Electronic Supplementary Material (ESI) for Chemical Science.

Supporting information

Symmetry Breaking and the Turn-On Fluorescence of Small, Highly Strained Carbon Nanohoops

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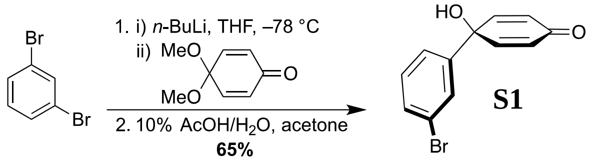
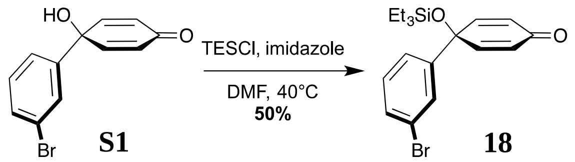
1. General Experimental Details. All glassware was flame dried and cooled under an inert atmosphere of nitrogen unless otherwise noted. Moisture sensitive reactions were carried out under nitrogen atmosphere using Schlenk and standard syringe/septa techniques. Tetrahydrofuran, dichloromethane, dimethylformamide and 1,4-dioxane were dried by filtration through alumina according to the methods describes by Grubbs.[1] Silica column chromatography was conducted with Zeochem Zeoprep 60 Eco 40-63 μm silica gel. Automated flash chromatography was performed using a Biotage Isolera One. Recycling gel permeation chromatography (GPC) was performed using a Japan Analytical Industry LC-9101 preparative HPLC with JAIGEL-1H/JAIGEL-2H columns in series using $CHCl_3$. 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. ^{1}H NMR spectra were recorded at 500 MHz or 600 MHz on a Bruker Advance-III-HD NMR spectrometer. ^{13}C NMR spectra were recorded 150 MHz on a Bruker Advance-III-HD NMR spectrometer. All ^{1}H NMR spectra were taken in $CDCl_3$ (referenced to TMS, δ 0.00 ppm) or DMSO-d_6 (referenced to residual DMSO, δ 2.50 ppm). All ^{13}C NMR spectra were taken in $CDCl_3$ (referenced to chloroform, δ 77.16 ppm) or DMSO-d_6 (referenced to DMSO, δ 39.52 ppm). Mass spectra were obtained from the University of Illinois at Urbana-Champaign Mass Spectrometry Lab using EI, ESI, ASAP, or MALDI or from University of Oregon CAMCOR using ASAP. HRMS was attempted for all compounds, but when not successful, LRMS is reported. Absorbance and fluorescence spectra were obtained in a 1 cm Quartz cuvette with dichloromethane using an Agilent Cary 100 UV-Vis spectrometer and a Horiba Jobin Yvon Fluoromax-4 Fluorimeter. Fluorescent quantum yield was measured in dichloromethane at room temperature using a Hamamatsu absolute PL quantum yield measurement system. Fluorescence lifetimes were measured in dichloromethane using a Horiba Jobin Yvon Tempro Fluorescence Lifetime System. A LUDOX® prompt was used and decay curves were fit to a single exponential function. Electrochemical experiments were performed using a Biologic SP-50 potentiostat with a Ag wire reference electrode, Pt wire counter electrode, and glassy carbon working electrode under nitrogen atmosphere in 100 mM solutions of Bu_4NPF_6 in DCM with ferrocene as a reference. All reagents were obtained commercially unless otherwise noted. Compounds *para*-benzoquinone mono-methyl ketal[2], **S2**[3], **S11**[4], PPh_3 Pd Gen III and SPhos Pd Gen III[5] were prepared according to literature procedure.

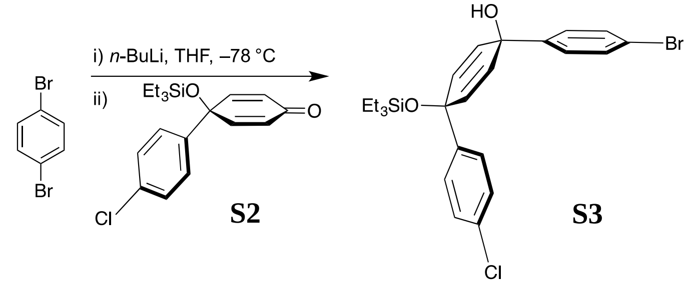


S1

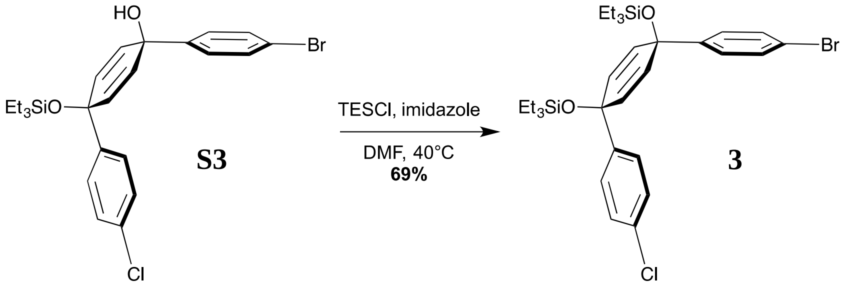
S1. 1,3-dibromobenzene (4.3 mL, 35.7 mmol, 1.1 equiv) was added to a 500 mL round bottom flask equipped with a stir bar. The reaction flask was capped with a septa, evacuated and refilled with nitrogen. Tetrahydrofuran (51 mL) was cannulated to the reaction flask, which was cooled to –78 °C over 30 min. *n*-BuLi (13.6 mL, 34.1 mmol, 1.05 equiv, 2.5 M in hexanes) was added to the reaction mixture dropwise over 10 min. This was followed by the dropwise addition of *para*-benzoquinone monomethyl ketal (4.6 mL, 32.4 mmol, 1 equiv) and the reaction stirred at –78 °C for 1 h. The reaction was quenched with deionized water (20 mL) at –78 °C and warmed to room temperature. The product was extracted with ethyl acetate (3 x 20 mL) and washed with brine (30 mL). The organic layers were dried over sodium sulfate, decanted and concentrated to yield the protected product as a slightly yellow solid. The protected product was dissolved in a minimal amount of acetone (20 mL) and a 10% acetic acid solution in water (20 mL) was added. This was stirred at room temperature for 1 h. The reaction was quenched with a saturated solution of sodium bicarbonate (50 mL). The product was extracted with ethyl acetate (3 x 20 mL), washed with brine (20 mL), dried over sodium sulfate and concentrated to yield the crude product as an orange solid. The product was purified by trituration with hexanes and ethanol to give **S1** as an off white solid (5.588 g, 65% 2 Steps). IR (neat) 1659, 1610 cm^{-1}; ^1H NMR (600 MHz, Chloroform-*d*) δ 7.67 (t, *J* = 1.9 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.25 (t, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 10.0 Hz, 2H), 6.23 (d, *J* = 10.0 Hz, 2H), 3.04 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 185.60, 150.34, 140.99, 131.53, 130.45, 128.54, 127.19, 124.04, 123.09, 70.58. HRMS (ESI-TOF) (m/z): $[M+H]^+$ calculated for $C_{12}H_{10}BrO_2$, 264.9864; found, 264.9871.



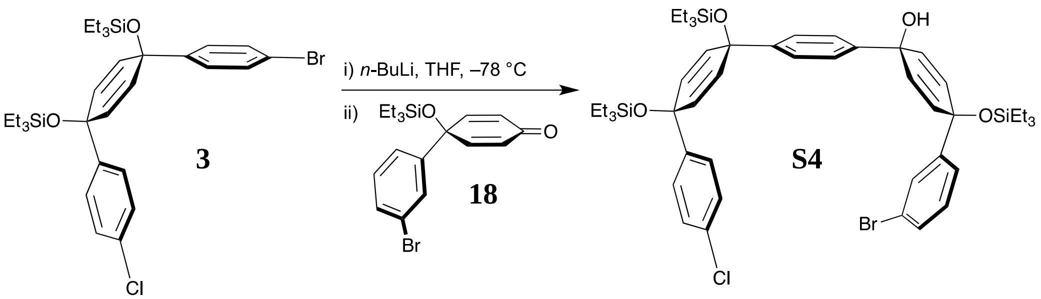
18. **S1** (5.588 g, 26.7 mmol, 1 equiv) and imidazole (5.74 g, 84.3 mmol, 4 equiv) were added to a 250 mL round bottom flask equipped with a stir bar and septum. Dimethylformamide (105 mL) was added to the flask followed by triethylsilyl chloride (4.2 mL, 89.8 mmol, 1.2 equiv). The reaction mixture was heated to 40 °C in an oil bath and stirred overnight. The reaction mixture was cooled to room temperature and quenched with a saturated solution of sodium bicarbonate (30 mL). The product was extracted with ethyl acetate (3 x 100 mL) and washed with 5% lithium chloride solution in water (3 x 100 mL). The organic layers were dried over sodium sulfate and concentrated to yield the crude product as a yellow oil. The product was purified by automated flash silica gel chromatography (0% to 10% ethyl acetate in hexanes) to give **18** as a slightly yellow oil (4.0 g, 50%). IR (neat) 2954, 2875, 1670, 1631 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (t, *J* = 1.9 Hz, 1H), 7.42 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.34 (ddd, *J* = 7.9, 1.8, 1.1 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 10.0 Hz, 2H), 6.24 (d, *J* = 10.0 Hz, 2H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.66 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 185.59, 151.35, 142.46, 131.10, 130.25, 128.60, 126.93, 124.08, 122.88, 72.70, 6.90, 6.22. HRMS (ESI-TOF) (m/z): $[M+H]^+$ calculated for $C_{18}H_{24}BrO_2Si$, 379.0729; found, 379.0732.



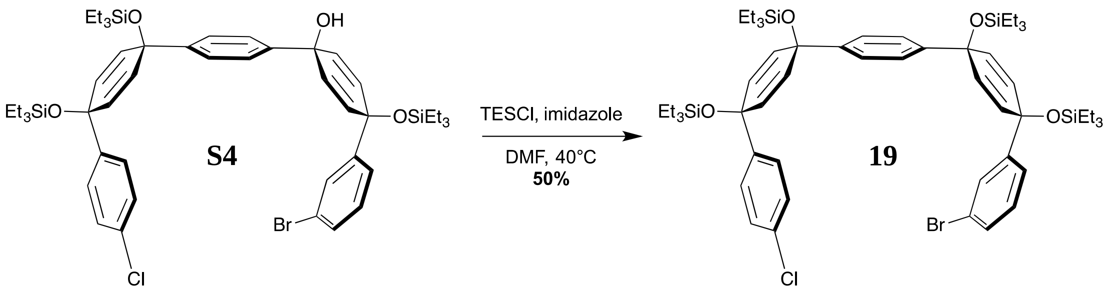
S3. 1,4-dibromobenzene (3.9 g, 16 mmol, 1.1 equiv) was added to a 100 mL round bottom flask equipped with a stir bar and septa. The flask was evacuated and filled with nitrogen. Tetrahydrofuran (23 mL) was added to the flask and this was cooled for 30 min at –78 °C. *n*-BuLi (6.5 mL, 16 mmol, 1.05 equiv, 2.4 M in hexanes) was added dropwise over 5 min. **S2** (4.6 mL, 15 mmol, 1 equiv) was added to the reaction flask dropwise and the reaction was stirred for 1 h at –78 °C. The reaction was quenched with deionized water (40 mL) while at –78 °C and warmed to room temperature. The product was extracted with ethyl acetate (3 x 70 mL) and washed with brine (3 x 40). The organic layers were dried over sodium sulfate, decanted and concentrated to yield the crude product **S3** as a yellow oil. The product was used as is for the next reaction.



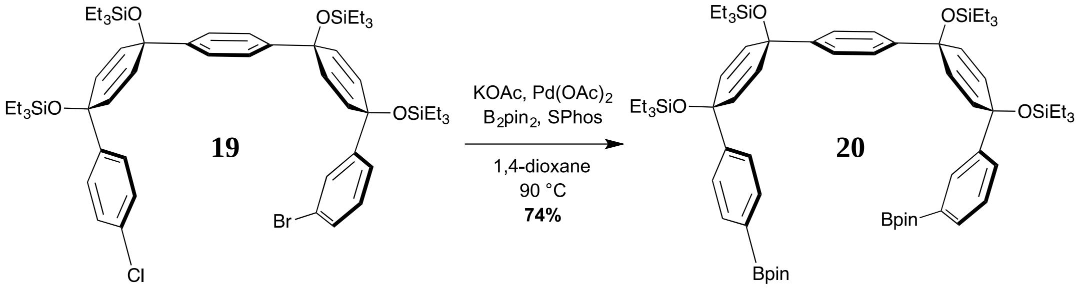
3. Crude **S3** and imidazole (2.3 g, 25 mmol, 4 equiv) were added to a 250 mL round bottom flask equipped with a stir bar and septum. Dimethylformamide (75 mL) was added to the flask followed by triethylsilyl chloride (3.0 mL, 18 mmol, 1.2 equiv). The reaction mixture was heated to 40 °C in an oil bath and stirred overnight. The reaction mixture was cooled to room temperature and quenched with a saturated solution of sodium bicarbonate (30 mL). The product was extracted with ethyl acetate (3 x 60 mL) and washed with 5% lithium chloride solution in water (30 mL) and brine (30 mL). The organic layers were dried over sodium sulfate and concentrated to yield the crude product as a yellow oil. The product was purified by automated flash silica gel chromatography (0% to 3% ethyl acetate in hexanes) to give **3** as a white solid (6.3 g, 69% 2 steps). IR (neat) 2952, 2871, 1483, 1401 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 0.9 Hz, 4H), 7.17 (d, *J* = 8.3 Hz, 2H), 5.95 (s, 4H), 0.95 – 0.89 (m, 18H), 0.59 (qd, *J* = 8.0, 2.5 Hz, 12H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.97, 144.41, 133.11, 131.46, 131.37, 131.25, 128.31, 127.60, 127.24, 121.29, 71.10, 71.04, 7.02, 6.41. HRMS (EI) (m/z): [M]$^{+}$ calculated for $C_{30}H_{42}BrClO_2Si_2$, 604.1595; found, 604.1594.



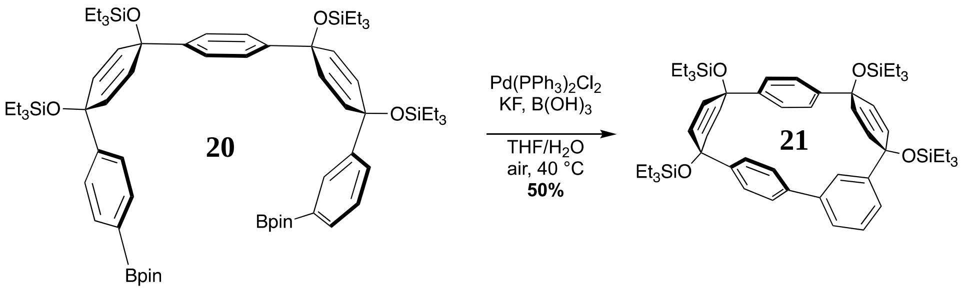
S4. **3** (1.5 g, 2.5 mmol, 1.1 equiv) was added to a 25 mL one-neck round bottom flask equipped with a stir bar and septa. The flask was evacuated and filled with nitrogen. Tetrahydrofuran (27 mL) was added to the flask and it was cooled for 30 min at –78 °C. *n*-BuLi (1.0 mL, 2.6 mmol, 1.05 equiv, 2.5 M in hexanes) was added dropwise over 3 min. **18** (0.72 mL, 2.5 mmol, 1 equiv) was added to the reaction flask dropwise and the reaction was stirred for 1 h at – 78 °C. The reaction was quenched with deionized water (10 mL) while at –78 °C and deionized water (5 mL) was added again when the ice bath was removed. The product was extracted with ethyl acetate (3 x 20 mL) and washed with brine (3 x 20 mL). The organic layers were dried over sodium sulfate and concentrated to yield the crude product **S4** as a colorless oil. The product was not purified.



19. Crude **S4** and imidazole (0.67 g, 9.9 mmol, 4 equiv) were added to a 100 mL round bottom flask equipped with a stir bar and septum. Dimethylformamide (10 mL) was added to the flask followed by triethylsilyl chloride (0.5 mL, 3.0 mmol, 1.2 equiv). The reaction mixture was heated to 40 °C in an oil bath and stirred overnight. The reaction mixture was cooled to room temperature and quenched with a saturated solution of sodium bicarbonate (20 mL). The product was extracted with ethyl acetate (3 x 100 mL) and washed with 5% lithium chloride solution in water (3 x 50 mL). The organic layers were dried over sodium sulfate and concentrated to yield the crude product as a yellow oil. The product was purified by automated flash silica gel chromatography (0% to 5% ethyl acetate in hexanes) to give **19** as a white solid (1.25 g, 50% 2 steps). IR (neat) 2953, 2874, 1457, 1405 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 1.5 Hz, 1H), 7.34 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.25 – 7.22 (m, 6H), 7.21 – 7.17 (m, 3H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.02 (d, *J* = 10.9 Hz, 2H), 6.00 (d, *J* = 9.9 Hz, 2H), 5.91 (d, *J* = 3.9 Hz, 2H), 5.90 (d, *J* = 3.5 Hz, 2H), 0.97 – 0.89 (m, 38H), 0.66 – 0.60 (m, 12H), 0.57 (q, *J* = 7.8 Hz, 13H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.41, 144.95, 144.83, 144.70, 131.91, 131.77, 131.06, 130.98, 130.14, 129.60, 129.14, 128.18, 127.28, 125.76, 125.70, 124.29, 122.35, 71.23, 71.15, 7.05, 7.03, 6.46, 6.41. HRMS (ESI-TOF) (m/z): [M+Na]$^+$ calculated for $C_{54}H_{80}BrClNaO_4Si_4$, 1041.3903; found, 1041.3909.

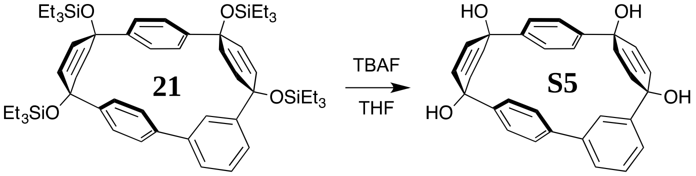


20. Potassium acetate (KOAc) (634.8 mg, 6.5 mmol, 6.6 equiv) that had been stored in an oven was added to a 25 mL round bottom flask equipped with a stir bar. **NOTE**: KOAc is extremely hygroscopic and the reaction is water sensitive, therefore it must be dried in an oven and weighed quickly while hot. The KOAc and flask were flame-dried again under vacuum until all apparent moisture was removed. Palladium(II) acetate (1.1 mg, 0.0049 mmol, 0.05 equiv), SPhos (50.3 mg, 0.12 mmol, 0.125 equiv), bis(pinacolato)diboron (994.8 mg, 3.9 mmol, 4 equiv) and **19** (1.0 g, 0.98 mmol, 1 equiv) were added to the flask, which was placed under vacuum for 1 h with stirring. The flask was purged with nitrogen and evacuated 3 times. 1,4- dioxane (3.3 mL) was purged with nitrogen for 1 h prior and added to the round bottom flask at room temperature. The round bottom flask was placed in an oil bath while it heated up to 90 °C. The reaction mixture changed from yellow to orange to red to a very dark red. The reaction was stirred at 90 °C overnight. Ethyl acetate (EtOAc) was added to the reaction mixture, which was filtered through a fritted suction funnel with 2 cm Celite®. The flask was rinsed several times with EtOAc and sonicated. The filtrate was transferred to a 250 mL flask and concentrated to yield a white waxy solid. This was rinsed with ethanol and suctioned through a Büchner funnel to yield **20** as a white solid (843.1 mg, 74%). IR (neat) 2953, 2875, 1357, 1317 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.22 (m, 3H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.02 (d, *J* = 9.8 Hz, 2H), 5.95 (d, *J* = 10.0 Hz, 2H), 5.93 (s, 4H), 1.34 (s, 12H), 1.30 (s, 12H), 0.96 – 0.88 (m, 36H), 0.65 – 0.54 (m, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.19, 145.31, 145.06, 144.72, 134.69, 133.60, 132.55, 131.64, 131.58, 131.37, 131.13, 128.62, 127.43, 125.61, 125.54, 125.15, 83.72, 83.61, 71.53, 71.36, 71.29, 71.25, 24.90, 24.88, 7.10, 7.06, 6.47, 6.45, 6.43. HRMS (ESI-TOF) (m/z): [M+Na]$^+$ calculated for $C_{66}H_{104}B_2NaO_8Si_4$, 1181.6892; found, 1181.6926.

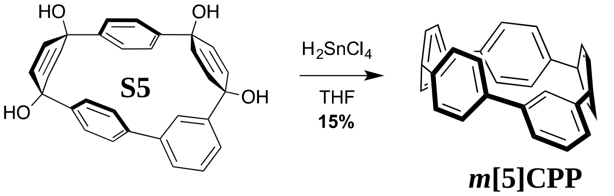


21. Diboronic ester **20** (400 mg, 0.417 mmol, 1.00 equiv) was added to a round bottom flask followed by bis(triphenylphosphine)palladium(II) dichloride (59 mg, 0.083 mmol, 0.2 equiv) and boric acid (129 mg, 2.09 mmol, 5.00 equiv). The solids were dissolved in tetrahydrofuran (200 mL) and the mixture was stirred vigorously for 10 min. Potassium fluoride (24 mg, 0.417 mmol, 1.00 equiv) dissolved in water (20 mL) was added to the mixture. The reaction was stirred at 40 °C open to the atmosphere overnight. The next day, the mixture was filtered through Celite® washing with EtOAc, dried over sodium sulfate, and concentrated to give the crude product as an orange oil. The product was purified by automated flash silica gel chromatography (0% to 30% dichloromethane in hexanes) to yield **21** as a white solid (190 mg, 50%). IR (neat) 2953, 2874, 1457, 1412 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 6.6 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.12 (d, *J* = 6.7 Hz, 2H), 6.92 (d, *J* = 6.7 Hz, 2H), 6.88 (d, *J* = 6.8 Hz, 2H), 6.58 (d, *J* = 6.9

Hz, 2H), 6.47 (s, 1H), 6.40 (d, *J* = 8.3 Hz, 2H), 6.12 (d, *J* = 8.3 Hz, 2H), 5.96 (d, *J* = 8.5 Hz, 2H), 5.86 (d, *J* = 8.5 Hz, 2H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.87 (t, *J* = 8.0 Hz, 9H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.72 (q, *J* = 7.9 Hz, 6H), 0.64 (q, *J* = 7.9 Hz, 6H), 0.50 (q, *J* = 7.9 Hz, 6H), 0.46 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.63, 143.99, 143.87, 143.13, 141.22, 141.11, 134.02, 132.79, 132.74, 131.05, 130.66, 128.60, 126.93, 126.75, 125.79, 125.61, 123.22, 122.78, 72.88, 72.53, 72.02, 71.46, 7.12, 7.03, 6.96, 6.95, 6.46, 6.44, 6.41, 6.40. HRMS (ESI-TOF) (m/z): $[M+Na]^+$ calculated for $C_{54}H_{80}NaO_4Si_4$, 927.5031; found, 927.5050.

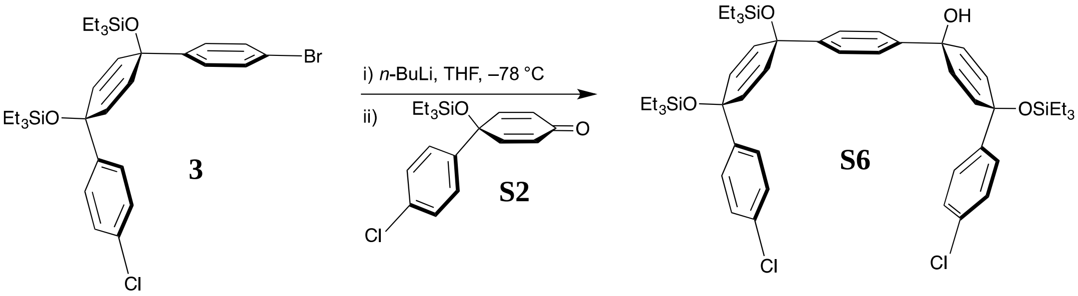


S5. **21** (33 mg, 0.036 mmol, 1 equiv) was dissolved in THF (0.9 mL). Tetra-*n*-butylammonium fluoride (0.22 mL, 0.22 mmol, 6 equiv, 1 M in tetrahydrofuran) was added and the reaction was stirred for 1 h. The reaction was quenched with water (1 mL) and the THF was removed by distillation. The resulting mixture was filtered to afford **S5** as a white solid that was rinsed with water and dichloromethane. The product was not purified further.

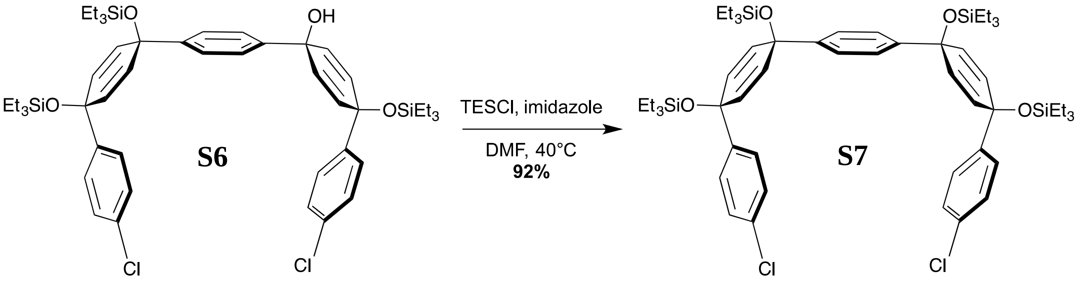


***m*[5]CPP**

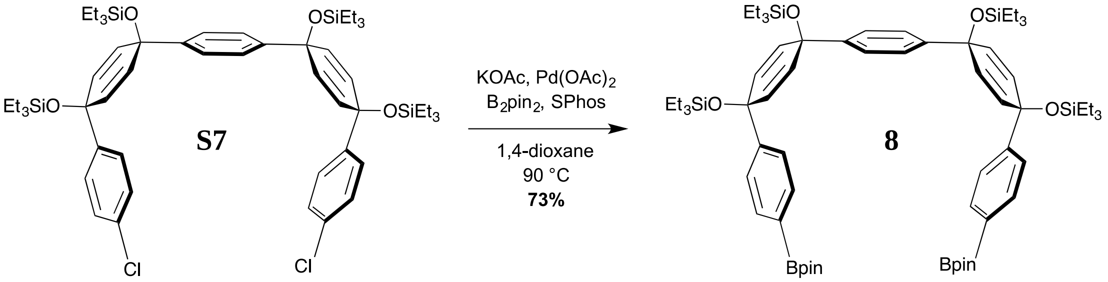
***m*[5]CPP**. Crude **S5** was dissolved in tetrahydrofuran (0.36 mL). A solution of tin(II) dichloride dihydrate (18 mg, 79 µmol, 2.2 eq) and concentrated hydrochloric acid (12 µL, 150 µmol, 4.2 eq) in THF (710 µL) was added and the reaction was stirred for 1 h at room temperature. A 1 M concentrated solution of NaOH (1 mL) was added and the mixture was extracted with dichloromethane (3 x 3 mL). The organic layers were concentrated and the product. The product was purified by preparative thin layer chromatography on alumina (50% dichloromethane in hexanes) to yield ***m*[5]CPP** as a yellow solid (2.0 mg, 15% 2 steps). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.31 (m, 15H), 7.06 (d, *J* = 8.7 Hz, 4H), 4.80 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.23, 142.82, 140.79, 139.05, 136.69, 135.38, 129.88, 128.64, 128.33, 127.54, 126.71, 121.18. HRMS (ASAP) (m/z): [M+H]$^+$ calculated for $C_{30}H_{21}$, 381.1643; found, 381.1642.



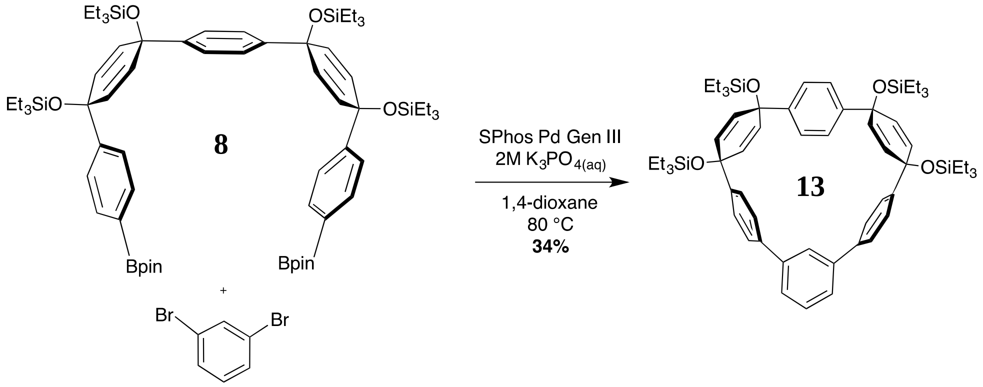
S6. **3** (6.0972 g, 10.1 mmol, 1.1 equiv) was added to a 100 mL round bottom flask equipped with a stir bar and septa. The flask was evacuated and filled with nitrogen. Tetrahydrofuran (15 mL) was added to the round bottom flask and was cooled for 30 min at –78 °C. *n*-BuLi (4.2 mL, 10.6 mmol, 1.05 equiv, 2.5 M in hexanes) was added dropwise. **S2** (3.12 mL, 10.1 mmol, 1 equiv) was added to the reaction flask dropwise and the reaction was stirred for 1 h at –78 °C. The reaction was quenched with deionized water (15 mL) at –78 °C and warmed to room temperature. The product was extracted with ethyl acetate (3 x 40 mL) and washed with brine (30 mL). The organic layers were dried over sodium sulfate and concentrated to yield the crude product **S6** as a colorless oil. The product was not purified.



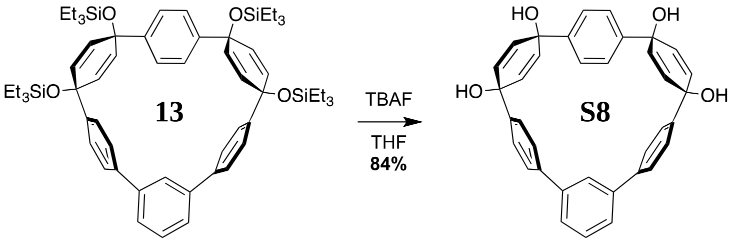
S7. Crude **S6** (8.67 g, 10.1 mmol, 1 equiv) and imidazole (2.74 g, 40.2 mmol, 4 equiv) were added to a 250 mL round bottom flask and was equipped with a stir bar and septum. Dimethylformamide (50 mL) was added to the flask followed by triethylsilyl chloride (2.0 mL, 12.1 mmol, 1.2 equiv). The reaction mixture was heated to 40 °C in an oil bath and stirred overnight. The reaction mixture was cooled to room temperature and quenched with a saturated solution of sodium bicarbonate (50 mL). The product was extracted with ethyl acetate (3 x 100 mL) and washed with 5% lithium chloride solution in water (3 x 100 mL). The organic layers were dried over sodium sulfate and concentrated to yield the crude product as a yellow oil. The product was purified by automated flash silica gel chromatography (0% to 15% ethyl acetate in hexanes) to give **S7** as a white solid (9.0 g, 92% 2 steps). IR (neat) 2952, 2874, 1481, 1456, 1405 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 (s, 4H), 7.22 (d, *J* = 8.4 Hz, 4H), 7.19 (d, *J* = 8.4 Hz, 4H), 6.01 (d, *J* = 10.1 Hz, 4H), 5.91 (d, *J* = 10.1 Hz, 4H), 0.94 (t, *J* = 7.9 Hz, 18H), 0.91 (t, *J* = 7.9 Hz, 18H), 0.62 (q, *J* = 7.9 Hz, 12H), 0.57 (q, *J* = 8.0 Hz, 12H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.98, 144.63, 132.91, 131.68, 131.17, 128.15, 127.31, 127.23, 125.73, 71.18, 71.13, 7.05, 7.03, 6.46, 6.40. HRMS (ESI-TOF) (m/z): [M+Na]$^+$ calculated for $C_{54}H_{80}Cl_2NaO_4Si_4$, 997.4409; found, 997.4455.



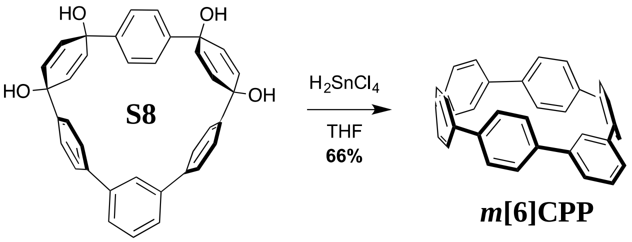
8. Potassium acetate (KOAc) (1.1 g, 12 mmol, 6.6 equiv) that had been stored in an oven was added to a 25 mL round bottom flask equipped with a stir bar. **NOTE**: KOAc is extremely hygroscopic and it is important to have none or very little moisture in the reaction, therefore it must be weighed very quickly while it is warm. The KOAc and flask were flame-dried again under vacuum until all apparent moisture was removed. Palladium(II) acetate (20 mg, 0.09 mmol, 0.05 equiv), SPhos (91 mg, 0.2 mmol, 0.13 equiv), bis(pinacolato)diboron (1.8 g, 7 mmol, 4 equiv) and **S7** (1.7 g, 1.2 mmol, 1 equiv) were added to the flask and was put under vacuum for 1 h with stirring. The flask was purged with nitrogen and evacuated 3 times. 1,4-dioxane (6 mL) was sparged with nitrogen for 1 h, added to the round bottom flask at room temperature and the mixture was stirred for 5 min. The flask was placed in an oil bath and heated to 90 °C. The color of the reaction mixture changed from yellow to orange to red to a very dark red. The reaction was stirred at 90 °C over 2 nights. EtOAc was added to the reaction mixture. This was filtered through Celite® in a fritted suction funnel. The reaction flask was rinsed several times with EtOAc with sonication. The filtrate was transferred to a 250 mL round bottom flask and concentrated to yield a white waxy solid. This was rinsed with ethanol and filtered using a Büchner funnel to yield **8** as a white solid (1.51 g, 73%). IR (neat) 2954, 2876, 1610, 1361 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.2 Hz, 4H), 7.32 (d, *J* = 8.2 Hz, 4H), 7.22 (s, 4H), 5.98 (d, *J* = 10.2 Hz, 4H), 5.94 (d, *J* = 10.2 Hz, 4H), 1.33 (s, 24H), 0.95 – 0.90 (m, 36H), 0.63 – 0.56 (m, 24H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.17, 144.91, 134.65, 131.61, 131.22, 125.68, 125.16, 83.68, 71.60, 71.25, 24.88, 7.07, 6.45. HRMS (ESI-TOF) (m/z): [M+Na]$^{+}$ calculated for $C_{66}H_{104}B_2NaO_8Si_4$, 1181.6892; found, 1181.6871.



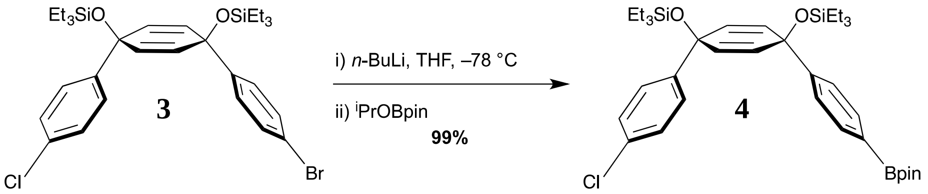
13. *m*-dibromobenzene (0.06 mL, 0.08 mmol, 1 equiv), **8** (666.5 mg, 0.058 mmol, 1.2 equiv) and SPhos Pd Gen III (38.1 mg, 0.0048 mmol, 0.1 equiv) were added to a 50 mL round bottom flask equipped with a stir bar. The flask was evacuated for 5 min and purged with nitrogen 5 times. 1,4-dioxane and a solution of 2 M K_3PO_4 were sparged with nitrogen for over 1 h prior to use. The round bottom flask was equipped with a septa and 1,4-dioxane (160 mL) was added to the round bottom flask and the solution was sparged for 20 min. The round bottom flask was heated to 80 °C for 10 min and K_3PO_4 (16 mL, 2 M in deionized water) was added. The reaction was stirred at 80 °C overnight. The reaction mixture was cooled to room temperature. It was filtered through a fritted suction funnel filled with Celite®. The round bottom flask was rinsed with dichloromethane and filtered through the Celite® plug. The filtrate was added to a separatory funnel along with deionized water (10 mL) and the product was extracted (3 x 30) with dichloromethane. The organic layer was washed with brine (20 mL), dried over sodium sulfate and concentrated to yield an orange oil. The product was purified by automated flash silica gel chromatography (5% to 45% dichloromethane in hexanes) to yield the product **13** as a white solid (193 mg, 34%). IR (neat) 2952, 2874, 1457, 1403, 1237 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.48 – 7.44 (m, 5H), 7.30 (d, *J* = 8.3 Hz, 4H), 6.93 (s, 4H), 6.24 (t, *J* = 1.9 Hz, 1H), 6.13 (d, *J* = 10.1 Hz, 4H), 5.72 (d, *J* = 10.1 Hz, 4H), 0.97 (t, *J* = 7.9 Hz, 18H), 0.93 (t, *J* = 7.9 Hz, 18H), 0.69 (q, *J* = 7.9 Hz, 12H), 0.58 (q, *J* = 7.9 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.92, 144.77, 143.15, 142.47, 141.76, 131.48, 131.43, 128.80, 128.69, 128.06, 125.99, 125.81, 125.73, 125.35, 122.39, 71.19, 70.58, 7.15, 7.04, 6.97, 6.80, 6.61, 6.50, 6.48, 6.42. HRMS (ESI-TOF) (m/z): [M+Na]$^+$ calculated for $C_{60}H_{84}NaO_4Si_4$, 1003.5344; found, 1003.5375.



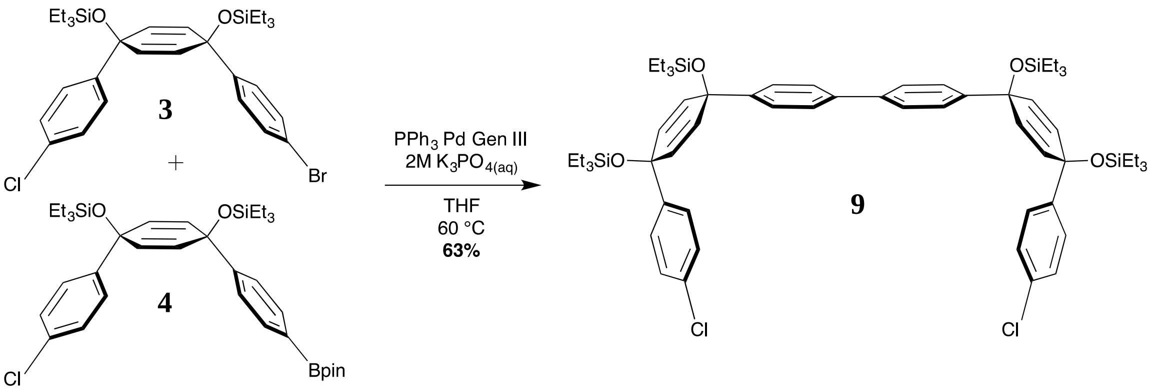
S8. Tetrahydrofuran (1.05 mL) was added to **13** (102.9 mg, 0.1 mmol, 1 equiv) and the vial was equipped with a stir bar and septa. Tetra-*n*-butylammonium fluoride (1.05 mL, 1 mmol, 10 equiv, 1 M in tetrahydrofuran) was added to the reaction flask and this was stirred for 2 h at room temperature. The reaction was quenched with deionized water (5 mL), filtered in a Büchner funnel and washed with deionized water and dichloromethane to yield **S8** as a white solid (46 mg, 84%). IR (neat) 3370, 3187, 1408 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.60 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 4H), 7.33 (d, *J* = 7.9 Hz, 4H), 6.88 (s, 4H), 6.17 (t, *J* = 2.0 Hz, 1H), 6.07 (d, *J* = 9.9 Hz, 4H), 5.65 (d, *J* = 9.8 Hz, 4H). ^{13}C NMR (151 MHz, DMSO) δ 145.94, 144.97, 142.45, 142.38, 131.85, 131.53, 129.54, 128.78, 126.26, 125.54, 122.79, 68.63, 68.09, 23.53, 19.70, 13.98. HRMS (ESI-TOF) (m/z): $[M+Na]^+$ calculated for $C_{36}H_{28}NaO_4$, 547.1885; found, 547.1869.



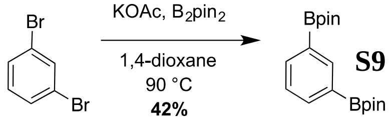
***m*[6]CPP.** $SnCl_2•H_2O$ (180.6 mg, 0.80 mmol) was added to a 100 mL round bottom flask equipped with a stir bar and septum. Tetrahydrofuran (20 mL) was added to the flask followed by hydrochloric acid (0.13 mL, 1.6 mmol, 12 M). This was stirred at room temperature for 30 min. H_2SnCl_2 solution (2.1 mL, 0.09 mmol, 2.2 equiv, 0.04 M) was added to the scintillation vial containing **S8** (20.3 mg, 0.04 mmol, 1 equiv) and was stirred for 1 h at room temperature. The reaction was quenched with saturated sodium bicarbonate (5 mL). The filtrate was transferred to a separatory funnel and the product was extracted with dichloromethane (5 x 7 mL). The organic layers were washed with brine (10 mL), dried over sodium sulfate and concentrated to give the crude product as a green solid. The product was purified by automated flash alumina column chromatography (10% to 45% dichloromethane in hexanes) to yield ***m*[6]CPP** as a green solid (12 mg, 66%). IR (neat) 2921, 2851, 1661, 1261 cm^{-1}; ^1H NMR (600 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 19H), 7.15 (d, *J* = 8.6 Hz, 4H), 5.62 (t, *J* = 1.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.79, 139.53, 139.04, 137.43, 136.42, 136.38, 129.45, 128.99, 128.08, 127.85, 127.58, 127.20, 122.20, 77.25, 77.03, 76.82. HRMS (ASAP-TOF) (m/z): $[M+H]^+$ calculated for $C_{36}H_{25}$, 457.1956; found, 457.1956.



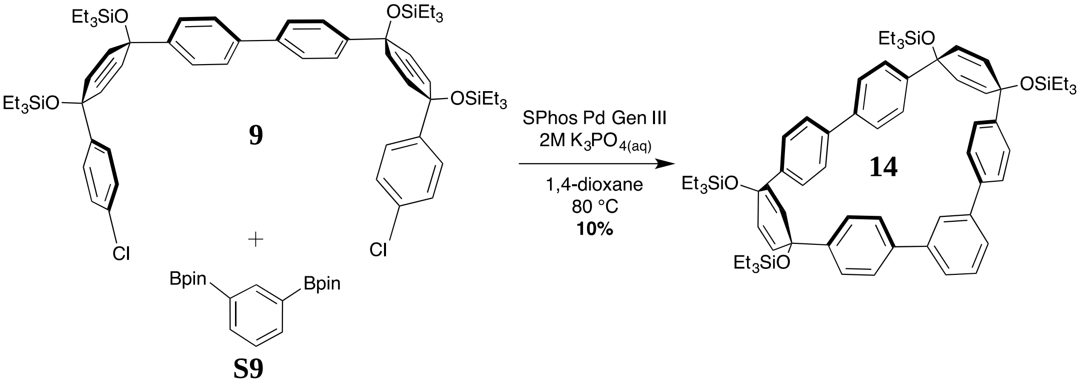
4. **3** (5 g, 8.25 mmol, 1.0 eq) was added to a 100 mL round bottom flask equipped with a stir bar. The reaction flask was capped with a septa and the flask was evacuated and refilled with nitrogen. Tetrahydrofuran (48 mL) was added to the reaction flask and the mixture was cooled for 30 min at –78 °C. *n*-BuLi (3.5 mL, 8.7 mmol, 1.05 eq, 2.5 M in hexanes) was added to the reaction mixture dropwise. This was followed by the dropwise addition of 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.4 mL, 16.5 mmol, 2 eq) and the reaction was stirred at –78 °C for 1 h. The reaction was quenched with deionized water (30 mL) at –78 °C and the reaction mixture was warmed to room temperature. The product was extracted with ethyl acetate (3 x 50 mL) and washed with brine (3 x 20 mL). The organic layers were dried over sodium sulfate, decanted into a round bottom flask and concentrated to yield a slightly yellow oil. Ethanol (20 mL) was added to the oil and was sonicated, producing a white precipitate. The product **4** was isolated by suction filtration to yield a white solid (5.3 g, 99%). IR (neat) 2955, 2874, 1399, 1359, 1321 $\mathrm{cm^{-1}}$; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.72 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 5.99 (d, J = 10.0 Hz, 2H), 5.92 (d, J = 10.0 Hz, 2H), 1.34 (s, 12H), 0.93 (t, J = 8.0 Hz, 9H), 0.91 (t, J = 7.9 Hz, 9H), 0.61 (q, J = 8.0 Hz, 6H), 0.57 (q, J = 7.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.90, 144.59, 134.73, 132.91, 131.60, 131.24, 128.21, 127.27, 125.15, 83.79, 71.45, 71.15, 24.88, 7.03, 6.45, 6.41. HRMS (ESI-TOF) (m/z): $[M+Na]^+$ calculated for $C_{36}H_{54}BClNaO_4Si_2$, 675.3240; found, 675.3246.



