A New Phototransformation of Methoxycarbonyl-Substituted (*E*,*Z*,*E*)-1,3,5-Hexatrienes: Easy Access to Ring-Annelated 8-Oxabicyclo[3.2.1]octa-2,6-diene Derivatives

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Abstract: On attempting photochemically induced electrocyclizations of the previously reported 1,6-bismethoxycarbonyl- or 1,6-bistrimethylsilyl-substituted ring-attached (*E*,*Z*,*E*)-1,3,5-hexatrienes **4b**, **4c** and **5b**, **5c**, equilibrium mixtures of the starting materials and their diastereomers, the corresponding (*E*,*Z*,*Z*)-hexatrienes **4b**, **4c** and **5b**, **5c** were obtained. The desired *trans*-disubstituted ring-annelated cyclohexadienes **9b** and **10b** were formed by subsequent thermal 6π-electrocyclization of the (*E*,*Z*,*Z*)-hexatrienes **4b** and **5b** in good yields (77–83%). Upon treating the bissilyl-substituted hexatrienes (*E*,*Z*,*E*)-**5c** or (*E*,*Z*,*Z*)-**5c** under the same conditions, 6π-electrocyclizations did occur, but the primary products immediately isomerized to a large extent, and mixtures of the cyclohexane-annelated cyclohexadienes **10c**–**12c** along with the dehydrogenation products **13**, **14c** were formed. When the bismethoxycarbonyl-substituted hexatriene (*E*,*Z*,*E*)-**5b** was irradiated for an extended period of time (4.5 h), the gradual formation of the oxabicyclo[3.2.1]octa-2,6-diene **17b** by a formal intramolecular hetero-Diels–Alder reaction was observed and **17b** could be isolated in up to 69% yield. To explore the scope of this new photochemical reaction, the new ring-attached (*E*,*Z*,*E*)-hexatrienes **4a**, **5a** and **6b** were synthesized by twofold Heck reactions from 1,2-dibromocycloalkenes **1**–**3** (59–66%). While irridiation of the cyclopentene-attached 1,3,5-hexatrienes only led to decomposition, the cyclohexene- and cycloheptene-attached hexatrienes gave the hetero-Diels–Alder products or other photoproducts depending on the size of the cycloalkene moiety and the nature of the alkoxycarbonyl substituents at the vinyl termini. The photoreaction products **17b** and **18b** which are bicyclic acetals, underwent cleavage upon treatment with a Lewis acid such as Me_3SiOTf to give the ring-annelated methoxycarbonyl-substituted tropone-carboxylates **21b** and **22b**.

Keywords: cycloaddition · Diels–Alder reaction · electrocyclic reaction · Heck reaction · photochemistry

Introduction

Palladium-catalyzed cross-coupling reactions often proceed in excellent yields, even when performed with oligohaloalkene and -arene derivatives.[1] Using this Heck methodology, alkenylations on 1,2-difunctionalized cycloalkenes give rise to 1,3,5-hexatrienes with a central cycloalkene skeleton, which are valuable intermediates for the synthesis of a broad spectrum of cyclic and bicyclic compounds.[2] Symmetrical (*E*,*Z*,*E*)-1,3,5-hexatrienes with two alkoxycarbonyl or phenyl substituents in the 1,6-position can be obtained by twofold Heck reaction of 1,2-dibromocycloalkenes with acrylates or styrene and afford ring-annelated cyclohexadienes after subsequent thermal 6π-electrocyclization.[2a] In addition, these hexatrienes can be utilized to prepare interesting bicyclic β-amino acids,[2b] strained 1,6-oxygen bridged cyclodeca-1,5-dienes[2c] as well as highly functionalized cyclodecenones and cycloundecenones.[2d] The preparation of unsymmetrical 1,3,5-hexatrienes by stepwise Heck reaction with two different alkenes turned out to be difficult even by using cycloalkenes with two leaving groups of different reactivity in the 1,2-positions.[2a,e] Towards this goal it is advantageous to first perform a cross-coupling reaction with alkenylstannanes—a so-called Stille reaction—on 2-bromocycloalk-1-enyl triflates which occurs chemoselectively at the

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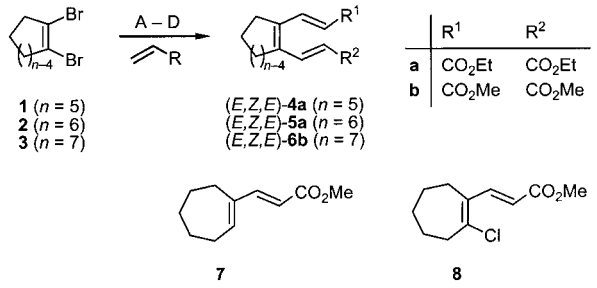
site of the triflate leaving group and then a Heck reaction on the resulting 2-bromo-1,3-butadienes.[2f,g] This sequence can be performed in a one-pot procedure, and its products can be transformed to yet another wide range of interesting cyclic skeletons. Moreover, it was shown that 1,6-bissilyl-(*E*,*Z*,*E*)-1,3,5-hexatrienes are obtained by twofold Heck reactions of 1,2-diiodocycloalkenes with alkenylsilanes, but unlike their counterparts with electron-withdrawing substituents—for example alkoxycarbonyl or phenyl groups—these compounds failed to undergo thermal 6π-electrocyclizations.[2a] This behavior was attributed to the steric demand of the two silyl groups which would have to end up *cis* with respect to each other on the cyclohexadiene moiety of the products due to the disrotatory ring closure under thermal conditions. This triggered our interest in the photochemical behavior of such 1,3,5-hexatrienes as, according to the Woodward–Hoffmann rules, their photochemical 6π-electrocyclization would occur conrotatorily[3] and lead to *trans*-5,6-disubstituted cyclohexadienes in which the steric interference between the silyl groups would be much smaller.

Photochemical conversions of 1,3,5-hexatrienes have been thoroughly investigated, mostly because the reverse reaction, the photochemical ring opening of a cyclohexa-1,3-diene to a 1,3,5-hexatriene, is the key step in the biogenesis of vitamin D.[4] According to the concept of ground state conformational control, the outcome of a photolysis of a 1,3,5-hexatriene with a (*Z*)-configured central double bond strongly depends on the predominant conformation of the starting material.[5] For the photochemical 6π-electrocyclization to occur, the starting 1,3,5-hexatrienes must adopt an s-*cis*,s-*cis* conformation and besides the expected cyclohexadienes, 3-vinylcyclobut-1-ene derivatives can be formed. 1,3,5-Hexatrienes with predominant s-*cis*,s-*trans* conformation upon irradiation, preferentially produce 3-vinylcyclobut-1-ene, bicyclo[3.1.0]hex-2-ene and 1,2,4-hexatriene derivatives. Finally, in photochemical conversions of open-chain 1,3,5-hexatrienes with an s-*trans*,s-*trans* conformation the (*Z*/*E*)-isomerization of the central double bond is favored. The steric constraints in the ring-attached 1,6-disubstituted (*E*,*Z*,*E*)-1,3,5-hexatrienes **4** and **5** would render a (*Z*/*E*)-isomerization of the central double bond improbable and further favor an s-*trans*,s-*trans* major conformation. This assumption is backed by the appearance of their UV/Vis spectra. The main absorption maximum shows up at approximately 290 nm for the bissilyl-, 320 nm for the bisalkoxycarbonyl- and 360 nm for the diphenyl-substituted hexatrienes and each is accompanied by shoulders at slightly higher and slightly lower wavelengths. These spectral data are characteristic for 1,3,5-hexatrienes with a predominant s-*trans*,s-*trans* conformation.[5d]

Results and Discussion

In addition to the previously published (*E*,*Z*,*E*)-hexatrienes **4b–d**, **5b–d** and **6d** the new ethoxycarbonyl-substituted analogues **4a**, **5a** as well as the cycloheptene-derived triene **6b**, were prepared. The (*E*,*Z*,*E*)-hexatrienes **4a** and **5a** with ethoxycarbonyl substituents were synthesized according to the established protocol (Scheme 1 and Table 1, entries 1,2).[2a] The twofold Heck reaction of ethyl acrylate with



Scheme 1. Heck reaction of 1,2-dibromocycloalkenes **1–3** with acrylates. For details see Table 1.

Table 1. Twofold Heck reaction of 1,2-dibromocycloalkenes **1–3** with acrylates.

Entry	Starting material	(*E*,*Z*,*E*)-Hexatriene	Conditions	*t* [h]	*T* [°C]	Yield[a] starting material	[%] Hexatriene
1	**1**	**4a**	A	24	100	–	59
2	**2**	**5a**	A	24	100	–	62
3	**3**	**6b**	A	16	100	–	14[b]
4	**3**	**6b**	B	8	90	20	30[c]
5	**3**	**6b**	C	7	90	38	28
6	**3**	**6b**	D	7	90	–	66

A: $[Pd(OAc)_2]$, PPh_3, NEt_3, DMF. B: $[Pd(OAc)_2]$, $(nBu)_4NBr$, LiCl, K_2CO_3, DMF. C: $[Pd(OAc)_2]$, $(nBu)_4NBr$, K_2CO_3, DMF. D: $[Pd_2(dba)_3]\cdot CHCl_3$, $(nBu)_4NBr$, K_2CO_3, DMF. [a] Isolated yields. [b] In addition 26% of the diene **7** was isolated. [c] In addition 8% of the chlorodienecarboxylate **8** was isolated.

dibromocyclopentene **1** and dibromocyclohexene **2** under classical conditions, that is, with triphenylphosphane and triethylamine as a soluble base, gave the desired products in 59 and 62%, respectively, isolated yield. For the preparation of the *tert*-butoxycarbonyl-substituted cycloheptene-derived hexatriene **6d** from 1,2-dibromocycloheptene (**3**)[2d] the modified conditions according to Jeffery had turned out to be better.[6] Indeed, the coupling of **3** with methyl acrylate under classical conditions afforded the hexatriene **6b** in a poor yield, and the reduced monoalkenylation product **7** predominated (entry 3). Under Jeffery's conditions, but with added lithium chloride, the formation of **7** was suppressed but the chlorodienecarboxylate **8** was formed in a considerable amount (entry 4), probably by a palladium-catalyzed bromine-chlorine[7] exchange due to the added lithium chloride. When the same reaction was run without lithium chloride, the yield of the hexatriene **6b** was not any better (28%), and the conversion less complete due to a premature precipitation of palladium black (entry 5). But with $[Pd_2(dba)_3]\cdot CHCl_3$ instead of $[Pd(OAc)_2]$ as a precatalyst, the yield of the desired hexatriene **6b** went up to 66% (entry 6).

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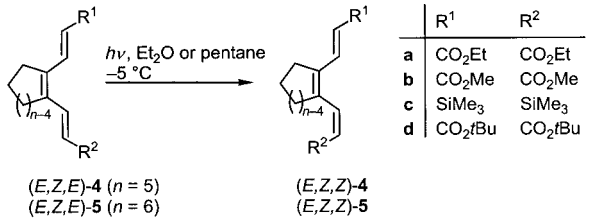
Upon irradiation of the 1,6-bissilyl-(*E*,*Z*,*E*)-1,3,5-hexatriene **4c** with a cyclopentene moiety in anhydrous deoxygenated diethyl ether or pentane with a 150 W medium pressure mercury lamp covered with a Pyrex glass filter, no electrocyclization took place, but (*E*)- to (*Z*)-isomerization of one of the exocyclic double bonds, as monitored by ^{1}H NMR spectroscopy. After 90 min, the ratio of the starting material (*E*,*Z*,*E*)-**4c** and the newly formed (*E*,*Z*,*Z*)-hexatriene **4c** had reached 44:56 (Scheme 2, Table 2, entry 1).



	R^1	R^2
a	CO_2Et	CO_2Et
b	CO_2Me	CO_2Me
c	$SiMe_3$	$SiMe_3$
d	CO_2tBu	CO_2tBu

Scheme 2. (*E*/*Z*)-Isomerization of **4** and **5**. For details see Table 2.

Table 2. Photochemical (*E*)- to (*Z*)-isomerization of silyl- and methoxycarbonyl-substituted (*E*,*Z*,*E*)-1,3,5-hexatrienes.

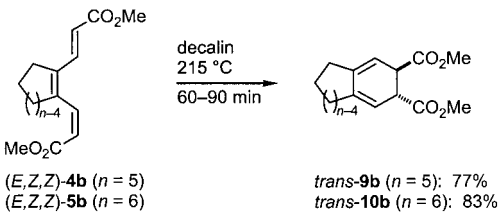
Entry	Hexatriene	Scale [mmol]	Solvent [mL]	*t* [h]	Ratio[a] (*E*,*Z*,*E*)/(*E*,*Z*,*Z*)	Yield[b] [%]
1	**4c**	0.20	Et_2O	0.5	55:45	–
			60	1.5	44:56	–
				2.5	**43**:**57**	–
2	**4c**	0.50	Et_2O	3	52:48	–
			60		72:28[d]	71
3	**5c**	1.00	pentane	1	26:74	–
			55	2	**8**:**92**	97
4	**5c**	1.00	pentane	3	8:92	–
			55	19	decomposition	
5	**4b**	0.22	Et_2O	0.3	81:19	–
			60	1.2	**68**:**32**	–
				3.2	66:34	–
				6.5	decomposition	
6	**4b**	0.22	Et_2O	2		51/24[e]
			60			
7	**5b**	0.50	Et_2O	0.7	33:67	25/51[e]
			60			
8	**4a**	0.20	Et_2O	2	decomposition	
			60			
9	**4d**	0.17	Et_2O	1	decomposition	
			60			

[a] Determined by ^{1}H NMR spectroscopy of small samples of the reaction mixture; ratios in bold indicate equilibrium composition. [b] Isolated yields after column chromatography. [c] Not isolated. [d] Ratio after column chromatography. [e] Isolated yields of (*E*,*Z*,*E*)- and (*E*,*Z*,*Z*)-isomers.

Prolonged irradiation did not change this ratio significantly. When a more concentrated (2.5 fold) solution was irradiated for 3 h, the ratio of (*E*,*Z*,*E*)-**4c**/(*E*,*Z*,*Z*)-**4c** in the isolated crude product (98% of the initial amount) was 52:48 (entry 2). Upon attempted separation by column chromatography on silica gel, the composition shifted to a ratio of 72:28 (71% of the initial amount) indicating that part of the (*E*,*Z*,*Z*)-isomer **4c** decomposed under these conditions. The analogous hexatriene (*E*,*Z*,*E*)-**5c** with a cyclohexene moiety also underwent photochemically induced (*E*/*Z*)-isomerization (entry 3). In this case the conversion to the (*E*,*Z*,*Z*)-isomer **5c** was even higher with a ratio 8:92 of the starting material (*E*,*Z*,*E*)-**5c** and the isomer (*E*,*Z*,*Z*)-**5c** after 2 h. In addition, trace amounts of two other products were detected, but according to their signals in the ^{1}H NMR spectrum none of them was the expected cyclohexadiene. Attempts to separate this mixture also failed, but unlike the (*E*,*Z*,*Z*)-isomer **4c**, the homologous (*E*,*Z*,*Z*)-isomer **5c** was stable on silica gel. Upon significantly extended irradiation (19 h) complete decomposition was observed (entry 4).

