Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Inherently chiral belt-shaped conjugated macrocycles with strong fluorescence and circularly polarized luminescence

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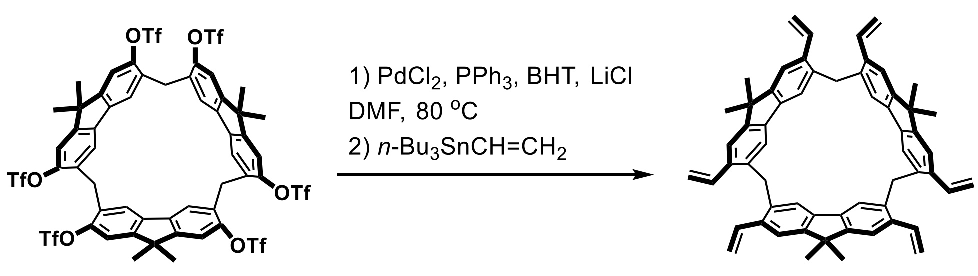
Contents

1. General information

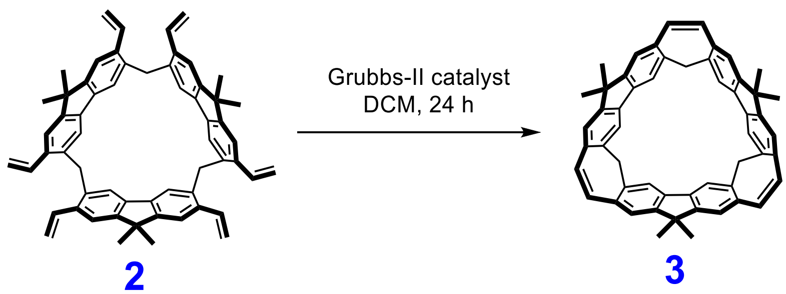
The commercially available reagents were used without further purification. Solvents were employed as purchased or dried with Molecular Sieves. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker 700 MHz spectrometer (or a Bruker 500 MHz spectrometer). High-resolution mass spectrum (HRMS) was obtained on an auto-flex TOF/TOF mass spectrometer. Single crystal data was collected on a Bruker Smart APEXII CCD diffractometer using graphite monochromated Cu Kα radiation. The UV-vis spectra were recorded on PerkinElmer® UV/Vis/NIR spectrometer (Lambda 950). Circular dichroism spectroscopy was recorded on a J-1700 spectrometer. Circularly polarized luminescence was recorded on a JASCO-300 spectrometer. Preparative silica gel plates separation and normal TLC analysis were performed on pre-coated, glass-backed silica gel plates. The energy-minimized structures were optimized using the Gaussian 16 program,[S1] based on the density functional theory (DFT) using the B3LYP functional and 6–31G(d) basis set.

2. Synthesis and characterizations

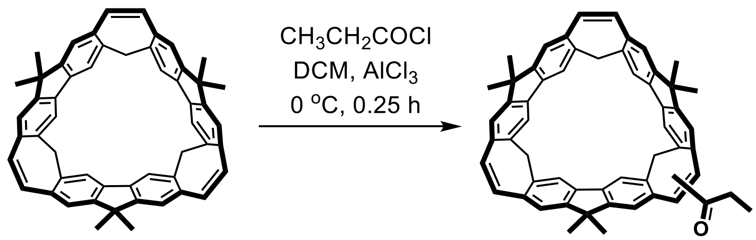


1 **2**

To a Schlenk tube was added **1** (750 mg, 0.5 mmol), $PdCl_2$(44 mg, 0.25 mmol), PPh_3 (131 mg, 0.5 mmol), BHT (55 mg, 0.25 mmol) and LiCl (840 mg, 20 mmol) under the protection of argon. Under the protection of argon, ultra-dry DMF (20 mL) was added. The reaction mixture was stirred at 80 ^{o}C under the protection of argon for 12h. The *n*-$Bu_3SnCH=CH_2$ (2.3 mL, 8 mmol) was added in one shot to the mixture, and the reaction mixture was stirred at 80 ^{o}C under the protection of argon for another 12h. After cooling down to room temperature, the reaction mixture was poured into and aqueous solution of KOH (~5M, 100 mL) and the resulting mixture was extracted with DCM (3 × 50 mL). The organic layer concentrated using a rotavapor. The residue was chromatographed on a silica gel column using a mixture of *n*-hexane and DCM (V: V = 8: 0 to 8: 1) as mobile phase to give pure product **2** (240 mg, 85%) as a white solid. M.p.: >280 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.53 (s, 6H), 7.44 (s, 6H), 7.12 (dd, *J* = 17.2, 11.0 Hz, 6H), 5.69 (d, *J* = 17.3 Hz, 6H), 5.32 (d, *J* = 10.9 Hz, 6H), 4.13 (s, 6H), 1.51 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ 152.3, 138.7, 137.1, 136.0, 135.5, 121.6, 120.2, 115.5, 46.6, 35.0, 27.5. MALDI-TOF-HRMS: *m/z* calcd for $[M]^{+}$: $C_{60}H_{54}^{+}$: 774.4226, found 774.4224.



To a Schlenk tube was added **2** (77.4 mg, 0.1 mmol) and the Grubbs-II catalyst (136mg, 0.16 mmol) in dry DCM (5 mL) under argon. The mixture was refluxed for 12 h. After cooling down to room temperature, the reaction mixture was concentrated using a rotavapor. The residue was chromatographed on a silica gel column (230-400 mesh) using a mixture of petroleum ether and DCM (V: V = 8: 1) as mobile phase to give pure product **3** (32 mg, 70%) as a white solid. M.p.: >280 °C. ^{1}H NMR (700 MHz, $CDCl_3$, 298 K): δ 7.57 (s, 6H), 7.08 (s, 6H), 7.07 (s, 6H), 3.96 (d, *J* = 11.8 Hz, 3H), 3.56 (d, *J* = 11.8 Hz, 3H), 1.48 (s, 9H), 1.06 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$, 298 K): δ 151.4, 140.3, 137.9, 133.8, 130.9, 121.0, 118.2, 47.0, 41.0, 28.8, 25.9. MALDI-TOF-HRMS: *m/z* calcd for $[M]^{+}$: $C_{54}H_{42}^{+}$: 690.3287, found 690.3281.



To a 5.0 mL flask was added **3** (13.8 mg, 0.02 mmol) and dry DCM (2.0 mL) under argon. The solution was cooled down to 0 °C, then $AlCl_3$ (2.7 mg, 0.02 mmol) was added quickly. The mixture was stirred for 5 minute and the solution of propionyl chloride (1.9 mg, 0.02 mmol) in dry DCM was added in one shot. The reaction was kept for 0.25 hour and quenched by adding distilled water. The mixture was heavily stirred for 1.0 hour and extracted three times. The organic phase was concentrated using a rotavapor at room temperature. The residue was chromatographed on a silica gel column (230 -400 mesh) using a mixture of *n*-hexane and DCM (V: V = 1: 5) as mobile phase to give pure product **4** (8.3 mg, 56%). M.p.: **>**280 °C. ^{1}H NMR (700 MHz, CD_2Cl_2, 298 K): δ 7.92 (s, 1H), 7.63 (s, 1H), 7.61 (s, 1H), 7.52 (s, 1H), 7.49 (s, 1H), 7.46 (d, *J* = 3.3 Hz, 2H), 7.19 (s, 1H), 7.18 (s, 1H), 7.18 (s, 1H), 7.07 (s, 1H), 7.06 (s, 1H), 7.05 (s, 1H), 7.04 (s, 1H), 5.61 (d, *J* = 2.9 Hz, 2H), 3.99 (d, *J* = 12.6 Hz, 1H), 3.91 (dd, *J* = 24.8, 12.1 Hz, 2H), 3.79 (d, *J* = 12.7 Hz, 1H), 3.61 (dd, *J* = 13.9, 12.1 Hz, 2H), 3.02 (ddd, *J* = 17.1, 14.6, 7.3 Hz, 1H), 2.90 (dq, *J* = 17.2, 7.3 Hz, 1H), 1.49 (s, 3H), 1.48 (s, 3H), 1.40 (s, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 1.08 (s, 6H), 1.01 (s, 3H). ^{13}C NMR (176 MHz, CD_2Cl_2, 298 K, TMS as standard): δ 202.7, 153.3, 153.2, 152.4, 152.2, 152.0, 151.9, 147.7, 141.93, 141.87, 141.41, 141.38, 141.2, 140.2, 139.89, 139.88, 139.75, 139.69, 139.6, 138.7, 138.4, 137.9, 136.8, 134.9, 133.3, 132.8, 131.5, 131.1, 130.6, 123.8, 122.2, 121.7, 121.1, 120.92, 120.86, 120.1, 120.0, 118.9, 118.72, 118.70, 118.5, 107.0, 48.2, 48.1, 46.7, 41.12, 41.11, 39.8, 33.2, 30.1, 29.6, 29.5, 28.7, 26.3, 25.2, 25.1, 9.0. MALDI-TOF-HRMS: *m/z* calcd for $[M]^{+}$: $C_{57}H_{46}^{+}$: 746.3549, found 746.3543.

3. NMR and mass spectra of new compounds

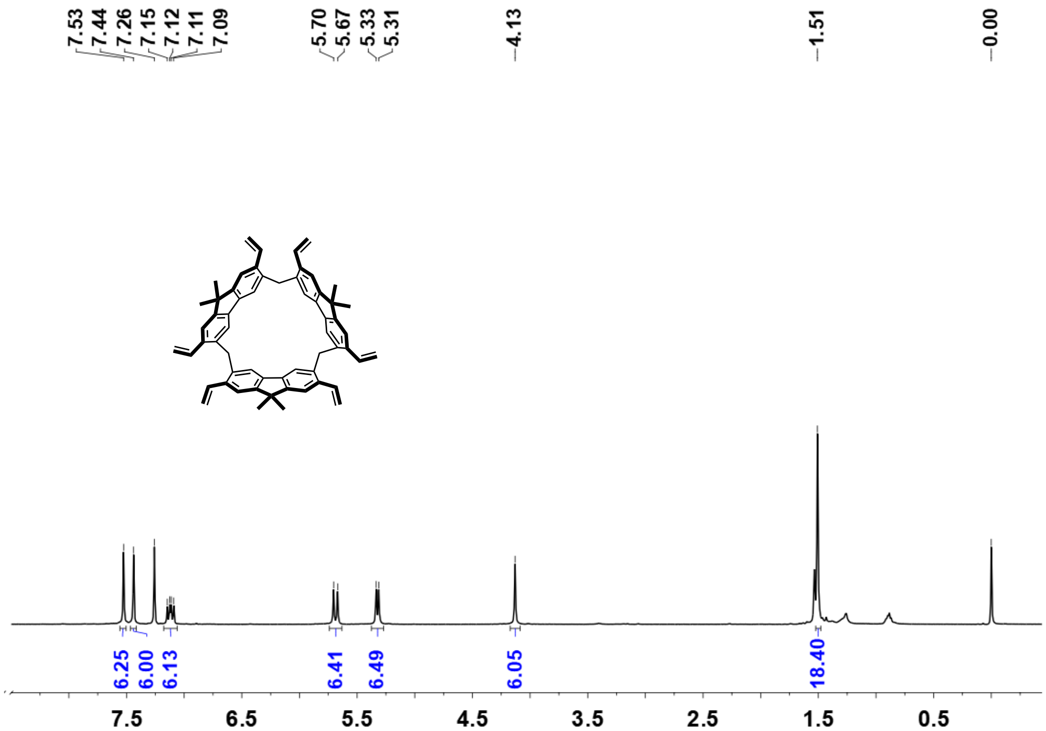


Fig. S1 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **2**.

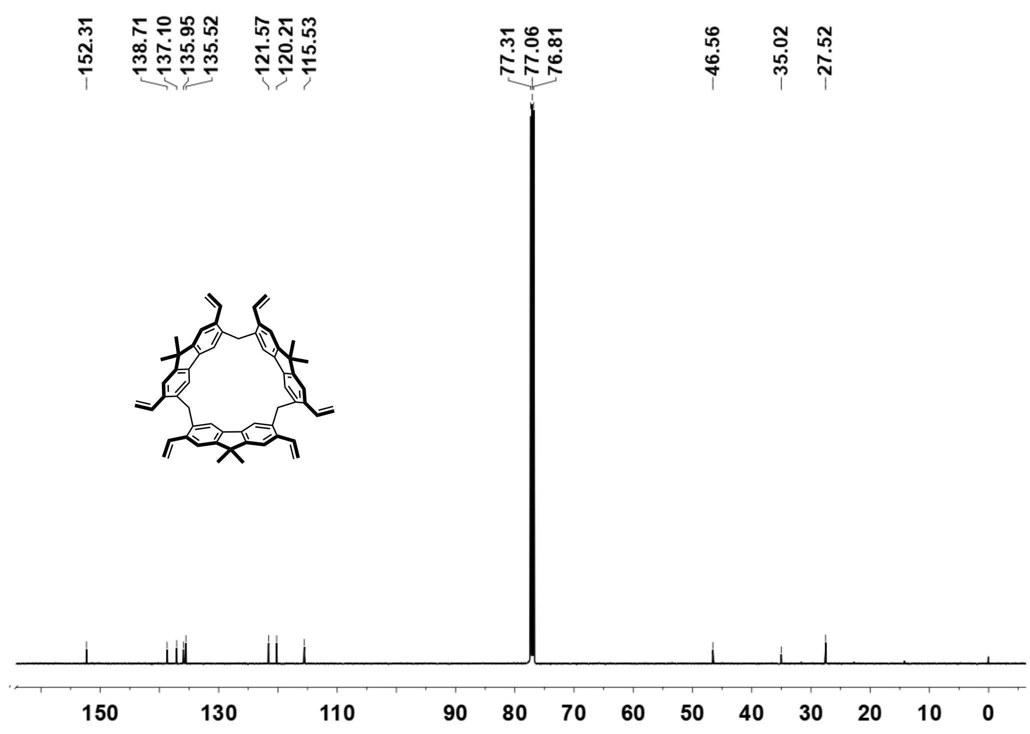


Fig. S2 ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 298 K) of **2**.

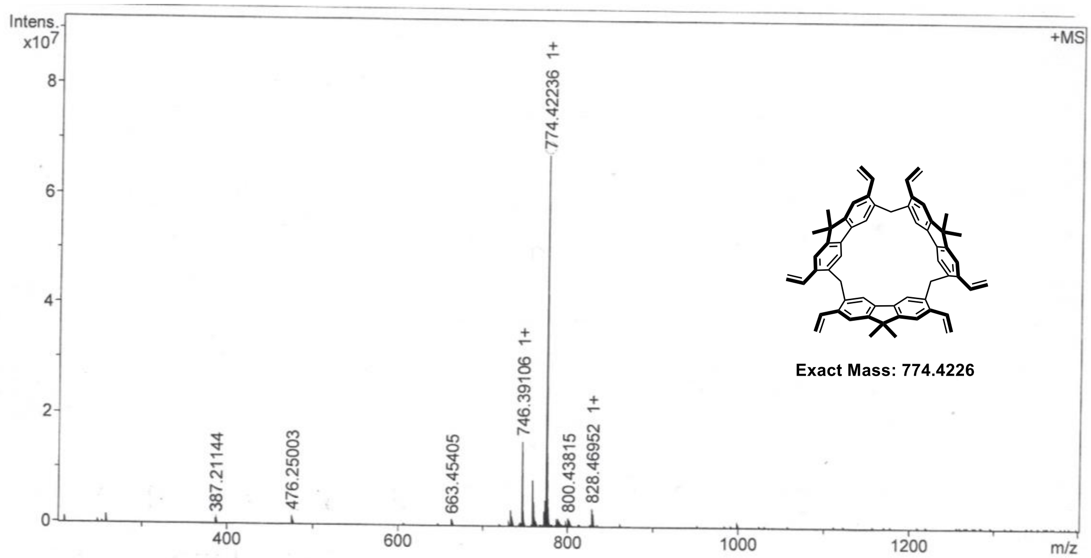


Fig. S3 MALDI-TOF-HRMS spectrum of **2**.

