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Photoreactions of Tricyclic α-Cyclopropyl Ketones and Unsaturated Enones – Synthesis of Polyquinanes and Analogous Ring Systems

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Polycyclic systems of both angular and propellane type have been synthesized through intramolecular radical cyclization reactions, by photochemically induced electron transfer of tricyclic α-cyclopropyl ketones or by photolysis of unsaturated enones. In general, tricyclic α-cyclopropyl ketones, each bearing an alkynyl or alkenyl side chain at the position γ to the carbonyl group, were used as starting materials. The reactions resulted in regioselective cleavage of one cyclopropyl bond with formation of tri- to tetracyclic ring systems by a tandem fragmentation-radical/radical anionic reaction pathway. The regioselectivity of the cyclization (*exo*/*endo*) depends on the length of the unsaturated side chain. In cases involving α-cyclopropane derivatives with alkoxymethyl side chains, various non-cyclization processes were observed. In addition, the photoinduced cyclization of the corresponding bicyclic enone derivatives with the same unsaturated side chains afforded tetra- and tricyclic products of propellane type in good yields and with high stereoselectivity.

Introduction

Over the last four decades new methods for the construction of specifically condensed cyclopentanoid natural products (polyquinanes) have been developed.[1–5] Most natural polyquinanes are tricyclic sesquiterpenes and can be classified according to ring fusion as linear, angular or bridged (also called propellanes) triquinanes.[1,4,5] These compounds have been found in plant, marine and microbial sources and often show wideranging biological activity.[5] Consequently, various synthetic methods for the construction of natural and artificial triquinanes involving sequential multistep pathways have been developed.[3–5]

In the 1980s, free-radical cascade cyclization reactions were successfully established as valuable synthetic tools in polyquinane chemistry, with the use of tin hydride becoming the method of choice among them.[6–9] Curran and coworkers explored a general radical-initiated polyolefinic cyclization approach to linear and angular condensed cyclopentanoides,[10–12] whilst an alternative method for efficient generation of radical or radical ion intermediates is one-electron transfer activation.[13] In this case reducing agents such as samarium(II) iodide are usually used.[14–17]

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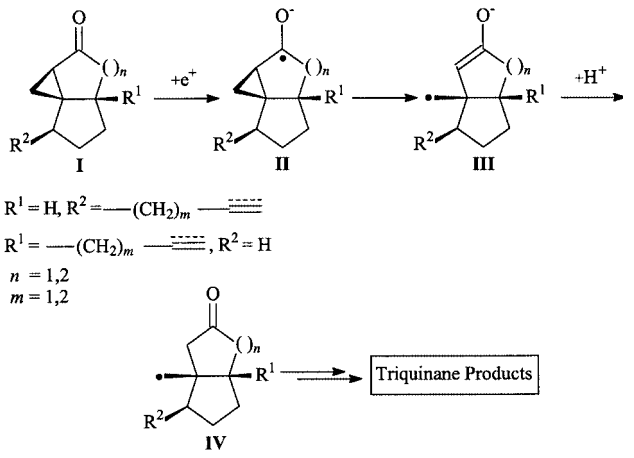
During the last decade, photoinduced electron transfer (PET) has become successfully established in organic synthesis.[18–20] Radical ions can easily be generated by oxidative[21–23] or reductive[24–27] single-electron transfer (SET) from neutral compounds. An alkyne-carbonyl cyclization reaction, for example, was used to prepare bicyclic tertiary cycloalkanols by photoreductively induced electron transfer from triethylamine (TEA) as a strong reducing agent in acetonitrile or by photoionization in pure hexamethylphosphoric triamide (HMPA).[28,29] Furthermore, one of the first examples of a PET-induced cleavage of a cyclobutane ring focused on organic synthesis was reported by Bischof and Mattay.[30] The most recent examples involved reductive PET reactions between α-cyclopropyl ketones and TEA as electron source and/or lithium perchlorate ($LiClO_4$) as additive to provide the ketyl radical anion and the corresponding donor radical cation.[24–27,31] This reaction is based on the well established ring-opening of the cyclopropylcarbinyl radical.[32–34]

In a previous communication[35] we reported a strategy for the synthesis of condensed cyclopentanoids of both angular and propellane type, with use of an intramolecular tandem fragmentation-radical cyclization promoted by reductive PET as key step. When starting from tricyclic α-cyclopropyl ketones with unsaturated side chains there are a number of necessary preconditions: (i) the cyclopropyl group and the unsaturated substituent units have to be *cis* to each other, and (ii) the side chain has to be of suitable length and in the position α to the cyclopropane unit.

Our concept of the tandem fragmentation-cyclization is illustrated for tricyclic alkanones (n = 1,2) with olefinic or acetylenic side substituents (m = 1,2) in Scheme 1. Irradia-

tion at a suitable wavelength produces the ketyl radical anion **II** after one-electron reduction of substrate (cyclopropyl ketone **I**). In polar solvents such as acetonitrile, back electron transfer is suppressed, favouring a subsequent cyclopropylcarbinyl-homoallyl rearrangement to the distonic γ-keto radical anion **III**, which – after protonation to afford the neutral radical **IV** – undergoes cyclization to the triquinane products.



Scheme 1. Formation of γ-keto radical anions by photoinduced electron transfer (PET).

The tricyclic cyclopropyl ketones were synthesized from the corresponding α-monosubstituted cyclopentanones by cyclopropanation. Depending on the position of the unsaturated side chain, either propellanes (pathway A) or angular triquinanes (pathway B) are accessible. In either case both *exo* and *endo* ring-closure reactions are possible (Scheme 2).

In this article we focus on the synthetic aspects of the novel PET reductive cyclization reactions of tricyclic cyclopropyl ketones functionalized with unsaturated side chains, to afford triquinane compounds of angular or propellane type. The influence of the substituents on the regiochemistry and stereochemistry of the cyclization step is investigated.

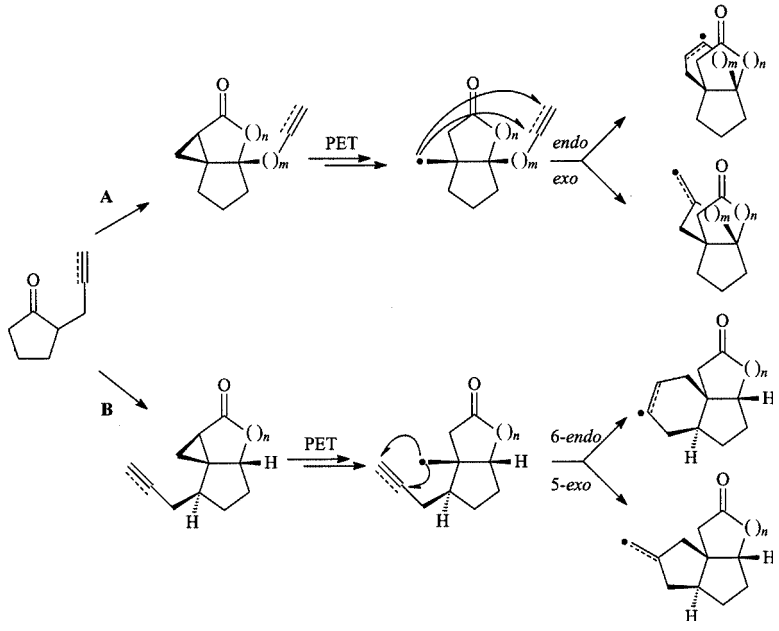
Results and Discussion

Synthesis of the Starting Materials:

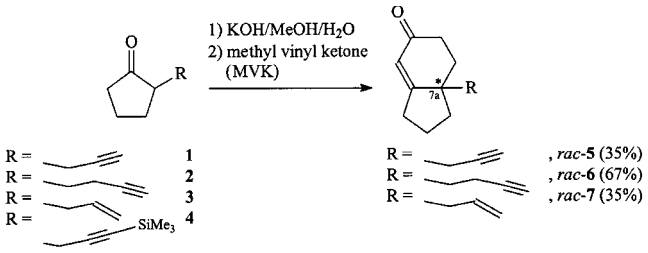
Following our strategy for the formation of bridged triquinane systems incorporating propellane structures, we started from bicyclo[4.3.0]nonenone derivatives possessing either alkynyl or an alkenyl side chains at their bridged carbon centres (7a). The hexahydroindenones **5**–**7** were synthesized from the corresponding α-monosubstituted cyclopentanones **1**–**4** by the well known Robinson annulation procedure (Scheme 3).[36–38] The extent of conversion of the starting materials was monitored by GC and/or GC-MS.

In the case of the trimethylsilylpropargyl-substituted substrate **4** we obtained the same product (**5**, in 18% yield) as we had from **1**. As Michael acceptor we generally used 1.15 molar equivalents of methyl vinyl ketone (MVK). The starting materials **1**–**4** were synthesized by known procedures.[39–42]

The synthesis of the hexahydroindenone derivatives **11** and **12** with longer heteroatom side chains of alkoxymethyl type is shown in Scheme 4.



Scheme 2. Reductive PET cyclization reactions of unsaturated α-cyclopropyl ketones to afford the corresponding propellane (pathway A) or angular triquinane systems (pathway B).



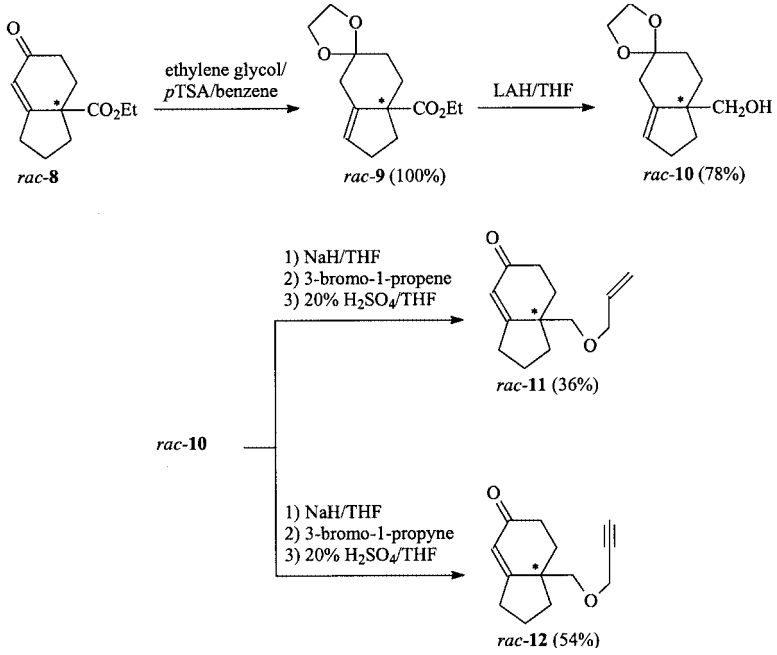
Scheme 3. Synthesis of the unsaturated indenone derivatives.

We started from ethyl hexahydroindenonecarboxylate **8**, which was synthesized in good yield by a known two-step procedure.[43–45] During ketalization,[46] **9** is formed with simultaneous migration of the double bond, as has also been observed in other systems.[47] It is known that substituents in the bicyclic systems can influence the location of the double bond in the formed ketal structure.[48] The ketal product **9** was purified by fast column chromatography and characterized by spectroscopic analysis (one- and two-dimensional NMR). A similar ketal product with a propargyl side chain was synthesized by the same procedure and the migration of the double bond into the β,γ-position was confirmed by X-ray analysis.[49] Reduction of the ethyl carboxylate side chain of **9** was performed under standard conditions as shown in Scheme 4. The syntheses of the allyl- and propynyloxymethyl-substituted hexahydroindenones **11** and **12** were carried out by alkylation with allyl and propargyl bromides.[50]

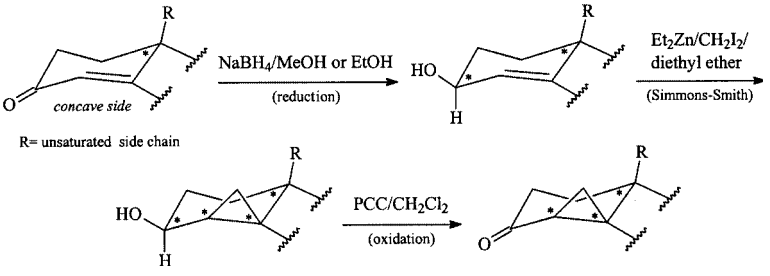
A direct cyclopropanization of **5** to **15** by the Corey method[51] failed due to preferred oxirane formation,[52] so we used the strategy shown in Scheme 5: reduction of the carbonyl group followed by stereoselective Simmons–Smith cyclopropanation.[53] The carbonyl group was regenerated by oxidation with pyridinium chlorochromate (PCC).

Although this procedure involves additional steps, the overall stereoselectivity is even higher, due to the directing effect of the secondary alcohol group. In this context the selective reduction of the enones **5**–**7**, **11** and **12** from the concave side, preferentially affording alcohols with the hydroxy group in the convex position (*cis* to the unsaturated side chain), is advantageous (Table 1).

In most cases the products were isolated by column chromatography on silica gel (**16**, **18**–**19** and **22**–**27**) or sim-

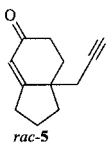
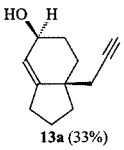
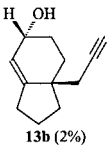
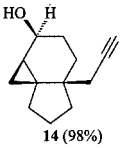
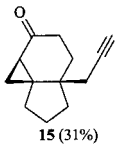
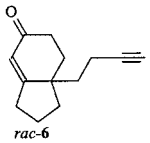
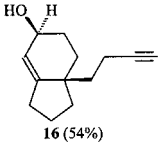
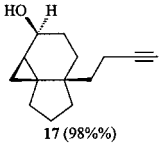
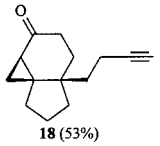
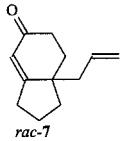
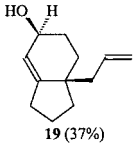
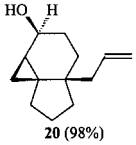
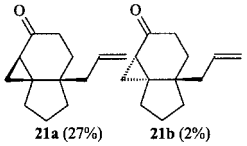
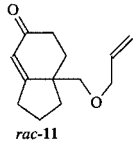
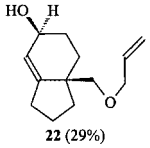
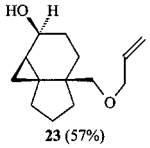
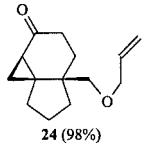
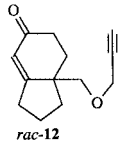
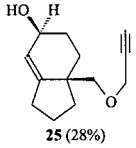
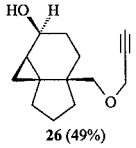
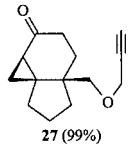


Scheme 4. Synthesis of the alkoxymethyl-substituted indenone derivatives.



Scheme 5. Synthetic strategy for the diastereoselective synthesis of α-cyclopropyl-substituted indenones.

Table 1. Diastereoselectively synthesized α-cyclopropyl indenones.

Indenone	Indenol		α-Cyclopropyl indenol	α-Cyclopropyl indenone
 *rac*-**5**	 **13a** (33%)	 **13b** (2%)	 **14** (98%)	 **15** (31%)
 *rac*-**6**	 **16** (54%)		 **17** (98%%)	 **18** (53%)
 *rac*-**7**	 **19** (37%)		 **20** (98%)	 **21a** (27%) **21b** (2%)
 *rac*-**11**	 **22** (29%)		 **23** (57%)	 **24** (98%)
 *rac*-**12**	 **25** (28%)		 **26** (49%)	 **27** (99%)

ply by filtration by flash chromatography (**14**, **17** and **20**). Compound **15** was first filtered through silica gel and subsequently purified by HPLC. The hexahydroindenol derivatives **13a/13b** and α-cyclopropyl octahydroindenone products **21a/21b** were separated by HPLC (see also Table 1). The structure determination of all products was accomplished by spectroscopic analysis, through the use of one- and two-dimensional NMR spectroscopy. Additionally, **18** was confirmed by X-ray crystal structure analysis[54] (Figure 1) and shows the same relative configuration as **15**, the X-ray structure of which had already been determined earlier.[35]

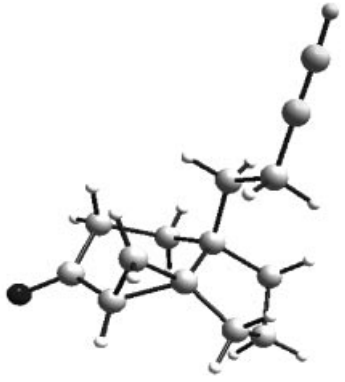
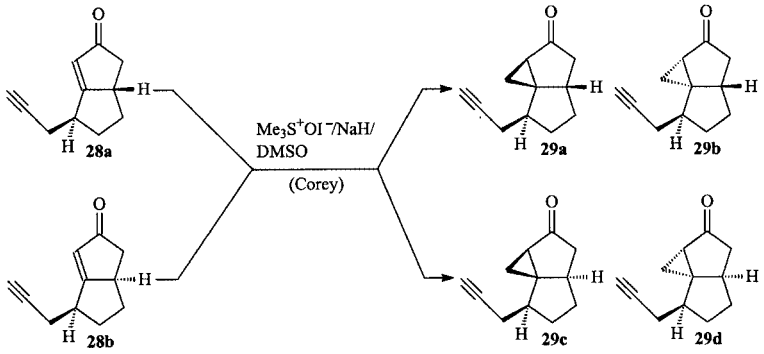


Figure 1. Structure of **18** in the crystalline state.

To search for possibilities for the formation of angular triquinanes by our strategy we chose the bicyclo[3.3.0]octenone pathway. The bicyclooctenone derivatives **28a** and **28b**, each with a propargyl side chain in the position γ to the carbonyl group were synthesized as an inseparable 94:6 mixture of two diastereomers (17% overall yield) by well known procedures.[35,50] The mixture of bicyclic octenones **28a/28b** was transformed into the corresponding cyclopropanes **29a**–**d** by Corey's method,[51] with sodium hydride/trimethylsulfoxonium iodide (1.37 equivalents) in dry dimethylsulfoxide (DMSO). The results are shown in Scheme 6.

The resulting mixture of four diastereoisomers was purified by column chromatography, giving a 65% combined



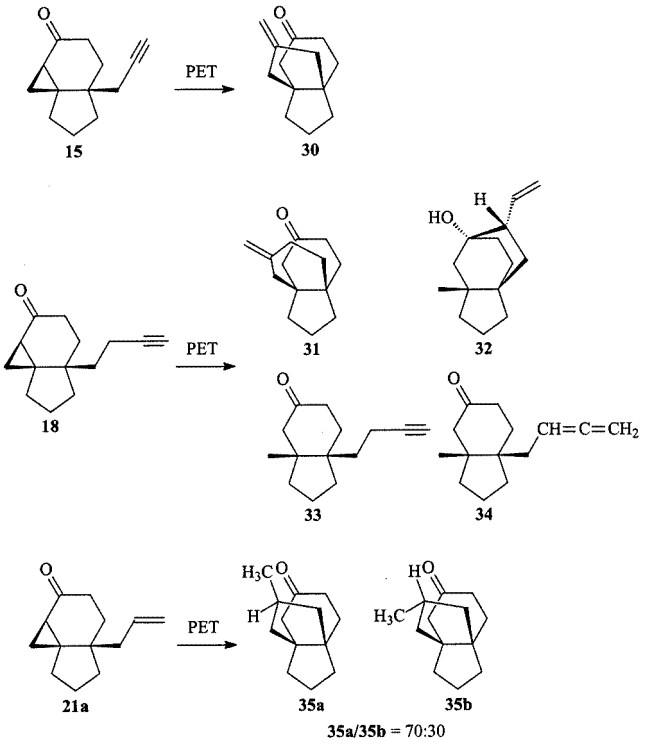
Scheme 6. Diastereoselective cyclopropanation of the diastereomeric mixture **28a/28b** to form the corresponding α-cyclopropyl bicyclo[3.3.0]-octanone derivatives **29a**–**d**.

isolated yield. The product ratio was determined by GC of the isolated mixture as 81:6:8:5 (**29a/29b/29c/29d**). The major *cis* diastereomeric product **29a** was separated from the mixture in 40% yield by preparative HPLC. Its structure and stereochemistry were assigned by modern spectroscopic NMR techniques (one- and two-dimensional NMR: COSY, HMQC and HMBC) and qualitative NOESY. From this it was deduced that **29a** was formed from the major diastereomer **28a** by a Michael-type addition of the sulfoxonium ylide from the convex side of the bicyclic system (*cis* to the propargyl side chain). The other diastereoisomers were detected as an inseparable mixture by GC/GC-MS (EI and CI).

