Supporting Information

Synthesis and Properties of [7]Helicene-like Compounds Fused with a Fluorene Unit

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General Procedures. All manipulations involving air- and/or moisture-sensitive compounds were carried out with the standard Schlenk technique under argon. Most of reagents were used without further purification unless otherwise specified. Analytical thin-layer chromatography was performed on a glass plates coated with 0.25-mm 230–400 mesh silica gel containing a fluorescent indicator. Column chromatography was performed by using silica gel (spherical neutral, particle size 63-210 μm). NMR spectra were recorded in $CDCl_3$ on a 500 MHz spectrometer (^{1}H 500 MHz; ^{13}C 126 MHz) or a 400 MHz spectrometer (^{1}H 400 MHz; ^{13}C 101 MHz). Chemical shifts are reported in ppm relative to the internal standard signal (0 ppm for Me_4Si in $CDCl_3$) or the residual solvent signal (7.26 ppm for $CHCl_3$ in $CDCl_3$) for ^{1}H and the deuterated solvent signal (77.16 ppm for $CDCl_3$) for ^{13}C. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances), coupling constant in hertz (Hz), and signal area integration in natural numbers. Melting points were determined on a melting point apparatus. High resolution mass spectra are taken by electrospray ionization-time-of-flight (ESI–TOF) method. UV-Vis absorption spectra were recorded on a UV−VIS scanning spectrophotometer. Photoluminescence spectra were recorded on a spectrofluorometer. Absolute quantum yields were determined by absolute quantum yield measurement system with an integrating sphere. Circular dichroism (CD) spectra were recorded on a CD spectrometer system. CPL spectra were measured by using a CPL spectrophotometer. Optical rotations were measured on a polarimeter using a 1-dm cell. HPLC analyses were carried out using a DAICEL CHIRAPAK® IF-3 column (4.6 mm × 250 mm).

Computational Studies. The DFT and TD–DFT calculations were performed by using the Gaussian 09 program[1] at the B3LYP/6–31G(d) level.

Synthetic Procedures and Characterization Data

4,5-Dibromo-9-fluorenone (6): A dry flask was charged with 2,2',6,6'-tetrabromobiphenyl (2.0 g, 4.3 mmol) and anhydrous THF (260 mL). To the mixture was added ^{n}BuLi (2.68 M in hexane, 3.2 mL, 8.5 mmol) at −78 °C. After stirring for 2 h, chloromethyl formate (0.96 mL, 12.8 mmol) was added. The reaction mixture was stirred for 30 min, and the reaction was quenched by the addition of saturated aqueous NH_4Cl (3 mL). After stirring for 30 min, water (20 mL) was added. The resulting mixture was extracted with Et_2O, and the combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica-gel column chromatography (CH_2Cl_2/hexane = 1/2 as an eluent) to afford the title compound as a yellow solid (0.75 g, 78% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76−7.70 (m, 4H), 7.26−7.21 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 190.5, 144.1, 142.0, 138.1, 130.7, 123.5, 117.1; HRMS-ESI$^+$ (*m*/*z*) calcd for $C_{14}H_{10}Br_2O_2Na^+$ ([M + Na + MeOH]$^+$) 390.8940, found 390.8943.

1,9-Bis{2-[(trimethlsilyl)ethynyl]phenyl}fluorenone: 1-Bromo-2-[(trimethylsilyl)ethynyl]-benzene (6.32 g, 25.0 mmol) in THF (100 mL) was cooled to –78 °C, and *t*-BuLi (1.60 *M* in pentane, 30.7 mL, 52.1 mmol) was added dropwise. After stirring for 40 minutes, the resulting solution was transferred to a mixture of $ZnCl_2$ (3.64 g, 26.4 mmol) and THF (100 mL) at 0 °C. The resulting mixture was stirred for 30 minutes, and **6** (3.34 g, 9.88 mmol) in THF (70 mL) and $Pd(PPh_3)_4$ (2.28 g, 1.90 mmol) was added to the solution. The resulting mixture was warmed to room temperature, and then refluxed for 22 h. The reaction was then quenched with saturated aqueous NH_4Cl (10 mL), and the resulting mixture was concentrated under reduced pressure. The resulting residue was extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica-gel column chromatography with CH_2Cl_2/hexane (1/4) as an eluent to give a mixture of *cis*- and *trans*-isomers of the title compound as a yellow solid (4.5 g). The obtained

mixture of isomers was further used without separation. HRMS–ESI$^+$ (*m*/*z*) calcd for $C_{35}H_{32}OSi_2Na^+$ ([M + Na]$^+$) 547.1884, found 547.1865.

1,9-Bis(2-ethynylphenyl)fluorenone (7): A mixture of 1,9-bis{2-[(trimethlsilyl)ethynyl]phenyl}-fluorenone (4.5 g, 8.6 mmol), K_2CO_3 (2.6 g, 19 mmol), CH_2Cl_2 (20 mL), MeOH (200 mL) was vigorously stirred until completion of the reaction, which was monitored by TLC. After water (10 mL) was added, the resulting mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by recrystallization from CH_2Cl_2/hexane to give a mixture of *cis*- and *trans*-isomers of **7** (2.96 g) as a yellow solid. The obtained mixture of isomers was further used without separation. HRMS–ESI$^+$ (*m*/*z*) calcd for $C_{29}H_{16}ONa^+$ ([M + Na]$^+$) 403.1093, found 403.1081.

***rac*-9*H*-Cyclopenta[1,2-*c*:4,3-*c*']diphenanthren-9-one (5):** A mixture of **7** (2.72 g, 7.15 mmol) and $PtCl_2$ (190 mg, 0.715 mmol) in toluene (200 mL) was refluxed for 18 h. The reaction mixture was concentrated under reduced pressure, and the crude residue was purified by silica-gel column chromatography with chloroform. The obtained solid was recrystallized from hexane/CH_2Cl_2 to give *rac*-**5** (2.64 g, 32% from compound **6**) as a red solid. *rac*-**5** can be separated into enatiomerically-pure (*P*)-**5** and (*M*)-**5** by HPLC equipped with a DICEL CHIEAPAK® IF-3 column (4.6 mm × 250 mm)[t_R = 3.5 min and 4.2 min (flow rate: 1.0 mL; eluent: CH_2Cl_2/hexane = 50/50)]: mp 187-188 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 2H), 6.30 (t, *J* = 7.7 Hz, 2H),; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.4, 147.2, 138.2, 135.2, 132.1, 130.7, 129.7 (2C), 128.5, 128.0, 127.7, 127.0, 126.7, 123.8, 120.8; HRMS-ESI$^+$ (*m*/*z*) calcd for $C_{29}H_{16}ONa^+$ ([M + Na]$^+$) 403.1093, found 403.1092.

***rac*-9*H*-Cyclopenta[1,2-*c*:4,3-*c*']diphenanthrene (3a):** A mixture of **5** (50 mg, 0.13 mmol) and hydrazine monohydrate (0.10 mL mg, 3.2 mmol), and KOH (22 mg, 0.40 mmol) in diethylene glycol (6 mL) was heated at 170 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into a solution of concentrated HCl at 0 °C. The resulting colorless precipitate was collected by filtration and washed with water to give a *rac*-**3a** (37 mg, 78%) as a colorless solid. *rac*-**3a** can be separated into enatiomerically-pure (*P*)-**3a** and (*M*)-**3a** by HPLC equipped with a DICEL CHIEAPAK® IF-3 column (4.6 mm × 250 mm)[t_R = 9.2 min and 10.8 min (flow rate: 1.0 mL; eluent: $CHCl_3$/hexane = 50/50)]: mp 178-179 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (d, J = 7.8 Hz, 2H), 7.88 (d, J = 7.6 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.09 (dt, J = 7.3, 1.0 Hz, 2H), 6.26 (dt, J = 7.7, 1.1 Hz, 2H), 4.35 (s,2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.1, 138.4, 131.9, 131.5, 130.7, 127.74, 127.71, 127.4, 126.9, 126.43, 126.40, 126.36, 123.2, 122.9, 38.5; HRMS-ESI$^+$ (*m*/*z*) calcd for $C_{29}H_{18}^+$ (M^+) 366.1403, found 366.1404.

