Supporting Information

Chiral Distorted Hexa-\textit{peri}-hexabenzocoronenes Bearing a Nonagon-Embedded Carbohelicene

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**General Details**

Unless otherwise stated, all reagents and solvents (DDQ, CF₃SO₂H, CH₂Cl₂, EtOAc, Hexane) were purchased from commercial sources and used without further purification. Anhydrous THF was freshly distilled over Na/benzophenone. HPLC grade solvents (hexane, CH₄Cl) were purchased from VWR. Anhydrous CH₂Cl₂ was purchased from Scharlab. 5,8,11,14-tetra-tet-butylidibenzof[g,i,j]benzo[7,8]cycloocta[1',2',3',4',5]phenanthro[9,10,123-pqrs]pentaphen-21(2H)-one (compound 4) was synthesized following the reported procedure. Flash column chromatography was carried out using Silica gel 60 (230-400 mesh, Scharlab, Spain) as the stationary phase. Analytical TLC was performed on aluminum sheets coated with silica gel with fluorescent indicator UV254 (Alugram SIL G/UV254, Mackerey-Nagel, Germany) and observed under UV light (254 nm) and/or stained with phosphomolybdic acid (5% methanol solution). All ¹H and ¹³C NMR spectra were recorded on Bruker Avance Neo (400 MHz or 500 MHz) spectrometers at a constant temperature of 298 K. Chemical shifts are reported in ppm and referenced to residual solvent. Multiplicities are abbreviated as follow: s = singlet, br s = broad singlet, d = doublet, t = triplet m = multiplet, dd = doublet of doublet, td = triplet of doublets. dd = doublet of doublet of doublets, dt = triplet of triplets. Coupling constants (J) are reported in Hertz (Hz).

**Synthetic procedures**

![Scheme S1. General synthetic route towards nona-[5]helicene derivatives 1-3. Reagents and conditions: a) i) BF₃·OEt₂, TMSCNHz. CH₂Cl₂, 0 ºC, 5 min; ii) Bu₄NF-3H₂O, THF, 1 h, 70%; b) Tebbe’s reagent, THF, 0 ºC, 5 min, 57%; c) SeO₂, dioxane, 100 ºC, 1 h; d) DMP, CH₂Cl₂, 0 ºC to rt, 4 h, 75%.

5,8,11,14-tetra-tet-butyl-22,23-dihydro-21H-dibenzo[g,i,j]benzo[8',9']cyclonona[1',2',3',4',5]phenanthro[9,10,123-pqrs]pentaphen-21-one (Compound 1, Helicene 1)

To a solution of compound 4 (450 mg, 0.57 mmol) in dry CH₂Cl₂ (10 mL) was added BF₃·OEt₂ (0.11 mL, 0.85 mmol) at 0 ºC. Then, TMSCNHz (0.42 mL, 0.85 mmol) was added dropwise and after 5 min stirring, TLC showed no starting material. The mixture was diluted with CH₂Cl₂ and washed with water and brine. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The crude was dissolved in THF and Bu₄NF·3H₂O (222.7 mg, 0.85 mmol) was added at RT. After 1 h stirring, the solvent was evaporated and the crude was diluted with CH₂Cl₂ and washed with water. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO₂, Hexane/CH₂Cl₂ mixtures) affording 1 (320 mg, 70 %) as a yellow solid. ¹H NMR (500 MHz, CD₂Cl₂) δ 9.22 (s, 1H), 9.20 (s, 1H), 9.13 (s, 1H), 9.03 (s, 1H), 9.00 (s, 1H), 8.82 (s, 2H), 8.51 (d, J = 8.0 Hz, 1H), 7.96 (dd, J = 7.9, 1.2 Hz, 1H), 7.53 (td, J = 7.8, 1.1 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.28 (td, J = 7.5, 1.4 Hz, 1H), 7.16 (dd, J = 9.0, 2.1 Hz, 1H), 7.02 (d, J = 7.3 Hz, 1H), 6.94 (d, J = 8.9 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 3.35 (ddd, J = 14.9, 13.1, 4.7 Hz, 1H), 2.92 (ddd, J = 16.9, 13.0, 4.0 Hz, 1H), 2.67 (dt, J = 16.6, 4.7 Hz, 1H), 2.45 (dt, J = 14.9, 4.4 Hz, 1H), 1.79 (s, 9H), 1.75 (s, 9H), 1.70 (s, 9H), 1.47 (s, 9H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 204.5 (C), 151.0 (C), 150.3 (C), 150.2 (C), 150.0 (C), 140.5 (C), 140.3 (C), 140.0 (C), 136.5 (C), 133.2 (C), 133.0 (C), 133.0 (C), 132.7 (C), 132.2 (C), 131.7 (C), 130.8 (C), 130.7 (C), 130.59 (C), 130.55 (C), 130.5 (C), 130.3 (C), 129.2 (CH), 128.5 (C), 128.4 (CH), 128.01 (CH), 127.96 (CH), 127.5 (CH), 126.0 (C), 125.2 (C), 124.5 (CH), 123.7 (C), 123.6 (C), 123.1 (C), 123.0 (C), 120.7 (CH), 120.4 (C), 120.3 (CH), 120.2 (CH),
5,8,11,14-tetra-tert-butyl-21-methylene-22,23-dihydro-21H-dibenzo[f,g,j]benzo[8',9']cyclonona[1',2',3',4':4,5]phenanthro[9,10,1,2,3-pqrst]pentaphene (Compound 2, Helicene 2)

A solution of 1 (60 mg, 0.075 mmol) in anhydrous THF (2 mL) was placed in an ice-water bath. Tebbe’s reagent (0.22 mL, 0.112 mmol) was added dropwise. After 5 minutes, the mixture was quenching with 1 M NaOH, diluted with CH₂Cl₂ and washed with 1 M NaOH and brine. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO₂, Hexane/CH₂Cl₂ 9:1, 73>R affording 2 (34 mg, 57 %) as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 9.14 (s, 1H), 9.12 (s, 1H), 9.07 (s, 1H), 8.99 (s, 1H), 8.94 (s, 1H), 8.79 (s, 1H), 8.75 (s, 1H), 8.42 (d, J = 7.7 Hz, 1H), 7.44–7.39 (m, 2H), 7.38 (t, J = 6.7 Hz, 1H), 7.13–7.07 (m, 2H), 7.00 (d, J = 7.2 Hz, 1H), 6.90 (d, J = 8.9 Hz, 1H), 6.55 (d, J = 7.5 Hz, 1H), 4.61 (s, 1H), 4.54 (s, 1H), 2.65 (dd, J = 15.4, 9.8 Hz, 1H), 2.58–2.49 (m, 2H), 2.43 (dd, J = 14.6, 9.2 Hz, 1H), 1.78 (s, 9H), 1.75 (s, 9H), 1.70 (s, 9H), 1.48 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 151.0 (C), 149.9 (C), 149.1 (C), 149.05 (C), 149.0 (C), 142.6 (C), 142.6 (C), 141.0 (C), 137.2 (C), 132.5 (CH), 132.3 (CH), 130.73 (C), 130.76 (C), 130.75 (C), 130.25 (C), 129.14 (C), 128.8 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 126.6 (CH), 125.7 (C), 124.6 (C), 123.6 (C), 122.3 (C), 122.7 (C), 122.4 (C), 119.5 (C), 119.2 (CH), 119.1 (CH), 118.9 (CH), 118.7 (CH), 118.6 (CH), 118.1 (CH), 111.4 (CH₂), 37.5 (CH₂), 35.9 (C), 35.84 (C), 35.80 (C), 35.0 (C), 32.2 (CH₂), 32.12 (CH₃), 31.5 (CH₃). (In theory there should be 42 aromatic peaks but only 40 aromatic peaks were observed, presumably some peaks have merged together.)