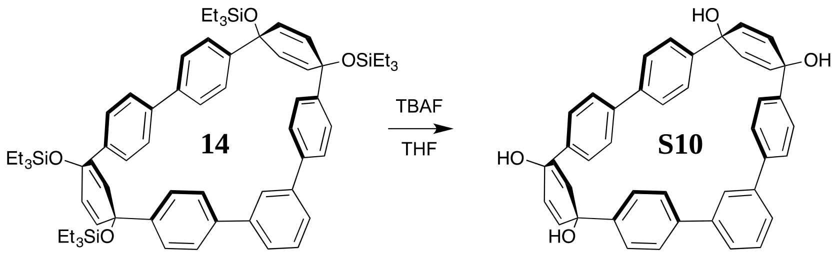
9. **3** (1.00 g, 1.65 mmol, 1 equiv), **4** (1.18 g, 1.82 mmol, 1.1 equiv) and PPh_3 Pd Gen III (31 mg,0.050 mmol, 0.03 equiv) dissolved in tetrahydrofuran (16 mL) and warmed to 60 °C. K_3PO_4 (1.6 mL, 2 M in deionized water) was added and the reaction was left overnight. The next day, the reaction was filtered through Celite®, dried over sodium sulfate and the solvent was removed under reduced pressure to yield an oil. The product was purified by automated flash silica column chromatography (0% to 30% dichloromethane in hexanes) to yield **9** as a white solid (1.1 g, 63%). IR (neat) 2951, 2873, 1490, 1456, 1401 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.50 (d, J = 8.2 Hz, 4H), 7.37 (d, J = 8.5 Hz, 4H), 7.28 (d, J = 8.3 Hz, 4H), 7.23 (d, J = 8.5 Hz, 4H), 6.03 (d, J = 10.0 Hz, 4H), 5.96 (d, J = 9.8 Hz, 4H), 0.94 (t, J = 7.9 Hz, 36H), 0.61 (q, J = 8.1 Hz, 24H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.90, 144.66, 139.59, 132.97, 131.78, 131.16, 128.23, 127.33, 126.76, 126.24, 71.27, 71.16, 7.05, 7.04, 6.47, 6.43. HRMS (ESI-TOF) (m/z): $[M+Na]^+$ calculated for $C_{60}H_{84}Cl_2NaO_4Si_4$, 1073.4722; found, 1073.4722.



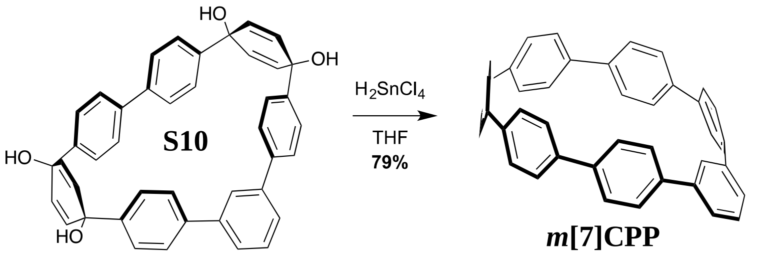
S9. 1,3-dibromobenzene (5.0 mL, 9.8 g, 41 mmol, 1 eqiv), $Pd(dppf)_2Cl_2$ (169 mg, 0.21 mmol, 0.005 eqiv) and bis(pinacolato)diboron (25 g, 99 mmol, 2.4 equiv) were added to a round bottomed flask. Oven dried hot KOAc (27 g, 270 mmol, 6.6 equiv) was added and the solids were placed under vacuum. The flask was refilled with nitrogen, 1,4-dioxane (40 mL) was added, and the reaction was warmed from room temperature to 90 °C. The reaction was stirred at this temperature overnight. The next day, the reaction was filtered through Celite® washing with ethyl acetate (80 mL) and the solvent of the filtrate was removed under reduced pressure until crystallization occurred. The crystals were collected by filtration and washed with cold ethanol to yield **S9** as a white solid (5.8 g, 42%). IR (neat) 2977, 1602, 1303 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 7.90 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 1.34 (s, 24H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.23, 137.62, 127.04, 83.73, 24.88. HRMS (ESI-TOF) (m/z): $[M+H]^+$ calculated for $C_{18}H_{29}B_2O_4$, 331.2252; found, 331.2244.



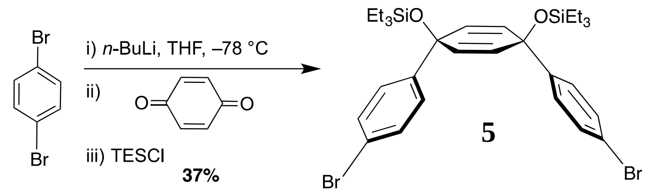
S14. **9** (157 mg, 0.475 mmol, 1 equiv), **S9** (500 mg, 0.475 mmol, 1 equiv), and Sphos Pd Gen III (37 mg, 0.048 mmol, 0.1 equiv) were dissolved in 1,4-dioxane (240 mL) and heated to 80 °C. K_3PO_4 (24 mL, 2 M in deionized water) was added and the reaction was stirred overnight. The reaction mixture was filtered through Celite® and the solvent was removed under reduced pressure to yield a golden oil. The product was purified by automated flash silica column chromatography (0% to 100% dichloromethane in hexanes) to yield a white solid. The solid was purified by recycling gel permeation chromatography to yield **14** as a white solid (50 mg, 10%). IR (neat) 2954, 2875, 1085 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.58 (dd, J = 7.5, 1.8 Hz, 2H), 7.50 (m, 2H), 7.40 (d, J = 8.4 Hz, 4H), 7.26 (d, J = 8.4 Hz, 4fH), 7.23 (d, J = 8.3 Hz, 4H), 7.04 (d, J = 8.3 Hz, 4H), 6.15 (d, J = 10.0 Hz, 4H), 6.07 (d, J = 10.0 Hz, 4H), 0.99 (t, J = 7.9 Hz, 18H), 0.98 (t, J = 7.9 Hz, 18H), 0.68 (q, J = 7.9 Hz, 12H), 0.66 (q, J = 7.9 Hz, 12H). ^{13}C NMR (151 MHz, CDCl3) δ 143.56, 142.92, 141.63, 140.33, 140.10, 132.46, 131.98, 129.16, 128.78, 127.09, 126.80, 126.68, 126.57, 124.89, 72.54, 72.35, 7.08, 7.06, 6.49. HRMS (ESI-TOF) (m/z): $[M+H]^+$ calculated for $C_{66}H_{89}O_4Si_4$, 1057.5838; found, 1057.5869.



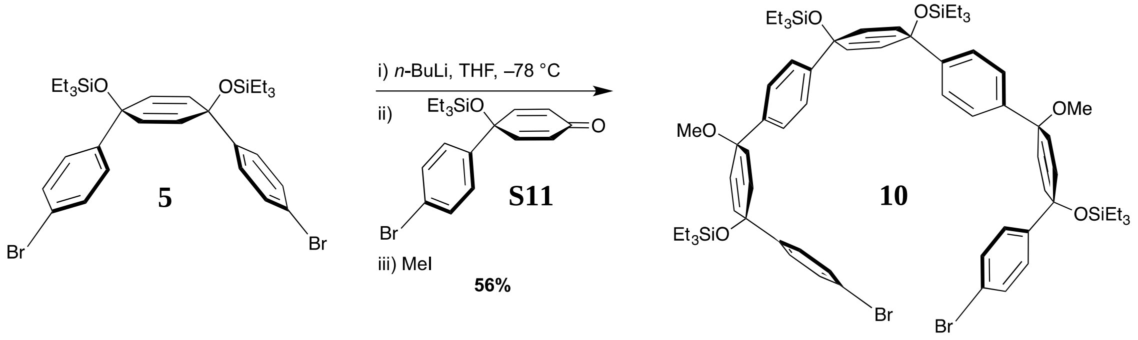
S10. **14** (50 mg, 0.047 mmol, 1 equiv) was dissolved in tetrahydrofuran (1.2 mL) and a Tetra-*n*-butylammonium fluoride (0.21 mL, 0.28 mmol, 6 equiv, 1 M in tetrahydrofuran) was added. The reaction was stirred for 1 h at room temperature and quenched with water. Solvent was removed from this mixture under reduced pressure. Filtration afforded **S10** as a white solid, which was washed with dichloromethane.



***m*[7]CPP**. Crude **S10** was dissolved in minimal tetrahydrofuran and to it was added a solution of tin(II) dichloride monohydrate (23 mg, 100 µmol, 2.1 eq) and concentrated aqueous hydrochloric acid (17 µL, 200 µmol, 4.2 eq) in THF (1 mL). The reaction was stirred at room temperature for 1 h and quenched with a 1 M aqueous solution of NaOH. This mixture was extracted with DCM and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the material was purified by preparative thin layer chromatography on alumina (25% dichloromethane in hexanes) to yield ***m*[7]CPP** as a yellow fluorescent solid. (20 mg, 79%). IR (neat) 3020, 2922, 2850, 1581, 1480, 1261 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.51 – 7.43 (m, 19H), 7.42 (d, J = 8.5 Hz, 4H), 7.21 (d, J = 8.4 Hz, 4H), 6.08 (t, J = 1.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.54, 141.91, 138.78, 137.57, 137.37, 137.30, 137.24, 136.58, 129.08, 128.90, 127.69, 127.51, 127.48, 127.43, 127.02, 123.02. HRMS (ASAP-TOF) (m/z): $[M+H]^+$ calculated for $C_{42}H_{29}$, 533.2269; found, 533.2278.

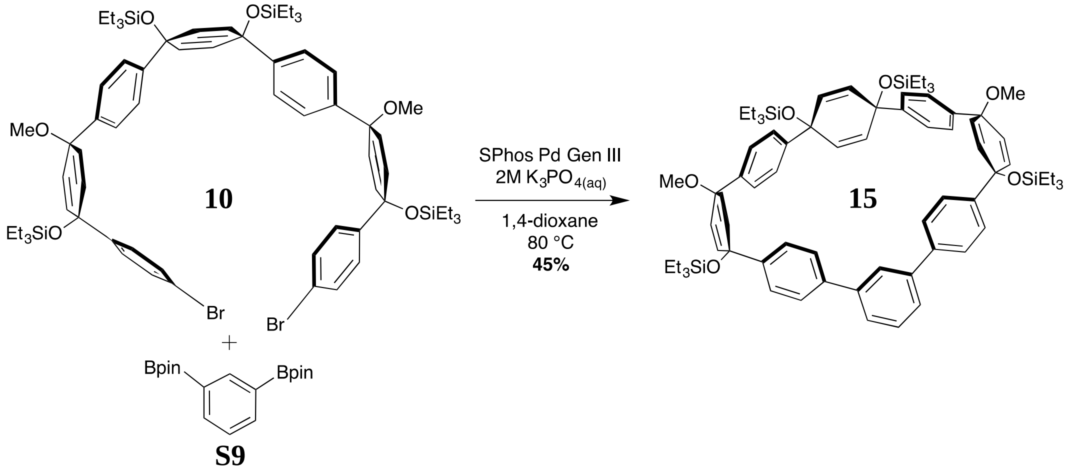


5. 1,4-dibromobenzene (5.00 g, 21.2 mmol, 2.8 equiv) was dissolved in tetrahydrofuran (125 mL) and cooled to –78 °C. *n*-BuLi (8.2 mL, 20.4 mmol, 2.7 equiv, 2.5 M in hexanes) was added followed by 1,4-benzoquinone (818 mg, 7.57 mmol, 1 equiv), which was added in fifths. After each fifth, the reaction turned blue and the next fifth was not added until the reaction became yellow. When the last fifth was added, the reaction was stirred for 1 h, triethylsilyl chloride (4.4 mL, 4.0 g, 26 mmol, 3.5 equiv) was added and the reaction was warmed to room temperature overnight. The next day, the reaction was quenched with water (60 mL) and extracted with ethyl acetate (3 x 60 mL). The combined extracts were washed with brine (60 mL), dried over anhydrous sodium sulfate and solvent was removed to yield an oil. The product was purified by automated flash silica column chromatography (0% to 20% dichloromethane in hexanes) to yield a clear colorless oil. This was mixed with an equal amount of ethanol and let sit to yield large crystals, which were filtered and washed with ethanol, to yield **5** as a white solid (1.80 mg, 37%). IR (neat) 2952, 2871, 1477, 1400 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.3 Hz, 4H), 7.17 (d, *J* = 8.3 Hz, 4H), 5.95 (s, 4H), 0.92 (t, *J* = 7.9 Hz, 18H), 0.59 (q, *J* = 8.0 Hz, 12H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 144.94, 131.39, 131.25, 127.60, 121.30, 71.09, 7.01, 6.41. HRMS (EI) (m/z): [M]$^+$ calculated for $C_{30}H_{42}Br_2O_2Si_2$, 648.1090; found, 648.1081.

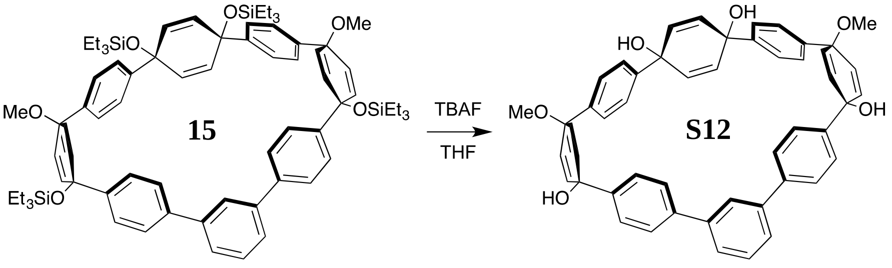


10. **5** (1.63 g, 2.50 mmol, 1 equiv) was dissolved in tetrahydrofuran (50 mL, 100 mM) and cooled to –78 °C. *n*-BuLi (2.0 mL, 5.0 mmol, 2 equiv, 2.5 M in hexanes) was added followed immediately by **S11** (1.5

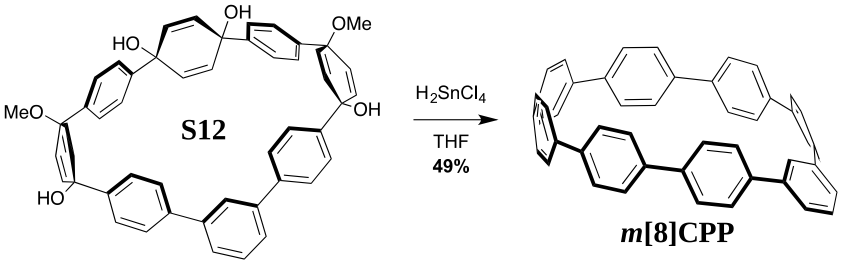
mL, 1.9 g, 5 mmol, 2 equiv) and the reaction was stirred for 1 h at –78 °C. It was quenched with methyl iodide (470 µL, 1.1 g, 7.5 mmol, 3 eq), warmed to room temperature and stirred overnight. The next day, water (20 mL) was added and the product was extracted with ethyl acetate (3 x 20 mL). The combined extracts were washed with brine (20 mL) and dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure to yield an oil. The product was purified by automated flash silica column chromatography (20% to 80% dichloromethane in hexanes) to yield **10** as a white solid (1.8 g, 56%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.6 Hz, 4H), 7.30 (d, *J* = 8.5 Hz, 4H), 7.26 (d, *J* = 8.5 Hz, 4H), 7.16 (d, *J* = 8.6 Hz, 4H), 6.09 (d, *J* = 10.2 Hz, 4H), 5.99 (d, *J* = 10.2 Hz, 4H), 5.96 (s, 4H), 3.33 (s, 6H), 0.96 (t, *J* = 7.9 Hz, 18H), 0.92 (t, *J* = 7.9 Hz, 18H), 0.66 (q, *J* = 7.9 Hz, 12H), 0.60 (q, *J* = 7.9 Hz, 12H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 145.68, 144.93, 141.99, 135.06, 131.40, 131.11, 129.35, 127.51, 126.02, 125.95, 121.07, 74.30, 71.68, 71.18, 52.06, 7.05, 6.49, 6.44. HRMS (ESI-TOF) (m/z): [M+Na]$^+$ calculated for $C_{68}H_{94}Br_2NaO_6Si_4$, 1299.4392; found, 1299.4379.



15. **S9** (206 mg, 0.63 mmol, 1 equiv), **10** (800 mg, 0.63 mmol, 1 equiv), and Sphos Pd Gen III (49 mg, 0.063 mmol, 0.1 equiv) were dissolved in 1,4-dioxane (125 mL) and heated to 80 °C. K_3PO_4 (12.5 mL, 2 M in deionized water) was added and the reaction was stirred overnight. The reaction mixture was filtered through Celite®, dried over sodium sulfate, and the solvent was removed under reduced pressure to yield a golden oil. The product was purified by automated flash silica column chromatography (20% to 80% dichloromethane in hexanes) to yield **15** as a white solid (340 mg, 45%). IR (neat) 2951, 2874, 1457, 1406 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 7.58 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 4H), 7.51 (d, *J* = 8.4 Hz, 4H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 4H), 7.42 (d, *J* = 8.3 Hz, 4H), 6.15 (s, 4H), 6.12 (d, *J* = 10.1 Hz, 4H), 6.01 (d, *J* = 10.2 Hz, 4H), 3.29 (s, 6H), 1.01 (t, *J* = 7.9 Hz, 18H), 0.89 (t, *J* = 8.0 Hz, 18H), 0.72 (q, *J* = 8.0 Hz, 12H), 0.53 (q, *J* = 8.0 Hz, 12H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 146.21, 145.04, 142.66, 141.06, 139.60, 135.49, 132.44, 131.12, 128.16, 127.82, 126.87, 126.31, 126.22, 125.87, 124.78, 73.80, 72.04, 69.76, 51.42, 7.12, 6.53. HRMS (ESI-TOF) (m/z): [M+Na]$^+$ calculated for $C_{74}H_{98}NaO_6Si_4$, 1217.6338; found, 1217.6381.

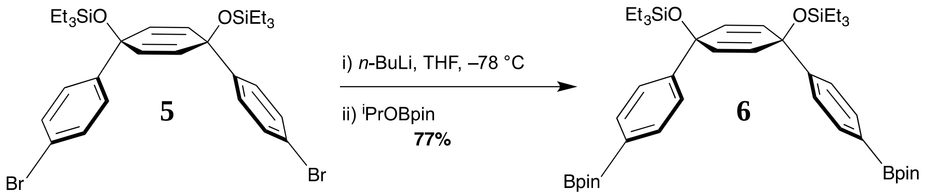


S12. **15** (100 mg, 0.084 mmol, 1 equiv) was dissolved in tetrahydrofuran (2.1 mL) and Tetra-*n*-butylammonium fluoride (0.50 mL, 0.50 mmol, 6 equiv, 1 M in tetrahydrofuran) was added. The reaction was stirred for 1 h at room temperature and was quenched with water. Tetrahydrofuran was removed from this mixture under reduced pressure and filtration afforded **S12** as a white solid, which was washed with dichloromethane. This crude material was used as is for the next reaction.

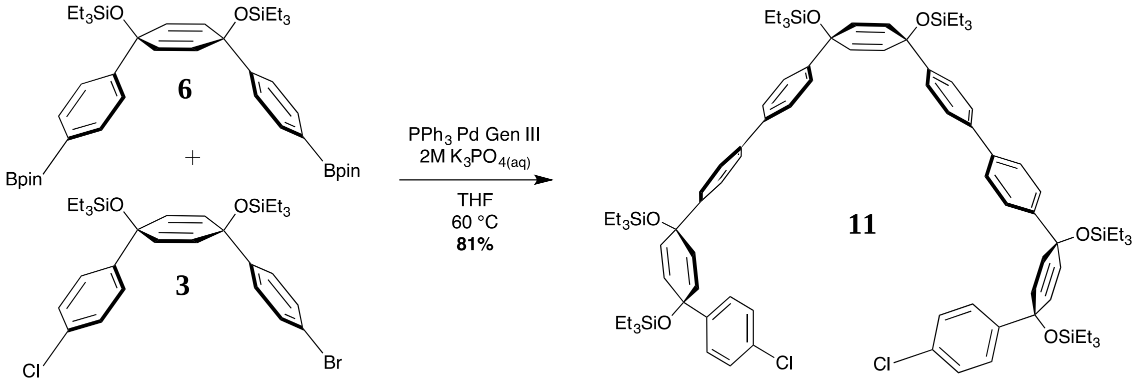


***m*[8]CPP**. Crude **S12** was dissolved in minimal tetrahydrofuran and to it was added a solution of tin(II) dichloride monohydrate (62 mg, 280 µmol, 3.3 eq) and concentrated aqueous hydrochloric acid (44 µL, 530 µmol, 6.3 eq) in THF (2.1 mL). The reaction was stirred at room temperature for 1 h and quenched with a 1 M aqueous solution of NaOH (1 mL). This mixture was extracted with dichloromethane (3 x 3 mL) and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the product was purified by automated flash silica column chromatography (0% to

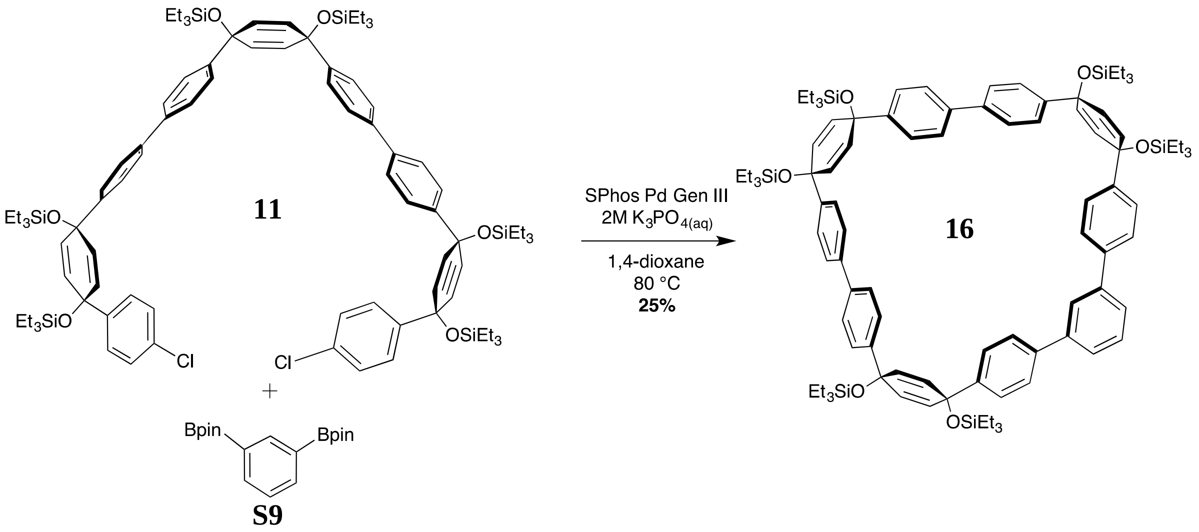
100% dichloromethane in hexanes) to yield ***m*****[8]CPP** as a yellow solid (25 mg, 49%). IR (neat) 3022, 1586, 1481, 1388 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.56 (dt, J = 7.7, 1.8 Hz, 2H), 7.52 – 7.44 (m, 17H), 7.40 – 7.36 (m, 8H), 7.32 (d, J = 8.2 Hz, 4H), 6.36 (t, J = 1.8 Hz, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 142.42, 141.12, 139.45, 138.47, 138.00, 137.83, 137.57, 137.23, 135.86, 128.93, 128.51, 127.52, 127.49, 127.27, 127.24, 127.14, 123.24. HRMS (ASAP-TOF) (m/z): [M+H]$^+$ calculated for C$_{48}$H$_{33}$, 608.2582; found, 609.2585.



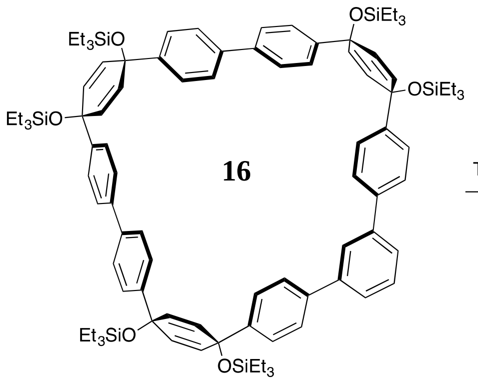
6. **5** (3.00 g, 4.61 mmol, 1 equiv) was dissolved in tetrahydrofuran (50 mL) and cooled to –78 °C. *n*-BuLi (3.9 mL, 9.7 mmol, 2.1 equiv, 2.5 M in hexanes) was added followed immediately by 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.1 mL, 1.9 g, 10 mmol, 2.2 equiv). The reaction was stirred for 30 min and warmed to room temperature. The reaction was quenched with water (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined extracts were washed with brine (20 mL), dried over anhydrous sodium sulfate, and solvent was removed under reduced pressure to yield an oil. The oil was mixed with an equal amount of ethanol and placed in the freezer until crystals formed, which was filtered to yield **6** as a white crystalline powder (2.65 g, 77%). IR (neat) 2949, 2872, 1607, 1355 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.6 Hz, 4H), 7.37 (d, *J* = 7.7 Hz, 4H), 5.99 (s, 4H), 1.37 (s, 24H), 0.95 (t, *J* = 7.8 Hz, 18H), 0.62 (q, *J* = 7.8 Hz, 12H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 149.08, 134.69, 131.41, 125.18, 83.72, 71.56, 24.89, 7.04, 6.45. HRMS (ESI-TOF) (m/z): [M+Na]$^+$ calculated for C$_{42}$H$_{66}$B$_2$NaO$_6$Si$_2$, 767.4482; found, 767.4514.



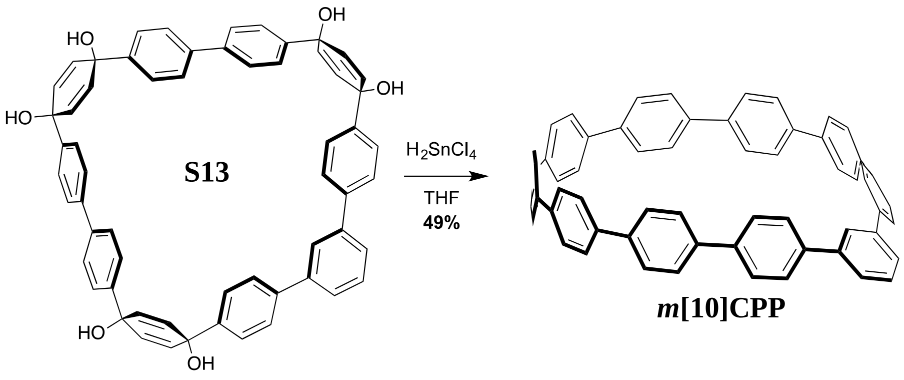
11. **6** (250 mg, 0.34 mmol, 1 equiv), **3** (407 mg, 0.67 mmol, 2 equiv), and PPh_3 Pd Gen III (11 mg, 0.017 mmol, 0.05 equiv) were dissolved in tetrahydrofuran (6.7 mL) and heated to 60 °C. K_3PO_4 (0.67 mL, 2 M in deionized water) was added and the reaction was left overnight. The next day, the reaction was cooled to room temperature, filtered through Celite® while rinsing with ethyl acetate (15 mL), and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the product was purified by automated flash silica column chromatography (0% to 50% dichloromethane in hexanes) to yield **11** as a white solid (421 mg, 81%). IR (neat) 2952, 2874, 1489, 1458, 1238 cm^{-1}; ^1H NMR (500 MHz, Chloroform-d) δ 7.50 (d, J = 8.2 Hz, 8H), 7.42 (d, J = 8.0 Hz, 4H), 7.36 (d, J = 7.9 Hz, 4H), 7.28 (d, 4H), 7.22 (d, J = 7.8 Hz, 4H), 6.04 (s, 4H), 6.03 (d, J = 8.8 Hz, 4H), 5.95 (d, J = 9.7 Hz, 4H), 0.94 (q, J = 8.3 Hz, 54H), 0.67 – 0.57 (m, 36H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.18, 144.83, 144.66, 139.70, 139.48, 132.99, 131.80, 131.52, 131.16, 128.23, 127.33, 126.78, 126.74, 126.33, 126.22, 71.38, 71.28, 71.18, 7.09, 7.06, 7.05, 6.51, 6.49, 6.45. HRMS (ESI-TOF) (m/z): $[M+Na]^+$ calculated for $C_{90}H_{126}Cl_2NaO_6Si_6$, 1563.7445; found, 1563.7485.



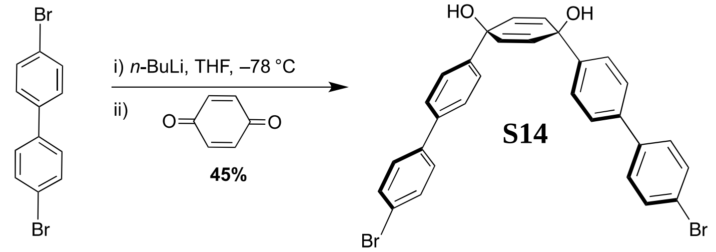
16. **11** (245 mg, 0.16 mmol, 1 equiv), **S9** (52 mg, 0.16 mmol, 1 equiv), and SPhos Pd Gen III (12 mg, 0.016 mmol, 0.1 equiv) were dissolved in 1,4-dioxane (80 mL) and heated to 80 °C. K_3PO_4 (8 mL, 2M in deionized water) was added and the reaction was stirred for 3 h. The reaction mixture was filtered through Celite® and dried over anhydrous sodium sulfate. Solvent was removed to yield a brown oil, which was purified by automated flash silica column chromatography (0% to 100% dichloromethane in hexanes) to yield a white solid. The product was purified by recycling gel permeation chromatography (chloroform) to yield **16** as a white solid (62 mg, 25%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.58 – 7.52 (m, 6H), 7.52 – 7.46 (m, 9H), 7.46 – 7.39 (m, 8H), 7.35 (d, *J* = 8.3 Hz, 4H), 6.11 (d, *J* = 9.8 Hz, 4H), 6.04 – 5.97 (m, 7H), 1.03 – 0.87 (m, 54H), 0.71 – 0.53 (m, 36H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.29, 145.22, 144.93, 141.64, 140.39, 139.46, 139.42, 131.80, 131.51, 131.36, 131.24, 129.12, 127.25, 126.75, 126.64, 126.51, 126.38, 126.13, 126.10, 71.57, 71.15, 71.11, 7.10, 7.07, 7.05, 6.49, 6.45. HRMS (ESI-TOF) (m/z): $[M+Na]^+$ calculated for $C_{96}H_{130}NaO_6Si_6$, 1569.8381; found, 1569.8341.



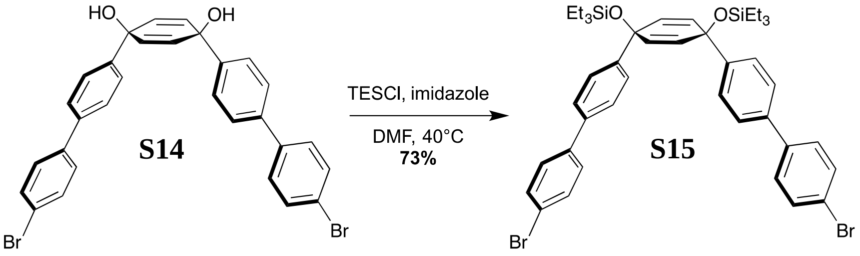
S13. Tetrahydrofuran (1.3 mL) was added to **16** (20 mg, 13 μmol, 1 equiv) and the vial was equipped with a stir bar and septa. Tetra-*n*-butylammonium fluoride (120 μL, 1 mmol, 9 equiv, 1 M in tetrahydrofuran) was added to the reaction flask and stirred for 1 h at room temperature. The reaction was quenched with deionized water (1 mL) and the tetrahydrofuran was removed under reduced pressure. This mixture was filtered through a Büchner funnel, washed with deionized water and dichloromethane yielding **S13** as a white solid. This solid was used as is for the next reaction.



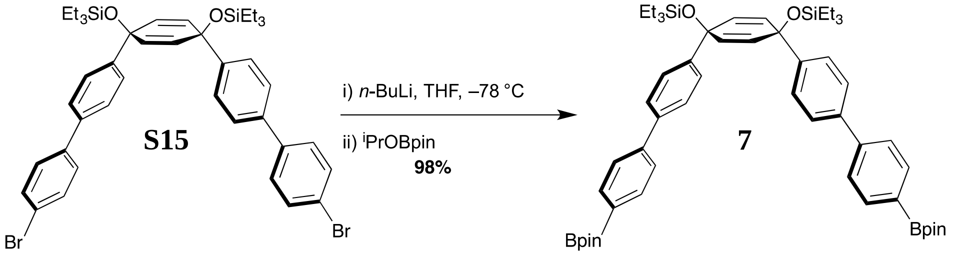
***m*[10]CPP**. Crude **S13** (11 mg, 17 μmol, 1 eq) was dissolved in tetrahydrofuran (300 μL) and to it was added a solution of tin(II) dichloride monohydrate (9.5 mg, 42 μmol, 3.3 eq) and concentrated aqueous hydrochloric acid (6.7 μL, 80 μmol, 6.3 eq) in THF (320 μL). The reaction was stirred at room temperature for 1 h and quenched with a 1 M aqueous solution of NaOH (1 mL). This mixture was extracted with dichloromethane (3 x 3 mL) and the combined extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the product was purified by preparative thin layer chromatography on alumina (50% dichloromethane in hexanes) to yield ***m*[10]CPP** as a white solid (2 mg, 21%). IR (neat) 2918, 2849, 1672, 1480, 1463 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.3 Hz, 8H), 7.60 – 7.56 (m, 19H), 7.55 – 7.50 (m, 8H), 7.43 (d, *J* = 7.9 Hz, 4H), 6.86 (s, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 142.37, 141.12, 139.51, 139.22, 138.49, 138.32, 138.20, 138.13, 138.00, 137.93, 133.39, 129.03, 128.54, 127.65, 127.53, 127.49, 127.45, 127.44, 127.33, 127.24, 127.12, 124.26. LRMS (MALDI) (m/z): [M]$^+$ calculated for $C_{60}H_{40}$, 760.3125; found, 760.244.



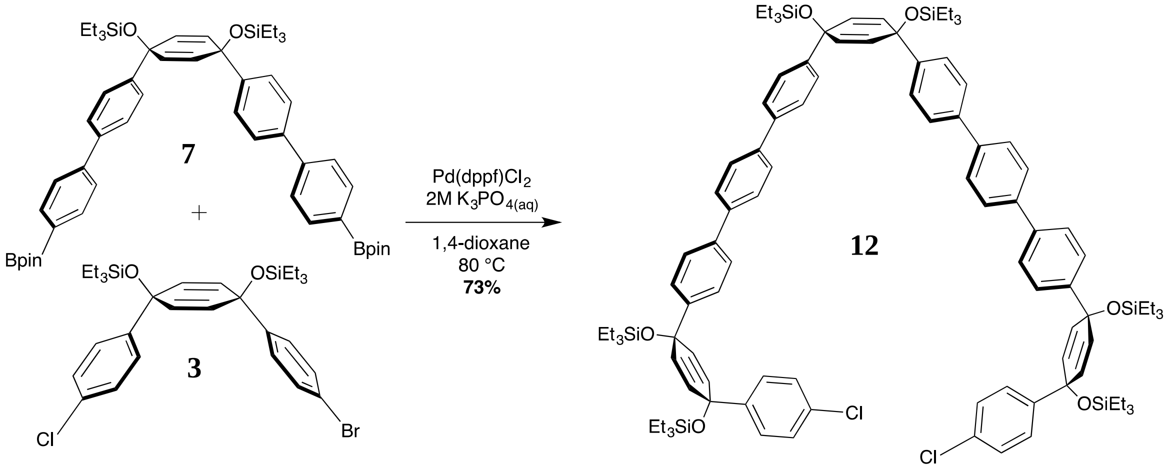
S14. 4,4'-Dibromobiphenyl (19 g, 0.061 mol, 3.3 eqiv) was added to a 1000 mL round bottom flask equipped with a stir bar. The reaction flask was capped with a septa and the round bottom flask was evacuated and purged with nitrogen. Tetrahydrofuran (370 mL) was added to the reaction flask and cooled for 30 min at –78 °C. *n*-BuLi (24.1 mL, 0.11 mol, 1.05 equiv, 2.3 M in hexanes) was added to the reaction mixture dropwise over 25 min. The light brown solution was stirred for 15 min producing a white precipitate in a brown solution. *p*-benzoquinone (14.5 mL, 0.10 mol, 1 equiv) was added to a 9 mL test tube and capped with a septa in order to weigh due to pungent odor. This was added portion-wise by removing the septa from the reaction flask (while a large flow of nitrogen was still flowing into the flask). As the benzoquinone was added, the reaction mixture turns blue momentarily before returning to brown. Benzoquinone was added until the blue color remained (2.3 g total). The reaction was stirred at –78 °C for 3 h. The reaction was quenched with deionized water (160 mL) at –78 °C. The reaction mixture was warmed to room temperature. The product was extracted with ethyl acetate (3 x 200 mL) and washed with brine (3 x 100 mL). The organic layers were dried over sodium sulfate, decanted and concentrated to yield the crude product as a dark orange solid. This was purified by automated flash silica gel chromatography (10% to 60% ethyl acetate in hexanes). The crude product **S14** was used as is for the next reaction.



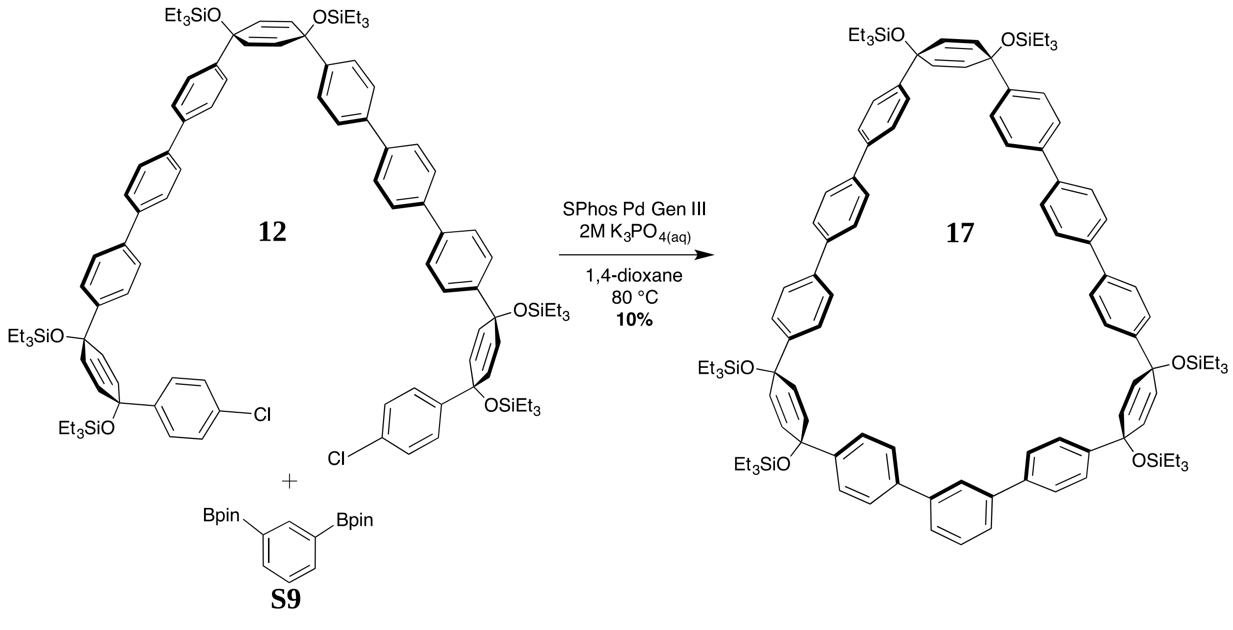
S15. **S14** (4.0 g, 7.0 mmol, 1 equiv) and imidazole (1.9 g, 28 mmol, 4 equiv) were added to a 250 mL round bottom flask equipped with a stir bar and septum. Dimethylformamide (35 mL) was added to the flask followed by triethylsilyl chloride (3.8 mL, 23 mmol, 1.2 equiv). The reaction mixture was heated to 40 °C in an oil bath and stirred overnight. The reaction mixture was cooled to room temperature and quenched with a saturated solution of sodium bicarbonate (30 mL). The product was extracted with ethyl acetate (3 x 100 mL) and washed with 5% lithium chloride solution in water (5 x 60 mL). The organic layers were dried over sodium sulfate and concentrated to yield the crude product as a brown solid. The product was purified by automated flash silica gel chromatography (0% to 10% ethyl acetate in hexanes) to give **S15** as a pale yellow solid (4.10 g, 39% 2 steps). IR (neat) 2952, 2874, 1481, 1458 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.53 (d, J = 8.4 Hz, 4H), 7.47 – 7.41 (m, 12H), 6.04 (s, 4H), 0.95 (t, J = 7.9 Hz, 18H), 0.63 (q, J = 7.9 Hz, 12H). ^{13}C NMR (151 MHz, CDCl3) δ 145.55, 139.66, 138.79, 131.83, 131.51, 128.62, 126.65, 126.45, 121.50, 71.32, 7.07, 6.46. LRMS (MALDI) (m/z): [M]$^+$ calculated for $C_{42}H_{50}Br_2O_2Si_2$, 802.17; found, 802.24.



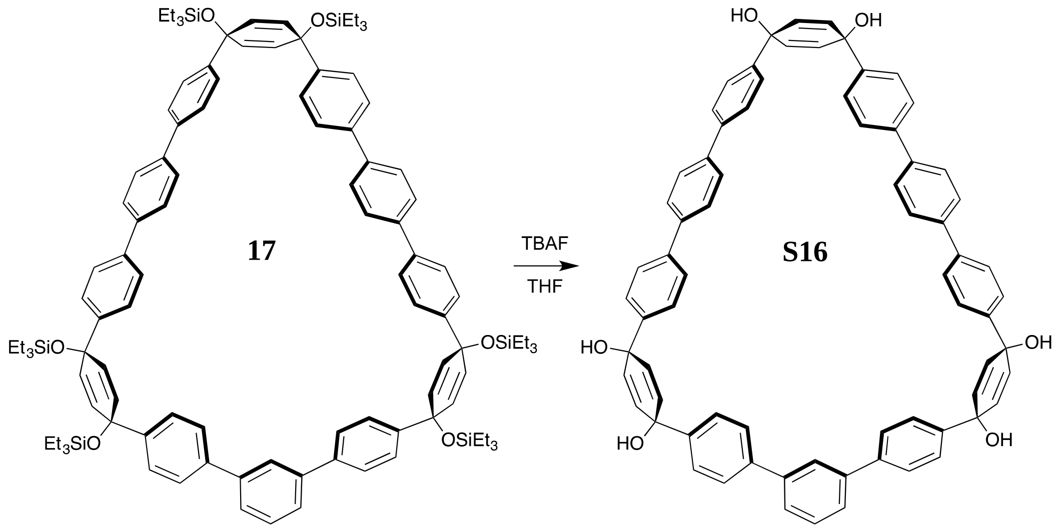
7. **S15** (3.0 g, 3.74 mmol, 1.0 eqiv) was added to a 100 mL round bottom flask equipped with a stir bar. The reaction flask was capped with a septa evacuated and refilled with nitrogen. Tetrahydrofuran (19 mL) was added to the reaction flask and the mixture was cooled for 30 min at –78 °C. *n*-BuLi (3.4 mL, 8.2 mmol, 2.2 equiv, 2.4 M in hexanes) was added to the reaction mixture dropwise, followed by the dropwise addition of 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.0 mL, 14.9 mmol, 4 equiv) and the reaction was stirred at –78 °C for 1 h. The reaction was quenched with deionized water (30 mL) at –78 °C and warmed to room temperature. The product was extracted with ethyl acetate (3 x 50 mL) and washed with brine (3 x 20 mL). The organic layers were dried over sodium sulfate and concentrated to yield **7** as a yellow solid (3.3 g, 98%). IR (neat) 2954, 2875, 1609, 1359 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.87 (d, J = 7.7 Hz, 4H), 7.63 – 7.41 (m, 12H), 6.04 (s, 4H), 0.96 (t, J = 7.8 Hz, 18H), 0.64 (q, J = 8.1 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.52, 143.50, 139.86, 135.33, 131.59, 127.02, 126.41, 83.84, 71.43, 24.94, 24.88, 7.17, 6.56. HRMS (ESI-TOF) (m/z): [M+Na]$^+$ calculated for $C_{54}H_{74}B_2O_6Si_2$, 919.5108; found, 919.5129.



