Regio- and Stereoselective Cyclization Reactions of Unsaturated Silyl Enol Ethers by Photoinduced Electron Transfer – Mechanistic Aspects and Synthetic Approach☆

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Oxidative photoinduced electron transfer (PET) reactions have been performed with various silyl enol ethers and silyloxy-2*H*-chromones bearing an olefinic or silylacetylenic side chain. The reactions result in regioselective ring closure with the formation of bi- to tetracyclic ring systems with a well-defined ring juncture, e.g. perhydrophenanthrenones **13** or benzo-annellated xanthenones **24**. Our investigations have focussed on the optimization of this cyclization method with regard to irradiation time and product yield. The irradiation times could be reduced by using the cosensitized PET method. Modifying the substrate at the silyl group led to enhanced yields. In addition, we found that solvent and pressure dependences are important tools, allowing control of the regiochemistry. Both the synthesis of 6-*endo* products by radical cationic reaction pathways, as well as 5-*exo* ring closure by radical intermediates was achieved. Mechanistic details, including findings from deuterium labelling experiments, are discussed.

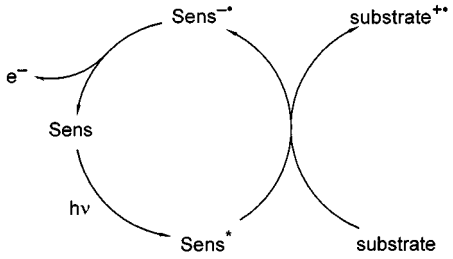
Introduction

During the last decade, photoinduced electron transfer (PET) has been the subject of extensive research.[1] PET reactions have been applied more and more in organic synthesis due to their frequently observed high efficiency and selectivity, and because of the mild reaction conditions. Starting from neutral compounds, PET leads to radical ion pairs as reactive intermediates by excitation of only one reactant.[2]

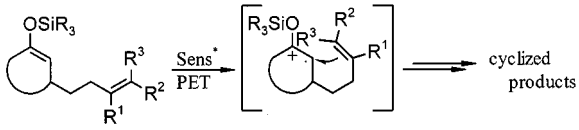
Radical cations can be generated by sensitized PET, using a catalytic amount of a PET sensitizer, such as 1,4-dicyanonaphthalene (DCN) or 9,10-dicyanoanthracene (DCA) in homogeneous solution.[3] Irradiation at a suitable wavelength leads to the singlet-excited sensitizer, which oxidizes the substrate. In polar solvents, back electron transfer is suppressed, favouring a subsequent reaction of the radical cation, such as isomerization[4], addition of nucleophiles[5], or cyclization.[6] In particular, cyclization reactions proceeding via radical cations generated from electron-rich olefins, arenes or amines, have been shown to be a useful synthetic tool for the construction of carbocyclic and heterocyclic ring systems in a highly regio- and stereoselective fashion.[7]

In previous studies, silyl enol ethers were shown to be chemically or electrochemically oxidized with the formation of silyloxy radical cations.[8][9] Due to our major interest in PET processes, we recently reported preliminary investigations concerning PET-oxidative cyclization reactions of unsaturated silyl enol ethers. The often observed 6-*endo* preference was shown to be an important feature of cyclization reactions involving silyloxy radical cations as reactive intermediates.[10]

Scheme 1. Substrate radical cations generated by PET



Scheme 2. PET-oxidative cyclization of monocyclic silyl enol ethers bearing an olefinic side chain



In this article we focus on the synthetic scope and limitations of the novel PET-oxidative cyclization reaction of monocyclic 1,6-unsaturated silyl enol ethers and silyloxy-2*H*-chromenes. The influence of the substituents at the double bond on the regiochemistry of the cyclization step is investigated, as well as the regio- and diastereoselective design of linear and angular annellated ring systems. Opti-

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mization of this cyclization method is achieved by using a sensitizer couple, such as DCA/phenanthrene, and by introducing a larger aliphatic silyl group.

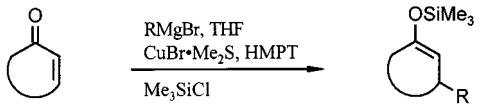
Mechanistic aspects are elucidated by deuterium labelling experiments. In addition, investigations on the regioselective control by solvent and high-pressure effects are described. The reaction is found to proceed by radical cationic as well as by radical reaction pathways, depending on the reaction conditions, leading either to 6-*endo* or 5-*exo* products. It should be emphasized that this is the first time that high-pressure effects on radical cationic cyclizations have been described in organic chemistry.

Results and Discussion

Starting Materials and PET Conditions

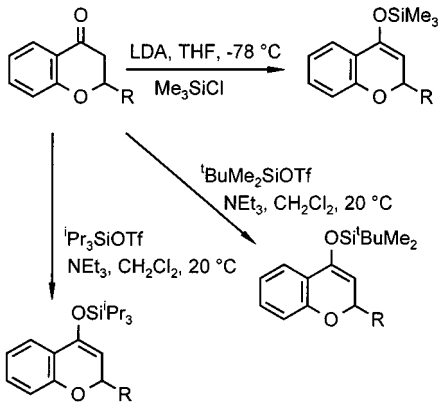
As starting materials, 3-substituted monocyclic silyl enol ethers were used. These are accessible by copper(I) and hexamethylphosphoric triamide catalysed conjugate addition of Grignard reagents to cycloalk-2-en-1-ones. The intermediate enolate is directly trapped with trimethylsilyl chloride as silylating agent. Distillation of the crude product leads to the silyl enol ether as a colourless liquid.[11]

Scheme 3. Generation of silyl enol ethers by 1,4-addition of Grignard reagents to enones



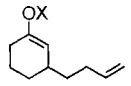
The 2-substituted chroman-4-ones were synthesized from chromone using the same procedure, with subsequent direct hydrolysis of the crude product. The trialkylsilyloxy-2*H*-chromenes are accessible by silylation of the 2-substituted chroman-4-ones with trimethylsilyl chloride and LDA at −78 °C.[12] Triisopropyl- and *tert*-butyldimethylsilyloxy-2*H*-chromene are generated by silylation of the corresponding chroman-4-one with the respective trialkylsilyl triflate and triethylamine at room temperature.[13]

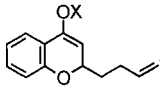
Scheme 4. Silylation of 2-substituted chroman-4-ones



Due to their electron-rich double bond, silyl enol ethers are easily oxidized with the formation of silyloxy radical cations.[8][9][10] In order to determine the exact oxidation potentials, we examined several silyl enol ethers by cyclic voltammetry. Their oxidation potentials were found to vary from 1.21 to 1.58 V and are more than 1 V lower than those of unfunctionalized double bonds. Therefore, electron transfer from our starting materials to the singlet-excited PET sensitizer ^{1}DCA* (E_{S1} = 2.89 V)[14] in acetonitrile, calculated from the simplified Rehm-Weller equation[15], is exergonic.

Table 1. Oxidation potentials and ΔG_{ET} from ^{1}DCA* in acetonitrile

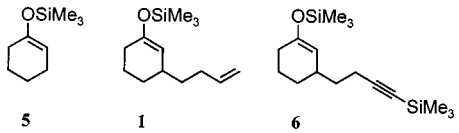




		E^{ox} (V)	ΔG_{ET} (kJ mol^{-1})			E^{ox} (V)	ΔG_{ET} (kJ mol^{-1})
X = $SiMe_3$	**1**	1.58	-48.9	X = $SiMe_3$	**3**	1.21	-81.7
X = Si^tBuMe_2	**2**	1.48	-55.7	X = Si^iPr_3	**4**	1.22	-80.8

In addition, luminescence quenching experiments showed that the fluorescence of ^{1}DCA* is quenched in acetonitrile at an almost diffusion-controlled rate upon addition of silyl enol ethers **1**, **5**, and **6**. The relatively low rate constant for the fluorescence quenching with **6** might be due to the steric bulk of the side chain.

Table 2. Fluorescence quenching rate constants of ^{1}DCA* in acetonitril



	5	**1**	**6**
k_q [10^9 L mol^{-1} s^{-1}]	8.40	8.79	6.29

Cyclization under PET Conditions

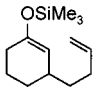
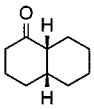
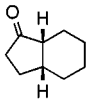
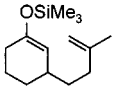
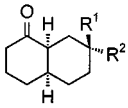
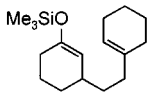
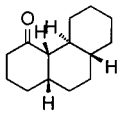
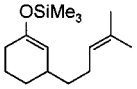
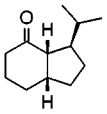
A deoxygenated 0.05 M solution of the respective silyl enol ether containing 10−20 mol-% of the PET sensitizer was irradiated in a Rayonet photochemical reactor. Irradiation at an appropriate wavelength (DCN: 350 nm; DCA: 419 nm) leads to excitation of the sensitizer. Due to the lower reduction potential of the sensitizer in its singlet-excited state, electron transfer occurs. In polar solvents, separation of the generated radical ion pairs is favoured. Hence, the silyloxy radical cations can react intramolecularly leading to cyclic products. Conversion of the starting material and formation of the products was monitored by gas chromatography using an internal standard.

Cyclizations in Acetonitrile

The results of the PET-oxidative cyclization reactions of silyl enol ethers bearing an olefinic side chain in pure acetonitrile are summarized in Table 3. Besides these bicyclic and tricyclic ketones, no other cyclic products and merely traces of the acyclic ketone could be detected by gas chromatography.

The products were isolated by HPLC and the structures were unambiguously determined by spectroscopic analysis. The assignment of the configuration of *cis*-1-decalone (**7**) was made on the basis of comparisons of its mass spectrum with those of purchased *trans*-1-decalone and a *cis*/*trans*

Table 3. PET-oxidative cyclizations in acetonitrile

entry	silyl enol ether		cyclized product		yield
1		**1**		**7**	25%
2		**8**		**9**	11%
3		**10**		R^1=CH_3, R^2=H **11a** 9% R^1=H, R^2=CH_3 **11b** 10%	
4		**12**		**13a**	26%
5		**14**		**15**	29%

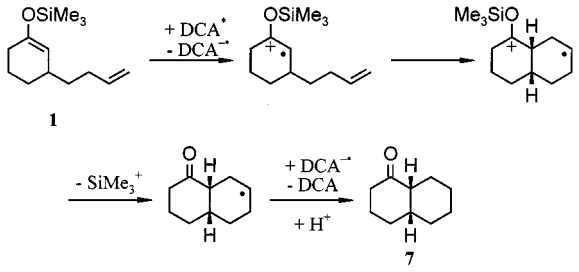
mixture. Additionally, the product could be isomerized in diethyl ether with basic aluminum oxide to form the thermodynamically more stable *trans* isomer. The structure of *cis*-1-hexahydroindanone (**9**) was established by comparison with reported ^{13}C-NMR data.[16] The configurations of the two separated isomeric products **11a** and **11b** were determined by double-resonance NMR experiments in combination with isomerization experiments. The structure of the dodecahydrophenanthren-4-one (**13a**) was ascertained by X-ray analysis. The stereochemistry of 3-isopropyl-4-hexahydroindanone (**15**) was determined by COSY experiments and comparison with the NMR data of **21a** and **21b**.

In most cases, we observed the exclusive formation of 6-*endo* products. Only the *gem*-disubstituted silyl enol ether **14** led exclusively to a 5-*exo* product (entry 5). In all cases, ring closure occurs between C-2 and the less substituted carbon atom of the side chain, leading to the thermodynamically favoured radical.

Besides the observed regioselectivity, the stereospecific *cis* ring juncture is an important feature of this cyclization method. In all cases, we obtained *cis*-connected rings, irrespective of the kinetic or thermodynamic stability of the product.[17] For example, the *cis*-1-hexahydroindanone (**9**) is thermodynamically more stable than the corresponding *trans* isomer, whereas in the case of 1-decalone the reverse is true. Consequently, *cis*-1-decalone (**7**) can be quantitatively converted to its *trans* isomer simply by stirring in diethyl ether under basic conditions at room temperature.

We assume the PET-generated silyloxy radical cation to be the reactive intermediate, which attacks the side-chain double bond intramolecularly. Subsequent desilylation leads to a radical species. Finally, formation of the product can either occur via back electron transfer regenerating the sensitizer followed by protonation, or via hydrogen transfer.

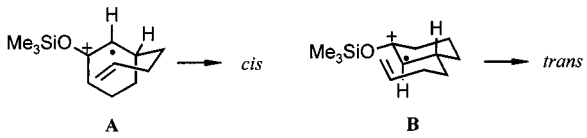
Scheme 5. Proposed mechanism of the PET-oxidative cyclization of **1**



At first glance, these monocyclic radicals may be compared to linear 1,2-disubstituted hexenyl systems that lead to *trans* products according to Beckwith′s concept of stereoelectronic control.[18] On the other hand, even Beckwith referred to the contrasting behaviour of monocyclic systems.[19] Since our radical cationic cyclizations also lead exclusively to *cis* isomers, we assume that the chair-like conformer **A** should be more favoured than **B**. Beckwith explained this unexpected stereoselectivity based on the inspection of models. These show that the overlap between the partially occupied orbital and the π* orbital in the reactive conformation is attained most efficiently if the two substituents are pseudoaxially oriented.

Clearly, in our radical cationic system, these stereoelectronic aspects also have a decisive effect. In analogy to the radical cyclization, the reactive chair-like conformer **A** should be more favoured than **B**, leading to a *cis* ring connection.

