Supplementary Information

Heptagon-Fusion Strategy as a Molecular Design Strategy for Distorted Acenes

Masato Hisada[1], Daiki Shimizu,[1]* and Kenji Matsuda[1,2]*

[1]Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan.

[2]Fukui Institute for Fundamental Chemistry, Kyoto University, Sakyo-ku, Kyoto 606-8103, Japan.

dshimizu@sbchem.kyoto-u.ac.jp (D.S.)

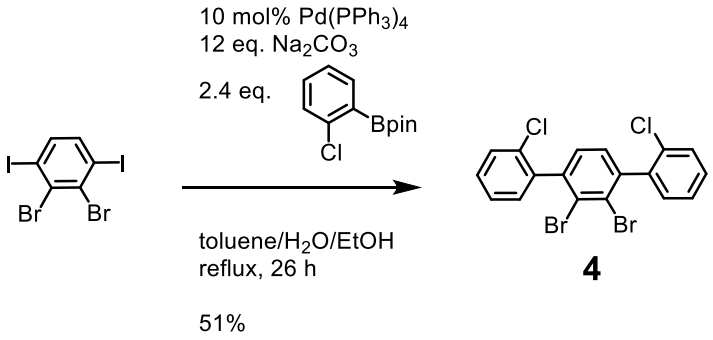
kmatsuda@sbchem.kyoto-u.ac.jp (K.M.)

Contents

1. Experimental Details

All reagents and solvents were obtained from commercial suppliers and used without further purification, unless noted. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Kanto Chemical Co., Inc., 63–210 mesh) or a Biotage Isolera One instrument with a Rening flash silica gel cartridge. Compounds **Naph7** and saddle-**Ant7** and twisted-**Ant7** were purified by preparative gel permeation chromatography (GPC) (Japan Analytical Industry Co., Ltd., JAIGEL-2HR-40, eluent: chloroform). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS400, ECZ500, or ECZ600 spectrometer. Tetramethylsilane (δ = 0 ppm for ^{1}H and ^{13}C in $CDCl_3$) and residual solvents (5.32 ppm for ^{1}H and 53.8 ppm for ^{13}C in CD_2Cl_2 and 5.97 ppm for ^{1}H and 73.39 ppm for ^{13}C in $(CD_2Cl)_2$ were used as internal references for NMR spectra. $(CD_2Cl)_2$ and CD_2Cl_2 for NMR spectroscopy were purified by passing through a short aluminum oxide pad before use. The quantitative ^{13}C NMR spectra for **4** were recorded with inverse gated decoupling at 10 s relaxation delay. Mass spectra were recorded on a Thermo Fisher Scientific EXACTIVE plus mass analyzer. Compounds **5**, **6** were synthesized in our previous report.[S1]

*2',3'-dibromo-2,2''-dichloro-1,1':4',1''-terphenyl (**4**).*



To a three-neck 1 L round-bottom flask containing 2,3-Dibromo-1,4-diiodobenzene (5.0 g, 10 mmol), (2-chlorophenyl)boronic acid (3.9 g, 25 mmol, 2.4 eq.), $Pd(PPh_3)_4$ (1.2 g, 1.0 mmol, 10 mol%), and Na_2CO_3 (13 g, 120 mmol, 12 equiv.), toluene (150 mL), water (60 mL) and EtOH (30 mL) were added under an atmosphere of N_2. The mixture was heated to reflux and stirred for 26 h. Then, the reaction mixture was diluted with CH_2Cl_2 and washed with water and brine. The organic phase was collected and dried over anhydrous Na_2SO_4. The residue, after concentration under reduced pressure, was purified by silica gel column chromatography (*n*-hexane), which afforded **4** as a colorless solid (2.4 g, 5.3 mmol, 51%). ^{1}H NMR (600 MHz, $(CD_2Cl)_2$, δ/ppm, as a mixture of two diastereomers): δ 7.51–7.48 (m, 2H), 7.39–7.26 (m, 8H); ^{13}C NMR (151 MHz, $(CD_2Cl)_2$, δ/ppm, a isomer): δ 141.9, 140.2, 132.8, 130.8, 129.4$_9$, 129.3$_6$, 129.2, 126.7$_8$, 126.7; ^{13}C NMR (151 MHz, $(CD_2Cl)_2$, δ/ppm, other isomer): δ 141.9, 140.3, 132.9, 130.7, 129.4$_8$, 129.4$_0$, 129.1, 126.8$_0$, 126.6; HR-APCI-orbitrapMS (*m*/*z*): $[M]^{+\cdot}$ calced for $C_{18}H_{10}Br_2Cl_2^{+\cdot}$, 453.8521; found, 453.8518.

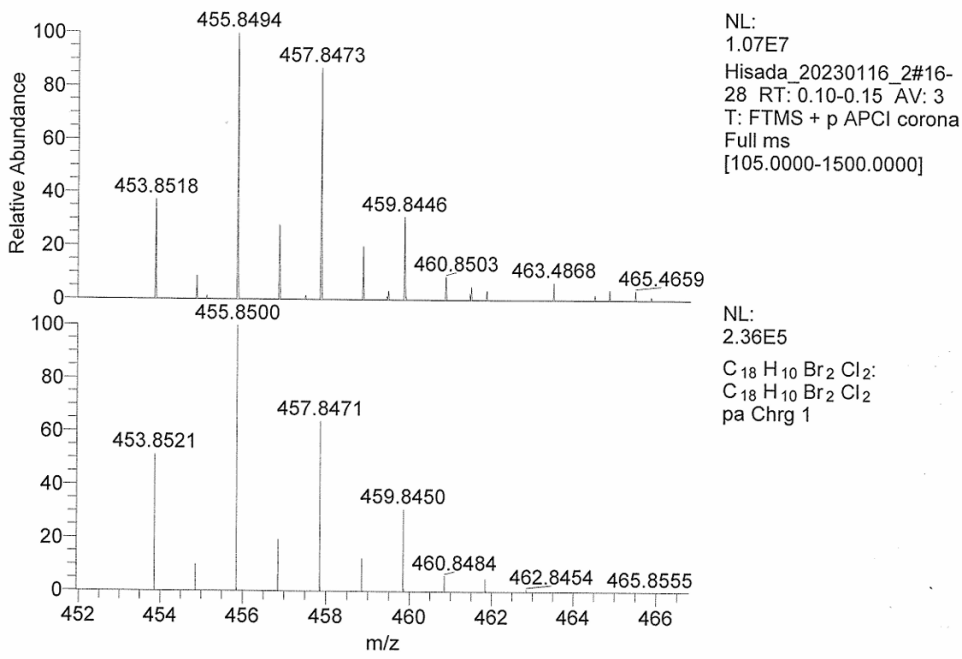


Figure S1. Observed and simulated high-resolution mass spectra of **4** (APCI-orbitrap, positive mode).

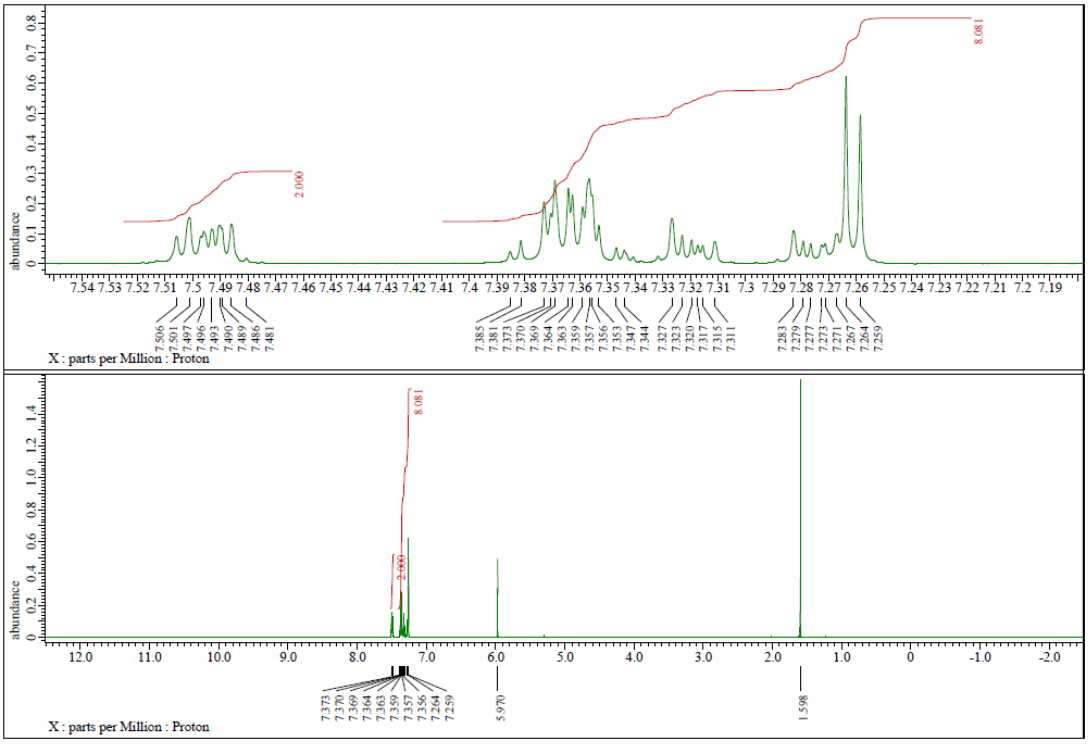


Figure S2. ^{1}H NMR spectrum of **4** as a mixture of two diastereomers at room temperature ($(CD_2Cl)_2$, 600 MHz).

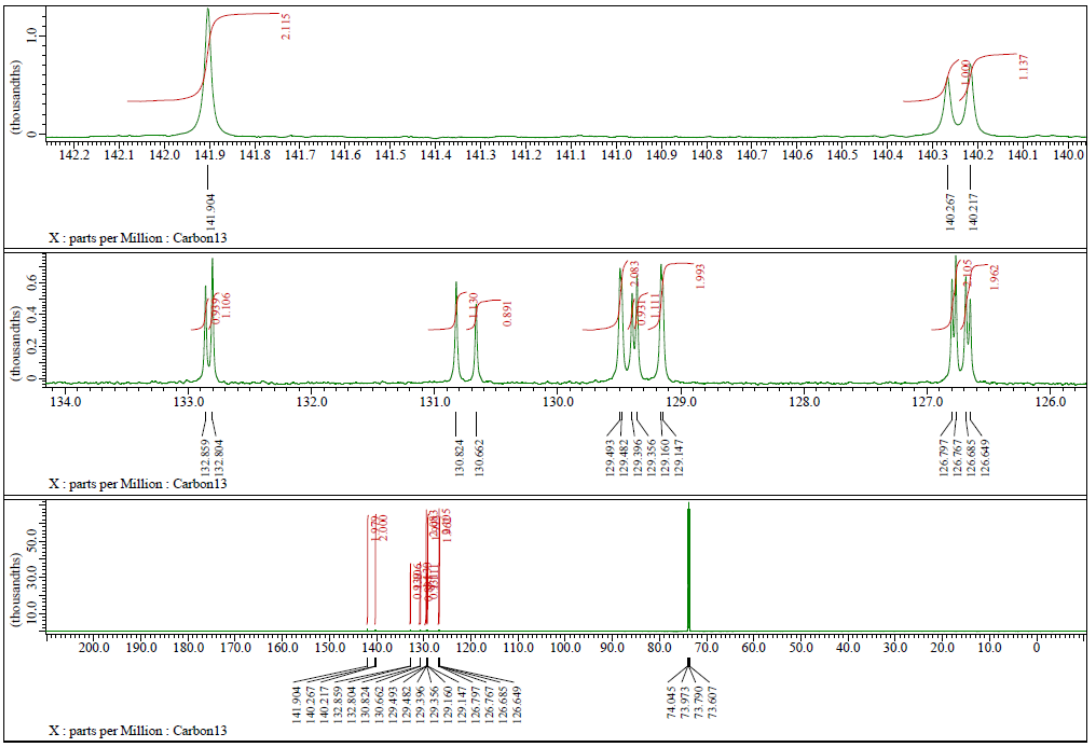
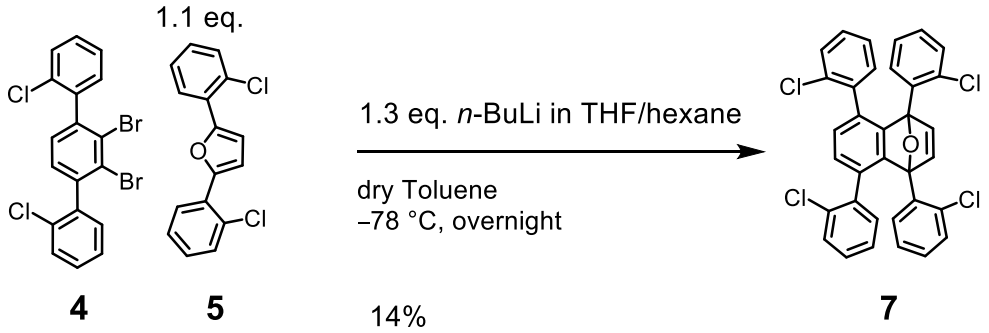


Figure S3. Quantitative ^{13}C NMR spectrum of **4** as a mixture of two diastereomers at room temperature ($(CD_2Cl)_2$, 151 MHz).

1,4,5,8-tetrakis(2-chlorophenyl)-1,4-dihydro-1,4-epoxynaphthalene (7).



To a three-neck 200 mL round-bottom flask containing **4** (440 mg, 1.0 mmol) and **5** (310 mg, 1.1 mmol, 1.1 eq.), dry toluene (24 mL) were added under an atmosphere of N_2. The mixture was cooled to −78 °C. To the mixture, *n*-butyllithium (1.6 M in THF, 0.78 mL, 1.2 mmol, 1.3 eq.) diluted in dry hexane (10 mL) was added dropwise over 1.5 h. The reaction mixture was warmed up to room temperature and stirred overnight. The reaction mixture was poured onto methanol and then diluted with EtOAc and washed with water and brine. The organic phase was collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/CH_2Cl_2 = 9/1), which afforded **6** as a colorless solid (80 mg, 0.14 mmol, 14 %).

^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): δ 8.02 (s, 1H), 7.72 (s, 1H), 7.30–6.88 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$, δ/ppm): δ 148.8, 143.4, 137.4, 134.5, 133.1, 132.8, 132.3, 131.0, 130.4, 130.1, 129.1, 128.3, 128.1, 127.1, 125.8, 125.6, 93.0; HR-ESI-orbitrapMS (*m*/*z*): $[M + H]^+$ calced for $C_{34}H_{20}OCl_4Na^+$, 607.0160; found, 607.0159.

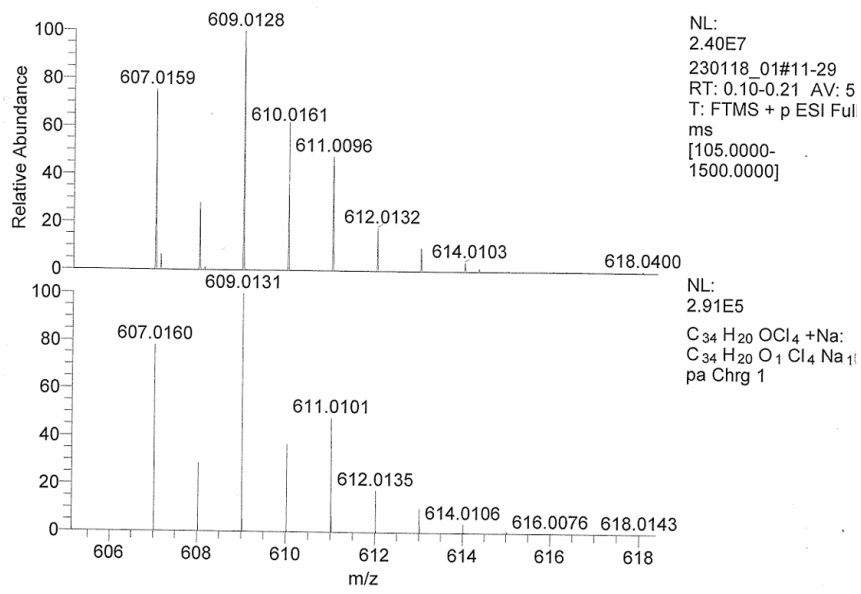


Figure S4. Observed and simulated high-resolution mass spectra of **7** (ESI-orbitrap, positive mode).

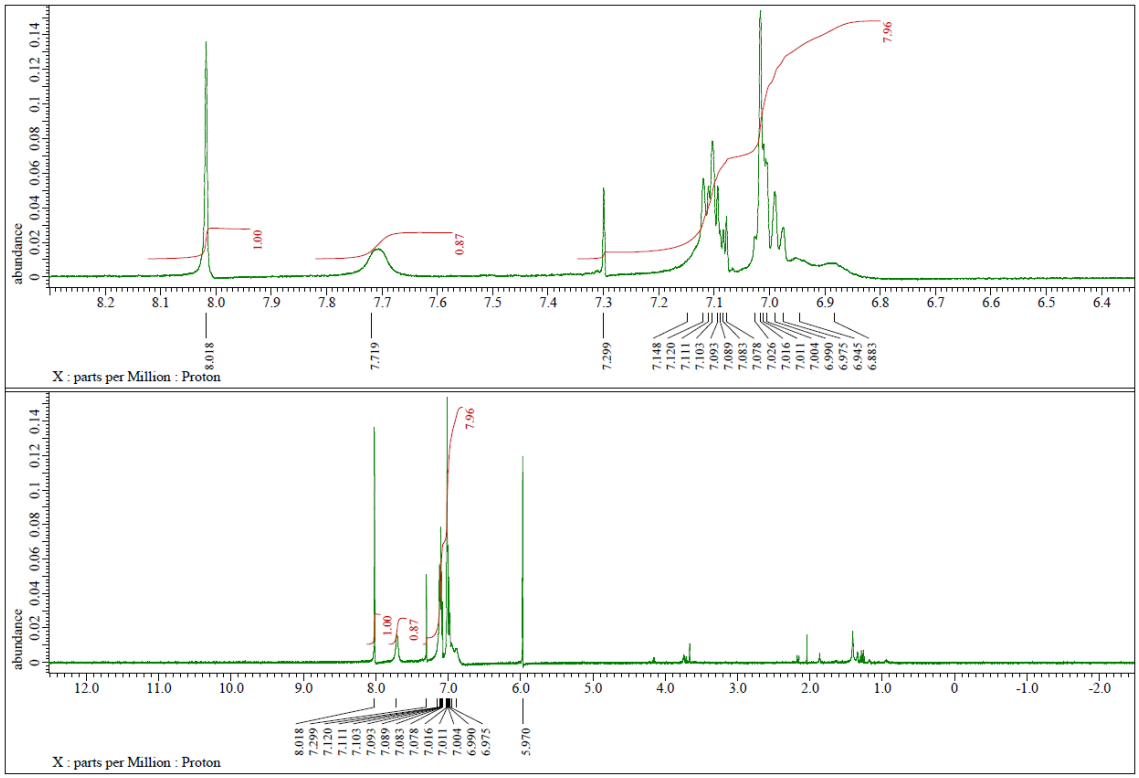


Figure S5. ^{1}H NMR spectrum of **7** at 120°C ($(CDCl_2)_2$, 500 MHz).

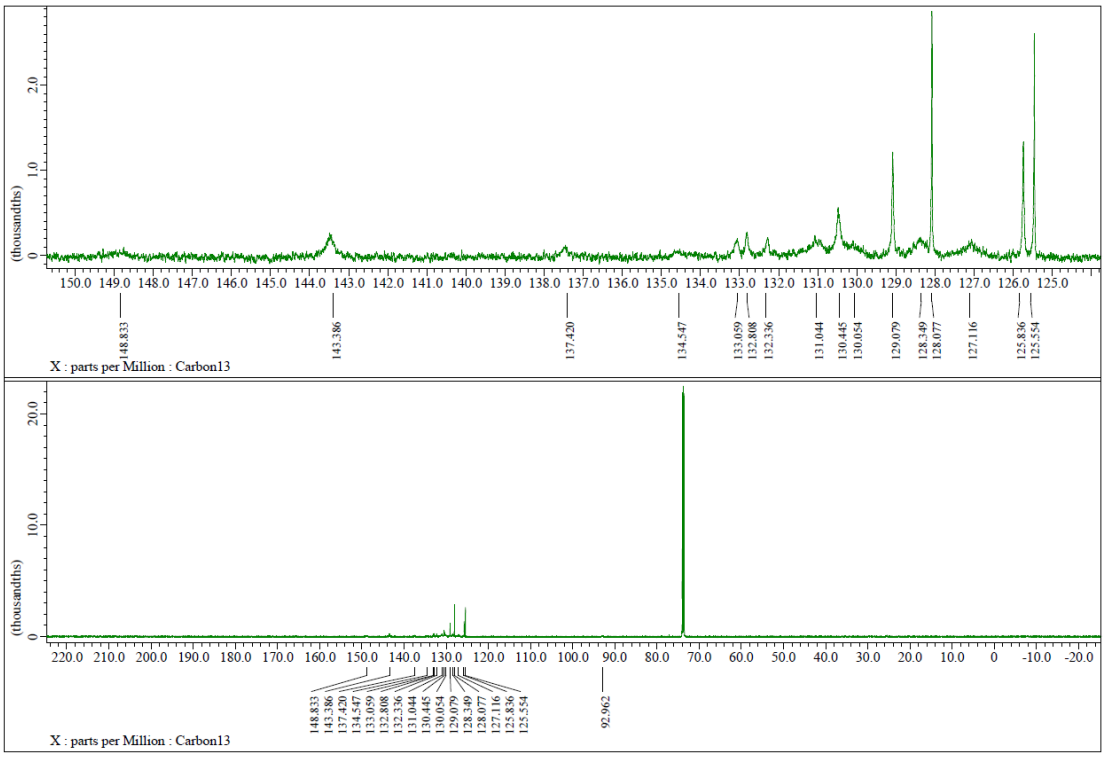
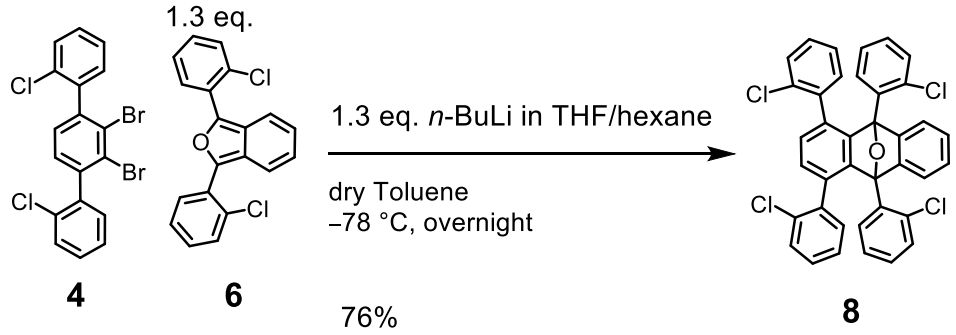


Figure S6. ^{13}C NMR spectrum of **7** at 120°C ($(CDCl_2)_2$, 126 MHz).

*1,4,9,10-tetrakis(2-chlorophenyl)-9,10-dihydro-9,10-epoxyanthracene (**8**).*



To a three-neck 200 mL round-bottom flask containing **4** (900 mg, 2.0 mmol) and **6** (930 mg, 2.7 mmol, 1.4 eq.), dry toluene (48 mL) were added under an atmosphere of N_2. The mixture was cooled to −78 °C. To the mixture, *n*-butyllithium (1.6 M in THF, 1.6 mL, 2.6 mmol, 1.3 eq.) diluted in dry hexane (21 mL) was added dropwise over 1.5 h. The reaction mixture was warmed up to room temperature and stirred overnight. The reaction mixture was poured onto methanol and then diluted with EtOAc and washed with water and brine. The organic phase was collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/CH_2Cl_2 = 9/1→1/1), which afforded **8** as a colorless solid (950 mg, 1.5 mmol, 76 %).

^{1}H NMR (600 MHz, $CDCl_3$, δ/ppm): δ 8.16–8.15 (m, 2H), 7.90 (br, 2H), 7.29–7.26 (m, 4H), 7.21–7.02 (m, 12H), 6.96–6.93 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$, δ/ppm): δ 150.5, 147.8, 137.1, 136.0, 133.0, 132.4, 132.2, 131.4, 131.2, 130.2, 129.3, 129.1, 128.1, 127.7, 125.2, 125.1, 125.0, 124.0, 91.0; HR-ESI-orbitrapMS (*m*/*z*): $[M + H]^+$ calced for $C_{38}H_{22}OCl_4Na^+$, 657.0317; found, 657.0304.

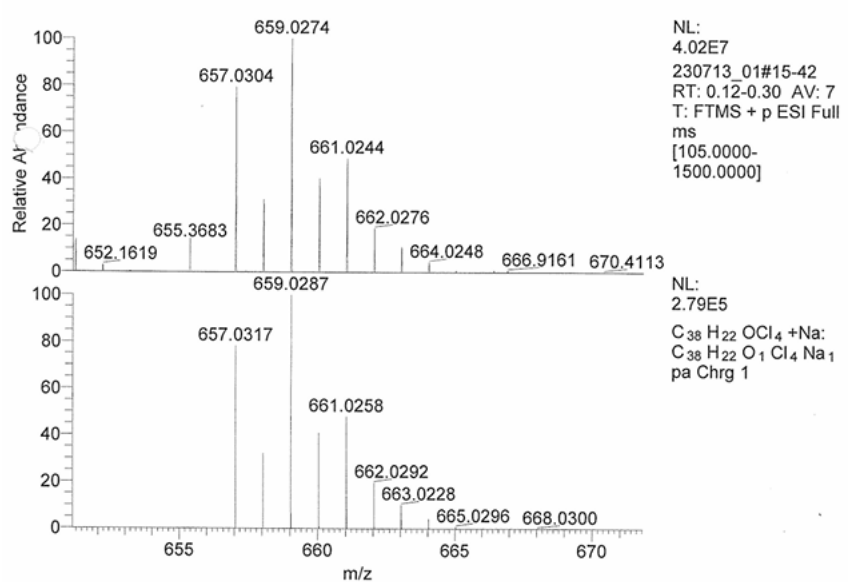


Figure S7. Observed and simulated high-resolution mass spectra of **8** (ESI-orbitrap, positive mode).