The irradiation of the methoxycarbonyl-substituted hexatrienes (*E*,*Z*,*E*)-**4b** and (*E*,*Z*,*E*)-**5b** led to similar results. In the case of the cyclopentene derivative **4b** a maximum ratio of 68:32 for (*E*,*Z*,*E*)-**4b**/(*E*,*Z*,*Z*)-**4b** was detected. These two isomers could be separated by column chromatography, and the isolated yields, 51% (*E*,*Z*,*E*)-**4b** and 24% (*E*,*Z*,*Z*)-**4b**, reflect the equilibrium ratio of the reaction mixture (entry 6). Longer reaction times just led to decomposition (entry 5). Irridiation of the cyclopentene-derived hexatrienes (*E*,*Z*,*E*)-**4a** and (*E*,*Z*,*E*)-**4d** also only led to decomposition of the starting material (entries 8, 9). In the case of the homologous cyclohexene derivative **5b**, a very fast (*E*/*Z*)-isomerization occurred, and after 42 min a 33:67 mixture of (*E*,*Z*,*E*)-**5b** and (*E*,*Z*,*Z*)-**5b** had formed from which the starting material (*E*,*Z*,*E*)-**5b** was isolated by column chromatography in 25% and its isomer (*E*,*Z*,*Z*)-**5b** in 51% yield (entry 7). Altogether, the intended photochemical 6π-electrocyclization was never observed.

However, a sequence of photochemical (*E*/*Z*)-isomerization to form (*E*,*Z*,*Z*)-hexatrienes and their subsequent thermal disrotatory 6π-electrocyclization should furnish the same products as a direct photochemical conrotatory cyclization. Indeed, upon heating the methoxycarbonyl-substituted (*E*,*Z*,*Z*)-hexatrienes **4b** and **5b** at 215 °C for 60–90 min in deoxygenated decalin in a sealed Pyrex bottle, they smoothly underwent 6π-electrocyclization to give the *trans*-disubstituted cyclohexadienes **9b** and **10b** in 77 and 83% yield, respectively (Scheme 3).



Scheme 3. Thermal electrocyclization of (*E*,*Z*,*Z*)-**4b** and (*E*,*Z*,*Z*)-**5b**.

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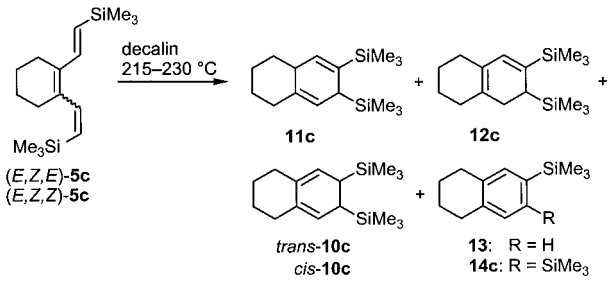
Under these conditions, the 1,6-bissilyl-(*E*,*Z*,*Z*)-hexatriene **5c** gave a mixture of six-ring-annelated cyclohexadienes which consisted mainly of the non-conjugated isomer **11c** (>95%) and only traces of the expected product *trans*-**10c** and a third isomer **12c** (Scheme 4 and Table 3, entry 1). After column chromatography on silica gel, the same mixture of isomeric cyclohexadienes was isolated in 54% yield and a small amount (7%) of the two tetralin derivatives **13** and **14c**, apparently formed by dehydrosilylation and dehydrogenation (oxidation), respectively. The bicyclic structure of all of the initial products was proven by treatment of the mixture with DDQ as an oxidant and subsequently with *p*-toluenesulfonic acid for protiodesilylation to yield tetrahydronaphthalene as the single product. When (*E*,*Z*,*Z*)-**5c** was heated in xylene at 150°C with NMR monitoring it became clear that the original 6π-electrocyclization product, the cyclohexadiene *trans*-**10c** is formed initially and then undergoes isomerization to **11c** and **12c** by formal 1,3- and 1,5-hydrogen shift, respectively. Encouraged by these results the cylization of the isomeric (*E*,*Z*,*E*)-hexatriene **5c** was reinvestigated, and indeed cyclization could be observed (entry 2). But again the product was not the expected cyclohexadiene *cis*-**10c** with *cis*-relationship of the silyl substituents. Instead, the isomer **12c** was the main product, accompanied by traces of the non-conjugated isomer **11c**. It is obvious that the primary cyclization product *cis*-**10c** would be destabilized by the steric interaction of the two silyl groups to such an extent that it would immediately undergo a thermally allowed 1,5-hydride shift to yield **12c**, but it is not understood, why the sterically far less congested *trans*-**10c**, the initial product from (*E*,*Z*,*Z*)-**5c**, would undergo a thermally forbidden 1,3-hydride shift under the same conditions.



Scheme 4. Thermal electrocyclization of (*E*,*Z*,*E*)-**5c** and (*E*,*Z*,*Z*)-**5c**. For details see Table 3.

Table 3. Thermal electrocyclization of hexatrienes (*E*,*Z*,*E*)-**5c** and (*E*,*Z*,*Z*)-**5c**.

Entry	Starting material	*t* [h]	Isolated fraction of start. amount [%]	Ratio[a] **11c**	**12c**	**10c**	**13/14c**
1	(*E*,*Z*,*Z*)-**5c**	3	crude product: 72	>95	trace	trace	–
			after CC: 54	>95	trace	trace	–
			after CC: 7	–	–	–	100
2	(*E*,*Z*,*E*)-**5c**	1	crude product: 95	trace	>95	–	–
			after CC: 86	trace	>95	–	–
			after CC: 7	–	–	–	100

CC = column chromatography. [a] Determined by ^{1}H NMR spectroscopy.

When the bismethoxycarbonyl-(*E*,*Z*,*E*)-hexatriene **5b** was irradiated for a relatively short time (42 min), only the (*E*/*Z*)-isomerization of one of the exocyclic double bonds was observed (see above). But upon extended irradiation, the gradual formation of another product was observed (Scheme 5 and Table 4, entry 1). After 4.5 h, the hexatriene (*E*,*Z*,*E*)-**5b** had been completely converted into the new product **17b**. The same reaction took place in benzene, but more slowly (entry 2). The structural assignment of **17b** as a six-ring-annelated 8-oxabicyclo[3.2.1]octa-2,6-diene derivative was ensured by extensive one- and two-dimensional NMR experiments and was later rigorously proven by the crystal structure of an analogous derivative (see below, Figure 1). Formally, the tricycle **17b** arises from an intramolecular hetero-Diels–Alder reaction, in which the carbonyl group of one of the acrylate functions acts as a dienophile which adds across the distal diene unit of the triene system. According to the Woodward–Hoffmann rules[3] this photochemical [4+2] cycloaddition cannot be a concerted reaction. Most probably, the triplet excited state of the molecule after (*E*/*Z*)-isomerization reacts as a 1,2-diradical on the carbonyl group. Due to its dipolar nature, this carbonyl then attacks the acceptor-substituted diene moiety in a 5-*exo*-*trig* mode to form the well stabilized diradical intermediate **16b** which finally undergoes a diastereoselective ring closure to yield **17b**. From the unsymmetrical (*E*,*Z*,*E*)-hexatriene **5e**, prepared along a sequence of Wittig-Horner-Emmons olefination of 2-bromocyclohexene-1-carbaldeyde and subsequent Heck coupling,[2a] the six-ring-annelated 4-cyano-8-oxabicyclo[3.2.1]octa-2,6-diene **17e** was formed upon irradiation as the sole product, albeit in only 28% yield (Scheme 5 and Table 4, entry 3). However, recrystallization of **17e** from hexane/dichloromethane furnished crystals suitable for an X-ray structure analysis which ultimately established the relative configuration at C-8 and C-9 (Figure 1).[8]

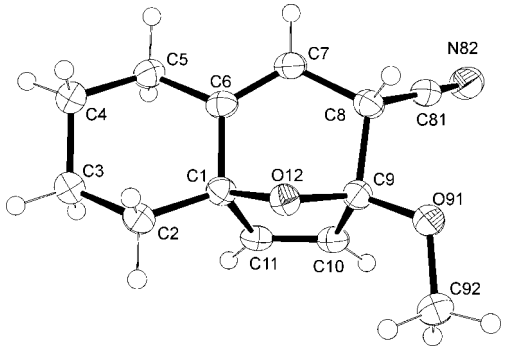


Figure 1. Structure of **17e** in the crystal. $C_{13}H_{15}NO_2$, monoclinic crystals of space group $P2_1/n$, $Z=4$, cell dimensions $a=12.366(3)$, $b=7.7669(16)$, $c=12.509(3)$ Å, $\alpha=90$, $\beta=110.83(3)$, $\gamma=90°$, $V=1122.9(4)$ Å^3.

Irradiation of the cycloheptene-derived hexatriene (*E*,*Z*,*E*)-**6b** led to a very fast formation within 90 min of the 13-oxatricyclo[8.2.1.0^{1,7}]tridecadiene (**18b**), which was isolat-

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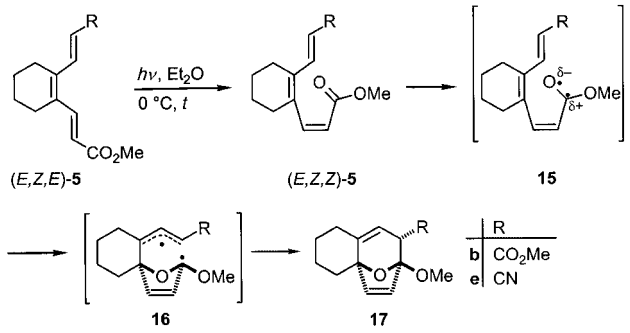


Scheme 5. Photoreaction of the hexatriene (*E*,*Z*,*E*)-**5** and proposed mechanism. For details see Table 4.

Table 4. Photoreaction of the (*E*,*Z*,*E*)-hexatrienes **5b**, **5e**, **6b**.

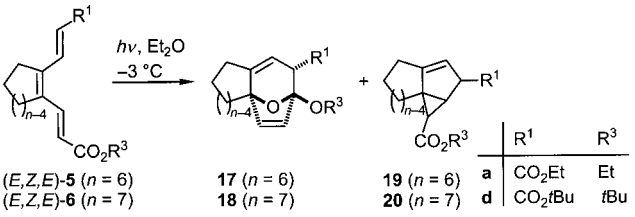
Entry	Scale [mmol]	(*E*,*Z*,*E*)-Hexatriene	Solvent [mL]	*t* [min]	Product	Ratio[a] (*E*,*Z*,*E*)/(*E*,*Z*,*Z*)/Product	Yield[b] [%]
1	0.25	**5b**	Et_2O	35	**17b**	18:71:11	–
			150	102		14:56:30	–
				272		0:0:100	69
2	0.22	**5b**	benzene	120	**17b**	34:51:15	–
			60	320		19:30:51	–[c]
3	0.20	**5e**	Et_2O	240	**17e**	0:0:100	28
			60				
4	0.19	**6b**	Et_2O	15	**18b**	48:36:16	–
			60	30		34:37:30	–
				60		17:22:61	–
				90		0:0:100	60

[a] Determined by ^{1}H NMR spectroscopy of small aliquots of the reaction mixture. [b] Isolated yields after column chromatography. [c] Not isolated.

ed in 60% yield (entry 4). When this transformation was monitored by ^{1}H NMR spectroscopy, the intermediate formation of (*E*,*Z*,*Z*)-**6b** was observed as well.

Upon irradiation of the ethoxycarbonyl-substituted hexatriene (*E*,*Z*,*E*)-**5a**, complete conversion was achieved within 5 h (Scheme 6 and Table 5, entry 1). After column chromatography, an inseparable 87:13 mixture of the 12-oxatricyclo[7.2.1.0^{1,6}]dodeca-6,10-diene (**17a**) and the tricyclo[4.4.0.0^{1,3}]dec-5-ene (**19a**) was isolated in 52% yield. The irradiation of the corresponding *tert*-butoxycarbonyl-substituted hexatriene (*E*,*Z*,*E*)-**5d** also gave a mixture of the two isomers **17d** and **19d** (entry 2), albeit in only 22% yield, and **17d** was the minor component. Finally, the *tert*-butoxycarbonyl-substituted triene (*E*,*Z*,*E*)-**6d** after 4 h of irradiation furnished an inseparable 29:71 mixture of isomers **18d** and **20d** in 30% isolated yield (entry 3).

These results show that the new photochemical transformation of cycloalkene-attached (*E*,*Z*,*E*)-1,3,5-hexatriene-1,6-dicarboxylates to ring-annelated 8-oxabicyclo[3.2.1]octa-2,6-diene derivatives competes with the already known transformation to bicyclo[3.1.0]-hex-2-ene derivatives.[5] In the case of methoxycarbonyl-substituted substrates with a central cyclohexene or cycloheptene moiety, only the new transformation with (*E*/*Z*)-isomerization and subsequent intramolecular formal hetero-Diels–Alder reaction takes place. With more bulky alkoxycarbonyl groups attached, the product formation is shifting towards the bicyclo[3.1.0]hex-2-ene derivatives **19** and **20**, respectively, which according to literature precedence, actually would be the expected products when the starting hexatrienes would adopt an s-*cis*,s-*trans* major conformation.[5] Along the same line, the isolated yields of products decrease probably because a larger fraction undergoes decomposition.



Scheme 6. Photoreaction of the hexatrienes (*E*,*Z*,*E*)-**5**, **6**. For details see Table 5.

Table 5. Photoreaction of the hexatrienes (*E*,*Z*,*E*)-**5a**, **5d**, **6d**.

Entry	Scale [mmol]	(*E*,*Z*,*E*)-Hexatriene	*t* [h]	Products	Ratio[a]	Yield[b] [%]
1	0.20	**5a**	5	**17a**, **19a**	87:13	52
2	0.20	**5d**	3.5	**17d**, **19d**	39:61	22
3	0.20	**6d**	4	**18d**, **20d**	29:71	30

[a] Determined by ^{1}H NMR spectroscopy of the isolated product. [b] Isolated yields after column chromatography.

