Supporting Information

Modular Synthesis, Racemization Pathway, and Photophysical Properties of Asymmetrically Substituted Cycloparaphenylenes†

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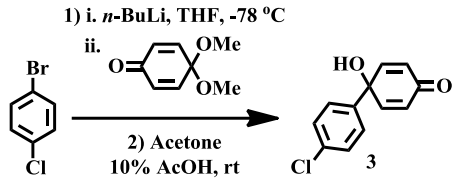
General Information

All glassware was oven-dried. Moisture and/or air sensitive reactions were carried out using standard Schlenk technique under nitrogen. Work-up and purification procedures were implemented with reagent-grade solvents under air. High resolution mass spectrometry (HR-MS) analysis were performed on an ESI-Orbitrap MS or MALDI-TOF MS. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker BioSpin (^{1}H 400 MHz, ^{13}C 100 MHz) NMR spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to residual peak of $CHCl_3$ (δ 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Coupling constants (*J*) are given in Hz. The apparent resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). ^{1}H NMR data are reported in the following form: chemical shift, multiplicity, coupling constant, and integration. Absorbance and fluorescence spectra were recorded on a UV1800 spectrophotometer and an F-4700 spectrophotometer, respectively. Cell viability was measured on a Multifunctional Enzyme Marker (SynergyHTX). Cell imaging experiments were performed on a confocal microscope (Zeiss Laser Scanning Confocal Microscope, LSM 880) with ZEN black software.

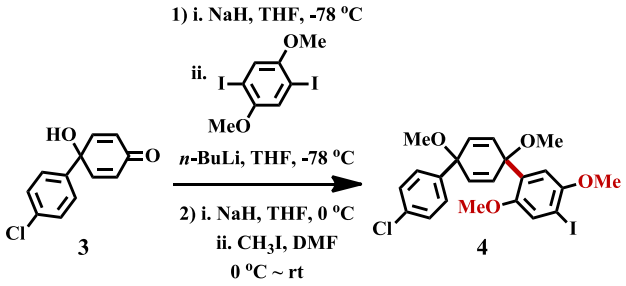
Materials

All solvents used for reactions were dried by distillation under nitrogen (tetrahydrofuran and 1,4-dioxane were distilled after reflux with sodium under nitrogen). Compound 4,4-dimethoxycyclohexa-2,5-dienone,[1] **8**,[2] **9**[3] was prepared according to previously reported procedures. Other reagents were obtained from commercial suppliers (Innochem or Energy Chemical) unless otherwise noted. Flash chromatography was performed on silica gel (300～400 mesh). Preparative thin-layer chromatography (PTLC) were performed on silica gel (GF 254) precoated plates. HepG2 cells were purchase from Beyotime Biotechnology.

Synthetic Details



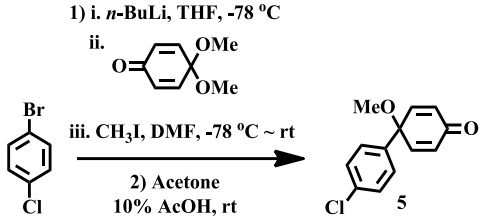
Synthesis of compound 3. To a solution of 1-bromo-4-chlorobenzene (15.45 g, 80.70 mmol, 1.3 equiv.) in anhydrous THF (200 mL) was slowly added *n*-butyllithium (27.3 mL, 2.5 M in hexane, 68.25 mmol, 1.1 equiv.) through a syringe (dropwise over 40 min) at -78 ℃. After stirring for 0.5 h at the same temperature, 4,4-dimethoxycyclohexa-2,5-dienone (9.58 g, 62.14 mmol, 1.0 equiv.) was added. The reaction mixture was allowed to stir for another 1 h at -78 ℃ before quenched by water. After extraction with CH_2Cl_2 (3 × 100 mL), the organic phase combined was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a brown oil, which was re-dissolved in acetone (23 mL). Precipitation began to appear while 10% acetic acid (88 mL) was added. The reaction mixture was allowed to stir for 16 h at room temperature before it was filtered off. The solid residue was washed thoroughly with CH_2Cl_2 to afford pure compound **3** as a white solid (10.97 g, 80% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.35 (dt, *J* = 8.8, 2.0 Hz, 2H), 6.86 (dt, *J* = 10.4, 2.0 Hz, 2H), 6.25 (dt, *J* = 10.4, 2.0 Hz, 2H), 2.50(s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 185.51, 150.38, 137.18, 134.43, 129.11, 127.12, 126.83, 70.67. Melting point: 177-178 ℃. HR-MS (ESI-Orbitrap MS) *m/z* calcd for $C_{12}H_{10}ClO_2$ $[M+H]^+$: 221.0369, found: 221.0371.



Synthesis of compound 4. A solution of compound **3** (2.24 g, 10.15 mmol, 1.0 equiv.) in anhydrous THF (30 mL) was slowly added to a slurry of sodium hydride (609 mg, 60% in mineral oil, 15.23 mmol, 1.5 equiv.) in THF (7.5 mL) at -78 ℃ through a syringe to generate deprotonated **3**. In a separate flask, *n*-butyllithium (7.7 mL, 1.6 M in hexane, 12.32 mmol, 1.2 equiv.) was added dropwise to a solution of 1,4-diiodo-2,5-

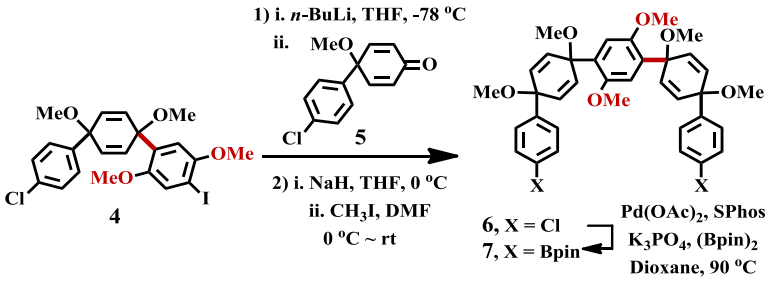
dimethoxybenzene (5.10 g, 13.08 mmol, 1.3 equiv.) in THF (65 mL) at -78 ℃, and the solution stirred for 1 h at this temperature. Then, it was transferred to the above slurry containing the deprotonated **3** through a steel needle under nitrogen. The reaction was allowed to proceed for another 2 h at -78 ℃ before quenched by water. After extraction with CH_2Cl_2 (3 × 30 mL), the combined organic phase was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography with petroleum ether/ethyl acetate (*v/v*, 2:1) as the eluent to give the diol (1.77 g), which could be used for the subsequent reaction although it contained a small amount of uncharacterized side products.

The obtained diol product (1.77 g, 3.55 mmol) was dissolved in anhydrous THF (30mL) and transferred to a suspension of sodium hydride (570 mg, 60% in mineral oil, 14.25 mmol, 4.0 equiv.) in THF (10 mL) at 0 ℃. After stirring for 1 h at this temperature, CH_3I (1.15 mL, 18.47 mmol, 5.2 equiv.) in DMF (4 mL) was added, and the reaction was allowed to warm to room temperature to proceed for an additional 24 h. The excess amount of sodium hydride was quenched by water carefully. After extraction with CH_2Cl_2 (3 × 30 mL), the combined organic phase was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The solid residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (*v/v*, 10:1) as the eluent to give compound **4** as a white solid (1.45 g, 28% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.28 (m, 3H), 7.22 (dt, *J* = 8.8, 2.4 Hz, 2H), 6.89 (s, 1H), 6.33 (dt, *J* = 10.4, 2.0 Hz, 2H), 6.06 (dt, *J* = 10.4, 2.0 Hz, 2H), 3.72 (s, 3H), 3.62 (s, 3H), 3.40 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.66, 152.52, 141.83, 133.21, 131.81, 131.75, 128.25, 127.62, 124.04, 110.96, 85.34, 74.36, 73.91, 57.09, 56.62, 51.99, 51.57. Melting point: 107-108 ℃. HR-MS (MALDI-TOF) *m/z* calcd for $C_{22}H_{22}ClIO_4$ $[M]^+$: 512.0251, found: 511.4963.



Synthesis of compound 5. To a solution of 1-bromo-4-chlorobenzene (6.13 g, 32.02 mmol, 1.3 equiv.) in anhydrous THF (80 mL) was slowly added *n*-butyllithium

(17.1 mL, 1.6 M in hexane, 27.36 mmol, 1.1 equiv.) through a syringe (dropwise over 30 min) at -78 ℃. After stirring for 0.5 h at the same temperature, 4,4-dimethoxycyclohexa-2,5-dienone **10** (3.83 g, 24.84 mmol, 1.0 equiv.) was added. The reaction mixture was allowed to stir for another 1 h at -78 ℃ before CH_3I (3.4 mL, 54.61 mmol, 2.2 equiv.) dissolved in DMF (8 mL) was added. Then, the reaction was warmed to room temperature and stirred for an additional 24 h. It was quenched by water and extracted with CH_2Cl_2 (3 × 80 mL). The combined organic phase was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a brown oil, which was re-dissolved in acetone (9 mL). Precipitation began to appear while 10% acetic acid (35 mL) was added. The reaction mixture was allowed to stir for 16 h at room temperature before it was filtered off. The solid residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (*v/v*, 5:1) as the eluent to afford compound **5** as a white solid (3.50 g, 60% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.33 (dt, *J* = 8.8, 2.0 Hz, 2H), 6.75 (dt, *J* = 10.4, 2.0 Hz, 2H), 6.41 (dt, *J* = 10.4, 2.0 Hz, 2H), 3.42(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 185.37, 150.07, 136.86, 134.29, 130.35, 128.95, 127.20, 52.96. Melting point: 100-101 ℃. HR-MS (ESI-Orbitrap MS) *m/z* calcd for $C_{13}H_{11}ClNaO_2$ $[M+Na]^+$: 257.0345, found: 257.0339.



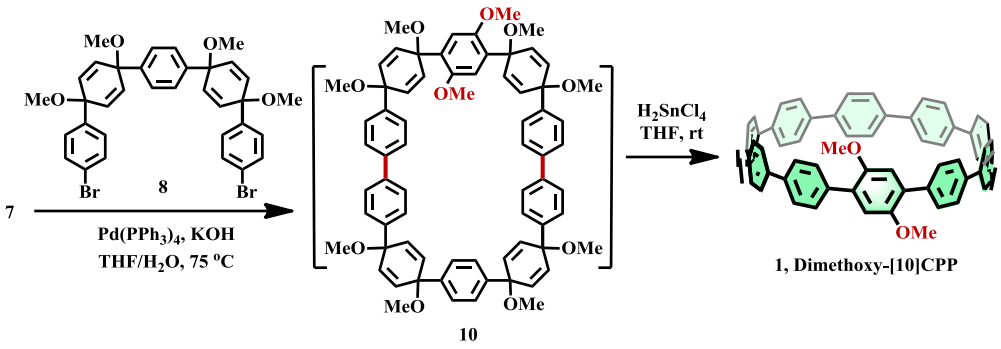
Synthesis of compound 6. To a solution of compound **4** (1.88 g, 3.67 mmol, 1.0 equiv.) in anhydrous THF (110 mL) was slowly added *n*-butyllithium (2.5 mL, 1.6 M in hexane, 4.00 mmol, 1.1 equiv.) through a syringe at -78 ℃. After stirring for 0.5 h at the same temperature, compound **5** (947 mg, 4.04 mmol, 1.1 equiv.) was added portionwise. The reaction mixture was allowed to stir for 3 h at -78 ℃ before quenched by water. After extraction with CH_2Cl_2 (3 × 30 mL), the combined organic phase was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography with petroleum ether/ethyl acetate (*v/v*, 2:1) as the eluent to

give the intermediate (1.75 g), which could be used for the subsequent reaction although it contained a small amount of uncharacterized side products.

The obtained intermediate (1.75 g, 2.82 mmol) was dissolved in anhydrous THF (30 mL) and transferred to a suspension of sodium hydride (225 mg, 60% in mineral oil, 5.63 mmol, 2.0 equiv.) in THF (10 mL) at 0 ℃. After stirring for 1 h at this temperature, CH_3I (0.45 mL, 7.23 mmol, 2.6 equiv.) in DMF (1.7 mL) was added, and the reaction was allowed to warm to room temperature to proceed for an additional 24 h. The excess amount of sodium hydride was quenched by water carefully. After extraction with CH_2Cl_2 (3 × 50 mL), the combined organic phase was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The solid residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (*v/v*, 5:1) as the eluent to give compound **6** as a white solid (1.43 g, 61% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.29 (dt, *J* = 8.8, 2.0 Hz, 4H), 7.20 (dt, *J* = 8.8, 2.0 Hz, 4H), 6.96 (s, 2H), 6.38 (dt, *J* = 10.0, 2.4 Hz, 4H), 6.03 (dt, *J* = 10.0, 2.4 Hz, 4H), 3.55 (s, 6H), 3.40 (s, 6H), 3.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.86, 142.01, 133.09, 132.89, 132.19, 131.04, 128.19, 127.62, 113.49, 74.43, 73.85, 56.60, 51.98, 51.58. Melting point: 227-229 ℃. HR-MS (MALDI-TOF) *m/z* calcd for $C_{36}H_{36}Cl_2O_6$ $[M]^+$: 634.1889, found: 634.1252.

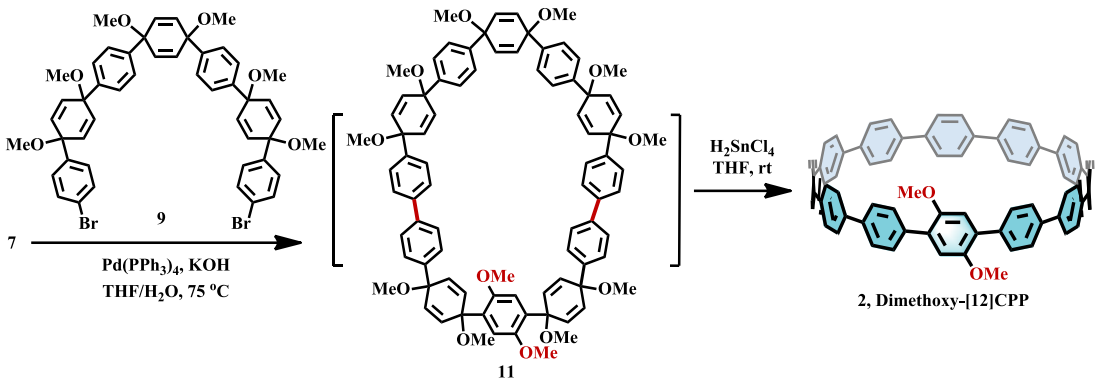
Synthesis of compound 7. To a 100-mL of round bottom flask containing **6** (850 mg, 1.34 mmol, 1.0 equiv.), dried K_3PO_4 (1.80 g, 8.48 mmol, 6.3 equiv.) and bis(pinacolato)diboron (2.04 g, 8.03 mmol, 6.0 equiv.) was added anhydrous 1,4-dioxane (50 mL). The mixture was degassed by argon for 1 h at room temperature before $Pd(OAc)_2$ (58 mg, 0.26 mmol, 0.19 equiv.) and SPhos (210 mg, 0.51 mmol, 0.38 equiv.) was added. The reaction was heated up to 90 ℃ and stirred for 24 h under inert atmosphere. After cooling down, the volatiles was vaporized under reduced pressure and the solid residue was purified by silica gel column chromatography using CH_2Cl_2 as the eluent to give the crude product, which was recrystallized from petroleum ether to obtain pure compound **7** as a white solid (890 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, *J* = 8.4 Hz, 4H), 7.37 (d, *J* = 8.4 Hz, 4H), 6.97 (s, 2H), 6.38 (d, *J* = 10.0 Hz, 4H), 6.06 (d, *J* = 10.0 Hz, 4H), 3.57 (s, 6H), 3.41 (s, 6H), 3.36 (s, 6H), 1.31 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.80, 146.49, 134.69, 132.95, 131.86, 130.88, 125.45, 113.28, 83.73, 74.84, 73.92, 56.56, 51.88, 51.54, 24.85. Melting point: 225-227 ℃. HR-MS (MALDI-TOF) *m/z* calcd for $C_{48}H_{60}B_2O_{10}$ $[M]^+$: 818.4373, found:

818.4317.



Synthesis of dimethoxy [10]CPP (1). A suspension of compound **7** (133 mg, 0.16 mmol, 1.0 equiv.), **8** (106 mg, 0.16 mmol, 1.0 equiv.), and KOH (119 mg, 2.12 mmol, 13.3 equiv.) in THF/H_2O (200 mL/20 mL) was degassed by argon for 1h at room temperature. Then, $Pd(PPh_3)_4$ (27 mg, 0.023 mmol, 0.14 equiv.) was added and the mixture was degassed for another 10 min. The reaction was heated up to 75 ℃ and stirred for 48 h under inert atmosphere. After cooling down to room temperature, water was added and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford crude product **10**, which could be used for the next step without further purification.

Concentrated aqueous HCl (264 μL, 3.17 mmol) was added to a degassed solution of $SnCl_2$ $2H_2O$ (357 mg, 1.58 mmol) in THF (30 mL) at room temperature, and the resulting solution was stirred for 0.5 h under nitrogen atmosphere. The crude product **10** was then added to the solution, and the mixture was stirred at room temperature for 2 h. Aqueous saturated sodium bicarbonate solution was added and the reaction mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The solid residue was purified by silica gel column chromatography using petroleum ether/CH_2Cl_2 (*v/v*, 2:1) as the eluent to obtain dimethoxy [10]CPP (**1)** as a yellow solid (7 mg, 5% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (m, 36H), 6.86 (s, 2H), 3.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.80, 138.57, 138.40, 138.28, 138.21, 138.11, 138.09, 138.02, 137.92, 136.51, 129.47, 129.00, 127.45, 127.42, 127.41, 127.34, 127.31, 127.22, 127.19, 126.63, 115.11, 56.63. Melting point: 167-169 ℃. HR-MS (MALDI-TOF) *m/z* calcd for $C_{62}H_{44}O_2$ $[M]^+$: 820.3341, found: 820.3177.



