171. New Results in the Synthesis of Styrylazulene Derivatives: Application of the 'Anil Synthesis' to the Preparation of Azulenes Substituted with Styryl Groups at the Seven-Membered Ring

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The synthesis of 4,6,8-trimethyl-1-[(*E*)-4-R-styryl]azulenes **5** (R=H, MeO, Cl) has been performed by *Wittig* reaction of 4,6,8-trimethylazulene-1-carbaldehyde (**1**) and the corresponding 4-(R-benzyl)(triphenyl)phosphonium chlorides **4** in the presence of EtONa/EtOH in boiling toluene (see *Table 1*). In the same way, guaiazulene-3-carbaldehyde (**2**) as well as dihydrolactaroviolin (**3**) yielded with **4a** the corresponding styrylazulenes **6** and **7**, respectively (see *Table 1*). It has been found that **1** and **4b** yield, in competition to the *Wittig* reaction, alkylation products, namely **8** and **9**, respectively (*cf. Scheme 1*). The reaction of 4,6,8-trimethylazulene (**10**) with **4b** in toluene showed that azulenes can, indeed, be easily alkylated with the phosphonium salt **4b**. 4,6,8-Trimethylazulene-2-carbaldehyde (**12**) has been synthesized from the corresponding carboxylate **15** by a reduction ($LiAlH_4$) and dehydrogenation (MnO_2) sequence (see *Scheme 2*). The *Swern* oxidation of the intermediate 2-(hydroxymethyl)azulene **16** yielded only 1,3-dichloroazulene derivatives (*cf. Scheme 2*). The *Wittig* reaction of **12** with **4a** and **4b** in the presence of EtONa/EtOH in toluene yielded the expected 2-styryl derivatives **19a** and **19b**, respectively (see *Scheme 3*). Again, the yield of **19b** was reduced by a competing alkylation reaction of **19b** with **4b** which led to the formation of the 1-benzylated product **20** (see *Scheme 3*). The 'anil synthesis' of guaiazulene (**21**) and the 4-R-benzanils **22** (R=H, MeO, Cl, Me_2N) proceeded smoothly under standard conditions (powered KOH in DMF) to yield the corresponding 4-[(*E*)-styryl]azulene derivatives **23** (see *Table 4*). In minor amounts, bis(azulen-4-yl) compounds of type **24** and **25** were also formed (see *Table 4*). The 'anil reaction' of **21** and 4-$NO_2C_6H_4CH{=}NC_6H_5$ (**22e**) in DMF yielded no corresponding styrylazulene derivative **23e**. Instead, (*E*)-1,2-bis(7-isopropyl-1-methylazulen-4-yl)ethene (**27**) was formed (see *Scheme 4*). The reaction of 4,6,8-trimethylazulene (**10**) and benzanil (**22a**) in the presence of KOH in DMF yielded the benzanil adducts **28** to **31** (*cf. Scheme 5*). Their direct base-catalyzed transformation into the corresponding styryl-substituted azulenes could not be realized (*cf. Scheme 6*). However, the transformation succeeded smoothly with KOH in boiling EtOH after *N*-methylation (*cf. Scheme 6*).

1. Introduction. – For a study of the thermo- and photochromic behavior of heptalenes [1], we have been interested in a versatile synthesis of methylazulenes with styryl substituents at C(1) or C(2) which should be reacted with dimethyl acetylenedicarboxylate to yield the corresponding 4- and 5-styryl-substituted heptalene-1,2-dicarboxylates (*cf.* [2]). It has already been shown that mixtures of 1-[(*E*)- and (*Z*)-styryl]azulenes can be obtained by *Wittig* reaction of azulene-1-carbaldehydes with (benzyl)(triphenyl)-phosphonium chloride in the presence of BuLi in Et_2O [3]. Also the reverse *Wittig* reaction, *i.e.*, the reaction of (azulen-1-yl)(methyl)(triphenyl)phosphonium iodides with benzaldehyde in the presence of BuLi in Et_2O, has been applied to the synthesis of 1-styryl- and 1,3-distyrylazulenes [4] [5]. A Me group at C(2) of the azulenes can be activated by strong π- and σ-acceptor substituents such as COOEt or CN at C(1) and/or C(3), so that these azulenes can be reacted with benzaldehydes already in EtOH/EtONa

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to yield the corresponding 2-styryl-substituted azulenes [6] [7]. Also the *Heck* reaction has been successfully applied to activated 1- and 2-halogen-substituted azulenes for the synthesis of the corresponding styryl-substituted azulenes [8].

We have been also interested in a plain synthesis of azulenes substituted with a styryl group at the seven-membered ring. Indeed, *Hafner*'s azulene synthesis (*cf.* [9]) has been performed with styryl-substituted pyrylium salts and sodium cyclopentadienide to yield the corresponding styryl-substituted azulenes [10]. Since Me groups at C(4), C(6), and C(8) of azulenes can easily be deprotonated by strong bases such as sodium methylphenylamide (*cf.* [11]), the formed carbanions can be reacted directly with benzaldehyde [12] to yield styryl-substituted azulenes, or, the carbanions can be transformed into the corresponding triphenylphosphonium salts which yield the styryl-substituted azulenes by a *Wittig* reaction with benzaldehyde [13]. Me groups at C(6) of azulene-1,3-dicarboxylates are much more acidic, so that they can react with aromatic aldehydes already in EtOH/EtONa to yield 6-styryl-substituted azulene-1,3-dicarboxylates [14]. Again, the *Heck* reaction has also been successfully performed with styrene and 6-bromoazulenes [8].

On grounds of simplicity, we applied a modified *Wittig* reaction to the synthesis of 1- and 2-styryl-substituted methylazulenes, starting from the corresponding methylazulene-1- and -2-carbaldehydes. We also investigated the 'anil synthesis' (*cf.* [15])[2]), which works well with acidic Me groups at aromatic or heteroaromatic hydrocarbons, for the preparation of azulenes with styryl substituents at the seven-membered ring.

2. Results and Discussions. – 4,6,8-Trimethylazulene-1-carbaldehyde (**1**) as well as guaiazulene-3-carbaldehyde (**2**) and dihydrolactaroviolin (**3**)[3]), and the (benzyl)(triphenyl)phosphonium chlorides **4** reacted smoothly in the presence of EtOH/EtONa in boiling toluene to yield – in most of the cases – (*E*)/(*Z*)-mixtures of the 1-styryl-substituted azulenes **5a–c**, **6**, and **7**, respectively (*cf. Table 1*).

These mixtures could easily be transformed into the pure (*E*)-isomers by heating in boiling toluene in the presence of catalytic amounts of I_2. All (*E*)-isomers showed in solution as well as in the crystals a green color[4]). The absorption regions in the UV spectra of the (*E*)-isomers are compiled in *Table 2*. Those of **5a–c** and **6**, *i.e.*, of azulenes with a Me substituent at C(8), show, as expected, a similar habitus with the longest-wavelength absorption in the range of 398–410 nm. The MeO-substituted styrylazulene **5b** possesses a clearly recognizable shoulder at the longer-wavelength flank (423 nm) of this absorption band. Weakly formed shoulders at *ca.* 430 nm are also visible in the spectra of the other styrylazulenes. In contrast, the spectrum of **7**, which carries an H-atom at C(8), exhibits a structured band at its longest-wavelength-absorption region with maxima at 400 and 380 nm. Again, a shoulder is recognizable at the longer-wavelength flank (423 nm). Also the other absorption regions are more structured for **7**.

The reaction of **1** and **4b** in the presence of EtOH/EtONa in boiling toluene led to the formation of two by-products (*Scheme 1*) whose structure could easily be established on

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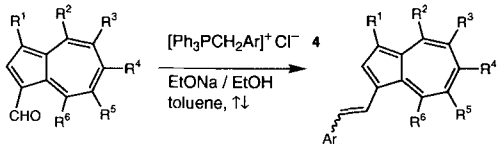
[2]) The term 'anil synthesis' has been coined for the synthesis of stilbene derivatives with anils [15]. Its broad application to the fabrication of stilbene derivatives as fluorescent whitening agents has exhaustively been studied by *Siegrist* (*cf.* [16] and literature cited there).

[3]) *Cf.* Footnote 2 in [17].

[4]) The corresponding (*Z*)-isomers which were identified only in the original reaction mixtures (*cf. Exper. Part*) showed on TLC (silica gel; hexane) as compared to the (*E*)-isomers the larger R_f values ($R_f(Z)/R_f(E) \approx 1.4$) and appeared as blue spots (*cf.* [3]).

Table 1. *1-Styryl-Substituted Azulenes Synthesized by* Wittig *Reaction of the Corresponding Azulene-1-carbaldehydes and Phosphoranes*



1–3 5–7

Aldehyde		Phosphonium salt		Azulene		
				[%]		(*E*)/(*Z*)[a]
1	$R^1 = R^3 = R^5 = H$, $R^2 = R^4 = R^6 = Me$	**4a**	Ar = Ph	**5a**	85	70:30
		4b	Ar = 4-$MeOC_6H_4$	**5b**	60[b])	100:0
		4c	Ar = 4-ClC_6H_4	**5c**	60[c])	100:0
2	$R^2 = R^4 = R^5 = H$, $R^1 = R^6 = Me$, R^3 = i-Pr	**4a**	Ar = Ph	**6**	90[d])	55:45
3	$R^1 = R^3 = R^4 = R^6 = H$, $R^2 = Me$, R^5 = i-Pr	**4a**	Ar = Ph	**7**	90	60:40

[a]) Ratio in the originally isolated material. Heating of the mixture in the presence of a catalytic amount of I_2 in boiling toluene yielded almost quantitatively the pure (*E*)-isomers.

[b]) (*E*)-**5b** was accompanied by 1-(4-methoxybenzyl)-4,6,8-trimethylazulene (**8**; 6.5%) and by 1-(4-methoxybenzyl)-3-[(*E*)-4-methoxystyryl]-4,6,8-trimethylazulene (**9**; 11%) in the original reaction mixture (see text).

[c]) 30% of **1** was recovered. Also 4,6,8-trimethylazulene-2-carbaldehyde (**12**; 7%) was isolated from the reaction mixture (see text).

[d]) See also [3].

Table 2. *UV Spectra* (hexane) *of 1-[(E)-4-R-Styryl]azulenes*[a])

Azulene[b])	R	λ_{max} (log ε) [nm]				λ_{min} (log ε) [nm]		
5a	H	398(4.42)	324(4.70)	257(4.48)	236(4.42)	374(4.31)	278(4.19)	240(4.42)
5b	MeO	428 (sh, 3.94)	324(4.54)	252(4.20)	232(4.20)	376(4.14)	283(4.06)	240(4.17)
		402(4.23)	271(4.24)				260(4.18)	
5c	Cl	402(4.33)	326(4.52)	262(4.27)	233(4.25)	374(4.20)	281(4.05)	244(4.20)
			267(4.29)					
6	H	410(4.48)	327(4.58)	268(4.45)	227(4.29)	369(4.23)	284(4.30)	242(4.22)
7	H	423 (sh, 3.95)	355(4.27)	255(4.38)		390(4.16)	275(4.09)	224(4.13)
		400(4.19)	342(4.30)			375(4.18)		
		380(4.19)	316(4.43)			332(4.29)		
			306(4.36)					

[a]) All azulenes showed in the VIS region a very broad and weak absorption band around 640 nm ($\log\varepsilon \approx 2.6$); sh: shoulder.

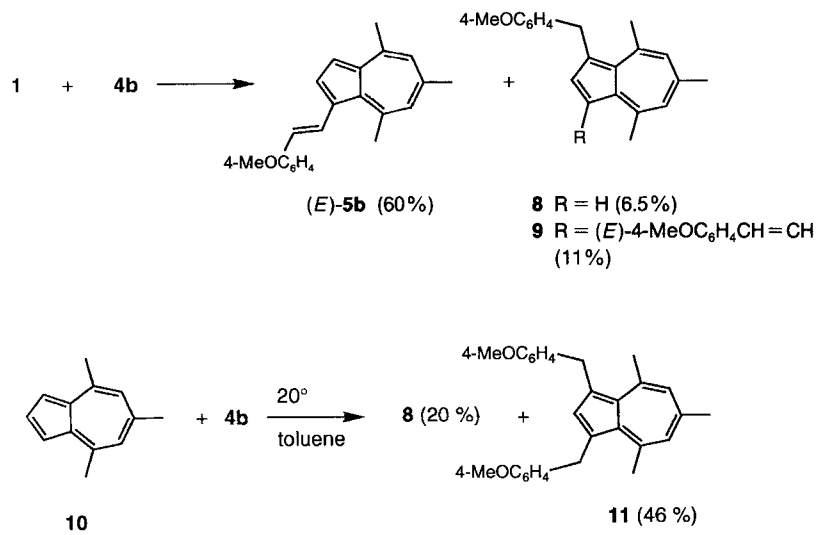
[b]) *Cf. Table 1.*

the basis of their ^{1}H-NMR spectra (see *Exper. Part*). From this observation, it can be concluded that **4b** in toluene is a strong alkylating agent for **1**[5]) as well as for (*E*)-**5b**. Indeed, when 4,6,8-trimethylazulene (**10**) was stirred in toluene with a 1.7-fold molar excess of **4b**, the formation of 20% **8** and 46% of the 1,3-bisalkylated azulene **11** was observed (*Scheme 1*), *i.e.*, the total yield of alkylation amounts to 66%[6]).

[5]) We suppose that **1** is alkylated by **4b** at C(1). Base-catalyzed extrusion of CO will lead to **8**.

[6]) Preliminary results with guaiazulene show that azulenes can quite generally be alkylated with π-donor substituted (benzyl)(triphenyl)phosphonium chlorides in toluene.

Scheme 1[a])



[a]) See *Table 1*.

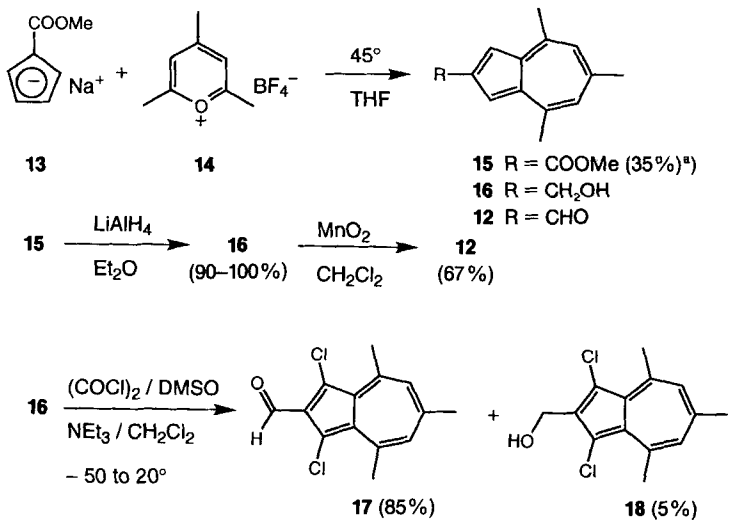
In the reaction of **1** with **4c**, which occurred under the usual reaction conditions (*cf. Exper. Part*) only to an extent of 70%, we observed – as we assume – an isomerization of the azulene-1-carbaldehyde **1** into the 2-carbaldehyde **12** (7%). So far, we have no explaination for the formation of **12**. The thermal rearrangement of azulene-1-carbaldehyde into -2-carbaldehyde has been observed in boiling ethyleneglycol [18]. However, the yield of the 2-carbaldehyde amounted only to 2%. Carbaldehyde **1** did not rearrange to its positional isomer **12** in boiling toluene.

We synthesized **12** by the sequence shown in *Scheme 2*. The sodium salt **13** was obtained from sodium cyclopentadienide and methyl chloroformate [19]. Its reaction with the pyrylium salt **14** [20] yielded a mixture of **15** and the corresponding 1-carboxylate which was separated chromatographically[7]). The ester **15** could not be transformed directly into the carbaldehyde **12** by reduction with DIBAH in toluene. At −70°, only the corresponding alcohol **16** was formed. The reduction of **15** to **16** took place quantitatively with $LiAlH_4$ in Et_2O at 0°. First attempts to obtain **12** from **16** by *Swern* oxidation failed completely, since the intermediate chlorodimethylsulfonium ions seem to be excellent chlorination agents for the azulene ring in **16** (*Scheme 2*). However, the dehydrogenation of **16** to yield the blue 2-carbaldehyde **12** could easily be performed with MnO_2 in CH_2Cl_2 (*Scheme 2*).

