Synthetic Applications in Radical/Radical Cationic Cascade Reactions[‡]

Heiko Rinderhagen and Jochen Mattay*[a]

Abstract: Oxidative photoinduced electron transfer (PET) reactions have been performed with various cyclic cyclopropyl(vinyl) silyl ethers bearing an olefinic or acetylenic side chain. The reactions result in bi- to tetracyclic ring systems via a fragmentation–radical/radical cationic addition reaction pathway with well defined ring juncture. The mode of cyclisation (*endo*/*exo*) can be partially controlled by addition of nucleophiles due to the suppression of radical cationic reaction pathways. Quantum chemical calculation of the cyclisation transition states underline the experimentally found selectivities. Additional mechanistic studies concerning the saturation step reveal that the final radical is saturated mostly by the solvent and traces of water in the solvent.

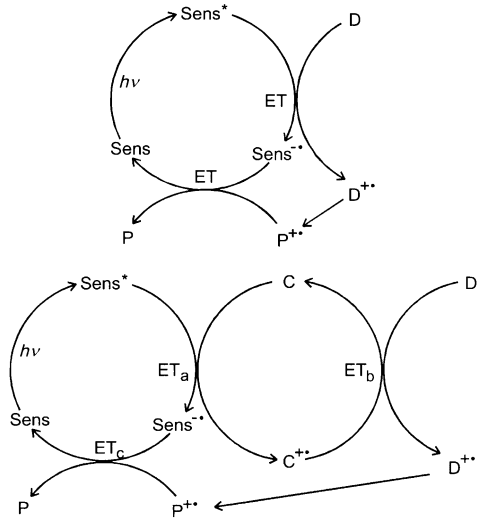
Keywords: domino reactions · electron transfer · polycycles · radical ions · radical reactions

Introduction

Radical cascade reactions had become very popular since their introduction to synthetic chemistry in the early 70s especially for synthesizing polycyclic compounds.[1–8] Though the tin hydride method, which was introduced by Giese et al., is still very important in radical chemistry, there are considerable interests to circumvent the toxic trap of tin chemistry.[9] One possibility for starting radical or radical ion reactions without tin chemistry is the electron transfer activation.[10] In these reactions oxidizing or reducing agents such as metal salts are usually used.

Alternatively the methodology of the photoinduced electron transfer (PET) can be used for carrying out such reactions.[11] The advantage of the PET is that the addition of inorganic salts can be circumvented, which among other advantages simplifies the work up procedures. The PET is based on the fact that the redox properties of molecules are drastically changed upon excitation, that is, both the electron donating as well as the electron accepting behavior of the excited species are approximately enhanced by excitation energy. For synthetic purposes PET reactions are often carried out using a sensitizer which has three characteristics. It is the substrate which is excited for the primary PET process, its resulting radical ion or radical is so inert, that it does not react with the substrate and in most cases the sensitizer is regenerated by back electron transfer. For generating radical cations 1,4-dicyanonaphthalene (DCN) or 9,10-dicyanoanthracene (DCA) are often used as sensitizers. A simplified mechanism of a sensitized PET reaction is shown in Scheme 1 (top).

Sensitized PET reactions are often very slow and have low quantum yields due to dominating back electron transfer. In these cases the addition of cosubstrates (e.g. biphenyl or phenanthrene to DCA or DCN sensitized reactions) is useful. In these reactions the substrate is not oxidized (or reduced) by the excited sensitizer but by the radical ion of the co-sensitizer via a thermal electron transfer step without the



Scheme 1. Simple sensitized (top) and co-sensitized (down) PET process. Sens: sensitizer, D: donor (substrate), C: co-sensitizer, P: product.

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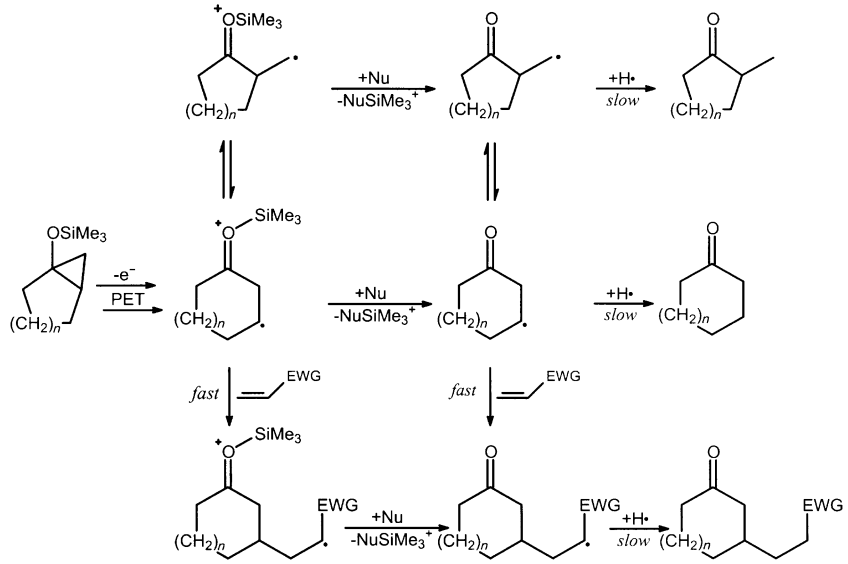
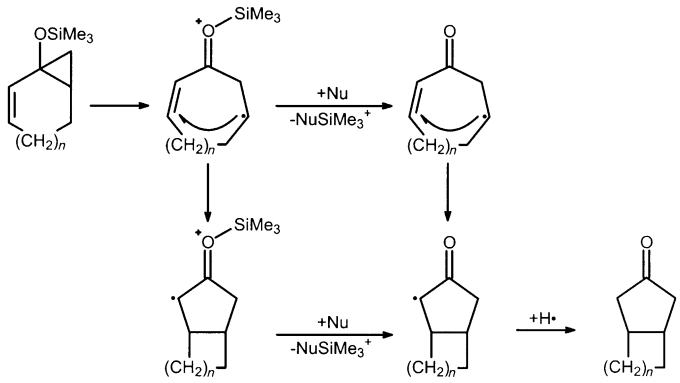
problems of back electron transfer (ET_b). The key step is still the primary PET process (ET_a) in which the co-sensitizer radical ion is formed (e.g. $\Phi_{fri}=0.83$ for DCA/biphenyl).[12] In co-sensitization systems the overall quantum yield is high and the reaction is fast (Scheme 1, bottom).

An additional effect of the co-sensitization may lead to different products or product ratios, which is caused by the efficient sensitizer radical ion substrate ion separation. This separation inhibits the early back electron transfer to the substrate radical ion or early intermediates and favors products of complex reaction pathways (late ET_c, Scheme 1, bottom).



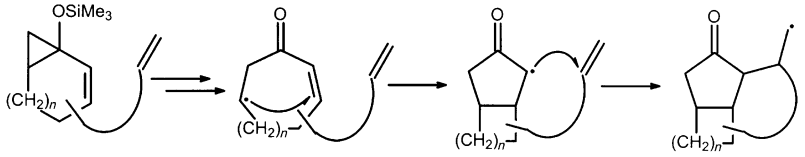
Scheme 2. Radical and radical cationic reaction pathways.

For synthetically and mechanistically reasons, we are interested in donor substituted strained systems, such as cyclopropyl silyl ethers, which react under chemical oxidation processes as well.[13,14] In former investigations we could show that cyclopropyl silyl ethers attached to cyclic systems predominantly undergo *endo*-cyclic fragmentation upon one-electron oxidation; this resulted in distonic radical cations or the corresponding radicals, which were formed by nucleophile assisted cleavage of the formal trialkylsilyl radical cation (Scheme 2).[15,16]



Scheme 3. Simple cascade reaction for building up bicyclic systems.

These radicalic species can be trapped by radicalophilic agents such as electron deficient alkenes. In the absence of such reagents the *endo* radicalic species rearrange to the corresponding *exo* radicals; the *exo*:*endo* product ratio is mostly determined by the interaction between the radical stability and the ring strain. In addition, studies on the concentration dependence have revealed a slow termination step. This complicates intermolecular radical additions due to the predominant polymerization but eases complex cascade reactions by avoiding an early saturation of intermediate radicals.

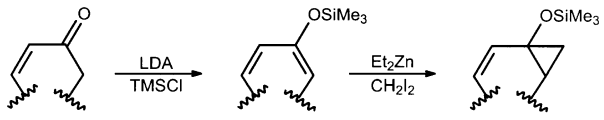


Scheme 4. Complex cascade reactions for building up polycyclic systems.

In this article we will focus on the synthetic scope and limitations of the PET induced fragmentation reactions of cyclopropyl silyl ethers suitable for radical cascade reactions resulting in bicyclic and tricyclic systems. (Schemes 3 and 4).

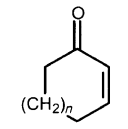
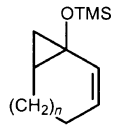
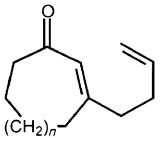
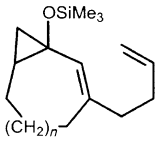
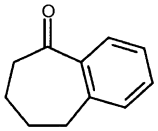
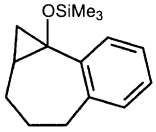
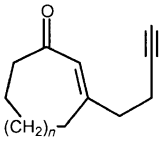
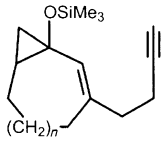
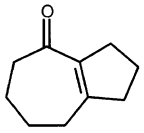
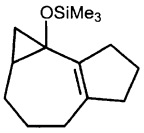
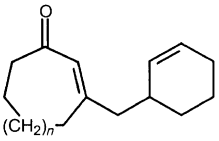
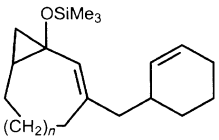
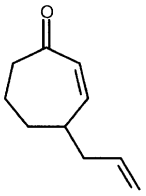
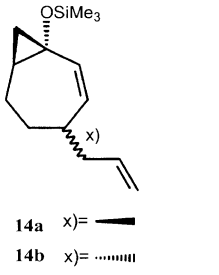
Results and Discussion

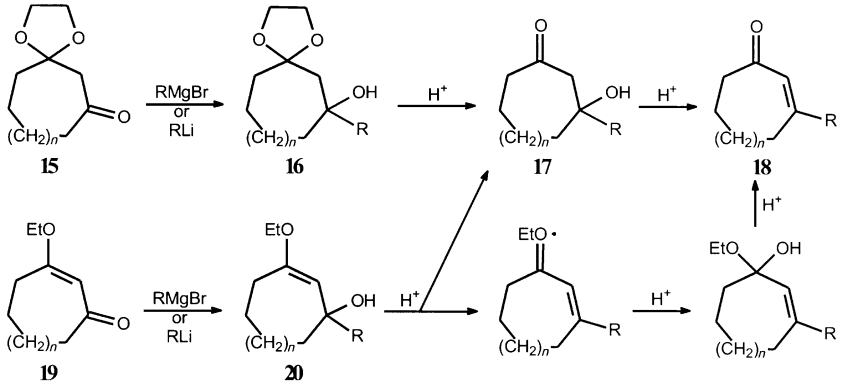
Synthesis of the starting materials: All vinylcyclopropyl silyl ethers **8–14** were synthesized starting from the corresponding ketone in a two-step reaction, using LDA/trimethylsilyl chloride for silylation and diethyl zinc/diiodomethane for cyclopropanisation (Scheme 5, Table 1). The cyclopropanisation was monitored by GC/GC-MS to circumvent reactions of the additional non-donor activated olefinic bonds in the starting materials. The desired cyclopropylsilyl ethers were obtained as colorless liquids after distillation or fast column chromatography of the crude products. The cyclopropana-



Scheme 5. Synthesis of the vinylcyclopropyl silyl ethers.

Table 1. Vinylcyclopropyl silyl ethers synthesized.

Ketone	Cyclopropyl silyl ether	Ketone	Cyclopropyl silyl ether
			
n = 1, 2, 3, 4 **1a-d**	n = 1, 2, 3, 4 **8a-d**	n = 1, 2 **4a, b**	n = 1, 2 **11a, b**
			
2	**9**	n = 1, 2 **5a, b**	n = 1, 2 **12a, b**
			
3	**10**	n = 1, 2 **6a, b**	n = 1, 2 **13a, b**
			
		7	**14a** x)= **14b** x)=



Scheme 6. Synthetic strategies for synthesizing 3-substituted cyclic enones.

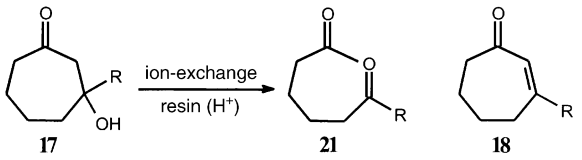
tion reaction resulting in cyclopropyl silyl ether **13** and **14** showed only negligible diastereoselectivity and therefore the products can be isolated in an approximately 1:1 mixture of the two diastereoisomers. Only in the case of the 4-substituted derivative **14** the diastereoisomers have been separated by preparative GC for mechanistic reasons (see below). Most of the ketones were synthesized according to known procedures (**1b–d**, **3**)[17,18] or following strategies shown in Scheme 6 for 3-substituted enones.

After reaction with Grignard or analogous lithium organic reagent of the semiprotected β-diketone **15**, the resulting β-hydroxy acetal **16** was hydrolyzed to the corresponding β-hydroxy ketone **17**. Acid-catalyzed elimination finally led to the desired product **18**.

For the elimination the use of 85% phosphoric acid and *n*-pentane as solvent at room temperature turned out to be the method of choice. When an acidic ion exchange resin under azeotropic removal of the reaction water was used instead, a 1:1 mixture of the enone and the open chain retro-aldol product was isolated as shown for the cycloheptanone derivative **18** in Scheme 7.

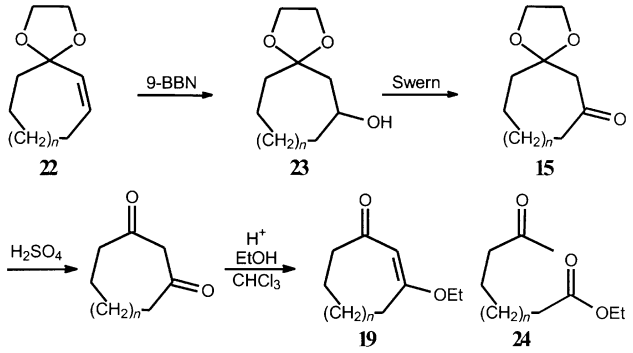
The alternative synthesis of 3-substituted enones **18** starting from the vinylogous esters **19** is recommended if the synthesis of the bromide is complicated or the elimination partially leads to retro-aldol products even under phosphoric acid conditions.

For the synthesis of the semiprotected β-diketones **15** two different strategies are suggested.[19,20] Starting from the easily accessible enone acetal **22** the product can be synthesized by oxymercuration and oxidation of the resulting alcohol **23**.[19] Alternatively the corresponding enone epoxide can be reduced to the alcohol which is again oxidized to the desired product.[20] However, the latter synthesis failed in our hands. Though we could synthesize an alcohol and a corresponding



Scheme 7. Retro-aldol reaction during elimination.

ketone by applying the suggested synthetic procedures in good yields (80–90%), the products turned out to be the α-hydroxy or the α-diketo regioisomers, respectively, unequivocally proven by one- and two-dimensional NMR experiments. To circumvent the use of mercury salts we developed an alternative route for the synthesis. Starting from the enone acetal after hydroboration using 9-BBN and Swern oxidation the product was obtained in good yields. The use of hydroboration reagents other than 9-BBN resulted in partially reduction of the acetal function (Scheme 8).



Scheme 8. Synthesis of the semiprotected β-diketone **15** and vinylogous acetal **19**.

The vinylogous esters **19** were synthesized by acid-catalyzed esterification. When carrying out this reaction it is advisable to thoroughly remove the reaction water, for example, by molecular sieves, otherwise, retro-crossed Claisen condensation products **24** are formed especially at longer reaction times (Scheme 8).

The required alkyl bromides (Scheme 6) for the metal organic reagents were either commercially available or synthesized according to known procedures.[21–24] For the synthesis of enones **5a**,**b** the corresponding trimethylsilyl protected derivatives were used. After the reaction the protective group was removed by tetrabutylammoniumfluoride (TBAF) in an aqueous THF solution. In case of the cyclohexenylmethyl side chain (product **6a**,**b**) the use of lithium organic compounds is necessary because the analogous Grignard reagent resulted in reduction of the carbonyl group due to its steric hindrance.

The 4-substituted derivative **7** was synthesized as shown in Scheme 9. Besides the desired enone the diastereoisomeric alcohols **26a** and **26b** were isolated, of which only the *cis*-isomer **26a** could was successfully converted to **7** by elimination.

Cyclization under PET conditions: The deoxygenated solutions of the respective cyclopropyl silyl ethers **8–14** containing the PET sensitizer, occasionally in presence of a co-sensitizer, were irradiated in a Rayonet photochemical reactor using the appropriate wavelength (DCN: 350 nm; DCA: 419 nm). The conversion of the starting material was monitored by GC or GC/MS.

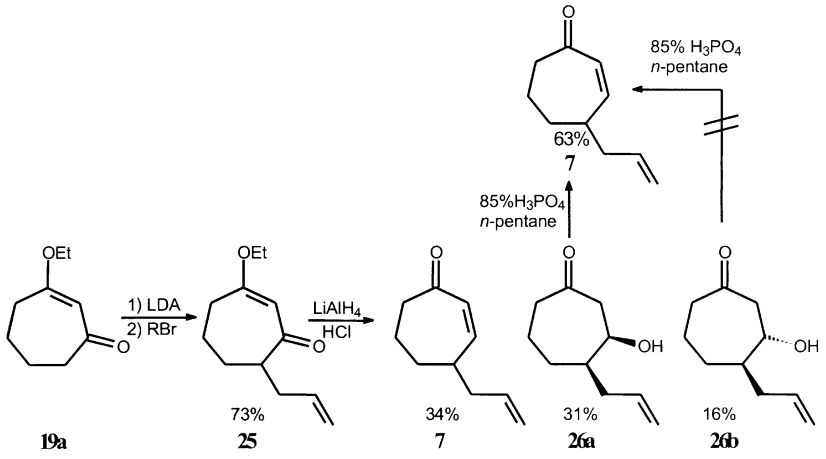
Simple cascade reactions: The results of the irradiations of the simple substrates **8–10** in pure acetonitrile are summarized in Scheme 10. The products were isolated by HPLC and unambiguously identified by spectroscopic analysis (mostly one and two dimensional NMR as reported in the Experimental Section). The stereochemistry of the cyclisation products **28** and **29** was assigned by comparison with reported NMR data.[25] The structure of the tricyclic compound **31** was established by comparison with the ^{1}H NMR data of the cyclisation products of the complex cascade reactions, which were identified by qualitative and partially quantitative NOESY spectroscopy (see Table 2).

Only the PET reactions of the seven- and eight-membered ring derivatives **8b**,**c** gave the desired cyclisation products. For the six- or nine-membered ring starting materials the ring strain of the four- (**8a**) or the seven- (**8d**) membered rings in the potential products suppresses the transannular cyclisation. The transannular addition towards the aromatic system of **9** is obviously reversible resulting in the more stable open chain product **33** as shown in Scheme 11 (for simplification only the radical reaction pathways are shown).

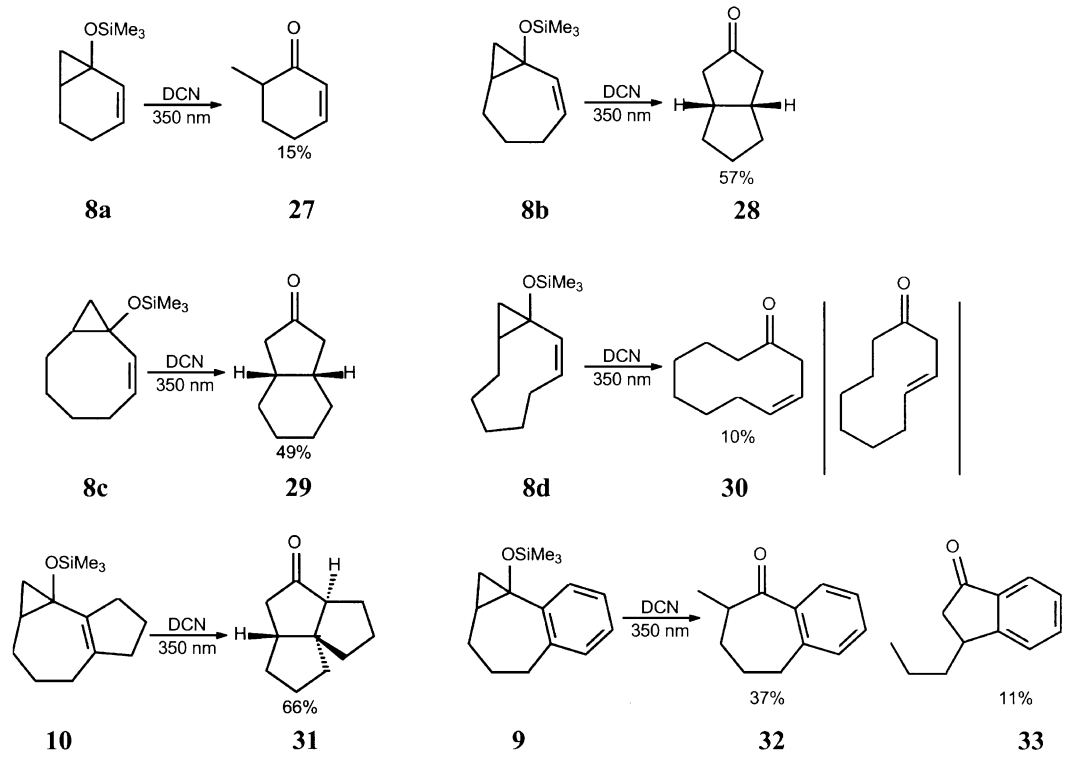
The unusual β,γ-unsaturated product **30** can be explained by a transannular hydrogen abstraction followed by a kinetic saturation of the allyl radical (Scheme 12).

Interestingly all cyclisation products exhibit only *cis*-ring connections. This is not surprising for products which contain a bicyclooctanone substructure because of the high ring strain of the corresponding *trans* products. Similar effects may also govern the energy of the transition state as expected for kinetically controlled reactions of this type.[26]

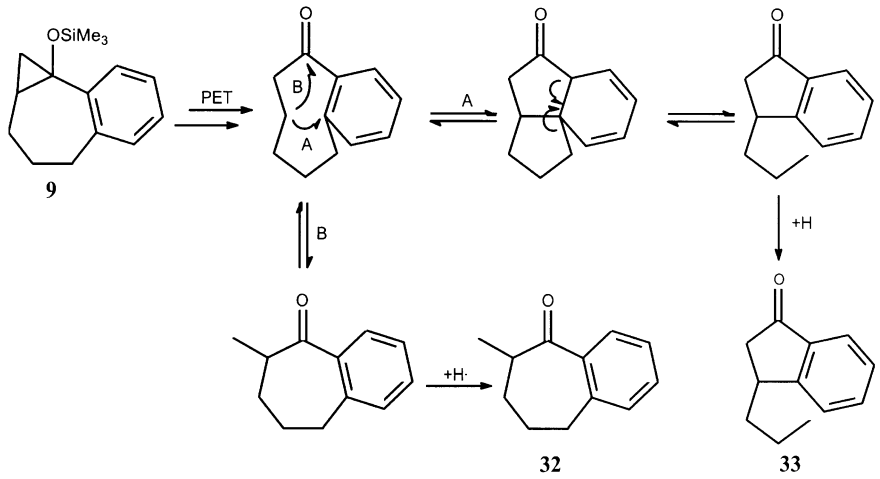
Complex cascade reactions: The results of the irradiations of the more complex substrates **11–14** in pure acetonitrile are summarized in Table 2. The products were isolated by



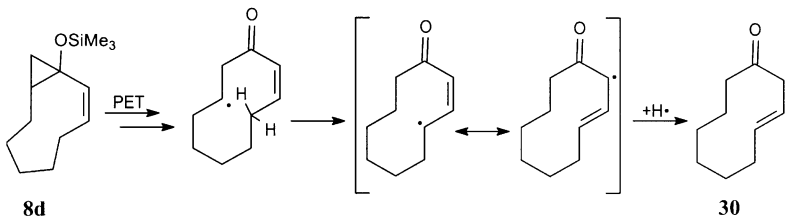
Scheme 9. Synthesis of the 4-substituted derivative **7**.



Scheme 10. Products of simple cascade reactions.



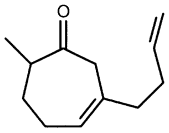
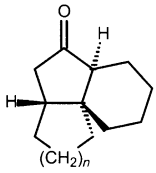
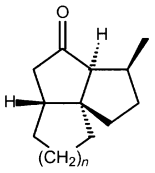
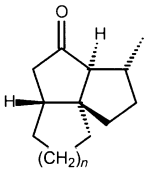
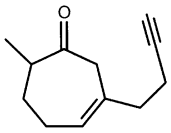
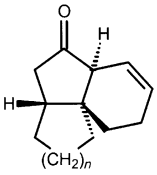
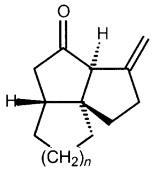
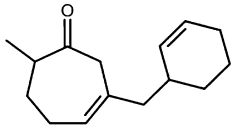
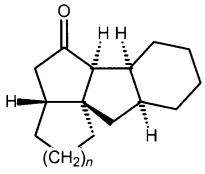
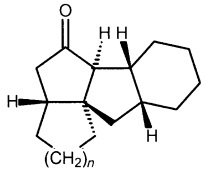
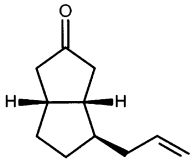
Scheme 11. Reversible addition towards the aromatic system.



Scheme 12. Transannular hydrogen abstraction followed by kinetic saturation.

HPLC and if necessary by preparative GC and unambiguously determined by spectroscopic analysis (mostly one- and two-dimensional NMR as reported in the Experimental Section). The stereochemistry of the cyclisation products was assigned using quantitative NOESY spectroscopy supported by molecular modeling assignments of the respective geometries using MMFF94 force field calculations and thoroughly evalution of the ^{1}H NMR coupling constants and the chemical shifts. Especially for the cyclisation products of the cycloheptane starting materials (**11a**/**12a**/**13a**), the relatively simple latter method allows partially stereochemical assignments due to the rigid molecular scaffold. For example, the agreement of the respective coupling constants and the chemical shifts of the α-carbonyl protons and the bridge head proton H^C indicates that all cyclisation products have the same A/B and A/C ring junction (Table 3). Additionally the order of magnitude of the respective coupling constants indicates a *cis*/*cis* junction. The relatively large coupling constant of the bridge head proton H^C and the *cis* connected α-carbonyl proton H^A indicates a small dihedral

Table 2. Isolated photoproducts.

	Not (completely) cyclized Product [%]	*endo*-Product [%]	*exo*-Product [%]	*exo*-Product [%]
11				
	34	**35**	**36**	**37**
a ($n=1$)	20	12	15	6
b ($n=2$)	–	22	9	17
12				
	38	**39**	**40**	
a ($n=1$)	15	6	30	
b ($n=2$)	–	32	12	
13				
	41		**42**	**43**
a ($n=1$)	19		11	12
b ($n=2$)	–		10	12
14				
	44			
a	40			
b	40			

using Boltzmann weighting are also shown as well for comparison (see Table 4).

The occurrence of the non-cyclised products **34**, **38** and **41** can be explained by a transannular allylic hydrogen abstraction of the *exo*-methyl radical (Scheme 13). The subsequent kinetic saturation of the resulting allylradical led to β,γ-unsaturated products. Probably the 3-substitution slows down the desired transannular addition (path A) and therefore the 1,2-rearrangement (path B) occurs, which results in the non-cyclised products. Interestingly the non-cyclised products are not stable upon prolonged reaction times in contrast to their cyclised counterparts. Obviously the non-cyclised products are more oxidative labile due to their highly substituted olefinic bond. The cyclisation products are resulting from two-step radical addition cascade reactions. All cyclisation products show only *cis*-ring connection of either the first- or the second step irrespective of the mode of cyclisation (*endo* or *exo*). Interestingly the second addition step leads to relatively large amounts of *endo* products in comparison to the classical *exo* preference of radical cyclisation reactions.[27] One reason for these unusual behavior is a radical cationic reaction pathway which will be discussed in more detail in the next paragraph (see below).

angle between these protons. In contrast the *trans* proton H^B shows only a small coupling constant towards H^C but an additional W coupling ($^4J^D$) towards the *cis*-connected α-carbonyl proton H^D.

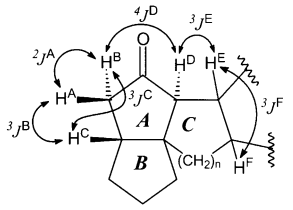
Additionally, the order of the $^3J^E$ coupling constants indicates the *cis*/*tran*s and the *cisoid*/*transoid* arrangement of the products **36a**/**37a** and **42a**/**43a**, respectively, while the $^3J^F$ constant indicates a *cis* junction of both tetracyclic compounds. However, especially the latter interpretations are only possible with additional NOESY experiments. These experiments were carried out and quantitatively evaluated for all products using diastereoisomeric geminal methylene groups as reference. In order to support these NOESY experiments additional population analysis was carried out. The respective H–H distances in each of the resulting conformers were measured for comparison. The results of one such evaluation are shown in Table 4.

