Mechanistic studies on PET-oxidative cyclization of unsaturated silyl enol ethers: dependence of the regioselectivity on alcohol addition and pressure effects

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Unsaturated silyl enol ethers are irradiated in the presence of electron transfer sensitizers. The efficiency of the cyclization reaction using different sensitizers is investigated. The *endo*/*exo* regiochemistry of the ring closure reaction can either be controlled by variation of the silyl group or by addition of alcohol. Furthermore, a dependence of the regiochemistry on pressure is revealed and it seems that it can be related to acetonitrile acting as a nucleophile at 1500 bar. As key intermediates radical cations and radicals are involved.

Introduction

Radical ions generated by single electron transfer (SET) from neutral compounds are known to be important intermediates in a variety of interesting chemical processes and reactions. Cyclization reactions *via* radical cations are getting more and more popular for constructing cyclic ring systems in a regio- and stereoselective fashion.[1] In contrast to the regioselective 5-*exo*-*trig* cyclization of the hex-5-enyl radical,[2,3] the analogous α,ε-diene radical cation cyclizes in a 6-*endo*-*trig* mode.[4] The generally observed preference for *endo*-cyclization is one important feature of radical cation ring closure reactions and is often quoted to distinguish between pathways involving radical cations and radicals as intermediates. Promising reactants for radical cation cyclization reactions are substrates containing an electron-rich double bond, *e.g.* enol ethers[5,6] or enol acetates,[7] and a non-activated double bond. Due to its lower oxidation potential a selective oxidation of the electron-rich double bond can be achieved.

Silyl enol ethers are easily oxidized either chemically[8] or by means of photoinduced electron transfer (PET).[9,10] Because of the often observed high selectivity and the mild reaction conditions the PET provides the chemist with a powerful tool for carrying out SET reactions. By photochemical excitation of either the electron donor or the acceptor the redox properties of the respective species change, *e.g.* 9,10-dicyanoanthracene (DCA) or 1,4-dicyanonaphthalene (DCN) can be used as strong oxidizing agents.[11]

We have recently reported that the PET-oxidative cyclization of monocyclic silyl enol ethers substituted by an olefinic or acetylenic side chain in the presence of catalytic amounts of 9,10-dicyanoanthracene (DCA) provides bicyclic or tricyclic ketones. Investigations concerning the mechanism have revealed that the *endo*/*exo* regiochemistry of the cyclization step can be controlled by the addition of alcohol.[12]

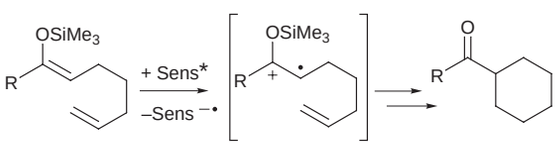
Preliminary studies regarding the pressure dependence of the PET-oxidative cyclization have revealed some unexpected results. In pure acetonitrile the almost exclusive generation of a 6-*endo* product is changed to the predominant formation of 5-*exo* compounds by applying high pressure.[13]

Results and discussion

I Synthetic aspects

For initial studies we chose δ,ε-unsaturated silyl enol ethers since the cyclization of hex-5-enyl radicals yielding cyclopentanemethyl radicals is faster than the formation of smaller or larger rings.[8] The trimethylsilyl enol ethers are accessible by deprotonation of the parent ketone with LDA and silylation with trimethylchlorosilane at −78 °C.

A deoxygenated 0.05 M solution of the respective trimethyl[(1*Z*)-hepta-1,6-dienyloxy]silanes **1**, **3**, **5** or **7** in acetonitrile containing about 10–20 mol% of the PET-sensitizer DCA is irradiated at 419 nm in a Rayonet photochemical reactor fitted with a merry-go-round insert. Due to the oxidation potential of the silyl enol ether, electron transfer occurs. In polar solvents like acetonitrile the separation of the radical ion pairs is favoured and the generated radical cations can react in an intramolecular fashion. The formation of the cyclic products **2**, **4**, **6** and **8**, respectively is monitored by gas chromatography using *n*-dodecane as an internal standard and the products are isolated by HPLC. The yields of the PET-oxidative cyclization reactions are summarized in Scheme 1. Besides the 6-*endo* ring closure products no other cyclic products and merely traces



R		
Bu^t	**1**	**2** (23%)
C_6H_{11}	**3**	**4** (37%)
Ph	**5**	**6** (38%)
p-MeOPh	**7**	**8** (26%)

Scheme 1

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of the non-cyclic ε,ζ-unsaturated ketones (2–5%) are detected by gas chromatography. In analogy to earlier studies[13] it is assumed that polymerization is the major side reaction. However, when optimizing the starting materials (*e.g.* cyclic enol ethers, higher substituted double bonds) the yields increase up to 70%.

Comparing the phenyl substituted compound **5** with the cyclohexyl-substituted derivative **3,** which gives nearly the same yield of cyclized product, shows that there is actually no evidence for any electronic effect caused by the substituent at C-1. This is further supported by the observation that the yield of the cyclization reaction of compound **7** is even decreased compared to that of **5**. Nevertheless the steric bulk of the substituent R seems to be crucial to prevent side reactions, *e.g.* polymerization of the intermediates. For example, in the case of R = CH_3 only 4% of the cyclization product is formed.[10c]

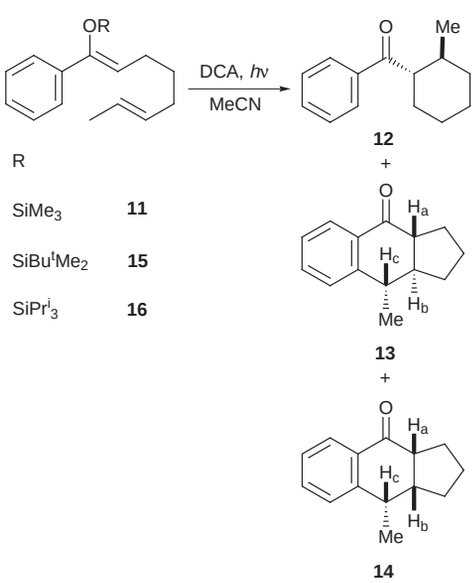
In Scheme 2 an example is given indicating that the ring

9 **10**

Scheme 2

closure reaction of the intermediary radical cation proceeds with high stereoselectivity. We assume that in the transition state both substituents take an equatorial position leading exclusively to the *cis* isomer. The yield of cyclized product, however, is not improved by substitution at the δ-position of the silyl enol ether **5** (yield of **10**: 33%).