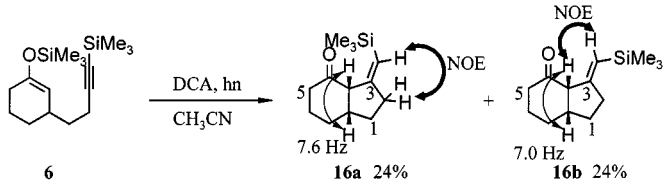
Scheme 6. Possible reactive conformers



Besides the investigated compounds with an olefinic side chain, the silyl enol ether **6** bearing a silylacetylenic side chain is also a promising candidate for the PET-oxidative cyclization. Higher functionalized products, the vinylsilane ketones **16a** and **16b** (1:1 ratio) were each obtained in a yield of 24% in acetonitrile. We presume that the 5-*exo* regioselectivity is due to the presence of the linear triple bond, which does not allow an attack at C-4 of the side chain for geometric reasons.

The products were characterized on the basis of their NMR spectra. The *cis* stereochemistry was confirmed by the coupling constants $^3J_{3a\text{-}H,7a\text{-}H}$ of 7.6 and 7.0 Hz. Since in both isomers the signal of the olefinic proton only exhibits allylic couplings, it follows that exclusively 5-*exo* ring closure had taken place. Furthermore, characteristic NOEs are seen. In compound **16a**, an NOE between the signals of the olefinic proton and one of the protons at C-2 is ob-

Scheme 7. PET-oxidative cyclization leading to the vinylsilane ketones **19a** and **19b**



served. In compound **16b**, there is an NOE between the signals of the olefinic proton and 3a-H.

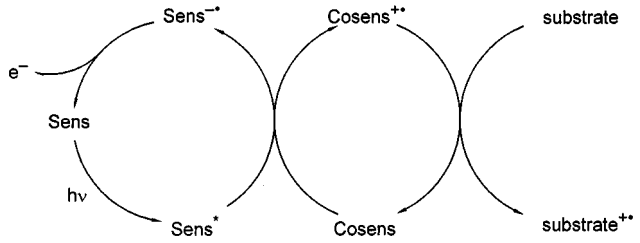
It should be noted that the nature of the R_3Si group may have an influence on the course of the reaction. In an earlier investigation of acyclic unsaturated silyl enol ethers, we showed that changing the trialkylsilyl group from trimethylsilyl to the more stable *tert*-butyldimethylsilyl or to the triisopropylsilyl (TIPS) group results in increasing amounts of tricyclic ketones.[10c] This clearly indicates the involvement of radical cationic intermediates.

Optimizations in Pure Acetonitrile

Prior to our studies, this cyclization method had two known disadvantages: high irradiation times and moderate yields. Therefore, we tried to improve the method and in the following the results of our efforts to optimize the process are described.

Shortened irradiation times were achieved by irradiation of the silyl enol ether **1** in the presence of a sensitizer/cosensitizer couple (cosensitized PET conditions: 0.01 equiv. Sens., 10 equiv. Cosens.). We assume that with an excess of cosensitizer, e.g. biphenyl or phenanthrene, two subsequent electron transfer steps are involved. Initially, the electron transfer occurs from the cosensitizer to the sensitizer. Subsequent electron transfer then leads to the substrate radical cation. The acceleration of the reaction is presumably due to the better separation of the radical ions. Direct back electron transfer plays only a subordinate role and hence the enol ether radical cations can cyclize more efficiently.

Scheme 8. Cosensitization scheme



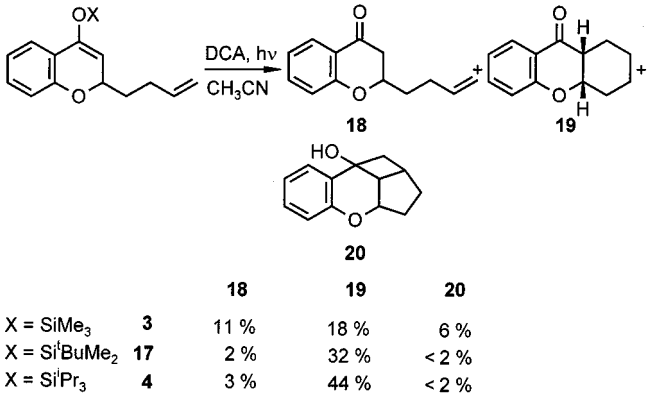
The best results in terms of the reaction time were achieved with 1,4-dicyanotetramethylbenzene (DCTMB)/phenanthrene as the sensitizer/cosensitizer couple (irradiation at 350 nm, cf. Table 4). Similar observations were made by Demuth and co-workers concerning the cyclization cascade of polyenes.[20] We assume that back electron transfer from the sterically hindered $DCTMB^{-\bullet}$ to the silyloxy radical cation is even more unfavourable than in the case of planar $DCA^{-\bullet}$. Unfortunately, the isolated yield of *cis*-1-decalone (**7**) could not be increased by cosensitization.

Table 4. Sensitized and cosensitized PET-oxidative cyclization of **1**

sensitizer (0.1 eq.)	cosensitizer (10 equiv.)	irradiation time [h] (total consumption)	*cis*-1-decalone (**7**) (isolated yield)
DCA	–	110	25%
DCA	biphenyl	75	23%
DCA	phenanthrene	75	29%
DCTMB	phenanthrene	46	26%

In order to investigate the effect of specific trialkylsilyl groups on the cyclization, we synthesized the 2-(3-butenyl)-4-trialkylsilyloxy-2*H*-chromenes **3**, **4**, and **17**. Irradiation of 2-(3-butenyl)-4-trimethylsilyloxy-2*H*-chromenes (**3**) in acetonitrile in the presence of DCA resulted in the formation of the three products **18**, **19** and **20**. Besides the acyclic ketone **18**, 16% of the 6-*endo* product **19**, and 6% of the unexpected alcohol **20** were isolated. At this stage of our investigations we can only speculate about the mechanism of formation of **20**. A [2+2] cycloaddition or two subsequent radical cyclization steps might be involved.

Scheme 9. Cyclization of the 2-(3-butenyl)-4-trialkylsilyloxy-2*H*-chromenes **3**, **4** and **17**



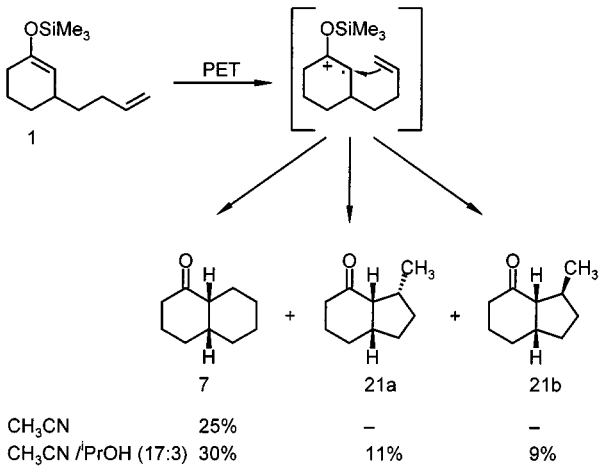
		18	19	20
X = $SiMe_3$	**3**	11 %	18 %	6 %
X = Si^tBuMe_2	**17**	2 %	32 %	< 2 %
X = Si^iPr_3	**4**	3 %	44 %	< 2 %

The compounds **3**, **4**, and **17** were irradiated under the same conditions in the presence of DCA. At total consumption, the yields of the products were determined by gas chromatography. Two trends concerning the product yields can clearly be seen. Firstly, the formation of **18** decreases with increasing size of the silyl group. Secondly, the formation of the 6-*endo* product **19** more than doubles. Obviously the product ratio is controlled by the stability of the silyl enol ethers. The TMS group is subjected to cleavage more easily than the bulky TBDMS and TIPS groups and therefore **18** is formed in relatively large amounts compared to the cyclization product **19**. From these results we conclude that TBDMS and TIPS stabilize the silyl enol ether even in its radical cation state and as a consequence, more silyloxy radical cations should react by cyclization, leading to **19**. It is also conceivable that acetonitrile assists the cleavage of the Si–O bond, leading to the acyclic ketone **18**. Therefore, the smaller the steric hindrance of the silyl group, the more acyclized ketone should be formed.

Cyclizations of 1 in Acetonitrile/Alcohol

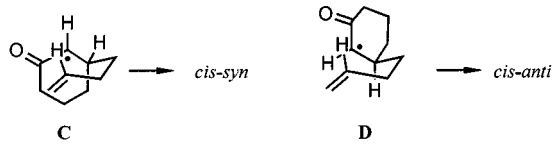
Irradiation of **1** in the presence of DCA in acetonitrile/2-propanol (17:3) led to a total yield of bicyclic ketones of 50%. To our surprise, two 5-*exo* diastereomers **21** were additionally formed. Comprehensive NMR analysis allowed the stereochemical assignment on the basis of the coupling constants $^3J_{3a\text{-}H,7a\text{-}H}$ and NOE experiments.

Scheme 10. PET-oxidative reaction of **1** in acetonitrile and acetonitrile/2-propanol (17:3)



The preferred stereochemistry of the 5-*exo* diastereomers is a *cis-syn* arrangement of the protons 7a-H, 3a-H, and 3-H in **21a**. This preference was observed throughout our investigations and might be explained according to the stereochemical analysis of radical cyclizations by Beckwith[19], which was later confirmed by several groups.[21] Due to a better overlap of the SOMO of the radical and the LUMO of the olefin, conformation **C** should be preferred.

Scheme 11. Possible reactive conformers



The results obtained in acetonitrile/2-propanol encouraged us to systematically investigate the effect of alcohols on the regiochemistry and to elucidate the reaction mechanism involved. Salient results are given in Scheme 12 and Table 5. On going from pure acetonitrile to acetonitrile/2-propanol (8:2), the amount of *cis*-1-decalone remains almost constant, whereas the formation of the 5-*exo* products clearly increases. At a solvent ratio of 1:1, the combined yield of the bicyclic ketones reaches a maximum of 68%. Unfortunately, desilylation leading to the acyclic ketone becomes the main process when the proportion of 2-propanol is increased still further. Irradiation in the absence of DCA shows that the formation of the acyclic ketone is predominantly the result of simple alcoholysis of the silyl enol ether. In pure 2-propanol, virtually no cyclization is observed.

This experiment demonstrates the significant influence of 2-propanol on the regioselectivity. The almost exclusive formation of the 6-*endo* product can be changed into predominant formation of the 5-*exo* diastereomers.

Scheme 12. Product distribution of the PET-oxidative cyclization of **1** depending on the solvent ratio CH_3CN/*i*PrOH

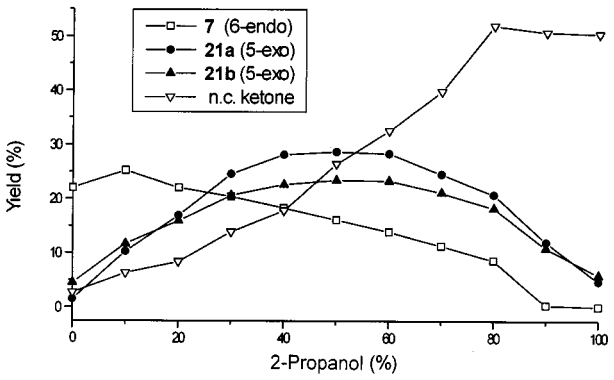


Table 5. *endo*/*exo* ratios taken from Scheme 12

solvent ratio (MeCN/*i*PrOH)	10:0	9:1	7:3	5:5	3:7	1:9
endo/*exo* ratio **7**/(**21a**+**21b**)	1:<0.2	1:0.9	1:2.1	1:3.1	1:4.0	1:4.9

An investigation with alcohols (30%) of varying bulkiness led to similar results. For example, in the presence of DCA, irradiation of **1** in acetonitrile/*tert*-butyl alcohol as in acetonitrile/2-propanol led to the predominant formation of *cis*-1-decalone (**7**) (*endo*/*exo* = 1:0.7). Unlike in the presence of a primary alcohol such as in acetonitrile/propanol (*endo*/*exo* = 1:2.4) or in acetonitrile/methanol (*endo*/*exo* = 1:3.6), formation of the 5-*exo* products **21** is clearly favoured. As summarized in Table 6, on going from a tertiary to a primary alcohol, the yield of *cis*-1-decalone (**7**) decreases, whereas the yields of the *cis*-3-methyl-4-hexahydroindanone diastereomers **21** increase. The total yield of isolated products is enhanced to 64% in acetonitrile/methanol.

