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Synthesis of angularly fused cyclopentanoids and analogous tricycles via photoinduced ketyl radical/radical anion fragmentation–cyclization reactions

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Abstract—Angular fused tricycles were synthesized through intramolecular tandem fragmentation–cyclization reactions by photochemically induced electron transfer (PET) of tricyclic α-cyclopropyl ketones with an unsaturated side chain at the position γ to the carbonyl group. The reactions resulted in regioselective cleavage of a β-cyclopropyl bond with formation of angular fused tricyclic ring systems via ketyl radical/radical anions as reactive intermediates. In general, triethylamine (TEA) was used as a strong reducing reagent in acetonitrile. The preferred regioselectivity of the cyclization step (*exo* vs *endo*) depending on the substitution pattern at the quaternary carbon center (Cβ′) of the tricyclic α-cyclopropyl ketones was investigated. In addition, we also checked a two-step pathway for the synthesis of angular dioxa-triquinanes including photolysis of an allyloxy-substituted cyclopenta[*c*]furanone derivative and subsequent β-cleavage of the resulted dioxa-[4.5.5.5]fenestrane under reductive PET conditions.

1. Introduction

Numerous natural products and important biochemical intermediates consist of an angularly fused tricyclo[6.3.0.0^{1,5}]-undecane (triquinane) framework as the core structural moiety.[1] For example, Silphinane and Silphiperfoliane represent two skeletal types differing from the arrangement of the four methyl groups on the basic angular triquinane framework (Fig. 1).[1a,b,d] (−)-1-Silphinene and (−)-5-Silphiperfolene were the first members of the small Silphane family of angular triquinane natural products isolated from the plants *Silphium perfoliatum* by Bohlmann and Jakupovic in 1980.[2] These sesquiterpenoids have received great interest for synthetic chemists due to their biological activity.[1b,d,3]

Although the angular triquinanes are most versatile and abundant in nature, they often form mixtures of isomers and therefore isolation of the pure tricyclopentanoids is a significant challenge.

Several synthetic strategies, in particular carbon–carbon ring-closure reactions and rearrangements, have been developed to prepare angularly fused tricyclopentaniods.[4] Among the synthetic strategies used for constructing angular triquinane carbocyclic skeletons the photoreductive cyclization via γ-ketyl radicals has been demonstrated to be efficient and selective.[5] We have recently reported an intramolecular tandem fragmentation–radical anion cyclization by photoreductive electron transfer of tricyclic α-cyclopropyl ketones with a propargyl group as a key step for the synthesis of a 6-*endo*-cyclized quasi-triquinane product.[5b,c] The

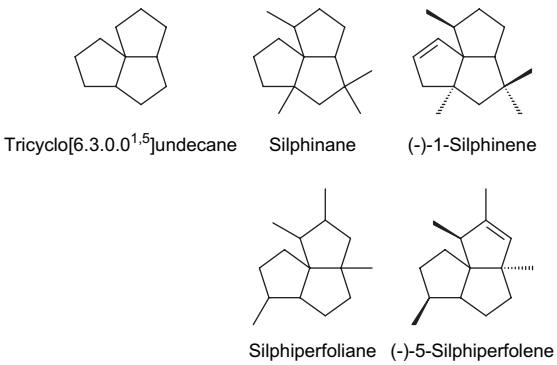

Figure 1. Angular triquinane frameworks.

Keywords: Angular triquinanes; Tricyclic α-cyclopropyl ketones; Photoinduced electron transfer (PET); Tandem fragmentation–cyclization reactions.
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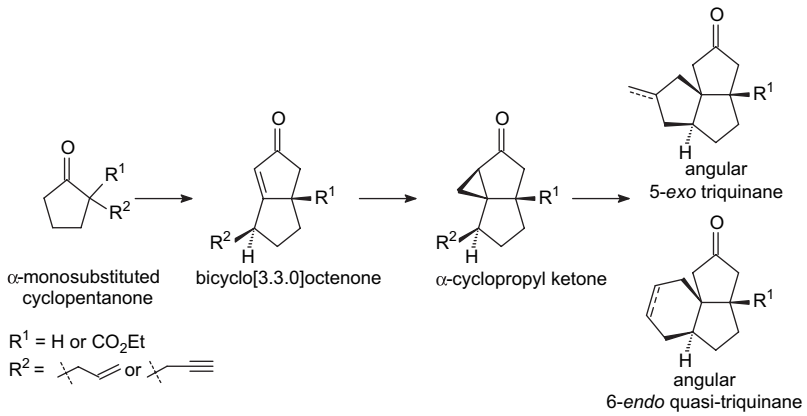


Figure 2. Synthesis of desired angular triquinanes and C_{12} tricycles.

efficiency of these photoreductive reactions strongly depends on the structure properties of the tricyclic α-cyclopropyl ketones. According to our concept for the construction of the desired angular triquinane and quasi-triquinane framework, the following preconditions are required: (i) the cyclopropyl group and the unsaturated side chain have to be cis to each other and (ii) the side chain with a suitable length has to be located γ to the carbonyl group and α to the cyclopropane unit.[5] The desired tricyclic α-cyclopropyl ketones could be easily prepared from the corresponding α-monosubstituted cyclopentanones in a couple of steps via γ-substituted bicyclo[3.3.0]octenone derivatives followed by a diastereoselective cyclopropanation step. The angular triquinanes are formed by a photoinduced cyclization in a 5-*exo*-ring-closure fashion, whereas C_{12} linearly fused tricycles are formed in a 6-*endo* cyclization mode (Fig. 2).

Figure 3 shows the simplified mechanism of the photoreductive process. Irradiation of a solution of the tricyclic α-cyclopropyl ketone **I** (electron acceptor, A) and triethylamine (TEA) as a strong reducing agent (electron donor, D) in acetonitrile at a suitable wavelength (λ=254 or 300 nm) leads to facile ring opening of the α-cyclopropyl ring yielding the distonic γ-keto radical anion **II**, which undergoes a cyclopropylcarbinyl–homoallyl rearrangement.[6,7] The resulting neutral γ-keto radical **III** may undergo a further intramolecular cyclization to form the desired angular triquinanes in a 5-*exo* (**V**) and/or 6-*endo* (**IV**) ring-closure mode (Fig. 3).

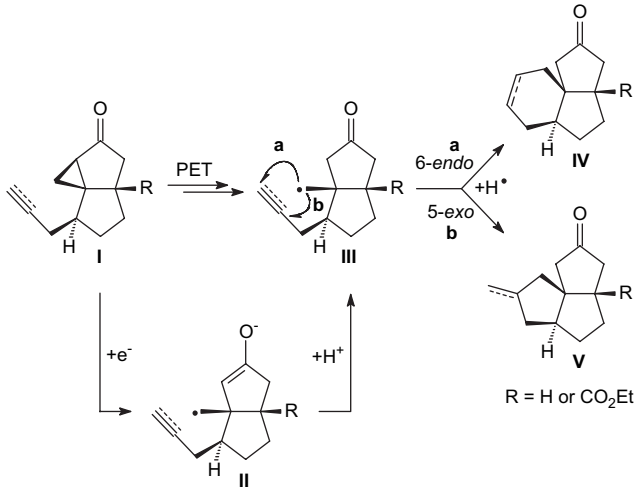


Figure 3. General concept for the formation of angularly fused tricycles via reductive PET.

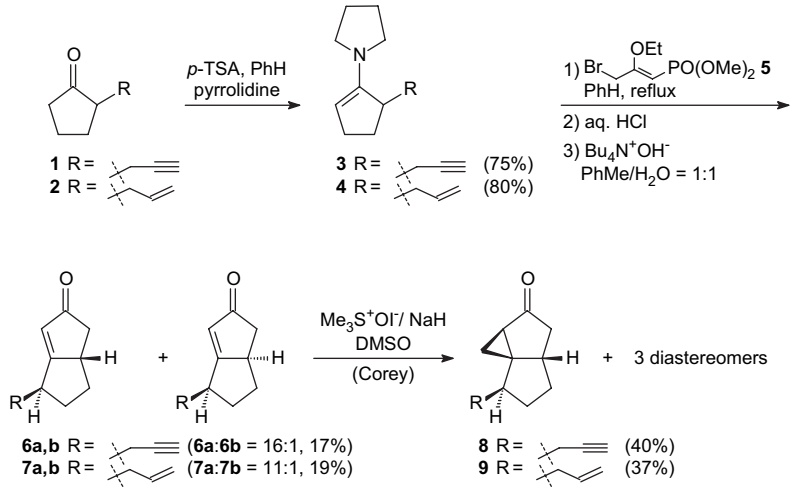
In this article we summarize an investigation of the influence of the substituents on the regio- and stereochemistry of the cyclization step of these novel PET photoreductive key reactions.

2. Results and discussion

2.1. Preparation of α-cyclopropyl octanones

Following our synthetic strategy for the formation of angularly fused tricycles with a bridgehead hydrogen atom, we started from the corresponding α-monosubstituted cyclopentanones **1** and **2** possessing a propargyl and allyl side chain, respectively (Scheme 1). The advantage of this method consists in the introduction of the unsaturated side chain in the very first synthetic step, namely formation of **1** and **2**. The cyclopentanones **1** and **2**, synthesized by well-known procedures,[8] were selectively transformed into the enamines **3** and **4** in 75% and 80% isolated yields, respectively.[8–10] Alkylation of **3** and **4** with dimethyl(3-bromo-2-ethoxyprop-1-enyl)phosphonate[11] followed by hydrolysis and an intramolecular cyclization of the Horner–Wadsworth–Emmons type[12] under phase transfer conditions led to the diastereomeric bicyclooctenones **6a/6b** (94:6 ratio) and **7a/7b** (92:8 ratio) in 17% and 19% overall yield, respectively.[5,13] The bicyclooctenones **6a/6b** were isolated after chromatographic purification as an inseparable mixture of two diastereomers,[14] whereas the bicyclooctenone **7a** was additionally separated from the diastereomeric mixture by HPLC as the predominant stereoisomer in 10% yield.

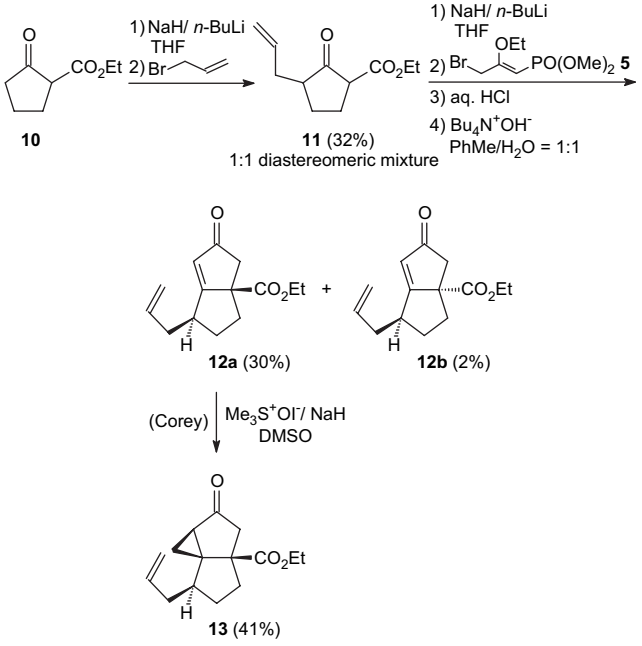
The diastereomeric mixture of the bicyclic octenones **6a/6b** and the pure isolated bicyclooctenone **7a** were converted into the corresponding mixtures of four and respective two α-ketocyclopropanes by Corey's method of cyclopropanation[15] using sodium hydride/trimethyl-sulfoxonium iodide (1.37 equiv) in dry dimethylsulfoxide (DMSO). The major cis-diastereomeric α-cyclopropyl octanones **8** and **9** were



Scheme 1. Synthesis of the tricyclic α-cyclopropyl octahydropentalenones **8** and **9**.

separated by preparative HPLC in 40% and 37% yield, respectively.[16] The other minor diastereomers were isolated as inseparable mixtures (three diastereomers by cyclopropanation of **6a/6b** and one trans-diastereoisomer containing small traces of **9** by cyclopropanation of **7a**) and were analyzed only by GC–MS (EI, CI) and GC methods.