Silyl enol ether **11** is irradiated under PET-conditions (Scheme 3). Only *trans*-benzoyl-2-methylcyclohexane (**12**) is



Scheme 3

detected as the 6-*endo*-cyclized product. The stereoselective formation of the *trans* isomer can be again explained by the assumption that both substituents take an equatorial position in the transition state leading to the *trans* isomer in this case. In addition to **12** the tricycles **13** and **14** are observed, formally the products of a tandem cyclization consisting of a 5-*exo* cyclization followed by a 6-*endo* cyclization with participation of the phenyl group.

The assignment of the stereochemistry of the isomer **13** is based upon the coupling constants $J_{Ha,Hb}$ = 13.6 Hz and $J_{Hb,Hc}$ = 10.7 Hz, which require that H_a, H_b and H_c are all axial.

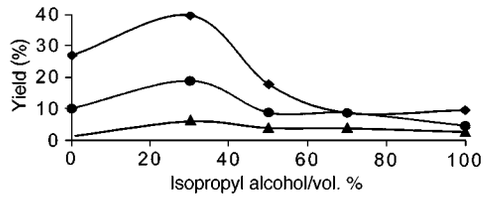


Fig. 1 Yield distribution of the products **12** (◆), **13** (●) and **14** (▲) in the reaction of **11** depending on the solvent ratio MeCN–Pr^iOH.

Table 1 Sensitized and cosensitized PET-oxidative cyclization of **5**

sensitizer	cosensitizer	λ/nm	*t*/h	**6** (%)
DCA	—	419	150	26
DCN	—	350	36	6
DCN	phenanthrene	350	30	10
DCTMB	phenanthrene	350	24	24
DCTMB	biphenyl	300	18	13

Table 2 Sensitized and cosensitized PET-oxidative cyclization of **11**

sensitizer	cosensitizer	λ/nm	*t*/h	**12** (%)	**12** + **13** + **14** (%)
DCA	—	419	131	27	38
DCN	—	350	36	11	16
DCN	phenanthrene	350	30	12	17
DCTMB	phenanthrene	350	24	15	22
DCTMB	biphenyl	300	18	13	19

The observed smaller couplings $J_{Ha,Hb}$ = 3.5 Hz and $J_{Hb,Hc}$ = 7.4 Hz for the *cis*-fused isomer **14** indicate that there are no axial–axial couplings.

With the intention of checking the potential of other sensitizers we tested DCN and 1,4-dicyano-2,3,5,6-tetramethylbenzene (DCTMB) instead of DCA as sensitizer. Further we tried to reduce the irradiation time by adding a cosensitizer like biphenyl or phenanthrene (conditions: 0.01 equiv. Sens, 10 equiv. Cosens). In Table 1 the yields of the sensitized and cosensitized PET-oxidative cyclization of **5** are summarized.

It is obvious that on the one hand the irradiation time can be reduced by adding a cosensitizer, but that on the other hand lower yields of cyclic product are obtained. Obviously the shorter excitation wavelength of 350 nm causes side reactions which lowers the yield, *e.g.* by the Norrish type II reaction. The PET-oxidative cyclization of silyl enol ether **11** shows similar results (Table 2).

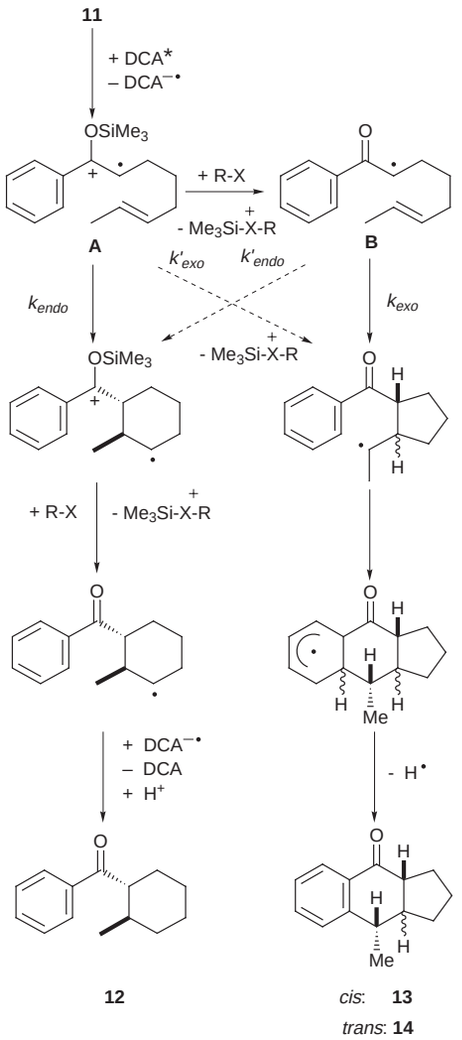
II Mechanistic aspects

PET-oxidative cyclization in acetonitrile–alcohol. In order to get more information about the factors which control the mechanism and the regioselectivity of the cyclizations we studied the reactions of **5**, **9**, and **11** in the presence of alcohols.[12,13] The most striking effect was observed in the case of **11**. For example, in propan-2-ol–acetonitrile mixtures we not only observed increasing total yields from 38% in pure acetonitrile up to 65% in a solvent containing 30% propan-2-ol but also an increased formation of the 5-*exo* cyclization products **13** and **14** (Fig. 1).

Methanol, *n*-propanol and *tert*-butyl alcohol show similar effects, however, the specific changes obviously depend on the type of alcohol. With methanol the optimal yield of product formation is reached at 15 volume per cent of alcohol whereas with the other alcohols the optimum corresponds to higher ratios. The specific influence of the alcohol is also reflected in the regioselectivity of cyclization (Table 3). For example, with methanol the most pronounced effect (*endo*/*exo* = 0.5) is observed in acetonitrile solutions containing 70% of the alco-

Table 3 Solvent dependence of the 6-*endo*:5-*exo* ratio **12**:(**13** + **14**) in the irradiation of **11** under oxidative PET-conditions in MeCN–ROH

Solvent ratio (MeCN–ROH)	10:0	7:3	5:5	3:7	0:10
6-*endo*/5-*exo* ratio (MeOH)	2.5	1.0	0.7	0.5	0.5
6-*endo*/5-*exo* ratio (Pr^iOH)	2.5	1.7	1.4	0.7	1.3
6-*endo*/5-*exo* ratio (Bu^tOH)	2.5	2.0	1.7	1.3	1.0



Scheme 4

hol whereas even in pure *tert*-butyl alcohol only a 1:1 mixture of *endo*- and *exo*-cyclization products is formed.

From these results we assume that the alcohol acts as a nucleophile facilitating the cleavage of the Si–O bond of the intermediate radical cation **A** (Scheme 4). Consequently, an α-keto radical **B** is generated which predominately cyclizes in a 5-*exo* mode according to the Baldwin rules. Obviously, the bulkiness of the alcohol influences this S_N2-type dissociation of the radical cation **A** showing the strongest effect with methanol even at relatively low concentration (Table 3).

