Synthesis and Characterization of New Heptalenes with Extended π-Systems Attached to Them

by **Sarah Maillefer-El Houar**[1]), **Peter Uebelhart**, **Anthony Linden**, and **Hans-Jürgen Hansen***

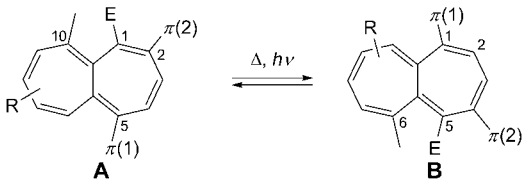
Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich (phone: +41-44-6354231; fax: +41-44-6354233; e-mail: hjhansen@oci.uzh.ch)

Methyl heptalenecarboxylates of type **A** and **B** with $\pi(1)$ and $\pi(2)$ substituents in 1,4-relation (*Scheme 1*) were synthetized starting with dimethyl 1-methylheptalene-4,5-dicarboxylates **5b** and **6b** derived from 7-isopropyl-1,4-dimethylazulene (= guaiazulene) and 1,4,6,8-tetramethylazulene by thermal reaction with dimethyl acetylenedicarboxylate. The further general way of proceeding for the introduction of the $\pi(1)$ and $\pi(2)$ substituents is displayed in *Scheme 3*, and the thus obtained methyl heptalene-5-carboxylates of type **A** and **B** are listed in *Table 1*. The C=C bonds of the 2-arylethenyl and 4-arylbuta-1,3-dien-1-yl groups of $\pi(1)$ and $\pi(2)$ were in all cases (*E*)-configured and showed s-*trans* conformation at the C–C bonds (X-ray and ^{1}H-NOE evidence) in the **B**-type as well as in the **A**-type heptalenes (*cf. Figs. 5–12*).

All **B**-type heptalenes showed a strongly enhanced heptalene band I in the wavelength region 440–490 nm in hexane/CH_2Cl_2 9:1 (*cf. Table 4* and *Figs. 13–20*). The **A**-type heptalenes showed in this region only weak absorption, recognizable as shoulders or simply tailing of the dominating heptalene bands II/III (*Table 5*). Absorption band I of the **B**-type heptalenes appeared almost at the same wavelength as the longest wavelength absorption band of comparable open-chain α,ω-diarylpolyenes (*cf. Fig. 21*). The cyclic double bond shift (DBS) of the **A**- and **B**-type heptalenes could be photochemically steered in one or the other direction by selective irradiation (*cf. Fig. 22*).

Introduction. – In a preliminary report, we have described new heptalenes of type **A** and **B**, wherein $\pi(1)$ and $\pi(2)$ represent conjugative substituents such as the 4-phenylbuta-1,3-dien-1-yl or the 4-methoxy- and 4-nitrostyryl group, which are located in 1,4-relation at the bicyclic [12]annulene core (*Scheme 1*) [1]. In heptalenes of type **A**, the C=C bonds are arranged in a way that $\pi(1)$ and $\pi(2)$ are not connected directly with each other *via* the twisted π-system of the heptalene skeleton. In this case, both π-substituents interact largely independently with the [12]annulene system. On the other hand, in the constitutionally isomeric heptalenes of type **B**, which can be generated from **A** by thermally or photochemically induced cyclic double-bond shifts (DBS), the

Scheme 1



[1]) Part of the Ph. D. Thesis of *S. M.-E.*, University of Zurich, 1998.

C=C bonds are located in a manner that $\pi(1)$ and $\pi(2)$ are now linked with each other *via* an s-*cis*-buta-1,3-diene substructure, which allows strong cooperative interactions of $\pi(1)$ and $\pi(2)$ with the annulene π-core. These different types of interactions of π-substituents with respect to the bonding situation in [4*n*]annulenes influence strongly the UV/VIS behavior of heptalenes of type **A** and **B**, *i.e.*, the **A** and **B** state of heptalenes represent thermo- and/or photochromic DBS isomers, which may serve as new types of molecular switches and/or data storage devices (see also [2]). *Fig. 1* shows, as an example, the UV/VIS spectra of the 2,5- and 1,4-bis[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]-substituted heptalenes (all-*E*)-**1a** and (all-*E*)-**1b**, respectively (*cf.* [1]). One recognizes in the spectrum of (all-*E*)-**1b** (*Fig. 1,b*), in which both π-substituents are situated at the termini of a local s-*cis*-buta-1,3-diene substructure (C(1)=C(2)–C(3)=C(4)), a strong enhancement of the heptalene band I at 439 nm (for band assignment, see [2]). The analogous band I arises in (all-*E*)-**1a** at the same wavelength (*cf. Fig. 1,a*), however, only as a just recognizable weak absorption. In this way, the thermo- and/or photochromic behavior of heptalenes are based on the respective hypo- and hyperchromisms of the UV/VIS absorption of the same basal chromogenic system of constitutionally isomeric structures such as (all-*E*)-**1a** and (all-*E*)-**1b**. A similar situation is found in thermally and/or photochemically induced (*E*)/(*Z*)-isomerizations of double-bond structures such as those in substituted ethylenes, azomethines, and azo compounds (*cf.* [3]) which may also lead to distinctly different UV/VIS spectra of the same basal chromophor of the diastereoisomeric (*E*)- and (*Z*)-isomers. As an example, the UV/VIS spectrum of the (*E*)- and (*Z*)-isomer of dimethyl 1-[6-(*tert*-butyl)azulen-1-yl]ethene-1,2-dicarboxylate ((*E*)- and (*Z*)-**2**) is reproduced in *Fig. 2* [4][2]). Whereas the typical azulene bands above 500 nm are almost not influenced by the substituted ethene chromophor attached to C(1) of the aromatic azulene core,

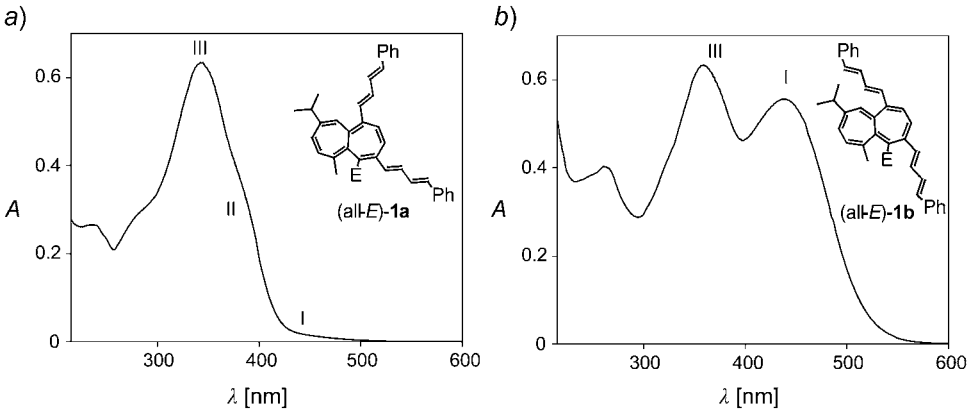


Fig. 1. *UV/VIS Spectra* (4% ^{i}PrOH/hexane) *of (all-*E*)-***1a** *and (all-*E*)-***1b** [1]. E = COOMe.

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[2]) According to AM1 calculations and in agreement with a number of X-ray crystal-structure analyses, (*E*)-configured dimethyl 1-(azulen-1-yl)ethene-1,2-dicarboxylates exhibit markedly larger torsion angles than the corresponding (*Z*)-configured dicarboxylates at the σ-bond, linking both chromogenic systems, especially when the azulenyl moieties carry additional Me substituents at C(2) and/or C(8). We will report on these 'green azulenes' later in this journal.

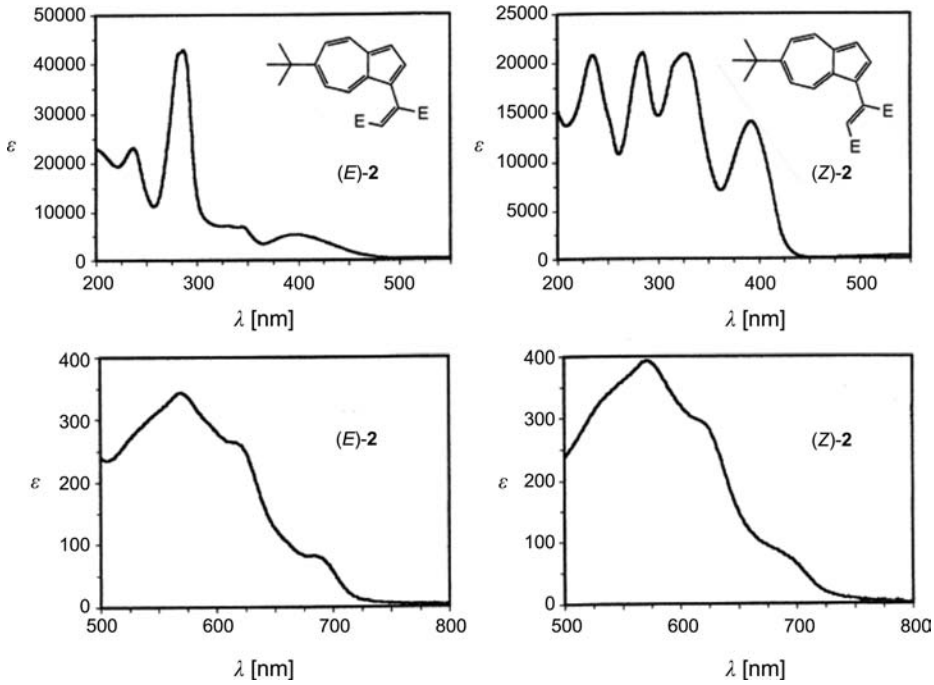


Fig. 2. *UV/VIS Spectra* (hexane) *of dimethyl 1-[(6-*(tert-*butyl)azulen-1-yl]fumarate* ((*E*)-**2**) *and dimethyl 1-[6-*(tert-*butyl)azulen-1-yl]maleate* ((*Z*)-***2***) (bottom, azulene bands) [4]. E = COOMe.

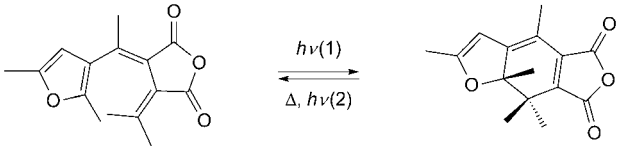
one observes significant differences in the spectra at 350 – 400 nm, caused by distinct changes in the conjugative interaction of both chromophoric systems in (*E*)- and (*Z*)-**2** due to altered torsion angles at the central σ-bond in the isomers, which are determined by the steric interactions of the azulenyl substituent at C(1) with the COOMe substituent at C(2) in (*E*)-**2** or with H–C(2) in (*Z*)-**2**.

Thermo- and photochromism, linked to UV/VIS absorption differences of two interconvertible structures with the same basal chromophoric system, are in contrast to the well-established chromism of two thermally and/or photochemically interrelated structures, which represent differing bonding states and, therefore, possess their individual excited states. A typical example is depicted in *Scheme 2*. The fulgide **3** with its longest-wavelength absorption at 345 nm is transformed photochemically into the dihydrobenzofuran **4** with an intense and broad absorption maximum at 494 nm due to the presence of a merocyanine chromophor [5]. In turn, irradiation of **4** at 494 nm or heating restores the fulgide structure of **3**. This photo- and thermochromic behavior of **3** and **4** has been amply applied in chemical actinometry [5][3]).

Since the described types of thermo- and photochromism are of fundamentally different origin, we call the former one, which is characterized by no overall change in bonding, *i.e.*, $\mathbf{A}(n\pi) \rightleftharpoons \mathbf{B}(n\pi)$, and is therefore based on hypo- and hyperchromic

[3]) The fulgide **3** has been sold under the trade name *Aberchrome 540* by *Aberchromics Ltd.*, University of Wales, Cardiff; dissolution, June 2000.

Scheme 2



3 (λ_{max} 345 nm) **4** (λ_{max} 494 nm)

effects, type-I thermo- and photochromism, and the latter one, which is characterized by changes in bonding, *i.e.*, $\mathbf{A}(n\pi) \rightleftarrows \mathbf{B}([n-m]\pi + m\sigma)$, and is thus based on hypso- and bathochromic effects, type II thermo- and photochromism.

The following chapters are dealing with the synthesis and characterization of π-substituted heptalenes of type **A** and **B** and their interconversion by thermally and photochemically induced DBS, and in this way, represent typical examples of compounds showing type-I thermo- and photochromic behavior.

Syntheses. – *Preamble.* Starting materials for our syntheses of heptalenes of type **A** and **B** (*Scheme 1*) were the heptalene-4,5-dicarboxylates **5b** and **6b** which are easily available from the corresponding azulenes by thermal reaction with an excess of dimethyl acetylenedicarboxylate (= dimethyl but-2-ynedioate) in toluene or MeCN (*cf.* [1][6][7]). Heptalene **5b** possesses three substituents in *peri*-position, and heptalenes derived from it undergo thermal DBS already at room temperature (*vide infra* as well as [8]). The other heptalene, **6b**, carries four substituents in *peri*-position, and its derivatives are set in thermal equilibrium with their DBS isomers at temperatures $>$ 60° (*vide infra* as well as [2]).

Our general synthetic approach to heptalenes of types **A** and **B** is depicted in *Scheme 3*. In a first step, Me–C(1) is transformed into the desired π(1) substituent by taking advantage of the enhanced acidity of the H-atoms of this group, caused by MeOOC–C(4), which stands in conjugative interaction with Me–C(1) *via* the involved heptalene π-bonds[4]) [1]. The π(1) substituted heptalenes **C**(1) can then selectively be reduced by way of the corresponding *pseudo*-esters **D**(1) to the 4-formylheptalene-5-carboxylates **E**(1). This procedure allows the introduction of the π(2) substituents at C(4) by established synthetic methodologies (*Wittig* and/or *Heck* reactions or variants of them; *vide infra*). We also synthesized the π(2)-substituted heptalenes **C**(2) by using the same procedures *via* **7b** and **8b** (*cf. Scheme 3*). The characterization of the spectroscopic properties of the synthesized heptalenes was also of interest in the frame of this work (see later). We will discuss in the following parts some characteristic features of the performed syntheses.

Introduction of the π(1) Substituents. In our first experiments with the heptalene-dicarboxylate **5b** as model compound, we tried to transform Me–C(1), on account of its

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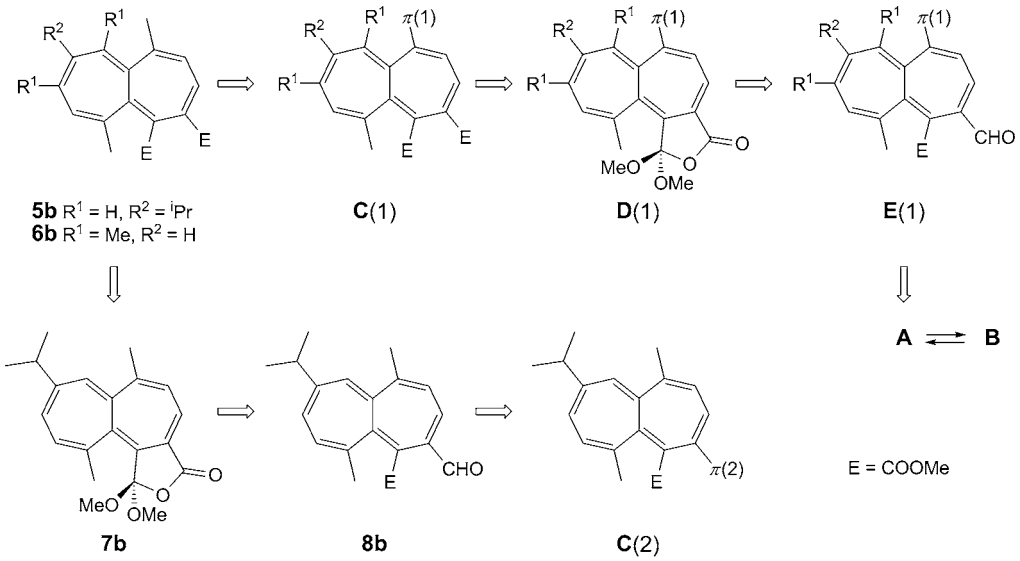
[4]) Indeed, X-ray analyses (*cf.*, *e.g.*, [2]) as well as AM1 calculations of heptalene-4,5-dicarboxylates of type **5b** and **6b** show the C=O group of MeOOC–C(4) mostly in almost ideal s-*cis* (sometimes s-*trans*) relation to C(3)=C(4) of the heptalene core with Θ(C(3)=C(4)–C=O) $<30°$ or $>150°$, respectively.

Scheme 3



allylic position, directly into a formyl group which would be useful for further coupling reactions of the *Wittig* type. However, the oxidation of **5b** with SeO_2 in boiling xylene led to a complex mixture from which only the intensely colored formyl-heptalenedicarboxylates **9b** and **10b** were isolated chromatographically in yields of 3 and 4%, respectively (*Scheme 4*[5]) [9]. Other oxidative agents such as MnO_2 or $Pb(OAc)_4$ gave no better results. The allylic bromination of **5b** with *N*-bromosuccinimide (NBS) under established conditions gave a 1:3 mixture of the (bromomethyl)heptalenedicarboxylates **11b** and **12b** in moderate yield and, moreover, in favor of the 'wrong' 6-(bromomethyl) derivative **12b** (*Scheme 4*). These preliminary experiments showed us that we had to search for other, more chemoselective procedures for the functionalization of Me–C(1).

Since **5b** (as well as **6b**) carries Me–C(1), in contrast to Me–C(6), in conjugative interaction with MeOOC–C(4), we investigated the base-induced halogenation of Me–C(1). The excellent results that we had observed in the low-temperature chlorination of alkyl phenyl sulfones with C_2Cl_6 in THF in the presence of ^{t}BuOK [10], led us to apply these conditions also to **5b**. They turned out to become a full success since only the 1-(chloromethyl) derivative **13b** of **5b** was formed and isolated in average yields of 90% after optimization of the reaction conditions (*Scheme 5*).

The heptalenedicarboxylate **6b**, in comparison to **5b**, behaved much more reluctant in the chlorination reaction due to the presence of Me–C(10) which hinders the deprotonation of Me–C(1) and – as we suppose – also the chlorination of the

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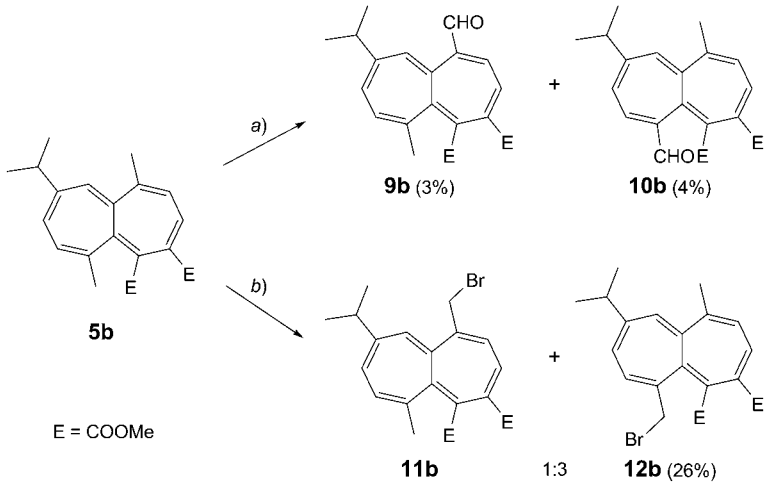
[5]) In later experiments, *Song* found that heptalenedicarboxylates, which carry only one Me group, can be transformed into the corresponding formyl-heptalenedicarboxylates with SeO_2 in yields up to 60% [9].

Scheme 4

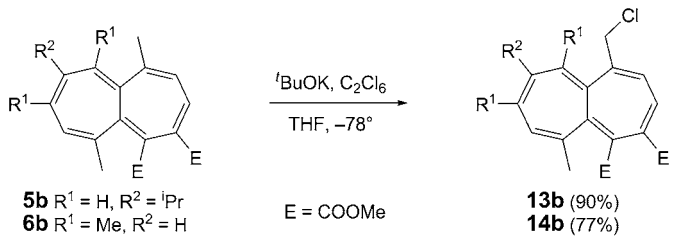


a) SeO_2, xylene, reflux, 1.5 h. *b*) NBS, dibenzoyl peroxide, CCl_4, reflux, 2 h.

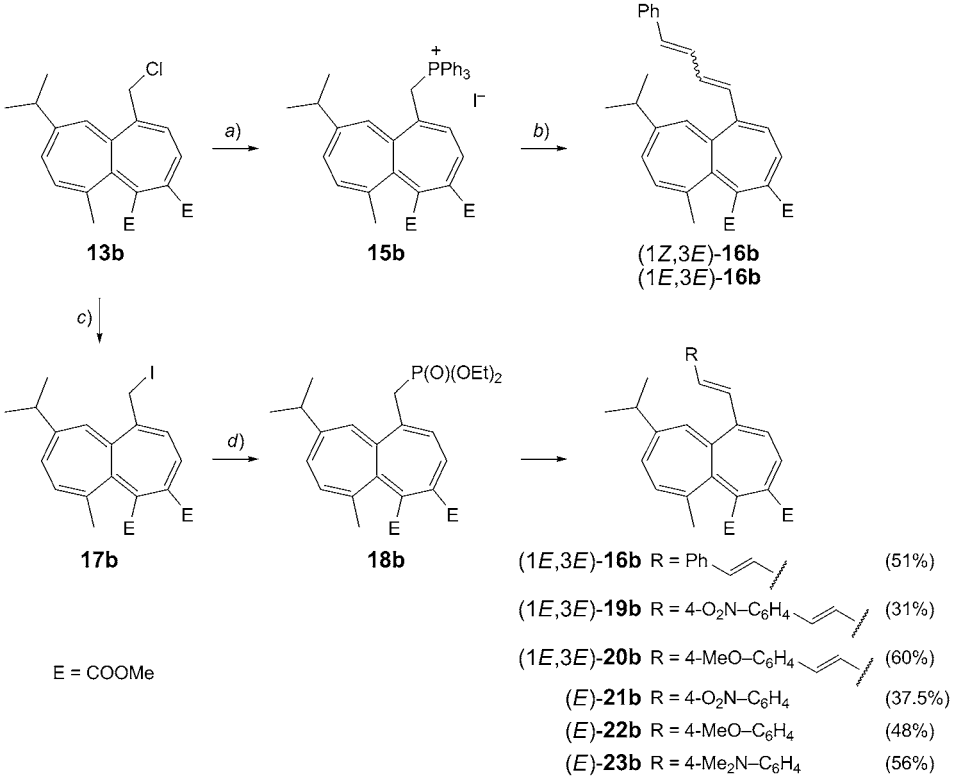
corresponding anion by C_2Cl_6. The reaction time had, therefore, to be prolonged, and the yield of the 1-(chlormethyl) derivative **14b** from **6b** dropped to 77% (*Scheme 5*).

The selective introduction of a chloro substituent at Me–C(1) of **5b** and **6b** opened the way for the construction of conjugative π-substituents at C(1) by *Wittig* and *Horner–Wadsworth–Emmons* reactions. Compound **13b** served as test substrate. Reaction of **13b** with Ph_3P in the presence of an excess of NaI in acetone at room temperature led just to the formation of the corresponding phosphonium iodide **15b** in excellent yield (*Scheme 6*). Its reaction with cinnamaldehyde in a two-phase system (2N aq. $NaOH/CH_2Cl_2$) at room temperature resulted in the formation of (1*Z*,3*E*)- and (1*E*,3*E*)-**16b** in 59% yield with the former stereoisomer in excess. On standing in Et_2O solution, both isomers **16b** cocrystallized from the mixture in dark orange to orange crystals that could be separated mechanically by hand (see *Exper. Part*). The 1-(iodomethyl)heptalene **17b** was obtained in good yield by the *Finkelstein* procedure (*Scheme 6*). *Michaelis–Arbusov* reaction of **17b** with triethyl phosphite ($P(OEt)_3$) formed the diethyl phosphonate **18b**, which was treated without further purification with cinnamaldehyde in THF at $-78°$ in the presence of sodium bis(trimethylsilyl)amide (NaHMDSA) as base. This reaction led exclusively to the formation of (1*E*,3*E*)-

Scheme 5



Scheme 6



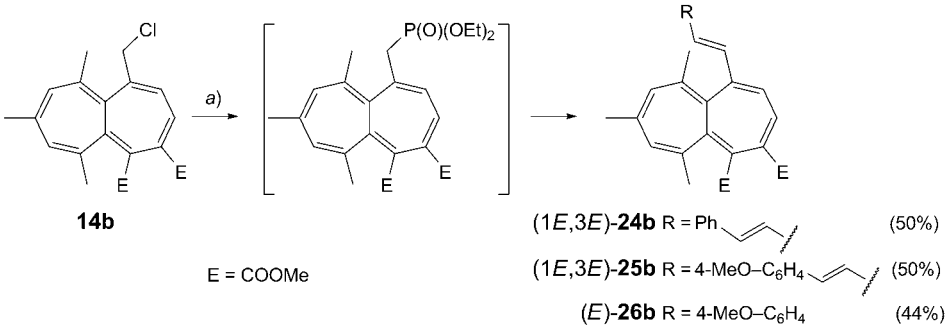
a) NaI, PPh_3, acetone, 25°; 88%. *b*) 2N NaOH, CH_2Cl_2, PhCH=CHCHO, 25°; 59%. *c*) NaI, acetone, 25°; 76%. *d*) 1. $P(OEt)_3$, 100°; 2. 2M NaHMDSA, THF, aldehyde, −78°.

16b in an overall yield of 51%. In the same manner, we synthesized 1-[4-(4-nitrophenyl)buta-1,3-dien-1-yl]-, 1-[4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-, 1-[2-(4-nitrophenyl)ethenyl]-, 1-[2-(4-methoxyphenyl)ethenyl]-, and 1-{2-[4-(dimethylamino)-phenyl]ethenyl}heptalenes (1*E*,3*E*)-**19b**, (1*E*,3*E*)-**20b**, (*E*)-**21b**, (*E*)-**22b**, and (*E*)-**23b**, respectively, in good to moderate yields (*Scheme 6*).

In comparison with **13b**, the reluctant S_N2 reactivity of 1-(chloromethyl)heptalene **14b** required harsher reaction conditions for the formation of the corresponding diethyl phosphonate (*Scheme 7*). Nevertheless, treatment of **14b** with $P(OEt)_3$ in the presence of NaI at 130° led to the phosphonate, which was not isolated but just treated with the aromatic aldehyde and sodium bis(trimethylsilyl)amide as base in THF. By this procedure, we synthesized the configurationally uniform 1-(4-phenylbuta-1,3-dien-1-yl)-, 1-[4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-, and 1-[2-(4-methoxyphenyl)ethenyl]-heptalenes (1*E*,3*E*)-**24b**, (1*E*,3*E*)-**25b**, and (*E*)-**26b**, respectively, in acceptable overall yields (*Scheme 7*).

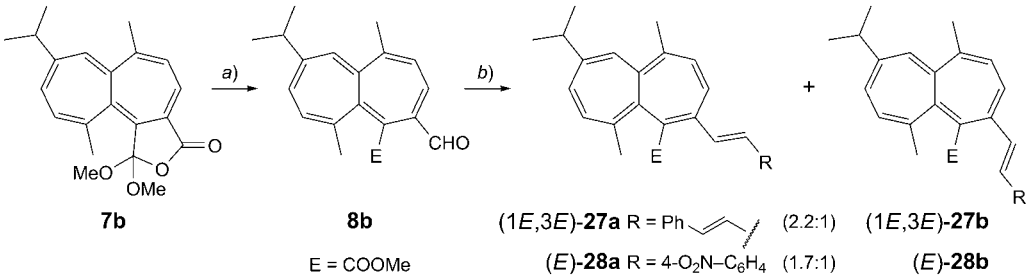
Introduction of the π(2) Substituents. The key step was here the successful reduction of the heptalene pseudoester **7b** [11] with diisobutylaluminium hydride (DIBAH) in

Scheme 7



a) 1. NaI, $P(OEt)_3$, 130°, 3 h; 2. 2M NaHMDSA, THF, aldehyde, r.t.

Scheme 8



a) 1M DIBAH, toluene, −78°; 78%. *b*) 2N NaOH, CH_2Cl_2, $(RPPh_3)Br$, r.t.; 31%/16%.

toluene to the corresponding 4-formylheptalene-5-carboxylate **8b** (*Scheme 8*). However, *Wittig* reactions of this aldehyde with resonance-stabilized (triphenylphosphonio)methanides in the described two-phase system were not very encouraging, especially, when electron-acceptor-substituted phosphoniomethanides were used. The formed π(2)-substituted heptalenes **27** and **28** were obtained as thermodynamically controlled mixtures of their two DBS isomers. On the other hand, following a procedure of *Corey* and *Fuchs* [12], the formyl group of **8b** could be transformed *via* **29** into an ethynyl (→ **30**) substituent, which could then be coupled in good yield to (*E*)-**31** in a *Heck* reaction with (*E*)-2-iodostyrene (*Scheme 9*) (*cf.* [13] and lit. cit. therein). The coupling product (*E*)-**31** was again obtained as a mixture of its two DBS isomers.

Treatment of **8b** with *Tebbe*'s reagent [14] in THF at −78 to 0° gave the corresponding ethenylheptalenecarboxylate **32** as a mixture of its two DBS forms, but unfortunately only in a yield of 19% (*Scheme 10*)[6]) [15]. Nevertheless, the *Heck* reaction of this mixture with (*E*)-2-iodostyrene proceeded smoothly and furnished

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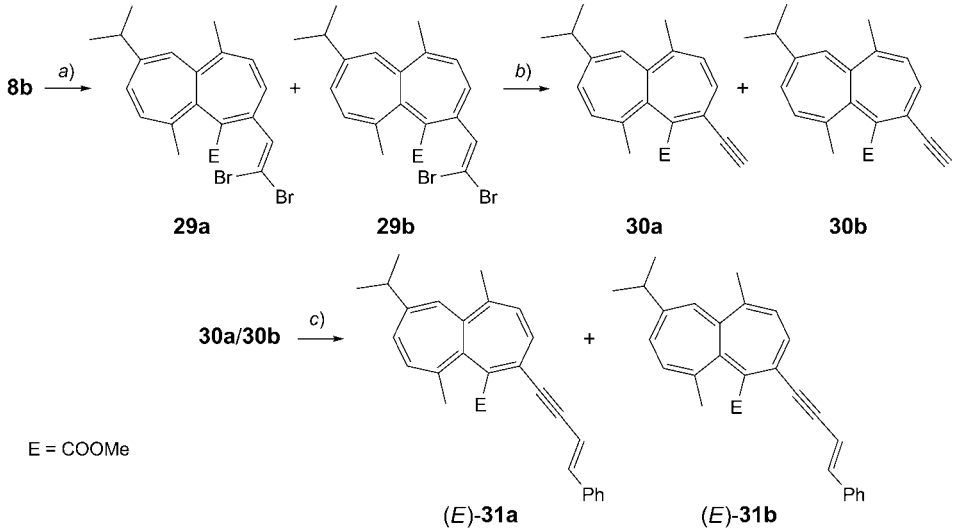
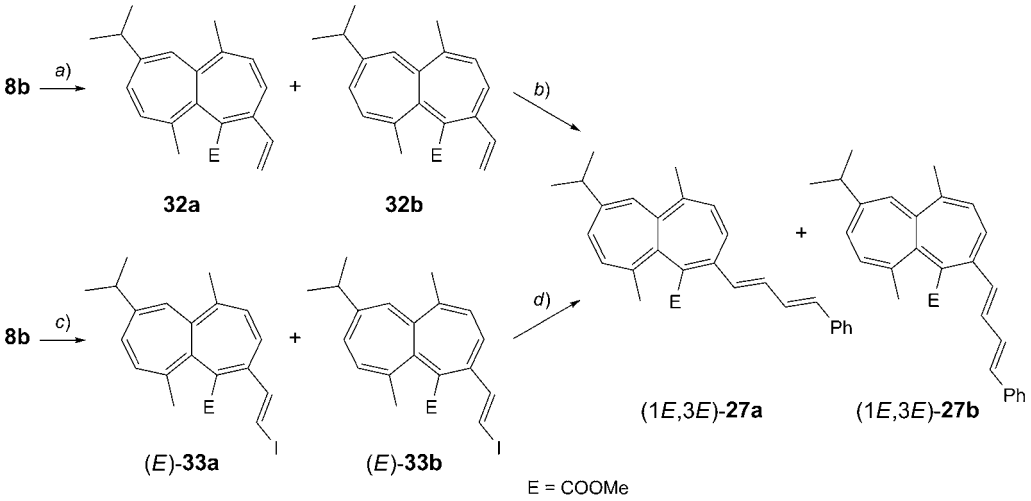
[6]) The reaction of heptalene-4,5-dicarboxylates of type **C**(1) with *Tebbe*'s or *Takai*'s reagent leads selectively, after hydrolysis, in yields >70% to the corresponding 4-acetylheptalene-5-carboxylates, which can easily and in high yields be transformed into 4-ethynylheptalene-5-carboxylates *via* their enol phosphates [15].

Scheme 9



a) CBr_4, Ph_3P, CH_2Cl_2, 1 h, 0°; 60%. *b*) BuLi, THF, −78°, 10 min; 48%. *c*) CuI, cat. $[Pd(Ph_3P)_4]$, $^{i}BuNH_2$, PhCH=CHI, DMF, r.t., 20 h; 76%.

Scheme 10



a) 1M *Tebbe*'s reagent in toluene, THF, −78° to 0°; 19%. *b*) PhCH=CHI, Ag_2CO_3, cat. $[Pd(OAc)_2]$, DMF, r.t., 12 h; 71%. *c*) $CrCl_2$, CHI_3, THF, 30 min, r.t.; 60%. *d*) Styrene, Ag_2CO_3, cat. $[Pd(OAc)_2]$, DMF, r.t., 12 h; 54%.

(1*E*,3*E*)-**27a** and -**27b** in good yield. Finally, the reversion of the two coupling steps turned out to be the procedure of choice for the transformation of the formyl group at C(4) into a 4-phenylbuta-1,3-dien-1-yl substituent. Following a procedure of *Takai* and co-workers [16], **8b** was treated with CHI_3 in the presence of $CrCl_2$ in THF to transform

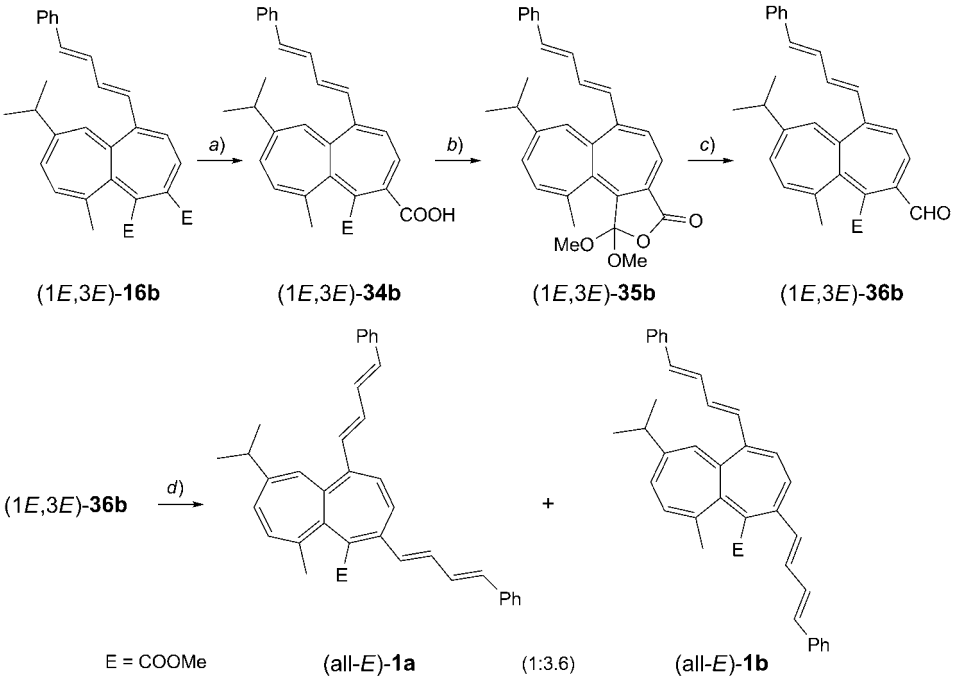
the formyl group into an (*E*)-2-iodoethenyl substituent. The thus formed mixture (*E*)-**33a**/(*E*)-**33b** was then subjected to the *Heck* reaction with styrene to deliver (1*E*,3*E*)-**27a**/(1*E*,3*E*)-**27b** in an overall yield of 32.4% with respect to **8b** as starting material.

Combined Introduction of the π(1) and π(2) Substituents. The reactivity of Me–C(1) of the heptalene-4,5-dicarboxylates **5b** and **6b** under basic conditions determined the sequence of the introduction of the π(1) and π(2) substituents (*cf. Scheme 3*). After formation of the π(1)-substituted heptalene-4,5-dicarboxylates of type **C**(1), MeOOC–C(4) has to be reduced to a formyl group *via* formation of the corresponding pseudoesters of type **D**(1). The formyl group can then be modified to an (*E*)-2-iodoethenyl substituent as a reactive residue for the final *Heck* coupling step, by which the π(2) substituents in the preferred (*E*)-configuration are generated.

We realized in our former experiments [11] the selective saponification of MeOOC–C(4) of heptalene-4,5-dicarboxylates of type **C**(1) with KOH in EtOH/H_2O. However, this procedure led in the case of the π(1)-substituted heptalenedicarboxylates to an appreciable extent of decomposition. We finally succeeded in selective saponification without decomposition by using LiOH instead of KOH and exchanging EtOH by MeOH. The sequence of transformations for the heptalene-4,5-dicarboxylate (1*E*,3*E*)-**16b** is displayed in *Scheme 11*.

The selective saponification gave the acid (1*E*,3*E*)-**34b** in 88% yield. The following formation of the pseudoester (1*E*,3*E*)-**35b** could be realized under standard conditions

Scheme 11



a) LiOH, MeOH/H_2O, 70°; 88%. *b*) 1. $(COCl)_2$, DMF, MeCN, 0°; 2. MeOH, r.t.; 81%. *c*) 1M DIBAH, toluene, −78°; 72%. *d*) 1. $CrCl_2$, CHI_3, THF; 2. styrene, cat. $[Pd(OAc)_2]$, Ag_2CO_3, DMF, r.t.; 43%.

in 81% yield. Reduction of the latter compound with DIBAH in toluene led to the 4-formylheptalene-5-carboxylate (1*E*,3*E*)-**36b** in 72% yield. The iodoethenylation and *Heck* coupling with styrene was performed as a 'one-pot' reaction without isolation and characterization of the intermediate 4-[(*E*)-2-iodoethenyl]heptalene-5-carboxylate. The bis[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]-substituted heptalene-5-carboxylate (all-*E*)-**1** was thus obtained in 43% yield with respect to the combined last two steps or in a 22% overall yield with respect to heptalene-4,5-dicarboxylate (1*E*,3*E*)-**16b**. Heptalene (all-*E*)-**1** represented a thermodynamically controlled 1:3.6 mixture of the two DBS isomers (all-*E*)-**1a** and -**1b**, respectively.