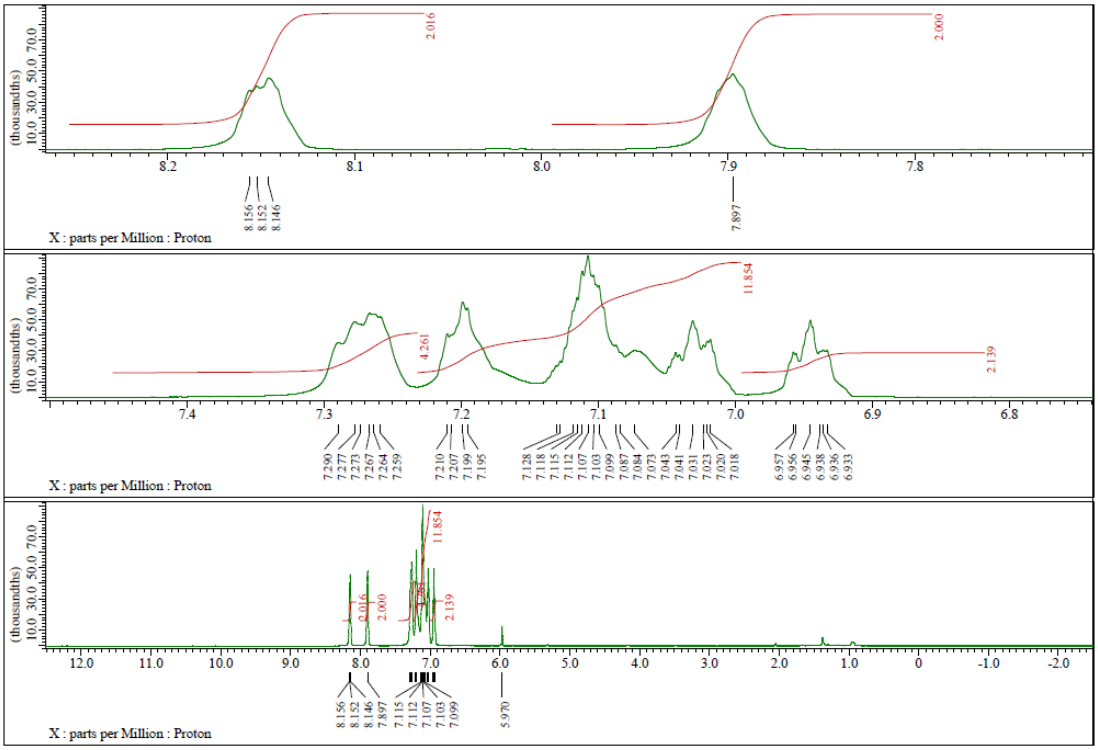


Figure S8. ^{1}H NMR spectrum of **8** at room temperature ($(CD_2Cl)_2$, 600 MHz).

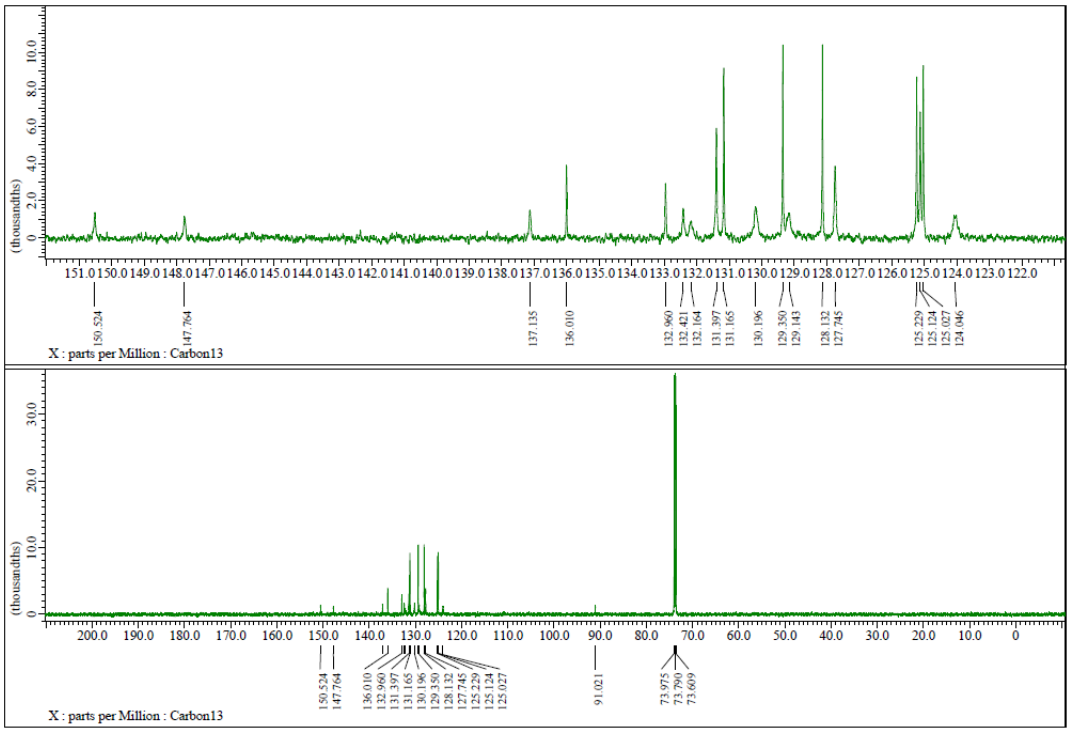
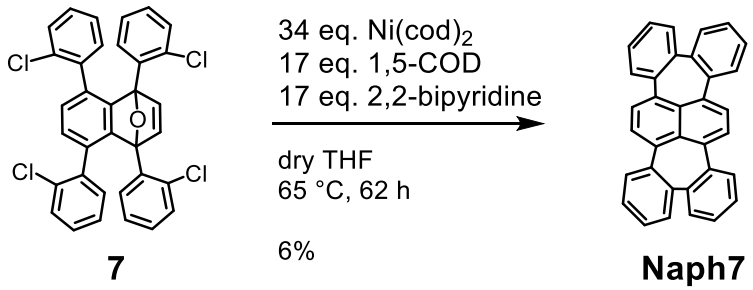


Figure S9. ^{13}C NMR spectrum of **8** at room temperature ($(CD_2Cl)_2$, 151 MHz).

*dibenzo[4,5:6,7]cyclohepta[1,2,3-de]dibenzo[4,5:6,7]cyclohepta[1,2,3-ij]naphthalene (**Naph7**).*



To a three-neck 300 mL round-bottom flask containing **7** (60 mg, 0.10 mmol), $Ni(cod)_2$ (480 g, 1.8 mmol, 17 eq.) and 2,2-bipyridyl (272 g, 1.7 mmol, 17 eq.), 1,5-COD (0.21 ml, 1.7 mmol, 17 eq.) and dry THF (120 mL) were added under an atmosphere of N_2. The mixture was heated at 65 °C and stirred for 22 h. Subsequently, additional $Ni(cod)_2$ (480 g, 1.8 mmol, 17 eq.) was added, and the mixture was stirred for further 40 h at 65 °C. The reaction mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/CH_2Cl_2 = 9/1) and GPC, which afforded **Naph7** as a white solid (10 mg, 0.023 mmol, 6%).

^{1}H NMR (600 MHz, CD_2Cl_2, δ/ppm): δ 7.66 (s, 4H), 7.63 (dd, J = 7.8, 1.4 Hz, 4H), 7.43 (td, J = 7.6, 1.4 Hz, 4H), 7.37 (td, J = 7.6, 1.4 Hz, 4H), 7.08 (dd, J = 7.8, 1.3 Hz, 4H); ^{13}C NMR (151 MHz, CD_2Cl_2, δ/ppm): δ 140.8, 139.2, 138.8, 136.5, 133.0, 130.6, 128.8, 128.2, 126.3, 125.0; HR-APCI-orbitrapMS (*m*/*z*): $[M + H]^+$ calced for $C_{34}H_{21}^+$, 429.1638; found, 429.1641.

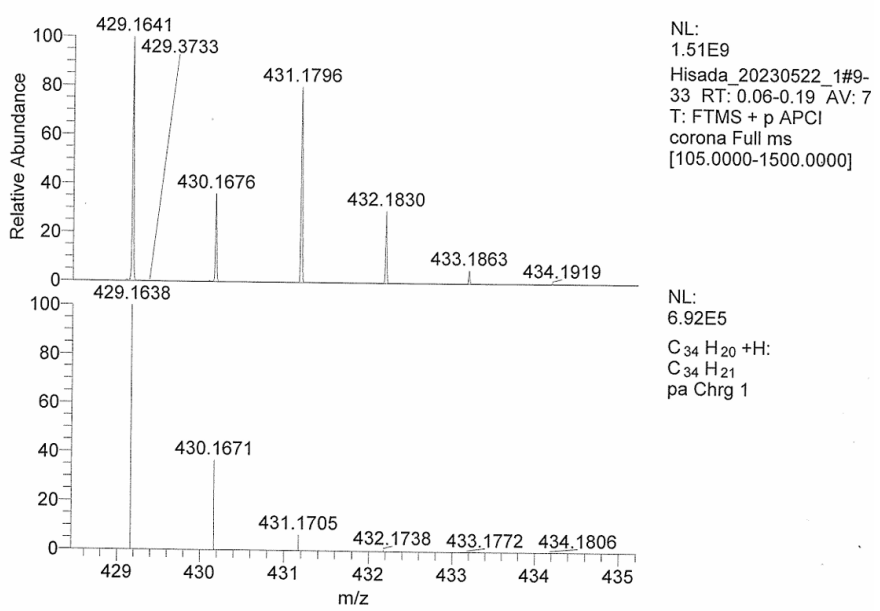


Figure S10. Observed and simulated high-resolution mass spectra of **Naph7** (APCI-orbitrap, positive mode).

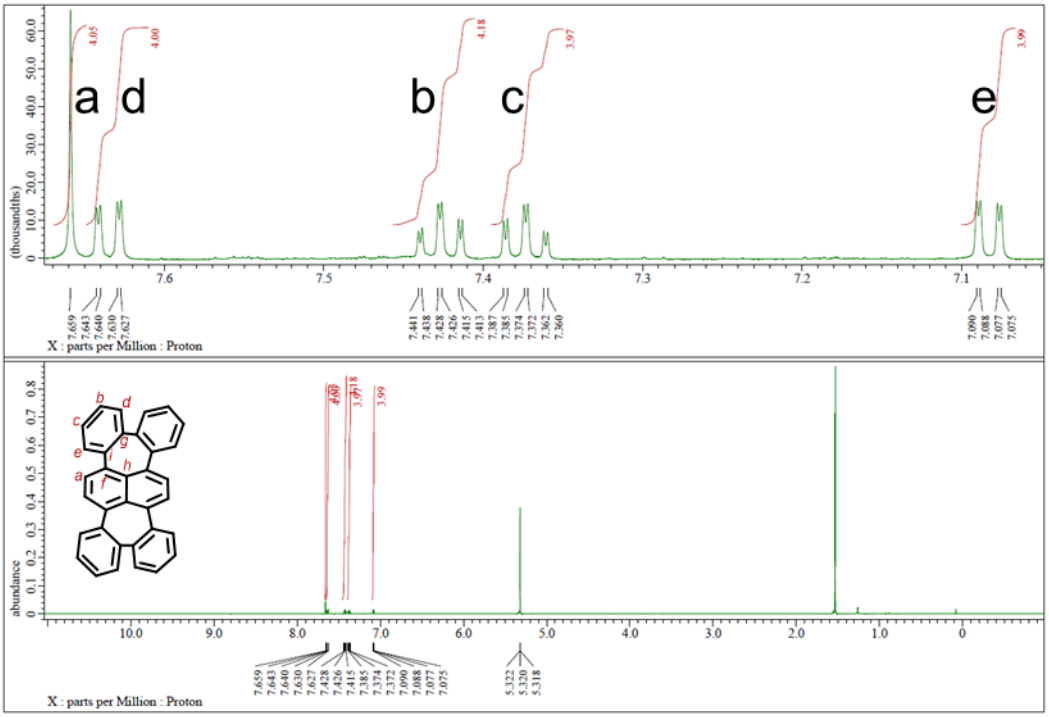


Figure S11. ^{1}H NMR spectrum of **Naph7** at room temperature (CD_2Cl_2, 600 MHz).

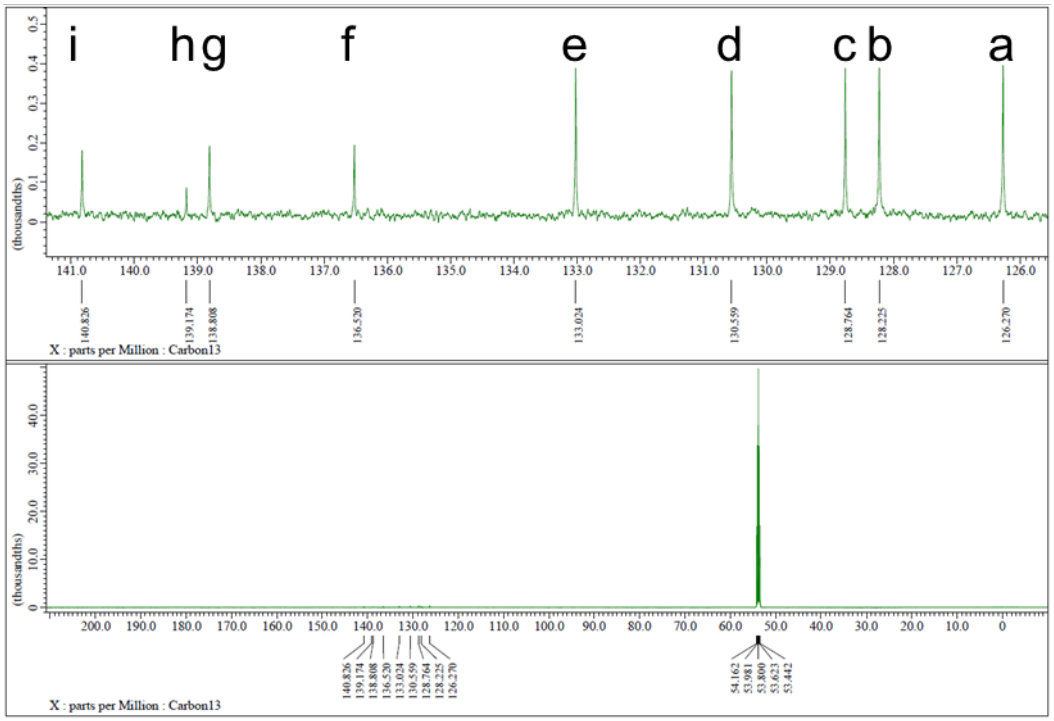


Figure S12. ^{13}C NMR spectrum of **Naph7** at room temperature (CD_2Cl_2, 151 MHz).

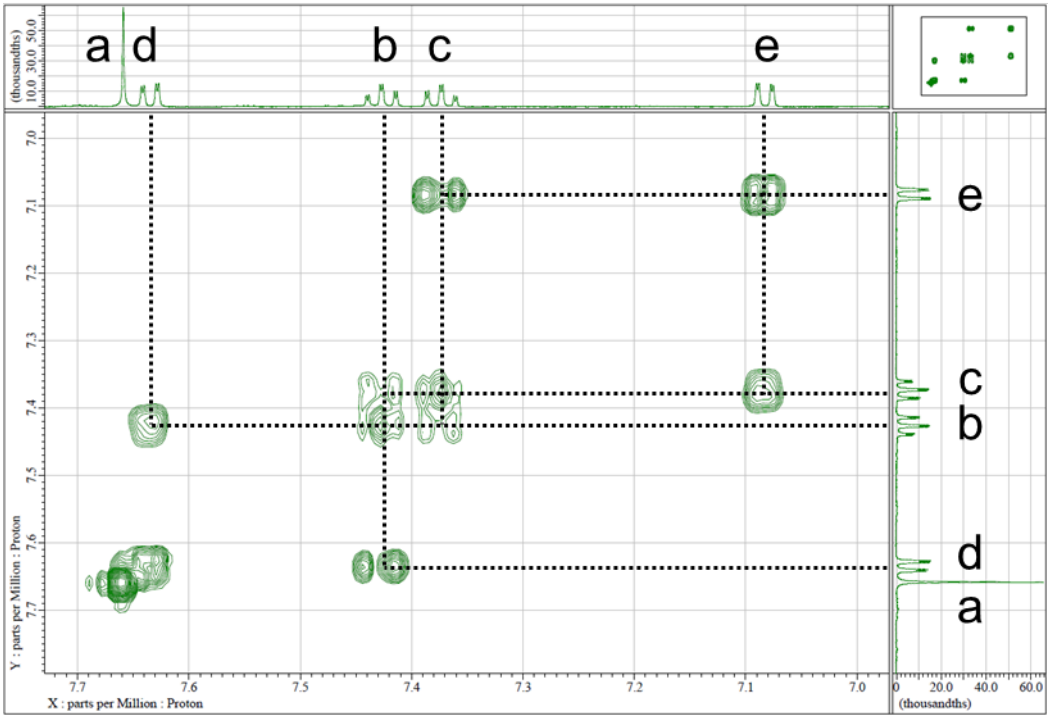


Figure S13. ^{1}H-^{1}H COSY spectrum of **Naph7** at room temperature (CD_2Cl_2, 600 MHz).

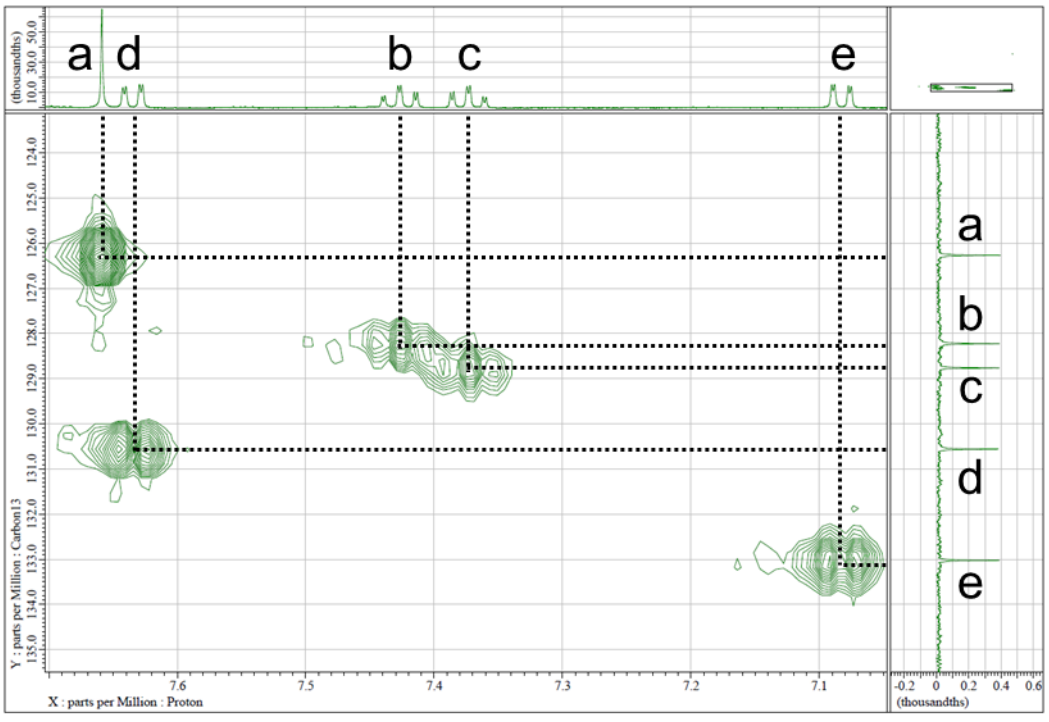


Figure S14. ^{13}C/^{1}H HMQC spectrum of **Naph7** at room temperature (CD_2Cl_2, 600 MHz).

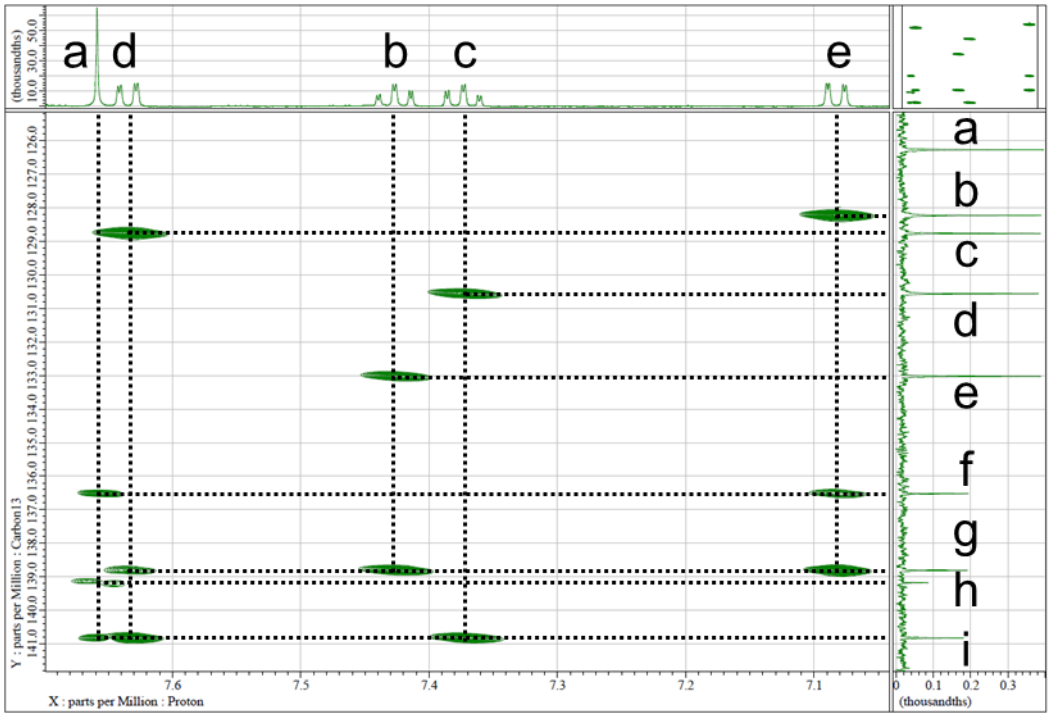
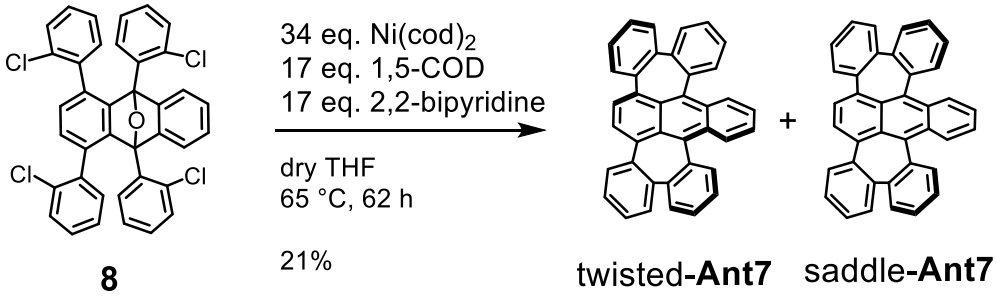


Figure S15. $^{13}C/^{1}H$ HMBC spectrum of **Naph7** at room temperature (CD_2Cl_2, 600 MHz).

*dibenzo[4,5:6,7]cyclohepta[1,2,3-de]dibenzo[4,5:6,7]cyclohepta[1,2,3-ij]naphthalene (**Ant7**).*



To a three-neck 500 mL round-bottom flask containing **8** (380 mg, 0.59 mmol), $Ni(cod)_2$ (2.8 g, 10 mmol, 17 eq.) and 2,2-bipyridyl (1.6 g, 10 mmol, 17 eq.), 1,5-COD (1.3 ml, 10 mmol, 17 eq.) and dry THF (180 mL) were added under an atmosphere of N_2. The mixture was heated at 65 °C and stirred for 22 h. Subsequently, additional $Ni(cod)_2$ (2.8 g, 10 mmol, 17 eq.) was added, and the mixture was stirred for further 40 h at 65 °C. The reaction mixture was diluted with EtOAc and washed with water and brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/CH_2Cl_2 = 9/1) and GPC, which afforded a mixture of saddle-**Ant7** and twisted-**Ant7** as an orange solid (58 mg, 0.12 mmol, 21% calculated for two isomers).

twisted-**Ant7**; ^{1}H NMR (600 MHz, CD_2Cl_2, δ/ppm): δ 8.24 (dd, *J* = 6.9, 3.3 Hz, 2H), 7.74 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.68 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.50 (s, 2H), 7.46–7.43 (m, 4H), 7.36-7.32 (m, 4H), 7.28 (td, *J* = 7.6, 1.4 Hz, 2H), 7.14 (dd, *J* = 7.9, 1.0 Hz, 2H), 7.04 (dd, *J* = 7.9, 1.0 Hz, 2H); ^{13}C NMR (151 MHz, CD_2Cl_2, δ/ppm): 141.8, 139.2, 139.0, 138.8, 136.8, 135.9, 135.2, 133.1, 132.4, 131.4, 131.1, 129.6, 128.6, 128.4, 128.0, 127.9, 127.3, 125.8, 125.1; HR-APCI-orbitrapMS (*m*/*z*): $[M + H]^+$ calced for $C_{38}H_{23}^+$, 479.1794; found, 479.1788.

saddle-**Ant7**; ^{1}H NMR (600 MHz, CD_2Cl_2, δ/ppm): δ 8.05 (dd, *J* = 6.7, 3.4 Hz, 2H), 7.85 (s, 2H), 7.83 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.76 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.51 (td, *J* = 7.5, 1.3 Hz, 2H), 7.45-7.41 (m, 4H), 7.34 (dd, *J* = 6.7, 3.2 Hz, 2H), 7.27-7.24 (m, 2H), 7.18 (dd, *J* = 7.7, 1.4 Hz, 2H), 6.94 (dd, *J* = 7.9, 1.2 Hz, 2H); HR-APCI-orbitrapMS (*m*/*z*): $[M + H]^+$ calced for $C_{38}H_{23}^+$, 479.1794; found, 479.1788.

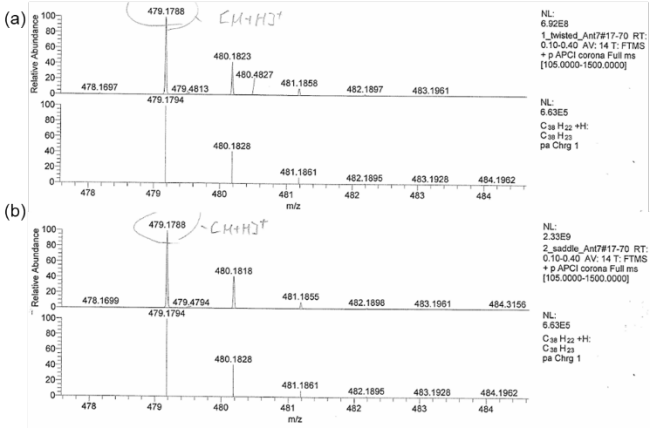


Figure S16. Observed and simulated high-resolution mass spectra of (a) twisted-**Ant7** and (b) saddle-**Ant7** (APCI-orbitrap, positive mode).