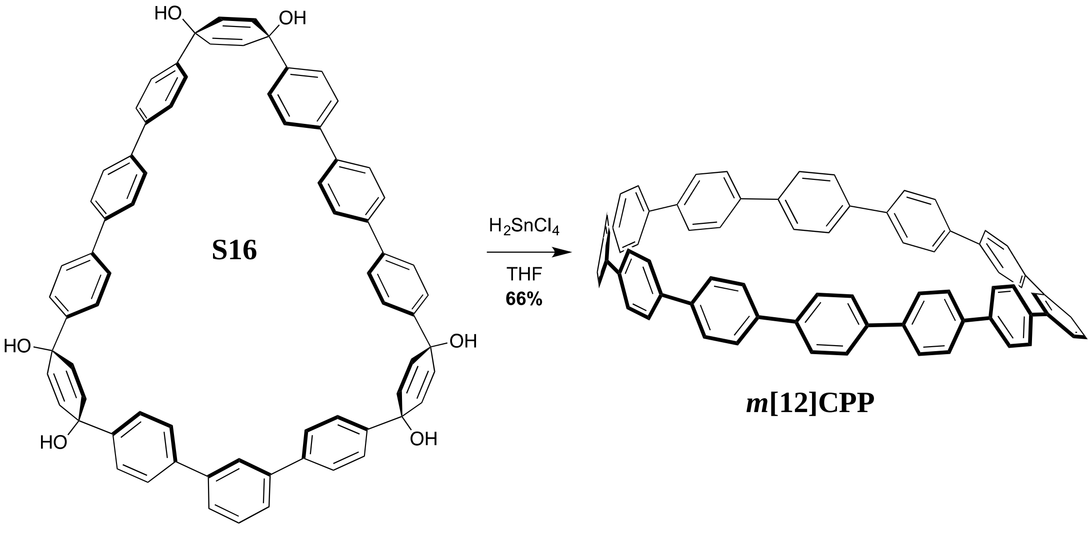
12. **7** (85.8 mg, 0.22 mmol, 1 equiv), **3** (270.3 mg, 0.45 mmol, 2 equiv) and Pd(dppf)$_2$Cl$_2$ (25.5 mg, 0.031 mmol, 0.07 equiv) were added to a 10 mL round bottom flask equipped with a stir bar. The flask was evacuated (5 min) and purged with nitrogen 5 times. 1,4-dioxane and 2 M aqueous K_3PO_4 were sparged with nitrogen for at least 1 h prior to use. The round bottom flask was equipped with a septa and 1,4-dioxane (2.2 mL) was added to the round bottom flask. The round bottom flask was heated to 80 °C over 5 min and K_3PO_4 (0.22 mL, 2 M in deionized water) was added. The reaction was stirred at 80 °C overnight. The reaction mixture was cooled to room temperature and filtered through a fritted suction funnel filled with Celite®. The round bottom flask was rinsed with dichloromethane, which was filtered through the Celite® plug. The filtrate was added to a separatory funnel along with deionized water (20 mL) and the product was extracted (3 x 20 mL) with dichloromethane. The organic layer was washed with brine (20 mL), dried over sodium sulfate and concentrated to yield the crude product as a brown solid. The product was purified by automated flash silica gel chromatography (5% to 25% dichloromethane in hexanes to yield **12** as a white solid (277 mg, 73%). IR (neat) 2952, 2874, 1485, 1457, 1401 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (s, 8H), 7.55 (t, *J* = 7.7 Hz, 8H), 7.46 (d, *J* = 8.1 Hz, 4H), 7.39 (d, *J* = 8.1 Hz, 4H), 7.30 (s, 4H), 7.23 (d, *J* = 8.4 Hz, 4H), 6.09 – 6.02 (m, 8H), 5.97 (d, *J* = 9.9 Hz, 4H), 0.99 – 0.92 (m, 54H), 0.67 – 0.59 (m, 36H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.26, 144.97, 144.68, 139.72, 139.61, 139.57, 139.48, 133.02, 131.82, 131.58, 131.21, 128.76, 128.28, 127.41, 127.38, 126.78, 126.76, 126.43, 126.32, 71.44, 71.32, 71.19, 18.66, 11.28, 7.14, 7.11, 7.09, 6.53, 6.51, 6.47, 6.34. LRMS (MALDI) (m/z): [M]$^{+}$ calculated for $C_{102}H_{134}Cl_2O_6Si_6$, 1693.82; found, 1694.838.



17. **S9** (34.7 mg, 0.11 mmol, 1 equiv), **12** (101.3 mg, 0.054 mmol, 1.05 equiv) and Pd Sphos Gen III 3.6 mg, 0.0045 mmol, 0.1 equiv) were added to a 100 mL round bottom flask equipped with a stir bar. The flask was evacuated (5 min) and purged with nitrogen 5 times. 1,4-dioxane and aqueous 2 M K_3PO_4 were sparged for at least 1 h prior to use. The round bottom flask was equipped with a septum and 1,4-dioxane (33 mL) was added to the round bottom flask and the solution was sparged for 30 min. The round bottom flask was heated to 80 °C over 10 min and K_3PO_4 (0.33 mL, 2 M in deionized water) was added. The reaction was stirred at 80 °C overnight. The reaction mixture was cooled to room temperature and filtered through a fritted suction funnel filled with Celite®. The round bottom flask was rinsed with dichloromethane, which was also filtered through the Celite® plug. The filtrate was added to a separatory funnel along with deionized water (30 mL) and the product was extracted (3 x 30 mL) with dichloromethane. The organic layer was washed with brine (40 mL), dried over sodium sulfate and concentrated to yield a brown oil. The product was purified by flash silica column chromatography (0% to 30% dichloromethane in hexanes) followed by recycling gel permeation chromatography yielding **17** as a white solid (18 mg, 10%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.77 (t, J = 1.7 Hz, 1H), 7.65 (d, J = 3.5 Hz, 2H), 7.62 – 7.45 (m, 25H), 7.36 (d, J = 8.1 Hz, 8H), 6.16 (d, J = 9.7 Hz, 4H), 6.05 (s, 4H), 6.00 (d, J = 9.8 Hz, 4H), 1.00 (t, J = 7.9 Hz, 18H), 0.97 (t, J = 7.9 Hz, 18H), 0.92 (t, J = 7.9 Hz, 18H), 0.71 (q, J = 7.9 Hz, 12H), 0.65 (q, J = 7.9 Hz, 12H), 0.57 (q, J = 7.9 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.33, 145.06, 144.75, 141.82, 140.68, 139.63, 139.48, 139.42, 139.27, 132.07, 131.64, 131.10, 127.39, 127.37, 127.30, 127.28, 126.74, 126.61, 126.56, 126.53, 126.18, 71.80, 71.72, 71.01, 7.14, 7.10, 7.05, 6.50, 6.48. LRMS (MALDI) (m/z): $[M+H]^+$ calculated for $C_{108}H_{139}O_6Si_6$, 1699.919; found, 1699.904.



S16. Tetrahydrofuran (0.11 mL) was added to **17** (18.2 mg, 0.01 mmol, 1 equiv) and the vial was equipped with a stir bar and septa. Tetra-*n*-butylammonium fluoride (0.11 mL, 0.1 mmol, 10 equiv, 1 M in tetrahydrofuran) was added to the reaction flask and this was stirred for 2 h at room temperature. The reaction was quenched with deionized water (5 mL) causing the product to precipitate. The resulting solution was filtered in a Büchner funnel, washed with deionized water and dichloromethane yielding **S16** as a white solid. The crude product was used as is for the following reaction.



***m*[12]CPP**. $SnCl_2$•H_2O (180.6 mg, 0.80 mmol) was added to a 100 mL round bottom flask equipped with a stir bar and septum. Tetrahydrofuran (20 mL) was added to the flask followed by hydrochloric acid (0.13 mL, 1.6 mmol, 12 M). This was stirred at room temperature for 30 min. H_2SnCl_2 solution (0.9 mL, 0.04

mmol, 3.3 equiv, 0.04 M) was added to the scintillation vial containing **S16** (11.1 mg, 0.01 mmol, 1 equiv) and was stirred for 1 h at room temperature. The reaction was quenched with saturated sodium bicarbonate (5 mL). The filtrate was transferred to a separatory funnel and the product was extracted with ethyl acetate (3 x 7 mL). The organic layers were washed with brine (10 mL), dried over sodium sulfate and concentrated to give the crude product as a yellow solid. The product was purified by preparative thin layer chromatography on alumina (50% dichloromethane in hexanes) and recycling gel permeation chromatography to give ***m*****[12]CPP** as a pale yellow solid (0.5 mg, 5% 2 steps). ***m*****[12]CPP** is too insoluble to record a ^{13}C spectrum. IR (neat) 2924, 2853, 1483 cm^{-1}; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.68 – 7.56 (m, 40H), 7.56 – 7.53 (m, 3H), 7.51 (d, J = 8.4 Hz, 4H), 7.12 (t, J = 1.8 Hz, 1H). LRMS (MALDI) (m/z): [M]$^{+}$ calculated for $C_{72}H_{48}$, 912.3751; found, 912.329.

2. Photophysical Characterization

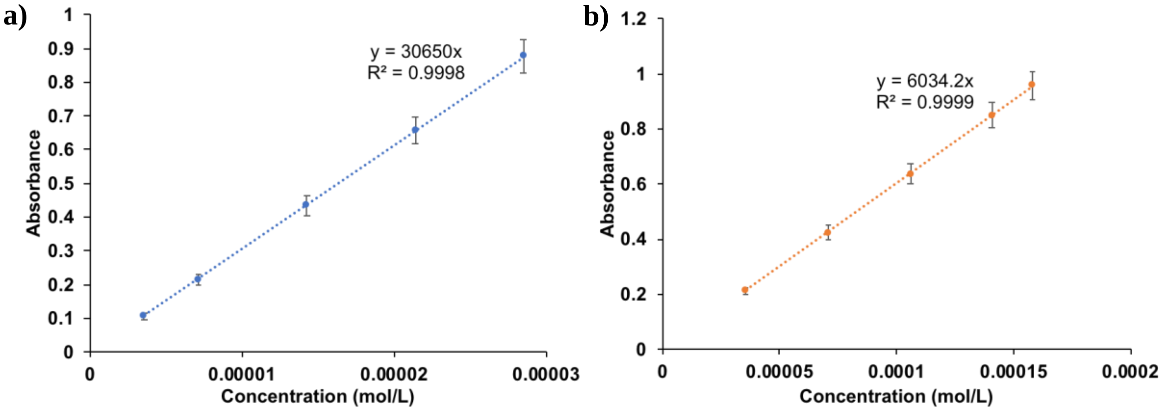


Figure S1. Extinction coefficient determination of ***m*****[5]CPP** at the a) absorbance maxima and b) HOMO→LUMO transition.

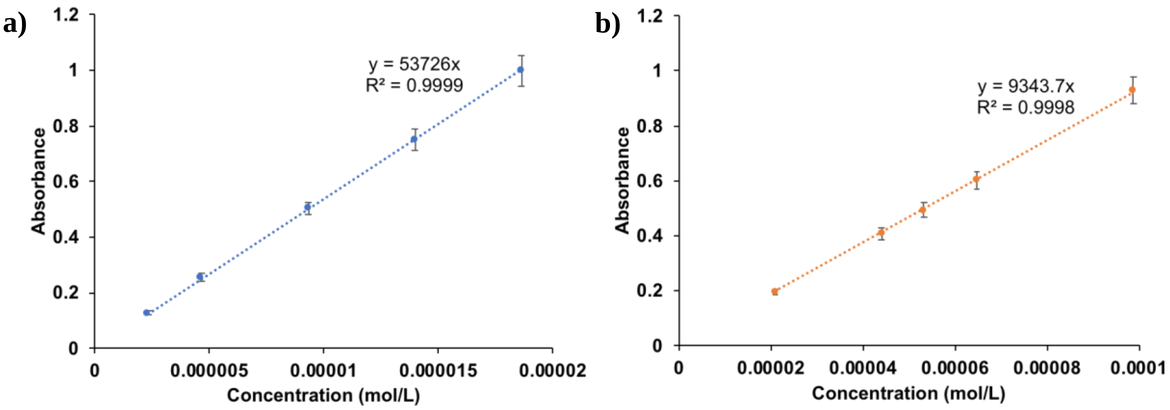


Figure S2. Extinction coefficient determination of ***m*[6]CPP** at the a) absorbance maxima and b) HOMO→LUMO transition.

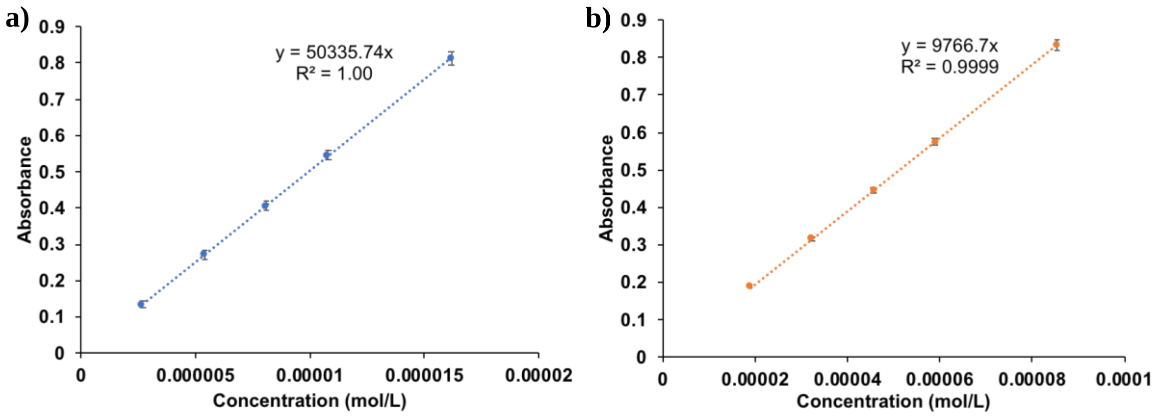


Figure S3. Extinction coefficient determination of ***m*[7]CPP** at the a) absorbance maxima and b) HOMO→LUMO transition.

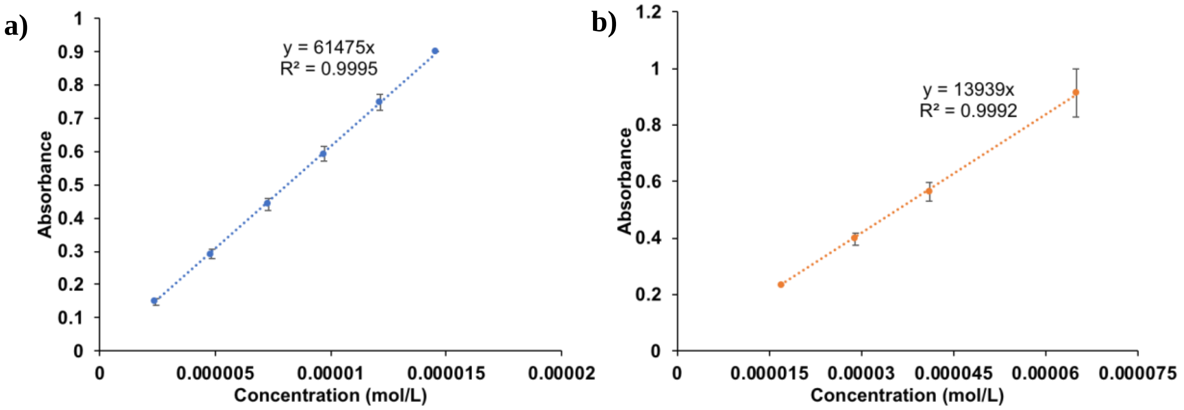


Figure S4. Extinction coefficient determination of ***m*[8]CPP** at the a) absorbance maxima and b) HOMO→LUMO transition.

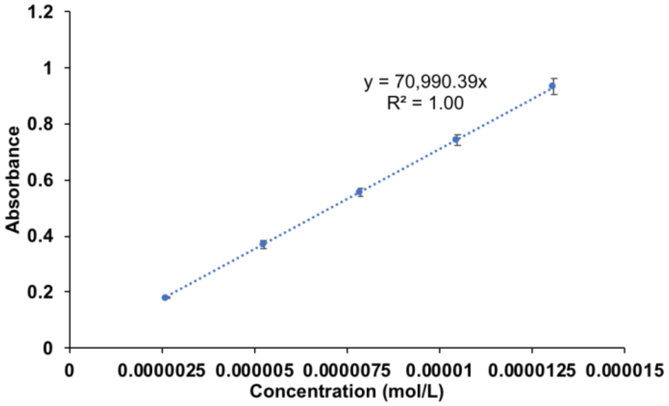


Figure S5. Extinction coefficient determination of ***m*[10]CPP** at the absorbance maxima.

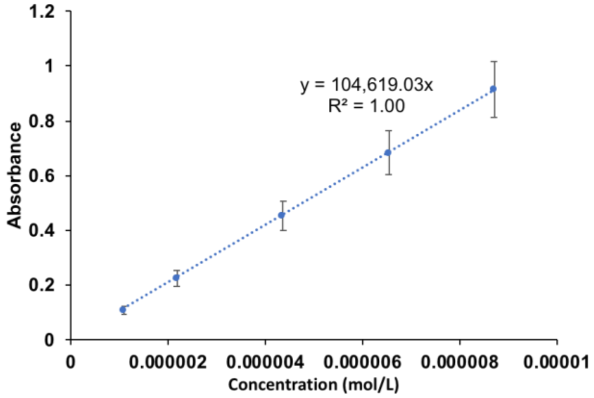


Figure S6. Extinction coefficient determination of ***m*[12]CPP** at the absorbance maxima.

m[*n*]CPP	Trial 1	Trial 2	Trial 3	$\Phi_{\text{Aver.}}$
5	0.013	0.014	0.014	0.014 ± 0.001
6	0.225	0.224	0.224	0.224 ± 0.001
7	0.453	0.445	0.451	0.450 ± 0.004
8	0.592	0.598	0.595	0.595 ± 0.003
10	0.726	0.729	0.722	0.726 ± 0.004
12	0.77	0.772	0.766	0.769 ± 0.003

Table S1. Triplicate quantum yield data, excited at the absorbance maxima.

m[*n*]CPP	Trial 1	Trial 2	Trial 3	$\Phi_{\text{Aver.}}$
5	0.015	0.015	0.014	0.015 ± 0.001
6	0.246	0.232	0.234	0.237 ± 0.008
7	0.47	0.471	0.474	0.472 ± 0.002
8	0.608	0.612	0.608	0.609 ± 0.002

Table S2. Triplicate quantum yield data, excited at HOMO→LUMO transition.

m[*n*]CPP	H→L Absorbance (nm)	$\varepsilon_{H\rightarrow L}$ ($M^{-1}cm^{-1}$)
5	428	$6.0 \times 10^3 \pm 0.3$
6	410	$9.4 \times 10^3 \pm 0.5$
7	394	$9.9 \times 10^3 \pm 0.08$
8	376	$1.4 \times 10^4 \pm 0.1$

Table S3. HOMO→LUMO absorbance maxima and extinction coefficients.

m[*n*]CPP	Lifetime (ns)	Rate of radiative decay (10^8 s^{-1})	Rate of non-radiative decay (10^8 s^{-1})
5	1.05	0.133	9.36
6	2.68	0.834	2.89
7	3.56	1.26	1.54
8	3.41	1.45	1.48
10	2.45	2.96	1.12
12	1.78	4.32	1.30

Table S4. Fluorescence lifetimes and calculated decay rates.

3. Electrochemical Analysis

The oxidation of these molecules proceeds similar to that off CPPs with a decreasing oxidation potential with decreasing size. Two reversible oxidations are observed in the electrochemical window of DCM except for *m*[5]CPP which had a single irreversible oxidation event. As the size of the *m*[*n*]CPP increases, the separation between the oxidations becomes smaller and both oxidations shift to higher potential.

m[*n*]CPP	1st Oxidation (V)	2nd Oxidation (V)	Difference (V)
6	0.50	0.68	0.18
7	0.65	0.82	0.17
8	0.70	0.85	0.15
10	0.79	0.90	0.11
12	0.86	0.94	0.08

Table S5. Oxidation potentials of *m*[*n*]CPPs.

m[*n*]CPP	1st Oxidation Peak (V)
5	0.47
6	0.53
7	0.67
8	0.74
10	0.81
12	0.88

Table S6. First oxidation peak of *m*[*n*]CPPs.

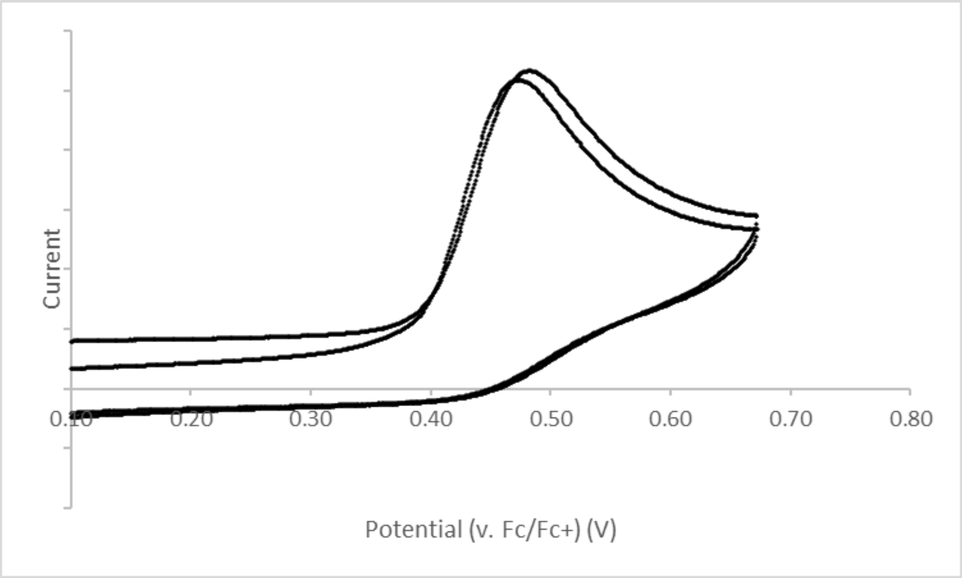


Figure S7. ***m*[5]CPP** Single irreversible oxidation (DCM) E = 0.47 V.

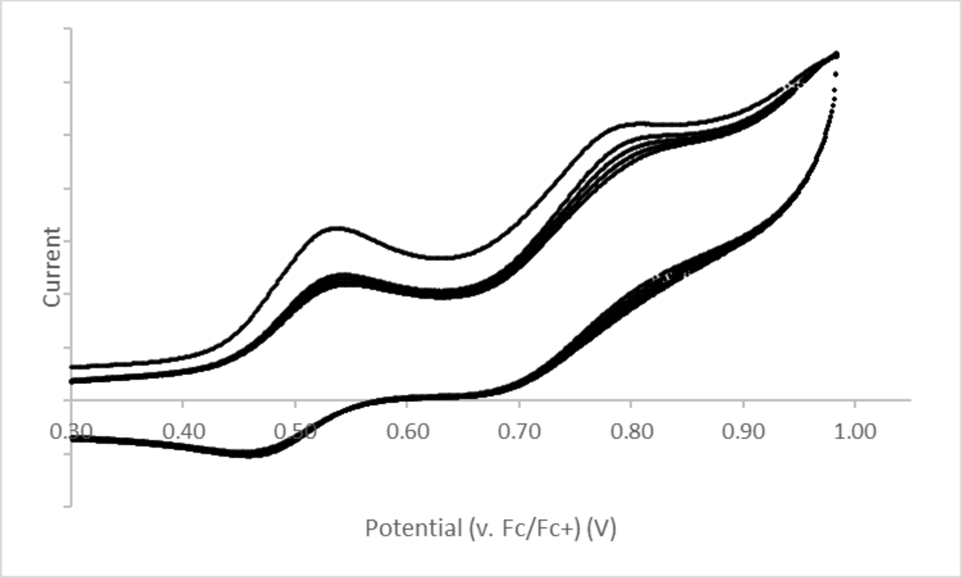


Figure S8. ***m*[6]CPP** Oxidation (DCM) $E_{1/2}$ = 0.50 V and 0.68 V.

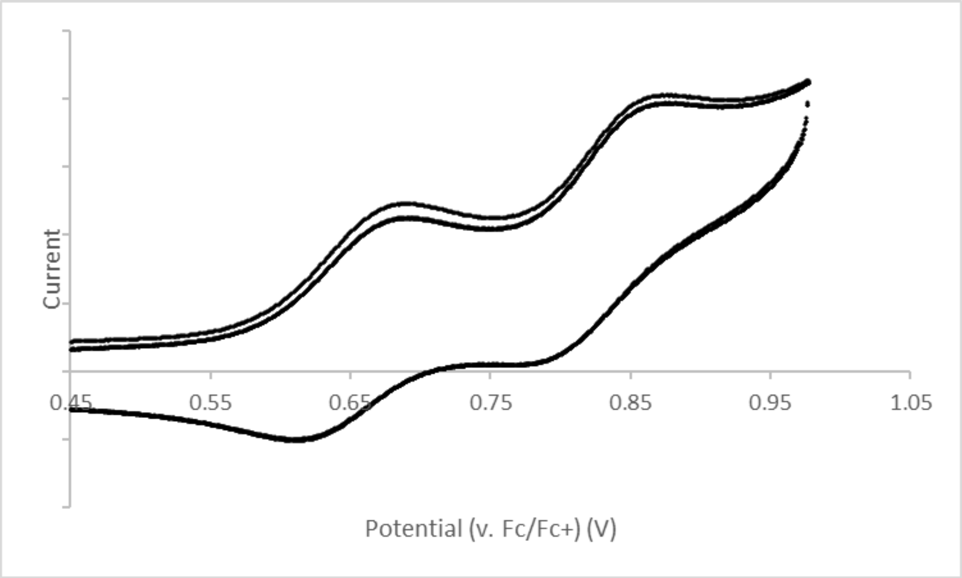


Figure S9. ***m*[7]CPP** Oxidation (DCM) $E_{1/2}$ = 0.65 V and 0.81 V.

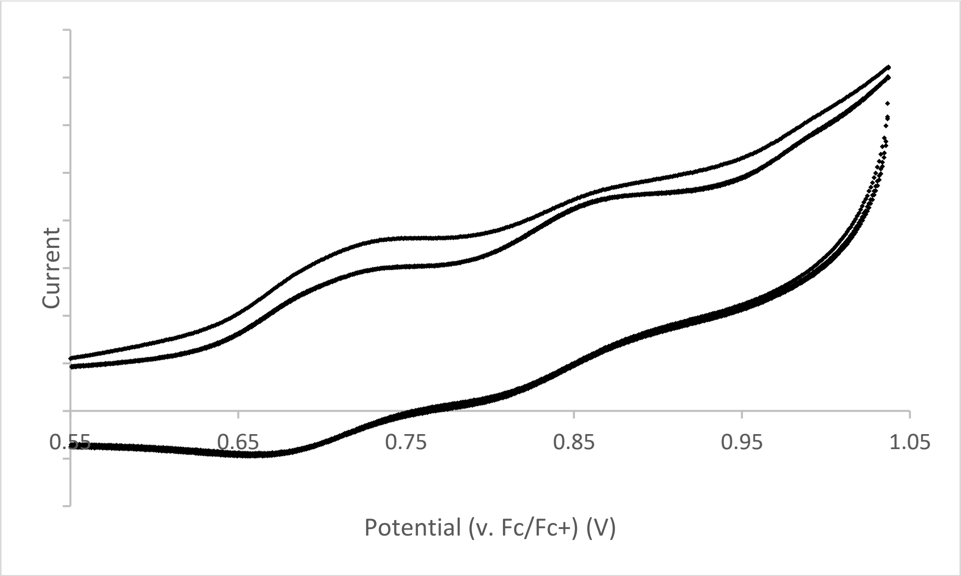


Figure S10. ***m*[8]CPP** Oxidation (DCM) $E_{1/2}$ = 0.69 V and 0.85 V.

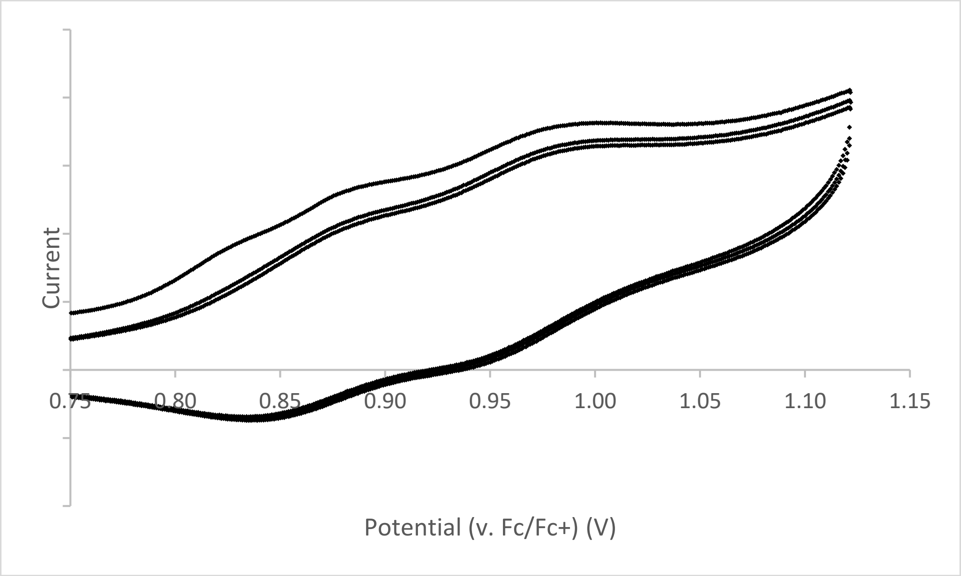


Figure S11. ***m*[10]CPP** Oxidation (DCM) $E_{1/2}$ = 0.80 V and 0.91 V.

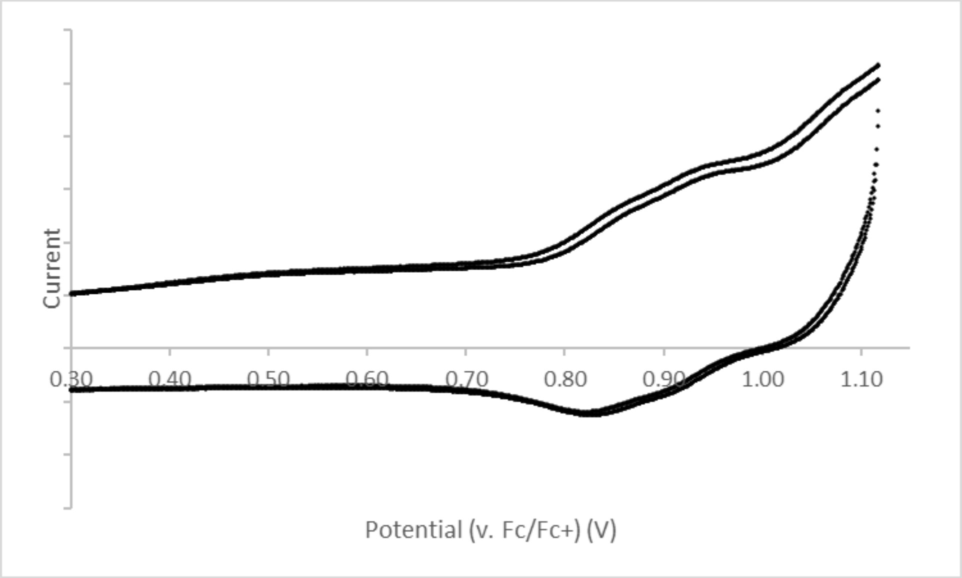


Figure S12. ***m*****[12]CPP** Oxidation (DCM) $E_{1/2}$ = 0.86 V and 0.95 V.

4. HOMO LUMO Level Calculations

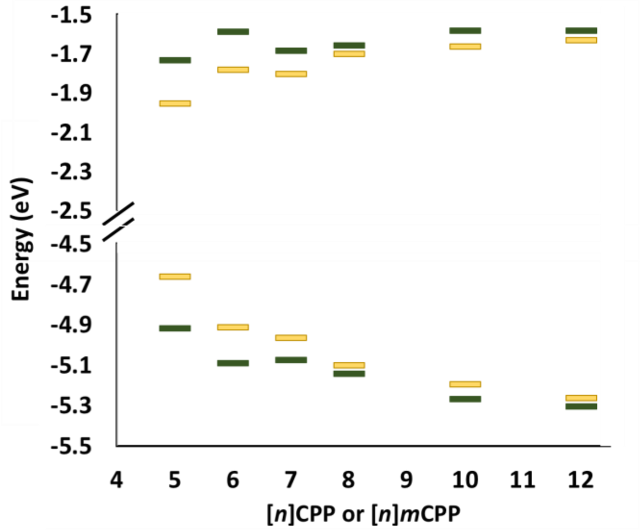


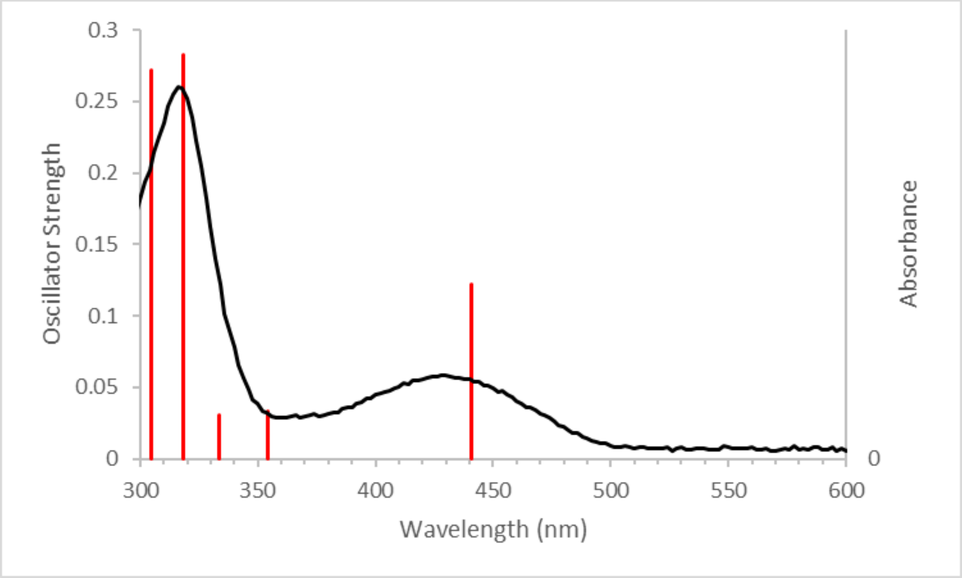
Figure S13. Comparison of HOMO and LUMO energy levels of [*n*]CPPs (yellow) and *m*[*n*]CPPs (green). Calculated using B3LYP/6-31G(d,p) level of theory.

5. Calculated Absorption Spectra

Geometries optimized using Gaussian 09[6] with B3LYP/6-31G(d,p), then using the same basis, a time dependent calculation of 12 states was performed. The results were analyzed using GaussSum.

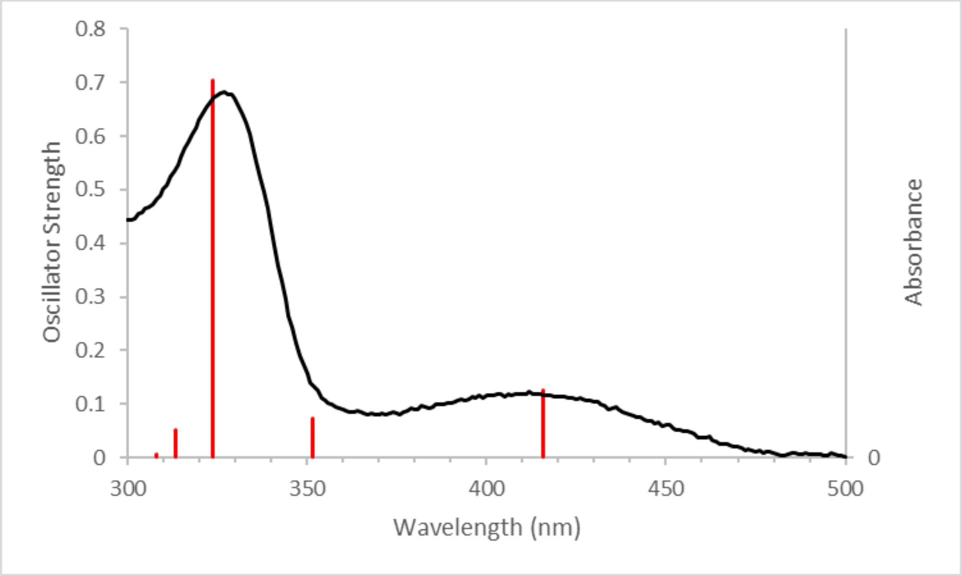
m[*n*]CPP	λmax (nm)	Oscillator strength	H→L Contribution (%)
5	441	0.122	98
6	416	0.126	97
7	404	0.172	97
8	397	0.176	95
10	388	0.227	91
12	383	0.281	86

Table S7. Calculated HOMO→LUMO absorption for *m*[*n*]CPPs.



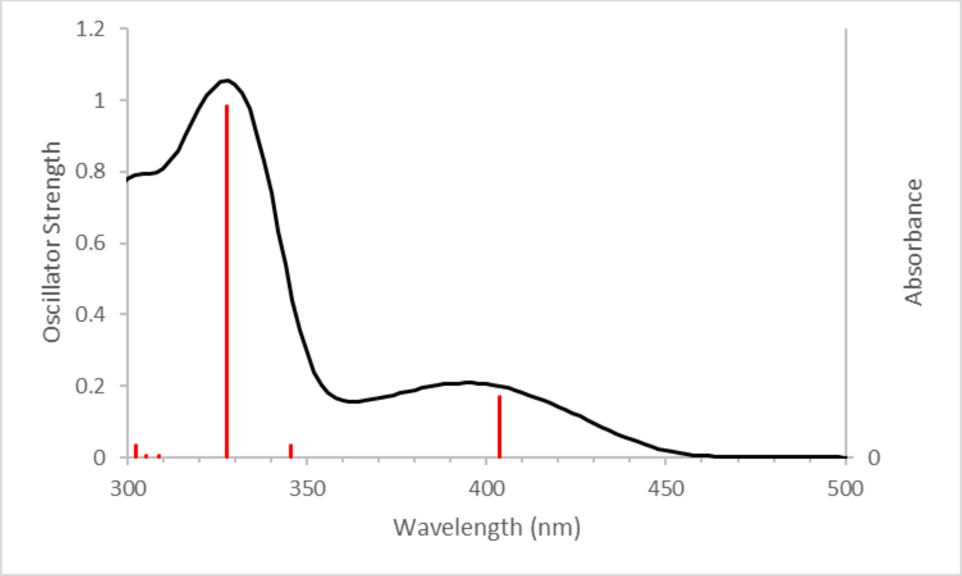
No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contributing transitions
1	22677.08	440.9738	0.1217	Singlet-A	HOMO->LUMO (98%)
2	28232.63	354.2001	0.033	Singlet-A	H-1->LUMO (27%), HOMO->L+1 (71%)
3	29990.92	333.4343	0.0309	Singlet-A	H-1->LUMO (15%), HOMO->L+2 (70%)
4	31409.65	318.3735	0.2824	Singlet-A	H-1->LUMO (38%), HOMO->L+1 (17%), HOMO->L+2 (13%), HOMO->L+3 (24%)
5	32829.18	304.607	0.272	Singlet-A	H-1->LUMO (17%), HOMO->L+3 (51%)
6	34168.07	292.6709	0.0064	Singlet-A	H-2->LUMO (73%), H-1->L+1 (16%)
7	34314.05	291.4258	0.0007	Singlet-A	H-1->L+1 (37%), HOMO->L+4 (51%)
8	34995.59	285.7503	0.0523	Singlet-A	H-4->LUMO (10%), H-2->LUMO (12%), H-1->L+1 (20%), HOMO->L+4 (30%)
9	35145.61	284.5306	0.002	Singlet-A	H-4->LUMO (12%), H-3->LUMO (12%), HOMO->L+5 (33%), HOMO->L+6 (10%)
10	35563.4	281.1879	0.0103	Singlet-A	H-4->LUMO (23%), H-3->LUMO (14%), HOMO->L+6 (21%)
11	35806.18	279.2814	0.0019	Singlet-A	H-3->LUMO (37%), HOMO->L+6 (15%)
12	36343.34	275.1536	0.0588	Singlet-A	H-7->LUMO (23%), H-4->LUMO (23%), HOMO->L+8 (13%)

Figure S14. ***m*[5]CPP** Calculated absorption (red lines) compared to experimental absorption (black trace) results and table of calculated transitions.



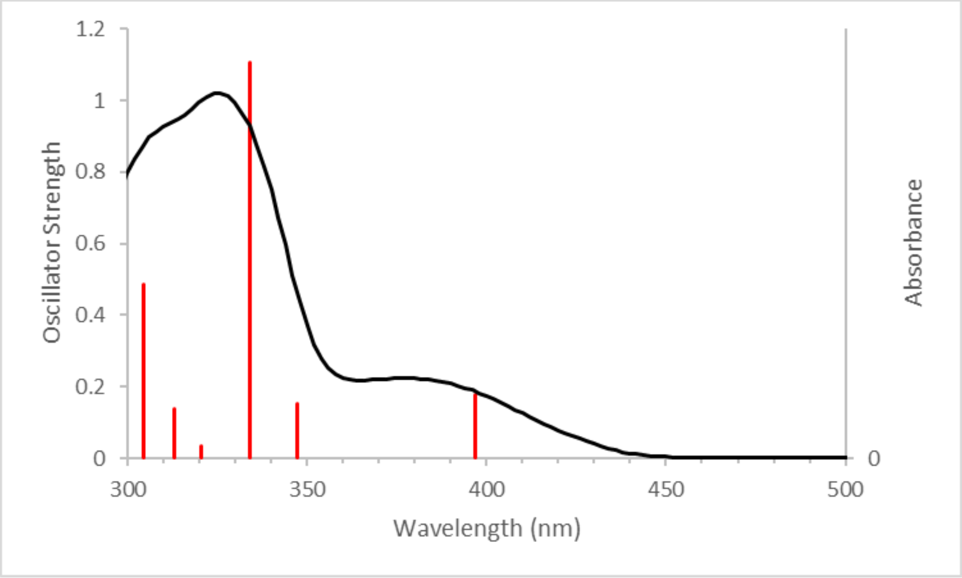
No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contributing transitions
1	24054.68	415.7195	0.126	Singlet-A	HOMO->LUMO (97%)
2	28438.3	351.6384	0.0731	Singlet-A	H-1->LUMO (25%), HOMO->L+1 (74%)
3	30893.45	323.6932	0.7042	Singlet-A	H-1->LUMO (70%), HOMO->L+1 (22%)
4	31889.55	313.5824	0.0502	Singlet-A	HOMO->L+2 (79%)
5	32471.07	307.9664	0.0069	Singlet-A	H-2->LUMO (15%), H-1->L+1 (80%)
6	33162.29	301.5473	0.0005	Singlet-A	H-2->LUMO (30%), HOMO->L+3 (58%)
7	33675.26	296.9539	0.1059	Singlet-A	H-2->LUMO (36%), HOMO->L+4 (31%)
8	35029.47	285.474	0.2921	Singlet-A	H-2->LUMO (15%), HOMO->L+3 (27%), HOMO->L+4 (40%)
9	35264.17	283.5739	0.0218	Singlet-A	H-6->LUMO (18%), HOMO->L+5 (23%), HOMO->L+6 (37%)
10	36278.82	275.6429	0.0251	Singlet-A	H-3->LUMO (23%), HOMO->L+5 (40%), HOMO->L+6 (13%)
11	36550.63	273.5931	0.0082	Singlet-A	H-7->LUMO (27%), HOMO->L+7 (32%), HOMO->L+8 (21%)
12	36911.96	270.9149	0.0143	Singlet-A	H-8->LUMO (17%), H-3->LUMO (15%), H-2->L+1 (36%), HOMO->L+9 (13%)

Figure S15. ***m*****[6]CPP** Calculated absorption (red lines) compared to experimental absorption (black trace) results and table of calculated transitions.



