Photoswitching neutral homoaromatic hydrocarbons
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1 Supporting Information

1.1 General Information

The numbering of the respective molecules in the main manuscript and supporting information do not necessarily follow IUPAC recommendations and were done at our own discretion in order to guide the reader.

All reactions were carried out in flame dried glassware under a nitrogen atmosphere using standard Schlenk techniques. Glassware and stir bars contaminated with transition metals were treated with *aqua regia* (conc. HCl/conc. HNO$_3$ 3:1) prior to cleaning. For cleaning, glassware and stir bars were kept in an iso-PrOH/KOH bath overnight, rinsed with H$_2$O, kept in a citric acid/H$_2$O bath overnight and finally rinsed with deionized H$_2$O and dried at 120 °C. Solutions and reagents were added with nitrogen-flushed disposable syringes/needles. Solvents were added using glass syringes and stainless steel needles (stored at 120 °C).

Analytical thin layer chromatography (TLC) was performed on silica gel 60 G/UV$_{254}$ aluminium sheets (*Macherey-Nagel*). Flash column chromatography was performed on silica gel Davisil LC60A (40-63 μm, pore size 60 Å, *Grace*) using the indicated solvents.

NMR spectra were recorded on Bruker Avance II 400, Bruker Avance III 500 or Bruker Avance III 700 instruments at 298 K at the Institute for Chemistry of *Technische Universität Berlin* and using a Bruker Avance II 300 and a Bruker Avance II 500, Bruker Avance II 600 at 298 K at the Department of Chemistry of the Humboldt University of Berlin. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard according to the standard literature$^{1,2}$. Data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, mc = centrosymmetric multiplet), coupling constants (Hz), integration and – if possible – atom assignment. The assignment refers to the atom number shown in the corresponding molecule figure and was achieved via analysis of DEPT (DEPT 135) and 2D NMR spectra (COSY, HMQC, HSQC, HMBC, NOESY). If a distinct assignment was not possible, atoms were marked with “*” and are interchangeable. Designation “Ar” refers to atoms of an aromatic system where a distinct assignment was not possible.

Melting points (m.p.) were determined using a Leica Galen III melting point apparatus (*Wagner & Munz*).

Infrared (IR) spectra were recorded on a Cary 630 FT-IR spectrometer equipped with an ATR unit (*Agilent Technologies*). Mass spectra (HRMS) were obtained from the Analytical Facility at the Institute for Chemistry at *Technische Universität Berlin* (ESI/APCI: LTQ Orbitrap XL, *Thermo Scientific*; EI: GC-system 5975C, HP-5MS, *Agilent Technologies*). Analytical gas chromatography (GC) of reaction mixtures and pure substances was performed using a gas
chromatograph 430-GC (Varian Inc.). The instrument was equipped with a FactorFour VF-WAXm capillary column (Varian Inc., length: 30 m, inner diameter: 0.25 mm, film thickness of the stationary phase: 0.25 μm). The following temperature program was used for the analysis: carrier gas N₂; injection temperature 270 °C; detector temperature 270 °C; flow rate 4.0 mL/min; temperature program: 40 °C start temperature, 20 °C/min heating rate to 250 °C for 10 min, then 20 °C/min heating rate to final temperature 260 °C for 5 min. The data was recorded with the program Galaxie 1.9.302.952 (Varian Inc.).

Ultra-Performance Liquid Chromatography with Mass Spectrometry coupling (UPLC/MS) was performed with a Waters ACQUITY UPLC H-Class, equipped with a quaternary solvent manager (QSM), a sample manager-flow through needle (SM-FTN), a column manager, a ACQUITY UPLC BEH Phenyl 1.7 μm, 2.1x100 mm column, an ACQUITY UPLC BEH C18 1.7 μm, 2.1 x 100 mm column and a photodiode array detector (PDA eλ), and a ACQUITY QDa detector. The mobile phase is a gradient of MeCN/H₂O individually optimized for each separation.

Ultraviolet–visible absorbance spectroscopy was performed on Agilent Cary 50 and Cary 60 instruments connected to a cryostat from Unisoku Scientific Instruments (temperature accuracy ±0.1 K) in 10 × 10 mm quartz cuvettes with 3 mL volume. Weighing of small quantities was performed on a Sartorius ME5 analytical microbalance. Ultraviolet–Visible Fluorescence Spectroscopy was performed on a Varian Cary Eclipse Fluorescence spectrometer using 10.0×10.0 mm quartz cuvettes. 305 nm mounted LED (LG Innotek, LEUVA66H100KU00, FWHM = 13 nm, 850 mW (min), 500 mA), 340 nm mounted LED (Seoul Viosys, CUD4AF1B, FWHM = 10 nm, 430 mW (min), 500 mA), 455 nm mounted LED (Osram OSLON SSL80, LD-CQ7P-1U3U, FWHM = 21 nm, 360 mW (min), 1000 mA).

The parameters for flash column chromatography are given as “(d × h, A/B = a:b, C, #n–m)”, with “d” = column diameter; “h” = filling height; “A/B” = eluent solvents; “a:b” = solvent ratio; “C” = fraction volume and #n–m = fraction number.

1.1.1 Solvents
THF and Et₂O were dried over sodium/benzophenone and distilled under N₂ atmosphere prior to use. Et₃N, CH₂Cl₂ and MeOH were dried over CaH₂ and distilled under N₂ atmosphere prior to use. Acetone and EtOH were distilled under reduced pressure prior to use. Solvents (technical grade) for extraction/chromatography (n-pentane, cyclohexane, CH₂Cl₂, tert-butyl methyl ether, EtOAc) were distilled under reduced pressure prior to use. MeCN for irradiation experiments was purged with Ar prior to use.
1.2 $^1$H NMR chemical shift comparison

For investigation of a present induced ring current, we compared the $^1$H NMR chemical shifts of elassovalene 3$^{3,4}$, homoannulenes 15 & 16 and related annulenes S1–S4$^{5,6}$ (Supplementary Figure 1). The chemical shift of the methine resonance $\delta_{methine} = 1.77$ ppm of elassovalene 3 (red) does not indicate a present ring current. Compared to the annulene S1, which is considered aromatic, the methine resonance $\delta_{methine} = -1.82$ ppm is significantly shifted up-field, indicative of an existing ring current. In homoannulene 15, the methine proton is facing away from the potential homoaromatic system with a chemical shift of $\delta_{methine} = 3.81$ ppm. The $\alpha$-carbonyl methine $^1$H NMR resonance of homoannulene carboxylic acid 16, placed directly on top of the homoaromatic system, is significantly shifted up-field to $\delta_{methine} = 0.89$ ppm, evidence for a present ring current. Although the chemical shift is not in the negative ppm range, it should be considered that it is $\alpha$ to a ketone. Comparing it to the annulene S2, which also has $\alpha$-carbonyl methine placed directly on top triene with $\delta_{methine} = 2.40$ ppm, $^1$H NMR resonance is not as up-field shifted as in homoannulene 16, suggesting the absence of a ring current. The related aromatic annulenes S3 and S4 show an even higher shielding of their respective methine protons ($\delta_{methine} = -1.16$ ppm and $\delta_{methine} = -0.87$ ppm). This comparison suggest a present induced ring current in 15 and 16, with weaker shielding effect compared to the aromatic annulenes S3 and S4, but with the right tendency towards (homo)aromaticity.

Supplementary Figure 1. Comparison of chemical shifts in $^1$H NMR of the elassovalene 3$^{3,4}$, homoannulenes 15 & 16 and related annulenes S1–S4$^{5,6}$. 
1.3 Investigation on conformational asymmetry in homoannulene 15

The $^1$H NMR of the homoannulene 15 showed a distinct AA’XX’ system of the olefinic hydrogen atoms. This suggests that the rotation of the ester group is restricted which breaks the plane of symmetry in 15, resulting in the observed diastereotopic alkene hydrogen atoms. This hypothesis is further supported by the comparison of the $^1$H NMR spectrum of homoannulene acid 16, in which no such restriction of rotation for the carboxyl group is expected and no such coupling pattern was observed. To investigate this barrier of rotation in homoannulene 15 we performed a variable temperature NMR study (Supplementary Figure 2). With increasing temperature, the coalesce of the olefinic protons was observed at ca. 100 °C. This supports the notion that there is a restricted rotation for the ester group.

Supplementary Figure 2. $^1$H NMR spectra of homoannulene 15 at different temperatures (500 MHz, C$_6$D$_5$Cl).
1.4 Comparison of bond lengths from X-ray crystal structures

The HOMA\(^7\)–\(^9\) (Harmonic Oscillator Model of Aromaticity) indices were calculated using the following equation with normalization factor $\alpha = 257.7 \text{Å}^{-2}$, the number of CC-bonds $n$, distances of $i$-th ring bond $R_i$ and the reference optimal bond in benzene $R_{\text{opt}} = 1.388 \text{Å}$. The HOMA index approaches 1 for aromatic compounds (benzene as reference) and approaches 0 for non-aromatic structures (cyclohexatriene as reference).

$$HOMA = 1 - \frac{\alpha}{n} \sum_{i=1}^{n} (R_i - R_{\text{opt}})^2$$

**Supplementary Equation 1.** HOMA index equation.

For triasterane 14a HOMA(14a) = −0.8860, which tends towards 0 and is considered not aromatic. For annulene 17 the HOMA index is 0.9097, which approaches 1 and is in accordance with the notion that it is aromatic. Homoannulenes 15 and 16 also show the tendency towards 1 with HOMA(15) = 0.8558 and HOMA(15) = 0.7614, suggesting that 15 and 16 show aromatic properties.

For barbaralane 4 the HOMA index of −2.9392 fails to reflect its homoaromatic character. The HOMA index shows how different to the perfect aromaticity in benzene the molecule in question is. The more different, unequal, and alternating the bonds are compared to benzene, the lower the HOMA index gets. It reflects similarity of the geometric properties to the aromatic geometry. Barbaralane 4 has one more single bond than double bond and the C-C-bond of the cyclopropyl (1.677 Å) differs greatly from the ideal C–C bond in benzene (1.388 Å), which is weighted in the equation disproportionally high. We concluded, that the HOMA index reaches the limit\(^8\) in the case of homoaromatic compounds which do not possess a fully conjugated system, such as in the case of barbaralane 4.
Supplementary Figure 3. Comparison of bond lengths from X-ray structures and HOMA (Harmonic Oscillator Model of Aromaticity) indices of triasterane 14a, homoannulenes 15 & 16, barbaralane 4 by Quast\textsuperscript{10} and methano[10]annulene 17 by Vogel\textsuperscript{11}. 
1.4.1 Plot of the C–C\=/C=C-bonds lengths

Supplementary Figure 4. Plot of the alternating bond lengths of annulene 17, barbaralane 4, homoannulene 15 and 16 and asterane 14a.
1.5 Proposed mechanism for the formation of homoannulene acid 16 and benzotropilidene S9

For the formation of homoannulene acid 16 and benzotropilidene S4 we propose that the donation of electrons of the homoaromatic system to the $\sigma^*$ C–C orbital, which weakens the C–C bond. (Supplementary Figure 5) Due to this interaction the hydroxide anion attacks the ketone carbonyl carbon and breaks the C–C bond in a retro-Claisen reaction. After a second deprotonation carbanion S5 is formed which can react further in two pathways: a) In a Claisen reaction homoannulene 16 is formed and b) the ring contracts and forms the carbanion S6. After protonation forming ester S7 it undergoes a [1,5] $H$-shift forming ester S8, which is driven by rearomatization. After a second saponification and work-up the benzotropilidene S9 is formed (X-ray structure available, see Section 2.1.8).

Supplementary Figure 5. Proposed mechanism for the formation of homoannulene acid 16 and benzotropilidene S6.
1.6 Synthesis

Supplementary Figure 6. Synthesis of homoannulene 15 and homoannulene acid 16. (Abbr.: CDI = N,N'-carbonyldiimidazole; hFacac = hexafluoroacetylacetonate; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone)
1.6.1 Optimization

1.6.1.1 Dearomative intramolecular cyclopropanation of 13

1.6.1.1.1 Procedure

A flame dried 2 mL microwave vial was charged with diazoacetate solution 13 (12.5 mM in CD$_2$Cl$_2$, 400 µL, 5.00 µmol, 1.00 equiv) with internal standard (mesitylene). Then catalyst solution (5.00 mM in CD$_2$Cl$_2$, 100 µL, 0.500 µmol, 10.0 mol%) was added and the microwave vial was sealed. When elevated temperatures were used, the reaction mixtures were heated under microwave reaction conditions (see Supplementary Table 1 & 2). After the indicated reaction time the reaction mixture allowed to cool to room temperature and the solution directly analyzed via $^1$H NMR spectroscopy.

Supplementary Table 1. Optimization of rhodium(II)- and copper(II)-based catalysts for dearomative intramolecular cyclopropanation of 13a.[a]

| Entry | Catalyst        | Temperature | Time | Conversion$^b$ | Yield 14a$^b$ |
|-------|-----------------|-------------|------|---------------|--------------|
| 1     | Rh$_2$(OAc)$_4$ | 100 °C      | 1 min| full conv.    | 0%           |
| 2     | Rh$_2$(esp)$_2$ | 100 °C      | 1 min| full conv.    | 0%           |
| 3     | Rh$_2$(TPA)$_4$ | 100 °C      | 1 min| full conv.    | 0%           |
| 4     | Rh$_2$(TFA)$_4$ | 100 °C      | 1 min| full conv.    | 20%          |
| 5[c]  | Rh$_2$(TFA)$_4$ | rt          | 18 h | full conv.    | 8%           |
| 6[c]  | Rh$_2$(TFA)$_4$ | 0 °C        | 18 h | full conv.    | 13%          |
| 7[c]  | Rh$_2$(TFA)$_4$ | –78 °C      | 18 h | full conv.    | 18%          |
| 8     | Cu(acac)$_2$    | 130 °C      | 1 min| no conv.      | 0%           |
| 9     | Cu(TMHD)$_2$    | 130 °C      | 1 min| no conv.      | 0%           |
| 10    | Cu(tFacac)$_2$  | 130 °C      | 1 min| no conv.      | 0%           |
| 11    | Cu(hFacac)$_2$  | 130 °C      | 1 min| full conv.    | 93%          |

[a] Reactions were performed with diazoacetate 13a (5 µmol) and catalyst (0.5 mmol) in CD$_2$Cl$_2$ (0.5 mL); [b] Determined via $^1$H NMR spectroscopy with mesitylene as internal standard; [c] Reaction was performed without the use of microwave conditions. Abbr.: esp = α,α,α',α'-tetramethyl-1,3-benzenedipropionate; TPA = triphenylacetate;
TMHD = 2,2,6,6-tetramethyl-3,5-heptandionate; tFacac = trifluoroacetylacetonate; hFacac = hexafluoroacetylacetonate.

**Supplementary Table 2.** Optimization of rhodium(II)- and copper(II)-based catalysts for the dearomative intramolecular cyclopropanation of 13b.[a]

| Entry | Catalyst      | Conversion[b] | Yield 14b[b] |
|-------|---------------|---------------|--------------|
| 1     | Rh$_2$(OAc)$_4$ | full conv.    | 0%           |
| 2     | Rh$_2$(TFA)$_4$ | full conv.    | 0%           |
| 3     | Rh$_2$(TPA)$_4$ | full conv.    | 0%           |
| 4     | Rh$_2$(esp)$_2$ | full conv.    | 0%           |
| 5     | Cu(acac)$_2$   | no conv.      | 0%           |
| 6     | Cu(TMHD)$_2$   | no conv.      | 0%           |
| 7     | Cu(tfacac)$_2$ | no conv.      | 0%           |
| 8     | Cu(hfacac)$_2$ | 85%           | 63%          |

[a] Reactions were performed with diazoacetate 13b (5 µmol) and catalyst (0.5 mmol) in CD$_2$Cl$_2$ (0.5 mL); [b] Determined via $^1$H NMR spectroscopy with mesitylene as internal standard. Abbr.: esp = α,α,α',α'-tetramethyl-1,3-benzenedipropionate; TPA = triphenylacetate; TMHD = 2,2,6,6-tetramethyl-3,5-heptandionate; tFacac = trifluoroacetylacetonate; hFacac = hexafluoroacetylacetonate.
1.6.1.2 Oxidative dehydrogenation of 14a

**Supplementary Table 3.** Probing different conditions for an oxidative dehydrogenation of triasterane 14a.

| Entry | Conditions          | Conversion [b] | Yield 15 [b] | Yield S12 [b] |
|-------|---------------------|----------------|--------------|---------------|
| 1     | 2.0 equiv DDQ       | full conv.     | 35%          | 0%            |
|       | 130 °C, 5 h         |                |              |               |
| 2     | 2.0 equiv p-chloranil | no conv.       | 0%           | 0%            |
|       | 130 °C, 3 h         |                |              |               |
| 3     | 2.0 equiv p-chloranil | no conv.       | 0%           | 0%            |
|       | 150 °C, 18 h        |                |              |               |
| 4     | 2.0 equiv o-chloranil | no conv.       | 0%           | 0%            |
|       | 130 °C, 3 h         |                |              |               |
| 5     | 10 mol% Pd/C        | full conv.     | 0%           | 96%           |
|       | 150 °C, 35 h        |                |              |               |
| 6     | 10 mol% Pd/C        | full conv.     | 0%           | 94%           |
|       | 1.0 equiv norbornene| 150 °C, 35 h   |              |               |
| 7     | 10 mol% (Ph₃P)₃RhCl | full conv.     | 0%           | 95%           |
|       | 160 °C, 22 h        |                |              |               |
| 8     | 1.0 equiv S₈        | no conv.       | 0%           | 0%            |
|       | 160 °C, 22 h        |                |              |               |

[a] Reactions were performed in J Youngs NMR tube with triasterane 14a (12.1 mg, 50.0 µmol, 1.00 equiv) and in C₆D₅Cl (0.5 mL); [b] Determined via ¹H NMR spectroscopy with mesitylene as internal standard. Abbr.: DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone
1.6.2 General procedures

1.6.2.1 GP1 – Synthesis of acetoacetate 12

A Schlenk flask is charged with carboxylic acid cis-11 (1.00 equiv) and dissolved in THF (7.5 mL/mmol carboxylic acid). N,N-carbonyldiimidazole (1.00 equiv) is added and the reaction mixture is stirred at room temperature for 3 h. In a separate Schlenk flask di-iso-propylamine (5.00 equiv) is dissolved in THF (1.5 mL/mmol di-iso-propylamine) and cooled down to –78 °C. nBuLi (5.00 equiv) is added dropwise and the reaction mixture is stirred at –78 °C for 1 h. A solution of acetate (2.50 equiv) and THF (1.5 mL/mmol acetate) is added dropwise to the LDA solution, and the mixture is stirred at –78 °C for 1 h. The solution of activated carboxylic acid is transferred dropwise to the enolate via a Teflon canula at –78 °C. After complete addition the reaction mixture is stirred at –78 °C for 3 h and is warmed up to room temperature. The reaction is quenched via addition of saturated aqueous NH₄Cl-solution (5 mL/mmol nBuLi), the layers are separated, and the aqueous layer is extracted with tert-butyldimethyl ether (3 × 10 mL/mmol). The combined organic layer was washed with saturated aqueous NaHCO₃-solution (2 × 10 mL/mmol) and brine and is dried over Na₂SO₄. After filtration and removal of all volatiles under reduced pressure the crude product is purified via flash column chromatography on silica gel.

1.6.2.2 GP2 – Diazo transfer reaction to diazoacetoacetate 13

A Schlenk flask is charged with 4-acetamidobenzenesulfonyl azide (1.2 equiv), dissolved in MeCN (10 mL/mmol) and the solution is cooled down to 0 °C. First triethylamine (1.2 equiv) then a solution of acetoacetate 12 (1.0 equiv) and MeCN (3.3 mL/mmol) is slowly added to the reaction mixture. The mixture is stirred at 0 °C for 1 h, is warmed up to room temperature and stirred for additional 15 h. After full conversion (monitored via TLC) the formed white precipitate is filtered off via a glass frit and washed with MeCN (3.3 mL/mmol). All volatiles of the filtrate are removed under reduced pressure and the crude product is purified via flash column chromatography on silica gel.
1.6.2.3 GP3 – Intramolecular Buchner dearomatization to triasterane 14

An Ace pressure tube is charged with copper(II) hexafluoroacetylacetonate hydrate (10 mol%) and CH$_2$Cl$_2$ (90 mL/mmol). A solution of diazoacetoacetate 13 (1.00 equiv) and CH$_2$Cl$_2$ (10 mL/mmol) is added to the catalyst solution and the pressure tube is tightly closed. The reaction mixture is heated to 130 °C in an oil bath for 2 h. After complete conversion (monitored via TLC) all volatiles are removed under reduced pressure and the crude product is purified via flash column chromatography on silica gel.

Alternative procedure:
A three-neck round-bottom flask is charged with copper(II) hexafluoroacetylacetonate hydrate (10 mol%) and chlorobenzene (45 mL/mmol) and is heated up till reflux. A solution of diazoacetoacetate 13 (1.00 equiv) and chlorobenzene (5 mL/mmol) is added to the catalyst solution under reflux via a syringe pump over 4 h. After complete conversion (monitored via TLC) all volatiles are removed under reduced pressure and the crude product is purified via flash column chromatography on silica gel.
1.6.3 Experimental details

1.6.3.1 Synthesis of annulene ester 15

1.6.3.1.1 1,4-Dihydronaphthalene (8)

According to a literature procedure\textsuperscript{12}, a Schlenk flask was charged with naphthalene (9, 12.8 g, 100 mmol, 1.00 equiv) and dry Et\textsubscript{2}O (200 mL). Sodium (5.75 g, 250 mmol, 2.50 equiv) was added in portions to the reaction mixture and stirred at room temperature for 15 min. tert-Butanol (18.5 g, 250 mmol, 2.50 equiv) was added dropwise to the reaction mixture and was stirred at room temperature for 14 h. The mixture was filtered through a glass frit and the filter cake was washed with Et\textsubscript{2}O (50 mL). The combined organic layers were washed with H\textsubscript{2}O (2 × 100 mL) and brine (100 mL), dried over Na\textsubscript{2}SO\textsubscript{4}. Filtration and removal of all volatiles under reduced pressure afforded 1,4-dihydronaphthalene (8) as a colourless oil and was used without further purification (12.6 g, 96.6 mmol, 97%).