The *Wittig* reaction of **12** with the phosphonium salt **4a** was performed in the usual way and yielded a 4:1 mixture of the (*E*)- and (*Z*)-isomer of the corresponding 2-styryl

[7]) It is difficult to separate 2-carboxylate **15** from the 1-carboxylate by chromatography on silica gel (R_f (**15**)/R_f (1-carboxylate) ≈ 1.0 (hexane/Et_2O 7:3)). In later runs, we learned that it is much easier to reduce and then dehydrogenate the mixture of **15** and 1-carboxylate. The red 1-carbaldehyde **1** and the blue 2-carbaldehyde **12** can be easily separated on silica gel (R_f (**12**)/R_f (**1**) ≈ 2.3).

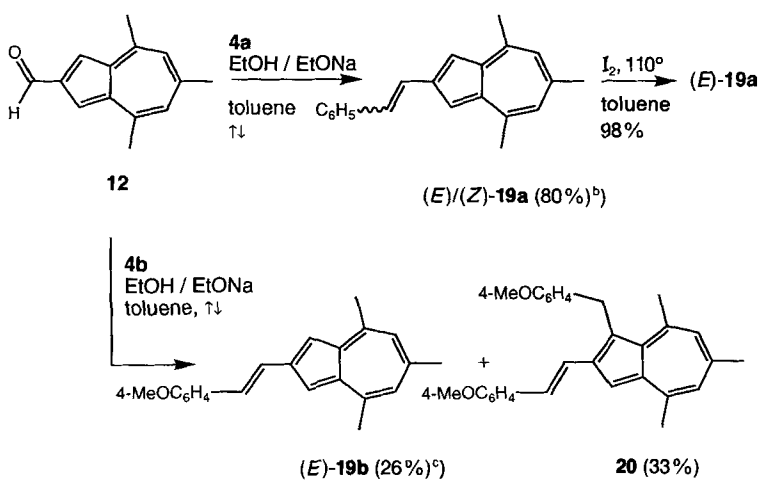
Scheme 2



a) A mixture of **15** and the corresponding methyl 4,6,8-trimethylazulene-1-carboxylate was obtained, from which **15** was separated by CC (see *Exper. Part*).

derivative **19a** (*Scheme 3*). Thermal isomerization of the mixture in the presence of catalytic amounts of I_2 in boiling toluene yielded the pure, dark-violet (*E*)-isomer. The reaction of **12** with **4b** was again hampered by the fact that the *Wittig* reaction with **4b** and the alkylation of the product (*E*)-**19b** by **4b** occurred with similar rates. Therefore, a mixture of (*E*)-**19** and its alkylation product **20** was obtained (*Scheme 3*), which could be separated chromatographically.

Scheme 3[a])



a) *Cf. Table 1.* b) 4:1 mixture of (*E*)- and (*Z*)-**19a**. c) Only the (*E*)-isomer was formed.

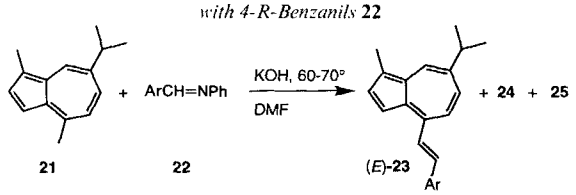
Table 3. *UV Spectra* (hexane) *of 2-[(E)-4-R-Styryl]azulenes*[a])

Azulene[b]) No.	R	λ_{max} (log ε) [nm]					λ_{min} (log ε) [nm]			
19a	H	426(4.46)	403(4.57)	384 (sh, 4.36)	326(4.97) 320(4.94)	255(4.34) 232(4.30)	416(4.39)	362(4.09)	274(3.90)	243(4.23)
19b	MeO	435(4.30)	411(4.36)	389 (sh, 4.13)	334(4.65)	263(4.01) 228(4.38)	424(4.18)	365(3.82)	272(3.87)	248(3.81)

[a]) The VIS region was not explored; sh = shoulder. [b]) *Cf. Scheme 3.*

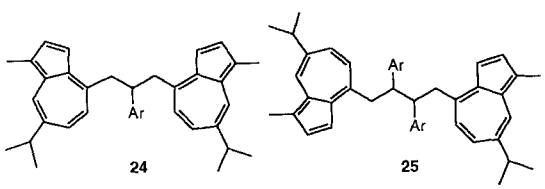
The UV maxima and minima of **19a** and **19b** are collected in *Table 3*. The spectra of both 2-styrylazulenes resemble in the longest-wavelength region those of **7** (*cf. Table 2*). However, the bands of **19a** and **19b** are more pronounced. On the other hand, the bathochromic influence of the *p*-MeO substituent of **19b** is more clearly recognizable as in the case of **5b**. This observation is in agreement with the fact that the 2-styryl substituent can strongly interact only with the LUMO of the azulene skeleton.

Table 4. *7-Isopropyl-1-methyl-4-[(E)-4-R-styryl]azulenes* **23** *by 'Anil Synthesis' of Guaiazulene* (**21**) *with 4-R-Benzanils* **22**



Benzanil	Ar	4-Styrylazulene ([%])	By-products[a])	
			24 ([%])	**25** ([%])
22a	Ph	**23a** (32)	**24a** (2)	**25a** (2)
22b	4-$MeOC_6H_4$	**23b** (31)	**24b** (2)	**25b** (2)
22c	4-ClC_6H_4	**23c** (30)	**24c** (10)	n.o.[b])[c])
22d	4-$Me_2NC_6H_4$	**23d** (82)	n.o.	n.o.

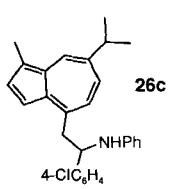
[a])



24 **25**

[b]) n.o. = not observed.

[c]) Instead of **25c**, compound **26c** was obtained in a yield of 2%.



26c

For the formation of azulenes with styryl groups at C(4), C(6), and/or C(8), we applied the 'anil synthesis' to guaiazulene (**21**) as well as to 4,6,8-trimethylazulene (**10**). Guaiazulene was chosen as a model azulene, because it carries a Me group at C(1) which should be unreactive in the 'anil synthesis', and a second one at C(4) which should be reactive (*cf.* metalation reactions of **21** [12]). Indeed, when **21** was reacted with the benzanils **22a–d** in *N,N*-dimethylformamide (DMF) in the presence of finely powdered KOH at 60–70°, the corresponding (*E*)-configurated 4-styryl-substituted azulenes **23a–d** were formed in all cases in moderate-to-good yields (*Table 4*).

No by-products were observed in the reaction of **21** with the 4-(dimethylamino)-substituted benzanil **22d**. However, in all other cases we found by-products of type **24** and **25** (*Table 2*). In the reaction with the 4-chlorobenzanil (**22c**), a compound of type **25** could not be detected. Instead, the anilino derivative **26c** (*Table 2*) could be isolated in a yield of 2%. Compounds of this type are considered to be intermediates in the formation of the stilbene-type products (*cf.* [21] and later). The formation of **24a** and **24b** can be explained by addition of the carbanion of **21** (deprotonated at the Me group at C(4)) to the styryl derivatives **23a** and **23b**, respectively. The products **25a** and **25b** are configurationally homogeneous. However, on the basis of their spectroscopic data, we were not able to distinguish unambiguously between the *meso*- and *rac*-configuration (*cf. Exper. Part*). An X-ray crystal-structure analysis of **25b** established its *meso*-configuration (*cf. Fig.*).

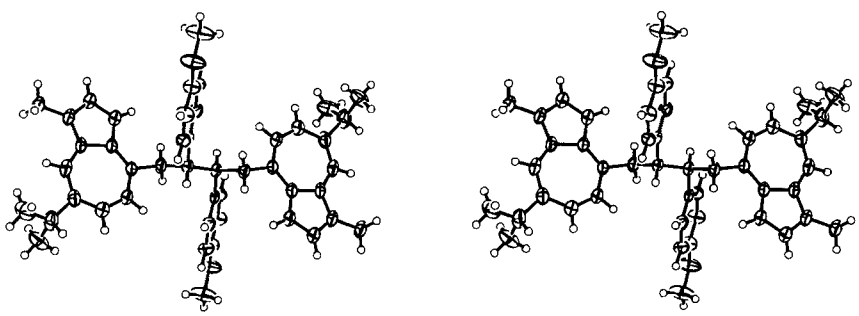


Figure. *Stereoscopic projection of the X-ray crystal structure of* meso-*1,4-bis(7-isopropyl-1-methylazulen-4-yl)-2,3-bis(4-methoxyphenyl)butane* (**25b**)

The *meso*-configuration of **25a** and **25b** excludes, in principle, the possibility that they are formed by dimerization of the corresponding 1-aryl-2-(azulen-4-yl)ethyl radicals, since similar radicals formed in ground-state reactions (*cf.* [22]) as well as *via* excited-state reactions (*cf.* [23] and lit. cit. there), in general, dimerize to yield *ca.* 1:1 mixtures of the corresponding *meso*- and *rac*-compounds. Therefore, the formation of the compounds of type **25** under the conditions of the anil synthesis is not quite clear at the moment.

The data of the UV spectra of the 4-[(*E*)-styryl]azulene derivatives are presented in *Table 5*. The bathochromic influence of the π-donor substituents (MeO, Me_2N) at C(4) of the styryl moiety at the seven-membered ring at C(4) is much more pronounced than in the case of the 1- or 2-styryl-substituted azulenes (*cf. Tables 1* and *3*). Indeed, π-donor substituents at C(4) should accentuate the dipolar ground state of the azulenes.

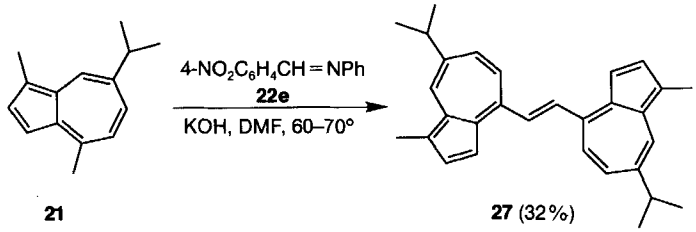
Table 5. *UV Spectra* (hexane) *of 7-Isopropyl-1-methyl-4-[(E)-4-R-styryl]azulenes*[a])

Azulene[b]) No.	R	λ_{max} (log ε) [nm]				λ_{min} (log ε) [nm]		
23a	H	396 (sh, 3.66) 364 (sh, 4.28) 344 (sh, 4.44)	317(4.55)	283(4.68)	260 (sh, 4.44)	306(4.58)	230(4.24)	
23b	MeO	[c]) 380 (sh, 4.29) 362 (sh, 4.39)	327(4.46)	291(4.56)	266(4.35) 244(4.30)	310(3.43)	254(4.28)	218(4.15)
23c	Cl	396 (sh, 3.73) 366 (sh, 4.33) 350 (sh, 4.47)	319(4.69)	282(4.71)	260(4.49)	301(4.61)	246(4.32)	215(4.30)
23d	Me_2N	430 (sh, 4.50) 413(4.60)	326 (sh, 4.21)	294(4.65)	258(4.64)	344(4.34)	273(4.52)	226(4.26)

[a]) The VIS region was not measured; sh = shoulder. [b]) *Cf. Table 4.* [c]) Strong tailing > 400 nm.

Another surprise has been offered by the reaction of **21** with 4-nitrobenzanil (**22e**). In this case, the expected styryl derivative **23e** was not detectable in the reaction mixture. Instead, the 1,2-bis(azulen-4-yl)ethene **27** could be isolated as black-green needles (*Scheme 4*).

Scheme 4



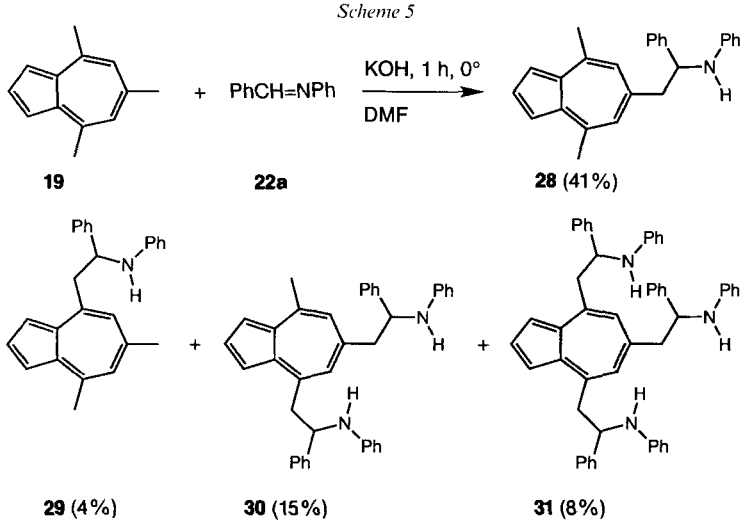
The (*E*)-configuration of **27** was deduced from an absorption band at 960 cm^{-1} in its IR spectrum (KBr) which would be in agreement with the out-of-plane vibration of the two H-atoms at the central C=C bond. We assume that **27** is formed by a SET mechanism which allows an electron transfer from the carbanion of **21** to the electron-accepting anil **22e**. Dimerization of the radicals formed from **21** and a new SET oxidation of the dihydrodimer of **21** would lead to **27**.

The 'anil synthesis' with 4,6,8-trimethylazulene (**10**) and benzanil (**22a**) in DMF in the presence of finely powdered KOH was performed at 0° and led under these conditions to a number of addition products of **10** and **22a** (*Scheme 5*).

According to the difference in the R_f values (silica gel; hexane/Et_2O 7:3) of the products they could easily be separated chromatographically (see *Exper. Part*). Their structure followed from their ^{1}H-NMR and mass spectra. The appearance of these four products as well as the missing of a possible second symmetric bisadduct demonstrates that *i*) under the conditions of the 'anil synthesis', Me–C(6) is kinetically more acidic[8])

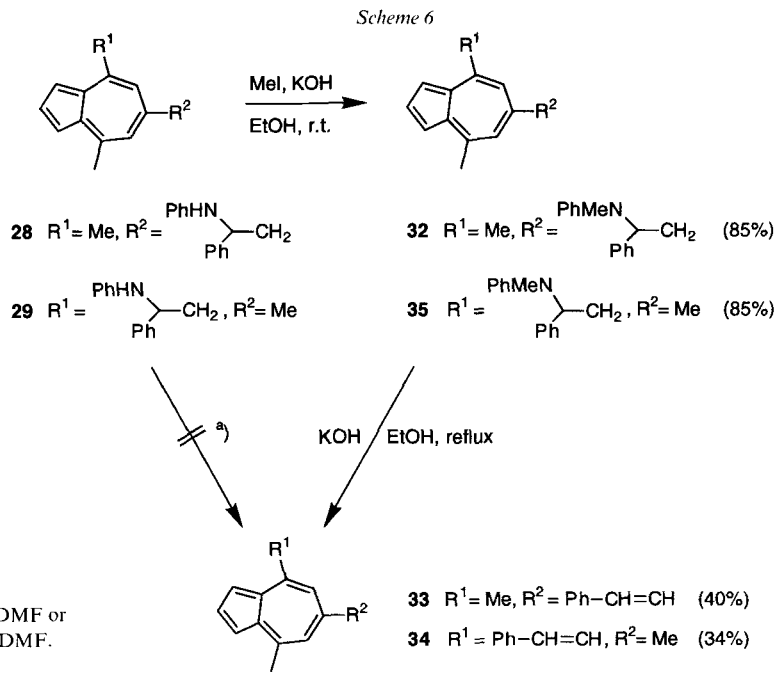
[8]) Sodium-salt formation of **10** with sodium methylphenylamide in Et_2O at −15° occurs according to *Hafner* and *Weldes* [24] exclusively at Me–C(4/8).

Scheme 5



than Me–C(4/8) assuming equal reactivities of the formed carbanions with **22a**, and *ii*) the acidities of the residual Me groups in the mono- and bisadducts **28** to **30** are of similar magnitude and close to those of the Me groups of **10**. The compounds **28**–**31** were stable under the reaction conditions, *i.e.*, no styryl derivatives were formed, when they were treated with KOH as well as with *t*-BuOK in DMF. However, azulene **28** could easily be *N*-methylated with MeI/KOH in EtOH to yield **32** (*Scheme 6*).

Scheme 6



[a]) KOH/DMF or *t*-BuOK/DMF.

