An Improved and Simplified Synthesis of 4-Styrylazulenes

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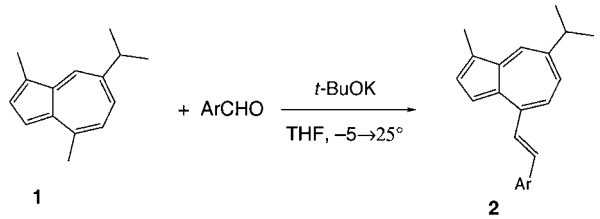
It is shown that 4- or 8-[(*E*)-styryl]-substituted azulenes can easily be prepared from 4- or 8-methylazulenes in the presence of potassium *tert*-butoxide (*t*-BuOK) with the corresponding benzaldehydes in tetrahydrofuran (THF) at −5 to 25° (see *Schemes 1* and *2*). 6-(*tert*-Butyl)-4,8-dimethylazulene (**5**) with both Me groups in reactive positions leads to the formation of a mixture of the mono- and distyryl-substituted azulenes **6** and **7**, respectively (*Scheme 3*). *Vilsmeier* formylation of **6** results in the formation of 3:2 mixture of the azulene-carbaldehydes **8a** and **8b**, which can be separated by chromatography on silica gel. Reduction of **8a** and **8b** with $NaBH_4$ in trifluoroacetic acid (TFA)/CH_2Cl_2 gives the 1-methyl forms **9a** and **9b**, respectively, in good yields (*Scheme 4*). The latter two azulenes are not separable on silica gel.

Some years ago, we reported on the preparation of 4-[(*E*)-styryl]-substituted azulenes by application of the 'anil synthesis' to corresponding 4-methylazulenes [1]. The 'anil procedure' is easily performed, since the corresponding benzanils are reacting with the 4-methylazulenes in the presence of powdered KOH in *N*,*N*-dimethylformamide (DMF) as solvent at 60–70°. DMF as solvent is necessary since it takes part in the reaction (*cf.* [1] and literature cited there). However, the yields of the 4-styryl-substituted azulenes did not exceed 30%, and a number of side products were also formed. Only the anil of 4-(dimethylamino)benzaldehyde gave the corresponding azulene in 82% yield. On the other hand, the anil of 4-nitrobenzaldehyde gave no styryl compound at all, and instead of that, a corresponding (*E*)-1,2-di(azulen-4-yl)ethene could be isolated in 32% yield. Since we are still interested in the synthesis of 4-styryl-substituted azulenes, we sought for a much more efficient and simpler method. Using *Hafner*'s deprotonation procedure with sodium *N*-methyl-*N*-phenylamide [2], *Kurokawa* prepared 7-isopropyl-1-methyl-4-[(*E*)-2-phenylethenyl]azulene (**2a**) from guaiazulene (**1**) and benzaldehyde (PhCHO) at ambient temperature in THF in good yield [3], however, also accompanied by side products. Nevertheless, the preparation of sodium *N*-methyl-*N*-phenylamide is somewhat laborious. Therefore, we have been looking for a cheaper and easily available base and found it in potassium *tert*-butoxide (*t*-BuOK). When **1** was treated with 2.6 mol-equiv. of *t*-BuOK in THF at −5° for 5 min and then 3 mol-equiv. of the corresponding benzaldehyde derivative were added, the expected 4-[(*E*)-styryl]-substituted azulenes **2** could be isolated after 2-h stirring at ambient temperature in good-to-excellent yields (see *Scheme 1*). Only the 4-[(*E*)-4-nitrostyryl]azulene (**2e**), which was not formed at all in the 'anil reaction', was obtained in moderate yield.

Under the same conditions, 1,4,7-trimethylazulene (**3a**) as well as the sterically more encumbered isomer, 1,5,8-trimethylazulene (**3b**) gave with PhCHO the corresponding 4- and 8-[(*E*)-styryl]azulenes **4a** and **4b**, respectively, in good yields (*Scheme 2*).