When we studied the cyclization reaction of **5** and **9** we only observed improved product yields by addition of alcohols. For **9** the optimal yields of 39% were reached with propan-2-ol in solutions containing 15% alcohol (Fig. 2). As in the reaction of **11** a further increase of the alcohol amount favours the solvolysis of the silyl enol ethers leading to the non-cyclized ketones.

However, for both **5** and **9** addition of alcohol does not have any pronounced effect on the regioselectivity of the cyclization. For example, in the case of **5** the formation of a new product was detected by the GC/MS-technique in the presence of alcohol. Since this compound is formed in less than 1% yield

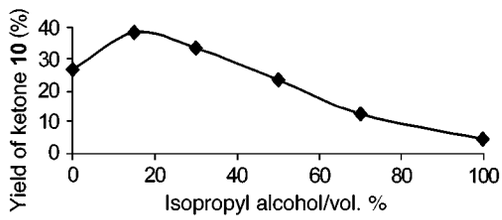


Fig. 2 Yield of ketone **11** in the irradiation of **9** in the presence of DCA depending on the solvent ratio MeCN–Pr^iOH.

Table 4 PET-oxidative cyclization under variation of the silyl group

Enol ether	R	**12** (6-*endo*) (%)	**13** (5-*exo*) (%)	**14** (5-*exo*) (%)
11	$SiMe_3$	27	10	1
15	$SiBu^tMe_2$	<1	12	1
16	$SiPr^i_3$	1	6	1

we tried to identify it by comparison with potential products independently synthesized according to literature procedures. Neither the 5-*exo* cyclization product prepared as described by Curran and Chang[14] nor the tandem-cyclized 6-*endo* ring closure product generated as described earlier[8] show the same retention time. Therefore we assume that this compound is the result of a 5-*exo* tandem-cyclization.

In the case of **9** only 4% of a 5-*exo* ring closure product is observed as well. We tentatively rationalize this different reaction pattern of **5** and **9** on the one hand and of **11** on the other hand in the following way: Firstly, depending on the suitable substitution of the alkene side chain the cyclization step of the radical cations of **5** and **9** is faster than the bimolecular nucleophile-assisted cleavage of the O–Si bond leading to the α-keto radical **B**. Secondly, even the cyclization of **B** only proceeds in the 6-*endo* mode resembling the 5-methylhex-5-enyl radical (5-*exo*:6-*endo* = 1:2).[15]

In order to investigate the impact of different trialkylsilyl groups on the regiochemistry of the cyclization reaction, we prepared the silyl enol ethers **15** and **16** by silylation of the corresponding ketone with the suitable trialkylsilyl triflate and triethylamine at room temperature. Irradiation of the silyl enol ethers in the presence of DCA as sensitizer results in the yields shown in Table 4.

By irradiating the more hydrolytically stable silyl enol ethers we expected higher yields of the 6-*endo* cyclization product **12**. However, in contrast to this prediction the main products are the 5-*exo* cyclized compounds **13** and **14**. We assume that this observation is the consequence of the different bulkiness of the distinct trialkylsilyl groups.

PET-oxidative cyclization under high pressure. Application of high pressure in compressed solutions has become more and more interesting since selectivity can be changed by pressure provided that the competitive or consecutive reactions investigated show different volumes of activation and hence a different response to pressure.[16] Generally, reactions accompanied with a decrease in volume (activation volume $\Delta V^{\ddagger} < 0$) are accelerated by raising the pressure while those accompanied by an increase in volume are retarded ($\Delta V^{\ddagger} > 0$).[16,17] In particular, reactions involving a charge separation (*e.g.* the Menshutkin-type S_N2-alkylation of pyridine) and cyclizations such as inter- and intramolecular Diels–Alder reactions show a dramatic decrease in volume and, hence, profit from high pressure.[17] This effect is frequently exploited for synthetic purposes.[18]

To elucidate the effect of pressure on the regiochemistry of the PET-oxidative cyclization we investigated the reaction of **11** in which the *endo* cyclization leading to **12** competes with *exo* cyclization leading to **13** and **14**. According to Scheme 4 there

Table 5 PET-oxidative cyclization of **11** in acetonitrile–toluene solution with different toluene mole fractions x at 1500 bar

x (toluene)	0.00	0.25	0.33
6-*endo*/5-*exo*	1.9	2.0	2.3

are two mechanistic alternatives to explain the formation of the *endo* and *exo* cyclization products. The first mechanism consists of the competitive product-determining *endo* and *exo* cyclization (k_{endo}/k_{exo}) of the primary radical cation generated by the sensitized photolysis. In this case the formation of the larger six-membered ring is expected to be favored over that of the five-membered ring at high pressure, so that the product ratio **12**:(**13** + **14**) should be shifted toward **12** by pressure.[17e,f]

In the product-determining step of the second mechanism the *endo* cyclization of the radical cation **A** competes with S_N2-type substitution of the trimethylsilyl group of the radical cation by the electron donor solvent which should have a more negative activation volume due to its bimolecular character than the intramolecular cyclization. In this case the product ratio **12**:(**13** + **14**) should be shifted toward (**13** + **14**) by pressure, provided that the free radical generated by the solvent assisted elimination of the trimethylsilyl group from the radical cation, cyclizes exclusively in the *exo* fashion.[19] In order to attain a conversion of about 30% after 5 h of irradiation we employed the sensitizer–cosensitizer couple DCN–biphenyl (conditions: 0.01 equiv. Sens, 2 equiv. Cosens). Using *n*-dodecane as an internal standard the conversion of the silyl enol ether was monitored by gas chromatography. A high-pressure mercury–xenon vapor lamp (1000 W) was used as the light source. The 6-*endo*/5-*exo* ratio obtained by irradiating in the high pressure cell at 1 bar resembles the results obtained in a Rayonet photochemical reactor as described above. This ratio shows a significant pressure dependence and changes at 20 °C from 2.6:1.0 at 1 bar to 1.9:1.0 at 1500 bar and 1.3:1.0 at 3000 bar. The difference in the activation volumes of the cyclization reactions was calculated from the pressure dependence of this ratio by the use of linear relation $\ln[\text{6-}endo/\text{5-}exo)_p] = a + bp$, $\Delta\Delta V^{\ddagger} = -bRT$ to be $\Delta\Delta V^{\ddagger} = [\Delta V^{\ddagger}$ (6-*endo*) $- \Delta V^{\ddagger}$ (5-*exo*)$] = +5.8 \pm 0.3$ cm^3 mol^{-1}.

