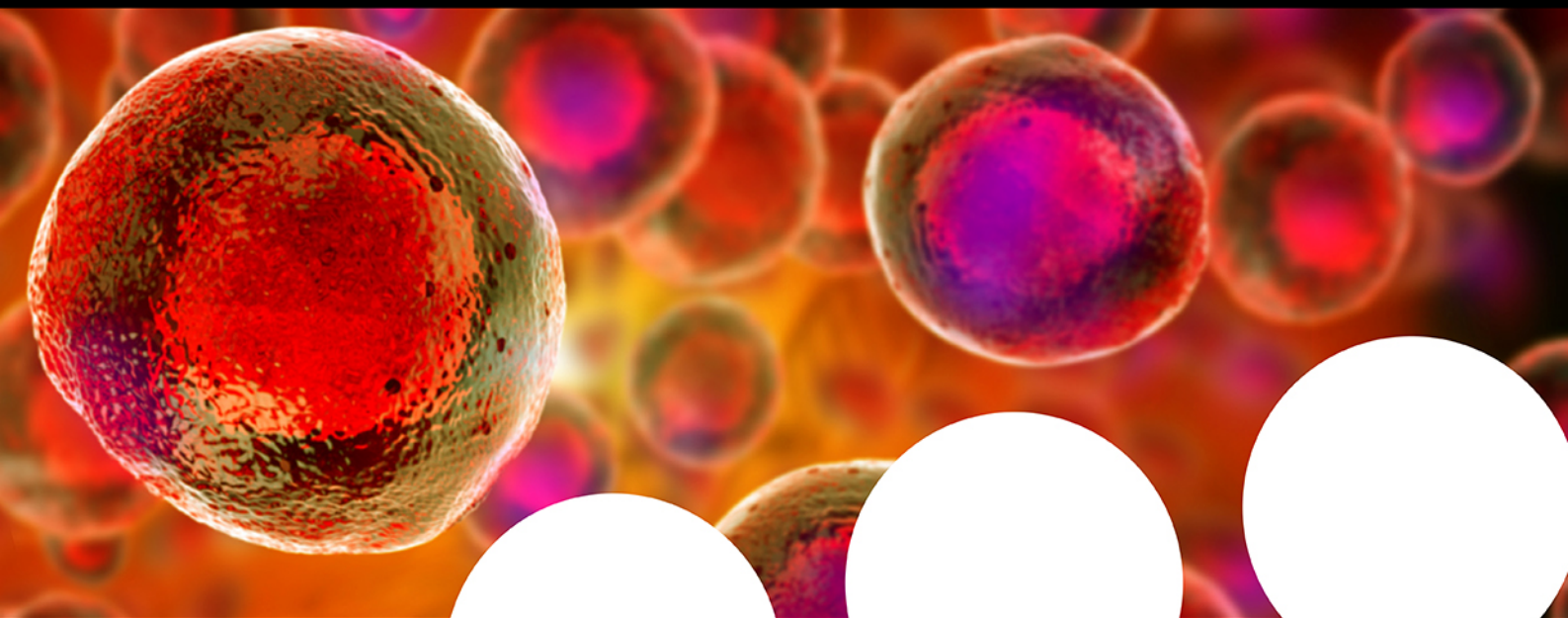


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# Ethynylazulenes – Building Blocks for Novel Oligoazulenes with Ethynyl and Butadiynyl Bridges

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*Dedicated to Professor Rolf Huisgen on the occasion of his 85th birthday*

**Keywords:** Azulenes / Cross-coupling / Oligoazulenes / Oxidative coupling / Palladium

The azulenes **3a,b**, **6a,b**, **9**, **12** and **15** ethynylated in the five-membered ring were prepared by Pd-catalysed cross-coupling of the corresponding iodoazulenes **1a,b**, **4a,b**, **7**, **10** and **13**, respectively, with trimethylsilylacetylene and subsequent desilylation. The synthesis of some acyclic oligomers **23–30**, **32–36** and **38–40** from these ethynylazulenes could be accomplished by oxidative Eglinton coupling as well as Pd/Cu-

catalysed cross-coupling reactions with the appropriate iodoazulenes **1a,b**, **4b**, **31** and **34**. The UV/Vis spectra of the novel oligomers **32**, **35** and **36** allow an estimation of the bandgap ( $E_g$ ) of poly(1,3-azulenyethynylene)s lower than 2 eV.

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## Introduction

Much attention has been focused in the last decades on aromatic compounds with extended  $\pi$ -electron systems because of their importance as materials with special optical and electrical properties for the design of molecular devices.<sup>[1–8]</sup> For this purpose, shape-persistent oligomers like oligophenylenes,<sup>[9]</sup> oligo(phenylenevinylene)s,<sup>[10]</sup> oligo(phenyleneethynylene)s<sup>[11–13]</sup> and oligo(thiopheneethynylene)s<sup>[14,15]</sup> have been prepared, characterized and functionalized to make them suitable modules for further constructions. However, up to now non-benzenoid aromatic or even antiaromatic  $\pi$ -electron systems have so far only scarcely been employed as building blocks for the synthesis of new materials with potentially useful properties, even though some of them should be particularly suitable as structural elements. The azulene system in particular, owing to its remarkable polarizability and tendency to form a stabilized tropylium cation as well as cyclopentadienyl anion, should be able to be utilized as a building block for the construction of advanced materials for electronic and photonic applications.<sup>[16,17]</sup> In this respect we recently developed a versatile procedure for the synthesis of mono- and polyethynyl azulenes<sup>[18]</sup> and studied their synthetic utility as building blocks for the construction of novel cyclic conjugated  $\pi$ -

electron systems.<sup>[19]</sup> In continuation of these studies we report here on the first syntheses of linear oligoazulenes with ethynyl and butadiynyl bridges and describe the experimental details for the preparation of their precursors.<sup>[20]</sup>

## Results and Discussion

### Synthesis of Mono-, Di- and Triethynylazulenes

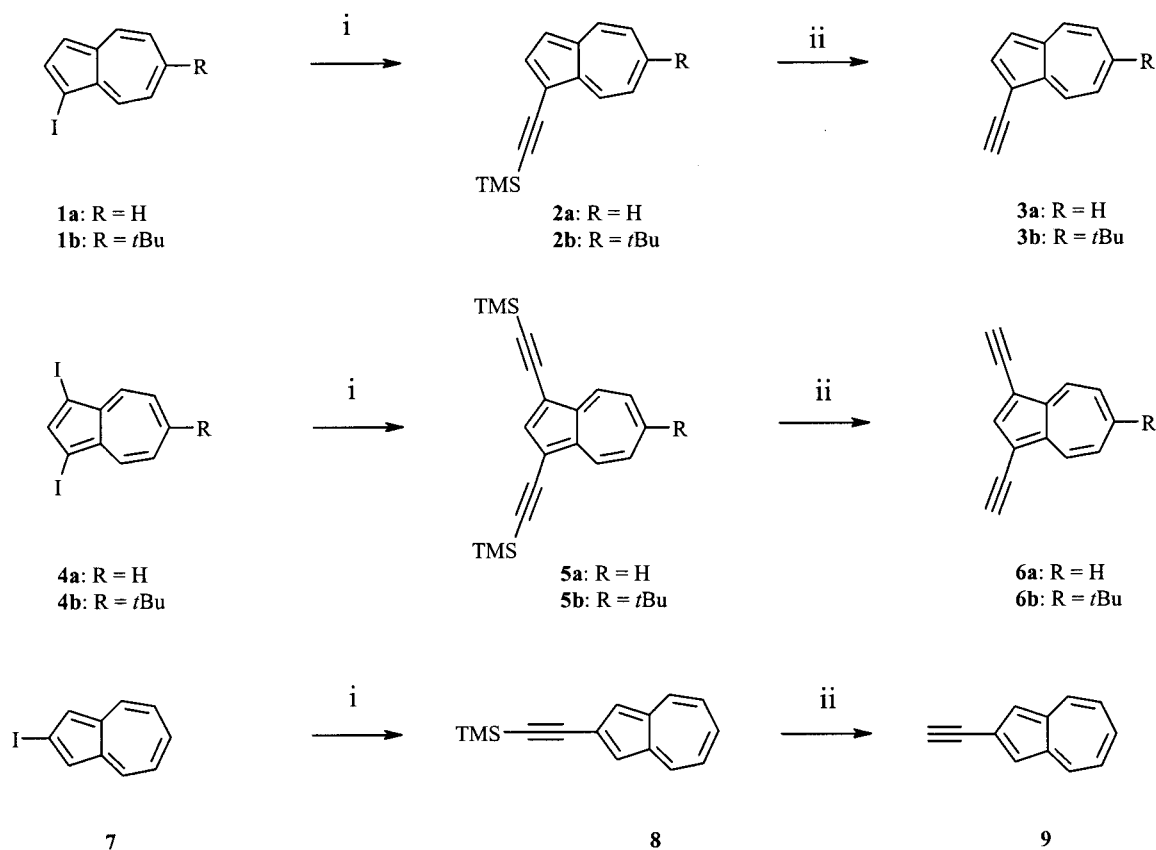
The ethynylation of azulenes at the five-membered ring by a Pd-catalysed cross-coupling reaction proved to be the most efficient synthesis for the series of mono-, di- and triethynylazulenes, as outlined in Schemes 1 and 2.

The iodoazulenes **1a,b** and **4a,b**, which are readily available by electrophilic substitution of azulene with *N*-iodosuccinimide in positions 1 and 3,<sup>[18,21]</sup> were chosen as the key intermediates. Pd<sup>0</sup>-catalysed alkynylation with trimethylsilylacetylene (TMSA) under Sonogashira<sup>[22–24]</sup> conditions furnished the protected monoethynyl- or diethynylazulenes **2a,b** and **5a,b**, respectively, which afforded the 1-ethynyl- and 1,3-diethynylazulenes **3a,b** and **6a,b**, respectively, as blue crystals in 38–99% yield, upon treatment with potassium hydroxide in methanol. In a similar reaction sequence, 2-ethynylazulene (**9**) could be prepared from 2-iodoazulene (**7**)<sup>[25]</sup> via the trimethylsilyl-protected derivative **8**.

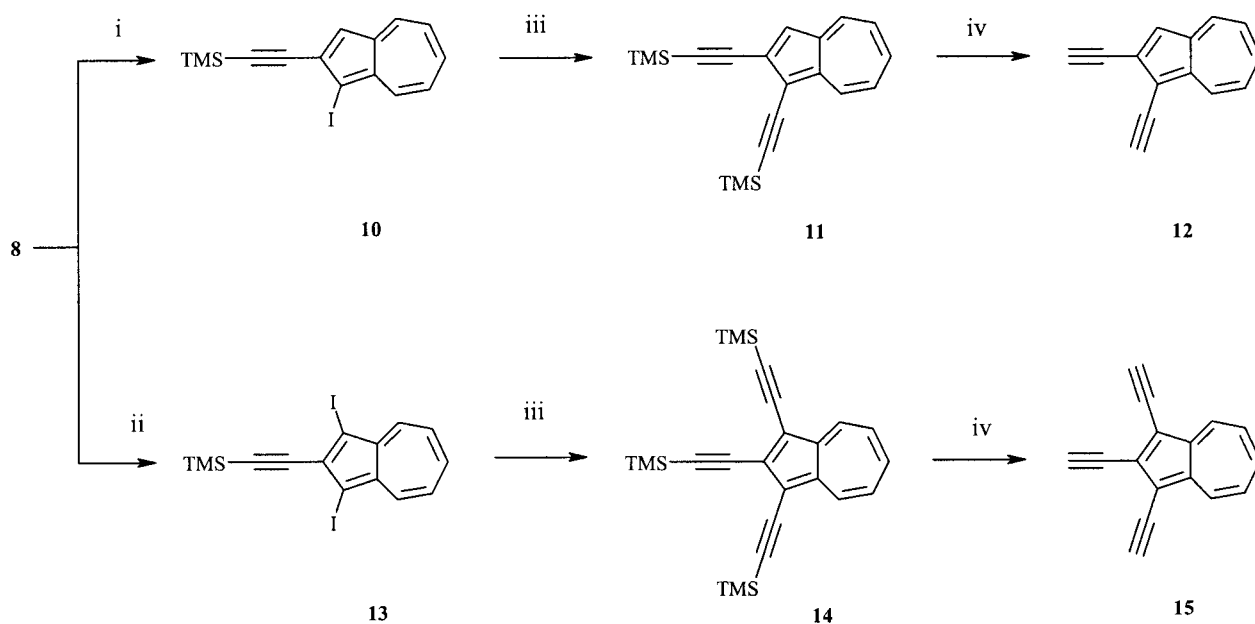
In analogy, the reaction of 2-(trimethylsilylethynyl)azulene (**8**) with one or two equivalents of *N*-iodosuccinimide led to the formation of the corresponding monoiodo- and diiodoazulenes **10** and **13**, respectively, which reacted with