Besides the NOESY evaluated distances the smallest, the largest and the average distance of the population analysis

The cyclisations of the cyclohexenyl methyl substituted starting materials **13a**,**b** gave an interesting selectivity behavior. During the cyclisation cascade four stereogenic centers are generated. Together with the stereocenter of the side chain the possible *exo* and *endo* products have five stereogenic centers. Though theoretically 16 *exo*- and *endo*-therefore 32 different diastereoisomeric products might be generated during the cyclisation cascade, only two diastereoisomers are formed.

The relatively high diastereoselectivity can be explained by the selectivities of the respective radical addition steps. The first addition step is completely *cis* selective at the ring junction but shows only negligible additional diastereoselectivity. Consequently the primary addition product **45a**,**b** is formed as a 1:1 diasteroisomeric mixture. The second addition step is completely diasteroselective as shown in

Table 3. ^{1}H NMR chemical shifts [ppm] and J coupling constants [Hz].



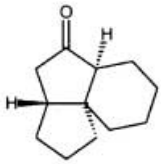
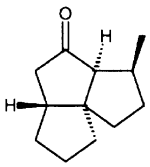
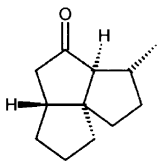
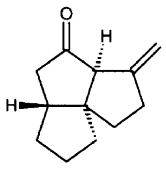
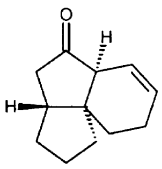
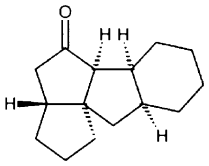
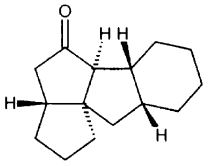
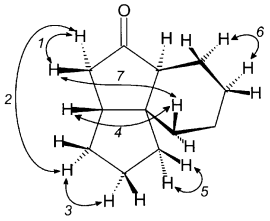
							
	35a	**36a**	**37a**	**40a**	**39a**	**42a**	**43a**
H^A	2.447	2.374	2.560	2.626	2.506	2.644	2.557
H^B	2.144	2.004	2.024	2.023	2.111	2.104	2.076
H^C	2.080	2.162	2.158	2.272	2.183	2.333	2.222
H^D	2.027	2.107	1.803	2.760	2.530	2.482	2.011
$^2J^A$	19.3	18.4	18.5	18.8	18.9	19.2	18.4
$^3J^B$	8.8	10.2	9.2	9.7	9.0	9.9	9.3
$^3J^C$	2.8	3.3	4.8	4.5	3.8	4.6	6.1
$^4J^D$	1.6	2.0	1.9	1.9	1.6	2.1	1.8
$^3J^E$	insignificant	10.5	5.5	not existent	insignificant	8.2	3.0
$^3J^F$	insignificant	insignificant	insignificant	insignificant	insignificant	5.0	5.3

Table 4. Exemplary NOESY evaluation.



No.	r_{NOE}	r_{Bolz}	r_{MIN}	r_{MAX}
1	1.79	1.79	1.79	1.80
2	2.28	2.49	2.28	2.65
3	2.13	2.36	2.30	2.41
4	2.62	2.75	2.37	2.80
5	≡1.77	1.77	1.76	1.77
6	2.35	2.46	2.35	2.48
7	2.65	2.72	2.58	3.74

r_{NOE}: Distance evaluated by NOESY spectroscopy (reference: "≡"). r_{Bolz}: Average distance of conformational analysis using Bolzmann weighting. r_{MIN}: smallest distance of conformational analysis. r_{MAX}: largest distance of conformational analysis.

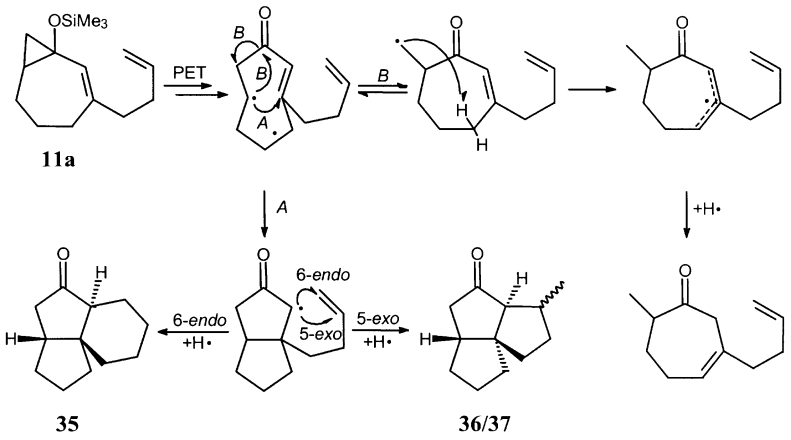
Scheme 14. The subsequent saturation is not important for the isomer distribution.

The 4-substituted starting material only partially cyclises under PET conditions. This is caused by the selectivity of the first addition step, which exhibits not only *cis* selectivity but takes place under equatorial alignment of the side chain (Scheme 15). This unfavorable alignment suppresses further cyclisation. Interestingly the partially cyclised product **44** is formed upon irradiation irrespective which diastereoisomeric starting material (**14a** or **14b**) is used, which underlines the proposed stepwise mechanism (fragmentation, addition) rather than a concerted one (e.g. cationic induced rearrangement).

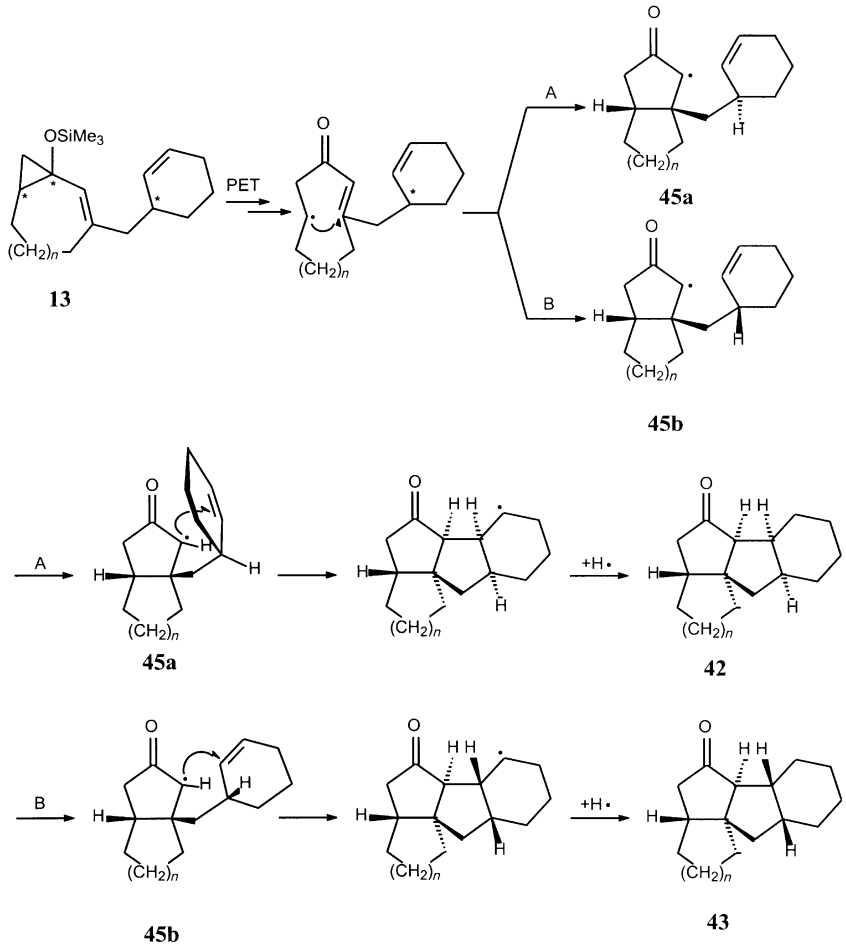
Mechanistic investigations

Radical ion versus radical reaction pathways: As mentioned above the second cyclisation step of the cascade reaction shows unusually large amounts of *endo*-cyclisation products. Usually pure radical (non-radical ionic) reactions prefer 5-*exo* cyclisations. This preference can be partially or predominately suppressed by steric effects. In this case the rigid bicyclic structure of the first addition step intermediate may cause the occurrence of the 6-*endo* cyclisation products. On the other hand radical cationic reaction pathways may be the reason for this unusual behavior. For example, silyl enol ether radical cations (e.g. **47**) predominately cyclize in a 6-*endo* fashion, as we have shown in former studies.[28–31] By addition of strong nucleophiles such as alcohols the *endo*/*exo* product ratio can be lowered due to the fast cleavage of the formal trimethyl silyl cation; this results in the α-carbonyl radical **48** which cyclises predominately in a 5-*exo* mode (Scheme 16).[28–31]

Analogous to these results the occurrence of relatively large amount of the *endo* products can be explained by radical cationic reaction pathways as shown in Scheme 17. On the one hand the distonic radical cation **49**, the result of the first fragmentation process, may lose the silyl group; this



Scheme 13. Reaction pathways in the cascade reactions.



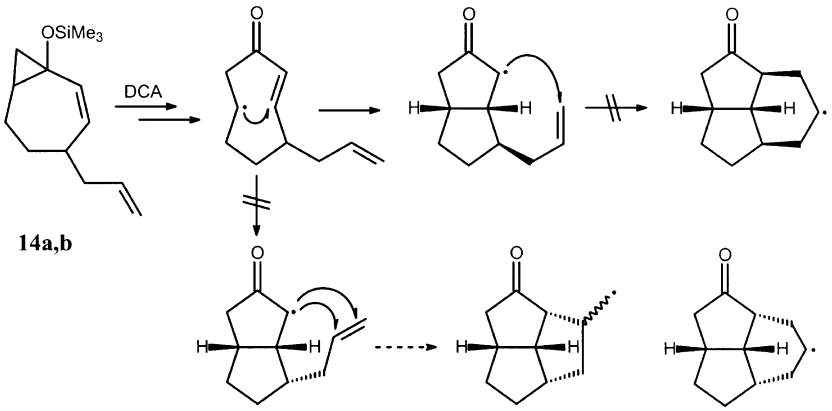
Scheme 14. Diastereoselectivity of the cascade reaction of **13** (only one enantiomer is shown).

would yield the β-carbonyl radical **50** which reacts to the *endo* or the *exo* products. On the other hand the radical center of the distonic radical **49** may add vinylogously to the cationic center resulting in the non-distonic radical cation **51** which is identical to the radical cation **47** of the silyl enol ether **46**. Analogous to our former published results this radical cation should cyclise predominantly in an *endo* fashion if not suppressed by steric effects.[28–31]

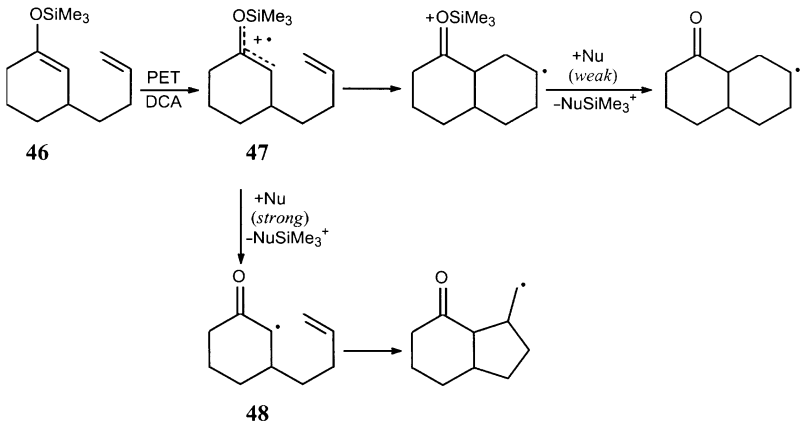
An investigation of the influence of isopropanol on the *endo*/*exo* ratio of the irradiation products of the cyclopropyl silyl ethers **11a**,**b** and **12a**,**b** in comparison with silyl enol ether **46** provides strong evidence that the *endo* products are partially caused by radical cationic reaction pathways. The addition of 20% of isopropanol lowers the amounts of the *endo* products of all cyclopropyl silyl ethers, caused by faster cleavage of the silyl group resulting in predominant radical reaction pathways (Scheme 18). As expected the effects are smaller compared with silyl enol ether **46**. The relevant cyclisation step is the last one of a three step (fragmentation; first cyclisation; second cyclisation) cascade reaction. This allows cleavage of the silyl group even in the absence of additional nucleophiles.

Deuterium labelling studies: For the last reaction step, that is the saturation of the radical, two mechanisms can be discussed. On the one hand a formal hydrogen radical transfer of a suitable donor (e.g. the solvent) by homolytic bond cleavage is possible. On the other hand a reduction of the radical by the sensitizer radical anion followed up by protonation (e.g. by traces of water in the highly hygroscopic acetonitrile) can be discussed as well (Scheme 19).

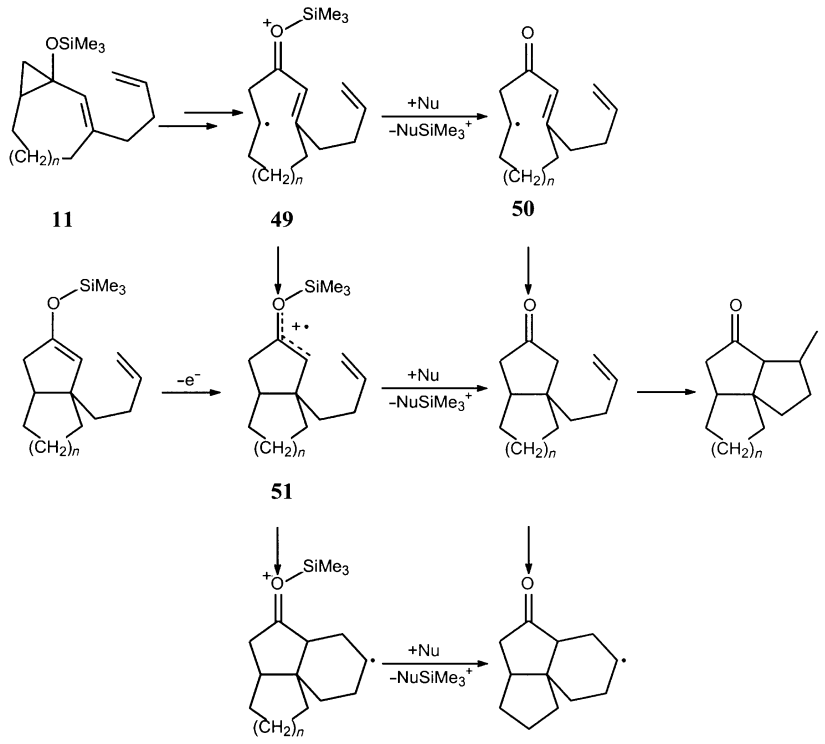
Both mechanisms are consistent with the observation that the saturation step is relatively slow, because neither good hydrogen-radical or proton-donor sources are added under standard reaction conditions. In order to elucidate this part of the reaction mechanism in more detail, we carried out deuterium labelling experiments using the easily synthesizable cyclopropyl ether **52** and various mixtures of deuterated and non-deuterated solvents (Scheme 20). The degree of deuteration was thoroughly ana-



Scheme 15. Partial cyclisation of the 4-substituted starting material **14a**, **b**.



Scheme 16. Regioselectivity controlled by radicalic and radical cationic reaction pathways.

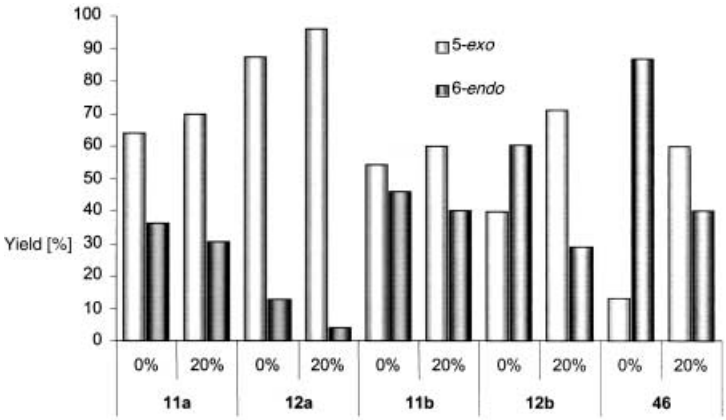


Scheme 17. Radical and radical ionic reaction pathways.

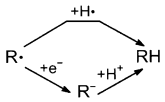
lyzed by mass range optimized GC-MS of the reaction mixtures.

At first sight two aspects can be concluded from the experimental results. Firstly, either acetonitrile or water are sources for the saturation. Secondly, at least one additional source is responsible for the saturation of the final radical. Additionally the experiments show three interesting effects.

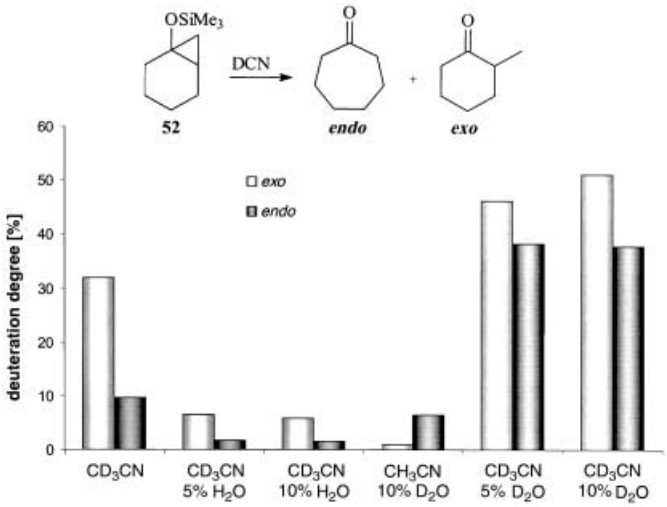
- In deuterated acetonitrile the deuteration degree of the *exo* product is much larger than that of the *endo* product. In contrast in non-deuterated acetonitrile containing D_2O the *endo* product exhibit the larger deuteration. This is consistent with the assumption that the primary *exo* radical is predominately saturated radically by the acetonitrile due to its higher reactivity, while the back electron transfer protonation reaction pathway play a more important role in case of the *endo* radical.
- The addition of water to deuterated acetonitrile results in partially suppression of the deuteration degree. Obviously the added water results in an acceleration of the non-radical pathway that is, in this case non-deuterated reaction.
- The last effect is the most interesting. If one compares the results of CD_3CN/10% D_2O with the two complementary experiments of CD_3CN/10% H_2O and CH_3CN/10% D_2O] one observation is amazing. The grade of deuteration of the fully deuterated experiment is much larger than the sum of the complementary experiments. This indicates a strong kinetic isotopic of one or both of the discussed saturation pathways.



Scheme 18. Amounts of *endo* and *exo* product with 0 and 20% isopropanol.



Scheme 19. Possible saturation pathways.



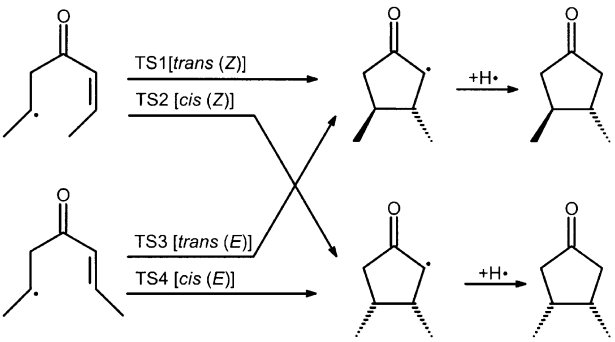
Scheme 20. Deuteration experiments for elucidation of saturation pathways.

Finally it can be concluded that the solvent and additional traces of water in the solvent are important sources for the saturation of the final radical. One or more additional saturation pathways (e.g. radical saturation pathways from the sensitizer or the silyl group) are not negligible. On the other hand, because of the strong kinetic isotopic effects of the major saturation pathways (acetonitrile/water), these additional pathways are less important than the quantitative values in Scheme 20 may suggest.[32]

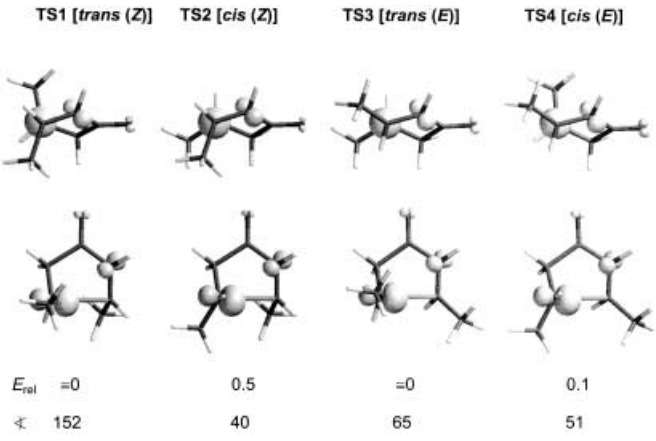
Theoretical investigation of the selectivities: All cyclisation cascade reactions exhibit strong *cis* diastereoselectivities concerning either the first or the second ring connection. For a deeper understanding of this selectivity we carried out quantumchemical calculations.[33] Because of the general irreversibility of radical addition reactions we calculated the relative energies of the respective transition states. Due to the large computational cost we confined our calculation to the radical reaction pathways.

In case of the first (transannular) addition step one has to take into consideration that the essential *Z* orientation of the cyclic enone determines the stereoselectivity of the addition step. For this reason we calculated the relative energies of the *cis* and *trans* transition states of either the (*E*)- or the (*Z*)-2-heptenen-4-one radical resulting in the corresponding *cis*- or *trans*-3,4-dimethyl-1-cyclopentanone products (Scheme 21). We used this open chain model compound for simplification and for circumventing problems while searching the transition states caused by ring strain effects. On the other hand the geometries of the transition states of the system are very useful for explaining the selectivities of the transannular addition (see below).

Interestingly the corresponding *cis*- and *trans*-transition states differ only slightly in energy while the structural differences mostly appear in the alignment of the methyl groups. This alignment is finally the reason for *cis*-selectivity in the corresponding cyclic systems. For example, the methyl groups in the transition state TS1 leading to the *trans*-product starting from the (*Z*)-olefin include a dihedral angle of 152°. In a cyclic system this dihedral angle would cause such a large ring strain that the respective product cannot be formed (Scheme 22).



Scheme 21. Transition states for the selectivity consideration of the first addition step.



Scheme 22. Geometries (B3LYP6-31 G*), relative energies [kcal mol^{-1}] and dihedral angles [°] in the transition states of the first addition step.

The energy differences of the *cis*- and the *trans* transitions states of the second addition step concerning the simple side chain starting material **11a**,**b** and **12a**,**b** exhibit a strong preference of the *cis* products underlining the experimental results. Generally the differences of the bicylononenone systems (starting materials **11b** and **12b**) are smaller than those of the bicyclooctanone systems due to the higher rigidity of the latter systems. This indicates that the selectivity of the second addition step is mostly caused by the rigid geometry of the bicyclic system formed in the first addition step (see Table 5)

Table 5. Energy differences of the *trans*- and *cis*-transition states of the second addition step (B3LYP6-31 G*).

Substrate	Mode of Cyclisation	$E=E_{trans}-E_{cis}$[a]	Substrate	Mode of Cyclisation	$E=E_{trans}-E_{cis}$[a]
11a	6-*endo*	11.4	**11b**	6-*endo*	7.4
	5-*exo trans*[b]	20.2		5-*exo trans*[b]	15.9
	5-*exo cis*[b]	21.4		5-*exo cis*[b]	16
12a	6-*endo*	13.8	**12b**	6-*endo*	13.7
	5-*exo*	21.0		5-*exo*	18.1

[a] *cis* and *trans* concerning the ring junction of the second addition step. [b] *cis* and *trans* concerning the alignment of the methyl group (product **36** or **37**).

Additionally stereoelectronic effects may support these selectivities as shown in Scheme 23. Due to the quasiequatorial attack of the olefinic group towards the radical center, the bond formed in the addition step and the carbonyl π-bond are nearly perpendicular. This partially suppresses a possible stabilizing conjugation, which results in a reduced spin density on the carbonyl oxygen.

For the selectivity calculations (relative energies of the transition states) of the second addition step of the cyclohexenyl methyl derivatives **13a**,**b** two different diastereoisomeric intermediates **45a** and **45b** must taken into consideration as depicted in Scheme 14. The energy differences in the respective group of transition states reveal that one diastereoisomer is energetically favored (Table 6). This underlines the experimental result of finding only two products (starting from two intermediate radicals) and the mechanistic explanation as discussed above (Scheme 14). Interestingly even simple AM1 calculations, which are known to be not suitable for evaluating regioselectivities and electronic influences of radical addition processes,[34] predict the selectivity of the stereochemistry quite well. This again indicates that the stereochemistry of these reactions are mostly governed by steric effects. In case of **13b** we only carried out AM1 calculation due to the large computational cost of this relatively large system.

Conclusion

PET-oxidative initiated reactions of cyclopropyl silyl ethers were carried out via β-carbonyl radical cationic and radical species generated by nucleophile assisted cleavage of a formal trimethyl silyl cation. These highly reactive intermediates react in radical/radical cationic reaction cascade reactions to polycyclic compounds, which have been structurally assigned by multiple NMR experiments supported by force field calculations. Due to the slow termination step partially cyclized products were not observed except for **14**. The termination step was proven to be either a hydrogen radical transfer from the solvent (acetonitrile) or a stepwise electron transfer/protonation by traces of water in the solvent process. The experimentally found stereoselectivities were evaluated and confirmed by quantum chemical calculations.

Scheme 23. 6-*endo cis*- and *trans*-transition states geometries (spin density: balls).

Table 6. Relative energies of the transition states of the second addition step of the cyclisation of **13** (cf. Scheme 14).

Diastereoisomers	Precursor radical	**13a** AM1		**13a** B3LYP6-31 G*		**13b** AM1	
		5-*exo*	6-*endo*	5-*exo*	6-*endo*	5-*exo*	6-*endo*
cis/*cis*/*cisoid*/*cis*	**45a**	≡0.0[a]	10.2	≡ 0.0[a]	8.2	≡0.0[a]	13.3
cis/*cis*/*transoid*/*trans*	**45a**	8.7	50.7	7.5	48.1	10.1	51.3
cis/*trans*/*transoid*/*cis*	**45a**	17.6	17.6	15.0	17.0	20.2	25.4
cis/*trans*/*cisoid*/*trans*	**45a**	41.3	78.2	39.2	76.4	37.7	73.2
cis/*cis*/*transoid*/*cis*[a]	**45b**	≡0.0[a]	8.3	≡0.0[a]	7.4	≡0.0[a]	9.8
cis/*cis*/*cisoid*/*trans*	**45b**	10.8	53.6	11.3	53.3	9.0	50.5
cis/*trans*/*cisoid*/*cis*	**45b**	25.8	26.2	23.57	25.1	26.2	30.0
cis/*trans*/*transoid*/*trans*	**45b**	31.2	38.9	29.4	37.7	30.8	66.6

[a] Relative energies [kcal mol^{-1}] were calculated within a group of the same radical precursor (**45a** or **45b**).

Experimental Section

General remarks: Melting points are uncorrected. IR: Perkin–Elmer IR-spectrometer 841 or Perkin–Elmer FT-IR-spectrometer1600. ^{1}H NMR:NMR: Bruker AC200P (200.132 MHz), AM250 (250.133 MHz), AM300 (300.133 MHz) or DRX500 (500.132 MHz); internal standard: TMS (0.00 ppm), $CHCl_3$ (7.24 ppm), C_6H_6 (7.15 ppm). ^{13}C NMR: Bruker AC 200 P (50.323 MHz), AM250 (62.896 MHz), AM300 (75.469 MHz) or DRX500 (125.772 MHz); internal Standard: TMS (0.00 ppm), $CDCl_3$ (77.00 ppm), C_6D_6 (128.00 ppm). Mass spectrometry: Micromass VG Autospec X or Finnigan MAT 8230. GC/MS: Shimadzu GC-17A ver. 3/MS QP 5050 A using Hewlett Packard 5MS (25 m, 0.2 mm, 0.33 μm) column, carrier gas: helium, pressure: 0.95 bar. GC: Shimadzu GC-17A/ver. 3, FID detector, using Class VP 4.2 software; Siemens Sichromat 3, FID detector, Specta Physics Integrator SP 4290; Siemens Sichromat 1-4, FID detector, Spectra Physics Integrator SP 4400; columns: Hewlett-Packard Ultra 2 (25 m, 0.2 mm, 0.33 μm), Hewlett-Packard 1MS (25 m, 0.2 mm, 0.33 μm), Hewlett-Packard 5MS (25 m, 0.2 mm, 0.33 μm); carrier gas: nitrogen. Preparative GC: Hewlett-Packard 5890 Series II; injektor and automatic fraction collector Fa. Gerstel; autosampler Hewlett-Packard 7673; column: Hewlett-Packard HP5 (30 m, 0.53 mm, 5.0 μm); carrier gas hydrogen (0.35–0.5 bar). HPLC: Kontron pump 420 or Merck pump L-6000; RI-detector Bischoff RI 8110; column 250 × 20 mm Merck LiChrosorb Si 60-7; flow 10 mL min^{-1}; reversed phase HPLC: column Macherey und Nagel PREP 2025 (250 × 20 mm) LiChrosorb RP 18 7.0 μm, precolumn: PREP 2005 (50 × 20 mm) LiChrosorb RP 18 7.0 μm, flow 10 mL min^{-1}.

NMR spectroscopy: ^{1}H NMR chemical shifts have been assigned either by thoroughly evaluation of the coupling patterns or by determination of the center of gravity of the HSQC/HMQC[35] correlation signals in case of complex overlapping multiplet signals. In the latter case the stated accuracy (digits) in experimental data reflects the resolution of the experiments used. All experiments for accurate signal assignments are stated in experimental data.