For the synthesis of the diastereomeric bicyclo[3.3.0]octenones **12a** and **12b** with an ethyl carboxylate group in the bridgehead position, we applied another well-known procedure[17] starting from ethyl 2-oxocyclopentanecarboxylate **10** (Scheme 2).



Scheme 2. Synthesis of tricyclic α-cyclopropyl octahydropentalenone ethyl carboxylate **12**.

Double deprotonation with sodium hydride/*n*-BuLi in dry tetrahydrofuran (THF) at 0 to −78 °C and reaction with allyl bromide at −60 °C led to alkylation in position γ to the β-keto ester group. The raw product was purified first by column chromatography followed by distillation in vacuum to give **11** in 32% yield as a 1:1 diastereomeric mixture. Subsequent alkylation of **11** with dimethyl(3-bromo-2-ethoxyprop-1-enyl)phosphonate[11] in THF at 0 °C followed by hydrolysis with aqueous hydrochloric acid and cyclization under phase transfer conditions (Horner–Wadsworth–Emmons reaction)[12] led to the formation of the diastereomeric bicyclic compounds **12a/12b**.[17] The mixture of **12a/12b** was separated by column chromatography and the diastereoisomer **12a** was isolated in an overall yield of 30%. Cyclopropanation of **12a** following Corey's procedure led to the tricyclic compound **13** as the predominant diastereoisomer, which was again isolated by column chromatography in a 41% yield.[18]

The high stereoselectivity of these cyclopropanation reactions may be caused both by the concave structure of **6**, **7**, and **12** and especially for **12a** by the sterically demanding ester group located at the bridgehead position of the octahydropentalenones.

2.2. Intramolecular tandem fragmentation–cyclizations under reductive PET conditions

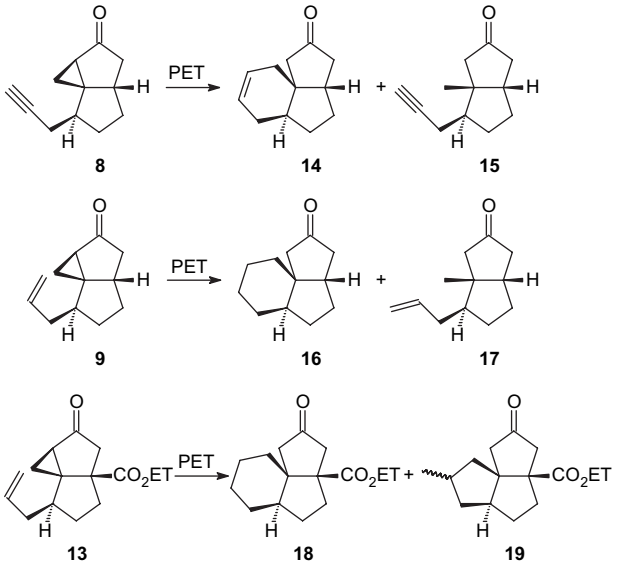
The proposed tandem fragmentation–cyclization under reductive PET conditions as key reaction to form the desired angular triquinanes and quasi-triquinanes was accomplished with tricyclic α-cyclopropyl ketones **8**, **9**, and **13** as starting materials.

After deoxygenation with argon solutions (usually 0.04 M) of the corresponding tricyclic α-cyclopropyl ketones (electron acceptor molecule) in acetonitrile were irradiated in the presence of triethylamine (TEA) as electron donor molecule (5 equiv) and/or lithium perchlorate salt ($LiClO_4$) as an additive (1 equiv). The irradiations were carried out in a Rayonet photochemical reactor at an appropriate wavelength, either by excitation of the donor molecule (TEA) at 254 nm (quartz tubes) or by excitation of the substrate molecule (ketone) at 300 nm (Duran tubes) until almost complete conversion of the starting material, which was monitored by GC and/or GC–MS (see also Section 4). Further addition of $LiClO_4$ did not improve the yields and did

not shorten the reaction time as well despite to our earlier observations.[5a,b,19]

The mechanistic details of the salt and solvent effects during PET reactions, e.g. formation of various types of ion pairs, have been described by us previously[20] and in accordance with earlier experience[6,21] we used 1 equiv $LiClO_4$ added to an acetonitrile solution of the α-cyclopropyl ketone and 5 equiv of TEA. The results of the PET reductive reactions of **8**, **9**, and **13** are presented in Scheme 3 and Table 1 and are summarized as follows:

(i) Better yields and low reaction times were obtained by irradiation at 254 nm with $LiClO_4$ as an additive (e.g. 40% rather than 29% for **14**).
(ii) Reductive PET cyclization of **8** and **9** led to the formation of two products: the *endo*-cyclized tricyclic products **14** and **16** and the non-cyclized minor products **15** and **17**. In both cases, 5-*exo* cyclization products were not observed.
(iii) Reductive PET cyclization of **13** led to the formation of both 6-*endo*- and 5-*exo*-cyclized products **18** and **19**, respectively, in a 1:1 ratio (6-*endo*/5-*exo* 1:1).
(iv) Alkynyl is preferred to alkenyl side substituent. Better yields were observed in the case of **8** with propargyl side substituent (cf. **14** and **16**).



Scheme 3. Tandem fragmentation–cyclization reactions under reductive PET conditions.

According to product formation both **8** and **9** follow the same PET mechanism via the distonic γ-radical anion (e.g. **20** as key intermediate in case of **9**). Obviously cyclization in 6-*endo* mode is most favorable. Simple hydrogen saturation of **20** provides the non-cyclized product **17** (Fig. 4).

In addition, the reductive PET reaction of **9** shows some interesting features: besides the angular quasi-triquinane **16** (6-*endo*-cyclized product) and non-cyclized product **17**, an unusual tricyclic hydroxy product is also isolated and characterized. The mechanistic details of this process are not well known so far.[22] We assume that this minor product is probably formed after reductive PET cyclization reaction from the more accessible concave face of the *endo*-conformer (trans-allyl isomer of **9**).[22]

Table 1. Reductive PET conditions and isolated photoproducts produced via Scheme 3

Ketone	PET conditions	Time (h)	*hν* (nm)	Product	Yield (%)
8	TEA 5.0 equiv, $LiClO_4$ 1.0 equiv, MeCN	3	254	14	40
				15	3
8	TEA 5.0 equiv, $LiClO_4$ 1.0 equiv, MeCN	5	300	14	29
				15	3
8	TEA 5.0 equiv, MeCN	21	300	14	29
				15	3
9	TEA 5.0 equiv, $LiClO_4$ 1.0 equiv, MeCN	3	254	16	30
				17	7
13	TEA 5.0 equiv, MeCN	5	300	18	11
				19	13

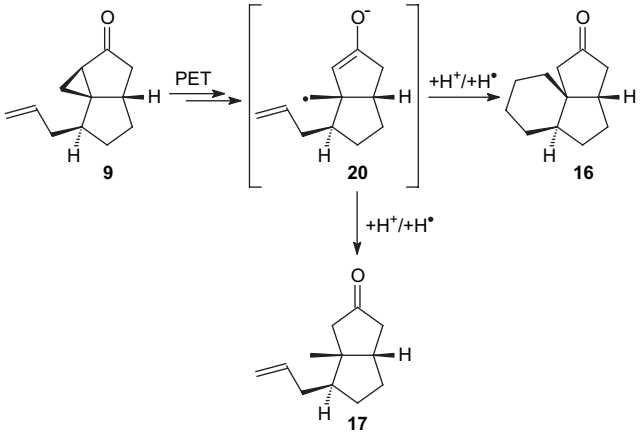


Figure 4. Mechanistic details for the reductive PET reaction of **9**.

The preferred regioselectivity of the ring-closure reaction (6-*endo* vs 5-*exo*) in case of **14** and **16** depends on the substitution pattern of the tricyclic framework, in particular, **14** and **16** are substituted by a hydrogen atom at Cβ (bridgehead carbon atom in relation to the carbonyl group). Interestingly, only the 6-*endo*-cyclized products **14** and **16** were formed, although, according to Baldwin rules,[23] 5-*exo* cyclization should be more favored. Preliminary quantum chemical calculations for the neutral cyclized 5-*exo* and 6-*endo* radicals (formed from **8**) indicate that 6-*endo* is preferred both energetically and kinetically.[5b,24–26]

If the substituent at Cβ is an electron-withdrawing group, e.g. ethoxycarbonyl as in **13**, 5-*exo* cyclization together with the 6-*endo* cyclization is observed. In Figure 5 the proposed mechanism of formation of both **18** and **19** is shown. The factors controlling the regioselectivity, i.e. the influence of steric and electronic effects, are not yet known in detail.[7b,27]

To investigate the potential of the reductive PET process for the synthesis of angular dioxa-triquinane systems bearing two dihydrofuran moieties, we also used an alternative pathway involving two photochemical key-step reactions (Scheme 4). This synthetic strategy was previously

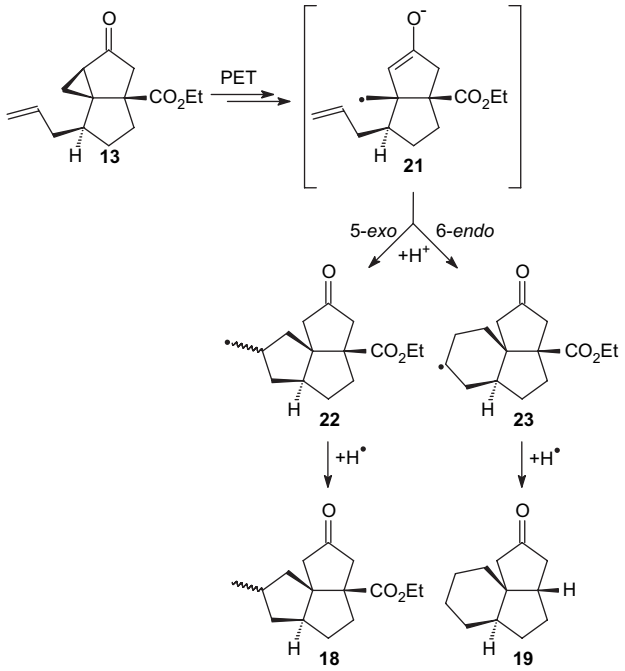


Figure 5. Reductive PET ring-closure reaction of **13** to give 5-*exo*- and 6-*endo*-cyclized products **18** and **19**.