Synthesis of dimethoxy [12]CPP (2). A suspension of compound **7** (133 mg, 0.16 mmol, 1.0 equiv.), **9** (141 mg, 0.16 mmol, 1.0 equiv.), and KOH (119 mg, 2.12 mmol, 13.3 equiv.) in THF/H_2O (200 mL/20 mL) was degassed by argon for 1h at room temperature. Then, $Pd(PPh_3)_4$ (27 mg, 0.023 mmol, 0.14 equiv.) was added and the mixture was degassed for another 10 min. The reaction was heated up to 75 ℃ and stirred for 48 h under inert atmosphere. After cooling down to room temperature, water was added and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford crude product **11**, which could be used for the next step without further purification.

Concentrated aqueous HCl (330 μL, 3.96 mmol) was added to a degassed solution of $SnCl_2$ $2H_2O$ (446 mg, 1.98 mmol) in THF (30 mL) at room temperature, and the resulting solution was stirred for 0.5 h under nitrogen atmosphere. The crude product **11** was then added to the solution, and the mixture was stirred at room temperature for 2 h. Aqueous saturated sodium bicarbonate solution was added and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The solid residue was purified by silica gel column chromatography using petroleum ether/CH_2Cl_2 (*v/v*, 3:2) as the eluent to obtain dimethoxy [12]CPP (**2**) as a yellow solid (8 mg, 5% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (m, 44H), 6.90 (s, 2H), 3.75 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.59, 138.91, 138.65, 138.63, 138.58, 138.52, 138.51, 138.38, 136.80, 129.70, 129.35, 127.46, 127.43, 127.39, 127.36, 127.31, 127.27, 126.64, 115.21, 56.67. Melting point: 188-190 ℃. HR-MS (MALDI-TOF) *m/z* calcd for $C_{74}H_{52}O_2$ $[M]^+$: 972.3967, found: 972.4055.

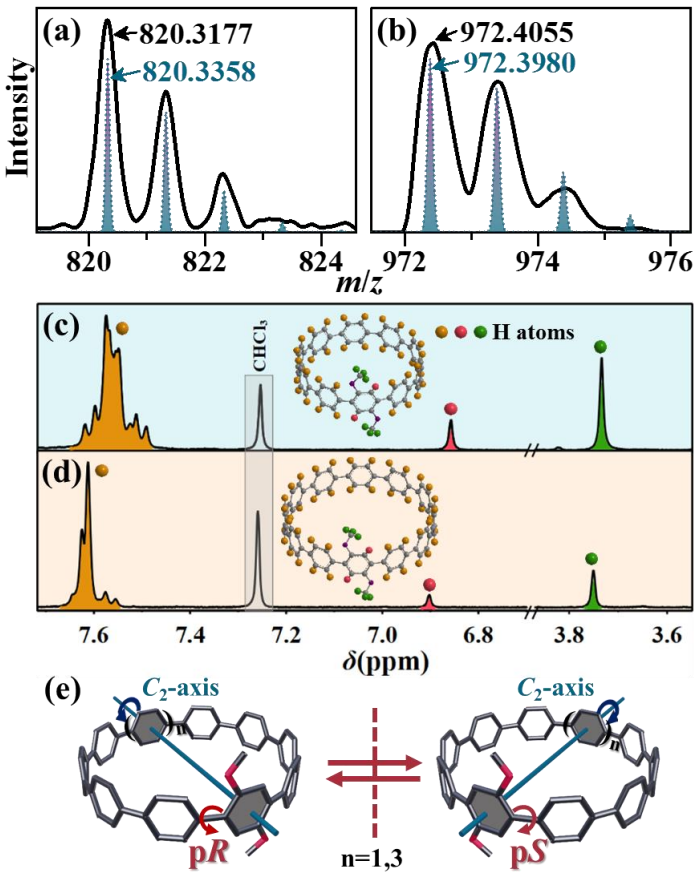


Fig. S1 HR-MS (MALDI-TOF MS) and simulated data for **1** (a) and **2** (b); Comparison of the ^{1}H NMR spectrum of **1** (c) and **2** (d) in $CDCl_3$; (e) Assignment of the absolute configurations of **1** and **2** with planar chirality descriptors (p*R* and p*S*), and the racemization process.

Computational Details

Geometrical optimizations were performed at the theoretical level of CAM-B3LYP[4]/6-311G(d,p)[5] without any symmetry assumptions and further validated by frequency analysis. Solvent effects of chloroform (ε = 4.7113) were implicitly taken into account by polarizable continuum model (PCM)[6, 7] developed by Tomasi's group in the framework of the self-consistent reaction field (SCRF)[8, 9]. Single point energy calculations were performed at the CAM-B3LYP/def2-TZVP[10] level in order to improve the relative energies. For the conformation analysis, potential energy surface (PES) scan was performed at the theoretical level of CAM-B3LYP[4]/6-311G(d,p) by changing the dihedral angles between dimethoxybenzene ring and adjacent phenyl units with a step size of -18° for 10 steps. The geometries at the minimum points were fully relaxed to get the most stable conformations, and the geometries at the maximum points were used as initial conformations to obtain the transition states by TS method, which were further validated by frequency analysis (one imaginary frequency). The strain energy was estimated by the reported hypothetical homodesmotic reaction method.[11, 12] As B3LYP[13] was more accurate for calculating orbital energy than CAM-B3LYP,[14] B3LYP/def2-TZVP theoretical level was applied to identify the energy level of frontier orbitals. Based on the optimized structures, time-dependent density functional theory (TD-DFT)[15] was performed to calculate the UV spectra. Due to the sensitivity of the vertical excitation energy to the functionals selected, a series of popular functionals (B3LYP, CAM-B3LYP and PBE0[16]) were tested. The results at the PBE0/def2-TZVP level were in accordance with the experimental data. All the calculations were carried out with Gaussian 16 package.[17] The wave function analysis were implemented in Multiwfn 3.8(dev) code,[18] and the visualizations of the isosurface maps were rendered with VMD software.[19]

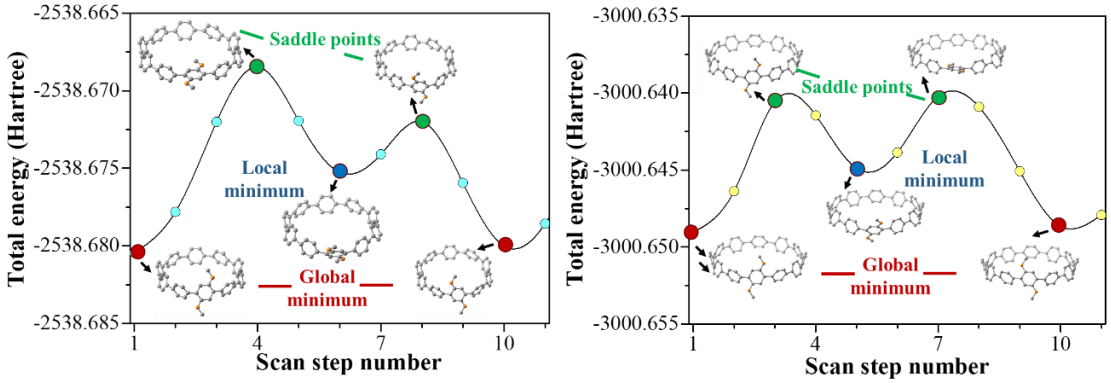


Fig. S2 1-D potential energy surface (PES) scan of **1** and **2** at the theoretical level of CAM-B3LYP/6-311G(d,p)/PCM by changing the dihedral angles between the dimethoxybenzene ring and adjacent phenyls with a step size of -18° for 10 steps. The geometries at the stationary points on the curves were used as initial geometries to find the most stable conformations (global minimum), the metastable conformations (local minimum) and the transition states (saddle points).

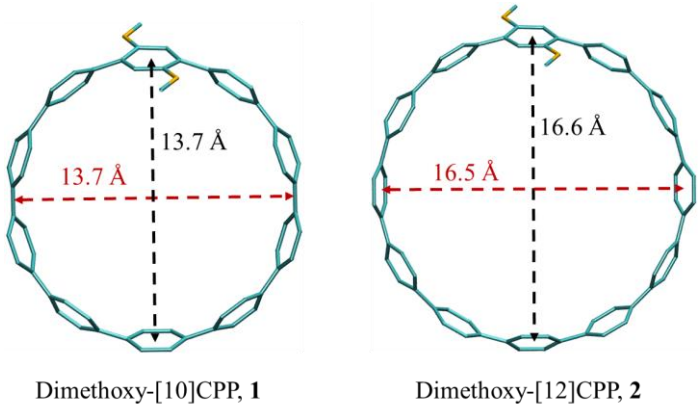


Fig. S3 The relaxed structures and calculated diameters of **1** and **2**.

Table S1. Uncorrected and thermal-corrected (298 K) energies of the relaxed structures of **1** and **2** (Unit: Hartree).[a]

Compounds	*E*	*E+ZPE*	*H*	*G*
1	-2538.998483	-2538.11884	-2538.068987	-2538.202398
2	-3001.024163	-2999.981241	-2999.921997	-3000.077444

[a]: *E*: Electronic energy; *ZPE*: Zero-point energy; *H*: Sum of electronic and thermal Enthalpies; *G*: Sum of electronic and thermal Free Energies

Table S2. The torsion angles (Unit: deg.) between adjacent phenyl rings of the relaxed structures of **1** and **2**.

	1	**2**
Torsion angles (deg.)	38	-43
	-35	37
	34	-34
	-35	36
	34	-35
	-34	36
	35	-35
	-33	35
	37	-36
	-38	35
	-	-36
	-	38
Average	**35**	**36**

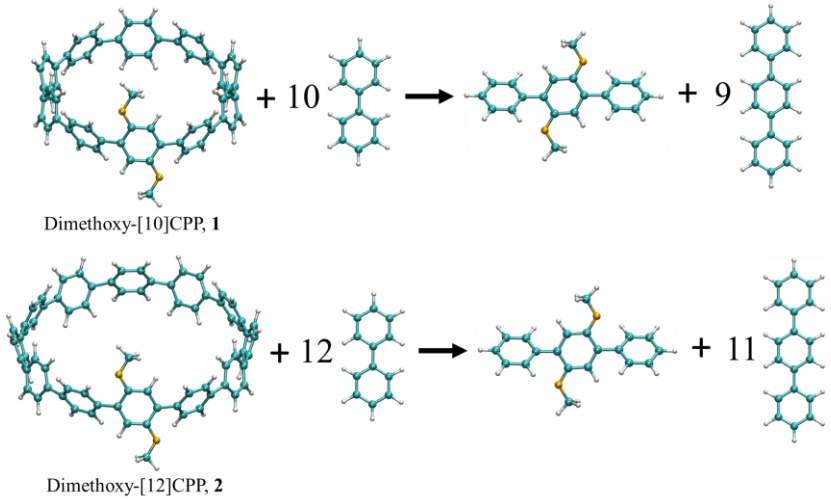


Fig. S4 The homodesmotic reactions for strain energy estimation.

Table S3. The calculated strain energies of **1** and **2** by homodesmotic reaction method.

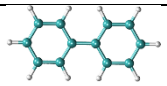
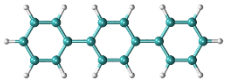
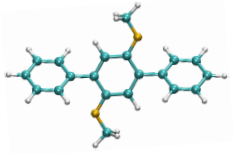
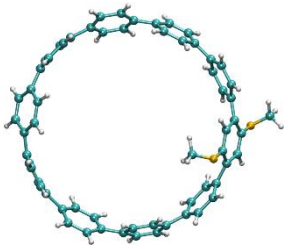
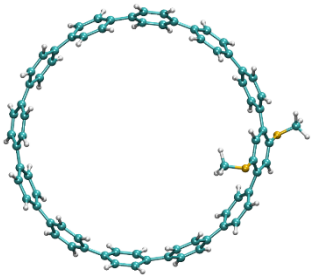
Optimized Structure	Total Energy (Hartree)	Strain Energy (ΔH, kcal mol^{-1})
	-463.005488	-
	-693.922719	-
	-922.899873	-
 **1**	-2538.068987	**50.50012227**
 **2**	-2999.921997	**38.86106679**

Table S4. Major electronic transitions for **1** and **2** determined by TD-DFT method at the PBE0/def2-TZVP level.

Compound	λ_{exp} (nm)	λ_{DFT} (nm)	Vertical excitation energy (eV)	Oscillator strengths f_{os}	Contributions
1	343	395	3.14	0.1280	HOMO→LUMO (88.3%)
		347	3.58	2.0051	HOMO-1→LUMO (43.5%) HOMO→LUMO+1 (27.5%) HOMO→LUMO+2 (12.8%) HOMO-2→LUMO (10%)
		346	3.59	2.0984	HOMO-2→LUMO (41.9%) HOMO→LUMO+2 (25.4%) HOMO→LUMO+1 (17.2%) HOMO-1→LUMO (11.6%)
2	341	343	3.61	2.7044	HOMO-1→LUMO (46.5%) HOMO→LUMO+1 (45.3%)
		342	3.63	2.4989	HOMO-2→LUMO (49.0%) HOMO→LUMO+2 (41.5%)

Table S5. The rate constant k_{298} and half-life at room temperature from theoretical data by kinetic analyses. $\Delta G^{\ddagger}$ were converted to k_{298} using the Eyring equation and calculated by TSTcalculator.[20] The very short half-life suggested the rapid racemization which made the isolation of pure enantiomers at ambient temperature unfeasible.[21]

	$\Delta G^{\ddagger}$ in kcal·mol^{-1}	k_{298} (sec^{-1})	Half-life $t_{1/2}$ (hr)
1-TS	7.34	2.59×10^{7}	7.44×10^{-12}
1-TS'	5.85	3.20×10^{8}	6.02×10^{-13}
2-TS	5.52	5.59×10^{8}	3.45×10^{-13}
2-TS'	5.99	2.53×10^{8}	7.62×10^{-13}

Table S6. Cartesian coordinates of optimized species.

1-p*S*

C	-5.336796	2.94813	-1.196862	C	6.973205	-2.447067	-0.0291	H	-3.345682	6.567405	-1.93918
C	-5.894953	-0.974545	1.335054	C	7.181969	1.809447	-0.069081	H	-3.981043	4.33495	-2.06888
C	-4.002976	-4.470573	-1.179448	C	4.843785	5.369516	0.066875	H	-5.588776	1.005335	2.069846
C	-0.650347	-7.052853	-1.186931	C	0.859603	6.882544	-0.020917	H	-4.909316	-2.70499	-1.94101
C	3.504736	-5.714979	-1.324801	C	-5.976403	3.369294	1.062607	H	-2.578597	-6.79848	-2.06655
C	6.966367	-3.284799	-1.148408	C	-6.70464	-1.091057	-0.913097	H	1.594433	-6.04349	-2.20095
C	6.940958	1.087724	-1.239152	C	-4.636421	-5.121138	1.025844	H	6.178231	-5.03956	-2.07242
C	5.659789	5.119552	-1.04039	C	-0.447573	-6.444093	1.110977	H	6.70197	-0.82197	-2.14649
C	1.48662	6.431192	-1.18337	C	3.789189	-6.468025	0.920877	H	7.109542	3.845566	-1.95088
C	-2.748645	6.475973	-1.039439	C	6.346842	-2.91753	1.126104	H	3.241028	5.615503	-2.06949
C	-4.567402	4.097091	-1.189875	C	7.68243	1.102619	1.028395	H	-1.068488	7.440504	-1.93371
C	-5.962519	0.410189	1.250288	C	5.078961	4.61676	1.2184	H	-6.526516	3.10012	1.95684
C	-4.875421	-3.399877	-1.111411	C	1.672112	7.136587	1.088114	H	-6.969226	-1.68762	-1.77455
C	-1.987933	-6.692405	-1.16411	C	-2.487374	5.781892	1.227995	H	-4.554111	-5.7869	1.877251
C	2.212483	-6.209877	-1.327603	C	-5.208988	4.524514	1.066666	H	0.149806	-6.28151	1.999423
C	6.215037	-4.448858	-1.164605	C	-6.831616	0.29088	-0.971647	H	4.394768	-6.58196	1.812377
C	7.022314	-0.29366	-1.257222	C	-5.51354	-4.04887	1.093986	H	6.335521	-2.30339	2.017926
C	6.54068	4.050024	-1.051449	C	-1.784969	-6.087597	1.134977	H	7.950158	1.634051	1.934096
C	2.825576	6.081403	-1.18459	C	2.495812	-6.96557	0.917123	H	4.473726	4.783741	2.100704
C	-1.454749	6.971695	-1.036283	C	5.597028	-4.080772	1.110225	H	1.237982	7.554561	1.98878
C	-4.416231	4.863457	-0.032029	C	7.764251	-0.280555	1.010137	H	-2.850801	5.268113	2.109319
C	-6.351752	1.074079	0.088901	C	5.958786	3.548436	1.207347	H	-5.178236	5.133753	1.962468
C	-5.587608	-3.113461	0.057176	C	3.012679	6.785751	1.08718	H	-6.089839	-3.89537	1.994389
C	-2.559604	-6.117379	-0.025464	C	-1.194595	6.276185	1.230884	H	-2.194824	-5.65763	2.040571
C	1.64939	-6.765724	-0.177674	O	-5.460724	-1.621088	2.450085	H	2.1194	-7.45876	1.805572
C	5.441143	-4.8223	-0.06186	C	-5.014841	-0.859001	3.556964	H	5.021877	-4.34169	1.989903
C	7.348499	-1.012474	-0.106118	O	-7.335338	0.954982	-2.049058	H	8.094177	-0.80036	1.901958
C	6.640682	3.187469	0.04424	C	-7.805061	0.201228	-3.151757	H	6.015199	2.911602	2.081362
C	3.594932	6.167499	-0.023254	H	-5.355439	2.329441	-2.082899	H	3.597276	6.936323	1.987208
C	-0.62009	6.801246	0.072229	H	-3.379408	-4.581507	-2.057946	H	-0.58493	6.133709	2.114459
C	-3.260678	5.790278	0.066058	H	-0.224195	-7.435797	-2.106746	H	-4.715428	-1.58074	4.313379
C	-5.981272	2.508337	-0.038061	H	3.858082	-5.177301	-2.195839	H	-4.155499	-0.23568	3.293828
C	-6.159651	-1.747701	0.194353	H	7.501264	-2.99094	-2.04391	H	-5.814095	-0.22886	3.957578
C	-3.800139	-5.303344	-0.07791	H	6.559534	1.598034	-2.114769	H	-8.194337	0.924851	-3.86406
C	0.170332	-6.848825	-0.073432	H	5.558894	5.728204	-1.931307	H	-8.607089	-0.48056	-2.85473
C	4.289413	-5.752929	-0.17121	H	0.895227	6.228449	-2.067498	H	-6.998622	-0.36921	-3.62214

