Electronic Supporting Information

Electronic Properties of Diastereomeric Möbius Shaped Cyclotris[5]helicenes

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Section S1: Semi-preparative HPLC on chiral stationary phases

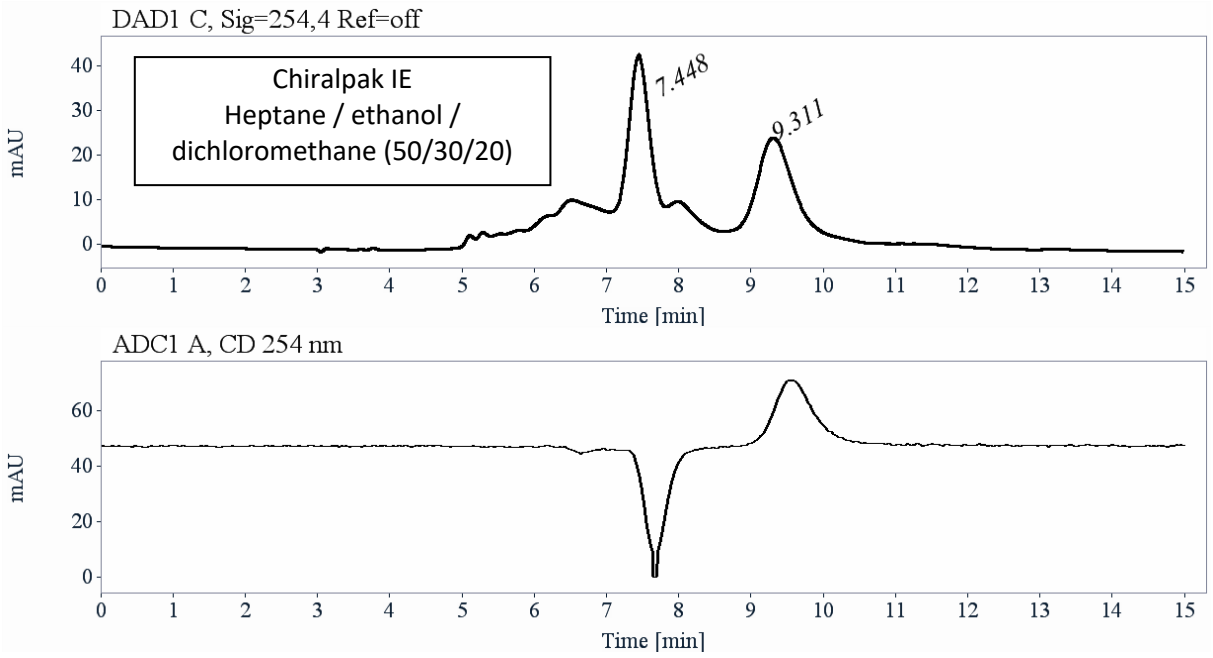
S1.1. General materials and methods

Chiral HPLC analyses were performed on an Agilent 1260 Infinity unit (pump G1311B, autosampler G1329B, DAD G1315D), with Igloo-Cil ovens, monitored by SRA Instruments Seleccol software (Version 1.2.3.0), Agilent OpenLAB CDS Chemstation LC and CE Drivers (A.02.08SP1) and Agilent OpenLAB Intelligent reporting (A.01.06.111). Chiroptical detection was performed with a Jasco CD-2095 circular dichroism detector. The analytical columns (250 x 4.6 mm) used were Chiralpak IE and Chiralpak ID. Heptane, ethanol and dichloromethane (HPLC grade) were degassed and filtered on a 0.45 mm Millipore membrane before use. Preparative chiral HPLC separation were performed on an Agilent 1260 Infinity unit (pump G1311C, autosampler G1329B, DAD G1365D and fraction collector G1364C), monitored by Agilent OpenLAB CDS Chemstation LC. The preparative columns (250 × 10 mm, 5 µm) used were Chiralpak IE and Chiralpak ID. Optical rotations were measured on a Jasco P-2000 polarimeter with a halogen lamp (589, 578 and 546 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

S1.2. Analytical chiral HPLC separation for compound D_3-3

The sample was dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak IE	heptane / ethanol / dichloromethane (50/30/20)	7.45 (-)	1.52	9.31 (+)	2.16	1.41	2.67

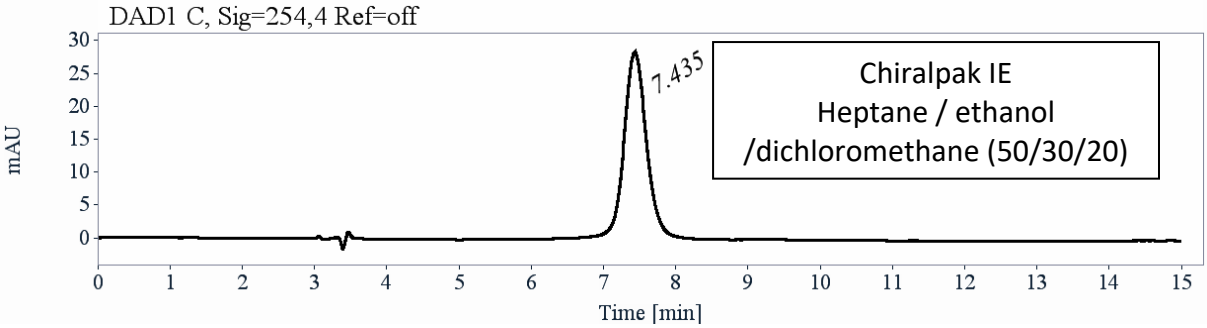


RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.45	637	45.08	1.52		
9.31	776	54.92	2.16	1.41	2.67
Sum	1413	100.00			

S1.3. Preparative chiral HPLC separation for compound D_3-3

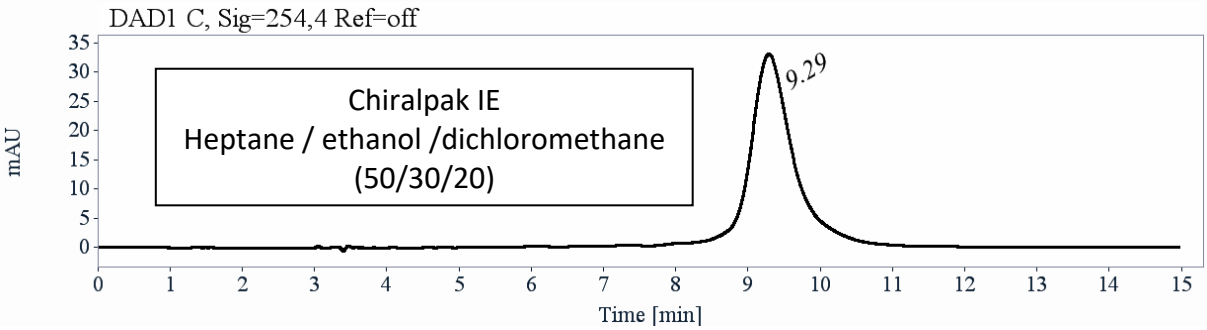
Sample preparation: 46 mg of ***D*$_3$-3** were dissolved in 1.7 mL of dichloromethane.
Chromatographic conditions: Chiralpak IE (250 × 10 mm), Heptane / ethanol / dichloromethane (50/30/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.
Injections (stacked): 85 times 20 µL, every 11.2 minutes.

First fraction: 8 mg of the first eluted enantiomer with *ee* > 99.5%



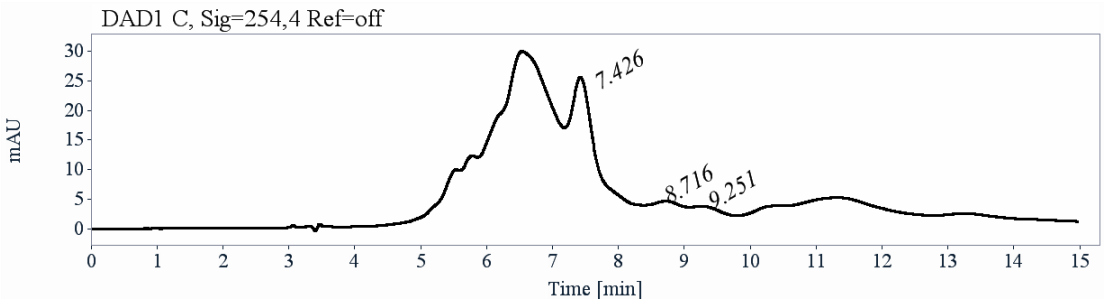
RT [min]	Area	Area%
7.44	549	100.00
Sum	549	100.00

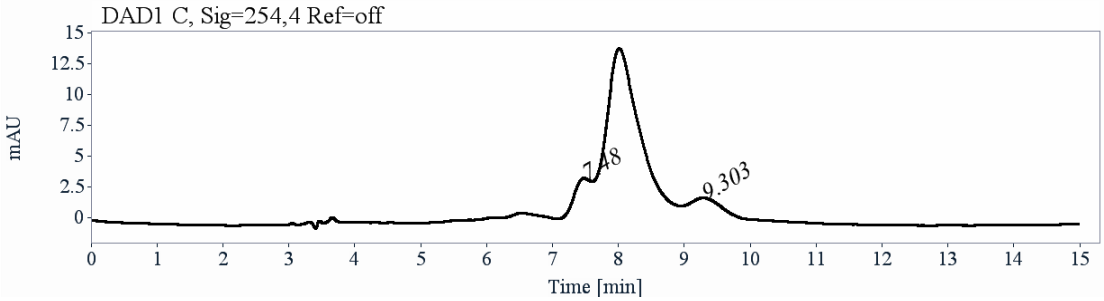
Second fraction: 11 mg of the second eluted enantiomer with *ee* > 99.5%



RT [min]	Area	Area%
9.29	1207	100.00
Sum	1207	100.00

Intermediate fractions: 22 mg (top chromatogram) and 5 mg (bottom chromatogram)

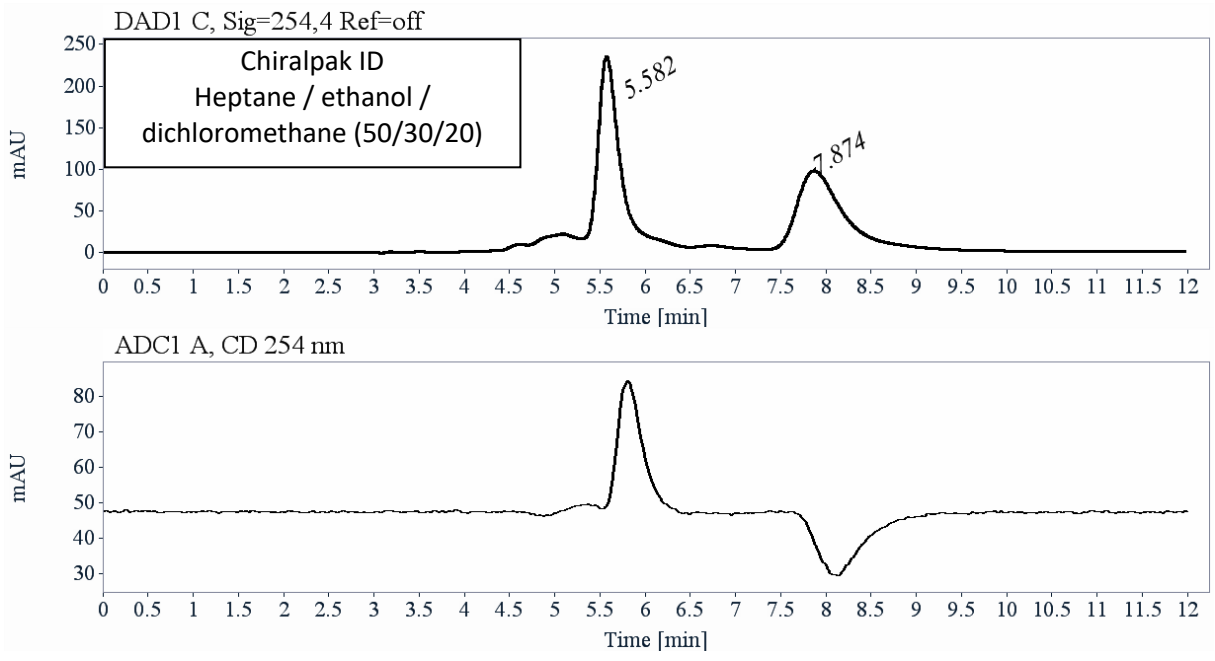




S1.4. Analytical chiral HPLC separation for compound C_2-3

The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak ID	Heptane / ethanol / dichloromethane (50/30/20)	5.58 (+)	0.89	7.87 (-)	1.67	1.87	3.63

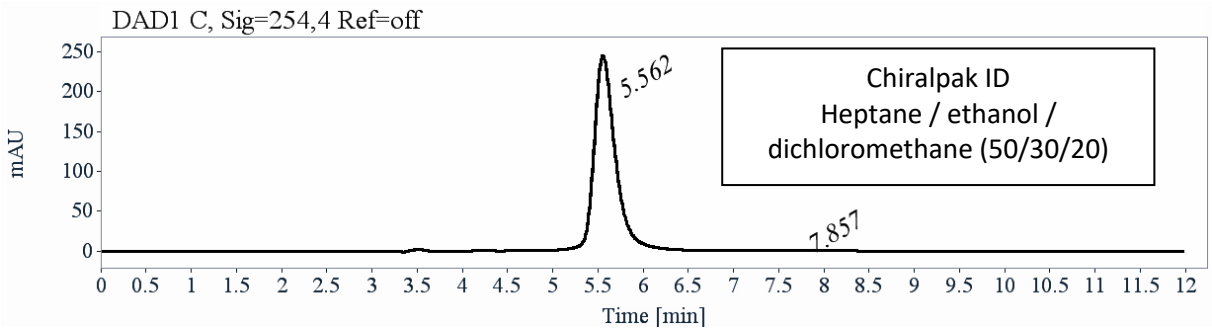


RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.58	3537	51.02	0.89		
7.87	3396	48.98	1.67	1.87	3.63
Sum	6934	100.00			

S1.5. Preparative chiral HPLC separation for compound C_2-3

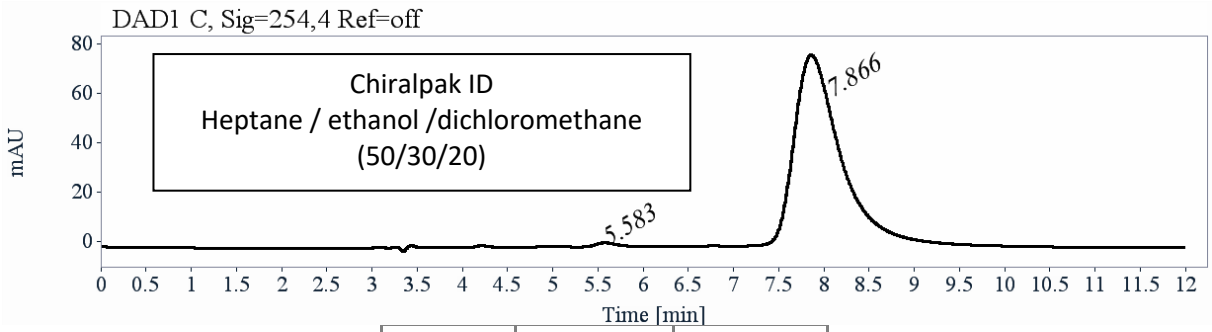
Sample preparation: 47 mg of ***C_2*-3** were dissolved in 2 mL of dichloromethane.
Chromatographic conditions: Chiralpak ID (250 × 10 mm), heptane / ethanol / dichloromethane (50/30/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.
Injections (stacked): 100 times 20 µL, every 9.6 minutes.

First fraction: 12 mg of the first eluted enantiomer with *ee* > 98.5%



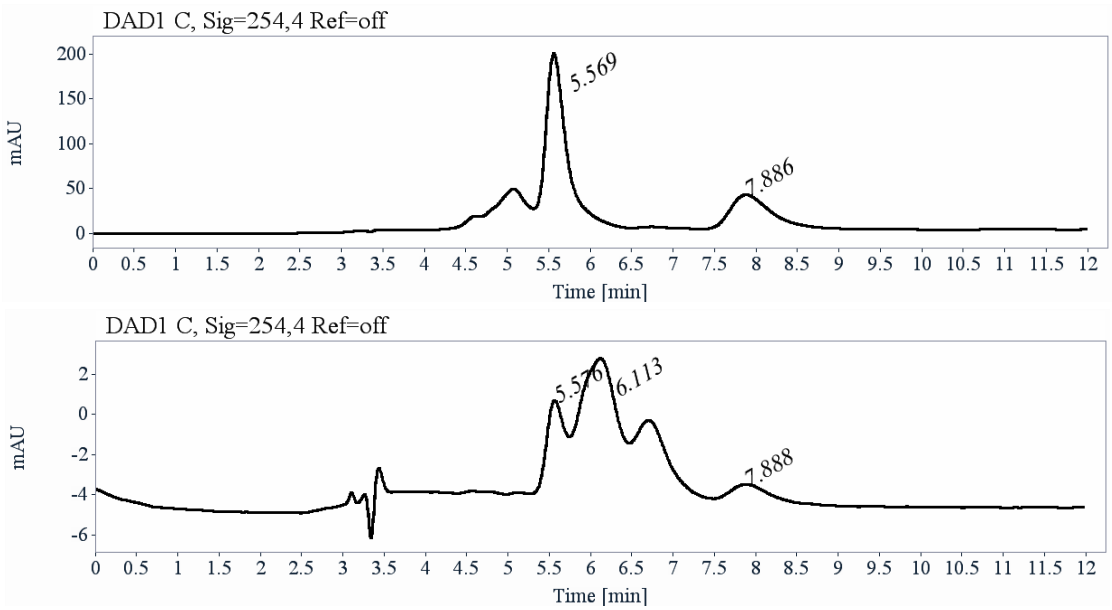
RT [min]	Area	Area%
5.56	3973	99.31
7.86	28	0.69
Sum	4001	100.00

Second fraction: 14 mg of the second eluted enantiomer with *ee* > 98 %



RT [min]	Area	Area%
5.58	26	0.92
7.87	2832	99.08
Sum	2858	100.00

• Intermediate fractions: 18 mg (top chromatogram) and 3 mg (bottom chromatogram)



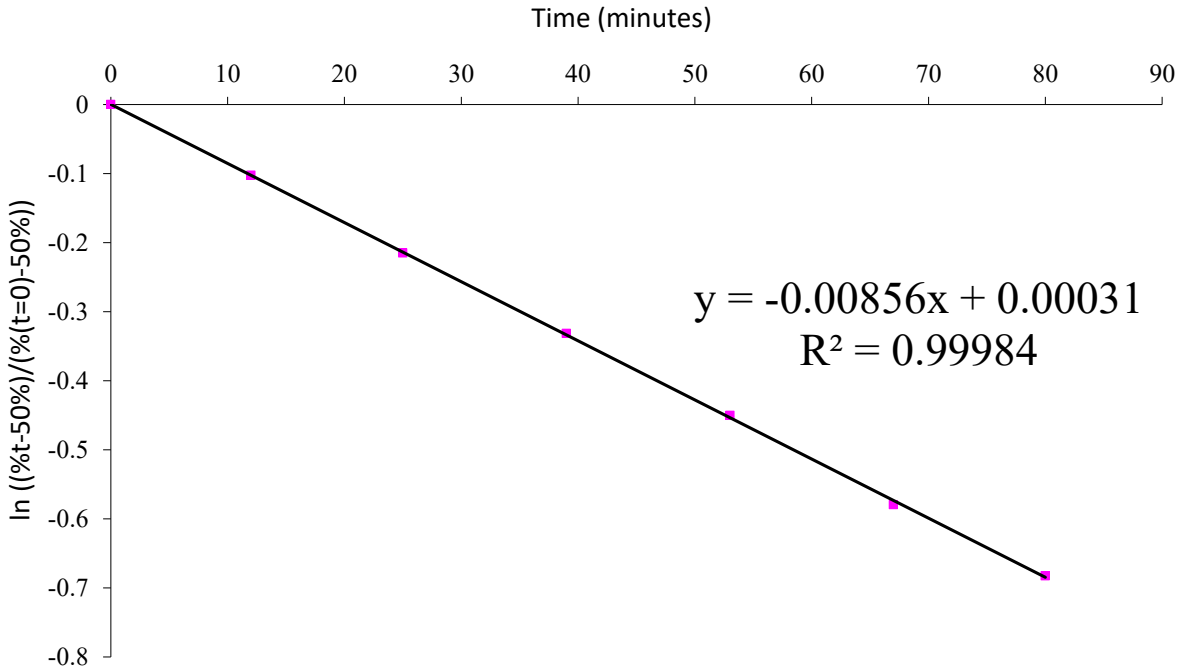
Section S2: Experimental conformational analysis

S2.1. Experimental determination of the barrier to enantiomerization of C_2-3

A solution of 0.7 mg of the second eluted enantiomer on Chiralpak ID of ***C*₂-3** (rt = 7.87 min) was refluxed in 25 mL of ethanol (bp = 78.4 °C). Samples (20 µL) were periodically taken and then analyzed on Chiralpak ID, heptane / ethanol / dichloromethane 50:30:20, 1 mL/min, UV 254 nm). The percentage decrease of the second eluted enantiomer on Chiralpak ID over time was found as reported in the Table below. This enantiomerization study revealed a clean process, with only the first eluted enantiomer on Chiralpak ID of ***C*₂-3** (rt = 5.58 min) formed overtime. This allowed to determine the kinetic constant of the enantiomerization of k_{enant}(***C*₂-3**). Then, using the Eyring equation, it was possible to calculate the corresponding barrier to enantiomerization $\Delta G^{\ddagger}_{enant}$(***C*₂-3**).

At the end of the kinetic study, the mixture of enantiomers was separated by preparative HPLC; the ECD spectra of these fractions were identical to the ECD spectra of the two enantiomers of ***C*₂-3**, confirming no decomposition.