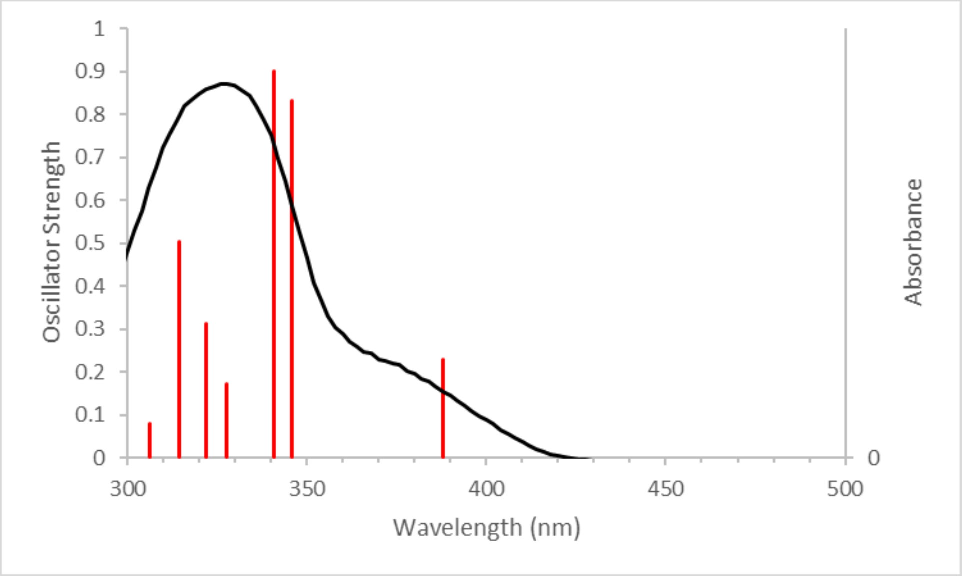
No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contributing transitions
1	24781.38	403.5287	0.1718	Singlet-A	HOMO->LUMO (97%)
2	28944.01	345.4946	0.0342	Singlet-A	H-1->LUMO (32%), HOMO->L+1 (66%)
3	30529.7	327.5499	0.9834	Singlet-A	H-1->LUMO (66%), HOMO->L+1 (31%)
4	32396.87	308.6718	0.0062	Singlet-A	H-2->LUMO (12%), H-1->L+1 (83%)
5	32745.3	305.3873	0.0071	Singlet-A	H-2->LUMO (48%), HOMO->L+2 (45%)
6	33070.34	302.3857	0.0326	Singlet-A	H-4->LUMO (10%), HOMO->L+4 (74%)
7	33687.36	296.8473	0.2207	Singlet-A	H-2->LUMO (23%), HOMO->L+2 (23%), HOMO->L+3 (25%)
8	34174.52	292.6157	0.1759	Singlet-A	H-2->LUMO (12%), HOMO->L+2 (22%), HOMO->L+3 (44%)
9	35339.18	282.972	0.079	Singlet-A	HOMO->L+5 (43%)
10	35952.16	278.1474	0.0225	Singlet-A	H-2->L+1 (59%), H-1->L+2 (24%)
11	36171.55	276.4604	0.0569	Singlet-A	H-3->LUMO (24%), H-2->L+1 (10%), HOMO->L+3 (16%), HOMO->L+6 (12%)
12	36332.86	275.233	0.014	Singlet-A	H-10->LUMO (12%), H-3->LUMO (20%), HOMO->L+8 (20%)

Figure S16. ***m*[7]CPP** Calculated absorption (red lines) compared to experimental absorption (black trace) results and table of calculated transitions.



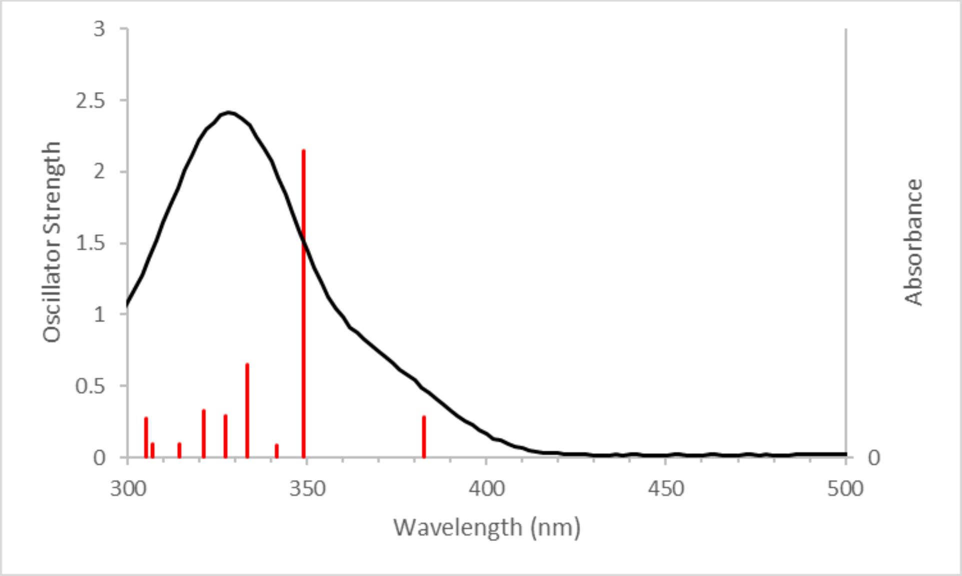
No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contributing transistions
1	25186.28	397.0416	0.1764	Singlet-A	HOMO->LUMO (95%)
2	28785.12	347.4017	0.1531	Singlet-A	H-1->LUMO (18%), HOMO->L+1 (81%)
3	29923.98	334.1802	1.1065	Singlet-A	H-1->LUMO (80%), HOMO->L+1 (18%)
4	31187.85	320.6377	0.0351	Singlet-A	H-1->L+1 (85%)
5	31941.17	313.0756	0.1391	Singlet-A	H-2->LUMO (76%), HOMO->L+2 (14%)
6	32853.38	304.3827	0.4857	Singlet-A	H-2->LUMO (12%), HOMO->L+2 (78%)
7	33596.22	297.6525	0.0011	Singlet-A	H-5->LUMO (13%), HOMO->L+3 (19%), HOMO->L+4 (52%)
8	34197.1	292.4224	0.086	Singlet-A	H-2->L+1 (88%)
9	34645.55	288.6374	0.0318	Singlet-A	H-3->LUMO (12%), HOMO->L+3 (59%), HOMO->L+4 (18%)
10	34857.67	286.8809	0.0563	Singlet-A	HOMO->L+5 (55%)
11	35451.29	282.0772	0.0355	Singlet-A	H-3->LUMO (13%), H-1->L+2 (14%), HOMO->L+6 (29%)
12	35921.51	278.3847	0.2387	Singlet-A	H-3->LUMO (28%), H-1->L+2 (60%)

Figure S17. ***m*[8]CPP** Calculated absorption (red lines) compared to experimental absorption (black trace) results and table of calculated transitions.



No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contributing transistions
1	25783.93	387.8384	0.2275	Singlet-A	HOMO->LUMO (91%)
2	28917.4	345.8126	0.8323	Singlet-A	HOMO->L+1 (98%)
3	29329.55	340.9531	0.9001	Singlet-A	H-1->LUMO (98%)
4	30510.34	327.7577	0.1709	Singlet-A	H-1->L+1 (88%)
5	31057.99	321.9783	0.3116	Singlet-A	H-2->LUMO (94%)
6	31807.28	314.3934	0.5032	Singlet-A	HOMO->L+2 (93%)
7	32663.84	306.1489	0.0805	Singlet-A	H-2->L+1 (89%)
8	33421.2	299.2113	0.0744	Singlet-A	H-3->LUMO (13%), HOMO->L+3 (78%)
9	33980.14	294.2896	0.2859	Singlet-A	H-1->L+2 (80%)
10	34545.53	289.473	0.0021	Singlet-A	H-6->LUMO (11%), H-3->LUMO (26%), HOMO->L+5 (37%)
11	34706.84	288.1276	0.054	Singlet-A	H-3->L+1 (10%), H-2->L+2 (48%), H-1->L+3 (27%)
12	34819.76	287.1932	0.0489	Singlet-A	H-3->LUMO (46%), HOMO->L+3 (13%), HOMO->L+5 (23%)

Figure S18. *m*[10]CPP Calculated absorption (red lines) compared to experimental absorption (black trace) results and table of calculated transitions.

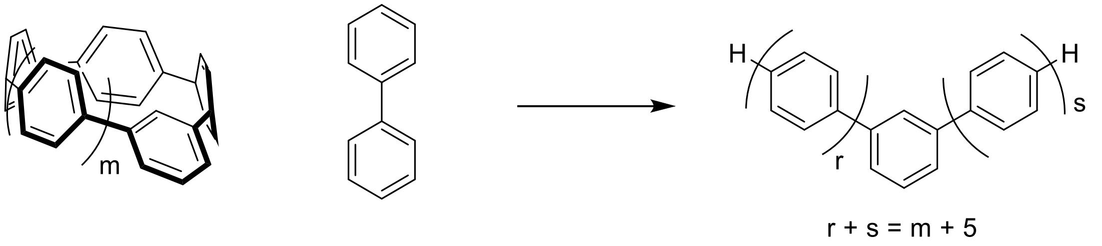


No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
1	26136.4	382.6082	0.2811	Singlet-A	H-1->L+1 (10%), HOMO->LUMO (86%)
2	28658.49	348.9367	2.1502	Singlet-A	H-1->LUMO (30%), HOMO->L+1 (67%)
3	29285.99	341.4602	0.0886	Singlet-A	H-1->LUMO (66%), HOMO->L+1 (30%)
4	29996.57	333.3715	0.647	Singlet-A	H-1->L+1 (74%), HOMO->LUMO (10%)
5	30553.89	327.2905	0.2915	Singlet-A	H-2->LUMO (88%)
6	31134.61	321.1859	0.3285	Singlet-A	HOMO->L+2 (92%)
7	31779.86	314.6647	0.0906	Singlet-A	H-2->L+1 (91%)
8	32568.67	307.0436	0.0951	Singlet-A	H-3->LUMO (18%), HOMO->L+3 (70%)
9	32750.95	305.3347	0.2706	Singlet-A	H-1->L+2 (82%)
10	33423.62	299.1897	0.031	Singlet-A	H-2->L+2 (64%), H-1->L+3 (21%)
11	33493.79	298.5628	0.0572	Singlet-A	H-3->LUMO (73%), HOMO->L+3 (23%)
12	33971.27	294.3664	0.3944	Singlet-A	H-3->L+1 (34%), H-2->L+2 (23%), H-1->L+3 (32%)

Figure S19. *m*[12]CPP Calculated absorption (red lines) compared to experimental absorption (black trace) results and table of calculated transitions.

6. Inherent Strain Calculation

Strain calculated by comparison of single point energy of optimized geometries of the molecules in the theoretical homodesmotic reaction shown below. Geometries optimized using Gaussian 09[6] with B3LYP/6-31G(d,p).



m[*n*]CPP	m	r	s	nanohoop	biphenyl	linear product	strain (hartrees)	strain (kcal/mol)
5	1	3	3	-1155.146	-463.3164	-1618.625	0.162858	102.2
6	2	4	3	-1386.234	-463.3164	-1849.674	0.123644	77.6
7	3	4	4	-1617.313	-463.3164	-2080.735	0.105867	66.4
8	4	5	4	-1848.389	-463.3164	-2311.795	0.090321	56.7
10	6	6	5	-2310.563	-463.3164	-2773.961	0.081901	51.4
12	8	7	6	-2772.704	-463.3164	-3236.089	0.068955	43.3

Table S8. Single point energies of compounds used in homodesmotic reactions and calculated strain.

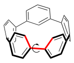
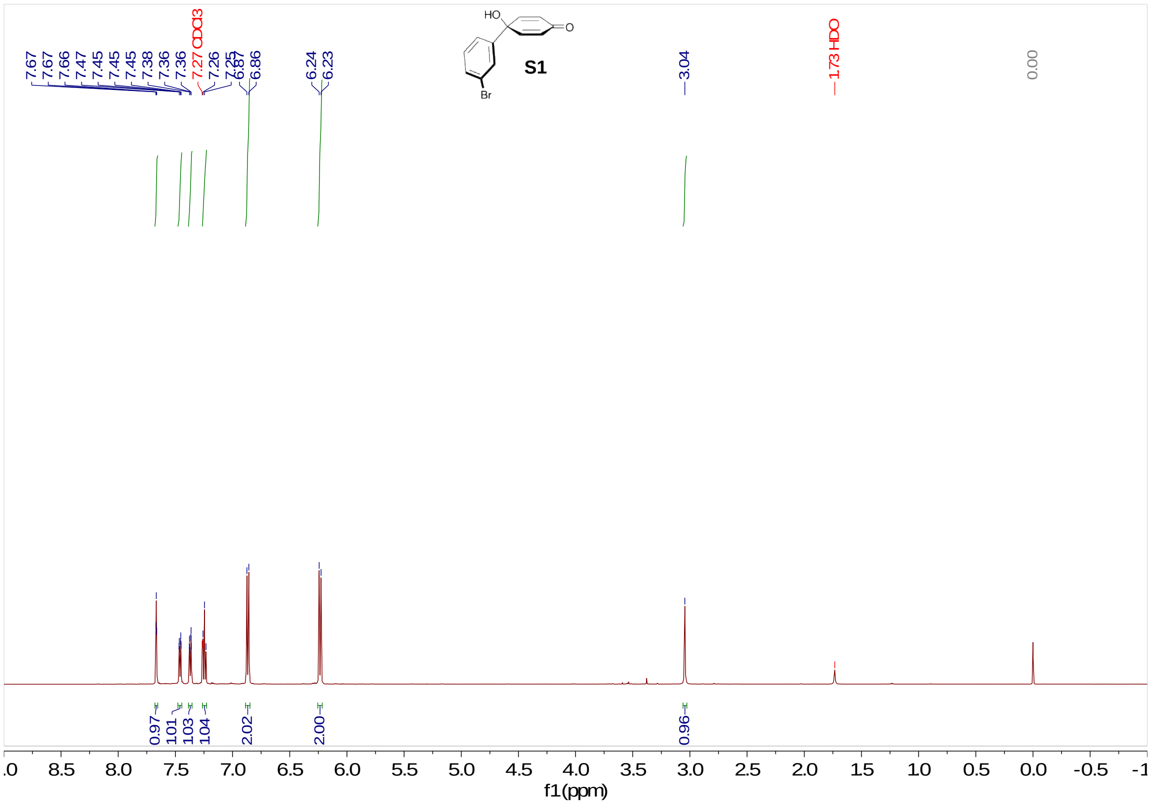
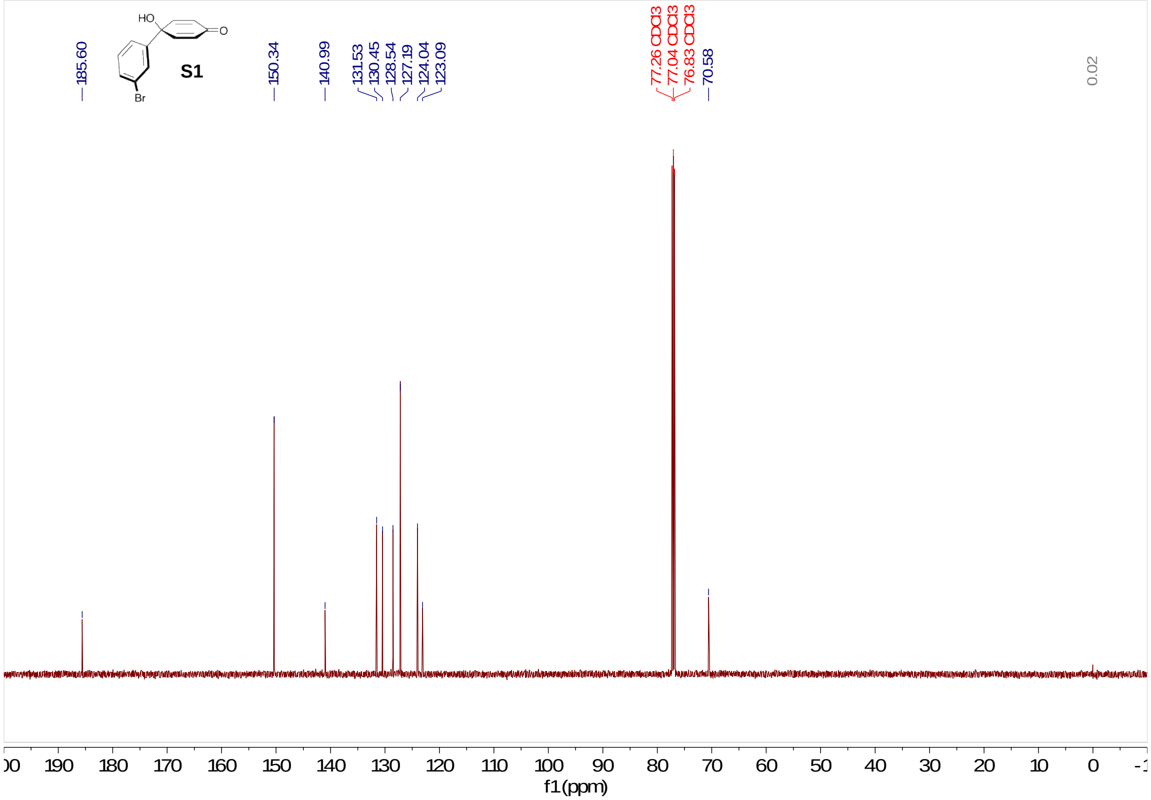
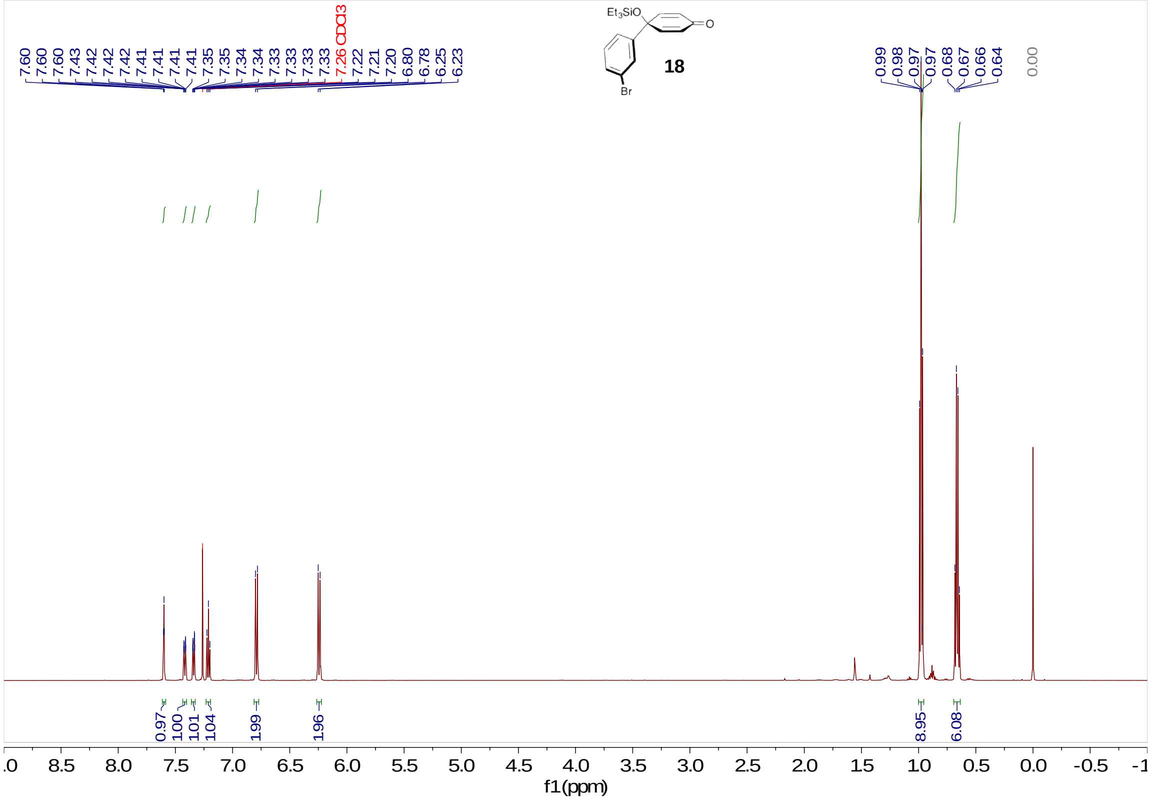
m[*n*]CPP	Strain energy (kcal/mol)	Strain per aryl ring (kcal/mol)	Phenylene *ipso* carbon deviation from planarity (°) 	Dihedral angle (°) 
5	102 (119)	20 (24)	17.0 (15.8)	23
6	78 (97)	13 (16)	14.1 (12.6)	25
7	66 (84)	9 (12)	12.0 (10.9)	28
8	57 (72)	7 (9)	10.6 (9.3)	30
10	51 (58)	5 (6)	8.4 (7.7)	31
12	43 (48)	4 (4)	7.0 (6.2)	34

Table S9. Calculated strain energy in *m*[*n*]CPPs, *ipso* carbon deviation, and dihedral angle. [*n*]CPP values in brackets.[7] It is noted that the strain for each aryl ring in *m*[*n*]CPPs are not equivalent due to asymmetry. *ipso* carbon deviations are for phenylenes opposite to the *meta* phenylene in the nanohoop.