Essentially, this new phototransformation constitutes an annelation of highly functionalized seven-membered rings onto cyclohexenes or cycloheptenes, provided that the bicyclic acetal functionality can be cleaved. Attempted cleavage of this functionality with Brønsted acids such as trifluoroacetic acid, oxalic acid or even diluted hydrochloric acid, which are well known to cleave acetals,[9] either led to no conversion or complete decomposition. However, Lewis acids turned out to be more suitable. Thus, upon treatment of the acetal **17b** with titanium tetrachloride/lithium iodide[10] or trimethylsilyl triflate, the six-ring-annelated troponecarboxylate **21b** was formed, apparently by cleavage of the acetal and subsequent dehydration in 30–33% yield (Scheme 7 and Table 6, entries 1, 2). With trimethylsilyl triflate, the acetal **18b** gave the seven-ring-annelated troponecarboxylate **22b** in 65% yield. Compounds **21b** and **22b** represent the first examples of tropones with this kind of substitution.

Interestingly, the 8-oxabicyclo[3.2.1]octa-2,6-diene fragment created in these phototransformations also occurs as a substructure in the known com-

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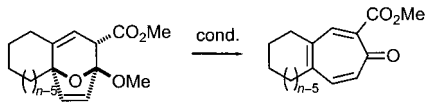


17b (n = 6)
18b (n = 7)

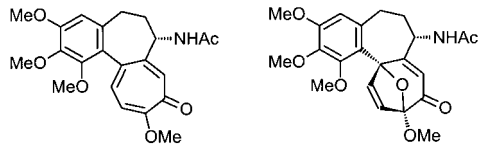
21b (n = 6)
22b (n = 7)

Scheme 7. Acetal cleavage of the photo products **17b** and **18b**. For more details see Table 6.

Table 6. Acetal cleavage of **17b** and **18b**.

Entry	Acetal	Product	Conditions	Yield [%]
1	**17b**	**21b**	$TiCl_4$, LiI, Et_2O, RT, 2.5 h	30
2	**17b**	**21b**	Me_3SiOTf, CH_2Cl_2, RT, 10 min	33
3	**18b**	**22b**	Me_3SiOTf, CH_2Cl_2, RT, 30 min	65

pound oxycolchicine **24**,[11] an oxidation product of the naturally occurring colchicine **23**. Colchicine is the principal alkaloid of the Autumn Crocus, and in view of its antimitotic properties many total syntheses have been developed.[12] Since the new photochemical formal hetero-Diels–Alder reaction appeared to be a promising tool for yet another novel access to this alkaloid and its derivatives, the benzocycloheptadienebisacrylate **27** was studied as a model to probe the feasibility of this approach.



23
Colchicine

24
Oxycolchicine

The trienedicarboxylate **27** was prepared from bromobenzosuberone **25**[13] via the bromoenol triflate **26** generated by deprotonation with lithium hexamethyldisilazide (LiHMDS) and trapping of the enolate with *N*-phenyltriflimide in 60% yield (Scheme 8). The twofold Heck reaction of **26** with methyl acrylate gave the hexatriene **27** in 51% isolated yield along with a small amount of the reduced monoalkenylation product **28**. Unfortunately, the irradiation of **27** under the usual conditions just furnished the two diastereomeric bicyclo[3.1.0]hex-2-ene derivatives **29** and **30** in 32 and 26% yield, respectively. The relative configuration of the isomer **29** was rigorously proved by X-ray structure analysis (Figure 2),[8] and the structure of **30** was assigned by one- and two-dimensional NMR experiments as well as by comparison with the spectra of the isomer **29**. Thus, the annelated aromatic ring which distinguishes the hexatriene **27** from hexatriene (*E*,*Z*,*E*)-**6b** completely changes the selectivity of the phototransformation. Interestingly, though, the transformation of **27** occurs with complete regioselectivity in that only the acrylate adjacent to the annelated benzene ring is involved.

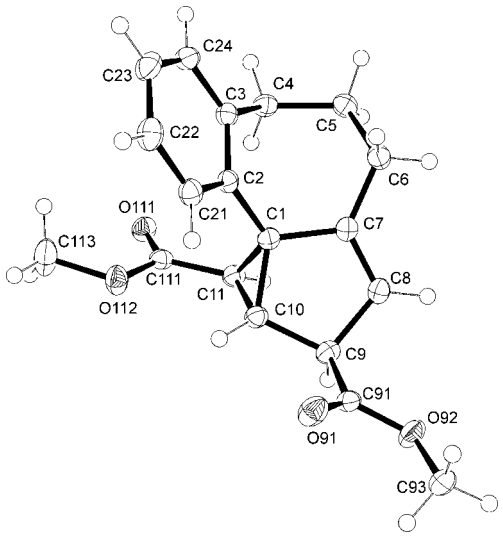
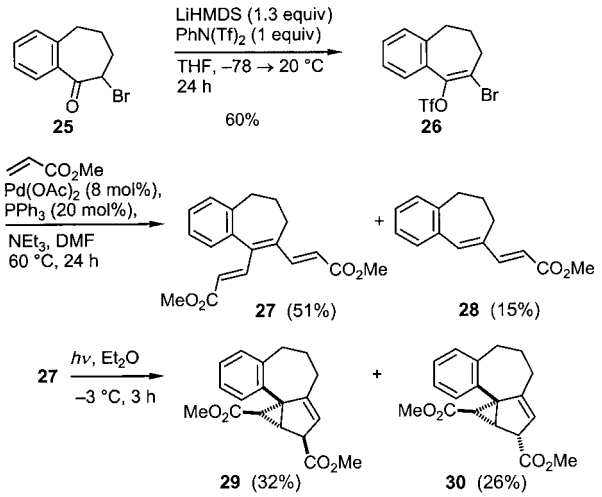


Figure 2. Structure of **29** in the crystal. $C_{19}H_{20}O_4$, monoclinic crystals of space group $P2_1/c$, $Z=4$, cell dimensions $a=11.634(2)$, $b=8.2145(16)$, $c=16.614(3)$ Å, $\alpha=90$, $\beta=98.39(3)$, $\gamma=90°$, $V=1570.7(5)$ Å^3.



Scheme 8. Synthesis and phototransformation of the hexatriene **27**.

Conclusion

1,6-Bisalkoxycarbonyl-substituted (*E*,*Z*,*E*)-1,3,5-hexatrienes with a central cycloalkene moiety, prepared from 1,2-dibromocycloalkenes or 2-bromocycloalkenol triflates by twofold Heck reaction with an acrylate, are suitable starting materials for fast and efficient annelations of both six- and seven-membered rings onto the cycloalkene ring. While the thermal disrotatory 6π-electrocyclization of this type of (*E*,*Z*,*E*)-hexatrienes is known to give cyclohexadienes with *cis*-relationship of the substituents in the former 1,6-position,[2a] the *trans*-configured compounds can be obtained by a sequence of photochemical double bond isomerization to form (*E*,*Z*,*Z*)-hexatrienes and their subsequent thermal disrotatory 6π-electrocyclization. Photochemical conrotatory 6π-electrocyclization was never observed, but after prolonged irradiation a formal hetero-Diels–Alder reaction took place to give highly functionalized oxygen-brigded cycloheptadiene

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derivatives. This new type of phototransformation probably proceeds via diradical intermediates, it appears to be a promising route to bicyclo[5.4.0]undecane and bicyclo[5.5.0]-dodecane derivatives.

Experimental Section

General: ^{1}H NMR: Bruker AM 250 (250 MHz) or Varian VXR 500S (500 MHz). Chemical shifts in $CDCl_3$ or C_6D_6 are reported as δ values relative to tetramethylsilane ($\delta = 0.00$), chloroform ($\delta = 7.26$) or [D_5]benzene ($\delta = 7.16$) as internal reference unless stated otherwise. ^{13}C NMR: Varian Mercury 200 (50.3 MHz) or Bruker AW250 (62.9 MHz). Chemical shifts in $CDCl_3$ or C_6D_6 are reported as δ values relative to chloroform ($\delta = 77.0$) or [D_6]benzene ($\delta = 128.0$); the multiplicity of the signals was determined by the ATP (50.3 MHz) or DEPT (62.9 MHz) technique and quoted as (+) for CH_3 and CH groups, (−) for CH_2 groups and (C_{quat}) for quaternary carbon atoms. IR spectra: Bruker IFS 66. UV/Vis: Varian-Cary 219 or Perkin–Elmer Lambda 2. Low-resolution EI mass spectra: Finnigan MAT 95, ionizing voltage 70 eV. High-resolution mass spectra: Finnigan MAT 95; preselected ion peak matching at $R \sim 10000$ to be within ± 2 ppm of the exact masses. Elemental analyses: Mikroanalytisches Labor des Instituts für Organische und Biomolekulare Chemie der Universität Göttingen, Germany. Melting points are uncorrected. Solvents for extraction and chromatography were of technical grade and distilled before use. Flash chromatography: Merck Kieselgel 60 (200–400 mesh). All reactions were carried out under dry nitrogen or argon in oven- and/or flame-dried glassware. *n*-Butyllithium was titrated according to the method of Suffert.[14] Ethyl ether, pentane, decalin and THF were distilled from sodium. Dichloromethane, NEt_3, DMF and hexamethyldisilazane (HMDS) were distilled from CaH_2. 1,2-Dibromocyclohexene (**2**),[2a] 1,2-dibromocycloheptene (**3**),[15] 6-bromo-6,7,8,9-tetrahydrobenzocyclohepten-5-one (**25**),[13] *N*-phenyltriflimide[16] and [$Pd_2(dba)_3$]·$CHCl_3$[17] were prepared according to literature procedures. 1,2-Dibromocyclopentene (**1**) was prepared by the same method as 1,2-dibromocyclohexene (**2**), but is also commercially available from Aldrich.

Methyl (*E*)-3-{2-[(*E*)-2-(methoxycarbonyl)ethenyl]-1-cyclopenten-1-yl}-acrylate [(*E*,*Z*,*E*)-4b]:[2a,e] UV (dichloromethane): λ_{max} ($\log\varepsilon$) = 322 nm (4.407), shoulder at 337 (2.107).

1,2-Bis[(*E*)-2-trimethylsilylethenyl]cyclopentene [(*E*,*Z*,*E*)-4c]:[2a] UV (isooctane): λ_{max} ($\log\varepsilon$) = 211.8 (3.998), 293.7 nm (4.655), shoulders at 282.1 (4.525) and 307.2 (4.542).

***tert*-Butyl (*E*)-3-{2-[(*E*)-2-(*tert*-butoxycarbonyl)ethenyl]-1-cyclopenten-1-yl}acrylate [(*E*,*Z*,*E*)-4d]**:[2a] UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 223.0 (3.930), 317.1 nm (4.080) shoulder at 331.0 (3.971).

Methyl (*E*)-3-{2-[(*E*)-2-(methoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}-acrylate [(*E*,*Z*,*E*)-5b]:[2b,e] UV (chloroform): λ_{max} ($\log\varepsilon$) = 317.5 nm (4.474).

1,2-Bis[(*E*)-2-trimethylsilylethenyl]cyclohexene [(*E*,*Z*,*E*)-5c]:[2a] UV (isooctane): λ_{max} ($\log\varepsilon$) = 214.6 (3.958), 291.4 nm (4.513), shoulder at 281.0 (4.449).

***tert*-Butyl (*E*)-3-{2-[(*E*)-2-(*tert*-butoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate [(*E*,*Z*,*E*)-5d]**:[2b] UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 229.5 (4.153), 314.0 nm (4.434).

Methyl (*E*)-3-{2-[(*E*)-2-cyanoethenyl]-1-cyclohexen-1-yl}acrylate [(*E*,*Z*,*E*)-5e]:[2a] UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 227.0 (4.003), 310.0 nm (4.291).

***tert*-Butyl (*E*)-3-{2-[(*E*)-2-(*tert*-butoxycarbonyl)ethenyl]-1-cyclohepten-1-yl}acrylate [(*E*,*Z*,*E*)-6d]**:[2d] UV (methanol): λ_{max} ($\log\varepsilon$) = 209.5 (3.826), 229.5 nm (3.679).

General procedure for the twofold Heck coupling of 1,2-dibromocycloalkenes 1–3 with acrylates (GP 1): In a Pyrex bottle containing a magnetic stirring bar were placed [$Pd(OAc)_2$] (0.18 g, 0.80 mmol, 4 mol% per Br), PPh_3 (0.53 g, 2.0 mmol) and the respective 1,2-dibromocycloalkene (10 mmol). DMF (50 mL) was added and the resulting suspension was purged with nitrogen in an ultrasonic bath for 10 min. To the stirred solution were added NEt_3 (5.6 mL, 40 mmol) and the acrylate (50 mmol, 2.5 equiv per Br). The bottle was sealed with a screw cap and heated with vigorous stirring for the stated time at the stated temperature. Then the reaction mixture was cooled to room temperture and poured into Et_2O and H_2O (200 mL each). The organic layer was washed with water (3×50 mL) and the aqueous layer was extracted back with Et_2O (50 mL). The combined organic layers were dried over $MgSO_4$, concentrated in vacuo, and the residue was purified by CC on silica gel.

Ethyl (*E*)-3-{2-[(*E*)-2-(ethoxycarbonyl)ethenyl]-1-cyclopenten-1-yl}acrylate [(*E*,*Z*,*E*)-4a]: 1,2-Dibromocyclopentene (**1**) (2.00 g, 8.85 mmol) was treated with ethyl acrylate (4.44 g, 44.4 mmol) for 24 h at 100 °C according to GP 1. After CC on silica gel (200 g, pentane/EtOAc 10:1), the hexatriene (*E*,*Z*,*E*)-**4a** was obtained as a colorless ductile oil (1.38 g, 59%). $R_f = 0.42$; IR (KBr): $\tilde{\nu} = 2980$ (C−H), 2843, 1711 (C=O), 1613 (C=C), 1458, 1393, 1366, 1312, 1163, 1096, 1038, 972 (*trans* HC=CH), 854, 717, 631 cm^{-1}; UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 227.5 (4.135), 318.5 nm (4.518), shoulder at 331.5 (4.434); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.27$ (t, J = 7.0 Hz, 6H, $CO_2CH_2CH_3$), 1.92 (quin, $J = 7.7$ Hz, 2H, 4′-H), 2.62 [t, J = 7.7 Hz, 4H, 3′(5′)-H], 4.20 (q, $J = 7.0$ Hz, 4H, $CO_2CH_2CH_3$), 5.87 [d, J = 15.6 Hz, 2H, 3(1″)-H], 7.79 [d, $J = 15.6$ Hz, 2H, 2(2″)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.15$ (+, 2C, $CO_2CH_2CH_3$), 21.13 (−, C-4′), 33.47 [−, 2C, C-3′(5′)], 60.38 (−, 2C, $CO_2CH_2CH_3$), 121.03 [+, 2C, C-2(2″)], 135.63 [+, 2C, C-1″(3)], 144.02 [C_{quat}, 2C, C-1′(2′)], 166.73 (C_{quat}, 2C, $CO_2CH_2CH_3$); MS (70 eV): m/z (%): 264 (26) [M^+], 235 (3) [$M^+ - CH_2CH_3$], 218 (57) [$M^+ - CH_2CH_3OH$], 206 (13) [$M^+ - 2CH_2CH_3$], 191 (46) [$M^+ - CO_2CH_2CH_3$], 172 (10) [$M^+ - 2CH_2CH_3OH$], 163 (23), 145 (66) [$M^+ - CO_2CH_2CH_3 - CH_2CH_3OH$], 144 (9), 121 (25), 117 (100) [$M^+ - CO_2CH_2CH_3 - CH_3CH_2CO_2H$], 115 (20), 105 (7), 91 (48), 77 (12), 55 (8), 41 (8); elemental analysis calcd (%) for $C_{15}H_{20}O_4$ (264.3): C 68.16, H 7.63; found C 67.98, H 7.36.