This result is good evidence for the second mechanism in which the *endo* cyclization competes with solvent-assisted elimination of the trimethylsilyl group from the radical cation. Further support of this mechanism comes from the finding that the 6-*endo*/5-*exo* ratio in different mixtures of acetonitrile and toluene is increased by raising the content of toluene in the solvent mixture (Table 5).

Experimental

General details

Substances and solvents were purified and/or distilled before use. Triisopropylsilyl trifluoromethanesulfonate (TIPSOTf) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf) were purchased from Fluka and used without purification. All reactions were carried out in dry solvents under argon. The irradiations were performed in a Rayonet RPR-100 Photoreactor (Southern New England) fitted with 16 lamps RPR-4190 Å or RPR-3500 Å and a merry-go-round inset using Pyrex tubes of 10 cm^3 volume. The solutions were deoxygenated with argon. For HPLC Kontron pump 420 and Merck pump L-6000, RI-detector Bischoff RI 8110, and a column 250 × 20 mm, Merck LiChrosorb Si 60-5 were used at a flow rate of 10 cm^3 min^{-1}, eluent cyclohexane–ethyl acetate. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 P, a Bruker WM 300, a Bruker AM 360 or a Bruker DRX 500 spectrometer, using TMS as reference and $CDCl_3$ as solvent. All chemical shifts are denoted by δ values and J values are given in Hz. The melting points were determined with a Büchi 510 and the IR spectra were recorded on a Perkin-Elmer 1600 (FT-IR) and on a Perkin-Elmer 298. Elemental analyses were performed with a Perkin-Elmer DIA CHN 240 or a Heraeus CHN-O-Rapid.

High pressure irradiations were performed in a Sitec 4 kbar high pressure cell with sapphire windows. The cell was assembled on a Dieckers high pressure vessel with 7 kbar pressure generator. For reasons of comparison the experiments at 1 bar were performed in the high pressure Sitec cell as well.

Procedure A: Silylation with LDA and trimethylchlorosilane

At −78 °C a solution of the respective ketone (25.0 mmol) in 10 cm^3 THF was added under an argon atmosphere to a solution of LDA (26.4 mmol) in 60 cm^3 THF. After stirring for 1 h at −78 °C trimethylchlorosilane (5.50 cm^3, 43.5 mmol) was added and the flask was allowed to warm to room temperature. After additional stirring for 1 h the solution was evaporated *in vacuo*. *n*-Pentane (50 cm^3) was added to the residue and the suspension was filtered. The resulting solution was evaporated *in vacuo* and distilled.

Procedure B: PET-oxidative cyclization

A 0.05 M argon-saturated solution of the respective silyl enol ether in dry MeCN, in a MeCN–alcohol or in a MeCN–toluene mixture was irradiated in the presence of a PET-sensitizer (10–20 mol%), *e.g.* 9,10-dicyanoanthracene (DCA) at 419 nm, or 1,4-dicyanonaphthalene (DCN) at 350 nm, for at least 30 h. The consumption was monitored by gas chromatography with *n*-dodecane as internal standard. After complete consumption the solvent was evaporated *in vacuo* and the residue was filtered over silica gel. The purification of the products was performed by HPLC (cyclohexane–ethyl acetate).

Synthesis of 6-methyl-1-phenylhept-6-en-1-one

At 0 °C 1-bromo-4-methylpent-4-ene[20] (28.5 g, 0.17 mmol) was added to a solution of Na (4.4 g, 0.19 mmol) and benzoyl ethyl acetate (44.2 g, 0.23 mmol) in 50 cm^3 absolute ethyl alcohol. After stirring at room temperature for 2 h and at 60 °C for 4 h NaBr was filtered off. The solution was concentrated and sodium hydroxide solution (10%; 100 cm^3) was added. Saponification was achieved by stirring for 2 h at room temperature and 3 h at 60 °C. The solution was carefully acidified with conc. HCl (pH 4) and extracted with diethyl ether. The combined organic layers were washed with saturated $NaHCO_3$ solution and H_2O, dried ($MgSO_4$) and evaporated *in vacuo*. 6-Methyl-1-phenylhept-6-en-1-one (10.2 g, 30%) was obtained by distillation *in vacuo* (bp 98 °C; 0.35 mbar) as a colourless liquid (Found: C, 83.1; H, 9.0. $C_{14}H_{18}O$ requires C, 83.05; H, 9.0%); ν_{max}/cm^{-1} 2900, 1670, 1640; δ_H(300 MHz; $CDCl_3$) 1.45–1.60 (2 H, m, 4-H), 1.65–1.80 (2 H, m, 3-H), 1.75 (3 H, s, 6-Me), 2.05 (2 H, t, J 7.5, 5-H), 2.95 (2 H, t, J 7.5, 2-H), 4.70 (2 H, d, J 6.5, 2-H), 7.40–7.60 (3 H, m), 7.95 (2 H, dd, J 2.0 and 7.0); δ_C(75 MHz; $CDCl_3$) 22.0 (C-8), 23.7 (C-3), 27.0 (C-4), 37.3 (C-5), 38.1 (C-2), 109.8 (C-7), 127.7 (C-3′), 128.2 (C-2′), 132.5 (C-4′), 136.8 (C-1′), 145.2 (C-6), 199.9 (C-1); *m*/*z* 202 (M^+, 7%), 120 (60), 105 (100), 77 (38).

Synthesis of (*E*)-1-phenyloct-6-en-1-one

HMPA (8.7 cm^3, 50 mmol) was added under argon atmosphere to a solution of LDA (60 mmol) in 120 cm^3 THF at room temperature. Acetophenone–cyclohexylimine[21] (10.1 g, 50 mmol) was added to the solution at 0 °C. After stirring for 10 min at 0 °C and 30 min at −78 °C (*E*)-1-bromohex-5-ene[22] (11.4 g, 53.3 mmol) was added and the resulting solution was stirred for an additional 16 h at −78 °C. After the flask was allowed to warm to room temperature HCl (2 mol dm^{-3}; 130 cm^3) was added and the reaction mixture was heated under reflux for 2 h.