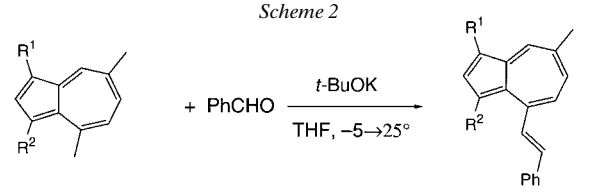
Scheme 1



1 **2**

2	Ar	Yield [%]
2a	Ph	91
2b	4-MeO–C_6H_4	94
2c	4-Cl–C_6H_4	77
2d	4-Me_2N–C_6H_4	85
2e	4-O_2N–C_6H_4	42

Scheme 2



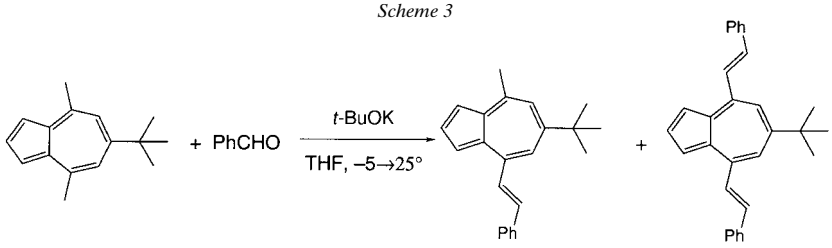
3a R^1 = Me, R^2 = H
3b R^1 = H, R^2 = Me

4a R^1 = Me, R^2 = H (70%)
4b R^1 = H, R^2 = Me (74%)

6-(*tert*-Butyl)-4,8-dimethylazulene (**5**), which carries both Me groups at reactive positions at the seven-membered ring, gave, after treatment with 1.5 mol-equiv. of *t*-BuOK and 2.6 mol-equiv. of PhCHO, indeed two substitution products, namely the mono- and distyryl-substituted azulenes **6** and **7**, in 20(33.5) and 9(14)%[1]) yield, respectively (*Scheme 3*). In this case, the starting azulene **5** could be recovered in 39% yield.

The *Vilsmeier* formylation of the azulene **6** led to the formation of a 3:2 mixture of the two azulene-carbaldehydes **8a** and **8b**, which could be quantitatively separated by

Scheme 3



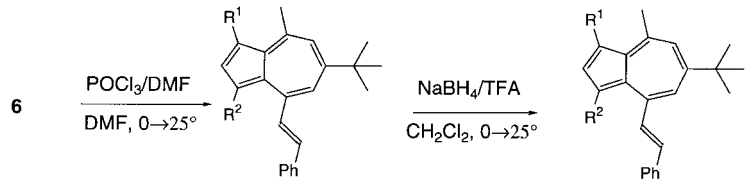
5[a]) **6** (20%) **7** (9%)

[a]) 39% of **5** were recovered

[1]) Yields in parentheses are with respect to reacted **5**.

column chromatography on silica gel (*Scheme 4*). The distinction between both isomers was achieved on the basis of ^{1}H-NOE measurements. Only **8a** showed strong reciprocal effects on the signal of the Me group at C(8) and the signal of the H-atom of the CHO group at C(1). The reduction of the CHO group by *Anderson* and *Breazeale*'s established procedure ($NaBH_4/BF_3 \cdot Et_2O$ in diglyme) [4] gave the expected 1-methylazulenes **9a** and **9b**, respectively, only in very poor yields and the *Kishner-Huang-Minlon* method (*cf.* [5]), also in the variant of *Kabalka* and *Baker* [6], failed almost completely. Finally, good results were obtained when **8a** and **8b** were reduced according to a protocol of *Ketcha* and *Gibble* with $NaBH_4$ in a mixture of CF_3COOH and CH_2Cl_2 [7].

Scheme 4



8a R^1 = CHO, R^2 = H (40%) **9a** R^1 = CH_3, R^2 = H (75%)[a])

8b R^1 = H, R^2 = CHO (59%) **9b** R^1 = H, R^2 = CH_3 (62%)[b])

[a]) 16% of **8a** were recovered. [b]) 30% of **8b** were recovered.

The described synthesis leads to pure **9a** and **9b**, respectively. The other conceivable way, to synthesize first 6-(*tert*-butyl)-1,4,8-trimethylazulene from **5** (*cf.* [8]) and then introduce the styryl substituent according to *Scheme 3*, will lead to the formation of a mixture of **9a** and **9b** which is difficult to separate, since **9a** and **9b** exhibit the same R_f values on silica gel.