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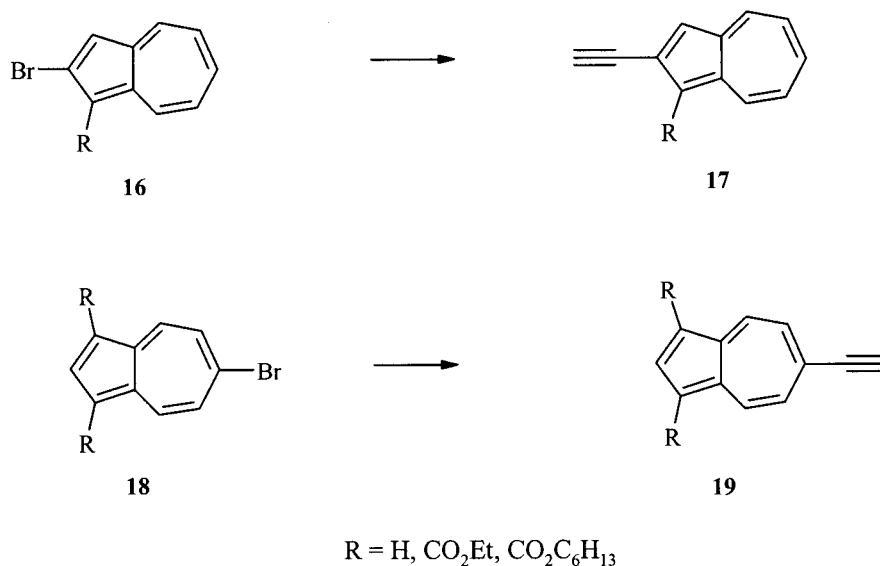
Scheme 1. i) 0.04 mol-%  $[\text{PdCl}_2(\text{PPh}_3)_2]$ , 0.08 mol-%  $\text{CuI}$ ,  $\text{NEt}_3$ , 1 or 2 equiv. TMSA, room temp.; ii) 1 M  $\text{KOH}$  in  $\text{H}_2\text{O}$ ,  $\text{MeOH}$ , room temp.



Scheme 2. i) 1 equiv.  $\text{NIS}$ ,  $\text{CH}_2\text{Cl}_2$ , room temp.; ii) 2 equiv.  $\text{NIS}$ ,  $\text{CH}_2\text{Cl}_2$ , room temp.; iii) 0.04 mol-%  $[\text{PdCl}_2(\text{PPh}_3)_2]$ , 0.08 mol-%  $\text{CuI}$ ,  $\text{NEt}_3$ , 1 or 2 equiv. TMSA, room temp.; iv) 1 M  $\text{KOH}$  in  $\text{H}_2\text{O}$ ,  $\text{MeOH}$ , room temp.

TMSA under  $\text{Pd/Cu}$ -catalysed coupling conditions to give the 1,2-bis(trimethylsilylethynyl)azulene (**11**) and 1,2,3-tris(trimethylsilylethynyl)azulene (**14**), respectively, as green crystals in 80–90% yield. Deprotection of **11** and **14** with

potassium hydroxide in methanol afforded 1,2-diethynyl- (**12**) and 1,2,3-triethynylazulene (**15**) as green or greenish blue crystals in 98% and 96% yields, respectively (Scheme 2).



Scheme 3.

Ito et al.<sup>[26–29]</sup> have recently used a similar methodology with 2-bromo- and 6-bromoazulenes **16** and **18** in order to synthesize 2-ethynyl- and 6-ethynylazulenes **17** and **19**, respectively (Scheme 3), and Makosza et al.<sup>[30]</sup> have prepared 6-ethynylazulenes as well as 1,6-di- and 1,3,6-triethynylazulenes by means of Vicarious Nucleophilic Substitution (VNS). Finally, Fujimori<sup>[31]</sup> also reported some time ago a synthesis of 1-ethynyl- and 2-ethynylazulenes (72%) as well as 1,2-diethynyl- and 1,3-diethynylazulenes (23–26%) from the corresponding aldehydes by treatment with lithium trimethylsilyldiazomethane, although without giving experimental details.

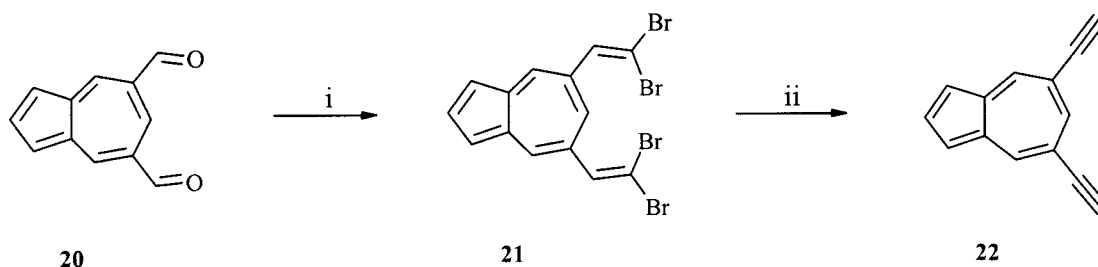
In addition to these syntheses of various ethynylazulenes, we also achieved an ethynylation of the 5- and 7-position of azulene by using the Corey–Fuchs<sup>[32]</sup> method for the conversion of aldehydes into acetylenes. Thus, treatment of the corresponding 5,7-diformylazulene (**20**)<sup>[33]</sup> with triphenylphosphane and tetrabromomethane in dichloromethane furnished the tetrabromo diolefin **21** as greenish-blue crystals in 70% yield. The latter could be converted into the 5,7-diethynylazulene (**22**; 86%) upon treatment with six equivalents of LDA (Scheme 4).

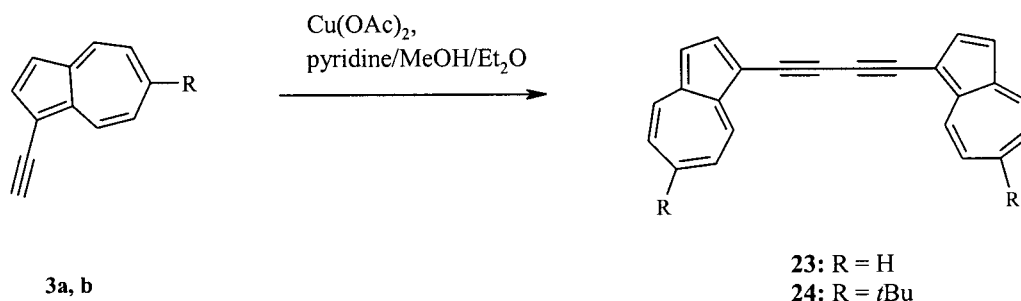
The deprotected ethynylazulenes are only slightly stable at room temperature, and after a few hours they form black solids with a metallic lustre that could not be characterized due to their insolubility. The stability of the ethynylazulene derivatives depends mainly on the number and position of the ethynyl groups at the azulene system.

#### Synthesis of Ethynylene- and Butadiynylene-Bridged Oligoazulenes

The ethynylazulenes **3a,b** and **6a,b** proved to be suitable building blocks for a synthesis of alkynyl-bridged oligoazulenes. Thus, oxidative Eglinton coupling<sup>[34,35]</sup> of 1-ethynylazulenes **3a,b** furnished **23** and **24** in 70% and 75% yields, respectively, as deep-green crystals (Scheme 5).

Higher oligomers with extended  $\pi$ -electron systems are accessible by the Eglinton coupling of 1,3-diethynylazulene **6b** in the presence of 1-ethynylazulene **3b** as end-capping reagent. As expected, butadiynylene-bridged trimer **25** and

Scheme 4. i) PPh<sub>3</sub>, CBr<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, room temp.; ii) 6 equiv. LDA, THF, –90 °C → room temp.

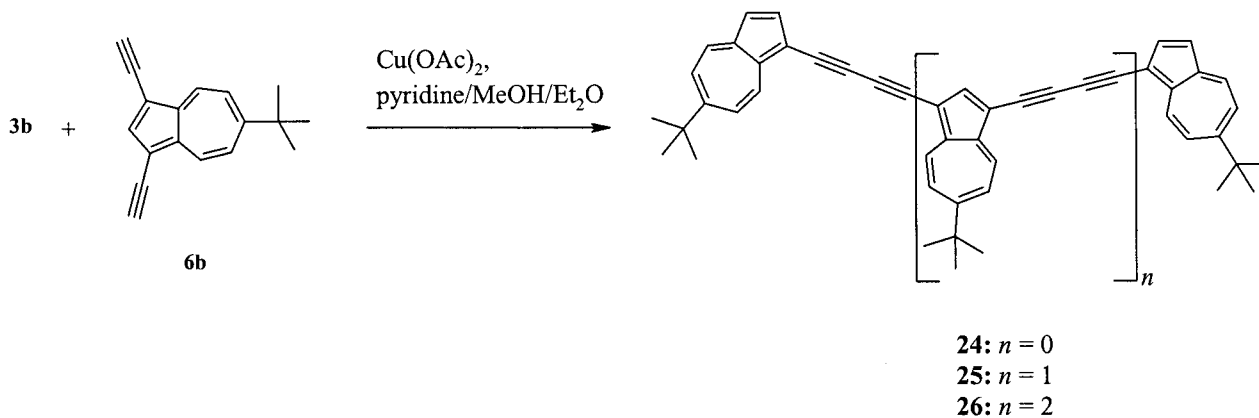


Scheme 5.

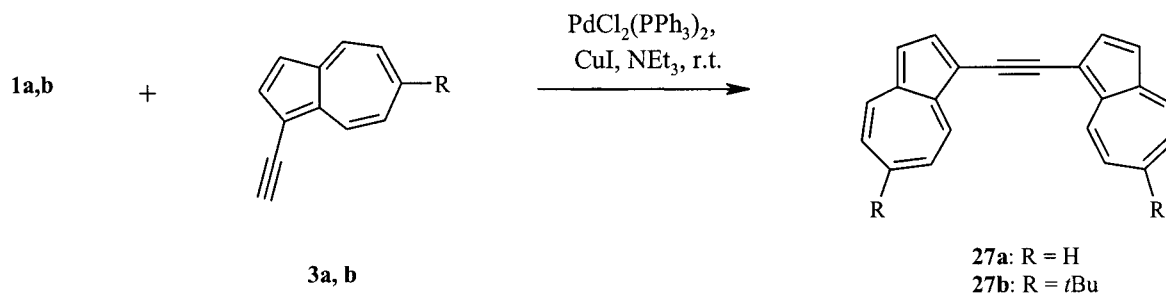
tetramer **26** were obtained as black crystals in 25% and 21% yields, respectively. As a result of homocoupling (oxidative acetylene dimerization) of **3b** the dimer **24** could also be isolated from the reaction mixture in 26% yield (Scheme 6). Ethynylazulenes **3b** and **6b** with *tert*-butyl groups in the seven-membered ring of the azulene moieties were chosen to ensure the solubility of the products.

On the other hand, Sonogashira coupling of the deprotected 1-ethynylazulenes **3a,b** with 1-iodoazulenes **1a,b** led to the likewise deep-green bis(azulen-1-yl)ethynes **27a,b** in 40% and 32% yields, respectively (Scheme 7).<sup>[36]</sup>

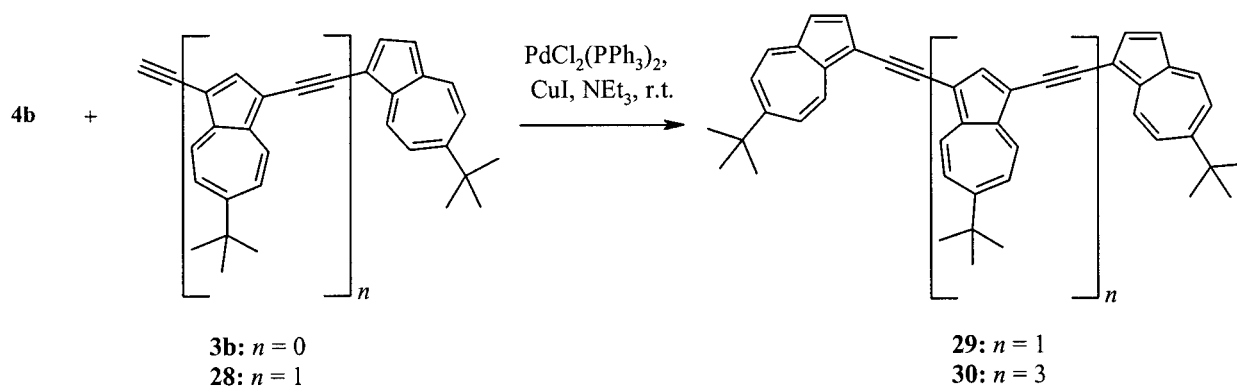
In order to extend the skeleton of **27** by substitution with additional azulenyne groups only the 6-*tert*-butylazulene derivatives were used to ensure sufficient solubility of the higher oligomers in organic solvents and thus to guarantee easier isolation and purification. For this reason, two equivalents of the ethynylazulenes **3b** as well as **28** could be coupled with 6-*tert*-butyl-1,3-diiodoazulene (**4b**) at room temperature under Sonogashira conditions to give 66% of the corresponding trimer **29** and 26% of the pentamer **30**, respectively, which could be isolated as brown or black high melting crystals (Scheme 8).