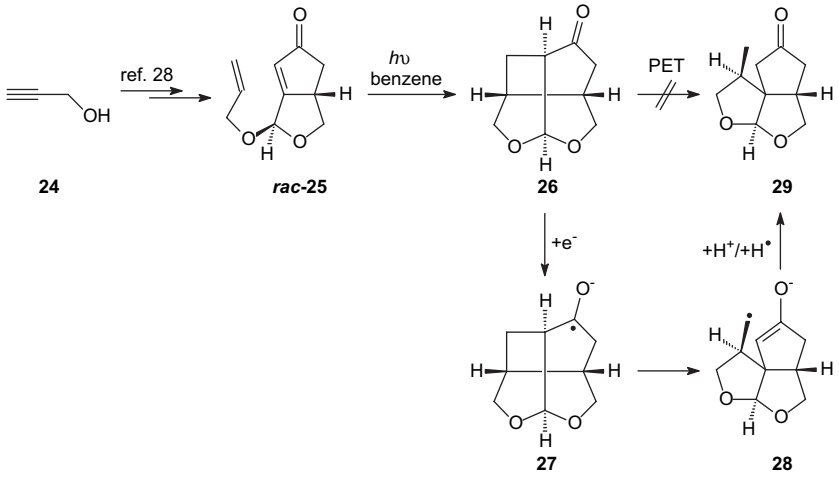
developed and reported by us.[5b,c,28] Starting from propargyl alcohol **24**, the allyloxy-substituted cyclopenta[*c*]furanone *rac*-**25** was synthesized following a five-step literature procedure,[29] which involves a cobalt-mediated Pauson–Khand (PK) reaction as last and decisive synthetic step.[17b,c,30] The cyclopenta[*c*]furanone *rac*-**25** was isolated by column chromatography on aluminum oxide with high diastereoselectivity (dr 98:2). The bicyclic *rac*-**25** was then photolyzed in dry benzene to provide all-*cis*-[4.5.5.5]dioxa-fenestrane product **26** in 58% yield using a 150 W Hg lamp via an intermolecular [2+2] cycloaddition.

In the following step, **26** was irradiated under reductive PET conditions[31] analogous to the synthesis of heterocyclic propellane systems reported previously by us.[5b] In this case, however, a β-C–C-bond cleavage of **26** to form the 5-*exo*-cyclized dioxa-triquinane **29** via the assumed distonic δ-*exo* radical anion **28** was not observed by means of GC and GC–MS analysis. The starting material of this irradiation reaction was completely isolated.

2.3. Structural assignments

cis Stereochemistry of the tricyclic α-cyclopropyl ketones and an *exo* configuration of the bicyclooctenone precursors during the corresponding cyclopropanation and cyclization reaction are essential preconditions for the successful reductive PET key-step reactions. The structural assignment of the new precursors (bicyclooctenones and tricyclic α-cyclopropyl ketones) reported here is based upon their spectral and physical properties as well as MMFF94 force field conformational analytical data.[24]

For example, the high diastereoselectivity (dr 94:6 for **6a/6b**, dr 92:8 for **7a/7b**, and dr 93:7 for **12a/12b**) in the intramolecular cyclization step in an *exo*-ring fusion under phase transfer conditions to afford the corresponding major bicyclooctenones **6a**, **7a**, and **12a** was determined on the basis of modern spectroscopic NMR techniques (one- and two-dimensional NMR: COSY, HMQC, and HMBC). The stereochemistry of the pure isolated cyclization products **7a** and **12a** was assigned by use of quantitative NOESY spectroscopy in combination with ^{1}H NMR analysis of the vicinal coupling constants and the chemical shifts. The bicyclooctenone diastereomeric pairs **6a/6b**, **7a/7b**, and **12a/12b** are resulting from three-step Michael type addition reactions. All cyclization products shown a predominantly cis-ring connection in an *exo*-cyclization mode. For the diastereomeric pair **6a/6b** we observed 88% diastereoselectivity for the major cis-product **6a**.[13] The relative configuration (*exo* or *endo*) and the stereochemistry, respectively, of the diastereomeric mixture **6a/6b** can be established by detailed analysis of the relative intensity of the signals on the ^{1}H and ^{13}C NMR spectra as well as on the basis of the NOESY experiment of the pure isolated cis connected cyclopropanation major product **8**. The observed cis stereochemistry of the tricyclic α-cyclopropyl ketone **8** indirectly indicates the predominant cis-diastereoselectivity of the bicyclooctenone precursor **6a**.



Scheme 4. Proposed synthetic pathway to form dioxa-triquinanes **29**.

The structures of the tricyclic α-cyclopropyl ketones **8**, **9**, and **13** were determined by spectroscopic analysis (one- and two-dimensional NMR). The C,H and H,H correlations for the tricyclic ring systems **8**, **9**, and **13** were obtained from heteronuclear NMR (HMQC and HMBC) and homonuclear NMR (COSY) measurements in combination with ^{1}H, ^{13}C, and DEPT 135 NMR methods. The stereochemistry of **8**, **9**, and **13** was assigned using qualitative NOESY spectroscopy in combination with ^{1}H NMR analysis. Additionally, the stereochemical determination was supported by molecular modeling of the respective geometries using MMFF94 force field calculations[24] assuming a favorable cis attack (from the more accessible convex face) of the in situ formed dimethyloxosulfoxonium-methylyde reagent during cyclopropanation. For example, the agreement of the NOE interactions, the respective coupling constants, and the chemical shifts of the α-carbonyl protons, the bridgehead proton H^F, and the C-1a, C-6 methine hydrogens H^C and H^I indicate that the cyclopropanation products **8** and **9** have the same C/B ring junction in an *exo* configuration (Table 2).

The relatively large coupling constant ($^{3}J_{DF}$~7.5 Hz) of the bridged head proton H^F and the cis connected α-carbonyl proton H^D indicates a small dihedral angle (H^D–C–C–H^F) between these protons. In contrast the order of magnitude ($^{4}J_{CI}$~2.2 Hz) of the respective long range coupling constants between C-1a and C-6 methine protons H^C and H^I indicates a trans-connection in a cis/cis junction, which is anticipated from the large coupling ($^{3}J_{HI}$) toward the trans-connected H^H and H^I protons. The qualitative analyses of two-dimensional NOESY spectra of **8** and **9** confirmed all assignments and revealed the expected through-space correlations of the cis-hydrogens H^A and H^D with bridged head proton H^F as well as between the axial methine proton H^C and the trans-hydrogen H^I. Additionally, the through-space correlations observed as cross-peaks between the bridgehead methine hydrogens H^F and C-6-substituent methylene hydrogens confirmed the cis-ring fusion of both tricyclic compounds **8** and **9**. The same NOE cis relationship between the bridged head CO_2Et group and α-cyclopropyl and C-6-substituent methylene hydrogens was observed for the tricyclic compound **13**. These results were additionally confirmed by molecular modeling assignments of the respective geometries.[24]

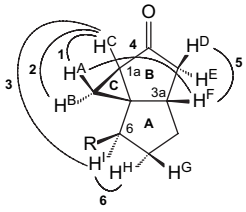
The structural analysis of the photoproducts **14**–**19** and **26** was carried out by one- and two-dimensional NMR as well as by mass spectroscopy, including HRMS (see also Section 4). The stereochemistry of these compounds was assigned by use of qualitative NOESY spectroscopy in combination with ^{1}H NMR analysis. The most important role for the stereochemical determination of the photoproducts **14**–**19** play the α-carbonyl protons (at the positions C-1 and C-2)[32] and their NOE interactions with the side substituents at the position C-3a, C-6a, and the methine proton H^E (Table 3).

For example, the NOE interactions between H^B and H^E protons and between the substituents at the positions C-6a and C-6 strongly support the proposed cis stereochemistry of the photoproducts **14**–**19**.

The structure determination of the dioxa-fenestrane photoproduct **26** was carried out by using heteronuclear correlation NMR (HMQC and HMBC) and homonuclear $^{1}H/^{1}H$ NMR (COSY) in combination with ^{1}H, ^{13}C, and DEPT 135 NMR methods. Additionally, the mass spectroscopy data (GC–MS), including HRMS (*m*/*z* 180 M^+), as well as the IR data proved the assumed structure of **26**. For example, the IR spectra of **26** show carbonyl stretching peak at 1737 cm^{-1} and its ^{13}C NMR spectra the presence of a carbonyl group (δ 215.4 ppm). The DEPT 135 for this compound indicated four CH, four CH_2, and the remaining two carbon atoms being quaternary. The analyses of HMQC and $^{1}H/^{1}H$-COSY spectra confirmed all structural assignments. The most important ^{1}H and ^{13}C NMR signals are shown in Table 4.

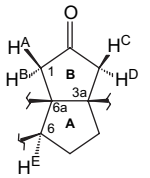
The all-cis configuration of **26** was proven by qualitative NOESY spectroscopy in combination with careful analysis of the ^{1}H NMR coupling constants. The analysis of two-dimensional NOESY spectra of **26** shows cross-peaks between the bridgehead methine protons (trans: 1-H with 6-H; cis: 4-H with 9-H). The observed stereochemistry of **26** is in agreement with the predominantly assigned all-cis

Table 2. NOE interactions, ^{1}H NMR chemical shifts δ (ppm), and coupling constants *J* (Hz) of the tricyclic α-cyclopropyl ketones **8** and **9**



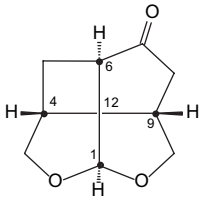
Nr.	NOE	**8**		**9**	
		^{1}H–^{1}H	*J*	^{1}H–^{1}H	*J*
1	H^A–H^C	1.51 (dd)–1.92 (dd)	^{3}J 9.9	0.82 (ddd)–1.53 (m)	^{3}J 9.3
2	H^B–H^C	1.21 (dd)–1.92 (dd)	^{3}J 3.2	0.66 (dd)–1.53 (m)	^{3}J 3.2
3	H^C–H^I	1.92 (dd)–2.47 (dt)	^{4}J 2.2	1.53 (m)–1.87 (m)	^{4}J —
4	H^A–H^F	1.51 (dd)–2.43 (dd)	^{4}J 4.9	0.82 (ddd)–1.89 (dd)	^{4}J 4.7
5	H^D–H^F	2.25 (dd)–2.43 (dd)	^{3}J 7.5	1.84 (dt)–1.89 (dd)	^{3}J 7.6
6	H^H–H^I	1.32 (ddt)–2.47 (dt)	^{3}J 9.5	1.20 (m)–1.87 (m)	^{3}J —

Table 3. Selected ^{1}H and ^{13}C NMR chemical shifts δ (ppm) and J coupling constants (Hz) of the isolated photoproducts **14–19**



Assignment	**14** (*endo*)	**15** (non-cyclization)	**16** (*endo*)	**17** (non-cyclization)	**18** (*exo*)	**19** (*endo*)
H^A	1.92 (d)	1.76 (dd)	1.79 (d)	1.78 (ddd)	2.33 (dd)	2.24 (ddd)
H^B	1.83 (ddd)	1.57 (ddd)	1.62–1.69 (m)	1.56 (ddd)	2.19 (ddd)	2.07 (td)
H^C	2.45 (ddd)	1.94 (dd)	2.12 (ddd)	2.14 (ddd)	3.17 (tdd)	3.19 (ddd)
H^D	2.15 (dd)	1.63 (dd)	1.93 (d)	1.85 (dd)	2.36 (ddd)	2.38 (ddd)
H^E	1.71–1.73 (m)	1.37–1.44 (m)	0.94–1.08 (m)	1.52–1.55 (m)	2.47 (dddd)	1.92 (dddd)
C-1	42.7	44.4	41.9	44.0	47.2	43.4
C-3	45.0	43.8	44.2	44.8	49.6	48.2
C-3a	44.6	48.5	45.3	49.5	65.3	55.3
C-6	43.5	47.1	48.8	47.0	53.5	46.1
C-6a	49.5	49.3	50.8	44.7	53.9	58.6