HR-MS (ESI-TOF): m/z calc. for C₄₈H₃₅Na [M + Na]⁺: 825.4229, found 825.4219. M.p.: 250 °C (decomp). IR (ATR): 2960, 2905, 2868, 1685, 1607, 1590, 1477, 1463, 1374, 1291, 1252, 1216, 871, 756, 731 cm⁻¹.

5,8,11,14-tetra-tert-butyl-21-methylene-22,23-dihydro-21H-dibenzo[f,g,j]benzo[8',9']cyclonona[1',2',3',4':4,5]phenanthro[9,10,1,2,3-pqrst]pentaphene-22-one (Compound 3, Helicene 3)

To a solution of 2 (34 mg, 0.042 mmol) in dioxane (5 mL) was added SeO₂ (5.6 mg, 0.050 mmol) and the reaction was heated at reflux for 2 h. The mixture was quenching with Na₂SO₄, extracted with CH₂Cl₂ and washed with water and brine. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was diluted with CH₂Cl₂ (3 mL). Then the solution was placed in an ice-water bath and Dess-Martin Periodinane was added (18.3 mg, 0.043 mmol). The mixture was stirred for 4 h. The reaction mixture was diluted with CH₂Cl₂ and washed with NaHCO₃, Na₂S₂O₅ and brine. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO₂, Hexane/CH₂Cl₂ 7:3) affording 3 (26 mg, 75 %) as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 9.13 (s, 1H), 9.09 (s, 1H), 9.06 (s, 1H), 8.97 (s, 1H), 8.95 (s, 1H), 8.84 (s, 1H), 8.73 (s, 1H), 8.56 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 7.9 Hz, 1H), 7.60 (d, J = 6.5 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.43 (td, J = 4.1, 1.4 Hz, 1H), 6.98 (dd, J = 8.9, 2.1 Hz, 1H), 6.95 (d, J = 7.4 Hz, 1H), 6.86 (d, J = 7.4 Hz, 1H), 6.41 (d, J = 8.9 Hz, 1H), 5.17 (s, 1H), 4.57 (s, 1H), 3.98 (d, J = 15.2 Hz, 1H), 3.16 (d, J = 15.2 Hz, 1H), 1.78 (s, 9H), 1.75 (s, 9H), 1.72 (s, 9H), 1.49 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 198.0 (C), 150.1 (C), 149.9 (C), 149.4 (C), 149.3 (C), 148.9 (C), 143.9 (C), 140.0 (C), 139.3 (C), 133.4 (C), 133.3 (C), 132.3 (CH), 131.5 (C), 130.5 (C), 130.4 (C), 130.3 (C), 130.2 (C), 130.1 (C), 129.9 (C), 129.8 (CH), 129.3 (C), 128.9 (CH), 128.8 (CH), 127.6 (CH), 127.5 (CH), 126.6 (C), 125.6 (C), 125.3 (C), 124.3 (C), 123.38 (C), 123.1 (C), 122.84 (C), 122.78 (C), 122.5 (CH), 120.3 (CH), 120.1 (C), 119.6 (CH), 119.1 (CH), 119.0 (CH), 118.9 (CH), 118.5 (CH), 118.2 (CH), 117.1 (CH₂),
51.3 (CH\textsubscript{2}), 35.9 (C), 35.84 (C), 35.79(C), 35.0 (C), 32.2 (CH\textsubscript{3}), 32.11 (CH\textsubscript{3}), 32.09 (CH\textsubscript{3}), 31.5 (CH\textsubscript{3}). (In theory there should be 16 secondary aromatic carbon signals but only 15 were observed, presumably two peaks have merged together.) HR-MS (ESI-TOF): m/z calc. for C\textsubscript{62}H\textsubscript{56}Na [M + Na]\textsuperscript{+}: 839.4229, found 839.4263. M.p.: 220 °C (decomp). IR (ATR): 2956, 2928, 1734, 1706, 1459, 1374 cm\textsuperscript{-1}.

### HPLC Traces

Separation of both enantiomers of compounds 1, 2 and 3 were carried out on an Agilent 1260 series equipped with the following modules: quaternary pump (G7111B 1260 Quat Pump), automatic sample injector (G2258A 1260 DL ALS), column thermostat (G1316A 1260 TCC), DAD detector (G7115A 1260 DADWR) and an automatic sample collector (G1364C 1260 FC-AS).

### Enantiomeric resolution of 1

The racemic resolution was achieved using a CHIRALPAK® IA semi-preparative chiral column packed with Amylose tris(3,5-dimethylphenylcarbamate) immobilized on 5 μm silica gel. The column temperature was set at 20 °C and the flow rate was constant during operation (3.6 mL/min). The mobile phase composition was hexane-CH\textsubscript{2}Cl\textsubscript{2} gradient and the gradient profile was as follows: from 80:20 to 60:40 and from 60:40 to 80:20 in 12 min. 360 nm was selected as reference wavelength for the peak detection.

| Time (min) | Hexane (%) | CH\textsubscript{2}Cl\textsubscript{2} (%) |
|-----------|------------|-----------------|
| 0         | 80         | 20               |
| 9         | 60         | 40               |
| 10        | 80         | 20               |

[Figure S1. Top: gradient profile. Medium: CSP-HPLC chromatogram of the separation of the enantiomers of 1. Bottom: HPLC traces of enantiopure samples.]

### Enantiomeric resolution of 2

The racemic resolution was achieved using a CHIRALPAK® IA semi-preparative chiral column packed with Amylose tris(3,5-dimethylphenylcarbamate) immobilized on 5 μm silica gel. The column temperature was set at 20 °C and the flow rate was constant during operation (3.6 mL/min). The mobile phase composition remained constant and it was hexane-CH\textsubscript{2}Cl\textsubscript{2} 95:5 in 10 min. 390 nm was selected as reference wavelength for the peak detection.
Enantiomeric resolution of 3

The racemic resolution was achieved using a CHIRALPAK® IA semi-preparative chiral column packed with Amylose tris(3,5-dimethylphenylcarbamate) immobilized on 5 μm silica gel. The column temperature was set at 20 °C and the flow rate was constant during operation (3.6 mL/min). The mobile phase composition was hexane-CH₂Cl₂ gradient and the gradient profile was as follows: from 80:20 to 60:40 and from 60:40 to 80:20 in 12 min. 360 nm was selected as reference wavelength for the peak detection.

| Time (min) | Hexane (%) | CH₂Cl₂ (%) |
|------------|------------|------------|
| 0          | 80         | 20         |
| 9          | 60         | 40         |
| 10         | 80         | 20         |

Figure S3. Top: gradient profile. Medium: CSP-HPLC chromatogram of the separation of the enantiomers of 3. Bottom: HPLC traces of enantiopure samples.
Photophysical study

Molar extinction coefficient

Absorption spectra were carried out at room temperature in an Analitik Jena SPECORD® 200 Plus double beam spectrophotometer equipped with a UV-Vis lamp.

Figure S4. Top: Absorbance spectra of 1 at different concentrations in CH2Cl2. Bottom: Absorbance vs Concentration plot of average weighing of compound 1 at the maximum (346 nm).
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Figure S5. Top: Absorbance spectra of 2 at different concentrations in CH$_2$Cl$_2$. Bottom: Absorbance vs Concentration plots at the maximum (343 nm) of compound 2.
Figure S6. Top: Absorbance spectra of 3 at different concentrations in CH₂Cl₂. Bottom: Absorbance vs Concentration plots at the maximum (349 nm) of compound 3.
Excitation and Emission spectra of compounds 1-3 in DCM at different excitation wavelengths

Fluorescence excitation/emission spectra were collected on a Jasco FP-8300 spectrofluorimeter (Jasco, Tokyo, Japan).

Figure S7. (a) Excitation and (b) emission spectra of compound 1 in DCM.

Figure S8. (a) Excitation and (b) emission spectra of compound 2 in DCM.