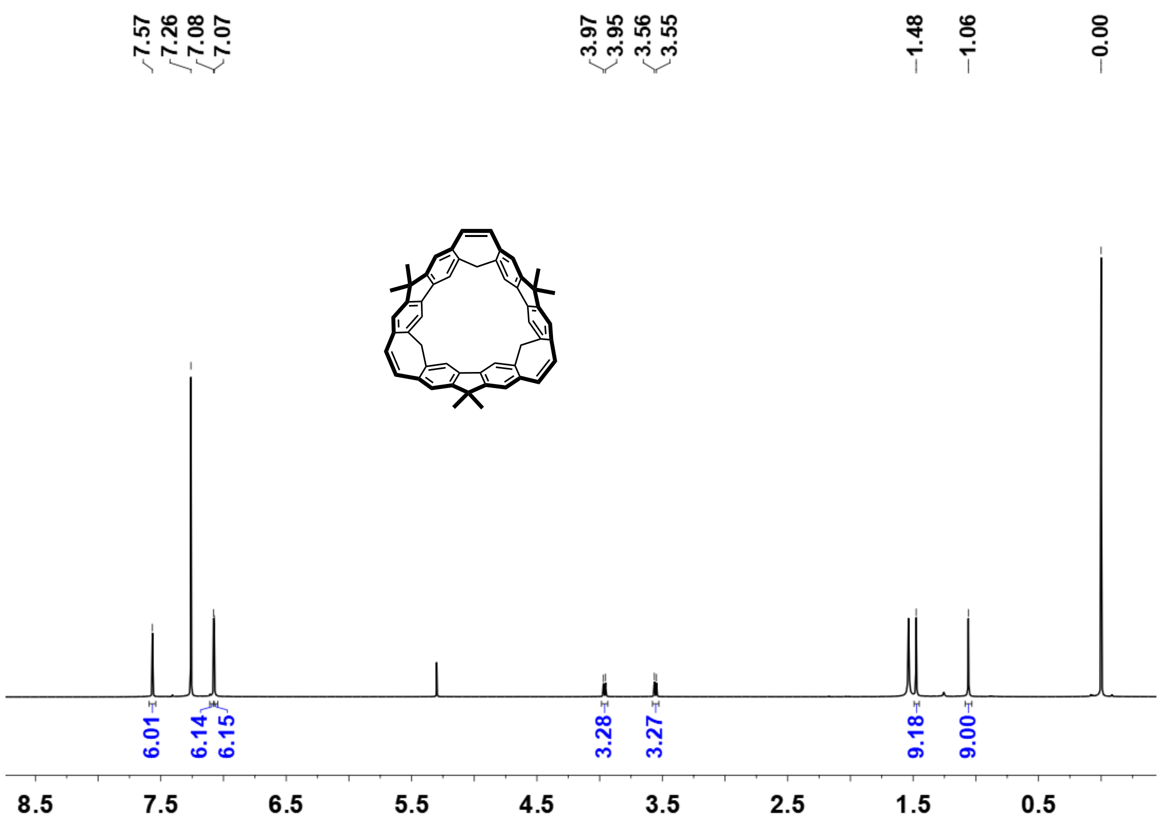


Fig. S4 ^{1}H NMR spectrum (700 MHz, $CDCl_3$, 298 K) of **3**.

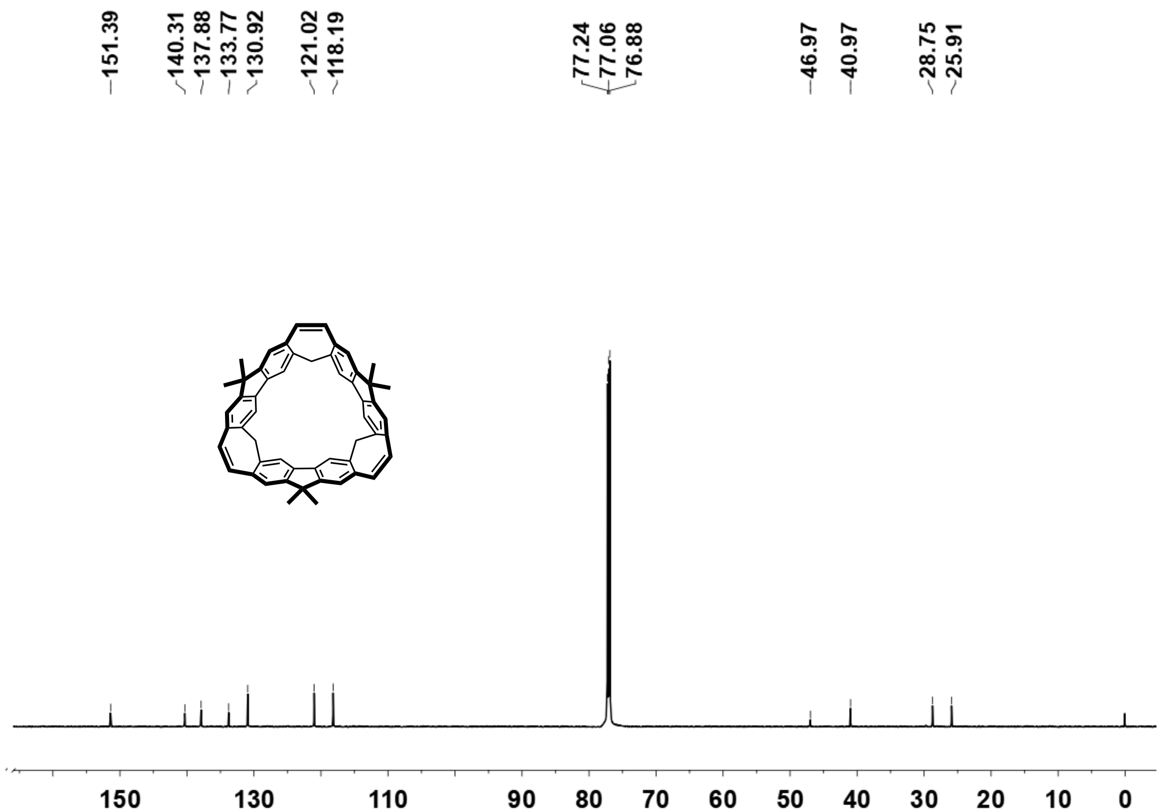


Fig. S5 ^{13}C NMR spectrum (176 MHz, $CDCl_3$, 298 K) of **3**.

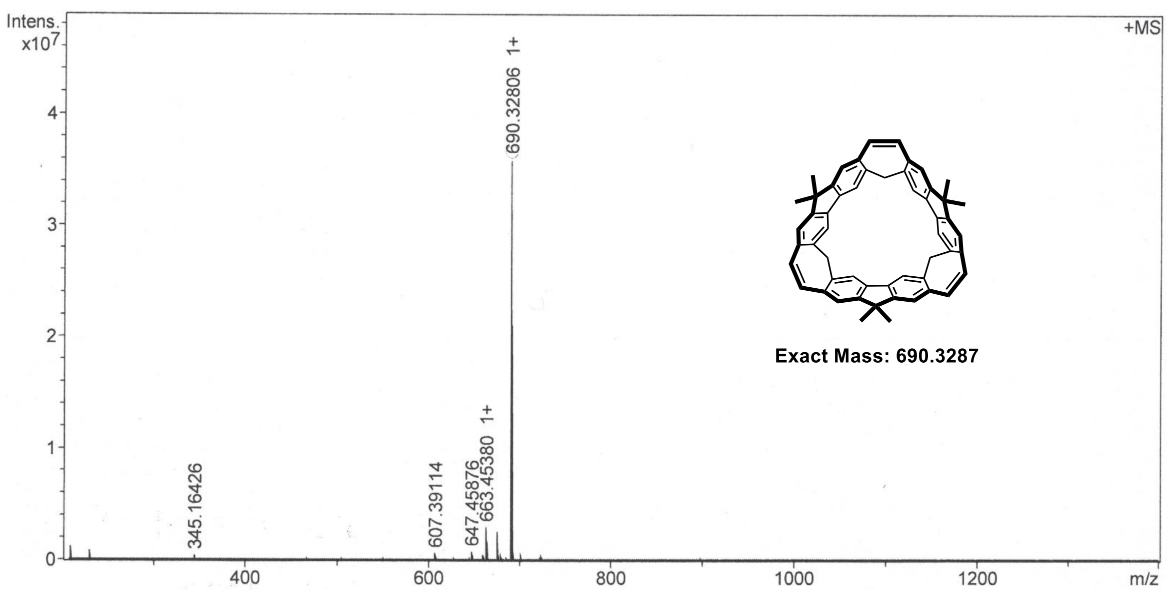


Fig. S6 MALDI-TOF-HRMS spectrum of **3**.

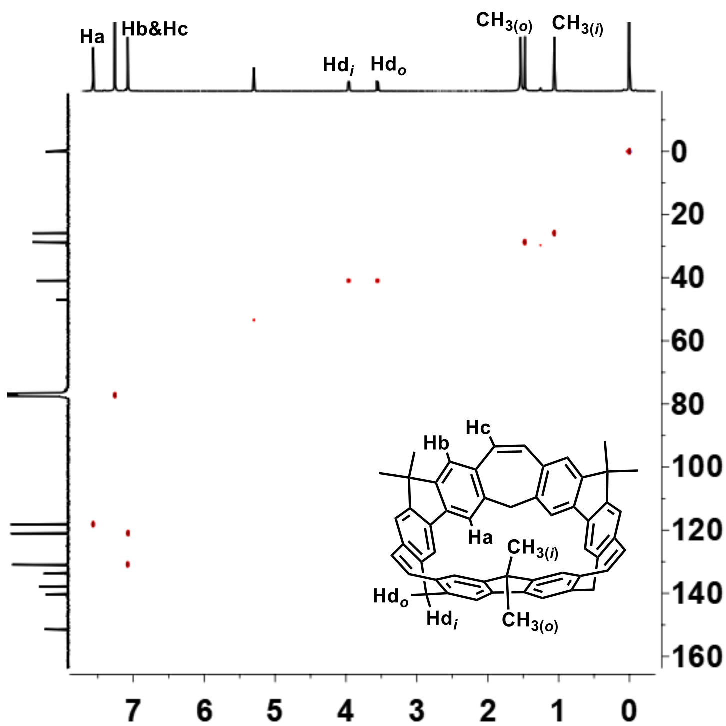


Fig. S7 ^{1}H-^{13}C HSQC spectrum (700 MHz, $CDCl_3$, 298 K) of **3**.

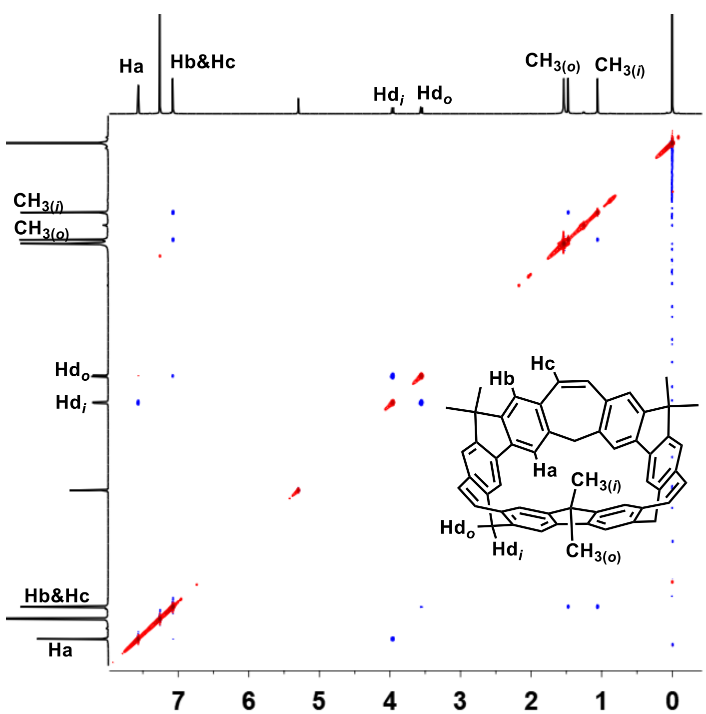


Fig. S8 2D NOESY spectrum (700 MHz, $CDCl_3$, 298 K) of **3**.

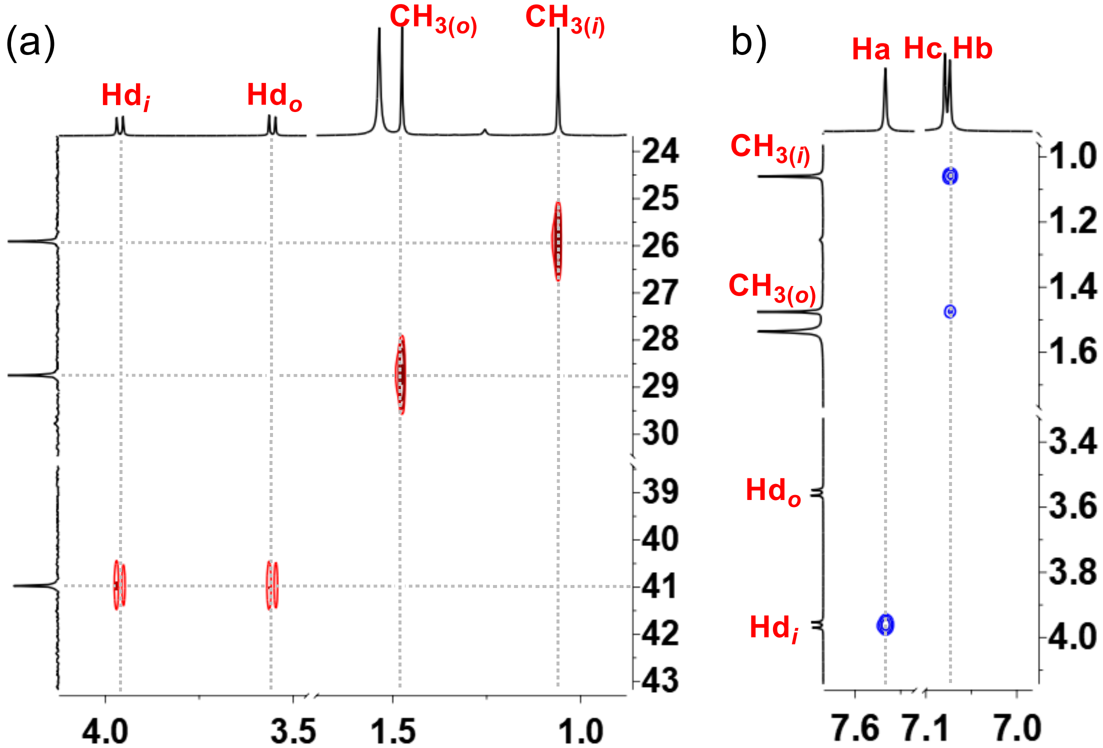


Fig. S9 (a) Partial ^{1}H-^{13}C HSQC spectrum and (b) partial NOESY spectrum of **3**.

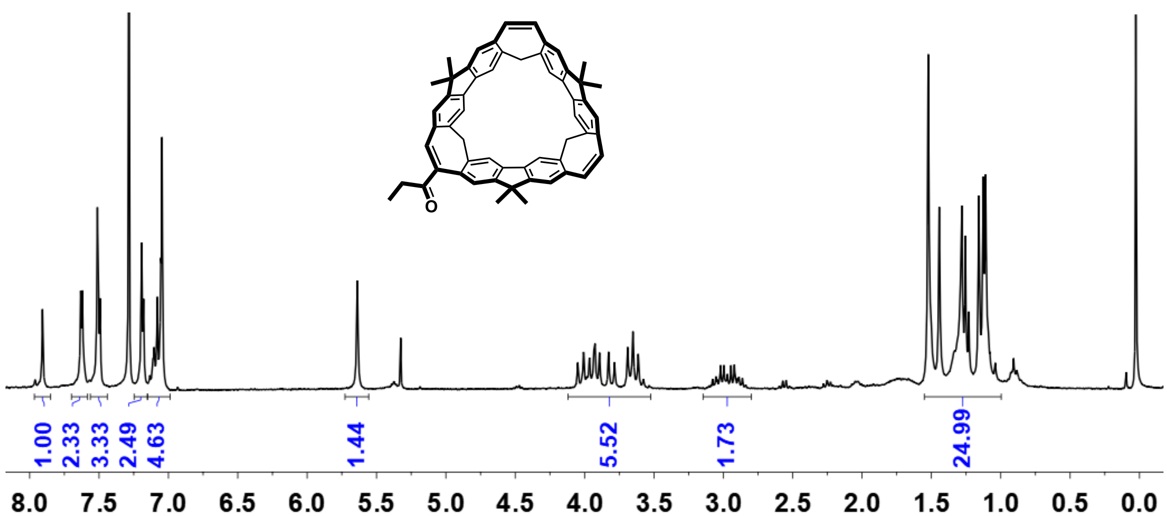


Fig. S10 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298K) of **4** before HPLC resolution.