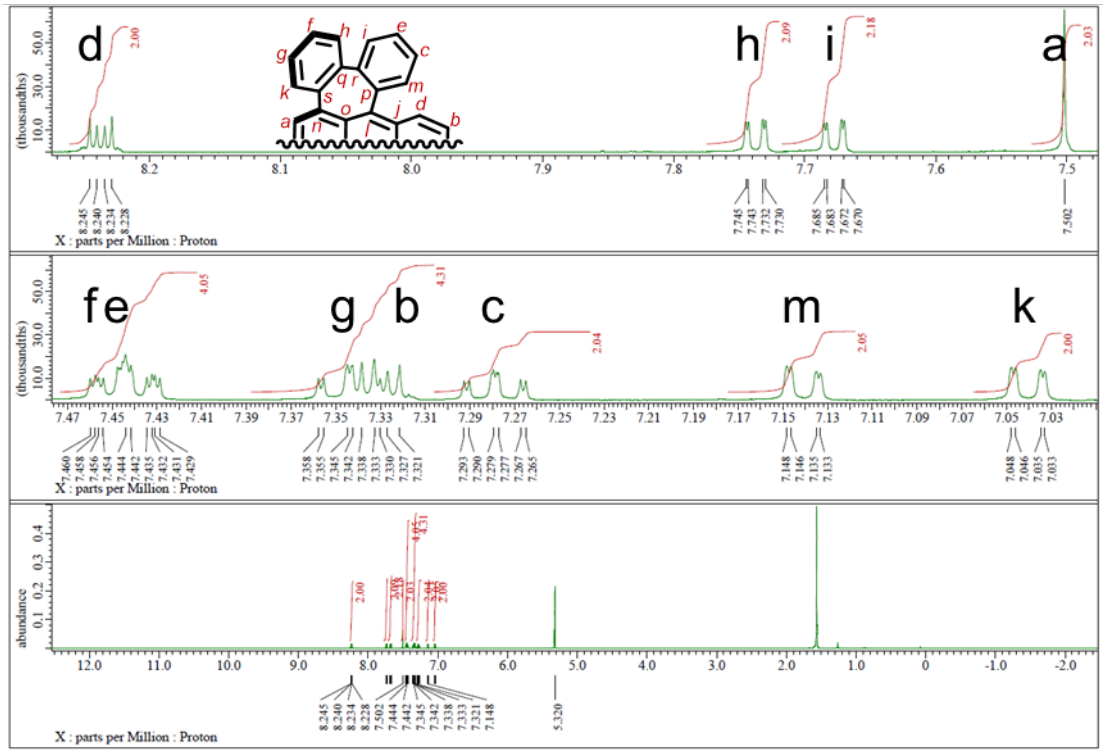


Figure S17. ^{1}H NMR spectrum of twisted-**Ant7** at room temperature (CD_2Cl_2, 600 MHz).

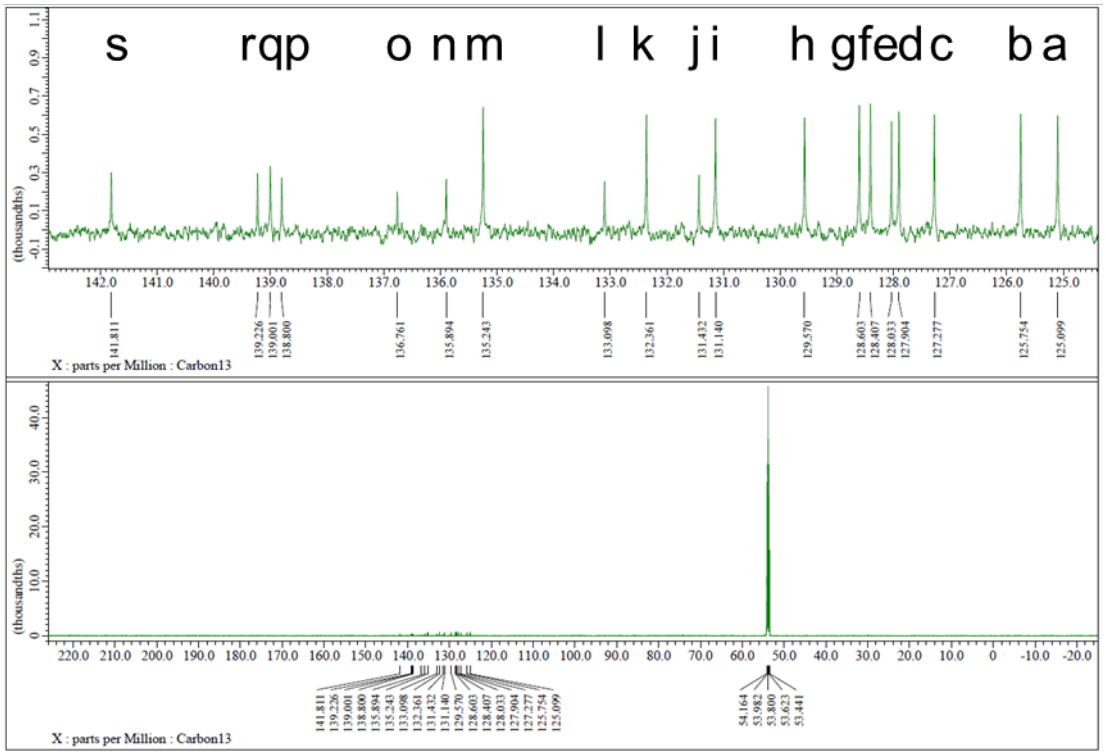


Figure S18. ^{13}C NMR spectrum of twisted-**Ant7** at room temperature (CD_2Cl_2, 151 MHz).

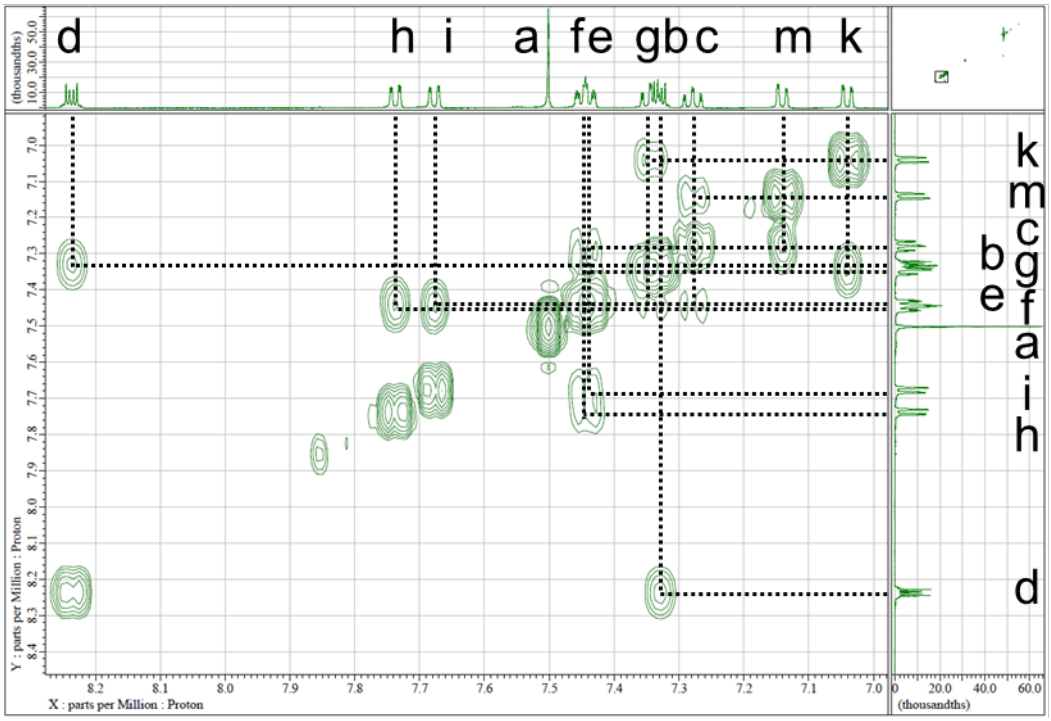


Figure S19. ^{1}H-^{1}H COSY spectrum of twisted-**Ant7** at room temperature (CD_2Cl_2, 600 MHz).

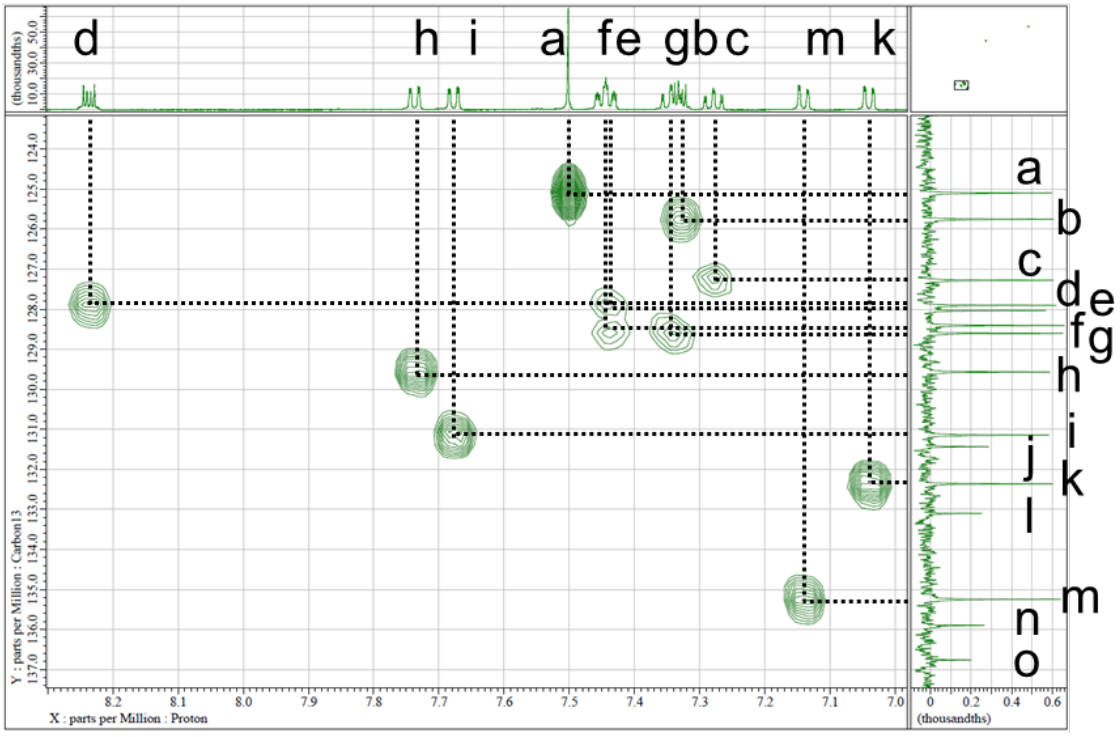


Figure S20. ^{13}C/^{1}H HMQC spectrum of twisted-**Ant7** at room temperature (CD_2Cl_2, 600 MHz).

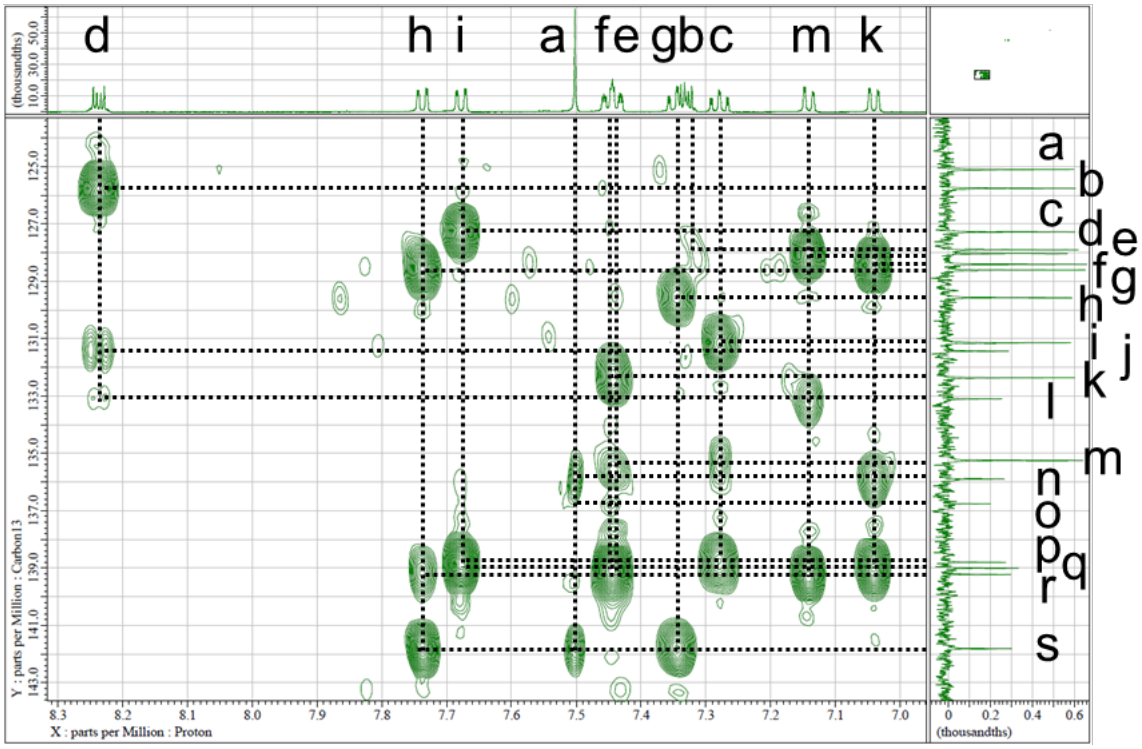


Figure S21. $^{13}C/^{1}H$ HMBC spectrum of twisted-**Ant7** at room temperature (CD_2Cl_2, 600 MHz).

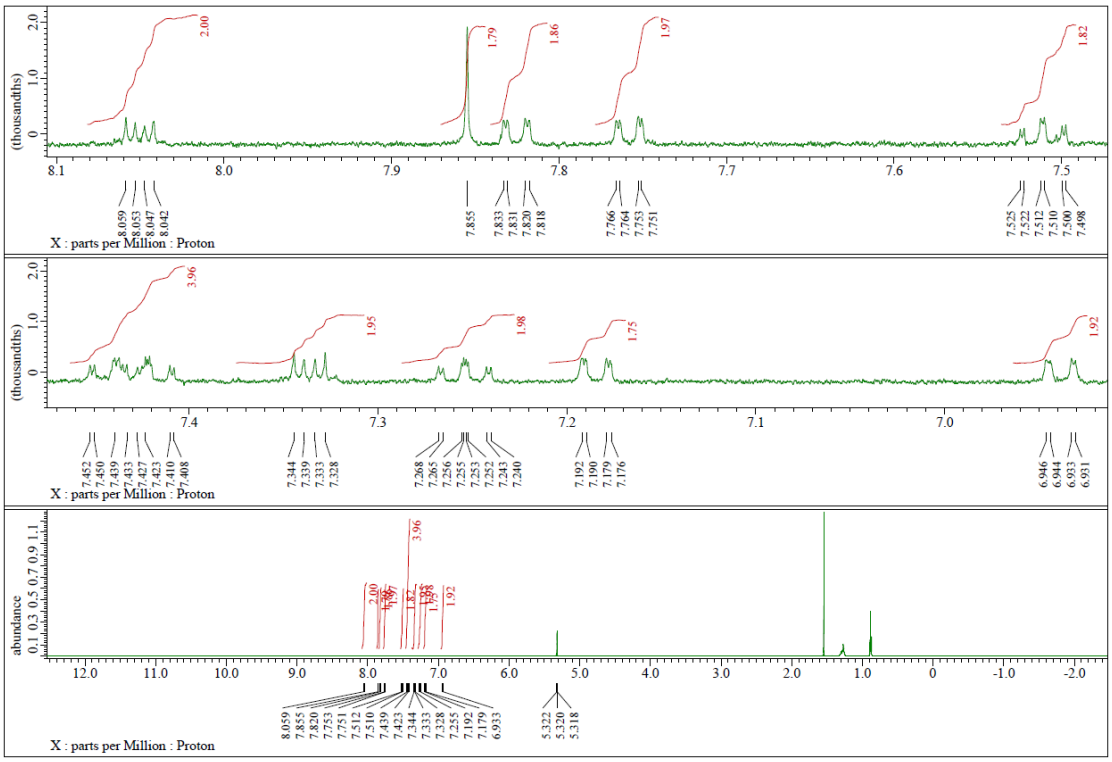


Figure S22. ^{1}H NMR spectrum of saddle-**Ant7** at room temperature (CD_2Cl_2, 600 MHz).

Practical Considerations for Synthesis: In the synthesis of **Naph7**, **Ant7**, and **Tet7**, the oxidative cyclization typically proceeds to full consumption of the precursor. However, the mass balance is dominated by a complex mixture of partially fused and dehalogenated byproducts. Due to the presence of multiple atropisomers with overlapping chromatographic profiles, the purification of the desired products from such byproducts requires meticulous silica gel column chromatography and recycle GPC-HPLC. This separation would be more difficult upon scale-up, and we recommend parallel small-scale reactions as a more practical approach for large-scale synthesis.

2. X-Ray Diffraction Analysis

X-Ray crystallographic data of a single crystal obtained by slow vapor diffusion were recorded using a Rigaku MicroMax 007-HF diffractometer equipped with a graphite monochromatic MoKα radiation source (λ = 0.71075 Å) and a Rigaku Saturn724+ CCD detector. The structures were solved using direct methods (SHELXT-2014/5),[S2] and structural refinements were carried out using SHELXL-2018/3.[S3] The data for saddle-**Tet7** and twisted-**Tet7** refer to our previous report.[S1]

Table S1. Crystallographic parameters of single-crystal X-ray diffraction analysis for compounds **7**, twisted-**Naph7** and twisted-**Ant7**.

compounds	**7**	twisted-**Naph7**	twisted-**Ant7**
CCDC	2534033	2534034	2534035
chemical formula	$C_{34}H_{20}Cl_4O$	$2(C_{17}H_{10})$	$C_{38}H_{22}$
formula weight	586.30	428.50	478.55
T / K	143.15	143.15	143.15
wavelength / Å	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
color	Colorless	Yellow	Orange
crystal size / mm^3	0.20 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.10 × 0.03 × 0.01
crystal system	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$I2/a$	$P2_1/n$
a / Å	15.6943(6)	13.3272(8)	8.8393(7)
b / Å	13.6478(4)	18.4614(7)	20.3510(15)
c / Å	12.3466(4)	18.4901(11)	13.6545(10)
α	90°	90°	90°
β	90°	110.580(7)	100.868(8)
γ	90°	90°	90°
V / $Å^3$	2644.55(15)	4259.0(4)	2412.2(3)
Z (molecules/unit cell)	4	8	4
Density (calculated)	1.473 g/cm^3	1.337 g/cm^3	1.318 g/cm^3
Data/restraints/parameters	6968 / 18 / 386	5616 / 0 / 308	6326 / 0 / 343
Goodness-of-fit on F^2	1.025	1.173	1.020
R_1 [$I > 2\sigma(I)$]	0.0565	0.1360	0.0947
wR_2 (for all data)	0.1263	0.3576	0.2212
Largest peak and hole /	0.686 and –0.406	0.685 and –0.479	0.280 and –0.293

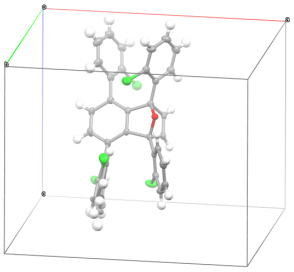


Figure S23. Asymmetric unit of **7** recorded at 143 K, showing a 50% probability of thermal ellipsoids.

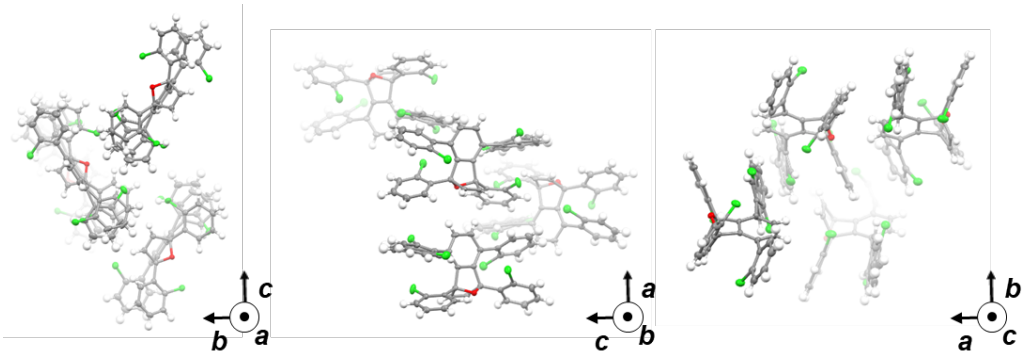


Figure S24. Crystal packing of **7** recorded at 143 K, showing a 50% probability of thermal ellipsoids.

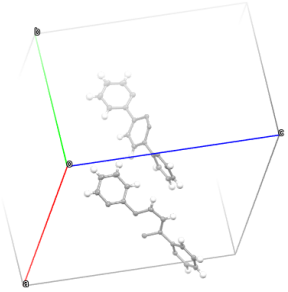


Figure S25. Asymmetric unit of twisted-**Naph7** recorded at 143 K, showing a 50% probability of thermal ellipsoids.

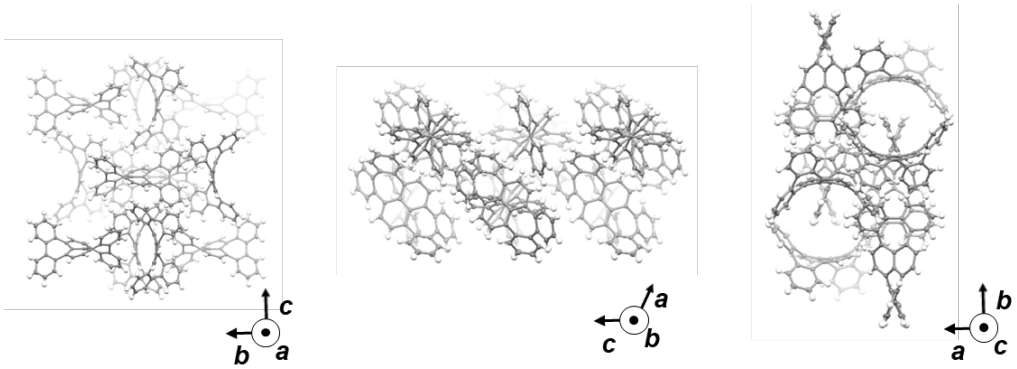


Figure S26. Crystal packing of twisted-**Naph7** recorded at 143 K, showing a 50% probability of thermal ellipsoids.

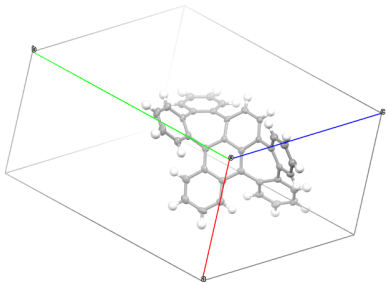


Figure S27. Asymmetric unit of twisted-**Ant7** recorded at 143 K, showing a 50% probability of thermal ellipsoids.

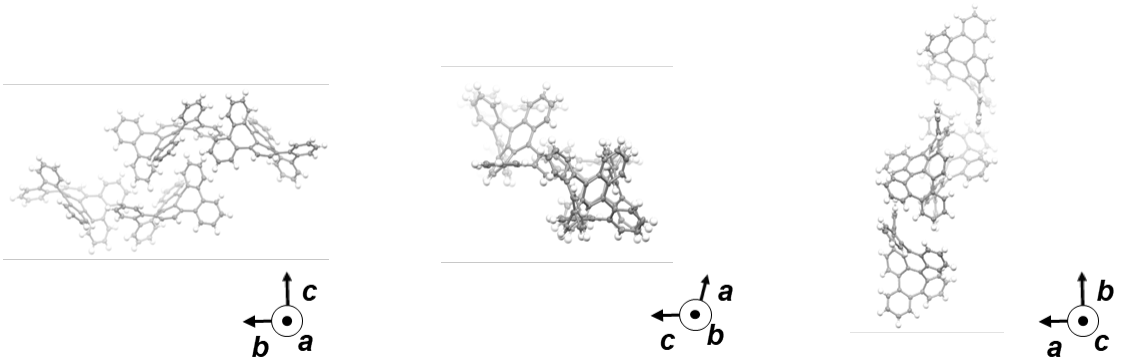


Figure S28. Crystal packing of twisted-**Ant7** recorded at 143 K, showing a 50% probability of thermal ellipsoids.

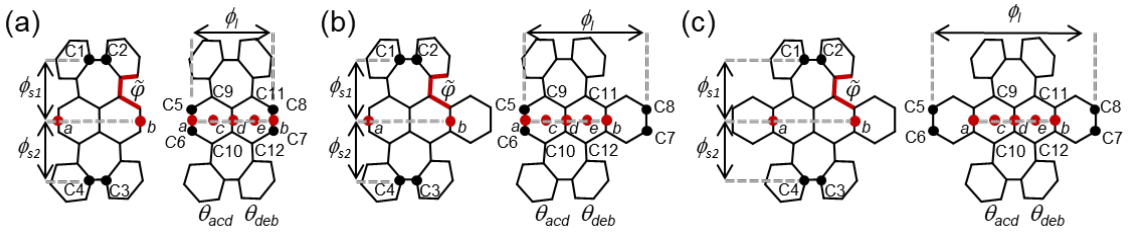


Figure S29. Definition of ϕ_{s1}, ϕ_{s2}, $\tilde{\varphi}$, ϕ_l, θ_{acd} and θ_{deb} in the structure of (a) **Naph7**, (b) **Ant7**, (c) **Tet7**. Dots (*a*,*b*,*d*) are the centroids of the C–C bonds, and dots(*c*,*e*) are the centroid between C9 and C10 **or** C11 and C12, respectively. ϕ_{s1}, ϕ_{s2} are torsion angles defined by two points and two atoms (C1, C2, *b*, *a* **or** *a*, *b*, C3, C4). $\tilde{\varphi}$ is defined as an average torsion angle between the acene moiety and the fused diphenylene moieties. ϕ_l is an end-to-end torsion angle defined by four carbon atoms at the edge of the acene moiety (C5, C6, C7, C8). θ_{acd} and θ_{deb} are angles defined by three points (*a*, *c*, *d* **or** *d*, *e*, *b*).