Scheme 6.



Scheme 7.

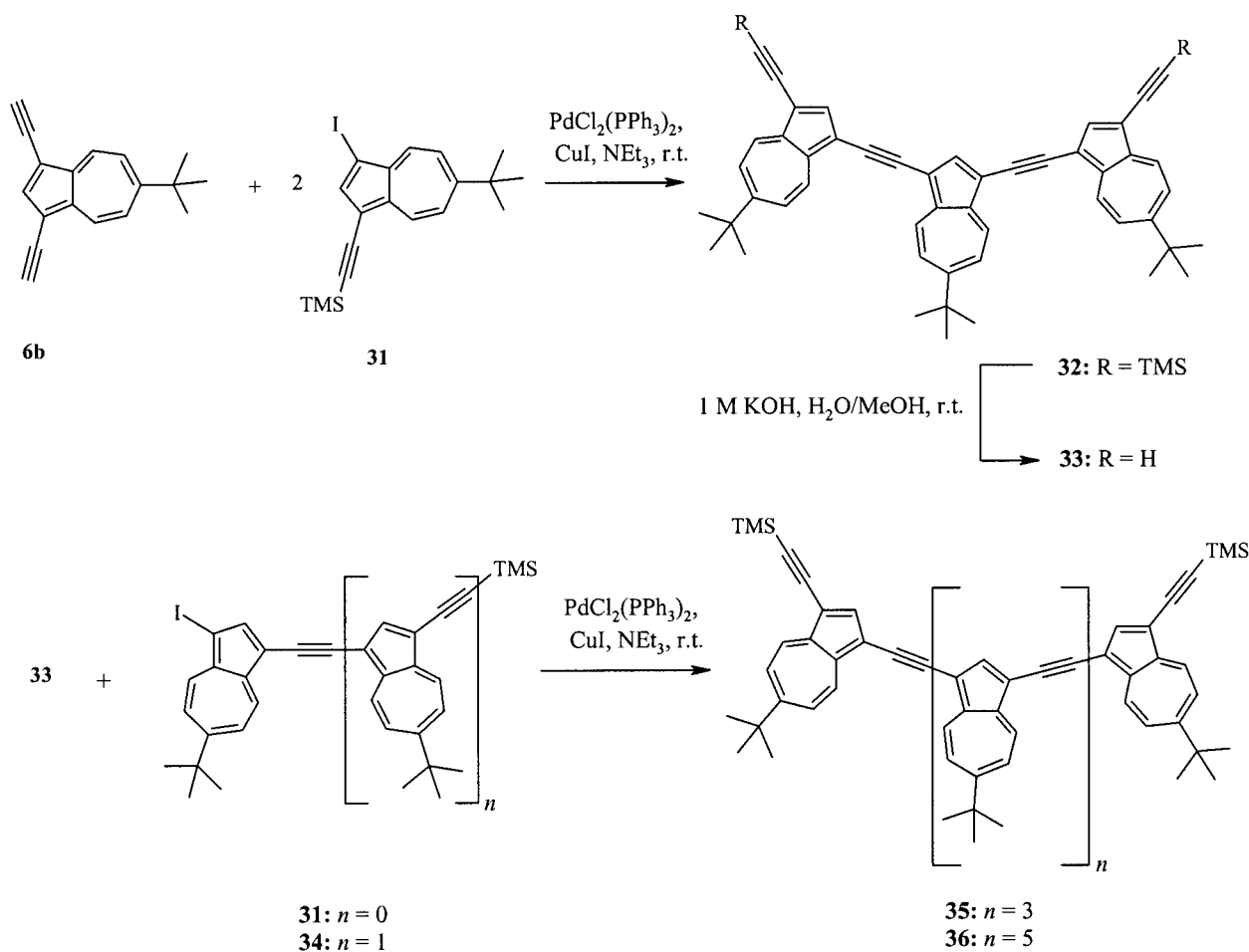


Scheme 8.

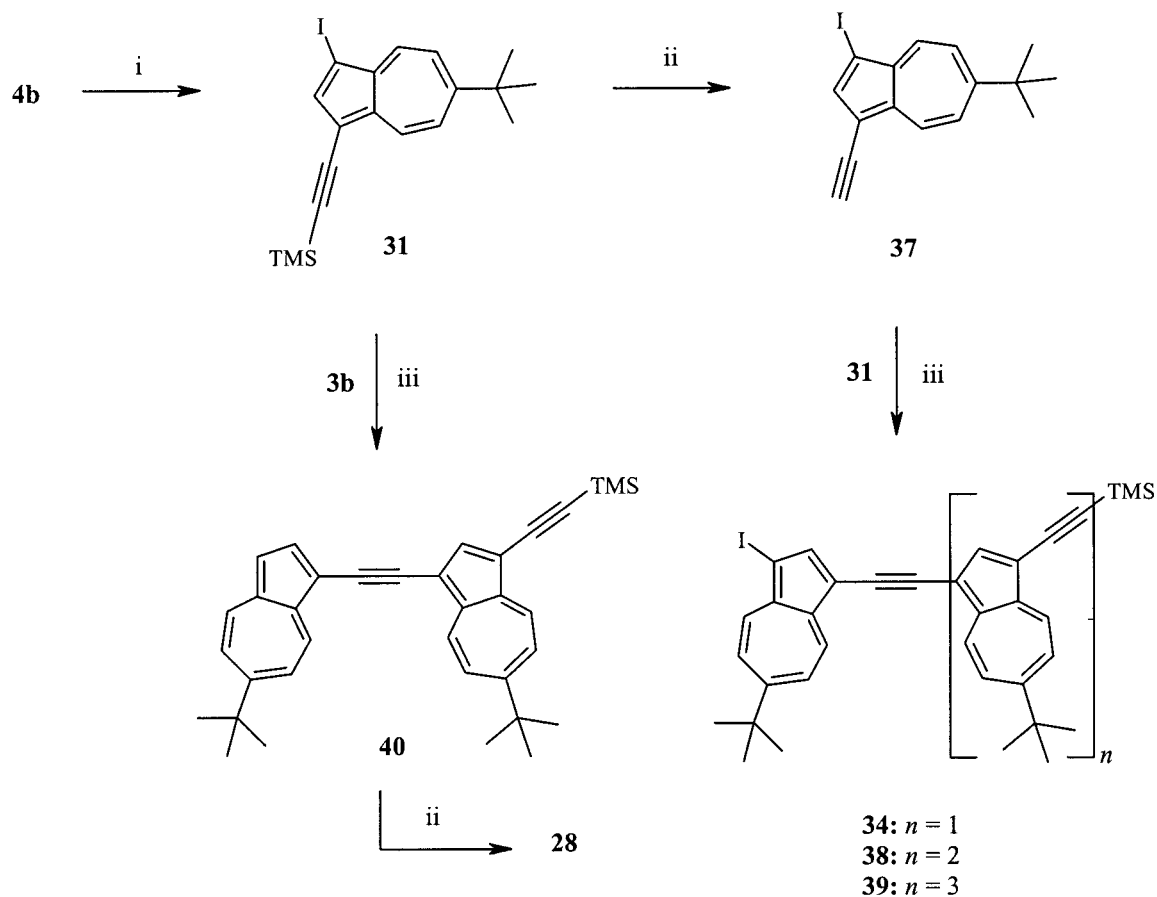
Furthermore, a cross-coupling reaction of 6-*tert*-butyl-1,3-diethynylazulene (**6b**) with 6-*tert*-butyl-3-iodo-1-(trimethylsilylethynyl)azulene (**31**) under similar conditions furnished the corresponding trimethylsilyl-protected trimer **32**, which was easily deprotected by treatment with methanolic potassium hydroxide to give greenish-black crystals, with a metallic lustre, of the 1,1'-diethynyl-trimer **33**, which is a promising building block for higher oligomers. Thus, Sonogashira coupling of the latter with **31** or its dimer **34**

led to the formation of 31% of the pentamer **35** and 19% of the heptamer **36** as green and brownish-black high melting crystals, respectively (Scheme 9).

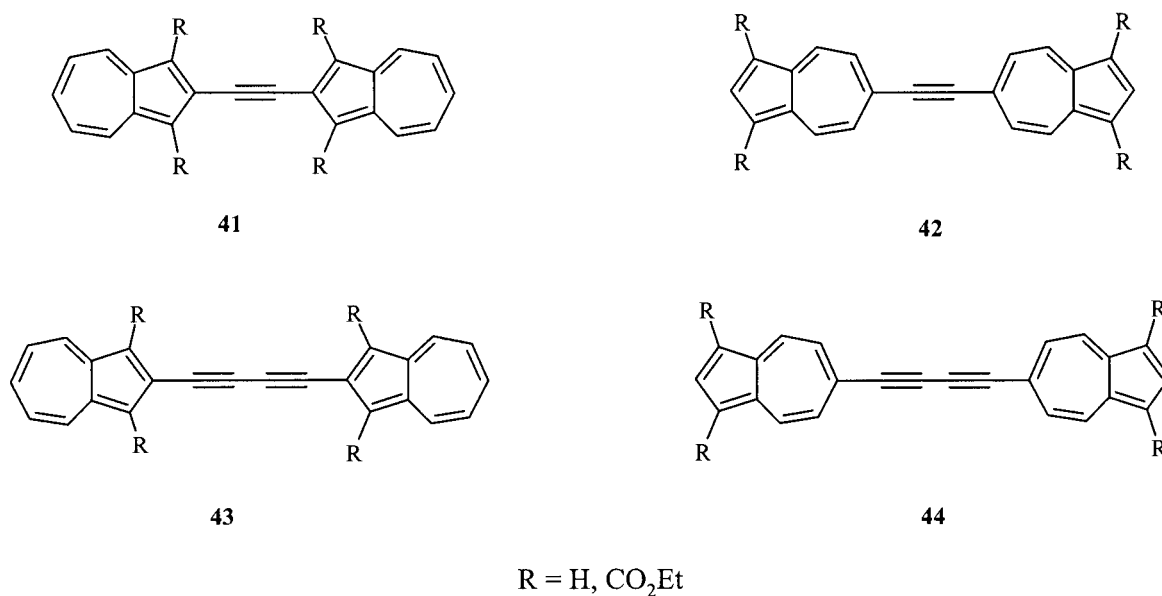
The trimethylsilyl-protected iodoethynylazulenes **31** and **34** were synthesized as outlined in Scheme 10. Cross-coupling of diiodoazulene **4b** with one equivalent of TMSA under Sonogashira conditions afforded **31**, which could be deprotected with potassium hydroxide in methanol to give 6-*tert*-butyl-1-ethynyl-3-iodoazulene (**37**). The Pd/Cu-cata-



Scheme 9.



Scheme 10. i) 0.04 mol-%  $[\text{PdCl}_2(\text{PPh}_3)_2]$ , 0.08 mol-% CuI,  $\text{NEt}_3$ , 1 equiv. TMSA, room temp.; ii) 1 M KOH in  $\text{H}_2\text{O}$ , MeOH, room temp.; iii) 0.04 mol-%  $[\text{PdCl}_2(\text{PPh}_3)_2]$ , 0.08 mol-% CuI,  $\text{NEt}_3$ , room temp.



lysed cross-coupling reaction of **37** with **31** afforded **34** in 68% yield together with 13% of the trimer **38** and 6% of the tetramer **39**. The deprotected ethynylazulene **28** was obtained by a Pd/Cu-catalysed cross-coupling reaction of **31**

with **3b** to give **40** (91%) and subsequent desilylation with methanolic potassium hydroxide.

