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Syntheses of Donor−Acceptor-Functionalized Dihydroazulenes

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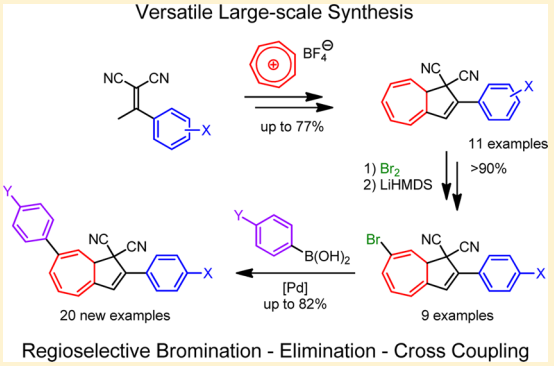
Supporting Information

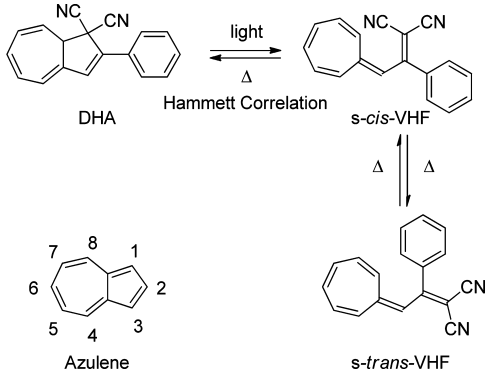
ABSTRACT: The dihydroazulene (DHA)/vinylheptafulvene (VHF) photo/thermoswitch has been of interest for use in molecular electronics and advanced materials. The switching between the two isomers has previously been found to depend strongly on the presence of donor and acceptor groups. The fine-tuning of optical and switching properties relies on ready access to new derivatives via efficient synthetic protocols. The central DHA core is conveniently prepared in a four-step synthesis starting from acetophenone and tropylium substrates. Here, the outcome of this reaction as a function of the nature of the substituent group on the phenyl unit of acetophenone is investigated in detail. A wide variety of functional groups (nitro, cyano, halo, alkyl, amido, and thioether) was tolerated, and the route provided access to a large selection of substituted DHA derivatives (position 2 of DHA). These compounds were investigated for their ability to undergo subsequent functionalization in the seven-membered ring by a regioselective bromination−elimination protocol, introducing a bromo substituent at position 7. Halo-substituted DHAs were subjected to palladium-catalyzed cyanation, Sonogashira, Cadiot−Chodkiewicz, and Suzuki couplings and for the latter reaction; optimized conditions were developed by varying the palladium catalyst. In general, our focus was on reducing the formation of fully unsaturated azulene byproducts.



INTRODUCTION

1,8a-Dihydroazulene-1,1-dicarbonitrile (DHA) is a photochromic molecule that, upon irradiation, undergoes a ring-opening reaction to form the corresponding vinylheptafulvene (VHF) (Scheme 1).[1] Over time, metastable isomer VHF converts via a thermally induced ring-closure reaction back to the more stable DHA isomer. The ring-opening reaction occurs with a high quantum yield[2] and is accompanied by significant changes in the physical properties of the molecule (e.g., dipole moment,[3] UV−vis absorption,[2] and single-molecule resistivity[4]). The VHF → DHA back reaction is relatively slow, but it is very solvent-dependent[2,5] and can easily be monitored either by UV−vis or NMR spectroscopies. We have recently shown that the rate constant, *k*, for the back reaction obeys linear free-energy relationships (Hammett correlations) for derivatives with substituent groups at positions 2 and 7. Thus, more than 70 derivatives with different electron-donating and electron-withdrawing groups were recently subjected to detailed kinetics studies.[6]

Scheme 1. Dihydroazulene (DHA)/Vinylheptafulvene (VHF) Photo/Thermoswitch[a]



[a]The inset shows the structure and numbering of azulene.

Here, we describe the synthetic protocols for achieving this large selection of donor−acceptor-substituted DHAs. Throughout the years, the need for functional-group tolerant and effective synthetic protocols to synthesize the DHA moiety has expanded, and the original procedure, starting from benzaldehydes and cyclooctatetraene,[7] has been supplemented with a more diverse route starting from acetophenones and tropylium.[5,8] To date, this route has allowed the synthesis of DHAs with a PhX substituent at position 2 of DHA, where X = H,[5] I,[8f] CO_2Me,[8g] C≡CSiMe$_3$,[8g] and *S*t-Bu.[8h,i] An expansion of this four-step synthesis to tolerate X = NO_2, CN, NHAc, OMe, Me, Br, and F is here presented. For X = NH_2, the method was not optimal, and other routes were devised.

In 2009,[9] we reported a regioselective bromination−elimination procedure for incorporation of a bromine substituent

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at position 7. This method was recently expanded to DHAs containing either an iodo- or thioether functionality at position 2.[4b,8h] We became interested in investigating the functional-group tolerance and hence the further scope of this protocol. DHAs with a halo substituent at position 7 or a halophenyl at position 2 are particularly interesting for further functionalization by palladium-catalyzed cross-coupling reactions such as Sonogashira,[10] Glaser–Hay,[11] Cadiot–Chodkiewicz,[12] and Suzuki[13] reactions. Here, we present optimized conditions for Suzuki coupling with a wide variety of substrates and different palladium catalysts. One particular challenge in the transformations of DHA compounds is finding conditions that prevent azulene formation, that is, generation of the fully unsaturated cores by elimination of HCN. All of the synthetic endeavors presented in this article are important for advancing the successful exploitation of suitably functionalized DHAs in photochromic advanced materials. In total, we have been able to prepare and study more than 70 photochromic DHAs as we developed these optimized conditions.

The compounds prepared were categorized into four overall structures, **1**–**4**, as shown in Figure 1.

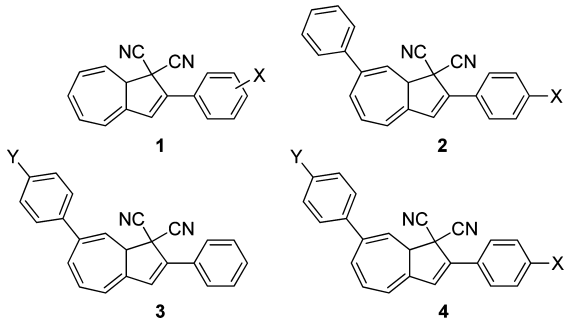


Figure 1. Structures of model compounds **1**–**4**.

RESULTS AND DISCUSSION

DHAs were prepared in four steps, expanding, with slight modification, the procedure of Diederich and co-workers.[8f] First, a Knoevenagel condensation between substituted acetophenones and malononitrile either by reflux in toluene using AcOH and NH_4OAc (**5.1**,[14] **5.2**,[15] **5.3**,[14] **5.4**,[8f] **5.5**, and **5.6**[14]) or in a hot mixture of AcOH and hexamethyldisilazane (HMDS) (**5.7**[16] and **5.8**[16]) gave a series of malononitrile derivatives, as shown in Scheme 2 and Table 1.

Although both procedures are effective, acetophenones with electron-withdrawing groups are in danger of a subsequent condensation between two product molecules if the reaction is not carefully monitored by TLC and stopped as the desired Knoevenagel condensation has finished.[16] In one example (X = NO_2), a significant amount of byproduct **6**, previously described in the literature,[16] was isolated, and the structure was confirmed by X-ray crystallography (Figure 2).

Electrophilic addition of (finely divided or mortared) tropylium tetrafluoroborate[5] to compounds **5.1**–**5.8** using Et_3N in CH_2Cl_2 at −78 °C gave the VHF precursors in almost quantitative yields (**7.1**–**7.8**). These were then treated with tritylium tetraflouroborate[5] in 1,2-dicloroethane (DCE) followed by Et_3N in toluene to yield the VHFs that were then, without isolation, directly converted into corresponding DHAs **1.1**–**1.8** by heating (Scheme 3 and Table 1). The DHAs were all isolated on a large scale and purified by means of dry column vacuum chromatography followed by a recrystallization as yellow crystals stable to light irradiation.

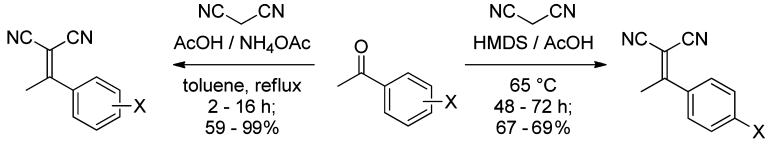
Interestingly, during the preparation of several of the VHF precursors by electrophilic addition of tropylium to **5.1**–**5.8** (Scheme 3), we found that if the reaction is not quenched at −78 °C, then overalkylation occurred in some cases; in one example, the corresponding product (**8.1**) was isolated, and the structure was confirmed by X-ray crystallographic analysis (Figure 3d). Additionally, in this reaction step, only finely powdered tropylium salt reacts smoothly. Thus, even small lumps of the starting material cause longer reaction times and sluggish reactions with poorer yields and side reactions such as overalkylation.

The hydride abstraction can be conveniently performed by either heating at reflux for 1 h in DCE or simply by stirring overnight in CH_2Cl_2 at rt; no significant difference in isolated yields was observed, although one or the other procedure may be more desirable when planning the synthesis.

In Table 1, the yields for the four-step synthesis are shown. Many of the compounds prepared using this strategy are known but were prepared by another, less efficient, procedure. The present methodology demonstrates a highly effective procedure to prepare DHAs with both electron-withdrawing and -donating groups in the phenyl ring placed at position 2 on DHA.

We note that using the four-step procedure for synthesis of the DHA **1.2** gave a lower yield than simply reducing nitro derivative **1.1** (Scheme 4).[7] Unfortunately, this procedure was not possible to perform on a gram scale. Even after some optimization, reduction of more than 2.5 mmol of **1.1** was not successful. Reduction using Zn(s) in AcOH also gave a low isolated yield of **1.2** (20%). For this reason, an efficient protocol for the preparation of **1.2** from either a protected aniline or from a halogenated DHA became desirable. Amination of iodo-DHA **1.4** using Fe_2O_3/CuI as catalyst[17] failed and afforded only azulenes by elimination of HCN because of basic conditions ($NaOH/NH_3$). This elimination is known to occur readily under basic conditions, in the presence of fluoride, or at high temperatures.[18] A better result was observed using slightly milder basic conditions; treatment with CuI, L-proline, K_2CO_3, and NH_4Cl in dimethyl sulfoxide (DMSO)[19] afforded desired amino-DHA **1.2**; unfortunately, it also resulted in azulene formation. Instead, a good result was

Scheme 2. Knoevenagel Condensations under Two Different General Sets of Conditions[a]



5.1-5.6
X = p-NO_2, p-NH_2, p-Me, p-I, m-I, p-F

5.7-5.8
X = OMe, Br

[a]For yields, see Table 1.

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Table 1. Yields for the Four-Step (or Five-Step) Synthesis of DHAs 1

X	compound	yield (%)[a]	compound	yield (%)[b]	compound	yield (%)[c]	total yield (%)[d]
p-NO_2	**5.1**	71	**7.1**	99	**1.1**	51	36[e]
p-NH_2	**5.2**	59 (36[f])	**7.2**	44	**1.2**		[e]
p-Me	**5.3**	71	**7.3**	99	**1.3**	56	39[e]
p-I	**5.4**	96 (81[f])	**7.4**	99	**1.4**	70	67
m-I	**5.5**	99	**7.5**	99	**1.5**	50	49
p-F	**5.6**	96	**7.6**	94	**1.6**	34	31
p-OMe	**5.7**	69	**7.7**	99	**1.7**	66	45[e]
p-Br	**5.8**	67	**7.8**	99	**1.8**	66	43[e]
p-NHAc	**5.9**	[g]	**7.9**	99	**1.9**	70	40[h]

[a]Isolated yield of the pure product. [b]Isolated yield of the crude product, with only minor impurities (traces of Et_3N and/or cycloheptatriene). [c]Isolated yield of the pure crystalline product. [d]Total yield from the commercially available acetophenone derivative. [e]Previously published compound but prepared by another procedure. [f]Isolated yield of recrystallized compound for long-term storage. [g]Prepared by acetylation of **5.2**. [h]Yield after five steps.

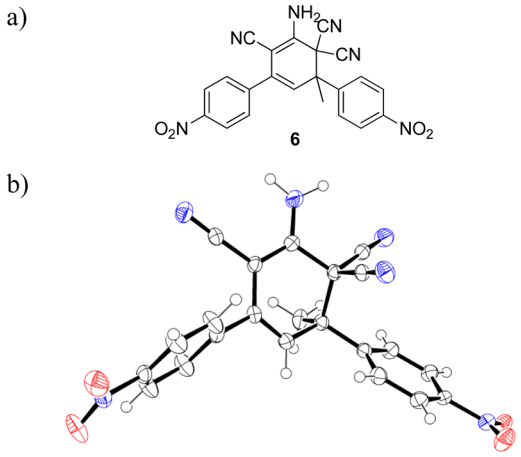


Figure 2. (a) Structure of observed byproduct of self-condensation between two **5.1** molecules. (b) Molecular structure of **6** (CCDC 953909; crystals grown from ethanol), with displacement ellipsoids at 50% probability for non-H atoms.

observed by simply protecting the aniline earlier in the sequence by acetylation of malononitrile **5.2**. The alkylation, oxidation, and ring closure now proceeded smoothly in high yield (Table 1), and the subsequent deprotection of the DHA **1.9** to give **1.2** could be performed using aqueous HCl (Scheme 4).

The protection was performed by treatment of **5.2** with Ac_2O in dioxane/water at 70 °C for 30 min, which gave protected compound **5.9** in quantitative yield (Scheme 5).

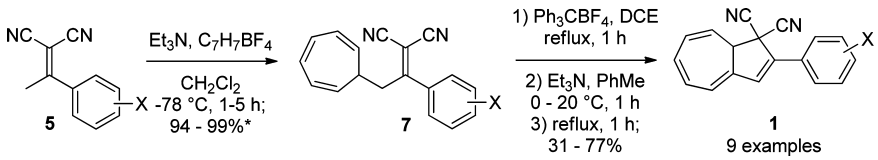
Three DHA-derivatives, namely, the methyl-, nitro-, and methoxy-derivatives **1.3**, **1.1**, and **1.7**, were characterized by X-ray crystallography, as shown in Figure 3a–c, whereas structures of the bromo-,[7a] iodo-,[8f] cyano-,[20] and hydrogen-derivatives[5] were previously reported. They all show the characteristic boat-shaped conformation of the seven-membered ring with the C7–C8 double bond out of plane, which eliminates effective conjugation with the rest of the double bonds and makes it susceptible to electrophilic attack.

The para- and meta-functionalized iodo-DHAs, **1.4** and **1.5**, acted as very useful precursors to other functionalized DHAs. Thus, a palladium-catalyzed cyanation of the iodo-DHAs was achieved when treated with $Zn(CN)_2$ in dimethylformamide (DMF) in the presence of catalytic amounts of $Pd(PPh_3)_4$ under microwave (MW) heating, which gave **1.10** and **1.11** in excellent yields of 96 and 84%, respectively (Scheme 6). A significantly lower yield was observed using *p*-bromo-DHA **1.8** because the reaction did not go to completion and because small amounts of the corresponding azulenes of starting material and product, **9.8** and **9.10**, were isolated.

By the means of Suzuki cross-couplings, functionalization with heteroaromatics, like thiophene and furan, was achieved. Starting from either the para- or meta-substituted iodo-DHAs, **1.4** and **1.5**, and the 2- and 3-furan or thiophene boronic acids allowed for a large host of functionalized DHAs to be prepared. Using $Pd(OAc)_2$/RuPhos (2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl) as a catalytic system, these reactions had a tendency to not go to completion in many examples. By using $Pd_2(dba)_3$ or $Pd(OAc)_2$ with Xantphos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) as the catalytic system instead, better results were obtained, and eight DHAs were prepared (Scheme 7). In Table 2, the reaction conditions and yields are shown. Unfortunately, no systematic behavior with respect to the choice of ligand was recognized.

Note that an unreactive ligand system for the Suzuki coupling often, eventually, resulted in azulene formation. The HCN, released during the azulene formation then participated in replacement of the halogen for a nitrile and thus the cyano-DHAs **1.10** and **1.11** were isolated. In the case of the cyanation of the bromo-DHA **1.8** shown in Scheme 6, azulenes **9.8** and **9.10** were then obtained as a result of this two-step elimination–cyanation because both DHA **1.8** and **1.10** can potentially eliminate HCN and the formed **9.8** can, in principle, also participate in the

Scheme 3. Synthesis of a Series of DHAs by Nucleophilic Addition by Tropylium Tetrafluoroborate Followed by a Two-Step Oxidation and Thermally Induced Ring Closure[a]



[a]For yields, see Table 1. The yield of X = NH_2 is not included.