Figure S9. (a) Excitation and (b) emission spectra of compound 3 in DCM.
Absorbance and fluorescence spectra in different solvents

**Figure S10.** Normalized absorbance (solid) and fluorescence ($\lambda_{\text{exc}} = 350$ nm, dashed) spectra of compound 1 in different solvents. Absorbance and fluorescence spectra were measured at 25 $^\circ$C. Color code: DCM (black), Hexane (red), MeCN (blue), MeOH (green).

**Figure S11.** Normalized absorbance (solid) and fluorescence ($\lambda_{\text{exc}} = 350$ nm, dashed) spectra of compound 2 in different solvents. Absorbance and fluorescence spectra were measured at 25 $^\circ$C. Color code: DCM (black), Hexane (red), MeCN (blue), MeOH (green).

**Figure S12.** Normalized absorbance (solid) and fluorescence ($\lambda_{\text{exc}} = 350$ nm, dashed) spectra of compound 3 in different solvents. Absorbance and fluorescence spectra were measured at 25 $^\circ$C. Color code: DCM (black), Hexane (red), MeCN (blue), MeOH (green).
Quantum yields, lifetimes and decay rate constants

The relative determination of the fluorescence quantum yield ($\Phi$) in a series of solvents was determined using a reference compound and the following formula:\[\text{S}2\]

$$
\Phi_x = \Phi_r \times \frac{F_x}{F_r} \times \frac{1 - 10^{-A_x(\lambda_{ex})}}{1 - 10^{-A_r(\lambda_{ex})}} \times \frac{n_r^2}{n_x^2}
$$

The subscripts $x$ and $r$ refer respectively to sample $x$ and reference (standard) fluorophore $r$ with known quantum yield $\Phi_r$ in a specific solvent; $F$ stands for the spectrally corrected, integrated fluorescence spectra; $A(\lambda_{ex})$ denotes the absorbance at the used excitation wavelength $\lambda_{ex}$; $n$ represents the refractive index of the solvent (in principle at the average emission wavelength). To minimize inner filter effects, the absorbance at the excitation wavelength $\lambda_{ex}$ was kept under 0.1. The measurements were performed using 10×10 mm cuvettes. Quinine in 0.1 M H$_2$SO$_4$ was used as fluorescence quantum yield reference ($\Phi_r = 0.52$) for compounds 1–3. All measurements were done on non-degassed samples at room temperature.

For the determination of fluorescence lifetimes, time-resolved fluorescence decay traces were collected in single photon timing (SPT) mode on a FluoTime 200 fluorometer (PicoQuant, GmbH). The excitation source was a 375-nm pulsed diode laser (LDH-P-375B, PicoQuant, GmbH) using a 20 MHz excitation frequency, and traces were recorded at two different wavelengths corresponding to the main bands of the emission spectra (each fluorescence lifetime results of the average of 3 measurements with a $\Delta \lambda =$5nm from the $\lambda_{max}$). The full width at half maximum (fwhm) of the laser pulses was around 40 ps. The fluorescence emission was collected at a 90° geometry, focused at the detector after crossing through a polarizer (set at the magic angle), 2-mm slits, and a 2-nm bandwidth monochromator. SPT was achieved by a TimeHarp200 board, set at 36 ps/channel. Fluorescence decay traces were collected for the necessary time to reach 20,000 counts at the peak channel and were fitted to a two or three-exponential function, by using a Levenberg-Marquard algorithm-based nonlinear least-squares error minimization deconvolution method (FluoFit 4.4 package, Picoquant GmbH). For each sample, the decay traces were fitted globally with the decay times linked as shared parameters, whereas the pre-exponential factors were local adjustable parameters. The quality of fittings was assessed by the value of the reduced chi-squared, $\chi^2$, parameter and random distributions of the weighted residuals and the autocorrelation functions.

The fluorescence emission ($k_f$) and nonradiative decay ($k_{nr}$) rate constants were determined at the maximum wavelength according to:

$$
\Phi = \frac{k_f}{k_f + k_{nr}} = k_f \tau_{av}
$$
Table S1. Quantum yields, lifetimes and decay rate constants of compound 1 in different solvents.

| Solvent     | Φ   | λ_{em} (nm) | τ_{1} (ns) | τ_{2} (ns) | τ_{3} (ns) | τ_{sw} (ns) | k_r (ns^{-1}) | k_{av} (ns^{-1}) |
|-------------|-----|-------------|------------|------------|------------|-------------|---------------|-----------------|
| CH_{2}Cl_{2} | 0.052 | 425-435 | 14.1±0.13 | 4.51±0.05 | 1.78±0.03 | 6.54        | 0.008         | 0.145           |
|             | 0.053 | 475-485 | 13.03±0.03 | 3.85±0.08 | -          | 12.77       | 0.004         | 0.074           |
| MeOH        | 0.006 | 460-470  | 15.49±0.19 | 3.01±0.09 | 0.32±0.005 | 6.21        | 0.016         | 0.145           |
| CH_{3}CN    | 0.016 | 475-485 | 16.27±0.33 | 5.43±0.17 | 1.96±0.01 | 4.12        | 0.004         | 0.239           |
| MeOH        | 0.005 | 535-545  | 8.66±0.17  | 2.61±0.07 | 0.37±0.005 | 2.57        | 0.016         | 0.145           |

Table S2. Quantum yields, lifetimes and decay rate constants of compound 2 in different solvents.

| Solvent     | Φ   | λ_{em} (nm) | τ_{1} (ns) | τ_{2} (ns) | τ_{3} (ns) | τ_{sw} (ns) | k_r (ns^{-1}) | k_{av} (ns^{-1}) |
|-------------|-----|-------------|------------|------------|------------|-------------|---------------|-----------------|
| CH_{2}Cl_{2} | 0.177 | 415-425 | 12.79±0.11 | 3.91±0.04 | 1.13±0.03 | 6.62        | 0.021         | 0.100           |
|             | 0.043 | 445-455 | 11.25±0.04 | 4.39±0.08 | 1.36±0.07 | 9.24        | 0.005         | 0.104           |
| CH_{3}CN    | 0.056 | 445-455 | 12.41±0.04 | 2.38±0.13 | -          | 11.79       | 0.005         | 0.080           |
| MeOH        | 0.051 | 450-460 | 13.20±0.4  | 2.82±0.15 | -          | 12.56       | 0.005         | 0.0075          |
| MeOH        | 0.051 | 455-465 | 12.59±0.08 | 5.77±0.04 | 2.01±0.07 | 8.14        | 0.005         | 0.0075          |

Table S3. Quantum yields, lifetimes and decay rate constants of compound 3 in different solvents.

| Solvent     | Φ   | λ_{em} (nm) | τ_{1} (ns) | τ_{2} (ns) | τ_{3} (ns) | τ_{sw} (ns) | k_r (ns^{-1}) | k_{av} (ns^{-1}) |
|-------------|-----|-------------|------------|------------|------------|-------------|---------------|-----------------|
| CH_{2}Cl_{2} | 0.109 | 445-455 | 16.90±0.13 | 8.26±0.04 | 1.93±0.08 | 10.92       | 0.010         | 0.082           |
|             | 0.049 | 445-455 | 9.31±0.03  | 4.45±0.05 | -          | 9.17        | 0.005         | 0.104           |
| CH_{3}CN    | 0.056 | 445-455 | 9.59±0.03  | 6.47±0.11 | -          | 8.99        | 0.006         | 0.105           |
| MeOH        | 0.062 | 455-465 | 18.36±0.11 | 3.07±0.17 | 0.13±0.002 | 13.73       | 0.0009        | 0.072           |

Decay rate constants were calculated at the maximum of emission.
Electronic circular dichroism (ECD) measurements

Electronic circular dichroism (ECD) was recorded in an Olis DSM172 spectrophotometer equipped with a xenon lamp of 150 W.

Compound 1

The ECD spectra were recorded after 50 scans at ca. $1.2 \times 10^{-5}$ M (for $P\cdot1$) and ca. $1.2 \times 10^{-5}$ M (for $M\cdot1$) in HPLC grade solvents and at 10 °C. For ECD measurements a fixed slit-width of 1 mm and 0.1 s of integration time were selected.

