Supporting Information

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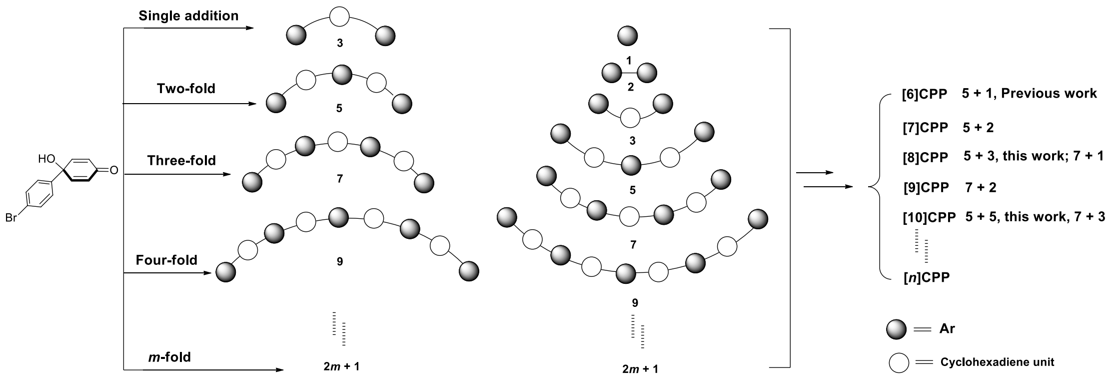


Figure S1. Suggested general synthetic approach—sequential oxidative dearomatization/ addition procedure—towards to [*n*]CPPs.

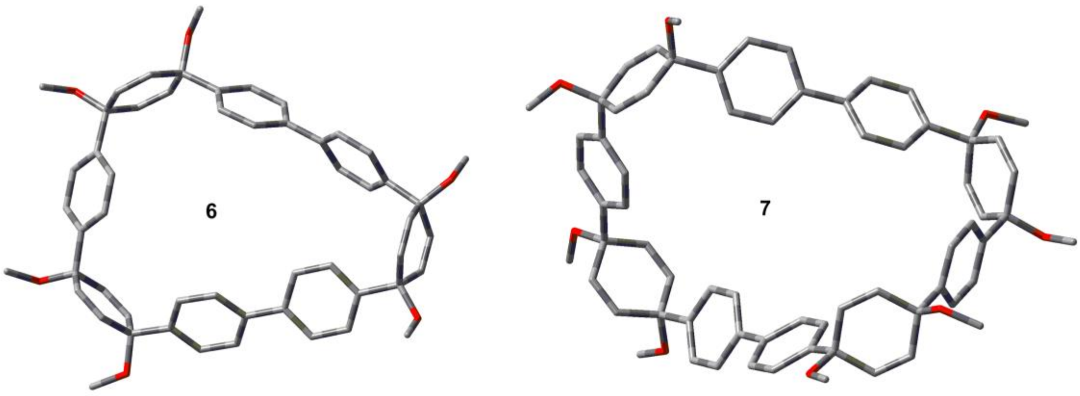


Figure S2. Optimized geometries of [8]- and [10]macrocycle.

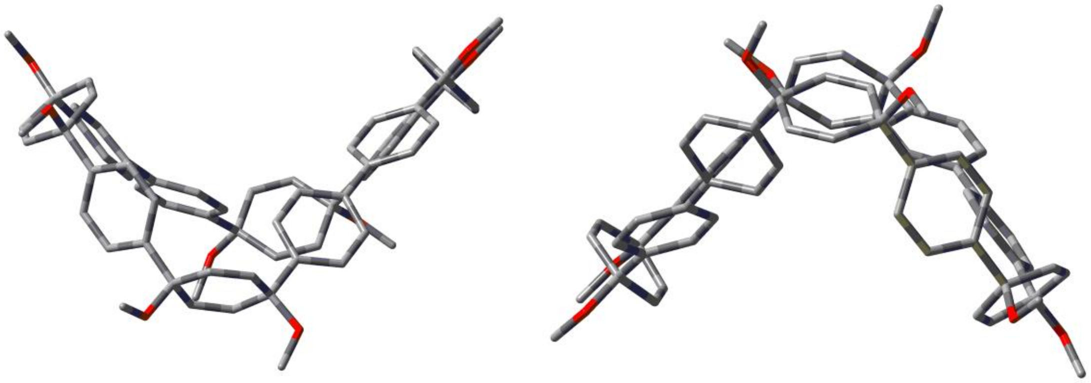


Figure S3. Optimized geometry of [10]macrocycle.

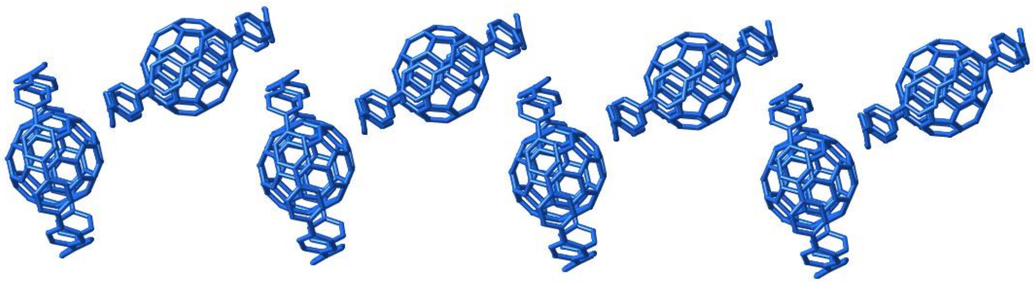


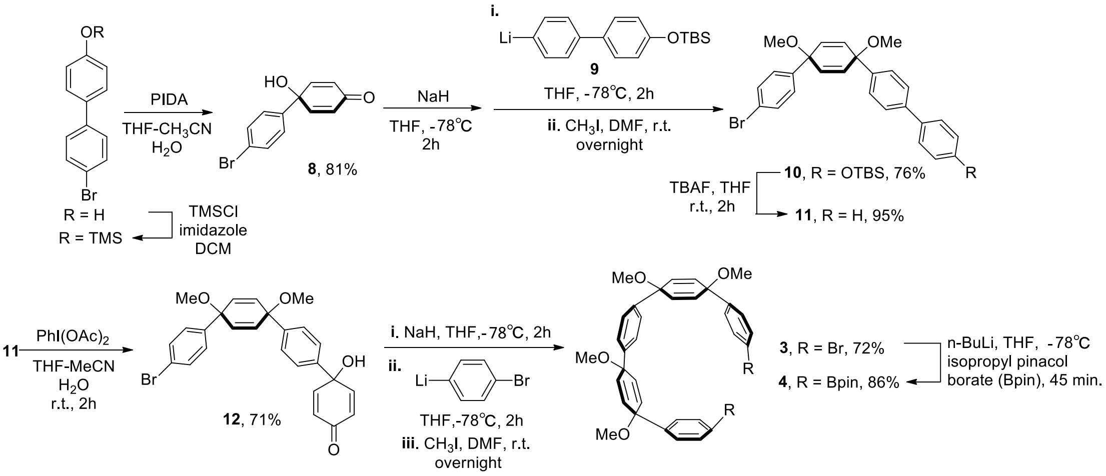
Figure S4. Packing structure of C_{60}@[10]CPP (Side View).

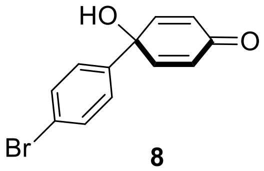
General Experimental Details. Moisture sensitive reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk technique. The starting materials 4-Bromo-4’[(tert-butyldimethylsilyl)oxy]biphenyl[1] and compound **5**[2] were prepared according to typical literature procedure. All other starting materials and chemicals were commercially available. All reagents were obtained commercially. Tetrahydrofuran, dicholoromethane, and dimethylformamide were dried by filtration through alumina according to the methods described by Grubbs[3].

^{1}H NMR spectra were recorded at 500 MHz or 400 MHz on a Varian VNMRS. ^{13}C NMR spectra were recorded at 125 MHz or 100 MHz on a Varian VNMRS. All NMR spectra were referenced to TMS. The matrix used for MALDI was a solution of 10 mg/ml of 7,7,8,8-tetracyanquinodimethane in THF with 1% silver trifluoroacetate as a promoter. Silica column chromatography was conducted with Zeochem Zeoprep 60 Eco 40-63 μm silica gel. Thin Layer Chromatography (TLC) was performed using Sorbent Technologies Silica Gel XHT TLC plates. Developed plates were visualized using UV light at wavelengths of 254 and 365 nm. All glassware was oven or flame dried and cooled under an inert atmosphere of nitrogen unless otherwise noted.