The aqueous phase was extracted with diethyl ether and the combined organic layers were washed with saturated $NaHCO_3$ solution and saturated NaCl solution and dried ($MgSO_4$). After evaporation *in vacuo* (*E*)-1-phenyloct-6-en-1-one (10.2 g, 30%) was obtained by distillation *in vacuo* (bp 106 °C; 0.2 mbar) as a colourless liquid (Found: C, 83.1; H, 9.0. $C_{14}H_{18}O$ requires C, 82.95; H, 9.0%), mp 34 °C; ν_{max}/cm^{-1} 2940, 1670, 1580, 1440; δ_H(300 MHz; $CDCl_3$) 1.35–1.40 (2 H, m, 4-H), 1.62 (3 H, m, 8-H), 1.65–1.80 (2 H, m, 3-H), 1.95–2.05 (2 H, m, 5-H), 2.92 (2 H, t, *J* 7.5, 2-H), 5.38–5.44 (2 H, m, 6-H, 7-H), 7.38–7.55 (3 H, m), 7.93 (2 H, d, *J* 7.5); δ_C(75 MHz; $CDCl_3$) 17.7 (C-8), 23.8 (C-3), 29.1 (C-4), 32.2 (C-5), 38.2 (C-2), 124.9 (C-7), 127.8 (C-3′), 128.3 (C-2′), 129.8 (C-6), 132.6 (C-4′), 136.9 (C-1′), 200.0 (C-1); *m*/*z* 202 (M^+, 14%), 120 (24), 105 (100), 77 (28).

Synthesis of trimethyl{[(3*Z*)-2,2-dimethylnona-3,8-dienyl]oxy}-silane (1)

2,2-Dimethylnon-8-en-3-one[23] (4.2 g, 25 mmol) was transformed into the silyl enol ether **1** according to procedure A. Purification by distillation *in vacuo* (bp 98 °C; 7 mbar) gave **1** (4.5 g, 72%) as a colourless liquid (Found: C, 68.9; H, 12.0. $C_{14}H_{28}OSi$ requires C, 69.95; H, 11.75%); ν_{max}/cm^{-1} 2900, 1655, 1450, 1245; δ_H(300 MHz, $CDCl_3$) 0.23 (9 H, s, $SiMe_3$), 1.15 (9 H, s, 1-H), 1.45 (2 H, tt, *J* 7.5 and 7.5, 6-H), 2.00 (4 H, m, 5-H, 7-H), 4.50 (1 H, t, *J* 6.5, 4-H), 4.90–5.05 (2 H, m, 9-H), 5.82 (1 H, ddt, *J* 10.0, 17.0 and 6.5, 8-H); δ_C(75 MHz, $CDCl_3$) 1.1 ($SiMe_3$), 25.8 (C-5), 28.6 (C-1), 29.3 (C-6), 33.7 (C-7), 36.2 (C-2), 103.7 (C-4), 114.4 (C-9), 138.7 (C-8), 158.3 (C-3); *m*/*z* 240 (M^+, 6%), 225 (8), 185 (90), 183 (20), 75 (26), 73 (100), 41 (13).

Synthesis of trimethyl{[(1*Z*)-1-cyclohexylhepta-1,6-dienyl]oxy}-silane (3)

1-Cyclohexylhept-6-en-1-one[23] (9.7 g, 50 mmol) was converted to **3** according to procedure A. Purification by distillation *in vacuo* (bp 75 °C; 0.15 mbar) gave an inseparable mixture (10.7 g, 79%) of trimethyl{[(1*Z*)-1-cyclohexylhepta-1,6-dienyl]oxy}-silane (**3**) (69%) and trimethyl{[(1*E*)-1-cyclohexylhepta-1,6-dienyl]oxy}silane (31%) as a colourless liquid (Found: C, 72.3; H, 11.6. $C_{16}H_{30}OSi$ requires C, 72.1; H, 11.35%); ν_{max}/cm^{-1} 2875, 1640, 1450, 1250; δ_H(300 MHz, $CDCl_3$) 0.18 (9 H, s, $SiMe_3$), 1.00–1.35 (4 H, m), 1.35–1.55 (1 H, m), 1.55–1.90 (8 H, m), 2.00 (4 H, m), 4.40 (1 H, t, *J* 7.0), 4.92 (1 H, dm, *J* 10.0, 7-H), 4.98 (1 H, dm, *J* 17.0, 7-H), 5.80 (1 H, ddt, *J* 10.0, 17.0 and 7.0, 6-H); δ_C(75 MHz, $CDCl_3$) 0.7 ($SiMe_3$), 25.0–34.0 (C-3, C-4, C-5, C-2′, C-3′, C-4′), 44.5 (C-1′), 105.4 (C-2), 114.2 (C-7), 138.9 (C-6), 155.2 (C-1); *m*/*z* 266 (M^+, 10%), 251 (5), 211 (35), 183 (42), 129 (15), 75 (30), 73 (100).

Synthesis of trimethyl{[(1*Z*)-1-phenylhepta-1,6-dienyl]oxy}-silane (5)

1-Phenylhept-6-en-1-one[24] (9.4 g, 50 mmol) was transformed into silyl enol ether **5** as described in the procedure A. Purification by distillation *in vacuo* (bp 92 °C; 0.05 mbar) gave **5** (10.7 g, 82%) as a colourless liquid (Found: C, 73.8; H, 9.3. $C_{16}H_{24}OSi$ requires C, 73.8; H, 9.4%); ν_{max}/cm^{-1} 2960, 1645, 1480, 1250; δ_H(300 MHz, $CDCl_3$) 0.15 (9 H, s, $SiMe_3$), 1.55 (2 H, m, 4-H), 2.15 (2 H, m), 2.25 (2 H, m), 4.95 (1 H, d, *J* 11.0, 7-H), 5.05 (1 H, d, *J* 17.0, 7-H), 5.25 (1 H, t, *J* 7.5, 2-H), 5.80 (1 H, ddt, *J* 11.0, 17.0 and 7.0, 6-H), 7.25 (3 H, m), 7.50 (2 H, d, *J* 7.5, 2′-H); δ_C(75 MHz, $CDCl_3$) 0.5 ($SiMe_3$), 25.7 (C-3), 28.9 (C-4), 33.6 (C-5), 110.9 (C-2), 114.4 (C-7), 125.3 (C-2′), 127.3 (C-4′), 127.9 (C-3′), 138.7 (C-6), 139.2 (C-1′), 149.1 (C-1); *m*/*z* 260 (M^+, 8%), 205 (25), 77 (12), 73 (100).

Synthesis of trimethyl{[(1*Z*)-1-(4-methoxyphenyl)hepta-1,6-dienyl]oxy}silane (7)

1-(4-Methoxyphenyl)oct-6-en-1-one[23] (4.4 g, 20 mmol) was converted to **7** according to procedure A. Purification by distillation *in vacuo* (bp 160 °C; 0.07 mbar) gave silyl enol ether **7** (4.9 g, 85%) as a colourless liquid; ν_{max}/cm^{-1} 2900, 1630, 1490, 1270, 1230; δ_H(300 MHz, $CDCl_3$) 0.05 (9 H, s, $SiMe_3$), 1.35 (2 H, tt, *J* 7.5 and 7.5, 4-H), 1.95 (4H, m, 3-H, 5-H), 3.76 (3 H, s, OMe), 4.90 (3 H, m, 2-H, 7-H), 5.83 (1 H, ddt, *J* 11.0, 17.0 and 7.0, 6-H), 6.80 (2 H, d, *J* 9.0, 3′-H), 7.35 (2 H, d, *J* 9.0, 2′-H); *m*/*z* 290 (M^+, 18%), 289 (34), 259 (44), 236 (22), 235 (96), 135 (16), 75 (16), 73 (100); high resolution MS calc. for $C_{17}H_{26}OSi$ 290.1702, found 290.1707.

