Supporting Information for:

A Non-Cross-Coupling Approach to Arene-Bridged Macrocycles: Synthesis, Structure and Direct, Regioselective Functionalization of a Cycloparaphenylene Fragment.

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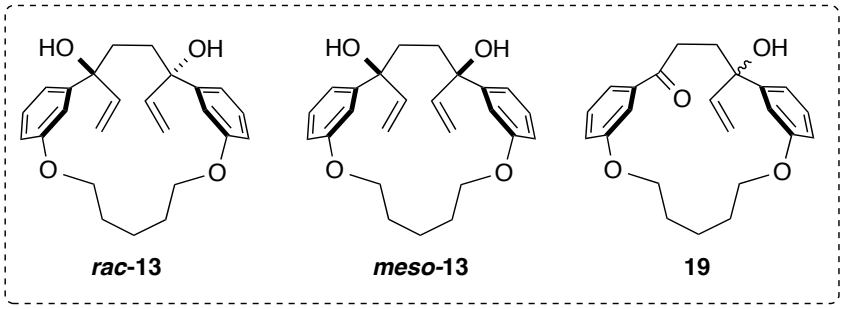


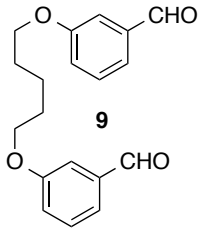
FIGURE SI-1: Structures/compounds not numbered in the manuscript that appear in the SI

General Experimental Conditions

All reactions were run in flame or oven-dried (120 °C) glassware and under a positive pressure of ultra high pure nitrogen or argon gas. All chemicals were used as received from commercial sources, unless otherwise stated. Anhydrous reaction solvents were purified and dried by passing HPLC grade solvents through activated columns of alumina (Glass Contour SDS). All solvents used for chromatographic separations were HPLC grade (hexanes, ethyl acetate, dichloromethane, chloroform, methanol, and acetone). Chromatographic separations were preformed using flash chromatography, as originally reported by Still and co-workers, on silica gel 60 (particle size 43-60 μm), and all chromatography conditions have been reported as height × diameter in centimeters. Reaction progress was monitored by thin layer chromatography (TLC), on glass-backed silica gel plates (pH = 7.0). TLC plates were visualized using a handheld UV lamp (254 nm) and stained using an aqueous ceric

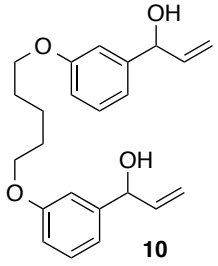
ammonium molybdate (CAM) solution. Plates were dipped, wiped clean, and heated from the back of the plate. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 400 or 600 MHz, calibrated using residual undeuterated solvent as an internal reference ($CHCl_3$, δ 7.27 and 77.2 ppm), reported in parts per million relative to trimethylsilane (TMS, δ 0.00 ppm), and presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets, m = multiplet, p = pentet), coupling constants (*J*, Hz). High-resolution mass spectrometric (HRMS) data were obtained using a quadrupole time-of-flight (Q-TOF) spectrometer and electrospray ionization (ESI).

Experimental procedures and compound characterization data are presented in numerical order



9

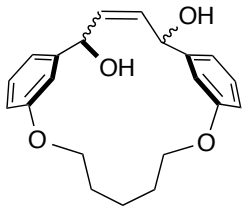
***Dialdehyde* 9:** 1,5-Diiodopentane (3.59 g, 11.1 mmol) was added to a stirred solution of 3-hydroxybenzaldehyde (3.01 g, 24.7 mmol), K_2CO_3 (3.41 g, 24.7 mmol) and tetrabutylammonium iodide (0.456 g, 1.24 mmol) in DMF (25 mL). The slurry was heated at 60 °C for 17 h, at which point water (100 mL) and 1 M HCl (50 mL) were added sequentially. The resulting mixture was extracted with ethyl acetate (3 × 50 mL). The organic extracts were combined and washed with a saturated solution of $NaHCO_3$ (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified via flash chromatography (15 cm × 5.0 cm; chloroform, 1:19 acetone/chloroform) to afford **9** as white solid (2.53 g, 73%): R_f = 0.35 (chloroform); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.98 (s, 2H), 7.48-7.42 (m, 4H), 7.41-7.38 (m, 2H), 7.20-7.16 (m, 2H), 4.06 (t, *J* = 6.4 Hz, 4H), 1.91 (p, *J* = 6.6 Hz, 4H), 1.72-1.66 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.4, 159.7, 137.9, 130.2, 123.7, 122.1, 112.7, 68.1, 29.0, 22.9; HRMS (ESI) calculated for $C_{19}H_{21}O_4$ ($[M+H]^+$) *m*/*z* = 313.1440, found 313.1432.



10

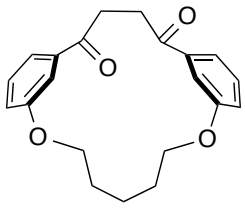
***Allylic alcohol* 10:** Vinylmagnesium chloride (1.6 M in THF, 5.4 mL, 8.7 mmol) was added to a stirred solution of dialdehyde **9** (1.08 g, 3.48 mmol) in THF (30 mL) at room temperature. After 1 h, the reaction mixture was poured into water (50 mL) and further diluted with 1 M HCl (30 mL). The resulting mixture was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4 filtered, and concentrated under

reduced pressure. The residue was purified via flash chromatography (18 cm × 2.5 cm; 3:7 EtOAc/hexanes) to afford compound **10** (1.06 g, 83 %): R_f = 0.26 (3:7 EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 6.98-6.92 (m, 4H), 6.85-6.81 (m, 2H), 6.04 (ddd, *J* = 17.1, 10.3, 6.0 Hz, 2H), 5.36 (dt, *J* = 17.1, 1.4 Hz, 2H), 5.20 (dt, *J* = 10.3, 1.4 Hz, 2H), 5.17 (d, *J* = 5.6 Hz, 2H), 4.00 (t, *J* = 6.4 Hz, 4H), 2.11 (d, *J* = 2.9 Hz, 2H), 1.92-1.81 (m, 4H), 1.72-1.62 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 144.4, 140.3, 129.8, 118.7, 115.4, 114.0, 112.5, 75.4, 67.9, 29.2, 22.9; HRMS (ESI) calculated for $C_{23}H_{29}O_4$ ([M-2H_2O]$^+$) *m*/*z* = 333.1855, found 333.1864.



11

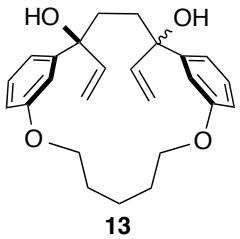
***Streamlined Synthesis of* 11**: Vinylmagnesium chloride (1.6 M in THF, 5.2 mL, 8.3 mmol) was added to a stirred solution of dialdehyde **9** (1.03 g, 3.32 mmol) in THF (30 mL) at room temperature. After 1 h, the reaction mixture was poured into water (50 mL) and further diluted with 1 M HCl (30 mL). The resulting mixture was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved in dichloromethane (220 mL, 15 mM) and Grubbs second-generation catalyst (0.073g, 0.086 mmol) was added. The reaction was heated to 40 °C for 2 h, cooled to room temperature, and concentrated under reduced pressure. The residue was pre-adsorbed onto silica and subjected to flash chromatography (18 × 2.5 cm, 3:2 EtOAc/hexanes) to give allylic diol **11** as a white solid (0.605 g, 54% from **9**): R_f = 0.24 (1:1 EtOAc/hexanes); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.22 (m, 2H), 7.10-7.02 (m, 2H), 6.88-6.76 (m, 4H), 6.06-5.94 (m, 2H), 5.34-5.25 (m, 2H), 4.10-3.95 (m, 4H), 2.00 (s, 2H), 1.89-1.76 (m, 4H), 1.74-1.64 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 144.53, 132.8, 129.9, 119.2, 114.7, 113.4, 74.0, 68.2, 28.7, 22.0; HRMS (ESI) calculated for $C_{22}H_{23}O_2$ ([M-(2H_2O)+H]$^+$) *m*/*z* = 319.1698, found 319.1703



12

***1,4-Dione* 12:** A hydrogen filled balloon was placed over a stirred slurry of 10% wt. Pd/C (0.063g) and allylic diol **11** (0.554 g, 1.64 mmol) in 1:1 MeOH/EtOAc (40 mL). After 2 h, the reaction was filtered through a short pad of Celite (4 cm) and the filtrate concentrated under reduced pressure. The solid white residue was subjected to flash chromatography (15 × 2.5 cm, 3:2 EtOAc/hexanes) to give 1,4-diol **17** as colorless solid (0.432 g, 78%): R_f = 0.42 (3:2 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.31-7.15 (m, 4H), 6.91-6.76 (m, 10H), 6.71-6.68 (m, 2H), 4.76 (t, *J* = 5.4 Hz, 2H), 4.68-4.54 (m, 2H), 4.20-3.94 (m, 8H), 3.02 (s, 2H), 1.90 (s, 2H), 1.86-1.78 (m, 12H), 1.76-1.64 (m, 6H), 1.55-1.44 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 159.1, 145.9, 145.4, 129.78, 129.74, 119.8, 118.5, 115.34, 115.24, 112.1, 111.6, 74.63, 73.49, 67.71, 67.62, 34.0, 33.9, 27.9, 27.6, 21.7, 21.4; HRMS (ESI) calculated for $C_{21}H_{25}O_3$ ([M-(H_2O)+H]$^+$) *m*/*z* = 325.1804, found 325.1816. Dess–Martin periodinane (1.58 g, 3.73 mmol) and $NaHCO_3$ (0.312 g, 3.75 mmol) were added to a stirred solution of 1,4-diol **17** (0.420 g, 1.24 mmol) in dichloromethane (15 mL) at room temperature. After 1 h, a 10% solution of $Na_2S_2O_3$ (40 mL) was added and the reaction was stirred for 10 min. The resulting mixture was extracted with dichlormethane (3 × 15 mL). The organic extracts were combined and washed with a saturated solution of $NaHCO_3$ (30 mL) and brine (40 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give 1,4-diketone **12** as a beige solid (0.384 g, 92%). R_f = 0.27 (1:4 EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (ddd, *J* = 7.7, 1.7, 1.0 Hz, 2H), 7.39-7.34 (m, 2H), 7.30 (dd, *J* = 2.5, 1.6 Hz, 2H), 7.07 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 2H), 4.11 (t, *J* = 6.2 Hz, 4H), 3.21 (s, 4H), 1.84 (p, *J* = 6.3 Hz, 4H), 1.75-1.66 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 159.1, 137.7, 130.3, 120.7, 119.6, 115.6, 68.0, 36.1, 27.9, 22.0; HRMS (ESI) calculated for $C_{21}H_{23}O_4$ ([M+H]$^+$) *m*/*z* = 339.1596, found 339.1598.

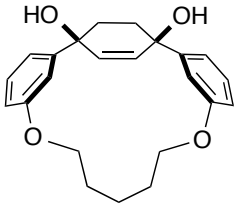


13

***Allylic alcohols* 13:** 1,4-diketone **12** (0.171 g, 0.488 mmol), as a solution in THF (6 mL), was added to a stirred 60 °C solution vinyl magnesium chloride (1.6 M in THF, 1.0 mL, 1.6 mmol). After 30 minutes, the reaction mixture was poured into water (30 mL) and further diluted with 1 M HCl (15 mL). The resulting mixture was extracted with dichloromethane (3 × 15 mL). The organic extracts were combined and washed with a saturated solution of $NaHCO_3$ (30 mL) and brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The solid residue was purified by flash chromatography (18 × 1.3 cm, 1:4 EtOAc/hexanes) to give hydroxyketone **18** (0.060 g, 34%) and allylic alcohols **13** (0.098 g, 51%; 77% based on recovery of **18**) as a mixture of diastereomers (dr = 5:1). A single column fraction produced pure sample of the major (slower moving) diastereomer, *syn*-(or *meso*)**13**: R_f = 0.20 (1:4 EtOAc/hexanes), 0.59 (1:1 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.12 (m, 2H), 7.03 (dd, *J* = 2.6, 1.7 Hz, 2H), 6.85-6.79 (m, 2H), 6.74 (ddd, *J* = 8.1, 2.6, 0.9 Hz, 2H), 6.18 (dd, *J* = 17.2, 10.7 Hz, 2H), 5.34 (dd, *J* = 17.2, 1.2 Hz, 2H), 5.18 (dd, *J* = 10.7, 1.2 Hz, 2H), 4.10 (dt, *J* = 10.5, 6.2 Hz, 2H), 3.97 (dt, *J* = 10.6, 6.4 Hz, 2H), 3.72 (s, 2H), 1.81-1.71 (m, 8H), 1.70-1.56 (m, 2H); ^{13}C NMR (101 MHz,

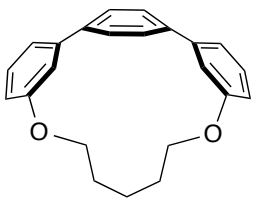
$CDCl_3$) δ 158.9, 147.5, 143.3, 129.3, 118.4, 114.3, 113.6, 112.3, 76.8, 67.6, 37.1, 27.8, 21.4; HRMS (ESI) calculated for $C_{25}H_{27}O_2$ ([M-(2H_2O)+H]$^+$) *m*/*z* = 359.2011, found 359.2023.

***Anti*-(or *rac*)13**. For isolation of this compound, see the experimental procedure below (compound **14**): R_f = 0.22 (1:4 EtOAc/hexanes), 0.59 (1:1 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.17-7.10 (m, 2H), 6.77 (ddd, *J* = 8.1, 2.5, 0.9 Hz, 2H), 6.58-6.52 (m, 2H), 6.08 (dd, *J* = 17.3, 10.6 Hz, 2H), 5.16 (dd, *J* = 17.2, 1.0 Hz, 2H), 5.02 (dd, *J* = 10.6, 1.0 Hz, 2H), 4.07-4.01 (m, 2H), 3.95 (td, *J* = 9.1, 4.0 Hz, 2H), 1.99-1.73 (m, 6H), 1.74-1.50 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 146.2, 145.6, 129.4, 117.4, 113.2, 112.32, 111.3, 76.8, 66.8, 35.7, 28.4, 24.7; HRMS (ESI) calculated for $C_{25}H_{27}O_2$ ([M-(2H_2O)+H]$^+$) *m*/*z* = 359.2011, found 359.2015.



14

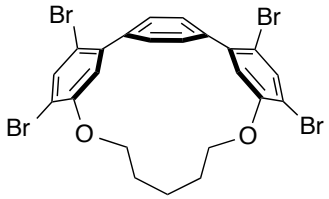
***Cyclohex-2-ene-1,4-diol* 14:** Grubbs' second-generation catalyst (0.0114 g, 0.0134 mmol) was added to a stirred solution of *syn*-**13** and *anti*-**13** (**dr = 5:1**, 0.101 g, 0.253 mmol) in dichloromethane (7 mL) and the reaction was heated to 40 °C. After 3 h, the solvent was evaporated under reduced pressure and residue was purified by flash chromatography (15 × 1.3 cm, 3:7 EtOAc/hexanes) to give *anti*-**13** as a colorless oil (0.017 g, 17%, R_f = 0.59 (1:1 EtOAc/hexanes)) and compound **14** as an off-white solid (0.071 g, 77%); R_f = 0.27 (1:1 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 4H), 7.04-6.98 (m, 2H), 6.88-6.81 (m, 2H), 6.05 (s, 2H), 4.18-4.07 (m, 2H), 4.07-3.96 (m, 2H), 2.22 (br s, 2H), 2.18-2.07 (m, 2H), 1.92-1.66 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 147.9, 134.8, 130.2, 117.9, 115.0, 114.1, 73.1, 69.6, 36.7, 28.9, 22.5; HRMS (ESI) calculated for $C_{23}H_{25}O_3$ ([M-(H_2O)+H]$^+$) *m*/*z* = 349.1804, found 349.1818.



15

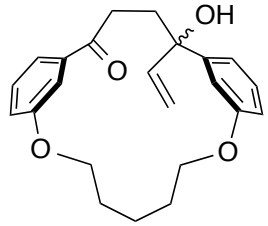
***1,7-dioxa[7](3,3″)p-Terphenylenophane* (*15*)**: *p*-Toluensulfonic acid monohydrate (1.22 g, 6.390 mmol) was added to a stirred solution of **14** (0.390 g, 1.07 mmol) in toluene (50 mL) and the reaction was heated at 50 °C for 4 h and 60 °C for 2 h. After 6 h, a saturated solution of $NaHCO_3$ (50 mL) was added to the reaction. The layers were separated and the aqueous phase was extracted with dichloromethane (3 × 30 mL). The organic extracts were combined and washed with brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by

flash chromatograph (15 × 2.5 cm, 1:19 EtOAc/hexanes) to afford **15** as a white solid (0.288 g, 82%): R_f = 0.32 (1:19 EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 4H), 7.35 (dd, *J* = 8.2, 7.4 Hz, 2H), 7.30-7.24 (m, 2H), 6.78 (ddd, *J* = 8.3, 2.8, 1.0 Hz, 2H), 5.81 (dd, *J* = 2.8, 1.5 Hz, 2H), 4.10-4.05 (m, 4H), 1.51-1.42 (m, 4H), 1.21-1.12 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 144.7, 144.1, 130.6, 129.5, 118.7, 115.9, 115.4, 68.5, 26.8, 23.3; HRMS (EI) calculated for $C_{23}H_{22}O_2$ ([M]$^+$) *m*/*z* = 330.1618, found, 330.1620.