1-p*R*

C	4.874094	-3.400135	-1.111763	C	-6.639696	3.188727	0.04385	H	2.576788	-6.79845	-2.06786
C	6.831886	0.289921	-0.970883	C	-7.348373	-1.01114	-0.105541	H	3.377417	-4.58097	-2.0583
C	4.568606	4.096576	-1.189022	C	-5.442057	-4.821529	-0.061205	H	6.969087	-1.68842	-1.77439
C	1.456517	6.971522	-1.036347	C	-1.650695	-6.765786	-0.17792	H	5.356596	2.328924	-2.08209
C	-2.82413	6.082528	-1.185375	C	5.513063	-4.050494	1.093021	H	3.347488	6.566702	-1.93878
C	-6.539336	4.050902	-1.05217	C	5.962364	0.408698	1.250956	H	-0.893759	6.229462	-2.06816
C	-7.022528	-0.292566	-1.25686	C	5.209523	4.523455	1.067794	H	-5.557246	5.728561	-1.93251
C	-6.21589	-4.447772	-1.163937	C	1.195786	6.276829	1.230948	H	-6.559626	1.598814	-2.11499
C	-2.214219	-6.210365	-1.327793	C	-3.011344	6.786642	1.086393	H	-7.501636	-2.98955	-2.04325
C	1.986341	-6.692532	-1.165249	C	-5.958029	3.550132	1.206918	H	-3.859896	-5.17788	-2.19584
C	4.001466	-4.470647	-1.180068	C	-7.763582	-0.278849	1.010743	H	0.222377	-7.43547	-2.1077
C	6.704528	-1.092082	-0.912793	C	-5.59789	-4.080034	1.110891	H	6.089752	-3.89761	1.993268
C	5.337689	2.947428	-1.195944	C	-2.496816	-6.965101	0.917276	H	5.588993	1.0039	2.070593

C	2.750279	6.475554	-1.039114	C	1.784077	-6.088662	1.134124	H	5.178685	5.13258	1.963683
C	-1.485111	6.432164	-1.183985	C	4.635739	-5.122615	1.024586	H	0.586066	6.134788	2.114563
C	-5.658313	5.120284	-1.04135	C	5.894431	-0.976043	1.335299	H	-3.595953	6.93727	1.986404
C	-6.940803	1.088816	-1.239066	C	5.97663	3.368026	1.063818	H	-6.01474	2.913742	2.081247
C	-6.966882	-3.283539	-1.147705	C	2.488443	5.782125	1.228402	H	-8.093394	-0.79835	1.902776
C	-3.5064	-5.715218	-1.32465	C	-1.670758	7.137277	1.087506	H	-5.022889	-4.34108	1.990634
C	0.648747	-7.05283	-1.187854	C	-5.07811	4.618404	1.21776	H	-2.120239	-7.45806	1.805795
C	3.799019	-5.304062	-0.07891	C	-7.681478	1.104281	1.028694	H	2.19421	-5.65923	2.039852
C	6.159216	-1.748838	0.194324	C	-6.347379	-2.916563	1.126806	H	4.553601	-5.78885	1.875642
C	5.981671	2.507216	-0.036973	C	-3.790051	-6.467273	0.92139	H	6.526421	3.098705	1.958204
C	3.26197	5.789931	0.066661	C	0.446589	-6.444967	1.110311	H	2.851526	5.268558	2.110001
C	-0.858071	6.88319	-0.021442	O	7.335529	0.954267	-2.048245	H	-1.236766	7.55514	1.988293
C	-4.842467	5.370627	0.066015	C	7.80655	0.2009	-3.15071	H	-4.473152	4.785647	2.100213
C	-7.181185	1.810839	-0.069096	O	5.460218	-1.623171	2.450071	H	-7.948804	1.635907	1.934405
C	-6.973529	-2.445778	-0.02837	C	5.010659	-0.861969	3.556149	H	-6.335863	-2.30253	2.018704
C	-4.290626	-5.752395	-0.170755	H	4.907766	-2.704725	-1.940907	H	-4.395231	-6.58091	1.813199
C	-0.171699	-6.849095	-0.074038	H	3.982669	4.334797	-2.068226	H	-0.150448	-6.28269	1.999052
C	2.558397	-6.117955	-0.026481	H	1.070645	7.440265	-1.933981	H	8.196247	0.924804	-3.86251
C	5.586891	-3.114559	0.056719	H	-3.239457	5.616822	-2.070435	H	8.608503	-0.48067	-2.85302
C	6.351925	1.072832	0.089759	H	-7.107999	3.846219	-1.951678	H	7.000748	-0.36968	-3.622
C	4.417207	4.862771	-0.031105	H	-6.702671	-0.821022	-2.146225	H	4.709717	-1.5843	4.311407
C	0.621517	6.801568	0.072076	H	-6.179309	-5.03838	-2.071822	H	4.151607	-0.23919	3.29087
C	-3.593622	6.168489	-0.024137	H	-1.596636	-6.044496	-2.201587	H	5.808324	-0.23145	3.959343

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C	-6.06669	-0.20135	-1.29022	C	6.930565	1.592925	-0.03109	H	-6.72052	3.913305	-1.84166
C	-3.23292	-3.23004	0.003894	C	4.746269	5.260632	-0.10023	H	-5.98377	1.762308	-2.10848
C	-0.74693	-6.39481	-1.16611	C	0.900591	7.107178	0.060025	H	-3.68166	-1.1364	-0.00382
C	3.456847	-6.66996	-0.93027	C	-3.30194	6.400311	0.040994	H	-2.36898	-5.42744	-2.16127
C	6.053055	-3.14588	-1.21574	C	-6.69424	-0.37504	1.0059	H	1.740271	-7.59985	-1.78768
C	7.394235	0.883469	-1.14274	C	-5.1488	-4.67742	-0.09247	H	4.712178	-4.57409	-2.04932
C	4.912568	4.496858	-1.25662	C	-1.01279	-6.75791	1.177146	H	7.76928	-1.02072	-2.03009
C	1.714007	7.292936	-1.06174	C	3.215878	-5.84771	1.294473	H	5.74258	2.749197	-2.14455
C	-2.55724	6.348341	-1.13862	C	6.708345	-3.5008	1.050404	H	3.598295	6.926606	-1.99469
C	-6.14759	4.139763	-0.95013	C	6.703698	0.869438	1.140744	H	-0.65008	6.544588	-2.06091
C	-6.22756	1.172739	-1.23353	C	5.56688	4.960408	0.990708	H	-5.31054	5.90111	-1.81676
C	-4.0811	-2.13969	-0.0303	C	1.502469	6.58747	1.207378	H	-6.85088	-0.96716	1.900017
C	-2.00911	-5.82974	-1.22143	C	-2.70969	7.020616	1.145023	H	-5.55363	-5.67934	-0.12939
C	2.140164	-7.10401	-0.91119	C	-5.47305	3.63522	1.280449	H	-0.63881	-7.10962	2.131211
C	5.302581	-4.3086	-1.1811	C	-6.85738	1.002659	1.062495	H	3.596468	-5.30577	2.151289
C	7.463388	-0.5007	-1.12989	C	-6.0052	-3.56895	-0.10825	H	7.258235	-3.20286	1.935386
C	5.735686	3.384063	-1.26727	C	-2.27203	-6.17748	1.123851	H	6.349024	1.381464	2.026589
C	3.016987	6.821524	-1.08614	C	1.899778	-6.27302	1.309534	H	5.517798	5.570982	1.88466
C	-1.22553	6.724529	-1.16145	C	5.955788	-4.66367	1.085828	H	0.909675	6.431684	2.100039
C	-5.34579	5.270248	-0.93623	C	6.771486	-0.51269	1.153115	H	-3.2769	7.147128	2.059769
C	-6.5228	1.811444	-0.02735	C	6.391344	3.846693	0.979793	H	-5.45661	2.977813	2.140569
C	-5.46505	-2.28505	-0.09343	C	2.804351	6.118606	1.183796	H	-7.15547	1.457643	1.999787
C	-2.74555	-5.61453	-0.05889	C	-1.37654	7.39818	1.121695	H	-2.84397	-6.06366	2.037597
C	1.302363	-6.82104	0.172475	C	-4.67517	4.765815	1.295864	H	1.295099	-6.04463	2.177558
C	5.161349	-5.04057	-0.00098	O	-1.87855	-3.12197	0.084465	H	5.93082	-5.24771	1.998381
C	7.069929	-1.23213	-0.00543	C	-1.304	-1.82954	0.128939	H	6.466667	-1.04038	2.048153
C	6.428147	2.987323	-0.12211	O	-7.36418	-3.6545	-0.15581	H	6.969336	3.610635	1.865522
C	3.560759	6.147715	0.01117	C	-7.95696	-4.9397	-0.18658	H	3.191628	5.611754	2.058951
C	-0.58183	7.17008	-0.00591	H	-5.71497	-0.65769	-2.20806	H	-0.93214	7.814102	2.018256

C	-4.51499	5.550483	0.152783	H	-0.14588	-6.41136	-2.06659	H	-4.06209	4.957187	2.167726
C	-6.14616	3.242254	0.122235	H	4.052273	-6.83406	-1.82095	H	-0.2293	-1.98362	0.190943
C	-6.19768	-0.98426	-0.14519	H	6.02818	-2.53748	-2.11126	H	-1.53432	-1.25619	-0.77396
C	-3.76741	-4.52583	-0.04727	H	7.64796	1.414776	-2.05252	H	-1.63955	-1.27081	1.007776
C	-0.17979	-6.768	0.055093	H	4.299525	4.700493	-2.12582	H	-9.03121	-4.77363	-0.21855
C	3.99189	-5.94538	0.138649	H	1.305716	7.756555	-1.95203	H	-7.70811	-5.51732	0.708705
C	6.695553	-2.6678	-0.07253	H	-2.98189	5.884345	-2.02013	H	-7.6526	-5.5	-1.07571

1-TS'

C	-5.570071	-3.64569	1.003873	C	6.870102	2.82223	-0.08482	H	-3.050597	-6.80512	1.590913
C	-6.204841	0.559696	1.504106	C	7.348037	-1.39959	0.199938	H	-4.423088	-5.23129	1.818656
C	-4.315065	4.492417	1.285272	C	5.216214	-5.090394	0.118323	H	-5.860785	-1.42465	2.15521
C	-1.019865	7.117571	0.782892	C	1.315671	-6.793147	0.022993	H	-5.212622	2.939796	2.414644
C	3.208428	5.985092	0.982072	C	-5.39998	-3.289913	-1.338284	H	-2.920582	6.923327	1.73211
C	6.795306	3.731721	0.97373	C	-6.700749	0.781509	-0.804384	H	1.295355	6.297568	1.861419
C	7.014562	-0.634727	1.318884	C	-4.909632	4.627428	-1.007864	H	5.887389	5.491627	1.766981
C	5.945299	-4.738241	1.257928	C	-0.820618	6.157854	-1.392678	H	6.622105	1.302475	2.109731
C	1.850721	-6.297448	1.212523	C	3.410059	6.508046	-1.336701	H	7.263733	-3.3401	2.185197
C	-2.389446	-6.610804	0.755815	C	6.224028	3.16736	-1.272922	H	3.510685	-5.38081	2.179663
C	-4.693997	-4.713095	0.907892	C	7.853951	-0.720622	-0.912735	H	-0.742872	-7.54109	1.746923
C	-6.157413	-0.815113	1.317638	C	5.484077	-4.383247	-1.055128	H	-5.654771	-2.74568	-2.23374
C	-5.151528	3.400762	1.444967	C	2.2022	-7.033503	-1.030479	H	-6.879801	1.39183	-1.67381
C	-2.338263	6.696774	0.846874	C	-1.961274	-5.745299	-1.419938	H	-4.843853	5.097248	-1.98227
C	1.888916	6.401513	0.961602	C	-4.546925	-4.374658	-1.435051	H	-0.227344	5.885513	-2.25685
C	5.969101	4.842073	0.90353	C	-6.771423	-0.594797	-0.960891	H	3.99311	6.56412	-2.24834
C	7.011339	0.748336	1.26459	C	-5.740351	3.531895	-0.85177	H	6.263827	2.492955	-2.1193
C	6.765605	-3.621031	1.264709	C	-2.13714	5.735393	-1.327646	H	8.193537	-1.28022	-1.77629
C	3.170317	-5.88346	1.282907	C	2.087464	6.921136	-1.358473	H	4.946546	-4.62678	-1.96285
C	-1.072882	-7.037113	0.845798	C	5.395661	4.273713	-1.341221	H	1.837992	-7.48391	-1.94649
C	-4.080807	-5.047762	-0.303008	C	7.847662	0.663788	-0.968472	H	-2.2553	-5.19612	-2.30345
C	-6.345682	-1.435621	0.083475	C	6.302839	-3.268234	-1.048391	H	-4.182865	-4.64327	-2.41798
C	-5.811	2.816755	0.355463	C	3.523701	-6.62519	-0.957409	H	-6.284561	3.19791	-1.72422
C	-2.897241	5.917794	-0.171071	C	-0.653018	-6.182791	-1.338092	H	-2.535295	5.144496	-2.14311
C	1.274544	6.793509	-0.228774	O	-6.052403	1.113354	2.738121	H	1.664908	7.288618	-2.28633
C	5.18065	5.084511	-0.225505	C	-5.908013	0.269758	3.867097	H	4.811803	4.430445	-2.23949
C	7.338978	1.42421	0.088208	O	-7.161996	-1.181412	-2.126835	H	8.180463	1.156767	-1.87442
C	6.889841	-2.810552	0.13237	C	-7.588124	-0.361328	-3.199817	H	6.379889	-2.67497	-1.95086
C	4.008779	-5.953632	0.168952	H	-5.969871	-3.405034	1.980446	H	4.167101	-6.76847	-1.81744
C	-0.155379	-6.762343	-0.170436	H	-3.734546	4.82074	2.138768	H	0.023218	-5.95894	-2.15382
C	-2.843966	-5.874001	-0.344047	H	-0.598769	7.662283	1.619852	H	-5.874634	0.932249	4.728911
C	-5.856043	-2.829727	-0.097488	H	3.606798	5.566535	1.897772	H	-6.759331	-0.40917	3.966357
C	-6.317353	1.411161	0.387163	H	7.338754	3.535829	1.890706	H	-4.980922	-0.30856	3.822533
C	-4.101546	5.077641	0.039537	H	6.626742	-1.121328	2.205115	H	-7.908349	-1.04173	-3.98537
C	-0.208047	6.779791	-0.303578	H	5.821357	-5.304996	2.173205	H	-6.773861	0.264843	-3.57621
C	3.97153	5.945996	-0.186129	H	1.19682	-6.108745	2.055294	H	-8.42972	0.272072	-2.90558

1-metastable conformation

C	5.764053	3.056811	1.282128	C	-7.02728	-2.11212	0.011068	H	3.822356	6.694577	1.552633
C	5.395024	-1.20792	1.488723	C	-7.00969	2.145261	0.175876	H	4.737052	4.776034	1.990867
C	4.035258	-5.25457	1.060482	C	-4.52203	5.603516	-0.04013	H	5.014655	0.797992	2.081025
C	0.33518	-7.33273	0.593012	C	-0.48525	6.960509	-0.14719	H	5.220413	-4.0126	2.31793
C	-3.74718	-5.70621	1.017017	C	5.888927	2.781123	-1.07983	H	2.292615	-7.37275	1.426896
C	-7.01312	-2.9936	1.095995	C	6.770541	-1.43499	-0.45369	H	-1.84421	-6.23717	1.815174
C	-6.7329	1.380105	1.309779	C	4.159859	-4.83084	-1.27574	H	-6.29391	-4.83035	1.908166
C	-5.28564	5.370854	1.107914	C	0.09945	-6.23532	-1.50921	H	-6.53773	-0.56586	2.151328