PET Cyclizations to Provide Propellanes and Angular Triquinanes

The proposed tandem fragmentation-cyclization under reductive PET conditions was accomplished with tricyclic α-cyclopropyl ketones **15**, **18**, **21a** and **29a**, which gave propellanes or angular triquinanes, depending on the position of the unsaturated side chain.

A deoxygenated solution (usually 0.04 M) of the particular α-cyclopropyl ketone in acetonitrile was irradiated in the presence of five equivalents of triethylamine (TEA) 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). The degree of conversion of the starting material was monitored by GC and/or GC-MS. In previous studies[35] we had found experimentally that further addition of one equivalent of lithium perchlorate ($LiClO_4$) provided better yields of the cyclized products and furthermore reduced the reaction time.[35,55] No changes in product distribution were found under these conditions. The mechanistic details of the solvent and salt effects with various type of ion pairs have been described by us previously.[56] In accordance with the described advantages,[24,25] we used a variant with one equivalent of $LiClO_4$ as an additive in the acetonitrile solution of the α-cyclopropyl ketone and five equivalents of TEA under standard PET conditions in the synthesis of polycyclic compounds of both angular triquinane and propellane type. The results of the PET reductive cyclization reactions of the α-cyclopropyl indenones **15**, **18** and **21a** are shown in Scheme 7 and Table 2.



Scheme 7. Tandem fragmentation-cyclization reactions predominantly affording propellanes.

The results can be summarized as follows:
i) The best results are obtained with **15** and confirm the importance of a suitable chain length of the unsaturated substituent, resulting in a preferred 5-*exo* cyclization.
ii) A longer chain dramatically reduces the yield (e.g., as shown for 6-*exo* cyclization of **18**).
iii) Alkynyl is preferred to alkenyl (cf. **15** and **21a**).
iv) Irradiation at 254 nm gives better yields (74% rather than 46% for **15**).

We also studied alternative methods such as the use of samarium(II) iodide (SmI_2).[57] However, as already shown for other unsaturated cyclopropyl ketones,[25] this procedure gave lower yields than the PET method: **30** was formed

Table 2. Isolated photoproducts of reductive PET reactions (see Scheme 7).

Entry	PET conditions	Time [h]	hν [nm]	Product	Yield [%]
15	5 equiv. Et_3N/1 equiv. $LiClO_4$ MeCN	2	254	**30**	74
15	5 equiv. Et_3N/1 equiv. $LiClO_4$ MeCN	15	300	**30**	46
18	15 equiv. Et_3N/1 equiv. $LiClO_4$ MeCN	3	254	**31**	7
				32	7
				33	3
18	5 equiv. Et_3N/1 equiv. $LiClO_4$ MeCN	3	254	**31**	
				34	29[a,c]
				33	17
21a	5 equiv. Et_3N/1 equiv. $LiClO_4$ MeCN	3	254	**35a**	34[b,c]
				35b	

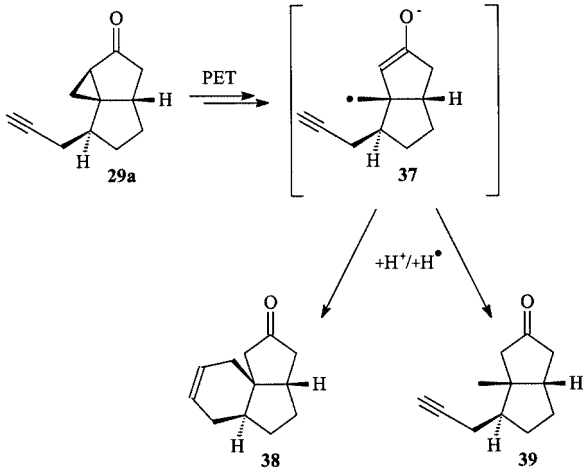
[a] Combined isolated yield of a 2:1 mixture of **34** and **31**. [b] Combined isolated yield of a mixture of **35a/b**. [c] Product ratio detected by GC in the mixture after purification.

from **15** in only 35% yield with SmI_2. The proposed mechanism of the PET cyclization of **15** is shown in Scheme 8. For saturation of the radical **36** we assume a hydrogen atom transfer from a suitable donor (e.g., TEA and/or solvent).[25]

The PET reaction of **18** shows some special features: besides the propellane **31**, which is probably formed by the usual PET-cyclization in analogy to **30** (Scheme 8), the non-cyclized product **33** and some unusual products (**32** and **34**) are also formed. At this stage we can only speculate about a mechanism of the reactions giving the latter products: **34** is a tautomer of **33** and may be formed through a radical-initiated isomerization after generation of the γ-keto radical, whilst **32** can only be formed with simultaneous reduction of the triple bond to the double bond. The mechanistic details of this process are not known so far. The necessity of a high excess of triethylamine as electron donor may indicate the involvement of PET processes (e.g., via the ketyl radical anions of **33** or **34**). The structural analysis of **31** and **33** was carried out by one- and two-dimensional NMR as well as by mass spectroscopy, including HRMS (see also the Experimental Section). For the structure determination of the tricyclic product **32** we used heteronuclear correlation NMR (HMQC and HMBC) and homonuclear $^1H/^1H$ NMR (COSY) in combination with ^1H, ^{13}C and DEPT NMR methods. Additionally, the stereochemistry of **32** was assigned by use of qualitative NOESY spectroscopy supported by MMFF94 force field conformational analysis[58] in combination with ^1H NMR analysis of the vicinal coupling constants and the chemical shifts. The calculated geometry of the lowest-energy conformer of tricyclic compound **32** is presented in Figure 2.

Figure 2. Calculated geometry (MMFF94) of **32**.[58]

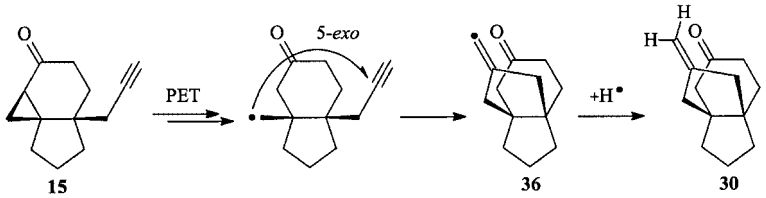
Reductive PET treatment of the α-cyclopropyl ketone **29a** in acetonitrile with TEA or TEA/$LiClO_4$ resulted in the formation of two products: the 6-*endo* cyclized compound **38** and the non-cyclized minor product **39** (Scheme 9).



Scheme 9. Reductive PET reaction giving the angular triquinane **38** and the bicyclic product **39**.

The products were determined by spectroscopic analysis (1D and 2D NMR) and the stereochemistry was assigned by qualitative NOESY in combination with careful analysis of the ^1H NMR coupling constants.

In this case we also observed that the addition of $LiClO_4$ reduced the reaction time by a factor of four and, further more, that irradiation at 254 nm increased the yield of the major product **38** by up to 40% (Table 3). As already discussed above, this is attributed to the special salt effect of $LiClO_4$ and to TEA as the light-absorbing species at 254 nm. The mechanism of this reaction is shown in Scheme 9. The initially formed ketyl radical anion of **29a**



Scheme 8. Regioselective 5-*exo* ring-closure reaction of **15** to give the propellane **30**.

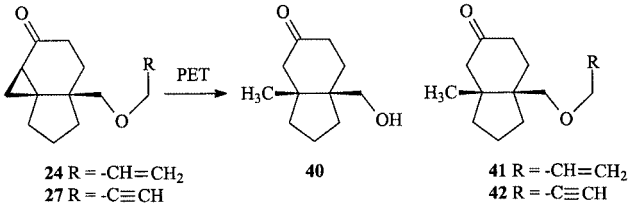
spontaneously opens to form the new distonic γ-radical anion **37**, which cyclizes to give **38** in a 6-*endo* fashion after protonation and tautomerization. Simple hydrogen saturation of the γ-radical provides the non-cyclized product **39**. Interestingly, only the 6-*endo* cyclized product **38** was formed from radical **37**, although, according to the Baldwin rules,[59] 5-*exo* cyclization should be more favoured. Preliminary quantum chemical calculations for the neutral cyclized 5-*exo* and 6-*endo* radicals (results from **37**) indicate that 6-*endo* is preferred both energetically and kinetically (by calculation of the transition state).[58,60] An analogous preference for 6-*endo* rather than 5-*exo* has also been observed in radical-type cascade reactions of alkynyl-substituted siloxycyclopropane derivatives.[23]

Table 3. Product yields from reductive reactions of **29a** depending on reaction conditions.

Entry	PET conditions	Time [h]	hν [nm]	Product	Yield [%]
29a	5 equiv. Et_3N/1 equiv. $LiClO_4$	3	254	**38**	40
	MeCN			**39**	3
29a	5 equiv. Et_3N/1 equiv. $LiClO_4$	5	300	**38**	29
	MeCN			**39**	3
29a	5 equiv. Et_3N/MeCN	21	300	**38**	29
				39	3

Limitation of PET Tandem Fragmentation-Cyclizations – Side Reactions of α-Cyclopropane Derivatives 24 and 27 and Alternative Photoinduced Pathway

To investigate the potential of this PET tandem procedure for the synthesis of heterocyclic propellanes we used the α-cyclopropyl indenone derivatives **24** and **27** as starting materials. However, both yielded two products in low yields rather than the expected propellanes after complete conversion of the starting materials under our general PET conditions (Scheme 10 and Table 4).



Scheme 10. Photolysis of α-cyclopropyl indenones **24** and **27** under reductive PET conditions.

Table 4. Photoproducts from **24** and **27**.

Entry	PET conditions	Time [h]	hν [nm]	Product	Yield [%]
24	5 equiv. Et_3N/1 equiv. $LiClO_4$	7	254	**40**	23[a]
	MeCN			**41**	12[a]
27	5 equiv. Et_3N/1 equiv. $LiClO_4$	4	254	**40**	44
	MeCN			**42**	11

[a] Isolated yield was determined by GC with reference to starting material consumed.

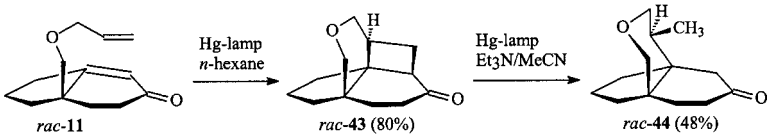
Beside the non-cyclized products **41** and **42**, the hydroxymethyl indenone derivative **40** was formed as the major product (Scheme 10). The formation of **41** and **42** can be explained in terms of simple hydrogen saturation of the corresponding radical intermediate **III** (see Scheme 1) in analogy to the formation of the non-cyclized product **33** (see also Scheme 7). For the formation of **40** we assume hydrogen abstraction from the position α to the ether substituent as the initiating step of this cleavage process. The products from **27** (**40** and **42**) were isolated by column chromatography and their structures were assigned by NMR techniques (HMQC and NOESY). In the case of **24** the observed products **40** and **41** were purified by column chromatography and the product ratio was determined by GC as 2:1 (**40**:**41**). Compound **41** was assigned only by GC-MS (EI) due to the small amounts of material in comparison with **42**.

We also investigated an alternative pathway for the synthesis of heterocyclic propellanes by a strategy previously developed by us.[27] The bicyclic enone derivative **11** was thus first photolysed to provide the intramolecular [2+2] cycloaddition product **43** in 80% yield. In the following step, **43** was cleaved to give the propellane **44** under reductive PET conditions in 48% yield (Scheme 11). Note that the high stereoselectivity of the newly formed methyl group is controlled by the preceding [2+2] cycloaddition (**11**→**43**).

The structures of **43** and **44** were determined from spectroscopic data (one- and two-dimensional NMR: COSY and HMQC) as well as by NOESY.

Conclusions

We have demonstrated that reductive PET-induced tandem fragmentation-cyclization reactions of α-cyclopropyl-substituted ketones can be used for the construction of novel polycyclic structures. Depending on the position of the unsaturated side chain in the tricyclic α-cyclopropyl skeleton, either angular triquinanes or propellanes are ac-



Scheme 11. Photochemical pathway for the regioselective synthesis of propellane structures *rac*-**44**.

cessible. For the synthesis of the α-cyclopropyl indenone derivatives with various side chains we used a general procedure that gave the desired starting materials with high diastereoselectivity. The PET reactions of the α-cyclopropyl ketones were carried out under standard reductive conditions, mostly by addition of $LiClO_4$, and provided the corresponding cyclized products in good yields and in highly regioselective manner, especially with substrate molecules with three or four carbon atoms in the unsaturated substituent unit. In general, five- or six-membered rings were formed by *exo*-cyclizations. In cases with α-cyclopropyl ketones with longer or heteroatom side chains, side reactions became the major process.

However, heterocyclic propellanes such as **44** are accessible from enones (e.g., **11**) by an alternative procedure, first by [2+2] cycloaddition and second by cleavage of the cyclobutane by reductive PET.

Experimental Section

General Remarks: ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 K with Bruker AM 250 or Bruker DRX 500 spectrometers. 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). IR spectra were recorded on a Perkin–Elmer 841 or a Matson Genesis Series ATT FT-IR spectrometer. 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, to 400 °C ± 0.8 °C). HRMS were recorded on a Micromass VG Autospec X (vacuum Generators, Manchester) or a Bruker FT-ICR APEX III (7.0 T). GC/MS were recorded on a Schimadzu GC-17A/MSQP 5050A fitted 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 (Schimadzu); carrier gas helium (pressure 0.95 bar). GC analysis were carried out with a Schimadzu GC-17A/ver. 3 (FID detector and Class VP 4.2 software) or a Schimadzu GC-2010 instrument fitted with a Hewlett–Packard HP-5MS capillary column (25 m, 0.2 mm, 0.33 μm); carrier gas nitrogen (pressure 1.0 bar). Preparative GC was performed on a Hewlett–Packard 5890 Series II chromatograph with use of an injector with automatic fraction collector (Gerstel) and autosampler (Hewlett–Packard 7673) with a Hewlett–Packard HP5 capillary column (30 m, 0.53 mm, 5.00 μm); carrier gas hydrogen (pressure 0.35–0.50 bar). HPLC was performed on an silica gel column (Merck LiChrospher Si 60–7, 250 × 20 mm; flow 10 mL min^{-1}) with use of a Kontron (420) or Merck pump (L-6000) and an RI-detector (Bischoff RI 8110). 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); aluminium oxide (0.20 mm) ALOX N/UV_{254} (Macherey & Nagel). Column chromatography was performed on silica gel MN-60 (40–63 μm or 63–200 μm; Macherey & Nagel). Photochemical reactions were performed in a Rayonet RPR-100 photochemical chamber reactor (Southern New England Ultraviolet Company, Brandford) fitted with 16 lamps: either RPR-2537 Å (emission maximum at 254 nm at half band width, each lamp 35 W) or RPR-3000 Å (emission maximum at 300 nm half band width, each lamp 21 W) and merry-go-round inset in quartz (10 mL volume, 1 cm diameter) or Duran (12 mL volume, 1 cm diameter) tubes. Solutions were deoxygenated with argon and use of an ultrasound bath (Bandelin Sonorex Super RK 255 H, Bandelin, Berlin) before irradiation. All reactions were carried out in dry solvents, mostly under argon. Starting materials and solvents were purified and/or distilled before use.[61] Compounds **1**–**4**,[41,42] **8**[43–45] and **28a/28b**[35,62,63] were synthesized by known procedures.

General Procedure A (Synthesis of the Alkyl-substituted Indenones by Robinson Annelation): A defined amount of finely pulverized potassium hydroxide (1.45 to 1.70 molar equivalents relative to the α-monosubstituted cyclopentanone) was dissolved in a methanol/water mixture (10:1; 1 mL per 1.10 mmol KOH). The solution was stirred until complete dissolution of KOH and was slowly cooled to –2 to 0 °C (ice/acetone cooling). A solution of the appropriate α-monosubstituted cyclopentanone in methanol (about 6–10 mL per 1.00 mmol) was added at this temperature over 10–15 min. The reaction mixture was cooled to –10 to –15 °C with ice/acetone/dry ice, and a solution of 1.15 molar equivalents methyl vinyl ketone (≈85% or 100%) in methanol was added dropwise. After stirring for 1 h the reaction mixture was allowed to warm slowly to room temperature, stirred for 3–5 days, and heated under reflux for 5–7 h (GC monitoring). The cooled solution was added to a mixture of HCl (2 N)/ice (2:1), and, depending on the amounts extracted, six times with Et_2O (100–300 mL). If necessary, the reaction mixture could be divided into two portions prior to extraction. The combined organic layers were washed with water (2 × 40 mL) and dried with Na_2SO_4, and the solvents were removed by evaporation. The remaining residue was purified either by column chromatography on silica gel or by distillation in vacuo. If necessary, the products could be additionally purified by Kugelrohr distillation (0.05 mbar for 50 min).

7a-Prop-2′-ynyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (*rac*-5): This compound was produced by GP A: 2-prop-2′-ynylcyclopentanone (**1**; 20.0 g, 160 mmol) was treated with methyl vinyl ketone (≈85%; 15.7 g, 184 mmol). Chromatography on silica gel (cyclohexane/ethyl acetate 85:15, R_f = 0.25) and Kugelrohr distillation afforded *rac*-**5** (9.95 g, 35%) as a colourless oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC. ^{1}H NMR (500 MHz, $CDCl_3$, ref. $CHCl_3$): δ = 1.40 (dddd, J = 1.88, 3.77, 10.72, 15.51 Hz, 1 H, 1-H), 1.73 (dddd, J = 1.41, 3.54, 6.95, 12.81 Hz, 1 H, 7-H), 1.82–1.89 (m, 2 H, 2-H), 2.02 (t, J = 2.67 Hz, 1 H, 3′-H), 2.22 (ddd, J = 3.22, 6.24, 13.05 Hz, 1 H, 1-H), 2.30 (dd, J = 1.35, 5.17 Hz, 1 H, 1′-H), 2.32 (dd, J = 1.49, 2.59 Hz, 1 H, 1′-H), 2.35 (dddd, J = 0.87, 2.59, 5.69, 16.33 Hz, 1 H, 6-H), 2.43 (dd, J = 1.88, 5.34 Hz, 1 H, 7-H), 2.45–2.50 (m, 1 H, 6-H), 2.51–2.55 (m, 1 H 3-H), 2.66 (dddd, J = 2.20, 6.32, 7.81, 19.51 Hz, 1 H, 3-H), 5.82 (t, J = 2.28 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, ref. $CHCl_3$): δ = 20.93 (C-2), 23.91 (C-1′), 30.72 (C-3), 32.52 (C-7), 33.35 (C-6), 37.34 (C-1), 45.70 (C-7a), 70.73 (C-3′), 80.57 (C-2′), 122.63 (C-4), 175.55 (C-3a), 199.08 (C-5) ppm. IR (film): $\tilde{\nu}$ = 3294, 2954, 2869, 2117, 1739, 1668, 1453, 1354, 1295, 1177, 1093, 930, 859 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 175 (7) $[M + 1]^+$, 174 (22) $[M]^+$, 173 (13), 159 (11), 146 (46), 135 (47), 131 (24), 117 (88), 115 (26), 107 (96), 105 (15), 104 (12), 93 (60), 92 (16), 91 (93), 79 (100), 78 (31), 77 (69), 67 (12), 65 (28), 55 (11), 53 (20), 51 (22), 41 (25), 39 (52). GC-MS (CI, isobutane): m/z (%) = 175 (100) $[M + H]^+$, 173 (2), 157 (3). HRMS: calcd. for $C_{12}H_{14}O$ $[M]^+$ m/z = 174.1045; found 174.1037; deviation, 2.90 ppm; elemental analysis calcd. (%) for $C_{12}H_{14}O$ (174.20): C 82.72, H 8.10; found C 82.23, H 8.23.