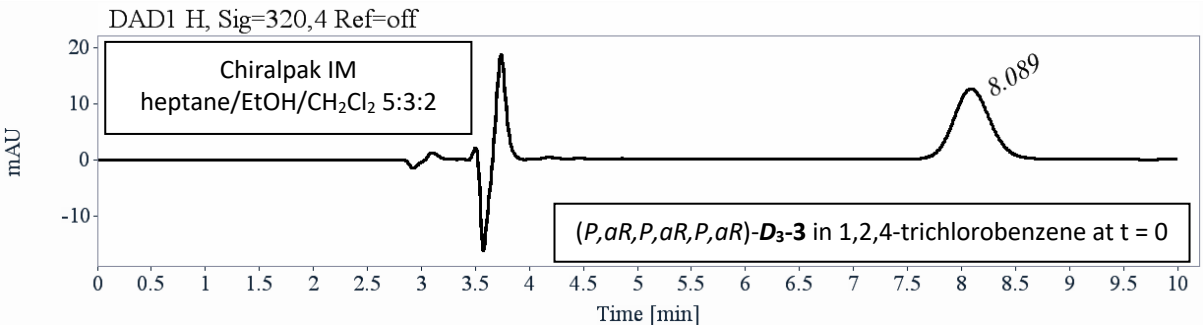
Time (min)	% second eluted enantiomer	ln ((%t-%e)/(%0-%e))
0	95.11	0.00000
12	90.72	-0.10238
25	86.38	-0.21508
39	82.38	-0.33156
53	78.76	-0.45012
67	75.27	-0.57949
80	72.80	-0.68234

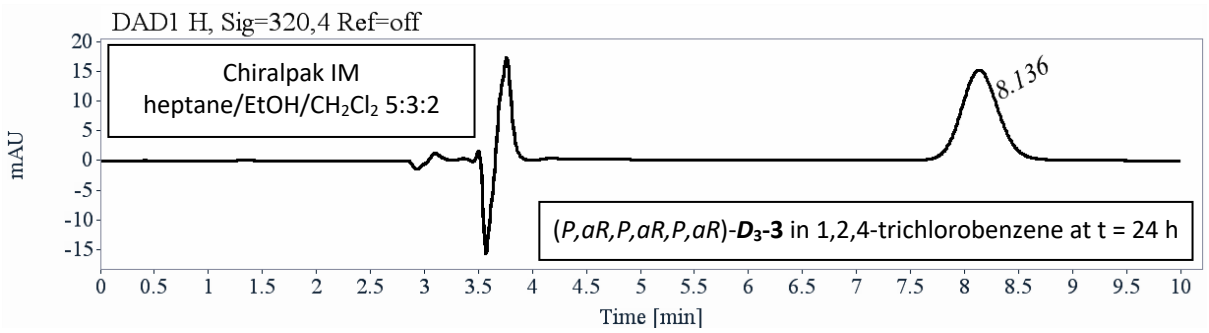


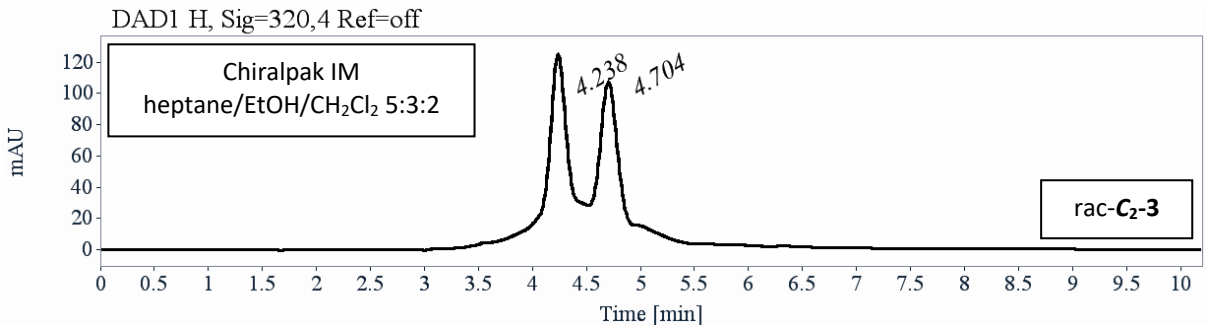
k_{enant}(***C*₂-3**) = 7.14 × 10^{-5} s^{-1}
$\Delta G^{\ddagger}_{enant}$(***C*₂-3**) = 114.4 kJ mol^{-1} (78 °C, ethanol)
$t_{1/2}$ = 81 min (78 °C, ethanol)

S2.2. Experimental verification of the barrier to diastereomers interconversion

A solution of 0.6 mg of the (*P,aR,P,aR,P,aR*)-***D*₃-3** enantiomer was refluxed in 15 mL of 1,2,4-trichlorobenzene (bp = 214 °C) for 24 hours. Periodic monitoring of the solution by chiral HPLC (Chiralpak IM, heptane/ethanol/dichloromethane 50:30:20, 1 mL/min, UV 320 nm) did not allow to detect any change. Considering that the conversion is less than 2% in 24 hours, this indicates that the barrier for the conversion of diastereomer ***D*₃-3** into diastereomer ***C*₂-3** is greater than 183 kJ mol^{-1}.







Section S3: Conformational calculations

S3.1. Methods

The enantiomerization mechanisms were investigated for ***D*₃-3** and ***C*₂-3** by DFT methods. For ***C*₂-3**, it was found that the inversion of configuration of a single [5]helicene fragment in a single step leads to a net enantiomerization of the entire molecule. In contrast, for ***D*₃-3**, no direct pathway connecting the (*P,aR,P,aR,P,aR*) and (*M,aS,M,aS,M,aS*) configurations, requiring the simultaneous inversion of the three [5]helicene fragments, could be identified. Instead, it was found that the enantiomerization path of ***D*₃-3** is a three-step process that goes through the formation of both enantiomers of ***C*₂-3**.

All calculations were performed within density functional theory (DFT) with the Gaussian16 package[1] using the B3LYP functional in conjunction with the 6-311G(d,p) basis set. To improve the agreement between calculated and experimental activation barriers, solvent effects were included using the SMD polarizable continuum solvation model. Different solvents, characterized by their dielectric constants, were considered in these calculations, namely ethanol, methanol, and hexane. All local minima and transition states were characterized by harmonic frequency calculations: no imaginary frequencies were found for minima, whereas a single imaginary frequency was obtained for each transition state. To verify the relevance of the located transition states, intrinsic reaction coordinate (IRC) calculations were performed; the geometries obtained after ten steps forward and ten steps backward along the IRC were subsequently fully optimized. For each identified transition state, an additional conformational analysis was carried out in order to locate the lowest-energy transition-state conformer. This conformational analysis was performed through a stochastic exploration of the potential energy surface (PES) of the two transition states, **TS₁** and **TS₂**. For the random PES exploration of each transition state, a simulated annealing procedure combined with the semi-empirical AM1 level of theory was employed. This approach was applied to geometries initially optimized at the DFT B3LYP/6-311G(d,p) level, including SMD(ethanol) solvation. During the simulated annealing process, only the dihedral angles were allowed to vary, while bond lengths and valence angles were kept fixed; naturally, the molecular fragment directly involved in the reaction mechanism was frozen. This strategy enables rapid identification of the major conformational families of the transition states. The

mechanisms presented in this study correspond to those derived from the lowest-energy transition states, **TS$_1$** and **TS$_2$**, identified using this approach. Intrinsic reaction coordinate (IRC) calculations confirmed that **TS$_1$** and **TS$_2$** correctly connect the expected minima. Analytical Hessian calculations were performed to obtain unscaled zero-point energies (ZPEs) and thermal corrections at 351.5 K and 1 atm, using standard ideal-gas statistical mechanics. The resulting activation barriers are reported in Figures SX and SX.

Several levels of theory were explored. The B3LYP functional was combined with different Gaussian basis sets and solvents (methanol, ethanol, and hexane). Attempts to optimize the transition states using the B3LYP functional augmented with the D3(BJ) dispersion correction scheme and the 6-311G(d,p) basis set were unsuccessful. These difficulties are attributed to the presence of several intramolecular CH–π interactions in the transition-state structures. Thus, the geometries were optimized at the SMD(ethanol)-B3LYP/6-311G(d,p) level of theory. The corresponding Gibbs energies calculated at 351.52 K are shown in Figure S1. These calculations realized without dispersion correction identify ***D*$_3$-3** as the thermodynamic diastereomer, with ***C*$_2$-3** calculated at ΔG = 29.1 kJ mol^{-1}.

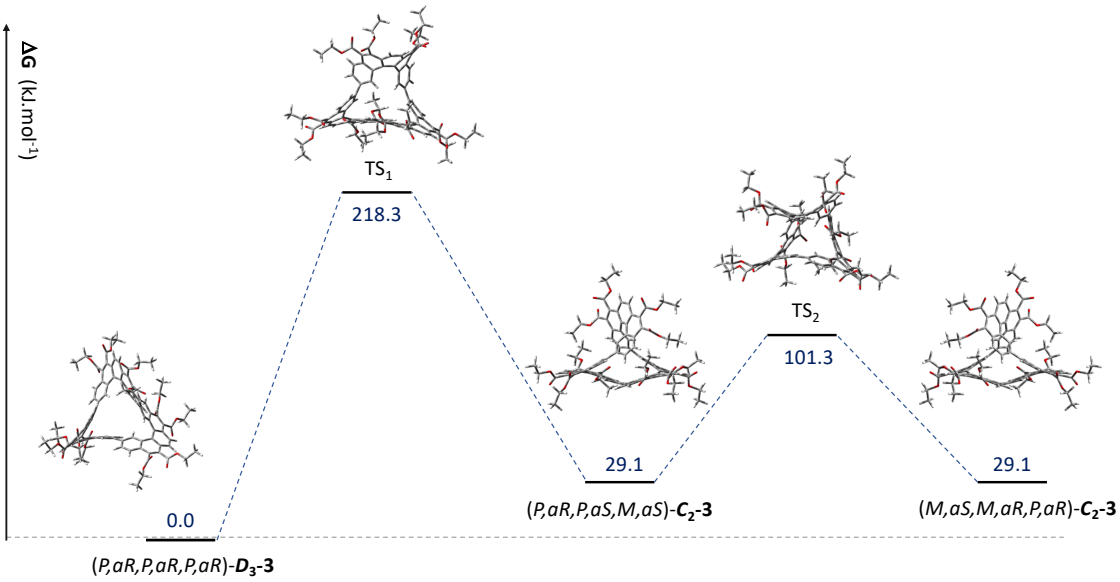


Figure S1. Enantiomerization barriers of cyclotris[5]helicenes ***D*$_3$-3** and ***C*$_2$-3**. Gibbs energies in kJ mol^{-1} computed at 351.52 K at the SMD(ethanol)-B3LYP/6-311G(d,p) level of theory.

In order to account for dispersion effects and improve the description of weak interactions, the D3(BJ) dispersion correction scheme[2] was included a posteriori in the single-point energy calculations of both transition states and minima optimized at the SMD(ethanol)/B3LYP/6-311G(d,p) level. The results obtained with SMD(methanol) and SMD(hexane) were very similar and are not reported. Now, with the D3(BJ) dispersion correction scheme included, the thermodynamic diastereomer is identified as ***C*$_2$-3**, with ***D*$_3$-3** calculated at ΔG = 25.8 kJ mol^{-1} at 351.52 K (Figure S2).

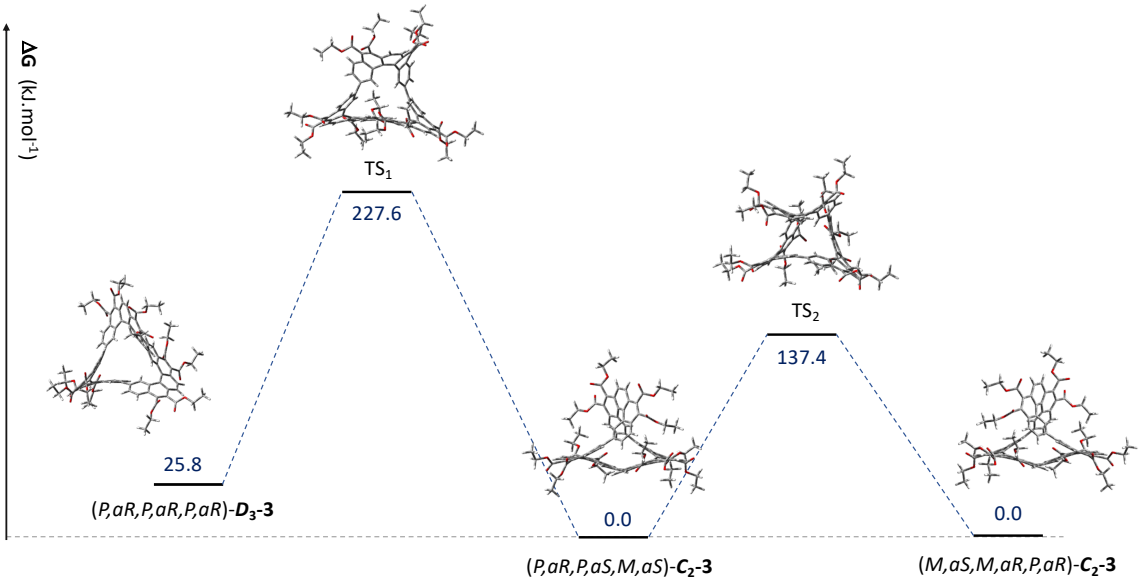


Figure S2. Enantiomerization barriers of cyclotris[5]helicenes ***D*$_3$-3** and ***C*$_2$-3**. Gibbs energies in kJ mol^{-1} computed at 351.52 K at the SMD(ethanol)-B3LYP-D3(BJ)/6-311G(d,p)//SMD(ethanol)-B3LYP/6-311G(d,p) level of theory.

Looking at the calculated barrier to enantiomerization for ***C*$_2$-3**, both levels of theory, without and with dispersion correction provided significantly different values, underestimating (largely) and overestimating (a little) the experimentally determined value:

- without dispersion, $\Delta G^{\ddagger}_{enant}$(***C*$_2$-3**) = 72.2 kJ mol^{-1} (351.52 K, ethanol)
- with D3(BJ) dispersion, $\Delta G^{\ddagger}_{enant}$(***C*$_2$-3**) = 137.4 kJ mol^{-1} (351.52 K, ethanol)
- experimental, $\Delta G^{\ddagger}_{enant}$(***C*$_2$-3**) = 114.4 kJ mol^{-1} (351.5 K, ethanol)

Table S1. Cartesian coordinates in the standard orientation of transition states **TS$_1$** and **TS$_2$**, and their connected minima (*P,aR,P,aR,P,aR*)-***D*$_3$-3** and (*P,aR,P,aS,M,aS*)-***C*$_2$-3** from IRC calculations at the SMD(ethanol)/B3LYP/6-311G(d,p) level of theory.

TS$_1$ Nimag = 1				**TS2** Nimag = 1			
C	1.088737	-2.866888	-0.892813	C	-0.143232	1.826731	-2.177128
C	-0.265690	-2.637941	-0.654097	C	-0.774645	2.475532	-1.133259
C	1.457706	-4.007941	-1.640529	C	-0.934656	1.229050	-3.180593
C	-1.236424	-3.646298	-0.899697	C	-2.181413	2.603048	-1.048162
H	-0.567529	-1.735374	-0.142304	H	-0.156413	2.953179	-0.389116
C	0.566322	-5.038457	-1.791533	C	-2.305549	1.365316	-3.154509
C	-0.733585	-4.941831	-1.246933	H	-0.462360	0.690702	-3.993843
C	-2.695456	-3.535821	-0.702081	C	-2.961396	2.103554	-2.135312
H	0.901520	-5.969855	-2.225709	C	-2.811961	3.379739	0.006487
C	-1.473984	-6.121409	-0.896645	H	-2.890040	0.933641	-3.953454
C	-3.329335	-4.716807	-0.198598	C	-4.365437	2.421917	-2.188694
C	-3.565406	-2.492341	-1.205655	C	-4.125278	3.855119	-0.215930
C	-2.673433	-5.990975	-0.251841	C	-2.112453	3.839796	1.185224
C	-0.943296	-7.512426	-1.112591	C	-4.911155	3.292064	-1.277285
C	-4.697834	-4.687345	0.177850	C	-5.292254	1.871040	-3.239471
C	-4.963135	-2.776863	-1.243954	C	-4.610822	4.952379	0.555650
C	-3.216056	-1.232671	-1.896584	C	-2.506783	5.074974	1.752329
C	-3.326120	-7.222461	0.325983	C	-1.061803	3.097578	1.856846
O	0.289424	-7.684000	-0.639693	C	-6.342496	3.736918	-1.442406
O	-1.601633	-8.394705	-1.626031	O	-4.859455	2.080003	-4.480913
C	-5.512301	-3.744784	-0.364993	O	-6.348192	1.338472	-2.965740
H	-5.120799	-5.490121	0.765958	C	-3.792414	5.601050	1.429709

C	-5.777173	-2.288773	-2.324853	H	-5.610475	5.329929	0.388023
C	-2.432662	-0.194035	-1.344665	C	-1.617808	5.749475	2.658393
C	-3.934613	-0.948946	-3.101283	C	-0.979437	1.685072	1.790429
O	-2.899141	-7.789482	1.309137	C	-0.170285	3.793244	2.722872
O	-4.391834	-7.614986	-0.367098	O	-6.754061	4.324315	-2.420293
C	0.875920	-9.017301	-0.780600	O	-7.087231	3.424033	-0.383153
H	-6.583632	-3.801189	-0.221569	C	-5.730096	1.642397	-5.573836
C	-5.203165	-1.586990	-3.350016	H	-4.141976	6.500650	1.917543
C	-7.223160	-2.706800	-2.368672	C	-0.444553	5.160049	3.066151
C	-2.310967	1.053711	-1.978544	C	-1.972779	7.112285	3.190884
H	-2.049535	-0.321134	-0.341012	C	0.009704	0.964850	2.449433
C	-3.551191	0.172134	-3.863429	H	-1.761167	1.164104	1.255261
C	2.251330	-8.971783	-0.157181	C	0.932332	3.075843	3.246351
H	0.219694	-9.729210	-0.276973	C	-5.055096	2.030899	-6.868459
H	0.911359	-9.262289	-1.843715	H	-5.869613	0.564382	-5.486910
C	-5.989854	-1.346163	-4.599055	H	-6.695608	2.135886	-5.449995
O	-7.439543	-3.682797	-3.247989	C	0.503714	5.917167	3.952591
O	-8.069356	-2.227544	-1.645501	O	-2.177557	7.997241	2.216346
C	-2.753708	1.145284	-3.317741	O	-2.054263	7.366679	4.374307
H	-3.998583	0.343546	-4.832408	C	1.030142	1.716733	3.095091
H	2.192850	-8.705744	0.901181	H	1.686470	3.593896	3.821357
H	2.714308	-9.959025	-0.238042	H	-4.089456	1.530706	-6.976865
H	2.892832	-8.249167	-0.667613	H	-5.690684	1.734050	-7.707247
O	-5.246502	-1.478150	-5.698541	H	-4.900422	3.111493	-6.921043
O	-7.177834	-1.090527	-4.610014	O	0.811825	7.106382	3.423657
C	-8.823120	-4.127123	-3.417518	O	0.934977	5.503274	5.007142
C	-8.820917	-5.216713	-4.464022	C	-2.550045	9.354415	2.616718
H	-9.187221	-4.484587	-2.452702	C	-2.722564	10.164277	1.353046
H	-9.418122	-3.263877	-3.721521	H	-3.471114	9.296203	3.199698
H	-8.202151	-6.061088	-4.149979	H	-1.756242	9.749523	3.252937
H	-9.843068	-5.575953	-4.611363	H	-3.515473	9.750662	0.724915
H	-8.447436	-4.842387	-5.420408	H	-2.993802	11.189906	1.617684
C	-5.913913	-1.261823	-6.981726	H	-1.794815	10.192581	0.776098
H	-6.744363	-1.966061	-7.055048	C	1.658711	8.005061	4.209392
H	-6.313149	-0.245812	-6.989901	H	1.361788	8.998160	3.874359
C	-4.886141	-1.481594	-8.067134	H	1.403383	7.887134	5.262318
H	-5.358878	-1.339216	-9.042743	C	3.127099	7.742425	3.943113
H	-4.060197	-0.771322	-7.979459	H	3.726047	8.486437	4.476578
H	-4.483952	-2.496932	-8.025710	H	3.424320	6.750873	4.290853
C	-5.074103	-8.825179	0.092882	H	3.349415	7.825177	2.876167
H	-5.410738	-8.658597	1.117776	C	-8.489337	3.842747	-0.410570
H	-4.349484	-9.641406	0.087906	H	-8.975310	3.334028	-1.245092
C	-6.223647	-9.079318	-0.853793	H	-8.520040	4.918986	-0.589108
H	-6.751060	-9.985676	-0.544204	C	-9.098721	3.467895	0.920134
H	-6.933499	-8.248429	-0.843572	H	-10.152004	3.761362	0.927764
H	-5.863811	-9.223163	-1.875601	H	-9.041916	2.390035	1.090349
C	2.110061	2.109418	0.342119	H	-8.593557	3.981042	1.742271
C	3.278407	1.410049	0.097594	C	-0.042865	-0.517914	2.613811
C	1.728793	3.084494	-0.618325	C	-1.007994	-1.321597	2.011353
C	4.053669	1.586365	-1.068782	C	0.840254	-1.145969	3.531382
H	3.626721	0.704569	0.831472	C	-1.222303	-2.668549	2.396174
C	2.518884	3.362986	-1.706550	H	-1.675683	-0.898491	1.273531
C	3.721873	2.651762	-1.950814	C	0.647702	-2.439109	3.942279
C	5.233439	0.783795	-1.320830	C	-0.445121	-3.200283	3.468823
H	2.220515	4.154196	-2.379676	C	-2.326088	-3.456789	1.867994
C	4.628587	2.979497	-3.016420	H	1.297145	-2.848458	4.702521
C	6.208139	1.283828	-2.214985	C	-0.836409	-4.434453	4.088129
C	5.516723	-0.422879	-0.590209	C	-2.856147	-4.461511	2.714071
C	5.854785	2.359812	-3.103754	C	-2.974301	-3.246492	0.588290
C	4.243565	4.035731	-4.015006	C	-2.047016	-4.999634	3.774314
C	7.529876	0.752012	-2.151379	C	0.028982	-5.056673	5.149156
C	6.868697	-0.786186	-0.392003	C	-4.204350	-4.879423	2.528010
C	4.489434	-1.295742	-0.056996	C	-4.339803	-3.619349	0.470403
C	6.844229	2.783918	-4.152104	C	-2.262047	-2.865134	-0.625431
O	4.326311	3.569120	-5.264106	C	-2.520968	-6.184979	4.570323
O	3.880237	5.156645	-3.729942	O	0.312796	-6.328141	4.848405
C	7.865909	-0.175504	-1.207714	O	0.422606	-4.480584	6.140050
H	8.294583	1.135038	-2.812520	C	-4.953989	-4.378467	1.508818
C	7.185419	-1.717381	0.660197	H	-4.655175	-5.562646	3.234566
C	3.218953	-1.443346	-0.680298	C	-5.072584	-3.280498	-0.721576
C	4.810468	-2.122708	1.052771	C	-0.845970	-2.868567	-0.710075