In addition to these novel ethynylazulene derivatives, Ito et al.<sup>[26–29]</sup> have reported recently on a synthesis of bis-



(azulenyl)ethynes **41** and **42** from the cross-coupling reactions of the appropriate ethynylazulenes **17** and **19** with the bromoazulenes **16** and **18**, respectively, in the presence of  $[\text{Pd}(\text{PPh}_3)_4]$  as a catalyst. Furthermore, these authors obtained bis(azulenyl)butadiynes **43** and **44**, in good yields by the Pd-catalysed oxidative coupling of the corresponding ethynylazulenes **17** and **19**, respectively.

### Electronic Spectra of the Ethynyl-Bridged Oligomers **32**, **35** and **36**

The UV/Vis spectra of the novel ethynyl-bridged oligomers **32**, **35** and **36** as well as the monomer **5b** are shown in Figure 1.

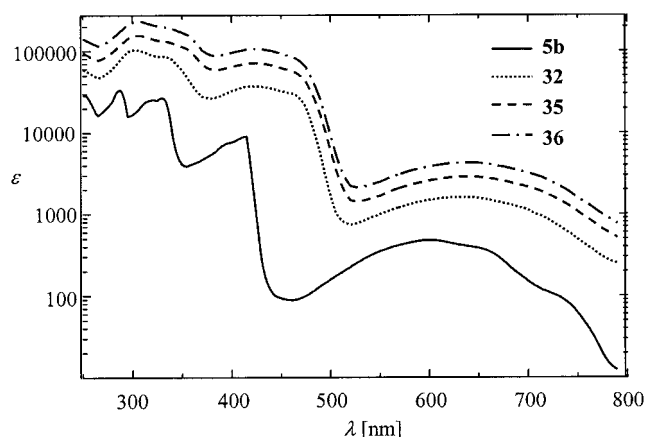


Figure 1. UV/Vis spectra of compounds **5b**, **32**, **35** and **36** in dichloromethane.

The longest wavelength absorption maximum ( $\lambda_{\text{max}}$ ) shifts bathochromically with increasing chain length (Table 1).

Table 1. Longest wavelength absorption ( $\lambda_{\text{max}}$ ) of compounds **5b**, **32**, **35** and **36** in dichloromethane.

Compound	<b>5b</b>	<b>32</b>	<b>35</b>	<b>36</b>
$\lambda_{\text{max}}$ (log $\epsilon$ ) [nm]	600 (2.67)	631 (3.26)	636 (3.48)	640 (3.63)

However, the shift differences diminish with enhancing length of the oligomers and tend towards a limiting value. This value can be determined by plotting the longest wavelength absorption ( $\lambda_{\text{max}}$ ) vs. reciprocal chain length  $1/n$ , which gives a linear relationship<sup>[37,38]</sup> (Figure 2). This allows an estimation of the bandgap ( $E_g$ ) of poly(1,3-azulenyl-ethynylene)s lower than 2 eV. For comparison, the corresponding value for polyacetylene was determined to be 1.4 eV, while the corresponding value for poly(*p*-phenyleneethynylene)s was determined to be about 3.25 eV.

Contrary to this, the analogous 1,3-butadiyne-1,4-diyl-bridged oligomers **24–26** show no significant bathochromic

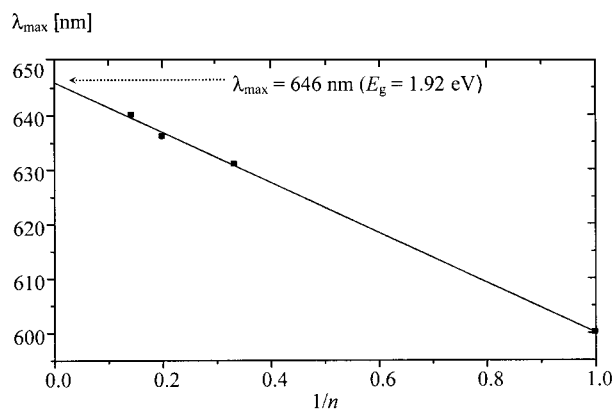


Figure 2. Longest wavelength absorption ( $\lambda_{\text{max}}$ ) vs. reciprocal chain length  $1/n$ .

shift of the longest wavelength absorption in their electronic spectra with increasing length of the oligomers, presumably due to a reduced conjugation.<sup>[39]</sup>

### Experimental Section

All melting points are uncorrected. IR spectra were measured with Beckman IR 5A and Perkin–Elmer 125 spectrometers. NMR spectra were recorded with a Bruker NMR spectrometer WM 300 in  $\text{CDCl}_3$  with tetramethylsilane as internal standard. UV/Vis spectra were recorded with a Beckman UV-5240 spectrometer. Mass spectra (MS) were obtained with a Varian 311A instrument or a Bruker–Frantzen–Esquire-LC. Elemental analyses: Perkin–Elmer CHN 240 B. Column chromatography: Basic alumina [activity B II–III (Brockmann) ICN Biomedicals] and silica gel [70–320 mesh (ASTM) Macherey–Nagel]. Elemental analyses of compounds **3a**, **6a**, **9**, **12**, **15** and **22** did not result in correct values because of a rapid decomposition.

**General Procedure for Iodination of Azulenes:** *N*-Iodosuccinimide (NIS) (1 mmol) was added to a cold solution (0 °C) of the appropriate azulene (1 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL). The reaction mixture was stirred at 0 °C for 2 h (for the preparation of diiodoazulene 2 mmol of NIS was used and the reaction mixture was stirred at room temperature for 4 h). The reaction mixture was then filtered through a short column of alumina (BII–III), the solvent was removed in vacuo, and the remaining material was used in the next step without further purification.

**General Procedure for the Preparation of Trimethylsilyl-Protected Ethynylazulenes:** Bis(triphenylphosphane)palladium(II) chloride (0.04 mol-%) and CuI (0.08 mol-%) were added to a solution of the appropriate iodoazulenes **1a**, **b**, **4a,b**, **7**, **10** or **13** (2 mmol) in triethylamine (TEA; 50 mL) and the reaction mixture was stirred at room temperature under  $\text{N}_2$  for 10 min. Trimethylsilylacetylene (1 or 2 equivalent) in TEA (10 mL) was then added and the reaction mixture was stirred for a further 10 h. It was then filtered through a short column of alumina (BII–III). The solvent was removed in vacuo and the remaining material was purified by chromatography on alumina (BII–III) using *n*-hexane as eluent to give **2a,b**, **5a,b**, **8**, **11**, **14** and **31**. Compounds **2a,b**, **11** and **31** were directly hydrolysed to the corresponding ethynyl derivatives. For further coupling reactions compound **31** was prepared in situ and used without isolation.

**1,3-Bis(trimethylsilylethynyl)azulene (5a):** Deep-green crystals (95%), m.p. 98–100 °C. FT-IR (KBr):  $\tilde{\nu}$  = 2950  $\text{cm}^{-1}$  (C–H), 2130



(C≡C), 1580, 1430, 1360, 1240, 1065, 955, 840, 755, 730. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.28 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>], 7.28 [t, <sup>3</sup>J<sub>H,H</sub> = 9.9 Hz, 2 H, 5-, 7-H], 7.65 (t, <sup>3</sup>J<sub>H,H</sub> = 9.9 Hz, 1 H, 6-H), 7.97 (s, 1 H, 2-H), 8.46 (d, <sup>3</sup>J<sub>H,H</sub> = 9.9 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.3 [Si(CH<sub>3</sub>)<sub>3</sub>], 98.7, 100.29 (C≡C), 110.2, 125.8, 137.0, 139.9, 142.2, 142.2 (C<sub>Az</sub>) ppm. UV/Vis (*n*-hexane): λ<sub>max</sub> (log ε) = 243 nm (4.44) sh, 254 (4.71), 267 (4.40), 273 (4.45), 279 (4.63) sh, 282 (4.78), 290 (4.14), 297 (4.23), 303 (4.32), 310 (4.47), 316 (4.44), 324 (4.40), 331 (4.55), 355 (3.46) sh, 360 (3.54) sh, 364 (3.59) sh, 368 (3.65) sh, 373 (3.74), 380 (3.78), 384 (3.83), 393 (3.88), 401 (3.88), 412 (4.16), 585 (2.42), 608 (2.48), 632 (2.54), 665 (2.44), 697 (2.42), 744 (1.96), 785 (1.91). MS (70 eV): *m/z* (%) = 320 (100) [M<sup>+</sup>], 305 (63), 247 (5), 145 (27). C<sub>20</sub>H<sub>24</sub>Si<sub>2</sub> (320.6): calcd. C 74.93, H 7.55; found C 75.31, H 7.69.

**6-tert-Butyl-1,3-bis(trimethylsilylethynyl)azulene (5b):** Green crystals (76%), m.p. 105 °C. FT-IR (KBr): ν̄ = 2957 cm<sup>-1</sup> (C-H), 2133 (C≡C), 1579, 1439, 1359, 1249, 1085, 845, 758. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.23 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.47 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.53 (d, <sup>3</sup>J<sub>H,H</sub> = 9.9 Hz, 2 H, 5-, 7-H), 7.92 (s, 1 H, 2-H), 8.45 (d, <sup>3</sup>J<sub>H,H</sub> = 9.9 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.5 [Si(CH<sub>3</sub>)<sub>3</sub>], 31.9 [C(CH<sub>3</sub>)<sub>3</sub>], 39.0 [C(CH<sub>3</sub>)<sub>3</sub>], 98.3, 100.8 (C≡C), 109.6, 124.3, 136.1, 141.3, 141.5, 164.3 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane): λ<sub>max</sub> (log ε) = 254 nm (4.58), 274 (4.38) sh, 288 (4.70), 313 (4.48), 319 (4.51), 327 (4.47), 334 (4.58), 363 (3.67), 372 (3.74), 392 (3.93), 412 (4.08), 600 (2.67), 640 (2.59) sh, 723 (2.01) sh. MS (EI, 70 eV): *m/z* (%) = 376 (100) [M<sup>+</sup>], 361 (26), 73 (41), 57 (12). C<sub>24</sub>H<sub>32</sub>Si<sub>2</sub> (376.7): calcd. C 76.53, H 8.56; found C 76.51, H 8.88.

**2-(Trimethylsilylethynyl)azulene (8):** Blue crystals (92%), m.p. 73–74 °C. FT-IR (KBr): ν̄ = 2957 cm<sup>-1</sup> (C-H), 2147 (C≡C), 1585, 1568, 1533, 1470, 1401, 1294, 1247, 1216, 1198, 1138, 1105, 1014, 977, 953, 927, 859, 841, 811, 757, 732, 700, 667, 645, 579, 471, 427. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.34 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>], 7.17 (dd, <sup>3</sup>J<sub>H,H</sub> = 9.8, 9.8 Hz, 2 H, 5-, 7-H), 7.45 (s, 2 H, 1-, 3-H), 7.54 (t, <sup>3</sup>J<sub>H,H</sub> = 9.9 Hz, 1 H, 6-H), 8.25 (d, <sup>3</sup>J<sub>H,H</sub> = 9.2 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.0 [Si(CH<sub>3</sub>)<sub>3</sub>], 101.2, 103.1 (C≡C), 121.0, 123.9, 130.2, 136.8, 137.7, 140.1 (C<sub>Az</sub>) ppm. UV/Vis (*n*-hexane): λ<sub>max</sub> (log ε) = 243 nm (4.20) sh, 252 (4.26) sh, 264 (4.52), 277 (4.39), 283 (4.53) sh, 292 (4.80), 300 (4.82), 304 (4.78), 314 (3.81), 322 (3.40), 330 (3.50) sh, 332 (3.52), 339 (3.52), 346 (3.78), 354 (3.72), 362 (4.16), 372 (3.80), 381 (4.41), 553 (2.42) sh, 584 (2.59), 592 (2.57) sh, 603 (2.53), 631 (2.60), 653 (2.33) sh, 664 (2.33) sh, 696 (2.30). MS (EI, 70 eV): *m/z* (%) = 224 (65) [M<sup>+</sup>], 209 (100), 179 (5), 105 (15). C<sub>15</sub>H<sub>16</sub>Si (224.4): calcd. C 80.29, H 7.19; found C 80.43, H 7.18.

