Supporting Information

Preparation and Physicochemical Properties of [6]Helicenes Fluorinated at Terminal Rings

Vladimír Církva,†[a‡] Pavel Jakubík,[†[a‡]] Tomáš Strašák,[a§] Jan Hrbáč,[b] Jan Sýkora,[†[a⊥]] Ivana Císařová,[c] Jan Vacek,[[d]] Jaroslav Žádný,[a‡] and Jan Storch[a‡]

[a‡] Department of Advanced Materials and Organic Synthesis, Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, v. v. i., Rozvojová 135, 165 02 Prague 6, Czech Republic

[a§] Department of Bioorganic Compounds and Nanocomposites, Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, v. v. i., Rozvojová 135, 165 02 Prague 6, Czech Republic

[a⊥] Department of Analytical Chemistry, Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, v. v. i., Rozvojová 135, 165 02 Prague 6, Czech Republic

[b] Institute of Chemistry, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic

[c] Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 128 40 Prague 2, Czech Republic

[d] Department of Medical Chemistry and Biochemistry, Faculty of Medicine and Dentistry, Palacký University, Hněvotinská 3, 775 15 Olomouc, Czech Republic

†These authors contributed equally to the paper as first authors.

E-mails: cirkva@icpf.cas.cz, sykora@icpf.cas.cz, jan.vacek@upol.cz
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1. Setup of Photoreactions

1.1. Batch Experiments

A 400-watt high-pressure Hg lamp (HQL 400W, Osram) was modified by cutting away the outer glass envelope from the screw base and it was connected to the corresponding power unit (ballast). The light beam was used inside a water-jacketed cylindrical (diameter = 6 cm) Pyrex photoreactor (Development workshop, IOCB CAS, Czech Republic). A solution of starting compound in a tall 2 L beaker was irradiated for appropriate time and the beaker was light-isolated to avoid unnecessary exposure to UV light. The operating temperature inside the photochemical reaction mixture was controlled by the magnetic stirrer with a hot plate and a slow stirring was maintained during the reaction (200 rpm).

1.2. Continuous Flow Experiments

The photochemical experiments were performed using a homemade flow photoreactor equipped with a high-pressure Hg lamp (HQL 400W, Osram) and a PTFE-diaphragm pump system (EW-07090-62, Masterflex, see Figure S1). A fluorinated ethylene propylene (FEP) tubing (ID/OD = 2/3 mm, total length = 50 m, BOLA Tubing) was tightly wrapped around the water-jacketed cylindrical (diameter = 6 cm) Pyrex photoreactor. The irradiation area of the FEP tubing was covered with two layers of aluminum foil to make the use of UV light effective. The temperature was set and maintained at 60°C using the magnetic stirrer with a hot plate. A solution of starting compound in reactant reservoir was passed continuously through the flow photoreactor system and collected. Solvent was removed by a rotary vacuum evaporator.

Figure S1. Flow photoreactor setup used in the present study (1 - water-jacketed cylindrical Pyrex photoreactor; 2 - high-pressure Hg lamp, 400 W; 3 - cryostat for water cooling; 4 - FEP tubing; 5 - reactant reservoir; 6 - magnetic stirrer with hot plate; 7 - PTFE-diaphragm pump; 8 - product collector).
2. Preparation of 8 and 9

2.1. Preparation of benzo[c]phenanthrene-2-carbaldehyde (8)

Benzo[c]phenanthrene-2-carbaldehyde (8) was prepared according to a following reaction scheme (Scheme S1) via synthesis of intermediates (i) and (ii).

![Scheme S1](image)

2.2. Preparation of (2,3,4,5-tetrafluorobenzyl)triphenylphosphonium bromide (9)

(2,3,4,5-Tetrafluorobenzyl)triphenylphosphonium bromide (9) was prepared according to a following reaction scheme (Scheme S2) via synthesis of intermediates (iii) and (iv).

![Scheme S2](image)
3. X-ray Crystallographic Studies

The crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

X-ray data of 1,2,3,4-tetrafluoro[6]helicene (6): C_{26}H_{12}F_{4}, M = 400.36 g.mol\(^{-1}\), orthorhombic system, space group \(P2_12_12_1\), a = 7.6014(3), b = 11.0951(4), c = 21.1486(10) Å, Z = 4, V = 1783.64(13) Å\(^3\), \(D_c = 1.49\) g.cm\(^{-3}\), \(\mu(\text{Mo K}\alpha) = 0.12\) mm\(^{-1}\), \(T = 100\) K, crystal dimensions of 0.12 x 0.25 x 0.70 mm, yellow prism. The structure converged to the final \(R = 0.0647\) and \(R_w = 0.155\) using 2122 independent reflections for 271 refined parameters (\(\theta_{\text{max}} = 27.19^\circ\)). CCDC registration number 1817597 (Figure S2).