Heating this azulene with KOH in boiling EtOH transformed it smoothly into the (*E*)-configurated 6-styrylazulene **33**. These observations are in accordance with proposals of *Fletcher* and *Siegrist* [15] who assume that, in the 'anil synthesis', the formed carbanions react in a concerted manner with the benzanils and DMF to yield corresponding orthoformic-acid intermediates from which the stilbene derivatives are formed by base-catalyzed elimination of DMF and aniline.

Under the same conditions as **33** was obtained from **28**, the benzanil adduct **29** yielded the corresponding styryl derivative **34** (*cf.* [13]) *via* **35**. Both **33** and **34** showed a blue color in solution as well as a deeply green color in the crystalline state (*cf. Exper. Part*). The advantage of the two-step 'anil synthesis' exercised with **10** and **22a** is the fact that the benzanil adducts **28–30** (as well as **31**) can be more easily separated by chromatography than the corresponding (*E*)-styryl derivatives **33** to **35**.

We thank Dr. *A. Linden* for the X-ray crystal-structure analysis, Prof. *M. Hesse* and his coworkers for mass spectra, Prof. *W. von Philipsborn* and his coworkers for NMR support and numerous ^{1}H-NOE measurements, and *H. Frohofer* for elemental analyses. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. See [25] and lit. cit. there. For ^{1}H-NOE: *s* = strong, *m* = medium, *w* = weak.

1. *4,6,8-Trimethyl-1-[(*E*)-2-phenylethenyl]azulene* ((*E*)-**5a**; cf. [26]). To 1.56 g (4.0 mmol) of *(benzyl)-(triphenyl)phosphonium chloride* (**4a**) in 20 ml of toluene were added under stirring 0.410 g (6.0 mmol) of NaOEt in 5 ml of EtOH, followed by 0.400 g (2.0 mmol) of *4,6,8-trimethylazulene-1-carbaldehyde* (**1**). The green mixture was then boiled under reflux for 10 min. After cooling, MeOH was added and the solvent mixture removed under reduced pressure. The residue was extracted with 20 ml of Et_2O and the extract washed with H_2O, sat. NaCl soln., and then dried ($MgSO_4$). Evaporation of Et_2O yielded 0.436 g (1.6 mmol) of a dark green oil. ^{1}H-NMR showed the presence of the (*E*)/(*Z*) isomers of **5a** in a ratio of 7:3. The (*Z*)-isomer appeared as a blue spot (R_f (hexane) 0.21) and the (*E*)-isomer as a green spot (R_f (hexane) 0.15) on TLC. The isomer mixture was boiled in toluene in presence of a catalytic amount of I_2 for 24 h. Toluene was removed (RE) and the (*E*)-isomer isolated after filtration over silica gel (hexane) to yield 0.425 g (1.56 mmol, 78%) of pure (*E*)-**5a** as green crystals. M.p. 152.0–153.0° (hexane). UV (hexane): λ_{max} 398 (4.42), 324 (4.70), 257 (4.48), 236 (4.42); λ_{min} 374 (4.31), 278 (4.19), 240 (4.42). IR (KBr): 1610*w*, 1590*m*, 1570*s*, 1560*m*, 1520*s*, 1490*w*, 1450*s*, 1420*m*, 1370*m*, 1340*s*, 1260*s*, 1220*w*, 1210*w*, 1190*w*, 1150*w*, 1100*w*, 1070*w*, 1020*w*, 960*s*, 840*s*, 790*s*, 750*s*, 720*s*, 690*s*. ^{1}H-NMR ($CDCl_3$): 8.02 (*d*, *J* = 15.9, PhCH=C*H*); 7.94 (*d*, *J* = 4.3, H–C(2)); 7.55 (*d*, *J* = 7.4, 2 arom. H); 7.41 (*d*, *J* = 7.4, 2 arom. H); 7.38 (*d*, *J* = 4.3, H–C(3)); 7.26 (*m*, 1 arom. H); 6.97 (*s*, H–C(5,7)); 6.93 (*d*, *J* = 15.9, PhC*H*=CH); 3.11 (*s*, Me–C(8)); 2.86 (*s*, Me–C(4)); 2.59 (*s*, Me–C(6)). ^{1}H-NOE ($CDCl_3$, 400 MHz): 2.59 (Me–C(6))→6.97 (*s*, H–C(5,7)); 2.86 (Me–C(4))→6.97 (*s*, H–C(5)); 7.38 (*m*, H–C(3)); 3.11 (Me–C(8))→6.97 (*s*, H–C(7)); 8.02 (*m*, MeCH=C*H*). ^{13}C-NMR ($CDCl_3$): 147.31 (*s*); 146.47 (*s*); 145.58 (*s*); 138.75 (*s*); 138.64 (*s*); 132.98 (*d*); 132.43 (*s*); 129.37 (*s*); 129.31 (*d*); 128.62 (*d*, 2 arom. CH); 127.57 (*d*); 127.40 (*d*); 127.06 (*d*); 126.58 (*d*); 125.97 (*d*, 2 arom. CH); 116.49 (*d*); 29.26 (*q*); 28.35 (*q*); 25.45 (*q*). CI-MS: 275 (4), 274 (19), 273 (100, $[M + 1]^+$). Anal. calc. for $C_{21}H_{20}$ (272.39): C 92.60, H 7.40; found: C 92.68, H 7.52.

2. *1-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-4,6,8-trimethylazulene* ((*E*)-**5b**). The phosphonium salt **4b** (3.77 g, 9.0 mmol) was formed by reaction of Ph_3P (2.36 g, 9.0 mmol) with 4-methoxybenzyl chloride (1.41 g, 9.0 mmol) in boiling toluene (50 ml; 2 h). Then, after cooling, **1** (0.547 g, 2.7 mmol) and EtONa (0.55 g, 8.1 mmol)/EtOH (15 ml) were added, and the reaction was completed as described in *1*. Workup and CC (silica gel; hexane) yielded **8** (0.051 g, 6.5%; violet crystals), (*E*)-**5b** (0.470 g, 60%; deeply green crystals), and **9** (0.125 g, 11%; dark green crystals).

*Data of (*E*)-***5b***: M.p. 125.0–126.0° (hexane). R_f (hexane/Et_2O 9:1) 0.28. UV (hexane): λ_{max} 428 (sh, 3.94), 402 (4.23), 324 (4.54), 271 (4.24), 252 (4.20), 232 (4.20); λ_{min} 376 (4.14), 283 (4.06), 260 (4.18), 240 (4.17). IR (KBr): 1610*m*, 1560*w*, 1540*w*, 1575*s*, 1510*s*, 1460*m*, 1440*m*, 1420*m*, 1390*w*, 1330*w*, 1300*w*, 1280*w*, 1260*s*, 1240*s*, 1210*m*, 1180*m*, 1175*s*, 1110*w*, 1070*w*, 1030*s*, 960*m*, 860*w*, 840*w*, 830*m*, 780*m*, 740*w*, 720*w*, 710*w*. ^{1}H-NMR ($CDCl_3$): 7.89 (*d*, *J* = 4.3, H–C(2)); 7.86 (*d*, *J* = 15.8, CH=C*H*–C(1)); 7.47 (*d*, *J* = 8.6, 2 arom. H); 6.93 (*d*, *J* = 8.6, 2 arom. H); 7.35 (*d*, *J* = 4.3, H–C(3)); 6.94 (*s*, H–C(5,7)); 6.86 (*d*, *J* = 15.8, C*H*=CH–C(1)); 3.84 (*s*, MeO); 3.08 (*s*,

Me–C(8)); 2.84 (*s*, Me–C(4)); 2.57 (*s*, Me–C(6)). ^{13}C-NMR ($CDCl_3$): 158.61 (*s*); 147.31 (*s*); 146.36 (*s*); 145.43 (*s*); 138.46 (*s*); 132.88 (*d*); 132.17 (*s*); 131.68 (*s*); 129.73 (*s*); 129.05 (*d*); 127.31 (*d*); 127.09 (*d*, 2 arom. CH); 126.73 (*d*); 125.55 (*d*); 116.40 (*d*); 114.11 (*d*, 2 arom. CH); 55.32 (*q*, MeO); 29.19 (*q*); 28.33 (*q*); 25.41 (*q*). CI-MS: 303 (25), 302 (100, $[M + 1]^+$), 288 (13), 287 (54), 272 (13). Anal. calc. for $C_{22}H_{22}O$ (302.42): C 87.38, H 7.33; found: C 87.53, H 7.17.

1-(4-Methoxybenzyl)-4,6,8-trimethylazulene (**8**): M.p. 115.5–116.5° (hexane). R_f (hexane/Et_2O 9:1) 0.34. IR (KBr): 1610*m*, 1570*s*, 1550*m*, 1530*s*, 1510*s*, 1440*s*, 1420*m*, 1370*w*, 1350*w*, 1330*w*, 1300*w*, 1260*m*, 1240*s*, 1180*s*, 1140*w*, 1100*m*, 1070*w*, 1030*s*, 990*w*, 940*w*, 910*w*, 900*w*, 880*w*, 820*w*, 840*m*, 820*w*, 805*s*, 790*m*, 760*m*, 740*w*, 720*w*, 700*w*, 640*w*. ^{1}H-NMR ($CDCl_3$): 7.42 (*d*, $J = 4.0$, H–C(2)); 7.33 (*d*, $J = 4.0$, H–C(3)); 6.97 (*dd*, $J = 8.7$, 2.1, 2 arom. H); 6.95 (*s*, H–C(7)); 6.89 (*s*, H–C(5)); 6.80 (*dd*, $J = 8.7$, 2.1, 2 arom. H); 4.58 (*s*, CH_2); 3.78 (*s*, MeO); 2.89 (*s*, Me–C(8)); 2.86 (*s*, Me–C(4)); 2.57 (*s*, Me–C(6)). CI-MS: 292 (9), 291 (100, $[M + 1]^+$). Anal. calc. for $C_{21}H_{22}O$ (290.41): C 86.85, H 7.63; found: C 86.63, H 7.42.

*1-(4-Methoxybenzyl)-3-[(*E*)-2-(4-methoxyphenyl)ethenyl]-4,6,8-trimethylazulene* (**9**): M.p. 139.2–140.4° (hexane). R_f (hexane/Et_2O 9:1) 0.11. IR (KBr): 1605*m*, 1575*m*, 1550*w*, 1505*s*, 1460*m*, 1450*m*, 1440*m*, 1390*w*, 1360*w*, 1300*w*, 1270*s*, 1240*s*, 1210*w*, 1170*s*, 1140*w*, 1100*w*, 1030*s*, 970*w*, 950*w*, 845*w*, 830*m*, 820*m*, 800*m*, 770*w*, 760*w*. ^{1}H-NMR ($CDCl_3$): 7.79 (*d*, $J = 15.9$, CH=C*H*–C(3)); 7.65 (*s*, H–C(2)); 7.44 (*d*, $J = 8.7$, 2 arom. H); 6.99 (*d*, $J = 8.7$, 2 arom. H); 6.92 (*d*, $J = 15.9$, C*H*=CH–C(3)); 6.91 (*d*, $J = 8.7$, 2 arom. H); 6.82 (*d*, $J = 8.7$, 2 arom. H); 6.79 (*s*, H–C(7)); 6.73 (*s*, H–C(5)); 4.54 (*s*, CH_2); 3.84 (*s*, MeO); 3.79 (*s*, MeO); 3.03 (*s*, Me–C(8)); 2.82 (*s*, Me–C(4)); 2.47 (*s*, Me–C(6)). ^{1}H-NOE ($CDCl_3$, 400 MHz): 2.47 (Me–C(6))→6.73 (*s*, H–C(5)); 6.79 (*s*, H–C(7)); 2.82 (Me–C(4))→6.73 (*s*, H–C(5)); 4.54 (*s*, CH_2); 3.03 (Me–C(8))→6.79 (*s*, H–C(7)); 7.79 (*s*, CH=C*H*–C(3)). CI-MS: 427 (16), 426 (15), 425 (53), 424 (35), 423 (100, $[M + 1]^+$), 422 (10, $M^{+\cdot}$). Anal. calc. for $C_{30}H_{30}O_2$ (422.57): C 85.27, H 7.15; found: C 85.21, H 7.30.

2.1. *Control Experiment.* The phosphonium salt **4b** was formed by boiling Ph_3P (0.80 g, 3.3 mmol) and 4-methoxybenzyl chloride (0.50 g, 3.3 mmol) in toluene (10 ml) for 2 h. After cooling, *4,6,8-trimethylazulene* (**10**; 0.34 g, 2.0 mmol) was added under stirring and stirring continued for 1 h at r.t. Workup and CC (silica gel; hexane) yielded, after a forerun of unreacted **10** (0.060 g, 20%), **8** (0.120 g, 20%; violet crystals), and **11** (0.378 g, 46%; blue needles).

1,3-Bis(4-methoxybenzyl)-4,6,8-trimethylazulene (**11**): M.p. 121.4–122.1° (hexane). R_f (hexane/Et_2O 9:1) 0.15. IR (KBr): 2960*m*, 2840*w*, 1610*m*, 1580*s*, 1560*w*, 1530*w*, 1510*s*, 1460*s*, 1440*s*, 1410*m*, 1390*w*, 1370*w*, 1330*w*, 1300*m*, 1270*m*, 1240*s*, 1190*w*, 1170*s*, 1100*m*, 1040*s*, 1010*w*, 900*w*, 890*w*, 840*m*, 800*s*, 770*w*, 750*w*, 730*w*, 690*w*, 650*w*. ^{1}H-NMR ($CDCl_3$): 7.22 (*s*, H–C(2)); 6.96 (*d*, $J = 8.7$, 4 arom. H); 6.81 (*d*, $J = 8.7$, 4 arom. H); 6.76 (*s*, H–C(5,7)); 4.54 (*s*, 2 CH_2); 3.78 (*s*, 2 MeO); 2.86 (*s*, 2 Me); 2.48 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 157.54 (*s*); 146.30 (*s*); 145.25 (*s*); 143.49 (*d*); 135.33 (*s*); 134.10 (*d*); 129.21 (*d*); 127.63 (*d*); 113.72 (*d*); 55.21 (*q*, MeO); 37.34 (*t*); 28.00 (*q*); 27.94 (*q*). CI-MS: 414 (5), 413 (18), 412 (31), 411 (100, $[M + 1]^+$). Anal. calc. for $C_{29}H_{30}O_2$ (410.56): C 84.84, H 7.36; found: C 85.05, H 7.56.

3. *1-[(*E*)-2-(4-Chlorophenyl)ethenyl]-4,6,8-trimethylazulene* ((*E*)-**5c**). The phosphonium salt **4b** was formed from Ph_3P (3.30 g, 20.2 mmol) and 4-chlorobenzyl chloride (5.3 g, 20.2 mmol) in toluene (80 ml) as described in *2*. Then, **1** (1.0 g, 5.0 mmol) and EtONa (1.03 g, 15.1 mmol)/EtOH (20 ml) were added and reacted as described in *1*. Usual workup and CC (silica gel; hexane) yielded 0.92 g (3.0 mmol, 60%) of (*E*)-**5c** as blue crystals, 0.30 g (1.5 mmol, 30%) of recovered **1** as red crystals, and 0.069 g (0.35 mmol, 7%) of *4,6,8-trimethylazulene-2-carbaldehyde* (**12**) as blue crystals.

*Data of (*E*)-***5c***: M.p. 172.6–173.4° (hexane). R_f (hexane) 0.32. UV (hexane): λ_{max} 402 (4.33), 326 (4.52), 267 (4.29), 262 (4.27), 233 (4.25); λ_{min} 374 (4.20), 281 (4.05), 244 (4.20). IR (KBr): 1600*m*, 1570*s*, 1520*m*, 1490*s*, 1450*m*, 1440*m*, 1430*m*, 1410*m*, 1340*m*, 1300*w*, 1250*w*, 1200*w*, 1180*w*, 1090*m*, 1080*w*, 1030*w*, 1010*w*, 960*m*, 860*m*, 840*w*, 810*s*, 760*w*, 740*w*, 720*w*, 690*w*. ^{1}H-NMR ($CDCl_3$): 7.89 (*d*, $J = 15.8$, CH=C*H*–C(1)); 7.82 (*d*, $J = 3.9$, H–C(2)); 7.38–7.19 (*m*, H–C(3), 4 arom. H); 6.90 (*s*, H–C(5,7)); 6.77 (*d*, $J = 15.8$, C*H*=CH–C(1)); 3.01 (*s*, Me–C(8)); 2.77 (*s*, Me–C(4)); 2.50 (*s*, Me–C(6)). ^{13}C-NMR ($CDCl_3$): 147.23 (*s*); 146.59 (*s*); 145.68 (*s*); 138.81 (*s*); 137.28 (*s*); 132.89 (*d*); 132.55 (*s*); 131.92 (*s*); 129.49 (*d*); 128.87 (*s*); 128.70 (*d*, 2 arom. C); 127.93 (*d*); 127.77 (*d*); 127.05 (*d*, 2 arom. C); 125.56 (*d*); 116.59 (*d*); 29.26 (*q*); 28.34 (*q*); 25.46 (*q*). EI-MS: 308 (36), 307 (25), 306 (100, $M^{+\cdot}$), 293 (17), 292 (13), 291 (49), 276 (10). Anal. calc. for $C_{21}H_{19}Cl$ (306.84): C 82.20, H 6.24; found: C 82.34, H 6.51.