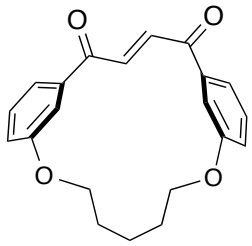
16

4,4",6,6"-Tetrabromo-1,7-dioxa[7](3,3")*p*-terphenylenophane (16): Bromine (0.105 g, 0.636 mmol) was added to a stirred solution of **15** (0.035 g, 0.11 mmol) in 1,2-dichlorbenzene (2 mL). The resulting mixture was heated to 70 °C for 6 h, and then cooled to room temperature under a stream of nitrogen gas. After evaporation of the solvent, the residue was dissolved in dichloromethane (10 mL), a solution of 5% $NaHSO_3$ (10 mL) was added, and the resulting mixture was stirred for 10 min. The layers were separated and the aqueous phase was extracted with dichloromethane (2 × 15 mL). The combined organic extracts were washed with a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 1.3 cm, 3:7 dichloromethane/hexanes) to yield tetrabromide **16** as a white solid (0.052 g, 80%): R_f = 0.48 (1:1 dichloromethane/hexanes); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (s, 2H), 7.50 (s, 4H), 5.73 (s, 2H), 4.18-4.07 (m, 4H), 1.54-1.43 (m, 4H), 1.18-1.09 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.4, 143.1, 142.8, 136.7, 129.7, 120.5, 110.5, 109.6, 69.96, 26.5, 23.4; HRMS (EI) calc'd for $C_{23}H_{18}O_2Br_4$ 641.8040, found 641.8038



18

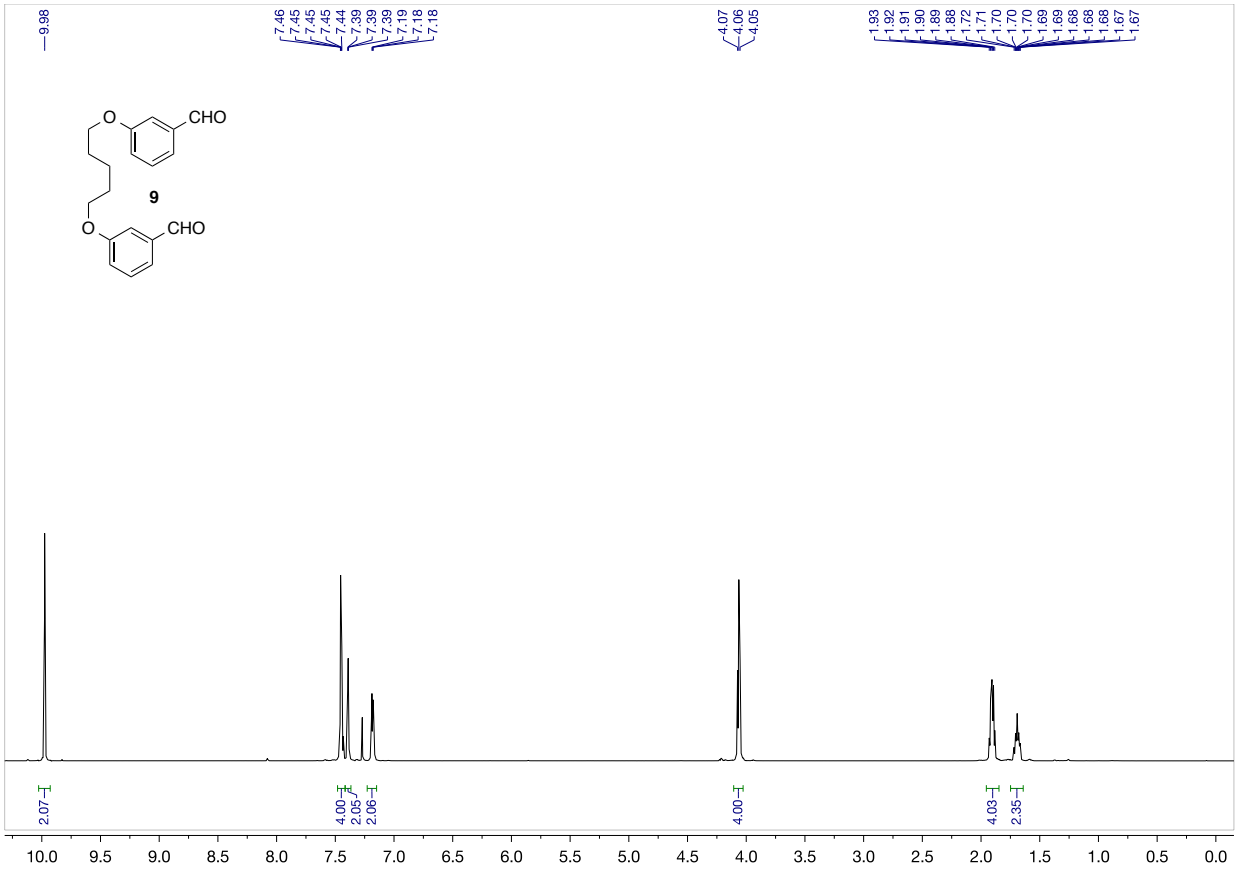
***Hydroxyketone* 18**: R_f = 0.29 (3% acetone/dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.35-7.24 (m, 2H), 7.15 (dd, *J* = 2.6, 1.7 Hz, 1H), 7.08-7.01 (m, 2H), 6.96 (ddd, *J* = 7.8, 1.8, 0.9 Hz, 1H), 6.81 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 6.30 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.39 (dd, *J* = 17.3, 0.9 Hz, 1H), 5.21 (dd, *J* = 10.7, 0.9 Hz, 1H), 4.19-4.02 (m, 4H), 2.91-2.81 (m, 1H), 2.68-2.58 (m, 1H), 2.40-2.23 (m, 2H), 2.03 (s, 1H), 1.92-1.68 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 158.9, 158.8, 145.7, 144.3, 138.1, 129.9, 129.7, 120.4, 120.2, 118.5, 115.0, 113.7, 113.5, 112.7, 76.7, 68.5, 66.7, 37.8, 33.8, 28.2, 27.6, 21.4; HRMS (ESI) calc'd for $C_{23}H_{25}O_3$ ([M-(H_2O)+H]$^+$) *m*/*z* = 349.1804, found 349.1793.

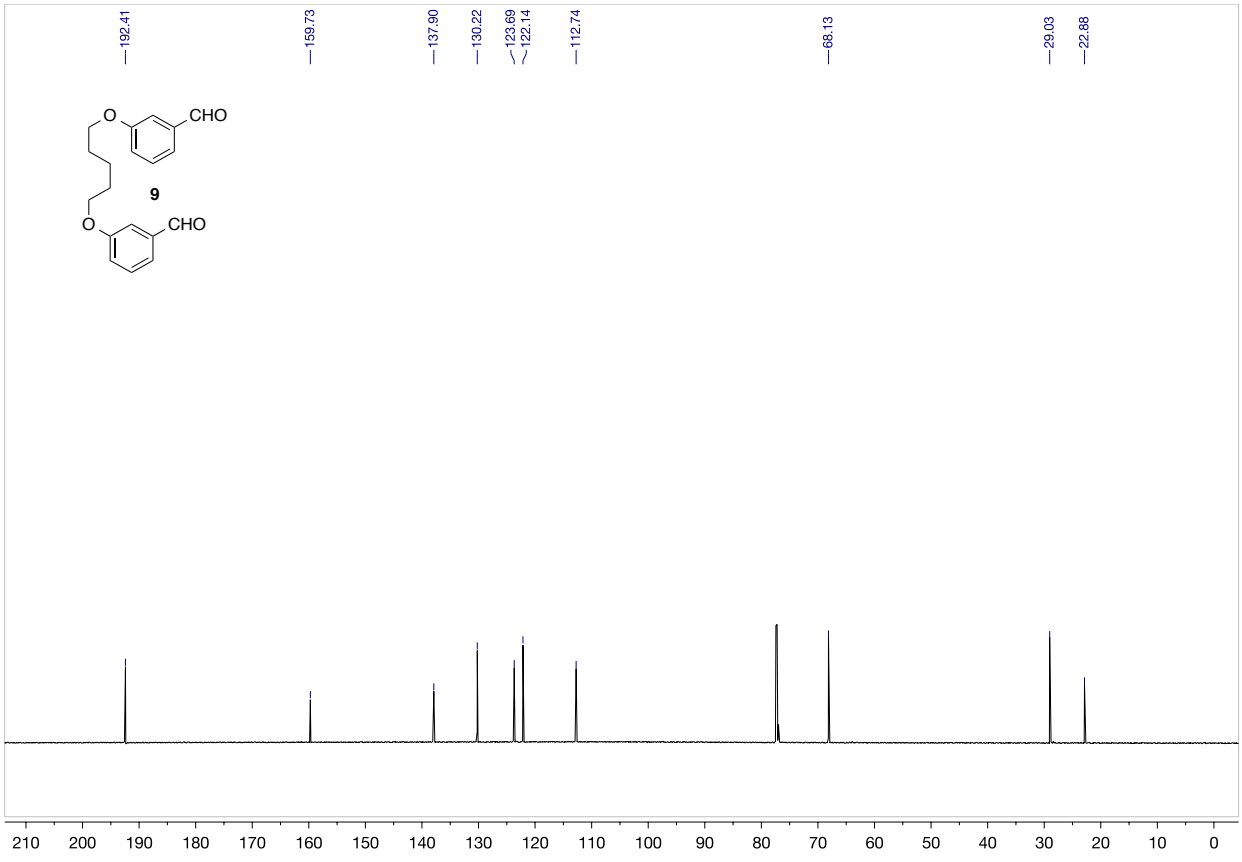


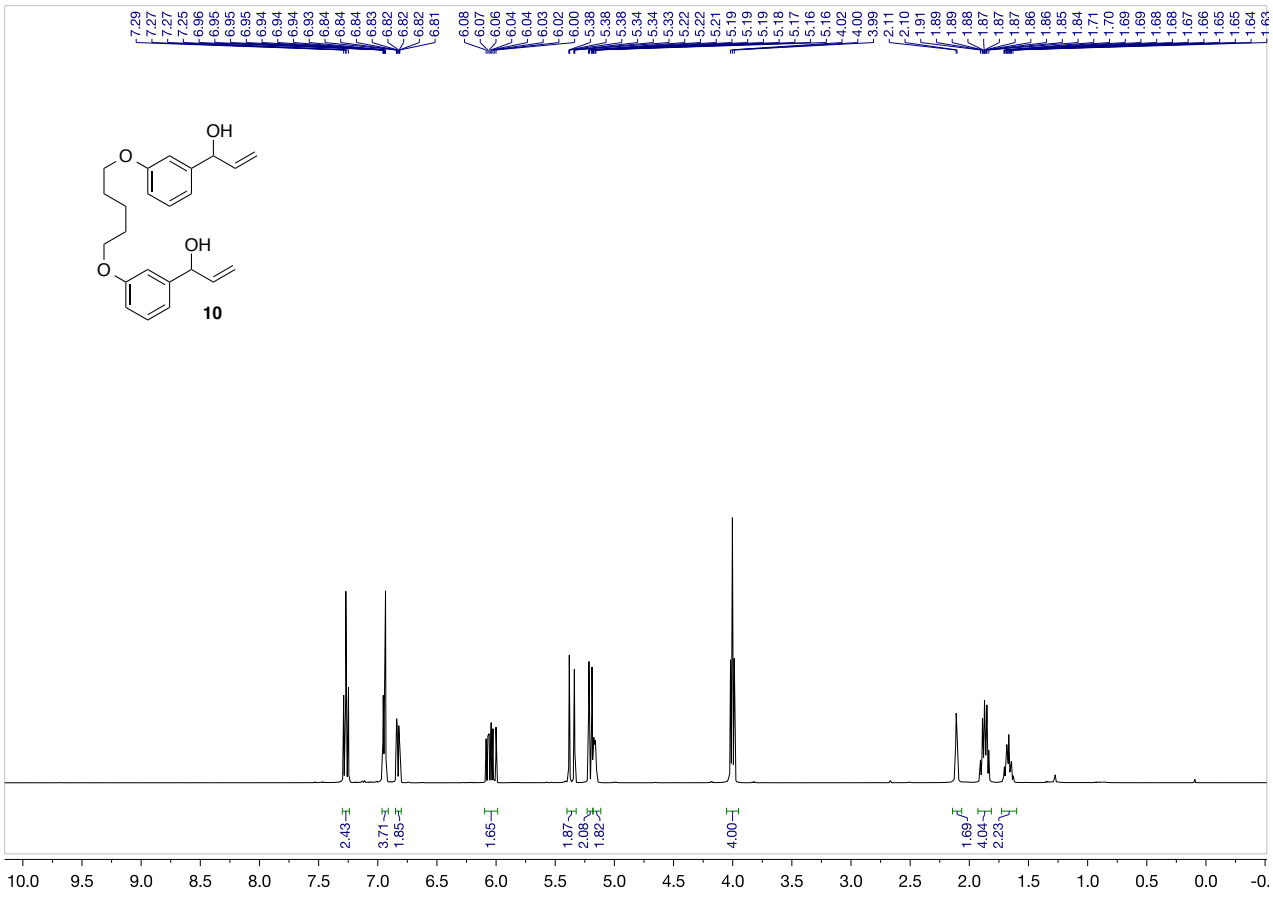
19

Ene-1,4-dione **19**: Dess–Martin periodinane (0.235 g, 0.556 mmol) and $NaHCO_3$ (0.0.47 g, 0.56 mmol) were added to a stirred solution of macrocyclic 1,4-diol **11** (0.063 g, 0.19 mmol) in dichloromethane (5 mL) at room temperature. After 1 h, a 10% solution of $Na_2S_2O_3$ (10 mL) was added and the reaction was stirred for 10 min. The resulting mixture was extracted with dichlormethane (3 × 10 mL). The organic extracts were combined and washed with a saturated solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give 1,4-diketone **12** as a white solid (0.058 g, 92%). R_f = 0.32 (1:4 EtOAc/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.49-7.44 (m, 4H), 7.38 (s, 2H), 7.21-7.17 (m, 2H), 4.16 (t, *J* = 6.6 Hz, 4H), 1.94 (p, *J* = 6.7 Hz, 4H), 1.81-1.71 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 159.0, 138.4, 130.9, 121.3, 121.0, 116.0, 69.2, 28.6, 22.5; HRMS (ESI) calculated for $C_{21}H_{21}O_4$ ($[M+H]^+$) *m*/*z* = 337.1440, found 337.1444.

