculated *via* ^{1}H-NMR analysis, using 1,3,5-trimethoxybenzene as internal standard.

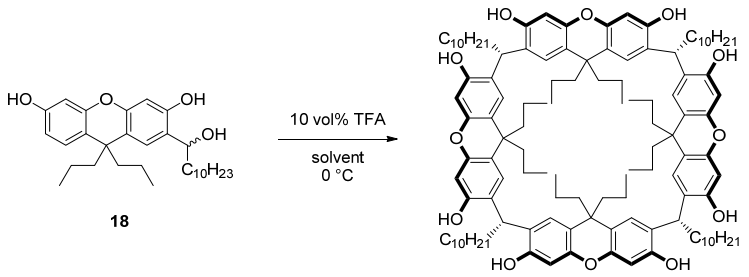
The initial screening (table S4) showed that the desired cyclization product **22** was formed, however it was found that it decomposes at room temperature under the reaction conditions. The decomposition was not observed at 0 °C. The best results were obtained at a concentration of 64 mM using 10 vol% TFA (cf. entry 11). An additional screening of solvents finally gave the best conditions in DCE (table S5, entry 18) with a yield of 10%.

Table S4: Macrocyclization of **18** using TFA:CH_2Cl_2



#	TFA [vol%]	Volume [mL]	T [°C]	T1 [h]/ *Yield* [%]	T2 [h]/ *Yield* [%]	T3 [h]/ *Yield* [%]	T4 [h]/ *Yield* [%]
1	1	0.1	rt	1.0/*3*	2.0/*3*	8.0/*3*	24/*3*
2	3	0.1	rt	1.0/*6*	2.0/*6*	8.0/*6*	24/*6*
3	3	0.3	rt	1.0/*6*	2.0/*6*	8.0/*6*	24/*6*
4	10	0.1	rt	1.0/*8*	2.0/*8*	8.0/*6*	24/-
5	10	0.3	rt	1.0/*6*	2.0/*5*	8.0/*2*	24/-
6	10	1.0	rt	1.0/*4*	2.0/*traces*	8.0/-	24/-
7	30	0.3	rt	1.0/*5*	2.0/*2*	8.0/-	24/-
8	3	0.1	0	0.5/*6*	1.0/*7*	6.5/*7*	24/*6*
9	3	0.3	0	0.5/*6*	1.0/*6*	6.5/*6*	24/*6*
10	10	0.03	0	0.5/*5*	1.0/*5*	6.5/*6*	24/*5*
11	10	0.1	0	0.5/*8*	1.0/*8*	6.5/*8*	24/*8*
12	10	0.3	0	0.5/*6*	1.0/*6*	6.5/*6*	24/*6*

Table S5: Macrocyclization of **18** using 10 vol% TFA at 0 °C in 0.1 mL solvent



18 **22**

#	Solvent	T1 [h]/ *Yield* [%]	T2 [h]/ *Yield* [%]	T3 [h]/ *Yield* [%]
13	CH_2Cl_2 anhydrous	0.5/*8*	4.5/*8*	20/*8*
14	Trichloroethene	0.5/*7*	4.5/*6*	20/*5*
15	Trifluorotoluene	0.5/*6*	4.5/*6*	20/*6*
16	MTBE	0.5/*traces*	4.5/*traces*	20/*traces*
17	CH_3Cl	0.5/*6*	4.5/*6*	20/*6*
18	**DCE**	**0.5/*10***	**4.5/*10***	**20/*9***
19	TCE	0.5/*7*	4.5/*7*	20/*7*
20	MeCN	0.5/*traces*	4.5/*traces*	20/*traces*

5 DOSY-NMR Studies

5.1 DOSY Coefficients of Compounds 19, 23, S4, 25 and RA

The diffusion values were determined using 5.0 mM solutions of macrocycles **19**, **23**, **S4**, **25** and *C*-undecylcalix[4]resorcinarene (**RA**) in toluene-d8 at 298 K. The results presented below show that the diffusion value of assembly **I**, formed from macrocycle **25**, remains the same upon addition of 1.0 eq of fullerene-C_{60} and is close to the assembly of **RA**. Diffusion values were determined for the alkyl signal of the macrocycle.

Table S6: Diffusion values for macrocycles **19**, **23**, **S4**, self-assembling macrocycles **25** and **RA** in toluene-d8 at 298 K.

Macrocycle	**19**	**23**	**S4**	**25**	**25** + C_{60}	**RA**
D [$\times 10^{-5}$ cm^2s^{-1}]	0.35	0.38	0.38	0.23	0.24	0.17

5.2 Estimation of the Hydrodynamic Radius of Assembly I in Toluene-d_8

The hydrodynamic radius r_h of assembly **I** was estimated using a semi-empirical approach towards the modified Stokes-Einstein equation (equation 1).[5] This approach has been used before for size estimation of similar systems.[6] The equation was solved numerically using the Math Input-function of Wolfram Alpha.[1]

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

Equation 1

D = Diffusion coefficient obtained from DOSY-measurements [2.3 10^{-10} $m^2 \cdot s^{-1}$]

k_B = Boltzmann constant [1.3806485 × 10^{-23} $m^2 \cdot kg \cdot s^{-1} \cdot K^{-1}$

T = Temperature [298 K]

r_{solv} = Hydrodynamic radius of the solvent [0.287 10^{-9} m]

r_h = Hydrodynamic radius of the analyte [m]

η = Viscosity of the solvent at 298 K [0.551 10^{-3} $kg \cdot m^{-1} \cdot s^{-1}$]

r_h = 1.7 nm

[1] https://www.wolframalpha.com/input/?i=0.23+*+%2810%5E%28-9%29%29+%3D+%281.3806485+*+%2810%5E%28+-23%29%29+*298%29%2F%28%286%2F%281%2B0.695+*+%280.287+*+%2810%5E%28+-9%29%29+%2Fx%29%5E2.234%29%29*%CF%80*0.551*10%5E%28-3%29*x

5.3 Comparison of the Size of Dimeric, Tetrameric and Octameric Structures with the Estimated Hydrodynamic Radius of Assembly I

For this purpose, molecular models of dimeric, tetrameric and octameric assemblies of macrocycle **25** were built using Spartan'18 (Wavefunction, Inc). The flexible alkyl feet were arranged in a compact way to from ball-shaped objects. Diameters were determined using the distance measurement tool in Spartan'18 (Wavefunction, Inc). Only the tetrameric assembly (radius approx. 1.6 nm) fits the experimentally determined hydrodynamic radius (1.7 nm, green circle) of assembly **I**.

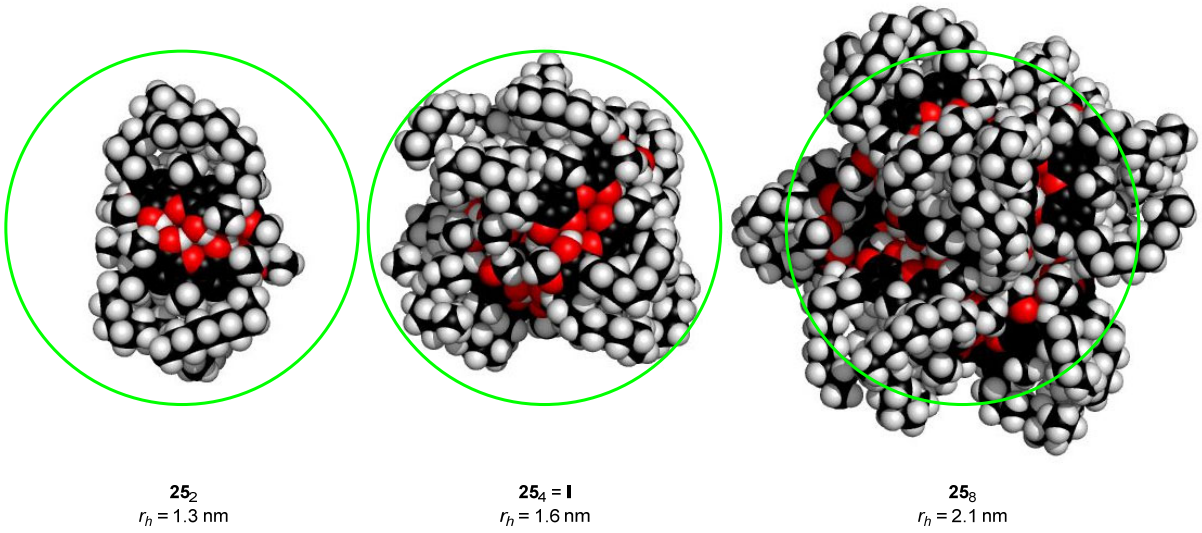


Figure S1: Comparison of the molecular models of dimeric, tetrameric and octameric assemblies of **25** with the experimentally determined hydrodynamic radius (1.7 nm, green circle) shows that the experimental data is only in good agreement with a tetrameric assembly **I**.

6 Model of Assembly I

The experimental evidence indicates that macrocycle **25** self-assembles to the tetrameric assembly **I**. The model was optimized (PM6 semi-empirical method) using the Spartan'18 software (Wavefunction, Inc). As can be seen in Fig. S2, a stable model was found that saturates all phenol hydrogen bond donor sites. Since steric hindrance of the methoxy groups does not allow the same orientation for all of them, most methoxy groups being part of the hydrogen bonding network are pointing outside of the assembly whereas the methoxy groups not included into the hydrogen bonding network are pointing inside.

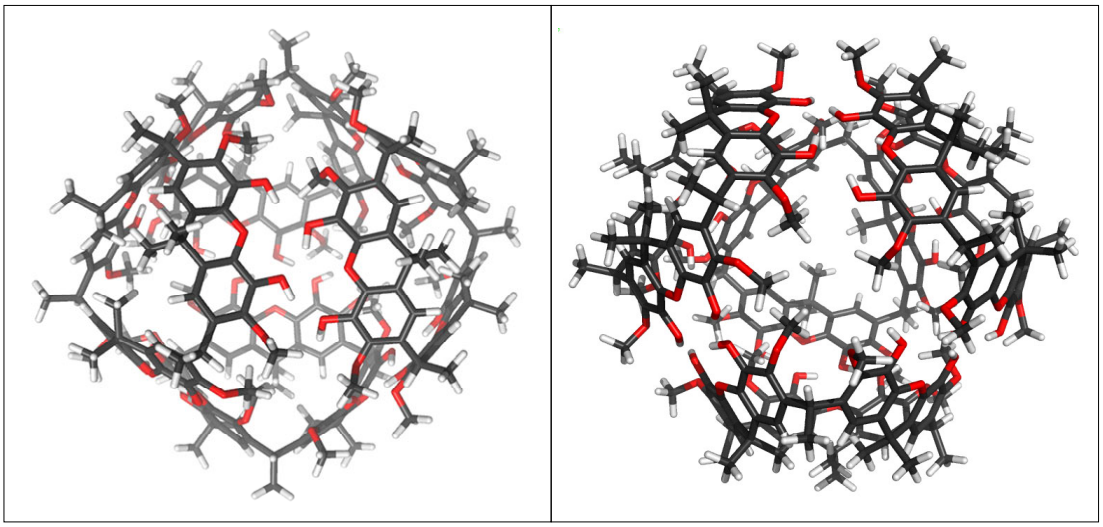


Figure S2: Model of assembly **I** constituted from four units of **25**.

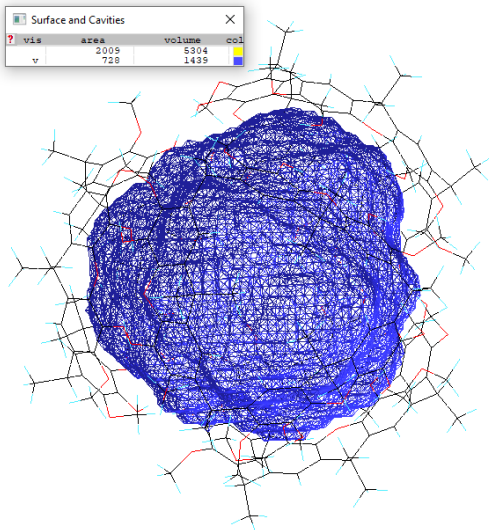


Figure S3: The cavity volume of capsule **I** was calculated using the SwissPdb Viewer v4.1.[7] The calculated cavity volume was 1439 Å^3. [2]

[2] http://www.expasy.org/spdbv/

7 Guest Uptake Studies

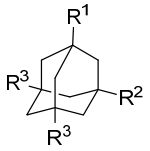
7.1 Overview of Tested Guests for Cavitand 23

The NMR guest uptake tests were performed at 298 K, measuring ^{1}H-NMR spectra at 500 MHz using a BRUKER UltraShield 500.

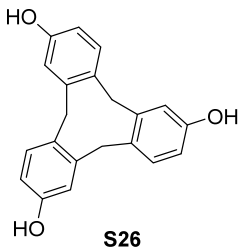
Cavitand **23** (1.56 mg, 1.00 µmol, 1.0 eq.) was dissolved in 600 µL of $CDCl_3$. To this solution, a stock solution of guest was added incrementally (0.5 – 5.0 eq.). The sample was heated to 50 °C for 30 min and subjected to NMR spectroscopy.

Table S7: Guest molecules tested for cavitand **23** in $CDCl_3$.

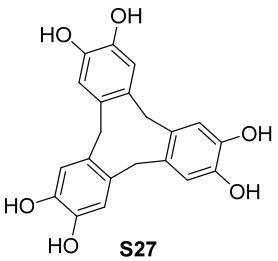
#	Guest	Observation
1	(*n*-CH_3)$_4N^+Br^-$	-
2	(*n*-C_2H_5)$_4N^+Br^-$	-
3	Adamantanemethanol **24**	Guest uptake
4-19	Adamantanes **S10**-**S25**	-
20	Cyclotribenzylene **S26**	-
21	Cyclotricatechylene **S27**	-
22	Fullerene-C_{60}	-
23	Fullerene-C_{70}	-



24: $R^1 = CH_2OH$; $R^{2-4} = H$
S10: $R^{1-4} = H$
S11: $R^1 = OH$; $R^{2-4} = H$
S12: $R^1 = NH_2$; $R^{2-4} = H$
S13: $R^1 = NH_3^+Cl^-$; $R^{2-4} = H$
S14: $R^1 = NHAc$; $R^{2-4} = H$
S15: $R^1 = CO_2H$; $R^{2-4} = H$
S16: $R^1 = CH_2NH_2$; $R^{2-4} = H$
S17: $R^1 = CH_2NH_3^+Cl^-$; $R^{2-4} = H$
S18: $R^1 = CH_2NHAc$; $R^{2-4} = H$
S19: $R^1 = CH_2CO_2H$; $R^{2-4} = H$
S20: $R^1 = CH_2CH_2OH$; $R^{2-4} = H$
S21: $R^{1-3} = OH$; $R^4 = H$
S22: $R^{1-3} = CH_2OH$; $R^4 = H$
S23: $R^{1-3} = CO_2H$; $R^4 = H$
S24: $R^1 = CH_2OH$; $R^{2-4} = CH_3$
S25: $R^1 = CH_2OH$; $R^{2-3} = CH_3$; $R^4 = H$



S26



S27

Figure S4: Structures of guest molecules investigated.

7.2 Encapsulation of 1-Adamantanemethanol (24) by Cavitand 23

Cavitand **23** (4.69 mg, 3.00 µmol, 1.0 eq.) was dissolved in 500 µL of $CDCl_3$ (freshly filtered through basic aluminium oxide). To this solution a stock solution of 1-adamantanemethanol (**24**) (60.0 mM in filtered $CDCl_3$, 50 µL, 3.00 µmol, 1.0 eq.) and a stock solution of 1,3,5-trimethoxybenzene (60.0 mM in filtered $CDCl_3$, 50 µL, 3.00 µmol, 1.0 eq.) were added. The sample was heated to 50 °C for 30 min and subjected to NMR spectroscopy.

Slow exchange on the NMR timescale was observed for the encapsulation of **24** at a temperature of 248 K and below. Concentrations of free guest [G] and host-guest complex [HG] were determined by integration of the corresponding ^{1}H-NMR signals (free guest: $\delta(^1H)$ = 3.20 ppm (s, 2H); host-guest complex: $\delta(^1H)$ = - 1.65 – - 1.86 ppm (m, 15H)) using the ^{1}H-NMR signal of 1,3,5-trimethoxybenzene ($\delta(^1H)$ = 3.77 ppm (s, 9H)) as the internal standard. A van't Hoff plot with a linear fit and the van't Hoff equation (equation 2) was used to calculate K_a, ΔH and ΔS.

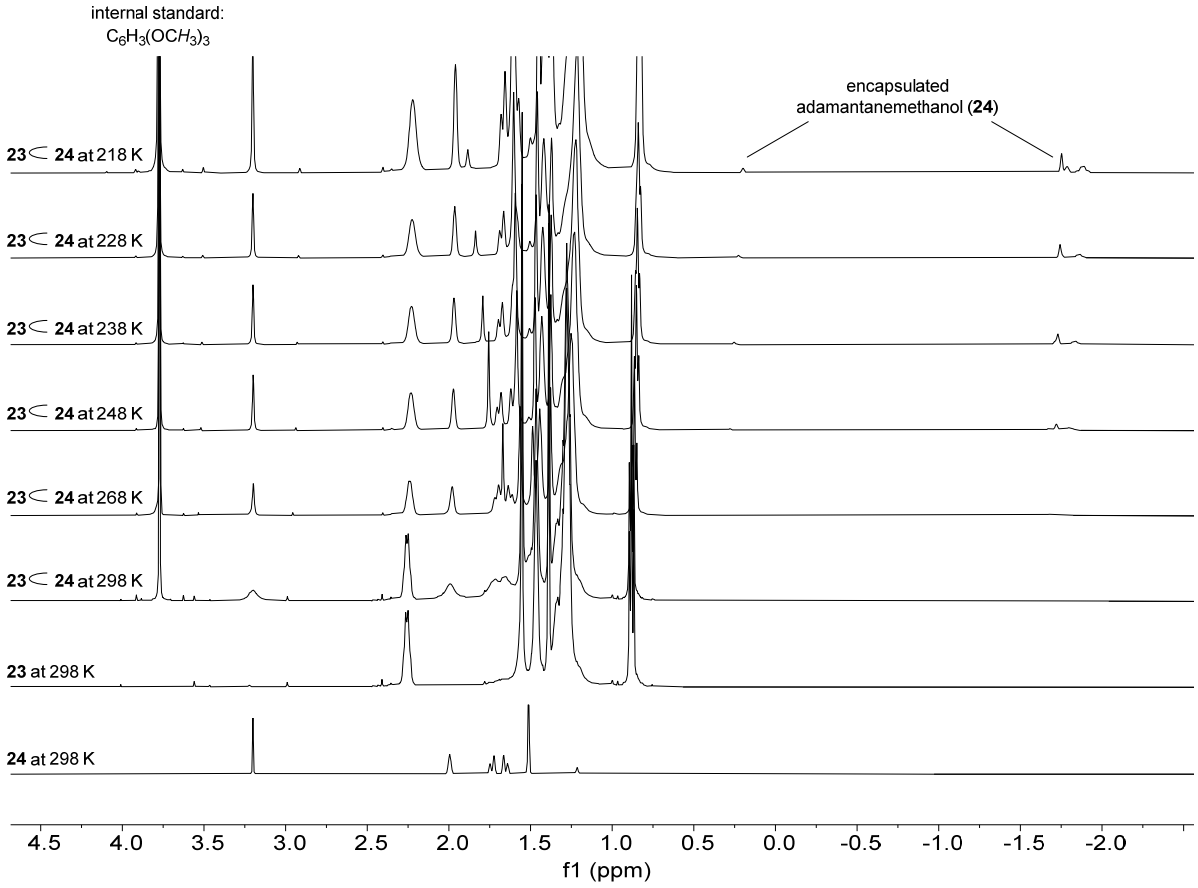


Figure S5: Excerpts from the ^{1}H-NMR spectra of 5.00 mM Cavitand **23** in $CDCl_3$ in the presence of 1.0 eq. 1-adamantanemethanol (**24**) and 1.0 eq. 1,3,5-trimethoxybenzene; T = 218 K -298 K.

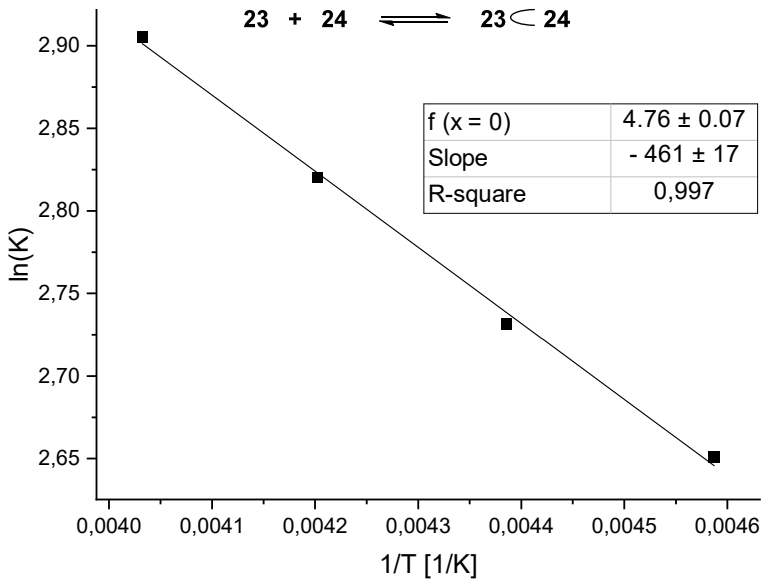


Figure S6: Temperature dependant stability constant in dependency of the reciprocal temperature (van't Hoff plot) for determination of the thermodynamic data of the encapsulation of **24** by Cavitand **23**.

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad \textbf{Equation 2}$$

K_a [M^{-1}]	ΔH [kJ/mol]	ΔS [J/(mol×K)]
23.9 ± 2.6	3.83 ± 0.14	39.6 ± 0.6

7.3 Overview of Tested Guests for Assembly I

The NMR guest uptake tests were performed at 298 K, measuring ^{1}H-NMR spectra at 500 MHz using a BRUKER UltraShield 500.

Macrocycle **25** (4.09 mg, 3.00 µmol, 4.0 eq.) was dissolved in 600 µL of $CDCl_3$. To this solution, a stock solution of guest was added incrementally (0.5 – 5.0 eq.). The sample was heated to 50 °C for 30 min and subjected to NMR spectroscopy.

Table S8: Guest molecules tested for assembly **I** in $CDCl_3$.

#	Guest	Observation
1	(*n*-C_2H_5)$_4N^+Br^-$	Precipitate
2	(*n*-C_4H_9)$_4N^+Br^-$	-
3	(*n*-C_5H_{11})$_4N^+Br^-$	-
4	$(Bn)_3$(*t*BuBn)N^+Br^-	-
5	Hexamethonium bromide	-
6	Geraniol	-
7	Nerol	-
8	Neryl acetate	-
9	Naphtalene[a]	-
10	Anthracene[a]	-
11	Adamantane	-
12	Adamantanemethanol **24**	-
13	Fullerene-C_{60}[b]	Guest uptake
14	Fullerene-C_{70}[b]	-

[a] ball-milling was tested as well. [b] also tested in toluene-d_8.