We synthesized in the same manner a number of further $\pi(1),\pi(2)$-substituted heptalene-5- or -1-carboxylates. All data of their synthesis are collected in *Table 1*. The heptalenecarboxylates **40**, **68**, **44**, **48**, and **52** derived from the heptalene-4,5-dicarboxylate **5b** (isopropyl series; see **19b** → **37b** → **38b** → **39b** → **40**; **20b** → **65b** → **66b** → **67b** → **68**; **25b** → **41b** → **42b** → **43b** → **44**; **22b** → **45b** → **46b** → **47b** → **48**; **21b** → **49b** → **50b** → **51b** → **52**) were isolated, as we expected, as thermodynamically controlled mixtures of their two DBS isomers **A** and **B** (or **a** and **b**), since thermal equilibration of the individual forms took place already at room temperature, and it was rapid at 40° (*cf.* [1]). Both isomers were characterized by their UV/VIS spectra, recorded in the course of their anal. HPLC separations at room temperature, and by the ^{1}H-NMR spectra of their mixtures, which allowed a full analysis only of the spectra of the major **A** forms (see also later). The heptalenecarboxylates **56**, **60**, and **64** derived form the heptalene-4,5-dicarboxylate **6b** (methyl series) were also obtained as mixtures of their DBS isomers **A** and **B** (or **a** and **b**) (see *Table 1*; **26b** → **53b** → **54b** → **55b** → **56**; **23b** → **57b** → **58b** → **59b** → **60**; **24b** → **61b** → **63b** → **64**). However, the DBS process started here slowly at temperatures $> 60°$, and it became rapid only at temperatures $> 80°$. Therefore, we were able to isolate the major **B** forms after chromatography (silica gel) in pure crystalline state, whereas the minor **A** forms were obtained as oils. For our model compounds of this series, *i.e.*, (all-*E*)-**60a** and (all-*E*)-**60b**, ($\pi(1) = \pi(2) =$ (1*E*,3*E*)-PhCH=CH–CH=CH) we demonstrated that (all-*E*)-**60a** is also a crystalline compound in the pure state, since irradiation of (all-*E*)-**60b** in 5% CH_2Cl_2/hexane at room temperature with a high-pressure Hg lamp through a *Pyrex* filter and 2N aqueous $[Cu(NH_3)_4]SO_4$ solution with a transparency window between 350 and 600 nm led to a mixture of (all-*E*)-**60a** and (all-*E*)-**60b**, which contained $> 60\%$ of (all-*E*)-**60a**. Chromatography (silica gel) gave then pure crystalline (all-*E*)-**60a**. No (*E*)/(*Z*)-isomerizations in the (1*E*,3*E*)-configured 4-phenylbuta-1,3-dien-1-yl side chains were observed in the course of the photochemically induced DBS process. Pictures of the crystal powder of (all-*E*)-**60a** and (all-*E*)-**60b** are reproduced in *Fig. 3*. The interruption of the conjugative interaction between the two π-substituents in (all-*E*)-**60a** is nicely demonstrated by the yellow color of its crystals, in contrast to the deep red color of the crystals of (all-*E*)-**60b**, where the two π-substituents, possessing an optimal planar s-*trans* arrangement with respect to C(1)=C(2) and C(3)=C(4) of the heptalene skeleton, interact conjugatively (see later).

Structural Assignment. – *X-Ray Crystal-Structure Analyses.* To get more insight into the spatial arrangements of the substituents at the twisted heptalene core, a number of analyses were performed under standard quality conditions (see *Exper. Part*,

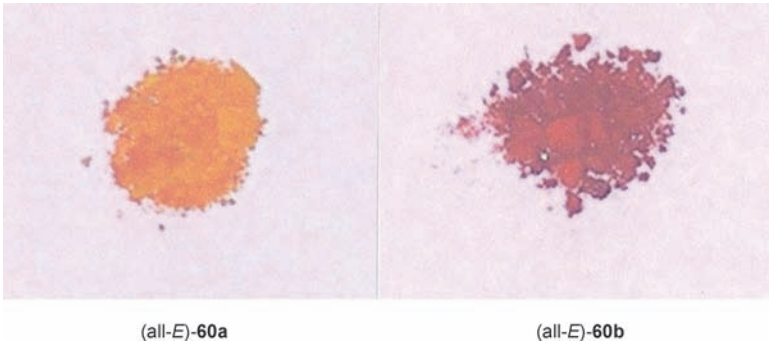


Fig. 3. *Picture of microcrystalline powder of (all-*E*)-***60a*** and (all-*E*)-***60b***

Table 7). Characteristic geometric parameters of the X-ray structures are listed in *Table 2*.

We mentioned already the remarkable different behavior of the two 1-(chloromethyl)heptalene-4,5-dicarbarboxylates **13b** and **14b** in nucleophilic substitution reactions (*Schemes 6* and *7*). For a better understanding of the marked reluctance of **14b** to undergo S_N2 reactions at the $ClCH_2$ group, we performed an X-ray crystal-structure analysis of a proper crystal of **14b** (*Fig. 4*,*a*). The structure reveals an interesting detail in that the chloromethyl substituent is turned inward with respect to the heptalene core. The torsion angle Θ of the Cl–CH_2–C(1)=C(2) part amounts to $-104°$. This conformation is stabilized by a weak intramolecular H-bond between the Cl-atom and one of the H-atoms of Me–C(6) ($d = 297$ pm). A second H-atom of Me–C(6) is involved in through-space bonding with the ether O-atom of MeOOC–C(5) ($d = 237$ pm). AM1 Calculations reflect the crystal structure of **14b** quite well, specifically with respect to the orientation of $ClCH_2$–C(1) (Θ(Cl–CH_2–C(1)=C(2)) $= -85°$) and the above mentioned H-bonding (d(Cl$\cdots$H–CH_2C(6)) $= 311$ pm). The calculations also demonstrated that the $ClCH_2$ substituent at C(1) may occupy another conformation of $\Theta = 47°$ with respect to C(1)=C(2) and with an almost equal ΔH_f^0 value[7]). Nevertheless, a linear nucleophilic attack at the C-atom of the CH_2Cl group is strongly hindered in both conformations. It is Me–C(10) of the actual structure and Me–C(6) of the second calculated structure of **14b**, which are expected to exert strong sterical hindrance on the nucleophilic substitution. Since it needed a temperature of 130° to realize the nucleophilic exchange, it seems that the temperature is needed to keep the thermal DBS equilibrium **14b** $\rightleftarrows$ **14a** alive[8]) [17], and it is indeed **14a**, which undergoes the nucleophilic exchange reaction. The AM1 calculated structure of **14a** (*Fig. 4*,*b*) shows $ClCH_2$–C(5) in an orientation almost parallel to Me–C(6) and with a torsion angle of $-110°$ for Θ(Cl–CH_2–C(5)=C(5a)). Moreover, one of the H-atoms of Me–C(6) is engaged in a H-bridge ($d = 280$ pm) with the neighboring Cl-atom, and Me–C(8) is too distant to block sterically effectively the nucleophilic exchange at $ClCH_2$–C(5). Therefore, it is reasonable assuming that **14a** is the actual reactant in the

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[7]) AM1: $\Delta H_f^0 = 99.21$ kcal·mol^{-1} for $\Theta = -85°$ and 99.18 kcal·mol^{-1} for $\Theta = 47°$ of **14b**. The sign of all discussed Θ values refer to the (*M*)-configuration of the heptalene core (*cf. Table 2*).

[8]) The equilibrium ratio of the comparable **6b**/**6a** amounts to 7.8:1 (100°, tetralin) [17].

Table 1. *Syntheses of π(1),π(2)-Substituted Methyl 6-Methylheptalene-5-carboxylates* (isomers **b** or **B**) *and Methyl 10-Methylheptalene-1-carboxylates* (isomers **a** and **A**)[a])

Substituents	π(1),π(2)-Heptalene precursors						π(1),π(2)-Heptalenes		
	C(1)	Acid		**D**(1)	**E**(1)		No. [%][b])		**a**/**b**[b])
	No.	No. [%]		No. [%]	No. [%]				
R^1 = H, R^2 = ^{i}Pr π(1) = PhCH=CH–CH=CH π(2) = PhCH=CH–CH=CH	**16b**	**34b**	88	**35b** 81	**36b**	72	**1**	43	1 : 3.5 (r.t.)
R^1 = H, R^2 = ^{i}Pr π(1) = 4-O_2N–C_6H_4CH=CH–CH=CH π(2) = 4-MeO–C_6H_4CH=CH–CH=CH	**19b**	**37b**	62	**38b** > 70	**39b**	47[c])	**40**	16	n.d.
R^1 = H, R^2 = ^{i}Pr π(1) = 4-MeO–C_6H_4CH=CH–CH=CH π(2) = 4-O_2N–C_6H_4CH=CH–CH=CH	**20b**	**65b**	83	**66b** 64	**67b**	85	**68**	25	1 : 5.7 (r.t.)
R^1 = H, R^2 = ^{i}Pr π(1) = 4-Me_2N–C_6H_4CH=CH π(2) = 4-O_2N–C_6H_4CH=CH–CH=CH	**23b**	**41b**	52	**42b** 90	**43b**	75	**44**	32	1 : 5.7 (r.t.)
R^1 = H, R^2 = ^{i}Pr π(1) = 4-MeO–C_6H_4CH=CH π(2) = 4-O_2N–C_6H_4CH=CH–CH=CH	**22b**	**45b**	72	**46b** 86	**47b**	79	**48**	≈3 (54)[d])	1 : 4.6 (55°)
R^1 = H, R^2 = ^{i}Pr π(1) = 4-O_2N–C_6H_4CH=CH π(2) = 4-MeO–C_6H_4CH=CH	**21b**	**49b**	71	**50b** 80	**51b**	77	**52**	74	1 : 2.6 (r.t.)
R^1 = Me, R^2 = H π(1) = 4-MeO–C_6H_4CH=CH π(2) = 4-O_2N–C_6H_4CH=CH–CH=CH	**26b**	**53b**	92	**54b** 77	**55b**	86	**56**	28	1 : 4.5 (r.t.)
R^1 = Me, R^2 = H π(1) = PhCH=CH–CH=CH π(2) = PhCH=CH–CH=CH	**24b**	**57b**	82	**58b** 77	**59b**	72	**60**	30	1 : 3.5 (80°)
R^1 = Me, R^2 = H π(1) = 4-MeO–C_6H_4CH=CH–CH=CH π(2) = 4-O_2N–C_6H_4CH=CH–CH=CH	**25b**	**61b**	< 85[e])	**62b** 55	**63b**	49	**64**	60	n.d.

[a]) See *Schemes 3*, *5*, *6*, and *11*; all compounds with (1*E*,3*E*)- and (all-*E*)-configuration, respectively. [b]) *Isopropyl series* (R^1 = H, R^2 = ^{i}Pr): yields are given for the DBS mixtures **a**/**b**. *Methyl series* (R^1 = Me, R^2 = H): yields are given for the easily crystallizing **b** forms. In parentheses, temperature of DBS equilibration (n.d. = not determined). [c]) (1*E*,3*E*)-**39b** was obtained as a 2 : 1 mixture with the corresponding lactone (yield 25%; *cf.* [1]). [d]) The yield in parentheses resulted from the *Tebbe* reaction of (*E*)-**47b** (≈ 40%), followed by Pd^{II} catalyzed *Heck* coupling with 1-iodo-4-nitrobenzene (*cf. Path b* in *Scheme 10*). [e]) (1*E*,3*E*)-**61b** contained still some nonreacted diester (1*E*,3*E*)-**24b**.

discussed substitution reaction, in contrast to **13b**, which reacts smoothly with NaI in acetone at room temperature (*Scheme 6*) due to the unoccupied C(10) position[9]) [8].

It was of interest for us to compare the X-ray crystal structures of (1*E*,3*E*)-**16b**, derived from **13b**, and of (1*E*,3*E*)-**24b**, derived from **14b**, both with a 4-phenylbuta-1,3-dien-1-yl group at C(1). A stereoscopic view of the (*M*)-configured structures is

[9]) The thermal equilibrium **13b** ⇌ **13a** takes place already at room temperature with *ca.* 0.5% of **13a** in equilibrium [8].

Table 2. *Characteristic Parameters of the Crystal Structures of* **14b**, *(1*E,*3*E*)-***16b***, *(1*E,*3*E*)-***24b***, *(1*E,*3*E*)-***25b***, (*all*-E)-***52b***, and (all*-E*)-***64b***[a])*

	14b	(1*E*,3*E*)-**16b**	(1*E*,3*E*)-**24b**	(1*E*,3*E*)-**25b**	(all-*E*)-**52b**	(all-*E*)-**64b**	
						A form	*B* form
Torsion angles Θ [°]:							
C(2)–C(1)–C(1′)–C(2′)	–	− 169.2(3)	− 179.9(2)	− 173.7(2)	− 178.6(1)	− 172.5(2)	− 178.9(2)
C(3)–C(4)–C(1″)–C(2″)	–	–	–	–	− 159.2(2)	− 161.8(2)	− 161.3(2)
C(1′)–C(2′)–C(3′)–C(4′)	–	− 173.4(3)	164.2(2)	177.2(3)	–	175.1(2)	175.6(2)
C(1″)–C(2″)–C(3″)–C(4″)	–	–	–	–	–	172.1(2)	177.7(2)
C(3′)–C(4′)–C_{ip}–C_o (s-*trans*)	–	171.6(3)	− 174.5(2)	− 174.4(3)	− 167.7(2)[b])	− 176.3(2)	− 3.9(4)
C(3″)–C(4″)–C_{ip}–C_o (s-*trans*)	–	–	–	–	− 158.8(2)[b])	− 170.6(3)	− 178.1(3)
C(1)–C(2)–C(3)–C(4)	− 29.7(5)	− 27.3(5)	− 30.7(4)	− 31.3(4)	− 30.2(3)	− 33.2(3)	− 31.2(4)
C(2)–C(3)–C(4)–C(5)	− 0.1(5)	− 2.6(5)	− 3.0(4)	3.0(4)	− 6.4(2)	− 6.5(3)	− 8.1(4)
C(3)–C(4)–C(5)–C(5a)	30.6(4)	30.4(5)	33.8(3)	35.6(3)	37.1(2)	42.6(3)	42.4(3)
C(3)–C(4)–C=O	− 153.2(3)	30.1(5)	− 167.5(2)[c])	− 164.6(2)	58.7(2)[d])	− 134.0(2)[d])	42.2(4)[d])
C(1)–C(10a)–C(5a)–C(5)	− 61.3(3)	− 63.9(4)	− 65.1(2)	− 64.4(3)	− 64.5(2)	− 67.4(2)	− 65.0(3)
C(1)–C(10a)–C(5a)–C(6)	114.2(3)	112.5(3)	112.2(2)	113.5(2)	113.3(2)	106.7(2)	111.9(2)
C(6)–C(5a)–C(10a)–C(10)	− 64.8(3)	− 63.8(4)	− 66.5(2)	− 68.1(3)	− 65.9(2)	− 69.8(2)	− 66.6(3)
C(1′)–C(1)–C(10a)–C(10)	64.0(4)	59.5(4)	61.9(3)	65.3(3)	58.6(2)	68.4(3)	62.9(3)
Interatomic distances *d* [pm]:							
C(1)–C(1′)	150.0(4)	146.2(4)	145.7(3)	135.2(3)	145.4(2)	144.9(3)	145.6(4)
C(1)–C(2)	134.7(4)	135.9(4)	136.2(3)	135.2(3)	135.9(2)	136.0(3)	136.1(4)
C(1)–C(10a)	149.1(4)	149.4(4)	148.9(3)	149.1(3)	149.3(2)	149.7(3)	149.1(3)
C(2)–C(3)	143.9(4)	143.8(4)	143.4(3)	144.2(3)	143.8(2)	143.0(3)	143.3(4)
C(10)–C(10a)	134.5(4)	134.6(4)	134.4(3)	135.7(3)	133.9(2)	134.5(3)	135.0(3)
C(10)–R ··· C(2′)[e])	–	314(3)	328.3(4)	349.0(4)	306	353.6(3)	332.1(4)
C(2′)–H ··· C(10)	–	274(3)	267.8(16)	294(2)	270	272	261
C(2′)–H ··· R–C(10)[e])	–	282(4)	289.8(18)	330(2)	265	312	287

[a]) In parentheses, e.s.d. values. The signs of Θ refer to the (*M*)-configuration of the heptalene core. C-atoms of the $\pi(1)$ chains are primed, those of the $\pi(2)$ chains are doubly primed. [b]) C(1′)–C(2′)–C_{ip}–C_o (s-*trans*) and C(1″)–C(2″)–C_{ip}–C_o (s-*trans*), respectively. [c]) MeOOC–C(4) occupies a second equal position with Θ(C(3)=C(4)–C=O) = − 9.5(3)°. [d]) C(5a)–C(5)–C=O. [e]) R = H and CH_3, respectively.

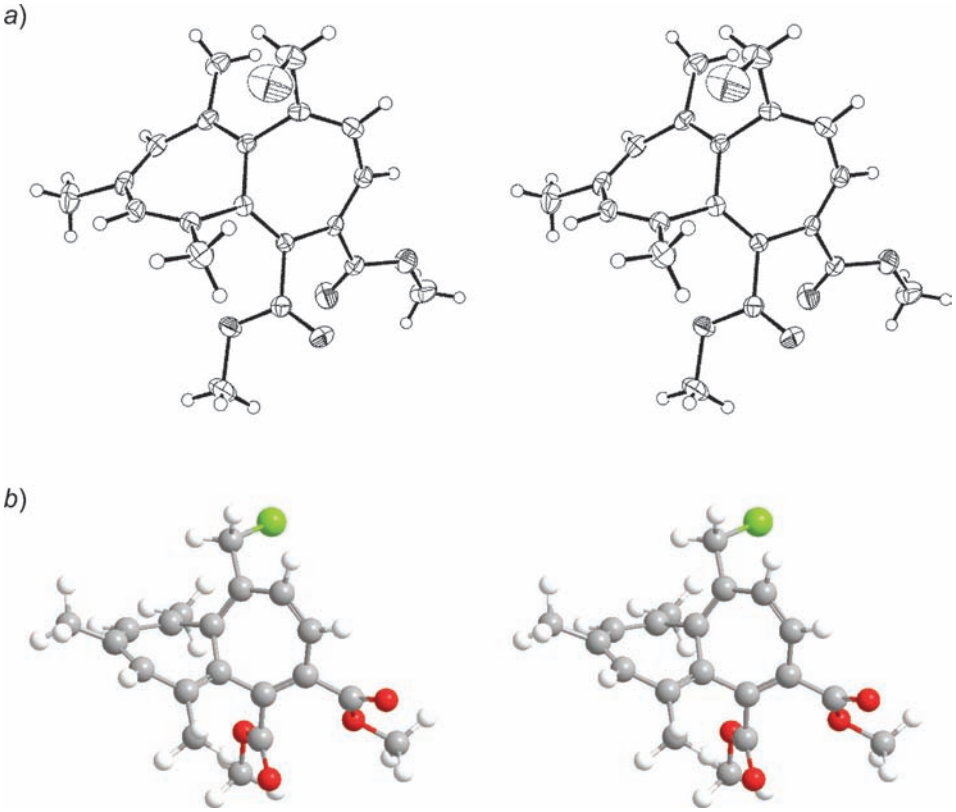


Fig. 4. a) *Stereoscopic view of the X-ray crystal structure of dimethyl 1-(chloromethyl)-6,8,10-trimethylheptalene-4,5-dicarboxylate* (**14b**) (atoms with 50% probability ellipsoids). b) *Stereoscopic view of the AM1 calculated structure of dimethyl 5-(chloromethyl)-6,8,10-trimethylheptalene-1,2-dicarboxylate* (**14a**)

displayed in *Figs. 5* and *6*. The buta-1,3-dien-1-yl chain adopts in both cases an almost perfect s-*trans*-conformation at their formal σ-bonds (*cf. Table 2*). As expected from our former investigations, the average value of the two torsion angles at the central σ-bond (C(5a)–C(10a)) of (1*E*,3*E*)-**16b** with three *peri*-substituents is slightly smaller than that of (1*E*,3*E*)-**24b** with four *peri*-substituents. This leads to quite similar interatomic distances between C(10)–*H* and C(2′) of (1*E*,3*E*)-**16b** and C(10)–*C*H_3 and C(2′) of (1*E*,3*E*)-**24b**, respectively (*cf.* last three lines of *Table 2*). This fact means that, in both cases, the 4-phenylbuta-1,3-dien-1-yl chain at C(1) can adopt a sterically undisturbed s-*trans* orientation with respect to C(1)=C(2) of the heptalene core providing thus optimal conjugation, which is further transmitted *via* C(1)=C(2)–C(3)=C(4) to the ester C=O group at C(4). This effect of conjugation is documented by Θ(C(3)=C(4)–C=O) of 30° for the (*M*)-configured (1*E*,3*E*)-**16b** and −168° for the (*M*)-configured (1*E*,3*E*)-**24b** (see *Footnote c* of *Table 2*).

The X-ray structures of the π(1),π(2)-substituted heptalene-5-carboxylates (all-*E*)-**52b** and (all-*E*)-**64b** demonstrate that there is also enough free space around C(4) for

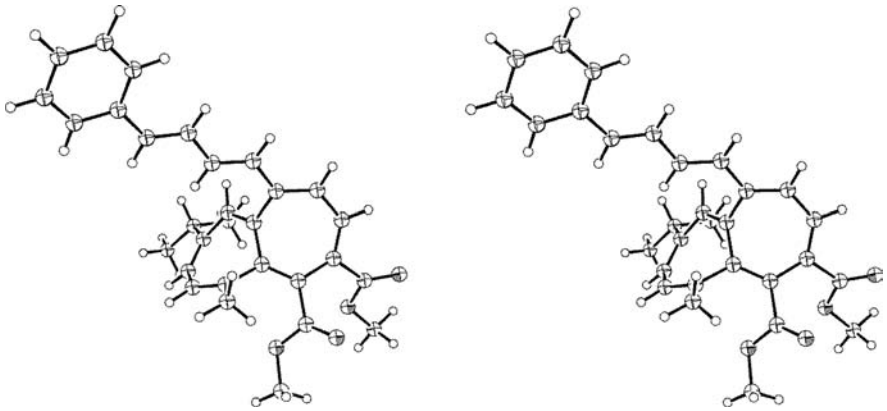


Fig. 5. *Stereoscopic view of the X-ray crystal structure of dimethyl 9-isopropyl-6-methyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**16b**) (atoms with 50% probability ellipsoids)

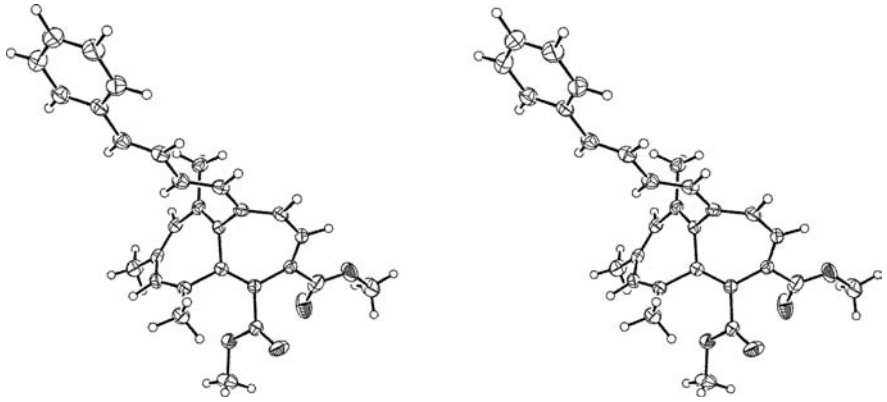


Fig. 6. *Stereoscopic view of the X-ray crystal structure of dimethyl 6,8,10-trimethyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**24b**) (atoms with 50% probability ellipsoids)

an extended $\pi(2)$ substituent, so that an (*E*)-configured 2-phenylethenyl as well as an (1*E*,3*E*)-configured 4-phenylbuta-1,3-dien-1-yl group can take the s-*trans*-conformation with respect to the C(3)=C(4) bond of the heptalene core – optimal for an effective conjugation between the two π-systems (*Figs. 7* and *8*, and *Table 2*). Moreover, as expected (*cf. Figs. 5* and *6*), the s-*trans*-conformation is also maintained between $\pi(1)$ and C(1)=C(2), in a way that $\pi(1)$–C(1)=C(2) and $\pi(2)$–C(4)=C(3) form an almost perfect (all-s-*trans*)-conformation in the crystals, which is only interrupted by the given s-*cis*-arrangement of C(1)=C(2)–C(3)=C(4) with Θ $-30°$ to $-33°$, *i.e.*, in a range where almost full through-conjugation is still possible. Heptalene (all-*E*)-**64b** is found in the crystals in two conformations *A* and *B* (*Fig. 8*, *a* and *b*), which differ only in their relative position of MeOOC–C(5) and of 4-MeO of $\pi(1)$. The conformation at

σ(C(5)–C(=O)) of (all-*E*)-**52b** and the form *B* of (all-*E*)-**64b** are similar with Θ(C(5a)=C(5)–C=O) = 59° and 42°, respectively (*cf. Table 2*). The position of the C=O group seems to be stabilized by weak H-bonding with one of the H-atoms of Me–C(6) (d = 273 pm for (all-*E*)-**52b** and 253 pm for (all-*E*)-**64b**) as well as with H–C(2″) of π(2) (d = 267 pm for (all-*E*)-**52b** and 281 pm for (all-*E*)-**64b**). In form *A*, MeOOC–C(5) is turned at σ(C(5)–C(=O) by *ca.* 180° (Θ(C(5a)=C(5)–C=O) = −134°) as compared with form *B*. Weak H-bonding of the MeO O-atom with one H-atom of Me–C(6) (d = 259 pm) and with H–C(2″) (d = 305 pm) seem to stabilize this conformation. It is also of interest to note that the remote 4-MeO group of π(1) at C(1) occupies opposite positions in forms *A* and *B* of (all-*E*)-**64b**. The torsion angles Θ of Me–O–C_{ip}–C_o amount (by clockwise counting of the fragment O–C_{ip}–C_o) to −1° (*A*) and −166° (*B*), respectively.

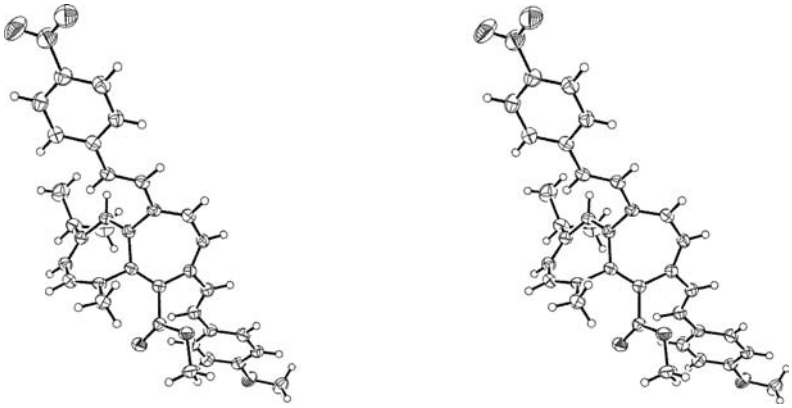


Fig. 7. *Stereoscopic view of the X-ray crystal structure of methyl 9-isopropyl-4-[(*E*)-2-(4-methoxyphenyl)ethenyl]-6-methyl-1-[(*E*)-2-(4-nitrophenyl)ethenyl]heptalene-5-carboxylate* ((all-*E*)-**52b**) (atoms with 50% probability ellipsoids)

NMR Analyses. The assignments of almost all H- and C-atoms of the π(1)- and π(2)-substituted heptalene-4,5-dicarboxylates and heptalene-5-carboxylates were realized with the usual NMR techniques. The corresponding DBS forms (*i.e.*, **a**) of the mentioned heptalenes were mostly characterized only in the thermodynamically controlled mixtures of the **a** and **b** forms (*cf. Table 1*). Of special interest for us, however, was the question of how the π-substituents, which in the crystals occupied always the s-*trans*-conformation, would behave in solution, especially after the DBS process of the heptalene core. For answering these questions, we performed ^{1}H-NOE measurements on heptalenes (1*E*,3*E*)-**16b**, (1*E*,3*E*)-**19b**, (all-*E*)-**60b**, and (all-*E*)-**60a** in $CDCl_3$ and for the DBS isomers of (all-*E*)-**60** also in C_6D_6[10]. The results of the measurements are visualized in *Figs. 9–12*. As expected, strong (*s*) to medium (*m*) ^{1}H-

[10] (all-*E*)-**60a** was obtained on irradiation of pure (all-*E*)-**60b** with filtered light of 400–500 nm in 60% yield. It was freed from residual (all-*E*)-**60b** by column chromatography (for details, see *Exper. Part*).

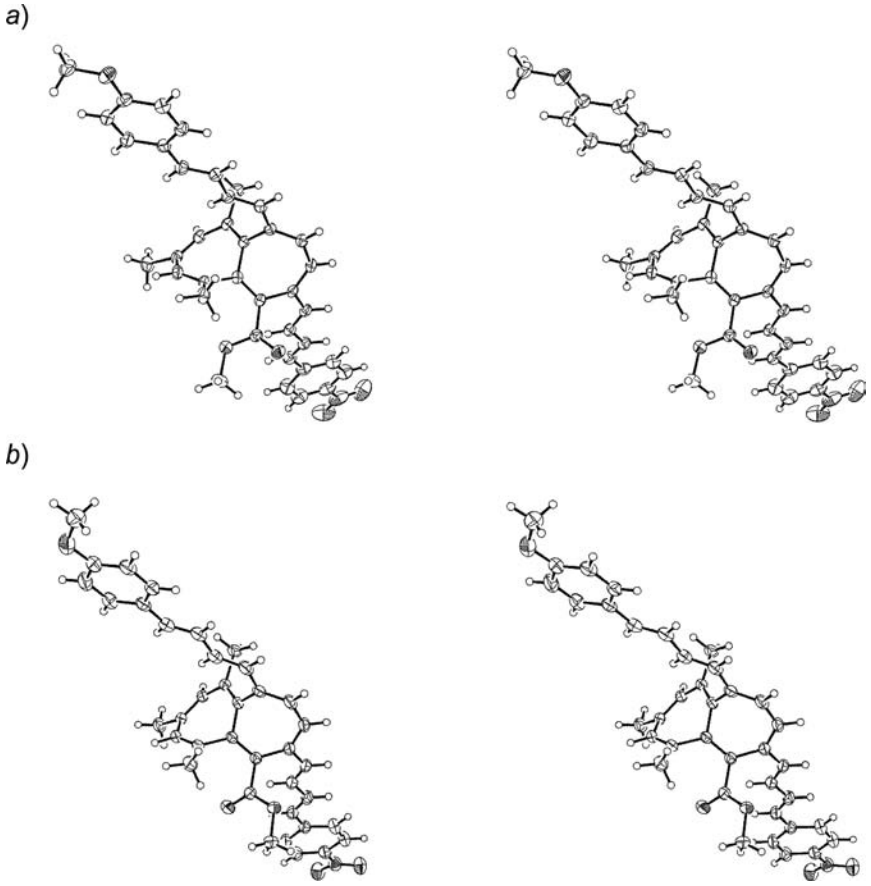


Fig. 8. *Stereoscopic views of the X-ray crystal structures of methyl 1-[(1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-6,8,10-trimethyl-4-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-5-carboxylate* ((all-*E*)-**64b**): a) *Conformation* A *and* b) *conformation* B (atoms with 50% probability ellipsoids)

NOEs were observed in all cases between the *ortho*-H-atoms of the terminal phenyl groups and H–C(3′) and H–C(4′) as well as H–C(3″) and H–C(4″), respectively. The detection of a strong ^{1}H-NOE between H–C(1′) of the buta-1,3-dien-1-yl chain and H–C(2) of the heptalene core of (1*E*,3*E*)-**16b** (*Fig. 9*) is in perfect agreement with an s-*trans* conformation at C(1)–C(1′) also in solution ($CDCl_3$). This fact is fully supported by the presence of a weak (*w*) ^{1}H-NOE between H–C(2′) and H–C(10) in accordance with the interatomic distance of these two H-atoms in the crystals structure of (1*E*,3*E*)-**16b** (*cf. Fig. 5* and *Table 2*). Similar ^{1}H-NOEs were found for (1*E*,3*E*)-**19b**, the 4-NO_2 analog of (1*E*,3*E*)-**16b** (*Fig. 10*). Despite the fact that the ^{1}H-NOE between H–C(1′) and H–C(2) was not identifiable (*n.i.*) in $CDCl_3$ due to the nearness of the signals of the two H-atoms, the realized strong ^{1}H-NOE of H–C(2′) and H–C(10) indicates the prevailing s-*trans* conformation of the π-substituent and the heptalene core. Nevertheless, the observed weak ^{1}H-NOE of H–C(1′) and H–C(10) speaks for the presence

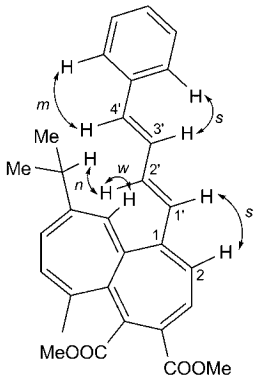


Fig. 9. *^{1}H-NOE Effects* (600 MHz, $CDCl_3$) *of dimethyl 9-isopropyl-6-methyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**16b**). *s* = strong, *m* = medium, *w* = weak, *n* = no effect.

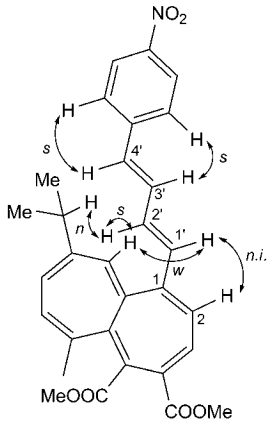


Fig. 10. *^{1}H-NOE Efects* (600 MHz, $CDCl_3$) *of dimethyl 9-isopropyl-6-methyl-1-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**19b**). *n.i.* = not identifiable due to overlapping shifts.

of a minor amount of the s-*cis*-conformer with respect to C(1′)–C(1) in the case of (1*E*,3*E*)-**19b** in $CDCl_3$ solution.

Most interesting were the ^{1}H-NOE investigations of (all-*E*)-**60b** and (all-*E*)-**60a** in $CDCl_3$ as well as in C_6D_6 (*Figs. 11* and *12*), since both DBS isomers were available in pure form as already mentioned. Several enhancement effects were not identifiable in $CDCl_3$ due to the nearness of the ^{1}H-signals. However, the realized weak ^{1}H-NOE between H–C(2′) and Me–C(10) of (all-*E*)-**60b** indicates an s-*trans* arrangement of C(2)=C(1)–C(1′)=C(2′)[11]. The s-*trans*-conformation of the π(2)-substituent with

[11]) For the comparable X-ray structures *A* and *B* of (all-*E*)-**64b**, one finds an average interatomic distance between *H*–C(2′) and the closest *H*–CH_2–C(10) of 290 pm, which is in accordance with the above discussed ^{1}H-NOE.

respect to the heptalene core is secured by a strong ^{1}H-NOE of H–C(3) and H–C(1″) in C_6D_6 as solvent. Support for the s-*trans*-conformation is given by a medium ^{1}H-NOE between H–C(1″) and MeOOC–C(5), an effect, which is not found in $CDCl_3$. It seems that MeOOC–C(5) of (all-*E*)-**60b** can attain different conformations, comparable with those (*A* and *B*) found in the crystal structure of (all-*E*)-**64b**.

The ^{1}H-NOE measurement of (all-*E*)-**60a** in $CDCl_3$ and in C_6D_6 were of particular interest in view of the relaxed conformations of the two 4-phenylbuta-1,3-dien-1-yl substituents with respect to the heptalene core. The observed effects (*Fig. 12*) clearly showed that the DBS process (all-*E*)-**60b** → (all-*E*)-**60a** is followed also by a 180° turn of both 4-phenylbuta-1,3-dien-1-yl substituents, so that the new conformations C(1)=C(2)–C(1″)=C(2″) and C(5a)=C(5)–C(1′)=C(2′) of (all-*E*)-**60a** are s-*trans* configured as it is found also for the other *σ*-bonds of the two unsaturated substituents. In other words, (all-*E*)-**60a** exists in solution mainly in all-s-*trans* conformation. MeOOC–C(1) seems to occupy also in (all-*E*)-**60a** two favored conformations as discussed for (all-*E*)-**60b**.

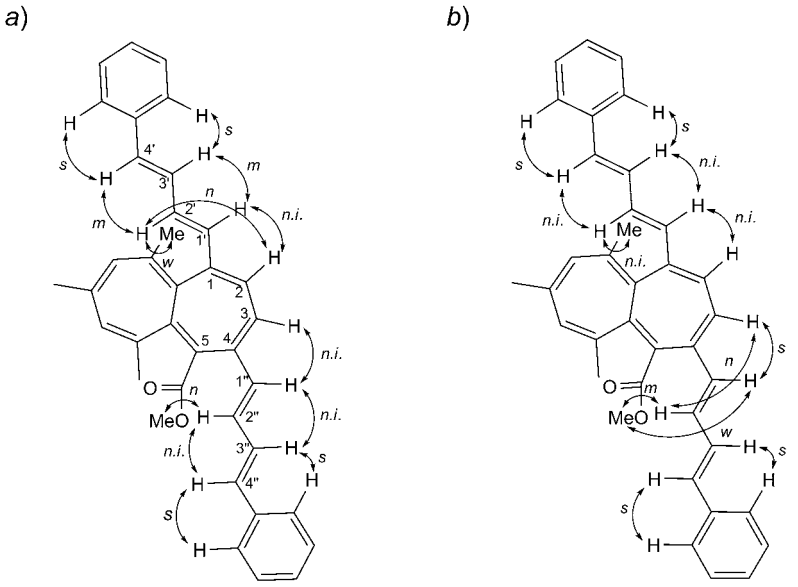


Fig. 11. *^{1}H-NOE Effects* (600 MHz) *of methyl 6,8,10-trimethyl-1,4-bis[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-5-carboxylate* ((all-*E*)-**60b**): a) *in $CDCl_3$ and* b) *in C_6D_6*

Of interest is also to note that the size of ^3J(H–C(2′),H–C(3′)) and of ^3J(H–C(2″),H–C(3″)) of the 4-phenylbuta-1,3-dien-1-yl substituents indicate with 10 – 8 Hz (*cf.* s-*trans*-buta-1,3-diene, $^3J = 10.4$ Hz [18]) also a preferred s-*trans*-conformation at the central *σ*-bond, whereby we mostly found that $^3J\ \pi(1) > {}^3J\ \pi(2)$. This finding would be in agreement with a higher internal s-*trans* mobility of the $\pi(2)$ chains as compared to those of $\pi(1)$. Steric interference with the neighboring MeOOC–C(5) group seems to be responsible for this effect.