7a-But-3′-ynyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (*rac*-6): :This compound was produced by GP A: 2-but-3′-ynylcyclopentanone (**2**; 3.18 g, 23.0 mmol) was treated with methyl vinyl ketone (100%; 2.03 g, 26.5 mmol). Chromatography on silica gel (cyclohexane/ethyl acetate 90:10, R_f = 0.08) gave *rac*-**6** (2.93 g, 67%) as a yellow oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.69 (dddd, J = 1.72,

3.96, 10.80, 21.44 Hz, 1 H, 1-H), 1.09 (ddt, *J* = 7.57, 12.15, 1.49 Hz, 1 H, 7-H), 1.17–1.24 (m, 2 H, 2-H), 1.19 (dd, *J* = 8.97, 10.64 Hz, 1 H, 1′-H), 1.38 (dd, *J* = 9.58, 21.33 Hz, 1 H, 1-H), 1.38 (dd, *J* = 8.77, 9.02 Hz, 1 H, 1′-H), 1.57 (ddd, *J* = 2.67, 4.55, 13.54 Hz, 1 H, 7-H), 1.72 (ddd, *J* = 1.89, 6.36, 12.85 Hz, 1 H, 2′-H), 1.73 (t, *J* = 1.57 Hz, 1 H, 4′-H), 1.75 (ddd, *J* = 1.67, 7.81, 12.75 Hz, 1 H, 2′-H), 1.82 (dddd, *J* = 2.11, 9.62, 11.68, 22.49 Hz, 1 H, 3-H), 1.95–2.03 (m, 1 H, 3-H), 2.10 (dd, *J* = 7.34, 12.17 Hz, 1 H, 6-H), 2.11 (dd, *J* = 4.63, 9.16 Hz, 1 H, 6-H), 5.74 (t, *J* = 2.04 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 14.39 (C-2′), 21.08 (C-2), 30.38 (C-3), 31.66 (C-1′), 31.73 (C-7), 33.49 (C-6), 36.18 (C-1), 45.26 (C-7a), 69.23 (C-4′), 83.86 (C-3′), 122.20 (C-4), 174.99 (C-3a), 196.77 (C-5) ppm. IR (film): $\tilde{\nu}$ = 3282, 2935, 2869, 2117, 1735, 1673, 1454, 1254, 1164, 1122 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 188 (12) $[M]^+$, 173 (4), 160 (78), 159 (23), 145 (12), 132 (41), 131 (55), 121 (75), 118 (13), 117 (68), 107 (27), 105 (15), 104 (17), 94 (21), 93 (30), 91 (70), 81 (15), 79 (84), 78 (27), 77 (97), 67 (21), 66 (15), 65 (60), 63 (23), 57 (18), 55 (38), 53 (56), 52 (25), 51 (38), 50 (17), 41 (61), 39 (100). HRMS: calcd. for $C_{13}H_{16}O$ $[M]^+$ *m*/*z* = 188.1201; found 188.1202; deviation, 0.21 ppm; elemental analysis calcd. (%) for $C_{13}H_{16}O$ (188.26): C 82.94, H 8.57; found C 83.00, H 8.57.

7a-Allyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (*rac*-7): This compound was produced by GP A: 2-prop-2′-enylcyclopentanone (**3**; 6.04 g, 49.0 mmol) was treated with methyl vinyl ketone (≈85%; 4.53 g, 53.0 mmol). Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 90:10, R_f = 0.22) afforded *rac*-**7** (3.00 g, 35%) as a colourless oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.81 (ddd, *J* = 1.72, 8.17, 11.74 Hz, 1 H, 1-H), 1.26 (ddd, *J* = 1.57, 5.57, 13.68 Hz, 1 H, 2-H), 1.28 (ddd, *J* = 2.12, 4.43, 8.89 Hz, 1 H, 3-H), 1.34 (ddd, *J* = 2.51, 7.46, 20.57 Hz, 1 H, 7-H), 1.59 (ddd, *J* = 2.75, 7.11, 12.72 Hz, 1 H, 1-H), 1.74 (dd, *J* = 2.19, 5.22 Hz, 1 H, 6-H), 1.77 (dd, *J* = 2.20, 5.10 Hz, 1 H, 6-H), 1.84 (ddd, *J* = 1.26, 7.23, 14.09 Hz, 1 H, 3-H), 1.91 (dtdt, *J* = 2.12, 1.96, 18.92, 2.20 Hz, 1 H, 7-H), 2.12 (m, 1 H, 2-H), 2.20 (ddd, *J* = 2.36, 5.61, 17.88 Hz, 1 H, 1′-H), 2.27 (ddd, *J* = 5.18, 13.98, 17.80 Hz, 1 H, 1′-H), 4.83 (ddd, *J* = 1.73, 3.53, 16.91 Hz, 1 H, 3′-H), 4.92 (dd, *J* = 2.36, 10.06 Hz, 1 H, 3′-H), 5.43 (dtd, *J* = 10.09, 15.87, 17.07 Hz, 1 H, 2′-H), 5.81 (t, *J* = 2.12 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 21.04 (C-2), 30.52 (C-3), 32.43 (C-7)*, 33.43 (C-6)*, 36.64 (C-1′), 37.69 (C-1), 45.53 (C-7a), 117.68 (C-3′), 122.27 (C-4), 134.27 (C-2′), 175.17 (C-3a), 196.94 (C-5) ppm; *) signal assignments are mutually interchangeable. IR (film): $\tilde{\nu}$ = 2950, 2865, 1666, 1454, 1268, 1214, 1184, 998 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 176 (30) $[M]^+$, 158 (6), 135 (51), 134 (31), 133 (8), 119 (7), 107 (87), 105 (12), 93 (52), 92 (17), 91 (48), 79 (100), 78 (19), 77 (45), 67 (23), 66 (10), 65 (36), 55 (24), 53 (30), 51 (30), 41 (50), 39 (56). HRMS: calcd. for $C_{12}H_{16}O$ $[M]^+$ *m*/*z* = 176.1201; found 176.1208; deviation, 4.03 ppm; elemental analysis calcd. (%) for $C_{12}H_{16}O$ (176.25): C 81.77, H 9.15; found C 81.83, H 9.16.

Ethyl 2′,4′,6′,7′-Tetrahydrospiro[1,3-dioxolan-2,5′-indene]-7a′(1′*H*)-carboxylate[40] (*rac*-9): Ethyl 6-oxo-1,2,3,4,5,6-hexahydro-3a*H*-indene-3a-carboxylate[37–39] (*rac*-**8**; 3.57 g, 18.0 mmol) in benzene (11 mL) was added under argon to a solution of *p*-toluenesulfonic acid (390 mg, 2.00 mmol, catalytic quantity) in benzene (45 mL) in a dry apparatus. Dry ethylene glycol (6.20 g, 100 mmol) in benzene (5 mL) was added, and the reaction mixture was heated under reflux for 2 h. The water formed was removed by means of a dropping funnel filled with freshly activated molecular sieves (4 Å). The solution was cooled to room temperature and washed successively with saturated aq. $NaHCO_3$ solution (10 mL) and water (10 mL). The aqueous layer was separated and extracted three times with Et_2O (100 mL). The combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. Column filtration through silica gel (EtOAc) afforded *rac*-**9** (4.60 g, 100%) as an orange oil. The product can be further used without additional purification. NMR experiments: ^{1}H, ^{13}C, ^{13}C-DEPT. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.88 (t, *J* = 7.14 Hz, 3 H, O–CH_2CH_3), 1.69–1.82 (m, 3 H, 2×6′-H and 7′-H), 2.11 (dt, *J* = 4.24, 13.90 Hz, 1 H, 1′-H), 2.18 (dqdq, *J* = 2.43, 9.64, 2.28, 9.42 Hz, 1 H, 7′-H), 2.33 (ddd, *J* = 2.43, 8.44, 13.99 Hz, 1 H, 1′-H), 2.44 (dddd, *J* = 1.88, 4.48, 8.42, 24.01 Hz, 1 H, 2′-H), 2.56 (dt, *J* = 3.37, 12.64 Hz, 1 H, 2′-H), 2.65 (dd, *J* = 2.67, 13.78 Hz, 1 H, 4′-H), 2.75 (dtddd, *J* = 4.55, 13.77, 2.35, 6.91, 13.78 Hz, 1 H, 4′-H), 3.42–3.55 (m, 4 H, O–CH_2CH_2–O), 3.91 (q, *J* = 7.14 Hz, 2 H, O–CH_2CH_3), 5.48 (dd, *J* = 2.52, 4.91 Hz, 1 H, 3′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 14.18 (O–CH_2CH_3), 31.76 (C-7′), 33.74 (C-2′), 34.38 (C-6′), 37.32 (C-1′), 38.19 (C-4′), 57.12 (C-7a′), 60.34 (O–CH_2CH_3), 64.27 (C-5)*, 64.45 (C-4)*, 109.42 (C-2/5′), 126.82 (C-3′), 141.59 (C-3′), 175.45 (C-1) ppm; *) signal assignments are mutually interchangeable. IR (film): $\tilde{\nu}$ = 2955, 1724, 1666, 1578, 1445, 1363, 1256, 1181, 1105, 1082, 1030, 1007 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 252 (5) $[M]^+$, 179 (24), 178 (13), 135 (14), 117 (9), 105 (7), 100 (32), 99 (100), 91 (23), 86 (16), 77 (16), 55 (63).

2′,4′,6′,7′-Tetrahydrospiro[1,3-dioxolan-2,5′-inden]-7a′-(1′H)-ylmethanol (*rac*-10): $LiAlH_4$ (2.77 g, 72.0 mmol) and dry THF (50 mL) were placed in a dry apparatus under argon and cooled to –2 to 0 °C with an ice/acetone/NaCl slurry. Ethyl 2′,4′,6′,7′-tetrahydrospiro[1,3-dioxolan-2,5′-indene]-7a′(1′H)-carboxylate (*rac*-**9**; 4.60 g, 18.0 mmol) in dry THF (12 mL) was added over 15 min and the suspension was stirred for 2 h at 0 °C and 2 h at room temperature. The solution was cooled with ice, saturated aq. sodium hydroxide (8 mL) was added, and vacuum filtration was carried out. The precipitate was washed with THF (4×50 mL), the combined organic layers were dried with Na_2SO_4, and the solvents were removed by evaporation. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 60:40, R_f = 0.28) yielded the title compound (*rac*-**10**; 2.99 g, 78%) as a yellowish oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 1.50 (ddd, *J* = 8.48, 10.24, 12.74 Hz, 1 H, 1′-H), 1.62 (dd, *J* = 2.51, 6.79 Hz, 1 H, 6′-H), 1.64 (dd, *J* = 1.18, 3.22 Hz, 1 H, O*H*), 1.66 (dd, *J* = 4.24, 6.12 Hz, 1 H, 7′-H), 1.81 (t, *J* = 14.21 Hz, 1 H, 6′-H), 1.88 (ddd, *J* = 2.64, 4.32, 10.13 Hz, 1 H, 7′-H), 2.09 (ddd, *J* = 1.96, 8.32, 12.79 Hz, 1 H, 1′-H), 2.18 (ddd, *J* = 2.04, 4.08, 14.86 Hz, 1 H, 2′-H), 2.24–2.33 (m, 2 H, 2′-H and 4′-H), 2.48 (dd, *J* = 2.59, 13.50 Hz, 1 H, 4′-H), 3.32 (s, 2 H, 1′′-H), 3.43–3.55 (m, 4 H, OCH_2CH_2O), 5.35 (dd, *J* = 2.28, 4.79 Hz, 1 H, 3′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 31.33 (C-2′), 32.25 (C-7′)*, 32.32 (C-6′)*, 35.90 (C-1′), 36.93 (C-4′), 51.20 (C-7a′), 64.25 (C-5)**, 64.38 (C-4)**, 64.67 (C-1′′), 109.67 (C-2/5′), 125.93 (C-3′), 142.55 (C-3a′) ppm; */**) signal assignments are mutually interchangeable. IR (film): $\tilde{\nu}$ = 3426, 2935, 2888, 1442, 1357, 1238, 1091, 948, 840 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 210 (8) $[M]^+$, 179 (24), 135 (26), 117 (17), 107 (11), 100 (32), 99 (100), 93 (10), 91 (36), 86 (19), 79 (23), 77 (22), 65 (11), 55 (69), 53 (17). HRMS: calcd. for $C_{12}H_{18}O_3$ $[M]^+$ *m*/*z* = 210.1256; found 210.1256; deviation, 0.19 ppm.

7a-Allyloxymethyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (*rac*-11): A suspension of NaH (60%; 930 mg, 28.0 mmol) in paraffin was washed with *n*-hexane (3×10 mL) under argon, the solvent was pipetted out and traces were then removed under reduced pressure, and the remaining material was suspended in anhydrous THF (50 mL). The mixture was cooled to –2 to 0 °C (ice/acetone/NaCl) and a solution of 2′,4′,6′,7′-tetrahydrospiro[1,3-dioxolan-2,5′-in-

den]-7a′(1′H)-ylmethanol (*rac*-**10**; 1.46 g, 6.90 mmol) in anhydrous THF (15 mL) was added dropwise. After the mixture had been stirred at 0 °C for 40 min, a solution of allyl bromide (1.26 g, 10.4 mmol) in anhydrous THF (2 mL) was added over 10 min and the system was stirred for 20 min at –2 to 0 °C and at room temperature for 6 days. Additional amounts of allyl bromide (2.52 g, 20.8 mmol), diluted each time in anhydrous THF (2 mL), were added to the reaction mixture after 2 and 5 days, respectively. After 80% conversion of the starting material (GC monitoring), the reaction mixture was cooled to 0 °C and carefully hydrolysed with water (20 mL), and THF (80 mL) was added. After phase separation the aqueous layer was extracted twice with Et_2O (100 mL), and the combined organic layers were washed with sat. aq. $NaHCO_3$ (10 mL), dried with Na_2SO_4 and concentrated in vacuo. Purification by Kugelrohr distillation (0.02 mbar for 45 min) to remove the last traces of the solvents afforded the *O*-alkylated product (1.60 g, 92%). The product was used directly in the next reaction.

A solution of the crude material in THF (11 mL) was treated with H_2SO_4 (20%, 11 mL), and the solution was stirred intensively for 5 h at room temperature and then diluted with Et_2O (50 mL). After phase separation the aqueous layer was extracted with Et_2O (2×40 mL), and the combined organic layers were washed with sat. aq. $NaHCO_3$ (3×30 mL) and water (3×20 mL) and dried with Na_2SO_4. Concentration in vacuo and column chromatography on silica gel (cyclohexane/ethyl acetate 80:20, R_f = 0.42) yielded the title compound (*rac*-**11**; 515 mg, 36%) as a colourless oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, HMBC. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.96 (ddd, J = 1.65, 8.64, 23.12 Hz, 1 H, 1-H), 1.25–1.30 (m, 1 H, 7-H), 1.34 (dddd, J = 2.59, 4.39, 8.83, 17.59 Hz, 1 H, 2-H), 1.41–1.52 (m, 1 H, 2-H), 1.91–1.99 (m, 1 H, 3-H), 2.01 (dd, J = 2.67, 7.58 Hz, 1 H, 1-H), 2.09–2.13 (m, 1 H, 3-H), 2.15 (ddd, J = 1.89, 5.65, 13.19 Hz, 1 H, 7-H), 2.26 (ddd, J = 1.89, 5.65, 18.21 Hz, 1 H, 6-H), 2.41 (ddd, J = 5.65, 13.82, 17.90 Hz, 1 H, 6-H), 2.86 (d, J = 9.42 Hz, 1 H, 1′-H), 2.96 (dd, J = 1.25, 9.42 Hz, 1 H, 1′-H), 3.61 (d, J = 1.26 Hz, 1 H, 1′′-H), 3.62 (d, J = 1.89 Hz, 1 H, 1′′-H), 4.98 (ddd, J = 1.88, 3.76, 10.68 Hz, 1 H, CH=C$H_{2\ cis}$), 5.12 (ddd, J = 1.89, 3.77, 17.58 Hz, 1 H, CH=C$H_{2\ trans}$), 5.68 (ddd, J = 5.02, 10.38, 22.61 Hz, 1 H, CH=CH$_2$), 5.89 (t, J = 1.88 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 21.23 (C-2), 31.05 (C-3), 31.37 (C-7), 33.66 (C-6), 35.71 (C-1), 47.14 (C-7a), 70.51 (C-1′), 71.95 (C-1′′), 116.22 (C-3′′), 123.75 (C-4), 134.88 (C-2′′), 171.72 (C-3a), 197.11 (C-5) ppm. IR (film): $\tilde{\nu}$ = 2931, 1740, 1672, 1453, 1350, 1298, 1189, 1091, 960, 886 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 206 (7) $[M]^+$, 176 (20), 135 (53), 134 (12), 107 (81), 93 (45), 91 (39), 79 (62), 77 (25), 55 (17), 41 (100). HRMS: calcd. for $C_{13}H_{18}O_2$ $[M]^+$ *m*/*z* = 206.1307; found 206.1305; deviation, 0.97 ppm.

7a-Prop-2′′-ynyloxymethyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (*rac*-12): A suspension of NaH (60%; 960 mg, 28.5 mmol) in paraffin was washed under argon atmosphere with *n*-hexane (3×10 mL), the solvent was pipetted out and traces were then removed under reduced pressure, and the remaining material was suspended in anhydrous THF (50 mL). The mixture was cooled to –2 to 0 °C (ice/acetone/NaCl) and a solution of 2′,4′,6′,7′-tetrahydrospiro[1,3-dioxolan-2,5′-inden]-7a′(1′H)-ylmethanol (*rac*-**10**; 1.50 g, 7.00 mmol) in anhydrous THF (15 mL) was added dropwise. After the mixture had been stirred at 0 °C for 50 min, a solution of propargyl bromide (≈80% in toluene; 1.53 g, 11.0 mmol) in anhydrous THF (2 mL) was added over 10 min, and the system was stirred for 20 min at –2 to 0 °C and at room temperature for 6 days. Additional amounts of the alkylation reagent (3.00 g, 22.0 mmol), each time diluted in anhydrous THF (2 mL), were added to the reaction mixture after 2 and 5 days. After 90% conversion of the starting material (GC monitoring), the reaction mixture was cooled to 0 °C and carefully hydrolysed with water (20 mL), and THF (80 mL) was added. After phase separation the aqueous layer was extracted twice with Et_2O (100 mL), and the combined organic layers were washed with sat. aq. $NaHCO_3$ (10 mL), dried with Na_2SO and concentrated in vacuo. Purification by Kugelrohr distillation (0.02 mbar for 45 min) to remove last traces of the solvents afforded the *O*-alkylated product (1.66 g, 94%). The product was used directly in the next reaction.

A solution of the crude material in THF (11 mL) was treated with H_2SO_4 (20%, 11 mL), and the solution was stirred intensively for 5 h at room temperature and then diluted with Et_2O (100 mL). After phase separation the aqueous layer was extracted with Et_2O (2×40 mL), and the combined organic layers were washed with sat. aq. $NaHCO_3$ (3×10 mL) and water (3×20 mL) and dried with Na_2SO_4. Concentration in vacuo and column chromatography on silica gel (cyclohexane/ethyl acetate 80:20, R_f = 0.26) yielded *rac*-**12** as a colourless oil (787 mg, 54%). NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, HMBC. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.93 (dddt, J = 1.41, 12.32, 19.59, 1.72 Hz, 1 H, 1-H), 1.26 (ddddt, J = 1.26, 1.18, 5.42, 27.24, 5.24 Hz, 1 H, 7-H), 1.33 (dddd, J = 2.51, 4.32, 8.82, 17.61 Hz, 1 H, 2-H), 1.42–1.52 (m, 1 H, 2-H), 1.91 (tdd, J = 1.88, 2.12, 18.76 Hz, 1 H, 3-H), 1.95 (t, J = 2.36 Hz, 1 H, 3′′-H), 1.99 (ddd, J = 2.67, 7.54, 12.76 Hz, 1 H, 1-H), 2.06–2.12 (m, 1 H, 3-H), 2.15 (ddd, J = 1.96, 5.58, 13.11 Hz, 1 H, 7-H), 2.23 (ddd, J = 2.28, 5.42, 18.01 Hz, 1 H, 6-H), 2.43 (ddd, J = 5.58, 14.29, 17.98 Hz, 1 H, 6-H), 2.92 (dd, J = 0.63, 9.27 Hz, 1 H, 1′-H), 3.05 (dd, J = 1.42, 9.26 Hz, 1 H, 1′-H), 3.67 (d, J = 2.35 Hz, 2 H, 1′′-H), 5.87 (t, J = 2.20 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 21.31 (C-2), 31.07 (C-3), 31.25 (C-7), 33.71 (C-6), 35.67 (C-1), 47.13 (C-7a), 58.29 (C-1′′), 69.78 (C-1′), 74.70 (C-3′′), 79.91 (C-2′′), 124.07 (C-4), 171.54 (C-3a), 197.23 (C-5) ppm. IR (film): $\tilde{\nu}$ = 3282, 2956, 2117, 1725, 1655, 1357, 1025, 886 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 205 (3) $[M + 1]^+$, 204 (23) $[M]^+$, 174 (10), 146 (14), 135 (83), 134 (15), 132 (16), 131 (15), 117 (24), 108 (13), 107 (87), 106 (17), 105 (19), 93 (65), 92 (16), 91 (68), 81 (14), 79 (76), 78 (17), 77 (42), 69 (75), 67 (22), 65 (22), 55 (27), 53 (31), 51 (22), 41 (81), 39 (100). HRMS: calcd. for $C_{13}H_{16}O_2$ $[M]^+$ *m*/*z* = 204.1150; found 204.1155; deviation, 2.25 ppm.