**1,2,3-Tris(trimethylsilylethynyl)azulene (14):** Green crystals (80%), m.p. 178–181 °C. FT-IR (KBr): ν̄ = 2960 cm<sup>-1</sup> (C-H), 2146 (C≡C), 1570, 1426, 1249, 975, 906, 877, 841, 758, 744, 698. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.32 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>], 0.33 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>], 7.27 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.0, 10.0 Hz, 2 H, 5-, 7-H), 7.58 (tt, <sup>3</sup>J<sub>H,H</sub> = 10.0, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, 1 H, 6-H), 8.39 (dd, <sup>3</sup>J<sub>H,H</sub> = 9.5, <sup>4</sup>J<sub>H,H</sub> = 1.1 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 0.1, 0.4 [Si(CH<sub>3</sub>)<sub>3</sub>], 98.0, 100.0, 101.7, 108.7 (C≡C), 113.4, 126.7, 135.8, 137.2, 139.9, 141.5 (C<sub>Az</sub>) ppm. UV/Vis (*n*-hexane): λ<sub>max</sub> (log ε) = 229 nm (4.24), 240 (4.21), 262 (4.45), 274 (4.36) sh, 279 (4.43) sh, 284 (4.59), 289 (4.57), 295 (4.53), 302 (4.84), 316 (4.30) sh, 322 (4.44) sh, 329 (4.58), 334 (3.75), 335 (4.70), 351 (4.85), 371 (3.79), 384 (3.90), 398 (3.67) sh, 403 (3.85) sh, 407 (4.05), 603 (2.46) sh, 645 (2.64), 707 (2.64), 791 (2.24). MS (EI, 70 eV): *m/z* (%) = 416 (100) [M<sup>+</sup>], 401 (6), 313 (15), 73 (76). C<sub>25</sub>H<sub>32</sub>Si<sub>3</sub> (416.8): calcd. C 72.04, H 7.74; found C 72.28, H 7.71.

**General Procedure for Deprotection of Trimethylsilylazulene Derivatives:** KOH (2 mL of a 1 M solution) was added to a suspension of

the appropriate trimethylsilylethynylazulene **2a,b**, **5a,b**, **8**, **11**, **14**, **31**, **32** or **40** (1 mmol) in methanol (30 mL) and the reaction mixture was stirred at room temperature for 2 h. After removal of the solvent in vacuo the remaining residue was extracted with diethyl ether, evaporated and purified by chromatography on alumina (BII-III), with *n*-hexane as an eluent for compounds **3a,b**, **6a,b**, **9**, **12**, **15**, **37** and with CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:4) for compounds **28** and **33**. Compound **28** was prepared in situ and used in the next coupling reactions without isolation.

**1-Ethynylazulene (3a):** Blue crystals (38%), m.p. 36–37 °C (dec.). FT-IR (KBr): ν̄ = 3287 cm<sup>-1</sup> (C≡C-H), 2092 (C≡C), 1577, 1560, 1406, 1393, 783, 736, 579. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 3.51 (s, 1 H, C≡C-H), 7.25 (t, <sup>3</sup>J<sub>H,H</sub> = 10.0 Hz, 1 H, 5-H), 7.27 (t, <sup>3</sup>J<sub>H,H</sub> = 9.6 Hz, 1 H, 7-H), 7.30 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 1 H, 3-H), 7.67 (t, <sup>3</sup>J<sub>H,H</sub> = 9.8 Hz, 1 H, 6-H), 8.00 (s, 1 H, 2-H), 8.32 (d, <sup>3</sup>J<sub>H,H</sub> = 9.8 Hz, 1 H, 4-H), 8.61 (d, <sup>3</sup>J<sub>H,H</sub> = 9.5 Hz, 1 H, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 80.2, 81.4 (C≡C), 109.1, 117.3, 124.1, 124.7, 136.1, 137.3, 138.6, 139.8, 141.3, 142.1 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane, qualitative): λ<sub>max</sub> = 262 nm, 280 sh, 286 sh, 291, 296, 303, 309, 324, 344 sh, 349, 358, 369, 377, 399, 578, 618, 685. HRMS: calcd. for C<sub>12</sub>H<sub>8</sub> 152.0626; found 152.0631.

**6-tert-Butyl-1-ethynylazulene (3b):** Blue crystals (42%), m.p. 67–69 °C. FT-IR (KBr): ν̄ = 3268 cm<sup>-1</sup> (C≡C-H), 2092 (C≡C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.48 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 3.52 (s, 1 H, C≡C-H), 7.23 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 1 H, 3-H), 7.44 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.3, <sup>4</sup>J<sub>H,H</sub> = 1.8 Hz, 1 H, 5-H), 7.50 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.5, <sup>4</sup>J<sub>H,H</sub> = 1.8 Hz, 1 H, 7-H), 7.94 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 1 H, 2-H), 8.27 (d, <sup>3</sup>J<sub>H,H</sub> = 10.3 Hz, 1 H, 4-H), 8.58 (d, <sup>3</sup>J<sub>H,H</sub> = 10.4 Hz, 1 H, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 32.0 [C(CH<sub>3</sub>)<sub>3</sub>], 38.9 [C(CH<sub>3</sub>)<sub>3</sub>], 80.7, 81.1 (C≡C), 108.8, 116.9, 122.6, 123.0, 135.3, 136.6, 139.1, 140.0, 140.9, 162.9 (C<sub>Az</sub>) ppm. UV/Vis (*n*-hexane): λ<sub>max</sub> (log ε) = 234 nm (4.19), 259 (4.03), 261 (4.03), 275 (4.17), 279 (4.31) (sh), 284 (4.45) (sh), 289 (4.61), 294 (4.71), 300 (4.64), 306 (4.79), 334 (3.55), 342 (3.64), 350 (3.74), 359 (3.84), 369 (3.69), 378 (4.01), 642 (2.44) (sh), 680 (2.06) (sh), 715 (2.02) (sh). MS (EI, 70 eV): *m/z* (%) = 208 (100) [M<sup>+</sup>], 193 (41), 178 (30), 152 (13), 57 (16). C<sub>16</sub>H<sub>16</sub> (208.3): calcd. C 92.26, H 7.74; found C 92.22, H 7.79.

**1,3-Diethynylazulene (6a):** Blue crystals (90%), m.p. 69–71 °C (dec). FT-IR (KBr): ν̄ = 3286 cm<sup>-1</sup> (C≡C-H), 2088 (C≡C), 1567, 1440, 1423, 1355, 1290, 1141, 979, 742, 592. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 3.45 (s, 2 H, C≡C-H), 7.26 (t, <sup>3</sup>J<sub>H,H</sub> = 10.0 Hz, 2 H, 5-, 7-H), 7.62 (t, <sup>3</sup>J<sub>H,H</sub> = 9.9 Hz, 1 H, 6-H), 8.05 (s, 1 H, 2-H), 8.49 (d, <sup>3</sup>J<sub>H,H</sub> = 10.0 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 79.1, 81.1 (C≡C), 108.9, 126.0, 137.5, 139.9, 142.2, 142.2 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane, qualitative): λ<sub>max</sub> = 245 nm, 266 sh, 272, 274, 290 sh, 296 sh, 301, 307, 314, 320, 354 sh, 363, 380, 393 sh, 399, 605, 645, 725. HRMS: calcd. for C<sub>14</sub>H<sub>8</sub> 176.0626; found 176.0649.

**6-tert-Butyl-1,3-diethynylazulene (6b):** Dark-blue crystals (99%), m.p. 102 °C. FT-IR (KBr): ν̄ = 3278 cm<sup>-1</sup> (C≡C-H), 2089 (C≡C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.46 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 3.44 (s, 2 H, C≡C-H), 7.54 (d, <sup>3</sup>J<sub>H,H</sub> = 11.0 Hz, 2 H, 5-, 7-H), 7.98 (s, 1 H, 2-H), 8.50 (d, <sup>3</sup>J<sub>H,H</sub> = 11.0 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 31.9 [C(CH<sub>3</sub>)<sub>3</sub>], 39.7 [C(CH<sub>3</sub>)<sub>3</sub>], 79.5, 81.2 (C≡C), 108.3, 124.4, 136.1, 141.2, 141.8, 164.6 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane): λ<sub>max</sub> (log ε) = 244 nm (4.55), 275 (4.43), 298 (4.37) (sh), 304 (4.50), 310 (4.56), 318 (4.55), 324 (4.67), 355 (3.63), 363 (3.70), 380 (3.82), 392 (3.86), 399 (4.02), 587 (2.66), 623 (2.59) (sh), 700 (2.07) (sh). MS (EI, 70 eV): *m/z* (%) = 232 (100) [M<sup>+</sup>], 217 (51), 202 (46), 176 (13), 57 (10). C<sub>18</sub>H<sub>16</sub> (232.3): calcd. C 93.06, H 6.94; found C 93.45, H 7.00.

**2-Ethynylazulene (9):** Blue crystals (99%), m.p. 66 °C. FT-IR (KBr):  $\tilde{\nu}$  = 3270 cm<sup>-1</sup> (C≡C–H), 1561, 1464, 1398, 815, 737, 656, 635, 624, 609, 577. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.52 (s, 1 H, C≡C–H), 7.19 (dd, <sup>3</sup>J<sub>H,H</sub> = 9.8, 9.8 Hz, 2 H, 5-, 7-H), 7.48 (s, 2 H, 1-, 3-H), 7.57 (tt, <sup>3</sup>J<sub>H,H</sub> = 9.9, <sup>4</sup>J<sub>H,H</sub> = 0.9 Hz, 1 H, 6-H), 8.27 (d, <sup>3</sup>J<sub>H,H</sub> = 9.2 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 81.8, 83.0 (C≡C), 121.0, 124.0, 129.1, 137.1, 138.0, 139.9 (C<sub>Az</sub>) ppm. UV/Vis (*n*-hexane, qualitative):  $\lambda_{\max}$  = 260 nm, 276 sh, 280 sh, 286 sh, 288, 295, 299, 310, 317, 327, 332, 340, 348, 356, 365, 373, 546 sh, 566 sh, 576 sh, 582, 592, 605, 618, 630, 638 sh, 651, 672, 696. MS (EI, 70 eV): *m/z* (%) = 152 (100) [M<sup>+</sup>], 126 (5), 76 (11).

**1,2-Diethynylazulene (12):** Green crystals (98%), m.p. 77–78 °C. FT-IR (KBr):  $\tilde{\nu}$  = 2095 cm<sup>-1</sup> (C≡C), 1570, 1469, 1445, 1415, 1384, 1292, 1245, 1148, 1071, 1020, 957, 810, 737, 723, 685, 670, 644, 625, 513. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.68 (s, 1 H, C≡C–H), 3.71 (s, 1 H, C≡C–H), 7.21 (dd, <sup>3</sup>J<sub>H,H</sub> = 9.8, 9.8 Hz, 1 H, 5-H), 7.26 (dd, <sup>3</sup>J<sub>H,H</sub> = 9.8, 9.8 Hz, 1 H, 7-H), 7.36 (s, 1 H, 3-H), 7.59 (t, <sup>3</sup>J<sub>H,H</sub> = 9.8 Hz, 1 H, 6-H), 8.19 (d, <sup>3</sup>J<sub>H,H</sub> = 9.6 Hz, 1 H, 4-H), 8.50 (d, <sup>3</sup>J<sub>H,H</sub> = 9.6 Hz, 1 H, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 78.4, 80.2, 83.9, 86.0 (C≡C), 112.2, 120.5, 125.3, 125.8, 131.5, 137.7, 137.9, 139.3, 141.7 (C<sub>Az</sub>) ppm. UV/Vis (*n*-hexane, qualitative):  $\lambda_{\max}$  = 245 nm, 270, 291 sh, 297 sh, 306, 319, 340, 345, 352, 362 sh, 369, 374, 382, 388, 578 sh, 606, 617, 646, 664, 679, 714, 739. MS (EI, 70 eV): *m/z* (%) = 176 (100) [M<sup>+</sup>].

**1,2,3-Triethynylazulene (15):** Greenish-blue crystals (96%), m.p. 77–78 °C. FT-IR (dichloromethane solution):  $\tilde{\nu}$  = 3303 cm<sup>-1</sup> (C≡C–H), 2098 (C≡C), 1601, 1569, 1452, 1429, 654, 590. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.63 (s, 2 H, 1-, 3-C≡C–H), 3.90 (s, 1 H, 2-C≡C–H), 7.35 (dd, <sup>3</sup>J<sub>H,H</sub> = 9.5, 9.5 Hz, 2 H, 5-, 7-H), 7.68 (tt, <sup>3</sup>J<sub>H,H</sub> = 9.9, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, 1 H, 6-H), 8.50 (d, <sup>3</sup>J<sub>H,H</sub> = 9.3 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 77.7, 78.8, 84.2, 89.2 (C≡C), 112.1, 127.1, 134.2, 137.6, 140.6, 141.7 (C<sub>Az</sub>) ppm. UV/Vis (*n*-hexane, qualitative):  $\lambda_{\max}$  = 231 nm, 253, 271, 276, 284, 287, 318 sh, 323, 339, 359, 371, 377, 388, 393, 578, 580, 615, 672, 692, 708 sh, 748, 774. MS (FD): *m/z* (%) = 200 (100) [M<sup>+</sup>].

