172. Thermal and Ru-catalyzed Reactions of Styryl-Substituted Azulenes with Dimethyl Acetylenedicarboxylate

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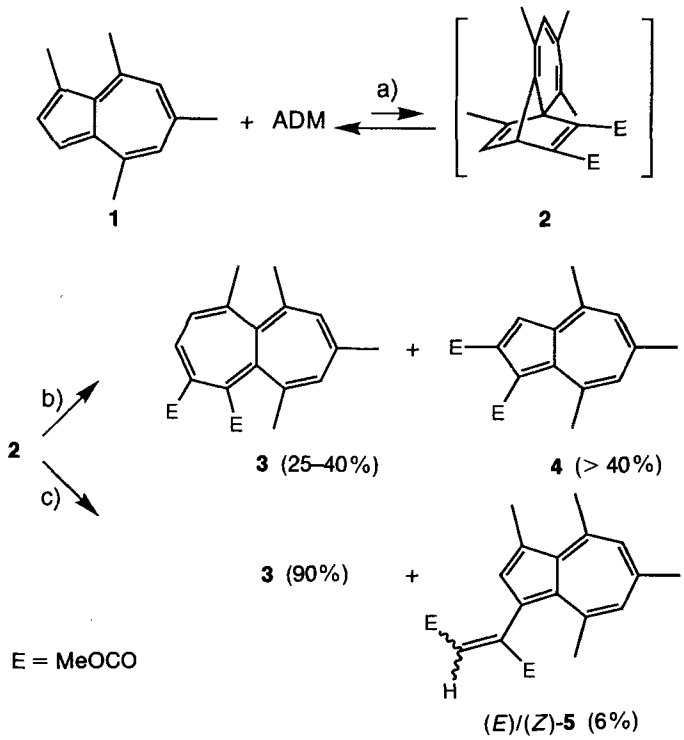
The thermal reaction of 1-[(*E*)-styryl]azulenes with dimethyl acetylenedicarboxylate (ADM) in decalin at 190–200° does not lead to the formation of the corresponding heptalene-1,2-dicarboxylates (*Scheme 2*). Main products are the corresponding azulene-1,2-dicarboxylates (see **4** and **9**), accompanied by the benzanellated azulenes *trans*-**10a** and *trans*-**11**, respectively. The latter compounds are formed by a *Diels-Alder* reaction of the starting azulenes and ADM, followed by an ene reaction with ADM (*cf. Scheme 3*). The $[RuH_2(PPh_3)_4]$-catalyzed reaction of 4,6,8-trimethyl-1-[(*E*)-4-R-styryl]azulenes (R=H, MeO, Cl; *Scheme 4*) with ADM in MeCN at 110° yields again the azulene-1,2-dicarboxylates as main products. However, in this case, the corresponding heptalene-1,2-dicarboxylates are also formed in small amounts (3–5%; *Scheme 4*). The benzanellated azulenes *trans*-**10a** and *trans*-**10b** are also found in small amounts (2–3%) in the reaction mixture. ADM Addition products at C(3) of the azulene ring as well as at C(2) of the styryl moiety are also observed in minor amounts (1–3%). Similar results are obtained in the $[RuH_2(PPh_3)_4]$-catalyzed reaction of 3-[(*E*)-styryl]guaiazulene ((*E*)-**8**; *Scheme 5*) with ADM in MeCN. However, in this case, no heptalene formation is observed, and the amount of the ADM-addition products at C(2) of the styryl group is remarkably increased (29%). That the substituent pattern at the seven-membered ring of (*E*)-**8** is not responsible for the failure of heptalene formation is demonstrated by the Ru-catalyzed reaction of 7-isopropyl-4-methyl-1-[(*E*)-styryl]azulene ((*E*)-**23**; *Scheme 11*) with ADM in MeCN, yielding the corresponding heptalene-1,2-dicarboxylate (*E*)-**26** (10%). Again, the main product is the corresponding azulene-1,2-dicarboxylate **25** (20%). Reaction of 4,6,8-trimethyl-2-[(*E*)-styryl]azulene ((*E*)-**27**; *Scheme 12*) and ADM yields the heptalene-dicarboxylates (*E*)-**30A**/**B**, purely thermally in decalin (28%) as well as Ru-catalyzed in MeCN (40%). Whereas only small amounts of the azulene-1,2-dicarboxylate **8** (1 and 5%, respectively) are formed, the corresponding benzanellated azulene *trans*-**29** ist found to be the second main product (21 and 10%, respectively) under both reaction conditions. The thermal reaction yields also the benzanellated azulene **28** which is not found in the catalyzed variant of the reaction. Heptalene-1,2-dicarboxylates are also formed from 4-[(*E*)-styryl]azulenes (*e.g.* (*E*)-**33** and (*E*)-**34**; *Scheme 14*) and ADM at 180–190° in decalin and at 110° in MeCN by $[RuH_2(PPh_3)_4]$ catalysis. The yields (30%) are much better in the catalyzed reaction. The formation of by-products (*e.g.* **39**–**41**; *Scheme 14*) in small amounts (0.5–5%) in the Ru-catalyzed reactions allows to understand better the reactivity of zwitterions (*e.g.* **42**) and their tricyclic follow-up products (*e.g.* **43**) built from azulenes and ADM (*cf. Scheme 15*).

1. Introduction. – We have already shown that the reaction of azulenes with dimethyl acetylenedicarboxylate (ADM) to yield heptalene-1,2-dicarboxylates can appreciably be improved as compared to the purely thermal reaction in apolar solvents (*cf.* [1–3]), when it is performed in the presence of catalytic amounts of $[RuH_2(PPh_3)_4]$ in polar solvents such as MeCN [4]. The reaction can as well be catalyzed by $[RhH(PPh_3)_4]$, Rh^I complexes of azulenes, and by other Rh^I complexes such as $[RhCl(cod)]_2$ (cod = (*Z*,*Z*)-cycloocta-1,5-diene) [5]. Also benz[*a*]azulenes and ADM can be transformed *via* expected tricyclic compounds into benzo[*d*]heptalene-6,7-dicarboxylates by catalytic amounts of

[1]) Part of the Ph. D. thesis of *A.A.S.B.*, University of Zurich, 1993.

Scheme 1

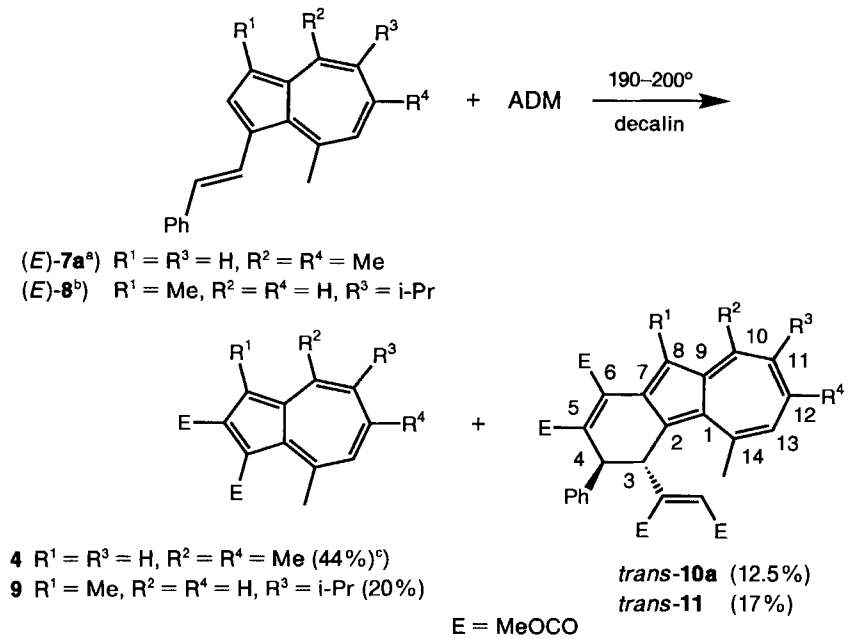


a) 180–208° in tetralin or decalin or 100° in MeCN in the presence of 2 mol-% of $[RuH_2(Ph_3P)_4]$ (**6**).
b) 180–208° in tetralin or decalin.
c) 100° in MeCN.

$[RuH_2(PPh_3)_4]$ [6] as well as by $[RhCl(cod)]_2$ [7]. The advantage of the catalyzed heptalene formation is the fact that azulenes and ADM already react at temperatures $< 100°$ (*cf.* [4]), and that, at this temperatures, the *retro-Diels-Alder* reaction of the primarily formed tricyclic intermediates to yield azulene-1,2-dicarboxylates cannot compete, in general, with the polar rearrangement of the tricyclic intermediates into heptalene-1,2-dicarboxylates (*cf.* [8]). An example is given in *Scheme 1*. 1,4,6,8-Tetramethylazulene (**1**) and ADM lead thermally at temperatures $> 180°$ in apolar solvents such as tetralin or decalin to 25–40% of the corresponding heptalene-1,2-dicarboxylate **3** and up to 40% of the dimethyl azulene-1,2-dicarboxylate **4** (*cf.* [1] [9]). However, in the presence of 2 mol-% of $[RuH_2(PPh_3)_4]$ (**6**) in MeCN, the reaction takes place already at 100°, and **3** is formed in a yield of 90%. Instead of **4**, small amounts of (*E*)- and (*Z*)-**5** are found [4]. For a study of the possible thermo- and photochromism of heptalenes [10], we were interested in the synthesis of styryl-substituted heptalene-1,2-dicarboxylates which should be obtained by the reaction of ADM with the corresponding styryl-substituted azulenes [11]. To find the best way to synthesize the styryl-substituted heptalenes, we compared the thermal with the Ru-catalyzed reaction of the corresponding azulenes with ADM. The results of these investigations are reported in this paper.

2. Results and Discussion. – 2.1. *1-Styryl-Substituted Azulenes.* – The thermal reaction of 4,6,8-trimethyl- ((*E*)-**7a**) and 5-isopropyl-3,8-dimethyl-1-[(*E*)-styryl]azulene ((*E*)-**8**) and ADM at 200° in decalin was disappointing, as no heptalene-dicarboxylate formation was observed (*Scheme 2*). Products that could be isolated and purified were the corresponding azulenedicarboxylates **4** and **9**, respectively, accompanied by the benzanellated azulenes *trans*-**10a** and *trans*-**11**, respectively. The formation of **4** and **9** shows that the

Scheme 2



[a]) ADM was applied in 1.5 molar excess. 20% of (*E*)-**7a** were recovered after 4 h at 200°.
[b]) ADM was applied in 2.1 molar excess. 24% of (*E*)-**8** were recovered after 7 h at 190°.
[c]) Yields with respect to reacted starting materials.

corresponding tricyclic intermediates of type **2** (*cf. Scheme 1*) had been formed. However, the tricyclic intermediates undergo in decalin the apolar *retro-Diels-Alder* reaction to yield **4** or **9** much more efficiently than the polar rearrangement into the corresponding heptalene-1,2-dicarboxylate (*cf.* [8]). The ^{1}H-NMR spectra ($CDCl_3$) of *trans*-**10a** and *trans*-**11** indicated the presence of four MeOCO groups and the disappearance of the *AB* system of the styryl substituent as well as of the signal of H–C(2) of the starting azulenes. Instead, the signals of two H-atoms in allylic/benzylic position (4.95/5.00 and 4.59/4.56 ppm[2])) with a small vicinal coupling constant (1.6/1.5 Hz) accompanied by the signal of a further H-atom at 5.05 and 5.10 ppm, respectively, were observed. ^{1}H-NOE Measurements of *trans*-**10a** revealed the spacial vicinity of Me–C(14) and the H-atom which appeared at 5.05 ppm and had to be assigned to a maleate or fumarate side chain. The

[2]) First value for *trans*-**10a** and the second one for *trans*-**11**.

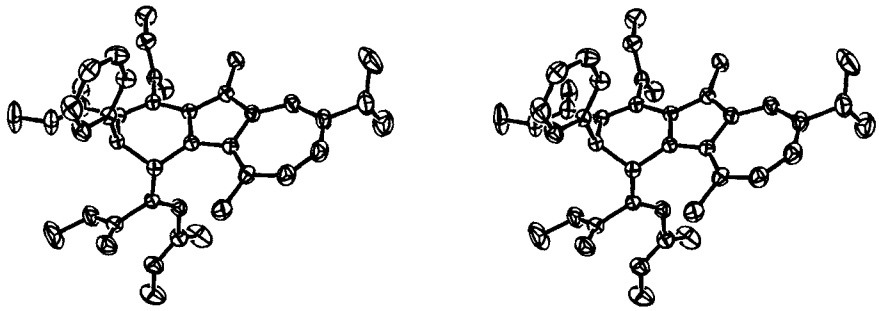
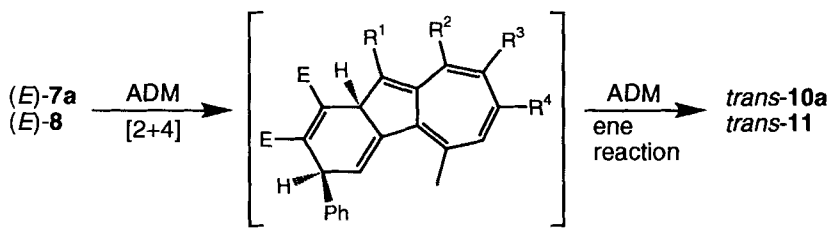


Fig. 1. *Stereoscopic view of the X-ray crystal structure of* trans-**11**

chemical shift of its H-atom suggested the (*Z*)-configuration. To eliminate any uncertainty with respect to the configuration of the side chain as well as of the relative configuration at C(3) and C(4), the structure of *trans*-**11a** was established by an X-ray crystal-structure analysis (*Fig. 1*). Indeed, it confirmed the assigned configuration and the fact that the maleate substituent at C(3) and the Ph group at C(4) occupy nearly pseudo-axial positions (Θ (C–C(3)–C(4)–C) = 159°) in the crystal structure. That the conformation of *trans*-**10a** and *trans*-**11** must be similar in solution is indicated by the observed small ^3J(H–C(3),H–C(4)) = 1.6/1.5 Hz (*cf.* [12]). The discussed configurational relations suggest that the formation of *trans*-**10a** and of *trans*-**11** is the result of two consecutive concerted reactions of the azulenes (*E*)-**7a** and (*E*)-**8**, respectively, and ADM as shown in *Scheme 3*. A thermal *Diels-Alder* reaction in the first step will lead to the formation of the *cis*-configurated derivatives **12**. A following ene reaction of these intermediates with ADM will yield – under re-establishment of the azulene system – the products with the observed *trans*- and (*Z*)-configurations.

Scheme 3[a])

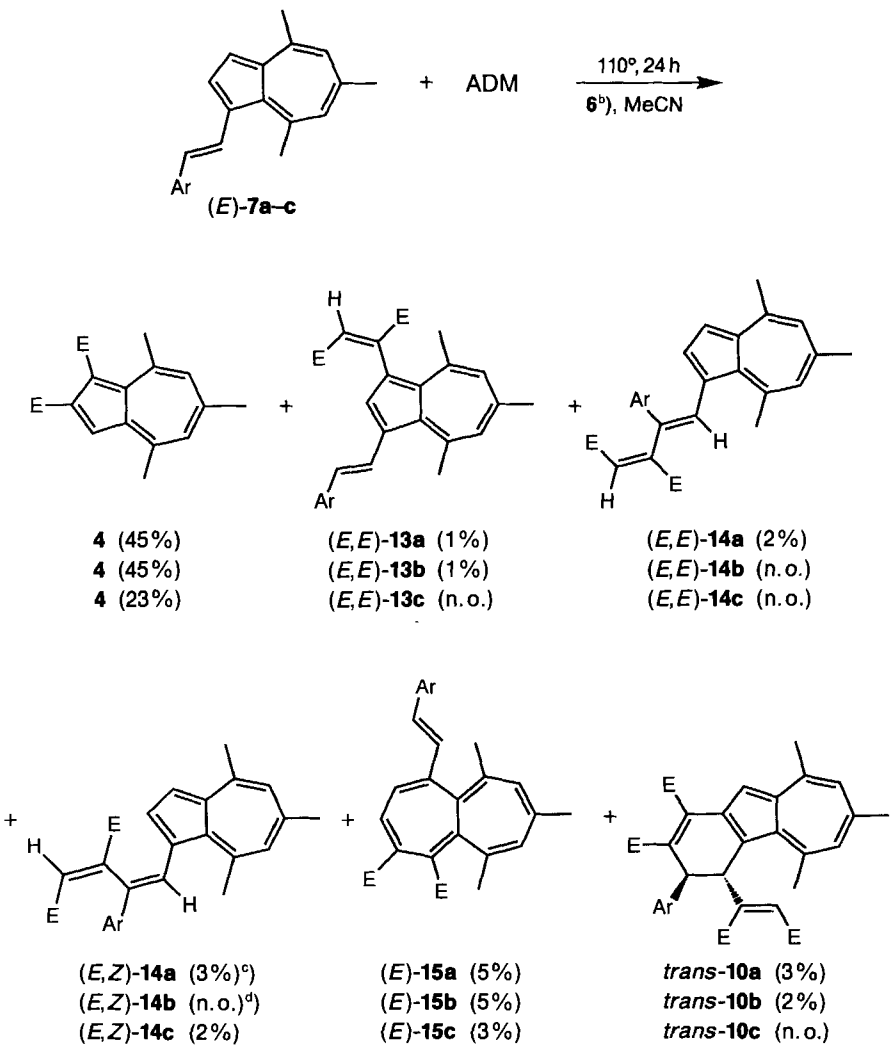


12 E = MeOCO

[a]) R^1–R^4 as defined in *Scheme 2*.

Since no heptalene-dicarboxylates were formed in the thermal reaction of (*E*)-**6a** and (*E*)-**7** with ADM, we examined the [$RuH_2(PPh_3)_4$]-catalyzed reaction. The results of the reaction of (*E*)-**7a** as well as of its 4-MeO and 4-Cl derivatives, (*E*)-**7b** and (*E*)-**7c**, respectively, with ADM in MeCN at 110° are shown in *Scheme 4*. The corresponding reaction with (*E*)-**8** and ADM is depicted in *Scheme 5*. Again, the azulene-1,2-dicarboxy-

Scheme 4[a])



a Ar = Ph, **b** Ar = 4-MeO–C_6H_4, **c** Ar = 4-Cl–C_6H_4

E = MeOCO

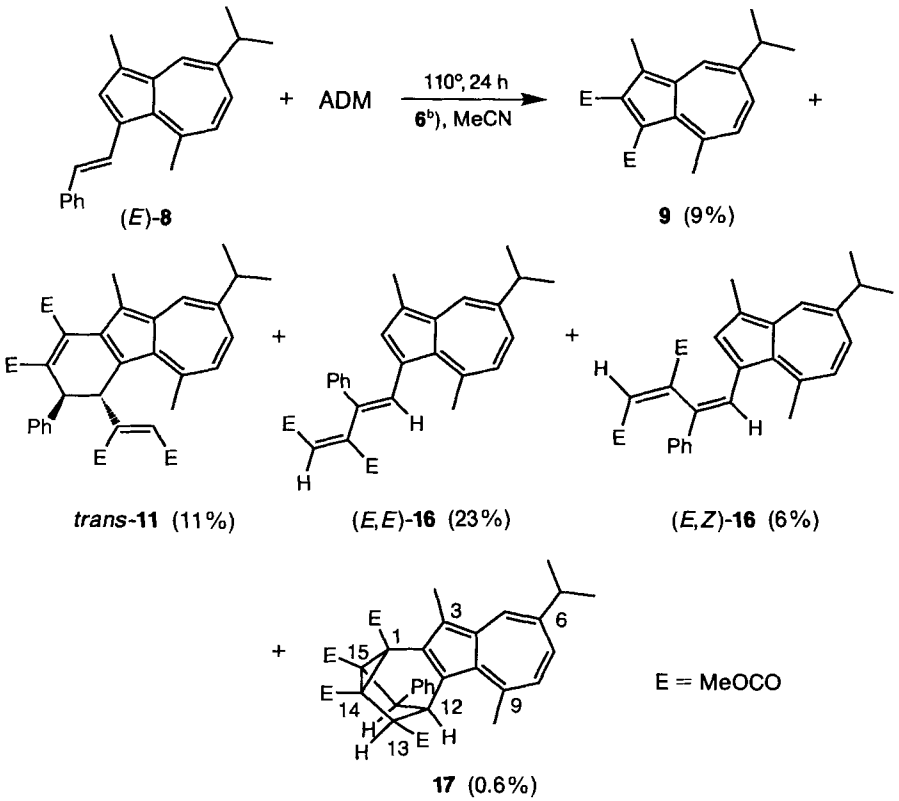
[a]) Yields are given with respect to isolated and purified materials. n.o.: not observed. All catalyzed reactions described in this and the following *Schemes* were performed under the given standard conditions. No optimization of the conditions with respect to the yield of heptalene-dicarboxylates was attempted.