General Procedure B (Reduction of Indenones to the Corresponding Alcohols): Finely pulverized $NaBH_4$ (8.00 molar equivalents relative to the indenone) was placed in a dry apparatus under argon and dissolved in a definite amount of dry alcohol (about 1.20–1.50 mL ethanol or methanol per 1.00 mmol enone). The alcohol mixture was stirred until complete dissolution of $NaBH_4$ (about 40–50 min). The reaction mixture was cooled to 0 °C with ice/acetone and a solution of the appropriate indenone in the corresponding solvent (1.50–4.50 mL dry ethanol or dry methanol per 1.00 mmol indenone) was added through a septum over 10–15 min. The reaction mixture was allowed to warm slowly to room temperature and intensively stirred for 2.5–5.5 h. The complete conversion of the starting material was monitored by GC. In some cases it is better to start the reaction with 4.00–5.00 molar equivalents of $NaBH_4$, followed by later addition of up to 8.00 molar equivalents. After complete conversion the clear mixture was carefully neutralized with acetic acid (100%) with ice cooling, followed by addition of Et_2O (100–200 mL) and water (10–40 mL). The aqueous layer was separated and extracted twice with Et_2O (50–100 mL). The combined organic layers were washed with saturated aq. $NaHCO_3$ solution (4×30 mL), brine (2×20 mL) and water (2×20 mL) and dried with Na_2SO_4. The solvent was removed by evaporation and the residue was purified by column chromatography on silica gel.

If necessary, the resulting diastereomers were additionally separated by HPLC.

General Procedure C (Cyclopropanization of Indenols to the Corresponding α-Cyclopropyl Indenols): A defined amount of the appropriate indenol in dry Et_2O (9–11 mL per 1.00 mmol indenol) was placed in a dry apparatus under argon and cooled to 0 °C (ice/acetone). Diethylzinc (1.0 M in *n*-hexane; 2.00 mL, 2.00 mmol) was added over 10 min through a septum and the mixture was stirred for 5 min at the same temperature. Diiodomethane (2.00 mmol) in dry Et_2O (1 mL per 1.00 mmol) was added over 10 min and the mixture was allowed to warm to room temperature and stirred for 20–29 h. The degree of conversion was checked by gas chromatography (note: low sensitivity of detection of diiodomethane by GC). GC analyses were carried out after 1, 2, 12 and 20 h. If required, additional diiodomethane and possibly diethylzinc solution were added and the mixture was stirred again for 12–24 h. As a rule, 1.00 to 3.00 molar equivalents of methylene iodide overall have to been used. After complete conversion the mixture was carefully hydrolysed with saturated aq. ammonium chloride solution with ice cooling until complete dissolution of the zinc salts, and Et_2O (50 mL) was added. The aqueous layer was separated and extracted three times with Et_2O (50 mL). The combined organic layers were washed with saturated aq. sodium hydrogencarbonate solution (20 mL) and water (20 mL) and dried with Na_2SO_4. The solvent was removed by evaporation and the residue was purified by column chromatography on silica gel. Alternatively, the crude product can be purified by Kugelrohr distillation (0.02 mbar for 50 min). The product can be directly used for the next reaction without additional purification.

General Procedure D (Oxidation of the α-Cyclopropyl Indenols to the Corresponding α-Cyclopropyl Indenones): A definite amount of pyridinium chlorochromate (PCC; 1.50–2.00 mmol relative to the cyclopropyl indenol) was suspended in dry dichloromethane (11–13 mL per 1.00 mmol PCC) under argon in a dry apparatus. A solution of the appropriate cyclopropyl indenol in dry dichloromethane (1–2 mL per 1.00 mmol indenol) was added. After the mixture had been intensively stirred for 2–3 h at room temperature, Et_2O (50 mL) was added and the reaction mixture was filtered by flash chromatography on silica gel. The combined organic layers were evaporated and the remaining residue was purified by fast chromatography on silica gel. If necessary, the resulting diastereomeric mixture was additionally separated by HPLC.

(5*S,7a*S**)-7a-Prop-2′-ynyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (13a):** Reduction of 7a-prop-2′-ynyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (*rac*-**5**; 5.00 g, 29.0 mmol) was carried out as described in GP B. The crude product was filtered through silica gel (cyclohexane/ethyl acetate 85:15), yielding a mixture of the two isomeric reducing products **13a** and **13b** (product ratio according to GC: 93.3:5.7, **13a/13b**). This mixture was separated by HPLC (cyclohexane/ethyl acetate 95:5), yielding (5*S**,7a*S**)-7a-prop-2′-ynyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (**13a**; 1.66 g, 33%) and (5*R**,7a*S**)-7a-prop-2′-ynyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (**13b**; 100 mg, 2%) as colourless oils.

(5*S,7a*S**)-7a-Prop-2′-ynyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (13a):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, HMBC, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 1.01 (dddd, J = 1.88, 2.51, 10.68, 12.56 Hz, 1 H, 1-H), 1.09 (dddd, J = 1.26, 1.88, 3.14, 13.71 Hz, 1 H, 7-H), 1.37–1.41 (m, 1 H, 2-H), 1.43 (ddd, J = 1.88, 4.40, 15.42 Hz, 1 H, 3-H), 1.46 (dd, J = 3.14, 13.81 Hz, 1 H, 6-H), 1.47 (dddd, J = 2.51, 5.02, 10.45, 17.59 Hz, 1 H, 2-H), 1.73 (t, J = 2.51 Hz, 1 H, 3′-H), 1.78 (ddd, J = 3.14, 6.91, 13.51 Hz, 1 H, 6-H), 1.93 (ddd, J = 1.88, 3.67, 15.21 Hz, 1 H, 3-H), 1.99 (ddd, J = 1.88, 2.51, 17.11 Hz, 1 H, 1′-H), 2.07 (dd, J = 3.77, 7.53 Hz, 1 H, O*H*), 2.11 (ddd, J = 2.51, 7.54, 11.30 Hz, 1 H, 1-H), 2.19 (dd, J = 2.51, 16.96 Hz, 1 H, 1′-H), 2.23 (ddd, J = 1.88, 3.77, 13.67 Hz, 1 H, 7-H), 4.05 (ddt, J = 2.51, 4.39, 8.47 Hz, 1 H, 5-H), 5.26 (dd, J = 2.51, 3.77 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 20.20 (C-2), 24.97 (C-1′), 28.74 (C-6), 29.80 (C-3), 32.33 (C-7), 37.63 (C-1), 44.34 (C-7a), 68.27 (C-5), 70.22 (C-3′), 82.20 (C-2′), 123.40 (C-4), 148.81 (C-3a) ppm. IR (film): $\tilde{\nu}$ = 3310, 2942, 2867, 2117, 1635, 1360, 1303, 1142, 1085, 990, 883 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 176 (1) [*M*]$^+$, 175 (2), 161 (9), 158 (3), 148 (10), 147 (13), 137 (42), 136 (12), 135 (14), 133 (20), 132 (9), 120 (16), 119 (80), 116 (27), 115 (10), 107 (10), 95 (15), 93 (19), 92 (13), 91 (100), 81 (16), 79 (37), 78 (11), 77 (38), 67 (53), 65 (30), 63 (12), 57 (15), 51 (21). HRMS: calcd. for $C_{12}H_{16}O$ [*M*]$^+$ *m*/*z* = 176.1201; found 174.1036* [*M* – 2]$^+$; deviation, 4.50 ppm; *) no [*M*]$^+$ signal detected.

(5*R,7a*S**)-7a-Prop-2′-ynyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (13b):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 1.01 (dddd, J = 1.88, 3.77, 11.30, 16.95 Hz, 1 H, 1-H), 1.29 (ddd, J = 2.51, 5.02, 13.49 Hz, 1 H, 7-H), 1.43 (ddd, J = 3.14, 7.54, 15.07 Hz, 1 H, 3-H), 1.47 (ddd, J = 3.14, 6.91, 13.19 Hz, 1 H, 6-H), 1.62 (ddd, J = 3.77, 7.53, 12.56 Hz, 1 H, 2-H), 1.65 (td, J = 2.51, 5.65 Hz, 1 H, 2-H), 1.74 (t, J = 2.51 Hz, 1 H, 3′-H), 1.93 (dddd, J = 2.51, 3.77, 7.53, 13.39 Hz, 1 H, 6-H), 1.99 (ddd, J = 7.55, 9.11, 15.37 Hz, 1 H, 3-H), 2.07 (dd, J = 3.77, 6.28 Hz, 1 H, O*H*), 2.11 (ddd, J = 3.77, 6.60, 11.80 Hz, 1 H, 1-H), 2.14 (ddd, J = 2.51, 5.65, 13.30 Hz, 1 H, 1′-H), 2.18 (ddd, J = 2.51, 5.66, 13.81 Hz, 1 H, 1′-H), 2.23 (ddd, J = 2.51, 5.02, 13.56 Hz, 1 H, 7-H), 3.87 (ddd, J = 1.88, 3.76, 8.22 Hz, 1 H, 5-H), 5.32 (dd, J = 1.88, 3.77 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 20.40 (C-2), 23.71 (C-1′), 27.50 (C-6), 28.30 (C-3), 29.11 (C-7), 37.57 (C-1), 44.26 (C-7a), 63.74 (C-5), 70.19 (C-3′), 81.95 (C-2′), 121.36 (C-4), 149.92 (C-3a) ppm. IR (film): $\tilde{\nu}$ = 3301, 2943, 2116, 1453, 1356, 1306, 1272, 1153, 1086, 1032, 988, 882 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 176 (1) [*M*]$^+$, 175 (2), 161 (9), 148 (22), 147 (22), 137 (44), 136 (17), 135 (16), 133 (14), 120 (15), 119 (75), 117 (26), 115 (10), 107 (13), 95 (13), 93 (18), 92 (13), 91 (100), 81 (17), 79 (39), 78 (12), 77 (33), 67 (49), 66 (10), 65 (28), 63 (14), 57 (20), 55 (61), 53 (31), 52 (14), 51 (60). HRMS: calcd. for $C_{12}H_{16}O$ [*M*]$^+$ *m*/*z* = 176.1201; found 174.1040* [*M* – 2]$^+$; deviation, 2.70 ppm; *) no [*M*]$^+$ signal detected.

(1a*R,2*S**,4a*S**,7a*S**)-4a-Prop-2′-ynyloctahydro-1*H*-cyclopropa[*d*]-inden-2-ol (14):** Cyclopropanization of (5*S**,7a*S**)-7a-prop-2′-ynyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (**13a**; 1.60 g, 9.10 mmol) was carried out as described in GP C. The cyclopropanized product was purified by flash chromatography (cyclohexane/ethyl acetate 90:10, R_f = 0.09), yielding **14** (1.74 g, 100%) as a colourless oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.22 (t, J = 5.65 Hz, 1 H, 1-H), 0.26 (dd, J = 5.66, 8.79 Hz, 1 H, 1-H), 0.56 (ddd, J = 2.51, 5.02, 13.50 Hz, 1 H, 3-H), 0.76 (dd, J = 2.51, 13.19 Hz, 1 H, 4-H), 0.80 (ddd, J = 3.77, 5.65, 14.44 Hz, 1 H, 1a-H), 1.00–1.05 (m, 1 H, 6-H), 1.35 (ddd, J = 2.28, 5.30, 9.13 Hz, 1 H, 5-H), 1.39 (ddd, J = 1.96, 5.18, 11.01 Hz, 1 H, 7-H), 1.46 (ddd, J = 1.49, 6.59, 13.25 Hz, 1 H, 3-H), 1.50 (dd, J = 3.61, 6.40 Hz, 1 H, 5-H), 1.54 (ddd, J = 2.12, 5.14, 13.70 Hz, 1 H, 4-H), 1.69 (t, J = 2.51 Hz, 1 H, 3′-H), 1.71 (dd, J = 3.77, 5.65 Hz, 1 H, 6-H), 1.89 (dd, J = 2.51, 16.65 Hz, 1 H, 1′-H), 1.97 (dd, J = 2.51, 16.64 Hz, 1 H, 1′-H), 2.02 (ddd, J = 2.51, 3.14, 9.42 Hz, 1 H, 7-H), 2.90 (s, 1 H, O*H*), 3.87 (dt, J = 5.65, 10.67 Hz, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 9.38 (C-1), 24.36 (C-5), 26.25 (C-3), 27.54 (C-1′), 27.84 (C-1a), 33.76 (C-4), 34.33 (C-7a), 39.47 (C-6), 40.07 (C-4a), 40.96

(C-7), 68.18 (C-2), 69.15 (C-2′), 83.27 (C-3′) ppm. IR (film): ṽ = 3304, 2939, 2864, 2116, 1451, 1351, 1290, 1076, 1020, 890 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 189 (1) [*M* – 1]$^+$, 157 (7), 151 (65), 139 (12), 133 (86), 132 (10), 131 (16), 129 (12), 118 (11), 117 (39), 115 (14), 109 (17), 107 (38), 105 (45), 93 (20), 91 (100), 81 (33), 79 (77), 78 (17), 77 (49), 67 (49), 65 (33), 63 (13), 57 (32), 55 (58), 53 (38), 51 (22). HRMS: calcd. for $C_{13}H_{18}O$ [*M*]$^+$ *m*/*z* = 190.1358; found 190.1126; deviation, 2.10 ppm.

(1a*R,4a*S**,7a*S**)-4a-Prop-2′-ynyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (15):** (1a*R**,2*S**,4a*S**,7a*S**)-4a-Prop-2′-ynyloctahydro-1*H*-cyclopropa[*d*]inden-2-ol (**14**; 1.74 g, 9.14 mmol) was oxidized as described in GP D. The crude product was filtered through silica gel (cyclohexane/ethyl acetate 70:30) and then purified by HPLC (cyclohexane/ethyl acetate 95:5), yielding (1a*R**,4a*S**,7a*S**)-4a-prop-2′-ynyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (**15**; 534 mg, 31%) as white crystals. The crystals of **15** were obtained in 100% purity after crystallization from petroleum ether. M.p. 97.4–101.3 °C; NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.46 (t, *J* = 5.18 Hz, 1 H, 1-H), 0.53 (dd, *J* = 5.49, 9.77 Hz, 1 H, 1-H), 0.70–0.75 (m, 1 H, 3-H), 1.15 (dd, *J* = 3.53, 13.62 Hz, 1 H, 4-H), 1.17–1.20 (m, 1 H, 5-H), 1.20–1.23 (m, 1 H, 7-H), 1.23–1-26 (m, 1 H, 5-H), 1.27 (ddd, *J* = 1.18, 2.36, 4.86 Hz, 1 H, 1a-H), 1.36 (ddd, *J* = 4.94, 9.15, 18.57 Hz, 1 H, 4-H), 1.42 (dd, *J* = 3.45, 9.70 Hz, 1 H, 3-H), 1.47 (dd, *J* = 4.01, 15.62 Hz, 1 H, 6-H), 1.51 (t, *J* = 2.67 Hz, 1 H, 3′-H), 1.62 (dd, *J* = 2.59, 16.72 Hz, 1 H, 1′-H), 1.67–1.69 (m, 1 H, 6-H), 1.69–1.76 (m, 1 H, 7-H), 1.72 (dd, *J* = 2.59, 16.72 Hz, 1 H, 1′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 17.15 (C-1), 23.67 (C-6), 27.12 (C-1′), 32.96 (C-5)*, 33.53 (C-1a), 36.09 (C-4), 37.83 (C-3), 39.57 (C-7)*, 40.19 (C-7a), 40.84 (C-4a), 69.67 (C-3′), 82.23 (C-2′), 206.83 (C-2) ppm; *) signal assignments are mutually interchangeable. IR (KBr): ṽ = 3304, 2954, 2867, 2117, 1691, 1453, 1324, 1267, 1191, 1071, 963, 866 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 188 (2) [*M*]$^+$, 187 (3), 173 (8), 169 (5), 160 (9), 159 (10), 155 (5), 149 (34), 148 (12), 146 (10), 145 (17), 131 (30), 129 (8), 121 (16), 118 (24), 117 (60), 115 (14), 107 (66), 105 (20), 93 (13), 92 (13), 91 (73), 79 (100), 78 (20), 77 (49), 67 (25), 65 (37), 63 (16), 57 (10), 55 (63), 53 (35), 51 (31). HRMS: calcd. for $C_{13}H_{16}O$ [*M*]$^+$ *m*/*z* = 188.1201; found 187.1117* [*M* – 1]$^+$; deviation, 3.00 ppm; *) no [*M*]$^+$ signal detected.

(5*S,7a*R**)-7a-But-3′-ynyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (16):** Reduction of 7a-but-3′-ynyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (*rac*-**6**; 2.90 g, 15.4 mmol) was carried out as described in GP B. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 70:30, R_f = 0.52) afforded (5*S**,7a*R**)-7a-but-3′-ynyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (**16**; 1.58 g, 54%) as a colourless oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.78 (ddd, *J* = 1.73, 10.80, 19.76 Hz, 1 H, 1-H), 0.85–0.93 (m, 1 H, 1′-H), 1.27–1.40 (m, 4 H), 1.41–1.53 (m, 2 H), 1.56–1.72 (m, 4 H), 1.78 (t, *J* = 2.67 Hz, 1 H, 4′-H), 1.91 (dt, *J* = 2.35, 2.67 Hz, 1 H, 2′-H), 1.91 (q, *J* = 2.52 Hz, 1 H, 2′-H), 2.12–2.19 (m, 1 H, 3-H), 4.03–4.08 (m, 1 H, 5-H), 5.24 (tdd, *J* = 2.67, 1.26, 6.83 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 14.40 (C-2′), 20.44 (C-2), 29.04 (C-3)**, 29.77 (C-6)**, 31.50 (C-1′)**, 33.41 (C-1)**, 36.75 (C-7), 43.85 (C-7a), 68.17 (C-5), 68.74 (C-4′), 84.74 (C-3′), 122.29 (C-4), 150.74 (C-3a) ppm; */**) signal assignments are mutually interchangeable. IR (film): ṽ = 3305, 2861, 2117, 1457, 1353, 1276, 1076, 991, 863 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 190 (1) [*M*]$^+$, 189 (1), 175 (4), 162 (23), 161 (55), 157 (6), 149 (12), 148 (21), 147 (38), 146 (12), 135 (13), 134 (20), 133 (55), 131 (17), 129 (18), 120 (19), 119 (39), 107 (17), 105 (25), 95 (17), 93 (25), 92 (20), 91 (100), 81 (23), 80 (10), 79 (60), 78 (18), 77 (60), 69 (11), 67 (71), 65 (38), 63 (15). HRMS: calcd. for $C_{13}H_{18}O$ [*M*]$^+$ *m*/*z* = 190.1358; found 190.1345/189.1282*** [*M* – 1]$^+$; deviation, 6.78/1.43 ppm; ***) because the molecule ion signal [*M*]$^+$ overlaps with the ^{13}C-isotope signal [*M* – H]$^+$, the mass of [*M*]$^+$ is not exactly determinable.

(1a*R,4a*R**,7a*S**)-4a-But-3′-ynyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (18):** Cyclopropanization of (5*S**,7a*R**)-7a-but-3′-ynyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (**16**; 1.56 g, 8.20 mmol) was carried out as described in GP C. The crude product was filtered through silica gel (cyclohexane/ethyl acetate 50:50), yielding (1a*R**,2*S**,4a*R**,7a*S**)-4a-but-3′-ynyloctahydro-1*H*-cyclopropa[*d*]-inden-2-ol (**17**; 1.54 g, 100%) as a yellowish oil. The product **17** of the cyclopropanization was analysed by GC and GC-MS methods, and used directly in the next oxidation reaction. GC-MS (EI, 70 eV): *m*/*z* (%) = 203 (1) [*M* – 1]$^+$, 185 (1), 175 (2), 171 (2), 161 (3), 158 (4), 147 (14), 145 (6), 143 (6), 131 (10), 129 (12), 120 (10), 119 (21), 117 (22), 105 (29), 95 (13), 93 (22), 91 (66), 81 (12), 79 (36), 77 (28), 67 (25), 65 (18), 57 (12), 55 (25), 53 (19), 52 (15), 51 (10), 43 (10), 41 (34), 39 (18), 32 (23), 28 (100).