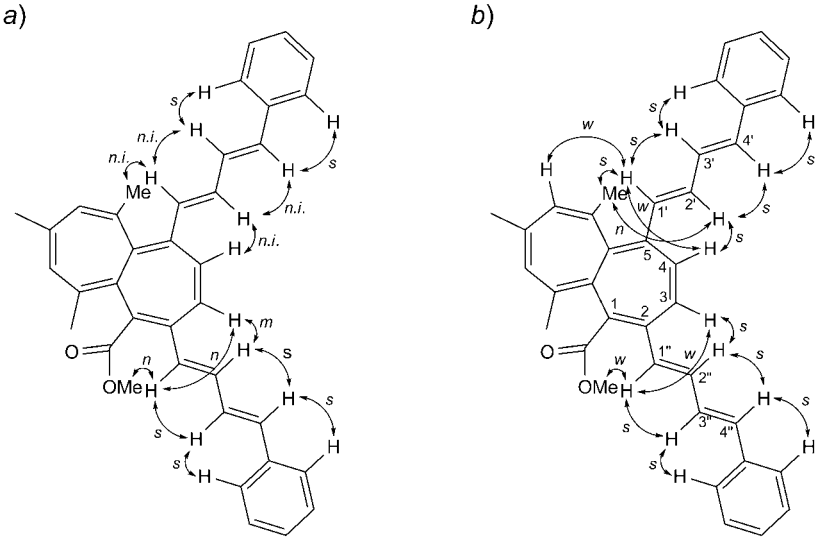


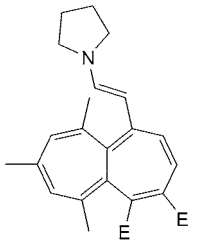
Fig. 12. *^{1}H-NOE Effects* (600 MHz) *of methyl 6,8,10-trimethyl-2,5-bis[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-1-carboxylate* ((all-*E*)-**60a**): a) *in $CDCl_3$ and* b) *in C_6D_6*

UV/VIS Spectra of the DBS Isomers. We measured most of the spectra in the course of anal. HPLC separations with CH_2Cl_2/hexane mixtures as mobile phase (see also [1][2][9])[12]) to avoid thermal DBS isomerizations, especially in the case of the thermally π-mobile heptalenes derived from **5b** (*Scheme 3*). In some cases, we used for optimal HPLC separation of the DBS isomers, 4% ^{i}PrOH/hexane as eluant. For crystalline **B** isomers, configurationally stable at room temperature, at least for the time of measurement, MeCN was used as standard solvent.

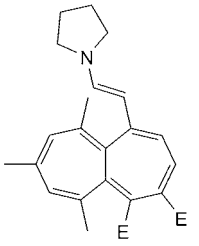
We reported already on the solvatochromism of the much stronger polarized merocyanine system of methyl 1-[(*E*)-2-(dialkylamino)ethenyl]heptalene-5-carboxylates [19]. The solvent dependence of the position of band I and III of dimethyl 6,8,10-trimethyl-1-[(*E*)-2-(pyrrolidin-1-yl)ethenyl]heptalene-4,5-dicarboxylate ((*E*)-**69b**) and its DBS isomer (*E*)-**69a** is listed in *Table 3*. One recognizes that the heptalene band I of the through-conjugated form (*E*)-**69b** exhibits a strong positive solvatochromic effect of +37 nm in going from hexane to MeCN. The effect is much less pronounced for the heptalene band III (+13 nm). Almost the same effects are found for (*E*)-**69a** what demonstrates that the heptalene π-skeleton in total takes part in the charge-transfer (CT) transitions. However, what changes in going by DBS from (*E*)-**69a** to (*E*)-**69b** is a stronger localization of the CT transition in the through-conjugated π-chain of (*E*)-**69b**, determined by length and electronic character of the $\pi(1)$ and $\pi(2)$ substituents at C(1) and C(4), respectively. Band II in π-substituted heptalenes is mostly difficult to determine and at best to make out as a shoulder sitting on the longer-

[12]) The UV/VIS spectra were measured directly with the photodiode-array detector of the HPLC system (see *Exper. Part*). The eluant was in all cases 15–30% CH_2Cl_2/hexane, CH_2Cl_2 containing as additive 0.5% MeOH.

Table 3. *Solvatochromism of Heptalene Band I and III of* **69a** *and* **69b**[a])



(*E*)-**69a**



(*E*)-**69b**

Solvent	(*E*)-**69a** [nm]		(*E*)-**69b** [nm]	
	I	III	I	III
Hexane	427	331	431	330
Hexane/CH_2Cl_2[b])	445	334	451	339
MeCN	465	338	468	343

[a]) For details, see [19]. [b]) Ratio 1.86 : 1 (*v*/*v*).

wavelength flanc of band III in **A-**type heptalenes or it may cause a certain asymmetry of band I at the lower-wavelength side of **B**-type heptalenes. The UV/VIS spectra of (all-*E*)-**1a** and (all-*E*)-**1b** (*Fig. 1*) as well as those of its 6,8,10-trimethyl variant (all-*E*)-**60a** and (all-*E*)-**60b** (*Fig. 13*) illustrate these facts. The introduction of a MeO and a NO_2 group as established electron-donor and electron-acceptor substituents at the 4-position of the phenyl groups at the π-chain termini, to enhance the CT character of the electronic transitions, has a marked influence, in that the position of the heptalene band I is strongly shifted to longer wavelengths (*Table 4*).

An inspection of the UV/VIS data and the corresponding *Figs. 13–20* show that the heptalene band I is bathochromically shifted by the additional donor/acceptor substituents by 28–37 nm taking the isopropyl series ($R^1 = H$, $R^2 = {}^iPr$) with (all-*E*)-**1b** as reference, or by at least 30 nm taking (all-*E*)-**60b** as reference for (all-*E*)-**64b**. And it seems that a 4-NO_2 group at $\pi(1)$ and a 4-MeO group at $\pi(2)$ shift band I stronger (+ 37 nm) than in the reverse situation (+28 nm), a fact which is also evident by comparison of the position of band I of (all-*E*)-**52b** and (all-*E*)-**48b** with the shorter π-chains (*Table 4*). Nevertheless, $\Delta\lambda$ ((all-*E*)-**52b** – (all-*E*)-**48b**) is with 11 nm about equal to $\Delta\lambda$ ((all-*E*)-**68b** – (all-*E*)-**40b**).

The influence of the donor/acceptor substituents on the position of heptalene band III is smaller than on that of band I and amounts to *ca.* + 14 nm (*Table 4*). In three cases, we found only a shoulder on the lower-wavelength flanc of band I at *ca.* 400 nm, *i.e.*, *ca.* 20 nm higher than in the other cases (*Table 4*). Therefore, we assume that this shoulder in the spectra of (all-*E*)-**56b**, (all-*E*)-**64b**, and (all-*E*)-**68b** represents heptalene band II of these heptalenes, and heptalene band III is weak and hidden under the further falling flanc of the dominating band I.

The UV/VIS spectra of the type-**A** heptalenes are easier to analyze since the dominating absorption is caused here by heptalene band III (*Table 5* and *Figs. 1* and *13–20*). Heptalene band II is sitting in most cases as clearly recognizable shoulder on

Table 4. *Absorption Maximum of the Heptalene Bands I and III of the π(1),π(2)-Substituted Type-***B** *Methyl Heptalene-5-carboxylates*[a])

π(1),π(2)[b])	Others	No.	I [nm]	III [nm]	Remarks
PhCH=CH–CH=CH PhCH=CH–CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**1b**	440	359	*Fig. 1*
4-O_2N–C_6H_4CH=CH–CH=CH 4-MeO–C_6H_4CH=CH–CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**40b**	477	378	*Fig. 19*
4-MeO–C_6H_4CH=CH–CH=CH 4-O_2N–C_6H_4CH=CH–CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**68b**	468	401 (sh)[c])	*Fig. 18*
4-Me_2N–C_6H_4CH=CH 4-O_2N–C_6H_4CH=CH–CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**44b**	486	378	*Fig. 17*
4-MeO–C_6H_4CH=CH 4-O_2N–C_6H_4CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**48b**	439	370	*Fig. 14*
4-O_2N–C_6H_4CH=CH 4-MeO–C_6H_4CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**52b**	450	356	*Fig. 15*
4-MeO–C_6H_4CH=CH 4-O_2N–C_6H_4CH=CH–CH=CH	6,8,10-Me_3	(all-*E*)-**56b**	451	400 (sh)[c])	*Fig. 16*
PhCH=CH–CH=CH PhCH=CH–CH=CH	6,8,10-Me_3	(all-*E*)-**60b**	439	365	*Fig. 13*
4-MeO–C_6H_4CH=CH–CH=CH 4-O_2N–C_6H_4CH=CH–CH=CH	6,8,10-Me_3	(all-*E*)-**64b**	469	400 (sh)[c])	*Fig. 20*

[a]) See *Figs.* and *Exper. Part* for further details. [b]) All π(1),π(2) substituents have (*E*)-configuration. [c]) Most probably heptalene band II; see text.

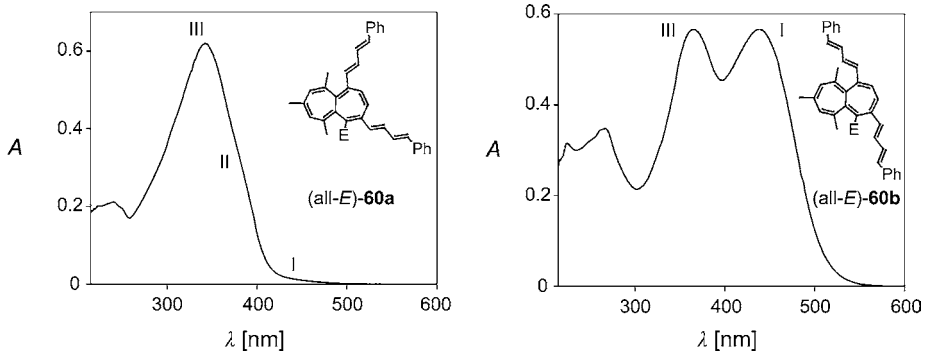


Fig. 13. *UV/VIS Spectra* (CH_2Cl_2/hexane) *of (*all-*E)-***60a** *and (*all-*E)-***60b**

the longer-wavelength flanc of band III, whereas band I appears only as tailing of band III, or at best as a weak broad shoulder in the range where the type-**B** heptalenes show the maximum of band I. As a rule, one finds band III of the type-**A** heptalenes at shorter wavelength than band III of the **B** forms.

Since we got a number of π(1) substituted heptalenes of type **C**(1), **D**(1), and **E**(1) in pure crystalline form, we measured their UV/VIS spectra in MeCN (*Table 6*). It was interesting to notice that band I of these type-**B** heptalenes appeared as broad maxima or shoulders at comparably long wavelength with respect to the corresponding π(1),π(2)-disubstituted type-**B** heptalenes derived from them – also if one takes into

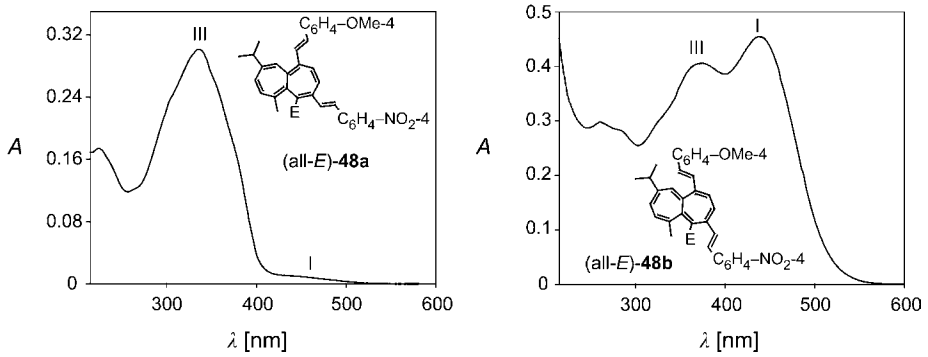


Fig. 14. *UV/VIS Spectra* (4% ^{i}PrOH/hexane) *of (*all-*E)*-**48a** *and (*all-*E)*-**48b** [1]

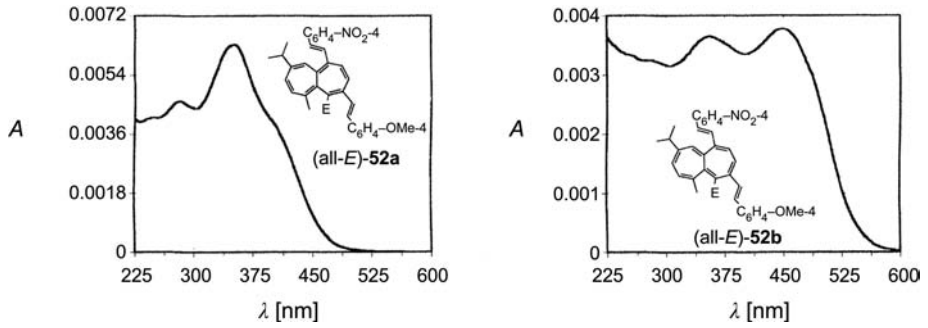


Fig. 15. *UV/VIS Spectra* (CH_2Cl_2/hexane) *of (*all-*E)*-**52a** *and (*all-*E)*-**52b**

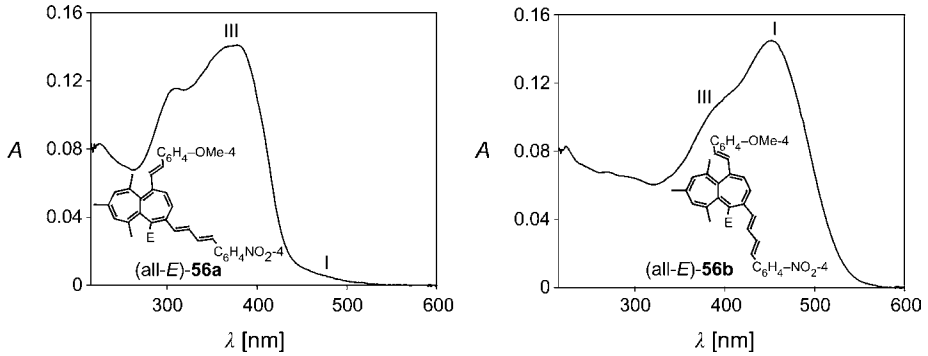


Fig. 16. *UV/VIS Spectra* (CH_2Cl_2/hexane) *of (*all-*E)*-**56a** *and (*all-*E)*-**56b**

account a polar solvent shift of *ca.* +17 nm in going from CH_2Cl_2/hexane to MeCN (*cf. Table 3*). Most obvious is this bathochromic shift for the corresponding **D**(1) heptaleno[3,4-*c*]furan-3-ones (*E*)-**42b** (*Table 6*). The correction of the solvent shift of +17 nm of the band I position of (*E*)-**42b** leads in comparison to its π(1),π(2)-

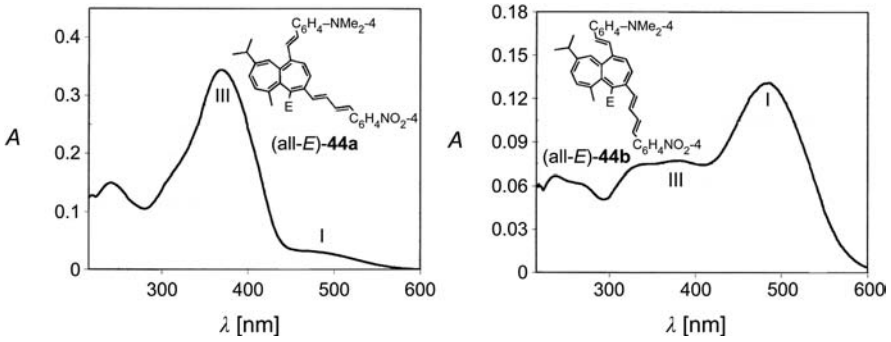


Fig. 17. *UV/VIS Spectra* (CH_2Cl_2/hexane) *of (*all-*E)*-**44a** *and (*all-*E)*-**44b**

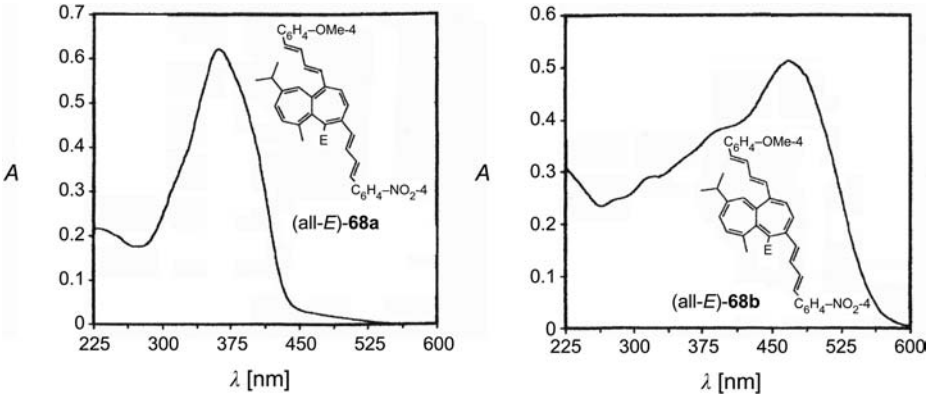


Fig. 18. *UV/VIS Spectra* (CH_2Cl_2/hexane) *of (*all-*E)*-**68a** *and (*all-*E)*-**68b**

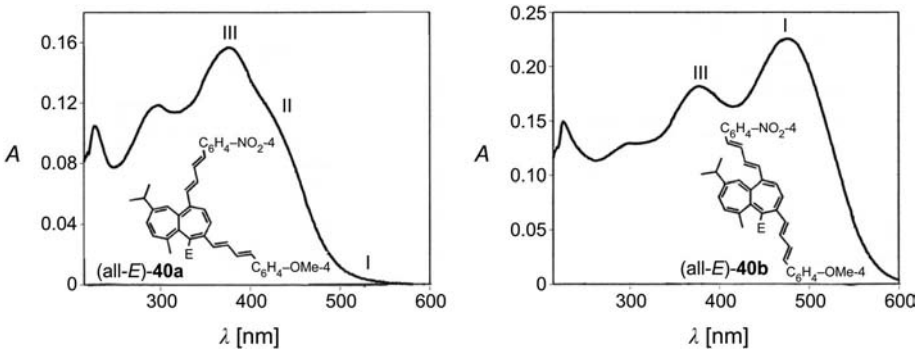


Fig. 19. *UV/VIS Spectra* (CH_2Cl_2/hexane) *of (*all-*E)*-**40a** *and (*all-*E)*-**40b**

disubstituted analog (all-*E*)-**44b** to almost the same wavelength of absorption. There must be reasons for the fact that the structure of (*E*)-**42b** compensates structurally and electronically the effect of the $\pi(2)$ substituent 4-(4-nitrophenylbuta-1,3-dien-1-yl) of

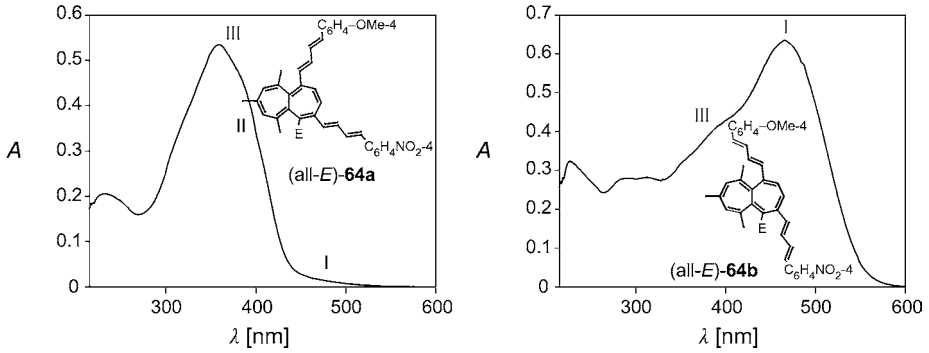


Fig. 20. *UV/VIS Spectra* (CH_2Cl_2/hexane) *of* (all-*E*)-**64a** *and* (all-*E*)-**64b**

Table 5. *Dominating Absorption Maximum of the π(1),π(2)-Substituted Type-***A** *Methyl Heptalene-1-carboxylates*[a])

π(1),π(2)[b])	Others	No.	λ [nm]	Remarks
PhCH=CH–CH=CH PhCH=CH–CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**1a**	343	*Fig. 1*
4-O_2N–C_6H_4CH=CH–CH=CH 4-MeO–C_6H_4CH=CH–CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**40a**	377	*Fig. 19*
4-MeO–C_6H_4CH=CH–CH=CH 4-O_2N–C_6H_4CH=CH–CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**68a**	351	*Fig. 18*
4-Me_2N–C_6H_4CH=CH 4-O_2N–C_6H_4CH=CH–CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**44a**	369	*Fig. 17*
4-MeO–C_6H_4CH=CH 4-O_2N–C_6H_4CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**48a**	337	*Fig. 14*
4-O_2N–C_6H_4CH=CH 4-MeO–C_6H_4CH=CH	9-^{i}Pr, 6-Me	(all-*E*)-**52a**	352	*Fig. 15*
4-MeO–C_6H_4CH=CH 4-O_2N–C_6H_4CH=CH–CH=CH	6,8,10-Me_3	(all-*E*)-**56a**	378	*Fig. 16*
PhCH=CH–CH=CH PhCH=CH–CH=CH	6,8,10-Me_3	(all-*E*)-**60a**	342	*Fig. 13*
4-MeO–C_6H_4CH=CH–CH=CH 4-O_2N–C_6H_4CH=CH–CH=CH	6,8,10-Me_3	(all-*E*)-**64a**	359	*Fig. 20*

[a]) See *Figs.* and *Exper. Part* for further details. [b]) All π(1),π(2) substituents have (*E*)-configuration.

(all-*E*)-**44b**. There are two structure arguments: The fusion of the five-membered ring in **D**(1) structures leads to a certain flattening of the heptalene skeleton, accompanied by a reduction of the torsion angles of the π-skeleton and a rigid almost perfect s-*cis* orientation of the C=O group with respect to the adjacent π-bonds[13]). Moreover, the

[13]) In connection with the synthesis of new heptalenes [9b], we performed an X-ray analysis of the structure of an analog of furanone (1*E*,3*E*)-**35b**, wherein Me–C(11) is substituted by an (*E*)-styryl group. In comparison with the X-ray structure of heptalenedicarboxylate (1*E*,3*E*)-**16b** (*cf. Table 2*), we found for the analog of (1*E*-3*E*)-**35b** torsion angles reduced by *ca.* 3°, and *Θ* (O=C–C(3a)=C(4)) amounted to 12.5°. AM1 Calculations of (*E*)-**25b** and (*E*)-**42b** with a Me_2N group at π(1) showed just the same tendencies in *Θ* of the heptalene skeleton.

C=O group of the furanone ring gains in electron-acceptor quality due to the three neighboring O-atoms of the cyclic semi-orthoanhydride structure [11], a fact, which enhances the polar character of the merocyanine part of the **D**(1) forms. An aldehyde group at the heptalene skeleton seems to adopt always an almost perfect s-*trans* arrangement with respect to the corresponding heptalene C=C bond (*cf.* [20]), thus allowing optimal conjugation within the merocyanine system of the **E**(1) forms (*cf. Table 6*).

A last point should be regarded. The **B** forms of the heptalenes contain a merocyanine chain, therefore, it is of interest to consider corresponding open-chain phenyl capped polyene systems and their donor/acceptor substituted variants as linear merocyanines (*Fig. 21*). Their longest-wavelength absorptions are close to those of the corresponding heptalene structures. Therefore, it can be concluded that the incorporated heptalene π-system with exception of the directly involved two π-bonds does not contribute markedly to the longest-wavelength absorption. A comparison of the position of heptalene band I of (all-*E*)-**48b** with the one of (all-*E*)-**52b** and of (all-*E*)-**40b** with the one of (all-*E*)-**68b** with an exchange of donor and acceptor group of $\pi(1)$ and $\pi(2)$ (*cf. Table 4*) indicates that a 4-NO_2 group at $\pi(1)$ and a 4-MeO group at $\pi(2)$ lead to a bathochromic shift of 11 and 18 nm, respectively, measured against the reverse situation. In other words, the merocyanine system of the **B**-type heptalenes are similar

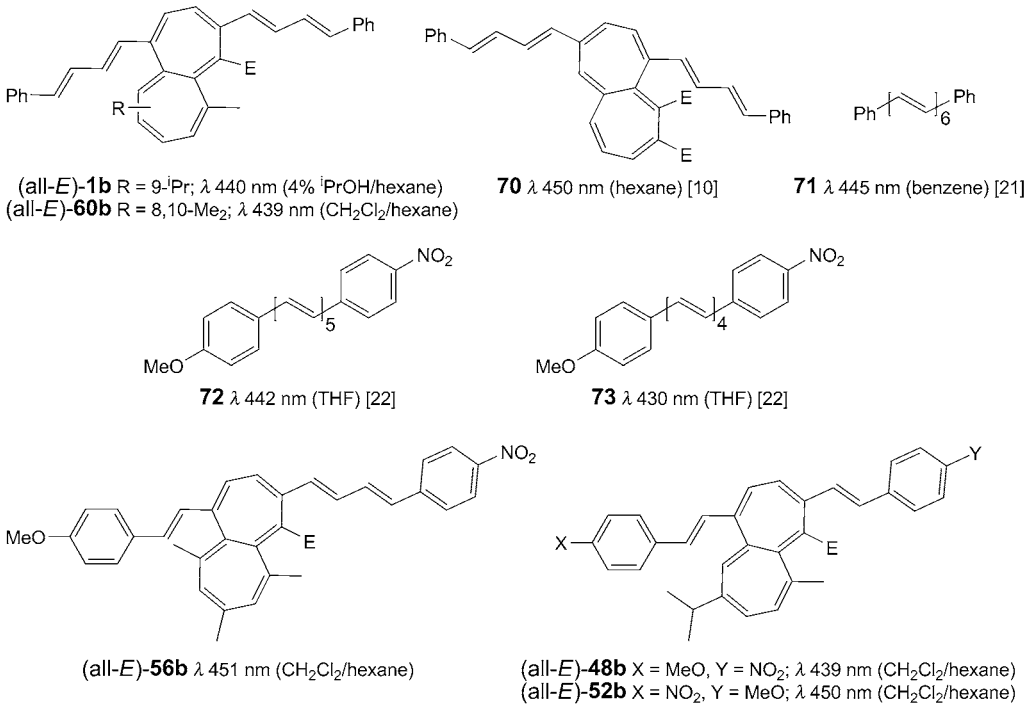


Fig. 21. *Position of the longest-wavelength band of α,ω-arylpolyenes in comparison with that of corresponding heptalene based polyenes*

Table 6. *Longest-Wavelength Absorption Maximum of Some Heptalene Intermediates of Type* **C**(1), **D**(1), *and* **E**(1)[a])

π(1)	PhCH=CH–CH=CH[b])			4-MeO–C_6H_4CH=CH[b])			4-Me_2N–C_6H_4CH=CH[b])			4-O_2N–C_6H_4CH=CH[b])		
	No.	λ ([nm]	log ε	No.	λ ([nm]	log ε	No.	λ ([nm]	log ε	No.	λ ([nm]	log ε
C(1)[c])	(1*E*,3*E*)-**16b**	403 (sh)[c])	4.14	(*E*)-**22b**	411 (sh)	4.04	(*E*)-**23b**	449	4.355	(1*E*)-**21b**	419sh	3.89
	(1*E*,3*E*)-**24b**	402 (sh)	4.14	(*E*)-**26b**	402 (sh)	3.99						
D(1)	(1*E*,3*E*)-**35b**	462	4.01	(*E*)-**46b**	464	3.93	(*E*)-**42b**	507	4.26	(1*E*)-**50b**	471	3.77
	(1*E*,3*E*)-**58b**	461 (sh)	3.85	(*E*)-**54b**	460	3.83						
E(1)	(1*E*,3*E*)-**36b**	416 (sh)	4.24	(*E*)-**47b**	428 (sh)	4.08	(*E*)-**43b**	473	4.356	(1*E*)-**51b**	422	4.21
	(1*E*,3*E*)-**59b**	413 (sh)	4.08	(*E*)-**55b**	413 (sh)	3.99						

[a]) See *Scheme 3*; solvent MeCN, sh = shoulder. [b]) π(1) Substituent has (*E*)-configuration. [c]) First line: isopropyl series (R^1 = H, R^2 = ^{i}Pr); second line: methyl series (R^1 = Me, R^2 = H).

to those of open-chain structures, however, they carry their own character, best documented by the unique thermal and photochemical convertibility of the **A** and **B** forms.

We studied the pure photochromism of heptalenes (all-*E*)-**56a** and (all-*E*)-**56b** at room temperature in hexane/CH_2Cl_2 9 : 1 in detail. Irradiation of (all-*E*)-**56b** with a Hg high-pressure lamp (150 W) through an interference filter with transmittance at 439 ± 20 nm led after 2 h to an almost complete conversion into (all-*E*)-**56a** (*Fig. 22*). On the other hand, when the thus obtained solution of (all-*E*)-**56a** was then irradiated through an interference filter with transmittance at 308 ± 20 nm for 2 h, a photo-equilibrated 1 : 3 mixture of (all-*E*)-**56a** and (all-*E*)-**56b** was generated (*Fig. 22*).

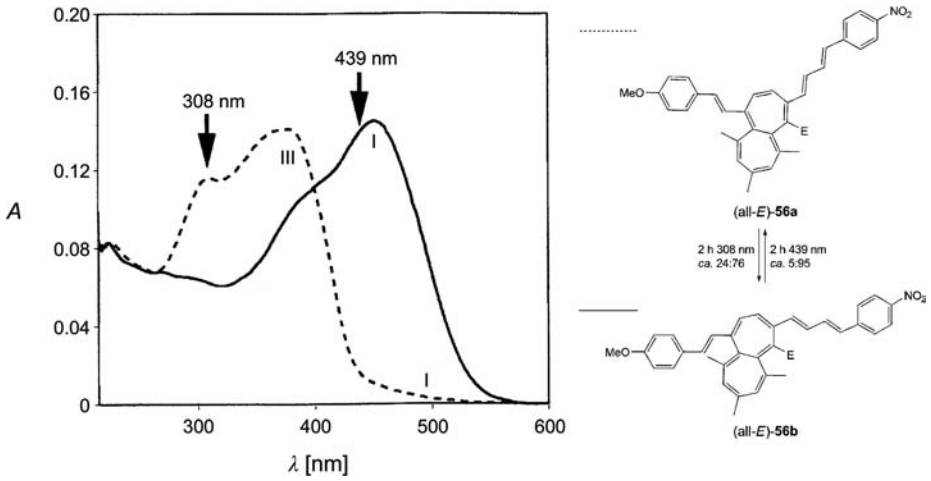


Fig. 22. *Testing the photochromic behavior of (all-*E*)-***56a*** and (all-*E*)-***56b***

We are thankful to our NMR laboratory for specific NMR measurements and to our MS laboratory for mass spectra. Financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. Anal. TLC: glass plates covered with silica gel *60* (SiO_2) with fluorescence indicator 254 nm (*Fluka*; layer thickness 0.25 mm, grain size 5–17 μm); detection with UV light (254 or 366 nm) or with appropriate spray reagents. Prep. column chromatography (CC): SiO_2 *60* (*Merck*; grain size 40–63 μm). Anal. HPLC: *Waters-991* instrument, equipped with a photodiode-array detector and a *Bischoff* pump and *Jasco MD-910* instrument, equipped with a photodiode-array detector and a *Milton-Roy-CM-4000* pump, *Spherisorb-S5-CN* column (*Phase Separations*; 5 μm, 20 × 250 mm). M.p.: *Mettler-FP-5* and *-FP-52* instruments; uncorrected. UV/VIS Spectra: recorded with the HPLC photodiode-array detectors (wavelength accuracy ± 1.5 nm) in relative intensities, or with a *Perkin–Elmer-Lambda-9* spectrophotometer; minima (min.) and maxima (max.) in nm; molar extinction coefficients ε [$dm^3/mol \cdot cm$] as log ε; sh = shoulder. IR Spectra: *Perkin–Elmer-FT-1600* IR spectrophotometer; solid compounds in KBr pills (*ca.* 0.1 g KBr/1 mg substance); in cm^{-1}. ^{1}H-NMR Spectra: *Bruker-AC-300*, *-ARX-300*, and *-AMX 600* instruments; chemical shifts δ in ppm with respect to Me_4Si (= 0 ppm), coupling constants *J* in Hz; if not otherwise stated, at 300 MHz; f.s. = fine structure. ^{13}C-NMR Spectra: *Bruker-ARX-300* and *-AMX-*

600 instruments; at 75 and 150 MHz; internal reference signal *C*DCl_3 at 77.00 ppm with $^1J(^{13}C,D) =$ 31.5 Hz; multiplicities determined with DEPT technique; if not otherwise stated, at 75 MHz. Mass spectra (MS): *Varian MAT-112S* and *-CH-7A* instruments for chemical ionization (CI) with NH_3; *Finnigan-MAT-SSQ-700* instrument, for electron-impact ionization (EI) at 70 eV; source temp. 250°, direct injection; in *m/z*, (rel. %).

1. *Syntheses of Dimethyl Heptalene-4,5-dicarboxylates.* 1.1. *Dimethyl 9-Isopropyl-1,6-dimethylheptalene-4,5-dicarboxylate* (**5b**). The diester was prepared in average yields of 68% by thermal reaction of guaiazulene with a three-fold molar amount of dimethyl but-2-ynedioate in toluene at 130° during 24 h. Recrystallization from Et_2O gave **5b**. Yellow crystals. M.p. 133.3–137.3° ([6]: 147° (Et_2O)).

1.2. *Dimethyl 1-Formyl-9-isopropyl-6-methyl- and 6-Formyl-9-isopropyl-1-methylheptalene-4,5-dicarboxylate* (**9b** and **10b**, resp.). Diester **5b** (3.10 g, 9.10 mmol) was dissolved in xylene (70 ml), and then SeO_2 (1.01 g, 9.10 mmol) was added. The mixture was heated under reflux, and additional amounts of SeO_2 (each time 1.01 g) were added after 30 and 60 min. Xylene was distilled off and the residue subjected to CC (SiO_2, hexane/Et_2O 4:1): **9b** (0.089 g, 3%) and **10b** (0.128 g, 4%), in this order. Other products which were visible on TLC were not isolated.

Data of **9b**: Red crystals from hexane/Et_2O. M.p. 161.5–162.8°. R_f (hexane/Et_2O 1:1) 0.24. UV/VIS (MeCN): max. 431 (2.80), 276 (sh, 4.12), 254 (4.15); min. 380 (2.79). IR (KBr): 2965*m*, 2843*w*, 1733*s*, 1711*s*, 1679*s*, 1644*w*, 1594*w*, 1565*w*, 1526*w*, 1435*m*, 1385*w*, 1356*w*, 1344*w*, 1277*s*, 1223*s*, 1184*m*, 1155*m*, 1170*m*, 1047*m*, 983*m*, 957*w*, 867*w*, 838*m*, 805*m*, 790*w*, 758*m*, 703*w*, 631*w*. ^{1}H-NMR ($CDCl_3$): 9.55 (*s*, CHO–C(1)); 7.66 (*d*, $^3J(2,3) = 6.1$, H–C(3)); 7.12 (*d*, $^3J(2,3) = 6.1$, H–C(2)); 6.33 (*d*, $^3J(7,8) = 6.6$, H–C(8)); 6.22 (*d*, $^3J(7,8) = 6.5$, H–C(7)); 5.71 (*s*, H–C(10)); 3.75, 3.71 (2*s*, COOMe); 2.50 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 1.96 (*s*, Me–C(6)); 1.08, 1.06 (2*d*, $^3J = 6.9$, 6.8, Me_2CH–C(9)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 189.90 (*d*, CHO); 169.78, 167.21 (2*s*, *C*OOMe); 149.19 (*s*, C(5a)); 148.78 (*s*, C(9)); 143.65 (*d*, C(3)); 140.81 (*s*, C(1)); 138.47 (*s*, C(10a)); 136.65 (*d*, C(2)); 130.99 (*d*, C(10)); 128.44 (*d*, C(7)); 127.84 (*s*, C(6)); 126.22 (*d*, C(8)); 123.94 (*s*, C(5)); 120.62 (*s*, C(4)); 52.50, 52.14 (2*q*, COO*Me*); 35.48 (*d*, Me_2CH–C(9)); 22.92, 22.55 (2*q*, Me_2CH–C(9)); 22.26 (*q*, *Me*–C(6)). EI-MS: 355 (18), 354 (100, $M^{+\bullet}$), 340 (21), 339 (16, $[M - Me]^+$), 325 (21, $[M - CHO]^+$), 311 (21, $[M - (Me + CO)]^+$), 295 (24, $[M - COOMe]^+$), 279 (21), 251 (8), 235 (8), 212 (17), 207 (7), 198 (8), 197 (6), 193 (7), 191 (8), 189 (7), 178 (7), 165 (12). Anal. calc. for $C_{21}H_{22}O_5$ (354.40): C 71.17, H 6.26; found: C 70.89, H 6.36.