[b]) 5 mol-% of the catalyst **6** were applied. The molar ratio of the azulenes and ADM was 1:3.

[c]) Two further products (both as green needles), presumably a pair of stereoisomers, were isolated in a yield of 2.2 and 4.4% (see the text).

[d]) A further product (green needles), presumably a compound comparable to those mentioned in *Footnote c* (see also the text), was isolated in a yield of 2%.

Scheme 5[a])



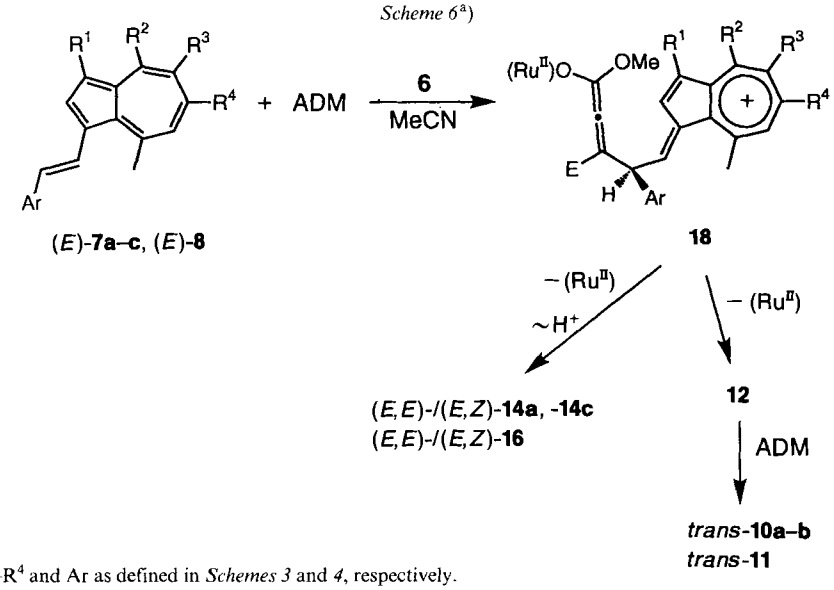
[a]) *Cf. Footnotes a* and *b* in *Scheme 4*.

lates **4** and **9**, respectively, are the main products. Their presence demonstrates the ease with which the tricyclic intermediates of type **2** (*cf. Scheme 1*) undergo the *retro-Diels-Alder* reaction to yield **4** or **9**, and (*E*)-ArCH=CH–C≡CH. The latter compounds were not detected as such in the reaction mixtures (however, see later). On the other hand, the heptalene-1,2-dicarboxylates (*E*)-**15a–c** were isolated from the corresponding reaction mixtures. However, no heptalene formation at all was observed in the case of the reaction of (*E*)-**8** with ADM. Instead, much higher amounts of the ADM adducts (*E,E*)- and (*E,Z*)-**16** were found as compared with the reaction mixtures of **7a–c** with ADM where the corresponding compounds (*E,E*)- and (*E,Z*)-**14a** as well as (*E,Z*)-**14c** were present only in minor amounts. Also the amount of the 'ene' adduct *trans*-**11**, which was also found in the purely thermal reaction of (*E*)-**8** with ADM, was much higher than the amount of the corresponding products *trans*-**10a** and *trans*-**10b** from the reaction of (*E*)-**7a** and (*E*)-**7b**, respectively, with ADM. A further product, **17**, of a complex structure (see later), was only found in the reaction mixture of (*E*)-**8** and ADM. On the other hand, the reaction mixtures of (*E*)-**7a** and (*E*)-**7c**, and ADM contained further products (*cf. Footnotes c* and *d* in *Scheme 4*), the analogous forms of which could not be detected in the reaction mixture of (*E*)-**8** and ADM.

The structures of the heptalene-1,2-dicarboxylates **15a–c** were mainly derived from their ^{1}H-NMR spectra ($CDCl_3$). The position of the C=C bonds in the heptalene perimeter was determined by the observed ^3J(H–C(3),H–C(4)) values of 6.3 to 6.4 Hz (*cf.* [13]). The preserved (*E*)-configuration of the styryl side chains at C(5) in the heptalene-1,2-dicarboxylates was secured by the observed vicinal coupling constants of 15.8 Hz. On irradiation with 366-nm light, **15a–c** rearranged partially into the corresponding heptalene-4,5-dicarboxylates which still contained an (*E*)-configurated styryl side chain at C(1) (*cf.* [10]).

The isolation of *trans*-**10a** and *trans*-**10b** as well as of *trans*-**11** shows that, also under catalytic conditions at 110°, the *Diels-Alder* reaction, followed by the ene reaction with ADM (*cf. Scheme 3*), takes place. However, the formation of (*E,E*)- and (*E,Z*)-**14a**, and (*E,E*)- and (*E,Z*)-**16** as well as of (*E,Z*)-**14c** in the Ru-catalyzed reactions in MeCN can be interpreted as a two-step mechanism of the initial *Diels-Alder* reaction (*cf. Scheme 6*).

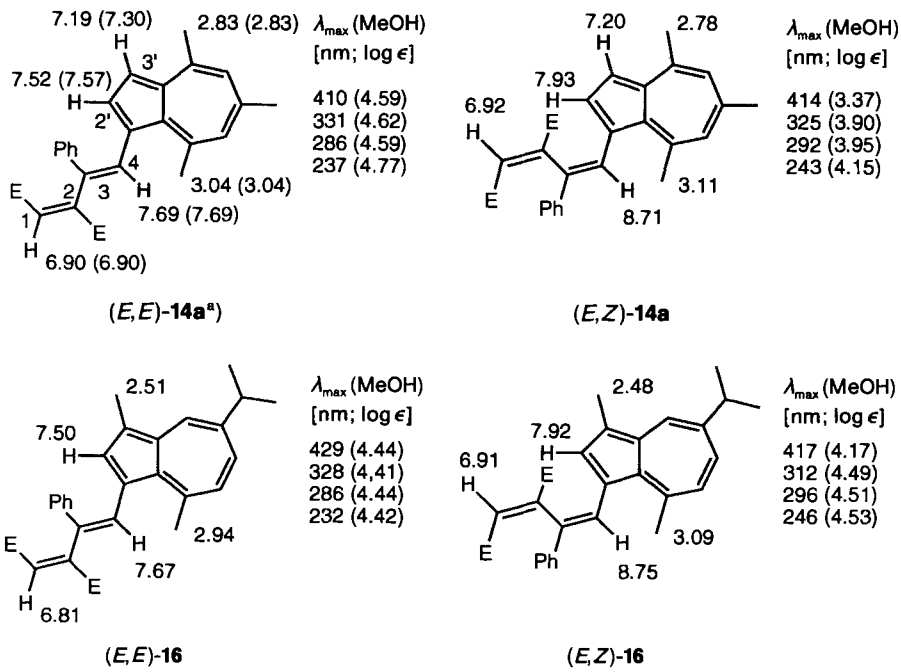
Scheme 6[a])



[a]) R^1–R^4 and Ar as defined in *Schemes 3* and *4*, respectively.

The formation of the *Diels-Alder* adducts **12** as well as of (*E,E*)- and (*E,Z*)-**14a**, (*E,E*)- and (*E,Z*)-**14c**, and (*E,E*)- and (*E,Z*)-**16** could arise from the common polar intermediate **18**. The structure of the (*E,E*)- and (*E,Z*)-isomers of **14a**, **14c**, and **16** were deduced from their ^{1}H-NMR spectra ($CDCl_3$) and UV data (*cf. Scheme 7*). ^{1}H-NOE Measurements of (*E,E*)- and (*E,Z*)-**16** revealed the spatial neighborhood of Me–C(8′) and H–C(4). The latter H-atom exhibited in both series of isomers an appreciable chemical-shift difference of > 1 ppm which is in agreement with the fact that the compounds are isomeric with respect to their C(3)=C(4) bond. That all compounds possess the (*E*)-configuration at their C(1)=C(2) band can be deduced from the chemical shift of H–C(1) which is almost the same for all compounds and close to the δ value of dimethyl (*E*)-1-(4,6,8-trimethylazulen-1-yl)ethene-1,2-dicarboxylate (7.10 ppm) [14] and other compounds of this type [15]. A chemical-shift difference of > 0.4 ppm is also observed for H–C(2′) in the two sets

Scheme 7[a])

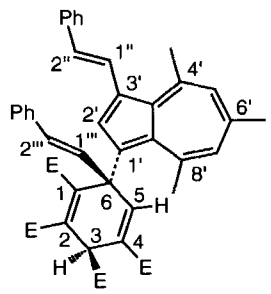


[a]) In parentheses are the δ values for (*E*,*E*)-**14c**, solvent $CDCl_3$.

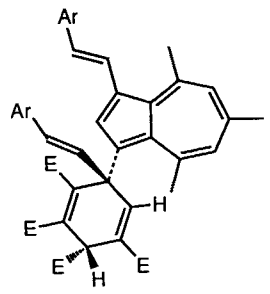
of isomers. The appearance of H–C(2′) at higher field in the (*E*,*Z*)-isomers is in agreement with the shielding effect of the Ph substituent at C(3). The UV spectra (MeOH) of both series of geometric isomers are very similar. However, the longest-wavelength UV absorption at 410 to 429 nm is more pronounced for the (*E*,*E*)-isomers as compared to that of their (*E*,*Z*)-forms. As expected, the conjugation between the azulene moiety and the MeOCO-substituted butadienyl side chain should be less disturbed, on steric grounds, in the case of the (*E*,*E*)-isomers (*cf.* [14] [15]).

In the reaction mixture of (*E*)-**7a** and ADM, we found two further products (*cf. Footnote c* in *Scheme 4*) which both crystallized as green needdles (*cf. Exper. Part*). Analogous products were not observed in the reaction mixture of (*E*)-**8** and ADM. However, at least one product, similar to those found in the reaction mixture of (*E*)-**7a** and ADM, was also isolated from the reaction mixture of (*E*)-**7b** and ADM. A proposal for the structure of these new products, based on the spectroscopic data of *trans*-**18a**, is given below[3]). The ^{1}H-NMR spectrum ($CDCl_3$) of *trans*-**18a** shows the presence of two (*E*)-configurated styryl moieties with quite different chemical shifts and shift differences within the two *AB* systems (7.76 and 6.73 ppm (J_{AB} = 16.0 Hz), and 6.98 and 6.63 ppm (J_{AB} = 16.3 Hz)). On the other hand, one can recognize a further *AB* system at 7.23 and 5.94 ppm with an allylic *J* value of 1.6 Hz. Three further *s* at 7.64, 6.93, and 6.90 ppm can

[3]) All three new products crystallized as fine green needles from different solvents and solvent mixtures. These needles were not suitable for an X-ray crystal-structure analysis.



trans-**18a**



cis-**18a** Ar = Ph
cis-**18b** Ar = 4-MeO–C_6H_4

E = MeOCO

be assigned to H–C(2′), H–C(5′), and H–C(7′), respectively. These assignments are supported by ^{1}H-NOE measurements. Irradiation of H–C(2′) causes strong signal-enhancement effects on H–C(5) at 7.23 ppm and on H–C(2″) at 6.73 ppm as well as a weak effect on H–C(3) at 5.94 ppm. The three Me groups at the azulene ring appear at 3.15, 3.00, and 2.54 ppm. Again, corresponding ^{1}H-NOE measurements allow their assignment. Irradiation of the Me signal at 3.15 ppm causes strong signal-enhancement effects on H–C(3) at 5.94 ppm as well as on H–C(7′) at 6.93 ppm, *i.e.*, the Me group, the resonance signal of which appears at 3.15 ppm, has to be placed at C(8′). In accordance with this assignment, the irradiation of the Me signal at 3.00 ppm causes strong enhancement effects on the signals of H–C(5′) at 6.90 ppm and of H–C(1″) at 7.76 ppm. Therefore, the signal at 3.00 ppm is due to Me–C(4′). As a consequence, the signal at 2.54 ppm must be attributed to the Me group at C(6′). Indeed, when this signal was irradiated, the signals of the flanking H-atoms at C(5′) and C(7′) were strongly enhanced. Since the ^{1}H-NMR spectrum of *trans*-**18a** showed the presence of four MeOCO groups, a molecular formula of $C_{43}H_{40}O_8$ could be calculated.

Indeed, the ^{13}C-NMR spectrum (150 MHz, $CDCl_3$) of *trans*-**18a** allows to identify 39 ^{13}C-signals which amounts to 43 C-atoms, taking into account the symmetric behavior of the two Ph rings. Of importance is the fact that, in addition to 14 signals of aromatic and olefinic CH groups, one finds a signal at 87.69 ppm of a quaternary C-atom (C(6)) and at 43.31 ppm of a tertiary C-atom (C(3)), strongly supporting the proposed structure for *trans*-**18a**.

In accordance with the structure of *trans*-**18a** is also its UV spectrum (MeOH) which resembles very much the UV spectrum of (*E*)-**7a** (hexane) [11] (*cf.* λ_{max} 398 (398), 325 (324), 257 (257), and λ_{min} 380 (374) and 280 (278) nm[4])). It shows that C(1′) of the azulene moiety must be linked to a saturated, *i.e.*, an sp^3-hybridized C-atom. Also of importance is the observation that it is very difficult to find the M^+ peak (EI) or the $[M+1]^+$ peak (CI) in the mass spectrum of *trans*-**18a**. The most prominent peak that is found in the mass spectrum (EI) of *trans*-**18a** is the peak at *m/z* 542 which corresponds to $[M - \text{ADM}]^+$. One would expect that a cyclohexa-1,4-diene moiety such as that of *trans*-**18a** would easily undergo a *retro-Diels-Alder* reaction, at least after ionization.

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[4]) In parentheses are the values of (*E*)-**7a**.

Table. *Comparison of the* ^{1}*H-NMR Data* ($CDCl_3$) *of* trans-**18a**, cis-**18a**, *and* cis-**18b**[a])

H-Atom(s)	Chemical shifts [ppm][b])		
	trans-**18a**	*cis*-**18a**	*cis*-**18b**
H–C(1″/2″)	7.76/6.73 (16.0)	7.85/6.82 (16.3)	7.72/6.82 (15.9)
H–C(1‴/2‴)	6.98/6.63 (16.3)	6.78/6.54 (16.3)	7.70/6.24 (16.3)
H–C(3/5)	5.94/7.23 (1.6)	5.79/6.52 (1.8)	5.70/5.63 (n.o.)
H–C(2′)	7.64	7.75	7.97
H–C(5′/7′)	6.90/6.93	6.87/6.89	6.89/6.95
MeOCO	3.77/3.69/3.57/3.11	3.88/3.86/3.82/3.74	3.93/3.76/3.73/3.69[c])
Me–C(4′)	3.00	2.97	2.97
Me–C(6′)	2.54	2.51	2.54
Me–C(8′)	3.15	3.03	3.05

[a]) The assignments for *cis*-**18a** and *cis*-**18b** are tentative.
[b]) In parentheses are the observed coupling constants; n.o. = not observed.
[c]) The two MeO groups give one *s* at 3.85 ppm.

We assume that the other compound obtained in 2.2% yield from the reaction mixture of (*E*)-**7a** and ADM respresents the corresponding *cis*-configurated product *cis*-**18a**. It shows a very similar ^{1}H-NMR spectrum ($CDCl_3$) as compared to that of *trans*-**18a** (*cf.* the *Table*). The largest chemical-shift difference is observed for H–C(5) in both structures. We assume that H–C(5) is shielded more by the azulene ring in the case of *cis*-**18a**. Again, the mass spectrum of *cis*-**18a** shows the most prominent fragment ion at *m/z* 542 which corresponds to $[M - \text{ADM}]^+$. The UV spectrum of *cis*-**18a** (MeOH) is nearly identical with that of *trans*-**18a** as well as with that of (*E*)-**7a** (*cf.* [11]).

Since the ^{1}H-NMR spectrum ($CDCl_3$) of the dimethoxy compound, isolated from the reaction mixture of (*E*)-**7b** and ADM, resembles more that of *cis*-**18a** than that of *trans*-**18a**, we assume that it has also the *cis*-configuration (*cis*-**18b**).

The assigned structures of *trans*- and *cis*-**18a** show that they can be built from (*E*)-**7a**, two molecules of ADM, and (*E*)-PhCH=CH–C≡CH. The latter molecule is expected to be formed in the *retro-Diels-Alder* reaction of the primary tricyclic intermediate of type **2** (*Scheme 1*; (*E*)-PhCH=CH at C(11) instead of Me) to yield the azulene-1,2-dicarboxylate **4** (*cf. Scheme 4*). It seems that the (*E*)-styrylacetylene adds, in the presence of the Ru catalyst, to ADM to yield the (*E*)- and (*Z*)-isomers **19** (*Scheme 8*)[5]). Polar addition of these isomers to (*E*)-**7** in the presence of the Ru catalyst will yield the (*E*)- and (*Z*)-isomers of **20**[6]). *Diels-Alder* reaction of the latter isomers with ADM then gives the observed products *trans*- and *cis*-**18a**[7]).

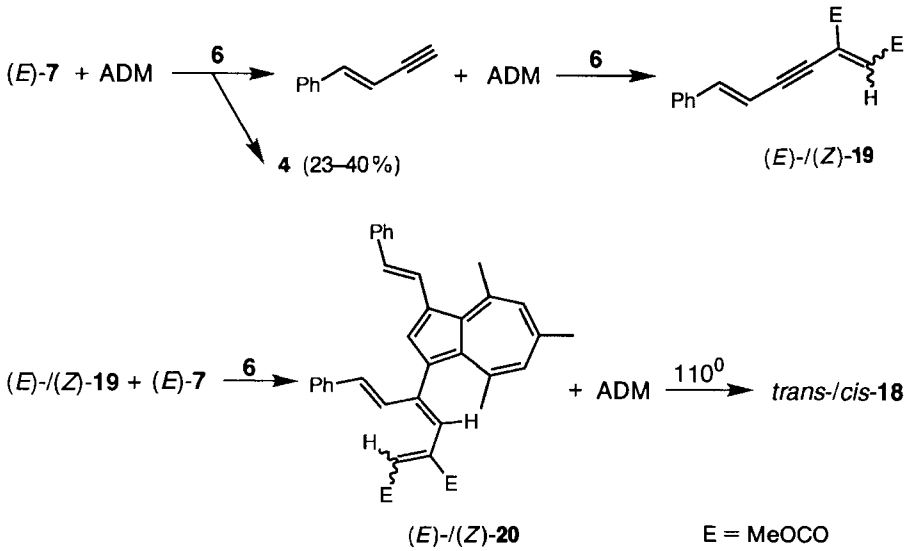
It should be noted that no compounds comparable to *trans*- and *cis*-**18a** were detected in the reaction mixture of (*E*)-**8** and ADM (*cf. Scheme 5*). This finding is in accordance

[5]) Transition-metal-catalyzed addition reactions of terminal acetylenes to disubstituted acetylenes in a '*Michael* sense' are well known (see [16] and lit. cit. there).

[6]) The polar addition of (*E*)/(*Z*)-**19** to (*E*)-**7** should occur in the same way as ADM reacts with azulenes in the presence of *Lewis* and *Brønstedt* acids (*cf.* [14] [15] as well as [17]).

[7]) In *Scheme 8*, only the (*E*)-isomer with respect to the C(3)=C(4) bond is shown. It might be that also the (*Z*)-isomer is formed. However, this will give no new isomer in the *Diels-Alder* reaction with ADM. Therefore, it might be that the reaction of (*E*)-styrylacetylene with ADM yields only one geometric isomer of **19**, and that the polar addition reaction of the latter with (*E*)-**7** leads to the formation of both possible isomers (or *vice versa* as shown in *Scheme 8*).