7. ^{1}H/^{13}C Spectra



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7.41
7.41
7.41
7.35
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7.34
7.34
7.33
7.33
7.33
7.33
7.33
7.26 CDCl3
7.22
7.21
7.20
6.80
6.78
6.25
6.23
Et3SiO
O
Br
18
0.99
0.98
0.97
0.97
0.68
0.67
0.66
0.64
0.00
0.97
1.00
1.01
1.04
1.99
1.96
8.95
6.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
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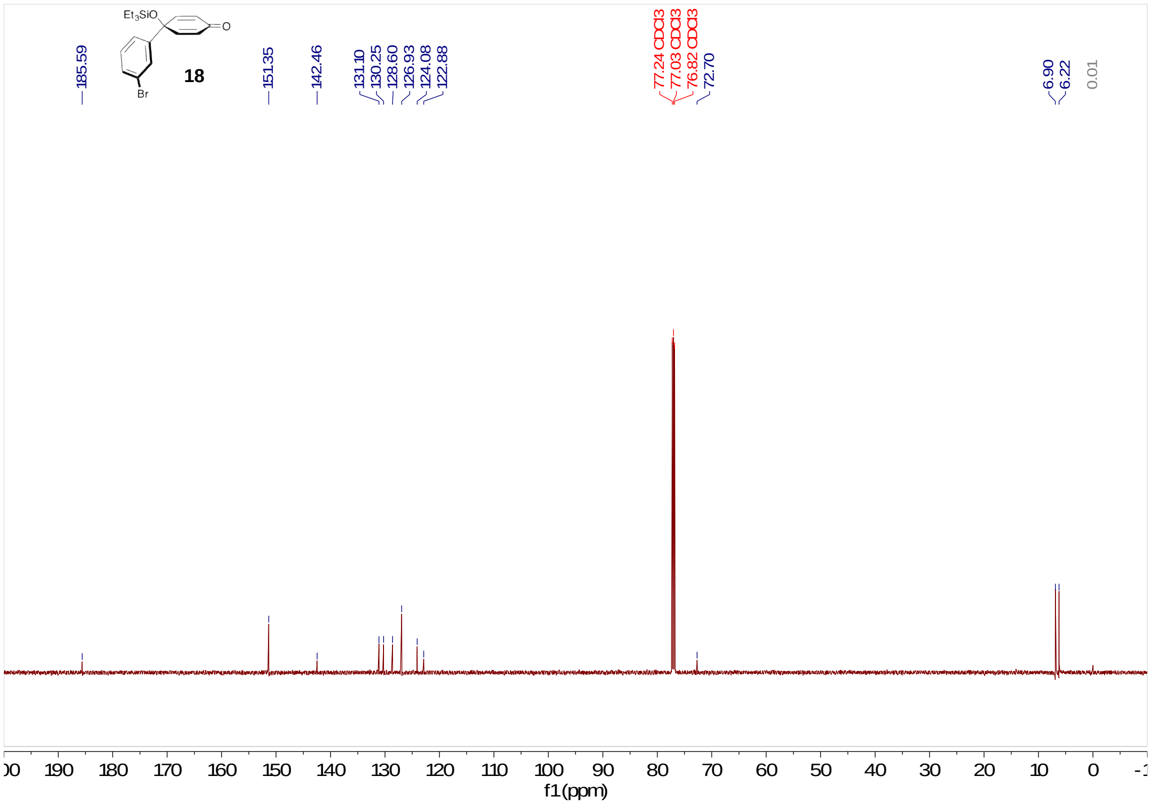
f1 (ppm)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130.25
128.60
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124.08
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77.24 CDCl3
77.03 CDCl3
76.82 CDCl3
72.70
6.90
6.22
0.01
190
180
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130
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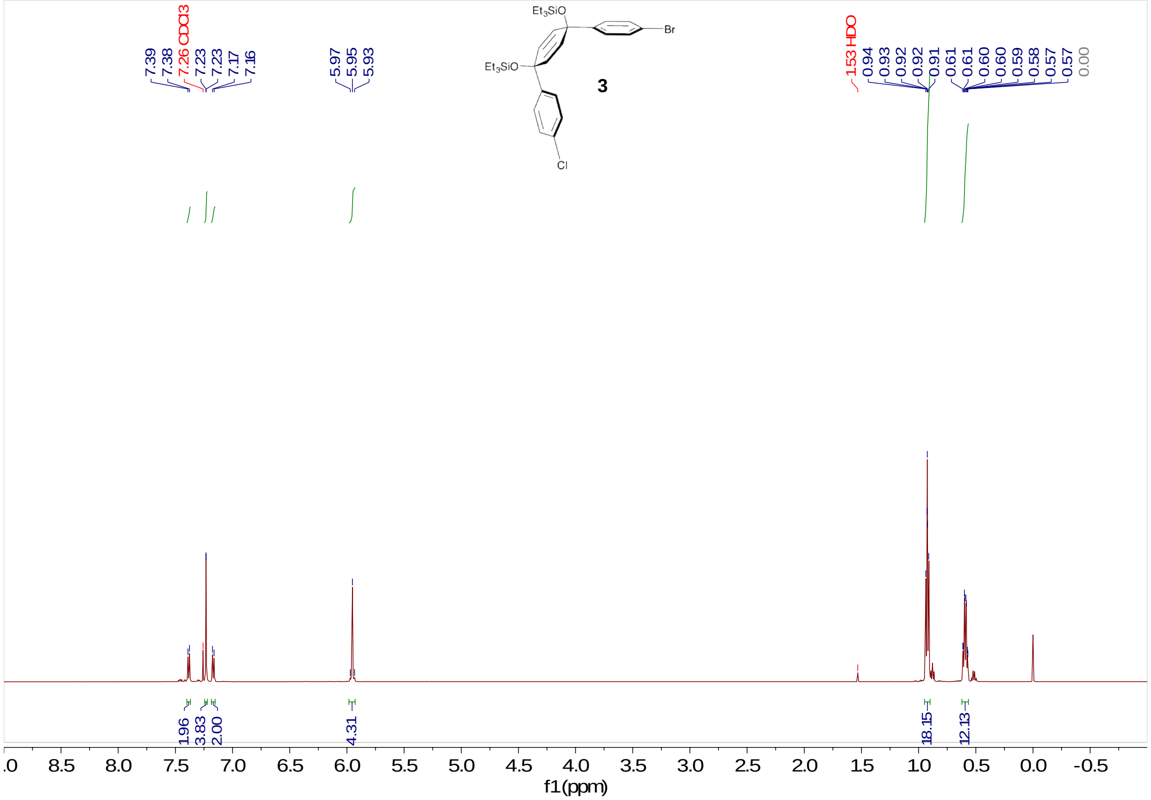
f1 (ppm)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Cl
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5.95
5.93
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0.93
0.92
0.92
0.91
0.61
0.60
0.60
0.59
0.58
0.57
0.57
0.00
1.96
3.83
2.00
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18.15
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9.0
8.5
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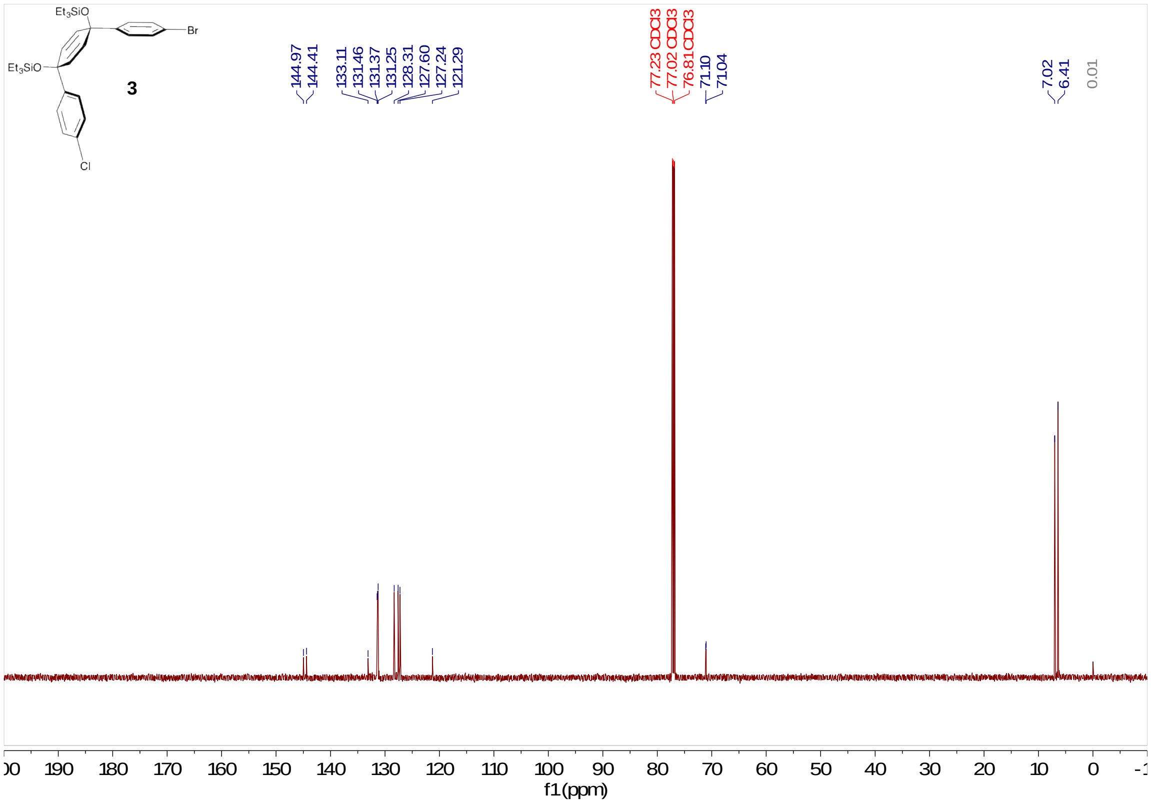
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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131.25
128.31
127.60
127.24
121.29
77.23 CDCl3
77.02 CDCl3
76.81 CDCl3
71.10
71.04
7.02
6.41
0.01
200
190
180
170
160
150
140
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120
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100
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80
70
60
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40
30
20
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0
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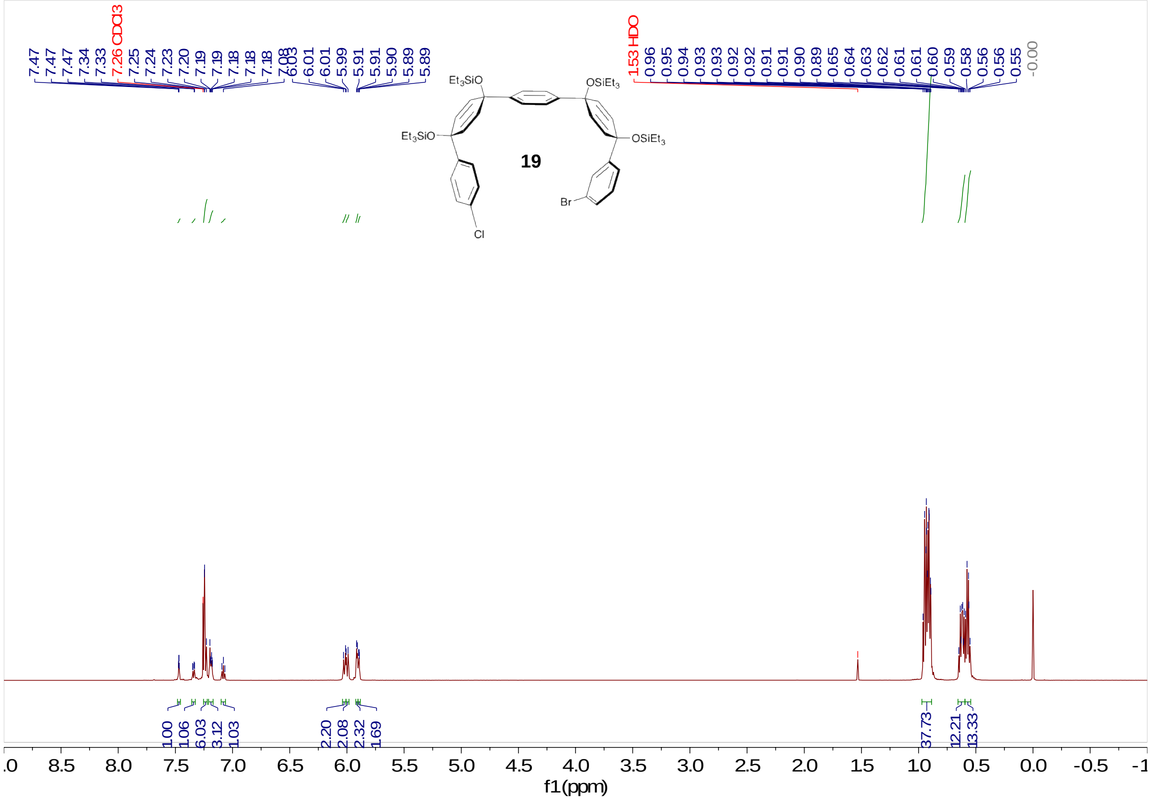
f1 (ppm)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7.26 CDCl3
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7.18
7.18
7.18
7.08
6.03
6.01
6.01
5.99
5.91
5.91
5.90
5.89
5.89
1.53 HDO
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0.95
0.94
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0.93
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0.92
0.91
0.91
0.90
0.89
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0.64
0.63
0.62
0.61
0.61
0.60
0.59
0.58
0.56
0.56
0.55
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Et3SiO
Et3SiO
OSiEt3
OSiEt3
19
Cl
Br
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1.06
6.03
3.12
1.03
2.20
2.08
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13.33
.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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0.0
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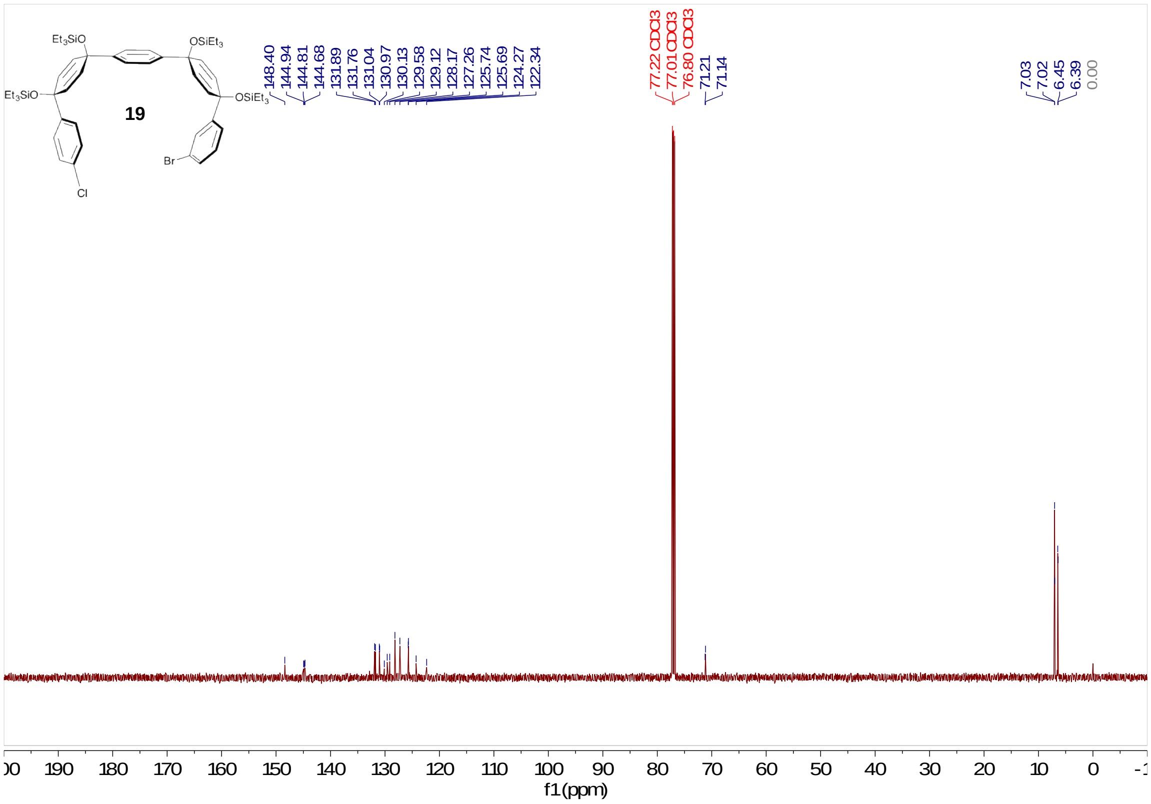
-1
f1(ppm)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OSiEt3
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Cl
Br
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131.04
130.97
130.13
129.58
129.12
128.17
127.26
125.74
125.69
124.27
122.34
77.22 CDCl3
77.01 CDCl3
76.80 CDCl3
71.21
71.14
7.03
7.02
6.45
6.39
0.00
00
190
180
170
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150
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30
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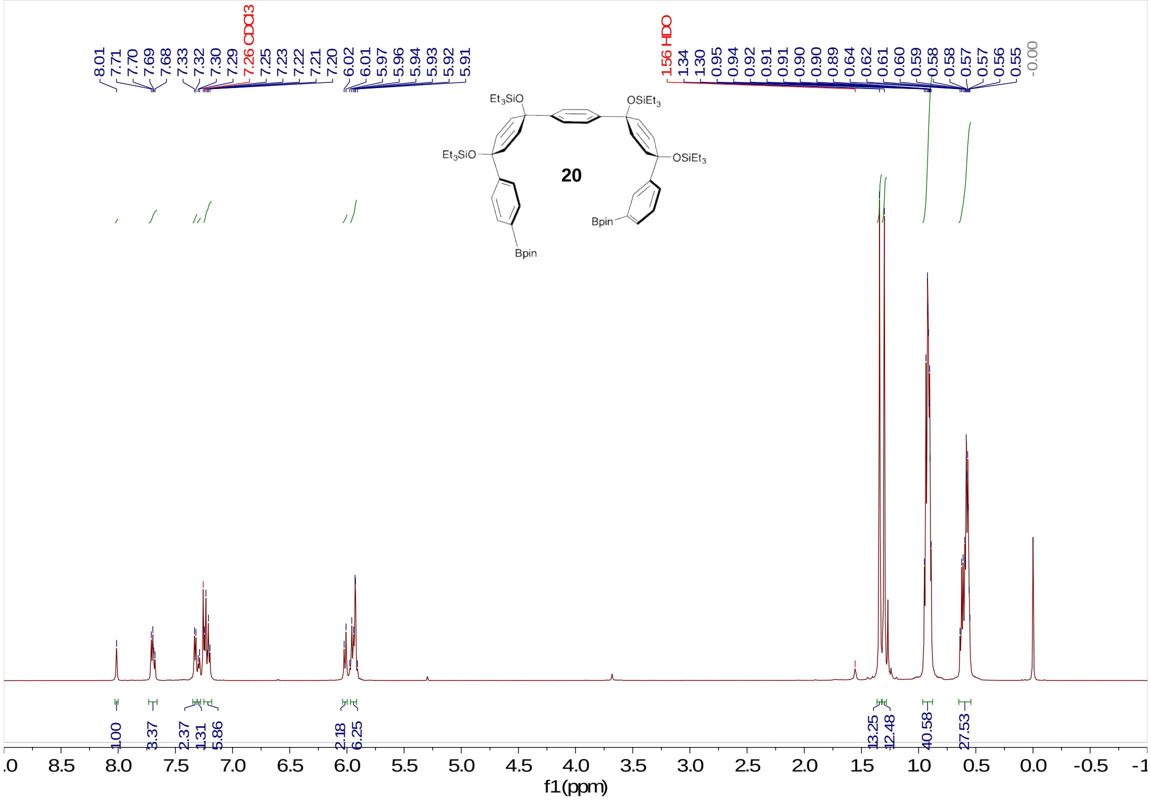
f1(ppm)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7.23
7.22
7.21
7.20
6.02
6.01
5.97
5.96
5.94
5.93
5.92
5.91
1.56 HDO
1.34
1.30
0.95
0.94
0.92
0.91
0.91
0.90
0.90
0.89
0.64
0.62
0.61
0.60
0.59
0.58
0.58
0.57
0.57
0.56
0.55
-0.00
Et3SiO
OSiEt3
Et3SiO
OSiEt3
20
Bpin
Bpin
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1.31
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2.18
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12.48
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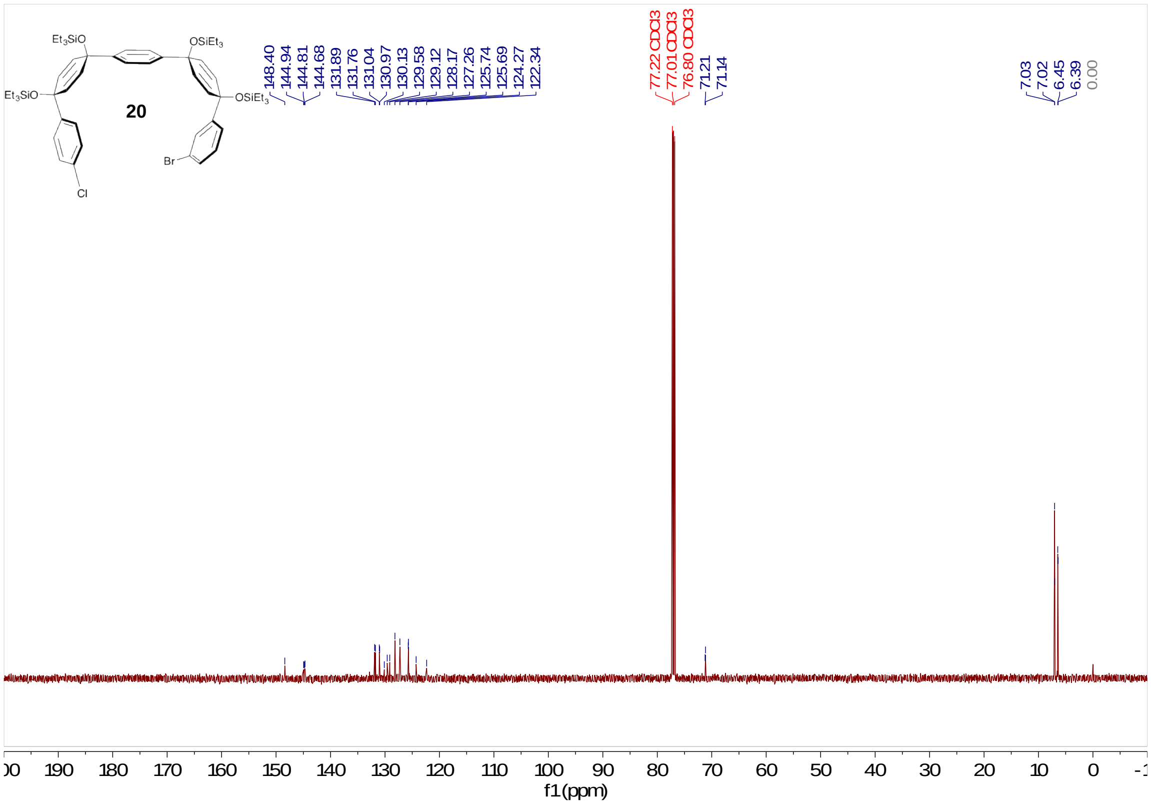
27.53
f1 (ppm)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125.69
124.27
122.34
77.22 CDCl3
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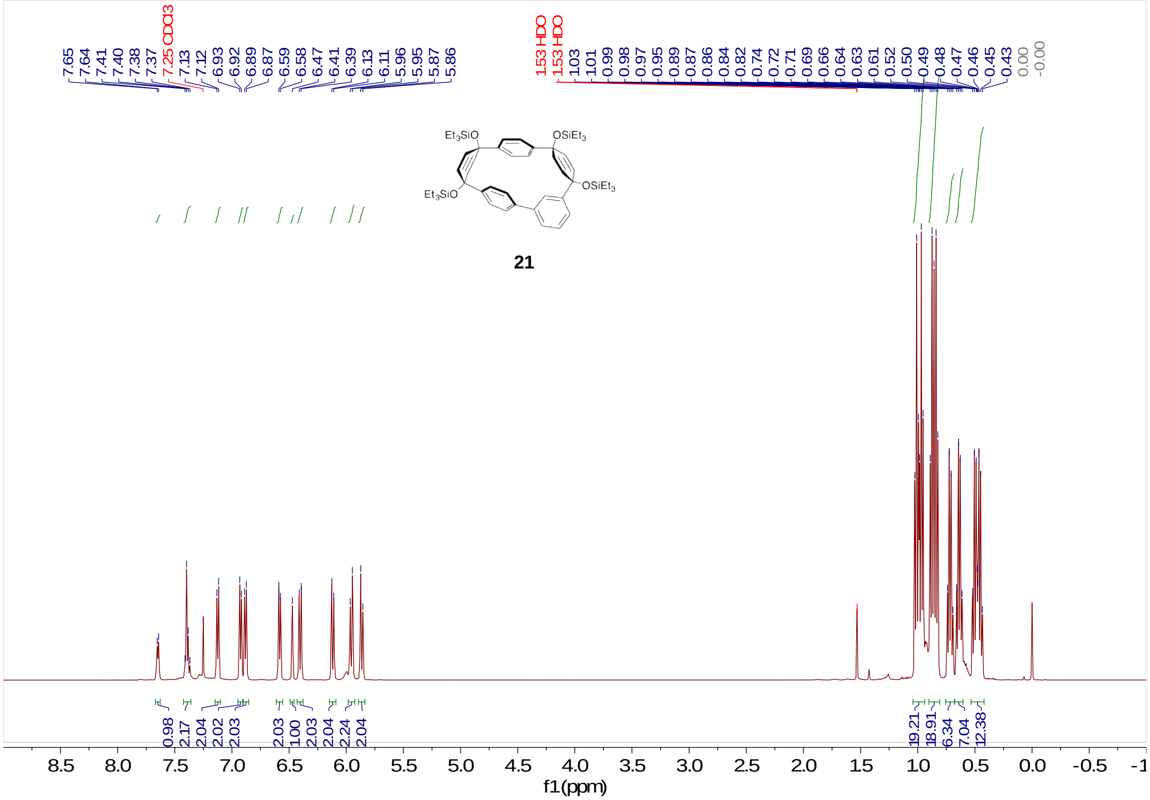
f1 (ppm)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5.96
5.95
5.87
5.86
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1.53 HDO
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1.01
0.99
0.98
0.97
0.95
0.89
0.87
0.86
0.84
0.82
0.74
0.72
0.71
0.69
0.66
0.64
0.63
0.61
0.52
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0.48
0.47
0.46
0.45
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Et3SiO
OSiEt3
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2.03
1.00
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2.04
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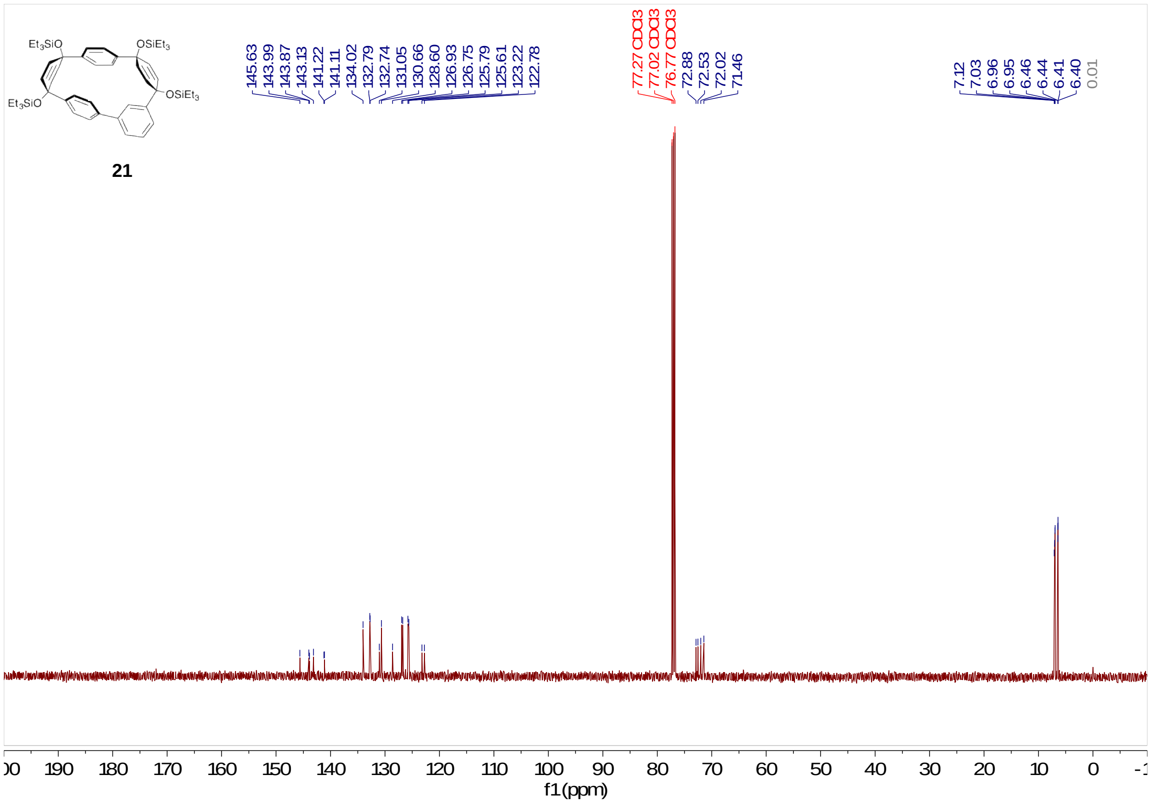
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132.74
131.05
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126.93
126.75
125.79
125.61
123.22
122.78
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77.02 CDCl3
76.77 CDCl3
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72.53
72.02
71.46
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7.03
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6.46
6.44
6.41
6.40
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00
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180
170
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120
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100
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80
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30
20
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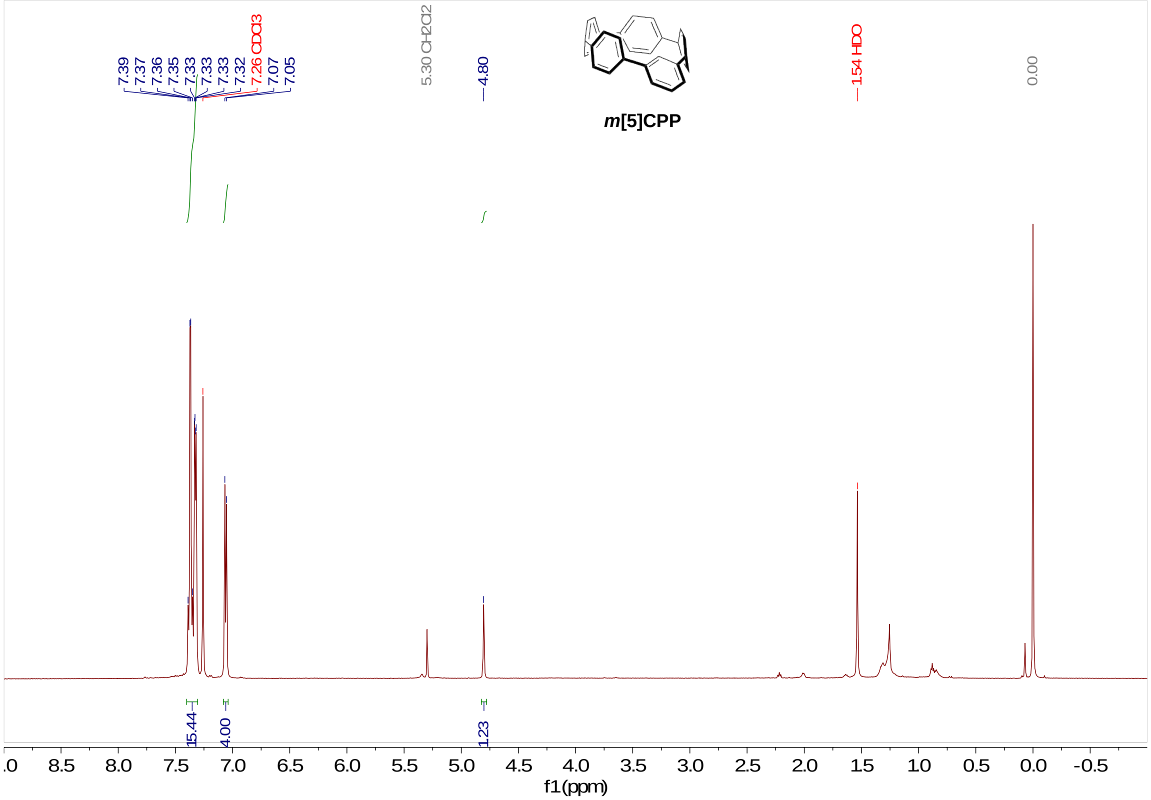
f1 (ppm)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7.05
5.30 CH2Cl2
4.80
1.54 HDO
0.00
m[5]CPP
15.44
4.00
1.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
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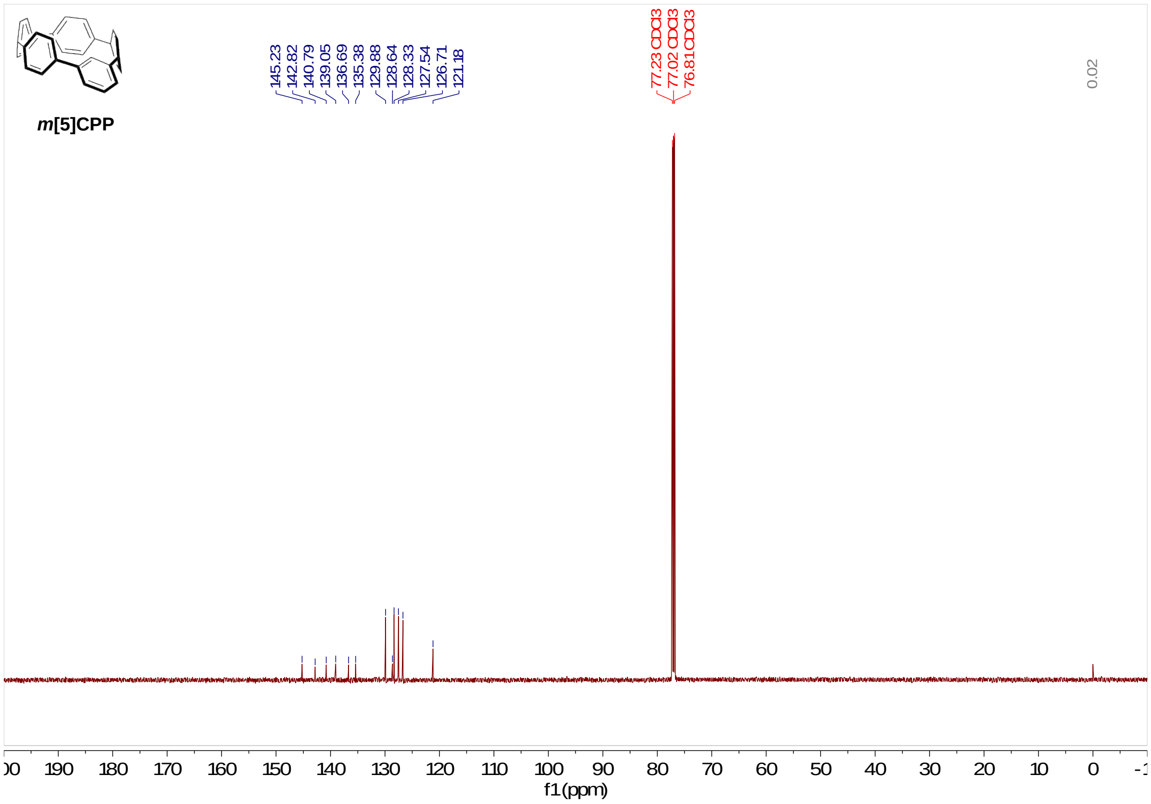
f1 (ppm)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126.71
121.18
77.23 CDCl3
77.02 CDCl3
76.81 CDCl3
0.02
190
180
170
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110
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90
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50
40
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10
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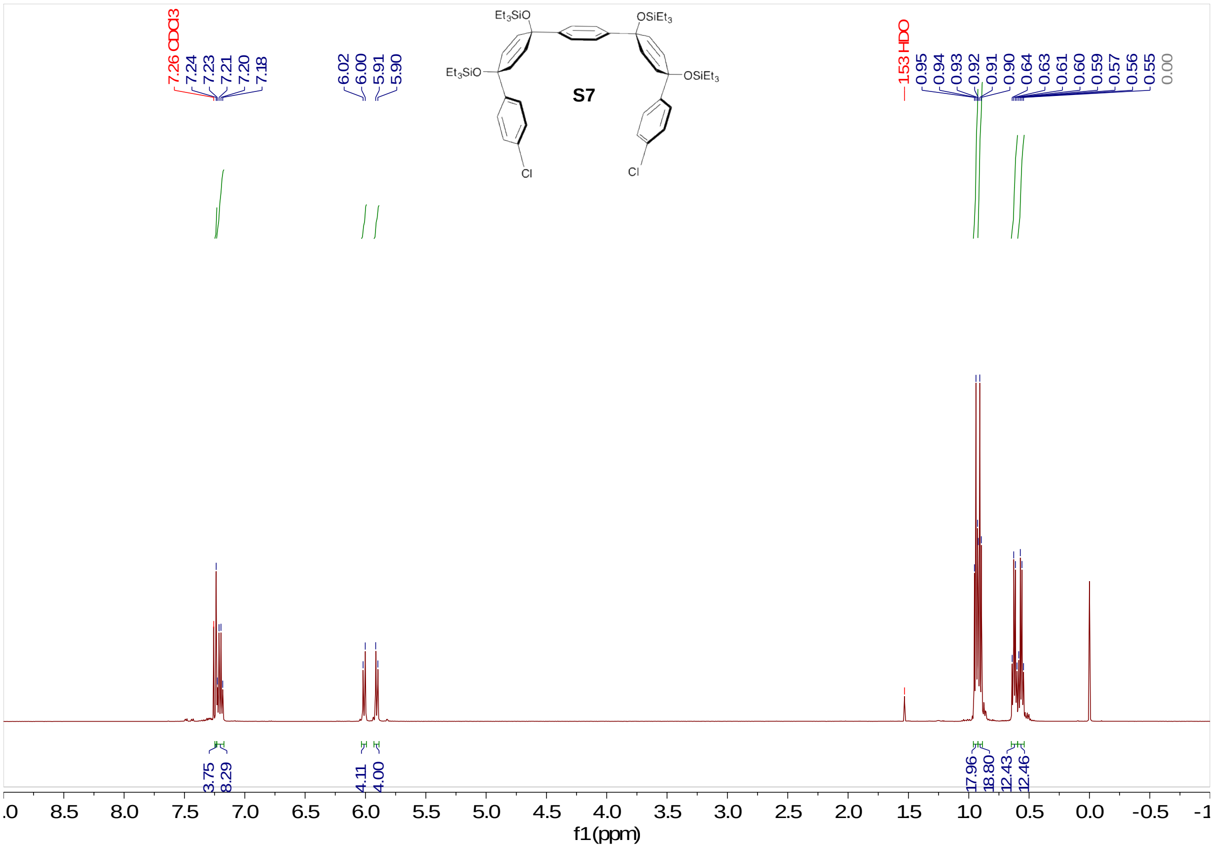
f1 (ppm)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5.90
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OSiEt3
Et3SiO
OSiEt3
S7
Cl
Cl
1.53 HDO
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0.94
0.93
0.92
0.91
0.90
0.64
0.63
0.61
0.60
0.59
0.57
0.56
0.55
0.00
3.75
8.29
4.11
4.00
17.96
18.80
12.43
12.46
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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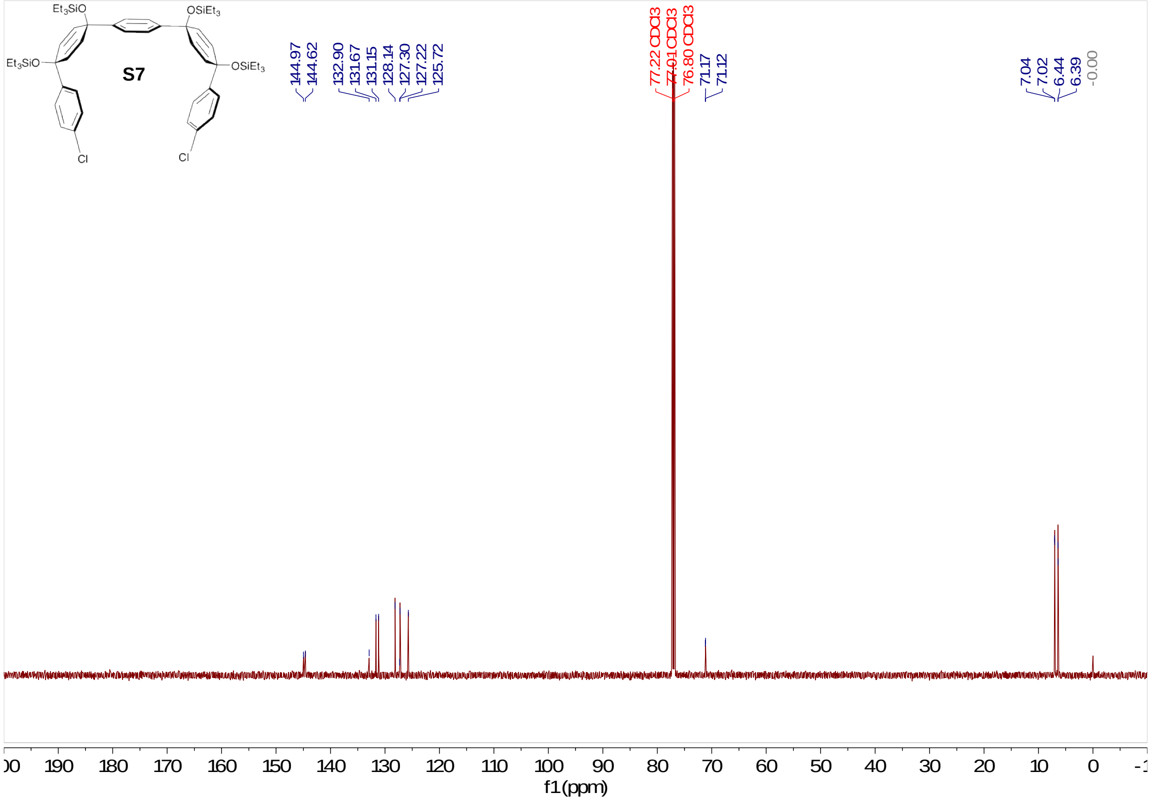
f1 (ppm)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Et3SiO
OSiEt3
S7
Cl
Cl
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132.90
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127.22
125.72
77.22 CDCl3
77.01 CDCl3
76.80 CDCl3
71.17
71.12
7.04
7.02
6.44
6.39
-0.00
190
180
170
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130
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110
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50
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10
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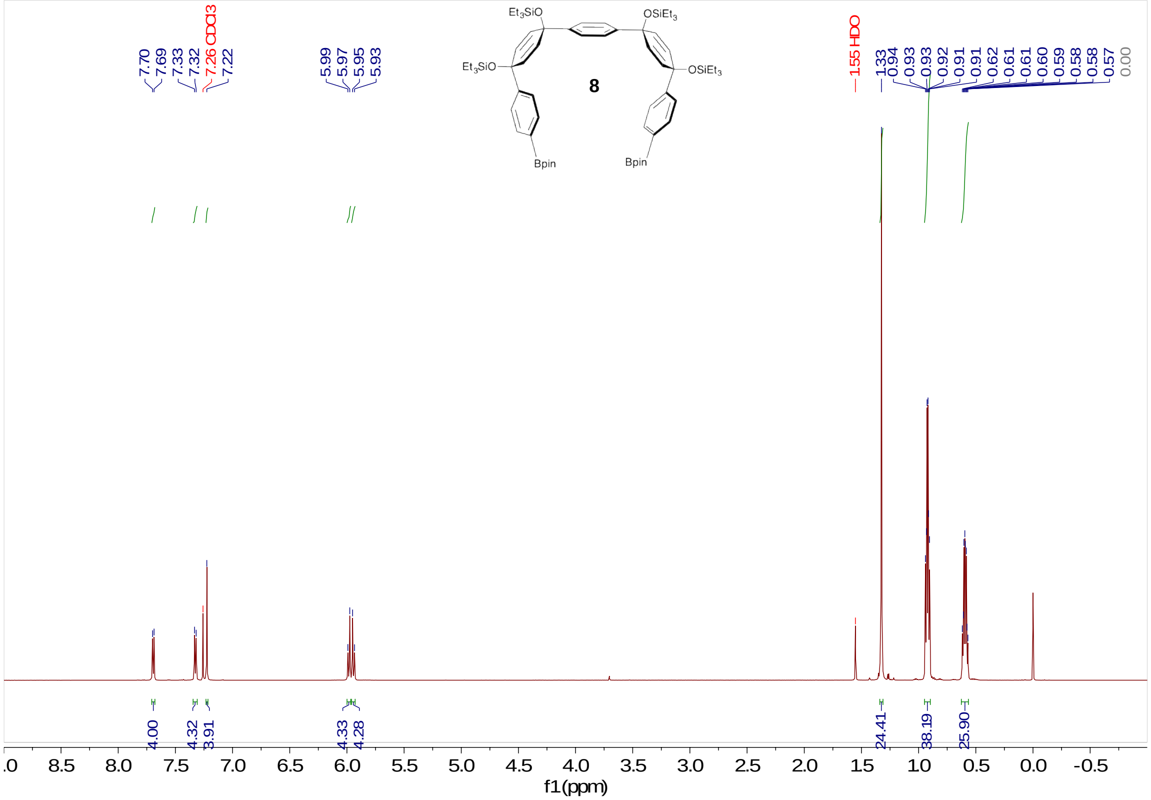
f1 (ppm)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OSiEt3
Et3SiO
OSiEt3
8
Bpin
Bpin
1.55 HDO
1.33
0.94
0.93
0.93
0.92
0.91
0.91
0.62
0.61
0.61
0.60
0.59
0.58
0.58
0.57
0.00
4.00
4.32
3.91
4.33
4.28
24.41
38.19
25.90
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
0.5
0.0
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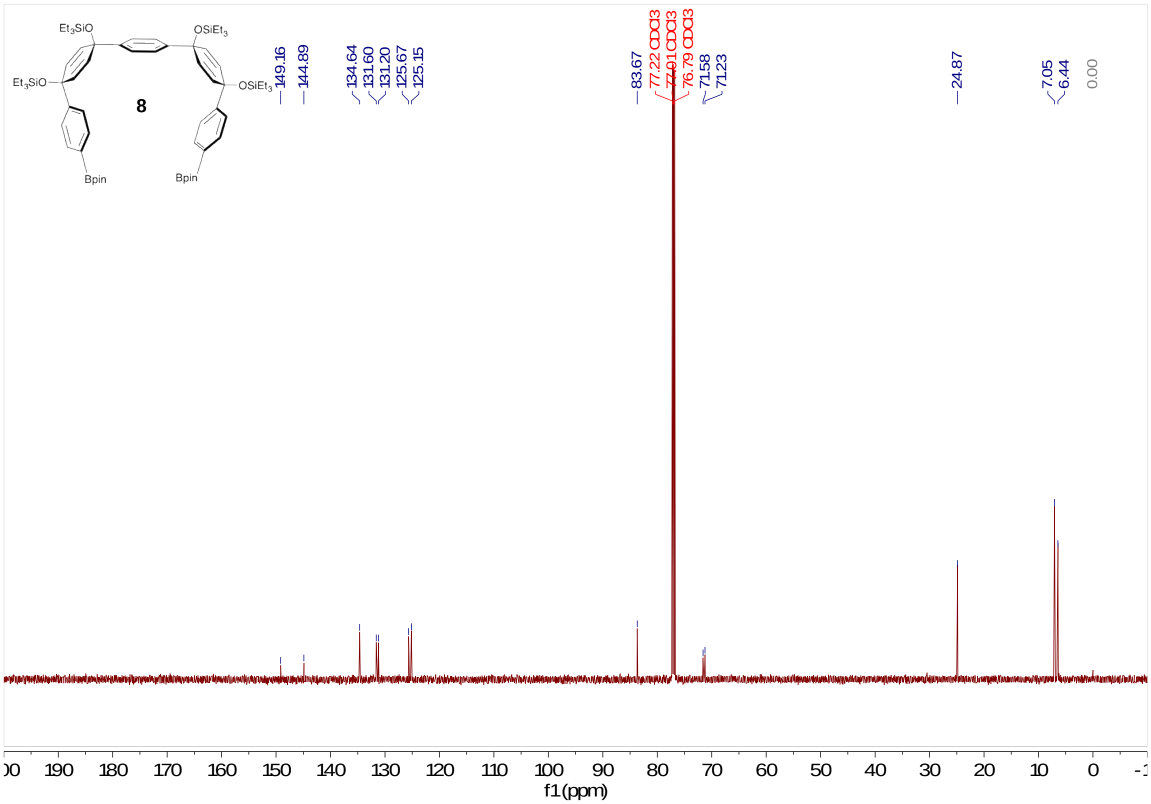
f1 (ppm)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OSiEt3
Et3SiO
OSiEt3
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Bpin
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125.67
125.15
83.67
77.22 CDCl3
77.01 CDCl3
76.79 CDCl3
71.58
71.23
24.87
7.05
6.44
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190
180
170
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120
110
100
90
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50
40
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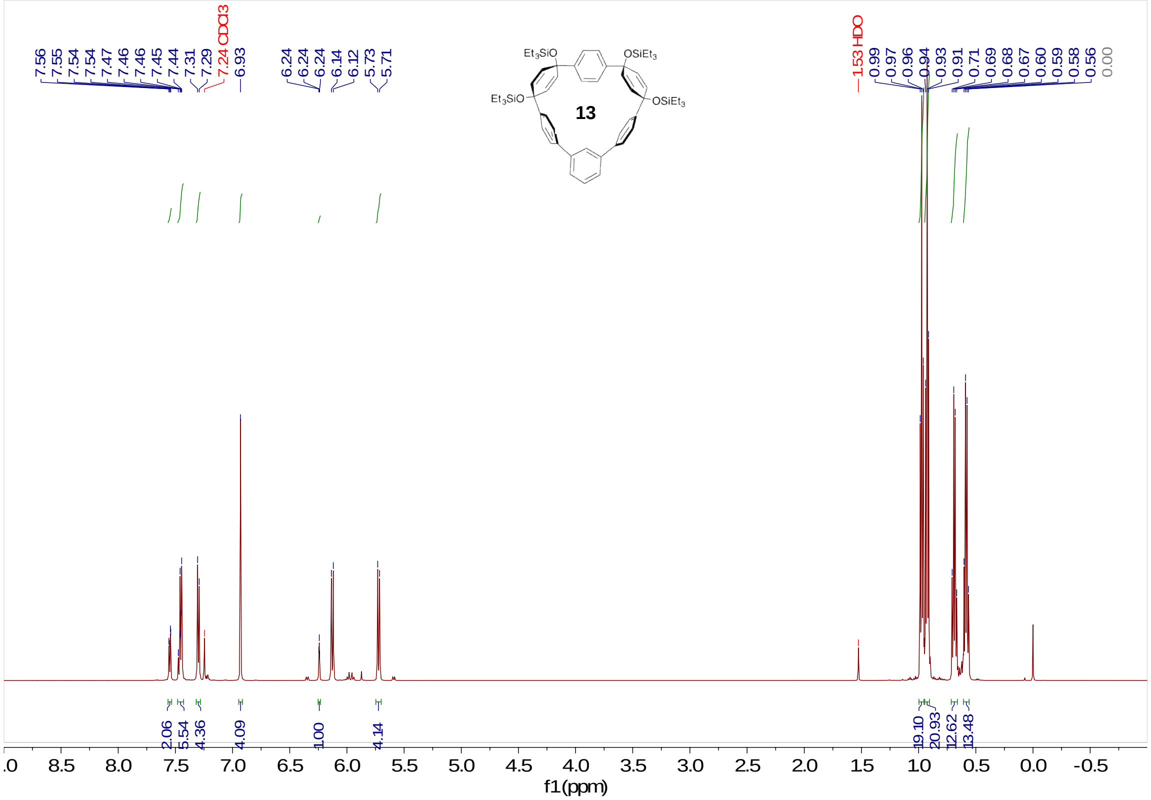
20
10
0
f1 (ppm)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7.31
7.29
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6.24
6.24
6.24
6.14
6.12
5.73
5.71
Et$_3$SiO
OSiEt$_3$
Et$_3$SiO
OSiEt$_3$
13
1.53 HDO
0.99
0.97
0.96
0.94
0.93
0.91
0.71
0.69
0.68
0.67
0.60
0.59
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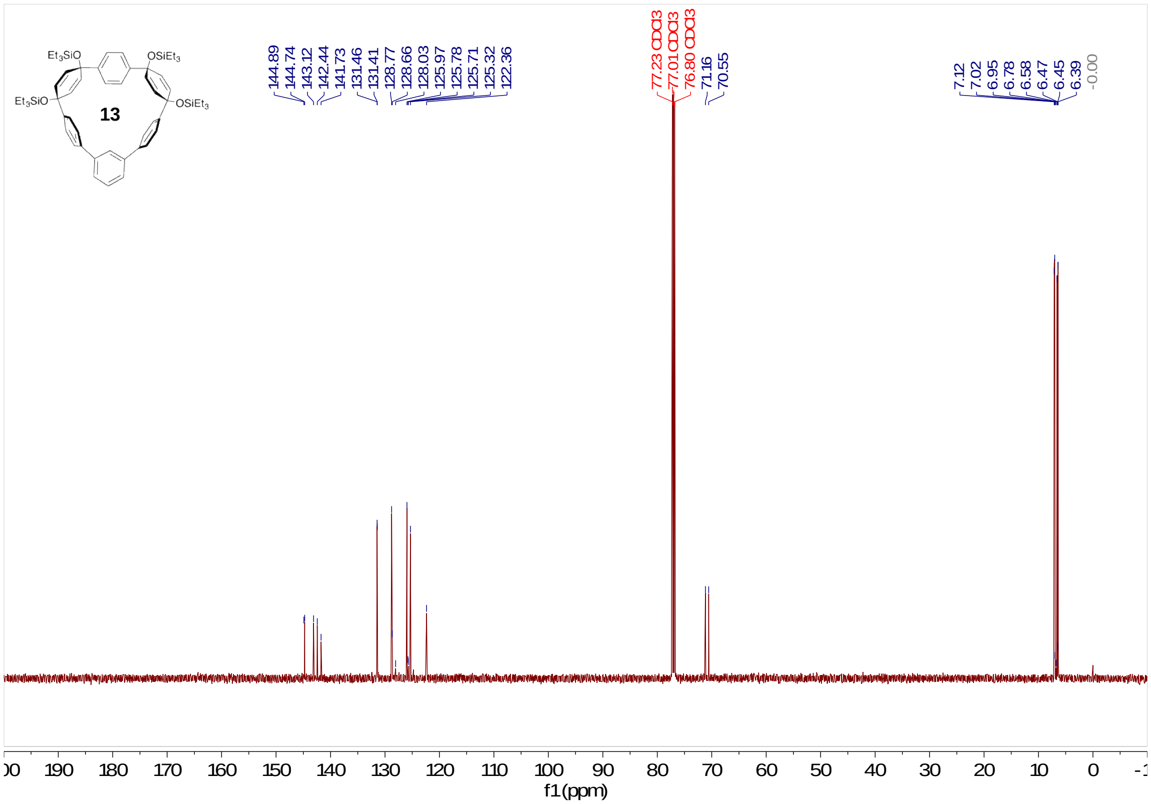
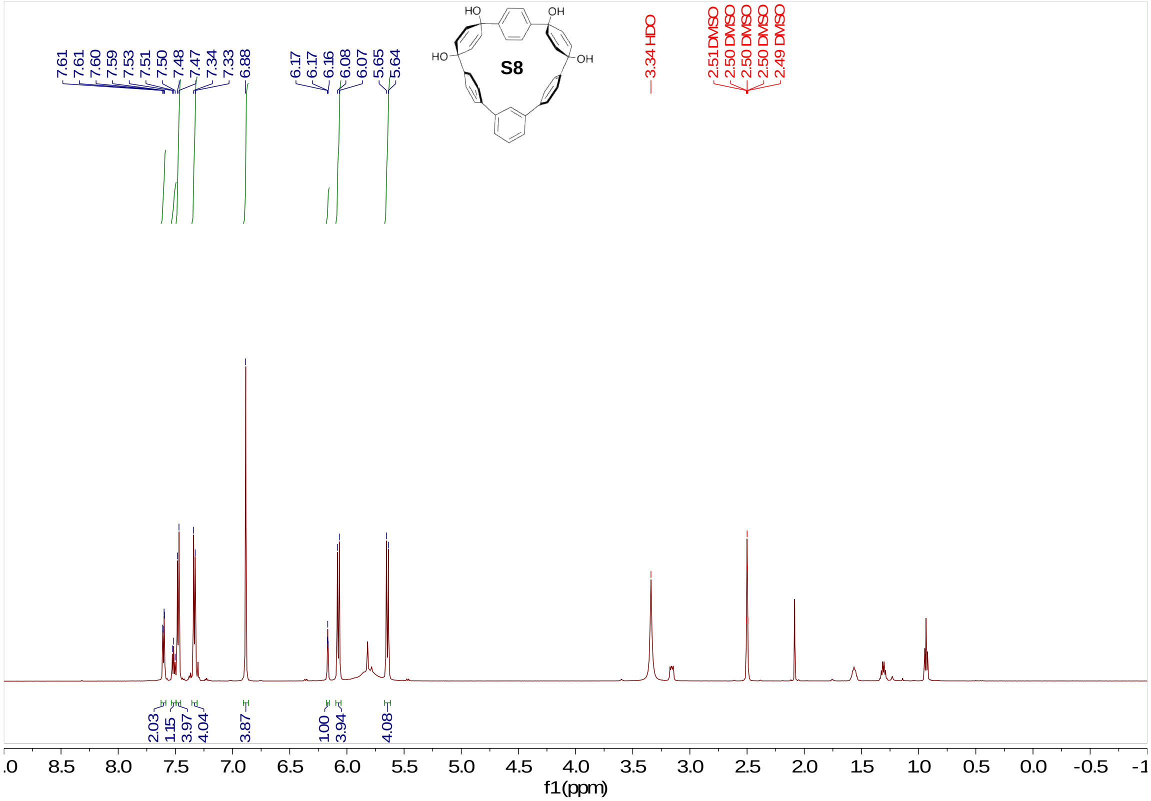
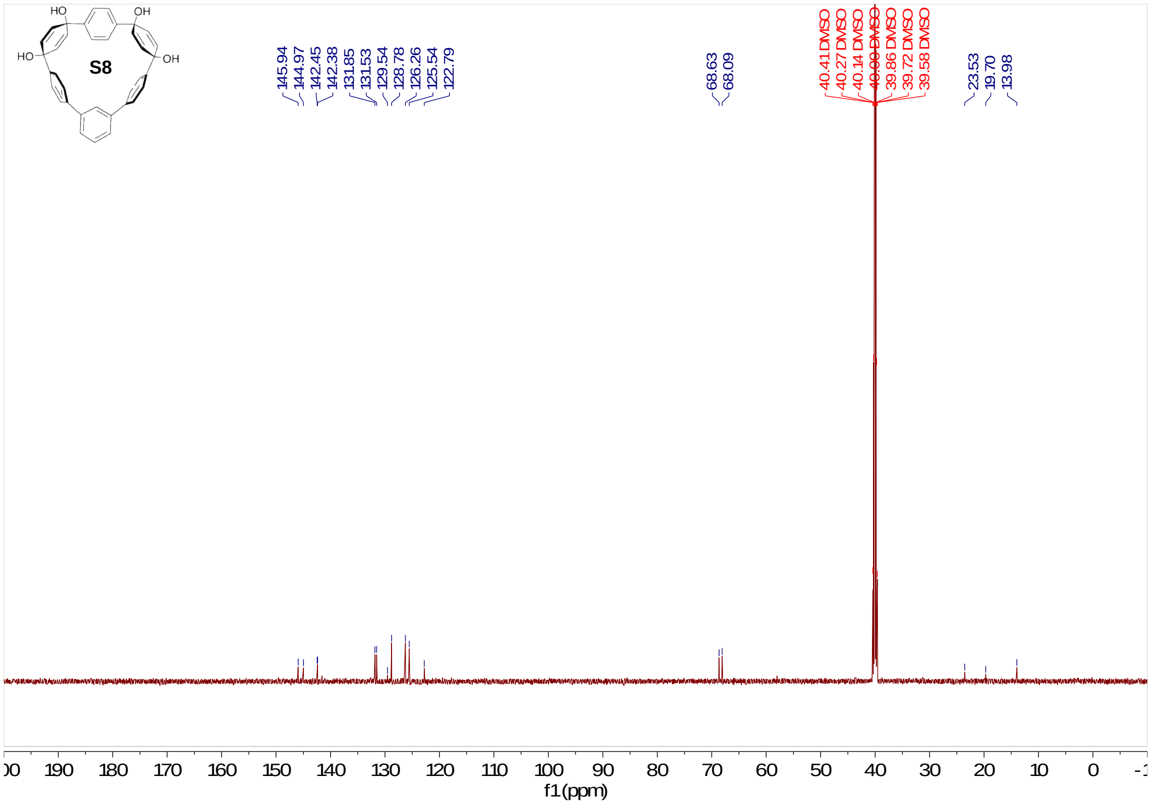
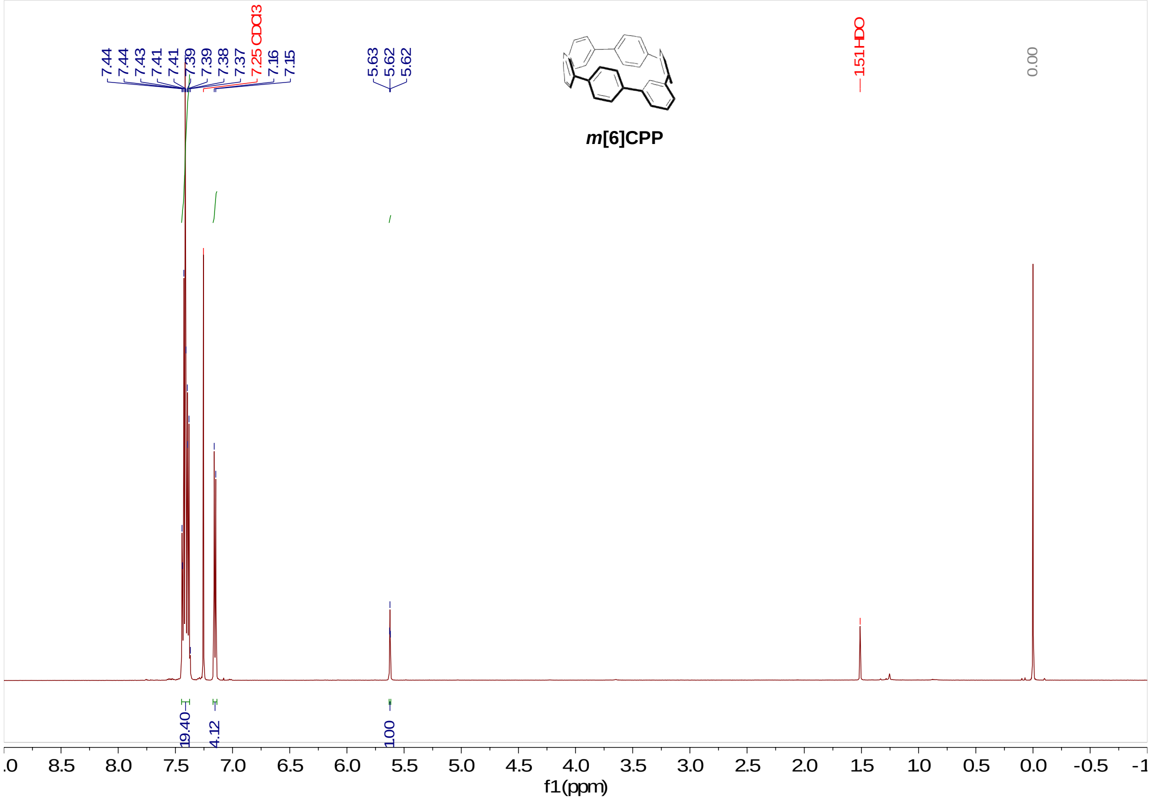
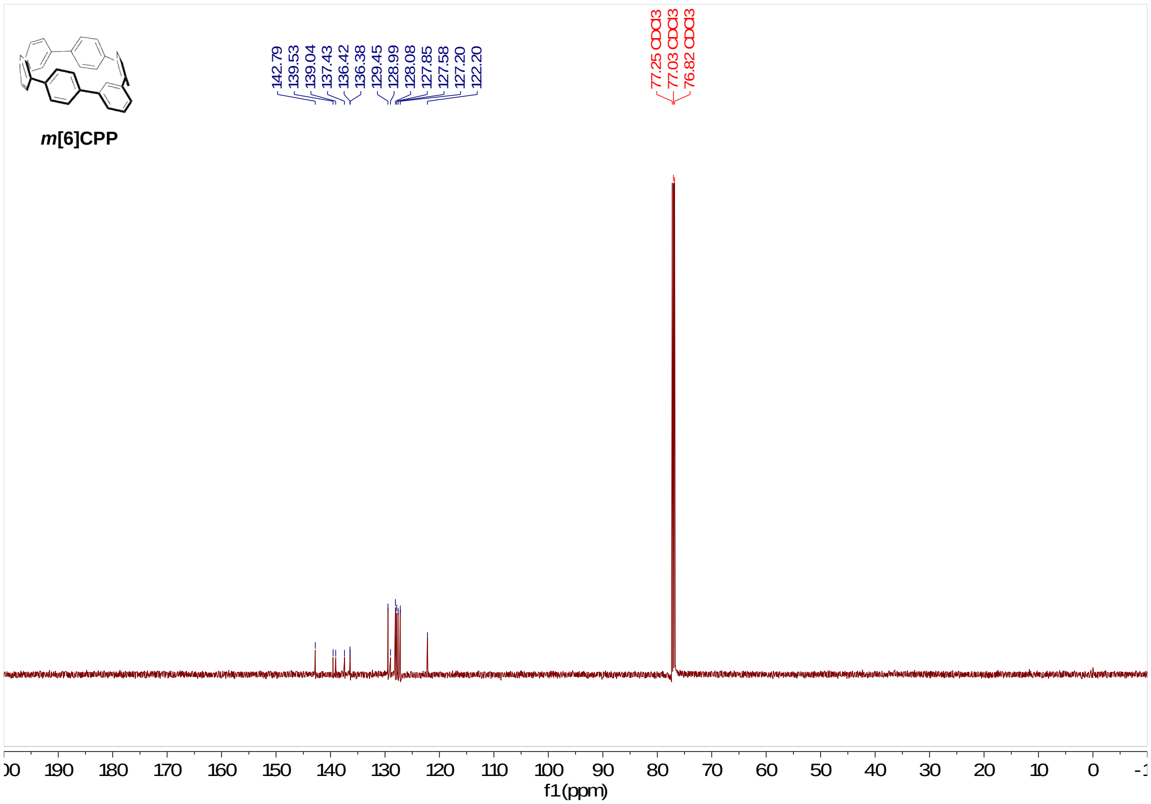
0.56
0.00
2.06
5.54
4.36
4.09
1.00
4.14
19.10
20.93
12.62
13.48
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

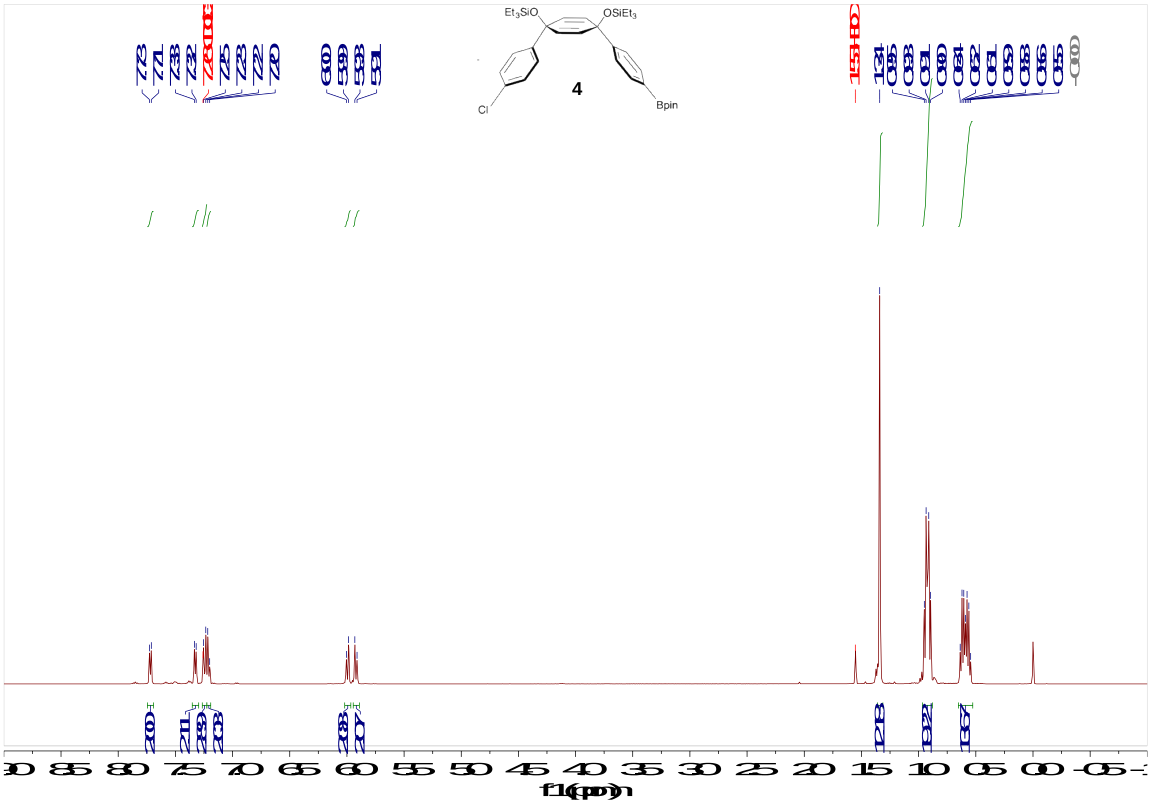

Et$_3$SiO
OSiEt$_3$
Et$_3$SiO
OSiEt$_3$
13
144.89
144.74
143.12
142.44
141.73
131.46
131.41
128.77
128.66
128.03
125.97
125.78
125.71
125.32
122.36
77.23 CDCl3
77.01 CDCl3
76.80 CDCl3
71.16
70.55
7.12
7.02
6.95
6.78
6.58
6.47
6.45
6.39
-0.00
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