Data of **10b**: Orange crystals from hexane/Et_2O. M.p. 165.7–166.6°. R_f (hexane/Et_2O 1:1) 0.12. UV/VIS (MeCN): max. 400 (3.11), 330 (sh, 3.54), 279 (4.28); min. 257 (4.21), 227 (4.30). IR (KBr): 2965*m*, 2908*w*, 2873*w*, 2843*w*, 1722*s*, 1677*s*, 1644*w*, 1608*w*, 1578*m*, 1528*w*, 1438*m*, 1385*w*, 1347*w*, 1300*w*, 1259*s*, 1226*m*, 1192*m*, 1166*m*, 1094*m*, 1070*w*, 1053*m*, 1043*m*, 989*w*, 957*w*, 876*w*, 862*w*, 833*w*, 734*w*. ^{1}H-NMR ($CDCl_3$): 9.46 (*s*, CHO–C(6)); 7.47 (*d*, $^3J(2,3) = 6.4$, H–C(3)); 7.06 (*d*, $^3J(7,8) = 6.6$, H–C(7)); 6.54 (*d*, $^3J(7,8) = 6.6$, H–C(8)); 6.24 (*d*, $^3J(2,3) = 6.5$, H–C(2)); 5.96 (*s*, H–C(10)); 3.70, 3.58 (2*s*, COOMe); 2.58 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 2.04 (*s*, Me–C(1)); 1.14, 1.12 (2*d*, $^3J = 6.9$, 6.8, Me_2CH–C(9)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 190.26 (*d*, CHO); 167.16, 167.01 (2*s*, COOMe); 157.16 (*s*, C(9)); 146.13 (*d*, C(3)); 142.94 (*s*, C(5a)); 140.24 (*d*, C(2)); 137.47 (*s*, C(1)); 133.17 (*s*, C(10a)); 132.15 (*s*, C(6)); 131.07 (*s*, C(4)); 127.74 (*d*, C(7)); 126.76 (*d*, C(10)); 126.62 (*s*, C(5)); 124.14 (*s*, C(8)); 52.00, 51.95 (2*q*, COO*Me*)); 36.45 (*d*, Me_2CH–C(9)); 25.41, 22.52 (2*q*, Me_2CH–C(9)); 22.06 (*q*, *Me*–C(1)). EI-MS: 354 (8, $M^{+\bullet}$), 296 (16), 295 (100, $[M - COOMe]^+$), 165 (8). Anal. calc. for $C_{21}H_{22}O_5$ (354.40): C 71.17, H 6.26; found: C 70.89, H 6.17.

1.3. *Dimethyl 1-(Bromomethyl)-9-isopropyl-6-methyl- and 6-(Bromomethyl)-9-isopropyl-1-methylheptalene-4,5-dicarboxylate* (**11b** and **12b**, resp.). Diester **5b** (1.00 g, 2.94 mmol) and NBS (0.55 g, 3.08 mmol) were dissolved in CCl_4. Then, dibenzoyl peroxide (0.038 g, 0.12 mmol) was added to start the bromination reaction under reflux, at an oil bath temp. of 90°. After 2 h at 90°, the mixture was cooled and the formed succinimide removed by filtration. The residue of the clear CCl_4 soln. was subjected to CC (SiO_2, hexane/Et_2O 4:1): crystalline mixture **12b**/**5b**/**11b** 3.1:1.7:1. Recrystallization from EtOH gave **12b** (0.32 g, 26%) in a purity of *ca.* 95%.

Data of **12b**: R_f (hexane/AcOEt 3:1) 0.31. ^{1}H-NMR ($CDCl_3$): 7.50 (*d*, $^3J(2,3) = 7.1$, H–C(3)); 6.42 (*d*, $^3J(7,8) = 6.5$, H–C(8)); 6.24 (*dd*, $^3J(2,3) = 7.2$, H–C(2)); 6.22 (*d*, $^3J(7,8) = 6.5$, H–C(7)); 5.85 (*s*, H–C(10)); 4.26, 4.04 (*AB*, $^2J_{AB} = 10.0$, $BrCH_2$–C(6)); 3.72, 3.68 (2*s*, COOMe); 2.49 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.20 (*s*, Me–C(1)); 1.09, 1.06 (2*d*, $^3J = 6.9$, Me_2CH–C(9)).

Data of **11b**: The compound was not purified. ^{1}H-NMR ($CDCl_3$; some signals taken from a mixture with **12b**): 5.86 (*s*, H–C(10)); 4.13, 3.95 (*AB*, $^2J_{AB} = 12.5$, $BrCH_2$–C(6)); 3.71, 3.70 (2*s*, COOMe); 2.07 (*s*, Me–C(6)).

1.4. *Dimethyl 1-(Chloromethyl)-9-isopropyl-6-methylheptalene-4,5-dicarboxylate* (**13b**). Diester **5b** (4.50 g, 13.2 mmol) and C_2Cl_6 (15.7 g, 66.1 mmol) were placed under Ar in a flame-dried flask and dissolved in dry THF (70 ml). The soln. was cooled to $-78°$, and a soln. of ^{t}BuOK (6.00 g, 53.5 mmol) in THF (20 ml) was slowly added. The dark yellow mixture was kept for 1.5 h at $-78°$ and then poured into H_2O. The aq. phase was extracted with Et_2O (3×), the combined org. extract washed with sat. aq. NaCl soln., dried (Na_2SO_4), and concentrated, and the powdery, red-to-yellow residue was washed with hexane and recrystallized from Et_2O: pure **13b** (4.50 g, 90%). Orange crystals. M.p. 108.5–110.8°. R_f (hexane/Et_2O 1:1) 0.36. UV/VIS (MeCN): max. 339 (sh, 3.50), 284 (4.04), 252 (4.15); min. 245 (4.15). IR (KBr): 2958*m*, 2908*w*, 2870*w*, 2843*w*, 1723*s*, 1644*w*, 1596*w*, 1574*w*, 1528*w*, 1434*m*, 1382*w*, 1362*w*, 1253*s*, 1226*m*, 1194*m*, 1162*w*, 1082*m*, 1047*w*, 988*w*, 794*w*, 750*w*, 721*w*, 621*w*. ^{1}H-NMR ($CDCl_3$): 7.49 (*d*, $^3J(2,3) = 6.2$, H–C(3)); 6.49 (*d*, $^3J(2,3) = 6.1$, H–C(2)); 6.23 (*d*, $^3J(7,8) = 6.5$, H–C(8)); 6.18 (*dq*-like, $^3J(7,8) = 6.6$, $^4J(7,\text{Me–C(6)}) = 1.4$, H–C(7)); 5.90 (*s*, H–C(10)); 4.22, 4.13 (2*dt*, *ABXY*, $^2J_{AB} = 12.3$, 12.2 $^4J(ClCH_2\text{–C(1)},2) \approx {}^5J(ClCH_2\text{–C(1)},3) = 0.7$, 1.1, $ClCH_2$–C(1)); 3.72, 3.71 (2*s*, COOMe); 2.50 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 2.03 (*s*, Me–C(6)); 1.09, 1.06 (2*d*, $^3J = 6.9$, (Me_2CH–C(9)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 167.50, 166.95 (2*s*, *C*OOMe); 148.03 (*s*, C(9)); 145.75 (*s*, C(5a)); 141.25 (*s*, C(1)); 138.21 (*d*, C(3)); 134.36 (*s*, C(10a)); 128.73 (*s*, C(6)); 128.42 (*d*, C(2)); 127.50 (*d*, C(7)); 127.21 (*s*, C(4)); 126.93 (*d*, C(10)); 126.14 (*d*, C(8)); 123.09 (*s*, C(5)); 52.14, 52.01 (2*q*, COO*Me*)); 47.64 (*t*, Cl*C*H_2–C(1)); 35.51 (*d*, Me_2CH–C(9)); 22.96, 22.82 (2*q*, Me_2CH–C(9)); 22.32 (*q*, *Me*–C(6)). EI-MS: 376, 374 (20, 66, $M^{+\bullet}$); 345, 343 (4, 11, $[M - \text{MeO}]^+$); 340 (29), 339 (100, $[M - \text{Cl}]^+$), 325 (6, $[M - ClCH_2]^+$), 308 (6), 307 (15), 281 (5), 279 (8), 255 (6), 221 (9), 205 (8), 198 (7), 197 (22), 191 (5), 189 (8), 179 (7), 178 (11), 165 (7).

1.5. *Dimethyl 1-(Iodomethyl)-9-isopropyl-6-methylheptalene-4,5-dicarboxylate* (**17b**). A soln. of **13b** (2.00 g, 5.33 mmol) and NaI (1.20 g, 8.01 mmol) in acetone (12 ml) was stirred for 1 h at r.t. under N_2. Then the suspension was poured into H_2O and extracted with CH_2Cl_2 (2×) and the extract washed with H_2O (2×), and dried (Na_2SO_4), and concentrated to 7 ml at 40°. Et_2O (20 ml) was added, followed by hexane (20 ml). After standing overnight, pure **17b** (1.90 g, 76%) had separated. Brown-to-orange crystals. M.p. 138.8–141.2° (Et_2O/CH_2Cl_2/hexane). R_f (hexane/Et_2O 1:1) 0.37. UV/VIS (MeCN): max. 333 (sh), 287, 247; min. 272, 235. IR (KBr): 2957*m*, 2872*w*, 1725*s*, 1640*w*, 1606*w*, 1571*w*, 1525*w*, 1428*m*, 1382*w*, 1362*w*, 1252*s*, 1228*m*, 1192*m*, 1160*w*, 1128*w*, 1099*w*, 1078*m*, 1048*w*, 987*w*, 876*w*, 841*w*, 794*w*, 771*w*, 748*w*. ^{1}H-NMR ($CDCl_3$): 7.39 (*dd*, $^3J(2,3) = 6.4$, $^5J(3,\ CH_2\text{–C(1)}) = 1.2$, H–C(3)); 6.47 (*d*, $^3J(2,3) = 6.4$, H–C(2)); 6.34 (*d*, $^3J(7,8) = 6.6$, H–C(8)); 6.20 (*dd*, $^3J(7,8) = 6.6$, $^4J(7,\ \text{Me–C(6)}) = 1.3$, H–C(7)); 5.92 (*s*, H–C(10)); 4.19, 4.04 (*ABXY*, $^2J(ICH_2\text{–C(1)}) = 9.0$, $^4J(IH_2C\text{–C(1)},2) \approx {}^5J(IH_2C\text{–C(1)},3) = 1.0$, ICH_2–C(1)); 3.72 (*s*, COOMe); 2.50 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.14 (*s*, Me–C(6)); 1.10, 1.06 (2*d*, $^3J = 6.9$, Me_2CH–C(9)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 167.71, 166.99 (2*s*, *C*OOMe); 148.09 (*s*, C(9)); 145.16 (*s*, C(5a)); 144.25 (*s*, C(1)); 138.35 (*d*, C(3)); 134.39 (*s*, C(10a)); 129.26 (*s*, C(6)); 128.29 (*d*, C(2)); 128.08 (*d*, C(7)); 127.86 (*s*, C(4)); 127.39 (*d*, C(10)); 126.39 (*d*, C(8)); 123.40 (*s*, C(5)); 52.14, 52.04 (2*q*, COO*Me*); 35.50 (*d*, Me_2CH–C(9)); 23.00, 22.96 (2*q*, Me_2CH–C(9)); 22.31 (*q*, *Me*–C(6)); 18.73 (*t*, I*C*H_2–C(1)). EI-MS: 340 (65), 339 (100, $[M - \text{I}]^+$), 309 (10, $[M - (\text{I} + CH_2O)]^+$), 308 (10, $[M - (\text{I} + \text{MeO})]^+$), 309 (10, $[M - (\text{I} + CH_2O)]^+$), 281 (13), 242 (12), 221 (12), 201 (15), 198 (27), 179 (10), 178 (12), 165 (11).

1.6. *{[9-Isopropyl-4,5-bis(methoxycarbonyl)-6-methylheptalen-1-yl]methyl}-triphenylphosphonium Iodide* (**15b**). A soln. of **13b** (0.30 g, 0.80 mmol), NaI (0.12 g, 1.20 mmol), and Ph_3P (0.42 g, 1.60 mmol) in dry acetone (15 ml) was stirred at r.t. until a suspension had formed (4 h). Et_2O (10 ml) and hexane (10 ml) were added. The precipitate was filtered off and re-dissolved in CH_2Cl_2 and the soln. concentrated to half the volume. The salt was precipitated with Et_2O and dried under h.v.: **15b** (0.513 g, 88%). IR (KBr): 2952*m*, 1728*s*, 1587*w*, 1437*s*, 1272*s*, 1227*m*, 1190*m*, 1152*m*, 1110*m*, 1046*m*, 996*w*, 860*w*, 747*m*, 719*m*, 690*m*, 521*m*. ^{1}H-NMR ($CDCl_3$): 7.84–7.60 (*m*, 15 arom. H); 7.26 (*dd*, $^3J(2,3) = 6.9$, $^5J(3,\text{P}) = 2.8$, H–C(3)); 6.40 (*dd*, $^3J(2,3) \approx {}^4J(2,\text{P}) = 5.5$, H–C(2)); 6.31 (*s*, H–C(10)); 6.16 (*d*, $^3J(7,8) = 6.5$, H–C(8)); 5.73 (*d*, $^3J(7,8) = 6.7$, H–C(7)); 5.45, 4.88 (2*t*, *ABX*, $^2J_{AB} = {}^2J_{AX} = {}^2J_{BX} = 16.0$, 15.5,

Ph_3PCH_2–C(1)); 3.69, 3.68 (2*s*, COOMe); 2.56 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 1.63 – 1.67 (*m*, Me–C(6)); 1.13, 1.10 (2*d*, $^3J = 7.0$, 6.9, Me_2CH–C(9)).

1.7. *Dimethyl 1,6,8,10-Tetramethylheptalene-4,5-dicarboxylate* (**6b**). The diester was prepared in average yields of 46% by thermal reaction of 1,4,6,8-tetramethylazulene with a three-fold molar amount of dimethyl but-2-ynedioate in toluene at 130° during 6 h. The DBS isomer *dimethyl 5,6,8,10-tetramethylheptalene-1,2-dicarboxylate* (**6a**) that was present in the original mixture in an amount of *ca.* 12% with respect to **6b** and was isolated together with **6b** after CC (SiO_2, hexane/Et_2O 6:1) and converted into **6b** by heating for 1 h at 120°. Recrystallization from Et_2O gave 46% of pure **6b**. Yellow crystals. M.p. 136.2 – 137.3° ([6]: 137 – 138° (Et_2O)).

1.8. *Dimethyl 1-(Chloromethyl)-6,8,10-trimethylheptalene-4,5-dicarboxylate* (**14b**). As described in *1.4*, with diester **6b** (1.00 g, 3.06 mmol), C_2Cl_6 (3.62 g, 16.83 mmol), THF (30 ml), and ^{t}BuOK (1.37 g, 12.24 mmol) in THF (12 ml); for 4 h at – 78°: pure **14b** (0.850 g, 77%). Orange crystals. M.p. 133.4 – 134.7°. R_f (hexane/Et_2O 1:1) 0.36. UV/VIS (MeCN): max. 391 (sh, 2.53), 271 (3.95); min. 248 (3.88). IR (KBr): 2951*w*, 2917*w*, 1711*s*, 1644*w*, 1564*w*, 1431*m*, 1397*w*, 1305*m*, 1278*s*, 1260*s*, 1205*w*, 1148*w*, 1086*m*, 1051*w*, 1002*w*, 959*w*, 772*w*. ^{1}H-NMR ($CDCl_3$): 7.53 (*d*, $^3J(2,3) = 5.9$, H–C(3)); 6.59 (*dt*, $^3J(2,3) = 5.9$, $^4J(2,ClCH_2$–C(1)) = 1.0, H–C(2)); 6.14 (*s*, H–C(9)); 6.03 (*d*, $^4J(7,$Me–C(6)) = 1.2, H–C(7)); 4.23, 4.02 (*dt*, *ABXY*, $^2J_{AB} = 12.4$, $^4J(ClCH_2$– C(1),2) ≈ $^5J(ClCH_2$–C(1),3) = 1.2, $ClCH_2$–C(1)); 3.70, 3.68 (2*s*, COOMe); 2.04 (*d*, $^4J(9,$Me–C(8)) = 1.2, Me–C(8)); 2.02 (*d*, $^4J(7,$Me–C(6)) = 1.2, Me–C(6)); 1.73 (*s*, Me–C(10)). EI-MS: 362, 360 (17, 58, $M^{+\bullet}$); 326 (22), 325 (100, $[M - Cl]^+$), 295 (16), 293 (32), 279 (12), 269 (14), 265 (28), 251 (15), 241 (10), 235 (10), 233 (16), 223 (12), 221 (13), 219 (16), 218 (11), 208 (17), 207 (53), 206 (36), 205 (30), 193 (29), 192 (53), 191 (64), 190 (39), 189 (67), 183 (70), 179 (24), 178 (34), 176 (16), 165 (41), 152 (19).

The structure of **14b** was confirmed by an X-ray crystal-structure analysis (*Fig. 4*,*a*, *Tables 2* and *7*).

2. *Syntheses of π(1)-Substituted Heptalene-4,5-dicarboxylates.* 2.1. *Dimethyl 9-Isopropyl-6-methyl-1-[(1Z,3E)- and (1E,3E)-4-phenylbuta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate* ((1*Z*,3*E*)- and (1*E*,3*E*)-**16b**, resp.) via Wittig *Reaction*. A soln. of **15b** (3.00 g, 4.12 mmol) and cinnamaldehyde (3.27 g, 24.7 mmol) in CH_2Cl_2 (250 ml) was mixed with 2N aq. NaOH (250 ml) and the two-phase system was intensely stirred under N_2 at r.t. for 12 h. The emulsion was neutralized with conc. aq. HCl soln. and extracted with CH_2Cl_2 (3×), the combined extract filtered, dried (Na_2SO_4), and concentrated and their residue subjected to CC (SiO_2; hexane/Et_2O 4:1): diastereoisomer mixture **16b** (1.10 g, 59%) as an orange oil. This oil was dissolved in a minimum amount of Et_2O and the soln. kept at 4°. After several weeks, both diastereoisomers crystallized side by side and could be separated mechanically.

Data of (1Z,3E)-**16b**: Dark orange crystals. M.p. 112.9 – 113.7°. R_f (hexane/Et_2O 2:1) 0.29. UV/VIS (MeCN): max. 408 (sh, 4.00), 367 (sh, 4.20), 336 (4.38), 268 (4.39); min. 297 (4.14), 242 (4.32). IR (KBr): 2994*w*, 2952*m*, 2868*w*, 1724*s*, 1634*w*, 1595*w*, 1578*w*, 1544*w*, 1510*w*, 1460*w*, 1428*m*, 1396*w*, 1380*w*, 1362*w*, 1337*w*, 1251*s*, 1215*s*, 1191*m*, 1160*m*, 1106*m*, 1081*m*, 1044*m*, 988*m*, 963*w*, 948*m*, 924*w*, 870*m*, 842*w*, 800*w*, 791*w*, 764*w*, 746*m*, 691*m*, 626*w*. ^{1}H-NMR ($CDCl_3$)[14]: 7.60 (*d*, $^3J(2,3) = 6.8$, H–C(3)); 7.32 – 7.20 (*m*, 5 arom. H); 6.97 (*dd*, $^3J(3',4') = 15.3$, $^3J(2',3') = 11.4$, H–C(3′)); 6.52 (*d*, $^3J(3',4') = 15.3$, H–C(4′)); 6.45 (*d*, $^3J(7,8) = 6.6$, H–C(8)); 6.43 (*d*, $^3J(2,3) = 6.8$, H–C(2)); 6.33 (*dd*, $^3J(7,8) = 6.6$, $^4J(7,$Me–C(6)) = 1.2, H–C(7)); 6.18 (*t*, $^3J(2',1') \approx {}^3J(2',3') \approx 11.6$, H–C(2′)); 6.06 (*d*, $^3J(1',2') = 11.8$, H–C(1′)); 5.96 (*s*, H–C(10)); 3.73, 3.72 (2*s*, COOMe); 2.51 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 1.96 (*s*, Me–C(6)); 1.04, 1.03 (2*d*, $^3J = 6.9$, 6.8, Me_2CH–C(9)). EI-MS: 455 (27, $[M + H]^+$), 454 (100, $M^{+\bullet}$), 395 (19, $[M - COOMe]^+$), 380 (15), 379 (67), 363 (14), 341 (14), 340 (86), 325 (14), 309 (18), 308 (16), 293 (23), 281 (22), 278 (13), 277 (26), 262 (11), 242 (21),198 (45), 183 (15).

Data of (1E,3E)-**16b**: Dark orange crystals. M.p. 159.4 – 161.4°. R_f (hexane/Et_2O 2:1) 0.29. UV/VIS (MeCN): max. 403 (sh, 4.14), 362 (sh, 4.32), 337 (4.46), 270 (4.12); min. 285 (4.07), 261 (4.10); *cf.* also Fig. 2 in [1]. IR (KBr): 3017*w*, 2956*m*, 2868*w*, 1731*s*, 1705*s*, 1639*w*, 1594*w*, 1581*w*, 1551*w*, 1517*w*, 1448*w*, 1433*m*, 1396*w*, 1383*w*, 1362*w*, 1341*w*, 1284*s*, 1252*s*, 1231*m*, 1200*m*, 1157*m*, 1144*m*, 1077*m*, 1054*w*, 1039*w*, 996*m*, 819*w*, 771*w*, 751*m*, 692*w*. ^{1}H-NMR ($CDCl_3$): 7.62 (*d*, $^3J(2,3) = 6.6$, H–C(3)); 7.40 – 7.20 (*m*, 5 arom. H); 6.83 (*dd*, $^3J(3',4') = 15.5$, $^3J(2',3') = 10.5$, H–C(3′)); 6.56 (*d*, $^3J(3',4') = 15.5$, H–C(4′)); 6.54 (*d*,

[14] The C-atoms of the ethenyl or buta-1,3-dien-1-yl groups of π(1) are primed and those of π(2) are doubly primed (see *Table 2*), irrespective of the DBS form **A** or **B** (*cf. Scheme 1* and *Table 2*).

$^3J(1',2') = 15.0$, H–C(1')); 6.40 (*dd*, $^3J(1',2') = 15.5$, $^3J(2',3') = 10.4$, H–C(2')); 6.37 (*d*, $^3J(7,8) = 6.6$, H–C(8)); 6.34 (*d*, $^3J(2,3) = 7.1$, H–C(2)); 6.28 (*dd*, $^3J(7,8) = 6.6$, $^4J(7,\text{Me–C}(6)) = 1.3$, H–C(7)); 5.87 (*s*, H–C(10)); 3.72, 3.71 (2*s*, COOMe); 2.51 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 1.97 (*s*, Me–C(6)); 1.09, 1.07 (2*d*, $^3J = 6.7$, 6.6, Me_2CH–C(9)). ^{13}C-NMR ($CDCl_3$): 167.68, 167.28 (2*s*, *C*OOMe); 148.27 (*s*, C(9)); 144.81 (*s*, C(5a)); 142.76 (*s*, C(1)); 139.08 (*d*, C(3)); 136.86 (*s*, arom. C); 135.29 (*d*, C(3')); 133.51 (*d*, C(1')); 132.87 (*d*, C(2')); 132.04 (*s*, C(10a)); 128.74 (*s*, C(6)); 128.61 (*d*, arom. C); 128.56 (*d*, C(4')); 127.94 (*d*, arom. C); 127.65 (*d*, C(2)); 127.50 (*d*, C(7), C(10)); 126.43 (*d*, arom. C); 125.47 (*d*, C(8)); 125.02 (*s*, C(4)); 123.61 (*s*, C(5)); 52.02, 51.98 (2*q*, COO*Me*); 35.41 (*d*, Me_2CH–C(9)); 23.11, 22.24 (2*q*, Me_2CH–C(9)); 21.82 (*q*, *Me*–C(6)). EI-MS: 455 (30, $[M+H]^+$), 454 (100, $M^{+\bullet}$), 395 (24, $[M-\text{COOMe}]^+$), 380 (15), 379 (58), 363 (16), 293 (11), 291 (10), 278 (14), 277 (21), 135 (31), 91 (13), 81 (11). Anal. calc. for $C_{30}H_{30}O_4$ (454.60): C 79.24, H 6.65; found: C 79.14, H 6.66.

The structure of (1*E*,3*E*)-**16b** was confirmed by an X-ray crystal-structure analysis (*Fig. 5* and *Tables 2* and *7*).

2.2. *Dimethyl 9-Isopropyl-6-methyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**16b**) via Horner–Wadsworth–Emmons *Reaction*. $P(OEt)_3$ (5 ml) was placed in a destillation apparatus, equipped with a two-neck flask and a dropping funnel. After heating to 100°, **17b** (2.60 g, 5.57 mmol) in CH_2Cl_2 (20 ml) was carefully added through the funnel under a pressure of 450 Torr. The mixture was then stirred at 90°/300 Torr during 40 min. The residual $P(OEt)_3$ was distilled off, leaving **18b** as dark viscous oil in the distillation flask. It was not further characterized and dissolved at r.t. in THF (20 ml) under N_2. The soln. was cooled to −78° and 2M NaHMDSA soln. in THF (3.08 ml, 6.16 mmol) was added dropwise. (→ dark red). The mixture was stirred during 30 min at −78°. Then, cinnamaldehyde (3.51 ml, 27.85 mmol) was added dropwise at −78°. Within 12 h, the mixture was brought under stirring to r.t. The orange soln. was poured into H_2O and extracted with Et_2O (3×), the extract was dried (Na_2SO_4) and concentrated, and the residue subjected to CC (SiO_2, hexane/Et_2O 4:1): pure, crystalline (1*E*,3*E*)-**16b** (1.29 g, 51%).

2.3. *Dimethyl 9-Isopropyl-6-methyl-1-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**19b**). As described in *2.2*, with $P(OEt)_3$ (20 ml), iodide **17b** (5.20 g, 11.15 mmol), 2M NaHMDSA in THF (6.13 ml, 12.27 mmol), and 4-nitrocinnamaldehyde (7.00 g, 39.5 mmol) in THF. The extraction of the aq. mixture was performed with CH_2Cl_2. CC (SiO_2, hexane/CH_2Cl_2 1:4) gave (1*E*,3*E*)-**19b** (1.73 g, 31%) as a red powder. A sample was recrystallized from CH_2Cl_2/pentane for analyses. Red crystals. M.p. 231.5–232.5°. R_f (hexane/Et_2O 2:1) 0.31. UV/VIS (MeCN): max. 425 (sh, 4.37), 386 (4.54), 245 (4.25), 278 (4.24); min. 283 (4.11). IR (KBr): 2951*w*, 2870*m*, 1722*s*, 1644*w*, 1586*m*, 1553*w*, 1508*m*, 1435*m*, 1333*s*, 1283*m*, 1251*s*, 1231*m*, 1202*m*, 1158*w*, 1106*w*, 1085*m*, 1046*w*, 994*m*, 865*m*, 829*w*, 747*w*. ^{1}H-NMR ($CDCl_3$): 8.16 (*d*-like, 2 arom. H); 7.62 (*d*, $^3J(2,3) = 6.6$, H–C(3)); 7.49 (*d*-like, 2 arom. H); 6.98 (*dd*, $^3J(3',4') = 15.5$, $^3J(2',3') = 10.8$, H–C(3')); 6.66 (*d*, $^3J(1',2') = 15.3$, H–C(1')); 6.60 (*d*, $^3J(3',4') = 15.8$, H–C(4')); 6.45–6.36 (*m*, H–C(2'), H–C(2), H–C(8)); 6.29 (*dd*, $^3J(7,8) = 6.6$, $^4J(7,\text{Me–C}(6)) = 1.1$, H–C(7)); 5.86 (*s*, H–C(10)); 3.72, 3.72 (2*s*, COOMe); 2.52 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 1.98 (*s*, Me–C(6)); 1.07, 1.05 (2*d*, $^3J = 6.6$, Me_2CH–C(9)). ^{13}C-NMR ($CDCl_3$): 167.54, 167.13 (2*s*, COOMe); 148.33 (*s*, C(9)); 146.73 (*s*, arom. C); 145.05 (*s*, C(5a)); 143.34 (*s*, arom. C); 142.07 (*s*, C(1)); 138.73 (*d*, C(3)); 136.48 (*d*, C(1')); 132.93 (*d*, C(3')); 132.84 (*s*, C(10a)); 132.31 (*d*, C(4')); 131.52 (*d*, C(2')); 129.35 (*d*, C(2)); 128.74 (*s*, C(6)); 127.74 (*d*, C(10)); 127.61 (*d*, C(7)); 126.69 (*d*, arom. C); 125.61 (*d*, C(8)); 124.63 (*s*, C(5)); 124.04 (*d*, arom. C); 123.69 (*s*, C(4)); 52.11, 52.02 (2*q*, COO*Me*); 35.39 (*d*, Me_2CH–C(9)); 23.08, 22.22 (2*q*, Me_2CH–C(9)); 21.81 (*q*, *Me*–C(6)). CI-MS (NH_3): 519 (13), 518 (32), 517 (100, $[M+NH_4]^+$), 502 (10), 501 (8), 500 (26, $[M+H]^+$), 470 (15), 469 (22), 468 (71, $[M-\text{MeO}]^+$). Anal. calc. for $C_{30}H_{29}NO_6$ (499.60): C 72.13, H 5.85, N 2.80; found: C 71.96, H 5.87, N 2.77.

2.4. *Dimethyl 9-Isopropyl-1-[(1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-6-methylheptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**20b**). Iodide **17b** (4.00 g, 8.59 mmol) was treated according to *2.2* and *2.3* to yield, after workup (CH_2Cl_2) and CC (SiO_2, hexane/CH_2Cl_2 1:4), (1*E*,3*E*)-**20b** (2.49 g, 60.0%). Orange crystals. R_f (Et_2O/hexane 3:2) 0.25.

2.5. *Dimethyl 1-{(*E*)-2-[4-(Dimethylamino)phenyl]ethenyl}-9-isoproplyl-6-methylheptalene-4,5-dicarboxylate* ((*E*)-**23b**). As described in *2.2*, with $P(OEt)_3$ (8 ml), iodide **17b** (2.00 g, 4.29 mmol), 2M NaHMDSA (2.4 ml, 4.72 mmol), and 4-(dimethylamino)benzaldehyde (3.20 g, 21.45 mmol). CC (SiO_2, toluene/AcOEt 10:1) gave crystalline (*E*)-**23b** (1.10 g, 56%). For analyses, a small sample was

recrystallized from MeOH. Dark red crystals. M.p. 152.9–153.9°. R_f (toluene/AcOEt 9:1) 0.37. UV/VIS (MeCN): max. 449 (4.355), 340 (4.18), 308 (sh, 4.17), 271 (sh, 4.19), 200 (4.63); min. 375 (4.14), 292 (4.15). IR (KBr): 2958*m*, 1721*s*, 1654*w*, 1603*s*, 1546*m*, 1523*s*, 1483*w*, 1432*m*, 1399*w*, 1363*s*, 1328*w*, 1283*s*, 1256*s*, 1222*m*, 1182*s*, 1168*s*, 1091*m*, 1044*w*, 975*w*, 965*w*, 948*w*, 928*w*, 840*w*, 808*w*, 773*w*, 755*w*. ^{1}H-NMR ($CDCl_3$): 7.65 (*d*, $^3J(2,3) = 6.7$, H–C(3)); 7.27 (*d*-like, 2 arom. H); 6.81 (*d*, $^3J(1',2') = 15.7$, H–C(1′)); 6.64 (*d*-like, 2 arom. H); 6.53 (*d*, $^3J(1',2') = 15.7$, H–C(2′)); 6.36 (*d*, $^3J(7,8) = 6.7$, H–C(8)); 6.33 (*d*, $^3J(2,3) = 6.7$, H–C(2)); 6.27 (*dd*, $^3J(7,8) = 6.5$, $^4J(7, CH_3–C(6)) = 1.1$, H–C(7)); 5.91 (*s*, H–C(10)); 3.82, 3.72 (2*s*, COOMe); 2.98 (*s*, Me_2N); 2.50 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 1.94 (*s*, Me–C(6)); 1.08, 1.06 (*d*, $^3J = 7.0$, 6.9, Me_2CH–C(9)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 167.86, 167.47 (2*s*, COOMe); 150.52 (*s*, arom. C); 148.22 (*s*, C(9)); 144.38 (*s*, C(5a)); 143.63 (*s*, C(1)); 139.56 (*d*, C(3)); 132.88 (*d*, C(2′)); 130.91 (*s*, C(10a)); 128.71 (*s*, C(6)); 128.68 (*s*, arom. C); 128.22 (*d*, arom. C, C(1′)); 127.41 (*d*, C(7)); 127.19 (*d*, C(10)); 125.45 (*d*, C(2)); 125.35 (*d*, C(8)); 124.92 (*s*, C(4)); 123.57 (*s*, C(5)); 112.10 (*d*, arom. C); 51.93 (*q*, COO*Me*); 40.21 (*q*, Me_2N); 35.45 (*d*, Me_2CH–C(9)); 23.08, 22.29 (2*q*, Me_2CH–C(9)); 21.75 (*q*, *Me*–C(6)).

2.6. *Dimethyl 9-Isopropyl-1-[(*E*)-2-(4-methoxyphenyl)ethenyl]-6-methylheptalene-4,5-dicarboxylate* ((*E*)-**22b**). As described in *2.2*, with iodide **17b** (1.30 g, 2.80 mmol), $P(OEt)_3$ (5 ml), 2M NaHMDSA (1.50 ml, 3.10 mmol), and 4-methoxybenzaldehyde (1.90 g, 13.9 mmol). CC (SiO_2, hexane/Et_2O 9:1) gave pure, crystalline (*E*)-**22b** (0.60 g, 48%). A small sample was recrystallized from Et_2O for analyses. Orange-red crystals. M.p. 160.9–162.2°. R_f (hexane/Et_2O 2:1) 0.31. UV/VIS (MeCN): max. *ca.* 411 (sh, 4.04), 367 (sh, 4.23), 330 (4.43), 259 (4.27); min. 279 (4.19). IR (KBr): 2998*w*, 2957*m*, 2833*w*, 1724*s*, 1702*s*, 1641*w*, 1603*m*, 1574*w*, 1551*m*, 1517*w*, 1511*m*, 1461*w*, 1434*m*, 1422*w*, 1400*w*, 1311*w*, 1263*s*, 1221*m*, 1193*m*, 1175*m*, 1157*m*, 1159*m*, 1088*w*, 1048*w*, 1038*m*, 992*w*, 980*w*, 967*w*, 851*w*, 840*w*, 832*w*, 816*w*, 771*w*, 750*w*. ^{1}H-NMR ($CDCl_3$): 7.65 (*d*, $^3J(2,3) = 6.6$, H–C(3)); 7.32 (*d*-like, 2 arom. H); 6.86 (*d*, $^3J(1',2') = 15.9$, H–C(1′)); 6.84 (*d*-like, 2 arom. H); 6.53 (*d*, $^3J(1',2') = 15.8$, H–C(2′)); 6.37 (*d*, $^3J(7,8) = 6.7$, H–C(8)); 6.37 (*d*, $^3J(2,3) = 6.7$, H–C(2)); 6.28 (*dd*, $^3J(7,8) = 6.5$, $^4J(7,Me–C(6)) = 1.1$, H–C(7)); 5.91 (*s*, H–C(10)); 3.81, 3.72 (2*s*, COOMe); 2.51 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 1.95 (*s*, Me–C(6)); 1.08, 1.06 (*d*, $^3J = 7.0$, 6.9, Me_2CH–C(9)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 167.72, 167.35 (2*s*, COOMe); 159.87 (*s*, arom. C); 148.25 (*s*, C(9)); 144.75 (*s*, C(5a)); 142.94 (*s*, C(1)); 139.28 (*d*, C(3)); 131.92 (*d*, C(2′)); 131.70 (*s*, C(10a)); 129.38 (*s*, C(6)); 128.68 (*s*, arom. C); 128.25 (*d*, arom. C); 127.48 (*d*, C(1′)); 127.43 (*d*, C(7)); 127.31 (*d*, C(10)); 126.76 (*d*, C(2)); 125.46 (*d*, C(8)); 125.00 (*s*, C(4)); 123.54 (*s*, C(5)); 114.10 (*d*, arom. C); 55.25 (*q*, MeO); 51.99, 51.96 (2*q*, COO*Me*); 35.44 (*d*, Me_2CH–C(9)); 23.08, 22.27 (2*q*, Me_2CH–C(9)); 21.75 (*q*, *Me*–C(6)). CI-MS (NH_3): 478 (16), 477 (31), 476 (100, $[M+NH_4]^+$), 462 (7), 461 (25), 460 (15), 459 (47, $[M+H]^+$), 429 (15), 428 (22), 427 (79, $[M-MeO]^+$). Anal. calc. for $C_{29}H_{30}O_5$ (458.60): C 75.95, H 6.59; found: C 75.50, H 6.58.

2.7. *Dimethyl 9-Isopropyl-6-methyl-1-[(*E*)-2-(4-nitrophenyl)ethenyl]heptalene-4,5-dicarboxylate* ((*E*)-**21b**). The olefination reaction was performed in analogy to *2.2*, with chloride **13b** (4.37 g, 11.66 mmol), NaI (3.50 g, 23.35 mmol), $P(OEt)_3$ (30 ml), 2M NaHMDSA (6.5 ml, 13 mmol), and 4-nitrobenzaldehyde (8.80 g, 58.30 mmol). CC (*Alox BIV*, *t*BuOMe/hexane 7:3), followed by recrystallization from CH_2Cl_2/Et_2O gave (*E*)-**21b** (2.07 g, 37.5%). Bright red crystal powder. R_f (*Alox N*, Et_2O/hexane) 0.25. UV/VIS (MeCN): max. 419 (sh, 3.89), 361 (4.32), 305 (sh, 4.09); min. 270 (4.01). IR (KBr): 1723*s* and 1708*s* (C=O), 1592*s* and 1510*s* (arom. NO_2). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.16 (*d*-like, $J_o =$ 8.9, H_m of Ar); 7.65 (*d*, $^3J(2,3) = 6.4$, H–C(2)); 7.49 (*d*-like, $J_o = 8.8$, H_o of Ar); 7.10 (*d*, $^3J(1',2') = 15.5$, H–C(1′)); 6.56 (*d*, $^3J(2',1') = 15.8$, H–C(2′)); 6.53 (*d*, $^3J(3,2) = 6.7$, H–C(3)); 6.40 (*d* with f.s., $^3J(8,7) = 6.3$, H–C(8)); 6.31 (*d* with f.s., $^3J(7,8) = 6.5$, H–C(7)); 5.89 (*s*, H–C(10)); 3.74, 3.72 (2*s*, COOMe); 2.55 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 1.97 (*s*, Me–C(6)); 1.09, 1.07 (*t*-like, $J = 6.8$, 6.7, Me_2CH–C(9)). EI-MS: 473 (100, $M^{+\bullet}$), 398 (39), 331 (77, $[M-MeOOC–C\equiv C–COOMe]^+$).