Synthesis of trimethyl{[(1*Z*)-6-methyl-1-phenylhepta-1,6-dienyl]-oxy}silane (9)

Ketone **17** (5.1 g, 25 mmol) was transformed into silyl enol ether **9** according to procedure A. Purification by distillation *in vacuo* (bp 85 °C; 0.5 mbar) gave **9** (5.2 g, 76%) as a colourless liquid (Found: C, 72.8; H, 9.5. $C_{17}H_{26}OSi$ requires C, 74.4; H, 9.55%); ν_{max}/cm^{-1} 2950, 1640, 1495, 1250; δ_H(300 MHz, $CDCl_3$) 0.25 (9 H, s, $SiMe_3$), 1.65 (2 H, m, 4-H), 1.80 (3 H, s, CH_3), 2.18 (2 H, t, *J* 7.5, 5-H), 2.31 (2 H, dt, *J* 7.5 and 7.5, 3-H), 4.82 (2 H, m, 7-H), 5.34 (1 H, t, *J* 7.5, 2-H), 7.2–7.4 (3 H, m), 7.56 (2 H, dd, *J* 2.0 and 7.0); δ_C(75 MHz, $CDCl_3$) 0.4 ($SiMe_3$), 22.3 (CH_3), 25.9 (C-3), 27.9 (C-4), 37.6 (C-5), 109.9 (C-7), 110.9 (C-2), 125.2 (C-2′), 127.2 (C-4′), 127.9 (C-3′), 139.2 (C-1′), 145.4 (C-6), 149.1 (C-1); *m*/*z* 274 (M^+, 24%), 205 (80), 73 (100).

Synthesis of trimethyl{[(1*Z*,6*E*)-1-phenylocta-1,6-dienyl]oxy}-silane (11)

Ketone **18** (1.4 g, 6.8 mmol) was transformed into silyl enol ether **11** according to procedure A. Purification by distillation *in vacuo* (bp 140 °C; 0.5 mbar) gave **11** (1.7 g, 89%) as a colourless liquid (Found: C, 74.7; H, 9.55. $C_{17}H_{26}OSi$ requires C, 74.4; H, 9.55%); ν_{max}/cm^{-1} 2940, 1640, 1440, 1250; δ_H(300 MHz, $CDCl_3$) 0.05 (9 H, s, $SiMe_3$), 1.55 (2 H, m), 1.65 (3 H, m, 8-H), 1.95 (2 H, m), 2.15 (2 H, m), 5.15 (1 H, t, *J* 7.5, 2-H), 5.3–5.4 (2 H, m, 6-H, 7-H), 7.05–7.21 (3 H, m), 7.37 (2 H, d, *J* 7.5); δ_C(75 MHz, $CDCl_3$) 0.5 ($SiMe_3$), 17.8 (C-8), 25.7 (C-3), 29.6 (C-4), 32.4 (C-5), 111.1 (C-2), 124.9 (C-7), 125.3 (C-2′), 127.2 (C-4′), 127.9 (C-3′), 131.2 (C-6), 139.3 (C-1′), 149.1 (C-1); *m*/*z* 274 (M^+, 6%), 205 (40), 73 (100).

Synthesis of (1,1-dimethylethyl)dimethyl{[(1*Z*,6*E*)-1-phenylhepta-1,6-dienyl]oxy}silane (15)

A solution of TBDMSOTf (2.8 cm^3, 12 mmol) in 10 cm^3 of CH_2Cl_2 was added at 25 °C to a solution of ketone **18** (2.2 g, 11 mmol) and Et_3N (4.8 cm^3, 34 mmol) in 50 cm^3 of CH_2Cl_2. The solution was stirred at room temperature for 24 h, diluted with 125 cm^3 CH_2Cl_2, washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$) and evaporated *in vacuo*. Purification by distillation *in vacuo* (bp 130 °C; 0.9 mbar) gave pure silyl enol ether **15** (2.6 g, 74%) as a colourless liquid; ν_{max}/cm^{-1} 2930, 1650, 1490, 1280; δ_H(200 MHz, $CDCl_3$) −0.04 (6 H, s, $Si(CH_3)_2$-$C(CH_3)_3$), 1.00 (9 H, s, $Si(CH_3)_2C(CH_3)_3$), 1.50 (2 H, m), 1.65 (3 H, m, 8-H), 2.05 (2 H, m), 2.20 (2 H, m), 5.10 (1 H, t, *J* 7.0, 2-H), 5.40–5.50 (2 H, m, 6-H, 7-H), 7.25 (3 H, m, 3′-H, 4′-H), 7.45 (2 H, m, 2′-H); δ_C(50 MHz, $CDCl_3$) −4.0 ($Si(CH_3)_2$-$C(CH_3)_3$), 17.9 (C-8), 18.4 ($Si(CH_3)_2C(CH_3)_3$), 25.8 (C-3), 25.9 ($Si(CH_3)_2C(CH_3)_3$), 29.6 (C-4), 32.5 (C-5), 111.8 (C-2), 125.0 (C-7), 125.9 (C-2′), 127.3 (C-4′), 127.9 (C-3′), 131.4 (C-6), 139.9 (C-1′), 149.4 (C-1); *m*/*z* 316 (M^+, 47%), 75 (95), 73 (100); high resolution MS calc. for $C_{20}H_{32}OSi$ 316.2222, found 316.2222.