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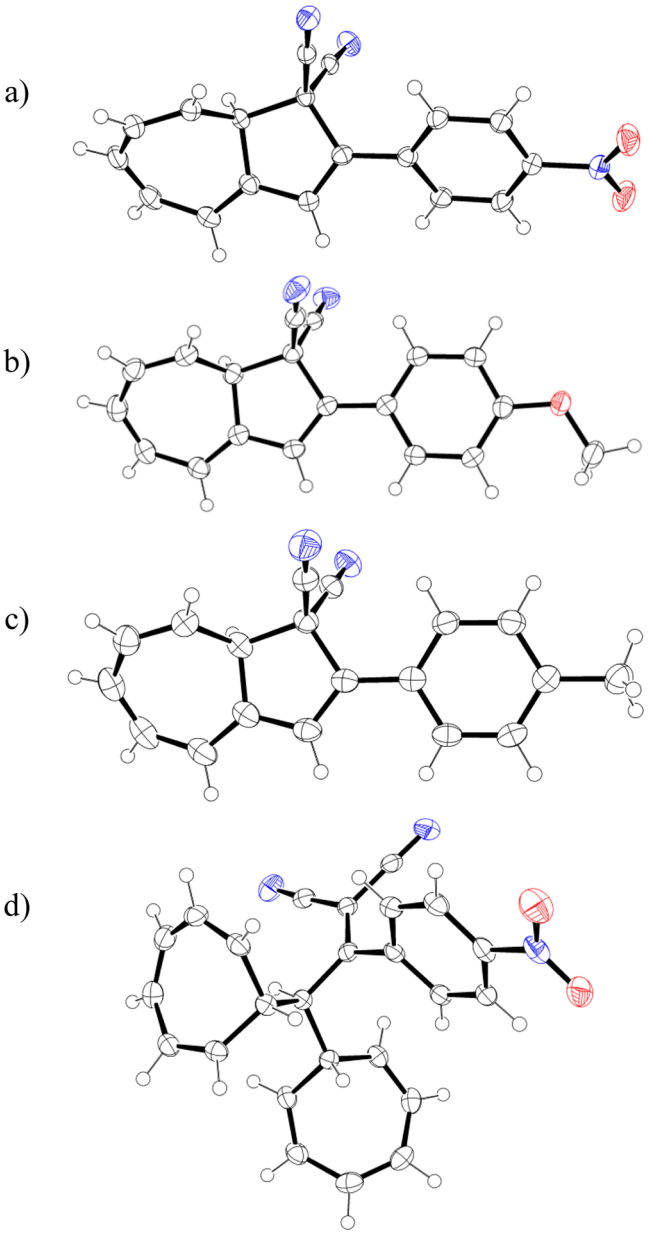
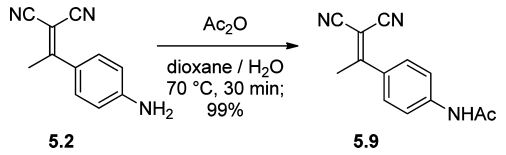


Figure 3. Molecular structures of (a) **1.1** (CCDC 912892; crystals grown from MeOH), (b) **1.7** (CCDC 912893; crystals grown from EtOH), (c) **1.3** (CCDC 912894; crystals grown from $CHCl_3$/heptanes), and (d) **8.1** (CCDC 912896; crystals grown from heptanes), with displacement ellipsoids at 50% probability for non-H atoms.

replacement reaction. The two-step elimination−cyanation reaction is shown in Scheme 8.

By using a Sonogashira cross-coupling protocol, functionalization of the phenyl ring with alkynes was achieved. In THF at room temperature, both trimethylsilylacetylene (TMS-acetylene) and triisopropylacetylene (TIPS-acetylene) were treated with the

Scheme 5. Acetylation of Aniline Derivative 1.2



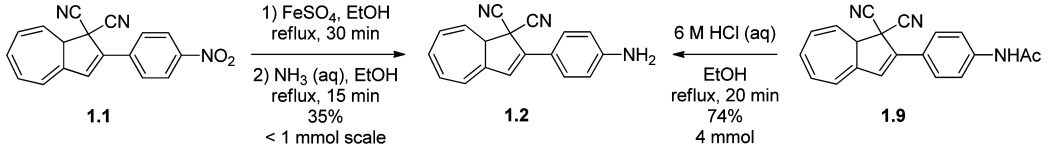
para- and meta-substituted iodo-DHAs **1.4** and **1.5**, which gave alkyne-functionalized DHAs **1.20**,[8g] **1.21**,[8g] and **1.22** in good to excellent yields. Desilylation of the TMS-protected alkyne can be effected as previously described by using either TBAF/AcOH[6a] in THF/MeOH (53% yield) or, in two steps, with $AgNO_3$ followed by KI (86%).[8g] With an optimized procedure using 2 mol equiv of TBAF and 10 mol equiv of AcOH in THF, deprotection was effected in 58% yield at rt. For the TIPS-protected alkynes, 2 mol equiv TBAF in refluxing THF/AcOH allowed for the formation of the terminal acetylenes in excellent yields (Scheme 9). No desilylation of TIPS-protected DHA **1.22** was observed using KF in THF/MeOH at reflux, and azulene formation and decomposition was achieved only using TBAF without the presence of AcOH. Both terminal alkynes are unstable and each one of them converts to an unidentified product over a few days under ambient conditions. The present preparations are improved conditions of those previously reported.[8g]

Terminal acetylene DHAs **1.23** and **1.24** act as precursors for a number of other functional groups. DHA **1.23** was reacted in a Glaser−Hay coupling with TMS-acetylene, using CuCl/TMEDA in CH_2Cl_2 to give butadiyne **1.25** in 73% yield together with its homocoupled product (Scheme 10). The TMS-protection group was removed by TBAF in THF/AcOH, which gave **1.26** in 92% yield (total yield, 67%). Alternatively, **1.25** can be prepared in two steps from **1.23** by treatment with NBS and $AgNO_3$ in acetone to give bromoalkyne **1.27**[21] in 92% yield. A subsequent modified Cadiot−Chodkiewicz[12] coupling with TMS-acetylene using $Pd(PPh_3)_4$, CuI, and NEt_3 in THF gave **1.25** in 44% yield. Preparation of the chloroalkyne was attempted by an in situ deprotection of TMS-ethynyl DHA **1.20** followed by chlorination using trichlorocyanuric acid and $AgNO_3$ in acetone.[22] Although the desired compound was presumably observed by thin-layer chromatography (TLC) analysis, isolation failed during the aqueous workup, presumably because of a lack of stability. However, the bromoalkyne showed stability in solution and as a solid that was sufficient enough for isolation and characterization.

The thioethers[8h] **1.28−1.29** were oxidized by treatment with either 1.0 or 2.2 equiv of *meta*-chloroperoxybenzoic acid (*m*-CPBA) in CH_2Cl_2 to give sulfoxides **1.30−1.31** (as a mixture of diastereoisomers) and sulfones **1.32−1.33**, respectively (Scheme 11).

The compounds were generally quite stable solids, although the VHF precursors, **7.1−7.9**, were low-melting solids or oils, generally difficult to purify, and only stable as solids. All DHAs are stable for storage under ambient conditions as solids. The reactions were done on a preparative scale, up to 10−15 g, and for proof-of-concept, two compounds, **1.3** and **1.7**, were prepared without the use of chromatography.

Scheme 4. Preparation of 1.2 by Either Reduction of Nitro-DHA 1.1 by Means of $FeSO_4$ and NH_3 or by Deprotection of Amide-DHA 1.9 Using Aqueous HCl



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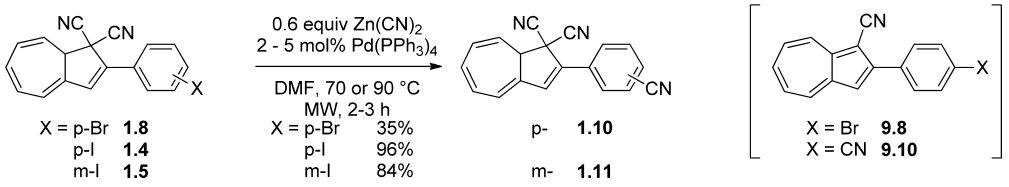
Scheme 6. Palladium-Catalyzed Cyanation of 1.4, 1.5, and 1.8 and Structures of Isolated Azulenes 9.8 and 9.10



Scheme 7. Synthesis of Heteroaromatic-Functionalized DHAs by Suzuki Coupling and Structures of Isolated Cyano-DHAs 1.10 and 1.11

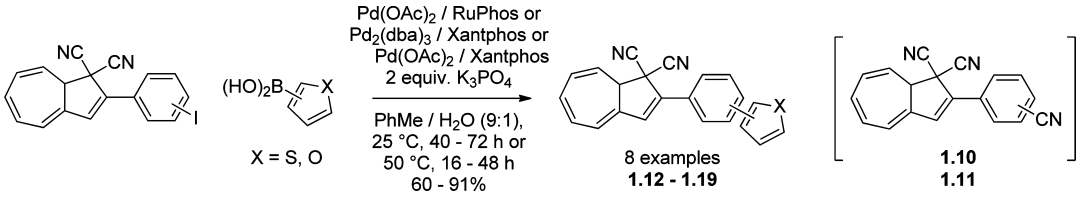
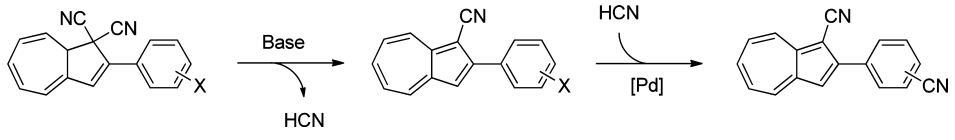


Table 2. Reaction Conditions and Isolated Yields of Heteroaromatic-Substituted DHAs[a]

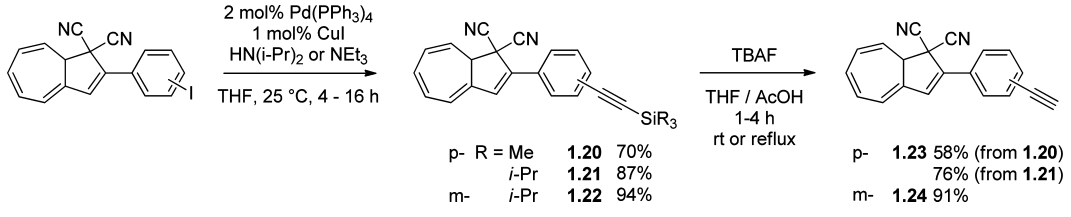
						unreacted SM[b]	
substituent	catalyst	temp (°C)	time (h)	product	yield (%)	1.4	1.5
p-(3-furyl)	$Pd(OAc)_2$/RuPhos	25	72	**1.12**	70[c]	none	
p-(2-furyl)	$Pd_2(dba)_3$/Xantphos	25	72	**1.13**	32[d]	>20%	
	$Pd(OAc)_2$/ Xantphos	50	48		91	none	
p-(2-thienyl)	$Pd(OAc)_2$/RuPhos	25	72	**1.14**	<30[d]	>20%	
	$Pd(OAc)_2$/ Xantphos	50	16		61[c,d]	<10%[e]	
p-(3-thienyl)	$Pd(OAc)_2$/RuPhos	25	16	**1.15**	<50	none	
	$Pd(OAc)_2$/ Xantphos	50	4		77[c]	none[e]	
m-(2-thienyl)	$Pd_2(dba)_3$/Xantphos	50	2	**1.16**	78[c]		none
m-(3-thienyl)	$Pd(OAc)_2$/RuPhos	50	48	**1.17**	19[d]		14%
	$Pd_2(dba)_3$/Xantphos	50	16		60[c]		<5%
m-(3-furyl)	$Pd(OAc)_2$/RuPhos	50	8	**1.18**	30[c,d]		55%[f]
	$Pd(OAc)_2$/ Xantphos	reflux	48		<20		none[f]
	$Pd_2(dba)_3$/Xantphos	50	10		<20		none[f]
	$Pd_2(dba)_3$/Xantphos	reflux	6		70[c]		none[f]
m-(2-furyl)	$Pd_2(dba)_3$/Xantphos	25	72	**1.19**	74		none

[a]General conditions: 5−10 mol % palladium catalyst, 2 equiv K_3PO_4 as activator of the boronic acid in toluene/H_2O (9:1) at 25 or 50 °C. RuPhos: 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl. Xantphos: 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene. [b]SM, starting material. [c]Higher catalyst loading. [d]Reaction did not go to completion. [e]A small amount of **1.4** or **1.10** and the corresponding azulenes were observed. [f]A small amount of **1.5** or **1.11** and the corresponding azulenes were observed.

Scheme 8. Base-Facilitated Elimination of HCN and Its Participation in a Palladium-Catalyzed Cyanation



Scheme 9. Functionalization with Alkynes by Sonogashira Cross-Couplings and Subsequent Desilylation



Gratifyingly, our previously reported bromination−elimination procedure[6a,b,8h,9] proved to be possible, with a series of DHAs demonstrating the tolerance of the procedure toward a variety of functional groups. In addition to the three recently published DHAs (X = H, I, and S*t*-Bu),[4b,6a,b,8h,9] the two-step incorporation of a bromo substituent at position 7 of the DHA tolerated a bromo, nitro, cyano, and methyl functionality. Under the same reaction conditions, Br_2 in CH_2Cl_2 at −78 °C, four derivatives of the DHA

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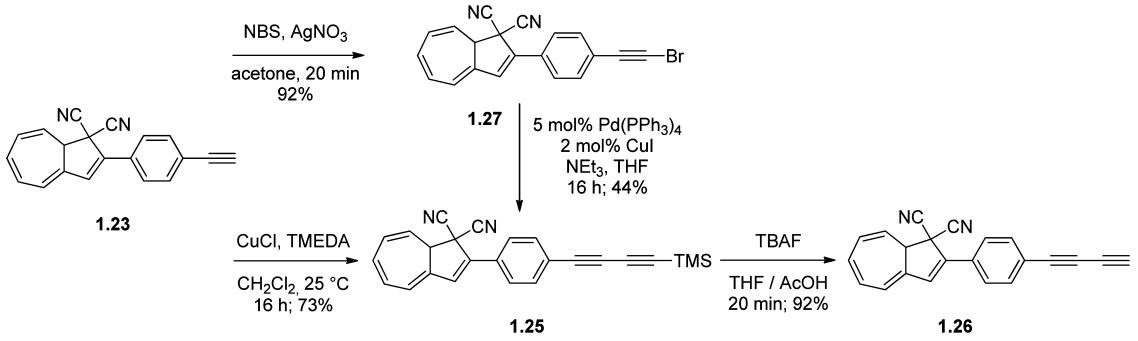
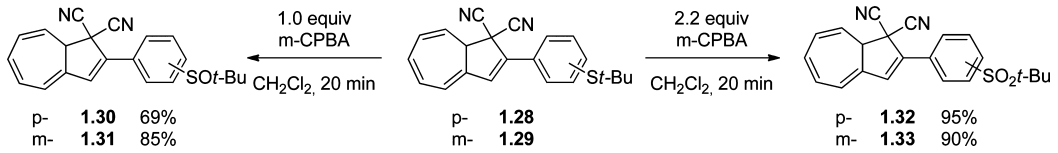
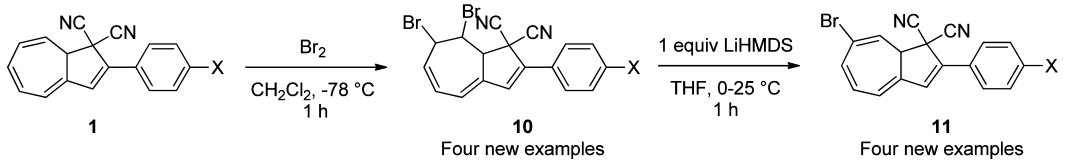
Scheme 10. Preparation of Butadiyne Derivative by Glaser−Hay Coupling and by Bromination Followed by Cadiot−Chodkiewicz Coupling



Scheme 11. Oxidation of Thioether Using *m*-CPBA



Scheme 12. Bromination−Elimination Procedure[a]



[a]LiHMDS, lithium hexamethyldisilazane. For yields, see Table 3.

were selectively brominated at the C7−C8 double bond, and HBr was selectively eliminated by treatment with lithium hexamethyldisilazane (LiHMDS) in THF at 0 °C (Scheme 12). The structure of **11.1** was determined by X-ray crystallography, confirming the position of the bromo substituent (Figure 4). No sign of electrophilic aromatic substitution or bromination directly on nitrogen was detected.

All dibromides **10.1**−**10.4**, **10.7**−**10.10**, and **10.34** were isolated as foams or powders and were very unstable. Thus, they could, in many instances, only be isolated long enough for characterization by NMR spectroscopy if the spectrum was acquired directly after evaporation of the solvent. Purification of 7-bromides **11** using column chromatography was not possible without significant loss of compound; thus, the compounds were used for subsequent reactions in crude form. A sample of each 7-bromide was, however, purified for characterization by tedious dry column vacuum chromatography followed by recrystallization.

The crude and isolated yields for the two-step bromination−elimination reactions are given in Table 3. For comparison, some previously published data are also shown.

In the case of the methoxy-DHA **1.7**, the procedure did not yield desired dibromide **10.7** as the major product. When treating **1.7** with bromine in CH_2Cl_2, the reaction mixture became dark green with a reddish glow. ^{1}H NMR spectroscopy did show about 10% conversion to the desired dibromide as well as signals attributed to the starting material and an unidentified compound (presumably an azulene). This mixture was treated with LiHMDS in THF. Despite a very low yield, a small amount of 7-bromide **11.7** was isolated relatively pure, for characterization by UV−vis spectroscopy, by repeated dry column vacuum chromatography followed by recrystallization. Alternatively,

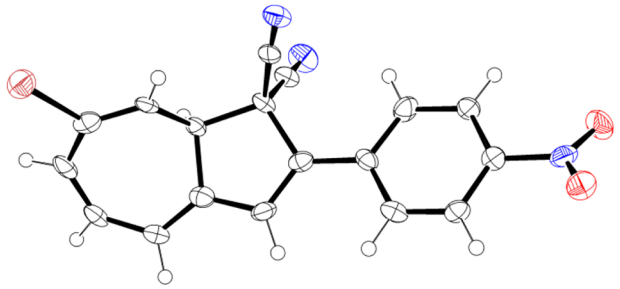


Figure 4. Molecular structure of **11.1** (CCDC 912891; crystals grown from CH_2Cl_2/heptanes), with displacement ellipsoids at 50% probability for non-H atoms.

bromination in AcOH at 0 °C also led to an undesired reaction product. Upon addition of bromine, the solution took a dark but bright red color (not from bromine), which eventually became purple−green. A green precipitate was collected and identified as 3-bromoazulene **12** in 53% yield (Scheme 13). Simply treating methoxy-DHA **1.7** with Br_2 at −78 °C and then stirring the reaction mixture for 2 days at rt also gave azulene **12** in about 50% yield, but the compound was not easily isolated by chromatography via this procedure.