![Figure S2. ORTEP projection of the X-ray structure 6 with 50% probability atomic displacement ellipsoids is displayed.](image)
X-ray data of \(P\)-1,2,3,4-tetrafluoro[6]helicene (6): \(\text{C}_{26}\text{H}_{12}\text{F}_4\), \(M = 400.36 \text{ g.mol}^{-1}\), orthorhombic system, space group \(P2_12_12_1\), \(a = 7.6059(2)\), \(b = 11.0958(3)\), \(c = 21.1436(10) \text{ Å}\), \(Z = 4\), \(V = 1784.38(9) \text{ Å}^3\), \(D_c = 1.49 \text{ g.cm}^{-3}\), \(\mu(\text{Cu K}\alpha) = 0.97 \text{ mm}^{-1}\), \(T = 121 \text{ K}\), crystal dimensions of 0.06 x 0.08 x 0.28 mm, yellow bar. The independent part of the lattice cell is formed by one disordered molecule. The occupancy factors of disordered atoms converged to ratio 0.88:0.12 at the end. The heavy atoms with occupancy 0.88 were refined anisotropically. The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors \(\text{Hiso(H)} = 1.2 \text{ Ueq(pivot atom)}\). The obtained molecule was used as a template for subsequent rigid body refinement of the minor disordered molecule. The molecule was rotated by 180° around central bond (C11-C24) and occupancy factors were adjusted. The heavy atoms with occupancy 0.12 were refined isotropically. The right-handed helicene provided Flack parameter 0.17(9). This structure model converged to the final \(R = 0.0495\) and \(R_w = 0.1185\) using 3341 independent reflections for 283 refined parameters (\(\theta_{\text{max}} = 70.09^\circ\)). CCDC registration number is 1817458 (Figure S3).

Figure S3. ORTEP projection of the X-ray structure \(P\)-6 with 50% probability atomic displacement ellipsoids is displayed.
X-ray data of $M$-1,2,3,4-tetrafluoro[6]helicene (6): $C_{26}H_{12}F_4$, $M = 400.36$ g.mol$^{-1}$, orthorhombic system, space group $P2_12_12_1$, $a = 7.6061(3)$, $b = 11.0989(3)$, $c = 21.1650(7)$ Å, $Z = 4$, $V = 1786.74(10)$ Å$^3$, $D_c = 1.49$ g.cm$^{-3}$, $\mu$ (Cu K$\alpha$) = 0.97 mm$^{-1}$, $T = 120$ K, crystal dimensions of 0.06 x 0.18 x 0.45 mm, yellow plate. The independent part of the lattice cell is also formed by one disordered molecule. The same procedure for structure refinement was used as for $P$-1,2,3,4-tetrafluoro[6]helicene (6). The final occupancy factors of disordered atoms converged to ratio 0.89:0.11. The left-handed helicene provided Flack parameter -0.14(10). The structure converged to the final $R = 0.0497$ and $R_w = 0.1324$ using 3376 independent reflections for 282 refined parameters ($\theta_{\text{max}} = 70.24^\circ$). CCDC registration number is 1817456 (Figure S4).

**Figure S4.** ORTEP projection of the X-ray structure $M$-6 with 50% probability atomic displacement ellipsoids is displayed.
X-ray data of cyclodimer 7: C_{26}H_{13}F_{5}, M = 420.38 g.mol^{-1}, monoclinic system, space group P2_1/n, a = 14.984(3), b = 7.7036(14), c = 15.893(2) Å, β = 96.609(9)° Z = 4, V = 1822.3(5) Å³, D_c = 1.53 g.cm^{-3}, μ(Mo Kα) = 0.12 mm^{-1}, T = 150 K, crystal dimensions of 0.05 x 0.30 x 0.44 mm, yellow plate. The independent part of the unit cell is formed by half of the dimer molecule. The structure converged to the final R = 0.0504 and R_w = 0.0975 using 2771 independent reflections for 331 refined parameters (θ_{max} = 27.49°). CCDC registration number is 1817457 (Figure S5).

**Figure S5.** ORTEP projection of the X-ray structure (1R,2R,3S,4S)-7 with 50% probability atomic displacement ellipsoids is displayed.
X-ray data of 1,2,3,4,13,14,15,16-octafluoro[6]helicene (15): C_{26}H_{8}F_{8}, M = 472.32 g.mol$^{-1}$, monoclinic system, space group $P2_1/c$, $a = 11.0004(6)$, $b = 21.2412(12)$, $c = 7.9354(4)$ Å, $\beta = 105.702(2)^\circ$, $Z = 4$, $V = 1785.00(17)$ Å$^3$, $D_c = 1.76$ g.cm$^{-3}$, $\mu$(Mo K$\alpha$) = 0.16 mm$^{-1}$, $T = 150$ K, crystal dimensions of 0.05 x 0.09 x 0.50 mm, yellow bar. The structure converged to the final $R = 0.0413$ and $R_w = 0.0962$ using 3150 independent reflections for 339 refined parameters ($\theta_{\text{max}} = 27.52^\circ$). CCDC registration number is 1817455 (Figure S6).