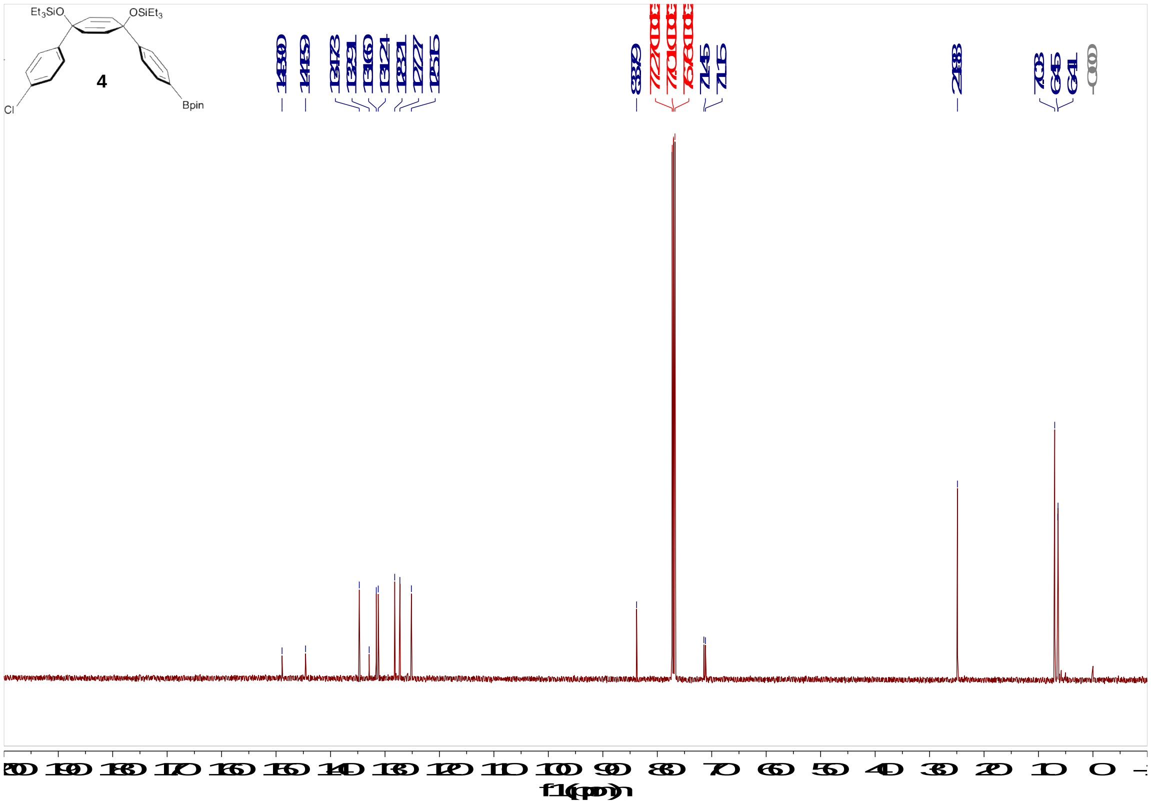

7.61
7.61
7.60
7.59
7.53
7.51
7.50
7.48
7.47
7.34
7.33
6.88
6.17
6.17
6.16
6.08
6.07
5.65
5.64
HO
OH
HO
OH
S8
3.34 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.03
1.15
3.97
4.04
3.87
1.00
3.94
4.08
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

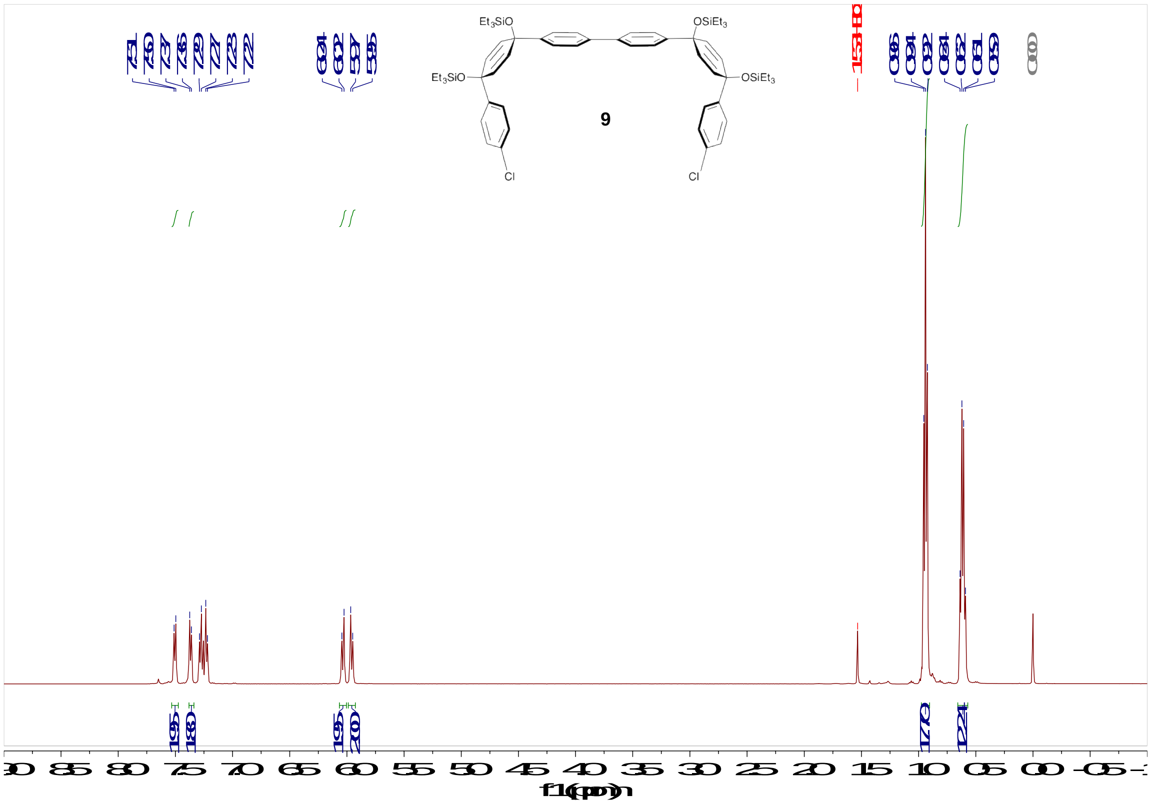

HO
OH
HO
OH
S8
145.94
144.97
142.45
142.38
131.85
131.53
129.54
128.78
126.26
125.54
122.79
68.63
68.09
40.41 DMSO
40.27 DMSO
40.14 DMSO
40.00 DMSO
39.86 DMSO
39.72 DMSO
39.58 DMSO
23.53
19.70
13.98
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

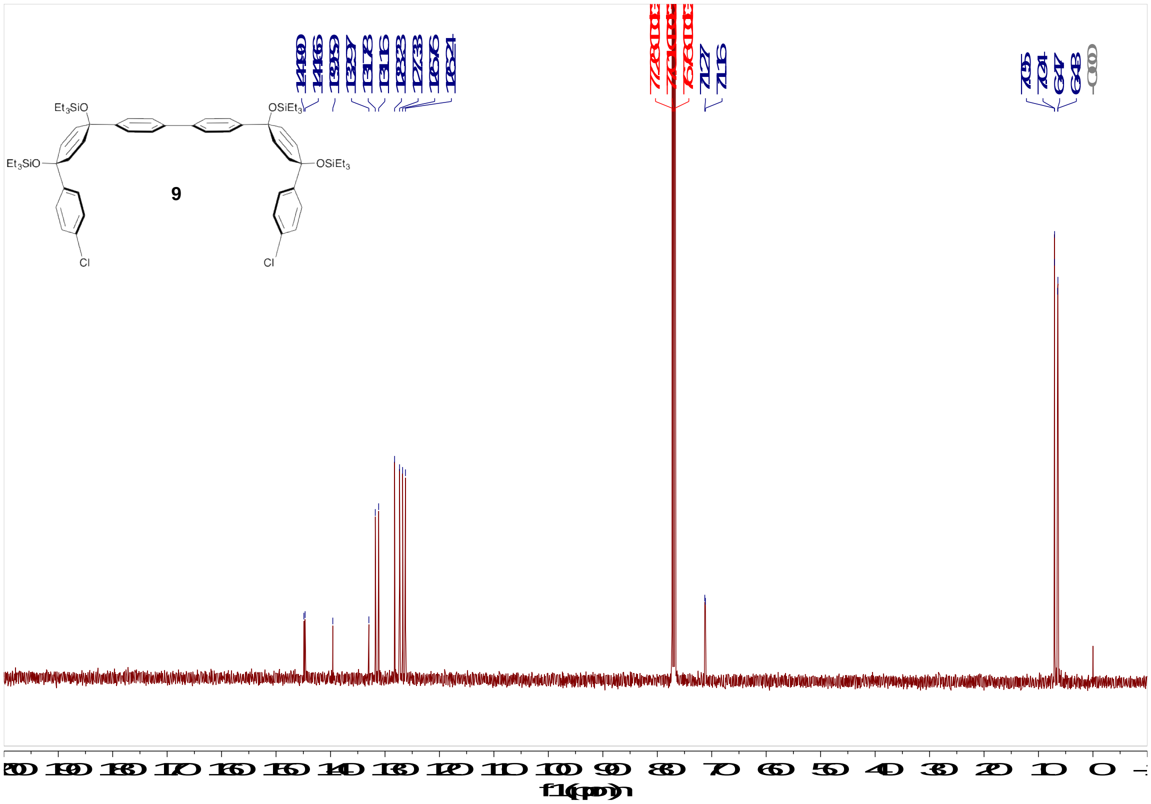

7.44
7.44
7.43
7.41
7.41
7.39
7.39
7.38
7.37
7.25 CDCl3
7.16
7.15
5.63
5.62
5.62
m[6]CPP
1.51 HDO
0.00
19.40
4.12
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

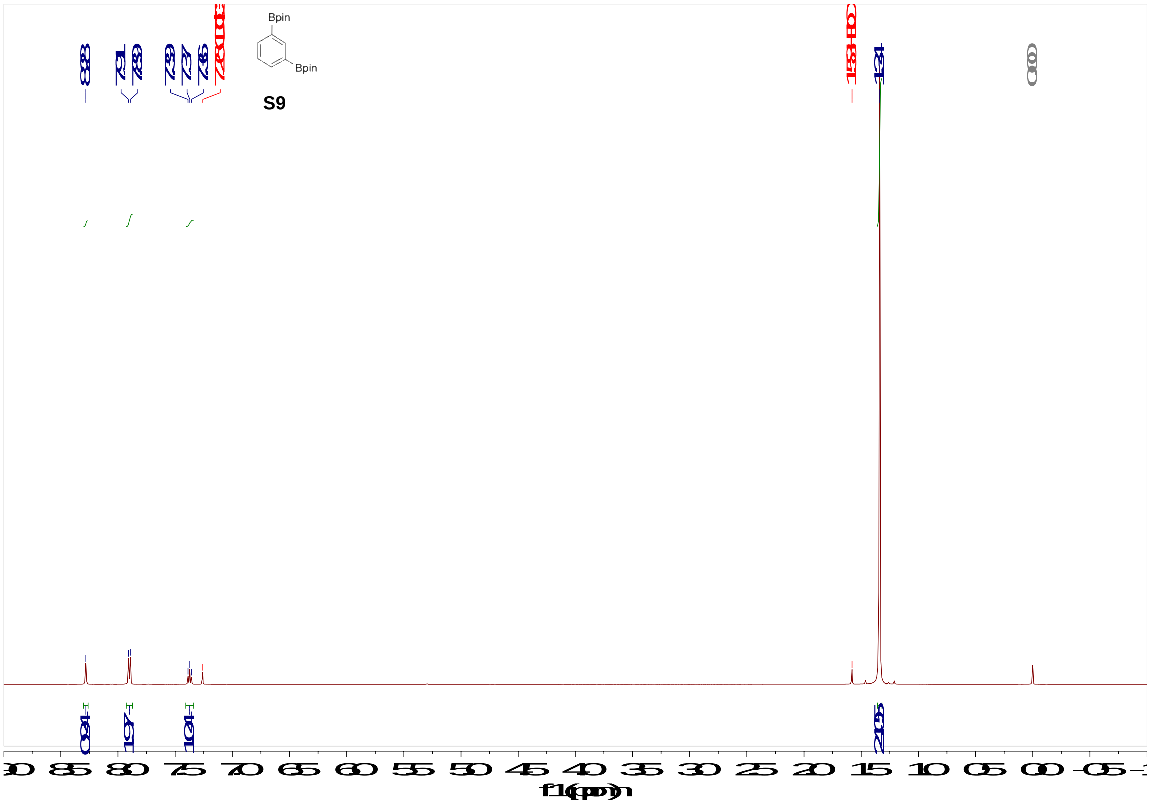

m[6]CPP
142.79
139.53
139.04
137.43
136.42
136.38
129.45
128.99
128.08
127.85
127.58
127.20
122.20
77.25 CDCl3
77.03 CDCl3
76.82 CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

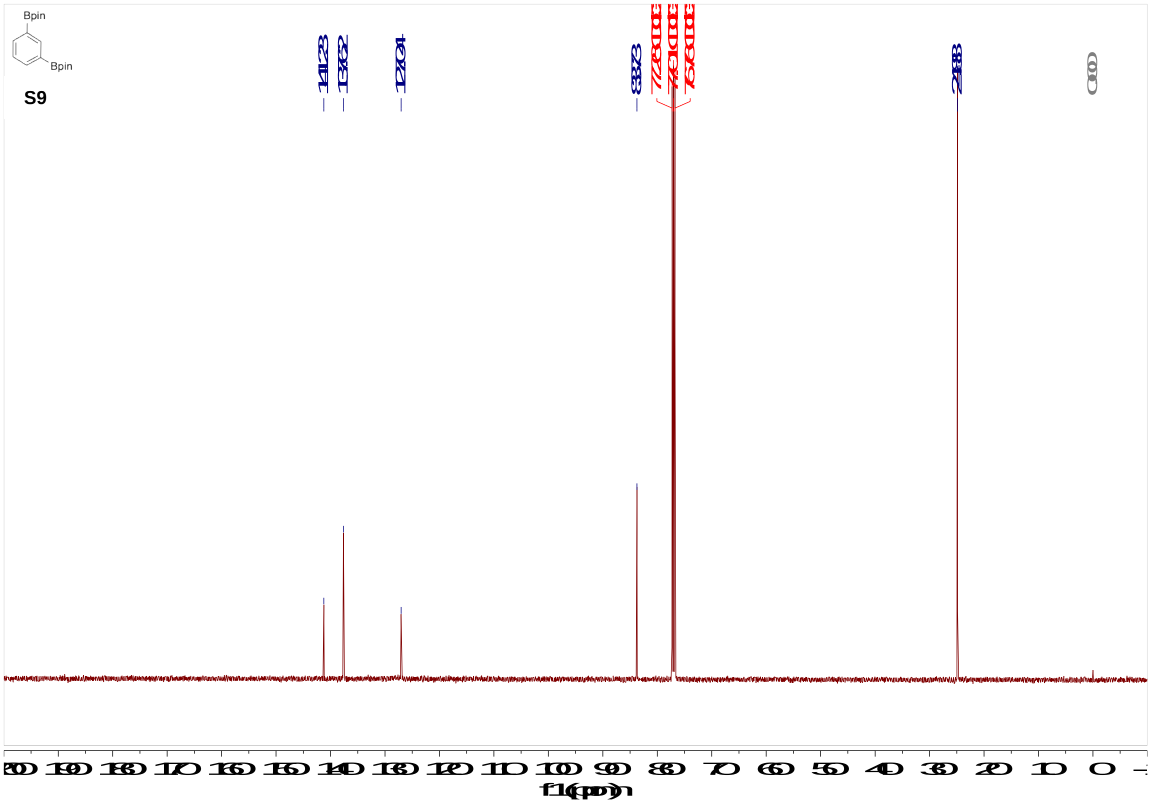

Et3SiO
OSiEt3
4
Cl
Bpin
f1 (ppm)

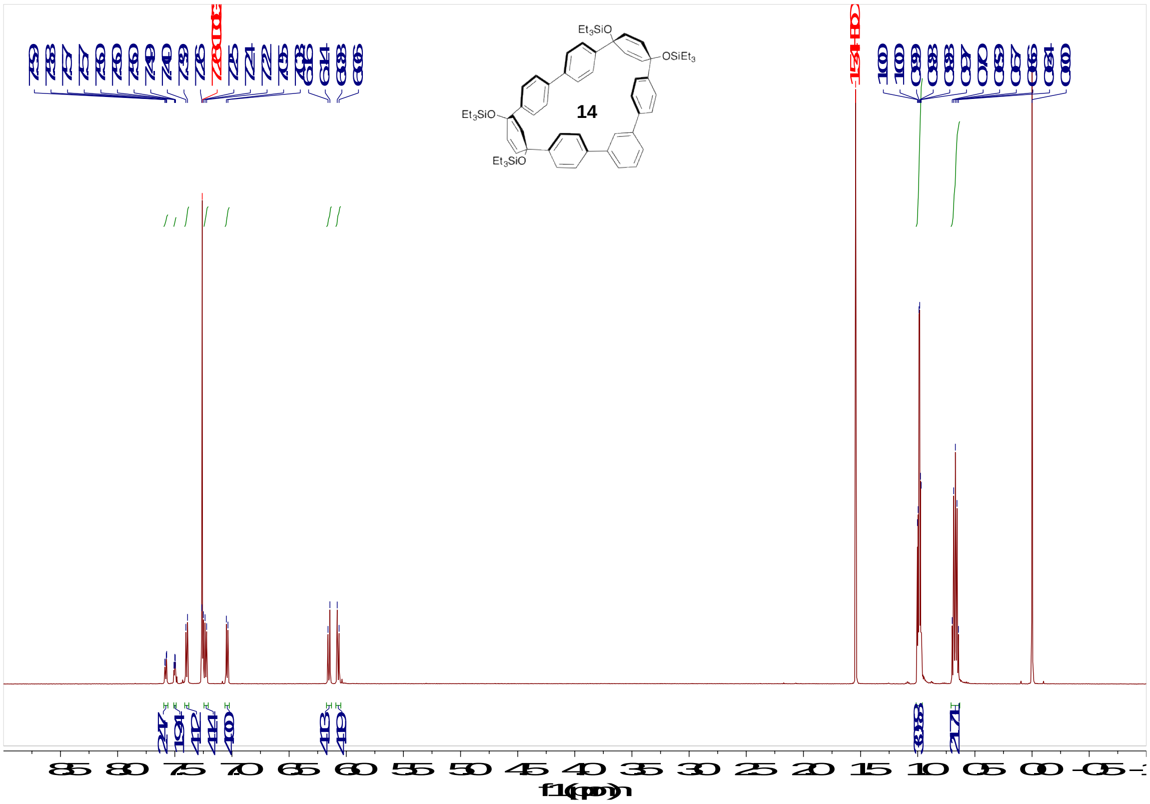

Et3SiO
OSiEt3
4
Cl
Bpin
f1 (ppm)

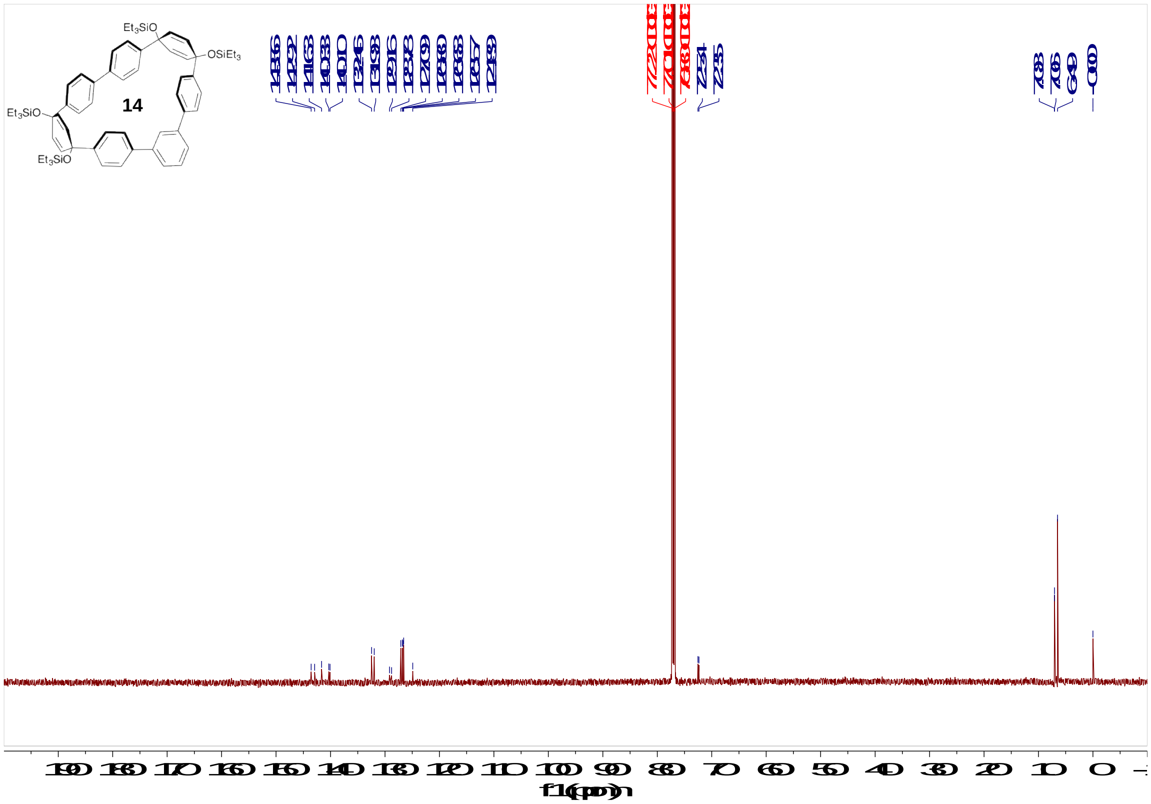

Et$_3$SiO
OSiEt$_3$
Et$_3$SiO
OSiEt$_3$
9
Cl
Cl
f1 (ppm)

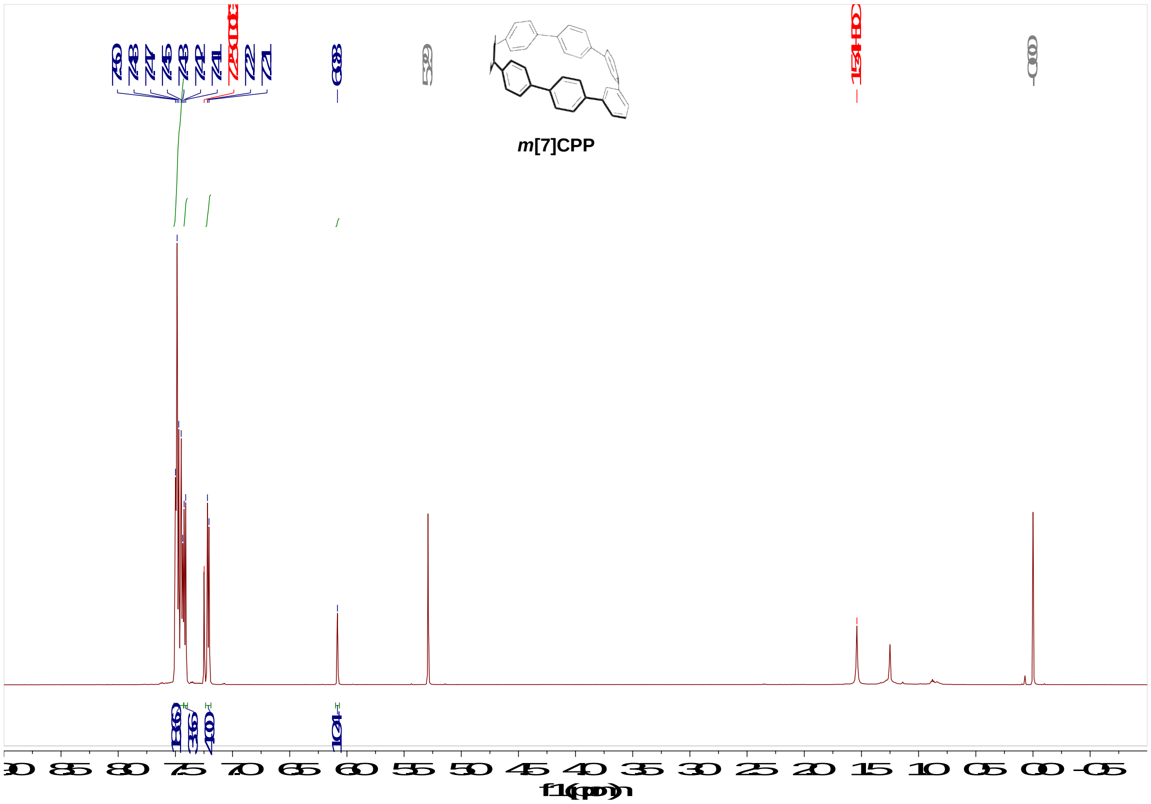

Et$_3$SiO
OSiEt$_3$
Et$_3$SiO
OSiEt$_3$
9
Cl
Cl
f1 (ppm)

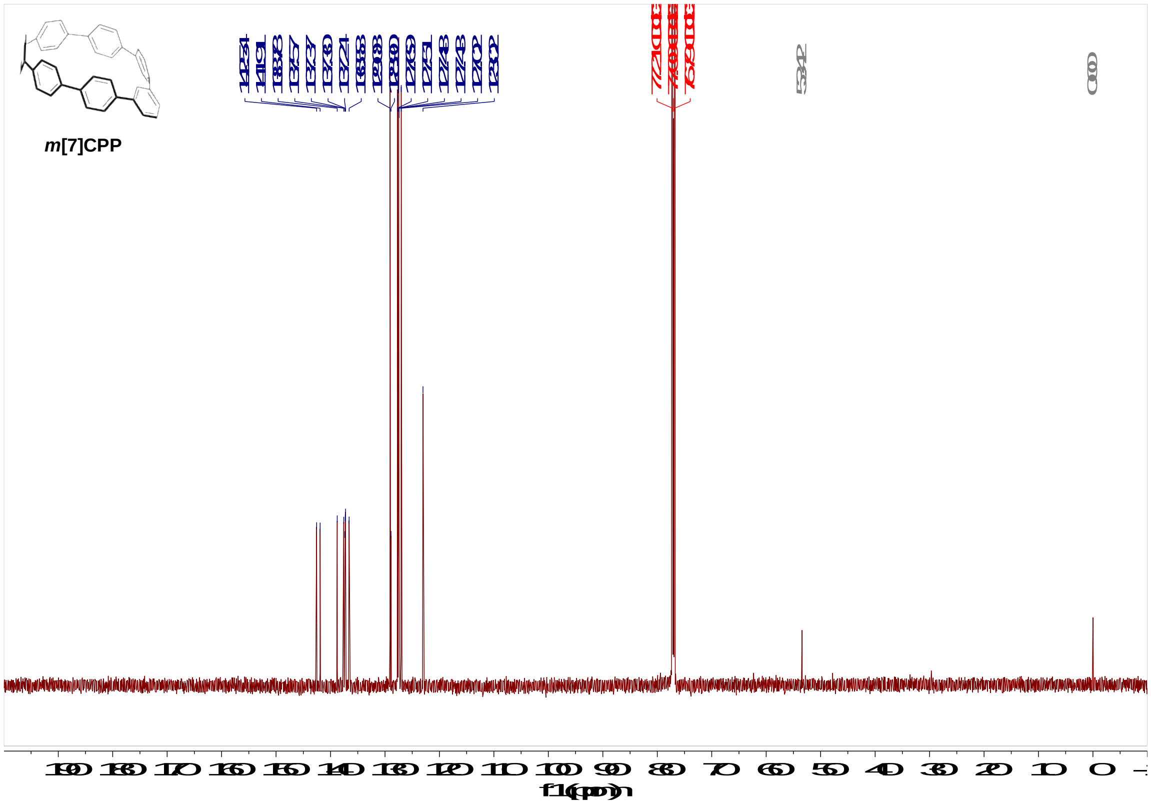

Bpin
Bpin
S9
f1 (ppm)

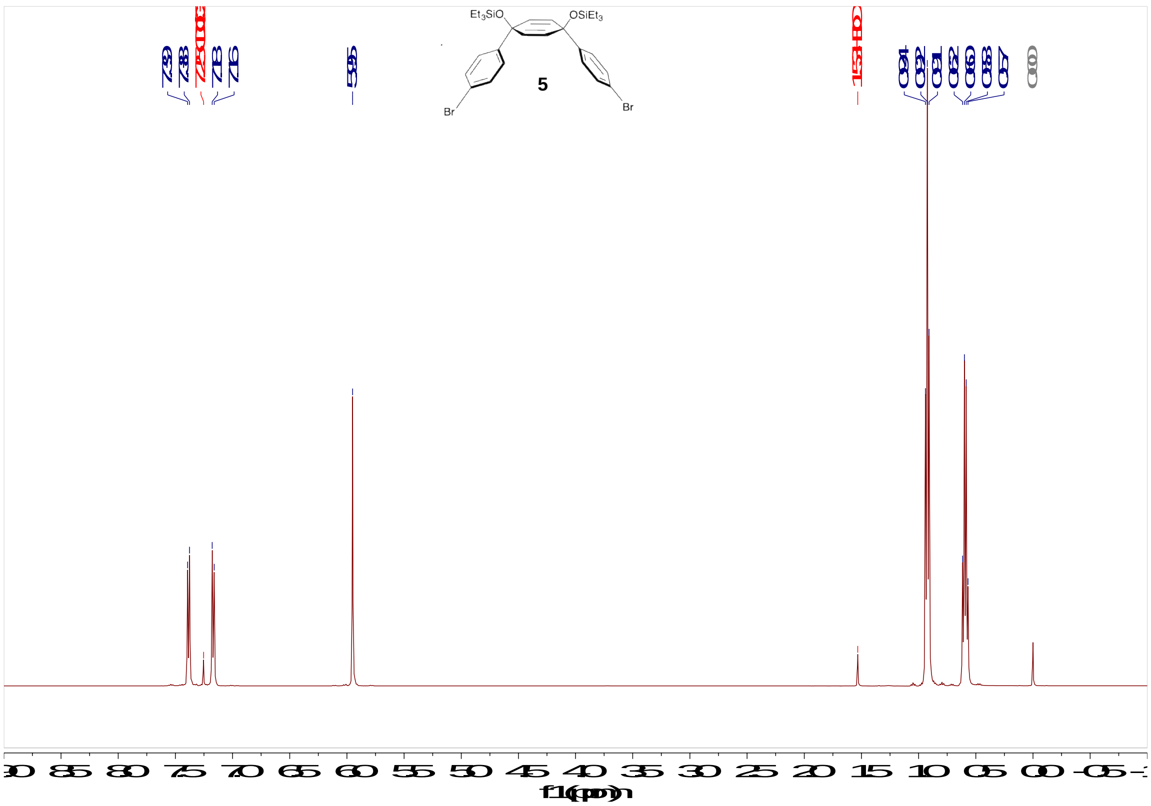

Bpin
Bpin
S9
f1 (ppm)

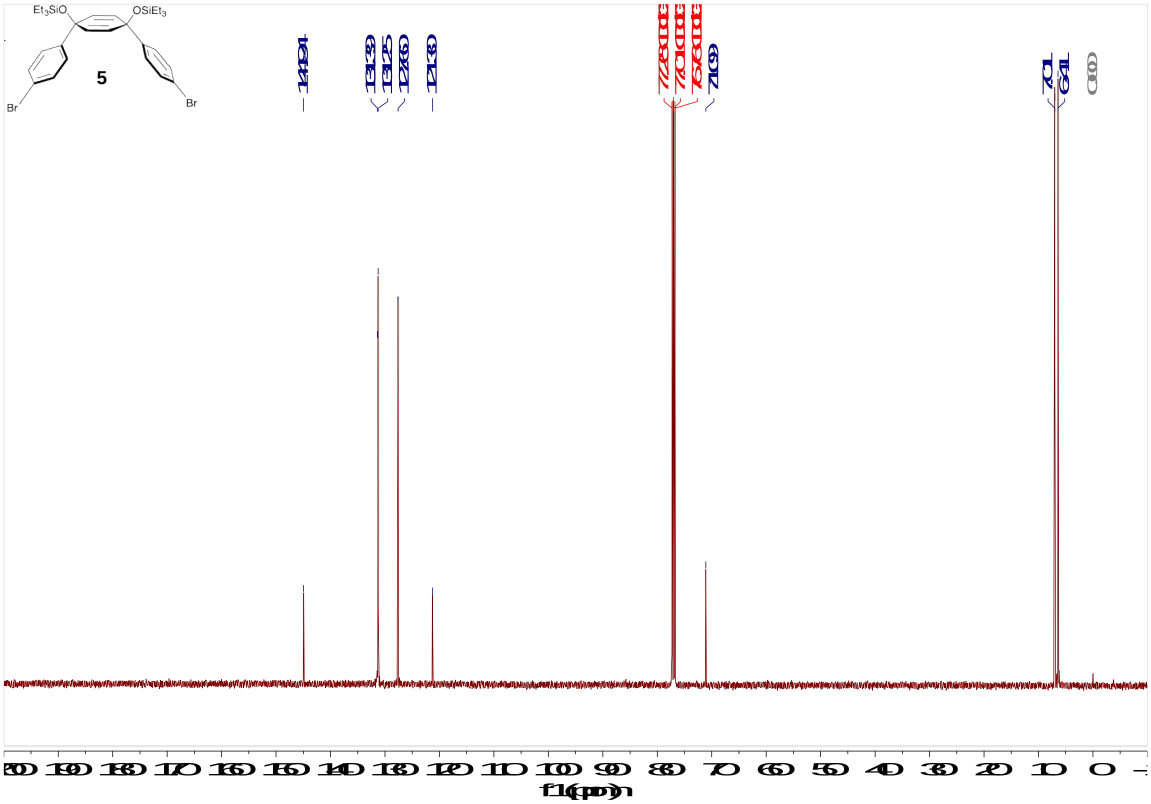

Et3SiO
OSiEt3
Et3SiO
Et3SiO
14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

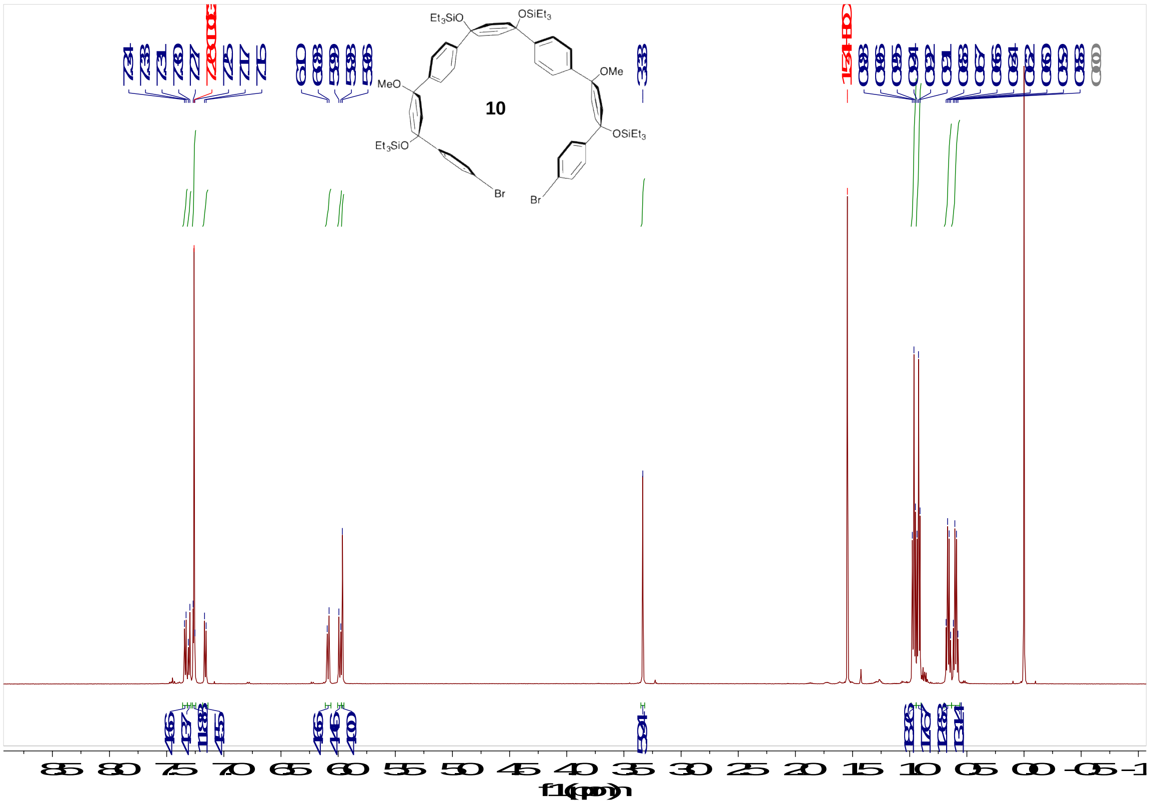

Et3SiO
OSiEt3
Et3SiO
Et3SiO
14
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


m[7]CPP
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
-0.5
f1 (ppm)

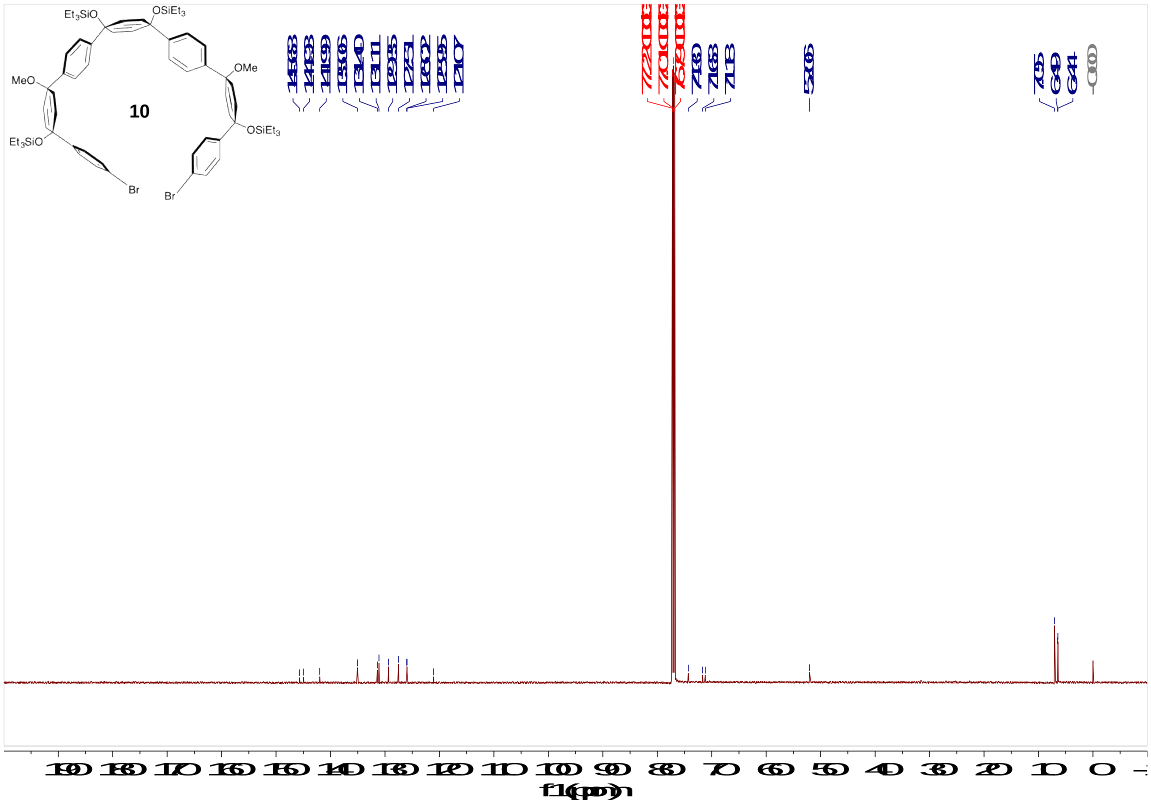

m[7]CPP
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Et3SiO
OSiEt3
5
Br
Br
f1 (ppm)

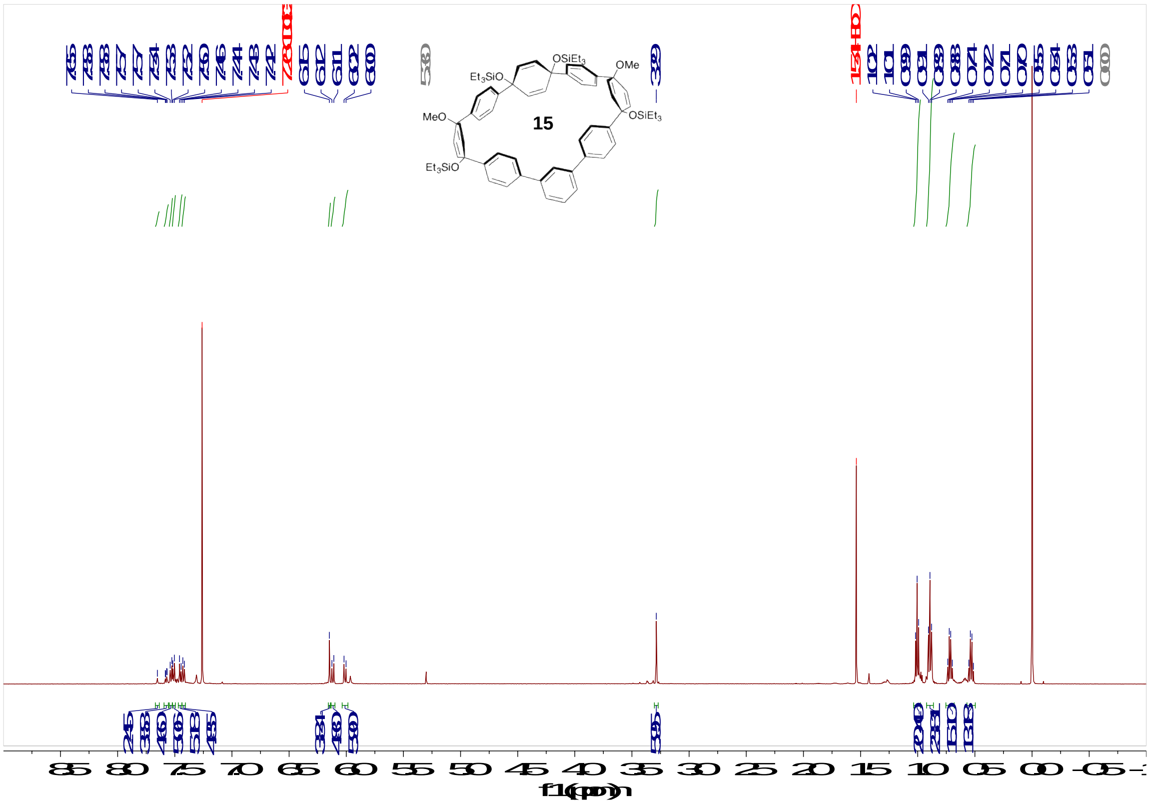

Et3SiO
OSiEt3
5
Br
Br
f1 (ppm)