\textbf{TLC} (SiO\textsubscript{2}, cyclohexane/EtOAc = 9:1, v/v): \(R_f = 0.62\);

\textbf{\textsuperscript{1}H NMR} (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta 3.38\) (d, \(3J_{4,5} = 1.3\) Hz, 4H, H\textsubscript{-4}), 5.93 (m, 2H, H\textsubscript{-5}), 7.12 (m, 4H, H\textsubscript{-1}, H\textsubscript{-2});

\textbf{\textsuperscript{13}C NMR} (101 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta 30.1\) (C\textsubscript{-4}), 125.2 (C\textsubscript{-5}), 126.2 (C\textsubscript{-1}), 128.7 (C\textsubscript{-2}), 134.7 (C\textsubscript{-3});

\textbf{HRMS} (m/z): [M+\textsuperscript{+}] calcd. for C\textsubscript{10}H\textsubscript{10}\textsuperscript{+}, 130.0777; found, 130.0771.

The data is in accordance with literature\textsuperscript{13}.

1.6.3.1.2 1-((1r,1aR,7aS)-1a,2,7,7a-Tetrahydro-1\textsubscript{H}-cyclopropa[b]naphthalen-1-yl)propan-1-one (10)

According to a literature procedure\textsuperscript{14,15}, a Schlenk flask was charged with Rh\textsubscript{2}(OAc)\textsubscript{4} (22 mg, 50 \(\mu\)mol, 0.10 mol%) and 1,4-dihydronaphthalene (8, 6.51 g, 50.0 mmol, 1.00 equiv). Ethyl diazoacetate (15\% in toluene, 57.2 g, 75.0 mmol, 1.50 equiv) was slowly added to the reaction mixture at room temperature over 16 h. The reaction mixture was filtered over a plug of Al\textsubscript{2}O\textsubscript{3} (3 × 5 cm, eluent: CH\textsubscript{2}Cl\textsubscript{2}, 100 mL). After removal of all volatiles under reduced pressure the crude product was purified via flash column chromatography on silica gel (9 × 12 cm, cyclohexane/EtOAc = 20:1, 100 mL, #17–25) to afford ester 10 as a colourless oil (10.8 g, 50.0 mmol, 100\%, trans/cis = 2:1).

\textbf{Alternative procedure:}

According to a literature procedure\textsuperscript{14,15}, a Schlenk flask was charged with Rh\textsubscript{2}(OAc)\textsubscript{4} (84.9 mg, 192 \(\mu\)mol, 0.10 mol%) and 1,4-dihydronaphthalene (8, 25.0 g, 192 mmol, 1.00 equiv). Ethyl diazoacetate (15\% in toluene, 245 mL, 288 mmol, 1.50 equiv) was slowly added to the reaction mixture at room temperature over 18 h. The reaction mixture was filtered over a plug of Al\textsubscript{2}O\textsubscript{3} (3 × 5 cm, eluent: CH\textsubscript{2}Cl\textsubscript{2}, 200 mL). After removal of all volatiles under reduced pressure the
crude product was purified via distillation under reduced pressure (3.3 × 10⁻¹ mbar), where the impurities were distilled out from the crude product mixture. The distillation was stopped when the head temperature exceeded 100 °C (oil bath temperature: 130 °C). Ester 10 was afforded as a yellow oil (39.3 g, 182 mmol, 95%, 2:1 dr). TLC (SiO₂, cyclohexane/EtOAc = 9:1, v/v): Rf = 0.47 (SiO₂, cyclohexane/EtOAc = 9:1); ¹H NMR (400 MHz, CDCl₃): δ 1.08 (t, 3J₁₈ = 7.1 Hz, 3H, H-9trans), 1.19 (t, 3J₁₈ = 7.1 Hz, 3H, H-9trans), 1.39 (t, 3J₁₄,₁₅ = 3.9 Hz, 1H, H-6trans), 1.69–1.73 (m, 3H, H-5cis, H-6trans), 1.91 (m, 2H, H-5trans), 2.95–3.15 (m, 4H, H-4), 3.77 (q, 3J₁₈ = 7.1 Hz, 2H, H-8cis), 4.04 (q, 3J₁₈ = 7.1 Hz, 2H, H-8trans), 7.00–7.12 (m, 4H, H-1, H-2); ¹³C NMR (101 MHz, CDCl₃): δ 14.3 (C-9cis), 14.5 (C-9trans), 17.3 (C-5cis), 19.1 (C-6trans), 21.3 (C-6cis), 22.4 (C-5trans), 25.1 (C-4cis), 28.6 (C-4trans), 60.2 (C-8cis), 60.6 (C-8trans), 125.9 (C-1cis), 126.8 (C-1trans), 128.6 (C-2cis), 129.2 (C-2trans), 134.2 (C-3trans), 136.4 (C-3cis), 174.4 (C-7trans), 176.5 (C-7cis); HRMS (m/z): [(M+H)⁺] calcd. for C₁₄H₁₇O₂⁺, 217.1223; found, 217.1230.

The data is in accordance with literature¹⁴⁻¹⁵.

1.6.3.1.3 (1r,1aR,7aS)-1a,2,7,7a-Tetrahydro-1H-cyclopropa[b]naphthalene-1-carboxylic acid (trans-11) & ethyl (1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalene-1-carboxylate (cis-10)

![Reaction Scheme](image)

A round-bottom flask was charged with ester 10 (trans/cis = 67:33, 8.60 g, 39.8 mmol, 1.00 equiv) and EtOH (75 mL). Potassium hydroxide (6.68 g, 119 mmol, 3.00 equiv) was added and the reaction mixture was stirred at room temperature for 8 h. Then H₂O (300 mL) was added, the layers were separated.

1.6.3.1.3.1 For isolation of trans-carboxylic acid trans-11:

The aqueous layer was washed with tert-butyl methyl ether (3 × 100 mL). Then conc. aqueous HCl-solution (32%) was added until pH ≤ 1 was set and the aqueous layer was extracted with tert-butyl methyl ether (3 × 100 mL). The combined organic layers were washed with brine and dried over Na₂SO₄. After filtration and removal of all volatiles under reduced pressure the crude product was purified via recrystallization in cyclohexane and EtOAc to afford acid trans-11 as a colourless solid (2.20 g, 11.7 mmol, 29%). TLC (SiO₂, cyclohexane/EtOAc = 9:1, v/v): Rf = 0.16; mp: 156 °C (cyclohexane/EtOAc); ¹H NMR (400 MHz, CDCl₃): δ 1.48 (t, 3J₁₈,₁₉ = 3.83 Hz, 1H, H-6), 2.03 (m, 2H, H-5), 3.06 (d, 3J₁₈,₁₉ = 15.9 Hz, 2H, H-4a), 3.14 (d, 3J₁₈,₁₉ = 15.9 Hz, 2H, H-4b), 6.99–7.03 (m, 2H, H-2), 7.11–7.14 (m, 2H, H-1), 11.43 (br s, 1H,
The crude product was purified via recrystallization in cyclohexane and EtOAc to afford acid (cis-10) (2.28 g, 10.5 mmol, 26%) as a colourless oil. TLC (SiO₂, cyclohexane/EtOAc = 9:1, v/v): Rf = 0.47; ¹H NMR (400 MHz, CDCl₃): δ 1.07 (t, J = 7.1 Hz, 3H, H₈), 1.69–1.76 (m, 3H, H₅, H₆), 3.03–3.14 (m, 4H, H₃, H₄, H₅), 3.76 (q, J = 7.1 Hz, 2H, H₈), 7.06 (m, 4H, H₁, H₂); ¹³C NMR (101 MHz, CDCl₃): δ 14.2 (C-9), 17.0 (C-5), 21.1 (C-6), 25.1 (C-4), 60.1 (C-8), 125.9 (C-1), 128.6 (C-2), 138.5 (C-3), 171.0 (C-7); HRMS (m/z): [(M+H)+] calcd. for C₁₄H₁₇O₂⁺: 217.1223; found, 217.1230; IR (ATR): 2979 (w), 2907 (w), 2340 (w), 1917 (w), 1715 (s), 1430 (m), 1369 (m), 1268 (m), 1148 (s), 1039 (m), 998 (m), 859 (m), 810 (m), 743 cm⁻¹ (s).

The data is in accordance with literature¹⁴⁻¹⁵.

1.6.3.1.4 (1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalene-1-carboxylic acid (cis-11)

A round-bottom flask was charged with ester cis-10 (1.50 g, 6.94 mmol, 1.00 equiv) and EtOH (15 mL). Potassium hydroxide (1.17 g, 20.8 mmol, 3.00 equiv) was added and the reaction mixture was stirred under reflux for 11 h. After full conversion (monitored via TLC) H₂O (100 mL) was added, and the aqueous layer was washed with tert-butyl methyl ether (2 × 20 mL). Then the aqueous layer was acidified with conc. aqueous HCl solution and extracted with tert-butyl methyl ether (3 × 30 mL). The combined organic layers were washed with brine and dried over Na₂SO₄. After filtration and removal of all volatiles under reduced pressure the crude product was purified by flash column chromatography on silica gel (2.5 × 12 cm, cyclohexane/EtOAc = 10:1, 20 mL, #2–7) to afford ester cis-10 (2.28 g, 10.5 mmol, 26%) as a colourless oil. TLC (SiO₂, cyclohexane/EtOAc = 9:1, v/v): Rf = 0.47; ¹H NMR (400 MHz, CDCl₃): δ 1.07 (t, J = 7.1 Hz, 3H, H₈), 1.69–1.76 (m, 3H, H₅, H₆), 3.03–3.14 (m, 4H, H₃, H₄, H₅), 3.76 (q, J = 7.1 Hz, 2H, H₈), 7.06 (m, 4H, H₁, H₂); ¹³C NMR (101 MHz, CDCl₃): δ 14.2 (C-9), 17.0 (C-5), 21.1 (C-6), 25.1 (C-4), 60.1 (C-8), 125.9 (C-1), 128.6 (C-2), 138.5 (C-3), 171.0 (C-7); HRMS (m/z): [(M+H)+] calcd. for C₁₄H₁₇O₂⁺: 217.1223; found, 217.1230; IR (ATR): 2979 (w), 2907 (w), 2340 (w), 1917 (w), 1715 (s), 1430 (m), 1369 (m), 1268 (m), 1148 (s), 1039 (m), 998 (m), 859 (m), 810 (m), 743 cm⁻¹ (s).
δ = 177.4 ppm was detected via HMBC; HRMS (m/z): [(M+H)+] calcd. for C_{13}H_{13}O_{5}^+, 189.0910; found, 189.0909; IR (ATR): 3021 (w), 2930 (w), 2853 (w), 2694 (w), 2538 (w), 2342 (w), 2118 (w), 1908 (w), 1750 (w), 1680 (s), 1452 (s), 1346 (m), 1313 (w), 1232 (m), 1214 (s), 1194 (s), 1118 (m), 926 (s), 847 (m), 798 (m), 738 (w), 1908 (w), 1750 (w), 1680 (s), 1452 (s), 1346 (m), 1313 (w), 1232 (m), 1214 (s), 1194 (s), 1118 (m), 926 (s), 847 (m), 798 (m), 738 (w).

1.6.3.1.5 Methyl 3-oxo-3-((1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-1-yl)propanoate (12a)

Prepared according to GP1 from carboxylic acid cis-11 (1.00 g, 5.31 mmol, 1.00 equiv), N,N-carbonyldiimidazole (947 mg, 5.31 mmol, 1.00 equiv), di-iso-propylamine (3.73 mL, 26.6 mmol, 5.00 equiv), nBuLi (2.61 M in n-hexane, 9.12 mL, 26.6 mmol, 5.00 equiv) and methyl acetate (1.06 mL, 13.3 mmol, 2.50 equiv) in THF (100 mL). Purification via flash column chromatography on silica gel (4.5 × 13 cm, cyclohexane/EtOAc = 20:1, 20 mL, #76–140) afforded acetoacetate 12a as a colourless oil (745 mg, 3.05 mmol, 57%). TLC (SiO₂, cyclohexane/EtOAc = 7:3, v/v): R₆ = 0.36; ¹H NMR (400 MHz, CDCl₃): δ 1.96–2.00 (m, 2H, H-5), 2.13 (t, J₆,₅ = 8.5 Hz, 1H, H-6), 2.86–3.03 (m, 4H, H-4), 3.52 (s, 2H, H-8), 3.72 (s, 3H, H-10) 7.09 (s, 4H, H-1, H-2); ¹³C NMR (101 MHz, CDCl₃): δ 22.6 (C-5), 23.9 (C-6), 28.5 (C-4), 51.8 (C-8), 52.3 (C-10), 125.9 (C-1), 128.4 (C-2), 136.5 (C-3) 168.0 (C-9), 200.7 (C-7); HRMS (m/z): [(M+H)+] calcd. for C₁₃H₁₃O₅⁺, 245.1172; found, 245.1170; IR (ATR): 3475 (w), 3357 (w), 3020 (w), 2919 (m), 2847 (w), 2318 (w), 2107 (w), 2082 (w), 1741 (s), 1678 (s), 1490 (m), 1398 (s), 1302 (s), 1258 (s), 1183 (m), 1140 (s), 1091 (s), 1036 (m), 964 (s), 892 (m), 816 (s), 751 (s), 667 cm⁻¹ (s).

1.6.3.1.6 tert-Butyl 3-oxo-3-((1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-1-yl)propanoate (12b)

Prepared according to GP1 from carboxylic acid cis-10 (1.00 g, 5.31 mmol, 1.00 equiv), N,N-carbonyldiimidazole (947 mg, 5.84 mmol, 1.00 equiv), di-iso-propylamine (3.73 mL, 26.6 mmol, 5.00 equiv), nBuLi (2.61 M in n-hexane, 10.2 mL, 26.6 mmol, 5.00 equiv) and tert-butyl acetate (1.79 mL, 13.3 mmol, 2.50 equiv) in THF (100 mL). Purification via flash column chromatography on silica gel (2.5 × 12 cm, cyclohexane/EtOAc = 20:1, 20 mL, #15–25) afforded acetoacetate 12c as a colourless solid (1.06 g, 0.35 mmol, 70%). TLC (SiO₂, cyclohexane/EtOAc = 9:1, v/v): R₆ = 0.46; mp: 95–100 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.48 (s, 9H, H-11), 1.95–1.98 (m, 2H, H-5), 2.15 (t, J₆,₅ = 8.2 Hz, 1H, H-6), 2.88–3.01 (m, 4H, H-4), 3.39 (s, 2H, H-8), 7.09 (s, 4H, H-1, H-2); ¹³C NMR (101 MHz, CDCl₃): δ 22.5 (C-5), 23.9 (C-6), 28.2 (C-11), 28.2 (C-6), 53.7 (C-8), 81.8 (C-10), 125.8 (C-1), 128.4 (C-2), 136.8 (C-3), 166.8 (C-9), 201.3 (C-7); HRMS (m/z): [(M–(C₄H₈)+2H)+]: calcd. for C₁₄H₁₅O₅⁺, 231.1016; found, 231.1016; IR (ATR): 2974 (m), 2927
IR was not detected. 83.0 (C(s, 4H, H(c, 9H, H(cyclohexane/EtOAc afforded diazoacetoacetate chromatography on silica gel (4.5 × 15 cm, cyclohexane/EtOAc = 30:1, 20 mL, #27–55) afforded diazoacetoacetate 13a as a yellow oil (693 mg, 2.56 mmol, 85%). TLC (SiO2, cyclohexane/EtOAc = 8:2, v/v): Rf = 0.50; 1H NMR (400 MHz, CDCl3): δ 2.02 (m, 2H, H-5) 2.88 (t, J = 8.4 Hz, 1H, H-6), 2.94–2.98 (m, 2H, H-4a), 3.02–3.08 (m, 2H, H-4b), 3.84 (s, 3H, H-10), 7.07 (m, 4H, H-1, H-2); 13C NMR (101 MHz, CDCl3): δ 22.0 (C-5), 24.7 (C-4), 26.3 (C-6), 52.3 (C-10), 125.8 (C-1)*, 128.4 (C-2)*, 136.4 (C-3), 162.4 (C-9), 189.5 (C-7). Carbon atom C-8 was not detected; HRMS (m/z): [(M+H)+] calcd. for C13H15N2O3+, 271.1077; found, 271.1074; IR (ATR): 3421 (w), 3015 (s). 13a

1.6.3.1.7 Methyl-2-diazo-3-oxo-3-((1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-1-yl)propanoate (13a)

Prepared according to GP2 from acetoacetate 12a (740 mg, 3.03 mmol, 1.00 equiv), 4-acetamidobenzenesulfonyl azide (875 mg, 3.64 mmol, 1.2 equiv), triethylamine (0.51 mL, 3.64 mmol, 1.2 equiv) and MeCN (50 mL). Purification via flash column chromatography on silica gel (4 × 15 cm, cyclohexane/EtOAc = 30:1, 20 mL, #27–55) afforded diazoacetoacetate 13a as a yellow oil (693 mg, 2.56 mmol, 85%). TLC (SiO2, cyclohexane/EtOAc = 8:2, v/v): Rf = 0.50; 1H NMR (400 MHz, CDCl3): δ 2.02 (m, 2H, H-5) 2.88 (t, J = 8.4 Hz, 1H, H-6), 2.94–2.98 (m, 2H, H-4a), 3.02–3.08 (m, 2H, H-4b), 3.84 (s, 3H, H-10), 7.07 (m, 4H, H-1, H-2); 13C NMR (101 MHz, CDCl3): δ 22.0 (C-5), 24.7 (C-4), 26.3 (C-6), 52.3 (C-10), 125.8 (C-1)*, 128.4 (C-2)*, 136.4 (C-3), 162.4 (C-9), 189.5 (C-7). Carbon atom C-8 was not detected; HRMS (m/z): [(M+H)+] calcd. for C13H15N2O3+, 271.1077; found, 271.1074; IR (ATR): 3421 (w), 3015 (s). 13a

1.6.3.1.8 tert-Butyl 2-diazo-3-oxo-3-((1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-1-yl)propanoate (13b)

Prepared according to GP2 from acetoacetate 12b (1.00 g, 3.90 mmol, 1.00 equiv), 4-acetamidobenzenesulfonyl azide (1.12 g, 4.68 mmol, 1.2 equiv), triethylamine (0.65 mL, 4.68 mmol, 1.20 equiv) and MeCN (50 mL). Purification via flash column chromatography on silica gel (4.5 × 15 cm, cyclohexane/EtOAc = 30:1, 20 mL, #26–36) afforded diazoacetoacetate 13c as a yellow solid (912 mg, 2.92 mmol, 75%). TLC (SiO2, cyclohexane/EtOAc = 8:2, v/v): Rf = 0.49; mp: 120–125 °C; 1H NMR (400 MHz, CDCl3): δ 1.55 (s, 9H, H-11), 1.99 (m, 2H, H-5), 2.86 (t, J = 8.5 Hz, 1H, H-6), 2.95–3.08 (m, 4H, H-4), 7.07 (s, 4H, H-1, H-2); 13C NMR (101 MHz, CDCl3): δ 21.9 (C-5), 24.8 (C-4), 26.2 (C-6), 28.5 (C-11), 83.0 (C-10), 125.7 (C-1), 128.4 (C-2), 136.5 (C-3), 161.3 (C-9), 190.1 (C-7). Carbon atom C-8 was not detected. HRMS (m/z): [(M+H)+] calcd. for C18H21N2O3+, 313.1547; found, 313.1548; IR (ATR): 2976 (w), 2918 (w), 2321 (w), 2129 (s), 1908 (w), 1697 (s), 1624 (s), 1454 (w), 1401 (m), 1302 (s), 1188 (s), 1128 (s), 1070 (s), 968 (s), 837 (m), 748 cm−1 (s).
1.6.3.1.9 Triasterane 14a

Prepared according to GP3 from diazoacetoacetate 13a (270 mg, 1.00 mmol, 1.00 equiv), copper(II) hexafluoroacetylacetonate hydrate (49 mg, 0.10 mmol, 10 mol%) and CH₂Cl₂ (100 mL). Purification via flash column chromatography on silica gel (2.5 × 13 cm, cyclohexane/EtOAc = 4:1, 20 mL, #8–15) afforded triasterane 14a as a colourless solid (195 mg, 805 µmol, 81%). TLC (SiO₂, cyclohexane/EtOAc = 8:2, v/v): Rᵣ = 0.24; mp: 160 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.86 (dd, 3 J₅,₆ = 8.2 Hz, 3 J₅,₄b = 1.6 Hz, 2H, H-5), 2.06 (t, 3 J₆,₅ = 8.2 Hz, 1H, H-6), 2.34 (d, 2 J₄a,₄b = 13.8 Hz, 2H, H-4a)*, 2.44 (dt, 2 J₄b,₄a = 13.8 Hz, 3 J₄b,₅ = 1.6 Hz, 2H, H-4b)*, 3.56 (s, 3H, H-10), 5.90–5.97 (m, 4H, H-1, H-2)*; ¹³C NMR (101 MHz, CDCl₃): δ 22.7 (C-5), 23.2 (C-4), 26.5 (C-6), 41.3 (C-8), 45.9 (C-3), 52.1 (C-10), 122.8 (C-1), 128.9 (C-2), 165.3 (C-9), 202.7 (C-7); HRMS (m/z): [(M+H)⁺] calcd. for C₁₅H₁₅O₃⁺, 243.1016; found, 243.1015; IR (ATR): 2907 (w), 2107 (w), 1731 (s), 1639 (s), 1458 (m), 1359 (m), 1288 (m), 1246 (s), 1129 (m), 1080 (m), 1029 (s), 966 (m), 904 (m), 852 (m), 735 cm⁻¹ (s).