(1a*R**,2*S**,4a*R**,7a*S**)-4a-But-3′-ynyloctahydro-1*H*-cyclopropa[*d*]inden-2-ol (**17**; 1.54 g, 7.54 mmol) was oxidized as described in GP D. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 80:20, R_f = 0.36) afforded (1a*R**,4a*R**,7a*S**)-4a-but-3′-ynyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (**18**; 878 mg, 53%) as colourless crystals with m.p. 48.4 °C. These were directly used for the X-ray crystallographic analysis. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.53 (dd, *J* = 5.26, 10.44 Hz, 1 H, 1-H), 0.56 (t, *J* = 5.42 Hz, 1 H, 1-H), 0.74 (dd, *J* = 4.37, 6.74 Hz, 1 H, 5-H), 0.99–1.04 (m, 1 H, 7-H), 1.08 (d, *J* = 3.61 Hz, 1 H, 1′-H), 1.10 (tdd, *J* = 3.57, 3.06, 6.91 Hz, 1 H, 1′-H), 1.17–1.37 (m, 7 H, 6-H, 7-H, 6-H, 5-H, 1a-H, 4-H, 3-H), 1.58 (ddd, *J* = 5.18, 12.33, 15.50 Hz, 1 H, 2′-H), 1.76 (dddd, *J* = 2.59, 4.91, 8.40, 15.79 Hz, 1 H, 2′-H), 1.79 (t, *J* = 2.59 Hz, 1 H, 4′-H), 1.84 (dd, *J* = 2.75, 6.44 Hz, 1 H, 3-H), 1.87 (ddd, *J* = 2.59, 5.85, 10.27 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 13.91 (C-2′), 17.20 (C-1), 23.66 (C-6), 32.90 (C-7), 33.33 (C-1a), 35.94 (C-1′)*, 36.01 (C-4)*, 38.00 (C-5)**, 38.30 (C-3)**, 40.11 (C-7a), 40.51 (C-4a), 68.71 (C-4′), 84.64 (C-3′), 207.06 (C-2) ppm; */**) signal assignments are mutually interchangeable. IR (KBr): ṽ = 3289, 2861, 2115, 1691, 1456, 1326, 1261, 1193, 960 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 202 (1) [*M*]$^+$, 173 (4), 159 (4), 145 (13), 131 (13), 117 (24), 107 (14), 105 (15), 93 (26), 91 (32), 79 (29), 77 (14), 65 (10), 55 (31), 53 (15), 44 (12), 41 (17), 39 (18), 32 (23), 28 (100). HRMS: calcd. for $C_{14}H_{18}O$ [*M*]$^+$ *m*/*z* = 202.1358; found 202.1356; deviation, 0.89 ppm.

X-ray Crystal Analysis of *rac*-18: $C_{14}H_{18}O$, *M* = 202.28, colourless crystals, monoclinic space group P 2(1)/n: *a* = 7.1520(1), *b* = 7.6630(1), *c* = 20.6610(3) Å; β = 95.8170(10)°, *V* = 1126.51(3) Å^3; *T* = 100(2) K; *Z* = 4; $d_{calcd.}$ = 1.193 g cm^{-3}; μ = 0.073 mm^{-1}; *F*(000) = 440; Crystal size = 0.30 × 0.30 × 0.30 mm; crystals of *rac*-**18** (Table 5) were removed from the mother liquor and immediately cooled to 100(2) *K* on a Nonius Kappa CCD device (Bruker Nonius GmbH), Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator. A total of 25979 reflections ($3 < \Theta < 27.5°$) were collected, of which 2571 (R_{int} = 0.027) reflections were unique. Index ranges $-9 \le h \le 9$, $-9 \le k \le 9$, $-26 \le l \le 26$; completeness to Θ = 27.5°: 99.7%. An empirical absorption correction using equivalent reflections was performed with the program Denzo and Scalepak (Otwinowski & Minor, 1997). The structure was solved with the program SHELXS-97 and refined with the aid of SHELXL-97 to R_1 = 0.0355 and wR_2 = 0.0910 for 2361 reflections with $I > 2*\sigma(I)$, R_1 = 0.0387 and wR_2 = 0.0937 for all reflections; Refinement method: full-matrix, least-squares on F_2; data/restraints/parameters: 2571/0/208; largest diff. peak and hole: 0.289 and –0.168 e Å^{-3}; Goodness-of-fit on F^2 =

1.044; Hydrogen atoms were refined isotopically; Structure graphics with SHELXTL-PLUS from Sheldrick, Germany, 1990 and DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, Germany, 2001.[54]

Table 5. Characteristics bond lengths [Å] and angles [°] for *rac*-**18**:.

O(1)–C(3)	1.2236(12)	C(3)–C(4)–H(4B)	108.7(7)
C(1)–C(10)	1.4855(13)	C(5)–C(4)–H(4B)	110.5(8)
C(1)–C(9)	1.5193(13)	H(4A)–C(4)–H(4B)	108.4(11)
C(1)–C(2)	1.5296(13)	C(4)–C(5)–C(6)	113.42(8)
C(1)–C(6)	1.5504(12)	C(4)–C(5)–H(5A)	108.5(7)
C(2)–C(3)	1.4780(13)	C(6)–C(5)–H(5A)	108.1(7)
C(2)–C(10)	1.5363(14)	C(4)–C(5)–H(5B)	110.0(7)
C(2)–H(2)	0.981(12)	C(6)–C(5)–H(5B)	108.8(7)
C(3)–C(4)	1.5068(14)	H(5A)–C(5)–H(5B)	107.9(10)
C(4)–C(5)	1.5351(14)	C(5)–C(6)–C(11)	109.08(7)
C(4)–H(4A)	0.995(13)	C(5)–C(6)–C(1)	111.27(7)
C(4)–H(4B)	0.981(13)	C(11)–C(6)–C(1)	112.28(7)
C(5)–C(6)	1.5398(12)	C(5)–C(6)–C(7)	108.98(7)
C(5)–H(5A)	1.015(12)	C(11)–C(6)–C(7)	112.03(7)
C(5)–H(5B)	0.997(13)	C(1)–C(6)–C(7)	103.08(7)
C(6)–C(11)	1.5414(13)	C(8)–C(7)–C(6)	105.88(7)
C(6)–C(7)	1.5601(12)	C(8)–C(7)–H(7A)	112.7(8)
C(7)–C(8)	1.5358(14)	C(6)–C(7)–H(7A)	110.0(8)
C(7)–H(7A)	0.994(13)	C(8)–C(7)–H(7B)	109.9(7)
C(7)–H(7B)	1.007(13)	C(6)–C(7)–H(7B)	111.7(7)
C(8)–C(9)	1.5295(14)	H(7A)–C(7)–H(7B)	106.7(10)
C(8)–H(8A)	0.987(13)	C(9)–C(8)–C(7)	102.18(8)
C(8)–H(8B)	0.982(14)	C(9)–C(8)–H(8A)	108.9(7)
C(9)–H(9A)	0.990(13)	C(7)–C(8)–H(8A)	110.4(7)
C(9)–H(9B)	1.015(12)	C(9)–C(8)–H(8B)	114.0(8)
C(10)–H(10A)	0.995(13)	C(7)–C(8)–H(8B)	111.6(8)
C(10)–H(10B)	0.964(13)	H(8A)–C(8)–H(8B)	109.5(11)
C(11)–C(12)	1.5403(13)	C(1)–C(9)–C(8)	102.18(7)
C(11)–H(11A)	0.987(12)	C(1)–C(9)–H(9A)	109.8(7)
C(11)–H(11B)	1.008(12)	C(8)–C(9)–H(9A)	109.2(7)
C(12)–C(13)	1.4663(14)	C(1)–C(9)–H(9B)	111.5(7)
C(12)–H(12A)	1.016(14)	C(8)–C(9)–H(9B)	115.2(7)
C(12)–H(12B)	0.999(13)	H(9A)–C(9)–H(9B)	108.8(10)
C(13)–C(14)	1.1886(15)	C(1)–C(10)–C(2)	60.79(6)
C(14)–H(14)	0.955(16)	C(1)–C(10)–H(10A)	119.5(7)
C(10)–C(1)–C(9)	121.78(8)	C(2)–C(10)–H(10A)	116.2(7)
C(10)–C(1)–C(2)	61.25(6)	C(1)–C(10)–H(10B)	118.5(7)
C(9)–C(1)–C(2)	116.68(8)	C(2)–C(10)–H(10B)	115.5(7)
C(10)–C(1)–C(6)	122.94(8)	H(10A)-C(10)–H(10B)	115.2(10)
C(9)–C(1)–C(6)	107.84(7)	C(12)–C(11)–C(6)	114.63(7)
C(2)–C(1)–C(6)	119.75(7)	C(12)–C(11)–H(11A)	107.6(7)
C(3)–C(2)–C(1)	120.34(8)	C(6)–C(11)–H(11A)	108.7(7)
C(3)–C(2)–C(10)	117.47(8)	C(12)–C(11)–H(11B)	108.9(7)
C(1)–C(2)–C(10)	57.96(6)	C(6)–C(11)–H(11B)	108.6(7)
C(3)–C(2)–H(2)	113.7(7)	H(11A)-C(11)–H(11B)	108.2(10)
C(1)–C(2)–H(2)	118.7(7)	C(13)–C(12)–C(11)	112.61(8)
C(10)–C(2)–H(2)	117.6(7)	C(13)–C(12)–H(12A)	110.4(8)
O(1)–C(3)–C(2)	121.08(9)	C(11)–C(12)–H(12A)	107.7(8)
O(1)–C(3)–C(4)	122.51(9)	C(13)–C(12)–H(12B)	107.6(8)
C(2)–C(3)–C(4)	116.35(8)	C(11)–C(12)–H(12B)	109.6(7)
C(3)–C(4)–C(5)	109.62(8)	H(12A)-C(12)–H(12B)	108.9(11)
C(3)–C(4)–H(4A)	108.5(7)	C(14)–C(13)–C(12)	178.91(11)
C(5)–C(4)–H(4A)	111.2(7)	C(13)–C(14)–H(14)	177.8(9)

(5*S,7a*S**)-7a-Allyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (19):** Reduction of 7a-allyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (*rac*-**7**; 2.96 g, 16.8 mmol) was carried out as described in GP B. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 70:30, R_f = 0.60) afforded (5*S**,7a*S**)-7a-allyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (**19**; 1.11 g, 37%) as a yellowish oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.91 (dq, J = 1.81, 7.35 Hz, 1 H, 1-H), 1.04 (ddd, J = 1.41, 3.06, 13.77 Hz, 1 H, 1-H), 1.45–1.56 (m, 2 H), 1.66–1.84 (m, 5 H), 1.87 (ddd, J = 1.34, 7.34, 12.66 Hz, 1 H, 6-H), 1.92 (ddd, J = 1.33, 7.38, 14.21 Hz, 1 H, 1′-H), 2.12 (dddd, J = 1.49, 2.91, 7.38, 10.52 Hz, 1 H, 1′-H), 2.25 (tdt, J = 5.18, 2.51, 13.89 Hz, 1 H, 6-H), 4.13 (dtd, J = 1.25, 7.93, 6.93 Hz, 1 H, 5-H), 4.94 (ddd, J = 1.81, 3.85, 12.44 Hz, 1 H, 3′-H), 5.00 (tdd, J = 2.59, 10.68, 12.71 Hz, 1 H, 3′-H), 5.35 (ddt, J = 2.75, 4.91, 2.51 Hz, 1 H, 4-H), 5.64 (dddtd, J = 7.38, 10.08, 17.04, 2.51, 5.26, 1 H, 2′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 20.36 (C-2), 27.18 (C-6)*, 29.07 (C-7)*, 29.64 (C-3)**, 37.13 (C-1′), 39.06 (C-1)**, 44.19 (C-7a), 68.34 (C-5), 117.02 (C-3′), 122.33 (C-4), 135.51 (C-2′), 150.77 (C-3a) ppm; */**) signal assignments are mutually interchangeable. IR (film): $\tilde{\nu}$ = 3336, 2861, 1677, 1639, 1454, 1334, 1284, 1193, 1076, 910 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 178 (1) $[M]^+$, 161 (2), 160 (7), 149 (3), 137 (79), 136 (11), 119 (100), 109 (6), 108 (4), 95 (15), 93 (22), 92 (10), 91 (96), 81 (17), 79 (42), 77 (31), 67 (79), 65 (27), 57 (23), 55 (72), 53 (24), 51 (18), 43 (38), 41 (73), 39 (41). HRMS: calcd. for $C_{12}H_{18}O$ $[M]^+$ *m*/*z* = 178.1358; found 178.1360; deviation, 1.46 ppm.

(1a*R,4a*S**,7a*S**)-4a-Allyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (21a):** Cyclopropanization of (5*S**,7a*S**)-7a-allyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (**19**; 980 mg, 5.50 mmol) was carried out as described in GP C. The crude product was filtered by flash chromatography over silica gel (cyclohexane/ethyl acetate 50:50), yielding (1a*R**,2*S**,4a*S**,7a*S**)-4a-allyloctahydro-1*H*-cyclopropa[*d*]-inden-2-ol (**20**; 1.05 g, 100%) as a yellowish oil. The product **20** of the cyclopropanization was analysed by GC and GC-MS methods and directly used for the next oxidation reaction. GC-MS (EI, 70 eV): *m*/*z* (%) = 192 (2) $[M]^+$, 176 (5), 167 (5), 151 (62), 149 (13), 135 (10), 134 (18), 133 (71), 119 (7), 109 (20), 107 (67), 105 (32), 95 (18), 93 (26), 92 (20), 91 (69), 83 (10), 81 (32), 80 (15), 79 (100), 77 (35), 71 (11), 69 (16), 67 (86), 65 (34).

(1a*R**,2*S**,4a*S**,7a*S**)-4a-Allyloctahydro-1*H*-cyclopropa[*d*]inden-2-ol (**20**; 1.00 g, 5.20 mmol) was oxidized as described in GP D. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 80:20) afforded a mixture of two diastereomers **21a** and **21b** (403 mg, 40%) as a yellowish oil (relative amounts according to GC: **21a/21b** 93:7). This mixture was separated by HPLC (cyclohexane/ethyl acetate 99:1), yielding (1a*R**,4a*S**,7a*S**)-4a-allyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (**21a**; 270 mg, 27%) and (1a*S**,4a*S**,7a*R**)-4a-allyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (**21b**; 20 mg, 2%) as colourless oils.

(1a*R,4a*S**,7a*S**)-4a-Allyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (21a):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.67 (dt, J = 3.64, 9.18 Hz, 1 H, 1-H), 0.84 (ddd, J = 1.65, 6.04, 15.86 Hz, 1 H, 1-H), 1.18 (dddd, J = 3.61, 6.87, 8.38, 13.56 Hz, 1 H, 3-H), 1.25 (dd, J = 3.61, 13.42 Hz, 1 H, 7-H), 1.30–1.42 (m, 5 H, 6-H, 1a-H, 3-H and 2 × 5-H), 1.47 (ddd, J = 6.52, 10.84, 12.48 Hz, 1 H, 1′-H), 1.53 (ddd, J = 6.82, 9.95, 12.48 Hz, 1 H, 1′-H), 1.71 (ddd, J = 4.08, 2.51, 13.31 Hz, 1 H, 4-H), 1.73 (dd, J = 4.08, 13.27 Hz, 1 H, 4-H), 1.84 (ddd, J = 1.57, 3.42, 4.91 Hz, 1 H, 6-H), 1.87 (ddd, J = 1.49, 3.45, 4.99 Hz, 1 H, 7-H), 4.92 (ddd, J = 1.49, 3.85, 16.97 Hz, 1 H, 3′-H), 5.01 (ddd, J = 2.35, 2.51, 10.16 Hz, 1 H, 3′-H), 5.59 (dddd, J = 2.12, 6.43, 8.16, 13.54 Hz, 1 H, 2′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 17.61 (C-1), 23.81 (C-6)*, 32.99 (C-7)*, 33.55 (C-1a), 36.39 (C-4)**, 38.09 (C-3)**, 38.77 (C-5), 40.32 (C-7a), 40.74 (C-4a), 41.45 (C-1′), 117.74 (C-3′), 135.34 (C-2′), 207.28 (C-2) ppm; */**) signal assignments are mutually interchangeable. IR (film): $\tilde{\nu}$ = 2950, 2861, 1731, 1693, 1450, 1376, 1195, 1068, 914 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 190 (7) $[M]^+$, 175 (2), 162 (3), 161 (5), 150 (6), 149 (60), 133 (6), 131 (6), 121 (13), 120 (29), 119 (10), 107 (86), 105

(23), 93 (14), 92 (31), 91 (62), 79 (100), 78 (16), 77 (40), 67 (41), 65 (32), 55 (63), 53 (30), 41 (51), 39 (42). HRMS: calcd. for $C_{13}H_{18}O$ $[M]^+$ m/z = 190.1358; found 190.1356; deviation, 0.79 ppm.

(1a*S,4a*S**,7a*R**)-4a-Allyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (21b):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.21 (dd, J = 4.95, 8.87 Hz, 1 H, 1-H), 0.80–0.98 (m, 4 H, 2×5-H, 7-H and 1-H), 1.04 (dtd, J = 3.88, 3.61, 6.21 Hz, 1 H, 3-H), 1.45 (dd, J = 13.34, 22.45 Hz, 1 H, 4-H), 1.50–1.61 (m, 3 H, 1a-H, 3-H and 4-H), 1.67–1.79 (m, 2 H, 2×6-H), 1.89 (ddd, J = 1.18, 8.51, 19.09 Hz, 1 H, 7-H), 1.96 (dddd, J = 1.65, 3.38, 6.55, 14.23 Hz, 1 H, 1′-H), 2.08 (ddd, J = 2.61, 9.34, 13.68 Hz, 1 H, 1′-H), 4.87 (ddd, J = 1.57, 3.61, 19.94 Hz, 1 H, 3′-H), 4.93 (ddd, J = 1.73, 3.38, 10.05 Hz, 1 H, 3′-H), 5.51 (dddd, J = 1.57, 6.59, 8.24, 13.52 Hz, 1 H, 2′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 18.83 (C-1), 21.38 (C-6), 25.34 (C-7)*, 30.79 (C-4)**, 31.89 (C-3)**, 32.12 (C-1a), 33.60 (C-1′), 37.64 (C-5)*, 40.87 (C-7a), 42.49 (C-4a), 117.27 (C-3′), 134.90 (C-2′), 205.98 (C-2) ppm; */**) signal assignments are mutually interchangeable. IR (film): $\tilde{\nu}$ = 2950, 2861, 1731, 1693, 1450, 1376, 1195, 914 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 190 (1) $[M]^+$, 175 (2), 150 (10), 149 (94), 133 (7), 131 (4), 121 (13), 108 (10), 107 (100), 105 (17), 93 (13), 92 (12), 91 (47), 79 (96), 78 (15), 77 (33), 67 (29), 65 (26), 55 (44), 53 (24), 51 (14), 41 (47), 39 (35). HRMS: calcd. for $C_{13}H_{18}O$ $[M]^+$ m/z = 190.1358; found 190.1353; deviation, 2.58 ppm.

(5*S,7a*R**)-7a-Allyloxymethyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (22):** Reduction of 7a-allyloxymethyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (*rac*-**11**; 504 mg, 2.40 mmol) was carried out as described in GP B. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 70:30, R_f = 0.39) afforded (5*S**,7a*R**)-7a-allyloxymethyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (**22**; 166 mg, 29%) as a colourless oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 1.06 (ddd, J = 1.18, 10.95, 20.78 Hz, 1 H, 1-H), 1.14 (ddd, J = 1.10, 3.57, 12.36 Hz, 1 H, 7-H), 1.49 (dddd, J = 2.28, 5.22, 9.48, 22.63 Hz, 1 H, 2-H), 1.56–1.69 (m, 3 H, 2-H, O*H* and 6-H), 1.80 (ddd, J = 3.37, 9.64, 13.31 Hz, 1 H, 6-H), 2.04 (dd, J = 7.46, 15.00 Hz, 1 H, 3-H), 2.14 (ddd, J = 2.43, 7.93, 12.56 Hz, 1 H, 1-H), 2.24 (dtd, J = 2.19, 6.44, 12.97 Hz, 1 H, 7-H), 2.28 (ddd, J = 2.44, 4.95, 11.22 Hz, 1 H, 3-H), 3.00 (dd, J = 1.18, 9.27 Hz, 1 H, 1′-H), 3.23 (dd, J = 1.49, 9.26 Hz, 1 H, 1′-H), 3.73 (dd, J = 1.57, 3.14 Hz, 1 H, 1′′-H), 3.74 (dd, J = 1.49, 3.06 Hz, 1 H, 1′′-H), 4.09–4.16 (m, 1 H, 5-H), 5.01 (ddd, J = 1.57, 3.30, 10.44 Hz, 1 H, 3′′-H, CH=C$H_{2\ cis}$), 5.18 (ddd, J = 1.80, 3.57, 17.23 Hz, 1 H, 3′′-H, CH=C$H_{2\ trans}$), 5.45 (dt, J = 1.26, 3.57 Hz, 1 H, 4-H), 5.77 (ddd, J = 5.34, 10.51, 22.49 Hz, 1 H, 2′′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 20.67 (C-2), 29.77 (C-6), 29.93 (C-3), 30.80 (C-7), 36.14 (C-1), 45.95 (C-7a), 68.00 (C-5), 71.88 (C-1′), 72.23 (C-1′′), 116.16 (C-3′′), 124.54 (C-4), 135.52 (C-2′′), 147.71 (C-3a) ppm. IR (film): $\tilde{\nu}$ = 3357, 2945, 2861, 1677, 1452, 1350, 1269, 1093, 1012, 986, 888 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 208 (1) $[M]^+$, 152 (5), 150 (21), 135 (10), 120 (64), 119 (36), 107 (11), 93 (16), 92 (23), 91 (61), 81 (11), 79 (28), 77 (23), 67 (42), 57 (13), 55 (42), 43 (23), 41 (100). HRMS: calcd. for $C_{13}H_{20}O_2$ $[M]^+$ m/z = 208.1463; found 208.1454; deviation, 4.47 ppm.