***rac*-9-Phenyl-9*H*-cyclopenta[1,2-*c*:4,3-*c*']diphenanthrene (3b):** To a solution of **5** (100 mg, 0.26 mmol) in THF (5 mL), phenyllithium in cyclohexane and diethylether (1.09 M, 0.30 mL, 0.33 mmol) was added dropwise at −78 ºC. After stirring −78 °C for 30 min, methanol and water were added to the mixture. The resulting mixture was concentrated under reduced pressure, extracted with CH_2Cl_2 (twice). The combined organic layers were dried over $MgSO_4$ and concentrated. The resulting residue was dissolved into CH_2Cl_2 under Ar atmosphere, and triethylsilane (0.10 mL) and trifluoroacetic acid (0.05 mL) were added to the solution at 0 °C. The resulting mixture was stirred at room temperature for 20 min, and concentrated. The crude residue was purified by silica-gel column chromatography using hexane/CH_2Cl_2 (3/1) as an eluent to afford **3b** (99 mg, 85% yield for two steps) as a colorless solid. *rac*-**3b** can be separated into enatiomerically-pure (*P*)-**3b** and (*M*)-**3b** by HPLC equipped with a DICEL CHIEAPAK® IF-3 column (4.6 mm × 250 mm) [t_R = 10.2 min and 12.2 min (flow rate: 0.75 mL; eluent: CH_2Cl_2/hexane = 10/90)] A crystal suitable for an X-ray diffraction

analysis was obtained by recrystallization by slow evaporation from CH_2Cl_2/hexane solution.: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.80–7.78 (m, 2H), 7.73–7.59 (m, 8H), 7.33–7.21 (m, 5H), 7.14–7.09 (m, 2H), 6.33–6.27 (m, 2H), 5.39 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 148.2, 141.1, 138.1, 137.7, 132.34, 132.27, 131.7, 131.5, 130.9, 130.8, 129.0, 128.8, 128.5, 128.2, 127.9, 127.6, 127.5, 127.3, 127.0, 126.9, 126.72, 126.70, 126.5, 126.4, 123.4, 123.32, 123.29, 122.8, 55.4; HRMS-ESI$^+$ (*m*/*z*) calcd for $C_{35}H_{22}^+$ (M^+) 442.1716, found 442.1714.

***rac*-9,9-Diphenyl-9*H*-cyclopenta[1,2-*c*:4,3-*c*']diphenanthrene (3c):** To a solution of PhMgBr (1.0 M solution in THF, 0.12 mL, 0.12 mmol) was added a mixture of **5** (30 mg, 79 μmol) in THF (1.0 mL). The resulting mixture was stirred for 30 min, and saturated aqueous NH_4Cl (0.1 mL) was added. The resulting mixture was then filtered through a pad of silica gel and concentrated to give a colorless solid (35 mg). The obtained solid was dissolved in a mixture of trifluoroacetic acid (12 μL, 0.13 mmol), and the resulting mixture was heated at 80 °C for 21 h. After the addition of saturated aqueous $NaHCO_3$ (0.1 mL), the resulting mixture was concentrated under reduced pressure. The crude residue was purified by silica-gel column chromatography using AcOEt/hexane (1/5) as an eluent to afford *rac*-**3c** (32 mg, 78% yield) as a colorless solid. *rac*-**3c** can be separated into enatiomerically-pure (*P*)-**3c** and (*M*)-**3c** by HPLC equipped with a DICEL CHIEAPAK® IF-3 column (4.6 mm × 250 mm) [t_R = 12.2 min and 16.1 min (flow rate: 1.0 mL; eluent: $CHCl_3$/hexane = 25/75)]: mp 185-186 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 8.0 Hz, 2H), 7.76–7.67 (m, 8H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.43–7.41 (m, 4H), 7.26–7.24 (m, 8H), 7.09 (t, *J* = 7.4, 2H), 6.31 (dt, *J* = 7.7, 2H), 4.35 (s,2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.1, 145.2, 137.2, 132.3, 131.7, 130.9, 128.8, 128.6, 128.5, 128.0, 127.4, 127.1, 126.9, 126.8, 126.6, 126.5, 123.7, 123.4, 66.0; HRMS-ESI$^+$ (*m*/*z*) calcd for $C_{41}H_{26}$ (M^+) 518.2029, found 518.2013.

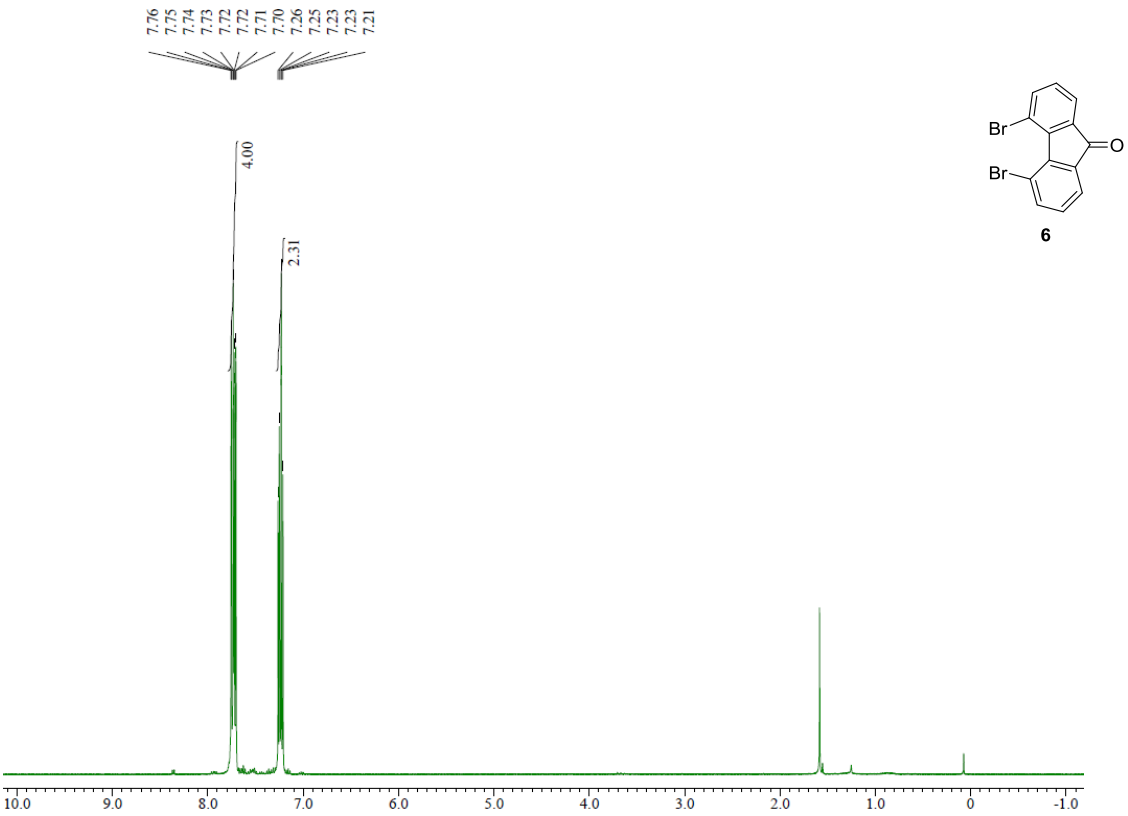

Figure S1. ^{1}H NMR spectrum of **6** ($CDCl_3$).

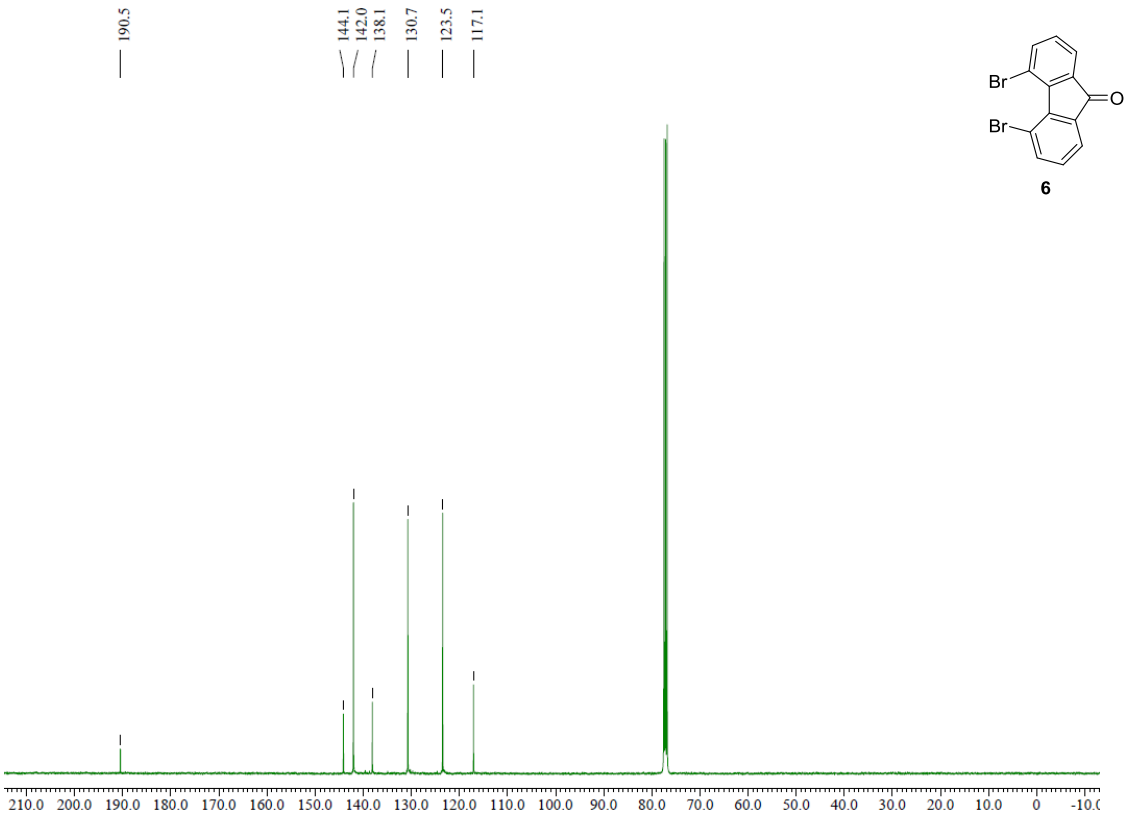

Figure S2. ^{13}C NMR spectrum of **6** ($CDCl_3$).