Table S2. Comparison of ϕ_{s1}, ϕ_{s2}, $\tilde{\varphi}$, ϕ_l, MPD (all carbon), θ_{acd}, θ_{deb}, MPD (acene moiety), and Ave. HOMA (acene moiety) in the X-ray and calculated structures of **Naph7**, **Ant7**, and **Tet7** at the B3LYP/6-31G(d) level.

compd.	**Naph7**					**Ant7**				**Tet7**				
isomer	twist			saddle		twist		saddle		twist		saddle		
	exp.[a]		calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.[a]		calc.
ϕ_{s1}[b]	54	54	53	N/A	−48	59	57	N/A	−51	61	60	−53	−53	−53
ϕ_{s2}[b]	55	58	53	N/A	48	58	57	N/A	51	59	60	52	53	53
$\tilde{\varphi}$[b]	36	37	36	N/A	35	41	41	N/A	38	45	45	43	41	42
ϕ_l[b]	32	34	31	N/A	0	30	29	N/A	0	26	28	0	0	0
MPD[c] (all carbon)	1.33	1.27	1.36	N/A	0.50	1.24	1.21	N/A	0.90	1.15	1.17	1.10	1.08	1.09
θ_{acd}[b]	179	179	180	N/A	164	179	180	N/A	166	180	180	161	161	161
θ_{deb}[b]	179	179	180	N/A	164	180	180	N/A	159	180	180	161	161	161
MPD[d] (acene moiety)	0.19	0.16	0.19	N/A	0.08	0.19	0.19	N/A	0.15	0.23	0.24	0.13	0.12	0.11
Ave. HOMA (acene moiety)	0.65	0.68	0.63	N/A	0.60	0.63	0.56	N/A	0.54	0.52	0.52	0.58	0.55	0.51

[a]two independent molecules in crystal, [b]values are in degrees, [c]calculated by all carbon atoms. values are in Å. [d]calculated by all carbon atoms of an acene moitety. values are in Å.
N/A = Not Available

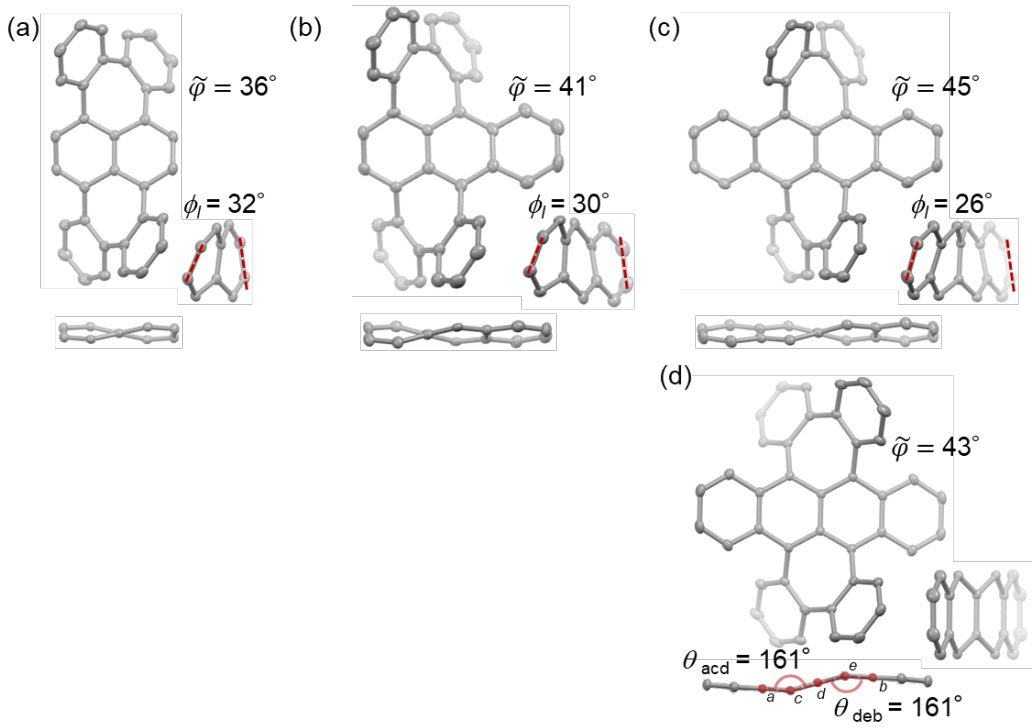


Figure S30. X-ray structures of (a) twisted-**Naph7**, (b) twisted-**Ant7**, (c) twisted-**Tet7**, and (d) saddle-**Tet7**.

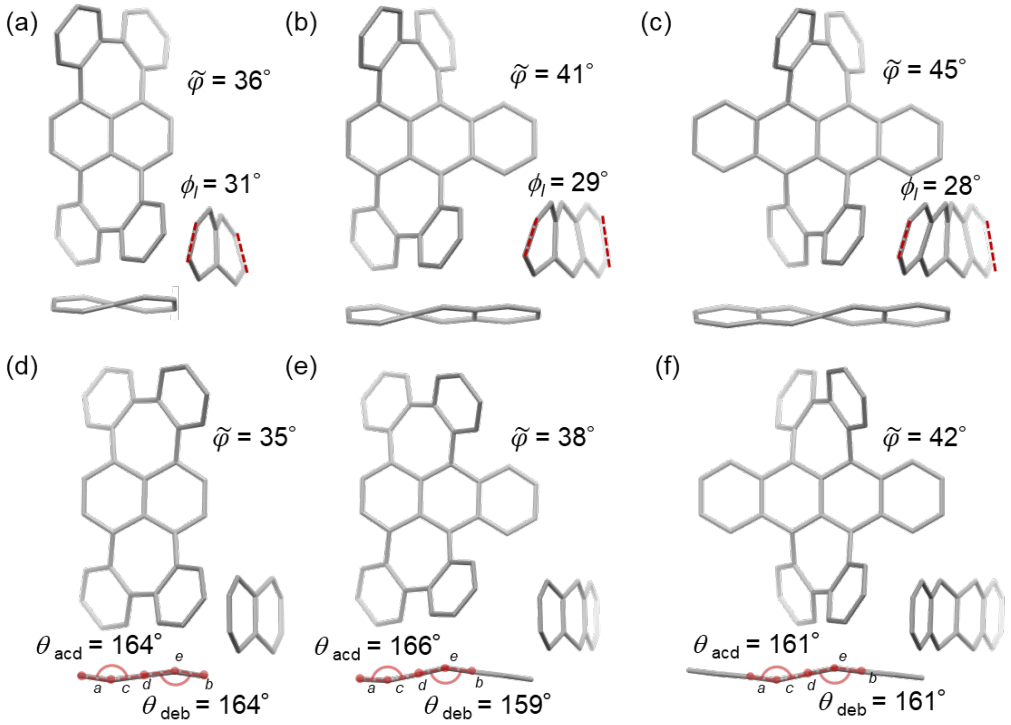


Figure S31. Calculated structures of (a) twisted-**Naph7**, (b) twisted-**Ant7**, (c) twisted-**Tet7**, (d) saddle-**Naph7**, (e) saddle-**Ant7**, and (f) saddle-**Tet7** at the B3LYP/6-31G(d) level.

3. Kinetics of the isomerization pathway between saddle and twisted isomers

A residual solvent (5.32 ppm for ^{1}H in dichloromethane-d_2) was used as an internal reference for NMR spectra. Dichloromethane-d_2 for NMR spectroscopy was purified by passing through a short aluminum oxide pad before use). The thermodynamics and kinetics of isomerization between the saddle and twisted isomers of **Naph7** and **Ant7** were studied by ^{1}H NMR spectroscopy. A solution of **Naph7** showed only single peak by HPLC analysis in some conditions. VT-NMR measurement of **Naph7** in CH_2Cl_2 did not change from 20 °C to −80 °C.(Figure S32) These results suggested two possibility: (i) **Naph7** predominantly exists as a single isomer in solution due to an significant energy difference between the major and minor conformers, and/or (ii) the interconversion between the isomers is too rapid on the NMR timescale due to the low isomerization barrier.

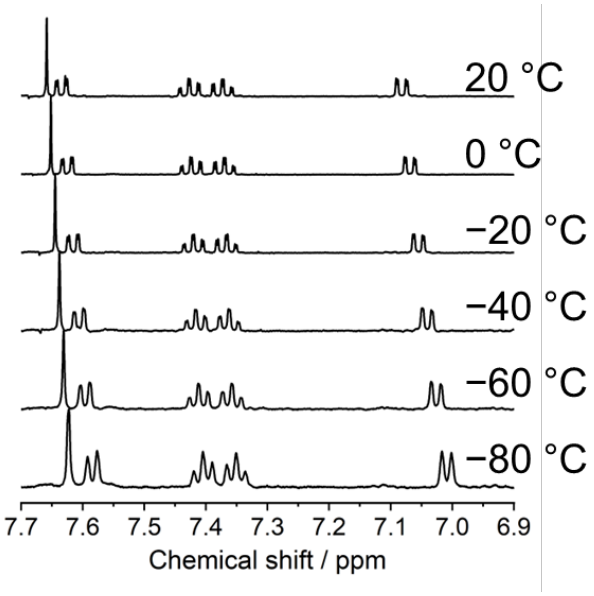


Figure S32. VT-^{1}H NMR spectra of **Naph7** in dichloromethane-d_2 from 20 °C to −80 °C.

In the case of **Ant7**, twited-**Ant7** and saddle-**Ant7** could be separated by HPLC (Figure S43). The concentration changes for isomerization between saddle and twisted isomers were measured, showing no intermediates or biproducts, indicating reversible first-order interconversion (Figure S33,S34). The solutions were stirred for adequate time (21 h at 25 °C, 85 h at 20 °C, 100 h at 15 °C), resulting in 0.131/1 at 25 °C, 0.125/1 at 20 °C, 0.123/1 at 15 °C of equilibrium mixture of saddle-**Ant7**/twisted-**Ant7**. In addition, the rate constants were determined by the following equation of reversible first-order interconversion.

$$\ln(([X]_0-[X]_{eq})/([X]-[X]_{eq})) = (k_{tw\rightarrow sa} + k_{sa\rightarrow tw})t \qquad \text{(S1)}$$

where [X] is the concentration of saddle-**Ant7** at a certain time t, $[X]_0$ is the initial concentration, $[X]_{eq}$ is the final (equilibrium) concentration, and $k_{tw\rightarrow sa}$ and $k_{sa\rightarrow tw}$ are the rate constants for the twisted-to-saddle and saddle-to-twisted isomerization, respectively. Using these data and the reaction equilibrium constant K, the rate constants $k_{sa\rightarrow tw}$ (4.8×10^{-5} s^{-1} at 25 °C, 3.0×10^{-5} s^{-1} at 20 °C, and 1.9×10^{-5} s^{-1} at 15 °C) and $k_{tw\rightarrow sa}$ (6.3×10^{-6} s^{-1} at 25 °C, 3.8×10^{-6} s^{-1} at 20 °C, and 2.4×10^{-6} s^{-1} at 15 °C) were determined (Figure S35). By Eyring plots using the ^{1}H NMR spectral change of **Ant7** solutions in dichloromethane-d_2 at 25 °C, 20 °C, and 15 °C, the activation barrier ($\Delta G^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$), and entropy ($\Delta S^{\ddagger}$) was determined to be 103.6 kJ·mol^{-1} at 25°C, and 68.2 kJ·mol^{-1} and −0.119 kJ·mol^{-1}·K^{-1} for the twisted-to-saddle isomerization and 97.7 kJ·mol^{-1} at 25°C, and 63.7 kJ·mol^{-1}, −0.114 kJ·mol^{-1}·K^{-1} for the saddle-to-twisted isomerization, respectively (Figure S36).

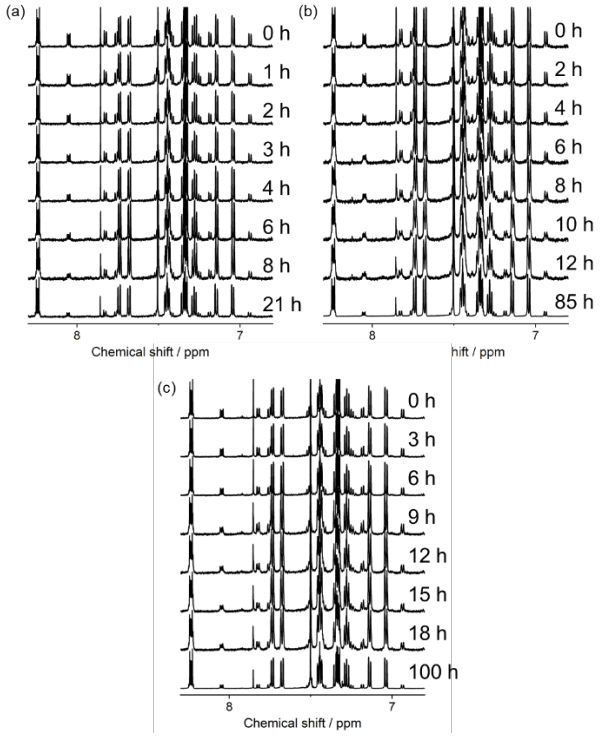


Figure S33. ^{1}H NMR spectral change of saddle-**Ant7** and twisted-**Ant7** during the progress of saddle-to-twisted isomerization in dichloromethane-d_2 at (a) 25 °C, (b) 20 °C, and (c) 15 °C.

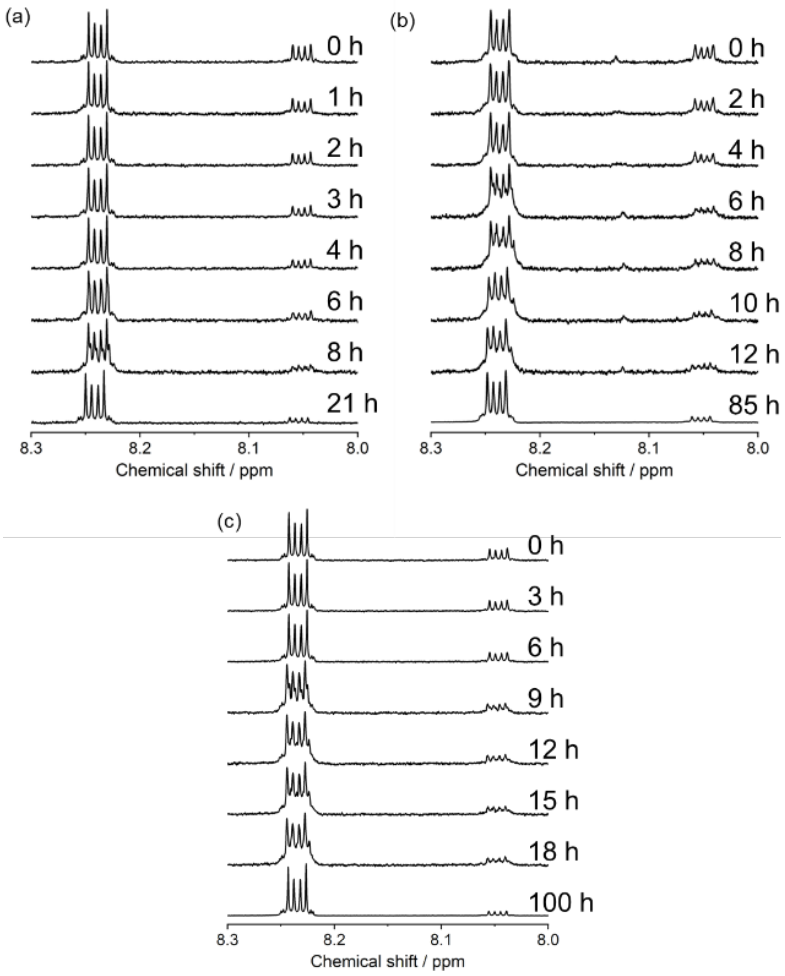


Figure S34. Extracted ^{1}H NMR spectral change of saddle-**Ant7** and twisted-**Ant7** during the progress of saddle-to-twisted isomerization in dichloromethane-d_2 at (a) 25 °C, (b) 20 °C, and (c) 15 °C.

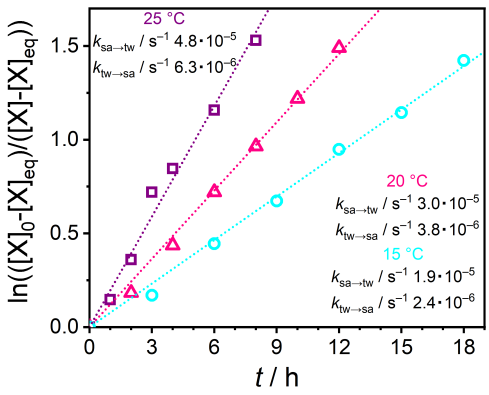


Figure S35. a plot for the isomerization of saddle-**Ant7** obtained by ^{1}H-NMR studies.

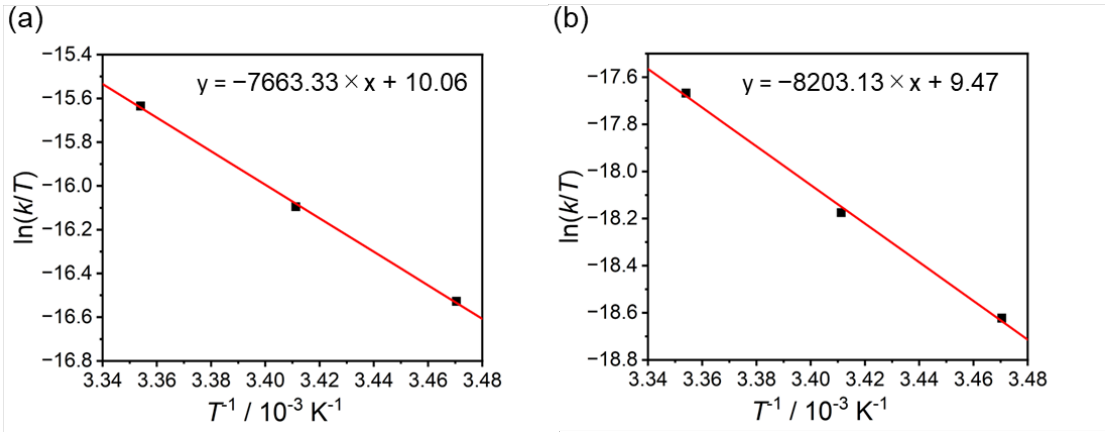


Figure S36. Eyring plots using the rate constants (a) $k_{sa \rightarrow tw}$ and (b) $k_{tw \rightarrow sa}$ determined by the ^{1}H NMR spectral change of **Ant7** solutions in dichlorobenzene-d_2 at 25 °C, 20 °C, and 15 °C.

4. Absorption and Fluorescence Measurement

UV–vis. Absorption spectra were measured on a JASCO (V-670 equipped with an ETCS-761 Peltier-type temperature controller and V-750) spectrophotometer (conditions: scan rate, 400 nm/min; bandwidth, 5 nm). Fluorescence and excitation spectra were measured on a JASCO (FP-8300) spectrophotometer (conditions: scan rate, 100 nm/min; bandwidth, 1 nm). Fluorescence quantum yields were determined on a Hamamatsu Photonics absolute quantum yield measurement system C6620-02G. Fluorescence lifetimes were recorded on a Hamamatsu Photonics picosecond fluorescence lifetime measurement system C11200 equipped with a picosecond light pulser PLP-10, a spectrograph C11119-01, and a streakscope C10627. Excitation was carried out by a laser diode emitting at λ = 378 nm for **Naph** and λ = 465 nm for **Ant7**. Fluorescence emission (k_f) and nonradiative decay (k_{nr}) rate constants were calculated from the fluorescence quantum yield (Φ_f) and the fluorescence lifetime (τ_f) by using the following equations,

$$\Phi_f = \frac{k_f}{k_f + k_{nr}} = \tau_f k_f \quad \text{(S2)}, \quad \tau_f = \frac{1}{k_f + k_{nr}} \quad \text{(S3)}$$

Sample concentration was typically set around 1×10^{-6} M for fluorescence spectroscopy to avoid distortion of the spectrum by self-absorption. The optical data for twitsed-**Ant7** and saddle-**Ant7** were recorded within 1 h.

UV−vis. absorption spectra of twitsed-**Ant7** and saddle-**Ant7** were measured immediately after isomerization by HPLC and solvent removal by a vacuum pump. The molar absorption coefficients (ε) of both isomers in toluene were determined by combining global fitting with an equilibrium ratio. First, the absorption spectrum of the equilibrium mixture of twisted-**Ant7** and saddle-**Ant7** in toluene at rt was recorded, and the concentration of the solution was determined by a total weight of twisted-**Ant7** and saddle-**Ant7**. Second, the equilibrium spectrum was deconvoluted into the spectra of twisted-**Ant7** and saddle-**Ant7**. Third, the deconvoluted spectra were converted by dividing them by the equilibrium ratio of 0.877 (twisted-**Ant7**) and 0.123 (saddle-**Ant7**) in toluene at room temperature, respectively, as determined independently by ^{1}H NMR spectroscopy. Finally, the molar absorption coefficients (ε) were calculated from using the concentrations and absorbance.

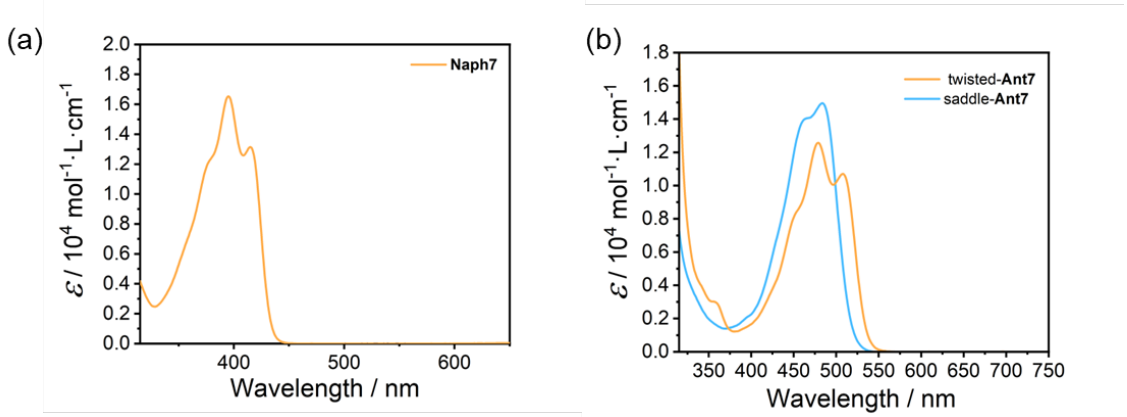


Figure S37. UV−vis. absorption spectra of (a) **Naph7** and (b) twisted-**Ant7** and saddle-**Ant7** in toluene.

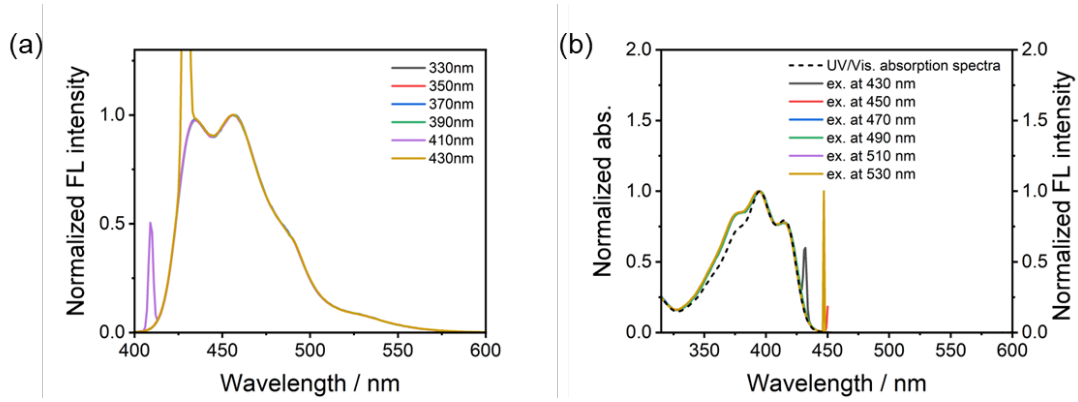


Figure S38. (a) Fluorescence and (b) excitation spectra of **Naph7** (fluorescence spectra: excitation at 330, 350, 370, 390, 410, and 430 nm; excitation spectra: recorded at 430, 450, 470, 490, 510, and 530 nm) in toluene.

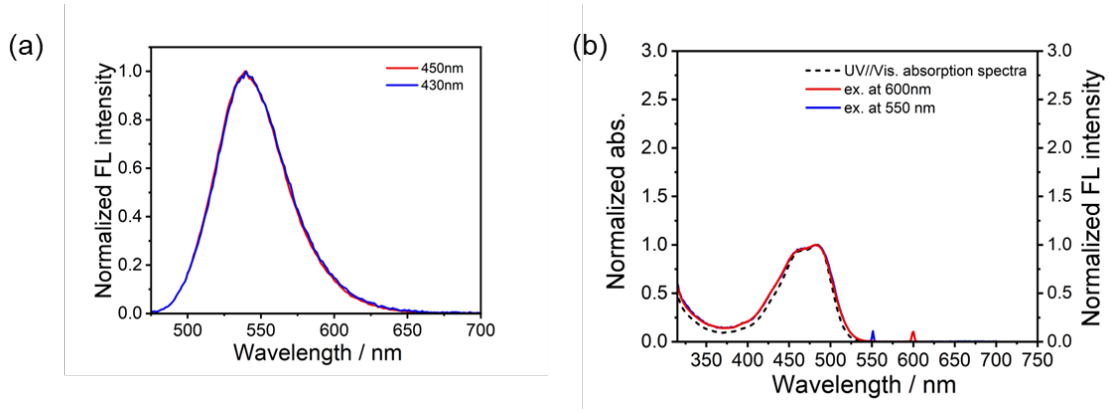


Figure S39. (a) Fluorescence and (b) excitation spectra of saddle-**Ant7** (fluorescence spectra: excitation at 430 and 450 nm; excitation spectra: recorded at 550 and 600 nm) in toluene.