The four 7-bromides **11.1**−**11.3**, **11.8**, and **11.10** together with three of the previously reported compounds **11.34** (X = H),[6a,b,9] **11.4** (X = I),[4b] and **11.28** (X = S*t*-Bu)[8h] now acted as the starting point for introduction of para-substituted benzene rings onto the 7-position. This series of 7-bromides was subjected to palladium-catalyzed Suzuki cross-coupling reactions to afford a number of derivatives bearing either one or two

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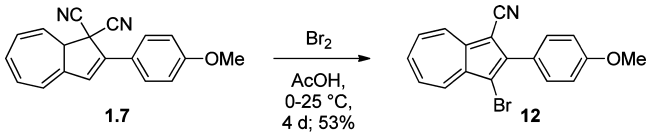
Table 3. Crude and Isolated Yields for the Bromination–Elimination Reactions

X	compound	yield (%)	compound	crude yield (%)	isolated yield (%)	ref
NO_2	**10.1**	99	**11.1**	>90	24	
NH_2	**10.2**		**11.2**			
Me	**10.3**	99	**11.3**	>90	74	
I	**10.4**[a]	99	**11.4**[a]	>90		4b
OMe	**10.7**	<10[b]	**11.7**			
Br	**10.8**	99	**11.8**	>90	72	
NHAc	**10.9**		**11.9**			
CN	**10.10**	99	**11.10**	>90	64	
*S*t-Bu	**10.28**[a]	99	**11.28**[a]	>90	20	8h
H	**10.34**[a]	99	**11.34**[a]	>90		6a, 6b, 9

[a]Known compound. [b]Only traces (<10%) of the dibromide **10.7** and 7-bromide were reproducibly prepared; however, from both bromination in CH_2Cl_2 (−78 °C) and in AcOH (0 °C), 3-bromoazulene derivative **12** was instead isolated.

Scheme 13. Synthesis of 12 by Bromination of 1.7 in AcOH



functional groups. Using this methodology, donor–acceptor, donor–donor, and acceptor–acceptor compounds were prepared to study systematically the influence of mesomeric and inductive effects (either electron withdrawing or donating).[6c]

Using the previously reported conditions (10–20 mol % $Pd(PPh_3)_4$ and $KF{\cdot}2H_2O$ in toluene/H_2O),[6b] three of the six 7-bromo DHAs, **11.1**, **11.3**, **11.10**, were treated with *p*-methoxy, *p*-nitrophenyl, and *p*-cyanophenyl boronic acid. and the six donor and acceptor DHAs were isolated in 10–37% yield (Scheme 14 and Table 4).

The structure of compound **4.1** was solved by X-ray crystallography, as shown in Figure 5, confirming the position of the nitrophenyl. The functionalization maintains the boat-like conformation of the DHA moiety, which was also in accordance with the UV–vis absorption spectroscopy.[6c]

Although all of the tested 7-bromides were reactive in the Suzuki coupling under the same general conditions, the isolated yields were relatively low. For this reason, other conditions, solvents, and reagents were tested to improve the procedure. Strong bases, like NaOH or NaO*t*-Bu, and the fluoride source tetrabutylammonium fluoride (TBAF) were deliberately avoided because of the unwanted elimination of HCN, which is known to occur readily. Simple 7-bromide **11.34** and *p*-cyanophenyl boronic acid were chosen as the main model compounds, although other substrates were also investigated.

Table 4. Reaction Conditions and Isolated Yields for Suzuki-Couplings between 7-Bromides and Para-Substituted Phenyl Boronic Acids[a]

product	X	Y	reactant	temp (°C)	time (h)	yield (%)
4.1	NO_2	NO_2	**11.1**	70–75	16	28
4.2	NO_2	OMe	**11.1**	90	24	37
4.3	Me	CN	**11.3**	70–75	48	<10
4.4	Me	OMe	**11.3**	90	16	22
4.5	CN	OMe	**11.10**	90	24	<15
4.6	CN	CN	**11.10**	90	48	<10[b]

[a]General conditions: $Pd(PPh_3)_4$, $KF{\cdot}2H_2O$ in toluene/water. [b]Reaction did not go to completion.

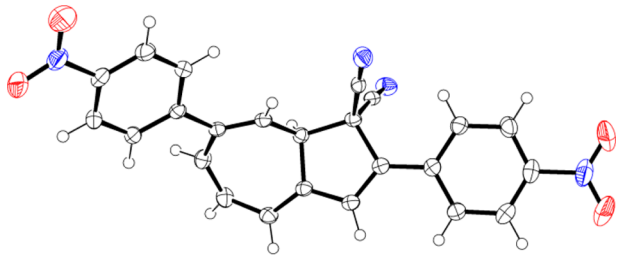
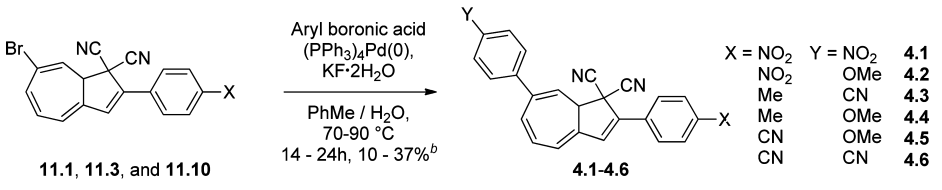


Figure 5. Molecular structure of **4.1** (CCDC 912895; crystals grown from CH_2Cl_2/heptanes), with displacement ellipsoids at 50% probability for non-H atoms.

During the screening, it was found that using amine bases (Et_3N or *i*-Pr_2NH) in THF at up to 100 °C (MW) with 10 mol % $Pd(PPh_3)_4$ as the catalyst gave no reaction, and if the reaction was heated at 140 °C, then azulene formation was observed. Decomposition of the starting material readily occurred in DMF at 70 °C (60 min), but in toluene, about 5–10% of the product could be obtained when the mixture was stirred at 120 °C (MW) for 40 min. Using $KF{\cdot}2H_2O$ in THF gave decomposition within hours, but in toluene, 15–20% of the product could be obtained, whereas a slightly better result was observed using K_3PO_4 in toluene/water. Although most of the attempted conditions gave poorer results than the initial conditions, K_3PO_4 in toluene/water proved to be better than the initial conditions. Good yields were finally obtained by simply changing the ligand system and employing K_3PO_4 as the activator of the boronic acid. Of the three attempted commercially available electron-donating phosphine ligands, P(*t*-Bu)$_3$ and RuPhos, shown in Figure 6, both gave approximately 50% yield in the first attempt (calculated for three steps), whereas Xantphos gave no reaction. The best sets of reaction conditions were then repeated for the Suzuki coupling between **11.3** and 4-methoxyphenylboronic acid, and the isolated yields of **4.4** are shown in Table 5.

With these very encouraging results, we chose to go with the $Pd(OAc)_2$/RuPhos catalyst using K_3PO_4 as the activator. The reactions were performed in toluene/water (9:1) because from time to time they did not proceed without water (probably

Scheme 14. Synthesis of Donor–Acceptor-Functionalized DHAs 4.1–4.6 under Known Conditions[a]



[a]For yields, see Table 4. [b]Yields calculated over three steps from pure DHA **1**.

dx.doi.org/10.1021/jo4020326 | J. Org. Chem. 2014, 79, 41–64

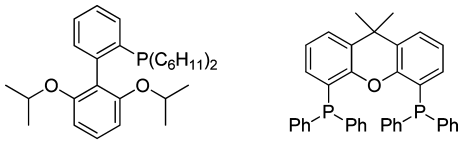


Figure 6. Structures of Ruphos (left) and Xantphos (right).

because of the lack of solubility of K_3PO_4 in toluene). The eight 7-bromides, **11.1**–**11.4**, **11.8**, **11.10**, **11.28**, and **11.34**, were reacted with a selection of functionalized phenylboronic acids (Y = OMe, Me, S*t*-Bu, SMe, Br, H, CN, and NO_2) to yield a selection of donor–acceptor and acceptor–acceptor substituted DHAs, **2.1**–**2.4**, **3.1**–**3.5**, **4.3**–**4.6**, **4.8**–**4.14**, and **4.16**. All substrates were reactive under the same general conditions, and the reactions were cleaner with higher isolated yields, lower catalyst loading, and shorter reaction times compared to the previously reported conditions.[6b] In the case of **4.7**, 4-(*N*,*N*-dimethylamino)phenylboronic pinacol ester was employed, as 4-(*N*,*N*-dimethylamino)phenyl boronic acid is very unstable and only commercially available as the hydrochloride salt. In this case, the activator was changed to a mixture of K_3PO_4 and $KF{\cdot}2H_2O$ (1.2 equiv). The products were generally extremely difficult to purify owing to poor separation by column chromatography in addition to their light sensitivity. Multiple column chromatography purifications were avoided, if possible, because of the danger of the loss of compound because of some unavoidable light exposure, resulting in a mixture of the 7- and 6-isomer as a result of isomerization.[6,9] The general reaction is shown in Scheme 15. These conditions were also employed in two recently published papers.[8h,18]

In Table 6, the recorded yields for the Suzuki couplings using $Pd(OAc)_2$/RuPhos together with some functional group transformations are listed.

We have recently reported that the aryliodide unit of DHA **11.4** is more reactive than the vinylbromide in the Suzuki cross-coupling (Scheme 16) using $KF{\cdot}2H_2O$ and $Pd(PPh_3)_4$.[4b,23] In the case of DHA **11.8**, the vinylbromide was found to be more reactive than the arylbromide. Suzuki coupling between **11.8** and methoxyphenyl boronic acid, using the mentioned conditions, gave **4.10**, which indicates the higher reactivity of the vinylbromide. Reaction for 30 min at 90 °C (MW) gave 2-fold-coupled DHA **4.11** in 42% yield, but when repeated at room temperature overnight, DHA **4.10** was almost exclusively obtained and isolated in 82% yield. In addition, phenyl boronic acid, bromophenyl boronic acid, and cyanophenyl boronic acid reacted selectively on the vinylbromide, although the amount of boronic acid added is crucial for the outcome; thus, the arylbromide reacts with any excess of boronic acid or if the temperature is elevated to 50 °C. In the case of bromophenyl boronic acid, an excess of the reagent was needed because it eventually polymerized. By ^1H and ^{13}C HMBC NMR, the positions of the phenyl substituents were determined.

As a proof of concept, nitro-DHA **3.6** was reduced using Zn(s) in AcOH to yield corresponding amino-DHA **3.7**, which was isolated crude in 74% yield, as shown in Scheme 17. This gives a useful alternative to using simply the amino phenyl boronic acid or ester, as this seemed to complicate the Suzuki coupling, although the compound, in this specific example, could not be purified.

Finally, the *tert*-butylthioether[8h] was oxidized using either 1.0 or 2.2 molar equiv of *m*-CPBA to yield the sulfoxide and the sulfone, respectively (Scheme 18).

CONCLUSIONS

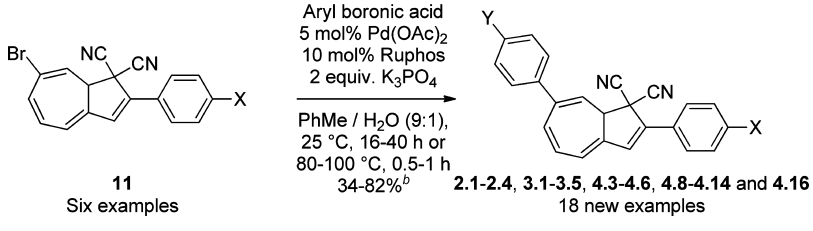
We have expanded the operationally simple large-scale synthesis of DHAs to tolerate a variety of functional groups: both electron withdrawing and donating (NO_2, CN, halo, alkyl, amido, and thioether). Several transition-metal-catalyzed functional-group transformations and cross couplings have been explored, demonstrating the usefulness of both para- and meta-substituted iodo-DHAs as synthetic precursors for larger functionalized systems. Here, the aim has been to find reaction conditions that reduce the formation of the fully unsaturated azulene, especially because these conditions usually require base, which can readily form azulene from DHA. Via a regioselective bromination–elimination cross-coupling protocol, we have prepared a large selection of donor–acceptor-functionalized DHAs. Optimum conditions for performing Suzuki couplings on dihydroazulenes incorporating halogen substituents were developed that tolerated both electron-withdrawing and electron-donating groups. These

Table 5. Reaction Conditions and Isolated Yields for Suzuki Couplings[a]

product	X	Y	solvent	catalyst	ligand	temp (°C)	time (min)	yield (%)
4.4	Me	OMe	PhMe	$PdCl_2(PhCN)_2$	P(*t*-Bu)$_3$	80 (MW)	30	nr
4.4	Me	OMe	PhMe/H_2O	$PdCl_2(PhCN)_2$	P(*t*-Bu)$_3$	100 (MW)	30	51
4.4	Me	OMe	PhMe/H_2O	$Pd(OAc)_2$	RuPhos	80 (MW)	30	52
4.4	Me	OMe	PhMe/H_2O	Pd_2dba_3	Xantphos	80 (MW)	30	nr

[a]General conditions: 0.30 mmol 7-bromide and 2 mol equiv K_3PO_4 as activator and 5 mol % [Pd] and 10 mol % ligand for RuPhos and P(*t*-Bu)$_3$ and 5 mol % for Xantphos. nr, no reaction; MW, microwave.

Scheme 15. Synthesis of Donor–Acceptor-Functionalized DHAs under Improved Conditions[a]



[a]For yields, see Table 6. [b]Yields calculated over three steps from pure DHA **1**.

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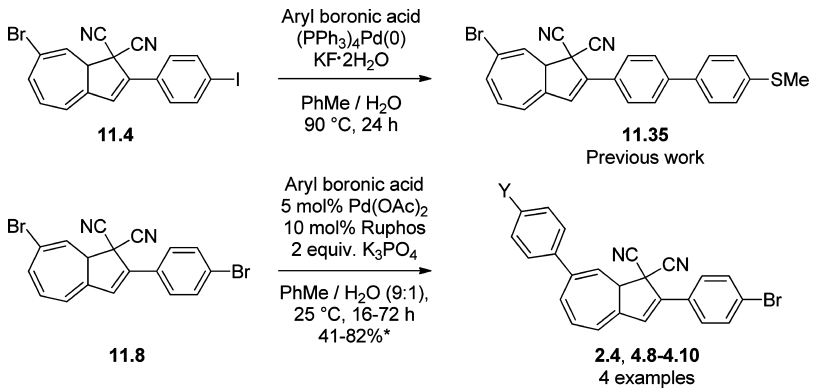
Table 6. Reaction Conditions and Isolated Yields for Suzuki Couplings, Reduction, Cyanation, and Oxidations[a]

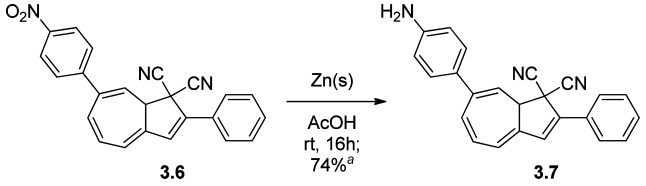
product	X	Y	reactant	temp (°C)[b]	time	yield (%)
2.1	Me	H	**11.3**	80	1 h	34
4.3	Me	CN	**11.3**	25	72 h	46
4.4	Me	OMe	**11.3**	25	16 h	70
4.5	CN	OMe	**11.10**	80 (MW)	30 min	52
	CN	OMe	**11.10**	25	16 h	41[c]
4.6	CN	CN	**11.10**	50	8 h	29
4.7[d]	CN	NMe_2	**11.10**	(1) 110, (2) 50	(1) 1 h, (2) 16 h	9
2.2[e]	CN	H	**11.10**	70	20 h	20
2.3	NO_2	H	**11.1**	80	1 h	55
3.1	H	SMe	**11.34**	90 (MW)	15 min	59
3.2	H	CN	**11.34**	25	72 h	60
3.3	H	Me	**11.34**	25	24 h	59
3.4	H	Br	**11.34**	25	48 h	64
3.5	H	S*t*-Bu	**11.34**	25	16 h	67
3.7[f]	H	NH_2	**3.6**[g]	25	6 h	74
3.8[h]	H	SO*t*-Bu	**3.5**	25	30 min	75
3.9[h]	H	SO_2*t*-Bu	**3.5**	25	20 min	92
2.4	Br	H	**11.8**	25	60 h	65
4.8	Br	Br	**11.8**	25	60 h	72
4.9	Br	CN	**11.8**	25	16 h	41
4.10	Br	OMe	**11.8**	25	16 h	82
4.11	C_6H_4OMe	OMe	**11.8**	90 (MW)	30 min	42
4.12	C_6H_5	H	**11.8**	25	60 h	12[i]
4.13	C_6H_4CN	CN	**11.8**	25	16 h	<5[i]
4.14	S*t*-Bu	S*t*-Bu	**11.28**	25	16 h	53
4.15[h]	SO_2*t*-Bu	SO_2*t*-Bu	**4.14**	25	20 min	82
4.16	C_6H_4SMe	SMe	**11.4**	50	7 h	46

[a]All Suzuki couplings were done using 2 mol equiv K_3PO_4 as activator, PhMe/H_2O (9:1) as solvent, 5 mol % $Pd(OAc)_2$, and 10 mol % RuPhos. [b]MW, microwave. [c]The compound was isolated in 41% yield. The rest of an estimated 60% yield was lost because of the lack of separation by column chromatography. [d]The boronic ester was used. As activator, a mixture of K_3PO_4 and KF·3H_2O was used (1.2 equiv). [e]Prepared by palladium-catalyzed cyanation using $Zn(CN)_2$ and 5−10 mol % $Pd(PPh_3)_4$ in DMF. [f]Prepared by reduction of **3.7**[6b] (7-(4-nitrophenyl)-2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile) using Zn(s) in neat AcOH and isolated crude. [g]Prepared according to ref 6b. [h]Prepared by oxidation using *m*-CPBA in CH_2Cl_2. [i]Isolated as byproducts.