Scheme 8



with the fact that both positions in (*E*)-**8**, prone to electrophilic attack, are occupied by substituents. However, careful examination of the reaction mixture of (*E*)-**8** and ADM lead to the isolation of a new product, namely **17** (*cf. Scheme 5*), whose structure could not be completely elucidated by spectroscopic data. Its blue color and its ^{1}H-NMR spectrum ($CDCl_3$) showed that the azulene skeleton was still present, and that two molecules of ADM had been incorporated into the starting azulene (*E*)-**8**. H–C(2) and the two H-atoms of the styryl moiety of the starting compound had been transformed into an *ABM* system which appeared in the range of 4.8 to 4.0 ppm with $J_{AM} = 5.5$, $J_{BM} = 5.1$, and $J_{AB} \approx 0$ Hz. It showed that C(2) of the starting azulene was involved in the new structure, and its H-atom must have been migrated within the new skeleton. The final structure of **17** was established by an X-ray crystal-structure analysis (*Fig. 2*).

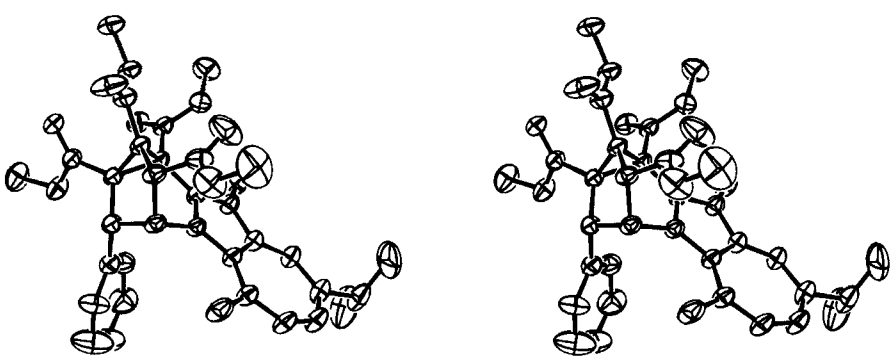
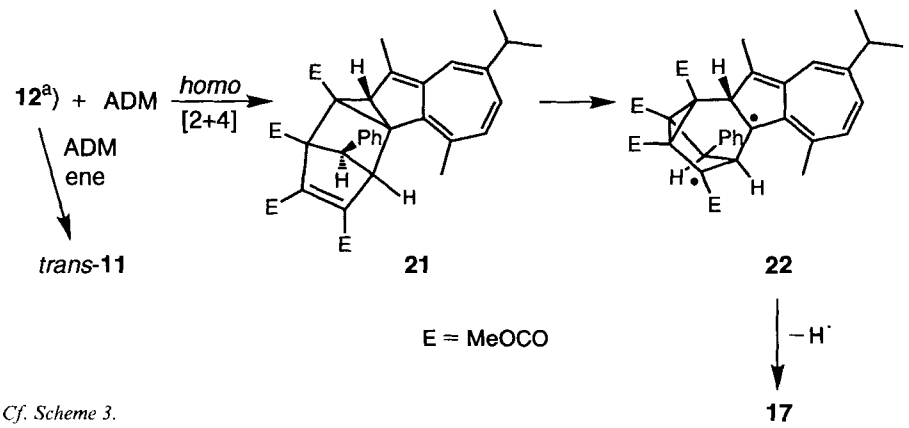


Fig. 2. *Stereoscopic view of the X-ray crystal structure of* **17**

As one can see, the basal structure of **17** represents a tricyclo[2.2.2.$0^{2,6}$]octene system where a guaiazulene moiety is anellated with its *b* side to the C=C double bond of the tricycle. The substituents at C(3) and C(5) (Ph and MeOCO, respectively) occupy positions which are in an *anti,anti*-relation to each other. The torsional angles in the *ABM* system (*i.e.*, Θ(H–A–M–H) and Θ(H–B–M–H)) are nearly the same and amount to ± 50° in good agreement with the observed ^3J values of 5.1 and 5.5 Hz.

One way to explain the formation of **17** is to assume that it has the same precursor as *trans*-**11**, *i.e.*, the *Diels-Alder* adduct **12** (*Scheme 3*; $R^2 = R^4 = H$, $R^1 = Me$, R^3 = i-Pr). A homo-*Diels-Alder* reaction of this compound instead of an ene reaction (→*trans*-**11**) would lead to the formation of the intermediate **21** (*Scheme 9*). The latter one can rearrange to yield the diradical **22**. H Migration within this diradical will lead to the formation of the observed product **17**[8]).

Scheme 9



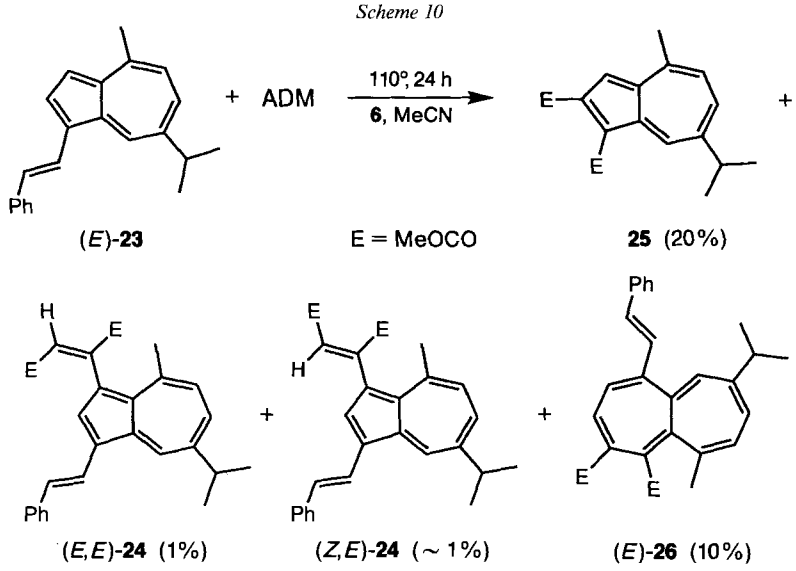
[a]) *Cf. Scheme 3.*

On grounds of comparison, we reacted 7-isopropyl-4-methyl-1-[(*E*)-styryl]azulene ((*E*)-**23**), which carries no substituent at C(8), with ADM in the presence of **6**. The results are shown in *Scheme 10*. In this case, we observed the formation of the corresponding heptalene derivative (*E*)-**26** as well as of the expected azulene-1,2-carboxylate **25** (*cf.* [2]). The heptalene-1,2-dicarboxylate (*E*)-**26** did not isomerize into its double-bond-shifted form, neither thermally nor photochemically (*cf.* [2] [18]). As further products, we found small amounts of the products of electrophilic addition of ADM to (*E*)-**23**, namely (*E,E*)- and (*Z,E*)-**24**. In addition, in intermediate fractions of the chromatographic separation, we could identify traces (< 1%) of an 'ene' product analogous to that of *trans*-**11** (*cf. Scheme 5*) as well as of an ADM adduct of (*E,E*)-**24** (*cf.* (*E,E*)-**16** in *Scheme 5*) by ^{1}H-NMR spectroscopy.

All experiments so far described show that, in the thermal as well as in the catalyzed reaction of the 1-(*E*)-styryl-substituted azulenes with ADM, the expected tricyclic inter-

[8]) It might be that the H shift occurs in a concerted manner leading to a pseudo-axially arranged E group which flips finally into the energetically more favourable pseudo-equatorial position of **17** *via* enolization of the E group.

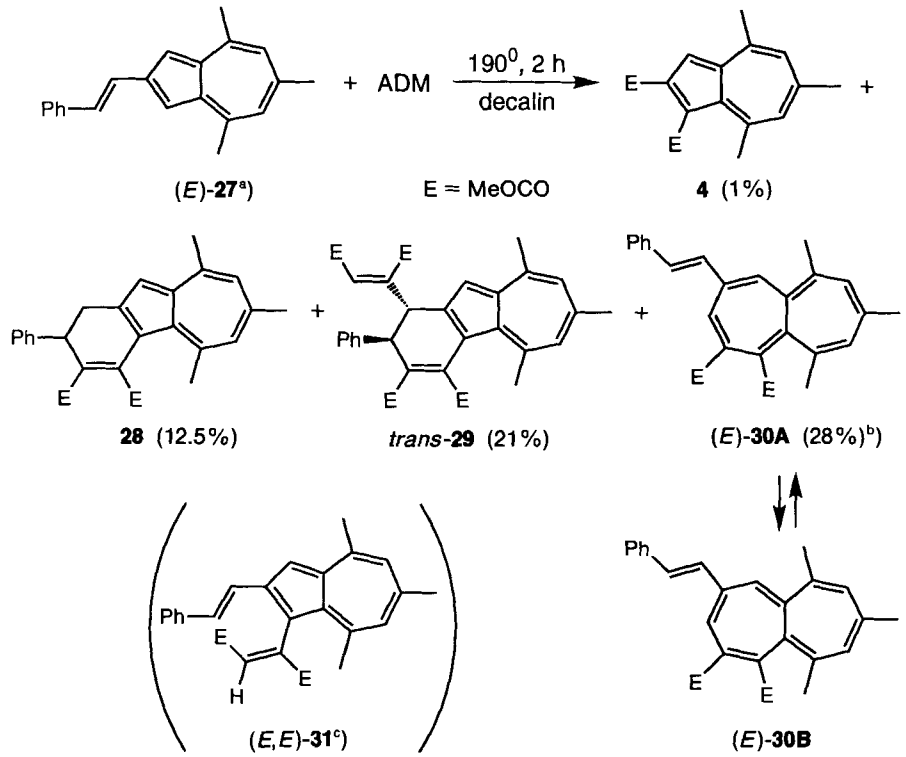
Scheme 10



mediates of type **2** are formed. However, in the thermal reactions the *retro-Diels-Alder* process, to yield the corresponding azulene-1,2-dicarboxylates, is the only observable pathway. In the catalyzed reactions, the *retro-Diels-Alder* process is still the dominant pathway; however, the formation of the heptalene-1,2-dicarboxylates is also observed. This is valid for all instances where the tricyclic intermediates of type **2**, which carry the (*E*)-styryl group at C(11), possess a Me substituent at C(6), which, in general, favor the formation of the heptalene-1,2-dicarboxylates (*cf.* [3]). A special case represents the reaction of (*E*)-**8** with ADM, since no heptalene formation is observed. However, in this case, also the formation of the corresponding azulene-1,2-dicarboxylate **9** is remarkably reduced as compared with all other catalyzed reactions. It seems that, as in other cases (*cf.* [3]), the formation of the tricyclic intermediate, which has to carry a Me substituent at C(8) (*cf. Scheme 1*), occurs less efficiently, and, on the other hand, the Me group at C(8) in the tricyclic intermediate favors the *retro-Diels-Alder* reaction (*cf.* the discussion in [3]). The longest C–C bonds in tricyclic intermediates of type **2** are the C(1)–C(10) and C(1)–C(11) bonds (*cf.* [8] [15a] [19] as well as [20]). They are, in average, 3–4% longer than their parallel counterpart bonds C(8)–C(9) and C(8)–C(12). It means that any substituent at C(11), that will further weaken the C(1)–C(11) bond due to steric congestion (*e.g. t*-Bu [4] [21]) or of conjugation as shown by (*E*)-styryl groups studied here as well as by aryl groups (*cf.* [10]), will also foster the *retro-Diels-Alder* reaction which leads to the azulene-1,2-dicarboxylates. Under these circumstances, it was of interest to study the thermal and catalyzed reaction of an azulene substituted with an (*E*)-styryl group at C(2) with ADM.

2.2. *4,6,8-Trimethyl-2-[(E)-styryl]azulene* ((*E*)-**27**). The result of the thermal reaction of (*E*)-**27** in the presence of a 2.2-fold molar excess of ADM at 190° in decalin is shown in *Scheme 11*. The fact that only very small amounts of the corresponding

Scheme 11



[a]) (*E*)-**27** was reacted with a 2.2-fold molar excess of ADM. After 2 h at 190°, 5.5% of (*E*)-**27** were recovered.

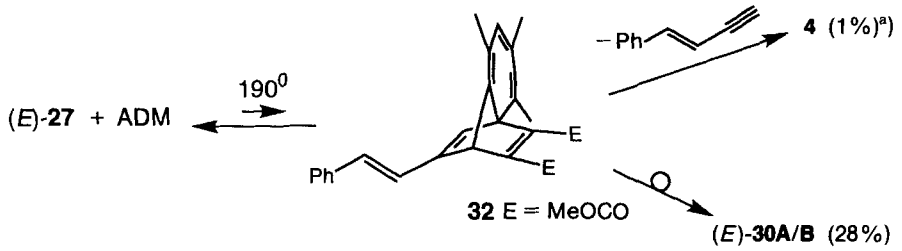
[b]) (*E*)-**30** and (*E*)-**30B** are in thermal equilibrium at r.t. The equilibrium mixture consists of 77% of (*E*)-**30A** and 23% of (*E*) **30B**.

[c]) Formed only in the Ru-catalyzed reaction.

azulene-1,2-dicarboxylate **4** are found attracts attention at once. It shows that a styryl group at C(12) in the tricyclic intermediate **32** does not favor the *retro-Diels-Alder* reaction to yield **4** (*cf. Scheme 12*), in contrast to the thermal behavior of the tricyclic intermediates arising from 1-styryl-substituted azulenes and ADM, which thermally react solely *via* the *retro-Diels-Alder* pathway (*vide supra*). As a consequence, no heptalene formation is observed in the thermal reaction of 1-styryl-substituted azulenes with ADM at 190° in decalin, whereas (*E*)-**27** yields the corresponding heptalene-1,2-dicarboxylates (*E*)-**30A/B** to an extent of 28%. It can be assumed that the yield of (*E*)-**30A/B** would be much better, when the 'internal' *Diels-Alder* reaction of (*E*)-**27** and ADM to yield **32** (*Scheme 12*) would not be competed by an external *Diels-Alder* reaction of (*E*)-**27** and ADM involving the (*E*)-styryl moiety to lead finally to **28** and *trans*-**29** (in analogy to *Scheme 3*). There is no doubt that **28** is the energetically favored prototropic form of the primary *Diels-Alder* adduct, and *trans*-**29** is its ene-trapping product with ADM.

The structure of **28** and *trans*-**29** follows clearly from their UV/VIS spectra (hexane and EtOH, respectively; see *Exper. Part*), which are nearly identical above 250 nm and

Scheme 12



a) 1% of **4** represents the lower limit of the formation of **4**, since we have not verified, if **4** is stable in the presence of ADM at 190° (*cf.* [18] for the thermal reactivity of the azulene-1,2-dicarboxylates in the presence of ADM).

resemble very much the UV/VIS spectrum of dimethyl (*Z*)-1-(4,6,8-trimethylazulene-1-yl)ethene-1,2-dicarboxylate [14], as well as from their ^{1}H-NMR spectra, including ^{1}H-NOE measurements. However, the *trans*-relation of the substituents at C(5) and C(6) in *trans*-**29** could not be derived conclusively from these measurements (*cf. Exper. Part*). Therefore, the structure of *trans*-**29** was established by an X-ray crystal-structure analysis (*cf. Fig. 3*) which showed as in the case of *trans*-**11a** (*cf. Fig. 1*) that, indeed, the Ph group at C(5) and the maleate substituent at C(6) are in a *trans*-relation and occupy pseudo-axial positions at the azulene-anellated benzo ring with Θ(C–C(5)–C(6)–C) = 158°. This is in agreement with the finding that the vicinal coupling constant between H–C(5) and H–C(6) is < 1.9 Hz (C_6D_6). In the ^{1}H-NMR spectrum ($CDCl_3$ and C_6D_6) of **28**, the H-atoms at C(5) and C(6) appear as an *ABX* system with the *X* part at 4.10 ppm and $^3J_{AX} + {}^3J_{BX} = 11.5$ Hz (C_6D_6). $\Delta\delta_{AB}$ amounts to < 1 ($CDCl_3$)–5 Hz (C_6D_6). In C_6D_6, $^2J_{AB} = 16.0$ Hz and $^3J_{AX} = 6.0$ as well as $^3J_{BX} = 5.5$ Hz is recognizable.

The heptalene structure of (*E*)-**30A** and (*E*)-**30b** was deduced from their ^{1}H-NMR spectra ($CDCl_3$) and their interconvertibility at room temperature in $CDCl_3$. From

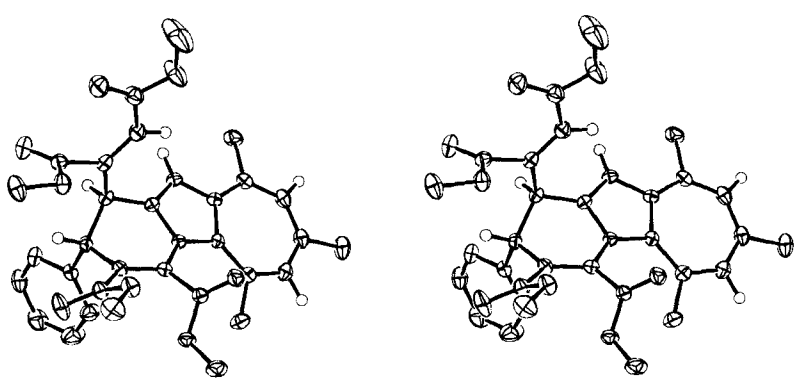


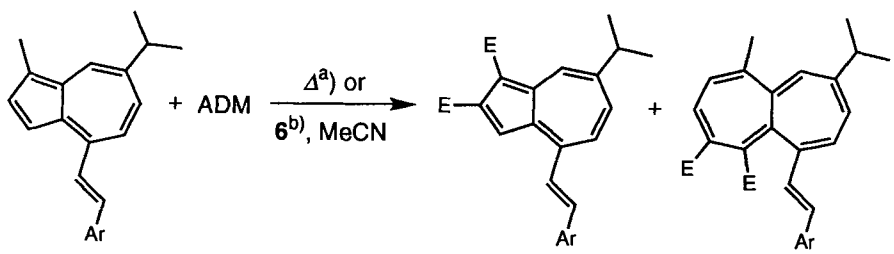
Fig. 3. *Stereoscopic view of the X-ray crystal structure of* trans-**29**

Et_2O/hexane only (*E*)-**30A** crystallizes[9]). When these crystals are dissolved in $CDCl_3$ at $-20°$ and subjected to ^{1}H-NMR analysis at this temperature, only the signals of (*E*)-**30A** are recognizable (*cf. Exper. Part*). At room temperature, the thermal equilibrium mixture of 77% of (*E*)-**30A** and 23% of (*E*)-**30B** is rapidly established. Both isomers show ^3J(HC=CH) = 16.3 Hz for the styryl group.

The Ru-catalyzed reaction of (*E*)-**27** and ADM under standard conditions in MeCN (*cf. Exper. Part*) proceeded smoothly and yielded besides 40% of (*E*)-**30A**/**30B**, 10% of *trans*-**29**, and 3% of **4** and also 3% of the fumarate derivative (*E,E*)-**31** (*cf. Scheme 11*). The rearranged *Diels-Alder* adduct **28** was not observed in the catalyzed reaction. As expected, the amount of by-products is reduced, and the total amount of the heptalenes is increased in the catalytic version of the reaction of (*E*)-**27**.

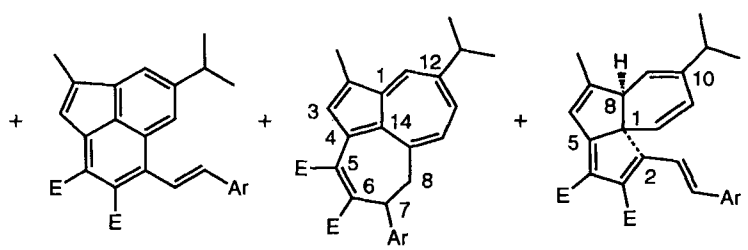
2.3. *4-Styryl-Substituted Azulenes.* 7-Isopropyl-1-methyl-4-[(*E*)-styryl]azulene ((*E*)-**33**) as well as its 4-methoxystyryl derivative (*E*)-**34** were reacted with ADM under thermal and catalytic conditions (*Scheme 13*). The thermal reactions proceeded quite

Scheme 13



(*E*)-**33** Ar = Ph
(*E*)-**34** Ar = 4-MeO–C_6H_4

(*E*)-**35** (17%/n.o.)[c]) (*E*)-**37** (6%/30%)
(*E*)-**36** (20%/n.o.) (*E*)-**38** (8%/30%)



39 (3%)[d]) Ar = Ph
n.o. Ar = 4-MeO–C_6H_4

40 (5%)[d])
n.o.

n.o.
41 (0.5%)[d])

E = MeOCO

[a]) (*E*)-**33** was reacted with 1.5 molar excess of ADM at 190° (4 h) and (*E*)-34 with 1.9 molar excess of ADM at 180° (5 h) in decalin.
[b]) *Cf. Scheme 4* and *Footnotes a* and *b* in *Scheme 4*.
[c]) In parentheses, yield of the thermal reaction/yield of the catalyzed reaction; n.o.: not observed.
[d]) Observed only in the catalyzed reaction.