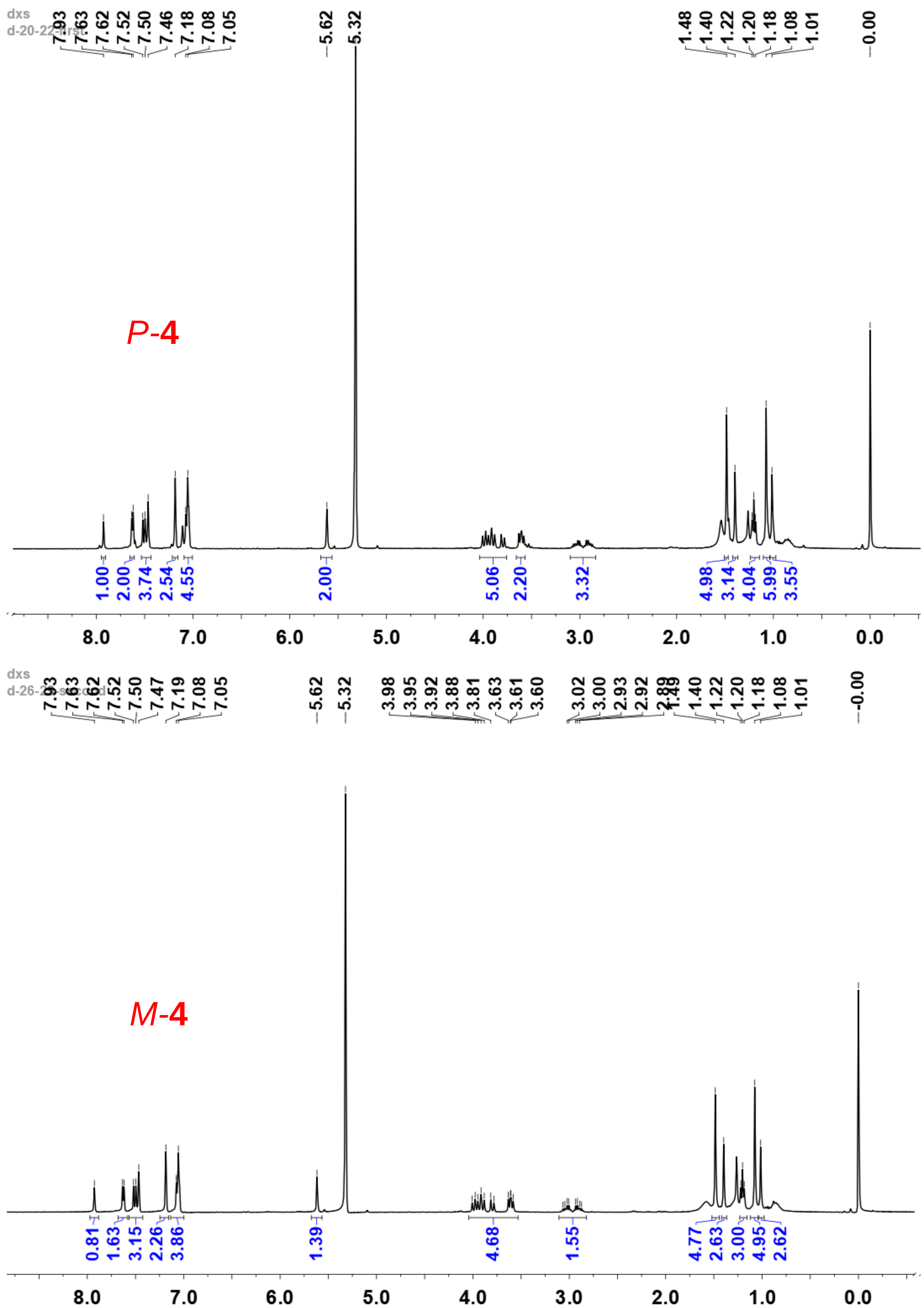


Fig. S11 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298K) of *P*-**4** and *M*-**4**.

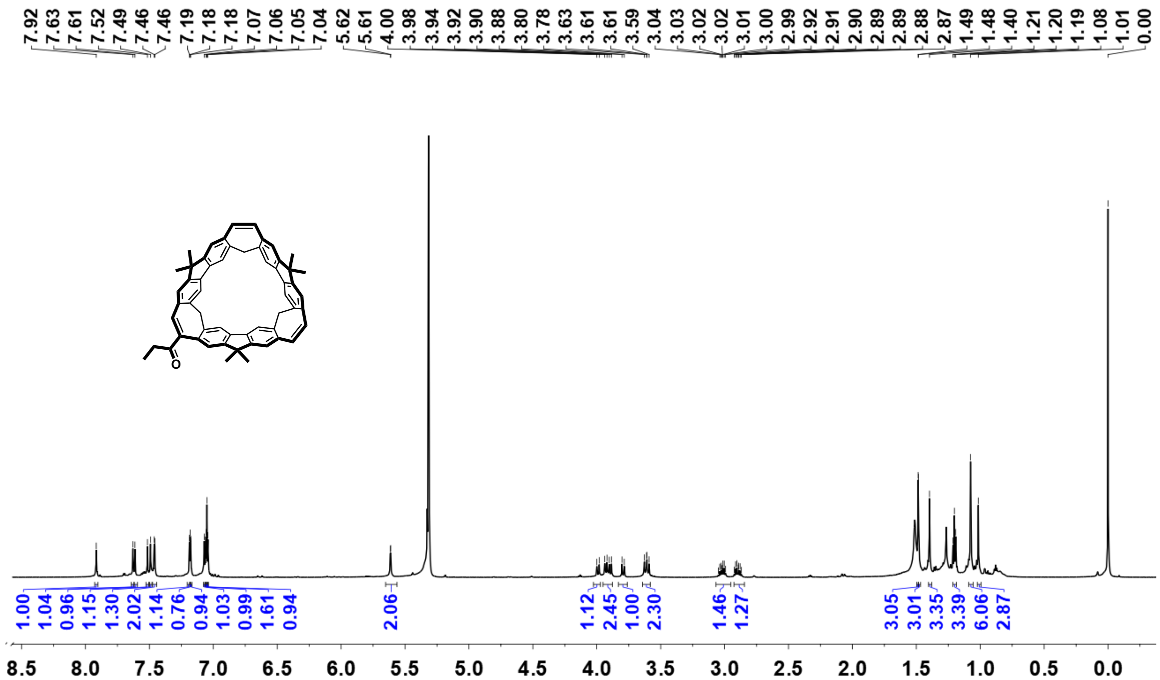


Fig. S12 ^{1}H NMR (700 MHz, CD_2Cl_2, 298 K) spectrum of *M*-**4**.

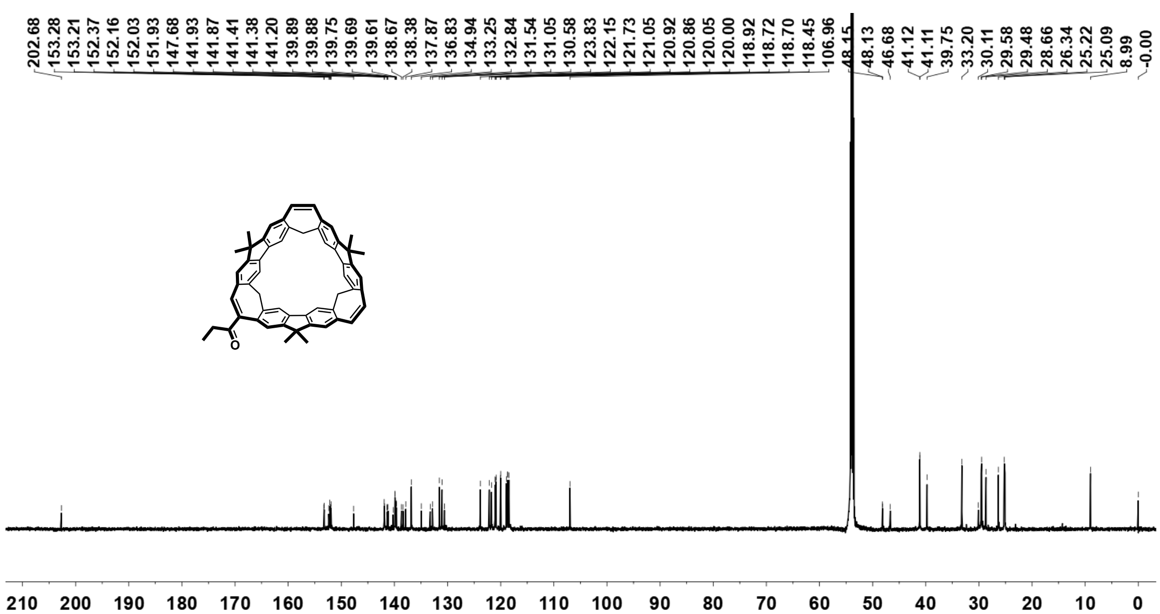


Fig. S13 ^{13}C NMR (176 MHz, CD_2Cl_2, 298 K) spectrum of *M*-**4**.

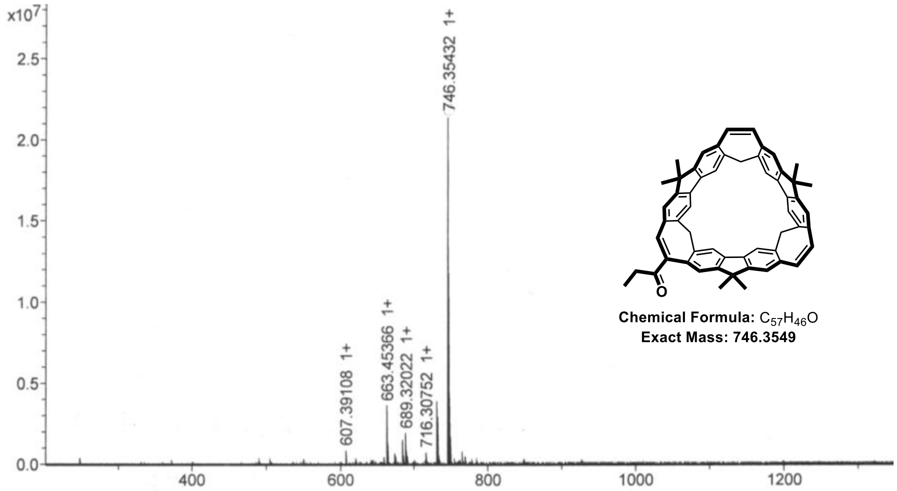


Fig. S14 MALDI-TOF-HRMS spectrum of **4**.

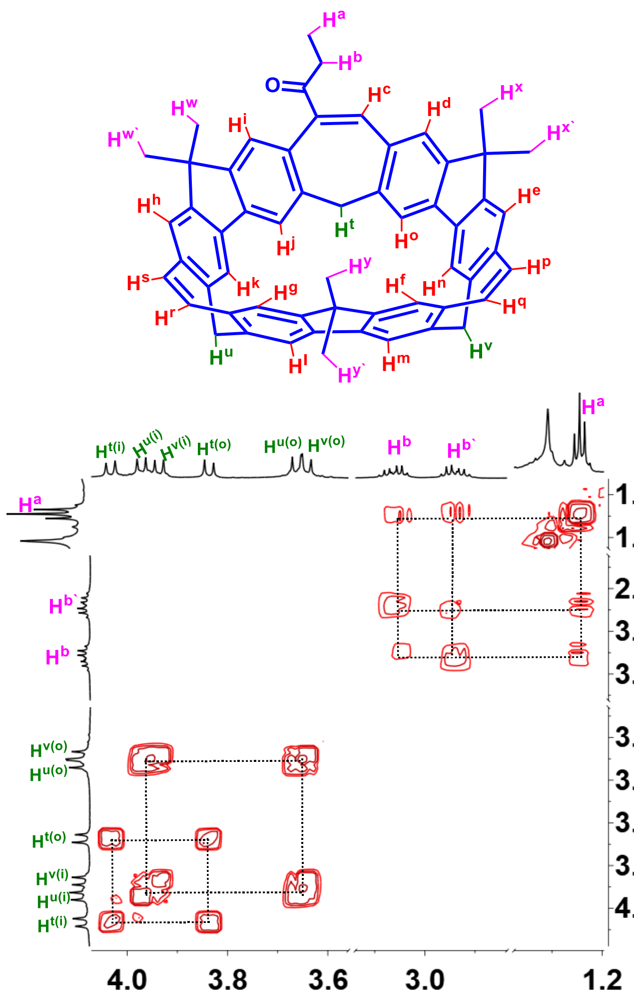


Fig. S15 ^{1}H-^{1}H COSY spectrum (700 MHz, $CDCl_3$, 298 K) of *M*-**4**.

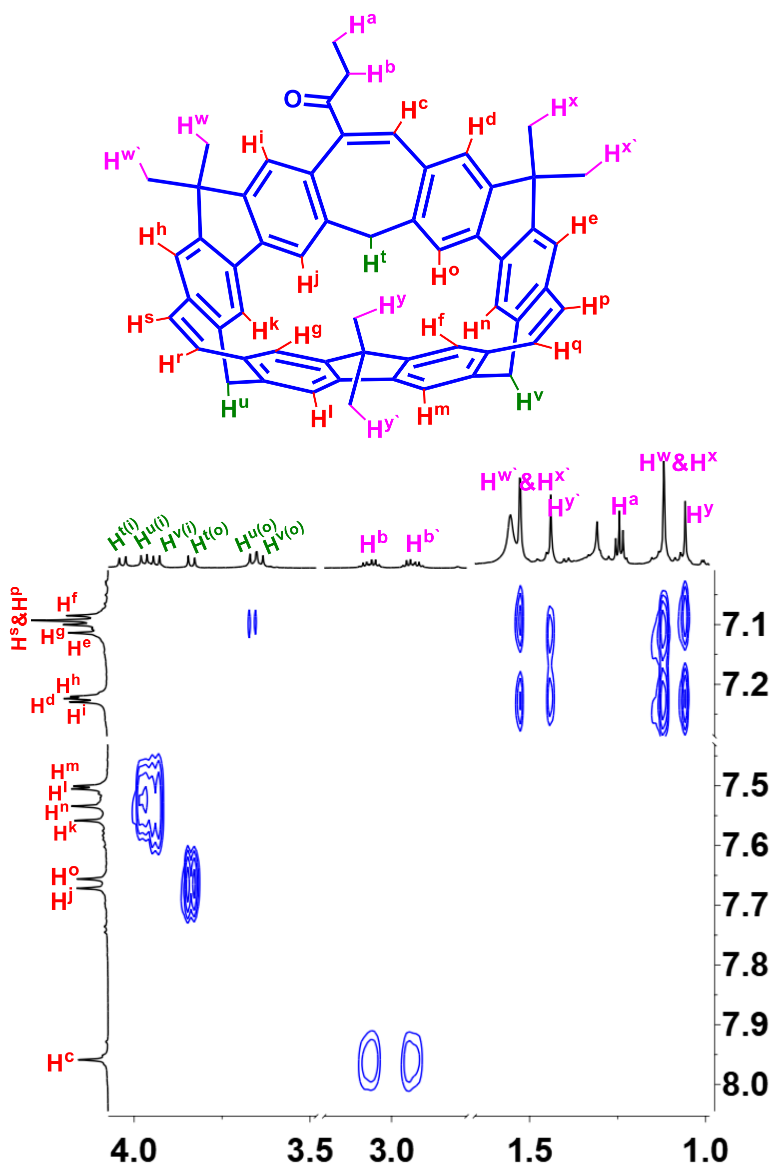


Fig. S16 2D NOESY spectrum (700 MHz, CDCl₃, 298 K) of *M*-**4**.