Scheme 16. Observed Selectivity between Aryliodide and Vinylbromide and between Arylbromide and Vinylbromide in the Suzuki Coupling on Halogen-Substituted DHAs



Scheme 17. Reduction of Nitro-DHA 3.6[a]



[a]Crude yield.

functionalizations are important for tuning the switching properties. Indeed, recent kinetics studies on the ring-closure reaction of the corresponding vinylheptafulvenes showed that the rate of this reaction was finely tuned by the electronic character of the substituent group and its position on the system, and the kinetics data followed Hammett correlations.

EXPERIMENTAL SECTION

General Methods. All reactions except for the Knoevenagel condensations were done under an argon atmosphere. All reactions

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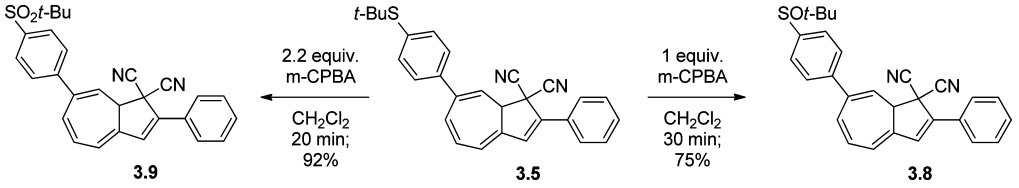
Scheme 18. Oxidation of Thioether Using *m*-CPBA



using palladium catalyst were performed in a solvent flushed with argon by letting argon flow through the solvent for at least 20 min as it was exposed to ultrasound. All handling of photochromic compounds was done in the dark. All operations involving DHAs (evaporation of solvents, column chromatography, and reactions) were done in glassware wrapped in tinfoil. Large amounts (>200 mg) of DHA compounds in solution turn red within minutes, whereas small amounts turn red within seconds in daylight, and traces of the VHF and/or isomerized DHA can be observed by NMR spectroscopy. Brominations were done in CH_2Cl_2 (stabilized with amylene) using a stock solution of bromine in CH_2Cl_2 (1.00 mL Br_2 in 25 mL CH_2Cl_2, 0.78 M). Elimination reactions were performed in THF (distilled over Na/benzophenone). THF for column chromatography were used as purchased. Thin-layer chromatography (TLC) was carried out on commercially available precoated plates (silica 60) with fluorescence indicator; color change from yellow to red or violet upon irradiation with UV light (366 nm, not 254 nm) indicated the presence of a DHA. All melting points are uncorrected, and if the compounds were not strongly colored (like the azulenes), then they were measured on an automatic melting-point apparatus. All spectroscopic measurements (including photolysis) were performed in a 1 cm path length cuvette. UV−vis absorption spectra were obtained by scanning the wavelengths from 800 to 200 nm. Absorption data for VHFs were obtained after light-induced ring opening of the corresponding DHAs using a 150 W Xenon arc lamp equipped with a monochromator; the DHA absorption maximum (lowest-energy absorption) for each individual species was chosen as the wavelength of irradiation (line width ±2.5 nm). The thermal back reaction was performed by heating the sample (cuvette) using a Peltier unit in the UV−vis spectrophotometer. All NMR spectra were acquired on a 500 MHz instrument equipped with a (noninverse) cryoprobe or, in a few examples, with a broadband probe. All chemical shift values in ^{1}H and ^{13}C NMR spectra are referenced to the residual solvent peak ($CDCl_3$ δ_H = 7.26 ppm and δ_C = 77.16 ppm; CD_3CN δ_H = 1.96 ppm and δ_C = 1.94 ppm; DMSO-d_6 δ_H = 2.50 ppm and δ_C = 39.52 ppm), and ^{13}C NMR values are given with one decimal except for the cases with very close signals. All processing of the NMR spectra, calculating of the coupling constants, peak-picking, and so forth were done without exponential apodization (line broadening), but NMR spectra presented in ESI are shown with exponential apodization equal to 0.3−0.5 Hz.

Synthesis. *2-(4′-Nitrophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.1**).* To a stirred solution of VHF precursor **7a** (prepared from 73.24 mmol of **5.1**) in 1,2-dichloroethane (250 mL) was added tritylium tetrafluoroborate (25.39 g, 76.90 mmol) (the solution immediately turned dark red), and the reaction mixture was refluxed for 1 h. The resulting dark solution was cooled to 0 °C, and Et_3N (10.21 mL, 73.24 mmol) was slowly added over 1 h, after which the temperature was allowed to rise to rt. The now strongly red reaction mixture was refluxed for 1 h (monitored by TLC) excluded from light. After the reaction mixture cooled to rt, saturated aqueous NH_4Cl (100 mL) was added, and the organic layer was separated. This was washed with water (100 mL) and brine (100 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo onto Celite. Purification by dry column vacuum chromatography (SiO_2, 113 cm^2, 0−100% toluene/heptanes, 10% steps, 150 mL fractions) gave **1.1** as a yellow oil (compounds removed should be triphenylmethane and triphenylmethanol). Recrystallization from boiling 96% ethanol (600 mL) gave **1.1** (11.19 g, 37.15 mmol, 51%) as yellow crystals. Crystals suitable for X-ray crystallography were grown from methanol. TLC (toluene): R_f = 0.37. mp 139.2−140.1 °C (methanol) (lit.[7a] mp 145−146 °C (methanol)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 9.0 Hz, 2H), 7.90 (d, J = 9.0 Hz, 2H), 7.06 (s, 1H), 6.64 (dd, J = 11.1, 6.1 Hz, 1H), 6.56 (dd, J = 11.1, 6.0 Hz, 1H), 6.47 (d, J = 6.1 Hz, 1H), 6.35 (ddd, J = 10.2, 6.0, 2.1 Hz, 1H), 5.83 (dd, J = 10.2, 3.9 Hz, 1H), 3.84 (dt, J = 3.9, 2.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 137.9, 137.6, 136.6, 136.3, 132.4, 130.9, 128.1, 127.1, 124.7, 123.6, 119.7, 114.7, 112.4, 51.1, 45.2 ppm. UV−vis (MeCN) λ_{max} (ε) = 386 nm (17.8 × 10^3 M^{-1} cm^{-1}).

*2-(4′-Aminophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.2**).* Method 1: A solution of $FeSO_4$ (3.33 g, 124 mmol) in water (60 mL) was added to a solution of DHA **1.1** (748 mg, 2.48 mmol) in 96% EtOH (60 mL), and the reaction mixture was heated to reflux for 30 min. Diluted aqueous ammonia (74 mL, 12%, 471 mmol) was added, and the reaction mixture was refluxed for a further 15 min. The reaction mixture was diluted with Et_2O (150 mL), and saturated aqueous NH_4Cl (150 mL) was added. The mixture was filtered, and the organic layer was separated. The aqueous phase was extracted with Et_2O (2 × 50 mL), the combined organic phases were dried with $MgSO_4$ and filtered, and the solvents were removed under vacuum. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% $CHCl_3$/heptanes, 12.5% steps, 40 mL fractions) gave **1.2** (235 mg, 0.865 mmol, 35%) as a yellow solid. Method 2: To a stirred suspension of DHA **1.1** (1.01 g, 3.35 mmol) in AcOH (50 mL) under an atmosphere of argon was added zinc dust (1.01 g, 15.4 mmol), and the reaction mixture was stirred at rt for 4 h. The resulting dark yellow suspension was diluted with Et_2O (100 mL), and, while stirring, saturated aqueous $NaHCO_3$ (765 mL) was carefully added over 4−6 h, until the yellow to red color was completely transferred into the organic phase. **Caution:** *gas evolution.* The phases were separated, and the organic phase was washed with brine (50 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% $CHCl_3$/heptanes, 12.5% steps, 40 mL fractions) gave **1.2** (183 mg, 0.67 mmol, 20%) as a yellow solid. Method 3: A suspension of DHA **1.9** (1.57 g, 5.00 mmol) in a mixture of 6 M aqueous HCl (100 mL) and EtOH (100 mL) was refluxed for 20 min. (The compound should dissolve. The reaction was monitored by TLC by taking a sample and neutralizing it with saturated aqueous $NaHCO_3$ and extracting with Et_2O.) The reaction mixture was allowed to cool, after which it was carefully transferred (over the course of several hours) into a vigorously stirring mixture of saturated aqueous $NaHCO_3$ (525 mL) and Et_2O (100 mL). (The yellow to red color should be in the organic layer. The pH of the mixture should be checked.) The phases were separated, and the aqueous layer was extracted with Et_2O (3 × 100 mL). The combined organic phases was washed with brine (100 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% $CHCl_3$/heptanes, 12.5% steps, 40 mL fractions) gave **1.2** (1.01 g, 3.72 mmol, 74%) as a yellow solid. TLC ($CHCl_3$): R_f = 0.30. TLC (50% THF/heptanes): R_f = 0.50. mp 184.5−185.5 °C dec (lit.[7a] mp 188 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.7 Hz, 2H), 6.72 (d, J = 8.7 Hz, 2H), 6.68 (s, 1H), 6.54 (dd, J = 11.2, 6.4 Hz, 1H), 6.41 (dd, J = 11.2, 6.1 Hz, 1H), 6.28 (ddd, J = 10.2, 6.1, 1.9 Hz, 1H), 6.24 (d, J = 6.4 Hz, 1H), 5.80 (dd, J = 10.2, 3.8 Hz, 1H), 3.99 (br s, 2H), 3.76 (dt, J = 3.8, 1.9 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 140.6, 139.5, 131.1, 129.8, 128.4, 127.8, 127.6, 120.5, 119.2, 119.1, 115.5, 115.1, 113.0, 51.2, 45.1 ppm. UV−vis (MeCN) $\lambda_{max\ DHA}$ (ε) = 389 nm (37.0 × 10^3 M^{-1} cm^{-1}). $\lambda_{max\ VHF}$ (ε) = 455 nm (40.2 × 10^3 M^{-1} cm^{-1}).

*2-(4′-Tolyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.3**).* To a stirred solution of VHF precursor **7.3** (from 73.24 mmol **5.3**) in 1,2-dichloroethane (250 mL) was added tritylium tetrafluoroborate (25.39 g, 76.90 mmol) (the solution immediately turned dark red), and the reaction mixture was refluxed for 1 h (TLC (toluene): R_f = 0.51 (**7.3**),

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R_f = 0.23 (VHF)). The resulting dark solution was diluted with toluene (250 mL) and cooled to 0 °C, after which Et_3N (10.21 mL, 73.24 mmol) was slowly added over 1 h and the temperature was then allowed to rise to rt. The now strongly red reaction mixture was refluxed for 1 h (TLC (toluene): R_f = 0.71 (DHA)) excluded from light. The reaction mixture was then concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 113 cm^2, 0−40% CH_2Cl_2/heptanes, 5% steps, 150 mL fractions) gave **1.3** (11.11 g, 41.09 mmol, 56%) as yellow crystals with minor impurities. Recrystallization from boiling heptanes or EtOH gave **1.3** (9.507 g, 35.17 mmol, 48%) as yellow crystals. Crystals suitable for X-ray crystallography was grown from $CHCl_3$/heptanes. Alternatively, purification can also be accomplished by extraction with boiling heptanes (5 × 250 mL) followed by cooling to rt. The resulting dark yellow or even black crystals were then recrystallized from boiling heptanes while treating with activated carbon to give **1.3** (7.097 g, 26.26 mmol to 14.16 g, 51.20 mmol, 36−71%) as yellow crystals. TLC (50% CH_2Cl_2/heptanes): R_f = 0.48. mp 150.8−152.0 °C (ethanol) (lit.[7a] mp 151 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66−7.62 (m, 2H), 7.30−7.26 (m, 2H), 6.84 (s, 1H), 6.56 (dd, J = 11.2, 6.4 Hz, 1H), 6.46 (dd, J = 11.2, 6.1 Hz, 1H), 6.31 (dd, J = 10.0, 6.4 Hz), 6.30−6.24 (m, 1H), 5.82 (dd, J = 10.0, 3.6 Hz, 1H), 3.78 (dd, J = 3.6, 1.8 Hz, 1H), 2.41 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 140.5, 139.1, 131.5, 131.4, 130.8, 130.1, 127.8, 127.7, 126.3, 120.6, 119.6, 115.4, 113.0, 51.3, 45.3, 21.6 ppm. UV−vis (MeCN) λ_{DHA} (ε): 358 nm (20.0 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 470 nm (31.4 × 10^3 M^{-1} cm^{-1}).

2-(4′-Iodophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (1.4).[8f] TLC (toluene): R_f = 0.73. UV−vis (MeCN) λ_{DHA} (ε): 358 nm (26.2 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 476 nm (33.8 × 10^3 M^{-1} cm^{-1}).

*2-(3′-Iodophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.5**).* Prepared according to the general procedure for **1.1**: **7.5** (prepared from 22.2 mmol of **5.5**) and tritylium tetrafluoroborate (7.792 g, 23.31 mmol, 1.05 equiv) in 1,2-dichloroethane (100 mL) were refluxed for 1 h. Afterward, it was diluted with toluene (100 mL), the reaction mixture was cooled to 0 °C, and Et_3N (3.09 mL, 22.2 mmol) was added over the course of 1 h. The reaction mixture was allowed to reach rt, after which it was refluxed for 1 h. The resulting black reaction mixture was then concentrated on Celite. Purification by dry column vacuum chromatography (SiO_2, 28.3 cm^2, 0−87.5% chloroform/heptanes, 6.25% steps, 80 mL fractions) followed by recrystallization from heptanes (300 mL) gave **1.5** (4.25 g, 11.11 mmol, 50%) as yellow crystals. TLC (toluene): R_f = 0.72. mp 101.9−105.4 °C (heptanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (t, J = 1.7 Hz, 1H), 7.82−7.68 (m, 2H), 7.22 (t, J = 7.9 Hz, 1H), 6.89 (s, 1H), 6.58 (dd, J = 11.3, 6.3 Hz, 1H), 6.50 (dd, J = 11.3, 6.1 Hz, 1H), 6.37 (d, J = 6.3 Hz, 1H), 6.31 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.81 (dd, J = 10.2, 3.8 Hz, 1H), 3.78 (dt, J = 3.9, 2.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 138.4, 138.3, 135.3, 133.7, 132.8, 131.5, 1310, 130.9, 127.9, 125.3, 121.9, 119.6, 115.0, 112.6, 95.1, 51.2, 45.2 ppm. Anal. Calcd for $C_{18}H_{11}N_2I$ (382.20): C, 56.57; H, 2.90; N, 7.33. Found: C, 56.58; H, 2.54; N, 7.25. HRMS (ESI+): m/z 383.0025 [MH^+] calcd for ($C_{18}H_{12}N_2I^+$): m/z 383.0040. UV−vis (MeCN) λ_{DHA} (ε): 358 nm (16.0 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 478 nm (28.3 × 10^3 M^{-1} cm^{-1}).

*2-(4′-Fluorophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.6**).* To a stirring solution **7.6** (8.30 g, 30.0 mmol) in CH_2Cl_2 (300 mL) was added tritylium tetrafluoroborate (11.30 g, 34.2 mmol) and the resulting mixture was stirred 16 h at rt, covered from light. The vessel was placed in an ice bath and NEt_3 (4.5 mL, 31.2 mmol) was added carefully over 10 min and the mixture was allowed to stir for 1 h. The solvent was removed in vacuum and the crude residue was dissolved in acetonitrile (50 mL) and the vessel subjected to heating at 50 °C for 20 min. The solvent was again removed and the crude material purified by flash column chromatography (SiO_2, eluent: 50% CH_2Cl_2/heptane) to obtain pure DHA **1.6** as a yellow crystalline solid (2.82 g, 10.3 mmol, 34%). TLC (50% CH_2Cl_2/heptane): R_f = 0.38. mp 119.5−121.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, J = 8.7, 5.1 Hz, 2H), 7.17 (dd, J = 8.7, 8.7 Hz, 2H), 6.82 (s, 1H), 6.57 (dd, J = 11.3, 6.3 Hz, 1H), 6.48 (dd, J = 11.3, 6.1 Hz, 1H), 6.35−6.30 (m, 2H), 5.81 (dd, J = 10.2, 3.8 Hz, 1H), 3.79 (dt, J = 3.8, 1.9 Hz, 1H)ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7 (d, J = 252 Hz), 139.2, 138.6, 132.4 (d, J = 2.0 Hz), 131.1 (d, J = 9.5 Hz), 128.4 (d, J = 8.4 Hz), 127.8, 127.0 (d, J = 3.6 Hz), 121.2, 119.5, 116.7, 116.6, 115.2, 112.8, 51.3, 45.5 ppm. Anal. Calcd for $C_{18}H_{11}N_2F$ (274.29): C, 78.81; H, 4.04; N, 10.22. Found: C, 78.64; H, 3.83; N, 10.22. MS (ESP+): m/z 297 [MNa^+]. UV−vis (MeCN) λ_{DHA} (ε): 354 nm (17.8 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 474 nm (29.0 × 10^3 M^{-1} cm^{-1}).