Figure S13. Experimental ECD spectra of $P\cdot1$ and $M\cdot1$ (navy/green), in CH$_2$Cl$_2$ at ca. $1.2 \times 10^{-5}$ M.
Compound 2

The ECD spectra were recorded after 50 scans at ca. $1.1 \times 10^{-5}$ M (for $P$) and ca. $1.0 \times 10^{-5}$ M (for $M$) in HPLC grade solvents and at 10°C. For ECD measurements a fixed slit-width of 1 mm and 0.1 s of integration time were selected.

Figure S14. Experimental ECD spectra of $P$ and $M$ (navy/green), in CH$_2$Cl$_2$ at ca. $1.1 \times 10^{-5}$ M and $1.0 \times 10^{-5}$ M.

Compound 3

The ECD spectra were recorded after 50 scans at ca. $1.4 \times 10^{-5}$ M (for $P$) and ca. $1.3 \times 10^{-5}$ M (for $M$) in HPLC grade solvents and at 10°C. For ECD measurements a fixed slit-width of 1 mm and 0.1 s of integration time were selected.

Figure S15. Experimental ECD spectra of $P$ and $M$ (green/navy), in CH$_2$Cl$_2$ at ca. $1.4 \times 10^{-5}$ M and $1.3 \times 10^{-5}$ M.
Determination and Analysis of Activation parameters by VT-CD

The value of the Gibbs activation energy ($\Delta G^\ddagger(T)$) for enantiomerization of 1-3 were obtained by following the decay of the enantiomeric excess (ee) in CD of the enantioenriched sample dissolved in n-heptane over time (t) at 90 °C ($\pm$ 0.2 °C) with the help of a peltier temperature control.

Remarkably, compounds 1-3 resist racemization. There are no hints of racemization at 90 °C. They were heated for 6 h without signal decay.

Figure S16. ECD signal decay of (M)-1 in n-heptane at 90 °C.

Figure S17. ECD signal decay of (P)-2 in n-heptane at 90 °C.
Figure S18. ECD signal decay of (M)-3 in n-heptane at 90 ºC.

The rate constant of racemization was calculated from the maximum time to which compounds 1-3 remain unchanged.

\[ t_{1/2} = \frac{\ln 2}{k_{rac}} \]

Since \( k_{rac} = 2k_e \), where \( k_e \) is the rate constant of enantiomerization, the \( k_e \) values were obtained and used to calculate the corresponding \( \Delta G^\ddagger(T) \) values by using the Eyring equation:

\[ \Delta G^\ddagger = -RT \ln \left( \frac{k_e h}{k_B T} \right) \]

where \( R \) is the gas constant (\( R = 1.98 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1} \)), \( h \) is the Planck constant (\( h = 6.62607 \times 10^{-34} \text{ J s} \)), \( k_B \) is the Boltzmann constant (\( k_B = 1.38064852 \times 10^{-23} \text{ J K}^{-1} \)), and \( \kappa \) is the transmission coefficient (\( \kappa = 0.5 \) or 1). The transmission coefficient \( \kappa = 0.5 \) was used due to the enantiomerization process is defined as a reversible first order reaction. Therefore, the corresponding \( \Delta G^\ddagger(T) \) value for 1-3 is at least 28.9 kcal mol\(^{-1}\) at 363 K.

We also tried to study the kinetics of the racemization at different temperatures by measurement the enantiomeric excess decay over time in (CSP)-HPLC. Unfortunately, when we heated a hexadecane solution of 1, 2 and 3 at 150°C over time, new chromatographic peaks appeared at the HPLC traces with new and unknown UV spectra. Therefore, instead of racemization, some kind of decomposition is observed. Those results prevent the study of the kinetics of racemization at different temperatures.
Cyclic Voltammetry (CV) and Square Wave Voltammetry (SWV) were carried out on a PGSTAT2014 potentiostat/galvanostat (Metrohm Autolab B. V.) with a three-electrode cell under Ar atmosphere at 25°C. A Pt wire counter electrode, an Ag wire quasireference electrode and a glassy carbon disk working electrode were used. CH₂Cl₂ was used as solvent to prepare a 0.1 M solution of tetra-n-butylammonium hexafluorophosphate (TBAPF₆) which was used as work solution. The scan rate was 0.05 V/s. Potential values are referred to the ferrocenium/ferrocene (FeCp²⁺/FeCp₂) system, Fc added as an internal reference after each measurement.

**Compound 1**

![Cyclic voltammogram of compound 1](image1.png)

*Figure S19. Cyclic (black) and Square Wave (red) voltammograms of compound 1 (2.5 mM).*

Cyclic voltammetry in CH₂Cl₂ shows a reversible oxidation wave at 0.83 V (vs Fc/Fc⁺) but no clear reduction potentials were observed.

**Compound 2**

![Cyclic voltammogram of compound 2](image2.png)

*Figure S20. Cyclic (black) and Square Wave (red) voltammograms of compound 2 (0.9 mM).*

Cyclic voltammetry in CH₂Cl₂ shows a reversible oxidation wave at 0.77 V (vs Fc/Fc⁺) but no clear reduction potentials were observed.
Cyclic voltammetry in CH$_2$Cl$_2$ shows a reversible oxidation wave at 0.78 V (vs Fc/Fc$^+$) but no clear reduction potentials were observed.
Figure S22. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 1.

Figure S23. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 1.
Figure S24. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 2.

Figure S25. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 2.
Figure S26. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3.

Figure S27. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 3.
2D-NMR spectra of compound 3

Figure S28. Multiplet analysis of compound 3.

Figure S29. Partial $^1$H-$^{13}$C HSQC (126 MHz, CD$_2$Cl$_2$) of compound 3.
Figure S30. Partial $^1$H-$^1$C HMBC (126 MHz, CD$_2$Cl$_2$) of compound 3.

Figure S31. Partial $^1$H-$^1$H COSY (500 MHz, CD$_2$Cl$_2$) of compound 3.
Figure S32. HRMS (ESI+) isotopic distribution of the [M+Na]+ signal of compound 1. Top: Calculated. Bottom: Experimental.

Figure S33. HRMS (ESI+) isotopic distribution of the [M+Na]+ signal of compound 2. Top: Calculated. Bottom: Experimental.
Figure S34. HRMS (ESI⁺) isotopic distribution of the [M+Na]⁺ signal of compound 3. Top: Calculated. Bottom: Experimental.
X-Ray Crystallography

X-ray diffraction-quality single crystals of compound 3 were grown by vapor diffusion of acetonitrile into a chloroform solution of 3. The diffraction data were collected on a Bruker D8 Venture diffractometer using a Mo radiation source and a Photon 100 detector. The structure was solved by direct methods using SHELXT\cite{S4} SHELX 2018\cite{S5} and the WinGX32\cite{S6} software were used for refinement, carried out with the full-matrix least-squares against $F^2$ procedure. C–H hydrogen atoms were placed in idealized positions ($U_{eq}(H) = 1.2U_{eq}(C)$ or $U_{eq}(H) = 1.5U_{eq}(C)$) and were allowed to ride on their parent atoms.

The structure of the title compound was readily and unequivocally determined. However, as usual in structures with tert-butyl groups, there was some disorder associated with them. Two of the groups were highly disordered and were split into two positions. Moreover, SIMU, DELU and ISOR instructions were needed to model the residue. For some of the remaining tert-butyl groups, large thermal ellipsoids were observed due to the thermal motion of these groups but the disorder could not be modeled.

Additionally, we observed a large amount of extra electron density in the unit cell, located in the void, corresponding to solvent. Thus, some acetonitrile molecules could be identified and modeled with the help of some restraints/constraints (DFIX, DANG, SIMU, DELU) in some cases. Nevertheless, large residual electron density was still present and could not be assigned to acetonitrile or chloroform molecules, although it probably corresponded to the same solvents. Therefore, the SQUEEZE\cite{S7} routine included in PLATON\cite{S8} was applied and a density of 349 e$^{-}$ in an approximately 1286 Å$^3$ volume was identified. This density was removed and the data refined against the model.