**6-tert-Butyl-1,3-bis-[(6-tert-butyl-3-ethynyl)azulene-1-yl]ethynylazulene (33):** Greenish-black crystals (67%), m.p. > 280 °C. FT-IR (KBr):  $\tilde{\nu}$  = 3288 cm<sup>-1</sup> (C≡C–H), 2964, 2928, 2870 (C–H), 2092 (C≡C), 1576, 1361, 837. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 1.48 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.49 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 3.47 (s, 2 H, C≡C–H), 7.48–7.57 (m, 6 H, 5-, 5'-, 7-, 7'-H), 8.09 (s, 2 H, 2'-H), 8.17 (s, 1 H, 2-H), 8.48 (d, <sup>3</sup>J<sub>H,H</sub> = 10.4 Hz, 2 H, 4'-H), 8.60 (d, <sup>3</sup>J<sub>H,H</sub> = 10.9 Hz, 2 H, 8'-H), 8.65 (d, <sup>3</sup>J<sub>H,H</sub> = 10.4 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 30.4, 31.9 [C(CH<sub>3</sub>)<sub>3</sub>], 39.0 [C(CH<sub>3</sub>)<sub>3</sub>], 79.7, 81.2, 89.2, 89.4 (C≡C), 108.7, 110.7, 111.0, 123.6, 124.0, 124.0, 135.9, 136.2, 136.4, 140.2, 140.5, 140.5, 141.2, 141.3, 164.4, 164.5 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 245 nm (4.77), 297 (4.98), 329 (4.88), 422 (4.57), 455 (4.49), 626 (3.26). MS (FD): *m/z* (%) = 644 (80) [M<sup>+</sup>], 220 (100). C<sub>50</sub>H<sub>44</sub> (644.9): calcd. C 93.12, H 6.88; found C 93.20, H 6.95.

**6-tert-Butyl-3-ethynyl-1-iodoazulene (37):** Deep-blue crystals (97%), m.p. 55–57 °C. FT-IR (KBr):  $\tilde{\nu}$  = 3310 cm<sup>-1</sup> (C≡C–H), 2961, 2866 (C–H), 2089 (C≡C), 1585, 1420, 1364, 1295, 856, 834, 810, 640, 543. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 1.45 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 3.48 (s, 1 H, C≡C–H), 7.48–7.57 (m, 2 H, 5-, 7-H), 7.95 (s, 1 H, 2-H), 8.16 (d, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, 1 H, 8-H), 8.45 (d, <sup>3</sup>J<sub>H,H</sub> = 10.4 Hz, 1 H, 4-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 31.9 [C(CH<sub>3</sub>)<sub>3</sub>], 39.1 [C(CH<sub>3</sub>)<sub>3</sub>], 79.2, 81.9 (C≡C), 73.1, 110.5, 123.5, 124.0, 135.2, 138.7, 139.4, 141.4, 145.3, 164.3 (C<sub>Az</sub>) ppm.

UV/Vis (dichloromethane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 243 nm (4.46), 266 (4.15), 301 (4.52) sh, 306 (4.60), 314 (4.61) sh, 319 (4.70), 340 (3.61), 348 (3.68), 357 (3.76), 369 (3.79), 382 (3.80) sh, 389 (3.98), 586 (2.66), 625 (2.61), 700 (2.11). MS (FD): *m/z* (%) = 334 (100) [M<sup>+</sup>], 57 (15). C<sub>16</sub>H<sub>15</sub>I (334.2): calcd. C 57.50, H 4.52; found C 57.59, H 4.47.

**5,7-Bis[(1',1'-dibromo)ethen-2'-yl]azulene (21):** Triphenylphosphane (12 mmol) and tetrabromomethane (6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added to a stirred solution of **20**<sup>[33]</sup> (2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then filtered through a short column of alumina (BII-III). The solvent was removed in vacuo and the remaining material was purified by chromatography on alumina (BII-III) using *n*-pentane as eluent to give the tetrabromo diolefin **21** as greenish-blue crystals (70%), m.p. 90–91 °C. FT-IR (KBr):  $\tilde{\nu}$  = 1410 cm<sup>-1</sup>, 1053, 965, 944, 914, 764, 630, 561, 358. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.50 (d, <sup>3</sup>J<sub>H,H</sub> = 3.8 Hz, 2 H, 1-, 3-H), 7.61 (s, 1 H, 6-H), 7.67 (s, 2 H, = CH), 7.92 (d, <sup>3</sup>J<sub>H,H</sub> = 3.8 Hz, 1 H, 2-H), 8.38 (d, <sup>4</sup>J<sub>H,H</sub> = 1.5 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 91.51 (CH=CBr<sub>2</sub>), 121.94, 128.97, 137.15, 137.83, 138.60, 138.72, 139.87 (CH=CBr<sub>2</sub>, C<sub>Az</sub>) ppm. UV/Vis (*n*-hexane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 233 nm (4.28), 293 (4.71), 298 (4.71), 390 (4.06), 533 (2.36) sh, 554 (2.52) sh, 574 (2.46), 596 (2.77), 618 (2.78), 651 (2.84), 680 (2.60), 721 (2.59). MS (EI, 70 eV): *m/z* (%) = 496 (52) [M<sup>+</sup>], 336 (28), 256 (7), 176 (100), 150 (35), 126 (21); each peak appears as a cluster of isotope peaks. C<sub>14</sub>H<sub>8</sub>Br<sub>4</sub> (495.8): calcd. C 33.91, H 1.63; found C 33.94, H 1.51.

**5,7-Diethynylazulene (22):** A solution of *n*BuLi (2.5 N in *n*-hexane, 1.7 mL) was added to a cold stirred solution (–90 °C) of diisopropylamine (4.3 mmol) in THF (5 mL). A solution of **21** (0.66 mmol) in anhydrous THF (10 mL) was then added. The reaction mixture was stirred for 10 min at –90 °C and then warmed to –30 °C. Ammonium chloride solution (10 mL) and diethyl ether (30 mL) were then added. The ether layer was separated, the solvent was removed in vacuo and the remaining solid was purified by chromatography on alumina (BII-III) using *n*-pentane as an eluent to give **22** as greenish-blue crystals (86%), m.p. 81–82 °C. FT-IR (KBr):  $\tilde{\nu}$  = 3305 cm<sup>-1</sup> (C≡C–H), 2088 (C≡C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.12 (s, 2 H, C≡C–H), 7.45 (d, <sup>3</sup>J<sub>H,H</sub> = 3.8 Hz, 2 H, 1-, 3-H), 7.92 (t, <sup>3</sup>J<sub>H,H</sub> = 3.8 Hz, 1 H, 2-H), 8.01 (t, <sup>4</sup>J<sub>H,H</sub> = 1.4 Hz, 1 H, 6-H), 8.45 (d, <sup>4</sup>J<sub>H,H</sub> = 1.4 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 76.0, 86.8 (C≡C), 115.8, 122.3, 138.6, 139.1, 140.2, 143.8 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane, qualitative):  $\lambda_{\max}$  = 258 nm, 286, 296, 321, 353, 366, 384, 555, 577, 600, 618, 652, 677, 721. MS (EI, 70 eV): *m/z* (%) = 176 (100) [M<sup>+</sup>], 150 (9), 126 (9), 88 (7). HRMS: calcd. for C<sub>14</sub>H<sub>8</sub> 176.0626; found 176.0639.

#### General Procedure for the Oxidative Coupling of Ethynylazulenes:

A solution of the appropriate ethynylazulene **3a,b** (4 mmol) or a mixture (3:1) of **3b** and **6b** (4 mmol) in pyridine (10 mL) was added slowly over a period of 30 min. to a boiling solution of copper(II) acetate (1.8 g, 10 mmol) in pyridine/methanol/diethyl ether (50 mL, 1:1:4) and the reaction mixture was heated under reflux for 2 h. The mixture was cooled to 0 °C and hydrolysed carefully with 2 N HCl (100 mL) and then dichloromethane (50 mL) was added to the resulting suspension. The layers were separated and the aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 × 50 mL). The combined organic layers were washed with water, dried with Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed in vacuo and the remaining residue was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:3) to give **23–26**.

**1,4-Bis(azulene-1-yl)-1,3-butadiyne (23):** Compound **3a** afforded **23** as deep-green crystals (70%), m.p. 215–217 °C. FT-IR (KBr):  $\tilde{\nu}$  =

2127 cm<sup>-1</sup> (C≡C), 1572, 1451, 1395, 1261, 1096, 1015, 805, 784, 733, 571. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.26 (dd, <sup>3</sup>J<sub>H,H</sub> = 9.9, 9.9 Hz, 2 H, 5-H), 7.30 (d, <sup>3</sup>J<sub>H,H</sub> = 4.1 Hz, 2 H, 3-H), 7.34 (dd, <sup>3</sup>J<sub>H,H</sub> = 9.9, 9.9 Hz, 2 H, 7-H), 7.67 (dd, <sup>3</sup>J<sub>H,H</sub> = 9.9, 9.9 Hz, 2 H, 6-H), 8.04 (d, <sup>3</sup>J<sub>H,H</sub> = 4.1 Hz, 2 H, 2-H), 8.31 (d, <sup>3</sup>J<sub>H,H</sub> = 9.6 Hz, 2 H, 4-H), 8.68 (d, <sup>3</sup>J<sub>H,H</sub> = 9.7 Hz, 2 H, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 79.5, 80.0 (C≡C), 109.5, 118.4, 125.2, 126.0, 137.1, 138.1, 139.69, 140.5, 142.3, 143.4 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane): λ<sub>max</sub> (log ε) = 235 nm (4.63), 259 (4.47), 288 (4.65), 308 (4.59), 320 (4.59), 327 (4.60), 393 (4.38) sh, 407 (4.48), 414 (4.48), 423 (4.42) sh, 451 (4.43), 578 (2.97) sh, 603 (3.00), 650 (2.86) sh. MS (EI, 70 eV): *m/z* (%) = 302 (100) [M<sup>+</sup>], 151 (13). C<sub>24</sub>H<sub>14</sub> (302.4): calcd. C 95.33, H 4.67; found C 94.64, H 4.86.

**1,4-Bis(6-tert-butylazulen-1-yl)-1,3-butadiyne (24):** Compound **3b** afforded **24** as deep-green crystals (75%), m.p. 244–245 °C. FT-IR (KBr): ν̄ = 2965 cm<sup>-1</sup> (C–H), 2134 (C≡C), 1577, 1404, 838, 779, 713. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.47 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.20 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 3-H), 7.44 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.3, <sup>4</sup>J<sub>H,H</sub> = 1.7 Hz, 2 H, 5-H), 7.50 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.5, <sup>4</sup>J<sub>H,H</sub> = 1.8 Hz, 2 H, 7-H), 7.95 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 2-H), 8.24 (d, <sup>3</sup>J<sub>H,H</sub> = 10.3 Hz, 2 H, 4-H), 8.62 (d, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, 2 H, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 31.9 [C(CH<sub>3</sub>)<sub>3</sub>], 38.8 [C(CH<sub>3</sub>)<sub>3</sub>], 79.1, 79.9 (C≡C), 109.0, 117.3, 122.9, 123.4, 135.7, 136.5, 139.4, 140.5, 142.8, 163.2 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane): λ<sub>max</sub> (log ε) = 263 nm (4.44) sh, 294 (4.68), 315 (4.64), 331 (4.68), 397 (4.39) sh, 409 (4.48), 417 (4.48), 425 (4.44) sh, 454 (4.44), 589 (3.11), 632 (2.99) sh. MS (EI, 70 eV): *m/z* (%) = 414 (100) [M<sup>+</sup>], 202 (7). C<sub>32</sub>H<sub>30</sub> (414.6): calcd. C 92.71, H 7.29; found C 92.65, H 7.45.