Compounds **1b–d**,[17,36] **3**,[37] **22**,[17] the bromides[21–24,38] and the sensitizers[39,40] were synthesized following known procedures.

General procedure A (hydroboration of olefins using 9-BBN): A 1.0 M borane solution (1.00 L, 1.00 mol) in THF was placed in a dry apparatus under argon atmosphere and cooled to 0–5 °C. 1,5-Cyclooctadiene (110 g, 1.02 mol) was added while inner temperature did not raise above 25 °C. The solution was diluted with dry THF (600 mL) and heated under reflux for 1 h.

The above 9-BBN solution was cooled to 0–5 °C and the respective olefin (700 mmol) was added while the temperature was kept below 25 °C. The solution was stirred at room temperature for 48 h.

Ethanol (400 mL) and a 6 N caustic soda solution (140 mL) were subsequently added. A 30% hydrogen peroxide solution (280 mL) was added such that the solution was gently boiling. The reaction was heated under reflux for 1 h and cooled to room temperature. The solution was saturated under vigorous stirring with potassium carbonate. The organic layer was separated and the remaining viscous aqueous layer was washed several times with Et_2O (4 × 50 mL). The volatile compounds were carefully removed in vacuum from the combined organic layers using low water bath temperature and protective shield. The residue was diluted in Et_2O (500 mL), eventually separating water was pipetted out and the organic layer was dried over potassium carbonate. The volatile components were carefully removed using an rotational evaporator (see below). Finally the remaining viscous residue had to be kept at for 2 h at 1–2 mbar in order to remove last traces of THF and ethanol. The residue was diluted with ethyl acetate (300 mL) and cyclohexane was added until slight persisting turbidity. For crystallization of the by-product (1,5-dihydroxycyclooctane) the mixture was first kept at room temperature and then at 4 °C for some hours. The bulb was heated to room temperature and cyclohexane was added again until slight persisting turbitity. The crystallisation procedure was repeated until most of the 1,5 dihydroxycyclooctane was removed.

The supernatant was decanted and the remaining 1,5-dihydroxycyclooctane was washed with cyclohexane/ethyl acetate (95:5). The combined organic layers were evaporated and the remaining residue was purified by fast chromatography.

General procedure B (Swern oxidation): Oxalylchloride (20.0 mL, 220 mmol) and methylene chloride (250 mL) were placed in a dry apparatus under argon atmosphere and cooled to −78 °C. Dry DMSO (34.0 mL, 440 mmol) diluted with dry methylene chloride (30 mL) was added at this temperature during 30 min. The respective alcohol (100 mmol) dissolved in dry methylene chloride (100 mL) was added during 30 min and the mixture was stirred for additional 30 min. Triethylamine (70 mL, 500 mmol) was added during 30 min and the mixture was warmed to −10 °C and kept at this temperature for 30 min. Water (100 mL) was added and the mixture was warmed to room temperature. The precipitating salts were mainly diluted by adding water. The organic layer was separated and the aqueous was extracted five times with methylene chloride. The combined organic layers were dried over Na_2SO_4 and evaporated.

The remaining residue was purified either by column chromatography or by distillation.

1,4-Dioxaspiro[4.6]undecan-7-ol (23a): Hydroboration of 1,4-dioxaspiro-[4.6]undec-6-ene (**22a**; 108 g, 700 mmol) was carried out according to GP A. Chromatography on silica gel (cyclohexane/ethyl acetate 55:45) yielded the title compound as a colorless oil (98.5 g, 82%). NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref. $CHCl_3$): δ = 1.35–1.44 (m, 1H, 9-H), 1.41–1.58 (m, 2H, 10-H), 1.55–1.63 (m, 1H, 8-H), 1.60–1.68 (m, 1H, 11-H), 1.63–1.72 (m, 1H, 9-H), 1.803 (ddd, J = 3.4/8.0/14.6 Hz, 1H, 11-H), 1.896 (dddd, J = 3.5/3.5/7.1/13.7 Hz, 1H, 8-H), 1.93–2.04 (m, 2H, 6-H), 3.80–3.91 (m, 4H, 3-H/4-H), 3.84–3.91 (m, 4H, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref. $CDCl_3$): δ = 22.71 (C-10), 24.08 (C-9), 38.09 (C-8), 38.53 (C-11), 46.17 (C-6), 63.92 (C-2), 64.09 (C-3), 67.89 (C-7), 110.79 (C-5); IR (film): $\tilde{\nu}$ = 3432, 2951, 2678, 1451, 1370, 1299, 1211, 1184, 1131, 1094, 1027, 972, 947, 902, 870, 812, 785, 695 cm^{-1}; GC-MS (70 eV): m/z (%): 172 (1) [M^+], 155 (10), 127 (3), 116 (6), 115 (100), 114 (3), 113 (7), 112 (3), 111 (4), 110 (5), 102 (9), 101 (4), 100 (9), 99 (81), 95 (3), 89 (3), 87 (18), 86 (22), 85 (9), 84 (10), 83 (5), 82 (5), 81 (7), 79 (5), 77 (3), 73 (7), 71 (16), 69 (6), 68 (3), 67 (15), 66 (3), 65 (3), 59 (3), 58 (11), 57 (22), 56 (10), 55 (58), 54 (5), 53 (10), 45 (14), 44 (11), 43 (61), 42 (20), 41 (34), 40 (4), 39 (11), 29 (16), 28 (8), 27 (10); GC-MS (CI): m/z (%): 175 (1) [MH$^+$+2], 174(9) [MH$^+$+1], 173(100) [MH$^+$].

1,4-Dioxaspiro[4.6]undecan-7-one (15a): 1,4-Dioxaspiro[4.6]undecan-7-ol (**23a**; 164 g, 952 mmol) was oxidized according to GP B. The distillation of the crude product in vacuo yielded in the title compound as a slightly yellow oil (138 g, 85%). NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC): ^{1}H NMR (500 MHz, $CDCl_3$, ref. $CHCl_3$): δ = 1.71–1.81 (m, 4H, 9-H/10-H), 1.898 (m, 2H, 11-H), 2.473 (m, 2H, 8-H), 2.840 (d, J = 0.7 Hz, 2H, 6-H), 3.885–3.965 (m, 4H, 2-H/3-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 23.38 (C-9), 24.29 (C-10), 39.97 (C-11), 43.50 (C-8), 53.11 (C-6), 64.31 (C-2/C-3), 107.35 (C-5), 209.14 (C-7); IR (film): $\tilde{\nu}$ = 2940, 1702, 1451, 1369, 1282, 1242, 1199, 1081, 1044, 1017, 1000, 978, 948, 909, 863, 835, 791, 737 cm^{-1}; GC-MS (70 eV): m/z (%): 170 (2) [M^+], 114 (3), 113 (40), 112 (82), 100 (11), 99 (100), 97 (7), 87 (5), 86 (51), 85 (3), 84 (3), 83 (4), 82 (3), 81 (5), 79 (4), 70 (4), 69 (12), 68 (7), 67 (10), 56 (12), 55 (63), 54 (7), 53 (11), 45 (5), 44 (3), 43 (29), 42 (48), 41 (43), 40 (8), 39 (26), 29 (17); GC-MS (CI): m/z (%): 172 (16) [MH$^+$+1], 171 (100) [MH$^+$].

3-Ethoxy-2-cyclohepten-1-one (19a): 1,4-Dioxaspiro[4.6]dodecan-7-ol (**23a**; 17.2 g, 100 mmol) was oxidized according to GP B without purification. The crude product was diluted with Et_2O (300 mL) and 1 M H_2SO_4 (50 mL) was added; the reaction mixture was vigorously stirred for 2 h. The aqueous layer was separated and additional 1 M H_2SO_4 (50 mL) was added to the organic layer and the reaction mixture was stirred for 2 h. The procedure was repeated until complete removal of the acetal group (GC control).

The combined aqueous layers were extracted with Et_2O (6 × 50 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuo. The residue was diluted in dry chloroform (400 mL) and ethanol (14.5 mL, 250 mmol) and *p*-toluenesulfonic acid (1.0 g, 5.8 mmol) were added. The mixture was heated under reflux for 36 h while the water formed was removed by a dropping funnel filled with freshly activated molecular sieve (4) Å). The solution was cooled to room temperature, water-free sodium carbonate (10 g) were added and the mixture was stirred for 10 min. The solid residue was filtered out and the filter cake was washed with chloroform. The solvent was removed and the residue was preliminarily cleaned by kugelrohr distillation (0.05 mbar). Chroma-

tography on silica gel (cyclohexane/ethyl acetate 30:70) yielded the title compound as a colorless oil (9.56 g, 62%).

Note: Both the acetal cleavage and the vinylogous esterification should be carried out under GC control while the probe should be deacidified before analysis by filtration over sodium carbonate. NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC): ^{1}H NMR (500 MHz, $CDCl_3$, ref. $CHCl_3$): $\delta =$ 1.299 (t, $J = 7.0$, 3H, 2′-H), 1.72–1.85 (m, 4H, 4-H/7-H), 2.50–2.56 (m, 4H, 5-H/6-H), 3.753 (q, $J = 7.0$ Hz, 2H, 1′-H), 5.330 (s, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref. $CDCl_3$): $\delta = 13.96$ (C-2′), 21.01 (C-6)*, 23.28 (C-5)*, 32.71 (C-4), 41.37 (C-7), 63.90 (C-1′), 105.50 (C-2), 176.04 (C-3), 202.12 (C-1); *: signal assignments are mutual interchangeable; IR (film): $\tilde{\nu} =$ 2986, 2945, 2873, 1699, 1647, 1607, 1476, 1453, 1423, 1378, 1361, 1340, 1324, 1266, 1238, 1184, 1145, 1112, 1092, 1055, 1032, 957, 898, 865, 810 cm^{-1}; GC-MS (70 eV): m/z (%): 155 (5) [M^++1], 154 (49) [M^+], 126 (15), 125 (62), 112 (2), 109 (7), 108 (3), 98 (18), 97 (76), 85 (5), 84 (12), 83 (7), 82 (10), 81 (12), 80 (3), 79 (7), 77 (3), 71 (4), 70 (9), 69 (100), 68 (5), 67 (13), 66 (3), 57 (6), 56 (2), 55 (43), 54 (12), 53 (16), 43 (10), 42 (8), 41 (42), 39 (22), 29 (41), 28 (12), 27 (41); GC-MS (CI): m/z (%): 156 (10) [MH$^+$+1], 155(100) [MH$^+$].

1,4-Dioxaspiro[4.7]dodecan-7-ol (23b): Hydroboration of 1,4-dioxaspiro-[4.7]dode-6-ene (**22b**; 108 g, 700 mmol) was carried out according to GP A. Chromatography on silica gel (cyclohexane/ethyl acetate 50:50) yielded the title compound as a white solid (70.8 g, 76%); m.p. 48°C; NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT): ^{1}H NMR (500 MHz, $CDCl_3$, ref. $CHCl_3$): $\delta = 1.34$ (ddddd, $J = 2.0/3.2/9.2/9.2/14.8$ Hz, 1H, 10-H), 1.44–1.53 (m, 2H, 11-H), 1.59 (m, 1H, 8-H), 1.57–1.79 (m, 4H, 9-H/10-H/12-H), 1.85 (ddd, $J = 0.9/10.0/14.9$ Hz, 1H, 12-H), 2.01 (m, 1H, 8-H), 2.03 (dd, $J = 6.8/14.8$ Hz, 1H, 6-H), 2.07 (dd, $J = 3.2/14.8$ Hz, 1H, 6-H), 2.46 (s, 1H, 7-H(OH)), 3.87–3.97 (m, 5H, 2-H/3-H/7-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref. $CDCl_3$): $\delta = 22.36$ (C-9)*[1], 22.36 (C-11)*[1], 28.90 (C-10), 35.70 (C-12)*[2], 36.32 (C-8)*[2], 40.03 (C-6), 63.98 (C-2)*[3], 64.47 (C-3)*[3], 68.55 (C-7), 111.54 (C-5); *: signal assignments are mutual interchangeable; IR (film): $\tilde{\nu} =$ 3432, 2931, 1693, 1468, 1359, 1282, 1224, 1146, 1114, 1050, 1006, 976, 948, 860, 836, 813, 777, 739 cm^{-1}; GC-MS (70 eV): m/z (%): 186 (<1) [M^+], 169 (14), 143 (4), 141 (6), 125 (6), 124 (5), 116 (5), 115 (74), 113 (8), 102 (4), 100 (5), 99 (68), 97 (3), 96 (3), 95 (3), 94 (3), 87 (24), 86 (81), 83 (3), 81 (10), 80 (3), 79 (7), 73 (7), 72 (4), 71 (22), 70 (3), 69 (8), 68 (3), 67 (10), 65 (3), 59 (7), 58 (11), 56 (9), 55 (86), 54 (8), 53 (14), 51 (3), 45 (15), 44 (19), 43 (100), 42 (37), 41 (46), 40 (7), 39 (22), 32 (9), 31 (8), 29 (32), 28 (36), 27 (25), 26 (3).

3-(Ethoxy)-2-cycloocten-1-one (19b): 1,4-Dioxaspiro[4.7]undecan-7-ol (**23b**; 18.6 g, 100 mmol) was treated analogously to the synthesis of 3-(ethoxy)-2-cyclohepten-1-one (see above). Purification by kugelrohr distillation (0.05 mbar) and chromatography on silica gel (cyclohexane/ethyl acetate 20:80) yielded the title compound as a colorless oil (10.8 g, 64%).

Note: Both the acetal cleavage and the vinylogous esterification should be carried out under GC control, while the probe should be deacidified before analysis by filtration over sodium carbonate. NMR (^{1}H,^{1}H-COSY, ^{13}C-APT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref. $CHCl_3$): $\delta = 1.30$ (t, $J = 7.0$ Hz, 3H, 2′-H), 1.52–1.57 (m, 2H, 6-H), 1.61–1.72 (m, 4H, 5-H/7-H), 2.73 (t, $J = 7.4$ Hz, 2H, 8-H), 2.75 (t, $J = 7.0$ Hz, 2H, 4-H), 3.77 (q, $J = 7.0$ Hz, 2H, 1′-H), 5.54 (s, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref. $CDCl_3$): $\delta = 13.92$ (C-2′), 22.76 (C-5)*, 22.97 (C-7)*, 23.39 (C-6), 32.76 (C-4), 41.13 (C-8), 63.61 (C-1′), 108.19 (C-2), 171.91 (C-3), 200.85 (C-1); *: signal assignments are mutual interchangeable; IR (film): $\tilde{\nu} =$ 2986, 2938, 2863, 1639, 1602, 1475, 1451, 1379, 1363, 1343, 1308, 1259, 1229, 1178, 1161, 1129, 1112, 1092, 1075, 1036, 946, 850, 825, 786, 748 cm^{-1}; GC-MS (70 eV): m/z (%): 169 (4) [M^++1], 168 (27) [M^+], 141 (4), 140 (40), 139 (11), 126 (10), 125 (83), 113 (8), 112 (13), 111 (12), 110 (8), 98 (20), 97 (100), 96 (3), 95 (4), 94 (3), 86 (9), 84 (37), 83 (27), 82 (7), 81 (10), 80 (10), 79 (10), 77 (7), 71 (7), 70 (9), 69 (76), 68 (17), 67 (15), 66 (9), 65 (5), 58 (9), 56 (7), 55 (78), 54 (8), 53 (18), 52 (3), 51 (3), 43 (32), 42 (23), 41 (44), 40 (11), 39 (35), 29 (46), 28 (15), 27 (33); GC-MS (CI): m/z (%): 170 (11) [MH$^+$+1], 169 (100) [MH$^+$].

General procedure C (synthesis of 3-substituted enones by reaction of semiprotected β-diketones with Grignard reagents): Magnesium (1.23 g, 50.0 mmol) and dry THF (30 mL) were placed in a dry apparatus under argon atmosphere and treated with ultrasound at 0°C for 1 h. The cooling source was removed and the bromine compound (45.0 mmol) was added such that the solution was slightly boiling. Then the mixture was heated under reflux for 1 h and the respective semiprotected β-diketone (35.0 mmol) in dry THF (20 mL) was added followed by heating under reflux for 1 h. Water (5 mL) and a saturated ammonium chloride solution (15 mL) were added carefully for hydrolysis and the mixture was stirred for 10 min.

Acetone (20 mL), a saturated ammonium chloride solution (10 mL), water (10 mL) and 85% phophoric acid (8 mL) were added and stirred over night for complete hydrolysis of the acetal. The organic layer was separated and the aqueous layer was extracted with Et_2O (4×50 mL). The combined organic layers were evaporated, the residue was diluted in Et_2O (100 mL), washed with saturated sodium bicarbonate (10 mL) and dried over Na_2SO_4. The solution was evaporated, the residue was diluted in *n*-pentane (200 mL), 85% phosphoric acid (5 mL) were added and the mixture was vigorously stirred for 24–72 h until complete conversion.

Water (10 mL) and a saturated sodium bicarbonate solution (60 mL) were added and the aqueous layer was saturated with sodium bicarbonate. The aqueous layer was separated and extracted Et_2O (3×). The combined organic layers were dried over Na_2SO_4 and evaporated. The remaining residue was purified either by column chromatography or by distillation.

Note: Both the acetal cleavage and the elimination should be carried out under GC control.

General procedure D (synthesis of 3-substituted enones by reaction of vinylogous esters with Grignard reagents): The Grignard reagent was prepared analogously to the GP C. The respective vinylogous ester (35.0 mmol) in dry THF (20 mL) was added and the solution was heated under reflux for 1 h. Water (10 mL) was added carefully. The mixture was acidified (pH 1–2) by adding 2 M HCl and stirred for 2 h. The organic layer was separated and the aqueous was extracted four times with Et_2O (50 mL). The combined organic layers were washed with aq sat $NaHCO_3$ and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography.

General procedure E (synthesis of 3-substituted enones by reaction of semiprotected β-diketones with lithium organic reagents): Lithium (1.04 g, 150.0 mmol) as a suspension in *n*-hexane were placed in an dry apparatus under argon atmosphere. A large excess of lithium generally did not reduce the yield, but in these reactions the hydrolysis must be carried out very cautiously. The solvent was carefully evaporated, dry Et_2O (70 mL) was added and the mixture was treated with ultrasound at 0°C for 3 h. A solution (0.5 mL) of the respective bromine (50.0 mmol) in dry Et_2O (10 mL) was added at room temperature. The mixture was cooled to −18°C and the remaining bromine solution was added within 30 min and stirred for additional 60 min. While cooling the reaction vessel with dry ice/acetone, the respective carbonyl compound (40.0 mmol) in dry Et_2O (10 mL) was added to the lithium organyl solution within 10 min. The mixture was stirred for 2 h at −18°C and for 30 min at 0°C. The hydrolyzation was carefully (!!) carried out by successive addition of ethanol and water saturated ammonium chloride solution. The organic layer was separated and the aqueous was extracted with Et_2O (5×50 mL). The combined organic layers were evaporated, the diphasic residue was diluted with Et_2O (50 mL), acetone (20 mL) and 2 M phosphoric acid (20 mL) and stirred until complete hydrolysis of the acetal group (GC control). The aqueous layer was separated and extracted with Et_2O (4×50 mL). The combined organic layers were evaporated and the residue was disoolved in Et_2O (100 mL), washed with aq sat $NaHCO_3$ (10 mL) and dried over Na_2SO_4. The solution was evaporated and diluted with *n*-pentane (200 mL). 85% Phosphoric acid (5 mL) was added and the mixture was vigorously stirred for 24–72 h until complete conversion.

Water (10 mL) and aq sat $NaHCO_3$ (60 mL) were added and the aqueous layer was saturated with sodium bicarbonate. The aqueous layer was separated and extracted with Et_2O (3×). The combined organic layers were dried over Na_2SO_4 and evaporated.

The remaining residue was purified either by column chromatography or by distillation.

Caution: Both the acetal cleavage and the elimination should be carried out under GC control. The excess of the ultrasound activated lithium powder is highly pyrophoric.

General procedure F (synthesis of 3-substituted enones by reaction of vinylogous esters with lithium organic reagents): The lithium organyl solu-

tion was prepared analogous to GP D. The respective vinylogous ester (40.0 mmol) in dry Et_2O (10 mL) was added at −78 °C (dry ice/acetone cooling) within 10 min. The mixture was warmed to −18 °C, stirred for 2 h, warmed to 0 °C and stirred for 30 min. Then it was carefully (!!) hydrolyzed by successive addition of ethanol and aq sat NH_4Cl.

The mixture was acidified (pH 1–2) by adding 2 M HCl and stirred for 2 h. The organic layer was separated and the aqueous was extracted with Et_2O (4 × 50 mL). The combined organic layers were evaporated and the residue was diluted with Et_2O (100 mL), washed with aq sat $NaHCO_3$ and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography.

3-(3-Butenyl)-2-cyclohepten-1-one (4a): Following GP C 1,4-dioxaspiro-[4.6]undecan-7-on (**15a**; 7.54 g, 44.3 mmol) was treated with 4-bromobut-1-ene. Chromatography on silica gel (cyclohexane/ethyl acetate 9:1) yielded 3-(3-butenyl)-2-cyclohepten-1-one (**4a**; 4.36 g, 60 %). NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 1.70–1.76 (m, 2H, 6-H), 1.74–1.80 (m, 2H, 5-H), 2.18–2.25 (m, 2H, 2′-H), 2.25–2.29 (m, 2H, 1′-H), 2.32–2.36 (m, 2H, 6-H), 2.47–2.51 (m, 2H, 7-H), 4.913 (tdd, J = 1.3/2.9/10.2 Hz, 1H, 4′-H), 4.96 (tdd, J = 1.5/2.9/16.9 Hz, 1H, 4′-H), 5.70 (tdd, J = 6.3/10.2/16.9 Hz, 1H, 3′-H), 5.82 (s, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 21.07 (C-6), 24.88 (C-5), 31.57 (C-2′), 32.42 (C-4), 40.11 (C-1′), 42.00 (C-7), 115.32 (C-4′), 129.35 (C-2), 137.01 (C-3′), 161.01 (C-3), 203.88 (C-1); IR (film): $\tilde{\nu}$ = 3082, 2942, 2870, 1660, 1452, 1417, 1372, 1344, 1266, 1199, 1122, 1050, 995, 912, 877 cm^{-1}; GC-MS (70 eV): m/z (%): 164 (8) [M^+], 149 (3), 136 (8), 135 (22), 122 (5), 121 (9), 120 (10), 109 (25), 108 (7), 107 (19), 106 (3), 105 (5), 104 (5), 98 (5), 97 (3), 96 (3), 95 (31), 94 (19), 93 (48), 92 (8), 91 (38), 82 (10), 81 (36), 80 (37), 79 (93), 78 (13), 77 (42), 68 (7), 67 (40), 66 (12), 65 (17), 55 (18), 54 (7), 53 (26), 52 (4), 51 (6), 43 (5), 42 (7), 41 (100), 40 (13), 39 (78), 38 (3), 29 (35), 28 (13), 27 (43), 26 (4); GC-MS (CI): m/z (%): 167 (1) [MH$^+$+2], 166 (12) [MH$^+$+1], 165 (100) [MH$^+$]; elemental analysis calcd (%) for $C_{11}H_{16}O_1$ (164.24): C 80.44, H 9.82; found: C 80.37, H 9.85.

3-[4-(Trimethylsilyl)-3-butynyl]-2-cyclohepten-1-one: Following GP C 1,4-dioxaspiro[4.6]undecan-7-on (**15a**; 16.5 g, 96.9 mmol) was treated with 4-bromo-1-trimethylsilylbut-1-yne. Chromatography on silica gel (cyclohexane/ethyl acetate 8:2) yielded 3-(2-butynyl)-2-cyclohepten-1-one (**5a**; 1.10 g, 7 %) and 3-[4-(trimethylsilyl)-3-butynyl]-2-cyclohepten-1-one (7.27 g, 32 %) as colorless oils. NMR (^{1}H,^{1}H-COSY, ^{13}C-APT, HMQC): ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 0.10 (s, 9H, 1″-H), 1.73–1.89 (m, 4H, 5-H/6-H), 2.35–2.43 (m, 6H, 4-H/1′-H/2′-H), 2.55 (m, 2H, 7-H), 5.89 (s, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = −0.12 (C-1″), 18.49 (C-2′), 21.03 (C-6), 24.91 (C-5), 32.29 (C-4), 39.35 (C-1′), 42.03 (C-7), 85.85 (C-4′), 105.14 (C-3′), 129.93 (C-2), 159.13 (C-3), 203.70 (C-1); IR (film): $\tilde{\nu}$ = 2960, 2871, 2177, 1664, 1451, 1424, 1372, 1331, 1249, 1199, 1040, 842, 759 cm^{-1}; GC-MS (70 eV): m/z (%): 234 (5) [M^+], 233 (5), 220 (8), 219 (30), 206 (6), 205 (7), 193 (4), 192 (3), 191 (8), 177 (6), 165 (4), 163 (4), 161 (7), 160 (5), 159 (3), 151 (3), 149 (5), 147 (6), 146 (3), 145 (13), 143 (7), 135 (6), 133 (8), 132 (40), 131 (11), 130 (6), 129 (9), 128 (4), 121 (4), 119 (4), 117 (14), 116 (3), 115 (8), 110 (3), 109 (9), 106 (3), 105 (6), 104 (8), 99 (3), 97 (7), 96 (9), 95 (9), 93 (5), 92 (4), 91 (18), 89 (3), 85 (3), 83 (15), 82 (3), 81 (17), 80 (3), 79 (11), 77 (11), 76 (5), 75 (60), 74 (9), 73 (100), 69 (6), 68 (3), 67 (8), 66 (3), 65 (4), 61 (4), 59 (16), 55 (8), 53 (7), 51 (4), 45 (9), 43 (9), 41 (11), 39 (7).

3-(2-Butynyl)-2-cyclohepten-1-on (5a): 3-[4-(Trimethylsilyl)-3-butynyl]-2-cyclohepten-1-one (6.50 g, 27.7 mmol) was diluted in THF (50 mL) and water (1 mL) and cooled to −78 °C. Tetrabutylammonium fluoride hexahydrate (14.5 g, 39.5 mmol) in THF (50 mL) was slowly added, the solution was slowly warmed to room temperature and stirred for 30 min. Brine (20 mL) and Et_2O (200 mL) were added and the organic layer was separated, dried over Na_2SO_4 and evaporated. Chromatography on silica gel (cyclohexane/ethyl acetate 85:15) yielded a colorless oil (4.36 g, 97 %). NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC): ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 1.72–1.82 (m, 4H, 5-H/6-H), 1.958 (t, J = 2.3 Hz, 2H, 4′-H), 2.33–2.42 (m, 6H, 4-H/1′-H/2′-H), 2.55 (m, 2H, 7-H), 5.90 (s, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 16.88 (C-4′), 21.00 (C-6), 24.88 (C-5), 32.28 (C-4), 39.07 (1′), 42.02 (C-7), 69.40 (C-4′), 82.47 (C-3′), 129.77 (C-2), 158.88 (C-3), 203.76 (C-3); IR (film): $\tilde{\nu}$ = 3297, 2938, 2871, 2175, 1660, 1450, 1373, 1345, 1258, 1201, 1118, 1053, 877, 844, 760, 632 cm^{-1}; GC-MS (70 eV): m/z (%): 163 (1) [M^++1], 162 (7) [M^+], 161 [$(M-1)^+$] (8), 147 (9), 134 (10), 133 (23), 131 (3), 129 (6), 121 (4), 120 (9), 119 (17), 118 (6), 117 (5), 115 (3), 109 (13), 107 (5), 106 (15), 105 (34), 104 (6), 103 (6), 95 (14), 94 (7), 93 (11), 92 (31), 91 (100), 89 (3), 84 (3), 81 (14), 80 (6), 79 (40), 78 (19), 77 (33), 68 (4), 67 (18), 66 (8), 65 (19), 63 (4), 55 (16), 54 (4), 53 (25), 52 (11), 51 (15), 50 (4), 43 (3), 42 (5), 41 (32), 40 (7), 39 (39), 38 (3), 29 (7), 28 (7), 27 (19); GC-MS (CI): m/z (%): 165 (2) [MH$^+$+2], 164 (11) [MH$^+$+1], 163 (100) [MH$^+$]; HRMS: m/z: calcd for $C_{11}H_{13}O$: 161.0959, found: 161.0966 [$(M-1)^+$].