**Figure S6.** ORTEP projection of the X-ray structure 15 with 50% probability atomic displacement ellipsoids is displayed.
4. Separation of Enantiomers and Racemization Barrier Determination

Racemic 1,2,3,4-tetrafluoro[6]helicene (6) was separated to enantiomers (\(M\))- and (\(P\))-6 on a preparative HPLC system using conditions described in Experimental Section. The optical purity of each enantiomer and racemization process were studied by integration of UV traces from analytical HPLC records (see Figure S7).

![Figure S7. Chiral HPLC chromatogram of racemic 6 (green). The retention times of (−)-(\(M\))-6 (red, 4.5 min) and (+)-(\(P\))-6 (blue, 8.1 min). Eluted peaks are detected by monitoring absorbance at 254 nm.](image)

The racemization process of 6 and 15 was studied computationally first. Both minima (\(P\))- and (\(M\))- were initially optimized using the Becke three-parameter Lee-Yang-Parr (B3LYP) functional and the 6-31(d) basis set. The transition states (TS) were localized by the quadratic synchronous transit approach by Schlegel and co-workers (QST3) method as implemented in Gaussian09. Vibrational frequencies were calculated to confirm the saddle point order, evaluate free energies, and calculate the barriers to racemization.

In order to confirm the calculation, a thermal racemization experiment with 6 was performed according to following experimental setup.

Enantiomerically pure (\(P\))-6 (2.2 mg) was dissolved in hexadecane (2.2 mL) in a capped (PP-cap and rubber/PTFE septum) vial equipped with a stirring bar. The vial was wrapped into aluminum foil and heated to a constant temperature (506 K) using a hot plate magnetic stirrer with Pt1000 probe and stirred Wood’s metal bath. The temperature was cross-checked using external mercury-in-glass thermometer with 0.5 °C accuracy. The concentration of (\(P\))- and (\(M\))-6 was monitored by chiral HPLC (Kromasil Cellucoat® column) in the course of time.

The Gibbs free energy (\(\Delta G^\circ\)), the rate constant of racemization (\(k_{\text{rac}}\)) and the rate constant of enantiomerization (\(k_e\), \(k_{\text{rac}} = 2k_e\)) values were determined. Three different approaches were used and mutually compared in order to obtain the best fit to the experimental data and reliable half-time of the racemization (\(t_{1/2}\)). \(\Delta G^\circ(T)\) values were calculated using Eyring equation \(\Delta G^\circ(T) = -RT \ln(k_e h/k_B T)\), where \(R\) is the gas constant (\(R = 8.31441\) J/K), \(h\) is the Planck constant (\(h = 6.626176\times10^{-34}\) J s), \(k_B\) is the Boltzmann constant (\(k_B = 1.380662 \times 10^{-23}\) J/K), and \(\kappa\) is the transmission coefficient (\(\kappa = 0.5\) for reversible first order reaction was used). The \(t_{1/2}\) was calculated from the equation \(t_{1/2} = \ln 2/k_{\text{rac}}\).

The first approach employed for the \(k_e\) and \(k_{\text{rac}}\) determination a linear fit of the \(\ln(ee/ee_0)\) values plotted against the \(t\) values (see Figure S8). This approach was recently used by Juríček and coworkers which follows the equation \(\ln(ee/ee_0) = -k_{\text{rac}}t\). However, the calculated \(t_{1/2}\) values do not match the experimentally obtained data satisfactorily.
Figure S8. Plot of $\ln(\text{ee}/\text{ee}_0)$ against time

Table S1. The thermodynamic data obtained by linear fit of $\ln(\text{ee}/\text{ee}_0)$ against $t$.

| $T$ (K) | 506      |
|---------|----------|
| $\Delta G^\ddagger$ (kcal/mol) | $38.51 \pm 0.05$ |
| $t_{1/2}$ (min) | $47.1 \pm 2.3$ |
| $k_{\text{rac}}$ (s$^{-1}$) | $(2.46 \pm 0.12) \times 10^{-4}$ |

The second approach used the plot of $(M)$-6 concentration ($c$, %) against time ($t$). The data set was exponentially fitted following the fitting equation $y = y_0 + A_1e^{-t/t_1/2}$ (see Figure S9). The $t_{1/2}$ was calculated from the 50 % ee ($c_{(M)-6} = 25 \%$) and equation $t_{1/2} = \ln 2/k_{\text{rac}}$ provided $k_{\text{rac}}$ consequently. Using this approach, a very good fit was achieved and a good agreement in computationally and experimentally obtained $t_{1/2}$ was achieved.