Table 4. For structural assignments of **26** important ^{1}H and ^{13}C NMR chemical shifts δ (ppm)



^{13}C assignment		^{13}H assignment	
C-1	112.2	1-H	5.19 (s)
C-4	40.8	4-H	1.94–1.97 (m)
C-6	41.2	6-H	2.12 (d)
C-9	43.2	9-H	1.90–1.92 (m)
C-12	60.6		

configuration of similar [4.5.5.5]fenestrane structures formed under same reaction conditions.[17]

3. Conclusion

In summary, we have demonstrated that reductive PET-induced tandem fragmentation–cyclization reactions of tricyclic α-cyclopropyl ketones with a suitable unsaturated side chain at the position γ to the carbonyl group can be successfully used for the construction of angularly fused tricycles. For the synthesis of the tricyclic α-cyclopropyl ketones with propargyl (**8**) and allyl (**9**) side substituents and Cβ bridgehead hydrogen atom we used a general double-enamine procedure followed by an intermolecular Horner–Wadsworth–Emmons type reaction[12] and cyclopropanation,[15] leading to the desired starting materials with high regio- and diastereoselectivity. In case of **13** with an ethyl carboxylate bridgehead substituent[17] at Cβ and for the synthesis of allyloxy-substituted cyclopenta[*c*]furanone[29] *rac*-**25** we used literature known procedures. Important observations arising from this study include the following points:

(1) the PET reactions of the tricyclic α-cyclopropyl ketones were carried out under standard reductive reaction conditions, reported earlier by us,[5] and provided the angular fused tricycles in high regioselective manner;
(2) the regioselectivity (5-*exo* vs 6-*endo*) of the ring-closure step of the in situ formed distonic γ-keto radicals depends on the substitution pattern of the β-carbon atom to the carbonyl function in the substrate molecules;
(3) 6-*endo* cyclization can be expected when the Cβ substituent is hydrogen atom (cf. **8**→**14** and **9**→**16**);
(4) 5-*exo* cyclization was observed only in case of electron-withdrawing group as Cβ substituent (cf. **13**→**18**);
(5) using an alternative two-step photochemical pathway for the construction of angular dioxa-triquinanes involving [2+2]photocycloaddition and photoinduced β-carbon bond cleavage failed so far.

4. Experimental

4.1. General

The starting materials, reagents, and solvents, obtained by commercial suppliers, were used without further purification as provided. Trimethylsulfoxonium iodide salt[33] and dimethyl(3-bromo-2-ethoxyprop-1-enyl)phosphonate[11b,c] (**5**) were synthesized by known procedures. The synthesis and chemical characterization of compounds **8**, **14**, and **15** have been previously published by us.[5b] Solvents for reactions were purified and/or distilled before use.[34] Solvents for routine isolation of products and chromatography were of reagent grade. Air and moisture sensitive reactions were performed in dry solvents under argon atmosphere. The reaction flasks were dried in an oven at 100 °C for 12 h before use. Column chromatography was performed on silica gel MN-60 (40–63 μm or 63–200 μm; Macherey & Nagel). Analytical thin-layer chromatography was performed on silica gel 60 (0.20 and 0.25 mm) with fluorescent indicator F_{254} (Merck) or silica gel (0.20 mm) SIL G/UV_{254} (Macherey & Nagel). HPLC was performed on a silica gel column Merck LiChrospher Si 60-7 (250×20 mm; flow 10 mL min^{-1}) using Kontron pump 420 or Merck pump L-6000 and an RI-detector Bischoff RI 8110. All reactions were monitored by GC analysis using Shimadzu GC-17A/ver. 3 (FID detector and Class VP 4.2 software) or Shimadzu

GC-2010 equipped with Hewlett–Packard HP-5MS capillary column (25 m, 0.2 mm, 0.33 μm); carrier gas nitrogen (pressure 1.0 bar). GC–MS were recorded on a Shimadzu GC-17A/MSQP 5050A equipped with a Hewlett–Packard 5MS capillary column (25 m, 0.2 mm, 0.33 μm); software Class 5000 V 2.0 and LabSolutions GCMSsolution V 1.02 (Shimadzu); carrier gas helium (pressure 0.95 bar). Melting points were measured with a Büchi B-540 instrument and are uncorrected (to 100 °C±0.3 °C, to 250 °C±0.5 °C). IR spectra were recorded on a Perkin–Elmer 841 or FT-IR ATT Matson Genesis Series spectrometer. HRMS were recorded on a Micromass VG Autospec X (Vacuum Generators, Manchester) or Bruker FT-ICR APEX III (7.0 T). ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 K using Bruker AM 250 or Bruker DRX 500 spectrometer. Spectra were recorded in $CDCl_3$ (δ_H=7.26 ppm, δ_C=77.00 ppm) or C_6D_6 (δ_H=7.20 ppm, δ_C=128.00 ppm). ^{1}H NMR data were reported in the order of chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), number of protons, and coupling constant J in Hertz (Hz). Description of the hydrogen atoms is as follows: *a* for axial, *e* for equatorial, and cis or trans to the substituents for the methine hydrogens. Photochemical reactions were performed in a Rayonet RPR-100 photochemical chamber reactor (Southern New England Ultraviolet Company, Brandford) fitted with 16 lamps RPR-2537 Å (emission maximum at 254 nm at half bandwidth, each lamp 35 W) or RPR-3000 Å (emission maximum at 300 nm half bandwidth, each lamp 21 W) and merry-go-round inset using quartz (10 mL volume, 1 cm diameter) or Duran (12 mL volume, 1 cm diameter) tubes. Solutions were deoxygenated with argon under using of ultrasound bad Bandelin Sonorex Super RK 255 H (Bandelin, Berlin) before irradiation.

4.2. General procedure A for preparation of α-substituted enamines

A solution of the corresponding α-monosubstituted ketone in dry benzene (90–120 mL), freshly distilled pyrrolidine (1.70 equiv), and catalytic amounts of *p*-toluenesulfonic acid were placed in a dry apparatus under argon atmosphere. The reaction mixture was heated under reflux for 4–6 h while the water formed was removed by a dropping funnel filled with freshly activated molecular sieve (4 Å). The solution was cooled to room temperature and the solvent removed under reduced pressure. The remaining residue was purified by distillation under vacuum. The product was used immediately in the next reaction.

4.2.1. 1-(5-Prop-2-ynylcyclopent-1-en-1-yl)pyrrolidine (3). According to GP A, 2-prop-2-ynylcyclopentanone (**1**, 12.0 g, 98.0 mmol) was stirred under reflux for 6 h. Purification by distillation yielded 15.9 g (92%) of **3** as colorless liquid, bp 68 °C (0.02 mbar). IR (film) 3311, 3066, 2953, 2840, 2118, 1628, 1486, 1380, 1276, 1243, 1174, 1056, 941, 883 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.81–1.83 (m, 4H), 1.91 (t, J=2.6 Hz, 1H, C≡C*H*), 2.02–2.22 (m, 4H), 2.40 (dt, J=3.1, 16.5 Hz, 2H, CH_2C≡CH), 2.79 (t, J=8.8 Hz, 1H, 5-H), 2.94–3.04 (m, 4H), 4.09 (s, 1H, 2-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.9 (*C*H$_2$C≡CH), 24.8 (2×CH$_2$), 28.4 (C-4), 29.0 (C-3), 44.3 (C-5), 48.7 (2×CH$_2$), 68.1 (C≡*C*H), 84.1 (*C*≡CH), 94.1 (C-2), 151.3 (C-1); GC–MS (EI, 70 eV) *m*/*z* (%) 175 (40) [M$^+$], 174 (30), 160 (11), 148 (13), 147 (100), 146 (45), 136 (46), 134 (24), 119 (11), 91 (12), 79 (15), 70 (20), 65 (16); GC–MS (CI, isobutane) *m*/*z* (%) 176 (100) [MH$^+$], 175 (35), 174 (20), 147 (18); HRMS (EI) calcd for $C_{12}H_{17}N$ *m*/*z* 175.1361, found *m*/*z* 175.1354, deviation 0.91 ppm.

4.2.2. 1-(5-Allylcyclopent-1-en-1-yl)pyrrolidine (4). According to GP A, 2-prop-2-enylcyclopentanone (**2**, 8.30 g, 66.9 mmol) was stirred under reflux for 4 h. Purification by distillation yielded 9.53 g (80%) of **4** as colorless liquid, bp 62–63 °C (0.04 mbar). IR (film) 3072, 2967, 2908, 2846, 1741, 1633, 1424, 1378, 1157, 993, 750; ^{1}H NMR (C_6D_6, 500 MHz) δ 1.48–1.52 (m, 4H), 1.84 (tdd, J=2.0, 7.9, 12.7 Hz, 1H), 2.05 (dddd, J=5.1, 8.8, 10.8, 19.6 Hz, 1H), 2.13–2.20 (m, 1H), 2.36–2.42 (m, 2H), 2.53–2.61 (m, 1H), 2.66 (dt, J=3.5, 9.0 Hz, 1H, 5-H), 2.77–2.83 (m, 2H), 2.89–2.95 (m, 2H), 4.28 (t, J=2.5 Hz, 1H, 2-H), 5.90 (ddd, J=3.8, 7.1, 17.1 Hz, 2H, CH=CH_2), 5.09 (ddd, J=1.8, 3.8, 17.1 Hz, 1H, C*H*=CH$_2$); ^{13}C NMR (C_6D_6, 125 MHz) δ 25.0, 28.9, 29.3, 38.3, 44.6 (C-5), 48.7 (2×CH$_2$), 94.2 (C-2), 115.7 (CH=*C*H$_2$), 137.9 (*C*H=CH$_2$), 152.0 (C-1); GC–MS (EI, 70 eV) *m*/*z* (%) 179 (2) [M$^+$+2H], 178 (13) [M$^+$+1H], 177 (95) [M$^+$], 176 (36), 162 (14), 148 (64), 136 (100), 135 (61), 134 (57), 121 (11), 120 (15), 107 (14), 94 (13), 91 (11), 79 (31), 77 (17), 70 (64), 67 (30), 65 (28); HRMS (EI) calcd for $C_{12}H_{19}N$ *m*/*z* 177.1518, found *m*/*z* 177.1495, deviation 2.24 ppm.