^{1}H and ^{13}C NMR Spectra



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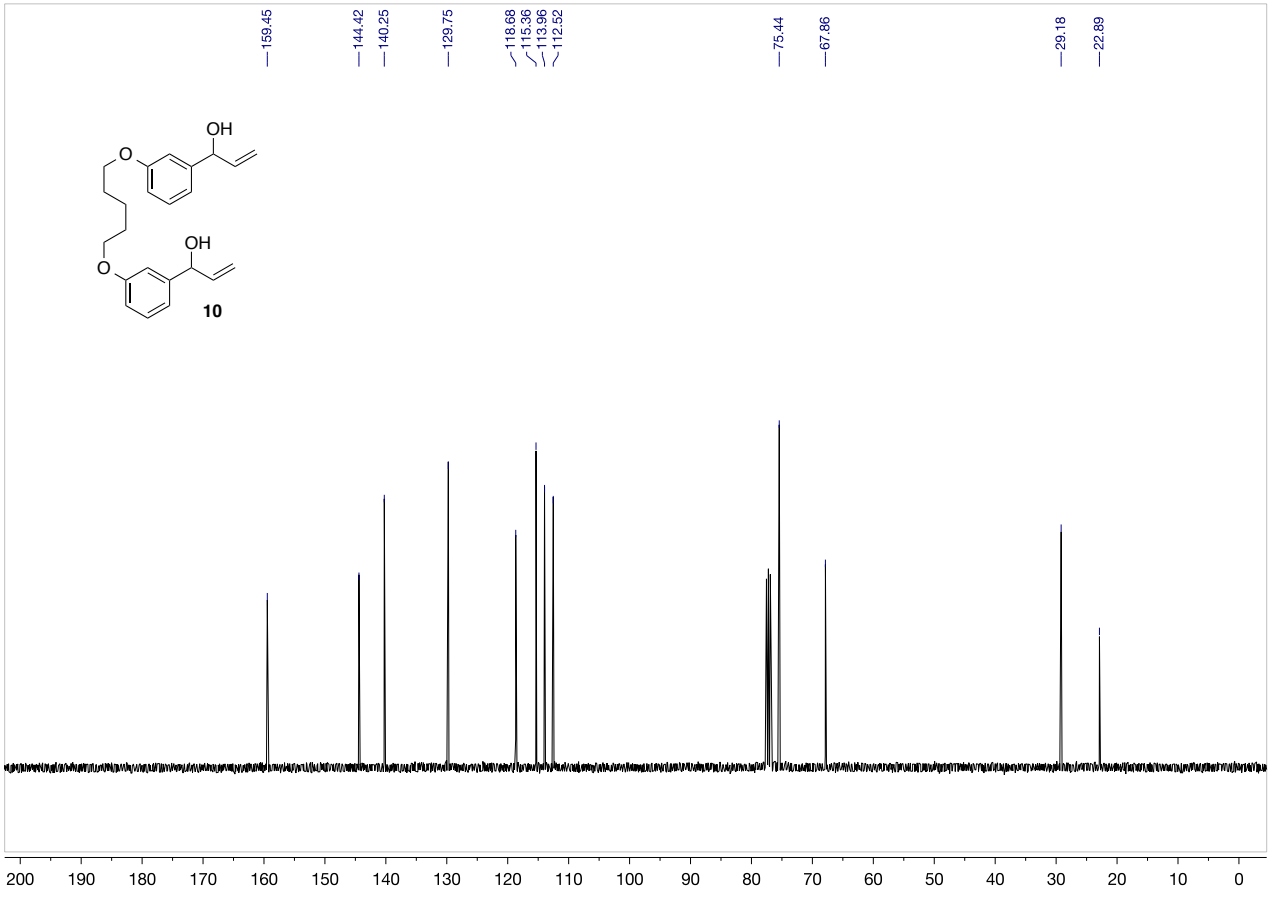
O
OH
O
10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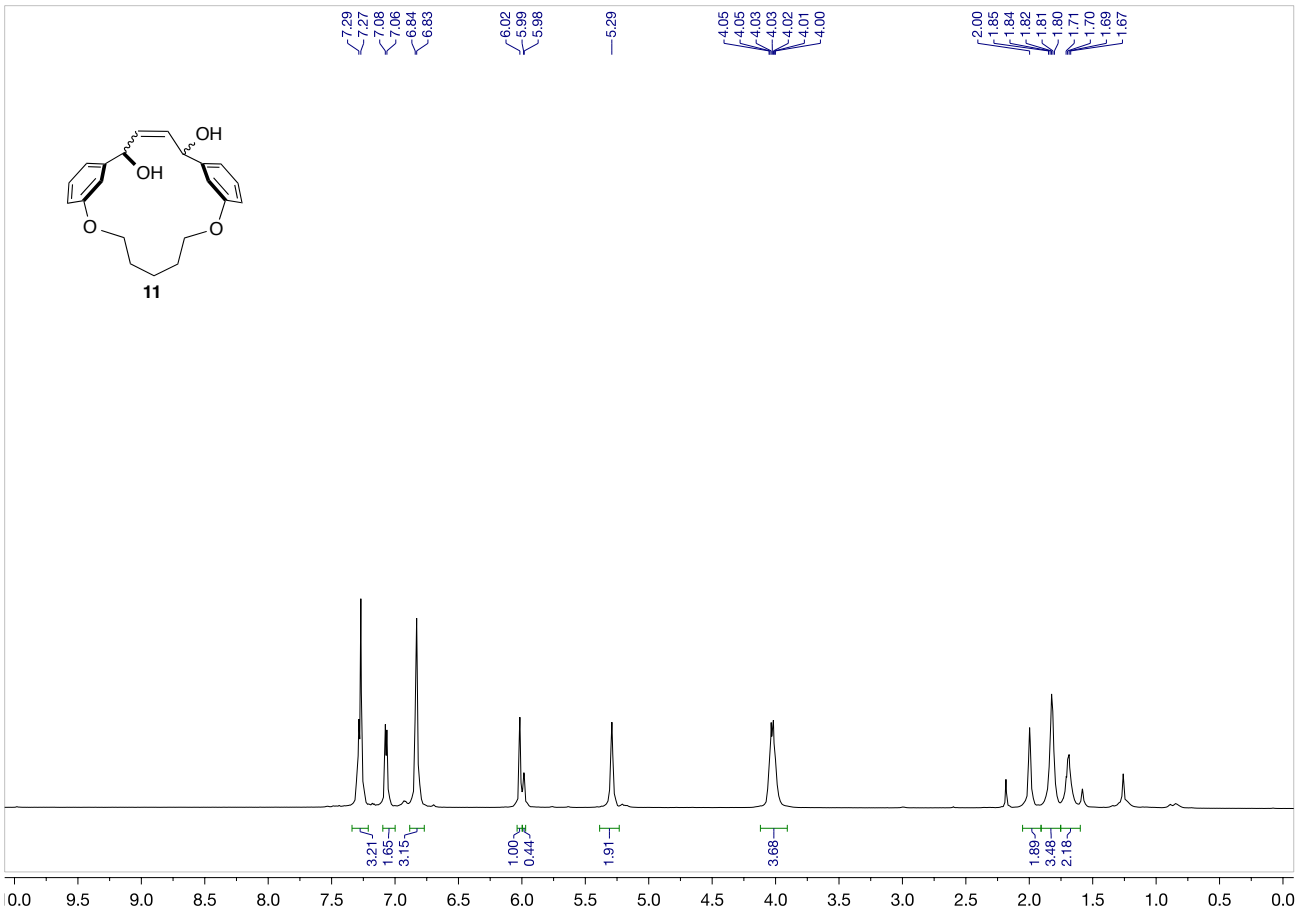
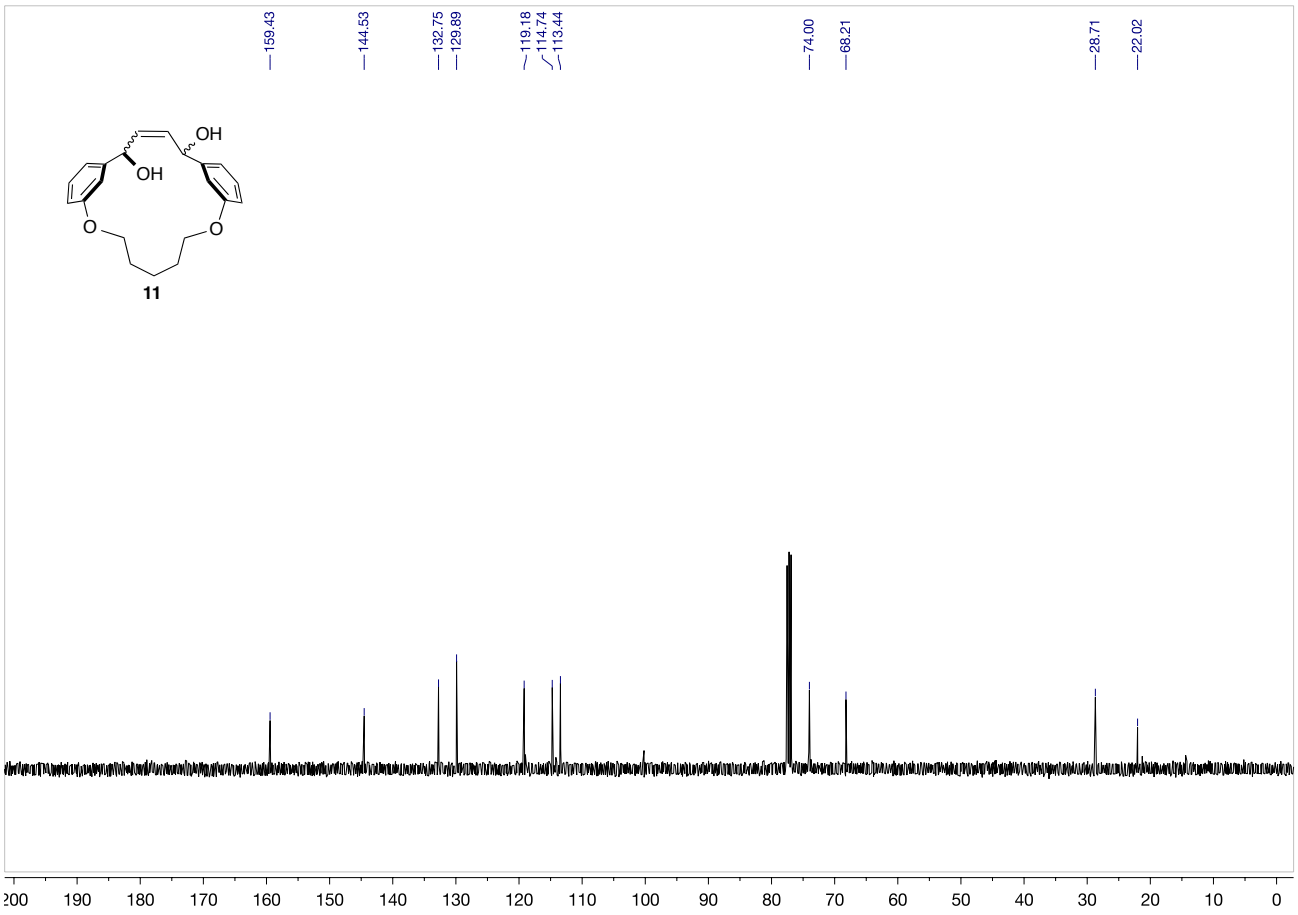
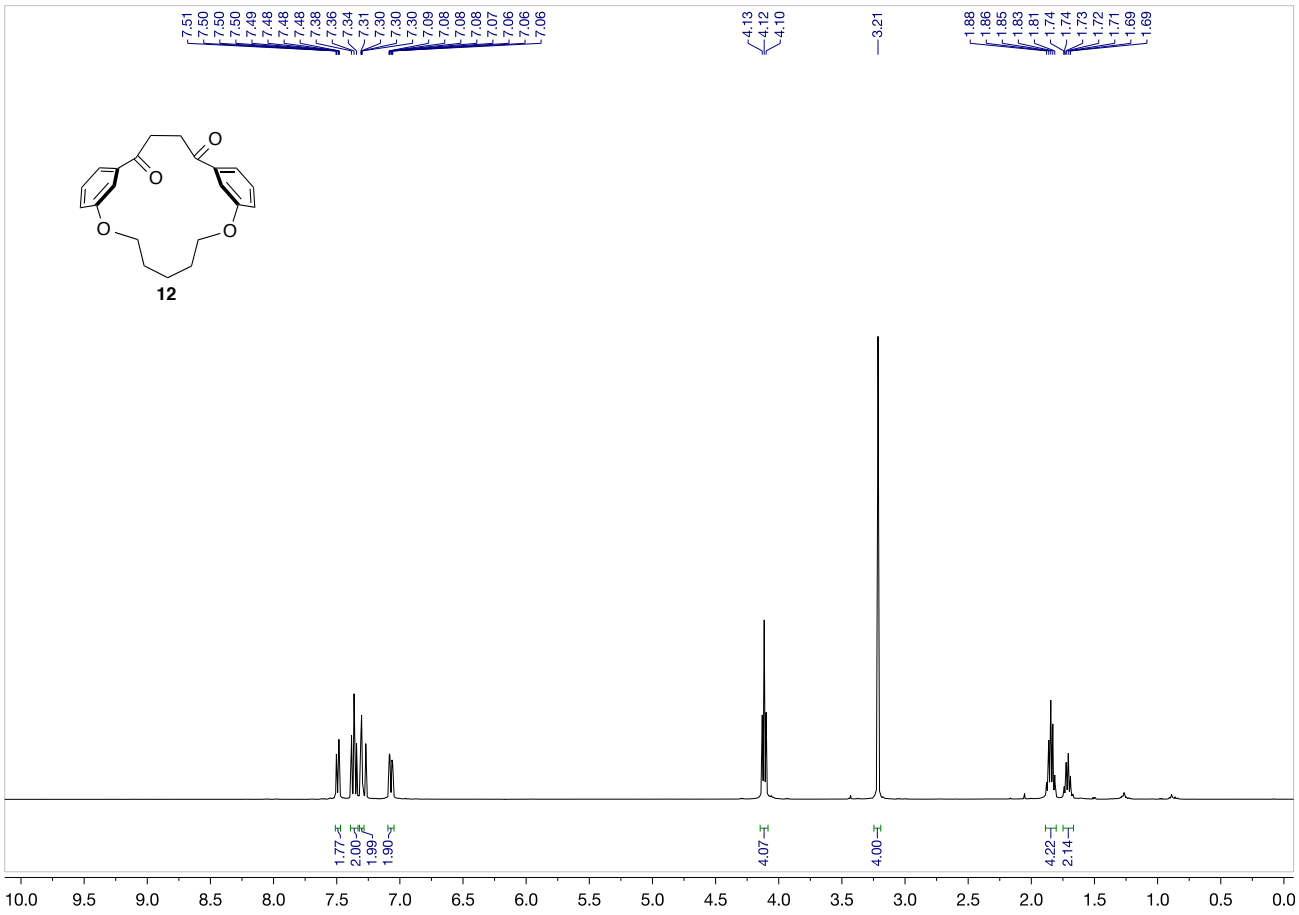
O
OH
O
10


7.29
7.27
7.08
7.06
6.84
6.83
6.02
5.99
5.98
5.29
4.05
4.05
4.03
4.03
4.02
4.01
4.00
2.00
1.85
1.84
1.82
1.81
1.80
1.71
1.70
1.69
1.67
OH
OH
O
O
11
3.21
1.65
3.15
1.00
0.44
1.91
3.68
1.89
3.48
2.18
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