Figure S9. Concentration of $(M)$-6 in the course of time at 506 K and its exponential fit used for calculation of $\Delta G^\ddagger(T)$ and $t_{1/2}$. 
Table S2. The thermodynamic data obtained by exponential fit of $c$ against time $t$.

| $T$ (K) | 506 |
|---------|-----|
| $\Delta G^\ddagger$ (kcal/mol) | 38.88 ± 0.09 |
| $t_{1/2}$ (min) | 67.9 ± 4.5 |
| $k_{rac}$ ($s^{-1}$) | $(1.70 \pm 0.11) \times 10^{-4}$ |

In the last approach the plot of $(M)$-6 concentration ($c$, %) against time ($t$) was used and the data set was exponentially fitted by $y = y_0 + A_1e^{kt}$ (see Figure S10). Additionally, the fitting curve was forced to intersect the zero point as the starting concentration of $(M)$-6 was 0 % and its concentration approaches 50 % in the limit using the presumption that the concentration of $(M)$-6 cannot exceed 50%. Similarly, to the previous approach, the $t_{1/2}$ was calculated from the 50 % ee ($c_{(M),6} = 25 \%$) and equation $t_{1/2} = \ln 2/k_{rac}$ provided $k_{rac}$ consequently. The fit of the experimental data was not satisfactory as without the restrictions.

![Figure S10. Plot of $(M)$-6 concentration against time with the applied restrictions](image)

Table S3. The thermodynamic data obtained by exponential fit of $c$ against time $t$ with the applied restrictions

| $T$ (K) | 506 |
|---------|-----|
| $\Delta G^\ddagger$ (kcal/mol) | 38.77 ± 0.06 |
| $t_{1/2}$ (min) | 61.2 ± 3.7 |
| $k_{rac}$ ($s^{-1}$) | $(1.89 \pm 0.11) \times 10^{-4}$ |

To summarize, the $\Delta G^\ddagger(T)$ values for racemization of 1,2,3,4-tetrafluoro[6]helicene (6) do not change significantly within three used approaches, whereas the values of racemization half-time and $k_{rac}$ depend significantly on used method.
5. DFT Calculations

Calculations of electrostatic potentials and HOMO/LUMO/gap energies were performed with the package Gaussian09.\(^5\) As functional we have used the Becke’s 3-parameter hybrid one, combined with the non-local correlation functional provided by Perdew/Wang denoted as B3PW91.\(^1,7\) As basis set we used 6-311++G(d,p). In the DFT calculations the chloroform solvent was simulated with the polarizable continuum model (IEFPCM). The vibrational analysis showed that all structures correspond to the local minima in the potential energy surface. Calculation details regarding the localization of TSs are presented above in chapter 4 (SI). Cartesian coordinates of [6]helicene, 6, 15 and their TSs are following.

### [6]Helicene

| Symbol | X     | Y     | Z      |
|--------|-------|-------|--------|
| C      | 2.2691260 | 2.8854560 | -0.8339390 |
| C      | 2.3770770 | 1.4848020 | -0.6155700 |
| C      | 1.2886440 | 0.7625000 | -0.0691520 |
| C      | 0.0007110 | 2.8431310 | -0.0002480 |
| C      | 1.1517870 | 3.5548130 | -0.4368800 |
| C      | 1.5756270 | -0.5432530 | 0.4988790 |
| C      | -1.2877810 | 0.7635830 | 0.0688130 |
| C      | -2.8242950 | -1.1683820 | -0.2134830 |
| C      | -3.8088030 | -0.4714680 | 0.5484570 |
| C      | -3.6103560 | 0.8262430 | 0.8960920 |
| C      | -2.3754070 | 1.4868290 | 0.6156090 |
| C      | -2.2662230 | 2.8874010 | 0.8338750 |
| C      | -1.1484100 | 3.5558010 | 0.4365500 |
| H      | -1.1010800 | 4.6394520 | 0.4810600 |
| H      | -3.1190930 | 3.4205870 | 1.2421130 |
| H      | 3.1225780 | 3.4179170 | -1.2419050 |
| H      | 1.1054310 | 4.6385100 | -0.4812970 |
| H      | -4.7435590 | -0.9725200 | 0.7806610 |
| H      | -4.3938660 | 1.3930160 | 1.3900230 |
| C      | 3.6116030 | 0.8231590 | -0.8954680 |
| C      | 3.8088360 | -0.4746800 | -0.5476030 |
| C      | 2.8233960 | -1.1707220 | 0.2139420 |
| H      | 4.3958020 | 1.3892450 | -1.3890960 |
| H      | 4.7432760 | -0.9765320 | -0.7793550 |
| H      | -4.3938660 | 1.3930160 | 1.3900230 |
| C      | 3.6116030 | 0.8231590 | -0.8954680 |
| C      | 3.8088360 | -0.4746800 | -0.5476030 |
| C      | 2.8233960 | -1.1707220 | 0.2139420 |
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| H      | -4.3938660 | 1.3930160 | 1.3900230 |
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| C      | 2.8233960 | -1.1707220 | 0.2139420 |
| H      | 4.3958020 | 1.3892450 | -1.3890960 |
| H      | 4.7432760 | -0.9765320 | -0.7793550 |
| H      | -4.3938660 | 1.3930160 | 1.3900230 |
| C      | 3.6116030 | 0.8231590 | -0.8954680 |
| C      | 3.8088360 | -0.4746800 | -0.5476030 |
| C      | 2.8233960 | -1.1707220 | 0.2139420 |
| H      | 4.3958020 | 1.3892450 | -1.3890960 |
| H      | 4.7432760 | -0.9765320 | -0.7793550 |
| H      | -4.3938660 | 1.3930160 | 1.3900230 |
| C      | 3.6116030 | 0.8231590 | -0.8954680 |
| C      | 3.8088360 | -0.4746800 | -0.5476030 |
| C      | 2.8233960 | -1.1707220 | 0.2139420 |
| H      | 4.3958020 | 1.3892450 | -1.3890960 |
| H      | 4.7432760 | -0.9765320 | -0.7793550 |
| H      | -4.3938660 | 1.3930160 | 1.3900230 |
| C      | 3.6116030 | 0.8231590 | -0.8954680 |
| C      | 3.8088360 | -0.4746800 | -0.5476030 |
| C      | 2.8233960 | -1.1707220 | 0.2139420 |
| H      | 4.3958020 | 1.3892450 | -1.3890960 |
### Helicene TS