General details for the X-ray diffraction analysis:[4] Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: OLEX2 (Dolmanov, *et al.* 2009); software used to prepare material for publication: PublCIF v.1.9.5_c (IUCr).

Experimental Section



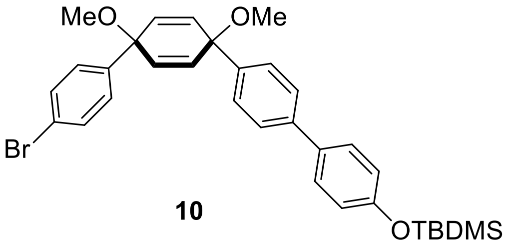


8

To a stirred slurry of 4’-bromo-(1,1’-biphenyl)-4-ol (50.5 g, 0.2 mol, 1 equiv.) and imidazole (22.1 g, 0.32 mol, 1.6 equiv.) in 300 mL dichloromethane was added neat chlorotrimethylsilane (33.0 mL, 0.26 mol, 1.3 equiv.) at 0 ℃. The mixture was then allowed to warm up to room temperature and stirred for 16 h. With stirring, 1 M aqueous sodium bicarbonate (150 mL) was added and the layers were separated. The organic layer was washed one additional time with 1 M aqueous sodium bicarbonate (150 mL) followed by a saturated brine solution (150 mL). The organic layer was then dried over sodium sulfate and concentrated under reduced pressure to afford the TMS-protected bisphenol as an off-white solid (64 g), which was used directly without further purification.

To a stirred solution of this TMS-protected bisphenol (64 g) in a mixture of THF (1000 mL), CH_3CN (250 mL) and H_2O (400 mL) was added (diacetoxyiodo)benzene

(97 g, 0.3 mol, 1.5 equiv) slowly as a solid over the course of 30 minutes. The reaction mixture was allowed to stir for another 16 h at room temperature before quenching with saturated $NaHCO_3$ solution. The mixture was then extracted with CH_2Cl_2 (3 × 200 mL), the organic phase was separated and washed with water (3 × 150 mL) and dried over sodium sulfate. After removing solvent under reduced pressure, The crude orange solid was then washed with CH_2Cl_2 (150 mL) to give ketone **8** as a white solid (43 g, 81% over two steps). ^1H NMR (400 MHz, $CDCl_3$):[5] δ(ppm) 7.51 (d, *J* = 8 Hz, 2H, Ar), 7.35 (d, *J* = 8 Hz, 2H, Ar), 6.85 (d, *J* = 10.0 Hz, 2H, CH=CH), 6.24 (d, *J* = 10.0 Hz, 2H, CH=CH), 2.57 (s, 1H, OH).

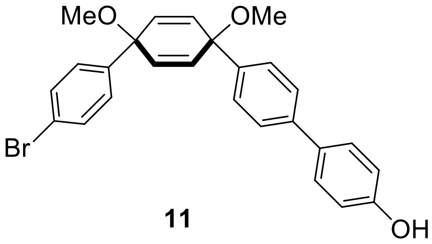


10

To a slurry of sodium hydride (5.88 g, 147 mmol, 60% in mineral oil) in 300 mL of THF was added slowly a solution of the ketone **8** (30 g, 113 mmol) in 500 mL of THF at –78 ℃, the reaction mixture was stirred for another 2 h at -78 ℃ to generate the deprotonated ketone.

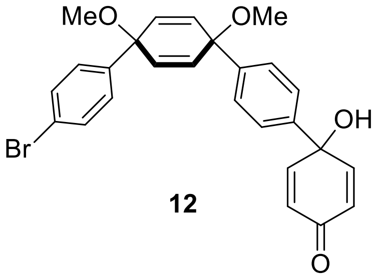
In a separate 1000 mL flask, 4-Bromo-4’[(tert-butyldimethylsilyl)oxy]biphenyl[1] (86 g, 237 mmol) was dissolved in 500 mL dry THF. This solution was cooled down to -78℃. n-BuLi (100 mL, 249 mmol, 2.5 M in hexane) was added slowly to this solution, then the reaction mixture was allowed to stir for 30 min at –78 ℃ to give **9**. This lithium reagent (**9**) was transferred to the slurry containing deprotonated ketone via cannula, and the resulting mixture was allowed to stir for another 2 h at –78 ℃.

CH_3I (28.2 mL, 452 mmol) and dry DMF (200 mL) were then added to quench the addition reaction, the reaction mixture was allowed to warm up to room temperature and stir for overnight. Water (400 mL) was added carefully to quench the methylation reaction, and the resulting mixture was extracted with diethyl ether (3 × 250 mL). The combined organic layer was washed with water (3 × 150 mL) and brine (200 mL) and dried over sodium sulfate. After concentrating under reduced pressure, the crude product was purified by column on silica gel (Ethyl Acetate/hexane = 1:4) to give compound **10** as a white solid (49.7 g, 76%, m.p. 125-127 ℃). ^{1}H NMR (400 MHz，$CDCl_3$): δ(ppm) 0.22 (s, 6H, Si-CH_3), 1.00 (s, 9H, C(CH_3)), 3.42 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 6.05 (d, *J* = 10 Hz, 2H, CH=CH), 6.16 (d, *J* = 10 Hz, 2H, CH=CH), 6.89 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.27 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.39-7.48 (m, 6H, Ar-H), 7.50 (d, *J* = 8.4 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) -4.39, 18.22, 25.68 (TBDMS), 51.97, 52.01 (OCH_3), 74.56, 74.59 (C-OMe), 120.31, 121.55, 126.28, 126.72, 127.83, 128.03, 131.39, 132.89, 133.69, 133.77, 140.26, 141.49, 142.56, 155.36 (Ar). HRMS (Q-TOF ES+) m/z calcd for $C_{32}H_{37}BrO_3Si$ $(M-OCH_3)^+$: 544.1433, Found: 544.1426. IR (neat): 2930, 2857, 1607, 1493, 1254, 1080, 822 cm^{-1}.



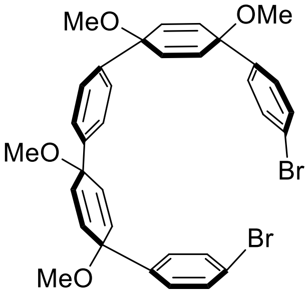
11

To a stirred solution of **10** (48 g, 83.1 mmol) in 400 mL THF was added 100 mL TBAF (100 mmol, 1 M in THF). The reaction mixture was allowed to stirred for 2 h at room temperature. Water (100 mL) was then added and the reaction mixture was extracted with diethyl ether (3 × 150 mL), the combined organic phase was washed with water (3 × 100 mL) and dried over sodium sulfate. After concentrating under reduced pressure, the crude yellow solid was passed through a short pad of silica (Ethyl Acetate/hexane = 1:1) to afford **11** as a white solid (36.7 g, 95%, m.p. 197 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 3.43 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 5.35 (s, 1H, OH), 6.07 (d, *J* = 10.4 Hz, 2H, CH=CH), 6.17 (d, *J* = 10.4 Hz, 2H, CH=CH), 6.83 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.27 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.39-7.49 (m, 8H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 51.97, 52.01 (OCH_3), 74.61, 74.68 (C-OMe), 115.64, 121.60, 126.32, 126.69, 127.82, 128.24, 131.42, 132.91, 133.19, 133.64, 140.18, 141.36, 142.40, 155.26 (Ar). HRMS (Q-TOF ES+) m/z calcd for $C_{26}H_{23}BrO_4$ $(M\text{-}OCH_3)^+$: 436.0602, Found: 436.0620. IR (neat): 3361, 1608, 1481, 1259, 1176, 822, 808 cm^{-1}.