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Experimental Part

General. See [1].

General Procedure for the Synthesis of 7-Isopropyl-1-methyl-4-[(*E*)-styryl]azulenes 2. To a stirred soln. of *guaiazulene* (**1**; 1.0 g, 5.0 mmol) in THF (20 ml) at −5° was added *t*-BuOK (1.46 g, 13.0 mmol) within 5 min. After 10 min, the corresponding benzaldehyde derivative (15.0 mmol) was introduced slowly. The temp. was then raised to 25° and stirring continued for 2 h. The reaction was quenched with H_2O and the mixture extracted with hexane. The residue of the hexane extracts was chromatographed on silica gel with hexane to yield the pure azulenes **2**.

*7-Isopropyl-1-methyl-4-[(*E*)-2-phenylethenyl]azulene* (**2a**) [1]: Deep-green crystals (1.30 g, 91%). M.p. 74.0–75.0°.

*7-Isopropyl-4-[(*E*)-2-(4-methoxyphenyl)ethenyl]-1-methylazulene* (**2b**) [1]: Deep-green crystals (1.50 g, 94%). M.p. 71.3–72.8° ([1]: 71.3–72.5°).

*4-[(*E*)-2-(4-Chlorophenyl)ethenyl]-7-isopropyl-1-methylazulene* (**2c**) [1]: Green needles (1.24 g, 77%). M.p. 87.0–88.1° ([1]: 87.1–87.6°).

*4-[(*E*)-2-[4-(Dimethylamino)phenyl]ethenyl]-7-isopropyl-1-methylazulene* (**2d**) [1]: Green needles (1.40 g, 85%). M.p. 121.3–122.1° ([1]: 121.5–122.5°).

*7-Isopropyl-1-methyl-4-[(*E*)-2-(4-nitrophenyl)ethenyl]azulene* (**2e**). Deep-green needles (0.70 g, 42%). M.p. 125.2–126.0° (hexane). R_f (hexane/Et_2O 95:5) 0.25. UV/VIS (hexane): λ_{max} 659 (3.20), 338 (4.50), 289 (4.61), 257 (4.33); λ_{min} 473 (2.99), 309 (4.32), 265 (4.25), 238 (4.21). IR (KBr): 2962*m*, 1595*m*, 1543*w*, 1516*s*, 1470*w*, 1386*m*, 1340*s*, 1109*m*, 1060*m*, 1022*m*, 958*m*, 918*m*, 866*m*, 831*m*, 767*m*, 742*m*, 683*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.29 (*d*, *J*(6,8) = 1.8, H–C(8)); 8.26 (*d*-like, *J* = 8.8, 2 arom. H); 8.20 (*d*, *J* = 16.2, CH=C*H*–C(4)); 7.80 (*d*, *J*(2, 3) = 3.9, H–C(2)); 7.71 (*d*-like, *J* = 8.8, 2 arom. H); 7.58 (*dd*, *J*(5, 6) = 11.0, *J*(6, 8) = 1.8, H–C(6)); 7.52 (*d*, *J*(2, 3) = 3.9, H–C(3)); 7.46 (*d*, *J*(5, 6) = 11.0, H–C(5)); 7.40 (*d*, *J* = 16.2, C*H*=CH–C(4)); 3.20 (*sept.*, *J* = 6.9, Me_2CH); 2.77 (*s*, Me–C(1)); 1.46 (*d*, *J* = 6.9 Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$): 169.98 (*s*); 147.09 (*s*); 143.50 (*s*); 140.91 (*s*); 140.25 (*s*); 137.47 (*d*); 136.89 (*s*); 134.79 (*d*); 134.04 (*d*); 133.34 (*d*); 131.14 (*d*); 127.29 (*d*, 2 arom. C); 126.27 (*s*); 124.05 (*d*, 2 arom. C); 120.10 (*d*); 111.90 (*d*); 38.31 (*d*, Me_2CH); 24.63 (*q*, Me_2CH); 12.94 (*q*). EI-MS: 332 (24, $[M+1]^+$), 331 (100, $M^{+\cdot}$), 316 (40, $[M-Me]^+$). Anal. calc. for $C_{22}H_{21}NO_2$ (331.42): C 79.73, H 6.39, N 4.23; found: C 79.87, H 6.61, N 4.38.