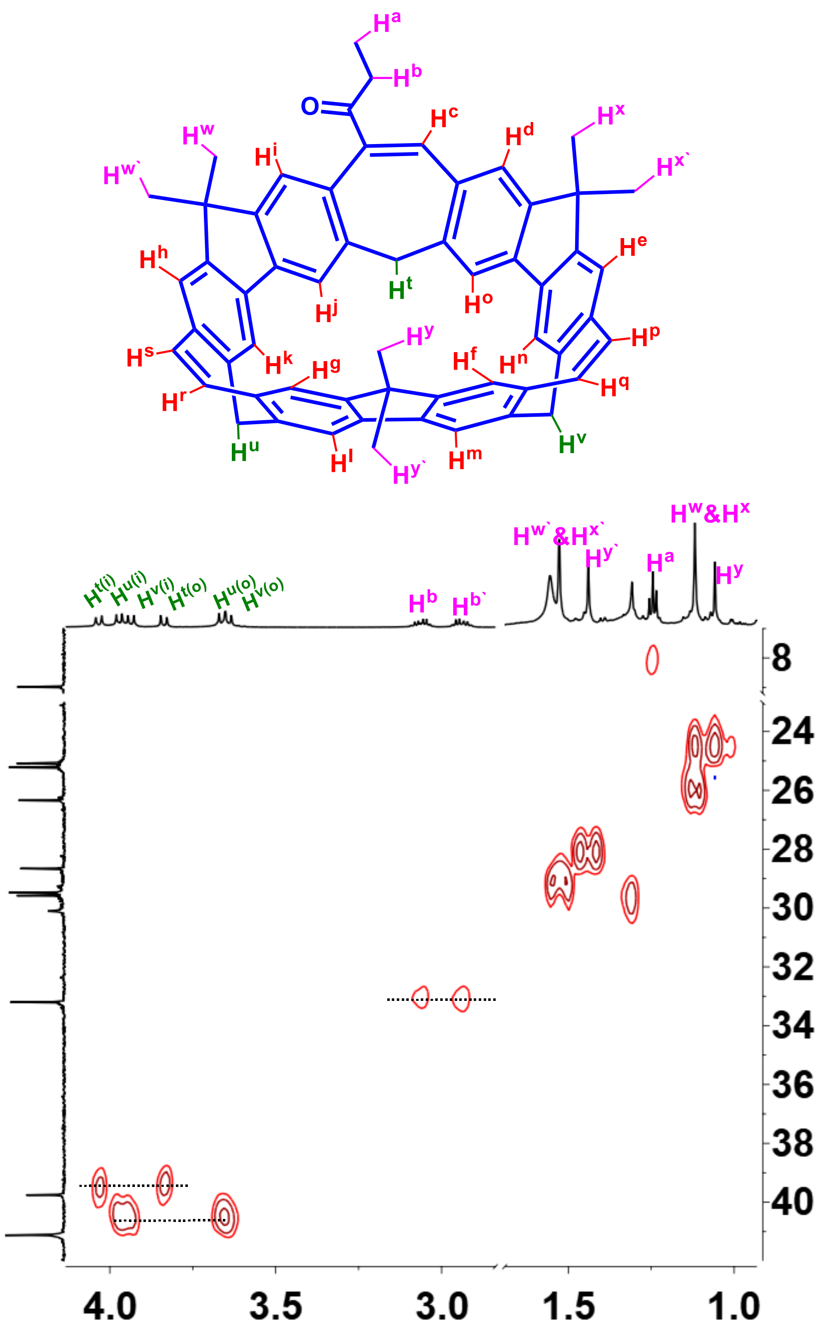


Fig. S17 ^{1}H-^{13}C HSQC spectrum (700 MHz, $CDCl_3$, 298 K) of *M*-**4**.

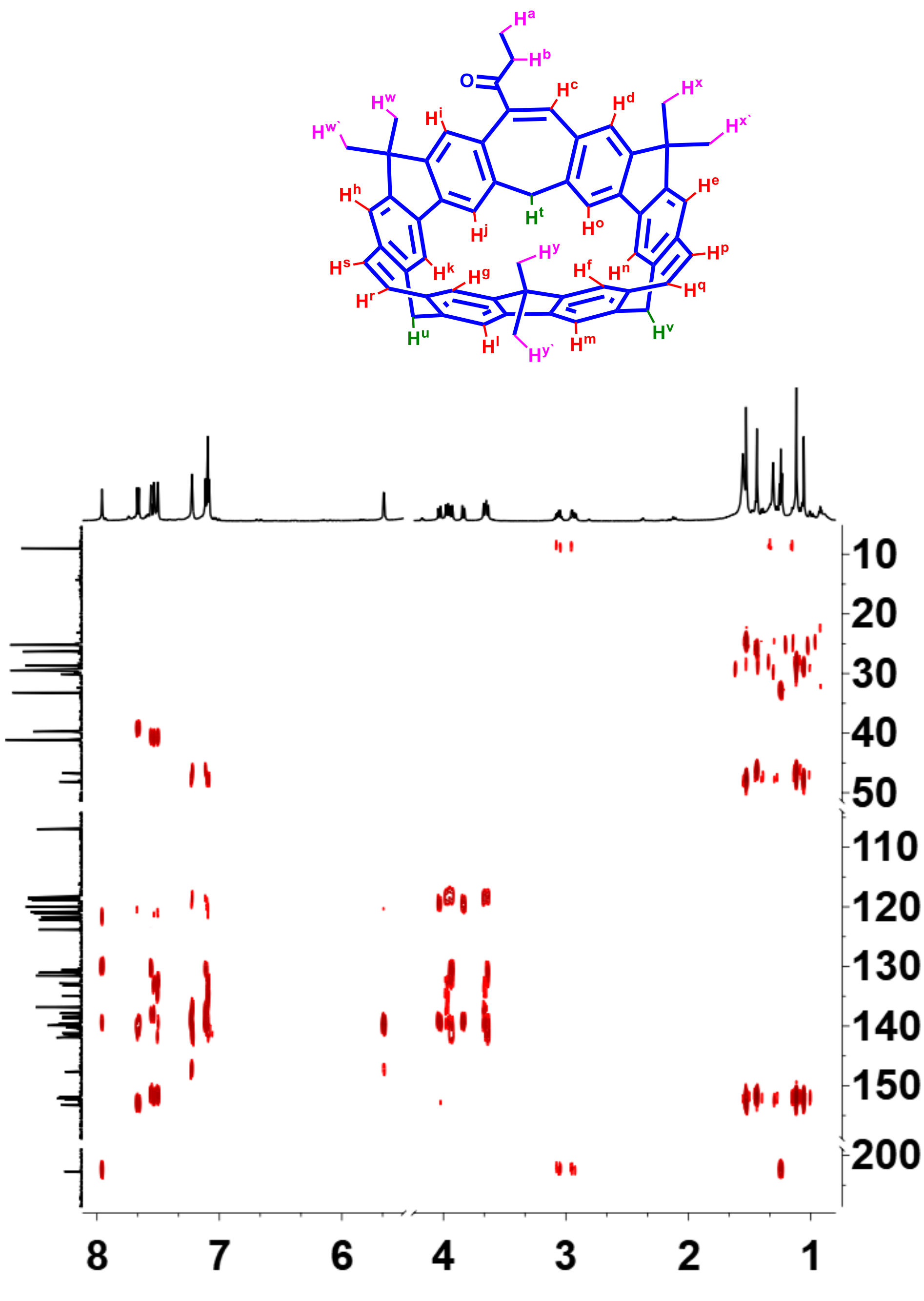


Fig. S18 ^{1}H-^{13}C HMBC spectrum (700 MHz, $CDCl_3$, 298 K) of *M*-**4**.

4. HPLC resolution

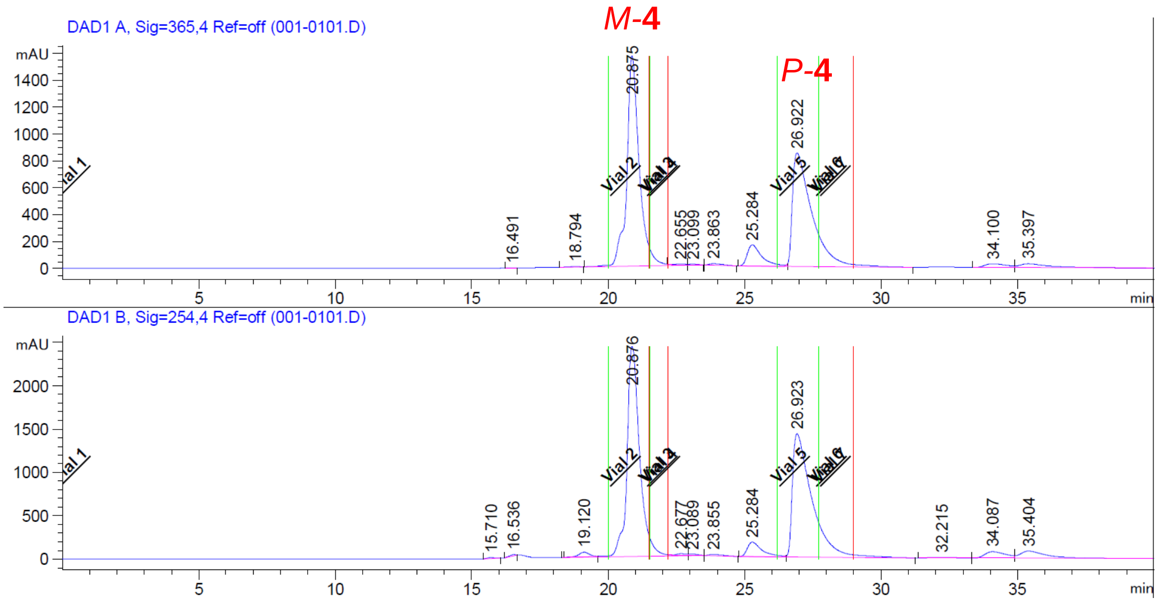


Fig. S19 HPLC resolution of **4**. DCM as mobile phase.

5. The X-ray crystal structures and crystallographic data

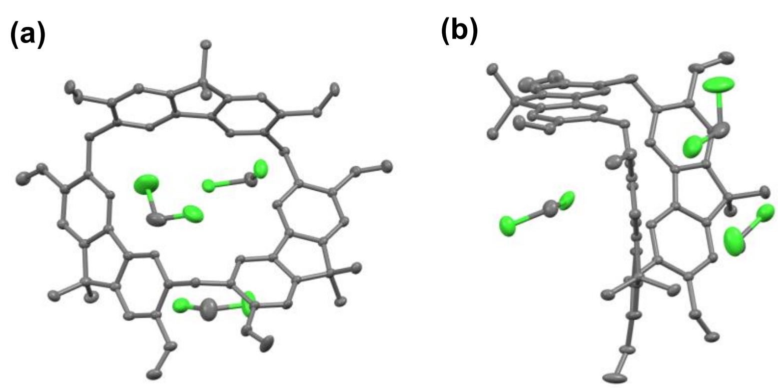


Fig. S20 ORTEP drawing of **2** from (a) top view and (b) side view (the thermal ellipsoids are displayed at a 30 % probability).

Table S1. Crystal Data and Structure Refinement for **2** (CCDC 2192655)

Compound	**2**
Empirical formula	$C_{63}H_{60}Cl_6$
Formula weight	1029.81
Temperature/K	170.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	12.9068(3)
b/Å	14.7144(3)
c/Å	16.1660(4)
α/°	71.467(2)
β/°	69.769(2)
γ/°	79.6845(19)
Volume/Å^3	2723.10(12)
Z	2
ρ_{calc}g/cm^3	1.256
μ/mm^{-1}	3.169
F(000)	1080.0
Crystal size/mm^3	0.28 × 0.18 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.064 to 154.666
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20
Reflections collected	35753
Independent reflections	10991 [R_{int} = 0.0242, R_{sigma} = 0.0225]
Data/restraints/parameters	10991/0/638
Goodness-of-fit on F^2	1.722
Final R indexes [I>=2σ (I)]	R_1 = 0.1003, wR_2 = 0.3483
Final R indexes [all data]	R_1 = 0.1033, wR_2 = 0.3549
Largest diff. peak/hole / e Å^{-3}	1.36/-1.49

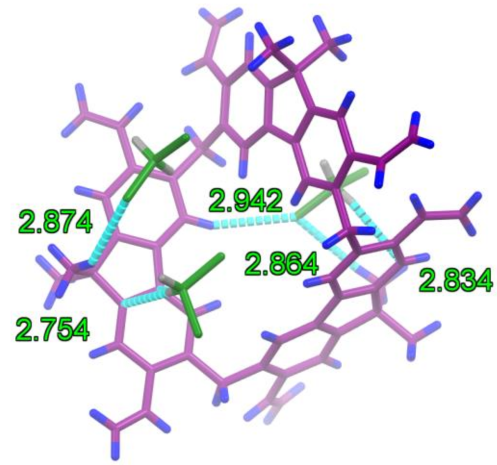


Fig. S21 Illustration of Cl_2C-H···π interaction between **2** and CH_2Cl_2.

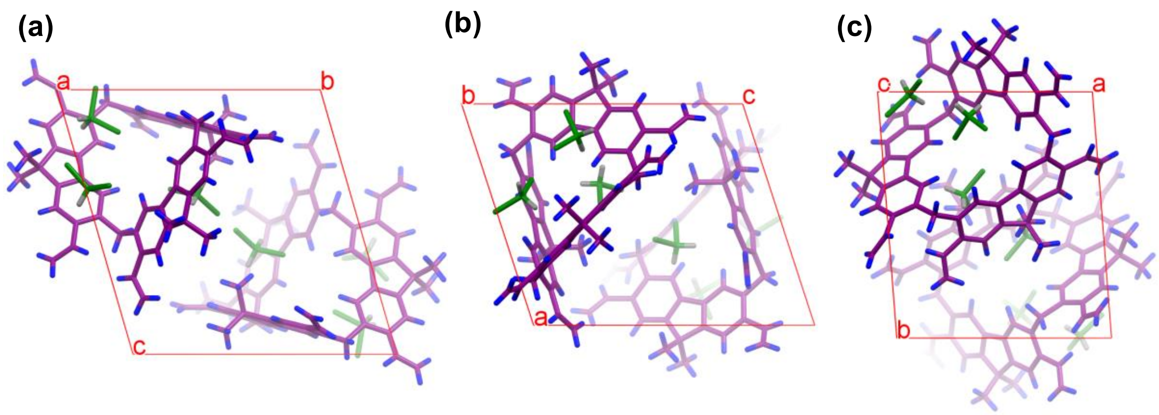


Fig. S22 Packing of **2** in the solid state.

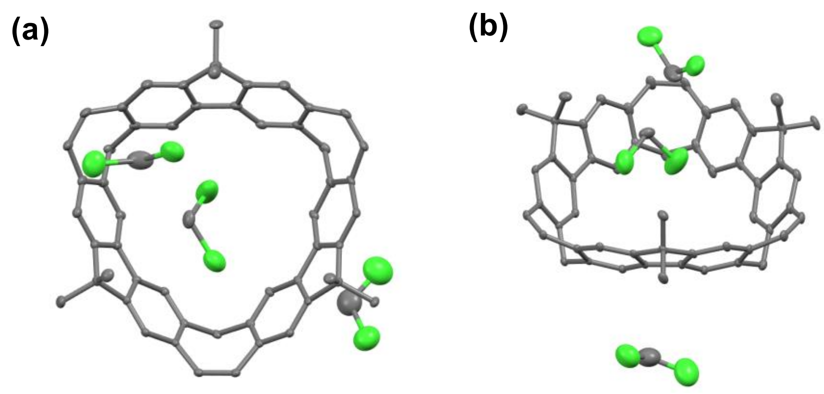


Fig. S23 ORTEP drawing of **3** from (a) top view and (b) side view (the thermal ellipsoids are displayed at a 60 % probability).