12

To a stirred solution of **11** (18 g, 38.84 mmol) in a mixture of THF (500 mL), CH_3CN (150 mL) and H_2O (200 mL) was added (diacetoxyiodo)benzene (18.76 g, 58.26 mmol) slowly as a solid over the course of 1h. The resulting mixture was stirred for 2 h at room temperature before quenching with saturated $NaHCO_3$ solution. The reaction mixture was extracted with dichloromethane (3 × 150 mL), and the combined organic phase was washed with water (3 × 100 mL) and dried over sodium sulfate. After removing solvent under reduced pressure, the crude yellow solid was purified by column on silica gel using ethyl acetate/hexane = 1:1 as eluent to give compound **12** as a white solid (13.25 g, 71%, m.p. 190-191 ℃). ^{1}H NMR (400 MHz，CDCl$_3$): δ(ppm) 2.99 (s, 1H, OH), 3.41 (s, 6H, OCH$_3$), 6.07 (dd, *J* = 10 Hz, 4H, CH=CH), 6.19 (d, *J* = 10 Hz, 2H, CH=CH), 6.85 (d, *J* = 10 Hz, 2H, CH=CH), 7.25 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.36-7.44 (m, 6H, Ar-H). ^{13}C NMR (100 MHz, CDCl$_3$): δ(ppm) 51.99, 52.01 (OCH$_3$), 70.77(C-OH), 74.39, 74.47 (C-OMe), 121.64, 125.42, 126.48, 126.76, 126.84, 127.72, 131.45, 133.18, 133.43, 138.12, 142.34, 143.49, 150.76 (Ar), 185.75 (C=O). HRMS (Q-TOF ES+) m/z calcd for $C_{26}H_{23}BrO_4$ (M)$^+$: 479.0858, Found: 479.0859. IR (neat): 3418, 2934, 1662, 1622, 1398, 1265, 1082, 1033, 947, 857, 737 cm^{-1}.

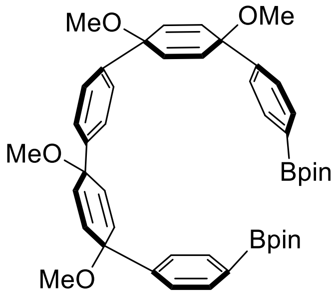


3

To a slurry of sodium hydride (2.17 g, 54.24 mmol, 60% in mineral oil) in 200 mL of THF was added a solution of ketone **12** (20 g, 41.72 mmol) in 300 mL dry THF at –78 ℃. The reaction mixture was stirred for another 2 h at –78 ℃ to generate the deprotonated ketone.

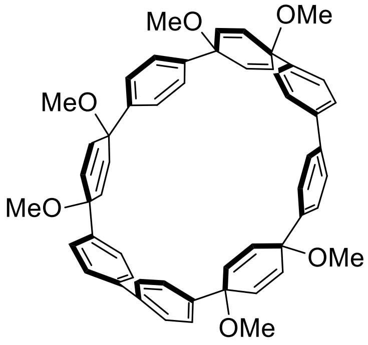
In a separate 500 mL round flask, 1,4-dibromobenzene (23.6 g, 100 mmol) was dissolved in 300 mL of THF, this solution was cooled down to –78 ℃, and then n-BuLi (42 mL, 105 mmol, 2.5 M in hexane) was added slowly to this solution. After the addition, the reaction mixture was stirred for 30 min to form the lithium reagent.

This mixture was then transferred to the slurry containing the deprotonated ketone via cannula, and the resulting mixture was allowed to stir for another 2 h at –78 ℃. CH_3I (10.42 mL, 167 mmol) and dry DMF (160 mL) were then added to quench the addition reaction, the reaction mixture was allowed to warm up to room temperature and stir for overnight. Water (300 mL) was added carefully to quench the methylation reaction, and the resulting mixture was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic layer was washed with water (3 × 150 mL) and brine (200 mL) and dried over sodium sulfate. After concentrating under reduced pressure, the crude off-white solid was purified by column on silica gel (Ethyl Acetate/hexane = 1:4) to give dibromide **3** as a white solid (20.1 g, 72%, m.p. 185-186 ℃). ^{1}H NMR (400 MHz，$CDCl_3$): δ(ppm) 3.41 (s, 12H, OCH_3), 6.04 (d, *J* = 10 Hz, 4H, CH=CH), 6.10 (d, *J* = 10 Hz, 4H, CH=CH), 7.25 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.33 (s, 4H, Ar-H), 7.42 (d, *J* = 8.4 Hz, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 51.97 (OCH_3), 74.46, 74.52 (C-OMe), 121.58, 126.03, 127.77, 131.40, 132.98, 133.63, 142.51, 142.66 (Ar). HRMS (Q-TOF ES+) m/z calcd for $C_{26}H_{23}BrO_4$ (M – 2OCH_3)$^+$: 601.3215, Found (isotopic pattern): 599.3282, 600.3158, 601.3227, 602.3257, 603.3302. IR (neat): 2948, 1483, 1400, 1270, 1072, 1010, 948, 818, 730 cm^{-1}.



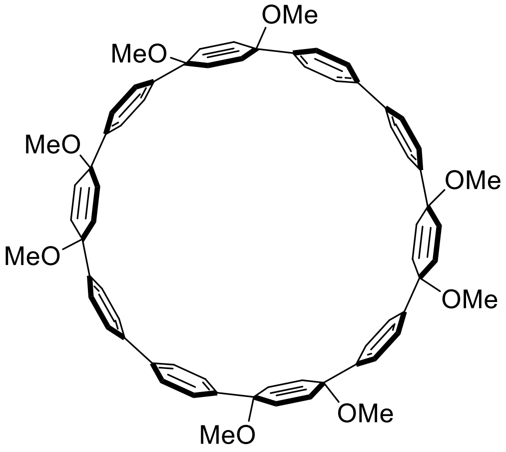
4

Dibromide **3** (10 g, 15 mmol) was dissolved in 240 mL of tetrahydrofuran and cooled down to –78 °C. To this solution was added n-BuLi (13.2 mL, 33 mmol, 2.5 M in hexane) over 6 min. After the addition of n-BuLi, neat isopropyl pinacol borate (11.84 mL, 60 mmol) was added immediately and rapidly, and the solution was stirred for 30 min at –78 °C. The reaction was then warmed up to room temperature and water (100 mL) was added to the solution and the mixture was allowed to stir for 15 min before extracting with CH_2Cl_2 (3 × 80 mL). The combined organic layers were washed with a saturated brine solution and then dried over magnesium sulfate. After removing the solvent under vacuum, the crude product was purified by recrystallization from hot ethyl acetate to afford compound **4** as a white solid (9.8 g, 86%, m.p. 251 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) 1.33 (s, 24 H, CH_3), 3.42 (d, *J* = 3.6 Hz, 12H, OCH_3), 6.08 (s, 8H, CH=CH), 7.34 (s, 4H, Ar), 7.39 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.74 (d, *J* = 8.4 Hz, 4H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 24.84 (CH_3), 51.92 (OCH_3), 74.61, 74.90 (C-OMe), 83.73 ($C(Me)_2$), 125.27, 126.05, 133.16, 133.35, 134.90, 142.70, 146.43 (Ar). HRMS (Q-TOF ES+) m/z calcd for $C_{46}H_{56}B_2O_8Na$ $(M + Na)^+$: 781.4075. Found: 781.4054. IR (neat): 2979, 2933, 2823, 1606, 1397, 1361, 1324, 1268, 1143, 1090, 1075, 1011, 947, 835 cm^{-1}.



6

Dibromide **3** (3.0 g, 4.5 mmol), diboronate **5** (2.45 g, 4.5 mmol), $Pd(OAc)_2$ (303 mg, 0.45 mmol, 0.1 equiv) and Cs_2CO_3 (7.33 g, 45 mmol, 5 equiv) were charged in a 2L flask under nitrogen, then 1650 mL degassed DMF/2-isopropanol (10:1) was added. The result mixture was heated to 100 ℃ and stirred for 24 h. After cooling to rt, the mixture was filtered through a short plug of Celite, and 500 mL water was added to the filtrate. After extraction with dichloromethane (3 × 150 mL), the combined organic phase was washed with water (8 × 100 mL) and dried over sodium sulflate. After removing the solvent under vacuum, the crude mixture was purified by silica column chromatography (ethyl acetate/hexane = 2:3) to give the [8]macrocycle **6** as a white solid (1.8 g, 50%). ^1H NMR (400 MHz，$CDCl_3$): δ(ppm) 3.40-3.48 (m, 18H, OCH_3), 6.06 (d, *J* = 10.4 Hz, 4H, CH=CH), 6.14 (d, *J* = 10.4 Hz, 4H, CH=CH), 6.26 (s, 4H, CH=CH), 7.13 (*J* = 8.4 Hz, 4H, Ar-H), 7.37 (*J* = 8.4 Hz, 4H, Ar-H), 7.50-7.53 (m, 12H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 51.81, 52.12, 52.14 (OCH_3), 74.02, 74.54, 75.91 (C-OMe), 126.23, 126.51, 126.82, 127.15, 132.78, 133.50, 139.66, 139.85, 140.49, 142.80, 143.32 (Ar). MALDI-TOF *m/z* calcd for $C_{54}H_{50}O_6$ $(M)^+$: 794.97, Found: 795.0. IR (neat): 3030, 2980, 2929, 2893, 2818, 1606, 1493, 1447, 1392, 1358, 1265, 1224, 1172, 1074, 1014, 948, 821 cm^{-1}. (melting point is not available because compound decomposed when the temperature was raised to 280 ℃.)