159.43
144.53
132.75
129.89
119.18
114.74
113.44
74.00
68.21
28.71
22.02
OH
OH
O
O
11
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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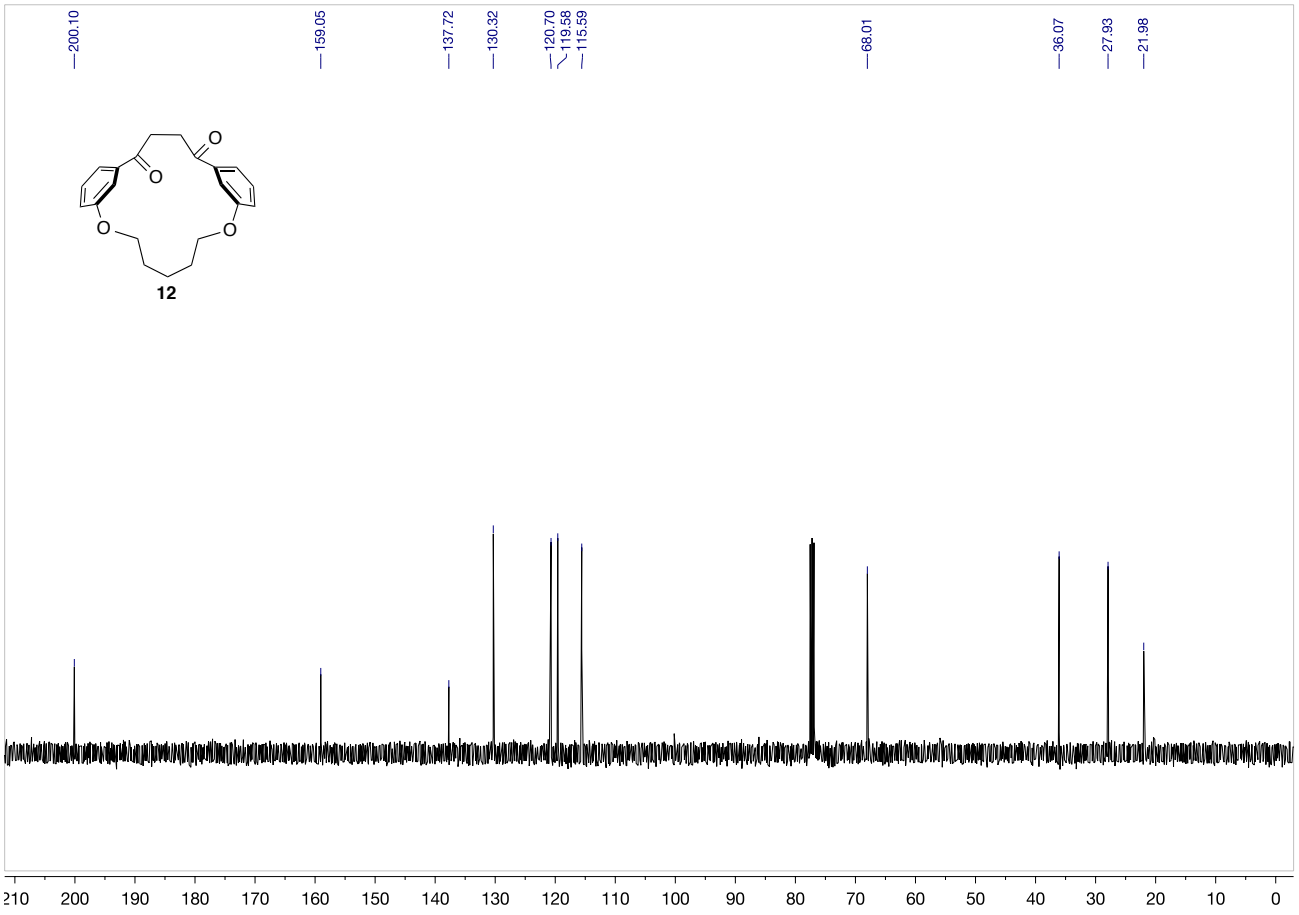
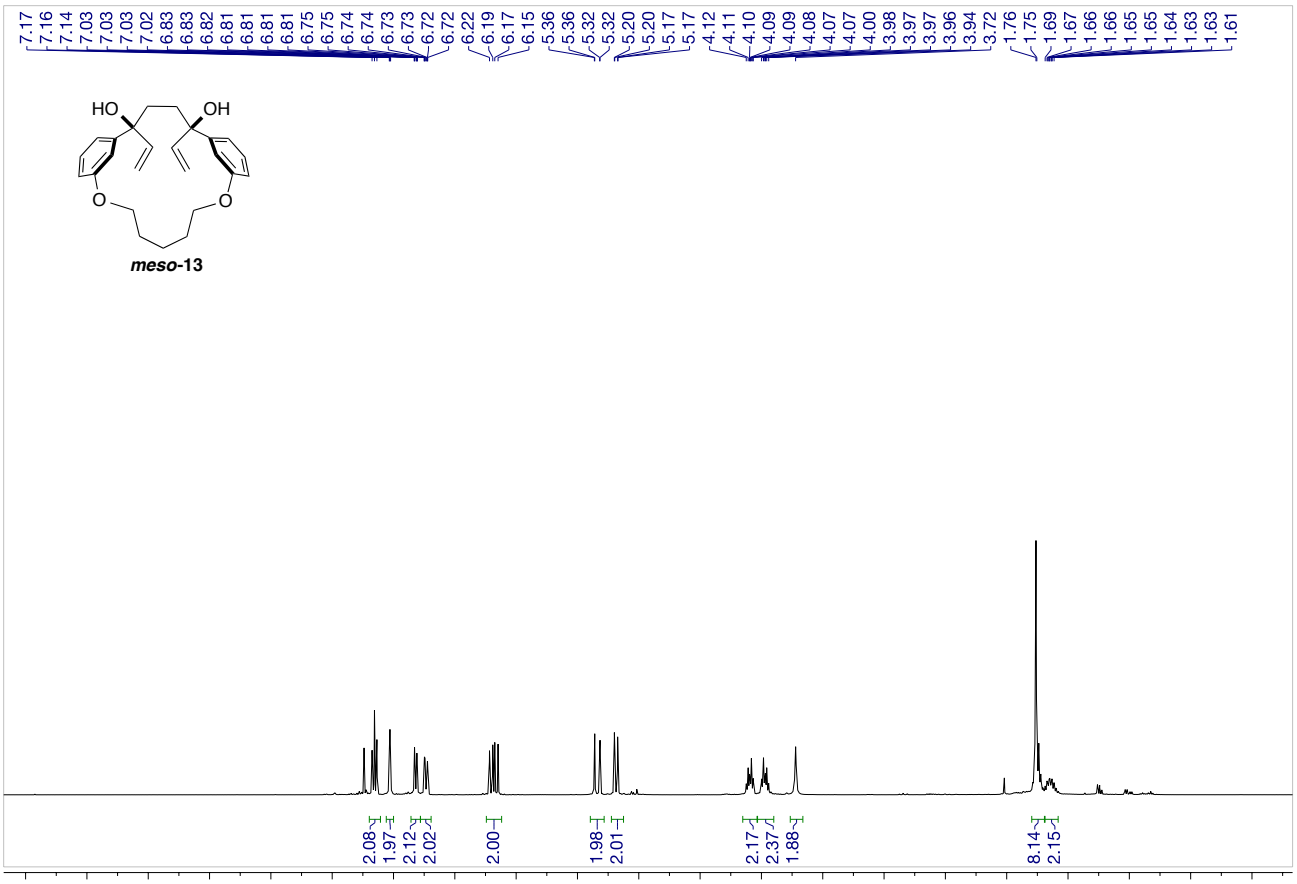
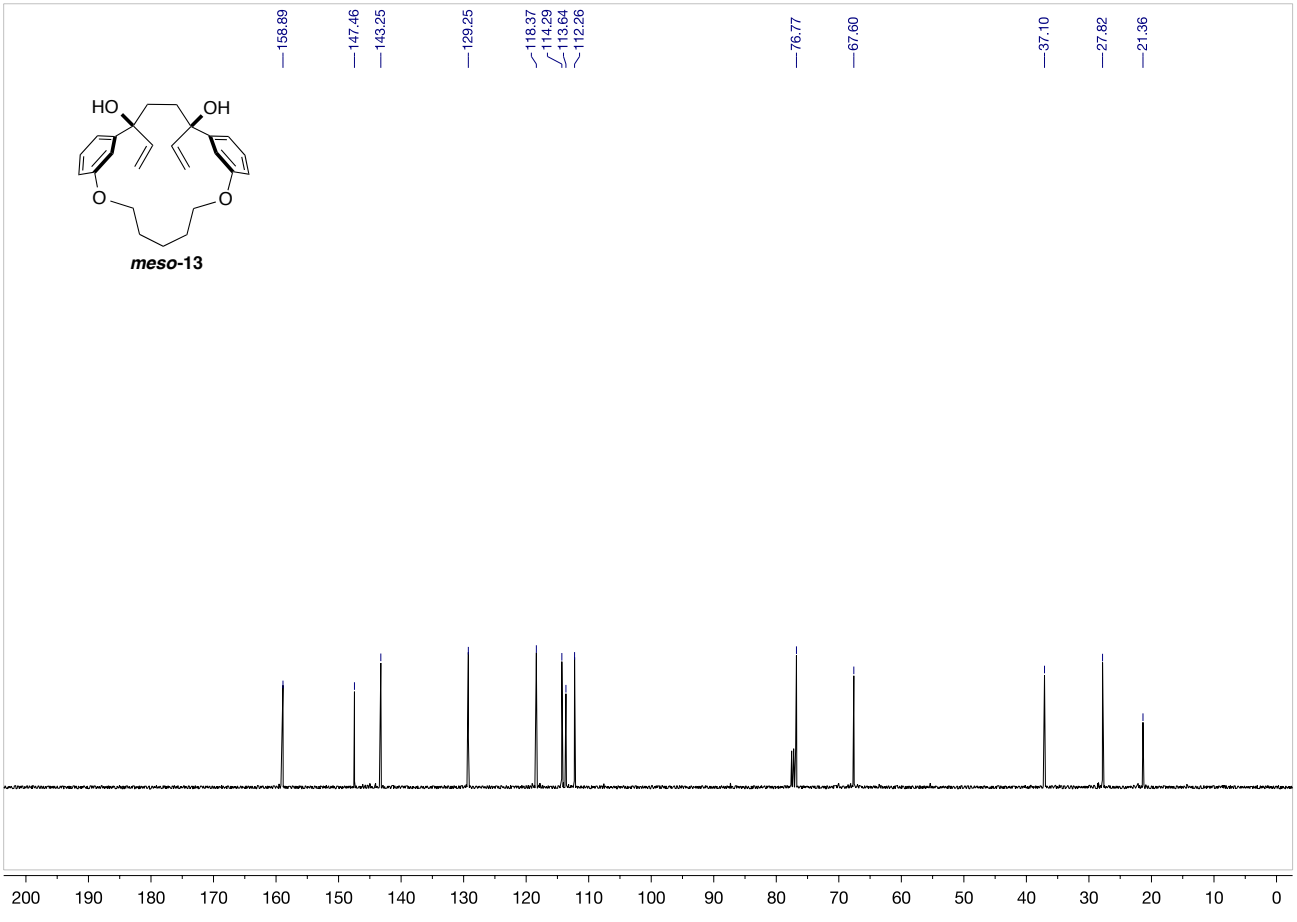
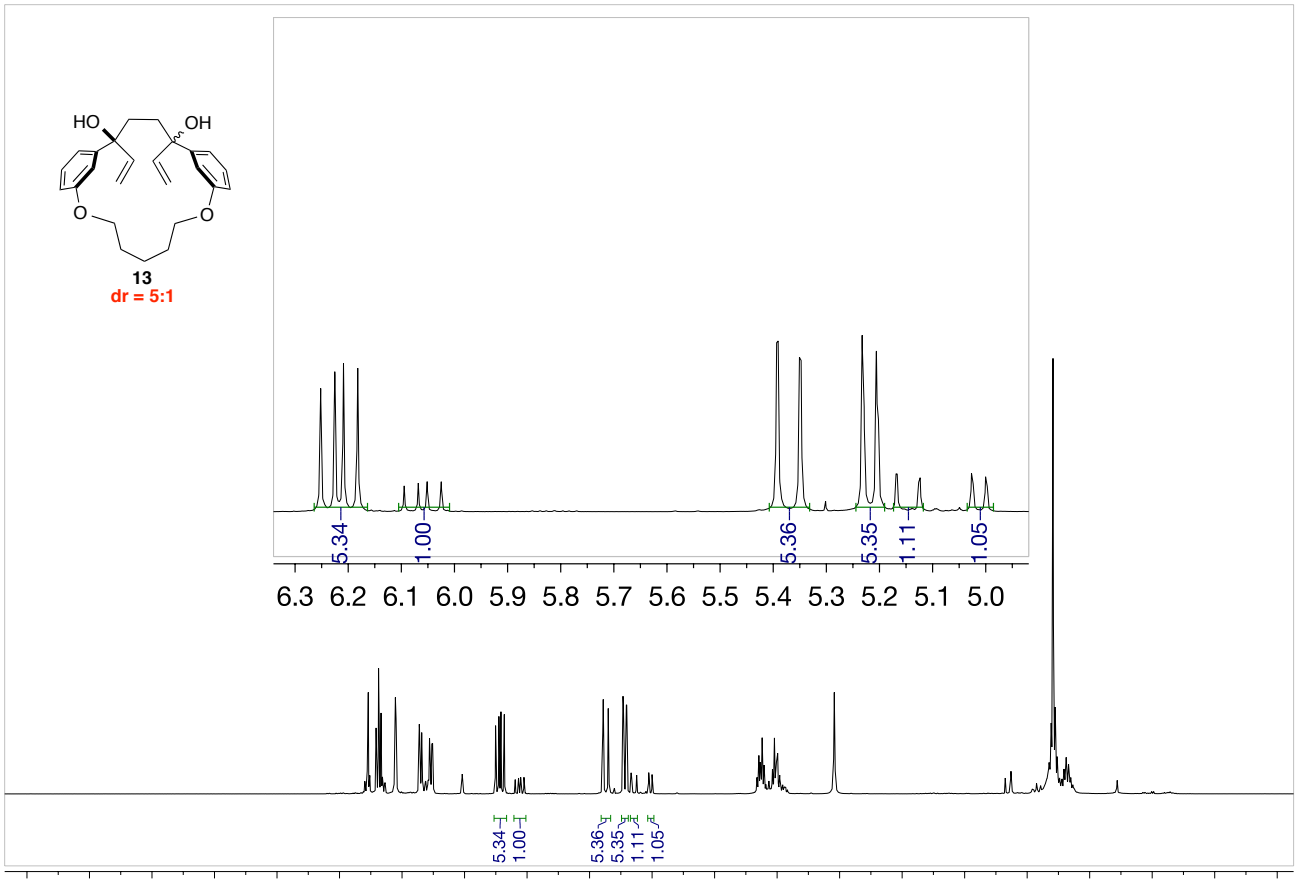
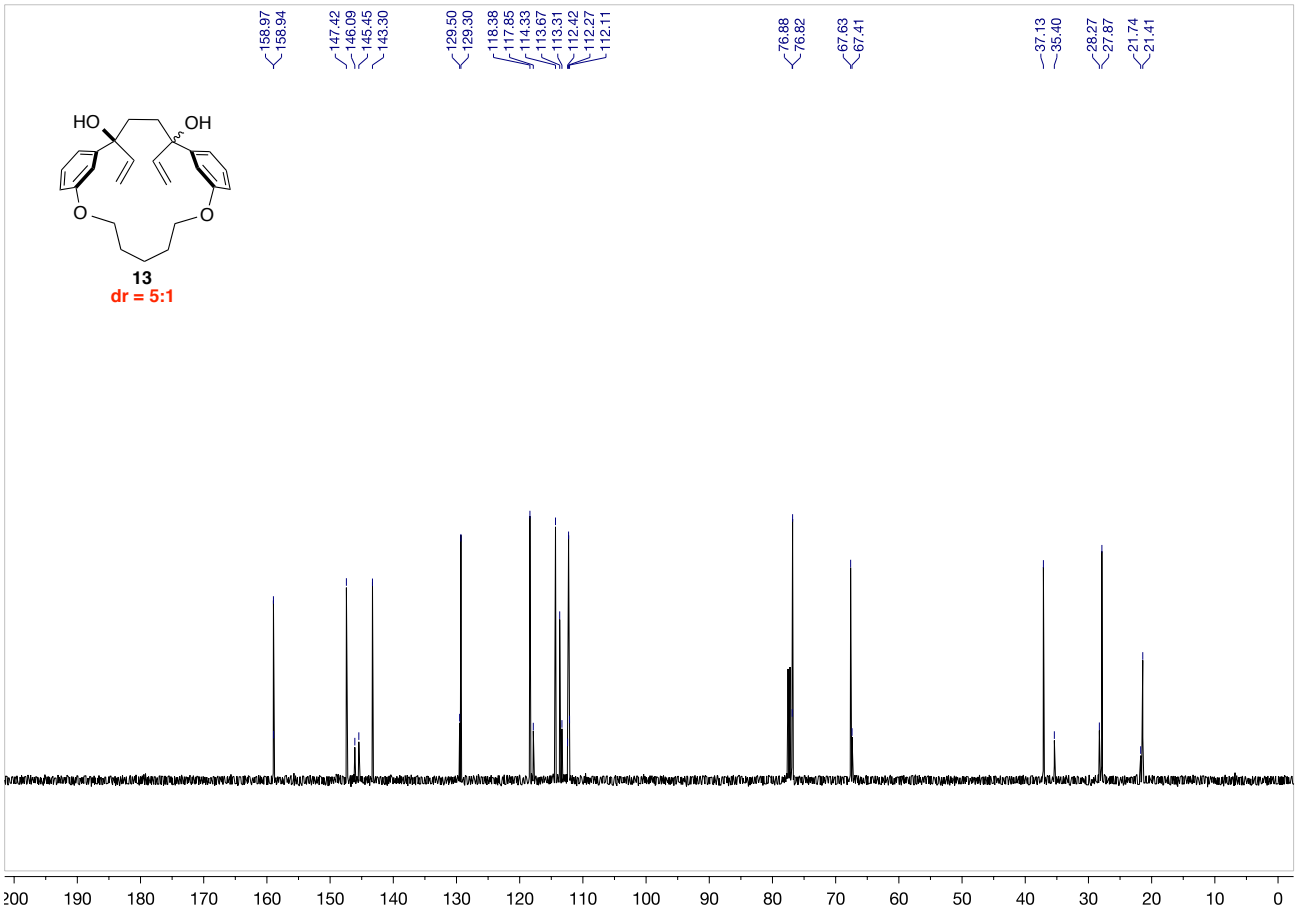
7.50
7.50
7.50
7.49
7.48
7.48
7.48
7.38
7.36
7.34
7.31
7.30
7.30
7.30
7.09
7.08
7.08
7.08
7.07
7.06
7.06
7.06
4.13
4.12
4.10
3.21
1.88
1.86
1.85
1.83
1.81
1.74
1.74
1.73
1.72
1.71
1.69
1.69
O
O
O
O
12
1.77
2.00
1.99
1.90
4.07
4.00
4.22
2.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