C	-1.08212	6.582738	1.056119	C	-4.11271	-6.21984	-1.28382	H	-6.7334	4.143354	2.08418
C	3.164669	6.505884	0.712903	C	-6.48506	-2.56895	-1.191	H	-2.82918	5.865742	2.036959
C	5.073096	4.243881	1.110021	C	-7.61588	1.496303	-0.9039	H	1.587888	7.658993	1.576166
C	5.561417	0.165508	1.399909	C	-4.85047	4.873848	-1.18393	H	6.192842	2.215831	-1.94933
C	4.936306	-4.22995	1.300117	C	-1.32876	7.20775	-1.23377	H	7.229951	-2.06898	-1.1985
C	1.689379	-7.03526	0.593283	C	2.715122	5.525082	-1.41173	H	3.883581	-5.04547	-2.30007
C	-2.48719	-6.27586	0.944262	C	5.215644	3.979013	-1.24987	H	-0.51488	-5.86545	-2.32084
C	-6.33559	-4.20072	1.027239	C	6.980577	-0.06141	-0.50389	H	-4.73916	-6.21502	-2.16787
C	-6.88525	0.004099	1.298551	C	5.037796	-3.78879	-1.03654	H	-6.48086	-1.91994	-2.0578
C	-6.2076	4.337188	1.156582	C	1.446776	-5.92522	-1.49957	H	-7.91244	2.066582	-1.77637
C	-2.43264	6.283856	1.120117	C	-2.84891	-6.78175	-1.35955	H	-4.28893	5.02496	-2.09717
C	1.894011	7.06055	0.725801	C	-5.80537	-3.77212	-1.25818	H	-0.9111	7.56947	-2.16615
C	4.691577	4.681751	-0.16054	C	-7.76873	0.119477	-0.91496	H	2.982438	4.878211	-2.23663
C	6.291907	0.779186	0.384483	C	-5.77377	3.844467	-1.13673	H	5.02463	4.323067	-2.25876
C	5.370488	-3.3972	0.265253	C	-2.68135	6.916553	-1.16688	H	5.385651	-3.20319	-1.87856
C	2.259185	-6.23932	-0.40717	C	1.453398	6.090607	-1.40715	H	1.834345	-5.32049	-2.3081
C	-1.9758	-6.73785	-0.26906	O	4.635946	-1.78325	2.459755	H	-2.51132	-7.19871	-2.30129
C	-5.64033	-4.57373	-0.12734	C	3.929911	-0.95687	3.367125	H	-5.29008	-4.0253	-2.17602
C	-7.321	-0.66371	0.153128	O	7.785845	0.541185	-1.42275	H	-8.1816	-0.35781	-1.79596
C	-6.40718	3.496997	0.05736	C	8.488141	-0.26966	-2.34714	H	-5.90631	3.223579	-2.01399
C	-3.24258	6.357352	-0.01438	H	5.973607	2.718501	2.289592	H	-3.29457	7.062305	-2.04822
C	0.982043	6.794674	-0.29844	H	3.629487	-5.78432	1.912808	H	0.779911	5.870669	-2.22631
C	3.570624	5.646424	-0.31404	H	-0.08365	-7.8841	1.426993	H	3.385054	-1.63346	4.021449
C	6.081529	2.238744	0.194587	H	-4.05178	-5.23695	1.944135	H	4.610821	-0.34723	3.967941
C	5.924719	-2.03563	0.485017	H	-7.48371	-2.70614	2.029004	H	3.219165	-0.30779	2.847923
C	3.545051	-5.51367	-0.22164	H	-6.27107	1.846511	2.171244	H	9.08818	0.411227	-2.94619
C	-0.50468	-6.86432	-0.42015	H	-5.11322	5.963691	1.998425	H	7.804253	-0.81819	-3.00156
C	-4.54985	-5.5822	-0.11829	H	-0.46188	6.392296	1.923545	H	9.147221	-0.97657	-1.83522

2-p*S*

C	8.379775	-0.261016	1.173821	C	-6.351189	-3.561786	-1.072991	H	5.626195	7.395395	-1.94694
C	8.731995	-0.95462	0.015185	C	-6.303882	-5.287847	1.075106	H	2.803512	7.21749	2.085116
C	9.068097	1.182529	-1.075268	C	-7.057534	-4.125832	1.136484	H	1.321058	7.535536	-2.06763
C	9.146514	-0.200682	-1.085998	C	-5.502735	-5.573249	-0.032768	H	-1.19745	8.823949	1.963845
C	8.301404	1.12078	1.18455	C	-5.599816	-4.721662	-1.133784	H	1.240144	8.951836	1.971173
C	8.107672	3.275275	-0.036048	C	-3.631649	-6.688674	1.16032	H	-1.10484	7.406306	-2.07458
C	8.571949	1.867677	0.037108	C	-4.407074	-6.573238	0.005945	H	-2.57966	6.955481	2.077442
C	7.462499	3.719273	-1.191162	C	-2.734628	-7.879817	-1.161963	H	-5.36753	6.797402	-1.97943
C	7.322303	5.275008	1.083796	C	-3.966538	-7.246565	-1.136446	H	-3.31513	8.118458	-1.97644
C	8.082029	4.116383	1.079666	C	-2.39926	-7.318597	1.133836	H	-4.62368	5.641973	2.074484
C	6.557163	5.639261	-0.02745	C	-0.442451	-8.167612	-0.142188	H	-5.62603	4.482582	-2.07615
C	6.703426	4.876484	-1.186951	C	-1.891769	-7.862246	-0.047221	H	-8.03865	3.004064	1.951025
C	4.666321	6.673954	1.207402	C	0.258773	-7.790089	-1.288372	H	-6.91274	5.17104	1.947831
C	5.451694	6.625866	0.054771	C	1.688676	-8.541448	0.949015	H	-6.78161	2.339291	-2.08147
C	3.77757	7.980769	-1.054963	C	0.3049	-8.613237	0.951518	H	-6.91862	0.968121	2.039004
C	5.014213	7.356113	-1.053524	C	2.381463	-8.02366	-0.148521	H	-8.37334	-1.76242	-1.75552
C	3.431145	7.298406	1.206203	C	1.640888	-7.720484	-1.291826	H	-6.31419	-2.8717	-1.90676
C	1.478615	8.205354	-0.032467	C	4.233821	-6.942083	1.103498	H	-6.29736	-5.95662	1.928051
C	2.928495	7.900853	0.05207	C	3.791712	-7.570176	-0.061645	H	-7.6147	-3.90343	2.034975
C	0.777706	7.859774	-1.188706	C	5.80022	-6.781475	-1.162855	H	-4.99313	-4.90837	-2.01139
C	-0.65178	8.543789	1.070524	C	4.638047	-7.53552	-1.17311	H	-3.94206	-6.18168	2.065672
C	0.731849	8.616627	1.074729	C	5.394286	-6.187793	1.11331	H	-2.40225	-8.34989	-2.08002
C	-1.344728	8.055823	-0.04069	C	7.15154	-4.926199	-0.108588	H	-4.57217	-7.23192	-2.03504
C	-0.604317	7.786334	-1.192633	C	6.162363	-6.030447	-0.041273	H	-1.77739	-7.28663	2.019905

C	-3.203815	6.961975	1.192419	C	7.208405	-4.133102	-1.255552	H	-0.28364	-7.43829	-2.15711
C	-2.755438	7.601599	0.035859	C	8.500609	-3.260747	1.021413	H	2.234654	-8.84672	1.833952
C	-4.763156	6.831533	-1.080628	C	7.874901	-4.496867	1.007424	H	-0.2026	-8.97444	1.838204
C	-3.598036	7.581199	-1.078857	C	8.428894	-2.404147	-0.080386	H	2.14189	-7.31668	-2.16293
C	-4.368076	6.213546	1.190765	C	7.833979	-2.898697	-1.241904	H	3.606373	-6.94793	1.986227
C	-6.13133	4.976542	-0.047044	O	-8.727945	0.881025	-2.052836	H	6.407452	-6.73598	-2.05922
C	-5.133434	6.071784	0.032339	C	-9.212072	0.118769	-3.143301	H	4.359535	-8.06393	-2.07731
C	-6.184192	4.18541	-1.196727	O	-6.752255	-1.660508	2.425617	H	5.643105	-5.62362	2.003621
C	-7.515315	3.325247	1.05794	C	-6.283999	-0.89012	3.517189	H	6.661258	-4.4316	-2.14115
C	-6.874492	4.555014	1.057042	H	8.053421	-0.810041	2.048416	H	9.009329	-2.9369	1.921809
C	-7.438904	2.469286	-0.043206	H	9.349452	1.733863	-1.964735	H	7.907637	-5.11472	1.897051
C	-6.827825	2.961412	-1.198693	H	9.487512	-0.703075	-1.983561	H	7.759304	-2.26524	-2.11715
C	-8.209287	0.225542	-0.977137	H	7.915697	1.615596	2.067292	H	-9.60653	0.837218	-3.85801
C	-7.727683	1.016363	0.075768	H	7.459937	3.095877	-2.076704	H	-8.4126	-0.45867	-3.61703
C	-7.222043	-1.020363	1.320643	H	7.284636	5.878049	1.983372	H	-10.0133	-0.55754	-2.83177
C	-7.299023	0.363227	1.229538	H	8.622928	3.836859	1.976121	H	-5.95724	-1.606	4.26784
C	-8.085087	-1.156498	-0.908339	H	6.12764	5.126892	-2.06934	H	-7.07794	-0.2657	3.937051
C	-7.04044	-3.201888	0.087967	H	4.971647	6.121237	2.087236	H	-5.43805	-0.25966	3.228675
C	-7.532168	-1.803757	0.199239	H	3.447234	8.495481	-1.949566				

2-p*R*

C	-8.30144	1.120983	1.183899	C	6.82768	2.961394	-1.19867	H	-6.40778	-6.73659	-2.05849
C	-8.57198	1.867813	0.03645	C	6.874861	4.554769	1.057195	H	-3.60641	-6.94731	1.986784
C	-9.14655	-0.20064	-1.08653	C	7.515687	3.325038	1.057822	H	-2.14215	-7.31662	-2.1622
C	-9.06813	1.182557	-1.0759	C	6.131452	4.976435	-0.04672	H	0.202606	-8.97437	1.838744
C	-8.3798	-0.26083	1.173263	C	6.184052	4.185424	-1.19645	H	-2.23466	-8.84671	1.834638
C	-8.42897	-2.40403	-0.08073	C	4.368105	6.213031	1.191351	H	0.283372	-7.43817	-2.15652
C	-8.73203	-0.95453	0.014723	C	5.13361	6.071664	0.03301	H	1.777315	-7.28579	2.020143
C	-7.83368	-2.89864	-1.242	C	3.598348	7.581509	-1.07784	H	4.572122	-7.23265	-2.03478
C	-7.87536	-4.49674	1.007342	C	4.763457	6.831846	-1.07973	H	2.40217	-8.35055	-2.07937
C	-8.50105	-3.26062	1.021087	C	3.203822	6.961458	1.193123	H	3.942	-6.18091	2.065539
C	-7.15165	-4.92615	-0.10845	C	1.344873	8.05566	-0.03989	H	4.992625	-4.90823	-2.01153
C	-7.20815	-4.13309	-1.25541	C	2.755562	7.601492	0.036775	H	7.615504	-3.90373	2.034085
C	-5.39439	-6.18743	1.113754	C	0.604553	7.78613	-1.19184	H	6.297936	-5.9568	1.927422
C	-6.16254	-6.0304	-0.04079	C	-0.73181	8.616541	1.075341	H	6.313903	-2.87166	-1.90717
C	-4.6383	-7.53583	-1.17229	C	0.651801	8.543683	1.071262	H	8.372305	-1.76225	-1.75681
C	-5.80046	-6.78178	-1.16218	C	-1.47851	8.205218	-0.03192	H	6.919936	0.967831	2.038892
C	-4.2339	-6.94172	1.104079	C	-0.77749	7.859572	-1.18804	H	6.781298	2.339376	-2.08152
C	-2.38162	-8.02357	-0.14781	C	-3.43111	7.297986	1.206349	H	6.91333	5.170774	1.94799
C	-3.79185	-7.57016	-0.06087	C	-2.92837	7.900776	0.052471	H	8.039286	3.003722	1.950703
C	-1.6411	-7.72038	-1.29111	C	-5.01407	7.356454	-1.05341	H	5.625756	4.48269	-2.07576
C	-0.30496	-8.61312	0.95212	C	-3.77741	7.981058	-1.0546	H	4.623616	5.641192	2.074931
C	-1.68873	-8.54135	0.949703	C	-4.66634	6.6736	1.207299	H	3.3156	8.119157	-1.97524
C	0.44234	-8.16746	-0.14164	C	-6.55715	5.639381	-0.02792	H	5.367996	6.798117	-1.97844
C	-0.25897	-7.78995	-1.28773	C	-5.45167	6.625884	0.054654	H	2.579587	6.954671	2.078094
C	2.399157	-7.31805	1.134064	C	-6.70311	4.87651	-1.18736	H	1.105137	7.406087	-2.07375
C	1.891635	-7.8621	-0.04676	C	-8.08243	4.116632	1.078859	H	-1.2402	8.951839	1.971701
C	3.966441	-7.24688	-1.13621	C	-7.32268	5.275224	1.08313	H	1.197407	8.82395	1.964589
C	2.734537	-7.88011	-1.1615	C	-8.10774	3.275384	-0.03679	H	-1.32077	7.535331	-2.06701
C	3.631598	-6.68818	1.160337	C	-7.46221	3.719291	-1.1917	H	-2.80354	7.2168	2.085284
C	5.502718	-5.57322	-0.03311	O	6.754032	-1.66086	2.425417	H	-5.62602	7.396078	-1.94684
C	4.407028	-6.57314	0.005964	C	6.285362	-0.8905	3.516856	H	-3.447	8.496054	-1.94901
C	5.599559	-4.72161	-1.13408	O	8.726219	0.881284	-2.05423	H	-4.97173	6.120646	2.086965
C	7.058021	-4.12602	1.135778	C	9.209724	0.118998	-3.14497	H	-6.12708	5.126829	-2.06962

C	6.304241	-5.28792	1.074563	H	-7.91575	1.615839	2.066626	H	-8.62367	3.837234	1.975147
C	7.040701	-3.20199	0.087294	H	-9.48758	-0.70311	-1.98404	H	-7.28534	5.878381	1.98264
C	6.351047	-3.56178	-1.07343	H	-9.34954	1.733831	-1.96538	H	-7.45939	3.09585	-2.07721
C	7.222974	-1.02063	1.320149	H	-8.05347	-0.80979	2.047913	H	5.958568	-1.60635	4.267508
C	7.532439	-1.80384	0.1985	H	-7.75873	-2.26523	-2.11725	H	7.079081	-0.26589	3.936852
C	8.208728	0.225601	-0.97811	H	-7.90844	-5.11458	1.896965	H	5.43939	-0.26023	3.228029
C	8.084614	-1.15639	-0.9094	H	-9.01008	-2.93673	1.921297	H	9.603747	0.837383	-3.85997
C	7.299812	0.363004	1.229139	H	-6.66074	-4.43161	-2.14083	H	8.410002	-0.4585	-3.61818
C	7.439018	2.469177	-0.04343	H	-5.64314	-5.62303	2.00394	H	10.01111	-0.55726	-2.8338
C	7.727878	1.01626	0.075264	H	-4.35988	-8.06455	-2.07634				