7.4 Encapsulation of Fullerene-C_{60} by Assembly I

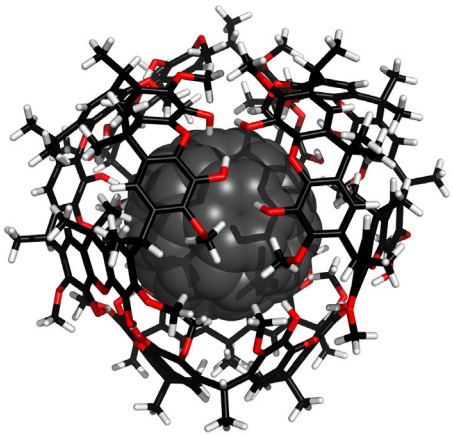


Figure S7: Molecular model of assembly **I** encapsulating fullerene-C_{60}.

The NMR titration was performed at 298 K, measuring ^{13}C-NMR spectra at 151 MHz using a 600 MHz BRUKER Avance III NMR spectrometer equipped with a cryogenic QCI-F probe.

Macrocycle **25** (4.09 mg, 3.00 µmol, 4.00 eq.) was dissolved in 600 µL of toluene-d8. To this solution, a stock solution of fullerene-C_{60} was added incrementally (2.50 mM in tol-d8). The sample was heated to 50 °C for 30 min and subjected to NMR spectroscopy.

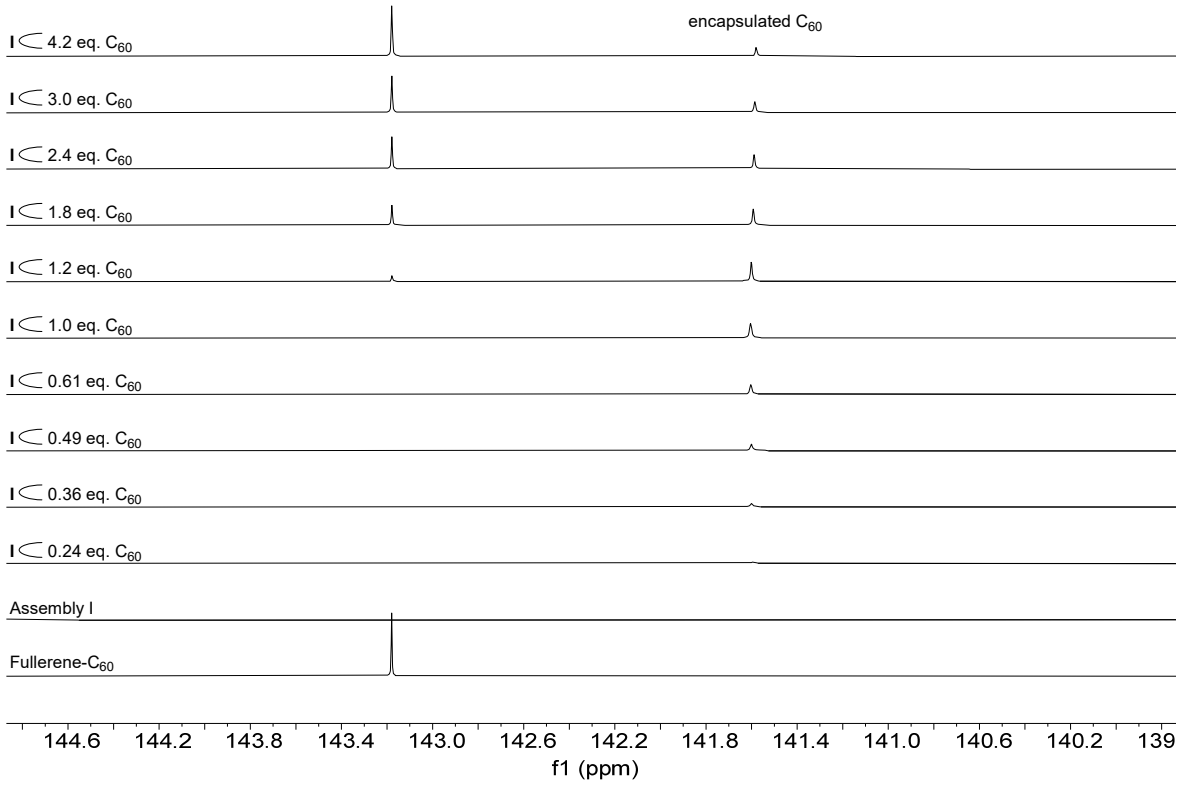
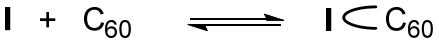


Figure S8: Excerpts from the ^{13}C-NMR spectra of assembly **I** in the presence of 0 – 4.2 eq. fullerene-C60.

Due to the low concentrations required for UV/Vis spectroscopy or ITC, those techniques are not suited for the determination of the binding constant, as such low concentrations prevent the self-assembly of **I**. As can be seen from the ^{13}C-NMR titration (figure S8) guest uptake of fullerene-C_{60} into the assembly **I** is almost quantitative upon addition of 1.0 eq. guest (figure S9) thereby making the exact determination of the binding constant difficult. From the ^{13}C-NMR titration, it can be estimated that the relaxation time of C_{60} is not significantly changed by the encapsulation. Taking into account the experimental error and the error caused by the integration of the free guest signal, the calculated K_a value can only be used as an estimate. The order of magnitude however is in accordance with the limit of NMR quantification for the K_a values (10^5 M^{-1}).[8]

Slow exchange on the NMR timescale was observed for the encapsulation of fullerene-C_{60} by assembly **I**. Concentrations of free guest [G] and host-guest complex [HG] were determined by integration of the corresponding ^{13}C-NMR signals (free guest: δ(^{13}C) = 143.15 ppm; host-guest complex: δ(^{13}C) = 141.57 ppm. The formation of the host-guest complex is described by the following equation, which was used to calculate K_a



$$K_a = \frac{[HG]}{[H_{frei}] \times [G_{frei}]}$$ **Equation 3**

$K_a = 7 \times 10^5$ M^{-1}

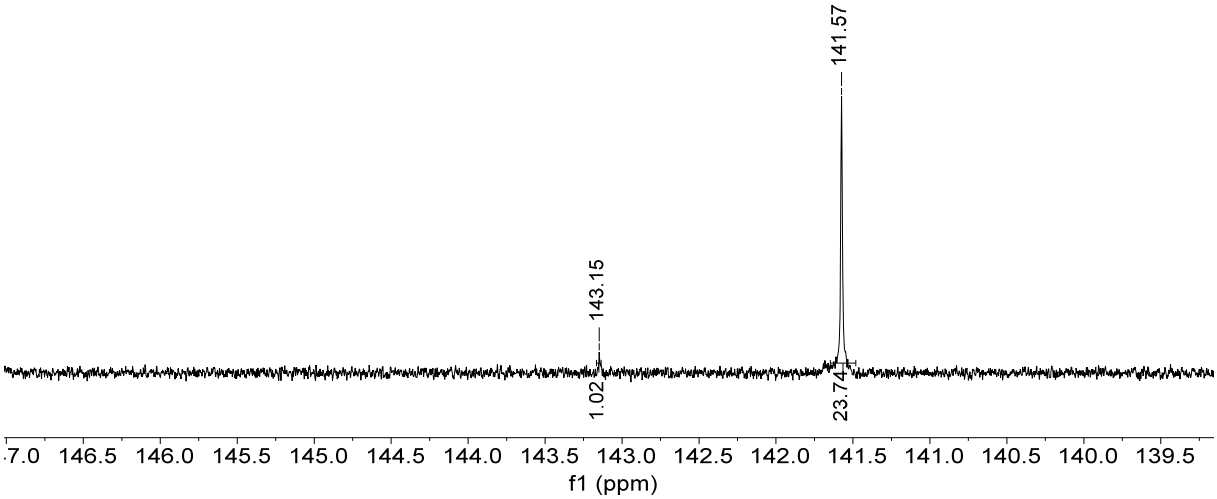


Figure S7: Excerpt from the ^{13}C-NMR spectrum in toluene-d_8 of capsule **I** and fullerene-C_{60} (both 0.85 mM) used to calculate K_a.

8 Photophysical Properties of O_6-Belt 26

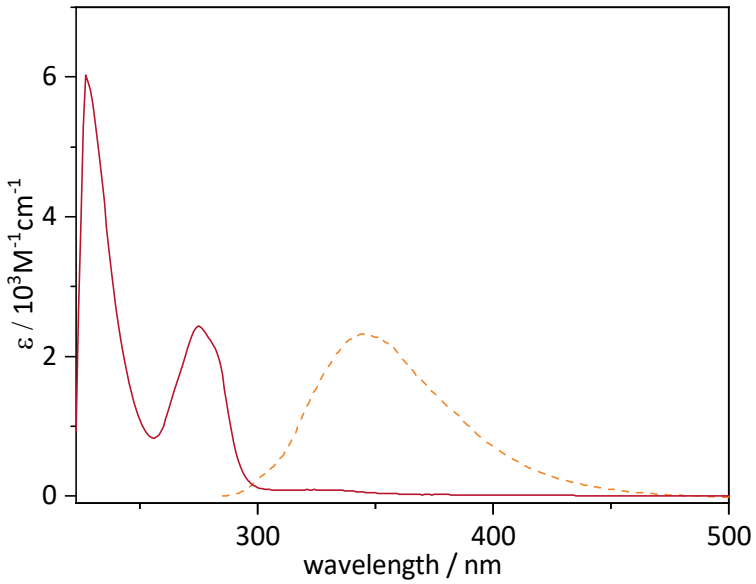


Figure S8: UV-Vis absorption (solid red line) and normalized luminescence spectrum (dashed orange line) of a $2 \cdot 10^{-5}$ M O_6-belt **26** solution in dry, deaerated CH_2Cl_2 at 293 K. For the luminescence spectrum, the excitation was at 275 nm.

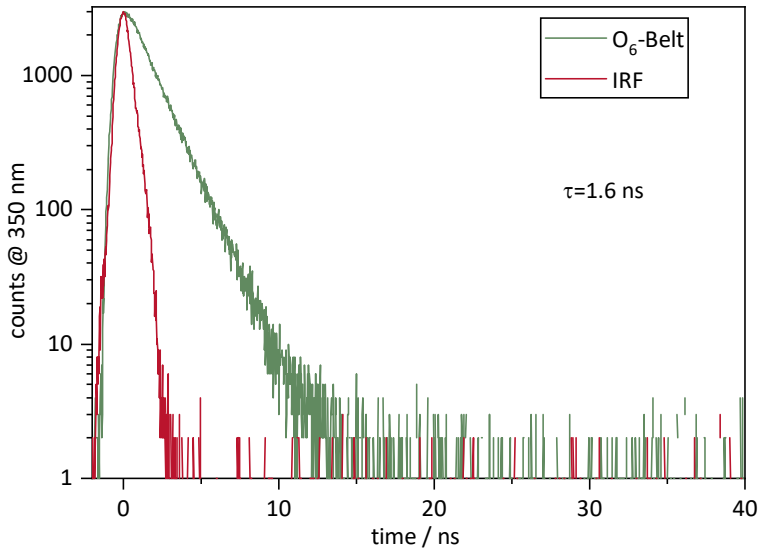


Figure S9: Luminescence decay at 350 nm of a $2 \cdot 10^{-5}$ M O_6-belt **26** solution in dry, deaerated CH_2Cl_2 at 293 K (green line) and the instrument response function (IRF, red line). Excitation was at 313 nm with laser pulses of ca. 60 ps duration in both cases.

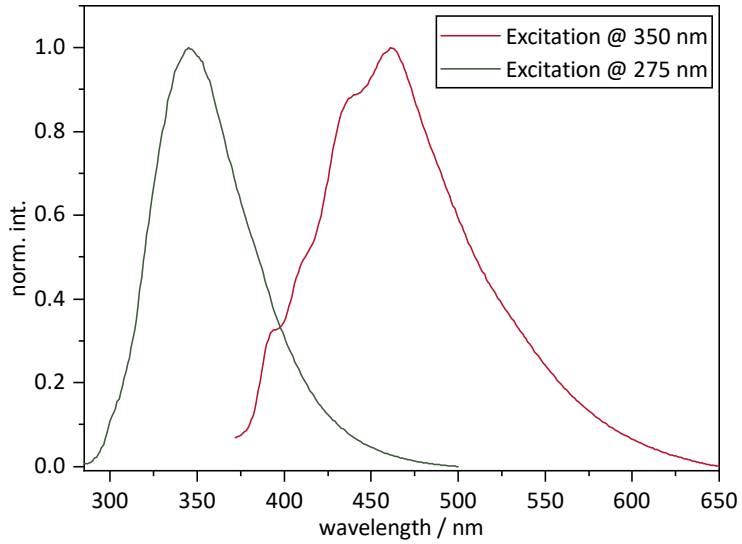


Figure S10: Normalized luminescence spectra of a $2 \cdot 10^{-5}$ M O_6-belt **26** solution in dry, deaerated CH_2Cl_2 at 293 K. Excitation was at 350 nm (red line) or 275 nm (green line).

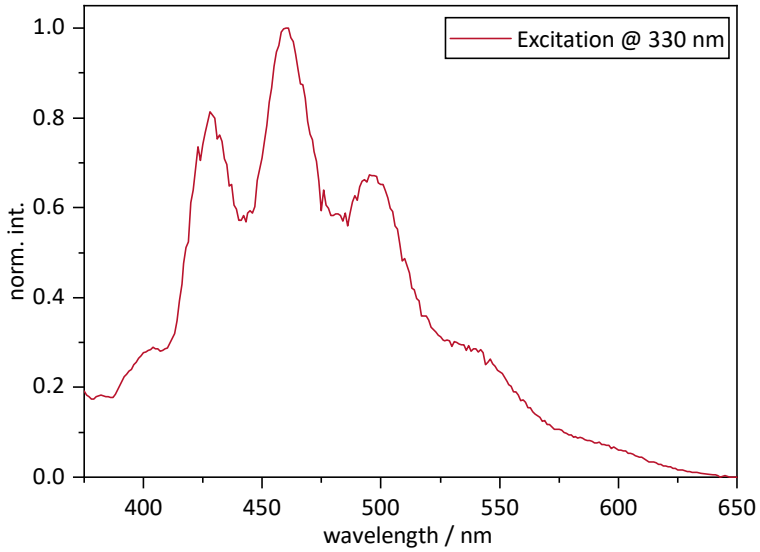


Figure S11: Normalized luminescence spectrum of a 10^{-5} M O_6-belt **26** solution recorded at 77 K in 2-methyl-THF. Excitation was at 330 nm.

9 MALDI-TOF-MS Studies Indicating Formation of Xanthene-4-arene S28 during the Cyclization of Benzylic Alcohol 15

The sample was prepared after flash column chromatography and before gel permeation chromatography of the crude product **19**. 1 mg of the material was diluted with 1 mL CH_2Cl_2. The resulting solution was used for MALDI-TOF-MS analysis.

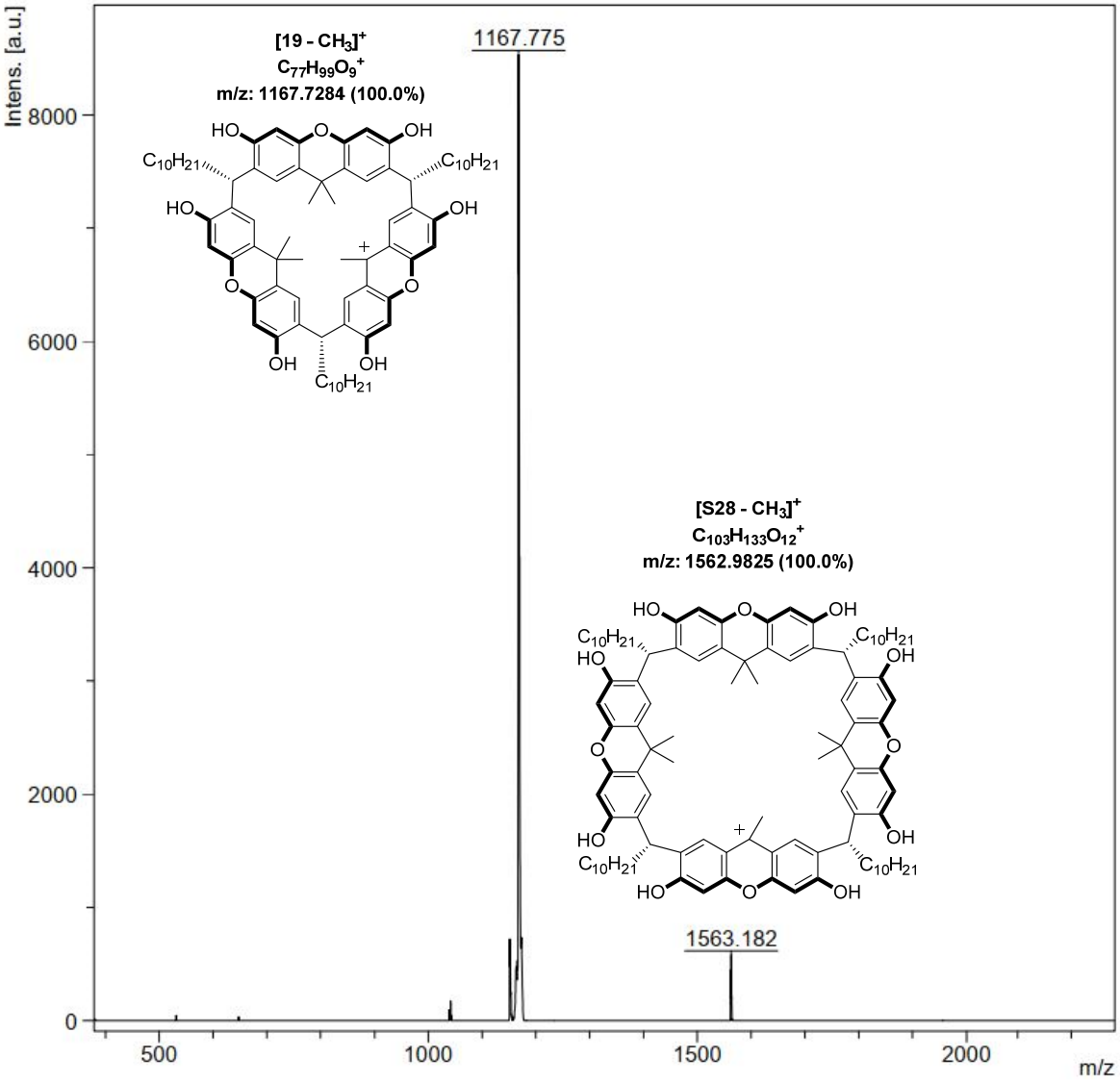
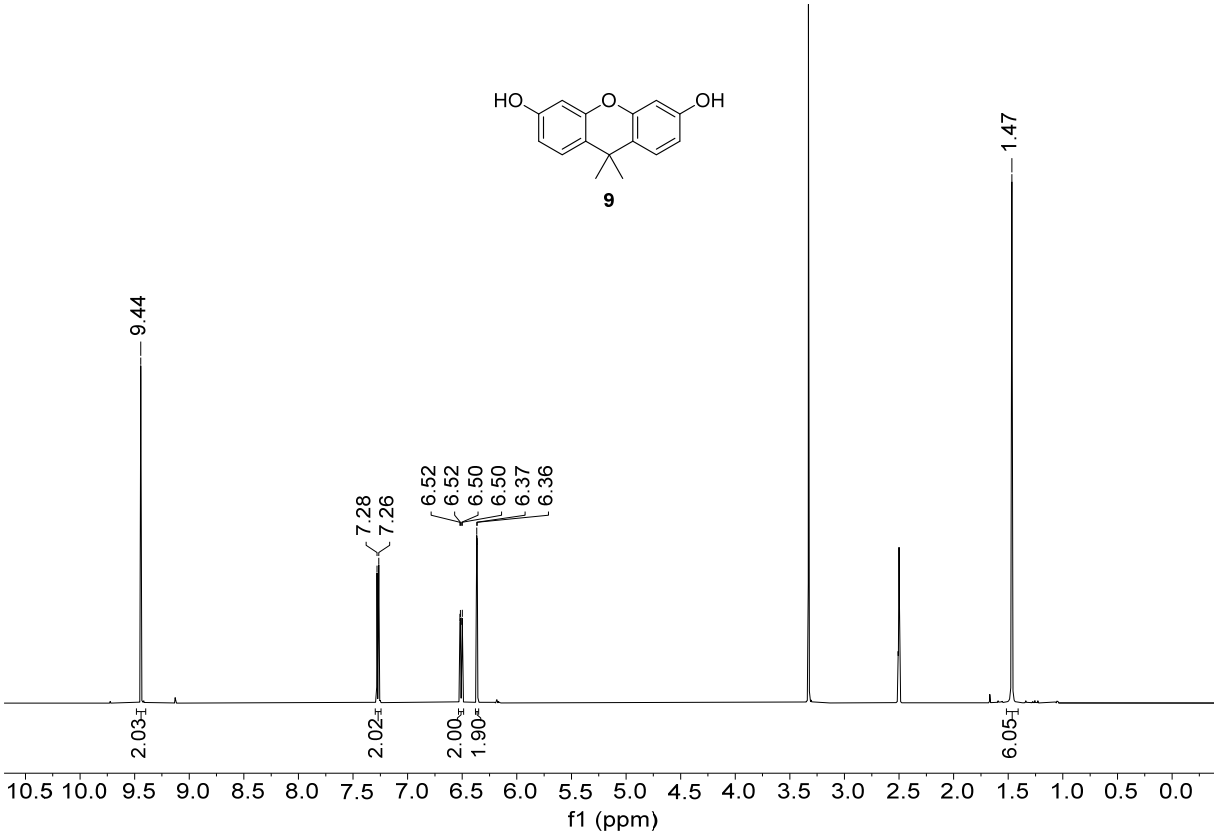
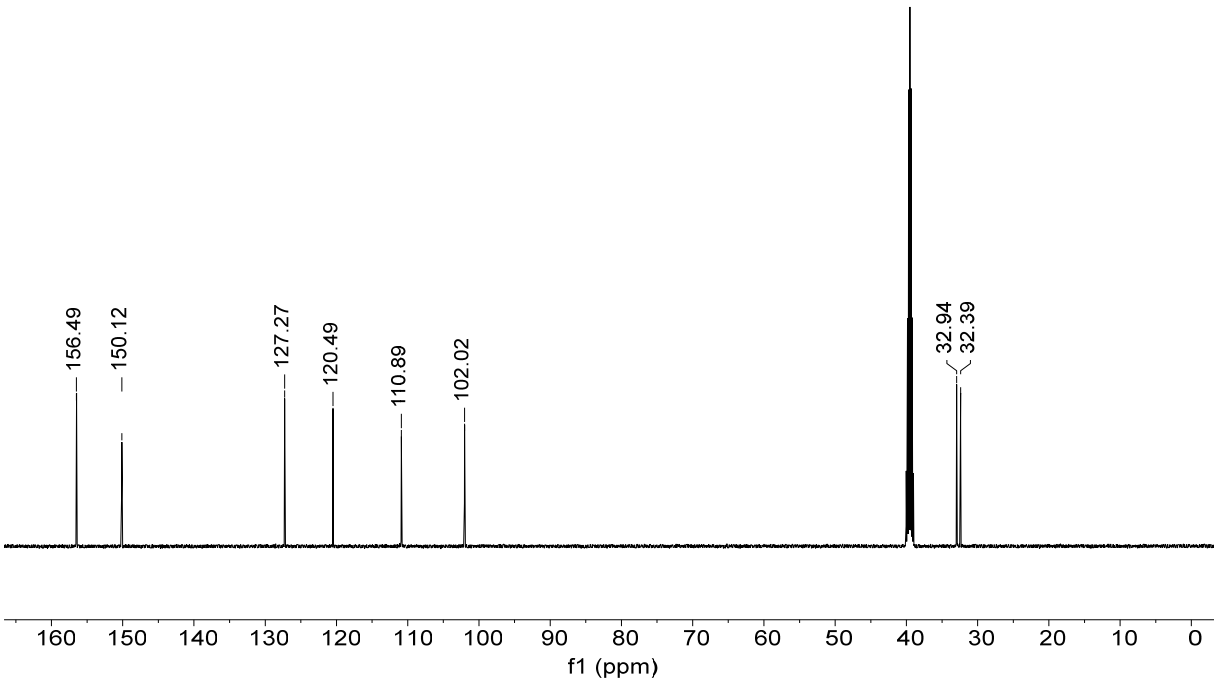


Figure S12: MALDI-TOF-MS analysis (positive scan) of the cyclization of benzylic alcohol **15**, indicating the formation of xanthene-4-arene **S28** in small amounts that were insufficient for isolation.