3-(2-Cyclohexenylmethyl)-2-cyclohepten-1-one (6a): According to the GP E 1,4-dioxaspiro[4.6]undecan-7-one (**15a**; 2.21 g, 13.0 mmol) was treated with 3-bromomethyl-1-cyclohexene. Chromatography on silica gel (cyclohexane/ethyl acetate 9:1) yielded a colorless oil (1.25 g, 47 %). NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 1.16–1.24 (m, 1H, 6″-H), 1.45–1.55 (m, 1H, 5″-H), 1.65–1.75 (m, 2H, 5″-H/6″-H), 1.75–1.79 (m, 4H, 5-H/6-H), 1.94–1.98 (m, 2H, 4″-H), 2.10 (dd, J = 8.2/13.1 Hz, 1H, 1′-H), 2.18 (ddd, J = 0.9/6.9/13.1 Hz, 1H, 1′-H), 2.26–2.35 (m, 1H, 1″-H), 2.38–2.41 (m, 2H, 4-H), 2.54–2.57 (m, 2H, 7-H), 5.48 (dddd, J = 2.4/2.4/2.4/10.0 Hz, 1H, 2″-H), 5.68 (dddd, J = 2.4/3.8/3.8/10.0 Hz, 1H, 3″-H), 5.88 (s, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 20.99 (C-5″)*, 21.08 (C-6)*, 24.93 (C-5), 25.03 (C-4″), 28.83 (C-6″), 32.17 (C-4), 33.21 (C-1″), 41.98 (C-7), 47.74 (C-1′), 127.86 (C-3″), 130.32 (C-2″), 130.72 (C-2), 160.25 (C-3), 203.81 (C-1); IR (film): $\tilde{\nu}$ = 3022, 2934, 2865, 1660, 1447, 1371, 1344, 1320, 1267, 1201, 1045, 953, 882, 863, 722, 699, 676 cm^{-1}; GC-MS (70 eV): m/z (%): 204 (3) [M^+], 125 (5), 124 (54), 109 (6), 96 (5), 95 (3), 91 (8), 83 (3), 82 (10), 81 (100), 80 (7), 79 (39), 78 (3), 77 (15), 69 (3), 67 (10), 66 (6), 65 (7), 55 (14), 53 (27), 51 (3), 43 (7), 41 (40), 39 (18), 29 (7), 27 (9); GC-MS (CI): m/z (%): 207 (2) [MH$^+$+2], 206 (17) [MH$^+$+1], 205 (100) [MH$^+$]; HRMS: m/z: calcd for $C_{14}H_{20}O$: 204.1514, found: 204.1518; elemental analysis calcd (%) for $C_{14}H_{20}O$ (204.31): C 82.30, H 9.87; found: C 82.20, H 10.20.

3-(3-Butenyl)-2-cycloocten-1-one (4b): Following GP D 3-(ethoxy)-2-cycloocten-1-one (**19b**; 2.50 g, 14.9 mmol) was treated with 4-bromobut-1-ene. Chromatography on silica gel (cyclohexane/ethyl acetate 9:1) yielded the title compound (1.87 g, 71 %). NMR (^{1}H,^{1}H-COSY, ^{13}C-APT, HMQC, HMBC): ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 1.50 (m, 2H, 6-H), 1.61 (tt, J = 6.0/6.8 Hz, 2H, 5-H), 1.714 (m, 2H, 7-H), 2.17–2.26 (m, 4H, 1′-H/2′-H), 2.56 (t, J = 6.8 Hz, 2H, 4-H), 2.68 (t, J = 7.2 Hz, 2H, 8-H), 6.00 (s, 1H, 2-H), 4.96 (tdd, J = 1.2/2.0/10.2 Hz, 1H, 4′-H), 5.00 (tdd, J = 1.3/2.0/18.6 Hz, 1H, 4′-H), 5.75 (m, 1H, 3′-H), 5.99 (m, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 22.77 (C-7), 23.55 (C-6), 23.84 (C-5), 31.51 (C-2′), 31.89 (C-4), 40.52 (C-1′), 41.87 (C-8), 115.18 (C-4′), 130.41 (C-2), 137.05 (C-3′), 155.58 (C-3), 203.69 (C-1); IR (film): $\tilde{\nu}$ = 3082, 2936, 2860, 1648, 1482, 1449, 1343, 1305, 1282, 1259, 1217, 1161, 1135, 1084, 994, 912 cm^{-1}; GC-MS (70 eV): m/z (%): 178 (7) [M^+], 163 (3), 150 (11), 149 (24), 137 (8), 136 (7), 135 (21), 134 (4), 124 (3), 123 (15), 122 (5), 121 (15), 120 (3), 117 (3), 111 (3), 109 (7), 108 (9), 107 (32), 105 (7), 104 (5), 96 (5), 95 (23), 94 (24), 93 (41), 92 (8), 91 (37), 83 (6), 82 (9), 81 (31), 80 (37), 79 (100), 78 (11), 77 (37), 69 (4), 68 (8), 67 (48), 66 (13), 65 (18), 55 (42), 54 (12), 53 (35), 52 (4), 51 (6), 43 (8), 42 (8), 41 (62), 40 (7), 39 (36), 29 (19), 28 (8), 27 (20); elemental analysis calcd (%) for $C_{12}H_{18}O$ (178.27): C 80.85, H 10.18; found: C 80.56, H 10.34.

3-(3-Butynyl)-2-cycloocten-1-one (5b): Following GP D 3-(ethoxy)-2-cycloocten-1-one (**19b**; 4.71 g, 28.0 mmol) was treated with 4-bromo-1-trimethylsilylbut-1-yne (8.00 g, 39.0 mmol). The raw product was diluted in THF (50 mL)/water (1 mL) and cooled to −18 °C. Tetrabutylammonium fluoride hexahydrate (11.5 g, 36.7 mmol) in THF (50 mL) was added and the mixture was allowed to warm slowly to room temperature and stirred for 30 min. Brine (20 mL) was added, the organic layer was separated and washed with brine (20 mL). The combined aqueous layers were washed three times with Et_2O (100 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. Chromatography on silica gel (cyclohexane/ethyl acetate 9:1) gave a colorless oil (3.51 g, 71 %). NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, ^{13}C-gated, HMQC, HMBC): ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 1.50–1.56 (m, 2H, 6-H), 1.59–1.66 (m, 2H, 5-H), 1.71–1.77 (m, 2H, 7-H), 1.95–1.97 (m, 1H, 4′-H), 2.36–2.37 (m, 4H, 1′-H/2′-H), 2.55 (t, J = 6.9 Hz, 2H, 4-H), 2.69 (t, J = 7.1 Hz, 2H, 8-H), 6.00 (s, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 16.90 (C-2′), 22.70 (C-7)*, 23.78 (C-5)*, 23.80 (C-6), 31.82 (C-4), 39.52 (C-1′), 42.04 (C-8), 69.39 (C-4′), 82.59 (C-3′), 130.63 (C-2), 153.37 (C-3), 203.95 (C-1); *: signal assignments are mutual interchangea-

ble; IR (film): $\tilde{\nu}$ =3295, 2935, 2862, 2120, 1648, 1483, 1447, 1345, 1305, 1283, 1259, 1218, 1158, 1134, 1066, 1024, 957, 889, 820, 634 cm^{-1}; GC-MS (70 eV): *m/z* (%): 176 (4) [M^+], 161 (4), 148 (6), 147 (12), 137 (5), 135 (3), 134 (10), 133 (52), 123 (8), 121 (4), 120 (23), 119 (26), 118 (3), 117 (5), 115 (4), 109 (3), 108 (4), 107 (10), 106 (14), 105 (61), 104 (3), 103 (11), 95 (9), 94 (8), 93 (12), 92 (30), 91 (100), 83 (3), 82 (3), 81 (11), 80 (8), 79 (53), 78 (17), 77 (48), 68 (4), 67 (25), 66 (8), 65 (27), 63 (4), 55 (35), 54 (4), 53 (35), 52 (9), 51 (11), 50 (4), 43 (5), 42 (7), 41 (43), 40 (5), 39 (41), 29 (14), 28 (6), 27 (22); GC-MS (CI): *m/z* (%): 179 (1) [MH$^+$+2], 178 (14) [MH$^+$+1], 177 (100) [MH$^+$]; elemental analysis calcd (%) for $C_{12}H_{16}O$ (176.25): C 81.77, H 9.15; found: C 81.09, H 9.86.

3-(2-Cyclohexenylmethyl)-2-cycloocten-1-one (6b): Following GP F 3-(ethoxy)-2-cycloocten-1-one (**19b**, 2.50 g, 14.9 mmol) was treated with 3-bromomethyl-1-cyclohexene (2.09 g, 18.6 mmol). Chromatography on silica gel (cyclohexane/ethyl acetate 9:1) gave a colorless oil (1.82 g, 56%). NMR (^{1}H,^{1}H-COSY, ^{13}C-APT, HMQC, HMBC): ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ=1.21 (m, 1H, 6″-H), 1.44–1.56 (m, 3H, 6-H/5″-H), 1.57–1.63 (m, 2H, 5-H), 1.63–1.76 (m, 4H, 7-H/5″-H/6″-H), 1.92–1.97 (m, 2H, 4″-H), 2.07 (dd, J=8.1/13.2 Hz, 1H, 1′-H), 2.14 (dd, J=7.0/13.2 Hz, 1H, 1′-H), 2.29 (m, 1H, 1″-H), 2.53–2.63 (m, 2H, 4-H), 2.66–2.75 (m, 2H, 8-H), 5.48 (dddd, J=2.3/2.3/2.3/10.1 Hz, 1H, 2″-H), 5.67 (dddd, J=3.1/3.2/3.3/10.1 Hz, 1H, 3″-H), 6.01 (s, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=20.94 (C-5″), 22.90 (C-7), 23.41 (C-6), 23.98 (C-5), 24.98 (C-4″), 28.83 (C-6″), 31.65 (C-4), 33.05 (C-1″), 41.76 (C-8), 48.27 (C-1′), 127.71 (C-3″), 130.32 (C-2″), 132.01 (C-2), 154.79 (C-3), 203.41 (C-1); IR (film): $\tilde{\nu}$ = 3022, 2933, 2861, 1648, 1619, 1481, 1447, 1364, 1258, 1128, 890, 722 cm^{-1}; GC-MS (70 eV): *m/z* (%): 219 (1) [M^++1], 218 (7) [M^+], 203 (2), 200 (3), 190 (5), 175 (9), 147 (8), 139 (4), 138 (36), 133 (3), 123 (5), 121 (4), 120 (3), 119 (6), 110 (21), 109 (11), 105 (5), 96 (5), 95 (14), 94 (8), 93 (5), 92 (4), 91 (17), 83 (13), 81 (100) [(cyclohexen−H)$^+$], 80 (17), 79 (49), 78 (5), 77 (17), 68 (3), 67 (13), 66 (6), 65 (8), 55 (16), 54 (3), 53 (20), 52 (3), 43 (5), 41 (24), 39 (10); GC-MS (CI): *m/z* (%): 220 (16) [MH$^+$+1], 219 (100) [MH$^+$]; elemental analysis calcd (%) for $C_{15}H_{22}O$ (218.33): C 82.52, H 10.16; found: C 81.12, H 10.28.

3-Ethoxy-7-(2-propenyl)-2-cyclohepten-1-one (25): Diisopropylamine (3.55 g, 35.1 mmol) in dry THF (40 mL) was placed in a dry apparatus under argon atmosphere and cooled to −78 °C. *n*-Butyllithium (20 mL, 32.0 mmol, in *n*-hexane) was added within 5 min. The mixture was warmed to 0 °C and stirred for 30 min. After cooling to −78 °C 3-(ethoxy)-2-cyclohepten-1-on (**19a**; 4.20 g, 27.2 mmol) in dry THF (25 mL) was added. The solution was stirred for 1 h and allyl bromide (3.30 g, 27.2 mmol) was added followed by stirring for 12 h at −78 °C (dry ice/acetone cooling), warming to room temperature within 1 h and again stirring for additional 30 min.

After hydrolysis with water (15 mL) the volatile compound except water were removed in a rotary evaporator and the diphasic residue was diluted in Et_2O (80 mL) and water (20 mL). The aqueous layer was separated and washed four times with Et_2O (50 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. Chromatography on silica gel (cyclohexane/ethyl acetate 7:3) yielded 3-(ethoxy)-7-(2-propenyl)-2-cyclohepten-1-one (2.71 g, 13.9 mmol, 51%) and the starting material **19a** (1.26 g) as colorless oils. NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ= 1.30 (dd, J=7.0/7.0 Hz, 3H, 2′-H), 1.41 (m, 1H, 6-H), 1.68 (m, 1H, 5-H), 1.85–1.95 (m, 2H, 5-H/6-H), 2.07 (ddd, J=7.1/6.9/14.0 Hz, 1H, 1″-H), 2.40 (dddd, J=1.6/2.8/6.0/16.9 Hz, 1H, 4-H), 2.54–2.66 (m, 3H, 4-H/7-H/1″-H), 3.73 (td, J=7.0/9.7 Hz, 1H, 1′-H), 3.77 (td, J=7.0/9.7 Hz, 1H, 1′-H), 4.96 (dddd, J=1.0/1.0/2.9/10.2 Hz, 1H, 3″-H), 5.01 (dddd, J=1.4/1.5/2.9/17.1 Hz, 1H, 3″-H), 5.34 (m, 1H, 2-H), 4.96 (dddd, J=5.8/7.9/10.2/17.1 Hz, 1H, 2″-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=14.13 (C-2′), 23.29 (C-5), 28.17 (C-6), 33.02 (C-4), 35.29 (C-1″), 48.80 (C-7), 63.89 (C-1′), 105.80 (C-2), 115.94 (C-3″), 136.94 (C-2″), 176.30 (C-3), 202.51 (C-1); IR (film): $\tilde{\nu}$ = 3079, 2940, 2942, 1871, 1650, 1608, 1476, 1444, 1377, 1360, 1305, 1241, 1184, 1158, 1112, 1033, 997, 911, 845, 808, 754 cm^{-1}; GC-MS (70 eV): *m/z* (%): 195 (8) [M^++1], 194 (40) [M^+], 193 (12) [(M−1)$^+$], 179 (4), 166 (10), 165 (20), 153 (3), 152 (14), 151 (27), 150 (6), 149 (5), 140 (16), 139 (8), 138 (8), 137 (13), 126 (6), 125 (44), 124 (13), 123 (14), 121 (5), 120 (3), 119 (3), 112 (23), 111 (11), 110 (7), 109 (9), 108 (3), 107 (7), 105 (4), 99 (7), 98 (26), 97 (94), 96 (7), 95 (19), 94 (4), 93 (11), 92 (4), 91 (14), 86 (8), 85 (5), 84 (31), 83 (11), 82 (23), 81 (31), 80 (15), 79 (40), 78 (4), 77 (17), 71 (14), 70 (10), 69 (100), 68 (20), 67 (28), 66 (6), 65 (10), 58 (4), 57 (9), 56 (4), 55 (51), 54 (19), 53 (28), 52 (5), 51 (4), 43 (40), 42 (15), 41 (81), 40 (15), 39 (48), 29 (53), 28 (13), 27 (36), 18 (18); GC-MS (CI): *m/z* (%): 196 (13) [MH$^+$+1], 195 (100) [MH$^+$], 194 (4) [M^+]; HRMS: *m/z*: calcd for $C_{12}H_{18}O_2$: 194.1307, found: 194.1306 [M^+].

4-(2-Propenyl)-2-cyclohepten-1-one (7): $LiAlH_4$ (420 mg, 11.1 mmol) and dry Et_2O (50 mL) were placed in a dry apparatus under argon atmosphere. 3-(Ethoxy)-7-(2-propenyl)-2-cyclohepten-1-one (2.52 g, 13.0 mmol) in dry Et_2O (20 mL) was added within 10 min and the suspension was heated under reflux 3 h. After hydrolysis by successive addition of wet Et_2O, water and saturated ammonium chloride solution the mixture was acidified (pH 1–2) by slow addition of 2 M HCl and stirred for 2 h. The aqueous layer was separated and extracted four times with Et_2O (40 mL). The combined organic layers were washed with saturated sodium bicarbonate solution and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (cyclohexane/ethyl acetate 75:25) to yield 4-(2-propenyl)-2-cyclohepten-1-one (**7**; 680 mg, 4.53 mmol, 34%), (3*R**,4*S**)-4-allyl-3-hydroxy-1-cycloheptanone (**26a**; 690 mg, 4.10 mmol, 32%) and (3*R**,4*S**)-4-allyl-3-hydroxy-1-cycloheptanone (**26b**; 350 mg, 2.08 mmol, 16%).

Synthesis of 7 starting with (3*R,4*S**)-4-allyl-3-hydroxy-1-cycloheptanone (26a)**: The alcohol (500 mg) was diluted in *n*-pentane (50 mL). 85% Phosphoric acid (3 mL) was added and the mixture was vigorously stirred for 24–72 h until complete conversion. Water (10 mL) and saturated sodium bicarbonate solution (40 mL) was added. The aqueous layer was separated and extracted three times with Et_2O (50 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated and the residue was purified by column chromatography (see above).

4-(2-Propenyl)-2-cyclohepten-1-one (7): NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ=1.48 (dddd, J=5.8/7.2/10.4/13.8 Hz, 1H, 5-H), 1.747–1.81 (m, 2H, 6-H), 1.94 (m, 1H, 5-H), 2.16–2.26 (m, 2H, 1′-H), 2.49–2.62 (m, 3H, 4-H/7-H), 5.03–5.09 (m, 2H, 3′-H), 5.75 (dddd, J=6.8/7.0/9.6/17.6 Hz, 1H, 2′-H), 5.90 (dd, J=2.6/12.3 Hz, 1H, 2-H), 6.37 (ddd, J=0.9/3.8/12.3 Hz, 1H, 3-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=20.54 (C-6), 31.79 (C-5), 39.87 (C-4), 40.25 (C-1′), 43.23 (C-7), 117.27 (C-3′), 131.33 (C-2), 135.71 (C-2′), 149.74 (C-3), 204.19 (C-1); IR (film): $\tilde{\nu}$ =3326, 3081, 2937, 2868, 1668, 1450, 1417, 1399, 1350, 1282, 1262, 1201, 1178, 995, 916, 794, 725 cm^{-1}; GC-MS (70 eV): *m/z* (%): 151 (3) [M^++1], 150 (12) [M^+], 149 (3), 135 (6), 132 (3), 122 (8), 121 (8), 117 (4), 109 (6), 108 (7), 107 (11), 106 (6), 105 (3), 104 (10), 95 (6), 94 (19), 93 (25), 92 (6), 91 (28), 84 (3), 82 (6), 81 (53), 80 (32), 79 (100), 78 (14), 77 (35), 68 (11), 67 (26), 66 (13), 65 (14), 55 (24), 54 (10), 53 (39), 52 (11), 51 (11), 50 (3), 43 (4), 42 (7), 41 (57), 40 (10), 39 (51), 29 (8), 28 (7), 27 (31); GC-MS (CI): *m/z* (%): 152 (11) [MH$^+$+1], 151 (100) [MH$^+$]; HRMS: *m/z*: calcd for $C_{10}H_{14}O$: 150.1045, found: 150.1042 [M^+].

(3*R,4*S**)-4-Allyl-3-hydroxy-1-cycloheptanone (26a)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ=1.53 (dddd, J=1.7/11.3/11.3/13.1 Hz, 1H, 5-H), 1.57–1.67 (m, 2H, 4-H/6-H), 1.67–1.73 (m, 1H, 5-H), 1.85 (m, 1H, 6-H), 2.05 (ddddd, J=1.3/1.3/7.0/7.0/14.0 Hz, 1H, 1′-H), 2.20 (ddddd, J=1.3/1.3/7.0/7.0/14.0 Hz, 1H, 1′-H), 2.40 (ddd, J=3.7/11.5/17.5 Hz, 1H, 7-H), 2.47 (dddd, J=1.4/3.7/5.2/17.5 Hz, 1H, 7-H), 2.47 (d, J=4.0 Hz, 1H, 3-H (OH)), 2.71 (dd, J=7.1/14.5 Hz, 1H, 2-H), 2.77 (dd, J=2.0/14.5 Hz, 1H, 2-H), 4.04 (dddd, J=2.0/2.4/4.0/7.1 Hz, 1H, 3-H), 4.99 (dddd, J=1.3/1.3/2.0/10.0 Hz, 1H, 3′-H), 5.05 (dddd, J=1.3/1.3/2.0/17.1 Hz, 1H, 3′-H), 5.76 (dddd, J=7.0/7.0/10.0/17.1 Hz, 1H, 2′-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=22.85 (C-6), 29.13 (C-5), 38.27 (C-1′), 44.04 (C-7), 46.32 (C-4), 49.93 (C-2), 68.20 (C-3), 116.48 (C-3′), 137.06 (C-2′), 213.59 (C-1); IR (film): $\tilde{\nu}$ = 3453, 3080, 2933, 2867, 1691, 1640, 1451, 1414, 1352, 1256, 1157, 1076, 1018, 996, 914, 873, 839, 790 cm^{-1}; GC-MS (70 eV): *m/z* (%): 149 (3)*, 126 (4), 111 (3), 110 (5), 109 (6), 108 (4), 107 (7), 98 (4), 97 (6), 96 (4), 95 (10), 93 (7), 91 (4), 86 (4), 85 (6), 84 (16), 83 (11), 82 (10), 81 (25), 80 (17), 79 (26), 77 (6), 71 (22), 70 (9), 69 (11), 68 (18), 67 (42), 66 (7), 65 (6), 59 (4), 58 (17), 57 (19), 56 (10), 55 (63), 54 (21), 53 (22), 52 (3), 51 (4), 50 (3), 45 (4), 44 (12), 43 (100), 42 (13), 41 (51), 40 (11), 39 (35), 32 (28), 31 (7), 29 (25), 28 (62), 27 (29); *no [M^+] detected; GC-MS (CI): *m/z* (%): 170 (2) [MH$^+$+1], 169 (15) [MH$^+$], 153 (5), 152 (11), 151 (100) [MH$^+$−H_2O].

(3*R,4*S**)-4-Allyl-3-hydroxy-1-cycloheptanone (26b)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): $\delta = 1.23$ (dddd, $J = 1.2/8.9/9.5/14.3$ Hz, 1H, 5-H), 1.67 (ddddd, $J = 1.6/4.8/9.7/9.7/14.6$ Hz, 1H, 6-H), 1.76 (ddddd, $J = 3.4/4.8/8.0/8.1/8.2$ Hz, 1H, 4-H), 1.81 (m, 1H, 6-H), 1.88 (m, 1H, 5-H), 2.02 (ddddd, $J = 1.3/1.7/7.8/7.8/14.2$ Hz, 1H, 1′-H), 2.29 (m, 1H, 1′-H), 2.30 (ddd, $J = 4.6/9.6/17.1$ Hz, 1H, 7-H), 2.44 (dddd, $J = 0.8/4.7/6.7/17.1$ Hz, 1H, 7-H), 2.69 (dd, $J = 2.4/13.0$ Hz, 1H, 2-H), 2.75 (d, $J = 4.3$ Hz, 1H, 3-H (OH)), 2.81 (dd, $J = 9.1/13.0$ Hz, 1H, 2-H), 3.64 (dddd, $J = 2.5/4.3/7.1/9.4$ Hz, 1H, 3-H), 4.99 (dddd, $J = 1.3/1.7/2.0/10.3$ Hz, 1H, 3′-H), 5.01 (dddd, $J = 1.3/1.7/2.0/16.9$ Hz, 1H, 3′-H), 5.37 (dddd, $J = 6.5/7.8/10.3/16.9$ Hz, 1H, 2′-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): $\delta = 20.40$ (C-6), 28.83 (C-5), 36.85 (C-1′), 43.78 (C-7), 46.04 (C-4), 49.78 (C-2), 70.95 (C-3), 116.72 (C-3′), 136.41 (C-2′), 212.50 (C-1); IR (film): $\tilde{\nu} = 3442$, 3080, 2936, 1697, 1640, 1443, 1415, 1351, 1263, 1226, 1033, 996, 912, 832, 748 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 126 (5)*, 110 (3), 109 (5), 108 (4), 107 (6), 98 (4), 97 (5), 96 (4), 95 (9), 94 (4), 93 (6), 92 (4), 91 (5), 86 (4), 85 (4), 84 (14), 83 (9), 82 (10), 81 (21), 80 (15), 79 (24), 78 (3), 77 (6), 71 (20), 70 (5), 69 (9), 68 (17), 67 (42), 66 (6), 65 (7), 59 (3), 58 (18), 57 (15), 56 (9), 55 (57), 54 (18), 53 (20), 52 (3), 51 (5), 45 (3), 44 (7), 43 (100), 42 (12), 41 (48), 40 (7), 39 (32), 32 (3), 31 (5), 29 (21), 28 (16), 27 (24); *no [M^+] detected; GC-MS (CI): *m*/*z* (%): 170 (1) [MH$^+$+1], 169 (12) [M^+], 153 (5), 152 (11), 151 (100) [MH$^+$ −H_2O].

General procedure G (synthesis of the silyl enol ethers): Diisopropylamine (360 mmol) in dry THF (500 mL) was placed in a dry apparatus under argon atmosphere and cooled to 0 °C. *n*-Butyllithium (1.6 M in *n*-hexane; 206 mL, 330 mmol) were added at this temperature within 30 min and stirred for additional 30 min. After cooling to −78 °C the respective ketone/enone (300 mmol) in dry THF (50 mL) were added. Then the solution was stirred for 1 h and trimethylsilyl chloride (450 mmol) were added. The mixture was warmed to room temperature within 1 h and stirred for an additional hour at this temperature. After evaporation of the solvent the residue was diluted in *n*-pentane (300 mL) the precipitating lithium chloride was filtered off. The solvent was evaporated and the residue was purified by fractional distillation. At small scales the residue was only purified by kugelrohr distillation and immediately converted to the corresponding cyclopropyl derivative according to GP H.

General procedure H (cyclopropanisation of silyl enol ethers containing additional reactive olefinic bonds): The respective silyl enol ether (100 mmol) in dry Et_2O (250 mL) was placed in a dry apparatus under argon atmosphere and cooled to 0 °C. Diethyl zinc (1.0 M in *n*-hexane; 150 mL, 150 mmol) were added within 30 min at this temperature. Methylene iodide (100 mmol) in Et_2O (20 mL) was added within 30 min and the mixture was warmed to room temperature and stirred for 12–24 h. The conversion was checked by gas chromatography. (Note the low sensitivity of detection of diiodo methane by gas chromatography.) If required additional methylene iodide and eventually diethyl zinc solution was added and the mixture was stirred again for 12–24 h. After complete conversion the mixture was carefully hydrolyzed with saturated ammonium chloride solution until complete dissolution of the zinc salts. The aqueous layer was separated and extracted two times with Et_2O (50 mL). The combined organic were washed with saturated sodium bicarbonate solution and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by fractional distillation or by fast column chromatography.

Eventually the product partially hydrolyzed during chromatography. In these cases the corresponding alkyl alcohol can be converted into the silyl alkyl ether by the following procedure. 2.0 Molar equivalents triethylamine and 1.3 equivalents trimethylsilyl trifluoromethanesulfonate were added to the hydrolyzed product diluted in methylene chloride (approx. 15 mL per 5 mmol alcohol). The mixture was stirred for 2 h diluted with methylene chloride and washed with saturated sodium bicarbonate solution. The organic layer was dried over $MgSO_4$, the solvent was evaporated and the residue was purified again by fast column chromatography.

1,5-Cyclohexadienyltrimethylsilyl ether: Silylation of 2-cyclohexen-1-one (**1a**; 28.8 g, 300 mmol) according to GP G yielded 1,5-cyclohexadienyltrimethylsilyl ether (40.9 g, 81 %) as a colorless liquid. B.p. 61 °C at 16 mbar; NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): $\delta = 0.16$ (s, 9H, 1′-H), 2.05 (m, 2H), 2.14 (m, 2H,), 4.85 (dt, $J = 2.1/4.5$ Hz, 1H, 2-H), 5.66 (qd, $J = 2.0/10.0$ Hz, 1H, 5-H), 5.83 (td, $J = 4.2/10.0$ Hz, 1H, 6-H); ^{13}C NMR (50 MHz, $CDCl_3$, ref.: $CDCl_3$): $\delta = 0.12$ (C-1′), 21.71 (CH_2), 22.57 (CH_2), 102.93 (C-2), 126.40 (C-5), 129.80 (C-6), 148.07 (C-1); IR (film): $\tilde{\nu} = 3053$, 2965, 2880, 2830, 2764, 2724, 2492, 1649, 1428, 1401, 1251, 1199, 1165, 981, 954, 910, 845, 805, 755 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 169 (10) [M^++1], 168 (80) [M^+], 167 (28), 152 (40), 151 (32), 77 (29), 75 (55), 74 (10), 73 (100), 59 (10), 45 (31).

1,6-Cycloheptadienyltrimethylsilyl ether: Silylation of 2-cyclohepten-1-one (**1b**; 16.0 g, 145 mmol) according to GP G yielded a colorless liquid (230.9 g, 87 %). B.p. 67 °C at 7.5 mbar; NMR (^{13}C,^{13}C-gated); ^{13}C NMR (50 MHz, $CDCl_3$, ref.: $CDCl_3$): $\delta = 0.17$ (C-1′), 26.61 (CH_2), 27.12 (CH_2), 31.27 (CH_2), 112.74 (C-2), 128.16 (C-7), 133.28 (C-6), 148.01 (C-1); GC-MS (70 eV): *m*/*z* (%): 183 (8) [M^++1], 182 (43) [M^+], 181 (7), 168 (6), 167 (43), 165(5), 155 (3), 154 (13), 151 (17), 149 (3), 139 (3), 93 (3), 92 (5), 91 (15), 85 (3), 83 (6), 81 (3), 79 (4), 78 (3), 77 (12), 76 (13), 75 (46), 74 (9), 73 (100), 65 (6), 61 (5), 59 (9), 53 (3), 47 (5), 45 (20), 43 (4), 41 (4), 39 (4); GC-MS (CI): *m*/*z* (%): 185 (6) [MH$^+$+2], 184 (17) [MH$^+$+1], 183 (100) [MH$^+$], 182 (10) [M^+].