These results provide strong evidence for a nucleophile-assisted Si−O bond cleavage of the silyloxy radical cation, opening up a new radical reaction pathway. In a previous paper, Schmittel et al. demonstrated by kinetic studies that chemically and electrochemically generated radical cations of sterically hindered silyl enol ethers undergo Si−O bond cleavage assisted by various nucleophiles.[22] Furthermore, an analogous nucleophile-assisted Si−C cleavage mechanism of trialkyl(benzyl)silane radical cations was elucidated by Dinnocenzo et al.[23]

Table 6. Product yields and *endo*/*exo* ratios of the cyclization of **1** in CH_3CN/ROH (17:3) with various alcohols

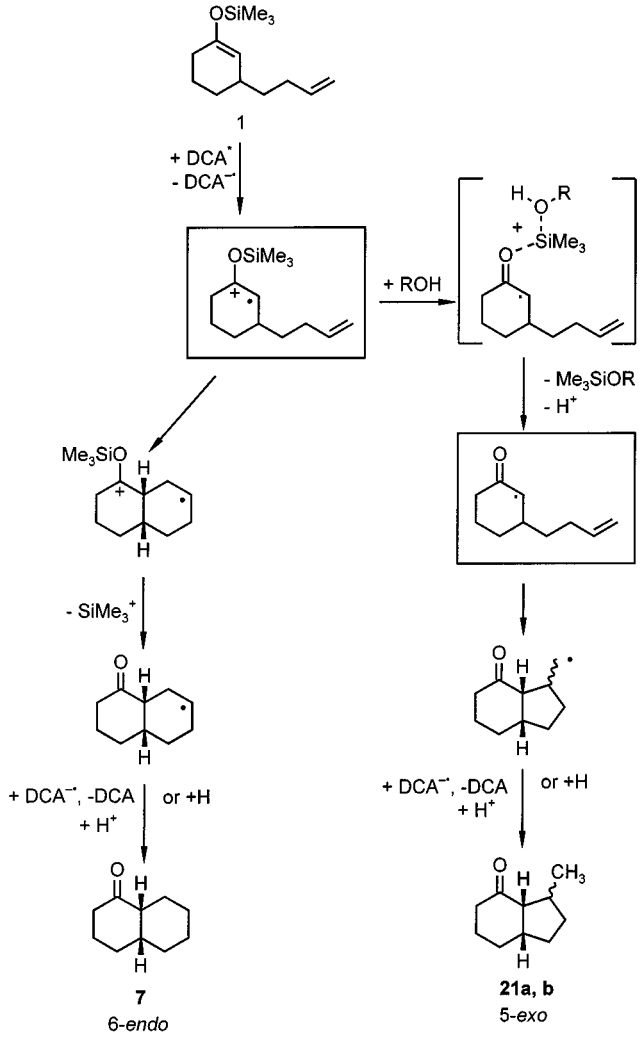
ROH	*t*BuOH	*i*PrOH	PrOH	MeOH
7 (6-*endo*)	27%	30%	13%	14%
21a (5-*exo*)	9%	11%	20%	29%
21b (5-*exo*)	11%	9%	12%	21%
total yield	46%	49%	46%	64%
endo/*exo* ratio **7**/(**21a**+**21b**)	1:0.7	1:0.7	1:2.4	1:3.6

In agreement with these mechanistic interpretations, we assume that the alcohol acts as a nucleophile and assists the

Si−O bond cleavage of the silyloxy radical cation, leading to an α-oxo radical as reactive intermediate. According to Baldwin's rule, this α-oxo radical predominantly cyclizes in a 5-*exo* mode, as confirmed for the radical cyclization of the corresponding α-iodo ketone via α-oxo radicals by Sha.[24]

Summarizing these results, the presence of an alcohol opens up a competing reaction pathway besides the already discussed radical cationic reaction pathway (cf. Scheme 13). This new radical reaction pathway is favoured by increasing the amount of alcohol and by decreasing its steric hindrance. As a consequence, by simple addition of an alcohol, it is possible to control and to invert the regiochemistry of the cyclization, and to improve the yield of the cyclic products. As far as we are aware, this is the first example of a synthetic application of nucleophile effects on PET-oxidative cyclization reactions.

Scheme 13. Competing reaction pathways − radical cationic versus radical cyclization



Deuterium Labelling Studies

In order to elucidate the reaction mechanism in more detail, we performed deuterium labelling experiments. **1** was irradiated with DCA as PET sensitizer in various deuterated and partially deuterated solvents. The reaction mixtures were analysed by GC-MS and the spectra were compared to those of the non-deuterated products. The results are summarized in Table 7. Firstly, it is clear that protons/deuterons in the final products are not derived from the acetonitrile or [D_3]methanol. Secondly, on the other hand, partially deuterated cyclic products were obtained by using deuterated proton donors such as [D_1]methanol and deuterated water. The detected acyclic ketone shows almost no deuterium incorporation, thus we can exclude a subsequent H/D exchange via the acidic protons of the α-carbon atom of the carbonyl group. The silyl group may also be excluded as a proton source, as shown by Heidbreder in a PET-oxidative cyclization of a similar silyl enol ether with a perdeuterated trimethylsilyl group.[25]

Table 7. Deuterium labelling experiments of the PET-oxidative cyclization of **1**

solvent	partial product deuteration (GC-MS analysis)
CD_3CN	negative
CH_3CN/CD_3OH (9:1)	negative
CH_3CN/CH_3OD (9:1)	positive
CH_3CN with D_2O (10 equiv.)	positive

In order to determine the position and extent of deuterium incorporation, we isolated **21a** and **21b** following irradiation in CH_3CN containing D_2O (10 equiv.). NMR analysis confirmed that the deuterium was located in the methyl group. By comparing the integrals of the proton signals of the methyl group and of the monodeuterated methyl group, the amount of deuterated product was estimated to be 11% in **21a** and 16% in **21b**. Unfortunately, the D-labelling of **7** could not be determined quantitatively due to the coupling with the other protons of the cyclohexane ring.

These deuterium labelling experiments indicate that in the presence of an alcohol, back electron transfer from the sensitizer radical anion to the radical product precursor and final protonation is only one of the reaction pathways followed. This is further supported by the fact that a catalytic amount of the sensitizer is sufficient. These results are in agreement with the reaction mechanism for the PET-promoted cyclization of α-silylated amines established by Mariano.[26] In pure acetonitrile, we have not as yet been able to establish the origin of the protons, but we assume that they may arise from the portion of the starting material not accounted for.

Further Cyclizations in Acetonitrile/Alcohol

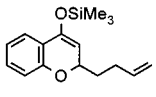
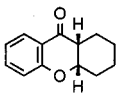
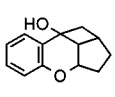
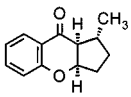
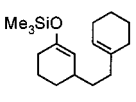
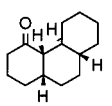
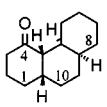
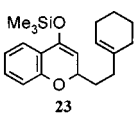
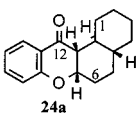
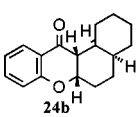
To check the effect of an alcohol on the regiochemistry of the cyclization and on the product yields, we investigated the PET-oxidative cyclization of **3**, **12**, and **23** in acetonitrile/alcohol. The preparative experiments were preceded by a gas-chromatographic inspection using a sequence of solvent ratios. The respective acetonitrile/alcohol ratios were chosen due to their favourable product ratio and yield. The results are summarized in Table 8.

As discussed above, cyclization of the silyloxy-2*H*-chromene in pure acetonitrile leads predominantly to the formation of xanthenone derivative **19** as a result of 6-*endo* cyclization. As expected, irradiation under the same conditions in acetonitrile/methanol (17:3) leads to **19** in decreased yield. Furthermore, a new cyclopenta[*b*]chromenone derivative **22** is formed. Although the yield amounts to only 3%, the formation of this 5-*exo* product evidently supports our proposal of an alcohol-assisted radical reaction pathway competing with the radical cationic one. The enhanced formation of the alcohol **20** indicates that it derives from two subsequent radical cyclization steps. Unfortunately, the total yield of cyclic products is not increased by using acetonitrile/methanol as solvent.

Irradiation of the silyl enol ether **12** in the presence of an alcohol does not lead to a change in the regiochemistry, though the total yield is doubled. In addition to the *cis-anti-trans* diastereomer **13a** (the exclusive product of the cyclization in pure acetonitrile), the *cis-anti-cis* diastereomer **13b** is formed in a yield of 24%. Due to its *cis* geometry it is a dynamic molecule, as is evident from high-temperature NMR analysis. The reason why the *cis-anti-cis* diastereomer **13b** is only detected in the presence of an alcohol has yet to be fully clarified.

Entry 10 indicates that the PET-oxidative cyclization method can also be applied to the synthesis of tetracyclic systems. The benzo[*a*]-annellated xanthenones **24a** and **24b** are built up with a definite stereochemistry. According to entry 8, no 5-*exo* product is formed in the presence of methanol. We assume that the formation of spirocyclic products is sterically unfavourable. Again, the structure of the dynamic molecule **24b** was ascertained by high-temperature NMR analysis.

Table 8. PET-oxidative cyclizations in acetonitrile/alcohol

entry	silyl enol ether	cyclized product (isolated yield)			
					
	3	**19**	**20**	**22**	
6	CH_3CN	16 %	6 %	-	
7	CH_3CN / CH_3OH (17:3)	6 %	8 %	3 %	
					
	12	**13a**	**13b**		
8	CH_3CN	26 %	-		
9	CH_3CN / CH_3OH (17:3)	27 %	24 %		
					
	23	**24a**	**24b**		
10	CH_3CN / CH_3OH (19:1)	14 %	6 %		

High-Pressure Experiments

As a fundamental property, pressure influences the values of various thermodynamic and kinetic parameters of chemical reactions. The pressure dependence gives information on the volume profile of a process and has often been used to elucidate reaction mechanisms.[27] In general, reactions with a negative reaction volume ΔV are accelerated under pressure. Furthermore, taking the activation volume $\Delta V^{\neq}$ into account, pressure allows us to distinguish between competing reaction pathways and to enhance the selectivity. Extensive studies have been carried out on pericyclic reactions using Eyring's transition state theory, e.g. on Diels-Alder reactions and Cope rearrangements.[28][29] In the following, we report our preliminary studies on the high-pressure effects on the PET-oxidative cyclization of silyl enol ethers.

As a model system, we chose the enol ether **1** and the sensitizer/cosensitizer couple DCN/phenanthrene. DCN is completely soluble in acetonitrile and through cosensitization a conversion of about 35% was attained after only 2 h of irradiation. The conversion and the product formation was monitored by gas chromatography using an internal standard. The result of the irradiation at 1 bar in the high-pressure cell with light of wavelength 313 nm resembles the preparative results described above.

Irradiation under high pressure[34] led to some unexpected results. In pure acetonitrile, by varying the pressure from 1 to 1500 bar, the *endo*/*exo* ratio changed from 3.4:1 to 0.5:1. The almost exclusive formation of the 6-*endo* product **7** is reversed to the predominant formation of the 5-*exo* products **21** simply by applying high pressure. The absolute formation of the 6-*endo* product **7** decreases, whereas more 5-*exo* products **21** are formed. In the presence of methanol, this pressure effect on the regioselectivity levels out. Furthermore, at 1500 bar, the regiochemistry of the ring closure is almost independent of the methanol concentration. These results lead to the conclusion that under pressure the alcohol plays only a subordinate role.

Table 9. *endo*/*exo* ratios of the PET-oxidative cyclization of **7** in CH_3CN/CH_3OH at various pressures

MeOH [%]	*endo*/*exo* = **7**/(**21a**+**21b**) 1 bar	750 bar	1500 bar
0	3.4:1	2.2:1	0.5:1
1.0	1.8:1		0.7:1
2.5	0.9:1	0.6:1	0.6:1
5.0	0.6:1		0.3:1

At this stage of our investigations, at least two explanations are conceivable for the preferred 5-*exo* regioselectivity under high pressure. On the one hand, the formation of the 5-*exo* products might be due to a new radical cationic reaction mechanism. On the other hand, the solvent acetonitrile may act as nucleophile, assisting the Si−O bond cleavage[30]. In the latter case, acetonitrile acts at 1500 bar in the same way as an alcohol does at 1 bar. Consequently, the radical cationic reaction pathway competes with the

radical reaction pathway leading to more of the 5-*exo* product under pressure.

The preference for 5-*exo* ring closures under high pressure is confirmed by MOLVOL calculations of the difference in the activation volume (*6-endo* versus 5-*exo*).[31] This parameter amounts to $+31 \pm 10$ cm^3 mol^{-1} in acetonitrile, and to $+7 \pm 4$ cm^3 mol^{-1} in acetonitrile containing 2.5% methanol. In both solvent systems, the activation volume for the 5-*exo* ring closure is smaller, i.e. more negative. Therefore, this reaction should be the more favoured one under pressure. Due to the stepwise nature of the reaction mechanism, these preliminary results leave much scope for speculation concerning the precise effect of pressure on the rate-determining step. As yet, there has been no possibility of determining which transition state might be most pressure-dependent.

Conclusion

PET-oxidative cyclizations of silyl enol ethers and silyloxy-2*H*-chromenes have been performed via silyloxy radical cations as reactive intermediates. These radical cations cyclize in a regioselective fashion, leading predominantly to 6-*endo* products. A second important feature is the stereoselective *cis* ring juncture, which is presumably due to a favoured reactive chair-like conformer with the substituents pseudoaxially arranged. Using the cosensitized PET method, the irradiation times were reduced by up to ca. 40%. Modifying the 2-substituted silyloxy-2*H*-chromenes at the silyl group resulted in enhanced yields of cyclic products.

The regiochemistry of cyclization can be controlled either by adding alcohols or by applying high pressure. The alcohol presumably acts as a nucleophile and assists the Si−O bond cleavage leading to α-oxo radicals as reactive intermediates. The precise details of the high-pressure effect are presently not known. The increased nucleophilicity of acetonitrile at high pressure and the smaller (more negative) activation volume for the 5-*exo* cyclization might be the controlling factors. Systematic studies aimed at elucidating this new process are currently in progress.

By applying this method, linear and angular annellated ketones and xanthenones are accessible with high regio- and stereoselectivity. The stereochemical assignments are confirmed by two-dimensional and high-temperature NMR experiments. The structure of perhydrophenanthrenone **13a** has been confirmed by X-ray analysis.

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Experimental Section

All reactions were carried out in dry solvents under argon. The solvents were dried by standard methods. Hexamethylphosphoric triamide was used as purchased from Aldrich. − The irradiations were performed in a Rayonet RPR-100 Photoreactor (Southern New England) fitted with 16 RPR-4190 A or RPR-3500 A lamps and a merry-go-round inset using Pyrex tubes of ca. 12 ml volume. All solutions were deoxygenated with argon. For HPLC, Kontron 420 and Merck L-6000 pumps, a Bischoff RI 8110 RI-detector, and a 250 × 20 mm Merck LiChrosorb Si 60-5 column were used, at a flow of 10 ml min^{-1}; solvent: cyclohexane/ethyl acetate. The PET sensitizers were prepared following known procedures: DCTMB[20], DCN[32], DCA[33].