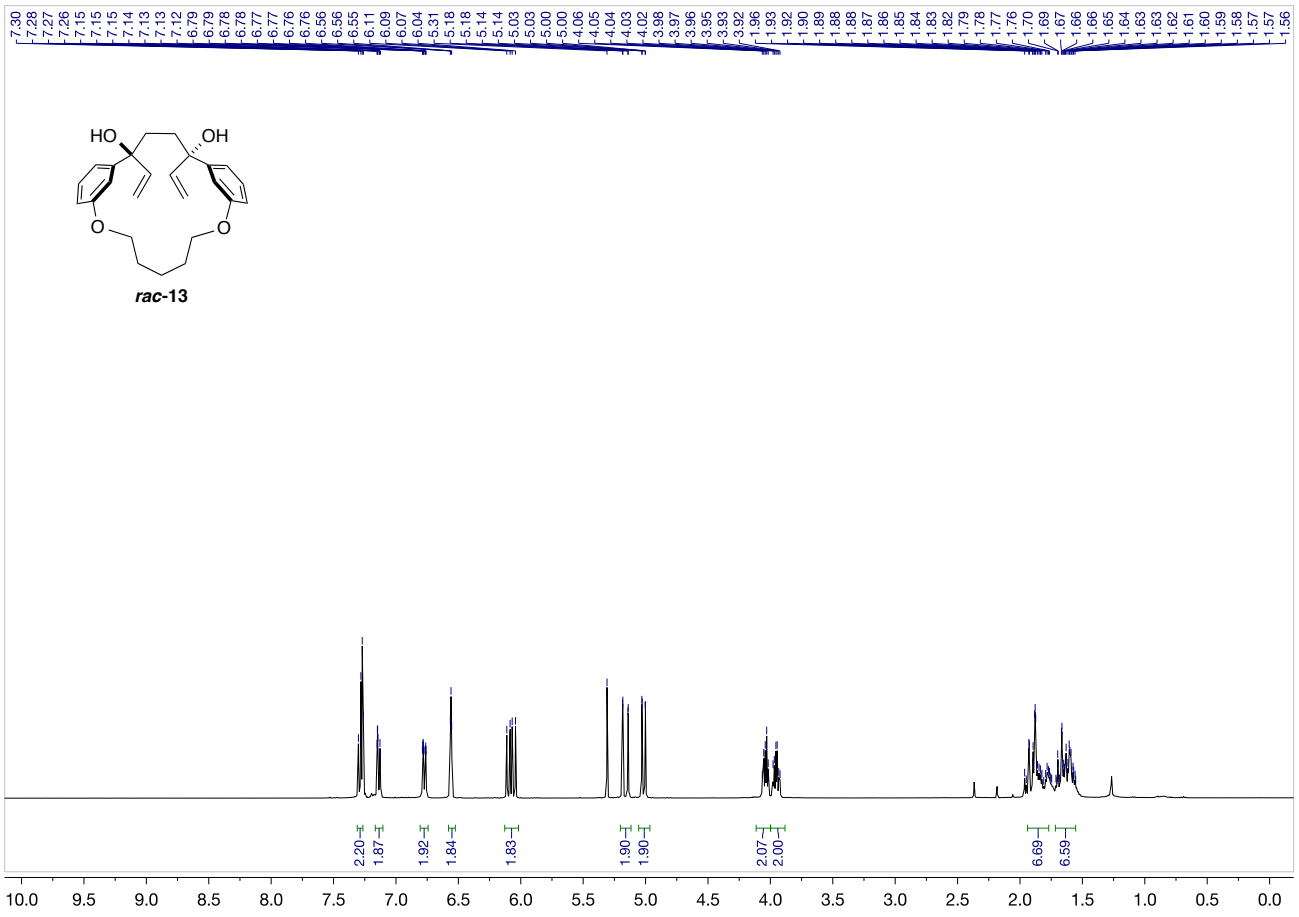

200.10
159.05
137.72
130.32
120.70
119.58
115.59
68.01
36.07
27.93
21.98
O
O
O
O
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

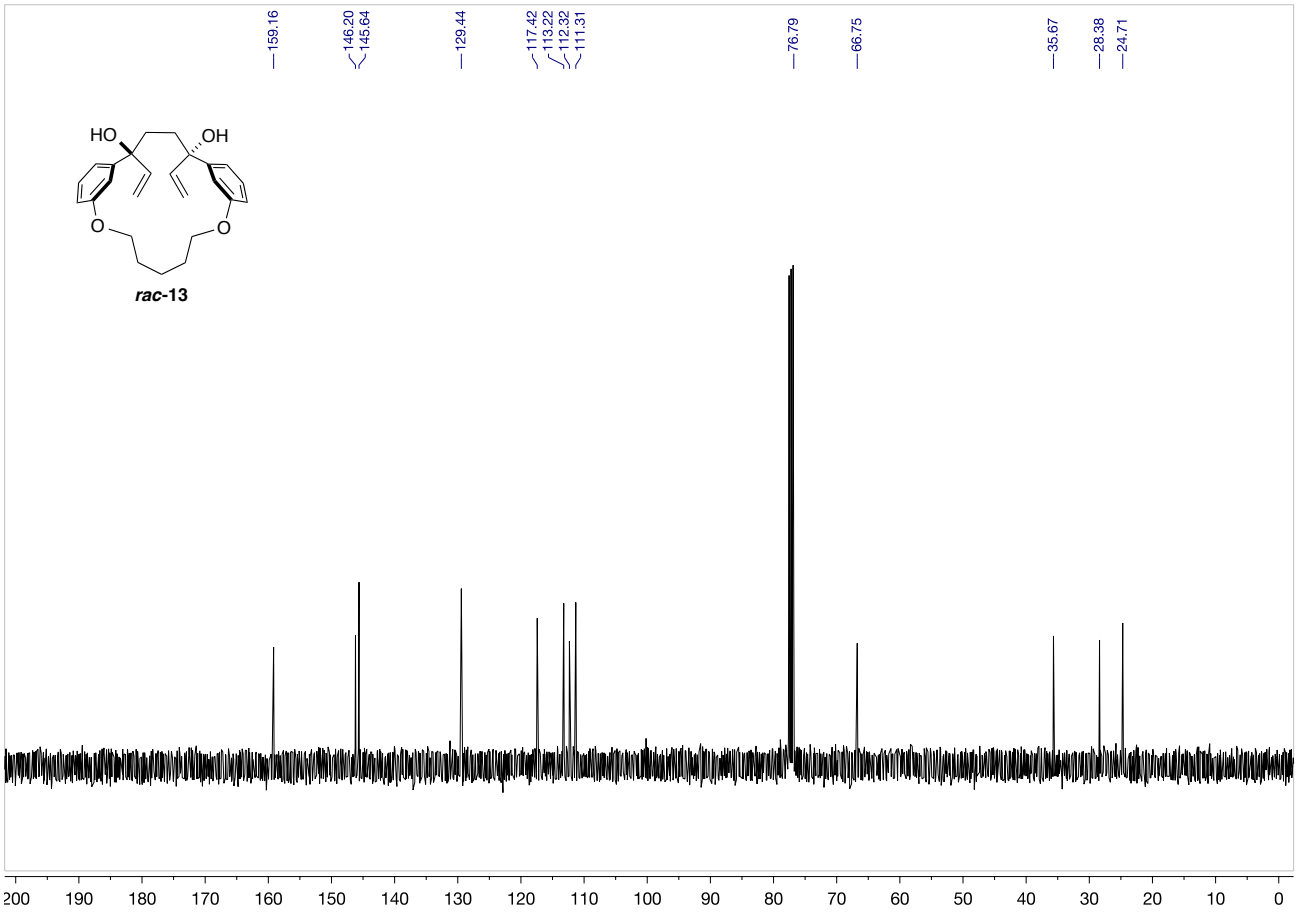

HO
OH
O
O
meso-13
7.17 7.16 7.14 7.03 7.03 7.03 7.02 6.83 6.83 6.82 6.81 6.81 6.81 6.81 6.75 6.75 6.74 6.74 6.73 6.73 6.72 6.72 6.22 6.19 6.17 6.15 5.36 5.36 5.32 5.32 5.20 5.20 5.17 5.17 4.12 4.11 4.10 4.09 4.09 4.08 4.07 4.07 4.00 3.98 3.97 3.97 3.96 3.94 3.72 1.76 1.75 1.69 1.67 1.66 1.66 1.65 1.65 1.64 1.63 1.63 1.61
2.08 1.97 2.12 2.02 2.00 1.98 2.01 2.17 2.37 1.88 8.14 2.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

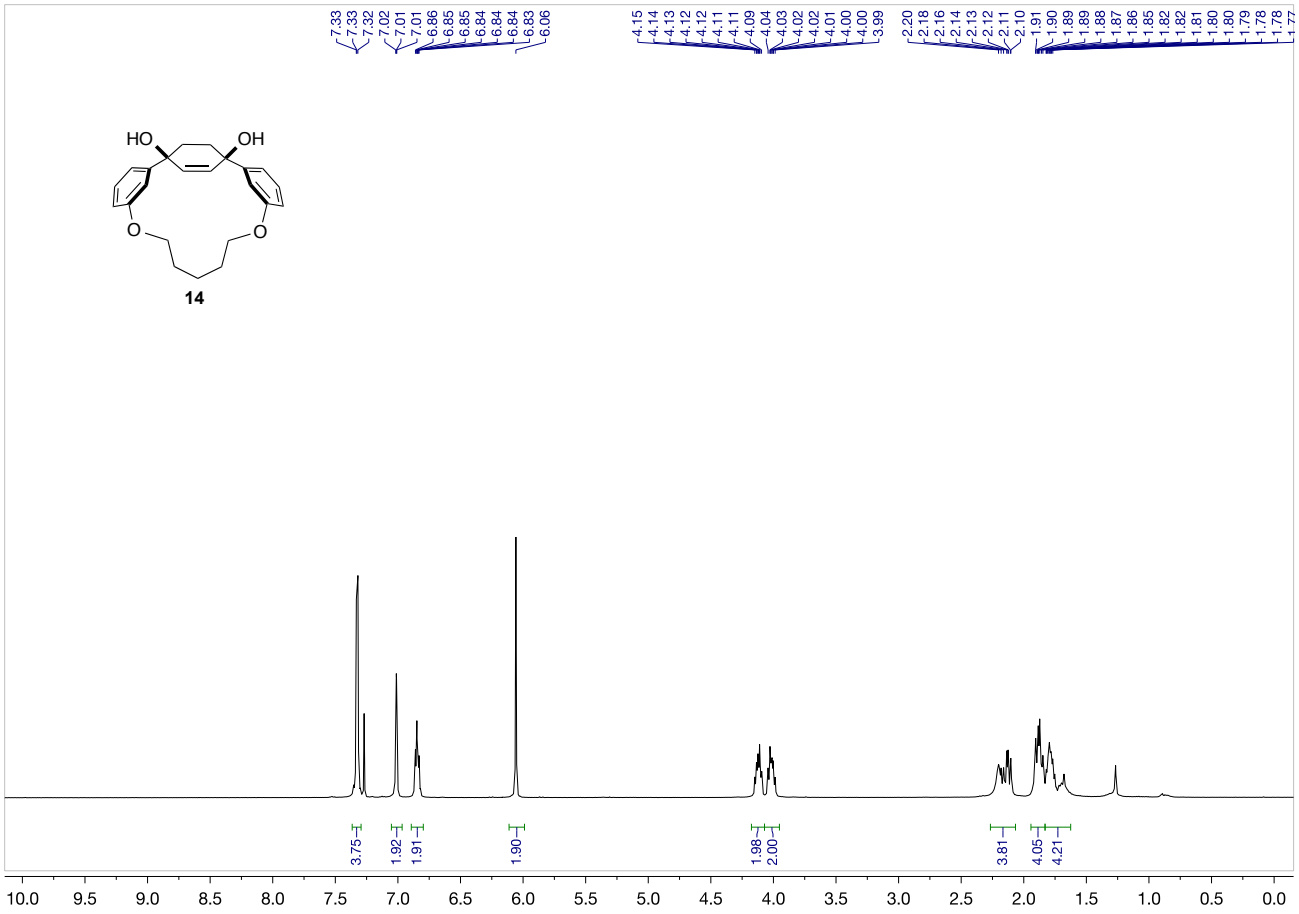

HO
OH
O
O
meso-13
158.89 147.46 143.25 129.25 118.37 114.29 113.64 112.26 76.77 67.60 37.10 27.82 21.36
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

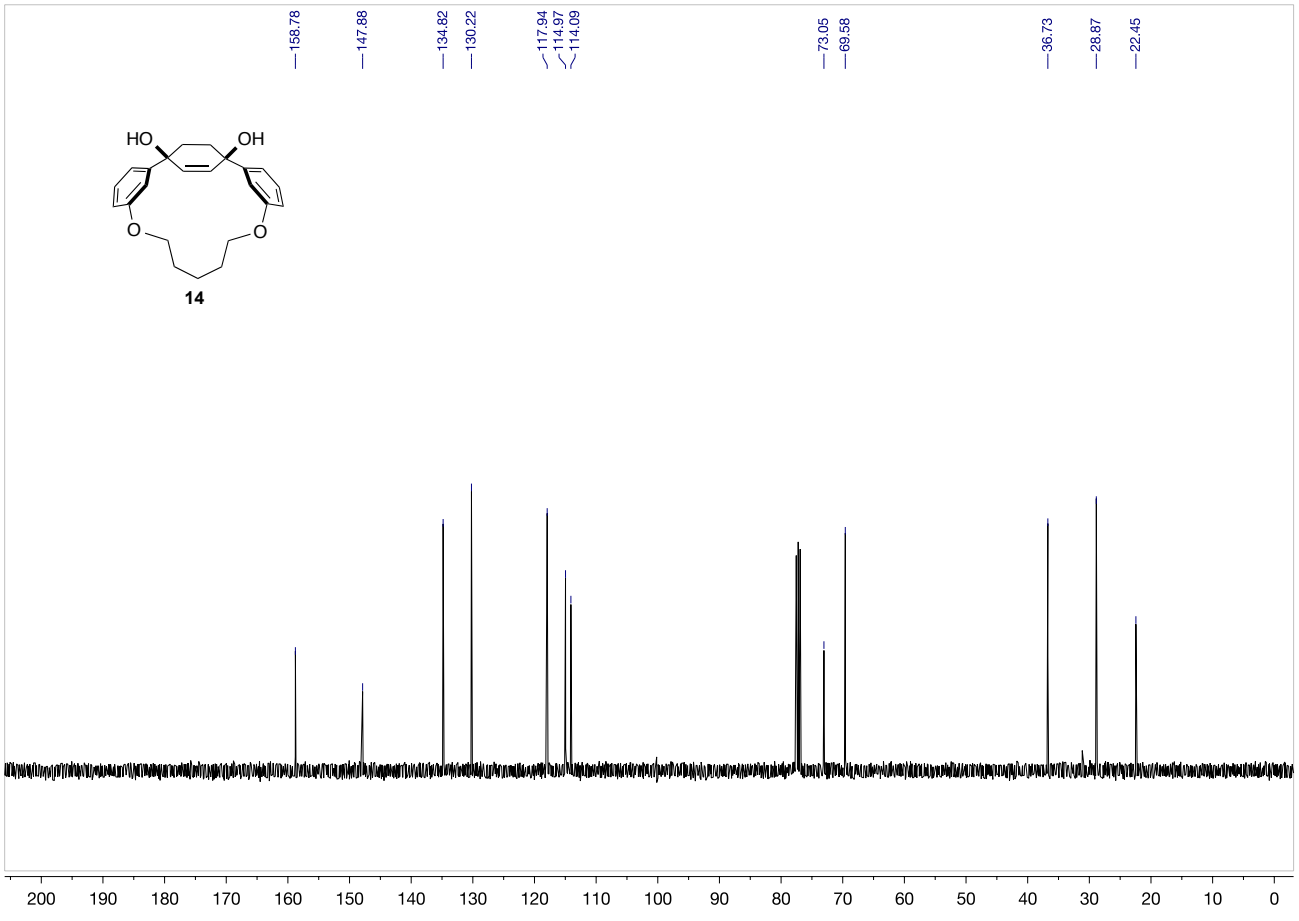

HO
OH
O
O
13
dr = 5:1
5.34
1.00
5.36
5.35
1.11
1.05
6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