4.3. General procedure for ethyl 3-allyl-2-oxocyclopentanecarboxylate[12b,35] (11)

A suspension of sodium hydride (60% in paraffin) was washed under argon atmosphere with *n*-hexane (3×10 mL) and the solvent was removed under reduced pressure. The remaining material (7.86 g, 0.38 mol) of sodium hydride was suspended under argon atmosphere in anhydrous THF (500 mL). The suspension was cooled to 0 °C (ice/acetone/NaCl) and a solution of 50.1 g (0.32 mol) of ethyl 2-oxocyclopentanecarboxylate (**10**) in anhydrous THF (50 mL) was slowly added. After stirring for 15 min at 0 °C, the reaction mixture was cooled to −78 °C and 200 mL of 1.6 M *n*-BuLi in hexane (0.32 mol) was added dropwise at −78 °C. After warming to −30 °C for 30 min, the mixture was cooled to −60 °C and a solution of 38.8 g (0.32 mol) of allyl bromide in anhydrous THF (10 mL) was added. After warming to room temperature and stirring overnight, the mixture was added to a 1:1 mixture of HCl (2 N)/ice (160 mL) and the water layer extracted with Et_2O (4×80 mL). The combined organic layers were washed with brine (100 mL) and water (100 mL), and dried with sodium sulfate. After evaporation, the remaining residue was purified by distillation in vacuo to give 19.9 g (32%) of a colorless oil containing **11** as mixture of diastereoisomers, bp 68 °C (0.09 mbar). IR (film) 2978, 1752, 1725, 1641, 1445, 1370, 1299, 1255, 1192, 1131, 1026, 918 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (t, J=7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.45–1.92 (m, 1H), 2.00–2.56 (m, 6H), 3.07–3.30 (m, 1H, 1-H), 4.19–4.20 (q, J=7.1 Hz, 2H, $CO_2CH_2CH_3$), 5.02–5.12 (m, 2H, CH=CH_2), 5.74 (tdd, J=17.1, 10.1, 7.1 Hz, 1H, C*H*=CH$_2$); *Diastereomeric mixture*: ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.2 ($CO_2CH_2CH_3$), 25.0 (CH_2), 25.1 (CH_2), 26.7 (CH_2), 26.9 (CH_2), 33.7 (CH_2), 34.2 (CH_2), 48.3 (C-3), 48.9 (C-3),

54.2 (C-1), 55.1 (C-1), 61.4 ($CO_2CH_2CH_3$), 116.8 ($CH{=}CH_2$), 116.9 ($CH{=}CH_2$), 135.3 ($CH{=}CH_2$), 135.5 ($CH{=}CH_2$), 169.3 (CO_2Et), 169.5 (CO_2Et), 212.5 (C-2), 213.2 (C-2); GC–MS (EI, 70 eV) *m/z* (%) 196 (30) [M^+], 178 (14), 168 (12), 154 (31), 150 (37), 149 (56), 123 (37), 122 (74), 109 (100), 108 (21), 105 (59), 101 (25), 95 (79), 94 (53), 79 (73), 78 (48), 72 (67), 68 (46), 67 (89).

4.4. General procedure B for alkylation of pyrrolidine enamines with dimethyl(3-bromo-2-ethoxyprop-1-enyl)phosphonate (5) followed by Horner–Wadsworth–Emmons reaction[11b,12]

A solution of freshly distilled dimethyl(3-bromo-2-ethoxyprop-1-enyl)phosphonate (**5**, 1.1–1.3 equiv/1 mmol enamine) in dry benzene (10 mL) was added to a solution of the corresponding pyrrolidine enamine in dry benzene (110 mL) under argon atmosphere. The reaction mixture was heated under reflux for 18 h, cooled to room temperature, water (30–40 mL) was added, and the resulting mixture was intensively stirred under reflux for 50 min. The solvent was removed under reduced pressure, the residue diluted with dichloromethane (200 mL), and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3×100 mL) and the combined organic layers were dried over sodium sulfate and evaporated.

The crude alkylation product (dark red oil) was diluted in acetone (150 mL), treated with aqueous hydrochloric acid (15 mL), and intensively stirred for 3 h at room temperature. The solution was neutralized by addition of saturated sodium bicarbonate solution (40–80 mL) and acetone was removed under reduced pressure. The residual material was extracted with ethyl acetate (6×100 mL), and the combined organic layers were dried over sodium sulfate and evaporated.

The remaining hydrolyzed product (dark red oil) was dissolved in a 1:1 toluene/water solution (300–400 mL), tetrabutylammoniumhydroxide (40%, 15 mL) was added, and the resulting mixture was intensively stirred for 3 h at room temperature. The aqueous layer was separated and extracted with diethylether (6×100 mL). The combined organic layers were dried with sodium sulfate and evaporated. The remaining residue was purified by column chromatography followed by HPLC.

4.4.1. (4*S,6a*S**)-4-Prop-2-ynyl-4,5,6,6a-tetrahydropentalen-2(1*H*)-one (6a) and (4*S**,6a*R**)-4-prop-2-ynyl-4,5,6,6a-tetrahydropentalen-2(1*H*)-one (6b).** Compounds **6a** and **6b** are obtained as 16:1 diastereomeric mixture.[36] Following GP B, 1-(5-prop-2-ynylcyclopent-1-en-1-yl)pyrrolidine (**3**; 12.8 g, 73.1 mmol) was treated with dimethyl(3-bromo-2-ethoxyprop-1-enyl)phosphonate (**5**; 21.8 g, 80.0 mmol). Chromatography on silica gel (80:20 cyclohexane/ethyl acetate, R_f=0.30) gave 1.94 g (16% for three steps) of diastereomeric mixture **6a/6b** (GC ratio **6a/6b** 16:1) as a colorless oil.

Major cis-isomer **6a**: IR (film) 3261, 2966, 2873, 2120, 1703, 1626, 1447, 1409, 1311, 1257, 1191, 1174, 1131, 1089, 1040, 940, 893 cm^{-1}; NMR experiments: ^1H, $^1H/^1H$-COSY, ^{13}C, ^{13}C-DEPT, HMQC, HMBC, NOESY; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.12 (ddd, *J*=7.5, 11.9, 24.1 Hz, 1H, 6-H_e), 1.72 (ddt, *J*=7.5, 13.4, 6.9 Hz, 1H, 5-H_e), 1.95 (t, *J*=2.5 Hz, 1H, C≡C*H*), 2.03 (dd, *J*=3.8, 17.4 Hz, 1H, 1-H_e), 2.13 (td, *J*=6.9, 7.2 Hz, 1H, 6-H_a), 2.23 (td, *J*=7.5, 13.3 Hz, 1H, 5-H_a), 2.34 (ddd, *J*=2.5, 7.2, 16.6 Hz, 1H, $CH_2C{\equiv}CH$), 2.45 (ddd, *J*=2.5, 6.3, 16.7 Hz, 1H, $CH_2C{\equiv}CH$), 2.60 (dd, *J*=6.3, 17.9 Hz, 1H, 1-H_a), 2.71–2.78 (m, 1H, 6a-H_{cis}), 2.94 (t, *J*=6.9 Hz, 1H, 4-H_{trans}), 5.94 (t, *J*=1.6 Hz, 1H, 3-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.5 ($CH_2C{\equiv}CH$), 30.8 (C-6), 32.5 (C-5), 37.7 (C-4), 42.5 (C-1), 45.9 (C-6a), 69.7 (C≡*C*H), 81.5 (*C*≡CH), 125.7 (C-3), 191.7 (C-3a), 210.9 (C-2); GC–MS (EI, 70 eV) *m/z* (%) 160 (14) [M^+], 145 (10), 132 (21), 131 (22), 121 (14), 118 (20), 117 (70), 115 (16), 104 (34), 103 (11), 93 (16), 91 (100), 79 (12), 78 (27), 77 (66), 65 (33); GC–MS (CI, isobutane) *m/z* (%) 161 (100) [MH^+]; HRMS (EI) calcd for $C_{11}H_{12}O$ *m/z* 160.0888, found *m/z* 160.0881, deviation 2.90 ppm; elemental analysis calcd (%) for $C_{11}H_{12}O$ (160.21): C 82.46; H 7.55, found (%): C 82.24; H 7.68.

Minor trans-isomer **6b**: IR (film) 3261, 2966, 2873, 2120, 1703, 1626, 1447, 1409, 1311, 1257, 1191, 1174, 1131, 1089, 1040, 940, 893 cm^{-1}; NMR experiments: ^1H, $^1H/^1H$-COSY, ^{13}C, ^{13}C-DEPT, HMQC, HMBC, NOESY; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.21 (ddd, *J*=8.8, 11.9, 22.6 Hz, 1H, 6-H_e), 1.82 (ddtd, *J*=1.9, 3.8, 22.5, 1.6, 4.4 Hz, 1H, 5-H_e), 1.92 (t, *J*=2.5 Hz, 1H, C≡C*H*), 2.03 (dd, *J*=3.5, 18.1 Hz, 1H, 1-H_e), 2.07–2.09 (m, 1H, 6-H_a), 2.27 (dd, *J*=3.1, 7.5 Hz, 1H, 5-H_a), 2.32 (dd, *J*=2.5, 16.9 Hz, 1H, $CH_2C{\equiv}CH$), 2.40 (dd, *J*=2.5, 6.3 Hz, 1H, $CH_2C{\equiv}CH$), 2.55 (d, *J*=17.9 Hz, 1H, 1-H_a), 2.98–3.04 (m, 2H, 4-H_{trans} and 6a-H_{trans}), 5.98 (t, *J*=2.5 Hz, 1H, 3-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 22.5 ($CH_2C{\equiv}CH$), 26.8 (C-6), 29.6 (C-5), 31.7 (C-1), 37.4 (C-4), 46.2 (C-6a), 69.3 (C≡*C*H), 81.8 (*C*≡CH), 125.0 (C-3), 192.3 (C-3a), 210.9 (C-2); GC–MS (EI, 70 eV) *m/z* (%) 160 (22) [M^+], 146 (14), 132 (20), 131 (32), 121 (16), 120 (16), 118 (34), 117 (86), 115 (15), 114 (10), 104 (27), 103 (18), 93 (25), 92 (24), 91 (100), 79 (20), 78 (43), 77 (80), 66 (19), 65 (43); GC–MS (CI, isobutane) *m/z* (%) 161 (100) [MH^+]; HRMS (EI) calcd for $C_{11}H_{12}O$ *m/z* 160.0888, found *m/z* 160.0881, deviation 2.90 ppm; elemental analysis calcd (%) for $C_{11}H_{12}O$ (160.21): C 82.46; H 7.55, found (%): C 82.24; H 7.68.