(1a*R,2*S**,4a*R**,7a*S**)-4a-(Allyloxymethyl)octahydro-1*H*-cyclopropa[*d*]inden-2-ol (23):** Cyclopropanization of (5*S**,7a*R**)-7a-allyloxymethyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (**22**; 134 mg, 0.64 mmol) was carried out as described in GP C. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 70:30, R_f = 0.42) yielded (1a*R**,2*S**,4a*R**,7a*S**)-4a-(allyloxymethyl)-octahydro-1*H*-cyclopropa[*d*]inden-2-ol (**23**; 82 mg, 57%) as a yellowish oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.29 (dd, J = 5.18, 8.75 Hz, 1 H, 1-H), 0.44 (t, J = 5.33 Hz, 1 H, 1-H), 0.78 (d, J = 3.13 Hz, 1 H, 4-H), 0.79 (t, J = 2.67 Hz, 1 H, 5-H), 0.81–0.87 (m, 1 H, 2-H), 1.06–1.11 (m, 1 H, 3-H), 1.41–1.51 (m, 4 H, O*H*, 5-H, 7-H and 6-H), 1.59 (ddd, J = 3.46, 6.59, 21.10 Hz, 1 H, 6-H), 1.71–1.75 (m, 1 H, 4-H), 1.76 (dd, J = 3.61, 6.40 Hz, 1 H, 3-H), 2.06 (ddd, J = 2.98, 5.18, 11.91 Hz, 1 H, 7-H), 3.01 (q, J = 8.79 Hz, 2 H, 1′-H), 3.78 (dt, J = 5.26, 1.73 Hz, 2 H, 1′′-H), 3.94 (ddd, J = 2.44, 5.65, 13.58 Hz, 1 H, 2-H), 5.04 (ddd, J = 1.64, 3.46, 10.46 Hz, 1 H, 3′′-H, CH=C$H_{2\ cis}$), 5.23 (ddd, J = 1.89, 3.77, 17.23 Hz, 1 H, 3′′-H, CH=C$H_{2\ trans}$), 5.82 (ddd, J = 5.18, 10.44, 22.49 Hz, 1 H, 2′′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 8.22 (C-1), 24.61 (C-6), 26.50 (C-5), 26.83 (C-1a), 31.61 (C-4), 32.86 (C-7a), 39.76 (C-3), 39.78 (C-7), 40.72 (C-4a), 68.51 (C-2), 72.22 (C-1′′), 74.94 (C-1′), 115.85 (C-3′′), 135.80 (C-2′′) ppm. IR (film): $\tilde{\nu}$ = 3368, 2999, 2944, 2863, 1651, 1420, 1268, 1025, 921 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 220 (1) $[M - 2]^+$, 163 (5), 151 (61), 149 (4), 146 (9), 133 (59), 109 (14), 107 (27), 105 (21), 93 (18), 91 (50), 81 (25), 79 (50), 77 (24), 69 (10), 67 (62), 65 (16), 57 (27), 55 (53), 53 (19), 43 (23), 41 (100). HRMS: calcd. for $C_{14}H_{22}O_2$ $[M]^+$ m/z = 222.1620; found 222.1616; deviation, 4.42 ppm; elemental analysis calcd. (%) for $C_{14}H_{22}O_2$ (222.32): C 75.63, H 9.97; found: C 75.50, H 9.47.

(1a*R,4a*R**,7a*S**)-4a-(Allyloxymethyl)octahydro-2*H*-cyclopropa[*d*]-inden-2-one (24):** (1a*R**,2*S**,4a*R**,7a*S**)-4a-(Allyloxymethyl)octahydro-1*H*-cyclopropa[*d*]inden-2-ol (**23**; 57.0 mg, 0.26 mmol) was oxidized as described in GP D. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 50:50) afforded (1a*R**,4a*R**,7a*S**)-4a-(allyloxymethyl)octahydro-2*H*-cyclopropa[*d*]inden-2-one (**24**; 57 mg, 100%) as a yellowish oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.68 (dd, J = 5.34, 9.77 Hz, 1 H, 1-H), 0.86 (t, J = 5.11 Hz, 1 H, 1-H), 0.88–0.93 (m, 1 H, 5-H), 1.29 (dd, J = 4.79, 13.54 Hz, 1 H, 3-H), 1.31–1.38 (m, 3 H, 4-H, 7-H and 6-H), 1.42–1.48 (m, 2 H, 1a-H and 6-H), 1.59 (ddd, J = 6.52, 10.48, 12.42 Hz, 1 H, 5-H), 1.71 (dt, J = 13.81, 4.24 Hz, 1 H, 3-H), 1.81 (dd, J = 2.82, 6.87 Hz, 1 H, 7-H), 1.91 (ddd, J = 1.49, 4.51, 9.97 Hz, 1 H, 4-H), 2.92 (q, J = 8.95 Hz, 2 H, 1′-H), 3.69 (dt, J = 5.18, 1.88 Hz, 2 H, 1′′-H), 5.02 (ddd, J = 1.57, 3.33, 10.46 Hz, 1 H, 3′′-H, CH=C$H_{2\ cis}$), 5.12 (ddd, J = 1.80, 3.57, 17.25 Hz, 1 H, CH=C$H_{2\ trans}$), 5.75 (ddd, J = 5.26, 10.48, 22.49 Hz, 1 H, 2′′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 16.86 (C-1), 23.91 (C-6), 32.50 (C-1a), 33.23 (C-4), 34.58 (C-3), 38.17 (C-7), 38.63 (C-5), 39.19 (C-7a), 41.34 (C-4a), 72.02 (C-1′′), 74.68 (C-1′), 115.87 (C-3′′), 135.21 (C-2′′), 207.40 (C-2) ppm. IR (film): $\tilde{\nu}$ = 2953, 2866, 1692, 1452, 1377, 1260, 1196, 990, 854 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 221 (2) $[M + 1]^+$, 220 (2) $[M]^+$, 179 (3), 163 (7), 162 (9), 150 (10), 149 (73), 134 (9), 121 (11), 107 (40), 105 (11), 93 (12), 91 (27), 79 (63), 77 (22), 71 (10), 67 (27), 65 (17), 55 (58), 53 (18), 43 (16), 41 (100). HRMS: calcd. for $C_{14}H_{20}O_2$ $[M]^+$ m/z = 220.1463; found 220.1462; deviation, 0.73 ppm.

(5*S,7a*R**)-7a-Prop-2′′-ynyloxymethyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (25):** Reduction of 7a-prop-2′′-ynyloxymethyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (*rac*-**12**; 591 mg, 2.89 mmol) was carried out as described in GP B. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 70:30, R_f = 0.46) afforded (5*S**,7a*R**)-7a-prop-2′′-ynyloxymethyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (**25**; 167 mg, 28%) as a colourless oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 1.03 (ddd, J = 3.77, 10.68, 21.36 Hz, 1 H, 1-H), 1.10 (dd, J = 3.14, 3.82 Hz, 1 H, 7-H), 1.48 (dddd, J = 1.88, 5.03, 9.42, 22.61 Hz, 1 H, 2-H), 1.57–1.68 (m, 3 H, 2-H, O*H* and 6-H), 1.81 (ddd, J = 3.14, 6.28, 13.19 Hz, 1 H, 6-H), 1.98 (t, J = 2.51 Hz, 1 H, 3′′-H), 2.03 (ddd, J = 6.28, 10.04, 21.98 Hz, 1 H, 3-H), 2.13 (ddd, J = 2.51, 7.54, 12.37 Hz, 1 H, 1-H), 2.22 (ddd, J = 2.51, 6.28,

24.81 Hz, 1 H, 3-H), 2.23 (dd, *J* = 3.14, 7.54 Hz, 1 H, 7-H), 3.06 (d, *J* = 8.17 Hz, 1 H, 1′-H), 3.12 (dd, *J* = 1.89, 9.11 Hz, 1 H, 1′-H), 3.78 (d, *J* = 2.51 Hz, 2 H, 1′′-H), 4.11 (dt, *J* = 4.39, 9.42 Hz, 1 H, 5-H), 5.42 (dd, *J* = 1.88, 5.65 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 20.57 (C-2), 29.64 (C-6), 29.80 (C-3), 30.72 (C-7), 35.95 (C-1), 45.79 (C-7a), 58.36 (C-1′′), 68.11 (C-5), 71.11 (C-1′), 74.36 (C-3′′), 80.38 (C-2′′), 124.69 (C-4), 147.44 (C-3a) ppm. IR (film): $\tilde{\nu}$ = 3297, 2944, 2117, 1452, 1359, 1248, 1092, 950, 886 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 207 (2) [*M* + 1]$^+$, 173 (2), 150 (12), 149 (13), 137 (23), 136 (15), 135 (26), 122 (16), 121 (17), 120 (71), 119 (61), 118 (17), 117 (14), 108 (19), 107 (22), 105 (13), 95 (15), 93 (23), 91 (100), 81 (18), 79 (48), 77 (37), 69 (16), 67 (76), 66 (13), 65 (31), 57 (21), 55 (78), 53 (31), 51 (22), 43 (41). HRMS: calcd. for $C_{13}H_{18}O_2$ [*M*]$^+$ *m*/*z* = 206.1307; found 206.1299; deviation, 2.21 ppm.

(1a*R,2*S**,4a*R**,7a*S**)-4a-(Prop-2′′-ynyloxymethyl)octahydro-1*H*-cyclopropa[*d*]inden-2-ol (26):** Cyclopropanization of (5*S**,7a*R**)-7a-prop-2′′-ynyloxymethyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-5-ol (**25**; 156 mg, 0.76 mmol) was carried out as described in GP C. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 70:30, R_f = 0.30) yielded (1a*R**,2*S**,4a*R**,7a*S**)-4a-(prop-2′′-ynyloxymethyl)octahydro-1*H*-cyclopropa[*d*]inden-2-ol (**26**; 82 mg, 49%) as a colourless oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.28 (dd, *J* = 5.26, 8.79 Hz, 1 H, 1-H), 0.42 (t, *J* = 5.34 Hz, 1 H, 1-H), 0.74–0.87 (m, 3 H, 4-H, 5-H and 1a-H), 1.06 (ddd, *J* = 2.35, 4.39, 14.36 Hz, 1 H, 3-H), 1.39–1.49 (m, 4 H, O*H*, 5-H, 7-H and 6-H), 1.54–1.61 (m, 1 H, 6-H), 1.67–1.74 (m, 2 H, 4-H and 3-H), 1.99 (t, *J* = 2.35 Hz, 1 H, 3′′-H), 2.03 (dd, *J* = 2.90, 6.79 Hz, 1 H, 7-H), 3.10 (q, *J* = 8.71 Hz, 2 H, 1′-H), 3.84 (d, *J* = 3.85 Hz, 2 H, 1′′-H), 3.92 (dt, *J* = 9.96, 5.97 Hz, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 8.22 (C-1), 24.56 (C-6), 26.43 (C-5), 26.81 (C-1a), 31.48 (C-4), 32.80 (C-7a), 39.68 (C-7), 39.67 (C-3), 40.53 (C-4a), 58.41 (C-1′′), 68.43 (C-2), 74.23 (C-3′′), 74.42 (C-1′), 80.56 (C-2′′) ppm. IR (film): $\tilde{\nu}$ = 3309, 2940, 2860, 2117, 1453, 1355, 1264, 1096, 959 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 202 (2) [*M* – 18]$^+$, 173 (2), 164 (5), 151 (94), 149 (11), 148 (4), 146 (6), 134 (11), 133 (92), 131 (11), 120 (20), 109 (16), 108 (10), 107 (36), 105 (27), 95 (16), 93 (21), 92 (13), 91 (82), 83 (12), 81 (36), 80 (10), 79 (86), 78 (17), 77 (42), 69 (20), 68 (10), 67 (91), 66 (11), 65 (26), 57 (51), 55 (93), 53 (39), 51 (13), 43 (30), 41 (92), 39 (100). HRMS: calcd. for $C_{14}H_{20}O_2$ [*M*]$^+$ *m*/*z* = 220.1463; found 220.1458; deviation, 1.71 ppm; elemental analysis calcd. (%) for $C_{14}H_{20}O_2$ (220.31): C 76.33, H 9.15; found: C 76.50, H 9.20.

(1a*R,4a*R**,7a*S**)-4a-(Prop-2′′-ynyloxymethyl)octahydro-2*H*-cyclopropa[*d*]inden-2-one (27):** (1a*R**,2*S**,4a*R**,7a*S**)-4a-(Prop-2′′-ynyloxymethyl)octahydro-1*H*-cyclopropa[*d*]inden-2-ol (**26**; 58.0 mg, 0.26 mmol) was oxidized as described in GP D. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate 50:50) afforded (1a*R**,4a*R**,7a*S**)-4a-(prop-2′′-ynyloxymethyl)octahydro-2*H*-cyclopropa[*d*]inden-2-one (**27**; 57 mg, 99%) as an orange oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.67 (dd, *J* = 5.33, 9.78 Hz, 1 H, 1-H), 0.82 (t, *J* = 5.18 Hz, 1 H, 1-H), 0.85–0.92 (m, 1 H, 5-H), 1.25 (dd, *J* = 4.16, 13.70 Hz, 1 H, 3-H), 1.28–1.39 (m, 3 H, 4-H, 7-H and 6-H), 1.39–1.47 (m, 2 H, 1a-H and 6-H), 1.52–1.59 (m, 1 H, 5-H), 1.67 (dt, *J* = 13.81, 4.16 Hz, 1 H, 3-H), 1.78–1.84 (m, 1 H, 7-H), 1.90 (dtdt, *J* = 1.57, 4.24, 1.34, 4.28 Hz, 1 H, 4-H), 1.97 (t, *J* = 2.43 Hz, 1 H, 3′′-H), 3.75 (t, *J* = 2.20 Hz, 2 H, 1′′-H), 3.08 (q, *J* = 8.79 Hz, 2 H, 1′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 17.06 (C-1), 24.09 (C-6), 32.62 (C-1a), 33.31 (C-4), 34.63 (C-3), 38.33 (C-7), 38.77 (C-5), 39.25 (C-7a), 41.32 (C-4a), 58.39 (C-1′′), 74.13 (C-1′), 74.47 (C-3′′), 80.19 (C-2′′), 207.35 (C-2) ppm. IR (film): $\tilde{\nu}$ = 2955, 2865, 2116, 1691, 1452, 1358, 1259, 1160, 1095, 870 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 218 (3) [*M*]$^+$, 179 (6), 162 (8), 161 (6), 150 (11), 149 (100), 148 (13), 134 (17), 133 (10), 121 (13), 120 (18), 119 (15), 107 (50), 105 (18), 93 (14), 91 (42), 81 (10), 80 (10), 79 (84), 77 (35), 69 (24), 67 (32), 65 (30), 55 (66), 53 (30). HRMS: calcd. for $C_{14}H_{18}O_2$ [*M*]$^+$ *m*/*z* = 218.1307; found 218.1321; deviation, 6.69 ppm.

(1a*R,3a*S**,6*S**,6a*S**)-6-Prop-2′-ynyl-1a,3a,4,5,6,6a-hexahydrocyclopropa[*c*]pentalen-2(3*H*)-one[51] (29a):** A suspension of sodium hydride (60%; 506 mg, 15.1 mmol) in paraffin was washed three times with *n*-hexane (10 mL). The solvent was pipetted out and residual traces were then removed under reduced pressure. The NaH was placed under argon in a dry apparatus, and trimethylsulfoxonium iodide salt (3.32 g, 15.1 mmol) was added, followed by dry DMSO (45 mL). The suspension was stirred for 45 min, until evolution of hydrogen ceased. 4-Prop-2′-ynyl-4,5,6,6a-tetrahydropentalen-2(1*H*)-one, as a 16:1 (**28a/28b**) mixture of two diastereomers in dry DMSO (30 mL), was added over 20 min with ice cooling. The reaction mixture was stirred for 2 h at room temperature, slowly warmed to 50 °C and stirred for 1.5–2 h at this temperature. The mixture was poured onto ice water and extracted with Et_2O (3 × 80 mL). The combined organic layers were washed with water (2 × 20 mL) and dried with Na_2SO_4. The solvent was removed by evaporation and the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 70:30, R_f = 0.34) to yield a mixture of four diastereomeric cyclopropanization products in a 81:6:8:5 (**29a/29b/29c/29d**) ratio as a colourless oil (1.25 g, 65%). Subsequent separation by HPLC (cyclohexane/ethyl acetate 85:15) yielded (1a*R**,3a*S**,6*S**,6a*S**)-6-prop-2′-ynyl-1a,3a,4,5,6,6a-hexahydrocyclopropa[*c*]pentalen-2(3*H*)-one (**29a**; 744 mg, 40%) as a colourless oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY. ^{1}H NMR (500 MHz, $CDCl_3$, ref. $CHCl_3$): δ = 1.21 (dd, *J* = 3.22, 4.86 Hz, 1 H, 1-H), 1.32 (ddt, *J* = 9.54, 20.73, 2.51 Hz, 1 H, 5-H), 1.51 (dd, *J* = 4.87, 9.54 Hz, 1 H, 1-H), 1.62 (ddd, *J* = 3.22, 5.10, 13.19 Hz, 1 H, 4-H), 1.65 (ddd, *J* = 3.22, 5.26, 13.39 Hz, 1 H, 4-H), 1.89 (t, *J* = 2.67 Hz, 1 H, 3′-H), 1.92 (dd, *J* = 2.75, 9.86 Hz, 1 H, 1a-H), 1.96 (ddd, *J* = 2.59, 4.99, 18.94 Hz, 1 H, 3-H), 1.98 (dt, *J* = 2.67, 6.99 Hz, 2 H, 1′-H), 2.01–2.07 (m, 1 H, 5-H), 2.25 (dd, *J* = 7.53, 18.65 Hz, 1 H, 3-H), 2.43 (dd, *J* = 7.06, 10.13 Hz, 1 H, 3a-H), 2.47 (dt, *J* = 7.07, 2.20 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, ref. $CHCl_3$): δ = 17.14 (C-1), 21.90 (C-1′), 30.71 (C-1a), 31.47 (C-4), 31.68 (C-5), 37.54 (C-6), 40.11 (C-3), 41.53 (C-3a), 46.30 (C-6a), 69.08 (C-3′), 82.47 (C-2′), 214.40 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3294, 2956, 2874, 2118, 1722, 1448, 1332, 1256, 1176, 967 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 175 (4) [*M* + 1]$^+$, 174 (2) [*M*]$^+$, 159 (4), 146 (12), 145 (11), 135 (32), 134 (25), 133 (7), 132 (10), 131 (37), 119 (10), 118 (23), 117 (44), 115 (20), 106 (11), 105 (30), 104 (29), 103 (16), 94 (34), 93 (33), 92 (29), 91 (100), 80 (28), 79 (66), 78 (32), 77 (83), 66 (18), 65 (12), 55 (73), 53 (22), 51 (15), 41 (26). GC-MS (CI, isobutane): *m*/*z* (%) = 175 (100) [*M* + H]$^+$, 147 (2), 131 (2), 105 (3). HRMS: calcd. for $C_{12}H_{14}O$ [*M*]$^+$ *m*/*z* = 174.1045; found 174.1031; deviation, 3.50 ppm; elemental analysis calcd. (%) for $C_{12}H_{14}O$ (174.24): C 82.72, H 8.10; found: C 82.79, H 8.03.

General Procedure E (PET Reductive Reaction): The appropriate tricyclic α-cyclopropyl ketone (1.00 mmol) and dry triethylamine (5.00 or 15.0 mmol) were dissolved in dry acetonitrile or in a dry acetonitrile/$LiClO_4$ (1.00 mmol) solution. The solution was apportioned in Duran (12 mL, 1 cm diameter) or quartz (10 mL, 1 cm diameter) irradiation tubes, these were sealed with septa, and the solutions were deoxygenated by use of argon and ultrasound irradiation for 1 h. The solutions were irradiated in a Rayonet RPR-100 photochemical reactor with use of lamps of the appropriate wavelength (quartz tubes: 254 nm; Duran tubes: 300 nm) for several hours. The reactions were monitored by gas chromatography. The irradiation was carried

out until maximum conversion of the starting material. The solvent was removed under reduced pressure and the residue was generally purified by column chromatography on silica gel and/or by HPLC. The reactions in the presence of lithium perchlorate were worked up as follows: ether (50 mL) and water (20 mL) were added, the aqueous layer was extracted with ethyl acetate (2×50 mL) after separation, the combined organic layers were dried with Na_2SO_4, and the solvents were removed by evaporation.