1,7-Cyclooctadienyl trimethylsilyl ether: Silylation of 2-cycloocten-1-one (**1c**; 10.2 g, 82.1 mmol) according to GP G yielded as a colorless liquid (12.4 g, 77 %). B.p. 56 °C at 2 mbar; NMR (^{1}H,^{13}C,^{13}C-gated); ^{1}H NMR (200 MHz, $CDCl_3$, ref.: $CHCl_3$): $\delta = 0.16$ (s, 9H, 1′-H), 1.32–1.61 (m, 4H), 1.98–2.28 (m, 4H), 4.96 (t, $J = 8.0$ Hz, H-2), 5.55–5.80 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, ref.: $CDCl_3$): $\delta = 0.39$ (C-1′), 22.39 (CH_2), 25.13 (CH_2), 25.48 (CH_2), 29.05 (CH_2), 110.22 (C-2), 125.07 (C-8), 133.12 (C-7), 148.42 (C-1); IR (film): $\tilde{\nu} = 3019$, 2930, 2857, 1643, 1446, 1251, 1205, 1177, 1165, 1151, 903, 886, 845 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 197 (5) [M^++1], 196 (26) [M^+], 195 (3), 182 (4), 181 (26), 169(4), 168 (21), 167 (34), 154 (3), 153 (4), 151 (6), 105 (3), 91 (9), 82 (4), 79 (5), 78 (4), 77 (10), 76 (4), 75 (44), 74 (9), 73 (100), 67 (3), 65 (3), 61 (4), 59 (6), 55 (4), 47 (4), 45 (16), 41 (3); GC-MS (CI): *m*/*z* (%): 199 (7) [MH$^+$+2], 198 (17) [MH$^+$+1], 197 (100) [MH$^+$], 196 (11) [M^+].

(1*Z*,8*Z*)-1,8-Cyclononadienyl trimethylsilyl ether: Silylation of 2-cyclononen-1-one (**1d**; 3.50 g, 25.4 mmol) according to GP G yielded a colorless liquid (3.70 g, 69 %). B.p. 65 °C at 2 mbar; NMR (^{1}H,^{13}C,^{13}C-gated): ^{1}H NMR (200 MHz, $CDCl_3$, ref.: $CHCl_3$): $\delta = 0.18$ (s, 9H, 1′-H), 1.32–1.71 (m, 6H), 1.96–2.35 (m, 4H), 4.96 (t, $J = 8.6$ Hz, H-2), 5.65–5.90(m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, ref.: $CDCl_3$): $\delta = 0.57$ (C-1′), 25.89 (CH_2), 26.95 (CH_2), 28.33 (CH_2), 29.97 (CH_2), 30.04 (CH_2), 110.90 (C-2), 125.47 (C-9), 135.32 (C-8), 147.87 (C-1); IR (film): $\tilde{\nu} = 3008$, 2925, 2853, 1650, 1634, 1454, 1406, 1251, 1207, 1172, 1157, 886, 844, 854 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 211 (2) [M^++1], 210 (11) [M^+], 195 (7), 181 (6), 169 (7), 168 (12), 167 (62), 157 (3), 156 (19), 155 (10), 154 (6), 151 (6), 127 (3), 91 (8), 79 (6), 77 (8), 76 (4), 75 (42), 74 (9), 73 (100), 67 (4), 61 (3), 59 (5), 55 (4), 47 (3), 45 (15), 43 (3), 41 (5), 39 (3); GC-MS (CI): *m*/*z* (%): 212 (2) [MH$^+$+1], 211 (12) [MH$^+$], 210 (5) [M^+], 209 (3) [$(M-1)^+$], 122 (10), 121 (100); HRMS: *m*/*z*: calcd for $C_{12}H_{22}OSi$: 210.1440, found: 210.1438 [M^+].

6,7-Dihydro-5*H*-benzo[*a*]cyclohepten-9-yltrimethylsilyl ether: Silylation of benzsuberon (**2**; 25.0 g, 156 mmol) according to GP G yielded a colorless liquid (31.5 g, 87 %). B.p. 73 °C at 0.5 mbar; NMR (^{1}H,^{13}C,^{13}C-gated); ^{1}H NMR (200 MHz, $CDCl_3$, ref.: $CHCl_3$): $\delta = 0.17$ (s, 9H, 1′-H), 1.83–2.08 (m, 4H, 6-H/7-H), 2.65 (t, $J = 6.3$ Hz, 2H, 5-H), 5.418 (t, $J = 6.6$ Hz, 1H, 8-H), 7.12–7.30 (m, 3H), 7.47 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, ref.: $CDCl_3$): $\delta = 0.24$ (C-1′), 23.84 (C-6), 33.03 (CH_2), 33.30 (CH_2), 109.39 (C-8), 125.77 (CH), 126.82 (CH), 127.46 (CH), 128.66 (CH), 138.18 (C-5a), 140.87 (C-9a), 149.50 (C-8)*, 140.35 (C-9)*; *: signal assignments are mutual interchangeable; IR (film): $\tilde{\nu} = 2935$, 2855, 1633, 1486, 1448, 1353, 1331, 1252, 1229, 1180, 1134, 1094, 1073, 889, 844, 770, 746 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 234 (3) [M^++2], 233 (13) [M^++1], 232 (61) [M^+], 231 (17), 219 (17), 218 (11), 217 (57), 215 (4), 205 (7), 204 (15), 203 (29), 201 (9), 189 (3), 185 (4), 143 (12), 142 (28), 141 (16), 131 (8), 130 (3), 129 (7), 128 (18), 127 (4), 116 (4), 115 (16), 101 (4), 91 (6), 89 (3), 77 (4), 76 (3), 75 (27), 74 (9), 73 (100), 59 (4), 45 (17), 43 (3); GC-MS (CI): *m*/*z* (%): 235 (5) [MH$^+$+2], 234 (21) [MH$^+$+1], 233 (100) [MH$^+$], 232 (10) [M^+], 231 (3) [$(M-1)^+$]; HRMS: *m*/*z*: calcd for $C_{14}H_{20}OSi$: 232.1283, found: 232.1283 [M^+].

6-(3-Butenyl)-1,6-cycloheptadienyltrimethylsilyl ether: Silylation of 3-(3-butenyl)-2-cyclohepten-1-one (**4a**; 3.65 g, 22.2 mmol) was carried out according to GP G. The title compound was isolated after kugelrohr distil-

lation as a colorless liquid (5.05 g, 96 %). NMR (^{1}H,^{13}C,^{13}C-DEPT); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9H, 1″-H), 1.81 (tt, J = 6.3/6.3 Hz, 2H, 4-H), 2.07 (dt, J = 5.8/6.1 Hz, 2H, 3-H), 2.11–2.20 (m, 6H, 5-H/1′-H/2′-H), 4.93 (tdd, J = 1.2/2.0/10.4/13.6 Hz, 1H, 4′-H), 5.00 (tdd, J = 1.6/2.0/17.0 Hz, 1H, 4′-H), 5.14 (dt, J = 1.7/5.8 Hz, 1H, 2-H), 5.44 (m, 1H, 7-H), 5.79 (tdd, J = 6.3/10.4/17.0 Hz, 1H, 3′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.22 (C-1″), 26.43 (CH_2), 28.31 (CH_2), 32.60 (CH_2), 33.63 (CH_2), 39.65 (CH_2), 111.38 (C-2), 114.66 (C-4′), 123.78 (C-7), 138.26 (C-3′), 145.88 (C-6), 147.94 (C-1); IR (film): $\tilde{\nu}$ = 2932, 1640, 1438, 1378, 1250, 1168, 1113 cm^{-1}; GC-MS (70 eV): m/z (%): 237 (6) [M^++1], 236 (30) [M^+], 235 (5), 221 (15), 208 (5), 207 (9), 195 (13), 194 (18), 193 (9), 182 (3), 181 (9), 180 (5), 179 (10), 168 (4), 167 (9), 165 (5), 131 (6), 117 (4), 106 (4), 105 (5), 104 (4), 91 (13), 79 (5), 77 (4), 75 (27), 74 (10), 73 (100), 61 (3), 59 (5), 55 (3), 47 (3), 45 (18), 41 (5).

(2*Z*)-Bicyclo[4.1.0]hept-2-en-1-yl trimethylsilyl ether (8a): Cyclopropanisation of 1,5-cyclohexadienyl trimethylsilyl ether (33.7 g, 200 mmol) was carried out according to GP H. Purification by spinning band column distillation yielded **8a** as a colorless liquid (27.7 g, 76 %). B.p. 76 °C at 10 mbar; NMR (^{1}H,^{1}H-COSY,^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 0.11 (s, 9H, 1′-H), 0.72 (dd, J = 5.3/6.2 Hz, 1H, 7-H), 0.94 (dd, J = 5.3/9.8 Hz, 1H, 7-H), 1.45 (ddddd, J = 1.6/2.0/4.0/6.2/9.8 Hz, 1H, 6-H), 1.51 (dddd, J = 2.0/2.4/6.2/12.7 Hz, 1H, 5-H), 1.57 (m, 1H, 4-H), 1.80 (m, 1H, 5-H), 1.93 (m, 1H, 4-H), 5.33 (dddd, J = 1.4/1.6/6.2/10.2 Hz, 1H, 3-H), 6.08 (ddd, J = 1.5/1.6/10.2 Hz, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 1.05 (C-1′), 17.42 (C-5), 17.74 (C-7), 20.21 (C-4), 22.98 (C-6), 53.85 (C-1), 121.20 (C-3), 133.42 (C-2); IR (film): $\tilde{\nu}$ = 3041, 3005, 2963, 2934, 2862, 1638, 1444, 1396, 1370, 1316, 1250, 1213, 1159, 1105, 1087, 1047, 1018, 1002, 977, 930, 863, 841, 753, 715 cm^{-1}; GC-MS (70 eV): m/z (%): 183 (3) [M^++1], 182 (16) [M^+], 181 (5), 168 (6), 167 (38), 165 (7), 154 (11), 153 (4), 152 (3), 151 (20), 149 (4), 91 (7), 77 (6), 76 (10), 75 (35), 74 (9), 73 (100), 65 (5), 61 (4), 59 (8), 55 (5), 53 (5), 51 (3), 47 (7), 45 (28), 44 (5), 43 (8), 41 (6), 39 (8), 29 (3), 28 (5), 27 (5); HRMS: m/z: calcd for $C_{10}H_{17}OSi$: 181.1049, found: 181.1036 [$(M-1)^+$].

(2*Z*)-Bicyclo[5.1.0]oct-2-en-1-yltrimethylsilyl ether (8b): Cyclopropanisation of 1,6-cycloheptadienyl trimethylsilyl ether (20.5 g, 112 mmol) according to GP H yielded **8b** as a colorless liquid (20.0 g, 91 %). B.p. 86 °C at 20 mbar; NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 0.10 (s, 9H, 1′-H), 0.39 (dd, J = 4.9/6.9 Hz, 1H, 8-H), 0.95 (dd, J = 4.9/9.9 Hz, 1H, 8-H), 1.26 (ddddd, J = 2.1/4.3/9.6/9.9/14.0 Hz, 1H, 4-H), 1.41–1.49 (m, 2H, 6-H/7-H), 1.64 (ddddd, J = 2.4/3.6/6.0/9.5/14.0 Hz, 1H, 5-H), 1.98 (m, 1H, 5-H), 2.06 (m, 1H, 4-H), 2.12 (m, 1H, 4-H), 5.37 (ddd, J = 4.2/6.9/11.3 Hz, 1H, 3-H), 5.85 (dm, J = 11.3 Hz, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 1.17 (C-1′), 22.07 (C-8), 23.99 (C-5), 28.28 (C-7), 28.44 (C-6), 30.29 (C-4), 59.00 (C-1), 126.75 (C-3), 132.58 (C-2); IR (film): $\tilde{\nu}$ = 2922, 1451, 1249, 1181, 1090, 984, 840, 753 cm^{-1}; GC-MS (70 eV): m/z (%): 197 (2) [M^++1], 196 (9) [M^+], 181 (9), 169 (3), 168 (10), 167 (49), 165 (3), 155 (2), 154 (7), 153 (2), 151 (5), 105 (3), 91 (6), 83 (2), 82 (2), 79 (4), 78 (3), 77 (7), 76 (3), 75 (29), 74 (8), 73 (100), 67 (3), 65 (2), 61 (2), 59 (5), 55 (3), 53 (2), 47 (3), 45 (16), 43 (2), 41 (3), 39 (3); GC-MS (CI): m/z (%): 197 (4) [MH$^+$], 196 (5) [M^+], 107 (100) [MH$^+$−Me$_3$SiOH]; HRMS: m/z: calcd for $C_{11}H_{19}OSi$: 195.1205, found: 195.1193 [$(M-1)^+$]; elemental analysis calcd (%) for $C_{11}H_{20}OSi$ (196.36): C 67.28, H 10.27; found: C 67.16, H 10.03.

(2*Z*)-Bicyclo[6.1.0]non-2-en-1-yl trimethylsilyl ether (8c): Cyclopropanisation of 1,7-cyclooctadienyl trimethylsilyl ether (4.20 g, 21.4 mmol) according to GP H yielded **8c** as a colorless liquid (3.56 g, 77 %). B.p. 64 °C at 4 mbar; NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-gated); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 0.05 (dd, J = 5.1/6.9 Hz, 1H, 9-H), 0.12 (s, 9H, 1′-H), 0.82 (dddd, J = 4.0/11.0/11.0/14.3 Hz, 1H, 7-H), 0.83 (dd, J = 5.1/10.0 Hz, 1H, 9-H), 1.05 (dddd, J = 3.3/6.9/10.0/11.4 Hz, 1H, 8-H), 1.38 (m, 1H, 5-H), 1.58–1.70 (m, 2H, 6-H), 1.87–1.98 (m, 3H, 4-H/5-H/7-H), 2.56 (m, 1H, 4-H), 5.59 (d, J = 10.5 Hz, 1H, 2-H), 5.74 (ddd, J = 5.0/7.4/10.7 Hz, 1H, 3-H); ^{13}C NMR (50 MHz, $CDCl_3$, ref.: TMS): δ = 1.56 (C-1′), 18.92 (C-9), 24.80 (CH_2), 27.32 (C-8), 29.15 (CH_2), 29.28 (CH_2), 30.08 (CH_2), 57.03 (C-1), 127.76 (C-3), 136.73 (C-2); GC-MS (70 eV): m/z (%): 211 (2) [M^++1], 210 (12) [M^+], 209 (4), 195 (4), 181 (7), 169 (6), 168 (11), 167 (47), 156 (7), 155 (7), 154 (6), 151 (4), 91 (7), 79 (5), 77 (6), 76 (4), 75 (33), 74 (9), 73 (100), 67 (3), 59 (5), 55 (4), 53 (3), 45 (14), 43 (4), 41 (5), 39 (3); GC-MS (CI): m/z (%): 212 (2) [MH$^+$+1], 211 (15) [MH$^+$/M^++1], 210 (5) [M^+], 209 (2) [$(M-1)^+$], 122 (100) [MH$^+$−Me$_3$SiOH+1], 121 (100) [MH$^+$−Me$_3$SiOH].

(2*Z*)-Bicyclo[7.1.0]dec-2-en-1-yl trimethylsilyl ether (8d): Cyclopropanisation of 1,8-cyclononadienyl trimethylsilyl ether (3.00 g, 14.3 mmol) was carried out according to GP H. Column chromatography on silica gel (Et$_2$O/*n*-pentane 1:200) yielded **8d** as a colorless liquid (1.81 g, 56 %). NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 0.07 (s, 9H, 1′-H), 0.08 (dd, J = 5.2/6.7 Hz, 1H, 10-H), 0.47 (dddd, J = 1.3/8.8/11.8/15.1 Hz, 1H, 8-H), 0.83 (dd, J = 5.2/10.1 Hz, 1H, 10-H), 1.07–1.22 (m, 3H, 6-H/7-H/9-H), 1.50 (m, 1H, 5-H), 1.62 (m, 1H, 5-H), 1.68–1.77 (m, 2H, 6-H/7-H), 1.99–2.11 (m, 2H, 4-H/8-H), 2.88 (m, 1H, 4-H), 5.61–5.68 (m, 2H, 2-H/3-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 1.27 (C-1′), 20.15 (C-10), 26.03 (C-7), 27.29 (C-4/C-5)*, 28.97 (C-6), 29.06 (C-9), 33.95 (C-8), 56.99 (C-1), 130.93 (C-2), 138.66 (C-3). *signal shows correlation signals with 4 protons in HMQC 2D experiment; IR (film): $\tilde{\nu}$ = 3008, 2956, 2923, 2854, 1455, 1248, 1202, 1164, 1089, 1042, 1018, 974, 944, 888, 840, 750, 701 cm^{-1}; GC-MS (70 eV): m/z (%): 224 (4) [M^+], 223 (2) [$(M-1)^+$], 209 (3), 195 (3), 182 (4), 181 (15), 171 (3), 170 (26), 169 (17), 168 (9), 167 (35), 156 (3), 155 (10), 154 (3), 151 (6), 142 (3), 127 (4), 93 (3), 92 (3), 91 (9), 81 (3), 79 (6), 77 (5), 76 (3), 75 (31), 74 (9), 73 (100), 67 (4), 59 (4), 55 (5), 53 (3), 47 (3), 45 (20), 43 (3), 41 (8), 39 (5); GC-MS (CI): m/z (%): 226 (2) [M+H$^+$+1], 225 (12) [M+H$^+$], 234 (2) [M^+], 223 (3) [$(M-1)^+$], 137 (4), 136 (11), 135 (100); HRMS: m/z: calcd for $C_{13}H_{24}OSi$: 223.1495, found: 223.1518 [$(M-1)^+$].

2-Trimethylsilyloxy-tricyclo[6.4.0.0^{2,4}]dodeca-1(8),9,11-triene (9): Cyclopropanisation of 6,7-dihydro-5*H*-benzo[*a*]cyclohepten-9-yltrimethylsilyl ether (14.6 g, 62.8 mmol) according to GP H yielded **9** as a colorless liquid (14.4 g, 93 %). B.p. 59 °C at 0.2 mbar; NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 0.04 (s, 9H, 1′-H), 0.11 (dddd, J = 6.5/12.1/12.3/14.2 Hz, 1H, 5-H), 0.51 (dd, J = 5.3/5.8 Hz, 1H, 3-H), 1.08 (dddd, J = 4.8/5.8/9.4/12.1 Hz, 1H, 4-H), 1.18 (dd, J = 5.3/9.4 Hz, 1H, 3-H), 1.49 (ddddd, J = 1.1/6.4/6.5/12.6/13.0 Hz, 1H, 6-H), 1.86 (ddddd, J = 1.4/5.9/7.2/12.3/13.0 Hz, 1H, 6-H), 1.94 (dddd, J = 1.1/4.8/5.9/14.2 Hz, 1H, 5-H), 2.55 (ddd, J = 1.4/6.4/13.0 Hz, 1H, 7-H), 3.36 (ddd, J = 7.2/12.6/13.0 Hz, 1H, 7-H), 7.08 (dd, J = 2.0/7.0 Hz, 1H, 9-H), 7.18 (dd, J = 2.0/7.0 Hz, 1H, 10-H)*, 7.20 (dd, J = 2.0/7.0 Hz, 1H, 11-H)*, 7.08 (dd, J = 2.0/7.0 Hz, 1H, 12-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 1.23 (C-1′), 19.71 (C-3), 21.64 (C-4), 24.71 (C-6), 26.88 (C-5), 30.38 (C-7), 59.53 (C-2), 126.18 (C-10), 128.27 (C-11), 128.64 (C-9), 130.11 (C-12), 139.39 (C-8)*, 140.35 (C-1)*; *: signal assignments are mutual interchangeable; IR (film): $\tilde{\nu}$ = 2934, 2858, 1451, 1249, 1219, 1206, 1190, 1112, 1088, 1042, 990, 931, 840, 752 cm^{-1}; GC-MS (70 eV): m/z (%): 247 (3) [M^++1], 246 (22) [M^+], 245 (3), 231 (12), 219 (5), 218 (10), 217 (41), 205 (10), 204 (22), 203 (20), 201 (3), 157 (4), 156 (7), 155 (4), 142 (3), 141 (12), 131 (4), 130 (3), 129 (9), 128 (12), 127 (3), 117 (3), 116 (3), 115 (13), 91 (8), 77 (3), 75 (24), 74 (10), 73 (100), 59 (4), 45 (20), 43 (3), 41 (3), 39 (3); GC-MS (CI): m/z (%): 248 (1) [MH$^+$+1], 247 (5) [MH$^+$], 246 (7) [M^+], 245 (3) [$(M-1)^+$], 159 (4), 158 (13), 157 (100); HRMS: m/z: calcd for $C_{15}H_{22}OSi$: 246.1440, found: 246.1439 [M^+]; elemental analysis calcd (%) for $C_{15}H_{22}OSi$ (246.42): C 73.11, H 9.00; found: C 73.41, H 8.96.

2-Trimethylsilyloxy-tricyclo[6.3.0.0^{2,4}]undec-1(8)-ene (10): Silylation of bicyclo[5.3.0]dec-1(7)-en-2-one (**3**; 3.24 g, 21.6 mmol) was carried out according to GP G. The crude product was purified by kugelrohr distillation and treated according to GP H. The cyclopropanisation product was purified by column chromatography (cyclohexane/ethyl acetate 98:2) yielding **10** (3.47 g, 68 %) as a colorless oil. NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 0.09 (s, 9H, 1′-H), 0.24 (dd, J = 4.8/6.8 Hz, 1H, 3-H), 0.92 (dd, J = 4.8/10.1 Hz, 1H, 3-H), 1.10 (dddd, J = 1.7/7.5/9.4/14.3 Hz, 1H, 5-H), 1.42 (dddd, J = 6.8/7.5/7.0/10.1 Hz, 1H, 4-H), 1.49 (ddddd, J = 1.6/5.1/5.4/8.9/14.2 Hz, 1H, 6-H), 1.66–1.81 (m, 3H, 6-H/10-H), 2.02 (ddddd, J = 1.3/2.6/5.1/10.0/17.7 Hz, 1H, 7-H), 2.14 (dddd, J = 1.9/6.9/8.9/14.3 Hz, 1H, 5-H), 2.14–2.30 (m, 3H, 7-H/11-H), 2.42 (m, 1H, 9-H), 2.67 (m, 1H, 9-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 1.06 (C-1′), 21.90 (C-10), 22.10 (C-3), 24.33 (C-6), 27.65 (C-4), 29.39 (C-5), 31.95 (C-7), 35.67 (C-9), 39.61 (C-11), 57.13 (C-2), 134.62 (C-8), 136.16 (C-1); IR (film): $\tilde{\nu}$ = 3078, 3000, 2931, 2844, 1671, 1449, 1369, 1346, 1324, 1305, 1260, 1248, 1182, 1137, 1121, 1096, 1079, 1054, 1020, 995, 943, 930, 842, 749, 688 cm^{-1}; GC-MS (70 eV): m/z (%): 237 (4) [M^++1], 236 (27) [M^+], 221 (12), 209

(8), 208 (25), 207 (79), 205 (6), 195 (4), 194 (23), 193 (6), 191 (7), 180 (5), 179 (3), 166 (10), 165 (3), 151 (3), 131 (8), 118 (4), 117 (7), 115 (5), 105 (7), 93 (6), 92 (3), 91 (16), 79 (9), 78 (4), 77 (9), 76 (3), 75 (33), 74 (10), 73 (100), 67 (4), 65 (4), 59 (7), 55 (4), 53 (5), 45 (20), 43 (3), 41 (13), 39 (6), 29 (4), 28 (3), 27 (4); GC-MS (CI): *m/z* (%): 237 (8) [MH$^+$+1], 236 (8) [M^+], 235 (6) [M^+−H], 149 (4), 148 (13), 147 (100); HRMS: *m/z*: calcd for $C_{14}H_{24}OSi$: 236.1596, found: 236.1596 [M^+].

3-(3-Butenyl)bicyclo[5.1.0]oct-2-en-1-yltrimethylsilyl ether (11a): Cyclopropanisation of 6-(3-butenyl)-1,6-cycloheptadienyltrimethylsilyl ether (4.63 g, 19.6 mmol) was carried out according to GP H. Column chromatography on silica gel (cyclohexane/ethyl acetate 99:1) yielded **11a** as a colorless oil (3.83 g, 78%). NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.09 (s, 9H, 1″-H), 0.24 (dd, J = 4.9/6.6 Hz, 1H, 8-H), 0.88 (dd, J = 4.9/9.9 Hz, 1H, 8-H), 1.00 (dddd, J = 4.7/8.0/9.7/14.2 Hz, 1H, 6-H), 1.19 (ddddd, J = 1.6/5.0/6.6/8.0/9.9 Hz, 1H, 7-H), 1.26 (ddddd, J = 4.7/4.8/6.5/11.3/13.6 Hz, 1H, 5-H), 1.63 (ddddd, J = 4.7/4.7/5.4/9.7/13.6 Hz, 1H, 5-H), 1.91 (ddd, J = 4.7/4.8/14.9 Hz, 1H, 4-H),1.96 (dddd, J = 4.7/5.0/6.5/14.2 Hz, 1H, 6-H), 1.99–2.05 (m, 2H, 1′-H), 2.06–2.19 (m, 2H, 2′-H), 2.42 (dddd, J = 2.1/5.4/11.3/14.9 Hz, 1H, 4-H), 4.92 (dddd, J = 1.2/1.2/2.0/10.3 Hz, 1H, 4′-H), 4.99 (dddd, J = 1.7/1.7/2.0/17.0 Hz, 1H, 4′-H), 5.63 (dddd, J = 1.6/1.6/1.6/2.1 Hz, 1H, 2-H), 5.77 (dddd, J = 6.5/6.5/10.3/17.0 Hz, 1H, 3′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.31 (C-1″), 20.92 (C-8), 22.57 (C-5), 25.07 (C-7), 28.33 (C-6), 30.99 (C-4), 32.11 (C-1′), 38.67 (C-2′), 57.45 (C-1), 114.53 (C-4′), 125.62 (C-2), 138.42 (C-3′), 140.27 (C-3); IR (film): $\tilde{\nu}$ = 3081, 2935, 2864, 1641, 1452, 1251, 1218, 1187, 1091, 1050, 1000, 926, 846, 751 cm^{-1}; GC-MS (70 eV): *m/z* (%): 250 (6) [M^+], 235 (7), 222 (4), 221 (24), 209 (8), 208 (11), 207 (4), 195 (19), 194 (3), 193 (10), 181 (12), 180 (4), 179 (5), 167 (6), 119 (4), 117 (3), 105 (5), 91 (10), 79 (4), 75 (18), 74 (8), 73 (100), 59 (3), 55 (4), 45 (17), 41 (5); GC-MS (CI): *m/z* (%): 252 (2) [MH$^+$+1], 251(10) [MH$^+$], 250(11) [M^+], 249(3) [M^+−H], 162 (13), 161 (100), 133 (7), 119 (5); elemental analysis calcd (%) for $C_{15}H_{26}OSi$ (250.45): C 71.93, H 10.46; found: C 71.80, H 10.22.

3-(3-Butynyl)bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ether (12a): Silylation of 3-(2-butynyl)-2-cyclohepten-1-one (2.17 g, 13.4 mmol) was carried out according to GP G. The crude product was purified by kugelrohr distillation and treated according to GP H. The cyclopropanisation product was purified by column chromatography (cyclohexane/ethyl acetate 99:1) yielding **12a** as a colorless oil (2.39 g, 72%). NMR (^{1}H,^{1}H-COSY, ^{13}C-APT, HMQC, HMBC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.09 (s, 9H, 1″-H), 0.26 (dd, J = 4.9/6.7 Hz, 1H, 8-H), 0.89 (dd, J = 4.9/9.9 Hz, 1H, 8-H), 1.04 (dddd, J = 4.6/8.0/9.7/14.2 Hz, 1H, 6-H), 1.20 (ddddd, J = 1.3/4.8/6.7/8.0/9.9 Hz, 1H, 7-H), 1.27 (ddddd, J = 4.5/4.6/6.5/11.3/13.7 Hz, 1H, 5-H), 1.63 (ddddd, J = 4.6/4.7/5.4/9.7/13.7 Hz, 1H, 5-H), 1.91 (ddd, J = 4.5/4.7/14.8 Hz, 1H, 4-H), 1.91 (dd, J = 2.6/2.6 Hz, 1H, 4′-H), 1.96 (dddd, J = 4.6/4.8/6.5/14.2 Hz, 1H, 6-H), 2.14–2.29 (m, 4H, 1′-H; 2′-H), 2.42 (dddd, J = 2.1/5.4/11.3/14.8 Hz, 1H, 4-H), 5.63 (dd, J = 1.3/2.1 Hz, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.29 (C-1″), 17.29 (C-2′), 20.93 (C-8), 22.57 (C-5), 25.13 (C-7), 28.21 (C-6), 30.85 (C-4), 38.00 (C-1′), 57.32 (C-1), 68.62 (C-4′), 83.94 (C-3′), 126.64 (C-2), 138.74 (C-3); IR (film): $\tilde{\nu}$ = 3317, 3077, 2934, 2865, 2122, 1450, 1249, 1218, 1186, 1088, 1050, 995, 927, 840, 754, 628 cm^{-1}; GC-MS (70 eV): *m/z* (%): 248 (0.41) [M^+], 233 (3), 219 (6), 206 (3), 195 (5), 143 (4), 129 (4), 105 (3), 91 (7), 79 (4), 77 (7), 75 (18), 74 (9), 73 (100), 59 (36), 45 (15), 43 (3), 41 (4), 39 (4); GC-MS (CI): *m/z* (%): 250 (2) [MH$^+$+1], 249 (6) [MH$^+$], 248 (5) [M^+], 247 (3) [(M−1)$^+$], 160 (13), 159 (100), 131 (11), 117 (14); HRMS: *m/z*: calcd for $C_{15}H_{23}OSi$: 247.1518, found: 247.1510 [(M−1)$^+$].