Summary of the X-ray diffraction measurement and refinement data: Chemical formula, C$_{130}$H$_{121}$N$_3$O$_2$; Mr, 1757.29; crystal size [mm$^3$], 0.636 x 0.372 x 0.235; temperature, 130(2) K; wavelength [Å], 0.71073 (Mo Ka), crystal system, monoclinic; space group, $P2_1/n$; a [Å], 13.6873(9); b [Å], 25.1606(14); c [Å], 31.4942(18); $\alpha$ [$^\circ$], 90; $\beta$ [$^\circ$], 94.602(2); $\gamma$ [$^\circ$], 90; V [Å$^3$], 10811.0(11); Z, 4; $\rho$\text{calcld} [Mg m$^{-3}$], 1.080; $\mu$ [mm$^{-1}$], 0.063; F(000), 3752; $\theta$ range [$^\circ$], 2.108 to 28.741; $hkl$ ranges, -18/16, -33/33, -42/40; reflections collected, 76671; independent reflections, 27741; $R_{int}$, 0.0292; completeness to $\theta = 25.242^\circ$, 99.6%; absorption correction, numerical; refinement method; full-matrix least-squares on $F^2$; Final $R$ indices [h-2$\theta$(i)], $R_I = 0.0698$, $wR_2 = 0.1878$; $R$ indices (all data), $R_I = 0.0903$, $wR_2 = 0.2024$; goodness-of-fit on $F^2$, 1.020.

CCDC-XXX contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Crystal structure of compound 3 showing the asymmetric unit in a ORTEP\cite{S9} type representation. H atoms and solvent molecules are omitted for clarity. The thermal ellipsoids are shown at 50% probability.}
\end{figure}
Figure S36. Different views of the crystal structure of compound 3 showing the dimensions of the saddle generated by the incorporation of the nine-membered ring into the [5]helicene moiety. Distances [Å]: a, 4.90-5.10; b, 3.08-3.14. Distance a was calculated as the C–C distance shown in the view on the right. Distance b was calculated as the distance between the centroid of distance a and the mean plane defined by the 4 central C atoms of the nonagon.
Computational details

The Gaussian 16 (Revision A.03) software package was used to perform theoretical studies over compounds 1–3. The optimized ground state geometries of the different compounds were obtained from DFT optimizations using the Coulomb-attenuated Becke three-parameters exchange function in combination with the Lee-Yang-Parr correlation functional (CAM-B3LYP). The basis set used for these optimizations was the 6-31G(d,p). Optimized geometries were confirmed to be stationary points by analysis of their vibrational frequencies. The 50 lowest energetic transitions were calculated by TD-DFT, using the CAM-B3LYP functional, selecting the 6-311++G(d,p) basis set and including solvent effects via the Polarizable Continuum Model (PCM) as implemented in Gaussian 16 with the dielectric constant of dichloromethane. The simulated UV-Vis/ECD spectra were plotted with a half-width at half-height of 0.2 eV using GaussView (version 6.1.1). The obtained spectra were corrected to better fit the experimental results by -0.5 eV (for 1), -0.6 eV (for 2) and -0.5 eV (for 3).

Figure S37. Different views of the optimized geometry of compound (M-1 (CAM-B3LYP/6-31G(d,p)) showing the interplanar angle between the two terminal rings of the helicene moiety. Hydrogens were omitted for clarity.

Figure S38. Different views of the optimized geometry of compound (M-2 (CAM-B3LYP/6-31G(d,p)) showing the interplanar angle between the two terminal rings of the helicene moiety. Hydrogens were omitted for clarity.
Figure S39. Different views of the optimized geometry of compound (M)-3 (CAM-B3LYP/6-31G(d,p)) showing the interplanar angle between the two terminal rings of the helicene moiety. Hydrogens were omitted for clarity.
Calculated electronic transitions and simulated UV-Vis and ECD spectra

Figure S40. Top: Oscillatory strength of the calculated first 50 electronic transitions (black), simulated UV-Vis spectrum (red) and experimental UV-Vis spectrum (gray) of 1. Bottom: Rotatory strength of the calculated first 50 electronic transitions (black), simulated ECD spectrum (red) and experimental ECD spectrum of (M-1).
Figure S41. Top: Oscillatory strength of the calculated first 50 electronic transitions (black), simulated UV-Vis spectrum (red) and experimental UV-Vis spectrum (gray) of 2. Bottom: Rotatory strength of the calculated first 50 electronic transitions (black), simulated ECD spectrum (red) and experimental ECD spectrum of (M-2).
Figure S42. Top: Oscillatory strength of the calculated first 50 electronic transitions (black), simulated UV-Vis spectrum (red) and experimental UV-Vis spectrum (gray) of 3. Bottom: Rotatory strength of the calculated first 50 electronic transitions (black), simulated ECD spectrum (red) and experimental ECD spectrum of (M-3).
Table S4. Calculated main parameters describing the $S_0 \rightarrow S_2$ transition in compounds ($M$)-1, ($M$)-2 and ($M$)-3.

| Compound | $|\mu|$ / 10⁻²⁰ esu cm | $|m|$ / 10⁻²⁰ erg G⁻¹ | $\cos(\theta_{\mu,m})$ | $D$ / 10⁻⁴⁰ esu² cm² | $G$ / 10⁻⁴⁰ erg G⁻² | $R$ / 10⁻⁴⁰ erg esu cm G⁻¹ | $f$ | $g_{abs.~calcd.}$ / 10⁻³ |
|----------|-----------------------|------------------------|-------------------|----------------------|----------------------|-----------------------------|-----|------------------------|
| 1        | 235                   | 0.116                  | 0.96              | 55,409               | 0.0134               | 26.26                       | 0.0745 | 1.9                   |
| 2        | 133                   | 0.1076                 | 0.84              | 17,688               | 0.0116               | 12.06                       | 0.0242 | 2.7                   |
| 3        | 158                   | 0.2839                 | 0.65              | 25,131               | 0.0806               | 29.43                       | 0.0341 | 4.7                   |

$|\mu|$ = Transition electric dipole moment; $|m|$ = Transition magnetic dipole moment; $D$ = Electric dipole strength; $G$ = Magnetic dipole strength; $R$ = Rotatory strength; $f$ = Oscillator strength.

Table S5. Calculated main parameters describing the $S_0 \rightarrow S_1$ transition in compounds ($M$)-1, ($M$)-2 and ($M$)-3.

| Compound | $|\mu|$ / 10⁻²⁰ esu cm | $|m|$ / 10⁻²⁰ erg G⁻¹ | $\cos(\theta_{\mu,m})$ | $D$ / 10⁻⁴⁰ esu² cm² | $G$ / 10⁻⁴⁰ erg G⁻² | $R$ / 10⁻⁴⁰ erg esu cm G⁻¹ | $f$ | $g_{abs.~calcd.}$ / 10⁻³ |
|----------|-----------------------|------------------------|-------------------|----------------------|----------------------|-----------------------------|-----|------------------------|
| ($M$)-1  | 27                    | 0.0544                 | −0.52             | 715                  | 0.0030               | −0.76                       | 0.0009 | −4.2                  |
| ($M$)-2  | 27                    | 0.0616                 | −0.44             | 736                  | 0.0038               | −0.74                       | 0.0010 | −4.0                  |
| ($M$)-3  | 113                   | 0.0360                 | −0.48             | 12,740               | 0.0013               | −1.93                       | 0.0166 | −0.6                  |
| ($M$)-S1 Doublebond | 71  | 0.0415                 | −0.66             | 5,051                | 0.0017               | −1.95                       | 0.0066 | −1.5                  |
| ($M$)-S2 keto extended | 248 | 0.2110                 | 0.21              | 61,534               | 0.0445               | 10.78                       | 0.0787 | 0.7                   |
| ($M$)-S3 Keto ch2 | 112  | 0.0496                 | −0.69             | 12,580               | 0.0025               | −3.87                       | 0.0160 | −1.2                  |

$|\mu|$ = Transition electric dipole moment; $|m|$ = Transition magnetic dipole moment; $D$ = Electric dipole strength; $G$ = Magnetic dipole strength; $R$ = Rotatory strength; $f$ = Oscillator strength.