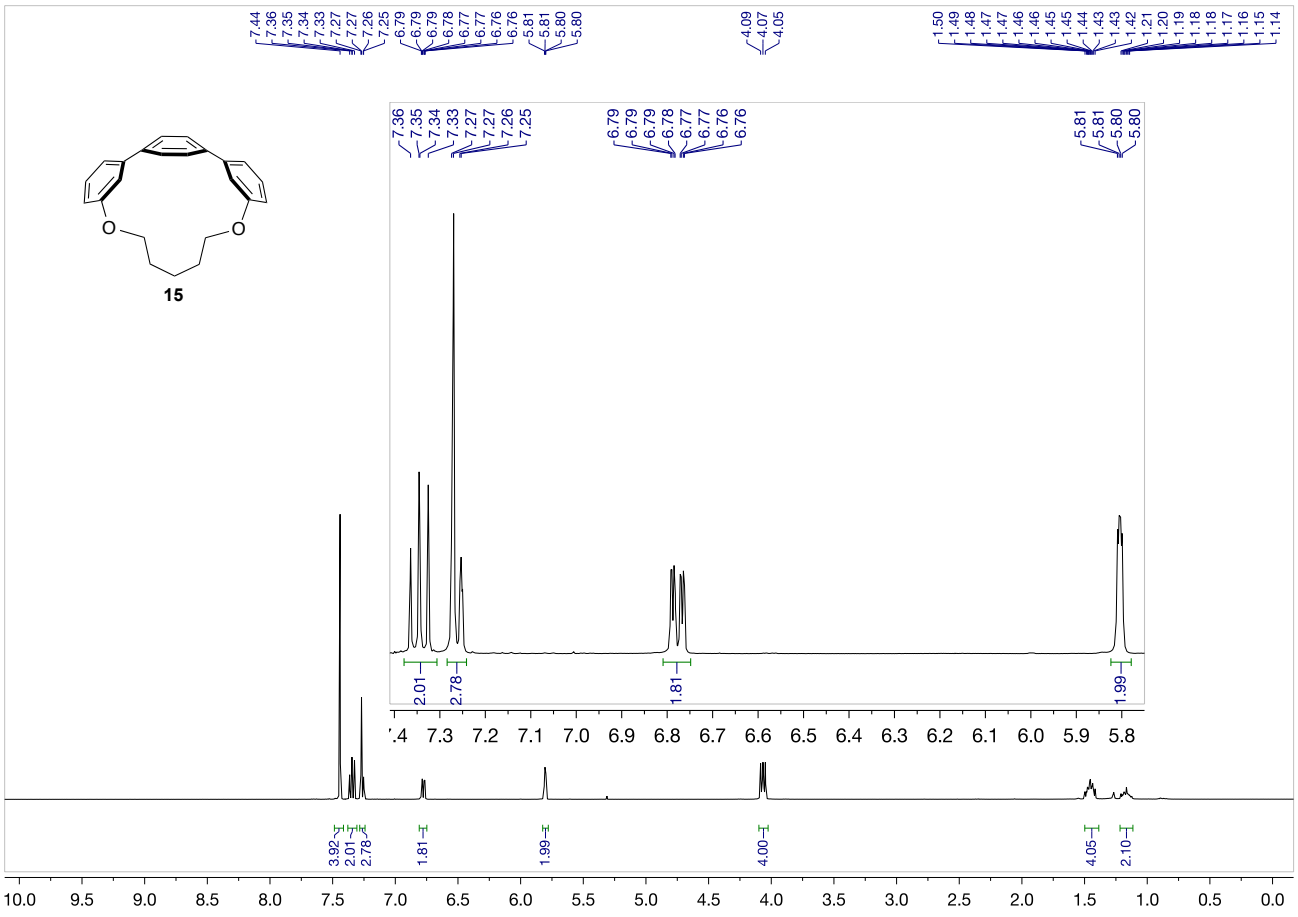

158.97
158.94
147.42
146.09
145.45
143.30
129.50
129.30
118.38
117.85
114.33
113.67
113.31
112.42
112.27
112.11
76.88
76.82
67.63
67.41
37.13
35.40
28.27
27.87
21.74
21.41
HO
OH
O
O
13
dr = 5:1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

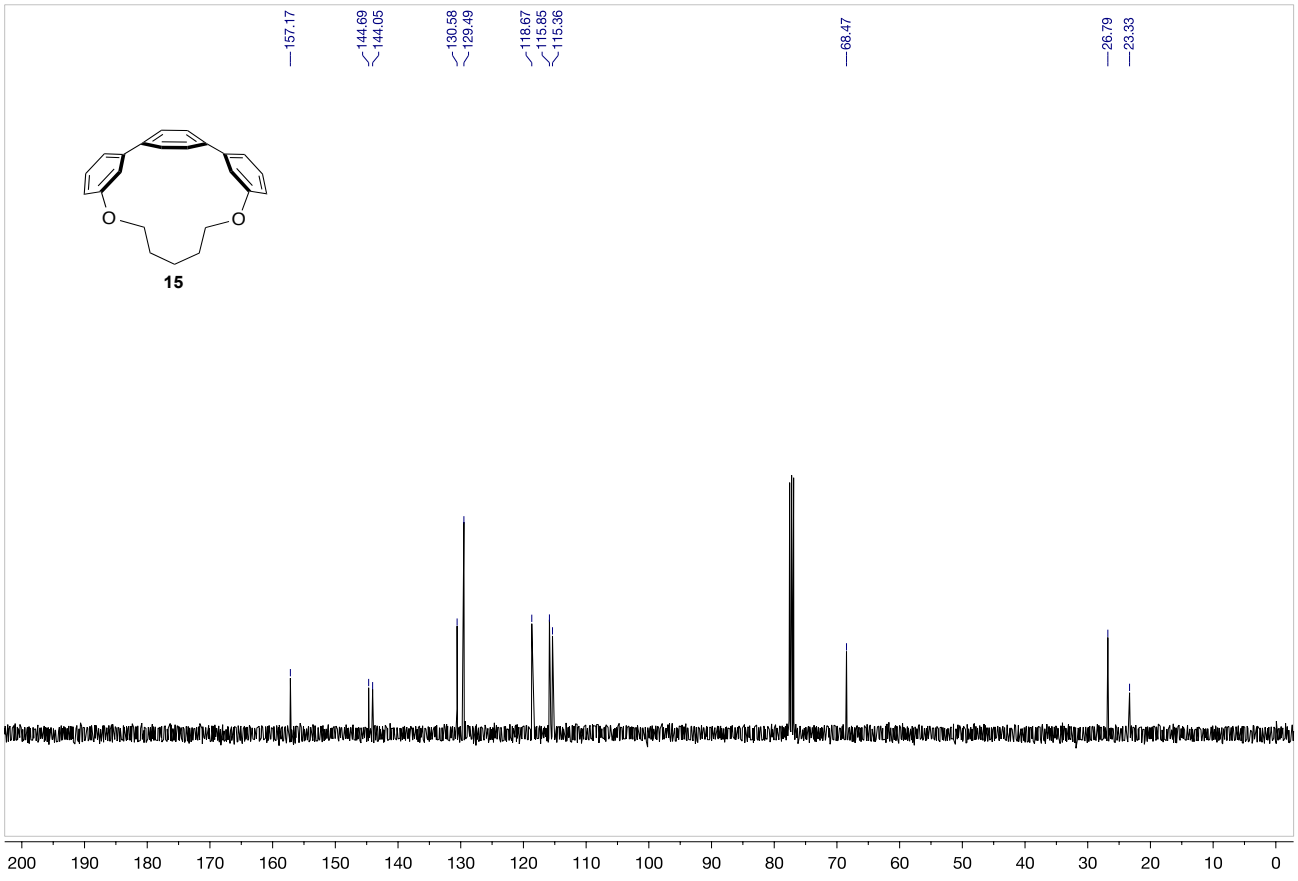

HO
OH
O
O
rac-13

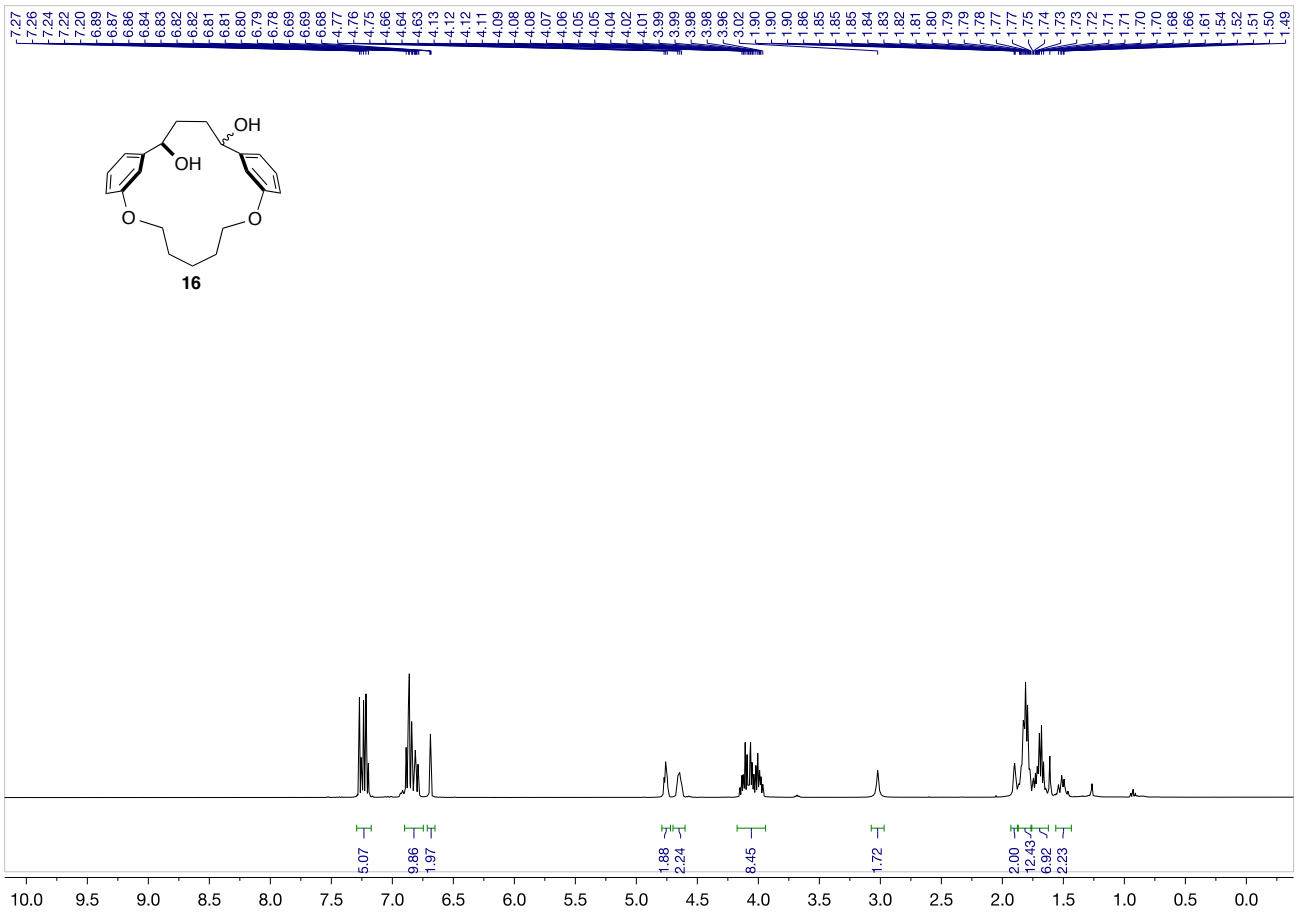

HO
OH
O
O
rac-13

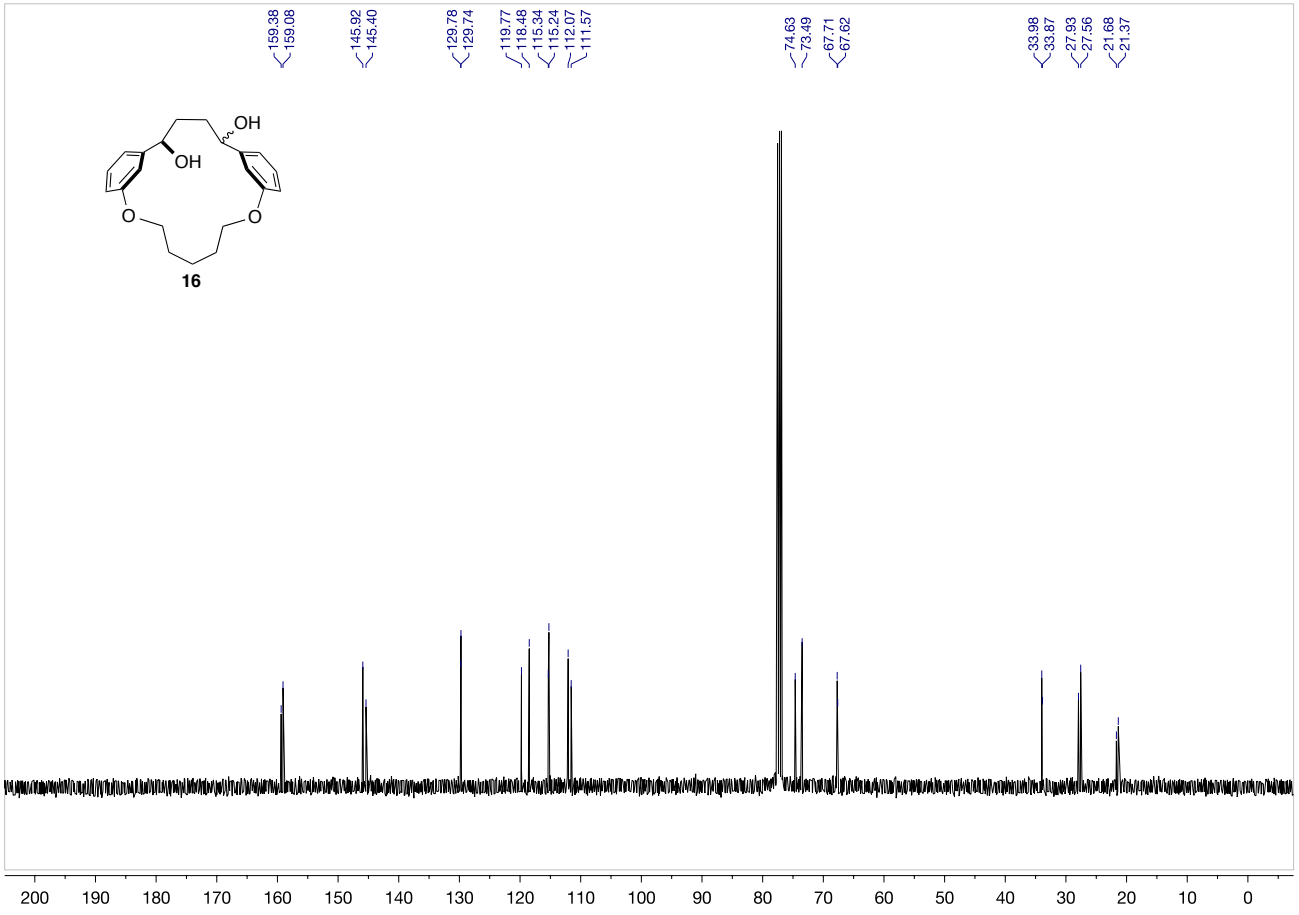

HO
OH
O
O
14
7.33
7.33
7.32
7.02
7.01
7.01
6.86
6.85
6.85
6.84
6.84
6.84
6.83
6.06
4.15
4.14
4.13
4.12
4.12
4.11
4.11
4.09
4.04
4.03
4.02
4.02
4.01
4.00
4.00
3.99
2.20
2.18
2.16
2.14
2.13
2.12
2.11
2.10
1.91
1.90
1.89
1.89
1.88
1.87
1.86
1.85
1.82
1.82
1.81
1.80
1.80
1.79
1.78
1.78
3.75
1.92
1.91
1.90
1.98
2.00
3.81
4.05
4.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

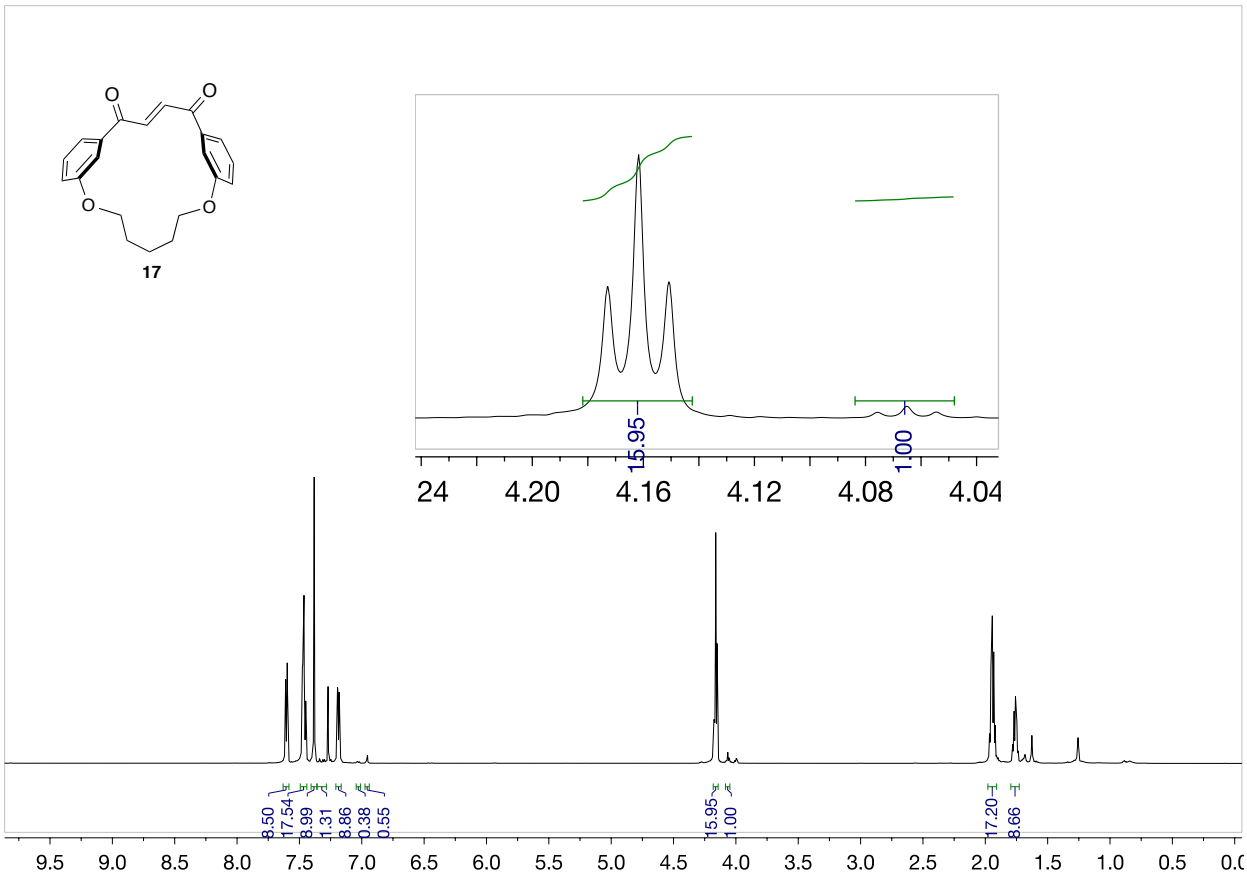

HO
OH
O
O
14
158.78
147.88
134.82
130.22
117.94
114.97
114.09
73.05
69.58
36.73
28.87
22.45
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