[9]) For an X-ray crystal-structure analysis of (*E*)-**30A**, see [10].

cleanly in a way that only the formation of the corresponding azulene-1,2-dicarboxylates (*cf.* (*E*)-**35** and (*E*)-**36**) and heptalene-1,2-dicarboxylates (*cf.* (*E*)-**37** and (*E*)-**38**) was observed. However, the yields of the heptalene-1,2-dicarboxylates were quite low (*cf. Scheme 13*). The formation of azulene-1,2-dicarboxylates was completely suppressed in the catalyzed reaction, and the yield of the heptalene-1,2-dicarboxylates increased to 30% (*Scheme 13*). However, (*E*)-**37** was accompanied in small amounts by the acenaphthylene derivative **39** and the dihydroaceheptylene derivative **40**. Analogous compounds were not found in the reaction mixture which contained (*E*)-**38**. Nevertheless, we could isolate and crystallize in very small amounts the tricyclic compound **41**. The structure of the heptalene-1,2-dicarboxylates, which showed, as expected (*cf.* [18]), no tendency to rearrange thermally or photochemically into their double-bond-shifted isomers, was unequivocally derived from their ^{1}H-NMR spectra ($CDCl_3$). The observed ^3J(H–C(3),H–C(4)) = 6.3 Hz and ^3J(H–C(8),H–C(9)) = 6.8 Hz is only in accordance with the structures (*E*)-**37** and (*E*)-**38** as shown in *Scheme 13*. All observed chemical shifts were close to those of the heptalene-1,2-dicarboxylate derived from guaiazulene and ADM [2] (see also [18]).

The ^{1}H-NMR spectrum ($CDCl_3$) of **39** showed the signals of an (*E*)-configurated styryl group with H–C(2) at 7.55 and H–C(1) at 6.90 ppm with ^3J(H–C(1),H–C(2)) = 16.4 Hz. Other signals of the core H-atoms appeared in the region of aromatic H-atoms. One H-atom (6.99 ppm) exhibited an allylic coupling (J = 1.6–1.7 ppm) with the Me group (2.43 ppm), quite typical for acenaphthylene derivatives. The structure of an acenaphthylene for **39** was strongly supported by the UV spectrum (hexane) which showed the characteristic broad-structured absorption bands in the long-wavelength region (361 and 346 nm) and an additional intense absorption band in the short-wavelength region (258 nm) of acenaphthylenes (*cf.* [22] [23]). *Scheme 13* shows the most probable position of the substituents at the acenaphthalene skeleton according to its formation from (*E*)-**37** and ADM (*cf. Scheme 14* and later)[10]).

Compound **40** showed an UV/VIS spectrum (hexane) which highly resembled that of **28** and *trans*-**29** (*cf. Scheme 11*) in the long-wavelength region. The broad absorption band of **28** at 408 nm (hexane) is shifted to 424 nm, with a strong shoulder at 442 nm, in **40**. The weak 'azulene band' of **40** was very broad and appeared at *ca.* 600 nm (539 nm for **28**)[11]). Therefore, it had to be assumed that the original azulene skeleton of (*E*)-**33** carried a maleate substituent at C(3). On the other hand, the ^{1}H-NMR spectrum ($CDCl_3$) of **40** indicated that the structure of **40** was asymmetric, since the i-Pr substituent exhibited diastereotopic Me groups with *d* signals at 1.29 and 1.31 ppm. Moreover, the signals of the (*E*)-styryl had disappeared. Instead, an *ABX* system was recognizable at 5.03 ppm with $^3J_{AX}$ = 6.3 and $^3J_{BX}$ = 2.1 Hz as well as at 3.63 and 3.53 ppm with J_{AB} = 14.5 Hz. The chemical shift of H_X was in agreement with a benzylic position next to the maleate structure. Therefore, the most probable structure for **40** is that shown in *Scheme 13* which was definitely established by an X-ray crystal-structure analysis (*Fig. 4*). It yielded torsion

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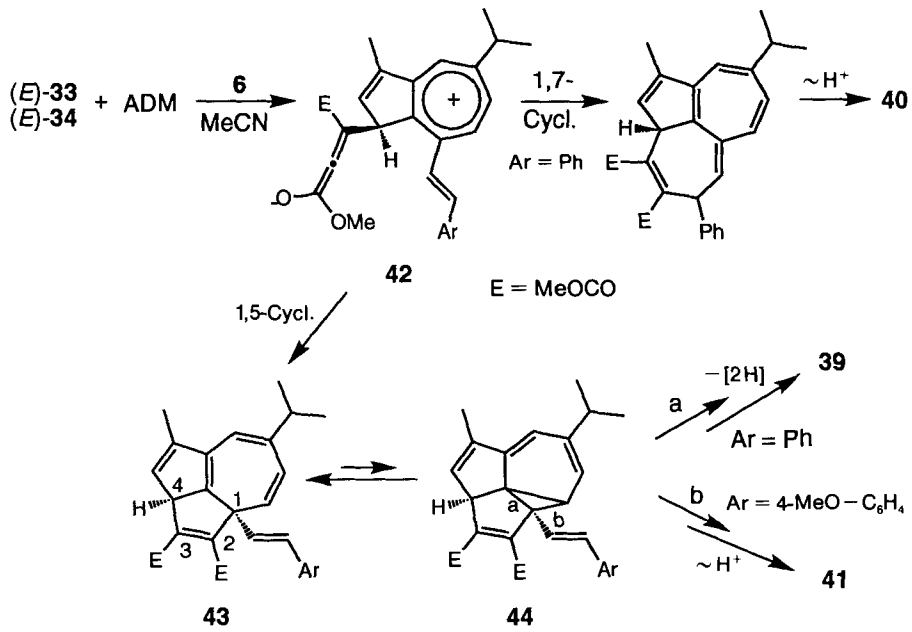
[10]) The definitive structure of **39** was established by an X-ray crystal-structure analysis (*cf. Exper. Part*).

[11]) The long-wavelength absorption bands of **28** at 408 nm (hexane) and of *trans*-**29** at 414 nm (EtOH) are slightly asymmetric at the longer-wavelength flank, *i.e.* the pronounced shoulder in **40** may have a much less pronounced pendant in **28** as well as in *trans*-**29** (*cf.* also[12])).

Scheme 14



angles between H–C(7) and CH_2(8) of -47 and 44° in perfect agreement with the observed vicinal coupling constants of 2.1 and 6.3 Hz, respectively, *i.e.*, the H-atom with $^3J = 2.1$ Hz is H_R and the other with $^3J = 6.3$ Hz is H_S. The torsional angles between the maleate substructure and the five-membered ring of the azulene skeleton amount to 15 and $-161°$, respectively, which explains the strong conjugative interaction of these two chromophors as expressed in the strong absorption band at 424 nm ($\log \varepsilon = 4.26$) with a pronounced shoulder at 442 nm ($\log \varepsilon = 4.19$). A similar hyperchromic effect is observed for the longest-wavelength UV absorption band of *trans*-**29** in EtOH which appears at 414 nm ($\log \varepsilon = 4.23$). The torsional angles of the maleate substructure and the five-mem-

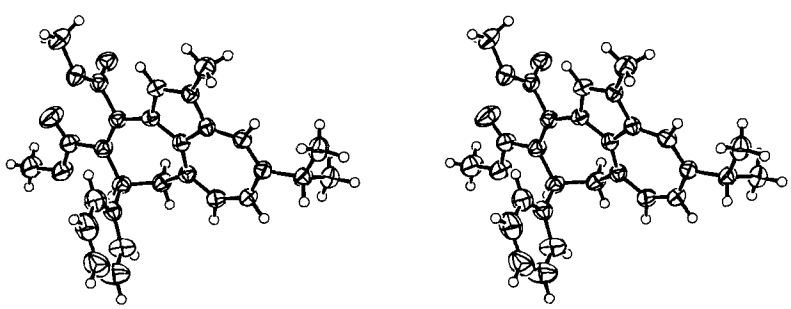


Fig. 4. *Stereoscopic view of the X-ray crystal structure of* **40**

bered ring of the azulene skeleton amount in this case, according to the X-ray crystal-structure analysis of *trans*-**29**, to 166 and −23°, respectively, *i.e.*, they are quite close to those of **40**[12]).

The third compound **41**, which we isolated only in small amounts from the reaction mixture of (*E*)-**34** and ADM (*cf. Scheme 14*), showed in the ^{1}H-NMR spectrum ($CDCl_3$) the presence of an intact (*E*)-4-methoxystyryl group as well as an olefinic *AB* system with $^3J_{AB} = 9.6$ Hz and, in addition, a coupling constant of 6.2 Hz between an olefinic H-atom at 5.83 ppm and an H-atom in allylic surrounding at 3.40 ppm. The $^3J_{AB}$ value pointed to the fact that the seven-membered ring of the azulene skeleton had been rearranged, presumably to a cyclohexadiene ring (*cf.* [24]). The value of the other vicinal coupling constant can be interpreted in a way that the torsional angle between the two involved H-atoms must be in a range of 30–50°. The final answer to the question of the structure of **41** gave an X-ray crystal-structure analysis (*Fig. 5*). It showed that **41** represents a cyclopenteno-bridged spiro[6.5]undecatetraene system with Θ(H–C(8)–C(9)–H) = 36°. It is most probably formed by a ring contraction of the seven-membered ring of the originally present azulene skeleton. A unified mechanistic

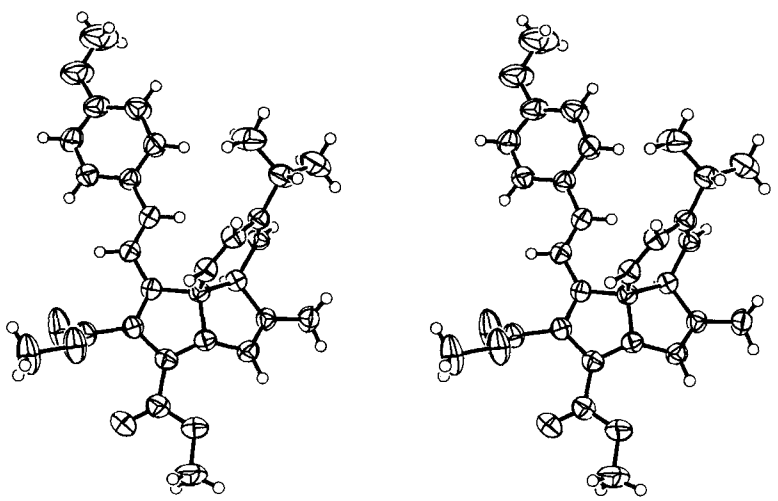


Fig. 5. *Stereoscopic view of the X-ray crystal structure of* **41**

[12]) A closer inspection of the stereoscopic projection of the X-ray crystal structure of **40** (*Fig. 4*) shows that the C=O group at C(6), which acts, with respect to the π-donating azulene ring, as a π-acceptor, is in an almost perfect s-*cis*-conformation with the C(5)=C(6) bond (Θ(O=C–C(6)–C(5)) = −9°). On the other hand, the X-ray crystal-structure analysis of *trans*-**29** (*cf. Exper. Part*) demonstrates that the corresponding C=O group at C(4) is in a more or less s-*trans*-conformation with the C(3)=C(4) bond (Θ(O=C–C(4)–C(3)) = 148°; *cf. Fig. 3*). Therefore, it might be that compounds such as **28**, *trans*-**29**, and **40**, where a given anellated ring fixes the maleate substructure at C(1) of an azulene in an s-*cis*- or s-*trans*-conformation with respect to C(2) of the azulene ring, show two more or less separated long-wavelength absorption bands above 400 nm, due to the fact that the π-acceptor C=O group at C(2) of the maleate substructure may occupy an s-*cis*- as well as an s-*trans*-conformation with the C(2′)=C(1′) bond of the maleate substructure. We will report on these effects in more detail very soon [15b].

picture of the formation of **39**–**41** is shown in *Scheme 15*. The central intermediates seem to be the zwitterions **42** (Ar = Ph or 4-MeO–C_6H_4) which may be formed by heterolysis of the C(1)–C(10) bond from the primary tricyclic compounds of type **2** (*cf. Scheme 1*) or directly by *Lewis*-acid-catalyzed addition of ADM to (*E*)-**33** or (*E*)-**34**. Direct 1,7-cyclization of **42** (R = Ph) will yield the prototropic precursor of **40**. On the other hand, 1,5-cyclization of **42** (R = Ph or 4-MeO–C_6H_4) will lead to the formation of the tricyclic intermediates **43**. These compounds may be in thermal equilibrium with their norcaradiene derivatives **44** (*cf.* [25]). Cleavage of bond *a* in **44** (R = Ph) results in the formation of a corresponding dihydro precursor of **39**, whereas cleavage of bond *b* in **44** (R = 4-MeO–C_6H_4) and a prototropic shift leads to **41**[13]). Whereas the formation of acenaphthylene derivatives has often been observed in thermal (*cf.* [1] [25]; see also [15a]) as well as in Ru-catalyzed reactions (*cf.* [4] [21]) of azulenes with ADM, the generation of the (6,5,5)-ring system of **41** has never been observed to our knowledge. The formation of **41** strongly supports the occurrence of structure types such as **44** as intermediates in the building of acenaphthylene derivatives.

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Experimental Part

General. See [3–5] [11] [2b]. For ^{1}H-NOE: *s* = strong, *m* = medium, and *w* = weak.

Thermal and [$RuH_2(PPh_3)_4$]-Catalyzed Reactions of Styrylazulenes with Dimethyl Acetylenedicarboxylates (ADM). For the synthesis of the styrylazulenes, see [11]. The Ru catalyst **6** was prepared according to [27].

Thermal Reactions. The styrylazulenes were heated with an excess of ADM in decalin at 190–200°. Decalin and the excess of ADM were removed by distillation *in vacuo* in a rotary evaporator (RE). The residues were then subjected to CC (silica gel; hexane/Et_2O 7:3). The products are given in the order of their elution. Where possible, they were further purified by crystallization. Yields are given for crystallized materials.

Ru-Catalyzed Reactions. All were performed in the same way: 1.0 mmol of the styryl-azulene, 3.0 mmol of ADM, and 0.05 mmol of **6** (2 mol-%) were placed together with 5 ml of MeCN in a 25-ml *Schlenk* vessel. The vessel was stoppered and heated under Ar for 24 h at 110°. The mixture was diluted with Et_2O and washed with H_2O (3 × 30 ml). After drying ($MgSO_4$), the solvent was distilled off (RE) and subjected to CC (*vide supra*).

1. *4,6,8-Trimethyl-1-[(*E*)-2-phenylethenyl]azulene* ((E)-**7a**) *and Dimethyl Acetylenedicarboxylate (ADM). Thermal Addition:* 0.665 g (2.44 mmol) of **7a** and 0.520 g (3.66 mmol) of ADM were heated in decalin (10 ml) for 4 h at 200°. CC yielded 0.130 g (20%) of (*E*)-**7a**, 0.240 g (35%) of *4,6,8-trimethylazulene-1,2-dicarboxylate* (**4**; violet crystals; [3]), and 0.140 g (10%) of *trans*-**10a** (green crystals).

Ru-Catalyzed Addition: The following products were eluted: 0.004 g (1%) of (*E,E*)-**13a** (brown crystals), 0.012 g (3%) of (*E,Z*)-**14a** (green crystals), 0.008 g (2%) of (*E,E*)-**14a** (brown crystals), 0.021 g (5%) of (*E*)-**15a** (orange crystals), 0.129 g (45%) of **4** (violet crystals; [3]), 0.017 g (3%) of *trans*-**10a** (green crystals), 0.030 g (4.4%) of *cis*-**18a** (green needles), and 0.015 g (2.2%) of *trans*-**18a** (green needles).

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[13]) At the moment, we accumulate evidences which demonstrate that the crucial intermediates in acenaphthylene formation from azulenes and ADM are not those of type **43** and **44** (*Scheme 15*), but their prototropic isomers with the H-atom at C(4) linked to C(2). However, there is also evidence that the rearrangement to acenaphthylene derivatives occurs more readily in polar solvents. Therefore, it might be that the rearrangement takes place in the deprotonated form of **44** or its prototropic isomers [7] [15].

Dimethyl (E)-1-{4,6,8-Trimethyl-3-[(E)-2-phenylethenyl]azulen-1-yl}ethene-1,2-dicarboxylate ((*E,E*)-**13a**): M.p. 124.0–125.0° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.48. ^{1}H-NMR (300 MHz)[14]: 7.90 (*d*, *J* = 15.9, PhCH=C*H*); 7.61 (*s*, H–C(2′)); 7.49 (*d*, *J* = 7.3, 2 arom. H); 7.36 (*t*, *J* = 7.4, 2 arom. H); 7.22 (*t*, *J* = 7.3, 1 arom. H); 7.10 (*s*, H–C(2)); 6.94 (*s*, H–C(7′)); 6.89 (*s*, H–C(5′)); 6.80 (*d*, *J* = 15.9, PhC*H*=CH); 3.78, 3.57 (2*s*, 2 MeOCO); 3.05 (*s*, Me–C(4′)); 2.70 (*s*, Me–C(8′)); 2.53 (*s*, Me–C(6′)). CI-MS: 417 (9), 416 (28), 415 (100, $[M + 1]^+$).

Dimethyl (1E,3Z)-4-(4,6,8-Trimethylazulen-1-yl)-3-phenylbuta-1,3-diene-1,2-dicarboxylate ((*E,Z*)-**14a**): M.p. 188.3–189.2° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.33. UV (MeOH): λ_{max} 414 (3.77), 325 (3.90), 282 (3.95), 243 (4.15); λ_{min} 374 (3.50), 314 (3.88), 274 (3.89). ^{1}H-NMR (300 MHz)[14]: 8.71 (*s*, H–C(4)); 7.93 (*d*, *J* = 4.4, H–C(2′)); 7.3 (*m*, 5 arom. H); 7.20 (*d*, *J* = 4.4, H–C(3′)); 7.09 (*s*, H–C(7′)); 7.05 (*s*, H–C(5′)); 6.92 (*s*, H–C(1)); 3.83, 3.63 (2*s*, 2 MeOCO); 3.11 (*s*, Me–C(8′)); 2.78 (*s*, Me–C(4′)); 2.59 (*s*, Me–C(6′)). CI-MS: 417 (29), 416 (31), 415 (100, $[M + 1]^+$).

Data of (E,E)-**14a**: M.p. 145.0° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.32. UV (MeOH): λ_{max} 410 (4.59), 331 (4.62), 286 (4.59), 237 (4.77); λ_{min} 383 (4.33), 310 (4.56), 268 (4.48). IR (KBr): 1720*s*, 1580*m*, 1450*w*, 1430*m*, 1350*w*, 1340*w*, 1220*s*, 1210*s*, 1180*m*, 1150*w*, 1010*m*, 920*w*, 830*w* (br.), 780*w*, 740*w*, 720*w*, 680*w*. ^{1}H-NMR (300 MHz): 7.69 (*s*, H–C(4)); 7.52 (*d*, *J* = 4.3, H–C(2′)); 7.19 (*d*, *J* = 4.3, H–C(3′)); 7.05 (*s*, H–C(5′,7′)); 6.90 (*s*, H–C(1)); 3.76, 3.69 (2*s*, 2 MeOCO); 3.04 (*s*, Me–C(8′)); 2.83 (*s*, Me–C(4′)); 2.59 (*s*, Me–C(6′)). CI-MS: 417 (14), 416 (25), 415 (100, $[M + 1]^+$). Anal. calc. for $C_{27}H_{26}O_4$ (414.50): C 78.24, H 6.32; found: C 77.92, H 6.05.