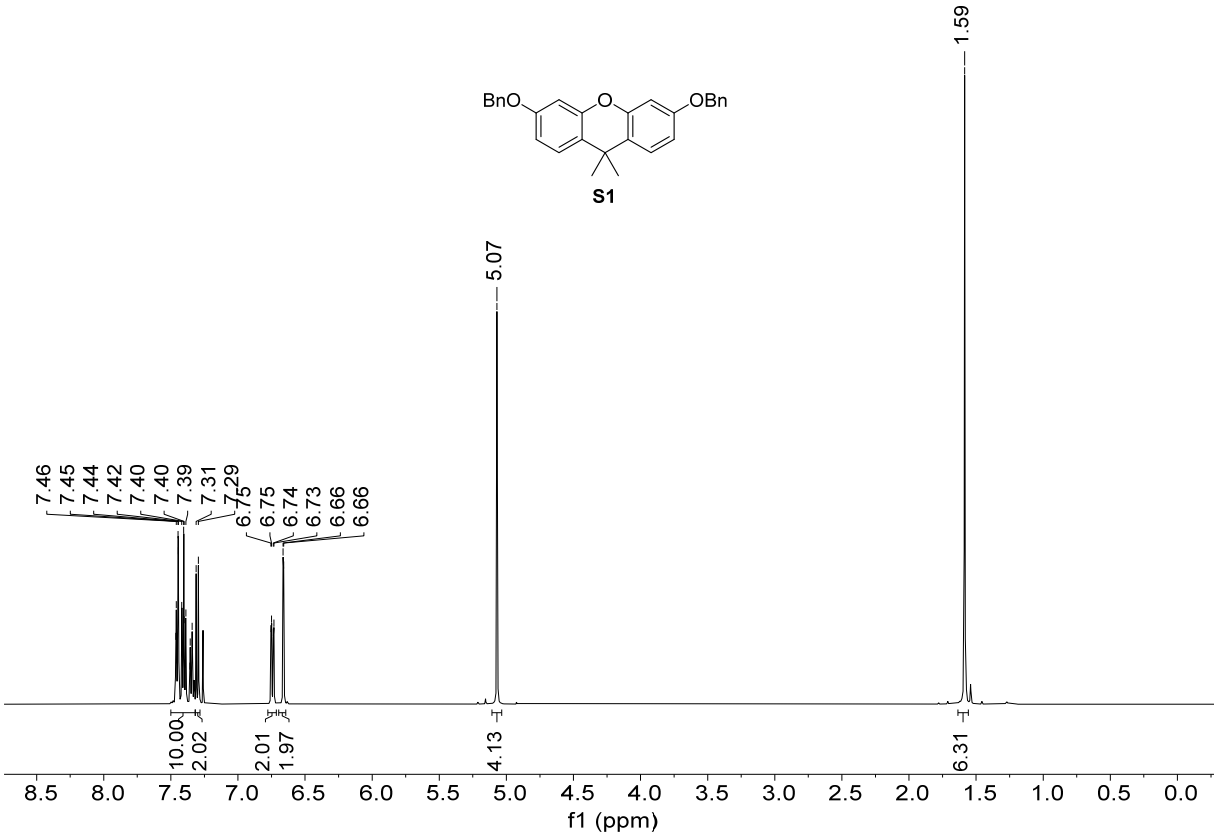
10 NMR-Spectra of New Compounds

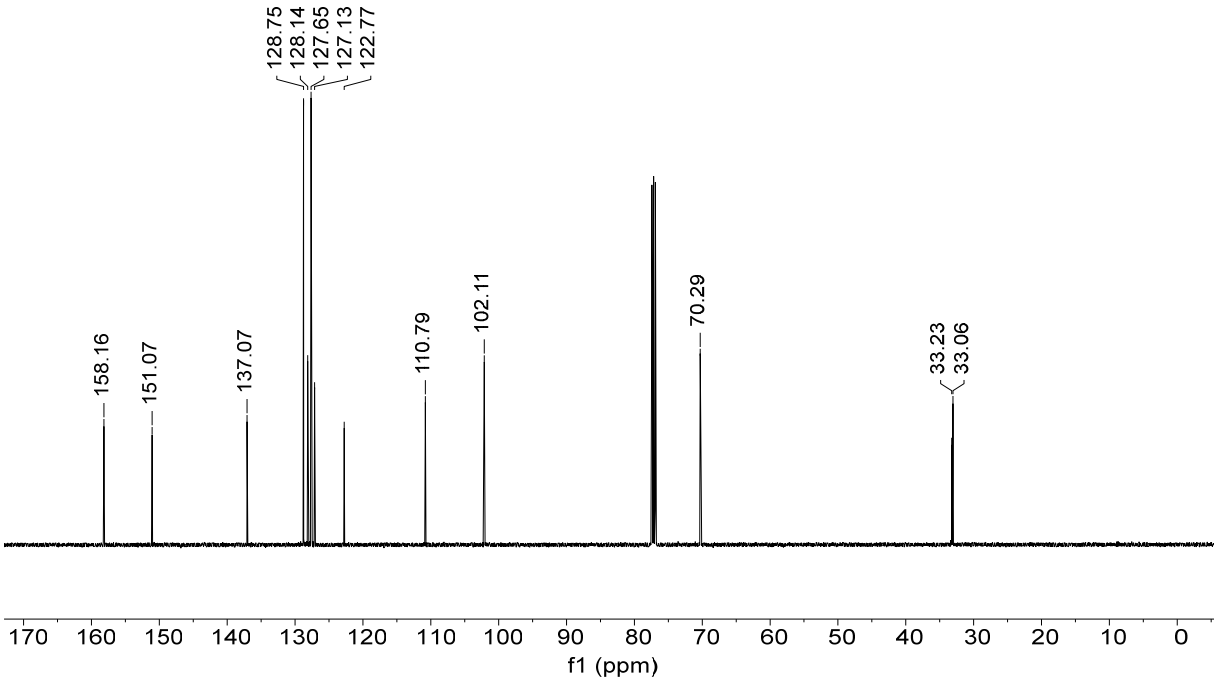
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **9** in DMSO-d6 at 298 K.



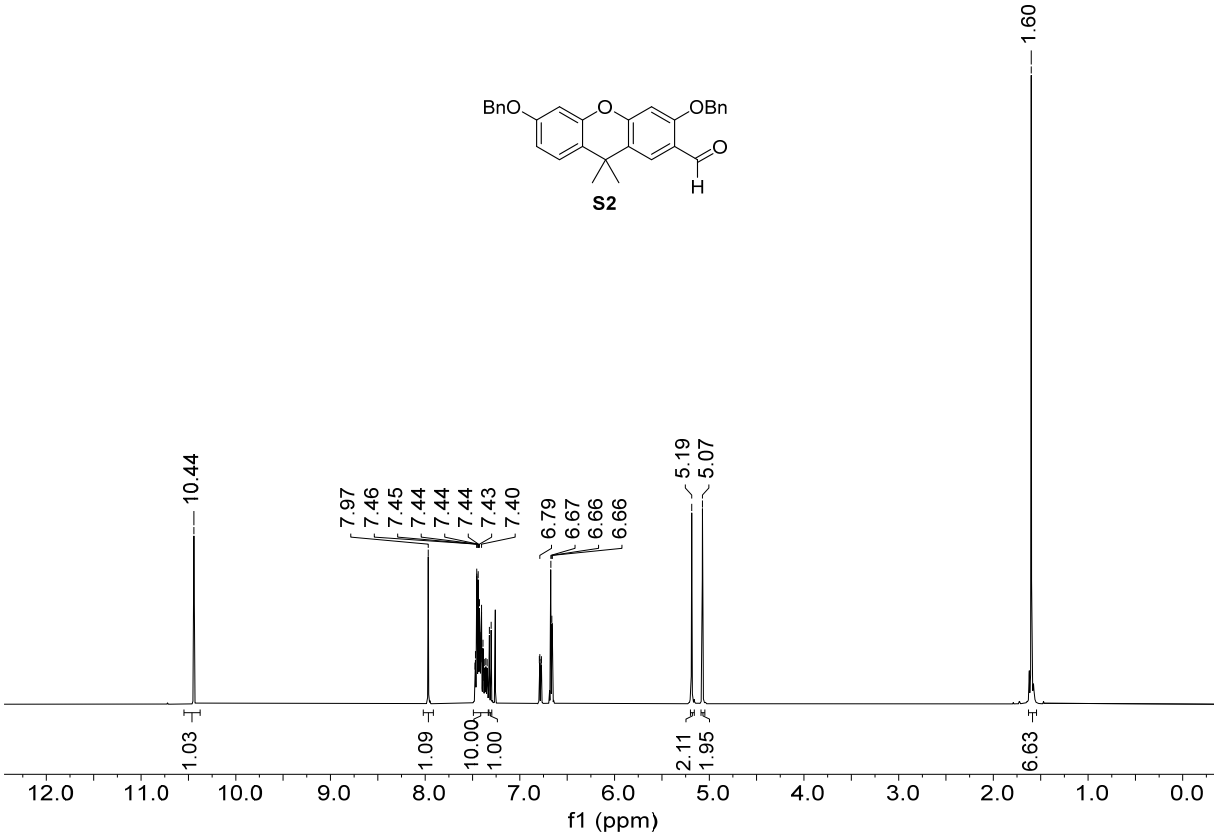


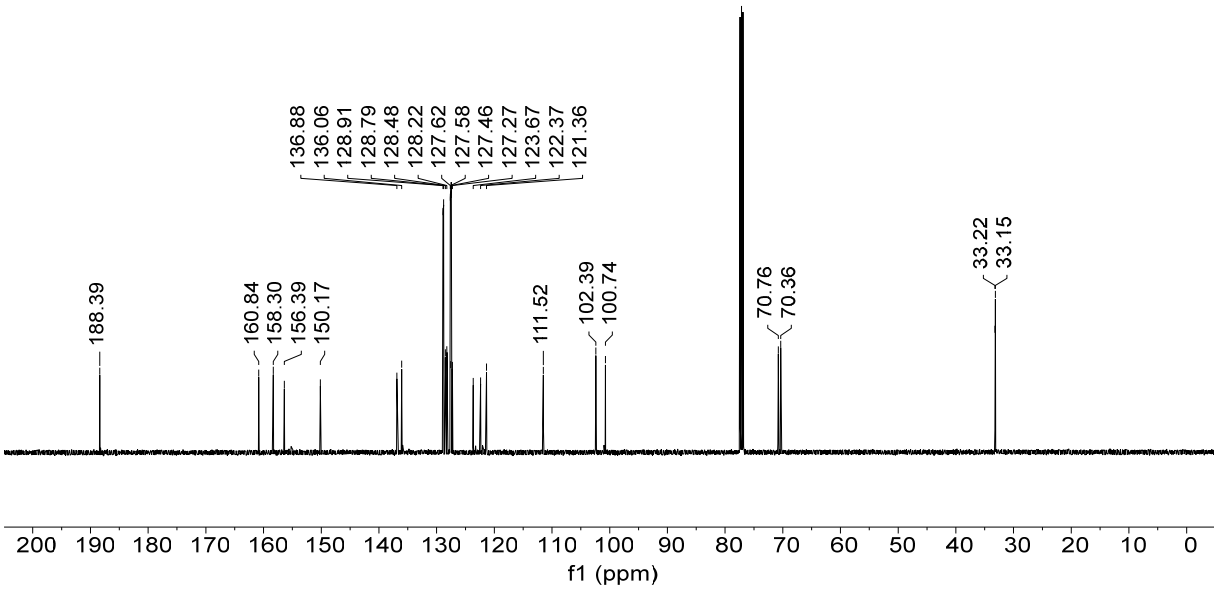
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **S1** in $CDCl_3$ at 298 K.



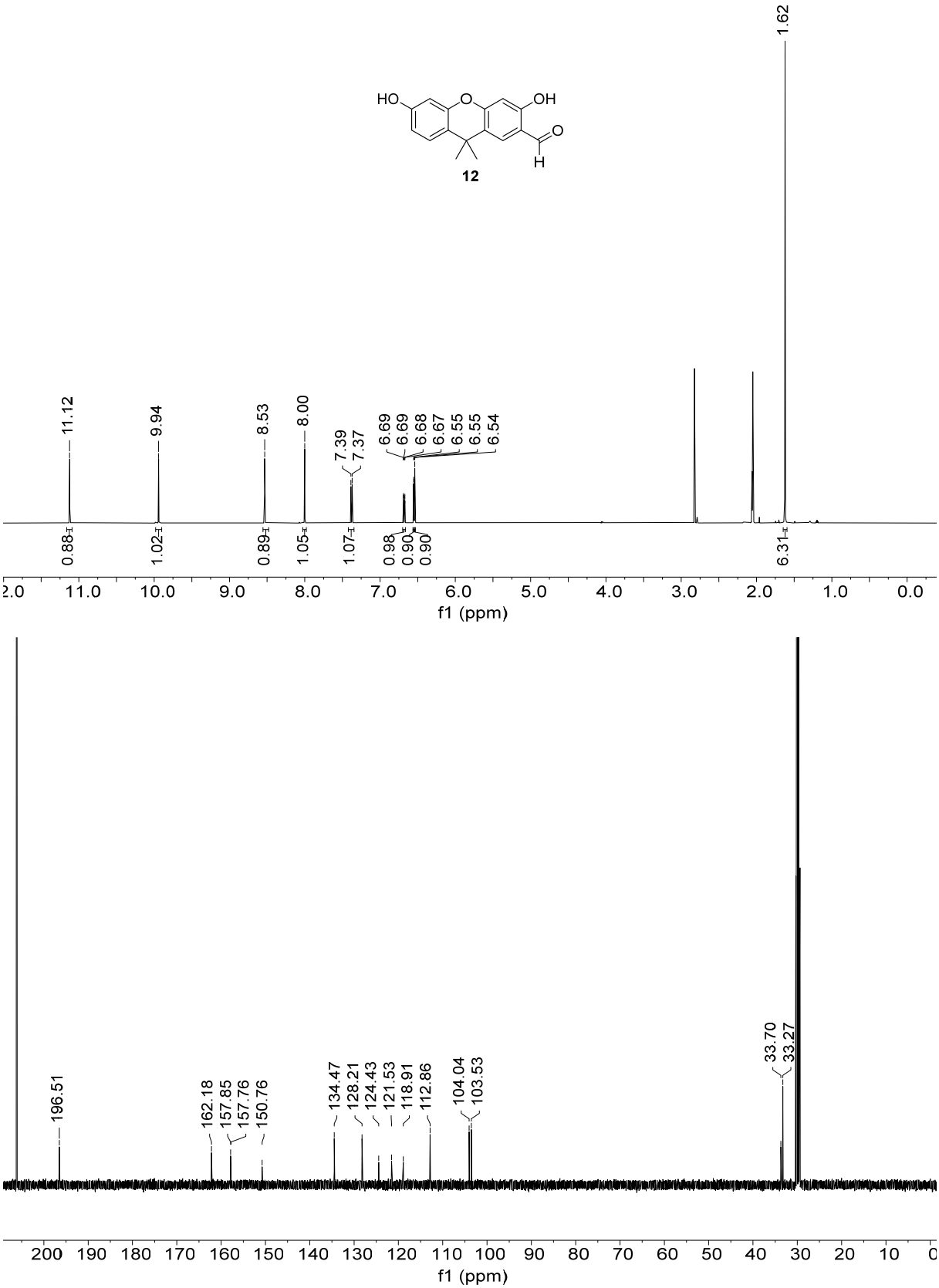


^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **S2** in $CDCl_3$ at 298 K.

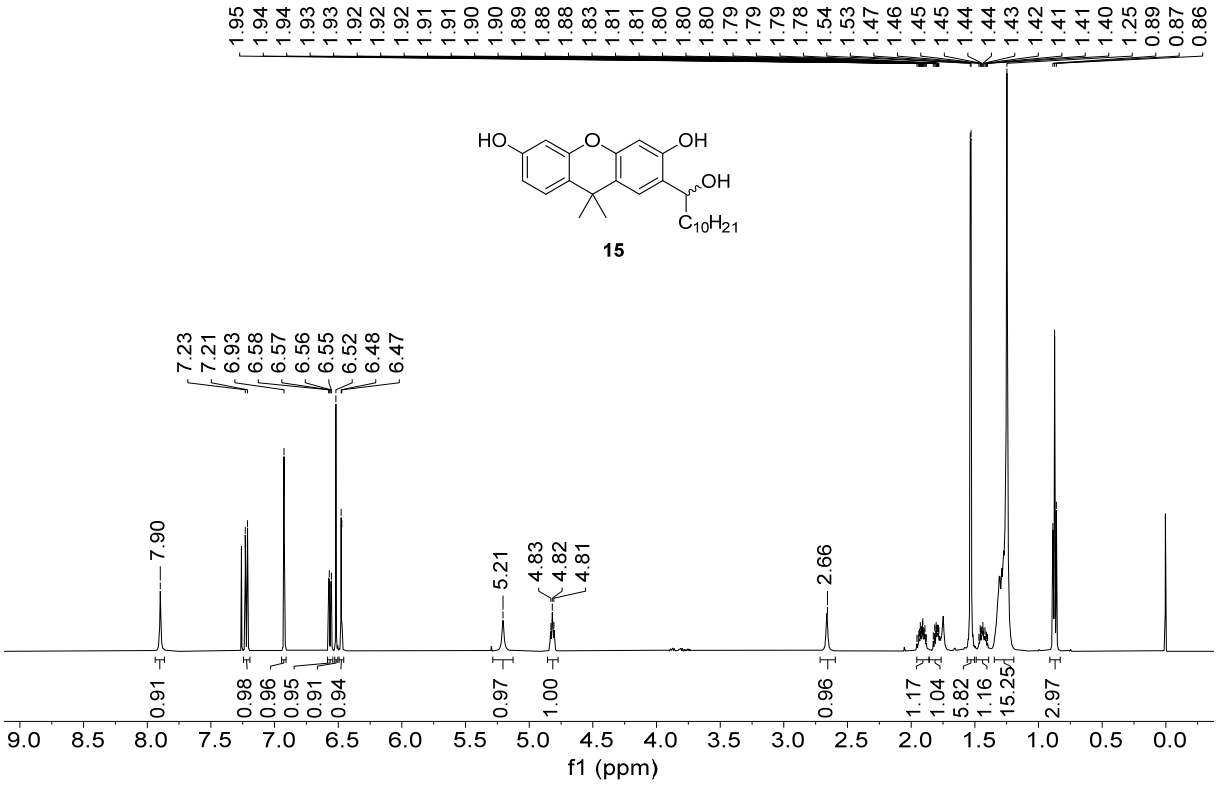




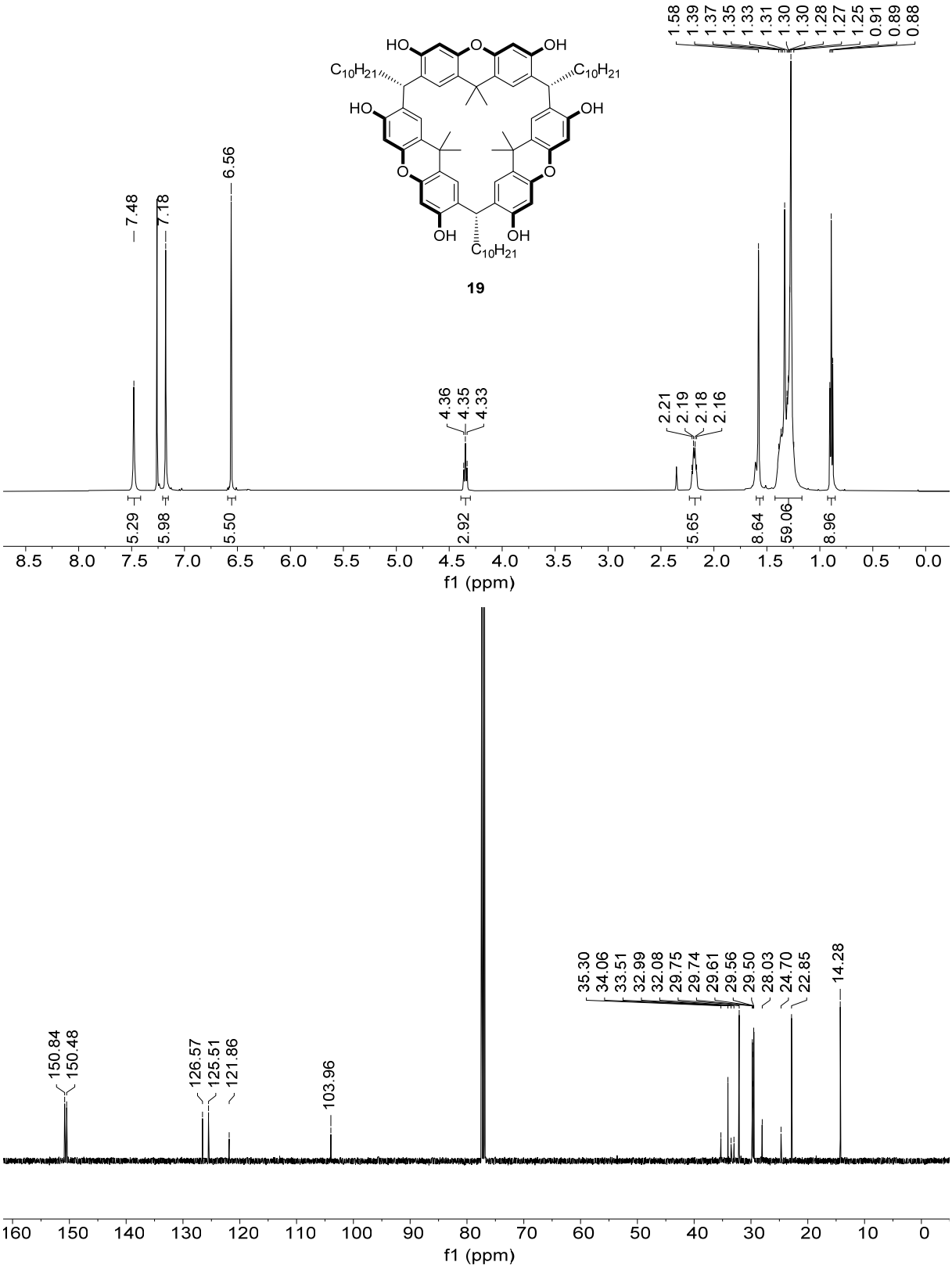
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **12** in acetone-d_6 at 298 K.