- **Imaginary frequencies:** -41.39
- **Zero-point correction =** 0.333976 (Hartree/Particle)
- **Thermal correction to Energy =** 0.350612
- **Thermal correction to Enthalpy =** 0.351557
- **Thermal correction to Gibbs Free Energy =** 0.291034
- **Sum of electronic and zero-point Energies =** -1000.049732
- **Sum of electronic and thermal Energies =** -1000.033096
- **Sum of electronic and thermal Enthalpies =** -1000.032152
- **Sum of electronic and thermal Free Energies =** -1000.092674

| Symbol | X      | Y      | Z      |
|--------|--------|--------|--------|
| C      | -0.0008850 | 1.3497320 | -0.5099950 |
| C      | 1.3223960  | 0.7667950  | -0.1967780 |
| C      | -1.3234610 | 0.7653240  | -0.1965680 |
| C      | 1.7521300  | -0.6346740 | -0.1729760 |
| C      | -1.7514200 | -0.6366340 | -0.1729010 |
| C      | 1.4314080  | -1.5616860 | -1.1877270 |
| C      | -1.4285900 | -1.5632730 | -1.1872150 |
| C      | -0.0017010 | 2.7648110  | -0.7721460 |
| C      | 1.1968680  | 3.5367340  | -0.7709610 |
| C      | -1.2012630 | 3.5353670  | -0.7709330 |
| C      | 2.3092250  | 3.0347220  | -0.1709590 |
| C      | -2.3130250 | 3.0320460  | -0.1709250 |
| C      | 2.3430260  | 1.6699150  | 0.2227450  |
| C      | -2.3452370 | 1.6672120  | 0.2228150  |
| C      | 3.4045020  | 1.2305670  | 1.0825590  |
| C      | -3.4065290 | 1.2265170  | 1.0821470  |
| C      | 3.5150410  | -0.0691510 | 1.4650280  |
| C      | -3.5157600 | -0.0733930 | 1.4643440  |
| C      | 2.7522530  | -1.0555430 | 0.7649820  |
| C      | -2.7514580 | -1.0587890 | 0.7645780  |
| C      | 3.1207990  | -2.4193410 | 0.8382260  |
| C      | -3.1181680 | -2.4230820 | 0.8376760  |
| C      | 2.6655460  | -3.3306970 | -0.0943220 |
| C      | -2.6610410 | -3.3383770 | -0.0941600 |
| C      | 1.8708350  | -2.8737250 | -1.1592520 |
| C      | -1.8661350 | -2.8759430 | -1.1589030 |
| H      | -0.9048450 | -1.2028270 | -2.0588470 |
| H      | -1.6070050 | -3.5465890 | -1.9735960 |
| H      | -2.9747320 | -4.3732010 | -0.0490300 |
| H      | -3.8352260 | -2.7251890 | 1.5974460  |
| H      | 4.2671100  | -0.3874410 | 2.1822560  |
| H      | -4.2677900 | -0.3926590 | 2.1811800  |
| H      | 4.0842210  | 1.9866960  | 1.4677620  |
| H      | -4.0873020 | 1.9817930  | 1.4671630  |
| H      | 3.1736130  | 3.6613650  | 0.0335070  |
| H      | -3.1781980 | 3.6576520  | 0.0333980  |
| H      | 1.1445120  | 4.5794240  | -1.0724460 |
| H      | -1.1501710 | 4.5781090  | -1.0724570 |
| H      | 0.9078560  | -1.2020630 | -2.0598740 |
| H      | 1.6133290  | -3.5446050 | -1.9742710 |
| H      | 2.9806780  | -4.3695800 | -0.0487340 |
| H      | 3.8378200  | -2.7204930 | 1.5984100  |
Tetrafluoro[6]helicene (6)