*2-(4′-Methoxyphenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.7**).* Prepared according to the general procedure for **1.1**: **7.7** (prepared from 73.24 mmol of **5.7**) and tritylium tetrafluoroborate (25.39 g, 76.90 mmol) in 1,2-dichloroethane (250 mL), were refluxed for 1 h and then diluted with toluene (250 mL). The reaction mixture was cooled to 0 °C, and Et_3N (10.21 mL, 73.24 mmol) was added over the course of 1 h. The reaction mixture was allowed to reach rt, after which it was refluxed for 1 h. The resulting black reaction mixture was then concentrated on Celite, and purification by dry column vacuum chromatography (SiO_2, 113 cm^2, 0−75% toluene/heptanes, 6.25% steps, 80 mL fractions) followed by recrystallization from boiling heptanes (600 mL) gave **1.7** (13.77 g, 48.09 mmol, 66%) as yellow crystals. Alternatively, the crude reaction mixture can be purified without the use of column chromatography by the following procedure. The reaction mixture was concentrated in vacuo, and the residue was extracted with boiling heptanes (6 × 250 mL). The extracts were not combined but were allowed to cool to rt separately. The resulting yellow precipitates were then subjected to TLC analysis, and the samples of similar purity (the two first extracts) were combined and recrystallized separately from boiling heptanes (250−350 mL) using activated carbon, which gave **1.7** (10.76 g, 37.61 mmol, 51%) as yellow crystals. Crystals suitable for X-ray crystallography were grown from ethanol. TLC (toluene): R_f = 0.45. mp 125.8−126.8 °C (heptanes) (lit.[7a] mp 125−126 °C (MeOH)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 9.0 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 6.75 (s, 1H), 6.55 (dd, J = 11.2, 6.3 Hz, 1H), 6.44 (dd, J = 11.2, 6.3 Hz, 1H), 6.31−6.28 (m, 2H), 5.82 (dd, J = 10.3, 3.8 Hz, 1H), 3.86 (s, 3H), 3.78 (dt, J = 3.8, 1.9 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 140.2, 139.2, 131.1, 130.5, 130.3, 128.0, 127.8, 123.2, 120.1, 119.5, 115.4, 114.9, 113.0, 55.6, 51.3, 45.4 ppm. UV−vis (MeCN) $\lambda_{max\ DHA}$ (ε) = 365 nm (20.0 × 10^3 M^{-1} cm^{-1}). $\lambda_{max\ VHF}$ (ε) = 471 nm (25.3 × 10^3 M^{-1} cm^{-1}).

*2-(4′-Bromophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.8**).* Prepared according to the general procedure for **1.1**: **7.8** (prepared from 73.24 mmol of **5.8**) and tritylium tetrafluoroborate (25.39 g, 76.90 mmol) in 1,2-dichloroethane (250 mL) were refluxed for 1 h and then diluted with toluene (250 mL). The reaction mixture was cooled to 0 °C, and Et_3N (10.21 mL, 73.24 mmol) was added over the course of 1 h. The reaction mixture was allowed to reach rt, after which it was refluxed for 1 h. Purification by dry column vacuum chromatography (SiO_2, 113 cm^2, 0−75% $CHCl_3$/heptanes, 6.25% steps, 160 mL fractions) followed by recrystallization from boiling heptanes (1150 mL) gave **1.8** (16.32 g, 48.69 mmol, 66%) as yellow crystals. TLC (toluene): R_f = 0.80. mp 157.2−157.8 °C (heptanes) (lit.[7a] mp 151 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (br s, 4H), 6.88 (s, 1H), 6.57 (dd, J = 11.3, 6.3 Hz, 1H), 6.49 (dd, J = 11.3, 6.1 Hz, 1H), 6.36 (d, J = 6.3 Hz, 1H), 6.31 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.81 (dd, J = 10.2, 3.8 Hz, 1H), 3.79 (dt, J = 3.8, 2.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 138.5, 133.1, 132.7, 131.4, 131.0, 129.5, 127.9, 127.8, 124.6, 121.6, 119.6, 115.1, 112.7, 51.2, 45.3 ppm. UV−vis (MeCN): λ_{DHA} (ε): 360 nm (19.4 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 474 nm (30.8 × 10^3 M^{-1} cm^{-1}).

*2-(4′-Acetaminophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.9**).* To a stirred solution of VHF precursor **7.9** (6.30 g, 20.0 mmol) in 1,2-dichloroethane (200 mL) was added tritylium tetrafluoroborate (7.26 g, 22.0 mmol). The reaction mixture was heated to reflux for 1 h, after which it was cooled to 0 °C, and NEt_3 (3.00 mL, 22.0 mmol) was added dropwise. The now strongly red reaction mixture was allowed to reach rt over 1 h and was then stirred for 3 h. The now red reaction mixture was then concentrated on Celite, and purification by dry column vacuum chromatography (SiO_2, 28.3 cm^2, 0−100% EtOAc/heptanes, 6.25% steps, then 6× fractions of neat EtOAc to collect product, 80 mL fractions; the compound moved very differently on the column compared to the movement on TLC) gave **1.9** (4.40 g, 14.1 mmol, 70%) as a yellow solid (crude fractions can be recrystallized from boiling EtOAc/heptanes). TLC (60% EtOAc/heptanes) R_f = 0.23−0.33. mp 207−209 °C dec. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.23 (s, 1H), 7.74 (s, 4H), 7.34 (s, 1H), 6.58 (dd, J = 11.3, 6.5 Hz, 1H), 6.45 (d, J = 11.3,

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6.5, 1H), 6.43 (d, J = 6.2, 1H), 6.35 (ddd, J = 10.2, 6.2, 2.1 Hz, 1H), 5.71 (dd, J = 10.2, 3.7 Hz, 1H), 3.92 (dt, J = 3.7, 2.1 Hz, 1H), 2.08 (s, 3H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.7, 140.7, 138.7, 138.5, 132.1, 130.9, 130.3, 127.7, 126.8, 124.7, 120.9, 119.5, 119.2, 115.1, 113.1, 50.6, 44.9, 24.1 ppm. Anal. Calcd for $C_{20}H_{15}N_3O$ (313.35): C, 76.66; H, 4.82; N, 13.41. Found: C, 76.56; H, 4.82; N, 13.47. MS (MALDI−): m/z 313 [M^-]. UV−vis (MeCN): λ_{DHA} (ε): 369 nm (27.5×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 472 nm (24.8×10^3 M^{-1} cm^{-1}).

*2-(4′-Cyanophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.10**).* Method 1: To a solution of iodo-DHA **1.4** (1.77 g, 4.63 mmol) in dry argon-flushed DMF (10 mL) in a glass container suitable for microwave irradiation were added tetrakis(triphenylphosphine)-palladium(0) (107 mg, 92.6 μmol, 2 mol %) and $Zn(CN)_2$ (326 mg, 2.78 mmol), and the reaction mixture was heated by microwave irradiation at 70 °C for 2 h. The reaction mixture was allowed to cool to rt, and it was then poured into EtOAc (100 mL) and washed with brine (3 × 50 mL). The water phases were kept and extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with water (3 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 10% steps, then 10 × 40 mL neat toluene, 40 mL fractions) gave **1.10** (1.25 g, 4.44 mmol, 96%) as a yellow solid. Recrystallization from EtOH (150 mL) gave **1.10** (950 mg, 3.38 mmol, 73%) as yellow crystals. TLC (toluene): R_f = 0.23. mp 214 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.01 (s, 1H), 6.60 (dd, J = 11.2, 6.1 Hz, 1H), 6.55 (dd, J = 11.2, 6.0 Hz, 1H), 6.45 (d, J = 6.1 Hz, 1H), 6.34 (ddd, J = 10.2, 6.0, 2.1 Hz, 1H), 5.82 (dd, J = 10.2, 3.8 Hz, 1H), 3.82 (dt, J = 3.8, 2.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 137.9, 135.6, 134.8, 133.1, 132.3, 130.9, 128.1, 126.8, 123.2, 119.7, 118.2, 114.8, 113.4, 112.4, 51.1, 45.1 ppm. Anal. Calcd for ($C_{19}H_{11}N_3$): C, 81.12; H, 3.94; N, 14.94. Found: C, 81.22; H, 4.02; N, 14.83. Corresponding VHF: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 6.80−6.73 (m, 1H), 6.52−6.46 (m, 2H), 6.41−6.35 (m, 1H), 6.35 (d, J = 4.2 Hz, 1H), 6.00 (dd, J = 12.0, 8.0 Hz, 1H), 5.79 (dd, J = 12.0, 2.9 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 154.4, 142.6, 139.8, 136.6, 135.7, 135.4, 135.0, 134.9, 133.6, 129.3, 118.3, 117.9, 114.9, 114.6, 114.1 ppm (1 signal is missing because of overlap). UV−vis (MeCN) λ_{DHA}: 368 nm. λ_{VHF}: 482 nm. Method 2: To a solution of bromo-DHA **1.8** (3.84 g, 11.4 mmol) in argon-flushed DMF (15 mL) in a glass container suitable for microwave irridiation were added $Pd(OAc)_2$ (64.3 mg, 286 μmol), RuPhos (267 mg, 573 umol), and $Zn(CN)_2$ (803 mg, 6.84 mmol), and the reaction mixture was heated by means of microwave irradiation at 70 °C for 30 min followed by 90 °C for 30 min. No reaction was observed. To the resulting black reaction mixture was added tetrakis(triphenylphosphine)-palladium(0) (662 mg, 573 μmol, 5 mol %), and the reaction mixture was heated by microwave irridiation at 90 °C for 60 min. The reaction mixture was allowed to cool to rt and was then poured into Et_2O (200 mL), washed with brine (100 mL), water (2 × 100 mL), and then with brine (100 mL) again (to prevent emulsions). The combined organic phases were dried with $MgSO_4$, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 10% steps, 40 mL fractions) gave **1.8** (1.54 g, 4.56 mmol, 40%) as a yellow solid, 2-(4-bromophenyl)azulene-1-carbonitrile **9.8** as a purple solid with minor impurities, **1.10** (1.13g, 3.99 mmol, 35%) as a yellow solid, and 2-(4-cyanophenyl)azulene-1-carbonitrile **9.10** (312 mg, 1.25 mmol, 11%) as a purple solid. For **1.10**: spectroscopic data are identical to those of **1.10** described above. For **9.8**: recrystallization from EtOH (50 mL) gave 2-(4-bromophenyl)azulene-1-carbonitrile **9.8** (316 mg, 1.03 mmol, 9%) as a purple solid. mp 162.5−163.0 °C (ethanol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, J = 9.8 Hz, 1H), 8.42 (d, J = 9.7 Hz, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.81 (t, J = 9.8 Hz, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.56 (t, J = 9.8 Hz, 1H), 7.52 (s, 1H), 7.50 (t, J = 9.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 145.8, 142.7, 139.4, 138.4, 136.2, 133.4, 132.5, 130.2, 128.4, 128.1, 124.1, 118.0, 116.4, 94.2 ppm. Anal. Calcd for $C_{17}H_{10}BrN$ (308.17): C, 66.26; H, 3.27; N, 4.55. Found: C, 66.18; H, 3.06; N, 4.45. MS (MALDI+): m/z 307, 309 [MH^+ $Br^{79/81}$]. For **9.10**: recrystallization from EtOH (80 mL) gave 2-(4-cyanophenyl)azulene-1-carbonitrile **9.10** (145 mg, 0.572 mmol, 5.0%) as dark-purple needles. For **9.10**: TLC (toluene): R_f = 0.10. mp 220−222 °C (ethanol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, J = 9.8 Hz, 1H), 8.49 (d, J = 9.8 Hz, 1H), 8.14 (d, J = 8.6 Hz, 2H), 7.88 (t, J = 9.8 Hz, 1H), 7.81 (d, J = 8.6 Hz, 2H), 7.61 (t, J = 9.8 Hz, 1H), 7.57 (s, 1H), 7.56 (t, J = 9.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 145.7, 142.6, 140.4, 139.4, 138.9, 137.2, 133.0, 129.2, 128.7, 128.4, 118.7, 117.6, 117.0, 112.8, 94.6 ppm. Anal. Calcd for $C_{18}H_{10}N_2$ (256.30): C, 84.35; H, 4.72; N, 10.93. Found: C, 83.91; H, 4.94; N, 10.82. MS (MALDI−): m/z 256 [M^-].

*2-(3′-Cyanophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.11**).* To a stirred solution of **1.5** (526 mg, 1.38 mmol) in argon-flushed DMF (8 mL) in a glass container suitable for microwave irradiation were added $Pd(PPh_3)_4$ (31.8 mg, 27.5 μmol, 2 mol %) and $Zn(CN)_2$ (96.9 mg, 0.826 mmol), and the reaction mixture was heated by microwave irradiation at 70 °C for 3 h. The reaction mixture was allowed to cool to rt and was then poured into EtOAc (100 mL) and washed with brine (3 × 50 mL). The water phases were kept and extracted with EtOAc (3 × 50 mL). The combined organic phases were then washed with water (3 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 10% steps, then 10 × 40 mL neat toluene, 40 mL fractions) gave **1.11** (325 mg, 1.16 mmol, 84%) as a yellow solid. Recrystallization from heptanes (75 mL) gave **1.11** (268 mg, 0.953 mmol, 69%) as a yellow powder. TLC (toluene): R_f = 0.27. mp 146.0−147.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (ddd, J = 7.9, 2.0, 1.1 Hz, 1H), 7.99−7.96 (m, 1H), 7.71 (dt, J = 7.9, 1.3, 1H), 7.63 (dt, J = 7.9, 0.7 Hz, 1H), 6.96 (s, 1H), 6.60 (ddt, J = 11.3, 6.3, 0.7 Hz, 1H), 6.54 (dd, J = 11.3, 6.1 Hz, 1H), 6.43 (d, J = 6.3 Hz, 1H), 6.34 (dddt, J = 10.2, 6.1, 2.1, 0.7 Hz, 1H), 5.81 (dd, J = 10.2, 3.8 Hz, 1H), 3.81 (dt, J = 3.9, 2.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 137.6, 134.9, 133.0, 132.04, 132.02, 130.9, 130.4, 130.04, 129.95, 128.0, 122.8, 119.6, 118.0, 114.7, 114.1, 112.4, 51.1, 45.3 ppm. Anal. Calcd for $C_{19}H_{11}N_3$ (281.31): C, 81.12; H, 3.94; N, 14.94. Found: C, 81.23; H, 3.71; N, 15.06. HRMS (ESP+): m/z 304.0846 [MNa^+], calcd for ($C_{19}H_{11}N_3Na^+$): m/z 304.0845. UV−vis (MeCN) λ_{DHA}: 351 nm. λ_{VHF}: 479 nm.

*2-[4′-(3″-Furyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.12**).* To a stirred solution of iodo-DHA **1.4** (143.0 mg, 0.3741 mmol) in a mixture of argon-flushed toluene (4.5 mL) and water (0.5 mL) were added 3-furyl boronic acid (69.3 mg, 0.619 mmol), K_3PO_4 (319 mg, 1.50 mmol), RuPhos (48.4 mg, 0.10 mmol, 27 mol %), and $Pd(OAc)_2$ (11.6 mg, 0.05 mmol, 13 mol %), and the reaction mixture was stirred for 72 h at rt. The reaction mixture was diluted with Et_2O (50 mL), washed with saturated aqueous NH_4Cl (2 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was redissolved in CH_2Cl_2 and concentrated on Celite. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−40% toluene/heptanes, 5% steps, then 40−65% toluene/heptanes, 2.5% fractions, 40 mL fractions) gave **1.12** (84.4 mg, 0.262 mmol, 70%) as a yellow to red solid. TLC (toluene): R_f = 0.62 (orange to red). mp 161.7−162.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, J = 1.4, 0.9 Hz, 1H), 7.75 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 8.7 Hz, 2H), 7.51 (dd, J = 1.9, 1.4 Hz, 1 H), 6.89 (s, 1H), 6.74 (dd, J = 1.9, 0.9 Hz, 1H), 6.58 (dd, J = 11.3, 6.4 Hz, 1H), 6.48 (dd, J = 11.3, 6.1 Hz, 1H), 6.35 (d, J = 6t.4 Hz, 1H), 6.31 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.83 (dd, J = 10.2, 3.8 Hz, 1H), 3.80 (dt, J = 3.8, 2.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 140.0, 139.4, 138.9, 134.3, 131.9, 131.1, 131.0, 129.1, 127.8, 126.9, 126.6, 125.8, 121.0, 119.6, 115.3, 112.9, 108.7, 51.3, 45.3 ppm. Anal. Calcd for $C_{22}H_{14}N_2O$ (322.36): C, 81.97; H, 4.38; N, 8.69. Found: C, 81.37; H, 4.01; N, 8.64. HRMS (ESP+): m/z 345.1001 [MNa^+], calcd for ($C_{22}H_{14}N_2ONa^+$): m/z 345.0998. UV−vis (MeCN) λ_{DHA} (ε): 370 nm (18.5×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 475 nm (20.7×10^3 M^{-1} cm^{-1}).

*2-[4′-(2″-Furyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.13**).* To a stirred solution of iodo-DHA **1.4** (104.9 mg, 0.274 mmol) in a mixture of argon-flushed toluene (9 mL) and water (1 mL) were added 2-furyl boronic acid (122.6 mg, 1.100 mmol), K_3PO_4 (122 mg, 0.574 mmol), Xantphos (11.2 mg, 0.019 mmol, 7.1 mol %), and $Pd_2(dba)_3$ (8.9 mg, 0.0097 mmol, 3.5 mol %) (the reaction mixture took a red color, which slowly faded to yellow). The reaction mixture was stirred for 48 h at 50 °C. The reaction mixture was diluted with Et_2O (50 mL),washed with saturated aqueous NH_4Cl (2 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was redissolved in CH_2Cl_2 and concentrated on Celite. Purification by dry column

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vacuum chromatography (SiO_2, 12.6 cm^2, 0–70% toluene/heptanes, 10% steps, then 70–90% toluene/heptanes, 5% steps, 40 mL fractions) gave **1.13** (79.7 mg, 0.247 mmol, 91%) as a yellow solid. TLC (75% toluene/heptanes): R_f = 0.38 (yellow → red). mp 158.4–160.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.52 (dd, J = 1.8, 0.7 Hz, 1H), 6.90(s, 1H), 6.76 (dd, J = 3.4, 0.7 Hz, 1H), 6.57 (dd, J = 11.2, 6.4 Hz, 1H), 6.51 (dd, J = 3.4, 1.8 Hz, 1H), 6.47 (dd, J = 11.2, 6.1 Hz, 1H), 6.35 (d, J = 6.4 Hz, 1H), 6.31 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.83 (dd, J = 10.2, 3.9 Hz, 1H), 3.80 (dt, J = 3.9, 2.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 143.1, 139.9, 138.9, 132.3, 132.0, 131.1, 131.0, 129.2, 127.8, 126.8, 124.5, 121.0, 119.6, 115.3, 112.9, 112.2, 106.9, 51.3, 45.2 ppm. Anal. Calcd for $C_{22}H_{14}N_2O$ (322.36): C, 81.97; H, 4.38; N, 8.69. Found: C, 81.92; H, 4.25; N, 8.77. HRMS (ESP+): m/z 345.0997 [MNa^+], calcd for ($C_{22}H_{14}N_2ONa^+$): m/z 345.0998. UV–vis (MeCN) λ_{DHA} (ε): 382 nm (25.2 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 476 nm (21.3 × 10^3 M^{-1} cm^{-1}).