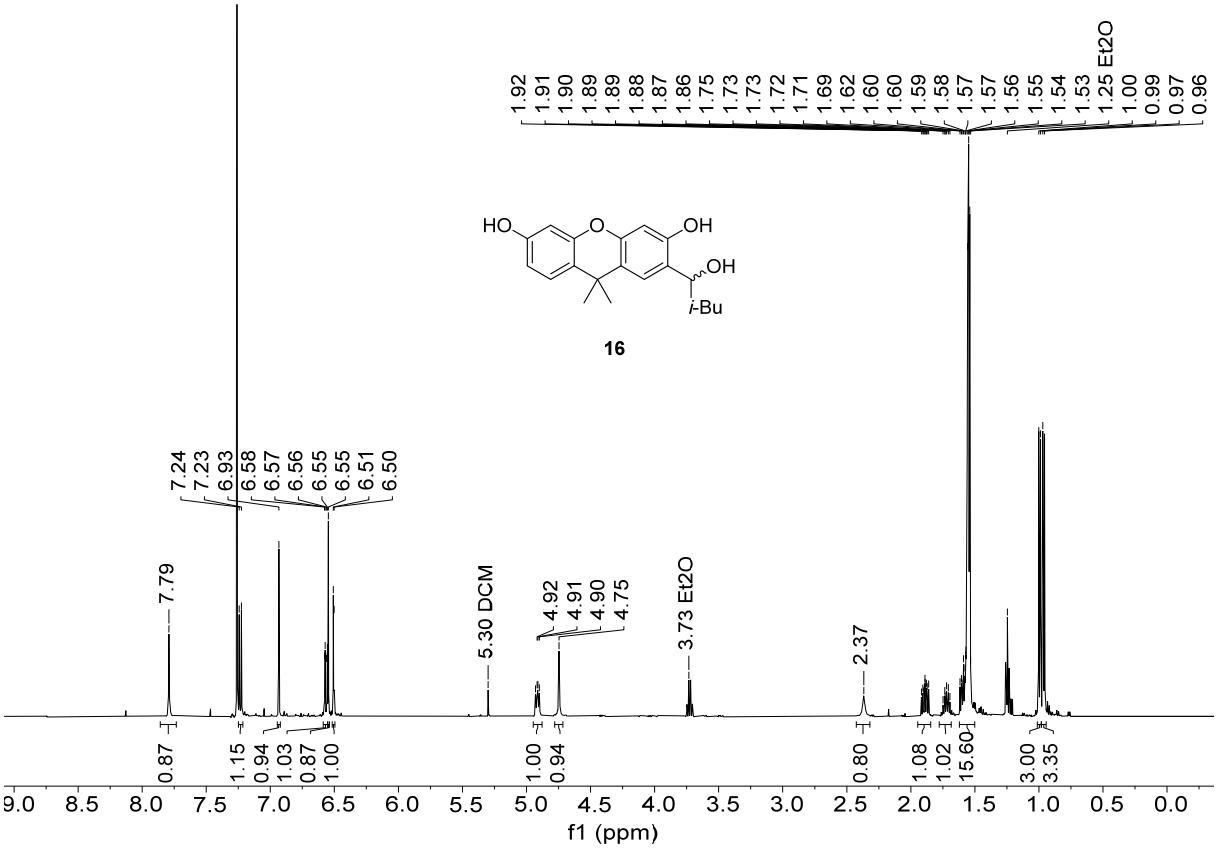
^{1}H-NMR (500 MHz) spectrum of **15** in $CDCl_3$ at 298 K.



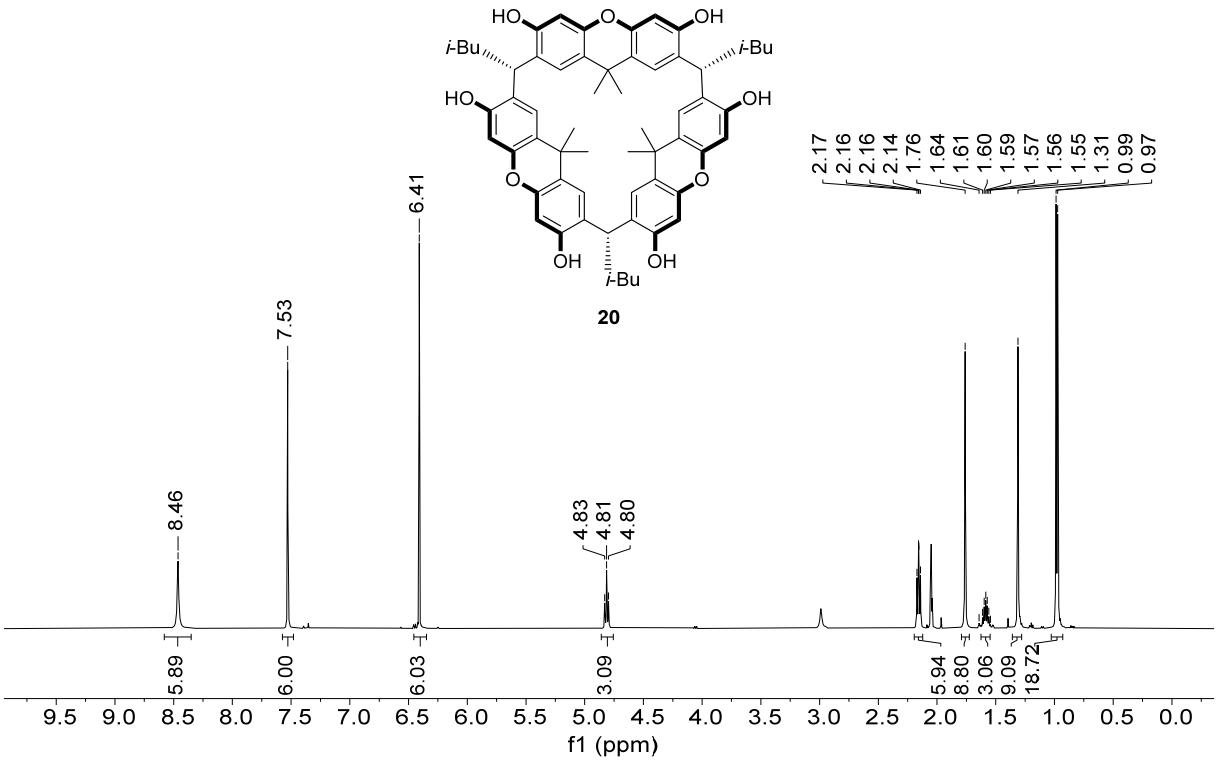
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **19** in $CDCl_3$ at 298 K.

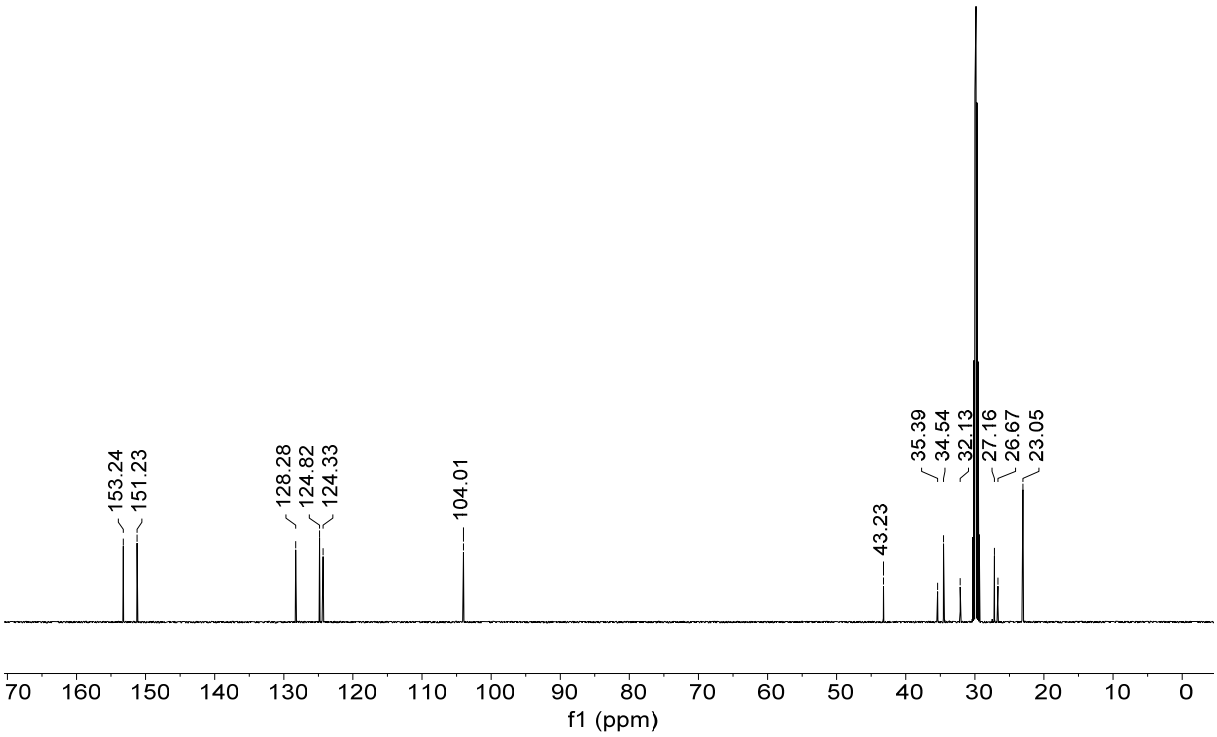


^{1}H-NMR (500 MHz) spectrum of **16** in $CDCl_3$ at 298 K.

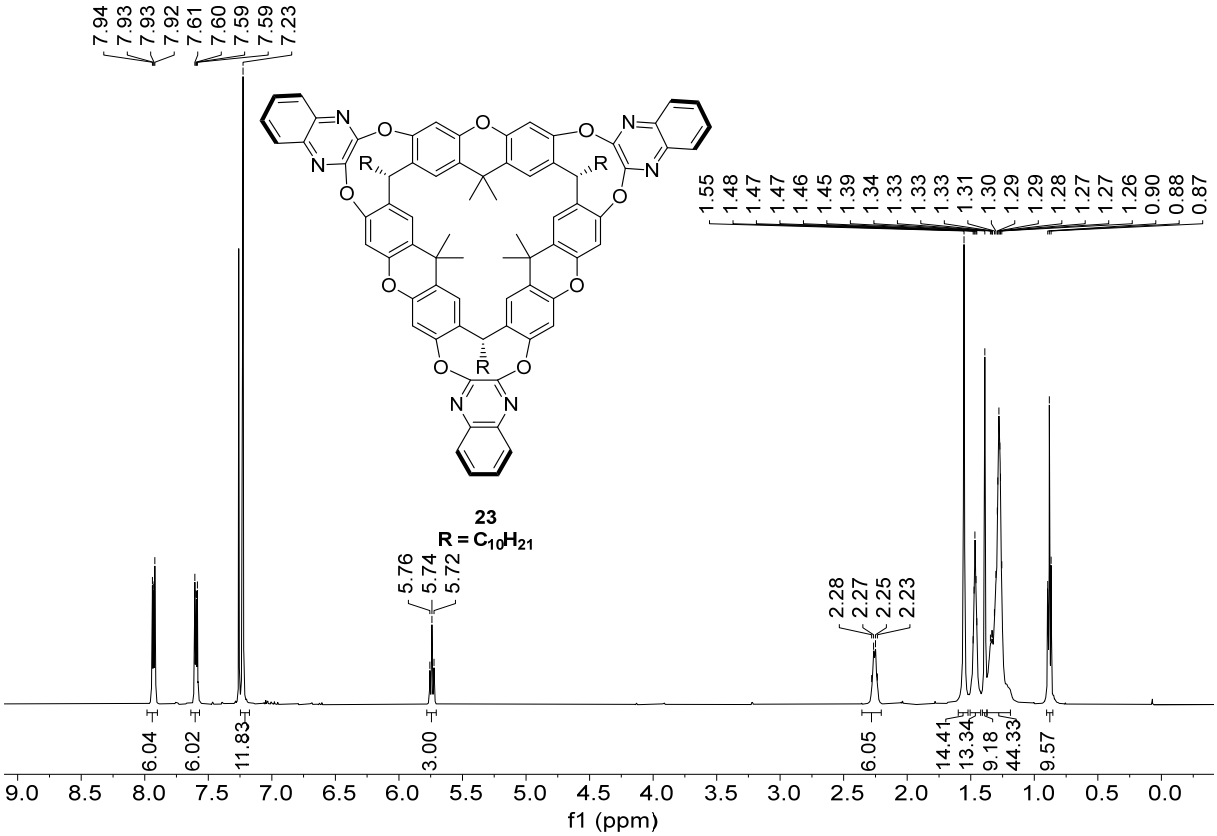


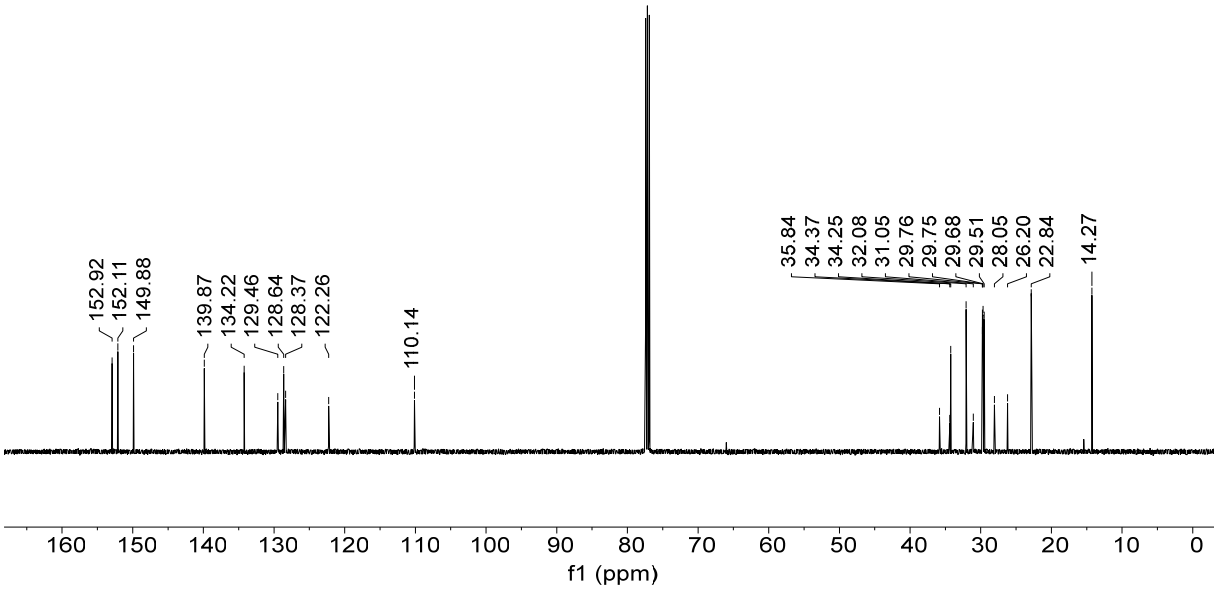
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **20** in acetone-d_6 at 298 K.



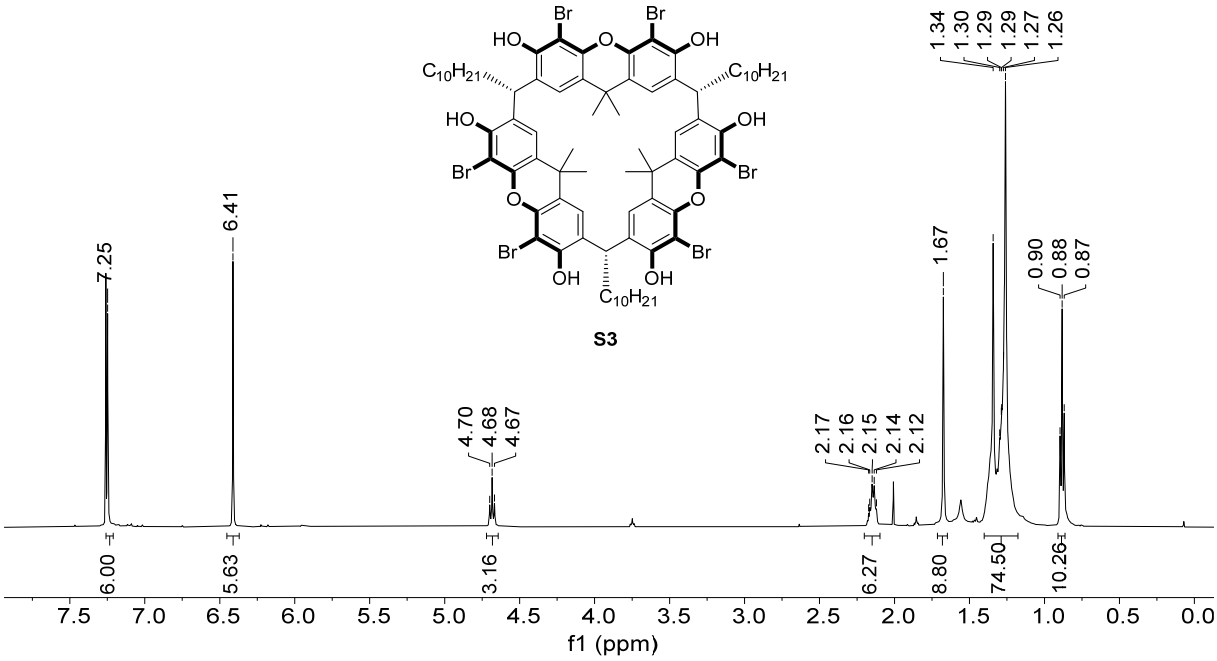


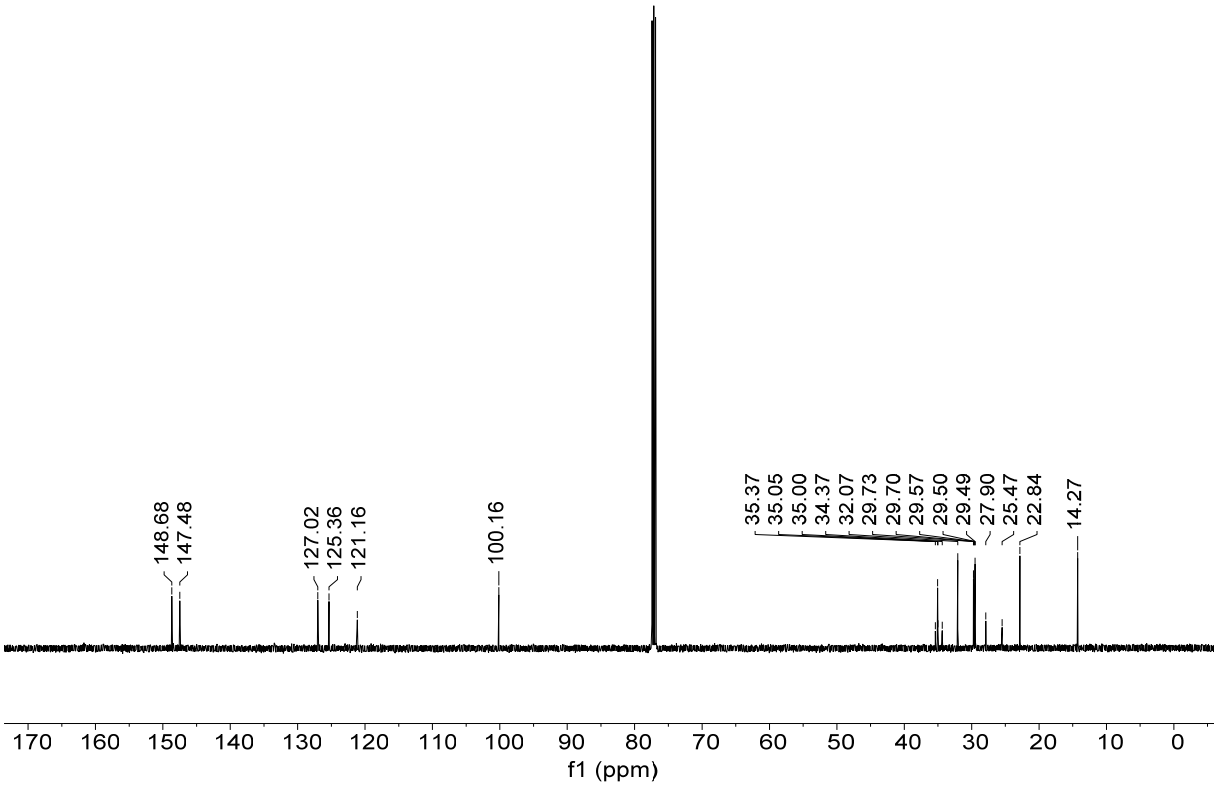
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **23** in $CDCl_3$ at 298 K.