4. *7-Isopropyl-1,4-dimethyl-3-[(*E*)-2-phenylethenyl]azulene* ((*E*)-**6**; *cf.* [3]). *5-Isopropyl-3,8-dimethylazulene-1-carbaldehyde* (= *guaiazulene-3-carbaldehyde*, **2**; 1.18 g, 5.2 mmol) [27] [28] and **4a** (4.04 g, 10.4 mmol) were reacted in the presence of EtONa (1.06 g, 15.6 mmol)/EtOH (20 ml) in toluene (30 ml) as described for **5a** (see *1*). Usual workup yielded 1.41 g (90%) of a 55:45 mixture of (*E*)- and (*Z*)-**6** as a green oil. Boiling of the mixture in toluene (10 ml) in the presence of catalytic amounts of I_2 for 24 h yielded quantitatively (*E*)-**6**. Crystallization from

hexane gave pure (*E*)-**6** (1.25 g, 80%) as green crystals. M.p. 87.0–88.0° (hexane); 87.0–88.0° (petroleum ether) [3]. R_f (hexane) 0.32. UV (hexane): λ_{max} 410 (4.48), 327 (4.58), 268 (4.45), 227 (4.29); λ_{min} 369 (4.23), 284 (4.30), 242 (4.22). IR (KBr): 2900*s*, 1595*s*, 1560*w*, 1540*s*, 1520*m*, 1490*w*, 1460*s*, 1450*s*, 1420*s*, 1380*m*, 1360*s*, 1310*w*, 1290*w*, 1260*w*, 1210*w*, 1180*m*, 1170*w*, 1120*w*, 1100*w*, 960*s*, 900*m*, 870*w*, 850*w*, 840*w*, 800*m*, 750*s*, 730*m*, 690*s*, 640*m*. ^{1}H-NMR ($CDCl_3$): 8.06 (*d*, *J* = 15.9, PhCH=C*H*); 8.03 (*s*, H–C(8)); 7.94 (*s*, H–C(2)); 7.54 (*d*, *J* = 7.3, 2 arom. H); 7.38 (*t*, *J* = 7.8, 2 arom. H); 7.27 (*m*, 1 arom. H); 7.25 (*d*, *J* = 9.60, H–C(5)); 6.95 (*d*, *J* = 15.9, PhC*H*=CH); 6.88 (*d*, *J* = 9.6, H–C(6)); 3.07 (*s*, Me–C(4)); 3.03 (*sept.*, *J* = 6.9, Me_2CH–C(7)); 2.66 (*s*, Me–C(1)); 1.37 (*d*, *J* = 6.9, *Me*$_2$CH–C(7)). ^{13}C-NMR ($CDCl_3$): 145.91 (*s*); 140.96 (*s*); 140.46 (*s*); 138.85 (*s*); 135.76 (*d*); 134.86 (*d*); 133.64 (*d*); 132.65 (*s*); 128.62 (*d*, 2 arom. C); 127.38 (*d*); 126.63 (*d*); 126.47 (*d*); 126.39 (*s*); 126.14 (*d*); 126.09 (*s*); 125.87 (*d*, 2 arom. C); 37.67 (*d*, Me_2CH); 28.45 (*q*); 24.42 (*q*, *Me*$_2$CH); 12.97 (*q*). EI-MS: 301 (19), 300 (100, $M^{+\cdot}$), 286 (6), 285 (34). Anal. calc. for $C_{23}H_{24}$: C 91.95, H 8.05; found: C 91.65, H 7.77.

5. *7-Isopropyl-4-methyl-1-[(*E*)-2-phenylethenyl]azulene* ((*E*)-**7**). Lactaroviolin (1.0 g, 4.71 mmol) was hydrogenated catalytically 10% Pd/C, 0.12 g, 3.5 bar) in dioxane (60 ml) at r.t. After stirring for 4 h, the mixture was filtered through *Celite* and the dioxane evaporated to yield 1.0 g (quant.) of the pure *7-isopropyl-4-methylazulene-1-carbaldehyde* (**3**) as red-violet crystals [17].

The *Wittig* reaction of **3** (0.500 g, 2.35 mmol) and **4a** was performed as described for **5a** (see *1*). Chromatographic workup (CC on silica gel; hexane) yielded 0.606 g (90%) of (*E*)/(*Z*)-**7** 60:40 as a green oil. Thermal isomerization (see *1*) led to pure (*E*)-**7**. R_f (hexane) 0.28. UV/VIS (hexane): λ_{max} 640 (2.64), 423 (3.95), 400 (4.19), 380 (4.19), 355 (4.27), 342 (4.30), 316 (4.43), 306 (4.36), 255 (4.38); λ_{min} 475 (1.71), 390 (4.16), 375 (4.18), 332 (4.29), 275 (4.09), 224 (4.13). IR ($CHCl_3$): 3005*m*, 2960*s*, 2930*m*, 2870*m*, 1790*w*, 1620*m*, 1600*s*, 1560*s*, 1520*m*, 1490*m*, 1460*m*, 1420*s*, 1390*s*, 1300*w*, 1260*s*, 1090*w*, 1030*m*, 950*s*, 820*m*, 690*s*, 650*w*. ^{1}H-NMR ($CDCl_3$): 8.52 (*d*, *J* = 1.8, H–C(8)); 8.20 (*d*, *J* = 4.3, H–C(2)); 7.70 (*d*, *J* = 16.0, Ph–CH=C*H*); 7.65 (*d*, J_{ortho} = 7.6, H–C(2′,6′)); 7.48 (*dd*, *J* = 10.7, *J* = 1.8, H–C(6)); 7.42 (*t*-like, J_{meta} = 7.6, H–C(3′,5′)); 7.40 (*d*, *J* = 4.7, H–C(3)); 7.27 (*t*-like, *J* = 7.3, H–C(4′)); 7.20 (*d*, *J* = 16.0, PhC*H*=CH); 7.11 (*d*, *J* = 10.8, H–C(5)); 3.18 (*sept.*, *J* = 6.9, Me_2CH); 2.89 (*s*, Me–C(4)); 1.44 (*d*, *J* = 6.9, *Me*$_2$CH). EI-MS: 287 (20), 286 (100, $M^{+\cdot}$), 271 (22, $[M - Me]^+$), 243 (6, $[M - Me_2CH]^+$), 228 (6, $[M - Me - Me_2CH]^+$), 178 (11), 165 (20), 152 (12), 143 (12), 128 (14), 122 (16), 115 (15), 114 (15), 107 (15), 105 (12), 91 (34), 77 (11).

(Z)-**7**: ^{1}H-NMR ($CDCl_3$; recognizable signals in the 3:2 mixture of (*E*)- and (*Z*)-**7**): 8.34 (*d*, *J* = 1.9, H–C(8)); 7.17 (*d*, *J* = 12.0, PhCH=C*H*); 6.65 (*d*, *J* = 12.1, PhC*H*=CH); 3.03 (*sept.*, *J* = 6.9, Me_2CH); 2.85 (*s*, Me–C(4)); 1.30 (*d*, *J* = 6.9, *Me*$_2$CH).

6. *4,6,8-Trimethyl-2-[(*E*)-2-phenylethenyl]azulene* ((*E*)-**19a**). 6.1. *Methyl-4,6,8-Trimethylazulene-2-carboxylate* (**15**). *Sodium (methoxycarbonyl)cyclopentadienide* (**13**; 6.0 g, 41.0 mmol; prepared according to [19]) was dissolved in THF (40 ml). After addition of *2,4,6-trimethylpyrylium tetrafluoroborate* (**14**; 6.0 g, 29.0 mmol) [20] under stirring, the temp. went up and the color changed spontaneously to red. Stirring for another h at r.t., evaporation of the THF under low pressure, and usual workup provided 2.32 g (10.0 mmol, 35%) of **15** as violet crystals. M.p. 169.0–170.0° (hexane). R_f (hexane/Et_2O 7:3) 0.36. IR (KBr): 1700*s*, 1630*w*, 1580*m*, 1540*w*, 1510*w*, 1485*w*, 1430*s*, 1330*s*, 1270*w*, 1230*s*, 1215*s*, 1150*m*, 1130*s*, 1030*w*, 1000*m*, 910*w*, 850*s*, 830*w*, 790*w*, 760*s*. ^{1}H-NMR ($CDCl_3$): 7.78 (*s*, H–C(1,3)); 7.09 (*s*, H–C(5,7)); 3.97 (*s*, MeO); 2.89 (*s*, Me–C(4,8)); 2.64 (*s*, Me–C(6)). ^{13}C-NMR ($CDCl_3$): 150.12 (*s*, 2 C); 150.06 (*s*, 2 C); 135.86 (*s*, 2 C); 133.39 (*s*, 1 C); 128.09 (*d*, 2 CH); 117.16 (*d*, 2 CH); 51.66 (*q*, MeO); 29.02 (*q*, 1 Me); 25.13 (*q*, 2 Me). CI-MS: 230 (15), 229 (100, $[M + 1]^+$), 228 (8). Anal. calc. for $C_{15}H_{16}O_2$ (228.29): C 78.92, H 7.06; found: C 78.80, H 7.21.

6.2. *4,6,8-Trimethylazulene-2-methanol* (**16**; *cf.* [29]). Under N_2, $LiAlH_4$ (0.832 g, 21.9 mmol) was dissolved in Et_2O (50 ml) and **15** (5 g, 21.9 mmol) added under stirring. After the color had changed from red-violet to pure blue, stirring was continued for 30 min at 0°. The reaction was interrupted by adding 10 ml of MeOH and 100 ml of H_2O. Extraction with Et_2O (3 × 30 ml), drying, and removal of the solvent (RE) yielded 4.38 g (21.9 mmol, 100%) of **16** as a blue solid. M.p. 124.4–125.5° (AcOEt/hexane; 117.6–118.6° (AcOEt/hexane) [29]). R_f (hexane/Et_2O 7:3): 0.08. Anal. calc. for $C_{14}H_{16}O$ (200.28): C 83.96, H 8.05; found: C 83.74, H 7.84.

6.3. *4,6,8-Trimethylazulene-2-carbaldehyde* (**12**; *cf.* [18]). Compound **16** (5.7 g, 28.5 mmol) and MnO_2 (*purum*, *Merck*; 12.4 g, 142.3 mmol) were stirred in CH_2Cl_2 (50 ml) for 24 h at r.t. CC (silica gel; hexane/Et_2O 7:3) yielded **12** (3.8 g, 67%) as blue crystals[9]. M.p. 101.5–103.0 (hexane). R_f (hexane/Et_2O 7:3) 0.28[9]. UV (hexane): λ_{max} 374 (2.99), 348 (2.81), 306 (3.81), 296 (3.79), 253 (3.51); λ_{min} 362 (2.75), 325 (2.61), 300 (3.74), 267 (3.09). IR (KBr): 1670*s*, 1580*m*, 1540*m*, 1500*w*, 1480*w*, 1440*w* (br.), 1370*w*, 1360*w*, 1310*w*, 1220*w*, 1170*m*, 1080*m*, 980*w*, 850*w*, 800*w*,

[9]) The isomeric 1-carbaldehyde **1** showed under the same conditions R_f of 0.12.

770*w*, 710*w*, 600*w*. ^{1}H-NMR ($CDCl_3$): 10.36 (*s*, CHO); 7.75 (*s*, H–C(1,3)); 7.11 (*s*, H–C(5,7)); 2.90 (*s*, Me–C(4,8)); 2.65 (*s*, Me–C(6)). ^{13}C-NMR ($CDCl_3$): 190.34 (*d*, CHO); 151.53 (*s*, 2 C); 151.40 (*s*, 1 C); 140.32 (*s*, 1 C); 136.41 (*s*, 2 C); 128.43 (*d*, 2 CH); 116.75 (*d*, 2 CH); 29.08 (*q*, 1 Me); 25.11 (*q*, 2 Me). CI-MS: 200 (12), 199 (100, $[M+1]^+$). Anal. calc. for $C_{14}H_{14}O$ (198.27): C 84.81, H 7.12; found: C 84.99, H 7.35.

6.4. Wittig *Reaction*. Phosphonium salt **4a** (1.33 g, 3.42 mmol) and **12** (3.40 g, 1.71 mmol) were reacted in the presence of EtONa (0.35 g, 5.13 mmol)/EtOH (5 ml) in toluene (15 ml) as described in *1*. After the usual workup, a 4:1 mixture of (*E*)- and (*Z*)-**19a** (0.372, 80%) was isolated as a dark violet oil. The usual thermal isomerization in the presence of I_2 gave the pure (*E*)-isomer in dark violet needles (0.363 g, 78%).

Data of (E)-**19a**: M.p. 126.3° (hexane). R_f (hexane) 0.16 UV (hexane): λ_{max} 426 (4.46), 403 (4.57), 384 (sh, 4.36), 326 (4.97), 320 (4.94), 255 (4.34), 232 (4.30); λ_{min} 416 (4.39), 362 (4.09), 274 (3.90), 243 (4.23). IR (KBr): 3020*m*, 2980*m*, 2900*w*, 1750*s*, 1550*s*, 1540*m*, 1500*s*, 1470*m*, 1440*m*, 1370*w*, 1330*s*, 1300*w*, 1280*w*, 1210*m*, 1180*w*, 1140*w*, 1090*w*, 1070*w*, 1030*w*, 980*w*, 950*s*, 910*w*, 840*s*, 800*s*, 750*s*, 690*s*, 630*m*. ^{1}H-NMR ($CDCl_3$): 7.60 (*d* with f.s., J_{ortho} = 7.3, H–C(2′,6′)); 7.46 (*d*, J = 16.6, PhCH=C*H*); 7.44 (*s*, H–C(1,3)); 7.40 (*t*, J_{ortho} = 7.5, H–C(3′,5′)); 7.40 (*d*, J = 16.2, PhC*H*=CH); 7.28 (*tt*, J_{ortho} = 7.3, J_{meta} = 1.3, H–C(4′)); 7.04 (*s*, H–C(5,7)); 2.88 (*s*, Me–C(4,8)); 2.62 (*s*, Me–C(6)). ^{1}H-NMR (C_6D_6): 7.65 (*s*, H–C(1,3)); 7.65–7.60 (*m*, 4 H); 7.27 (*m*, 3 H); 6.90 (*s*, H–C(5), H–C(7)); 2.77 (*s*, Me–C(4,8)); 2.39 (*s*, Me–C(6)). ^{13}C-NMR ($CDCl_3$): 145.03 (*s*); 144.40 (*s*); 143.47 (*s*); 137.80 (*s*); 137.23 (*s*); 130.90 (*d*); 128.66 (*d*, 2 CH); 127.98 (*d*, 2 CH); 127.51 (*d*); 126.54 (*d*, 2 CH); 125.15 (*d*); 113.85 (*d*); 28.65 (*q*); 25.00 (*q*). CI-MS: 274 (22), 273 (100, $[M+1]^+$). Anal. calc. for $C_{21}H_{20}$ (272.39): C 92.60, H 7.40; found: C 92.32, H 7.44.

Data of (Z)-**19**: ^{1}H-NMR ($CDCl_3$; taken from the 4:1 mixture with (*E*)-**19a**): 7.50–7.25 (*m*, 5 arom. H); 7.17 (*s*, H–C(1,3)); 6.97 (*s*, H–C(5,7)); 6.90 (*d*, J = 12.1, PhCH=C*H*); 6.75 (*d*, J = 12.1, PhC*H*=CH); 2.69 (*s*, Me–C(4,8)); 2.58 (*s*, Me–C(6)).