2.8. *Dimethyl 6,8,10-Trimethyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**24b**). As described in *2.7*, with chloride **14b** (0.580 g, 1.61 mmol), NaI (0.483 g, 3.22 mmol), $P(OEt)_3$ (6 ml), 2M NaHMDSA (0.89 ml, 1.77 mmol), and cinnamaldehyde (1.01 ml, 8.05 mmol). CC (SiO_2, hexane/Et_2O 5:1) gave pure, crystalline (1*E*,3*E*)-**24b** (0.350 g, 50%). A sample was recrystallized from Et_2O for analyses. Dark orange crystals. M.p. 183.2–185.5°. R_f (hexane/Et_2O 1:1) 0.48. UV/VIS (MeCN): max. 402 (sh, 4.14), 341 (4.52), 277 (4.22); min. 382 (4.22), 259 (4.15). IR (KBr): 3021*w*, 2946*m*, 2910*w*, 1719*s*, 1643*w*, 1596*w*, 1550*w*, 1511*m*, 1434*m*, 1398*w*, 1374*w*, 1300*m*, 1254*s*, 1201*m*, 1157*w*, 1145*w*,

1087*m*, 1053*m*, 995*m*, 915*w*, 892*m*, 843*w*, 773*m*, 752*w*, 691*w*, 615*w*. ^{1}H-NMR ($CDCl_3$): 7.64 (*d*, $^3J(2,3) = 6.4$, H–C(3)); 7.39–7.21 (*m*, 5 arom. H); 6.84 (*dd*, $^3J(3',4') = 15.5$, $^3J(2',3') = 10.7$, H–C(3′)); 6.55 (*d*, $^3J(3',4') = 15.5$, H–C(4′)); 6.49 (*d*, $^3J(1',2') = 15.0$, H–C(1′)); 6.45 (*d*, $^3J(2,3) = 6.8$, H–C(2)); 6.21 (*s*, H–C(9)); 6.18 (*dd*, $^3J(1',2') = 14.9$, $^3J(2',3') = 10.7$, H–C(2′)); 6.12 (*s*, H–C(7)); 3.48, 3.46 (2*s*, COOMe); 2.14 (*d*, ^4J(7,Me–C(6)) = 1.0, Me–C(6)); 1.83 (*d*, ^4J(9,Me–C(8)) = 1.0, Me–C(8)); 1.58 (*s*, Me–C(10)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 167.66, 167.42 (2*s*, *C*OOMe); 146.49 (*s*); 142.22 (*s*); 139.70 (*s*); 138.58 (*d*, C(3)); 136.90 (*s*); 135.02 (*d*, C(9)); 132.70 (*d*, C(1′)); 131.93 (*s*); 131.73 (*d*, C(3′)); 130.83 (*s*); 130.83 (*s*); 130.83 (*d*, C(4′)), 129.25 (*d*, C(7)); 128.69 (*d*, arom. C); 128.60 (*d*, arom. C); 127.87 (*d*, C(2), C(2′)); 126.39 (*d*, arom. C); 123.16 (*d*, C(4)); 119.98 (*d*, C(5)); 52.02, 51.85 (2*q*, COO*Me*); 25.08 (*q*, *Me*–C(8)); 21.63 (*q*, *Me*–C(6)); 18.57 (*q*, *Me*–C(10)). EI-MS: 441 (30, $[M+H]^+$), 440 (100, $M^{+\bullet}$), 393 (27), 381 (18, $[M-COOMe]^+$), 349 (35), 331 (17), 321 (36), 304 (26), 291 (28), 277 (14), 228 (44), 215 (26), 202 (25), 196 (27), 189 (34), 165 (27), 152 (22), 115 (36), 91 (48). Anal. calc. for $C_{29}H_{28}O_4$ (440.50): C 79.07, H 6.41; found: C 78.43, H 6.15.

The structure of (1*E*,3*E*)-**24b** was confirmed by an X-ray crystal-structure analysis (*Fig. 6* and *Tables 2* and *7*).

2.9. *Dimethyl 1-[(1*E*,3*E*)-4-(4-Methoxyphenyl)buta-1,3-dien-1-yl]-6,8,10-trimethylheptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**25b**). As described in *2.7*, with **14b** (4.00 g, 11.08 mmol), NaI (3.32 g, 22.16 mmol), $P(OEt)_3$ (30 ml), 2M NaHMDSA (6.1 ml, 12.19 mmol), and 4-methoxycinnamaldehyde (8.98 g, 55.4 mmol). CC (SiO_2, hexane/Et_2O 5:1) gave crystalline (1*E*,3*E*)-**25b** (2.60 g, 50%). A sample for analyses was recrystallized from Et_2O. Orange crystals. M.p. 188.5–190.4°. R_f (hexane/Et_2O 1:1) 0.47. IR (KBr): 3016*w*, 2948*w*, 2909*w*, 1718*s*, 1708*s*, 1605*w*, 1580*w*, 1546*w*, 1508*s*, 1439*m*, 1399*w*, 1374*w*, 1302*m*, 1252*s*, 1200*m*, 1172*m*, 1158*w*, 1142*w*, 1106*w*, 1090*m*, 1054*w*, 1036*w*, 983*m*, 962*w*, 851*w*, 830*w*, 812*w*, 801*w*, 774*m*. ^{1}H-NMR ($CDCl_3$): 7.64 (*d*, $^3J(2,3) = 6.4$, H–C(3)); 7.32 (*d*-like, 2 arom. H); 6.86 (*d*-like, 2 arom. H); 6.72 (*dd*, $^3J(3',4') = 15.5$, $^3J(2',3') = 10.8$, H–C(3′)); 6.51 (*d*, $^3J(3',4') = 15.6$, H–C(4′)); 6.45 (*d*, $^3J(1',2') = 15.1$, H–C(1′)); 6.43 (*d*, $^3J(2,3) = 6.4$, H–C(2)); 6.21 (*d*, ^4J(9,Me–C(8)) = 1.6, H–C(9)); 6.18 (*dd*, $^3J(1',2') = 15.0$, $^3J(2',3') = 10.7$, H–C(2′)); 6.12 (*s*, H–C(7)); 3.81 (*s*, MeO); 3.72, 3.69 (2*s*, COOMe); 2.10 (*d*, ^4J(7,Me–C(6)) = 1.0, Me–C(6)); 1.89 (*d*, ^4J(9,Me–C(8)) = 1.1, Me–C(8)); 1.63 (*s*, Me–C(10)).

The structure of (1*E*,3*E*)-**25b** was confirmed by an X-ray crystal-structure analysis (*Tables 2* and *7*).

2.10. *Dimethyl 1-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-6,8,10-trimethylheptalene-4,5-dicarboxylate* ((*E*)-**26b**). As described in *2.7*, with **14b** (3.70 g, 10.3 mmol), NaI (3.07 g, 20.5 mmol), $P(OEt)_3$ (20 ml), 2M NaHMDSA (5.7 ml, 11.3 mmol), and 4-methoxybenzaldehyde (7.01 g, 51.5 mmol). CC (SiO_2, hexane/Et_2O 5:1) gave crystalline (*E*)-**26b** (2.03 g, 44%). A sample for analyses was recrystallized from Et_2O. Orange crystals. M.p. 167.1–168.2°. R_f (hexane/Et_2O 1:1) 0.28. UV/VIS (MeCN): max. *ca.* 402 (sh, 3.99), 332 (4.35), 307 (sh, 4.27), 270 (4.27); min. 277 (4.21), 254 (4.19). IR (KBr): 2947*w*, 2911*w*, 2837*w*, 1707*s*, 1642*w*, 1604*m*, 1574*w*, 1550*w*, 1511*s*, 1434*m*, 1397*w*, 1373*w*, 1302*m*, 1252*s*, 1195*m*, 1174*s*, 1156*w*, 1086*w*, 1052*w*, 1031*w*, 968*w*, 841*w*, 820*w*, 776*w*, 766*w*, 571*w*. ^{1}H-NMR ($CDCl_3$): 7.66 (*d*, $^3J(2,3) = 6.3$, H–C(3)); 7.32 (*d*-like, 2 arom. H); 6.83 (*d*-like, 2 arom. H); 6.81 (*d*, $^3J(1',2') = 15.5$, H–C(1′)); 6.49 (*d*, $^3J(2,3) = 6.4$, H–C(2)); 6.32 (*d*, $^3J(1',2') = 15.7$, H–C(2′)); 6.21 (*s*, H–C(9)); 6.12 (*s*, H–C(7)); 3.80 (*s*, MeO); 3.72, 3.69 (2*s*, COOMe); 2.10 (*d*, ^4J(7,Me–C(6)) = 1.1, Me–C(6)); 1.88 (*d*, ^4J(9,Me–C(8)) = 1.1, Me–C(8)); 1.64 (*s*, Me–C(10)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 167.70, 167.49 (2*s*, COOMe); 159.81 (*s*, MeO–C_{ar}); 146.41 (*s*); 142.38 (*s*); 139.62 (*s*); 138.75 (*d*, C(3)); 131.90 (*s*); 131.64 (*d*, C(9)); 131.16 (*s*); 130.85 (*s*); 130.06 (*d*, C(1′)); 129.56 (*s*); 129.21 (*d*, C(7)); 128.19 (*d*, arom. C); 127.05 (*d*, C(2)); 125.45 (*d*, C(2′)); 123.08 (*d*, C(4)); 120.04 (*d*, C(5)); 114.07 (*d*, arom. C); 55.26 (*q*, MeO); 52.00, 51.83 (2*q*, COO*Me*); 25.07 (*q*, *Me*–C(8)); 21.53 (*q*, *Me*–C(6)); 18.59 (*q*, *Me*–C(10)).

3. *Syntheses of π(2)-Substituted Heptalene-5- and -1-carboxylates.* 3.1. *Methyl 4-Formyl-9-isopropyl-1,6-dimethylheptalene-5-carboxylate* (**8b**). To furanone **7b** [11] (2.40 g, 7.10 mmol) in dry toluene (200 ml) at −78°, 1M DIBAH in hexane (7.8 ml, 7.8 mmol) was slowly added through a syringe (TLC monitoring). After all of the DIBAH soln. had been added, TLC showed, beside **8b**, the presence of small amounts of starting material and two by-products, possibly the corresponding 4-methanol and 4,5-dimethanol. The dark yellow mixture was poured on pre-cooled MeOH (10 ml). The cooling bath was removed and the mixture poured into H_2O under vigorous stirring until a yellow jelly was formed. Et_2O was added, the mixture acidified with conc. HCl soln., and the product extracted with Et_2O. The extract was washed with H_2O, dried (Na_2SO_4) and concentrated, and the residue purified by CC (SiO_2, hexane/Et_2O 4:1): **8b**

(1.72 g, 78%). Dark yellow oil. R_f (hexane/Et_2O 2:1) 0.21. ^{1}H-NMR ($CDCl_3$): 9.37 (*s*, CHO–C(4)); 7.09 (*d*, ^3J(2,3) = 6.0, H–C(3)); 6.30 (*dd*, ^3J(2,3) = 6.1, ^4J(2,Me–C(1)) = 1.4, H–C(2)); 6.25 (*d*, ^3J(7,8) = 6.4, H–C(8)); 6.13 (*dd*, ^3J(7,8) = 6.5, ^4J(7,Me–C(6)) = 1.1, H–C(7)); 5.87 (*s*, H–C(10)); 3.71 (*s*, COOMe); 2.46 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 2.12 (*s*, Me–C(1)); 2.00 (*s*, Me–C(6)); 1.08, 1.04 (2*d*, ^3J = 6.9, 6.8, Me_2CH–C(9)).

3.2. *Methyl 7-Isopropyl-5,10-dimethyl-2-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-1-carboxylate* ((1*E*,3*E*)-**27a**) *and Methyl 9-Isopropyl-1,6-dimethyl-4-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-5-carboxylate* ((1*E*,3*E*)-**27b**) via Wittig *Reaction*. Aldehyde **8b** (0.50 g, 1.61 mmol) and cinnamyltriphenylphosphonium bromide (2.22 g, 4.84 mmol) were added under N_2 to a vigorously stirred mixture of CH_2Cl_2 (100 ml) and 2N aq. NaOH (100 ml). Stirring was continued during 2 h at r.t. The emulsion was then neutralized with conc. HCl soln., the aq. phase extracted with CH_2Cl_2 (3×), the extract dried (Na_2SO_4) and concentrated, and the residue subjected to CC (SiO_2, hexane/Et_2O 7:1): (1*Z*,3*E*)-**27b**/(1*Z*,3*E*)-**27a**/(1*E*,3*E*)-**27a**/(1*E*,3*E*)-**27b** 6.5:2.7:2.2:1 (by ^{1}H-NMR). TLC (hexane/AcOEt 9:1): R_f 0.55 ((1*E*,3*E*)-**27a**), 0.49 ((1*Z*,3*E*)-**27a**), 0.45 ((1*E*,3*E*)- and (1*Z*,3*E*)-**27b**). This dark yellow mixture (0.20 g, 31%) was dissolved in hexane/Et_2O 1:1 (20 ml), and trace amounts of I_2 were added. The soln. was stirred at r.t. during 10 h. The solvent was removed by distillation and the residue subjected to CC (SiO_2, hexane/Et_2O 5:1): pure (1*E*,3*E*)-**27a**/(1*E*,3*E*)-**27b** 2.23:1 (at r.t. (by ^{1}H-NMR); 0.13 g, 19%). Yellow oil.

*Data of (1*E*,3*E*)-***27a***: R_f: see above. UV/VIS (4% ^{i}PrOH/hexane; see Fig. 3 in [1]): max. *ca.* 425 (sh, 0.04), *ca.* 350 (sh, 0.94), 332 (1.00); min. 258 (0.39). ^{1}H-NMR ($CDCl_3$; taken from the thermal-equilibrium mixture with (1*E*,3*E*)-**27b**): 7.64 (*d*, ^3J(1′,2′) = 15.4, H–C(1′)); 7.45–7.19 (*m*, 5 arom. H); 6.99 (*dd*, ^3J(3′,4′) = 15.5, ^3J(2′,3′) = 10.6, H–C(3′)); 6.79 (*d*, ^3J(3,4) = 12.1, H–C(4)); 6.68 (*d*, ^3J(3′,4′) = 15.5, H–C(4′)); 6.52 (*d*, ^3J(3,4) = 12.0, H–C(3)); 6.39 (*d*, ^3J(8,9) = 11.9, H–C(9)[15]); 6.33 (*d*, ^3J(8,9) = 11.9, H–C(8))[15]); 5.80 (*s*, H–C(6)); 3.65 (*s*, MeOOC–C(1)); 2.56 (*sept.*, ^3J = 6.9, Me_2CH–C(7)); 1.78 (*s*, Me–C(5)); 1.68 (*s*, Me–C(10)); 1.14, 1.12 (2*d*, ^3J = 6.8, Me_2CH–C(7)).

*Data of (1*E*,3*E*)-***27b***: R_f: see above. UV/VIS (4% ^{i}PrOH/hexane; see Fig. 3 in [1]): max. *ca.* 465 (sh, 0.04), *ca.* 374 (sh, 0.53), 332 (1.00), 268 (0.61); min. 285 (0.56), 255 (0.59). ^{1}H-NMR ($CDCl_3$; recognizable signals in the thermal equilibrium mixture with (1*E*,3*E*)-**27a**): 6.08–6.04 (*m*, 2 H); 5.78 (*s*, H–C(10)); 3.63 (*s*, MeOOC–C(5)); 2.42 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 1.98 (*s*, Me–C(1)); 1.92 (*s*, Me–C(6)); 1.02, 0.98 (2*d*, ^3J = 7.2, 6.8, Me_2CH–C(9)).

3.3. *Methyl 7-Isopropyl-5,10-dimethyl-2-[(*E*)-2-(4-nitrophenyl)ethenyl]-heptalene-1-carboxylate* ((*E*)-**28a**) *and Methyl 9-Isopropyl-1,6-dimethyl-4-[(*E*)-2-(4-nitrophenyl)ethenyl]heptalene-5-carboxylate* ((*E*)-**28b**). As described in *3.2*, with **8b** (1.40 g, 4.51 mmol), (4-nitrobenzyl)triphenylphosphonium bromide (4.32 g, 9.0 mmol), CH_2Cl_2 (300 ml), and 2N aq. NaOH (300 ml). After 1 h, additional phosphonium bromide (4.32 g, 9.0 mmol) was added. This procedure was repeated three times. Then the emulsion was worked up according to *3.2*. CC (SiO_2, hexane/Et_2O 7:1) gave a mixture (*Z*)-**28a**/(*Z*)-**28b**/(*E*)-**28a**/(*E*)-**28b** and two not identified by-products (0.30 g). A (*Z*) → (*E*) isomerization with a cat. amount of I_2 in hexane/Et_2O could not be realized. However, CC delivered a small amount of pure (*E*)-**28a** (0.020 g, 1%) as an orange oil, which rapidly formed at r.t. the equilibrium mixture with (*E*)-**28b**; ratio 1.67:1 (by ^{1}H-NMR).

*Data of (*E*)-***28a***: R_f (hexane/Et_2O 1:1) 0.50. UV/VIS (hexane/CH_2Cl_2): max. 421 (sh, 0.09), 349 (1.00), 279 (0.78); min. 304 (0.68), 252 (0.71). ^{1}H-NMR ($CDCl_3$; taken from the thermal equilibrium mixture with (*E*)-**28b**): 8.30 (*d*, ^3J(1′,2′) = 16.3, H–C(1′)); 8.20 (*d*-like, 2 arom. H); 7.64 (*d*-like, 2 arom. H); 6.92 (*d*, ^3J(1′,2′) = 16.3, H–C(2′)); 6.80 (*d*, ^3J(3,4) = 11.9, H–C(3)); 6.60 (*d*, ^3J(3,4) = 11.8, H–C(4)); 6.42 (*d*, ^3J(8,9) = 11.9, H–C(8)); 6.36 (*d*, ^3J(8,9) = 12.0, H–C(9)); 5.81 (*s*, H–C(6)); 3.67 (*s*, MeOOC–C(1)); 2.57 (*sept.*, ^3J = 6.8, Me_2CH–C(7)); 1.80 (*s*, Me–C(5)); 1.70 (*s*, Me–C(10)); 1.22 (*d*, ^3J = 7.0, Me_2CH–C(7)).

*Data of (*E*)-***28b***: R_f (hexane/Et_2O 1:1) 0.40. UV/VIS (hexane/CH_2Cl_2): max. 500–350 (tailing), 350 (1.00); min. 300 (0.56). ^{1}H-NMR ($CDCl_3$; taken from the thermal equilibrium mixture with (*E*)-**28a**): 8.13 (*d*-like, 2 arom. H); 7.45 (*d*-like, 2 arom. H); 6.92 (*d*, ^3J(1′,2′) = 16.3, H–C(1′)); 6.60 (*d*, ^3J(2,3) = 7.2, H–C(3)); 6.45 (*d*, ^3J(1′,2′) = 16.3, H–C(2′)); 6.33 (*d*, ^3J(2,3) = 7.2, H–C(8)[15])); 6.18 (*m*, H–C(2),

[15]) The chemical shifts of H–C(8) and H–C(9) or of H–C(7) and H–C(8) could be inverse.

H–C(7)[15])); 5.88 (*s*, H–C(10)); 3.68 (*s*, MeOOC–C(5)); 2.50 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.08 (*s*, Me–C(1)); 2.02 (*s*, Me–C(6)); 1.15, 1.12 (*d*, $^3J = 6.9$, 7.0, Me_2CH–C(9)).

3.4. *Methyl 7-Isopropyl-5,10-dimethyl-2-[(*E*)-4-phenylbut-3-en-1-yn-1-yl]heptalene-1-carboxylate* ((*E*)-**31a**) *and Methyl 9-Isopropyl-1,5-dimethyl-4-[(*E*)-4-phenylbut-3-en-1-yn-1-yl]heptalene-5-carboxylate* ((*E*)-**31b**). 3.4.1. *Methyl 2-(2,2-Dibromoethenyl)-7-isopropyl-5,10-dimethylheptalene-1-carboxylate* (**29a**) *and Methyl 4-(2,2-Dibromoethenyl)-9-isopropyl-1,6-dimethylheptalen-5-carboxylate* (**29b**). To a soln. of Ph_3P (2.2 g, 8.4 mmol) in CH_2Cl_2 at 0°, a soln. of CBr_4 (1.44 g, 4.5 mmol) in CH_2Cl_2 (5 ml) was added drop by drop (→ yellow soln.). Aldehyde **8b** (1.00 g, 3.20 mmol) in CH_2Cl_2 (5 ml) was slowly added to this soln. The mixture was stirred for one additional hour at 0° and then poured on H_2O. The aq. phase was extracted with Et_2O (3×), the combined extract washed with aq. sat. NaCl soln., dried (Na_2SO_4), and concentrated, and the residue subjected to CC (SiO_2, hexane): thermodynamically controlled mixture **29a**/**29b** (0.90 g, 60%). Yellow oil. R_f (hexane/Et_2O 4:1) 0.92 (**29a**) and 0.79 (**29b**).

3.4.2. *Methyl 2-Ethynyl-7-isopropyl-5,10-dimethylheptalene-1-carboxylate* (**30a**) *and Methyl 4-Ethynyl-9-isopropyl-1,6-dimethylheptalene-5-carboxylate* (**30b**). To a soln. of **29a**/**29b** (0.770 g, 1.65 mmol) in THF (10 ml) under Ar in a flame-dry flask cooled to −78°, 1.6M BuLi in hexane (2.4 ml, 3.84 mmol) was added drop by drop through a syringe. The dark brown mixture was stirred for additional 10 min at −78° and then poured into H_2O under vigorous stirring. The aq. phase was extracted with Et_2O (3×). The combined org. extract was washed with sat. aq. NaCl soln., dried (Na_2SO_4), and concentrated, and the residue subjected to CC (SiO_2, hexane/Et_2O 9:1): thermodynamically controlled mixture **30a**/**30b** 1.27:1 (0.240 g, 48%). Yellow oil.

Data of **30a**: R_f (hexane/Et_2O 4:1) 0.48. ^{1}H-NMR ($CDCl_3$; taken from the thermal-equilibrium mixture with **30b**): 6.47 (*d*, $^3J(3,4) = 11.5$, H–C(3)); 6.43 (*d*, $^3J(3,4) = 11.5$, H–C(4)); 6.39 (*d*, $^3J(8,9) = 11.4$, H–C(8)); 6.34 (*d*, $^3J(8,9) = 11.4$, H–C(9)); 5.75 (*s*, H–C(6)); 3.69 (*s*, MeOOC–C(1)); 3.46 (*s*, HC≡C–C(2)); 2.55 (*sept.*, $^3J = 6.8$, Me_2CH–C(7)); 1.75 (*d*, $^5J(6,\text{Me–C}(5)) = 0.7$, Me–C(5)); 1.64 (*s*, Me–C(10)); 1.14, 1.13 (2*d*, $^3J = 6.9$, 7.0, Me_2CH–C(7)).

Data of **30b**: R_f (hexane/Et_2O 4:1) 0.41. ^{1}H-NMR ($CDCl_3$; taken from the thermal equilibrium mixture with **30a**): 6.75 (*d*, $^3J(2,3) = 6.4$, H–C(3)); 6.22 (*d*, $^3J(7,8) = 6.6$, H–C(8)); 6.12 (*dq*-like, $^3J(7,8) = 6.5$, $^4J(7,\text{Me–C}(6)) = 1.1$, H–C(7)); 6.04 (*dq*-like, $^3J(2,3) = 6.4$, $^4J(2,\text{Me–C}(1)) = 1.4$, H–C(2)); 5.81 (*s*, H–C(10)); 3.76 (*s*, MeOOC–C(5)); 2.98 (*s*, HC≡C–C(4)); 2.48 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.06 (*s*, Me–C(1)); 1.99 (*s*, Me–C(6)); 1.11, 1.07 (2*d*, $^3J = 7.0$, 6.8, Me_2CH–C(9)).

3.4.3 Heck *Reaction of* **30a**/**30b** *with [(*E*)-2-Iodoethenyl]benzene.* At r.t. under N_2, a mixture of [(*E*)-2-iodoethenyl]benzene (0.167 g, 0.73 mmol), [$Pd(PPh_3)_4$] (0.090 g, 0.078 mmol), CuI (0.028 g, 0.15 mmol), ^{i}BuNH$_2$ (0.146 ml, 1.46 mmol), and DMF (0.7 ml) was prepared. Then, a soln. of **30a**/**30b** (0.100 g, 0.33 mmol) in DMF (0.7 ml) was added under stirring. Afterwards, the mixture was stirred during 20 h at r.t. The mixture was diluted with H_2O and extracted several times with Et_2O, the combined Et_2O extract washed with sat. aq. NaCl soln., dried (Na_2SO_4), and concentrated, and the dark brown residue subjected to CC (SiO_2, hexane/Et_2O 9:1): pure, thermodynamically controlled mixture (*E*)-**31a**/(*E*)-**31b** 1.08:1 (0.104 g, 76%). Yellow oil.

*Data of (*E*)-***31a***:* R_f (hexane/Et_2O 4:1) 0.48. UV/VIS (hexane/CH_2Cl_2): max. 420 (sh) 320, 283 (sh); min. 250. ^{1}H-NMR ($CDCl_3$; taken from the thermal equilibrium mixture with (*E*)-**31b**): 7.43–7.24 (*m*, 5 arom. H); 7.07 (*d*, $^3J(3'',4'') = 16.2$, H–C(3″)); 6.46 (*d*, $^3J(3,4) = 11.0$, H–C(3)); 6.44 (*d*, $^3J(3,4) = 11.0$, H–C(4)); 6.43 (*d*, $^3J(4'',3'') = 16.2$, H–C(4″)); 6.40 (*d*, $^3J(8,9) = 11.8$, H–C(8)); 6.35 (*d*, $^3J(8,9) = 11.9$, H–C(9)); 5.83 (*s*, H–C(6)); 3.71 (*s*, MeOOC–C(1)); 2.56 (*sept.*, $^3J = 6.9$, Me_2CH–C(7)); 1.76 (*d*, $^5J(5,6) = 0.6$, Me–C(5)); 1.66 (*s*, Me–C(10)); 1.14, 1.13 (2*d*, $^3J = 6.9$, 7.1, Me_2CH–C(7)).

*Data of (*E*)-***31b***:* R_f (hexane/Et_2O 4:1) 0.39. UV/VIS (hexane/CH_2Cl_2): max. *ca.* 400 (sh), 332, 264; min. 285, 250. ^{1}H-NMR ($CDCl_3$; taken from the thermal equilibrium mixture with (*E*)-**31a**): 7.43–7.24 (*m*, 5 arom. H); 6.86 (*d*, $^3J(3'',4'') = 16.2$, H–C(3″)); 6.69 (*d*, $^3J(2,3) = 6.0$, H–C(3)); 6.24 (*d*, $^3J(4'',3'') = 16.3$, H–C(4″)); 6.23 (*d*, $^3J(7,8) = 6.5$, H–C(8)); 6.13 (*dq*-like, $^3J(7,8) = 6.5$, $^4J(7,\text{Me–C}(6)) = 1.2$, H–C(7)); 6.07 (*dq*-like, $^3J(2,3) = 6.4$, $^4J(2,\text{Me–C}(1)) = 1.4$, H–C(2)); 5.76 (*s*, H–C(10)); 3.79 (*s*, MeOOC–C(5)); 2.48 (*sept.*, $^3J = 6.9$, Me_2CH–C(9)); 2.07 (*s*, Me–C(1)); 2.00 (*s*, Me–C(6)); 1.11, 1.08 (2*d*, $^3J = 7.2$; 6.8, Me_2CH–C(9)).

3.5. *Methyl 7-Isopropyl-5,10-dimethyl-2-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-1-carboxylate* ((1*E*,3*E*)-**27a**) *and Methyl 9-Isopropyl-1,6-dimethyl-4-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]hepta-*

lene-5-carboxylate ((1*E*,3*E*)-**27b**) via Heck *Reaction*. 3.5.1. *With [(*E*)-2-Iodoethenyl]benzene*. 3.5.1.1. *Methyl 2-Ethenyl-7-isopropyl-5,10-dimethylheptalene-1-carboxylate* (**32a**) *and 4-Ethenyl-9-isopropyl-1,6-dimethylheptalene-5-carboxylate* (**32b**). To a soln. of **8b** (0.100 g, 0.32 mmol) in THF (10 ml) under Ar in a flame-dried flask cooled to −78°, 1M *Tebbe*'s reagent in toluene (0.32 ml, 0.32 mmol) was added through a syringe. The temp. was then raised within 6 h to 0°, and the mixture was poured into H_2O. The aq. phase was extracted with Et_2O (3×) the combined extract treated as usual, and the residue subjected to CC (SiO_2, hexane/Et_2O 9:1): thermodynamically controlled mixture **32a**/**32b** 1.86:1 (by ^{1}H-NMR; 0.019 g, 19%). Dark yellow oil.

Data of **32a**: R_f (hexane/Et_2O 4:1) 0.45. ^{1}H-NMR ($CDCl_3$; taken from the thermal equilibrium mixture with **31b**): 7.43 (*dd*, $^3J_{trans}$(1″,2″) = 17.6, $^3J_{cis}$(1″,2″) = 11.0, H–C(1″)); 6.62 (*d*, ^3J(3,4) = 11.9, H–C(3)); 6.44 (*d*, ^3J(3,4) = 11.9, H–C(4)); 6.32 (*d*, ^3J(8,9) = 11.5, H–C(8)); 6.25 (*d*, ^3J(8,9) = 11.8, H–C(9)); 5.70 (*s*, H–C(6)); 5.47 (*dd*, $^3J_{trans}$(1″,2″) = 17.6, ^2J(2″,2″) = 1.3, H_{cis}–C(2″)); 5.32 (*dd*, $^3J_{cis}$(1″,2″) = 11.0, ^2J(2″,2″) = 1.3, H_{trans}–C(2″)); 3.56 (*s*, MeOOC–C(1)); 2.48 (*sept.*, ^3J = 6.8, Me_2CH–C(7)); 1.69 (*s*, Me–C(5)); 1.60 (*s*, Me–C(10)); 1.06 (*d*, ^3J = 7.0, Me_2CH–C(7)).

Data of **32b**: R_f (hexane/Et_2O 4:1) 0.38. ^{1}H-NMR ($CDCl_3$; taken from the thermal equilibrium mixture with **32a**): 6.32 (*d*, ^3J(2,3) = 6.8, H–C(3)); 6.28 (*dd*, $^3J_{trans}$(1″,2″) = 17.5, $^3J_{cis}$(1″,2″) = 10.8, H–C(1″)); 6.19 (*d*, ^3J(7,8) = 6.5, H–C(8)); 6.05 (*dq*-like, ^3J(7,8) = 6.8, ^4J(7,Me–C(6)) = 1.3, H–C(7)); 6.03 (*dq*-like, ^3J(2,3) = 6.8, ^4J(2,Me–C(1)) = 1.4, H–C(2)); 5.76 (*s*, H–C(10)); 5.32 (*d*, $^3J_{cis}$(1″,2″) = 11.0, H_{trans}–C(2″)); 5.02 (*d*, $^3J_{trans}$(1″,2″) = 17.6, H_{cis}–C(2″)); 3.62 (*s*, MeOOC–C(5)); 2.41 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 1.97 (*s*, Me–C(1)); 1.91 (*s*, Me–C(6)); 1.01, 0.98 (2*d*, ^3J = 6.9, 6.8, Me_2CH–C(9)).

3.5.1.2. Heck *Reaction.* A mixture **32a**/**32b** (0.100 g, 0.35 mmol), [(*E*)-2-iodoethenyl]benzene (0.243 g, 1.05 mmol), [$Pd(OAc)_2$] (7.8 mg, 0.035 mmol), and Ag_2CO_3 (0.096 g, 0.35 mmol) in DMF (1 ml) was stirred under N_2 at r.t. during 12 h. The mixture was then poured into H_2O and the product isolated as usual (see *2.2*): thermodynamically controlled mixture (1*E*,3*E*)-**27a**/(1*E*,3*E*)-**27b** (0.102 g, 71%).

3.5.2. *With Styrene.* 3.5.2.1. *Methyl 2-[(*E*)-2-Iodoethenyl]-7-isopropyl-5,10-dimethylheptalene-1-carboxylate* ((*E*)-**33a**) *and Methyl 4-[(*E*)-2-Iodoethenyl]-9-isopropyl-1,6-dimethylheptalene-5-carboxylate* ((*E*)-**33b**). To a suspension of $CrCl_2$ (0.315 g, 2.56 mmol) in THF (8 ml) at r.t. under Ar, CHI_3 (0.252 g, 0.64 mmol) was added. To the dark brown mixture (*cf.* [16]), aldehyde **8b** (0.100 g, 0.32 mmol) was added. After 30 min stirring at r.t., the mixture was poured into H_2O and extracted with Et_2O (5×). The product was isolated in the usual manner. CC (SiO_2, hexane/Et_2O 7:1) gave a pure, thermodynamically controlled mixture (*E*)-**33a**/(*E*)-**33b** 1.5:1 (0.230 g, 60%). Yellow oil.

*Data of (*E*)-***33a***:* R_f (hexane/Et_2O 2:1) 0.79. ^{1}H-NMR ($CDCl_3$; taken from the thermal equilibrium mixture with (*E*)-**33b**): 8.25 (*d*, ^3J(1″,2″) = 14.9, H–C(1″)); 6.71 (*d*, ^3J(1″,2″) = 14.8, H–C(2″)); 6.49 (*d*, ^3J(3,4) = 11.9, H–C(3)); 6.44 (*d*, ^3J(3,4) = 12.0, H–C(4)); 6.31 (*d*, ^3J(8,9) = 11.4, H–C(8)); 6.26 (*d*, ^3J(8,9) = 11.2, H–C(9)); 5.70 (*s*, H–C(6)); 3.57 (*s*, MeOOC–C(1)); 2.48 (*sept.*, ^3J = 6.8, Me_2CH–C(7)); 1.68 (*s*, Me–C(5)); 1.58 (*s*, Me–C(10)); 1.06 (*d*, ^3J = 6.9, Me_2CH–C(7)).

*Data of (*E*)-***33b***:* R_f (hexane/Et_2O 2:1) 0.65. ^{1}H-NMR ($CDCl_3$; taken from the thermal-equilibrium mixture with (*E*)-**33a**): 6.98 (*d*, ^3J(1″,2″) = 14.9, H–C(1″)); 6.25 (*d*, ^3J(2,3) = 7.0, H–C(3)); 6.19 (*d*, ^3J(7,8) = 6.3, H–C(8)); 6.13 (*d*, ^3J(1″,2″) = 14.9, H–C(2″)); 6.05 (*d*, ^3J(7,8) = 6.5, H–C(7)); 6.00 (*d*, ^3J(2,3) = 6.4, H–C(2)); 5.77 (*s*, H–C(10)); 3.64 (*s*, MeOOC–C(5)); 2.42 (*sept.*, ^3J = 6.8, Me_2CH–C(9)); 1.95 (*s*, Me–C(1)); 1.90 (*s*, Me–C(6)); 1.02, 0.99 (2*d*, ^3J = 6.9, 6.8, Me_2CH–C(9)).

3.5.2.2. Heck *Reaction*. The mixture (*E*)-**33a**/(*E*)-**33b** (0.060 g, 0.14 mmol), styrene (0.044 g, 0.42 mmol), [$Pd(OAc)_2$] (3.1 mg, 0.014 mmol), and Ag_2CO_3 (0.039 g, 0.14 mmol) in DMF (0.5 ml) was stirred under N_2 at r.t. during 12 h. The isolation of the product was performed as described: thermodynamically controlled mixture of (1*E*,3*E*)-**27a**/(1*E*,3*E*)-**27b** (0.031 g, 54%). Yellow oil.

4. *Syntheses of the π(1),π(2)-Substituted Heptalene-1- and -5-carboxylates.* 4.1. *Methyl 7-Isopropyl-10-methyl-2,5-bis[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-1-carboxylate* ((all-*E*)-**1a**) *and Methyl 9-Isopropyl-6-methyl-1,4-bis[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-5-carboxylate* ((all-*E*)-**1b**). 4.1.1. *5-Methyl Hydrogen 9-Isopropyl-6-methyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**34b**). To a soln. of (1*E*,3*E*)-**16b** (2.50 g, 5.50 mmol) in MeOH (200 ml), a soln. of LiOH (5.00 g, 0.119 mol) in H_2O (30 ml) was added, and the mixture was heated at 70° during 2 h. After cooling, the mixture was acidified to pH 1 with 6N aq. HCl soln. One half of the MeOH was distilled off, whereby the product precipitated. It was filtered and washed with H_2O and then dried at 50° under h.v.:

(1*E*,3*E*)-**34b** (2.20 g, 88%). Yellow powder. M.p. 152.7–154.3° (dec. under formation of the cyclic anhydride). R_f (CH_2Cl_2/MeOH 9:1) 0.43. UV/VIS (MeCN): max. 402 (sh), 335, 270; min. 284, 261. IR (KBr): 3022*m*, 2957*m*, 2868*w*, 1732*s*, 1678*s*, 1593*w*, 1580*w*, 1548*w*, 1513*m*, 1434*m*, 1383*w*, 1363*w*, 1348*w*, 1304*s*, 1286*s*, 1238*m*, 1212*m*, 1195*m*, 1167*m*, 1145*m*, 1066*m*, 1039*w*, 993*m*, 816*w*, 784*m*, 761*m*, 748*m*, 690*m*, 670*w*, 626*w*. ^{1}H-NMR ($CDCl_3$): 7.71 (*d*, $^3J(2,3) = 6.6$, H–C(3)); 7.40–7.20 (*m*, 5 arom. H); 6.84 (*dd*, $^3J(3',4') = 15.4$, $^3J(2',3') = 10.5$, H–C(3′)); 6.58 (*d*, $^3J(3',4') = 15.5$, H–C(4′)); 6.56 (*d*, $^3J(1',2') = 14.9$, H–C(1′)); 6.42 (*dd*, $^3J(1',2') = 14.9$, $^3J(2',3') = 10.4$, H–C(2′)); 6.37 (*d*, $^3J(2,3) = 6.6$, H–C(2)); 6.35 (*d*, $^3J(7,8) = 6.5$, H–C(8)); 6.28 (*d*, $^3J(7,8) = 6.5$, H–C(7)); 5.88 (*s*, H–C(10)); 3.71 (*s*, COOMe); 2.51 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 1.96 (*s*, Me–C(6)); 1.09, 1.07 (2*d*, $^3J = 6.7$, Me_2CH–C(9)); signal of COO*H* not recognizable. ^{13}C-NMR ($CDCl_3$; tentative assignment): 172.12 (*s*, COOH); 167.63 (*s*, *C*OOMe); 148.27 (*s*, C(9)); 144.98 (*s*, C(5a)); 143.66 (*s*, C(1)); 140.86 (*d*, C(3)); 136.82 (*s*, arom. C); 135.61 (*d*, C(3′)); 133.47 (*d*, C(1′)); 133.36 (*d*, C(2′)); 131.24 (*s*, C(10a)); 128.73 (*s*, C(6)); 128.63 (*d*, arom. C); 128.51 (*d*, C(4′)); 128.01 (*d*, arom. C); 127.65 (*d*, C(2)); 127.53 (*d*, C(7), C(10)); 126.47 (*d*, arom. C); 125.60 (*d*, C(8)); 124.92 (*s*, C(4)); 123.50 (*s*, C(5)); 52.10 (*q*, COO*Me*); 35.40 (*d*, Me_2CH–C(9)); 23.11, 22.24 (2*q*, Me_2CH–C(9)); 21.78 (*q*, *Me*–C(6)). EI-MS: 440 (16, $M^{+\cdot}$), 409 (20, $[M - MeO]^+$), 408 (20, $[M - MeOH]^{+\cdot}$), 366 (22), 365 (100, $[M - (CO_2 + MeO)]^+$), 337 (26), 293 (14), 291 (17), 281 (12), 135 (19), 91 (11).