Synthesis of tri(1-methylethyl){[(1*Z*,6*E*)-1-phenylhepta-1,6-dienyl]oxy}silane (16)

At 25 °C a solution of TIPSOTf (3.3 cm^3, 11 mmol) in 10 cm^3 of CH_2Cl_2 was added to a solution of ketone **18** (2.2 g, 11 mmol) and Et_3N (2.4 cm^3, 17 mmol) in 50 cm^3 of CH_2Cl_2. The solution was stirred at room temperature for 1 h, diluted with

250 cm^3 CH_2Cl_2, washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$) and evaporated *in vacuo*. Purification by chromatography on neutral Al_2O_3 (*n*-pentane–diethyl ether, 9:1; containing 0.5% pyridine) gave silyl enol ether **16** (2.5 g, 65%) as a colourless liquid; ν_{max}/cm^{-1} 2940, 1680, 1460, 1280; δ_H(200 MHz, $CDCl_3$) 0.90–1.10 [21 H, m, $Si(CH(CH_3)_2)_3$], 1.50 (2 H, m), 1.65 (3 H, m, 8-H), 2.05 (2 H, m), 2.20 (2 H, m), 5.00 (1 H, t, *J* 7.5, 2-H), 5.35–5.50 (2 H, m, 6-H, 7-H), 7.20–7.35 (3 H, m, 3′-H, 4′-H), 7.45 (2 H, m, 2′-H); δ_C(75 MHz, $CDCl_3$) 13.5 [$Si(CH(CH_3)_2)_3$], 17.9 [$Si(CH(CH_3)_2)_3$], 18.0 (C-8), 25.8 (C-3), 29.6 (C-4), 32.5 (C-5), 111.2 (C-2), 124.9 (C-7), 126.0 (C-2′), 127.2 (C-4′), 127.9 (C-3′), 131.3 (C-6), 140.4 (C-1′), 150.3 (C-1); *m*/*z* 358 (M^+, 79%), 131 (100), 75 (48), 73 (28); high resolution MS calc. for $C_{23}H_{38}OSi$ 358.2692, found 358.2691.

Synthesis of 1-cyclohexyl-2,2-dimethylpropan-1-one (2)

Following procedure B a solution of trimethyl{[(3*Z*)-2,2-dimethylnona-3,8-dienyl]oxy}silane (**1**) (157.4 mg, 0.654 mmol) in dry MeCN (10 cm^3) was irradiated in the presence of DCA (12 mg, 0.05 mmol) for 335 h. Purification by HPLC (cyclohexane–ethyl acetate, 99:1) gave ketone **2** (25.2 mg, 23%); ν_{max}/cm^{-1} 2880, 1685, 1440; δ_H(300 MHz, $CDCl_3$) 1.10 (9 H, s, 3-H), 1.20–1.45 (5 H, m), 1.55–1.90 (5 H, m), 2.85 (1 H, tt, *J* 3.5 and 11.5, 1′-H); δ_C(75 MHz, DMSO-d_6) 25.2 (CH_2), 25.4 (CH_2), 25.7 (C-3), 29.7 (CH_2), 43.8 (C-1′), 44.1 (C-2), 217.5 (C=O); *m*/*z* 168 (M^+, 4%), 111 (20), 83 (100), 57 (35), 55 (36), 41 (38).

Synthesis of dicyclohexyl ketone (4)

Following procedure B a solution of trimethyl{[(1*Z*)-1-cyclohexylhepta-1,6-dienyl]oxy}silane (**3**) (1.38 g, 5.19 mmol) in dry MeCN (100 cm^3) was irradiated in the presence of DCA (70 mg, 0.31 mmol) for 120 h. Purification by HPLC (cyclohexane–ethyl acetate, 199:1) gave ketone **4** (370 mg, 37%); the structure of compound **4** was assigned by comparison with an authentic sample.

Synthesis of benzoylcyclohexane (6)

Following procedure B a solution of trimethyl{[(1*Z*)-1-phenylhepta-1,6-dienyl]oxy}silane (**5**) (1.83 mg, 5.30 mmol) in dry MeCN (100 cm^3) was irradiated in the presence of DCA (144 mg, 0.63 mmol) for 150 h. Purification by HPLC (cyclohexane–ethyl acetate, 99:1) gave ketone **6** (259 mg, 26%) as colourless crystals, mp 57 °C; ν_{max}/cm^{-1} 2930, 1670, 1445, 1250; δ_H(200 MHz, $CDCl_3$) 1.20–1.55 (5 H, m), 1.65–1.80 (1 H, m), 1.85–1.95 (4 H, m), 3.25 (1 H, tt, *J* 3.0 and 11.0, 1-H), 7.45–7.55 (3 H, m, 3′-H, 4′-H), 7.95 (2 H, m, 2′-H); δ_C(50 MHz, $CDCl_3$) 25.9 (CH_2), 26.0 (CH_2), 29.4 (CH_2), 45.6 (C-1), 128.3 (CH), 128.6 (CH), 132.7 (C-4′), 136.3 (C-1′), 203.9 (C=O); *m*/*z* 188 (M^+, 27%), 133 (11), 120 (6), 105 (100), 77 (27).

Synthesis of *p*-anisoylcyclohexane (8)

Following procedure B a solution of trimethyl{[(1*Z*)-1-(4-methoxyphenyl)hepta-1,6-dienyl]oxy}silane (**7**) (1.01 g, 3.48 mmol) in dry MeCN (50 cm^3) was irradiated in the presence of DCA (62 mg, 0.27 mmol) for 113 h. Purification by HPLC (cyclohexane–ethyl acetate, 95:5) gave ketone **8** (200 mg, 26%) as colourless crystals, mp 89–92 °C (Found: C, 77.15; H, 8.25. $C_{14}H_{18}O$ requires C, 77.0; H, 8.3%); ν_{max}/cm^{-1} 2950, 1660, 1450, 1250; δ_H(300 MHz, $CDCl_3$) 1.15–1.55 (5 H, m), 1.70 (1 H, m), 1.75–1.90 (4 H, m), 3.20 (1 H, tt, *J* 3.5 and 11.0, 1-H), 3.80 (3 H, s, 7′-H), 6.89 (2 H, d, *J* 9.0, 3′-H), 7.90 (2 H, d, *J* 9.0, 2′-H); δ_C(75 MHz, $CDCl_3$) 25.8 (CH_2), 25.9 (C-4), 29.4 (CH_2), 45.2 (C-1), 55.2 (C-7′), 113.6 (C-3′), 129.2 (C-1′), 130.3 (C-2′), 163.1 (C-4′), 202.2 (C-7); *m*/*z* 218 (M^+, 20%), 187 (5), 163 (7), 150 (12), 136 (15), 135 (100), 107 (12), 92 (19), 77 (18).