6.5. *Attempted* Swern *Oxidation of* **16**. Oxalyl chloride (0.04 ml, 44 mmol) was dissolved in CH_2Cl_2 (1 ml) and the soln. cooled to −50° to −60°. At this temp. DMSO (0.07 ml, 0.88 mmol) was added, followed after 1 min by a soln. of **16** (0.080 g, 0.40 mmol) in CH_2Cl_2 (1 ml). Stirring at −50° to −60° was continued for 15 min, and then Et_3N (0.28 ml, 2.0 mmol) was added. The temp. was allowed to rise to r.t. H_2O (20 ml) was added and the reaction mixture extracted with CH_2Cl_2. After drying and evaporation (RE), the residue was subjected to CC (silica gel; hexane/Et_2O 4:1). Two products were eluted, namely **17** (0.091 g, 85%) as green needles followed by **18** (0.005 g, 5%) as blue needles.

1,3-Dichloro-4,6,8-trimethylazulene-2-carbaldehyde (**17**): M.p. 197.0–198.0° (hexane). R_f (hexane/Et_2O 7:3) 0.34. IR (KBr): 1680*s*, 1670*s*, 1580*s*, 1500*m*, 1480*m*, 1460*s*, 1440*m*, 1390*w*, 1370*m*, 1170*w*, 1060*s*, 1020*w*, 910*w*, 850*w*. ^{1}H-NMR ($CDCl_3$): 10.62 (*s*, CHO); 6.85 (*s*, H–C(5,7)); 3.15 (*s*, Me–C(4,8)); 2.52 (*s*, Me–C(6)). CI-MS: 271 (10), 270 (9), 269 (65), 268 (15), 267 (100, M^+), 235 (18), 234 (7), 233 (52, $[M-Cl]^+$), 199 (8, $[M-2Cl]^+$). Anal. calc. for $C_{14}H_{12}Cl_2O$ (267.16): C 62.94, H 4.53; found: C 62.69, H 4.79.

1,3-Dichloro-4,6,8-trimethylazulene-2-methanol (**18**): M.p. 149.0–151.0° (Et_2O/hexane). R_f (hexane/Et_2O 7:3) 0.19. IR (KBr): 1580*s*, 1550*w*, 1510*m*, 1480*m*, 1440*m*, 1370*m*, 1240*w*, 1060*s*, 1020*w*, 1000*m*, 990*m*, 780*w*. ^{1}H-NMR ($CDCl_3$): 6.85 (*s*, H–C(5,7)); 4.99 (*s*, CH_2OH); 3.14 (*s*, Me–C(4,8)); 2.52 (*s*, Me–C(6)). CI-MS: 270 (20, $[M+1]^+$), 268 (100), 235 (13).

7. *2-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-4,6,8-trimethylazulene* ((*E*)-**19b**). The phosphonium salt **4b** was formed from Ph_3P (2.4 g, 10 mmol) and 4-methoxybenzyl chloride (1.57, 10 mmol) in toluene (50 ml) as usual. The *Wittig* reaction with **12** (1.0 g, 5.0 mmol) was performed in the usual manner (see *1*). CC (silica gel, hexane/Et_2O 7:3) of the worked up reaction mixture gave two products: (*E*)-**19b** (0.390 g, 26%) as dark-violet oil, followed by **20** (0.690 g, 33%) as green crystals.

Data of (E)-**19b**: M.p. 107.5–108.7° (hexane). R_f (hexane/Et_2O 7:3) 0.55. UV (hexane): λ_{max} 435 (4.30), 411 (4.36), 389 (sh, 4.13), 334 (4.65), 321 (4.60), 263 (4.01), 228 (4.38); λ_{min} 424 (4.18), 365 (3.82), 272 (3.87), 248 (3.81). IR (KBr): 2960*w*, 2940*w*, 1600*m*, 1580*w*, 1510*s*, 1460*w*, 1450*w*, 1440*m*, 1330*w*, 1300*m*, 1250*s*, 1180*s*, 1140*w*, 1110*w*, 1090*w*, 1030*s*, 960*m*, 940*w*, 850*w*, 830*s*, 810*w*, 790*w*, 720*w*, 630*w*. EI-MS: 303 (38), 302 (100, $M^{+\cdot}$), 301 (35), 288 (8), 287 (12), 286 (14), 272 (21), 244 (9), 243 (9), 229 (13), 228 (12), 227 (10), 121 (17).

*1-(4-Methoxybenzyl)-2-[(*E*)-2-(4-methoxyphenyl)ethenyl]-4,6,8-trimethylazulene* (**20**): M.p. 110.6–111.2° (hexane). R_f (hexane/Et_2O 7:3) 0.37. IR (KBr): 3000*w*, 2940*w*, 2900*w*, 2820*w*, 1700*w*, 1600*w*, 1590*m*, 1580*w*, 1550*w*, 1530*w*, 1510*s*, 1470*m*, 1450*m*, 1440*m*, 1370*w*, 1330*w*, 1320*w*, 1300*w*, 1280*m*, 1260*m*, 1240 (sh), 1210*m*, 1180*m*, 1110*w*, 1030*m*, 980*w*, 960*w*, 900*w*, 870*w*, 830*m*, 800*m*, 750*w*, 640*w*. ^{1}H-NMR ($CDCl_3$): 7.50 (*d*, J = 8.8, 2 arom. H); 7.35 (*s*, H–C(3)); 7.25 (*d*, J = 8.7, 2 arom. H); 7.23 (*d*, J = 16.2, CH=C*H*–C(2)); 6.81 (*d*, J = 15.9, C*H*=CH–C(2)); 6.96 (*s*, H–C(5,7)); 6.83 (*d*, J = 8.8, 2 arom. H); 6.79 (*d*, J = 8.7, 2 arom. H); 4.30 (*s*, CH_2); 3.76 (*s*, MeO); 3.72 (*s*, MeO); 2.70 (*s*, Me–C(4,8)); 2.54 (*s*, Me–C(6)). ^{1}H-NMR (C_6D_6): 7.78 (*s*, H–C(3)); 7.74–7.70 (*m*,

5 H); 7.50–7.43 (*m*, 3 H); 6.94–6.87 (*m*, 5 H); 4.62 (*s*, CH_2); 3.42 (*s*, MeO); 3.37 (*s*, MeO); 2.71 (*s*, Me–C(4,8)); 2.36 (*s*, Me–C(6)). ^{13}C-NMR ($CDCl_3$): 157.94 (*s*); 156.83 (*s*); 144.02 (*s*); 143.49 (*s*); 141.81 (*s*); 138.83 (*s*); 135.66 (*s*); 134.82 (*s*); 130.79 (*s*); 128.24 (*d*); 126.73 (*d*); 125.17 (*d*); 124.01 (*d*); 115.36 (*d*); 113.09 (*d*); 113.00 (*d*); 122.77 (*d*); 54.23 (*q*); 54.18 (*q*); 35.38 (*t*); 27.64 (*q*); 24.14 (*q*); 23.91 (*q*). CI-MS: 425 (16), 424 (32), 423 (36, $[M + 1]^+$). Anal. calc. for $C_{30}H_{30}O_2$ (422.57): C 85.27, H 7.15; found: C 85.13, H 7.02.

8. *General Procedure of the 'Anil Synthesis' with 7-Isopropyl-1,4-dimethylazulene* (= *Guaiazulene*, **21**). 8.1. Schiff's *Bases* **22**. They were prepared in the usual way. The corresponding benzaldehyde (0.1 mol) and aniline (0.1 mol) were stirred at r.t. during 20 min. Then, EtOH (50 ml) was added and the mixture cooled in an ice-bath. The resulting benzanils **22a–e** were filtered off, crystallized from EtOH, and dried under high vacuum.

8.2. *Anil Syntheses*. They were performed according to the following procedure: **21** (1.0 g, 5.0 mmol), the benzanil **22** (5.0 mmol), and finely powdered KOH (1.4 g; 25.0 mmol) were stirred at r.t. in 20 ml of DMF. The mixture was warmed up to 60° during 30 min. After cooling to r.t., the mixture was added to 100 ml of H_2O and extracted with Et_2O (3 × 50 ml). The Et_2O extracts were dried ($MgSO_4$). Evaporation of the solvent resulted in a blue oil which was subjected to CC (silica gel; hexane).

8.2.1. *7-Isopropyl-1-methyl-4-[(E)-2-phenylethenyl]azulene* ((*E*)-**23a**). The following fractions were eluted: 1) (*E*)-**23a** (0.458 g, 32%) as dark green crystals; 2) **25a** (0.121 g, 5%) as dark blue crystals, and 3) **24a** (0.057 g, 2%) as blue powder.

Data of (E)-**23a**: M.p. 74.0–75.0° (hexane). R_f (hexane/Et_2O 9:1) 0.48. UV (hexane): λ_{max} 396 (sh, 3.66), 364 (sh, 4.28), 344 (sh, 4.44), 317 (4.65), 283 (4.68), 260 (sh, 4.44); λ_{min} 306 (4.58), 230 (4.24). IR (KBr): 3060*w*, 3030*w*, 2960*s*, 2920*m*, 2860*m*, 1630*w*, 1600*m*, 1580*w*, 1550*s*, 1520*s*, 1490*m*, 1460*s*, 1450*s*, 1430*s*, 1420*s*, 1390*s*, 1370*m*, 1360*m*, 1330*w*, 1300*w*, 1290*w*, 1220*w*, 1200*w*, 1190*w*, 1180*w*, 1070*w*, 1060*m*, 1020*s*, 950*s*, 930*s*, 880*w*, 865*w*, 840*w*, 810*m*, 780*s*, 750*s*, 720*m*, 690*s*, 650*w*, 620*m*. ^{1}H-NMR ($CDCl_3$): 8.24 (*d*, *J* = 1.4, H–C(8)); 8.06 (*d*, *J* = 16.1, PhCH=C*H*); 7.72 (*d*, *J* = 3.9, H–C(2)); 7.68 (*m*, 2 arom. H); 7,54 (*m*, H–C(6)); 7.52 (*d*, *J* = 3.9, H–C(3)); 7.45 (*m*, H–C(5)); 7.45 (*m*, 2 arom. H); 7.43 (*d*, *J* = 16.1, PhC*H*=CH); 7.36 (*m*, 1 arom. H); 3.15 (*sept.*, *J* = 6.9, Me_2CH–C(7)); 2.73 (*s*, Me–C(1)); 1.43 (*d*, *J* = 6.9, *Me*$_2$CH–C(7)). ^{1}H-NOE ($CDCl_3$, 400 MHz): 1.42 (Me_2CH)→8.24 (*s*, H–C(8)), 7.54 (*s*, H–C(6)), 3.15 (*s*, Me_2CH); 2.73 (Me–C(1))→8.24 (*s*, H–C(8)), 7.72 (*s*, H–C(2)); 3.15 (MeC*H*)→8.24 (*s*, H–C(8)), 7.54 (*s*, H–C(6)), 1.42 (*Me*$_2$CH); 8.06 (PhCH=C*H*)→7.68 (*s*, 2 arom. H), 7.52 (*s*, H–C(3)), 7.43 (*m*, PHC*H*=CH). ^{13}C-NMR ($CDCl_3$): 141.8 (*s*); 140.1 (*s*); 137.3 (*s*); 136.8 (*d*); 136.4 (*s*); 134.9 (*d*); 133.9 (*d*); 133.1 (*d*); 129.6 (*d*); 128.8 (*d*, 2 arom. C); 128.3 (*d*); 127.0 (*d*, 2 arom. C); 125.8 (*s*); 120.3 (*d*); 111.9 (*d*); 38.3 (*d*, Me_2CH); 24.7 (*q*, *Me*$_2$CH); 13.0 (*q*). EI-MS: 288 (5), 287 (23), 286 (100, $M^{+\cdot}$), 285 (11), 272 (12), 271 (58, $[M - CH_3]^+$), 256 (6), 255 (8), 243 (25, $[M - Me_2CH]^+$), 242 (6), 241 (11), 239 (8), 229 (5), 228 (7). Anal. calc. for $C_{22}H_{22}$ (286.42): C 92.26, H 7.74; found: C 92.40, H 7.65.

1,3-Bis(7-isopropyl-1-methylazulen-4-yl)-2-phenylpropane (**24a**): M.p. 149.0–150.0° (hexane). R_f (hexane/Et_2O 9:1) 0.39. UV (hexane): λ_{max} 370 (4.03), 352 (4.14), 305 (sh, 4.47), 290 (sh, 5.05), 285 (5.07), 249 (4.93); λ_{min} 361 (4.01), 339 (3.99), 263 (4.70), 226 (4.55). IR (KBr): 3060*w*, 3020*m*, 2960*s*, 2940*s*, 2860*s*, 1600*w*, 1550*s*, 1530*s*, 1490*s*, 1470*s*, 1460*s*, 1430*m*, 1390*s*, 1370*m*, 1360*m*, 1330*w*, 1310*w*, 1290*w*, 1220*w*, 1210*w*, 1180*w*, 1170*w*, 1150*w*, 1080*w*, 1060*w*, 1030*m*, 960*w*, 920*m*, 900*w*, 880*w*, 860*w*, 820*m*, 780*s*, 750*m*, 730*w*, 720*w*, 700*w*, 700*s*, 650*w*, 630*m*. ^{1}H-NMR ($CDCl_3$): 8.24 (*d*, *J* = 1.9, H–C(8,8′)); 7.60 (*d*, *J* = 3.8, H–C(2,2′)); 7.34 (*dd*, *J* = 10.8, *J* = 1.9, H–C(6,6′)); 7.27 (*m*, 5 arom. H); 7.05 (*d*, *J* = 3.8, H–C(3,3′)); 6.85 (*d*, *J* = 10.7, H–C(5,5′)); 3.89 (*quint.*-like, *X* of A_2B_2X, J_{vic} = 6.9, H–C(2)); 3.75 (*dd*, *A* of A_2B_2X, J_{AB} = 12.9, J_{AX} = 6.7, H–C(1,3)); 3.51 (*dd*, *B* of A_2B_2X, J_{AB} = 12.9, J_{BX} = 7.7, H–C(1,3)); 3.13 (*sept.*, *J* = 6.9, 2 Me_2CH); 2.74 (*s*, Me–C(1,1′)); 1.43 (*d*, *J* = 6.9, 2 *Me*$_2$CH). ^{13}C-NMR ($CDCl_3$): 146.62 (*s*); 145.21 (*s*); 139.74 (*s*); 137.59 (*s*); 136.33 (*d*); 136.10 (*s*); 134.48 (*d*); 133.05 (*d*); 128.19 (*d*); 127.63 (*d*); 126.29 (*d*); 125.22 (*d*); 124.89 (*s*); 112.32 (*d*); 48.95 (*d*); 45.00 (*t*); 38.14 (*d*, Me_2CH); 24.71 (*q*, *Me*$_2$CH); 12.92 (*q*). CI-MS: 488 (2), 487 (10), 486 (34), 485 (100, $[M + 1]^+$). Anal. calc. for $C_{37}H_{40}$ (484.73): C 91.68, H 8.32; found: C 91.90, H 8.05.

meso-*1,4-Bis(7-isopropyl-1-methylazulen-4-yl)-2,3-diphenylbutane* (**25a**): M.p. 263.0–264.0° (hexane). R_f (hexane/Et_2O 9:1) 0.21. UV (Et_2O): λ_{max} 369 (3.71), 351 (3.83), 305 (sh, 4.15), 287 (4.76), 248 (4.60), 221 (4.33); λ_{min} 362 (3.50), 317 (3.15), 263 (4.30), 230 (4.22). IR (KBr): 3060*w*, 3020*w*, 2960*s*, 1920*m*, 2900*w*, 2830*w*, 1600*w*, 1550*s*, 1525*m*, 1490*m*, 1465*s*, 1450*s*, 1430*m*, 1420*m*, 1390*m*, 1360*w*, 1320*w*, 1280*w*, 1210*w*, 1170*w*, 1160*w*, 1070*w*, 1030*m*, 960*w*, 950*w*, 950*w*, 920*m*, 820*w*, 785*s*, 760*m*, 740*w*, 700*s*, 630*m*. ^{1}H-NMR ($CDCl_3$): 8.06 (*d*, *J* = 1.7, H–C(8,8′)); 7.53 (*d*, *J* = 3.8, H–C(2,2′)); 7.27 (*m*, 10 arom. H); 6.99 (*dd*, *J* = 10.8, 1.8, H–C(6,6′)); 6.80 (*d*, *J* = 3.8, H–C(3,3′)); 6.31 (*d*, *J* = 10.8, H–C(5,5′)); 3.60 (*m*, *A* of $A_2B_2X_2$, H–C(1,4)); 3.44 (*dd*, *B* of $A_2B_2X_2$, J_{AB} = 12.7, J_{BX} = 7.0, H–C(1,4)); 2.99 (*m*, *X* of $A_2B_2X_2$, H–C(2,3)); 2.93 (*sept.*, *J* = 6.9, 2 Me_2CH); 2.63 (*s*, Me–C(1,1′)); 1.29–1.26 (2*d*, *J* = 6.9, 2 *Me*$_2$CH). ^{1}H-NOE ($CDCl_3$, 400 MHz): 2.93 (2 Me_2CH)→8.06 (*s*, H–C(8,8′)), 6.99 (*s*, H–C(6,6′)), 3.44 (CH_2)→6.80 (*s*, H–C(3,3′)), 2.99 (*s*, CH); 3.69 (*m*, CH_2)→6.80 (*m*, H–C(3,3′)), 3.44 (*m*, CH_2), 7.27 (*s*, 10 arom. H). ^{13}C-NMR ($CDCl_3$): 147.12 (*s*); 143.61 (*s*); 139.32 (*s*); 137.32 (*s*);

135.99 (*d*); 135.83 (*s*); 134.11 (*d*); 132.70 (*d*); 128.72 (*d*, 2 arom. C); 128.36 (*d*, 2 arom. C); 126.66 (*d*); 125.53 (*d*); 124.48 (*s*); 112.48 (*d*); 54.13 (*d*); 43.77 (*t*); 38.01 (*d*, Me_2CH); 24.65 (*q*, Me_2CH); 24.60 (*q*, Me_2CH); 12.92 (*q*). CI-MS: 577 (10), 576 (31), 575 (100, $[M + 1]^+$). Anal. calc. for $C_{44}H_{46}$ (574.86): C 91.94, H 8.06; found: C 91.58, H 8.25.