15


15


OH
OH
O
O
16


OH
OH
O
O
16


17
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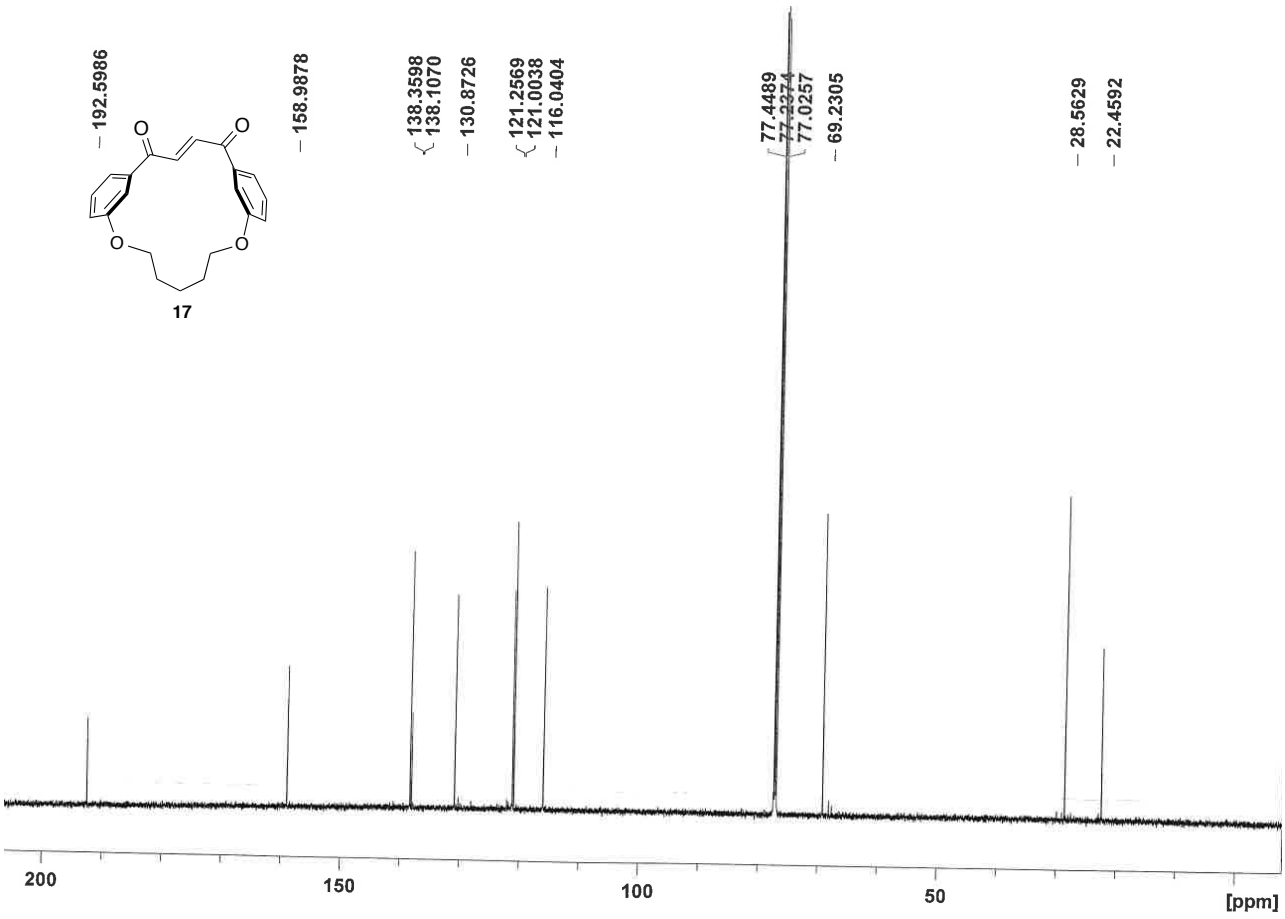
1.00
24
4.20
4.16
4.12
4.08
4.04
8.50
17.54
8.99
1.31
8.86
0.38
0.55
15.95
1.00
17.20
8.66
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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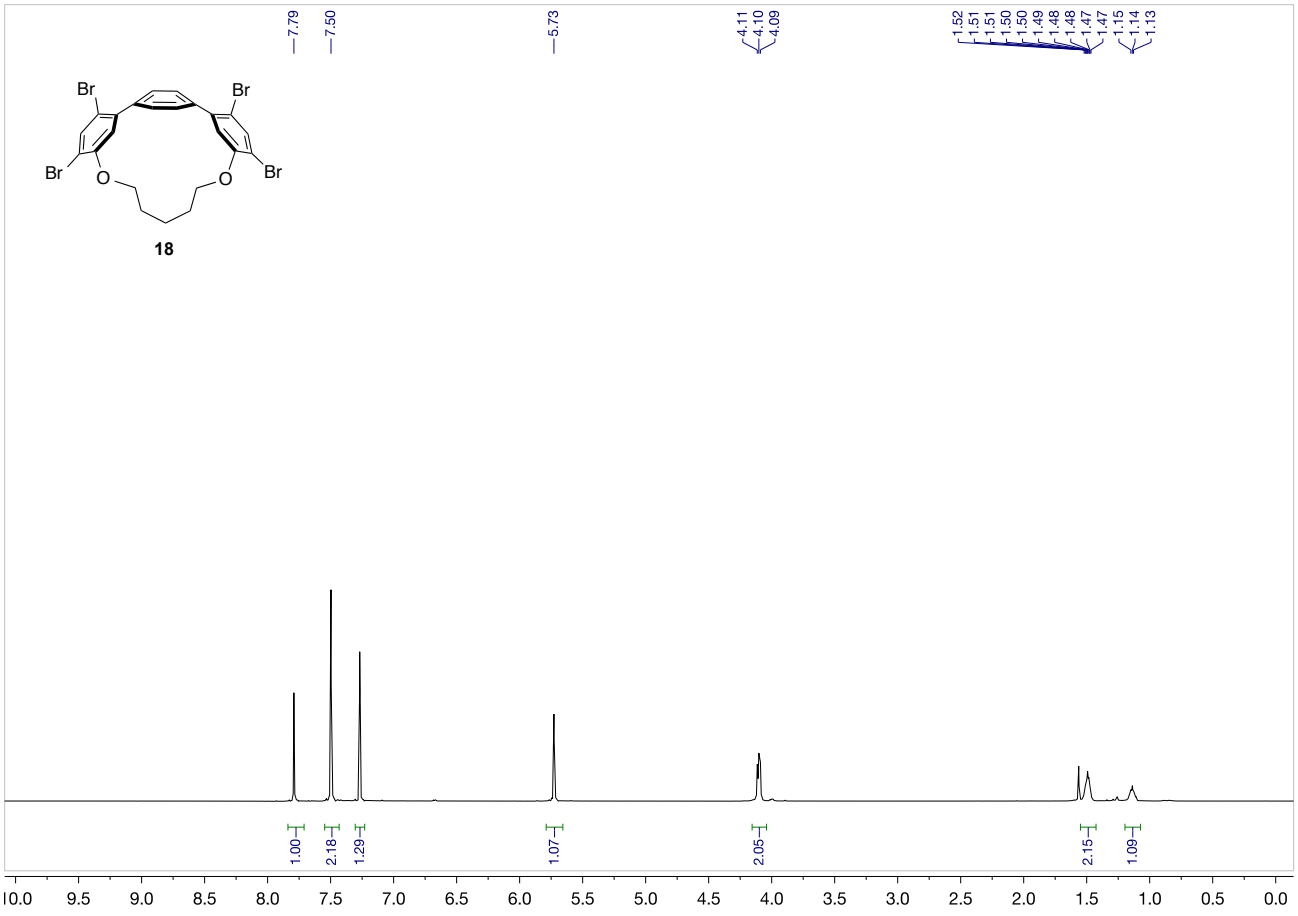
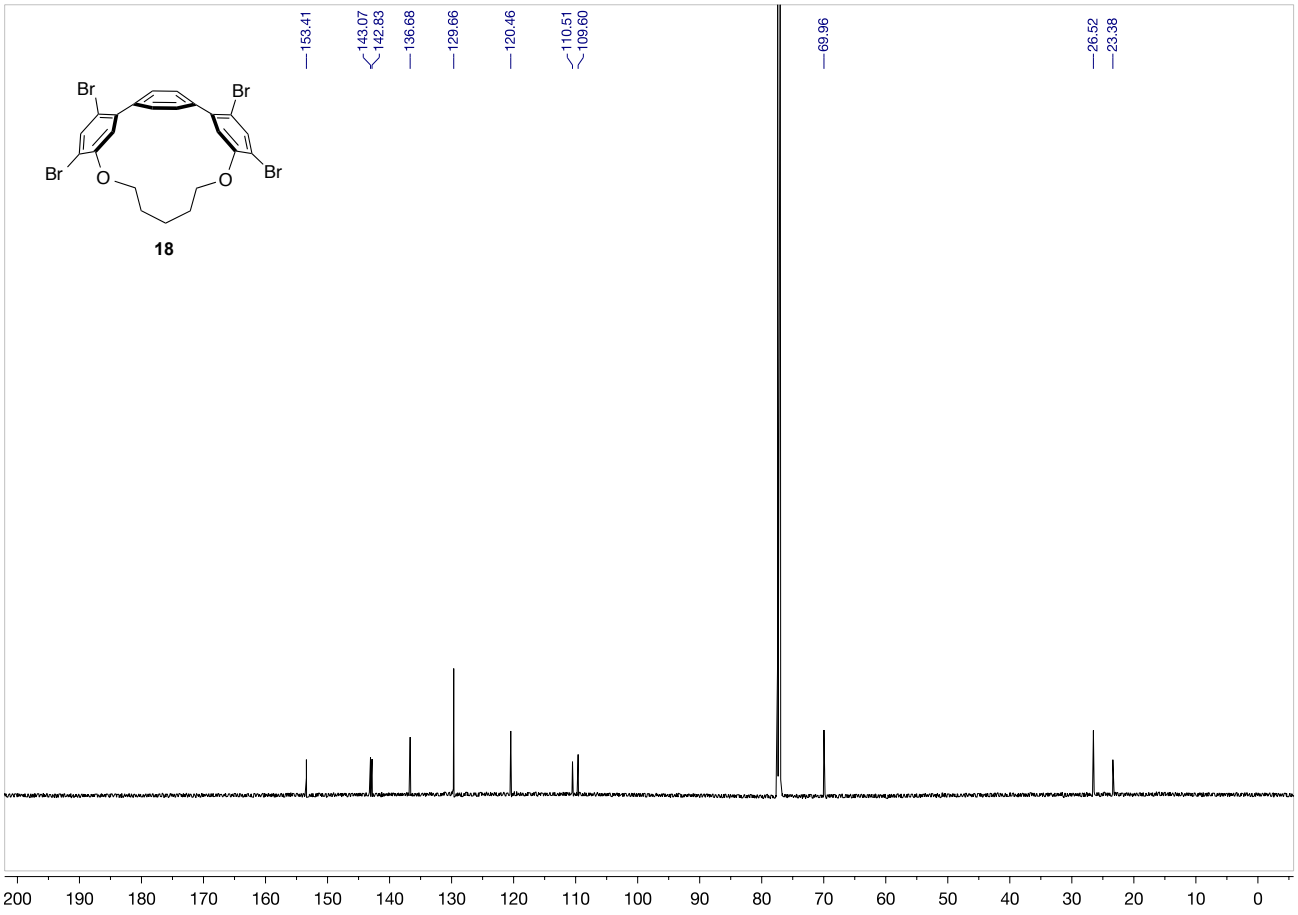
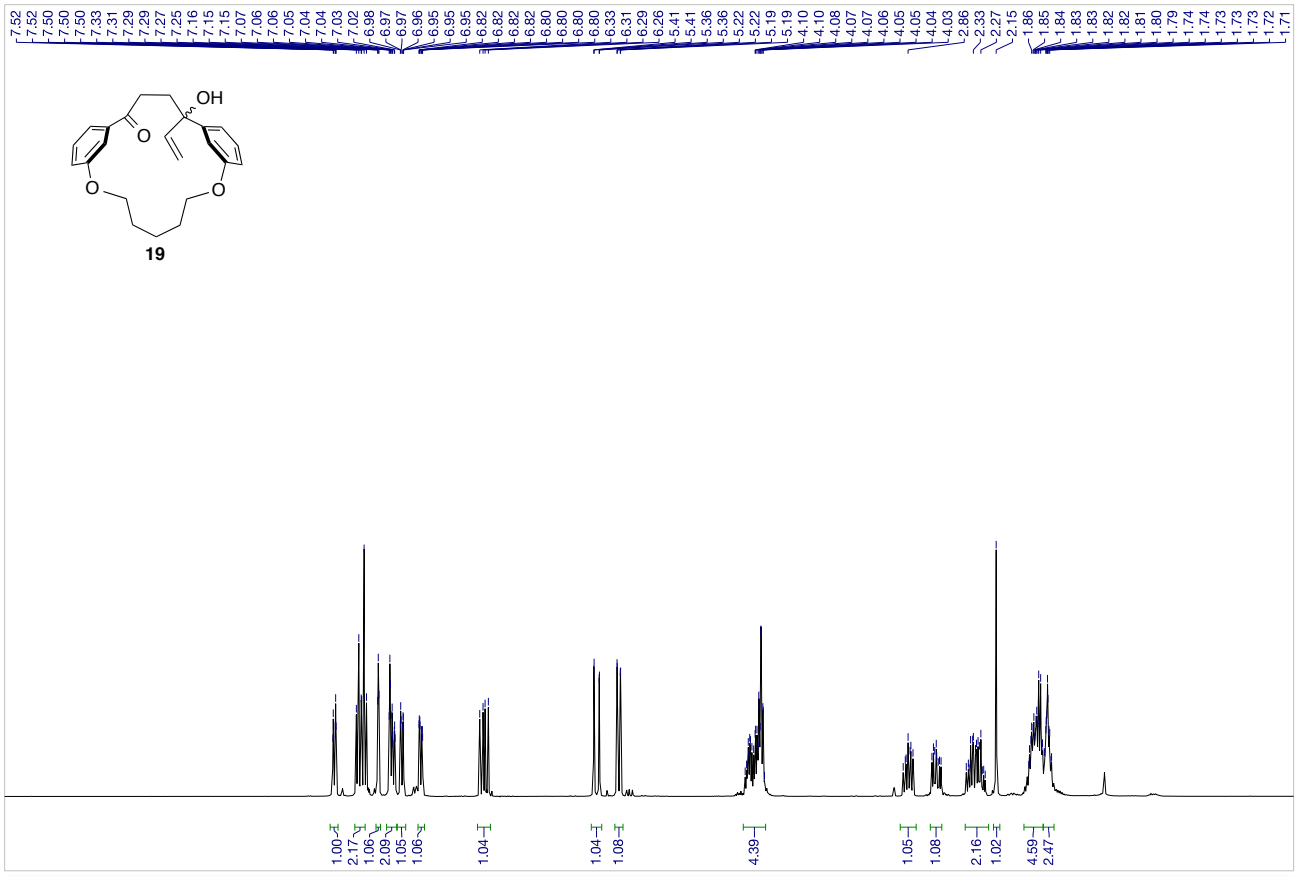
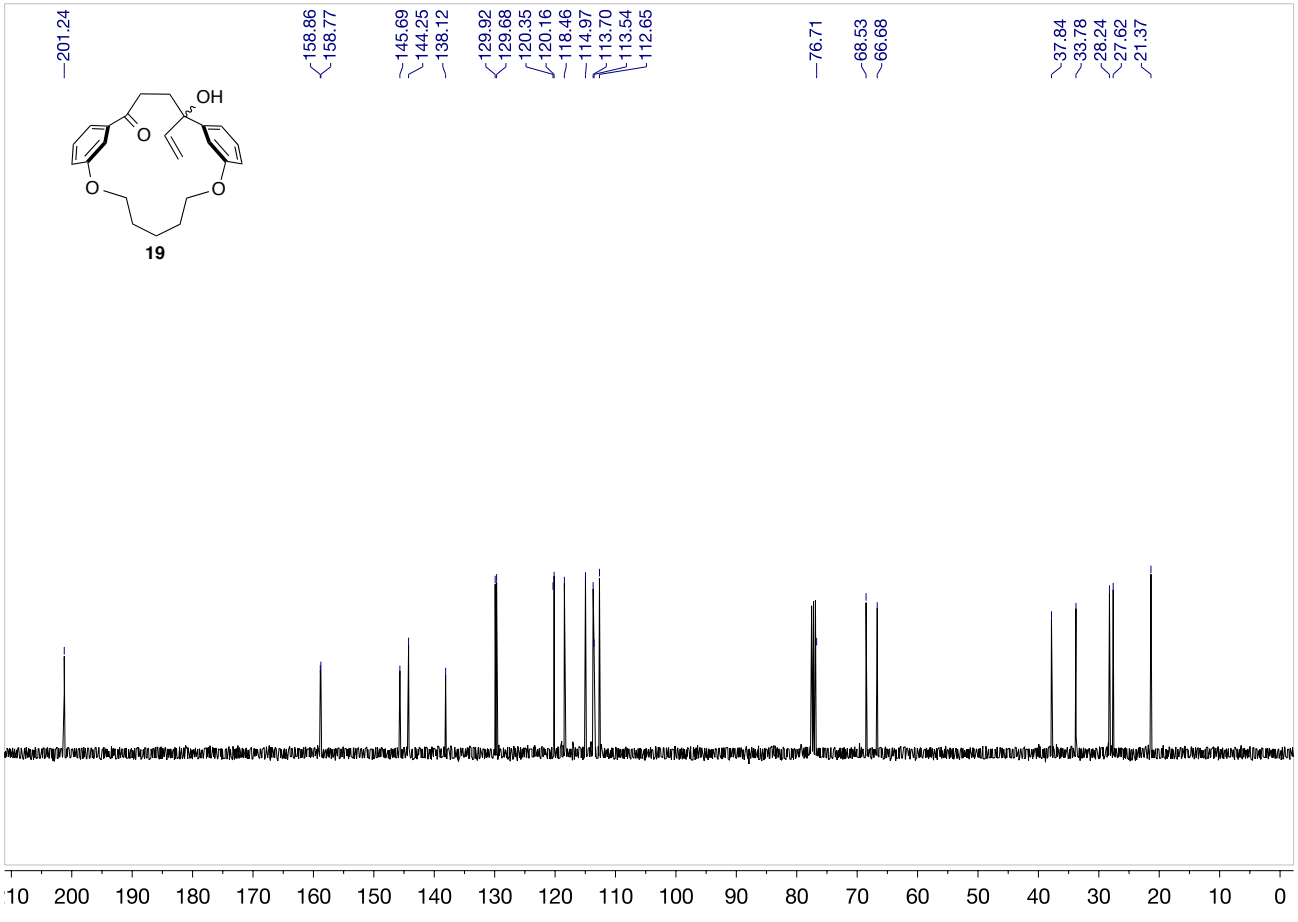
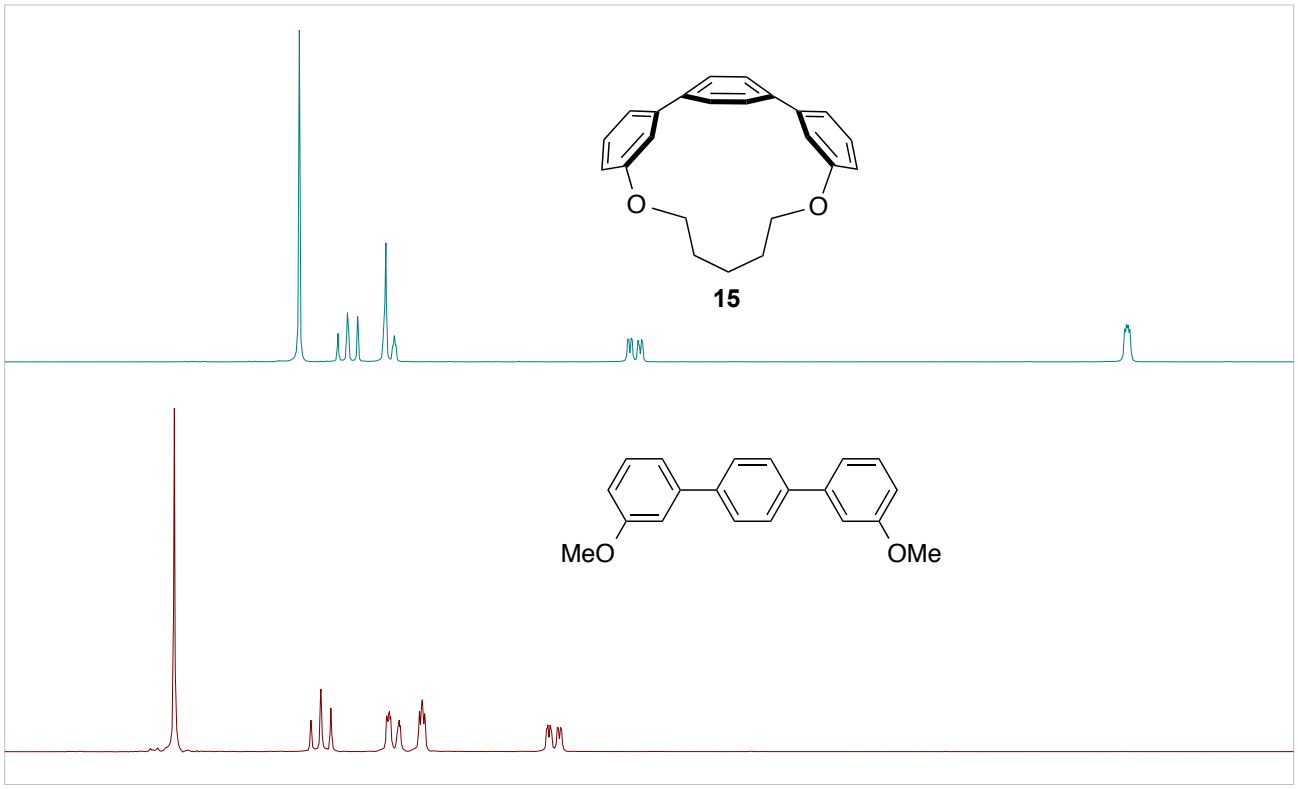
158.9878
138.3598
138.1070
130.8726
121.2569
121.0038
116.0404
77.4489
77.3374
77.0257
69.2305
28.5629
22.4592
17
200
150
100
50
[ppm]