O	7.407338	2.020423	-4.907334	C	-2.995929	-2.676066	-1.837051
O	7.042589	4.105008	-4.136128	O	-2.552371	-6.206368	5.783524
C	3.992870	4.494239	-6.346436	O	-2.882407	-7.205582	3.793934
H	8.897591	-0.483708	-1.110414	C	1.078947	-7.105935	5.823445
C	6.191163	-2.275865	1.428160	H	-5.996572	-4.646891	1.430370
C	8.631340	-2.001247	0.956382	C	-4.425554	-2.800147	-1.831107
C	2.251455	-2.272082	-0.148138	C	-6.569943	-3.432314	-0.741578
H	3.040983	-0.947594	-1.626440	C	-0.176850	-2.703474	-1.910785
C	3.762878	-2.852750	1.668892	C	-2.293354	-2.478509	-3.050760
C	4.088290	3.722894	-7.642236	C	2.569152	-6.942628	5.602849
H	2.985605	4.875040	-6.168881	H	0.774973	-6.800181	6.824354
H	4.694972	5.329220	-6.308839	H	0.757092	-8.131293	5.645418
C	6.524957	-3.133239	2.614971	C	-5.185040	-2.494863	-3.091708
O	8.955637	-1.644362	2.200982	O	-7.153468	-2.268019	-1.036835
O	9.410227	-2.468432	0.153503	O	-7.174692	-4.456206	-0.505287
C	2.513654	-2.899031	1.101286	C	-0.923963	-2.501007	-3.092810
H	3.958707	-3.424951	2.566091	H	-2.844684	-2.332475	-3.968847
H	3.384136	2.887122	-7.652423	H	2.890105	-5.916341	5.793271
H	3.844502	4.387581	-8.475448	H	3.106906	-7.602699	6.289880
H	5.097581	3.333587	-7.796999	H	2.843096	-7.216164	4.580706
O	7.341460	-4.137432	2.289344	O	-5.971188	-3.512701	-3.449864
O	6.082915	-2.944189	3.728103	O	-5.071474	-1.467231	-3.725441
C	10.335495	-1.880607	2.625493	C	-8.612606	-2.249729	-1.122009
H	1.742967	-3.510212	1.556671	H	-0.410454	-2.369034	-4.037848
C	10.487159	-1.295570	4.010321	C	-9.020778	-0.842755	-1.492551
H	10.515881	-2.957047	2.608101	H	-8.922116	-2.981560	-1.870101
H	10.999066	-1.402050	1.903453	H	-9.010205	-2.551257	-0.151037
H	9.804882	-1.771646	4.718806	H	-8.624595	-0.560400	-2.470340
H	11.511174	-1.456572	4.358157	H	-10.111942	-0.783365	-1.531075
H	10.292217	-0.220211	4.003510	H	-8.661580	-0.124667	-0.751468
C	7.767694	-5.029143	3.367574	C	-6.786438	-3.344201	-4.651997
H	8.330099	-4.438843	4.093378	H	-7.479222	-2.518650	-4.479401
H	6.874302	-5.424270	3.853921	H	-6.123292	-3.080242	-5.477475
C	8.603950	-6.122230	2.744012	C	-7.501885	-4.652644	-4.896218
H	8.940269	-6.807774	3.526587	H	-6.787575	-5.464132	-5.056639
H	8.021646	-6.692094	2.015571	H	-8.147093	-4.914588	-4.054215
H	9.485113	-5.711623	2.245052	H	-8.123865	-4.560751	-5.790734
C	7.958823	4.655191	-5.133900	C	-3.380942	-8.407004	4.463255
H	7.545019	4.451926	-6.123410	H	-4.249494	-8.126494	5.062101
H	8.914140	4.136077	-5.040338	H	-2.598122	-8.773068	5.129807
C	8.088429	6.135299	-4.858541	C	-3.727180	-9.409780	3.387534
H	8.768582	6.578932	-5.590711	H	-4.097680	-10.325645	3.855986
H	7.122038	6.639130	-4.937535	H	-4.505742	-9.023877	2.724829
H	8.496066	6.312400	-3.860079	H	-2.848035	-9.661778	2.789186
C	1.265311	1.795322	1.525958	H	1.887356	1.225079	3.531772
C	0.157465	2.568731	1.824450	H	1.650494	-0.594169	3.984432
C	1.512238	0.671133	2.359634	H	-0.261255	-3.084160	0.171326
C	-0.756180	2.243415	2.849310	C	1.352555	1.888164	-2.220177
H	-0.015877	3.470833	1.264031	C	2.140498	1.005224	-1.493179
C	0.708196	0.392628	3.438697	C	1.964264	2.976578	-2.864667
C	-0.439270	1.174324	3.729402	C	3.526856	1.191166	-1.285521
C	-1.941325	3.042375	3.084973	H	1.631412	0.214000	-0.982963
H	0.959898	-0.446087	4.073750	C	3.285091	3.256794	-2.603031
C	-1.232689	0.994815	4.914051	C	4.058028	2.441406	-1.744677
C	-2.538552	2.999136	4.366118	C	4.434209	0.273751	-0.560211
C	-2.449962	3.969982	2.110598	H	3.717197	4.162553	-3.005748
C	-2.197035	1.916539	5.253259	C	5.268780	2.961404	-1.166618
C	-0.946751	-0.182318	5.802465	C	5.511213	0.915296	0.126215
C	-3.452240	4.032933	4.727545	C	4.484597	-1.182998	-0.652180
C	-3.149938	5.109871	2.568308	C	5.856447	2.289853	-0.134423
C	-2.298939	3.788296	0.680542	C	5.797453	4.310055	-1.563946
C	-2.947447	1.784576	6.549817	C	6.413697	0.162391	0.921610
O	-0.698326	0.194875	7.060100	C	5.654695	-1.838846	-0.167048
O	-0.929204	-1.329307	5.410374	C	3.550954	-2.080160	-1.348313
C	-3.670895	5.094064	3.896534	C	6.953556	2.921636	0.681578
H	-3.917622	4.020495	5.702877	O	6.106533	4.363232	-2.858539
C	-3.318546	6.225938	1.675117	O	5.936380	5.231604	-0.787185
C	-2.204485	2.505342	0.082239	C	6.506900	-1.182700	0.754372
C	-2.357883	4.932617	-0.159223	H	7.114269	0.667388	1.572298
O	-2.983802	2.640678	7.407268	C	6.085813	-3.089344	-0.738263
O	-3.591866	0.617810	6.623782	C	2.148637	-2.014320	-1.239323

C	-0.444340	-0.851175	8.052674	C	4.084923	-3.183591	-2.087811
H	-4.274020	5.921198	4.243591	O	6.842512	3.143425	1.867677
C	-2.838253	6.172159	0.384247	O	8.048203	3.163491	-0.041431
C	-3.972579	7.477158	2.187613	C	6.606461	5.638173	-3.375371
C	-2.017536	2.339836	-1.283022	H	7.285628	-1.735137	1.263242
H	-2.366536	1.640070	0.711454	C	5.420942	-3.638302	-1.799986
C	-1.969113	4.767695	-1.514453	C	7.355624	-3.711276	-0.219476
C	1.025898	-1.216246	8.092086	C	1.301360	-2.800268	-2.012201
H	-0.770031	-0.403269	8.990436	H	1.714793	-1.387427	-0.478822
H	-1.074147	-1.709527	7.820658	C	3.223947	-3.934080	-2.918568
C	-2.873995	7.394557	-0.489521	C	6.840034	5.461314	-4.857504
O	-4.936550	7.897920	1.363067	H	5.861425	6.406784	-3.162349
O	-3.680182	8.028040	3.227579	H	7.526667	5.881743	-2.842040
C	-1.768645	3.519596	-2.044806	C	6.036284	-4.799315	-2.521875
H	-1.872767	5.632659	-2.155690	O	8.364784	-3.586501	-1.079832
H	1.640329	-0.333364	8.285776	O	7.439195	-4.233451	0.870802
H	1.193902	-1.934612	8.899915	C	1.866415	-3.711333	-2.924597
H	1.348576	-1.674481	7.154829	H	3.629075	-4.734961	-3.521198
O	-2.279842	8.431792	0.107787	H	5.910916	5.213864	-5.376947
O	-3.354568	7.434515	-1.601899	H	7.227750	6.395150	-5.273612
C	-5.636244	9.128387	1.727991	H	7.571207	4.671528	-5.047291
C	-6.726052	9.347382	0.704356	O	5.994034	-4.649854	-3.845458
H	-6.038681	9.004353	2.734767	O	6.538788	-5.751407	-1.959868
H	-4.908833	9.942335	1.739751	C	9.632519	-4.216963	-0.710194
H	-7.435842	8.516310	0.705769	C	10.615249	-3.938379	-1.823244
H	-7.269984	10.263923	0.948566	H	9.958470	-3.794314	0.241725
H	-6.310188	9.451821	-0.300754	H	9.449739	-5.285089	-0.578034
C	-2.257325	9.698889	-0.621333	H	10.768332	-2.863852	-1.951723
H	-1.792286	9.523196	-1.592907	H	11.577391	-4.395167	-1.575953
H	-3.289051	10.018458	-0.779323	H	10.268220	-4.360729	-2.769559
C	-1.473032	10.684395	0.213513	C	6.568927	-5.724565	-4.654858
H	-0.447563	10.338469	0.365793	H	7.617030	-5.837214	-4.372430
H	-1.437401	11.646411	-0.304899	H	6.039393	-6.649141	-4.417541
H	-1.940875	10.836664	1.189257	C	6.410126	-5.330093	-6.104581
C	-4.336834	0.345268	7.852657	H	6.842091	-6.109701	-6.737948
H	-5.061472	1.148961	7.994536	H	5.356033	-5.217438	-6.370129
H	-3.632232	0.356639	8.686293	H	6.928866	-4.391295	-6.314269
C	-5.005303	-0.999295	7.685471	C	9.203760	3.749660	0.645950
H	-5.575962	-1.231663	8.588758	H	10.049432	3.423209	0.042278
H	-5.694085	-0.991121	6.836967	H	9.272489	3.301165	1.636933
H	-4.267767	-1.790932	7.532177	C	9.115652	5.260576	0.714431
H	2.354022	0.019314	2.172915	H	10.027472	5.643020	1.183111
H	0.810251	3.642162	-0.503920	H	9.036953	5.696977	-0.283656
H	2.487800	-4.133605	-1.953238	H	8.262319	5.585150	1.312708
H	-2.602126	2.049776	-3.888655	H	1.376748	3.648739	-3.479374
H	-1.474249	3.448554	-3.083152	H	1.224823	-4.311598	-3.558915

Table S1 (continued). Cartesian coordinates in the standard orientation of transition states **TS_1** and **TS_2**, and their connected minima (*P,aR,P,aR,P,aR*)-***D*$_3$-3** and (*P,aR,P,aS,M,aS*)-***C*$_2$-3** from IRC calculations at the SMD(ethanol)/B3LYP/6-311G(d,p) level of theory.

(*P,aR,P,aR,P,aR*)-***D*$_3$-3** Nimag = 0				(*P,aR,P,aS,M,aS*)-***C*$_2$-3** Nimag = 0			
C	-0.948164	-3.072350	0.419006	C	-0.214563	-2.440344	0.790644
C	0.357192	-3.435320	0.122841	C	-0.359109	-1.556496	1.846669
C	-1.430157	-3.327174	1.728880	C	0.973803	-3.215687	0.732667
C	1.178140	-4.132256	1.040141	C	0.577735	-1.491680	2.906052
H	0.745922	-3.231166	-0.863708	H	-1.266822	-0.973834	1.921338
C	-0.669586	-4.023186	2.634968	C	1.884144	-3.198765	1.762548
C	0.618033	-4.507816	2.294483	C	1.674129	-2.396928	2.912210
C	2.485721	-4.638470	0.664059	C	0.336888	-0.667319	4.073441
H	-1.093552	-4.260467	3.601994	H	2.748190	-3.848086	1.709093
C	1.329663	-5.425940	3.133729	C	2.423358	-2.569662	4.129725
C	3.000203	-5.745967	1.375732	C	0.872400	-1.088596	5.311022
C	3.219286	-4.167037	-0.487745	C	-0.509091	0.488543	4.047586
C	2.462344	-6.056949	2.678276	C	1.963332	-2.025491	5.304824

C	0.826632	-5.681812	4.533496	C	3.644183	-3.440826	4.179669
C	3.970379	-6.573646	0.734048	C	0.318965	-0.554832	6.509914
C	4.038417	-5.085063	-1.180825	C	-1.170086	0.880154	5.235251
C	3.261778	-2.774831	-0.892962	C	-0.630831	1.338919	2.881073
C	3.119417	-7.052425	3.588506	C	2.692967	-2.307100	6.593821
O	-0.258710	-6.452234	4.543649	O	4.548187	-3.089541	3.265843
O	1.345527	-5.206593	5.519950	O	3.800514	-4.336249	4.984668
C	4.384449	-6.311226	-0.538518	C	-0.731257	0.319484	6.470420
H	4.328563	-7.462514	1.233179	H	0.690389	-0.891041	7.469016
C	4.551164	-4.729452	-2.479357	C	-2.273583	1.806264	5.134293
C	2.943355	-1.732807	0.008653	C	0.412027	1.448263	1.929144
C	3.806781	-2.429285	-2.163409	C	-1.735635	2.225856	2.792544
O	2.501779	-7.826890	4.292720	O	3.799205	-1.878868	6.841238
O	4.449481	-6.960916	3.579410	O	1.970075	-3.059712	7.420735
C	-0.826965	-6.780644	5.851311	C	5.811276	-3.828337	3.265926
H	5.033045	-7.015397	-1.040387	H	-1.193650	0.636147	7.393904
C	4.386957	-3.459202	-2.979028	C	-2.610337	2.363150	3.922973
C	5.205100	-5.790083	-3.315526	C	-3.047422	2.172688	6.364760
C	3.092720	-0.393541	-0.317831	C	0.361562	2.366866	0.894135
H	2.626771	-1.998254	1.006537	H	1.318099	0.877221	2.080496
C	3.822191	-1.061384	-2.536750	C	-1.849364	3.049560	1.645299
C	-2.016786	-7.679952	5.610493	C	6.723310	-3.160438	2.263853
H	-0.051266	-7.274011	6.439707	H	6.220121	-3.796458	4.277025
H	-1.106240	-5.848916	6.346732	H	5.595686	-4.866706	3.006820
C	4.789063	-3.165198	-4.401765	C	-3.807632	3.270978	3.793124
O	6.337693	-5.359490	-3.878417	O	-4.365810	2.064514	6.181147
O	4.756802	-6.907371	-3.464796	O	-2.536280	2.534461	7.404135
C	3.477264	-0.075323	-1.645824	C	-0.832274	3.118356	0.724747
H	4.177024	-0.777028	-3.517597	H	-2.723234	3.675731	1.512254
H	-1.716443	-8.596321	5.096339	H	6.902775	-2.117433	2.536683
H	-2.460849	-7.954564	6.571175	H	7.684716	-3.681171	2.251046
H	-2.778689	-7.173773	5.012357	H	6.300569	-3.194895	1.257713
O	5.786161	-2.287558	-4.485836	O	-4.775139	2.682450	3.094687
O	4.241327	-3.675306	-5.356120	O	-3.858862	4.394056	4.246203
C	7.012394	-6.276588	-4.795491	C	-5.224002	2.498971	7.283579
C	8.292651	-5.610313	-5.242131	C	-6.653593	2.210630	6.889908
H	7.200882	-7.211208	-4.264798	H	-4.928384	1.950973	8.179511
H	6.336295	-6.475424	-5.629568	H	-5.046526	3.563858	7.447020
H	8.941474	-5.397987	-4.388612	H	-6.799698	1.144373	6.699595
H	8.827219	-6.279932	-5.921437	H	-7.315856	2.506700	7.708119
H	8.089173	-4.676126	-5.771149	H	-6.940711	2.771508	5.997406
C	6.217157	-1.897333	-5.829213	C	-6.011467	3.434363	2.869805
H	6.509788	-2.800099	-6.367627	H	-6.274525	3.949001	3.794078
H	5.364689	-1.444829	-6.339340	H	-5.809365	4.176935	2.095418
C	7.367510	-0.931023	-5.669822	C	-7.069084	2.442061	2.445569
H	7.717646	-0.623608	-6.659008	H	-8.001092	2.975508	2.239979
H	7.059191	-0.036958	-5.122206	H	-6.770712	1.913747	1.538082
H	8.201566	-1.398303	-5.140350	H	-7.256475	1.710407	3.235308
C	5.184269	-7.875841	4.452100	C	2.577828	-3.401706	8.707864
H	4.942333	-8.897906	4.154423	H	2.799297	-2.473302	9.237470
H	4.839157	-7.717489	5.475282	H	3.514059	-3.925602	8.507474
C	6.654624	-7.566527	4.293402	C	1.590330	-4.266246	9.455883
H	7.232727	-8.227912	4.944494	H	2.019888	-4.549995	10.420541
H	6.983363	-7.726163	3.263479	H	0.656597	-3.729196	9.640817
H	6.870046	-6.533032	4.576019	H	1.367479	-5.178904	8.897557
C	-2.227947	2.213447	0.468270	C	-0.379802	0.618392	-3.222071
C	-3.182645	1.304920	0.037099	C	-1.625201	0.116528	-2.875376
C	-2.277950	2.633016	1.821893	C	-0.235998	2.016709	-3.368210
C	-4.246834	0.871860	0.861356	C	-2.719693	0.936222	-2.528494
H	-3.149235	0.955607	-0.983993	H	-1.739034	-0.950586	-2.817034
C	-3.310208	2.251190	2.643253	C	-1.295818	2.849335	-3.115679
C	-4.362774	1.429313	2.167847	C	-2.547416	2.348190	-2.676386
C	-5.310448	0.027868	0.345509	C	-4.009889	0.393737	-2.108321
H	-3.356942	2.650106	3.646341	H	-1.173207	3.913288	-3.259656
C	-5.570064	1.208029	2.917244	C	-3.637981	3.231363	-2.382364
C	-6.572676	0.095453	0.978983	C	-5.103555	1.299994	-2.058447
C	-5.189628	-0.766806	-0.851728	C	-4.287300	-1.020149	-1.894855
C	-6.660667	0.627772	2.313882	C	-4.877625	2.721265	-2.101492
C	-5.654588	1.664616	4.347759	C	-3.412825	4.719270	-2.397041
C	-7.729175	-0.306566	0.248660	C	-6.436515	0.804227	-2.066612
C	-6.352968	-1.003853	-1.621543	C	-5.615705	-1.469393	-2.130518

C	-3.966335	-1.442491	-1.246316	C	-3.334422	-2.026266	-1.422985
C	-7.962885	0.504769	3.053385	C	-6.023445	3.650066	-1.814076
O	-6.005480	0.655794	5.150523	O	-3.669452	5.260102	-1.201402
O	-5.415954	2.788809	4.733160	O	-3.028483	5.347491	-3.359011
C	-7.627531	-0.734238	-1.042672	C	-6.677947	-0.526563	-2.203403
H	-8.707338	-0.214307	0.699962	H	-7.268232	1.494454	-2.048472
C	-6.207827	-1.506799	-2.964520	C	-5.875880	-2.871417	-2.334960
C	-2.966498	-1.771297	-0.302045	C	-2.214839	-1.719517	-0.605494
C	-3.846768	-1.956415	-2.567894	C	-3.596972	-3.402745	-1.697394
O	-8.598033	-0.523917	3.146736	O	-6.732704	3.573249	-0.832720
O	-8.344734	1.671671	3.579589	O	-6.169147	4.568772	-2.770816
C	-6.146213	0.954690	6.575060	C	-3.507684	6.711058	-1.082270
H	-8.525660	-0.939891	-1.607262	H	-7.694034	-0.873327	-2.323909
C	-4.979748	-1.886655	-3.448809	C	-4.869983	-3.794217	-2.230867
C	-7.421121	-1.566050	-3.850633	C	-7.260382	-3.311724	-2.724223
C	-1.863619	-2.546483	-0.627913	C	-1.325602	-2.695969	-0.166519
H	-3.103668	-1.458272	0.722650	H	-2.056415	-0.691441	-0.306815
C	-2.660801	-2.647300	-2.920201	C	-2.644183	-4.375306	-1.313533
C	-6.476738	-0.342359	7.276156	C	-3.862673	7.096885	0.334556
H	-5.206030	1.383353	6.926208	H	-2.472325	6.954378	-1.327000
H	-6.935594	1.699783	6.689746	H	-4.162179	7.186003	-1.814764
C	-4.810749	-2.316571	-4.878111	C	-5.103017	-5.237053	-2.580910
O	-7.264475	-0.808273	-4.938530	O	-7.263856	-3.902391	-3.921112
O	-8.422790	-2.200630	-3.598637	O	-8.248820	-3.140080	-2.044053
C	-1.698940	-2.932735	-1.982657	C	-1.534305	-4.032394	-0.587399
H	-2.533111	-3.012984	-3.930732	H	-2.813551	-5.415954	-1.555494
H	-5.677462	-1.075253	7.140312	H	-3.208722	6.602025	1.056729
H	-6.590787	-0.153242	8.347020	H	-3.742141	8.177616	0.449651
H	-7.410867	-0.767535	6.900877	H	-4.899636	6.842055	0.566215
O	-5.652267	-3.298455	-5.207955	O	-6.107281	-5.762904	-1.877526
O	-3.988094	-1.838712	-5.629547	O	-4.440003	-5.848161	-3.391059
C	-8.365186	-0.787994	-5.901965	C	-8.545698	-4.408421	-4.412623
H	-0.843314	-3.527098	-2.277177	H	-0.851802	-4.810713	-0.270826
C	-8.001742	0.206247	-6.980034	C	-8.313547	-4.943300	-5.806523
H	-8.490322	-1.798533	-6.295192	H	-8.892030	-5.181363	-3.724220
H	-9.274952	-0.502827	-5.371137	H	-9.260798	-3.584201	-4.403560
H	-7.080690	-0.083135	-7.491942	H	-7.582932	-5.755889	-5.802374
H	-8.807357	0.245846	-7.718262	H	-9.255665	-5.330150	-6.204367
H	-7.871207	1.207010	-6.560668	H	-7.957608	-4.154136	-6.473568
C	-5.602020	-3.786999	-6.585949	C	-6.449085	-7.160745	-2.141650
H	-5.882716	-2.964925	-7.246989	H	-6.781540	-7.238259	-3.178436
H	-4.573398	-4.077737	-6.805291	H	-5.545447	-7.759638	-2.017196
C	-6.555075	-4.955255	-6.685115	C	-7.529390	-7.552799	-1.160760
H	-6.543046	-5.342602	-7.707526	H	-7.809857	-8.595474	-1.333032
H	-6.256861	-5.760844	-6.009454	H	-7.174860	-7.458374	-0.131303
H	-7.577524	-4.654882	-6.443473	H	-8.420475	-6.932386	-1.283485
C	-9.581542	1.678819	4.359441	C	-7.221066	5.568567	-2.584803
H	-9.443911	1.021570	5.220141	H	-6.980421	6.150130	-1.692909
H	-10.379287	1.274323	3.734268	H	-8.162375	5.042823	-2.417171
C	-9.849383	3.109245	4.766237	C	-7.259262	6.418849	-3.833151
H	-10.769431	3.148845	5.355686	H	-8.034878	7.181801	-3.724398
H	-9.033784	3.507423	5.374697	H	-6.303496	6.921490	-3.999750
H	-9.976332	3.747775	3.888388	H	-7.495006	5.812693	-4.711454
C	-1.257643	2.827002	-0.476697	C	0.783235	-0.300717	-3.239236
C	-0.056684	3.361820	-0.035204	C	2.018921	0.161154	-2.811290
C	-1.594554	2.991599	-1.844697	C	0.635337	-1.681354	-3.507013
C	0.779318	4.138603	-0.870068	C	3.090635	-0.696992	-2.482775
H	0.225251	3.236631	0.999796	H	2.142366	1.220490	-2.674484
C	-0.813900	3.754697	-2.677857	C	1.676908	-2.541680	-3.279159
C	0.353490	4.401692	-2.202066	C	2.907463	-2.090615	-2.738878
C	1.947431	4.823754	-0.346024	C	4.370087	-0.209910	-1.973709
H	-1.133218	3.909818	-3.699800	H	1.548484	-3.590298	-3.511178
C	1.029731	5.415275	-2.964427	C	3.988253	-3.003239	-2.523958
C	2.365764	6.008299	-0.997116	C	5.462284	-1.124409	-1.989054
C	2.621171	4.434553	0.867850	C	4.638094	1.173557	-1.597890
C	1.939870	6.244077	-2.353772	C	5.235113	-2.530572	-2.208182
C	0.665269	5.595351	-4.410190	C	3.740240	-4.477694	-2.699609
C	3.195603	6.926012	-0.288631	C	6.790018	-0.644179	-1.814636
C	3.265710	5.438168	1.627157	C	5.976953	1.632800	-1.725578
C	2.790613	3.054134	1.285582	C	3.670838	2.135674	-1.064725
C	2.547132	7.393214	-3.110157	C	6.382525	-3.499013	-2.121831