4.1.2. *8-Isopropyl-1,1-dimethoxy-11-methyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)heptaleno[4,5-c]furan-3(1*H*)-one* ((1*E*,3*E*)-**35b**). In analogy to our earlier experiments (*cf.* [11]), (1*E*,3*E*)-**34b** (0.130 g, 0.29 mmol) was treated with oxalyl chloride (0.081 g, 0.64 mmol) and DMF (0.143 g, 1.95 mmol) in MeCN, followed by addition of MeOH (0.12 ml, 4 mmol). After workup, CC (SiO_2, hexane/Et_2O 5:1) furnished (1*E*,3*E*)-**35b** (0.110 g, 81%). A sample for analyses was recrystallized from Et_2O. Dark brown crystals. M.p. 180.2–180.7°. R_f (hexane/Et_2O 1:1) 0.57. UV/VIS (MeCN): max. 462 (4.01), 365 (sh, 4.34), 336 (4.42), 282 (4.26); min. 442 (4.01), 298 (4.24), 264 (4.18). IR (KBr): 3022*w*, 2954*m*, 2870*w*, 2841*w*, 1760*s*, 1640*s*, 1609*w*, 1597*w*, 1554*w*, 1495*m*, 1461*m*, 1446*w*, 1400*w*, 1365*w*, 1286*m*, 1250*m*, 1230*w*, 1199*w*, 1176*w*, 1162*w*, 1134*m*, 1088*w*, 1060*w*, 1010*w*, 990*m*, 922*m*, 882*w*, 860*w*, 845*w*, 810*w*, 780*w*, 768*w*, 746*w*, 690*w*, 660*w*. ^{1}H-NMR ($CDCl_3$): 7.40 (*d*, $^3J(4,5) = 7.1$, H–C(4)); 7.34–7.21 (*m*, 5 arom. H); 6.86 (*dd*, $^3J(3',4') = 15.4$, $^3J(2',3') = 9.8$, H–C(3′)); 6.69 (*dd*, $^3J(1',2') = 14.8$, $^3J(2',3') = 9.8$, H–C(2′)); 6.63 (*d*, $^3J(3',4') = 15.4$, H–C(4′)); 6.60 (*d*, $^3J(1',2') = 14.8$, H–C(1′)); 6.47 (*d*, $^3J(4,5) = 7.0$, H–C(5)); 6.36 (*dd*, $^3J(9,10) = 6.6$, $^4J(7,9) = 1.3$, H–C(9)); 6.23 (*d*, $^3J(9,10) = 6.6$, H–C(10)); 5.76 (*d*, $^4J(7,9) = 0.9$, H–C(7)); 3.46, 3.16 (2*s*, 2 MeO–C(1)); 2.47 (*sept.*, $^3J = 6.8$, Me_2CH–C(8)); 2.19 (*s*, Me–C(4)); 1.05, 1.04 (2*d*, $^3J = 6.8$, Me_2CH–C(8)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 167.85 (*s*, C(3)=O); 150.43 (*s*, C(8)); 138.31 (*s*, C(6)); 136.82 (*s*, arom. C); 135.93 (*d*, C(4)); 135.77 (*s*, C(11a)); 133.74 (*d*, C(3′)); 133.29 (*d*, C(1′)); 132.71 (*d*, C(2′)); 132.42 (*s*, C(6a)); 130.20 (*d*, C(4′)); 129.99 (*d*, C(5)); 129.40 (*d*, arom. C); 128.73 (*s*, C(11)); 128.64 (*d*, arom. C); 128.49 (*d*, C(10)); 128.22 (*s*, C(3a)); 128.07 (*d*, C(7)); 126.49 (*d*, arom. C); 124.68 (*d*, C(9)); 118.96 (*s*, C(1)); 52.53, 50.69 (2*q*, *Me*O–C(1)); 35.78 (*d*, Me_2CH–C(8)); 23.11, 23.06 (*q*, Me_2CH–C(8)); 22.40 (*q*, *Me*–C(11)). CI-MS (NH_3): 459 (8), 458 (13), 457 (44), 456 (32, $[M + H]^+$), 455 (100, $M^{+\cdot}$).

4.1.3. *Methyl 4-Formyl-9-isopropyl-6-methyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-5-carboxylate* ((1*E*,3*E*)-**36b**). As described in *3.1*, with (1*E*,3*E*)-**35b** (3.40 g, 7.50 mmol) and 1M DIBAH (7.5 ml, 7.5 mmol) in toluene: (1*E*,3*E*)-**36b** (2.30 g, 72%). A sample for analyses was recrystallized from Et_2O. Red crystals. M.p. 138.4–140.0°. R_f (hexane/Et_2O 1:1) 0.29. UV/VIS (MeCN): max. 416 (sh, 4.24), 371 (sh, 4.35), 340 (4.44), 274 (4.16); min. 287 (4.13), 262 (4.13). IR (KBr): 3025*w*, 2995*w*, 2955*m*, 2868*w*, 2819*w*, 2722*w*, 1721*s*, 1642*w*, 1595*w*, 1548*w*, 1507*s*, 1462*w*, 1448*w*, 1431*m*, 1417*m*, 1384*w*, 1363*w*, 1334*w*, 1277*s*, 1258*m*, 1236*m*, 1210*m*, 1192*m*, 1140*w*, 1120*m*, 1062*m*, 1051*m*, 992*m*, 914*w*, 891*w*, 847*w*, 822*w*, 792*w*, 750*m*, 693*w*, 613*w*. ^{1}H-NMR ($CDCl_3$): 9.42 (*s*, CHO); 7.39 (*d*, $^3J(2,3) = 7.1$, H–C(3)); 7.34–7.21 (*m*, 5 arom. H); 6.85 (*dd*, $^3J(3',4') = 15.6$, $^3J(2',3') = 10.2$, H–C(3′)); 6.62 (*d*, $^3J(3',4') = 15.6$, H–C(4′)); 6.58 (*d*, $^3J(1',2') = 15.0$, H–C(1′)); 6.48 (*dd*, $^3J(1',2') = 15.0$, $^3J(2',3') = 10.0$, H–C(2′)); 6.46 (*d*, $^3J(2,3) = 6.7$, H–C(2)); 6.35 (*d*, $^3J(7,8) = 6.6$, H–C(8)); 6.28 (*dq*-like, $^3J(7,8) = 6.5$, $^4J(7,\text{Me–C(6)}) = 0.9$, H–C(7)); 5.88 (*s*, H–C(10)); 3.73 (*s*, COOMe); 2.50 (*sept.*, $^3J = 6.8$, Me_2CH–C(9)); 1.98 (*s*, Me–C(6)); 1.08, 1.05 (2*d*, $^3J = 6.7$, 6.6, Me_2CH–C(9)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 191.97 (*s*, CHO); 167.66 (*s*, *C*OOMe); 148.34 (*s*, C(9)); 147.30 (*d*, C(3)); 145.10 (*s*, C(5a)); 144.30 (*s*, C(1)); 140.25 (*s*, C(10a)); 136.71 (*s*, arom. C); 136.20 (*d*, C(3′)); 134.13 (*d*, C(1′)); 133.38 (*d*, C(2′)); 129.09 (*s*, C(6)); 128.65 (*d*, arom. C,

C(4′)); 128.38 (*d*, C(7), C(10)); 128.16 (*d*, C(2)); 128.12 (*d*, arom. C); 126.54 (*d*, arom. C); 125.71 (*d*, C(8)); 125.15 (*s*, C(4)); 122.68 (*s*, C(5)); 52.13 (*q*, COO*Me*); 35.40 (*d*, Me_2*C*H–C(9)); 23.07, 22.18 (*q*, *Me*$_2$CH–C(9)); 21.82 (*q*, *Me*–C(6)). CI-MS (NH_3): 442 (32, $[M+NH_4]^+$), 427 (23), 426 (32), 425 (100, $[M+H]^+$). Anal. calc. for $C_{29}H_{28}O_3$ (424.54): C 82.05, H 6.65; found: C 82.25, H 6.77.

4.1.5. *Formation of (all-*E*)-***1a***/(all-*E*)-***1b*** via the Corresponding [(*E*)-2-Iodoethenyl]heptalene.* As described in *3.5.2.1*, with $CrCl_2$ (0.231 g, 1.88 mmol), THF (10 ml), CHI_3 (0.185 g, 0.46 mmol), and (1*E*,3*E*)-**36b** (0.100g, 0.23 mmol). The combined Et_2O extract was dried (Na_2SO_4) and concentrated. DMF (0.5 ml) was added under N_2 to the orange oily residue, followed by styrene (0.073 g, 0.70 mmol), [$Pd(AcO)_2$] (5.3 mg, 0.023 mmol), and Ag_2CO_3 (0.065 g, 0.23 mmol). The mixture was stirred during 12 h at r.t. and then poured into H_2O. The mixture was extracted with Et_2O, the extract concentrated, and the residue subjected to CC (SiO_2, hexane/Et_2O 7:1): thermodynamically controlled mixture (all-*E*)-**1a**/(all-*E*)-**1b** 1:3.6 (by ^{1}H-NMR) (0.053 g, 43%). Dark orange oil. In later experiments, we succeeded in the crystallization of the main DBS isomer (all-*E*)-**1b** from Et_2O/hexane[16]).

*Data of (all-*E*)-***1a***:* R_f (hexane/Et_2O 3:1) 0.48. UV/VIS (4% ^{i}PrOH/hexane; *Fig. 1*; taken from [1]): max. 440 (sh, 0.03), 380 (sh, 0.58), 343 (1.00), 280 (sh, 0.45); min. 258 (0.33). ^{1}H-NMR ($CDCl_3$; recognizable signals; taken from the thermal-equilibrium mixture with (all-*E*)-**1b**): 6.01 (*s*, H–C(6)); 3.64 (*s*, COOMe); 2.63 (*sept.*, ^3J = 6.9, Me_2*C*H–C(7)); 1.73 (*s*, Me–C(10)); 1.20, 1.19 (2*d*, ^3J = 7.1, 6.8, *Me*$_2$CH–C(7)).

*Data of (all-*E*)-***1b***:* Red-orange crystals. M.p. 97–107°. R_f (hexane/Et_2O 3:1) 0.27. UV/VIS (4% ^{i}PrOH/hexane; *Fig. 1*; taken from [1]): max. 440 (0.88), 359 (1.00), 261 (0.63); min. 397 (0.73), 295 (0.46). ^{1}H-NMR ($CDCl_3$; taken from the thermal-equilibrium mixture with (all-*E*)-**1a**): 7.45–7.19 (*m*, 10 arom. H); 6.84 (*dd*, ^3J(3′,4′) = 15.4, ^3J(2′,3′) = 10.6, H–C(3′)); 6.79 (*dd*, ^3J(3″,4″) = 14.7, ^3J(2″,3″) = 9.8, H–C(3″)); 6.62 (*d*, ^3J(2,3) = 7.0, H–C(3)); 6.52 (*d*-like, H–C(4″), H–C(4′), H–C(1′)); 6.43–6.31 (*m*, H–C(2), H–C(1″), H–C(2″), H–C(2), H–C(8), H–C(2′)); 6.28 (*d*, ^3J(7,8) = 6.4, H–C(7)); 5.88 (*s*, H–C(10)); 3.71 (*s*, COOMe); 2.52 (*sept.*, ^3J = 6.9, Me_2*C*H–C(9)); 1.97 (*s*, Me–C(6)); 1.08, 1.06 (*d*, ^3J = 7.0, 6.9, *Me*$_2$CH–C(9)).

4.2. *Methyl 7-Isopropyl-2-[(1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-10-methyl-5-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-1-carboxylate* ((all-*E*)-**40a**) *and Methyl 9-Isopropyl-4-[(1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-6-methyl-1-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-5-carboxylate* ((all-*E*)-**40b**). 4.2.1. *5-Methyl Hydrogen 9-Isopropyl-6-methyl-1-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**37b**). To a soln. of diester (1*E*,3*E*)-**19b** (2.00 g, 4.00 mmol) in MeOH (152 ml) and $ClCH_2CH_2Cl$ (50 ml), LiOH (4.00 g, 95.3 mmol) in H_2O (20 ml) was introduced and the mixture heated under reflux during 6 h. Additional LiOH (1.00 g, 23.8 mmol) was added and refluxing continued for 8 h. The mixture was kept during 12 h at 4° and the $ClCH_2CH_2Cl$ phase, which contained still some diester, separated. The aq. phase was acidified with conc. HCl soln. until pH 1 was attained. MeOH (100 ml) was added and the solvent slowly distilled off until the product precipitated. After storage during 4 h in a refrigerator, the compound was filtered and dried during 2 h at 50° under h.v.: *(1*E*,3*E*)-***37b*** (1.20 g, 62%). Red powder. M.p. 213.5–232.5° (dec. under formation of the cyclic anhydride). R_f (CH_2Cl_2/MeOH 9:1) 0.51. IR (KBr): 3418*m*, 2958*m*, 2625*w*, 1715*s*, 1589*m*, 1548*w*, 1515*s*, 1435*m*, 1417*m*, 1338*s*, 1269*s*, 1162*m*, 1109*m*, 1044*m*, 990*m*, 890*w*, 864*m*, 828*w*, 814*w*, 788*w*, 764*w*, 747*m*, 689*w*, 629*w*. ^{1}H-NMR ($CDCl_3$): 8.17 (*d*-like, 2 arom. H); 7.71 (*d*, ^3J(2,3) = 6.6, H–C(3)); 7.50 (*d*-like, 2 arom. H); 7.00 (*dd*, ^3J(3′,4′) = 15.4, ^3J(3′,4′) = 10.8, H–C(3′)); 6.67 (*d*, ^3J(1′,2′) = 15.0, H–C(1′)); 6.61 (*d*, ^3J(3′,4′) = 15.6, H–C(4′)); 6.43 (*d*, ^3J(2,3) = 6.7, H–C(2)); 6.42 (*dd*, ^3J(1′,2′) = 14.9, ^3J(2′,3′) = 10.8, H–C(2′)); 6.39 (*d*, ^3J(7,8) = 6.5, H–C(8)); 6.29 (*d*, ^3J(7,8) = 6.5, H–C(7)); 5.87 (*s*, H–C(10)); 3.71 (*s*, COOMe); 2.51 (*sept.*, ^3J = 6.8, Me_2*C*H–C(9)); 1.97 (*s*, Me–C(6)); 1.09, 1.07 (2*d*, ^3J = 6.7, 6.6, *Me*$_2$CH–C(9)). ^{13}C-NMR ($CDCl_3$): 171.83 (*s*, COOH); 167.50 (*s*, *C*OOMe); 148.32 (*s*, C(9)); 146.79 (*s*, arom. C); 145.25 (*s*, C(5a)); 143.27 (*s*, arom. C); 142.97 (*s*, C(1)); 140.52 (*d*, C(3)); 136.38 (*d*, C(1′)); 132.84 (*d*, C(3′)); 132.63 (*d*, C(4′)); 132.00 (*s* + *d*, C(10a)), C(2′)); 129.18 (*d*, C(2)); 128.71 (*s*, C(6)); 127.93 (*d*, C(10)); 127.76 (*d*, C(7)); 126.73 (*d*, arom. C); 125.75 (*d*, C(8)); 124.51 (*s*, C(5)); 124.05 (*d*, arom. C); 123.55 (*s*, C(4)); 52.14 (*q*, COO*Me*); 35.38 (*d*, Me_2*C*H–C(9)); 23.08, 22.22 (2*q*,

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[16]) We thank Dr. *Stefan Rosenberger* for the synthesis of a larger amount of (all-*E*)-**1a** and (all-*E*)-**1b**, which allowed the crystallization of (all-*E*)-**1b**.

Me$_2$CH–C(9)); 21.77 (*q*, *Me*–C(6)). CI-MS (NH_3): 518 (11), 517 (36), 474 (9), 473 (35), 472 (30), 471 (100, $[(M+NH_4)-MeOH]^+$), 470 (11), 469 (30), 454 (14, $[(M+1)-MeOH]^+$), 441 (8, $[M-CO_2]^+$), 424 (9).

4.2.2. *8-Isopropyl-1,1-dimethoxy-11-methyl-6-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptaleno[4,5-c]furan-3(1*H*)-one* ((1*E*,3*E*)-**38b**). Acid (1*E*,3*E*)-**37b** (1.10 g, 2.27 mmol) was treated with oxalyl chloride (0.87 g, 6.81 mmol) and DMF (1.08 g, 14.76 mmol) in MeCN, followed by addition of MeOH (0.94 ml, 31.3 mmol). CC (SiO_2, hexane/Et_2O 5:1) furnished (1*E*,3*E*)-**38b** as a dark brown powder, which was contaminated with diester (1*E*,3*E*)-**19a**. The two compounds could not be separated (in total 0.80 g; yield of (1*E*,3*E*)-**38b** >70%). *(1*E*,3*E*)-**38b**: R_f (hexane/Et_2O 1:1): 0.55. ^{1}H-NMR ($CDCl_3$): 8.17 (*d*-like, 2 arom. H); 7.50 (*d*-like, 2 arom. H); 7.30 (*d*, $^3J(4,5)=6.9$, H–C(4)); 6.99 (*dd*, $^3J(3',4')=15.3$, $^3J(2',3')=9.8$, H–C(3′)); 6.70–6.63 (*m*, H–C(2′), H–C(1′), H–C(4′)); 6.54 (*d*, $^3J(4,5)=6.9$, H–C(5)); 6.37 (*d*, $^3J(9,10)=6.5$, H–C(9)); 6.25 (*d*, $^3J(9,10)=6.8$, H–C(10)); 5.74 (*d*, $^4J(7,9)=1.1$, H–C(7)); 3.47, 3.16 (*s*, 2 MeO–C(1)); 2.48 (*sept.*, $^3J=6.9$, Me_2CH–C(8)); 2.20 (*s*, Me–C(4)); 1.05, 1.04 (*d*, $^3J=6.8$, *Me*$_2$CH–C(8)).

4.2.3. *Methyl 4-Formyl-9-isopropyl-6-methyl-1-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-5-carboxylate* ((1*E*,3*E*)-**39b**). As described in *3.1*, with (1*E*,3*E*)-**38b** (0.75 g, 1.50 mmol, contaminated with diester (1*E*,3*E*)-**19b**) and 2M DIBAH (0.75 ml, 1.5 mmol) in toluene (80 ml) and CH_2Cl_2. CC (SiO_2; hexane/CH_2Cl_2 2:1) yielded a *ca.* 2:1 mixture (0.50 g, corresponding to 47% yield of the formyl compound) of (1*E*,3*E*)-**39b** and the corresponding lactone, as a result of the partial reduction of the diester; the two compounds were not separated. *(1*E*,3*E*)-**39b**: R_f (hexane/Et_2O 1:1) 0.25. ^{1}H-NMR ($CDCl_3$; taken from the mixture with the lactone): 9.44 (*s*, CHO); 8.19–8.15 (*d*-like, 2 arom. H); 7.51 (*d*-like, 2 arom. H); 7.26 (*d*, $^3J(2,3)=6.4$, H–C(3)); 6.99 (*dd*, $^3J(3',4')=15.2$, $^3J(3',4')=10.6$, H–C(3′)); 6.69 (*d*, $^3J(1',2')=14.7$, H–C(1′)); 6.59 (*d*, $^3J(3',4')=15.6$, H–C(4′)); 6.54 (*d*, $^3J(2,3)=6.6$, H–C(2)); 6.47 (*dd*, $^3J(1',2')=14.6$, $^3J(2',3')=8.9$, H–C(2′)); 6.37 (*d*, $^3J(7,8)=6.5$, H–C(8)); 6.30 (*dq*-like, $^3J(7,8)=6.5$, $^4J(7,Me–C(6))=1.2$, H–C(7)); 5.87 (*s*, H–C(10)); 3.74 (*s*, COOMe); 2.50 (*sept.*, $^3J=6.9$, Me_2CH–C(9)); 1.99 (*s*, Me–C(6)); 1.09, 1.06 (*d*, $^3J=6.7$, 6.6, *Me*$_2$CH–C(9)).

4.2.4. *Formation of the Thermodynamically Controlled Mixture (all-*E*)-***40a***/(all-*E*)-***40b***.* As described in *3.5.2.1* and *4.1.5* with (1*E*,3*E*)-**39b**/lactone (0.160 g, 0.68 mmol), $CrCl_2$ (0.334 g, 2.72 mmol), CHI_3 (0.268 g, 0.68 mmol) in THF, 4-methoxystyrene (0.137 g, 1.02 mmol), $[Pd(AcO)_2]$ (7.6 mg, 0.034 mmol), and Ag_2CO_3 (0.093 g, 0.34 mmol) in DMF. CC (SiO_2, hexane/CH_2Cl_2 3:1) gave (all-*E*)-**40a**/(all-*E*)-**40b** (0.030 g, 16%), as a red oil showing some impurities. It was not further purified.

*Data of (all-*E*)-***40a***:* R_f (hexane/Et_2O 1:1) 0.50. UV/VIS (hexane/CH_2Cl_2; *Fig. 19*): max. *ca.* 500 (sh, 0.08), 405 (sh, 0.83), 377 (1.00), 298 (0.76); min. 317 (0.73), 248 (0.43).

*Data of (all-*E*)-***40b***:* R_f (hexane/Et_2O 1:1) 0.41. UV/VIS (hexane/CH_2Cl_2; *Fig. 19*): max. 477 (1.00), 378 (0.81), 300 (0.53); min. 415 (0.73), 263 (0.50).

4.3. *Methyl 7-Isopropyl-5-[(1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-10-methyl-2-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-1-carboxylate* ((all-*E*)-**68a**) *and Methyl 9-Isopropyl-6-methyl-1-[(1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-4-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-5-carboxylate* ((all-*E*)-**68b**). 4.3.1. *5-Methyl Hydrogen 9-Isopropyl-6-methyl-1-[(1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate* ((1*E*,3*E*)-**65b**). As described in *4.1.1*, with diester (1*E*,3*E*)-**20b** (2.30 g, 4.73 mmol) and LiOH (4.68 g, 111 mmol) in boiling MeOH/H_2O 6.5:1: (1*E*,3*E*)-**65b** (1.85 g, 83%). Orange powder.

4.3.2. *8-Isopropyl-1,1-dimethoxy-6-[(1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-11-methylheptaleno[4,5-c]furan-3(1*H*)-one* ((1*E*,3*E*)-**66b**). As described in *4.1.2*, with acid (1*E*,3*E*)-**65b** (1.50 g, 3.19 mmol), oxalyl chloride (0.52 ml, 6.06 mmol), DMF (1.60 ml, 20.72 mmol), and MeOH (0.39 ml, 9.6 mmol). Recrystallization from Et_2O/hexane 1:1 gave (1*E*,3*E*)-**66b** (0.991 g, 64%). Red crystals. M.p. 178–179°.

4.3.3. *Methyl 4-Formyl-9-isopropyl-1-[(1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-6-methylheptalene-5-carboxylate* ((1*E*,3*E*)-**67b**). As described in *3.1*, with furanone (1*E*,3*E*)-**66b** (0.524 g, 1.08 mmol), toluene (8 ml), and 2M DIBAH (0.54 ml, 1.08 mmol). CC (SiO_2, hexane/Et_2O 5:1) gave (1*E*,3*E*)-**67b** (0.390 g, 85%). Red crystals. R_f (Et_2O/hexane) 0.19.

4.3.4. *Formation of the Thermodynamically Controlled Mixture (all-*E*)-***68a***/(all-*E*)-***68b***.* As described in *3.5.2.1* and *4.1.5*, with aldehyde (1*E*,3*E*)-**67b** (0.390 g, 0.875 mmol), CHI_3 (0.689 g, 1.75 mmol), and

$CrCl_2$ (0.860 g, 7.00 mmol) in THF (→4-(2-iodoethenyl) derivative (*ca.* 0.500 g, 0.87 mmol)); then with DMF (2 ml), 4-nitrostyrene (0.396 g, 2.63 mmol), $[Pd(OAc)_2]$ (0.020 g, 0.088 mmol), and Ag_2CO_3 (0.241 g, 0.87 mmol). CC (SiO_2, hexane/CH_2Cl_2 3:1) gave (all-*E*)-**68b** (0.129 g, 25%) as dark red crystals. Dissolved at r.t. in $CDCl_3$, a thermodynamically controlled mixture of 15% (all-*E*)-**68a** and 85% (all-*E*)-**68b** was obtained.

*Data of (*all-E*)*-**68a**: UV/VIS (hexane/CH_2Cl_2; *Fig. 18*): max. *ca.* 450 (sh, 0.06), *ca.* 375 (sh, 0.92), 361 (1.00); min. 274 (0.28). ^{1}H-NMR ($CDCl_3$, 600 MHz; recognizable signals in the presence of 85% of (all-*E*)-**68b**): 8.19 (*d*, J_o = 8.8, H_m of Ar″); 7.55 (*d*, J_o = 8.8, H_o of Ar″); 7.35 (*d*, J_o = 8.8, H_o of Ar′); 6.89 (*d*, J_o = 8.7, H_m of Ar′); 7.13 (*dd*, ^3J(3″,4″) = 15.5, ^3J(3″,2″) = 10.8, H–C(3″)); 6.80 (*dd*, ^3J(3′,4′) = 15.6, ^3J(3′,2′) = 10.9, H–C(3′)); 6.53 (*d*, ^3J(4′,3′) = 15.6, H–C(4′)); 6.01 (*s*, H–C(6)); 3.813 (*s*, MeOOC–C(1)); 3.65 (*s*, MeO–C_p of Ar′); 2.63 (*sept.*, ^3J = 6.8, Me_2CH–C(7)); 1.72 (*s*, Me–C(10)); 1.190, 1.187 (2*d*, ^3J = 6.8, 6.9, Me_2CH–C(7)).

*Data of (*all-E*)*-**68b**: R_f (Et_2O/hexane 3:2) 0.32. UV/VIS (hexane/CH_2Cl_2; *Fig. 18*): max. 468 (1.00), 401 (sh, 0.71), 356 (sh, 0.65), 322 (0.56); min. 264 (0.43). ^{1}H-NMR ($CDCl_3$, 600 MHz; assignable signals in the presence of 15% of (all-*E*)-**68a**): 8.15 (*d*, J_o = 8.8, 2 H_m of Ar″); 7.46 (*d*, J_o = 8.8, 2 H_o of Ar″); 7.32 (*d*, J_o = 8.8, 2 H_o of Ar′); 6.93 (*dd*, ^3J(3″,4″) = 15.4, ^3J(3″,2″) = 10.6, H–C(3″)); 6.84 (*d*, J_o = 8.8, 2 H_m of Ar′); 6.71 (*dd*, ^3J(3′,4′) = 15.4, ^3J(3′,2′) = 10.7, H–C(3′)); 6.67 (*d*, ^3J(3,2) = 7.0, H–C(3)); 6.52 (*d*, ^3J(1′,2′) = 15.3, H–C(1′)); 6.49 (*d*, ^3J(4′,3′) = 15.5, H–C(4′)); 6.39 (*d*, ^3J(8,7) = 6.6, H–C(8)); 6.27 (*dq*-like, ^3J(7,8) = 6.5, ^4J(7,Me–C(6)) = 1.1, H–C(7)); 6.30 (*d*, ^3J(2,3) = 7.0, H–C(2)); 3.81 (*s*, MeOOC–C(5)); 3.72 (s, MeO–C_p of Ar′); 2.52 (*sept.*, ^3J = 6.8, Me_2CH–C(9)); 1.97 (*s*, Me–C(6)); 1.08, 1.07 (2*d*, ^3J = 6.9, 6.8, Me_2CH-C(9)). Residual signals in the range of δ(H) 6.87–6.30 could not be assigned due to too much overlap.

4.4. *Methyl 5-{(*E*)-2-[4-(Dimethylamino)phenyl]ethenyl}-7-isopropyl-10-methyl-2-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-1-carboxylate* ((all-*E*)-**44a**) *and Methyl 1-{(*E*)-2-[4-(Dimethylamino)phenyl]ethenyl}-9-isopropyl-6-methyl-4-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-5-carboxylate* ((all-*E*)-**44b**). 4.4.1. *5-Methyl Hydrogen 1-{(*E*)-2-[4-(Dimethylamino)phenyl]ethenyl}-9-isopropyl-6-methyl-heptalene-4,5-dicarboxylate* ((*E*)-**41b**). As described in *4.1*, with diester (*E*)-**23b** (1.00 g, 2.12 mmol) and LiOH (2.00 g, 44.66 mmol) in a MeOH (76 ml) and H_2O (10 ml) (4 h reflux). After cooling, CH_2Cl_2 was added and the mixture neutralized with conc. HCl soln. under vigorous stirring until the mixture turned red. The CH_2Cl_2 phase was separated, filtered, and dried (Na_2SO_4), and concentrated. CC (SiO_2, hexane/Et_2O 1:2 → AcOEt/MeOH 9:1) of the residue gave (*E*)-**41b** (0.500 g, 52%). Dark red powder. M.p. 122.9–124.3° (dec. under formation of the cyclic anhydride). R_f (CH_2Cl_2/MeOH 9:1) 0.44. UV/VIS (MeCN): max. 442 (4.26), 335 (4.24), 269 (sh, 4.15), 236 (sh, 4.22), 199 (4.60); min. 371 (4.06), 289 (4.13). IR (KBr): 3424*w*, 2957*m*, 1716*s*, 1647*s*, 1600*s*, 1523*s*, 1432*m*, 1364*s*, 1330*m*, 1255*s*, 1222*s*, 1182*s*, 1165*s*, 1040*m*, 967*w*, 975*w*, 945*w*, 926*w*, 868*w*, 812*m*, 787*w*. ^{1}H-NMR ($CDCl_3$): 7.72 (*d*, ^3J(2,3) = 6.6, H–C(3)); 7.28 (*d*-like, 2 arom. H); 6.82 (*d*, ^3J(1′,2′) = 15.7, H–C(1′)); 6.68–6.65 (*d*-like, 2 arom. H); 6.55 (*d*, ^3J(1′,2′) = 15.7, H–C(2′)); 6.36 (*d*, ^3J(7,8) = 6.4, H–C(8)); 6.33 (*d*, ^3J(2,3) = 6.6, H–C(2)); 6.26 (*dq*-like, ^3J(7,8) = 6.4, ^4J(7,Me–C(6)) = 1.1, H–C(7)); 5.91 (*s*, H–C(10)); 3.70 (*s*, COOMe); 2.98 (*s*, Me_2N); 2.50 (*sept.*, ^3J = 6.8, Me_2CH–C(9)); 1.94 (*s*, Me–C(6)); 1.08, 1.06 (2*d*, ^3J = 7.0, 6.9, Me_2CH–C(9)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 171.97 (*s*, COOH); 167.81 (*s*, *C*OOMe); 159.60 (*s*, arom. C); 150.60 (*s*, C(9)); 148.20 (*s*, C(5a)); 144.50 (*s*, C(1)); 141.25 (*d*, C(3)); 133.37 (*d*, C(2′)); 131.95 (*s*, C(10a)); 130.13 (*s*, C(6)); 128.72 (*s*, arom. C); 128.32 (*d*, arom. C); 127.54 (*d*, C(7)); 127.36 (*d*, C(10)); 127.3 (*d*, C(1′)); 125.37 (*d*, C(2)); 124.89 (*d*, C(8)); 124.76 (*s*, C(4)); 123.54 (*s*, C(5)); 112.13 (*d*, arom. C); 52.04 (*q*, COO*Me*); 40.22 (*q*, Me_2N); 35.43 (*d*, Me_2CH–C(9)); 23.07, 22.28 (2*q*, Me_2CH–C(9)); 21.72 (*q*, *Me*–C(6)).

4.4.2. *6-{(*E*)-2-[4-(Dimethylamino)phenyl]ethenyl}-8-isopropyl-1,1-dimethoxy-11-methylheptaleno[4,5-c]furan-3(1*H*)-one* ((*E*)-**42b**). In analogy to our earlier experiments (*cf.* [11]), acid (*E*)-**41b** (0.300 g, 0.66 mmol) was treated with oxalyl chloride (0.250 g, 1.97 mmol) and DMF (0.314 g, 4.29 mmol) in MeCN, followed by addition of MeOH (0.27ml, 32 mmol). After workup, CC (SiO_2, hexane/Et_2O 5:1) furnished (*E*)-**42b** (0.280 g, 90%). A sample for analyses was recrystallized from Et_2O. Black-brown crystals. M.p. 171.7–173.3°. R_f (hexane/Et_2O 1:1) 0.65. UV/VIS (MeCN): max. 507 (4.26), 438 (sh, 4.15), 285 (4.26), 245 (4.24), 200 (4.56); min. 382 (4.02), 324 (4.10), 263 (4.19), 233 (4.21). IR (KBr): 2953*w*, 1753*s*, 1610*m*, 1587*s*, 1551*m*, 1524*s*, 1481*s*, 1434*m*, 1402*w*, 1362*s*, 1332*w*, 1288*s*, 1249*m*, 1222*m*, 1202*m*,

1183*s*, 1164*s*, 1136*s*, 1063*m*, 1015*w*, 965*w*, 948*w*, 920*m*, 870*w*, 844*w*, 811*m*, 780*w*, 660*w*. ^{1}H-NMR ($CDCl_3$): 7.32–7.28 (*m*, 2 arom. H, H–C(4)); 6.88, 6.82 (*AB*, $^3J_{AB}$ = 15.7, H–C(1′), H–C(2′)); 6.64 (*d*-like, 2 arom. H); 6.45 (*d*, ^3J(4,5) = 6.8, H–C(5)); 6.34 (*d*, ^3J(9,10) = 6.1, H–C(10)); 6.21 (*d*, ^3J(9,10) = 6.3, H–C(9)); 5.80 (*s*, H–C(7)); 3.44, 3.16 (2*s*, 2 MeO–C(1)); 2.98 (*s*, Me_2N); 2.46 (*sept.*, ^3J = 6.8, Me_2C*H*–C(8)); 2.16 (*s*, Me–C(11)); 1.04 (*d*, ^3J = 6.7, *Me*$_2$CH–C(8)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 168.20 (*s*, C(3) = O); 150.66 (*s*, arom. C)); 150.24 (*s*, C(8)); 139.37 (*s*, C(6)); 134.81 (*s*, C(11a)); 133.71 (*d*, C(4)); 132.85 (*s*, C(6a)); 132.42 (*d*, C(2′)); 129.83 (*d*, C(10)); 129.76 (*d*, C(7)); 128.62 (*s*, C(11)); 128.48 (*d*, arom. C, C(1′)); 127.50 (*s*, C(3a)); 127.16 (*d*, C(5)); 124.91 (*s*, arom. C); 124.59 (*d*, C(9)); 118.95 (*s*, C(1)); 112.11 (*d*, arom. C); 52.50, 50.64 (2*q*, *Me*O–C(1)); 40.20 (*q*, Me_2N); 35.81 (*d*, Me_2*C*H–C(8)); 23.07, 22.95 (2*q*, *Me*$_2$CH–C(8)); 22.45 (*q*, *Me*–C(11)). EI-MS: 472 (15, $[M+H]^+$), 471 (100, $M^{+\bullet}$), 428 (22), 369 (12), 338 (12), 310 (25), 266 (14), 265 (22), 219 (49), 189 (34), 154 (24), 134 (44), 120 (16).

4.4.3. *Methyl 1-[(*E*)-2-[4-(Dimethylamino)phenyl]ethenyl]-4-formyl-9-isopropyl-6-methylheptalene-5-carboxylate* ((*E*)-**43b**). As described in *3.1*, with furanone (*E*)-**42b** (0.250 g, 0.53 mmol) and 1M DIBAH (6.4 ml, 6.4 mmol) in toluene. CC (SiO_2, hexane/Et_2O 4:1) gave (*E*)-**43b** (0.175 g, 75%). A sample for analyses was recrystallized from Et_2O. Dark red crystals. M.p. 178.9–182.1°. R_f (hexane/Et_2O 1:1) 0.26. UV/VIS (MeCN): max. 473 (4.356), 315 (4.17), 271 (4.197), 201 (4.60); min. 376 (4.06), 296 (4.14), 252 (4.186). IR (KBr): 2958*w*, 2806*w*, 1716*s*, 1677*s*, 1599*s*, 1523*s*, 1423*m*, 1365*s*, 1328*m*, 1303*w*, 1277*m*, 1256*m*, 1224*m*, 1206*w*, 1182*s*, 1124*m*, 1062*m*, 976*w*, 946*w*, 916*w*, 902*w*, 830*w*, 810*w*, 794*w*. ^{1}H-NMR ($CDCl_3$): 9.40 (*s*, CHO); 7.30 (*d*-like, 2 arom. H); 7.25 (*d*, ^3J(2,3) = 6.6, H–C(3)); 6.84 (*d*, ^3J(1′,2′) = 15.6, H–C(1′)); 6.64 (*d*-like, 2 arom. H); 6.62 (*d*, ^3J(1′,2′) = 15.5, H–C(2′)); 6.44 (*d*, ^3J(7,8) = 6.6, H–C(8)); 6.34 (*d*, ^3J(2,3) = 6.9, H–C(2)); 6.27 (*dq*-like, ^3J(7,8) = 6.6, ^4J(7,Me–C(6)) = 1.3, H–C(7)); 5.92 (*s*, H–C(10)); 3.72 (*s*, COOMe); 2.98 (*s*, Me_2N); 2.48 (*sept.*, ^3J = 6.8, Me_2C*H*–C(9)); 1.96 (*s*, Me–C(6)); 1.06, 1.04 (2*d*, ^3J = 7.1, 7.0, *Me*$_2$CH–C(9)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 192.00 (*d*, CHO); 167.84 (*s*, *C*OOMe); 150.76 (*s*, arom. C); 148.25 (*s*, C(9)); 147.97 (*d*, C(3)); 145.34 (*s*, C(1)); 144.55 (*s*, C(5a)); 139.38 (*s*, C(10a)); 134.35 (*d*, C(2′)); 129.08 (*s*, C(6)); 128.53 (*s*, arom. C); 128.06 (*d*, C(7)); 128.02 (*d*, C(10)); 125.61 (*d*, C(1′)); 125.49 (*d*, arom. C); 125.29 (*d*, C(2)); 124.71 (*d*, C(8)); 124.46 (*s*, C(4)); 122.69 (*s*, C(5)); 112.03 (*d*, arom. C); 52.07 (*q*, COO*Me*); 40.16 (*q*, Me_2N); 35.44 (*d*, Me_2*C*H–C(9)); 23.04, 22.23 (2*q*, *Me*$_2$CH–C(9)); 21.77 (*q*, *Me*–C(6)). EI-MS: 442 (23, $[M+1]^+$), 441 (100, $M^{+\bullet}$), 366 (18), 329 (19), 310 (16), 265 (14), 252 (15), 239 (16), 220 (21), 202 (22), 189 (31), 171 (34), 165 (27), 154 (20), 134 (45), 120 (19). Anal. calc. for $C_{29}H_{31}NO_3$ (441.60): C 78.88, H 7.07, N 3.17; found: C 79.09, H 6.85 N 3.17.