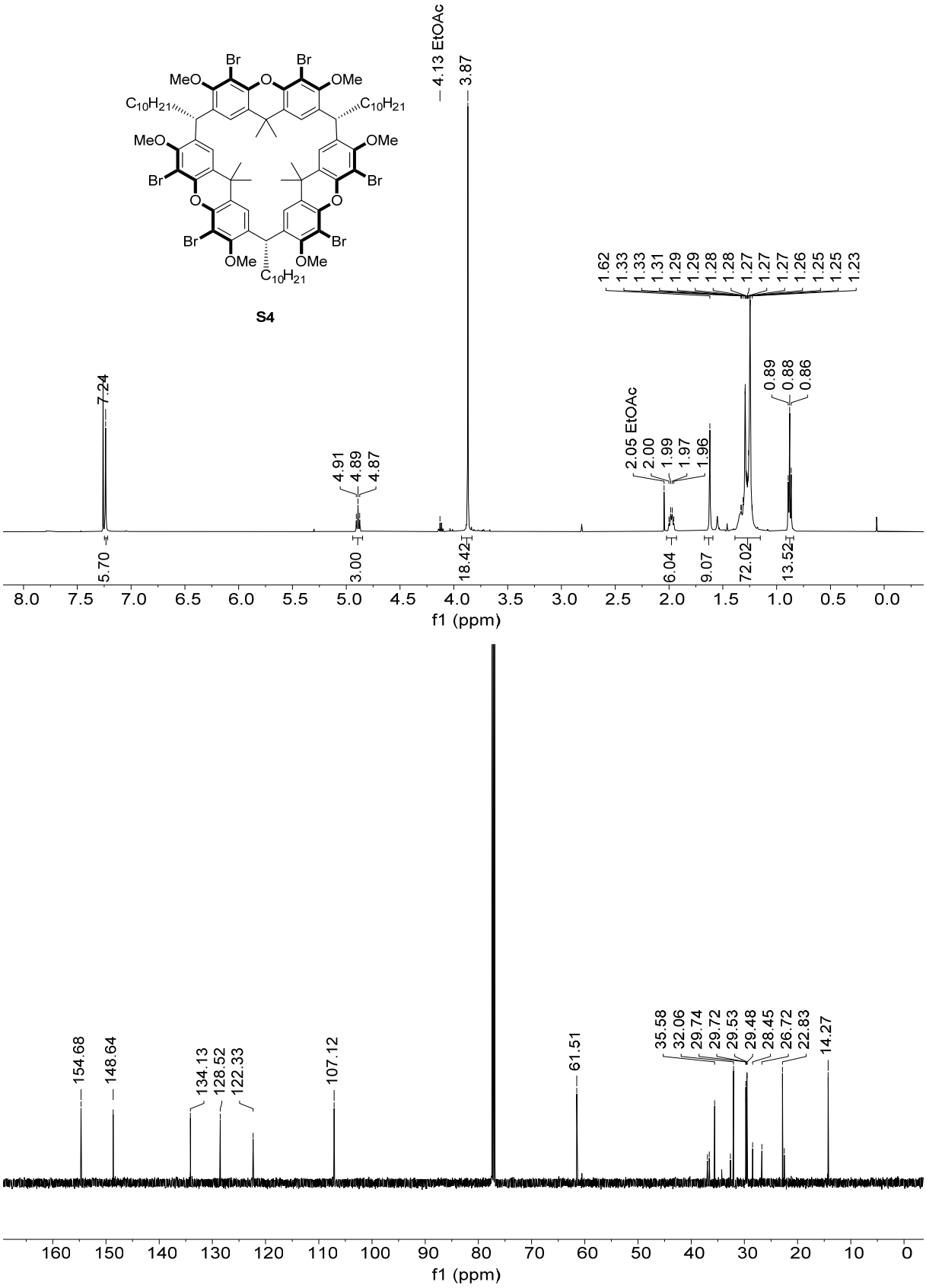


^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **S3** in $CDCl_3$ at 298 K.

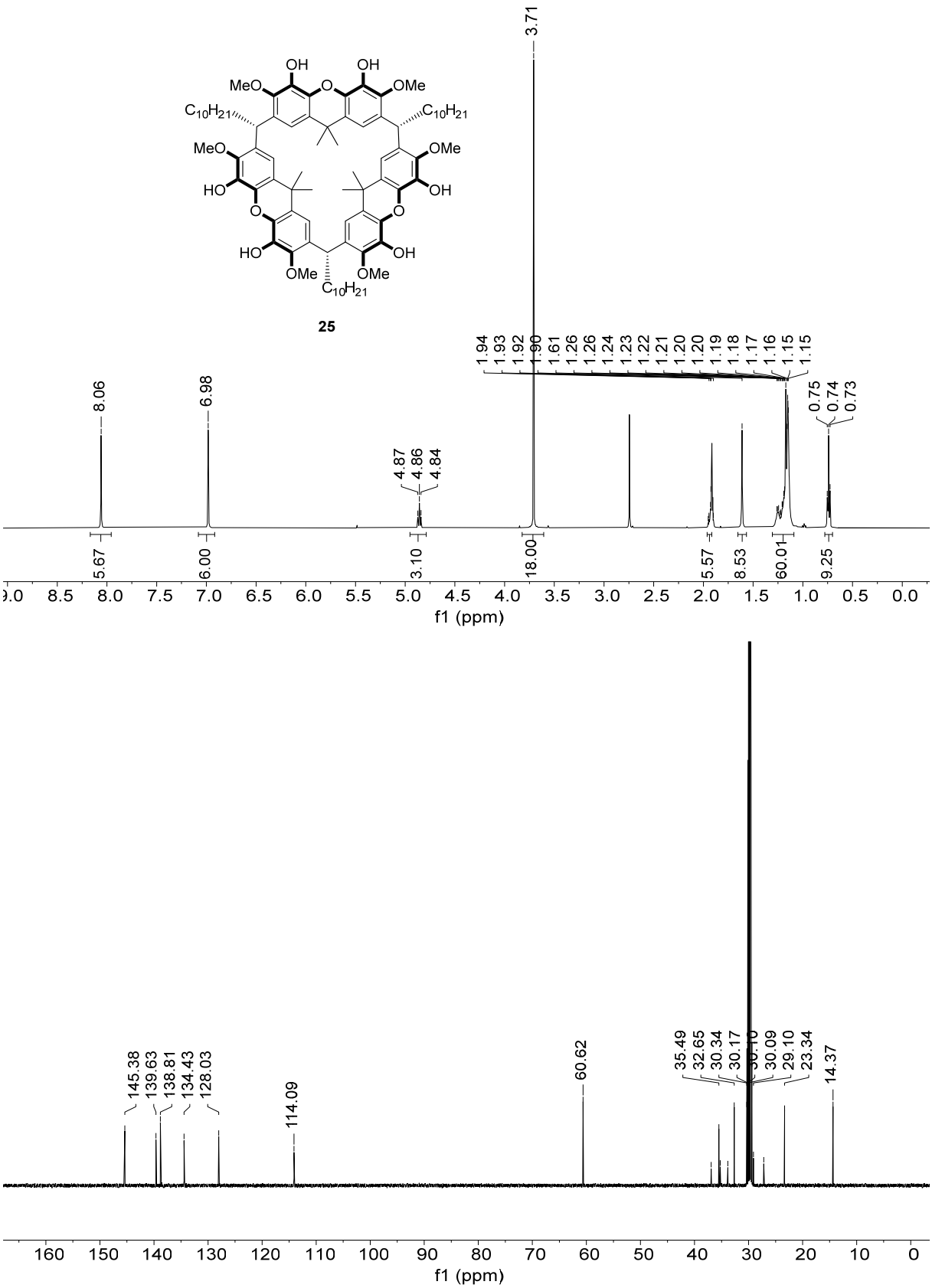




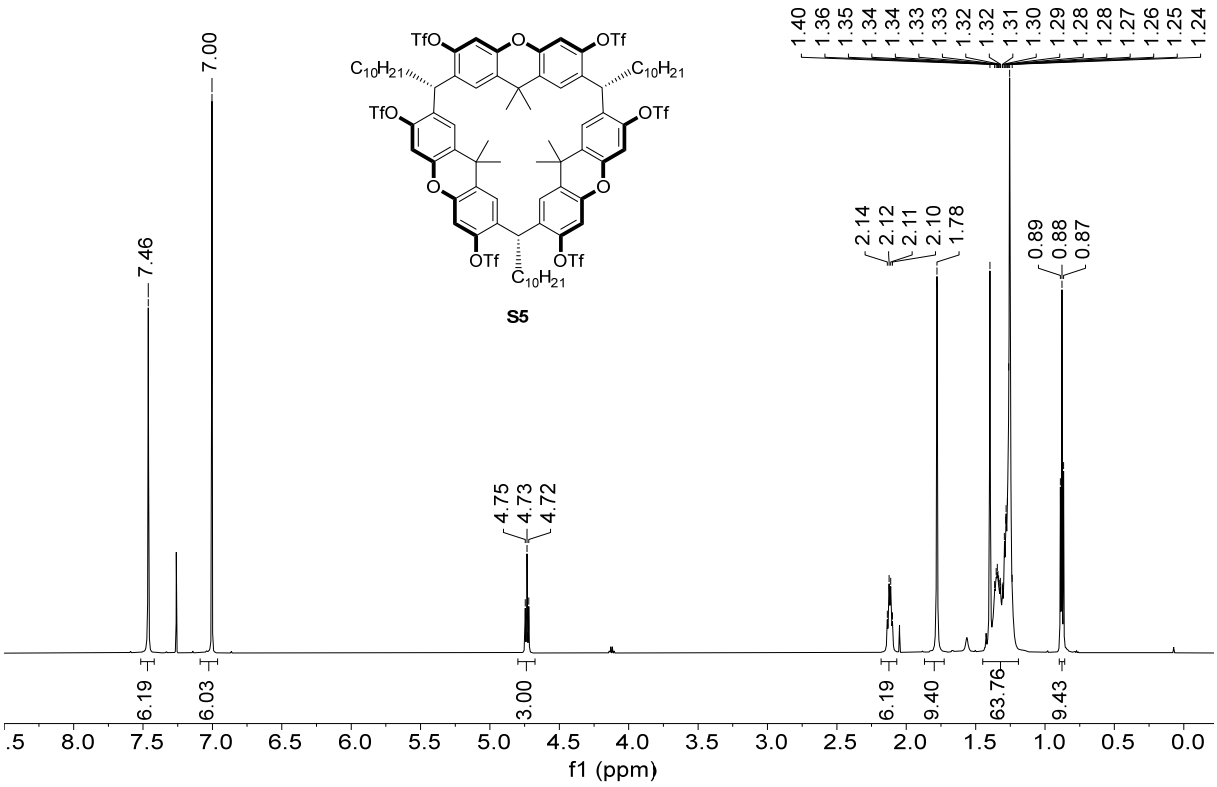
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **S4** in $CDCl_3$ at 298 K.

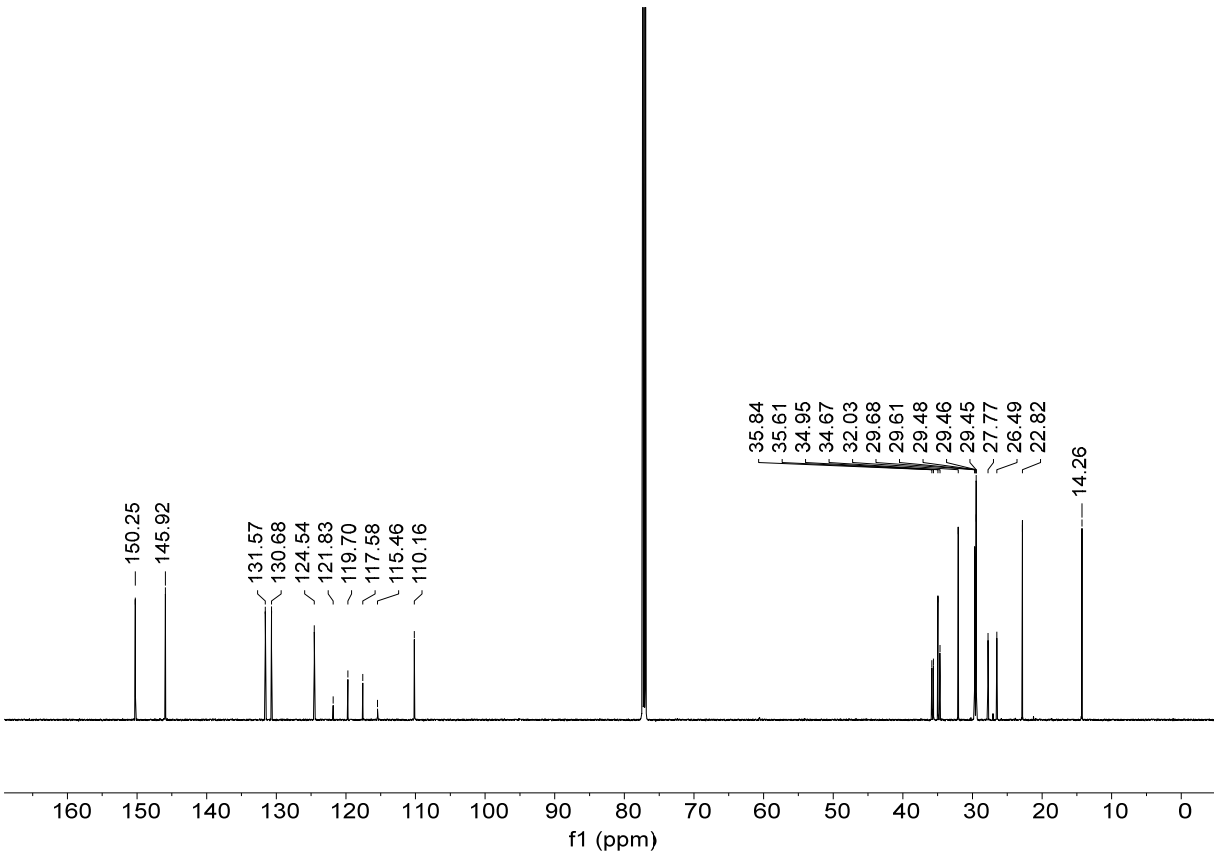


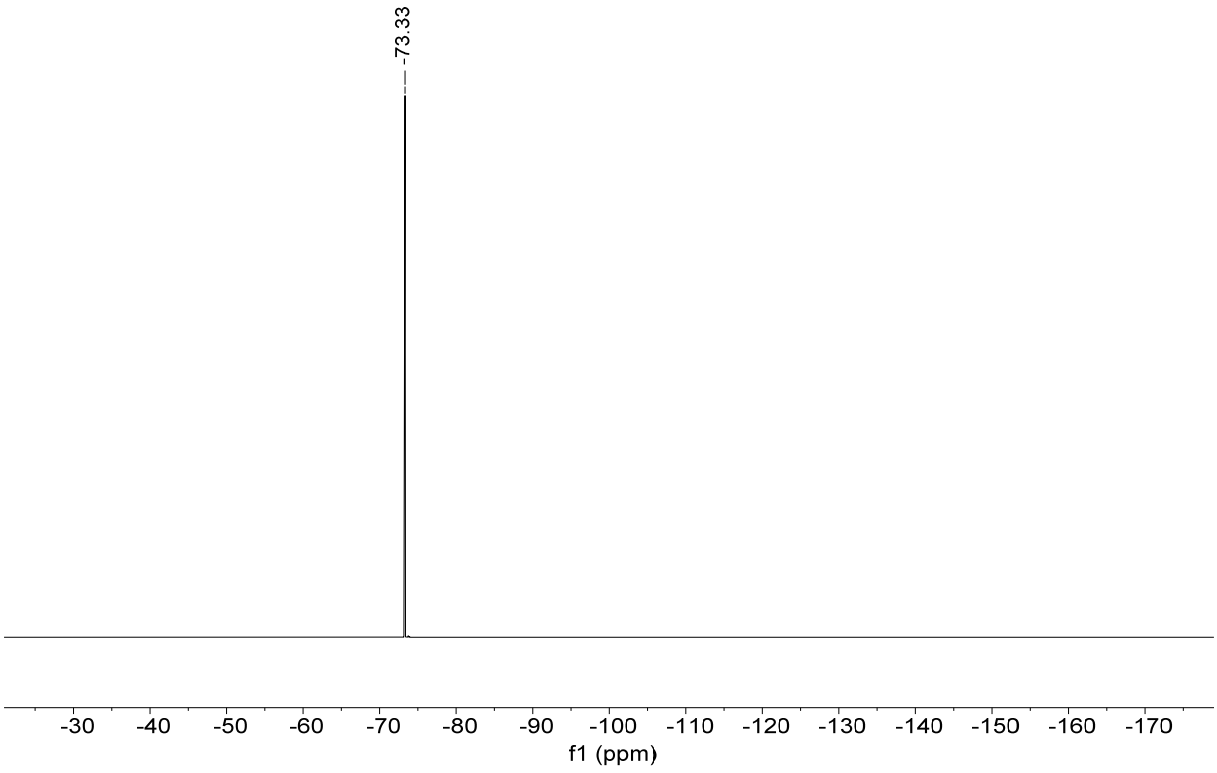
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **25** in acetone-d_6 at 298 K.



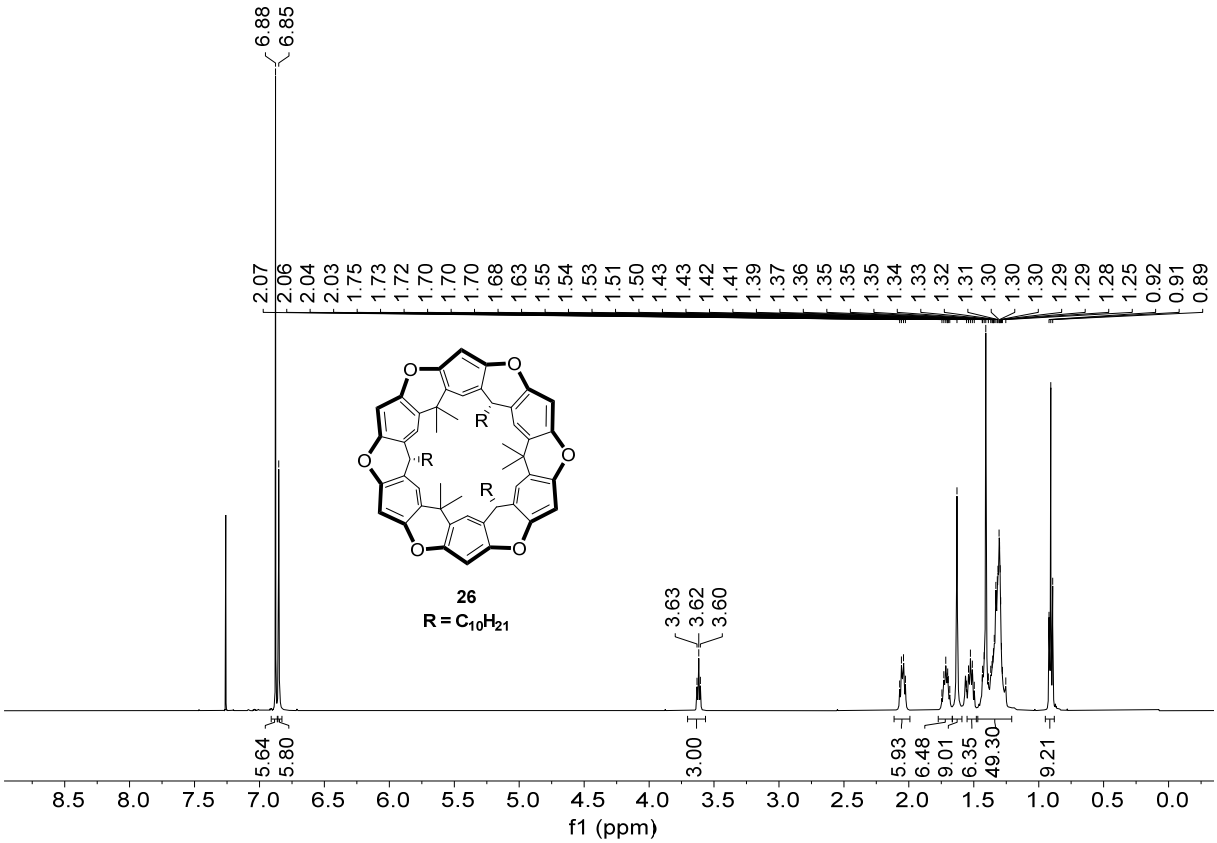
^{1}H-NMR (600 MHz), ^{13}C-NMR (151 MHz) and ^{19}F-NMR (565 MHz) spectrum of **S5** in $CDCl_3$ at 298 K.