Zero-point correction = 0.301094 (Hartree/Particle)
Thermal correction to Energy = 0.322235
Thermal correction to Enthalpy = 0.323179
Thermal correction to Gibbs Free Energy = 0.252366
Sum of electronic and zero-point Energies = -1396.878272
Sum of electronic and thermal Energies = -1396.857130
Sum of electronic and thermal Enthalpies = -1396.856186
Sum of electronic and thermal Free Energies = -1396.926999

| Symbol | X           | Y           | Z           |
|--------|-------------|-------------|-------------|
| C      | 4.0905500   | 0.6258860   | -0.9710790  |
| C      | 3.2389870   | -0.4325650  | -0.5507430  |
| C      | 1.9871200   | -0.1472780  | 0.0430440   |
| C      | 1.4918850   | 1.2076220   | -0.0407790  |
| C      | 2.4461600   | 2.2418780   | -0.2537280  |
| C      | 3.7438770   | 1.9212990   | -0.7367890  |
| C      | 1.3340260   | -1.2179880  | 0.7739140   |
| C      | 0.1103330   | 1.6130850   | 0.0908120   |
| C      | -2.3261410  | 1.1690250   | 0.2504130   |
| C      | -2.4995730  | 2.4200860   | 0.9122740   |
| C      | -1.4654640  | 3.2973330   | 0.9632820   |
| C      | -0.1577840  | 2.9360480   | -1.2208500  |
| C      | 2.1082750   | 3.5924900   | 0.0260930   |
| H      | 2.8707380   | 4.3574720   | -0.0996910  |
| H      | 0.6378320   | 4.9252090   | 0.8139270   |
| H      | 5.0519460   | 0.3780980   | -1.4099190  |
| H      | 4.4355030   | 2.7314270   | -0.9448210  |
| H      | -3.4783490  | 2.6834140   | 1.2929400   |
| H      | -1.6126280  | 4.2943060   | 1.3660220   |
| C      | 3.6746090   | -1.7842720  | -0.6945080  |
| C      | 2.9472520   | -2.814960   | -0.1911860  |
| C      | 1.7927650   | -2.5573470  | 0.6053530   |
| H      | 4.6059640   | -1.9694480  | -1.2208500  |
| H      | 3.2711740   | -3.8422650  | -0.3266720  |
| C      | 1.1504920   | -3.6117310  | 1.2919560   |
| C      | 0.1307240   | -3.3633650  | 2.1813390   |
| H      | 1.5014250   | -4.6261260  | 1.1271650   |
| H      | -0.3461390  | -4.1807110  | 2.7121390   |
| C      | -3.4372640  | 0.3483420   | -0.0031430  |
| C      | -3.3436480  | -0.7758540  | -0.7833740  |
| C      | 0.3282570   | -0.9955340  | 1.7429860   |
| H      | 0.0329260   | 0.0179990   | 1.9802900   |
| C      | -0.2573790  | -2.0363220  | 2.4309240   |
| H      | -1.0137450  | -1.8249340  | 3.1797430   |
| C      | -1.0391920  | 0.7913510   | -0.2413860  |
| C      | -2.1127690  | -1.0908150  | -1.3636650  |
| C      | -1.0021460  | -0.3166790  | -1.1120030  |
| F      | 0.1015910   | -0.6333990  | -1.7977050  |
| F      | -2.0349480  | -2.1305080  | -2.1947450  |
| F      | -4.4070190  | -1.5384330  | -1.0353750  |
| F      | -4.6372940  | 0.6874960   | 0.4907670   |

Tetrafluoro[6]helicene (6) TS

Imaginary frequencies: -19.44
Zero-point correction = 0.300783 (Hartree/Particle)
Thermal correction to Energy = 0.321151
Thermal correction to Enthalpy = 0.322095
Thermal correction to Gibbs Free Energy = 0.253599
Sum of electronic and zero-point Energies = -1396.987201
Sum of electronic and thermal Energies = -1396.966833
Sum of electronic and thermal Enthalpies = -1396.965888