O	0.301868	6.852281	-4.680523	O	4.489598	-4.989627	-3.677745
O	0.688768	4.694691	-5.221387	O	2.942123	-5.107724	-2.038869
C	3.536859	6.695431	1.011842	C	7.040203	0.690629	-1.787381
H	3.497022	7.849752	-0.761574	H	7.616012	-1.338663	-1.794483
C	3.683268	5.140258	2.972550	C	6.264563	3.041514	-1.759411
C	2.694370	1.986980	0.362939	C	2.487148	1.758984	-0.374031
C	3.241722	2.770337	2.607207	C	3.967652	3.532523	-1.151913
O	2.463771	8.553842	-2.770606	O	7.407592	-3.411279	-2.762754
O	3.213302	6.970483	-4.186762	O	6.128744	-4.482218	-1.252229
C	-0.031039	7.187003	-6.066651	C	4.386781	-6.426887	-3.945663
H	4.072761	7.456612	1.561721	H	8.063586	1.037701	-1.780531
C	3.600340	3.861744	3.471985	C	5.271158	3.965116	-1.568238
C	4.180545	6.263036	3.838492	C	7.661970	3.497259	-2.079195
C	2.976326	0.674427	0.710007	C	1.563573	2.694572	0.079584
H	2.446962	2.217137	-0.662521	H	2.298306	0.708073	-0.198601
C	3.396971	1.413320	2.986567	C	2.979545	4.469170	-0.766015
C	-1.492491	6.911082	-6.357294	C	3.271052	-6.718765	-4.928396
H	0.196418	8.249649	-6.138007	H	5.361254	-6.681739	-4.359669
H	0.631320	6.627527	-6.726751	H	4.245637	-6.946615	-2.998603
C	3.937385	3.591553	4.912587	C	5.567291	5.431776	-1.727150
O	5.341334	5.957033	4.424689	O	8.108776	4.371722	-1.173767
O	3.607773	7.322949	3.975762	O	8.305408	3.116672	-3.033384
C	3.269895	0.398880	2.069829	C	1.806333	4.064004	-0.188107
H	3.697391	1.172434	3.996079	H	3.174392	5.526127	-0.874196
H	-2.135979	7.447431	-5.655283	H	3.407910	-6.150656	-5.851953
H	-1.726464	7.256111	-7.368760	H	3.284916	-7.784203	-5.176330
H	-1.716609	5.843886	-6.300170	H	2.293044	-6.479808	-4.505475
O	3.185590	4.338197	5.726414	O	6.048467	5.691604	-2.945878
O	4.761751	2.789113	5.294591	O	5.385263	6.273286	-0.874082
C	5.915470	6.951770	5.329414	C	9.441741	4.933982	-1.387919
C	7.254570	6.423186	5.788541	C	9.750402	5.821312	-0.204441
H	6.011177	7.891924	4.783702	H	10.148523	4.107193	-1.476558
H	5.220369	7.097264	6.158510	H	9.429761	5.487253	-2.328829
H	7.929706	6.280570	4.941010	H	9.749867	5.246723	0.725226
H	7.710087	7.144120	6.472822	H	10.742247	6.262619	-0.334819
H	7.145670	5.471535	6.314337	H	9.022216	6.631325	-0.116825
C	3.414475	4.195595	7.163846	C	6.409008	7.078290	-3.240755
H	3.289784	3.143157	7.424363	H	5.530471	7.701487	-3.065116
H	4.444374	4.489148	7.374799	H	7.196816	7.379468	-2.548048
C	2.410998	5.078497	7.868573	C	6.862791	7.127474	-4.681151
H	1.388277	4.772380	7.634567	H	6.061284	6.813696	-5.354619
H	2.555604	4.995566	8.949177	H	7.142838	8.153387	-4.935240
H	2.537901	6.126011	7.584247	H	7.730636	6.483650	-4.843913
C	3.823941	7.994079	-5.034897	C	7.128473	-5.545563	-1.146064
H	4.506077	8.581984	-4.418351	H	8.064072	-5.096184	-0.808612
H	3.030851	8.647753	-5.402384	H	7.281178	-5.965970	-2.141436
C	4.543318	7.280092	-6.155373	C	6.604362	-6.570962	-0.168134
H	5.016001	8.019499	-6.807569	H	7.332273	-7.382046	-0.078140
H	5.321810	6.620823	-5.763229	H	6.455758	-6.134177	0.822185
H	3.849207	6.686639	-6.755537	H	5.657944	-6.996442	-0.510156
H	-2.517216	2.576557	-2.230410	H	-0.295965	-2.066796	-3.902836
H	-1.538533	3.325076	2.204958	H	0.707877	2.441033	-3.687599
H	-2.437355	-3.039341	2.002739	H	1.155990	-3.865171	-0.114304
H	3.575470	0.958598	-1.951396	H	-0.930266	3.790523	-0.118300
H	3.472895	-0.616270	2.386972	H	1.092578	4.811236	0.135143

Section S4: IR/VCD and UV-vis/ECD spectroscopy

Section S4.1. Materials and methods

Vibrational Circular Dichroism (VCD) and IR spectra measurements

Infrared (IR) and vibrational circular dichroism (VCD) spectra were recorded using a Bruker PMA 50 module coupled to a Vertex 70 Fourier-transform infrared spectrometer. A photoelastic modulator (Hinds PEM-90) set to λ/4 retardation was operated at 50 kHz to modulate the handedness of the circularly polarized light, and the signal was demodulated with an SR830 DSP lock-in amplifier. A low-pass optical filter (< 1800 cm^{-1}), placed upstream of the modulator, was used to improve the signal-to-noise ratio.
A transmission cell fitted with CaF_2 windows and a 200 µm optical pathlength was employed. Solutions (0.09 mol L^{-1}) were prepared by dissolving the solid samples in CD_2Cl_2. The VCD spectra of the first-eluted and second-eluted pure enantiomers of ***D*₃-3** and ***C*₂-3**, respectively, were measured at room temperature. Baseline correction was performed using the standard half-subtraction procedure applied to the spectra of each enantiomer. Approximately 12 000 scans were co-added for each spectrum at 4 cm^{-1} resolution (≈ 3 h acquisition time).
For IR absorption spectra, the reference measurement was obtained using the same cell filled with CD_2Cl_2. All spectra are shown without smoothing or further post-processing.

Electronic Circular Dichroism (ECD) and UV-vis spectra measurements

UV and electronic circular dichroism (ECD) spectra were recorded on a JASCO J-815 spectropolarimeter equipped with a Peltier-controlled cell holder (JASCO PTC-423) maintained at 20.0 °C. A quartz photoelastic modulator set to λ/4 retardation and operated at 50 kHz was used to modulate the handedness of the circularly polarized light. Measurements were conducted in a quartz cell with a 1 mm optical path length. Solutions of the first-eluted and second-eluted enantiomers of ***D*₃-3** and ***C*₂-3** (1 mmol L^{-1}) were prepared by dissolving the isolated solids in HPLC-grade acetonitrile. The ECD spectrometer was continuously purged with nitrogen during data acquisition. UV absorption and ECD spectra were measured using acetonitrile as the reference solvent and are presented without smoothing or additional post-processing. Acquisition parameters were as follows: 0.1 nm data pitch, 100 nm min^{-1} scan speed, and 2 nm bandwidth.

UV-vis/ECD and IR/VCD spectra simulations

To determine the absolute configuration by VCD and ECD, it is necessary to simulate the theoretical spectra using DFT and TD-DFT methods for a selected absolute configuration. The first step in this simulation workflow is a conformational analysis aimed at identifying the most populated conformers, which are then used to generate the Boltzmann-weighted averaged spectra. These calculated spectra are subsequently compared with the experimentally measured ones.

Conformational analysis:
This step was carried out through a stochastic exploration of the potential energy surface (PES) of the (*P,aR,P,aR,P,aR*)-***D*₃-3** and (*P,aR,P,aS,M,aS*)-***C*₂-3** enantiomers. For the random PES exploration of each enantiomer, we employed a simulated annealing procedure combined with the semi-empirical AM1 level of theory. This approach was applied to geometries that were initially optimized using density functional theory (DFT) with the B3LYP functional and the 6-311G(d,p) Gaussian basis set. During the simulated annealing process, only the dihedral angles of the molecules were allowed to vary, while bond lengths and valence angles were kept fixed. This strategy enables rapid identification of the major conformational families.
From the structures generated by this procedure, the lowest-energy geometries were reoptimized at the DFT level using the B3LYP functional and the 6-311G(d,p) basis set. To enhance the agreement between calculated and experimental spectra, solvent effects were included during geometry

optimization using the SMD polarizable continuum model (CH_2Cl_2 for IR/VCD calculations, acetonitrile for UV-vis/ECD calculations). To limit computational cost, this solvation correction was applied only to the conformers selected for spectral averaging, namely those exhibiting Boltzmann populations greater than 5%, as determined at the B3LYP/6-311G(d,p) level (Tables S2 and S3).
Analytical Hessians were computed to obtain unscaled zero-point energies (ZPEs) and thermal corrections at 298.15 K and 1 atm using standard statistical-mechanics relationships for an ideal gas. These parameters provided the relative enthalpies used to compute the conformational weighting factors for generating the Boltzmann-averaged spectra. From the set of converged calculations, the enthalpies of each conformer were extracted and used to determine the corresponding Boltzmann populations.

Table S2. Enthalpies and Boltzmann population of conformations A_1-A_5, for the (*P,aR,P,aR,P,aR*)-***D*₃-3** enantiomer, calculated using the B3LYP/6-311G(d,p) level of theory.

Conformations	H^{298K} (in a.u)	ΔH^{298K} (in kcal mol^{-1})	Boltzmann Distribution
A_1	-5742.606075	0.0	0.79
A_2	-5742.604752	0.8	0.19
A_3	-5742.601891	2.6	0.01
A_4	-5742.60083	3.3	0.00
A_5	-5742.599197	4.3	0.00

Table S3. Enthalpies and Boltzmann population of conformations B_1-B_9, for the (*P,aR,P,aS,M,aS*)-***C*₂-3** enantiomer, calculated using the B3LYP/6-311G(d,p) level of theory.

Conformations	H^{298K} (in a.u)	ΔH^{298K} (in kcal mol^{-1})	Boltzmann Distribution
B_1	-5742.598727	0.0	0.80
B_2	-5742.597354	0.9	0.19
B_3	-5742.594344	2.8	0.01
B_4	-5742.593281	3.4	0.00
B_5	-5742.591486	4.5	0.00
B_6	-5742.59075	5.0	0.00
B_7	-5742.588009	6.7	0.00
B_8	-5742.586412	7.7	0.00
B_9	-5742.585372	8.4	0.00

For both enantiomers, (*P,aR,P,aR,P,aR*)-***D*₃-3** and (*P,aR,P,aS,M,aS*)-***C*₂-3**, two conformations were retained for spectral modelling, denoted A_1 and A_2 for the former, and B_1 and B_2 for the latter. These four conformers were fully optimized while accounting for average solvent effects using the SMD implementation of the IEF-PCM continuum solvation model. Overall, the inclusion of solvent effects only weakly affects the optimized geometries. Therefore, only gas-phase optimized structures are shown in Figure 1. For both ***D*₃-3** and ***C*₂-3**, the molecular core composed of the three helicene units is highly rigid and common to all conformations. The relative orientations of the twelve ethyl ester groups constitute the main source of conformational variability, thereby modulating the relative energies and global properties of the enantiomers.

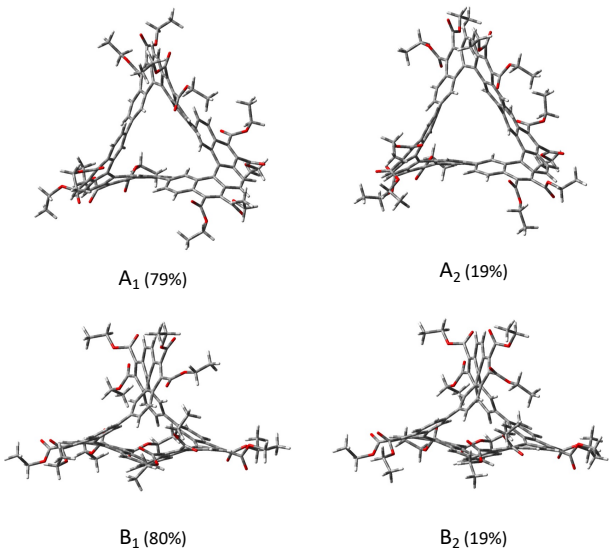


Figure S3. Calculated geometries of conformers A_1/A_2 and B_1/B_2 used for the spectra simulations of (*P,aR,P,aR,P,aR*)-**D_3-3** and (*P,aR,P,aS,M,aS*)-**C_2-3** at the B3LYP/6-311G(d,p) level of theory.

Table S4. Cartesian coordinates in the standard orientation of the conformers A_1, A_2, B_1 and B_2 at the B3LYP/6-311G(d,p) level of theory.

A_1 – (*P,aR,P,aR,P,aR*)-***D_3*-3** Nimag = 0				A_2 – (*P,aR,P,aR,P,aR*)-***D_3*-3** Nimag = 0			
O	3.433618	-2.474243	5.467945	C	-1.358487	-2.806368	0.253394
O	4.849254	-4.229520	5.378261	C	-0.116562	-3.364666	-0.005631
O	-2.623033	-6.737601	-4.430588	C	-1.903344	-2.986384	1.549593
O	-4.471356	-1.206810	5.407844	C	0.563423	-4.179151	0.928813
O	-6.624959	-1.644741	4.889512	H	0.332489	-3.217555	-0.977467
C	1.993025	-3.179531	2.936766	C	-2.149258	-2.143766	-0.815005
H	1.820896	-3.483859	3.959796	C	-1.278545	-3.782224	2.476967
C	4.280874	-3.310711	4.839817	H	-2.864140	-2.551384	1.798219
C	2.127897	-3.722298	7.138264	C	-0.070103	-4.457711	2.172453
H	1.954474	-3.820515	8.213789	C	1.784938	-4.880517	0.575611
H	1.186973	-3.418118	6.673724	C	-3.123448	-1.202092	-0.523675
H	2.415181	-4.701853	6.752790	C	-2.010553	-2.545684	-2.166087
C	1.150948	-2.928269	0.672181	H	-1.739691	-3.929320	3.444337
C	3.219518	-2.696698	6.886483	C	0.460861	-5.496584	3.012070
H	2.942371	-1.713354	7.265735	C	2.079669	-6.080649	1.265426
H	4.164074	-3.005766	7.334575	C	2.635756	-4.491573	-0.521463
C	0.958449	-3.252872	2.037956	C	-4.023143	-0.708710	-1.496431
H	0.002574	-3.638048	2.372677	H	-3.240446	-0.865453	0.496666
C	2.393425	-2.442856	0.295343	C	-2.870644	-2.091732	-3.135220
H	2.560539	-2.173271	-0.737742	H	-1.263266	-3.282159	-2.437143
O	-0.402853	9.006123	2.476962	C	1.454721	-6.323131	2.543486
O	-1.183106	7.601799	4.062669	C	-0.171747	-5.717856	4.357671
C	-7.054042	-1.203526	6.202992	C	2.977384	-7.010531	0.664351
H	-7.983955	-1.746343	6.373758	C	3.376013	-5.495656	-1.189339
H	-6.310057	-1.514601	6.936831	C	2.878924	-3.109848	-0.897147
C	-2.305068	-7.298620	-5.730360	C	-3.935243	-1.209708	-2.827183
H	-2.958698	-8.167500	-5.810290	C	-5.143655	0.136959	-1.123035
H	-2.568730	-6.571674	-6.498985	H	-2.762522	-2.458420	-4.145647
C	-0.591015	7.886189	2.884595	C	1.966618	-7.458699	3.385737
C	-7.273601	0.298700	6.235342	O	-0.574104	-6.994731	4.509264
H	-7.690846	0.593150	7.202719	O	-0.344401	-4.856053	5.182726
H	-6.333356	0.834169	6.095597	C	3.514499	-6.770282	-0.566818
H	-7.973407	0.605553	5.454841	H	3.163048	-7.955414	1.154127
C	-5.718130	-5.490339	6.978712	C	3.969024	-5.191998	-2.468756
H	-6.263464	-6.080612	7.719964	C	2.683082	-2.051118	0.019487
H	-4.827517	-6.049759	6.684687	C	3.503740	-2.821847	-2.143194