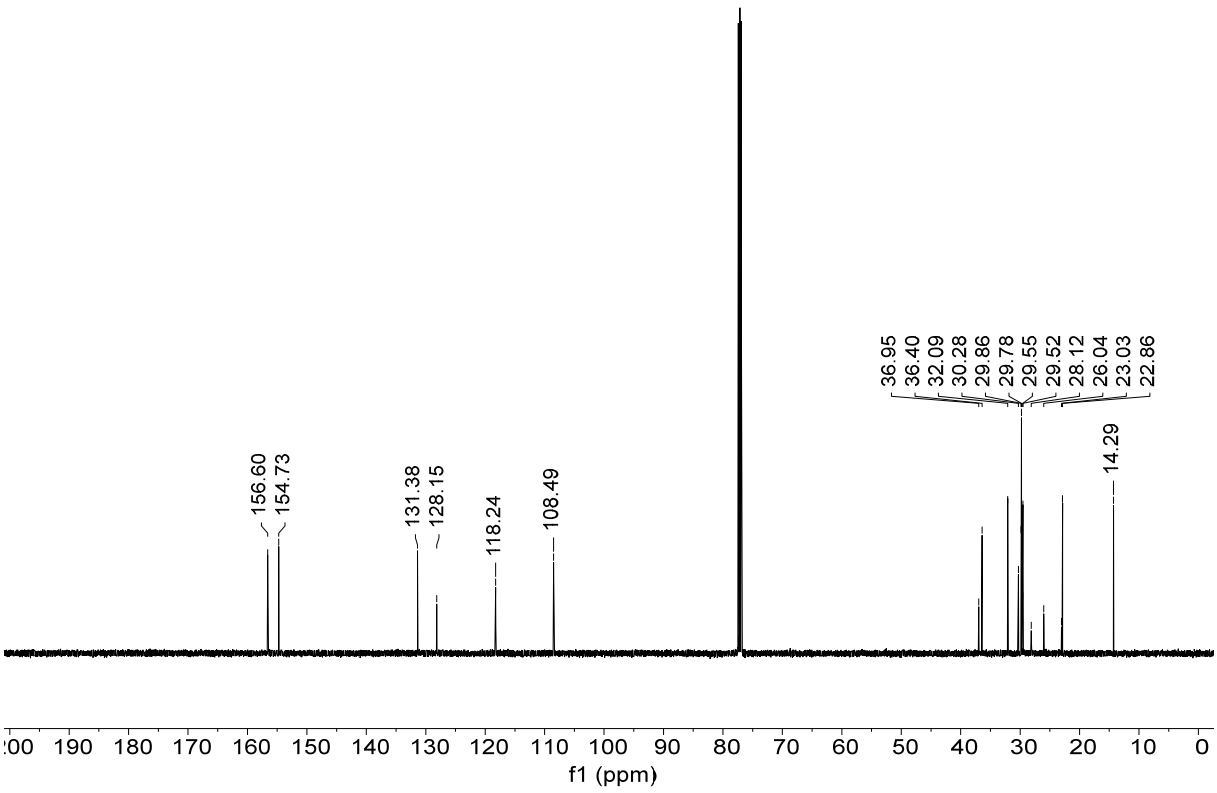




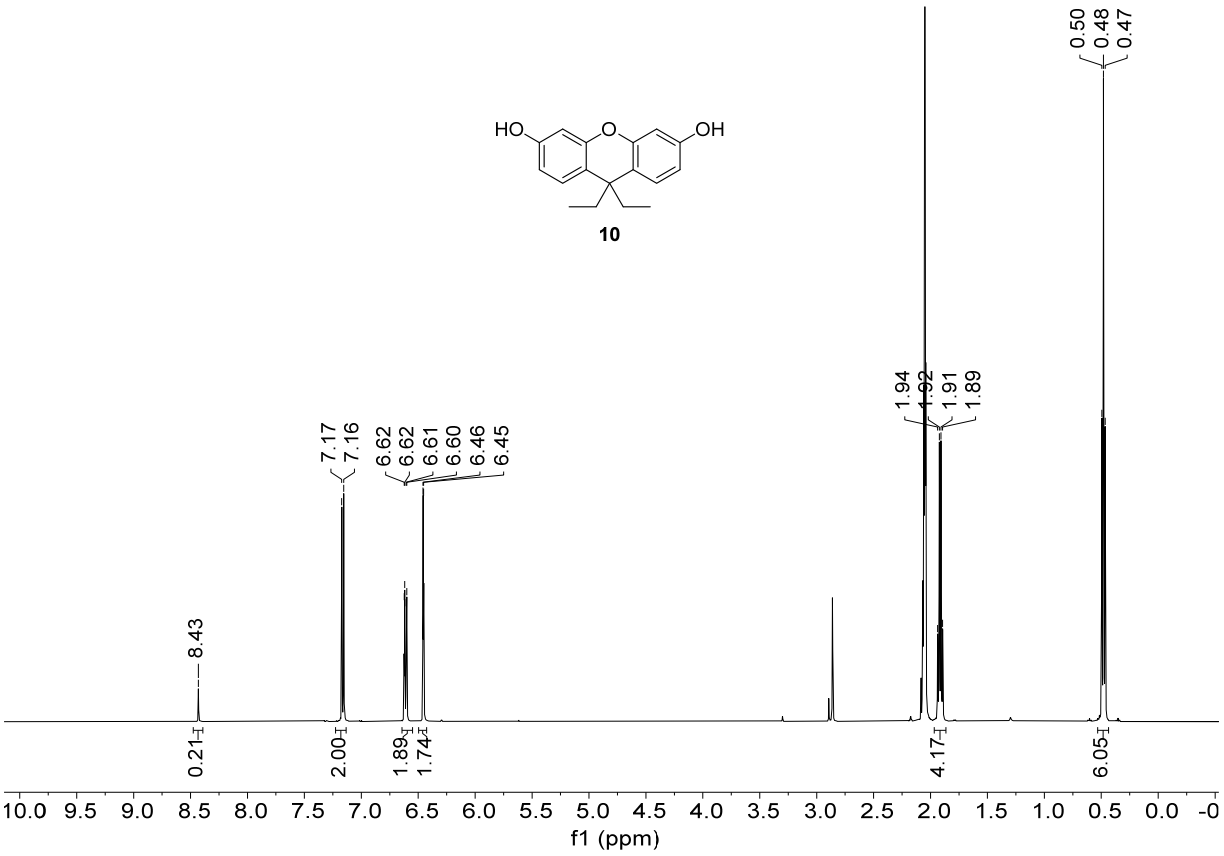

-73.33
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

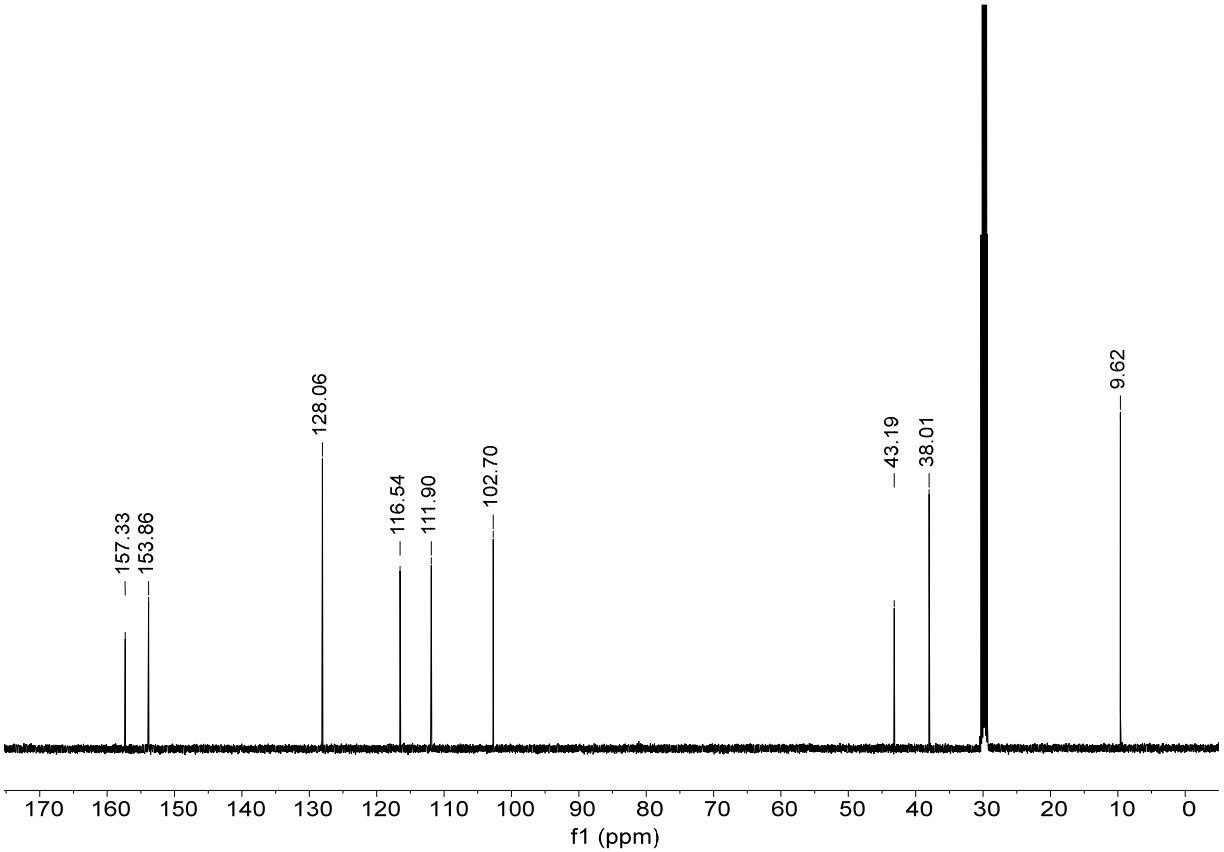
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **26** in $CDCl_3$ at 298 K.



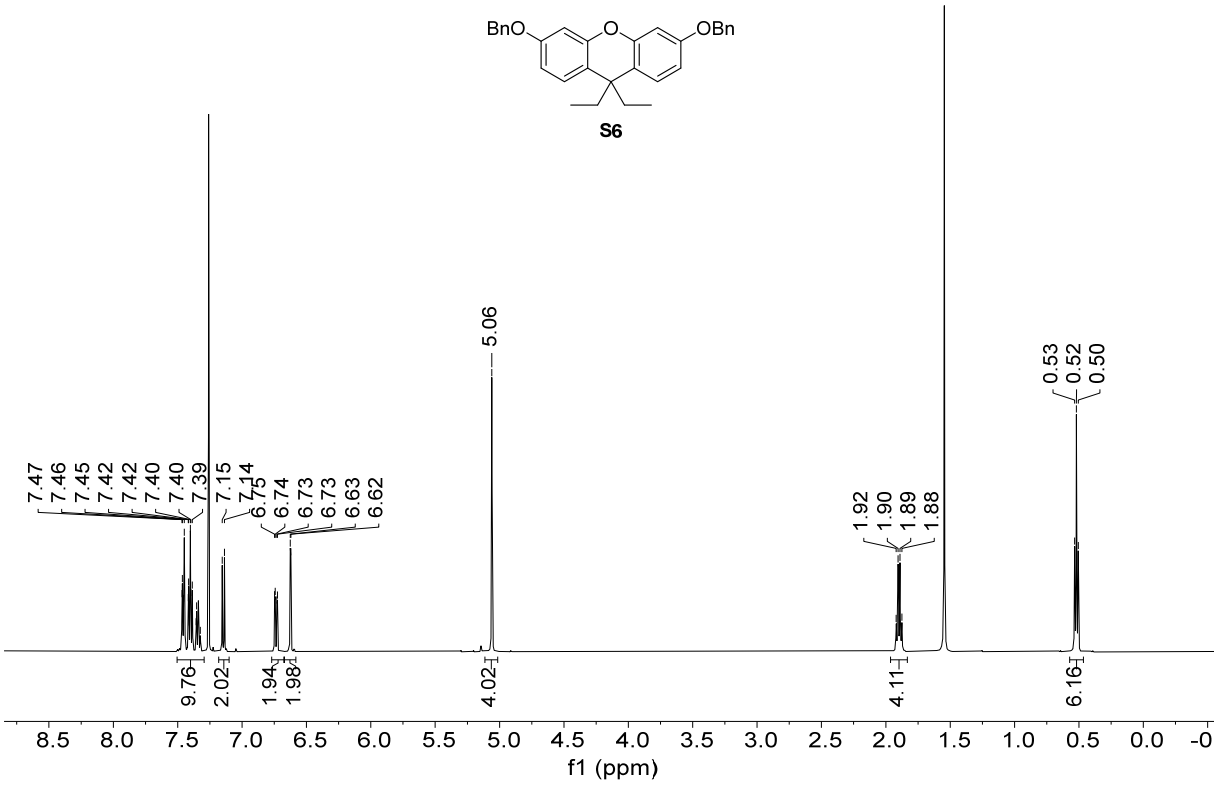


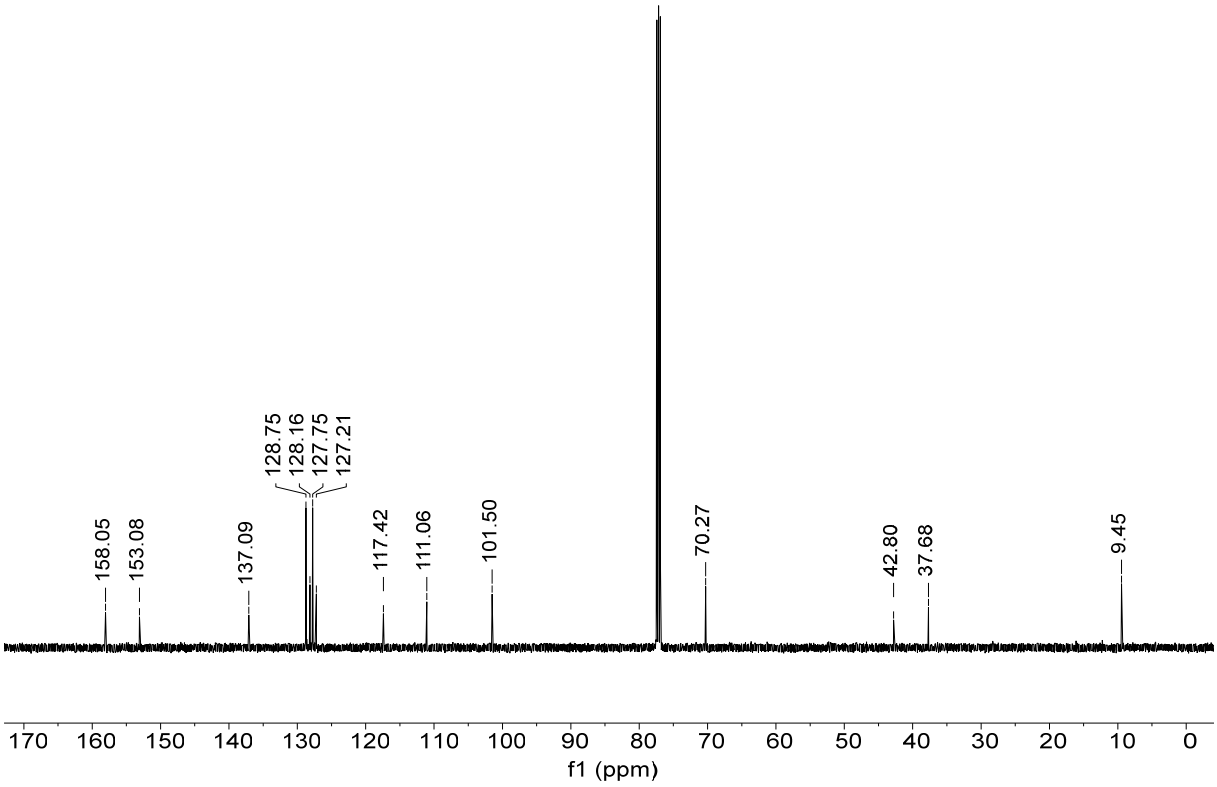
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **10** in acetone-d6 at 298 K.



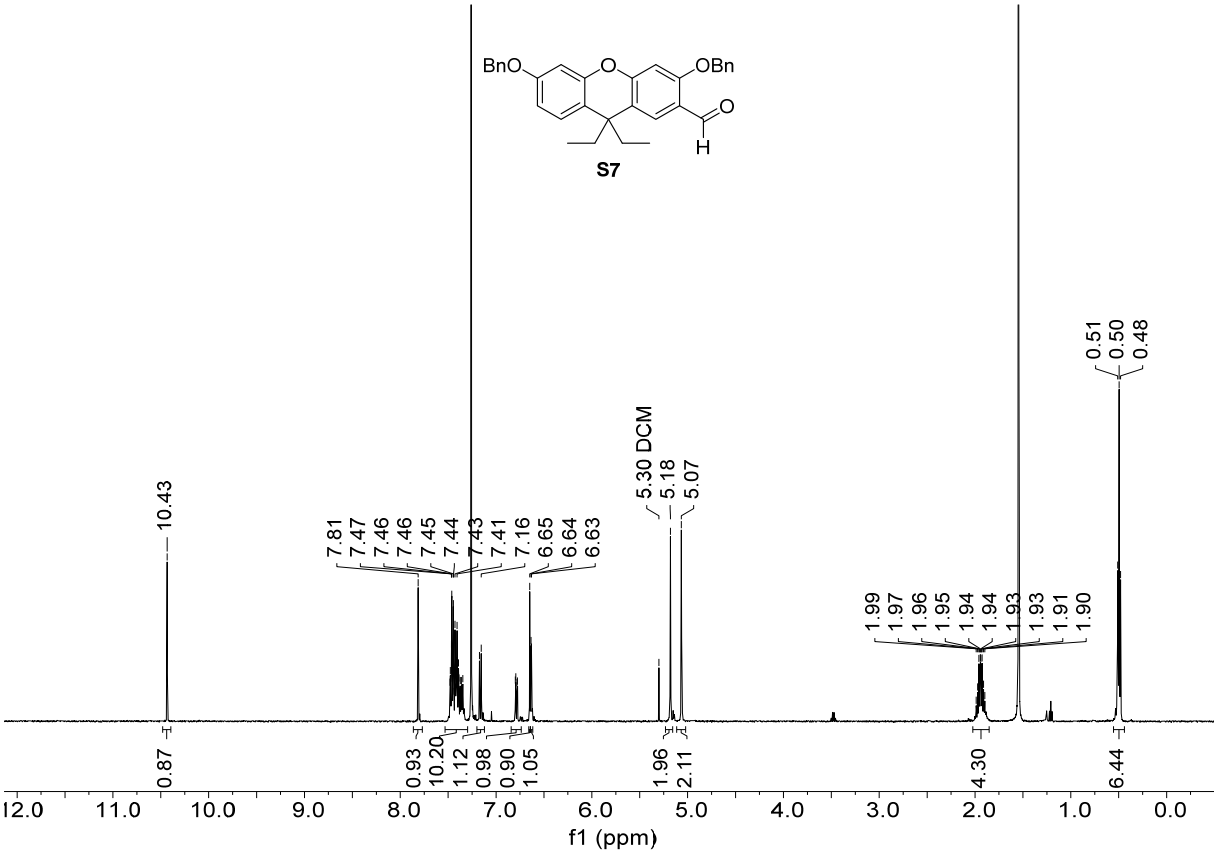


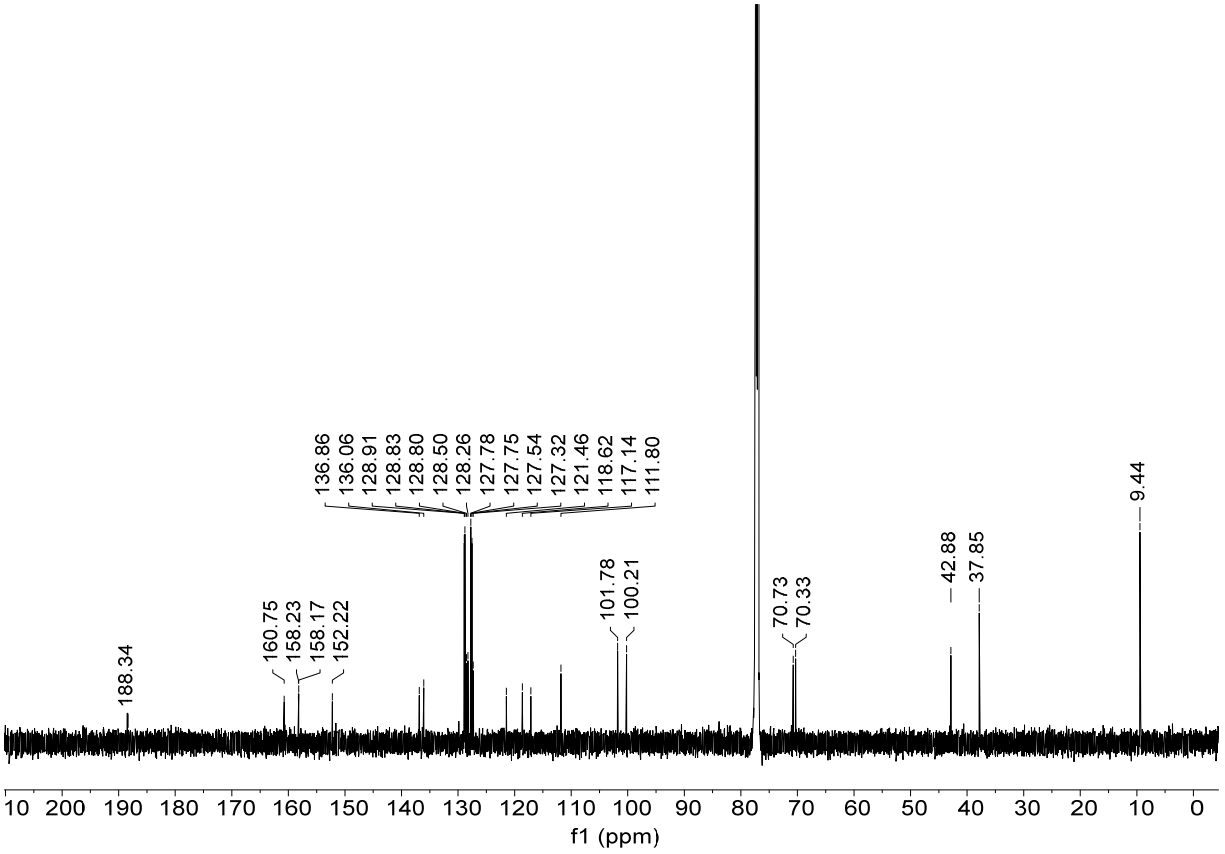
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **S6** in $CDCl_3$ at 298 K.



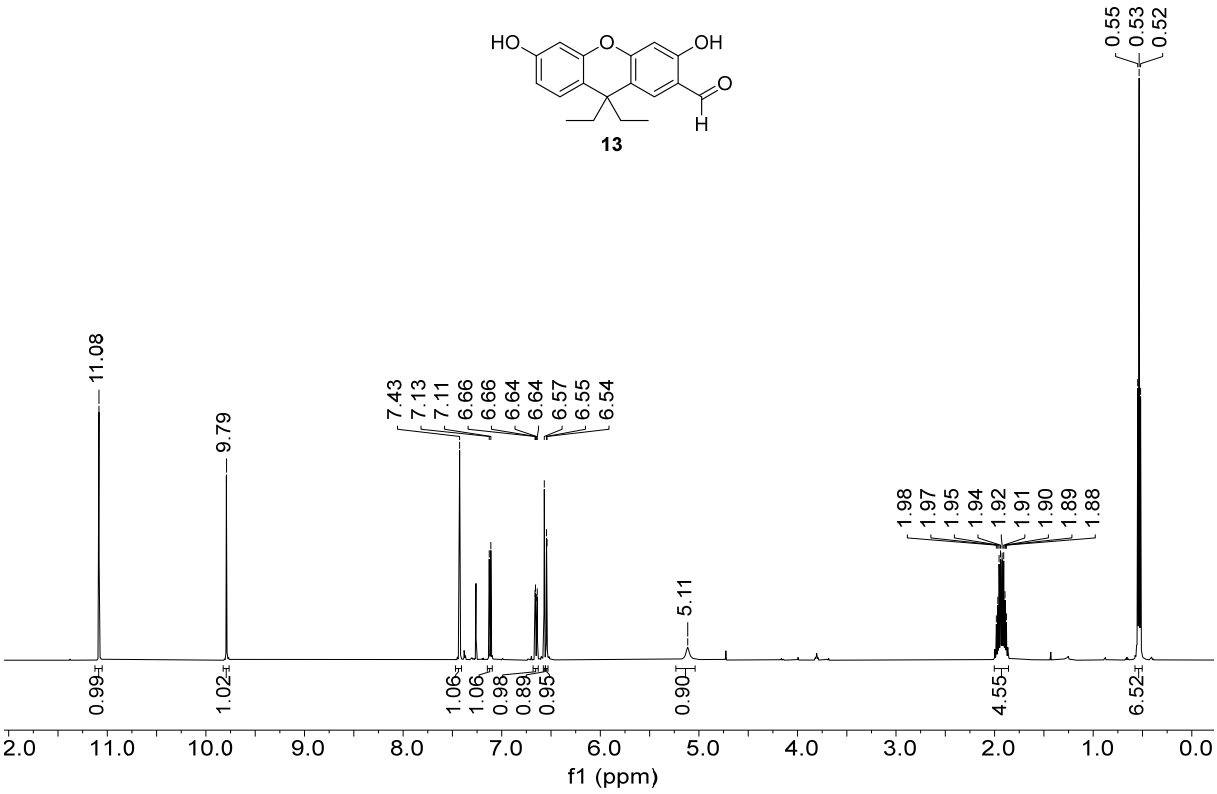


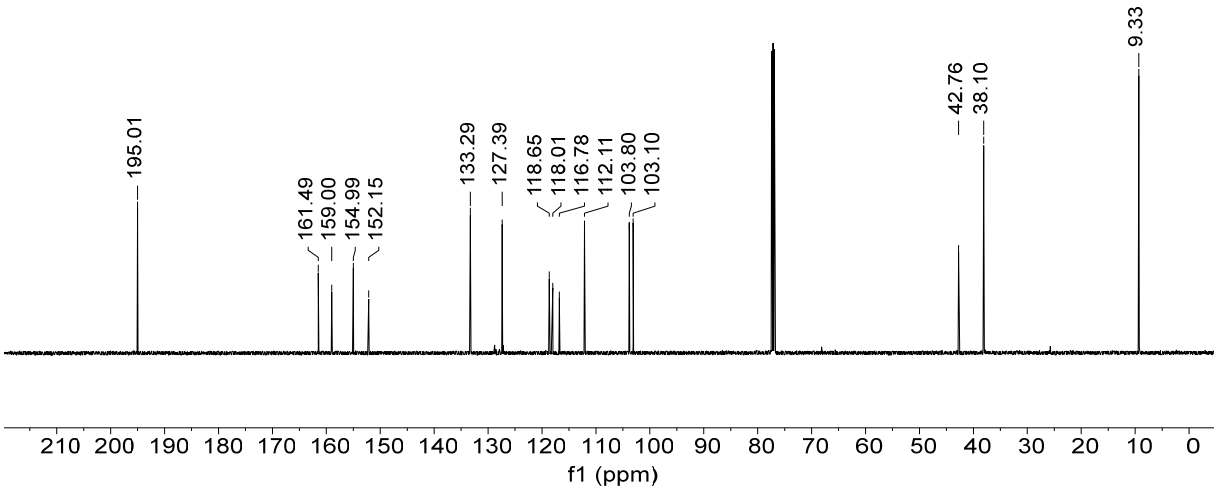
^{1}H-NMR (500 MHz) and ^{13}C-NMR (151 MHz) spectrum of **S7** in $CDCl_3$ at 298 K.