S15
Sum of electronic and thermal Free Energies = -1397.034384

| Symbol | X     | Y     | Z      |
|--------|-------|-------|--------|
| C      | -1.4568010 | 1.1705800 | -0.4288040 |
| C      | -0.0470870  | 1.5794770  | -0.5465850 |
| C      | -1.9712730  | -0.0798020  | 0.15666000 |
| C      | 1.1585430   | 0.7731790   | -0.2769860 |
| C      | -1.5931380  | -1.4483040  | -0.1529480 |
| C      | 1.4942060   | -0.4562970  | -0.8737900 |
| C      | -1.2763770  | -1.8496180  | -1.4701150 |
| C      | -2.4295810  | 2.2231530   | -0.5301450 |
| C      | -2.0851350  | 3.5003820   | -1.0535410 |
| C      | -3.6968740  | 2.1341460   | 0.12165800 |
| C      | -0.7794060  | 3.8855480   | -1.0693140 |
| C      | -3.9102210  | 1.1543570   | 1.04419900 |
| C      | 0.2217880   | 2.9775220   | -0.6294940 |
| C      | -3.0288730  | 0.0373890   | 1.09901900 |
| C      | 1.4185010   | 3.5405800   | -0.0688030 |
| C      | -3.2563490  | -1.0090440  | 2.05315600 |
| C      | 2.2890630   | 2.7774680   | 0.64215000 |
| C      | -2.5826920  | -2.1907760  | 1.98366800 |
| C      | 2.2062460   | 1.3540670   | 0.51625400 |
| C      | -1.8228730  | -2.4869950  | 0.80901200 |
| C      | 3.2681090   | 0.5492300   | 0.97025500 |
| C      | -1.4631530  | -3.8176960  | 0.49690000 |
| C      | 3.4304110   | -0.7500600  | 0.53472900 |
| C      | -1.0410720  | -4.1564620  | -0.7748970 |
| C      | 2.5560000   | -1.2362270  | -0.4423970 |
| C      | -1.0042490  | -3.1707760  | -1.7779400 |
| H      | -1.2885570  | -1.1029540  | 2.25314100 |
| H      | -0.7722600  | -3.4466820  | -2.8025900 |
| H      | -0.7986260  | -5.1881320  | -1.0467000 |
| H      | -1.5980130  | -4.5850560  | 1.25553700 |
| H      | 3.1113670   | 3.2107780   | 1.19930600 |
| H      | -2.7274660  | -2.9655610  | 2.73218600 |
| H      | 1.5348180   | 4.6203320   | -0.1073010 |
| H      | -3.9805420  | -0.8256130  | 2.84317800 |
| H      | -0.4988650  | 4.9127650   | 1.28672400 |
| H      | -4.7783160  | 1.1720330   | 1.69802400 |
| H      | -2.8799420  | 4.2111770   | 1.26397200 |
| H      | -4.3993500  | 2.9540150   | 0.00046800 |
| F      | 4.2100810   | 1.0855320   | 1.77007100 |
| F      | 4.4598120   | -1.4989910  | 0.94539200 |
| F      | 2.8141480   | -2.4088590  | -1.0341910 |
| F      | 0.9036770   | -0.8440410  | -2.0136880 |

**Octafluoro[helicene (15)]**

Zero-point correction = 0.268444 (Hartree/Particle)
Thermal correction to Energy = 0.293269
Thermal correction to Enthalpy = 0.294213
Thermal correction to Gibbs Free Energy = 0.215379
Sum of electronic and zero-point Energies = -1793.805020
Sum of electronic and thermal Energies = -1793.780195
Sum of electronic and thermal Enthalpies = -1793.779251
Sum of electronic and thermal Free Energies = -1793.858085

| Symbol | X     | Y     | Z     |
|--------|-------|-------|-------|
| C      | 3.6909540  | 2.2537610  | 0.8613280 |
| C      | 2.2856840  | 2.3516210  | 0.6770920 |
| C      | 1.5705380  | 1.2794560  | 0.0931400 |
| C      | 2.2293550  | -0.0009350  | -0.000650 |
| C      | 3.6521750  | -0.0015330  | -0.001400 |
| C      | 4.3628780  | 1.1475320  | 0.4376830 |
| C      | 0.2369870  | 1.5711500  | -0.3976440 |
Octafluoro[6]helicene (15) TS

| Symbol | X      | Y       | Z       |
|--------|--------|---------|---------|
| C      | 2.2095430 | 0.0008560 | 0.5010770 |
| C      | 1.6223800 | 1.3066270 | 0.1636740 |
| C      | 1.6234750 | -1.3054790 | 0.1639590 |
| C      | 0.2136370 | 1.6842060 | 0.0611520 |
| C      | 0.2150600 | -1.6842290 | 0.0613940 |
| C      | -0.07179640 | 1.5029020 | 1.1002420 |
| C      | -0.71193090 | -1.5032370 | 1.1002030 |
| C      | 3.6237400 | 0.0014750 | 0.7485900 |
| C      | 4.3849640 | 1.2074540 | 0.7261710 |
| C      | 1.3859400 | -1.2038970 | 0.7265740 |
| C      | 3.8728830 | 2.3050180 | 0.1020050 |
| C      | 3.8747890 | -2.3020570 | 0.1026970 |
| C      | 2.5090970 | 2.3185430 | -0.3008620 |
| C      | 2.5110440 | -2.3140900 | -0.3002740 |
| C      | 2.0585540 | 3.2893720 | -1.2570830 |
| C      | 2.0613640 | -3.2882920 | -1.2562780 |
| C      | 0.7804240 | 3.2918800 | -1.7255590 |
| C      | 0.7832870 | -3.2918460 | -1.7258980 |