Ethyl (*E*)-3-{2-[(*E*)-2-(ethoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate [(*E*,*Z*,*E*)-5a]: 1,2-Dibromocyclohexene (**2**) (2.00 g, 8.33 mmol) was treated with ethyl acrylate (4.15 g, 41.5 mmol) for 24 h at 100 °C according to GP 1. After CC on silica gel (200 g, pentane/EtOAc 20:1), the hexatriene (*E*,*Z*,*E*)-**5a** was obtained as a colorless solid (1.43 g, 62%). M.p. 102–104 °C; $R_f = 0.47$; IR (KBr): $\tilde{\nu} = 2984$ (C−H), 2937 (C−H), 2863, 1707 (C=O), 1609 (C=C), 1456, 1396, 1370, 1269, 1238, 1164, 1044, 966 cm^{-1} (*trans*-HC=CH), 849; UV (acetonitrile): λ_{max} ($\log\varepsilon$) = 228.5 (4.063), 314.0 nm (4.310); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.31$ (t, $J = 7.1$ Hz, 6H, $CO_2CH_2CH_3$), 1.68 [m, 4H, 4′(5′)-H], 2.34 [m, 4H, 3′(6′)-H], 4.23 (q, J = 7.1 Hz, 4H, $CO_2CH_2CH_3$), 5.98 [d, $J = 15.5$ Hz, 2H, 2(2″)-H], 8.06 [d, J = 15.5 Hz, 2H, 1″(3)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.28$ (+, 2C, $CO_2CH_2CH_3$), 21.79 [−, 2C, C-4′(5′)], 26.62 [−, 2C, C-3′(6′)], 60.48 (−, 2C, $CO_2CH_2CH_3$), 119.00 [+, 2C, C-2(2″)], 137.95 [C_{quat}, 2C, C-1′(2′)], 139.91 [+, 2C, C-1″(3)], 167.14 (C_{quat}, 2C, $CO_2CH_2CH_3$); MS (70 eV): m/z (%): 278 (14) [M^+], 248 (9) [$M^+ - CH_3CH_3$], 232 (33) [$M^+ - CH_2CH_3OH$], 220 (24), 205 (100) [$M^+ - CO_2CH_2CH_3$], 204 (67) [$M^+ - CH_3CH_2CO_2H$], 186 (12), 177 (26), 175 (30) [$M^+ - CO_2CH_2CH_3 - CH_3CH_3$], 159 (55) [$M^+ - CO_2CH_2CH_3 - CH_2CH_3OH$], 147 (9), 133 (22), 131 (99) [$M^+ - CO_2CH_2CH_3 - CH_3CH_2CO_2H$], 119 (27), 104 (13), 91 (72), 77 (14), 65 (3), 55 (5), 41 (6); elemental analysis calcd (%) for $C_{16}H_{22}O_4$ (278.3): C 69.04, H 7.97; found C 69.33, H 7.71.

Methyl (*E*)-3-{2-[(*E*)-2-(methoxycarbonyl)ethenyl]-1-cyclohepten-1-yl}-acrylate [(*E*,*Z*,*E*)-6b], variant A: 1,2-Dibromocycloheptene (**3**) (254 mg, 1.00 mmol) was treated with methyl acrylate (430 mg, 5.00 mmol) for 16 h at 100 °C according to GP 1. After CC on silica gel (60 g, pentane/EtOAc 20:1), the hexatriene (*E*,*Z*,*E*)-**6b** was obtained as a colorless solid (36 mg, 14%). M.p. 67–70 °C; $R_f = 0.22$ (pentane/EtOAc 10:1); IR (KBr): $\tilde{\nu} = 2923$ (C−H), 2848, 1699 (C=O), 1610, 1437, 1277, 1247, 1201, 1171, 1135, 1038, 1022, 969 cm^{-1} (*trans*-HC=CH), 856; UV (chloroform): λ_{max} ($\log\varepsilon$) = 327.0 nm (4.391); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.45$–1.63 [m, 4H, 4′(5′,6′)-H], 1.71–1.83 [m, 2H, 4′(6′)-H], 2.54 [m, 4H, 3′(7′)-H], 3.79 (s, 6H, CO_2CH_3), 6.02 [d, $J = 15.5$ Hz, 2H, 2(2″)-H], 8.01 [d, $J = 15.5$ Hz, 2H, 3(1″)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 25.31$ [−, 2C, C-4′(6′)], 29.39 [−, 2C, C-3′(7′)], 31.36 (−, C-5′), 51.71 (+, 2C, CO_2CH_3), 118.94 [+, 2C, C-2(2″)], 140.30 [+, 2C, C-3(1″)], 144.32 [C_{quat}, 2C, C-1′(2′)], 167.61 (C_{quat}, 2C, CO_2CH_3); MS (70 eV): m/z (%): 264 (16) [M^+], 231 (47) [$M^+ - CH_3OH$], 205 (100) [$M^+ - CO_2CH_3$], 190 (10) [$M^+ - CO_2CH_3 - CH_3$], 173 (52) [$M^+ - CO_2CH_3 - CH_3OH$], 172 (24), 164 (19) [$M^+ - CHCHCO_2CH_3 - CH_3$], 145 (78) [$M^+ - CH_3CO_2H - CO_2CH_3$], 131 (24), 117 (20), 105 (41), 91 (26), 77 (10), 59 (14) [$CO_2CH_3^+$], 41 (6); elemental analysis calcd (%) for $C_{15}H_{20}O_4$ (264.3): C 68.16, H 7.63; found C 68.35, H 7.41.

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As the first fraction after CC, methyl (*E*)-3-(cyclohept-1-enyl)acrylate (**7**) was obtained as a colorless oil (47 mg, 26%). R_f=0.68 (pentane/EtOAc 10:1); IR (film): $\tilde{\nu}$=2925 (C–H), 2853, 1719 (C=O), 1622 (C=C), 1436, 1309, 1272, 1193, 1168, 1038, 982 (*trans*-HC=CH), 845 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=1.47–1.56 [m, 4H, 4′(5′,6′)-H], 1.72–1.79 [m, 2H, 4′(6′)-H], 2.24–2.33 [m, 4H, 3′(7′)-H], 3.73 (s, 3H, CO_2CH_3), 5.79 (d, J=15.8 Hz, 1H, 2-H), 6.30 (t, J=6.8 Hz, 1H, 2′-H), 7.27 (d, J=15.8 Hz, 1H, 3-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=25.84 (–, C-5′), 26.16 (–, C-4′), 27.09 (–, C-6′), 29.04 (–, C-3′), 31.85 (–, C-7′), 51.40 (+, CO_2CH_3), 114.04 (+, C-2), 141.89 (C_{quat}, C-1′), 143.97 (+, C-2′), 149.30 (+, C-3), 168.22 (C_{quat}, C-1); MS (70 eV): *m*/*z* (%): 180 (100) [M^+], 165 (17) [M^+-CH_3], 162 (8), 149 (24) [M^+-OCH_3], 137 (25), 131 (13), 121 (35) [$M^+-CO_2CH_3$], 120 (18), 105 (14), 93 (18), 91 (31), 81 (12), 79 (31), 77 (23), 67 (12), 53 (7), 51 (4), 41 (10); MS: *m*/*z*: calcd for $C_{11}H_{16}O_2$ (180.2): 180.1150 (correct HRMS).

Variant B: In a Pyrex bottle containing a magnetic stirring bar were placed [$Pd(OAc)_2$] (18 mg, 0.080 mmol), Bu_4NBr (322 mg, 1.00 mmol), LiCl (174 mg, 4.10 mmol), K_2CO_3 (691 mg, 5.00 mmol), and 1,2-dibromocycloheptene (**3**) (254 mg, 1.00 mmol). DMF (15 mL) was added, and the resulting suspension was purged with nitrogen in an ultrasonic bath for 10 min. To the stirred solution was added methyl acrylate (430 mg, 5.00 mmol). The bottle was sealed with a screw cap, and the solution was stirred for 8 h at 90°C. The reaction mixture was cooled down to room temperature and worked up according to GP 1. After CC on silica gel (56 g, pentane/EtOAc 10:1) besides the starting material **3** (fraction 1; 50 mg, 20%) and hexatriene (*E*,*Z*,*E*)-**6b** (fraction 3; 79 mg, 30%), methyl (*E*)-3-[(2-chloro)cyclohept-1-enyl]acrylate (**8**) (fraction 2; 18 mg, 8%) was obtained as a colorless oil. R_f=0.66; **8**: IR (film): $\tilde{\nu}$=2930 (C–H), 2855, 1718 (C=O), 1617 (C=C), 1436, 1302, 1276, 1172, 1097, 1038, 982 (*trans*-HC=CH), 859, 733 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=1.51 (m, 2H, 5′-H), 1.62 (m, 2H, 6′-H), 1.76 (m, 2H, 4′-H), 2.40 (m, 2H, 7′-H), 2.74 (m, 2H, 3′-H), 3.76 (s, 3H, CO_2CH_3), 5.91 (d, J=15.8 Hz, 1H, 2-H), 7.88 (d, J=15.8 Hz, 1H, 3-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=24.90 (–, C-5′), 25.24 (–, C-6′), 27.98 (–, C-4′), 31.27 (–, C-7′), 39.78 (–, C-3′), 51.63 (+, CO_2CH_3), 117.75 (+, C-2), 134.64 (C_{quat}, C-1′), 142.40 (+, C-3), 143.09 (C_{quat}, C-2′), 167.73 (C_{quat}, C-1); MS (70 eV): *m*/*z* (%): 216/214 (3/9) [M^+], 179 (100) [M^+-Cl]; MS (DCI, NH_3, 200 eV): *m*/*z* (%): 448/446 (23/37) [$2M+NH_4^+$], 251/249 (34/100) [$M+NH_3+NH_4^+$], 234/232 (26/76) [$M+NH_4^+$], 216/214 (13/74) [M^+]; elemental analysis calcd (%) for $C_{11}H_{15}O_2Cl$ (214.7): C 61.54, H 7.04; found C 61.83, H 6.87.

Variant C: In a Pyrex bottle containing a magnetic stirring bar were placed [$Pd_2(dba)_3$]·$CHCl_3$ (209 mg, 0.200 mmol), Bu_4NBr (1.61 g, 5.00 mmol), K_2CO_3 (3.46 g, 25.0 mmol), and 1,2-dibromocycloheptene (**3**) (1.27 g, 5.00 mmol). DMF (40 mL) was added, and the resulting suspension was purged with nitrogen in an ultrasonic bath for 10 min. To the stirred solution was added methyl acrylate (2.15 g, 25.0 mmol). The bottle was sealed with a screw cap and the solution was stirred at 90°C for 7 h. The reaction mixture was cooled down to room temperature and worked up according to GP 1. CC on silica gel (150 g, petroleum ether/EtOAc 10:1) yielded the hexatriene (*E*,*Z*,*E*)-**6b** (870 mg, 66%).

General procedure for the phototransformation of (*E*,*Z*,*E*)-1,3,5-hexatrienes (GP 2): A solution of the respective hexatriene **4**, **5** or **6** in anhydrous, degassed diethyl ether or pentane was irradiated with a 150 W medium pressure mercury lamp in a photoreaction vessel with a Pyrex filter sleeve at the stated temperature for the stated time. To monitor the reaction, irradiation was interrupted to take a sample which was analyzed by ^1H NMR spectroscopy. Subsequently the sample was returned to the reaction mixture and the irradiation was continued. After the conversion had ceased, the mixture was concentrated in vacuo, and the residue was purified by column chromatography (CC) on silica gel.

1-[(*E*)-2-Trimethylsilylethenyl]-2-[(*Z*)-2-trimethylsilylethenyl]cyclopentene [(*E*,*Z*,*Z*)-4c]: A solution of 1,2-bis[(*E*)-2-trimethylsilylethenyl]cyclopentene [(*E*,*Z*,*E*)-**4c**] (132 mg, 0.499 mmol) in diethyl ether (60 mL) was irradiated according to GP 2 under ^1H NMR monitoring at −5°C for 3 h. After concentration in vacuo, a mixture was obtained (130 mg, 98%) containing the (*E*,*Z*,*Z*)-1,3,5-hexatriene **4c** and the starting material (*E*,*Z*,*E*)-**4c** in a ratio of 48:52. After CC on silica gel (6 g, pentane), a colorless oil (94 mg, 71%) was obtained which consisted of the triene (*E*,*Z*,*Z*)-**4c** and the starting material (*E*,*Z*,*E*)-**4c** in a ratio of 28:72. R_f=0.86; ^1H NMR (250 MHz, $CDCl_3$); the signals marked with "#" agree with the signals for (*E*,*Z*,*E*)-**4c**:[2a] δ=0.02 [s, 9H, $Si(CH_3)_3$], 0.05 [s, 9H, $Si(CH_3)_3$], 0.06 [s, 18H, $Si(CH_3)_3$]#, 1.76–1.97 (m, 2H, 4-H)#, 2.50–2.64 [m, 4H, 3(5)-H]#, 5.72 (d, J=15.7 Hz, 1H, 2″-H), 5.77 (d, J=18.9 Hz, 1H, 2′-H), 5.84 [d, J=18.8 Hz, 2H, 2′(2″)-H]#, 6.96 (d, J=18.9 Hz, 1H, 1′-H), 7.11 [d, J=18.8 Hz, 2H, 1′(1″)-H]#. The signal for 1″-H is hidden by the doublet at 7.11. ^{13}C NMR (62.9 MHz, $CDCl_3$); the signals marked with "#" agree with the signals for (*E*,*Z*,*E*)-**4c**:[2a] δ=−1.18 [+, $Si(CH_3)_3$]#, −0.48 [+, $Si(CH_3)_3$], 21.18 (–, C-4)#, 22.01 (–, C-4), 32.68 (–, C-5*), 33.66 [–, C-3(5)]#, 37.17 (–, C-3*), 130.68 (+, C-2″*), 131.37 [+, C-2′(2″)]#, 131.61 (C_{quat}, C-2*), 132.50 (+, C-2′*), 136.77 [+, C-1′(1″)]#, 138.21 (+, C-1′*), 140.15 [C_{quat}, C-1(2)]#, 140.39 (+, C-1″*), 140.81 (C_{quat}, C-1*).