Cyclic voltammetry: Potentiostat PGSTAT 20 and VA Stand 663 from Metrohm, solvent: acetonitrile, 0.25 M $LiClO_4$, vs. Ag/AgCl. − Fluorescence spectroscopy: Perkin-Elmer LS 50B. − Melting points: Büchi 510. − IR: Perkin-Elmer 1600 (FT-IR), Perkin-Elmer 298. − ^{1}H- and ^{13}C NMR: Bruker AC 200 P, WM 300, and DRX 500; δ in ppm; *J* in Hz. − MS: Finnigan MAT C 312 and MAT 8230. − GC/MS: Varian MAT CH 7A with GC Varian 1400, SS 200 data system, and Finnigan MAT 8230 with GC Varian 3400, SS 300 data system, or Varian Saturn 2. − Elemental analysis: Heraeus CHN-O-Rapid or Perkin-Elmer DIA CHN 240.

General Procedure A. − Catalytic Conjugate Addition of Copper Reagents to α,β-Unsaturated Ketones and Chromone: Under argon, magnesium turnings (0.85 g, 35 mmol) were placed in dry THF (10 ml). To initiate the Grignard reaction, a few drops of the respective bromoolefin or -alkyne were added. The remaining bromoolefin or -alkyne (35 mmol) was diluted with THF (25 ml) and added at room temp. over a period of 1 h. The mixture was then refluxed for 1 h while further THF (25 ml) was added. After cooling to −78°C, $CuBr \cdot Me_2S$ (0.26 g, 1.25 mmol) was added to the reaction mixture. Hexamethylphosphoric triamide (10.5 ml, 60 mmol) and a mixture of the respective enone (25 mmol) and trimethylsilyl chloride (6.4 ml, 50 mmol) were then added dropwise. After stirring for 2 h at −78°C, triethylamine (7 ml) was added. The mixture was allowed to warm to room temp. while hexane (100 ml) was added, and was then quickly washed with one portion of iced water. The organic layer was separated and dried with $MgSO_4$. The solvent was removed and the crude product was purified by distillation in vacuo.

General Procedure B. − Silylation with Triethylamine/Trialkylsilyl Triflates: Under argon, 2-(3-butenyl)chroman-4-one (**19**) (1.04 g, 5.1 mmol) and triethylamine (0.8 ml, 7.5 mmol) were dissolved in dry CH_2Cl_2 (13 ml). At room temp., the respective trialkylsilyl trifluoromethanesulfonate (5.0 mmol) was added and the solution was stirred for 1 h. CH_2Cl_2 (80 ml) was added and the organic solution was extracted twice with saturated aqueous $NaHCO_3$ solution and once with water, and then dried with $MgSO_4$. After removal of the solvent, the residue was distilled in vacuo.

General Procedure C. − PET-Oxidative Reaction: A 0.05 M argon-saturated solution of the respective silyl enol ether in dry CH_3CN or in a CH_3CN/alcohol mixture was irradiated in the presence of a PET sensitizer (10−20 mol-%), e.g. 9,10-dicyanoanthracene (DCA), excited at 419 nm, or 1,4-dicyanonaphthalene (DCN), excited at 350 nm, for at least 60 h. The consumption was monitored by gas chromatography with *n*-decane as internal standard. After complete consumption, the solvent was evaporated and the residue was filtered through silica gel. The products were isolated by HPLC (cyclohexane/ethyl acetate).

3-(3-Butenyl)-1-trimethylsilyloxy-1-cyclohexene (**1**): Following procedure A, cyclohex-2-en-1-one (2.4 ml, 25 mmol) was treated with 1-bromo-3-butene (4.72 g, 35 mmol). 3-(3-Butenyl)-1-trimethylsilyloxy-1-cyclohexene (**1**) (4.58 g, 82%) was obtained by distillation in vacuo (b.p. 52°C, 0.05 mbar) as a colourless liquid. − IR (film): ν = 3076, 2926, 2850, 1664, 1641, 1453, 1369, 1297, 1251, 1187, 987, 905, 845, 747 cm^{-1}. − ^{1}H NMR (300 MHz; $CDCl_3$):

δ = 0.20 [s, 9 H, $Si(CH_3)_3$], 1.10 (m, 1 H), 1.30−1.82 (m, 6 H), 1.92−2.12 (m, 4 H), 4.78 (m, 1 H, 2-H), 4.91 (d, *J* = 10.3 Hz, 1 H, 4′-H_a), 4.98 (d, *J* = 16.9 Hz, 1 H, 4′-H_b), 5.79 (ddt, *J* = 16.9, 10.3, 6.7 Hz, 1 H, 3′-H). − ^{13}C NMR (75 MHz; $CDCl_3$): δ = 0.3 [$Si(CH_3)_3$], 21.7 (CH_2), 28.8 (CH_2), 30.0 (CH_2), 31.2 (CH_2), 33.8 (C-3), 36.4 (CH_2), 109.2 (CH), 114.2 (C-4′), 139.1 (C-3′), 150.5 (C-1). − MS (EI): *m/z* (%) = 224 (4) [M^+], 209 (4), 194 (4), 182 (17), 169 (100) [$M^+ - C_4H_7$], 75 (18), 73 (94) [$Si(CH_3)_3^+$], 45 (18), 39 (17). − CV: E^{ox} = +1.58 V. − $C_{13}H_{24}OSi$ (224.3): calcd. C 69.61, H 10.78; found C 69.02, H 10.74.

3-(3-Butenyl)-1-tert-butyldimethylsilyloxy-1-cyclohexene (**2**): Followig procedure A, cyclohex-2-en-1-one (2.4 ml, 25 mmol) was treated with 1-bromo-3-butene (4.72 g, 35 mmol). The intermediate enolate was trapped with *tert*-butyldimethylsilyl chloride (7.54 g, 50 mmol). 3-(3-Butenyl)-1-*tert*-butyldimethylsilyloxy-1-cyclohexene (**2**) (2.61 g, 28%) was obtained by distillation in vacuo (b.p. 89°C, 1.20 mbar) as a colourless liquid. − IR (film): ν = 2928, 2857, 1665, 1641, 1472, 1367, 1257, 1197, 1175, 993, 908, 837, 778 cm^{-1}. − ^{1}H NMR (300 MHz; C_6D_6): δ = 0.22 [s, 6 H, $Si(CH_3)_2$], 1.07 [s, 9 H, $C(CH_3)_3$], 1.18 (m, 1 H), 1.32−1.74 (m, 6 H), 2.10 (m, 4 H), 4.98 (m, 1 H, 3-H), 5.06 (m, 1 H, 4′-H_a), 5.12 (ddt, *J* = 16.9, 1.7, 1.7 Hz, 1 H, 4′-H_b), 5.88 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1 H, 3′-H). − ^{13}C NMR (75 MHz; C_6D_6): δ = −3.4 [$Si(CH_3)_2$], 18.63 [$C(CH_3)_3$], 22.4 (CH_2), 26.3 [$C(CH_3)_3$], 29.4 (CH_2), 30.8 (CH_2), 32.0 (CH_2), 34.8 (C-3), 37.2 (CH_2), 109.3 (C-2), 114.8 (C-4′), 139.5 (C-3′), 151.4 (C-1). − MS (CI, isobutane): *m/z* (%) = 267 (100) [MH^+]; MS (EI): *m/z* (%) = 266 (11) [M^+], 224 (14), 212 (17), 211 (100) [$M^+ - C_4H_7$], 209 (16), 75 (65), 73 (74). − CV: E^{ox} = +1.48 V. − HRMS: 266.20650 ($C_{16}H_{30}OSi$; calcd. 266.20660).

3-(3-Butenyl)-1-trimethylsilyloxy-1-cyclopentene (**8**): Following procedure A, cyclopent-2-en-1-one (2.1 ml, 25 mmol) was allowed to react with 1-bromo-3-butene (4.72 g, 35 mmol). 2-(3-Butenyl)-4-trimethylsilyloxy-1-cyclopentene (**8**) (2.89 g, 55%) was obtained by distillation in vacuo (b.p. 46°C, 0.05 mbar) as a colourless liquid. − IR (film): ν = 3074, 2919, 2848, 1641, 1345, 1252, 1186, 992, 927, 845, 754 cm^{-1}. − ^{1}H NMR (300 MHz; C_6D_6): δ = 0.20 [s, 9 H, $Si(CH_3)_3$], 1.42 (m, 3 H), 2.00 (m, 3 H), 2.41 (m, 2 H), 2.66 (m, 1 H), 4.75 (m, 1 H, 2-H), 5.02 (d, *J* = 10.3 Hz, 1 H, 4′-H_a), 5.08 (d, *J* = 17.0 Hz, 1 H, 4′-H_b), 5.84 (ddt, *J* = 17.0, 10.3, 6.9 Hz, 1 H, 3′-H). − ^{13}C NMR (75 MHz; $CDCl_3$): δ = 0.3 [$Si(CH_3)_3$], 28.7 (CH_2), 32.5 (CH_2), 34.0 (CH_2), 37.3 (CH_2), 42.2 (C-3), 106.8 (C-2), 114.6 (C-4′), 139.6 (C-3′), 155.6 (C-1). − MS (EI): *m/z* (%) = 210 (5) [M^+], 181 (4), 155 (91) [$M^+ - C_4H_7$], 75 (25), 73 (100) [$Si(CH_3)_3^+$], 45 (21), 43 (9). − $C_{12}H_{22}OSi$ (210.3); calcd. C 68.54, H 10.54; found C 68.12, H 10.64.

3-(3-Methyl-3-butenyl)-1-trimethylsilyloxy-1-cyclohexene (**10**): Following procedure A, cyclohex-2-en-1-one (2.4 ml, 25 mmol) was allowed to react with 1-bromo-1-methyl-3-butene (5.22 g, 35 mmol). 3-(3-Methyl-3-butenyl)-1-trimethylsilyloxy-1-cyclohexene (**10**) (3.32 g, 40%) was obtained by distillation in vacuo (b.p. 67°C, 0.05 mbar) as a colourless liquid. − IR (film): ν = 3065, 2915, 2845, 1660, 1445, 1365, 1250, 1185, 1085, 1050, 960, 890, 840, 750 cm^{-1}. − ^{1}H NMR (300 MHz; C_6D_6): δ = 0.22 [s, 9 H, $Si(CH_3)_3$], 1.10 (m, 1 H), 1.35−1.68 (m, 6 H), 1.68 (s, 3 H, CH_3), 2.06 (m, 4 H), 4.82 (m, 2 H, 4′-H), 4.97 (m, 1 H, 2-H). − ^{13}C NMR (75 MHz; C_6D_6): δ = 0.5 [$Si(CH_3)_3$], 22.1 (CH_2), 22.5 (CH_3), 29.2 (CH_2), 30.5 (CH_2), 34.8 (C-3), 35.6 (CH_2), 35.7 (CH_2), 108.8 (C-2), 110.2 (C-4′), 146.0 (C-3′), 151.1 (C-1). − MS (EI): *m/z* (%) = 238 (2) [M^+], 223 (2) [$M^+ - CH_3$], 195 (4), 169 (80) [$M^+ - C_5H_9$], 75 (21), 73 (100) [$Si(CH_3)_3^+$], 45 (18), 41 (17), 39 (20).

3-(2-Cyclohex-1-enylethyl)-1-trimethylsilyloxy-1-cyclohexene (**12**): Following procedure A, cyclohex-2-en-1-one (2.4 ml, 25 mmol) was treated with 1-(2-bromoethyl)cyclohex-1-ene (6.62 g, 35 mmol). 3-(2-Cyclohex-1-enylethyl)-1-trimethylsilyloxy-1-cyclohexene (**12**) (2.99 g, 43%) was obtained by distillation in vacuo (b.p. 118°C, 0.10 mbar) as a colourless liquid. − IR (film): ν = 3040, 2920, 2825, 2815, 1660, 1440, 1365, 1250, 1190, 910, 894, 843, 750 cm^{-1}. − ^{1}H NMR (300 MHz; C_6D_6): δ = 0.19 [s, 9 H, $Si(CH_3)_3$], 1.10 (m, 1 H), 1.30−2.30 (m, 18 H), 4.97 (m, 1 H, 2-H), 5.44 (m, 1 H, 2′′-H). − ^{13}C NMR (75 MHz; C_6D_6): δ = 0.5 [$Si(CH_3)_3$], 22.1 (CH_2), 23.0 (CH_2), 23.5 (CH_2), 25.6 (CH_2), 28.7 (CH_2), 29.6 (CH_2), 30.6 (CH_2), 34.6 (C-3), 35.8 (CH_2), 35.9 (CH_2), 109.0 (C-2), 121.1 (C-2′′), 138.0 (C-1′′), 151.0 (C-1). − MS (CI, isobutane): *m/z* (%) = 279 (100) [MH^+]; MS (EI): *m/z* (%) = 278 (1) [M^+], 183 (15), 182 (100), 169 (42) [$M^+ - C_8H_{13}$], 73 (36) [$Si(CH_3)_3^+$], 67 (8), 45 (8).