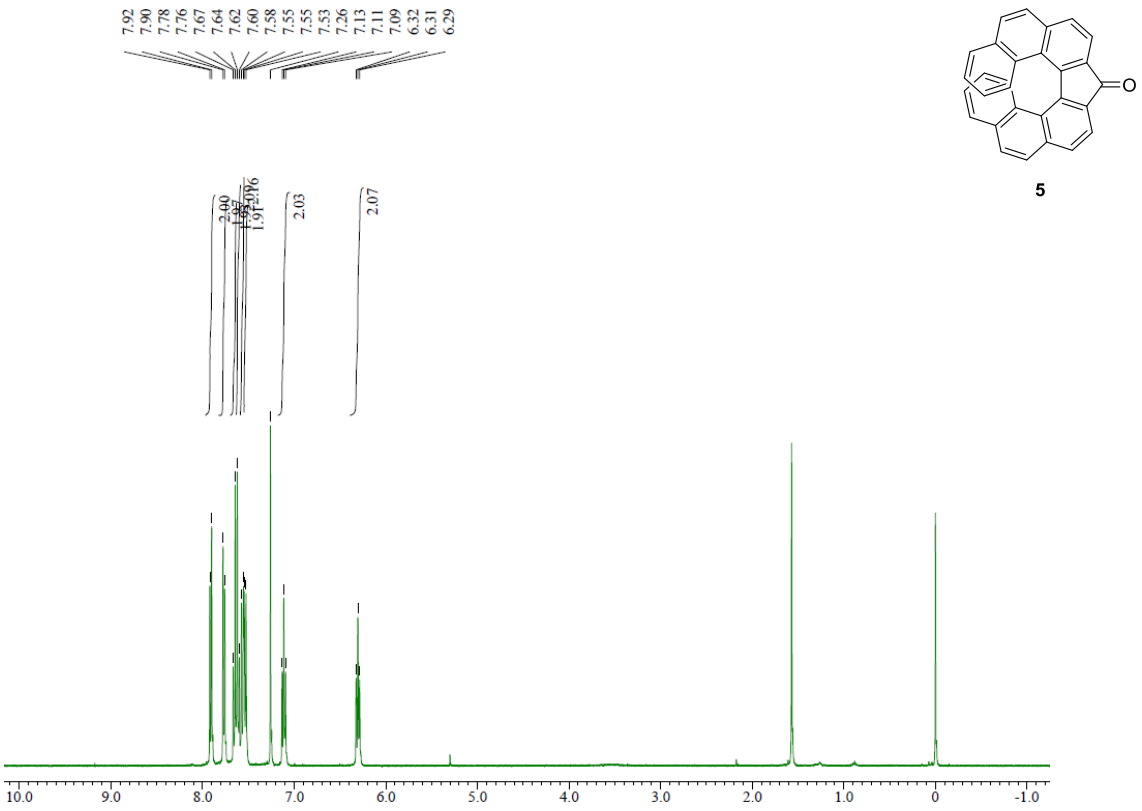

Figure S3. ^{1}H NMR spectrum of **5** ($CDCl_3$).

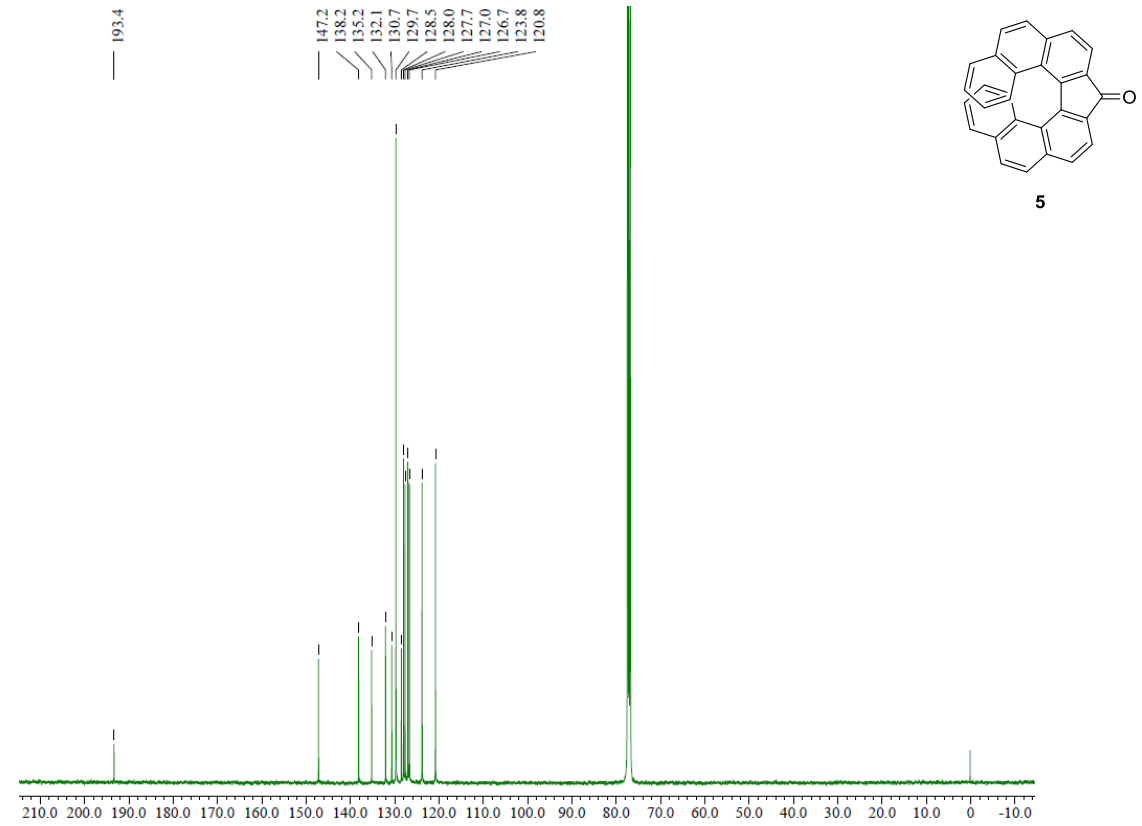

Figure S4. ^{13}C NMR spectrum of **5** ($CDCl_3$).