1.6.3.1.10 Triasterane 14b

Prepared according to GP3 from diazoacetoacetate 13b (500 mg, 1.60 mmol, 1.00 equiv), copper(II) hexafluoroacetylacetonate hydrate (76 mg, 0.10 mmol, 10 mol%) and CH₂Cl₂ (160 mL). Purification via flash column chromatography on silica gel (3 × 13 cm, cyclohexane/EtOAc = 7:3, 20 mL, #14–30) afforded triasterane 14b as a colourless solid (250 mg, 879 µmol, 55%). TLC (SiO₂, cyclohexane/EtOAc = 8:2, v/v): Rᵣ = 0.11; mp: 168 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.34 (s, 9H, H-11), 1.83 (d, 3 J₅,₆ = 8.2 Hz, 2H, H-5), 2.03 (t, 3 J₆,₅ = 8.2 Hz, 1H, H-6), 2.31 (d, 2 J₄a,₄b = 13.8 Hz, 2H, H-4a)*, 2.51 (d, 2 J₄b,₄a = 13.8 Hz, 2H, H-4b)*, 5.87–5.90 (m, 2H, H-2), 5.94–5.97 (m, 2H, H-1)*; ¹³C NMR (101 MHz, CDCl₃): δ 22.6 (C-5), 23.2 (C-4), 26.6 (C-6), 28.0 (C-11), 41.3 (C-8), 45.6 (C-3), 81.1 (C-10), 122.8 (C-1), 128.9 (C-2), 164.0 (C-9), 203.3 (C-7). HRMS (m/z): [(M+H)⁺] calcd. for C₁₅H₁₅O₃⁺, 285.1485; found, 285.1485; IR (ATR): 3034 (w), 2970 (w), 2922 (w), 2257 (w), 2123 (w), 1731 (s), 1655 (s), 1354 (m), 1248 (s), 1158 (s), 1084 (s), 1029 (s), 920 (m), 880 (m), 820 (m), 732 cm⁻¹ (s).

1.6.3.1.11 Methyl 1-oxo-1,2-dihydro-9αH-2,9-ethenobenzo[7]annulene-9α-carboxylate (15)

A pressure tube was charged with triasterane 14a (200 mg, 826 µmol, 1.00 equiv) and chlorobenzene (17 mL). 2,3-Dichloro-5,6-dicyano-p-benzoquinone (375 mg, 1.65 mmol, 2.00 equiv) was added and the pressure tube was closed. The reaction mixture was stirred at 130 °C for 3 h. After full conversion (monitored via TLC) the reaction mixture was filtered over a plug of
silica (4 × 5 cm, eluent: CH₂Cl₂, 100 mL). After removal of all volatiles under reduced pressure the crude product was purified via flash column chromatography on silica gel (2.5 × 12 cm, cyclohexane/EtOAc = 20:1, 20 mL, #23–55) to afford annulene 15 as a yellow solid (63 mg, 262 mmol, 32%). TLC (SiO₂, cyclohexane/EtOAc = 6:4, v/v): Rf = 0.53, mp: 165 °C; ¹H NMR (400 MHz, CDCl₃): δ 3.78 (s, 3H, H-10), 3.81 (pseudo t, 3J₆,₅ = 6.5 Hz, 3J₅,₆ = 6.5 Hz, 1H, H-6), 5.31 (dd, 3J₅,₄ = 9.0 Hz, 3J₆,₅ = 6.5 Hz, 1H, H-5), 5.35 (dd, 3J₅,₄ = 8.9 Hz, 3J₆,₅ = 6.5 Hz, 1H, H-5*), 6.70 (d, 3J₄,₅ = 8.9 Hz, 1H, H-4*), 6.71 (d, 3J₆,₅ = 9.0 Hz, 1H, H-4), 6.75 (d, 3J₅,₄ = 6.7 Hz, 1H, H-2)*, 6.83 (d, 3J₆,₅ = 6.7 Hz, 1H, H-2)*, 6.96 (dd, 3J₁,₁ = 10.7 Hz, 3J₁,₂ = 6.7 Hz, 1H, H-1)**, 7.06 (dd, 3J₁,₁ = 10.7 Hz, 3J₁,₂ = 6.7 Hz, 1H, H-1)**; ¹³C NMR (101 MHz, CDCl₃): δ 45.3 (C-6), 52.1 (C-10), 61.6 (C-8), 111.0 (C-5), 111.3 (C-5*), 121.6 (C-3), 121.8 (C-3*), 123.9 (C-2)*, 124.0 (C-2)*, 127.4 (C-4'), 127.4 (C-4'), 127.4 (C-1)*, 127.9 (C-4), 129.5 (C-1)*, 166.5 (C-9), 203.0 (C-7); HRMS (m/z): [(M+H)+] calcd. for C₁₅H₁₃O₃⁺: 241.0859; found, 241.0858; IR (ATR): 3446 (w), 2947 (w), 2339 (w), 2339 (w), 2220 (w), 2088 (w), 1912 (w), 1724 (s), 1436 (m), 1353 (w), 1237 (s), 1113 (m), 1066 (s), 933 (s), 831 (s), 788 (s) 738 cm⁻¹ (s).

Note: During the publication process it was found that DMF is the superior solvent compared to chlorobenzene in the oxidative dehydrogenation and should be used instead.

1.6.3.1.122-Diazo-1-((1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-1-y1)ethan-1-one (S10)

A Schlenk flask was charged with carboxylic acid cis-11 (500 mg, 2.66 mmol, 1.00 equiv), dissolved in CH₂Cl₂ (20 mL) and cooled down to 0 °C. Oxalyl chloride (161 mg, 1.27 mmol, 1.20 equiv) and DMF (1 drop) were added, and the reaction mixture was stirred at 0 °C for 2 h. All volatiles were removed under reduced pressure and the residue was dissolved in MeCN (10 mL). A separate Schlenk flask was charged with trimethylsilyl diazomethane (2M in hexane, 3.99 mL, 7.98 mmol, 3.00 equiv) and MeCN (10 mL) and cooled down to 0 °C. The acid chloride solution was added dropwise to the trimethylsilyl diazomethane solution and stirred at 0 °C for 1 h and at room temperature for 1 h. After removal of all volatiles under reduced pressure via the Schlenk line the crude product was purified via flash column chromatography on silica gel (3.5 × 15 cm, cyclohexane/EtOAc = 20:1 (#1–50) → 10:1 (#51-100), 20 mL, #59–73) to afford diazoketone S10 as a yellow solid (382 mg, 1.80 mmol, 68%). TLC (SiO₂, cyclohexane/EtOAc = 8:2, v/v): Rf = 0.33; mp: 99 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.71–1.78 (m, 1H, H-6) 1.80–1.83 (m, 2H, H-5), 3.07–3.08 (m, 4H, H-4), 5.31 (br s, 1H, H-8), 7.05–7.10 (m, 4H, H-1, H-2); ¹³C NMR (101 MHz, CDCl₃): δ 20.0 (C-5), 24.9 (C-4), 27.2 (C-6), 56.2 (C-8), 125.9 (C-1)*, 128.4 (C-2)*, 136.3 (C-3), 192.2 (C-7); HRMS (m/z): [(M+H)+] calcd. for C₁₅H₁₃N₂O⁺, 213,1022; found, 213,1022; IR (ATR): 3213 (w), 3084 (m), 3003 (w), 2913 (w),
2623 (w), 2371 (w), 2263 (w), 2091 (s), 1918 (w), 1608 (s), 1491 (m), 1410 (s), 1314 (s), 1089 (s), 1089 (s), 1045 (s), 965 (s), 941 (m), 864 (m), 808 (m), 744 (m).

1.6.3.1.13 Triasterane S11

A Schlenk tube was charged with Rh₂(OAc)₄ (22 mg, 50 µmol, 10 mol%) and dissolved in CH₂Cl₂ (20 mL). A solution of diazoketone S10 (106 mg, 0.50 mmol, 1.00 equiv) and CH₂Cl₂ (5 mL) was slowly added to the catalyst solution via a syringe pump at room temperature over 5 h. After complete addition of the diazoketone solution all volatiles were removed under reduced pressure and the crude product was purified via flash column chromatography on silica gel (2 × 11 cm, cyclohexane/EtOAc = 8:1, 20 mL, #10–25) to afford ketone S11 as a colourless solid (71 mg, 0.39 mmol, 77%). TLC (SiO₂, cyclohexane/EtOAc = 8:2, v/v): Rf = 0.13; mp: 135 °C; 1H NMR (400 MHz, CDCl₃): δ 0.87 (d, J₆,6 = 2.12 Hz, 1H, H-8), 1.81–1.83 (m, 2H, H-5), 1.92 (m, 1H, H-6), 2.32 (d, J₄a,4b = 13.8 Hz, 2H, H-4a)*, 2.44 (d, J₄a,4b = 13.5 Hz, 2H, H-4b)*, 5.86–5.90 (m, 2H, H-1), 5.94–5.98 (m, 2H, H-2); 13C NMR (101 MHz, CDCl₃): δ 23.0 (C-4), 23.5 (C-5), 27.0 (C-6), 34.7 (C-8), 43.8 (C-3), 121.6 (C-1), 130.8 (C-2), 208.2 (C-7); HRMS (m/z): [(M+H)+] calcd. for C₁₃H₁₃O⁺, 185.0961; found, 185.0960; IR (ATR): 3261 (w), 3035 (m), 2902 (m), 2846 (m), 2623 (w), 2371 (w), 2263 (w), 2091 (s), 1918 (w), 1608 (s), 1491 (m), 1410 (s), 1314 (s), 1089 (s), 1089 (s), 1045 (s), 965 (s), 941 (m), 864 (m), 808 (m), 744 (m).

1.6.3.1.14 Methyl-2-(2a1,2b,3b,7b-tetrahydrobenzo[g]cyclopropa[cd]benzofuran-2(2aH)-ylidene)acetate (tentative structure, S12)

A pressure tube was charged with triasterane 14a (12.1 mg, 50.0 µmol, 1.00 equiv) and chlorobenzene (1 mL). Pd/C (10 wt%, 5.3 mg, 5.0 µmol, 10 mol%) was added and the pressure tube was closed. The reaction mixture was stirred at 150 °C for 35 h. After full conversion (monitored via TLC) the reaction mixture was filtered over a plug of silica (0.5 × 5 cm, eluent: CH₂Cl₂, 20 mL). After removal of all volatiles under reduced pressure ester S12 was afforded a yellow oil (10.1 mg, 41.7 µmol, 83%). TLC (SiO₂, cyclohexane/EtOAc = 6:4, v/v): Rf = 0.68; 1H NMR (400 MHz, CDCl₃): δ 2.01 (m, 1H, H-5), 2.37 (dd, J₆a,4b = 17.0 Hz, J₆a,5 = 3.3 Hz, 1H, H-4a), 2.52 (m, 1H, H-7), 3.17 (dd, J₅b,4a = 17.0 Hz, J₅b,5 = 8.6 Hz, 1H, H-4b), 3.59 (dd, J₅a,5 = 8.6 Hz, J₆,7 = 6.2 Hz, 1H, H-6), 3.70 (s, 3H, H-15), 5.32 (s, 1H, H-13), 5.60 (d, J₅a,7 = 5.2 Hz, 1H, H-8), 7.18–7.21 (m, 2H, H-2, H-11), 7.26–7.30 (m, 2H, H-1, H-10); 13C NMR (101 MHz, CDCl₃): δ 19.9 (C-5), 24.3 (C-4), 26.5 (C-7), 29.9 (C-6), 50.9 (C-15), 81.7 (C-8), 89.7 (C-13), 126.3 (C-11), 128.2 (C-10), 128.5 (C-2), 129.3 (C-1), 134.4 (C-9), 138.1 (C-3), 169.5 (C-14), 174.6 (C-12). HRMS (m/z): [(M+H)+] calcd. for C₁₅H₁₃O₃⁺, 243.1016; found, 243.1014.
1.6.3.2 Follow-Up

1.6.3.2.1 Saponification

1.6.3.2.1.1 1-Oxo-1,9a-dihydro-2,2,9-ethenobenzo[7]annulene-2-carboxylic acid (16)

A Schlenk tube was charged with annulene 15 (30.0 mg, 125 µmol, 1.00 equiv) and MeOH/H₂O (1:1, 1 mL). Then potassium hydroxide (21 mg, 375 µmol, 3.00 equiv) was added and the reaction mixture was stirred for 24 h. Additional potassium hydroxide (7.00 mg, 125 µmol, 1.00 equiv) was added and the reaction was stirred for 3 h. After full conversion (monitored via TLC) H₂O (5 mL) was added and the aqueous layer was washed with tert-butyl methyl ether (3 × 2 mL). The aqueous layer was acidified with aqueous HCl-solution (2 M) and then extracted with EtOAC (5 × 2 mL). The combined organic layer was washed with brine and dried over Na₂SO₄. After filtration and removal of all volatiles under reduced pressure the crude product purified via recrystallization from EtOAc to afford carboxylic acid 16 (6.0 mg, 27 µmol, 22%) as a colourless solid. X-ray crystal structure of side product S9 was isolated (see Supporting Information Section 2.1.8). TLC (SiO₂, cyclohexane/EtOAc = 6:4, v/v): Rf = 0.06; 'H NMR (400 MHz, CDCl₃): δ 0.86 (s, 1H, H-8), 5.61 (d, 3J₅,₄ = 8.9 Hz, 2H, H-5), 6.75 (m, 2H, H-2), 6.79 (d, 3J₄,₅ = 8.9 Hz, 2H, H-4), 7.17 (m, 2H, H-1). The ¹H NMR spectrum contains signals of tert-butyl methyl ether; ¹³C NMR (101 MHz, CDCl₃): δ 48.7 (C-8), 58.0 (C-6), 115.7 (C-5), 121.1 (C-3), 123.1 (C-2), 126.8 (C-4), 129.1 (C-1), 176.4 (C-9), 205.6 (C-7). Carbon atom C-9 and C-7 were detected via ¹H, ¹³C HMBC NMR. The ¹³C NMR spectrum contains signals of tert-butyl methyl ether; HRMS (m/z): [(M+H)+] calcd. for C₁₄H₁₁O₃+, 227.0703; found, 227.0707.
1.6.3.2.2 Irradiation experiments

1.6.3.2.2.1 Methyl 10-oxo-9,10-dihydro-10aH,1,9-(metheno)heptalene-10a-carboxylate (18)

A quartz cuvette was charged with 2.5 mL of a prior prepared degassed solution of annulene 15 (4.97 mg, 20.7 µmol in 5 mL MeCN). The cuvette (2.5 mL) was then irradiated with a 305 nm LED (LG Innotek, FWHM = 13 nm) for 25 min. This procedure was repeated and the resulting solutions were combined. The crude product was purified via preparative HPLC. After removal of all volatiles under reduced pressure the ester 18 was afforded as a yellow solid (3.2 mg, 13 µmol, 64%). The product is sensitive to air and light. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): δ 3.56 (s, 3H, H-$^15$), 3.70 (dd, $^3$J$_{5,6}=8.2$ Hz, $^3$J$_{5,4}=2.3$ Hz, 1H, H-$^5$), 4.48 (d, $^3$J$_{4,5}=2.3$ Hz, 1H, H-$^4$), 5.53 (dd, $^3$J$_{6,7}=10.8$ Hz, $^3$J$_{6,5}=8.2$ Hz, 1H, H-$^6$), 6.04 (dd, $^3$J$_{11,10}=11.6$ Hz, $^3$J$_{11,1}=7.8$ Hz, 1H, H-$^{11}$), 6.10 (d, $^3$J$_{6,7}=8.2$ Hz, 1H, H-$^8$), 6.18 (dd, $^3$J$_{1,2}=11.4$ Hz, $^3$J$_{1,11}=7.8$ Hz, 1H, H-$^1$), 6.19 (dd, $^3$J$_{7,6}=10.8$ Hz, $^3$J$_{7,8}=8.2$ Hz, 1H, H-$^7$), 6.72 (d, $^3$J$_{2,1}=11.4$ Hz, 1H, H-$^2$), 6.97 (d, $^3$J$_{10,11}=11.6$ Hz, 1H, H-$^{10}$); $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): δ 52.1 (C-$^5$), 52.6 (C-$^{15}$), 68.0 (C-$^{13}$), 93.6 (C-$^4$), 120.1 (C-$^6$), 121.0 (C-$^8$), 122.5 (C-$^{11}$), 124.0 (C-$^7$), 127.4 (C-$^1$), 129.2 (C-$^2$), 133.7 (C-$^3$), 134.4 (C-$^9$), 135.3 (C-$^{10}$), 167.9 (C-$^{14}$), 205.8 (C-$^{12}$); $^1$H NMR (600 MHz, CDCl$_3$): δ 3.62 (s, 3H, H-$^15$), 3.73 (dd, $^3$J$_{5,6}=8.2$ Hz, $^3$J$_{5,4}=2.3$ Hz, 1H, H-$^5$), 4.47 (d, $^3$J$_{4,5}=2.3$ Hz, 1H, H-$^4$), 5.52 (dd, $^3$J$_{6,7}=11.7$ Hz, $^3$J$_{6,5}=7.9$ Hz, 1H, H-$^6$), 6.06 (dd, $^3$J$_{11,10}=11.6$ Hz, $^3$J$_{11,1}=7.8$ Hz, 1H, H-$^{11}$), 6.11 (dd, $^3$J$_{6,7}=8.2$ Hz, $^3$J$_{6,10}=1.0$ Hz, 1H, H-$^6$), 6.19 (m, 2H, H-$^1$), 6.74 (d, $^3$J$_{2,1}=11.4$ Hz, 1H, H-$^2$), 6.99 (d, $^3$J$_{10,11}=11.7$ Hz, 1H, H-$^{10}$); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 51.7 (C-$^5$), 52.7 (C-$^{15}$), 67.7 (C-$^4$), 93.2 (C-$^3$), 119.8 (C-$^9$), 121.0 (C-$^8$), 122.3 (C-$^{11}$), 123.9 (C-$^7$), 127.3 (C-$^1$), 128.9 (C-$^2$), 133.3 (C-$^{10}$), 134.0 (C-$^9$), 135.0 (C-$^{10}$), 167.8 (C-$^{14}$), 205.5 (C-$^{12}$). HRMS (m/z): [(M+H)$^+$] calcd. for C$_{15}$H$_{12}$O$_3$+, 241.0859; found, 241.0861.
1.7 UV/vis Absorption Experiments

In the following, a full irradiation cycle (forth and back irradiation) refers to the irradiation of compound 15 using a 305 nm LED until the photostationary state of 15 and 18 was reached. Afterwards, this solution was irradiated with a 455 nm LED until no 18 could be observed in the UV/vis absorption trace of the HPLC chromatogram. All UV/vis experiments were conducted at 25 °C if not stated otherwise.

Supplementary Figure 7. UV/vis spectrum (molar extinction coefficient \( \varepsilon \)) of compound 15 in MeCN (\( c(15) = 1.1 \times 10^{-4} \text{ mol L}^{-1} \)).

Supplementary Figure 8. UV/vis-absorption of compound 15 in cyclohexane (\( c(15) = 3.7 \times 10^{-5} \text{ mol L}^{-1} \)) before irradiation and after one full irradiation cycle.
**Supplementary Figure 9.** UV/vis absorption (300 nm – 650 nm) trace of the HPLC chromatogram obtained from the spectroscopy cyclohexane solutions of Supplementary Figure 8. Before irradiation (top) and after one irradiation cycle (bottom). $t_R = 3.01$ min: minor unknown impurity from the irradiation cycle.
1.7.1 Switching in polar medium: MeCN

The photoswitching experiments were further conducted in MeCN as an alternative solvent with increased polarity as compared to the initially studied cyclohexane medium (see main text). This control experiment further indicated a non-polar transition state as is expected for a pericyclic [1,11] sigmatropic shift of a hydrocarbon scaffold. The reaction kinetics are approximately identical to the irradiation experiments in cyclohexane. (Supplementary Figure 8–9)

Supplementary Figure 10. UV/vis absorption of 15 in MeCN ($c = 7.8 \times 10^{-6}$ mol L$^{-1}$) before irradiation (cyan graph) and of isolated 18 (green graph) after irradiation ($c = 1.1 \times 10^{-4}$ mol L$^{-1}$). The molar absorptivity is equal at 350 nm for 15 and 18, which is the analytical wavelengths of choice for further analysis of the UV/vis traces in the HPLC analysis.

Supplementary Figure 11. UV/vis absorption of 15 in MeCN ($c(15) = 1.1 \times 10^{-4}$ mol L$^{-1}$) before irradiation (cyan graph), upon irradiation with a 305 nm LED with 5 s time intervals (grey graphs) and at the PSS consisting of 15 and 18 (green graph) after total irradiation time of 80 s.
**Supplementary Figure 12.** UV/vis absorption of 15 and 18 in MeCN ($c_{\text{start}}(15) = 1.1 \times 10^{-4}$ mol L$^{-1}$) at the PSS$_{305}$ nm (green graph), upon irradiation with a 455 nm LED for 2 s, 12 s, 22 s, 42 s, 102 s, 322 s, 564 s 1044 s (17.4 min) (grey graphs) and at the PSS$_{455}$ nm consisting only of 15 according to the HPLC analysis (cyan graph).