3-(4-Methylpent-3-enyl)-1-trimethylsilyloxy-1-cyclohexene (**14**): Following procedure A, cyclohex-2-en-1-one (2.4 ml, 25 mmol) was allowed to react with 1-bromo-4-methyl-3-pentene (5.71 g, 35 mmol). 3-(4-Methylpent-3-enyl)-1-trimethylsilyloxy-1-cyclohexene (**14**) (5.16 g, 58%) was obtained by distillation in vacuo (b.p. 78°C, 0.06 mbar) as a colourless liquid. − IR (film): ν = 3040, 2900, 2840, 1660, 1440, 1370, 1250, 1185, 1050, 960, 895, 840, 750 cm^{-1}. − ^{1}H NMR (300 MHz; C_6D_6): δ = 0.23 [s, 9 H, $Si(CH_3)_3$], 1.13 (m, 1 H), 1.62 (s, 3 H, CH_3), 1.33−1.70 (m, 6 H), 1.72 (s, 3 H, CH_3), 2.11 (m, 4 H), 5.02 (m, 1 H, 2-H), 5.25 (tsept, *J* = 7.2, 1.4 Hz, 1 H, 3′-H). − ^{13}C NMR (75 MHz; C_6D_6): δ = 0.5 [$Si(CH_3)_3$], 17.7 (CH_3), 22.1 (CH_2), 24.9 (CH_3), 26.0 (CH_2), 29.3 (CH_2), 30.6 (CH_2), 34.6 (C-3), 37.7 (CH_2), 108.9 (C-2), 125.4 (C-3′), 131.0 (C-4′), 151.0 (C-1). − MS (EI): *m/z* (%) = 252 (15) [M^+], 237 (2), 209 (6), 195 (52), 182 (64), 169 (64) [$M^+ - C_6H_{11}$], 75 (21), 73 (100) [$Si(CH_3)_3^+$], 45 (19), 41 (37), 39 (21). − $C_{13}H_{28}OSi$ (252.4); calcd. C 71.39, H 11.18; found C 70.99, H 11.53.

3-(4-Trimethylsilyl-3-butynyl)-1-trimethylsilyloxy-1-cyclohexene (**6**): Following procedure A, cyclohex-2-en-1-one (1.2 ml, 12.5 mmol) was treated with 4-bromo-1-trimethylsilylbut-1-yne (3.59 g, 17.5 mmol). 3-(4-Trimethylsilyl-3-butynyl)-1-trimethylsilyloxy-1-cyclohexene (**6**) (2.69 g, 52%) was obtained by distillation in vacuo (b.p. 81°C, 0.05 mbar) as a colourless liquid. − IR (film): ν = 3040, 2956, 2932, 2174, 1663, 1449, 1369, 1250, 1193, 895, 843, 759 cm^{-1}. − ^{1}H NMR (200 MHz; $CDCl_3$): δ = 0.13 [s, 9 H, $Si(CH_3)_3$], 0.17 [s, 9 H, $Si(CH_3)_3$], 1.10 (m, 1 H), 1.40−1.80 (m, 4 H), 1.96 (m, 2 H), 2.24 (m, 4 H, 2′-H, 6-H), 4.76 (m, 1 H, 2-H). − ^{13}C NMR (75 MHz; C_6D_6): δ = 0.3 [$Si(CH_3)_3$], 0.4 [$Si(CH_3)_3$], 17.8 (C-2′), 21.7 (CH_2), 28.4 (CH_2), 30.4 (CH_2), 34.0 (C-3), 36.1 (CH_2), 84.6 (C-4′), 107.9 (C-3′), 108.0 (C-2), 151.3 (C-1). − MS (EI): *m/z* (%) = 294 (8) [M^+], 221 (35), 183 (11), 182 (43), 169 (48) [$M^+ - C_4H_4Si(CH_3)_3$], 147 (12), 133 (12), 131 (13), 117 (12), 75 (18), 73 (100) [$Si(CH_3)_3^+$], 45 (21), 43 (12). − HRMS: 294.18360 ($C_{16}H_{30}OSi_2$, calcd. 294.18353).

2-(3-Butenyl)chroman-4-one (**18**). − *Direct Hydrolysis of the Crude 3-Substituted Silyloxy-2H-chromene:* Copper(I)-catalysed conjugate addition of the Grignard reagent of 1-bromo-3-butene (4.72 g, 35 mmol) to chromone (3.65 g, 25 mmol) was carried out according to procedure A. The crude product was dissolved in ethanol (10 ml) containing 2 M hydrochloric acid (1 ml) and the mixture was stirred for 2 h at room temp. Water (30 ml) was then added and the solution was extracted three times with Et_2O (20 ml). The combined organic layers were dried with $MgSO_4$ and the solvent was evaporated. The residue was worked-up by distillation in vacuo (b.p. 94°C, 0.02 mbar). 2-(3-Butenyl)-chroman-4-one (**18**) (3.03 g, 60%) was obtained as a yellow liquid. − IR (film): ν = 3076, 2925, 1693, 1641, 1608, 1577, 1473, 1464, 1306, 1228, 1149, 1118, 1030, 915, 765 cm^{-1}. − ^{1}H NMR (200 MHz; $CDCl_3$): δ =

1.78 (m, 1 H), 2.00 (m, 1 H), 2.30 (m, 2 H), 2.70 (m, 2 H, 3-H), 4.47 (m, 1 H, 2-H), 5.02 (ddt, J = 10.1, 1.6, 1.3 Hz, 1 H, 4′-H_a), 5.13 (ddt, J = 16.9, 1.6, 1.6 Hz, 1 H, 4′-H_b), 5.85 (ddt, J = 16.9, 10.1, 6.6 Hz, 1 H, 3′-H), 6.98 (dm, J = 8.1 Hz, 1 H, 8-H), 7.00 (dd, J = 8.6, 7.2 Hz, 1 H, 6-H), 7.43 (ddd, J = 8.1, 7.2, 0.7 Hz, 1 H, 7-H), 7.88 (ddd, J = 8.6, 1.8, 0.7 Hz, 1 H, 5-H). − ^{13}C NMR (50 MHz; $CDCl_3$): δ = 29.05 (C-2′), 34.0 (C-1′), 42.9 (C-3), 77.1 (C-2), 115.6 (C-4′), 117.9 (C-8), 121.0 (C-4a), 121.2 (C-6), 127.0 (C-5), 136.0 (C-7), 137.2 (C-3′), 161.6 (C-8a), 192.4 (C-4). − MS (EI): *m/z* (%) = 202 (46) [M^+], 160 (55), 147 (50) [$M^+ - C_4H_7$], 121 (100) [retro-DA + H], 120 (72) [retro-DA], 92 (37), 65 (15), 64 (10), 41 (10), 39 (13). − $C_{13}H_{14}O$ (202.2); calcd. C 77.20, H 6.98; found C 77.14, H 7.17.

2-(3-Butenyl)-4-trimethylsilyloxy-2H-chromene (**3**): Following procedure A, chromone (3.65 g, 25 mmol) was treated with 1-bromo-3-butene (4.72 g, 35 mmol). 2-(3-Butenyl)-4-trimethylsilyloxy-2*H*-chromene (**3**) (5.06 g, 74%) was obtained by distillation in vacuo (b.p. 110°C, 0.07 mbar) as a yellow liquid. − IR (film): ν = 3050, 2957, 2920, 1680, 1648, 1484, 1454, 1358, 1254, 1225, 1094, 985, 882, 846, 757 cm^{-1}. − ^{1}H NMR (200 MHz; $CDCl_3$): δ = 0.27 [s, 9 H, $Si(CH_3)_3$], 1.80 (m, 2 H), 2.24 (m, 2 H), 4.82 (d, J = 3.6 Hz, 1 H, 3-H), 4.91−5.11 (m, 3 H, 2-H, 4′-H), 5.84 (ddt, J = 17.2, 10.1, 7.7 Hz, 1 H, 3′-H), 6.80 (dd, J = 8.0, 1.2 Hz, 1 H, 8-H), 6.89 (ddd, J = 7.5, 7.5, 1.2 Hz, 1 H, 6-H), 7.13 (ddd, J = 8.0, 7.5, 1.7 Hz, 1 H, 7-H), 7.30 (dd, J = 7.5, 1.7 Hz, 1 H, 5-H). − ^{13}C NMR (50 MHz; $CDCl_3$): δ = 0.1 [$Si(CH_3)_3$], 29.1 (C-2′), 35.3 (C-1′), 75.2 (C-3), 102.6 (C-2), 114.9 (C-4′), 115.6 (C-8), 120.5 (C-6), 121.5 (C-4a), 122.3 (C-5), 129.5 (C-7), 138.0 (C-3′), 145.5 (C-8a), 154.7 (C-4). − MS (CI, isobutane): *m/z* (%) = 275 (100) [MH^+]; MS (EI): *m/z* (%) = 274 (5) [M^+], 259 (4), 232 (5), 221 (6), 220 (22), 219 (100) [$M^+ - C_4H_7$], 217 (6), 203 (3), 75 (4), 73 (30). − CV: E^{ox} = +1.21 V. − HRMS: 274.13880 ($C_{16}H_{22}O_2Si$, calcd. 274.13892); calcd. C 70.03, H 8.08; found C 69.50, H 8.01.

2-(3-Butenyl)-4-tert-butyldimethylsilyloxy-2H-chromene (**17**): Following procedure B, 2-(3-butenyl)chroman-4-one (**18**) (1.04 g, 5.1 mmol) was silylated with *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.1 ml, 5.0 mmol). 2-(3-Butenyl)-4-*tert*-butyldimethylsilyloxy-2*H*-chromene (**17**) (0.99 g, 62%) was obtained by vacuum distillation (b.p. 125°C, 0.01 mbar) as a yellowish liquid. − IR (film): ν = 3080, 2944, 2929, 2857, 1644, 1610, 1484, 1454, 1357, 1270, 1234, 1095, 877, 840, 781, 756 cm^{-1}. − ^{1}H NMR (200 MHz; $CDCl_3$): δ = 0.20 [s, 6 H, $Si(CH_3)_2$], 0.99 [s, 9 H, $SiC(CH_3)_3$], 1.65−2.00 (m, 2 H), 2.24 (m, 2 H), 4.80 (d, J = 3.6 Hz, 1 H, 3-H), 4.90−5.10 (m, 3 H, 2-H, 4′-H), 5.85 (ddd, J = 16.8, 10.1, 6.6 Hz, 1 H, 3′-H), 6.78 (dd, J = 8.0, 1.2 Hz, 1 H, 8-H), 6.88 (ddd, J = 7.5, 7.5, 1.2 Hz, 1 H, 6-H), 7.13 (ddd, J = 8.0, 7.5, 1.7 Hz, 1 H, 7-H), 7.34 (dd, J = 7.5, 1.7 Hz, 1 H, 5-H). − ^{13}C NMR (50 MHz; $CDCl_3$): δ = −4.6 [$Si(CH_3)_2$], 18.3 [$SiC(CH_3)_3$], 25.8 [$SiC(CH_3)_3$], 29.2 (C-2′), 35.4 (C-1′), 75.3 (C-3), 102.3 (C-2), 114.9 (C-4′), 115.7 (C-8), 120.6 (C-6), 121.8 (C-4a), 122.4 (C-5), 129.6 (C-7), 138.1 (C-3′), 145.8 (C-8a), 154.6 (C-4). − MS (CI, isobutane): *m/z* (%) = 317 (100) [MH^+]; MS (EI): *m/z* (%) = 316 (4) [M^+], 262 (22), 261 (100) [$M^+ - C_4H_7$], 203 (8), 147 (6), 73 (36). − HRMS: 316.18590 ($C_{19}H_{28}O_2Si$, calcd. 316.18585); calcd. C 72.10, H 8.92; found C 71.32, H 9.00.

2-(3-Butenyl)-4-triisopropylsilyloxy-2H-chromene (**4**): Following procedure B, 2-(3-butenyl)chroman-4-one (**19**) (1.04 g, 5.1 mmol) was silylated with triisopropylsilyl trifluoromethanesulfonate (1.5 ml, 5.0 mmol). 2-(3-Butenyl)-4-triisopropylsilyloxy-2*H*-chromene (**4**) (1.27 g, 71%) was obtained by vacuum distillation (b.p. 125°C, 0.01 mbar) as a yellowish liquid. − IR (film): ν = 3076, 2944, 2866, 1644, 1607, 1485, 1454, 1356, 1231, 1150, 1096, 1013, 912, 882, 755, 685 cm^{-1}. − ^{1}H NMR (200 MHz; $CDCl_3$): δ = 1.06 {d, J = 5.9 Hz, 18 H, $Si[CH(CH_3)_2]_3$}, 1.17 {m, 3 H, $Si[CH(CH_3)_2]_3$}, 1.72 (m, 1 H), 1.92 (m, 1 H), 2.24 (m, 2 H), 4.73 (d, J = 3.6 Hz, 1 H, 3-H), 4.81−5.03 (m, 3 H, 2-H, 4′-H), 5.77 (ddt, J = 16.8, 10.2, 6.6 Hz, 1 H, 3′-H), 6.71 (dd, J = 8.0, 1.2 Hz, 1 H, 8-H), 6.81 (ddd, J = 7.5, 7.5, 1.2 Hz, 1 H, 6-H), 7.06 (ddd, J = 8.0, 7.5, 1.7 Hz, 1 H, 7-H), 7.35 (dd, J = 7.5, 1.7 Hz, 1 H, 5-H). − ^{13}C NMR (50 MHz; $CDCl_3$): δ = 12.8 {$Si[CH(CH_3)_2]_3$}, 18.1 {$Si[CH(CH_3)_2]_3$}, 29.3 (C-2′), 35.4 (C-1′), 75.3 (C-3), 101.3 (C-2), 114.9 (C-4′), 115.9 (C-8), 120.6 (C-6), 121.8 (C-4a), 122.5 (C-5), 129.5 (C-7), 138.1 (C-3′), 146.0 (C-8a), 154.8 (C-4). − MS (CI, isobutane): *m/z* (%) = 359 (100) [MH^+]; MS (EI): *m/z* (%) = 358 (8) [M^+], 316 (4), 304 (26), 303 (100) [$M^+ - C_4H_7$], 273 (3), 185 (3), 173 (3), 147 (6), 131 (10), 121 (8), 115 (18), 102 (12), 87 (9), 73 (10). − CV: E^{ox} = +1.22 V. − HRMS: 358.23250 ($C_{22}H_{34}O_2Si$, calcd. 358.23282); calcd. C 73.69, H 9.56; found C 73.11, H 9.62.