7.79
7.50
5.73
4.11
4.10
4.09
1.52
1.51
1.51
1.50
1.50
1.49
1.48
1.48
1.47
1.47
1.15
1.14
1.13
Br
Br
Br
Br
O
O
18
1.00
2.18
1.29
1.07
2.05
2.15
1.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

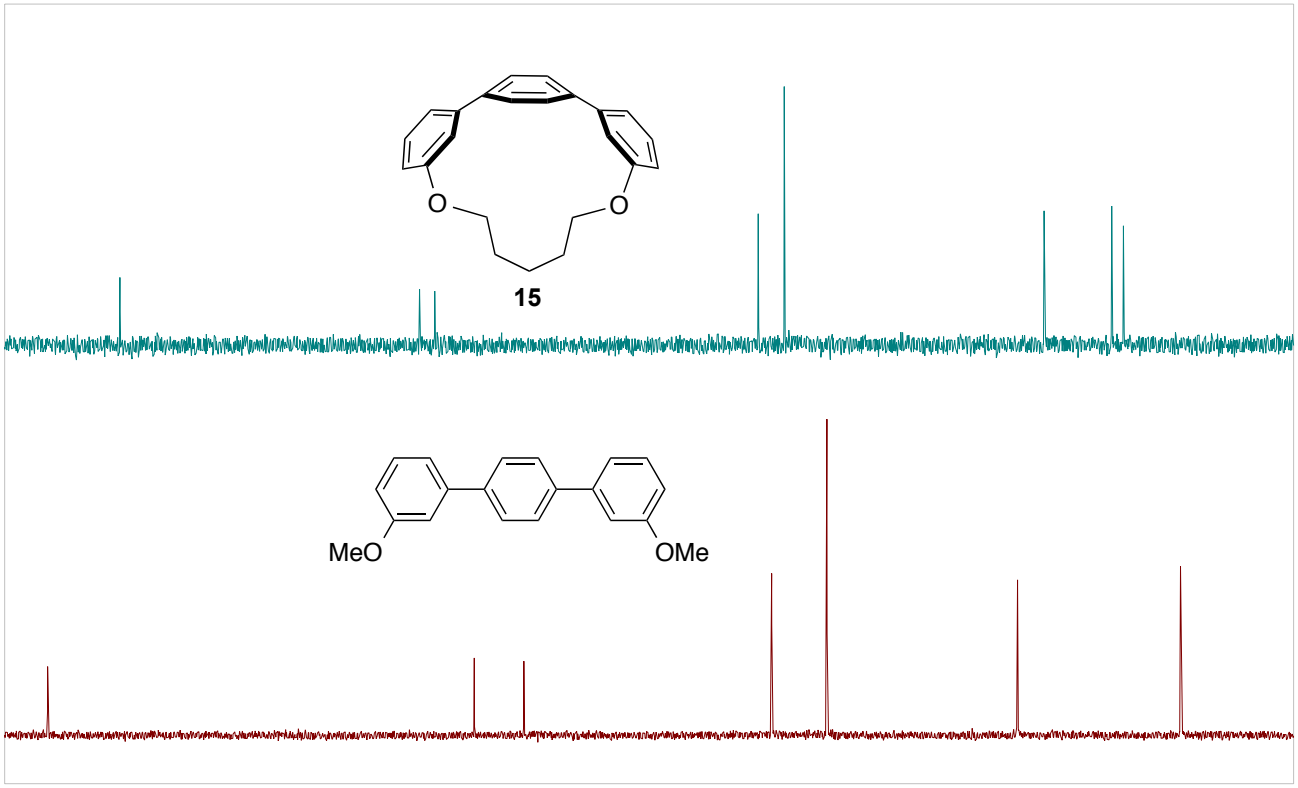

153.41
143.07
142.83
136.68
129.66
120.46
110.51
109.60
69.96
26.52
23.38
Br
Br
Br
Br
O
O
18
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OH
O
O
O
19


OH
O
O
O
19


O
O
15
MeO
OMe

8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5


O
O
15
MeO
OMe

160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110

X-ray Crystal Structure and Relevant Data for Compound 15

Table SI-1: Crystal Data and Structure Refinement for (Merner112414b) Compound **15**

Identification code	Merner112414b	
Empirical formula	C_{23} H_{24} O_2	
Formula weight	332.42	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.099(3) Å	α = 90°
	b = 13.445(4) Å	β = 90°
	c = 16.407(5) Å	γ = 90°
Volume	1786.6(9) Å3	
Z	4	
Density (calculated)	1.236 g/cm3	
Absorption coefficient	0.077 mm-1	
F(000)	712	
Crystal size	0.05 x 0.08 x 0.10 mm3	
Theta range for data collection	1.96 to 22.73°	
Index ranges	-8<=h<=8, -14<=k<=14, -17<=l<=17	
Reflections collected	10323	
Independent reflections	2402 [R(int) = 0.0708]	
Completeness to theta = 22.73°	99.9%	
Absorption correction	Multiscan	
Max. and min. transmission	0.9960 and 0.9920	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	2402 / 0 / 226	
Goodness-of-fit on F2	0.973	
Final R indices [I>2sigma(I)]	R1 = 0.0404, wR2 = 0.0680	
R indices (all data)	R1 = 0.0587, wR2 = 0.0721	
Absolute structure parameter	1.9(10)	
Largest diff. peak and hole	0.151 and -0.127	

Table SI-2: Bond Lengths and Angles for (Merner112414b) Compound 15

O1-C26	1.371(4)
O1-C2	1.442(4)
O8-C21	1.377(4)
O8-C6	1.440(4)
C16-C15	1.376(5)
C16-C26	1.395(5)

C26-C17	1.382(4)
C2-C3	1.529(4)
C3-C4	1.515(4)
C4-C5	1.527(4)
C5-C6	1.523(4)
C21-C20	1.381(4)
C21-C9	1.392(4)
C9-C10	1.384(5)
C15-C14	1.387(5)
C14-C25	1.397(4)
C25-C17	1.395(4)
C25-C24	1.485(4)
C24-C18	1.391(4)
C24-C13	1.392(4)
C18-C19	1.385(4)
C19-C23	1.394(4)
C23-C12	1.389(4)
C23-C22	1.484(4)
C22-C11	1.383(4)
C22-C20	1.399(5)
C11-C10	1.390(5)
C12-C13	1.385(4)

C26-O1-C2	117.2(3)
C21-O8-C6	117.5(3)
C15-C16-C26	119.1(3)
O1-C26-C17	123.8(3)
O1-C26-C16	117.0(3)
C17-C26-C16	119.1(3)
O1-C2-C3	114.8(3)
C4-C3-C2	111.2(3)
C3-C4-C5	115.1(3)
C6-C5-C4	112.5(3)
O8-C6-C5	114.0(3)
O8-C21-C20	123.5(3)
O8-C21-C9	117.7(3)
C20-C21-C9	118.8(3)
C10-C9-C21	119.8(3)
C16-C15-C14	122.4(3)
C15-C14-C25	118.6(3)
C17-C25-C14	119.0(3)
C17-C25-C24	113.7(3)
C14-C25-C24	126.5(3)
C18-C24-C13	117.8(3)
C18-C24-C25	119.8(3)
C13-C24-C25	118.7(3)

C19-C18-C24	120.6(3)
C18-C19-C23	120.6(3)
C12-C23-C19	117.7(3)
C12-C23-C22	119.8(3)
C19-C23-C22	119.3(3)
C11-C22-C20	119.5(3)
C11-C22-C23	127.7(3)
C20-C22-C23	112.5(3)
C22-C11-C10	119.0(3)
C9-C10-C11	121.4(3)
C26-C17-C25	121.7(3)
C21-C20-C22	121.4(3)
C13-C12-C23	120.6(3)
C12-C13-C24	120.6(3)

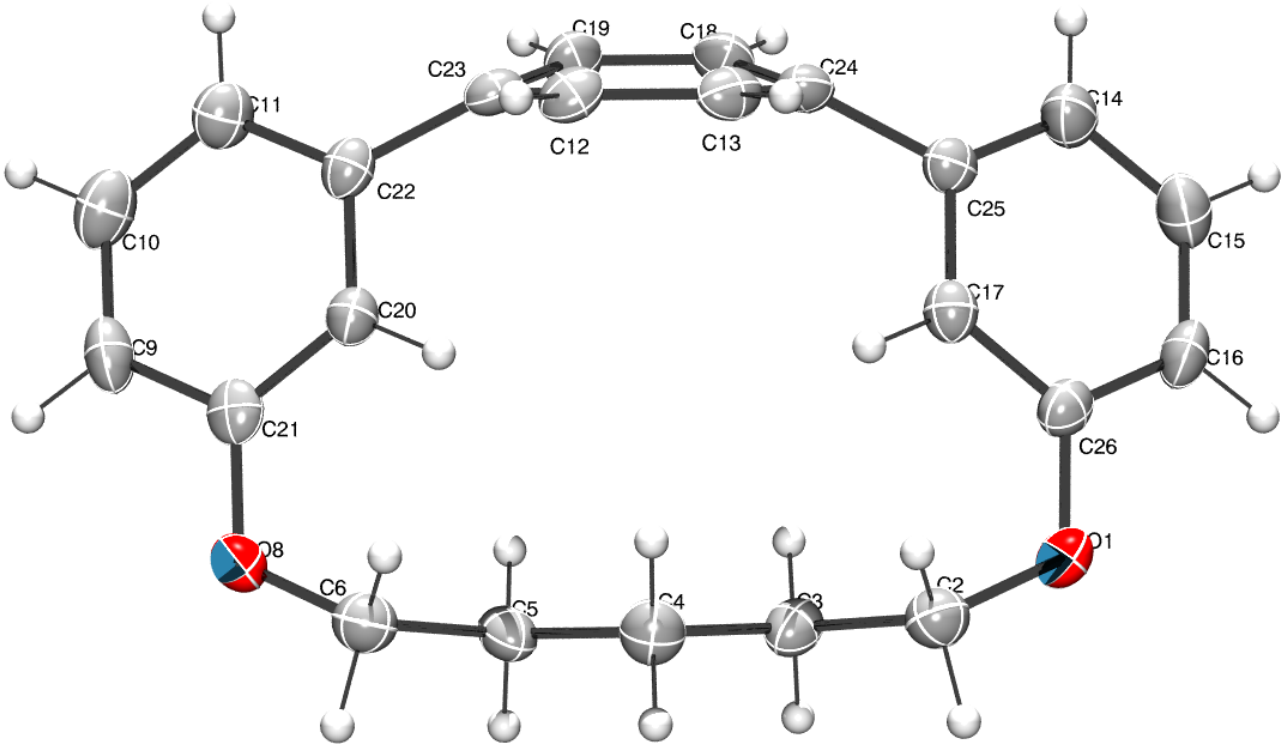


FIGURE SI-2: X-ray crystal structure of compound 15