*1,7-Dimethyl-4-[(*E*)-2-phenylethenyl]azulene* (**4a**). The preparation from **3a** (125 mg, 0.73 mmol) was carried out as described for **2** to yield **4a** (133 mg, 70%) as deep-blue crystals. M.p. 132.2–133.1° (hexane). R_f (hexane/Et_2O 95:5) 0.51. UV/VIS (hexane): λ_{max} 651 (2.79), 317 (4.50), 283 (4.50); λ_{min} 446 (1.51), 299 (4.42), 283 (4.12). IR (KBr): 3061*w*, 3025*w*, 2901*w*, 2854*w*, 1545*m*, 1519*s*, 1492*w*, 1461*w*, 1446*m*, 1417*m*, 1380*w*, 1368*w*, 1187*w*, 1028*w*, 959*s*, 925*m*, 877*w*, 806*m*, 781*m*, 748*s*, 716*w*, 689*s*, 605*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 8.18 (*s*, H–C(8)); 8.03 (*d*, *J* = 16.1, CH=C*H*–C(4)); 7.70 (*d*, *J*(2, 3) = 3.8, H–C(2)); 7.66 (*d*-like, *J* = 7.4, 2 arom. H); 7.50 (*d*, *J*(5, 6) = 11.0, H–C(6)); 7.49 (*d*, *J*(2, 3) = 3.8, H–C(3)); 7.44 (*t*-like, *J* = 7.6, 2 arom. H); 7.42 (*d*, *J*(5, 6) = 11.0, H–C(5)); 7.40 (*d*, *J* = 16.1, C*H*=CH–C(4)); 7.36 (*t*-like, *J* = 7.4, 1 arom. H); 2.69 (*s*, Me–C(1)); 2.67 (*s*, Me–C(7)). ^{13}C-NMR (150 MHz, $CDCl_3$)[2]): 141.72 (*s*); 137.30 (*s*); 137.16 (*d*, C(6)); 136.98 (*d*, C(2)); 136.17 (*s*); 135.25 (*d*, C(8)); 133.79 (*d*, CH=CH–C(6)); 129.64 (*d*, CH=CH–C(6)); 129.24 (*s*); 128.80 (*d*, 2 arom. C); 128.31 (*d*, 1 arom. C); 127.04 (*d*, 2 arom. C); 125.51 (*s*); 119.83 (*d*, C(5)); 111.92 (*d*, C(3)); 26.32 (*q*, *Me*–C(7)); 12.96 (*q*, *Me*–C(1)). EI-MS: 259 (19, $[M+1]^+$), 258 (100, $M^{+\cdot}$), 243 (77, $[M-Me]^+$). Anal. calc. for $C_{20}H_{18}$ (258.36): C 92.98, H 7.02; found: C 92.95, H 6.95.

*1,5-Dimethyl-8-[(*E*)-2-phenylethenyl]azulene* (**4b**). The preparation from **3b** (10 mg, 0.059 mmol) was carried out as described for **2** to yield **4b** (11 mg, 74%) as deep-blue crystals. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.18 (*d*, *J* = 16.1, CH=C*H*–C(8)); 8.12 (*d*, *J* = 1.2, H–C(4)); 7.62 (*d*, *J*(2, 3) = 3.7, H–C(2)); 7.59 (*m*, 2 arom. H); 7.43 (*m*, 2 arom. H); 7.36 (*d*, *J*(6, 7) = 10.0, H–C(6)); 7.33 (*m*, 1 arom. H); 7.17 (*d*, *J*(6, 7) = 10.0, H–C(7)); 7.16 (*d*, *J*(2, 3) = 3.7, H–C(3)); 7.04 (*d*, *J* = 16.1, C*H*=CH–C(8)); 2.88 (*s*, Me–C(1)); 2.57 (*s*, Me–C(5)). ^{13}C-NMR (125 MHz, $CDCl_3$): 145.04 (*s*); 141.96 (*s*); 139.99 (*d*, C(2)); 138.61 (*d*, C(4)); 137.25 (*s*); 136.99 (*d*, C(6)); 132.92 (*d*, CH=CH–C(8)); 132.81 (*d*, CH=CH–C(8)); 131.86 (*s*); 129.94 (*s*); 128.84 (*m*, 2 arom. C); 128.07 (*m*, 1 arom. C); 126.72 (*m*, 2 arom. C); 125.27 (*s*); 122.29 (*d*, C(7)); 116.96 (*d*, C(3)); 25.58 (*q*, *Me*–C(5)); 18.77 (*q*, *Me*–C(7)). EI-MS: 259 (19, $[M+1]^+$), 258 (100, $M^{+\cdot}$), 243 (28, $[M-Me]^+$).