Dimethyl 6,8,10-Trimethyl-5-[(E)-2-phenylethenyl]heptalene-1,2-dicarboxylate ((*E*)-**15a**): M.p. 192.5–193.0° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.27. UV: see [10]. IR (KBr): 1720*s*, 1700*s*, 1550*w*, 1520*w*, 1430*m*, 1300*m*, 1280*m*, 1260*s*, 1190*m*, 1150*w*, 1110*w*, 1080*m*, 1050*m*, 980*w*, 830*w*, 840*w*, 770*w*, 750*w*, 690*w*. ^{1}H-NMR (300 MHz): 7.69 (*d*, *J* = 6.3, H–C(3)); 7.4–7.25 (*m*, 5 arom. H); 6.95 (*d*, *J* = 15.8, PhCH=C*H*); 6.56 (*d*, *J* = 6.3, H–C(4)); 6.37 (*d*, *J* = 15.8, PhC*H*=CH); 6.24 (*s*, H–C(7)); 6.14 (*s*, H–C(9)); 3.75, 3.71 (2*s*, 2 MeOCO); 2.12 (*d*, *J* = 1.1, Me–C(10)); 1.90 (*d*, *J* = 1.2, Me–C(8)); 1.65 (*s*, Me–C(6)). CI-MS (NH_3): 434 (7), 433 (28), 432 (100, $[M + 1 + NH_3]^+$), 415 (39, $[M + 1]^+$), 414 (8), 384 (6), 383 (31). EI-MS: 415 (23), 414 (100, $M^{+\cdot}$), 399 (10), 383 (13), 382 (6), 368 (14), 367 (77), 356 (9), 355 (39), 354 (27), 352 (7), 351 (12), 350 (5), 349 (9), 340 (17), 339 (31), 325 (8), 324 (24), 323 (100), 322 (16), 297 (14), 296 (57), 295 (46), 294 (12), 293 (12), 292 (9), 291 (35), 273 (9), 272 (29, $[M - ADM]^+$), 271 (7), 267 (13), 266 (39), 265 (67), 264 (19), 262 (31).

Dimethyl trans-*3-[(Z)-1,2-Bis(methoxycarbonyl)ethenyl]-10,12,14-trimethyl-4-phenyltricyclo[7.5.0.0^{2,7}]-tetradeca-1(14),2(7),5,8,10,12-hexaene-5,6-dicarboxylate* (*trans*-**10a**): M.p. 103.7–104.7°. UV/VIS (hexane): λ_{max} 612 (2.47), 580 (2.46), 414 (3.77), 394 (3.80), 326 (4.40), 319 (sh, 4.37), 274 (sh, 4.07), 263 (sh, 4.21), 255 (4.23); λ_{min} 591 (2.45), 504 (2.30), 405 (3.72), 366 (3.58), 283 (4.01), 272 (4.07). ^{1}H-NMR (300 MHz): 7.33 (*s*, H–C(8)); 7.1 (*m*, 5 arom. H); 6.99 (*s*, H–C(11)); 6.87 (*s*, H–C(13)); 5.05 (*s*, MeOCOC*H*); 4.95 (*d*, *J* = 1.6, H–C(3)); 4.59 (*d*, *J* = 1.7 H–C(4)); 4.03, 3.98, 3.72, 3.60 (4*s*, 4 MeOCO); 2.83 (*s*, Me–C(10)); 2.77 (*s*, Me–C(14)); 2.52 (*s*, Me–C(12)). ^{1}H-NOE ($CDCl_3$; 400 MHz): 2.52 (Me–C(12))→6.87 (*s*, H–C(13)); 6.99 (*s*, H–C(11)); 2.77 (Me–C(14))→4.95 (*m*, H–C(3)); 5.05 (*s*, MeOCOC*H*), 6.87 (*s*, H–C(13)); 2.83 (Me–C(10))→6.99 (*s*, H–C(11)); 7.33 (*s*, H–C(8)). CI-MS: 558 (11), 557 (36, $[M + 1]^+$), 556 (7), 527 (12), 526 (18), 525 (100, $[M + 1 - MeOH]^+$), 524 (47), 523 (67), 522 (18).

Tetramethyl cis-*6-{4,6,8-Trimethyl-3-[(E)-2-phenylethenyl]azulen-1-yl}-6-[(E)-2-phenylethenyl]cyclohexa-1,4-diene-1,2,3,4-tetracarboxylate* (*cis*-**18a**): M.p. 189.5–190.0° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.10. UV (MeOH): λ_{max} 400 (3.24), 323 (3.53), 266 (3.48); λ_{min} 374 (3.14), 286 (3.23). IR (KBr): 2940*w*, 1740*s*, 1720*s*, 1640*w*, 1620*w*, 1590*w*, 1580*w*, 1490*w*, 1440*m*, 1430*m*, 1340*w*, 1310*s*, 1270*s* (br.), 1200*m*, 1150*w*, 1120*w*, 1100*w*, 1050*w*, 1020*m*, 1010*w*, 960*m*, 830*w*, 810*w*, 780*w*, 740*m*, 690*w*. ^{1}H-NMR (300 MHz): 7.85 (*d*, *J* = 16.3, H–C(1″)); 7.75 (*s*, H–C(2′)); 7.52 (*d*, *J* = 7.2, 2 arom. H); 7.36 (*d*, *J* = 8.0, 2 arom. H); 7.25 (*t*-like, 1 arom. H); 6.89 (*s*, H–C(7′)); 6.87 (*s*, H–C(5′)); 6.82 (*d*, *J* = 16.3, H–C(2″)); 6.78 (*d*, *J* = 16.3, H–C(1‴)); 6.54 (*d*, *J* = 16.3, H–C(2‴)); 6.52 (*d*, *J* = 1.8, H–C(5)); 5.79 (*d*, *J* = 1.8, H–C(3)); 3.88, 3.86, 3.82, 3.74 (4*s*, 4 MeOCO); 3.03 (*s*, Me–C(8′)); 2.97 (*s*, Me–C(4′)); 2.51 (*s*, Me–C(6′)). ^{1}H-NMR (C_6D_6): 8.41 (*s*, 1 H); 8.00 (*d*, *J* = 16.0, PhCH=C*H*); 7.39 (*d*, *J* = 7.7, 2 arom. H); 7.18 (*d*, *J* = 7.7, 2 arom. H); 7.06 (*m*, 6 H); 6.83 (*d*, *J* = 16.2, PhC*H*=CH); 6.64 (*s*, 1 H); 6.60 (*s*, 1 H); 6.40 (*s*, 1 H); 3.93, 3.68, 3.47, 3.41 (4*s*, 4 MeOCO); 3.11 (*s*, Me); 2.86 (*s*, Me); 2.16 (*s*, Me). EI-MS: 684 (≪ 1, $M^{+\cdot}$), 544 (8), 543 (41), 542 (100, $[M - ADM]^+$), 484 (18), 483 (51, $[M - ADM - MeOCO]^+$), 468 (10).

Data of trans-**18a**: M.p. 187.0–187.5° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.20. UV (MeOH): λ_{max} 398 (3.82), 325 (4.20), 257 (4.21); λ_{min} 380 (3.78), 288 (3.93). IR (KBr): 1730*s*, 1720*s*, 1630*w*, 1610*w*, 1590*w*, 1580*w*, 1510*w*,

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[14]) For the sake of clarity, the locants of the azulenyl substituents are primed where necessary.

1490*w*, 1440*m*, 1430*m*, 1370*w*, 1340*w*, 1300*s* (br.), 1240*m*, 1200*w*, 1170*w*, 1150*w*, 1110*w*, 1050*w*, 1000*w*, 960*m*, 840*w*, 830*w*, 770*w*, 740*w*, 690*w*. ^{1}H-NMR (300 and 600 MHz): 7.76 (*d*, *J* = 16.0, H–C(1″)); 7.64 (*s*, H–C(2′)); 7.50 (*d*-like, *J* = 7.5, 2 H_o of Ph–C(2″)); 7.45 (*d*-like, *J* = 7.6, 2 H_o of Ph–C(2‴)); 7.35 (*t*-like, *J* = 7.5, 2 H_m of Ph–C(2″)); 7.33 (*t*-like, *J* = 7.5, H_m of Ph–C(2‴)); 7.29 (*t*-like, *J* = 7.7, H_p of Ph–C(2″)); 7.23 (*d*, *J* = 1.7, H–C(5)); 7.20 (*t*-like, *J* = 7.7, H_p of Ph–C(2‴)); 6.98 (*d*, *J* = 16.3, H–C(1‴)); 6.93 (*s*, H–C(7′)); 6.90 (*s*, H–C(5′)); 6.73 (*d*, *J* = 16.0, H–C(2″)); 6.63 (*d*, *J* = 16.3, H–C(2‴)); 5.94 (*d*, *J* = 1.5, H–C(3)); 3.77, 3.69, 3.57, 3.11 (4*s*, 4 MeOCO); 3.15 (*s*, Me–C(8′)); 3.00 (*s*, Me–C(4′)); 2.54 (*s*, Me–C(6′)). ^{1}H-NOE (400 MHz; $CDCl_3$): 7.64 (H–C(2′))→7.23 (*s*, H–C(5)), 6.73 (v*s*, H–C(2″)); 5.94 (*w*, H–C(3)); 3.15 (Me–C(8))→6.93 (*s*, H–C(7′)), 5.94 (v*s*, H–C(3)); 3.00 (Me–C(4′))→7.76 (*s*, H–C(1″)), 6.90 (*s*, H–C(5′)); 2.54 (Me–C(6′))→6.93 (*s*, H–C(7′)), 6.90 (*s*, H–C(5′)). ^{13}C-NMR (150 MHz; $CDCl_3$; incl. $^1J(^1H,^{13}C)$ correlation): 172.00 (MeO*C*O–C(3)); 164.84, 160.84, 158.81 (3 MeO*C*O); 154.45; 146.84, 146.54; 146.09; 144.86; 138.78 (C(1) of Ph–C(2‴)); 137.49 (C(5)); 137.43 (C(2′)); 137.38 (C(1) of Ph–C(2″)); 135.92; 135.11; 134.99; 134.88 (C(1‴)); 130.48 (C(7′)), 129.41 (C(5′)); 128.61 (C(3,5) of Ph–C(2″)); 128.55 (C(3,5) of Ph–C(2‴)); 128.36 (C(4) of Ph–C(2″)); 127.37 (C(2″)); 127.04 (C(1″)); 126.84 (C(2,6) of Ph–C(2‴)); 126.59 (C(4) of Ph–C(2‴)); 126.02 (C(2,6) of Ph–C(2″)); 120.50 (C(2‴)); 119.81 (C(3′)); 115.33 (C(1′)); 87.79 (C(6)); 77.01 ($CDCl_3$); 55.20 (3.57)[15]), 52.46 (3.77), 52.33 (3.69), 51.51 (3.11; 4 *Me*OCO); 43.43 (C(3)); 29.86 (*Me*–C(8′)); 28.61 (*Me*–C(4′)); 28.06 (*Me*–C(6′)). EI-MS: 674 (≪ 1, $M^{+\cdot}$), 544 (10), 543 (43), 542 (100, $[M - ADM]^{+\cdot}$), 484 (18), 483 (55, $[M - ADM - MeOCO]^+$), 468 (10).

2. *1-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-4,6,8-trimethylazulene* ((*E*)-**7b**) *and ADM. Ru-Catalyzed Addition*: The following products were eluted: 0.004 g (1%) of (*E,E*)-**13b** (brown crystals), 0.022 g (5%) of (*E*)-**15b** (orange crystals), 0.129 g (45%) of **4** (violet crystals; [3]), 0.012 g (2%) of *trans*-**10b** (green crystals), 0.015 g (2%) of *cis*-**18b** (green needles).

*Dimethyl (*E*)-1-{3-[(*E*)-2-(4-Methoxyphenylethenyl]-4,6,8-trimethylazulen-1-yl}ethene-1,2-dicarboxylate* ((*E,E*)-**13b**): M.p. 148.8–149.8° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.36. IR (KBr): 1720*s*, 1630*w*, 1600*m*, 1580*m*, 1510*s*, 1450*m*, 1430*m* (br.), 1410*w*, 1370*w*, 1320*w*, 1300*w*, 1240*s*, 1200*m*, 1180*s*, 1100*w*, 1070*w*, 1050*w*, 1030*m*, 1010*m*, 970*w*, 850*w*, 820*w*. ^{1}H-NMR (300 MHz): 7.74 (*d*, *J* = 16.3, CH=C*H*–C(3′)); 7.58 (*s*, C(2′)); 7.43 (*d*, *J* = 9.8, 2 arom. H); 7.09 (*s*, H–C(2)); 6.92 (*s*, H–C(5′)); 6.90 (*d*, *J* = 9.8, 2 arom. H); 6.87 (*s*, H–C(7′)); 6.75 (*d*, *J* = 16.3, C*H*=CH–C(3′)); 3.84 (*s*, MeO); 3.78, 3.56 (2*s*, 2 MeOCO); 3.04 (*s*, Me–C(4′)); 2.69 (*s*, Me–C(8′)); 2.52 (*s*, Me–C(6′)). CI-MS: 447 (12), 446 (30), 445 (100, $[M + 1]^+$).

*Dimethyl 5-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-6,8,10-trimethylheptalene-1,2-dicarboxylate* ((*E*)-**15b**): M.p. 174.0–175.0° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.23[14]). IR (KBr): 3000*w*, 2940*w*, 2900*w*, 1710*s*, 1640*w*, 1600*m*, 1550*w*, 1510*m*, 1450*w*, 1430*m*, 1390*w*, 1320*w*, 1300*m*, 1270*s*, 1260*s*, 1250*s*, 1200*w*, 1190*w*, 1170*m*, 1150*w*, 1110*w*, 1090*m*, 1050*m*, 1030*m*, 990*w*, 960*w*, 950*w*, 920*w*, 860*w*, 840*w*, 820*w*, 800*w*, 770*w*, 760*w*, 710*w*, 650*w*. ^{1}H-NMR (300 MHz): 7.68 (*d*, *J* = 6.4, H–C(3)); 7.34 (*d*, *J* = 8.9, 2 arom. H); 6.85 (*d*, *J* = 8.8, 2 arom. H); 6.82 (*d*, *J* = 15.8, CH=C*H*–C(5)); 6.50 (*d*, *J* = 6.4, H–C(4)); 6.32 (*d*, *J* = 15.8, C*H*=CH–C(5)); 6.23 (*s*, H–C(7)); 6.13 (*s*, H–C(9)); 3.82 (*s*, MeO); 3.74, 3.71 (2*s*, 2 MeOCO); 2.12 (*d*, *J* = 1.0, Me–C(10)); 1.89 (*d*, *J* = 1.1, Me–C(8)); 1.65 (*s*, Me–C(6)). CI-MS (NH_3): 464 (7), 463 (31), 462 (100, $[M + 1 + NH_3]^+$), 446 (5), 445 (18, $[M + 1]^+$), 414 (17), 413 (61). Anal. calc. for $C_{28}H_{28}O_5$ (444.53): C 75.66, H 6.35; found: C 75.43, H 6.09.

Dimethyl trans-*3-[(Z)-1,2-Bis(methoxycarbonyl)ethenyl]-10,12,14-trimethyl-4-(4-methoxyphenyl)tricyclo-[7.5.0.0^{2,7}]tetradeca-1(14),2(7),5,8,10,12-hexaene-5,6-dicarboxylate* (*trans*-**10b**): M.p. 85.8–86.4° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.05. UV/VIS (hexane): λ_{max} 593 (2.54), 414 (3.77), 395 (3.80), 320 (4.44), 254 (sh, 4.28); λ_{min} 508 (2.43), 406 (3.72), 379 (3.66), 278 (4.12). ^{1}H-NMR (300 MHz): 7.32 (*s*, H–C(8)); 7.00 (*s*, H–C(11)); 6.92 (*dd*, *J* = 8.8, 2.1, 2 arom. H); 6.87 (*s*, H–C(13)); 6.66 (*dd*, *J* = 8.8, 2.1, 2 arom. H); 5.02 (*t*-like, MeOCOC*H*); 4.94 (*d*, *J* = 1.5, H–C(3)); 4.54 (br. *s*, H–C(4)); 4.02, 3.97 (2*s*, 2 MeOCO); 3.83 (*s*, MeO); 3.73, 3.60 (2*s*, 2 MeOCO); 2.83 (*s*, Me–C(10)); 2.78 (*s*, Me–C(14)); 2.53 (*s*, Me–C(12)). EI-MS: 588 (9), 587 (38), 586 (81, $M^{+\cdot}$), 585 (25), 584 (68), 570 (11), 569 (22), 555 (13), 554 (16), 553 (34), 552 (37), 537 (14), 527 (16), 526 (20), 525 (13), 496 (14), 495 (32), 494 (8), 493 (16), 479 (11), 468 (18), 467 (18), 444 (10), 443 (38), 442 (100), 436 (8), 435 (16), 412 (13), 411 (37), 396 (12), 395 (22), 385 (8), 384 (17), 379 (13), 363 (12), 337 (8), 323 (8), 289 (8), 277 (14), 276 (11), 263 (10), 192 (26), 177 (12), 169 (8), 161 (8), 151 (17), 149 (9), 138 (10), 135 (11), 121 (15), 77 (10).

Tetramethyl cis-*6-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-6-{3-[(*E*)-2-(4-methoxyphenyl)ethenyl]-4,6,8-trimethylazulen-1-yl}cyclohexa-1,4-diene-1,2,3,4-tetracarboxylate* (*cis*-**18b**): M.p. 218.5–219.0° (Et_2O/hexane). UV (MeOH): λ_{max} 350 (sh, 4.02), 327 (4.10), 278 (3.94), 240 (3.63); λ_{min} 288 (3.91), 254 (3.51), 213 (3.47). ^{1}H-NMR (300 MHz): 7.97 (*s*, H–C(2′)); 7.72 (*d*, *J* = 15.9, H–C(1″)); 7.70 (*d*, *J* = 16.3, H–C(1‴)); 7.46 (*d*, *J* = 8.7, 2 arom. H); 7.16 (*d*, *J* = 8.8, 2 arom. H); 6.95 (*s*, H–C(7′)); 6.92 (*d*, *J* = 8.8, 2 arom. H); 6.89 (*s*, H–C(5′)); 6.82 (*d*, *J* = 16.3,

[15]) In parentheses δ(H) of the correlating MeOCO.

H–C(2″)); 6.67 (*d*, *J* = 8.8, 2 arom. H); 6.24 (*d*, *J* = 16.3, H–C(2‴)); 5.70 (*s*, H–C(3)); 5.63 (*s*, H–C(5)); 3.85 (*s*, 2 MeO); 3.93, 3.76, 3.73, 3.69 (4*s*, 4 MeOCO); 3.05 (*s*, Me–C(8′)); 2.97 (*s*, Me–C(4′)); 2.54 (*s*, Me–C(6′)). EI-MS: 744 (M^+, not detectable), 374 (10), 373 (27), 372 (100, M^{2+}), 341 (10), 340 (29), 313 (18), 307 (26), 299 (7).

3. *1-[(*E*)-2-(4-Chlorophenyl)ethenyl]-4,6,8-trimethylazulene* ((*E*)-**7c**) *and ADM. Ru-Catalyzed Addition*: The following products were eluted: 0.009 g (2%) of (*E,E*)-**14c** (brown crystals), 0.013 g (3%) of (*E*)-**15c** (yellow crystals), and 0.066 g (23%) of **4** (violet crystals; [3]).