8.2.2. *7-Isopropyl-4-[(*E*)-2-(4-methoxyphenyl)ethenyl]-1-methylazulene* ((*E*)-**23b**). The following fractions were eluted: 1) 0.490 g (1.55 mmol, 31%) of (*E*)-**23b** as dark green crystals; 2) 0.125 g (0.25 mmol, 5%) of **25b** as dark-blue crystals, and 3) 0.063 g (0.1 mmol, 2%) of **24b** as blue powder.

Data of (E)-**23b**: M.p. 71.3–72.5° (hexane). R_f (hexane/Et_2O 9:1) 0.32. UV (hexane): λ_{max} 380 (sh, 4.29), 362 (sh, 4.39), 327 (4.46), 291 (4.56), 266 (4.35), 244 (4.30); λ_{min} 310 (3.43), 254 (4.28), 218 (4.15). IR (KBr): 3060*w*, 3000*w*, 2960*m*, 2930*w*, 2860*w*, 1620*w*, 1600*s*, 1570*m*, 1540*m*, 1520*s*, 1510*s*, 1460*m*, 1440*m*, 1420*m*, 1390*m*, 1370*w*, 1360*w*, 1330*w*, 1310*w*, 1280*m*, 1250*s*, 1190*w*, 1180*s*, 1110*w*, 1065*w*, 1030*s*, 970*m*, 960*w*, 920*w*, 870*w*, 825*s*, 780*m*, 730*w*, 710*w*, 650*w*, 640*w*, 620*w*, 610*w*. ^{1}H-NMR ($CDCl_3$): 8.21 (*s*, H–C(8)); 7.92 (*d*, J = 16.1, CH=C*H*–C(4)); 7.69 (*d*, J = 3.9, H–C(2)); 7.61 (*d*, J = 8.7, 2 arom. H); 7.52 (*m*, H–C(5,6)); 7.51 (*d*, J = 3.9, H–C(3)); 7.39 (*d*, J = 16.1, C*H*=CH–C(4)); 6.98 (*d*, J = 8.7, 2 arom. H); 3.88 (*s*, MeO); 3.13 (*sept.*, J = 6.9, Me_2CH); 2.72 (*s*, Me–C(1)); 1.42 (*d*, J = 6.9, Me_2CH). ^{13}C-NMR ($CDCl_3$): 159.91 (*s*); 142.18 (*s*); 139.82 (*s*); 136.67 (*s*); 136.49 (*d*); 136.23 (*s*); 134.84 (*d*); 133.47 (*d*); 132.98 (*d*); 130.13 (*s*); 128.37 (*d*, 2 arom. C); 127.39 (*d*); 125.76 (*s*); 120.15 (*d*); 114.26 (*d*, 2 arom. C); 111.83 (*d*); 55.35 (*q*, MeO); 38.27 (*d*, Me_2CH); 24.72 (*q*, Me_2CH); 13.04 (*q*). EI-MS: 316 (100, $M^{+\cdot}$), 315 (11), 302 (17), 301 (68, $[M - Me]^+$), 286 (6), 284 (9), 274 (6), 273 (27, $[M - Me_2CH]^+$), 271 (6). Anal. calc. for $C_{23}H_{24}O$ (316.45): C 87.30, H 7.64; found: C 87.46, H 7.40.

1,3-Bis(7-isopropyl-1-methylazulen-4-yl)-2-(4-methoxyphenyl)propane (**24b**): M.p. 129.0–131.0° (hexane). R_f (hexane/Et_2O 9:1) 0.26. UV (MeOH): λ_{max} 369 (3.88), 350 (4.01), 284 (4.78), 247 (4.77); λ_{min} 363 (3.85), 343 (3.97), 263 (4.59), 228 (4.62). IR (KBr): 3050*w*, 3000*w*, 2940*s*, 2920*s*, 2860*m*, 2820*w*, 1610*s*, 1580*w*, 1500*m*, 1510*s*, 1460*s*, 1440*s*, 1420*m*, 1380*s*, 1365*m*, 1360*m*, 1320*w*, 1300*m*, 1290*w*, 1250*s* (br.), 1230*w*, 1210*m*, 1180*s*, 1140*w*, 1110*w*, 1050*w*, 1040*m*, 1020*m*, 1000*w*, 970*w*, 960*w*, 920*m*, 880*w*, 840*m*, 820*s*, 780*w*, 750*w*, 710*w*, 640*w*, 620*w*. ^{1}H-NMR ($CDCl_3$): 8.16 (*d*, J = 1.8, H–C(8,8′)); 7.53 (*d*, J = 3.8, H–C(2,2′)); 7.28 (*dd*, J = 10.8, J = 1.9, H–C(6,6′)); 7.09 (*d*, J = 8.7, 2 arom. H); 6.97 (*d*, J = 3.8, H–C(3,3′)); 6.78 (*d*, J = 10.8, H–C(5,5′)); 6.78 (*d*, J = 8.7, 2 arom. H); 3.79 (*s*, 2 MeO); 3.79 (*m*, *X* of A_2B_2X, J_{vic} = 6.8, H–C(2)); 3.65 (*dd*, *A* of A_2B_2X, J_{AB} = 12.8, J_{AX} = 6.6, H–C(1,3)); 3.39 (*dd*, *B* of A_2B_2X, J_{AB} = 12.8, J_{BX} = 7.7, H–C(1,3)); 3.06 (*sept.*, J = 6.9, 2 Me_2CH); 2.66 (*s*, Me–C(1,1′)); 1.36 (*d*, J = 6.9, Me_2CH). ^{13}C-NMR ($CDCl_3$): 157.97 (*s*); 146.78 (*s*); 139.70 (*s*); 137.58 (*s*); 137.35 (*s*); 136.28 (*d*); 136.05 (*d*); 134.51 (*d*); 133.03 (*d*); 128.47 (*d*); 125.27 (*d*); 124.84 (*s*); 113.55 (*d*); 112.29 (*d*); 55.14 (*d*, MeO); 48.11 (*d*); 45.20 (*t*); 38.13 (*q*, Me_2CH); 24.71 (*q*, Me_2CH); 12.92 (*q*). EI-MS: 514 (27, $M^{+\cdot}$), 317 (42), 316 (100), 315 (30), 301 (15), 198 (38), 167 (72), 165 (26), 155 (16), 152 (15), 137 (31), 121 (66). Anal. calc. for $C_{38}H_{42}O$ (514.76): C 88.67, H 8.03; found: C 88.77, H 8.27.

meso-*1,4-Bis(7-isopropyl-1-methylazulen-4-yl)-2,3-bis(4-methoxyphenyl)butane* (**25b**): M.p. 227.5–229.0° (hexane). R_f (hexane/Et_2O 9:1) 0.12. UV (Et_2O) λ_{max} 369 (3.84), 351 (3.96), 286 (4.85), 247 (4.74), 230 (4.72); λ_{min} 362 (3.67), 318 (3.68), 262 (4.49), 238 (4.68), 209 (4.51). IR (KBr): 3020*w*, 2980*m*, 2940*w*, 2920*w*, 2880*w*, 2860*w*, 1620*m*, 1560*w*, 1530*w*, 1520*s*, 1470*m*, 1450*m*, 1440*m*, 1390*m*, 1375*w*, 1335*w*, 1310*w*, 1290*m*, 1250*s*, 1220*w*, 1180*s*, 1160*w*, 1110*w*, 1040*s*, 930*w*, 835*s*, 820*w*, 790*m*, 720*m*, 640*w*. ^{1}H-NMR ($CDCl_3$): 8.08 (*d*, J = 1.8, H–C(8,8′)); 7.55 (*d*, J = 3,6, H–C(2,2′)); 7.18 (*d*, J = 8.4, 4 arom. H); 7.04 (*dd*, J = 10.8, 1.9, H–C(6,6′)); 6.86 (*d*, J = 8.4, 4 arom. H); 6.84 (*d*, J = 3.6, H–C(3,3′)); 6.36 (*d*, J = 10.8, H–C(5,5′)); 3.83 (*s*, 2 MeO); 3.52 (*m*, *A* of $A_2B_2X_2$, H–C(1,4)); 3.44 (*m*, *B* of $A_2B_2X_2$, H–C(1,4)); 3.00 (*m*, *X* of $A_2B_2X_2$, H–C(2,3)); 2.98 (*sept.*, J = 6.9, Me_2CH); 2.65 (*s*, Me–C(1,1′)); 1.29–1.30 (2*d*, J = 6.9, 2 Me_2CH–C(7,7′)). ^{13}C-NMR ($CDCl_3$): 158.26 (*s*); 147.48 (*s*); 139.26 (*s*); 137.33 (*s*); 135.94 (*d*); 135.82 (*s*); 134.16 (*d*); 132.68 (*d*); 129.51 (*d*, 2 arom. C); 125.62 (*d*); 124.43 (*s*); 113.74 (*d*, 2 arom. C); 112.17 (*d*); 55.25 (*q*, MeO); 53.51 (*d*, C(2,3)); 43.81 (*t*); 38.01 (*d*, Me_2CH); 24.67 (*q*, Me_2CH); 24.61 (*q*, Me_2CH); 12.93 (*q*). EI-MS: 635 (11), 634 (22, $M^{+\cdot}$), 438 (8), 437 (27), 436 (26), 435 (14), 319 (17), 318 (84), 317 (73), 198 (19), 197 (51), 196 (5), 168 (11), 167 (65), 166 (9), 165 (18), 122 (11), 121 (100). Anal. calc. for $C_{46}H_{50}O_2$ (634.91): C 87.02, H 7.94; found: C 87.22, H 8.14.

The relative configuration of **25b** was determined by an X-ray crystal-structure analysis at −100°. *Crystal data*: space group and cell dimensions: monoclinic $P2_1$ (# 4) with a = 896.0, b = 1777.5, c = 1156.3 pm and β = 101.51°. The refinement of the structure (*cf. Fig.*) was carried out using the space group $P2_1/C$ (# 14), taking into account disorder of the two i-Pr groups as well as of the two MeO groups.

8.2.3. *4-[(*E*)-2-(4-Chlorophenyl)ethenyl]-7-isopropyl-1-methylazulene* ((*E*)-**23c**). The following fractions were eluted: 1) 0.481 g (1.5 mmol, 30%) of (*E*)-**23c** as green needles, 2) 0.260 g (0.5 mmol, 10%) of **24c** as blue crystals, and 3) 0.041 g (0.1 mmol, 2%) **26c** as green powder.

Data of (E)-**23c**: M.p. 87.1–87.6° (hexane). R_f (hexane/Et_2O 9:1) 0.61. UV (hexane): λ_{max} 396 (sh, 3.73), 366 (sh, 4.33), 350 (sh, 4.47), 319 (4.69), 282 (4.71), 260 (4.49); λ_{min} 301 (4.61), 246 (4.32), 2.15 (4.30). IR (KBr): 2960*m*,

2920*m*, 2900*m*, 2860*m*, 1620*w*, 1590*w*, 1540*m*, 1520*m*, 1490*s*, 1460*m*, 1450*m*, 1430*m*, 1410*m*, 1400*m*, 1380*m*, 1370*m*, 1360*m*, 1330*m*, 1310*w*, 1290*w*, 1210*w*, 1200*w*, 1190*w*, 1160*w*, 1120*w*, 1100*w*, 1090*s*, 1060*m*, 1040*w*, 1010*s*, 960*s*, 940*w*, 920*m*, 900*w*, 880*w*, 860*w*, 810*m*, 800*m*, 770*s*, 750*w*, 710*m*. ^{1}H-NMR ($CDCl_3$): 8.23 (*d*, *J* = 1.7, H–C(8)); 8.00 (*d*, *J* = 16.2, CH=C*H*–C(4)); 7.72 (*d*, *J* = 3.8, H–C(2)); 7.57 (*d*, *J* = 8.5, 2 arom. H); 7.50 (*m*, H–C(5,6)); 7.49 (*d*, *J* = 3.9, H–C(3)); 7.40 (*d*, *J* = 8.5, 2 arom. H); 7.35 (*d*, *J* = 16.2, C*H*=CH–C(4)); 3.14 (*sept.*, *J* = 6.9, Me_2CH); 2.72 (*s*, Me–C(1)); 1.42 (*d*, *J* = 6.9, *Me*$_2$CH). ^{13}C-NMR ($CDCl_3$): 141.35 (*s*); 140.27 (*s*); 136.92 (*d*); 136.76 (*s*); 136.52 (*s*); 135.75 (*s*); 134.84 (*d*); 133.91 (*s*); 133.15 (*d*); 130.17 (*d*); 128.93 (*d*, 2 arom. C); 128.14 (*d*, 2 arom. C); 125.95 (*s*); 120.17 (*d*); 111.89 (*d*); 38.30 (*d*, Me_2CH); 24.69 (*q*, *Me*$_2$CH); 13.01 (*q*). CI-MS: 324 (9), 323 (38), 322 (22), 321 (100, $[M + 1]^+$). Anal. calc. for $C_{22}H_{21}Cl$ (320.87): C 82.35, H 6.60, Cl 11.05; found: C 82.48, H 6.62, Cl 10.78.

2-(4-Chlorophenyl)-1,3-bis(7-isopropyl-1-methylazulen-4-yl)propane (**24c**): M.p. 156.0–157.0° (hexane). R_f (hexane/Et_2O 9:1) 0.49. UV (hexane): λ_{max} 370 (3.96), 352 (4.08), 304 (4.44), 290 (4.99), 285 (5.02), 247 (4.94), 217 (4.92); λ_{min} 362 (3.79), 321 (3.75), 263 (4.70), 231 (4.80). IR (KBr): 3050*w*, 3020*w*, 2960*s*, 2920*s*, 2900*s*, 2860*m*, 2870*m*, 1590*w*, 1550*s*, 1520*s*, 1490*s*, 1460*s*, 1450*s* (br.), 1415*s*, 1380*s*, 1360*s*, 1330*m*, 1300*w*, 1280*w*, 1220*w*, 1200*w*, 1170*w*, 1150*w*, 1120*w*, 1100*w*, 1090*m*, 1060*w*, 1050*w*, 1030*m*, 1010*m*, 990*w*, 960*w*, 920*m* (br.), 880*w*, 870*w*, 820*s*, 780*s*, 740*w*, 710*m*, 620*w*. ^{1}H-NMR ($CDCl_3$): 8.16 (*d*, *J* = 1.8, H–C(8,8′)); 7.54 (*d*, *J* = 3.8, H–C(2,2′)); 7.28 (*dd*, *J* = 10.7, 1.8, H–C(6,6′)); 7.18 (*d*, *J* = 8.5, 2 arom. H); 7.08 (*d*, *J* = 8.5, 2 arom. H); 6.96 (*d*, *J* = 3.8, H–C(3,3′)); 6.74 (*d*, *J* = 10.7, H–C(5,5′)); 3.81 (*quint.*-like, *X* of A_2B_2X, $J_{vic} \approx 7.1$, H–C(2)); 3.65 (*dd*, *A* of A_2B_2X, J_{AB} = 12.9, J_{AX} = 6.5, H–C(1,3)); 3.41 (*dd*, *B* of A_2B_2X, J_{AB} = 12.9, J_{BX} = 8.0, H–C(1,3)); 3.06 (*sept.*, *J* = 6.9, 2 Me_2CH); 2.66 (*s*, Me–C(1,1′)); 1.36 (*d*, *J* = 6.9, *Me*$_2$CH). ^{13}C-NMR ($CDCl_3$): 146.08 (*s*); 143.56 (*s*); 139.92 (*s*); 137.45 (*s*); 136.42 (*d*); 136.17 (*s*); 134.54 (*d*); 133.17 (*d*); 131.85 (*s*); 128.94 (*d*); 128.28 (*d*); 125.10 (*d*); 125.04 (*d*); 112.24 (*d*); 48.28 (*d*, C(2)); 44.96 (*t*); 38.14 (*d*, Me_2CH); 24.70 (*q*, *Me*$_2$CH); 12.91 (*q*). CI-MS: 523 (6), 522 (17), 521 (48), 520 (40, $[M + 1]^+$), 519 (100). EI-MS: 520 (94), 519 (39, $M^{+\cdot}$), 518 (79), 322 (39), 321 (39), 320 (100), 319 (20), 305 (22), 198 (72), 167 (26), 165 (14), 155 (12). Anal. calc. for $C_{37}H_{39}Cl$ (519.18): C 85.60, H 7.57, Cl 6.83; found: C 85.37, H 7.40, Cl 6.61.