**Supplementary Figure 13.** UV/vis absorption of 15 in MeCN ($c_{\text{start}}(15) = 1.1 \times 10^{-4}$ mol L$^{-1}$) before irradiation (cyan graph) and after one full irradiation cycle (dashed cyan graph).
Supplementary Figure 14. UV/vis absorption trace (at 350 nm) of the HPLC chromatogram obtained from the spectroscopy MeCN solutions of Supplementary Figure 11 & 12. Before irradiation (top), at the PSS$_{305}$ nm and after one irradiation cycle (PSS$_{455}$ nm bottom). The composition at the PSS$_{305}$ nm in MeCN is $15/18$ 20:80 based on the integration of the HPLC 350nm-UV/vis trace (middle graph).
1.7.2 Photoswitch-Cycling monitored by HPLC (in MeCN)

Supplementary Figure 15. UV/vis absorption trace of the HPLC chromatogram obtained from the cycling experiments conducted with 15 in MeCN. Top chromatogram before irradiation, second chromatogram after irradiation with a 305 nm LED, third chromatogram after irradiation with 455 nm continuing till the last chromatogram presenting the end of the fourth cycle. The sum of absorption (300–650 nm) at the UV/vis absorption diode detector was used as analytical probe (ordinate).
Supplementary Figure 16. UV/vis absorption at 390 nm of the spectroscopy (MeCN) solutions of the photo-cycling experiments of 15/18.
1.7.3 Thermal Stability Test

Testing the thermal stability at the reached PSS leads to the classification of a “type p” photoswitch that undergoes photochemical backreaction exclusively (no thermal backreaction observed, Supplementary Figure 17 & 18).

**Supplementary Figure 17.** UV/vis absorption of 15/18 at the PSS$_{305}$ nm in MeCN ($c_{\text{start}}(15) = 2.1 \times 10^{-4}$ mol L$^{-1}$) upon heating the solution to 55 °C for 555 min.
Supplementary Figure 18. UV/vis absorption trace of the HPLC chromatogram obtained from the thermal stability tests (Supplementary Figure 17) conducted with a solution of 15/18 in MeCN at the PSS$_{305}$ nm. Top before heating, bottom after heating for 555 min at 55 °C. The sum of absorption (300–650 nm) at the UV/vis absorption diode detector was used as analytical probe (ordinate) to detect any sort of new forming byproduct.
1.7.4 UV/vis absorption spectroscopy and irradiation of purified (isolated) 18

The irradiation control experiments of HPLC-purified 18 exclude (photo-)side reactions from other species in the PSS, such as 15 (Supplementary Figure 19–20). The formed trace impurity was found to arise with 455 nm irradiation of prior isolated 18 at $t_n = 3.02$ min, see Supplementary Figure 21, bottom chromatogram).

Supplementary Figure 19. UV/vis absorption of isolated 18 ($c(18) = 8.6 \times 10^{-5}$ mol L$^{-1}$) in MeCN.

Supplementary Figure 20. UV/vis absorption of 18 in MeCN ($c_{\text{start}}(18) = 8.6 \times 10^{-5}$ mol L$^{-1}$) upon irradiation with a 455 nm LED.
**Supplementary Figure 21.** UV/vis absorption trace of the HPLC chromatogram obtained from the irradiation of 18 shown in Supplementary Figure 20. Top HPLC chromatogram of isolated 18, bottom spectroscopy solution after irradiation with a 455 nm LED. The sum of absorption (300–650 nm) at the UV/vis absorption diode detector was used as analytical probe (ordinate) to detect any sort of new forming byproduct.
1.7.5 Long-time irradiation / Fatigue Experiment

We intentionally promoted the fatigue-causing side reaction by constant irradiation of a solution of 15 and 18 (at the PSS) with 340 nm for 30 min (Supplementary Figure 22). Analytical HPLC revealed the formation two trace side products (at 1.30 min and 2.06 min) as well as one minor side product (3.02 min, molecular structure not determined), thus rationally explaining the observed fatigue resistance.

Supplementary Figure 22. UV/vis absorption trace of the HPLC chromatogram obtained from pure 15, after the irradiation with a 305 LED (PSS305 15/18) (middle) and after irradiating the spectroscopy solution represented in the middle for 30 min with a 340 nm LED to investigate the possible degradation products. The sum of absorption (300–650 nm) at the UV/vis absorption diode detector was used as analytical probe (ordinate) to detect any sort of new forming byproduct.
1.8 Computational Analysis

All calculations were conducted with Gaussian 16 Revision A.03\textsuperscript{16} on the chccs-cluster of the Department of Chemistry of Humboldt University of Berlin starting from pre-optimized MM2 force field models. The structures are confirmed ground-state minima according to the analysis of their analytical frequencies computed at the same level, which show no imaginary frequencies.

\textbf{Supplementary Figure 23.} Overlap of the geometry-optimized structures of elassovalene 3 (in cyan), Me-15 (in green), and Me-18 (in pink) at the B3LYP-D3/def2TZVP level of theory.
Supplementary Figure 24. Overview of selected C—C distances and C—C—C bond angles of geometry-optimized structures of elassovalene 3 (in cyan), Me-15 (in green), and Me-18 (in pink) at the B3LYP-D3/def2TZVP level of theory.
1.8.1 NICS Scans\textsuperscript{17–21}

NICS values were calculated using GIAO methods at the B3LYP/6-311G(d,p) level of theory on previously geometry-optimized MM2 force field structures followed by a DFT geometry optimization at the B3LYP-D3/def2TZVP level of theory. Performing NICS scans on a system as 15 and 18 bears several challenges. The ring-system is not planar and in the case of 18 not symmetric. Therefore we decided to calculate the NICS\textsubscript{ZZ} metric surfaces at various heights above the ring planes additionally to the widely known NICS-XY scans\textsuperscript{20}. According to a detailed analysis by Gershoni-Poranne and Stanger, this is the recommended approach for non-planar molecules, in which it is not feasible to separate the $\pi$ and $\sigma$ contributions to the NICS value\textsuperscript{21}. A calculated reference of benzene is given at the beginning of this section.

Supplementary Figure 25. Schematic representation of the becquerel surface (10 Å x 10 Å grid with 0.5 Å distance intervals between the probes) placed under the homoaromatic ring-system centroid of Me-18. The distance $d$ is selected as either 1.8 Å, 2.0 Å, or 2.2 Å to minimize the influence of the $\sigma$–bond-electrons on the NICS value as recommended by Gershoni-Poranne and Stanger\textsuperscript{21}.

Supplementary Figure 26. NICS\textsubscript{ZZ}-XY heat maps of benzene showing the plane below the molecule at the distances –2.2 Å, –2.0 Å, or –1.8 Å. Note the slightly different scale of this NICS-2D map at 1.8 Å (from –20.30 to 2.000 ppm) compared to the other NICS-2D plots (from –20.00 to 2.000 ppm).
**Supplementary Figure 27.** NICS\_ZZ-XY heat maps of cycloheptatriene (top row) and norcaradiene (bottom row) at the plane below the molecule with the distances \(-2.2\ \text{Å}, -2.0\ \text{Å},\) or \(-1.8\ \text{Å}.

**Supplementary Figure 28.** NICS\_ZZ-XY heat maps of elassovalene showing the plane below the molecule at the distances \(-2.2\ \text{Å}, -2.0\ \text{Å},\) or \(-1.8\ \text{Å}.

**Supplementary Table 4.** Calculated NICS\textsubscript{zz} values of the central becquerel, extracted from the GIAO calculations

| Molecule                     | NICS\textsubscript{zz} (ppm) | Distance (Å) |
|------------------------------|-----------------------------|--------------|
| Cycloheptatriene             | –10.7                       | –1.8         |
|                              | –9.5                        | –2.0         |
|                              | –8.3                        | –2.2         |
|                              | –9.3                        | –1.8         |
| Norcaradiene                 | –8.5                        | –2.0         |
|                              | –7.6                        | –2.2         |
| Elassovalene (7 membered ring)| –15.6                       | –1.8         |
|                              | –14.0                       | –2.0         |
|                              | –12.5                       | –2.2         |
| Elassovalene (below bridge)  | –12.5                       | –1.8         |
|                              | –11.6                       | –2.0         |
|                              | –10.7                       | –2.2         |
| Benzene                      | –20.2                       | –1.8         |
|                              | –17.4                       | –2.0         |
|                              | –14.9                       | –2.2         |
Supplementary Figure 29. NICS$_{zz}$-XY heat maps of compound Me-18 showing the plane below the molecule at the distances –2.2 Å, –2.0 Å, or –1.8 Å. Without (Top) and with an overlayed DFT-optimized model of Me-18 (bottom).

Supplementary Figure 30. NICS$_{zz}$-XY heat maps of compound Me-15 showing the plane below the molecule at the distances –2.2 Å, –2.0 Å, or –1.8 Å. Without (Top) and with an overlayed computer model of Me-15 (bottom).
1.8.2 ACID Plots

ACID plots\textsuperscript{22,23} were generated for cycloheptatriene, 15 and 18, which were previously geometry-optimized using an MM2 force field followed by a DFT geometry optimization at the B3LYP-D3/def2TZVP level of theory. We calculated the ACID plots at the HF/6-311G(d,p) and the B3LYP-D3/def2TZVP level of theory, as was earlier compared by Herges and co-workers in their initial report\textsuperscript{22,23}. We prioritize the hybrid functional B3LYP method with Grimme’s D3 dispersion for our conclusion although both methods give the same qualitative results. The critical isosurface value (CIV) (the lowest ACID value in space between two interacting units) is defined as a measure of the strength of a conjugation\textsuperscript{22,23}. The values for cycloheptatriene are shown for comparison, as its homoaromatic character has been discussed previously\textsuperscript{24}.

**ACID Plots of Cycloheptatriene**

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ACID_plots}
\caption{ACID plots of cycloheptatriene at iso-surface(is)-values of 0.1, 0.028, 0.027, 0.026 showing that the topology of the ACID boundary surface changes at an is-value of 0.027(CIV). The calculations gave the same CIV using either HF/6-311G(d,p) and B3LYP-D3/def2TZVP.}
\end{figure}
ACID Plots of Norcaradiene

Supplementary Figure 32. (a) top-view on ACID plots of norcaradiene at is-values of 0.059, 0.058, 0.057, 0.056 and 0.055 showing the changes of topology of the ACID boundary surface at an is-value of 0.057 (encircled in red), level of theory: B3LYP-D3/def2TZVP; (b) bottom-view on ACID plots of norcaradiene as in panel a; (c) ACID plot of norcaradiene with the vector field on the 0.04 is-value (the alignment of the external magnetic field as green arrow at the right). The clockwise alignment —accounting for a diatropic ring current— is significantly disturbed.
ACID Plots of Elassovalene

Supplementary Figure 33. (a) ACID plots of elassovalene at is-values of 0.032 and 0.031 showing the changes of topology of the ACID boundary surface at an is-value of 0.031 (encircled in red), but a second change does not even occur at an is-value of 0.01, calculated at the B3LYP-D3/def2TZVP level of theory; (b) ACID plot of elassovalene with the vector field (the alignment of the external magnetic field as green arrow at the right).
**ACID Plots of 15**

For the ACID plots at the HF/6-311G(d,p) the topology of the ACID boundary surface changes first between the central bridged C-atoms C(4) and C(9) (encircled in red, see above) with a CIV of 0.033. In comparison, using B3LYP-D3/def2TZVP the topology of the ACID boundary surface changes first between the upper bridged C-atoms C(2) and C(11) (encircled in red, see below) with a CIV of 0.034.

**Supplementary Figure 34.** ACID plots of 15 at is-values of 0.034, 0.033 and 0.027 showing that the topology of the ACID boundary surface changes at an is-value (= CIV) of 0.033 (encircled in red) and a second occurs at an is-value of 0.027 (encircled in green), calculated at the HF/6-311G(d,p) level of theory.

**Supplementary Figure 35.** ACID plots of 15 at is-values of 0.035, 0.034, 0.033, 0.027 and 0.026 showing that the topology of the ACID boundary surface changes at an is-value of 0.034 (encircled in red) and a second change occurs at an is-value of 0.026 (encircled in green), calculated at the B3LYP-D3/def2TZVP level of theory.
**ACID Plots of 18**

For the ACID plots at the HF/6-311G(d,p) the topology of the ACID boundary surface changes first between the upper bridged C-atoms C(1) and C(10) (encircled in red, see above) with a CIV of 0.033. In comparison using B3LYP-D3/def2TZVP the topology of the ACID boundary surface changes between the upper bridged C-atoms C(1) and C(10) as well (encircled in red, see below), but with a higher CIV of 0.041.

**Supplementary Figure 36.** ACID plots of 18 at is-values of 0.034, 0.033 and 0.01 showing that the topology of the ACID boundary surface changes at an is-value of 0.033 (encircled in red), but a second change does not even occur at an is-value of 0.01 (circled in green), calculated at the HF/6-311G(d,p) level of theory

**Supplementary Figure 37.** ACID plots of 18 at is-values of 0.041, 0.040, 0.039 and 0.01 showing that the topology of the ACID boundary surface changes at an is-value of 0.040 (encircled in red), but a second topology change (at the central C(4) and C(9)) does not occur even at an is-value of 0.01 (the absence is circled in green), calculated at the B3LYP-D3/def2TZVP level of theory.
1.8.3 Calculated $^1$H NMR chemical shifts of 15, 18, Me-15, Me18, norcaradiene, cycloheptatriene, elassovalene and benzene

$^1$H-NMR chemical shifts were calculated using GIAO methods at the B3LYP/6-311G(d,p) level of theory on optimized geometries obtained at the DFT:B3LYP-D3/def2TZVP level of theory. A reference of TMS was used for calibration purposes. The results are summarized in the following table. In agreement with the experimental values, the hydrogen atoms above the ring currents in 15 and 18 show significant up-field shifts, while in contrast the hydrogen atoms H(20) in elassovalene shows only a moderate up-field shift.

**Supplementary Table 5.** Calculated isotropic magnetic shielding vectors of selected compounds at the DFT:B3LYP/6-311G(d,p) (GIAO) level of theory.

| Compound        | Isotropic magnetic shielding vector (ppm) | Isotropic magnetic shielding vector (ppm), relative to TMS | Experimental chem. shifts (ppm) |
|-----------------|------------------------------------------|----------------------------------------------------------|-------------------------------|
| TMS             | Average: 32.07257                         | 0                                                        | 0                             |
| Compound 15     | H19 24.9336                               | H19 7.13897                                              |                               |
|                 | H20 24.7207                               | H20 7.35187                                              |                               |
|                 | H21 24.8360                               | H21 7.23657                                              |                               |
|                 | H22 25.0872                               | H22 6.98537                                              |                               |
|                 | H23 25.1480                               | H23 6.92457                                              |                               |
|                 | H24 25.2668                               | H24 6.80577                                              |                               |
|                 | H25 27.0042                               | H25 5.06837                                              |                               |
|                 | H26 27.0680                               | H26 5.00457                                              |                               |
|                 | H27 28.5223                               | H27 3.55027                                              |                               |
|                 | H28 28.6249                               | H28 3.44767                                              |                               |
|                 | H29 29.0227                               | H29 3.04987                                              |                               |
|                 | H30 28.4697                               | H30 3.60287                                              |                               |
| Compound-Me-15  | H16 24.7137                               | H16 7.35887                                              | N/A                           |
|                 | H17 24.7142                               | H17 7.35837                                              |                               |
|                 | H18 24.9980                               | H18 7.07457                                              |                               |
|                 | H19 24.9987                               | H19 7.07387                                              |                               |
|                 | H20 25.2481                               | H20 6.82447                                              |                               |
|                 | H21 25.2463                               | H21 6.82627                                              |                               |
| Compound 18 |  | Compound-Me-18 |
|------------|----------------|----------------|
| H22 | 27.1827 | H22 | 4.88987 |
| H23 | 27.1823 | H23 | 4.89027 |
| H24 | 28.3686 | H24 | 3.70397 |
| H25 | 32.7787 | H25 | -0.70613 |
| H26 | 32.5125 | H26 | -0.43993 |
| H27 | 32.5076 | H27 | -0.43503 |
| H19 | 25.5282 | H19 | 6.54437 |
| H20 | 25.8499 | H20 | 6.22267 |
| H21 | 24.3894 | H21 | 7.68317 |
| H22 | 24.9935 | H22 | 7.07907 |
| H23 | 25.7629 | H23 | 6.30967 |
| H24 | 28.6321 | H24 | 3.44047 |
| H25 | 28.4925 | H25 | 3.58007 |
| H26 | 25.6646 | H26 | 6.40797 |
| H27 | 26.6699 | H27 | 5.40267 |
| H28 | 28.4591 | H28 | 3.61347 |
| H29 | 28.8230 | H29 | 3.24957 |
| H30 | 28.4618 | H30 | 3.61077 |

| Norcaradiene |  | Cycloheptatriene |
|--------------|----------------|-----------------|
| H8 | 30.1817 | H8 | 1.89087 |
| H9 | 25.6852 | H9 | 6.38737 |
| H10 | 26.0246 | H10 | 6.04797 |
| H11 | 26.0253 | H11 | 6.04727 |
| H12 | 25.6847 | H12 | 6.38787 |
| H13 | 30.1810 | H13 | 1.89157 |
| H14 | 33.0605 | H14 | -0.98793 |
| H15 | 30.5118 | H15 | 1.56077 |

| H8 | 25.1746 | H8 | 6.89797 |
| H9 | 25.1742 | H9 | 6.89837 |
| H10 | 25.5414 | H10 | 6.53117 |
| H11 | 25.5412 | H11 | 6.53137 |
| H12 | 26.7523 | H12 | 5.32027 |
| H13 | 26.7518 | H13 | 5.32077 |
| H14 | 30.4726 | H14 | 1.59997 |
| H15 | 29.1132 | H15 | 2.95937 |

Source: SDBS database
https://sdbs.db.aist.go.jp/
(SDBS No. 3886HSP-49-492)
### Comparison of chemical shifts of selected hydrogen atoms shows that the level of theory is appropriate for evaluation of the magnetic shielding analysis, such as our NICS calculations. The deviation is in the range of $\Delta \delta_{\text{calc-obs}}$ ca. –0.3 ppm, depending on solvent effects.

### 1.8.4 TD-DFT Results, Orbital Energy Levels of 15 and 18 and Orbital Plots

Vertical transitions were calculated for 15 and 18 on the geometry obtained from B3LYP-D3/def2-TZVP optimizations for the first 50 transitions at the TD-DFT-D3(BJ)/UCAM-B3LYP/def2-TZVP level of theory using MeCN as SMD solvent model. Die original dataset of the first 10 transitions can be found in the appendix, section S2.3. The obtained transitions were simulated to obtain a spectral trace using the SpecDis software, developed by Bringmann and co-workers.\(^{25}\)
Supplementary Figure 38. Comparison of the UV/Vis spectra of 15 in MeCN at 295 K (cyan solid graph, \(c = 1.1 \times 10^{-4} \text{ M}\)) and the TD-DFT-calculated spectra (black dotted graph, level of theory: TD-DFT-D3(BJ)/UCAM-B3LYP/def2-tzvp/SMD(MeCN). The calculated spectrum is shown with a UV correction of \(-13\) nm, a scaling factor of 0.2648, and a standard deviation (graph width fitting parameter \(\sigma\)) of \(\sigma = 0.24\) eV. The comparison was performed using the SpecDis software, which computed a similarity factor of 99.8\%.\textsuperscript{25}

Supplementary Figure 39. Comparison of the UV/Vis spectra of 18 in MeCN at 295 K (gren solid graph, \(c = 8.6 \times 10^{-5} \text{ M}\)) and the TD-DFT-calculated spectra (black dotted graph, level of theory: TD-DFT-D3(BJ)/UCAM-B3LYP/def2-tzvp/SMD(MeCN). The calculated spectrum is shown with a UV correction of \(-18\) nm, a scaling factor of 0.2111, and a standard deviation (graph width fitting parameter \(\sigma\)) of \(\sigma = 0.29\) eV. The comparison was performed using the SpecDis software, which computed a similarity factor of 96.0\%.\textsuperscript{25}
Supplementary Figure 40. Orbital energy diagram of 15 and 18 at the B3LYP-D3/def2-TZVP level of energy (black values) and the lowest vertical transition calculated at the TD-DFT-D3(BJ)/UCAM-B3LYP/def2-TZVP/SMD(MeCN) level of theory (blue transitions). In 15, this transition is composed of a 69% HOMO→LUMO and a 10% HOMO−1→LUMO+1 combination (energy in nm, \( f \) is the calculated oscillator strengths). In 18, this transition is purely composed of a HOMO→LUMO transition. The orbital depictions are plotted at the 0.02 e Å⁻³ isosurface at the B3LYP/def2-TZVP level of theory.
**Supplementary Figure 41.** HOMO orbital plots for 1–3 and 6 at the 0.03 e Å⁻³ isosurface at the B3LYP/def2-TZVP level of theory. Note that compound 6 of the introduction was later introduced as 15.
1.8.5 Strain Analysis on H-15, H-18, Elasovalene

The strain energy of an organic compound can usually be derived from its heat of formation of the elements. The difference in the heat of formation of the strained isomer vs the unstrained isomer can then be regarded as the strain energy. As this method is not feasible for the investigated molecules due to limited synthetic access to strain free version of 15, 18, elasovalene. We therefore decided to choose a recently developed program to investigate the strain energies theoretically. As the absolute values cannot be compared to experimental results the consistent method used allows internal comparison.\textsuperscript{26} StrainViz\textsuperscript{27} is based on the analysis of DFT calculations performed with Gaussian. While it has not been benchmarked for tricyclic molecular scaffolds and especially not for homoaromatic compounds, where disruption of the diatropic ring currents is necessary throughout the analysis, the obtained results visualize and support our findings. We adopt the nomenclature for strain energy terms as in the cited work of Jasti and co-workers.\textsuperscript{27} This strain energy differs from the strain energy as defined by A. von Baeyer.\textsuperscript{28} All calculations were performed on the geometry optimized structures of elasovalene, and on the H-subsituted parent scaffolds of 15 (H-15) and 18 (H-18) that were obtained at the DFT:B3LYP/def2TZVP level of theory. The absolute energies obtained depend on the selected fragments used in the calculations and are therefore given as well in the Appendix. All StrainViz calculations were performed at B3LYP/6-311G(d).