*Dimethyl (1*E,*3*E*)-3-(4-Chlorophenyl)-4-(4,6,8-trimethylazulen-1-yl)buta-1,3-diene-1,2-dicarboxylate* ((*E,E*)-**14c**): M.p. 148.6–149.5° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.36. IR (KBr): 1730*s*, 1710*s*, 1580*m*, 1520*w*, 1480*w*, 1430*w*, 1340*m*, 1250*m*, 1200*m* (br.), 1140*m*, 1100*w*, 1080*w*, 1000*m*, 890*w*, 870*w*, 840*w*, 830*w*, 810*w*, 780*w*, 760*w*, 720*w*. ^{1}H-NMR (300 MHz)[14]): 7.69 (*s*, H–C(4)); 7.57 (*d*, *J* = 4.8, H–C(2′)); 7.30 (*d*, *J* = 4.8, H–C(3′)); 7.06 (*s*, H–C(5′,7′)); 6.90 (*s*, H–C(1)); 3.77, 3.69 (2*s*, 2 MeOCO); 3.04 (*s*, Me–C(8′)); 2.83 (*s*, Me–C(4′)); 2.60 (*s*, Me–C(6′)). CI-MS: 469 (7), 468 (16), 466 (8, $[M + 1 + NH_3]^+$), 465 (24), 453 (10), 452 (13), 451 (41), 450 (32), 449 (100, $[M + 1]^+$), 448 (39), 447 (98).

*Dimethyl 5-[(*E*)-2-(4-Chlorophenyl)ethenyl]-6,8-10-trimethylheptalene-1,2-dicarboxylate* ((*E*)-**15c**): M.p. 203.0–204.0° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.30. UV: see [10]. IR (KBr): 3000*w*, 2950*w*, 2900*w*, 1710*s*, 1640*w*, 1610*w*, 1550*w*, 1520*w*, 1490*m*, 1430*m*, 1390*w*, 1370*w*, 1300*m*, 1280*s*, 1250*s*, 1200*m*, 1190*m*, 1180*m*, 1150*m*, 1090*m*, 1050*m*, 1010*w*, 960*m*, 840*m*, 810*m*, 770*m*. ^{1}H-NMR ($CDCl_3$): 7.68 (*d*, *J* = 6.3, H–C(3)); 7.31 (*d*, *J* = 8.8, 2 arom. H); 7.28 (*d*, *J* = 8.8, 2 arom. H); 6.90 (*d*, *J* = 15.8, CH=C*H*–C(5)); 6.56 (*d*, *J* = 6.3, H–C(4)); 6.30 (*d*, *J* = 15.8, C*H*=CH–C(5)); 6.23 (*s*, H–C(7)); 6.13 (*s*, H–C(9)); 3.74, 3.71 (2*s*, 2 MeOCO); 2.12 (*s*, Me–C(10)); 1.89 (*s*, Me–C(8)); 1.64 (*s*, Me–C(6)). EI-MS: 450 (33), 449 (27), 448 (100, M^+), 403 (22), 402 (16), 401 (71), 390 (21), 389 (43), 388 (36), 374 (20), 373 (26), 359 (22), 358 (21), 357 (54), 332 (19), 331 (27), 330 (60), 329 (35), 323 (29), 316 (16), 315 (30), 314 (30), 313 (18), 306 (34, $[M - ADM]^{+\cdot}$), 300 (15), 299 (19), 294 (22), 293 (18), 292 (17), 291 (44), 290 (16).

4. *7-Isopropyl-1,4-dimethyl-3-[(*E*)-2-phenylethenyl]azulene* (= *3-(2-Phenylethenylguaiazulene*; (*E*)-**8**) *and ADM. Thermal Addition:* 0.150 g (0.50 mmol) of (*E*)-**8** and 0.168 g (1.18 mmol) of ADM were heated in decalin (2 ml) for 7 h at 190°. CC (silica gel; hexane/Et_2O 4:1) yielded 0.036 g (24%) of (*E*)-**8**, 0.024 g (15%) of **9** (blue crystals; [18]), and 0.039 g (13%) of *trans*-**11**.

Ru-Catalyzed Addition: The following products were eluted: 0.026 g (23%) of (*E,Z*)-**16** (brown oil), 0.102 g (23%) of (*E,E*)-**16** (olive colored oil), 0.028 g (9%) of **9** (blue crystals; [18]), 0.064 g (0.6%) of **17** (blue crystals), and 0.035 g (11%) of *trans*-**11** (blue crystals).

*Dimethyl (1*E,*3*Z*)-4-(5-Isopropyl-3,8-dimethylazulen-1-yl)-3-phenylbuta-1,3-diene-1,2-dicarboxylate* ((*E,Z*)-**16**): UV (MeOH): λ_{max} 427 (4.17), 328 (sh, 4.45), 313 (4.49), 296 (4.51), 246 (4.53); λ_{min} 376 (3.93), 274 (4.43). ^{1}H-NMR (300 MHz)[14]): 8.75 (*s*, H–C(4)); 8.00 (*d*, *J* = 2.1, H–C(4′)); 7.92 (*s*, H–C(2′)); 7.25 (*m*, 5 arom. H); 7.34 (*dd*, *J* = 10.8, 1.9, H–C(6′)); 7.05 (*d*, *J* = 10.8, H–C(7′)); 6.91 (*s*, H–C(1)); 3.82, 3.67 (2*s*, 2 MeOCO); 3.09 (*s*, Me–C(8′)); 3.02 (*sept.*, *J* = 6.9, Me_2CH); 2.48 (*s*, Me–C(3′)); 1.33 (*d*, *J* = 6.9, Me_2CH). ^{1}H-NOE (400 MHz, $CDCl_3$): 2.48 (Me–C(3′))→8.00 (*s*, H–C(4)); 7.92 (*s*, H–C(2′)); 3.09 (Me–C(8))→8.75 (*s*, H–C(4)); 7.05 (*s*, H–C(7′)). CI-MS: 444 (33), 443 (100, $[M + 1]^+$), 411 (8).

*Data of (*E,E*)-***16**. UV (MeOH): λ_{max} 429 (4.44), 328 (4.41), 286 (4.44), 232 (4.42), 224 (4,42); λ_{min} 373 (4.06), 332 (4.35), 265 (4.34), 224 (4.41). ^{1}H-NMR (300 MHz)[14]): 8.00 (*d*, *J* = 2.0, H–C(4′)); 7.67 (*s*, H–C(4)); 7.50 (*s*, H–C(2′)); 7.27 (*d*, *J* = 10.8, H–C(6′)); 7.25 (*m*, 5 arom. H); 6.94 (*d*, *J* = 10.8, H–C(7′)), 6.81 (*s*, H–C(1)); 3.69, 3.65 (2*s*, 2 MeOCO); 2.98 (*sept.*, *J* = 6.9, Me_2CH); 2.94 (*s*, Me–C(8′)); 2.51 (*s*, Me–C(3′)); 1.28 (*d*, *J* = 6.9, Me_2CH). ^{1}H-NOE (400 MHz, $CDCl_3$): 2.51 (Me–C(3))→8.00 (*s*, H–C(4′)), 7.50 (*s*, H–C(2′)); 2.94 (Me–C(8′))→7.67 (*s*, H–C(4)), 6.94 (*s*, H–C(7′)). CI-MS: 445 (9), 444 (26), 443 (100, $[M + 1]^+$).

Dimethyl trans-*3-[(*Z*)-1,2-Bis(methoxycarbonyl)ethenyl]-11-isopropyl-8,14-dimethyl-4-phenyltricyclo-[7.5.0.0^{2,7}]tetradeca-1(14),2(7),5,8,10,12-hexaene-5,6-dicarboxylate* (*trans*-**11**). M.p. 164–165° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.09. UV/VIS (hexane): λ_{max} 697 (2.89), 651 (sh, 2.87), 412 (4.03), 394 (4.04), 327 (4.79), 261 (4.40); λ_{min} 472 (2.41), 402 (3.97), 282 (3.99), 240 (4.18). IR (KBr): 2925*m*, 1740*s*, 1730*s*, 1715*s*, 1640*m*, 1600*m*, 1550*w*, 1520*w*, 1490*m*, 1460*m*, 1450*m*, 1430*s*, 1390*w*, 1370*w*, 1360*w*, 1340*m*, 1300 (sh), 1260 (sh), 1220*s*, 1190*s*, 1170 (sh), 1110*m*, 1085*m*, 1075*m*, 1100*m*, 1030*m*, 995*m*, 960*w*, 910*w*, 885*w*, 860*w*, 830*w*, 810*w*, 790*w*, 770*w*, 750*w*, 690*m*, 660*w*, 630*w*. ^{1}H-NMR (300 MHz): 8.14 (*d*, *J* = 1.9, H–C(10)); 7.22 (*dd*, *J* = 10.6, 2.0, H–C(12)); 7.12 (*m*, 5 arom. H); 6.78 (*d*, *J* = 10.6, H–C(13)); 5.10 (*t*-like, *J* = 1.4, MeOCO–C*H*); 5.00 (*d*, *J* = 1.6, H–C(3)); 4.56 (*d*, *J* = 1.4, H–C(4)); 4.02, 3.95, 3.73, 3.61 (4*s*, 4 MeOCO); 2.98 (*sept.*, *J* = 6.9, Me_2CH); 2.74 (*s*, Me–C(14)); 2.59 (*s*, Me–C(8)); 1.32 (*d*, *J* = 6.9, Me_2CH). CI-MS (NH_3): 604 (13), 603 (29), 602 (86, $[M + 1 + NH_3]^+$), 587 (16), 586 (36), 585 (100, $[M + 1]^+$), 584 (12). Anal. calc. for $C_{35}H_{36}O_8$ (584.67): C 71.90, H 6.21; found: C 71.62, H 6.03.

The structure of *trans*-**11** was confirmed by an X-ray crystal-structure analysis (*cf. Fig. 1*). *Crystal data*: space group and cell dimensions: monoclinic $P2_1/c$ with $a = 1130.0$, $b = 909.0$, $c = 3084.5$ pm, and $\beta = 96.74°$; D_{calc}: 1.234 Mg m^{-3}, $Z = 4$; $\mu(CuK_\alpha) = 6.750$ cm^{-1}; measured reflections (23 ± 1°): 5335, observed 3800; $R = 0.047$. Selected torsion angles [°]: C(1)–C(2)–C(3)–C(MeOCO)=CHCOOMe, –88.8(3); C(1)–C(2)–C(3)–C(4), 148.2(2); C(2)–C(3)–C(4)-Ph, –78.2(2); C(2)–C(3)–C(4)–C(5), 51.0(2); MeOCOCH=(MeOCO)C–C(3)–C(4)–Ph, 158.8(2); C(3)–C(4)–C(5)–C(6), –35.4(3); C(4)–C(5)–C(6)–C(7), 2.0(3.0), O=C–C(5)–C(6), 3.9(4); MeO–C–C(5)–C6), –177.5(2); C(5)–C(6)–C(7)–C(2), 15.3(3); C(5)–C(6)–C7)–C(8), –164.2(2); O=C–C(6)–C(5), –101.7(3); MeO–C–C(6)–C(5), 81.7(3); C(6)–C(7)–C(8)–C(9), 178.9(2); H–C(3)–C(4)–H, –75.8(3).

Tetramethyl (1RS,12RS,13RS,14RS,15RS,16RS)-6-Isopropyl-3,9-dimethyl-16-phenylpentacyclo[10.2.2.0^{2,11}.0^{4,10}.0^{14,15}]hexadeca-2,4,6,8,10-pentaene-1,13,14,15-tetracarboxylate (**17**): M.p. 190.0–190.5° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.05. ^{1}H-NMR (300 MHz): 8.08 (*d*, $J = 2.0$, H–C(5); 7.16 (*dd*, $J = 10.6$, 2.0, H–C(7)); 6.89 (*m*, 3 arom. H); 6.81 (*m*, 2 arom. H); 6.67 (*d*, $J = 10.6$, H–C(8)); 4.79 (*t*, $J = 5.4$, H–C(12)); 4.18 (*d*, $J = 5.1$, H–C(13)); 4.03 (*d*, $J = 5.5$, H–C(16)); 4.03, 3.83, 3.66, 3.19 (4*s*, 4 MeOCO); 2.98 (*sept.*, $J = 7.0$, Me_2CH); 2.62 (*s*, Me–C(9)); 2.57 (*s*, Me–C(3)); 1.30 (*d*, $J = 7.0$, Me_2CH). CI-MS: 587 (9), 586 (29), 585.1 (100, $[M + 1]^+$). EI-MS: 586 (8), 585 (32), 584 (100, M^+); 525 (11), 524 (27); 494 (9), 493 (28); 466 (8), 465 (19), 422 (19), 391 (23).

The structure of **17** was confirmed by an X-ray crystal-structure analysis (*cf. Fig. 2*). *Crystal data*: space group and cell dimensions: triclinic $P\bar{1}$ with MeCN (one molecule per two molecules of **17** assumed), $a = 1159.9$, $b = 1517.1$, $c = 1018.2$ pm, $\alpha = 98.24$, $\beta = 96.31$, $\gamma = 75.12°$; D_{calc} (with one MeCN per two molecules of **17**): 1.176 Mg m^{-3}, $Z = 2$; $\mu(CuK_\alpha) = 6.415$ cm^{-1}; measured reflections (23 ± 1°): 5392, observed 3878; $R = 0.073$. Selected torsion angles [°]: MeOOC–C(1)–C(2)–C(3), –8.3(6); C(1)–C(2)–C(11)–C(12), 4.7(4); C(10)–C(11)–C(12)–C(13), 129.7(4); C(10)–C(11)–C(12)–C16), –120.2(4); C(10)–C(11)–C(2)–C(1), 179.4(3); C(11)–C(12)–C(13)–COOMe, –53.0(4); C(11)–C(12)–C(16)–Ph, 55.8(4); MeOOC–C(13)–C(12)–C(16), –167.0(3); Ph–C(16)–C(12)–C(13), 170.2(3); C(12(–C(13)–C(14)–C(1), –37.7(4); C(12)–C(13)–C(14)–C(15), 26.3(3); C(12)–C(16)–C(15)–C(1), 40.4(4); C(12)–C(16)–C(15)–C(14), –25.1(3); C(13)–C(14)–C(1)–C(2), –9.9(4); C(16)–C(15)–C(1)–C(2), 11.3(4); MeOOC–C(13)–C(14)–C(1), 86.9(4); MeOOC–C(13)–C(14)–C(15), 151.0(3); Ph–C(16)–C(15)–C(1), –84.4(4); Ph–C(16)–C(15)–C(14), –149.9(3). H–C(3)–C(4)–H, –48(1), H–C(4)–C(16)–H, 49(1).

5. *7-Isopropyl-4-methyl-1-[(*E*)-2-phenylethenyl]azulene* ((*E*)-**23**) *and ADM. Ru-Catalyzed Addition*: The following products were eluted: 0.005 g (1%) of (*E,E*)-**24** (brown crystals)[16]), 0.040 g (10%) of (*E*)-**26** (yellow crystals), 0.060 g (20%) of **25** (blue-violet crystals; [2]).

*Dimethyl (*E*)-1-{5-Isopropyl-8-methyl-3-[(*E*)-2-phenylethyl]azulen-1-yl}ethene-1,2-dicarboxylate* ((*E,E*)-**24**): R_f (hexane/Et_2O 1:1) 0.49. UV (hexane +5% i-PrOH; qual.): λ_{max} 400 (sh, 0.57, 385 (sh, 0.61), 360 (sh, 0.71), 346 (0.73), 319 (100), 255 (0.95); λ_{min} 338 (0.73), 280 (0.45), 228 (0.73). ^{1}H-NMR (300 MHz)[14]): 8.45 (*d*, $J = 2.1$, H–C(4′)); 7.90 (*s*, H–C(2′)); 7.68 (*d*, $J = 15.8$, PhCH=C*H*); 7.58 (*d*, $J = 7.4$, 2 arom. H); 7.40 (*d*, $J = 10.9$, H–C(6′)); 7.38 (*t*-like, $J = 7.2$, 2 arom. H); 7.22 (*d*, $J = 7.3$, 1 arom. H); 7.17 (*s*, H–C(2)); 7.10 (*d*, $J = 15.8$, PhC*H*=CH); 6.98 (*d*, $J = 10.9$, H–C(7′)); 3.78, 3.56 (2*s*, 2 MeOCO); 3.11 (*sept.*, $J = 7.0$, Me_2CH); 2.72 (*s*, Me–C(8)); 1.38 (*d*, $J = 6.9$, Me_2CH). CI-MS (NH_3); 430 (31), 429 (100, $[M + 1]^+$), 428 (11).

*Data of (*Z,E*)-***24**: UV (hexane + 5% i-PrOH; qual.): λ_{max} 422 (sh, 0.31), 381 (sh, 0.64), 360 (sh, 0.84), 342 (0.93), 319 (1.00), 256 (0.81); λ_{min} 333 (0.92), 272 (0.48), 230 (0.58). ^{1}H-NMR (300 MHz)[14]): 8.48 (br. *s*, H–C(4′)); 8.18 (*s*, H–C(2′)); 7.64 (*d*, $J = 16.1$, PhCH=C*H*); 7.58 (*d*, $J = 7.4$, 2 arom. H); 7.50 (*dd*, $J = 10.8$, *ca.* 2, H–C(6′)); 7.38 (*t*-like, $J = 7.6$, 2 arom. H); 7.25 (*t*-like (partly covered by the signal of $CHCl_3$), $J = 7.4$, 1 arom. H); 7.15 (*d*, $J = 16.2$, PhC*H*=CH); 7.14 (*d*, $J = 10.7$, H–C(7′)); 5.80 (*s*, H–C(2)); 3.92, 3.81 (2*s*, MeOCO); 3.13 (*sept.*, $J = 6.8$, Me_2CH); 2.89 (*s*, Me–C(8′)); 1.39 (*d*, $J = 6.9$, Me_2CH).

*Dimethyl 7-Isopropyl-10-methyl-5-[(*E*)-2-phenylethenyl]heptalene-1,2-dicarboxylate* ((*E*)-**26**): R_f (hexane/Et_2O 1:1) 0.36. UV: see [10]. ^{1}H-NMR (300 MHz): 7.65 (*d*, $J = 6.6$, H–C(3)); 7.37 (*d*, $J = 7.8$, 2 arom. H); 7.31 (*t*-like, $J = 7.2$, 2 arom. H); 7.24 (*t*-like, $J = 7.2$, 1 arom. H); 6.97 (*d*, $J = 15.8$, PhCH=C*H*); 6.57 (*d*, $J = 15.8$, PhC*H*=CH); 6.42 (*d*, $J = 6.6$, H–C(4)); 6.38 (*d*, $J = 6.6$, H–C(9)); 6.29 (*d*, $J = 6.7$, H–C(8)); 5.91 (*s*, H–C(6)); 3.73, 3.72 (2*s*, 2 MeOCO); 2.52 (*sept.*, $J = 6.8$, Me_2CH); 1.96 (*s*, Me–C(10)); 1.09, 1.06 (2*d*, $J = 7.1$, Me_2CH).

*Isomer (*Z*)-***26**. When a 3:2 mixture of (*E*)- and (*Z*)-**23** (*cf.* [10]; especially Table 1 in [10]) was reacted with ADM under the usual $[RuH_2(PPh_3)_4]$ catalysis, isolated **26** represented also a 3:2 mixture of its (*E*)- and

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[16]) HPLC (*Spherisorb CN* column; hexane + 4% i-PrOH) of mixed fractions from CC allowed to isolate *ca.* 1% of pure (*Z,E*)-**24**.

(*Z*)-isomer, respectively. ^{1}H-NMR (300 MHz; recognizable signals for (*Z*)-**26** were taken from the 3:2 mixture): 7.38 (*d*, *J* = 7.2, H–C(3)); 7.20 (*m*, 5 arom. H); 6.59 (*d*, *J* = 12.4, PhCH=C*H*); 6.40 (*d*, *J* = 7.2, H–C(4)); 6.24 (*d*, *J* = 6.6, H–C(9)); 6.12 (*dd*, *J* = 6.6, 1.3, H–C(8)); 5.96 (*d*, *J* = 12.4, PhC*H*=CH); 5.90 (*s*, H–C(6)); 3.73, 3.72 (2*s*, 2 MeOCO); 2.46 (*sept.*, *J* = 6.7, Me_2CH); 2.05 (*s*, Me–C(10)); 1.05 (*d*, *J* = 7.0, Me_2CH).

6. *4,6,8-Trimethyl-2-[(*E*)-2-phenylethenyl]azulene* ((*E*)-**27**) *and ADM. Thermal Addition*: 0.143 g (0.53 mmol) of (*E*)-**27** and 0.168 g (1.18 mmol) of ADM were heated in decalin (2.5 ml) at 190° for 2 h. CC yielded 0.008 g (6%) of (*E*)-**27**, 0.0014 g (1%) of **4** (violet crystals; [3]), 0.061 g (28%) of (*E*)-**30A**/**30B** (red crystals), 0.027 g (12.5%) of **28** (brown oil), and 0.067 g of *trans*-**29** (dark-red crystals).