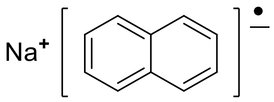
7

Method A: A mixture of dibromide **3** (664 mg, 1 mmol), diboronate **4** (759 mg, 1 mmol), Pd(OAc)$_2$ (135 mg, 0.2 mmol, 0.2 equiv), S-Phos (82 mg, 0.2 mmol, 0.2 equiv) and K_3PO_4 (849 mg, 4 mmol, 4 equiv) in DMF/H_2O (200 mL/20 mL, 10:1) was stirred at 100 ℃ for 16 h under nitrogen. After cooling down to rt, the mixture was filtered through a short plug of Celite, and 150 mL water was added to the filtrate. After extraction with dichloromethane (3 × 60 mL), the combined organic phase was washed with water (8 × 60 mL) and dried over sodium sulfate. After removing the solvent under vacuum, the crude mixture was purified by silica column chromatography (ethyl acetate/hexane = 2:3) to give the [10]macrocycle **7** as a white solid (556 mg, 55%). ^{1}H NMR (400 MHz，CDCl$_3$): δ(ppm) 3.45 (s, 12 H, OCH$_3$), 3.45 (s, 12 H, OCH$_3$), 6.02 (d, *J* = 11 Hz, 8H, CH=CH), 6.06 (d. *J*=11 Hz, 8H, CH=CH) 7.31 (s, 8H, Ar), 7.38 (d, *J* = 8 Hz, 8H, Ar), 7.46 (d, *J* = 8 Hz, 8H, Ar). ^{13}C NMR (100 MHz, CDCl$_3$): δ(ppm) 51.97, 52.03 (OCH$_3$), 74.80, 74.81 (C-OMe), 125.98, 126.27, 126.95, 133.26, 133.36, 139.63, 142.50, 142.82 (sp$_2$). MALDI-TOF *m/z* calcd for $C_{68}H_{64}O_8$ (M)$^+$: 1009.23, Found: 1009.2. IR (neat): 2920, 2847, 2820, 1739, 1593, 1486, 1449, 1402, 1183, 1074, 1014, 953, 823 cm^{-1}. (melting point is not available because compound decomposed when the temperature was raised to 300 ℃.)

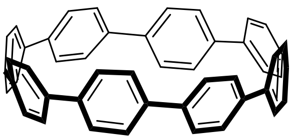
Method B. Dibromide **3** (3.19 g, 4.8 mmol), diboronate **4** (3.64 g, 4.8 mmol), Pd(OAc)$_2$ (324 mg, 0.48 mmol, 0.1 equiv) and Cs$_2$CO$_3$ (7.82 g, 48 mmol, 5 equiv) were charged in a 2L flask under nitrogen, then the degassed DMF (1600 mL) and 2-isopropanol (160 mL) was added. The result mixture was heated to 100 ℃ and stirred for 24 h. After cooling down to rt, the mixture was filtered through a short plug of Celite, and 500 mL water was added to the filtrate. After extraction with dichloromethane (3 × 150 mL), the combined organic phase was washed with water (8 × 100 mL) and dried over sodium sulfate. After removing the solvent under vacuum, the crude mixture was purified by silica column chromatography (ethyl acetate/hexane = 2:3) to give the [10]macrocycle **7** as a white solid (2.15 g, 44%).

Gram-scale procedures for [8]- and [10]CPP.

Preparation of sodium naphthalenide (1.0 M in THF):

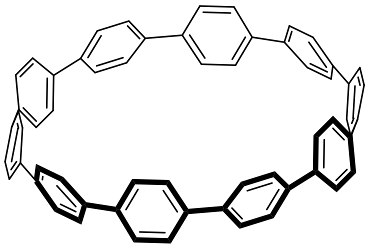


To a 50 mL dry roundbottom flask charged with a solution of naphthalene (3.85 g, 30 mmol) in 30 mL dry THF was added sodium metal (1.04 g, 45 mmol) under nitrogen. The reaction mixture was stirred for 18 h at room temperature. After this time, a green solution containing sodium naphthalenide (1.0 M in THF) was formed.



1, [8]-CPP

[8]macrocycle **6** (1.8 g, 2.26 mmol) was dissolved in 160 mL THF under nitrogen and cooled down to –78 ℃. At this point, the freshly prepared sodium naphthalenide (18 mL, 18 mmol, 1.0 M in THF (see above)) was added. The reaction mixture was stirred for 2 h at –78 ℃ before the addition of I_2 (15 mL of a 1 M solution in THF). Then the resulting mixture was warmed up to room temperature and sodium thiosulfate (saturated solution) was carefully added to remove excess I_2. Water (60 mL) was then added and the mixture was extracted with dichloromethane (3 × 60 mL), which was combined and washed brine (60 mL) and dried over sodium sulfate. After removing the solvent under reduced pressure, the crude yellow solid was purified by column on silica gel (CH_2Cl_2/Hexanes = 1:1) to give [8]CPP **1** as a yellow solid (1.04 g, 75%). ^1H NMR (400 MHz，$CDCl_3$): δ(ppm) 7.48 (s, 32H). ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 127.44, 137.63. MALDI-TOF *m/z* calcd for $C_{48}H_{32}$ $(M)^+$: 608.25, Found: 608.4.



2, [10]-CPP

[10]macrocycle **7** (2.1 g, 2.08 mmol) was dissolved in 160 mL THF under nitrogen and cooled down to –78 ℃. At this point, the freshly prepared sodium naphthalenide (25 mL, 25 mmol, 1.0 M in THF (see above)) was added. The reaction mixture was stirred for 2 h at –78 ℃ before the addition of I_2 (15 mL of a 1 M solution in THF). Then the resulting mixture was warmed up to room temperature and

sodium thiosulfate (saturated solution) was carefully added to remove excess I_2. Water (60 mL) was then added and the mixture was extracted with dichloromethane (3 × 60 mL), which was combined and washed brine (60 mL) and dried over sodium sulfate. After removing the solvent under reduced pressure, the crude yellow solid was purified by column on silica gel (CH_2Cl_2/Hexanes = 1:1) to give [10]CPP **2** as a yellow solid (1.03 g, 65%). ^{1}H NMR (400 MHz，$CDCl_3$): δ(ppm) 7.56 (s, 32H). ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 127.34, 138.14. MALDI-TOF *m/z* calcd for $C_{60}H_{40}$ $(M)^+$: 760.31. Found: 760.5.

Table S1. Crystal data, data collection and refinement of [8]CPP (**1**).

Compound **1** ([8]CPP)	
$C_{48}H_{32}$	V = 1934.66 (5) Å^3
M_r = 608.74	Z = 2
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, λ = 1.54178 Å
a = 12.9325 (2) Å	μ = 0.45 mm^{-1}
b = 8.0103 (1) Å	T = 100 K
c = 19.3676 (3) Å	0.15 × 0.09 × 0.09 mm
β = 105.363 (1)°	Block, yellow
θ = 3.7–65.7°	D_x = 1.045 Mg m^{-3}
Bruker Proteum-R diffractometer	3374 independent reflections
Absorption correction: multi-scan SADABS (Sheldrick, 1997)	3192 reflections with I > 2s(I)
Tmin = 0.657, Tmax = 0.753	Rint = 0.0000

3374 measured reflections	$h = -15 \rightarrow 10$ $k = 0 \rightarrow 9$ $l = -10 \rightarrow 22$
$R[F^2 > 2\sigma(F^2)] = 0.041$	0 restraints
$wR(F^2) = 0.113$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.09$	$\Delta\rangle_{\mathrm{max}} = 0.22$ e Å^{-3}
3374 reflections	$\Delta\rangle_{\mathrm{min}} = -0.16$ e Å^{-3}
220 parameters	

Table S2. Crystal data, data collection and refinement of [10]CPP (**2**).