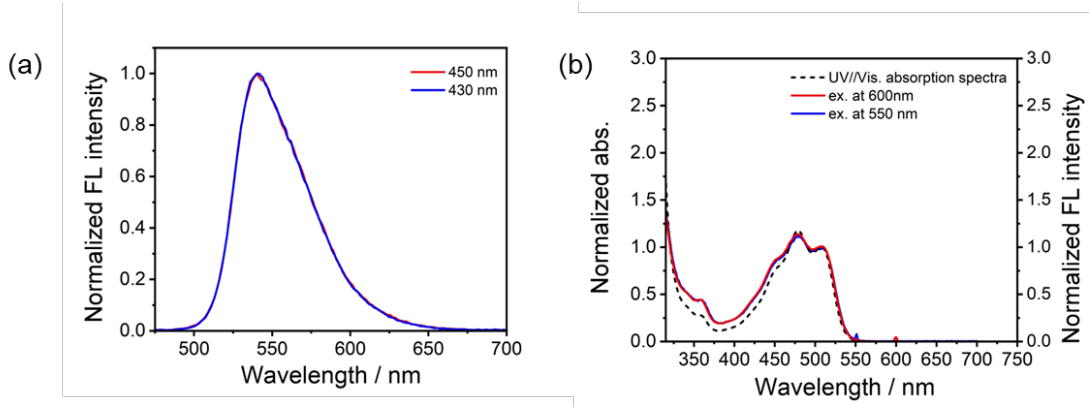


Figure S40. (a) Fluorescence and (b) excitation spectra of twisted-**Ant7** (fluorescence spectra: excitation at 430 and 450 nm; excitation spectra: recorded at 550 and 600 nm) in toluene.

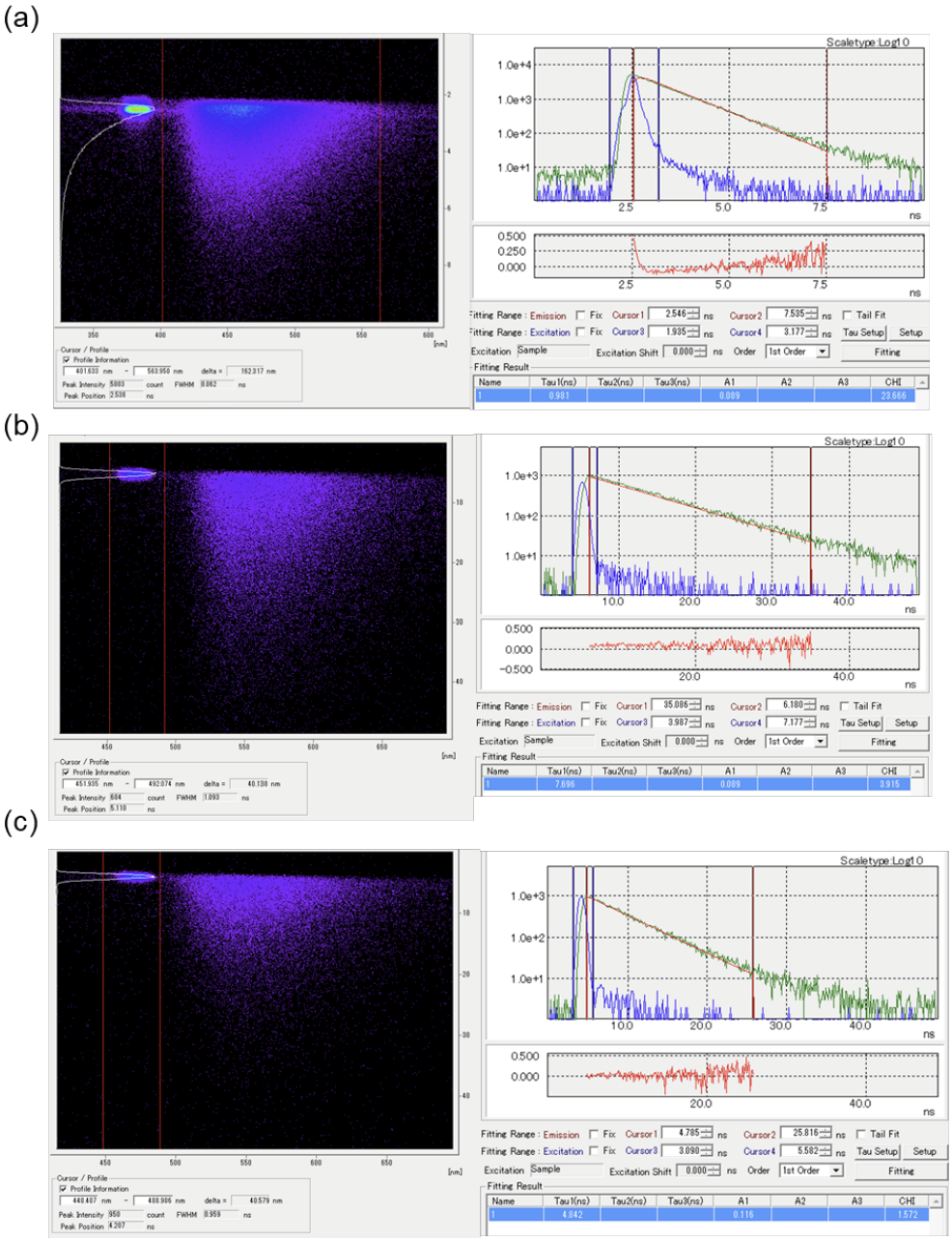


Figure S41. Streak images and fluorescence decay profiles of (a) **Naph7** and (b) twisted-**Ant7**, and (c) saddle-**Ant7**. Red lines denote the curves of the best fit by single exponential functions.

5. Chiral HPLC details and Circular Dichroism (CD) Analysis

The chirality of and heptagon-fused compounds (saddle-**Naph7**, twisted-**Naph7**, saddle-**Ant7**, twisted-**Ant7**, saddle-**Tet7** and twisted-**Tet7**) was specified by the longitudinal helicities of the two seven-membered ring moieties (Figure S42). The enantiomeric resolution of *rac*-twisted-**Ant7** and saddle-**Ant7** was performed using preparative HPLC on CHIRALPAK IB 250-10 (5 μm) with hexanes/CH_2Cl_2 = 85/15 as an eluent (flow rate = 5 mL/min). Circular dichroism (CD) spectra of separated (*P*,*P*)-twisted-**Ant7** and (*M*,*M*)-twisted-**Ant7** were measured on a JASCO J-720WI (conditions: scan rate, 100 nm/min; response, 1 sec; slit width, 1 nm).

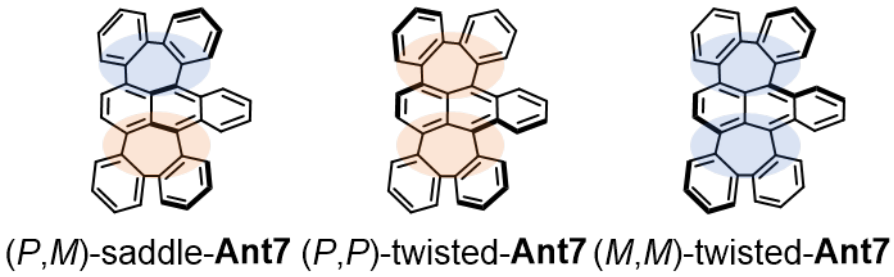


Figure S42. Description of the longitudinal helicities of seven-membered ring moieties of saddle-**Ant7** and twisted-**Ant7**.

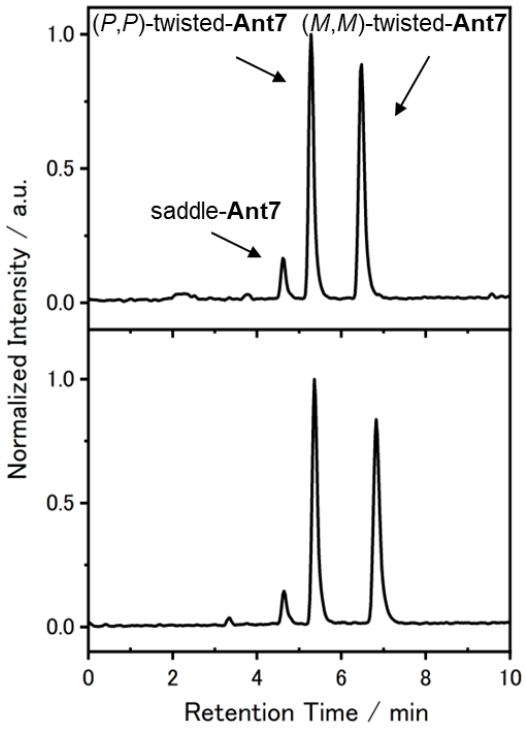


Figure S43. (a) Chiral HPLC chart for (a) an equilibrium solution of *rac*-twisted-**Ant7** and saddle-**Ant7**, (b) a separated solution of 1st fraction (saddle-**Ant7**) after 45 h at room temperature.

6. Theoretical Calculations

(TD-)DFT calculations were conducted using the Gaussian 16 program (revision C.01).[S4]

Convergence at a local minimum structure was confirmed by the absence of imaginary frequencies in the frequency analysis.

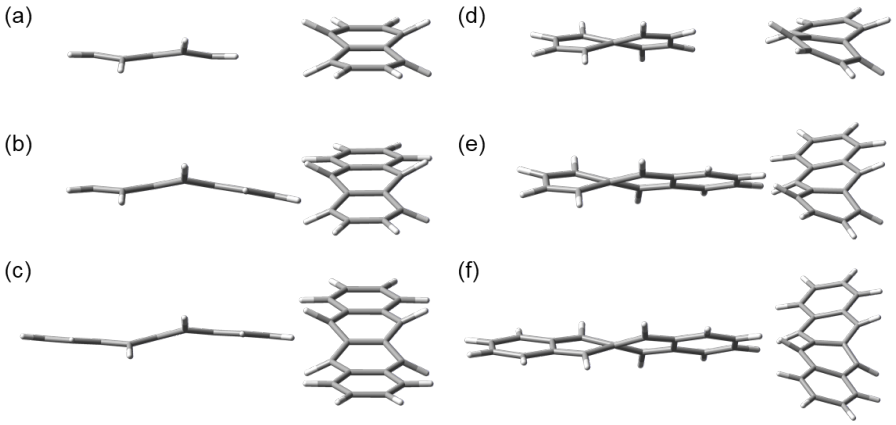


Figure S44. Calculated structures of (a) saddle-**Naph7-H**, (b) saddle-**Ant7-H**, (c) saddle-**Tet7-H**, (d) twisted-**Naph7-H**, (e) twisted-**Ant7-H**, and (f) twisted-**Tet7-H**. The extracted acenes were generated by substituting the diphenylene moieties of energy-minimized structures of **Naph7**, **Ant7**, and **Tet7**, calculated at the B3LYP/6-31G(d) level, with hydrogen atoms. The C–H bond lengths at substituted positions were fixed at 1.084 Å.

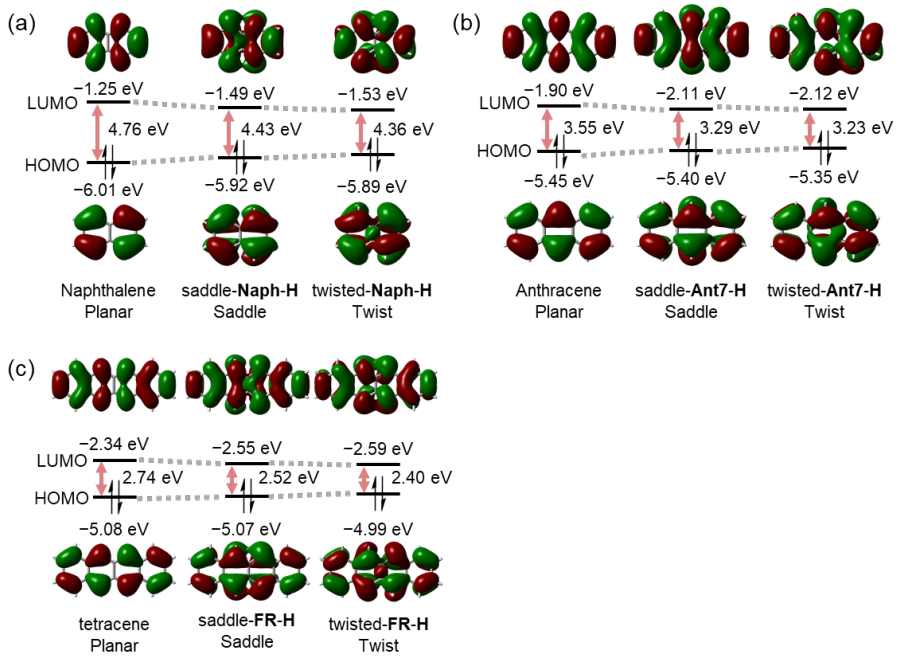


Figure S45. Molecular orbital diagram of (a) (energy-minimized) naphthalene, saddle-**Naph-H**, and twisted-**Naph-H**, (b) (energy-minimized) anthracene, saddle-**Ant-H**, and twisted-**Ant-H**, and (c) (energy-minimized) tetracene, saddle-**Tet7-H**, and twisted- **Tet7-H**. Single point calculations of naphthalene, anthracene, and tetracene were performed at the B3LYP/6-31G(d)//B3LYP/6-311G(2d,p) level. Single point calculations of the other structures were performed at the B3LYP/6-311G(2d,p) level.

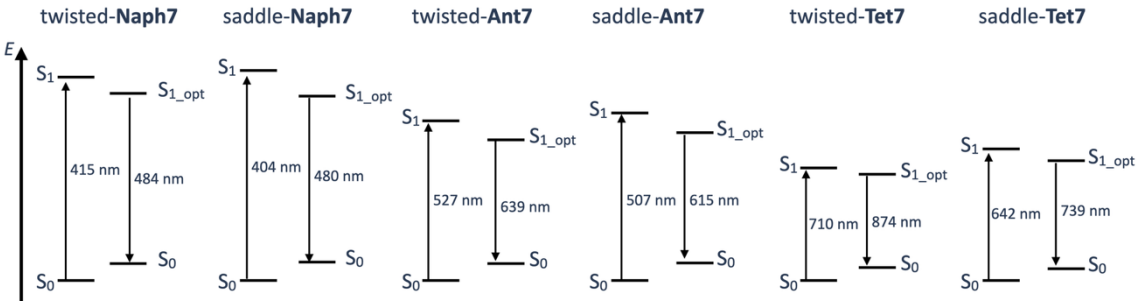


Figure S46. Calculated lowest-energy electronic transitions of **Naph7**, **Ant7**, and **Tet7** based on the energy-minimized S_0 and S_1 geometry. Calculations were conducted at the TD-B3LYP/6-31G(d)//B3LYP/6-311G(2d,p) level.

Table S3. Calculated ΔE_{HL}, $\Delta\Delta E_{HL}$, ΔE_{dist}, and $\Delta E_{\pi\text{-ext}}$ of naphthalene, saddle-**Naph7**, twisted-**Naph7** and their hydrogen-substituted analogues (saddle-**Naph-H** and twisted-**Naph7-H**) calculated at the B3LYP/6-31G(d)//B3LYP-6-311G(2d,p) level.

compound	ΔE_{HL}	$\Delta E_{HL} - \Delta E_{HL,\ naphthalene}$	$\Delta\Delta E_{HL} - \Delta E_{dist,}$
naphthalene	4.76	---	---
saddle-**Naph7-H**	4.43	$-0.33 = \Delta E_{dist}$	---
twisted-**Naph7-H**	4.36	$-0.40 = \Delta E_{dist}$	---
saddle-**Naph7**	3.48	$-1.28 = \Delta\Delta E_{HL}$	$-0.95 = \Delta E_{\pi\text{-ext}}$
twisted-**Naph7**	3.42	$-1.34 = \Delta\Delta E_{HL}$	$-0.94 = \Delta E_{\pi\text{-ext}}$

Table S4. Calculated ΔE_{HL}, $\Delta\Delta E_{HL}$, ΔE_{dist}, and $\Delta E_{\pi\text{-ext}}$ of anthracene, saddle-**Ant7**, twisted-**Ant7** and their hydrogen-substituted analogues (saddle-**Ant7-H** and twisted-**Ant7-H**) calculated at the B3LYP/6-31G(d)//B3LYP-6-311G(2d,p) level.

compound	ΔE_{HL}	$\Delta E_{HL} - \Delta E_{HL,\ anthracene}$	$\Delta\Delta E_{HL} - \Delta E_{dist,}$
anthracene	3.55	---	---
saddle-**Ant7-H**	3.29	$-0.26 = \Delta E_{dist}$	---
twisted-**Ant7-H**	3.23	$-0.32 = \Delta E_{dist}$	---
saddle-**Ant7**	2.78	$-0.78 = \Delta\Delta E_{HL}$	$-0.52 = \Delta E_{\pi\text{-ext}}$

twisted-**Ant7**	2.75	–0.80 = $\Delta\Delta E_{HL}$	–0.48 = $\Delta E_{\pi\text{-ext}}$

Table S5. Calculated ΔE_{HL}, $\Delta\Delta E_{HL}$, ΔE_{dist}, and $\Delta E_{\pi\text{-ext}}$ of tetracene, saddle-**Tet7**, twisted-**Tet7** and their hydrogen-substituted analogues (saddle-**Tet7-H** and twisted-**Tet7-H**) calculated at the B3LYP/6-31G(d)//B3LYP-6-311G(2d,p) level.

compound	ΔE_{HL}	$\Delta E_{HL} - \Delta E_{HL,\ tetracene}$	$\Delta\Delta E_{HL} - \Delta E_{dist,}$
tetracene	2.74	---	---
saddle-**Tet7-H**	2.52	$-0.22 = \Delta E_{dist}$	---
twisted-**Tet7-H**	2.40	$-0.34 = \Delta E_{dist}$	---
saddle-**Tet7**	2.22	$-0.52 = \Delta\Delta E_{HL}$	$-0.30 = \Delta E_{\pi\text{-ext}}$
twisted-**Tet7**	2.11	$-0.63 = \Delta\Delta E_{HL}$	$-0.29 = \Delta E_{\pi\text{-ext}}$

7. Supporting References

S1. M. Hisada, K. Bulgarevich, Y. Tsutsui, K. Miyata, D. Shimizu, S. Seki, K. Takimiya, K. Matsuda. Fused Rubrene Derivatives with Embedded Seven-membered Rings: Curvature-dependent Photophysical and Semiconductor Properties, *J. Am. Chem. Soc.* **2026**, *148*, 6716–6726.

S2. G. M. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3–8.

S3. G. M. Sheldrick, Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.

S4. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A., Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. J. Cossi, M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

8. Molecular Geometries, Excitations, and Thermodynamic Parameters by Theoretical Calculations

Atomic numbers 1, 6, and 7 correspond to hydrogen, carbon, and nitrogen, respectively.

Table S6. Molecular geometries, excitations, and thermodynamic parameters of the optimized structure of (*P*,*P*)-twisted-**Naph7** in the global minimum state (S_0) calculated at the B3LYP/6-31G(d) level of theory. Frequency vibrational and TD-DFT calculations were performed at B3LYP/6-311G(2d,p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.399451	-0.279810	1.237176
2	6	0	0.676365	-0.188294	2.416045
3	6	0	-0.676324	0.188174	2.416064
4	6	0	-1.399428	0.279745	1.237211
5	6	0	2.733398	-0.942673	1.258232
6	6	0	-2.733361	0.942636	1.258302
7	6	0	3.836129	-0.590849	0.446863
8	6	0	5.009175	-1.364749	0.522961
9	6	0	5.125329	-2.448955	1.385229
10	6	0	4.044714	-2.790772	2.197132
11	6	0	2.869664	-2.051622	2.118475
12	6	0	-2.869596	2.051554	2.118591
13	6	0	-4.044616	2.790749	2.197263
14	6	0	-5.125233	2.449016	1.385326
15	6	0	-5.009114	1.364837	0.523019
16	6	0	-3.836102	0.590885	0.446912
17	6	0	0.717165	-0.000019	-0.000006
18	6	0	-0.717165	-0.000020	0.000007
19	6	0	-1.399451	-0.279795	-1.237179
20	6	0	-0.676365	-0.188265	-2.416048
21	6	0	0.676324	0.188203	-2.416062
22	6	0	1.399428	0.279760	-1.237207
23	6	0	-2.733398	-0.942658	-1.258244
24	6	0	2.733361	0.942651	-1.258289
25	6	0	3.836103	0.590891	-0.446905
26	6	0	5.009114	1.364843	-0.523004
27	6	0	5.125233	2.449033	-1.385298
28	6	0	4.044616	2.790776	-2.197229
29	6	0	2.869595	2.051580	-2.118565
30	6	0	-2.869664	-2.051596	-2.118501
31	6	0	-4.044714	-2.790745	-2.197166
32	6	0	-5.125329	-2.448938	-1.385258
33	6	0	-5.009175	-1.364743	-0.522976
34	6	0	-3.836128	-0.590844	-0.446870
35	1	0	1.170674	-0.386551	3.362067
36	1	0	-1.170617	0.386390	3.362103
37	1	0	5.839876	-1.112858	-0.129030
38	1	0	6.043615	-3.029278	1.409369
39	1	0	4.103192	-3.643573	2.867991
40	1	0	2.014223	-2.357045	2.711984
41	1	0	-2.014151	2.356922	2.712122
42	1	0	-4.103069	3.643520	2.868161
43	1	0	-6.043491	3.029383	1.409470
44	1	0	-5.839816	1.113005	-0.128994
45	1	0	-1.170674	-0.386510	-3.362072
46	1	0	1.170618	0.386431	-3.362098
47	1	0	5.839817	1.113004	0.129005
48	1	0	6.043491	3.029399	-1.409435
49	1	0	4.103067	3.643556	-2.868117
50	1	0	2.014150	2.356955	-2.712091
51	1	0	-2.014224	-2.357011	-2.712015
52	1	0	-4.103193	-3.643537	-2.868037
53	1	0	-6.043615	-3.029261	-1.409405
54	1	0	-5.839876	-1.112860	0.129018

SCF Done: E(RB3LYP) = -1307.68858551 A.U. after 6 cycles

imaginary vibration = 0

Zero-point correction= 0.425195 (Hartree/Particle)

Thermal correction to Energy= 0.447448

Thermal correction to Enthalpy= 0.448392

Thermal correction to Gibbs Free Energy= 0.376140

Sum of electronic and zero-point Energies= -1307.587648

Sum of electronic and thermal Energies= -1307.565394

Sum of electronic and thermal Enthalpies= -1307.564450

Sum of electronic and thermal Free Energies= -1307.636702

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	2.1608	0.0000	-0.0001	4.6690	0.3414
2	0.0000	0.1318	0.0000	0.0174	0.0014
3	0.0000	-0.0000	0.2982	0.0889	0.0080
4	-0.0000	-0.0000	0.2170	0.0471	0.0043
5	-0.0000	0.3299	0.0000	0.1088	0.0102
6	0.0000	-0.0000	0.0000	0.0000	0.0000
7	0.0000	0.6983	0.0000	0.4877	0.0479
8	-0.2940	0.0000	0.0001	0.0864	0.0085
9	-0.0001	0.0000	0.4388	0.1925	0.0203
10	-0.0000	-0.0000	0.5064	0.2564	0.0275
11	0.0000	-0.0000	0.0000	0.0000	0.0000
12	1.9311	0.0000	-0.0000	3.7291	0.4066
13	0.0000	-0.0000	0.0000	0.0000	0.0000
14	-0.0075	0.0000	-0.5051	0.2552	0.0288
15	1.4436	0.0000	-0.0023	2.0839	0.2351
16	-0.0000	-0.0001	0.0000	0.0000	0.0000

Ground to excited state transition velocity dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	-0.2374	-0.0000	0.0000	0.0564	0.3427
2	-0.0000	-0.0160	-0.0000	0.0003	0.0014
3	-0.0000	-0.0000	-0.0416	0.0017	0.0085
4	0.0000	0.0000	-0.0282	0.0008	0.0039
5	0.0000	-0.0463	-0.0000	0.0021	0.0101
6	-0.0000	0.0000	-0.0000	0.0000	0.0000
7	-0.0000	-0.1074	-0.0000	0.0115	0.0522
8	0.0412	-0.0000	-0.0000	0.0017	0.0076
9	0.0000	-0.0000	-0.0699	0.0049	0.0206
10	0.0000	0.0000	-0.0829	0.0069	0.0285
11	-0.0000	0.0000	-0.0000	0.0000	0.0000
12	-0.3169	-0.0000	0.0000	0.1004	0.4095
13	-0.0000	0.0000	-0.0000	0.0000	0.0000
14	0.0013	-0.0000	0.0850	0.0072	0.0285
15	-0.2434	-0.0000	0.0004	0.0592	0.2334
16	0.0000	0.0000	-0.0000	0.0000	0.0000

Ground to excited state transition magnetic dipole moments (Au):

state	X	Y	Z
1	-0.3137	0.0000	-0.0000
2	0.0000	2.4722	0.0000
3	-0.0000	-0.0000	0.8146
4	-0.0001	-0.0000	1.0569
5	0.0000	1.1267	0.0000
6	-0.0000	-0.0000	0.0000
7	0.0000	0.4793	0.0000
8	-0.0640	-0.0000	0.0001
9	0.0001	0.0000	-1.1531
10	-0.0000	-0.0000	0.6105
11	-0.0000	0.0000	0.0000
12	-0.2730	-0.0000	-0.0003
13	-0.0000	-0.0000	0.0000
14	0.0009	0.0000	-1.2384
15	-0.1700	-0.0000	-0.0062
16	0.0000	0.0001	0.0000