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C	6.294996	5.084713	-1.14262	C	-7.23713	-0.73497	1.264476	H	8.871816	-2.64248	2.026087
C	6.12832	5.854583	0.009518	C	-8.20273	0.449571	-1.03442	H	6.673114	-4.28894	-2.06105
C	7.663284	4.36053	1.142092	C	-7.96378	-0.91758	-1.00328	H	5.676848	-5.52724	2.081572
C	6.884717	5.506669	1.131746	C	-7.88322	1.260088	0.057569	H	4.539483	-8.00375	-2.02058
C	7.073042	3.940188	-1.13247	C	-7.47619	0.62859	1.234159	H	6.532148	-6.59555	-1.97504
C	8.226007	2.123969	0.111413	C	-7.11158	3.239468	-1.22515	H	3.696808	-6.93324	2.037233
C	7.717806	3.5159	0.030338	C	-7.694	2.728576	-0.06426	H	2.308248	-7.27909	-2.12846
C	7.970667	1.36943	1.257372	C	-7.25605	4.85866	1.003964	H	-0.07854	-8.98042	1.827953
C	8.905561	0.07895	-0.99587	C	-7.82895	3.597009	1.022352	H	2.358654	-8.87343	1.843574
C	8.764402	1.457273	-0.99229	C	-6.54016	4.499857	-1.24395	H	-0.1153	-7.37152	-2.13943
C	8.513499	-0.68881	0.103851	C	-5.55429	6.421352	-0.02169	H	-1.60701	-7.29078	2.058356
C	8.111364	-0.00751	1.253659	C	-6.52667	5.30265	-0.10241	H	-4.30556	-6.7965	-2.03334
C	7.741869	-2.68695	-1.15373	C	-4.8015	6.579961	1.14294	H	-2.25217	-8.12727	-2.09216
C	8.29038	-2.15321	0.013268	C	-4.01133	7.921279	-1.13495	H	-3.68114	-6.00747	2.119578
C	7.843586	-4.27015	1.104204	C	-5.17712	7.172377	-1.13827	H	-6.89554	-6.20995	0.282042
C	8.395555	-2.99925	1.120427	C	-3.17568	7.949511	-0.01502	H	-4.88444	-1.75207	-0.22858
C	7.189366	-3.95562	-1.16941	C	-3.63704	7.327804	1.146178	H	-6.82327	-1.18413	2.159638
C	6.233177	-5.90233	0.040178	C	-1.01557	8.087715	-1.233	H	-8.573	0.899585	-1.94813
C	7.162126	-4.74607	-0.01925	C	-1.75796	8.382835	-0.08846	H	-8.13634	-1.51059	-1.89382
C	5.462436	-6.09872	1.187043	C	0.322524	8.911769	1.035282	H	-7.23035	1.22365	2.10501
C	4.78727	-7.46908	-1.1111	C	-1.06235	8.867705	1.022391	H	-6.99368	2.600223	-2.09132
C	5.917715	-6.66846	-1.08547	C	0.36761	8.132917	-1.22056	H	-7.32746	5.483032	1.886821
C	3.927988	-7.5373	-0.01117	C	2.511342	8.143318	0.034267	H	-8.33554	3.260981	1.919465
C	4.334153	-6.90014	1.162211	C	1.067921	8.474291	-0.0627	H	-5.99189	4.811128	-2.12447
C	1.798002	-7.69405	-1.26805	C	2.995694	7.541729	1.196794	H	-5.063	6.017311	2.030533
C	2.527062	-8.01498	-0.12224	C	4.599674	7.563969	-1.04865	H	-3.72034	8.447533	-2.03644
C	0.43748	-8.61085	0.949687	C	3.370038	8.202287	-1.06645	H	-5.77259	7.127588	-2.04257
C	1.822327	-8.55122	0.958625	C	5.020562	6.840297	0.070196	H	-3.02068	7.330085	2.036608
C	0.415568	-7.74836	-1.27442	C	4.223769	6.903628	1.21427	H	-1.51789	7.709272	-2.11458
C	-1.7346	-7.76308	-0.03546	O	-3.16046	-3.81655	-0.3315	H	0.831655	9.24495	1.931995
C	-0.29834	-8.13027	-0.13726	C	-2.54124	-2.55266	-0.47949	H	-1.60767	9.167232	1.909606
C	-2.21502	-7.23295	1.16406	O	-8.62872	-4.11963	0.327506	H	0.909981	7.789866	-2.09292
C	-3.73373	-6.93315	-1.12277	C	-9.26093	-5.37758	0.475059	H	2.359357	7.475681	2.070675
C	-2.56265	-7.67678	-1.15686	H	5.724945	5.321646	-2.03245	H	5.220587	7.590232	-1.93634
C	-4.12145	-6.26941	0.038084	H	8.200466	4.095455	2.045132	H	3.053904	8.713851	-1.96797
C	-3.38815	-6.49935	1.199417	H	6.82912	6.114799	2.026922	H	4.515772	6.355628	2.101563
C	-4.50976	-3.86202	-0.158	H	7.091101	3.312085	-2.01454	H	-1.47952	-2.7534	-0.60204
C	-5.08385	-5.12949	0.005402	H	7.552546	1.850295	2.133089	H	-2.91274	-2.02457	-1.36279
C	-7.27541	-4.08872	0.173922	H	9.281927	-0.41068	-1.88629	H	-2.68974	-1.9268	0.405549
C	-6.46218	-5.22723	0.157485	H	9.033716	2.017592	-1.87986	H	-10.3234	-5.16885	0.576627
C	-5.3152	-2.73747	-0.12458	H	7.799224	-0.56766	2.126413	H	-8.90952	-5.90017	1.369786
C	-7.39982	-1.51499	0.121978	H	7.643758	-2.06327	-2.03367	H	-9.10055	-6.01199	-0.40183

C	-6.6937	-2.82865	0.050354	H	7.899798	-4.88053	1.997796			

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C	-8.480396	-0.485451	-1.06042	C	7.006535	-3.923405	0.97735	H	-5.820342	7.369277	1.708358
C	-8.764256	-1.15249	0.132202	C	6.005715	-4.643641	-1.476558	H	-2.986936	6.983834	-2.30206
C	-9.089348	1.008332	1.177963	C	6.776917	-3.502245	-1.352049	H	-1.533264	7.65151	1.837351
C	-9.139437	-0.375468	1.231091	C	5.621487	-5.396048	-0.363923	H	0.997262	8.635612	-2.27162
C	-8.427741	0.896289	-1.112531	C	6.210851	-5.049832	0.854684	H	-1.442195	8.708221	-2.31027
C	-8.220199	3.08888	0.03699	C	3.561125	-6.263546	-1.467614	H	0.89389	7.583108	1.876332
C	-8.658946	1.671007	0.025163	C	4.495146	-6.363921	-0.433194	H	2.435417	6.785403	-2.19211
C	-7.559439	3.589735	1.159731	C	2.981369	-7.916862	0.66161	H	5.161997	7.103576	1.897099
C	-7.49456	5.056364	-1.1773	C	4.202982	-7.262968	0.598078	H	3.079267	8.366307	1.733784
C	-8.234148	3.886661	-1.110516	C	2.351592	-6.929655	-1.415713	H	4.511615	5.529941	-2.03
C	-6.71467	5.477893	-0.097448	C	0.583056	-8.098924	-0.148019	H	5.452656	4.812946	2.231753
C	-6.823662	4.760118	1.0944	C	2.006589	-7.717449	-0.317262	H	7.996166	3.027083	-1.564
C	-4.841946	6.466398	-1.393287	C	-0.058138	-7.833191	1.062008	H	6.837601	5.114449	-1.80234
C	-5.628104	6.478307	-0.240252	C	-1.592159	-8.47673	-1.140913	H	6.635025	2.728358	2.486928
C	-3.982388	7.933462	0.780032	C	-0.210272	-8.494533	-1.227528	H	8.385438	1.18096	-1.56054
C	-5.20639	7.285485	0.819272	C	-2.235991	-8.050582	0.024349	H	7.07525	-1.68135	2.146873
C	-3.617854	7.11121	-1.431116	C	-1.440561	-7.805021	1.144939	H	7.40255	-3.68147	1.955511
C	-1.685866	8.136652	-0.250259	C	-4.1828	-7.008205	-1.109769	H	5.647681	-4.90983	-2.46261
C	-3.129073	7.797388	-0.318413	C	-3.659155	-7.628001	0.026208	H	6.979741	-2.90894	-2.22994
C	-0.989016	7.909904	0.937537	C	-5.624586	-6.893134	1.239507	H	5.987713	-5.61837	1.748426
C	0.448552	8.424059	-1.361405	C	-4.443394	-7.616275	1.182955	H	3.730877	-5.58017	-2.28826
C	-0.936491	8.46477	-1.383291	C	-5.363418	-6.289699	-1.054661	H	2.769934	-8.56154	1.506995
C	1.140533	8.05531	-0.2049	C	-7.09006	-5.082082	0.253098	H	4.918118	-7.42558	1.39479
C	0.393887	7.870681	0.959808	C	-6.071814	-6.155678	0.140218	H	1.620011	-6.74995	-2.19392
C	3.04557	6.89554	-1.304032	C	-7.099122	-4.266222	1.385239	H	0.527592	-7.53007	1.9216
C	2.563532	7.634738	-0.222732	C	-8.548196	-3.477658	-0.827596	H	-2.177731	-8.74389	-2.01241
C	4.57118	7.032883	0.991513	C	-7.892284	-4.697779	-0.824733	H	0.258924	-8.76835	-2.16533
C	3.389273	7.748979	0.898845	C	-8.428842	-2.593405	0.247737	H	-1.901001	-7.47673	2.068549
C	4.22766	6.180583	-1.21194	C	-7.755139	-3.047167	1.382653	H	-3.606666	-6.99219	-2.02626
C	5.991471	5.114271	0.176973	O	7.300363	0.839263	2.795591	H	-6.180943	-6.86327	2.169045
C	4.97571	6.173467	-0.033724	C	7.066161	-0.023442	3.894495	H	-4.103105	-8.13827	2.069467
C	6.03316	4.442071	1.395662	O	8.579512	-1.392131	-2.063416	H	-5.677544	-5.73315	-1.92888
C	7.445449	3.390854	-0.707896	C	9.083589	-0.567736	-3.098331	H	-6.491827	-4.53197	2.24176
C	6.77991	4.595648	-0.852481	H	-8.185891	-1.053262	-1.934308	H	-9.11818	-3.18648	-1.70204
C	7.356227	2.625367	0.466518	H	-9.340221	1.578878	2.064342	H	-7.96265	-5.33687	-1.69702
C	6.699076	3.237322	1.542014	H	-9.426693	-0.858282	2.157806	H	-7.643863	-2.39128	2.23734
C	7.511282	0.308658	1.559679	H	-8.092608	1.371469	-2.026032	H	6.998503	0.621764	4.767377
C	7.733222	1.178952	0.474034	H	-7.52571	3.002214	2.068774	H	6.128388	-0.5746	3.78211
C	8.164764	-0.814183	-0.901234	H	-7.484579	5.623191	-2.100917	H	7.891601	-0.72772	4.029273
C	8.138422	0.559819	-0.716026	H	-8.789293	3.563882	-1.983316	H	9.406033	-1.24361	-3.88689
C	7.432565	-1.060425	1.341567	H	-6.235222	5.057128	1.953767	H	9.93891	0.021587	-2.75586
C	7.229252	-3.062791	-0.103118	H	-5.136731	5.852677	-2.235584	H	8.312969	0.10181	-3.49166
C	7.680684	-1.661795	0.109761	H	-3.664732	8.512403	1.639154			

2-metastable conformation

C	8.122418	1.852783	-1.057621	C	-7.321229	2.668337	1.335092	H	6.907003	-6.29826	1.87846
C	8.260265	2.59837	0.114081	C	-7.020419	3.702492	-1.198054	H	4.238223	-6.54311	-2.2526
C	8.956423	0.567319	1.237431	C	-7.501239	2.415152	-1.028451	H	2.759737	-7.47274	1.856056
C	8.75076	1.937759	1.243575	C	-6.583925	4.465708	-0.111337	H	0.61627	-8.78655	-2.37919
C	8.327864	0.484425	-1.063771	C	-6.827295	3.950184	1.16323	H	3.034089	-8.45978	-2.30168
C	8.520943	-1.673012	0.150017	C	-4.826024	5.682863	-1.380691	H	0.355084	-7.82376	1.782095
C	8.680108	-0.19822	0.101488	C	-5.688215	5.638028	-0.283024	H	-1.004082	-6.99773	-2.26638

C	7.925067	-2.26036	1.267027	C	-4.408199	7.452831	0.69367	H	-3.990945	-8.11593	1.483055
C	8.237585	-3.776581	-1.017827	C	-5.498773	6.597328	0.71682	H	-1.741339	-9.04928	1.415345
C	8.734497	-2.48449	-0.967598	C	-3.745283	6.545305	-1.411082	H	-3.223219	-6.0352	-2.183
C	7.509161	-4.310139	0.048561	C	-2.115284	7.991653	-0.237602	H	-4.949195	-6.22758	2.028639
C	7.430259	-3.552377	1.217722	C	-3.470091	7.395386	-0.339498	H	-6.685075	-3.68971	-1.80636
C	5.917508	-5.665658	-1.28546	C	-1.411792	7.878409	0.961984	H	-5.321397	-5.65486	-2.20039
C	6.639	-5.502641	-0.102201	C	-0.043395	8.639434	-1.310423	H	-6.390556	-4.31862	2.413511
C	5.254604	-7.224179	0.892738	C	-1.414719	8.449947	-1.35604	H	-8.561244	-2.55429	-1.04507
C	6.329847	-6.352516	0.96279	C	0.684004	8.369498	-0.147568	H	-6.215234	0.476974	1.994251
C	4.841057	-6.532084	-1.353303	C	-0.039807	8.060172	1.005143	H	-7.434372	2.282368	2.340927
C	3.084921	-7.881323	-0.228998	C	2.747192	7.578285	-1.282624	H	-6.92016	4.089946	-2.20457
C	4.440984	-7.277081	-0.242627	C	2.154611	8.167055	-0.164262	H	-7.754398	1.823383	-1.89689
C	2.309137	-7.804286	0.928863	C	4.228799	7.799235	1.034637	H	-6.538598	4.516333	2.039927
C	1.08294	-8.508785	-1.44126	C	2.950748	8.33159	0.972705	H	-4.931499	4.959678	-2.17887
C	2.454312	-8.319566	-1.397194	C	4.02497	7.051065	-1.222748	H	-4.259634	8.142695	1.516376
C	0.288598	-8.278022	-0.315465	C	5.940952	6.191192	0.098158	H	-6.182564	6.644757	1.555727
C	0.939329	-8.002719	0.887559	C	4.765026	7.08562	-0.040189	H	-3.041308	6.474356	-2.23115
C	-1.665164	-7.27882	-1.455768	C	6.086111	5.430743	1.259195	H	-1.9237	7.530137	1.850891
C	-1.176128	-8.061204	-0.409364	C	7.642576	4.81044	-0.933917	H	0.475357	8.948822	-2.20992
C	-3.34445	-7.861336	0.652064	C	6.791331	5.902677	-0.972357	H	-1.940577	8.609525	-2.29015
C	-2.06647	-8.397421	0.612664	C	7.675965	3.961228	0.17549	H	0.485392	7.846869	1.927844
C	-2.934291	-6.731977	-1.407305	C	6.935326	4.338061	1.296748	H	2.164579	7.430309	-2.18316
C	-4.954439	-6.064129	-0.116795	O	-5.662505	-2.084607	2.354406	H	4.799053	7.899585	1.95073
C	-3.779656	-6.951922	-0.317513	C	-4.924012	-1.212753	3.190249	H	2.549731	8.83967	1.84169
C	-5.355653	-5.704955	1.171926	O	-9.235058	0.031252	-1.277219	H	4.407084	6.507077	-2.07773
C	-6.339175	-4.262743	-0.954646	C	-9.965906	-0.824255	-2.136801	H	5.445356	5.625787	2.110386
C	-5.544029	-5.373404	-1.178753	H	7.74349	2.328245	-1.953776	H	8.252995	4.586478	-1.80077
C	-6.602912	-3.804333	0.339811	H	9.291264	0.080137	2.145626	H	6.751809	6.510577	-1.86861
C	-6.168539	-4.60681	1.397222	H	8.929407	2.493903	2.156319	H	6.936097	3.706465	2.176534
C	-6.537063	-1.557828	1.454756	H	8.10389	-0.073322	-1.964566	H	-4.28734	-1.85256	3.79694
C	-7.131823	-2.428575	0.527791	H	7.744021	-1.66475	2.153245	H	-4.298003	-0.53221	2.606111
C	-8.337685	-0.520688	-0.4134	H	8.374217	-4.360637	-1.920378	H	-5.580285	-0.63323	3.84594
C	-8.066549	-1.883696	-0.356977	H	9.25154	-2.084147	-1.831657	H	-10.63376	-0.17918	-2.70284
C	-6.778223	-0.19559	1.366143	H	6.875509	-3.933545	2.066324	H	-10.55835	-1.54757	-1.56922
C	-7.574824	1.836819	0.242043	H	6.127723	-5.025181	-2.133097	H	-9.307185	-1.35702	-2.82907
C	-7.632548	0.362175	0.417021	H	5.015774	-7.835025	1.755246				

Cell Imaging Experiments

Cell Culture

HepG2 cells were cultured in Dulbecco's modified Eagle's medium (DMEM) containing 10% fetal bovine serum (FBS) and 1% penicillin/streptomycin at 36.5℃ under 5% CO_2 atmosphere within an incubator.