4-[2-(4-Chlorophenyl)-2-(phenylamino)ethyl]-7-isopropyl-1-methylazulene (**26c**): ^{1}H-NMR ($CDCl_3$): 8.23 (*d*, *J* = 1.9, H–C(8)); 7.85 (*d*, *J* = 8.7, 2 arom. H); 7.75 (*d*, *J* = 3.8, H–C(2)); 7.53 (*d*, *J* = 8.3, 2 arom. H); 7.33 (*d*, *J* = 8.5, 2 arom. H); 7.00 (*d*, *J* = 7.3, H–C(6)); 6.97 (*d*, *J* = 3.8, H–C(3)); 6.96 (*d*, *J* = 7.3, H–C(5)); 6.60 (*t*, *J* = 7.3, 1 arom. H); 6.30 (*d*, *J* = 8.7, 2 arom. H); 4.80 (*dd*, *J* = 8.4, *J* = 5.8, 4-ClC_6H_4CH); 4.35 (br. *s*, N*H*); 3.53 (*d*, *J* = 8.5, 1 H, CH_2); 3.52 (*d*, *J* = 5.7, 1 H, CH_2); 3.09 (*sept.*, *J* = 6.9, Me_2CH); 2.72 (*s*, Me–C(1)); 1.38 (*d*, *J* = 6.9, *Me*$_2$CH). CI-MS: 416 (8), 414 (17, $[M + 1]^+$), 218 (6), 216 (18, $[4\text{-}ClC_6H_4CHNH - C_6H_5]^+$), 200 (16), 199 (100, $[(M + 1) - (4\text{-}ClC_6H_4CHNHC_6H_5)]^+$).

8.2.4. *Attempted 'Anil Synthesis' with (4-Nitrobenzylidene)(phenyl)amine* (**22e**). After a forerun of **21**, a green fraction was eluted. After evaporation of the solvent, *(E)-1,2-bis(7-isopropyl-1-methylazulen-4-yl)ethene* (**27**; 0.527 g, 32%) was obtained as black-green needles. M.p. 137.8–138.1° (hexane). R_f (hexane) 0.25. UV (hexane): λ_{max} 380 (sh, 4.57), 328 (4.94), 274 (5.16), 230 (4.71); λ_{min} 306 (4.83), 214 (4.68). IR (KBr): 3060*w*, 2960*s*, 2920*w*, 2900*w*, 2840*w*, 1540*s*, 1520*s*, 1460*m*, 1450*m*, 1435*m*, 1415*m*, 1385*s*, 1365*m*, 1320*w*, 1210*s*,1160*w*, 1060*m*, 1020*m*, 960*w*, 940*m*, 910*m*, 880*w*, 850*w*, 810*w*, 770*s*, 700*s*, 660*w*, 620*m*. ^{1}H-NMR (C_6D_6): 8.39 (*s*, C*H*=C*H*); 8.28 (*d*, *J* = 1.6, H–C(8,8′)); 7.74 (*d*, *J* = 3.9, H–C(2,2′)); 7.64 (*d*, *J* = 3.9, H–C(3,3′)); 7.51 (*d*, *J* = 10.8, H–C(5,5′)); 7.35 (*dd*, *J* = 10.8, 1.9, H–C(6,6′)); 2.92 (*sept.*, *J* = 6.9, 2 Me_2CH); 2.67 (*s*, Me–C(1,1′)); 1.32 (*d*, *J* = 6.9, 2 *Me*$_2$CH). ^{13}C-NMR ($CDCl_3$): 141.71 (*s*); 140.55 (*s*); 137.19 (*d*); 136.88 (*s*); 136.75 (*s*); 134.92 (*d*); 134.87 (*d*); 133.28 (*d*); 125.99 (*s*); 120.67 (*d*); 112.17 (*d*); 38.37 (*d*, Me_2CH); 24.72 (*q*, *Me*$_2$CH); 12.99 (*q*). EI-MS: 394 (5), 393 (29), 392 (100, $M^{+\cdot}$), 378 (10), 377 (36, $[M - CH_3]^+$), 350 (16), 349 (57, $[M - Me_2CH]^+$), 334 (11), 333 (9), 319 (12), 318 (5), 317 (6), 221 (48), 196 (21), 181 (31). Anal. calc. for $C_{30}H_{32}$ (392.59): C 91.78, H 8.22; found: C 92.07, H 8.05.

8.2.5. *4-{(E)-2-[4-(Dimethylamino)phenyl]ethenyl}-7-isopropyl-1-methylazulene* ((*E*)-**23d**). The 'anil synthesis' yielded pure (*E*)-**23d** (1.35 g, 82%) as dark-green needles. M.p. 121.5–122.5° (hexane). R_f (hexane/Et_2O 9:1) 0.18 UV (hexane) λ_{max} 430 (sh, 4.50), 413 (4.60), 326 (sh, 4.21), 294 (4.65), 258 (4.64); λ_{min} 344 (4.34), 273 (4.52), 226 (4.26). IR (KBr): 2950*m*, 2900*w*, 2840*w*, 2800*w*, 1600*s*, 1550*w*, 1540*m*, 1520*s*, 1450*m*, 1440*m*, 1380*m*, 1360*s*, 1330*w*, 1310*w*, 1270*w*, 1220*w*, 1180*s*, 1160*m*, 1120*w*, 1060*w*, 1020*w*, 960*m*, 910*w*, 820*m*, 770*m*, 710*w*. ^{1}H-NMR ($CDCl_3$): 8.17 (*s*, H–C(8)); 7.85 (*d*, *J* = 16.1, CH=C*H*–C(4)); 7.65 (*d*, *J* = 3.9, H–C(2)); 7.56 (*d*, *J* = 8.9, 2 arom. H); 7.51 (*d*, *J* = 3.9, H–C(3)); 7.50 (*m*, H–C(5,6)); 7.38 (*d*, *J* = 16.1, C*H*=CH–C(4)); 6.77 (*d*, *J* = 8.9, 2 arom. H); 3.10 (*sept.*, *J* = 6.9, Me_2CH); 3.04 (*s*, Me_2N); 2.69 (*s*, Me–C(1)); 1.39 (*d*, *J* = 6.9, *Me*$_2$CH). ^{13}C-NMR ($CDCl_3$): 150.59 (*s*); 142.77 (*s*); 139.32 (*s*); 136.48 (*s*); 135.99 (*d*); 135.88 (*s*); 134.73 (*d*); 134.25 (*d*); 132.73 (*d*); 128.32 (*d*, 2 arom. C); 125.56 (*s*); 124.78 (*d*); 119.99 (*d*); 112.27 (*d*, 2 arom. C); 111.68 (*d*); 40.29 (*q*, Me_2N); 38.20 (*d*, Me_2CH); 24.72 (*q*, *Me*$_2$CH); 13.06 (*q*). CI-MS: 332 (17), 331 (24), 330 (100, $[M + 1]^+$). Anal. calc. for $C_{24}H_{27}N$ (329.49): C 87.49, H 8.26, N 4.25; found: C 87.56, H 8.27, N 4.30.

9. *Reaction of* **10** *and (Benzylidene)(phenyl)amine* (**22a**). Azulene **10** (0.340 g, 2.0 mmol), **22a** (0.362 g, 2.0 mmol), and finely powdered KOH (0.56 g, 10 mmol) were reacted in DMF (10 ml) at 0° for 1 h. H_2O (50 ml) was added to the mixture, followed by extraction with Et_2O (3 × 20 ml). The org. phase was washed with H_2O, dried (Na_2SO_4), and evaporated (RE) to yield after CC (silica gel; hexane/Et_2O 7:3) 4 fractions in the following order of elution: 0.288 g (0.82 mmol, 41%) of **28**, 0.028 g (0.08 mmol, 4%) of **29**, 0.160 g (0.30 mmol, 15%) of **30**, and 0.110 g (0.15 mmol, 8%) of **31**.

4,8-Dimethyl-6-[2-(phenylamino)-2-phenylethyl]azulene (**29**): M.p. 112.0–113.0° (hexane). R_f (hexane/Et_2O 7:3) 0.70. IR (KBr): 3400*m*, 3060*w*, 3020*w*, 2960*w*, 2920*w*, 2840*w*, 1600*s*, 1580*s*, 1540*w*, 1500*s*, 1450*m*, 1430*s*, 1370*w*, 1350*w*, 1320*m*, 1270*m*, 1240*w*, 1220*w*, 1180*w*, 1150*w*, 1100*w*, 1080*w*, 1030*w*, 1010*w*, 990*w*, 870*w*, 840*w*, 750*s*, 730*m*, 690*s*. ^{1}H-NMR ($CDCl_3$): 7.75 (*t*, *J* = 4.0, H–C(2)); 7.43 (*d*, *J* = 3.9, H–C(1,3)); 7.34 (*m*, *Ph*CH); 7.08 (*dt*, *J* = 7.4, *J* = 1.1, 2 H, *Ph*NH); 6.96 (*s*, H–C(5,7)); 6.67 (*dt*, *J* = 7.3, *J* = 1.1, 1 H, *Ph*NH); 6.49 (*dd*, *J* = 8.8, 1.0, 2 H, *Ph*NH); 4.73 (*dd*, J_{vic} = 6.4, 7.4, PhC*H*); 4.24 (br. *s*, N*H*); 3.32 (*dd*, J_{gem} = 13.0, J_{vic} = 6.2, 1 H, CH_2); 3.21 (*dd*, J_{gem} = 13.0, J_{vic} = 7.6, 1 H, CH_2); 2.88 (*s*, Me–C(4,6)). ^{13}C-NMR ($CDCl_3$): 146.88 (*s*); 145.65 (*s*); 144.97 (*s*); 142.77 (*s*); 136.42 (*s*); 133.27 (*d*); 129.00 (*d*, 2 arom. C); 128.57 (*d*, 2 arom. C); 127.30 (*d*, 2 arom. C); 127.20 (*d*); 126.54 (*d*, 2 arom. C); 117.72 (*d*); 116.33 (*d*, 2 CH); 113.78 (*d*, 2 CH); 60.17 (*d*); 51.52 (*t*); 25.10 (*q*). CI-MS: 353 (27), 352 (96, $[M + 1]^+$), 259 (22, $[(M + 1) - NHC_6H_5]^+$), 183 (8), 182 (63, $[CHC_6H_5NHC_6H_5]^+$), 172 (12), 171 (100, $[M - CHC_6H_5NHC_6H_5]^+$). Anal. calc. for $C_{26}H_{25}N$ (351.50): C 88.85, H 7.17, N 3.98; found: C 88.55, H 7.37, N 3.71.

4,6-Dimethyl-8-[2-(phenylamino-)2-phenylethyl]azulene (**29**): M.p. 152.0–153.0° (hexane). R_f (hexane/Et_2O 7:3) 0.61. IR (KBr): 3400*m*, 3060*w*, 3020*w*, 2960*w*, 2940*w*, 2820*w*, 1600*s*, 1580*s*, 1500*s*, 1490*s*, 1450*m*, 1430*s*, 1370*w*, 1350*m*, 1320*s*, 1300*m*, 1270*m*, 1220*w*, 1210*w*, 1180*w* (br.), 1150*w*, 1120*w*, 1100*w*, 1080*w*, 1070*w*, 1030*w*, 990*w*, 870*w*, 840*w*, 750*s*, 700*s*, 690*s*. ^{1}H-NMR ($CDCl_3$): 7.77 (*t*, *J* = 3.9, H–C(2)); 7.59 (*dd*, *J* = 3.9, 1.5, H–C(1)); 7.49 (*dd*, *J* = 8.6, 1.6, 2 H, *Ph*CH); 7.44 (*dd*, *J* = 4.0, 1.5, H–C(3)); 7.37 (*t*, *J* = 7.5, 1.5, 2 H, *Ph*CH); 7.30 (*m*, 1 H, *Ph*CH); 7.08 (*s*, H–C(5)); 6.96 (*m*, *J* = 7.4, 2 H, *Ph*NH); 6.89 (*s*, H–C(7)); 6.57 (*t*, *J* = 7.3, 1 H, *Ph*NH); 6.33 (*d*, *J* = 7.5, 2 arom. H, *Ph*NH); 4.82 (*dd*, J_{vic} = 8.4, J_{vic} = 5.7, PhC*H*); 4.35 (br. *s*, NH); 3.50 (*m*, CH_2); 2.90 (*s*, Me–C(4)); 2.57 (*s*, Me–C(6)). ^{1}H-NOE ($CDCl_3$, 400 MHz): 2.57 (Me–C(6))→6.89 (*s*, H–C(7)), 7.08 (*s*, H–C(5)); 2.90 (Me–C(4))→7.08 (*s*, H–C(5)), 7.44 (*s*, H–C(3)). CI-MS: 354 (4), 353 (16), 352 (62, $[M + 1]^+$), 183 (6), 182 (45), 173 (2), 172 (12), 171 (100).

4-Methyl-6,8-bis[2-(phenylamino)-2-phenylethyl]azulene (**30**): M.p. 105.8–106.6° (Et_2O/hexane). R_f (hexane/Et_2O 7:3) 0.42. IR (KBr): 3400*s*, 3040*w*, 3020*w*, 2920*w*, 2850*w*, 1600*s*, 1580*m*, 1500*s*, 1450*m*, 1430*m*, 1350*m*, 1320*m*, 1270*w*, 1180*w*, 1150*w*, 1120*w*, 1100*w*, 1080*w*, 1070*w*, 1030*w*, 1020*w*, 990*w*, 870*w*, 750*s*, 700*s*. ^{1}H-NMR ($CDCl_3$): 7.83 (*t*, *J* = 3.9, H–C(2)); 7.61 (*dd*, *J* = 3.9, 1.30, H–C(1)); 7.47 (*dd*, *J* = 3.9, 1.4, H–C(3)); 7.40–7.25 (*m*, 2 *Ph*CH); 7.08 (*t*, *J* = 7.4, 1.0, 2 H, *Ph*NH); 7.01 (*t*, *J* = 7.4, 1.0, 2 H, *Ph*NH); 6.92 (*s*, H–C(5)); 6.81 (*s*, H–C(7)); 6.67 (*t*, *J* = 7.3, 1 H, *Ph*NH); 6.60 (*t*, *J* = 7.3, 1 H, *Ph*NH); 6.47 (*dd*, *J* = 7.7, 1.0, 2 H, *Ph*NH); 6.32 (*dd*, *J* = 8.5, 1.0, 2 H, *Ph*NH); 4.70 (*dd*, J_{vic} = 5.2, J_{vic} = 8.8, PhC*H*); 4.59 (*t*-like, *J* = 7.0, PhC*H*); 4.25 (br. *s*, 2 N*H*); 3.62 (*dd*, J_{vic} = 8.8, J_{gem} = 13.5, 1 H, CH_2); 3.51 (*dd*, J_{vic} = 5.2, J_{gem} = 13.6, 1 H, CH_2); 3.20 (*dd*, J_{vic} = 6.4, J_{gem} = 13.2, 1 H, CH_2); 3.11 (*dd*, J_{vic} = 7.4, J_{gem} = 13.2, 1 H, CH_2); 2.87 (*s*, Me–C(4)). ^{13}C-NMR ($CDCl_3$): 147.04 (*s*); 146.87 (*s*); 145.72 (*s*); 145.15 (2*s*); 143.78 (*s*); 142.69 (*s*); 137.48 (*s*); 136.74 (*s*); 134.07 (*d*); 129.03 (*d*); 128.91 (*d*); 128.87 (*d*); 128.61 (*d*); 127.85 (*d*); 127.27 (*d*); 127.23 (*d*); 126.85 (*d*); 126.54 (*d*); 126.27 (*d*); 117.75 (*d*); 117.43 (*d*); 117.16 (*d*); 115.64 (*d*); 113.79 (*d*); 113.61 (*d*, 2 CH); 59.80 (*d*); 59.73 (*d*); 51.27 (*t*); 47.64 (*t*); 25.22 (*q*). ^{1}H-NOE ($CDCl_3$, 400 MHz): 2.87 (Me–C(4))→6.92 (*s*, H–C(5)), 7.47 (*s*, H–C(3)). CI-MS: 534 (14), 533 (33, $[M + 1]^+$), 353 (10), 352 (35), 182 (25), 172 (14), 171 (100). Anal. calc. for $C_{39}H_{36}N_2$ (532.73): C 87.93, H 6.81, N 5.26; found: C 87.74, H 7.05, N 5.11.