1-[(*E*)-2-Trimethylsilylethenyl]-2-[(*Z*)-2-trimethylsilylethenyl]cyclohexene [(*E*,*Z*,*Z*)-5c]: A solution of 1,2-bis[(*E*)-2-trimethylsilylethenyl]cyclohexene [(*E*,*Z*,*E*)-**5c**] (278 mg, 1.0 mmol) in pentane (55 mL) was irradiated according to GP 2 under ^1H NMR monitoring at −5°C for 2 h. After CC on silica gel (12 g, petroleum ether), a colorless oil was obtained (270 mg, 97%) which consisted of the (*E*,*Z*,*Z*)-1,3,5-hexatriene **5c** and the starting material (*E*,*Z*,*E*)-**5c** in a ratio of 92:8, as well as traces of two other products. R_f=0.95; (*E*,*Z*,*Z*)-**5c**: IR (film): $\tilde{\nu}$=2952 (C–H), 2896 (C–H), 2859 (C–H), 2836 (C–H), 1620 (C=C), 1586, 1435, 1318, 1247, 993, 839, 764, 728, 690, 658, 613, 510 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.01 [s, 9H, $Si(CH_3)_3$], 0.06 [s, 9H, $Si(CH_3)_3$], 1.54–1.70 [m, 4H, 4(5)-H], 2.08 (m, 2H, 3*-H), 2.18 (m, 2H, 6*-H), 5.69 (d, J=15.1 Hz, 1H, 2″-H), 5.71 (d, J=19.1 Hz, 1H, 2′-H), 6.75 (d, J=15.1 Hz, 1H, 1″-H), 7.02 (d, J=19.1 Hz, 1H, 1′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=−1.10 [+, $Si(CH_3)_3$], −0.44 [+, $Si(CH_3)_3$], 22.46 (–, C-4*), 22.49 (–, C-5*), 24.47 (–, C-6*), 30.98 (–, C-3*), 124.75 (+, C-2″*), 130.92 (C_{quat}, C-2*), 132.45 (+, C-2′*), 139.60 (C_{quat}, C-1*), 144.29 (+, C-1″*), 146.83 (+, C-1′*); elemental analysis calcd (%) for $C_{16}H_{30}Si_2$ (278.6): C 68.98, H 10.85; found C 68.68, H 10.77.

Methyl (*E*)-3-{2-[(*Z*)-2-(methoxycarbonyl)ethenyl]-1-cyclopenten-1-yl} acrylate [(*E*,*Z*,*Z*)-4b]: A solution of methyl (*E*)-3-{2-[(*E*)-2-(methoxycarbonyl)ethenyl]-1-cyclopenten-1-yl}acrylate [(*E*,*Z*,*E*)-**4b**] (204 mg, 0.863 mmol) in diethyl ether (240 mL) was irradiated according to GP 2 in four portions at −5°C for 2 h each. The combined reaction mixtures were purified by CC (40 g, petroleum ether/EtOAc 8:1). The (*E*,*Z*,*Z*)-hexatriene **4b** was obtained as a colorless solid (48 mg, 24%). M.p. 34°C; R_f=0.43.

As the second fraction after CC, the starting material (*E*,*Z*,*E*)-**4b** was obtained (105 mg, 51%). R_f=0.36; (*E*,*Z*,*Z*)-**4b**: IR (KBr): $\tilde{\nu}$=2951 (C–H), 1721 (C=O), 1616 (C=C), 1437, 1307, 1286, 1251, 1198, 1166, 1022, 972, 855, 824 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=1.92 (quin, J=7.5 Hz, 2H, 4′-H), 2.56 (m, 2H, 3′*-H), 2.76 (m, 2H, 5′*-H), 3.71 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 5.86 (d, J=15.5 Hz, 1H, 2-H), 5.89 (d, J=12.5 Hz, 1H, 2″-H), 6.88 (dt, ^4J=1.1, J=12.5 Hz, 1H, 3″-H), 7.66 (d, J=15.5 Hz, 1H, 3-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=22.44 (–, C-4′), 32.61 (–, C-5′*), 36.06 (–, C-3′*), 51.53 (+, OCH_3), 51.61 (+, OCH_3), 119.69 (+, C-2″*), 120.60 (+, C-2*), 134.04 (+, C-3′*), 136.80 (+, C-3*), 142.47 (C_{quat}, C-2′*), 145.00 (C_{quat}, C-1′*), 166.60 (C_{quat}, C-1″*), 167.55 (C_{quat}, C-1*); elemental analysis calcd (%) for $C_{13}H_{16}O_4$ (236.3): C 66.09, H 6.83; found C 66.10, H 6.95.

Methyl (*E*)-3-{2-[(*Z*)-2-(methoxycarbonyl)ethenyl]-1-cyclohexen-1-yl} acrylate [(*E*,*Z*,*Z*)-5b]: A solution of methyl (*E*)-3-{2-[(*E*)-2-(methoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate [(*E*,*Z*,*E*)-**5b**] (125 mg, 0.499 mmol) in diethyl ether (60 mL) was irradiated according to GP 2 at −5°C for 42 min. After CC on silica gel (40 g, petroleum ether/EtOAc 10:1) the (*E*,*Z*,*Z*)-hexatriene **5b** was isolated as a colorless oil (64 mg, 51%). R_f=0.32.

As the second fraction after CC, the starting material (*E*,*Z*,*E*)-**5b** was obtained (31 mg, 25%). R_f=0.25; (*E*,*Z*,*Z*)-**5b**: IR (film): $\tilde{\nu}$=2934 (C–H), 2860 (C–H), 1726 (C=O), 1619 (C=C), 1436, 1399, 1300, 1276, 1196, 1174, 1038, 1016, 982, 920, 859, 817, 734 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=1.65–1.76 [m, 4H, 4′(5′)-H], 2.21–2.26 [m, 4H, 3′(6′)-H], 3.65 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 5.80 (d, J=15.7 Hz, 1H, 2-H), 5.93 (d, J=12.0 Hz, 1H, 2″-H), 6.79 (d, J=12.0 Hz, 1H, 3″-H), 7.51 (d, J=15.7 Hz, 1H, 3-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.91 (–, C-4′*), 22.07 (–, C-5′*), 24.65 (–, C-6′*), 29.99 (–, C-3′*), 51.37 (+, OCH_3), 51.42 (+, OCH_3), 115.36 (+, C-2″*), 121.73 (+, C-2*), 129.36 (C_{quat}, C-2′*), 142.65 (C_{quat}, C-1′*), 143.30 (+, C-3″*), 144.96 (+, C-3*), 165.57 (C_{quat}, C-1″*),

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167.95 (C_{quat}, C-1*); elemental analysis calcd (%) for $C_{14}H_{18}O_4$ (250.3): C 67.18, H 7.25; found C 66.89, H 7.27.

General procedure for the 6π-electrocyclization of (*E*,*Z*,*Z*)-1,3,5-hexatrienes under thermal conditions (GP 3): In a Pyrex bottle containing a magnetic stirring bar, the hexatriene **4** or **5** (0.10 mmol) was dissolved in decalin (10 mL), and the mixture was purged with nitrogen in an ultrasonic bath for 15 min. The bottle was sealed with a screw cap, and the solution was stirred for a given time at 215 °C. The reaction mixture was cooled down to room temperature, and the reaction mixture was separated by CC on silica gel as a solution in decalin or after concentration in vacuo (50 °C, 0.01 Torr).

Dimethyl 2,3,5,6-tetrahydro-1*H*-indene-*trans*-5,6-dicarboxylate (*trans*-9b): According to GP 3, the hexatriene (*E*,*Z*,*Z*)-**4b** (26 mg, 0.11 mmol) was heated in decalin (10 mL) at 215 °C for 60 min. CC on degassed silica gel with degassed solvents (10 g, petroleum ether/EtOAc 10:1) afforded the tetrahydroindene *trans*-**9b** as a colorless solid (20 mg, 77 %). M.p. 57 °C; R_f = 0.31; IR (KBr): $\tilde{\nu}$ = 2956 (C–H), 1738 (C=O), 1440, 1322, 1289, 1266, 1217, 1174, 1152, 1053, 1026, 1006, 949, 903, 816, 799, 738 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.71 (quin, J = 7.2 Hz, 2H, 2-H), 2.34 [m, 4H, 1(3)-H], 3.73 (s, 6H, OCH_3), 3.85 [m, 2H, 5(6)-H], 5.54 [m, 2H, 4(7)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.74 (–, C-2), 30.96 [–, C-1(3)], 42.61 [+, C-5(6)], 52.27 (+, OCH_3), 112.22 [+, C-4(7)], 140.64 [C_{quat}, C-3a(7a)], 174.04 (C_{quat}, CO_2CH_3); MS (70 eV): *m*/*z* (%): 236 (11) [M^+], 204 (7) [M^+-HOCH_3], 177 (100) [$M^+-CO_2CH_3$], 145 (60) [$M^+-HOCH_3-CO_2CH_3$], 117 (36) [$M^+-CH_3CO_2H-CO_2CH_3$], 105 (48), 91 (15), 59 (20) [$CO_2CH_3^+$]; elemental analysis calcd (%) for $C_{13}H_{16}O_4$ (236.3): C 66.09, H 6.83; found. C 66.22, H 6.90.

Dimethyl 2,3,5,6,7,8-hexahydronaphthalene-*trans*-2,3-dicarboxylate (*trans*-10b): According to GP 3, the hexatriene (*E*,*Z*,*Z*)-**5b** (30 mg, 0.12 mmol) was heated in decalin (10 mL) at 215 °C for 90 min. CC on degassed silica gel with degassed solvents (26 g, petroleum ether/EtOAc 10:1) afforded the cyclization product *trans*-**10b** as a colorless solid (25 mg, 83 %). M.p. 64 °C; R_f = 0.36; IR (KBr): $\tilde{\nu}$ = 2922 (C–H), 1735 (C=O), 1725 (C=O), 1439, 1300, 1288, 1252, 1241, 1172, 1011 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.40–1.49 [m, 2H, 6(7)-H], 1.64–1.70 [m, 2H, 6(7)-H], 2.16–2.37 [m, 4H, 5(8)-H], 3.63 [m, 2H, 2(3)-H], 3.73 (s, 6H, OCH_3), 5.46 [m, 2H, 1(4)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.19 [–, C-6(7)], 30.67 [–, C-5(8)], 42.05 [+, C-2(3)], 52.26 (+, OCH_3), 116.79 [+, C-1(4)], 135.89 [C_{quat}, C-4a(8a)], 173.94 (C_{quat}, CO_2CH_3); MS (70 eV): *m*/*z* (%): 250 (10) [M^+], 218 (6) [M^+-HOCH_3], 191 (100) [$M^+-CO_2CH_3$], 159 (58) [$M^+-HOCH_3-CO_2CH_3$], 131 (27) [$M^+-CH_3CO_2H-CO_2CH_3$], 105 (75), 91 (17), 59 (17) [$CO_2CH_3^+$]; elemental analysis calcd (%) for $C_{14}H_{18}O_4$ (250.3): C 67.18, H 7.25; found C 66.94, H 7.04.

6,7-Bis(trimethylsilyl)-1,2,3,4,4a,7-hexahydronaphthalene (11c): According to GP 3 the (*E*,*Z*,*Z*)-hexatriene **5c** (54 mg, 0.19 mmol) was heated in decalin (10 mL) at 215 °C for 3 h. After concentration in vacuo at 50 °C 39 mg (72 % of the initial amount) of 6,7-bis(trimethylsilyl)-1,2,3,4,4a,7-hexahydronaphthalene (**11c**) was obtained which contained traces of 6,7-bis(trimethylsilyl)-1,2,3,4,5,6-hexahydronaphthalene (**12c**) (see below) and 6,7-bis(trimethylsilyl)-1,2,3,4,6,7-hexahydronaphthalene (*trans*-**10c**). CC on silica gel (6 g, pentane) gave 29 mg (54 % of the initial amount) of a mixture of **11c** together with traces of **12c** and *trans*-**10c** (R_f = 0.93) and 4 mg (7 % of the starting amount) of trimethyl-(5,6,7,8-tetrahydronaphthalen-2-yl)silane (**13**) (see below) (R_f = 0.83); **11c**: IR (film): $\tilde{\nu}$ = 2952 (C–H), 2926 (C–H), 2856 (C–H), 1457, 1246, 1191, 1152, 1090, 837, 792, 747, 726, 687, 656 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$); signals, which can be assigned to the by-product *trans*-**10c**, are marked with "#": δ = –0.04 [s, 9H, $Si(CH_3)_3$], 0.01 [s, 9H, $Si(CH_3)_3$], 1.51–1.97 [m, 10H, 1(2,3,4,4a,7)-H], 5.18 [m, 2H, 5(8)-H]#, 5.36–5.47 [m, 2H, 5(8)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$); signals, which can be assigned to the by-product *trans*-**10c**, are marked with "#": δ = –3.35 [+, $Si(CH_3)_3$], –3.07 [+, $Si(CH_3)_3$]#, –1.07 [+, $Si(CH_3)_3$], 23.22 (–, C-3*), 23.29 (–, C-2*), 27.14 (+, C-7), 28.12 (–, C-4), 30.34 (+, C-4a), 31.57 (–, C-1), 120.59 [+, C-5(8)]#, 124.84 (C_{quat}, C-6*), 124.99 (+, C-5*), 126.62 (+, C-8*), 128.79 (C_{quat}, C-8a*), 132.90 [C_{quat}, C-4a(8a)]#; DCI-MS (NH_3): *m*/*z* (%): 281/280/279 (6/22/100) [M+H^+].