4.4.4. *Formation of the Thermodynamically Controlled Mixture (all-*E*)-***44a***/(all-*E*)-***44b***.* As described in *3.5.2.1* and *4.1.5*, with aldehyde (*E*)-**43b** (0.050 g, 0.113 mmol), $CrCl_2$ (0.112 g, 0.906 mmol), and CHI_3 (0.089 g, 0.226 mmol) in THF; then, after removal of THF, with 4-nitrostyrene (0.051 g, 0.339 mmol), [$Pd(OAc)_2$] (2.5 mg, 0.011 mmol), Ag_2CO_3 (0.031 g, 0.113 mmol), and DMF (0.5 ml). CC (SiO_2, hexane/Et_2O 6:1) gave (all-*E*)-**44a**/(all-*E*)-**44b** 1:5.7 (0.020 g, 32%). Deep red oil.

*Data of (all-*E*)-***44a***:* UV/VIS (hexane/CH_2Cl_2; *Fig. 17*): max. *ca.* 475 (sh, 0.09), 369 (1.00); min. 280 (0.31).

*Data of (all-*E*)-***44b***:* R_f (hexane/Et_2O 1:1) 0.51. UV/VIS (hexane/CH_2Cl_2; *Fig. 17*): max. 486 (1.00), 378 (0.60), 340 (0.57); min. 408 (0.57), 293 (0.39).

4.5. *Methyl 7-Isopropyl-5-[(*E*)-2-(4-methoxyphenyl)ethenyl]-10-methyl-2-[(*E*)-2-(4-nitrophenyl)-ethenyl]heptalene-1-carboxylate* ((all-*E*)-**48a**) *and Methyl 9-Isopropyl-1-[(*E*)-2-(4-methoxyphenyl)ethenyl]-6-methyl-4-[(*E*)-2-(4-nitrophenyl)ethenyl]heptalene-5-carboxylate* ((all-*E*)-**48b**). 4.5.1. *5-Methyl Hydrogen 9-Isopropyl-1-[(*E*)-2-(4-methoxyphenyl)ethenyl]-6-methylheptalene-4,5-dicarboxylate* ((*E*)-**45b**). As described in *4.1.1*, with diester (*E*)-**22b** (0.950 g, 2.07 mmol) and LiOH (1.90 g, 45.2 mmol) in MeOH/H_2O. Drying under h.v. at 50° gave (E)-**45b** (72%). Orange powder. M.p. 143.3–144.3° (dec. under formation of the cyclic anhydride). R_f (CH_2Cl_2/MeOH 9:1) 0.46. UV/VIS (MeCN): max. 416 (sh), 364 (sh), 328, 259; min. 280, 249. IR (KBr): 3428*w*, 2958*m*, 1725*s*, 1677*s*, 1603*m*, 1550*m*, 1512*s*, 1462*w*, 1433*m*, 1421*w*, 1253*s*, 1219*m*, 1193*m*, 1173*s*, 1157*m*, 1091*w*, 1039*w*, 966*w*, 840*w*, 842*w*, 816*w*, 788*w*, 750*w*. ^{1}H-NMR ($CDCl_3$): 7.73 (*d*, ^3J(2,3) = 6.6, H–C(3)); 7.33 (*d*-like, 2 arom. H); 6.87 (*d*, ^3J(1′,2′) = 15.7, H–C(1′)); 6.84 (*d*-like, 2 arom. H); 6.55 (*d*, ^3J(1′,2′) = 15.7, H–C(2′)); 6.38 (*d*, ^3J(2,3) = 6.6, H–C(2)); 6.36 (*d*, ^3J(7,8) = 6.5, H–C(8)); 6.27 (*dq*-like, ^3J(7,8) = 6.5, ^4J(7,Me–C(6)) = 1.1, H–C(7)); 5.91 (*s*, H–C(10)); 3.81 (*s*, MeO); 3.70 (*s*, COOMe); 2.50 (*sept.*, ^3J = 6.8, Me_2C*H*–C(9)); 1.95 (*s*, Me–C(6)); 1.08, 1.06 (2*d*, ^3J = 7.0, 6.9, *Me*$_2$CH–C(9)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 172.04 (*s*, COOH); 167.66 (*s*, *C*OOMe);

159.60 (*s*, arom. C); 148.24 (*s*, C(9)); 144.89 (*s*, C(5a)); 143.84 (*s*, C(1)); 141.05 (*d*, C(3)); 132.41 (*d*, C(2′)); 130.91 (*s*, C(10a)); 129.31 (*s*, C(6)); 128.68 (*s*, arom. C); 128.34 (*d*, arom. C); 127.62 (*d*, C(7), C(10)); 127.28 (*d*, C(1′)); 126.66 (*d*, C(2)); 125.60 (*d*, C(8)); 124.91 (*s*, C(4)); 123.45 (*s*, C(5)); 114.12 (*d*, arom. C); 55.26 (*q*, MeO); 52.07 (*q*, COO*Me*); 35.42 (*d*, Me_2*C*H–C(9)); 23.07, 22.26 (*q*, *Me*$_2$CH–C(9)); 21.71 (*q*, *Me*–C(6)). CI-MS (NH_3): 476 (82), 461 (14, $[M+NH_3]^+$), 460 (11), 459 (35), 436 (8), 434 (29), 433 (15), 432 (57), 431 (29), 430 (100, $[(M+NH_4)-MeOH)]^+$), 429 (11), 428 (17), 427 (53, $[(M+1)-H_2O)]^+$), 418 (11), 417 (22), 416 (15), 415 (48), 414 (18), 413 (56, $[(M+1)-MeOH)]^+$), 136 (13).

4.5.2. *8-Isopropyl-1,1-dimethoxy-6-[(*E*)-2-(4-methoxyphenyl)ethenyl]-11-methylheptaleno[4,5-*c*]furan-3(1*H*)-one* ((*E*)-**46b**). In analogy to our earlier experiments (*cf.* [11]), acid (*E*)-**45b** (0.450 g, 1.01 mmol) was treated with oxalyl chloride (0.384 g, 3.03 mmol) and DMF (0.481 g, 6.58 mmol) in MeCN, followed by addition of MeOH (0.42 ml, 14 mmol). After workup, CC (SiO_2, hexane/Et_2O 5:1) furnished (*E*)-**46b** (0.400 g, 86%). A sample for analyses was recrystallized from Et_2O. Dark brown crystals. M.p. 150.2–151.0°. R_f (hexan/Et_2O 1:1) 0.70. UV/VIS (MeCN): max. 464 (3.93), 382 (4.18), 323 (4.27), 267 (4.28); min. 442 (3.91), 359 (4.16), 300 (4.15), 232 (4.24). IR (KBr): 2951*m*, 2837*w*, 1755*s*, 1596*m*, 1570*w*, 1552*w*, 1512*s*, 1461*w*, 1442*w*, 1421*w*, 1400*w*, 1362*w*, 1287*s*, 1254*s*, 1218*w*, 1194*m*, 1172*s*, 1130*m*, 1090*w*, 1059*w*, 1036*w*, 1011*w*, 963*w*, 926*m*, 881*w*, 831*m*, 812*w*, 781*w*, 770*w*, 659*w*. ^{1}H-NMR ($CDCl_3$): 7.36 (*d*-like, 2 arom. H); 7.31 (*d*, $^3J(4,5)=7.0$, H–C(4)); 6.93 (*d*, $^3J(1',2')=15.7$, H–C(1′)); 6.85 (*d*-like, 2 arom. H); 6.81 (*d*, $^3J(1',2')=15.7$, H–C(2′)); 6.51 (*d*, $^3J(4,5)=7.0$, H–C(5)); 6.35 (*dq*-like, $^3J(9,10)=6.6$, $^4J(10,\text{Me–C}(11))=1.2$, H–C(10)); 6.23 (*d*, $^3J(9,10)=6.6$, H–C(9)); 5.79 (*s*, H–C(7)); 3.82 (*s*, MeO); 3.46, 3.16 (2*s*, 2 MeO–C(1)); 2.47 (*sept.*, $^3J=6.8$, Me_2*C*H–C(8)); 2.17 (*s*, Me–C(11)); 1.04, 1.03 (2*d*, $^3J=6.9$, 6.7, *Me*$_2$CH–C(8)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 167.95 (*s*, C(3)=O); 160.08 (*s*, arom. C)); 150.35 (*s*, C(8)); 138.50 (*s*, C(6)); 135.51 (*s*, C(11a)); 133.49 (*d*, C(4)); 132.35 (*s*, C(6a)); 131.70 (*d*, C(2′)); 130.07 (*d*, C(10)); 129.96 C(7)); 129.25 (*s*, C(11)); 128.48 (*s*, arom. C); 128.43 (*d*, arom. C, C(1′)); 128.23 (*s*, C(3a)); 127.43 (*d*, C(5)); 124.69 (*d*, C(9)); 118.96 (*s*, C(1)); 114.16 (*d*, arom. C); 55.26 (*q*, MeO); 52.52, 50.67 (2*q*, *Me*O–C(1)); 35.80 (*d*, Me_2*C*H–C(8)); 23.07, 22.97 (2*q*, *Me*$_2$CH–C(8)); 22.43 (*q*, *Me*–C(11)). CI-MS (NH_3): 462 (10), 461 (36), 460 (30), 459 (100, $[M+1]^+$), 423 (17), 422 (61), 300 (7), 277 (6), 213 (13), 210 (7), 152 (10). Anal. calc. for $C_{29}H_{30}O_5$ (458.60): C 75.95, H 6.59; found: C 76.01, H 6.58.

4.5.3. *Methyl 4-Formyl-9-isopropyl-1-[(*E*)-2-(4-methoxyphenyl)ethenyl]-6-methylheptalene-5-carboxylate* ((*E*)-**47b**). As described in *3.1*, with furanone (*E*)-**46b** (2.00 g, 4,40 mmol) and with 1M DIBAH (4.4 ml, 4.4 mmol) in toluene. CC (SiO_2, hexane/Et_2O 4:1) gave (*E*)-**47b** (1.50 g, 79%). A sample for analyses was recrystallized from Et_2O. Red crystals. M.p. 172.9–174.9°. R_f (hexane/Et_2O 1:1) 0.28. UV/VIS (MeCN): max. 428 (sh, 4.08), 377 (4.25), 335 (4.31), 262 (4.18); min. 362 (4.24), 284 (4.12), 253 (4.17). IR (KBr): 3000*w*, 2961*m*, 2834*w*, 1719*s*, 1682*s*, 1603*m*, 1573*w*, 1552*w*, 1546*m*, 1513*s*, 1458*w*, 1431*w*, 1417*w*, 1382*w*, 1363*w*, 1317*w*, 1279*m*, 1252*s*, 1223*m*, 1192*m*, 1177*s*, 1125*w*, 1082*w*, 1060*w*, 1036*m*, 988*w*, 977*w*, 905*w*, 888*w*, 843*m*, 823*w*, 780*w*, 770*w*. ^{1}H-NMR ($CDCl_3$): 9.43 (*s*, CHO); 7.35 (*d*-like, 2 arom. H); 7.27 (*d*, $^3J(2,3)=6.5$, H–C(3)); 6.90 (*d*, $^3J(1',2')=15.7$, H–C(1′)); 6.85 (*d*-like, 2 arom. H); 6.62 (*d*, $^3J(1',2')=15.7$, H–C(2′)); 6.50 (*d*, $^3J(2,3)=6.6$, H–C(2)); 6.35 (*d*, $^3J(7,8)=6.7$, H–C(8)); 6.28 (*d*, $^3J(7,8)=6.7$, H–C(7)); 5.91 (*s*, H–C(10)); 3.82 (*s*, MeO); 3.73 (*s*, COOMe); 2.49 (*sept.*, $^3J=6.8$, Me_2*C*H–C(9)); 1.97 (*s*, Me–C(6)); 1.07, 1.05 (2*d*, $^3J=7.0$, 6.9, *Me*$_2$CH–C(9)). ^{13}C-NMR ($CDCl_3$; tentative assignment): 192.00 (*d*, CHO); 167.69 (*s*, *C*OOMe); 160.17 (*s*, arom. C); 148.30 (*s*, C(9)); 147.60 (*d*, C(3)); 145.00 (*s*, C(5a)); 144.53 (*s*, C(1)); 140.04 (*s*, C(10a)); 133.24 (*d*, C(2′)); 129.13 (*s*, C(6)); 129.04 (*s*, arom. C); 128.50 (*d*, arom. C); 128.31 (*d*, C(7)); 28.10 (*d*, C(10)); 127.20 (*d*, C(1′)); 126.65 (*d*, C(2)); 125.71 (*d*, C(8)); 125.14 (*s*, C(4)); 122.63 (*s*, C(5)); 114.17 (*d*, arom. C); 55.27 (*q*, MeO); 52.10 (*q*, COO*Me*); 35.42 (*d*, Me_2*C*H–C(9)); 23.04, 22.21 (2*q*, *Me*$_2$CH–C(9)); 21.77 (*q*, *Me*–C(6)). CI-MS (NH_3): 432 (6), 431 (24), 430 (29), 429 (100, $[M+1]^+$), 423 (14), 422 (49), 399 (7), 213 (12). Anal. calc. for $C_{28}H_{28}O_4$ (428.50): C 78.48, H 6.59; found: C 77.84, H 6.64.

4.5.4. *Formation of the Thermodynamically Controlled Mixture (all-*E*)-***48a***/(all-*E*)-***48b*** via Wittig Reaction.* As described in *2.1.*, with aldehyde (*E*)-**47b** (0.150 g, 0.35 mmol) and (4-nitrobenzyl)triphenylphosphonium bromide (1.67 g, 3.50 mmol) in CH_2Cl_2 (15 ml) and 2N aq. NaOH (15 ml). CC (SiO_2, hexane/Et_2O 7:1) gave (all-*E*)-**48a**/(all-*E*)-**48b** and (1′*E*,1″*Z*)-**48a**/(1′*E*,1″*Z*)-**48b** as well as some not identified by-products in smaller amounts (in total 0.075 g). The (*Z*) → (*E*) isomerization could not be realized by cat. amounts of I_2. However, a second CC allowed the separation of dark orange (all-*E*)-**48a**

(5 mg, 2.6%) from the mixture. It rapidly isomerized at r.t. to the thermodynamically controlled mixture of (all-*E*)-**48a** (18%) and (all-*E*)-**48b** (82%).

Data of (all-E*)*-**48a**: Red crystals (Et_2O/hexane). M.p. 166.5–168.5°. R_f (hexane/Et_2O 1:1) 0.50. UV/VIS (4% ^{i}PrOH/hexane; *Fig. 14*): max. *ca.* 440 (sh, 0.04), 337 (1.00); min. 257 (0.40). ^{1}H-NMR ($CDCl_3$; recognizable signals in the thermal equilibrium mixture with 82% of (all-*E*)-**48b**): 6.04 (*s*, H–C(6)); 3.82 (*s*, MeO–C_p of Ar′); 3.67 (*s*, MeOOC–C(5)); 2.64 (*sept.*, ^3J = 6.9, Me_2CH–C(7)); 1.75 (*s*, Me–C(10)).

Data of (all-E*)*-**48b**: See also *4.5.5*. R_f (hexane/Et_2O 1:1) 0.41. UV/VIS (4% ^{i}PrOH/hexane; *Fig. 14*): max. 439 (1.00), 370 (0.90), 332 (sh, 0.69); min. 400 (0.85), 302 (0.56). ^{1}H-NMR ($CDCl_3$; taken from the thermal equilibrium mixture with (all-*E*)-**48a**): 8.14 (*d*-like, 2 arom. H); 7.46 (*d*-like, 2 arom. H); 7.32 (*d*-like, 2 arom. H); 6.98 (*d*, $^3J(1'',2'')$ = 16.2, H–C(1″)); 6.85 (*d*-like, 2 arom. H); 6.84 (*d*, $^3J(1',2')$ = 15.0, H–C(1′)); 6.80 (*d*, $^3J(2,3)$ = 6.8, H–C(3)); 6.49 (*d*, $^3J(1',2')$ = 16.0, H–C(2′)); 6.47 (*d*, $^3J(1'',2'')$ = 16.3, H–C(2″)); 6.41 (*d*, $^3J(7,8)$ = 7.0, H–C(8)); 6.39 (*d*, $^3J(2,3)$ = 7.2, H–C(2)); 6.31 (*d*, $^3J(7,8)$ = 6.5, H–C(7)); 5.95 (*s*, H–C(10)); 3.81 (*s*, MeO); 3.69 (*s*, COOMe); 2.53 (*sept.*, ^3J = 6.9, Me_2CH–C(9)); 1.97 (*s*, Me–C(6)); 1.08, 1.06 (*d*, ^3J = 6.8, 6.7, Me_2CH–C(9)).

4.5.5. *Formation of the Thermodynamically Controlled Mixture (all*-E*)*-**48a**/*(all*-E*)*-**48b** via Heck *Reaction*. A soln. of aldehyde (*E*)-**47b** (0.090 g, 0.21 mmol) in THF (6 ml) at −70° was treated with 0.5M *Tebbe*'s reagent (0.42 ml, 0.21 mmol) (*cf. 3.5.1.1*). After warming to r.t. over 3 h, the mixture was poured in ice water and worked up. Flash CC (SiO_2, Et_2O/hexane 3:2) gave the corresponding 4-(ethenyl)heptalene as an unstable bright red oil (40.5 mg, *ca.* 30%), which was just dissolved in DMF (0.5 ml) and subjected to the *Heck* reaction at r.t. with 1-iodo-4-nitrobenzene (0.052 g, 0.21 mmol) in the presence of $[Pd(OAc)_2]$ (2.0 mg) and Ag_2CO_3 (23.5 mg) (*cf. 3.5.1.2*). After removal of nonreacted 1-iodo-4-nitrobenzene by CC (*Alox B IV*, Et_2O/hexane 3:2), (all-*E*)-**48a** and (all-*E*)-**48b** were separated by prep. HPLC (*Spherisorb CN*, 5 μm; hexane/^{i}PrOH 95:5): 1.4 mg of (all-*E*)-**48a** (recrystallized from Et_2O/hexane; see *4.5.4*) and 5.5 mg of (all-*E*)-**48b** (recrystallized from Et_2O/CH_2Cl_2).

Data of (all-E*)*-**48b**: Red crystals. M.p. 171.9–172.8°. R_f (hexane/Et_2O 1:1) 0.41. UV/VIS (4% ^{i}PrOH/hexane; *Fig. 14*): max. 439 (1.00), 370 (0.90), 332 (sh, 0.69); min. 400 (0.85), 302 (0.56). ^{1}H-NMR (500 MHz, $CDCl_3$ at 233 K; $CHCl_3$ at δ 7.260; full assignment): 8.16 (*d*, J_o = 8.7, 2 H_m of Ar–C(2″)); 7.48 (*d*, J_o = 8.7, 2 H_o of Ar–C(2″)); 7.35 (*d*, J_o = 8.6, 2 H_o of Ar–C(2′)); 7.013 (*d*, $^3J(1'',2'')$ = 16.3, H–C(1″)); 6.883 (*d*, $^3J(1',2')$ = 15.9, H–C(1′)); 6.849 (*d*, J_o = 8.6, 2 H_m of Ar–C(2′)); 6.809 (*d*, $^3J(3,2)$ = 6.7, H–C(3)); 6.435 (*d*, $^3J(2',1')\approx$ 15.1, H–C(2′)); 6.417 (*d*, $^3J(2'',1'')\approx$ 16.6, H–C(2″)); 6.414 (*d*, $^3J(2,3)\approx$ 7.1, H–C(3)); 6.394 (*d*, $^3J(8,7)\approx$ 6.6, H–C(8)); 6.309 (*d*, $^3J(7,8)$ = 6.6, H–C(7)); 5.944 (br. *s*, H–C(10)); 3.82 (*s*, MeO); 3.69 (*s*, COOMe); 2.51 (*sept.*, ^3J = 6.8, Me_2CH–C(9)); 1.96 (*s*, Me–C(6)); 1.044, 1.030 (2*d*, ^3J = 6.9, 6.8, Me_2CH–C(9)). ^{13}C-NMR (125 MHz, $CDCl_3$ at 233 K; $CDCl_3$ at δ 77.00; full assignment): 169.29 (MeO*O*C); 159.30 (C_p of Ar–C(2′)); 148.27 (C(9)); 144.88 (C(5a)); 145.92 (C_p of Ar–C(2″)); 143.81 (C_{ip} of Ar–C(2″)); 140.55 (C(1)); 138.74 (C(4)); 135.79 (C(1″)); 135.71 (C(3)); 130.26 (C(2′)); 129.20 (C_{ip} of Ar–C(2′)); 128.26 (C(2)); 127.61 (C(1′)); 127.26 (C(10)); 127.05 (C(7)); 126.52 (C_o of Ar–C(2″)); 126.20 (C(2″)); 124.87 (C(10a)); 124.50 (C(8)); 124.05 (C_m of Ar–C(2″)); 113.78 (C_m of Ar–C(2′)); 55.32 (MeO); 52.77 (COO*Me*); 35.40 (Me_2CH–C(9)); 23.13, 22.14 (*Me*$_2$CH–C(9)); 22.01 (*Me*–C(6)). EI-MS: 548 (18, $[M+1]^+$), 547 (60, $M^{+\bullet}$), 504 (14, $[M-{}^i\mathrm{Pr}]^{+\bullet}$), 532 (9), 504 (10), 488 (11), 472 (11), 374 (23), 317 (20), 316 (100), 121 (78).

4.6. *Methyl 7-Isopropyl-2-[(*E*)-2-(4-methoxyphenyl)ethenyl]-10-methyl-5-[(*E*)-2-(4-nitrophenyl)-ethenyl]heptalene-1-carboxylate* ((all-*E*)-**52a**) *and Methyl 9-Isopropyl-4-[(*E*)-2-(4-methoxyphenyl)ethenyl]-6-methyl-1-[(*E*)-2-(4-nitrophenyl)ethenyl]heptalene-5-carboxylate* ((all-*E*)-**52b**). 4.6.1. *5-Methyl Hydrogen 9-Isopropyl-6-methyl-1-[(*E*)-2-(4-nitrophenyl)ethenyl]-4,5-dicarboxylate* ((*E*)-**49b**): Semi-saponification of diester (*E*)-**21b** (1.87 g, 3.95 mmol) in the usual manner with LiOH (3.73 g, 0.156 mol) in boiling H_2O/MeOH gave (*E*)-**49b** (1.34 g, 71%). Yellow micro-crystalline powder. M.p. 216–217° (dec. to the cylic anhydride). UV/VIS (MeCN): max. 439 (sh, 3.83), 393 (sh, 3.98), 362 (4.24), 336 (sh, 3.95), 290 (sh, 4.13), 214 (sh, 4.19); min. 270 (3.95). IR (KBr): 1702*s* and 1698*s* (C=O), 1592*s* and 1516*s* (arom. NO_2). ^{1}H-NMR ($CDCl_3$): Almost identical to that of (*E*)-**21b**; OH (not visible); 3.72 (*s*, COOMe). CI-MS: 445 (100, $[(M-\mathrm{MeOH})+NH_4]^+$), 428 (10, $[(M-\mathrm{MeOH})+\mathrm{H}]^+$), 398 (7).

4.6.2. *8-Isopropyl-1,1-dimethoxy-11-methyl-6-[(*E*)-2-(4-nitrophenyl)ethenyl]heptaleno[4,5-*c*]furan-3(1*H*)-one* ((*E*)-**50b**). The iminium salt was formed from DMF (3 ml) and oxalyl chloride (0.26 g) in MeCN (3 ml). The mixture with the suspended iminium salt was cooled with an ice bath, and acid (*E*)-

49b (0.300 g, 0.653 mmol) in MeCN (3 ml) was slowly added drop by drop. Stirring was continued at 0° for 10 min. Then, dry MeOH (3 ml) was added and the mixture stirred for an additional hour at 0°. The mixture was poured in H_2O and then extracted with CH_2Cl_2 (3×). After drying ($MgSO_4$), the soln. was filtered over a column of *Alox BIV*. After evaporation of CH_2Cl_2, the dark red residue, which contained still a small amount of DMF, was treated with Et_2O and a little hexane: (*E*)-**50b** (0.249 g, 80%). Dark red crystals with an almost black gleam. M.p. 235–236° (AcOEt). R_f (CH_2Cl_2/MeOH 19:1) 0.67. UV/VIS (MeCN): max. 471 (3.77), 375 (4.42), 296 (4.17), 245 (4.29); min. 431 (3.70), 307 (4.16), 272 (4.11), 235 (4.28). IR (KBr): 1758*vs* (5-ring lactone), 1590*s* and 1516*s* (arom. NO_2). ^{1}H-NMR ($CDCl_3$): 8.17 (*d*-like, J_o = 8.8, 2 H_m of Ar); 7.52 (*d*-like, J_o = 8.7, 2 H_o of Ar); 7.34 (*d*, ^3J(2,3) = 6.8, H–C(2)); 7.16 (*d* with f.s., ^3J(2′,1′) = 15.8, H–C(2′)); 6.83 (*d*, ^3J(1′,2′) = 15.8, H–C(1′)); 6.66 (*d*, ^3J(3,2) = 6.8, H–C(3)); 6.40 (*dd*, ^3J(8,7) = 6.7, ^4J(8,10) = 1.4, H–C(8)); 6.27 (*dq*-like, ^3J(7,8) = 6.8, ^4J(7,Me–C(6)) ≤ 0.6, H–C(7)); 5.78 (*d*, ^4J(10,8) = 1.2, H–C(10)); 3.47, 3.16 (2*s*, 2 MeO–C(1)); 2.49 (*sept.*, ^3J = 6.8, Me_2CH–C(9)); 2.20 (*s*, Me–C(6)); 1.05 (*d*, ^3J = 6.8, Me_2CH–C(9)).

4.6.3. *Methyl 4-Formyl-9-isopropyl-6-methyl-1-[(*E*)-2-(4-nitrophenyl)ethenyl]heptalene-5-carboxylate* ((*E*)-**51b**). Furanone (*E*)-**50b** (0.164 g, 0.345 mmol) in toluene (23 ml) was reduced at −78° in the usual manner with 1.5M DIBAH in toluene (0.3 ml). After 20 min, the reaction was quenched with MeOH (5 ml), the mixture warmed to r.t. and then poured into aq. 10% *Seignette* salt soln. (*E*)-**51b** was extracted with ^{t}BuOMe (3×) and then subjected to CC (*Alox B IV*, CH_2Cl_2) followed by crystallization from Et_2O/hexane: (*E*)-**51b** (0.118 g, 77%). Dark red crystals. M.p. 226.9–227.9°. R_f (*Alox B IV*, Et_2O/hexane) 0.21. UV/VIS (MeCN): max. 422 (sh, 4.21), 349 (4.36), 231 (sh, 4.23); min. 272 (3.97). IR (KBr): 1718*s* (C=O, ester), 1688*s* (C=O, aldehyde), 1590*s* and 1512*s* (NO_2). ^{1}H-NMR ($CDCl_3$): 9.46 (*s*, CHO); 8.17 (*d*, J_o = 8.8, 2 H_m of Ar); 7.51 (*d*, J_o = 8.8, 2 H_o of Ar); 7.29 (*d*, ^3J(2,3) = 6.5, H–C(2)); 7.13 (*d* with f.s., ^3J(2′,1′) = 16.0, H–C(2′)); 6.66 (*d*, ^3J(3,2) = 6.5, H–C(3)); 6.65 (*d*, ^3J(1′,2′) = 16.3, H–C(1′)); 6.38 (*d*-like, ^3J(8,7) = 6.9, H–C(8)); 6.32 (*dq*-like, ^3J(7,8) = 6.9, H–C(7)); 5.90 (*s*, H–C(10)); 3.76 (*s*, COOMe); 2.52 (*sept.*, ^3J = 6.8, Me_2CH–C(9)); 2.00 (*s*, Me–C(6)); 1.07 (*t*-like, Me_2CH–C(9)). EI-MS: 443 (100, $M^{+\bullet}$).

4.6.4. *Formation of (all-*E*)-***52a***/(all-*E*)-***52b***.* At r.t., aldehyde (*E*)-**51b** (0.028 g, 0.063 mmol) and (4-methoxybenzyl)triphenylphosphonium chloride (0.032 g, 0.076 mmol) were added to CH_2Cl_2 (0.5 ml), followed by KOH (8.5 mg, 0.152 mmol) and immediately by 50–100 µl of a 2% soln. of [18]Crown-6 in CH_2Cl_2. After 10 min, half-conc. aq. NaCl soln. was added, the mixture extracted with CH_2Cl_2, the combined extract washed with H_2O, dried, and concentrated, and the red residue subjected to CC (SiO_2, ^{t}BuOMe/hexane 7:3). The obtained red oil was crystallized from Et_2O and a second time from Et_2O/pentane: pure (all-*E*)-**52b** (0.0264 g, 77%).

*Data of (all-*E*)-***52b***:* Red plates. M.p. 166.1–167.5°. R_f (^{t}BuOMe/hexane 7:3) 0.38. UV/VIS (hexane/CH_2Cl_2; *Fig. 15*): max. 450 (1.00), 356 (0.97); min. 401 (0.89), 305 (0.84). IR (KBr): 1724*s* (C=O, ester), 1587*s* and 1509*s* (arom. NO_2). ^{1}H-NMR ($CDCl_3$, 500 MHz, 233 K; $CHCl_3$ at δ 7.26; full assignment): 8.16 (*d*, J_o = 8.85, 2 H_m of Ar′); 7.51 (*d*, J_o = 8.83, 2 H_o of Ar′); 7.33 (*d*, J_o = 8.73, 2 H_o of Ar″); 6.84 (*d*, J_o = 8.77, 2 H_m of Ar″); 7.14 (*d*, ^3J(1′,2′) = 15.7, H–C(1′)); 6.75 (*d*, ^3J(1″,2″) = 16.3, H–C(1″)); 6.70 (*d*, ^3J(3,2) = 6.9, H–C(3)); 6.53 (*d*, ^3J(2,3) = 6.8, H–C(2)); 6.44 (*d*, ^3J(2′,3′) = 15.4, H–C(2′)); 6.43 (*d*, ^3J(2″,3″) = 15.9, H–C(2″)); 6.42 (*d*, ^3J(8,7) = 6.2, H–C(8)); 6.32 (br. *d*, ^3J(7,8) = 6.4, H–C(7)); 5.91 (*s*, H–C(10)); 3.80 (*s*, MeO); 3.69 (*s*, COOMe); 2.51 (*sept.*, ^3J = 6.8, Me_2CH–C(9)); 1.97 (*s*, Me–C(6)); 1.04, 1.03 (2*d*, *J* = 6.8, 6.6, Me_2CH–C(9)). ^{13}C-NMR ($CDCl_3$, 500 MHz, 233 K; $CDCl_3$ at δ 76.00; full assignment): 168.16 (MeO*O*C); 157.90 (C_p of Ar″); 147.33 (C(9)); 144.93 (C_p of Ar′); 143.13 (C_{ip} of Ar′); 142.59 (C(5a)); 140.56 (C(4)); 136.42 (C(1)); 133.62 (C(1′)); 131.77 (C(2)); 130.57 (C(3)); 128.56 (C(2″)); 128.40 (C_{ip} of Ar″); 127.67 (C(1″)); 126.73 (C(6)); 126.64 (C_o of Ar″); 126.52 (C(10)); 126.17 (C(7)); 125.90 (C_o of Ar′); 125.56 (C(2′)); 123.84 (C(8)); 123.62 (C(10a)); 123.58 (C(5a)); 123.12 (C(5)); 123.00 (C_m of Ar′); 112.71 (C_m of Ar″); 54.27 (MeO); 51.81 (*Me*OOC); 34.35 (Me_2CH–C(9)); 21.04 (*Me*–C(6)); 22.12, 21.09 (Me_2CH–C(9)). EI-MS: 547 (29, $M^{+\bullet}$).

The structure of (all-*E*)-**52b** was confirmed by an X-ray crystal structure analysis (see *Fig. 7* and *Tables 2* and *7*).

*Data of (all-*E*)-***52a***:* Red oil. R_f (^{t}BuOMe/hexane 7:3) 0.44. UV/VIS (hexane/CH_2Cl_2; *Fig.15*): max. 397 (sh, 0.64), 352 (1.00), 281 (0.73); min. 304 (0.69). ^{1}H-NMR ($CDCl_3$; recognizable signals in a 1:3 mixture with (*E*)-**52b**): 8.05 (*d*, ^3J(1′,2′) = 16.1, H–C(1′)); 6.63 (*d*, ^3J(1″,2″) = 16, H–C(1″)); 6.08 (*s*,

H–C(6)); 3.83 (*s*, MeO); 3.65 (*s*, MeOOC–C(1)); 2.67 (*sept.*, $^3J = 6.8$, Me_2CH–C(7)); 1.78 (*s*, Me–C(10)); 1.21 (*t*-like, Me_2CH–C(7).

Irradiation of (*E*)-**52b** (0.5 mg) in hexane/CH_2Cl_2 9:1 (4 ml) at *ca.* −30° with light of λ 439 ± 20 nm (interference filter) led to 100% conversion into (*E*)-**52a**. Heating of the soln. at 60° established within 15 min the thermal equilibrium of (*E*)-**52b**/(*E*)-**52a**. The same ratio of (*E*)-**52b**/(*E*)-**52a** was also reached by heating of pure (*E*)-**52b** at 60° in the same solvent mixture.

4.7. *Methyl 5-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-6,8,10-trimethyl-2-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-1-carboxylate* ((all-*E*)-**56a**) *and Methyl 1-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-6,8,10-trimethyl-4-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-5-carboxylate* ((all-*E*)-**56b**). 4.7.1. *5-Methyl Hydrogen 1-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-6,8,10-trimethylheptalene-4,5-dicarboxylate* ((*E*)-**53b**). The partial saponification of (*E*)-**26b** (1.90 g, 4.27 mmol) in boiling MeOH/H_2O with LiOH (4.00 g, 95.3 mmol) was performed as described before: (*E*)-**53b** (1.70 g, 92%). Orange powder. M.p. 185.5–186.4° (dec. under formation of the cyclic anhydride). R_f (CH_2Cl_2/MeOH 9:1) 0.43. IR (KBr): 2950*m*, 2835*w*, 2635*w*, 1702*s*, 1682*s*, 1603*m*, 1573*w*, 1547*m*, 1511*s*, 1437*m*, 1418*m*, 1373*w*, 1302*m*, 1250*s*, 1206*m*, 1174*s*, 1107*w*, 1039*m*, 984*w*, 967*w*, 922*w*, 892*w*, 840*m*, 825*w*, 803*w*, 778*w*, 578*w*. ^{1}H-NMR ($CDCl_3$ 300 MHz): 7.75 (*d*, $^3J(2,3) = 6.3$, H–C(3)); 7.32 (*d*-like, 2 arom. H); 6.84 (*d*-like, 2 arom. H); 6.81 (*d*, $^3J(1',2') = 16.0$, H–C(1′)); 6.50 (*d*, $^3J(2,3) = 6.5$, H–C(2)); 6.34 (*d*, $^3J(1',2') = 15.7$, H–C(2′)); 6.21 (*s*, H–C(9)); 6.12 (*s*, H–C(7)); 3.80 (*s*, MeO); 3.68 (*s*, COOMe); 2.10 (*d*, ^4J(7,Me–C(6)) = 1.0, Me–C(6)); 1.88 (*d*, ^4J(9,Me–C(8)) = 1.0, Me–C(8)); 1.64 (*s*, Me–C(10)). ^{13}C-NMR ($CDCl_3$, 75 MHz; tentative assignment): 171.99 (*s*, COOH); 167.64 (*s*, *C*OOMe); 159.88 (*s*, MeO–C_p); 146.66 (*s*); 143.27 (*s*); 140.46 (*d*, C(3)); 139.72 (*s*); 132.10 (*d*, C(9)); 130.82 (*s*); 130.36 (*s*); 130.09 (*d*, C(1′)); 129.50 (*s*); 129.33 (*d*, C(7)); 128.28 (*d*, arom. C); 126.96 (*d*, C(2)); 125.43 (*d*, C(2′)); 122.92 (*d*, C(4)); 119.92 (*d*, C(5)); 114.09 (*d*, arom. C); 55.27 (*q*, MeO); 51.97 (*q*, COO*Me*); 25.07 (*q*, *Me*–C(8)); 21.50 (*q*, *Me*–C(6)); 18.61 (*q*, *Me*–C(10)).