PET Reductive Reactions of (1a*R,4a*S**,7a*S**)-4a-Prop-2′-ynyloctahydro-2*H*-cyclopropa[d]inden-2-one (15):** As described in General Procedure E, a solution of (1a*R**,4a*S**,7a*S**)-4a-prop-2′-ynyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (**15**; 160 mg, 0.85 mmol) in dry acetonitrile (0.04 M) was irradiated in the presence of $LiClO_4$ (91.0 mg, 0.85 mmol) and dry TEA (4.25 mmol) at 254 nm (quartz tubes) for 2 h. The crude product was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 80:20, R_f = 0.53), yielding (3a*S**,7a*S**)-2-methylenetetrahydro-1*H*-3a,7a-propanoinden-5-one (**30**; 120 mg, 74%) as a yellowish oil. Irradiation of **15** (161 mg, 0.86 mmol) in dry acetonitrile (0.04 M) at 300 nm for 15 h was carried out as described in GP E, yielding **30** (75 mg, 46%) as a yellowish oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, HMBC. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 1.14 (ddd, J = 1.65, 5.34, 12.33 Hz, 1 H, 8-H), 1.21–1.23 (m, 1 H, 7-H), 1.24–1.35 (m, 6 H, 2×6-H, 2×9-H, 7-H and 8-H), 1.85 (ddd, J = 2.04, 2.30, 14.96 Hz, 1 H, 3-H), 1.89–1.91 (m, 1 H, 1-H), 1.92–1.94 (m, 1 H, 3-H), 1.95 (q, J = 6.67 Hz, 2 H, 2×10-H), 1.97–2.01 (m, 1 H, 1-H), 2.06 (d, J = 14.60 Hz, 2 H, 2×4-H), 4.75 (dd, J = 1.81, 3.61 Hz, 1 H, 1′-H), 4.78 (dd, J = 1.81, 3.57 Hz, 1 H, 1′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 22.84 (C-9), 32.00 (C-7), 35.74 (C-10)*, 39.67 (C-6), 40.69 (C-8)*, 46.77 (C-3)**, 47.67 (C-1)**, 48.98 (C-4), 49.44 (C-7a), 51.79 (C-3a), 107.02 (C-1′), 149.58 (C-2), 210.40 (C-5) ppm; */**) signal assignments are mutually interchangeable. IR (film): $\tilde{\nu}$ = 2866, 1715, 1666, 1455, 1378, 1293, 1181, 1072, 997 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 191 (3) $[M + 1]^+$, 190 (23) $[M]^+$, 162 (14), 161 (30), 157 (5), 149 (9), 148 (36), 147 (19), 136 (12), 135 (100), 134 (27), 133 (43), 132 (33), 123 (21), 120 (78), 119 (98), 117 (23), 107 (30), 106 (19), 105 (40), 93 (31), 91 (95), 79 (95), 77 (61), 67 (29), 65 (42), 63 (11), 55 (60), 53 (36), 51 (22). HRMS: calcd. for $C_{13}H_{18}O$ $[M]^+$ m/z = 190.1358; found 190.1355; deviation, 1.37 ppm.

PET Reductive Reactions of (1a*R,4a*R**,7a*S**)-4a-But-3′-ynyloctahydro-2*H*-cyclopropa[d]inden-2-one (18)**

Irradiation in the Presence of Five Equivalents of TEA: As described in General Procedure E, a solution of (1a*R**,4a*R**,7a*S**)-4a-but-3′-ynyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (**18**; 17.0 mg, 0.08 mmol) in dry acetonitrile (0.04 M) was irradiated in the presence of $LiClO_4$ (9.00 mg, 0.08 mmol) and dry TEA (0.40 mmol) at 254 nm (quartz tubes) for 3 h. The crude material was filtered through silica gel (cyclohexane/ethyl acetate 50:50) and purified by HPLC (cyclohexane/ethyl acetate 99:1), yielding (3a*R**,7a*R**)-7a-but-3′-ynyl-3a-methyloctahydro-5*H*-inden-5-one (**33**; 3 mg, 17%) and a mixture (5 mg, 29%) of (4a*R**,8a*S**)-7-methylenehexahydro-4a,8a-propanonaphthalen-2-one (**31**) and (3a*R**,7a*S**)-7a-buta-2′,3′-dienyl-3a-methyloctahydro-5*H*-inden-5-one (**34**) as yellowish oils. The product ratio was determined by GC directly from the reaction mixture as 67:33 (**34/31**). The structural and stereochemical assignments were carried out by direct comparison with the analogous spectra of the same compounds, isolated by irradiation of **18** with 15 equivalents of TEA (**31**; see below) and by reduction of **18** with SmI_2 (**34**).[64]

Irradiation in the Presence of 15 Equivalents of TEA: The compound was again produced by GP E, a solution of (1a*R**,4a*R**,7a*S**)-4a-but-3′-ynyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (**18**; 291 mg, 1.44 mmol) in dry acetonitrile (0.04 M) being irradiated in the presence of $LiClO_4$ (51.0 mg, 1.44 mmol) and dry TEA (21.6 mmol) at 254 nm (quartz tubes) for 3 h. The crude material was filtered through silica gel (cyclohexane/ethyl acetate 50:50) and separated by HPLC (cyclohexane/ethyl acetate 98:2), yielding (4a*R**,8a*S**)-7-methylenehexahydro-4a,8a-propanonaphthalen-2-one (**31**; 21 mg, 7%) and (3a*R**,7a*R**)-7a-but-3′-ynyl-3a-methyloctahydro-5*H*-inden-5-one (**33**; 9 mg, 3%) as yellowish oils and (3a*S**,5*S**,6*R**,7a*R**)-7a-methyl-5-vinylhexahydro-3a,6-ethanoinden-6(1*H*)-ol (**32**; 22 mg, 7%) as a white solid with m.p. 50.8 °C.

(4a*R,8a*S**)-7-Methylenehexahydro-4a,8a-propanonaphthalen-2-one (31):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 1.12 (dt, J = 5.67, 13.64 Hz, 1 H, 5-H), 1.15–1.19 (m, 1 H, 9-H), 1.23 (dd, J = 6.14, 14.07 Hz, 1 H, 6-H), 1.27 (dd, J = 3.40, 9.35 Hz, 1 H, 5-H), 1.29–1.33 (m, 2 H, 2×10-H), 1.34 (dd, J = 3.40, 5.95 Hz, 1 H, 6-H), 1.39–1.46 (m, 2 H, 2×11-H), 1.46–1.50 (m, 1 H, 9-H), 1.52 (d, J = 13.97 Hz, 1 H, 8-H), 1.80 (d, J = 13.60 Hz, 1 H, 8-H), 1.92 (dd, J = 1.70, 14.26 Hz, 1 H, 1-H), 1.93 (dd, J = 13.99, 15.86 Hz, 1 H, 4-H), 1.95–1.99 (m, 1 H, 4-H), 2.00 (dd, J = 1.79, 6.14 Hz, 1 H, 3-H), 2.03 (dd, J = 1.61, 8.08 Hz, 1 H, 3-H), 2.18 (dd, J = 1.04, 14.26 Hz, 1 H, 1-H), 4.53 (s, 1 H, 1′-H), 4.72 (s, 1 H, 1′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 18.60 (C-10), 30.49 (C-4), 31.51 (C-5), 33.46 (C-6), 34.00 (C-9)*, 36.18 (C-11)*, 37.32 (C-3), 42.25 (C-8a), 42.47 (C-8), 47.17 (C-1), 49.77 (C-4a), 109.84 (C-1′), 146.24 (C-7), 209.54 (C-2) ppm; */**) signal assignments are mutually interchangeable. IR (film): $\tilde{\nu}$ = 2954, 2923, 2873, 1715, 1467, 1316, 886 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 204 (17) $[M]^+$, 186 (4), 176 (4), 171 (4), 162 (4), 147 (14), 146 (15), 135 (17), 133 (100), 132 (28), 131 (13), 119 (11), 117 (14), 109 (14), 107 (14), 105 (32), 96 (10), 94 (15), 93 (32), 91 (72), 79 (61), 77 (46), 67 (26), 65 (27), 55 (23), 53 (16). HRMS: calcd. for $C_{14}H_{20}O$ $[M]^+$ m/z = 204.1514; found 204.1511; deviation, 0.98 ppm.

(3a*S,5*S**,6*R**,7a*R**)-7a-Methyl-5-vinylhexahydro-3a,6-ethanoinden-6(1*H*)-ol (32):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.83 (s, 3 H, CH_3), 1.02 (dddd, J = 1.64, 3.03, 6.56, 12.34 Hz, 1 H, 5-H), 1.07 (ddd, J = 3.14, 8.64, 12.24 Hz, 1 H, 3-H), 1.25 (dd, J = 7.38, 13.23 Hz, 1 H, 1′-H), 1.28 (s, 1 H, OH), 1.30 (dd, J = 3.14, 5.97 Hz, 1 H, 3-H), 1.33 (dd, J = 1.28, 7.62 Hz, 1 H, 4-H), 1.39–1.42 (m, 1 H, 1-H), 1.42 (dd, J = 3.22, 12.48 Hz, 1 H, 7-H), 1.51–1.54 (m, 1 H, 2-H), 1.57 (ddd, J = 2.57, 5.50, 11.15 Hz, 1 H, 1-H), 1.58–1.61 (m, 1 H, 4-H), 1.63 (dd, J = 4.16, 7.85 Hz, 1 H, 2-H), 1.64–1.67 (m, 1 H, 5-H), 1.73 (q, J = 4.24 Hz, 1 H, 7-H), 1.75 (dd, J = 3.38, 13.39 Hz, 1 H, 1′-H), 2.41 (dq, J = 2.12, 8.76 Hz, 1 H, 2′-H), 5.02 (d, J = 1.02 Hz, 1 H, 4′-H), 5.05 (ddd, J = 1.02, 2.05, 5.59 Hz, 1 H, 4′-H), 5.74 (tdd, J = 5.57, 8.56, 13.54 Hz, 1 H, 3′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 21.43 (C-2), 26.84 (CH_3), 30.83 (C-4), 32.18 (C-5), 32.91 (C-3), 35.93 (C-1′), 39.64 (C-1), 41.42 (C-3a), 44.21 (C-7a), 46.62 (C-2′), 49.78 (C-7), 71.63 (C-6), 117.34 (C-4′), 140.30 (C-3′) ppm. IR (KBr): $\tilde{\nu}$ = 3463, 2872, 2279, 1617, 1451, 1329, 1088, 916, 812 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 206 (5) $[M]^+$, 191 (19) $[M - 15]^+$, 189 (4), 188 (5), 178 (4), 177 (5), 165 (10), 164 (85), 151 (15), 149 (13), 136 (15), 133 (12), 123 (20), 122 (25), 121 (53), 119 (15), 110 (19), 109 (30), 108 (14), 105 (15), 96 (14), 95 (100), 94 (74), 93 (92), 91 (47), 81 (33), 80 (17), 79 (67), 77 (35), 69 (15), 68 (20), 67 (77), 65 (17), 55 (65), 53 (24). HRMS: calcd. for $C_{14}H_{22}O$ $[M]^+$ m/z = 206.1671; found 191.1431 $[M - CH_3]^+$*; deviation, 0.52 ppm; *) no $[M]^+$ signal detected.

(3a*R,7a*R**)-7a-But-3′-ynyl-3a-methyloctahydro-5*H*-inden-5-one (33):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.49 (s, 3 H, CH_3), 1.05 (dd, J = 4.32, 8.32 Hz, 1 H, 3-H), 1.08 (dd, J = 3.76, 12.56 Hz, 1 H, 2-

H), 1.09–1.11 (m, 1 H, 6-H), 1.12 (dd, *J* = 1.88, 6.91 Hz, 1 H, 7-H), 1.15 (ddd, *J* = 3.53, 6.51, 12.78 Hz, 1 H, 2-H), 1.28 (ddd, *J* = 2.51, 4.40, 8.50 Hz, 1 H, 1-H), 1.31 (ddd, *J* = 3.38, 5.57, 13.76 Hz, 1 H, 1′-H), 1.35 (dd, *J* = 5.57, 12.05 Hz, 1 H, 1-H), 1.38 (tdd, *J* = 2.51, 1.89, 17.59 Hz, 1 H, 3-H), 1.48 (dd, *J* = 10.04, 13.82 Hz, 1 H, 1′-H), 1.74 (dd, *J* = 1.25, 14.44 Hz, 1 H, 4-H), 1.78 (dd, *J* = 2.99, 8.64 Hz, 1 H, 2′-H), 1.79 (t, *J* = 2.51 Hz, 1 H, 4′-H), 1.80–1.86 (m, 2 H, 6-H and 2′-H), 1.89 (dtd, *J* = 1.89, 5.02, 14.44 Hz, 1 H, 7-H), 2.02 (dd, *J* = 1.88, 14.45 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 14.77 (C-2′), 19.04 (C-2), 23.56 (*C*H$_3$), 29.77 (C-1′), 31.84 (C-7), 33.81 (C-6), 37.37 (C-1), 37.50 (C-3), 44.90 (C-3a), 48.79 (C-7a), 49.11 (C-4), 68.87 (C-4′), 84.77 (C-3′), 208.64 (C-5) ppm. IR (film): $\tilde{\nu}$ = 3292, 2874, 2118, 1713, 1451, 1379, 1245, 1084 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 204 (19) [*M*]$^+$, 203 (4) [*M* – 1]$^+$, 189 (8), 176 (5), 175 (9), 160 (9), 148 (13), 147 (25), 134 (10), 133 (32), 131 (11), 121 (16), 120 (19), 118 (33), 109 (27), 108 (16), 107 (30), 106 (23), 105 (66), 95 (26), 94 (16), 93 (46), 92 (26), 91 (100), 81 (41), 80 (21), 79 (77), 78 (21), 77 (51), 69 (18), 68 (26), 67 (76), 65 (23), 55 (76), 53 (49). HRMS: calcd. for $C_{14}H_{20}O$ [*M*]$^+$ *m*/*z* = 204.1514; found 204.1507; deviation, 1.03 ppm.

(3a*R,7a*S**)-7a-Buta-2′,3′-dienyl-3a-methyloctahydro-5*H*-inden-5-one (34):** NMR experiments*: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT; *) the spectroscopic data of **34** were taken from the combined spectra of the compound mixture with the product **31** (**34/31** 67:33). ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.55 (s, 3 H, C*H*$_3$), 1.14 (dd, *J* = 2.75, 4.87 Hz 1 H, 3-H), 1.22–1.42 (m, 4 H, 2×2-H, 7-H and 3-H), 1.46 (t, *J* = 5.81 Hz, 1 H, 6-H), 1.48 (dd, *J* = 5.81, 11.07 Hz, 1 H, 1-H), 1.78 (d, *J* = 14.44 Hz, 1 H, 4-H), 1.78–1.82 (m, 1 H, 1-H), 1.92 (dd, *J* = 1.73, 14.78 Hz, 1 H, 1′-H), 1.97–2.02 (m, 1 H, 7-H), 2.01 (dd, *J* = 5.81, 8.64 Hz, 1 H, 6-H), 2.07 (d, *J* = 14.75 Hz, 1 H, 4-H), 2.11 (dd, *J* = 1.34, 14.25 Hz, 1 H, 1′-H), 4.56 (dd, *J* = 1.72, 3.38 Hz, 1 H, 4′-H), 4.57 (dd, *J* = 1.88, 3.30 Hz, 1 H, 4′-H), 4.84 (ddd, *J* = 6.75, 8.94, 13.70 Hz, 1 H, 2′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 19.11 (C-2), 23.36 (*C*H$_3$), 30.86 (C-1), 33.09 (C-1′), 33.83 (C-7), 37.39 (C-6), 38.03 (C-3), 45.72 (C-3a), 45.60 (C-7a), 49.54 (C-4), 73.87 (C-4′), 87.15 (C-2′), 208.91 (C-3′), 209.84 (C-5) ppm. IR (film): $\tilde{\nu}$ = 3069, 2933, 2873, 1954, 1714, 1466, 1378, 1316, 1238, 1204, 1163, 861 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 204 (29) [*M*]$^+$, 150 (30), 135 (28), 133 (47), 117 (25), 109 (26), 108 (64), 105 (44), 95 (56), 91 (100), 80 (22), 79 (80), 77 (35), 67 (47), 65 (27), 55 (39), 53 (70). HRMS: calcd. for $C_{14}H_{20}O$ [*M*]$^+$ *m*/*z* = 204.1514; found 204.1508; deviation, 2.89 ppm.

PET Reductive Reaction of (1a*R,4a*S**,7a*S**)-4a-Allyloctahydro-2*H*-cyclopropa[*d*]inden-2-one (21a):** As described in General Procedure E, a solution of (1a*R**,4a*S**,7a*S**)-4a-allyloctahydro-2*H*-cyclopropa[*d*]-inden-2-one (**21a**; 264 mg, 1.39 mmol) in dry acetonitrile (0.04 M) was irradiated in the presence of $LiClO_4$ (148 mg, 1.39 mmol) and dry TEA (6.95 mmol) at 254 nm (quartz tubes) for 3 h. The crude product was filtered through silica gel (cyclohexane/ethyl acetate 90:10) and the product fraction from the column chromatography (R_f = 0.46) was further purified by HPLC (cyclohexane/ethyl acetate 99:1), yielding a mixture (91 mg, 34%) of the two isomeric cyclization products (3a*S**,7a*S**)-*syn*-2-methyl-6,7,9,10-tetrahydro-1*H*-3a,7a-propanoinden-5-one (**35a**) and (3a*S**,7a*S**)-*anti*-2-methyl-6,7,9,10-tetrahydro-1*H*-3a,7a-propanoinden-5-one (**35b**) as a colourless oil. The product ratio was determined by GC directly from the reaction mixture (**35a/35b** 69:31). The mixture was separated by preparative gas chromatography (180 °C isotherm for 15 min/ 0.43 mbar) for spectroscopic characterization.

(3a*S,7a*S**)-*syn*-2-Methyl-6,7,9,10-tetrahydro-1*H*-3a,7a-propanoinden-5-one (35a):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.83 (d, *J* = 9.36 Hz, 3 H, C*H*$_3$), 0.84 (t, *J* = 12.32 Hz, 1 H, 3-H), 0.89 (t, *J* = 12.32 Hz, 1 H, 1-H), 0.97 (dd, *J* = 6.51, 11.54 Hz, 1 H, 8-H), 1.15 (dd, *J* = 5.02, 9.82 Hz, 1 H, 10-H), 1.17 (dd, *J* = 5.97, 9.82 Hz, 1 H, 10-H), 1.24 (dd, *J* = 4.48, 8.36 Hz, 1 H, 7-H), 1.26–1.32 (m, 4 H, 3-H, 8-H, 2×9-H),1.33 (dd, *J* = 2.82, 7.93 Hz, 1 H, 7-H), 1.43 (ddd, *J* = 2.51, 5.81, 12.44 Hz, 1 H, 1-H), 1.60 (ddd, *J* = 6.04, 12.21, 24.33 Hz, 1 H, 2-H), 1.98 (dd, *J* = 2.12, 5.18 Hz, 1 H, 6-H), 1.99 (d, *J* = 4.48 Hz, 1 H, 6-H), 2.02 (d, *J* = 14.68 Hz, 1 H, 4-H), 2.19 (d, *J* = 14.76 Hz, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 18.65 (*C*H$_3$), 22.05 (C-9), 31.60 (C-2), 31.94 (C-7), 35.39 (C-6), 37.64 (C-10), 40.03 (C-8), 42.38 (C-7a), 45.05 (C-3a), 49.80 (C-4), 51.05 (C-3), 51.62 (C-1), 210.98 (C-5) ppm. IR (film): $\tilde{\nu}$ = 2865, 1714, 1457, 1375, 1249, 1191, 1064, 736 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 193 (3) [*M* + 1]$^+$, 192 (28) [*M*]$^+$, 177 (7), 174 (6), 164 (11), 163 (19), 150 (40), 149 (25), 145 (12), 137 (100), 136 (43), 135 (46), 134 (37), 123 (20), 122 (59), 121 (96), 120 (13), 119 (11), 109 (21), 108 (55), 107 (55), 106 (14), 105 (19), 95 (31), 94 (49), 93 (93), 92 (14), 91 (45), 81 (39), 80 (18), 79 (80), 78 (12), 77 (40), 67 (38), 65 (21), 57 (10), 55 (63), 53 (37), 51 (15). HRMS: calcd. for $C_{13}H_{20}O$ [*M*]$^+$ *m*/*z* = 192.1514; found 192.1514; deviation, 0.16 ppm.