Cell Viability Evaluation by MTT Assays

HepG2 cells were seeded in 96-well plates at a density of 5000 cells per well and the outer wells were filled with sterile phosphate-buffered saline (PBS). After culturing overnight, the medium in each well was replaced by fresh medium containing the sample dimethoxy [10]CPP **1** or dimethoxy [12]CPP **2** at different concentrations (0.5, 2.5, 5, 10, 25 μM) with 0.5% DMSO. The cells were incubated for a series of time periods (2, 5, 8, 12, 18 and 24 h). Then, 20 μL of MTT solution (5 mg/mL in PBS) was added to each well and the cells were incubated for another 4 h. After removal of the supernatant, 150 μL of DMSO was added to each well. The optical density (OD) was measured at 490 nm. The percentage of the viable cells was evaluated according to the formula (eq.1):

$$\text{cell viability (\%)} = \frac{\text{absorbance of test sample} - \text{absorbance of positive control}}{\text{absorbance of negative control} - \text{absorbance of positive control}} \quad \text{(eq.1)}$$

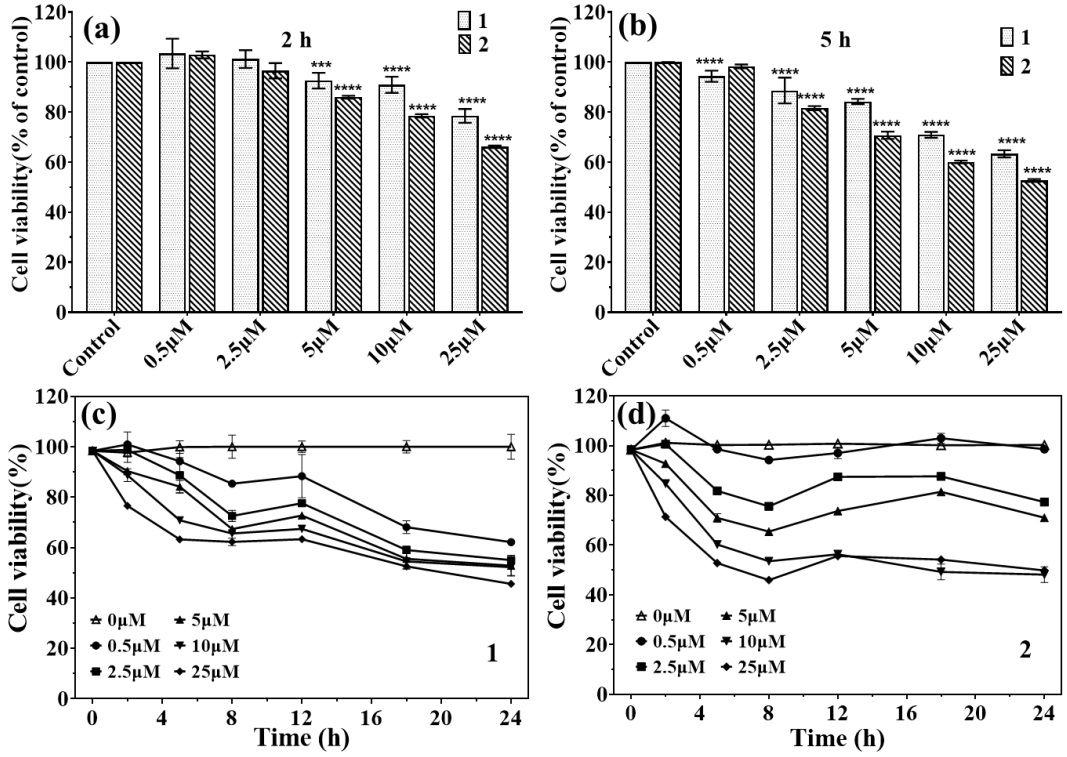

Fig. S5 Cell viability of **1** and **2** in HepG2 cells was evaluated by MTT assay. The results are expressed as the mean value with error bars representing the standard error in measurements (n=5). (a, b) Concentration-dependent analysis of cell viability after treatments with **1** or **2** for 2 h (a) or 5 h (b). ***, $p = 0.0004$ vs. control; ****, $p < 0.0001$ vs. control. (c, d) Time-dependent analysis of cell viability after treatments with different concentrations of **1** (c) or **2** (d).

Cell Imaging

To increase water-dispersion in aqueous medium, surfactant diacylphospholipid-polyethyleneglycol (F127) was used to solubilize the nanohoops. Typically, F127 (6.7 mg), nanohoop **1** (0.4 mg) were dissolved in DMSO (0.5 mL), and then H_2O (3.5 mL) was added dropwise. After stirring for 2 h, the resulting solution was freeze-dried. For cell imaging, HepG2 cells were seeded in 24-well plate containing glass coverslips at a density of 50000 cells per well and incubated for 24 h. Then, the medium was removed and 0.5 mL of DMEM media containing 10 μM F127 solublized dimethoxy-[10]CPP was added into each well and incubated for different times (2h, 5h, 8h) at 37℃. The coverslips with cells were then placed in empty wells, treated with 1 mL of 4% formaldehyde in PBS, and allowed to sit at room temperature for 30 min. After washing with PBS for three times, the cells were analyzed on a confocal microscope (Zeiss Laser Scanning Confocal Microscope, LSM 880). Nanohoops were excited at 405 nm (0.5% laser power) with photoluminescence detected at the range of 410-489 nm.

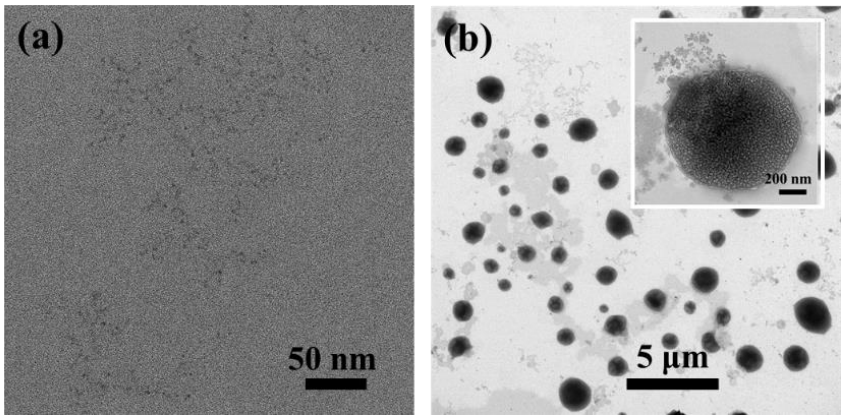

Fig. S6 TEM images of **1** (a) and **1** solubilized by F127 (b) in PBS. The size of pure **1** was observed to be about 1 nm in accord with the calculated diameter. Aggregation was also observed due to its hydrophobicity. After modified by F127, well-dispersed spherical porous particles were formed with the diameter in a range of hundreds of nanometers.

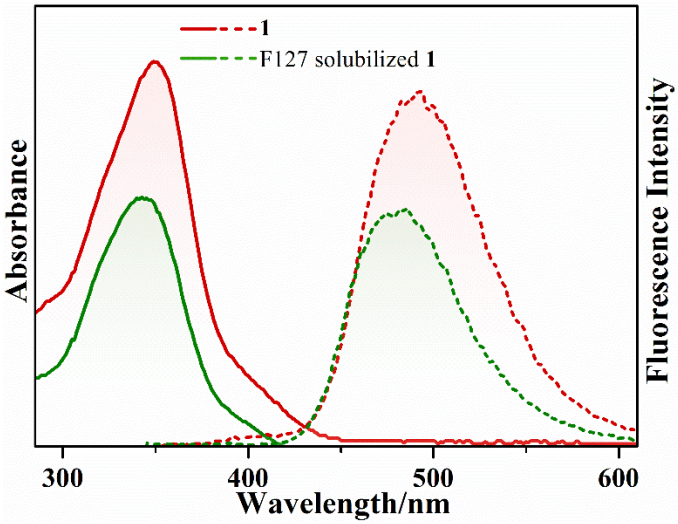

Fig. S7 UV-Vis absorption (solid lines) and fluorescence spectra (dash lines) of **1** in DMSO (red) or solubilized by F127 in PBS (green) with the same concentration of 3.0 $\times 10^{-6}$ M at room temperature.

NMR Spectra

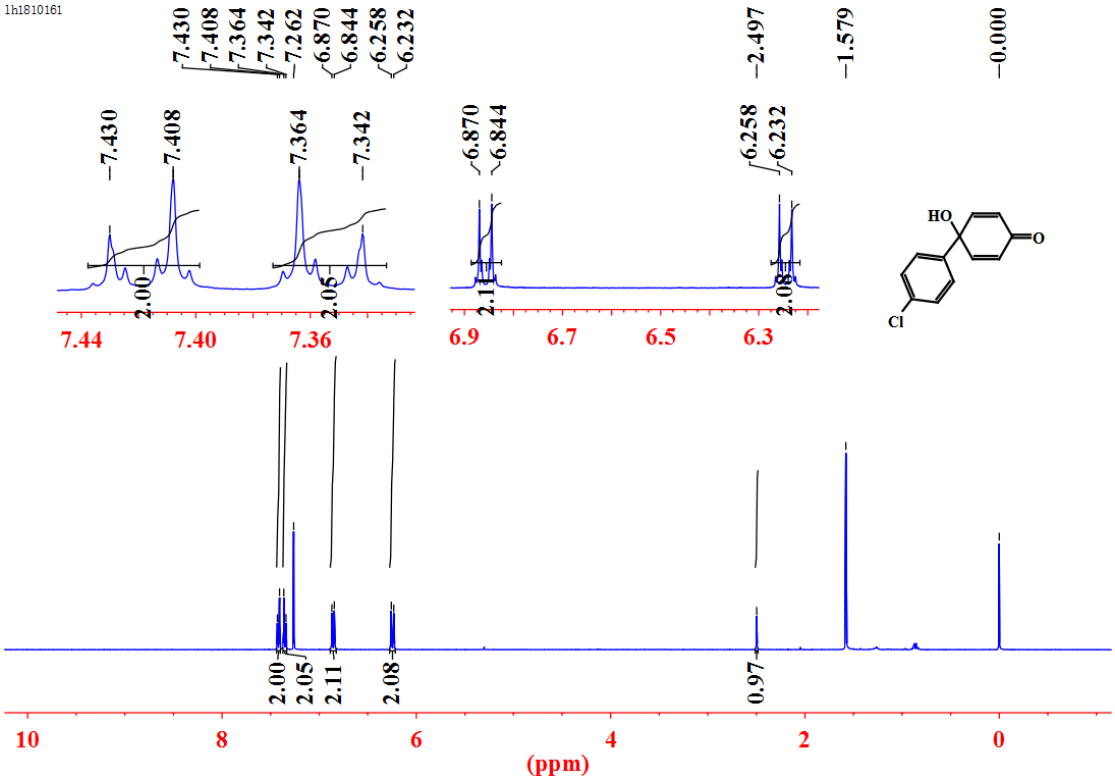

Fig. S8 ^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$).

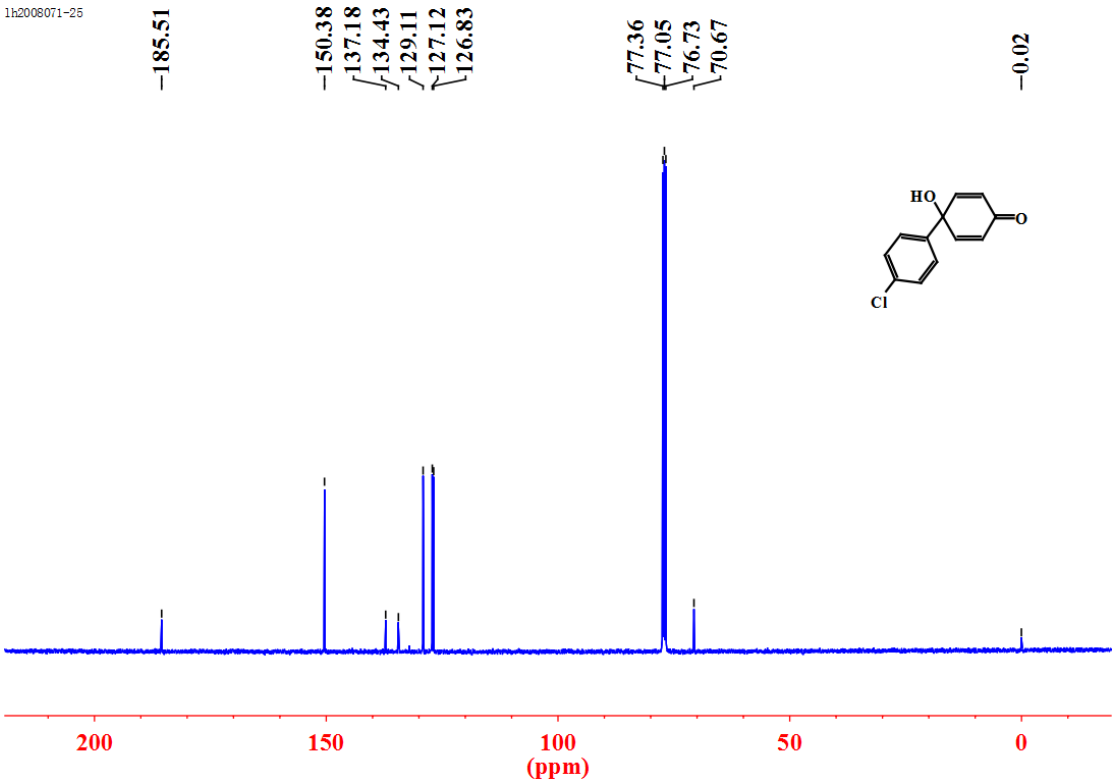

Fig. S9 ^{13}C NMR spectrum of compound **3** (100 MHz, $CDCl_3$).

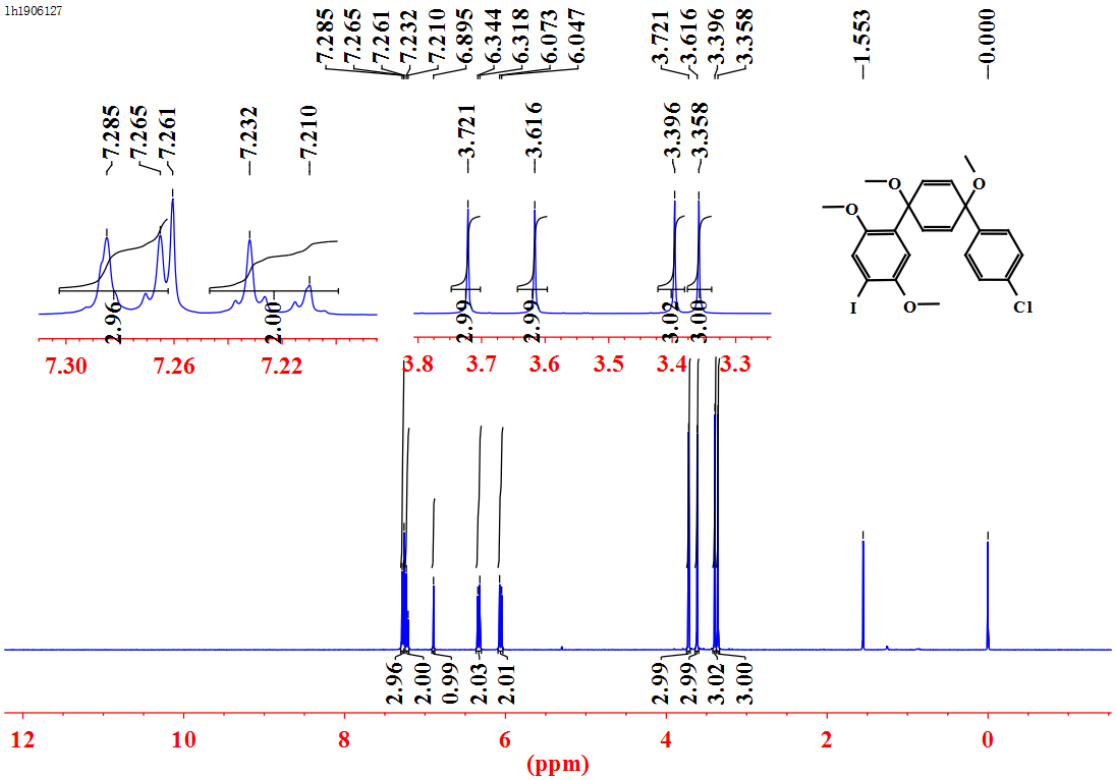

Fig. S10 ^{1}H NMR spectrum of compound **4** (400 MHz, $CDCl_3$).

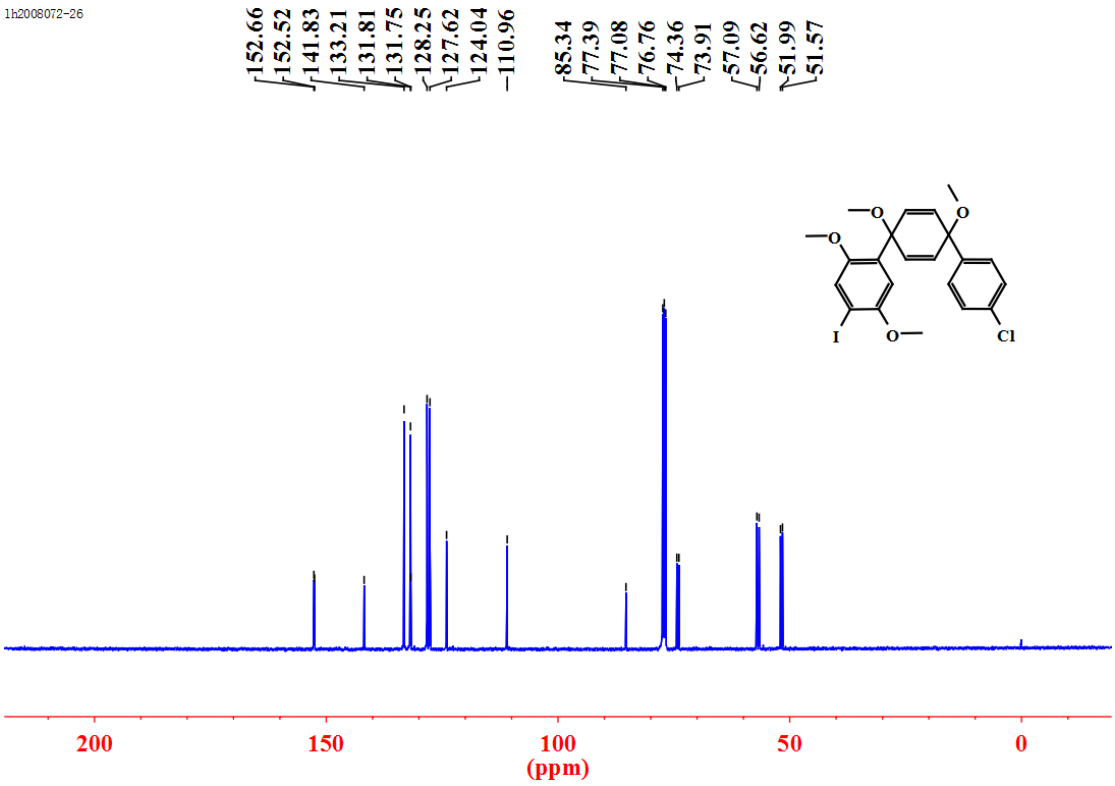

Fig. S11 ^{13}C NMR spectrum of compound **4** (100 MHz, $CDCl_3$).