*6-(*tert*-Butyl)-8-methyl-4-[(*E*)-2-phenylethenyl]azulene* (**6**). To a stirred soln. of *6-(*tert*-butyl)-4,8-dimethylazulene* (**5**; 3.98 g, 18.4 mmol) in THF (60 ml), *t*-BuOK (3.09 g, 27.6 mmol) was introduced within 5 min, followed, after 10 min, by the addition of PhCHO (4.75 ml, 47 mmol). The temp. was raised to 25° and stirring continued for 2 h. After workup, CC (silica gel; hexane) afforded the following fractions: *1*) 1.50 g (39%) of starting material **5**; *2*) 1.13 g (20%) of **6** as dark-blue crystals; *3*) 0.62 g (9%) of **7** as deep-green crystals.

Data of **6**: M.p. 92.6–93.4° (hexane). R_f (hexane/Et_2O 95:5) 0.56. UV/VIS (hexane): λ_{max} 586 (3.13), 306 (4.58), 285 (4.58); λ_{min} 439 (2.89), 295 (4.55), 239 (4.21). IR (KBr): 3096*w*, 3061*w*, 3027*w*, 2950*s*, 1623*w*, 1578*s*, 1242*s*, 1486*m*, 1446*m*, 1430*m*, 1392*w*, 1374*w*, 1360*m*, 1337*s*, 1241*m*, 1222*w*, 1208*m*, 1071*w*, 1012*w*, 954*s*, 869*w*, 737*s*, 686*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.10 (*d*, *J* = 16.1, CH=C*H*–C(4)); 7.73 (*s*, H–C(5)); 7.72 (*t*, *J*(1, 2) ≈ *J*(2, 3) ≈ 4.0, H–C(2)); 7.65 (*m*, *J* = 7.2, 2 arom. H), 7.54 (*dd*, *J*(1, 3) = 1.5, *J*(1, 2) = 4.0, H–C(1)); 7.45 (*m*, 2 arom. H); 7.38 (*dd*, *J*(1, 3) = 1.5, *J*(2, 3) = 3.8, H–C(3)); 7.37 (*m*, 1 arom. H); 7.36 (*s*, H–C(7)); 7.30 (*d*, *J* = 16.7, C*H*=CH–C(4)); 2.94 (*s*, Me–C(8)); 1.48 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 158.04; 145.16; 143.21; 137.34; 136.82; 135.74; 134.11; 133.51; 131.52; 128.84 (2 arom. C); 128.35; 127.09 (2 arom. C); 124.22; 119.30; 116.31; 115.06; 39.06 (*s*, Me_3C); 32.34 (*q*, Me_3C); 25.90 (*q*, *Me*–C(8)). EI-MS: 300 (100, $M^{+\cdot}$), 285 (59, $[M-Me]^+$), 243 (49). Anal. calc. for $C_{23}H_{24}$ (300.44): C 91.95, H 8.05; found: C 91.89, H 8.00.

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[2]) The signals for two quaternary C-atoms coincided.