Supplementary Figure 42. The calculated total strain energy, bond strain energy, dihedral strain energy, and angle strain energy of H-15.
Supplementary Figure 43. The calculated total strain energy, bond strain energy, dihedral strain energy, and angle strain energy of H-18.

Supplementary Figure 44. The calculated total strain energy, bond strain energy, dihedral strain energy, and angle strain energy of elassovalene (3).

The total strain energies are in a similar range from 28.35 kcal mol\(^{-1}\) to 31.21 kcal mol\(^{-1}\) for elasovalene, H-15 and H-18. It is distributed among several bonds in the molecular scaffold of H-15, H-18. In contrast the strain energy in elasovalene is concentrated at the two (red) bonds bridging the two cyclopentenylene fragments. This difference in strain distribution might cause different reactivity and stability within the studied series of molecules.
Appendix

2.1 Crystallographic Data

2.1.1 (1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalene-1-carboxylic acid (cis-11)

Supplementary Table 6. Crystal data and structure refinement for cis-11.

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| CCDC number                           | 2128305                                    |
| Empirical formula                     | C_{12}H_{12}O_{2}                          |
| Formula weight                        | 188.22                                     |
| Temperature                           | 150.00(10) K                              |
| Wavelength                            | 1.54184 Å                                  |
| Crystal system                        | Triclinic                                  |
| Space group                           | P-1                                       |
| Unit cell dimensions                  |                                          |
| \(a\)                                 | 7.5990(5) Å \(\alpha = 65.320(6)^\circ\)  |
| \(b\)                                 | 8.0638(5) Å \(\beta = 79.717(5)^\circ\)   |
| \(c\)                                 | 8.5252(5) Å \(\gamma = 84.980(6)^\circ\)  |
| Volume                                | 467.01(5) Å³                              |
| \(Z\)                                 | 2                                         |
| Density (calculated)                  | 1.338 Mg/m³                                |
| Absorption coefficient                | 0.726 mm⁻¹                                 |
| \(F(000)\)                            | 200                                       |
| Crystal size                          | 0.37 x 0.22 x 0.17 mm³                     |
| Theta range for data collection       | 5.78 to 67.45°                             |
| Index ranges                          | \(-8 \leq h \leq 9, -9 \leq k \leq 9, -6 \leq l \leq 10\) |
| Reflections collected                 | 2725                                       |
| Independent reflections               | 1677 \([R(\text{int}) = 0.0118]\)         |
| Completeness to \(\theta = 67.45^\circ\) | 99.4%                                     |
| Absorption correction                 | Semi-empirical from equivalents           |
Max. and min. transmission 0.8853 and 0.7755
Refinement method Full-matrix least-squares on $F^2$
Data / restraints / parameters 1677 / 0 / 131
Goodness-of-fit on $F^2$ 1.028
Final $R$ indices [$I>2\sigma(I)$] $R1 = 0.0346$, $wR2 = 0.0888$
$R$ indices (all data) $R1 = 0.0366$, $wR2 = 0.0903$
Largest diff. peak and hole 0.195 and $-0.195$ e $^{-}$ Å$^{-3}$

**Supplementary Table 7.** Bond lengths [Å] and angles [$^\circ$] for cis-11.

| Bond | Length [Å] |
|------|------------|
| O(1)-C(12) | 1.2265(15) |
| O(2)-C(12) | 1.3250(14) |
| C(1)-C(12) | 1.4667(16) |
| C(1)-C(3) | 1.5337(15) |
| C(1)-C(2) | 1.5347(16) |
| C(2)-C(3) | 1.4917(16) |
| C(2)-C(7) | 1.5213(17) |
| C(3)-C(4) | 1.5200(16) |
| C(4)-C(5) | 1.5149(16) |
| C(5)-C(8) | 1.3888(17) |
| C(5)-C(6) | 1.3997(16) |
| C(6)-C(11) | 1.3904(17) |
| C(6)-C(7) | 1.5123(16) |
| C(8)-C(9) | 1.3906(18) |
| C(9)-C(10) | 1.3832(19) |
| C(10)-C(11) | 1.3887(18) |
| C(12)-C(1)-C(3) | 123.27(10) |
| C(12)-C(1)-C(2) | 123.40(10) |
| C(3)-C(1)-C(2) | 58.18(7) |
| C(3)-C(2)-C(7) | 115.47(10) |
| C(3)-C(2)-C(1) | 60.88(7) |
| C(7)-C(2)-C(1) | 124.44(10) |
| C(2)-C(3)-C(4) | 115.22(10) |
| C(2)-C(3)-C(1) | 60.95(7) |
| C(4)-C(3)-C(1) | 124.12(10) |
| C(5)-C(4)-C(3) | 109.07(9) |
| C(8)-C(5)-C(6) | 119.67(11) |
| C(8)-C(5)-C(4) | 122.97(10) |
C(6)-C(5)-C(4)   117.32(10)
C(11)-C(6)-C(5)  119.40(11)
C(11)-C(6)-C(7)  123.05(11)
C(5)-C(6)-C(7)   117.51(10)
C(6)-C(7)-C(2)   108.94(9)
C(5)-C(8)-C(9)   120.55(11)
C(10)-C(9)-C(8)  119.76(11)
C(9)-C(10)-C(11) 120.08(11)
C(10)-C(11)-C(6) 120.54(11)
O(1)-C(12)-O(2)  122.14(11)
O(1)-C(12)-C(1)  125.45(11)
O(2)-C(12)-C(1)  112.41(10)

Symmetry transformations used to generate equivalent atoms:
2.1.2 tert-Butyl 3-oxo-3-((1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-1-yl)propanoate (12b)

![Chemical structure diagram]

**Supplementary Table 8.** Crystal data and structure refinement for 12b.

| Description                                      | Value                      |
|--------------------------------------------------|----------------------------|
| CCDC number                                      | 2128302                    |
| Empirical formula                                | C18 H22 O3                 |
| Formula weight                                   | 286.36                     |
| Temperature                                      | 150.01(10) K               |
| Wavelength                                       | 1.54184 Å                  |
| Crystal system                                   | Monoclinic                 |
| Space group                                      | P2_1/c                     |
| Unit cell dimensions                             | a = 5.73381(13) Å         |
|                                                  | b = 10.6147(2) Å          |
|                                                  | c = 24.6993(5) Å          |
| Volume                                           | 1503.02(5) Å^3            |
| Z                                                | 4                          |
| Density (calculated)                             | 1.265 Mg/m^3               |
| Absorption coefficient                           | 0.677 mm^-1                |
| F(000)                                           | 616                        |
| Crystal size                                     | 0.38 x 0.21 x 0.20 mm^3    |
| Theta range for data collection                  | 3.58 to 67.47°             |
| Index ranges                                     | -6 ≤ h ≤ 6, -12 ≤ k ≤ 12, -23 ≤ l ≤ 29 |
| Reflections collected                            | 5408                       |
| Independent reflections                          | 2705 [R(int) = 0.0144]     |
| Completeness to \( \theta = 67.47^{\circ} \)    | 99.9 %                     |
| Absorption correction                            | Semi-empirical from equivalents |
| Max. and min. transmission                       | 0.8787 and 0.7810          |
| Refinement method                                | Full-matrix least-squares on \( F^2 \) |
| Data / restraints / parameters                    | 2705 / 0 / 193             |
|                                                   | 61                         |
Goodness-of-fit on $F^2$ 1.057

Final $R$ indices [$>2\sigma(I)$] $R1 = 0.0343$, $wR2 = 0.0866$

$R$ indices (all data) $R1 = 0.0378$, $wR2 = 0.0900$

Largest diff. peak and hole 0.174 and $-0.263 \text{ e}^{-}\AA^{-3}$

**Supplementary Table 9.** Bond lengths [Å] and angles [°] for 12b.

| Bond (Å)        | Value       |
|-----------------|-------------|
| O(1)-C(1)       | 1.3349(14)  |
| O(1)-C(15)      | 1.4878(13)  |
| O(2)-C(1)       | 1.2060(14)  |
| O(3)-C(3)       | 1.2131(14)  |
| C(1)-C(2)       | 1.5100(16)  |
| C(2)-C(3)       | 1.5181(16)  |
| C(3)-C(4)       | 1.4748(16)  |
| C(4)-C(5)       | 1.5296(17)  |
| C(4)-C(6)       | 1.5307(16)  |
| C(5)-C(6)       | 1.4910(17)  |
| C(5)-C(10)      | 1.5084(18)  |
| C(6)-C(7)       | 1.5122(17)  |
| C(7)-C(8)       | 1.5098(17)  |
| C(8)-C(9)       | 1.3959(16)  |
| C(8)-C(11)      | 1.3980(17)  |
| C(9)-C(14)      | 1.3957(17)  |
| C(9)-C(10)      | 1.5123(17)  |
| C(11)-C(12)     | 1.3813(18)  |
| C(12)-C(13)     | 1.3895(19)  |
| C(13)-C(14)     | 1.3841(19)  |
| C(15)-C(16)     | 1.5138(18)  |
| C(15)-C(18)     | 1.5185(17)  |
| C(15)-C(17)     | 1.5191(17)  |
| C(1)-O(1)-C(15) | 121.51(9)   |
| O(2)-C(1)-O(1)  | 125.79(11)  |
| O(2)-C(1)-C(2)  | 123.17(11)  |
| O(1)-C(1)-C(2)  | 111.03(9)   |
| C(1)-C(2)-C(3)  | 112.77(10)  |
| O(3)-C(3)-C(4)  | 124.65(11)  |
| O(3)-C(3)-C(2)  | 121.68(10)  |
| C(4)-C(3)-C(2)  | 113.66(10)  |
C(3)-C(4)-C(5)  122.80(10)
C(3)-C(4)-C(6)  120.80(10)
C(5)-C(4)-C(6)  58.32(8)
C(6)-C(5)-C(10)  120.38(10)
C(6)-C(5)-C(4)  60.88(8)
C(10)-C(5)-C(4)  122.40(10)
C(5)-C(6)-C(7)  120.80(11)
C(5)-C(6)-C(4)  60.81(8)
C(7)-C(6)-C(4)  122.22(10)
C(8)-C(7)-C(6)  115.94(10)
C(9)-C(8)-C(11)  118.64(11)
C(9)-C(8)-C(7)  122.60(11)
C(11)-C(8)-C(7)  118.72(10)
C(14)-C(9)-C(8)  119.12(11)
C(14)-C(9)-C(10)  118.21(10)
C(8)-C(9)-C(10)  122.67(11)
C(5)-C(10)-C(9)  116.46(10)
C(12)-C(11)-C(8)  121.79(11)
C(11)-C(12)-C(13)  119.46(12)
C(14)-C(13)-C(12)  119.27(12)
C(13)-C(14)-C(9)  121.63(11)
O(1)-C(15)-C(16)  110.49(10)
O(1)-C(15)-C(18)  101.95(9)
C(16)-C(15)-C(18)  111.15(11)
O(1)-C(15)-C(17)  109.22(9)
C(16)-C(15)-C(17)  112.62(11)
C(18)-C(15)-C(17)  110.89(11)

Symmetry transformations used to generate equivalent atoms:
2.1.3 *tert*-Butyl 2-diazo-3-oxo-3-((1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[b]naphthalen-1-yl)propanoate (13b)

Supplementary Table 10. Crystal data and structure refinement for 13b.

| Parameter                              | Value                              |
|----------------------------------------|------------------------------------|
| CCDC number                            | 2128309                            |
| Empirical formula                      | C18 H20 N2 O3                      |
| Formula weight                         | 312.36                             |
| Temperature                            | 150.01(10) K                       |
| Wavelength                             | 1.54184 Å                          |
| Crystal system                         | Orthorhombic                       |
| Space group                            | Pnma                               |
| Unit cell dimensions                   | a = 15.0492 (4) Å                  |
|                                       | b = 9.0381 (2) Å                   |
|                                       | c = 11.6981 (3) Å                  |
| Volume                                 | 1591.13 (7) Å^3                    |
| Z                                      | 4                                  |
| Density (calculated)                   | 1.304 Mg m\(^{-3}\)               |
| Absorption coefficient                 | 0.73 mm\(^{-1}\)                   |
| \(F(000)\)                             | 664                                |
| Crystal size                           | 0.55 × 0.44 × 0.33 mm\(^3\)        |
| Theta range for data collection        | 5.9 to 72.5°                       |
| Reflections collected                  | 2657                               |
| \(R(F^2 > 2\sigma(F^2)) = 0.035\)     |                                    |
| H-atom parameters constrained          |                                    |
| Largest diff. peak and hole            | −0.21 and −0.16 e\(^-\) Å\(^{-3}\) |
**Supplementary Table 11.** Bond lengths [Å] and angles [°] for 13b.

| Bond                                    | Length/Angle (Å/°) |
|-----------------------------------------|--------------------|
| O(1)-C(8)                               | 1.209 (2)          |
| O(2)-C(8)                               | 1.340 (2)          |
| O(2)-C(7)                               | 1.496 (2)          |
| O(3)-C(11)                              | 1.233 (2)          |
| N(1)-N(2)                               | 1.116 (2)          |
| N(1)-C(5)                               | 1.340 (2)          |
| C(5)-C(8)                               | 1.468 (2)          |
| C(5)-C(11)                              | 1.475 (2)          |
| C(6)-C(12)                              | 1.3916 (17)        |
| C(6)-C(6i)                              | 1.394 (2)          |
| C(6)-C(9)                               | 1.5093 (17)        |
| C(7)-C(16)                              | 1.5107 (17)        |
| C(7)-C(16i)                             | 1.5107 (17)        |
| C(7)-C(17)                              | 1.520 (3)          |
| C(9)-C(10)                              | 1.5175 (18)        |
| C(10)-C(10i)                            | 1.490 (2)          |
| C(10)-C(13)                             | 1.5424 (18)        |
| C(11)-C(13)                             | 1.469 (3)          |
| C(12)-C(15)                             | 1.3830 (19)        |
| C(15)-C(15i)                            | 1.380 (3)          |
| C(8)-O(2)-C(7)                          | 122.01 (13)        |
| N(2)-N(1)-C(5)                          | 176.02 (17)        |
| N(1)-C(5)-C(8)                          | 116.02 (15)        |
| N(1)-C(5)-C(11)                         | 111.48 (15)        |
| C(8)-C(5)-C(11)                         | 132.50 (16)        |
| C(12)-C(6)-C(6i)                        | 119.36 (7)         |
| C(12)-C(6)-C(9)                         | 120.21 (11)        |
| C(6i)-C(6)-C(9)                         | 120.42 (7)         |
| O(2)-C(7)-C(16)                         | 109.70 (9)         |
| O(2)-C(7)-C(17)                         | 109.70 (9)         |
| Bond                  | Angle (°)      |
|----------------------|---------------|
| C(16)-C7-C(17)       | 112.44 (15)   |
| O2-C7-C(17)          | 101.84 (14)   |
| C(16)-C7-C(17)       | 111.32 (10)   |
| C(17)-C7-C(17)       | 111.32 (10)   |
| O(1)-C(8)-O(2)       | 126.53 (16)   |
| O(1)-C(8)-C(5)       | 124.10 (16)   |
| O(2)-C(8)-C(5)       | 109.38 (14)   |
| C(6)-C(9)-C(10)      | 112.62 (10)   |
| C(10i)-C(10)-C(9)    | 118.18 (7)    |
| C(10i)-C(10)-C(13)   | 61.12 (5)     |
| C(9)-C(10)-C(13)     | 122.96 (12)   |
| O(3)-C(11)-C(13)     | 123.51 (16)   |
| O(3)-C(11)-C(5)      | 118.48 (16)   |
| C(13)-C(11)-C(5)     | 118.01 (15)   |
| C(15)-C(12)-C(6)     | 120.74 (13)   |
| C(11)-C(13)-C(10)    | 120.99 (13)   |
| C(11)-C(13)-C(10i)   | 120.99 (13)   |
| C(10)-C(13)-C(10i)   | 57.77 (11)    |
| C(15i)-C(15)-C(12)   | 119.90 (8)    |

Symmetry code: (i) x, −y+1/2, z.
### 2.1.4 Triasterane 14a

![Triasterane 14a structure](image)

**Supplementary Table 12.** Crystal data and structure refinement for 14a.

| Property                                | Value                                      |
|-----------------------------------------|--------------------------------------------|
| CCDC number                             | 2128304                                    |
| Empirical formula                       | C15 H14 O3                                 |
| Formula weight                          | 242.26                                     |
| Temperature                             | 150.01(10) K                              |
| Wavelength                              | 1.54184 Å                                 |
| Crystal system                          | Triclinic                                  |
| Space group                             | P-1                                        |
| Unit cell dimensions                    | a = 11.5389(4) Å, \( \alpha = 82.438(3)^\circ \)  |
|                                        | b = 14.7506(4) Å, \( \beta = 69.164(3)^\circ \)  |
|                                        | c = 15.0755(5) Å, \( \gamma = 84.945(3)^\circ \)  |
| Volume                                  | 2374.90(14) Å\(^3\)                      |
| Z                                       | 8                                          |
| Density (calculated)                    | 1.355 Mg/m\(^3\)                          |
| Absorption coefficient                  | 0.765 mm\(^{-1}\)                         |
| \( F(000) \)                            | 1024                                       |
| Crystal size                            | 0.38 x 0.27 x 0.09 mm\(^3\)               |
| Theta range for data collection         | 3.03 to 67.49°                            |
| Index ranges                            | \(-11 \leq h \leq 13, -14 \leq k \leq 17, -18 \leq l \leq 18\) |
| Reflections collected                   | 16013                                      |
| Independent reflections                 | 8552 [\( R(int) = 0.0179 \) ]             |
| Completeness to \( \theta = 67.49^\circ \)| 99.9 %                                    |
| Absorption correction                   | Semi-empirical from equivalents            |
| Max. and min. transmission              | 0.9330 and 0.7599                          |

![Triasterane 14a structure](image)
Refinement method
Full-matrix least-squares on $F^2$

Data / restraints / parameters
8552 / 0 / 652

Goodness-of-fit on $F^2$
1.041

Final $R$ indices [$I>2\sigma(I)$]
$R_1 = 0.0393$, $wR_2 = 0.1103$

$R$ indices (all data)
$R_1 = 0.0441$, $wR_2 = 0.1151$

Largest diff. peak and hole
0.326 and $-0.326$ e$^{-}$ Å$^{-3}$

**Supplementary Table 13.** Bond lengths [Å] and angles [°] for 14a.

| Bond          | Distance     |
|---------------|--------------|
| O(1)-C(4)     | 1.2249(17)   |
| O(2)-C(14)    | 1.3329(15)   |
| O(2)-C(15)    | 1.4424(16)   |
| O(3)-C(14)    | 1.1994(16)   |
| O(4)-C(19)    | 1.2252(15)   |
| O(5)-C(29)    | 1.3415(15)   |
| O(5)-C(30)    | 1.4442(15)   |
| O(6)-C(29)    | 1.1961(15)   |
| O(7)-C(34)    | 1.2211(18)   |
| O(8)-C(44)    | 1.3286(15)   |
| O(8)-C(45)    | 1.4419(16)   |
| O(9)-C(44)    | 1.1953(16)   |
| O(10)-C(49)   | 1.2241(15)   |
| O(11)-C(59)   | 1.3404(15)   |
| O(11)-C(60)   | 1.4450(15)   |
| O(12)-C(59)   | 1.1988(15)   |
| C(1)-C(4)     | 1.4605(19)   |
| C(1)-C(2)     | 1.529(2)     |
| C(1)-C(3)     | 1.5331(19)   |
| C(2)-C(3)     | 1.4756(19)   |
| C(2)-C(5)     | 1.5071(19)   |
| C(3)-C(6)     | 1.5052(18)   |
| C(4)-C(7)     | 1.4845(17)   |
| C(5)-C(8)     | 1.5109(18)   |
| C(6)-C(9)     | 1.5176(17)   |
| C(7)-C(14)    | 1.5023(16)   |
| C(7)-C(8)     | 1.5426(17)   |
| C(7)-C(9)     | 1.5437(16)   |
| C(8)-C(10)    | 1.4747(17)   |
| C(8)-C(9)     | 1.5254(17)   |