H	-5.394906	-4.560200	7.451160	C	-5.004475	-0.933066	-3.754382
C	-6.604412	-5.217611	5.781950	C	-6.294372	0.091703	-1.943175
H	-7.500547	-4.651767	6.047711	C	-5.199025	0.910441	0.091102
H	-6.928940	-6.136333	5.289283	O	2.327455	-7.018591	4.608374
C	-2.003405	7.905127	-6.100920	O	2.083470	-8.602277	3.018695
H	-3.047408	7.974201	-6.415870	C	-1.175077	-7.330656	5.783472
H	-1.742982	8.847252	-5.614364	H	4.124992	-7.525416	-1.040851
C	-1.074443	7.576192	-7.250230	C	3.968168	-3.908860	-2.962610
H	-1.130204	8.359593	-8.010812	C	4.522550	-6.328807	-3.283666
H	-0.040010	7.505647	-6.907428	C	3.050666	-0.743596	-0.258009
H	-1.343304	6.625751	-7.716138	H	2.277502	-2.287815	0.992672
O	-1.974587	-4.686780	-5.118574	C	3.759638	-1.466008	-2.467310
C	2.898720	8.530486	5.583045	C	-6.179788	-0.394122	-3.290703
H	3.305717	8.773647	6.568211	C	-4.932917	-1.304896	-5.206884
H	3.727925	8.474081	4.874701	C	-7.537539	0.533759	-1.409142
H	2.242178	9.345784	5.271886	C	-6.464504	1.165332	0.671011
O	6.994136	-2.397568	4.748564	C	-4.042710	1.557873	0.684598
C	8.048902	-2.688837	5.699050	C	2.827107	-8.008119	5.544348
H	9.002302	-2.709509	5.167667	C	-1.621893	-8.775281	5.708061
H	7.868821	-3.685809	6.106947	H	-2.007947	-6.648629	5.966027
C	8.009973	-1.614526	6.764818	H	-0.434793	-7.163965	6.569779
H	8.795615	-1.793832	7.503659	C	4.542169	-3.590706	-4.314158
H	8.169157	-0.625177	6.329999	O	3.926759	-6.387237	-4.490717
H	7.048943	-1.609740	7.283748	O	5.350994	-7.119736	-2.906201
O	7.728239	-4.068601	3.425763	C	3.544185	-0.461968	-1.556748
C	6.912000	-3.221104	3.689097	C	3.047045	0.306375	0.792822
C	-2.942628	9.235724	4.551971	H	4.171418	-1.220804	-3.436787
H	-3.239483	10.019141	5.255357	C	-7.339994	-0.164908	-4.233168
H	-2.961311	9.658656	3.546460	O	-3.726739	-1.040533	-5.742289
H	-3.678399	8.430391	4.608328	O	-5.863729	-1.750472	-5.835748
C	-1.555662	8.725604	4.901214	C	-7.635478	0.952955	-0.114771
H	-0.803753	9.507677	4.793263	H	-8.430277	0.468583	-2.017260
H	-1.520571	8.323442	5.913961	C	-6.525724	1.640272	2.032382
C	-0.841566	-7.694139	-5.816795	C	-2.898183	1.861568	-0.087569
H	-0.649421	-8.204286	-6.765158	C	-4.126565	2.069861	2.010128
H	-0.195585	-6.816269	-5.768798	C	4.325015	-8.203586	5.389751
H	-0.574234	-8.373403	-5.004274	H	2.576083	-7.597642	6.522647
C	-4.734419	4.940114	-6.582838	H	2.284584	-8.941167	5.390216
H	-3.922784	4.731891	-7.280437	H	-0.778064	-9.440429	5.512674
H	-5.149985	5.926412	-6.790469	H	-2.082638	-9.073128	6.653744
C	-5.804241	3.863774	-6.636733	H	-2.355329	-8.915209	4.911169
H	-6.274956	3.856021	-7.624137	O	5.763308	-4.140466	-4.471715
H	-5.374632	2.876715	-6.459460	O	3.999535	-2.899343	-5.140553
H	-6.580111	4.049887	-5.890734	C	4.389549	-7.430392	-5.382876
C	9.992882	-1.490822	-3.646779	H	3.828236	0.549756	-1.820733
H	10.631071	-0.608658	-3.596720	C	2.971376	1.653514	0.474596
H	9.744751	-1.697400	-4.687974	C	3.238684	-0.036914	2.154747
C	10.646165	-2.692689	-2.986682	O	-8.313510	-1.068330	-4.039518
H	11.585086	-2.929606	-3.495480	O	-7.384188	0.743922	-5.021767
H	10.875519	-2.489381	-1.937834	C	-3.575563	-1.279311	-7.166927
H	10.000798	-3.570380	-3.045277	H	-8.600994	1.212329	0.295507
O	4.625148	0.027303	-5.345900	C	-5.387030	2.010393	2.707030
C	2.662361	1.570088	-0.640059	C	-7.870779	1.622747	2.708201
C	-3.629383	-3.880121	-0.390810	C	-1.844348	2.616349	0.402617
O	6.853039	0.129186	-5.032751	H	-2.875219	1.532743	-1.116579
O	-5.292983	-5.607208	-4.300472	C	-2.992281	2.733572	2.541693
C	-3.097993	0.417635	0.420685	H	4.853225	-7.252756	5.489776
C	-2.530060	3.403821	-2.640901	H	4.694025	-8.882142	6.164354
C	-2.755110	1.383730	-0.654439	H	4.563845	-8.637486	4.417649
C	2.758266	1.900265	-2.014237	C	6.421107	-3.933305	-5.747871
H	2.214874	2.752397	-2.405374	C	3.549407	-7.358148	-6.640286
C	5.506340	-0.387494	-3.156925	H	4.291755	-8.391505	-4.874175
C	-1.874722	-4.220695	-2.116396	H	5.451740	-7.269268	-5.582060
C	3.480500	-2.350127	1.194657	C	3.180591	2.675862	1.428917
C	-3.161126	1.146812	-1.991770	H	2.797277	1.942126	-0.552095
H	-3.635955	0.209513	-2.256110	C	3.458129	0.927950	3.105719
C	-4.178856	-3.189538	0.749131	H	3.287049	-1.078389	2.449543
C	0.846577	4.452256	2.007219	C	-9.433697	-1.024433	-4.963012
C	4.419338	0.159841	-2.380371	C	-3.219072	-2.725769	-7.462791
C	-0.776093	6.452450	0.807528	H	-2.776174	-0.599395	-7.460334
C	3.368008	0.462584	-0.197748	H	-4.500400	-0.987559	-7.664562

H	3.294241	0.171527	0.840363	C	-5.426827	2.468639	4.137342
C	0.878848	3.253908	-0.115886	O	-7.866421	0.783235	3.761311
H	0.513768	3.153491	-1.128030	O	-8.848823	2.214769	2.325273
C	0.091047	-3.219928	-0.326394	C	-1.891848	3.000721	1.765464
C	-1.989028	3.614994	-1.341292	C	-0.762530	3.111068	-0.486612
C	3.293166	-2.784735	2.537259	H	-3.007987	3.073294	3.567606
C	-3.829510	-1.825688	1.105857	C	7.221598	-2.642907	-5.751668
C	-0.522023	-4.077393	-2.514962	H	7.067763	-4.804226	-5.856907
H	-0.224945	-4.390489	-3.506529	H	5.666892	-3.937972	-6.535205
C	-1.248962	-3.242327	0.026767	H	3.651359	-6.386402	-7.128261
H	-1.534859	-2.932699	1.021841	H	3.865867	-8.131444	-7.345364
C	0.429319	-3.596355	-1.650265	H	2.492918	-7.515074	-6.412668
H	1.463985	-3.577137	-1.971572	C	3.508426	2.302196	2.762697
C	0.302951	4.249240	0.707384	C	3.257610	4.072578	1.037998
C	-1.481706	4.927747	-0.982449	H	3.636115	0.629896	4.129877
C	-0.686119	5.180361	0.193352	C	-10.507066	-0.052565	-4.504890
C	-3.296719	-0.927815	0.152273	H	-9.798886	-2.051143	-4.977661
H	-3.087376	-1.302556	-0.839369	H	-9.052066	-0.764858	-5.950222
C	-4.200286	-1.318271	2.382854	H	-2.301469	-3.019564	-6.947322
C	-2.258384	-3.718151	-0.841220	H	-3.055725	-2.852884	-8.536926
C	3.602365	1.216740	-2.854691	H	-4.025459	-3.396414	-7.162431
H	3.676875	1.520753	-3.888644	O	-6.436774	3.334063	4.358708
C	2.362565	2.585921	1.646710	O	-4.618104	2.152023	4.975402
H	3.172539	1.969095	2.017540	C	-9.133698	0.611184	4.443051
C	4.239779	-0.269987	-1.035296	H	-1.081686	3.579242	2.193465
O	0.884565	4.940859	5.014272	C	0.489538	3.443939	0.006228
C	1.930069	2.453334	0.303189	C	-1.018800	3.365550	-1.857265
C	-1.814924	7.338291	-1.198904	H	7.930807	-2.623617	-4.921183
H	-2.185833	8.181536	-1.763656	H	7.786229	-2.557816	-6.684700
C	4.441709	-2.946582	3.389239	H	6.564670	-1.775297	-5.673846
C	-3.347376	0.867241	1.741808	C	4.000889	3.303098	3.670732
H	-3.189829	1.907996	1.998700	C	4.028885	4.941166	1.846291
O	1.634401	6.948379	4.316846	C	2.704150	4.588013	-0.189496
O	-5.519284	-7.193337	-2.716626	H	-10.862489	-0.302998	-3.502115
C	6.461730	-1.158943	-2.537838	H	-11.362547	-0.097268	-5.185327
C	-4.997421	-2.135760	3.257555	H	-10.131387	0.971714	-4.502411
C	1.836443	3.549576	2.469875	C	-6.492033	3.951085	5.671595
H	2.215610	3.648828	3.478032	C	-8.939051	-0.447114	5.507680
C	-1.901911	6.031720	-1.761645	H	-9.885221	0.321683	3.705661
C	-3.876705	0.027168	2.689378	H	-9.438004	1.573290	4.860688
H	-4.089126	0.412049	3.677499	C	1.463890	4.108780	-0.773806
C	-2.133281	2.591177	-0.376545	H	0.718907	3.235848	1.041580
H	-1.788408	2.785811	0.628868	C	-0.102435	4.021628	-2.640372
C	-4.033103	-5.331637	-2.337645	H	-1.980467	3.108301	-2.285087
C	-4.421109	-4.863887	-1.029290	C	4.316413	4.558236	3.206905
C	0.473302	5.625987	2.748429	C	4.257322	2.910095	5.098172
C	4.816446	-2.016811	0.731587	C	4.502229	6.161124	1.281221
C	-5.207315	-3.820747	1.488203	C	3.328182	5.705635	-0.793053
C	-1.372018	7.522444	0.078418	C	-7.187862	3.079251	6.701139
H	-1.391505	8.510698	0.514529	H	-7.035279	4.879572	5.497383
C	-3.049112	2.121950	-2.950883	H	-5.472364	4.182332	5.981867
H	-3.401040	1.920275	-3.953295	H	-8.624009	-1.393400	5.062806
C	-2.830314	-4.964013	-2.892934	H	-9.878455	-0.615950	6.040953
C	-2.411552	5.796219	-3.090296	H	-8.182856	-0.143670	6.234400
C	-5.540527	-3.311562	2.796100	C	1.130727	4.474519	-2.108592
C	5.085037	-1.322768	-0.501764	H	-0.344603	4.233047	-3.672898
C	-6.207268	-6.335657	-5.155961	C	4.902757	5.593312	4.127923
H	-7.131495	-6.515767	-4.603241	O	5.505260	3.245797	5.483816
H	-5.765372	-7.308213	-5.385598	O	3.464448	2.332922	5.800282
C	-5.569594	-5.364202	-0.349188	C	4.250657	6.472412	-0.023157
H	-6.148260	-6.155722	-0.803277	H	5.139518	6.803661	1.871655
C	6.300811	-1.588203	-1.173006	C	3.002755	6.034340	-2.159345
O	-5.831534	-4.436556	4.837965	H	-8.212966	2.853972	6.400463
C	-2.650462	4.519462	-3.540688	H	-7.227001	3.606489	7.658907
C	-0.254626	6.622420	2.142217	H	-6.645846	2.144944	6.850345
C	5.704034	-2.907530	2.847011	C	1.983665	5.389109	-2.819067
C	-5.881715	-4.934214	0.907635	O	4.114252	5.776894	5.204520
H	-6.706720	-5.386872	1.438765	O	5.913191	6.218678	3.922059
O	-4.180435	5.065346	-5.248002	C	5.874352	2.948960	6.854918
O	-3.266592	7.955409	-3.742718	H	4.688665	7.360434	-0.455753
O	7.568159	-2.606966	-4.101040	C	3.856216	7.049502	-2.869366

O	-7.538471	-4.534147	3.370794	C	1.665085	5.694610	-4.255460
O	8.782857	-1.083527	-2.956325	C	4.580543	6.737374	6.183520
O	-2.694239	3.419861	-5.674606	C	6.425036	1.539770	6.984768
C	-5.300746	-1.622596	4.636622	H	6.631350	3.696559	7.092884
C	-2.436353	-5.411681	-4.272558	H	5.002074	3.097315	7.492005
C	5.586071	-0.063913	-4.619649	O	4.398692	6.522417	-3.984230
O	-1.887212	6.837070	-5.129246	O	4.075872	8.170365	-2.482330
C	7.331591	-2.279949	-0.474937	O	1.582264	7.023377	-4.468538
H	8.278435	-2.459846	-0.965259	O	1.468674	4.859455	-5.103511
C	7.642779	-1.704018	-3.307069	C	3.522671	6.836140	7.262064
C	-5.010519	-6.173602	-3.111414	H	4.749942	7.691668	5.680788
C	0.989106	5.777253	4.151925	H	5.542039	6.394744	6.573433
C	5.910209	-2.524117	1.472733	H	7.258759	1.383866	6.296497
C	-6.439783	-4.139430	3.672981	H	6.787873	1.374398	8.003399
C	7.178358	-2.637757	0.832438	H	5.652833	0.797740	6.776503
H	8.000266	-3.091753	1.367691	C	5.228163	7.409788	-4.773466
C	-2.604389	6.980285	-3.998132	C	1.304997	7.459056	-5.824243
C	-6.433650	-5.497406	-6.396197	H	3.359004	5.870214	7.744693
H	-7.120457	-6.011729	-7.073746	H	3.834612	7.553434	8.025928
H	-6.868730	-4.529499	-6.138419	H	2.571233	7.173026	6.845130
H	-5.496921	-5.317836	-6.928160	C	5.782652	6.604466	-5.929376
C	-3.142267	4.262511	-4.937188	H	6.015925	7.810783	-4.132567
C	7.051521	0.358267	-6.453242	H	4.615206	8.250309	-5.107673
H	6.282405	1.049164	-6.800130	C	-0.189211	7.526865	-6.086064
H	8.023274	0.849776	-6.500617	H	1.765790	8.445248	-5.884708
C	7.033341	-0.937110	-7.246623	H	1.802171	6.780853	-6.518217
H	7.289270	-0.731091	-8.290245	H	4.980294	6.202336	-6.551673
H	7.753298	-1.653746	-6.847753	H	6.417708	7.237830	-6.554556
H	6.043806	-1.394398	-7.222828	H	6.384363	5.767721	-5.568266
C	2.149617	7.216136	5.643465	H	-0.684683	8.159985	-5.346690
H	1.309229	7.247117	6.341270	H	-0.374630	7.950728	-7.077288
H	2.793608	6.385990	5.940737	H	-0.637258	6.532588	-6.054644

Table S4 (continued). Cartesian coordinates in the standard orientation of the conformers A_1, A_2, B_1 and B_2 at the B3LYP/6-311G(d,p) level of theory.

B_1 – (*P,aR,P,aS,M,aS*)-***C*$_2$-3** Nimag = 0				B_2 – (*P,aR,P,aS,M,aS*)-***C*$_2$-3** Nimag = 0			
C	0.126593	2.257834	0.839180	C	0.198653	1.985532	1.491814
C	0.204284	1.334752	1.866080	C	0.367916	0.841275	2.251719
C	-1.095987	2.960888	0.671639	C	-1.044136	2.669281	1.583033
C	-0.840897	1.163373	2.804464	C	-0.602306	0.409287	3.186012
H	1.130805	0.798980	2.024834	H	1.314217	0.317898	2.213497
C	-2.116802	2.840077	1.584701	C	-1.987488	2.291820	2.508243
H	-1.226195	3.635104	-0.167280	H	-1.250979	3.518761	0.942141
C	-1.983663	2.008129	2.727316	C	-1.758061	1.205761	3.390065
C	-0.688682	0.275361	3.935611	C	-0.356191	-0.710455	4.068109
H	-3.003520	3.445997	1.466639	H	-2.898587	2.872909	2.592540
C	-2.892043	2.039506	3.845216	C	-2.578832	0.954634	4.541279
C	-1.394790	0.573009	5.122184	C	-0.965029	-0.707261	5.343442
C	0.231918	-0.825293	3.935008	C	0.565157	-1.756614	3.736252
C	-2.541725	1.439560	5.038770	C	-2.144446	0.109702	5.538037
C	-4.224177	2.720243	3.705257	C	-3.855656	1.745569	4.673260
C	-0.922352	0.006225	6.344880	C	-0.398632	-1.539217	6.355159
C	0.796023	-1.239265	5.159637	C	1.220312	-2.442484	4.780289
C	0.510763	-1.611344	2.752477	C	0.760348	-2.225235	2.380372
C	-3.353894	1.677667	6.281075	C	-2.900157	0.000882	6.829709
O	-5.196504	1.943029	4.225105	O	-4.778772	1.270379	3.820099
O	-4.437999	3.780015	3.165828	O	-4.018964	2.693738	5.398346
C	0.191622	-0.784058	6.369930	C	0.711172	-2.297617	6.103741
H	-1.441054	0.223362	7.267634	H	-0.813007	-1.511938	7.351784
C	1.949886	-2.099469	5.128744	C	2.373494	-3.242360	4.460386
C	-0.428480	-1.684395	1.694921	C	-0.257385	-2.072893	1.405046
C	1.640340	-2.476146	2.736793	C	1.898966	-3.021990	2.076225
O	-3.686479	0.833020	7.075070	O	-2.389315	-0.074336	7.921876
O	-3.625537	2.991487	6.433798	O	-4.232188	-0.022614	6.628864
C	-6.543465	2.468600	4.193343	C	-6.078044	1.905218	3.851402

H	0.567452	-1.149020	7.316104	H	1.163640	-2.861571	6.908253
C	2.417437	-2.626086	3.944529	C	2.761932	-3.445123	3.154707
C	2.657465	-2.359260	6.434589	C	3.168165	-3.805164	5.611648
C	-0.258633	-2.530616	0.615553	C	-0.154464	-2.626758	0.142803
H	-1.356833	-1.137319	1.790661	H	-1.186013	-1.600098	1.696932
C	1.864520	-3.242054	1.563714	C	2.050589	-3.464953	0.737429
C	-7.448692	1.428905	4.820423	C	-6.937949	1.219138	2.811145
H	-6.560752	3.417568	4.735212	H	-6.488232	1.800027	4.858519
H	-6.812644	2.674418	3.155385	H	-5.953307	2.972633	3.653802
C	3.656663	-3.478044	3.989354	C	4.010876	-4.244906	2.904713
O	3.892738	-1.832197	6.432556	O	4.393124	-3.258606	5.672349
O	2.150392	-2.905876	7.381490	O	2.729749	-4.590221	6.414051
C	0.952874	-3.263271	0.536431	C	1.064456	-3.267177	-0.197540
H	2.761686	-3.836746	1.480103	H	2.950252	-3.986702	0.447815
H	-7.153734	1.218079	5.850536	H	-7.012879	0.149001	3.014766
H	-8.481985	1.786214	4.823566	H	-7.946701	1.640571	2.819181
H	-7.411910	0.492369	4.260185	H	-6.520344	1.348200	1.810621
O	4.445096	-3.289218	2.919224	O	4.720534	-3.772851	1.866992
O	3.918995	-4.233631	4.896031	O	4.346397	-5.193521	3.575145
C	4.707407	-2.122196	7.595017	C	5.283562	-3.807927	6.674634
C	6.031739	-1.412627	7.409718	C	6.583633	-3.036116	6.598546
H	4.177929	-1.783033	8.487749	H	4.807107	-3.719677	7.653157
H	4.822542	-3.206080	7.662548	H	5.417584	-4.870110	6.459132
H	6.680474	-1.602869	8.269036	H	6.421000	-1.973861	6.794395
H	6.542995	-1.764890	6.511260	H	7.288057	-3.417322	7.342832
H	5.889383	-0.333203	7.321204	H	7.041638	-3.135931	5.612129
C	5.678400	-4.060125	2.858892	C	5.958304	-4.464925	1.538961
H	6.297659	-3.501105	2.160515	H	6.519064	-3.732033	0.963239
H	6.133098	-4.053897	3.850099	H	6.479786	-4.690714	2.469732
C	5.441415	-5.474601	2.361969	C	5.708792	-5.719164	0.721279
H	5.008931	-5.461959	1.360292	H	5.199632	-5.473855	-0.212528
H	6.398400	-5.999995	2.296809	H	6.666801	-6.177005	0.459502
H	4.792036	-6.029397	3.040655	H	5.121931	-6.448180	1.281846
C	-4.414797	3.353322	7.591456	C	-5.072420	-0.049368	7.813815
H	-3.929739	2.952461	8.483703	H	-4.637250	-0.750414	8.526695
H	-5.394445	2.875699	7.507875	H	-6.018015	-0.450397	7.448681
C	-4.511894	4.864220	7.619520	C	-5.241305	1.331575	8.423875
H	-3.521320	5.316398	7.702120	H	-5.604595	2.047434	7.684748
H	-4.984126	5.246581	6.711906	H	-5.961630	1.282809	9.246065
H	-5.107323	5.184560	8.478674	H	-4.295152	1.700204	8.821011
C	-1.355244	-2.787048	-0.352814	C	-1.311973	-2.707396	-0.786901
C	-2.219835	-1.808286	-0.825366	C	-2.233569	-1.688911	-0.997611
C	-1.573768	-4.123428	-0.765840	C	-1.511841	-3.935063	-1.462824
C	-3.315693	-2.109954	-1.674854	C	-3.358891	-1.846805	-1.850559
H	-2.053568	-0.776482	-0.540939	H	-2.086284	-0.736483	-0.503390
C	-2.663047	-4.461165	-1.525424	C	-2.625524	-4.150240	-2.229858
C	-3.592528	-3.482246	-1.950883	C	-3.601684	-3.141199	-2.404478
C	-4.228718	-1.090971	-2.183869	C	-4.325172	-0.779505	-2.110212
H	-2.832211	-5.498041	-1.779993	H	-2.775015	-5.116264	-2.690312
C	-4.853788	-3.855617	-2.531876	C	-4.869887	-3.439316	-3.014475
C	-5.556776	-1.516151	-2.455369	C	-5.642213	-1.194182	-2.447135
C	-3.909570	0.313234	-2.390365	C	-4.070668	0.651107	-2.024331
C	-5.840276	-2.913831	-2.665849	C	-5.887458	-2.526507	-2.930834
C	-5.072059	-5.287317	-2.928299	C	-5.068918	-4.762553	-3.694465
C	-6.588974	-0.544275	-2.554110	C	-6.715985	-0.271061	-2.342881
C	-4.981593	1.249071	-2.362600	C	-5.182628	1.520518	-1.824795
C	-2.593701	0.816973	-2.775819	C	-2.777563	1.280864	-2.282142
C	-7.190455	-3.314005	-3.209798	C	-7.243991	-2.852725	-3.510474
O	-6.229098	-5.776744	-2.444844	O	-6.242045	-5.328796	-3.353890
O	-4.288422	-5.929221	-3.584613	O	-4.272532	-5.263942	-4.450732
C	-6.324213	0.781012	-2.401086	C	-6.504744	1.012261	-1.948462
H	-7.610153	-0.866042	-2.698054	H	-7.725232	-0.607801	-2.533117
C	-4.705823	2.665486	-2.339563	C	-4.973062	2.916573	-1.525024
C	-1.505312	-0.026674	-3.091022	C	-1.667752	0.580511	-2.805621
C	-2.385466	2.224069	-2.911345	C	-2.619003	2.684128	-2.071042
O	-7.363557	-3.746596	-4.320865	O	-7.456978	-2.967519	-4.690562
O	-8.171597	-3.097399	-2.314285	O	-8.175919	-2.980232	-2.548858
C	-6.579349	-7.130053	-2.838587	C	-6.610461	-6.548901	-4.049028
H	-7.130593	1.498359	-2.420942	H	-7.343257	1.681975	-1.832973
C	-3.443693	3.136118	-2.596098	C	-3.720098	3.467426	-1.599455
C	-5.797933	3.626625	-1.953227	C	-6.138288	3.781612	-1.131610