*Data of 6-(*tert*-Butyl)-4,8-bis[(*E*)-2-phenylethenyl]azulene* (**7**): M.p. 160.2–161.3° (hexane). R_f (hexane/Et_2O 95:5) 0.54. UV (hexane): λ_{max} 615 (3.28), 333 (4.77); λ_{min} 449 (3.07), 268 (4.28). IR (KBr): 3025*w*, 2963*m*, 1622*w*, 1570*m*, 1540*s*, 1486*s*, 1437*m*, 1361*w*, 1338*m*, 1241*m*, 1224*m*, 1199*m*, 1014*w*, 964*s*, 743*s*, 692*s*, 570*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.08 (*d*, *J* = 16.1, CH=C*H*–C(4,8); 7.77 (*s*, H–C(5, 7)); 7.75 (*t*, *J*(1, 2) = 3.9, H–C(2)); 7.67 (*m*, 4 arom. H); 7.59 (*d*, *J*(1, 2) = 4.0, H–C(1, 3)); 7.44 (*m*, 4 arom. H); 7.36 (*m*, 2 arom. H); 7.33 (*d*, *J* = 16.0, C*H*=CH–C(4, 8)); 1.57 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 157.82; 143.28; 137.28; 136.22; 134.14; 133.86; 131.48; 129.70 (4 arom. C); 128.83; 127.08 (4 arom. C); 119.90; 115.70; 39.40 (*s*, Me_3C); 32.26 (*q*, *Me*$_3$C). EI-MS: 389 (24, $[M+1]^+$), 388 (100, $M^{+\cdot}$), 375 (20, $[M-Me]^+$). Anal. calc. for $C_{30}H_{28}$ (388.55): C 92.74, H 7.26; found: C 92.53, H 7.26.

*6-(*tert*-Butyl)-8-methyl-4-[(*E*)-2-phenylethenyl]azulene-1-carbaldehyde* (**8a**). $POCl_3$ (1.05 ml, 11.5 mmol) was added to DMF (5 ml) under stirring at 0° within 10 min. This *Vilsmeier* reagent was introduced slowly into the stirred soln. of **6** (3.0 g, 10 mmol) in DMF (15 ml) at 0°. After additional stirring at 25° for 30 min, the red mixture was poured into ice-water. Extraction by Et_2O (mixed with 5% of CH_2Cl_2) and CC (silica gel; hexane/Et_2O/CH_2Cl_2 80:5:15) yielded **8b** (1.92 g, 58.5%) as a first fraction and **8a** (1.30 g, 39.6%) as a second fraction.

Data of **8a**: Violet crystals. M.p. 173.0–173.6° (CH_2Cl_2/hexane). R_f (hexane/Et_2O 1:1) 0.34. UV/VIS (hexane): λ_{max} 545 (3.46), 334 (4.61), 307 (4.62), 248 (4.41); λ_{min} 445 (3.39), 320 (4.58), 276 (4.19), 235 (4.36). IR (KBr): 2960*w*, 1633*s*, 1581*w*, 1541*w*, 1499*m*, 1478*w*, 1448*w*, 1425*w*, 1337*s*, 1305*m*, 1228*m*, 1208*m*, 956*m*, 768*m*, 752*m*, 692*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 10.67 (*s*, CHO); 8.32 (*d*, *J*(2, 3) = 4.6, H–C(2)); 7.99 (*d*, *J* = 15.9, CH=C*H*–C(4)); 7.99 (*s*, H–C(5)); 7.69 (*s*, H–C(7)); 7.64 (*d*-like, *J* = 7.4, 2 arom. H); 7.46 (*d*, *J*(2, 3) = 4.6, H–C(3)); 7.44 (*t*-like, *J* = 7.4, 2 arom. H); 7.38 (*t*-like, *J* = 7.4, 1 arom. H); 7.26 (*d*, *J* = 16.0, C*H* = CH–C(4)); 3.23 (*s*, Me–C(8)); 1.56 (*s*, *t*-Bu). ^{1}H-NOE (600 MHz, $CDCl_3$): 10.67 (CHO) → 8.32 (*s*, H–C(2)), 3.23 (*s*, Me–C(8)); 3.23 (*s*, Me–C(8)) → 10.67 (*s*, CHO), 7.69 (*s*, H–C(7)). ^{13}C-NMR (75 MHz, $CDCl_3$): 186.87 (CHO); 159.77 (*s*); 147.74 (*s*); 145.97 (*s*); 141.88 (*s*); 138.03 (*d*); 137.97 (*s*); 136.61 (*s*); 135.74 (*d*); 130.85 (*d*); 130.56 (*d*); 130.25 (*s*); 128.86 (*d*, 2 arom. C); 128.81 (*d*); 127.13 (*d*, 2 arom. C); 124.90 (*d*); 116.45 (*d*); 39.06 (*s*, Me_3C); 31.93 (*q*, *Me*$_3$C); 31.60 (*q*). EI-MS: 329 (15, $[M+1]^+$), 328 (63, $M^{+\cdot}$), 299 (100). Anal. calc. for $C_{24}H_{24}O$ (328.45): C 87.76, H 7.36; found C 87.71, H 7.36.