Ru-Catalyzed Addition: The following products were eluted: 0.012 g (3%) of (*E,E*)-**31** (brown crystals); 0.008 g (3%) of **4** (violet crystals; [3]), 0.166 g (40%) of (*E*)-**30A**/**30B** (red crystals), and 0.056 g (10%) of *trans*-**29** (dark-red crystals).

*Dimethyl (*E*)-1-{4,6,8-Trimethyl-2-[(*E*)-2-phenylethenyl]azulen-1-yl}ethene-1,2-dicarboxylate* ((*E,E*))-**31**). M.p. 162.3–163.1° (Et_2O/hexane). ^{1}H-NMR (300 MHz)[14]: 7.63 (*s*, H–C(3′)); 7.52 (*d*, *J* = 7.7, 2 arom. H); 7.38 (*d*, *J* = 6.9, 2 arom. H); 7.36 (*d*, *J* = 16.2, PhCH=C*H*); 7.34 (*s*, H–C(2)); 7.27 (*m*, 1 arom. H); 7.11 (*d*, *J* = 16.2, PhC*H*=CH); 7.02 (*s*, H–C(5′)); 6.96 (*s*, H–C(7′)); 3.76, 3.48 (2*s*, MeOCO); 2.88 (*s*, Me–C(4′)); 2.74 (*s*, Me–C(8)); 2.57 (*s*, Me–C(6)). CI-MS (NH_3): 417 (12); 416 (34); 415 (100, $[M+1]^+$). EI-MS: 414 ($M^{+\cdot}$), 355 ($[M-COOMe]^+$), 323 ($[M-COOMe-MeOH]^{+\cdot}$), 296 ($[M-2\,COOMe]^{+\cdot}$), 265 ($[M-2\,COOMe-MeO]^+$).

*Dimethyl 6,8,10-Trimethyl-4-[(*E*)-2-phenylethenyl]heptalene-1,2-dicarboxylate* ((*E*)-**30A**): M.p. 189.1–190.0° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.28. UV: See [10]. IR (KBr): 2940*w*, 1740*s*, 1720*s*, 1640*w*, 1590*w*, 1580*w*, 1560*w*, 1490*w*, 1440*m*, 1430*m*, 1400*w*, 1370*m*, 1340*w*, 1300*m*, 1270*s*, 1260*s*, 1240*s*, 1210*m*, 1200*m*, 1170*m*, 1125*s*, 1080*w*, 1060*m*, 1030*w*, 1000*m*, 980*m*, 920*w*, 890*w*, 870*w*, 840*m*, 785*m*, 760*m*, 700*m*, 660*w*, 620*w*. ^{1}H-NMR (300 MHz; −20°): 7.97 (*s*, H–C(3)); 7.50 (*d*, *J* = 7.3, 2 arom. H), 7.38 (*t*, *J* = 7.7, 2 arom. H); 7.29 (*t*, *J* = 7.2, 1 arom. H); 6.98 (*d*, *J* = 16.3, PhCH=C*H*); 6.75 (*d*, *J* = 16.3, PhC*H*=CH); 6.17 (*s*, H–C(5)); 6.16 (*s*, H–C(7)); 5.97 (*s*, H–C(9)); 3.78, 3.71 (2*s*, 2 MeOCO); 2.03 (*s*, Me–C(8)); 2.00 (*s*, Me–C(10)); 1.82 (*s*, Me–C(6)). CI-MS (NH_3): 433 (12); 432 (55, $[M+1+NH_3]$); 417 (7); 416 (22); 415 (100, $[M+1]^+$); 383 (6). EI-MS: 415 (20), 414 (100, $M^{+\cdot}$), 367 (10), 356 (8), 355 (17, $[M-COOMe]^+$), 354 (8), 323 (15), 295 (10, $[M-2\,COOMe]^{+\cdot}$), 296 (9), 272 (10, $[M+1+NH_3]$). Anal. calc. for $C_{27}H_{26}O_4$ (414.51): C 78.24, H 6.32; found: C 78.30, H 6.43.

*Dimethyl 6,8,10-Trimethyl-2-[(*E*)-2-phenylethenyl]heptalene-4,5-dicarboxylate* ((*E*)-**30B**). When the crystals of (*E*)-**30A** were dissolved at r.t. in $CDCl_3$, or the soln. of (*E*)-**30A** at −20° was warmed up to r.t., the presence of 23–25% of (*E*)-**30B** could be detected by ^{1}H-NMR. ^{1}H-NMR (600 MHz; C*H*Cl_3 at 7.260 ppm; 75% (*E*)-**30A** and 25% (*Z*)-**30B**): 7.93 (*s*, H–C(3) of **A**); 7.47 (*d*, *J* = 7.6, 2 H_o of Ph in **A**); 7.42 (*d*, *J* = 7.6, 2 H_o of Ph in **B**); 7.35 (*t*, *J* = 7.8, 2 H_m of Ph in **A**); 7.32 (*t*, *J* = 7.5, 2 H_m of Ph in **B**); 7.26 (*t*, partly covered by C*H*Cl_3, H_p of Ph in **A**); 7.25 (*t*, partly covered by C*H*Cl_3, H_p of Ph in **B**); 6.93, 6.77 (*AB*, J_{AB} = 16.3, PhC*H*=C*H* of **A**); 6.80 (*AB*, $\Delta\delta < 1$, $J_{AB} \approx 16.6$, PhC*H*=C*H* of **B**); 6.57 (*s*, H–C(3) of **B**); 6.16 (*s*, H–C(7) of **A**); 6.15 (*s*, H–C(5) of **A**, H–C(7) of **B**); 6.11 (*s*, H–C(1) of **B**); 5.96 (*s*, H–C(9) of **A** and **B**); 3.85, 3.73 (2*s*, 2 MeOCO of **B**); 3.77, 3.70 (2*s*, 2 MeOCO of **A**); 2.19 (*s*, Me–C(10) of **B**); 2.04 (br. *s*, Me–C(10) of **A**); 2.00 (*s*, Me–C(8) of **A** and **B**); 1.81 (*s*, Me–C(6) of **A**); 1.67 (*s*, Me–C(6) of **B**). ^{1}H-NMR (300 MHz; 75% (*E*)-**30A** and 25% (*E*)-**30B** in C_6D_6; C_6D_5H at 7.160): 8.27 (*s*, H–C(3) of **A**); 7.10–7.00 (arom. H of **A** and **B**); 6.84 (*s*, H–C(3) of **B**); 6.77 (*AB*, $\Delta\delta_{AB} < 1$, J_{AB} = 16.8, PhC*H*=C*H* of **A**); 6.64, 6.61 (*AB*, $\Delta\delta_{AB}$ = 9.8, J_{AB} = 16.3, PhC*H*=C*H* of **B**); 6.21 (*s*, H–C(1) of **B**); 6.07 (*s*, H–C(5) of **A**); 6.02 (*s*, H–C(7) of **A**); 6.00 (*s*, H–C(7) of **B**); 5.89 (*s*, H–C(9) of **A**); 5.77 (*s*, H–C(9) of **B**); 3.56 (*s*, MeOCO of **B**); 3.45 (*s*, MeCOO of **A**); 3.40 (*s*, MeOCO of **B**); 3.29 (*s*, MeOCO of **A**); 2.08 (br. *s*, Me–C(8) of **A**); 2.07 (br. *s*, Me–C(8) of **B**); 1.80 (br. *s*, Me–C(10) of **A**); 1.74 (br. *s*, Me–C(10) of **B**); 1.73 (*s*, Me–C(6) of **B**); 1.68 (*s*, Me–C(6) of **A**).

Dimethyl 10,12,14-Trimethyl-5-phenyltricyclo[7.5.0.0^{2,7}]tetradeca-1(14),2(7),3,8,10,12-hexaene-3,4-dicarboxylate (**28**): UV/VIS (hexane): λ_{max} 539 (2.76), 408 (4.15), 336 (4.41), 310 (4.40), 244 (4.32); λ_{min} 477 (2.60), 378 (3.90), 322 (4.36), 274 (3.84), 224 (4.24). IR ($CHCl_3$): 3015*m*, 2952*m*, 2360*m*, 2340*m*, 1719*s*, 1580*m*, 1434*m*, 1259*s*, 1105*m*, 1013*m*. ^{1}H-NMR (300 MHz): 7.34 (*d*, *J* = 7.4, 2 arom. H); 7.20 (*t*-like, *J* = 2 arom. H); 7.14 (*t*-like, *J* = 7.0, 1 arom. H); 7.02 (*s*, H–C(11,13)); 6.98 (*s*, H–C(8)); 4.11 (*t*, *X* of *ABX*, $J_{AX} \approx J_{BX}$ = 6.0, H–C(5)); 3.82, 3.66 (2*s*, 2 MeOCO); 3.36 (*AB* of *ABX*, $\Delta\delta < 1$, $J_{AB} \approx 17$, 2 H–C(6)); 2.75 (*s*, Me–C(14)); 2.70 (*s*, Me–C(10)); 2.54 (*s*, Me–C(12)). ^{1}H-NMR (300 MHz; C_6D_6): 7.46 (*d*, *J* = 7.6, 2 arom. H); 7.07 (*t*, *J* = 7.6, 2 arom. H); 6.95 (*tt*-like, *J* = 7.4, *ca.* 1, 1 arom. H); 6.81 (*s*, H–C(8)); 6.67 (*s*, H–C(13)); 6.63 (*s*, H–C(11)); 4.10 (*t*, *X* of *ABX*, $J_{AX} \approx J_{BX}$ = 5.7, H–C(5)); 3.57, 3.42 (2*s*, 2 MeOCO); 3.15 (*AB* of *ABX*, $\Delta\delta_{AB} \approx 5$ Hz, J_{AB} = 16.8, J_{AX} = 6.0, J_{BX} = 5.4, 2 H–C(6)); 2.71 (*s*, Me–C(14)); 2.41 (*s*, Me–C(10)); 2.11 (*s*, Me–C(12)). ^{1}H-NOE (400 MHz; $CDCl_3$): 4.11 (H–C(5))→7.34 (*s*, 2 arom. H), 3.36 (*s*, 2 H–C(6)); 3.36 (2 H–C(6))→7.34 (*s*, 2 arom. H), 6.98 (*s*, H–C(8)), 4.11 (*s*, H–C(5)). EI-MS: 415 (26), 414 (100, $M^{+\cdot}$), 383 (8), 355 (33), 324 (13), 323 (11), 296 (22).

Dimethyl trans-*6-[(Z)-1,2-Bis(methoxycarbonyl)ethenyl]-10,12,14-trimethyl-5-phenyltricyclo[7.5.0.0^{2,7}]-tetradeca-1(14),2(7),3,8,10,12-hexaene-3,4-dicarboxylate* (*trans*-**29**): M.p. 188.9–189.1° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.05. UV/VIS (EtOH): λ_{max} 534 (3.07), 414 (4.23), 340 (4.38), 312 (4.42), 232 (4.40); λ_{min} 488 (3.00), 379 (3.91), 326 (4.34), 236 (4.40), 224 (4.39). IR (KBr): 2940*w*, 1730*s*, 1700*s*, 1640*w*, 1580*w*, 1560*w*, 1510*w*, 1490*w*, 1450*w*, 1430*m*, 1390*w*, 1360*m*, 1330*w*, 1310*w*, 1250*s*, 1200*m*, 1160*m*, 1140*m*, 1100*m*, 1085*w*, 1040*w*, 1020*w*, 990*w*, 930*w*, 840*w*, 750*w*, 690*w*. ^{1}H-NMR (300 MHz): 7.32 (*d*, *J* = 7.1, 2 arom. H); 7.16 (*t*, *J* = 7.6, 2 arom. H); 7.12 (*t*, *J* = 7.5, 1 arom. H); 7.06 (*s*, H–C(11,13)); 6.96 (*s*, H–C(8)); 5.41 (*d*, *J* = 1.4, MeOCOC*H*); 4.34 (*s*, H–C(5,6)); 3.86, 3.83, 3.71, 3.63 (4*s*, 4 MeOCO); 2.74 (*s*, Me–C(14)); 2.73 (*s*, Me–C(10)); 2.54 (*s*, Me–C(12)). ^{1}H-NMR (300 MHz; C_6D_6): 7.65 (*d*, *J* = 7.6, 2 arom. H); 7.04 (*t*, *J* = 7.5, 2 arom. H); 6.90 (*t*, *J* = 7.3, 1 arom. H); 6.80 (*s*, H–C(8)); 6.63 (*s*, H–C(13)); 6.53 (*s*, H–C(11)); 5.75 (*d*, *J* = 1.3, MeOCOC*H*); 4.87 (*d*, *J* = 1.9, H–C(5)); 4.65 (*s*, H–C(6)); 3.64, 3.55, 3.39, 3.04 (4*s*, 4 MeOCO); 2.71 (*s*, Me–C(14)); 2.23 (*s*, Me–C(10)); 2.23 (*s*, Me–C(10)); 2.05 (*s*, Me–C(12)). ^{1}H-NOE (400 MHz, C_6D_6): 2.05 (Me–C(12))→6.63 (*s*, H–C(13)), 6.53 (*s*, H–C(11)); 2.23 (Me–C(10))→6.53 (*s*, H–C(11)), 6.80 (*s*, H–C(8)); 2.71 (Me–C(14))→6.63 (*s*, H–C(13)); 6.80 (H–C(8))→5.75 (*s*, MeOCOC*H*), 4.65 (*s*, H–C(6)), 2.23 (*s*, Me–C(10)); 7.65 (H_o of Ph–C(5))→7.04 (*s*, H_m of Ph–C(5)), 4.86 (*s*, H–C(5)), 4.65 (*s*, H–C(6)). CI-MS (NH_3): 575 (20), 574 (56, $[M + 1 + NH_3]^+$), 559 (9), 558 (37), 557 (100, $[M + 1]^+$), 556 (7), 526 (15), 525 (45, $[M + 1 - MeOH]^+$). EI-MS: 557 (23), 556 (70, $M^{+\cdot}$), 525 (13), 524 (5), 510 (7), 509 (23), 497 (13), 494 (10), 493 (28), 465 (9), 464 (9), 438 (7), 437 (8), 433 (11), 405 (8), 391 (11), 377 (8), 373 (9), 320 (6), 319 (9). Anal. calc. for $C_{33}H_{32}O_8$ (556.62): C 71.21, H 5.79; found: C 70.99, H 6.00.

The structure of *trans*-**29** was confirmed by an X-ray crystal-structure analysis (*cf. Fig. 3*). *Crystal data*: space group and cell dimensions: monoclinic *C*2/*c* with *a* = 2781.1, *b* = 1533.6, *c* = 1486.8 pm, and β = 113.40°; D_{calc}: 1.270 Mg m^{-3}, *Z* = 8; μ (MoK_α) = 0.850 cm^{-1}; measured reflections (–100 ± 1°): 8943, observed 5929, *R* = 0.040. Selected torsion angles [°]: C(1)–C(2)–C(3)–C(4), –166.3(1); C(2)–C(3)–C(4)–C(5), 8.0(2); O=C–C(3)–C(4), –123.7(2); MeO–C–C(3)–C(4), 56.1(2); C(3)–C(4)–C(5)-Ph, 80.8(2); C(3)–C(4)–C(5)–C(6), –46.0(2); C(3)–C(2)–C(1)–C(14), 24.3(3); C(4)–C(5)–C(6)–C(7), 52.2(2); O=O–C(4)–C(3), –148.2(2); MeO–C–C(4)–C(3), 35.1(2); Ph–C(5)–C(6)–C(COOMe)=CHCOOMe, 158.4(1); Ph–C(5)–C(6)–C(7), –75.3(1); MeOCOCH=C(COOMe)–C(6)–C(7)–C(8), –81.6(2), C(6)–C(7)–C(8)–C(9), –178.4(1); C(8a)–C(1)–C(2)–C(2a), 0.1(3), H–C(5)–C(6)–H, –74(1).

7. *7-Isopropyl-1-methyl-4-[(E)-2-phenylethenyl]azulene* ((*E*)-**33**) *and ADM. Thermal Addition*: 1.15 g (4.0 mmol) of (*E*)-**33** and 0.850 g (6.0 mmol) of ADM were heated in decalin (10 ml) at 190° for 4 h. CC yielded 0.103 g (6%) of (*E*)-**37** (orange crystals) and 0.264 g (17%) of (*E*)-**35** (green-black crystals).

Ru-Catalyzed Addition: The following products were eluted: 0.013 g (3%) of **39** (orange crystals), 0.129 g (30%) of (*E*)-**37** (orange crystals), and 0.021 g (5%) of **40** (green crystals).

Dimethyl 7-Isopropyl-5-methyl-10-[(E)-2-phenylethenyl]heptalene-1,2-dicarboxylate ((*E*)-**37**): M.p. 174.8 175.5° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.36. UV (MeOH): λ_{max} 355 (sh), 306, 259, 242; λ_{min} 340, 275, 247 (see also [10]). IR (KBr): 2940*w*, 1740*s*, 1715*s*, 1640*w*, 1600*w*, 1570*m*, 1550*w*, 1460*w*, 1450*m*, 1430*m*, 1390*w*, 1380*w*, 1360*w*, 1270*s*, 1230*m*, 1190*m*, 1160*m*, 1140*w*, 1090*m*, 1050*m*, 1040*w*, 985*m*, 980*m*, 880*w*, 850*w*, 820*w*, 790*w*, 770*w*, 750*m*, 700*m*. ^{1}H-NMR (300 MHz): 7.60 (*d*, *J* = 6.3, H–C(3)); 7.35 (*d*-like, *J* = 7.1, 2 arom. H); 7.25 (*d*-like, *J* = 7.0, 2 arom. H); 7.20 (*t*-like, *J* = 7.2, 1 arom. H); 6.88 (*d*, *J* = 16.2, PhC*H*=CH); 6.56 (*d*, *J* = 16.2, PhCH=C*H*); 6.44 (*d*, *J* = 6.8, H–C(8)); 6.42 (*d*, *J* = 6.8, H–C(9)); 6.34 (*d*, *J* = 6.4, H–C(4)); 5.94 (*s*, H–C(6)); 3.73, 3.50 (2*s*, 2 MeOCO); 2.54 (*sept.*, *J* = 6.9, Me_2CH); 2.08 (*s*, Me–C(5)); 1.13, 1.09 (2*d*, *J* = 6.9, 6.8, Me_2CH). ^{1}H-NOE (400 MHz; $CDCl_3$): 1.10 (Me_2CH)→6.44 (*m*, H–C(8)), 5.94 (*s*, H–C(6)); 2.08 (Me–C(5))→6.34 (*s*, H–C(4)), 5.94 (*s*, H–C(6)); 2.54 (Me_2CH)→5.94 (*m*, H–C(6)), 6.44 (*m*, H–C(8)); 6.42 (H–C(9))→6.88 (*s*, PhC*H*=CH). ^{13}C-NMR (50 MHz): 167.68 (*s*); 167.23 (*s*); 150.24 (*s*); 144.15 (*s*); 140.35 (*d*); 137.2 (*s*); 136.80 (*s*); 133.53 (*s*); 131.86 (*s*); 130.21 (*s*); 130.03 (*d*); 128.75 (*d*); 128.50 (*d*, 2 arom. C); 127.59 (*d*); 127.42 (*d*); 126.45 (*d*, 2 arom. C); 126.06 (*d*); 125.72 (*d*); 52.08, 51.97 (2*q*, 2 *Me*OCO); 36.05 (*d*, Me_2CH); 25.06 (*q*, Me–C(5)); 23.01, 22.43 (2*q*, *Me*$_2$CH). EI-MS: 428 (43, $M^{+\cdot}$), 396 (13), 370 (24), 369 (100, $[M - COOMe]^+$), 368 (24), 355 (13), 338 (13), 337 (58), 326 (11), 310 (52, $[M - 2\ COOMe]^+$), 309 (16), 295 (19), 279 (11), 268 (11), 267 (21), 266 (21), 265 (18), 253 (12), 252 (24), 239 (14). Anal. calc. for $C_{28}H_{28}O_4$ (428.53): C 78.48, H 6.59; found: C 78.34, H 6.40.