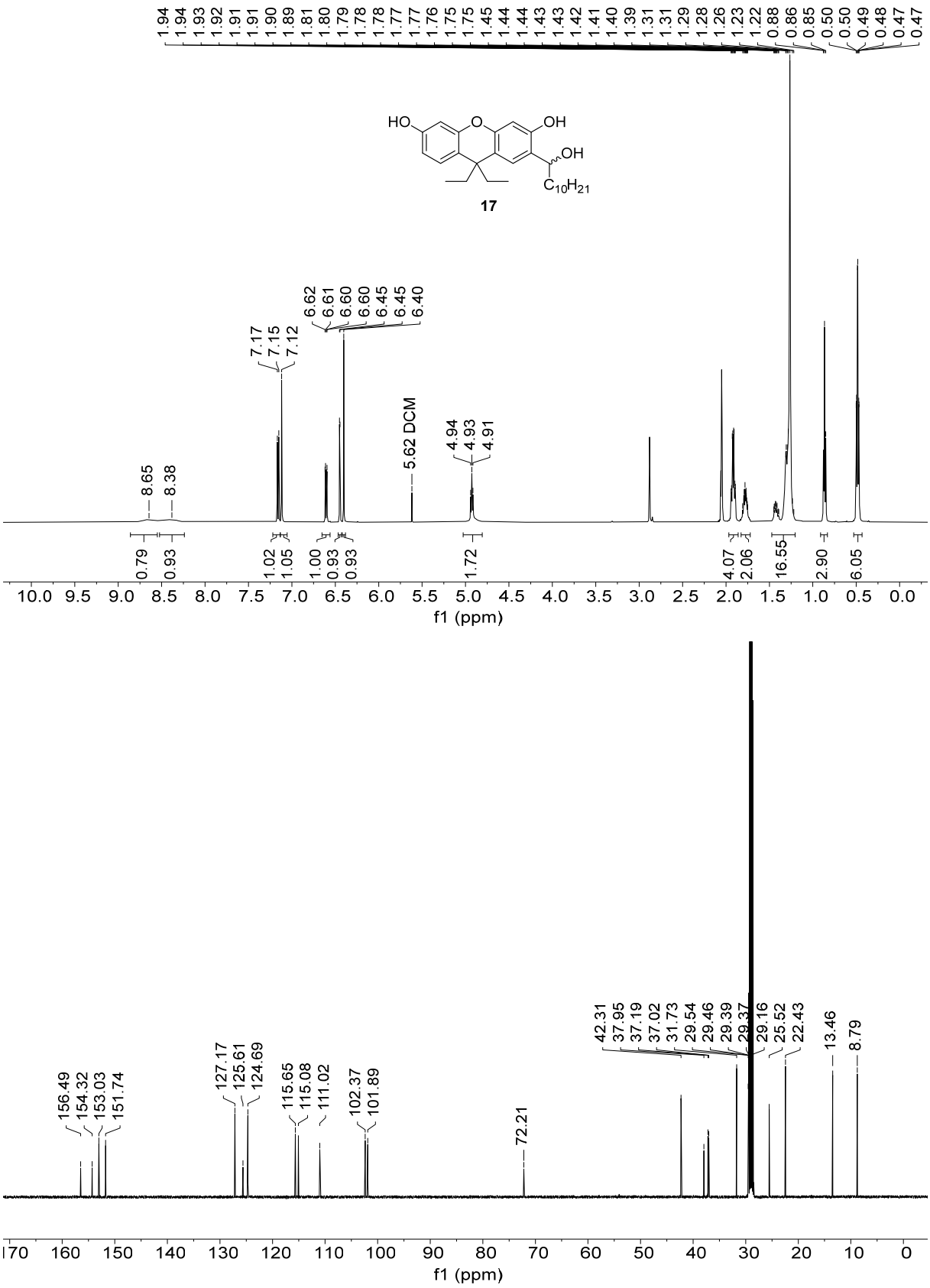


^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **13** in $CDCl_3$ at 298 K.

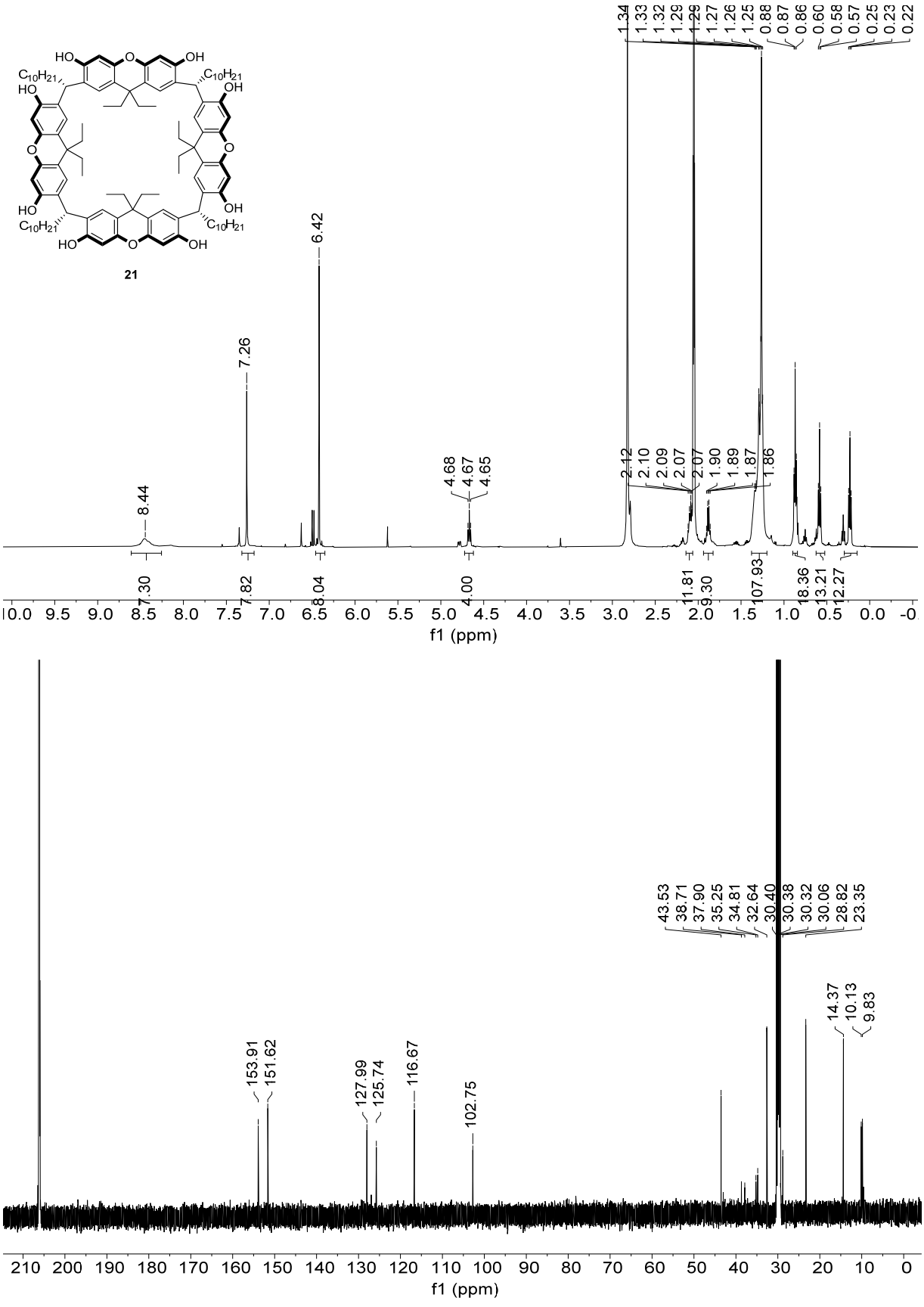




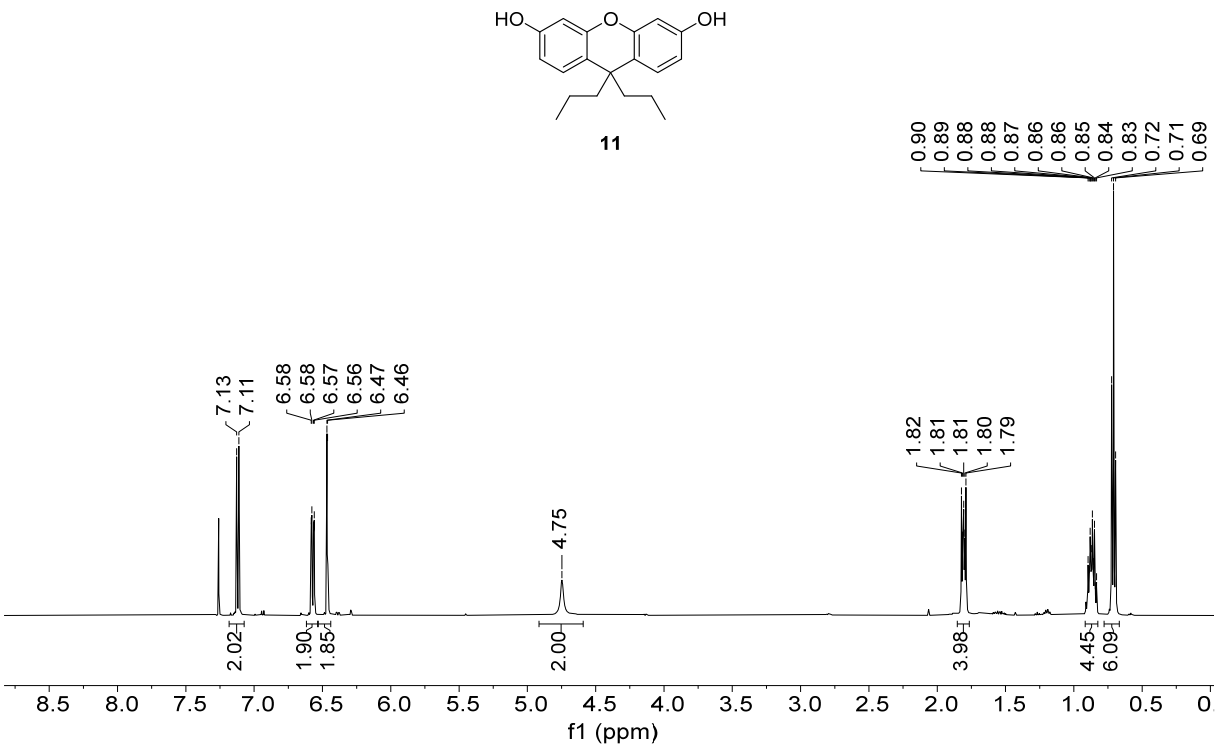
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **17** in acetone-d6 at 298 K.

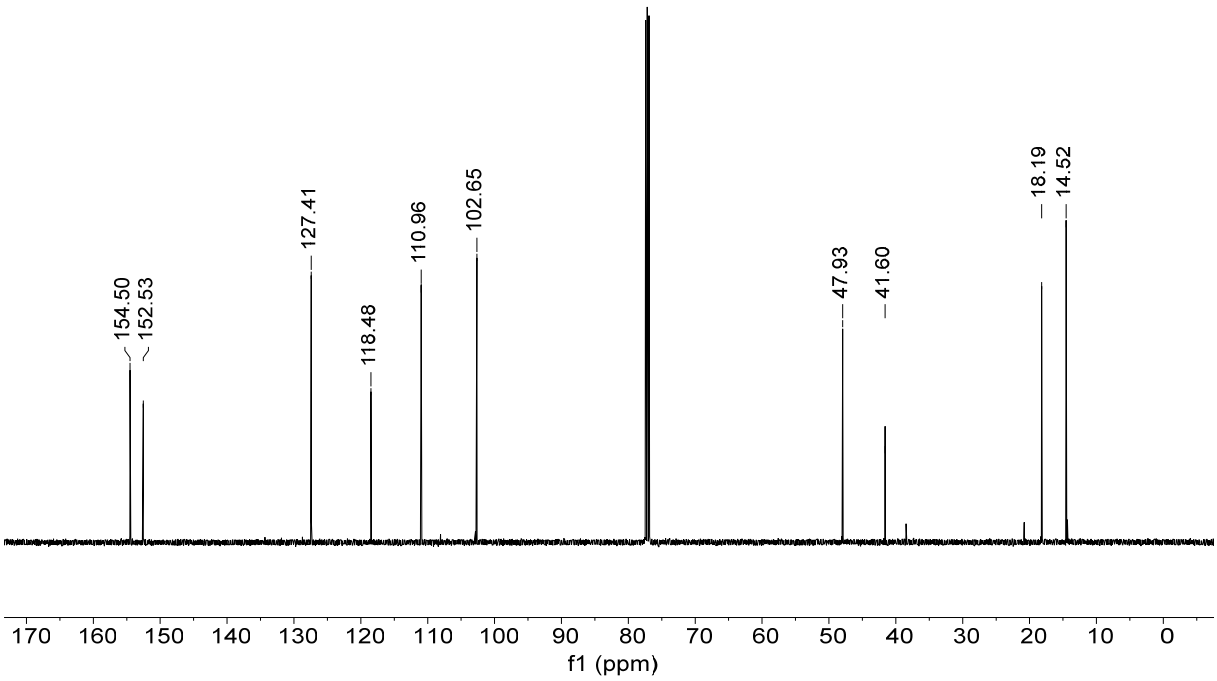


^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **21** in acetone-d6 at 298 K.

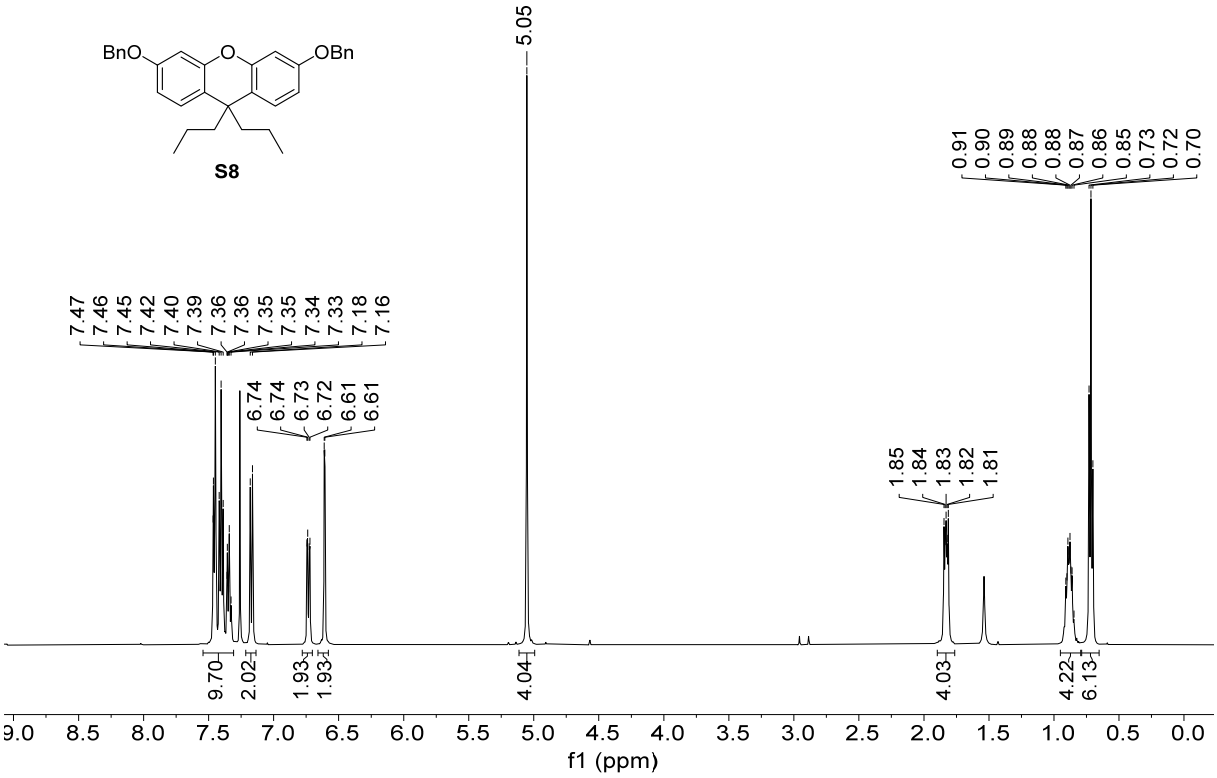


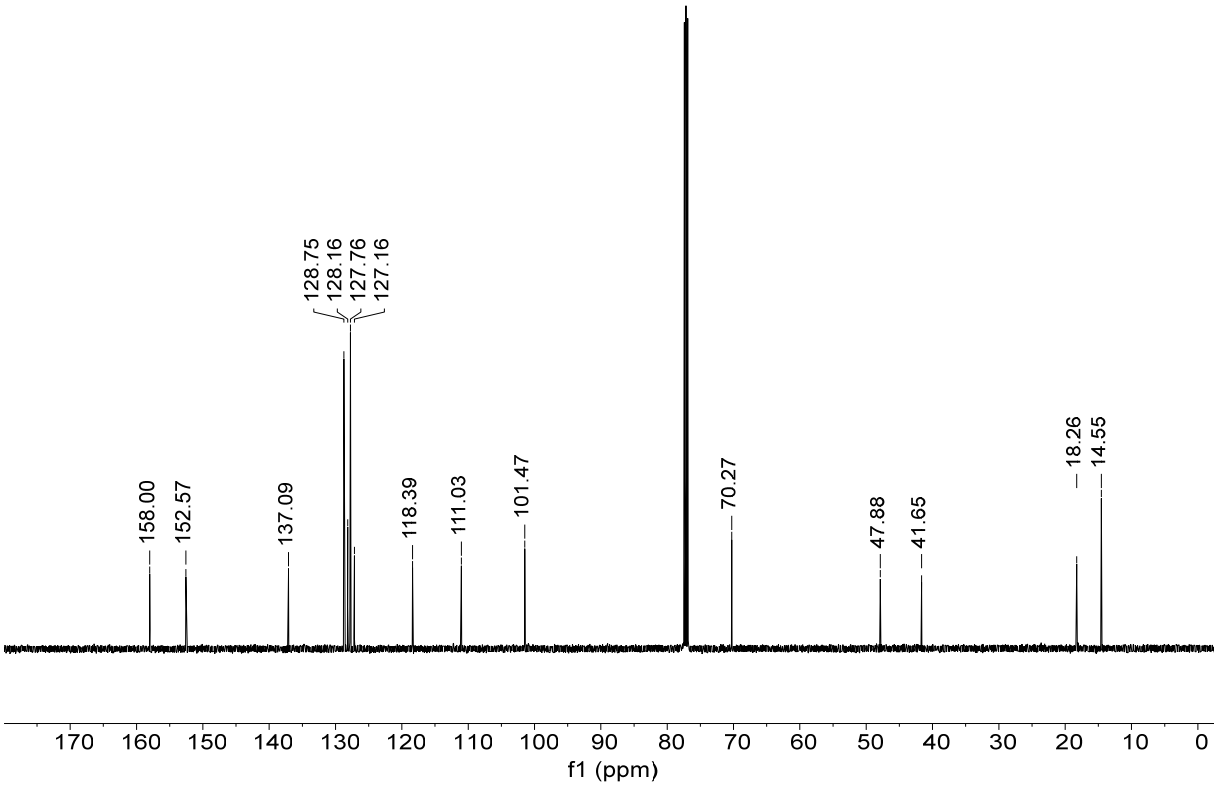
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **11** in $CDCl_3$ at 298 K.