*2-[4′-(2″-Thienyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.14**).* To a stirred solution of iodo-DHA **1.4** (148.6 mg, 0.3888 mmol) in a mixture of argon-flushed toluene (9 mL) and water (1 mL) were added 2-thienyl boronic acid (128.0 mg, 1.000 mmol), K_3PO_4 (212 mg, 1.000 mmol), Xantphos (39 mg, 0.068 mmol, 18 mol %), and $Pd(OAc)_2$ (7.6 mg, 0.034 mmol, 9 mol %), and the reaction mixture was stirred for 16 h at 50 °C. The resulting dark yellow reaction mixture was diluted with Et_2O (50 mL), washed with saturated aqueous NH_4Cl (2 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was redissolved in CH_2Cl_2 and concentrated on Celite. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0–60% toluene/heptanes, 5% steps, then 60–75% toluene/heptanes, 2.5% steps, 40 mL fractions) gave **1.14** (80.7 mg, 238 μmol, 61%) as a dark yellow solid. A stable crystalline solid can be obtained by recrystallization from $CHCl_3$/heptanes. TLC (toluene): R_f = 0.69. mp 159.0–159.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.8 Hz, 2H), 7.40 (dd, J = 3.6, 1.1 Hz, 1H), 7.35 (dd, J = 5.1, 1.1 Hz, 1H), 7.12 (dd, J = 5.1, 3.6 Hz, 1H), 6.90 (s, 1H), 6.58 (dd, J = 11.2, 6.3 Hz, 1H), 6.48 (dd, J = 11.2, 6.1 Hz, 1H), 6.36 (d, J = 6.3 Hz, 1H), 6.32 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.83 (dd, J = 10.2, 3.8 Hz, 1H), 3.80 (dt, J = 3.8, 2.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 139.8, 138.9, 136.1, 132.1, 131.1, 131.1, 129.4, 128.5, 127.8, 126.9, 126.6, 126.1, 124.2, 121.1, 119.6, 115.3, 112.9, 51.3, 45.2 ppm. Anal. Calcd for $C_{22}H_{14}N_2S$ (338.43): C, 78.08; H, 4.17; N, 8.28. Found: C, 77.90; H, 3.76; N, 8.26. HRMS (ESP+): m/z 361.0793 [MNa^+] calcd for ($C_{22}H_{14}N_2SNa^+$): m/z 361.0770. UV–vis (MeCN) λ_{DHA} (ε): 380 nm (23.3 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 476 nm (20.5 × 10^3 M^{-1} cm^{-1}).

*2-[4′-(3″-Thienyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.15**).* To a stirred solution of iodo-DHA **1.4** (146.2 mg, 0.3825 mmol) in a mixture of argon-flushed toluene (9 mL) and water (1 mL) were added 3-thienyl boronic acid (108.2 mg, 0.847 mmol), K_3PO_4 (201 mg, 0.948 mmol), Xantphos (39.3 mg, 0.068 mmol, 18 mol %), and $Pd(OAc)_2$ (7.6 mg, 0.034 mmol, 9 mol %), and the reaction mixture was stirred for 4 h at 50 °C. The resulting dark yellow reaction mixture was diluted with Et_2O (50 mL), washed with saturated aqueous NH_4Cl (2 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was redissolved in CH_2Cl_2 and concentrated on Celite. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0–60% toluene/heptanes, 5% steps, then 60–75% toluene/heptanes, 2.5% steps, 40 mL fractions) gave **1.15** (99.6 mg, 294 μmol, 77%) as a dark yellow solid. A stable crystalline solid can be obtained by recrystallization from $CHCl_3$/heptanes. TLC (toluene): R_f = 0.67. mp 151.1–152.1 °C ($CHCl_3$/heptanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.7 Hz, 2H), 7.56–7.54 (m, 1H), 7.43 (s, 1H), 7.43–7.42 (m, 1H), 6.90 (s, 1H), 6.58 (dd, J = 11.2, 6.4 Hz, 1H), 6.48 (dd, J = 11.2, 6.1 Hz, 1H), 6.35 (d, J = 6.4 Hz, 1H), 6.32 (ddd, J = 10.2, 6.1, 2.2 Hz, 1H), 5.84 (dd, J = 10.2, 3.8 Hz, 1H), 3.81 (dt, J = 3.8, 2.0 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 139.9, 138.9, 137.4, 132.0, 131.1, 131.0, 129.2, 127.8, 127.2, 126.9, 126.9, 126.2, 121.6, 121.0, 119.6, 115.3, 112.9, 51.3, 45.3 ppm. Anal. Calcd for $C_{22}H_{14}N_2S$ (338.43): C, 78.08; H, 4.17; N, 8.28. Found: C, 78.25; H, 3.85; N, 8.18. MS (MALDI TOF+): m/z 339 [MH^+]. UV–vis (MeCN) λ_{DHA} (ε): 373 nm (22.8 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 475 nm (23.1 × 10^3 M^{-1} cm^{-1}).

*2-[3′-(2″-Thienyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.16**).* To a stirred solution of **1.5** (164 mg, 0.429 mmol) in a mixture of argon-flushed toluene (18 mL) and water (2 mL), were added 2-thienyl boronic acid (110 mg, 0.857 mmol), K_3PO_4 (182 mg, 0.857 mmol), $Pd_2(dba)_3$ (19.6 mg, 0.0214 mmol), and Xantphos (12.4 mg, 0.0215 mmol), and the reaction mixture was stirred at 50 °C for 2 h. The resulting dark yellow reaction mixture was diluted with Et_2O (100 mL), washed with saturated aqueous NH_4Cl (3 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was redissolved in CH_2Cl_2 and concentrated on Celite. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0–50% toluene/heptanes, 10% steps, then 50–75%, 5% steps, 40 mL fractions) gave **1.16** (133 mg, 0.335 μmol, 78%) as a bright yellow solid. TLC (75% toluene/heptanes): R_f = 0.41 (yellow → red). mp 135.1–136.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dt, J = 1.9, 0.5 Hz, 1H), 7.68–7.65 (m, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.41 (dd, J = 3.6, 1.0 Hz, 1H), 7.37 (dd, J = 5.1, 1.0 Hz, 1H), 7.15 (dd, J = 5.1, 3.6 Hz, 1H), 6.97 (s, 1H), 6.61 (dd, J = 11.3, 6.3 Hz, 1H), 6.52 (dd, J = 11.3, 6.1 Hz, 1H), 6.41 (d, J = 6.3 Hz, 1H), 6.32 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.83 (dd, J = 10.2, 3.8 Hz, 1H), 3.84 (dt, J = 3.8, 2.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 139.9, 138.7, 135.7, 133.1, 131.3, 131.2, 131.0, 130.0, 128.4, 127.8, 127.7, 125.8, 125.2, 124.1, 123.9, 121.4, 119.7, 115.3, 112.8, 51.3, 45.5 ppm. Anal. Calcd for $C_{22}H_{14}N_2S$ (338.43): C, 78.08; H, 4.17; N, 8.28. Found: C, 77.98; H, 4.21; N, 8.20. HRMS (ESP+): m/z 361.0761 [MNa^+], calcd for ($C_{22}H_{14}N_2S$): m/z 361.0770. UV–vis (MeCN) λ_{DHA} (ε): 358 nm (22.8 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 475 nm (23.1 × 10^3 M^{-1} cm^{-1}).

*2-[3′-(3″-Thienyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.17**).* Method 1: To a stirred solution of iodo-DHA **1.5** (152.2 mg, 0.3532 mmol) in a mixture of argon-flushed toluene (4.5 mL) and water (0.5 mL) were added 3-thienyl boronic acid (108.4 mg, 0.847 mmol), K_3PO_4 (113 mg, 0.532 mmol), RuPhos (16.6 mg, 0.035 mmol, 10 mol %), and $Pd(OAc)_2$ (4.0 mg, 0.018 mmol, 5 mol %), and the reaction mixture was stirred for 16 h at 50 °C. To the dark yellow reaction mixture, RuPhos (16.6 mg, 0.035 mmol, 10 mol %) and $Pd(OAc)_2$ (4.0 mg, 0.018 mmol, 5 mol %) were added again, and it was then stirred for another 16 h at 50 °C. The reaction mixture was diluted with ether (50 mL), washed with saturated aqueous NH_4Cl (2 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was redissolved in CH_2Cl_2 and concentrated on Celite. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0–50% toluene/heptanes, 5% steps, then 50–62.5% toluene/heptanes, 2.5% steps, 40 mL fractions) gave **1.17** (24.9 mg, 0.0736 mmol, 19%) as a yellow to red solid and **1.5** (21.2 mg, 0.0555 mmol, 14%) as a yellow solid. Method 2: To the stirred solution of iodo-DHA **1.5** (106.8 mg, 0.279 mmol) in a mixture of argon-flushed toluene (9 mL) and water (1 mL) were added 3-thienyl boronic acid (60.2 mg, 0.470 mmol), K_3PO_4 (122 mg, 0.574 mmol), Xantphos (12.6 mg, 0.0218 mmol, 7.8 mol %), and $Pd_2(dba)_3$ (10.3 mg, 0.0112 mmol, 3.9 mol %), and the reaction mixture was stirred for 16 h at 50 °C. The reaction mixture was diluted with ether (50 mL), washed with saturated aqueous NH_4Cl (2 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was redissolved in CH_2Cl_2 and concentrated on Celite. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0–50% toluene/heptanes, 5% steps, then 50–62.5% toluene/heptanes, 2.5% steps, 40 mL fractions) gave **1.17** (57.2 mg, 0.169 mmol, 60%) as a yellow solid. For **1.17**: TLC (75% toluene/heptanes): R_f = 0.41 (yellow → orange-red). mp 128.3–129.2 °C ($CHCl_3$/heptanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dt, J = 1.9, 0.4 Hz, 1H), 7.67 (ddd, J = 7.8, 1.9, 1.0 Hz, 1H), 7.65 (ddd, J = 7.8, 1.7, 1.0 Hz, 1H), 7.52(dd, J = 2.8, 1.5 Hz, 1H), 7.51 (td, J = 7.5, 0.4 Hz, 1H), 7.43 (m, 2 H), 6.94 (s, 1H), 6.58 (dd, J = 11.3, 6.4 Hz, 1H), 6.49 (dd, J = 11.3, 6.1 Hz, 1H), 6.37 (d, J = 6.4 Hz, 1H), 6.32 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.84 (dd, J = 10.2, 3.8 Hz, 1H), 3.81 (dt, J = 3.8, 2.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5, 140.2, 138.8, 137.1, 132.8, 131.18, 131.14, 131.05, 129.9, 128.3, 127.8, 126.9, 126.4, 125.0, 124.5, 121.4, 121.3, 119.7, 115.3, 112.9, 51.3, 45.5 ppm. Anal. Calcd for $C_{22}H_{14}N_2S$ (338.43): C, 78.08; H, 4.17; N, 8.28. Found: C, 77.81; H, 3.90; N, 8.28. HRMS (ESP+): m/z 699.1638 [$2MNa^+$], calcd for ($C_{44}H_{28}N_4S_2Na^+$): m/z 699.1648. UV–vis (MeCN) λ_{DHA} (ε): 359 nm (14.7 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 474 nm (29.0 × 10^3 M^{-1} cm^{-1}).

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*2-[3′-(3″-Furyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.18**).* To a stirred solution of **1.5** (257 mg, 0.672 mmol) in a mixture of argon-flushed toluene (18 mL) and water (2 mL) were added 3-furyl boronic acid (150 mg, 1.34 mmol), K_3PO_4 (301 mg, 1.34 mmol), $Pd(OAc)_2$ (13.2 mg, 0.0588 mmol, 9 mol %), and RuPhos (56.1 mg, 0.1176 mmol), and the reaction mixture was stirred at 50 °C for 16 h. The resulting black reaction mixture was diluted with Et_2O (80 mL), washed with saturated aqueous NH_4Cl (3 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was redissolved in CH_2Cl_2 and concentrated on Celite. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−75% toluene/heptanes, 7.5% steps, 40 mL fractions) gave **1.18** (153 mg, 0.474 mmol, 70%) as a yellow oil or solid. (In case the compound comes out as an oil, a stable solid was obtained by simply passing the compound through a plug of silica using CH_2Cl_2/heptanes 2:1.) TLC (toluene): R_f = 0.64. mp 99.9−101.4 °C ($CHCl_3$/heptanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (app t, J = 1.9 Hz, 1H), 7.79 (app dd, J = 1.5, 0.9 Hz, 1H), 7.65 (ddd, J = 7.7, 2.0, 1.1 Hz, 1H), 7.54 (dt, J = 7.7, 1.4 Hz, 1 H), 7.51 (app dd, J = 2.0, 1.6 Hz, 1 H), 7.48 (dt, J = 7.7, 0.5 Hz, 1H), 6.93 (s, 1H), 6.74 (app dd, J = 1.9, 0.9 Hz, 1H), 6.58 (ddt, J = 11.2, 6.2, 0.5 Hz, 1H), 6.49 (dd, J = 11.2, 6.1 Hz, 1H), 6.37 (d, J = 6.2 Hz, 1H), 6.32 (dddt, J = 10.2, 6.1, 2.1, 0.5 Hz, 1H), 5.83 (dd, J = 10.2, 3.8 Hz, 1H), 3.81 (dt, J = 3.8, 2.1 Hz, 1H) ppm. Anal. Calcd for $C_{22}H_{14}N_2O$ (322.36): C, 81.97; H, 4.38; N, 8.69. Found: C, 81.89; H, 4.46; N, 7.52. HRMS (ESP+): m/z 345.0991 [MNa^+], calcd for ($C_{22}H_{14}N_2ONa^+$): m/z 345.0998. UV−vis (MeCN) λ_{DHA} (ε): 357 nm (14.7 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 474 nm (26.7 × 10^3 M^{-1} cm^{-1}).

*2-(3′-(2″-Furyl)phenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.19**).* To a stirred solution of iodo-DHA **1.5** (101.2 mg, 0.265 mmol) in a mixture of argon-flushed toluene (9 mL) and water (1 mL) were added 2-furyl boronic acid (122.6 mg, 1.100 mmol), K_3PO_4 (122 mg, 0.574 mmol), Xantphos (12.4 mg, 0.0214 mmol, 8.1 mol %), $Pd_2(dba)_3$ (8.9 mg, 0.0097 mmol, 3.6 mol %) (the reaction mixture took a red color, which slowly faded to yellow), and the reaction mixture was stirred for 72 h at 25 °C. The reaction mixture was diluted with ether (50 mL), washed with saturated aqueous NH_4Cl (2 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was redissolved in CH_2Cl_2 and concentrated on Celite. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−75% toluene/heptanes, 7.5% steps, 40 mL fractions) gave **1.19** (65.4 mg, 0.203 mmol, 74%) as a yellow solid. TLC (toluene): R_f = 0.67. mp 126.2−127.7 °C ($CHCl_3$/heptanes), dec > 150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (app t, J = 1.8 Hz, 1H), 7.71 (app ddd, J = 7.8, 1.6, 1.0 Hz, 1H), 7.64 (app ddd, J = 7.8, 2.0, 1.0 Hz, 1H), 7.51 (app dd, J = 1.8, 0.8 Hz, 1H), 7.49 (app dt, J = 7.8, 0.5 Hz, 2H), 6.96 (s, 1H), 6.75 (app dd, J = 3.4, 0.7 Hz, 1H), 6.58 (dd, J = 11.3, 6.3 Hz, 1H), 6.51 (dd, J = 3.4, 1.8 Hz, 1H), 6.49 (dd, J = 11.3, 6.2, 1H), 6.37 (d, J = 6.3 Hz, 1H), 6.32 (ddd, J = 10.2, 6.2, 2.1 Hz, 1H), 5.84 (dd, J = 10.2, 3.8 Hz, 1H), 3.81 (dt, J = 3.8, 2.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 142.8, 140.1, 138.7, 133.0, 132.0, 131.2, 131.1, 131.0, 129.8, 127.8, 125.4, 125.0, 121.6, 121.3, 119.7, 115.3, 112.8, 112.0, 106.3, 51.3, 45.4 ppm. HRMS (ESP+): m/z 345.0995 [MNa^+], calcd for ($C_{22}H_{14}N_2ONa^+$): m/z 345.0998. UV−vis (MeCN) λ_{DHA} (ε): 358 nm (14 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 475 nm (27 × 10^3 M^{-1} cm^{-1}).