C	-0.244835	0.451786	-3.413563	C	-0.429879	1.168859	-3.016602
C	-1.133938	2.694608	-3.380813	C	-1.385360	3.298100	-2.400184
C	-5.973002	-8.154066	-1.895510	C	-6.066822	-7.774607	-3.336837
H	-7.668014	-7.144380	-2.797303	H	-7.700504	-6.534553	-4.048881
H	-6.255501	-7.286986	-3.867125	H	-6.250379	-6.485791	-5.075566
C	-3.141086	4.609193	-2.577180	C	-3.462489	4.904835	-1.238144
O	-5.360449	4.450106	-0.978474	O	-5.878437	4.446757	0.014790
O	-6.914991	3.657704	-2.409321	O	-7.174732	3.882502	-1.741295
C	-0.087837	1.842118	-3.612433	C	-0.318579	2.568549	-2.850118
H	-0.985934	3.756065	-3.524428	H	-1.273280	4.366948	-2.274871
H	-6.332798	-9.154488	-2.153061	H	-6.439602	-8.681770	-3.821303
H	-4.884571	-8.157296	-1.968783	H	-4.976652	-7.795594	-3.372726
H	-6.255801	-7.946808	-0.860816	H	-6.384793	-7.791553	-2.291811
O	-3.974715	5.291137	-3.382402	O	-4.195564	5.747084	-1.985394
O	-2.240099	5.115162	-1.950187	O	-2.658773	5.264299	-0.411333
C	-6.273511	5.474509	-0.503568	C	-6.854239	5.438877	0.431124
H	0.863552	2.242543	-3.943248	H	0.611808	3.074619	-3.078923
C	-7.064633	4.979530	0.693283	C	-7.972722	4.824908	1.253021
H	-5.622949	6.306543	-0.233309	H	-6.271315	6.148051	1.019085
H	-6.923890	5.769763	-1.326802	H	-7.243115	5.935496	-0.458305
H	-7.721396	4.154354	0.409482	H	-8.562833	4.130707	0.653690
H	-6.394000	4.649140	1.488955	H	-7.572607	4.293821	2.119107
H	-7.689086	5.788950	1.083445	H	-8.638740	5.612695	1.616735
C	-3.827280	6.734737	-3.423594	C	-4.028539	7.162587	-1.716398
H	-4.829726	7.095660	-3.653689	H	-4.315652	7.353655	-0.679894
H	-3.532611	7.083887	-2.433857	H	-2.970175	7.411698	-1.816310
C	-2.825831	7.154759	-4.484680	C	-4.891593	7.917247	-2.704742
H	-3.097963	6.745280	-5.459998	H	-5.944437	7.648121	-2.596780
H	-2.805925	8.245362	-4.566383	H	-4.793869	8.993339	-2.538748
H	-1.820251	6.816456	-4.229387	H	-4.589539	7.700650	-3.731465
C	-9.532607	-3.363134	-2.746454	C	-9.514432	-3.343486	-2.978410
H	-9.631621	-3.066313	-3.791181	H	-9.932749	-3.865260	-2.117756
H	-10.137944	-2.704061	-2.123768	H	-9.432347	-4.035254	-3.816835
C	-9.910543	-4.819135	-2.546189	C	-10.339350	-2.123702	-3.350396
H	-9.341320	-5.462069	-3.217938	H	-10.402484	-1.421251	-2.515716
H	-9.724158	-5.129899	-1.515813	H	-9.912562	-1.611286	-4.214012
H	-10.974279	-4.958619	-2.759782	H	-11.357116	-2.429779	-3.609152
H	1.165492	-3.866418	-0.337812	H	1.221797	-3.629167	-1.206082
H	-0.912261	-4.904801	-0.411082	H	-0.809197	-4.745617	-1.310778
H	-1.631475	-1.091571	-3.006518	H	-1.762924	-0.474757	-2.992306
C	1.324406	2.623240	0.038433	C	1.330419	2.576139	0.730265
C	2.309835	1.719946	-0.346755	C	2.309107	1.827274	0.084460
C	1.513441	3.991959	-0.272357	C	1.466642	3.985810	0.742645
C	3.502943	2.128434	-0.997369	C	3.443862	2.422394	-0.525511
H	2.167475	0.665658	-0.143108	H	2.206412	0.749912	0.043497
C	2.684270	4.428611	-0.832505	C	2.583587	4.587092	0.227058
C	3.726551	3.528482	-1.155094	C	3.620346	3.828925	-0.365769
C	4.556926	1.200855	-1.406897	C	4.489216	1.658176	-1.206679
H	2.830491	5.489870	-0.985429	H	2.694553	5.659780	0.321599
C	5.027225	4.011525	-1.516368	C	4.877405	4.436529	-0.690381
C	5.879782	1.723912	-1.422572	C	5.793303	2.227989	-1.191071
C	4.376820	-0.199631	-1.757016	C	4.321436	0.367058	-1.856598
C	6.092409	3.149341	-1.529136	C	5.960214	3.647522	-0.977377
C	5.229528	5.492492	-1.710242	C	5.023050	5.928800	-0.540276
C	6.981948	0.825398	-1.375816	C	6.920501	1.393315	-1.430710
C	5.500427	-1.064379	-1.659284	C	5.473190	-0.444532	-2.038815
C	3.167942	-0.759498	-2.353767	C	3.087667	-0.099698	-2.482354
C	7.491471	3.669964	-1.713826	C	7.325821	4.259688	-1.129650
O	4.571271	5.925672	-2.800901	O	4.274530	6.577747	-1.449718
O	5.876990	6.196279	-0.976695	O	5.694110	6.472757	0.299572
C	6.786096	-0.519589	-1.396265	C	6.760235	0.081859	-1.749278
H	7.979890	1.223337	-1.271000	H	7.911992	1.801251	-1.305940
C	5.352755	-2.479385	-1.856232	C	5.354490	-1.780839	-2.548197
C	2.102541	0.050658	-2.795477	C	1.968206	0.739405	-2.650687
C	3.059040	-2.166516	-2.584545	C	3.004155	-1.419746	-3.026102
O	8.439196	3.351516	-1.036635	O	8.333474	3.831583	-0.620355
O	7.567425	4.518310	-2.755576	O	7.293994	5.338252	-1.933836
C	4.696525	7.332944	-3.132015	C	4.321932	8.025385	-1.406105
H	7.638790	-1.177757	-1.304736	H	7.634650	-0.542477	-1.871689
C	4.158613	-3.027451	-2.248534	C	4.151883	-2.283281	-2.974436
C	6.515167	-3.387552	-1.525874	C	6.573560	-2.675012	-2.527779

C	0.924641	-0.453769	-3.322486	C	0.769504	0.318699	-3.203303
H	2.177207	1.114626	-2.660560	H	2.025096	1.745646	-2.277801
C	1.893403	-2.662519	-3.222206	C	1.809886	-1.806215	-3.686157
C	3.683849	8.182279	-2.383522	C	3.368885	8.542038	-2.462865
H	5.716709	7.651415	-2.917239	H	4.049468	8.356356	-0.401490
H	4.529090	7.363465	-4.208571	H	5.350757	8.341910	-1.591145
C	4.099949	-4.519824	-2.410878	C	4.130997	-3.704958	-3.459180
O	7.486200	-3.308493	-2.443919	O	7.412165	-2.392493	-3.530988
O	6.559261	-4.068226	-0.528954	O	6.763167	-3.519790	-1.685621
C	0.845766	-1.843412	-3.561502	C	0.716608	-0.979639	-3.756787
H	1.818547	-3.719812	-3.434044	H	1.751141	-2.787323	-4.135271
H	3.755271	9.222205	-2.715144	H	3.382321	9.635119	-2.475684
H	2.664908	7.837052	-2.574406	H	3.654111	8.184265	-3.454430
H	3.871288	8.158459	-1.308903	H	2.345988	8.215392	-2.262801
O	2.986390	-5.071144	-1.888176	O	3.050981	-4.396843	-3.042287
O	4.975124	-5.171490	-2.928656	O	5.009723	-4.199092	-4.124166
C	8.643490	-4.173122	-2.271611	C	8.558983	-3.269246	-3.699358
C	8.433309	-5.499021	-2.979328	C	9.745430	-2.810752	-2.870034
H	9.465762	-3.606300	-2.708972	H	8.254319	-4.283232	-3.442061
H	8.822557	-4.307274	-1.204911	H	8.768970	-3.217706	-4.767254
H	7.596724	-6.046195	-2.544602	H	10.020320	-1.781262	-3.112258
H	8.222859	-5.343618	-4.039232	H	9.527793	-2.876992	-1.802826
H	9.336064	-6.110965	-2.891204	H	10.610351	-3.447315	-3.078053
C	2.896288	-6.518685	-1.991146	C	3.000639	-5.789420	-3.457184
H	2.970356	-6.794940	-3.044770	H	3.034867	-5.825711	-4.547877
H	3.754724	-6.951315	-1.474122	H	3.894712	-6.290178	-3.081448
C	1.582096	-6.948896	-1.376624	C	1.729299	-6.394725	-2.902841
H	0.734064	-6.506621	-1.904097	H	0.844822	-5.881059	-3.286153
H	1.487599	-8.036213	-1.437500	H	1.664178	-7.445072	-3.198515
H	1.525223	-6.663693	-0.323942	H	1.712782	-6.349608	-1.811794
C	8.866386	5.115910	-3.018864	C	8.548458	6.048238	-2.126140
H	8.801052	5.417866	-4.064153	H	8.393488	6.591575	-3.058291
H	9.625883	4.339949	-2.916330	H	9.339400	5.310924	-2.268059
C	9.154991	6.295292	-2.106667	C	8.863872	6.983274	-0.971730
H	10.101210	6.759187	-2.401261	H	9.764532	7.558761	-1.206017
H	8.367066	7.047331	-2.169958	H	8.044360	7.680461	-0.790998
H	9.239113	5.975125	-1.068195	H	9.044062	6.423918	-0.053711
H	0.754123	4.713562	0.003227	H	0.715444	4.592437	1.233585
H	-0.035662	-2.270116	-4.027223	H	-0.181093	-1.327876	-4.255270

Calculation of averaged IR, VCD, UV-vis and ECD spectra:

The vibrational frequencies, IR absorption and VCD intensities were calculated using the same theoretical level as for geometry optimization SMD(CH_2Cl_2)/B3LYP/6-311G(d,p). All the geometries selected have no imaginary frequency and are therefore local minima. Computed harmonic frequencies are generally larger than those experimentally observed. They have been calibrated using a scaling factor of 0.98. IR absorption and VCD averaged spectra were constructed from calculated dipole and rotational strengths assuming Lorentzian band shape with a half-width at half maximum of 8 cm^{-1}.

Based on the SMD(CH_3CN)/B3LYP/6-311G(d,p) optimized geometries, the ECD and UV spectra were calculated using time dependent density functional theory (TD-DFT) with CAM-B3LYP functional and def2svp basis set and with the SMD(CH_3CN) solvation model. Calculations were performed for vertical 1A singlet excitation using 150 states. For a comparison between theoretical results and the experimental values, a Gaussian function with a half-width of 0.37 eV was used to build UV and ECD spectra. Due to the approximations of the theoretical model used, an offset almost constant was observed between measured and calculated frequencies. Using the experimental UV-vis spectra as preferences, all frequencies were calibrated by a factor of 1.05. All calculations were performed using Gaussian16 package.[1] All the molecular pictures were generated using AGUI from the AMPAC 11 package (http://www.semichem.com/ampac/ampacgui-features.php).

Section S4.2. Detailed data

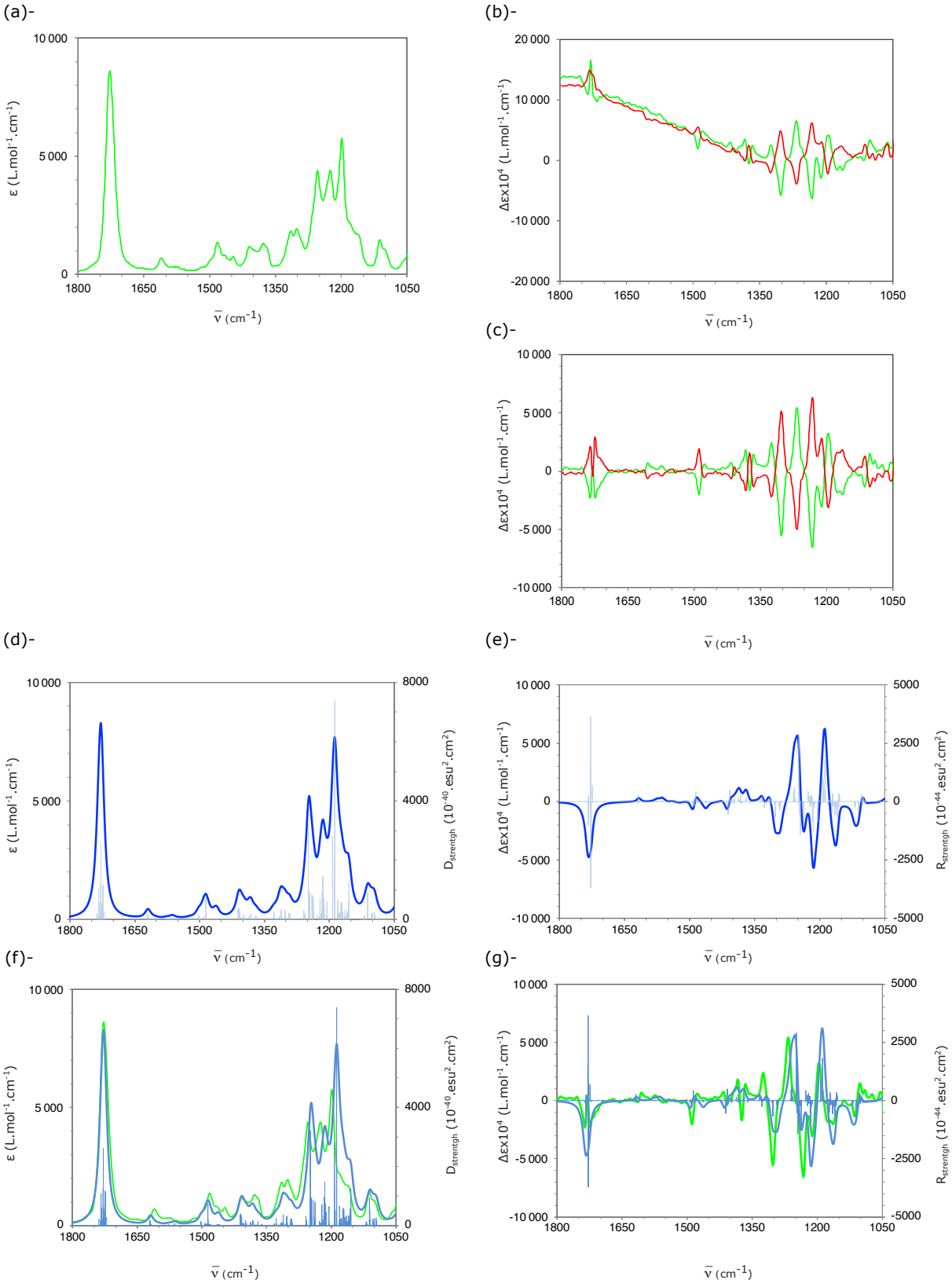


Figure S4. IR (left) and VCD (right) spectra measured (top) for (1st eluted)-***D*₃-3** (green) and (2nd eluted)-***D*₃-3** (red) sample and calculated (middle) for (*P,aR,P,aR,P,aR*)-***D*₃-3** (blue) enantiomer at the SMD(CH_2Cl_2)-B3LYP/6-311G(d,p) level. Experimental VCD spectra are given without (b) and with (c) half difference baseline corrections.

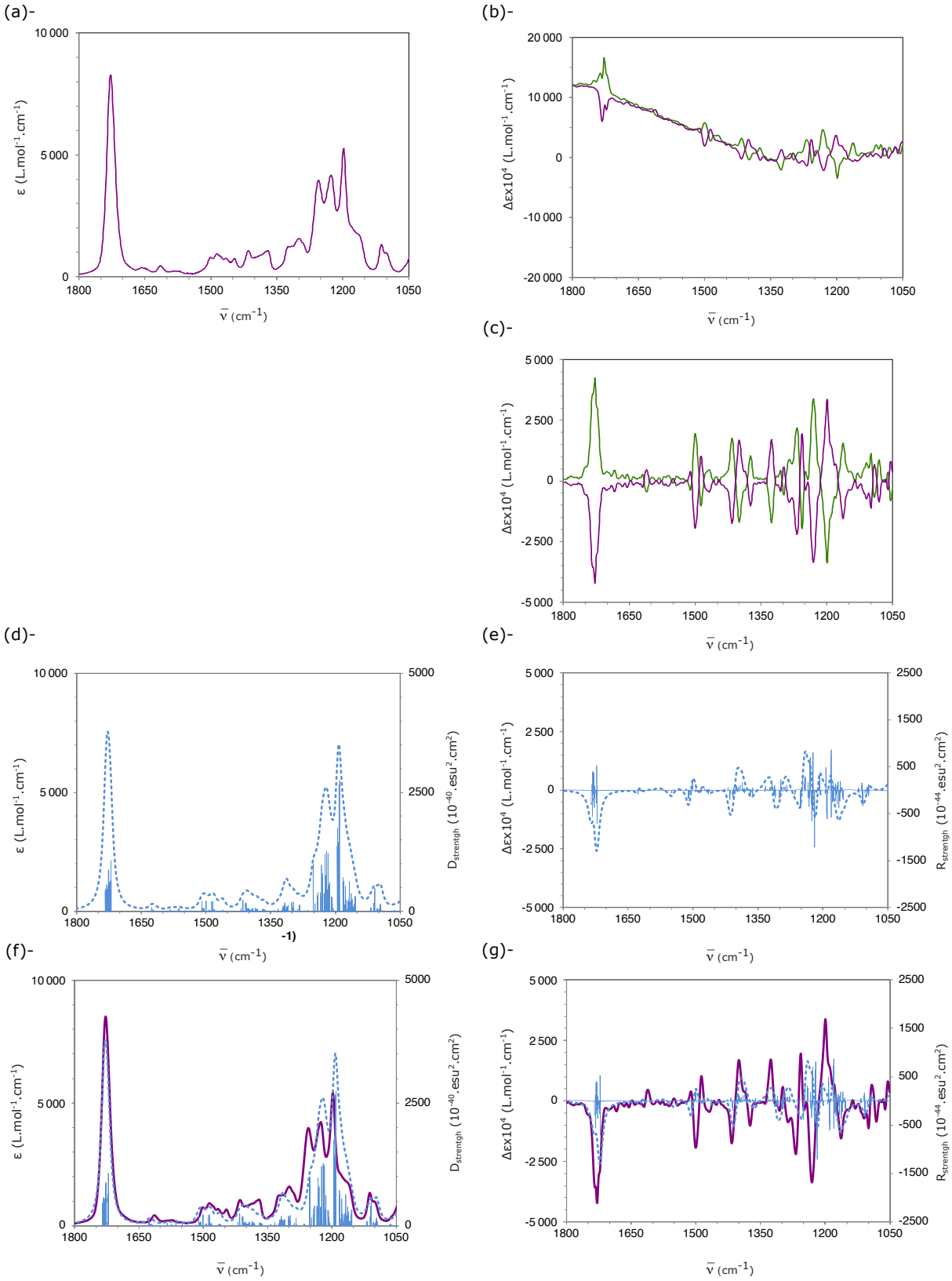


Figure S5. IR (left) and VCD (right) spectra measured (top) for (1st eluted)-***C*$_2$-3** (dark-green) and (2nd eluted)-***C*$_2$-3** (purple) sample and calculated (middle) for (*P,aR,P,aS,M,aS*)-***C*$_2$-3** (dashed-blue) enantiomer at the SMD(CH_2Cl_2)-B3LYP/6-311G(d,p) level of theory. Experimental VCD spectra are given without (b) and with (c) half difference baseline corrections.

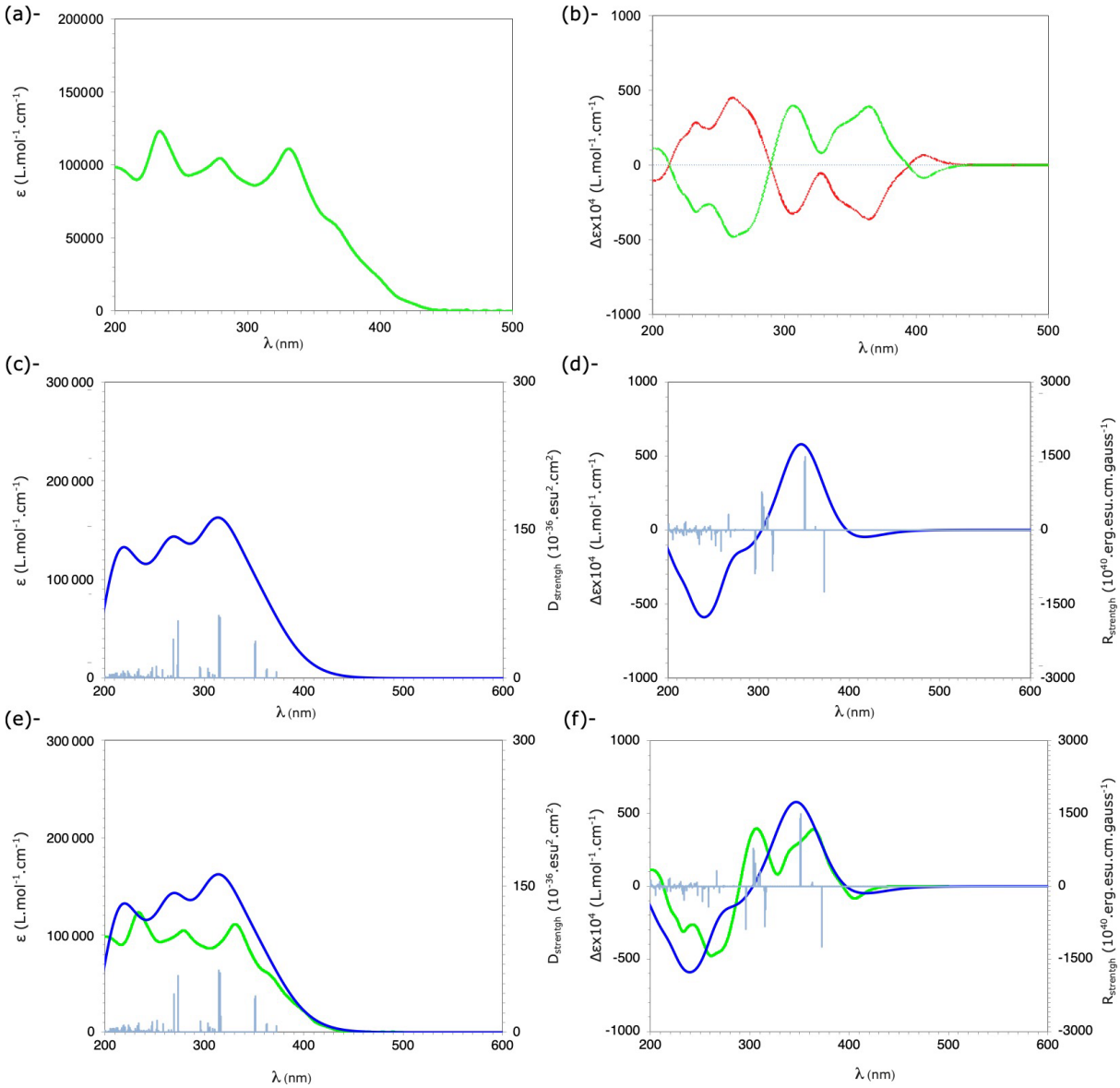


Figure S6. UV (left) and ECD (right) spectra measured (top) for (1st eluted)-***D*₃-3** (green) and (2nd eluted)-***D*₃-3** (red) sample and calculated (middle) for (*P,aR,P,aR,P,aR*)-***D*₃-3** (blue) enantiomer at the SMD(CH_3CN)-CAM-B3LYP/def2svp//SMD(CH_3CN)-B3LYP/6-311G(d,p).