Compound **2** ([10]CPP)	
$C_{60}H_{40}$	$V = 2544.84\ (12)$ Å^3
$M_r = 760.92$	$Z = 2$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 15.9075\ (4)$ Å	$\mu = 0.43$ mm^{-1}
$b = 8.1405\ (2)$ Å	$T = 100$ K
$c = 20.7418\ (6)$ Å	0.08 × 0.07 × 0.06 mm
$\beta = 108.655\ (2)°$	$D_x = 0.993$ Mg m^{-3}
Block, yellow	$\theta = 2.9–65.7°$
Bruker Proteum-R diffractometer	4384 independent reflections
Absorption correction: multi-scan *SADABS* (Sheldrick, 1997)	3596 reflections with $I > 2\sigma(I)$

T_{min} = 0.684, T_{max} = 0.753	R_{int} = 0.040
4384 measured reflections	$h = -18 \rightarrow 17$
	$k = 0 \rightarrow 9$
	$l = 0 \rightarrow 24$
$R[F^2 > 2\sigma(F^2)] = 0.051$	0 restraints
wR(F2) = 0.146	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0964P)^2 + 0.2599P]$
	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.10	$\Delta\rangle_{max}$ = 0.42 e Å^{-3}
4384 reflections	$\Delta\rangle_{min}$ = -0.19 e Å^{-3}
271 parameters	$(\Delta/\sigma)_{max} < 0.001$

Table S3. Crystal data, data collection and refinement of C_{60}@[10]CPP.

The encapsulation of C_{60} by [10]CPP	
$C_{60}H_{40}\cdot C_{60}$	$Z = 3$
M_r = 1481.52	$F(000)$ = 2280
Triclinic, P-1	D_x = 1.212 Mg m^{-3}
Hall symbol: -P 1	Cu $K\alpha$ radiation, λ = 1.54178 Å
a = 12.8737 (3) Å	Cell parameters from 9958 reflections
b = 19.0556 (4) Å	θ = 2.5–65.6°
c = 27.2224 (6) Å	μ = 0.53 mm^{-1}
α = 69.540 (2)°	T = 100 K
β = 79.038 (2)°	Block, purple
γ = 79.051 (2)°	0.14 × 0.04 × 0.03 mm
V = 6087.1 (2) Å^3	

Bruker Proteum-R diffractometer	19873 independent reflections
Radiation source: rotating anode	12766 reflections with $I > 2\sigma(I)$
multilayer	$R_{\text{int}} = 0.075$
ϕ & ω scans	$\theta_{\max} = 66.3°$, $\theta_{\min} = 2.5°$
Absorption correction: multi-scan SADABS (Sheldrick, 1997)	$h = -13 \rightarrow 13$
Tmin = 0.697, Tmax = 0.753	$k = -20 \rightarrow 22$
19873 measured reflections	$l = 0 \rightarrow 32$
Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full with fixed elements per cycle	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.077$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.224$	H-atom parameters constrained
S = 1.09	$w = 1/[\sigma^2(F_o^2) + (0.0905P)^2 + 5.2616P]$ where $P = (F_o^2 + 2F_c^2)/3$
19873 reflections	$(\Delta/\sigma)_{\max} = 0.025$
1621 parameters	$\Delta\rangle_{\max} = 0.30$ e Å^{-3}
0 restraints	$\Delta\rangle_{\min} = -0.31$ e Å^{-3}

Computational Details

The Gaussian 03 program[6] running on an IBM pSeries 655 system was used for optimization of structure **6** and **7** at the (B3LYP/6-31G*) level of theory. Structures were minimized with no symmetry restrictions.

Energy minimized structure of the ground state of [8]macrocycle (**6**):

C	-5.15820000	2.73487100	-0.84512200
H	-5.83826700	2.96636400	-1.65955000
C	-3.86966200	3.26247400	-0.86304900
H	-3.55524100	3.88953000	-1.69345600
C	-2.97007400	3.00633200	0.18505700
C	-1.56864300	3.50189600	0.14534400

C	-0.73151900	3.18561800	-0.93276500
H	-1.12227700	2.58867600	-1.75281600
C	0.60407800	3.59020300	-0.94973500
H	1.23221900	3.29654800	-1.78509400
C	1.14018100	4.34838100	0.09620700
C	3.35187100	4.49716400	-1.14479800
H	2.94690700	4.92381900	-2.06000500
C	4.44898900	3.74037800	-1.21483300
H	4.90751900	3.55902100	-2.18469500
C	5.23562700	1.58315000	-0.10592400
C	4.31528600	0.80590000	-0.81623800
H	3.52478700	1.28966700	-1.38329300
C	4.38341100	-0.58938100	-0.79027500
H	3.64584200	-1.16758200	-1.33936300
C	5.37127200	-1.24819600	-0.05084800
C	4.83466900	-3.50331000	-1.10788900
H	5.32199000	-3.31684500	-2.06255000
C	3.30872600	4.20353200	1.32710500
H	2.85811500	4.42462300	2.29074300
C	4.41946200	3.47426700	1.26137500
H	4.88222200	3.09021700	2.16687700
C	6.29529100	-0.46786000	0.65843300
H	7.06825300	-0.96218100	1.23862000
C	6.22985100	0.92185500	0.62946900
H	6.95468600	1.51015000	1.18353900
C	4.66731600	-3.14921900	1.36027700
H	5.05063000	-2.68242800	2.26441400
C	3.61576200	-3.96602400	1.40671300
H	3.12395400	-4.17505700	2.35438700
C	1.54500400	-4.30658600	0.07549700
C	0.60714900	-4.86134400	0.95773500
H	0.93395000	-5.59289600	1.68942500
C	-0.73271700	-4.48718800	0.90610600
H	-1.42501200	-4.90737100	1.63032900
C	-1.19643200	-3.55638000	-0.04033400
C	-2.61531800	-3.12355600	-0.09111400
C	-2.95074700	-1.83910200	-0.55055400
H	-2.16426400	-1.14519300	-0.83081900
C	-4.27284600	-1.41724900	-0.62812800
H	-4.48617800	-0.41943300	-0.99366000
C	-5.32167700	-2.25167400	-0.22361700
C	-4.99756800	-3.52658000	0.25841800
H	-5.79431500	-4.19025400	0.57933100
C	-3.67222100	-3.95793900	0.31130400

H	-3.46113200	-4.96849200	0.65022000
C	-7.10333300	-1.08423000	1.07905200
H	-7.25415000	-1.76848300	1.91047500
C	-7.19800500	0.23550600	1.24318800
H	-7.41858600	0.63758500	2.22867500
C	-5.58389500	1.89763400	0.19890800
C	0.29301300	4.69249900	1.16156700
H	0.67579800	5.31419300	1.96563300
C	-1.03024800	4.26387600	1.19520800
H	-1.66489300	4.53789900	2.03404800
C	-3.41820500	2.22598600	1.25890400
H	-2.74047200	2.01042900	2.08063600
C	-4.69774700	1.67040500	1.25805500
H	-4.99024300	1.02131400	2.07674700
C	-7.11840100	0.52852000	-1.21375500
H	-7.28929300	1.18461700	-2.06298800
C	-0.25408200	-3.02880800	-0.93772800
H	-0.57635300	-2.33987700	-1.71257800
C	1.08963600	-3.38646700	-0.87313800
H	1.78627100	-2.94903200	-1.58162100
C	3.80209000	-4.34680000	-1.05245800
H	3.46290700	-4.86051500	-1.95043300
C	5.13894100	3.11924800	-0.02031400
C	2.60857400	4.81595500	0.13420800
O	6.45873700	3.68574700	0.15972400
O	2.65047500	6.23670600	0.42239800
C	7.35008700	3.59762400	-0.94160000
H	7.08130800	4.29459200	-1.74704300
H	8.33440400	3.87717400	-0.55621300
H	7.40694000	2.57999000	-1.35205500
C	2.07377300	7.10424500	-0.54121800
H	2.04592400	8.09333800	-0.07617700
H	2.67782700	7.16870700	-1.45714000
H	1.04999500	6.80929200	-0.80878900
C	5.41080600	-2.78281800	0.09296400
C	3.02891700	-4.67546600	0.20450600
O	6.76532200	-3.22441000	0.35104100
O	3.03234100	-6.10590600	0.42101100
C	7.69422300	-3.10425400	-0.71648600
H	8.68068000	-3.28181100	-0.27949000
H	7.52076100	-3.85339500	-1.50101000
H	7.68280900	-2.10334000	-1.16899000
C	4.30447000	-6.69705700	0.65335300
H	4.79000900	-6.29849100	1.55324200

H	4.11468600	-7.76512700	0.78749100
H	4.98565700	-6.55596400	-0.19635100
C	-6.97824700	1.23141000	0.12256700
C	-6.78727100	-1.75768000	-0.24230400
C	-7.02801000	-0.78977500	-1.38012300
H	-7.08920500	-1.21021100	-2.38006400
O	-8.01328400	2.23816400	0.08570300
O	-7.69415400	-2.87658100	-0.27829900
C	-8.08376800	3.12916700	1.18611200
H	-8.40695900	2.63055500	2.11103500
H	-7.12707300	3.63504500	1.37252700
H	-8.83526800	3.87698000	0.91917100
C	-7.77437900	-3.60715500	-1.49250300
H	-6.78407900	-3.86263700	-1.89312800
H	-8.30683500	-4.53207600	-1.25431800
H	-8.34400700	-3.06738800	-2.26116800

Total energy: -2538.98603702228 a.u.