2-(2-Cyclohex-1-enylethyl)chroman-4-one. − Direct Hydrolysis of the Crude 3-Substituted Silyloxy-2H-chromene: Copper(I)-catalysed conjugate addition of the Grignard reagent of 1-(2-bromoethyl)cyclohex-1-ene (9.85 g, 52 mmol) to chromone (5.41 g, 37 mmol) was carried out according to procedure A. The crude product was dissolved in ethanol (10 ml) containing 2 M hydrochloric acid (1 ml) and the mixture was stirred for 2 h at room temp. Water (30 ml) was then added and the solution was extracted three times with Et_2O (20 ml). The combined organic layers were dried with $MgSO_4$ and the solvent was removed. The residue was subjected to HPLC (cyclohexane/ethyl acetate, 95:5). 2-(2-Cyclohex-1-enylethyl)chroman-4-one (1.12 g, 12%) was obtained as a colourless oil. − IR (film): ν = 3080, 2924, 2860, 2820, 1693, 1607, 1577, 1472, 1464, 1315, 1307, 1228, 1148, 1118, 1031, 884, 764 cm^{-1}. − ^{1}H NMR (200 MHz; $CDCl_3$): δ = 1.60 (m, 3 H), 1.80 (m, 1 H), 1.96 (m, 6 H), 2.15 (m, 2 H), 2.69 (m, 2 H, 3-H), 4.43 (m, 1 H, 2′′-H), 5.46 (m, 1 H, 2′′-H), 6.98 (dm, J = 7.7 Hz, 1 H, 8-H), 7.00 (dd, J = 7.4, 7.2 Hz, 1 H, 6-H), 7.47 (dd, J = 7.7, 7.2 Hz, 1 H, 7-H), 7.88 (dm, J = 7.4 Hz, 1 H, 5-H). − ^{13}C NMR (50 MHz; $CDCl_3$): δ = 22.5 (CH_2), 22.9 (CH_2), 25.2 (CH_2), 28.3 (CH_2), 32.9 (CH_2), 33.1 (CH_2), 43.0 (C-3), 77.4 (C-2), 117.9 (C-8), 121.0 (C-4a), 121.1 (C-6), 121.9 (C-2′′), 126.9 (C-5), 136.0 (C-7), 136.3 (C-1′′), 161.7 (C-8a), 192.6 (C-4). − MS (EI): *m/z* (%) = 256 (16) [M^+], 173 (49), 160 (100), 147 (89) [$M^+ - C_8H_{13}$], 121 (46) [retro-DA + H], 120 (15) [retro-DA], 93 (11), 92 (15), 91 (11), 79 (12), 67 (13). − $C_{17}H_{20}O_2$ (256.2); calcd. C 79.65, H 7.86; found C 79.57, H 7.73.

2-(2-Cyclohex-1-enylethyl)-4-trimethylsilyloxy-2H-chromene (**23**). − *Silylation of 2-(2-Cyclohex-1-enylethyl)chroman-4-one with LDA/Trimethylsilyl Chloride:* Under argon, diisopropylamine (6 ml, 4.2 mmol) was diluted with THF (5 ml) and the solution was cooled to −78°C. A 1.6 M solution of *n*BuLi in hexane (2.5 ml, 3.5 mmol) was then added by means of a syringe over a period of 10 min and the mixture was stirred for 30 min. at 0°C. At −78°C, 2-(2-cyclohex-1-enylethyl)chroman-4-one (0.90 g, 3.5 mmol) in THF (1 ml) was added and the mixture was stirred for 1 h. Trimethylsilyl chloride (1.0 ml, 24.4 mmol) was added and stirring was continued for a further 1 h at room temp. After evaporation of the solvent, the residue was dissolved in dry *n*-pentane and the solution was filtered to remove LiCl. The solvent was evaporated from the filtrate and the crude product was subjected to distillation in vacuo (b.p. 152°C, 0.02 mbar). 2-(2-Cyclohex-1-enylethyl)-4-trimethylsilyloxy-2*H*-chromene (**23**) (0.54 g, 47%) was obtained as an orange liquid. − IR (film): ν = 3040, 2926, 2850, 2834, 1648, 1606, 1483, 1454, 1357, 1253, 1232, 1152, 1134, 1098, 882, 845, 757 cm^{-1}. − ^{1}H NMR (200 MHz; $CDCl_3$): δ = 0.30 [s, 9 H, $Si(CH_3)_3$], 1.48−1.68 (m, 5 H), 1.80 (m, 1 H), 1.88−2.06 (m, 4 H), 2.06−2.21 (m, 2 H), 4.85 (d, J = 3.4 Hz, 1 H, 3-H), 4.92 (m, 1 H, 2-H), 5.45

(br. m, 1 H, 2′′-H), 6.79 (dd, J = 7.8, 1.2 Hz, 1 H, 8-H), 6.88 (dt, J = 1.2, 7.5 Hz, 1 H, 6-H), 7.15 (ddd, J = 7.8, 7.5, 1.7 Hz, 1 H, 7-H), 7.32 (dd, J = 7.5, 1.2 Hz, 1 H, 5-H). − ^{13}C NMR (50 MHz; $CDCl_3$): δ = 0.2 [Si(CH_3)$_3$], 22.5 (CH_2), 23.0 (CH_2), 25.2 (CH_2), 28.4 (CH_2), 33.2 (CH_2), 34.3 (CH_2), 75.5 (C-2), 102.8 (C-3), 115.7 (C-8), 120.5 (C-6), 121.2 (C-2′′), 121.6 (C-4a), 122.3 (C-5), 129.5 (C-7), 137.0 (C-1′′), 145.4 (C-4), 154.8 (C-8a). − MS (EI): *m/z* (%) = 328 (2) [M^+], 327 (7), 245 (10), 233 (11), 232 (10), 221 (15), 220 (52), 219 (100) [$M^+ - C_8H_{13}$], 218 (8), 217 (7), 121 (4), 73 (8).

cis-1-Decalone (**7**), *(3R*,3aR*,7aS*)-cis-3-Methyl-4-hexahydroindanone* (**21a**), *and (3R*,3aS*,7aR*)-cis-3-Methyl-4-hexahydroindanone* (**21b**): Following procedure C, a solution of 3-(3-butenyl)-1-trimethylsilyloxy-1-cyclohexene (**1**) (677 mg, 3.00 mmol) in dry CH_3CN/*i*PrOH (17:3) (60 ml) was irradiated in the presence of DCA (103 mg, 0.45 mmol) for 180 h. Separation of the products by HPLC (cyclohexane/ethyl acetate, 95:5) led to the cyclized products in order of increasing polarity: *cis*-1-decalone (**7**) (137 mg, 30%), (3*R**,3a*S**,7a*R**)-*cis*-3-methyl-4-hexahydroindanone (**21b**) (41 mg, 9%), and (3*R**,3a*R**,7a*S**)-*cis*-3-methyl-4-hexahydroindanone (**21a**) (50 mg, 11%) were obtained as colourless oils.

Using CH_3CN/MeOH (17:3) instead of CH_3CN/*i*PrOH (17:3), *cis*-1-decalone (**7**) (64 mg, 14%), (3*R**,3a*S**,7a*R**)-*cis*-3-methyl-4-hexahydroindanone (**21b**) (96 mg, 21%), and (3*R**,3a*R**,7a*S**)-*cis*-3-methyl-4-hexahydroindanone (**21a**) (132 mg, 29%) were isolated.

cis-1-Decalone (**7**): IR (film): $\tilde{\nu}$ = 2931, 2851, 1708 (C=O), 1446, 1314, 1232, 1186, 1153, 1133, 1102, 1007, 827 cm^{-1}. − ^{1}H NMR (300 MHz; $CDCl_3$): δ = 1.15−1.67 (m, 7 H), 1.67−2.15 (m, 6 H), 2.20 (m, 1 H), 2.31 (m, 1 H), 2.46 (m, 1 H). − ^{13}C NMR (75 MHz; $CDCl_3$): δ = 23.1 (CH_2), 23.4 (CH_2), 24.6 (CH_2), 25.2 (CH_2), 29.1 (2 CH_2), 39.1 (C-4a), 40.6 (C-2), 50.7 (C-8a), 213.4 (C-1). − MS (EI): *m/z* (%) = 152 (45) [M^+], 137 (84), 119 (22), 110 (77), 109 (44), 97 (71), 93 (24), 81 (100), 79 (40), 67 (60), 55 (28), 53 (22), 41 (58), 39 (93). − $C_{10}H_{16}O$ (152.2): calcd. C 78.90, H 10.59; found C 78.92, H 10.73.

(3R,3aR*,7aS*)-cis-3-Methyl-4-hexahydroindanone* (**21a**): IR (film): ν = 2941, 2868, 1698 (C=O), 1461, 1380, 1320, 1222, 1170 cm^{-1}. − ^{1}H NMR (300 MHz; $CDCl_3$): δ = 0.98 (d, J = 7.3 Hz, 3 H, CH_3), 1.34 (m, 1 H), 1.46 (m, 1 H), 1.64 (m, 2 H), 1.83 (m, 3 H), 1.96 (m, 1 H), 2.05 (m, 1 H, 5-H), 2.38 (m, 1 H, 7a-H), 2.40 (m, 1 H, 3-H), 2.45 (m, 1 H, 5-H), 2.70 (ddd, J = 9.1, 8.4, 1.9 Hz, 1 H, 3a-H). − ^{13}C NMR (75 MHz; $CDCl_3$): δ = 18.1 (CH_3), 23.6 (CH_2), 29.8 (CH_2), 31.5 (CH_2), 32.9 (CH_2), 37.4 (C-7a), 41.2 (C-3), 42.6 (C-5), 55.6 (C-3a), 214.9 (C-4). − MS (EI): *m/z* (%) = 152 (19) [M^+], 137 (7), 123 (8), 110 (34), 109 (9), 97 (100), 81 (38), 67 (14), 55 (14), 41 (15). − $C_{10}H_{16}O$ (152.2): calcd. C 78.90, H 10.59; found C 78.74, H 10.76.

(3R,3aS*,7aR*)-cis-3-Methyl-4-hexahydroindanone* (**21b**): IR (film): ν = 2951, 2918, 2868, 1704 (C=O), 1454, 1380, 1320, 1315, 1240, 1145, 1023 cm^{-1}. − ^{1}H NMR (300 MHz; $CDCl_3$): δ = 1.00 (d, J = 6.7 Hz, 3 H, CH_3), 1.20 (m, 1 H), 1.43 (m, 2 H), 1.75 (m, 3 H), 1.96 (m, 2 H), 2.12 (ddd, J = 9.0, 7.7, 1.1 Hz, 1 H, 3a-H), 2.32 (m, 3 H, 3-H, 5-H), 2.47 (m, 1 H, 7a-H). − ^{13}C NMR (75 MHz; $CDCl_3$): δ = 20.0 (CH_3), 24.4 (CH_2), 28.6 (CH_2), 31.2 (CH_2), 33.0 (CH_2), 36.2 (C-7a), 39.2 (C-5), 42.7 (C-3), 61.2 (C-3a), 214.1 (C-4). − MS (EI): *m/z* (%) = 152 (58) [M^+], 151 (23), 137 (78), 135 (18), 137 (14), 123 (18), 119 (22), 110 (74), 109 (42), 97 (22), 95 (19), 93 (22), 81 (100), 79 (17), 67 (21), 55 (16), 53 (17), 41 (22), 39 (79). − $C_{10}H_{16}O$ (152.2): calcd. C 78.90, H 10.59; found C 78.27, H 10.60.

cis-1-Hexahydroindanone (**9**): Following procedure C, a solution of 3-(3-butenyl)-1-trimethylsilyloxy-1-cyclopentene (**8**) (1.05 g, 5.0 mmol) in dry CH_3CN (100 ml) was irradiated in the presence of DCA (114 mg, 0.5 mmol) for 113 h. The cyclized product was isolated by HPLC (cyclohexane/ethyl acetate, 95:5). *cis*-1-Hexahydroindanone (**8**) (75 mg, 11%) was obtained as a colourless oil. − IR (film): ν = 2910, 2840, 1730 (C=O), 1440, 1400, 1320, 1160, 1100, 1050, 1030, 900, 840 cm^{-1}. − ^{1}H NMR (300 MHz; C_6D_6): δ = 0.60−1.40 (m, 9 H), 1.73−1.82 (m, 2 H), 1.92 (m, 2 H), 2.12 (m, 1 H). − ^{13}C NMR (75 MHz; $CDCl_3$): δ = 22.6 (CH_2), 23.0 (CH_2), 24.1 (CH_2), 25.7 (CH_2), 28.3 (CH_2), 35.0 (C-2), 36.3 (C-3a), 49.7 (C-7a), 220.8 (C-1). − MS (EI): *m/z* (%) = 138 (41) [M^+], 109 (32), 96 (56), 94 (35), 83 (30), 81 (66), 79 (38), 67 (100), 54 (30), 41 (43), 39 (79).

(4aR,7S*,8aS*)-cis-7-Methyl-1-decalone* (**11a**) *and (4aR*,7R*,8aS*)-cis-7-Methyl-1-decalone* (**11b**): Following procedure C, a solution of 3-(3-methyl-3-butenyl)-1-trimethylsilyloxy-1-cyclohexene (**10**) (834 mg, 3.50 mmol) in dry CH_3CN (70 ml) was irradiated in the presence of DCN (84 mg, 0.60 mmol) for 68 h. The products were separated by HPLC (cyclohexane/ethyl acetate, 95:5). (4a*R**,7*S**,8a*S**)-*cis*-7-Methyl-1-decalone (**11a**) (50 mg, 9%) and (4a*R**,7*R**,8a*S**)-*cis*-7-methyl-1-decalone (**11b**) (55 mg, 10%) were obtained as colourless oils.