*2-[4′-(Trimethylsilylethynyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.20**).* To a stirred solution of DHA **1.4** (390 mg, 1.02 mmol), $(PPh_3)_4Pd$ (56 mg, 49 μmol, 5 mol %), and CuI (4.1 mg, 22 μmol) in argon-flushed THF (10 mL) were added (i-Pr_2)NH (0.57 mL, 4.1 mmol) and trimethylsilylacetylene (0.58 mL, 4.1 mmol), and the reaction mixture was stirred at rt for 16 h. The dark yellow reaction mixture was concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−30% THF/heptanes, 5% steps, 40 mL fractions) gave **1.20** (252 mg, 0.714 mmol, 70%) as a yellow oil that solidifies. TLC (30% THF/heptanes): R_f = 0.54. Other spectroscopic analyses are in accordance with the literature.[8g]

*2-[4′-(Triisopropylsilylethynyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.21**).* To a stirred mixture of DHA **1.4** (1.02 g, 2.62 mmol), $(PPh_3)_4Pd$ (60 mg, 0.052 mmol, 2 mol %), and CuI (5 mg, 0.026 mmol, 1 mol %) in argon-flushed THF (40 mL) were added triisopropylacetylene (1.18 mL, 0.956 g, 5.24 mmol) and Et_3N (1.46 mL, 1.06 g, 10.5 mmol). The reaction mixture was stirred for 16 h at rt, after which saturated aqueous NH_4Cl (50 mL) was added, and the mixture was extracted with Et_2O (3 × 100 mL). The combined organic phases were washed with saturated aqueous NH_4Cl (3 × 75 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−45% toluene/heptanes, 7.5% steps, then 45−75% toluene/heptanes, 5% steps, 40 mL fractions) gave **1.21** (1.00 g, 2.29 mmol, 87%) as a dark yellow solid (a purple band at slightly lower R_f was observed). TLC (50% toluene/heptanes): R_f = 0.42 and (75% toluene/heptanes): R_f = 0.71. UV−vis (MeCN) λ_{DHA} (ε): 371 nm (28.3 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 479 nm (29.7 × 10^3 M^{-1} cm^{-1}). Other spectroscopic analyses are in accordance with the literature.[8g]

*2-[3′-(Triisopropylsilylethynyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.22**).* To a stirred mixture of **1.5** (469 mg, 1.22 mmol), $Pd(PPh_3)_4$ (30 mg, 0.026 mmol, 2 mol %), and CuI (10 mg, 0.053 mmol) in argon-flushed THF (10 mL) were added TIPS-acetylene (1.0 mL, 0.81 g, 4.5 mmol) and argon-flushed (i-Pr)$_2$NH (1.0 mL, 0.72 g, 7.1 mmol). The reaction mixture was stirred for 4 h at rt, after which saturated aqueous NH_4Cl (20 mL) was added, and the mixture was extracted with Et_2O (2 × 50 mL). The combined organic phases were washed with water (3 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−70% toluene/heptanes, 5% steps, 40 mL fractions) gave **1.22** (499 mg, 1.11 mmol, 94%) as a dark yellow solid. TLC (75% toluene/heptanes): R_f = 0.61 (yellow → red). mp 128.9−129.8 °C ($CHCl_3$/heptanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (app. td, J = 1.7, 0.5 Hz, 1H), 7.72 (app. ddd, J = 7.9, 2.0, 1.0 Hz, 1H), 7.52 (app. dt, J = 7.9, 1.3 Hz, 1H), 7.43 (app. td, J = 7.9, 0.5 Hz, 1H), 6.91 (s, 1H), 6.58 (dd, J = 11.3, 6.2 Hz, 1H), 6.49 (dd, J = 11.3, 6.1 Hz, 1H), 6.36 (d, J = 6.2 Hz, 1H), 6.31 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.81 (dd, J = 10.2, 3.8 Hz, 1H), 3.79 (dt, J = 3.8, 2.1 Hz, 1H), 1.14 (s, 21H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 138.6, 133.6, 133.3, 131.3, 131.0, 130.9, 130.0, 129.3, 127.8, 125.8, 124.9, 121.5, 119.7, 115.1, 112.7, 106.0, 92.5, 51.3, 45.4, 18.8, 11.4 ppm. Anal. Calcd for $C_{29}H_{32}N_2Si$ (436.66): C, 79.77; H, 7.39; N, 6.42. Found: C, 79.35; H, 7.42; N, 6.41. MS (ESP+): m/z 437.2 [MH^+], 459.2 [MNa^+]. UV−vis (MeCN) λ_{DHA} (ε): 358 nm (15.7 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 476 nm (27.3 × 10^3 M^{-1} cm^{-1}).

*2-(4′-Ethynylphenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.23**).* To a stirred solution of DHA **1.20** (252 mg, 0.714 mmol) in THF (5 mL) were added AcOH (0.08 mL, 1.4 mmol) and a solution of tetrabutylammonium fluoride (1.43 mL, 1.43 mmol, 1 M) in THF, and the reaction mixture was stirred at rt for 2 h. The resulting dark yellow solution was diluted with Et_2O (50 mL), washed with water (3 × 50 mL) and brine (25 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−50% toluene/heptanes, 12.5% steps, then 50−100% toluene/heptanes, 6.25% steps, 40 mL fractions) gave **1.23** (117 mg, 0.417 mmol, 58%) as a yellow foam or solid. TLC (50% toluene/heptanes): R_f = 0.24 (yellow → red). UV−vis (MeCN) λ_{DHA} (ε): 366 nm (22.1 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 478 nm (29.5 × 10^3 M^{-1} cm^{-1}). Other spectroscopic analyses are in accordance with the literature.[8g]

*2-(3′-Ethynylphenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.24**).* To a stirred solution of **1.22** (230.3 mg, 0.527 mmol) in THF (40 mL) were added dropwise AcOH (0.30 mL, 0.32 g, 5.3 mmol) and a solution of tetrabutyl ammonium fluoride (1.05 mL, 1.05 mmol, 1 M, 2 equiv) in THF. The reaction mixture was refluxed for 4 h (the yellow solution took a light yellow-brown color), after which it was diluted with Et_2O (50 mL), washed with water (3 × 50 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−50% toluene/heptanes, 5 steps, then 50−65% toluene/heptanes, 2.5% steps, 40 mL fractions) gave **1.24** (134.3 mg, 0.479 mmol, 91%) as a yellow solid. TLC (75% toluene/heptanes): R_f = 0.41 (yellow → red). mp 108.0−108.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (t, J = 1.6 Hz, 1H), 7.74 (ddd, J = 7.8, 2.0, 1.1 Hz, 1H), 7.54 (dt, J = 7.8, 1.2 Hz, 1H), 7.45 (td, J = 7.8, 0.4 Hz, 1H), 6.91 (s, 1H), 6.58 (dd, J = 11.2, 6.3 Hz, 1H), 6.50 (dd, J = 11.2, 6.1 Hz, 1H), 6.36 (d, J = 6.3 Hz, 1H), 6.32 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.82 (dd, J = 10.2, 3.9 Hz, 1H), 3.79 (dt, J = 3.9, 2.1 Hz, 1H), 3.15 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 138.5, 133.5, 133.5, 131.4, 130.99, 130.95, 130.0, 129.5, 127.9, 126.4, 123.6, 121.7, 119.6, 115.1,

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112.7, 82.7, 78.7, 51.3, 45.3 ppm. Anal. Calcd for $C_{20}H_{12}N_2$ (280.32): C, 85.69; H, 4.31; N, 9.99. Found: C, 85.38; H, 4.05; N, 9.93. HRMS (ESP+): m/z 303.0940 [MNa^+], calcd for ($C_{20}H_{12}N_2Na^+$): m/z 303.0898. UV−vis (MeCN) λ_{DHA} (ε): 357 nm (24.6×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 477 nm (46.2×10^3 M^{-1} cm^{-1}).

*2-[4′-(Trimethylsilyl-1,3-butadiynyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.25**).* Method 1: To a stirred solution of **1.23** (218 mg 0.779 mmol) in CH_2Cl_2 (20 mL) were added CuCl (16 mg, 0.163 mmol), TMS-acetylene (1.11 mL, 7.80 mmol), and TMEDA (0.12 mL, 0.77 mmol), and the mixture was stirred for 1 h while passing through oxygen and then overnight under an oxygen atmosphere. The reaction mixture was washed with brine (3 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−50% toluene/heptanes, 6.25% steps, then 50−85% toluene/heptanes, 5% steps, then neat toluene, then 0−15% EtOAc/toluene, 5% steps (to collect homocoupled byproduct of **1.23** by chromatography, TLC (75% toluene/heptanes): R_f = 0.26 (yellow → orange)), 40 mL fractions) gave **1.25** (214 mg, 0.568 mmol, 73%) as a yellow oil. Method 2: To a stirred solution of **1.27** (72 mg, 0.20 mmol) in argon-flushed THF (20 mL) were added argon-flushed Et_3N (0.28 mL, 2.0 mmol), TMS-acetylene (0.29 mL, 2.0 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol, 5 mol %), and CuI (0.4 mg, 2 μmol, 1 mol %), and the reaction mixture was stirred at rt overnight. The reaction mixture was diluted with Et_2O (100 mL), washed with saturated aqueous NH_4Cl (2 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−60% toluene/heptanes, 6.25% steps, then neat toluene, then 0−15% EtOAc/toluene, 5% steps (to collect homocoupled byproduct of **1.23** by chromatography, TLC (75% toluene/heptanes): R_f = 0.26 (yellow → orange)), 40 mL fractions) gave **1.25** (33 mg, 87 μmol, 44%) as a yellow oil that solidifies. A stable compound was obtained by recrystallization from $CHCl_3$/heptanes. For **1.25**: TLC (75% toluene/heptanes): R_f = 0.52 (yellow → red). mp 107.3−109.0 °C ($CHCl_3$/heptanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H), 6.91 (s, 1H), 6.57 (dd, J = 11.3, 6.3 Hz, 1H), 6.50 (dd, J = 11.3, 6.1 Hz, 1H), 6.37 (d, J = 6.3 Hz, 1H), 6.31 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.81 (dd, J = 10.2, 3.8 Hz, 1H), 3.79 (dt, J = 3.8, 2.1 Hz, 1H), 0.25 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 138.5, 133.6, 133.5, 131.5, 131.1, 131.0, 127.9, 126.2, 123.2, 122.0, 119.6, 115.0, 112.6, 92.6, 87.7, 76.8, 75.9, 51.2, 45.1, −0.3 ppm. Anal. Calcd for $C_{25}H_{20}N_2Si$ (376.53): C, 79.75; H, 5.35; N, 7.44. Found: C, 79.89; H, 5.45; N, 7.52. HRMS (ESP+): m/z 399.1281 [MNa^+], calcd for ($C_{25}H_{20}N_2SiNa^+$): m/z 399.1288. UV−vis (MeCN) λ_{DHA} (ε): 376 nm (33.8×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 480 nm (27.8×10^3 M^{-1} cm^{-1}).

*2-[4′-(1,3-Butadiynyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.26**).* To a stirred solution of **1.25** (11.3 mg, 30.0 μmol) in THF (20 mL) were added acetic acid (17 μL, 0.30 mmol) and a solution of TBAF (60 μL, 60 μmol, 1 M) in THF. The reaction mixture was stirred for 20 min at rt, after which it was diluted with Et_2O (40 mL), washed with aqueous NH_4Cl (2 × 25 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−60% toluene/heptanes, 6.25% steps, 40 mL fractions) gave **1.26** (8.4 mg, 28 μmol, 92%) as a yellow to red oil (that solidifies). mp < 80 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 6.92 (s, 1H), 6.58 (dd, J = 11.3, 6.3 Hz, 1H), 6.50 (dd, J = 11.3, 6.1 Hz, 1H), 6.38 (d, J = 6.3 Hz, 1H), 6.34−6.30 (m, 1H), 5.82 (dd, J = 10.2, 3.8 Hz, 1H), 3.79 (br s, 1H), 2.57 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 138.3, 133.6, 133.5, 131.4, 131.3, 130.9, 127.8, 126.1, 122.6, 122.0, 119.5, 114.9, 112.5, 76.0, 74.5, 72.7, 67.9, 51.1, 45.0 ppm. HRMS (ESP+): m/z 327.0890 [MNa^+], calcd for ($C_{22}H_{12}N_2Na^+$): m/z 327.0893. UV−vis (MeCN) λ_{DHA} (ε): 375 nm (24.0×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 480 nm (23.3×10^3 M^{-1} cm^{-1}).

*2-[4′-(tert-Butylsulfinyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.30**).* To a solution of DHA **1.28** (92 mg, 0.267 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (72 mg, 0.32 mmol, 70% w/w), and the resulting solution was stirred for 20 min at rt. The solution was treated simultaneously with saturated aqueous sodium thiosulfate (1 mL) and saturated sodium bicarbonate (1 mL) and was then diluted with both water (10 mL) and CH_2Cl_2 (10 mL). The phases were separated, and the organic phase was dried over sodium sulfate. Filtration and removal of the solvent under reduced pressure gave an orange residue, which was subjected to flash column chromatography (gradient elution 0−10% EtOAc/CH_2Cl_2) to furnish **1.30** (66 mg, 69%) as a gummy orange oil. In addition, unreacted starting material **1.28** (20 mg, 22%) and sulfone **1.32** (11 mg, 8%) were isolated. TLC (10% EtOAc/CH_2Cl_2): R_f = 0.44. ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.84 (d, J = 8.7 Hz, 2H), 7.69 (d, J = 8.6 Hz, 1H), 6.99 (s, 1H), 6.58−6.51 (m, 1H), 6.50 (dd, J = 11.2, 6.1 Hz, 1H), 6.40 (br d, J = 6.2 Hz, 1H), 6.32 (ddd, J = 10.1, 6.1, 2.0 Hz, 1H), 5.83−5.80 (m, 1H), 3.81−3.79 (m, 1H), 1.20 (s, 9H) ppm.^{13} ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 138.7, 138.2, 138.2, 134.3, 134.3, 131.6, 131.0, 127.9, 127.9, 127.3, 126.1, 122.2, 119.6, 119.5, 115.0, 115.0, 112.6, 112.6, 56.7, 51.2, 51.2, 45.2, 45.2, 22.9 ppm (mixture of two diastereoisomers). HRMS (ESP+): m/z 383.1205 [MNa^+], 743.2494 [$2MNa^+$], calcd for ($C_{22}H_{20}N_2OSNa^+$): 383.1189, calcd for ($C_{44}H_{40}N_4O_2S_2Na^+$): 743.2485. UV−vis (MeCN) λ_{DHA} (ε): 365 nm (17.8×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 477 nm (24.3×10^3 M^{-1} cm^{-1}).

*2-[3′-(tert-Butylsulfinyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.31**).* To a solution of DHA **1.29** (82 mg, 0.238 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (60 mg, 0.27 mmol, 70% w/w), and the resulting solution was stirred for 20 min at rt. The solution was treated simultaneously with saturated aqueous sodium thiosulfate (1 mL) and saturated aqueous sodium bicarbonate (1 mL) and was then diluted with both water (10 mL) and CH_2Cl_2 (10 mL). The phases were separated, and the organic phase was dried over sodium sulfate. Filtration and removal of the solvent under reduced pressure gave an orange residue, which was subjected to flash column chromatography (gradient elution 0−10% EtOAc/CH_2Cl_2) to furnish pure sulfoxide **1.31** (73 mg, 85%) as a viscous orange oil. In addition, unreacted starting material **1.29** (5 mg 6%) and sulfone **1.33** (4 mg, 4%) were obtained. TLC (10% EtOAc/CH_2Cl_2): R_f = 0.42. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (br m, 1H), 7.88−7.86 (m, 1H), 7.61−7.60 (m, 1H), 7.00 and 7.01 (s, 1H), 6.60−6.56 (m, 1H), 6.50 (dd, J = 11.2, 6.0 Hz, 1H), 6.38 (br d, J = 6.2 Hz, 1H), 6.31 (dd, J = 10.0, 6.0 Hz, 1H), 5.81 (dd, J = 10.0, 3.6 Hz, 1H), 3.81−3.79 (m, 1H), 1.21 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 138.7, 138.3, 138.2, 134.2, 134.2, 129.4, 128.5, 127.9, 127.6, 123.9, 122.1, 122.1, 119.6, 119.5, 115.0, 114.9, 112.6, 112.6, 56.5, 51.2, 51.1, 45.3, 45.3, 22.9 ppm (mixture of two diastereoisomers). HRMS (ESP+): m/z 383.1186 [MNa^+], 743.2474 [$2MNa^+$], calcd for $C_{22}H_{20}N_2OSNa^+$: 383.1189, calcd for $C_{44}H_{40}N_4O_2S_2Na^+$: 743.2485. UV−vis (MeCN) λ_{DHA} (ε): 355 nm (11.9×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 475 nm (19.2×10^3 M^{-1} cm^{-1}).

*2-[4′-(tert-Butylsulfonyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.32**).* To a solution of DHA **1.28** (71 mg, 0.206 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (116 mg, 70% w/w, 0.52 mmol), and the resulting solution was stirred for 20 min at rt. The solution was treated simultaneously with saturated aqueous sodium thiosulfate (1 mL) and saturated aqueous sodium bicarbonate (1 mL) and was then diluted with both water (10 mL) and CH_2Cl_2 (10 mL). The phases were separated, and the organic phase was dried over sodium sulfate. Filtration and removal of the solvent under reduced pressure gave an orange residue, which was subjected to flash column chromatography (gradient elution 0−2% EtOAc/CH_2Cl_2) to furnish pure **1.32** (74 mg, 95%) as a crystalline yellow solid. This compound could be crystallized from CH_2Cl_2/methanol. TLC (2% EtOAc/CH_2Cl_2): R_f = 0.63. mp 210−223 °C (decomposes). ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.98 (d, J = 8.7 Hz, 2H), 7.89 (d, J = 8.7 Hz, 2H), 7.05 (s, 1H), 6.60 (dd, J = 11.2, 6.2 Hz, 1H), 6.54 (dd, J = 11.2, 6.0 Hz, 1H), 6.45 (broad d, J = 6.2 Hz, 1H), 6.34 (ddd, J = 10.2, 6.0, 2.0 1H), 5.83 (dd, J = 10.2, 3.8 Hz, 1H), 3.83 (dt, J = 3.8, 2.0 Hz, 1H), 1.37 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 137.9, 136.5, 135.7, 135.5, 132.2, 131.48, 130.9, 128.0, 126.4, 123.1, 119.7, 114.8, 112.4, 60.4, 51.2, 45.2, 23.8 ppm. Anal. Calcd for $C_{22}H_{20}N_2O_2S$ (376.47): C, 70.19; H, 5.35; N, 7.44. Found: C, 69.95; H, 5.13; N, 7.46. MS (ESP+): m/z 399 [MNa^+]. UV−vis (MeCN) λ_{DHA} (ε): 367 nm (17.9×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 481 nm (24.6×10^3 M^{-1} cm^{-1}).