Ground to excited state transition velocity quadrupole moments (Au):

state	XX	YY	ZZ	XY	XZ	YZ
1	0.0000	-0.0000	0.0000	-0.0000	-0.0000	0.3958
2	-0.0000	-0.0000	0.0000	0.0000	0.0788	0.0000
3	-0.0000	-0.0000	0.0000	0.1172	-0.0000	0.0000
4	-0.0000	0.0000	0.0000	0.3591	0.0000	-0.0000
5	-0.0001	-0.0000	0.0000	-0.0000	0.2386	-0.0000
6	0.7575	0.0581	-0.1980	0.0000	0.0000	0.0000
7	0.0001	-0.0000	-0.0000	-0.0000	0.6579	0.0000
8	-0.0000	0.0000	-0.0000	0.0000	0.0000	-0.2213
9	-0.0000	-0.0000	0.0000	0.0651	0.0000	-0.0000
10	-0.0000	-0.0000	-0.0000	0.1483	-0.0000	-0.0000
11	0.2955	0.1786	0.0050	0.0000	-0.0000	0.0000

```
12          -0.0000      -0.0000       0.0000      -0.0001       0.0000
0.4559
13           0.4440       0.3370      -0.0941       0.0000      -0.0000
0.0000
14          0.0000      0.0000     -0.0000     -1.3567     -0.0000     -
0.0028
15          -0.0000      -0.0000       0.0000      -0.0068      -0.0000
0.5403
16        -0.6077     -0.2845     -0.0242      0.0000     -0.0001     -
0.0000
<0|del|b> * <b|rxdel|0> + <0|del|b> * <b|delr+rdel|0>
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)
state         XX          YY          ZZ    R(velocity)    E-M Angle
1       -0.0000    -62.8827    543.1298    160.0824      90.00
2     -113.1139     -0.0000   -120.5592    -77.8911      90.00
3     -101.2345    -75.7697      0.0000    -59.0014      90.00
4     -102.9564    -50.7411     -0.0000    -51.2325      90.00
5     -102.8917     -0.0000   -158.1682    -87.0200      90.00
6       -0.0000     -0.0000      0.0000     -0.0000      90.00
7       46.0605     -0.0000   -293.2836    -82.4077      90.00
8       -0.0000    -28.0141     15.4399     -4.1914      90.00
9      170.0189    190.3565      0.0000    120.1251      90.00
10     -138.2488    -84.2017     -0.0000    -74.1502      90.00
11        0.0000     -0.0000      0.0000      0.0000      90.00
12       -0.0000   -125.2936    499.4974    124.7346      90.00
13        0.0000     -0.0000     -0.0000     -0.0000      90.00
14     -460.9465     21.0097      0.0097   -146.6424     179.10
15       -0.0107   -188.3055    361.2692     57.6510       2.18
16        0.0000      0.0000      0.0000      0.0000      90.00
1/2[<0|r|b>*<b|rxdel|0> + (<0|rxdel|b>*<b|r|0>)*]
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)
state         XX          YY          ZZ     R(length)
1      479.3009     -0.0000     -0.0000    159.7670
2       -0.0000   -230.4781     -0.0000    -76.8260
3        0.0000     -0.0000   -171.8036    -57.2679
4       -0.0000     -0.0000   -162.1747    -54.0582
5        0.0000   -262.8437     -0.0000    -87.6146
6        0.0000     -0.0000     -0.0000     -0.0000
7       -0.0000   -236.6904     -0.0000    -78.8968
8      -13.3116      0.0000     -0.0000     -4.4372
9        0.0000     -0.0000    357.7989    119.2663
10       -0.0000     -0.0000   -218.6322    -72.8774
11        0.0000      0.0000     -0.0000      0.0000
12      372.8619      0.0000     -0.0000    124.2873
13        0.0000     -0.0000     -0.0000     -0.0000
14        0.0049     -0.0000   -442.3397   -147.4449
15      173.5787      0.0000     -0.0103     57.8562
16        0.0000      0.0000     -0.0000      0.0000
1/2[<0|del|b>*<b|r|0> + (<0|r|b>*<b|del|0>)*] (Au)
state         X           Y           Z        Dip. S.   Osc.(frdel)
1       -0.5130     -0.0000     -0.0000      0.5130      0.3420
2       -0.0000     -0.0021     -0.0000      0.0021      0.0014
3       -0.0000      0.0000     -0.0124      0.0124      0.0083
4       -0.0000     -0.0000     -0.0061      0.0061      0.0041
5       -0.0000     -0.0153     -0.0000      0.0153      0.0102
6       -0.0000     -0.0000     -0.0000      0.0000      0.0000
7       -0.0000     -0.0750     -0.0000      0.0750      0.0500
8       -0.0121     -0.0000     -0.0000      0.0121      0.0081
9       -0.0000     -0.0000     -0.0307      0.0307      0.0205
10       -0.0000     -0.0000     -0.0420      0.0420      0.0280
11       -0.0000     -0.0000     -0.0000      0.0000      0.0000
12       -0.6120     -0.0000     -0.0000      0.6120      0.4080
13       -0.0000     -0.0000     -0.0000      0.0000      0.0000
14       -0.0000     -0.0000     -0.0429      0.0429      0.0286
15       -0.3513     -0.0000     -0.0000      0.3513      0.2342
16       -0.0000     -0.0000     -0.0000      0.0000      0.0000

Excitation energies and oscillator strengths:

Excited State   1:       Singlet-A       2.9842 eV  415.47 nm  f=0.3414
<S**2>=0.000
112 ->113        0.69945
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) =  -1307.90317475
Copying the excited state density for this state as the 1-particle RhoCI
density.

Excited State   2:       Singlet-A       3.2537 eV  381.05 nm  f=0.0014
<S**2>=0.000
112 ->114        0.70391

Excited State   3:       Singlet-A       3.6840 eV  336.55 nm  f=0.0080
<S**2>=0.000
108 ->113        0.34900
112 ->115        0.53079
112 ->116       -0.29489

Excited State   4:       Singlet-A       3.7366 eV  331.81 nm  f=0.0043
<S**2>=0.000
108 ->113       -0.20379
112 ->115        0.42532
112 ->116        0.50696

Excited State   5:       Singlet-A       3.8423 eV  322.68 nm  f=0.0102
<S**2>=0.000
111 ->113        0.64561
112 ->117       -0.27399

Excited State   6:       Singlet-A       3.8812 eV  319.44 nm  f=0.0000
<S**2>=0.000
110 ->113        0.69565

Excited State   7:       Singlet-A       4.0054 eV  309.54 nm  f=0.0479
<S**2>=0.000
109 ->114        0.18271
111 ->113        0.25428
112 ->117        0.62319

Excited State   8:       Singlet-A       4.0375 eV  307.08 nm  f=0.0085
<S**2>=0.000
109 ->113        0.69521

Excited State   9:       Singlet-A       4.3060 eV  287.94 nm  f=0.0203
<S**2>=0.000
107 ->113       -0.26605
108 ->113       -0.36665
110 ->114        0.44162
112 ->116       -0.16471
112 ->119       -0.21418

Excited State  10:       Singlet-A       4.3767 eV  283.28 nm  f=0.0275
<S**2>=0.000
107 ->113       -0.28231
108 ->113       -0.22540
110 ->114       -0.17869
112 ->116       -0.19721
112 ->119        0.51831

Excited State  11:       Singlet-A       4.3934 eV  282.21 nm  f=0.0000
<S**2>=0.000
106 ->113       -0.26061
107 ->114        0.11696
111 ->115        0.12324
112 ->118        0.62317

Excited State  12:       Singlet-A       4.4499 eV  278.62 nm  f=0.4066
<S**2>=0.000
111 ->114        0.63251
112 ->120       -0.24382

Excited State  13:       Singlet-A       4.5663 eV  271.52 nm  f=0.0000
<S**2>=0.000
106 ->113        0.55997
108 ->114        0.26765
111 ->115        0.21316
111 ->116       -0.16615
112 ->118        0.16976

Excited State  14:       Singlet-A       4.6021 eV  269.41 nm  f=0.0288
<S**2>=0.000
107 ->113        0.45420
110 ->114        0.37973
112 ->116       -0.11843
112 ->119        0.33471

Excited State  15:       Singlet-A       4.6040 eV  269.30 nm  f=0.2351
<S**2>=0.000
105 ->113       -0.12226
111 ->114        0.26341
112 ->120        0.63314

Excited State  16:       Singlet-A       4.6441 eV  266.97 nm  f=0.0000
<S**2>=0.000
```

106 ->113 -0.27994
107 ->114 -0.14376
108 ->114 0.57363
111 ->116 -0.21502

Table S7. Molecular geometries, excitations, and thermodynamic parameters of the optimized structure of saddle-**Naph7** in a local minimum state (S_0) calculated at the B3LYP/6-31G(d) level of theory. Frequency vibrational and TD-DFT calculations were performed at B3LYP/6-311G(2d,p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.423518	-1.068048	-0.662210
2	6	0	-0.700123	-1.865541	-1.539789
3	6	0	0.700110	-1.865538	-1.539794
4	6	0	1.423513	-1.068049	-0.662218
5	6	0	-2.766845	-1.548278	-0.229589
6	6	0	2.766844	-1.548281	-0.229617
7	6	0	-3.875187	-0.733261	0.093993
8	6	0	-5.051348	-1.340467	0.573841
9	6	0	-5.167086	-2.717664	0.717540
10	6	0	-4.082365	-3.528599	0.386035
11	6	0	-2.905167	-2.943589	-0.065607
12	6	0	2.905179	-2.943594	-0.065664
13	6	0	4.082379	-3.528602	0.385973
14	6	0	5.167090	-2.717664	0.717507
15	6	0	5.051340	-1.340466	0.573835
16	6	0	3.875179	-0.733262	0.093985
17	6	0	-0.727551	-0.000048	0.000048
18	6	0	0.727552	-0.000048	0.000048
19	6	0	1.423516	1.067947	0.662348
20	6	0	0.700114	1.865352	1.539993
21	6	0	-0.700127	1.865355	1.539988
22	6	0	-1.423520	1.067947	0.662340
23	6	0	2.766797	1.548254	0.229682
24	6	0	-2.766798	1.548252	0.229654
25	6	0	-3.875131	0.733299	-0.094140
26	6	0	-5.051192	1.340579	-0.574134
27	6	0	-5.166865	2.717791	-0.717747
28	6	0	-4.082176	3.528665	-0.385990
29	6	0	-2.905062	2.943582	0.065777
30	6	0	2.905075	2.943587	0.065834
31	6	0	4.082191	3.528668	-0.385927
32	6	0	5.166870	2.717790	-0.717714
33	6	0	5.051185	1.340577	-0.574127
34	6	0	3.875123	0.733300	-0.094133
35	1	0	-1.222190	-2.604705	-2.140130
36	1	0	1.222173	-2.604696	-2.140146
37	1	0	-5.884545	-0.705413	0.858171
38	1	0	-6.087452	-3.149916	1.100621
39	1	0	-4.139673	-4.607206	0.504751
40	1	0	-2.047732	-3.576874	-0.266637
41	1	0	2.047752	-3.576885	-0.266712
42	1	0	4.139698	-4.607211	0.504664
43	1	0	6.087455	-3.149916	1.100590
44	1	0	5.884529	-0.705409	0.858182
45	1	0	1.222167	2.604480	2.140392
46	1	0	-1.222184	2.604488	2.140376
47	1	0	-5.884366	0.705572	-0.858637
48	1	0	-6.087153	3.150101	-1.100949
49	1	0	-4.139436	4.607285	-0.504611
50	1	0	-2.047639	3.576828	0.266978
51	1	0	2.047660	3.576839	0.267052
52	1	0	4.139462	4.607290	-0.504524
53	1	0	6.087157	3.150101	-1.100917
54	1	0	5.884351	0.705567	-0.858648

SCF Done: E(RB3LYP) = -1307.68258132 A.U. after 1 cycles

imaginary vibration = 0
Zero-point correction= 0.425057 (Hartree/Particle)
Thermal correction to Energy= 0.447284
Thermal correction to Enthalpy= 0.448228
Thermal correction to Gibbs Free Energy= 0.375923
Sum of electronic and zero-point Energies= -1307.581424
Sum of electronic and thermal Energies= -1307.559198
Sum of electronic and thermal Enthalpies= -1307.558253
Sum of electronic and thermal Free Energies= -1307.630558

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	-2.2537	0.0000	0.0000	5.0794	0.3824
2	0.0005	-0.0000	0.0000	0.0000	0.0000
3	-0.0000	0.4164	0.0484	0.1757	0.0160
4	-0.0002	0.0000	0.0000	0.0000	0.0000
5	0.0000	-0.0000	-0.0000	0.0000	0.0000
6	0.0000	-0.3763	0.0023	0.1416	0.0136
7	0.0000	-0.0000	-0.0000	0.0000	0.0000
8	-0.2947	-0.0000	0.0000	0.0868	0.0086
9	0.0000	-0.1215	0.1893	0.0506	0.0053
10	-0.0000	-0.4247	-0.2228	0.2300	0.0247
11	-0.0000	0.0059	0.0031	0.0000	0.0000
12	-2.3701	0.0000	0.0000	5.6176	0.6109
13	-0.0000	-0.0003	0.0000	0.0000	0.0000
14	0.0000	1.1271	-0.1660	1.2980	0.1461
15	0.0000	-0.0018	0.0003	0.0000	0.0000
16	-0.5884	-0.0000	-0.0000	0.3462	0.0396

Ground to excited state transition velocity dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	0.2552	-0.0000	-0.0000	0.0651	0.3845
2	-0.0001	0.0000	-0.0000	0.0000	0.0000
3	0.0000	-0.0589	-0.0048	0.0035	0.0170
4	0.0000	-0.0000	0.0000	0.0000	0.0000
5	-0.0000	0.0000	0.0000	0.0000	0.0000
6	0.0000	0.0534	-0.0010	0.0029	0.0132
7	0.0000	0.0000	0.0000	0.0000	0.0000
8	0.0415	0.0000	0.0000	0.0017	0.0077
9	-0.0000	0.0194	-0.0299	0.0013	0.0053
10	0.0000	0.0684	0.0371	0.0061	0.0251
11	0.0000	-0.0009	-0.0005	0.0000	0.0000
12	0.3875	-0.0000	-0.0000	0.1501	0.6135
13	0.0000	0.0001	-0.0000	0.0000	0.0000
14	-0.0000	-0.1926	0.0305	0.0380	0.1501
15	-0.0000	0.0003	-0.0001	0.0000	0.0000
16	0.0987	0.0000	0.0000	0.0097	0.0379

Ground to excited state transition magnetic dipole moments (Au):

state	X	Y	Z
1	-0.0000	0.0003	-0.0005
2	0.0000	0.8201	-2.5150
3	-0.0001	0.0000	0.0000
4	-0.0000	0.4988	-0.9101
5	0.1790	0.0000	-0.0000
6	0.0001	0.0001	-0.0001
7	0.0000	-0.5592	0.0281
8	0.0000	0.0002	0.0002
9	0.0001	-0.0000	-0.0000
10	0.0005	-0.0000	0.0000
11	0.0336	0.0000	-0.0000
12	-0.0000	0.0000	0.0002
13	-0.0239	-0.0000	-0.0000
14	-0.0001	0.0006	0.0028
15	0.0000	0.3779	1.7403
16	0.0000	-0.0001	-0.0000

Ground to excited state transition velocity quadrupole moments (Au):

state	XX	YY	ZZ	XY	XZ	YZ
1	0.0000	0.0000	-0.0000	0.0001	-0.0000	0.0000
2	0.0000	-0.0000	-0.0000	0.2410	-0.0981	-0.0000
3	0.0000	-0.0000	0.0000	0.0000	-0.0000	-0.0000
4	0.0000	-0.0000	-0.0000	0.4533	-0.1116	-0.0000
5	-0.8260	0.0613	0.0826	0.0000	-0.0000	0.1426
6	-0.0002	0.0000	0.0000	0.0001	-0.0000	0.0000
7	0.0000	-0.0000	0.0000	-1.1470	0.1696	0.0000
8	-0.0000	0.0000	0.0000	0.0004	-0.0001	0.0000
9	0.0001	0.0001	-0.0000	-0.0000	0.0000	-0.0000
10	-0.0044	-0.0020	0.0005	-0.0000	0.0000	0.0011
11	-0.3039	-0.1474	0.0351	-0.0000	-0.0000	0.0788
12	0.0000	0.0000	-0.0000	-0.0001	-0.0000	0.0000
13	-0.4875	-0.4323	0.1824	-0.0000	0.0000	0.2409
14	-0.0000	-0.0002	0.0001	0.0028	-0.0004	0.0001
15	0.0000	-0.0000	0.0000	1.7649	-0.2461	-0.0000

```
16           0.0000       0.0000      -0.0000      -0.0001       0.0000
0.0000
<0|del|b> * <b|rxdel|0> + <0|del|b> * <b|delr+rdel|0>
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)
state         XX          YY          ZZ    R(velocity)    E-M Angle
1        0.0000      0.0002     -0.0032     -0.0010      90.00
2        0.0031      0.0018      0.0012      0.0021      90.00
3       -0.0043     -0.0000     -0.0019     -0.0021      90.00
4       -0.0061     -0.0008     -0.0037     -0.0036      90.00
5        0.0000     -0.0008     -0.0001     -0.0003      90.00
6        0.0101      0.0005      0.0067      0.0057      90.00
7       -0.0058      0.0025     -0.0018     -0.0017      90.00
8        0.0000      0.0017      0.0002      0.0006      90.00
9        0.0033     -0.0003     -0.0008      0.0007      90.00
10      -0.0014      0.0003     -0.0008     -0.0007      90.00
11      -0.0000      0.0007     -0.0003      0.0001      90.00
12      -0.0000      0.0020     -0.0103     -0.0028      90.00
13      -0.0000      0.0037     -0.0045     -0.0003      90.00
14      -0.0600     -0.0028     -0.0888     -0.0505      90.00
15       0.0392      0.0026      0.0862      0.0427      90.00
16      -0.0000      0.0012      0.0005      0.0006      90.00
1/2[<0|r|b>*<b|rxdel|0> + (<0|rxdel|b>*<b|r|0>)*]
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)
state         XX          YY          ZZ     R(length)
1       -0.0029     -0.0000      0.0000     -0.0010
2       -0.0000      0.0026      0.0033      0.0020
3       -0.0000     -0.0059     -0.0002     -0.0020
4       -0.0000     -0.0101      0.0007     -0.0031
5       -0.0006      0.0000     -0.0000     -0.0002
6       -0.0000      0.0170      0.0002      0.0057
7       -0.0000     -0.0057      0.0001     -0.0019
8        0.0020      0.0000     -0.0000      0.0007
9       -0.0000     -0.0029      0.0051      0.0007
10       0.0000     -0.0024      0.0004     -0.0007
11       0.0004     -0.0000      0.0000      0.0001
12      -0.0083     -0.0000     -0.0000     -0.0028
13      -0.0008     -0.0000      0.0000     -0.0003
14       0.0000     -0.4981      0.3238     -0.0581
15      -0.0000      0.4881     -0.3351      0.0510
16       0.0018     -0.0000     -0.0000      0.0006
1/2[<0|del|b>*<b|r|0> + (<0|r|b>*<b|del|0>)*] (Au)
state         X           Y           Z       Dip. S.   Osc.(frdel)
1       -0.5752     -0.0000     -0.0000      0.5752      0.3834
2       -0.0000     -0.0000     -0.0000      0.0000      0.0000
3       -0.0000     -0.0245     -0.0002      0.0248      0.0165
4       -0.0000     -0.0000      0.0000      0.0000      0.0000
5       -0.0000     -0.0000     -0.0000      0.0000      0.0000
6        0.0000     -0.0201     -0.0000      0.0201      0.0134
7        0.0000     -0.0000     -0.0000      0.0000      0.0000
8       -0.0122     -0.0000      0.0000      0.0122      0.0082
9       -0.0000     -0.0024     -0.0057      0.0080      0.0053
10      -0.0000     -0.0291     -0.0083      0.0373      0.0249
11      -0.0000     -0.0000     -0.0000      0.0000      0.0000
12      -0.9183     -0.0000     -0.0000      0.9183      0.6122
13      -0.0000     -0.0000     -0.0000      0.0000      0.0000
14      -0.0000     -0.2170     -0.0051      0.2221      0.1481
15      -0.0000     -0.0000     -0.0000      0.0000      0.0000
16      -0.0581     -0.0000     -0.0000      0.0581      0.0387

Excitation energies and oscillator strengths:

Excited State   1:       Singlet-A       3.0726 eV  403.52 nm  f=0.3824
<S**2>=0.000
112 ->113        0.69792
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) =  -1307.89356544
Copying the excited state density for this state as the 1-particle RhoCI
density.

Excited State   2:       Singlet-A       3.2635 eV  379.91 nm  f=0.0000
<S**2>=0.000
112 ->114        0.70386

Excited State   3:       Singlet-A       3.7152 eV  333.72 nm  f=0.0160
<S**2>=0.000
108 ->113        0.19191
112 ->115        0.67428

Excited State   4:       Singlet-A       3.8451 eV  322.45 nm  f=0.0000
<S**2>=0.000
110 ->113        0.62599
112 ->116        0.31540

Excited State   5:       Singlet-A       3.8806 eV  319.50 nm  f=0.0000
<S**2>=0.000
110 ->115        0.10163
111 ->113        0.69329

Excited State   6:       Singlet-A       3.9119 eV  316.94 nm  f=0.0136
<S**2>=0.000
106 ->113        0.10269
108 ->113        0.47694
112 ->115       -0.13613
112 ->117       -0.45726
112 ->119        0.16298

Excited State   7:       Singlet-A       3.9836 eV  311.24 nm  f=0.0000
<S**2>=0.000
109 ->114        0.17871
110 ->113       -0.29595
112 ->116        0.60635

Excited State   8:       Singlet-A       4.0360 eV  307.20 nm  f=0.0086
<S**2>=0.000
109 ->113        0.69325

Excited State   9:       Singlet-A       4.3064 eV  287.90 nm  f=0.0053
<S**2>=0.000
106 ->113        0.19470
108 ->113       -0.21494
111 ->114        0.54009
112 ->117       -0.12332
112 ->119        0.29189

Excited State  10:       Singlet-A       4.3852 eV  282.73 nm  f=0.0247
<S**2>=0.000
106 ->113       -0.33093
108 ->113        0.26071
112 ->117        0.35109
112 ->119        0.40920

Excited State  11:       Singlet-A       4.3866 eV  282.64 nm  f=0.0000
<S**2>=0.000
106 ->114       -0.10479
107 ->113       -0.26921
110 ->115        0.12596
112 ->118        0.61992

Excited State  12:       Singlet-A       4.4387 eV  279.33 nm  f=0.6109
<S**2>=0.000
110 ->114        0.67913

Excited State  13:       Singlet-A       4.5597 eV  271.92 nm  f=0.0000
<S**2>=0.000
107 ->113        0.59137
108 ->114        0.23712
110 ->115        0.20105
110 ->117       -0.10319
112 ->118        0.17900

Excited State  14:       Singlet-A       4.5952 eV  269.81 nm  f=0.1461
<S**2>=0.000
106 ->113        0.40396
108 ->113       -0.10481
111 ->114       -0.36539
111 ->116        0.11762
112 ->117        0.11886
112 ->119        0.38189

Excited State  15:       Singlet-A       4.5992 eV  269.58 nm  f=0.0000
<S**2>=0.000
107 ->115       -0.11372
109 ->114        0.63719
109 ->116       -0.11521
111 ->115       -0.10986
112 ->116       -0.15326

Excited State  16:       Singlet-A       4.6662 eV  265.71 nm  f=0.0396
<S**2>=0.000
105 ->113       -0.13924
110 ->116       -0.12212
112 ->120        0.65320
```

Table S8. Molecular geometries, excitations, and thermodynamic parameters of the optimized structure of (*P*,*P*)-twisted-**Ant7** in the global minimum state (S_0) calculated at the B3LYP/6-31G(d). Frequency vibrational and TD-DFT calculations were performed at B3LYP/6-311G(2d,p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.393543	-1.652482	-0.305029
2	6	0	0.674689	-2.824451	-0.212744
3	6	0	-0.674672	-2.824390	0.213559
4	6	0	-1.393532	-1.652398	0.305495
5	6	0	2.700034	-1.646872	-1.019883
6	6	0	-2.700015	-1.646582	1.020362
7	6	0	3.809200	-0.846385	-0.665879
8	6	0	4.961663	-0.880389	-1.469864
9	6	0	5.047024	-1.691903	-2.596215
10	6	0	3.960016	-2.494272	-2.942274
11	6	0	2.805388	-2.458134	-2.167198
12	6	0	-2.805349	-2.457498	2.167923
13	6	0	-3.959966	-2.493407	2.943025
14	6	0	-5.046981	-1.691145	2.596740
15	6	0	-4.961640	-0.879969	1.470145
16	6	0	-3.809188	-0.846202	0.666133
17	6	0	0.718644	-0.404118	0.009146
18	6	0	-0.718641	-0.404126	-0.009060
19	6	0	-1.402580	0.803454	-0.294329
20	6	0	-0.700199	2.033012	-0.178404
21	6	0	0.700176	2.033070	0.177798
22	6	0	1.402574	0.803550	0.294065
23	6	0	-2.724449	0.745213	-0.986510
24	6	0	2.724435	0.745508	0.986283
25	6	0	3.824267	-0.039681	0.574727
26	6	0	4.985180	-0.062713	1.369445
27	6	0	5.080189	0.656560	2.554928
28	6	0	3.988088	1.413265	2.979654
29	6	0	2.832501	1.444891	2.207293
30	6	0	-2.832522	1.444213	-2.207738
31	6	0	-3.988110	1.412343	-2.980086
32	6	0	-5.080203	0.655756	-2.555127
33	6	0	-4.985184	-0.063155	-1.369425
34	6	0	-3.824273	-0.039864	-0.574712
35	6	0	-1.363679	3.297043	-0.305152
36	6	0	-0.696169	4.481836	-0.140034
37	6	0	0.696100	4.481887	0.138757
38	6	0	1.363631	3.297151	0.304202
39	1	0	1.155183	-3.768389	-0.452047
40	1	0	-1.155160	-3.768258	0.453150
41	1	0	5.799419	-0.242132	-1.204532
42	1	0	5.948045	-1.687485	-3.203489
43	1	0	3.998597	-3.126779	-3.825019
44	1	0	1.944331	-3.045202	-2.470248
45	1	0	-1.944285	-3.044471	2.471138
46	1	0	-3.998532	-3.125648	3.825961
47	1	0	-5.947993	-1.686547	3.204027
48	1	0	-5.799400	-0.241791	1.204637
49	1	0	5.815968	-0.687144	1.054772
50	1	0	5.987641	0.608355	3.150590
51	1	0	4.025563	1.962484	3.916547
52	1	0	1.976716	2.010954	2.559302
53	1	0	-1.976737	2.010167	-2.559930
54	1	0	-4.025588	1.961271	-3.917149
55	1	0	-5.987653	0.607356	-3.150775
56	1	0	-5.815960	-0.687506	-1.054566
57	1	0	-2.428613	3.306148	-0.504818
58	1	0	-1.232552	5.423254	-0.223063
59	1	0	1.232464	5.423338	0.221528
60	1	0	2.428562	3.306329	0.503867