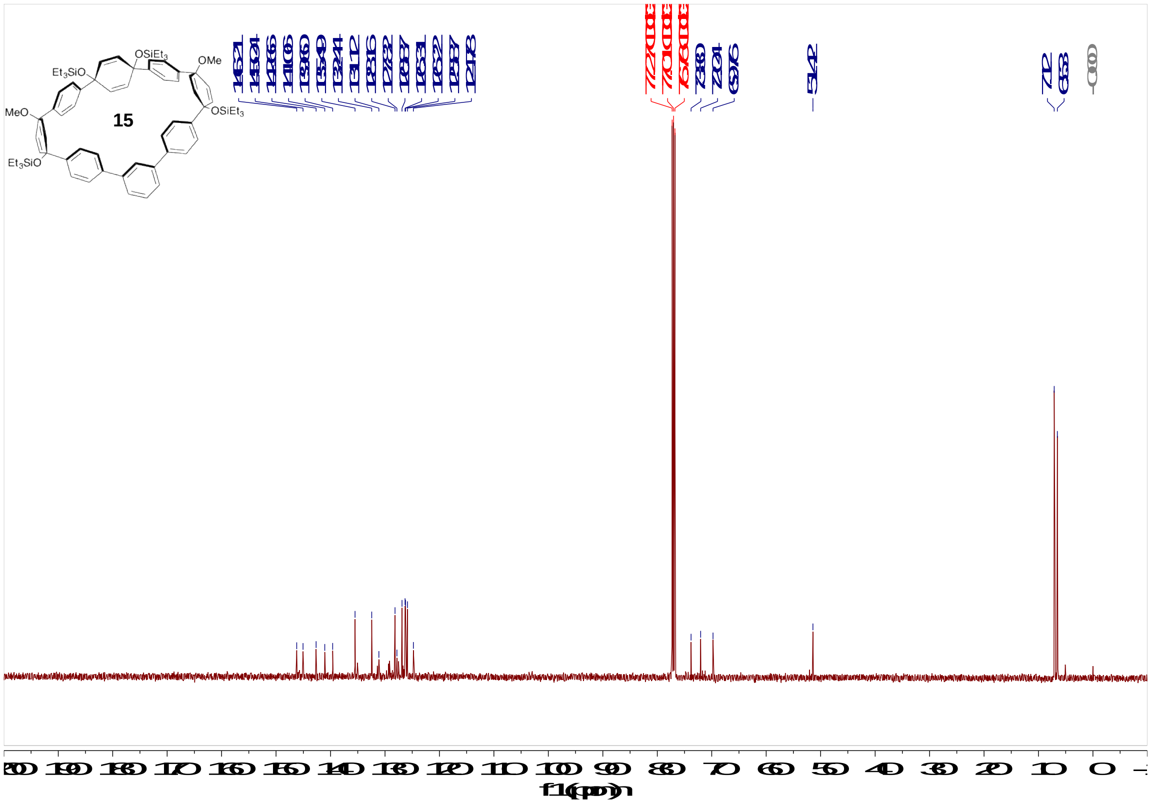


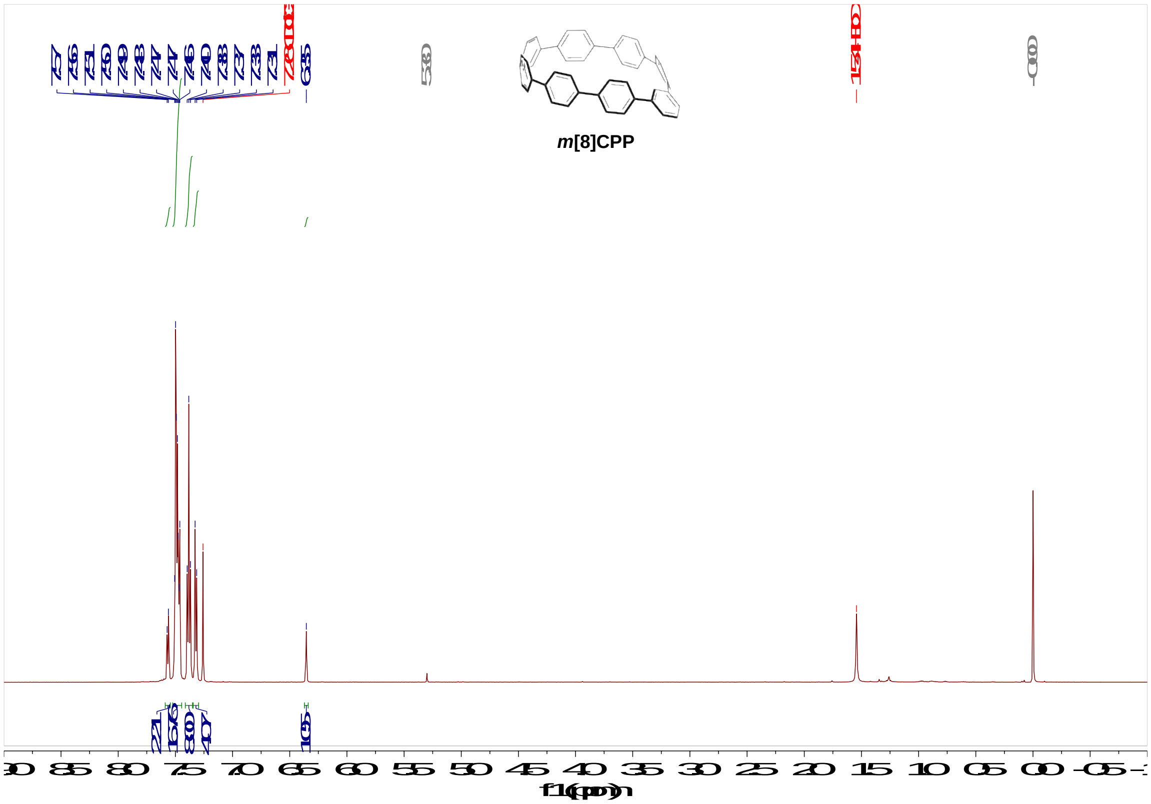
Et3SiO
OSiEt3
MeO
OMe
10
Et3SiO
OSiEt3
Br
Br
f1 (ppm)

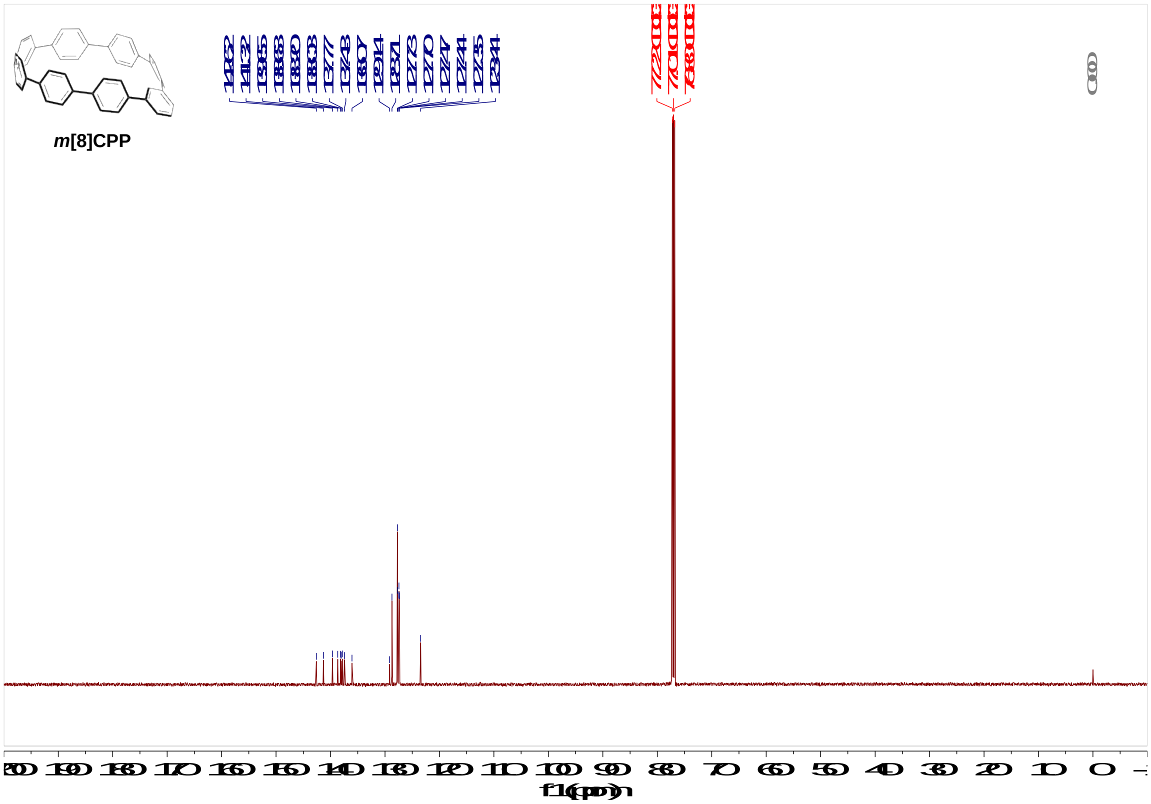


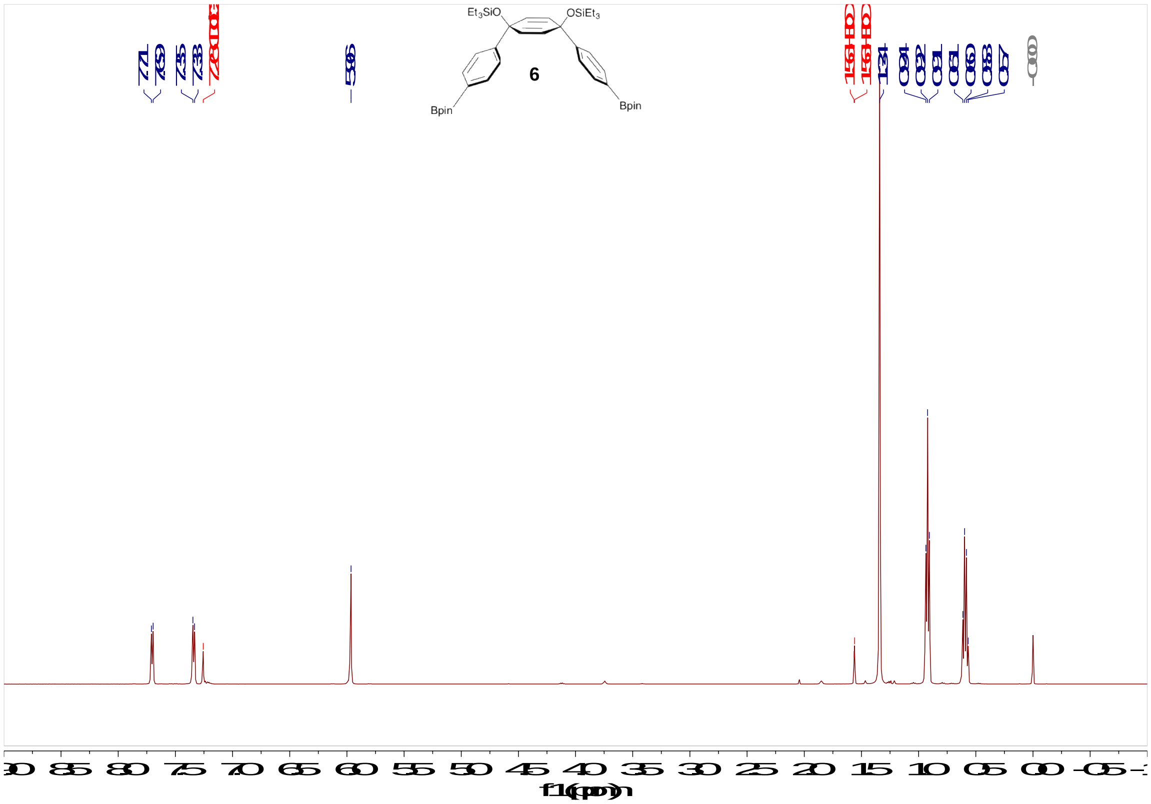
Et3SiO
OSiEt3
MeO
OMe
10
Et3SiO
OSiEt3
Br
Br
f1 (ppm)

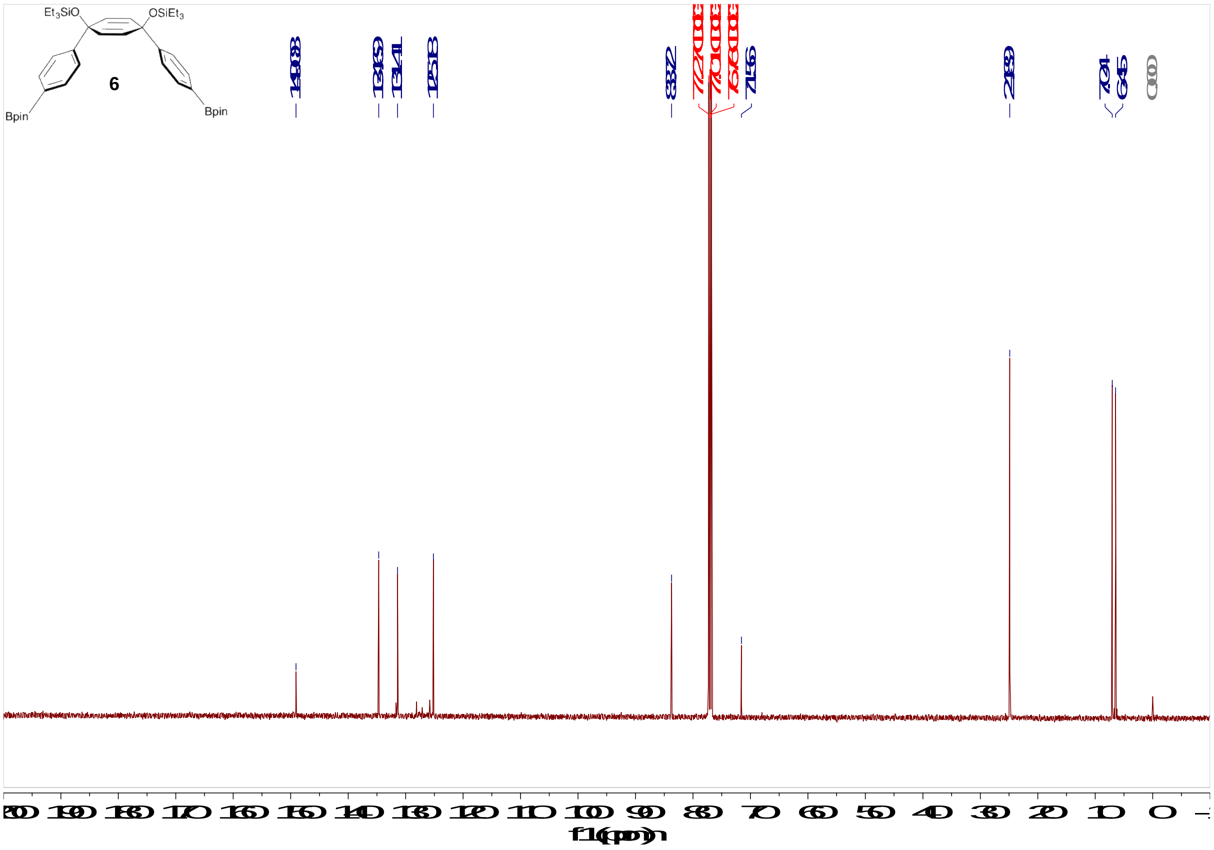

Et3SiO
OSiEt3
OMe
MeO
OSiEt3
Et3SiO
15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

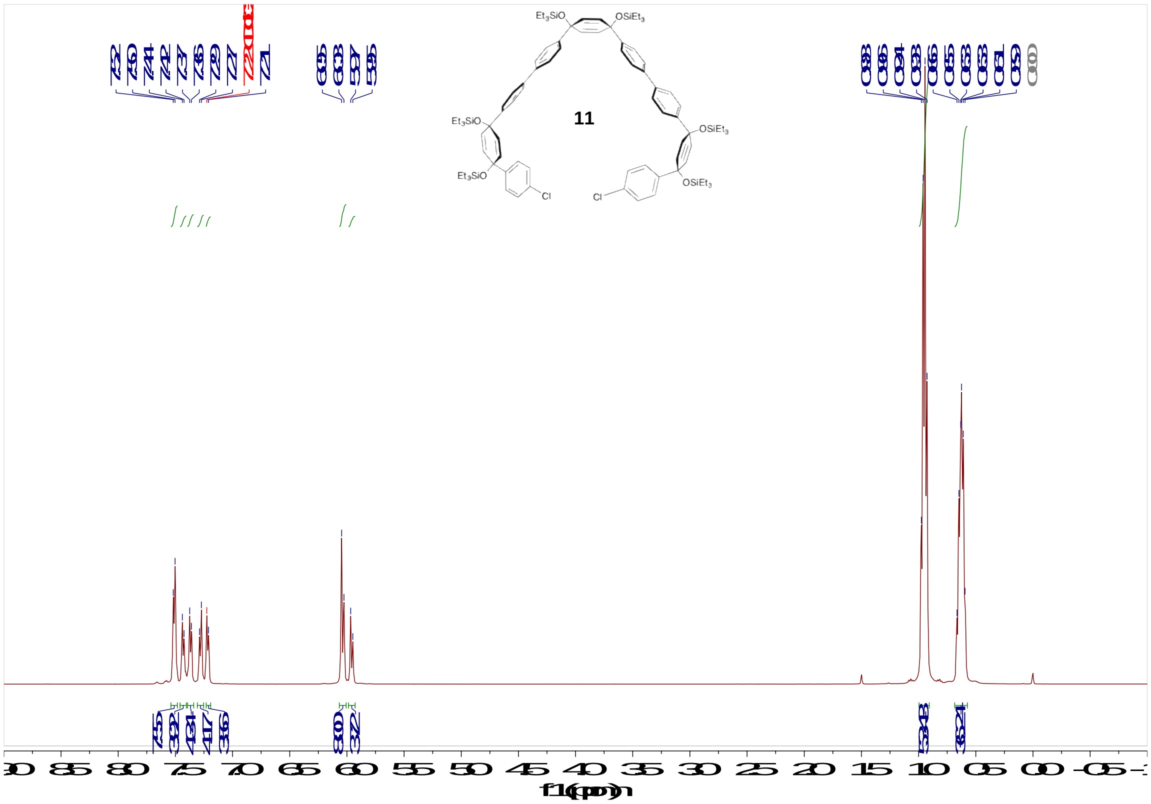

Et3SiO
OSiEt3
OMe
MeO
OSiEt3
Et3SiO
15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

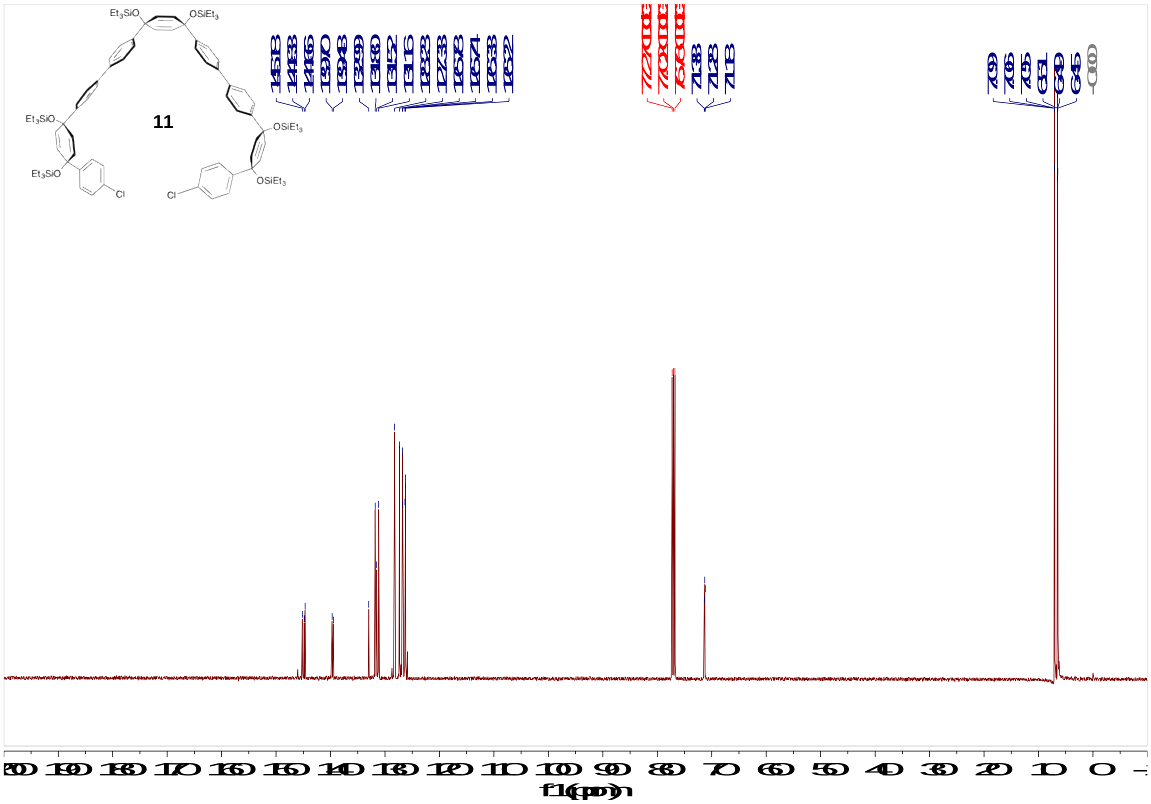

7.57
7.56
7.51
7.50
7.49
7.48
7.47
7.47
7.46
7.40
7.38
7.37
7.33
7.31
7.26 CDCl3
6.35
5.30
1.54 H2O
0.00
m[8]CPP
2.21
15.6
8.01
4.07
1.95
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

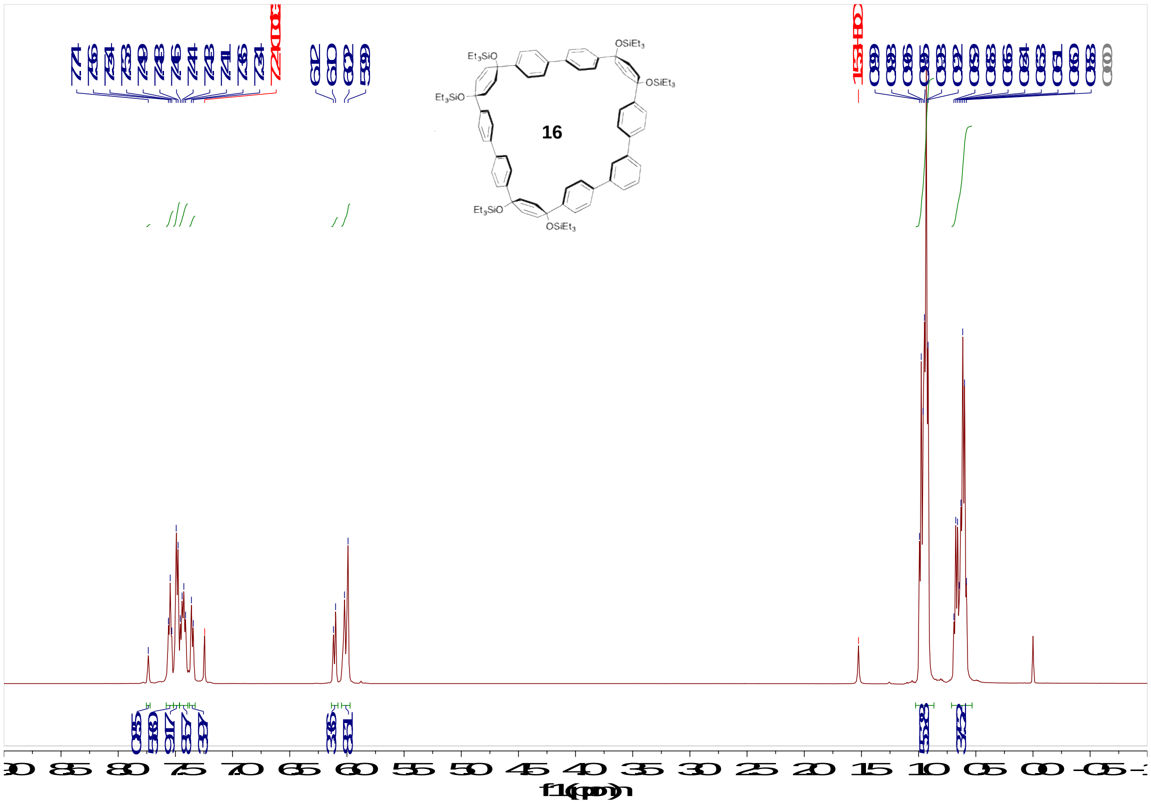

m[8]CPP
142.62
141.32
139.55
138.68
138.30
138.03
137.77
137.43
136.07
129.14
128.71
127.73
127.70
127.47
127.44
127.25
123.44
77.22 CDCl3
77.00 CDCl3
76.80 CDCl3
0.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

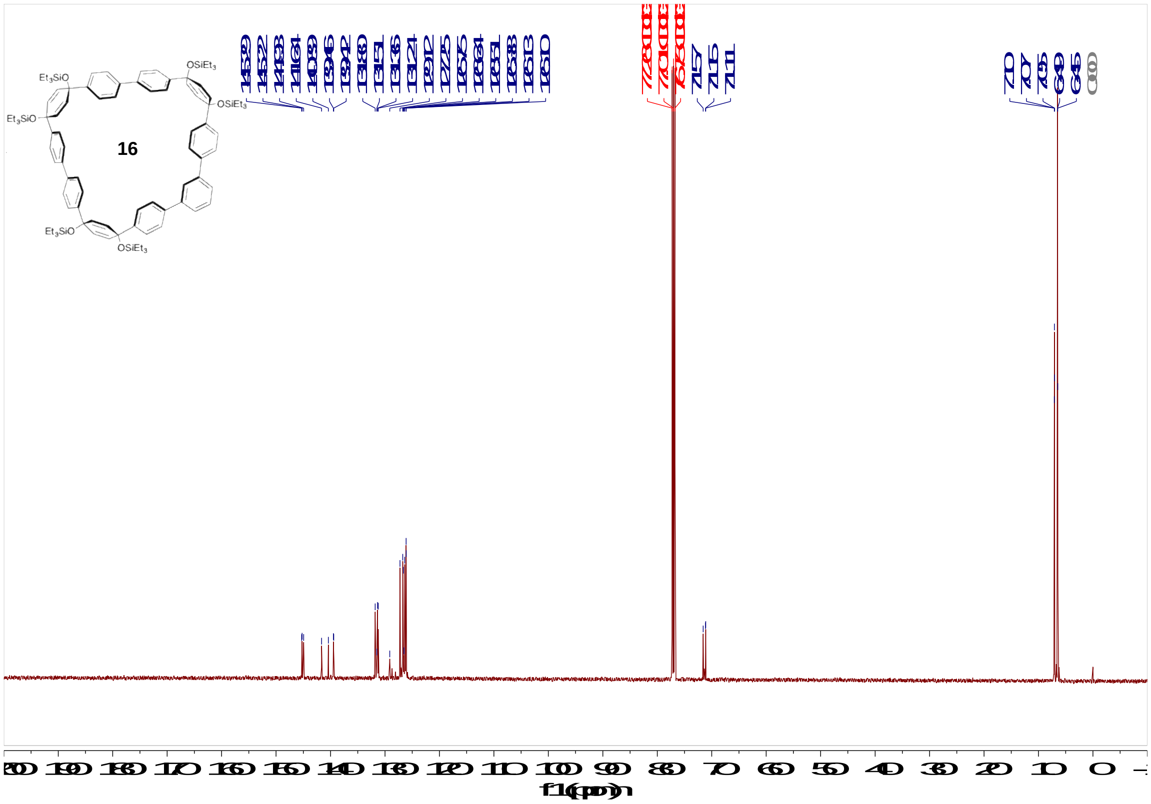

Et3SiO
OSiEt3
6
Bpin
Bpin
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

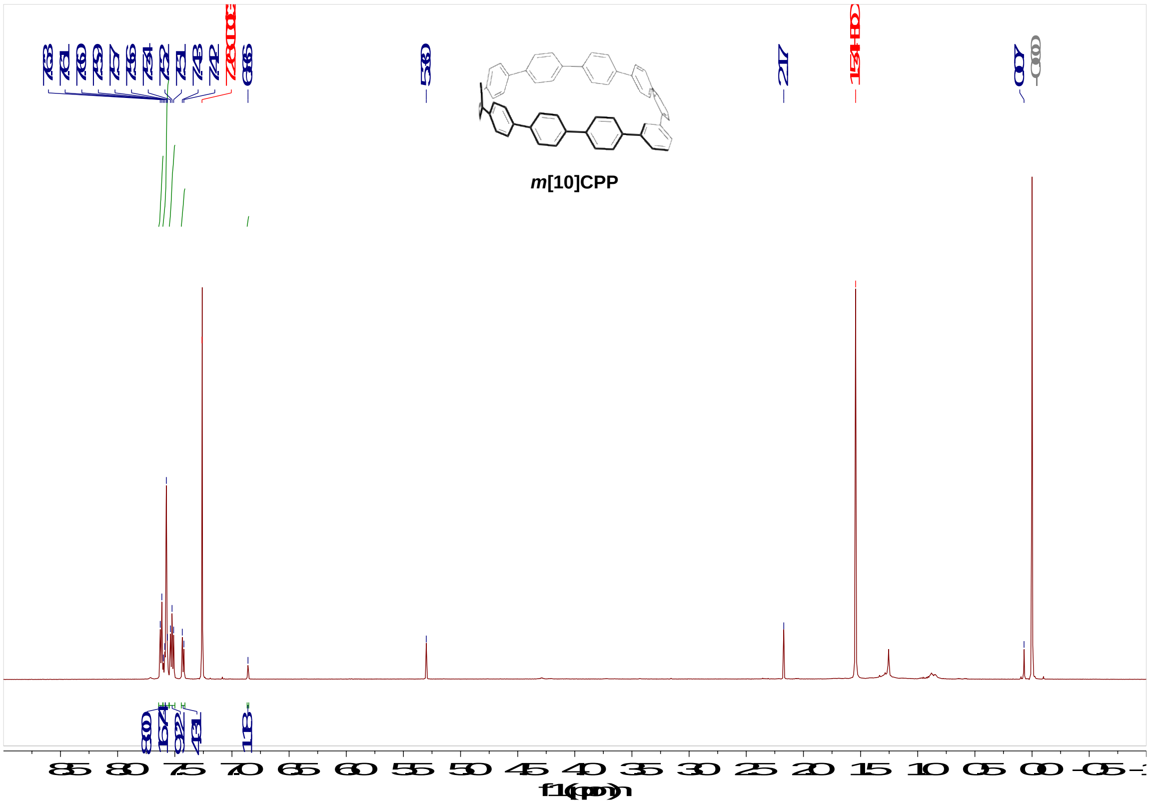

Et3SiO
OSiEt3
6
Bpin
Bpin
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Et₃SiO
OSiEt₃
Et₃SiO
OSiEt₃
Et₃SiO
OSiEt₃
Cl
Cl
11
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 -0.5
f1 (ppm)

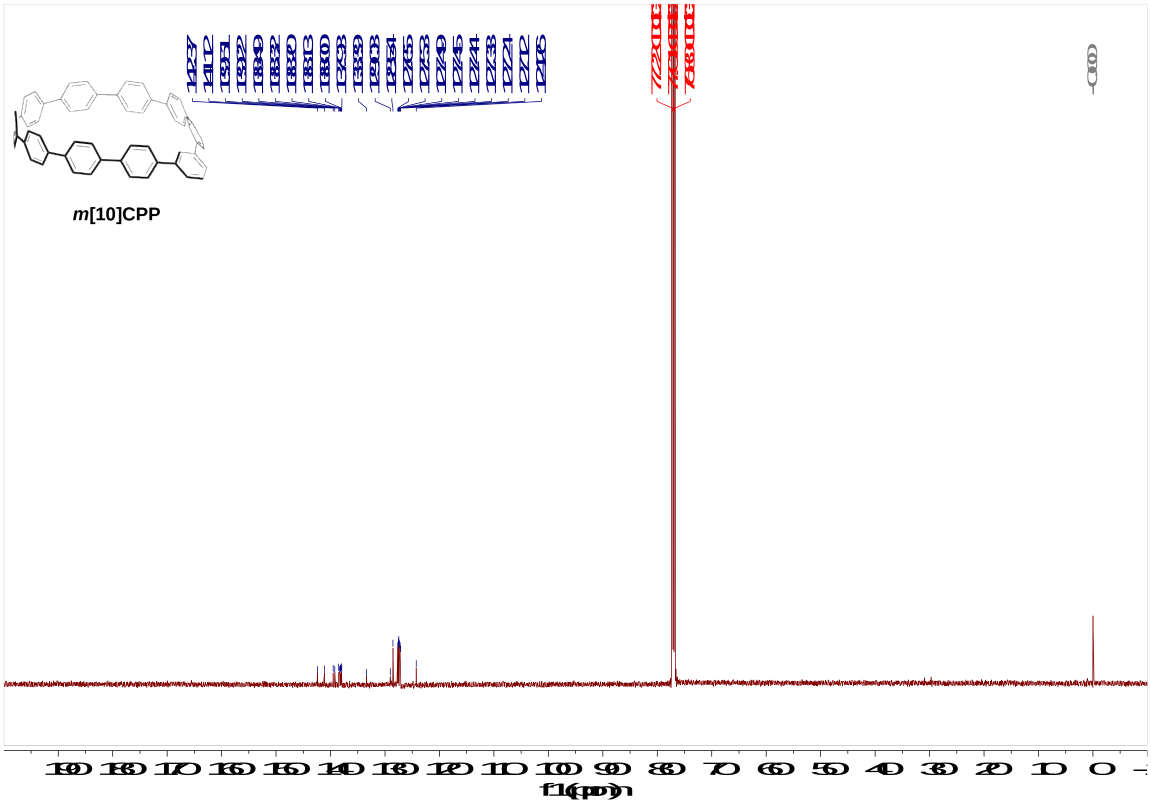

Et₃SiO
OSiEt₃
Et₃SiO
OSiEt₃
Et₃SiO
OSiEt₃
Cl
Cl
11
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Et3SiO
Et3SiO
OSiEt3
OSiEt3
16
Et3SiO
OSiEt3
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 -0.5
f1 (ppm)

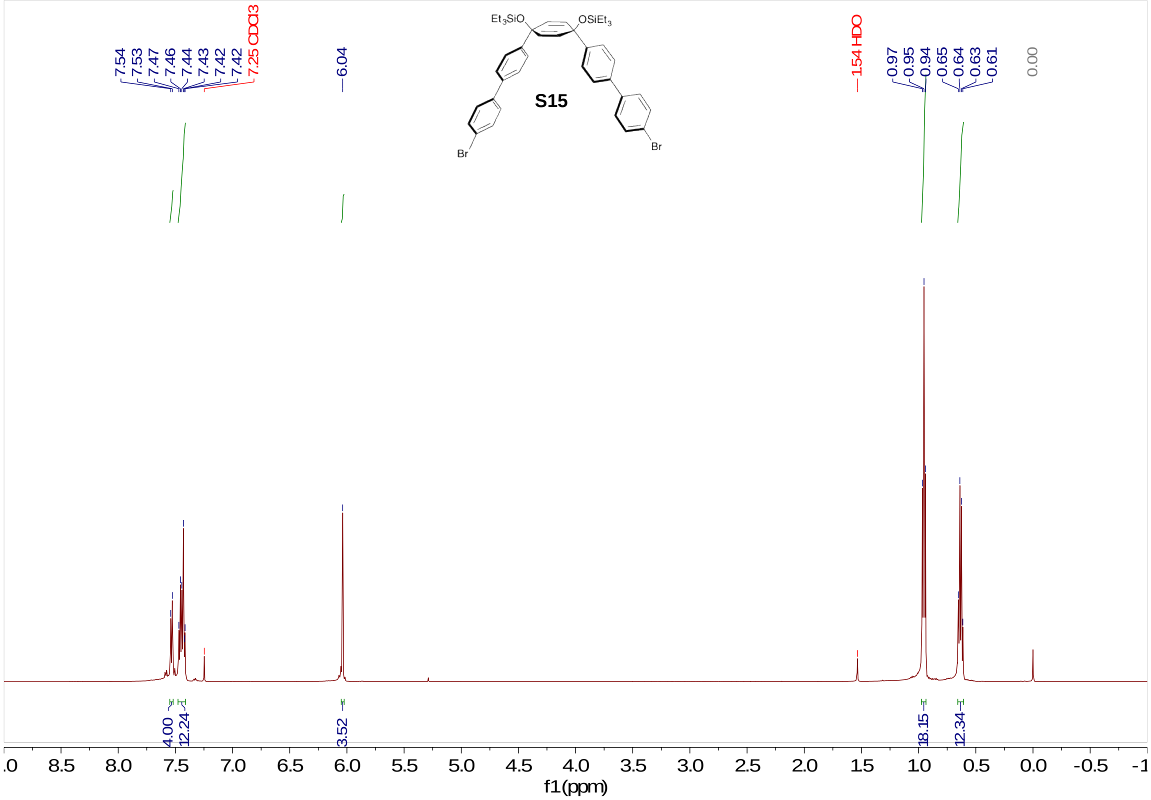

Et3SiO
Et3SiO
OSiEt3
OSiEt3
16
Et3SiO
OSiEt3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

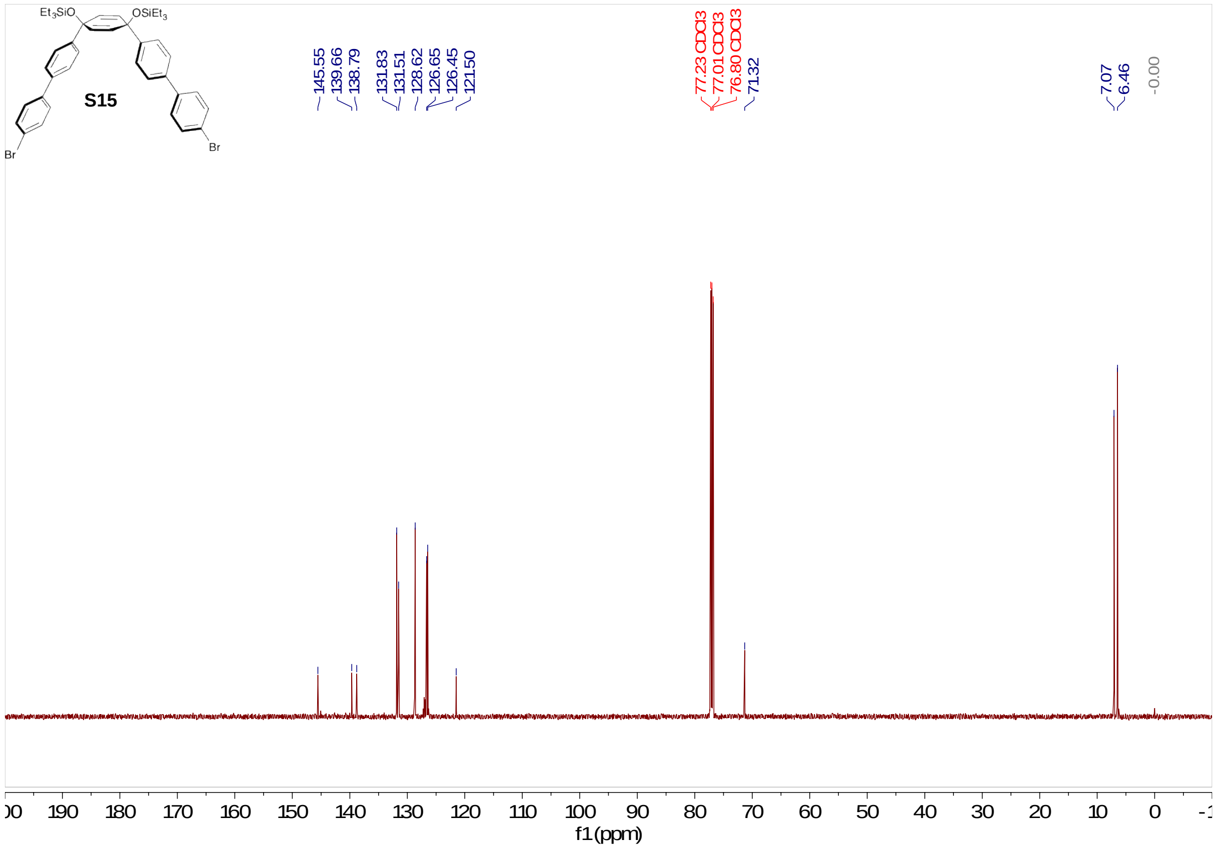


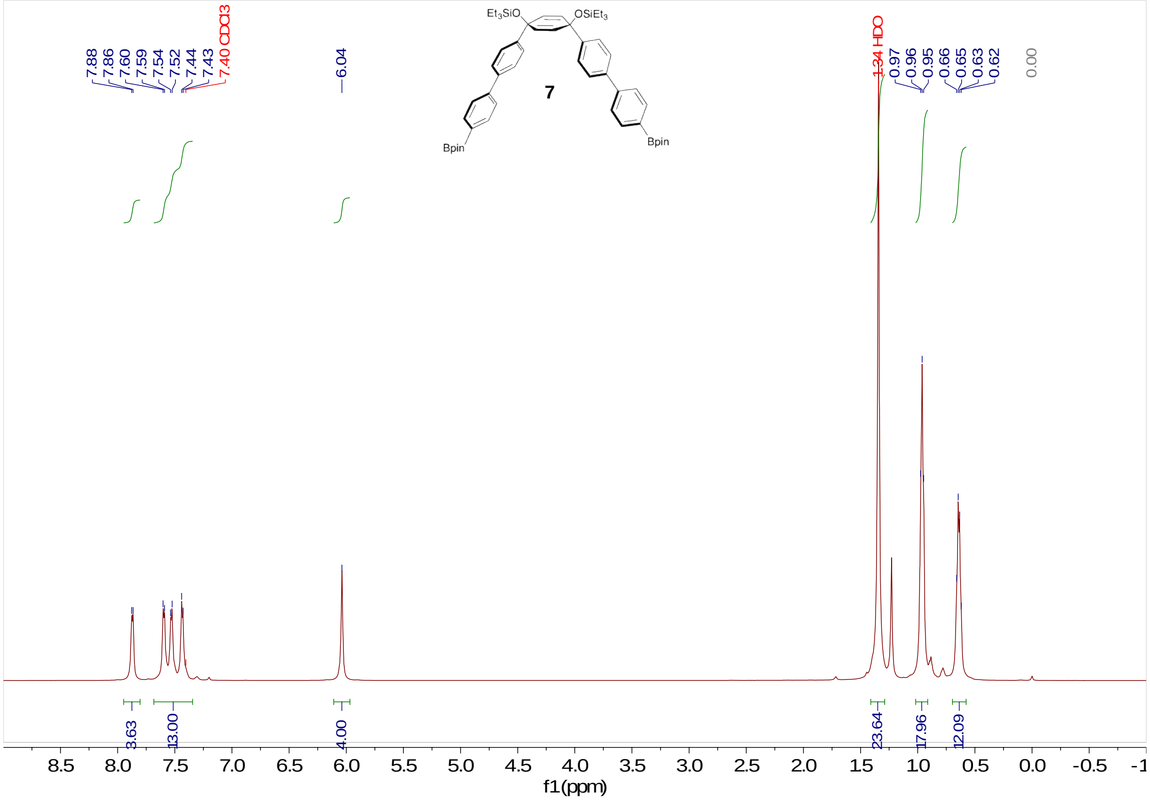
m[10]CPP
7.63
7.61
7.60
7.59
7.57
7.56
7.54
7.52
7.51
7.48
7.42
7.26 CDCl3
6.96
5.30
2.17
1.54 HDO
0.07
0.00
8.00
15.74
9.92
4.13
1.18
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