6,7-Bis(trimethylsilyl)-1,2,3,4,5,6-hexahydronaphthalene (12c): According to GP 3 the (*E*,*Z*,*E*)-hexatriene **5c** (70 mg, 0.25 mmol) was heated in decalin (10 mL) at 230 °C for 60 min. After concentration in vacuo at 50 °C CC on silica gel (12 g, pentane) afforded 60 mg (86 % of the starting amount) of a colorless oil (R_f = 0.92), which consisted mostly of the cyclization product **12c** along with traces of the cyclohexadiene **11c** and unidentified by-products as well as 5 mg (7 % of the initial amount) of a colorless oil (R_f = 0.83), which consisted of the arene **13** and traces of the arene **14c** and unidentified by-products. **12c**: IR (film): $\tilde{\nu}$ = 2952 (C–H), 2928 (C–H), 2857 (C–H), 2832 (C–H), 1557, 1437, 1246, 1146, 1110, 1035, 975, 931, 834, 752, 687, 618 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = –0.04 [s, 9H, $Si(CH_3)_3$], 0.10 [s, 9H, $Si(CH_3)_3$], 1.55–1.98 [m, 11H, 1(2,3,4,5,6)-H], 5.94 (s, 1H, 8-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –0.88 [+, $Si(CH_3)_3$], –0.51 [+, $Si(CH_3)_3$], 22.96 (–, C-3*), 23.13 (–, C-2*), 27.58 (+, C-6), 27.66 (–, C-5), 30.31 (–, C-4*), 30.99 (–, C-1*), 129.20 (C_{quat}, C-7*), 130.46 (C_{quat}, C-8a*), 135.46 (+, C-8), 139.16 (C_{quat}, C-4a*); DCI-MS (NH_3): *m*/*z* (%): 282/281/280/279 (2/10/29/100) [M+H^+]; **13**: IR (film): $\tilde{\nu}$ = 2932 (C–H), 2858 (C–H), 1437, 1247, 1196, 1102, 876, 861, 836, 754, 690, 652 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.27 [s, 9H, $Si(CH_3)_3$], 1.82 [m, 4H, 6(7)-H], 2.80 [m, 4H, 5(8)-H], 7.08–7.11 (m, 1H, Ar-H), 7.25–7.29 (m, 2H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –1.05 [+, $Si(CH_3)_3$], 23.14 (–, C-6*), 23.28 (–, C-7*), 29.36 [–, C-5(8)], 128.67 (+, Ar-C), 130.36 (+, Ar-C), 134.32 (+, Ar-C), 136.45 (C_{quat}, Ar-C), 136.94 (C_{quat}, Ar-C), 138.02 (C_{quat}, Ar-C); DCI-MS (NH_3): *m*/*z* (%): 205 (64) [M+H^+], 107 (100).

Methyl (1*R,8*R**,9*R**)-9-methoxy-12-oxatricyclo[7.2.1.0^{1,6}]dodeca-6,10-diene-8-carboxylate (17b)**: A solution of methyl (*E*)-3-{2-[(*E*)-2-(methoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate [(*E*,*Z*,*E*)-**5b**] (62 mg, 0.25 mmol) in diethyl ether (150 mL) was irradiated according to GP 2 under ^1H NMR monitoring at 0 °C for 4.5 h. After CC on silica gel (8 g, petroleum ether/EtOAc 6:1) the cyclization product **17b** was isolated as a colorless oil (43 mg, 69 %). R_f = 0.28 (petroleum ether/EtOAc 10:1); IR (film): $\tilde{\nu}$ = 2933 (C–H), 1740 (C=O), 1436, 1329, 1316, 1278, 1195, 1171, 1146, 1122, 1113, 1008 cm^{-1}; ^1H NMR (500 MHz, C_6D_6): δ = 1.06 [m, 2H, 3(4)-H], 1.37–1.43 (m, 1H, 4-H), 1.45–1.51 (m, 1H, 3-H), 1.75 (dt, J = 4.5, J = 13.5 Hz, 1H, 2-H), 1.79–1.91 [m, 2H, 2(5)-H], 2.12–2.17 (m, 1H, 5-H), 3.28 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3), 4.04 (m, 1H, 8-H), 5.23 (m, 1H, 7-H), 6.21 (d, J = 5.8 Hz, 1H, 10-H), 6.45 (d, J = 5.8 Hz, 1H, 11-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.94 (–, C-3), 24.84 (–, C-4), 31.10 (–, C-5), 32.25 (–, C-2), 49.59 (+, C-8), 51.00 (+, OCH_3), 51.89 (+, OCH_3), 84.10 (C_{quat}, C-1), 109.58 (C_{quat}, C-9), 116.59 (+, C-7), 128.65 (+, C-10), 143.78 (+, C-11), 144.43 (C_{quat}, C-6), 170.58 (C_{quat}, CO_2); MS (70 eV): *m*/*z* (%): 250 (1) [M^+], 218 (29) [M^+-HOCH_3], 191 (22) [$M^+-CO_2CH_3$], 175 (7), 159 (20) [$M^+-HOCH_3-CO_2CH_3$], 147 (7), 131 (100), 121 (39), 105 (24), 91 (63), 59 (26) [$CO_2CH_3^+$]; elemental analysis calcd (%) for $C_{14}H_{18}O_4$ (250.3): C 67.18, H 7.25; found C 66.91, H 7.42.

(1*R,8*R**,9*R**)-9-Methoxy-12-oxatricyclo[7.2.1.0^{1,6}]dodeca-6,10-diene-8-carbonitrile (17e)**: A solution of methyl (*E*)-3-{2-[(*E*)-2-cyanoethyl]-1-cyclohexen-1-yl}acrylate [(*E*,*Z*,*E*)-**5e**] (86 mg, 0.40 mmol) in diethyl ether (120 mL) was irradiated according to GP 2 in two portions at 0 °C for 4 h each. The combined reaction mixtures were purified by CC on silica gel (2 g, pentane/Et_2O 59:1) yielding the cyclization product **17e** as colorless crystals (23 mg, 28 %). M.p. 110–112 °C; R_f = 0.34; IR (KBr): $\tilde{\nu}$ = 2946 (C–H), 2858, 2242 (C≡N), 1457, 1330, 1285, 1243, 1145, 1045, 980, 909, 850, 771 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.24–2.14 [m, 7H, 2(3,4,5)-H], 2.36–2.42 (m, 1H, 5-H), 3.44 (s, 3H, OCH_3), 3.66 (m, 1H, 8-H), 5.02 (m, 1H, 7-H), 6.04 (d, J = 5.8 Hz, 1H, 10-H), 6.80 (d, J = 5.8 Hz, 1H, 11-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.62 (–, C-3), 24.43 (–, C-4), 30.85 (–, C-5), 31.89 (–, C-2), 35.02 (+, C-8), 51.26 (+, OCH_3), 84.64 (C_{quat}, C-1), 108.57 (C_{quat}, C-9), 112.94 (+, C-7), 116.75 (C_{quat}, C≡N), 126.58 (+, C-10), 144.93 (+, C-11), 145.61 (C_{quat}, C-6); MS (70 eV): *m*/*z* (%): 217 (4) [M^+], 190 (3) [M^+-HCN], 188 (19), 185 (100) [M^+-CH_3OH], 184 (42), 170 (13), 158 (45), 145 (14), 130 (29), 129 (37), 116 (31), 104 (8), 91 (14), 79 (4), 77 (11), 65 (6), 55 (2), 51 (3), 41 (7); elemental analysis calcd (%) for $C_{13}H_{15}O_2N$ (217.3): C 71.87, H 6.96, N 6.45; found C 71.58, H 6.69, N 6.25.

Methyl (1*R,9*R**,10*R**)-10-methoxy-13-oxatricyclo[8.2.1.0^{1,7}]trideca-7,11-diene-9-carboxylate (18b)**: A solution of methyl (*E*)-3-{2-[(*E*)-2-(methoxycarbonyl)ethenyl]-1-cyclohepten-1-yl}acrylate [(*E*,*Z*,*E*)-**6b**] (50 mg, 0.19 mmol) in diethyl ether (60 mL) was irradiated according to GP 2 under ^1H NMR monitoring at 0 °C for 90 min. After CC on silica gel (2 g, pentane/Et_2O 5:1), the cyclization product **18b** was isolated as a colorless oil (30 mg, 60 %). R_f = 0.40 (pentane/Et_2O 4:1); IR (film): $\tilde{\nu}$ = 2927 (C–H), 2851, 1734 (C=O), 1437, 1313, 1269, 1198, 1161, 1125, 1082, 1034,

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1005, 919, 856, 819, 734 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.24–1.37$ (m, 2H, 4-H), 1.46–2.09 [m, 7H, 2(3,5,6)-H], 2.25–2.32 (m, 1H, 6-H), 3.46 (s, 3H, CH_3), 3.57 (m, 1H, 9-H), 3.67 (s, 3H, CO_2CH_3), 5.29 (m, 1H, 8-H), 5.94 (d, $J = 5.8$ Hz, 1H, 11-H), 6.48 (d, $J = 5.8$ Hz, 1H, 12-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 24.00$ (–, C-4), 31.27 (–, C-3), 31.46 (–, C-5), 34,06 (–, C-6), 35.22 (–, C-2), 49.35 (+, C-8), 51.12 (+, OCH_3), 51.90 (+, OCH_3), 87.69 (C_{quat}, C-1), 110.77 (C_{quat}, C-10), 120.24 (+, C-9), 128.02 (+, C-11), 144.83 (+, C-12), 148.73 (C_{quat}, C-7), 170.58 (C_{quat}, CO_2CH_3); MS (70 eV): *m/z* (%): 264 (4) [M^+], 236 (3), 232 (60) [$M^+ - CH_3OH$], 205 (65) [$M^+ - CO_2CH_3$], 204 (75), 200 (20), 179 (13) [$M^+ - CHCHCO_2CH_3$], 177 (28), 173 (45) [$M^+ - CO_2CH_3 - CH_3OH$], 164 (13) [$M^+ - CHCHCO_2CH_3 - CH_3$], 145 (100), 131 (21), 121 (46), 105 (35), 91 (31), 77 (13), 65 (6), 59 (17) [$CO_2CH_3^+$], 43 (6), 41 (11); elemental analysis calcd (%) for $C_{15}H_{20}O_4$ (264.3): C 68.16, H 7.63; found C 68.10, H 7.52; MS: *m/z*: 264.1361 (correct HRMS).

Ethyl (1*R,8*R**,9*R**)-9-ethoxy-12-oxatricyclo[7.2.1.0^{1,6}]dodeca-6,10-diene-8-carboxylate (17a) and diethyl tricyclo[4.4.0.0^{1,3}]dec-5-ene-2,4-dicarboxylate (19a)**: A solution of ethyl (*E*)-3-{2-[(*E*)-2-(ethoxycarbonyl)-ethenyl]-1-cyclohexen-1-yl}acrylate [(*E*,*Z*,*E*)-**5a**] (56 mg, 0.20 mmol) in diethyl ether (60 mL) was irradiated according to GP 2 at 0 °C for 5 h. The reaction mixture was purified by CC on silica gel (2 g, pentane/Et_2O 5:1) yielding a 87:13 mixture (29 mg, 52 %) of 12-oxatricyclo[7.2.1.0^{1,6}]dodeca-6,10-diene (**17a**) and tricyclo[4.4.0.0^{1,3}]dec-5-ene (**19a**). $R_f = 0.39$; ^1H NMR (250 MHz, $CDCl_3$); signals which can be assigned to the product **17a** are marked with "#", signals which can be assigned to the by-product **19a** are marked with "##": $\delta = 1.10–1.26$ (m, 6H, $CO_2CH_2CH_3$), 1.29–2.15 (m), 2.32–2.38 (m, 1H, 5-H)$^{\#}$, 3.61–4.21 (m, 5H, $CO_2CH_2CH_3$, 8-H)$^{\#}$, 5.04 (m, 1H, 5-H)$^{\#\#}$, 5.13 (m, 1H, 7-H)$^{\#}$, 5.98 (d, $J = 5.8$ Hz, 1H, 10-H)$^{\#}$, 6.69 (d, $J = 5.8$ Hz, 1H, 11-H)$^{\#}$; ^{13}C NMR (50.3 MHz, $CDCl_3$); signals which can be assigned to the product **17a** are marked with "#", signals which can be assigned to the by-product **19a** are marked with "##": $\delta = 14.09$ (+, CH_2CH_3)$^{\#}$, 14.17 (+, CH_2CH_3)$^{\#\#}$, 14.26 (+, CH_2CH_3)$^{\#\#}$, 15.60 (+, CH_2CH_3)$^{\#}$, 22.96 (–, C-3)$^{\#}$, 23.99 (–, C-7*)$^{\#\#}$, 24.43 (–, C-8*)$^{\#\#}$, 24.87 (–, C-4)$^{\#}$, 25.24 (–, C-9*)$^{\#\#}$, 26.97 (–, C-10*)$^{\#\#}$, 30.50 (+, C-3)$^{\#\#}$, 31.10 (–, C-5)$^{\#}$, 31.54 (+, C-2)$^{\#\#}$, 32.33 (–, C-2)$^{\#}$, 43.35 (–, C-1)$^{\#\#}$, 49.92 (+, C-8)$^{\#}$, 51.35 (+, C-4)$^{\#\#}$, 59.08 (–, CH_2CH_3)$^{\#}$, 60.23 (–, 2C, CH_2CH_3)$^{\#\#}$, 60.54 (–, CH_2CH_3)$^{\#}$, 83.75 (–, C-1)$^{\#}$, 109.36 (–, C-9)$^{\#}$, 116.74 (+, C-7)$^{\#}$, 118.28 (+, C-5)$^{\#\#}$, 129.32 (+, C-10)$^{\#}$, 143.15 (+, C-11)$^{\#}$, 144.44 (–, C-6)$^{\#}$, 149.36 (–, C-6)$^{\#\#}$, 170.19 (–, CO_2)$^{\#}$, 171.12 (–, CO_2)$^{\#\#}$, 172.82 (–, CO_2)$^{\#\#}$.