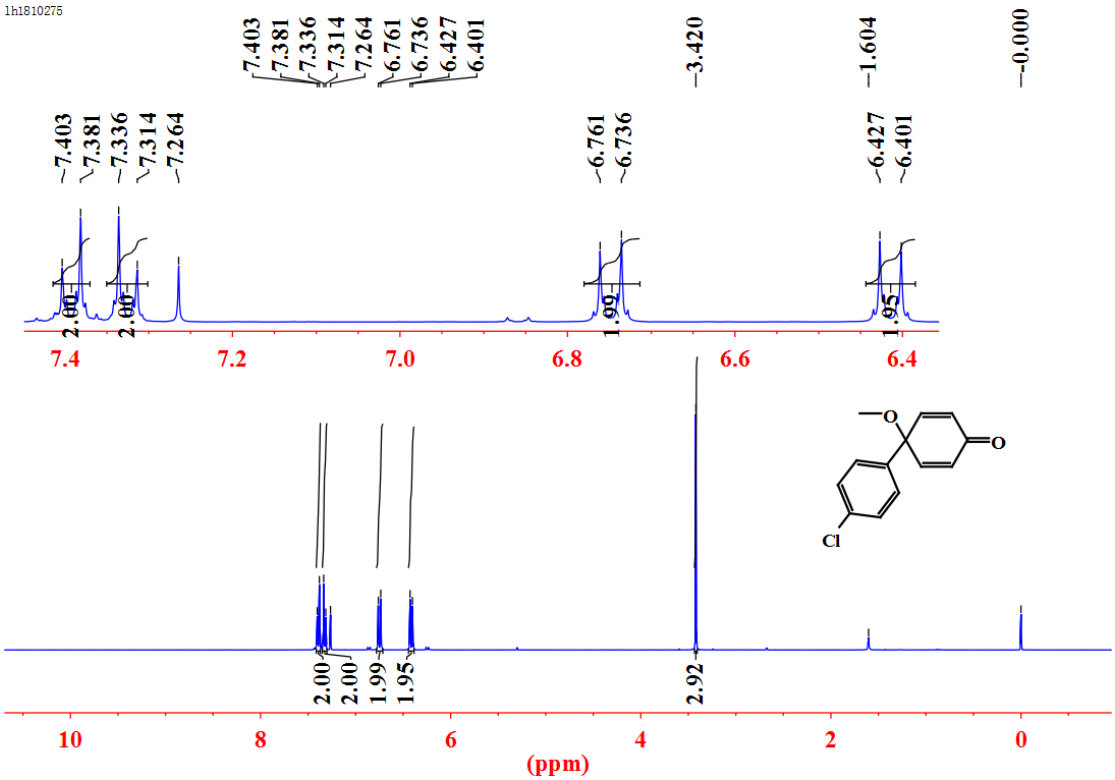

Fig. S12 ^{1}H NMR spectrum of compound **5** (400 MHz, $CDCl_3$).

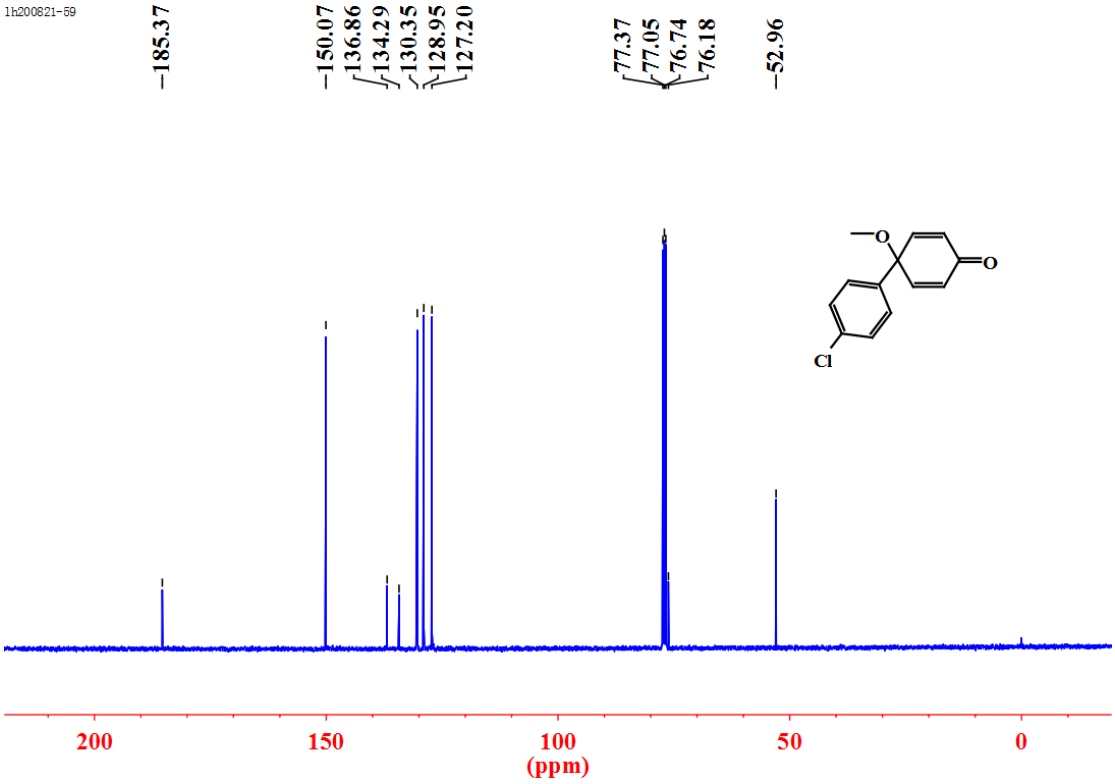

Fig. S13 ^{13}C NMR spectrum of compound **5** (100 MHz, $CDCl_3$).

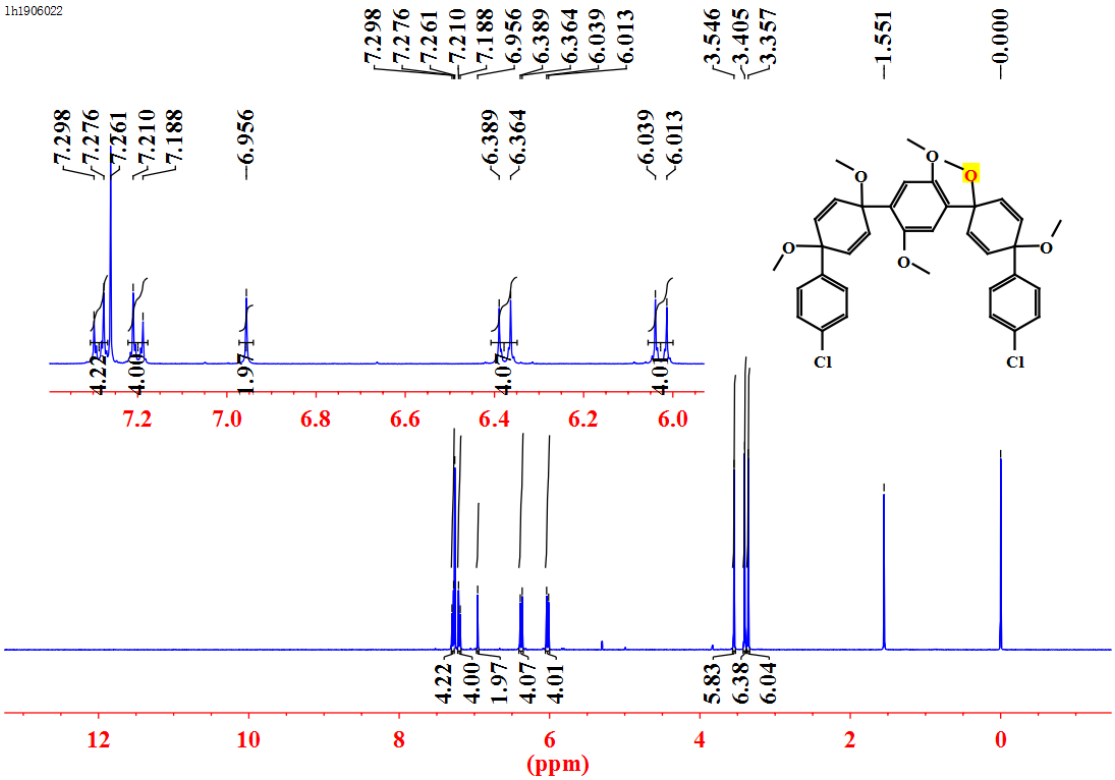

Fig. S14 ^{1}H NMR spectrum of compound **6** (400 MHz, $CDCl_3$).

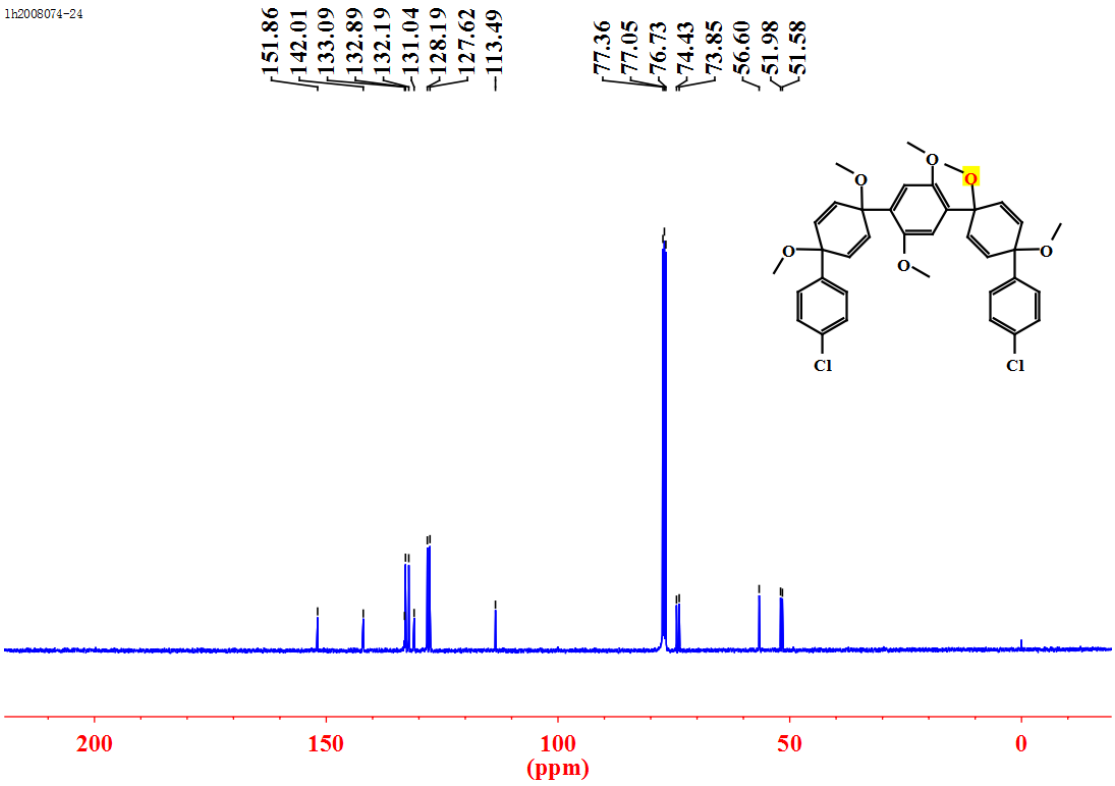

Fig. S15 ^{13}C NMR spectrum of compound **6** (100 MHz, $CDCl_3$).

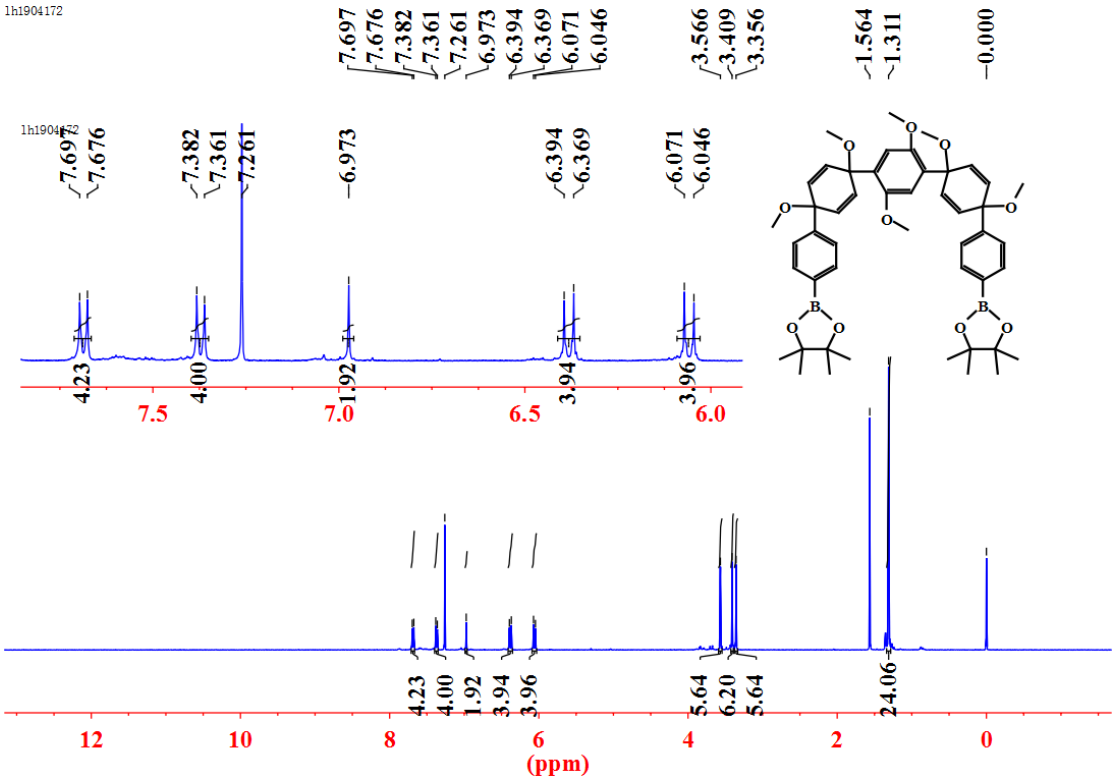

Fig. S16 ^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$).

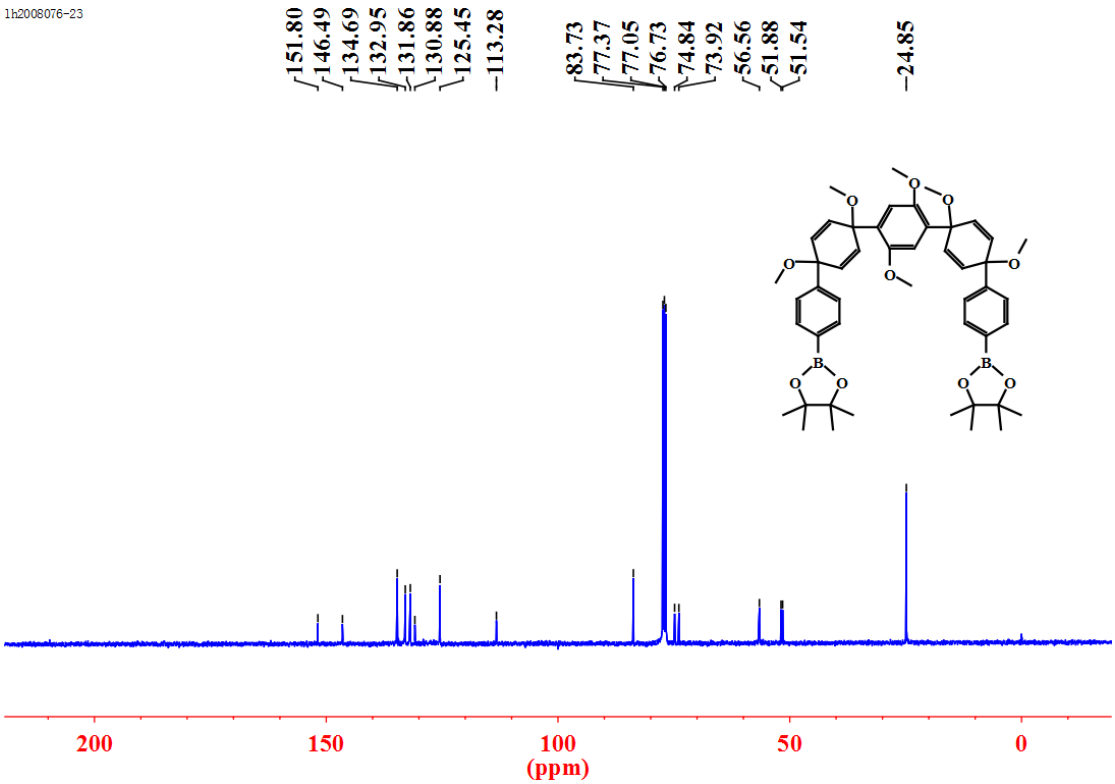

Fig. S17 ^{13}C NMR spectrum of compound **7** (100 MHz, $CDCl_3$).