Table S2. Crystal Data and Structure Refinement for **3** (CCDC 2192656)

Compound	**3**
Empirical formula	$C_{57}H_{48}Cl_6$
Formula weight	945.65
Temperature/K	169.99(11)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.6999(2)
b/Å	27.5753(4)
c/Å	14.7599(2)
α/°	90
β/°	117.155(2)
γ/°	90
Volume/Å^3	4961.36(16)
Z	4
ρ_{calc}g/cm^3	1.266
μ/mm^{-1}	3.434
F(000)	1968.0
Crystal size/mm^3	0.28 × 0.18 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.41 to 156.104
Index ranges	-17 ≤ h ≤ 17, -34 ≤ k ≤ 32, -18 ≤ l ≤ 15
Reflections collected	71868
Independent reflections	10177 [R_{int} = 0.0494, R_{sigma} = 0.0259]
Data/restraints/parameters	10177/46/593
Goodness-of-fit on F^2	2.244
Final R indexes [I>=2σ (I)]	R_1 = 0.1510, wR_2 = 0.4300
Final R indexes [all data]	R_1 = 0.1564, wR_2 = 0.4451
Largest diff. peak/hole / e Å^{-3}	2.05/-1.65

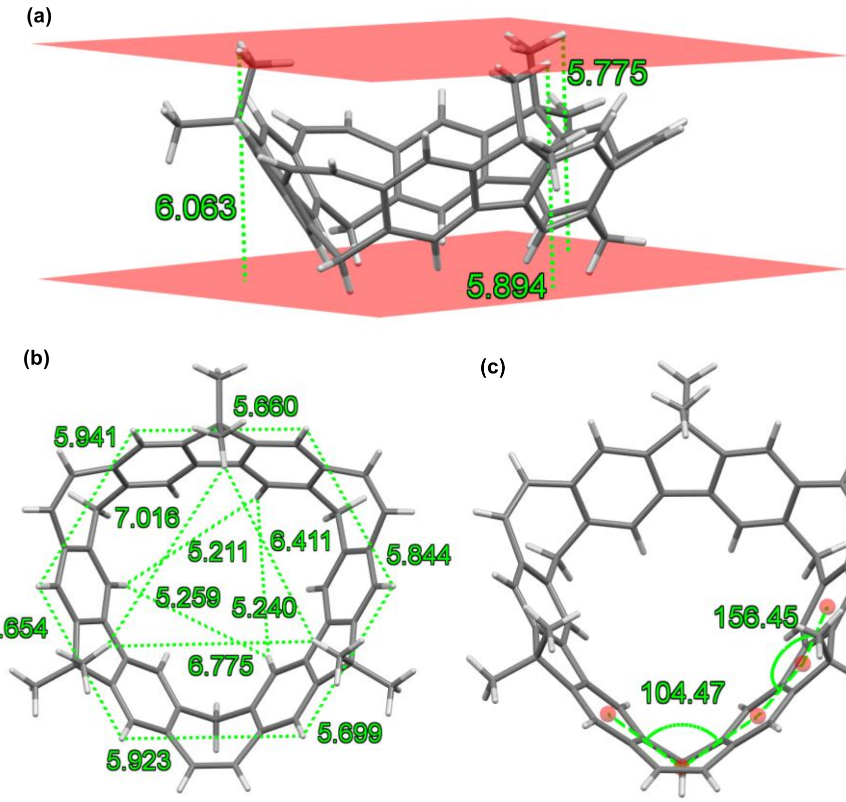


Fig. S24 Cavity size and distorsion angle measurements of **3**.

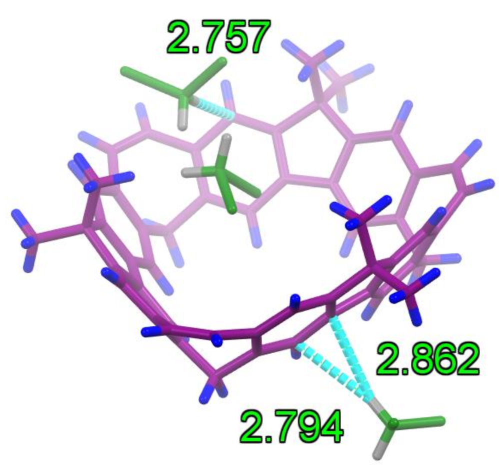


Fig. S25 Illustration of Cl_2C-H···π interaction between **3** and CH_2Cl_2.

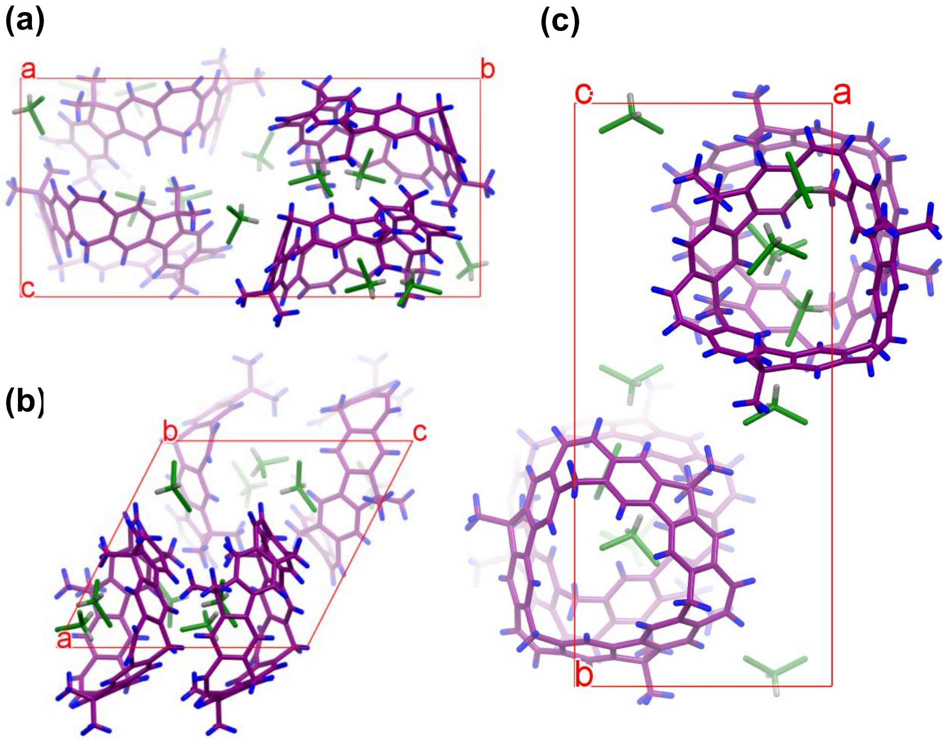


Fig. S26 Packing of **3** in the solid state.

6. Photophysical properties

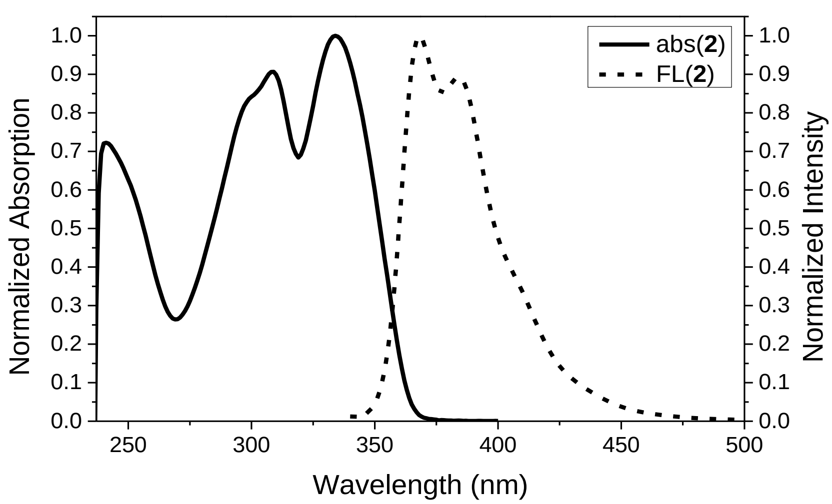


Fig. S27 UV-vis absorption spectrum (solid line) and normalized fluorescent spectrum (dashed line) of **2**, [**2**] = 1.0×10^{-5} M.

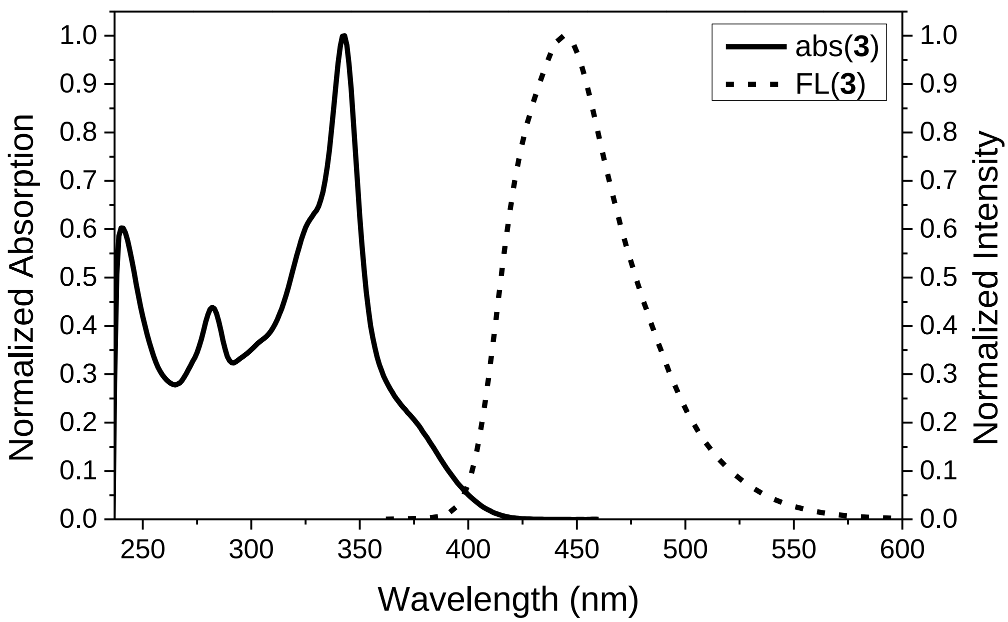


Fig. S28 UV-vis absorption spectrum (solid line) and normalized fluorescent spectrum (dashed line) of **3**, [**3**] = 1.0 × 10^{-5} M.

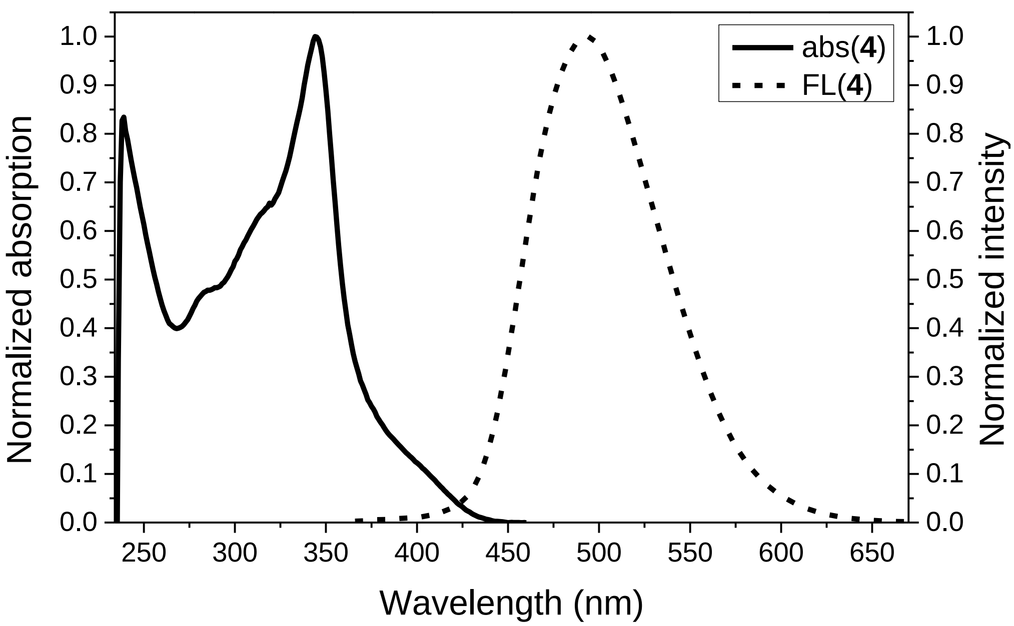


Fig. S29 UV-vis absorption spectrum (solid line) and normalized fluorescent spectrum (dashed line) of **4**, [**4**] = 1.0 × 10^{-5} M.

7. Circular dichroism

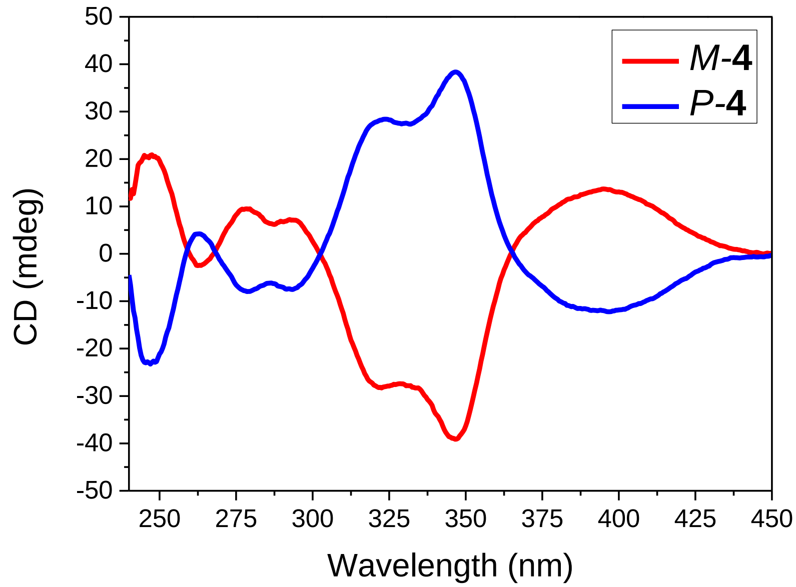


Fig. S30 CD spectra of **4**, [**4**] = 1.0 × 10^{-5} M.

8. Circularly polarized luminescence

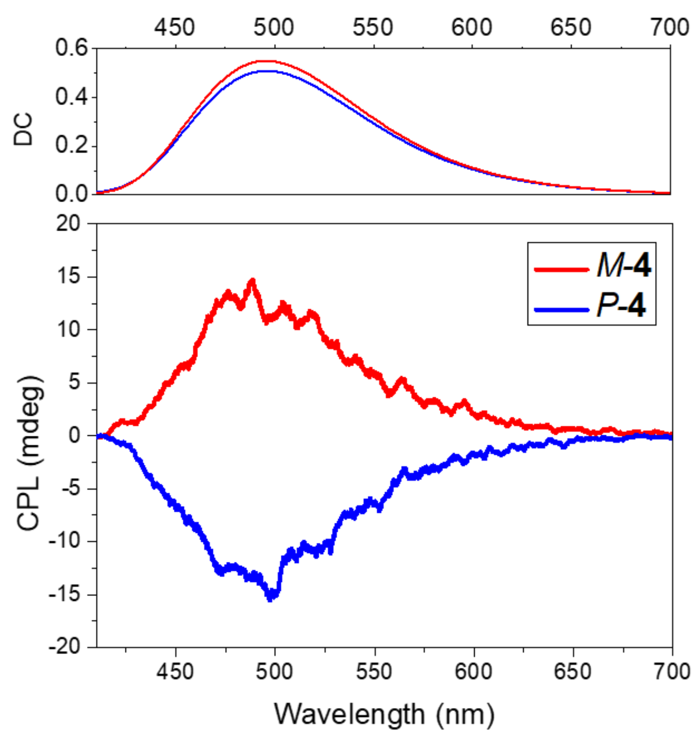


Fig. S31 CPL of **4**, [**4**] = 1.0 × 10^{-5} M.

9. Theoretical calculations

9.1 Calculated UV-vis spectra

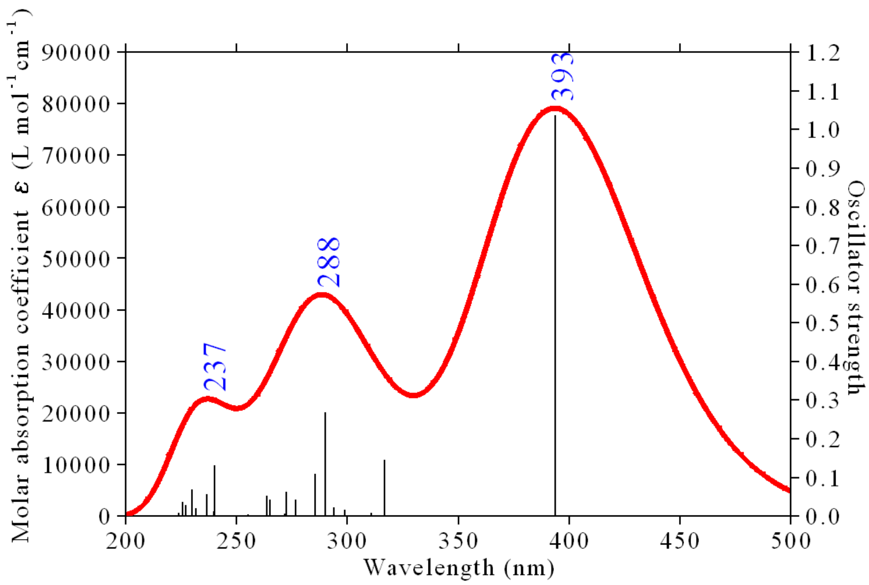


Fig. S32 Simulated UV-vis spectrum of **3**.