Figure S43. Representation of the transition electric dipole moments ($|\mu|$, yellow capped arrows), transition magnetic dipole moments ($|m|$, blue capped arrows) and the angle between them of the lowest energy transition of compounds ($M$)-1 (left), ($M$)-2 (middle) and ($M$)-3 (right). *Represented using a.u. obtained from TD-DFT calculation **Module of the transition electric dipole moment of compound ($M$)-3 is shown 10 times lower for an easier interpretation.
### Compound 1

| Orbitals contributing to the lowest energy transition \((S_0 \rightarrow S_1)\) | Contribution to excitation \((\text{Gaussian coefficient})\) |
|---------------------------------------------------------------|---------------------------------------------------------------|
| HOMO-1 → LUMO                                                  | 42% \((-0.43217)\)                                           |
| HOMO-1 → LUMO+2                                                | 5% \((-0.14714)\)                                            |
| HOMO → LUMO+1                                                  | 50% \((-0.46861)\)                                           |
| HOMO → LUMO+3                                                  | 3% \(0.10776)\)                                              |

---

**HOMO-1**

**LUMO**

**HOMO**

**LUMO+1**
### Compound 2

| Orbitals contributing to the lowest energy transition \((S_0 \rightarrow S_1)\) | Contribution to excitation \(\text{Gaussian coefficient}\) |
|---|---|
| HOMO-1 \(\rightarrow\) LUMO | 36\% \((0.39887)\) |
| HOMO-1 \(\rightarrow\) LUMO+1 | 13\% \((0.23701)\) |
| HOMO \(\rightarrow\) LUMO | 15\% \((-0.25604)\) |
| HOMO \(\rightarrow\) LUMO+1 | 36\% \((0.39751)\) |

![HOMO-1](image1) ![HOMO](image2) ![LUMO](image3) ![LUMO+1](image4)
### Compound 3

| Orbitals contributing to the lowest energy transition ($S_0 \rightarrow S_1$) | Contribution to excitation (Gaussian coefficient) |
|-------------------------------------------------|--------------------------------------------------|
| HOMO-1 → LUMO | 10% (-0.20514) |
| HOMO-1 → LUMO+1 | 33% (-0.37107) |
| HOMO → LUMO | 48% (0.44929) |
| HOMO → LUMO+1 | 10% (-0.20415) |
| HOMO → LUMO+3 | 5% (0.14969) |

![HOMO-1](image1.png)  ![HOMO](image2.png)  ![LUMO](image3.png)  ![LUMO+1](image4.png)
**Optimized geometries**

**Compound 1**

| Atom | X | Y | Z | Atom | X | Y | Z |
|------|---|---|---|------|---|---|---|
| C    | -1.41808000 | -5.35506900 | 2.44000500 | C    | -1.00560600 | -4.10951500 | 2.89912000 |
| C    | -0.79834300 | -3.07553300 | 1.99945000 | C    | -0.99755600 | -3.23466700 | 0.62174000 |
| C    | -1.43288200 | -4.49326300 | 0.16782600 | C    | -1.62968800 | -5.53088200 | 1.08556200 |
| C    | -0.60791800 | -1.97978500 | -0.13516200 | C    | 0.74661900 | -1.92861300 | -0.51952800 |
| C    | 1.50086000 | -3.11606100 | -0.91548500 | C    | 0.95717400 | -4.07420500 | -1.80196500 |
| C    | 1.63345400 | -3.74472100 | -2.28656700 | C    | 1.80381900 | -4.80854100 | -1.24461900 |
| C    | 2.84695500 | -3.22824500 | -0.51726800 | C    | 3.50842100 | -4.44835000 | -0.71900400 |
| C    | 2.88377000 | -5.48197400 | -1.38767400 | C    | 3.59126300 | -1.90380900 | 0.26437600 |
| C    | 1.64258700 | -5.26623700 | -1.98603100 | C    | 1.35327900 | -0.77709400 | -0.03875100 |
| C    | -0.66199100 | 0.45989500 | -0.15516200 | C    | 0.74959100 | 0.47782500 | -0.22089900 |
| C    | 1.45411700 | -0.72616200 | -0.37113000 | C    | -2.81463200 | -0.74160300 | -2.28657000 |
| C    | -1.36678200 | 1.72111900 | -0.12481100 | C    | 1.48615900 | 1.71455800 | -0.16396100 |
| C    | 2.88585800 | -0.77127300 | -0.18336100 | O    | -2.20923500 | 5.91908200 | -1.54791500 |
| C    | 3.60375200 | -1.90380900 | -0.26437600 | C    | -4.96770200 | -1.86216400 | -0.42990600 |
| C    | -5.65493800 | -0.64204100 | 0.49473900 | C    | -4.89653600 | 0.50281900 | 0.35665200 |
| C    | -3.50187100 | 0.48991700 | 0.16765300 | C    | -2.77547800 | 1.74806300 | -0.16932200 |
| C    | -3.43799000 | 2.97149900 | -0.08904100 | C    | -2.76503500 | 4.18024300 | -0.23398900 |
| C    | -1.37928700 | 4.14245900 | -0.28108900 | C    | -0.66289700 | 2.94594300 | -0.21783800 |
| C    | 0.80258800 | 2.94321000 | -0.20756000 | C    | 1.54460700 | 4.12774400 | -0.21400000 |
| C    | 2.93682300 | 4.13574200 | -0.18014700 | C    | 3.59126300 | 2.91228700 | -0.10912600 |
| C    | 2.89668100 | 1.70265600 | -0.08287500 | C    | 3.59780800 | 0.42288300 | 0.04818900 |
| C    | 4.93481900 | 0.34647400 | 0.43806000 | C    | 5.03086900 | -0.08979200 | 0.59410300 |
| C    | 4.88402300 | -2.03660800 | 0.32519800 | C    | 3.54921200 | -2.01458900 | -0.07622300 |
| C    | -3.56232300 | 5.48438000 | -0.32234500 | C    | -2.65580400 | 6.70890020 | -0.47633800 |
| C    | -4.50101000 | 5.42221300 | -1.53932400 | C    | -4.39617900 | 5.63522800 | 0.95851300 |
| C    | -7.16936000 | -0.62175000 | 0.75016600 | C    | -7.50747600 | -1.32203400 | 0.20818900 |
| C    | -7.73732000 | 0.80219700 | 0.74936200 | C    | -7.84862000 | -1.37155600 | -0.45927100 |
| C    | 3.68422900 | 5.47197800 | -0.21408800 | C    | 5.20465600 | 5.28789100 | -0.17522500 |
| C    | 3.26911100 | 6.31625600 | -0.02990900 | C    | 3.32217600 | 6.22387800 | -1.50619000 |
| C     | 7.05522400 | -0.88019200 | 1.05280200 |
| C     | 7.62002100 | -2.29966000 | 1.16352000 |
| C     | 7.15734000 | -0.21150400 | 2.43436100 |
| C     | 7.91060200 | -0.09822800 | 0.04140000 |
| H     | -1.57785800 | -6.17485600 | 3.13515300 |
| H     | -0.83702000 | -3.94051100 | 3.95739900 |
| H     | -0.46168800 | -2.11105100 | 2.36313500 |
| H     | -1.96662300 | -6.48133500 | 0.69166000 |
| C     | -0.16990200 | -3.73757800 | -2.76955000 |
| H     | 4.53197300 | -4.57723400 | -0.39035900 |
| H     | 3.39934900 | -6.42527000 | 1.53207100 |
| H     | 1.23074900 | -6.01598100 | -2.65443700 |
| H     | -3.14474100 | -2.87398000 | 0.23173600 |
| H     | -5.50595100 | -2.80018600 | 0.51334400 |
| H     | -5.39990800 | 1.45518100  | 0.40363700  |
| H     | -4.51706900 | 2.99498800  | -0.04320500 |
| H     | -0.83881500 | 5.07143800  | -0.37286000 |
| H     | 1.03051600  | 5.07826200  | -0.24549200 |
| H     | 4.67061100  | 2.89287400  | 0.08995600  |
| H     | 5.47025700  | 1.26011400  | 0.65729300  |
| H     | 5.38174600  | 2.98922700  | 0.43084500  |
| H     | -1.98236700 | 6.82692300  | 0.37739900  |
| H     | -2.05176000 | 6.65592600  | -1.38643700 |
| H     | -3.26967800 | 7.61201600  | -0.53930500 |
| H     | -5.20565100 | 4.59024700  | -1.46655400 |
| H     | -3.93102700 | 5.30022100  | -2.46467500 |
| H     | -5.08196600 | 6.34618200  | -1.61562900 |
| H     | -5.09932600 | 4.83408600  | 1.10774900  |
| H     | -3.75037400 | 5.07034000  | 1.83987400  |
| H     | -4.97463500 | 6.58571700  | 0.90944600  |
| H     | -7.16443300 | -2.35936600 | 2.03762600  |
| H     | -7.04013700 | -0.80502800 | 2.87105800  |
| H     | -8.58965500 | -1.32622100 | 2.18813000  |
| H     | -7.54671500 | 1.34355500  | -0.18276700 |
| H     | -7.30333000 | 1.37974800  | 1.57342700  |
| H     | -8.81370200 | 0.76264500  | 0.90000800  |
| H     | -7.62314300 | -0.89034700 | -1.41580400 |
| H     | -7.51259800 | -2.41039500 | 0.51954500  |
| H     | -8.93161300 | -1.37608200 | -0.32415500 |
| H     | 5.56604600  | 4.71397000  | 1.03312400  |
| H     | 5.52945900  | 4.78237900  | 0.73855000  |
| H     | 5.69116800  | 6.26634300  | -0.20286400 |
| H     | 2.19602600  | 6.52221900  | 1.00786600  |
| H     | 3.51726800  | 5.80291300  | 1.93585900  |
| H     | 3.79311900  | 7.27666900  | 0.99242700  |
| H     | 2.25032700  | 6.42576900  | -1.57168000 |
| H     | 3.60950500  | 5.64394000  | -2.38751900 |
| H     | 3.84590300  | 7.18275100  | -1.54407600 |
| H     | 7.59965700  | -2.82142020 | 0.20243900  |
| H     | 7.06916100  | -2.90049900 | 1.89278600  |
| H     | 8.66133600  | -2.25323500 | 1.49262200  |
| H     | 6.81152100  | 0.82477000  | 2.41060500  |
| H     | 6.55638900  | -0.74991600 | 3.17260100  |
| H     | 8.19651900  | -0.20904300 | 2.77672300  |
| H     | 7.58471200  | 0.94082900  | -0.04849100 |
| H     | 7.85516800  | -0.55518200 | -0.95064900 |
| H     | 8.95828000  | -0.09343500 | 0.35673200  |
| H     | -1.91441200 | -2.76789300 | -1.89649000 |
| H     | -2.29076600 | -3.98347500 | -3.12397000 |
| H     | 0.04213100  | -2.75616300 | -3.20310200 |
| H     | -0.09300900 | -4.46063500 | -3.58415500 |
### Zero-point correction