3-(2-Cyclohexenylmethyl)bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ether (13a): Silylation of 3-(2-cyclohexenylmethyl)-2-cyclohepten-1-one (950 mg, 4.65 mmol) was carried out according to GP G. The crude product was purified by kugelrohr distillation and treated according to GP H. The cyclopropanisation product was purified by column chromatography (cyclohexane/ethyl acetate 99:1) yielding of **13a** (640 mg, 47%) as a colorless oil. NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.097/0.099 (s, 9H, 1‴-H), 0.24–0.28 (m, 1H, 8-H), 0.86–0.91 (m, 1H, 8-H), 0.97–1.08 (m, 1H, 6-H), 1.12–1.30 (m, 3H, 5-H/7-H/6″-H), 1.42–1.54 (m, 1H, 5″-H), 1.58–1.74 (m, 3H, 5-H/5″-H/6″-H), 1.84–2.01 (m, 6H, 4-H/6-H/1′-H/4″-H), 2.36–2.45 (m, 1H, 4-H), 2.14–2.23 (m, 1H, 1″-H), 5.46–5.55 (m, 1H, 2″-H), 5.5871/5.570 (s, 1H, 2-H), 5.61–5.67 (m, 1H, 3″-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.29 (C-1‴), 21.00/21.06 (C-8), 21.24/21.36 (C-5″), 22.53/22.69 (C-5), 25.05/25.24 (C-7), 25.29/25.31 (C-4″), 28.41/28.44 (C-6), 28.99/29.28 (C-6″), 30.55/30.90 (C-4), 33.21 (C-1″), 46.19/46.24 (C-1′), 57.53/57.58 (C-1), 127.01/127.02 (C-3″)*, 127.11/127.14 (C-2)*, 131.48/131.76 (C-2″), 139.09/139.20 (C-3); *: signal assignments are mutual interchangeable; IR (film): $\tilde{\nu}$ = 3075, 3021, 2932, 2863, 1745, 1648, 1450, 1379, 1309, 1249, 1219, 1184, 1127, 1090, 1050, 1000, 973, 944, 926, 840, 750, 720 cm^{-1}; GC-MS (70 eV): *m/z* (%): 291 (2) [M^++1], 291 (7) [M^+], 262 (3), 261 (13), 248 (5), 247 (4), 211 (5), 210 (28), 209 (21), 196 (6), 195 (29), 182 (6), 181 (29), 169 (4), 168 (19), 167 (10), 119 (6), 117 (3), 105 (4), 91 (9), 80 (3), 79 (16), 77 (4), 75 (17), 74 (8), 73 (100), 53 (5), 45 (8), 41 (6); GC-MS (CI): *m/z* (%): 292 (2) [MH$^+$+1], 291(8) [MH$^+$/M^++1], 290 (5) [M^+], 289 (3) [M^+−H], 203 (6), 202 (18), 201 (100); HRMS: *m/z*: calcd for $C_{18}H_{30}OSi$: 290.2066, found: 290.2056 [M^+].

3-(3-Butenyl)bicyclo[6.1.0]non-2-en-1-yl trimethylsilyl ether (11b): Silylation of 3-(3-butenyl)-2-cycloocten-1-one (**4b**; 1.70 g, 4.65 mmol) was carried out according to GP G. The crude product was purified by kugelrohr distillation and treated according to GP H. The cyclopropanisation product was purified by column chromatography (cyclohexane/ethyl acetate 99:1) yielding **11b** (1.41 g, 56%) as a colorless oil. NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.03 (dd, J = 5.0/6.8 Hz, 1H, 9-H), 0.08 (s, 9H, 1″-H), 0.71 (dddd, J = 1.9/11.4/11.6/14.0 Hz, 1H, 7-H), 0.78 (dd, J = 5.0/10.1 Hz, 1H, 9-H), 1.062 (dddd, J = 3.2/6.8/10.1/10.6 Hz, 1H, 8-H), 1.29 (m, 1H, 5-H), 1.58 (m, 1H, 6-H), 1.670 (m, 1H, 6-H), 1.77–1.90 (m, 3H, 4-H/5-H/7-H), 2.015–2.255 (m, 4H, 1′-H/2′-H), 2.72 (m, 1H, 4-H), 4.94 (dddd, J = 1.4/1.4/1.9/10.2 Hz, 1H, 4′-H), 5.01 (dddd, J = 1.6/1.6/1.9/17.1 Hz, 1H, 4′-H), 5.39 (m, 1H, 2-H), 5.81 (dddd, J = 6.6/6.6/10.2/17.1 Hz, 1H, 3′-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.52 (C-1″), 18.75 (C-9), 25.91 (C-5), 28.46 (C-8), 29.66 (C-7), 30.17 (C-6), 31.25 (C-4), 32.16 (C-2′), 36.35 (C-1′), 57.57 (C-1), 114.48 (C-4′), 123.69 (C-2), 138.55 (C-3′), 148.48 (C-3); IR (film): $\tilde{\nu}$ = 3080, 2926, 2856, 1658, 1641, 1448, 1383, 1317, 1295, 1249, 1204, 1188, 1159, 1095, 1079, 1020, 995, 976, 952, 910, 894, 844, 752, 709, 687 cm^{-1}; GC-MS (70 eV): *m/z* (%): 264 (2) [M^+], 223 (8), 222 (6), 221 (24), 211 (3), 210 (10), 209 (52), 208 (5), 207 (4), 193 (5), 181 (6), 180 (4), 179 (5), 167 (7), 156 (5), 155 (3), 133 (3), 131 (3), 119 (3), 117 (3), 105 (4), 93 (3), 91 (12), 79 (6), 77 (4), 75 (20), 74 (9), 73 (100), 67 (4), 59 (3), 55 (4), 45 (9), 41 (7), 39 (3); GC-MS (CI): *m/z* (%): 266 (3) [MH$^+$+1], 265 (10) [MH$^+$/M^++1], 264 (4) [M^+], 176 (16), 175 (100); HRMS: *m/z*: calcd for $C_{16}H_{28}OSi$: 264.1909, found: 264.1890 [M^+]; elemental analysis calcd (%) for $C_{16}H_{28}OSi$ (264.48): C 72.66, H 10.67; found: C 71.61, H 10.52.

3-(3-Butynyl)bicyclo[6.1.0]non-2-en-1-yl trimethylsilyl ether (12b): Silylation of 3-(3-butynyl)-2-cycloocten-1-one (**5b**; 1.95 g, 13.4 mmol) was carried out according to GP G. The crude product was purified by kugelrohr distillation and treated according to procedure H. The cyclopropanisation product was purified by column chromatography (cyclohexane/ethyl acetate 99:1) yielding **12b** (1.21 g, 41%) as a colorless oil. NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.05 (dd, J = 5.1/6.8 Hz, 1H, 9-H), 0.07 (s, 9H, 1″-H), 0.72 (dddd, J = 1.9/11.4/11.5/14.3 Hz, 1H, 7-H), 0.79 (dd, J = 5.1/10.1 Hz, 1H, 9-H), 1.062 (ddddd, J = 0.7/3.3/6.8/10.2/11.4 Hz, 1H, 8-H), 1.29 (m, 1H, 5-H), 1.59 (m, 1H, 6-H), 1.68 (m, 1H, 6-H), 1.77–1.90 (m, 3H, 4-H/5-H/7-H), 1.93 (dd, J = 2.5/2.5 Hz, 1H, 4′-H), 2.17–2.37 (m, 4H, 1′-H/2′-H), 2.72 (m, 1H, 4-H), 5.41 (m, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.52 (C-1″), 17.32 (C-2′), 18.72 (C-9), 25.84 (C-5), 28.42 (C-8), 29.57 (C-7), 30.16 (C-6), 31.15 (C-4), 36.85 (C-1′), 57.41 (C-1), 68.62 (C-4′), 84.20 (C-3′), 124.44 (C-2), 147.15 (C-3); IR (film): $\tilde{\nu}$ = 3316, 3074, 2995, 2927, 2857, 2122, 1661, 1445, 1383, 1316, 1294, 1249, 10204, 1189, 1157, 1139, 1094, 1079, 1047, 1021, 978, 951, 893, 840, 753 cm^{-1}; GC-MS (70 eV): *m/z* (%): 262 (1) [M^+], 261 (1) [(M−1)$^+$], 247 (3), 233 (4), 223 (3), 221 (4), 220 (5), 219 (21), 210 (8), 209 (39), 207 (3), 206 (4), 205 (9), 181 (3), 179 (4), 167 (4), 165 (3), 157 (3), 156 (6), 155 (3), 143 (3), 131 (3), 129 (5), 117 (3), 115 (3), 105 (4), 91 (11), 79 (5), 77 (6), 75 (20), 74 (9), 73 (100), 67 (3), 59 (3), 55 (3), 45 (11), 41 (4), 39 (4); GC-MS (CI): *m/z* (%): 264 (5) [MH$^+$+1], 263 (19) [MH$^+$/M^++1], 262 (4) [M^+], 174 (13), 173 (100); HRMS: *m/z*: calcd for $C_{16}H_{25}OSi$: 261.1675, found: 261.1659 [(M−1)$^+$]; elemental analysis calcd (%) for $C_{16}H_{26}OSi$ (262.46): C 73.22, H 9.98; found: C 70.85, H 10.60.

3-(2-Cyclohexenylmethyl)bicyclo[6.1.0]non-2-en-1-yl trimethylsilyl ether (13b): Silylation of 3-(2-cyclohexenylmethyl)-2-cycloocten-1-one (**6b**; 1.48 g, 6.77 mmol) was carried out according to GP G. The crude product was purified by kugelrohr distillation and treated according to GP H.

The cyclopropanisation product was purified by column chromatography (cyclohexane/ethyl acetate 99:1) yielding **13b** (1.10 g, 53%) as a colorless oil. NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.01–0.07 (m, 1H, 9-H), 0.084/0.086 (s, 9H, 1‴-H), 0.68–0.77 (m, 1H, 7-H), 0.78–0.83 (m, 1H, 9-H), 1.03–1.10 (m, 8-H), 1.13–1.25 (m, 1H, 6″-H), 1.25–1.34 (m, 1H, 5-H), 1.45–1.77 (m, 5H), 1.77–2.09 (m, 7H), 2.21–2.34 (m, 1H, 1″-H), 2.62–2.72 (m, 1H, 4-H), 5.366/5.378 (s, 1H, 2-H), 5.51–5.59 (m, 1H, 2″-H), 5.62–5.69 (m, 1H, 3″-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.52 (C-1‴), 18.73/18.83 (C-9), 21.12/21.50 (C-5″), 25.33/25.34 (C-4″), 25.56/25.72 (C-5), 28.43/28.52 (C-8), 28.87/29.60 (C-6″), 29.69/29.73 (C-7), 30.17/30.20 (C-6), 30.90/31.44 (C-4), 33.18/33.29 (C-1″), 43.97/44.18 (C-1′), 57.65 (C-1), 125.10/125.30 (C-2), 126.87/127.11 (C-3″), 131.54/131.89 (C-2″), 146.89/147.04 (C-3); IR (film): $\tilde{\nu}$ = 3072, 3022, 2926, 2857, 1656, 1446, 1314, 1293, 1248, 1204, 1188, 1095, 1079, 1017, 953, 893, 839, 752, 720 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 304 (5) [M^+], 223 (14), 222 (5), 221 (9), 210 (10), 209 (25), 208 (5), 207 (9), 181 (12), 168 (8), 167 (13), 155 (8), 134 (5), 133 (8), 131 (8), 129 (4), 117 (7), 115 (4), 91 (11), 81 (21), 80 (5), 79 (25), 77 (5), 75 (25), 74 (8), 73 (100), 67 (7), 59 (5), 55 (5), 53 (5), 45 (8), 41 (8), 39 (10); GC-MS (CI): *m*/*z* (%): 306 (30) [MH^++1], 305 (100) [MH^+]; HRMS: *m*/*z*: calcd for $C_{19}H_{32}OSi$: 304.2222, found: 304.2211 [M^+].

4-(2-Propenyl)bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ether (14a,b): Silylation of 4-(2-propenyl)-2-cyclohepten-1-one (**7**; 650 mg, 4.33 mmol) was carried out according to GP G. The crude product was purified by kugelrohr distillation and treated according to procedure H. The cyclopropanisation product was purified by HPLC (cyclohexane/ethyl acetate 130:1) yielding a mixture of the isomeric 4-(2-propenyl)bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ethers (**14a**,**b**) as a colorless oil (480 mg, 47%). For identification and for mechanistic reasons the isomers were separated by preparative gas chromatography.

(1*S,4*R**,7*S**)-4-(2-Propenyl)bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ether (14a)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 0.10 (s, 9H, 1″-H), 0.36 (dd, *J* = 4.9/7.1 Hz, 1H, 8-H^A), 0.93 (dd, *J* = 4.9/10.2 Hz, 1H, 8-H^B), 0.96 (dddd, *J* = 3.5/9.4/10.6/13.9 Hz, 1H, 5-H^B), 1.37 (m, 1H, 7-H), 1.46 (dddd, *J* = 3.5/6.0/8.0/14.0 Hz, 1H, 6-H^A), 1.59 (dddd, *J* = 3.6/3.8/7.4/13.9 Hz, 1H, 5-H^A), 1.91 (dddd, *J* = 3.8/4.0/9.7/14.0 Hz, 1H, 6-H^B), 2.02–2.13 (m, 2H, 1′-H), 2.29 (m, 1H, 4-H), 4.99 (dm, *J* = 10.2 Hz, 3′-H^A), 5.002 (dm, *J* = 17.0 Hz, 3′-H^B), 5.26 (ddd, *J* = 0.9/3.8/11.2 Hz, 1H, 3-H), 5.75 (dddd, *J* = 6.9/6.9/10.2/17.0 Hz, 1H, 2′-H), 5.83 (ddd, *J* = 1.4/2.6/11.2 Hz, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 1.16 (C-1″), 21.17 (C-8), 27.12 (C-6), 27.13 (C-7), 29.28 (C-5), 38.69 (C-4), 41.25 (C-1′), 58.62 (C-1), 116.12 (C-3′), 131.45 (C-2), 132.47 (C-3), 136.98 (C-2′); **IR** (film): $\tilde{\nu}$ = 3081, 3014, 2962, 2853, 1656, 1640, 1441, 1415, 1378, 1250, 1190, 1125, 1095, 1015, 991, 955, 912, 840, 750 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 236 (1) [M^+], 235 (<1) [$(M-1)^+$], 221 (5), 207 (6), 195 (7), 194 (8), 193 (6), 182 (3), 181 (4), 180 (4), 179 (5), 168 (7), 167 (27), 154 (3), 151 (3), 105 (3), 91 (4), 79 (4), 77 (5), 75 (18), 74 (9), 73 (100), 59 (3), 45 (7), 41 (3); GC-MS (CI): *m*/*z* (%): 237 (9) [MH^+], 236 (8) [M^+], 149 (4), 148 (13), 147 (100); HRMS: *m*/*z*: calcd for $C_{14}H_{23}OSi$: 235.1518, found: 235.1513 [$(M-1)^+$].

(1*S,4*S**,7*S**)-4-(2-Propenyl)bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ether (14b)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 0.12 (s, 9H, 1″-H), 0.39 (dd, *J* = 4.8/6.8 Hz, 1H, 8-H^A), 0.95 (dd, *J* = 4.8/10.1 Hz, 1H, 8-H^B), 1.09 (dddd, *J* = 3.0/7.1/7.6/14.9 Hz, 1H, 6-H^A), 1.44 (ddddd, *J* = 1.6/6.8/6.9/7.1/10.1 Hz, 1H, 7-H), 1.55–1.67 (m, 2H, 5-H), 2.06–2.21 (m, 3H, 4-H/1′-H), 2.25 (dddd, *J* = 2.2/6.4/8.7/14.7 Hz, 1H, 6-H^B), 4.99 (dm, *J* = 10.1 Hz, 3′-H^A), 5.02 (dm, *J* = 17.1 Hz, 3′-H^B), 5.23 (dd, *J* = 4.4/12.1 Hz, 1H, 3-H), 5.76 (dddd, *J* = 7.0/7.0/10.1/17.1 Hz, 1H, 2′-H), 5.84 (ddd, *J* = 2.6/1.6/12.3 Hz, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 1.48 (C-1″), 23.91 (C-8), 26.65 (C-6), 27.95 (C-7), 30.10 (C-5), 40.03 (C-1′), 42.19 (C-4), 58.02 (C-1), 116.03 (C-3′), 129.88 (C-3), 131.01 (C-2), 137.15 (C-2′); IR (film): $\tilde{\nu}$ = 3081, 3004, 2962, 2861, 1658, 1640, 1451, 1413, 1379, 1250, 1182, 993, 912, 840, 751 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 236 (2) [M^+], 235 (3) [$(M-1)^+$], 221 (5), 207 (5), 195 (9), 194 (7), 193 (7), 182 (3), 181 (4), 180 (4), 179 (5), 168 (6), 167 (21), 154 (3), 151 (3), 105 (4), 91 (4), 79 (4), 77 (5), 75 (18), 74 (9), 73 (100), 59 (3), 45 (7), 41 (3); GC-MS (CI): *m*/*z* (%): 237 (9) [MH^+], 236 (6) [M^+], 149 (4), 148 (13), 147 (100); HRMS: *m*/*z*: calcd for $C_{14}H_{23}OSi$: 235.1518, found: 235.1523 [$(M-1)^+$].

General procedure I (PET oxidative reaction): The respective cyclopropylsilyl ether and sensitizer (10–40 mol%) were dissolved in dry acetonitrile. The solution was either poured into an immersion well reactor or apportioned to pyrex irradiation tubes (12 mL, 1 cm diameter). Note, that DCA is only slightly soluble in acetonitrile leading to a suspension of the sensitizer at the beginning of the irradiation. The tubes or the reactor were sealed with a septum. The solution was deoxygenated with argon and ultrasound irradiation (1 h: pyrex tubes/3 h: immersion well reactor) and irradiated in a Rayonet photochemical reactor using lamps of the appropriate wavelength (DCN: 350 nm/DCA: 420 nm) for at least 24 h. The reaction was monitored by GC. The solvent was removed and the residue was purified (generally by column chromatography and/or HPLC).

PET oxidative reaction of bicyclo[4.1.0]hept-2-en-1-yl trimethylsilyl ether (8a): Bicyclo[4.1.0]hept-2-en-1-yl trimethylsilyl ether (**8a**; 993 mg, 5.45 mmol) and DCN (422 mg, 2.37 mmol) were dissolved in acetonitrile (215 mL), apportioned to 12 pyrex tubes and irradiated according to GP I for 48 h. The crude product was purified by kugelrohr distillation yielding 6-methylcyclohex-2-enone (**27**; 91 mg, 15%). NMR (^{1}H, ^{13}C,^{13}C-DEPT); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 1.09 (d, *J* = 6.8 Hz, 3H, 1′-H), 1.68 (dddd, *J* = 6.7/8.4/11.9/13.4 Hz, 1H, 5-H), 2.02 (ddddd, *J* = 1.2/4.4/4.5/4.6/13.4 Hz, 1H, 5-H), 2.30–2.39 (m, 3H, 4-H/6-H), 5.928 (ddd, *J* = 2.0/2.0/10.0 Hz, 1H, 2-H), 6.88 (dddd, *J* = 1.2/3.3/4.6/10.0 Hz, 1H, 3-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 14.80 (C-1′), 25.27 (C-5), 30.57 (C-4), 41.35 (C-6), 129.03 (C-2), 149.71 (C-3), 202.23 (C-1); IR (film): $\tilde{\nu}$ = 2936, 2877, 1678, 1455, 1427, 1389, 1376, 1215, 1130, 1056, 951, 801 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 110 (17) [M^+], 68 (100), 41 (15), 40 (20), 39 (43), 27 (15).

PET oxidative reaction of bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ether (8b): Bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ether (**8b**; 1.31 g, 6.68 mmol) and DCN (422 mg, 2.37 mmol) were dissolved in acetonitrile (400 mL) and irradiated in an immersion well reactor according to GP I for 72 h. The crude product was filtered over silica (cyclohexane/ethyl acetate 80:20) and purified by HPLC (cyclohexane/ethyl acetate 85:15) yielding (3a*R**, 6a*S**)-hexahydro-2(1*H*)pentalenone (**28**; 489 mg, 57%). NMR (^{1}H,^{13}C,^{13}C-gated); ^{1}H NMR (300 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 1.26–1.40 (m, 2H), 1.48–1.77 (m, 2H), 1.80–2.02 (m, 4H), 2.33–2.49 (m, 2H), 2.55–2.71 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ref.: TMS): δ = 25.19 (C-5), 33.13 (C-4/6), 39.31 (C-3a/6a), 44.39 (C-1/3), 220.88 (C-2). *The stereochemical assignment was carried out by direct comparison with the original spectra of the *cis*-compound: IR (film): $\tilde{\nu}$ = 2935, 2842, 1725, 1440 cm^{-1}; GC-MS (CI): *m*/*z* (%): 126 (9) [MH^++1] 125 (100) [MH^+].

PET oxidative reaction of bicyclo[6.1.0]non-2-en-1-yl trimethylsilyl ether (8c): Bicyclo[6.1.0]non-2-en-1-yl trimethylsilyl ether (**8c**; 1.20 g, 5.70 mmol) and DCN (500 mg, 2.81 mmol) were dissolved in acetonitrile (400 mL) and irradiated in an immersion well reactor according to GP I for 90 h. The crude product was first prepurified by kugelrohr distillation and secondly by HPLC (cyclohexane/ethyl acetate 90:10) yielding (3a*R**,7a*S**)-octahydro-2*H*-inden-2-one (**29**; 385 mg, 49%) as a colorless oil. NMR (^{1}H,^{13}C,^{13}C-gated); ^{1}H NMR (300 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 1.33–1.68 (m, 8H), 2.05–2.35 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, ref.: TMS): δ = 22.39 (C-5/6), 27.37 (C-4/7), 35.46 (C-3a/7a), 43.23 (C-1/3), 220.35 (C-2); IR (film): $\tilde{\nu}$ = 2930, 2857, 1744, 1462, 1449, 1405, 1366, 1235, 1161, 1140, 1119, 1073, 916, 732 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 139 (8) [M^++1], 138 (63) [M^+], 120 (4), 110 (4), 109 (9), 96 (14), 95 (39), 94 (95), 93 (3), 92 (3), 91 (5), 83 (4), 82 (37), 81 (100), 80 (9), 79 (31), 78 (4), 77 (16), 70 (4), 68 (11), 68 (52), 67 (97), 66 (12), 65 (15), 57 (6), 56 (8), 55 (36), 54 (48), 53 (43), 52 (5), 51 (6), 43 (9), 42 (12), 41 (86), 40 (12), 39 (53), 29 (23), 28 (12), 27 (30); GC-MS (CI): *m*/*z* (%): 140 (1) [MH^++2], 139 (10) [MH^++1] 138 (100) [MH^+]. *The stereochemical assignment was carried out by direct comparison with the original spectra of the analogous *trans*-compound.

PET oxidative reaction of bicyclo[7.1.0]dec-2-en-1-yl trimethylsilyl ether (8d): Bicyclo[7.1.0]dec-2-en-1-yl trimethylsilyl ether (**8d**; 1.01 g, 4.50 mmol) and DCN (300 mg, 1.69 mmol) were dissolved in acetonitrile (192 mL), apportioned to 12 pyrex tubes and irradiated according to GP I for 48 h. The crude product was purified by kugelrohr distillation yielding 6-methlycyclohex-2-enone (**27**; 91 mg, 15%). The crude product was filtered over silica gel (cyclohexane/ethyl acetate 80:20) and purified by stepwise HPLC (cyclohexane/ethyl acetate prepurification: 90:10; fine purification 95:5) yielding (*Z*)-3-cyclodecen-1-one (**30**; 67 mg, 10%) as

the major product. The corresponding *E* isomer was detectable in ^{1}H NMR of the crude product mixture but had not been isolated as pure product.

(*Z*)-3-Cyclodecen-1-one (30): NMR (^{1}H, ^{13}C,^{13}C-DEPT); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: TMS): $\delta = 1.33$ (m, 2H), 1.39 (m, 2H), 1.46 (m, 2H), 1.688 (m, 2H), 2.16 (m, 2H, 5-H), 2.49 (m, 2H, 10-H), 3.14 (dd, $J =$ 1.2/8.3 Hz, 1H, 2-H), 5.60 (ttd, $J = 1.2/8.3/10.8$ Hz, 3-H)*, 5.77 (ttd, $J =$ 1.2/8.3/10.8 Hz, 4-H)*; ^{13}C NMR (125 MHz, $CDCl_3$, ref.: TMS): $\delta = 22.54$ (CH_2), 23.66 (CH_2), 24.55 (CH_2), 25.26 (CH_2), 26.37 (CH_2), 39.04 (C-5), 43.24 (C-2), 123.79 (C-3)*, 133.81 (C-4)*, 214.42 (C-1); *: signal assignments are mutual interchangeable.

PET oxidative reaction of 2-trimethylsilyloxy-tricyclo[6.3.0.0^{2,4}]undec-1(8)-ene (10): Compound **10** (370 mg, 1.57 mmol) was dissolved in acetonitrile (243 mL), apportioned together with DCA (119 mg, 0.52 mmol; 7 mg each tube) to 17 pyrex tubes and irradiated according to GP I for 48 h. The crude product was purified by column chromatography on silica (cyclohexane/ethyl acetate 925:75) yielding (3a*S**,5a*R**,8a*S**)-3-octahydrocyclopenta[*c*]pentalen-4(5*H*)-one (**31**; 170 mg, 66%). NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): $\delta = 1.35$ (m, 1H, 2-H), 1.37 (m. 1H, 6-H^B), 1.58 (m, 1H, 1-H), 1.61 (m, 1H, 2-H), 1.62 (m, 1H, 7-H), 1.64 (m, 1H, 8-H), 1.65 (m, 1H, 7-H), 1.69 (m, 1H, 1-H), 1.73 (m, 1H, 8-H), 1.79–1.87 (m, 2H, 3-H), 1.93 (m, 1H, 6-H^A), 2.08 (ddd, $J = 1.8/6.0/18.3$ Hz, 1H, 5-H^B), 2.16 (dddd, $J =$ 4.4/6.0/8.4/9.0 Hz, 1H, 5a-H), 2.23 (ddd, $J = 1.8/6.3/6.9$ Hz, 1H, 3a-H), 2.49 (dd, $J = 9.0/18.3$ Hz, 1H, 5-H^A); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): $\delta = 25.70$ (C-7), 26.76 (C-2), 30.81 (C-3), 34.41 (C-6), 40.75 (C-8), 41.92 (C-1), 44.74 (C-5a), 46.40 (C-5), 58.55 (C-8a), 59.43 (C-3a), 223.70 (C-4); IR (film): $\tilde{\nu} = 2945$, 2868, 1738, 1469, 1449, 1409, 1314, 1267, 1211, 1163, 1113, 1040, 946, 924, 907, 775 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 165 (3) [M^++1], 164 (31) [M^+], 146 (7), 136 (25), 135 (5), 123 (34), 122 (31), 121 (56), 120 (12), 119 (4), 117 (3), 108 (14), 107 (18), 105 (7), 104 (4), 96 (11), 95 (25), 94 (41), 93 (43), 92 (6), 91 (33), 83 (3), 82 (16), 81 (34), 80 (47), 79 (100), 78 (10), 77 (50), 76 (5), 68 (16), 67 (86), 66 (14), 65 (23), 55 (37), 54 (15), 53 (26), 52 (5), 51 (6), 42 (6), 41 (58), 40 (9), 39 (32), 29 (14), 27 (16); GC-MS (CI): *m*/*z* (%): 165 (100) [MH$^+$+1], 164 (12) [MH$^+$]; HRMS: *m*/*z*: calcd for $C_{11}H_{16}O$: 164.1201, found: 164.1199 [M^+].

PET oxidative reaction of 2-trimethylsilyloxy-tricyclo[6.4.0.0^{2,4}]dodeca-1(8),9,11-triene (9): Compound **9** (1.57 g, 6.37 mmol) and DCN (398 mg, 2.33 mmol)) were dissolved in acetonitrile (500 mL) and irradiated in an immersion well reactor according to GP I for 84 h. The crude product was filtered over silica gel (cyclohexane/ethyl acetate 85:15) and purified by HPLC (cyclohexane/ethyl acetate 90:10) yielding 6-methyl-6,7,8,9-tetrahydro-5*H*-benzo[*a*]cyclohepten-5-one (**32**; 366 mg, 34%) and 3-propyl-1-indanone (**33**; 125 mg, 11%) as colorless oils.