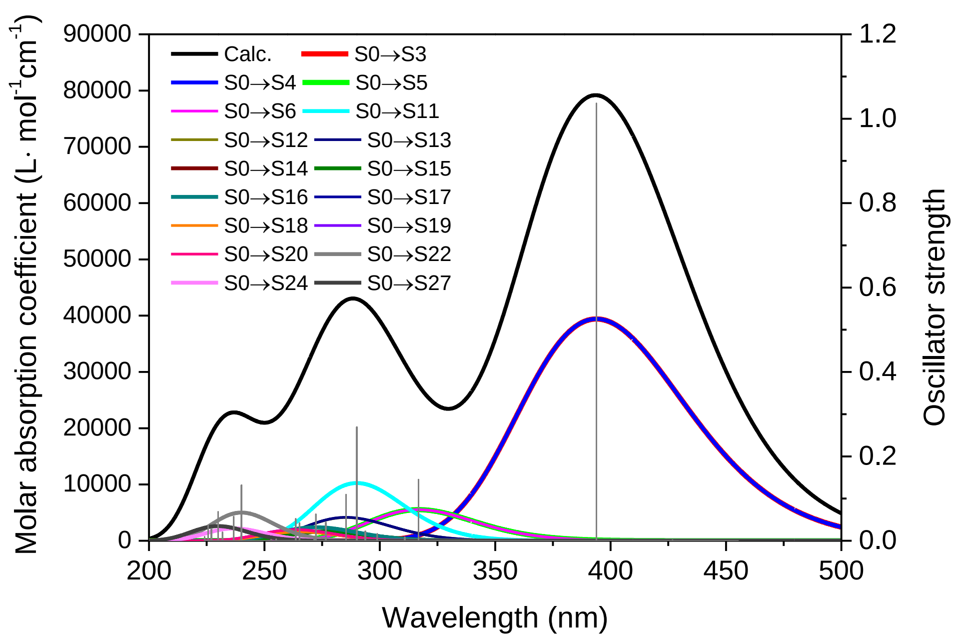


Fig. S33 Major electronic transitions (f >0.02) of the main absorption bands for **3**.

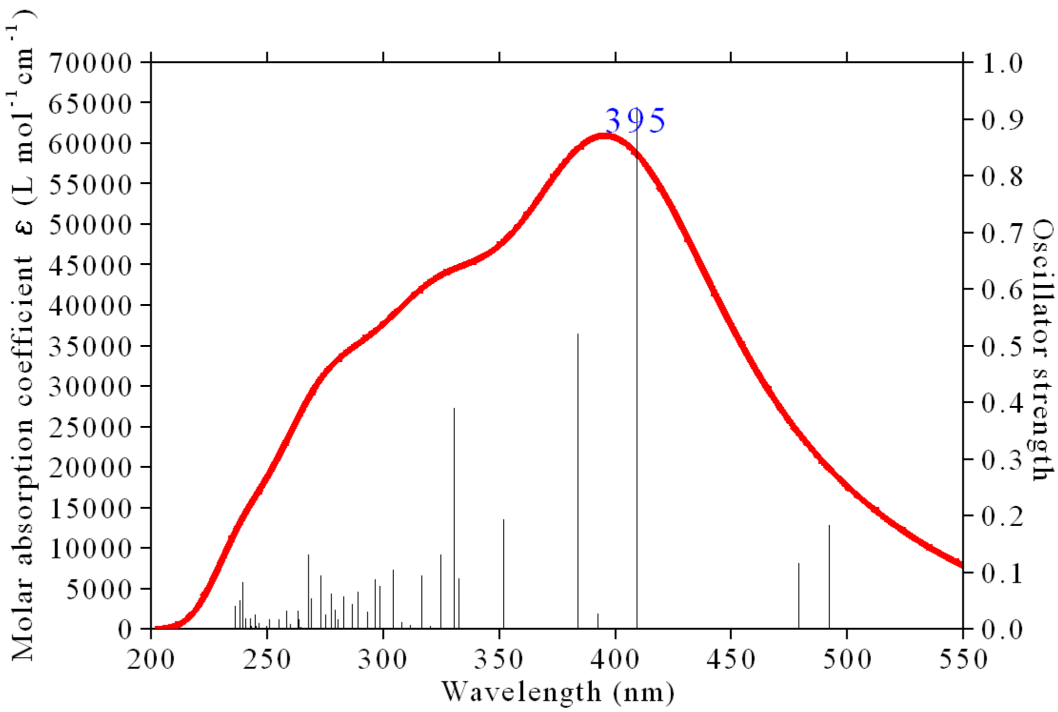


Fig. S34 Simulated UV-vis spectrum of **4**.

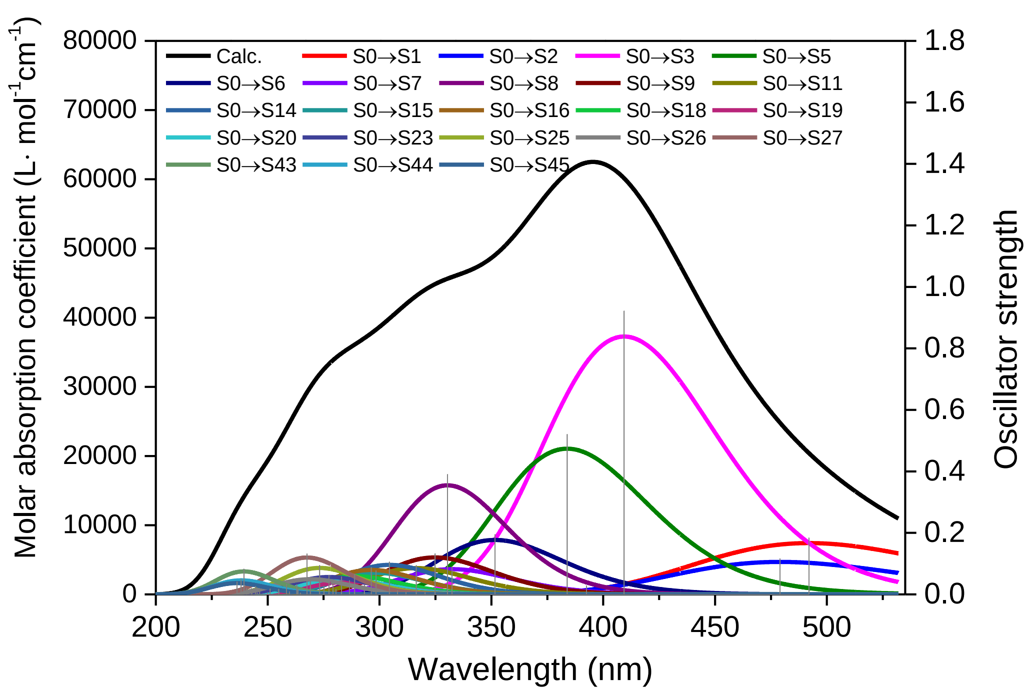


Fig. S35 Major electronic transitions (*f* >0.04) of the main absorption bands for **4**.

9.2 Calculated ECD spectra of 4

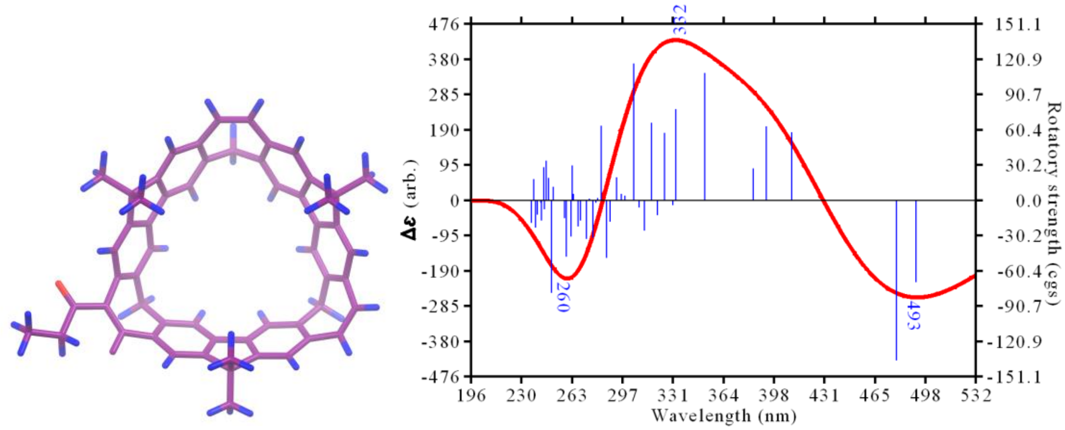


Fig. S36 Simulated ECD spectrum of *P*-**4**.

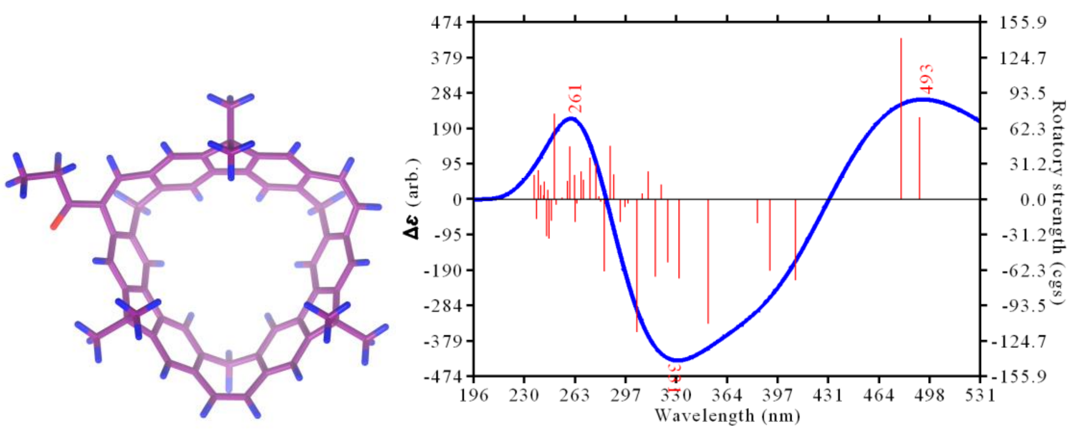


Fig. S37 Simulated ECD spectrum of *M*-**4**.

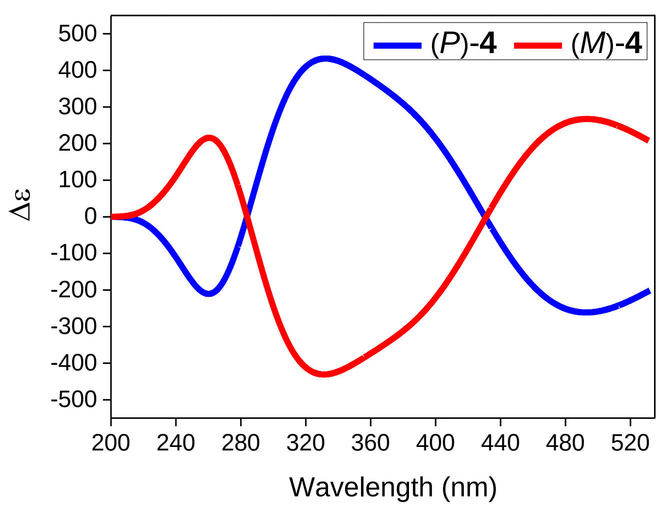


Fig. S38 Simulated ECD spectrum of **4**.

9.3 TD-DFT vertical one-electron excitations

Table S3. Major Electronic Transitions for **3** by TD-DFT Method Using B3LYP/6-31G(d).

	energy (eV)	Excitation [nm]	Oscillator strength (f)	Description
S1	2.7220	455.49	0.00000	H →L 49.8%, H-1 → L+1 49.6%
S2	2.9047	426.84	0.00160	H-1 → L 49.7%, H → L+1 49.7%
S3	3.1480	393.85	1.03590	H-1 → L+1 42.4%, H → L 42.2%, H → L+1 7.3%, H-1 → L 7.3%
S4	3.1480	393.85	1.03620	H → L+1 42.3%, H-1 → L 42.3%, H-1 → L+1 7.3%, H → L 7.3%
S5	3.9137	316.80	0.14520	H → L+2 47.3%, H-2 → L 27.3%
S6	3.9139	316.78	0.14520	H-1 → L+2 47.3%, H-2 → L+1 27.4%
S7	3.9888	310.83	0.00810	H-2 → L 49.3%, H → L+2 36.1%, H-3 → L+1 7.8%
S8	3.9890	310.82	0.00810	H-2 → L+1 49.2%, H-1 → L+2 36.1%, H-3 → L 7.8%
S9	4.1479	298.91	0.01660	H-5 → L 31.1%, H-4 → L+1 31.0%, H-4 → L 6.7%, H-5 → L+1 6.6%, H → L+5 5.6%, H-1 → L+6 5.6%
S10	4.2207	293.75	0.02290	H-3 → L 67.3%, H → L+3 19.9%, H-2 → L+1 6.1%
S11	4.2210	293.73	0.02280	H-3 → L+1 67.3%, H-1 → L+3 19.9%, H-2 → L 6.0%
S12	4.2743	290.07	0.26910	H-4 → L 13.9%, H-5 → L+1 13.4%, H-4 → L+1 13.4%, H-5 → L 13.0%, H-1 → L+3 10.5%, H-2 → L 8.8%, H → L+4 6.6%, H → L+2 5.2%
S13	4.2744	290.06	0.26960	H-5 → L 13.7%, H-4 → L+1 13.5%, H-4 → L 13.4%, H-5 → L+1 12.9%, H → L+3 10.6%, H-2 → L+1 8.8%, H-1 → L+4 6.6%, H-1 → L+2 5.2%
S14	4.2912	288.93	0.00000	H-5 → L+1 20.1%, H-4 → L 19.1%, H-1 → L+5 12.7%, H → L+6 12.5%, H-1 → L+6 7.6%, H → L+5 7.4%
S15	4.3445	285.38	0.10870	H → L+3 45.8%, H-3 → L 14.4%, H-1 → L+4 14.1%, H-5 → L+1 6.0%, H-4 → L 6.0%
S16	4.3446	285.38	0.10940	H-1 → L+3 45.8%, H-3 → L+1 14.4%, H → L+4 14.2%, H-4 → L+1 6.0%, H-5 → L 6.0%
S17	4.4367	279.45	0.00000	H-4 → L 21.0%, H-5 → L+1 21.0%, H → L+6 12.2%, H-1 → L+5 12.0%, H → L+5 7.3%, H-1 → L+6 7.0%
S18	4.4818	276.64	0.04340	H → L+5 29.9%, H-1 → L+6 29.8%, H-6 → L 12.7%
S19	4.4818	276.64	0.04330	H-1 → L+5 30.0%, H → L+6 29.7%, H-6 → L+1 12.6%