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| Bond          | Distance (Å) |
|--------------|--------------|
| C(9)-C(13)   | 1.4762(17)   |
| C(10)-C(11)  | 1.335(2)     |
| C(11)-C(12)  | 1.441(2)     |
| C(12)-C(13)  | 1.339(2)     |
| C(16)-C(19)  | 1.4642(17)   |
| C(16)-C(18)  | 1.5304(18)   |
| C(16)-C(17)  | 1.5353(17)   |
| C(17)-C(18)  | 1.4869(19)   |
| C(17)-C(20)  | 1.5080(17)   |
| C(18)-C(21)  | 1.5057(18)   |
| C(19)-C(22)  | 1.4847(16)   |
| C(20)-C(23)  | 1.5156(16)   |
| C(21)-C(24)  | 1.5128(16)   |
| C(22)-C(29)  | 1.5016(16)   |
| C(22)-C(24)  | 1.5471(16)   |
| C(22)-C(23)  | 1.5482(16)   |
| C(23)-C(28)  | 1.4817(16)   |
| C(23)-C(24)  | 1.5267(16)   |
| C(24)-C(25)  | 1.4768(17)   |
| C(25)-C(26)  | 1.3398(19)   |
| C(26)-C(27)  | 1.4486(19)   |
| C(27)-C(28)  | 1.3376(19)   |
| C(31)-C(34)  | 1.463(2)     |
| C(31)-C(32)  | 1.522(2)     |
| C(31)-C(33)  | 1.5273(19)   |
| C(32)-C(33)  | 1.483(2)     |
| C(32)-C(35)  | 1.503(2)     |
| C(33)-C(36)  | 1.5038(18)   |
| C(34)-C(37)  | 1.4856(17)   |
| C(35)-C(38)  | 1.5090(18)   |
| C(36)-C(39)  | 1.5161(16)   |
| C(37)-C(44)  | 1.5020(17)   |
| C(37)-C(39)  | 1.5402(16)   |
| C(37)-C(38)  | 1.5447(17)   |
| C(38)-C(40)  | 1.4761(18)   |
| C(38)-C(39)  | 1.5285(17)   |
| C(39)-C(43)  | 1.4743(17)   |
| C(40)-C(41)  | 1.337(2)     |
| C(41)-C(42)  | 1.442(2)     |
C(42)-C(43)  1.335(2)
C(46)-C(49)  1.4632(17)
C(46)-C(47)  1.5299(18)
C(46)-C(48)  1.5358(17)
C(47)-C(48)  1.486(2)
C(47)-C(50)  1.5038(19)
C(48)-C(51)  1.5054(18)
C(49)-C(52)  1.4874(16)
C(50)-C(53)  1.5124(17)
C(51)-C(54)  1.5142(17)
C(52)-C(59)  1.5003(16)
C(52)-C(53)  1.5473(16)
C(52)-C(54)  1.5485(16)
C(53)-C(55)  1.4769(17)
C(53)-C(54)  1.5262(17)
C(54)-C(58)  1.4792(17)
C(55)-C(56)  1.339(2)
C(56)-C(57)  1.447(2)
C(57)-C(58)  1.338(2)

C(14)-O(2)-C(15)  115.75(10)
C(29)-O(5)-C(30)  114.48(10)
C(44)-O(8)-C(45)  115.75(11)
C(59)-O(11)-C(60)  114.74(10)
C(4)-C(1)-C(2)  117.82(11)
C(4)-C(1)-C(3)  116.60(11)
C(2)-C(1)-C(3)  57.61(9)
C(3)-C(2)-C(5)  119.85(12)
C(3)-C(2)-C(1)  61.33(9)
C(5)-C(2)-C(1)  118.49(11)
C(2)-C(3)-C(6)  120.66(11)
C(2)-C(3)-C(1)  61.06(9)
C(6)-C(3)-C(1)  117.09(11)
O(1)-C(4)-C(1)  122.70(12)
O(1)-C(4)-C(7)  120.44(12)
C(1)-C(4)-C(7)  116.85(11)
C(2)-C(5)-C(8)  112.53(11)
C(3)-C(6)-C(9)  112.98(10)
C(4)-C(7)-C(14)  112.76(10)
| Bond | Angle       |
|------|------------|
| C(4)-C(7)-C(8) | 118.30(10) |
| C(14)-C(7)-C(8) | 119.85(10) |
| C(4)-C(7)-C(9)  | 116.30(10) |
| C(14)-C(7)-C(9) | 120.61(10) |
| C(8)-C(7)-C(9)  | 59.24(8)   |
| C(10)-C(8)-C(5) | 116.00(11) |
| C(10)-C(8)-C(9) | 116.26(11) |
| C(5)-C(8)-C(9)  | 119.43(10) |
| C(10)-C(8)-C(7) | 116.39(10) |
| C(5)-C(8)-C(7)  | 116.89(11) |
| C(9)-C(8)-C(7)  | 60.42(8)   |
| C(13)-C(9)-C(6) | 115.47(11) |
| C(13)-C(9)-C(8) | 116.66(11) |
| C(6)-C(9)-C(8)  | 118.58(10) |
| C(13)-C(9)-C(7) | 118.41(10) |
| C(6)-C(9)-C(7)  | 116.31(10) |
| C(8)-C(9)-C(7)  | 60.34(8)   |
| C(11)-C(10)-C(8) | 122.13(14) |
| C(10)-C(11)-C(12) | 121.33(13) |
| C(13)-C(12)-C(11) | 121.78(13) |
| C(12)-C(13)-C(9) | 121.51(14) |
| O(3)-C(14)-O(2) | 123.67(11) |
| O(3)-C(14)-C(7) | 125.51(11) |
| O(2)-C(14)-C(7) | 110.81(10) |
| C(19)-C(16)-C(18) | 117.84(11) |
| C(19)-C(16)-C(17) | 115.75(10) |
| C(18)-C(16)-C(17) | 58.03(8)   |
| C(18)-C(17)-C(20) | 120.22(11) |
| C(18)-C(17)-C(16) | 60.82(8)   |
| C(20)-C(17)-C(16) | 117.07(10) |
| C(17)-C(18)-C(21) | 119.98(11) |
| C(17)-C(18)-C(16) | 61.15(8)   |
| C(21)-C(18)-C(16) | 118.03(10) |
| O(4)-C(19)-C(16) | 122.48(11) |
| O(4)-C(19)-C(22) | 120.23(11) |
| C(16)-C(19)-C(22) | 117.26(10) |
| C(17)-C(20)-C(23) | 113.47(10) |
| C(18)-C(21)-C(24) | 113.21(10) |
| C(19)-C(22)-C(29) | 111.86(10) |
\begin{align*}
C(34) - C(37) - C(39) & \quad 116.86(10) \\
C(44) - C(37) - C(39) & \quad 120.49(10) \\
C(34) - C(37) - C(38) & \quad 116.97(11) \\
C(44) - C(37) - C(38) & \quad 121.14(10) \\
C(39) - C(37) - C(38) & \quad 59.40(8) \\
C(34) - C(37) - C(39) & \quad 120.49(10) \\
C(44) - C(37) - C(39) & \quad 121.14(10) \\
C(39) - C(37) - C(38) & \quad 60.15(8) \\
C(35) - C(38) - C(39) & \quad 116.21(11) \\
C(40) - C(38) - C(39) & \quad 115.50(12) \\
C(35) - C(38) - C(37) & \quad 117.27(10) \\
C(39) - C(38) - C(37) & \quad 117.07(11) \\
C(40) - C(38) - C(37) & \quad 60.44(8) \\
C(44) - C(39) - C(36) & \quad 115.08(11) \\
C(43) - C(39) - C(38) & \quad 116.86(11) \\
C(46) - C(39) - C(38) & \quad 118.93(10) \\
C(43) - C(39) - C(37) & \quad 118.17(10) \\
C(46) - C(39) - C(37) & \quad 116.56(10) \\
C(38) - C(39) - C(37) & \quad 60.44(8) \\
C(42) - C(41) - C(39) & \quad 122.64(14) \\
C(40) - C(41) - C(42) & \quad 121.34(13) \\
C(43) - C(42) - C(41) & \quad 121.26(13) \\
C(42) - C(43) - C(39) & \quad 122.05(14) \\
O(9) - C(44) - O(8) & \quad 123.78(12) \\
O(9) - C(44) - C(37) & \quad 124.74(12) \\
O(8) - C(44) - C(37) & \quad 111.44(10) \\
C(49) - C(46) - C(47) & \quad 117.87(11) \\
C(49) - C(46) - C(48) & \quad 115.84(10) \\
C(47) - C(46) - C(48) & \quad 58.00(9) \\
C(48) - C(47) - C(50) & \quad 119.96(11) \\
C(48) - C(47) - C(46) & \quad 61.20(9) \\
C(48) - C(48) - C(50) & \quad 118.21(11) \\
C(47) - C(48) - C(51) & \quad 120.44(11) \\
C(47) - C(48) - C(46) & \quad 60.80(9) \\
C(51) - C(48) - C(46) & \quad 116.93(10) \\
O(10) - C(49) - C(46) & \quad 122.58(11) \\
O(10) - C(49) - C(52) & \quad 120.16(11) \\
C(46) - C(49) - C(52) & \quad 117.22(10) \\
C(47) - C(50) - C(53) & \quad 113.07(11) \\
C(48) - C(51) - C(54) & \quad 113.35(10) \\
C(49) - C(52) - C(59) & \quad 112.03(10)
\end{align*}
C(49)-C(52)-C(53)  118.16(10)
C(59)-C(52)-C(53)  121.34(10)
C(49)-C(52)-C(54)  116.03(10)
C(59)-C(52)-C(54)  120.76(10)
C(53)-C(52)-C(54)  59.08(7)
C(55)-C(53)-C(50)  115.32(11)
C(55)-C(53)-C(54)  116.38(11)
C(50)-C(53)-C(54)  119.00(11)
C(55)-C(53)-C(52)  118.15(10)
C(50)-C(53)-C(52)  116.57(10)
C(54)-C(53)-C(52)  60.50(7)
C(58)-C(54)-C(51)  115.50(10)
C(58)-C(54)-C(53)  116.48(11)
C(51)-C(54)-C(53)  119.28(10)
C(58)-C(54)-C(52)  118.45(10)
C(51)-C(54)-C(52)  115.62(10)
C(53)-C(54)-C(52)  60.42(7)
C(56)-C(55)-C(53)  122.18(13)
C(55)-C(56)-C(57)  121.37(12)
C(58)-C(57)-C(56)  121.48(13)
C(57)-C(58)-C(54)  122.02(12)
O(12)-C(59)-O(11)  123.97(11)
O(12)-C(59)-C(52)  125.09(11)
O(11)-C(59)-C(52)  110.87(10)

Symmetry transformations used to generate equivalent atoms:
### Supplementary Table 14. Crystal data and structure refinement for 14b.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| CCDC number                                   | 2128306                                    |
| Empirical formula                             | C18 H20 O3                                 |
| Formula weight                                 | 284.34                                     |
| Temperature                                   | 150.01(10) K                              |
| Wavelength                                    | 1.54184 Å                                 |
| Crystal system                                | Monoclinic                                 |
| Space group                                   | P2₁/n                                      |
| Unit cell dimensions                          |                                             |
| a                                             | 6.04138(18) Å                             |
| b                                             | 14.0715(5) Å                              |
| c                                             | 17.1606(5) Å                              |
| Volume                                        | 1456.69(8) Å³                             |
| Z                                             | 4                                          |
| Density (calculated)                          | 1.297 Mg/m³                                |
| Absorption coefficient                        | 0.698 mm⁻¹                                 |
| F(000)                                        | 608                                        |
| Crystal size                                  | 0.28 x 0.16 x 0.12 mm³                     |
| Theta range for data collection               | 4.07 to 67.48°                             |
| Index ranges                                  | −5 ≤ h ≤ 7, −16 ≤ k ≤ 14, −20 ≤ l ≤ 20    |
| Reflections collected                         | 5300                                       |
| Independent reflections                       | 2627 [R(int) = 0.0275]                     |
| Complement to θ = 67.48°                      | 99.7 %                                     |
| Absorption correction                         | Semi-empirical from equivalents           |
| Max. and min. transmission                    | 0.9221 and 0.8285                          |
| Refinement method                             | Full-matrix least-squares on F²           |
| Data / restraints / parameters                 | 2627 / 0 / 193                             |
Goodness-of-fit on $F^2$ 1.120
Final $R$ indices [$>2\sigma$ (I)] $R1 = 0.0628$, $wR2 = 0.1658$
$R$ indices (all data) $R1 = 0.0688$, $wR2 = 0.1688$
Largest diff. peak and hole 0.283 and $-0.272$ e $\cdot$ Å$^{-3}$

**Supplementary Table 15.** Bond lengths [Å] and angles [°] for 14b.

| Bond                  | Length [Å] |
|-----------------------|------------|
| O(1)-C(1)             | 1.344(3)   |
| O(1)-C(15)            | 1.469(3)   |
| O(2)-C(1)             | 1.203(3)   |
| O(3)-C(3)             | 1.227(3)   |
| C(1)-C(2)             | 1.496(4)   |
| C(2)-C(3)             | 1.489(4)   |
| C(2)-C(8)             | 1.547(4)   |
| C(2)-C(9)             | 1.550(4)   |
| C(3)-C(4)             | 1.453(4)   |
| C(4)-C(6)             | 1.531(4)   |
| C(4)-C(5)             | 1.543(4)   |
| C(5)-C(6)             | 1.492(4)   |
| C(5)-C(10)            | 1.502(4)   |
| C(6)-C(7)             | 1.507(4)   |
| C(7)-C(8)             | 1.507(4)   |
| C(8)-C(11)            | 1.477(4)   |
| C(8)-C(9)             | 1.527(4)   |
| C(9)-C(14)            | 1.464(4)   |
| C(9)-C(10)            | 1.519(4)   |
| C(11)-C(12)           | 1.335(4)   |
| C(12)-C(13)           | 1.453(4)   |
| C(13)-C(14)           | 1.338(5)   |
| C(15)-C(18)           | 1.516(5)   |
| C(15)-C(16)           | 1.517(4)   |
| C(15)-C(17)           | 1.518(4)   |
| C(1)-O(1)-C(15)       | 121.7(2)   |
| O(2)-C(1)-O(1)        | 125.8(3)   |
| O(2)-C(1)-C(2)        | 126.0(3)   |
| O(1)-C(1)-C(2)        | 108.2(2)   |
| C(3)-C(2)-C(1)        | 112.2(2)   |
| C(3)-C(2)-C(8)        | 118.6(2)   |
C(1)-C(2)-C(8)  118.6(2)
C(3)-C(2)-C(9)  117.0(2)
C(1)-C(2)-C(9)  121.9(2)
C(8)-C(2)-C(9)  59.08(17)
O(3)-C(3)-C(4)  123.6(3)
O(3)-C(3)-C(2)  119.5(3)
C(4)-C(3)-C(2)  116.9(2)
C(3)-C(4)-C(6)  118.1(2)
C(3)-C(4)-C(5)  115.9(3)
C(6)-C(4)-C(5)  58.09(19)
C(6)-C(5)-C(10)  119.6(3)
C(6)-C(5)-C(4)  60.55(19)
C(10)-C(5)-C(4)  117.9(2)
C(5)-C(6)-C(7)  119.2(3)
C(5)-C(6)-C(4)  61.4(2)
C(7)-C(6)-C(4)  118.6(2)
C(8)-C(7)-C(6)  113.1(2)
C(11)-C(8)-C(7)  117.2(2)
C(11)-C(8)-C(9)  115.3(2)
C(7)-C(8)-C(9)  119.3(2)
C(11)-C(8)-C(2)  115.5(2)
C(7)-C(8)-C(2)  116.7(2)
C(9)-C(8)-C(2)  60.57(17)
C(14)-C(9)-C(10)  115.7(2)
C(14)-C(9)-C(8)  117.2(2)
C(10)-C(9)-C(8)  117.6(2)
C(14)-C(9)-C(2)  119.3(2)
C(10)-C(9)-C(2)  115.5(2)
C(8)-C(9)-C(2)  60.35(17)
C(5)-C(10)-C(9)  114.0(2)
C(12)-C(11)-C(8)  122.9(3)
C(11)-C(12)-C(13)  121.2(3)
C(14)-C(13)-C(12)  120.8(3)
C(13)-C(14)-C(9)  122.4(3)
O(1)-C(15)-C(18)  102.1(2)
O(1)-C(15)-C(16)  108.9(2)
C(18)-C(15)-C(16)  110.3(3)
O(1)-C(15)-C(17)  110.0(2)
C(18)-C(15)-C(17)  111.5(3)
C(16)-C(15)-C(17)  113.4(3)

Symmetry transformations used to generate equivalent atoms:
2.1.6 Methyl 1-oxo-1,2-dihydro-9aH-2,9-ethenobenzo[7]annulene-9-carboxylate (15)

Supplementary Table 16. Crystal data and structure refinement for 15.

| Property                        | Value                          |
|---------------------------------|-------------------------------|
| CCDC number                     | 2128303                       |
| Empirical formula               | C15 H12 O3                    |
| Formula weight                  | 240.25                        |
| Temperature                     | 150.01(10) K                  |
| Wavelength                      | 1.54184 Å                     |
| Crystal system                  | Orthorhombic                  |
| Space group                     | Pna2₁                         |
| Unit cell dimensions            | a = 12.5081(2) Å, α = 90°     |
|                                 | b = 13.8918(2) Å, β = 90°     |
|                                 | c = 6.63025(10) Å, γ = 90°    |
| Volume                          | 1152.07(3) Å³                 |
| Z                               | 4                             |
| Density (calculated)            | 1.385 Mg/m³                   |
| Absorption coefficient          | 0.788 mm⁻¹                    |
| F(000)                          | 504                           |
| Crystal size                    | 0.27 x 0.12 x 0.02 mm³        |
| Theta range for data collection | 4.76 to 67.42°                |
| Index ranges                    | -14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -6 ≤ l ≤ 7 |
| Reflections collected           | 7091                          |
| Independent reflections         | 1779 [R(int) = 0.0181]         |
| Completeness to θ = 67.42°     | 100.0 %                       |
| Absorption correction           | Semi-empirical from equivalents |
| Max. and min. transmission      | 0.9860 and 0.8167             |
| Refinement method               | Full-matrix least-squares on F² |
Data / restraints / parameters 1779 / 1 / 176
Goodness-of-fit on $F^2$ 1.083
Final $R$ indices [$>2\sigma(I)$] $R_1 = 0.0269, \text{w}R_2 = 0.0691$
$R$ indices (all data) $R_1 = 0.0278, \text{w}R_2 = 0.0697$
Absolute structure parameter 0.17(19)
Largest diff. peak and hole 0.251 and $-0.161$ e$^-\text{Å}^{-3}$

**Supplementary Table 17.** Bond lengths [Å] and angles [°] for 15.

| Bond          | Length [Å] |
|---------------|------------|
| O(1)-C(6)     | 1.2088(19) |
| O(2)-C(14)    | 1.200(2)   |
| O(3)-C(14)    | 1.3301(18) |
| O(3)-C(15)    | 1.4494(18) |
| C(1)-C(2)     | 1.512(2)   |
| C(1)-C(7)     | 1.5187(18) |
| C(1)-C(6)     | 1.5323(18) |
| C(1)-C(14)    | 1.534(2)   |
| C(2)-C(13)    | 1.370(2)   |
| C(2)-C(3)     | 1.447(2)   |
| C(3)-C(4)     | 1.342(2)   |
| C(3)-H(3A)    | 1.03(2)    |
| C(4)-C(5)     | 1.510(2)   |
| C(4)-H(4A)    | 0.9500     |
| C(5)-C(6)     | 1.494(2)   |
| C(5)-C(9)     | 1.517(2)   |
| C(5)-H(5A)    | 1.0000     |
| C(7)-C(10)    | 1.364(2)   |
| C(7)-C(8)     | 1.4495(19) |
| C(8)-C(9)     | 1.341(2)   |
| C(8)-H(8A)    | 0.9500     |
| C(9)-H(9A)    | 0.9500     |
| C(10)-C(11)   | 1.420(2)   |
| C(10)-H(10A)  | 0.946(19)  |
| C(11)-C(12)   | 1.376(3)   |
| C(11)-H(11A)  | 0.998(19)  |
| C(12)-C(13)   | 1.416(2)   |
| C(12)-H(12A)  | 1.002(19)  |
| C(13)-H(13A)  | 0.9500     |
| C(15)-H(15A)  | 0.9800     |
| Bond                        | Distance (Å) |
|-----------------------------|--------------|
| C(15)-H(15B)                | 0.9800       |
| C(15)-H(15C)                | 0.9800       |
| C(14)-O(3)-C(15)            | 116.34(13)   |
| C(2)-C(1)-C(7)              | 100.66(11)   |
| C(2)-C(1)-C(6)              | 110.12(13)   |
| C(7)-C(1)-C(6)              | 109.36(11)   |
| C(2)-C(1)-C(14)             | 115.33(12)   |
| C(7)-C(1)-C(14)             | 115.16(12)   |
| C(6)-C(1)-C(14)             | 106.14(12)   |
| C(13)-C(2)-C(3)             | 122.29(15)   |
| C(13)-C(2)-C(1)             | 118.80(14)   |
| C(3)-C(2)-C(1)              | 118.42(13)   |
| C(4)-C(3)-C(2)              | 122.19(16)   |
| C(4)-C(3)-H(3A)             | 123.8(10)    |
| C(2)-C(3)-H(3A)             | 113.9(10)    |
| C(3)-C(4)-C(5)              | 121.70(15)   |
| C(3)-C(4)-H(4A)             | 119.2        |
| C(5)-C(4)-H(4A)             | 119.2        |
| C(6)-C(5)-C(4)              | 108.67(12)   |
| C(6)-C(5)-C(9)              | 106.60(13)   |
| C(4)-C(5)-C(9)              | 109.49(13)   |
| C(6)-C(5)-H(5A)             | 110.7        |
| C(4)-C(5)-H(5A)             | 110.7        |
| C(9)-C(5)-H(5A)             | 110.7        |
| O(1)-C(6)-C(5)              | 125.06(13)   |
| O(1)-C(6)-C(1)              | 122.69(14)   |
| C(5)-C(6)-C(1)              | 112.23(12)   |
| C(10)-C(7)-C(8)             | 123.13(13)   |
| C(10)-C(7)-C(1)             | 119.14(13)   |
| C(8)-C(7)-C(1)              | 117.39(12)   |
| C(9)-C(8)-C(7)              | 123.44(14)   |
| C(9)-C(8)-H(8A)             | 118.3        |
| C(7)-C(8)-H(8A)             | 118.3        |
| C(8)-C(9)-C(5)              | 120.73(13)   |
| C(8)-C(9)-H(9A)             | 119.6        |
| C(5)-C(9)-H(9A)             | 119.6        |
| C(7)-C(10)-C(11)            | 125.69(15)   |
| C(7)-C(10)-H(10A)           | 115.9(12)    |
C(11)-C(10)-H(10A)  118.1(12)
C(12)-C(11)-C(10)  125.31(15)
C(12)-C(11)-H(11A)  117.2(12)
C(10)-C(11)-H(11A)  116.4(11)
C(11)-C(12)-C(13)  125.39(14)
C(11)-C(12)-H(12A)  117.4(12)
C(13)-C(12)-H(12A)  115.8(13)
C(2)-C(13)-C(12)  125.60(16)
C(2)-C(13)-H(13A)  117.2
C(12)-C(13)-H(13A)  117.2
O(2)-C(14)-O(3)  125.13(14)
O(2)-C(14)-C(1)  124.75(14)
O(3)-C(14)-C(1)  109.94(13)
O(3)-C(15)-H(15A)  109.5
O(3)-C(15)-H(15B)  109.5
H(15A)-C(15)-H(15B)  109.5
O(3)-C(15)-H(15C)  109.5
H(15A)-C(15)-H(15C)  109.5
H(15B)-C(15)-H(15C)  109.5