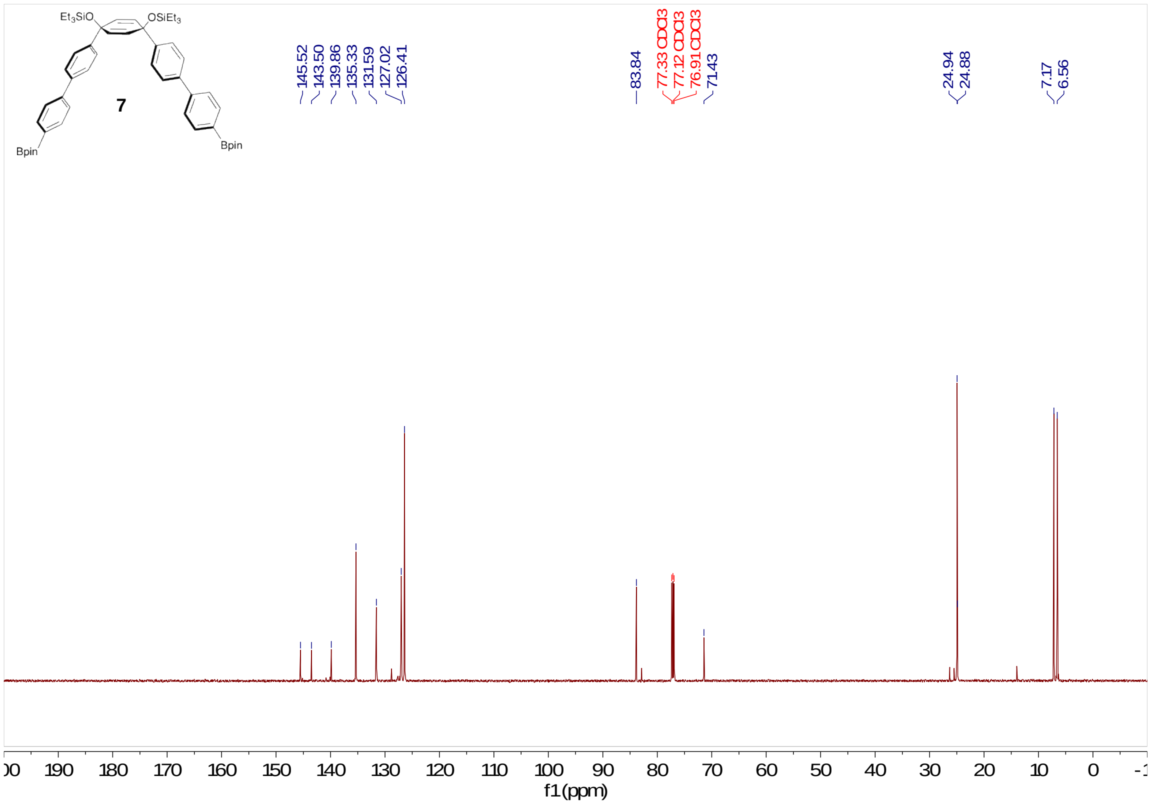


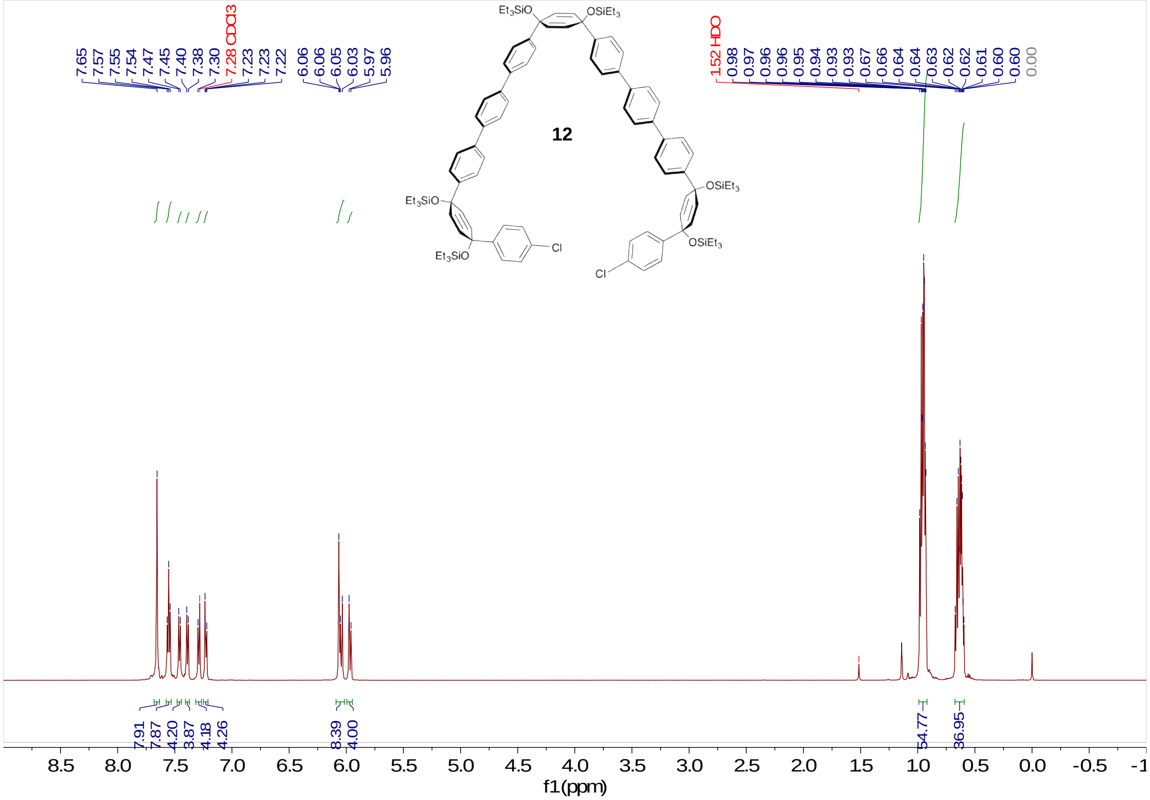
m[10]CPP
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
0.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

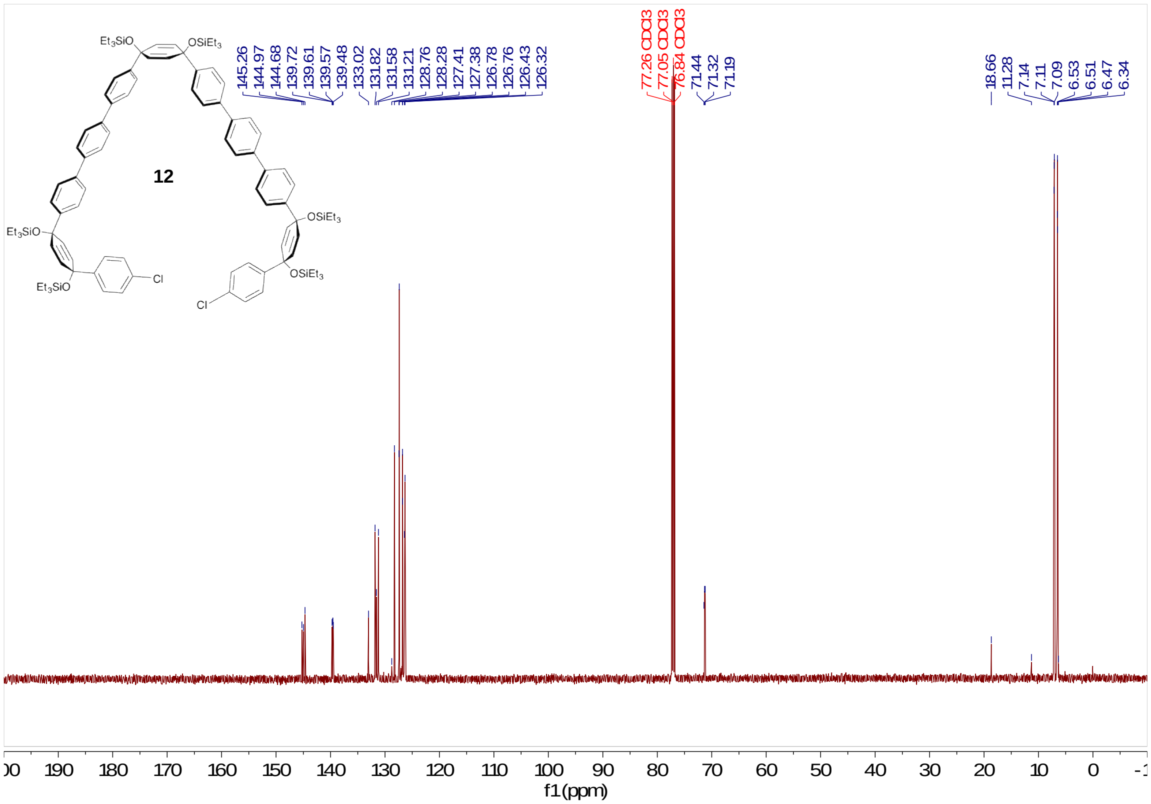

7.54
7.53
7.47
7.46
7.44
7.43
7.42
7.42
7.25 CDCl3
6.04
Et3SiO
OSiEt3
S15
Br
Br
1.54 HDO
0.97
0.95
0.94
0.65
0.64
0.63
0.61
0.00
4.00
12.24
3.52
18.15
12.34
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1(ppm)


Et3SiO
OSiEt3
S15
Br
Br
145.55
139.66
138.79
131.83
131.51
128.62
126.65
126.45
121.50
77.23 CDCl3
77.01 CDCl3
76.80 CDCl3
71.32
7.07
6.46
-0.00
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1(ppm)


Et3SiO
OSiEt3
7
Bpin
Bpin
7.88
7.86
7.60
7.59
7.54
7.52
7.44
7.43
7.40 CDCl3
6.04
1.34 HDO
0.97
0.96
0.95
0.66
0.65
0.63
0.62
0.00
3.63
13.00
4.00
23.64
17.96
12.09
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
-0.5
-1
f1 (ppm)


Et3SiO
OSiEt3
7
Bpin
Bpin
145.52
143.50
139.86
135.33
131.59
127.02
126.41
83.84
77.33 CDCl3
77.12 CDCl3
76.91 CDCl3
71.43
24.94
24.88
7.17
6.56
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.65
7.57
7.55
7.54
7.47
7.45
7.40
7.38
7.30
7.28 CDCl3
7.23
7.23
7.22
6.06
6.06
6.05
6.03
5.97
5.96
1.52 HDO
0.98
0.97
0.96
0.96
0.95
0.94
0.93
0.93
0.67
0.66
0.64
0.64
0.63
0.62
0.62
0.61
0.60
0.60
0.00
Et3SiO
OSiEt3
12
Cl
7.91
7.87
4.20
3.87
4.18
4.26
8.39
4.00
54.77
36.95
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 -0.5 -1
f1 (ppm)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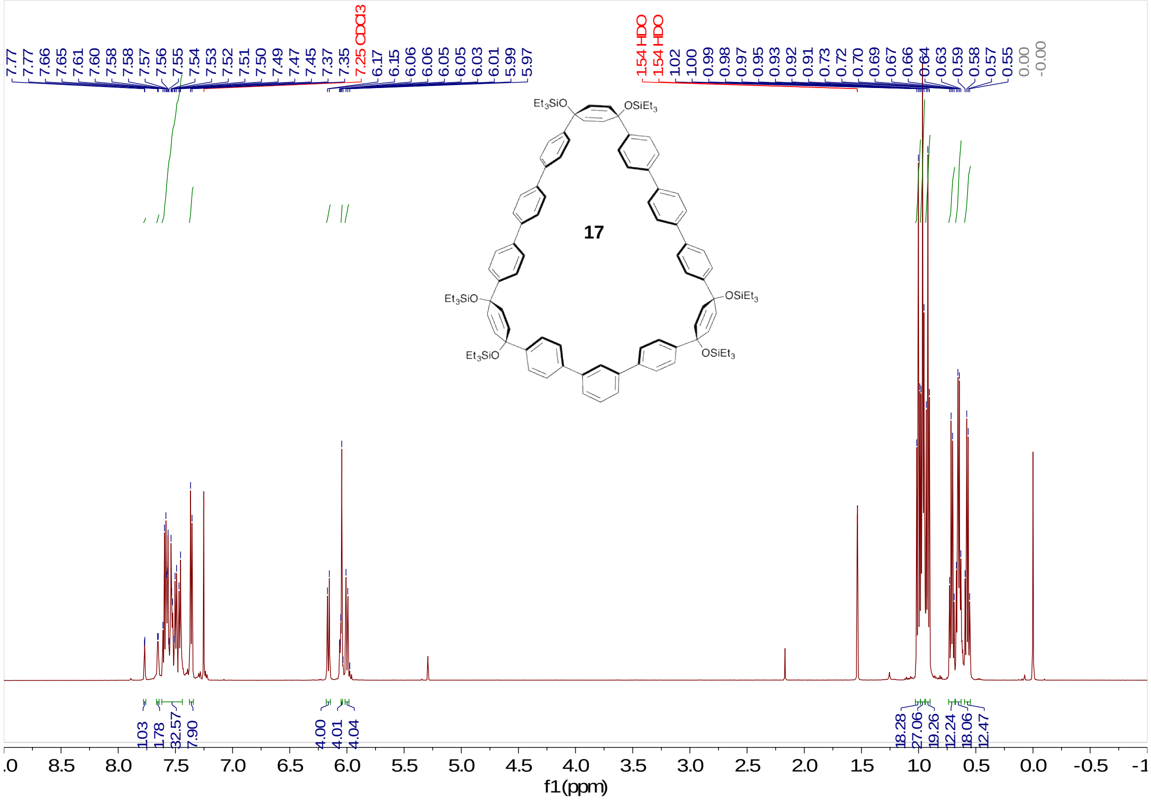
144.97
144.68
139.72
139.61
139.57
139.48
133.02
131.82
131.58
131.21
128.76
128.28
127.41
127.38
126.78
126.76
126.43
126.32
77.26 CDCl3
77.05 CDCl3
76.84 CDCl3
71.44
71.32
71.19
18.66
11.28
7.14
7.11
7.09
6.53
6.51
6.47
6.34
Et3SiO
OSiEt3
12
Cl
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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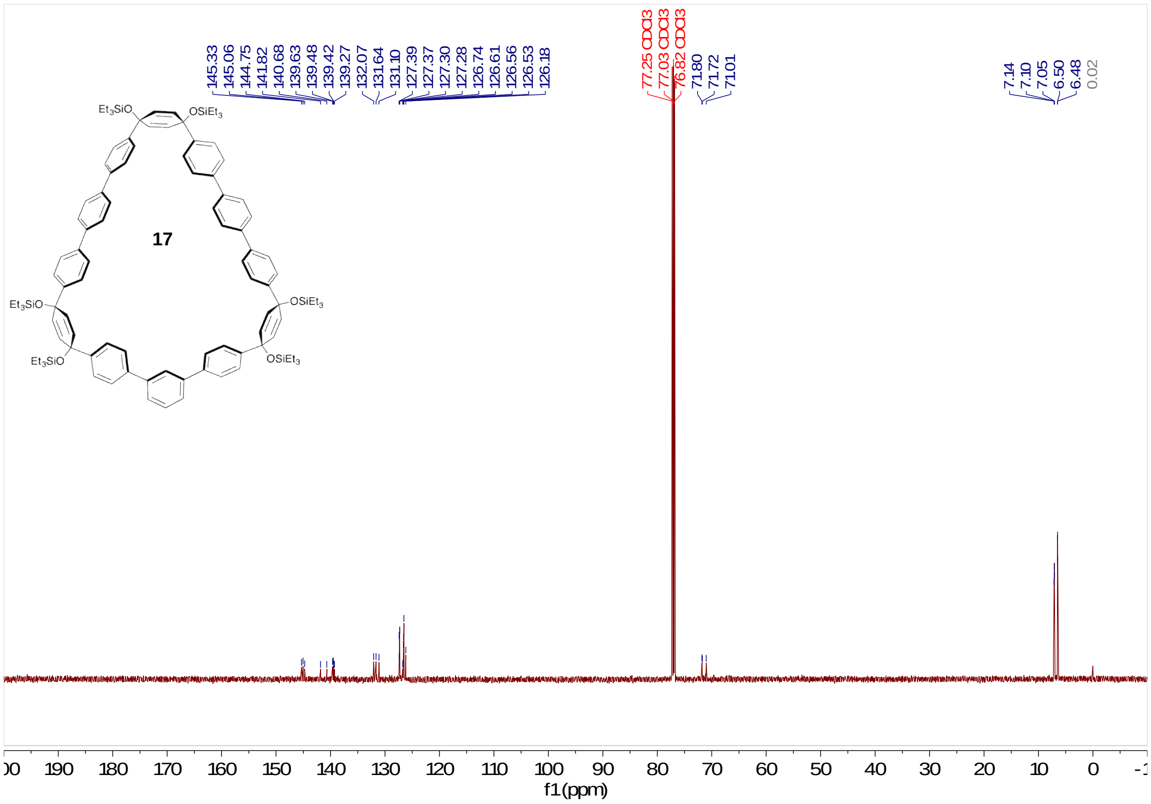
7.77
7.66
7.65
7.61
7.60
7.58
7.58
7.57
7.56
7.55
7.54
7.53
7.52
7.51
7.50
7.49
7.47
7.45
7.37
7.35
7.25 CDCl3
6.17
6.15
6.06
6.06
6.05
6.05
6.03
6.01
5.99
5.97
1.54 HDO
1.54 HDO
1.02
1.00
0.99
0.98
0.97
0.95
0.93
0.92
0.91
0.73
0.72
0.70
0.69
0.67
0.66
0.64
0.63
0.59
0.58
0.57
0.55
0.00
-0.00
Et3SiO
OSiEt3
17
Et3SiO
OSiEt3
Et3SiO
OSiEt3
1.03
1.78
32.57
7.90
4.00
4.01
4.04
18.28
27.06
19.26
12.24
18.06
12.47
.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
-0.5
-1
f1(ppm)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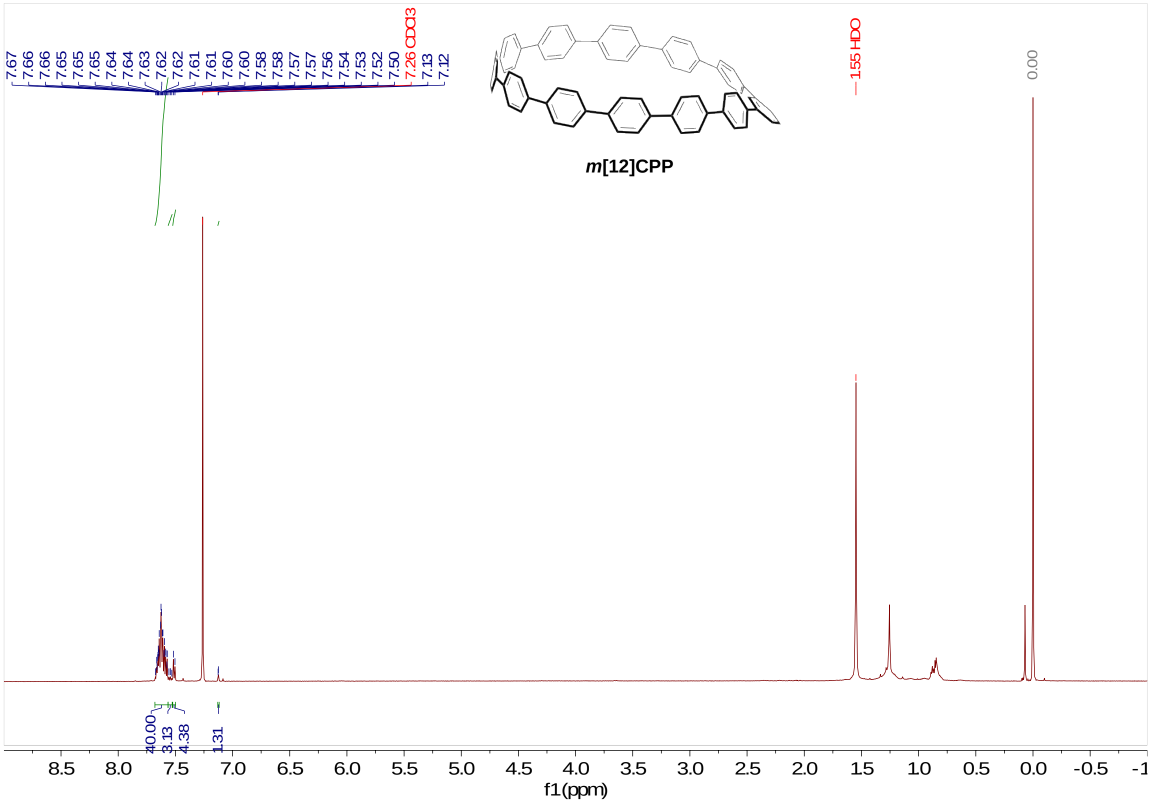
145.06
144.75
141.82
140.68
139.63
139.48
139.42
139.27
132.07
131.64
131.10
127.39
127.37
127.30
127.28
126.74
126.61
126.56
126.53
126.18
77.25 CDCl3
77.03 CDCl3
76.82 CDCl3
71.80
71.72
71.01
7.14
7.10
7.05
6.50
6.48
0.02
Et3SiO
OSiEt3
17
Et3SiO
OSiEt3
Et3SiO
OSiEt3
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1(ppm)



7.67
7.66
7.66
7.65
7.65
7.65
7.64
7.64
7.63
7.62
7.62
7.62
7.61
7.61
7.60
7.60
7.58
7.58
7.57
7.57
7.56
7.54
7.53
7.52
7.50
7.26 CDCl3
7.13
7.12
1.55 HDO
0.00
m[12]CPP
40.00
3.13
4.38
1.31
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
-0.5
-1
f1 (ppm)

8. X-ray Crystallography. Diffraction intensities were collected at 173 K on a Bruker Apex2 Duo CCD diffractometer with a micro-focus Incoatec *IμS* Cu source, CuKα radiation, λ= 1.54178 Å. Absorption correction was applied by SADABS.[8] Space group was determined based on systematic absences. Structure was solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms were found on the residual density map and refined with isotropic thermal parameters. The Flack parameter is 0.016(7). All calculations were performed by the Bruker SHELXL-2014/7 package.[9]

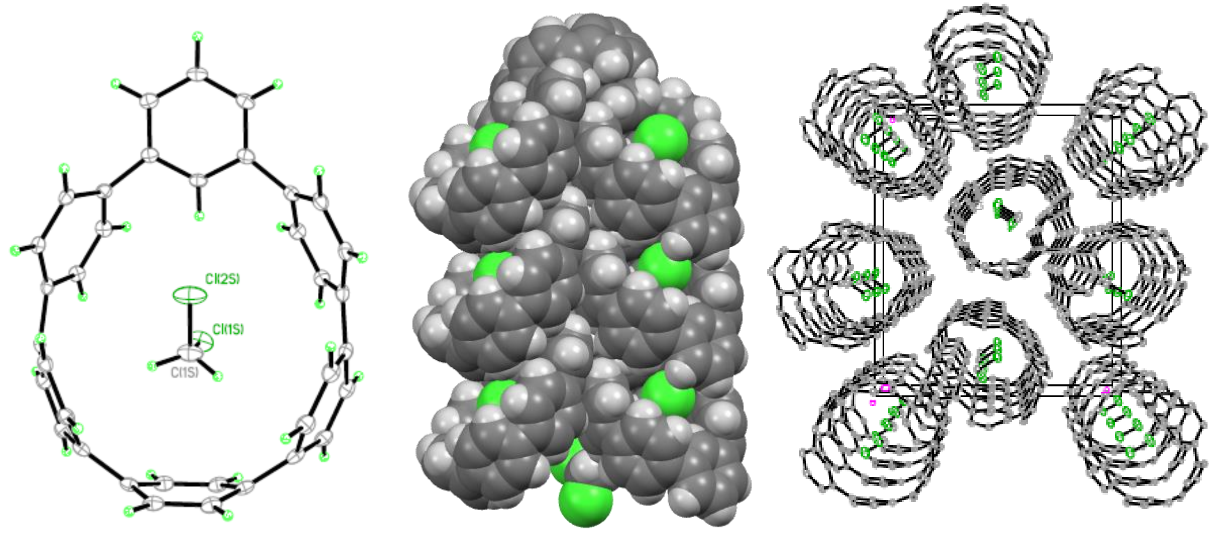


Figure S20. ORTEP representation (thermal ellipsoids shown at 30% probability), space-filling model showing herringbone packing, and ORTEP representation showing columnar packing for ***m*[6]CPP**. One chlorine atom from a dichloromethane solvent molecule is located in the center of each hoop.

Crystallographic Data for ***m*[6]CPP**:

Empirical formula	C37 H26 Cl2
Formula weight	541.48
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic

Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.2031(2) Å	a= 90°.
	b = 16.7290(4) Å	b= 90°.
	c = 19.7339(5) Å	g = 90°.
Volume	2708.08(12) $Å^3$	
Z	4	
Density (calculated)	1.328 Mg/m^3	
Absorption coefficient	2.337 mm^{-1}	
F(000)	1128	
Crystal size	0.130 x 0.100 x 0.070 mm^3	
Theta range for data collection	3.463 to 66.635°.	
Index ranges	-9<=h<=9, -16<=k<=19, -23<=l<=23	
Reflections collected	22179	
Independent reflections	4784 [R(int) = 0.0554]	
Completeness to theta = 66.635°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6795	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4784 / 0 / 456	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0318, wR2 = 0.0792	
R indices (all data)	R1 = 0.0342, wR2 = 0.0808	
Absolute structure parameter	0.016(7)	
Largest diff. peak and hole	0.292 and -0.362 $e.Å^{-3}$	

9. Input files for calculations

Input file for *m*[5]CPP UV-vis calculation

```
#n B3LYP/6-31G(d,p) SP TD=nstate=12

 5mcppUV

0 1
C     -3.23436    -1.21721     0.11310
C     -2.28233    -2.37789     0.12588
C     -1.64276    -2.77633     1.31149
C     -0.33440    -3.25386     1.29447
C      0.40747    -3.29639     0.09432
C      1.86116    -2.94656     0.07848
C      2.43356    -2.35931     1.22516
C      3.31701    -1.29252     1.11743
C      3.66960    -0.76807    -0.14289
C      3.44286    -1.63332    -1.23686
C      2.55341    -2.69809    -1.12802
C     -0.34381    -3.19415    -1.09454
C     -1.66328    -2.74544    -1.07963
C     -4.53462    -1.15275    -0.40151
C     -5.14971     0.09485    -0.56946
C     -4.47716     1.29025    -0.29174
C     -3.17417     1.25041     0.22433
C     -2.18833     2.36994     0.34070
C     -1.75515     3.06102    -0.80484
C     -0.44292     3.52652    -0.90380
C      0.48677     3.29273     0.13036
C      1.91116     2.93514    -0.13882
C      2.20403     2.33233    -1.37789
C      3.06772     1.24645    -1.45593
C      3.66939     0.71634    -0.29662
```

```
C       3.70028      1.58414      0.81902
C       2.83415      2.67113      0.89754
C      -0.05152      2.89917      1.37278
C      -1.36106      2.44356      1.47408
C      -2.60703     -0.01172      0.45929
H      -2.12330     -2.58840      2.26780
H       0.15260     -3.44235      2.24574
H       2.03810     -2.58140      2.21004
H       3.54561     -0.73542      2.01979
H       3.82733     -1.38255     -2.22135
H       2.28568     -3.23440     -2.03339
H       0.14864     -3.28065     -2.05721
H      -2.14763     -2.50753     -2.02274
H      -5.05785     -2.05976     -0.69036
H      -6.16306      0.13647     -0.95925
H      -4.96002      2.24296     -0.49045
H      -2.39204      3.09192     -1.68495
H      -0.10636      3.92893     -1.85506
H       1.59025      2.55161     -2.24511
H       3.07850      0.67887     -2.38010
H       4.27988      1.32107      1.69940
H       2.77216      3.21813      1.83431
H       0.60578      2.76339      2.22510
H      -1.69193      1.99221      2.40525
H      -1.57819     -0.05529      0.79734
```

Input file for *m*[6]CPP UV-vis calculation

```
#n B3LYP/6-31G(d,p) SP TD=nstate=12

 6mcppUV

0 1
C       4.03404      1.23403      0.13588
C       3.12656      2.41283      0.25771
```

C	2.32399	2.55461	1.40187
C	1.11465	3.23729	1.34844
C	0.65207	3.80607	0.14600
C	-0.82119	3.89931	-0.05296
C	-1.73059	4.01739	1.01832
C	-2.98554	3.41661	0.96302
C	-3.38010	2.66478	-0.16365
C	-4.19117	1.42005	-0.05453
C	-4.11009	0.69484	1.14940
C	-4.11011	-0.69473	1.14942
C	-4.19121	-1.41997	-0.05450
C	-4.62930	-0.69603	-1.18392
C	-4.62928	0.69611	-1.18394
C	-2.60394	2.83624	-1.32579
C	-1.35266	3.43914	-1.27151
C	1.57422	3.87821	-0.91575
C	2.78662	3.18907	-0.86328
C	5.32935	1.22061	-0.40022
C	5.96872	-0.00006	-0.64109
C	5.32931	-1.22072	-0.40025
C	4.03400	-1.23412	0.13586
C	3.12649	-2.41289	0.25768
C	2.78652	-3.18911	-0.86332
C	1.57411	-3.87822	-0.91578
C	0.65198	-3.80608	0.14599
C	-0.82129	-3.89930	-0.05294
C	-1.35277	-3.43915	-1.27150
C	-2.60404	-2.83623	-1.32576
C	-3.38017	-2.66472	-0.16361
C	-2.98560	-3.41653	0.96307
C	-1.73066	-4.01733	1.01836
C	1.11458	-3.23733	1.34842
C	2.32394	-2.55466	1.40184
C	3.43169	-0.00003	0.42280

H	2.59197	2.01991	2.30865
H	0.45429	3.19176	2.20830
H	-1.41336	4.48295	1.94737
H	-3.61002	3.42897	1.85199
H	-3.83279	1.20352	2.06666
H	-3.83282	-1.20341	2.06668
H	-4.84440	-1.21770	-2.11239
H	-4.84436	1.21777	-2.11241
H	-2.88213	2.32055	-2.23879
H	-0.71290	3.37037	-2.14528
H	1.29560	4.37777	-1.83931
H	3.41063	3.14682	-1.75194
H	5.83315	2.15368	-0.63645
H	6.97730	-0.00007	-1.04506
H	5.83308	-2.15381	-0.63649
H	3.41052	-3.14685	-1.75199
H	1.29546	-4.37776	-1.83934
H	-0.71303	-3.37041	-2.14528
H	-2.88224	-2.32055	-2.23877
H	-3.61007	-3.42886	1.85206
H	-1.41343	-4.48287	1.94741
H	0.45423	-3.19179	2.20829
H	2.59193	-2.01999	2.30863
H	2.40466	-0.00002	0.76885

Input file for *m*[7]CPP UV-vis calculation

#n B3LYP/6-31G(d,p) SP TD=nstate=12

7mcppUV

0 1

C	-4.95556	-1.16924	-0.02976
C	-4.10857	-2.40190	0.04387

C	-3.64985	-2.90924	1.26876
C	-2.52642	-3.73091	1.32984
C	-1.78548	-4.04067	0.17293
C	-0.34546	-4.41538	0.23758
C	0.41247	-4.02798	1.35731
C	1.78886	-3.86127	1.27711
C	2.47987	-4.06426	0.06874
C	3.72446	-3.28044	-0.15062
C	4.57329	-2.88963	0.90435
C	5.27060	-1.68601	0.85365
C	5.14084	-0.81950	-0.25109
C	4.54094	-1.36022	-1.40362
C	3.84891	-2.56491	-1.35503
C	1.76028	-4.68389	-0.97097
C	0.38092	-4.85961	-0.88555
C	-2.35889	-3.67983	-1.06050
C	-3.50085	-2.88500	-1.12426
C	-6.25965	-1.08929	-0.53258
C	-6.86101	0.16186	-0.70737
C	-6.16936	1.34318	-0.42832
C	-4.86152	1.28792	0.07554
C	-3.95053	2.45444	0.24612
C	-3.69639	3.34258	-0.81240
C	-2.55029	4.13776	-0.82202
C	-1.61565	4.07587	0.22715
C	-0.18626	4.45349	0.06448
C	0.44667	4.16449	-1.15696
C	1.81849	3.94903	-1.22172
C	2.62355	4.01628	-0.06955
C	3.85110	3.17699	-0.01850
C	4.54154	2.76365	-1.17618
C	5.19015	1.53246	-1.22404
C	5.17613	0.66207	-0.11519
C	4.75396	1.21584	1.10772

C	4.10585	2.44392	1.15487
C	2.02570	4.55996	1.08519
C	0.65036	4.76659	1.15290
C	-1.97770	3.33280	1.36609
C	-3.11718	2.53711	1.37341
C	-4.29447	0.02321	0.29409
H	-4.13362	-2.59775	2.19035
H	-2.17550	-4.06130	2.30259
H	-0.08780	-3.69985	2.26173
H	2.30358	-3.40631	2.11700
H	4.60383	-3.47762	1.81752
H	5.82877	-1.36574	1.72897
H	4.44696	-0.75031	-2.29605
H	3.24540	-2.84856	-2.21138
H	2.26832	-4.95163	-1.89338
H	-0.14519	-5.27118	-1.74185
H	-1.83699	-3.90675	-1.98426
H	-3.84898	-2.53066	-2.09039
H	-6.79755	-1.99471	-0.79832
H	-7.87723	0.21629	-1.08770
H	-6.64321	2.30490	-0.60408
H	-4.34252	3.33015	-1.68591
H	-2.33809	4.74769	-1.69572
H	-0.15581	3.94098	-2.03170
H	2.23464	3.55887	-2.14461
H	4.48035	3.35861	-2.08310
H	5.61404	1.19985	-2.16748
H	4.75769	0.60393	2.00363
H	3.63376	2.73826	2.08631
H	2.62589	4.73267	1.97400
H	0.21139	5.09354	2.09150
H	-1.29280	3.27712	2.20629
H	-3.31688	1.90017	2.23026
H	-3.26547	-0.03456	0.63285

Input file for *m*[8]CPP UV-vis calculation

```
#n B3LYP/6-31G(d,p) SP TD=nstate=12

 8mcppUV

0 1
C        -5.70344         1.23062         0.01847
C        -4.86113         2.44822         0.17327
C        -4.67208         3.34964        -0.88726
C        -3.61056         4.25407        -0.87933
C        -2.69921         4.29489         0.19057
C        -1.33991         4.88444         0.07343
C        -0.63244         4.72578        -1.13052
C         0.75480         4.81117        -1.16621
C         1.50140         5.06378        -0.00112
C         2.91630         4.61165         0.05340
C         3.72850         4.50392        -1.09245
C         4.78574         3.59930        -1.14274
C         5.07843         2.76185        -0.04865
C         5.70516         1.42234        -0.20097
C         5.44420         0.69498        -1.37622
C         5.44424        -0.69483        -1.37621
C         5.70522        -1.42216        -0.20094
C         6.22464        -0.69589         0.88886
C         6.22461         0.69612         0.88884
C         4.42479         3.05356         1.16223
C         3.36911         3.95560         1.21177
C         0.77794         5.43463         1.14879
C        -0.61049         5.34120         1.18691
C        -2.99437         3.50831         1.31877
C        -4.04905         2.60335         1.30841
C        -7.00420         1.21688        -0.50596
```

C	-7.64640	-0.00013	-0.74782
C	-7.00414	-1.21712	-0.50597
C	-5.70339	-1.23081	0.01845
C	-4.86102	-2.44837	0.17324
C	-4.04895	-2.60349	1.30838
C	-2.99423	-3.50841	1.31874
C	-2.69903	-4.29496	0.19053
C	-1.33971	-4.88447	0.07341
C	-0.61030	-5.34122	1.18689
C	0.77814	-5.43461	1.14879
C	1.50160	-5.06373	-0.00110
C	2.91650	-4.61157	0.05344
C	3.36927	-3.95549	1.21181
C	4.42492	-3.05342	1.16227
C	5.07857	-2.76169	-0.04861
C	4.78592	-3.59917	-1.14268
C	3.72871	-4.50383	-1.09240
C	0.75502	-4.81113	-1.16620
C	-0.63223	-4.72577	-1.13054
C	-3.61038	-4.25416	-0.87937
C	-4.67193	-3.34978	-0.88730
C	-5.08907	-0.00008	0.29198
H	-5.30261	3.27562	-1.76897
H	-3.44763	4.88671	-1.74731
H	-1.15794	4.38816	-2.01840
H	1.26796	4.53190	-2.08073
H	3.47947	5.07204	-1.98427
H	5.33351	3.48139	-2.07350
H	5.06855	1.21108	-2.25380
H	5.06861	-1.21097	-2.25378
H	6.54339	-1.22196	1.78436
H	6.54333	1.22221	1.78434
H	4.63028	2.45018	2.04036
H	2.79115	4.02405	2.12756

H	1.31052	5.72777	2.04899
H	-1.13036	5.56215	2.11495
H	-2.32263	3.52538	2.17123
H	-4.20221	1.95257	2.16435
H	-7.51156	2.15245	-0.72365
H	-8.65897	-0.00015	-1.14146
H	-7.51147	-2.15271	-0.72367
H	-4.20213	-1.95272	2.16434
H	-2.32250	-3.52546	2.17121
H	-1.13017	-5.56219	2.11492
H	1.31071	-5.72775	2.04899
H	2.79130	-4.02395	2.12759
H	4.63038	-2.45002	2.04039
H	5.33369	-3.48125	-2.07345
H	3.47971	-5.07196	-1.98422
H	1.26818	-4.53183	-2.08071
H	-1.15773	-4.38815	-2.01842
H	-3.44741	-4.88678	-1.74736
H	-5.30246	-3.27576	-1.76901
H	-4.05942	-0.00006	0.63262

Input file for *m*[10]CPP UV-vis calculation

#n B3LYP/6-31G(d,p) SP TD=nstate=12

10mcppUV

0 1

C	7.37665	-1.22928	-0.08666
C	6.56829	-2.46559	0.08454
C	6.46826	-3.42421	-0.93708
C	5.49922	-4.42494	-0.89049
C	4.59658	-4.51236	0.18314
C	3.36210	-5.33568	0.12899
C	2.77793	-5.89438	1.27972

C	1.46482	-6.35522	1.26954
C	0.67042	-6.26876	0.11128
C	-0.81098	-6.36078	0.15425
C	-1.58610	-6.67086	-0.97889
C	-2.94286	-6.36343	-1.03122
C	-3.58880	-5.73457	0.04900
C	-4.86128	-4.98385	-0.09932
C	-5.09519	-4.26984	-1.28724
C	-5.99321	-3.20949	-1.32450
C	-6.70178	-2.81349	-0.17636
C	-7.21999	-1.42371	-0.09786
C	-7.62745	-0.69602	-1.23197
C	-7.62743	0.69608	-1.23201
C	-7.21996	1.42382	-0.09794
C	-7.02048	0.69482	1.08768
C	-7.02049	-0.69465	1.08771
C	-6.61766	-3.65664	0.94778
C	-5.71592	-4.71617	0.98638
C	-2.85257	-5.59024	1.23793
C	-1.49747	-5.89393	1.28859
C	1.30537	-5.84789	-1.07046
C	2.62026	-5.39546	-1.06266
C	4.78269	-3.62825	1.26034
C	5.74418	-2.62576	1.21025
C	8.68211	-1.21515	-0.60048
C	9.32648	-0.00006	-0.84078
C	8.68214	1.21503	-0.60042
C	7.37668	1.22918	-0.08661
C	6.56835	2.46549	0.08463
C	5.74423	2.62565	1.21032
C	4.78275	3.62815	1.26043
C	4.59667	4.51230	0.18326
C	3.36220	5.33563	0.12911
C	2.77801	5.89432	1.27983

C	1.46490	6.35518	1.26962
C	0.67054	6.26875	0.11134
C	-0.81087	6.36078	0.15426
C	-1.49740	5.89395	1.28857
C	-2.85251	5.59029	1.23785
C	-3.58869	5.73462	0.04889
C	-4.86118	4.98392	-0.09946
C	-5.71587	4.71630	0.98620
C	-6.61763	3.65678	0.94761
C	-6.70173	2.81360	-0.17650
C	-5.99310	3.20953	-1.32462
C	-5.09505	4.26986	-1.28737
C	-2.94269	6.36346	-1.03131
C	-1.58594	6.67088	-0.97891
C	1.30551	5.84789	-1.07040
C	2.62039	5.39544	-1.06257
C	5.49933	4.42490	-0.89036
C	6.46835	3.42415	-0.93697
C	6.75558	-0.00005	0.17772
H	7.10450	-3.33748	-1.81333
H	5.41195	-5.11930	-1.72133
H	3.34673	-5.93163	2.20446
H	1.03540	-6.74587	2.18750
H	-1.11047	-7.11016	-1.85102
H	-3.49618	-6.56474	-1.94416
H	-4.46553	-4.45125	-2.15256
H	-6.03503	-2.59417	-2.21746
H	-7.88012	-1.22355	-2.14737
H	-7.88009	1.22357	-2.14743
H	-6.71636	1.21448	1.99057
H	-6.71637	-1.21426	1.99063
H	-7.21535	-3.43958	1.82852
H	-5.62851	-5.30373	1.89590
H	-3.31287	-5.11029	2.09565

```
H      -0.94094      -5.64296       2.18577
H       0.72885      -5.76231      -1.98602
H       3.03726      -4.97367      -1.97202
H       4.10732      -3.67332       2.10912
H       5.82665      -1.92287       2.03402
H       9.19262      -2.15166      -0.80599
H      10.34246      -0.00007      -1.22541
H       9.19267       2.15153      -0.80591
H       5.82667       1.92272       2.03407
H       4.10737       3.67320       2.10920
H       3.34679       5.93155       2.20458
H       1.03547       6.74583       2.18758
H      -0.94092       5.64297       2.18577
H      -3.31286       5.11036       2.09556
H      -5.62848       5.30389       1.89571
H      -7.21535       3.43976       1.82834
H      -6.03488       2.59417      -2.21755
H      -4.46534       4.45121      -2.15266
H      -3.49597       6.56477      -1.94427
H      -1.11026       7.11016      -1.85103
H       0.72901       5.76235      -1.98597
H       3.03742       4.97368      -1.97192
H       5.41208       5.11928      -1.72118
H       7.10459       3.33743      -1.81322
H       5.72377      -0.00004       0.51272
```

Input file for *m*[12]CPP UV-vis calculation

```
#n B3LYP/6-31G(d,p) SP TD=nstate=12

 12mcppUV

0 1
C      -9.04086      -1.22858      -0.18732
```

C	-8.25351	-2.47598	-0.00601
C	-8.21271	-3.46784	-0.99959
C	-7.30497	-4.52222	-0.92575
C	-6.40676	-4.63317	0.14903
C	-5.26755	-5.58441	0.14050
C	-4.53509	-5.79160	-1.04026
C	-3.31086	-6.45113	-1.02189
C	-2.76323	-6.94264	0.17590
C	-1.34051	-7.36233	0.22451
C	-0.55578	-7.04127	1.34557
C	0.82961	-7.14541	1.31126
C	1.50090	-7.57108	0.15208
C	2.96020	-7.33146	0.02966
C	3.47720	-6.80448	-1.16601
C	4.74265	-6.23045	-1.21216
C	5.55375	-6.15906	-0.06609
C	6.69017	-5.20465	-0.03421
C	6.90657	-4.43329	1.12078
C	7.68006	-3.27959	1.08304
C	8.27469	-2.83878	-0.11198
C	8.70815	-1.42339	-0.22107
C	9.20000	-0.69577	0.87821
C	9.19998	0.69588	0.87827
C	8.70811	1.42358	-0.22095
C	8.38607	0.69515	-1.37924
C	8.38607	-0.69488	-1.37929
C	8.19521	-3.69848	-1.22275
C	7.42159	-4.85514	-1.18434
C	5.09902	-6.82884	1.08470
C	3.83061	-7.39909	1.13250
C	0.71061	-8.01374	-0.92349
C	-0.67733	-7.91433	-0.88667
C	-3.55474	-6.84138	1.33432
C	-4.77532	-6.17344	1.31818

C	-6.51814	-3.69424	1.18902
C	-7.41862	-2.63810	1.11147
C	-10.35050	-1.21407	-0.69126
C	-10.99664	-0.00016	-0.92922
C	-10.35052	1.21378	-0.69135
C	-9.04088	1.22835	-0.18740
C	-8.25357	2.47578	-0.00617
C	-8.21279	3.46758	-0.99981
C	-7.30508	4.52199	-0.92602
C	-6.40690	4.63305	0.14877
C	-5.26773	5.58435	0.14023
C	-4.53522	5.79150	-1.04051
C	-3.31100	6.45106	-1.02210
C	-2.76345	6.94263	0.17569
C	-1.34073	7.36232	0.22438
C	-0.67748	7.91433	-0.88675
C	0.71047	8.01376	-0.92347
C	1.50068	7.57110	0.15215
C	2.96000	7.33151	0.02982
C	3.47709	6.80458	-1.16584
C	4.74255	6.23058	-1.21194
C	5.55358	6.15916	-0.06582
C	6.69003	5.20478	-0.03393
C	7.42152	4.85537	-1.18404
C	8.19518	3.69873	-1.22248
C	8.27461	2.83896	-0.11177
C	7.67990	3.27967	1.08325
C	6.90638	4.43335	1.12103
C	5.09875	6.82887	1.08498
C	3.83033	7.39909	1.13272
C	0.82932	7.14542	1.31127
C	-0.55607	7.04127	1.34549
C	-3.55500	6.84138	1.33409
C	-4.77556	6.17343	1.31791

C	-6.51829	3.69420	1.18883
C	-7.41872	2.63802	1.11133
C	-8.41510	-0.00010	0.06954
H	-8.85411	-3.37530	-1.87134
H	-7.26995	-5.25211	-1.72946
H	-4.88032	-5.34394	-1.96723
H	-2.72692	-6.49818	-1.93563
H	-1.02598	-6.60382	2.22044
H	1.40507	-6.78697	2.15902
H	2.83634	-6.73453	-2.03945
H	5.05486	-5.72476	-2.12038
H	6.36245	-4.66745	2.03013
H	7.71736	-2.64595	1.96341
H	9.53600	-1.22515	1.76522
H	9.53597	1.22520	1.76532
H	8.00573	1.21841	-2.25089
H	8.00575	-1.21809	-2.25098
H	8.70455	-3.43264	-2.14466
H	7.34437	-5.46961	-2.07671
H	5.72812	-6.86359	1.96941
H	3.49333	-7.86674	2.05306
H	1.19071	-8.41035	-1.81356
H	-1.25343	-8.24094	-1.74747
H	-3.19774	-7.26748	2.26723
H	-5.34647	-6.08690	2.23807
H	-5.83999	-3.75366	2.03478
H	-7.45329	-1.90543	1.91233
H	-10.86383	-2.15097	-0.88729
H	-12.01569	-0.00018	-1.30558
H	-10.86387	2.15065	-0.88744
H	-8.85416	3.37496	-1.87157
H	-7.27008	5.25184	-1.72978
H	-4.88039	5.34379	-1.96747
H	-2.72702	6.49808	-1.93582

H	-1.25352	8.24094	-1.74759
H	1.19063	8.41038	-1.81351
H	2.83628	6.73468	-2.03932
H	5.05483	5.72495	-2.12017
H	7.34435	5.46990	-2.07636
H	8.70458	3.43298	-2.14438
H	7.71714	2.64596	1.96357
H	6.36219	4.66743	2.03036
H	5.72780	6.86359	1.96973
H	3.49299	7.86670	2.05328
H	1.40473	6.78698	2.15907
H	-1.02632	6.60382	2.22033
H	-3.19804	7.26751	2.26701
H	-5.34676	6.08689	2.23778
H	-5.84017	3.75371	2.03462
H	-7.45340	1.90542	1.91225
H	-7.38122	-0.00008	0.39867

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