(4aR,7S*,8aS*)-cis-7-Methyl-1-decalone* (**11a**): IR (film): $\tilde{\nu}$ = 2920, 2860, 2840, 1710 (C=O), 1440, 1425, 1370, 1320, 1250, 1220, 1210, 1185, 1150, 1130, 1105, 1010, 880, 840 cm^{-1}. − ^{1}H NMR (300 MHz; $CDCl_3$): δ = 0.68−0.93 (m, 2 H), 0.93 (d, J = 6.4 Hz, 3 H, CH_3), 1.11−1.28 (m, 1 H), 1.31−1.28 (m, 1 H), 1.30−2.00 (m, 8 H), 2.03−2.33 (m, 3 H), 2.55 (m, 1 H). − ^{13}C NMR (75 MHz; $CDCl_3$): δ = 22.5 (CH_3), 22.6 (CH_2), 27.6 (C-7), 28.4 (CH_2), 30.7 (CH_2), 33.7 (CH_2), 34.8 (CH_2), 39.7 (C-4a), 41.8 (C-2), 49.9 (C-8a), 212.7 (C-1). − MS (EI): *m/z* (%) = 166 (4) [M^+], 148 (2), 133 (2), 123 (8), 110 (100), 97 (25), 95 (12), 81 (11), 79 (10), 67 (18), 55 (13), 41 (22), 39 (28). − HRMS: 166.13577 ($C_{11}H_{18}O$, calcd. 166.13548).

(4aR,7R*,8aS*)-cis-7-Methyl-1-decalone* (**11b**): IR (film): $\tilde{\nu}$ = 2940, 2920, 2860, 1705 (C=O), 1460, 1425, 1375, 1345, 1320, 1265, 1230, 1195, 1140, 1145, 1045, 990, 760 cm^{-1}. − ^{1}H NMR (300 MHz; C_6D_6): δ = 0.82−1.71 (m, 12 H), 0.77 (d, J = 6.0 Hz, 3 H, CH_3), 2.04 (m, 1 H, 2-H), 2.16 (m, 1 H, 2-H), 2.44 (dt, J = 12.0, 4.5 Hz, 1 H, 8a-H). − ^{13}C NMR (75 MHz; $CDCl_3$): δ = 22.6 (CH_3), 24.6 (CH_2), 25.6 (CH_2), 29.3 (CH_2), 30.4 (CH_2), 32.4 (C-7), 33.5 (C-8), 36.4 (C-4a), 37.6 (C-4a), 53.3 (C-8a), 215.2 (C-1). − MS (EI): *m/z* (%) = 166 (41) [M^+], 148 (27), 133 (20), 123 (59), 110 (54), 106 (24), 95 (74), 93 (26), 84 (32), 81 (60), 79 (30), 69 (30), 67 (82), 55 (42), 53 (24), 41 (74), 39 (100). − HRMS: 166.13577 ($C_{11}H_{18}O$, calcd. 166.13548).

cis-anti-trans-Dodecahydrophenanthren-4-one (**13a**) *and cis-anti-cis-Dodecahydrophenanthren-4-one* (**13b**): Following procedure C, a solution of 3-(2-cyclohex-1-enylethyl)-1-trimethylsilyloxy-1-cyclohexene (**12**) (770 mg, 2.77 mmol) in 50 ml of dry CH_3CN/*i*PrOH (17:3) was irradiated in the presence of DCA (128 mg, 0.55 mmol) for 280 h. Separation of the products by HPLC (cyclohexane/ethyl acetate, 93:7) led to the cyclic products in order of increasing polarity: *cis-anti-trans*-dodecahydrophenanthren-4-one (**13a**) (154 mg, 27%) and *cis-anti-cis*-dodecahydrophenanthren-4-one (**13b**) (134 mg, 24%) were obtained as colourless crystals, and 3-(2-cyclohex-1-enylethyl)-1-cyclohexanone (91 mg, 16%) as a colourless oil.

cis-anti-trans-Dodecahydrophenanthren-4-one (**13a**): M.p. 48°C. − IR (KBr): ν = 2890, 2817, 1695 (C=O), 1436, 1335, 1330, 1268, 1249, 1220, 1190, 1118 cm^{-1}. − ^{1}H NMR (300 MHz; C_6D_6): δ = 0.69 (m, 1 H), 0.74−1.31 (m, 18 H), 1.98 (ddd, J = 13.8, 13.8, 5.8 Hz, 1 H, 3-H), 2.13 (m, 2 H, 3-H, 4a-H). − ^{13}C NMR (75 MHz; C_6D_6): δ = 26.0 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 27.2 (CH_2), 29.3

(CH_2), 31.1 (CH_2), 31.4 (CH_2), 34.8 (CH_2), 38.6 (C-3), 39.2 (CH), 40.0 (CH), 43.2 (CH), 60.4 (C-4a), 210.4 (C-4). − MS (EI): *m/z* (%) = 206 (21) [M^+], 188 (18), 163 (14), 123 (47), 110 (100), 97 (36), 93 (18), 91 (18), 79 (31), 77 (14), 67 (28), 55 (15), 41 (33), 39 (34). − $C_{14}H_{22}O$ (206.3): calcd. C 81.50, H 10.75; found C 81.42, H 10.92. − Crystals of **13a**, $C_{14}H_{22}O$, M_r = 206.23, from ethanol are orthorhombic, space group $P2_12_12_1$, a = 5.450(1), b = 14.580(1), c = 14.802(1) A; Z = 4; $d_{calcd.}$ = 1.165 g/cm^3; μ = 5.36 cm^{-1}, $F(000)$ = 456, crystal dimensions 0.7 × 0.1 × 0.05 mm^3, CAD-4 diffractometer, λ = 1.54178 A, 1416 independent reflections and 1182 observed reflections, R = 0.042 and wR^2 = 0.115 for the observed, R = 0.057 and wR^2 = 0.128 for all reflections, 137 parameters, largest diff. peak and hole: 0.21 and −0.17 eA^{-3}, *Goof* = 1.052, Flack parameter −0.3(7). Hydrogen atoms were placed in calculated positions and refined as a riding model. Programs used: SHELXS-86, SHELXL-93, SCHAKAL-92. Further information can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404816. Characteristic bond lengths and angles: C(4)−O 1.218(3), C(4)−C(4A) 1.512(3); O−C(4)−C(3) 112.3(2), C(5A)−C(4A)−C(10A) 112.4(2).

cis-anti-cis-Dodecahydrophenanthren-4-one (**13b**): M.p. 50°C. − IR (CH_2Cl_2): ν = 2923, 2853, 1708 (C=O), 1470, 1447, 1315, 1106, 1010 cm^{-1}. − ^{1}H NMR (500 MHz; $CDCl_3$): δ = 1.10−1.70 (br. m, 16 H), 1.70−2.00 (br. m, 3 H), 2.27 (br. m, 2 H), 2.35 (br. m, 1 H). − ^{1}H NMR (200 MHz; $C_2D_2Cl_4$, 70°C): δ = 1.10−2.00 (m, 19 H), 2.10−2.40 (m, 3 H). − ^{13}C NMR (50 MHz; $C_2D_2Cl_4$, 70°C): δ = 22.2 (CH_2), 23.0 (CH_2), 25.4 (CH_2), 26.2 (CH_2), 26.7 (CH_2), 28.3 (CH_2), 29.5 (CH_2), 30.2 (CH_2), 32.8 (CH), 33.8 (CH), 35.8 (CH), 40.9 (C-3), 54.8 (C-4a), 212.0 (C-4). − MS (EI): *m/z* (%) = 206 (13) [M^+], 123 (24), 111 (9), 110 (100), 97 (25), 95 (6), 93 (6), 91 (6), 79 (11), 77 (5), 67 (11). − $C_{14}H_{22}O$ (206.3): calcd. C 81.50, H 10.75; found C 81.36, H 10.85.

(3R,3aS*,5aS*)-cis-3-Isopropyl-4-hexahydroindanone* (**15**): Following procedure C, a solution of 3-(4-methylpent-3-enyl)-1-trimethylsilyloxy-1-cyclohexene (**14**) (833 mg, 3.50 mmol) in dry CH_3CN (70 ml) was irradiated in the presence of DCN (84 mg, 0.60 mmol) for 70 h. The cyclic product was isolated by HPLC (cyclohexane/ethyl acetate, 95:5). (3*R**,3a*S**,5a*S**)-*cis*-3-Isopropyl-4-hexahydroindanone (**15**) (170 mg, 29%) was obtained as a colourless oil. − IR (film): ν = 2952, 2932, 2868, 1705 (C=O), 1467, 1445, 1366, 1138 cm^{-1}. − ^{1}H NMR (300 MHz; C_6D_6): δ = 0.86 (d, J = 8.4 Hz, 3 H, CH_3), 0.88 (d, J = 8.4 Hz, 3 H, CH_3), 1.07 (m, 3 H), 1.41 (m, 5 H), 1.63 (m, 1 H), 1.99 (m, 2 H), 2.11 (m, 1 H), 2.16 (t, J = 7.0 Hz, 1 H, 3a-H), 2.34 (tt, J = 8.4, 7.0 Hz, 1 H, 3-H). − ^{13}C NMR (75 MHz; C_6D_6): δ = 19.8 (CH_3), 21.5 (CH_3), 23.9 (CH_2), 27.8 (CH_2), 28.1 (CH_2), 31.6 (CH_2), 32.2 (C-8), 40.1 (C-5), 43.6 (C-7a), 46.4 (C-3), 56.5 (C-3a), 214.9 (C-4). − MS (EI): *m/z* (%) = 180 (15) [M^+], 147 (6), 137 (76), 123 (52), 110 (100), 97 (31), 91 (22), 79 (20), 67 (41), 55 (18), 41 (55), 39 (50). − $C_{12}H_{20}O$ (180.2): calcd. C 79.94, H 11.18; found C 79.26, H 11.20.

cis-(3Z)-Trimethylsilylmethylidenoctahydroinden-4-one (**16a**) *and cis-*(3*E*)-*Trimethylsilylmethylidenoctahydroinden-4-one* (**16b**): Following procedure C, a solution of 3-(4-trimethylsilyl-3-butynyl)-1-trimethylsilyloxy-1-cyclohexene (**6**) (1.47 g, 5.00 mmol) in dry CH_3CN (100 ml) was irradiated in the presence of DCA (114 mg, 0.50 mmol) for 60 h. Separation of the products by HPLC (cyclohexane/ethyl acetate, 95:5) led to the following products in order of increasing polarity: *cis*-(3*Z*)-trimethylsilylmethylidenoctahydroinden-4-one (**16a**) (265 mg, 24%), *cis*-(3*E*)-trimethylsilylmethylidenoctahydroinden-4-one (**16b**) (272 mg, 24%), and 3-(4-trimethylsilyl-3-butynyl)-1-cyclohexanone (126 mg, 11%). These were obtained as yellowish oils.

cis-(3Z)-Trimethylsilylmethylidenoctahydroinden-4-one (**16a**): IR (film): ν = 2948, 1713 (C=O), 1629, 1460, 1426, 1306, 1245, 1102, 841, 836 cm^{-1}. − ^{1}H NMR (300 MHz; $CDCl_3$): δ = 0.04 [s, 9 H, $Si(CH_3)_3$], 1.41 (m, 1 H), 1.59 (m, 1 H), 1.71 (m, 1 H), 1.95 (m, 3 H), 2.22−2.58 (m, 4 H), 2.64 (m, 1 H), 3.28 (dm, J = 7.6 Hz, 1 H, 3a-H), 5.51 (dt, J = 1.3, 2.3 Hz, 1 H, 8-H). − ^{13}C NMR (75 MHz; $CDCl_3$): δ = −0.2 [$Si(CH_3)_3$], 23.7 (C-6), 26.5 (CH_2), 27.8 (CH_2), 34.6 (C-2), 41.7 (C-5), 44.6 (C-7a), 58.8 (C-3a), 124.5 (C-8), 156.7 (C-3), 209.8 (C-4). − MS (EI): *m/z* (%) = 222 (3) [M^+], 208 (20), 207 (100), 133 (11), 131 (13), 91 (11), 75 (55), 73 (20), 59 (17). − $C_{13}H_{22}OSi$ (222.4): calcd. C 70.21, H 10.04; found C 70.26, H 9.99.

cis-(3E)-Trimethylsilylmethylidenoctahydroinden-4-one (**16b**): IR (film): ν = 2950, 2865, 1706 (C=O), 1614, 1447, 1320, 1247, 1145, 1039, 880, 852, 839, 750 cm^{-1}. − ^{1}H NMR (300 MHz; $CDCl_3$): δ = 0.06 [s, 9 H, $Si(CH_3)_3$], 1.31 (m, 1 H), 1.52−1.80 (m, 4 H), 1.92 (m, 1 H), 2.25 (m, 2 H), 2.45 (m, 3 H), 3.14 (m, 1 H, 3a-H), 5.25 (q, J = 2.6 Hz, 1 H, 8-H). − ^{13}C NMR (50 MHz; $CDCl_3$): δ = −0.7 (C-9), 24.9 (C-6), 26.7 (C-1), 29.4 (CH_2), 30.7 (CH_2), 38.3 (C-5), 42.6 (C-7a), 62.2 (C-3a), 121.7 (C-8), 157.6 (C-3), 211.8 (C-4). − MS (EI): *m/z* (%) = 222 (13) [M^+], 208 (19), 207 (100), 133 (11), 131 (14), 91 (13), 75 (59), 73 (40), 59 (19), 45 (15). − $C_{13}H_{22}OSi$ (222.4): calcd. C 70.21, H 10.04; found C 69.92, H 9.77.

cis-1,2,3,4,4a,9a-Hexahydroxanthen-9-one (**19**) *and (1R*,5R*,7R*,10S*)-Benzo[c]-2-oxatricyclo[5.2.1.0^{5,10}]decan-5-ol* (**20**): Following procedure C, a solution of 2-(3-butenyl)-4-trimethylsilyloxy-2*H*-chromene (**3**) (823 mg, 3.00 mmol) in dry CH_3CN (60 ml) was irradiated in the presence of DCA (191 mg, 0.40 mmol) for 180 h. Separation of the products by HPLC (cyclohexane/ethyl acetate, 95:5 and 98:2) led to the following products in order of increasing polarity: (1*R**,5*R**,7*R**,10*S**)-benzo[*c*]-2-oxatricyclo[5.2.1.0^{5,10}]decan-5-ol (**20**) (38 mg, 6%) as colourless crystals, and *cis*-1,2,3,4,4a,9a-hexahydroxanthen-9-one (**19**) (96 mg, 16%) as a colourless oil.