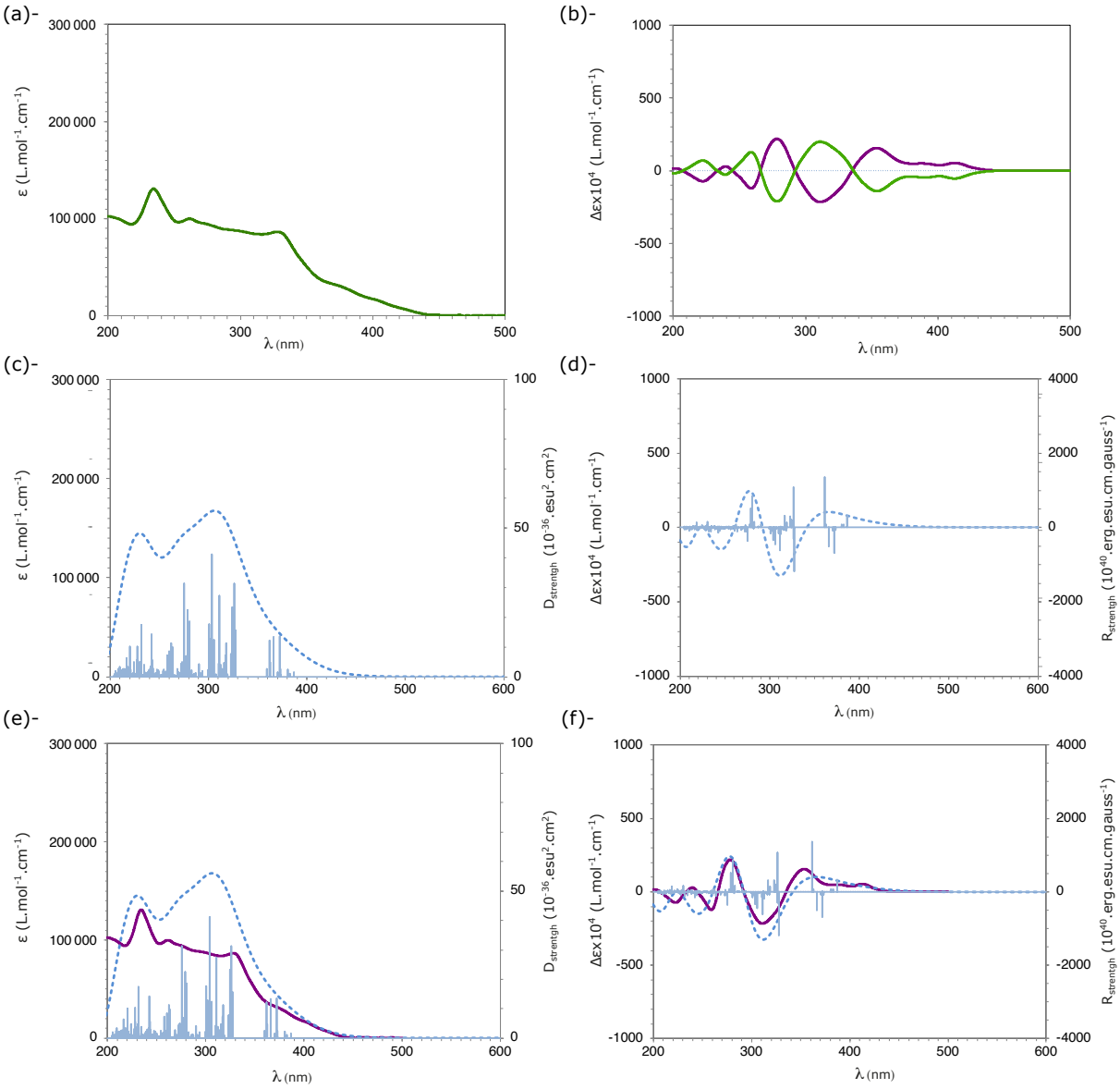


Figure S7. UV (left) and ECD (right) spectra measured (top) for (1st eluted)-***C*$_2$-3** (dark-green) and (2nd eluted)-***C*$_2$-3** (purple) sample and calculated (middle) for (*P,aR,P,aS,M,aS*)-***C*$_2$-3** (dashed-blue) enantiomer at the SMD(CH_3CN)-CAM-B3LYP/def2svp//SMD(CH_3CN)-B3LYP/6-311G(d,p).

Section S5: Luminescence spectroscopy

Steady-state luminescence spectra were measured using an Edinburgh FS920 Steady State Fluorimeter combined with a FL920 Fluorescence Lifetime Spectrometer. The spectra were corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Life-times measurements were conducted with 375 nm diode laser excitation (EPL-series) plugged to a TCSPC pulsed source interface. Absolute fluorescence quantum yields were recorded with a Hamamatsu C9920-03 integrating sphere. The circularly polarized luminescence (CPL) measurements were performed using a JASCO 300 CPL spectrofluoropolarimeter. The following parameters were used: emission slit width ≈ 20 mm, integration time = 4 s, scan speed = 50 nm/min,

accumulations = 8, with excitation at 350 nm. The concentration of all the samples was *ca*. 10^{-5}–10^{-6} M.

For the simulations, it was necessary to reduce the size of the systems, i.e., using their stripped-down versions without the ester substituents: only the π-conjugated polycyclic macrocyclic carbon backbone of both ***D*$_3$-3** and ***C*$_2$-3** was considered in the calculation (with 'only' 102 atoms vs 210 atoms for the full systems). Of course, for the sake of comparison, pristine [5]helicene was used instead of the tetraester [5]helicene in these calculations. Geometries optimization and frequency calculations were done at the B3LYP-D4/def2-TZVP level of theory using Orca 6.1.[3] Fluorescence and phosphorescence spectra were obtained using the Excited State Dynamics[4] using the full adiabatic Hessian method: geometries of each state were optimized, their Hessian fully computed (no approximation) at the B3LYP-D4/def2-TZVP level of theory. Note that due to some numerical issues, the phosphorescence spectrum of ***C*$_2$-3** required to use a cutoff at wavenumber 400 (hence frequencies below this value were discarded in the vibronic coupling).

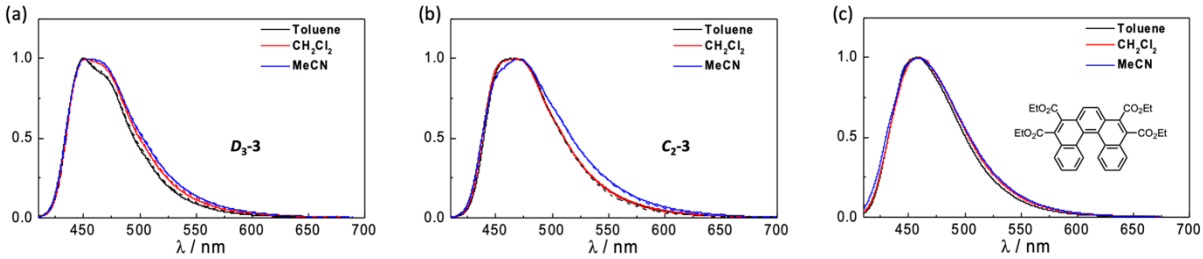


Figure S8. Normalized fluorescence profile of (a) ***D*$_3$-3**, (b) ***C*$_2$-3** and (c) the parent tetraethyl ester [5]helicene fragment in three solvents of different polarity.

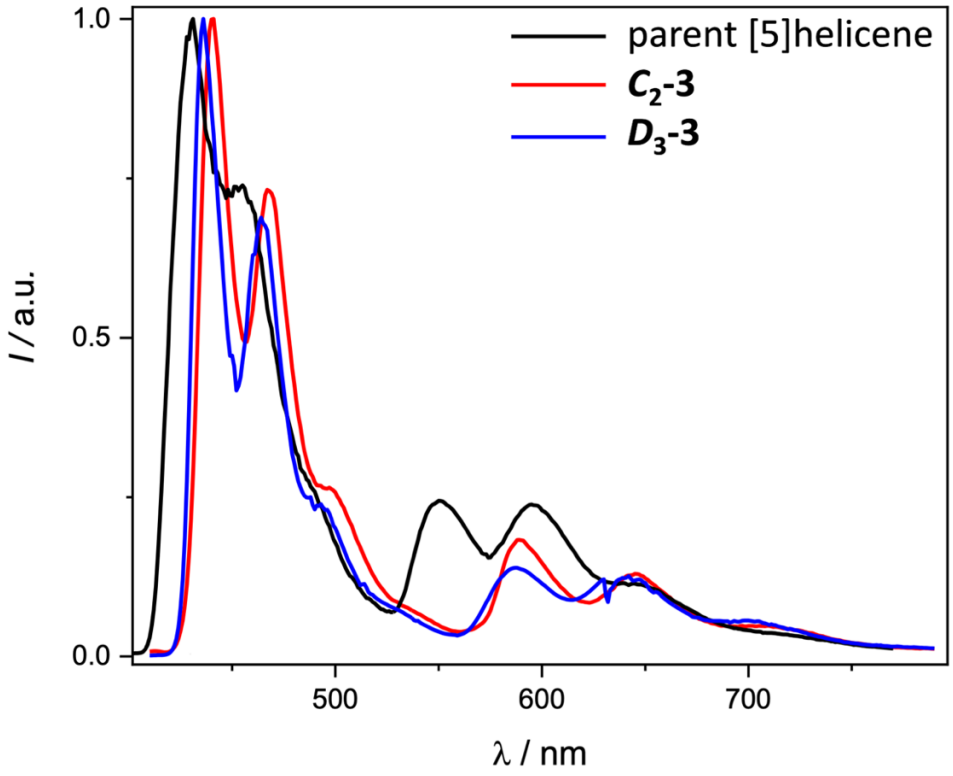


Figure S9. Normalized fluorescence and phosphorescence spectra of ***D*$_3$-3**, ***C*$_2$-3** and the parent [5]helicene in a frozen 2-MeTHF matrix at 77 K.

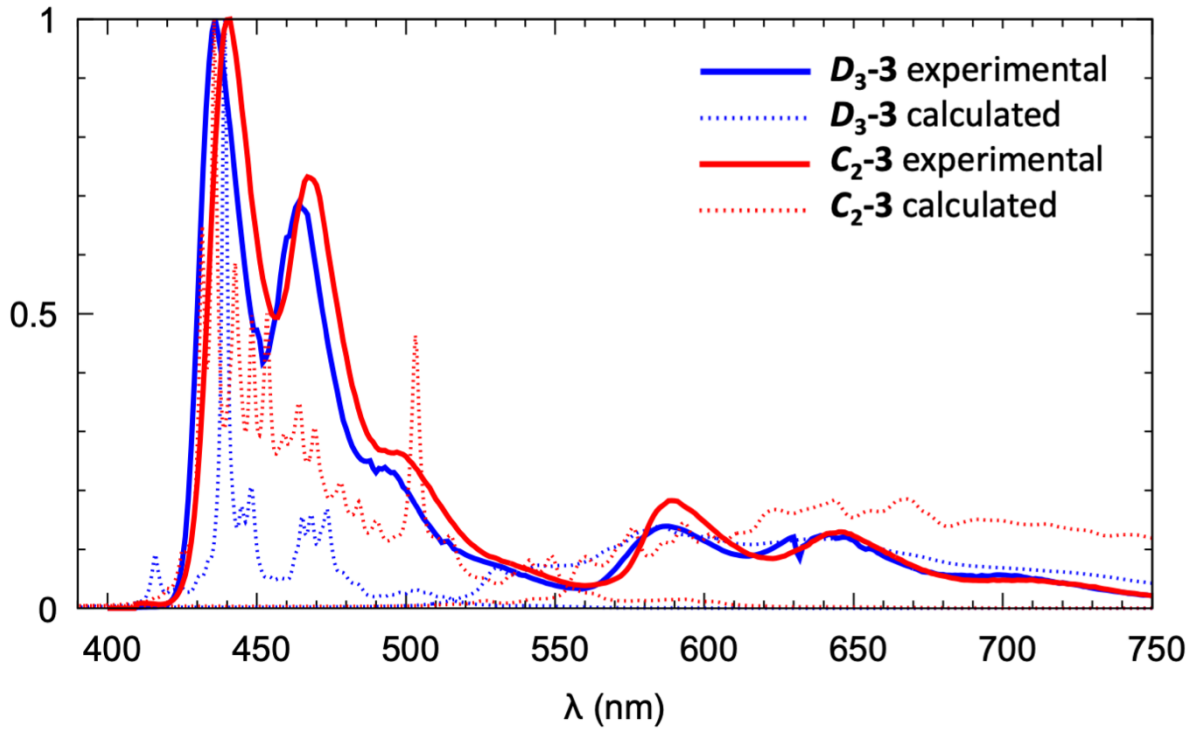


Figure S10. Normalized fluorescence and phosphorescence spectra of ***D*$_3$-3** and ***C*$_2$-3** in a frozen 2-MeTHF matrix at 77 K; the calculated spectra were obtained using the B3LYP-D4/def2-TZVP level of theory.

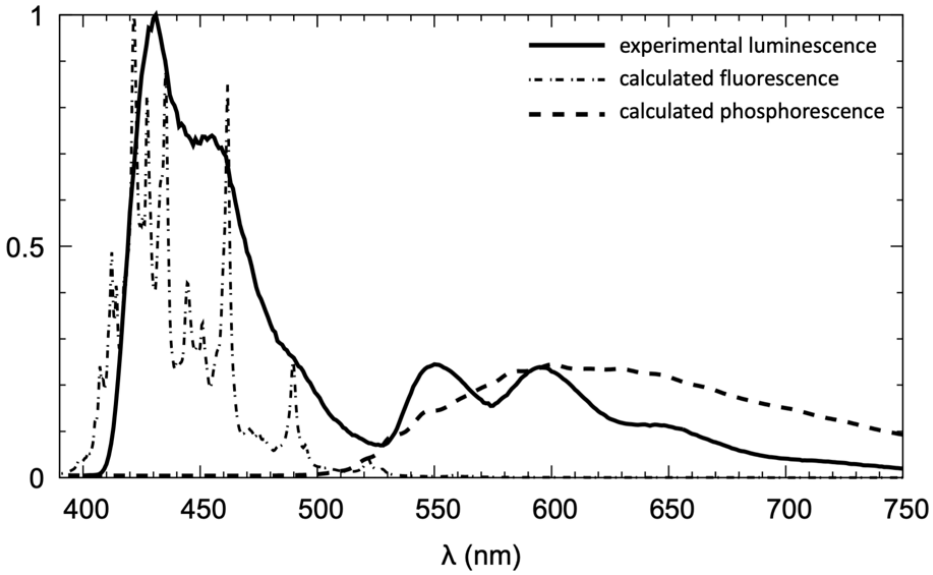


Figure S11. Normalized fluorescence and phosphorescence spectra of the parent [5]helicene in a frozen 2-MeTHF matrix at 77 K. The calculated spectra were obtained using the B3LYP-D4/def2-TZVP level of theory.

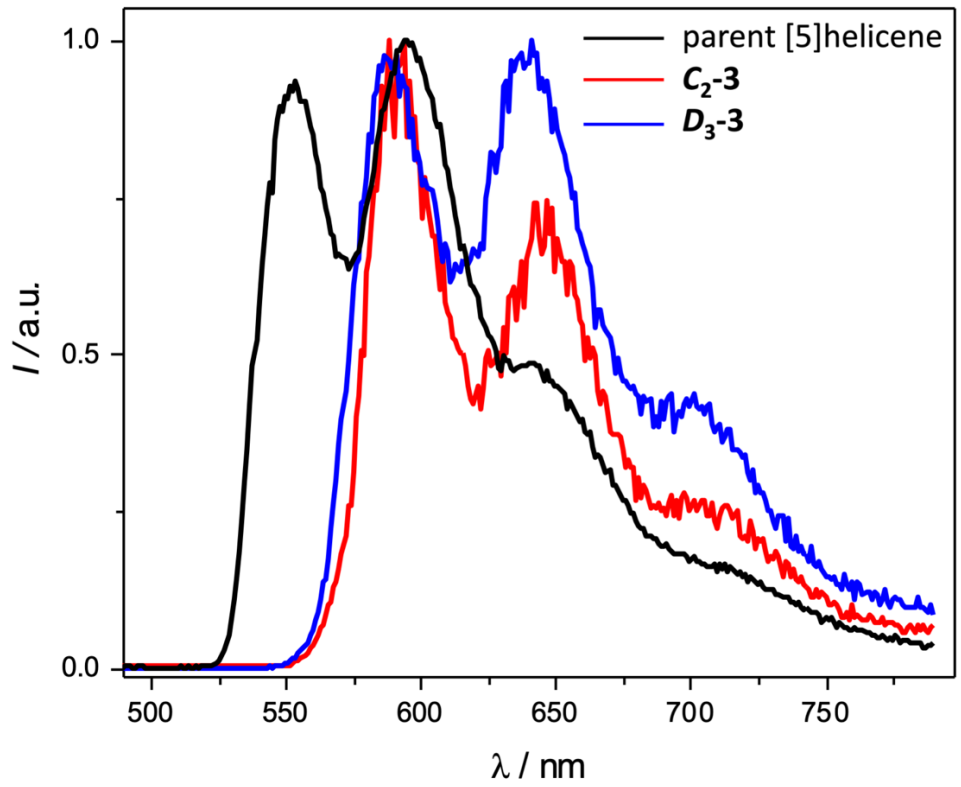


Figure S12. Normalized time-gated experimental measurements of the phosphorescence spectra of ***D*$_3$-3**, ***C*$_2$-3** and the parent [5]helicene in a frozen 2-MeTHF matrix at 77 K. $\tau_{phospho}$ = 1.1 s for the parent [5]helicene, and $\tau_{phospho}$ = 0.5–0.6 s for ***D*$_3$-3** and ***C*$_2$-3**.

Table S5. Cartesian coordinates of the geometries of stripped-down analogues of ***D*$_3$-3** and ***C*$_2$-3** (no ester substituents), and pristine [5]helicene in the S_0 state at the B3LYP-D4/def2-TZVP level of theory.