Energy minimized structure of the ground state of [10]macrocycle (**7**):

C	3.44841200	3.91895600	-1.95846200
C	3.24252600	3.04786300	-0.88009000
H	3.97530400	2.27599100	-0.66252400
C	2.10008400	3.14459700	-0.09302600
H	1.96753300	2.46068800	0.74093400
C	1.11951300	4.11734200	-0.35369500
C	-0.13806000	4.17150400	0.43225700
C	-0.73588300	5.39377000	0.78318600
H	-0.24180100	6.32510500	0.51939100
C	-1.93854000	5.43207200	1.48292100
H	-2.37804700	6.38718100	1.75398800
C	-2.59317700	4.25037500	1.85978600
C	5.13028500	-4.47422500	2.04462600
H	5.11719000	-5.50842300	1.70558200
C	6.18413300	-3.69242300	1.80206600
H	7.02955900	-4.09584100	1.24930400
C	6.38688500	-1.28416800	1.02729000
C	6.56317600	0.08558100	1.26306500
H	6.65154900	0.44608900	2.28361100
C	6.64386400	0.99441500	0.20908300
H	6.75243000	2.05057200	0.43381300
C	6.58724500	0.56369500	-1.12344900
C	6.86361000	2.96786500	-1.88568800
H	7.77090300	3.21083500	-1.33727700

C	5.96116900	3.92488100	-2.11074100
H	6.13019300	4.94142000	-1.76036800
C	5.48967200	1.37148500	-3.22137700
H	5.38141600	0.39357900	-3.68255300
C	4.60505800	2.33504900	-3.47168300
H	3.75489500	2.15367600	-4.12585400
C	1.35129300	5.00742000	-1.41332100
H	0.60372500	5.75935700	-1.65162800
C	2.49516700	4.91129100	-2.20602700
H	2.63823800	5.58844000	-3.03915100
C	-1.99707700	3.03093700	1.52148300
H	-2.48718200	2.09864000	1.78620200
C	-0.79144600	2.99222000	0.82348300
H	-0.36725200	2.03075500	0.54734700
C	6.32580300	-1.71513200	-0.30461200
H	6.18560200	-2.76796000	-0.52820900
C	6.44318200	-0.81007700	-1.35894300
H	6.43307900	-1.18162400	-2.37922600
C	4.06016200	-2.63887900	3.35327500
H	3.24528200	-2.29257300	3.98543800
C	5.10141800	-1.85050900	3.09250100
H	5.15521400	-0.85208300	3.51828100
C	-3.42029600	-3.84372500	-1.86075400
C	-2.72848600	-2.68180100	-1.50250100
H	-3.13713300	-1.70852300	-1.75683300
C	-1.51953300	-2.75337900	-0.81157500
H	-1.01712700	-1.83381800	-0.52446900
C	-0.96095100	-3.98842600	-0.44852400
C	0.30143100	-4.05495700	0.32869100
C	0.46258200	-4.98358400	1.36818300
H	-0.34550300	-5.67299100	1.59810400
C	1.61649600	-5.00442300	2.15111200
H	1.70569100	-5.70915700	2.96859700
C	2.65109500	-4.09393800	1.91546400
C	-4.29582000	3.07664700	3.32886600
H	-3.60006700	2.80158700	4.11882200
C	-5.35869900	2.30370200	3.09853700
H	-5.51046900	1.41543200	3.70817000
C	-6.52901600	1.40392700	1.03181200
C	-7.66868800	1.33020900	0.22013000
H	-8.45307600	2.07135100	0.34245000
C	-7.82084700	0.31595200	-0.72366800
H	-8.71223900	0.27579800	-1.33716700
C	-6.83559400	-0.66649200	-0.87825400

C	-5.96908400	-1.62191500	-3.02230000
H	-6.07445100	-0.70374400	-3.59725000
C	-5.00306800	-2.49858200	-3.30699800
H	-4.30348500	-2.30851200	-4.11910400
C	-6.83310300	-3.14471300	-1.23524200
H	-7.57178900	-3.36064000	-0.46572800
C	-5.87223600	-4.02420900	-1.52659900
H	-5.81053400	-4.97246200	-0.99576600
C	-1.65503600	-5.15153800	-0.82288900
H	-1.23276200	-6.12427200	-0.58525900
C	-2.85914300	-5.08188600	-1.51709500
H	-3.36309100	-5.99417000	-1.81712300
C	2.51455000	-3.18669900	0.85594400
H	3.31223300	-2.47983500	0.64459100
C	1.36118500	-3.16640400	0.07823600
H	1.28352800	-2.45745700	-0.74158300
C	-5.54297300	0.42439100	0.86837500
H	-4.64444100	0.45218400	1.47799900
C	-5.69581900	-0.59770500	-0.06873100
H	-4.92210300	-1.35460700	-0.15848800
C	-5.01956900	4.61178800	1.50309400
H	-4.86374200	5.52279400	0.93075500
C	-6.07804600	3.83925500	1.27169400
H	-6.80244200	4.11041200	0.50797100
C	-6.98613500	-1.79882800	-1.91132100
C	-4.78704400	-3.79765500	-2.56297500
O	-4.74318100	-4.90273000	-3.49497400
O	-8.31978000	-1.65600100	-2.43747200
C	-8.71611000	-2.59103500	-3.42618000
H	-9.73540600	-2.31394500	-3.70757000
H	-8.07474400	-2.54914100	-4.31658000
H	-8.71748800	-3.62080700	-3.04451000
C	-5.92317900	-5.14825600	-4.24267800
H	-6.78550000	-5.36825900	-3.59892100
H	-6.18214300	-4.30465700	-4.89688100
H	-5.70729600	-6.02335200	-4.86131900
C	-3.96677000	4.33333100	2.55314000
C	-6.39672200	2.57011700	2.03063000
O	-4.01906500	5.50217000	3.40476500
O	-7.68801400	2.85216300	2.62458400
C	-3.19388100	5.49077000	4.55973500
H	-2.15213400	5.23080000	4.32633500
H	-3.22179700	6.50790200	4.96005500
H	-3.57049600	4.80362800	5.32985500

C	-8.23813900	1.85188500	3.46789600
H	-9.26800500	2.16013200	3.66772700
H	-8.25107400	0.86325000	2.98913800
H	-7.70518300	1.77912100	4.42608500
C	4.66929200	3.72217200	-2.87328800
C	6.70054500	1.52761600	-2.32453200
O	4.55870100	4.71969000	-3.90277400
O	7.79403400	1.10693800	-3.17821800
C	5.56373500	4.69005700	-4.90642600
H	5.56365900	3.74343400	-5.46220900
H	5.32702400	5.50928300	-5.59000300
H	6.56776500	4.84552600	-4.49009800
C	9.09457100	1.11153200	-2.61178700
H	9.14194200	0.54603200	-1.67129500
H	9.74362000	0.62872200	-3.34732800
H	9.46969600	2.12922000	-2.43427900
C	6.28352100	-2.24396600	2.23088100
C	3.89959900	-4.04081400	2.81176300
O	3.65106400	-4.96429400	3.88690100
O	7.41392400	-2.03073400	3.11404400
C	8.70154000	-2.31712600	2.59157300
H	8.88612400	-1.80944100	1.63504600
H	9.41554000	-1.94567200	3.33159200
H	8.86713600	-3.39558700	2.46033900
C	4.67265500	-5.06714300	4.86913700
H	4.30542300	-5.78581500	5.60613200
H	5.61720400	-5.43449700	4.44657500
H	4.86609900	-4.10701800	5.36456600

Total energy: -3231.29453752 a.u.