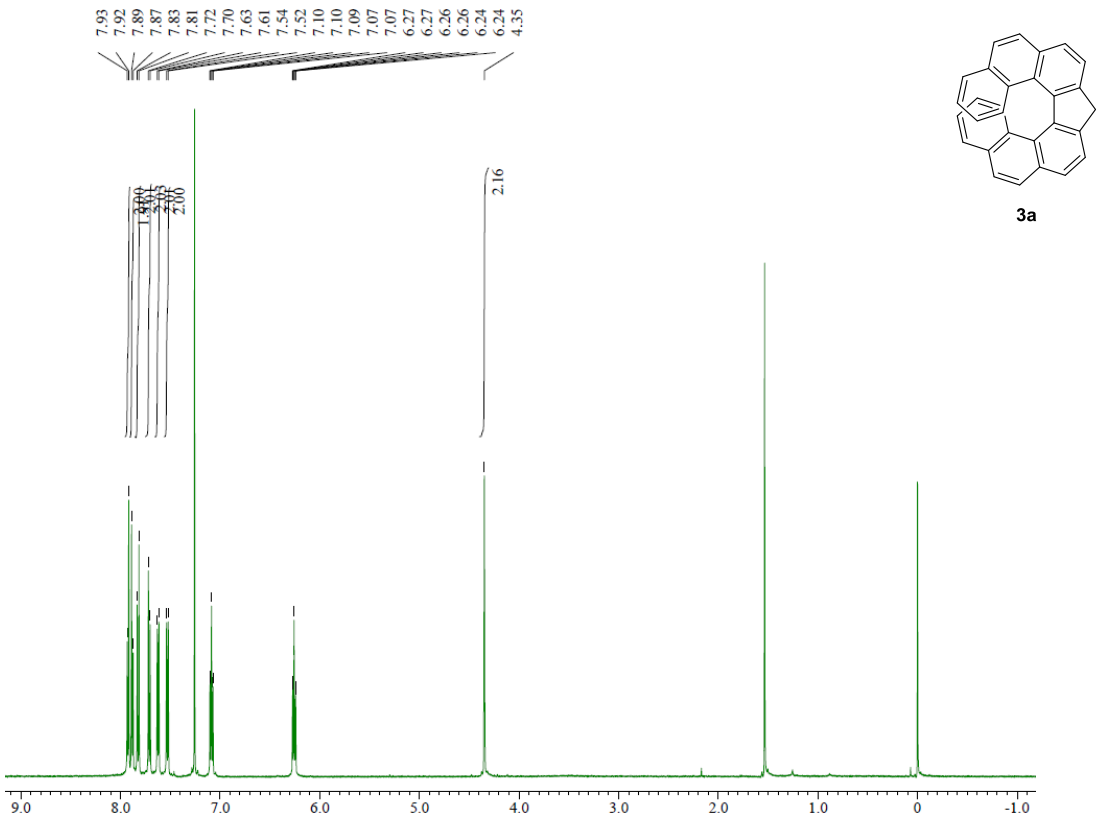

Figure S5. ^{1}H NMR spectrum of **3a** ($CDCl_3$).

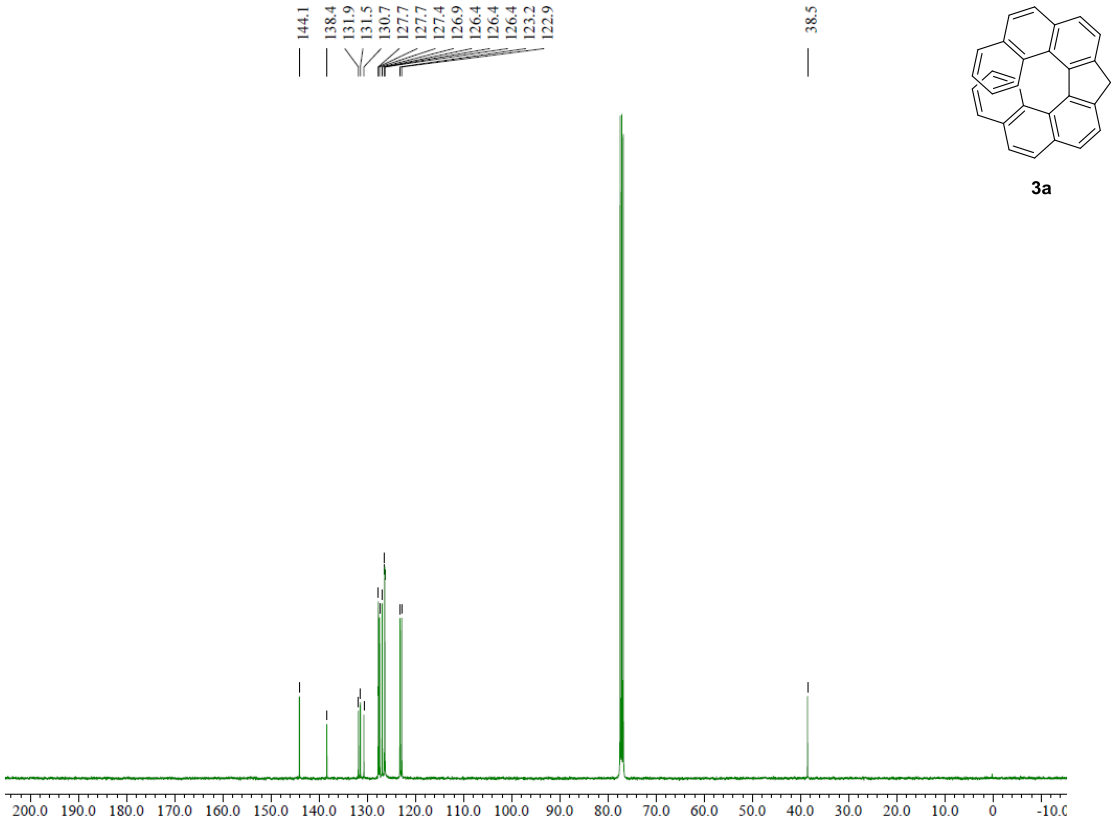

Figure S6. ^{13}C NMR spectrum of **3a** ($CDCl_3$).

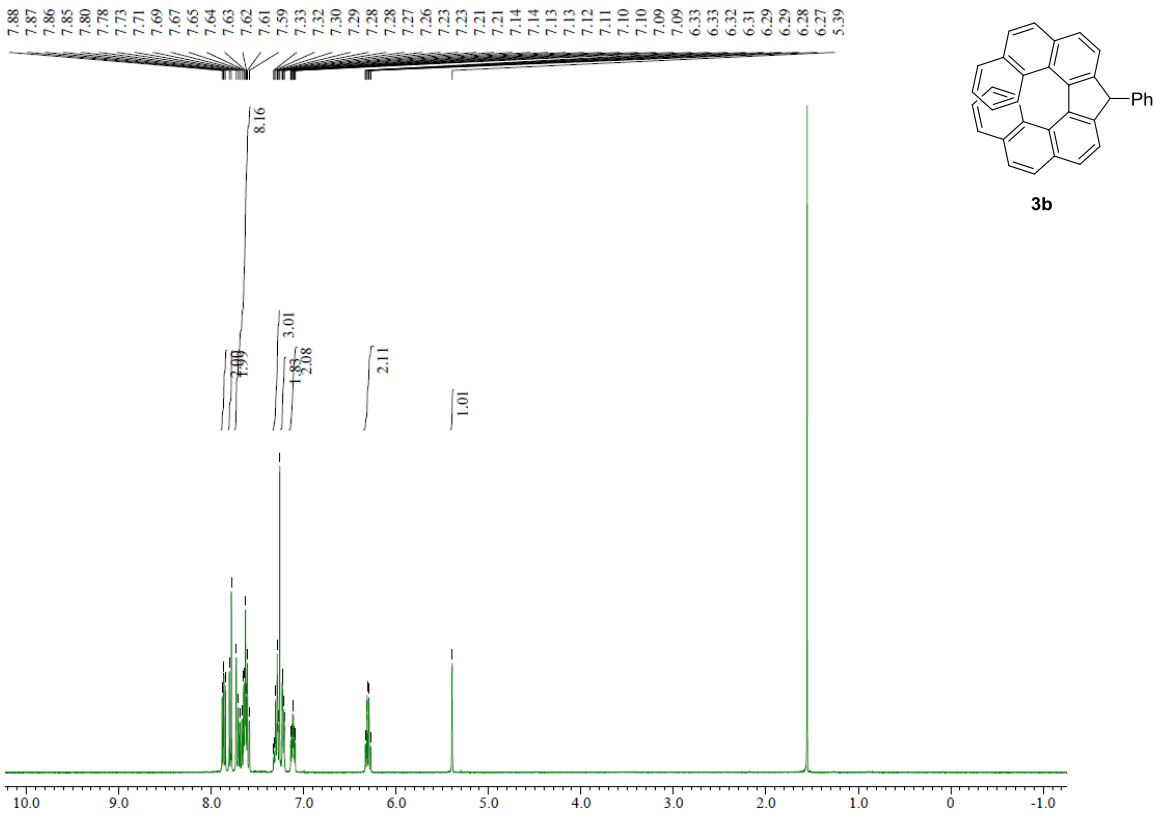

Figure S7. ^{1}H NMR spectrum of **3b** ($CDCl_3$).