tert*-Butyl (1*R**,8*R**,9*R**)-9-*tert*-butoxy-12-oxatricyclo[7.2.1.0^{1,6}]dodeca-6,10-diene-8-carboxylate (17d) and di-*tert*-butyl tricyclo[4.4.0.0^{1,3}]dec-5-ene-2,4-dicarboxylate (19d)**: A solution of *tert*-butyl (*E*)-3-{2-[(*E*)-2-(*tert*-butoxycarbonyl)ethenyl]-1-cyclohexen-1-yl}acrylate [(*E*,*Z*,*E*)-**5d**] (67 mg, 0.20 mmol) in diethyl ether (60 mL) was irradiated according to GP 2 at 0 °C for 3.5 h. The reaction mixture was purified by CC on silica gel (2 g, pentane/Et_2O 20:1) yielding a 39:61 mixture (15 mg, 22 %) of the 12-oxatricyclo[7.2.1.0^{1,6}]dodeca-6,10-diene (**17d**) and the tricyclo[4.4.0.0^{1,3}]dec-5-ene (**19d**). $R_f = 0.37$; ^1H NMR (250 MHz, $CDCl_3$); signals which can be assigned to the product **17d** are marked with "#", signals which can be assigned to **19d** are marked with "##": $\delta = 1.18–2.37$ (m), 1.34 [s, $C(CH_3)_3$], 1.43 [s, $C(CH_3)_3$], 2.41–2.47 (m, 1H, 5-H)$^{\#}$, 3.48 (m, 1H, 8-H)$^{\#}$, 3.82 (m, 1H, 4-H)$^{\#\#}$, 5.01 (m, 1H, 5-H)$^{\#\#}$, 5.10 (m, 1H, 7-H)$^{\#}$, 6.07 (d, $J = 5.8$ Hz, 1H, 10-H)$^{\#}$, 6.55 (d, $J = 5.8$ Hz, 1H, 11-H)$^{\#}$; ^{13}C NMR (62.9 MHz, $CDCl_3$); signals which can be assigned to the product **17d** are marked with "#", signals which can be assigned to **19d** are marked with "##": $\delta = 23.05$ (–, C-3)$^{\#}$, 23.93 (–, C-7***)$^{\#\#}$, 24.53 (–, C-8***)$^{\#\#}$, 24.96 (–, C-4***)$^{\#}$, 25.37 (–, C-9***)$^{\#\#}$, 27.02 (–, C-10***)$^{\#\#}$, 28.05 [+, $C(CH_3)_3$], 28.22 [+, $C(CH_3)_3$], 30.66 (+, C-3)$^{\#\#}$, 30.96 [+, $C(CH_3)_3$], 31.09 (–, C-5)$^{\#}$, 32.53 (–, C-2)$^{\#}$, 32.57 (+, C-2)$^{\#\#}$, 43.07 (C_{quat}, C-1)$^{\#\#}$, 52.43 (+, C-8)$^{\#}$, 52.69 (+, C-4)$^{\#\#}$, 80.01 [C_{quat}, $C(CH_3)_3$]**, 80.46 [C_{quat}, $C(CH_3)_3$]**, 80.53 [C_{quat}, $C(CH_3)_3$]**, 82.78 (C_{quat}, C-1**)$^{\#}$, 108.80 (C_{quat}, C-9)$^{\#}$, 117.58 (+, C-7*)$^{\#}$, 118.50 (+, C-5*)$^{\#\#}$, 130.78 (+, C-10)$^{\#}$, 139.73 (+, C-11)$^{\#}$, 143.61 (C_{quat}, C-6)$^{\#}$, 149.21 (C_{quat}, C-6)$^{\#\#}$, 170.06 (C_{quat}, CO_2), 170.66 (C_{quat}, CO_2), 172.28 (C_{quat}, CO_2).

***tert*-Butyl (1*R**,9*R**,10*R**)-10-*tert*-butoxy-13-oxatricyclo[8.2.1.0^{1,7}]trideca-7,11-diene-9-carboxylate (18d) and di-*tert*-butyl tricyclo[5.4.0.0^{1,10}]undec-7-ene-9,11-dicarboxylate (20d)**: A solution of *tert*-butyl (*E*)-3-{2-[(*E*)-2-(*tert*-butoxycarbonyl)ethenyl]-1-cyclohepten-1-yl}acrylate [(*E*,*Z*,*E*)-**6d**] (70 mg, 0.20 mmol) in diethyl ether (60 mL) was irradiated according to GP 2 under ^1H NMR monitoring at 0 °C for 4 h. After CC on silica gel (2 g, pentane/Et_2O 20:1), a 29:71 mixture (21 mg, 30 %) of the oxatricyclo[8.2.1.0^{1,7}]trideca-7,11-diene (**18d**) and the tricyclo[5.4.0.0^{1,10}]undec-7-ene (**20d**) was isolated as a colorless oil. $R_f = 0.26$; ^1H NMR (250 MHz, $CDCl_3$) signals which can be assigned to the product **18d** are marked with "#", signals which can be assigned to **20d** are marked with "##": $\delta = 1.28–1.89$ (m), 1.35 [s, $C(CH_3)_3$], 1.43 [s, $C(CH_3)_3$], 1.44 [s, $C(CH_3)_3$], 2.24–2.58 (m), 3.37 (m, 1H, 9-H)$^{\#}$, 3.78 (m, 1H, 9-H)$^{\#\#}$, 5.02 (m, 1H, 8-H)$^{\#\#}$, 5.23 (m, 1H, 8-H)$^{\#}$, 6.07 (d, $J = 5.8$ Hz, 1H, 11-H)$^{\#}$, 6.30 (d, $J = 5.8$ Hz, 1H, 12-H)$^{\#}$; ^{13}C NMR (62.9 MHz, $CDCl_3$); signals which can be assigned to the product **18d** are marked with "#", signals which can be assigned to **20d** are marked with "##": $\delta = 24.07$ (–)$^{\#}$, 26.65 (–)$^{\#\#}$, 28.00 [+, $C(CH_3)_3$], 28.10 [+, $C(CH_3)_3$], 28.80 (–)$^{\#\#}$, 30.75 (–)$^{\#\#}$, 30.87 [+, $C(CH_3)_3$]$^{\#}$, 31.22 (–)$^{\#}$, 31.38 (–)$^{\#}$, 32.20 (–)$^{\#\#}$, 33.21 (+, C-10)$^{\#\#}$, 33.39 (+, C-11)$^{\#\#}$, 34.23 (–, C-6)$^{\#}$, 35.54 (–, C-2)$^{\#}$, 47.35 (C_{quat}, C-1)$^{\#\#}$, 52.26 (+, C-9)$^{\#}$, 53.00 (+, C-9)$^{\#\#}$, 79.86 [C_{quat}, $C(CH_3)_3$], 80.41 [C_{quat}, $C(CH_3)_3$], 86.29 (C_{quat}, C-1)$^{\#}$, 109.92 (C_{quat}, C-10)$^{\#}$, 119.77 (+, C-8)$^{\#\#}$, 121.01 (+, C-8)$^{\#}$, 130.01 (+, C-11)$^{\#}$, 140.72 (+, C-12)$^{\#}$, 148.05 (C_{quat}, C-7)$^{\#}$, 154.00 (C_{quat}, C-7)$^{\#\#}$, 170.03 (C_{quat}, CO_2)$^{\#}$, 170.93 (C_{quat}, CO_2)$^{\#\#}$, 172.16 (C_{quat}, CO_2)$^{\#\#}$.

Methyl 7-oxo-2,3,4,7-tetrahydro-1*H*-benzocycloheptene-6-carboxylate (21b): Distilled titanium tetrachloride (14 μL, 0.12 mmol) was added dropwise with a syringe into a stirred solution of methyl (1*R**,8*R**,9*R**)-9-methoxy-12-oxatricyclo[7.2.1.0^{1,6}]dodeca-6,10-diene-8-carboxylate (**17b**) (31 mg, 0.12 mmol) in diethyl ether (2 mL) at 0 °C. Lithium iodide (16 mg, 0.12 mmol) was then added to the resulting solution, and the brown reaction mixture was stirred for 2.5 h. Then water (2 mL) was added. The reaction mixture was diluted with diethyl ether (5 mL), and the organic layer was successively washed with aqueous $Na_2S_2O_3$ solution (2 mL, 10 %), saturated aqueous Na_2CO_3 solution (2 mL) and water (2 mL) and then dried over $MgSO_4$. The extract was concentrated in vacuo, and the residue was purified by CC on silica gel (8 g, pentane/Et_2O 1:6) to give the troponecarboxylate **21b** as a colorless solid (8 mg, 30 %). M.p. 78–80 °C; $R_f = 0.45$; IR (KBr): $\tilde{\nu} = 2955$ (C–H), 2868, 1734 (C=O), 1630 (C=C), 1578, 1528, 1453, 1434, 1305, 1247, 1196, 1034, 918, 858, 821, 792 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.75$ [m, 4H, 2(3)-H], 2.67 [m, 4H, 1(4)-H], 3.88 (s, 3H, CO_2CH_3), 6.88 [s, 2H, 8(9)-H], 7.37 (s, 1H, 5-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.76$ (–, C-2), 21.89 (–, C-3), 33.40 [–, 2 C, C-1(4)], 52.68 (+, CO_2CH_3), 138.61 (+, C-5*), 138.90 (C_{quat}, C-9a**), 140.43 (C_{quat}, C-4a**), 140.60 (+, C-9*), 142.14 (+, C-8*), 145.13 (C_{quat}, C-6**), 168.32 (C_{quat}, CO_2CH_3), 183.65 (C_{quat}, C-7); ^1H NMR (250 MHz, C_6D_6): $\delta = 1.11$ [m, 4H, 2(3)-H], 1.86 [m, 4H, 1(4)-H], 3.57 (s, 3H, CO_2CH_3), 5.98 (d, $J = 12.6$ Hz, 1H, 9-H), 6.71 (d, $J = 12.6$ Hz, 1H, 8-H), 7.03 (s, 1H, 5-H); ^{13}C NMR (62.9 MHz, C_6D_6): $\delta = 21.77$ (–, C-2), 21.87 (–, C-3), 32.91 (–, C-1), 33.05 (–, C-4), 52.15 (+, CO_2CH_3), 138.43 (+, C-5*), 139.66 (C_{quat}, C-9a**), 139.91 (+, C-9*), 140.33 (C_{quat}, C-4a**), 140.88 (+, C-8*), 143.62 (C_{quat}, C-6**), 168.76 (C_{quat}, CO_2CH_3), 183.34 (C_{quat}, C-7); MS (70 eV): *m/z* (%): 218 (37) [M^+], 190 (23) [$M^+ - CO$], 187 (10) [$M^+ - OCH_3$], 175 (3), 159 (50) [$M^+ - CO_2CH_3$], 131 (100), 115 (12), 103 (6), 91 (19), 77 (10), 63 (3), 51 (4); elemental analysis calcd (%) for $C_{13}H_{14}O_3$ (218.3): C 71.54, H 6.47; found C 71.36, H 6.34; MS: *m/z*: found: 218.1943 (correct HRMS).

Methyl 3-oxo-3,6,7,8,9,10-hexahydroheptalene-2-carboxylate (22b): TMSOTf (64 μL, 0.36 mmol) was added at room temperature with a syringe to a solution of methyl (1*R**,9*R**,10*R**)-10-methoxy-13-oxatricyclo[8.2.1.0^{1,7}]trideca-7,11-diene-9-carboxylate (**18b**) (47 mg, 0.18 mmol) in dichloromethane (5 mL). The reaction mixture was stirred for 30 min and then poured into H_2O and CH_2Cl_2 (15 mL each). The aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by CC on silica gel (10 g, petroleum ether/EtOAc 2:1) to give the troponecarboxylate **22b** as a colorless solid (27 mg, 65 %). M.p. 79–81 °C; $R_f = 0.33$ (pentane/Et_2O 1:3); IR (KBr): $\tilde{\nu} = 2930$ (C–H), 2852, 1728 (C=O), 1617 (C=C), 1571, 1505, 1456, 1430, 1306, 1250, 1212, 1040, 962, 937, 837, 794 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.63$ [m, 4H, 7(9)-H], 1.84 (m, 2H, 8-H), 2.79 [m, 4H, 6(10)-H], 3.87 (s, 3H, CO_2CH_3), 6.92 (d, $J = 12.6$ Hz, 1H, 5-H), 7.06 (d, $J = 12.6$ Hz, 1H, 4-H), 7.55 (s, 1H, 1-H); ^{13}C NMR: (62.9 MHz, $CDCl_3$): $\delta = 25.86$ (–, C-7), 25.94 (–, C-9), 31.62 (–, C-8), 39.47 (–, C-6), 39.55 (–, C-10), 52.83 (+, CO_2CH_3), 139.60 (C_{quat}, C-5a**), 140.05 (+, C-1*), 141.00 (+, C-5*), 142.34 (+, C-4*), 147.57 (C_{quat}, C-10a**), 152.42 (C_{quat}, C-2**), 168.31 (C_{quat}, CO_2CH_3), 183.06 (C_{quat}, C-3); MS (70 eV): *m/z* (%): 232 (33) [M^+], 204 (50) [$M^+ - CO$], 173 (74) [$M^+ - CO_2CH_3$], 145 (100), 131 (14), 117 (19), 115 (24),

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103 (10), 91 (19), 77 (14), 63 (7), 51 (8); elemental analysis calcd (%) for $C_{14}H_{16}O_3$ (232.3): C 72.39, H 6.94; found C 72.61, H 6.73.

6-Bromo-5-trifluoromethanesulfonyloxy-8,9-dihydro-7*H*-benzocycloheptene (26): *n*-Butyllithium (2.75 mL, 6.50 mmol, 2.36 M in hexane) was added at −78 °C to hexamethyldisilazane (HMDS) (1.09 g, 6.75 mmol) in THF (20 mL). After 20 min, a solution of 6-bromo-6,7,8,9-tetrahydrobenzocyclohepten-5-one (**25**) (1.20 g, 5.00 mmol) in THF (5 mL) was added within 10 min. After an additional 10 min, *N*-phenyltriflimide (1.79 g, 5.00 mmol) in THF (5 mL) was added within 8 min. The mixture was stirred at −78 °C for 30 min and at room temp for 22 h. The mixture was diluted with ethyl ether (200 mL) and washed with H_2O (3×50 mL). The aqueous layers were reextracted with diethyl ether (50 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. CC on silica gel (60 g, pentane/Et_2O 50:1) yielded **26** as a colorless solid (1.11 g, 60%). M.p. 68–70 °C; R_f = 0.76 (pentane/Et_2O 20:1); IR (KBr): $\tilde{\nu}$ = 3056 (C–H), 2932, 1706, 1416, 1220, 1130, 1099, 1017, 993, 966, 849, 800, 787, 768, 721, 669, 655, 617, 602 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 2.31 (quin, J = 7.0 Hz, 2H, 8-H), 2.51 (t, J = 7.0 Hz, 2H, 9-H), 2.77 (t, J = 7.0 Hz, 2H, 7-H), 7.24–7.43 [m, 4H, 1(2,3,4)-H]; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 31.24 (–, C-8), 33.90 (–, C-9), 35.00 (–, C-7), 118.18 (q, J_{CF} = 320.6 Hz, C_{quat}, CF_3), 118.30 (C_{quat}, C-6), 126.50 (+, aromatic C), 126.54 (+, aromatic C), 129.46 (+, aromatic C), 130.15 (+, aromatic C), 130.29 (C_{quat}, C-5), 140.86 (C_{quat}, C-9a*), 142.84 (C_{quat}, C-4a*); MS (70 eV): *m*/*z* (%): 372/370 (5/5) [M^+], 211/209 (5/5), 141 (3), 129 (100), 115 (18), 90 (18), 77 (25), 69 (15) [CF_3^+]; elemental analysis calcd (%) for $C_{12}H_{10}BrF_3O_3S$ (371.2): C 38.83, H 2.72; found C 39.08, H 2.63.