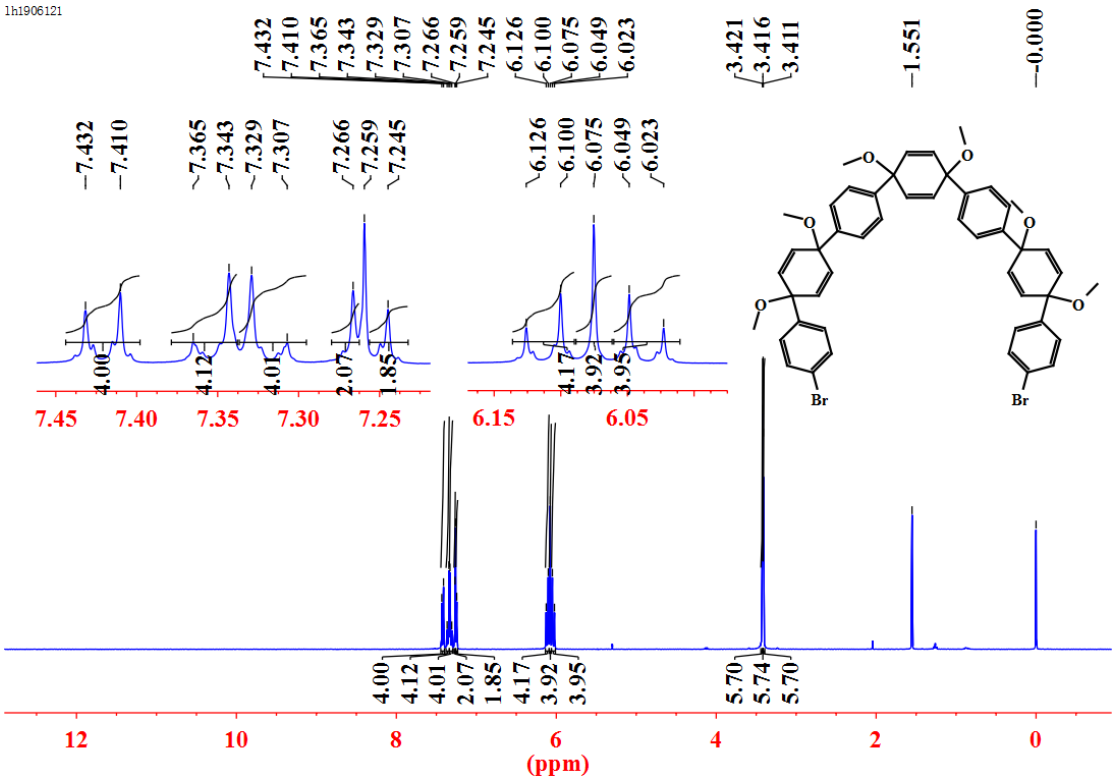

Fig. S18 ^{1}H NMR spectrum of compound **9** (400 MHz, $CDCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (d, *J* = 8.8 Hz, 4H), 7.35 (d, *J* = 8.8 Hz, 4H), 7.32 (d, *J* = 8.8 Hz, 4H), 7.26 (d, *J* = 8.4 Hz, 4H), 6.11 (d, *J* = 10.4 Hz, 4H), 6.08 (s, 4H), 6.04 (d, *J* = 10.4 Hz, 4H), 3.42 (s, 6H), 3.42 (s, 6H), 3.41 (s, 6H).

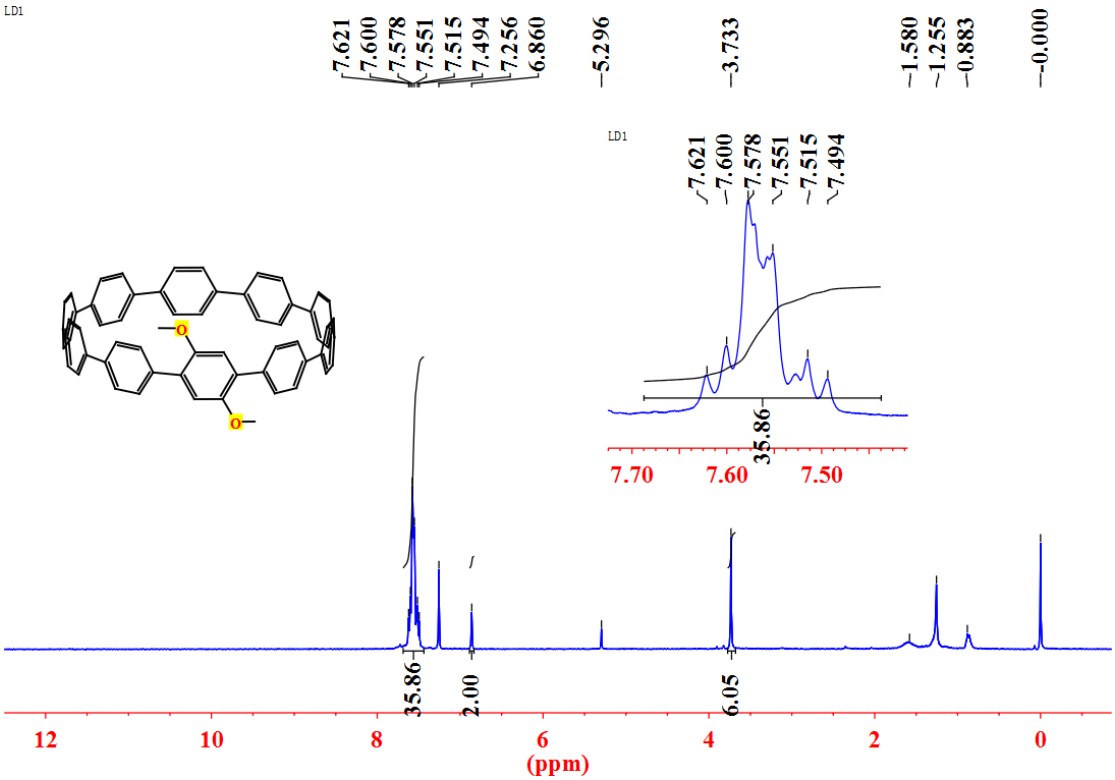

Fig. S19 ^{1}H NMR spectrum of compound **1** (400 MHz, $CDCl_3$).

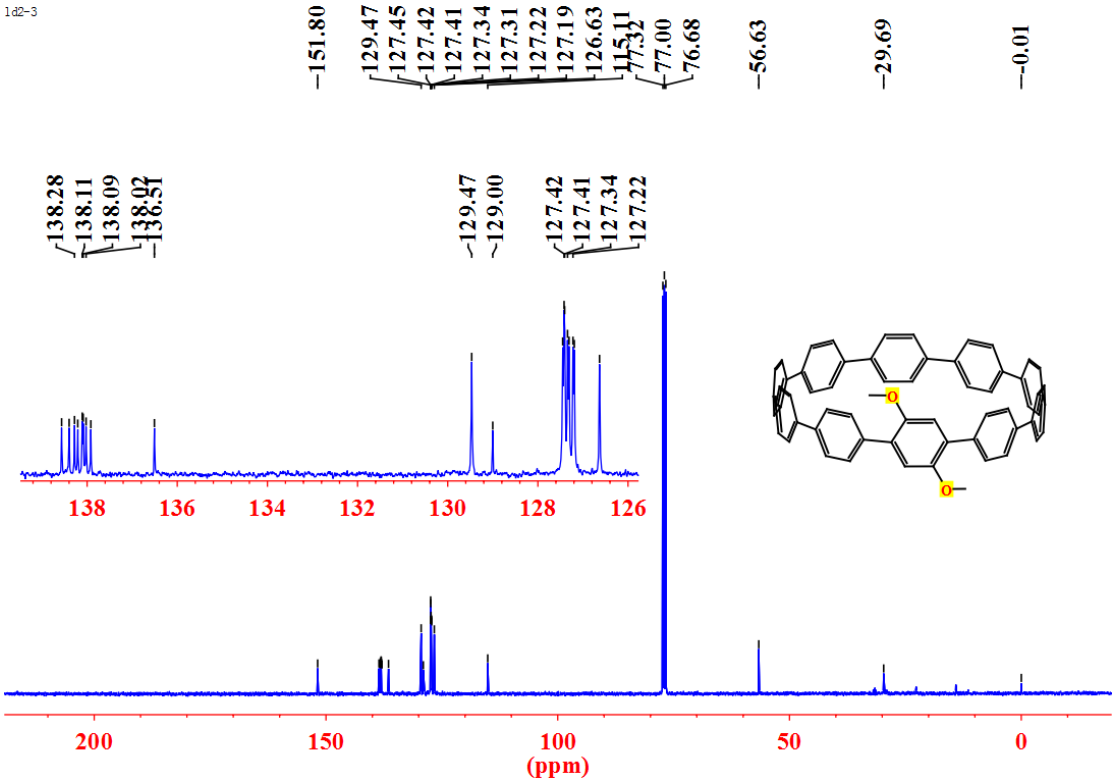

Fig. S20 ^{13}C NMR spectrum of compound **1** (100 MHz, $CDCl_3$).

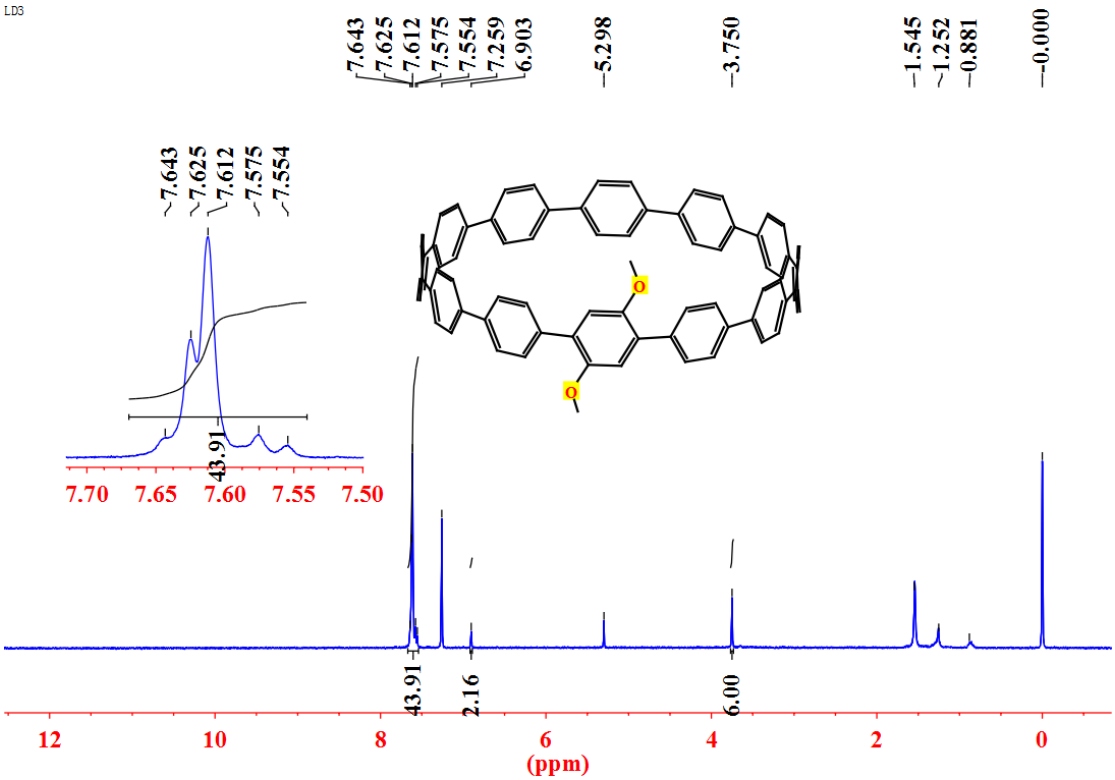

Fig. S21 ^{1}H NMR spectrum of compound **2** (400 MHz, $CDCl_3$).

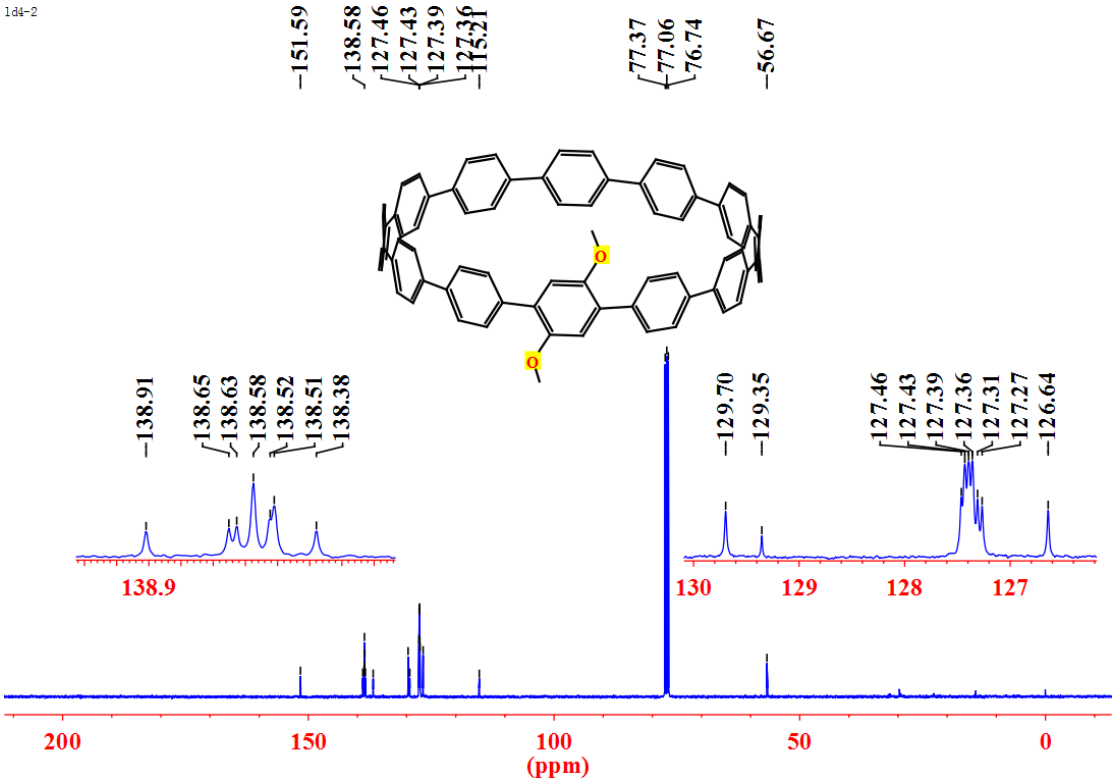

Fig. S22 ^{13}C NMR spectrum of compound **2** (100 MHz, $CDCl_3$).

HR-MS and Simulated Spectra for 1 and 2

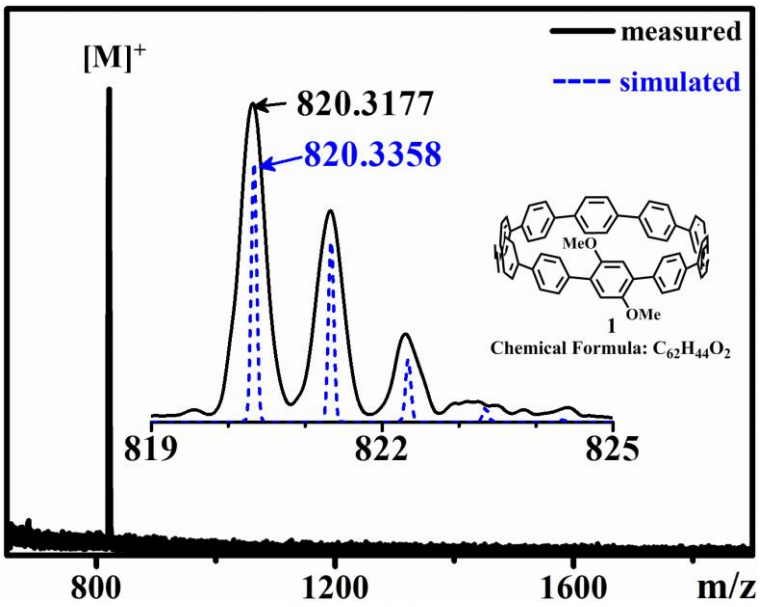

Fig. S23 HR-MS (MALDI-TOF MS) and simulated data for **1**.

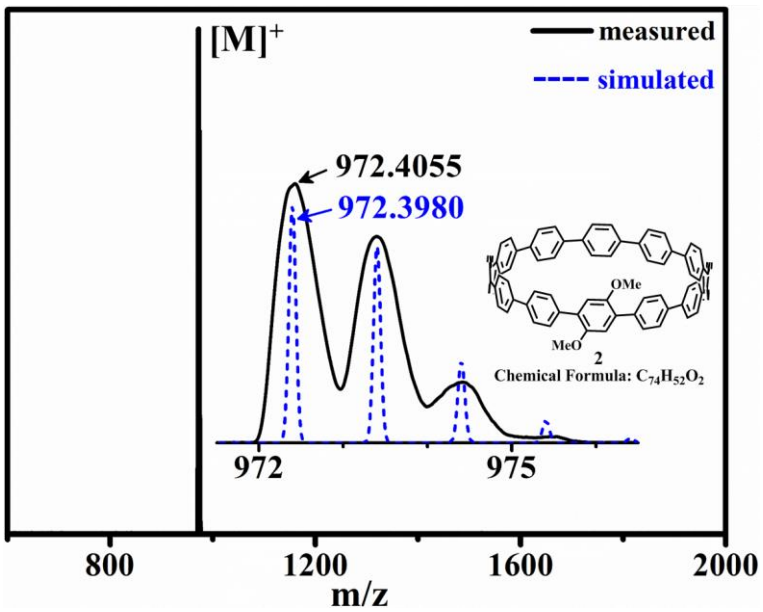

Fig. S24 HR-MS (MALDI-TOF MS) and simulated data for **2**.

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