**Dimer 24, Trimer 25 and Tetramer 26:** Compounds **3b** and **6b** afforded a mixture of **24** (26%), **25** and **26**, which were separated by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:3). **25:** Black crystals (25%), m.p. 203–205 °C. FT-IR (KBr): ν̄ = 2958 cm<sup>-1</sup> (C–H), 2145, 2123 (C≡C), 1578, 1400, 839. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.48 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.49 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.22 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 3'-H), 7.45 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.4, <sup>4</sup>J<sub>H,H</sub> = 1.6 Hz, 2 H, 5'-H), 7.52 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.5, <sup>4</sup>J<sub>H,H</sub> = 1.7 Hz, 2 H, 7'-H), 7.57 (d, <sup>3</sup>J<sub>H,H</sub> = 10.9 Hz, 2 H, 5-, 7-H), 7.96 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 2'-H), 8.07 (s, 1 H, 2-H), 8.26 (d, <sup>3</sup>J<sub>H,H</sub> = 10.3 Hz, 2 H, 4'-H), 8.57 (d, <sup>3</sup>J<sub>H,H</sub> = 10.8 Hz, 2 H, 8'-H), 8.62 (d, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 31.9, 32.0 [C(CH<sub>3</sub>)<sub>3</sub>], 38.9, 39.1 [C(CH<sub>3</sub>)<sub>3</sub>], 78.6, 79.0, 79.3, 80.2 (C≡C), 108.7, 109.3, 117.5, 123.1, 123.7, 125.1, 135.9, 136.7, 139.6, 140.7, 142.1, 142.4, 142.6, 163.4, 165.31 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane): λ<sub>max</sub> (log ε) = 244 nm (4.82), 303 (4.88), 325 (4.91) sh, 330 (4.93), 345 (4.79) sh, 409 (4.80), 438 (4.71) sh, 589 (3.36). MS (FD): *m/z* (%) = 644 (100) [M<sup>+</sup>], 322 (4). C<sub>50</sub>H<sub>44</sub> (644.9): calcd. C 93.12, H 6.88; found C 92.78, H 7.24.

**26:** Black crystals (21%), m.p. 170–185 °C. FT-IR (KBr): ν̄ = 2962 cm<sup>-1</sup>, 2932, 2850 (C–H), 2176, 2164, 2132 (C≡C), 1640, 1577, 1508, 1447, 1400, 1350, 1293, 1111, 1051, 859, 836, 749. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.47 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.48 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.22 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 3'-H), 7.45 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.4, <sup>4</sup>J<sub>H,H</sub> = 1.7 Hz, 2 H, 5'-H), 7.52 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.5, <sup>4</sup>J<sub>H,H</sub> = 1.8 Hz, 2 H, 7'-H), 7.59 (d, <sup>3</sup>J<sub>H,H</sub> = 10.8 Hz, 4 H, 5-, 7-H), 7.95 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 2'-H), 8.07 (s, 1 H, 2-H), 8.26 (d, <sup>3</sup>J<sub>H,H</sub> = 10.4 Hz, 2 H, 4'-H), 8.55–8.63 (m, <sup>3</sup>J<sub>H,H</sub> = 10.8 Hz, 6 H, 4-, 8-, 8'-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 31.9, 32.0 [C(CH<sub>3</sub>)<sub>3</sub>], 38.9, 39.2 [C(CH<sub>3</sub>)<sub>3</sub>], 78.5, 78.8, 79.0, 79.3, 80.2 (C≡C), 108.7, 108.9, 109.3, 117.5, 123.2, 123.7, 125.2, 135.9, 136.7, 139.6, 140.7, 142.2, 142.5, 142.7, 142.8, 163.5, 165.4 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane): λ<sub>max</sub> (log ε) = 243 nm (4.86), 306 (4.93) sh, 326

(4.99), 330 (4.99), 409 (4.87), 439 (4.79) sh, 594 (3.41). MS (FD): *m/z* (%) = 874 (9) [M<sup>+</sup>], 437 (100). C<sub>68</sub>H<sub>58</sub> (875.2): calcd. C 93.32, H 6.68; found C 92.97, H 6.99.

**General Procedure for the Palladium/Copper-Catalysed Coupling of Ethynylazulenes with Iodoazulenes:** Bis(triphenylphosphane)palladium(II) chloride (0.04 mol-%) and CuI (0.08 mol-%) were added to a solution of the appropriate iodoazulene **1a,b**, **4a,b**, **31** or **34** (2 mmol) in TEA (50 mL) and the reaction mixture was stirred at room temperature under N<sub>2</sub> for 10 min. The appropriate ethynylazulene **3a,b**, **6b**, **28**, **33** or **37** (1 or 2 equiv.) in TEA (10 mL) was then added slowly over a period of 6 h. The reaction mixture was stirred for a further 10 h and then filtered through a short column of alumina (BII-III). The solvent was removed in vacuo and the remaining product was purified by chromatography on alumina (BII-III), with CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:4) for compounds **27a,b**, **29**, **32** and **40** and CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:3) for compounds **30**, **34**, **35**, **36**, **38** and **39**.

**Bis(azulen-1-yl)ethyne (27a):** Compounds **1a** and **3a** afforded **27a** as deep-green crystals (40%), m.p. 158–160 °C. FT-IR (KBr): ν̄ = 1570 cm<sup>-1</sup>, 1450, 1420, 1393, 1288, 988, 941, 872, 780, 734, 672, 572, 542. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.20 (t, <sup>3</sup>J<sub>H,H</sub> = 9.8 Hz, 2 H, 5-H), 7.27 (t, <sup>3</sup>J<sub>H,H</sub> = 9.8 Hz, 2 H, 7-H), 7.39 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 3-H), 7.64 (t, <sup>3</sup>J<sub>H,H</sub> = 9.9 Hz, 2 H, 6-H), 8.12 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 2-H), 8.30 (d, <sup>3</sup>J<sub>H,H</sub> = 9.6 Hz, 2 H, 4-H), 8.75 (d, <sup>3</sup>J<sub>H,H</sub> = 9.6 Hz, 2 H, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 90.3 (C≡C), 111.9, 118.0, 123.8, 124.5, 136.7, 137.3, 138.8, 139.4, 140.8, 141.49 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane): λ<sub>max</sub> (log ε) = 276 nm (4.63), 287 (4.53) sh, 309 (4.57), 318 (4.56), 392 (4.26) sh, 410 (4.33), 422 (4.33), 446 (4.37), 623 (2.91). MS (EI, 70 eV): *m/z* (%) = 278 (100) [M<sup>+</sup>], 250 (5), 139 (12). C<sub>22</sub>H<sub>14</sub> (278.4): calcd. C 94.93, H 5.07; found C 95.07, H 4.88.

**Bis(6-tert-butylazulen-1-yl)ethyne (27b):** Compounds **1b** and **3b** afforded **27b** as deep-green crystals (32%), m.p. 169–171 °C. FT-IR (KBr): ν̄ = 2961 cm<sup>-1</sup>, 2867 (C–H), 1575, 1459, 1401, 840, 769. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.48 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.30 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 3-H), 7.37 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.3, <sup>4</sup>J<sub>H,H</sub> = 1.7 Hz, 2 H, 5-H), 7.48 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.5, <sup>4</sup>J<sub>H,H</sub> = 1.8 Hz, 2 H, 7-H), 8.02 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 2-H), 8.24 (d, <sup>3</sup>J<sub>H,H</sub> = 10.3 Hz, 2 H, 4-H), 8.70 (d, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, 2 H, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 32.0 [C(CH<sub>3</sub>)<sub>3</sub>], 38.8 [C(CH<sub>3</sub>)<sub>3</sub>], 90.2 (C≡C), 111.5, 117.3, 122.1, 122.4, 135.6, 136.6, 138.5, 139.5, 140.2, 162.7 ppm. UV/Vis (dichloromethane): λ<sub>max</sub> (log ε) = 283 nm (4.71), 292 (4.63) sh, 316 (4.61), 324 (4.62), 396 (4.30) sh, 413 (4.37), 424 (4.38), 450 (4.41), 610 (3.02). MS (FD): *m/z* (%) = 390 (100) [M<sup>+</sup>], 195 (2). C<sub>30</sub>H<sub>30</sub> (390.6): calcd. C 92.26, H 7.74; found C 91.88, H 7.87.

**Trimer 29:** Compounds **4b** and **3b** afforded **29** as brown needles (66%), m.p. 240–242 °C. FT-IR (KBr): ν̄ = 2961 cm<sup>-1</sup>, 2866 (C–H), 1574, 1401, 831. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.49 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.50 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.20 (d, <sup>3</sup>J<sub>H,H</sub> = 3.9 Hz, 2 H, 3'-H), 7.39 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.3, <sup>4</sup>J<sub>H,H</sub> = 1.7 Hz, 2 H, 5'-H), 7.49 (d, <sup>3</sup>J<sub>H,H</sub> = 10.9 Hz, 2 H, 5-, 7-H), 7.50 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.5, <sup>4</sup>J<sub>H,H</sub> = 1.8 Hz, 2 H, 7'-H), 8.04 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 2'-H), 8.20 (s, 1 H, 2-H), 8.25 (d, <sup>3</sup>J<sub>H,H</sub> = 10.3 Hz, 2 H, 4'-H), 8.64 (d, <sup>3</sup>J<sub>H,H</sub> = 10.8 Hz, 2 H, 8'-H), 8.70 (d, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C): δ = 31.9, 32.0 [C(CH<sub>3</sub>)<sub>3</sub>], 38.9, 39.0 [C(CH<sub>3</sub>)<sub>3</sub>], 89.4, 90.4 (C≡C), 111.2, 111.4, 117.4, 122.3, 122.6, 123.3, 135.6, 136.1, 136.4, 138.6, 139.7, 140.3, 140.4, 162.8, 164.1 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane): λ<sub>max</sub> (log ε) = 286 nm (4.86), 315 (4.77), 330 (4.78), 412 (4.63), 444 (4.55) sh, 618 (3.21). MS (FD): *m/z* (%) = 596 (100) [M<sup>+</sup>], C<sub>46</sub>H<sub>44</sub> (596.9): calcd. C 92.57, H 7.43; found C 92.13, H 7.80.



**Pentamer 30:** Compounds **4b** and **28** afforded **30** as black crystals (26%), m.p. > 270 °C. FT-IR (KBr):  $\tilde{\nu}$  = 2959 cm<sup>-1</sup>, 2887 (C–H), 1575, 1459, 1403, 1361, 1239, 863. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 1.50 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.52 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.53 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.32 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 3''-H), 7.42 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.3, 1.4 Hz, 2 H, 5''-H), 7.53–7.59 (m, 8 H, 5-, 5'-, 7-, 7'-, 7''-H), 8.03 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 2 H, 2''-H), 8.20 (s, 2 H, 2'-H), 8.23 (s, 1 H, 2-H), 8.29 (d, <sup>3</sup>J<sub>H,H</sub> = 10.3 Hz, 2 H, 4''-H), 8.65–8.73 (m, 8 H, 4-, 4'-, 8-, 8'-, 8''-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 32.0, 32.0 [C(CH<sub>3</sub>)<sub>3</sub>], 39.1, 39.3 [C(CH<sub>3</sub>)<sub>3</sub>], 89.6, 89.9, 89.9, 90.9 (C≡C), 111.1, 111.2, 111.3, 111.7, 117.7, 122.8, 123.2, 124.2, 135.8, 136.5, 136.8, 138.7, 139.9, 140.2, 140.4, 140.5, 140.6, 140.7, 163.6, 165.1 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 294 nm (5.03), 313 (5.01), 329 (5.01), 409 (4.87), 625 (3.44). MS (FD): *m/z* (%) = 1008 (100) [M<sup>+</sup>], 505 (5). C<sub>78</sub>H<sub>72</sub> (1009.4): calcd. C 92.81, H 7.19; found C 92.23, H 7.81.

**Trimer 32:** Compounds **6b** and **31** afforded **32** as green crystals (43%), m.p. > 270 °C. FT-IR (KBr):  $\tilde{\nu}$  = 2960 cm<sup>-1</sup>, 2928, 2856 (C–H), 2138 (C≡C), 1576, 1359, 1247, 1096, 840, 759. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.36 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.49 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.50 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.48–7.56 (m, 6 H, 5-, 5'-, 7-, 7'-H), 8.09 (s, 2 H, 2'-H), 8.19 (s, 1 H, 2-H), 8.48 (d, <sup>3</sup>J<sub>H,H</sub> = 10.6 Hz, 2 H, 4'-H), 8.61 (d, <sup>3</sup>J<sub>H,H</sub> = 10.7 Hz, 2 H, 8'-H), 8.64 (d, <sup>3</sup>J<sub>H,H</sub> = 10.5 Hz, 2 H, 4-, 8-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.5 [Si(CH<sub>3</sub>)<sub>3</sub>], 31.9 [C(CH<sub>3</sub>)<sub>3</sub>], 39.0 [C(CH<sub>3</sub>)<sub>3</sub>], 89.4, 98.5, 101.0 (C≡C), 110.0, 110.8, 111.1, 123.6, 124.0, 136.1, 136.2, 136.3, 140.3, 140.5, 141.0, 141.5, 164.3 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 250 nm (4.79), 301 (5.02), 333 (4.94), 420 (4.56), 457 (4.48), 631 (3.26). MS (FD): *m/z* (%) = 788 (100) [M<sup>+</sup>], 394 (9). C<sub>56</sub>H<sub>60</sub>Si<sub>2</sub> (789.3): calcd. C 85.22, H 7.66; found C 85.27, H 7.72.