*Data of 6-(*tert*-Butyl)-4-methyl-8-[(*E*)-2-phenylethenyl]azulene-1-carbaldehyde* (**8b**): Violet crystals. M.p. 166.2–166.8° (CH_2Cl_2/hexane). R_f (hexane/Et_2O 1:1) 0.47. UV (hexane): λ_{max} 553 (3.39), 310 (4.58), 265 (4.40); λ_{min} 448 (3.24), 282 (4.29), 240 (4.35). IR (KBr): 2968*w*, 2869*w*, 1619*s*, 1577*m*, 1526*w*, 1496*m*, 1461*m*, 1446*w*, 1422*m*, 1338*s*, 1312*m*, 1245*m*, 1226*s*, 1100*w*, 1052*w*, 967*w*, 913*w*, 796*m*, 773*m*, 758*m*, 736*m*, 696*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 10.58 (*s*, CHO); 8.29 (*d*, *J*(2, 3) = 4.5, H–C(2)); 8.08 (*d*, *J* = 16.0, CH=C*H*–C(8)); 7.98 (*s*, H–C(7)); 7.66 (*s*, H–C(5)); 7.63 (*d*-like, *J* = 7.5, 2 arom. H); 7.44 (*t*-like, *J* = 7.5, 2 arom. H); 7.36 (*t*-like, *J* = 7.4, 1 arom. H); 7.33 (*d*, *J*(2, 3) = 4.5, H–C(3)); 7.23 (*d*, *J* = 16.0, C*H*=CH–C(8)); 2.99 (*s*, Me–C(4)); 1.56 (*s*, *t*-Bu). ^{1}H-NOE (600 MHz, $CDCl_3$): 10.58 (CHO) → 8.29 (*s*, H–C(2)), 8.08 (*s*, CH=C*H*–C(8)); 2.99 (Me–C(4)) → 7.66 (*s*, H–C(5)), 7.33 (*s*, H–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 186.67 (CHO); 160.17 (*s*); 147.96 (*s*); 146.11 (*s*); 143.34 (*s*); 137.38 (*d*); 136.41 (*s*); 136.37 (*s*); 134.56 (*d*); 134.36 (*d*); 129.46 (*d*); 129.28 (*s*); 128.94 (*d*, 2 arom. C); 128.82 (*d*); 127.18 (*d*, 2 arom. C); 126.47 (*d*); 117.15 (*d*); 39.07 (*s*, Me_3C); 31.94 (*q*, *Me*$_3$C); 26.58 (*q*). EI-MS: 329 (27, $[M+1]^+$), 328 (100, $M^{+\cdot}$), 313 (29), 299 (100). Anal. calc. for $C_{24}H_{24}O$ (328.45): C 87.76, H 7.36; found: C 87.53, H 7.11.