6-Methyl-6,7,8,9-tetrahydro-5*H*-benzo[*a*]cyclohepten-5-one (32): NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): $\delta = 1.12$ (d, $J = 6.6$ Hz, 3H, 1′-H), 1.57 (dddd, $J =$ 5.0/6.5/11.3/13.3 Hz, 1H, 7-H), 1.68 (ddddd, $J =$ 3.3/6.5/8.5/11.8/13.3 Hz, 1H, 8-H), 1.89 (dddd, $J =$ 5.2/6.9/8.5/13.4 Hz, 1H, 7-H), 2.09 (ddddd, $J =$ 3.3/5.2/6.8/6.8/13.8 Hz, 1H, 8-H), 2.90 (ddd, $J =$ 3.3/6.8/15.5 Hz, 1H, 9-H), 2.90 (dtd, $J =$ 5.2/6.6/11.3 Hz, 1H, 6-H), 1.67 (ddd, $J =$ 3.3/11.0/15.5 Hz, 1H, 9-H), 7.18 (d, $J = 7.5$ Hz, 1H, 4-H), 7.35 (ddd, $J =$ 1.5/7.5/7.5 Hz, 1H, 3-H), 7.25 (dd, $J =$ 7.7/7.5 Hz, 1H, 2-H), 7.65 (dd, $J =$ 1.5/7.7 Hz, 1H, 1-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): $\delta = 16.33$ (C-1′), 25.38 (C-8), 31.80 (C-7), 33.47 (C-9), 43.93 (C-6), 126.15 (C-3), 128.22 (C-1), 129.65 (C-4), 131.15 (C-2), 139.46 (C-4a), 141.76 (C-9a), 207.61 (C-5); IR (film): $\tilde{\nu} = 3069$, 3025. 2937, 2867, 1679, 1598, 1481, 1448, 1375, 1348, 1322, 1276, 1251, 1223, 1204, 1160, 1122, 1106, 1091, 1072, 989, 970, 895, 852, 822, 782, 760, 737, 711 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 175 (10) [M^++1], 174 (78) [M^+], 173 (4), 159 (11), 156 (14), 147 (4), 146 (39), 145 (42), 144 (32), 143 (6), 142 (3), 141 (15), 133 (6), 132 (34), 131 (100), 130 (33), 129 (24), 128 (22), 127 (9), 120 (12), 119 (21), 118 (29), 117 (18), 116 (19), 115 (36), 105 (10), 104 (34), 103 (30), 102 (10), 92 (5), 91 (55), 90 (50), 89 (46), 79 (5), 78 (27), 77 (54), 76 (13), 75 (4), 65 (24), 64 (9), 63 (12), 55 (15), 53 (4), 52 (4), 51 (10), 50 (4), 43 (5), 41 (13), 39 (16), 29 (8); GC-MS (CI): *m*/*z* (%): 176 (14) [MH$^+$+1], 175 (100) [MH$^+$]; HRMS: *m*/*z*: calcd for $C_{12}H_{14}O$: 174.1045, found: 174.1037 [M^+].

3-Propyl-1-indanone (33): NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): $\delta = 0.93$ (dd, $J = 7.2/7.2$ Hz, 3H, 3′-H), 1.34–1.48 (m, 3H, 1′-H/2′-H), 1.86 (m, 1H, 1′-H), 2.32 (dd, $J =$ 3.3/19.0 Hz, 1H, 2-H), 2.81 (dd, $J = 7.5/19.0$ Hz, 1H, 2-H), 3.33 (dddd, $J =$ 3.3/4.2/7.5/8.3 Hz, 1H, 3-H), 7.33 (dddd, $J = 0.9/0.9/7.7/7.4$ Hz, 1H, 6-H), 7.467 (dddd, $J = 0.9/0.9/0.9/7.7$ Hz, 1H, 4-H), 7.56 (ddd, $J = 1.2/7.3/7.7$ Hz, 1H, 5-H), 7.69 (ddd, $J = 0.9/1.2/7.7$ Hz, 1H, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): $\delta = 14.06$ (C-3′), 20.72 (C-2′), 37.95 (C-3), 38.26 (C-1′), 43.00 (C-2), 123.38 (C-7), 125.52 (C-4), 127.33 (C-6), 134.52 (C-5), 136.62 (C-7a), 158.93 (C-3a), 206.45 (C-1); IR (film): $\tilde{\nu} = 3074$, 2962, 2933, 2876, 1714, 1605, 1463, 1406, 1378, 1328, 1281, 1236, 1209, 1196, 1150, 1094, 1042, 1015, 971, 758 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 175 (6) [M^++1], 174 (27) [M^+], 145 (8), 133 (10), 132 (100), 131 (40), 129 (3), 128 (4), 118 (3), 117 (6), 116 (4), 115 (14), 104 (10), 103 (45), 102 (16), 91 (12), 90 (4), 89 (5), 78 (7), 77 (34), 65 (5), 51 (11), 50 (3), 43 (3), 41 (7), 39 (7); GC-MS (CI): *m*/*z* (%): 176 (13) [MH$^+$+1], 175 (100) [MH$^+$]; HRMS: *m*/*z*: calcd for $C_{12}H_{14}O$: 174.1045, found: 174.1039 [M^+].

PET oxidative reaction of 3-(3-butenyl)bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ether (11a) Compound **11a** (560 mg, 2.24 mmol) and phenanthrene (1.98 g) were dissolved in acetonitrile (164 mL), apportioned together with DCA (180 mg, 0.79 mmol) to 12 pyrex tubes and irradiated according to GP I for 48 h. The crude product was purified by column chromatography on silica gel (Et_2O/*n*-pentane 1:18) yielding 3-(3-butenyl)-7-methyl-3-cyclohepten-1-on (**34a**; 80 mg, 20%) and a mixture (133 mg, 33%) of the three isomeric cyclisation products **35a**, **36a** and **37a** (relative amounts according to GC: 12:15:6). This mixture was separated for spectroscopic characterizaction by reversed phase-HPLC (RP-18, acetonitrile/water 70:30) and preparative GC (155°C isotherm/0.38 bar).

3-(3-Butenyl)-7-methyl-3-cyclohepten-1-one (34a): NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$MS): $\delta = 1.07$ (d, $J = 6.9$ Hz, 3H, 1″-H), 1.59 (dddd, $J =$ 3.7/9.9/9.9/13.7 Hz, 1H, 6-H), 1.93 (dddd, $J =$ 3.3/5.2/8.3/13.8 Hz, 1H, 6-H), 2.07–2.30 (m, 6H, 5-H/1′-H/2′-H), 2.64 (dqd, $J =$ 5.1/6.9/9.9 Hz, 1H, 7-H), 3.07 (d, $J =$ 13.8 Hz, 1H, 2-H), 3.16 (dd, $J =$ 1.1/13.8 Hz, 1H, 2-H), 4.93 (dddd, $J =$ 0.9/0.9/1.6/11.2 Hz, 1H, 4′-H), 4.98 (dddd, $J =$ 1.6/1.6/1.6/17.2 Hz, 1H, 4′-H), 5.53 (dd, $J =$ 5.5/5.5 Hz, 1H, 4-H), 5.74 (dddd, $J =$ 6.4/.6.4/10.3/17.2 Hz, 1H, 3′-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): $\delta = 16.60$ (C-1″), 26.46 (C-5), 31.87 (C-2′), 32.39 (C-6), 39.23 (C-1′), 45.37 (C-2), 47.79 (C-7), 114.81 (C-4′), 125.67 (C-4), 133.36 (C-3), 137.97 (C-3′), 210.87 (C-1); GC-MS (CI): *m*/*z* (%): 180 (13) [MH$^+$+1], 179 (100) [MH$^+$].

(3a*R,5a*S**,9a*R**)-Octahydro-1*H*-cyclopenta[*c*]inden-5(5a*H*)-one (35a)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HSQC, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: TMS): $\delta = 1.10$ (m, 1H, 7-H^B), 1.22 (m, 1H, 9-H^A), 1.260 (m, 1H, 8-H^B), 1.41 (m, 1H, 3-H^B), 1.42 (m, 1H, 6-H^A), 1.461 (m, 1H, 9-H^B), 1.48 (m, 1H, 7-H^A), 1.53 (m, 1H, 8-H^A), 1.560 (m, 1H, 1-H^A), 1.75 (m, 1H, 2-H^A), 1.83 (m, 1H, 2-H^B), 1.843 (m, 1H, 1-H^B), 1.99 (m, 1H, 6-H^B), 2.03 (dd, $J = 4.1/8.0/8.4/12.4$ Hz, 1H, 3-H^A), 2.03 (m, 1H, 5a-H), 2.09 (dddd, $J = 2.7/8.8/8.9/9.0$ Hz, 1H, 3a-H), 2.14 (ddd, $J =$ 1.6/2.7/19.4 Hz, 1H, 4-H^B), 2.45 (dd, $J =$ 8.8/19.4 Hz, 1H, 4-H^A); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): $\delta = 21.18$ (C-6), 23.18 (C-7), 23.40 (C-8), 24.68 (C-2), 32.49 (C-3), 35.64 (C-9), 36.78 (C-1), 41.41 (C-4), 44.13 (C-3a), 50.16 (C-9a), 52.95 (C-5a), 220.05 (C-5); IR (film): $\tilde{\nu} = 2931$, 2862, 1738, 1447, 1408 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 179 (13) [M^++1], 178 (100) [M^+], 163 (3), 161 (3), 150 (15), 149 (62), 137 (9), 136 (77), 135 (47), 134 (10), 133 (3), 124 (3), 123 (34), 122 (12), 121 (29), 120 (10), 119 (6), 117 (4), 110 (4), 109 (12), 108 (31), 107 (30), 106 (4), 105 (11), 97 (4), 96 (15), 95 (36), 94 (40), 93 (60), 92 (13), 91 (50), 83 (5), 82 (13), 81 (75), 80 (26), 79 (97), 78 (12), 77 (35), 69 (5), 68 (17), 67 (66), 66 (11), 65 (17), 56 (3), 55 (29), 54 (9), 53 (23), 52 (4), 51 (6), 43 (6), 42 (9), 41 (89), 40 (5), 39 (42), 29 (31); HRMS: *m*/*z*: calcd for $C_{12}H_{18}O$: 178.1358, found: 178.1353 [M^+].

(3*S,3a*S**,5a*R**,8a*S**)-3-Methyloctahydrocyclopenta[*c*]pentalen-4(5*H*)-one (36a)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HSQC, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: TMS): $\delta = 0.91$ (d, $J = 7.0$ Hz, 3H, 1′-H), 1.16 (dddd, $J =$ 6.3/11.5/12.2/11.5 Hz, 1H, 2-H^A), 1.26 (dddd, $J =$ 5.2/5.2/7.0/12.8 Hz, 1H, 6-H^B), 1.48 (ddddd, $J =$ 7.0/7.0/8.2/8.4/12.4 Hz, 1H, 7-H^B), 1.57 (ddddd, $J =$ 5.2/5.5/6.2/6.7/12.4 Hz, 1H, 7-H^A), 1.64 (ddd, $J =$ 6.2/8.2/12.6 Hz, 1H, 8-H^A), 1.66 (ddd, $J =$ 5.5/7.0/12.6 Hz, 1H, 8-H^B), 1.67 (ddd, $J =$ 6.3/12.2/12.5 Hz, 1H, 1-H^B), 1.75 (ddd, $J =$ 2.1/6.3/12.5 Hz, 1H, 1-H^A), 1.78 (dddd, $J =$ 2.1/5.9/6.3/12.2 Hz, 1H, 2-H^B), 1.91 (dddd, $J =$ 6.7/8.4/8.5/12.8 Hz, 1H, 6-H^A), 2.00 (ddd, $J =$ 2.0/3.3/18.4 Hz, 1H, 5-H^B), 2.11 (dd, $J =$ 2.0/10.5 Hz, 1H, 3a-H), 2.16 (dddd, $J =$ 3.3/5.2/8.5/10.2 Hz,

1H, 5a-H), 2.25 (dqdd, J=5.9/7.0/10.5/11.5 Hz, 1H, 3-H), 2.37 (ddd, J= 0.6/10.2/18.4 Hz, 1H, 5-H^A); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=15.77 (C-1′), 25.90 (C-7), 35.31 (C-6), 35.60 (C-2), 39.14 (C-3), 40.98 (C-1), 41.10 (C-8), 46.00 (C-5a), 48.79 (C-5), 59.78 (C-8a), 63.19 (C-3a), 222.39 (C-4); IR (film): $\tilde{\nu}$ =2944, 2866, 1735, 1715, 1480 cm^{-1}; GC-MS (70 eV): m/z (%): 179 (14) [M^++1], 178 (72) [M^+], 163 (4), 161 (3), 150 (16), 149 (100), 137 (11), 136 (69), 135 (22), 131 (3), 124 (7), 123 (75), 122 (5), 121 (33), 120 (10), 119 (5), 110 (3), 109 (6), 108 (20), 107 (51), 106 (4), 105 (16), 96 (32), 95 (32), 94 (32), 93 (78), 92 (13), 91 (67), 82 (9), 81 (79), 80 (19), 79 (87), 78 (12), 77 (45), 69 (8), 68 (7), 67 (37), 66 (10), 65 (17), 55 (26), 54 (6), 53 (23), 52 (5), 51 (5), 43 (7), 42 (7), 41 (83), 40 (9), 39 (46), 38 (33), 29 (39); HRMS: m/z: calcd for $C_{12}H_{18}O$: 178.1358, found: 178.1347 [M^+].

(3*R,3a*S**,5a*R**,8a*S**)-3-Methyloctahydrocyclopenta[*c*]pentalen-4(5*H*)-one (37a)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HSQC, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: TMS): δ=1.04 (d, J=6.9 Hz, 3H, 1′-H), 1.27 (m, 1H, 6-H^B), 1.29 (m, 1H, 2-H^B), 1.58 (m, 1H, 7-H^A), 1.61 (m, 1H, 7-H^B), 1.63 (m, 1H, 1-H^A), 1.65 (m, 1H, 8-H^A), 1.69 (m, 1H, 2-H^A), 1.69 (m, 1H, 8-H^B), 1.76 (m, 1H, 1-H^B), 1.80 (dd, J=1.8/5.5 Hz, 1H, 3a-H), 1.91 (dddd, J=6.8/7.2/8.6/13.4 Hz, 1H, 6-H^A), 2.02 (ddd, J=1.9/4.9/18.5 Hz, 1H, 5-H^B), 2.05 (m, 1H, 3-H), 2.16 (dddd, J= 4.9/5.3/8.6/9.2 Hz, 1H, 5a-H), 2.56 (ddd, J=0.6/9.2/18.5 Hz, 1H, 5-H^A); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=20.78 (C-1′), 25.90 (C-7), 34.48 (C-6), 35.53 (C-2), 40.14 (C-3), 40.81 (C-1), 41.76 (C-8), 44.95 (C-5a), 45.69 (C-5), 59.22 (C-8a), 67.44 (C-3a), 222.68 (C-4); IR (film): $\tilde{\nu}$ = 2942, 2865, 1735, 1701 cm^{-1}; GC-MS (70 eV): m/z (%): 179 (13) [M^++1], 178 (88) [M^+], 163 (5), 151 (5), 150 (35), 149 (53), 137 (3), 136 (34), 135 (30), 134 (8), 133 (3), 123 (17), 122 (8), 121 (36), 120 (4), 119 (6), 117 (3), 110 (3), 109 (8), 108 (37), 107 (90), 106 (5), 105 (17), 103 (3), 97 (3), 96 (8), 95 (27), 94 (89), 93 (91), 92 (12), 91 (74), 83 (4), 82 (11), 81 (100), 80 (20), 79 (88), 78 (13), 77 (51), 69 (11), 68 (12), 67 (42), 66 (11), 65 (18), 55 (26), 54 (5), 53 (22), 52 (3), 51 (5), 43 (5), 42 (6), 41 (87), 40 (6), 39 (48), 29 (41); HRMS: m/z: calcd for $C_{12}H_{18}O$: 178.1358, found: 178.1352 [M^+].

PET oxidative reaction of 3-(3-butynyl)bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ether (12a): Compound **12a** (580 mg, 2.33 mmol) was dissolved in acetonitrile (205 mL), apportioned together with DCA (100 mg, 0.44 mmol) to 14 pyrex tubes and irradiated according to GP I for 96 h. The crude product was filtered over silica (cyclohexane/ethyl acetate 90:10) and purified by HPLC (cyclohexane/ethyl acetate 95:5) yielding 3-(3-butynyl)-7-methyl-3-cyclohepten-1-one (**38a**; 62 mg, 15%), (3a*R**,5a*S**,9a*S**)-2,3,3a,4,8,9-hexahydro-1*H*-cyclopenta[*c*]inden-5(5a*H*)-one (**39a**; 25 mg, 15%) and (3a*S**,5a*R**,8a*S**)-3-methylenoctahydrocyclopenta[*c*]pentalen-4(5*H*)-one (**40a**; 123 mg, 30%) as colorless oils.

3-(3-Butynyl)-7-methyl-3-cyclohepten-1-one (38a): NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ= 1.063 (d, J=6.9 Hz, 3H, 1″-H), 1.600 (dddd, J=3.5/9.8/10.1/13.4 Hz, 1H, 6-H), 1.92 (dd, J=2.5/2.5 Hz, 1H, 4′-H), 1.94 (dddd, J=3.3/5.2/8.6/13.4 Hz, 1H, 6-H), 2.16–2.32 (m, 6H, 5-H/1′-H/2′-H), 2.665 (dqd, J=5.2/6.9/10.1 Hz, 1H, 7-H), 3.08 (dd, J=1.0/14.0 Hz, 1H, 2-H), 3.17 (dddd, J= 1.0/1.1/1.2/14.0 Hz, 1H, 2-H), 5.60 (dddd, J=1.0/1.0/5.1/6.1 Hz, 1H, 4-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=16.57 (C-1″), 17.33 (C-2′), 26.44 (C-5), 32.33 (C-6), 38.51 (C-1′), 45.21 (C-2), 47.71 (C-7), 68.76 (C-4′), 83.61 (C-3′), 126.81 (C-4), 132.22 (C-3), 210.57 (C-1); IR (film): $\tilde{\nu}$ = 3293, 2936, 2119, 1706, 1458, 1376, 1169, 1049 cm^{-1}; GC-MS (70 eV): m/z (%): 176 (1) [M^+], 161 (25), 143 (3), 134 (9), 133 (7), 132 (3), 119 (11), 118 (3), 109 (3), 107 (4), 106 (14), 105 (30), 104 (5), 103 (3), 98 (9), 95 (6), 93 (9), 92 (16), 91 (100), 82 (5), 81 (8), 80 (5), 79 (40), 78 (25), 77 (29), 69 (8), 67 (16), 66 (7), 65 (20), 56 (3), 55 (16), 54 (5), 53 (6), 52 (13), 43 (5), 42 (11), 41 (78), 40 (4), 39 (48), 29 (16); GC-MS (CI): m/z (%): 178 (12) [MH$^+$+1], 177 (100) [MH$^+$].

(3a*R,5a*S**,9a*S**)-2,3,3a,4,8,9-Hexahydro-1*H*-cyclopenta[*c*]inden-5(5a*H*)-one (39a)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: TMS): δ=1.43 (dddd, J=2.2/7.0/13.7/15.6 Hz, 1H, 3-H^B), 1.44–1.49 (m, 2H, 9-H), 1.67–1.83 (m, 3H, 1-H/2-H), 1.55 (m, 1H, 1-H), 1.97–2.06 (m, 3H, 3-H/8-H), 2.11 (ddd, J=1.6/3.8/18.9 Hz, 1H, 4-H^B), 2.18 (dddd, J=3.8/7.0/8.2/9.0 Hz, 1H, 3a-H), 2.51 (dd, J=9.0/18.9 Hz, 1H, 3-H^A), 2.53 (m, 1H, 5a-H), 5.69 (dddd, J=2.1/2.1/4.3/9.9 Hz, 1H, 6-H), 5.85 (dddd, J=2.3/3.9/3.9/3.9 Hz, 1H, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=22.90 (C-8), 24.07 (C-2), 31.11 (C-9), 33.06 (C-3), 37.78 (C-1), 42.72 (C-4), 43.25 (C-3a), 49.08 (C-9a), 55.31 (C-5a), 122.18 (C-6), 129.23 (C-7), 219.05 (C-5); GC-MS (70 eV): m/z (%): 177 (4) [M^++1], 176 (33) [M^+], 158 (5), 148 (8), 147 (12), 135 (5), 134 (33), 133 (12), 132 (16), 131 (6), 130 (12), 129 (6), 121 (3), 120 (8), 119 (18), 118 (3), 117 (8), 115 (3), 107 (9), 106 (19), 105 (29), 104 (18), 103 (6), 98 (5), 95 (3), 94 (9), 93 (17), 92 (38), 91 (100), 81 (5), 80 (11), 79 (38), 78 (18), 77 (38), 67 (10), 66 (6), 65 (12), 63 (3), 55 (6), 53 (14), 52 (6), 51 (8), 43 (3), 42 (6), 41 (35), 40 (5), 39 (24), 29 (6); GC-MS (CI): m/z (%): 178 (13) [MH$^+$+1], 177 (100) [MH$^+$]; HRMS: m/z: calcd for $C_{12}H_{16}O$: 176.1201, found: 176.1203 [M^+].

(3a*S,5a*R**,8a*S**)-3-Methylenoctahydrocyclopenta[*c*]pentalen-4(5*H*)-one (40a)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ=1.39 (dddd, J=4.5/4.7/5.0/14.7 Hz, 1H, 6-H^B), 1.55–1.72 (m, 3H, 7-H/8-H), 1.72–1.81 (m, 3H, 8-H/1-H), 1.96 (m, 1H, 6-H^A), 2.023 (ddd, J=1.9/4.5/18.8 Hz, 1H, 5-H^B), 2.27 (dddd, J= 4.2/4.5/8.9/9.7 Hz, 1H, 5a-H), 2.30–2.43 (m, 2H, 2-H), 2.63 (dd, J=9.7/18.8 Hz, 1H, 5-H^A), 2.76 (dddd, J=1.9/2.0/2.2/2.2 Hz, 1H, 3a-H), 4.95 (ddd, J=2.2/2.2/2.2 Hz, 1H, 1′-H), 5.02 (ddd, J=2.2/2.2/2.2 Hz, 1H, 1′-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=25.43 (C-7), 33.63 (C-2), 34.35 (C-6), 39.16 (C-8)*, 39.19 (C-1)*, 44.03 (C-5a), 45.39 (C-5), 59.56 (C-8a), 64.66 (C-3a), 108.40 (C-1′), 149.33 (C-3), 218.09 (C-4); *: signal assignments are mutual interchangeable; IR (film): $\tilde{\nu}$ =2947, 2866, 2163, 1737, 1650, 1447, 1407, 1222, 1167, 1042, 888 cm^{-1}; GC-MS (70 eV): m/z (%): 177 (8) [M^++1], 176 (58) [M^+], 161 (10), 149 (3), 148 (18), 147 (37), 135 (9), 134 (84), 133 (35), 132 (15), 131 (4), 121 (4), 120 (14), 119 (32), 117 (8), 115 (4), 107 (10), 106 (45), 105 (38), 104 (5), 103 (8), 95 (3), 94 (18), 93 (21), 92 (31), 91 (100), 82 (5), 81 (6), 80 (12), 79 (55), 78 (22), 77 (46), 67 (8), 66 (4), 65 (17), 63 (3), 55 (8), 54 (3), 53 (18), 52 (7), 51 (9), 42 (4), 41 (33), 40 (5), 39 (27), 29 (8), 27(11); GC-MS (CI): m/z (%): 178 (13) [MH$^+$+1], 177 (100) [MH$^+$], 176 (7) [M^+]; HRMS: m/z: calcd for $C_{12}H_{16}O$: 176.1201, found: 176.1193 [M^+].

PET oxidative reaction of 3-(2-cyclohexenylmethyl)bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ether (13a): Compound **13a** (268 mg, 0.93 mmol) was dissolved in acetonitrile (128 mL), apportioned together with DCA (100 mg, 0.44 mmol) to 14 pyrex tubes and irradiated according to GP I for 96 h. The crude product was filtered over silica (cyclohexane/ethyl acetate 75:25) and purified by HPLC (cyclohexane/ethyl acetate 95:5) yielding 3-(2-cyclohexenylmethyl)-7-methyl-3-cyclohepten-1-one (**41a**; 38 mg, 19%), (3a*R**,5a*S**,5b*S**,9a*S**,10a*S**)-dodecahydropentaleno[1,6a-*a*]-inden-5(1*H*)-one (**42a**; 22 mg, 11%) and (3a*R**,5a*S**,5b*R**,9a*R**,10a*S**)-dodecahydropentaleno[1,6a-*a*]inden-5(1*H*)-one (**43a**; 24 mg, 12%) as colorless oils.

3-(2-Cyclohexenylmethyl)-7-methyl-3-cyclohepten-1-one (41a): NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$MS): δ=1.063/1.061 (d, J=6.8 Hz, 3H, 1‴-H), 1.09–1.17 (m, 1H, 6″-H), 1.44–1.53 (m, 1H, 5″-H), 1.55–1.68 (m, 3H, 6-H/5″-H/6″-H), 1.90–2.05 (m, 5H, 6-H/1′-H/4″-H), 2.14–2.32 (m, 3H, 5-H/1″-H), 2.59–2.68 (m, 1H, 7-H), 3.03–3.09 (m, 1H, 2-H), 3.12–3.19 (m, 1H, 2-H), 5.45–5.53 (m, 2H, 4-H/2″-H), 5.61–5.67 (m, 1H, 3″-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=16.57/16.66 (C-1‴), 21.22 (C-5″), 25.26 (C-4″), 26.50/26.57 (C-5), 28.71/28.90 (C-6), 32.30/32.34 (C-6″), 32.54/32.56 (C-1″), 45.04/45.13 (C-2), 46.73 (C-1′). 47.82/47.89 (C-7), 127.06/127.07 (C-4), 127.22 (C-3″), 131.03/131.16 (C-2″), 132.16/132.22 (C-3), 210.82 (C-1); IR (film): $\tilde{\nu}$=3022, 2933, 1708, 1662, 1448, 1376, 1324, 1279, 1214, 1137, 1051, 957, 862, 784, 721 cm^{-1}; GC-MS (70 eV): m/z (%): 218 (11) [M^+], 175 (7), 138 (21), 123 (3), 121 (4), 110 (19), 109 (5), 107 (3), 105 (6), 96 (5), 95 (15), 94 (4), 93 (5), 92 (3), 91 (13), 82 (8), 81 (100), 80 (19), 79 (44), 78 (3), 77 (12), 69 (4), 68 (4), 67 (10), 66 (4), 65 (6), 55 (10), 53 (17), 43 (4), 42 (3), 41 (31), 39 (10), 29 (4); GC-MS (CI): m/z (%): 220 (17) [MH$^+$+1], 219 (100) [MH$^+$]; HRMS: m/z: calcd for $C_{15}H_{22}O$: 218.1671, found: 218.1672 [M^+].

(3a*R,5a*S**,5b*S**,9a*S**,10a*S**)-Dodecahydropentaleno[1,6a-*a*]inden-5(1*H*)-one (42a)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HSQC, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: TMS): δ=0.95 (dddd, J=3.2/12.0/12.9/12.9 Hz, 1H, 6-H^A), 1.11 (ddddd, J=3.1/3.3/12.0/12.9/12.9 Hz, 1H, 7-H^B), 1.27 (m, 1H, 3-H^B), 1.32 (ddddd, J=3.3/4.4/12.8/12.8/13.1 Hz, 1H, 8-H^A), 1.46 (dddddd, J=1.6/3.3/3.3/3.3/4.8/13.1 Hz, 1H, 8-H^B), 1.52 (m, 1H, 6-H^B), 1.56 (dddd, J=4.8/4.8/13.5/13.6 Hz, 1H, 9-H^A), 1.57 (dd, J=7.0/12.6 Hz, 1H, 10-H^B), 1.59 (m, 1H, 2-H), 1.63 (dm, J=13.5 Hz, 1H, 9-H^B), 1.64 (m, 1H, 2-H), 1.64 (m, 1H, 7-H^A), 1.66 (m, 1H, 1-H^B), 1.73 (m, 1H, 1-H^A), 2.01 (dd, J=12.3/13.0 Hz, 1H, 10-H^A), 2.04 (m, 1H, 3-H^A), 2.10 (ddd, J=2.1/4.6/19.2 Hz, 1H, 4-H^B), 2.22 (m, 1H, 9a-H), 2.24

(ddddd, J=1.2/5.0/5.9/8.2/12.0 Hz, 1H, 5b-H), 2.33 (dddd, J=4.6/5.8/8.5/10.1 Hz, 1H, 3a-H), 2.48 (dd, J=2.1/8.2 Hz, 1H, 5a-H), 2.64 (ddd, J=0.8/9.9/19.2 Hz, 1H, 4-H^A); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: TMS): δ= 21.02 (C-8), 24.35 (C-6), 25.70 (C-7), 26.15 (C-2), 26.51 (C-9), 35.26 (C-3), 40.96 (C-9a), 42.11 (C-5b), 43.86 (C-1), 44.16 (C-10), 46.35 (C-3a), 49.09 (C-4), 58.43 (C-10a), 65.52 (C-5a), 222.95 (C-5); IR (film): $\tilde{\nu}$ = 2931, 2863, 1730, 1467, 1447, 1407, 1316, 1270, 1248, 1166, 1039 cm^{-1}; GC-MS (70 eV): m/z (%): 218 (6) [M$^+$], 190 (3), 189 (12), 176 (7), 175 (4), 147 (4), 138 (6), 137 (9), 136 (3), 133 (7), 124 (16), 123 (100), 122 (14), 121 (4), 119 (6), 117 (3), 108 (3), 107 (5), 106 (4), 105 (10), 97 (4), 96 (43), 95 (28), 94 (11), 93 (14), 92 (8), 91 (33), 82 (3), 81 (23), 80 (8), 79 (34), 78 (6), 77 (18), 67 (19), 66 (4), 65 (5), 55 (15), 53 (9), 52 (5), 43 (6), 42 (3), 41 (35), 39 (6), 29 (6); GC-MS (CI): m/z (%): 220 (17) [MH$^+$+1], 219 (100) [MH$^+$]; HRMS: m/z: calcd for $C_{15}H_{22}O$: 218.1671, found: 218.1674 [M^+].