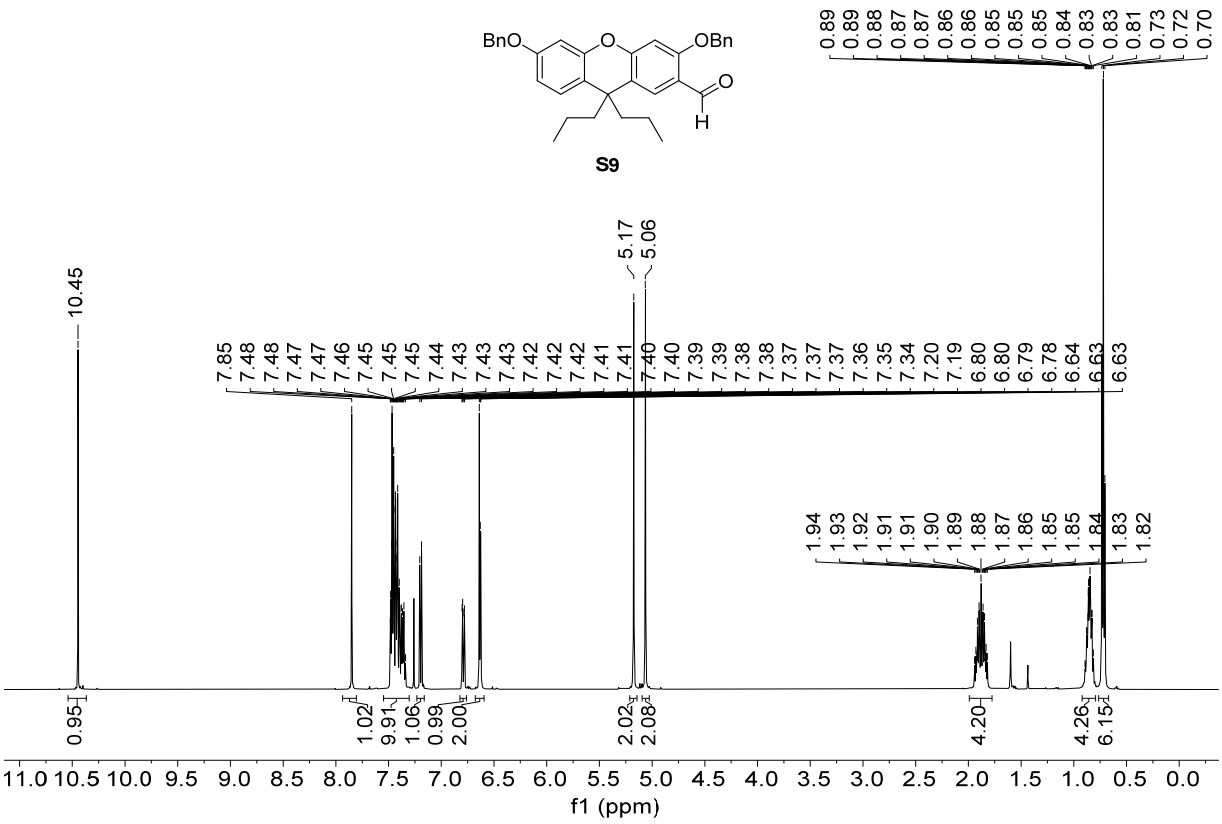


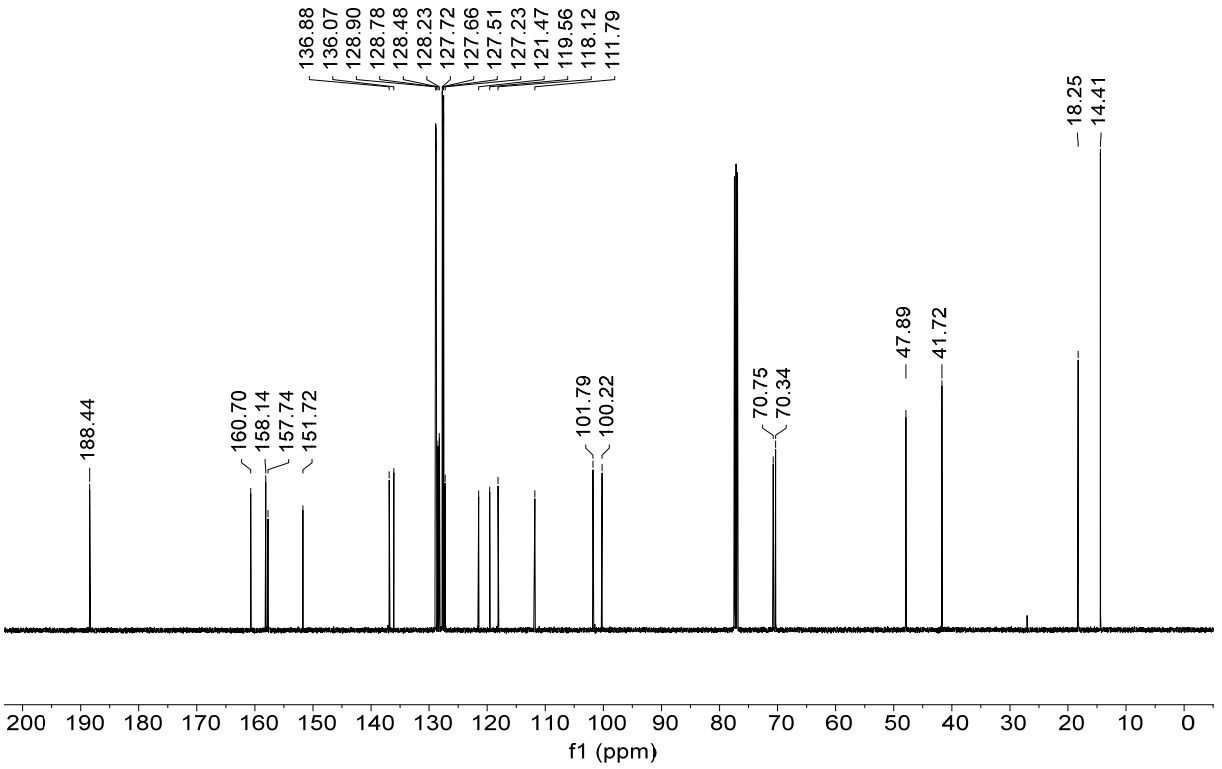
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **S8** in $CDCl_3$ at 298 K.



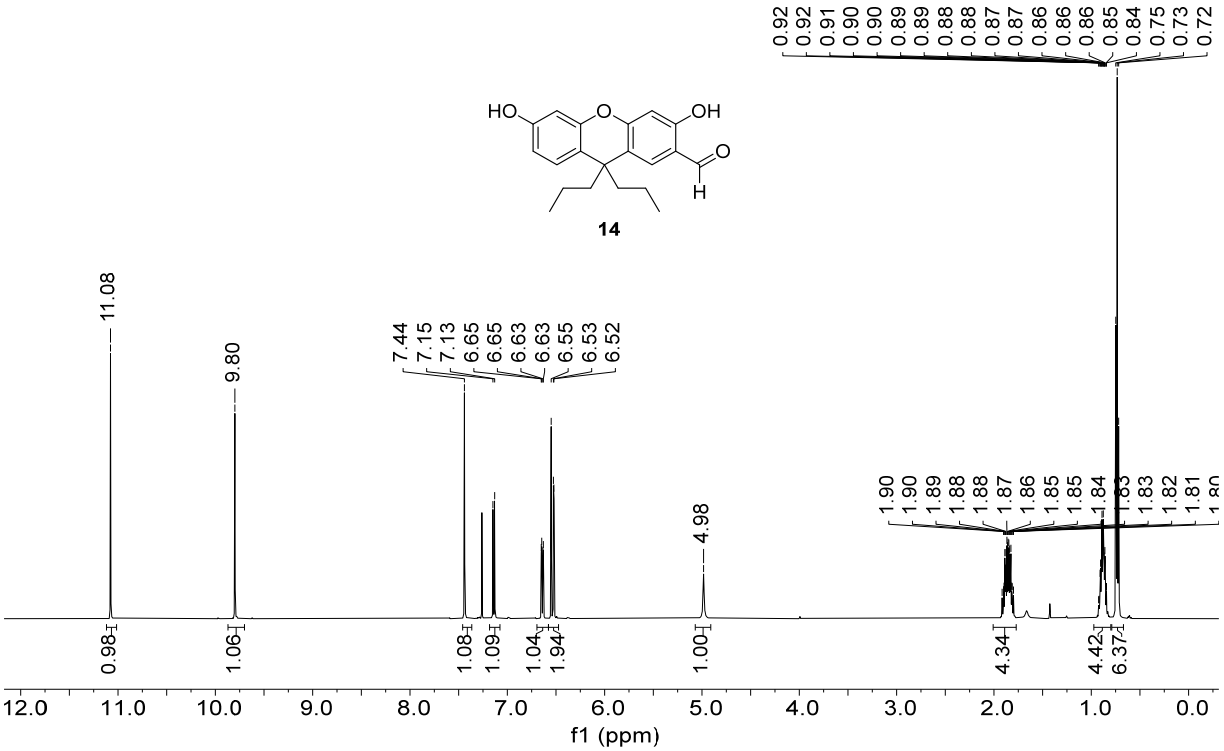


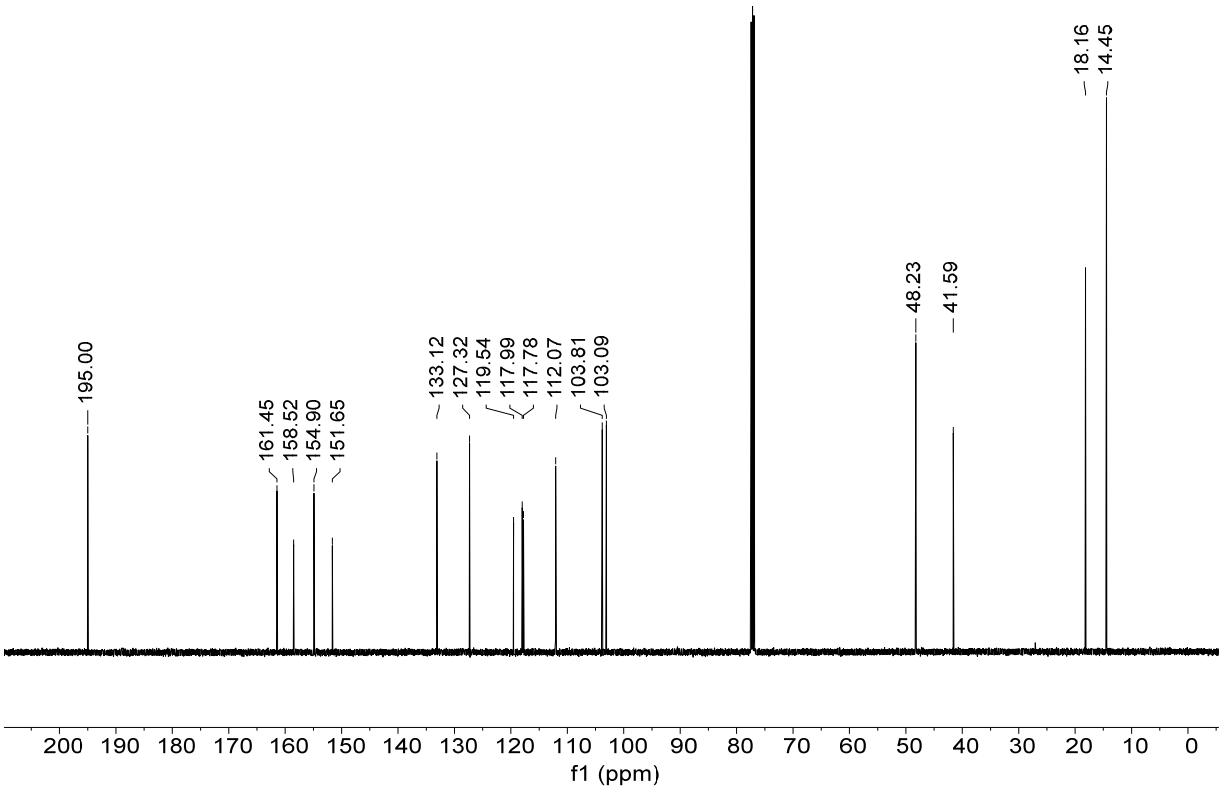
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **S9** in $CDCl_3$ at 298 K.



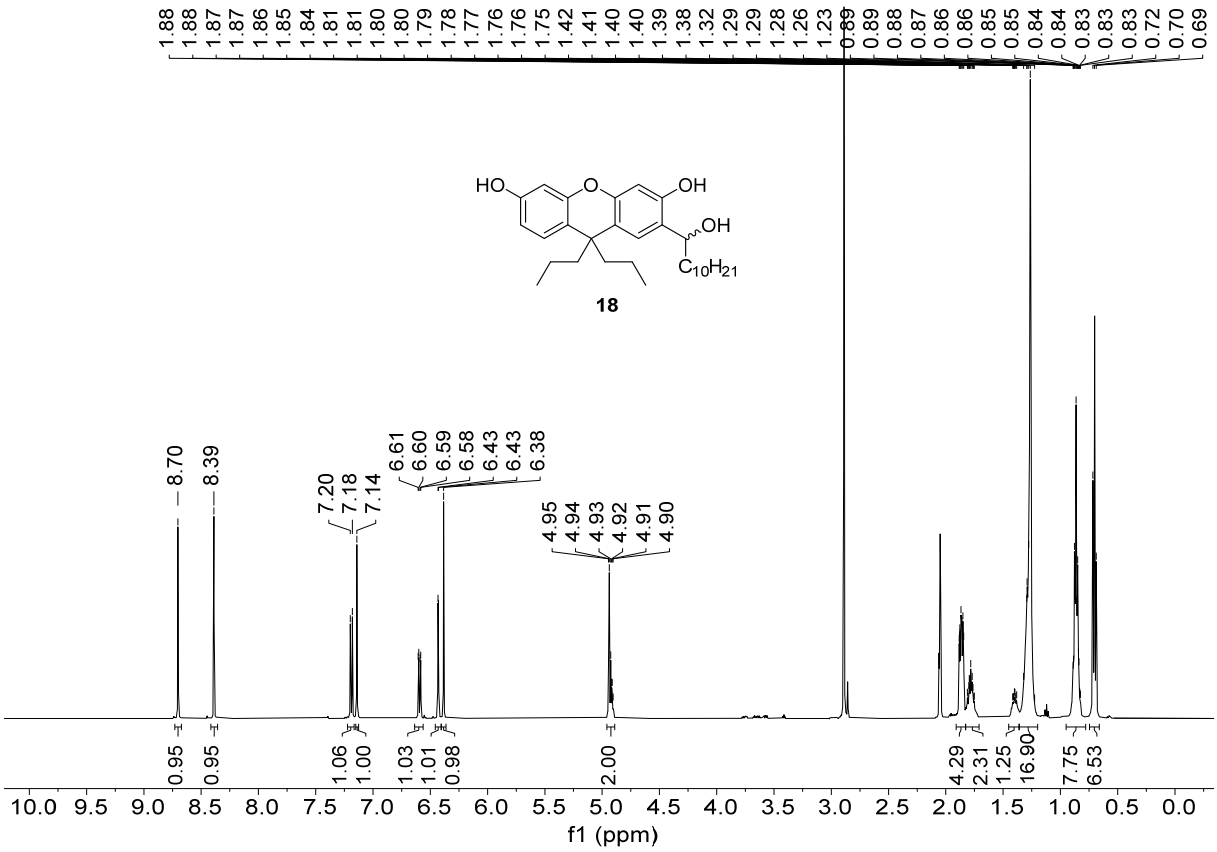


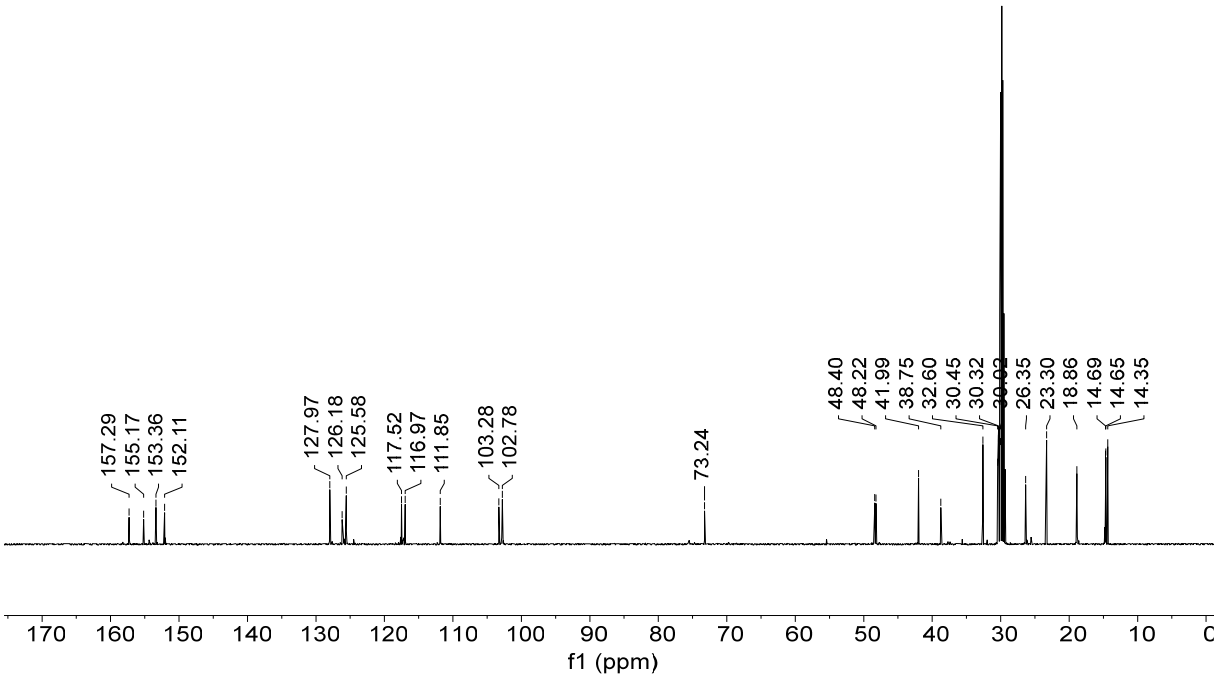
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **14** in $CDCl_3$ at 298 K.



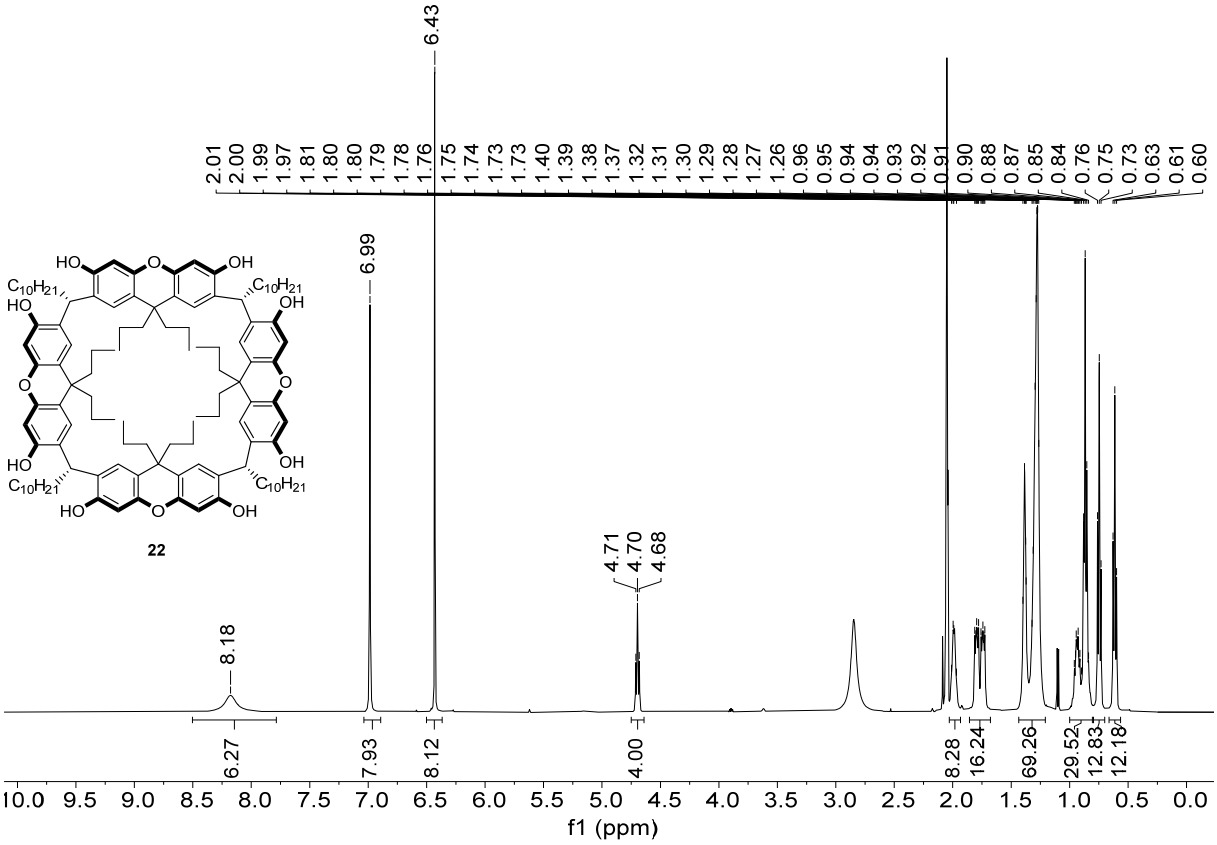


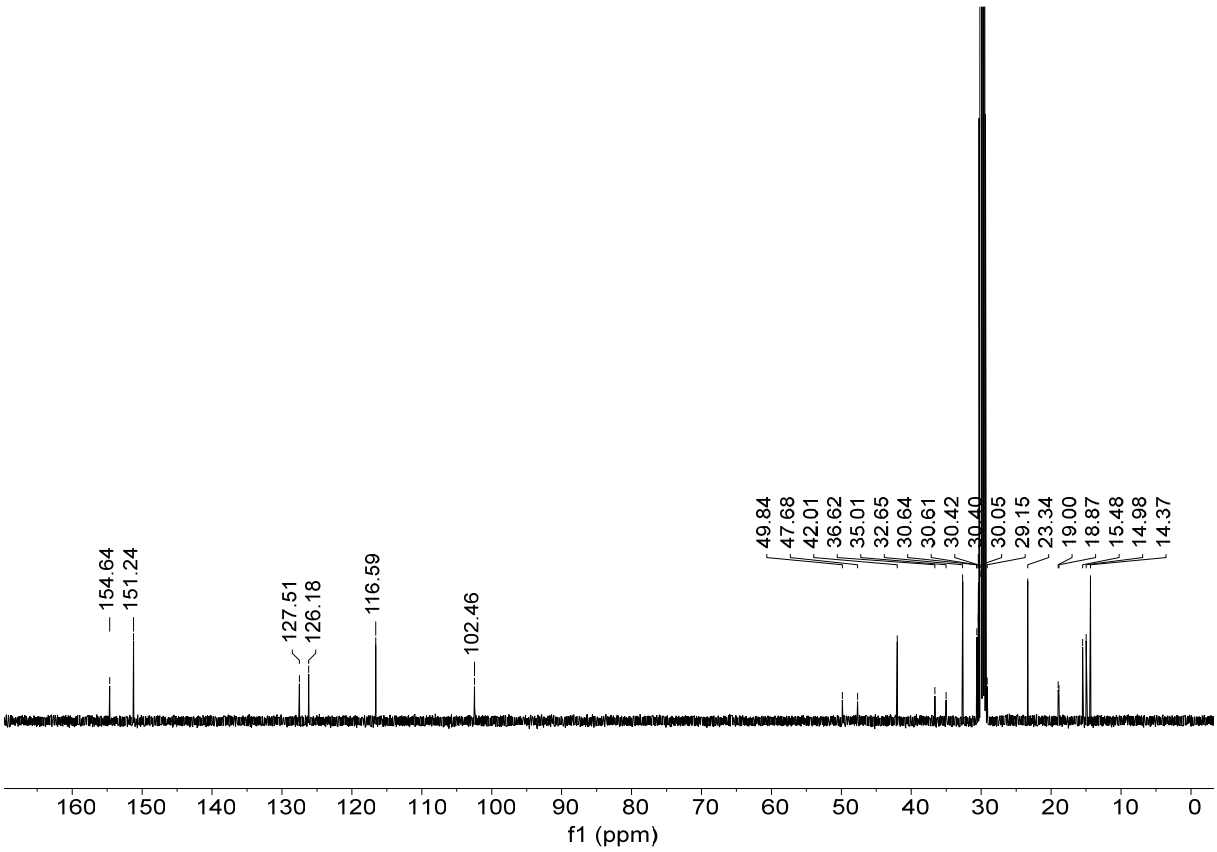
^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **18** in acetone-d6 at 298 K.





^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectrum of **22** in acetone.d6 at 298 K.





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