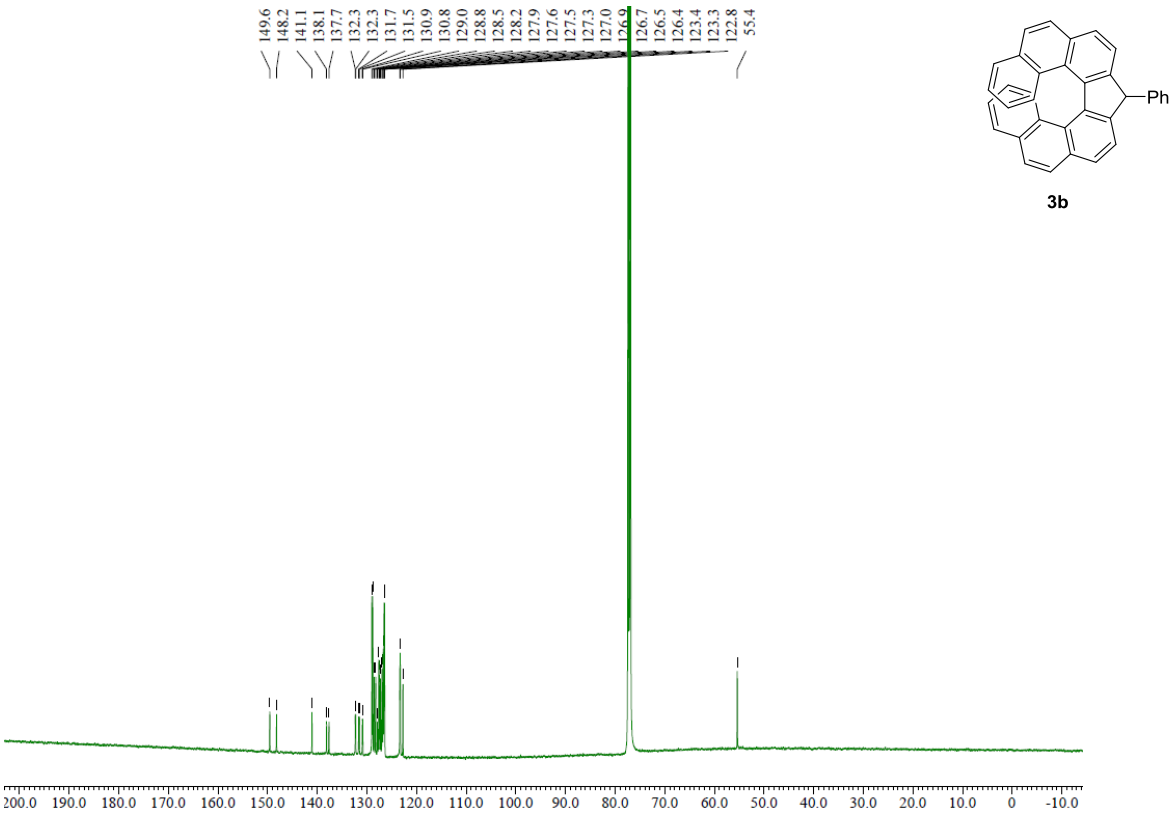

Figure S8. ^{13}C NMR spectrum of **3b** ($CDCl_3$).

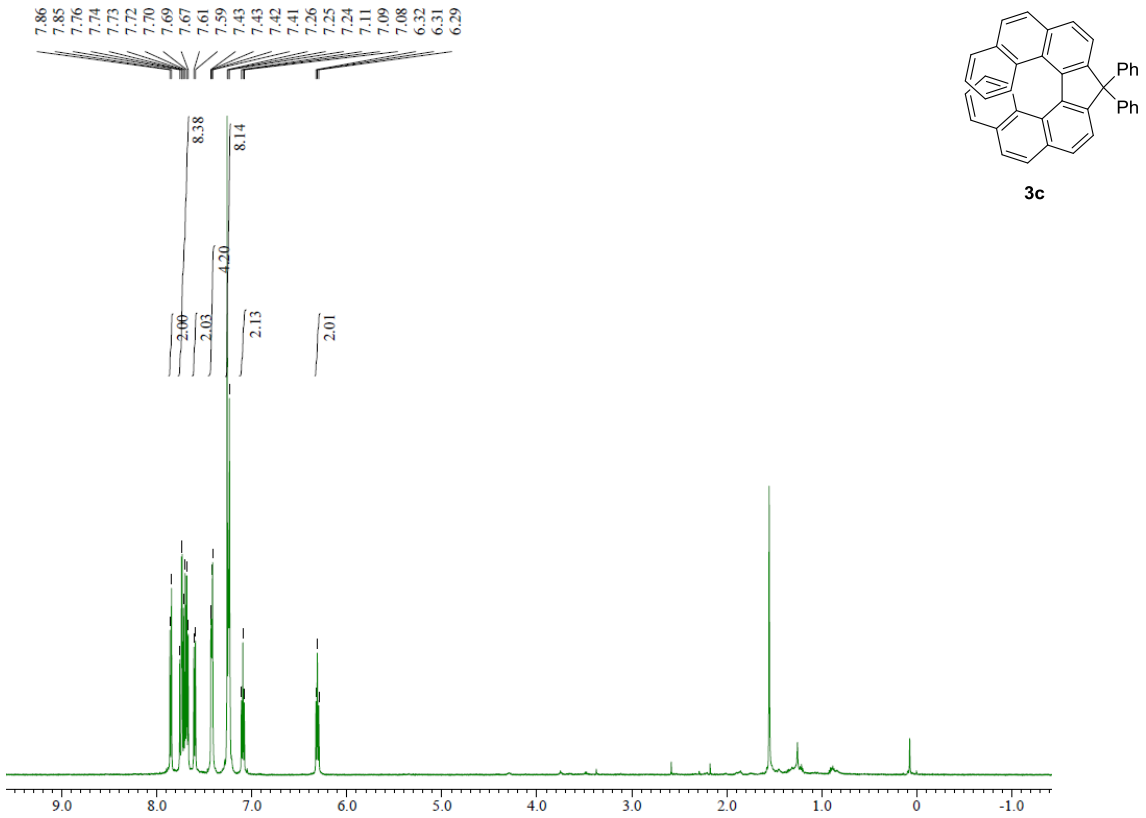

Figure S9. ^{1}H NMR spectrum of **3c** ($CDCl_3$).

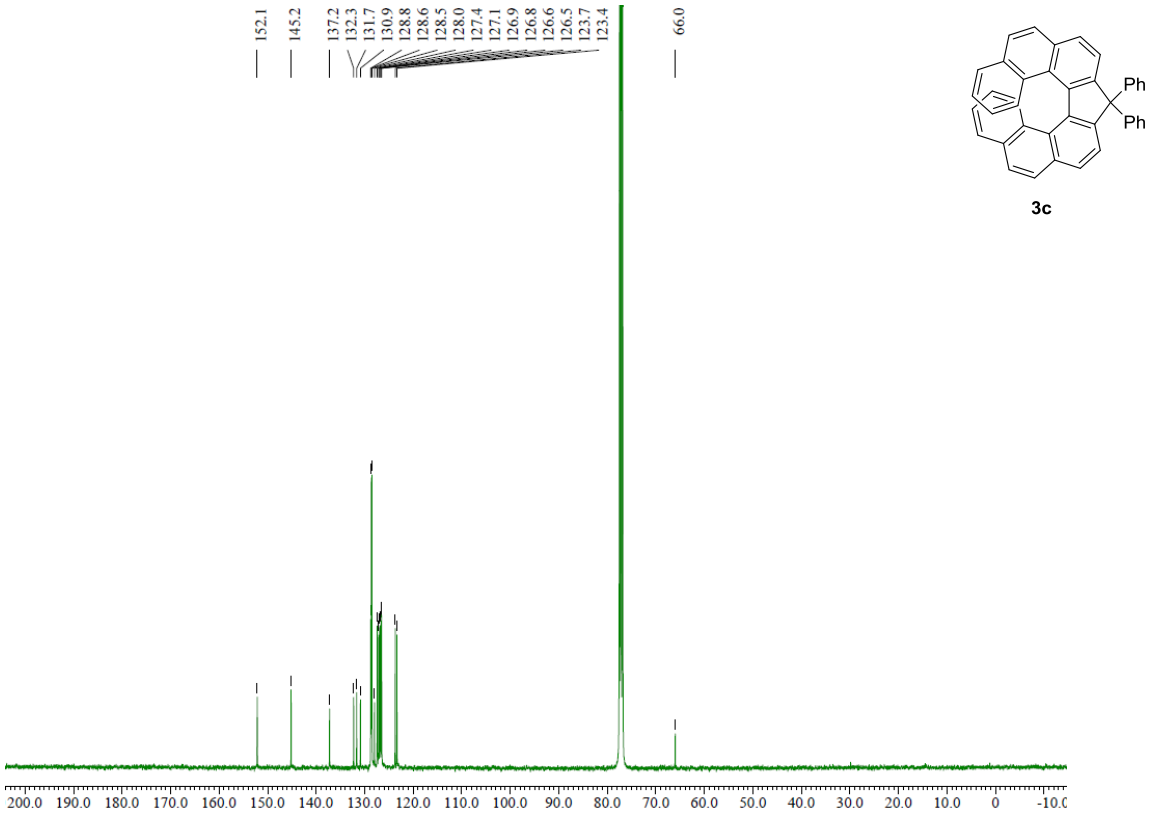

Figure S10. ^{13}C NMR spectrum of **3c** ($CDCl_3$).