Symmetry transformations used to generate equivalent atoms:
2.1.7 1-Oxo-1,9a-dihydro-2H-2,9-ethenobenzo[7]annulene-2-carboxylic acid (16)

Supplementary Table 18. Crystal data and structure refinement for 16.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| CCDC number                     | 2128308                                    |
| Empirical formula               | C14 H10 O3                                 |
| Formula weight                  | 226.22                                     |
| Temperature                     | 150.01(10) K                              |
| Wavelength                      | 1.54184 Å                                 |
| Crystal system                  | Monoclinic                                 |
| Space group                     | P2₁/n                                      |
| Unit cell dimensions            | a = 6.6629(2) Å, b = 13.3174(4) Å, c = 12.3559(4) Å |
|                                | α = 90°, β = 104.574(3)°, γ = 90°         |
| Volume                          | 1061.10(6) Å³                             |
| Z                               | 4                                          |
| Density (calculated)            | 1.416 Mg/m³                                |
| Absorption coefficient          | 0.821 mm⁻¹                                 |
| F(000)                          | 472                                        |
| Crystal size                    | 0.31 x 0.30 x 0.07 mm³                    |
| Theta range for data collection | 4.97 to 67.46°                             |
| Index ranges                    | -5 ≤ h ≤ 7, -15 ≤ k ≤ 15, -14 ≤ l ≤ 14   |
| Reflections collected           | 3719                                       |
| Independent reflections         | 1901 [R(int) = 0.0131]                     |
| Completeness to θ = 67.46°     | 99.9 %                                     |
| Absorption correction          | Semi-empirical from equivalents           |
| Max. and min. transmission      | 0.9433 and 0.7850                         |
| Refinement method               | Full-matrix least-squares on F²           |
| Data / restraints / parameters  | 1901 / 0 / 158                            |
|                                 | 83                                          |
Goodness-of-fit on $F^2$  1.087
Final $R$ indices [$>2\sigma (I)$]  $R_1 = 0.0371$, $wR_2 = 0.0924$
$R$ indices (all data)  $R_1 = 0.0400$, $wR_2 = 0.0957$
Largest diff. peak and hole  0.228 and $-0.201$ e Å$^{-3}$

**Supplementary Table 19.** Bond lengths [Å] and angles [°] for 16.

| Bond                  | Length [Å]   |
|-----------------------|--------------|
| O(1)-C(14)            | 1.2222(17)   |
| O(2)-C(14)            | 1.3096(17)   |
| O(3)-C(6)             | 1.2054(17)   |
| C(1)-C(14)            | 1.5136(19)   |
| C(1)-C(7)             | 1.5239(18)   |
| C(1)-C(6)             | 1.5255(18)   |
| C(1)-C(2)             | 1.5256(19)   |
| C(2)-C(3)             | 1.342(2)     |
| C(3)-C(4)             | 1.440(2)     |
| C(4)-C(10)            | 1.364(2)     |
| C(4)-C(5)             | 1.5115(18)   |
| C(5)-C(6)             | 1.4947(18)   |
| C(5)-C(9)             | 1.5085(19)   |
| C(7)-C(8)             | 1.337(2)     |
| C(8)-C(9)             | 1.4443(19)   |
| C(9)-C(13)            | 1.362(2)     |
| C(10)-C(11)           | 1.424(2)     |
| C(11)-C(12)           | 1.370(2)     |
| C(12)-C(13)           | 1.428(2)     |
| C(14)-C(1)-C(7)       | 112.52(11)   |
| C(14)-C(1)-C(6)       | 108.72(11)   |
| C(7)-C(1)-C(6)        | 105.66(11)   |
| C(14)-C(1)-C(2)       | 113.15(11)   |
| C(7)-C(1)-C(2)        | 109.29(11)   |
| C(6)-C(1)-C(2)        | 107.07(11)   |
| C(3)-C(2)-C(1)        | 121.97(13)   |
| C(2)-C(3)-C(4)        | 122.92(13)   |
| C(10)-C(4)-C(3)       | 125.38(13)   |
| C(10)-C(4)-C(5)       | 117.24(13)   |
| C(3)-C(4)-C(5)        | 117.05(12)   |
| C(6)-C(5)-C(9)        | 111.35(11)   |
| Bond                        | Angle (°) |
|-----------------------------|-----------|
| C(6)-C(5)-C(4)              | 111.36(11) |
| C(9)-C(5)-C(4)              | 102.09(10) |
| O(3)-C(6)-C(5)              | 124.33(12) |
| O(3)-C(6)-C(1)              | 123.97(13) |
| C(5)-C(6)-C(1)              | 111.67(11) |
| C(8)-C(7)-C(1)              | 121.98(12) |
| C(7)-C(8)-C(9)              | 122.85(13) |
| C(13)-C(9)-C(8)             | 125.73(13) |
| C(13)-C(9)-C(5)             | 117.16(12) |
| C(8)-C(9)-C(5)              | 116.94(12) |
| C(4)-C(10)-C(11)            | 124.18(13) |
| C(12)-C(11)-C(10)           | 125.39(13) |
| C(11)-C(12)-C(13)           | 125.99(13) |
| C(9)-C(13)-C(12)            | 124.29(14) |
| O(1)-C(14)-O(2)             | 123.85(13) |
| O(1)-C(14)-C(1)             | 122.24(12) |
| O(2)-C(14)-C(1)             | 113.89(12) |

Symmetry transformations used to generate equivalent atoms:
2.1.8 9-(Carboxymethyl)-7H-benzo[7]annulene-2-carboxylic acid (S9)

Supplementary Table 20. Crystal data and structure refinement for S9.

| Property                          | Value                        |
|-----------------------------------|------------------------------|
| CCDC number                       | 2128307                      |
| Empirical formula                 | C14 H12 O4                   |
| Formula weight                    | 244.24                       |
| Temperature                       | 150.00(10) K                 |
| Wavelength                        | 1.54184 Å                    |
| Crystal system                    | Monoclinic                   |
| Space group                       | P2₁/c                        |
| Unit cell dimensions              | a = 13.4532(5) Å, α = 90°    |
|                                  | b = 6.5900(2) Å, β = 110.134(4)° |
|                                  | c = 13.8727(5) Å, γ = 90°    |
| Volume                            | 1154.74(7) Å³               |
| Z                                 | 4                            |
| Density (calculated)              | 1.405 Mg/m³                  |
| Absorption coefficient            | 0.860 mm⁻¹                   |
| F(000)                            | 512                          |
| Crystal size                      | 0.26 x 0.13 x 0.06 mm³       |
| Theta range for data collection   | 3.50 to 67.48°               |
| Index ranges                      | -16 ≤ h ≤ 15, -7 ≤ k ≤ 7, -16 ≤ l ≤ 13 |
| Reflections collected             | 3941                         |
| Independent reflections           | 2082 [R(int) = 0.0155]       |
| Completeness to θ = 67.48°       | 99.9 %                       |
| Absorption correction            | Semi-empirical from equivalents |
| Max. and min. transmission        | 0.9518 and 0.8099            |
| Refinement method                 | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters    | 2082 / 0 / 171               |
| Goodness-of-fit on $F^2$          | 1.090                        |
|                                   | 86                           |
Final $R$ indices [$>2\sigma (I)$] $R1 = 0.0332$, $wR2 = 0.0819$

$R$ indices (all data) $R1 = 0.0368$, $wR2 = 0.0848$

Largest diff. peak and hole 0.152 and $-0.194$ e Å$^{-3}$

**Supplementary Table 21.** Bond lengths [Å] and angles [°] for S9.

| Bond                  | Distance (Å) |
|-----------------------|--------------|
| O(1)-C(13)            | 1.2333(15)   |
| O(2)-C(13)            | 1.3033(14)   |
| O(3)-C(14)            | 1.2170(14)   |
| O(4)-C(14)            | 1.3173(15)   |
| C(1)-C(8)             | 1.4018(16)   |
| C(1)-C(2)             | 1.4207(17)   |
| C(1)-C(7)             | 1.4838(16)   |
| C(2)-C(11)            | 1.4044(17)   |
| C(2)-C(3)             | 1.4645(17)   |
| C(3)-C(4)             | 1.3349(18)   |
| C(4)-C(5)             | 1.495(2)     |
| C(5)-C(6)             | 1.5045(18)   |
| C(6)-C(7)             | 1.3363(16)   |
| C(7)-C(12)            | 1.5131(16)   |
| C(8)-C(9)             | 1.3908(16)   |
| C(9)-C(10)            | 1.3930(17)   |
| C(9)-C(14)            | 1.4815(16)   |
| C(10)-C(11)           | 1.3766(17)   |
| C(12)-C(13)           | 1.5021(16)   |
| C(8)-C(1)-C(2)        | 117.87(10)   |
| C(8)-C(1)-C(7)        | 118.44(11)   |
| C(2)-C(1)-C(7)        | 123.43(10)   |
| C(11)-C(2)-C(1)       | 118.55(11)   |
| C(11)-C(2)-C(3)       | 116.44(11)   |
| C(1)-C(2)-C(3)        | 124.94(11)   |
| C(4)-C(3)-C(2)        | 126.61(12)   |
| C(3)-C(4)-C(5)        | 122.91(11)   |
| C(4)-C(5)-C(6)        | 110.33(10)   |
| C(7)-C(6)-C(5)        | 124.24(11)   |
| C(6)-C(7)-C(1)        | 124.15(11)   |
| C(6)-C(7)-C(12)       | 118.74(11)   |
| C(1)-C(7)-C(12)       | 117.08(10)   |
| Bond                  | Angle (°)  |
|----------------------|-----------|
| C(9)-C(8)-C(1)       | 122.30(11) |
| C(8)-C(9)-C(10)      | 119.47(11) |
| C(8)-C(9)-C(14)      | 121.24(11) |
| C(10)-C(9)-C(14)     | 119.27(10) |
| C(11)-C(10)-C(9)     | 119.14(11) |
| C(10)-C(11)-C(2)     | 122.53(12) |
| C(13)-C(12)-C(7)     | 114.97(10) |
| O(1)-C(13)-O(2)      | 123.53(11) |
| O(1)-C(13)-C(12)     | 122.33(11) |
| O(2)-C(13)-C(12)     | 114.12(11) |
| O(3)-C(14)-O(4)      | 122.07(11) |
| O(3)-C(14)-C(9)      | 124.02(11) |
| O(4)-C(14)-C(9)      | 113.90(10) |

Symmetry transformations used to generate equivalent atoms:
2.1.9 Triasterane S11

Supplementary Table 22. Crystal data and structure refinement for S11.

| Parameter                        | Value                        |
|----------------------------------|------------------------------|
| CCDC number                      | 2133482                      |
| Empirical formula                | C13 H12 O                    |
| Formula weight                   | 184.23                       |
| Temperature                      | 150.01(10) K                 |
| Wavelength                       | 1.54184 Å                    |
| Crystal system                   | Orthorhombic                 |
| Space group                      | Cmc2₁                        |
| Unit cell dimensions             | a = 9.2806(3) Å, \( \alpha = 90^\circ \) |
|                                  | b = 12.9060(4) Å, \( \beta = 90^\circ \) |
|                                  | c = 7.4518(3) Å, \( \gamma = 90^\circ \) |
| Volume                           | 892.54(5) Å³                 |
| Z                                | 4                            |
| Density (calculated)             | 1.371 Mg/m³                  |
| Absorption coefficient           | 0.664 mm⁻¹                   |
| F(000)                           | 392                          |
| Crystal size                     | 0.21 x 0.10 x 0.07 mm³       |
| Theta range for data collection  | 5.87 to 67.42°               |
| Index ranges                     | \(-11 \leq h \leq 10, -15 \leq k \leq 15, -8 \leq l \leq 8\) |
| Reflections collected            | 2849                         |
| Independent reflections          | 813 \( [R(int) = 0.0177] \)  |
| Completeness to \( \theta = 67.42^\circ \) | 100.0 %                     |
| Absorption correction            | Semi-empirical from equivalents |
| Max. and min. transmission       | 0.9525 and 0.8732             |
| Refinement method                | Full-matrix least-squares on \( F^2 \) |
| Data / restraints / parameters    | 813 / 1 / 70                 |
| Goodness-of-fit on \( F^2 \)     | 1.103                        |

89
Final $R$ indices [l>2$\sigma$(l)]

$R1 = 0.0272, wR2 = 0.0715$

$R$ indices (all data)

$R1 = 0.0274, wR2 = 0.0717$

Absolute structure parameter

0.2(3)

Largest diff. peak and hole

0.097 and $-0.170$ e$^{-}$ Å$^{-3}$

**Supplementary Table 23.** Bond lengths [Å] and angles [$^\circ$] for S11.

| Bond                  | Length [Å]   |
|-----------------------|--------------|
| O(1)-C(1)             | 1.228(2)     |
| O(1)-C(1)-C(6)        | 122.81(16)   |
| C(1)-C(6)             | 1.461(3)     |
| C(1)-C(2)             | 1.469(2)     |
| C(2)-C(3)#1           | 1.5473(18)   |
| C(2)-C(3)             | 1.5473(18)   |
| C(3)-C(7)             | 1.4728(15)   |
| C(3)-C(4)             | 1.5116(16)   |
| C(3)-C(3)#1           | 1.531(2)     |
| C(4)-C(5)             | 1.5062(16)   |
| C(5)-C(5)#1           | 1.490(3)     |
| C(5)-C(6)             | 1.537(2)     |
| C(6)-C(5)#1           | 1.537(2)     |
| C(7)-C(8)             | 1.3373(18)   |
| C(8)-C(8)#1           | 1.452(3)     |
| O(1)-C(1)-C(6)-O(1)   | 120.83(16)   |
| O(1)-C(1)-C(2)-C(6)   | 116.35(16)   |
| C(6)-C(1)-C(2)-C(3)   | 118.50(12)   |
| C(3)#1-C(2)-C(3)-C(7) | 59.32(10)    |
| C(7)-C(3)-C(4)        | 117.55(10)   |
| C(7)-C(3)-C(3)#1      | 116.43(7)    |
| C(4)-C(3)-C(3)#1      | 117.73(6)    |
| C(7)-C(3)-C(2)        | 115.60(11)   |
| C(4)-C(3)-C(2)        | 116.71(10)   |
| C(3)#1-C(3)-C(2)      | 60.34(5)     |
| C(5)-C(4)-C(3)        | 113.60(10)   |
| C(5)#1-C(5)-C(4)      | 118.73(6)    |
| C(5)#1-C(5)-C(6)      | 61.02(6)     |
| C(4)-C(5)-C(6)        | 118.93(12)   |
| C(1)-C(6)-C(5)#1      | 117.49(12)   |
C(1)-C(6)-C(5)  117.49(12)
C(5)#1-C(6)-C(5)  57.96(12)
C(8)-C(7)-C(3)  121.76(12)
C(7)-C(8)-C(8)#1  121.32(7)

Symmetry transformations used to generate equivalent atoms:
#1  -x,y,z
2.2 Spectral Data

2.2.1 1,4-Dihydronaphthalene (8)

$^1$H NMR

![NMR Spectrum](image)
$^{13}$C NMR

![Carbon-13 NMR spectrum diagram](image-url)

- Peaks at 134.7, 128.7, 128.3, 125.2, 30.1 ppm
$^1\text{H}, ^1\text{H COSY}$

![Diagram of a chemical structure with a COSY spectrum](image-url)
$^{1}H, ^{13}C$ HSQC
$^{1}H, ^{13}C$ HMBC

[Diagram of a molecule with chemical shifts on a 2D spectrum]
2.2.2 1-((1r,1aR,7aS)-1a,2,7,7a-Tetrahydro-1H-cyclopropa[b]naphthalen-1-yl)propan-1-one (10)

$^1$H NMR
$^{13}$C NMR

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
$^1\text{H}, ^{13}\text{C} \text{HSQC}$
$^{1}H, ^{13}C$ HMBC
2.2.3 \((1r,1aR,7aS)-1a,2,7,7a\)-Tetrahydro-1\(H\)-cyclopropa[b]naphthalene-1-carboxylic acid (trans-11)

\(^1\)H NMR
$^1$H, $^1$H COSY

trans-11
$^{1}H$, $^{13}C$ HSQC
$^{1}H, ^{13}C$ HMBC
$^1$H, $^1$H NOESY

[Diagram of a chemical structure with labels and a graph showing NMR spectra.]
IR spectra

Agilent Resolutions Pro
2.2.4 Ethyl (1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropane[b]naphthalene-1-carboxylate (cis-10)

$^1$H NMR
$^1$H, $^1$H COSY
$^1$H, $^{13}$C HMBC
$^1\text{H}$, $^1\text{H}$ NOESY

[Chemical structure image]

[Chemical spectrum diagram]
HRMS
IR spectra

![IR spectrum image]

- Wavenumber range: 3800 to 800 cm⁻¹
- Important peaks:
  - 2970 cm⁻¹
  - 2807 cm⁻¹
  - 2340 cm⁻¹
  - 1917 cm⁻¹
  - 1715 cm⁻¹
  - 1490 cm⁻¹
  - 1389 cm⁻¹
  - 1286 cm⁻¹
  - 1099 cm⁻¹
  - 868 cm⁻¹
  - 810 cm⁻¹
  - 743 cm⁻¹

Date: 2021-08-04
Time: 13:04
2.2.5 (1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalene-1-carboxylic acid (cis-11)

$^1$H NMR
$^{13}$C NMR
$^1H, ^1H$ COSY
$^{1}H, ^{13}C$ HSQC
IR spectra

C_{12}H_{12}O_{2}

M = 188.23 g/mol

% Transmittance

Wavenumber
2.2.6  Methyl 3-oxo-3-\((1s,1aR,7aS)-1a,2,7,7a\)-tetrahydro-1\(H\)-cyclopropa[b]naphthalen-1-yl)propanoate (12a)

\(^1H\) NMR

![NMR Spectrum](image-url)
$^{13}$C NMR
$^1$H, $^1$H COSY
$^{1}H, ^{13}C$ HSQC
$^1H, ^1H$ NOESY

![Chemical Structure](image)
HRMS

[Chemical structure image]

THN<sup>0.028</sup> (APCI) m/z 2.22; RT: 8.64 s. 55%, AV: 80 mL: 5.03 mEU
T. THN<sup>0</sup>S+C<sup>APCI</sup> corona Fullscan [160.00-500.00]
2.2.7 *tert*-Butyl 3-oxo-3-((1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-1-yl)propanoate (12b)

\[\text{\textsuperscript{1}H NMR}\]

![NMR spectrum](image)
$^1$H, $^1$H COSY
$^{1}H, ^{13}C$ HSQC
$^{1}H,^{13}C$ HMBC

![Chemical Structure](image)

![NMR Spectrogram](image)
2.2.8 Methyl-2-diazo-3-oxo-3-((1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-1-yl)propanoate (13a)

$^1$H NMR
$^{1}H$, $^{1}H$ COSY
$^{1}H$, $^{13}C$ HMBC
$^1$H, $^1$H NOESY
HRMS
2.2.9 tert-Butyl 2-diazo-3-oxo-3-\((1s,1aR,7aS)-1a,2,7,7a\)-tetrahydro-1H-cyclopropa[b]naphthalen-1-yl)propanoate (13b)

\(^1\text{H NMR}\)
$^{13}$C NMR
$^1\text{H},^1\text{H COSY}$
$^{1}H, ^{13}C$ HSQC
2.2.10 Triasterane 14a

$^1$H NMR
$^{13}$C NMR

![Chemical Structure](image)

Peaks at ppm:
- 62.1
- 60.9
- 47.3
- 26.5
- 23.2
- 22.7

Peaks at ppm range:
- 80 - 120
- 120 - 160
- 160 - 210
$^{1}H, ^{1}H$ COSY
$^1\text{H}, ^{13}\text{C}$ HSQC
$^{1}H, ^{13}C$ HMBC
\(^1H\), \(^1H\) NOESY

\[ 164 \]
2.2.11 Triasterane 14b

$^1$H NMR
$^{13}$C NMR

![Chemical Structure](image)