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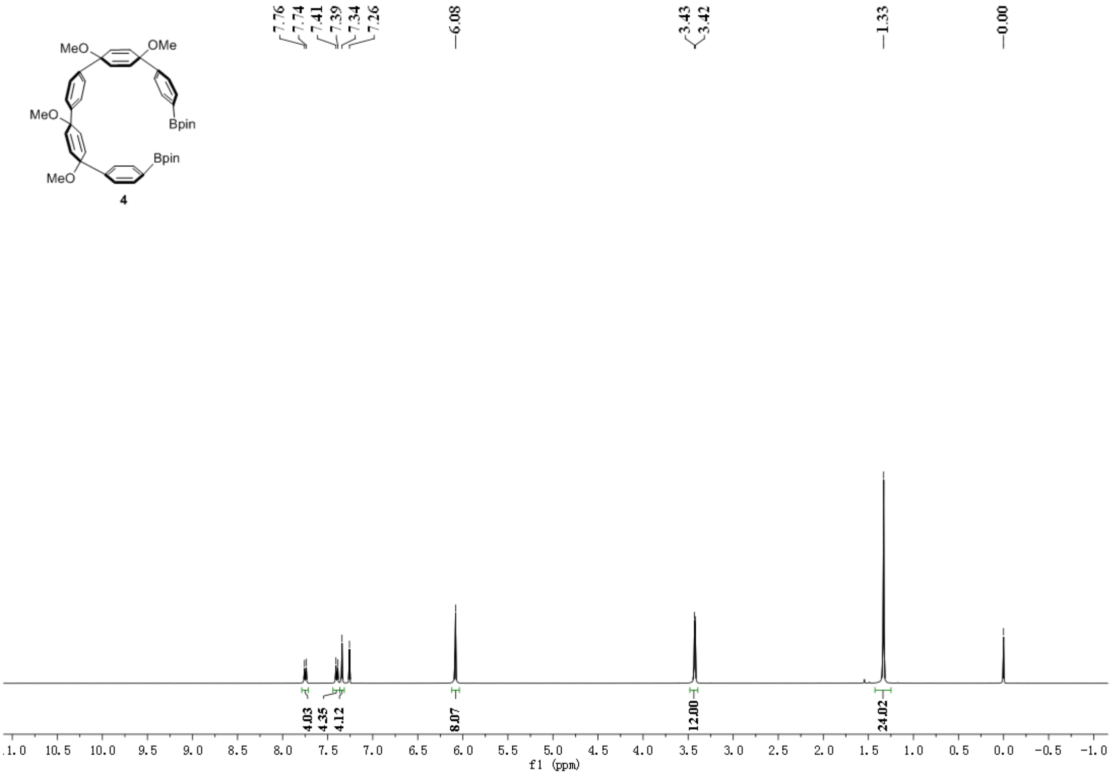