(3a*S,7a*S**)-*anti*-2-Methyl-6,7,9,10-tetrahydro-1*H*-3a,7a-propanoinden-5-one (35b):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C*, ^{13}C-DEPT*; *) signals were taken from the ^{13}C spectra of the isomeric mixture. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.74 (d, *J* = 10.05 Hz, 3 H, C*H*$_3$), 1.13 (dd, *J* = 2.51, 3.64 Hz, 1 H, 7-H), 1.19 (dd, *J* = 2.51, 12.55 Hz, 1 H, 3-H), 1.20 (dd, *J* = 2.51, 12.55 Hz, 1 H, 3-H), 1.24–1.33 (m, 6 H), 1.37 (dt, *J* = 10.05, 2.51 Hz, 1 H, 1-H), 1.41 (dd, *J* = 2.51, 6.28 Hz, 1 H, 7-H), 1.49 (dd, *J* = 2.51, 9.08 Hz, 1 H, 1-H), 1.51–1.61 (m, 1 H, 2-H),1.93–1.96 (m, 2 H, 2×6-H), 2.40 (ddd, *J* = 9.42, 11.42, 14.46 Hz, 1 H, 4-H), 2.48 (ddd, *J* = 1.80, 4.05, 11.85 Hz, 1 H, 4-H) ppm. ^{13}C NMR* (125 MHz, C_6D_6, ref. C_6H_6): δ = 23.07 (*C*H$_3$), 26.11 (C-9), 32.86 (C-2, *C*H), 33.19 (C-7), 35.54 (C-6), 38.53 (C-10), 39.88 (C-8), 46.13 (C-7a), 46.93 (C-3a), 50.27 (C-4), 51.47 (C-3), 52.06 (C-1), 212.68 (C-5) ppm. IR (film): $\tilde{\nu}$ = 2865, 1714, 1457, 1375, 1249, 1181, 736 cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 191 (12) [*M* – 1]$^+$, 190 (74) [*M* – 2]$^+$, 175 (6), 172 (19), 162 (35), 161 (32), 149 (28), 148 (24), 147 (19), 136 (17), 135 (39), 134 (31), 133 (35), 132 (13), 131 (24), 121 (20), 120 (63), 119 (39), 118 (24), 117 (19), 115 (10), 109 (14), 108 (16), 107 (66), 106 (25), 105 (56), 96 (17), 94 (21), 93 (33), 92 (36), 91 (90), 81 (16), 79 (100), 78 (25), 77 (51), 70 (10), 67 (36), 65 (32), 57 (16), 55 (52), 53 (36), 51 (21). HRMS: calcd. for $C_{13}H_{20}O$ [*M*]$^+$ *m*/*z* = 192.1514; found 190.1359** [*M* – 2]$^+$; deviation, 0.16 ppm; **) no [*M*]$^+$ signal detected.

PET Reductive Reactions of (1a*R,3a*S**,6*S**,6a*S**)-6-Prop-2′-ynyl-1a,3a,4,5,6,6a-hexahydrocyclopropa[*c*]pentalen-2(3*H*)-one (29a):** As described in General Procedure E, a solution of (1a*R**,3a*S**,6*S**,6a*S**)-6-prop-2′-ynyl-1a,3a,4,5,6,6a-hexahydrocyclopropa[*c*]pentalen-2(3*H*)-one (**29a**; 172 mg, 0.98 mmol) in dry acetonitrile (0.04 M) was irradiated in the presence of $LiClO_4$ (0.98 mmol) and dry TEA (4.90 mmol) at 254 nm (quartz tubes) for 9 h. The crude product was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 80:20), yielding (3a*S**,5a*S**,9a*S**)-3a,4,5,5a,6,9-hexahydro-1*H*-cyclopenta[*c*]inden-2(3*H*)-one (**38**; 71 mg, 40%, R_f = 0.60) as a colourless oil and a mixture of traces of **38** with (3a*S**,4*S**,6a*S**)-3a-methyl-4-prop-2′-ynyl-1,3,3a,4,5,6-hexahydropentalen-2(3*H*)-one (**39**; R_f = 0.49) as a orange oil. The mixture was then separated by HPLC (cyclohexane/ethyl acetate 99:1), yielding **39** (6 mg, 3%) as a colourless oil.

Irradiation of **29a** (257 mg, 1.48 mmol) in dry acetonitrile (0.04 M) in the presence of dry TEA (7.40 mmol) and $LiClO_4$ (1.48 mmol) at 300 nm (Duran tubes) was carried out for 5 h as described in GP E, yielding **38** (76 mg, 29%) and **39** (8 mg, 3%) as colourless oils.

Irradiation of **29a** (100 mg, 0.57 mmol) in dry acetonitrile (0.05 M) in the presence of dry TEA (2.85 mmol) at 300 nm (Duran tubes) was carried out for 21 h as described in GP E (without $LiClO_4$ additive), yielding **38** (28 mg, 29%) and **39** (3 mg, 3%) as colourless oils.

(3a*S,5a*S**,9a*S**)-3a,4,5,5a,6,9-Hexahydro-1*H*-cyclopenta[*c*]inden-2(3*H*)-one (38):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, HMBC, NOESY. ^{1}H NMR (500 MHz, $CDCl_3$, ref. $CHCl_3$): δ = 1.18–1.27 (m, 1 H, 5-H), 1.27–1.36 (m, 1 H, 4-H), 1.66–1.70 (m, 1 H, 6-H), 1.71–1.73 (m, 1 H, 5a-H $_{trans}$), 1.74–1.80 (m, 1 H, 4-H), 1.83 (ddd, J = 1.41, 2.51, 18.99 Hz, 1 H, 1-H), 1.92 (d, J = 18.99 Hz, 1 H, 1-H), 2.02–2.04 (m, 2 H, 2×9-H), 2.04–2.08 (m, 1 H, 5-H), 2.15 (dd, J = 1.02, 18.69 Hz, 1 H, 3-H), 2.18–2.21 (m, 1 H, 6-H), 2.21–2.25 (m, 1 H, 3a-H $_{cis}$), 2.45 (ddd, J = 1.65, 7.93, 18.76 Hz, 1 H, 3-H), 5.53–5.58 (m, 1 H, 8-H $_{cis}$), 5.63–5.68 (m, 1 H, 7-H $_{cis}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, ref. $CHCl_3$): δ = 28.83 (C-4), 29.43 (C-6), 30.72 (C-5), 38.10 (C-9), 42.68 (C-1), 43.46 (C-5a), 44.64 (C-3a), 44.96 (C-3), 49.48 (C-9a), 125.42 (C-8), 128.16 (C-7), 220.86 (C-2) ppm. IR (film): $\tilde{\nu}$ = 2887, 1743, 1637, 1470, 1404, 1305, 1235, 1183, 1154, 1060, 968, 885 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 177 (13) $[M + 1]^+$, 176 (89) $[M]^+$, 175 (5), 158 (4), 148 (7), 135 (14), 134 (18), 133 (42), 132 (7), 122 (11), 120 (14), 119 (41), 118 (54), 117 (25), 106 (14), 105 (25), 94 (12), 93 (45), 92 (33), 91 (100), 80 (47), 79 (88), 78 (28), 77 (62), 68 (11), 65 (40), 55 (19), 53 (31), 52 (13), 51 (20). GC-MS (CI, isobutane): m/z (%) = 177 (100) $[M + H]^+$, 159 (1), 135 (10), 118 (2). HRMS: calcd. for $C_{12}H_{16}O$ $[M]^+$ m/z = 176.1201; found 176.1198; deviation, 0.21 ppm.

(3a*S,4*S**,6a*S**)-3a-Methyl-4-prop-2′-ynyl-1,3,3a,4,5,6-hexahydropentalen-2(3*H*)-one (39):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, HMBC, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.56 (s, 3 H, CH_3), 0.65 (dddt, J = 3.76, 10.28, 20.52, 6.28 Hz, 1 H, 5-H), 0.96 (dddt, J = 7.77, 10.44, 23.71, 7.69 Hz, 1 H, 5-H), 1.34 (d, J = 17.74 Hz, 1 H, 6-H), 1.37–1.44 (m, 2 H, 6-H and 4-H $_{trans}$), 1.47 (dd, J = 2.67, 8.95 Hz, 1 H, 1′-H), 1.51 (dd, J = 2.59, 8.98 Hz, 1 H, 1′-H), 1.57 (dd, J = 3.77, 9.14 Hz, 1 H, 3-H), 1.59–1.61 (m, 1 H, 6a-H $_{cis}$), 1.59 (t, J = 2.67 Hz,1 H, 3′-H), 1.63 (dd, J = 2.82, 18.48 Hz, 1 H, 1-H), 1.76 (ddd, J = 2.74, 5.34, 16.47 Hz, 1 H, 3-H), 1.94 (ddd, J = 1.41, 8.36, 18.80 Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 19.99 (C-1′), 25.48 (*C*H$_3$), 30.08 (C-5), 30.19 (C-6), 43.78 (C-1), 44.43 (C-3), 47.06 (C-4), 48.49 (C-6a), 49.26 (C-3a), 69.27 (C-3′), 83.41 (C-2′), 216.18 (C-2) ppm. IR (film): $\tilde{\nu}$ = 3297, 2876, 2119, 1742, 1642, 1451, 1380, 1266, 1177, 1032, 808 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 177 (2) $[M + 1]^+$, 176 (20) $[M]^+$, 161 (12), 147 (9), 137 (4), 134 (9), 133 (58), 120 (11), 119 (11), 107 (10), 106 (13), 105 (17), 95 (31), 94 (12), 93 (20), 92 (13), 91 (47), 81 (25), 80 (14), 79 (49), 78 (10), 77 (31), 69 (13), 68 (41), 67 (100), 66 (10), 65 (27), 55 (45), 53 (31), 51 (16). GC-MS (CI, isobutane): m/z (%) = 176 (100) $[M]^+$, 174 (4), 148 (12), 131 (4), 105 (2). HRMS: calcd. for $C_{12}H_{16}O$ $[M]^+$ m/z = 176.1201; found 176.1199; deviation, 2.16 ppm.

PET Reaction of (1a*R,4a*R**,7a*S**)-4a-(Prop-2′′-ynyloxymethyl)octahydro-2*H*-cyclopropa[d]inden-2-one (27):** As described in General Procedure E, a solution of (1a*R**,4a*R**,7a*S**)-4a-(prop-2′′-ynyloxymethyl)octahydro-2*H*-cyclopropa[*d*]inden-2-one (**27**; 44.0 mg, 0.20 mmol) in dry acetonitrile (0.04 M) was irradiated in the presence of $LiClO_4$ (20.0 mg, 0.20 mmol) and dry TEA (1.00 mmol) at 254 nm (quartz tubes) for 4 h. The crude product was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 70:30), yielding (3a*R**,7a*R**)-7a-hydroxymethyl-3a-methyloctahydro-5*H*-inden-5-one (**40**; 16 mg, 44%, R_f = 0.62) as a orange oil and (3a*R**,7a*R**)-3a-methyl-7a-(prop-2′′-ynyloxymethyl)octahydro-5*H*-inden-5-one (**42**; 5 mg, 11%, R_f = 0.86) as a colourless oil.

(3a*R,7a*R**)-7a-Hydroxymethyl-3a-methyloctahydro-5*H*-inden-5-one (40):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.64 (t, J = 1.80 Hz, 3 H, CH_3), 1.19 (dd, J = 3.84, 8.05 Hz, 1 H, 3-H), 1.28 (ddd, J = 1.89, 4.63, 11.27 Hz, 1 H, 1-H), 1.34–1.45 (m, 6 H, O*H*, 2-H, 3-H, 2-H, 7-H and 1-H), 1.60 (dd, J = 5.83, 14.17 Hz, 1 H, 7-H), 1.99 (dd, J = 1.41, 14.09 Hz, 1 H, 4-H), 2.07 (ddd, J = 1.57, 11.93, 14.76 Hz, 1 H, 6-H), 2.10 (dd, J = 1.49, 13.97 Hz, 1 H, 4-H), 2.27 (dddd, J = 1.33, 4.63, 9.54, 15.37 Hz, 1 H, 6-H), 3.05 (d, J = 10.28 Hz, 1 H, 1′-H), 3.16 (d, J = 10.28 Hz, 1 H, 1′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 19.77 (C-2), 23.06 (*C*H$_3$), 30.56 (C-7), 33.22 (C-1), 37.77 (C-6), 39.49 (C-3), 46.74 (C-7a), 47.26 (C-3a), 50.67 (C-4), 66.99 (C-1′), 209.86 (C-5) ppm. IR (film): $\tilde{\nu}$ = 3413, 2875, 1714, 1668, 1547, 1461, 1378, 1041, 665 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 220 (5) $[M + 38]^+$, 168 (8), 151 (7), 149 (6), 140 (7), 94 (6), 93 (8), 81 (5), 69 (11), 67 (17), 57 (23), 56 (10), 55 (28), 42 (15), 41 (21), 32 (42), 28 (100). HRMS: calcd. for $C_{11}H_{18}O_2$ $[M]^+$ m/z = 182.1307; found 182.1302; deviation, 0.22 ppm.

(3a*R,7a*R**)-3a-Methyl-7a-(prop-2′′-ynyloxymethyl)octahydro-5*H*-inden-5-one (42):** NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.70 (s, 3 H, CH_3), 1.21 (dd, J = 1.88, 12.05 Hz, 1 H, 3-H), 1.28–1.54 (m, 6 H, 1-H, 2-H, 3-H, 2-H, 7-H and 1-H), 1.68 (dt, J = 14.44, 5.65 Hz, 1 H, 7-H), 1.97 (t, J = 2.51 Hz, 1 H, 3′′-H), 2.09 (dd, J = 5.65, 10.68 Hz, 1 H, 6-H), 2.13 (s, 2 H, 4-H), 2.41 (ddd, J = 5.65, 10.67, 14.44 Hz, 1 H, 6-H), 3.10 (d, J = 8.79 Hz, 1 H, 1′-H), 3.27 (d, J = 8.79 Hz, 1 H, 1′-H), 3.71 (dd, J = 2.51, 4.40 Hz, 2 H, 1′′-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 19.85 (C-2), 23.41 (*C*H$_3$), 31.76 (C-7), 34.19 (C-1), 38.09 (C-6), 39.31 (C-3), 45.95 (C-7a), 47.44 (C-3a), 50.56 (C-4), 58.42 (C-1′′), 74.46 (C-3′′), 75.28 (C-1′), 80.14 (C-2′′), 209.73 (C-5) ppm. IR (film): $\tilde{\nu}$ = 2876, 2116, 1712, 1641, 1459, 1358, 1249, 1092, 665 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 220 (3) $[M]^+$, 165 (7), 163 (6), 151 (16), 149 (21), 133 (16), 121 (9), 109 (18), 108 (10), 107 (13), 96 (10), 95 (19), 93 (28), 81 (22), 79 (24), 77 (13), 69 (28), 68 (20), 67 (63), 65 (14), 57 (13), 55 (100), 53 (17), 43 (25), 41 (59). HRMS: calcd. for $C_{14}H_{20}O_2$ $[M]^+$ m/z = 220.1463; found 220.1458; deviation, 2.45 ppm.

(1*S,2a*R**,5a*R**,8a*S**)-Hexahydro-6*H*-1,5a-(methanooxymethano)cyclobuta[*d*]inden-3(1*H*)-one (*rac*-43):** A solution of 7a-allyloxymethyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one (*rac*-**11**; 20.0 mg, 0.10 mmol) in dry *n*-hexane (5 mL) was placed in one irradiation tube (6 mL, Duran glass, 1 cm diameter), degassed with argon for 1 h and irradiated with a mercury lamp (150 W) for 9 h. The degree of conversion (91%) of the starting material was monitored by GC. The solution was concentrated in vacuo and the residue was purified by column chromatography (cyclohexane/ethyl acetate 80:20) to afford *rac*-**43** (16 mg, 80%) as a colourless oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, HMQC, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.75–0.82 (m, 1 H, 6-H), 0.98–1.06 (m, 1 H 7-H), 1.14–1.26 (m, 3 H, 6-H, 5-H and 8-H), 1.28–1.36 (m, 2 H, 7-H and 8-H), 1.65 (ddd, J = 4.08, 8.44, 10.40 Hz, 1 H, 2a-H), 1.84 (ddd, J = 1.88, 8.48, 18.76 Hz, 1 H, 2-H), 1.89 (d, J = 10.59 Hz, 1 H, 2-H), 1.98 (dddd, J = 0.63, 5.41, 14.64, 18.15 Hz, 1 H, 4-H), 2.25 (ddd, J = 2.82, 4.24, 18.10 Hz, 1 H, 4-H), 2.41 (t, J = 10.13 Hz, 1 H, 1-H), 2.47 (dt, J = 4.24, 14.41 Hz, 1 H, 5-H), 2.55 (d, J = 11.45 Hz, 1 H, 11-H), 3.04 (dd, J = 4.08, 12.17 Hz, 1 H, 9-H), 3.28 (d, J = 11.46 Hz, 1 H, 11-H), 3.36 (d, J = 12.25 Hz, 1 H, 9-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 23.95 (C-7), 25.44 (C-2), 30.39 (C-5), 35.17 (C-4), 35.51 (C-2a), 35.91 (C-6), 39.30 (C-5a), 41.04 (C-8), 47.50 (C-8a), 49.80 (C-1), 67.60 (C-9), 74.48 (C-11), 209.86 (C-3) ppm. IR (film): $\tilde{\nu}$ = 2864, 1702, 1672, 1410, 1251, 1190, 1115, 922 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 207 (3) $[M + 1]^+$, 206 (4) $[M]^+$, 190 (4), 188 (7), 178 (7), 175 (9), 173 (12), 160 (9), 159 (7), 149 (12), 148 (16), 147 (12), 136 (35), 135 (43), 134 (22), 133 (13), 123 (12), 122 (21), 121 (21), 119 (15), 117 (24), 109 (11), 108 (27), 107

(70), 106 (13), 105 (15), 104 (32), 95 (16), 94 (33), 93 (38), 92 (21), 91 (100), 83 (10), 82 (12), 81 (15), 80 (23), 79 (94), 78 (33), 77 (71), 67 (56). HRMS: calcd. for $C_{13}H_{18}O_2$ $[M]^+$ m/z = 206.1307; found 206.1294; deviation, 6.26 ppm.

(4*S,4a*R**,8a*R**)-4-Methyl-1,5,7,8-tetrahydro-4a,8a-propanoisochromen-6-one (*rac*-44):** A solution of (1*S**,2a*R**,5a*R**,8a*S**)-hexahydro-6*H*-1,5a-(methanooxymethano)cyclobuta[*d*]inden-3(1*H*)-one (*rac*-**43**; 15.0 mg, 0.09 mmol) and dry TEA (0.46 mmol) in dry acetonitrile (6 mL) was placed in one irradiation tube (12 mL, Duran glass, 1 cm diameter), degassed with argon for 1 h and irradiated with a mercury lamp (150 W) for 30 h. The degree of conversion (80%) of the starting material was monitored by GC. The reaction mixture (21 mg, reddish oil) was concentrated in vacuo and the residue was purified by HPLC (cyclohexane/ethyl acetate 98:2) to afford (4*S**,4a*R**,8a*R**)-4-methyl-1,5,7,8-tetrahydro-4a,8a-propanoisochromen-6-one (*rac*-**44**; 7 mg, 48%) as a yellowish oil. NMR experiments: ^{1}H, H/H-COSY, ^{13}C, ^{13}C-DEPT, NOESY. ^{1}H NMR (500 MHz, C_6D_6, ref. C_6H_6): δ = 0.21 (d, J = 6.99 Hz, 3 H, CH_3), 0.89 (dd, J = 2.66, 6.21 Hz, 1 H, 8-H), 0.90–0.96 (m, 1 H, 9-H), 1.31 (dd, J = 5.18, 14.36 Hz, 1 H, 7-H), 1.34–1.41 (m, 4 H, 11-H, 10-H, 11-H and 10-H), 1.44 (ddd, J = 4.40, 6.99, 11.34 Hz, 1 H, 4-H), 1.86 (dd, J = 6.28, 8.56 Hz, 1 H, 8-H), 1.90 (dd, J = 1.80, 14.01 Hz, 2 H, 2×5-H), 1.93 (dd, J = 1.88, 9.27 Hz, 1 H, 7-H), 2.25 (dt, J = 13.5, 9.44 Hz, 1 H, 9-H), 2.87 (d, J = 11.54 Hz, 1 H, 3-H), 3.27 (d, J = 11.69 Hz, 1 H, 1-H), 3.37 (d, J = 11.70 Hz, 1 H, 3-H), 3.45 (dd, J = 4.56, 12.08 Hz, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, C_6D_6, ref. C_6H_6): δ = 10.15 (CH_3), 18.44 (C-10), 32.00 (C-8), 33.11 (C-11), 33.23 (C-4), 33.30 (C-9), 37.63 (C-7), 40.18 (C-5), 42.49 (C-8a), 49.15 (C-4a), 68.41 (C-1), 69.67 (C-3), 209.45 (C-6) ppm. IR (film): $\tilde{\nu}$ = 2876, 1715, 1650, 1557, 1473, 1106, 1053 cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 208 (9) $[M]^+$, 166 (10), 150 (29), 148 (20), 136 (29), 135 (24), 134 (11), 125 (12), 122 (12), 109 (18), 108 (31), 107 (25), 105 (18), 95 (27), 94 (71), 93 (39), 92 (10), 91 (36), 81 (15), 79 (53), 77 (28), 68 (11), 67 (17), 65 (17), 55 (35), 53 (27), 43 (33), 42 (46), 41 (100). HRMS: calcd. for $C_{13}H_{20}O_2$ $[M]^+$ m/z = 208.1463; found 208.1454; deviation, 1.78 ppm.

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