X-ray Crystallography. For X-ray crystallographical analyses, suitable single crystals were selected under ambient conditions, mounted with perfluoroalkyl ether to the glass fiber, and transferred to the goniometer of a VariMax diffractometer with a graphite-monochromated Mo−Kα radiation (λ = 0.71075 Å) or Cu−Kα irradiation (λ = 1.54187 Å). The structures were solved by a direct method (SIR 2002[2]) and refined by full-matrix least-squares techniques against $F2$ (SHELXL-97[3]). The intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

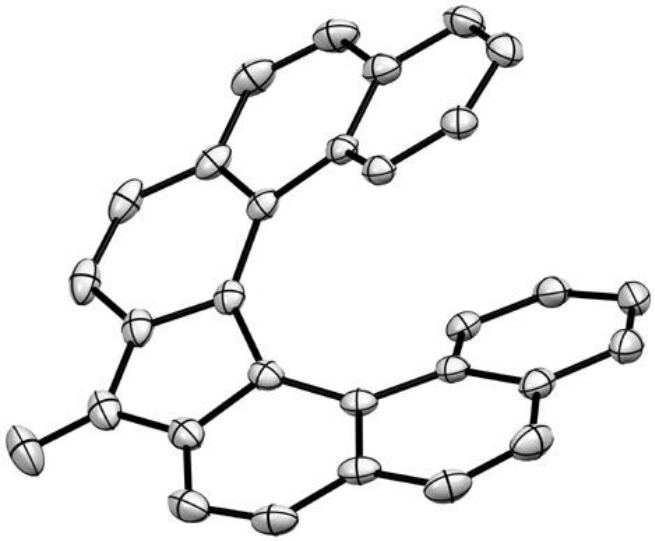

Figure S11. ORTEP drawing of **5** (50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.)

Table S1. Crystallographic data and structure refinement details for **5**

Formula	$C_{29}H_{16}O$	
Formula weight	380.42	
Temperature	293(2) K	
Wavelength	0.71075 Å	
Crystal system	'orthorhombic'	
Space group	'*P*bca'	
Unit cell dimensions	a = 13.816(2) Å	α = 90°
	b = 13.862(3) Å	β = 90°
	c = 19.248(4) Å	γ = 90°
Volume	3686.3(12) Å^3	
Z	8	
Density (calculated)	1.371 g/cm^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	1584	
Crystal size	0.25 × 0.20 × 0.10 mm^3	
Theta range for data collection	3.30 to 25.00°	
Index ranges	–16<=h<=16, –16<=k<=15, –17<=l<=22	
Reflections collected	23178	
Independent reflections	3219 [R_{int} = 0.0420]	
Completeness to theta = 25.00°	99.0%	
Max. and min. transmission	0.9919 and 0.9799	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3219 / 0 / 271	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R_1 = 0.0394, wR_2 = 0.1259	
R indices (all data)	R_1 = 0.0439, wR_2 = 0.1324	
Largest diff. peak and hole	0.193 and –0.180 e/Å^3	

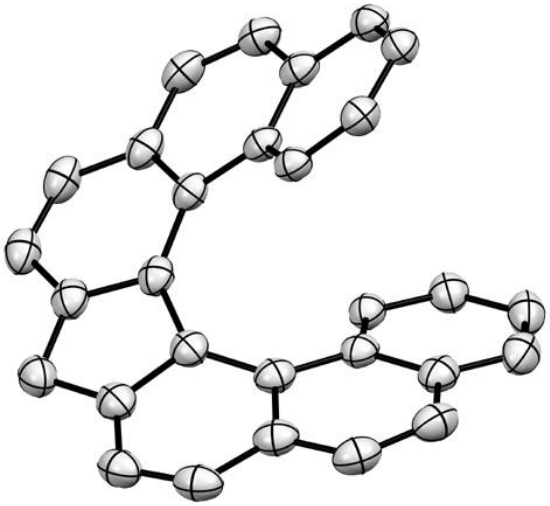

Figure S12. ORTEP drawing of **3a** (50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.)

Table S2. Crystallographic data and structure refinement details for **3a**

Formula	$C_{29}H_{18}$	
Formula weight	366.43	
Temperature	93(2) K	
Wavelength	1.54187 Å	
Crystal system	'orthorhombic'	
Space group	'$P2_12_12_1$'	
Unit cell dimensions	a = 8.051(3) Å	α = 90°
	b = 14.010(6) Å	β = 90°
	c = 16.659(6) Å	γ = 90°
Volume	1879.0(13) Å^3	
Z	4	
Density (calculated)	1.295 g/cm^3	
Absorption coefficient	0.557 mm^{-1}	
F(000)	768	
Crystal size	0.20 × 0.20 × 0.20 mm^3	
Theta range for data collection	4.123 to 73.770°	
Index ranges	–10<=h<=9, –17<=k<=17, –20<=l<=20	
Reflections collected	28093	
Independent reflections	3735 [R_{int} = 0.0515]	
Completeness to theta = 25.00°	99.1%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3735/ 0 / 262	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R_1 = 0.0438, wR_2 = 0.1070	
R indices (all data)	R_1 = 0.0456, wR_2 = 0.1087	
Largest diff. peak and hole	0.124 and –0.217 e/Å^3	

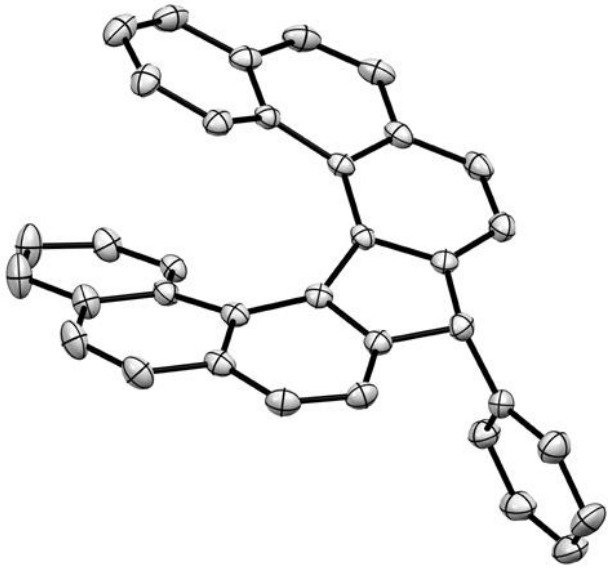

Figure S13. ORTEP drawing of **3b** (50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.)

Table S3. Crystallographic data and structure refinement details for **3b**

Formula	$C_{35}H_{22}$	
Formula weight	442.52	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	'monoclinic'	
Space group	'$P2_1$/c'	
Unit cell dimensions	a = 12.558(4) Å	α = 90 °
	b = 14.180(4) Å	β = 102.720(5) °
	c = 26.385(8) Å	γ = 90 °
Volume	4583(2) Å^3	
Z	8	
Density (calculated)	1.283 Mg/cm^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	1856	
Crystal size	0.500 × 0.500 × 0.05 mm^3	
Theta range for data collection	2.456 to 27.499 °	
Index ranges	–16<=h<=16, –18<=k<=18, –34<=l<=34	
Reflections collected	72605	
Independent reflections	10523	
R_{int}	0.0874	
Data / restraints / parameters	10523 / 0 / 631	
Goodness-of-fit on F^2	1.257	
Final R indices [I>2sigma(I)]	R_1 = 0.0817, wR_2 = 0.1464	
R indices (all data)	R_1 = 0.0985, wR_2 = 0.1540	
Largest diff. peak and hole	0.227 and –0.236 e/Å^3	

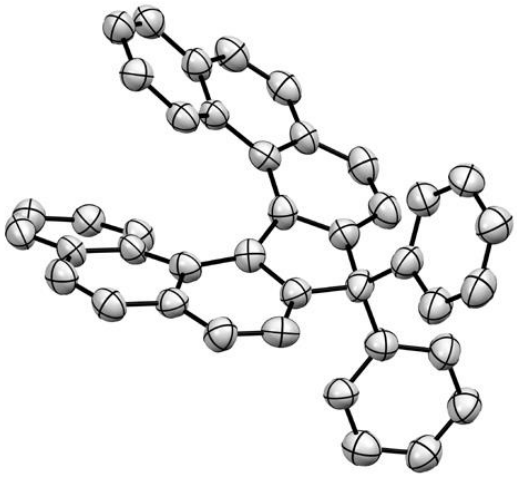

Figure S14. ORTEP drawing of **3c** (50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.)