Synthesis of *cis*-benzoyl-3-methylcyclohexane (10)

Following procedure B a solution of trimethyl{[(1*Z*)-6-methyl-1-phenylhepta-1,6-dienyl]oxy}silane (**9**) (903 mg, 3.29 mmol) in dry MeCN (50 cm^3) was irradiated in the presence of DCA (54 mg, 0.23 mmol) for 90 h. Purification by HPLC (cyclohexane–ethyl acetate, 99:1) gave ketone **10** (220 mg, 33%) as a colourless liquid; ν_{max}/cm^{-1} 2930, 1680, 1450, 1270; δ_H(200 MHz, $CDCl_3$) 0.95 (3 H, d, *J* 6.5, CH_3), 1.15 (1 H, m, 3-H), 1.40 (2 H, m), 1.55 (1 H, m), 1.70 (2 H, m), 1.90 (3 H, m), 3.32 (1 H, tt, *J* 3.5 and 11.5, 1-H), 7.40–7.60 (3 H, m, 3′-H, 4′-H), 7.95 (2 H, dd, *J* 1.5 and 8.0, 2′-H); δ_C(50 MHz, $CDCl_3$) 22.7 (CH_3), 25.8 (CH_2), 29.0 (CH_2), 32.4 (C-3), 34.7 (CH_2), 37.8 (CH_2), 45.7 (C-1), 128.2 (CH), 128.6 (CH), 132.7 (C-4′), 136.4 (C-1′), 203.7 (C=O); *m*/*z* 202 (M^+, 17%), 146 (8), 133 (10), 105 (100), 77 (22); high resolution MS calc. for $C_{14}H_{18}O$ 202.1358, found 202.1361.

Synthesis of *trans*-benzoyl-2-methylcyclohexane (12), (3a*R**,7*S**,7a*S**)-*trans*-7-methylhexahydrobenzo[*f*]indan-4-one (13) and (3a*R**,7*S**,7a*R**)-*cis*-7-methylhexahydrobenzo[*f*]indan-4-one (14)

Following the procedure B a solution of trimethyl{[(1*Z*)-phenylocta-1,6-dienyl]oxy}silane (**11**) (1.4 g, 5.0 mmol) in dry MeCN–MeOH (80 cm^3; 17:3) was irradiated in the presence of DCA (110 mg, 0.51 mmol) for 140 h. Purification by HPLC (cyclohexane–ethyl acetate, 99:1) gave ketone **12** (173 mg, 17%) and an inseparable 1.2:1 mixture of the diastereomers **13** and **14** (202 mg, 20%) according to increasing polarity.

***trans*-Benzoyl-2-methylcyclohexane (12).** (Found: C, 83.1; H, 9.0. $C_{14}H_{18}O$ requires C, 82.0; H, 8.7%); ν_{max}/cm^{-1} 2930, 1680, 1440, 1260; δ_H(200 MHz, $CDCl_3$) 0.82 (3 H, d, *J* 7.0, CH_3), 1.00–1.20 (1 H, m), 1.25–1.45 (3 H, m), 1.70–2.00 (5 H, m), 3.05 (1 H, ddd, *J* 3.5, 11.0 and 11.0, 1-H), 7.40–7.60 (3 H, m, 3′-H, 4′-H), 7.95 (2 H, m, 2′-H); δ_C(75 MHz, $CDCl_3$) 20.9 (CH_3), 26.0 (CH_2), 26.1 (CH_2), 30.9 (CH_2), 34.1 (C-2), 34.7 (CH_2), 52.3 (C-1), 128.2 (CH), 128.6 (CH), 132.8 (C-4′), 137.5 (C-1′), 204.6 (C=O); *m*/*z* 202 (M^+, 30%), 146 (7), 133 (8), 120 (7), 105 (100), 77 (29).

(3a*R,7*S**,7a*S**)-*trans*-7-Methylhexahydrobenzo[*f*]indan-4-one (13).** Mp 95 °C; ν_{max}/cm^{-1} 2960, 1690, 1450, 1240; δ_H(500 MHz, $CDCl_3$) 1.44 (3 H, d, *J* 6.8, CH_3), 1.48 (1 H, dddd, *J* 4.0, 7.8, 10.4 and 12.0, 1-H), 1.73 (1 H, ddddd, *J* 4.4, 8.0, 10.4, 11.0 and 12.5, 2-H), 1.80 (1 H, dddd, *J* 4.0, 6.5, 10.7 and 13.6, 7a-H), 1.83 (1 H, ddddd, *J* 2.5, 6.7, 7.8, 9.0 and 12.5, 2-H), 1.94 (1 H, dddd, *J* 6.7, 10.2, 11.0 and 13.4, 3-H), 2.05 (1 H, dddd, *J* 4.4, 8.0, 9.0 and 13.4, 3-H), 2.14 (1 H, dddd, *J* 2.5, 6.5, 8.0 and 12.0, 1-H), 2.52 (1 H, ddd, *J* 8.0, 10.2 and 13.6, 3a-H), 2.86 (1 H, qd, *J* 10.7 and 6.8, 7-H), 7.32 (1 H, dd, *J* 7.2 and 7.9, 10-H), 7.45 (1 H, md, *J* 7.9, 8-H), 7.52 (1 H, ddd, *J* 1.5, 7.2 and 7.9, 9-H), 8.04 (1 H, dd, *J* 1.5 and 7.9, 11-H); δ_C(125 MHz, $CDCl_3$) 18.6 (CH_3), 22.2 (C-2), 24.0 (C-3), 31.1 (C-1), 40.5 (C-7), 51.3 (C-7a), 55.1 (C-3a), 126.3 (C-10), 126.7 (C-8), 127.0 (C-11), 133.2 (C-9), 133.6 (C-5), 148.6 (C-6), 200.1 (C-4); *m*/*z* 200 (M^+, 100%), 171 (38), 167 (31), 159 (20), 132 (76), 104 (46), 77 (28); high resolution MS calc. for $C_{14}H_{16}O$ 200.1201, found 200.1201.

(3a*R,7*S**,7a*R**)-*cis*-7-Methylhexahydrobenzo[*f*]indan-4-one (14).** δ_H(500 MHz, $CDCl_3$) 1.24–1.34 (2 H, m, CH_2), 1.36 (3 H, d, *J* 6.8, CH_3), 1.53–1.60 (2 H, m, CH_2), 1.84–1.90 (2 H, m, CH_2), 2.38 (1 H, dddd, *J* 3.5, 7.4, 7.4 and 10.0, 7a-H), 2.99 (1 H, ddd, *J* 4.7, 7.4 and 11.2, 3a-H), 3.01 (1 H, dq, *J* 7.0 and 3.5, 7-H), 7.27 (1 H, m, CH), 7.29 (1 H, m, CH), 7.49 (1 H, dd, *J* 1.5 and 7.5, 8-H), 7.95 (1 H, dd, *J* 1.5 and 7.0, 11-H); δ_C(125 MHz, $CDCl_3$) 23.6 (C-2), 24.3 (CH_3), 30.0 (C-3), 31.0 (C-1), 35.6 (C-7), 45.6 (C-7a), 47.4 (C-3a), 126.6 (C-10), 127.3 (C-8), 128.8 (C-11), 131.2 (C-5), 133.6 (C-9), 147.8 (C-6), 201.4 (C-4);

m/*z* 200 (M^+, 100%), 171 (38), 167 (31), 159 (20), 132 (76), 104 (46), 77 (28).

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Paper 8/07683I