(1R,5R*,7R*,10S*)-Benzo[c]-2-oxatricyclo[5.2.1.0^{5,10}]decan-5-ol* (**20**): M.p. 45°C. − IR (KBr): ν = 3450 (br), 3060, 2957, 2930, 1609, 1583, 1485, 1452, 1306, 1250, 1212, 1171, 1140, 1101, 1080, 1039, 976, 888, 840, 760 cm^{-1}. − ^{1}H NMR (200 MHz; $CDCl_3$): δ = 1.50−1.75 (m, 3 H), 1.90−2.10 (m, 3 H), 2.70−2.95 (m, 3 H), 4.74 (ddd, J = 8.1, 8.1, 6.6 Hz, 1 H, 6-H), 6.81 (dd, J = 8.1, 1.3 Hz, 1 H, 13-H), 6.92 (ddd, J = 7.4, 7.4, 1.3 Hz, 1 H, 11-H), 7.14 (ddd, J = 8.1, 7.4, 1.8 Hz, 1 H, 12-H), 7.28 (dd, J = 7.4, 1.8 Hz, 1 H, 14-H). − ^{13}C NMR (50 MHz; $CDCl_3$): δ = 29.3 (CH_2), 30.3 (CH_2), 31.4 (C-3), 44.9 (C-5), 46.7 (C-10), 67.9 (C-1), 79.5 (C-6), 117.7 (C-11), 121.3 (C-13), 126.6 (C-12), 128.4 (C-14), 130.7 (C-9), 152.0 (C-8). − MS (CI, isobutane): *m/z* (%) = 203 (100) [MH^+]; MS (EI): *m/z* (%) = 202 (51) [M^+], 173 (13), 147 (21), 121 (100), 120 (86), 92 (30), 65 (11). − $C_{13}H_{14}O_2$ (202.1); calcd. C 77.20, H 6.98; found C 76.69, H 6.89.

cis-1,2,3,4,4a,9a-Hexahydroxanthen-9-one (**19**): IR (film): $\tilde{\nu}$ = 3060, 2936, 2861, 1688 (C=O), 1606, 1578, 1462, 1362, 1308, 1230, 1189, 1151, 1122, 1016, 965, 906, 868, 777, 758, 590 cm^{-1}. − ^{1}H NMR (200 MHz; C_6D_6): δ = 0.90−1.25 (m, 3 H), 1.30−1.65 (m, 4 H), 1.80 (m, 1 H), 2.27 (ddd, J = 11.0, 4.9, 3.2 Hz, 1 H, 9a-H), 4.06 (ddd, J = 4.9, 2.8, 2.1 Hz, 1 H, 4a-H), 6.72 (ddd, J = 7.9, 7.0, 1.2 Hz, 1 H, 7-H), 6.92 (ddd, J = 8.3, 7.0, 1.8 Hz, 1 H, 5-H), 7.07 (ddd, J = 8.3, 7.0, 1.8 Hz, 1 H, 6-H), 8.20 (ddd, J = 7.9, 1.8, 0.6 Hz, 1 H, 8-H). − ^{13}C NMR (50 MHz; $CDCl_3$): δ = 20.5 (C-1), 23.9 (CH_2), 24.0 (CH_2), 29.3 (C-4), 47.9 (C-9a), 76.1 (C-4a), 117.9 (C-5), 119.6 (C-8a), 121.1 (C-7), 127.4 (C-8), 135.9 (C-6), 161.2 (C-10a), 195.8 (C-9). − MS (CI, isobutane): *m/z* (%) = 203 (100) [MH^+]; MS (EI): *m/z* (%) = 202 (77) [M^+], 173 (45), 134 (33), 121

(100), 120 (97), 93 (10), 92 (30), 65 (14). − $C_{13}H_{14}O_2$ (202.1): calcd. C 77.20, H 6.98; found C 77.15, H 7.13.

(1R,3aR*,9aS*)-1-Methyl-2,3,3a,9a-tetrahydro-1H-cyclopenta[b]chromen-9-one* (**22**): Following procedure C, a solution of 2-(3-butenyl)-4-trimethylsilyloxy-2*H*-chromene (**3**) (686 mg, 2.50 mmol) in dry CH_3CN/MeOH (17:3) (50 ml) was irradiated in the presence DCA (86 mg, 0.38 mmol) for 110 h. The products were isolated by HPLC (cyclohexane/ethyl acetate, 95:5). In addition to **19** and **20**, (1*R**,3a*R**,9a*S**)-1-methyl-2,3,3a,9a-tetrahydro-1*H*-cyclopenta[b]chromen-9-one (**22**) (13 mg, 3%) was isolated as a colourless oil. − IR (KBr): ν = 3050, 2962, 2930, 1682 (C=O), 1607, 1578, 1462, 1354, 1310, 1224, 1121, 1027, 759 cm^{-1}. − ^1H NMR (300 MHz; $CDCl_3$): δ = 0.88 (d, *J* = 7.2 Hz, 3 H, CH_3), 1.71 (m, 1 H), 1.97 (m, 1 H), 2.12 (m, 1 H), 2.29 (m, 1 H), 2.70 (m, 1 H), 2.84 (dd, *J* = 10.1, 4.7 Hz, 1 H, 9a-H), 4.94 (ddd, *J* = 4.7, 4.7, 1.4 Hz, 1 H, 3a-H), 6.93 (dd, *J* = 8.3, 1.3 Hz, 1 H, 5-H), 7.00 (ddd, *J* = 8.0, 7.1, 1.3 Hz, 1 H, 7-H), 7.46 (ddd, *J* = 8.3, 7.1, 1.8 Hz, 1 H, 6-H), 7.90 (dd, *J* = 8.0, 1.8 Hz, 1 H, 8-H). − ^{13}C NMR (75 MHz; $CDCl_3$): δ = 18.3 (C-10), 32.4 (CH_2), 33.3 (CH_2), 36.0 (C-1), 54.0 (C-9a), 83.4 (C-3a), 118.1 (C-5), 121.2 (C-7), 121.5 (C-8a), 126.5 (C-8), 136.0 (C-6), 161.4 (C-4a), 194.5 (C-9). − MS (CI, isobutane): *m/z* (%) = 203 (100) [MH^+]; MS (EI): *m/z* (%) = 202 (23) [M^+], 173 (4), 160 (9), 147 (100), 121 (39), 120 (49), 92 (26), 81 (6), 67 (7). − HRMS: 202.10300 ($C_{13}H_{14}O_2$, calcd. 202.09938).

cis-anti-trans-1,2,3,4,4a,5,6,a,12a,12b-Decahydrobenzo[a]xanthen-12-one (**24a**) *and cis-anti-cis-1,2,3,4,4a,5,6,6a,12a,12b-Decahydrobenzo[a]xanthen-12-one* (**24b**): Following procedure C, a solution of 2-(2-cyclohex-1-enylethyl)-4-trimethylsilyloxy-2*H*-chromene (**23**) (341 mg, 1.07 mmol) in CH_3CN/MeOH (19:1) (20 ml) was irradiated in the presence of DCA (68 mg, 0.16 mmol) for 250 h. Separation of the products by HPLC (cyclohexane/ethyl acetate, 98:2) led to the cyclized products in order of increasing polarity: *cis-anti-cis*-1,2,3,4,4a,5,6,6a,12a,12b-decahydrobenzo[*a*]xanthen-12-one (**24b**) (17 mg, 6%) as colourless crystals, and *cis-anti-trans*-1,2,3,4,4a,5,6,a,12a,12b-decahydrobenzo[*a*]xanthen-12-one (**24a**) (38 mg, 14%) as a colourless oil.

cis-anti-trans-1,2,3,4,4a,5,6,a,12a,12b-Decahydrobenzo[a]xanthen-12-one (**24a**): IR (film): ν = 3050, 2923, 2854, 1686 (C=O), 1608, 1578, 1470, 1464, 1350, 1306, 1224, 1151, 1130, 1107, 1030, 950, 894, 767, 754, 596 cm^{-1}. − ^1H NMR (200 MHz; $CDCl_3$): δ = 0.90−1.20 (m, 4 H), 1.30−1.40 (m, 1 H), 1.50−1.80 (m, 8 H), 2.14 (dd, *J* = 11.3, 2.3 Hz, 1 H, 12a-H), 2.19 (m, 1 H), 4.60 (q, *J* = 2.3 Hz, 1 H, 6a-H), 6.97 (d, *J* = 7.9 Hz, 1 H, 8-H), 7.00 (ddd, *J* = 8.3, 7.1, 1.1 Hz, 1 H, 10-H), 7.48 (ddd, *J* = 7.9, 7.1, 1.8 Hz, 1 H, 9-H), 7.81 (dd, *J* = 8.3, 1.8 Hz, 1 H, 11-H). − ^{13}C NMR (125 MHz; $CDCl_3$): δ = 26.1 (CH_2), 26.1 (CH_2), 27.7 (CH_2), 29.7 (CH_2), 30.1 (CH_2), 33.9 (CH_2), 37.9 (CH), 41.5 (CH), 53.9 (C-12a), 76.6 (C-6a), 117.7 (C-8), 119.6 (C-11a), 121.0 (C-10), 127.4 (C-11), 135.7 (C-9), 161.2 (C-7a), 195.0 (C-12). − MS (CI, isobutane): *m/z* (%) = 257 (100) [MH^+]; MS (EI): *m/z* (%) = 256 (35) [M^+], 174 (11), 173 (90), 148 (10), 147 (100), 121 (43), 120 (14), 93 (11), 92 (14), 79 (10), 77 (10), 67 (12). − HRMS: 256.14630 ($C_{17}H_{20}O_2$, calcd. 256.14633).

cis-anti-cis-1,2,3,4,4a,5,6,6a,12a,12b-Decahydrobenzo[a]xanthen-12-one (**24b**): M.p. 73°C. − IR (KBr): ν = 3063, 2928, 2857, 1677 (C=O), 1606, 1577, 1474, 1464, 1447, 1365, 1323, 1304, 1232, 1210, 1150, 1125, 1030, 1000, 959, 902, 860, 774, 758 cm^{-1}. − ^1H NMR (300 MHz; $CDCl_3$): δ = 1.20−2.00 (m, 13 H), 2.28 (m, 1 H), 2.83 (dd, *J* = 9.8, 3.5 Hz, 1 H, 12a-H), 4.67 (m, 1 H, 6a-H), 6.94 (dd, *J* = 8.3, 1.1 Hz, 1 H, 8-H), 6.98 (ddd, *J* = 8.0, 7.2, 1.1 Hz, 1 H, 10-H), 7.46 (ddd, *J* = 8.3, 7.2, 1.8 Hz, 1 H, 9-H), 7.87 (dd, *J* = 8.0, 1.8 Hz, 1 H, 11-H). − ^1H NMR (300 MHz; 73°C, $C_2D_2Cl_4$): δ = 1.30−1.80 (m, 9 H), 1.80−2.10 (m, 4 H), 2.36 (m, 1 H), 2.83 (dd, *J* = 9.3, 3.7 Hz, 1 H, 12a-H), 4.70 (ddd, *J* = 6.5, 3.7, 3.2 Hz, 1 H, 6a-H), 6.98 (dd, *J* = 8.3, 1.1 Hz, 1 H, 8-H), 7.00 (ddd, *J* = 8.5, 7.2, 1.1 Hz, 1 H, 10-H), 7.47 (ddd, *J* = 8.3, 7.2, 1.8 Hz, 1 H, 9-H), 7.87 (dd, *J* = 8.5, 1.8 Hz, 1 H, 11-H). − ^{13}C NMR (50 MHz; 73°C, $C_2D_2Cl_4$): δ = 22.2 (CH_2), 24.6 (CH_2), 25.4 (CH_2), 25.6 (CH_2), 27.1 (CH_2), 27.3 (CH_2), 32.4 (CH), 34.0 (CH), 47.1 (C-12a), 76.5 (C-6a), 117.6 (C-8), 119.9 (C-11a), 120.6 (C-10), 127.0 (C-11), 135.3 (C-9), 160.6 (C-7a), 194.3 (C-12). − MS (CI, isobutane): *m/z* (%) = 257 (100) [MH^+]; MS (EI): *m/z* (%) = 256 (31) [M^+], 174 (11), 173 (78), 160 (16), 148 (10), 147 (100), 121 (26), 120 (12), 95 (12), 95 (6), 91 (6), 83 (6), 79 (8), 77(6), 71 (6); HRMS: 256.14630 ($C_{17}H_{20}O_2$, calcd. 256.14633).

☆ Dedicated to the photochemists born in 1938: *Bob Liu, Dave Neckers, Jack Saltiel, Nick Turro, Pete Wagner,* and *Dave Whitten.*

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