Methyl (*E*)-3-{6-[(*E*)-2-(methoxycarbonyl)ethenyl]-8,9-dihydro-7*H*-benzocyclohepten-5-yl}acrylate (27): 6-Bromo-5-trifluoromethanesulfonyloxy-8,9-dihydro-7*H*-benzocycloheptene (**26**) (0.900 g, 2.43 mmol) was treated with methyl acrylate (1.05 g, 12.2 mmol) for 24 h at 60 °C according to GP 1. After CC on silica gel (100 g, pentane/EtOAc 10:1) hexatriene **27** was obtained as a colorless solid (383 mg, 51%). M.p. 73–75 °C; R_f = 0.24; IR (film): $\tilde{\nu}$ = 2949 (C–H), 2859, 1717 (C=O), 1616 (C=C), 1436, 1311, 1195, 1173, 1040, 1017, 977 (*trans* HC=CH), 914, 982, 766, 734 cm^{-1}; UV (chloroform): λ_{max} (log ε) = 260.0 (4.048), 335.5 nm (4.368); ^1H NMR (250 MHz, $CDCl_3$): δ = 2.04–2.22 [m, 4H, 7′(8′)-H], 2.51 (t, J = 6.8 Hz, 2H, 9′-H), 3.76 (s, 3H, CO_2CH_3), 3.81 (s, 3H, CO_2CH_3), 5.79 (d, J = 15.5 Hz, 1H, 2-H), 6.17 (d, J = 15.6 Hz, 1H, 2″-H), 7.17–7.29 [m, 4H, 1′(2′,3′,4′)-H], 8.12 (d, J = 15.6 Hz, 1H, 1″-H), 8.16 (d, J = 15.5 Hz, 1H, 3-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.95 (–, C-8′), 31.20 (–, C-7′), 32.55 (–, C-9′), 51.69 (+, CO_2CH_3), 51.80 (+, CO_2CH_3), 119.94 (+, C-2), 123.51 (+, C-2″), 126.03 (+, aromatic C), 128.54 (+, aromatic C), 128.57 (+, aromatic C), 129.35 (+, aromatic C), 137.37 (C_{quat}, C-6′*), 139.47 (+, C-1″), 139.64 (+, C-3), 140.48 [C_{quat}, 2 C, C-5′(4a′)*], 141.15 (C_{quat}, C-9a′*), 167.31 (C_{quat}, CO_2CH_3), 167.44 (C_{quat}, CO_2CH_3); MS (70 eV): *m*/*z* (%): 312 (15) [M^+], 280 (32) [M^+−CH_3OH], 253 (83) [M^+−CO_2CH_3], 252 (89) [M^+−CH_3CO_2H], 221 (72) [M^+−CO_2CH_3−CH_3OH], 193 (100) [M^+−CO_2CH_3−CH_3CO_2H], 178 (59), 165 (60), 152 (21), 128 (12), 115 (19), 89 (7), 77 (4), 59 (25) [$CO_2CH_3^+$], 51 (3); as the first fraction after CC, methyl (*E*)-3-(8,9-dihydro-7*H*-benzocyclohepten-6-yl)acrylate (**28**) was obtained as a colorless solid (83 mg, 15%). M.p. 40–42 °C; R_f = 0.52; IR (film): $\tilde{\nu}$ = 3015 (C–H), 2944, 1716 (C=O), 1616 (C=C), 1434, 1312, 1285, 1158, 1021, 973 (*trans* HC=CH), 840, 770, 735 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 2.06 (m, 2H, 8′-H), 2.51 (t, J = 6.4 Hz, 2H, 7′-H), 2.83 (m, 2H, 9′-H), 3.78 (s, 3H, CO_2CH_3), 5.94 (d, J = 15.7 Hz, 1H, 2-H), 6.83 (s, 1H, 5′-H), 7.10–7.26 [m, 4H, 1′(2′,3′,4′)-H], 7.51 (d, J = 15.7 Hz, 1H, 3-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.43 (–, C-8′), 30.12 (–, C-7′), 35.28 (–, C-9′), 51.39 (+, CO_2CH_3), 115.62 (+, C-2), 126.05 (+, C-5′*), 128.09 (+, C-1′*), 129.05 (+, C-2′*), 132.32 (+, C-3′*), 134.94 (C_{quat}, C-6′**), 137.80 (C_{quat}, C-4a′**), 140.23 (+, C-4′*), 142.23 (C_{quat}, C-9a′**), 150.35 (+, C-3), 167.68 (C_{quat}, CO_2CH_3); MS (70 eV): *m*/*z* (%): 228 (100) [M^+], 197 (17) [M^+−OCH_3], 196 (33), 181 (13), 169 (43) [M^+−CO_2CH_3], 168 (45), 167 (44), 153 (33), 141 (39), 131 (49), 115 (35), 103 (25), 91 (22), 77 (24), 63 (10), 51 (15), 41 (5); elemental analysis calcd (%) for $C_{15}H_{16}O_2$ (228.3): C 78.92, H 7.06; found C 78.77, H 6.80; MS: *m*/*z*: found: 228.1150 (correct HRMS).

Dimethyl (1*S,9*R**,10*R**,11*R**)-benzotricyclo[5.4.0.0^{1,10}]undeca-2,7-diene-9,11-dicarboxylate (29) and dimethyl (1*S**,9*S**,10*R**,11*R**)-benzotricyclo[5.4.0.0^{1,10}]undeca-2,7-diene-9,11-dicarboxylate (30)**: A solution of methyl (3*E*)-3-{6-[(*E*)-2-(methoxycarbonyl)ethenyl]-8,9-dihydro-7*H*-benzocyclohepten-5-yl}acrylate (**27**) (66 mg, 0.21 mmol) in diethyl ether (60 mL) was irradiated according to GP 2 under ^1H NMR monitoring at 0 °C for 180 min. After CC on silica gel (18 g, pentane/Et_2O 4:1) cyclization product **29** as colorless crystals (21 mg, 32%), and diastereoisomer **30** as a colorless oil (17 mg, 26%). **29**: M.p. 105–107 °C; R_f = 0.48; IR (KBr): $\tilde{\nu}$ = 2928 (C–H), 2864, 1731 (C=O), 1707, 1458, 1431, 1324, 1271, 1233, 1198, 1069, 1015, 830, 777 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.78–1.99 [m, 3H, 5(6)-H], 1.86 (d, J = 3.7 Hz, 1H, 11-H), 2.31–2.41 (m, 1H, 6-H), 2.71 (dd, J = 14.0, J = 7.3 Hz, 1H, 4-H), 3.13–3.26 (m, 1H, 4-H), 3.33–3.36 (m, 1H, 10-H), 3.36 (s, 3H, CO_2CH_3), 3.60 (br. s, 1H, 9-H), 3.74 (s, 3H, CO_2CH_3), 5.24 (br. s, 1H, 8-H), 6.90–7.33 (m, 4H, aromatic H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 23.64 (–, C-5), 26.56 (–, C-6), 29.73 (+, C-10), 30.53 (–, C-4), 37.35 (+, C-11), 49.17 (C_{quat}, C-1), 51.45 (+, CO_2CH_3), 52.10 (+, CO_2CH_3), 52.17 (+, C-9), 118.40 (+, C-8), 125.94 (+, aromatic C), 127.57 (+, aromatic C), 128.37 (+, aromatic C), 128.66 (+, aromatic C), 133.30 (C_{quat}, C-2), 140.09 (C_{quat}, C-3), 151.03 (C_{quat}, C-7), 169.52 (C_{quat}, CO_2CH_3), 172.55 (C_{quat}, CO_2CH_3); MS (70 eV): *m*/*z* (%): 312 (5) [M^+], 280 (59) [M^+−CH_3OH], 253 (94) [M^+−CO_2CH_3], 252 (100) [M^+−CH_3CO_2H], 237 (9) [M^+−CH_3CO_2H−CH_3], 221 (76) [M^+−CO_2CH_3−CH_3OH], 193 (75) [M^+−CO_2CH_3−CH_3CO_2H], 178 (40), 165 (31), 152 (10), 115 (11), 91 (7), 84 (77), 73 (20), 61 (10), 45 (21), 43 (8); elemental analysis calcd (%) for $C_{19}H_{20}O_4$ (312.4): C 73.06, H 6.45; found C 72.79, H 6.22; **30**: R_f = 0.40; IR (film): $\tilde{\nu}$ = 2950 (C–H), 2863, 1733 (C=O), 1653, 1437, 1350, 1257, 1199, 1168, 967, 766, 737 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.74–1.96 [m, 3H, 5(6)-H], 2.18 (d, J = 3.6 Hz, 1H, 11-H), 2.30–2.40 (m, 1H, 6-H), 2.70 (dd, J = 13.9, J = 7.7 Hz, 1H, 4-H), 3.12–3.26 [m, 2H, 4(10)-H], 3.36 (s, 3H, CO_2CH_3), 3.74 (s, 3H, CO_2CH_3), 4.08 (m, 1H, 9-H), 5.17 (br. s, 1H, 8-H), 7.11–7.24 (m, 4H, aromatic H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 23.53 (–, C-5), 26.44 (–, C-6), 28.88 (+, C-10), 30.58 (–, C-4), 34.81 (+, C-11), 49.55 (C_{quat}, C-1), 51.31 (+, CO_2CH_3), 51.49 (+, C-9), 52.08 (+, CO_2CH_3), 118.76 (+, C-8), 125.83 (+, aromatic C), 127.61 (+, aromatic C), 128.01 (+, aromatic C), 128.91 (+, aromatic C), 133.20 (C_{quat}, C-2), 140.36 (C_{quat}, C-3), 150.32 (C_{quat}, C-7), 169.60 (C_{quat}, CO_2CH_3), 172.93 (C_{quat}, CO_2CH_3); MS (70 eV): *m*/*z* (%): 312 (11) [M^+], 280 (49) [M^+−CH_3OH], 253 (54) [M^+−CO_2CH_3], 252 (100) [M^+−CH_3CO_2H], 237 (6) [M^+−CH_3CO_2H], 221 (49) [M^+−CO_2CH_3−CH_3OH], 193 (74) [M^+−CO_2CH_3−CH_3CO_2H], 178 (43), 165 (39), 152 (11), 115 (9), 89 (4), 59 (15) [$CO_2CH_3^+$], 51 (2), 43 (1); elemental analysis calcd (%) for $C_{19}H_{20}O_4$ (312.4): C 73.06, H 6.45; found C 72.98, H 6.27; MS: *m*/*z*: found 312.1362 (correct HRMS).

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[1] For reviews see: a) S. Bräse, A. de Meijere in *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**, pp. 217–315; b) A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, *106*, 2473–2506; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379–2411; c) R. F. Heck in *Comprehensive Organic Synthesis*, *Vol. 4* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, pp. 833–863; d) R. F. Heck, *Org. React.* **1982**, *27*, 345–390.

[2] a) K. Voigt, P. von Zezschwitz, K. Rosauer, A. Lansky, A. Adams, O. Reiser, A. de Meijere, *Eur. J. Org. Chem.* **1998**, 1521–1534; b) K. Voigt, A. Lansky, M. Noltemeyer, A. de Meijere, *Liebigs Ann. Chem.* **1996**, 899–911; c) P. von Zezschwitz, K. Voigt, A. Lansky, M. Noltemeyer, A. de Meijere, *J. Org. Chem.* **1999**, *64*, 3806–3812; d) P. von Zezschwitz, K. Voigt, M. Noltemeyer, A. de Meijere, *Synthesis* **2000**, 1327–1340; e) A. Lansky, O. Reiser, A. de Meijere, *Synlett* **1990**, 405–407; f) P. von Zezschwitz, F. Petry, A. de Meijere, *Chem. Eur. J.* **2001**, *7*, 4035–4046; g) H. W. Sünnemann, A. de Meijere, *Angew. Chem.* **2004**, *116*, 913–915; *Angew. Chem. Int. Ed.* **2004**, *43*, 895–897.

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[3] I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley, London, **1976**.
[4] a) A. Windaus, O. Linsert, A. Lüttringhaus, G. Weidlich, *Justus Liebigs Ann. Chem.* **1932**, *492*, 226–241; b) L. F. Fieser, M. Fieser, *Steroide*, Verlag Chemie, Weinheim, **1961**, Chapter 4, pp. 97–183; c) J. L. M. A. Schlatmann, J. Pot, E. Havinga, *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 1173–1184.
[5] a) W. G. Dauben, E. L. McInnis, D. M. Michno in *Rearrangements in Ground and Excited States*, *Vol. 3* (Ed.: P. de Mayo), Academic Press, New York, **1980**, pp. 91–129; b) H. Prinzbach, E. Druckrey, *Tetrahedron Lett.* **1965**, 2959–2965; c) P. J. Vroegop, L. Lugtenburg, E. Havinga, *Tetrahedron* **1973**, *29*, 1393–1398; d) E. Druckrey, *Dissertation*, Universität Freiburg, **1966**.
[6] a) T. Jeffery, *J. Chem. Soc. Chem. Commun.* **1984**, 1287–1289; b) T. Jeffery, *Tetrahedron Lett.* **1985**, *26*, 2667–2670; c) T. Jeffery, *Tetrahedron* **1996**, *52*, 10113–10130.
[7] K. Hirakawa, E. Ogiue, J. Motoyoshiya, T. Kakurai, *J. Org. Chem.* **1986**, *51*, 1083–1087.
[8] Supporting information available: X-ray data and details for the X-ray data acquisition for compounds **17e** and **29**. CCDC-228627 (**17e**) and -228628 (**29**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).
[9] T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, Wiley, 3rd ed., New York, **1999**.
[10] G. Balme, J. Goré, *J. Org. Chem.* **1983**, *48*, 3336–3338.
[11] a) A. D. Cross, F. Šantavý, B. Trivedi, *Collect. Czech. Chem. Commun.* **1963**, *28*, 3402–3412; b) G. L. Buchanan, A. McKillop, A. L. Porte, J. K. Sutherland, *Tetrahedron* **1964**, *20*, 1449–1453.
[12] T. Graening, H.-G. Schmalz, *Angew. Chem.* **2004**, *116*, 3292–3318; *Angew. Chem. Int. Ed.* **2004**, *43*, 3230–3256.
[13] D. S. Tarbell, H. F. Wilson, E. Ott, *J. Am. Chem. Soc.* **1952**, *74*, 6263–6266.
[14] J. Suffert, *J. Org. Chem.* **1989**, *54*, 509–510.
[15] G. Wittig, R. Pohlke, *Chem. Ber.* **1961**, *94*, 3276–3286.
[16] J. B. Hendrickson, R. Bergeron, *Tetrahedron Lett.* **1973**, 4607–4610.
[17] T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, J. A. Ibers, *J. Organomet. Chem.* **1974**, *65*, 253–266.

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