4.4.2. (4*S,6a*S**)-4-Allyl-4,5,6,6a-tetrahydropentalen-2(1*H*)-one (7a).** Following GP B 1-(5-allylcyclopent-1-en-1-yl)pyrrolidine (**4**; 8.36 g, 47.2 mmol) was treated with dimethyl(3-bromo-2-ethoxyprop-1-enyl)phosphonate (**5**; 16.3 g, 63.5 mmol). Chromatography on silica gel (90:10 cyclohexane/ethyl acetate, R_f=0.11) gave 1.45 g (19% for three steps) of diastereomeric mixture **7a/7b** (GC ratio **7a/7b** 11:1). Subsequent separation by HPLC (90:10 cyclohexane/ethyl acetate) yielded 763 mg (10%) of pure cyclization product **7a** as a colorless oil. IR (film) 3075, 2958, 2906, 2865, 1708, 1625, 1446, 1411, 1355, 1309, 1257, 1176, 995, 850 cm^{-1}; NMR experiments: ^1H, $^1H/^1H$-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY; ^1H NMR (C_6D_6, 500 MHz) δ 0.52 (dq, *J*=7.7, 11.9 Hz, 1H, 6-H_e), 1.04–1.13 (m, 1H, 5-H_e), 1.51 (dt, *J*=7.2, 11.9 Hz, 1H, 6-H_a), 1.65 (dt, *J*=7.8, 13.0 Hz, 1H, 5-H_a), 1.73 (dd, *J*=3.5, 17.4 Hz, 1H, 1-H_e), 1.84 (dt, *J*=1.5, 7.2 Hz, 1H, $CH_2CH{=}CH_2$), 1.86 (dt, *J*=1.4, 7.2 Hz, 1H, $CH_2CH{=}CH_2$), 2.18–2.28 (m, 2H,

6a-H_{cis}, 4-H_{trans}), 2.31 (dd, J=6.4, 17.4 Hz, 1H, 1-H_a), 4.88 (q, J=1.7 Hz, 1H, CH=CH_2), 4.92 (q, J=1.7 Hz, 1H, CH=CH_2), 5.51 (ddd, J=7.0, 10.2, 24.0 Hz, 1H, CH=CH$_2$), 5.73 (dd, J=1.9, 3.9 Hz, 1H, 3-H); ^{13}C NMR (C_6D_6, 125 MHz) δ 30.9 (C-6), 32.8 (C-5), 38.6 (C-6a), 39.1 (CH_2CH=CH$_2$), 42.4 (C-1), 45.3 (C-6), 116.6 (CH=CH_2), 125.5 (C-3), 136.03 (CH=CH$_2$), 190.9 (C-3a), 208.7 (C-2); GC–MS (EI, 70 eV) m/z (%) 163 (4) [M$^+$+H], 162 (26) [M$^+$], 161 (3), 147 (4), 134 (41), 121 (30), 120 (31), 119 (25), 118 (25), 117 (13), 105 (20), 93 (31), 92 (43), 91 (100), 79 (29), 78 (26), 77 (81), 67 (15), 66 (33), 65 (52); HRMS (EI) calcd for $C_{11}H_{14}O$ m/z 162.1045, found m/z 162.1042, deviation 1.54 ppm.

4.5. Ethyl(1*S**,3a*R**)-1-allyl-5-oxo-2,3,4,5-tetrahydropentalene-3a(1*H*)-carboxylate (12a) and ethyl-(1*S**,3a*S**)-1-allyl-5-oxo-2,3,4,5-tetrahydropentalene-3a(1*H*)-carboxylate (12b)

A solution of 5.88 g (30.0 mmol) of ethyl 3-allyl-2-oxocyclopentanecarboxylate (**11**) in anhydrous THF (30 mL) was slowly added to a suspension of 744 mg (31.0 mmol) of sodium hydride (60% suspension in paraffin, prepared as described in Section 4.3) in anhydrous THF (120 mL) under argon atmosphere at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and a solution of 8.75 g (32.0 mmol) of dimethyl(3-bromo-2-ethoxyprop-1-enyl)-phosphonate (**5**) in anhydrous THF (30 mL) was added. After stirring for 3 h at 0 °C and 16 h at room temperature, the reaction mixture was neutralized with ice water (150 mL). The water phase was extracted with Et_2O (6×50 mL), and the combined organic phases were washed and dried with sodium sulfate.

After evaporation, the crude alkylation product (12.1 g colorless oil) was diluted in acetone (300 mL), treated with aqueous hydrochloric acid (5 mL), and intensively stirred for 1 h at room temperature. The solution was neutralized by addition of saturated sodium bicarbonate solution (9 mL) and acetone was removed under reduced pressure. The residual material was extracted with ethyl acetate (3×60 mL), and the combined organic layers were dried over magnesium sulfate and evaporated.

The remaining hydrolyzed product (8.80 g colorless oil) was dissolved in a 1:1 toluene/water solution (400 mL), tetrabutylammoniumhydroxide (40%, 13 mL) was added, and the resulted mixture was intensively stirred for 1 h 30 min at room temperature. The aqueous layer was separated and extracted with diethylether (6×80 mL). The combined organic layers were dried over magnesium sulfate and evaporated. The remaining residue was purified by column chromatography on silica gel (80:20 cyclohexane/ethyl acetate) to give 2.11 g (30% for three steps) of **12a** and 170 mg (2% for three steps) of **12b** as colorless oils.

Major cis-isomer **12a**: R_f=0.34 (80:20 cyclohexane/ethyl acetate); IR (film) 3076, 2978, 1722, 1630, 1443, 1413, 1266, 1249, 1184, 1095, 1024, 913, 858 cm^{-1}; NMR experiments: ^{1}H, ^{1}H/^{1}H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.84 (t, J=7.1 Hz, 3H, CO_2CH_2CH3), 0.85 (ddd, J=8.6, 11.6, 13.0 Hz, 1H, 3-H_e), 1.72 (dddd, J=7.2, 7.2, 11.8, 13.0 Hz, 1H, 2-H_e), 1.80 (dtd, J=1.2, 8.3, 14.3 Hz, 1H, 2-H_a), 1.98 (dd, J=0.8, 16.9 Hz, 1H, 4-H_e), 2.06 (tddd, J=8.2, 1.2, 6.8, 14.4 Hz, 2H, CH_2CH=CH$_2$), 2.38 (tt, J=7.9, 7.9 Hz, 1H, 1-H_{trans}), 2.59 (tdd, J=7.1, 1.2, 12.4 Hz, 1H, 3-H_a), 2.72 (d, J=16.9 Hz, 1H, 4-H_a), 3.80 (dq, J=10.6, 7.1 Hz, 2H, $CO_2CH_2CH_3$), 4.9 (tdd, J=2.1, 1.4, 16.7 Hz, 1H, CH=CH_2), 5.01 (tdd, J=2.1, 0.9, 10.5 Hz, 1H, CH=CH_2), 5.63 (tdd, J=7.1, 10.5, 16.7 Hz, 1H, CH=CH$_2$), 5.89 (s, 1H, 6-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1 ($CO_2CH_2CH_3$), 32.2 (C-2), 33.6 (C-3), 39.1 (CH_2–CH=CH$_2$), 39.3 (C-1), 48.9 (C-4), 60.4 (C-3a), 61.6 ($CO_2CH_2CH_3$), 115.9 (CH=CH_2), 127.8 (C-6), 135.6 (CH=CH$_2$), 172.9 ($CO_2CH_2CH_3$), 188.3 (C-6a), 208.9 (C-5); GC–MS (EI, 70 eV) m/z (%) 234 (29) [M$^+$], 206 (11), 161 (37), 160 (14), 133 (52), 119 (39), 105 (23), 92 (15), 91 (100), 79 (20), 67 (14), 65 (16); elemental analysis calcd (%) for $C_{14}H_{18}O_3$ (234.29): C 71.77; H 7.74, found (%): C 71.35; H 7.68.

Minor trans-isomer **12b**: R_f=0.38 (80:20 cyclohexane/ethyl acetate); IR (film) 2979, 1720, 1630, 1444, 1263, 1182, 1047, 1020, 918 cm^{-1}; NMR experiments: ^{1}H, ^{1}H/^{1}H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.23 (t, J=7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.48 (dddd, J=1.2, 8.6, 10.6, 12.9 Hz, 1H, 3-H_e), 1.69 (dddd, J=2.4, 5.3, 9.9, 13.5 Hz, 1H, 2-H_e), 2.21 (tddd, J=1.4, 6.5, 8.0, 14.5 Hz, 1H, CH_2CH=CH$_2$), 2.31 (d, J=17.6 Hz, 1H, 4-H_e), 2.39 (m, 1H, 2-H_a), 2.47 (ddddd, J=1.4, 1.4, 5.9, 6.9, 14.4 Hz, 1H, CH_2CH=CH$_2$), 2.61 (ddd, J=2.4, 8.4, 12.9 Hz, 1H, 3-H_a), 2.88 (dd, J=0.4, 17.6 Hz, 1H, 4-H_a), 2.98 (ddddd, J=2.3, 5.6, 5.6, 8.0, 11.1 Hz, 1H, 1-H_{trans}), 4.13 (dq, J=10.8, 7.1 Hz, 1H, $CO_2CH_2CH_3$), 4.15 (dq, J=10.8, 7.1 Hz, 1H, $CO_2CH_2CH_3$), 5.08 (tdd, J=1.8, 1.3, 10.4 Hz, 1H, CH=CH_2), 5.11 (tdd, J=1.6, 1.6, 17.1 Hz, 1H, CH=CH_2), 5.81 (tdd, J=6.7, 10.3, 17.0 Hz, 1H, CH=CH$_2$), 6.02 (s, 1H, 6-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0 ($CO_2CH_2CH_3$), 30.7 (C-2), 32.5 (C-3), 37.2 (CH_2–CH=CH$_2$), 37.4 (C-1), 48.0 (C-4), 60.5 (C-3a), 61.7 ($CO_2CH_2CH_3$), 115.7 (CH=CH_2), 125.1 (C-6), 135.6 (CH=CH$_2$), 173.1 ($CO_2CH_2CH_3$), 189.4 (C-6a), 208.9 (C-5); GC–MS (EI, 70 eV) m/z (%) 234 (29) [M$^+$], 161 (34), 160 (12), 133 (48), 132 (23), 119 (32), 105 (24), 92 (16), 91 (100), 79 (22), 77 (20), 67 (14), 65 (17); elemental analysis calcd (%) for $C_{14}H_{18}O_3$ (234.29): C 71.77; H 7.74, found (%): C 71.48; H 7.76.

4.6. General procedure C for cyclopropanation of the corresponding bicyclo[3.3.0]octenones by Corey's method[15]

A suspension of sodium hydride (60% in paraffin) was washed with *n*-hexane (3×10 mL) and the solvent was removed under reduced pressure. The remaining material of sodium hydride (1.37 equiv/1.00 mmol of bicyclooctenone) was placed under argon atmosphere in a dry apparatus and trimethylsulfoxonium iodide salt (1.37 equiv/1.00 mmol of bicyclooctenone) was added, followed by dry DMSO (3 mL/1.00 mmol of reagent). The suspension was stirred for 1 h until evolution of hydrogen ceased. A solution of the corresponding bicyclo[3.3.0]octenone in dry DMSO (3 mL/1.00 mmol of enone) was slowly added under ice cooling. The reaction mixture was stirred for 2–3 h at room temperature, slowly warmed to 50 °C, and stirred for

additional 3 h at this temperature. The mixture was poured into ice water and extracted with Et_2O (3×100 mL). The combined organic extracts were washed with water (2×20 mL) and dried with sodium sulfate. The solvent was removed by evaporation and the residue was purified by column chromatography and/or subsequent separation by HPLC.