- 1.009185 (Hartree/Particle)

### Thermal correction to Energy
- 1.061681

### Thermal correction to Enthalpy
- 1.062625

### Thermal correction to Gibbs Free Energy
- 0.924165

### Sum of electronic and zero-point Energies
- -2431.437644

### Sum of electronic and thermal Energies
- -2431.385148

### Sum of electronic and thermal Enthalpies
- -2431.384204

### Sum of electronic and thermal Free Energies
- -2431.522664

**Compound 2**

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 2.48449500| -5.80142900| -0.72295500|
| C       | 1.53312600| -5.29434200| -1.60047700|
| C       | 0.90465500| -4.09046900| -1.31181300|
| C       | 1.21491200| -3.37705300| -0.15283000|
| C       | 2.13996900| -3.90936200| 0.75258000  |
| C       | 0.58372500| -2.03159400| 0.03823900  |
| C       | -0.77965500| -2.00576300| 0.38879300  |
| C       | -1.51727600| -3.19312300| 0.84859300  |
| C       | -0.98582500| -4.17579000| 1.72488000  |
| C       | 1.14552900| -2.88787800| 2.84685000  |
| C       | 2.38333500| -3.23421700| 2.04962300  |
| C       | 2.77135400| -5.11677900| 0.45030000  |
| C       | 0.58832700| -2.03159400| 0.03823900  |
| C       | 0.82854300| -2.03159400| 0.03823900  |
| C       | 1.57127600| -3.19312300| 0.84859300  |
| C       | 0.98582500| -4.17579000| 1.72488000  |
| C       | 1.14552900| -2.88787800| 2.84685000  |
| C       | 2.38333500| -3.23421700| 2.04962300  |
| C       | 2.77135400| -5.11677900| 0.45030000  |
| C       | 0.58832700| -2.03159400| 0.03823900  |
| C       | 0.82854300| -2.03159400| 0.03823900  |
| C       | 1.57127600| -3.19312300| 0.84859300  |
| C       | 0.98582500| -4.17579000| 1.72488000  |
| C       | 1.14552900| -2.88787800| 2.84685000  |
| C       | 2.38333500| -3.23421700| 2.04962300  |
| C       | 2.77135400| -5.11677900| 0.45030000  |
| C       | 0.58832700| -2.03159400| 0.03823900  |
| C       | 0.82854300| -2.03159400| 0.03823900  |
| C       | 1.57127600| -3.19312300| 0.84859300  |
| C       | 0.98582500| -4.17579000| 1.72488000  |
| C       | 1.14552900| -2.88787800| 2.84685000  |
| C       | 2.38333500| -3.23421700| 2.04962300  |
| C       | 2.77135400| -5.11677900| 0.45030000  |
| C       | 0.58832700| -2.03159400| 0.03823900  |
| C       | 0.82854300| -2.03159400| 0.03823900  |
| C       | 1.57127600| -3.19312300| 0.84859300  |
| C       | 0.98582500| -4.17579000| 1.72488000  |
| C       | 1.14552900| -2.88787800| 2.84685000  |
| C       | 2.38333500| -3.23421700| 2.04962300  |
| C       | 2.77135400| -5.11677900| 0.45030000  |
| C       | 0.58832700| -2.03159400| 0.03823900  |
| C       | 0.82854300| -2.03159400| 0.03823900  |
| C       | 1.57127600| -3.19312300| 0.84859300  |
| C       | 0.98582500| -4.17579000| 1.72488000  |
| C       | 1.14552900| -2.88787800| 2.84685000  |
|   |   |   |   |
|---|---|---|---|
| C | 7.57639000 | 0.94661400 | -1.26408300 |
| C | 7.72199800 | -1.50404500 | 1.29339400 |
| C | 7.30308700 | 6.13373500 | -0.10673800 |
| C | -8.0527000 | -1.06813200 | -1.29829600 |
| C | -7.10852700 | -1.21092900 | -2.60528400 |
| H | 2.98524200 | -6.73950200 | 0.93981200 |
| H | 1.28229800 | -5.83242200 | 2.50880600 |
| H | 0.17797800 | -3.67624200 | -2.00329100 |
| H | 3.47855200 | 5.52707200 | 1.16378100 |
| H | 0.27308500 | 3.97622500 | -2.81998700 |
| H | 4.51788300 | 4.69278300 | 0.19006300 |
| H | -1.25012600 | -6.11446000 | 2.46739200 |
| H | 2.91225500 | -2.68201300 | -1.49647000 |
| H | 5.23360300 | -2.50400800 | 2.02759800 |
| H | 5.27223900 | 1.50440600 | -0.58722500 |
| H | 4.41621900 | 2.88405300 | 0.40224100 |
| H | 3.12073900 | 6.56589000 | 1.29221700 |
| H | 1.25012600 | 6.11446000 | 2.46739200 |
| H | 1.82820000 | 6.32485000 | 1.29221700 |
| H | 3.59619200 | 4.78345500 | 3.12050600 |
| H | 4.22295200 | 5.93568000 | 2.56656400 |
| H | 7.48546000 | 1.15708900 | 0.19440500 |
| H | 7.10854000 | 1.76671800 | -1.81507000 |
| H | 6.40928000 | 0.94775500 | -1.54308000 |
| H | 7.61608400 | -1.36531000 | 0.22194900 |
| H | 7.35290500 | -2.50269800 | -1.10370000 |
| H | 8.78848800 | -1.47293900 | -1.10370000 |
| H | 7.13927000 | 4.60520100 | 0.73975000 |
| H | 7.56539000 | 4.86140100 | -1.02957400 |
| H | 8.01498000 | 6.15058000 | -0.10645600 |
| H | -2.27583900 | 6.42142900 | -1.17886000 |
| H | -3.55407700 | 5.88669700 | -1.25206100 |
| H | -3.87648500 | 7.16634600 | -1.22904100 |
| H | -2.43700600 | 6.34641800 | 1.40398000 |
| H | -3.80206800 | 5.58832200 | 2.16775600 |
| H | -4.03577500 | 7.08987300 | 1.30240300 |
| H | -7.63090300 | -3.00303000 | -0.32820000 |
| H | -7.93593000 | -3.10456900 | 2.01546400 |
| H | -8.69536800 | -2.47316300 | -1.63123600 |
| H | -6.89329400 | 0.61428100 | -2.60371100 |
| H | -6.61832100 | -0.96869700 | -3.33611800 |
| H | -8.26512000 | -0.44434400 | -2.94604700 |
| H | -7.67385300 | 0.76181500 | -0.13985300 |
|    | X        | Y        | Z        |
|----|----------|----------|----------|
| H  | -7.91955200 |-0.72163700 | 0.78633400 |
| H  | -9.02856600 |-0.30181100 | -0.72163700 |
| H  | 0.72859100 | -2.51646000 | 3.89018800 |
| H  | -0.52850400 | -3.84319300 | 3.72602900 |
| H  | 0.57415900 | -4.94972000 | 2.96001000 |
| H  | 3.61386600 | -3.01509800 | 2.50900100 |
| H  | 3.78190300 | -2.56581300 | 3.48292400 |
| H  | 4.49038800 | -3.25140100 | 1.91513500 |