SCF Done: E(RB3LYP) = -1461.31519674 A.U. after 6 cycles

imaginary vibration = 0
Zero-point correction= 0.471126 (Hartree/Particle)
Thermal correction to Energy= 0.496134
Thermal correction to Enthalpy= 0.497078
Thermal correction to Gibbs Free Energy= 0.419327
Sum of electronic and zero-point Energies= -1461.205208
Sum of electronic and thermal Energies= -1461.180200
Sum of electronic and thermal Enthalpies= -1461.179256
Sum of electronic and thermal Free Energies= -1461.257007

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	1.8900	-0.0000	0.1111	3.5844	0.2063
2	0.1800	0.0000	0.1813	0.0653	0.0048
3	-0.2247	0.0003	0.5074	0.3080	0.0247
4	0.0002	0.2588	-0.0004	0.0670	0.0054
5	0.0000	0.2948	0.0000	0.0869	0.0074
6	0.0000	-0.1943	-0.0000	0.0377	0.0033
7	0.0255	0.0000	-0.0833	0.0076	0.0007
8	-0.1521	0.0001	-0.5602	0.3370	0.0306
9	-0.5279	0.0001	0.1777	0.3103	0.0292
10	-0.0001	-1.1542	0.0001	1.3322	0.1287
11	-0.0001	0.3394	-0.0001	0.1152	0.0115
12	0.0000	-0.3544	0.0000	0.1256	0.0127
13	0.2659	0.0007	-0.0613	0.0745	0.0076
14	-0.0004	0.8295	-0.0001	0.6880	0.0709
15	0.0062	-1.3862	0.0011	1.9215	0.2016
16	2.0756	0.0043	0.3153	4.4077	0.4629

Ground to excited state transition velocity dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	-0.1648	0.0000	-0.0093	0.0272	0.2104
2	-0.0207	-0.0000	-0.0199	0.0008	0.0050
3	0.0270	-0.0000	-0.0614	0.0045	0.0249
4	-0.0000	-0.0326	0.0000	0.0011	0.0059
5	-0.0000	-0.0369	-0.0000	0.0014	0.0071
6	-0.0000	0.0257	0.0000	0.0007	0.0034
7	-0.0022	-0.0000	0.0111	0.0001	0.0006
8	0.0225	-0.0000	0.0806	0.0070	0.0343
9	0.0739	-0.0000	-0.0248	0.0061	0.0287
10	0.0000	0.1691	-0.0000	0.0286	0.1315
11	0.0000	-0.0513	0.0000	0.0026	0.0117
12	0.0000	0.0546	-0.0000	0.0030	0.0130
13	-0.0435	-0.0001	0.0097	0.0020	0.0086
14	0.0001	-0.1280	0.0000	0.0164	0.0707
15	-0.0010	0.2196	-0.0002	0.0482	0.2044
16	-0.3273	-0.0007	-0.0502	0.1097	0.4642

Ground to excited state transition magnetic dipole moments (Au):

state	X	Y	Z
1	-0.3505	-0.0001	0.0869
2	0.0283	0.0002	1.8512
3	0.0687	0.0005	1.2695
4	-0.0001	0.4646	-0.0008
5	0.0000	1.0123	-0.0002
6	0.0000	-0.2522	0.0000
7	0.0652	-0.0001	-0.4836
8	-0.2691	0.0000	0.1678
9	-0.1341	-0.0000	0.7233
10	0.0000	0.4362	-0.0001
11	0.0000	-0.0475	0.0000
12	0.0001	-0.1766	-0.0000
13	-0.0986	-0.0006	-0.6961
14	0.0000	-0.4304	0.0009
15	-0.0004	0.9135	-0.0045
16	-0.1515	-0.0030	-1.4263

Ground to excited state transition velocity quadrupole moments (Au):

state	XX	YY	ZZ	XY	XZ	YZ
1	-0.0000	-0.0001	0.0001	0.0741	-0.0000	-0.2397
2	-0.0000	0.0000	0.0000	-0.0786	0.0000	-0.0105
3	0.0001	-0.0000	-0.0000	-0.3620	0.0001	0.0916
4	0.1718	-0.1318	0.0596	0.0003	0.0781	-0.0000
5	0.0479	0.0545	0.0172	-0.0001	-0.2338	-0.0000
6	-0.6371	0.2960	-0.0691	0.0000	0.1078	-0.0001
7	0.0001	-0.0001	0.0000	0.0359	-0.0000	-0.1112
8	0.0001	-0.0001	0.0000	0.3433	-0.0001	-0.0271
9	0.0001	0.0000	-0.0000	-0.3492	0.0001	0.2000
10	-0.2908	0.4559	-0.1418	0.0000	0.2754	-0.0000
11	-0.2433	-0.0403	-0.1254	-0.0001	-0.2417	-0.0000
12	-0.5654	0.4572	-0.2812	-0.0001	-0.5425	-0.0001
13	0.0008	-0.0007	0.0004	-0.0724	-0.0002	-0.0044
14	1.0684	-0.8202	0.4882	0.0000	-0.1414	0.0002
15	-0.3144	0.8509	-0.0491	0.0005	-0.3528	-0.0015

16 0.0010 -0.0028 0.0004 0.1822 0.0011 -
0.4953
<0|del|b> * <b|rxdel|0> + <0|del|b> * <b|delr+rdel|0>
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)
state XX YY ZZ R(velocity) E-M Angle
1 -6.1261 397.9067 74.7315 155.5040 17.15
2 -112.5180 -123.6709 -2.5634 -79.5841 134.74
3 -163.6809 -281.5467 -1.8143 -149.0140 153.15
4 -36.9904 -0.0001 -51.9362 -29.6422 90.00
5 -126.6696 0.0000 -79.1337 -68.6011 90.00
6 -25.2939 0.0000 -10.1444 -11.8128 90.00
7 -13.1695 -15.0138 -1.0308 -9.7380 176.45
8 106.9482 -54.0108 -14.1233 12.9380 73.64
9 -23.2772 -54.5333 -61.9272 -46.5792 119.06
10 66.3405 0.0000 293.4760 119.9388 90.00
11 -23.5012 0.0000 34.9851 3.8280 90.00
12 46.3662 -0.0000 -91.1258 -14.9199 90.00
13 -17.1408 -3.6279 9.4126 -3.7854 94.52
14 84.6650 0.0001 167.5193 84.0615 0.12
15 624.9530 0.0061 276.7618 300.5736 0.33
16 140.1160 656.4539 -252.6352 181.3116 75.22
1/2[<0|r|b>*<b|rxdel|0> + (<0|rxdel|b>*<b|r|0>)*]
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)
state XX YY ZZ R(length)
1 468.4023 -0.0000 -6.8254 153.8590
2 -3.5980 -0.0000 -237.3504 -80.3162
3 10.9238 -0.0001 -455.5453 -148.2072
4 0.0000 -85.0166 -0.0002 -28.3389
5 -0.0000 -211.0145 0.0000 -70.3382
6 -0.0000 -34.6520 0.0000 -11.5507
7 -1.1763 0.0000 -28.4975 -9.8913
8 -28.9475 -0.0000 66.4674 12.5066
9 -50.0620 0.0000 -90.8910 -46.9843
10 0.0000 356.0629 0.0000 118.6876
11 0.0000 11.3902 0.0000 3.7967
12 -0.0000 -44.2602 0.0000 -14.7534
13 18.5324 0.0003 -30.1790 -3.8821
14 0.0000 252.4520 0.0000 84.1507
15 0.0016 895.4892 0.0035 298.4981
16 222.3880 0.0090 318.0769 180.1580
1/2[<0|del|b>*<b|r|0> + (<0|r|b>*<b|del|0>)*] (Au)
state X Y Z Dip. S. Osc.(frdel)
1 -0.3115 -0.0000 -0.0010 0.3125 0.2083
2 -0.0037 -0.0000 -0.0036 0.0073 0.0049
3 -0.0061 -0.0000 -0.0312 0.0372 0.0248
4 -0.0000 -0.0084 -0.0000 0.0084 0.0056
5 -0.0000 -0.0109 -0.0000 0.0109 0.0073
6 -0.0000 -0.0050 -0.0000 0.0050 0.0033
7 -0.0001 -0.0000 -0.0009 0.0010 0.0007
8 -0.0034 -0.0000 -0.0452 0.0486 0.0324
9 -0.0390 -0.0000 -0.0044 0.0434 0.0289
10 -0.0000 -0.1952 -0.0000 0.1952 0.1301
11 -0.0000 -0.0174 -0.0000 0.0174 0.0116
12 0.0000 -0.0193 -0.0000 0.0193 0.0129
13 -0.0116 -0.0000 -0.0006 0.0122 0.0081
14 -0.0000 -0.1062 -0.0000 0.1062 0.0708
15 -0.0000 -0.3044 -0.0000 0.3044 0.2030
16 -0.6795 -0.0000 -0.0158 0.6953 0.4635

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.3490 eV 527.82 nm f=0.2063
<S**2>=0.000
125 -> 126 0.70370
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1461.59001047
Copying the excited state density for this state as the 1-particle RhoCI
density.

Excited State 2: Singlet-A 3.0103 eV 411.87 nm f=0.0048
<S**2>=0.000
125 -> 127 0.69888

Excited State 3: Singlet-A 3.2764 eV 378.42 nm f=0.0247
<S**2>=0.000
124 -> 126 0.69162

Excited State 4: Singlet-A 3.2821 eV 377.75 nm f=0.0054
<S**2>=0.000
121 -> 126 -0.40299
125 -> 128 0.52013
125 -> 129 -0.23986

Excited State 5: Singlet-A 3.4956 eV 354.69 nm f=0.0074
<S**2>=0.000
121 -> 126 0.18389
125 -> 128 0.39293
125 -> 129 0.53908

Excited State 6: Singlet-A 3.5237 eV 351.86 nm f=0.0033
<S**2>=0.000
123 -> 126 0.69446

Excited State 7: Singlet-A 3.6348 eV 341.10 nm f=0.0007
<S**2>=0.000
122 -> 126 0.69448
125 -> 130 -0.10555

Excited State 8: Singlet-A 3.7077 eV 334.40 nm f=0.0306
<S**2>=0.000
122 -> 126 0.10080
125 -> 130 0.66475
125 -> 131 0.16691

Excited State 9: Singlet-A 3.8346 eV 323.33 nm f=0.0292
<S**2>=0.000
118 -> 126 -0.10487
125 -> 130 -0.16252
125 -> 131 0.67008

Excited State 10: Singlet-A 3.9446 eV 314.32 nm f=0.1287
<S**2>=0.000
120 -> 126 0.44199
121 -> 126 -0.38429
125 -> 128 -0.15933
125 -> 129 0.23911
125 -> 132 0.18864
125 -> 133 0.12070

Excited State 11: Singlet-A 4.0817 eV 303.76 nm f=0.0115
<S**2>=0.000
119 -> 126 0.36773
121 -> 126 0.10567
125 -> 132 0.57334

Excited State 12: Singlet-A 4.1419 eV 299.34 nm f=0.0127
<S**2>=0.000
119 -> 126 -0.16508
120 -> 126 -0.34713
123 -> 127 0.11326
125 -> 129 0.14867
125 -> 132 0.11041
125 -> 133 0.53124

Excited State 13: Singlet-A 4.1902 eV 295.89 nm f=0.0076
<S**2>=0.000
118 -> 126 0.61968
124 -> 127 0.30739

Excited State 14: Singlet-A 4.2036 eV 294.95 nm f=0.0709
<S**2>=0.000
119 -> 126 0.39362
120 -> 126 0.26107
121 -> 126 0.11785
123 -> 127 0.13271
124 -> 128 -0.10314
125 -> 132 -0.28566
125 -> 133 0.36455

Excited State 15: Singlet-A 4.2818 eV 289.56 nm f=0.2016
<S**2>=0.000
119 -> 126 0.39103
120 -> 126 -0.31714
121 -> 126 -0.28691
123 -> 127 -0.18399
125 -> 128 -0.14749
125 -> 129 0.21767
125 -> 132 -0.13193
125 -> 133 -0.11331

Excited State 16: Singlet-A 4.2863 eV 289.25 nm f=0.4629
<S**2>=0.000
118 -> 126 -0.30512
124 -> 127 0.61642

Table S9. Molecular geometries, excitations, and thermodynamic parameters of the optimized structure of saddle-**Ant7** in a local minimum state (S_0) calculated at the B3LYP/6-31G(d) level of theory. Frequency vibrational and TD-DFT calculations were performed at B3LYP/6-311G(2d,p).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.427136	1.575426	-0.609662
2	6	0	-0.703858	2.539796	-1.286883
3	6	0	0.703858	2.539796	-1.286883
4	6	0	1.427136	1.575426	-0.609662
5	6	0	-2.784073	1.935212	-0.110050
6	6	0	2.784073	1.935212	-0.110049
7	6	0	-3.884142	1.052927	-0.028449
8	6	0	-5.091531	1.514201	0.527494
9	6	0	-5.239949	2.818622	0.984208
10	6	0	-4.161036	3.698087	0.896309
11	6	0	-2.955316	3.251614	0.366901
12	6	0	2.955317	3.251613	0.366903
13	6	0	4.161036	3.698086	0.896311
14	6	0	5.239949	2.818621	0.984210
15	6	0	5.091531	1.514200	0.527494
16	6	0	3.884142	1.052926	-0.028448
17	6	0	-0.732351	0.393060	-0.156728
18	6	0	0.732351	0.393060	-0.156728
19	6	0	1.420663	-0.777114	0.248571
20	6	0	0.719161	-1.722891	1.046380
21	6	0	-0.719161	-1.722891	1.046380
22	6	0	-1.420663	-0.777114	0.248571
23	6	0	2.717433	-1.172990	-0.368361
24	6	0	-2.717433	-1.172990	-0.368361
25	6	0	-3.831451	-0.324107	-0.561920
26	6	0	-4.952585	-0.812591	-1.258652
27	6	0	-5.003328	-2.108245	-1.757895
28	6	0	-3.909072	-2.952671	-1.568324
29	6	0	-2.790069	-2.483564	-0.891284
30	6	0	2.790069	-2.483564	-0.891286
31	6	0	3.909072	-2.952670	-1.568326
32	6	0	5.003328	-2.108244	-1.757897
33	6	0	4.952585	-0.812590	-1.258653
34	6	0	3.831451	-0.324107	-0.561920
35	6	0	1.398752	-2.702287	1.834365
36	6	0	0.709418	-3.606361	2.603093
37	6	0	-0.709418	-3.606361	2.603093
38	6	0	-1.398752	-2.702287	1.834366
39	1	0	-1.222926	3.397489	-1.704581
40	1	0	1.222927	3.397489	-1.704581
41	1	0	-5.921762	0.819996	0.615773
42	1	0	-6.182995	3.139327	1.418379
43	1	0	-4.247339	4.718246	1.260432
44	1	0	-2.104773	3.925057	0.347486
45	1	0	2.104774	3.925057	0.347488
46	1	0	4.247340	4.718245	1.260435
47	1	0	6.182995	3.139325	1.418380
48	1	0	5.921762	0.819995	0.615773
49	1	0	-5.789663	-0.142341	-1.428562
50	1	0	-5.880245	-2.448805	-2.301631
51	1	0	-3.916098	-3.965425	-1.962106
52	1	0	-1.931783	-3.136072	-0.775682
53	1	0	1.931783	-3.136072	-0.775684
54	1	0	3.916097	-3.965424	-1.962110
55	1	0	5.880244	-2.448803	-2.301634
56	1	0	5.789662	-0.142340	-1.428563
57	1	0	2.483526	-2.690915	1.849501
58	1	0	1.250379	-4.313302	3.226309
59	1	0	-1.250379	-4.313302	3.226309
60	1	0	-2.483526	-2.690915	1.849501

SCF Done: E(RB3LYP) = -1461.31461057 A.U. after 1 cycles

imaginary vibration = 0
Zero-point correction= 0.470896 (Hartree/Particle)
Thermal correction to Energy= 0.495913
Thermal correction to Enthalpy= 0.496858
Thermal correction to Gibbs Free Energy= 0.419002
Sum of electronic and zero-point Energies= -1461.204502
Sum of electronic and thermal Energies= -1461.179485
Sum of electronic and thermal Enthalpies= -1461.178541
Sum of electronic and thermal Free Energies= -1461.256396

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	-2.1135	-0.0000	0.0000	4.4668	0.2679
2	-0.1354	0.0000	0.0000	0.0183	0.0013
3	-0.2076	-0.0000	-0.0000	0.0431	0.0035
4	-0.0000	-0.1935	0.1084	0.0492	0.0041
5	0.0000	-0.1956	-0.0180	0.0386	0.0033
6	0.0000	0.5276	-0.0368	0.2797	0.0243
7	0.1240	-0.0000	-0.0000	0.0154	0.0014
8	0.0793	0.0000	-0.0000	0.0063	0.0006
9	-0.3415	0.0000	0.0000	0.1166	0.0110
10	0.0000	-0.7006	0.4138	0.6621	0.0642
11	-0.0000	0.4231	-0.1255	0.1947	0.0194
12	0.0000	0.3740	0.1699	0.1687	0.0171
13	0.0000	0.3626	-0.3713	0.2694	0.0278
14	1.2121	-0.0000	0.0000	1.4692	0.1517
15	-1.9194	0.0000	-0.0000	3.6839	0.3898
16	0.0000	0.4989	-1.0808	1.4169	0.1513

Ground to excited state transition velocity dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	0.1922	0.0000	-0.0000	0.0369	0.2737
2	0.0154	0.0000	-0.0000	0.0002	0.0015
3	0.0254	-0.0000	0.0000	0.0006	0.0035
4	0.0000	0.0255	-0.0120	0.0008	0.0043
5	0.0000	0.0249	0.0033	0.0006	0.0032
6	-0.0000	-0.0692	0.0042	0.0048	0.0246
7	-0.0179	0.0000	0.0000	0.0003	0.0016
8	-0.0119	-0.0000	-0.0000	0.0001	0.0007
9	0.0473	-0.0000	-0.0000	0.0022	0.0105
10	0.0000	0.1020	-0.0621	0.0143	0.0653
11	0.0000	-0.0638	0.0192	0.0044	0.0198
12	-0.0000	-0.0575	-0.0274	0.0041	0.0178
13	-0.0000	-0.0561	0.0569	0.0064	0.0275
14	-0.1902	0.0000	-0.0000	0.0362	0.1557
15	0.3032	-0.0000	0.0000	0.0919	0.3860
16	-0.0000	-0.0790	0.1752	0.0369	0.1537

Ground to excited state transition magnetic dipole moments (Au):

state	X	Y	Z
1	0.0000	0.1214	0.1748
2	-0.0000	0.2308	2.0844
3	-0.0000	-0.4927	-0.8553
4	0.1170	0.0000	0.0000
5	-0.0583	0.0000	-0.0000
6	-0.2362	0.0000	0.0000
7	0.0000	-0.2505	0.5796
8	-0.0000	-0.0955	-0.5699
9	-0.0000	-0.5106	-0.5075
10	-0.1333	0.0000	0.0000
11	0.0387	-0.0000	0.0000
12	-0.0890	0.0000	-0.0000
13	-0.0479	0.0000	0.0000
14	-0.0000	0.0877	1.5445
15	-0.0000	-0.0156	-1.0718
16	0.0837	-0.0000	0.0000

Ground to excited state transition velocity quadrupole moments (Au):

state	XX	YY	ZZ	XY	XZ	YZ
1	0.0000	0.0000	-0.0000	-0.0289	-0.1675	0.0000
2	0.0000	0.0000	0.0000	-0.2130	-0.1389	0.0000
3	0.0000	-0.0000	-0.0000	0.6551	0.2340	-0.0000
4	0.2085	0.0201	-0.0168	-0.0000	-0.0000	0.0803
5	-0.4995	0.1186	0.0228	-0.0000	-0.0000	-0.1255
6	-0.5801	0.0914	0.0981	0.0000	0.0000	-0.1611
7	-0.0000	-0.0000	-0.0000	0.6864	0.3450	-0.0000
8	-0.0000	-0.0000	-0.0000	0.1150	0.0994	-0.0000
9	-0.0000	-0.0000	0.0000	0.3644	-0.0727	0.0000
10	0.4798	-0.1009	-0.1557	-0.0000	0.0000	0.3557
11	0.3081	0.0743	0.0699	-0.0000	0.0000	0.0511
12	0.1028	0.0302	0.0629	-0.0000	-0.0000	0.0969
13	-1.1600	0.0111	0.2054	-0.0000	0.0000	-0.7218
14	0.0000	-0.0000	-0.0000	-0.1169	0.0011	0.0000
15	-0.0000	0.0000	0.0000	-0.0817	-0.5137	-0.0000

```
16         -0.5789      0.5438      0.2633     -0.0000      0.0000     -
0.6014
<0|del|b> * <b|rxdel|0> + <0|del|b> * <b|delr+rdel|0>
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)
state          XX          YY          ZZ    R(velocity)    E-M Angle
1         0.0002      0.0020     -0.0008      0.0005      90.00
2        -0.0012     -0.0015     -0.0001     -0.0009      90.00
3         0.0003     -0.0011      0.0002     -0.0002      90.00
4         0.0002     -0.0001      0.0000      0.0000      90.00
5         0.0002     -0.0000     -0.0001      0.0000      90.00
6         0.0000      0.0002     -0.0001      0.0000      90.00
7        -0.0004     -0.0001     -0.0000     -0.0002      90.00
8         0.0001      0.0002     -0.0000      0.0001      90.00
9         0.0003      0.0003      0.0001      0.0003      90.00
10       -0.0011     -0.0004      0.0007     -0.0003      90.00
11        0.0003      0.0002     -0.0000      0.0002      90.00
12       -0.0002     -0.0001     -0.0000     -0.0001      90.00
13        0.0011      0.0040     -0.0024      0.0009      90.00
14       -0.0005     -0.0011      0.0017      0.0000      90.00
15       -0.0013     -0.0031      0.0010     -0.0011      90.00
16       -0.0002      0.0012     -0.0010      0.0000      90.00
1/2[<0|r|b>*<b|rxdel|0> + (<0|rxdel|b>*<b|r|0>)*]
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)
state          XX          YY          ZZ     R(length)
1         0.0013      0.0000     -0.0002      0.0004
2        -0.0001     -0.0000     -0.0011     -0.0004
3        -0.0001     -0.0000     -0.0005     -0.0002
4         0.0001      0.0001     -0.0001      0.0000
5         0.0000      0.0002     -0.0000      0.0001
6         0.0000     -0.0002      0.0001     -0.0000
7        -0.0002     -0.0006      0.0003     -0.0002
8         0.0001      0.0001     -0.0001      0.0000
9        -0.0002      0.0002      0.0001      0.0001
10        0.0000      0.0001     -0.0009     -0.0002
11        0.0000      0.0002      0.0003      0.0002
12        0.0001     -0.0006      0.0002     -0.0001
13        0.0003     -0.0002      0.0026      0.0009
14        0.0011      0.0001     -0.0015     -0.0001
15       -0.0017      0.0000     -0.0024     -0.0014
16       -0.0003      0.0003      0.0000      0.0000
1/2[<0|del|b>*<b|r|0> + (<0|r|b>*<b|del|0>)*] (Au)
state          X           Y           Z       Dip. S.   Osc.(frdel)
1        -0.4061     -0.0000     -0.0000      0.4061      0.2708
2        -0.0021      0.0000     -0.0000      0.0021      0.0014
3        -0.0053      0.0000     -0.0000      0.0053      0.0035
4        -0.0000     -0.0049     -0.0013      0.0062      0.0042
5         0.0000     -0.0049     -0.0001      0.0049      0.0033
6        -0.0000     -0.0365     -0.0002      0.0366      0.0244
7        -0.0022     -0.0000     -0.0000      0.0022      0.0015
8        -0.0009     -0.0000      0.0000      0.0009      0.0006
9        -0.0161     -0.0000     -0.0000      0.0161      0.0108
10        0.0000     -0.0714     -0.0257      0.0971      0.0648
11       -0.0000     -0.0270     -0.0024      0.0294      0.0196
12       -0.0000     -0.0215     -0.0047      0.0262      0.0175
13       -0.0000     -0.0203     -0.0211      0.0415      0.0276
14       -0.2306     -0.0000     -0.0000      0.2306      0.1537
15       -0.5819     -0.0000     -0.0000      0.5819      0.3879
16       -0.0000     -0.0394     -0.1893      0.2287      0.1525

Excitation energies and oscillator strengths:

Excited State   1:       Singlet-A       2.4478 eV  506.51 nm  f=0.2679
<S**2>=0.000
125 -> 126       0.70284
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) =  -1461.58544284
Copying the excited state density for this state as the 1-particle RhoCI
density.

Excited State   2:       Singlet-A       2.9627 eV  418.49 nm  f=0.0013
<S**2>=0.000
125 -> 127       0.70116

Excited State   3:       Singlet-A       3.3227 eV  373.15 nm  f=0.0035
<S**2>=0.000
124 -> 126       0.68843
125 -> 129      -0.11439

Excited State   4:       Singlet-A       3.3766 eV  367.19 nm  f=0.0041
<S**2>=0.000
121 -> 126       0.30801

Excited State   5:       Singlet-A       3.5302 eV  351.21 nm  f=0.0033
<S**2>=0.000
121 -> 126      -0.32737
123 -> 126       0.51506
125 -> 128       0.14834
125 -> 130       0.29591

Excited State   6:       Singlet-A       3.5440 eV  349.84 nm  f=0.0243
<S**2>=0.000
121 -> 126       0.29654
123 -> 126       0.46810
125 -> 128      -0.26336
125 -> 130      -0.32085
125 -> 133      -0.11213

Excited State   7:       Singlet-A       3.6398 eV  340.63 nm  f=0.0014
<S**2>=0.000
124 -> 126       0.10051
125 -> 129       0.67559
125 -> 131      -0.14053

Excited State   8:       Singlet-A       3.6553 eV  339.19 nm  f=0.0006
<S**2>=0.000
122 -> 126       0.70095

Excited State   9:       Singlet-A       3.8410 eV  322.79 nm  f=0.0110
<S**2>=0.000
125 -> 129       0.13515
125 -> 131       0.67900

Excited State  10:       Singlet-A       3.9568 eV  313.34 nm  f=0.0642
<S**2>=0.000
119 -> 126       0.17056
120 -> 126       0.31765
121 -> 126      -0.26388
125 -> 130      -0.35543
125 -> 132       0.36063
125 -> 133       0.16415

Excited State  11:       Singlet-A       4.0767 eV  304.13 nm  f=0.0194
<S**2>=0.000
119 -> 126      -0.35416
121 -> 126       0.16185
125 -> 130       0.16622
125 -> 132       0.53167
125 -> 133      -0.12974

Excited State  12:       Singlet-A       4.1320 eV  300.06 nm  f=0.0171
<S**2>=0.000
119 -> 126      -0.19970
120 -> 126      -0.18356
123 -> 127      -0.22147
125 -> 130      -0.11496
125 -> 133       0.58295

Excited State  13:       Singlet-A       4.2080 eV  294.64 nm  f=0.0278
<S**2>=0.000
119 -> 126      -0.32830
120 -> 126       0.54823
124 -> 128      -0.10100
125 -> 132      -0.22980

Excited State  14:       Singlet-A       4.2152 eV  294.14 nm  f=0.1517
<S**2>=0.000
118 -> 126       0.41504
124 -> 127       0.55177

Excited State  15:       Singlet-A       4.3194 eV  287.04 nm  f=0.3898
<S**2>=0.000
118 -> 126       0.54766
124 -> 127      -0.41545

Excited State  16:       Singlet-A       4.3588 eV  284.44 nm  f=0.1513
<S**2>=0.000
119 -> 126       0.41166
120 -> 126       0.18590
121 -> 126       0.18824
123 -> 127      -0.38011
```

Table S10. Molecular geometries and thermodynamic parameters of the optimized structure of Intermediate-**Ant7** in a local minimum calculated at the B3LYP/6-31G(d) level of theory. Frequency vibrational calculation was performed at B3LYP/6-311G(2d,p).