Table S4. Crystallographic data and structure refinement details for **3c**

Formula	$C_{41}H_{26}$	
Formula weight	5182.62	
Temperature	296(2) K	
Wavelength	1.54187 Å	
Crystal system	'orthorhombic'	
Space group	'$P2_12_12_1$'	
Unit cell dimensions	a = 9.8499(2) Å	α = 90°
	b = 11.1882(4) Å	β = 90°
	c = 24.6237(4) Å	γ = 90°
Volume	2713.60(9) Å^3	
Z	4	
Density (calculated)	1.269 g/cm^3	
Absorption coefficient	0.546 mm^{-1}	
F(000)	1088	
Crystal size	0.10 × 0.10 × 0.10 mm^3	
Theta range for data collection	3.59 to 66.97°	
Index ranges	–11<=h<=11, –13<=k<=13, –29<=l<=29	
Reflections collected	31160	
Independent reflections	4830 [R_{int} = 0.0336]	
Completeness to theta = 25.00°	100%	
Max. and min. transmission	0.9474 and 0.9474	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4830 / 0 / 371	
Goodness-of-fit on F^2	1.777	
Final R indices [I>2sigma(I)]	R_1 = 0.0758, wR_2 = 0.2675	
R indices (all data)	R_1 = 0.1146, wR_2 = 0.1882	
Absolute structure parameter	–1(4)	
Largest diff. peak and hole	0.359 and –0.312 e/Å^3	

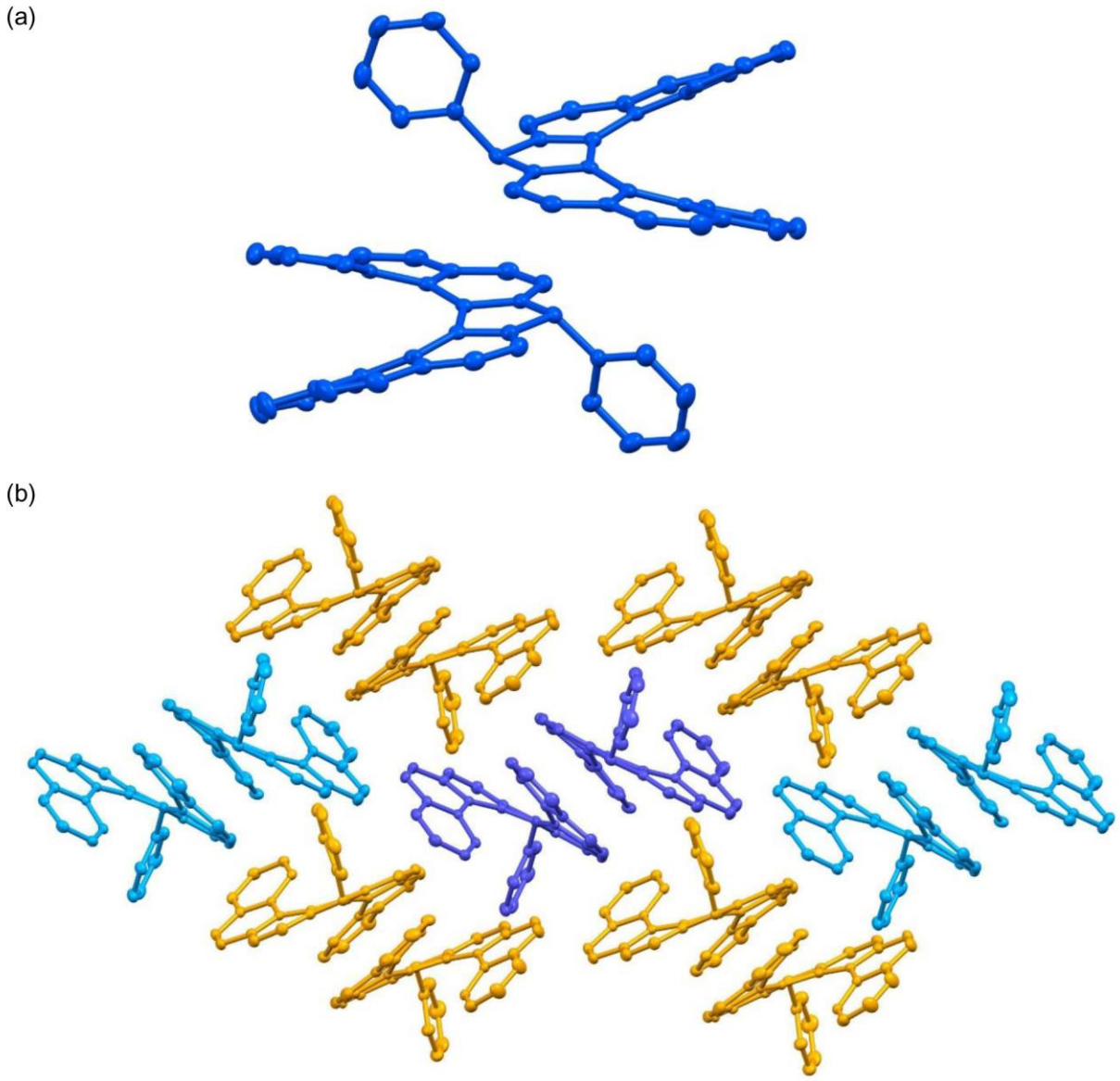

Figure S15. (a) Dimer and (b) packing structures of *rac*-**3b**.

Table S5. Coordinates (Å) and Absolute Energy of the Optimized Structure for **3a**[a]

atom	x	y	z	atom	x	y	z
C	-0.548767	-1.028563	-1.553853	C	-4.080074	-0.077137	0.576651
H	0.208705	-0.281737	-1.751328	H	-5.028248	0.204976	1.028165
C	-1.766554	0.584573	-0.040717	C	-3.372894	2.264980	0.818254
C	-2.666373	-1.685144	-0.558245	H	-4.373439	2.489418	1.179288
C	1.626227	-0.713185	0.692207	C	-2.532666	-2.947918	-1.180472
C	1.142748	2.923581	-0.270364	H	-3.327558	-3.678210	-1.046903
C	-0.745667	1.587627	0.067805	C	3.872646	-1.345366	-0.138616
C	-1.440012	-3.241162	-1.972754	H	4.643940	-2.104428	-0.244646
H	-1.355307	-4.211614	-2.454357	C	2.666793	-1.684565	0.558323
C	-1.626019	-0.713578	-0.692156	C	3.372206	2.265591	-0.818856
C	0.549032	-1.028387	1.553963	H	4.372540	2.490077	-1.180449
H	-0.208576	-0.281723	1.751414	C	3.064786	0.933291	-0.459261
C	-1.143348	2.923406	0.270724	C	2.533357	-2.947362	1.180615
C	0.745302	1.587828	-0.067615	H	3.328341	-3.677537	1.046930
C	1.766473	0.584840	0.040645	C	-0.000329	3.863167	0.000372
C	-3.065154	0.932804	0.458794	H	0.228906	4.522656	0.850086
C	-3.872397	-1.346155	0.138586	H	-0.229556	4.523245	-0.848870
H	-4.643407	-2.105483	0.244814	C	1.440810	-3.240783	1.972933
C	-0.454737	-2.258789	-2.179639	H	1.356312	-4.211203	2.454632
H	0.385422	-2.461744	-2.838045	C	2.442261	3.272261	-0.648398
C	-2.442973	3.271845	0.648271	H	2.701941	4.311607	-0.833273
H	-2.702922	4.311107	0.833300	C	4.079933	-0.076387	-0.577058
C	0.455332	-2.258572	2.179812	H	5.028015	0.205845	-1.028714
H	-0.384755	-2.461697	2.838260				
absolute energy *E* (B3LYP): -1115.94597398 au							

[a]Calculated by DFT method [B3LYP/6-31G(d)]

Table S6. Coordinates (Å) and Absolute Energy of the Optimized Structure for **3b**[a]

atom	x	y	z	atom	x	y	z
C	-2.668076	-0.428945	-0.971459	H	0.557958	4.983093	-1.323112
H	-2.955447	-0.745170	-1.986321	C	2.780289	0.734340	2.457397
C	0.322464	1.705567	-0.262360	H	2.932318	-0.074703	3.166510
C	0.721236	-1.806596	-0.236961	C	-3.951079	-0.250445	-0.169869
C	1.462275	1.715930	0.648739	C	3.789424	-0.201285	-1.781530
C	-1.962548	-2.771661	-0.095095	H	4.033624	0.651678	-2.408698
H	-2.985428	-3.137575	-0.113790	C	-3.905318	0.103032	1.187208
C	-1.305689	3.105755	-1.500083	H	-2.941638	0.247536	1.668710
H	-1.558643	4.073568	-1.925693	C	2.004786	4.014970	-0.097010
C	-0.385362	-0.903429	-0.370928	H	2.680474	4.866300	-0.065429
C	0.417591	-3.130961	0.223078	C	3.669534	1.823945	2.431490
C	-1.681822	-1.446948	-0.438588	H	4.520559	1.852198	3.106603
C	2.104099	-1.527160	-0.610075	C	3.431081	2.872284	1.564480
C	-0.919596	-3.580737	0.312113	H	4.081420	3.744101	1.563186
H	-1.106799	-4.594533	0.657069	C	2.786817	-3.680765	0.405288
C	3.132426	-2.451194	-0.245987	H	3.585414	-4.361151	0.690981
C	-0.052957	2.953106	-0.861737	C	-5.079999	0.269966	1.917385
C	1.706370	0.684948	1.586687	H	-5.026845	0.544360	2.967739
H	1.024678	-0.153230	1.642968	C	4.807206	-1.069445	-1.346881
C	-0.517912	0.577300	-0.548093	H	5.841723	-0.880575	-1.620613
C	-1.812301	0.818844	-1.042156	C	4.475072	-2.182129	-0.598747
C	-2.216825	2.068762	-1.518670	H	5.242963	-2.889153	-0.293046
H	-3.219709	2.207227	-1.913537	C	-6.323350	0.086607	1.303627
C	2.473301	-0.427593	-1.420311	H	-7.238875	0.217302	1.874311
H	1.706250	0.240474	-1.788639	C	-6.380327	-0.265531	-0.044135
C	1.484183	-4.024603	0.580393	H	-7.340905	-0.412019	-0.531223
H	1.217997	-4.993803	0.995383	C	-5.199766	-0.432884	-0.774159
C	2.320206	2.858863	0.689555	H	-5.250465	-0.709694	-1.825165
C	0.841130	4.075389	-0.795638				
absolute energy *E* (B3LYP): -1346.99097542 au							