- 203.1
- 164.0
- 138.9
- 122.8
- 81.1
- 45.6
- 41.3
- 28.0
- 26.6
- 23.2
- 22.6

ppm
$\text{H, }^{13}\text{C HMBC}$
$^1H, ^1H$ NOESY
HRMS

14b

THMB-132_APCI #4 .22 FT: 0.07 0.65 AM:16 NL: 0.8527
1: HRMS = 3 APCI corona Fullms 100-800 LQ
2.2.12 Methyl 1-oxo-1,2-dihydro-9aH-2,9-ethenobenzo[7]annulene-9a-carboxylate (15)

$^1$H NMR

[Chemical structure image]

[Graph displaying NMR spectrum with various peaks labeled with ppm values]
$^{1}H$, $^{1}H$ COSY

![Chemical Structure]

![NMR Spectrum]
$^1$H, $^1$H NOESY
2.2.13 1-Oxo-1,9a-dihydro-2,9-ethenobenzo[7]annulene-2-carboxylic acid (16)

$^1$H NMR
$^{13}$C NMR
$^{1}H, ^{13}C$ HMBC
$^1$H, $^1$H NOESY
2.2.14 Methyl 10-oxo-9,10-dihydro-10aH-1,9-(metheno)heptalene-10a-carboxylate (18 – CD$_2$Cl$_2$)

$^1$H NMR
$^1\text{H}, ^1\text{H COSY}$
$^{1}H, ^{13}C$ HMBC
2.2.15 Methyl 10-oxo-9,10-dihydro-10aH-1,9-(metheno)heptalene-10a-carboxylate (18– CDCl₃)

1H NMR
$^{1}H, ^{13}C$ HSQC
$^{1}H, ^{13}C$ HMBC
$^1$H, $^1$H NOESY
$^1$H, $^1$H TOCSY
HRMS
2.2.16 2-Diazo-1-((1s,1aR,7aS)-1a,2,7,7a-tetrahydro-1\textit{H}-cyclopropa[b]naphthalen-1-yl)ethan-1-one (S10)

\[^1H\text{ NMR}\]

![NMR Spectrum](image)

ppm
$^{13}$C NMR
$^{1}H, ^{13}C$ HSQC
$^{1}H, ^{13}C$ HMBC
2.2.17 Triasterane S11

$^1$H NMR

![NMR spectrum of Triasterane S11]
$^1$H, $^1$H COSY
$^{1}H, ^{13}C$ HMBC
$^1$H, $^1$H NOESY

![Chemical structure](image)

**217**
2.2.18 Methyl-2-(2a,2b,3,7b-tetrahydrobenzo[g]cyclopropa[cd]benzofuran-2(2H)-ylidene)acetate (S12)

$^1$H NMR
$^1$H, $^1$H COSY

Diagram of a 2D NMR spectrum with ppm axes.
2.3 Atomic coordinates, methods and energies of calculated compounds, and TD-DFT results, template input files and fragmentation used for strain energy analysis

Energies in the following are Gibbs Energies: \( \Delta G \)

**Me-15**

Energy (E) + Thermal free Energy Correction: \( -1617246.41869 \) kJ/mol  
Method: B3LYP-D3  
Basis set: def2-TZVP  

**XYZ-Coordinates:**

|   | C     | C     | C     | C     | C     | C     | C     | C     | C     | C     | O     | H     | H     | H     | H     | H     | H     | H     | H     | H     | H     |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|   | 2.24394800 | -1.32745400 | 1.11421800 | 2.05513600 | -2.07728500 | -0.03176300 | 0.84187900 | -2.19910900 | -0.73622500 | -0.21726700 | -1.31959900 | -0.70872700 | 0.09744600 | -0.07010600 | 1.20071200 | 1.25357300 | -0.56431700 | 1.76215300 | -0.00058500 | 0.13474400 | -0.30659700 | 1.19531200 | -0.95476800 | -0.63101400 | -1.25134400 | 1.95387300 | -1.29152500 | 3.16840900 | -1.49001900 | 1.65613300 | 2.84651800 | -2.76842400 | -0.29776900 | 0.67879200 | -3.13869900 | -1.25598100 | 1.35340400 | -0.45938200 | 2.83582400 | -1.68344200 | 2.80776800 | -1.23737500 | -0.98356500 | 0.01169300 | 3.07107000 | -3.19145600 | 0.31482800 | 2.08919100 | -3.64175100 | -1.47281800 | -0.64291700 | -3.36387000 | 0.97136000 | -0.29299600 | 2.12753700 | 0.30694700 | -0.76795700 | 1.03489900 | 0.88504300 | -2.02998900 | 1.27320800 | 1.84092000 | -0.57325700 |

**15**

Energy (E) + Thermal free Energy Correction: \( -2112465.95335 \) kJ/mol  
Method: B3LYP-D3  
Basis set: def2-TZVP  

**XYZ-Coordinates:**

|   | C     | C     | C     | C     | C     | C     | C     | C     | C     | C     | O     | H     | H     | H     | H     | H     | H     | H     | H     | H     | H     |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|   | 2.25801800 | -1.25054900 | 1.09462000 | 2.07466100 | -2.00016500 | -0.04970100 | 0.84240700 | -2.19962000 | -0.70497000 | -0.22622500 | -1.33908500 | -0.67757400 | 0.07273500 | -0.09614700 | 1.24277600 | 1.23583100 | -0.57257300 | 1.79277700 | -0.01158300 | 0.10694700 | -0.25886500 | -1.57673900 | -1.78669100 | -0.89912000 | -1.25668000 | 0.10714600 | 2.01611000 | 226
H-15

Energy (E) + Thermal free Energy Correction: -1514055.88811 kJ/mol
Method: B3LYP-D3
Basis set: def2-TZVP
XYZ-Coordinates:

|  C  |       |       |       |
|-----|-------|-------|-------|
| -2.33323900 | 0.29576400 | 1.45522400 |
| -2.65336300 | -1.04336000 | -0.59193600 |
| -2.50507500 | 0.36222200 | -0.04872900 |
| 1.20232900 | 0.75608200 | -0.96917200 |
| 1.59764000 | 0.34975600 | -2.02244500 |
| 1.79748500 | 1.82780200 | -0.41955200 |
| 1.29312900 | 2.56848900 | -0.69393900 |
| -1.24310100 | 0.94148900 | -0.62248000 |
| -1.19296600 | 1.94876500 | -1.28010200 |
| 3.21412500 | -1.34851200 | 1.59478700 |
| 2.90324600 | -2.62322400 | -0.36346200 |
| 0.70303300 | -3.14142200 | -1.22003800 |
| 0.05507500 | -0.13683200 | 1.27321300 |
| 1.23817500 | -0.58435700 | 1.79540800 |
| 0.03138000 | 0.02027800 | -0.22660300 |
| 1.62493400 | -1.82257000 | -0.87906600 |
| 1.14469800 | 0.08465600 | 2.03547000 |
| -2.33612300 | 0.30469200 | 1.44800000 |
| -2.67155500 | -1.02715000 | -0.58754600 |
| -2.48104300 | 0.38285000 | -0.06033800 |
| -1.18095000 | 0.90968700 | -0.61932400 |
| -1.07256700 | 1.90551100 | -1.28932500 |
| 3.23232300 | -1.29746500 | 1.51075400 |
| 2.91234900 | -2.56806900 | -0.43094700 |
| 0.70748800 | -3.19374000 | -1.22327900 |
| 1.38194500 | -0.51564400 | 2.86924400 |
| -1.79629300 | -2.84238200 | -1.20341700 |
| -1.08519300 | -0.01786800 | 3.11278800 |
| -3.23806400 | 0.38107900 | 2.04117700 |
| -3.68547200 | -1.39549900 | -0.67402500 |
| -3.30391000 | 1.03327200 | -0.35031900 |
| 0.90149300 | 0.40533700 | -0.63231200 |
### Me-18

**Energy (E) + Thermal free Energy Correction:** \(-1617677.41293\) kJ/mol

**Method:** B3LYP-D3  
**Basis set:** def2-TZVP

**XYZ-Coordinates:**

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -0.9929460 | -0.3774750 | 0.4116740 |
| C    | -0.99037200 | -1.1107550 | -0.83427100 |
| C    | -1.92377200 | -1.12970100 | -1.80527500 |
| C    | -3.09997700 | -0.27848600 | -1.81759900 |
| C    | -2.96474600 | 1.10862800 | 0.10344600 |
| C    | -1.89766600 | 0.52333600 | 0.87030700 |
| C    | -2.88075100 | 1.17534800 | -1.41006700 |
| C    | -4.32274100 | -0.85320800 | -1.96828100 |
| C    | -4.16953600 | 1.55200700 | 0.53750700 |
| C    | -5.07690200 | 1.92263800 | -0.60615100 |
| C    | -5.97630800 | 0.74060300 | -0.88863100 |
| C    | -1.62723800 | 1.81223100 | -2.00266400 |
| C    | -4.09868400 | 2.03531100 | -1.76199200 |
| O    | -4.23349400 | 2.69929100 | -2.75206400 |
| H    | -0.22070800 | -0.67682100 | 1.11133100 |
| H    | -0.17065900 | -1.82456600 | -0.93231900 |
| H    | -1.85117500 | -1.89974600 | -2.57543000 |
| H    | -1.82237900 | 0.82732000 | 1.90869300 |
| H    | -4.31216600 | -1.89209300 | -2.28309900 |
| H    | -4.50228500 | 1.52028500 | 1.56659000 |
| H    | -5.65601000 | 2.83615400 | -0.47736800 |
| H    | -6.40638900 | -1.12613200 | -1.65932000 |
| H    | -6.99593300 | 0.81642300 | -0.53019900 |
| H    | -0.72521000 | 1.27836400 | -1.72291600 |
| H    | -1.70822100 | 1.82858300 | -3.08910800 |
| H    | -1.54540200 | 2.84268000 | -1.65585400 |

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**Energy (E) + Thermal free Energy Correction:** \(-2112409.60749\) kJ/mol

**Method:** B3LYP-D3  
**Basis set:** def2-TZVP

**XYZ-Coordinates:**

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -0.9929460 | -0.3774750 | 0.4116740 |
| C    | -0.99037200 | -1.1107550 | -0.83427100 |
| C    | -1.92377200 | -1.12970100 | -1.80527500 |
| C    | -3.09997700 | -0.27848600 | -1.81759900 |
| C    | -2.96474600 | 1.10862800 | 0.10344600 |
| C    | -1.89766600 | 0.52333600 | 0.87030700 |
| C    | -2.88075100 | 1.17534800 | -1.41006700 |
| C    | -4.32274100 | -0.85320800 | -1.96828100 |
| C    | -4.16953600 | 1.55200700 | 0.53750700 |
| C    | -5.07690200 | 1.92263800 | -0.60615100 |
| C    | -5.97630800 | 0.74060300 | -0.88863100 |
| C    | -1.62723800 | 1.81223100 | -2.00266400 |
| C    | -4.09868400 | 2.03531100 | -1.76199200 |
| O    | -4.23349400 | 2.69929100 | -2.75206400 |
| H    | -0.22070800 | -0.67682100 | 1.11133100 |
| H    | -0.17065900 | -1.82456600 | -0.93231900 |
| H    | -1.85117500 | -1.89974600 | -2.57543000 |
| H    | -1.82237900 | 0.82732000 | 1.90869300 |
| H    | -4.31216600 | -1.89209300 | -2.28309900 |
| H    | -4.50228500 | 1.52028500 | 1.56659000 |
| H    | -5.65601000 | 2.83615400 | -0.47736800 |
| H    | -6.40638900 | -1.12613200 | -1.65932000 |
| H    | -6.99593300 | 0.81642300 | -0.53019900 |
| H    | -0.72521000 | 1.27836400 | -1.72291600 |
| H    | -1.70822100 | 1.82858300 | -3.08910800 |
| H    | -1.54540200 | 2.84268000 | -1.65585400 |
H-18
Energy (E) + Thermal free Energy Correction: \(-1513994.945 \text{ kJ/mol}\)
Basis set: def2-TZVP
XYZ-Coordinates:
C                  1.35157773    0.00000000 -0.04110105
C                  0.66863618 -1.17459592 -0.04110469
C                  0.76459070 -1.31502790 -0.50235000
C                  0.76459280  1.31503419  1.84107860
O                  2.42930645  0.00000000 -0.04110105
H                  1.45903200  1.45903200 -1.74325200

Cycloheptatriene
Energy (E) + Thermal free Energy Correction: \(-712929.831345 \text{ kJ/mol}\)
Method: B3LYP-D3
Basis set: def2-TZVP
XYZ-Coordinates:
C                  1.35157773    0.00000000 -0.04110105
C                  0.66863618 -1.17459592 -0.04110469
C                  0.76459070 -1.31502790 -0.50235000
C                  0.76459280  1.31503419  1.84107860
O                  2.42930645  0.00000000 -0.04110105
H                  1.45903200  1.45903200 -1.74325200
Ellassovalene:
Energy (E) + Thermal free Energy Correction: \(-1216399.03157\) kJ/mol
Method: B3LYP-D3
Basis set: def2-TZVP

XYZ-Coordinates:

|   | X   | Y   | Z   |
|---|-----|-----|-----|
| C | 1.22320000 | 0.00000000 | -0.00000259 |
| C | 1.54674801 | 1.29726742 | -0.24460293 |
| C | 0.68685825 | 2.41437601 | -0.00006693 |
| C | -0.68638350 | 2.41433237 | 0.00006903 |
| C | -1.54672052 | 1.29731705 | -0.24439379 |
| C | -1.22320457 | -0.00000171 | 0.00000554 |
| C | -1.89905641 | -1.20571111 | -0.4245369 |
| C | -1.24888472 | -2.30814363 | -0.00382482 |
| C | 0.00019139 | -1.96381013 | 0.78087975 |
| C | 1.24972273 | -2.30809099 | -0.00293664 |
| C | 1.89958675 | -1.20557931 | -0.42399241 |
| C | 0.00003954 | -0.40447590 | 0.79072574 |
| H | 2.51473768 | 1.51206489 | -0.69087339 |
| H | -2.51439472 | 1.51223890 | -0.69043751 |
| H | -2.79334205 | -1.20318650 | -1.03610107 |
| H | -1.53605448 | -3.32836820 | -0.22627990 |
| H | -0.00045843 | -2.41434500 | 1.77899048 |
| H | 1.53740638 | -3.32830420 | -0.22450385 |
| H | 2.79391827 | -1.20268988 | -1.03524774 |
| H | 0.00011547 | 0.04383788 | 1.78757748 |
| H | -1.16772061 | 3.38739267 | 0.04528972 |
| H | 1.16789843 | 3.38742534 | 0.04522118 |

Norcaradiene:
Energy : \(-712893.531179\) kJ/mol
Method: B3LYP-D3
Basis set: def2-TZVP

XYZ-Coordinates:

|   | X   | Y   | Z   |
|---|-----|-----|-----|
| C | 1.45811516 | 0.00000000 | -0.06362797 |
| C | 0.71284241 | -1.25888626 | 0.00000001 |
| C | -0.63065236 | -1.29557436 | -0.04763795 |
| C | -1.42159584 | -0.08632487 | 0.04837202 |
| C | -0.84263419 | 1.11934180 | 0.18875941 |
| C | 0.60165863 | 1.30932043 | 0.04011429 |
| C | 1.28744867 | 0.92024419 | -1.23721028 |
| H | 2.43378750 | 0.00940637 | 0.40576442 |
| H | 1.28084819 | -2.17407049 | 0.11532077 |
| H | -1.14497048 | -2.24816479 | -0.03397168 |
| H | -2.49696662 | -0.18114107 | 0.13030570 |
| H | -1.43986665 | 1.98584996 | 0.44559175 |
| H | 1.03785957 | 2.14371315 | 0.57479219 |
| H | 0.66231257 | 0.57560122 | -2.04951704 |
| H | 2.14781647 | 1.50619658 | -1.52850104 |
Benzene:
Energy: \(-609860.39146\) kJ/mol
Method: B3LYP-D3
Basis set: def2-TZVP

XYZ-Coordinates:
\[
\begin{array}{cccc}
\text{C} & 1.39018413 & 0.00000000 & -0.00014980 \\
\text{C} & 0.69508158 & 1.20395173 & -0.00014442 \\
\text{C} & -0.69511151 & 1.20393075 & 0.00000637 \\
\text{C} & -1.39018499 & 0.00000558 & 0.00015146 \\
\text{C} & -0.69510743 & -1.20391400 & 0.00015176 \\
\text{H} & 2.47265077 & 0.00002858 & -0.00026899 \\
\text{H} & 1.23634528 & 2.14137844 & 0.00025867 \\
\text{H} & -1.23637695 & 2.14135512 & 0.00000615 \\
\text{H} & -2.47265145 & 0.00003753 & 0.00026939 \\
\text{H} & -1.23630982 & -2.14137691 & 0.00026992 \\
\text{H} & 1.23630517 & -2.14137280 & 0.00000781 \\
\end{array}
\]

TD-DFT results
15
Level of Theory: cam-B3LYP-D3/def2tzvp Solvent: SMD(MeCN)

Excited State 1: Singlet 3.6555 eV 339.17 nm f=0.1373 <S**2>=0.000
   62 -> 65  0.10140
   63 -> 64  0.69332

Excited State 2: Singlet 3.9910 eV 310.66 nm f=0.1016 <S**2>=0.000
   62 -> 64  0.62034
   63 -> 65  -0.32042

Excited State 3: Singlet 4.2126 eV 294.32 nm f=0.0153 <S**2>=0.000
   59 -> 66  0.15939
   61 -> 66  -0.36795
   63 -> 66  0.56464

Excited State 4: Singlet 4.6249 eV 268.08 nm f=1.4129 <S**2>=0.000
   62 -> 64  0.31808
   63 -> 65  0.62178

Excited State 5: Singlet 5.0982 eV 243.19 nm f=0.2101 <S**2>=0.000
   62 -> 65  0.68832

Excited State 6: Singlet 5.2472 eV 236.29 nm f=0.0012 <S**2>=0.000
   57 -> 66  -0.12629
   59 -> 66  -0.18061
   61 -> 64  0.13416
   61 -> 66  0.47751
   63 -> 66  0.40938

Excited State 7: Singlet 5.4277 eV 228.43 nm f=0.0493 <S**2>=0.000
   62 -> 66  0.68748

Excited State 8: Singlet 5.5180 eV 224.69 nm f=0.1177 <S**2>=0.000
   61 -> 64  0.67339
   61 -> 66  -0.12337

Excited State 9: Singlet 5.6764 eV 218.42 nm f=0.0075 <S**2>=0.000
   60 -> 64  -0.37675
   63 -> 67  0.56237
   63 -> 68  0.12511

Excited State 10: Singlet 5.7561 eV 215.39 nm f=0.1120 <S**2>=0.000
   59 -> 64  -0.12153
Excited State 1: Singlet 3.2179 eV 385.30 nm f=0.1825 <S**2>=0.000

Excited State 2: Singlet 4.0949 eV 302.78 nm f=0.0573 <S**2>=0.000

Excited State 3: Singlet 4.1705 eV 297.29 nm f=0.0259 <S**2>=0.000

Excited State 4: Singlet 4.4602 eV 277.98 nm f=0.7525 <S**2>=0.000

Excited State 5: Singlet 4.7569 eV 260.64 nm f=0.0079 <S**2>=0.000

Excited State 6: Singlet 5.1019 eV 243.01 nm f=0.2291 <S**2>=0.000

Excited State 7: Singlet 5.3040 eV 233.76 nm f=0.1635 <S**2>=0.000

Excited State 8: Singlet 5.4257 eV 228.51 nm f=0.0365 <S**2>=0.000

Excited State 9: Singlet 5.5150 eV 224.81 nm f=0.0102 <S**2>=0.000

18

Level of Theory: cam-B3LYP-D3/def2tzvp Solvent: SMD(MeCN)

Total Energy, E(TD-HF/TD-DFT) = -804.235515510
60 -> 64  0.10744
61 -> 65  -0.14584
61 -> 66  -0.18089
62 -> 66  -0.32193
63 -> 67  0.53793

Excited State 10: Singlet 5.5621 eV 222.91 nm f=0.0243 <S**2>=0.000
60 -> 64  -0.34511
60 -> 65  -0.10798
60 -> 66  -0.21429
61 -> 66  0.15382
62 -> 66  0.32398
63 -> 67  0.39518
Templates for Input Files

Geometry Optimization

%chk=cal137.chk
%nprocshared=10
%mem=10GB
# opt freq=noraman b3lyp def2tzvp empiricaldispersion=gd3bj nosymmetry output=wfn

cal137

0 1
####Coordinates####
cal137.wfn

ACID Calculation

nprocshared=10
%mem=10GB
# b3lyp def2tzvp empiricaldispersion=gd3bj scf=tight nmr=csgt iop(10/93=1)

AICD022 from cal137

0 1
####Coordinates####
AICD022.txt

NICS-XY-Scan/ Plane
%chk=cal152.chk
%nprocshared=10
%mem=10GB
# nmr=giao b3lyp/6-311g(d,p)

cal152

0 1

####Coordinates####

---------------------------------------------------------------------------------------------------------------------------
Fragmentation of **H-15**, **H-18** and elassovalene for StrainViz Calculations.

|            | **H-15** | **H-18** | Elassovalene |
|------------|----------|----------|--------------|
| Geometry optimized structure | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| Fragment 1 | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| Fragment 2 | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |
| Fragment 3 | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| Fragment 4 | ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) |
| Fragment 5 | ![Image](image16.png) | ![Image](image17.png) | ![Image](image18.png) |
| Fragment 6 | ![Image](image19.png) | ![Image](image20.png) | ![Image](image21.png) |
3 References

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