Imaginary frequencies:

-30.82

Zero-point correction = 0.267448 (Hartree/Particle)
Thermal correction to Energy = 0.291685
Thermal correction to Enthalpy = 0.292629
Thermal correction to Gibbs Free Energy = 0.215658
Sum of electronic and zero-point Energies = -1793.920015
Sum of electronic and thermal Energies = -1793.895779
Sum of electronic and thermal Enthalpies = -1793.894834
Sum of electronic and thermal Free Energies = -1793.971806
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7. NMR Spectra

Figure S11. $^1$H NMR spectrum of compound 2 (400 MHz, CDCl$_3$)

Figure S12. $^{13}$C{$^1$H} NMR spectrum of compound 2 (101 MHz, CDCl$_3$)
Figure S13. $^{19}$F-$^1$H NMR spectrum of compound 2 (376 MHz, CDCl$_3$)

Figure S14. $^1$H NMR spectrum of compound 3 (400 MHz, CDCl$_3$)
Figure S15. $^{19}$F-$^1$H NMR spectrum of compound 3 (376 MHz, CDCl$_3$)

Figure S16. $^1$H NMR spectrum of compound 4 (400 MHz, CDCl$_3$)
Figure S17. $^{19}$F/$^1$H NMR spectrum of compound 4 (376 MHz, CDCl$_3$)

Figure S18. $^1$H NMR spectrum of compound 5 (400 MHz, CDCl$_3$)
Figure S19. $^{19}$F-$^1$H NMR spectrum of compound 5 (376 MHz, CDCl$_3$)

Figure S20. $^1$H NMR spectrum of compound 6 (400 MHz, CDCl$_3$)
Figure S21. $^{13}$C{$^{1}$H} NMR spectrum of compound 6 (101 MHz, CDCl$_3$)

Figure S22. $^{19}$F{$^{1}$H} NMR spectrum of compound 6 (376 MHz, CDCl$_3$)
Figure S23. $^1$H NMR spectrum of compound 7 (500 MHz, CDCl$_3$)

Figure S24. $^{13}$C\{$^1$H}\ spectrum of compound 7 (126 MHz, CDCl$_3$)
Figure S25. $^{19}$F-$^1$H NMR spectrum of compound 7 (471 MHz, CDCl$_3$)

Figure S26. $^1$H NMR spectrum of compound 9 (400 MHz, CDCl$_3$)
Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 9 (101 MHz, CDCl$_3$)

Figure S28. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of compound 9 (376 MHz, CDCl$_3$)
Figure S29. $^{31}$P/$^1$H NMR spectrum of compound 9 (162 MHz, CDCl$_3$)

Figure S30. $^1$H NMR spectrum of compound (E)-10 (400 MHz, CDCl$_3$)
Figure S31. $^{19}$F-$^1$H NMR spectrum of compound (E)-10 (376 MHz, CDCl$_3$)

Figure S32. $^1$H NMR spectrum of compound 12 (400 MHz, CDCl$_3$)
Figure S33. $^1$H NMR spectrum of compound (E,Z)-12 (500 MHz, CH$_3$CN/D$_2$O)

Figure S34. $^{19}$F/$^1$H NMR spectrum of compound 12 (376 MHz, CDCl$_3$)
Figure S35. $^1$H NMR spectrum of compound (Z,Z)-14 (500 MHz, CH$_3$CN/D$_2$O)

Figure S36. $^1$H NMR spectrum of compound (E,Z)-14 (500 MHz, CH$_3$CN/D$_2$O)
Figure S37. $^1$H NMR spectrum of compound (E,E)-14 (500 MHz, CH$_3$CN/D$_2$O)

Figure S38. $^{19}$F($^1$H) NMR spectrum of compound 14 (376 MHz, CDCl$_3$)
Figure S39. $^1$H NMR spectrum of compound 15 (400 MHz, C$_6$D$_6$)

Figure S40. $^{13}$C{$^1$H} NMR spectrum of compound 15 at 95 °C (126 MHz, C$_2$D$_2$Cl$_4$)
Figure S41. $^{19}$F/$^1$H NMR spectrum of compound 15 (376 MHz, CDCl$_3$)

Figure S42. $^1$H NMR spectrum of compound (iii) (400 MHz, DMSO-$d_6$)
Figure S43. $^{13}$C-$^1$H NMR spectrum of compound (iii) \((101\text{ MHz, CDCl}_3)\)

Figure S44. $^{19}$F-$^1$H NMR spectrum of compound (iii) \((376\text{ MHz, CDCl}_3)\)
Figure S45. $^1$H NMR spectrum of compound (iv) (400 MHz, CDCl$_3$)

Figure S46. $^{13}$C\{\textit{H}\} NMR spectrum of compound (iv) (101 MHz, CDCl$_3$)
Figure S47. $^{19}$F-$^1$H NMR spectrum of compound (iv) (376 MHz, CDCl$_3$)