4,6,8-Tris[2-(phenylamino)-2-phenylethyl]azulene (**31**): M.p. 97.1–98.1° (Et_2O/hexane). R_f (hexane/Et_2O 7:3) 0.27. IR (KBr): 3400*m*, 3060*w*, 3020*w*, 1600*s*, 1500*s*, 1450*m*, 1430*m*, 1360*w*, 1320*m*, 1270*m*, 1180*w*, 1150*w*, 1120*w*, 1100*w*, 1080*w*, 1060*w*, 1030*w*, 990*w*, 870*w*, 750*s*, 700*s*. ^{1}H-NMR ($CDCl_3$): 7.82 (*t*-like, *J* = 3.9, H–C(2)); 7.57 (*d*-like, *J* = 4.0, 2 H, H–C(1,3)); 7.34–7.16 (*m*, 3 *Ph*CH); 7.09–6.92 (*m*, *Ph*NH); 6.75 (*m*, 2 H, *Ph*NH); 6.73 (*m*, H–C(5,7)); 6.60 (*t*, *J* = 7.4, 2 H, *Ph*NH); 6.38 (*t*-like, *J* = 7.5, 2 H, *Ph*NH); 6.30 (*dd*, *J* = 7.7, 5.0, 4 H, *Ph*NH); 4.73 (*m*, 2 PhC*H*); 4.42 (*q*-like, *J* = 3.8, PhC*H*); 4.23 (br. *s*, 3 PhN*H*); 3.63–3.48 (2*m*, 3 CH_2). CI-MS: 715 (53), 714 (100 $[M + 1]^+$), 713 (22). Anal. calc. for $C_{52}H_{47}N_3$ (713.97): C 87.48, H 6.63, N 5.88; found: C 87.26, H 6.87, N 6.05.

9.1. *4,8-Dimethyl-6-[(E)-2-phenylethenyl]azulene* (**33**): To a soln. of 0.250 g (0.7 mmol) of **28** (R_f (hexane/Et_2O 9:1): 0.22) in 10 ml EtOH, 0.5 ml (7 mmol) of MeI and 0.820 g (14 mmol) of KOH were added. The mixture was stirred at r.t. for 24 h. H_2O (20 ml) was added to the mixture, followed by extraction with Et_2O (3 × 10 ml). The org. phase was washed with H_2O, dried (Na_2SO_4), and evaporated (RE) to yield after CC (silica gel; hexane/Et_2O 9:1) 0.220 g (0.6 mmol, 85%) of **32** as violet crystals.

Compound **32** (0.180 g, 0.5 mmol) and 0.300 g (5 mmol) of KOH were boiled in 10 ml EtOH for 24 h. After usual workup, 0.052 g (0.2 mmol, 40%) of **33** was obtained as green needles.

*4,8-Dimethyl-6-[2-(*N*-methyl-*N*-phenylamino)-2-phenylethyl]azulene* (**32**): M.p. 115.0° (Et_2O). R_f (hexane/Et_2O 9:1) 0.35. IR (KBr): 3090*w*, 3060*w*, 3020*w*, 2960*w*, 2890*w*, 2800*w*, 1600*s*, 1570*s*, 1490*s*, 1450*s*, 1430*s*, 1370*m*, 1340*w*, 1330*m*, 1300*m*, 1280*w*, 1250*w*, 1215*m*, 1190*w*, 1170*w*, 1160*w*, 1100*m*, 1080*w*, 1050*w*, 1030*m*, 1020*w*, 990*w*, 970*w*, 900*w*, 870*w*, 850*w*, 830*m*, 820*w*, 770*m*, 750*s*, 730*w*, 710*m*, 690*s*, 660*w*, 640*w*, 610*w*. ^{1}H-NMR ($CDCl_3$): 7.71 (*t*, J = 3.9, H–C(2)); 7.38 (*d*, J = 3.9, H–C(1,3)); 7.34–7.29 (*m*, *Ph*CH); 7.16 (*t*-like, J = 7.0, 2 H, *Ph*NMe); 7.07 (*s*, H–C(5,7)); 6.72 (*d*-like, J = 8.0, 3 H, *Ph*NMe); 5.39 (*dd*, J_{vic} = 8.7, J_{vic} = 6.3, PhC*H*); 3.58 (*dd*, J_{gem} = 13.6, J_{vic} = 6.3, 1 H, CH_2); 3.52 (*dd*, J_{gem} = 13.7, J_{vic} = 8.8, 1 H, CH_2); 2.85 (*s*, Me–C(4,8)); 2.82 (*s*, *Me*NPh). EI-MS: 197 (20), 196 (100, $[CHPhNMePh]^+$), 195 (90), 180 (22), 165 (13), 153 (29), 135 (12), 128 (17), 115 (21), 107 (11), 104 (14), 91 (30), 77 (73), 51 (17). Anal. calc. for $C_{27}H_{27}N$ (365.52): C 88.72, H 7.44, N 3.88; found: C 88.93, H 7.02, N 4.09.

Data of **33**: M.p. 108.5–110.5° (hexane). R_f (hexane/Et_2O 9:1) 0.51. UV/VIS (hexane): λ_{max} 595 (2.70), *ca.* 402 (sh, 4.10), 387 (4.26), 322 (4.66), 257 (sh, 4.11), 241 (4.20); λ_{min} 453 (2.06), 362 (4.01), 276 (3.96), 223 (4.09). IR (KBr): 3022*m*, 2920*m*, 1562*s*, 1536*s*, 1486*m*, 1426*s*, 1331*m*, 1208*m*, 1071*m*, 1011*m*, 1054*m*, 876*m*, 830*m*, 742*s*, 689*s*. ^{1}H-NMR ($CDCl_3$): 7.61 (*t*, J = 3.9, H–C(2)); 7.56 (*dd*, J = 7.1, 1.4, 2 arom. H); 7.32–7.20 (*m*, 10 H); 7.18 (*s*, H–C(5,7)); 2.88 (*s*, Me–C(4,8)). ^{1}H-NMR (C_6D_6): 7.92 (*t*, J = 3.9, H–C(2)); 7.56 (*d*, J = 3.9, H–C(1,3)); 7.48 (*d*, J = 7.0, 2 arom. H); 7.27 (*m*, 7 H); 2.81 (*s*, Me–C(4,8)). EI-MS: 259 (19), 258 (100, M^+), 243 (9, $[M - CH_3]^+$), 228 (15, $[M - 2\,Me]^+$), 215 (10), 165 (34), 152 (19), 141 (10), 128 (30), 119 (20), 115 (38), 107 (19), 101 (14), 91 (23), 77 (12). Anal. calc. for $C_{20}H_{18}$ (258.37): C 92.98, H 7.02; found: C 93.18, H 7.22.

9.2. *4,6-Dimethyl-8-[(*E*)-2-phenylethenyl]azulene* (**34**): To a soln. of 0.030 g (0.08 mmol) of **29** (R_f (hexane/Et_2O 9:1) 0.22) in 5 ml EtOH, 0.5 ml (8 mmol) of MeI and 1.0 g (16 mmol) of KOH were added, and the mixture was stirred at r.t. for 24 h. H_2O (10 ml) was added to the mixture, followed by extraction with Et_2O (3 × 5 ml). The org. phase was washed with H_2O, dried (Na_2SO_4), and evaporated (RE) to yield after CC (silica gel; hexane/Et_2O 9:1) 0.025 g (0.07 mmol, 85%) **35** as violet crystals.

Compound **35** (0.010 g, 0.03 mmol) and 0.020 g (0.3 mmol) of KOH were boiled in 5 ml of EtOH for 24 h. After usual workup, 0.003 g (0.01 mmol, 34%) **34** was obtained as green needles.

*4,6-Dimethyl-8-[2-(*N*-methyl-*N*-phenylamino)-2-phenylethyl]azulene* (**35**): R_f (hexane/Et_2O 9:1) 0.37. IR ($CHCl_3$): 1597*s*, 1577*s*, 1504*s*, 1449*m*, 1375*m*, 1332*m*, 1108*m*, 1076*m*, 1031*m*. ^{1}H-NMR ($CDCl_3$): 7.78 (*t*, J = 3.9, H–C(2)); 7.44 (*dd*, J = 4.0, 1.4, H–C(1)); 7.43 (*dd*, J = 3.9, 1.4, H–C(3)); 7.33 (*m*, *Ph*CH); 7.03 (*m*, 2 H, *Ph*NMe); 7.00 (*s*, H–C(5)); 6.92 (*s*, H–C(7)); 6.61 (*t*, J = 7.3, 1 H, *Ph*NMe); 6.49 (*d*, J = 8.1, 2 H, *Ph*NMe); 5.61 (*dd*, J_{vic} = 9.4, J_{vic} = 5.1, *PhCH*); 4.03 (*dd*, J_{vic} = 5.1, J_{gem} = 13.5, 1 H, CH_2); 3.83 (*dd*, J_{vic} = 9.4, J_{gem} = 13.5, 1 H, CH_2); 2.87 (*s*, Me–C(8)); 2.76 (*s*, Me–C(6)); 2.45 (*s*, *Me*NPh). EI-MS: 197 (12), 196 (100, $[CHPhNMePh]^+$), 180 (19), 165 (12), 153 (23), 128 (17), 115 (17), 107 (11), 104 (18), 91 (32), 77 (81), 51 (17).

Data of **34**: R_f (hexane/Et_2O 9:1) 0.51. UV/VIS (hexane): λ_{max} 587 (2.57), *ca.* 400 (sh, 3.50), 383 (3.65), 310 (4.31), 298 (4.30), 245 (4.03); λ_{min} 465 (2.15), 374 (3.63), 302 (4.29), 256 (4.01), 226 (4.01). IR ($CHCl_3$): 1600*s*, 1572*s*, 1487*m*, 1433*m*, 1374*w*, 1333*m*, 1262*w*, 1075*w*, 1027*w*, 961*m*. ^{1}H-NMR ($CDCl_3$): 8.07 (*d*, J = 16.1, PhCH=C*H*); 7.71 (*t*, J = 3.9, H–C(2)); 7.66 (*d*, J = 7.2, 2 arom. H); 7.58 (*d*, J = 3.9, H–C(1)); 7.5 (*d*, J = 3.9, H–C(3)); 7.48 (*s*, H–C(5)); 7.43 (*d*, J = 7.3, 2 arom. H); 7.35 (*t*, J = 7.3, 1 arom. H); 7.34 (*d*, J = 16.3, PhC*H*=CH); 7.11 (*s*, H–C(7)); 2.91 (*s*, Me–C(8)); 2.72 (*s*, Me–C(6)). EI-MS: 259 (23), 258 (61, $M^{+\cdot}$), 257 (60), 256 (14), 243 (33, $[M - Me]^+$), 242 (29), 241 (14), 228 (13, $[M - 2\,Me]^+$), 227 (12), 226 (10), 215 (9), 181 (32), 179 (15), 178 (11), 166 (15), 165 (52), 153 (11), 152 (17), 147 (19), 137 (27), 129 (31), 128 (22), 123 (10), 122 (50), 121 (100), 120 (25), 119 (14), 117 (10), 115 (33), 105 (93), 101 (12), 91 (45), 77 (71).

REFERENCES

[1] A. Briquet, H.-J. Hansen, *Helv. Chim. Acta* **1994,** in preparation.
[2] A. Briquet, H.-J. Hansen, *Helv. Chim. Acta* **1994,** *77,* 1940.
[3] R. N. Mc Donald, W. S. Stewart, *J. Org. Chem.* **1965,** *30,* 270.
[4] J. O. Currie, R. A. Labar, R. D. Breazeale, A. G. Anderson, *Liebigs Ann. Chem.* **1973,** 166.
[5] J. O. Currie, R. A. Labar, R. D. Breazeale, A. G. Anderson, *Org. Prep. Proc. Int.* **1976,** *8,* 169.
[6] M. Saito, T. Morita, K. Takase, *Chem. Lett.* **1974,** 289.
[7] M. Saito, T. Morita, K. Takase, *Bull. Chem. Soc. Jpn.* **1980,** *53,* 3276.
[8] H. Horino, T. Asao, N. Inoue, *Bull. Chem. Soc. Jpn.* **1991,** *64,* 183.
[9] K. Hafner, H. Kaiser, *Liebigs Ann. Chem.* **1958,** *618,* 140.
[10] Y. N. Porshnev, E. M. Tereshchenko, M. I. Cherkashin, *Zh. Org. Khim.* **1978,** *14,* 243.

[11] K. Hafner, H. Pelster, H. Patzelt, *Liebigs Ann. Chem.* **1961,** *650,* 80.
[12] M. Scholz, L. N. Vien, G. Fischer, B. Tschapke, M. Mühlstadt, *Chem. Ber.* **1967,** *100,* 375.
[13] K. Hafner, G. L. Knaup, H. J. Lindne, *Bull. Chem. Soc. Jpn.* **1988,** *61,* 155.
[14] D. Balschukat, E. V. Dehmlov, *Chem. Ber.* **1986,** *119,* 2272.
[15] I. J. Fletcher, A. E. Siegrist, *Adv. Heterocycl. Chem.* **1978,** *23,* 171.
[16] A. E. Siegrist, *Helv. Chim. Acta* **1981,** *64,* 662.
[17] A. Magnussen, P. Uebelhardt, H.-J. Hansen, *Helv. Chim. Acta* **1993,** *76,* 2887.
[18] Y. N. Porshnev, E. M. Tereschenko, *Zh. Org. Khim.* **1975,** *11*(2), 462.
[19] W. P. Hart, D. Shihua, M. D. Rausch, *J. Organomet. Chem.* **1985,** *282,* 111.
[20] A. J. Rippert, Ph. D. thesis, University of Zurich, 1994.
[21] H.-D. Becker, *J. Org. Chem.* **1964,** *29,* 2891.
[22] R. Schönenberger, S. Sunkel, H. Schönenberger, *Arzneim.-Forsch.* **1972,** *22,* 1952 as well as D. C. Sayles, M. S. Kharasch, *J. Org. Chem.* **1961,** *26,* 4210.
[23] Y. Romanens, Ph. D. thesis No. 878, University of Fribourg, 1985.
[24] K. Hafner, H. Weldes, *Liebigs Ann. Chem.* **1957,** *606,* 90.
[25] A. Briquet, H.-J. Hansen, *Helv. Chim. Acta* **1994,** *77,* 1577.
[26] Y. N. Porshnev, T. N. Ivanova, L. V. Efimova, E. M. Tereshchenko, M. I. Cherkashin, K. M. Dryumaev, *Zh. Org. Khim.* **1982,** *18,* 132.
[27] K. Hafner, C. Bernhard, *Liebigs Ann. Chem.* **1959,** *625,* 108.
[28] K. Hafner, *Angew. Chem.* **1957,** *69,* 533.
[29] Y. Chen, R. W. Kunz, P. Uebelhart, R. H. Weber, H.-J. Hansen, *Helv. Chim. Acta* **1992,** *75,* 2447.