Zero-point correction= 1.032043 (Hartree/Particle)
Thermal correction to Energy= 1.084858
Thermal correction to Enthalpy= 1.85802
Thermal correction to Gibbs Free Energy= 0.947763

Sum of electronic and zero-point Energies= -2395.303140
Sum of electronic and thermal Energies= -2395.250325
Sum of electronic and thermal Enthalpies= -2395.249381
Sum of electronic and thermal Free Energies= -2395.387420

Compound 3

|    | X        | Y        | Z        |
|----|----------|----------|----------|
| C  | 2.69493300 | -5.69897600 | 0.67268300 |
| C  | 1.67215000 | -5.32314600 | -1.53751600 |
| C  | 0.95125000 | -4.15963400 | -1.29785800 |
| C  | 1.24363200 | -3.36030400 | -0.19339100 |
| C  | 2.23569890 | -3.77133100 | 0.70470300 |
| C  | 0.56860200 | -2.03271200 | 0.02165600 |
| C  | -0.79579200 | -2.01192200 | 0.32165600 |
| C  | -1.53698800 | -3.19442500 | 0.78448800 |
| C  | -1.00464600 | -4.19289800 | 1.66028800 |
| C  | 1.11168100 | -2.82037300 | 2.72424400 |
| C  | 2.38368400 | -2.97246500 | 1.93874700 |
| C  | -2.88746500 | -3.32265200 | 0.36918700 |
| C  | -3.55268900 | -4.53751400 | 0.56698000 |
| C  | -2.93810400 | -5.57539000 | 1.23690000 |
| C  | -1.69943900 | -5.36310900 | 1.82636100 |
| C  | 1.25579800 | -0.81729900 | -0.27939700 |
| C  | 0.55251400 | 0.39957700 | -1.02681100 |
| C  | -0.85190300 | 0.38977000 | -0.00208800 |
| C  | -1.53166600 | -0.82800300 | 1.29435000 |
| C  | 2.66977400 | -0.71032900 | 0.69325200 |
| C  | 1.24679300 | 1.66054500 | 0.00269600 |
| C  | -1.60073400 | 1.62004000 | -0.19098000 |
| C  | -2.96030600 | -0.88096600 | -0.04430500 |
| C  | 3.51411300 | -2.43931300 | 2.39538000 |
| C  | 3.36948000 | -1.73364000 | -1.36448400 |
| C  | 4.69682900 | -1.61777700 | -1.70171100 |
| C  | 5.42981400 | -0.46067900 | -1.40424700 |
| C  | 4.73227700 | 0.57768000 | -0.81626100 |
| C  | 3.37067500 | 0.49489800 | -0.47545500 |
| C  | 2.65777400 | 1.68891600 | -0.10165000 |
| C  | 3.31154500 | 2.86887700 | 0.33255100 |
| C  | 2.62376600 | 4.04328200 | 0.63472600 |
| C  | 1.23809500 | 4.02026900 | 0.54268000 |
| C  | 0.53235300 | 2.85878000 | 0.21987800 |
| C  | -0.92892500 | 2.85633800 | 0.09702200 |
| C  | -1.67746200 | 4.03054700 | 0.07924800 |
| C  | -3.06771800 | 4.02946900 | -0.02497800 |
| C  | -3.70907500 | 2.80122100 | -1.03143500 |
| C  | -3.00586500 | 1.59481400 | -1.14462200 |
| C  | -3.68649400 | 0.30385700 | -0.28989600 |
|   |   |   |   |
|---|---|---|---|
| H | -3.85521600 | 5.53263800 | 2.15523500 |
| H | -4.06733500 | 7.07217700 | 1.30425700 |
| H | -7.65192800 | -3.00348300 | -0.42276100 |
| H | -7.09909400 | -3.10167800 | -2.10527900 |
| H | -8.70417100 | -2.47082500 | -1.73432700 |
| H | -6.89291100 | 0.61858200 | -2.68349700 |
| H | -6.61218100 | -0.96281200 | -3.41724800 |
| H | -8.26207200 | -0.43865400 | -3.04033100 |
| H | -7.69565800 | 0.76085500 | -0.22656400 |
| H | -7.94938600 | -0.72440600 | 0.69437700 |
| H | -9.04684500 | -0.30188800 | -0.63088600 |
| H | 3.50732800 | -1.86789100 | 3.31722600 |
| H | 4.44991400 | -2.54250700 | 1.85668100 |
| O | 0.93202500 | -1.90445000 | 3.49719400 |
| C | 0.14285700 | -4.00108600 | 2.65924900 |
| H | -0.33829200 | -3.98197500 | 3.64200000 |
| H | 0.75301000 | -4.90955900 | 2.61907000 |

Zero-point correction = 1.012640 (Hartree/Particle)
Thermal correction to Energy = 1.066210
Thermal correction to Enthalpy = 1.067155
Thermal correction to Gibbs Free Energy = 0.927299

Sum of electronic and zero-point Energies = -2469.316774
Sum of electronic and thermal Energies = -2469.26204
Sum of electronic and thermal Enthalpies = -2469.262260
Sum of electronic and thermal Free Energies = -2469.402115
SUPPORTING INFORMATION

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