4.6.1. (1a*R,3a*S**,6*S**,6a*S**)-6-Allyl-1a,3a,4,5,6,6a-hexahydrocyclopropa[*c*]pentalen-2(3*H*)-one (9).** Cyclopropanation of (4*S**,6*S**)-4-allyl-4,5,6,6a-tetrahydropentalen-2(1*H*)-one (**7a**; 630 mg, 3.88 mmol) was carried out according to GP C. The crude product (7:1 mixture of two diastereoisomers) was purified by HPLC (90:10 cyclohexane/ethyl acetate) yielding **9** (253 mg, 37%) as a colorless oil. IR (film) 3073, 2944, 2867, 1724, 1641, 1444, 1415, 1313, 1247, 1176, 1043, 914, 773 cm^{-1}; NMR experiments: ^1H, $^1H/^1H$-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY; ^1H NMR (C_6D_6, 500 MHz) δ 0.66 (dd, J=3.2, 4.7 Hz, 1H, 1-H_e), 0.82 (ddd, J=0.6, 4.7, 9.3 Hz, 1H, 1-H_a), 0.91–1.00 (m, 1H, 4-H_e), 1.15–1.24 (m, 1H, 5-H_e), 1.26–1.33 (m, 1H, CH_2CH=CH_2), 1.38–1.45 (m, 1H, CH_2CH=CH_2), 1.51–1.63 (m, 3H, 5-H_a, 4-H_a, 1a-H), 1.78 (dd, J=1.3, 4.4 Hz, 1H, 3-H_e), 1.84 (dt, J=1.0, 7.6 Hz, 1H, 3-H_a), 1.86–1.88 (m, 1H, 6-H_{trans}), 1.89 (dd, J=0.9, 5.1 Hz, 1H, 3a-H_{cis}), 4.85 (ddd, J=1.6, 3.8, 17.1 Hz, 1H, CH=CH_2), 4.88 (ddd, J=1.3, 3.5, 10.3 Hz, 1H, CH=CH_2), 5.48 (ddd, J=3.5, 7.0, 17.1 Hz, 1H, CH=CH_2); ^{13}C NMR (C_6D_6, 125 MHz) δ 15.5 (C-1), 30.0 (C-1a), 31.0 (C-5), 31.6 (C-4), 36.6 (*C*H_2CH=CH_2), 38.3 (C-3a), 40.4 (C-3), 41.0 (C-6), 45.7 (C-6a), 115.6 (CH=*C*H_2), 137.3 (*C*H=CH_2), 211.5 (C-2); GC–MS (EI, 70 eV) *m*/*z* (%) 178 (1) [M^+], 177 (1) [M^+-1H], 176 (4), 148 (5), 135 (20), 134 (17), 120 (11), 107 (12), 106 (23), 91 (35), 80 (11), 79 (39), 77 (29), 67 (21), 55 (100), 41 (36), 39 (44); HRMS (EI) calcd for $C_{12}H_{16}O$ *m*/*z* 176.1210, found *m*/*z* 176.1197, deviation 2.44 ppm.

4.6.2. (1a*R,3a*R**,6*S**,6a*R**)-6-Allyl-2-oxo-1a,3a,4,5,6,6a-hexahydrocyclopropa[*c*]pentalene-3a(4*H*)-carboxylate (13).** Cyclopropanation of (1*S**,3a*R**)-1-allyl-5-oxo-2,3,4,5-tetrahydropentalene-3a(1*H*)-carboxylate (**12a**; 2.85 g, 12.2 mmol) was carried out according to GP C. The crude product (10:1 mixture of two diastereoisomers) was purified by column chromatography on silica gel (60:40 cyclohexane/ethyl acetate) yielding **13** (1.25 g, 42%) as a colorless oil. R_f=0.50 (60:40 cyclohexane/ethyl acetate); IR (film) 3075, 2976, 1725, 1640, 1445, 1367, 1227, 1178, 1129, 1021, 915, 862 cm^{-1}; NMR experiments: ^1H, $^1H/^1H$-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.29 (t, J=7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.42 (ddd, J=0.4, 1.1, 5.8 Hz, 1H, 1-H_e), 1.44 (dd, J=4.7, 5.4 Hz, 1H, 1-H_a), 1.52 (dddd, J=4.3, 7.3, 10.2, 12.9 Hz, 1H, 5-H_e), 1.62 (ddd, J=7.1, 10.3, 13.4 Hz, 1H, 4-H_e), 1.72 (tddd, J=1.4, 6.8, 9.5, 14.0 Hz, 1H, CH_2CH=CH_2), 1.84 (m, 1H, 1a-H), 1.85 (tddd, J=1.4, 5.2, 6.5, 14.1 Hz, 1H, CH_2CH=CH_2), 2.21 (dddd, J=7.0, 8.9, 8.9, 12.8 Hz, 1H, 5-H_a), 2.24 (dd, J=1.3, 18.6 Hz, 1H, 3-H_e), 2.40 (ddd, J=4.5, 8.9, 13.4 Hz, 1H, 4-H_a), 2.59 (dddd, J=5.1, 7.3, 9.3, 9.3 Hz, 1H, 6-H_{trans}), 2.79 (dd, J=1.1, 18.6 Hz, 1H, 3-H_a), 4.19 (q, J=7.1 Hz, 2H, $CO_2CH_2CH_3$), 4.99 (tdd, J=1.9, 1.2, 10.2 Hz, 1H, CH=CH_2), 5.02 (tdd, J=1.9, 1.8, 17.1 Hz, 1H, CH=CH_2), 5.73 (tdd, J=6.8, 10.2, 17.1 Hz, 1H, CH=CH_2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.3 ($CO_2CH_2CH_3$), 15.0 (C-1), 30.4 (C-1a), 30.5 (C-5), 35.1 (C-4), 36.3 (*C*H_2CH=CH_2), 37.5 (C-6), 44.0 (C-3), 48.3 (C-6a), 55.1 (C-3a), 61.1 ($CO_2CH_2CH_3$), 116.0 (CH=*C*H_2), 136.5 (*C*H=CH_2), 174.8 ($CO_2CH_2CH_3$), 211.4 (C-2); GC–MS (EI, 70 eV) *m*/*z* (%) 207 (26) [$M^+-C_3H_5$], 175 (19), 165 (13), 151 (18), 139 (26), 133 (33), 125 (40), 111 (66), 109 (36), 97 (98), 95 (52), 85 (70), 83 (84), 81 (51), 71 (100), 69 (85); elemental analysis calcd (%) for $C_{15}H_{20}O_3$ (248.32): C 72.75; H 8.12, found (%): C 72.48; H 8.54.

4.7. PET reductive reaction of (1a*R**,3a*S**,6*S**,6a*S**)-6-allyl-1a,3a,4,5,6,6a-hexahydrocyclopropa[*c*]pentalen-2(3*H*)-one (9)

A solution of (1a*R**,3a*S**,6*S**,6a*S**)-6-allyl-1a,3a,4,5,6,6a-hexahydrocyclopropa[*c*]pentalen-2(3*H*)-one (**9**; 145 mg, 0.82 mmol) in dry acetonitrile (21 mL, 0.04 M) was treated with lithium perchlorate (88.0 mg, 0.82 mmol) and dry triethylamine (0.6 mL, 4.11 mmol). The solution was apportioned in two quartz irradiation tubes, these were sealed with septa, and the solutions were deoxygenated using argon and ultrasound irradiation for 1 h. The solutions were irradiated in a Rayonet RPR-100 photochemical reactor with use of merry-go-round inset at 254 nm for 2 h 30 min. The conversion of the staring material was monitored by GC. The solvent was removed under reduced pressure and ethyl acetate (20 mL) was added. The organic phase was washed with water (3×20 mL) and the aqueous layer extracted with ethyl acetate (3×50 mL). The combined organic layers were dried with sodium sulfate, the solvent was removed, and the crude product purified by column chromatography on silica gel (20:80 cyclohexane/ethyl acetate). Separation by HPLC (90:10 cyclohexane/ethyl acetate) yielded **16** (44 mg, 30%) and **17** (10 mg, 7%) as colorless oils.

4.7.1. (3a*S,5a*R**,9a*S**)-3a,4,5,5a,6,7,8,9-Octahydro-1*H*-cyclopenta[*c*]inden-2(3*H*)-one (16).** IR (film) 2948, 2923, 2859, 1741, 1635, 1448, 1403, 1376, 1174, 1149, 1074, 1035, 914 cm^{-1}; NMR experiments: ^1H, $^1H/^1H$-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY; ^1H NMR (C_6D_6, 500 MHz) δ 0.71 (dd, J=3.8, 2.5 Hz, 1H, 6-H_a), 0.83 (dt, J=2.3, 2.5 Hz, 1H, 5-H_e), 0.86 (d, J=7.3 Hz, 1H, 9-H_a), 0.92 (d, J=7.1 Hz, 1H, 8-H_e), 0.94–1.08 (m, 3H, 3a-H_{cis}, 7-H_e, 4-H_e), 1.31 (ddd, J=2.1, 3.4, 11.9 Hz, 1H, 9-H_a), 1.34–1.40 (m, 2H, 4-H_a, 8-H_a), 1.41–1.46 (m, 1H, 6-H_e), 1.47–1.52 (m, 1H, 7-H_a), 1.62–1.69 (m, 3H, 1-H_e, 5a-H_{trans}, 5-H_a), 1.79 (d, J=18.9 Hz, 1H, 1-H_a), 1.93 (d, J=17.9 Hz, 1H, 3-H_e), 2.12 (ddd, J=2.4, 6.6, 18.2 Hz, 1H, 3-H_a); ^{13}C NMR (C_6D_6, 125 MHz) δ 22.6 (C-8), 26.3 (C-7), 27.8 (C-6), 28.6 (C-4), 30.2 (C-5), 36.2 (C-9), 41.9 (C-1), 44.2 (C-3), 45.3 (C-3a), 48.8 (C-5a), 50.8 (C-9a), 216.9 (C-2); GC–MS (EI, 70 eV) *m*/*z* (%) 179 (11) [M^++1H], 178 (96) [M^+], 163 (6), 160 (9), 149 (37), 136 (19), 135 (59), 134 (15), 121 (66), 120 (91), 108 (16), 107 (17), 95 (26), 93 (38), 91 (25), 81 (35), 79 (66), 77 (32), 68 (42), 67 (100), 65 (30); HRMS (EI) calcd for $C_{12}H_{18}O$ *m*/*z* 178.1358, found *m*/*z* 178.1360, deviation 1.40 ppm.

4.7.2. (3a*S,4*S**,6a*S**)-4-Allyl-3a-methyl-3,3a,4,5,6,6a-hexahydropentalen-2(1*H*)-one (17).** IR (film) 2937, 2867, 1731, 1643, 1456, 1403, 1170, 1151, 1031, 993, 912 cm^{-1};

NMR experiments: ^{1}H, ^{1}H/^{1}H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY; ^{1}H NMR (C_6D_6, 500 MHz) δ 0.79 (s, 3H, CH_3), 0.84 (ddd, J=3.4, 6.9, 10.2 Hz, 1H, 5-H$_e$), 0.97 (dddd, J=0.6, 1.2, 6.9, 13.2 Hz, 1H, 6-H$_e$), 1.35 (dddd, J=1.2, 4.5, 10.5, 17.9 Hz, 1H, 4-H$_e$), 1.48 (dd, J=6.6, 10.2 Hz, 1H, CH_2CH=CH$_2$), 1.52–1.55 (m, 1H, 6-H$_a$), 1.56 (ddd, J=1.3, 4.4, 19.3 Hz, 1H, 3-H$_e$), 1.59 (td, J=6.3, 10.5 Hz, 1H, 5-H$_a$), 1.65–1.70 (m, 1H, 6a-H$_{cis}$), 1.78 (ddd, J=1.4, 4.8, 19.1 Hz, 1H, 3-H$_a$), 1.85 (dd, J=8.5, 18.6 Hz, 1H, 1-H$_e$), 1.93 (dtd, J=6.4, 2.1, 10.2 Hz, 1H, CH_2CH=CH$_2$), 2.14 (ddd, J=1.9, 8.3, 18.7 Hz, 1H, 1-H$_a$), 4.92 (t, J=1.7 Hz, 1H, CH=CH_2), 4.96 (dd, J=1.9, 3.7 Hz, 1H, CH=CH_2), 5.62 (dd, J=6.9, 7.2 Hz, 1H, CH=CH$_2$); ^{13}C NMR (C_6D_6, 125 MHz) δ 25.5 (CH_3), 30.0 (C-6), 30.5 (C-5), 35.9 (CH_2CH=CH$_2$), 44.0 (C-3), 44.7 (C-3a), 44.8 (C-1), 47.0 (C-4), 49.5 (C-6a), 115.1 (CH=CH_2), 138.2 (CH=CH$_2$), 216.7 (C-2); GC–MS (EI, 70 eV) m/z (%) 179 (4) [M$^+$+1H], 178 (38) [M$^+$], 163 (35), 149 (33), 137 (13), 136 (11), 135 (16), 121 (9), 109 (44), 107 (10), 96 (20), 95 (66), 93 (24), 91 (11), 81 (23), 79 (29), 77 (19), 68 (59), 67 (100), 65 (21), 55 (63), 53 (39), 43 (30), 41 (72), 39 (58); HRMS (EI) calcd for $C_{12}H_{18}O$ m/z 178.1358, found m/z 178.1362, deviation 1.60 ppm.