4.7.2. *1,1-Dimethoxy-6-[(*E*)-2-(4-methoxyphenyl)ethenyl]-7,9,11-trimethylheptaleno[4,5-c]furan-3(1*H*)-one* ((*E*)-**54b**): As described in *4.1.2*, with acid (*E*)-**53b** (1.50 g, 3.50 mmol), oxalyl chloride (1.30 g, 10.50 mmol), and DMF (1.70 g, 22.60 mmol) in MeCN, and MeOH (1.2 ml, 40 mmol). After workup, CC (SiO_2, hexane/Et_2O 5:1) furnished (*E*)-**54b** (1.40 g, 77%). For analyses, a sample was recrystallized from Et_2O. Dark brown crystals. M.p. 247.3–249.5°. R_f (hexane/Et_2O 1:1): 0.70. UV/VIS (MeCN): max. 460 (3.83), 375 (4.37), 269 (4.28); min. 305 (4.12). IR (KBr): 2947*w*, 2911*w*, 2838*w*, 1805*s*, 1763*s*, 1597*m*, 1571*w*, 1549*w*, 1510*s*, 1497*m*, 1463*w*, 1441*w*, 1420*w*, 1397*w*, 1375*w*, 1298*m*, 1252*s*, 1212*w*, 1194*w*, 1172*s*, 1141*m*, 1092*w*, 1060*w*, 1033*w*, 1014*w*, 960*w*, 912*m*, 882*w*, 868*w*, 837*m*, 742*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.36 (*d*-like, 2 arom. H); 7.34 (*d*, $^3J(4,5) = 6.8$, H–C(4)); 6.89 (*d*, $^3J(1',2') = 16.0$, H–C(1′)); 6.85 (*d*-like, 2 arom. H); 6.68 (*d*, $^3J(4,5) = 6.8$, H–C(5)); 6.55 (*d*, $^3J(1',2') = 15.7$, H–C(2′)); 6.24 (*s*, H–C(8)); 6.19 (*t*, ^4J(10,Me–C(11)) = 1.3, H–C(10)); 3.81 (*s*, MeO–C_p); 3.44, 3.20 (2*s*, 2 MeO–C(1)); 2.10 (*d*, ^4J(10,Me–C(11)) = 1.3, Me–C(11)); 2.05 (*d*, ^4J(8,Me–C(7)) = 1.2, Me–C(7)); 1.63 (*s*, Me–C(9)).^{13}C-NMR ($CDCl_3$, 75 MHz; tentative assignment): 168.09 (*s*, C=O); 160.04 (*s*, MeO–C_p); 139.21 (*s*); 137.92 (*s*); 136.79 (*s*); 133.87 (*s*); 133.36 (*s*); 133.01 (*d*, C(4)); 131.60 (*d*, C(8)); 131.43 (*d*, C(9)); 131.26 (*d*, C(1′)); 129.42 (*s*); 128.56 (*d*, C(5)); 128.37 (*d*, arom. C); 127.60 (*s*); 125.64 (*d*, C(2′)); 122.99 (*d*, C(3a)); 118.85 (*d*, C(1)); 114.14 (*d*, arom. C); 55.27 (*q*, *Me*O–C_p); 51.96, 50.67 (2*q*, *Me*O–C(1)); 25.14 (*q*, *Me*–C(9)); 22.52 (*q*, *Me*–C(11)); 18.06 (*q*, *Me*–C(7)).

4.7.3. *Methyl 4-Formyl-1-[(*E*)-2-(4-methoxyphenyl)ethenyl]-6,8,10-trimethylheptalene-5-carboxylate* ((*E*)-**55b**). As described in *3.1*, with furanone **54b** (1.06 g, 2.37 mmol), toluene (2.4 ml), and 1M DIBAH in hexane (2.40 mmol). CC (SiO_2, hexane/Et_2O 4:1) yielded (*E*)-**55b** (0.85 g, 86%). For analyses, a sample was recrystallized from Et_2O. Red crystals. M.p. 176.8–178.2°. R_f (hexane/Et_2O 1:1) 0.28. UV/VIS (MeCN): max. 413 (sh, 3.99), 362 (sh, 4.20), 335 (4.27), 295 (4.29), 278 (4.24); min. 322 (4.26), 255 (4.18). IR (KBr): 2942*w*, 2909*w*, 2836*w*, 1733*m*, 1707*s*, 1682*s*, 1641*w*, 1603*m*, 1571*w*, 1544*m*, 1514*s*, 1432*m*, 1416*m*, 1383*w*, 1301*m*, 1281*m*, 1253*s*, 1202*m*, 1173*s*, 1130*m*, 1112*w*, 1060*m*, 1029*m*, 998*w*, 980*w*, 907*w*, 838*m*, 808*w*, 606*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.34 (*d*-like, 2 arom. H); 7.29 (*d*, $^3J(2,3) = 6.2$, H–C(3)); 6.85 (*d*-like, 2 arom. H); 6.85 (*d*, $^3J(1',2') = 15.6$, H–C(1′)); 6.62 (*d*, $^3J(2,3) = 6.2$, H–C(2)); 6.41 (*d*, $^3J(1',2') = 15.7$, H–C(2′)); 6.19 (*s*, H–C(9)); 6.13 (*s*, H–C(7)); 3.80 (*s*, MeO–C_p); 3.71 (*s*, COOMe); 2.08 (*d*, ^4J(7,Me–C(6)) = 0.9, Me–C(6)); 1.89 (*d*, ^4J(9,Me–C(8)) = 1.2, Me–C(8)); 1.64 (*s*, Me–C(10)). ^{13}C-NMR ($CDCl_3$, 75 MHz; tentative assignment): 192.31 (*s*, CHO), 167.67 (*s*, *C*OOMe); 160.10 (*s*,

MeO–C_p); 146.86 (*d*, C(3)); 146.71 (*s*); 143.91 (*s*); 139.91 (*s*); 139.38 (*s*); 132.95 (*d*, C(9)); 132.53 (*s*); 131.14 (*s*); 130.13 (*d*, C(1′)); 129.76 (*d*, C(7)); 129.31 (*s*); 128.43 (*d*, arom. C); 126.89 (*d*, C(2)); 125.32 (*d*, C(2′)); 122.15 (*d*, C(4)); 120.24 (*d*, C(5)); 114.14 (*d*, arom. C); 55.27 (*q*, *Me*O–C_p); 52.01 (*q*, COO*Me*); 25.06 (*q*, *Me*–C(8)); 21.53 (*q*, *Me*–C(6)); 18.70 (*q*, *Me*–C(10)).

4.7.4. *Formation of (all-*E*)-***56a***/(all-*E*)-***56b***.* As described in *3.5.2.1* and *4.1.5*, with aldehyde (*E*)-**55b** (0.400 g, 0.97 mmol), $CrCl_2$ (0.950 g, 7.72 mmol), and CHI_3 (0.760 g, 1.93 mmol) in THF; then after removal of THF, with 4-nitrostyrene (0.290 g, 0.339 mmol), [$Pd(OAc)_2$] (21 mg, 0.096 mmol), Ag_2CO_3 (0.266 g, 0.96 mmol), and DMF (10 ml). CC (SiO_2, hexane/Et_2O 6:1) resulted in the separation of (all-*E*)-**56a** and (all-*E*)-**56b**. Crystallization from Et_2O gave (all-*E*)-**56b** (0.150 g, 28%).

*Data of (all-*E*)-***56a***:* Red oil. R_f (hexane/Et_2O 1:1) 0.65. UV/VIS (hexane/CH_2Cl_2; *Fig. 16*): max. 378 (1.00), 364 (sh, 0.99), 310 (0.70); min. 319 (0.69), 261 (0.48).

*Data of (all-*E*)-***56b***:* Red crystals. M.p. 202.9–205.2°. R_f (hexane/Et_2O 1:1) 0.48. UV/VIS (CH_2Cl_2/hexane; *Fig. 16*): max. 451 (1.00), 400 (sh, 0.72); min. 321 (0.42). ^{1}H-NMR ($CDCl_3$; 300 MHz): 8.15 (*d*-like, 2 arom. H); 7.47 (*d*-like 2 arom. H); 7.32 (*d*-like, 2 arom. H); 6.94 (*dd*, ^3J(3″,4″) = 15.7, ^3J(2″,3″) = 10.4, H–C(3″)); 6.84 (*d*-like, 2 arom. H); 6.79 (*d*, ^3J(3″,4″) = 15.7, H–C(4″)); 6.73 (*d*, ^3J(2,3) = 6.5, H–C(3)); 6.55 (*d*, ^3J(1″,2″) = 15.5, H–C(1″)); 6.51 (*d*, ^3J(1′,2′) = 15.5, H–C(2′)); 6.48 (*d*, ^3J(2,3) = 6.5, H–C(2)); 6.35 (*dd*, ^3J(1″,2″) = 15.4, ^3J(2″,3″) = 10.3, H–C(2″)); 6.24 (*s*, H–C(9)); 6.23 (*d*, ^3J(1′,2′) = 15.7, H–C(1′)); 6.13 (*s*, H–C(7)); 3.81 (*s*, MeO–C_p); 3.70 (*s*, COOMe); 2.14 (*d*, ^4J(7,Me–C(6)) = 1.0, Me–C(6)); 1.89 (*d*, ^4J(9,Me–C(8)) = 1.0, Me–C(8)); 1.65 (*s*, Me–C(10)). ^{13}C-NMR ($CDCl_3$, 75 MHz; tentative assignment): 168.87 (*s*, *C*OOMe); 159.54 (*s*, MeO–C_p); 146.38 (*q*, O_2N–C_p); 146.09 (*s*); 143.97 (*s*, arom. C); 139.46 (*s*); 139.19 (*s*); 138.80 (*s*); 138.67 (*d*, C(4″)); 134.01 (*d*, C(3″)); 133.40 (*d*, C(3)); 131.60 (*s*); 130.25 (*d*, C(9)); 130.21 (*s*); 130.11 (*d*, C(1′)); 130.02 (*s*); 129.71 (*d*, C(1″)); 129.12 (*d*, C(2″)); 129.03 (*d*, C(7)); 128.76 (*d*, C(2)); 127.97 (*d*, arom. C); 126.47 (*d*, arom. C); 126.03 (*d*, C(2′)); 124.05 (*d*, arom. C); 123.66 (*s*); 120.86 (*s*); 114.10 (*s*); 55.34 (*q*, *Me*O–C_p); 52.12 (*q*, COO*Me*); 25.16 (*q*, *Me*–C(8)); 21.63 (*q*, *Me*–C(6)); 18.84 (*q*, *Me*–C(10)).

4.8. *Methyl 6,8,10-Trimethyl-2,5-bis[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-1-carboxylate* ((all-*E*)-**60a**) *and Methyl 6,8,10-Trimethyl-1,4-bis[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-5-carboxylate* ((all-*E*)-**60b**). 4.8.1. *5-Methyl Hydrogen-6,8,10-Trimethyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalene-4,5-dicarboxylate Acid* ((1*E*,3*E*)-**57b**). Diester **24b** (0.450 g, 1.02 mmol) was semi-saponified in boiling MeOH/H_2O (2 h) in the presence of LiOH (0.950 g, 22.60 mmol): **57b** (0.357 g, 82%). Orange powder. M.p. 191.2–193.5° (dec. under formation of the cyclic anhydride). R_f (CH_2Cl_2/MeOH 9:1) 0.43. UV/VIS (MeCN): max. 404 (sh), 338, 282; min. 259. IR (KBr): 2947*m*, 2911*m*, 2626*w*, 2532*w*, 1729*s*, 1620*s*, 1609*w*, 1546*w*, 1513*m*, 1434*s*, 1374*w*, 1277*s*, 1239*s*, 1202*s*, 1146*w*, 1105*w*, 1050*m*, 990*m*, 917*w*, 890*w*, 843*w*, 817*w*, 796*w*, 774*m*, 750*m*, 689*m*, 579*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.72 (*d*, ^3J(3,2) = 6.4, H–C(3)); 7.40–7.20 (*m*, 5 arom. H); 6.85 (*dd*, ^3J(3′,4′) = 15.4, ^3J(2′,3′) = 10.7, H–C(3′)); 6.57 (*d*, ^3J(3′,4′) = 15.7, H–C(4′)); 6.51 (*d*, ^3J(1′,2′) = 15.2, H–C(1′)); 6.47 (*d*, ^3J(2,3) = 6.7, H–C(2)); 6.22 (*s*, H–C(9)); 6.22 (*dd*, ^3J(1′,2′) = 15.2, ^3J(2′,3′) = 10.7, H–C(2′)); 6.13 (*s*, H–C(7)); 3.46 (*s*, COOMe); 2.10 (*d*, ^4J(7,Me–C(6)) = 1.1, Me–C(6)); 1.90 (*d*, ^4J(9,Me–C(9)) = 1.1, Me–C(8)); 1.64 (*s*, Me–C(10)). CI-MS (NH_3): 458 (42), 440 (17), 426 (4, $M^{+\bullet}$); 412 (100), 410 (16), 394 (54).

4.8.2. *1,1-Dimethoxy-7,9,11-trimethyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptaleno[4,5-*c*]furan-3(1*H*)-one* ((1*E*,3*E*)-**58b**). The iminium salt was formed in the usual manner from DMF (2.12 g, 29.0 mmol) and oxalyl chloride (1.71 g, 13.5 mmol) in MeCN. Then, (1*E*,3*E*)-**57b** (1.90 g, 4.50 mmol) was added. Workup and CC (SiO_2, hexane/Et_2O 5:1) yielded (1*E*,3*E*)-**58b** (1.51 g, 77%). For analyses, a sample was recrystallized from Et_2O. Dark brown crystals. M.p. 189.8–190.7°. R_f (hexane/Et_2O 1:1) 0.70. UV/VIS (MeCN): max. 461 (sh, 3.85), 347 (3.87), 320 (4.36), 291 (sh, 4.31); min. 323 (4.35), 263 (4.15). IR (KBr): 2977*w*, 2945*w*, 2843*w*, 1758*s*, 1610*w*, 1553*w*, 1494*m*, 1446*w*, 1399*w*, 1374*w*, 1298*m*, 1275*m*, 1241*m*, 1197*w*, 1147*m*, 1097*w*, 1062*w*, 1016*w*, 991*w*, 908*m*, 870*w*, 849*m*, 779*w*, 747*m*, 725*w*, 695*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.39 (*d*, ^3J(4,5) = 7.1, H–C(4)); 7.33–7.23 (*m*, 5 arom. H); 6.88 (*dd*, ^3J(3′,4′) = 15.5, ^3J(2′,3′) = 10.6, H–C(3′)); 6.64 (*d*, ^3J(4,5) = 6.9, H–C(5)); 6.62 (*d*, ^3J(4′,3′) = 15.7, H–C(4′)); 6.59 (*d*, ^3J(1′,2′) = 15.1, H–C(1′)); 6.42 (*dd*, ^3J(2′,1′) = 15.0, ^3J(2′,3′) = 10.6, H–C(2′)); 6.24 (*s*, H–C(8)); 6.20 (*s*, H–C(10)); 3.45, 3.20 (2*s*, 2 MeO–C(1)); 2.12 (*d*, ^4J(10,Me–C(11)) = 1.0, Me–C(11)); 2.06 (*d*, ^4J(8,Me–C(9)) = 1.0, Me–C(9)); 1.63 (*s*, Me–C(7)). Anal. calc. for $C_{29}H_{28}O_4$ (440.50): C 79.07, H 6.41; found: C 78.90, H 6.39.

4.8.3. *Methyl 4-Formyl-9-isopropyl-6-methyl-1-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]heptalen-5-carboxylate* ((1*E*,3*E*)-**59b**). As described in *3.1*, with furanone **58b** (1.50 g, 3.40 mmol), toluene (4 ml), and 2M DIBAH in hexane (3.40 mmol). CC (SiO_2, hexane/Et_2O 4:1) yielded (1*E*,3*E*)-**59b** (1.02 g, 72%). For analyses, a sample was recrystallized from Et_2O. Red crystals. M.p. 206.4–208.3°. R_f (hexane/Et_2O 1:1) 0.29. UV/VIS (MeCN): max. 413 (sh, 4.08), 343 (4.47), 320 (4.46), 284 (sh, 4.27); min. 327 (4.45), 261 (4.17). IR (KBr): 3007*w*, 2943*w*, 2904*w*, 2717*w*, 1734*s*, 1643*w*, 1596*w*, 1547*w*, 1515*m*, 1432*m*, 1415*w*, 1380*w*, 1356*m*, 1242*s*, 1202*m*, 1177*w*, 1128*m*, 1099*w*, 1059*m*, 989*m*, 914*w*, 900*w*, 881*w*, 843*w*, 794*w*, 752*w*, 696*w*, 607*w*. ^{1}H-NMR ($CDCl_3$; 300 MHz): 9.43 (*s*, CHO); 7.39 (*d*, ^3J(2,3) = 7.1, H–C(3)); 740–7.21 (*m*, 5 arom. H); 6.87 (*dd*, ^3J(3′,4′) = 15.4, ^3J(3′,2′) = 10.8, H–C(3′)); 6.60 (*d*, ^3J(4′,3′) = 15.6, H–C(4′)); 6.58 (*d*, ^3J(2,3) = 6.8, H–C(2)); 6.54 (*d*, ^3J(1′,2′) = 15.0, H–C(1′)); 6.28 (*dd*, ^3J(2′,1′) = 14.9, ^3J(2′,3′) = 10.8, H–C(2′)); 6.19 (*s*, H–C(9)); 6.14 (*s*, H–C(7)); 3.71 (*s*, COOMe); 2.09 (*d*, ^4J(7,Me–C(6)) = 1.1, Me–C(6)); 1.91 (*d*, ^4J(9,Me–C(8)) = 1.1, Me–C(8)); 1.64 (*s*, Me–C(10)).

4.8.4. *Formation of (all-*E*)-***60a***/(all-*E*)-***60b***.* As described in *3.5.2.1* and *4.1.5*, with aldehyde (1*E*,3*E*)-**59b** (0.200 g, 0.49 mmol), $CrCl_2$ (0.482 g, 3.92 mmol), and CHI_3 (0.384 g, 0.98 mmol) in THF; then after removal of THF, with styrene (0.153 g, 0.147 mmol), [Pd(OAc)$_2$] (11 mg, 0.049 mmol), Ag_2CO_3 (0.135 g, 0.49 mmol), and DMF (5 ml). CC (SiO_2, hexane/Et_2O 7:1) resulted in the separation of (all-*E*)-**60a** and (all-*E*)-**60b**. Crystallization from Et_2O gave red crystals of (all-*E*)-**60b** (0.075 g, 30%). Pure (all-*E*)-**60a** was obtained by irradiation of (all-*E*)-**60b** (0.050 g) in hexane/CH_2Cl_2 20:1 (170 ml) with a high-pressure Hg lamp through a cooled filter soln. of 2N aq. $[Cu(NH_3)_4]SO_4$ [23]. CC as above gave pure (all-*E*)-**60a** (0.030 g) after recrystallization from Et_2O.

*Data of (all-*E*)-***60a***: Yellow crystals (*cf. Fig. 3*). M.p.: at 120–130°, crystal color changed from yellow to red); >149° crystals started to melt; at higher temp., the little oily drops took a sharp contour; at 202.2°, melting of orange micro-crystals. R_f (hexane/Et_2O 1:1) 0.77. UV/VIS (hexane/CH_2Cl_2; *Fig. 13*): max. *ca.* 440 (sh, 0.04), *ca.* 380 (sh, *ca.* 0.5), 342 (1.00); min. 258 (0.27). IR (KBr): 3058*w*, 3022*m*, 2945*m*, 2910*m*, 1701*s*, 1636*w*, 1600*m*, 1537*w*, 1494*m*, 1446*m*, 1431*m*, 1373*w*, 1319*w*, 1234*s*, 1211*s*, 1190*s*, 1099*m*, 1071*w*, 1046*w*, 988*s*, 936*w*, 909*w*, 875*w*, 841*w*, 794*w*, 746*s*, 689*s*, 609*w* 547*w*, 503*w*. ^{1}H-NMR ($CDCl_3$, 600 MHz): 7.58 (*d*, ^3J(1′,2′) = 15.5, H–C(1′)); 740–7.22 (*m*, 10 arom. H); 7.01 (*dd*, ^3J(3′,4′) = 15.4, ^3J(2′,3′) = 10.6, H–C(3′)); 6.98 (*d*, ^3J(3,4) = 12.0, H–C(3)); 6.90 (*ddd*, ^3J(3″,4″) = 15.6, ^3J(3″,2″) = 9.1, ^4J(1″,3″) = 0.7, H–C(3″)); 6.86 (*d*, ^3J(4,3) = 12.4, H–C(4)); 6.82 (*dd*, ^3J(2′,1′) = 15.5, ^3J(2′,3′) = 10.6, H–C(2′)); 6.74 (*d*, ^3J(4′,3′) = 15.5, H–C(4′)); 6.61 (*d*, ^3J(4″,3″) = 15.6, H–C(4″)); 6.52–6.47 (*m*, H–C(1″), H–C(2″)); 6.17 (*s*, H–C(9)); 6.10 (*s*, H–C(7)); 3.69 (*s*, COOMe); 2.12 (*s*, Me–C(6)); 2.05 (*s*, Me–C(8)); 1.74 (*s*, Me–C(10)). ^{1}H-NMR (C_6D_6, 600 MHz): 8.11 (*d*, ^3J(1′,2′) = 15.4, H–C(1′)); 7.24–7.00 (*m*, 10 arom. H); 7.01 (*d*, ^3J(3,4) = 12.4, H–C(3)); 6.89 (*dd*, ^3J(3′,4′) = 15.3, ^3J(2′,3′) = 10.7, H–C(3′)); 6.89 (*d*, ^3J(3,4) = 12.0, H–C(4)); 6.80 (*dd*, ^3J(2′,1′) = 15.4, ^3J(2′,3′) = 10.8, H–C(2′)); 6.79 (*dd*, ^3J(3″,4″) = 15.5, ^3J(3″,2″) = 10.6, H–C(3″)); 6.71 (*d*, ^3J(1″,2″) = 15.4, H–C(1″)); 6.55 (*dd*, ^3J(2″,1″) = 15.4, ^3J(2″,3″) = 10.5, H–C(2″)); 6.49 (*d*, ^3J(4″,3″) = 15.5, H–C(4″)); 6.48 (*d*, ^3J(4′,3′) = 15.4, H–C(4′)); 6.13 (*s*, H–C(9)); 6.04 (*s*, H–C(7)); 3.37 (*s*, COOMe); 2.17 (*s*, Me–C(6)); 1.88 (*s*, Me–C(8)); 1.87 (*s*, Me–C(10)).

*Data of (all-*E*)-***60b***: Brick-red crystals (*cf. Fig. 3*). M.p. 199.8–201.2°. R_f (hexane/Et_2O 1:1) 0.63. UV/VIS (hexane/CH_2Cl_2; *Fig. 13*): max. 439 (1.00), 365 (1.00), 267 (0.61); min. 397 (0.81), 302 (0.39). IR (KBr): 302*m*, 2944*m*, 2909*m*, 2852*w*, 1724*s*, 1640*w*, 1599*m*, 1494*m*, 1447*m*, 1433*m*, 1373*w*, 1242*s*, 1201*s*, 1096*m*, 1056*s*, 990*s*, 912*w*, 882*w*, 845*w*, 794*w*, 749*s*, 691*s*, 614*w*, 523*w*, 505*w*. ^{1}H-NMR ($CDCl_3$, 600 MHz): 7.38–7.20 (*m*, 10 arom. H); 6.86 (*dd*, ^3J(3′,4′) = 15.4, ^3J(3′,2′) = 11.0, H–C(3′)); 6.80 (*dd*, ^3J(3″,4″) = 15.6, ^3J(2″,3″) = 8.6, H–C(3″)); 6.67 (*d*, ^3J(3,2) = 6.5, H–C(3)); 6.55 (*d*, ^3J(4″,3″) = 15.1, H–C(4″)); 6.52 (*d*, ^3J(4′,3′) = 15.1, H–C(4′)); 6.48 (*d*, ^3J(1′,2′) = 14.9, H–C(1′)); 6.45 (*d*, ^3J(2,3) = 6.5, H–C(2)); 6.39 (*d*, ^3J(1″,2″) = 15.2, H–C(1″)); 6.37 (*dd*, ^3J(2″,1″) = 15.5, ^3J(2″,3″) = 8.7, H–C(2″)); 6.24 (*s*, H–C(9)); 6.14 (*s*, H–C(7)); 6.12 (*dd*, ^3J(2′,1′) = 14.8, ^3J(2′,3′) = 11.1, H–C(2′)); 3.71 (*s*, COOMe); 2.15 (*s*, Me–C(8)); 1.88 (*s*, Me–C(6)); 1.87 (*s*, Me–C(10)). ^{1}H-NMR (C_6D_6, 600 MHz): 7.38–7.20 (*m*, 10 arom. H); 6.83 (*ddd*, ^3J(3′,4′) = 15.6, ^3J(3′,2′) = 10.3, ^4J(3′,1′) = 0.8, H–C(3′)); 6.68 (*dd*, ^3J(3″,4″) = 15.4, ^3J(3″,2″) = 10.6, H–C(3″)); 6.61 (*d*, ^3J(3,2) = 6.7, H–C(3)); 6.58 (*dd*, ^3J(2″,1″) = 15.3, ^3J(2″,3″) = 10.6, H–C(2″)); 6.45–6.39 (*m*, H–C(1′), H–C(2′)); 6.39 (*d*, ^3J(1″,2″) = 15.5, H–C(1″)); 6.37 (*d*, ^3J(2,3) = 6.1, H–C(2)); 6.35 (*d*, ^3J(4′,3′) = 15.2, H–C(4′)); 6.24 (*s*, H–C(9)); 6.12 (*d*, ^3J(4″,3″) = 15.7, H–C(4″)); 6.11 (*s*, H–C(7)); 3.43 (*s*, COOMe); 2.03 (*s*, Me–C(6)); 1.98 (*s*, Me–C(8)); 1.76 (*s*, Me–C(10)).

4.9. *Methyl 5-[(1*E,*3*E*)-4-(4-Methoxyphenyl)buta-1,3-dien-1-yl]-6,8,10-trimethyl-2-[(1*E,*3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-1-carboxylate* ((all-*E*)-**64a**) *and Methyl 1-[(1*E,*3*E*)-4-(4-Methoxyphenyl)buta-1,3-dien-1-yl]-6,8,10-trimethyl-4-[(1*E,*3*E*)-4-(4-nitrophenyl)buta-1,3-dien-1-yl]heptalene-5-carboxylate* ((all-*E*)-**64b**). 4.9.1. *5-Methyl Hydrogen-1-[(1*E,*3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-6,8,10-trimethylheptalene-4,5-dicarboxylate* ((1*E*,3*E*-**61b**). Diester (1*E*,3*E*)-**25b** (2.50 g, 5.31 mmol) was semi-saponified with LiOH (4.95 g, 118 mmol) in boiling MeOH/H_2O (2 h). The usual workup gave (1*E*,3*E*)-**61b** (2.20 g), which contained still some diester **25b**.

4.9.2. *1,1-Dimethoxy-7,9,11-trimethyl-6-[(1*E,*3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]heptaleno[4,5-c]furan-3(1*H*)-one* ((1*E*,3*E*)-**62b**). The iminim salt of DMF and oxalyl chloride (2.92 g, 23.0 mmol) in MeCN was formed in the usual manner and treated with acid **61b** (1.5 g, 2.30 mmol). CC (SiO_2, hexane/Et_2O 5:1) gave (1*E*,3*E*)-**62b** (0.60 g, 55%) as dark brown crystals.

4.9.3. *Methyl 4-Formyl-1-[(1*E,*3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl]-6,8,10-trimethylheptalene-5-carboxylate* ((1*E*,3*E*)-**63b**). The reduction of (1*E*,3*E*)-**62b** (0.50 g, 1.06 mmol) in toluene with 2M DIBAH in hexane (0.53 ml, 1.06 mmol) at $-78°$ was performed in the usual manner. Workup and CC (SiO_2, hexane/Et_2O 4:1) gave (1*E*,3*E*)-**63b** (0.23 g, 49%) as a red oil, which was not further purified.

4.9.4. *Formation of (all-*E*)-***64a***/(all-*E*)-***64b***.* As described in *3.5.2.1* and *4.1.5*, with aldehyde (1*E*,3*E*)-**63b** (0.100 g, 0.227 mmol), $CrCl_2$ (0.419 g, 4.41 mmol), and CHI_3 (179 g, 0.454 mmol) in THF, then after evaporation with 4-nitrostyrene in DMF, [$Pd(OAc)_2$] (5.1 mg, 0.023 mmol), and Ag_2CO_3 (63 mg, 0.23 mmol). The formed (all-*E*)-**64a** and (all-*E*)-**64b** were separated by CC (SiO_2, hexane/Et_2O 6:1). Crystallization from Et_2O delivered pure (all-*E*)-**64b** (0.80 g, 60%).

*Data of (all-*E*)-***64a***:* R_f (hexane/Et_2O 1:1) 0.65. UV/VIS (hexane/CH_2Cl_2; *Fig. 20*): max. *ca.* 462 (sh, 0.04), *ca.* 378 (sh, 0.89), 359 (1.00); min. 269 (0.30).

*Data of (all-*E*)-***64b***:* Red crystals. M.p. 215.1–217.0°. R_f (hexane/Et_2O 1:1) 0.48. UV/VIS (hexane/CH_2Cl_2; *Fig 20*): max. 466 (1.00), 400 (sh, 0.67), 311 (0.44), 289 (0.44); min. 328 (0.43), 263 (0.38). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.15 (*d*-like, 2 arom. H); 7.47 (*d*-like, 2 arom. H); 7.32 (*d*-like, 2 arom. H); 6.94 (*dd*, $^3J(3'',4'')=15.6$, $^3J(3'',2'')=10.4$, H–C(3'')); 6.84 (*d*-like, 2 arom. H); 6.73 (*dd*, $^3J(3',4')=16.8$, $^3J(3',2')=10.8$, H–C(3')); 6.71 (*d*, $^3J(3,2)=7.1$, H–C(3)); 6.55, 6.50, 6.48 (3*d*, $^3J=15.3-13.6$, H–C(1'), H–C(1''), H–C(4')); 6.43 (*d*, $^3J(3'',4'')=14.3$, H–C(4'')); 6.42 (*d*, $^3J(2,3)=6.9$, H–C(2)); 6.34 (*dd*, $^3J(2'',1'')=15.4$, $^3J(2'',3'')=10.3$, H–C(2'')); 6.30 (*s*, H–C(9)); 6.13 (*s*, H–C(7)); 6.10 (*dd*, $^3J(1',2')=14.8$, $^3J(2',3')=10.7$, H–C(2')); 3.84 (*s*, MeO–C_p); 3.81 (*s*, COOMe); 2.14 (*s*, Me–C(6)); 1.91 (*s*, Me–C(8)); 1.64 (*s*, Me–C(10)). EI-MS: 586 (38, $[M+1]^+$), 585 (100, $M^{+\cdot}$), 584 (23), 583 (42), 121 (56).

The structure of (all-*E*)-**64b** was confirmed by an X-ray crystal-structure analysis (*Fig. 8* and *Tables 2* and *7*).

5. *X-Ray Crystal-Structure Determinations of Compounds* **14b**, (1*E*,3*E*)-**16b**, (1*E*,3*E*)-**24b**, (1*E*,3*E*)-**25b**, (all-*E*)-**52b**, *and* (all-*E*)-**64b** (see *Tables 2* and *7* and *Figs. 4*, *a*, *5*, *6*, *7*, and *8*)[17]). All measurements of **14b**, (1*E*,3*E*)-**16b**, (1*E*,3*E*)-**24b**, and (1*E*,3*E*)-**25b** were conducted at low-temp. with a *Rigaku-AFC5R* diffractometer with graphite-monochromated MoK_α radiation (λ 0.71073 Å) and a 12 kW rotating-anode generator, while those of (all-*E*)-**52b** and (all-*E*)-**64b** were made with an *Agilent-Technologies-SuperNova* area-detector diffractometer [24] with CuK_α radiation (λ 1.54184 Å) from a micro-focus X-ray source and an *Oxford-Instruments-Cryojet XL* cooler. The intensities for each structure were corrected for *Lorentz* and polarization effects, and in the case of (all-*E*)-**52b** and (all-*E*)-**64b**, an empirical absorption correction with spherical harmonics [25] was applied. The data collection and refinement parameter are given in *Table 7*.

Each structure was solved by direct methods with SHELXS86 [25] or SHELXS97 [26], which revealed the positions of all non-H-atoms. The asymmetric unit of (all-*E*)-**64b** contains two symmetry-independent molecules. In (1*E*,3*E*)-**24b**, the ester group at C(4) is disordered in that the positions of the C=O and MeO groups in one orientation are exchanged in the other orientation. Mean positions were used for the overlapping C=O and MeO O-atoms, while two positions with relative site occupation factors initially refined and then fixed at 0.488:0.512 were defined for the disordered Me groups. The non-H-atoms of each structure were refined anisotropically. The H-atoms in (1*E*,3*E*)-**16b**, (1*E*,3*E*)-**24b**,

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[17]) CCDC-887343–887348 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table 7. *Crystallographic Data for Compounds* **14b**, *(1*E,*3*E*)*-**16b**, *(1*E,*3*E*)*-**24b**, *(1*E,*3*E*)*-**25b**, *(all-*E*)*-**52b**, *and (all-*E*)*-**64b**

	14b	(1*E*,3*E*)-**16b**	(1*E*,3*E*)-**24b**	(1*E*,3*E*)-**25b**	(all-*E*)-**52b**	(all-*E*)-**64b**
Crystallized from	Et_2O/hexane	CH_2Cl_2/Et_2O/pentane	Et_2O/hexane	hexane/Et_2O	hexane/CH_2Cl_2	$CHCl_3$/hexane
Empirical formula	$C_{20}H_{21}ClO_4$	$C_{30}H_{30}O_4$	$C_{29}H_{28}O_4$	$C_{30}H_{30}O_5$	$C_{35}H_{33}NO_5$	$C_{38}H_{35}NO_5$
M_r	360.83	454.56	440.54	470.56	547.65	585.70
Crystal color, habit	orange, plate	crimson, prism	orange, prism	orange, plate	red, plate	red, plate
Crystal dimensions [mm]	0.15 × 0.45 × 0.50	0.35 × 0.40 × 0.45	0.38 × 0.38 × 0.50	0.15 × 0.28 × 0.40	0.02 × 0.20 × 0.25	0.04 × 0.12 × 0.23
Temperature [K]	173(1)	173(1)	173(1)	173(1)	160(1)	160(1)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	4	4	4	4	4	4
Reflections for cell determination	25	25	25	25	8752	17111
2θ Range for cell determination [°]	35 – 39	24 – 26	38 – 40	33 – 40	3 – 149	6 – 147
Unit cell parameters:						
a [Å]	7.434(2)	14.009(2)	14.557(2)	23.469(2)	10.85190(14)	9.5704(2)
b [Å]	25.925(5)	14.184(2)	9.639(2)	10.405(2)	10.64281(13)	12.8805(4)
c [Å]	9.858(3)	13.095(2)	17.674(2)	10.373(2)	25.7003(4)	26.4300(7)
α [°]	90	90	90	90	90	92.559(2)
β [°]	104.16(2)	95.02(1)	97.33(1)	98.13(1)	100.4867(14)	93.805(2)
γ [°]	90	90	90	90	90	105.588(2)
V [Å^3]	1842.1(8)	2592.1(6)	2459.6(6)	2507.7(7)	2918.68(7)	3124.7(1)
F(000)	760	968	936	1000	1160	1240
D_x [g cm^{-3}]	1.301	1.165	1.190	1.246	1.246	1.245
μ(MoK_α) [mm^{-1}]	0.228	0.0761	0.0781	0.0838	–	–
μ(CuK_α) [mm^{-1}]	–	–	–	–	0.667	0.658
Scan type	ω	ω/2θ	ω/2θ	ω/2θ	ω	ω
2$\theta_{(max)}$ [°]	55	55	55	55	148.8	147
Transmission factors (min; max)	–	–	–	–	0.403; 1.000	–
Total reflections measured	4643	5954	6203	6420	22702	23061
Symmetry independent reflections	4222	5466	5644	5770	5847	12064
R_{int}	0.027	0.020	0.077	0.054	0.025	0.043
Reflections with $I > 2\sigma(I)$	3043	3690	3564	3610	4579	8755
Parameters refined	226	428	432	437	375	803
$R(F)$ ($I > 2\sigma(I)$ reflections)	0.0589	0.0654	0.0486	0.0493	0.0405	0.0532

Table 7 (cont.)

	14b	(1*E*,3*E*)-**16b**	(1*E*,3*E*)-**24b**	(1*E*,3*E*)-**25b**	(all-*E*)-**52b**	(all-*E*)-**64b**
$wR(F^2)$ (all data)	–	–	–	–	0.1124	0.1459
$wR(F)$ ($I > 2\sigma(I)$ reflections)	0.0609	0.0612	0.0388	0.0441	–	–
Weights: p in $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$	0.005	0.005	0.005	0.005	–	–
Weighting parameters [a; b][a])	–	–	–	–	0.0525; 0.7840	0.0547; 1.5619
Secondary extinction coefficient	–	$1.6(1) \cdot 10^{-6}$	$1.14(7) \cdot 10^{-6}$	$5.1(4) \cdot 10^{-7}$	–	–
Goodness of fit	2.472	3.054	1.844	1.672	1.033	1.074
Final Δ_{max}/σ	0.0006	0.001	0.0001	0.0005	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	1.14; −0.52	0.37; −0.33	0.23; −0.19	0.24; −0.20	0.30; −0.26	0.41; −0.21
$\sigma(d_{(C-C)})$ [Å]	0.004	0.004–0.005	0.002–0.003	0.003	0.002–0.003	0.003–0.005

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$.

and (1*E*,3*E*)-**25b** were placed in the positions indicated by difference *Fourier* maps, and their positions were allowed to be refined together with individual isotropic displacement parameters. All H-atoms in the remaining structures were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom (1.5 U_{eq} for the Me groups in (all-*E*)-**52b** and (all-*E*)-**64b**).

The structures of **14b**, (1*E*,3*E*)-**16b**, (1*E*,3*E*)-**24b**, and (1*E*,3*E*)-**25b** were refined on *F* by full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o|-|F_c|)^2$. For (all-*E*)-**52b** and (all-*E*)-**64b**), the refinement was carried out on F^2 by minimizing the corresponding function based on F^2. Corrections for secondary extinction were applied in the case of (1*E*,3*E*)-**16b**, (1*E*,3*E*)-**24b**, and (1*E*,3*E*)-**25b**. For **14b**, the largest peak of residual electron density was 1.14 e Å^{-3} and was located near the Cl-atom and about 1.42 Å from C(11). The next largest peak of 0.75 e Å^{-3} was also near the Cl-atom. All other residual peaks were less than 0.31 e Å^{-3}. Neutral atom scattering factors for non-H-atoms were taken from [27a], and the scattering factors for H-atoms were taken from [28]. Anomalous dispersion effects were included in F_c [29]; the values for f' and f'' were those of [27b]. The values of the mass attenuation coefficients were those of [27c]. All calculations for (all-*E*)-**52b** and (all-*E*)-**64b**) were performed with SHELXL97 [26], while the teXsan crystallographic software package [30] was used for the remaining structures. The crystallographic diagrams were drawn with ORTEPII [31].

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