[a]Calculated by DFT method [B3LYP/6-31G(d)]

Table S7. Coordinates (Å) and Absolute Energy of the Optimized Structure for **3c**[a]

atom	x	y	z	atom	x	y	z
C	2.344287	-1.740650	0.250438	H	-0.830048	3.879523	2.332233
C	-1.289189	-1.028618	-0.568249	C	1.732432	-3.761700	-1.643922
C	0.042511	0.699264	0.262614	H	1.459833	-4.551894	-2.339301
C	3.322055	-2.703625	-0.150993	C	4.578789	2.740465	-0.496382
C	1.051681	1.706384	0.426512	H	5.314047	3.467890	-0.159882
C	0.716073	2.820911	1.263430	C	4.859963	-1.901764	1.557022
C	3.871233	-1.011342	2.013241	H	5.825730	-1.948326	2.052918
H	4.064640	-0.379918	2.875990	C	4.578745	-2.740386	0.496292
C	1.051703	-1.706214	-0.426751	H	5.314014	-3.467793	0.159776
C	2.344312	1.740746	-0.250599	C	4.860064	1.901763	-1.557033
C	2.996056	3.676521	1.152185	H	5.825850	1.948312	-2.052892
H	3.761019	4.386963	1.456067	C	-3.122769	-0.578030	1.151827
C	3.322078	2.703725	0.150861	C	-2.701961	1.696173	-1.885546
C	0.042543	-0.699089	-0.262935	H	-1.792368	2.215267	-1.603311
C	1.732396	3.761833	1.643701	C	-4.299656	0.071688	1.558770
H	1.459783	4.552045	2.339055	H	-4.656143	0.934889	1.005465
C	0.716106	-2.820777	-1.263649	C	-1.624581	2.174125	1.296145
C	-2.267864	0.000025	-0.000091	H	-2.657415	2.373360	1.563326
C	-1.624540	-2.173962	-1.296453	C	-3.123193	0.577903	-1.151627
H	-2.657376	-2.373212	-1.563631	C	-5.033635	0.384461	-2.654052
C	3.871366	1.011309	-2.013247	H	-5.943059	-0.135907	-2.943597
H	4.064831	0.379813	-2.875932	C	-4.605027	-1.503257	3.371688
C	2.646618	-0.935625	1.374059	H	-5.177403	-1.862831	4.222563
H	1.894922	-0.260805	1.761356	C	-3.436014	2.154544	-2.981325
C	-1.289218	1.028749	0.567960	H	-3.087890	3.026281	-3.529376
C	-2.701145	-1.696257	1.885556	C	-5.032739	-0.384828	2.654821
H	-1.791589	-2.215238	1.603028	H	-5.942138	0.135414	2.944676
C	-0.611624	-3.018433	-1.705773	C	-3.434807	-2.154727	2.981572
H	-0.829994	-3.879402	-2.332476	H	-3.086405	-3.026437	3.529490
C	2.646713	0.935632	-1.374136	C	-4.300140	-0.071929	-1.558216
H	1.895043	0.260772	-1.761414	H	-4.656387	-0.935170	-1.004812
C	2.996083	-3.676381	-1.152374	C	-4.606291	1.502927	-3.371060
H	3.761069	-4.386801	-1.456251	H	-5.178972	1.862429	-4.221761
C	-0.611675	3.018576	1.705498				
absolute energy *E* (B3LYP): -1578.02594106 au							

[a]Calculated by DFT method [B3LYP/6-31G(d)]

Table S8. The selected absorption peaks of **3** calculated by TD–DFT method [B3LYP/6-31G(d)]

	electron transition	transition energy (eV)	wavelength (nm)	main transition configuration (CI expansion coefficient)	oscillator strength *f*
3a	$S_0 \rightarrow S_1$	3.26	381	**HOMO → LUMO (0.670)**	0.2401
				HOMO → LUMO+1 (−0.168)	
3b	$S_0 \rightarrow S_1$	3.22	385	**HOMO → LUMO (0.674)**	0.1675
				HOMO–1 → LUMO (−0.153)	
3c	$S_0 \rightarrow S_1$	3.16	392	**HOMO → LUMO (0.677)**	0.1361
				HOMO–1 → LUMO (−0.137)	

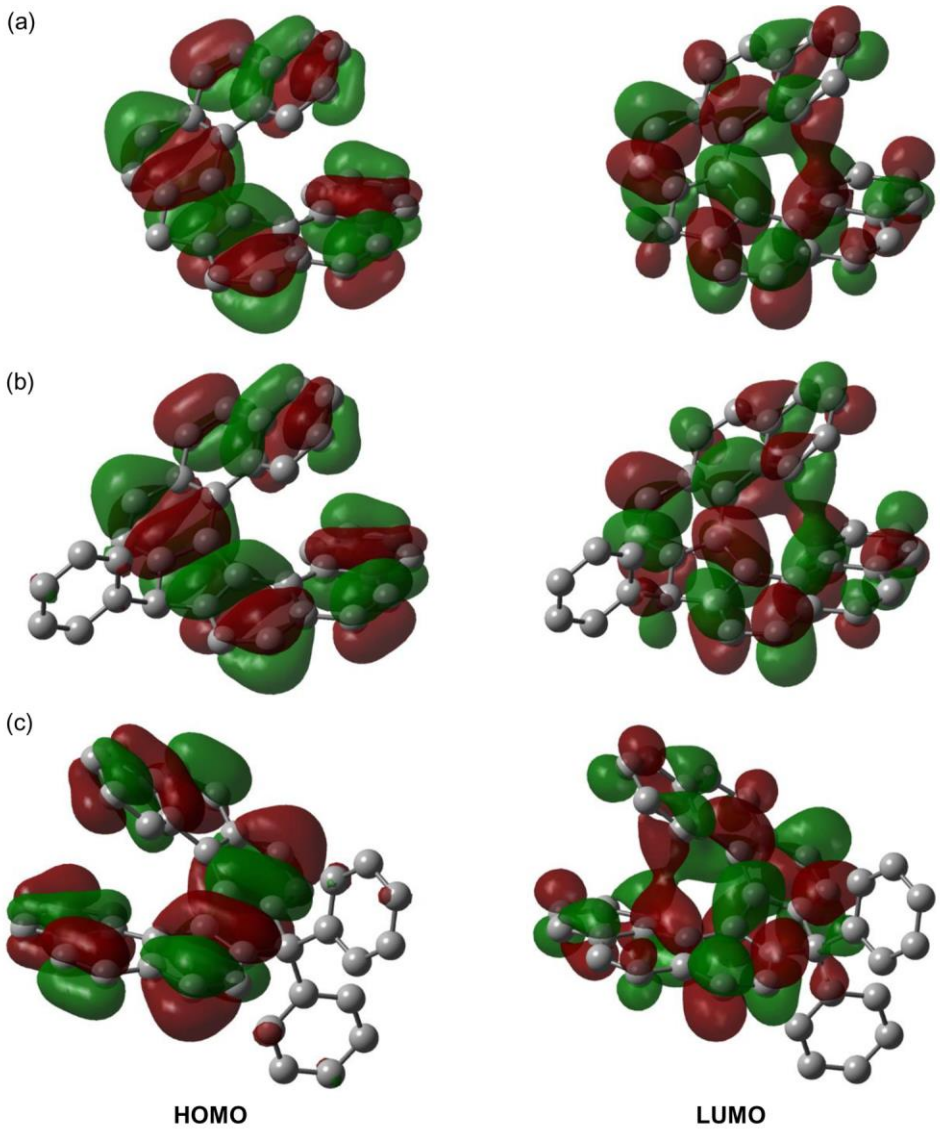

Figure S16. The HOMOs and LUMOs of (a) **3a**, (b) **3b**, and (c) **3c** calculated by DFT method [B3LYP /6-31G(d)].

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