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.41149600	0.71970200	-0.43741400
C	-0.74806700	-0.37853900	0.16319200
C	0.71141100	-0.39553200	0.16347300
C	1.41278800	0.84522400	0.01391000
C	0.59799900	2.03646800	0.08041600
C	-0.77353600	1.97430800	-0.35845400
C	-1.50250800	-1.43534700	0.79272100
C	-0.82370100	-2.56669300	1.18764700
C	0.54325300	-2.71090700	0.91380300
C	1.31948900	-1.69769600	0.37061400
C	2.88657900	1.04308500	-0.04914900
C	3.91013400	0.12336800	0.35134300
C	5.15069900	0.66083800	0.75321400
C	5.51616100	1.97938500	0.51167000
C	4.64523300	2.77412200	-0.23108100
C	3.36351100	2.30425800	-0.49077400
C	2.68677000	-2.10887500	-0.03654600
C	2.79552500	-3.41587100	-0.56451900
C	4.01125200	-3.99678900	-0.89677000
C	5.17770500	-3.25362300	-0.73525200
C	5.08680700	-1.94292300	-0.28799400
C	3.86225100	-1.33489300	0.07587800
C	-2.88807700	-1.22414600	1.30233800
C	-3.94527700	-0.64876200	0.56247900
C	-5.20771900	-0.51069500	1.16735700
C	-5.44778300	-0.92903400	2.47125400
C	-4.40632700	-1.49218700	3.20826000
C	-3.14972900	-1.62627500	2.62762000
C	-2.63556100	0.51609500	-1.25382000
C	-2.59120300	0.99824500	-2.57804100
C	-3.63211800	0.77919700	-3.47395600
C	-4.75203300	0.05414500	-3.06474700
C	-4.81636300	-0.42250900	-1.75981200
C	-3.77965800	-0.19856700	-0.83667300
C	1.03902300	3.29876400	0.59181900
C	0.27265000	4.43448200	0.49894100
C	-0.99783900	4.39362500	-0.12939300
C	-1.50903400	3.19008000	-0.53719200
H	-1.34733600	-3.36291700	1.70712700
H	1.02012500	-3.64969900	1.17097400
H	5.86894400	-0.00236900	1.22332100
H	6.48739800	2.34755800	0.82982600
H	4.93935100	3.76114900	-0.57682900
H	2.68620000	2.94758700	-1.03646900
H	1.88567300	-3.97806800	-0.74022300
H	4.03990100	-5.00395500	-1.30323400
H	6.14586300	-3.66660100	-1.00481500
H	5.99171700	-1.34879400	-0.27446600
H	-6.00688900	-0.04166500	0.60124300
H	-6.43203000	-0.79818000	2.91259700
H	-4.56313200	-1.80694600	4.23641800
H	-2.33400000	-2.02808400	3.21994200
H	-1.70718000	1.53715600	-2.90445700
H	-3.55908800	1.15718700	-4.49008000
H	-5.56535800	-0.14504200	-3.75714700
H	-5.68061000	-0.99850900	-1.44249800
H	1.99288000	3.35170700	1.10094800
H	0.63492500	5.36410000	0.92940500
H	-1.58967700	5.29996700	-0.22362300
H	-2.52301800	3.12731700	-0.91623900

SCF Done: E(RB3LYP) = -1461.28153066 A.U. after 16 cycles

imaginary vibration = 0

Zero-point correction=	0.471000 (Hartree/Particle)
Thermal correction to Energy=	0.495958
Thermal correction to Enthalpy=	0.496902
Thermal correction to Gibbs Free Energy=	0.419045
Sum of electronic and zero-point Energies=	-1461.172071
Sum of electronic and thermal Energies=	-1461.147113
Sum of electronic and thermal Enthalpies=	-1461.146169
Sum of electronic and thermal Free Energies=	-1461.224027

Table S11. Molecular geometries and thermodynamic parameters of the optimized structure of TS1-**Naph7** in a transition state calculated at the B3LYP/6-31G(d) level of theory. Frequency vibrational calculation was performed at B3LYP/6-311G(2d,p).

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.49415900	-1.25110100	-0.13371200
C	-0.79265700	-0.00470100	-0.02825000
C	0.66418000	0.03212300	-0.08886000
C	1.34712500	-1.13517100	-0.58491800
C	0.58034200	-2.27418000	-0.83865100
C	-0.78792600	-2.34921900	-0.58656500
C	-1.52640400	1.21309400	0.17811100
C	-0.85382200	2.26673400	0.76173600
C	0.52916100	2.21483700	0.95432700
C	1.33076400	1.21683900	0.39664300
C	2.81441200	-1.34670000	-0.76868700
C	3.86143600	-0.81511600	0.03915700
C	5.06324800	-1.56050800	0.07788300
C	5.33718500	-2.61832200	-0.77707600
C	4.41154100	-2.93797400	-1.76778600
C	3.17326300	-2.31461200	-1.73725400
C	2.79560800	1.50691600	0.44461900
C	3.13102600	2.88346000	0.45758500
C	4.37800800	3.36655700	0.82306500
C	5.35822000	2.45160600	1.19435200
C	5.10211300	1.09712200	1.03853000
C	3.86600300	0.57556500	0.59043400
C	-2.85945900	1.46038800	-0.43829800
C	-3.96120300	0.57844900	-0.40558800
C	-5.12716600	0.91699700	-1.11575500
C	-5.23548800	2.10678300	-1.82711800
C	-4.15898900	2.99319200	-1.84171400
C	-2.99038800	2.66194900	-1.16387900
C	-2.82056600	-1.49283900	0.50739100
C	-2.92522500	-2.65258300	1.30364900
C	-4.09704900	-2.99436600	1.96959200
C	-5.21042100	-2.16086700	1.87126400
C	-5.12535700	-1.00474200	1.10460300
C	-3.95196700	-0.65286500	0.41194400
H	1.07556200	-3.18990300	-1.13230100
H	-1.28766700	-3.30711700	-0.69199200
H	-1.39512000	3.16588500	1.04253500
H	0.99140600	3.02585900	1.50129000
H	5.83939500	-1.28807200	0.77993300
H	6.28718500	-3.14020200	-0.70423700
H	4.63389000	-3.67737800	-2.53189100
H	2.43694400	-2.59110300	-2.48307300
H	2.37244600	3.59891000	0.16534800
H	4.57326300	4.43516800	0.82002800
H	6.33637500	2.78008900	1.53441200
H	5.93054100	0.42856100	1.22286000
H	-5.95775100	0.21766400	-1.11679300
H	-6.14727900	2.33300600	-2.37314600
H	-4.21675900	3.92534600	-2.39715100
H	-2.13710500	3.33066300	-1.21751600
H	-2.04957900	-3.28191700	1.42329700
H	-4.12973100	-3.89330200	2.57917700
H	-6.12927300	-2.39657700	2.40118000
H	-5.97907200	-0.33603600	1.05339900

SCF Done: E(RB3LYP) = -1307.65723452 A.U. after 15 cycles

imaginary vibration = 1

Zero-point correction=	0.425051 (Hartree/Particle)

Thermal correction to Energy=	0.446541
Thermal correction to Enthalpy=	0.447485
Thermal correction to Gibbs Free Energy=	0.377134
Sum of electronic and zero-point Energies=	-1307.557003
Sum of electronic and thermal Energies=	-1307.535513
Sum of electronic and thermal Enthalpies=	-1307.534569
Sum of electronic and thermal Free Energies=	-1307.604919

Table S12. Molecular geometries and thermodynamic parameters of the optimized structure of TS1-**Ant7** in a transition state calculated at the B3LYP/6-31G(d) level of theory. Frequency vibrational calculations were performed at B3LYP-6-31G(d) and B3LYP/6-311G(2d,p).

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.47040700	0.76962700	-0.18303100
C	-0.76263600	-0.44664300	-0.01249400
C	0.70159200	-0.42397500	-0.02538800
C	1.35723200	0.82468700	0.16832800
C	0.54453000	1.92317900	0.61914400
C	-0.85575900	1.94829000	0.28767700
C	-1.47928100	-1.67736700	0.20664200
C	-0.76118500	-2.85190900	0.17732800
C	0.61856800	-2.85211700	-0.05859200
C	1.37829700	-1.69503800	-0.19296700
C	2.80657400	1.12386700	0.01600700
C	3.91239000	0.27017300	0.31949100
C	5.12864700	0.91346100	0.64266900
C	5.36234000	2.26392400	0.41837300
C	4.37173800	3.02156500	-0.20159400
C	3.11777400	2.45073500	-0.36939600
C	2.82644500	-1.94296000	-0.45108300
C	3.10068400	-3.12275400	-1.18601600
C	4.36431400	-3.68153500	-1.29307600
C	5.42582600	-3.04837800	-0.65293100
C	5.20642000	-1.82016700	-0.04779400
C	3.93901900	-1.19435800	0.02687800
C	-2.85932400	-1.70941900	0.77258900
C	-3.94962800	-0.94551700	0.30083600
C	-5.20029100	-1.07399900	0.93176400
C	-5.39689000	-1.93574100	2.00473500
C	-4.32262500	-2.68773500	2.47952100
C	-3.07759200	-2.56407500	1.87232500
C	-2.71122600	0.82556500	-1.00057100
C	-2.71076600	1.74345200	-2.07154300
C	-3.76702400	1.82319800	-2.97245200
C	-4.86030100	0.96776100	-2.82988000
C	-4.88192900	0.06041700	-1.77645500
C	-3.82868500	-0.02385200	-0.84848400
C	1.04629800	3.01766900	1.39483100
C	0.26731100	4.10257800	1.70907000
C	-1.07194300	4.18236200	1.24648400
C	-1.61546600	3.13230900	0.55501700
H	-1.25836900	-3.79675900	0.37298200
H	1.12007600	-3.81115200	-0.05039700
H	5.94710600	0.33230400	1.04643600
H	6.32794000	2.69435500	0.66883400
H	4.55139400	4.04821100	-0.50738200
H	2.32125600	3.06041900	-0.77805700
H	2.27945800	-3.60982300	-1.69760000
H	4.51320300	-4.59011400	-1.86969700
H	6.42893500	-3.46473300	-0.68027700
H	6.08014400	-1.30529600	0.32472400
H	-6.02532500	-0.46178700	0.58013000
H	-6.37317900	-2.00363500	2.47689200
H	-4.44528000	-3.35183600	3.33081300
H	-2.23713900	-3.12123800	2.27323200
H	-1.84812900	2.38946400	-2.20028600
H	-3.72621700	2.53672500	-3.79098600
H	-5.68509000	1.00100300	-3.53644700
H	-5.72418700	-0.61694200	-1.67080500
H	2.06103900	2.96978600	1.76969000
H	0.67438300	4.89707800	2.32856800
H	-1.67890400	5.05153300	1.48516300
H	-2.66134300	3.14877800	0.26870200

SCF Done: E(RB3LYP) = -1461.28055811 A.U. after 16 cycles

B3LYP/6-311G(2d,p)
imaginary vibration = 0

Zero-point correction=	0.470935 (Hartree/Particle)
Thermal correction to Energy=	0.496017
Thermal correction to Enthalpy=	0.496962
Thermal correction to Gibbs Free Energy=	0.418316
Sum of electronic and zero-point Energies=	-1461.171443
Sum of electronic and thermal Energies=	-1461.146360
Sum of electronic and thermal Enthalpies=	-1461.145416
Sum of electronic and thermal Free Energies=	-1461.224062

B3LYP/6-31G(d)
imaginary vibration = 1

Zero-point correction=	0.475570 (Hartree/Particle)
Thermal correction to Energy=	0.500165
Thermal correction to Enthalpy=	0.501109
Thermal correction to Gibbs Free Energy=	0.423588
Sum of electronic and zero-point Energies=	-1460.804988
Sum of electronic and thermal Energies=	-1460.780393
Sum of electronic and thermal Enthalpies=	-1460.779449
Sum of electronic and thermal Free Energies=	-1460.856970

Table S13. Molecular geometries and thermodynamic parameters of the optimized structure of TS2-**Ant7** in a transition state calculated at the B3LYP/6-31G(d) level of theory. Frequency vibrational calculation was performed at B3LYP/6-31G(d).

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.32493400	0.64490600	-0.52167700
C	-0.68114100	-0.31590300	0.27950000
C	0.76492900	-0.27230600	0.33658400
C	1.44837000	0.98428000	0.22962000
C	0.57892100	2.13056700	0.00895500
C	-0.69950300	1.90840800	-0.64006000
C	-1.41248700	-1.32692000	1.01924100
C	-0.71691600	-2.41008200	1.50125100
C	0.62952200	-2.59487000	1.11778900
C	1.35466200	-1.60169800	0.49482600
C	2.93219600	1.11217100	0.48364200
C	3.87976800	0.03824200	0.41531700
C	5.16823100	0.19705000	0.96263400
C	5.63802900	1.40505900	1.45582700
C	4.81278100	2.51290900	1.31012500
C	3.51769000	2.35578800	0.82918300
C	2.55265900	-2.00530100	-0.26688000
C	2.49743100	-3.21227400	-0.99245800
C	3.55837900	-3.63466100	-1.78575900
C	4.69563300	-2.83354200	-1.89269000
C	4.75650400	-1.63581100	-1.18826800
C	3.70181900	-1.21194500	-0.35654600
C	-2.79791300	-1.06302800	1.49409000
C	-3.84389600	-0.57848300	0.67554500
C	-5.10627000	-0.34683500	1.24948000
C	-5.35699200	-0.59205500	2.59545800
C	-4.32948500	-1.07761800	3.40412900
C	-3.07055400	-1.29918100	2.85525100
C	-2.52312600	0.26531700	-1.31540900
C	-2.45217300	0.46210200	-2.70891900
C	-3.48179400	0.07024700	-3.55795800
C	-4.61570800	-0.54514100	-3.02652200
C	-4.69833000	-0.75457900	-1.65413900
C	-3.67057700	-0.35959700	-0.77905600
C	0.79952200	3.49343000	0.39547400
C	0.03923800	4.53984200	-0.07338700
C	-1.04353000	4.30937900	-0.94966400
C	-1.42426000	3.01454900	-1.18582200

H	-1.21791500	-3.15984300	2.10565600
H	1.09856700	-3.56123200	1.27698500
H	5.81967300	-0.67105800	0.97149600
H	6.63315300	1.48410500	1.88403000
H	5.15858200	3.50862400	1.57480900
H	2.96843100	3.26315700	0.69068800
H	1.58879900	-3.80427400	-0.95389500
H	3.48386500	-4.56691400	-2.33906400
H	5.52248300	-3.12895600	-2.53284000
H	5.62958900	-0.99928600	-1.29087900
H	-5.89817400	0.05103600	0.62168800
H	-6.34100900	-0.39224700	3.01065100
H	-4.49881900	-1.26285400	4.46137900
H	-2.26195800	-1.63715400	3.49588900
H	-1.55804400	0.91648300	-3.12470100
H	-3.38952600	0.23004100	-4.62874200
H	-5.42300700	-0.87238800	-3.67591500
H	-5.56773800	-1.25737600	-1.24110700
H	1.51160100	3.72823400	1.16794400
H	0.25284300	5.54711600	0.27417700
H	-1.62492200	5.13797600	-1.34368900
H	-2.34665200	2.81232700	-1.71681300

SCF Done: E(RB3LYP) = -1461.27556576 A.U. after 16 cycles

imaginary vibration = 1

Zero-point correction=	0.470626 (Hartree/Particle)
Thermal correction to Energy=	0.494971
Thermal correction to Enthalpy=	0.495915
Thermal correction to Gibbs Free Energy=	0.419832
Sum of electronic and zero-point Energies=	-1461.167559
Sum of electronic and thermal Energies=	-1461.143214
Sum of electronic and thermal Enthalpies=	-1461.142270
Sum of electronic and thermal Free Energies=	-1461.218353

Table S14. Molecular geometries of twisted-**Naph7-H** generated by substituting the diphenylene moieties of the energy-minimized structure of twisted-**Naph7**, calculated at the B3LYP/6-31G(d) level, with hydrogen atoms. Single point calculation was performed at B3LYP/6-311G(2d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.386898	0.273675	-1.236925
2	6	0	0.676364	0.188372	-2.416004
3	6	0	-0.676328	-0.188158	-2.416025
4	6	0	-1.386877	-0.273545	-1.236963
5	6	0	0.717147	0.000047	0.000006
6	6	0	-0.717148	0.000047	-0.000006
7	6	0	-1.386898	0.273660	1.236929
8	6	0	-0.676363	0.188343	2.416006
9	6	0	0.676328	-0.188186	2.416023
10	6	0	1.399413	-0.279789	1.237156
11	1	0	1.170574	0.386829	-3.362043
12	1	0	-1.170522	-0.386557	-3.362084
13	1	0	-1.170573	0.386788	3.362048
14	1	0	1.170523	-0.386597	3.362079
15	1	0	2.357557	0.756007	-1.252176
16	1	0	2.370048	-0.762169	1.252427
17	1	0	-2.357557	0.755992	1.252187
18	1	0	-2.357512	-0.755924	-1.252240

Table S15. Molecular geometries of saddle-**Naph7-H** generated by substituting the diphenylene moieties of the energy-minimized structure of saddle-**Naph7**, calculated at the B3LYP/6-31G(d) level, with hydrogen atoms. Single point calculation was performed at B3LYP/6-311G(2d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.410902	-1.063538	-0.666273
2	6	0	-0.700123	-1.865541	-1.539789
3	6	0	0.700110	-1.865538	-1.539794
4	6	0	1.423513	-1.068049	-0.662218
5	6	0	-0.727551	-0.000048	0.000048
6	6	0	0.727552	-0.000048	0.000048
7	6	0	1.410901	1.063436	0.666411
8	6	0	0.700114	1.865352	1.539993
9	6	0	-0.700127	1.865355	1.539988
10	6	0	-1.410905	1.063436	0.666403
11	1	0	-1.222190	-2.604705	-2.140130
12	1	0	1.222173	-2.604696	-2.140146
13	1	0	1.222167	2.604480	2.140392
14	1	0	-1.222184	2.604488	2.140376
15	1	0	2.387677	1.412695	0.351795
16	1	0	2.400324	-1.417253	-0.347650
17	1	0	-2.387709	-1.412740	-0.351690
18	1	0	-2.387677	1.412693	0.351773

Table S16. Molecular geometries of twisted-**Ant7-H** generated by substituting the diphenylene moieties of the energy-minimized structure of twisted-**Ant7**, calculated at the B3LYP/6-31G(d) level, with hydrogen atoms. Single point calculation was performed at B3LYP/6-311G(2d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.414387	1.572046	-0.614356
2	6	0	-0.703858	2.539796	-1.286883
3	6	0	0.703858	2.539796	-1.286883
4	6	0	1.414387	1.572046	-0.614356
5	6	0	-0.732351	0.393060	-0.156728
6	6	0	0.732351	0.393060	-0.156728
7	6	0	1.420663	-0.777114	0.248571
8	6	0	0.719161	-1.722891	1.046380
9	6	0	-0.719161	-1.722891	1.046380
10	6	0	-1.408475	-0.773393	0.254369
11	6	0	1.398752	-2.702287	1.834365
12	6	0	0.709418	-3.606361	2.603093
13	6	0	-0.709418	-3.606361	2.603093
14	6	0	-1.398752	-2.702287	1.834366
15	1	0	-1.222926	3.397489	-1.704581
16	1	0	1.222927	3.397489	-1.704581
17	1	0	2.483526	-2.690915	1.849501
18	1	0	1.250379	-4.313302	3.226309
19	1	0	-1.250379	-4.313302	3.226309
20	1	0	-2.483526	-2.690915	1.849501
21	1	0	2.401529	1.833782	-0.250899
22	1	0	2.364332	-1.065196	-0.200375
23	1	0	-2.352145	-1.061475	-0.194577
24	1	0	-2.401529	1.833782	-0.250899

Table S17. Molecular geometries of saddle-**Ant7-H** generated by substituting the diphenylene moieties of the energy-minimized structure of saddle-**Ant7**, calculated at the B3LYP/6-31G(d) level, with hydrogen atoms. Single point calculation was performed at B3LYP/6-311G(2d,p) level.

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	1.381210	-1.652524	-0.298471
2	6	0	0.674625	-2.824427	-0.212782
3	6	0	-0.674717	-2.824339	0.213620
4	6	0	-1.381268	-1.652388	0.298943
5	6	0	0.718622	-0.404115	0.009064
6	6	0	-0.718652	-0.404090	-0.008982
7	6	0	-1.402610	0.803553	-0.294231
8	6	0	-0.700213	2.033091	-0.178307
9	6	0	0.700236	2.033101	0.177794
10	6	0	1.390220	0.804135	0.287450
11	6	0	-1.363630	3.297162	-0.304950
12	6	0	-0.696064	4.481924	-0.139754
13	6	0	0.696214	4.481913	0.139016
14	6	0	1.363719	3.297139	0.304347
15	1	0	1.155064	-3.768391	-0.452085
16	1	0	-1.155184	-3.768214	0.453217
17	1	0	-2.428565	3.306309	-0.504575
18	1	0	-1.232398	5.423357	-0.222879
19	1	0	1.232585	5.423331	0.222072
20	1	0	2.428648	3.306235	0.504049
21	1	0	2.349776	0.761979	0.789976
22	1	0	2.332183	-1.648493	-0.818750
23	1	0	-2.332236	-1.648162	0.819229
24	1	0	-2.362147	0.761229	-0.796777

Table S18. Molecular geometries of twisted-**Tet7-H** generated by substituting the diphenylene moieties of the energy-minimized structure of twisted-**Tet7-H**, calculated at the B3LYP/6-31G(d) level, with hydrogen atoms. Single point calculation was performed at B3LYP/6-311G(2d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.219757	1.397089	-0.316402
2	6	0	0.000000	0.718311	-0.000021
3	6	0	-0.000001	-0.718309	-0.000022
4	6	0	1.219762	-1.397096	0.316296
5	6	0	2.440265	-0.697520	0.201288
6	6	0	2.440264	0.697515	-0.201392
7	6	0	-1.219748	1.397098	0.316358
8	6	0	-2.440260	0.697524	0.201383
9	6	0	-2.440269	-0.697510	-0.201299
10	6	0	-1.219771	-1.397089	-0.316343
11	6	0	-3.708807	1.351453	0.368929
12	6	0	-4.889675	0.690506	0.175220
13	6	0	-4.889680	-0.690513	-0.175048
14	6	0	-3.708814	-1.351449	-0.368808
15	6	0	3.708810	-1.351453	0.368825
16	6	0	4.889677	-0.690510	0.175099
17	6	0	4.889678	0.690510	-0.175166
18	6	0	3.708810	1.351450	-0.368907
19	1	0	-3.718397	2.406649	0.615275
20	1	0	-5.832572	1.219517	0.284604
21	1	0	-5.832577	-1.219528	-0.284399
22	1	0	-3.718399	-2.406643	-0.615167
23	1	0	3.718397	-2.406648	0.615182
24	1	0	5.832574	-1.219522	0.284475
25	1	0	5.832575	1.219525	-0.284522
26	1	0	3.718400	2.406647	-0.615250
27	1	0	-1.163411	-2.339347	-0.849286
28	1	0	1.163393	-2.339374	0.849204
29	1	0	1.163364	2.339343	-0.849350
30	1	0	-1.163344	2.339371	0.849270

Table S19. Molecular geometries of saddle-**Tet7-H** generated by substituting the diphenylene moieties of the energy-minimized structure of saddle-**Tet7-H**, calculated at the B3LYP/6-31G(d) level, with hydrogen atoms. Single point calculation was performed at B3LYP/6-311G(2d,p) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.218837	1.424248	0.267453
2	6	0	0.000027	0.735384	0.000128
3	6	0	0.000026	-0.735382	0.000128
4	6	0	-1.218837	-1.424247	0.267452
5	6	0	-2.438867	-0.722005	0.118956
6	6	0	-2.438867	0.722005	0.118956
7	6	0	1.218771	1.424233	-0.267313
8	6	0	2.438882	0.721970	-0.118942
9	6	0	2.438881	-0.721970	-0.118943
10	6	0	1.218771	-1.424233	-0.267312
11	6	0	3.695915	1.400095	-0.012961
12	6	0	4.872700	0.710972	0.119078
13	6	0	4.872700	-0.710974	0.119078
14	6	0	3.695913	-1.400095	-0.012961
15	6	0	-3.695918	-1.400119	0.012875
16	6	0	-4.872663	-0.710993	-0.119302
17	6	0	-4.872663	0.710992	-0.119302
18	6	0	-3.695919	1.400118	0.012875
19	1	0	3.695540	2.484691	0.008442
20	1	0	5.807634	1.250804	0.242752
21	1	0	5.807633	-1.250807	0.242751
22	1	0	3.695539	-2.484691	0.008442
23	1	0	-3.695509	-2.484729	-0.008341
24	1	0	-5.807606	-1.250796	-0.243009
25	1	0	-5.807608	1.250795	-0.243009
26	1	0	-3.695510	2.484728	-0.008341
27	1	0	1.214739	-2.379526	-0.779615
28	1	0	-1.214838	-2.379444	0.779936
29	1	0	-1.214839	2.379445	0.779936
30	1	0	1.214739	2.379527	-0.779615