S20	4.5527	272.33	0.06320	H-1 → L+6 24.4%, H → L+5 24.3%, H-1 → L+5 14.5%, H → L+6 14.3%, H-4 → L+1 7.7%, H-5 → L 7.6%
S21	4.5640	271.66	0.00620	H → L+4 43.4%, H-6 → L 22.1%, H-1 → L+3 11.2%
S22	4.5642	271.64	0.00620	H-1 → L+4 43.5%, H-6 → L+1 22.2%, H → L+3 11.2%
S23	4.6751	265.20	0.04200	H-6 → L 20.5%, H-9 → L+1 14.5%, H → L+4 13.8%, H-6 → L+1 7.4%, H-9 → L 5.3%
S24	4.6751	265.20	0.04140	H-6 → L+1 20.0%, H-9 → L 14.8%, H-1 → L+4 13.7%, H-6 → L 7.5%, H-9 → L+1 5.3%
S25	4.7035	263.60	0.05250	H-6 → L+1 21.8%, H-9 → L 15.3%, H-8 → L 10.5%, H-7 → L+1 10.3%, H → L+6 6.6%, H-1 → L+5 6.6%, H-6 → L 5.4%
S26	4.7036	263.59	0.05170	H-6 → L 21.3%, H-9 → L+1 15.8%, H-7 → L 10.6%, H-8 → L+1 10.3%, H → L+5 6.6%, H-1 → L+6 6.6%, H-6 → L+1 5.4%
S27	4.7624	260.34	0.00000	H-8 → L+1 28.9%, H-7 → L 28.6%, H-7 → L+1 10.2%, H-8 → L 10.2%, H-1 → L+5 5.5%, H → L+6 5.5%
S28	4.8592	255.15	0.00390	H-8 → L 34.3%, H-7 → L+1 34.3%, H-7 → L 12.3%, H-8 → L+1 12.1%
S29	4.9031	252.87	0.00260	H-9 → L 41.0%, H-8 → L+1 21.8%, H-7 → L 21.6%, H-9 → L+1 7.0%
S30	4.9033	252.86	0.00260	H-9 → L+1 41.0%, H-7 → L+1 21.7%, H-8 → L 21.5%, H-9 → L 7.1%
S31	5.0098	247.48	0.00000	H-2 → L+2 90.9%
S32	5.1477	240.85	0.00000	H → L+7 44.4%, H-1 → L+8 41.3%
S33	5.1647	240.06	0.13190	H-1 → L+7 29.9%, H → L+8 28.0%, H-1 → L+8 8.2%, H → L+7 7.7%, H-5 → L+2 6.1%
S34	5.1648	240.06	0.13170	H-1 → L+8 30.2%, H → L+7 27.7%, H → L+8 8.0%, H-1 → L+7 7.9%, H-4 → L+2 6.1%
S35	5.1684	239.89	0.01200	H-3 → L+2 46.1%, H → L+8 20.4%, H-1 → L+7 18.5%, H-2 → L+3 9.8%
S36	5.2370	236.75	0.05770	H-3 → L+2 46.8%, H → L+8 19.8%, H-1 → L+7 19.7%
S37	5.3486	231.81	0.02040	H-2 → L+3 71.6%, H-3 → L+4 9.9%
S38	5.3922	229.93	0.06840	H-4 → L+2 76.4%, H-1 → L+9 6.0%
S39	5.3923	229.93	0.06850	H-5 → L+2 76.4%, H → L+9 6.0%
S40	5.4608	227.04	0.02860	H-10 → L 26.0%, H-11 → L+1 25.6%, H → L+9 16.1%, H → L+10 8.7%, H-1 → L+11 8.6%
S41	5.4609	227.04	0.02830	H-11 → L 26.0%, H-10 → L+1 25.9%, H-1 → L+9 15.8%, H → L+11 8.7%, H-1 → L+10 8.7%
S42	5.4952	225.62	0.03620	H → L+9 55.0%, H-10 → L 7.7%, H-11 → L+1 7.5%, H-2 → L+5 6.3%
S43	5.4953	225.62	0.03640	H-1 → L+9 55.3%, H-11 → L 7.5%, H-10 → L+1 7.5%, H-2 → L+6 6.3%
S44	5.5079	225.10	0.00000	H-2 → L+4 67.1%, H-3 → L+3 24.1%

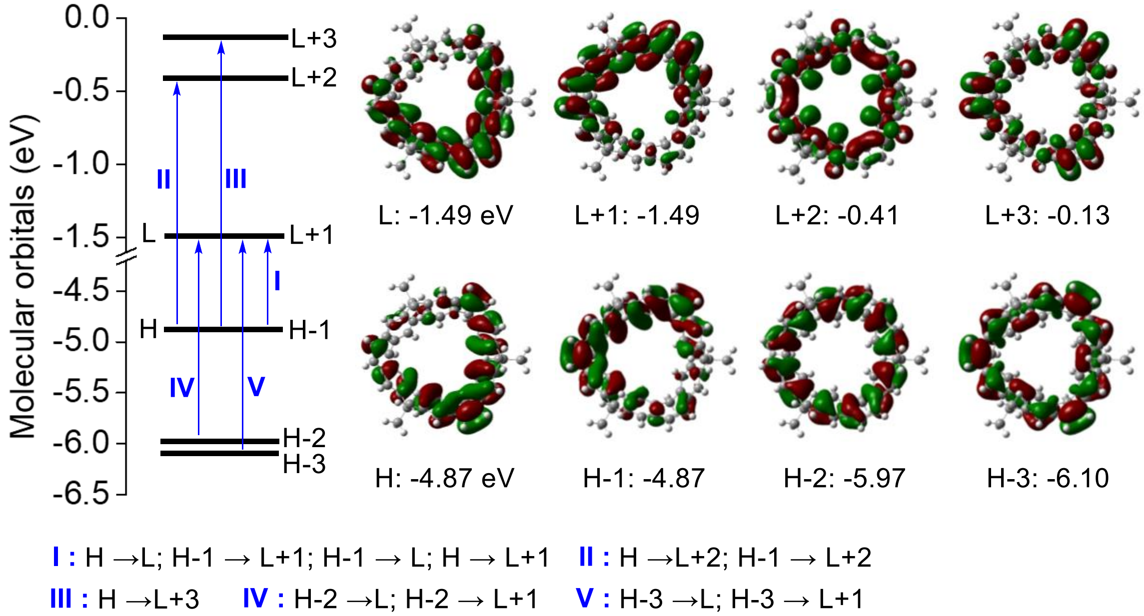


Fig. S39 Calculated frontier molecular orbital profiles, energy diagram, and major electronic transitions of **3**.

Table S4. Major Electronic Transitions for (*P*)-**4** by TD-DFT Method Using B3LYP/6-31G(d).

	energy (eV)	Excitation [nm]	Oscillator strength (f)	Description
S1	2.5202	491.96	0.18330	H → L 97.5%
S2	2.5885	478.98	0.11600	H-1 → L 76.9%, H → L+1 21.9%
S3	3.0286	409.38	0.92150	H → L+1 74.0%, H-1 → L 20.9%
S4	3.1591	392.47	0.02810	H-3 → L 48.2%, H-6 → L 17.5%, H-2 → L 14.3%
S5	3.2297	383.89	0.52070	H-1 → L+1 95.9%
S6	3.5259	351.64	0.19440	H-2 → L 72.8%, H-6 → L 9.4%
S7	3.7293	332.46	0.09010	H-6 → L 29.6%, H → L+2 21.5%, H-3 → L 19.3%, H-4 → L 11.9%, H-7 → L 5.6%
S8	3.7528	330.38	0.38970	H → L+2 71.6%, H-6 → L 7.2%, H-4 → L 7.0%
S9	3.8167	324.85	0.13200	H-4 → L 44.2%, H-5 → L 18.2%, H-3 → L 13.9%, H-1 → L+2 8.6%, H-2 → L+1 6.8%
S10	3.8698	320.39	0.00560	H-1 → L+2 31.5%, H-5 → L 29.4%, H → L+3 18.9%, H-4 → L 5.3%
S11	3.9182	316.43	0.09390	H-5 → L 37.3%, H-1 → L+2 14.5%, H-2 → L+1 14.1%, H → L+3 11.4%, H-6 → L 6.6%
S12	3.9766	311.78	0.00690	H-1 → L+2 32.3%, H → L+3 30.4%, H-4 → L 11.2%

S13	4.0251	308.03	0.01200	H-2 → L+1 43.1%, H → L+3 17.0%, H-7 → L 12.1%, H-1 → L+3 7.5%
S14	4.0736	304.36	0.10540	H-7 → L 27.4%, H-1 → L+3 17.8%, H-2 → L+1 10.8%, H → L+3 10.7%, H-6 → L 7.9%
S15	4.1539	298.48	0.07690	H-3 → L+1 63.1%, H-1 → L+3 7.0%, H-2 → L+1 6.6%
S16	4.1838	296.34	0.08730	H-1 → L+3 20.2%, H-7 → L 18.7%, H-10 → L 14.5%, H-5 → L+1 14.1%, H-9 → L 6.8%, H-6 → L 5.3%
S17	4.2282	293.23	0.02990	H-5 → L+1 40.6%, H-10 → L 12.7%, H-9 → L 10.4%, H → L+6 7.4%, H-3 → L+1 6.2%, H → L+4 5.0%
S18	4.2915	288.91	0.06540	H-1 → L+3 25.4%, H-10 → L 18.1%, H-7 → L 10.8%, H-9 → L 9.8%, H-3 → L+1 8.3%, H → L+5 5.6%
S19	4.3262	286.59	0.04470	H-4 → L+1 28.8%, H-10 → L 18.5%, H-8 → L 8.9%, H → L+4 7.7%, H → L+5 7.2%, H-1 → L+3 7.1%
S20	4.3819	282.95	0.05750	H-4 → L+1 29.6%, H-8 → L 25.6%, H-9 → L 24.0%, H-10 → L 6.1%
S21	4.4192	280.56	0.01670	H-8 → L 53.3%, H → L+4 16.1%, H-10 → L 11.5%, H-9 → L 5.9%, H-4 → L+1 5.1%
S22	4.4411	279.17	0.03340	H → L+5 25.4%, H-9 → L 23.6%, H-4 → L+1 16.9%, H → L+6 7.7%, H-6 → L+1 5.2%
S23	4.4694	277.41	0.06200	H → L+4 43.1%, H-5 → L+1 9.0%, H → L+6 6.8%, H → L+5 6.7%, H-7 → L+1 5.9%, H-8 → L 5.7%
S24	4.5067	275.11	0.02640	H-6 → L+1 69.7%, H-8 → L+1 6.6%
S25	4.5376	273.24	0.09450	H → L+6 33.2%, H-1 → L+4 16.1%, H → L+5 16.0%, H-5 → L+1 9.2%, H-2 → L+2 5.6%
S26	4.6080	269.06	0.05420	H-1 → L+4 53.9%, H → L+5 10.4%, H-9 → L 5.3%
S27	4.6342	267.54	0.13170	H-7 → L+1 48.7%, H-1 → L+6 12.7%, H-1 → L+5 11.3%, H-6 → L+1 5.3%
S28	4.6859	264.59	0.00430	H-1 → L+5 25.8%, H → L+6 20.5%, H-8 → L+1 18.2%, H-2 → L+2 16.1%
S29	4.7046	263.54	0.01650	H-3 → L+2 29.4%, H-2 → L+2 20.7%, H-8 → L+1 20.6%, H-1 → L+4 5.1%
S30	4.7137	263.03	0.03170	H-1 → L+5 34.4%, H-7 → L+1 23.7%, H-8 → L+1 10.5%
S31	4.7732	259.75	0.00820	H-1 → L+6 52.0%, H-8 → L+1 14.4%, H-7 → L+1 8.9%, H-3 → L+2 7.8%
S32	4.7987	258.37	0.03300	H-2 → L+2 36.4%, H-3 → L+2 20.5%, H-9 → L+1 17.7%
S33	4.8632	254.94	0.01670	H-9 → L+1 42.9%, H → L+7 12.9%, H-10 → L+1 8.7%, H-2 → L+2 7.4%, H-1 → L+5 7.1%
S34	4.9377	251.10	0.01790	H → L+7 49.2%, H-10 → L+1 14.1%, H-9 → L+1 11.8%
S35	4.9619	249.87	0.00480	H-10 → L+1 26.3%, H-2 → L+3 21.1%, H-4 → L+2 12.6%, H → L+7 11.6%, H-5 → L+2 7.0%

S36	5.0018	247.88	0.00050	H-2 → L+3 38.3%, H-10 → L+1 17.0%, H → L+7 8.5%, H-4 → L+2 7.1%, H-11 → L 6.4%
S37	5.0315	246.42	0.01100	H-5 → L+2 32.7%, H-10 → L+1 15.5%, H → L+8 12.6%, H-6 → L+2 9.9%, H-2 → L+3 7.1%
S38	5.0541	245.31	0.00550	H-11 → L 45.1%, H-4 → L+2 19.5%, H-2 → L+3 11.6%, H-12 → L 5.9%
S39	5.0681	244.64	0.02530	H-1 → L+7 54.3%, H-4 → L+2 12.9%, H-11 → L 10.3%, H-6 → L+2 7.9%
S40	5.1027	242.98	0.00480	H-6 → L+2 31.0%, H → L+8 26.4%, H-3 → L+2 7.8%, H-11 → L 6.1%
S41	5.1069	242.78	0.01900	H-4 → L+2 27.6%, H-12 → L 27.3%, H-11 → L 10.0%, H-1 → L+7 6.9%, H-2 → L+3 5.6%, H → L+8 5.1%
S42	5.1529	240.61	0.01930	H-5 → L+2 31.5%, H → L+8 30.9%, H-6 → L+2 10.9%, H-1 → L+7 6.9%
S43	5.1805	239.33	0.08200	H-3 → L+3 50.5%, H → L+9 10.5%, H-12 → L 5.3%
S44	5.2061	238.15	0.05010	H-12 → L 31.7%, H → L+9 25.6%, H-1 → L+8 6.0%, H → L+8 5.7%, H-11 → L 5.0%
S45	5.2466	236.31	0.04030	H-3 → L+3 28.4%, H → L+9 16.4%, H-12 → L 13.1%, H-1 → L+7 8.6%

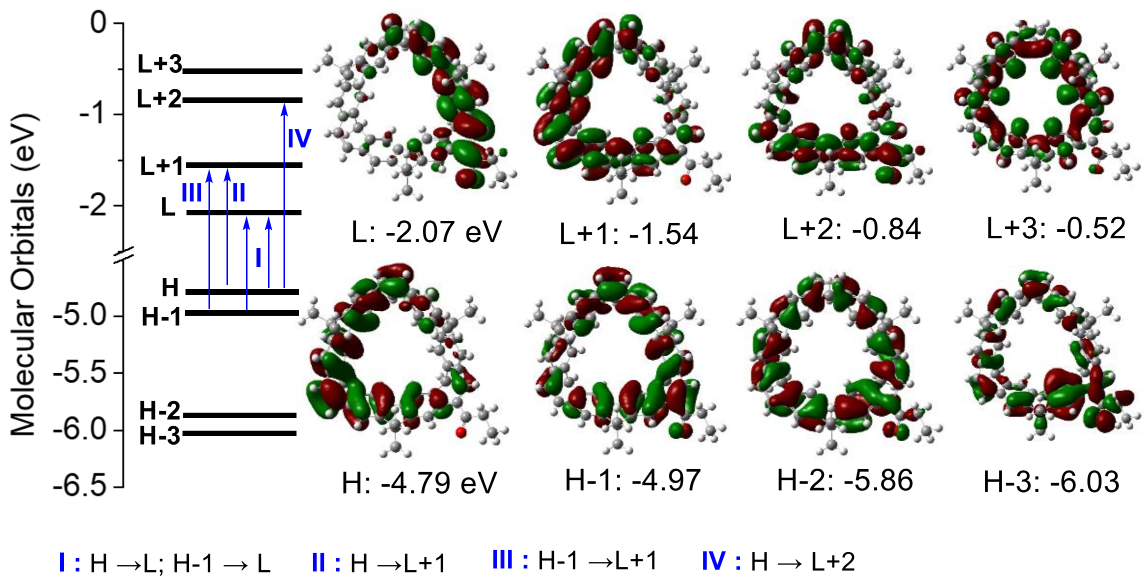


Fig. S40 Calculated frontier molecular orbital profiles, energy diagram, and major electronic transitions of (*P*)**-4**.