S_0_***D*$_3$-3**				S_0_***C*$_2$-3**				S_0_[5]helicene			
C	-1.76969	2.52974	-0.50342	C	0.49182	0.86701	-2.39132	C	-4.06784	-0.59655	0.80464
C	-0.68252	3.31497	-0.13954	C	0.48380	1.89186	-1.45477	H	-5.05077	-1.03835	0.98666
C	-2.22935	2.60813	-1.84778	C	-0.60267	0.78158	-3.29663	C	-3.95949	0.65589	0.23427
C	-0.09912	4.25999	-1.01804	C	-0.49231	2.91816	-1.46847	H	-4.85568	1.22824	-0.02077
H	-0.30198	3.25042	0.87771	H	1.32337	1.98380	-0.76765	C	-2.69155	1.24999	0.00744
C	-1.70086	3.53575	-2.71921	C	-1.55588	1.77636	-3.34798	C	-1.50005	0.51065	0.29164
C	-0.68429	4.43422	-2.30717	C	-1.47216	2.91289	-2.50276	C	-1.65133	-0.74013	0.94645
C	0.93300	5.18319	-0.57878	C	-0.37981	4.07987	-0.60857	H	-0.76579	-1.27796	1.27929
H	-2.12002	3.64086	-3.72367	H	-2.35612	1.72813	-4.09139	C	-2.89790	-1.28209	1.19588
C	-0.33152	5.57761	-3.09129	C	-2.23797	4.09873	-2.74382	H	-2.97482	-2.24363	1.70971
C	1.04586	6.42081	-1.26394	C	-0.94757	5.29866	-1.05485	C	-2.59396	2.61335	-0.41530
C	1.75838	4.96510	0.57905	C	0.37906	4.08004	0.60818	H	-3.51213	3.16035	-0.64504
C	0.44241	6.56862	-2.55497	C	-1.92688	5.26637	-2.10127	C	-1.38331	3.24076	-0.43263
C	1.72024	7.50922	-0.63440	C	-0.49662	6.52284	-0.47484	H	-1.31256	4.30933	-0.65289
C	2.27242	6.09699	1.26344	C	0.94663	5.29900	1.05424	C	-0.17138	2.52452	-0.16961
C	2.19888	3.65265	1.01906	C	0.49177	2.91848	1.46827	C	-0.20182	1.11514	0.02240
C	2.22374	7.37631	0.63359	C	0.49548	6.52300	0.47401	C	1.06052	3.23320	-0.06382
H	1.77129	8.46805	-1.15704	H	-0.91121	7.46410	-0.84566	H	1.05198	4.31958	-0.18435
C	2.87054	5.92801	2.55434	C	1.92594	5.26706	2.10068	C	2.21443	2.57168	0.25503
C	2.23751	2.54172	0.14178	C	-0.48415	1.89200	1.45473	H	3.14460	3.11870	0.42931
C	2.79466	3.51558	2.30788	C	1.47161	2.91356	2.50256	C	2.24290	1.14730	0.29082
H	2.65308	8.23527	1.15608	H	0.90992	7.46440	0.84466	C	1.05875	0.40379	0.02809
C	3.05385	4.68433	3.09121	C	2.23722	4.09958	2.74343	C	3.47535	0.46721	0.55465
C	2.79415	1.32180	0.50634	C	-0.49196	0.86728	2.39141	H	4.34637	1.06801	0.82973
H	1.87337	2.67207	-0.87515	H	-1.32374	1.98367	0.76760	C	3.56574	-0.89095	0.47172
C	3.23358	2.23215	2.72086	C	1.55555	1.77718	3.34796	H	4.50221	-1.40570	0.70205
C	3.23314	1.16355	1.85056	C	0.60254	0.78220	3.29673	C	2.46197	-1.65658	-0.02075
H	3.65035	2.11731	3.72527	H	2.35580	1.72923	4.09137	C	1.22103	-1.00485	-0.30764

C	-1.30710	-2.79906	-0.50667	C	0.51172	-2.78520	0.53700	C	0.24813	-1.74678	-1.02815
C	-2.52997	-2.24873	-0.14220	C	1.83606	-2.52880	0.20989	H	-0.66083	-1.25030	-1.36198
C	-1.14663	-3.23769	-1.85078	C	0.17012	-2.84521	1.91568	C	0.43711	-3.07989	-1.33972
C	-3.64121	-2.21658	-1.01931	C	2.81186	-2.15893	1.15937	H	-0.33083	-3.61596	-1.90313
H	-2.66185	-1.88525	0.87479	H	2.12299	-2.55718	-0.83175	C	1.61779	-3.74630	-0.94773
C	-2.21521	-3.24399	-2.72096	C	1.12674	-2.62081	2.87900	H	1.75392	-4.80567	-1.17944
C	-3.50099	-2.81185	-2.30797	C	2.45439	-2.25642	2.53845	C	2.61658	-3.03607	-0.31245
C	-4.95619	-1.78366	-0.57904	C	4.15975	-1.75469	0.78328	H	3.56267	-3.51993	-0.05436
H	-2.09851	-3.66046	-3.72529	H	0.86442	-2.70927	3.93679				
C	-4.66837	-3.07763	-3.09127	C	3.44290	-2.03800	3.54387				
C	-6.08521	-2.30393	-1.26344	C	5.13870	-1.73339	1.81730				
C	-5.17867	-0.95994	0.57906	C	4.59146	-1.49571	-0.57605				
C	-5.91306	-2.90107	-2.55442	C	4.74427	-1.82668	3.19069				
C	-7.36473	-2.26228	-0.63346	C	6.52455	-1.68490	1.49055				
C	-6.41565	-1.07947	1.26425	C	5.97417	-1.66403	-0.87108				
C	-4.26077	0.07682	1.01866	C	3.73621	-1.05190	-1.67532				
C	-7.50037	-1.75961	0.63455	C	6.92708	-1.74367	0.18537				
H	-8.22126	-2.69632	-1.15605	H	7.25582	-1.67784	2.30295				
C	-6.56664	-0.47704	2.55541	C	6.41672	-1.76084	-2.22963				
C	-3.31860	0.66502	0.14031	C	2.51632	-0.34851	-1.49103				
C	-4.43815	0.66094	2.30781	C	4.18816	-1.24815	-3.01696				
H	-8.45887	-1.81586	1.15728	H	7.98684	-1.81924	-0.07149				
C	-5.57977	0.30212	3.09184	C	5.53688	-1.64956	-3.26561				
C	-2.53913	1.75634	0.50423	C	1.69223	0.00948	-2.55482				
H	-3.25202	0.28483	-0.87695	H	2.21228	-0.08372	-0.47917				
C	-3.54495	1.68215	2.71992	C	3.31325	-0.94782	-4.09039				
C	-2.62004	2.21551	1.84859	C	2.08797	-0.36215	-3.86874				
H	-3.65232	2.10070	3.72441	H	3.65190	-1.14326	-5.11152				
H	-2.00653	3.05817	2.17161	H	1.45439	-0.09889	-4.71730				
C	-0.25244	-3.07885	0.50087	C	-0.51129	-2.78517	-0.53708				
C	1.08243	-3.20873	0.13723	C	-1.83564	-2.52895	-0.20988				
C	-0.60986	-3.37779	1.84539	C	-0.16974	-2.84501	-1.91578				
C	2.06277	-3.72997	1.01621	C	-2.81151	-2.15907	-1.15928				
H	1.37814	-2.96073	-0.88007	H	-2.12252	-2.55746	0.83177				
C	0.31408	-3.91236	2.71694	C	-1.12643	-2.62061	-2.87904				
C	1.64502	-4.17591	2.30509	C	-2.45411	-2.25639	-2.53839				
C	3.42004	-4.00572	0.57799	C	-4.15944	-1.75500	-0.78311				
H	0.00494	-4.21474	3.72133	H	-0.86413	-2.70899	-3.93685				
C	2.52594	-4.98578	3.08928	C	-3.44267	-2.03797	-3.54374				
C	4.14142	-5.01793	1.26284	C	-5.13844	-1.73373	-1.81708				
C	4.02358	-3.39943	-0.57833	C	-4.59115	-1.49620	0.57626				
C	3.69436	-5.45101	2.55336	C	-4.74406	-1.82683	-3.19050				
C	5.27365	-5.61592	0.63340	C	-6.52429	-1.68546	-1.49027				
C	5.03907	-4.11613	-1.26327	C	-5.97383	-1.66478	0.87134				
C	3.74152	-2.04349	-1.01658	C	-3.73594	-1.05232	1.67554				
C	5.64234	-5.24556	-0.63389	C	-6.92676	-1.74443	-0.18509				
H	5.80188	-6.41820	1.15543	H	-7.25560	-1.67839	-2.30264				
C	5.46976	-3.66707	-2.55387	C	-6.41629	-1.76180	2.22991				
C	3.21588	-1.06562	-0.13742	C	-2.51621	-0.34864	1.49121				
C	4.18511	-1.62376	-2.30564	C	-4.18779	-1.24876	3.01719				
H	6.44705	-5.77010	-1.15590	H	-7.98650	-1.82017	0.07182				
C	4.99896	-2.50094	-3.08986	C	-5.53642	-1.65045	3.26585				
C	3.07922	0.26853	-0.50113	C	-1.69215	0.00948	2.55497				
H	2.96982	-1.36304	0.87986	H	-2.21246	-0.08373	0.47929				
C	3.91487	-0.29420	-2.71743	C	-3.31287	-0.94828	4.09058				
C	3.37592	0.62718	-1.84577	C	-2.08775	-0.36231	3.86887				
H	4.21523	0.01663	-3.72191	H	-3.65141	-1.14384	5.11172				
H	-1.64660	-3.26667	2.16741	H	0.84855	-3.07996	-2.22597				
H	-0.19169	-3.65570	-2.17369	H	-0.84817	-3.08026	2.22578				
H	-3.06889	1.99028	-2.17064	H	-0.66557	-0.05937	-3.98721				
H	3.65612	0.21099	2.17401	H	0.66558	-0.05866	3.98741				
H	3.25968	1.66316	-2.16839	H	-1.45418	-0.09896	4.71741				
H	4.31208	-6.16650	3.10294	H	5.86443	-1.78483	-4.29965				
H	2.20325	-5.30355	4.08434	H	7.47568	-1.95975	-2.41420				
H	3.49036	4.56530	4.08646	H	5.52066	-1.73782	3.95527				
H	3.17941	6.82160	3.10351	H	3.15065	-2.10030	4.59559				
H	0.61490	7.49782	-3.10485	H	-5.52048	-1.73798	-3.95505				
H	-0.76961	5.68920	-4.08672	H	-3.15046	-2.10013	-4.59549				
H	-4.54677	-3.51362	-4.08643	H	-7.47520	-1.96090	2.41451				
H	-6.80501	-3.21486	-3.10345	H	-5.86390	-1.78587	4.29990				
H	-5.69363	0.73954	4.08731	H	3.00472	4.08111	3.52187				

H	-7.49494	-0.65454	3.10522	H	2.42440	6.20087	2.37479	
H	6.18804	-4.28144	-3.10357	H	-3.00546	4.08002	-3.52225	
H	5.31498	-2.17699	-4.08507	H	-2.42550	6.20004	-2.37554	

Table S6. Cartesian coordinates of the geometries of stripped-down analogues of ***D*$_3$-3** and ***C*$_2$-3** (no ester substituents), and pristine [5]helicene in the T_1 state at the B3LYP-D4/def2-TZVP level of theory.

T_1_***D*$_3$-3**				T_1_***C*$_2$-3**				T_1_[5]helicene			
C	-1.78718	2.49850	-0.49791	C	0.50524	0.85631	-2.41662	C	-4.02740	-0.66523	0.79075
C	-0.69428	3.27626	-0.13315	C	0.48533	1.86684	-1.46354	H	-5.00491	-1.12911	0.94554
C	-2.24092	2.57498	-1.84439	C	-0.57599	0.78875	-3.33911	C	-3.93513	0.58946	0.20869
C	-0.10495	4.21820	-1.01167	C	-0.48845	2.89647	-1.47591	H	-4.83946	1.13410	-0.07647
H	-0.31653	3.21156	0.88541	H	1.31551	1.94687	-0.76349	C	-2.67734	1.21497	0.01285
C	-1.70324	3.49580	-2.71721	C	-1.53235	1.77992	-3.38275	C	-1.48005	0.49758	0.33605
C	-0.68495	4.39138	-2.30341	C	-1.46052	2.90189	-2.51842	C	-1.61179	-0.73645	0.99522
C	0.92306	5.14467	-0.56842	C	-0.37908	4.05442	-0.60919	H	-0.71768	-1.25414	1.34095
H	-2.11771	3.59977	-3.72374	H	-2.32362	1.74298	-4.13626	C	-2.85867	-1.31753	1.21705
C	-0.32850	5.53324	-3.08839	C	-2.22981	4.08631	-2.75345	H	-2.92205	-2.28283	1.72518
C	1.03489	6.38247	-1.25363	C	-0.94656	5.27504	-1.05312	C	-2.59002	2.57716	-0.39350
C	1.74237	4.93158	0.59444	C	0.37876	4.05430	0.60935	H	-3.50542	3.12070	-0.63835
C	0.44005	6.52675	-2.54908	C	-1.92412	5.24909	-2.10099	C	-1.35713	3.24437	-0.35402
C	1.69858	7.47487	-0.61959	C	-0.49660	6.49923	-0.47319	H	-1.31934	4.31908	-0.55297
C	2.24326	6.06675	1.28326	C	0.94646	5.27476	1.05338	C	-0.16711	2.57682	-0.08153
C	2.19256	3.62224	1.03479	C	0.48808	2.89619	1.47586	C	-0.16732	1.12270	0.07532
C	2.19176	7.34569	0.65285	C	0.49667	6.49909	0.47364	C	1.09091	3.29495	-0.03224
H	1.74859	8.43352	-1.14270	H	-0.91225	7.44008	-0.84383	H	1.06314	4.38503	-0.11119
C	2.83210	5.90141	2.57891	C	1.92418	5.24850	2.10110	C	2.26138	2.63939	0.13872
C	2.25273	2.51547	0.15385	C	-0.48586	1.86670	1.46347	H	3.20519	3.18330	0.23191
C	2.78112	3.48894	2.32770	C	1.46037	2.90127	2.51816	C	2.29798	1.19132	0.18633
H	2.61149	8.20731	1.17877	H	0.91248	7.43982	0.84437	C	1.04661	0.44261	-0.03250
C	3.02209	4.65841	3.11554	C	2.22985	4.08555	2.75327	C	3.44987	0.50743	0.51223
C	2.82882	1.30306	0.51730	C	-0.50566	0.85596	2.41634	H	4.35225	1.07512	0.75548
H	1.89303	2.64345	-0.86525	H	-1.31619	1.94697	0.76363	C	3.49410	-0.91587	0.53969
C	3.23363	2.20986	2.74007	C	1.53226	1.77910	3.38223	H	4.41268	-1.43007	0.83097
C	3.25687	1.14529	1.86553	C	0.57576	0.78807	3.33858	C	2.40552	-1.67159	0.02467
H	3.64331	2.09720	3.74765	H	2.32370	1.74188	4.13555	C	1.20448	-0.99243	-0.36893
C	-1.29915	-2.73560	-0.50653	C	0.48121	-2.77197	0.51607	C	0.27557	-1.69168	-1.14268
C	-2.56121	-2.24278	-0.13135	C	1.88124	-2.59997	0.20710	H	-0.59829	-1.16769	-1.53055
C	-1.13535	-3.12153	-1.87751	C	0.13431	-2.75962	1.91899	C	0.42643	-3.06046	-1.41529
C	-3.66583	-2.22831	-1.00147	C	2.81005	-2.14965	1.13350	H	-0.33205	-3.57974	-2.00588
H	-2.71058	-1.89935	0.88877	H	2.20195	-2.74705	-0.81684	C	1.53647	-3.75296	-0.92272
C	-2.21042	-3.16932	-2.73107	C	1.07361	-2.49401	2.86644	H	1.64668	-4.82403	-1.11077
C	-3.51781	-2.80605	-2.30148	C	2.43480	-2.15880	2.52778	C	2.52127	-3.06267	-0.22043
C	-4.98813	-1.81169	-0.56032	C	4.17230	-1.76193	0.75974	H	3.42063	-3.58163	0.12244
H	-2.08158	-3.55300	-3.74698	H	0.80113	-2.52218	3.92487				
C	-4.67800	-3.10627	-3.07017	C	3.40450	-1.94053	3.51185				
C	-6.11007	-2.35563	-1.23981	C	5.14922	-1.73550	1.80505				
C	-5.21747	-0.97686	0.58587	C	4.59918	-1.51335	-0.59131				
C	-5.92883	-2.95933	-2.52458	C	4.74262	-1.78209	3.16336				
C	-7.39052	-2.31880	-0.61085	C	6.53784	-1.70071	1.47513				
C	-6.45600	-1.09647	1.27026	C	5.98623	-1.68061	-0.88895				
C	-4.30298	0.06674	1.02118	C	3.73726	-1.08159	-1.69511				
C	-7.53305	-1.79556	0.64825	C	6.93831	-1.76046	0.17025				
H	-8.24220	-2.76971	-1.12707	H	7.26973	-1.69427	2.28703				
C	-6.61278	-0.48215	2.55478	C	6.42327	-1.78742	-2.24427				
C	-3.35677	0.65018	0.14413	C	2.51807	-0.37933	-1.51210				
C	-4.48362	0.65652	2.30699	C	4.19228	-1.28016	-3.03582				
H	-8.49196	-1.85275	1.17016	H	7.99795	-1.83856	-0.08678				
C	-5.62884	0.30292	3.08875	C	5.54030	-1.68252	-3.28215				
C	-2.56953	1.73592	0.50866	C	1.70148	-0.00755	-2.57808				
H	-3.28882	0.26812	-0.87208	H	2.20924	-0.12140	-0.50012				
C	-3.58801	1.67600	2.71899	C	3.32137	-0.97329	-4.11072				
C	-2.65427	2.19998	1.85115	C	2.10117	-0.37620	-3.89147				
H	-3.69871	2.09924	3.72116	H	3.66128	-1.16856	-5.13149				
H	-2.03628	3.03929	2.17449	H	1.47514	-0.10367	-4.74263				
C	-0.25161	-2.97072	0.47058	C	-0.48086	-2.77208	-0.51565				
C	1.09373	-3.28007	0.06185	C	-1.88089	-2.60045	-0.20681				
C	-0.51621	-3.02285	1.87089	C	-0.13384	-2.75961	-1.91855				

C	2.05815	-3.71958	0.93845	C	-2.80982	-2.15066	-1.13338
H	1.37022	-3.14813	-0.98296	H	-2.20167	-2.74746	0.81710
C	0.40621	-3.52870	2.75597	C	-1.07316	-2.49445	-2.86612
C	1.68409	-4.02148	2.30606	C	-2.43447	-2.15986	-2.52762
C	3.42746	-4.04770	0.49992	C	-4.17223	-1.76343	-0.75971
H	0.14959	-3.63092	3.81393	H	-0.80052	-2.52252	-3.92451
C	2.49248	-4.86352	3.05252	C	-3.40426	-1.94211	-3.51179
C	4.08190	-5.14169	1.18272	C	-5.14909	-1.73754	-1.80505
C	4.08083	-3.41855	-0.57625	C	-4.59920	-1.51472	0.59128
C	3.63405	-5.50684	2.44894	C	-4.74239	-1.78418	-3.16337
C	5.20224	-5.77529	0.53648	C	-6.53771	-1.70320	-1.47520
C	5.11286	-4.14290	-1.27028	C	-5.98620	-1.68238	0.88892
C	3.81708	-2.04583	-1.00914	C	-3.73746	-1.08239	1.69498
C	5.64485	-5.33452	-0.67764	C	-6.93820	-1.76282	-0.17029
H	5.66504	-6.63900	1.02131	H	-7.26973	-1.69717	-2.28699
C	5.55394	-3.67919	-2.53490	C	-6.42331	-1.78898	2.24426
C	3.29441	-1.07784	-0.12917	C	-2.51842	-0.37994	1.51195
C	4.26734	-1.62371	-2.29493	C	-4.19247	-1.28077	3.03571
H	6.44600	-5.86263	-1.20201	H	-7.99781	-1.84127	0.08673
C	5.08797	-2.49811	-3.07375	C	-5.54039	-1.68350	3.28212
C	3.14253	0.26057	-0.49041	C	-1.70195	-0.00783	2.57792
H	3.04261	-1.38166	0.88526	H	-2.20912	-0.12215	0.50007
C	3.99719	-0.29316	-2.70164	C	-3.32175	-0.97346	4.11063
C	3.44638	0.62404	-1.82929	C	-2.10162	-0.37621	3.89139
H	4.30367	0.02371	-3.70240	H	-3.66178	-1.16865	5.13137
H	-1.49681	-2.73209	2.24974	H	0.88759	-2.96821	-2.23351
H	-0.16520	-3.46728	-2.23460	H	-0.88700	-2.96860	2.23406
H	-3.08346	1.96169	-2.16810	H	-0.62621	-0.03463	-4.05076
H	3.69133	0.19777	2.18861	H	0.62600	-0.03550	4.05001
H	3.32645	1.66041	-2.14972	H	-1.47565	-0.10341	4.74251
H	4.16447	-6.28596	3.00192	H	5.86826	-1.82221	-4.31541
H	2.20442	-5.12907	4.07288	H	7.48170	-1.98743	-2.43113
H	3.45204	4.54167	4.11392	H	5.50803	-1.70329	3.93938
H	3.12914	6.79691	3.13147	H	3.11068	-1.96586	4.56483
H	0.61376	7.45562	-3.09915	H	-5.50781	-1.70577	-3.93942
H	-0.76129	5.64217	-4.08643	H	-3.11041	-1.96739	-4.56476
H	-4.55393	-3.54113	-4.06560	H	-7.48167	-1.98932	2.43109
H	-6.81441	-3.29881	-3.06837	H	-5.86825	-1.82302	4.31544
H	-5.74684	0.74709	4.08074	H	2.99336	4.06994	3.53565
H	-7.54214	-0.65748	3.10351	H	2.42312	6.18360	2.36983
H	6.27453	-4.28760	-3.08870	H	-2.99316	4.07095	-3.53599
H	5.42035	-2.16996	-4.06189	H	-2.42289	6.18431	-2.36964

Section S6: Aromaticity

Section S6.1. Methods

All calculations were performed with the Gaussian16 package.[1] Geometries were optimized at the B3LYP-D3(BJ)/def2-SVP level of theory[2] and analytical Hessians were computed to verify their minima nature (zero imaginary frequencies). As previously described,[5] additional dummy atoms were added at all zig-zag, K, bay and fjord regions with the *Chemcraft* software to obtain a smooth surface, and pseudo-Van der Waals surfaces were generated by means of a purpose-made code (ims3d.py) by overlapping spheres made of ghost atoms of 1 Å radius. NMR-GIAO[6] calculations were performed at all ghost atoms thus generated at the B3LYP-GIAO/6-311++G(d,p) level of theory. Output .vtk files were visualized with the *Paraview* software. All .vtk files are available as ESI.

$EDDB_H(r)$ isosurfaces[7] were computed at the CAM-B3LYP/6-311G(d,p) level of theory using the *NBO 6.0* software[8] first to obtain the natural atomic orbitals and then running the *EDDB* program available at www.aromaticity.eu. The $EDDB_H(r)$ isosurfaces were generated using the *Formchk* and *Cubegen* tools implemented in the Gaussian16 package. Molecular graphics and analyses were performed with UCSF *Chimera*.

Section S6.2. Aromaticity in D_3-4

In addition to the data discussed in the manuscript, and for the interest of comparison, the analysis of the recently reported Möbius-shaped molecule ***D*$_3$-4**,[9] a diastereomer of ***C*$_2$-4**, was also realized. In full agreement with the reported properties of its π system, ***D*$_3$-4** was found Möbius aromatic. The 3DIMS map of ***D*$_3$-4** (Figure S13) shows only blue color, indicating its aromatic character. The dark blue areas indicate intense delocalization, which is visibly occurring in each 22-electron semi-local circuits at each [5]helicene fragments. Looking at the single bonds connecting the [5]helicene fragments, the 3DIMS map allows to visualize the uninterrupted π conjugation across these single bonds: from any 3D perspective, a continuum of light blue (or medium blue) color between the C atoms is visible. The $EDDB_H(r)$ analysis also confirmed the global Möbius aromatic character of ***D*$_3$-4**, with the delocalization of its π electrons extending to 79.5%.

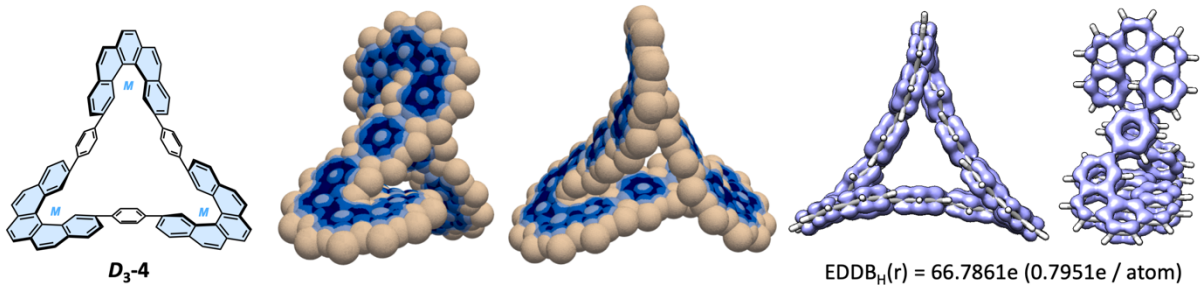


Figure S13. 3DIMS map and $EDDB_H(r)$ plot (isovalue = 0.02) of (*M,M,M*)-***D*$_3$-4**.

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