*6-(*tert*-Butyl)-1,8-dimethyl-4-[(*E*)-2-phenylethenyl]azulene* (**9a**). $NaBH_4$ (3.11 g, 82.2 mmol) was added to CF_3COOH (45 ml) at 0° in 30 min. To this mixture, a soln. of **8a** (0.90 g, 2.74 mmol) in CH_2Cl_2 (45 ml) was added at 10° under stirring within 40 min. After the mixture was stirred overnight at 25°, diluted with H_2O, made basic by the addition of NaOH pellets at 0°, it was extracted with Et_2O and chromatographed (silica gel; hexane; Et_2O) to yield 0.15 g (16%) of the starting material **8a** and 0.64 g (75%) of **9a** as deep-blue crystals. M.p. 115.8–116.6° (hexane). R_f (hexane/Et_2O 95:5) 0.55. UV/VIS (hexane): λ_{max} 614 (2.65), 313 (4.47), 285 (4.53); λ_{min} 459 (1.91), 299 (4.43), 240 (4.10). IR (KBr): 3032*w*, 2955*m*, 1567*s*, 1541*m*, 1509*s*, 1446*m*, 1395*w*, 1362*w*, 1242*m*, 1193*w*, 1177*w*, 964*s*, 949*m*, 852*w*, 780*m*, 754*s*, 694*s*. ^{1}H-NMR (600 MHz, $CDCl_3$): 8.07 (*d*, *J* = 16.0, CH=C*H*–C(4)); 7.67 (*m*, 2 arom. H); 7.54 (*s*, H–C(5)); 7.53 (*d*, *J*(2, 3) = 4.1, H–C(2)); 7.47 (*d*, *J*(2, 3) = 4.3, H–C(3)); 7.45 (*m*, 2 arom. H); 7.36 (*m*, 1 arom. H); 7.28 (*d*, *J* = 16.1, C*H*=CH–C(4)); 7.16 (*s*, H–C(7)); 3.11 (*s*, Me–C(8)); 2.99 (*s*, Me–C(1)); 1.56 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz, $CDCl_3$)[2]): 157.67 (*s*); 146.74 (*s*); 143.07 (*s*), 137.77 (C(2)); 137.40 (*s*); 136.62 (*s*); 133.46 (*d*, CH=C–CH(6)); 132.09 (*d*, CH=CH–C(6)); 128.74 (*d*, 2 arom. C); 128.11 (*d*, 1 arom. C); 126.99 (*s*); 126.93 (*d*, 2 arom. C); 124.08 (C(7)); 118.28 (C(5)); 113.75 (C(3)); 38.71 (*s*, *Me*$_3$C); 32.02 (*q*, Me_3C); 28.41 (*Me*–C(8)); 19.65 (*Me*–C(1)). EI-MS: 315 (23, $[M+1]^+$), 314 (99, $M^{+\cdot}$), 299 (100, $[M-Me]^+$). Anal. calc. for $C_{24}H_{26}$ (314.47): C 91.67, H 8.33; found: C 91.66, H 8.28.

*6-(*tert*-Butyl)-1,4-dimethyl-8-[(*E*)-2-phenylethenyl]azulene* (**9b**). The reduction of **8b** (0.79 g, 2.41 mmol) was performed as described for **8a** to yield 0.24 g (30%) of the starting material **8b** and 0.47 g (62%) of **9b** as

deep-blue crystals. M.p. 90.2–91.0°. R_f (hexane/Et_2O 95:5) 0.55. UV/VIS (hexane): λ_{max} 609 (2.74), 291 (4.56); λ_{min} 460 (2.06), 232 (4.15). IR (KBr): 2951*m*, 2863*w*, 1570*s*, 1509*s*, 1459*w*, 1448*m*, 1417*w*, 1362*w*, 1341*m*, 1243*w*, 1199*w*, 1179*w*, 1044*w*, 988*m*, 975*s*, 778*s*, 755*s*, 732*m*, 717*s*, 690*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.18 (*d*, *J* = 16.0, CH=C*H*–C(8)); 7.60 (*m*, 2 arom. H); 7.51 (*d*, *J*(2, 3) = 4.0, H–C(2)); 7.43 (*m*, 2 arom. H); 7.39 (*s*, H–C(7)); 7.33 (*m*, 1 arom. H); 7.28 (*d*, *J*(2, 3) = 4.0, H–C(3)); 7.18 (*s*, H–C(5)); 6.98 (*d*, *J* = 16.1, C*H*=CH–C(8)); 2.90 (*s*, Me–C(4)); 2.82 (*s*, Me–C(1)); 1.48 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): 157.44 (*s*); 145.55 (*s*); 144.61 (*s*); 137.86 (*s*); 137.42 (*d*); 137.27 (*s*); 134.76 (*d*); 132.39 (*d*); 131.54 (*s*); 128.78 (*d*, 2 arom. C); 127.94 (*d*); 126.64 (*d*, 2 arom. C); 126.14 (*s*); 123.12 (*d*); 121.10 (*d*); 114.58 (*d*); 38.61 (*s*, Me_3C); 31.95 (*q*, Me_3C); 25.90 (*q*, *Me*–C(4)); 19.18 (*q*, *Me*–C(1)). EI-MS: 315 (26, $[M+1]^+$), 314 (100, $M^{+\cdot}$), 299 (18, $[M-Me]^+$). Anal. calc. for $C_{24}H_{26}$ (314.47): C 91.67, H 8.33; found: C 91.66, H 8.41.

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