4.8. PET reductive reaction of (1a*R**,3a*R**,6*S**,6a*R**)-6-allyl-2-oxo-1a,3a,4,5,6,6a-hexahydrocyclopropa[*c*]-pentalene-3a(4*H*)-carboxylate (13)

A solution of (1a*R**,3a*R**,6*S**,6a*R**)-6-allyl-2-oxo-1a,3a,4,-5,6,6a-hexahydrocyclopropa[*c*]pentalene-3a(4*H*)-carboxylate (**13**; 400 mg, 1.61 mmol) in dry acetonitrile (96 mL, 0.02 M) was treated with dry triethylamine (1.2 mL, 8.05 mmol). The solution was apportioned in eight Duran irradiation tubes, these were sealed with septa, and the solutions were deoxygenated using argon and ultrasound irradiation for 1 h. The solutions were irradiated in a Rayonet RPR-100 photochemical reactor with use of merry-go-round inset at 300 nm for 5 h. The conversion of the staring material was monitored by GC. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (20:80 cyclohexane/ethyl acetate). Separation by HPLC (90:10 cyclohexane/ethyl acetate) yielded **18** (45 mg, 13%) and **19** (35 mg, 11%) as colorless oils.

4.8.1. Ethyl(3a*R,5a*R**,9a*S**)-2-oxo-3a,4,5,6,5a,6,7,8,9-octahydro-1*H*-cyclopenta[*c*]indene-3a(4*H*)-carboxylate (18).** IR (film) 2952, 2867, 1742, 1718, 1451, 1312, 1224, 1193, 1175, 1104, 1081, 1038, 809 cm^{-1}; NMR experiments: ^{1}H, ^{1}H/^{1}H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, HMBC, NOESY; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.99 (dddd, J=3.1, 12.5, 12.5, 12.6 Hz, 1H, 6-H$_e$), 1.12 (dddd, J=1.6, 3.6, 12.5, 12.5 Hz, 1H, 9-H$_e$), 1.18 (m, 1H, 7-H$_e$), 1.25 (m, 1H, 8-H$_e$), 1.30 (t, J=7.1 Hz, 3H, CO$_2$CH$_2$CH_3), 1.38 (m, 1H, 5-H$_e$), 1.41 (m, 1H, 4-H$_e$), 1.67 (m, 1H, 9-H$_a$), 1.69 (m, 1H, 8-H$_a$), 1.69 (m, 1H, 7-H$_a$), 1.75 (m, 1H, 6-H$_a$), 1.88 (dddd, J=2.1, 9.5, 11.6, 18.8 Hz, 1H, 5-H$_a$), 1.92 (dddd, J=1.2, 7.2, 11.4, 12.2 Hz, 1H, 5a-H$_{trans}$), 2.07 (td, J=1.6, 19.3 Hz, 1H, 1-H$_e$), 2.24 (ddd, J=1.4, 1.4, 19.3 Hz, 1H, 1-H$_a$), 2.38 (ddd, J=1.2, 1.2, 18.3 Hz, 1H, 3-H$_e$), 2.56 (ddd, J=1.1, 6.7, 9.3 Hz, 1H, 4-H$_a$), 3.19 (ddd, J=1.4, 1.4, 18.3 Hz, 1H, 3-H$_a$), 4.18 (dq, J=10.8, 7.1 Hz, 1H, CO$_2$CH_2CH$_3$), 4.19 (dq, J=10.8, 7.1 Hz, 1H, CO$_2$CH_2CH$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.4 (CO$_2$CH$_2$CH_3), 22.3 (C-8), 25.5 (C-7), 27.7 (C-6), 28.5 (C-5), 33.3 (C-9), 34.1 (C-4), 43.4 (C-1), 46.1 (C-5a), 48.2 (C-3), 55.3 (C-3a), 58.6 (C-9a), 61.0 (CO$_2$CH_2CH$_3$), 174.8 (CO_2CH$_2$CH$_3$), 216.8 (C-2); GC–MS (EI, 70 eV) m/z (%) 250 (17) [M$^+$], 193 (82), 192 (73), 177 (100), 119 (34), 91 (27), 67 (25); elemental analysis calcd (%) for $C_{15}H_{22}O_3$ (250.34): C 71.97; H 8.86, found (%): C 72.18; H 8.54.

4.8.2. Ethyl(3a*R,5a*S**,8a*S**)-7-methyl-2-oxo-3,4,5,5a,6,7,8,8a-oxooctahydrocyclopenta[*c*]pentalene-3a(1*H*)-carboxylate (19).** IR (film) 2952, 2869, 1746, 1721, 1451, 1313, 1224, 1193, 1175, 1104, 1081, 1038, 809 cm^{-1}; NMR experiments: ^{1}H, ^{1}H/^{1}H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, HMBC, NOESY; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.76 (ddd, J=8.6, 11.8, 13.2 Hz, 1H, 6-H$_a$), 1.04 (d, J=7.3 Hz, 3H, CH_3), 1.09 (dd, J=2.7, 12.5 Hz, 1H, 8-H$_e$), 1.29 (t, J=7.1 Hz, 3H, CO$_2$CH$_2$CH_3), 1.40 (dddd, J=8.2, 10.0, 12.4, 12.4 Hz, 1H, 5-H$_e$), 1.61 (dd, J=10.9, 12.5 Hz, 1H, 8-H$_a$), 1.71 (dddd, J=2.1, 6.8, 8.9, 12.4 Hz, 1H, 5-H$_a$), 1.76 (ddd, J=2.1, 9.9, 14.3 Hz, 1H, 4-H$_e$), 1.84 (ddd, J=5.9, 7.7, 11.8 Hz, 1H, 6-H$_e$), 2.19 (ddd, J=0.8, 2.0, 19.3 Hz, 1H, 1-H$_e$), 2.33 (dd, J=1.4, 13.2 Hz, 1H, 1-H$_a$), 2.36 (ddd, J=1.2, 1.2, 18.3 Hz, 1H, 3-H$_e$), 2.47 (dddd, J=5.9, 6.8, 12.7, 12.7 Hz, 1H, 5a-H$_{trans}$), 2.59 (m, 1H, 7-H), 3.01 (dddd, J=1.3, 8.2, 8.9, 14.3 Hz, 1H, 4-H$_a$), 3.17 (tdd, J=1.2, 0.6, 18.3 Hz, 1H, 3-H$_a$), 4.19 (q, J=7.1 Hz, 2H, CO$_2$CH_2CH$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.4 (CO$_2$CH$_2$CH_3), 23.0 (CHCH_3), 23.2 (C-5), 33.6 (C-6), 37.9 (C-7), 38.6 (C-8), 41.2 (C-4), 47.2 (C-1), 49.6 (C-3), 53.5 (C-5a), 53.9 (C-8a), 61.0 (CO$_2$CH_2CH$_3$), 65.3 (C-3a), 174.6 (CO_2CH$_2$CH$_3$), 217.0 (C-2); GC–MS (EI, 70 eV) m/z (%) 250 (45) [M$^+$], 207 (15), 205 (25), 204 (87), 195 (18), 193 (93), 192 (32), 177 (100), 161 (31), 148 (39), 141 (91), 139 (59), 135 (39), 133 (49), 119 (38), 113 (52), 109 (94), 107 (50), 100 (64), 95 (53), 93 (60), 91 (69), 81 (50), 69 (37), 67 (58); elemental analysis calcd (%) for $C_{15}H_{22}O_3$ (250.33): C 71.97; H 8.86, found (%): C 72.32; H 8.96.

4.9. (1*R**,4*R**,6*R**,9*S**)-2,11-Dioxatetracyclo-[5.4.1.0^{1,12}.0^{6,12}]dodecan-7-one (26)

A solution of (1*R**,3a*S**)-1-(allyloxy)-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (*rac*-**25**; 31.0 mg, 0.17 mmol) in dry benzene (7 mL) was placed in one irradiation tube (Duran glass), degassed with argon by use of ultrasound for 1 h, and irradiated with a mercury lamp (150 W) for 8 h. The degree of conversion of the starting material was monitored by GC. The solution was concentrated in vacuo and the residue was purified by 10 cm column on silica gel (80:20 cyclohexane/ethyl acetate) to afford **26** (19 mg, 58%) as a colorless oil. IR (film) 3429, 2959, 2926, 1737, 1639, 1408, 1369, 1260, 1168, 1090, 1026, 934, 801 cm^{-1}; NMR experiments: ^{1}H, ^{1}H/^{1}H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY; ^{1}H NMR (C_6D_6, 500 MHz) δ 1.49 (m, 1H, 5-H$_e$), 1.90–1.92 (m, 1H, 9-H$_{cis}$), 1.94–1.97 (m, 1H, 4-H$_{cis}$), 1.98 (dd, J=6.3, 13.1 Hz, 1H, 8-H$_e$), 2.03 (td, J=6.9, 13.8 Hz, 1H, 5-H$_a$), 2.12 (d, J=8.3 Hz, 1H, 6-H$_{trans}$), 2.43 (dd, J=8.5, 13.0 Hz, 1H, 8-H$_a$), 2.87 (td, J=8.6, 16.3 Hz, 1H, 10-H$_a$), 3.52 (dd, J=9.4, 13.6 Hz, 1H, 3-H$_a$), 3.98 (td, J=8.6, 16.1 Hz, 1H, 10-H$_e$), 4.06 (td, J=7.9, 13.6 Hz, 1H, 3-H$_e$), 5.19 (s, 1H, 1-H$_{trans}$); ^{13}C NMR (C_6D_6, 125 MHz) δ 24.7 (C-5), 40.8 (C-4), 41.2 (C-6), 43.2 (C-9), 44.4

(C-8), 60.6 (C-12), 74.0 (C-10), 75.8 (C-3), 112.2 (C-1), 215.4 (C-7); GC–MS (EI, 70 eV) *m/z* (%) 180 (14) [M^+], 150 (49), 122 (100), 107 (43), 104 (22), 92 (33), 90 (58), 80 (31), 79 (93), 77 (51), 67 (61), 66 (70), 65 (54); HRMS (EI) calcd for $C_{10}H_{12}O_3$ *m/z* 180.0787, found *m/z* 180.0786, deviation 0.22 ppm.

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124 (25), 123 (22), 110 (11), 109 (100), 96 (42), 95 (18), 81 (17), 79 (11), 67 (14), 55 (21), 43 (21), 41 (25), 39 (12); HRMS (EI) calcd for $C_{12}H_{20}O$ *m/z* 180.1514, found *m/z* 180.1512, deviation 1.22 ppm.

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