(3a*R,5a*S**,5b*R**,9a*R**,10a*S**)-Dodecahydropentaleno[1,6a-*a*]inden-5(1*H*)-one (43a)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, ^{13}C-gated, HSQC, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: TMS): δ=1.24 (m, 1H, 7-H), 1.36–1.42 (m, 2H, 8-H), 1.36 (dddd, J=3.0/10.4/13.1/15.2 Hz, 1H, 6-H), 1.38 (dddd, J=4.5/5.8/6.2/12.7 Hz, 1H, 3-H^B)*, 1.49–1.54 (m, 2H, 9-H), 1.567 (m, 1H, 6-H), 1.587 (m, 1H, 7-H), 1.63 (m, 1H, 2-H), 1.680 (m, 1H, 2-H), 1.69 (m, 1H, 10-H^A), 1.77 (ddd, J=6.4/8.3/12.6 Hz, 1H, 1-H^A), 1.82 (dddd, J=6.3/6.3/12.6 Hz, 1H, 1-H^B), 1.919 (m, 1H, 9a-H), 1.93 (m, 1H, 10-H^B), 1.96 (dddd, J=6.6/8.2/8.3/12.7 Hz, 1H, 3-H^A), 2.01 (dd, J=1.8/3.0 Hz, 1H, 5a-H), 2.08 (ddd, J=1.8/6.1/18.4 Hz, 1H, 4-H^B), 2.09 (dddd, J=3.0/5.2/5.2/10.4 Hz, 1H, 5b-H), 2.22 (dddd, J=4.5/6.1/8.3/9.3 Hz, 1H, 3a-H), 2.56 (ddd, J=0.7/9.3/18.4 Hz, 1H, 4-H^A); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: TMS): δ=21.58 (C-8), 24.76 (C-7), 26.13 (C-2), 26.61 (C-9), 27.86 (C-6), 34.54 (C-3), 39.07 (C-9a), 43.08 (C-1), 44.84 (C-10), 45.08 (C-5b), 46.59 (C-4), 46.70 (C-3a), 57.26 (C-10a), 65.99 (C-5a), 223.42 (C-5); IR (film): $\tilde{\nu}$ =2929, 2862, 1736, 1659, 1529, 1465, 1446, 1407, 1252, 1166, 1061 cm^{-1}; GC-MS (70 eV): m/z (%): 218 (6) [M^+], 189 (6), 176 (4), 175 (3), 161 (3), 149 (3), 148 (5), 147 (13), 134 (6), 133 (7), 124 (15), 123 (100), 121 (10), 120 (3), 119 (7), 117 (4), 108 (3), 107 (4), 106 (4), 105 (12), 96 (13), 95 (12), 94 (9), 93 (17), 92 (9), 91 (34), 81 (17), 80 (9), 79 (39), 78 (6), 77 (19), 67 (21), 66 (4), 65 (5), 55 (15), 53 (4), 52 (6), 51 (3), 43 (5), 42 (3), 41 (25), 39 (10), 29 (8); GC-MS (CI): m/z (%): 220 (16) [MH$^+$+1], 219 (100) [MH$^+$]; HRMS: m/z: calcd for $C_{15}H_{22}O$: 218.1671, found: 218.1673 [M^+].

PET oxidative reaction of 3-(3-butenyl)bicyclo[6.1.0]non-2-en-1-yl trimethylsilyl ether (11b): Compound **11b** (650 mg, 2.45 mmol) was dissolved in acetonitrile (205 mL), apportioned together with DCA (160 mg, 0.70 mmol) to 15 pyrex tubes and irradiated according to GP I for 96 h. The crude product was filtered over silica gel (cyclohexane/ethyl acetate 75:25) and purified by HPLC (cyclohexane/ethyl acetate 95:5) yielding (3*R**,3a*S**,5a*R**,9a*S**)-3-methyldecahydro-4*H*-cyclopenta[*c*]inden-4-one (**36b**; 43 mg, 9%) and a mixture (175 mg, 37%; relative amount according to GC 22:17) of the two isomeric cyclisation products (4a*S**,6a*R**,10a*S**)-decahydrobenzo[*c*]inden-5(1*H*)-one (**35b**) and (3*R**,3a*S**,5a*R**,9a*S**)-3-methyldecahydro-4*H*-cyclopenta[*c*]inden-4-one (**37b**). The mixture was separated by preparative GC (190°C isotherm/0.45 bar) for spectroscopic characterization.

(4a*S,6a*R**,10a*S**)-Decahydrobenzo[*c*]inden-5(1*H*)-one (35b)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ=1.06–1.33 (m, 6H), 1.34–1.48 (m, 5H), 1.51–1.67 (m, 3H), 1.80–1.99 (m, 3H, 4-H/6a-H/10-H), 1.94 (ddd, J=1.4/2.9/19.5 Hz, 1H, 6-H), 2.22 (m, 1H, 4a-H), 2.40 (dd, J=8.3/19.5 Hz, 1H, 6-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=20.99 (C-8/C-9)*, 21.29 (C-4), 23.35 (C-3), 24.30 (C-2), 28.69 (C-7), 32.84 (C-10), 35.79 (C-1), 37.72 (C-6a), 39.70 (C-10a), 42.57 (C-6), 49.66 (C-4a), 221.19 (C-5); *signal shows correlation signals with 4 protons in HMQC 2D experiment; IR (film): $\tilde{\nu}$ =2929, 2860, 1737, 1449, 1413, 1356, 1296, 1262, 1230, 1196, 1184, 1154, 1107, 1070, 1040, 1002, 909, 892, 878, 850 cm^{-1}; GC-MS (70 eV): m/z (%): 193 (5) [M^++1], 192 (34) [M^+], 163 (3), 150 (9), 149 (21), 138 (14), 137 (100), 136 (17), 135 (14), 134 (6), 122 (7), 121 (10), 110 (5), 109 (8), 108 (10), 107 (15), 105 3), 98 (3), 97 (4), 96 (8), 95 (18), 94 (14), 93 (18), 92 (4), 91 (12), 83 (7), 82 (15), 81 (33), 80 (10), 79 (32), 78 (4), 77 (12), 69 (5), 68 (16), 67 (45), 66 (5), 65 (8), 55 (32), 54 (11), 53 (18), 52 (4), 51 (5), 43 (4), 42 (3), 41 (37), 40 (4), 39 (17), 29 (11), 28 (6), 27 (15).

(3*R,3a*S**,5a*R**,9a*S**)-3-Methyldecahydro-4*H*-cyclopenta[*c*]inden-4-one (36b)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ=0.99 (m, 1H, 6-H), 1.05 (d, J=6.9 Hz, 3H, 1′-H), 1.15 (dddd, J=9.0/10.7/11.3/13.0 Hz, 1H, 2-H^A), 1.22–1.32 (m, 2H, 7-H/8-H), 1.37 (m, 1H, 9-H), 1.47–1.55 (m, 2H, 7-H/8-H), 1.54 (ddd, J=8.2/10.7/13.6 Hz, 1H, 1-H^B), 1.64 (m, 1H, 9-H), 1.65 (m, 1H, 6-H), 1.813 (dddd, J=2.1/6.4/8.2/13.0 Hz, 1H, 2-H^B), 1.84 (ddd, J=2.1/9.0/13.6 Hz, 1H, 1-H^A), 1.95 (dddd, J=4.0/5.3/7.1/9.8 Hz, 1H, 5a-H), 2.03 (ddd, J=1.8/4.0/17.1 Hz, 1H, 5-H^B), 2.11 (dd, J=1.8/9.2 Hz, 1H, 3a-H), 2.23 (dqdd, J=6.4/6.9/9.2/11.3 Hz, 1H, 3-H), 2.31 (dd, J=7.1/17.1 Hz, 1H, 5-H^A); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=16.02 (C-1′), 23.39 (C-7)*, 23.70 (C-8)*, 30.00 (C-6), 34.65 (C-2), 36.34 (C-9), 38.27 (C-3), 40.67 (C-1), 40.69 (C-5a), 47.19 (C-5), 51.14 (C-9a), 58.40 (C-3a), 221.91 (C-4); *: signal assignments are mutual interchangeable; IR (film): $\tilde{\nu}$ =2928, 2861, 1735, 1449, 1413, 1380, 1257, 1193, 1165, 1114, 1034, 934 cm^{-1}; GC-MS (70 eV): m/z (%): 193 (3) [M^++1], 192 (14) [M^+], 149 (10), 138 (11), 137 (100), 136 (11), 135 (5), 134 (3), 121 (4), 108 (5), 107 (12), 95 (9), 94 (6), 93 (9), 92 (8), 91 (15), 82 (4), 81 (24), 80 (5), 79 (27), 78 (4), 77 (12), 69 (5), 68 (3), 67 (19), 66 (3), 65 (4), 55 (15), 53 (7), 51 (3), 43 (4), 42 (3), 41 (30), 40 (5), 39 (9), 29 (9); GC-MS (CI): m/z (%): 194 (14) [MH$^+$+1], 193 (100) [MH$^+$]; HRMS: m/z: calcd for $C_{13}H_{20}O$: 192.1514, found: 192.1517 [M^+].

(3*R,3a*S**,5a*R**,9a*S**)-3-Methyldecahydro-4*H*-cyclopenta[*c*]inden-4-one (37b)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC*, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ=1.08 (d, J=6.8 Hz, 3H, 1′-H), 1.35 (m, 1H, 8-H), 1.38 (dddd, J=8.4/8.9/8.9/12.4 Hz, 1H, 2-H^B), 1.38 (m, 1H, 6-H^B), 1.40 (m, 1H, 7-H), 1.41 (m, 1H, 9-H^A), 1.42 (m, 1H, 7-H), 1.45 (m, 1H, 8-H), 1.57 (m, 1H, 1-H^B), 1.59 (ddd, J=4.4/8.4/13.1 Hz, 1H, 9-H^B), 1.64 (dddd, J=5.4/5.4/8.0/13.3 Hz, 1H, 6-H^A), 1.71 (ddd, J=7.8/8.9/13.1 Hz, 1H, 1-H^A), 1.79 (dd, J=1.5/7.4 Hz, 1H, 3a-H), 1.90 (dddd, J=4.4/7.7/7.8/12.4 Hz, 1H, 2-H^A), 2.02 (dddd, J=5.0/5.0/7.5/9.4 Hz, 1H, 5a-H), 2.10 (qddd, J=6.7/7.4/7.4/8.9 Hz, 1H, 3-H), 2.22 (ddd, J=1.5/9.4/17.9 Hz, 1H, 5-H^B), 2.31 (dd, J=7.5/17.9 Hz, 1H, 5-H^A); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=20.80 (C-1′), 21.70 (C-7), 23.18 (C-8), 26.64 (C-6), 34.77 (C-9), 35.30 (C-2), 37.73 (C-1), 38.19 (C-3), 39.25 (C-5a), 43.25 (C-5), 51.42 (C-9a), 66.59 (C-3a), 221.45 (C-4); IR (film): $\tilde{\nu}$ =2928, 2858, 1736, 1450, 1413, 1375, 1346, 1315, 1234, 1197, 1156, 1123 cm^{-1}; GC-MS (70 eV): m/z (%): 193 (9) [M^++1], 192 (50) [M^+], 165 (6), 164 (49), 163 (23), 150 (11), 149 (36), 148 (5), 147 (3), 138 (6), 137 (45), 136 (21), 135 (28), 134 (4), 133 (3), 131 (3), 123 (3), 122 (11), 121 (23), 119 (3), 110 (5), 109 (9), 108 (23), 107 (74), 105 (12), 97 (5), 96 (6), 95 (28), 94 (61), 93 (50), 92 (11), 91 (42), 83 (7), 82 (14), 81 (92), 80 (20), 79 (79), 78 (11), 77 (35), 69 (13), 68 (13), 67 (59), 66 (15), 65 (15), 55 (44), 54 (9), 53 (11), 51 (8), 43 (7), 42 (12), 41 (100), 40 (9), 39 (34), 29 (20); GC-MS (CI): m/z (%): 194 (13) [MH$^+$+1], 193 (100) [MH$^+$]; HRMS: m/z: calcd for $C_{13}H_{20}O$: 192.1514, found: 192.1514 [M^+].

PET oxidative reaction of 3-(3-butynyl)bicyclo[6.1.0]non-2-en-1-yl trimethylsilyl ether (12b): Compound **12b** was dissolved in acetonitrile (172 mL), apportioned together with DCA (200 mg, 0.88 mmol) to 12 pyrex tubes and irradiated according to GP I for 134 h. The crude product was filtered over silica gel (cyclohexane/ethyl acetate 95:5) and purified by HPLC (cyclohexane/ethyl acetate 95:5) yielding (4a*S**,6a*R**,10a*S**)-2,4a,6,6a,7,8,9,10-octahydrobenzo[*c*]inden-5(1*H*)-one (**39b**; 139 mg, 32%) and (3a*S**,5a*R**,9a*S**)-3-methylendecahydro-4*H*-cyclopenta[*c*]-inden-4-one (**40b**; 52 mg, 12%) as colorless oils.

(4a*S,6a*R**,10a*S**)-2,4a,6,6a,7,8,9,10-Octahydrobenzo[*c*]inden-5(1*H*)-one (39b)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ=1.16–1.40 (m, 4H, 7-H/8-H/9-H/10-H), 1.23 (ddd, J=6.4/6.7/13.3 Hz, 1H, 1-H^B), 1.47–1.57 (m, 2H, 8-H/9-H), 1.63 (m, 1H, 7-H), 1.65 (m, 1H, 10-H), 1.80 (ddd, J=5.7/7.6/13.3 Hz, 1H, 1-H^A), 1.95 (ddddd, J=2.1/3.8/6.4/7.6/18.3 Hz, 1H, 2-H), 1.99–2.09 (m, 2H, 2-H/6a-H), 2.08 (ddd, J=1.2/6.1/18.6 Hz, 1H, 6-H^B), 2.41 (dd, J=7.7/18.6 Hz, 1H, 6-H^A), 2.55–2.59 (m, 1H, 4a-H), 5.58 (dddd, J=2.1/2.2/4.4/9.9 Hz, 1H, 4-H), 5.74 (dddd, J=2.4/3.6/3.8/9.9 Hz, 1H, 3-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ=21.23 (C-2)*, 21.39 (C-9)*, 22.65 (C-8)*, 27.17 (C-7), 29.65 (C-1), 32.56 (C-10), 36.24 (C-6a), 38.71 (C-10a), 41.73 (C-6), 53.75 (C-4a), 122.28 (C-4), 128.29 (C-3), 219.17 (C-5); *: signal assignments are mutual interchangeable; IR (film): $\tilde{\nu}$ =3032, 2928, 2855, 1741, 1449, 1412, 1343, 1280, 1256, 1240, 1225, 1200, 1163, 1146, 1128, 1100, 1065, 1010, 949, 921, 902, 872, 834, 816, 774, 744,

713 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 191 (10) [*M*$^+$+1], 190 (59) [*M*$^+$], 172 (9), 163 (3), 162 (21), 161 (8), 149 (7), 148 (50), 147 (31), 146 (10), 145 (8), 144 (6), 143 (4), 135 (3), 134 (19), 133 (29), 132 (3), 131 (6), 130 (11), 129 (5), 121 (5), 120 (12), 119 (16), 118 (4), 117 (10), 115 (4), 108 (6), 107 (8), 106 (14), 105 (29), 104 (31), 103 (6), 96 (3), 95 (30), 94 (16), 93 (22), 92 (37), 91 (100), 81 (17), 80 (23), 79 (65), 78 (26), 77 (48), 68 (3), 67 (19), 66 (7), 65 (16), 55 (11), 54 (3), 53 (13), 52 (4), 51 (7), 43 (4), 42 (4), 41 (39), 40 (4), 39 (21), 29 (8); GC-MS (CI): *m*/*z* (%): 192 (13) [*M*H$^+$+1], 191 (100) [*M*H$^+$], 190 (5) [*M*$^+$]; HRMS: *m*/*z*: calcd for $C_{13}H_{18}O$: 190.1358, found: 190.1352 [*M*$^+$].

(3a*S,5a*R**,9a*S**)-3-Methylendecahydro-4*H*-cyclopenta[*c*]-inden-4-one (40b)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 1.27 (dddd, *J* = 3.7/6.9/7.4/13.0 Hz, 1H, 6-H), 1.37–1.48 (m, 5H, 7-H/8-H/9-H), 1.48 (ddd, *J* = 7.0/8.9/13.0 Hz, 1H, 1-H), 1.63–1.73 (m, 2H, 6-H/9-H), 1.91 (ddd, *J* = 6.9/8.2/13.0 Hz, 1H, 1-H), 2.03 (dddd, *J* = 6.0/6.2/7.4/7.7 Hz, 1H, 5a-H), 2.17 (ddd, *J* = 1.5/7.7/18.2 Hz, 1H, 5-H), 2.39 (dd, *J* = 7.4/18.2 Hz, 1H, 5-H), 2.36–2.49 (m, 2H, 2-H), 2.74 (d, *J* = 1.5 Hz, 1H, 3a-H), 4.95 (ddd, *J* = 2.3/2.4/2.4 Hz, 1H, 1′-H), 5.07 (ddd, *J* = 2.4/2.4/2.4 Hz, 1H, 1′-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 22.31 (C-7)*, 22.81 (C-8)*, 27.52 (C-6), 31.76 (C-2), 33.27 (C-9), 36.00 (C-1), 36.63 (C-5a), 42.85 (C-5), 51.35 (C-9a), 62.97 (C-3a), 109.23 (C-1′), 148.10 (C-3), 217.57 (C-4); *: signal assignments are mutual interchangeable; GC-MS (70 eV): *m*/*z* (%): 191 (8) [*M*$^+$+1], 190 (59) [*M*$^+$], 175 (3), 163 (3), 162 (22), 161 (12), 149 (8), 148 (70), 147 (46), 146 (12), 135 (3), 134 (22), 133 (39), 132 (3), 131 (6), 121 (6), 120 (16), 119 (30), 118 (3), 117 (10), 115 (5), 108 (4), 107 (13), 106 (24), 105 (42), 104 (6), 103 (7), 95 (8), 94 (17), 93 (30), 92 (31), 91 (100), 82 (6), 81 (15), 80 (28), 79 (71), 78 (25), 77 (67), 69 (3), 68 (4), 67 (20), 66 (7), 65 (23), 63 (3), 55 (18), 54 (5), 53 (24), 52 (5), 51 (8), 43 (3), 42 (4), 41 (40), 40 (4), 39 (20), 29 (10); GC-MS (CI): *m*/*z* (%): 192 (3) [*M*H$^+$+2], 192 (13) [*M*H$^+$+1], 191 (100) [*M*H$^+$], 190 (4) [*M*$^+$].

PET oxidative reaction of 3-(2-cyclohexenylmethyl)bicyclo[6.1.0]non-2-en-1-yl trimethylsilyl ether (13b): Compound **13b** (470 mg, 1.54 mmol) was dissolved in acetonitrile (211 mL), apportioned together with DCA (150 mg, 0.66 mmol) to 15 pyrex tubes and irradiated according to GP I for 68 h. The crude product was filtered over silica (cyclohexane/ethyl acetate 95:5) and purified by HPLC (cyclohexane/ethyl acetate 95:5) yielding (4a*R**,6a*S**,6b*S**,10a*S**,11a*S**)-tetradecahydro-6*H*-indeno[1,7a-*a*]-inden-6-one (**42b**; 36 mg, 10%) and (4a*R**,6a*S**,6b*R**,10a*R**,11a*S**)-tetradecahydro-6*H*-indeno[1,7a-*a*]inden-6-one (**43b**; 43 mg, 12%) as colorless oils.

(4a*R,6a*S**,6b*S**,10a*S**,11a*S**)-Tetradecahydro-6*H*-indeno[1,7a-*a*]inden-6-one (42b)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HSQC, HMBC, NOESY); ^{1}H NMR (500 MHz, C_6D_6 (trace of $CDCl_3$)*, ref.: TMS): δ = 0.81 (dddd, *J* = 3.4/12.7/12.8/12.9 Hz, 1H, 7-H^A), 0.99 (ddddd, *J* = 3.3/3.3/12.8/12.8/12.8 Hz, 1H, 8-H^B), 1.061 (m, 1H, 1-H^B), 1.08 (m, 1H, 3-H), 1.09 (m, 1H, 2-H), 1.19 (m, 1H, 1-H^A), 1.22 (m, 1H, 9-H), 1.27 (m, 1H, 4-H^B), 1.29 (m, 1H, 3-H), 1.32 (ddd, *J* = 0.6/7.5/12.6 Hz, 1H, 11-H^B), 1.36 (m, 1H, 9-H), 1.36–1.44 (m, 2H, 10-H), 1.37 (m, 1H, 4-H^A), 1.39 (m, 1H, 2-H), 1.45 (dd, *J* = 12.8/12.9 Hz, 1H, 11-H^A), 1.55 (dddddd, *J* = 1.3/3.4/3.4/3.4/3.4/12.8 Hz, 1H, 8-H^A), 1.77 (m, 1H, 7-H^B)*, 1.790 (m, 1H, 4a-H)*, 1.93 (ddddd, *J* = 2.7/5.3/5.4/7.5/12.9 Hz, 1H, 10a-H), 1.98 (ddd, *J* = 1.0/7.0/16.9 Hz, 1H, 5-H^A)*, 2.02 (dddd, *J* = 5.4/5.4/7.5/12.7 Hz, 1H, 6b-H), 2.13 (ddd, *J* = 1.0/1.4/7.6 Hz, 1H, 6a-H), 2.19 (ddd, *J* = 1.4/13.5/16.9 Hz, 1H, 5-H^B); *For better signal separation the NMR measurements was carried out in benzene containing traces of chloroform. In pure benzene the chemical slightly differ from the stated above. This is important for the *marked signal, because these signals overlap and change their sequence; ^{13}C NMR (125 MHz, $CDCl_3$, ref.: TMS): δ = 20.06 (C-3), 21.22 (C-9), 23.82 (C-2), 25.56 (C-4), 25.69 (C-7), 25.85 (C-8), 26.84 (C-10), 36.04 (C-1), 40.72 (C-11), 40.85 (C-10a), 41.26 (C-6b), 43.67 (C-4a), 45.31 (C-5), 49.01 (C-11a), 66.87 (C-6a), 216.70 (C-6); IR (film): $\tilde{\nu}$ = 2924, 2857, 1732, 1446, 1411, 1249, 1227, 1196, 1164, 1080 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 232 (4) [*M*$^+$], 189 (3), 138 (14), 137 (100), 136 (30), 119 (3), 109 (3), 107 (3), 105 (5), 96 (7), 95 (8), 94 (5), 93 (10), 92 (4), 91 (17), 81 (10), 80 (4), 79 (20), 77 (7), 67 (10), 65 (4), 55 (9), 53 (4), 43 (5), 41 (14), 39 (6), 29 (4); GC-MS (CI): *m*/*z* (%): 234 (17) [*M*H$^+$+1], 233 (100) [*M*H$^+$]; HRMS: *m*/*z*: calcd for $C_{16}H_{24}O$: 232.1827, found: 232.1825 [*M*$^+$].

(4a*R,6a*S**,6b*R**,10a*R**,11a*S**)-Tetradecahydro-6*H*-indeno[1,7a-*a*]inden-6-one (43b)**: NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HSQC, HMBC, NOESY); ^{1}H NMR (500 MHz, C_6D_6, ref.: TMS): δ = 1.08 (m, 1H, 3-H), 1.09 (m, 1H, 2-H), 1.13 (m, 1H, 10-H), 1.15 (m, 1H, 9-H), 1.20 (m, 1H, 4-H), 1.21 (dd, *J* = 6.0/13.1 Hz, 1H, 11-H^B), 1.23–1.35 (m, 2H, 1-H), 1.23 (m, 1H, 3-H), 1.26 (m, 1H, 8-H), 1.30 (m, 1H, 2-H), 1.33 (m, 1H, 10-H), 1.35 (m, 1H, 4-H), 1.35 (m, 1H, 9-H), 1.413 (m, 1H, 8-H), 1.43 (m, 1H, 7-H^B), 1.48 (dd, *J* = 7.3/13.1 Hz, 1H, 11-H^A), 1.62 (dddd, *J* = 3.6/5.3/7.0/12.3 Hz, 1H, 4a-H), 1.69 (m, 1H, 7-H^A), 1.82 (ddddd, *J* = 0.6/5.9/6.0/7.3/12.8 Hz, 1H, 10a-H), 1.96 (dd, *J* = 6.9/17.0 Hz, 1H, 5-H^A), 2.04 (d, *J* = 7.7 Hz, 1H, 6a-H), 2.07 (m, 1H, 6b-H), 2.1 (ddd, *J* = 1.3/12.3/17.0 Hz, 1H, 5-H^B); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: TMS): δ = 20.98 (C-3), 22.94 (C-8), 23.72 (C-2), 23.94 (C-9), 25.30 (C-4), 26.98 (C-7), 28.75 (C-10), 36.52 (C-1), 40.38 (C-10a), 40.77 (C-4a), 41.86 (C-6b), 43.17 (C-11), 43.26 (C-5), 49.20 (C-11a), 62.97 (C-6a), 217.73 (C-6); IR (film): $\tilde{\nu}$ = 2927, 2856, 1733, 1446, 1415, 1362, 1332, 1232, 1199, 1158, 1129, 1020 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 233 (2) [*M*$^+$+1], 232 (10) [*M*$^+$], 189 (4), 162 (4), 161 (4), 149 (3), 147 (9), 138 (13), 137 (100), 136 (30), 134 (4), 133 (4), 121 (10), 120 (3), 119 (4), 109 (3), 108 (4), 107 (4), 105 (8), 96 (4), 95 (8), 94 (6), 93 (16), 92 (6), 91 (25), 81 (12), 80 (6), 79 (22), 77 (10), 67 (18), 66 (3), 65 (4), 55 (16), 53 (5), 43 (3), 42 (4), 41 (27), 39 (9), 29 (5); GC-MS (CI): *m*/*z* (%): 234 (18) [*M*H$^+$+1], 233 (100) [*M*H$^+$]; HRMS: *m*/*z*: calcd for $C_{16}H_{24}O$: 232.1827, found: 232.1826 [*M*$^+$].

PET oxidative reaction of 4-(2-propenyl)bicyclo[5.1.0]oct-2-en-1-yl trimethylsilyl ether (14a,b): The two isomeric trimethylsilyl ether **14a** and **14b** (overall 277 mg) and DCA (90 mg; 10 mg/tube) were apportioned in different isomer ratios to 9 pyrex tubes and dissolved in acetonitrile (12 mL each) and irradiated according to GP I for 72 h. The GC analysis of each tube showed that irrespective of the isomeric ratio (3a*R**,4*R**,6a*R**)-4-allylhexahydro-2(1*H*)pentalenone (**44**) was formed as the major product. The contents of the tubes were combined and the solvent was evaporated. The crude product was purified by column chromatography (cyclohexane/ethyl acetate 925:75) yielding (3a*R**,4*R**,6a*R**)-4-allylhexahydro-2(1*H*)pentalenone (**44**; 78 mg, 40%) as a colorless oil. NMR (^{1}H,^{1}H-COSY, ^{13}C,^{13}C-DEPT, HMQC, HMBC, NOESY); ^{1}H NMR (500 MHz, $CDCl_3$, ref.: $CHCl_3$): δ = 1.26–1.40 (m, 2H, 5-H/6-H), 1.65 (ddddd, *J* = 7.0/7.3/7.5/7.6/7.7 Hz, 1H, 4-H), 1.91 (dddd, *J* = 4.0/6.8/7.0/12.3 Hz, 1H, 5-H), 1.97 (ddd, *J* = 2.1/5.6/19.1 Hz, 1H, 1-H^B), 1.97–2.06 (m, 2H, 1′-H/6-H), 2.06 (ddd, *J* = 2.1/4.6/18.8 Hz, 1H, 3-H^B), 2.15 (ddddd, *J* = 1.1/1.5/6.8/7.0/13.8 Hz, 1H, 1′-H), 2.25 (dddd, *J* = 4.8/7.6/9.2/9.2 Hz, 1H, 3a-H), 2.43 (ddd, *J* = 1.5/9.2/18.8 Hz, 1H, 3-H^A), 2.45 (ddd, *J* = 1.5/10.1/19.2 Hz, 1H, 1-H^A), 2.692 (m, 1H, 6a-H), 4.95 (dddd, *J* = 1.1/1.1/2.2/10.1 Hz, 1H, 3′-H), 4.97 (dddd, *J* = 1.5/1.5/2.2/17.1 Hz, 1H, 3′-H), 5.75 (dddd, *J* = 7.0/7.0/10.1/17.1 Hz, 1H, 2′-H); ^{13}C NMR (125 MHz, $CDCl_3$, ref.: $CDCl_3$): δ = 32.54 (C-6)*[1], 32.56 (C-5)*[1], 39.24 (C-1′)*[2], 39.26 (C-6a)*[2], 43.88 (C-3), 44.86 (C-1), 45.56 (C-3a), 46.73 (C-4), 115.59 (C-3′), 137.35 (C-2′), 220.89 (C-2); *: signal assignments are mutual interchangeable; IR (film): $\tilde{\nu}$ = 3080, 2950, 2866, 1740, 1700, 1678, 1660, 1640, 1547, 1438, 1404, 1242, 1159, 994, 911 cm^{-1}; GC-MS (70 eV): *m*/*z* (%): 164 (<1) [*M*$^+$], 123 (7), 122 (58), 121 (3), 96 (6), 95 (94), 94 (13), 93 (28), 92 (4), 91 (11), 82 (7), 81 (100), 80 (84), 79 (63), 78 (11), 77 (26), 68 (8), 67 (45), 66 (11), 65 (9), 55 (21), 54 (14), 53 (35), 51 (5), 43 (5), 42 (11), 41 (98), 40 (8), 39 (55), 29 (7); GC-MS (CI): *m*/*z* (%): 166 (12) [*M*H$^+$+1], 165 (100) [*M*H$^+$]; HRMS: *m*/*z*: calcd for $C_{11}H_{16}O$: 164.1201, found: 164.1198 [*M*$^+$].

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