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      2.9927 eV  414.28 nm  f=0.6517
<S**2>=0.000
    182 -> 184       -0.42105
    182 -> 185       -0.25976
    183 -> 184       -0.25937
    183 -> 185        0.42102
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -2083.05937231
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:      Singlet-A      2.7148 eV  456.71 nm  f=0.0008
<S**2>=0.000
    182 -> 184       -0.49580
    183 -> 185       -0.49587

 Excited State   3:      Singlet-A      2.5275 eV  490.54 nm  f=0.0000
<S**2>=0.000
    182 -> 185        0.49585
    183 -> 184       -0.49661
```

Fig. S41 Excitation energies and oscillator strengths for **3**.

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      2.5363 eV  488.84 nm  f=0.1068
<S**2>=0.000
    197 -> 200       -0.11214
    198 -> 199        0.69078
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -2274.77144170
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:      Singlet-A      2.6015 eV  476.58 nm  f=0.0690
<S**2>=0.000
    197 -> 199        0.59042
    198 -> 200        0.37212

 Excited State   3:      Singlet-A      3.0378 eV  408.13 nm  f=0.0816
<S**2>=0.000
    192 -> 199        0.16686
    193 -> 199        0.14109
    194 -> 199        0.14706
    195 -> 199        0.40337
    195 -> 201       -0.10015
    196 -> 199        0.38967
    197 -> 199        0.10873
    198 -> 200       -0.23286
```

Fig. S42 Excitation energies and oscillator strengths for **4**.

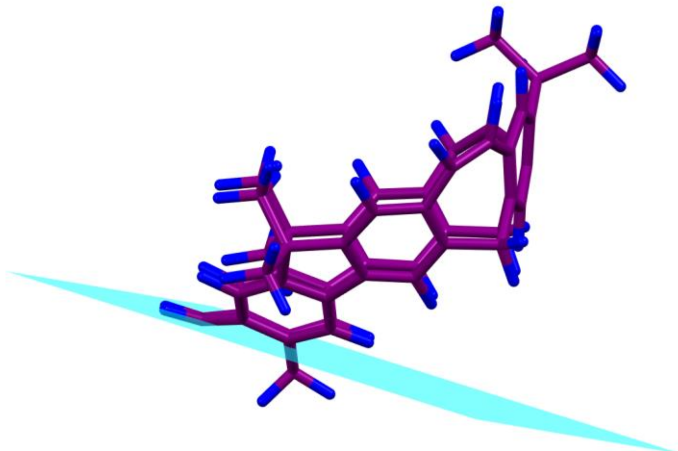


Fig. S43 Illumination of the shielding effect from the vinyl plane to $CH_{2(o)}$ for **3**.

10. Cartesian coordinates of the optimized structures

3

C	3.9736	-1.558	1.8681	**C**	3.0802	2.9800	0.4095
C	1.1386	-3.9825	0.0006	**C**	2.1363	3.4186	1.2467
C	-0.0633	-4.7008	-0.5918	**C**	1.4188	4.5015	0.9039
C	-1.1094	-3.9457	0.2126	**C**	1.6355	5.1444	-0.2607
C	-0.548	-3.1494	1.1319	**C**	2.7089	4.7848	-1.0011
C	0.785	-3.1713	1.0063	**C**	5.0906	0.5356	-0.966
C	1.6995	-2.4393	1.6484	**C**	4.8312	-0.5584	-0.2141
C	2.9596	-2.423	1.1828	**C**	4.1614	-0.3933	0.9438
C	3.3102	-3.1272	0.0884	**C**	3.6102	0.7881	1.2682
C	2.4100	-3.9919	-0.4328	**C**	-3.4651	-1.4358	2.5692
C	-2.4391	-3.9123	0.0242	**C**	-4.3595	1.8558	0.1676
C	-3.1974	-3.0203	0.7017	**C**	-4.4522	3.1329	-0.6521
C	-2.6258	-2.3313	1.7092	**C**	-3.2154	3.7894	-0.0598
C	-1.3021	-2.3900	1.9313	**C**	-2.7148	3.0762	0.9575
C	0.3218	4.9615	1.8155	**C**	-3.3933	1.9296	1.0925
C	3.404	3.6792	-0.6863	**C**	-3.1448	0.8994	1.9057
C	4.486	2.9845	-1.4975	**C**	-3.7846	-0.2627	1.6931
C	4.5081	1.7094	-0.6699	**C**	-4.664	-0.4022	0.6813
C	3.7349	1.8118	0.4191	**C**	-5.0242	0.7023	-0.0115

C	-2.5562	4.873	-0.5023	**C**	-5.724	3.9233	-0.3269
C	-1.3516	5.1946	0.0224	**H**	-2.3613	0.9613	2.6761
C	-0.9414	4.541	1.1275	**H**	-5.7458	0.6508	-0.8429
C	-1.6168	3.481	1.6017	**H**	-2.9474	5.3796	-1.3994
C	-0.5716	6.0882	-0.627	**H**	-1.2105	2.905	2.447
C	0.7774	6.0653	-0.755	**H**	-1.0685	6.7121	-1.3962
C	-5.1266	-1.6076	0.2793	**H**	1.1414	6.6747	-1.6059
C	-4.4642	-2.7901	0.2886	**H**	-5.9881	-1.6001	-0.4174
C	4.4845	-2.9373	-0.5547	**H**	-4.9032	-3.537	-0.4023
C	5.1716	-1.777	-0.6913	**H**	4.7621	-3.696	-1.313
H	4.9306	-2.1062	2.0255	**H**	5.8877	-1.7954	-1.5366
H	3.6497	-1.2463	2.8861	**H**	6.6315	3.1525	-1.9147
C	-0.2015	-4.4486	-2.0992	**H**	6.1268	3.9137	-0.3645
C	-0.0552	-6.1945	-0.2501	**H**	5.7508	4.7227	-1.927
H	1.4149	-1.7823	2.4842	**H**	-0.9986	-6.6834	-0.5834
H	2.6438	-4.6007	-1.3212	**H**	0.045	-6.3618	0.8466
H	-2.8543	-4.5104	-0.8031	**H**	0.7937	-6.7121	-0.7516
H	-0.8452	-1.7451	2.6972	**H**	-5.7199	4.9114	-0.8405
H	0.3541	6.0657	1.9595	**H**	-5.8204	4.1094	0.7671
H	0.4117	4.5351	2.8395	**H**	-6.6315	3.3696	-0.6584
C	4.0461	2.7257	-2.9447	**H**	-1.1445	-4.8846	-2.4985
C	5.8205	3.7336	-1.4201	**H**	0.636	-4.9129	-2.6665
H	1.8775	2.8541	2.1553	**H**	-0.2058	-3.3586	-2.3288
H	2.9414	5.2809	-1.9573	**H**	4.7992	2.1181	-3.4949
H	5.6418	0.463	-1.9176	**H**	3.9237	3.6778	-3.5079
H	2.9869	0.8732	2.1712	**H**	3.0754	2.1804	-2.9818
H	-2.9468	-1.1382	3.5079	**H**	-4.2563	3.8167	-2.7335
H	-4.3932	-1.953	2.9044	**H**	-5.1618	2.2847	-2.5536
C	-4.3003	2.8664	-2.1557	**H**	-3.3712	2.2917	-2.3735

P-**4**

C	2.0311	0.8111	-3.7459	**C**	-2.2741	-3.0761	-3.0551
C	-0.0762	-2.7639	-3.4836	**C**	-2.0238	-1.7746	-3.2492
C	-1.0339	-3.9271	-3.2767	**C**	-0.7204	-1.5921	-3.4946

C	-0.0346	-0.4555	-3.6251	**C**	-3.2148	3.0691	1.2618
C	1.3091	-0.4977	-3.6353	**C**	-1.5114	3.6705	4.3571
C	2.0068	-1.6518	-3.5405	**C**	-0.1874	3.8324	4.1173
C	1.2657	-2.7885	-3.5336	**C**	3.9372	-0.7934	-2.4629
C	-3.4784	-3.4634	-2.6031	**C**	3.3548	-1.6716	-3.3284
C	-4.4099	-2.5392	-2.2751	**C**	-6.1244	-2.2207	-0.584
C	-4.1782	-1.2543	-2.6098	**C**	-5.4888	-2.9213	-1.5547
C	-2.9869	-0.8626	-3.0917	**C**	-4.6254	-0.4213	4.0122
C	-1.4172	4.6697	1.7059	**C**	-6.5354	1.2498	3.7963
C	2.2463	2.6804	1.8053	**C**	3.5131	0.6058	2.519
C	3.5098	1.855	1.6278	**C**	4.7722	2.7041	1.8107
C	3.2687	1.5132	0.1667	**C**	-0.6787	-4.7562	-2.035
C	2.2051	2.1604	-0.3277	**C**	-1.1554	-4.7902	-4.5371
C	1.5978	2.8516	0.6456	**H**	4.9199	-1.0805	-2.0583
C	0.4541	3.5403	0.5994	**H**	-5.6897	-4.0098	-1.5047
C	-0.1063	3.9447	1.7518	**H**	-1.7406	3.5066	5.4287
C	0.4621	3.6686	2.9425	**C**	5.5433	-2.9898	-3.2879
C	1.7	3.1242	2.9493	**O**	3.6689	-3.5809	-4.526
C	3.9105	0.6078	-0.5895	**H**	2.9019	0.75	-4.4375
C	3.4414	0.2879	-1.8178	**H**	1.3947	1.6301	-4.1486
C	2.4589	1.0505	-2.3329	**H**	-0.5577	0.513	-3.6381
C	1.831	1.9838	-1.5981	**H**	1.7009	-3.7868	-3.379
C	-5.2484	-0.2269	-2.3989	**H**	-3.6172	-4.5306	-2.3656
C	-5.3852	0.3697	1.7268	**H**	-2.7895	0.2053	-3.2711
C	-5.2248	0.731	3.1951	**H**	-1.6504	5.066	0.6925
C	-4.226	1.8555	2.9712	**H**	-1.4088	5.5633	2.371
C	-4.0641	2.122	1.6685	**H**	-0.0742	3.696	-0.3535
C	-4.7513	1.2409	0.931	**H**	2.2192	2.8851	3.8915
C	-4.7593	1.0891	-0.3958	**H**	4.7284	0.0395	-0.1175
C	-5.2943	-0.0281	-0.9149	**H**	0.9706	2.5269	-2.0176
C	-5.8182	-0.9862	-0.1248	**H**	-6.2301	-0.5819	-2.7881
C	-5.9558	-0.7242	1.1952	**H**	-5.0455	0.7182	-2.9503
C	-3.4548	2.4777	3.8783	**H**	-4.25	1.81	-1.0532
C	-2.4647	3.3043	3.4708	**H**	-6.3853	-1.4661	1.8878
C	-2.4176	3.655	2.1703	**H**	-3.5472	2.1643	4.9307

H	-3.0885	3.2985	0.1929	**H**	4.8692	3.0497	2.8649
H	0.4287	3.7728	5.0363	**H**	5.6851	2.1186	1.5579
C	4.0881	-2.7656	-3.7286	**H**	-1.4528	-5.529	-1.8289
H	-6.7297	-2.8622	0.0867	**H**	0.2872	-5.2932	-2.1669
H	-3.674	-0.7855	3.5614	**H**	-0.5902	-4.1127	-1.1301
H	-4.4087	-0.1071	5.0577	**H**	-1.4153	-4.1753	-5.4287
H	-5.3264	-1.2837	4.0719	**H**	-0.197	-5.3144	-4.7536
H	-6.9588	2.0851	3.1933	**H**	-1.9475	-5.5633	-4.4148
H	-7.2998	0.4412	3.8402	**C**	6.2527	-4.1982	-3.9236
H	-6.3755	1.6259	4.8322	**H**	5.5611	-3.1534	-2.1828
H	3.5758	0.8768	3.5967	**H**	6.1493	-2.0898	-3.5547
H	2.5888	0.0013	2.3729	**H**	7.2998	-4.285	-3.5509
H	4.3861	-0.0481	2.2973	**H**	6.3056	-4.1044	-5.0327
H	4.7554	3.6062	1.1576	**H**	5.7361	-5.1538	-3.6753

M-**4**

C	2.9501	0.6906	-5.3967	**C**	4.1135	1.4652	-1.4681
C	0.7682	-2.8608	-5.2069	**C**	3.0705	2.1106	-2.0072
C	-0.2168	-4.0076	-5.0432	**C**	2.4345	2.8226	-1.0678
C	-1.4477	-3.1329	-4.8653	**C**	1.3017	3.5248	-1.1622
C	-1.1697	-1.8393	-5.0735	**C**	0.7122	3.9548	-0.034
C	0.1438	-1.6778	-5.2764	**C**	1.227	3.6851	1.1802
C	0.8361	-0.5428	-5.4042	**C**	2.4581	3.1259	1.2331
C	2.1758	-0.5903	-5.3205	**C**	4.7713	0.5398	-2.1856
C	2.8223	-1.7547	-5.1137	**C**	4.3314	0.2003	-3.4185
C	2.1103	-2.9036	-5.1681	**C**	3.3669	0.9549	-3.9816
C	-2.6685	-3.4905	-4.4334	**C**	2.7316	1.9116	-3.2839
C	-3.5842	-2.5423	-4.1299	**C**	-4.3625	-0.2085	-4.2749
C	-3.3205	-1.2662	-4.4742	**C**	-4.5332	0.4187	-0.1552
C	-2.1164	-0.9058	-4.948	**C**	-4.3989	0.7897	1.313
C	-0.5741	4.7135	-0.1146	**C**	-3.4001	1.917	1.1021
C	3.0407	2.6616	0.1158	**C**	-3.1862	2.1488	-0.1973
C	4.3065	1.8293	-0.0055	**C**	-3.8619	1.2673	-0.9449

C	-3.8489	1.1022	-2.2703
C	-4.4101	-0.0018	-2.7915
C	-4.9709	-0.9406	-2.0037
C	-5.1201	-0.6658	-0.6878
C	-2.677	2.5725	2.0249
C	-1.6871	3.4362	1.6849
C	-1.5691	3.7003	0.3643
C	-2.3085	3.0806	-0.5722
C	-0.7885	3.8965	2.6035
C	0.5467	3.9149	2.3272
C	4.809	-0.9252	-3.9964
C	4.1275	-1.8095	-4.7647
C	-5.3067	-2.1688	-2.4594
C	-4.6796	-2.8924	-3.4185
C	-3.811	-0.3592	2.1435
C	-5.7207	1.3075	1.8901
C	4.2759	0.5955	0.9064
C	5.5648	2.678	0.2056
C	0.0789	-4.8486	-3.794
C	-0.3073	-4.8624	-6.3117
H	5.7309	-1.3551	-3.557
H	-4.9079	-3.9752	-3.362
C	-0.7831	4.5133	6.4461
C	-0.1711	4.2771	5.0543
O	-2.3432	4.0878	4.2543
H	0.4452	5.1789	4.8194
C	-1.1771	4.0444	3.9159
H	0.4824	3.3752	5.1441
H	0.0145	4.6684	7.2094
H	-1.3907	3.6406	6.7796
H	3.8342	0.5897	-6.0669
H	2.3537	1.5251	-5.8285
H	0.3254	0.4296	-5.4734
H	2.5874	-3.885	-5.0143
H	-2.8331	-4.5511	-4.1832
H	-1.8941	0.1566	-5.1301
H	-0.7894	5.0888	-1.1397
H	-0.5602	5.6206	0.5314
H	0.8088	3.6798	-2.1339
H	2.9491	2.8997	2.1936
H	5.5642	-0.0335	-1.6784
H	1.8844	2.4503	-3.7349
H	-5.3514	-0.5379	-4.6684
H	-4.1309	0.7291	-4.8279
H	-3.315	1.8093	-2.9233
H	-5.5818	-1.3897	0.0031
H	-2.8298	2.2091	3.0516
H	-2.1298	3.2805	-1.6398
H	1.2276	3.9433	3.1916
H	4.6136	-2.8039	-4.8152
H	-5.9367	-2.7893	-1.7916
H	-2.8491	-0.7195	1.7124
H	-3.6173	-0.0448	3.1934
H	-4.5093	-1.2247	2.1889
H	-6.1359	2.1388	1.276
H	-6.4837	0.4972	1.9255
H	-5.5793	1.6891	2.9267
H	4.3036	0.8847	1.9809
H	3.3552	-0.0089	0.7397
H	5.1539	-0.0643	0.7254
H	5.5727	3.5693	-0.4624
H	5.628	3.0407	1.2566
H	6.4837	2.086	-0.0073
H	-0.7127	-5.6121	-3.6225
H	1.0423	-5.3972	-3.8931
H	0.1414	-4.2117	-2.8822
H	-0.5223	-4.239	-7.2094
H	0.6485	-5.4037	-6.4948
H	-1.1181	-5.6206	-6.2225
H	-1.4315	5.4194	6.4598

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