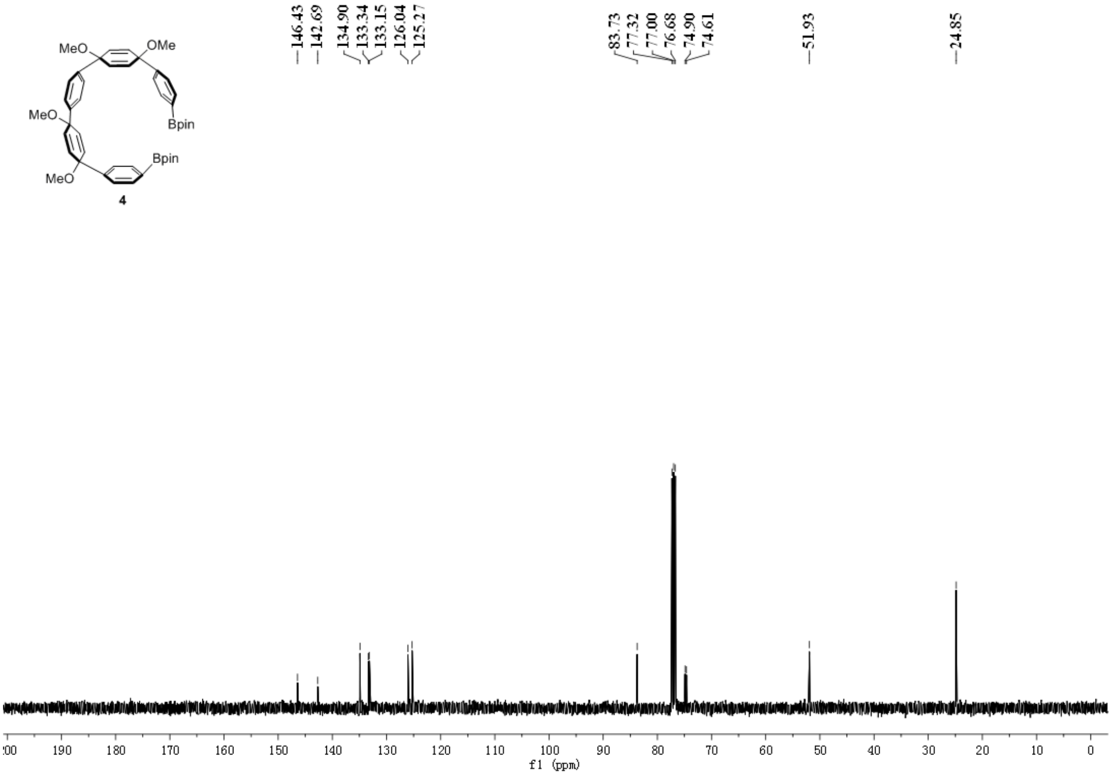

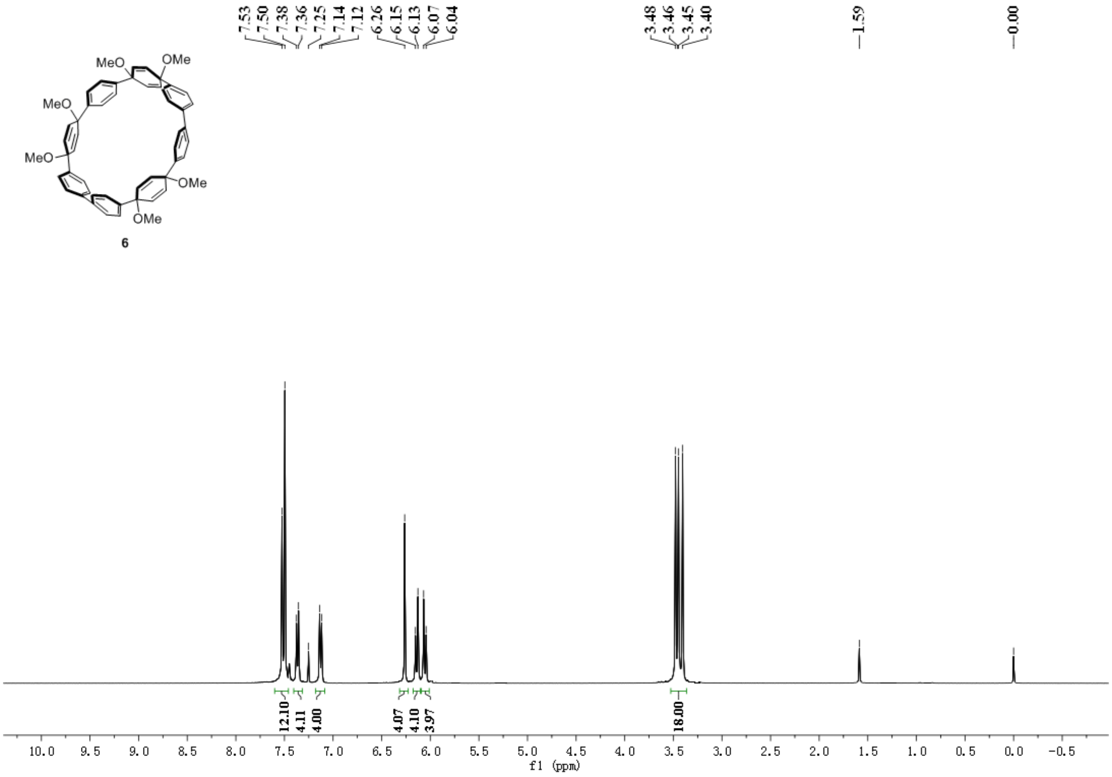
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OMe
OMe
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6.26
6.15
6.13
6.07
6.04
3.48
3.46
3.45
3.40
1.59
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4.11
4.00
4.07
4.10
3.97
18.00
10.0
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9.0
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8.0
7.5
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6.5
6.0
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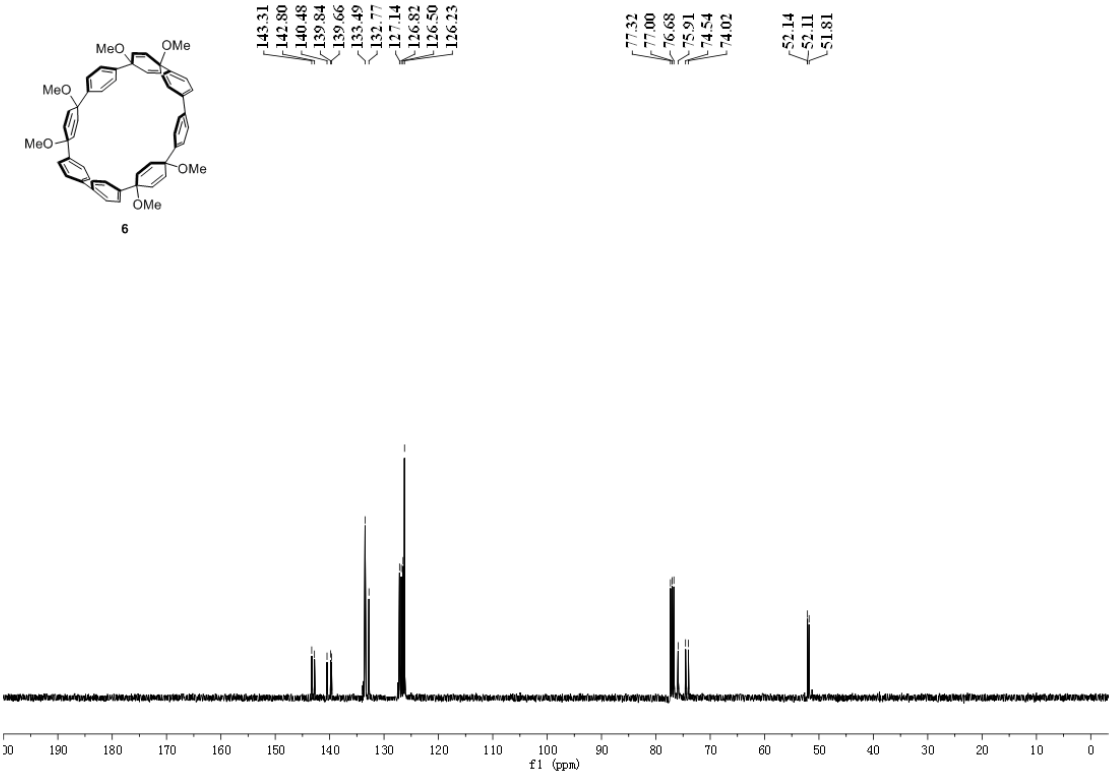
f1 (ppm)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126.82
126.50
126.23
77.32
77.00
76.68
75.91
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74.02
52.14
52.11
51.81
00
190
180
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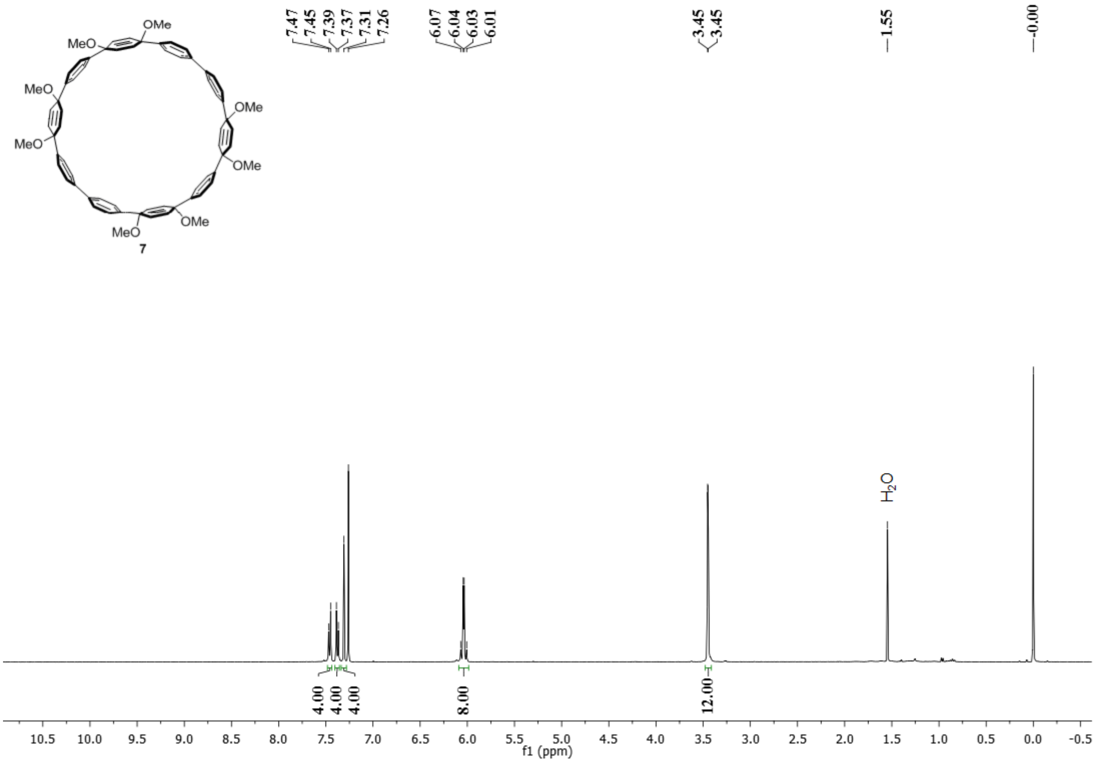
f1 (ppm)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4.00
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8.00
12.00
10.5
10.0
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9.0
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5.0
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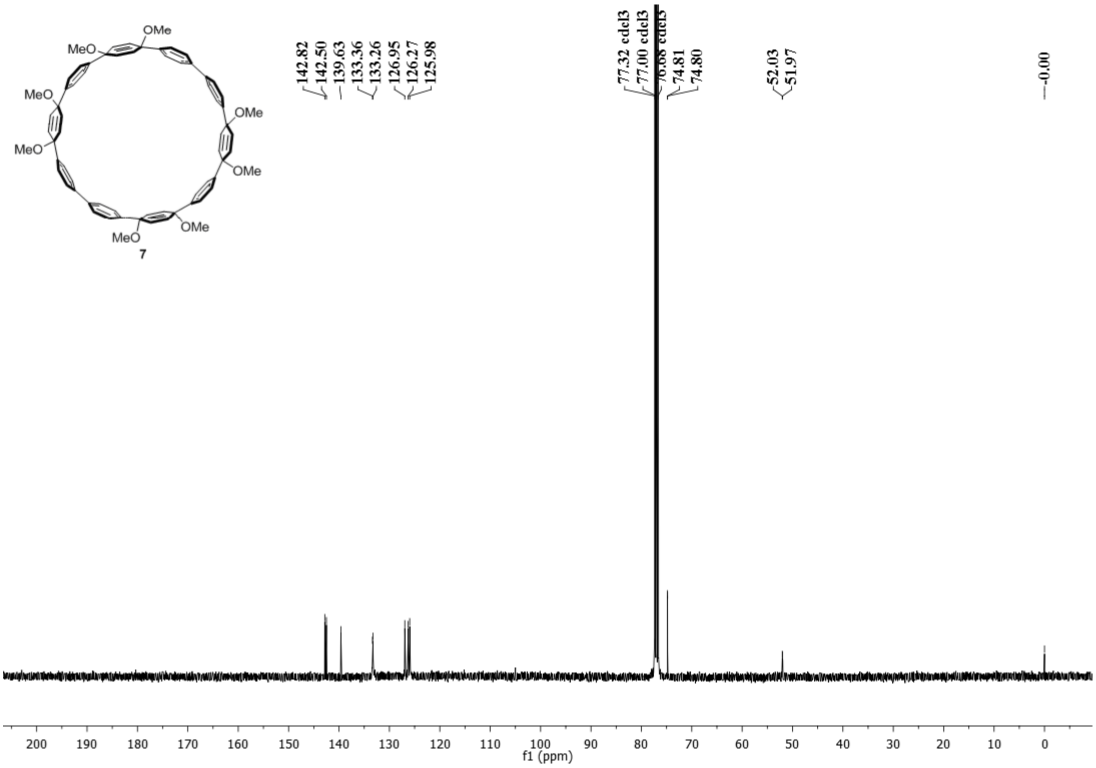
-0.5
f1 (ppm)

7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MeO
OMe
OMe
OMe
MeO
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133.36
133.26
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126.27
125.98
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
74.81
74.80
52.03
51.97
-0.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

7