**Pentamer 35:** Compounds **33** and **31** afforded **35** as green crystals (31%), m.p. > 270 °C. FT-IR (KBr):  $\tilde{\nu}$  = 2960 cm<sup>-1</sup>, 2928, 2852 (C–H), 2132 (C≡C), 1654, 1560, 1542, 1508, 1388, 1356, 1292, 1242, 852, 836. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.34 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.49 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.50 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.51 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.50–7.56 (m, 10 H, 5-, 5'-, 5''-, 7-, 7'-, 7''-H), 8.08 (s, 2 H, 2''-H), 8.20 (s, 2 H, 2'-H), 8.22 (s, 1 H, 2-H), 8.47 (d, <sup>3</sup>J<sub>H,H</sub> = 10.6 Hz, 2 H, 4''-H), 8.59–8.66 (m, 8 H, 4-, 4'-, 8-, 8'-, 8''-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.5 [Si(CH<sub>3</sub>)<sub>3</sub>], 31.9 [C(CH<sub>3</sub>)<sub>3</sub>], 39.0 [C(CH<sub>3</sub>)<sub>3</sub>], 89.4, 89.5, 98.5, 101.0 (C≡C), 109.9, 110.8, 111.0, 111.1, 123.6, 124.0, 136.0, 136.2, 136.3, 140.3, 140.5, 141.0, 141.5, 164.3 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 249 nm (4.95), 303 (5.18), 330 (5.10), 422 (4.83), 458 (4.75) sh, 636 (3.48). MS (FD): *m/z* (%) = 1200 (3) [M<sup>+</sup>], 600 (100). C<sub>88</sub>H<sub>88</sub>Si<sub>2</sub> (1201.8): calcd. C 87.95, H 7.38; found C 88.00, H 7.42.

**Heptamer 36:** Compounds **33** and **34** afforded **36** as brownish-black crystals (19%), m.p. > 270 °C. FT-IR (KBr):  $\tilde{\nu}$  = 2960 cm<sup>-1</sup>, 2920, 2862 (C–H), 2135 (C≡C), 1578, 1361, 1246, 854, 836. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.34 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.43 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.50 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.52 [s, 27 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.49–7.57 (m, 14 H, 5-, 5'-, 5''-, 5'''-, 7-, 7'-, 7''-, 7'''-H), 8.08 (s, 2 H, 2'''-H), 8.20 (s, 2 H, 2''-H), 8.22 (s, 2 H, 2'-H), 8.23 (s, 1 H, 2-H), 8.47 (d, <sup>3</sup>J<sub>H,H</sub> = 10.6 Hz, 2 H, 4'''-H), 8.60–8.68 (m, 12 H, 4-, 4'-, 4''-, 8-, 8'-, 8''-, 8'''-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.5 [Si(CH<sub>3</sub>)<sub>3</sub>], 31.9, 32.0 [C(CH<sub>3</sub>)<sub>3</sub>], 39.0 [C(CH<sub>3</sub>)<sub>3</sub>], 89.4, 89.6, 98.5, 101.0 (C≡C), 110.0, 110.8, 111.1, 111.2, 123.6, 123.9, 136.0, 136.2, 140.3, 140.5, 141.0, 141.5, 164.3 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 249 nm (5.08), 305 (5.30), 330 (5.24), 417 (5.00), 459 (4.91) sh, 640 (3.63). MS (FD): *m/z* (%) = 1612 (100) [M<sup>+</sup>], 806 (20). C<sub>120</sub>H<sub>116</sub>Si<sub>2</sub> (1614.4): calcd. C 89.28, H 7.24; found C 89.07, H 7.32.

**Dimer 34, Trimer 38 and Tetramer 39:** Compounds **37** and **31** afforded a mixture of **34**, **38** and **39**, which were separated by column chromatography on alumina (BII-III) with CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:3).

**Dimer 34:** Brown needles (68%), m.p. 175–177 °C. FT-IR (KBr):  $\tilde{\nu}$  = 2960 cm<sup>-1</sup>, 2924, 2856 (C–H), 2132 (C≡C), 1560, 854, 835. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.33 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.47 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.48–7.53 (m, 4 H, 5-, 5'-, 7-, 7'-H), 8.03, 8.05 (2 s, each 1 H, 2-, 2'-H), 8.14, 8.50, 8.56, 8.57 (4 d, <sup>3</sup>J<sub>H,H</sub> = 10.6 Hz, each 1 H, 4-, 4'-, 8-, 8'-H), ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.5 [Si(CH<sub>3</sub>)<sub>3</sub>], 31.9 [C(CH<sub>3</sub>)<sub>3</sub>], 39.0 [C(CH<sub>3</sub>)<sub>3</sub>], 88.8, 90.1, 98.5, 100.9 (C≡C), 73.8, 110.0, 110.6, 112.8, 123.1, 123.5, 124.0, 135.4, 136.1, 136.2, 138.5, 139.5, 140.2, 141.0, 141.5, 144.6, 164.1, 164.3 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 249 nm (4.62), 288 (4.79), 307 (4.76), 323 (4.70), 333 (4.68), 422 (4.31), 435 (4.31), 460 (4.31), 626 (3.08). MS (FD): *m/z* (%) = 612 (3) [M<sup>+</sup>], 78 (35). C<sub>35</sub>H<sub>37</sub>Si (612.7): calcd. C 68.62, H 6.09; found C 68.74, H 6.07.

**Trimer 38:** Black crystals (13%), m.p. > 270 °C. FT-IR (KBr):  $\tilde{\nu}$  = 2960 cm<sup>-1</sup>, 2866 (C–H), 2132 (C≡C), 1576, 1560, 1456, 1400, 840. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.33 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.48 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.49 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.48–7.55 (m, 6 H, 5-, 5'-, 5''-, 7-, 7'-, 7''-H), 8.06, 8.08, 8.15 (3 s, each 1 H, 2-, 2'-, 2''-H), 8.16–8.64 (m, 6 H, 4-, 4'-, 4''-, 8-, 8'-, 8''-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.5 [Si(CH<sub>3</sub>)<sub>3</sub>], 31.9 [C(CH<sub>3</sub>)<sub>3</sub>], 39.0 [C(CH<sub>3</sub>)<sub>3</sub>], 88.9, 89.3, 89.4, 90.2, 98.5, 100.9 (C≡C), 73.9, 109.9, 110.7, 110.9, 111.0, 112.9, 123.1, 123.5, 123.7, 124.0, 135.4, 136.1, 136.2, 136.3, 138.5, 139.5, 140.2, 140.3, 140.4, 140.5, 141.0, 141.4, 144.7, 164.1, 164.3 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 248 nm (4.71), 297 (4.90), 325 (4.84), 330 (4.84) sh, 420 (4.54), 455 (4.48) sh, 631 (3.22). MS (FD): *m/z* (%) = 818 (100) [M<sup>+</sup>], C<sub>51</sub>H<sub>51</sub>Si (819.0): calcd. C 74.80, H 6.28; found C 75.20, H 6.54.

**Tetramer 39:** Black crystals (6%), m.p. > 270 °C. FT-IR (KBr):  $\tilde{\nu}$  = 2960 cm<sup>-1</sup>, 2870 (C–H), 2136 (C≡C), 1561, 858, 835. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.34 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.49 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.51 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.50–7.56 (m, 8 H, 5-, 5'-, 5''-, 5'''-, 7-, 7'-, 7''-, 7'''-H), 8.09 (s, 1 H, 2-H), 8.13 (s, 1 H, 2''-H), 8.16 (d, <sup>3</sup>J<sub>H,H</sub> = 10.8 Hz, 1 H, 4-H), 8.19 (s, 2 H, 2'-, 2''-H), 8.46 (d, <sup>3</sup>J<sub>H,H</sub> = 10.6 Hz, 1 H, 4'''-H), 8.58–8.65 (m, 6 H, 4'-, 4''-, 8-, 8'-, 8''-, 8'''-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.5 [Si(CH<sub>3</sub>)<sub>3</sub>], 31.9 [C(CH<sub>3</sub>)<sub>3</sub>], 39.0 [C(CH<sub>3</sub>)<sub>3</sub>], 89.0, 89.4, 89.5, 90.2, 98.5, 101.0 (C≡C), 73.8, 110.0, 110.8, 111.0, 111.1, 112.9, 123.1, 123.6, 123.9, 135.4, 136.0, 136.2, 138.5, 139.6, 140.3, 140.5, 141.0, 141.5, 144.7, 164.1, 164.3 (C<sub>Az</sub>) ppm. UV/Vis (dichloromethane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 247 nm (4.86), 299 (5.05), 330 (4.98) sh, 422 (4.74), 455 (4.66) sh, 633 (3.39). MS (FD): *m/z* (%) = 1024 (100) [M<sup>+</sup>], 513 (85), 79 (75). C<sub>67</sub>H<sub>65</sub>Si (1025.2): calcd. C 78.49, H 6.39; found C 78.12, H 6.35.

**6-tert-Butyl-1-[(6-tert-butylazulen-1-yl)ethynyl]-3-(trimethylsilyl)ethynylazulene (40):** Compounds **3b** and **31** afforded **40** as greenish blue crystals (91%), m.p. 177–179 °C. FT-IR (KBr):  $\tilde{\nu}$  = 2960 cm<sup>-1</sup> (C–H), 2135 (C≡C), 1577, 1460, 1430, 1403, 1357, 1248, 1084, 994, 919, 896, 840, 759, 682. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.36 [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.48 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 1.49 [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>], 7.29 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 1 H, 3'-H), 7.38 (dd, <sup>3</sup>J<sub>H,H</sub> = 10.3, <sup>4</sup>J<sub>H,H</sub> = 1.7 Hz, 1 H, 5'-H), 7.44–7.54 (m, 3 H, 5-, 7-, 7'-H), 8.01 (d, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, 1 H, 2'-H), 8.08 (s, 1 H, 2-H), 8.23 (d, <sup>3</sup>J<sub>H,H</sub> = 10.3 Hz, 1 H, 4'-H), 8.47 (d, <sup>3</sup>J<sub>H,H</sub> = 10.6 Hz, 1 H, 4-H), 8.65 (m, 2 H, 8-, 8'-H) ppm. <sup>13</sup>C NMR (75.40 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.5 [Si(CH<sub>3</sub>)<sub>3</sub>], 31.9, 32.0 [C(CH<sub>3</sub>)<sub>3</sub>], 38.9, 39.0 [C(CH<sub>3</sub>)<sub>3</sub>], 89.2, 90.2, 98.4, 101.1 (C≡C), 109.9, 111.0, 111.2, 117.4, 122.3, 122.6, 123.8, 135.5, 136.0, 136.3, 136.4, 136.6, 138.6, 139.7,

140.2, 140.3, 141.0, 141.4, 162.8, 164.2 (C<sub>Az</sub>) ppm. UV/Vis (*n*-hexane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 251 nm (4.57), 283 (4.71), 302 (4.72), 317 (4.67), 327 (4.67), 362 (4.20), 387 (4.26), 414 (4.32), 432 (4.28), 447 (4.23), 612 (2.94), 627 (2.96), 650 (2.93) sh, 688 (2.81) sh, 725 (2.59) sh. MS (EI, 70 eV): *m/z* (%) = 486 (100) [M<sup>+</sup>], 471 (5), 73 (19). C<sub>35</sub>H<sub>38</sub>Si (486.8): calcd. C 86.36, H 7.87; found C 86.80, H 8.15.

## Acknowledgments

This work was generously supported by the Fonds der Chemischen Industrie and the Dr. Otto Röhm Gedächtnisstiftung, Darmstadt. A. H. M. E. thanks the Alexander von Humboldt Foundation for a research fellowship.

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Received: August 11, 2005

Published Online: November 30, 2005