Dimethyl 7-Isopropyl-4-[(E)-2-phenylethenyl]azulene-1,2-dicarboxylate ((*E*)-**35**): M.p. 125.0–126.0° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.36. UV (MeOH): λ_{max} 586 (3.38), 365 (4.55), 307 (4.80), 251 (4.54), 220 (4.51); λ_{min} 400 (2.90), 346 (4.56), 272 (4.38), 232 (4.47). IR (KBr): 2960*w*, 1720*s*, 1690*s*, 1630*w*, 1450*s*, 1390*s*, 1340*m*, 1230*s*, 1200*s*,1150*m*, 1110*w*, 1060*w*, 1020*w*, 780*w*, 750*w*, 740*w*. ^{1}H-NMR (300 MHz): 9.48 (*s*, H–C(8)); 7.98 (*d*, *J* = 16.1, PhCH=C*H*); 7.82 (*m*, 1 arom. H); 7.79 (*dd*, *J* = 11.2, 1.8, H–C(6)); 7.68 (*s*, H–C(3)); 7.66 (*m*, 2 arom. H); 7.38 (*m*, 2 arom. H); 7.45 (*d*, *J* = 16.1, PhC*H*=CH); 7.44 (*d*, *J* = 11.2, H–C(5)); 3.99, 3.96 (2*s*, 2 MeOCO); 3.21 (*sept.*,

J = 6.9, Me_2CH); 1.42 (*d*, J = 6.9, Me_2CH). ^{13}C-NMR (50 MHz): 165.65 (*s*); 147.91 (*s*, 2 C); 146.92 (*s*); 140.13 (*s*); 139.72 (*s*); 138.83 (*d*); 138.77 (*d*); 136.81 (*d*); 136.42 (*s*); 129.17 (*d*); 128.93 (*d*, 2 arom. C); 128.23 (*d*); 127.36 (*d*, 2 arom. C); 125.61 (*d*); 115.18 (*s*); 113.83 (*d*); 52.27, 51.57 (2*q*, 2 *Me*OCO); 38.60 (*d*, Me_2CH); 24.43 (*q*, Me_2CH). EI-MS: 389 (13), 388 (100, $M^{+\cdot}$), 357 (11), 329 (38, $[M - COOMe]^+$), 297 (10), 270 (16, $[M - 2\,COOMe]^+$). Anal. calc. for $C_{25}H_{24}O_4$ (388.47): C 77.30, H 6.23; found: C 77.37, H 5.95.

*Dimethyl 7-Isopropyl-1-methyl-5-[(*E*)-2-phenylethenyl]acenaphthylene-3,4-dicarboxylate* (**39**): M.p. 129.0–129.5° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.40. UV (hexane): λ_{max} 361 (4.01), 346 (4.04), 258 (4.61), *ca.* 290 (sh, 4.26); λ_{min} 353 (4.01), 318 (3.85), 228 (4.41). IR (KBr): 2950*m*, 1730*s*, 1710*s*, 1590*w*, 1550*w*, 1490*w*, 1460*m*, 1440*s*, 1330*m*, 1370*m*, 1320*w*, 1300*w*, 1270*s*, 1240*m*, 1210*m*, 1190*m*, 1160*s*, 1110*w*, 1060*w*, 1000*w*, 980*m*, 940*w*, 870*w*, 860*w*, 830*w*, 800*w*, 750*w*, 700*w*, 690*w*, 670*w*, 650*w*, 630*w*. ^{1}H-NMR (300 MHz): 7.79 (*s*, H–C(6)); 7.58 (*d*, J = 7.5, 2 arom. H); 7.55 (*d*, J = 16.4, PhCH=C*H*); 7.54 (*s*, H–C(8)); 7.42 (*t*, J = 7.6, 1 arom. H); 7.35 (*d*, J = 7.1, 2 arom. H); 6.99 (*d*, J = 1.6, H–C(2)); 6.90 (*d*, J = 16.4, PhC*H*=CH); 3.99, 3.91 (2*s*, 2 MeOCO); 3.12 (*sept.*, J = 6.9, Me_2CH); 2.43 (*d*, J = 1.7, Mc–C(1)); 1.35 (*d*, J = 7.0, Me_2CH). CI-MS (NH_3): 445 (8), 444 (33, $[M + 1 + NH_3]^+$), 428 (7), 427 (24, $[M + 1]^+$), 426 (20), 397 (14), 396 (30), 395 (100, M^+). EI-MS: 427 (24), 426 (100, $M^{+\cdot}$), 395 (14), 394 (9), 379 (29), 366 (10), 351 (16), 337 (12), 336 (10), 335 (14), 308 (12, $[M - 2\,COOMe]^+$), 293 (11). Anal. calc. for $C_{28}H_{26}O_4$ (426.52): C 78.85, H 6.14; found: C 78.58, H 5.94.

The structure of **39** was confirmed by an X-ray crystal-structure analysis (*cf. Scheme 13*). *Crystal data*: space group and cell dimensions: monoclinic $P2_1/n$ with a = 1263.1, b = 759.8, c = 2497.7 pm, and β = 101.81°; D_{calc}: 1.212 Mg m^{-3}, Z = 4; μ(CuK_α) = 6.070 cm^{-1}; measured reflections (23 ± 1°): 3998, observed 2939; R = 0.042. Selected torsion angles [°]: C(2)–C(2a)–C(3)–COOMe, 1.7(4); O=C–C(3)–C(2a), –45.7(3); O=C–C(3)–C(4), 136.4(3); MeO–C–C(3)–C(2a), 138.8(2); MeO–C–C(3)–C(4), –46.2(3); MeOCC–C(3)–C(4)–COOMe, –6.8(3); C(3)–C(4)–C=O, –51.8(3); C(3)–C(4)–C–OMe, 127.2(2); O=C–C(4)–C(5), 124.3(2); MeO–C–C(4)–C(5), –56.7(3); MeOCC–C(4)–C(5)–CH=CHPh, 3.5(3); C(4)–C(5)–CH=CHPh, 138.4(2); C(5a)–C(5)–CH=CH–Ph, –44.3(3); C(5)–CH=CH–Ph, –177.0(3); CH=CH–C_{ip}–X_o, 1.3(4) (*ip* = *ipso*); CH=CH–C_{ip}–$C_{o'}$, 179.2(3).

Dimethyl 12-Isopropyl-2-methyl-7-phenyltricyclo[7.4.1.0^{4,14}]tetradeca-1(13),2,4(14),5,9(10),11-hexaene-5,6-dicarboxylate (**40**): M.p. 141.0–142.0° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.27. UV/VIS (hexane): λ_{max} *ca.* 600 (2.8), 442 (sh, 4.19), 424 (4.26), 339 (4.25), 250 (4.42), 234 (sh, 4.39); λ_{min} 495 (2.6), 370 (357), 304 (3.98), 222 (4.48). IR (KBr): 2940*w*, 1720*s*, 1700*w*, 1580*s*, 1550*w*, 1530*m*, 1490*w*, 1450*m*, 1430*m*, 1410*s*, 1330*w*, 1300*w*, 1270*s*, 1260*s*, 1230*s* (br.), 1190*m*, 1180*m*, 1130*m*, 1120*s*, 1080*m*, 1060*m*, 1010*w*, 980*w*, 900*w*, 830*w*, 780*w*, 750*w*, 690*w*, 650*w*, 630*w*. ^{1}H-NMR (300 MHz): 8.10 (*d*, J = 2.0, H–C(13)); 7.58 (*s*, H–C(3)); 7.34 (*dd*, J = 10.7, 1.9, H–C(11)); 7.02 (*m*, 5 arom. H); 6.84 (*d*, J = 10.7, H–C(10)); 5.03 (*dd*, J = 6.3, 2.1, H–C(7)); 4.07, 3.73 (2*s*, 2 MeOCO); 3.63 (*dd*, J = 14.4, 2.1, H–C(8)); 3.53 (*dd*, J = 14.6, 6.5, H–C(8)); 3.02 (*sept.*, J = 6.9, Me_2CH); 2.56 (*s*, Me–C(2)); 1.31, 1.29 (2*d*, J = 6.9, Me_2CH). CI-MS: 430 (22), 429 (100, $[M + 1]^+$), 398 (12), 397 (43). EI-MS: 429 (28), 428 (100, $M^{+\cdot}$), 397 (9), 370 (18), 369 (71, $[M - COOMe]^+$), 368 (11), 353 (24), 337 (12), 310 (12, $[M - 2\,COOMe]^+$), 309 (13), 307 (23), 295 (13), 293 (11), 279 (21), 278 (10), 277 (10), 267 (12), 266 (13), 265 (17), 253 (11), 252 (17). Anal. calc. for $C_{28}H_{28}O_4$ (428.53): C 78.48, H 6.58; found: C 78.28, H 6.43.

The structure of **40** was confirmed by an X-ray crystal-structure analysis (*cf. Fig. 4*). *Crystal data*: space group and cell dimensions: orthorhombic $P2_12_12_1$ with a = 1127.7, b = 2209.4, and c = 911.9 pm; D_{calc}: 1.253 Mg m^{-3}, Z = 4; μ(CuK_α) = 6.240 cm^{-1}; measured reflections (23 ± 1°): 3083, observed 2361, R = 0.034. Selected torsion angles [°]: C(3)–C(4)–C(5)–COOMe, 20.2(3); C(3)–C(4)–C(5)–C(6), –161.3(3); C(4)–C(5)–C(6)–C(7), –3.9(4); O=C–C(5)–C(6), –90.5(3); MeO–C–C(5)–C(6), 95.6(3); C(5)–C(6)–C(7)–Ph, 86.5(3); O=C–C(6)–C(5), –9.3(5); MeO–C–C(6)–C(5), 170.6(3), C(5)–C(6)–C(7)–C(8), –43.7(3); Ph–C(7)–C(8)–C(9), –50.8(3); C(7)–C(8)–C(9)–C(10), 126.8(3); C(7)–C(8)–C(9)–C(14), –55.4(3); C(8)–C(9)–C(14)–C(4), 5.6(4); C(9)–C(14)–C(4)–C(5), 6.3(4); C(14)–C(4)–C(5)–COOMe, –163.7(3); C(14)–C(4)–C(5)–C(6), 14.8(5), H–C(3)–C(4)–H_R, 73.7(3); H–C(3)–C(4)–H_s – 43.9(3).

8. *7-Isopropyl-1-methyl-4-[(*E*)-2-(4-methoxyphenyl)ethenyl]azulene* ((*E*)-**34**) *and ADM. Thermal Addition*: 1.77 g (5.6 mmol) of (*E*)-**34** and 1.53 g (10.8 mmol) of ADM were heated in decalin (10 ml) at 180° for 5 h. CC yielded 0.205 g (8%) of (*E*)-**38** (orange crystals) and 0.469 g (20%) of (*E*)-**36** (green crystals).

Ru-Catalyzed Addition: The following products were eluted: 0.002 g (0.5%) of **41** (orange crystals), and 0.138 g (30%) of (*E*)-**38** (orange crystals).

*Dimethyl 7-Isopropyl-5-methyl-10-[(*E*)-2-(4-methoxyphenyl)ethenyl]heptalene-1,2-dicarboxylate* ((*E*)-**38**): M.p. 197.8–199.0° (Et_2O/hexane). R_f (hexane/Et_2O 1:1) 0.20. UV (MeOH): λ_{max} 312, 260, 242, 232; λ_{min} 280, 245, 235 (see also [10]). IR (KBr): 2950*w*, 1730*s*, 1710*s*, 1610*w*, 1510*m*, 1435*w*, 1270*s*, 1250*s*, 1225*w*, 1190*w*, 1175*m*, 1160*w*, 1050*w*, 1030*w*, 985*w*, 830*w*. ^{1}H-NMR (300 MHz): 7.59 (*d*, J = 6.3, H–C(3)); 7.29 (*d*, J = 8.7, 2 arom. H);

6.83 (*d*, *J* = 8.7, 2 arom. H); 6.75 (*d*, *J* = 16.1, CH=C*H*–C(10)); 6.51 (*d*, *J* = 16.1, C*H*=CH–C(10)); 6.43 (*d*, *J* = 6.8, H–C(8)); 6.36 (*d*, *J* = 6.8, H–C(9)); 6.34 (*d*, *J* = 6.3, H–C(4)); 5.93 (*s*, H–C(6)); 3.80, 3.73 (2*s*, 2 MeOCO); 3.50 (*s*, MeO); 2.53 (*sept.*, *J* = 6.8, Me_2CH); 2.07 (*s*, Me–C(5)); 1.13, 1.09 (2*d*, *J* = 6.8, Me_2CH). ^{13}C-NMR (50 MHz): 167.75 (*s*); 167.28 (*s*); 159.25 (*s*); 149.79 (*s*); 144.23 (*s*); 140.34 (*d*); 137.04 (*s*); 133.37 (*s*); 131.87 (*s*); 130.49 (*s*); 130.05 (*s*); 129.08 (*d*); 127.69 (*d*, 2 arom. C); 127.25 (*d*); 126.69 (*d*); 126.44 (*d*); 126.02 (*d*); 125.82 (*d*); 125.66 (*s*); 114.02 (*d*, 2 arom. C); 55.28 (*q*, Me); 52.07, 51.95 (2*q*, 2 *Me*OCO); 36.04 (*d*, Me_2CH); 25.08 (*q*, Me–C(5)); 23.05, 22.45 (2*q*, Me_2CH). EI-MS: 459 (7), 458 (26, $M^{+\cdot}$), 426 (7), 400 (25), 399 (100, $[M - COOMe]^+$), 398 (15), 368 (12), 367 (47), 341 (14), 340 (50, $[M - 2COOCH_3]^+$), 339 (14), 335 (23), 325 (20), 324 (6), 297 (15), 296 (8). Anal. calc. for $C_{29}H_{30}O_5$ (458.56): C 75.96, H 6.59; found: C 76.03, H 6.68.

*Dimethyl 7-Isopropyl-4-[(*E*)-2-(4-methoxyphenyl)ethenyl]azulene-1,2-dicarboxylate* ((*E*)-**36**): R_f (hexane/Et_2O 1:1) 0.20. UV/VIS (MeOH): λ_{max} 580, 406, 310, 255; λ_{min} 490, 355, 277. IR (KBr): 2960*w*, 1730*s*, 1690*s*, 1610*m*, 1580*w*, 1520*m*, 1450*m*, 1390*m*, 1340*w*, 1250*s*, 1230*s*, 1200*s*, 1175*s*, 1140*w*, 1110*w*, 1060*w*, 1030*w*, 960*w*, 930*w*, 830*w*, 780*w*. ^{1}H-NMR (300 MHz): 9.42 (*d*, *J* = 1.8, H–C(8)); 7.83 (*d*, *J* = 16.1, CH=C*H*–C(4)); 7.82 (*d*, *J* = 11.2, H–C(5)); 7.74 (*dd*, *J* = 11.2, 1.9, H–C(6)); 7.67 (*s*, H–C(3)); 7.57 (*d*, *J* = 8.8, 2 arom. H); 7.40 (*d*, *J* = 16.0, C*H*=CH–C(4)); 6.96 (*d*, *J* = 8.8, 2 arom. H); 3.99, 3.96 (2*s*, 2 MeOCO); 3.86 (*s*, MeO); 3.18 (*sept.*, *J* = 6.8, Me_2CH); 1.40 (*d*, *J* = 6.9, Me_2CH). ^{13}C-NMR (50 MHz); 165.72 (*s*); 160.59 (*s*); 147.52 (*s*); 147.37 (*s*); 139.93 (*s*); 139.21 (*s*); 138.67 (*d*); 138.48 (*d*); 136.55 (*d*); 129.19 (*s*); 128.85 (*d*, 2 arom. C); 128.03 (*s*); 125.80 (*d*); 125.35 (*d*); 114.37 (*d*, 2 arom. C); 113.82 (*d*); 113.57 (*s*); 55.34 (*q*, MeO); 52.21, 51.51 (2*q*, 2 *Me*OCO); 38.52 (*d*, Me_2CH); 24.39 (*q*, Me_2CH). EI-MS: 419 (26), 418 (100, $M^{+\cdot}$), 388 (9), 387 (29), 386 (10), 360 (13), 359 (56, $[M - COOMe]^+$), 358 (10), 328 (8), 327 (10), 301 (7), 300 (25, $[M - 2COOMe]^+$), 299 (7). Anal. calc. for $C_{26}H_{26}O_5$ (418.49): C 74.62, H 6.26; found: C 74.82, H 6.47.

*Dimethyl 10-Isopropyl-7-methyl-2-[(*E*)-2-(4-methoxyphenyl)ethenyl]tricyclo[6.4.0.0^{1,5}]dodeca-2,4,6,9,11-pentaene-3,4-dicarboxylate* (**41**): M.p. 168.0–169.0° (Et_2O/hexane). ^{1}H-NMR (300 MHz): 7.32 (*d*, *J* = 8.8, 2 arom. H); 7.07 (*d*, *J* = 16.2, CH=C*H*–C(2)); 6.85 (*d*, *J* = 8.8, 2 arom. H); 6.66 (*d*, *J* = 16.2, C*H*=CH–C(2)); 6.57 (*s*, H–C(6)); 6.01 (*d*, *J* = 9.6, H–C(11)); 5.83 (*d*, *J* = 6.2, H–C(9)); 5.08 (*d*, *J* = 9.6, H–C(12)); 3.91, 3.82 (2*s*, 2 MeOCO); 3.80 (*s*, MeO); 3.40 (*d*, *J* = 6.2, H–C(8)); 2.46 (*sept.*, *J* = 6.8, Me_2CH); 1.97 (*s*, Me–C(7)); 1.16, 1.14 (2*d*, *J* = 6.8, Me_2CH). EI-MS: 459 (21), 458 (74, $M^{+\cdot}$), 426 (14), 399 (22, $[M - COOMe]^+$), 398 (23), 383 (21), 368 (10), 367 (32), 352 (12), 351 (36), 340 (12, $[M - 2\,COOMe]^+$), 339 (19).

The structure of **41** was confirmed by an X-ray crystal-structure analysis (*cf. Fig. 5*). *Crystal data*: space group and cell dimensions: triclinic *P*1 with *a* = 1128.4, *b* = 1158.8, *c* = 1108.6 pm, and α = 107.12, β = 111.83, γ = 71.21°; D_{calc}: 1.220 Mg m^{-3}, *Z* = 2; μ(CuK_α) = 6.290 cm^{-1}; measured reflection (23 ± 1°): 3937, observed 3301; *R* = 0.044. Selected torsion angles [°]: C(1)–C(2)–C(3)–C(4), −10.7(2); C(1)–C(2)–*C*H=*C*HC$_6$H$_4$OMe, 10.5; C(1)–C(5)–C(6)–C(7), −13.9(2); MeOC$_6$H$_4$*C*H=*C*H–C(2)–C(3), −178.3(2); C$_o$–C$_{ip}$–CH=CH, −4.7(4), (*ip* = *ipso*); C$_o$–C$_{ip}$–CH=CH, 174.2(2); CH–C(2)–C(3)–COOMe, −7.8(3); C(2)–C(3)–C=O, 58.5(4); C(2)–C(3)–C–OMe, −119.0(2); C(2)–C(3)–C(4)–COOMe, −170.1(2); MeOCC–C(3)–C(4)-COOMe, 14.6(3); C(3)–C(4)–C(5)–C(1), 9.2(2); MeOCC–C(3)–C(4)–C(5), −174.2(2); O=C–C(4)–C(5), −165.6(2); MeO–C–C(4)–C(5), 13.7(2); MeOOC–C(4)–C(5)–C(1), −179.8(2); MeOOC–C(4)–C(5)–C(6), 17.5(4); C(4)–C(5)–C(6)–C(7), 148.9(3); C(5)–C(6)–C(7)–C(8), 1.7(2); C(6)–C(7)–C(8)–C(9), 135.7(2); C(7)–C(8)–C(9)–C(10), −95.2(2); C(8)–C(9)–C(10)–C(11), −3.2(3); C(9)–C(10)–C(11)–C(12), −8.7(3); C(10)–C(11)–C(12)–C(1), 0.4(3); C(11)–C(12)–C(1)–C(2), −123.5(2); C(11)–C(12)–C(1)–C(8), 17.2(3); H–C(8)–C(9)–H, −35.5(3).

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