*2-[3′-(tert-Butylsulfonyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**1.33**).* To a solution of DHA **1.29** (89 mg, 0.258 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (146 mg, 0.65 mmol, 70% w/w), and the resulting solution was stirred for 20 min at rt. The solution was

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treated simultaneously with saturated aqueous sodium thiosulfate (1 mL) and saturated aqueous sodium bicarbonate (1 mL) and was then diluted with both water (10 mL) and CH_2Cl_2 (10 mL). The phases were separated, and the organic phase was dried over sodium sulfate. Filtration and removal of the solvent under reduced pressure gave an orange residue, which was subjected to flash column chromatography (gradient elution 0−2% EtOAc/CH_2Cl_2) to give sulfone **1.33** (87 mg, 90%) as a pale yellow solid. TLC (2% EtOAc/CH_2Cl_2): R_f = 0.66. mp 144−164 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (t, J = 1.7 Hz, 1H), 8.03 (ddd, J = 7.9, 1.7, 1.0 Hz, 1H), 7.93 (ddd, J = 7.9, 1.7, 1.0 Hz, 1H). 7.70 (t, J = 7.9 Hz, 1H), 7.02 (s, 1H), 6.60 (dd, J = 11.3, 6.3 Hz, 1H), 6.53 (dd, J = 11.3, 6.1 Hz, 1H), 6.42 (br d, J = 6.3 Hz, 1H), 6.33 (ddd, J = 10.2, 6.1, 2.1 Hz, 1H), 5.82 (dd, J = 10.2, 3.8 Hz, 1H), 3.82 (dt, J = 3.8, 2.1 Hz, 1H), 1.39 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 137.0, 134.8, 131.9, 131.6, 131.3, 131.0, 130.6, 130.0, 128.4, 128.0, 122.7, 119.6, 114.8, 112.5, 60.4, 51.1, 45.4, 23.8 ppm (one signal is missing due to overlap). Anal. Calcd for $C_{22}H_{20}N_2O_2S$ (376.47): C, 70.19; H, 5.35; N, 7.44. Found: C, 69.93; H, 5.35; N, 7.28. MS (ESP+): m/z 399.1133 [MNa^+], calcd for ($C_{22}H_{20}N_2SO_2Na^+$): m/z 399.1138. UV−vis (MeCN) λ_{DHA}: 359 nm. λ_{VHF}: 478 nm.

*7-Phenyl-2-(4′-tolyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**2.1**).* General Procedure. To a stirred solution of 7-bromide **11.3** (crude, prepared in two steps from **1e** (1.00 mmol) with a purity of >90%) in a mixture of thoroughly argon-flushed toluene (9 mL) and water (1 mL) were added phenyl boronic acid (244 mg, 2.00 mmol), K_3PO_4 (425 mg, 2.00 mmol), RuPhos (47 mg, 0.10 mmol), and $Pd(OAc)_2$ (11 mg, 0.050 mmol). (Pellets of K_3PO_4 can be added before degassing of the solvent.) The reaction mixture was heated at 80 °C for 1 h (Progress of reaction was monitored by TLC. A dark red or purple spot is sign of formation of product, whereas starting material is orange or red), after which it was diluted with Et_2O (100 mL), washed with brine (3 × 50 mL), dried with $MgSO_4$, and filtered, and the solvents were removed in vacuo. The residue was redissolved in CH_2Cl_2 and concentrated on Celite. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, (1) 0−75% toluene/heptanes, 5% steps, (2) 0−20% EtOAc/heptanes, 1% steps (the product is isolated as the first of two yellow bands), 40 mL fractions) gave **2.1** (118 mg, 340 μmol, 34%) as a yellow solid. (The product is only stable as a crystalline solid. If not already crystalline after chromatographic purification, then this can be obtained by a careful recrystallization from $CHCl_3$/heptanes. The compound is dissolved in $CHCl_3$ (3 mL), after which heptanes (3 mL) is carefully put on top of the $CHCl_3$. The mixture is left in the dark in a container that allows for a slow evaporation of the more volatile $CHCl_3$. After evaporation to approximately half of the volume, a bright yellow crystalline solid can be collected.) TLC (75% toluene/heptanes): R_f = 0.50 (yellow → purple). mp 123.3−124.6 °C ($CHCl_3$/heptanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78−7.73 (m, 2H), 7.50−7.42 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 6.90 (s, 1H), 6.80−6.75 (m, 2H), 6.36 (d, J = 5.5 Hz, 1H), 5.97 (d, J = 4.6 Hz, 1H), 3.83 (dd, J = 4.6, 1.7 Hz, 1H), 2.36 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 140.7, 139.8, 138.1, 137.3, 132.42, 132.38, 131.8, 130.6, 130.3, 129.4, 129.4, 127.7, 126.5, 120.4, 115.6, 115.4, 113.1, 51.1, 45.2, 21.3 ppm. Anal. Calcd for $C_{25}H_{18}N_2$ (346.42): C, 86.68; H, 5.24; N, 8.09. Found: C, 86.56; H, 4.79; N, 8.05. HRMS (ESP+): m/z 369.1362 [MNa^+], calcd for ($C_{25}H_{18}N_2Na^+$): m/z 369.1362. UV−vis (MeCN) λ_{DHA} (ε): 358 nm (18.0 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 488 nm (34.8 × 10^3 M^{-1} cm^{-1}).

*7-Phenyl-2-(4′-cyanophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**2.2**).* Prepared according to the general procedure for **2.1**: 7-bromide **11.10** (crude, prepared in two steps from **1.1** (1.00 mmol) with a purity of >90%), phenyl boronic acid (240 mg, 2.04 mmol), K_3PO_4 (855 mg, 4.03 mmol), RuPhos (95 mg, 0.204 mmol), and palladium(II)acetate (22 mg, 0.098 mmol) in toluene (50 mL) and water (10 mL). Heating for 20 h at 70 °C. Worked up according to the general procedure for **2.1**. The residue was subsequently purified by flash column chromatography (SiO_2, 0.5% ethyl acetate/toluene) to afford the title compound, which was crystallized from concentrated ethanol to give **2.2** as a fluffy yellow solid (72 mg, 20% over the three steps). R_f = 0.38 (0.5% ethyl acetate/toluene). mp 155−158 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.8 Hz, 2H), 7.77 (dd, J = 8.8 Hz, 2H), 7.41−7.35 (m, 5H), 7.03 (s, 1H), 6.86−6.81 (m, 2H), 6.47 (dt, J = 4.0, 1.8 Hz, 1H), 5.99 (d, J = 4.6 Hz, 1H), 3.87 (dd, J = 4.6, 1.8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 139.9, 139.7, 138.9, 134.8, 134.7, 133.4, 133.1, 132.3, 128.8, 128.4, 127.8, 126.8, 122.5, 118.2, 116.2, 114.8, 113.5, 112.6, 50.9, 45.0 ppm. Anal. Calcd for $C_{25}H_{15}N_3$ (357.41): C, 84.00; H, 4.23; N, 11.76. Found: C, 84.01; H, 4.04; N, 11.72. MS (ESP+): m/z 380 [MNa^+]. UV−vis (MeCN) λ_{DHA} (ε): 364 nm (17.3 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 502 nm (35.2 × 10^3 M^{-1} cm^{-1}).

*7-Phenyl-2-(4′-nitrophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**2.3**).* Prepared according to the general procedure for **2.1**: 7-bromide **11.1** (crude, prepared in two steps from **1.1** (1.00 mmol) with a purity of >90%), phenyl boronic acid (244 mg, 2.00 mmol), K_3PO_4 (425 mg, 2.00 mmol), RuPhos (47 mg, 0.10 mmol), and palladium(II)acetate (11 mg, 0.050 mmol) in toluene (9 mL) and water (1 mL). Heating for 1 h at 80 °C. (TLC (60% toluene/heptanes: R_f = 0.20 (starting material, orange) and R_f = 0.26 (products, purple). TLC (60% CH_2Cl_2/heptanes: R_f = 0.42 (starting material, orange-red) and R_f = 0.58 (products, orange-purple.) Worked up according to the general procedure for **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 6.25% steps, 40 mL fractions) gave **2.3** (208 mg, 550 mmol, 55%) as a yellow crystalline solid. (A stable solid can be obtained by recrystallization from ethanol.) TLC (toluene): R_f = 0.50. mp 174.8−175.6 °C (ethanol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 9.0 Hz, 2H), 7.91 (d, J = 9.0 Hz, 2H), 7.45−7.33 (m, 5H), 7.07 (s, 1H), 6.91−6.80 (m, 2H), 6.50 (dd, J = 4.8, 1.6 Hz, 1H), 6.00 (d, J = 4.6 Hz, 1H), 3.89 (dd, J = 4.6, 1.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 139.9, 139.7, 138.6, 136.6, 135.5, 133.6, 132.3, 128.8, 128.4, 128.1, 127.8, 127.2, 124.7, 122.8, 116.3, 114.8, 112.6, 51.0, 45.1 ppm. Anal. Calcd for $C_{24}H_{15}N_3O_2$ (377.39): C, 76.38; H, 4.01; N, 11.13. Found: C, 76.58; H, 3.70; N, 11.07. HRMS (ESP+): m/z 400.1087 [MNa^+], calcd for ($C_{24}H_{15}N_3O_2Na^+$): m/z 400.1056. UV−vis (MeCN) λ_{DHA} (ε): 383 nm (15.3 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 506 nm (24.0 × 10^3 M^{-1} cm^{-1}).

*7-Phenyl-2-(4′-bromophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**2.4**).* Prepared according to the general procedure for **2.1**: 7-bromide **11.8** (crude, prepared in two steps from **1.8** (1.07 mmol with a purity of >90%), phenyl boronic acid (126 mg, 1.07 mmol), K_3PO_4 (254 mg, 2.14 mmol), RuPhos (49.9 mg, 107 μmol), and palladium(II)acetate (12.0 mg, 53.5 μmol) in toluene (18 mL) and water (2 mL). Stirred for 60 h at rt (TLC (30% EtOAc/heptanes: R_f = 0.36 (starting material, yellow → orange) and R_f = 0.43 (products, yellow → purple)). Worked up according to the procedure of **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−50% toluene/heptanes, 5% steps, then 50−65% toluene/heptanes, 2.5% steps, 40 mL fractions) gave **2.4** (286 mg, 0.696 mmol, 65%) and **4.12** (52.5 mg, 0.128 mmol, 12%) as yellow to red solids. For **2.4**: TLC (60% toluene/heptanes): R_f = 0.38. mp 122.4−124.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 4H), 7.40−7.36 (m, 5H), 6.90 (s, 1H), 6.82−6.79 (m, 2H), 6.42−6.36 (m, 1H), 5.98 (d, J = 4.6 Hz, 1H), 3.84 (dd, J = 4.6, 1.7 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 140.07, 140.06, 140.03, 132.7, 132.52, 132.48, 132.3, 129.5, 128.7, 128.3, 127.8, 124.7, 120.9, 116.2, 115.1, 112.9, 51.0, 45.1 ppm (one signal missing due to overlap). HRMS (ESP+): m/z 433.0303, 435.0279 [$MNa^{+\,79/81}Br$], calcd for ($C_{24}H_{15}N_2BrNa^+$): m/z 433.0311, 435.0291. UV−vis (MeCN) λ_{DHA} (ε): 357 nm (17.5 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 494 nm (33.2 × 10^3 M^{-1} cm^{-1}). For **4.12**: TLC (60% toluene/heptanes): R_f = 0.32. mp 209−211 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ7.84 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.44−7.32 (m, 6H), 6.95 (s, 1H), 6.84−6.77 (m, 2H), 6.39 (d, J = 5.7 Hz, 1H), 6.02 (d, J = 4.6 Hz, 1H), 3.87 (dd, J = 4.6, 1.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 140.9, 140.8, 140.2, 140.0, 139.9, 132.6, 132.2, 131.5, 129.4, 129.1, 128.7, 128.21, 128.18, 128.0, 127.8, 127.2, 126.9, 120.4, 116.3, 115.4, 113.2, 51.1, 45.1 ppm. HRMS (ESP+): m/z 431.1526 [MNa^+], calcd for ($C_{30}H_{20}N_2Na^+$): m/z 431.1519.

*7-(4-Thiomethoxyphenyl)-2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (**3.1**).* Prepared according to the general procedure for **2.1**: 7-bromide **10.34** (85.9 mg, 256 μmol), 4-thiomethoxyphenyl boronic acid (64.6 mg, 384 μmol), K_3PO_4 (109 mg, 513 mg), RuPhos (12.0 mg, 25.6 μmol), and palladium(II)acetate (2.9 mg, 13 μmol) in toluene (5 mL) and water (0.5 mL). Heated by microwave irradiation at 90 °C

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for 15 min. Worked up according to the general procedure for **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, (1) 0−100% $CHCl_3$/heptanes, 10% steps, 40 mL fractions. (2) 0−30% toluene/CS_2, 3% steps, 40 mL fractions) gave **3.1** (56.8 mg, 150 μmol, 59%) as a dark yellow to red solid. TLC (CH_2Cl_2): R_f = 0.90. mp 145−155 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.49−7.44 (m, 3H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.90 (s, 1H), 6.81 (dd, *J* = 11.5, 6.0 Hz, 1H), 6.74 (d, *J* = 11.5 Hz, 1H), 6.36 (d, *J* = 6.0 Hz, 1H), 5.97 (d, *J* = 4.6 Hz, 1H), 3.82 (dd, *J* = 4.6, 1.6 Hz, 1H), 2.50 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 140.8, 139.3, 138.9, 136.9, 132.7, 132.0, 131.7, 130.6, 130.3, 129.4, 128.2, 126.6, 126.5, 120.3, 115.8, 115.3, 113.1, 51.1, 45.2, 15.9 ppm. Anal. Calcd for $C_{25}H_{18}N_2S$ (378.49): C, 79.33; H, 4.79; N, 7.40. Found: C, 79.03; H, 4.63; N, 7.45. HRMS (ESP+): *m*/*z* 401.1080 [MNa^+], calcd for ($C_{25}H_{18}N_2SNa^+$): *m*/*z* 401.1083. UV−vis (MeCN) λ_{DHA} (ε): 348 nm (15×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 500 nm (33×10^3 M^{-1} cm^{-1}).

*7-(4-Cyanophenyl)-2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (**3.2**).* Prepared according to the general procedure for **2.1**: 7-bromide **10.34** (312 mg, 931 μmol), 4-cyanophenyl boronic acid (150 mg, 1.02 mmol), K_3PO_4 (395 mg, 1.86 mg), RuPhos (21.7 mg, 46.5 μmol), and palladium(II)acetate (5.22 mg, 23.3 μmol) were stirred for 72 h at 25 °C. Worked up according to the procedure of **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, (1) 0−50% THF/heptanes, 5% steps, 40 mL fractions, (2) 0−30% EtOAc/heptanes, 3.75% steps, 40 mL fractions, (3) 0−100% $CHCl_3$/heptanes, 20% steps, 40 mL fractions, 400 mL neat $CHCl_3$ was passed through) gave **3.2** (200 mg, 0.559 mmol, 60%) as a dark yellow solid. TLC (CH_2Cl_2): R_f = 0.86. mp 181.2−181.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78−7.74 (m, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.52−7.48 (m, 5H), 6.92 (s, 1H), 6.87 (dd, *J* = 11.5, 6.2 Hz, 1H), 6.71 (d, *J* = 11.5 Hz, 1H), 6.40 (d, *J* = 6.2 Hz, 1H), 6.04 (d, *J* = 4.7 Hz, 1H), 3.86 (dd, *J* = 4.7, 1.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 141.8, 140.9, 138.5, 133.6, 132.6, 131.5, 130.7, 130.6, 130.3, 129.5, 128.4, 126.5, 120.4, 118.8, 118.4, 115.1, 113.00, 111.9, 51.0, 45.1 ppm. Anal. Calcd for $C_{25}H_{15}N_3$ (357.41): C, 84.01; H, 4.23; N, 11.76. Found: C, 83.96; H, 3.78; N, 11.75. MS (MALDI−): *m*/*z* 357 [M^-]. UV−vis (MeCN) λ_{DHA} (ε) = 357 nm (18.4×10^3 M^{-1} cm^{-1}), λ_{VHF} (ε) = 479 nm (41.7×10^3 M^{-1} cm^{-1}).

*7-(4-Tolyl)-2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (**3.3**).* Prepared according to the general procedure for **2.1**: 7-Bromide **11.34** (crude, prepared in two steps from 1.00 mmol with a purity of >90%), 4-tolyl boronic acid (272 mg, 2.00 mmol), K_3PO_4 (225 mg, 2.00 mmol), RuPhos (46.7 mg, 100 μmol), and palladium(II)acetate (11.2 mg, 50.0 μmol) in toluene (9 mL) and water (1 mL) were stirred for 24 h at rt. Worked up according to the general procedure for **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−60% toluene/heptanes, 7.5% steps, then 60−85% toluene/heptanes, 5% steps, 40 mL fractions) gave **3.3** (204 mg, 0.589 mmol, 59%) as a yellow solid. TLC (toluene): R_f = 0.73. mp 120.9−122.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78−7.74 (m, 2H), 7.51−7.41 (m, 3H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.90 (s, 1H), 6.82−6.74 (m, 2H), 6.36 (dd, *J* = 4.7, 0.8 Hz, 1H), 5.97 (d, *J* = 4.6 Hz, 1H), 3.83 (dd, *J* = 4.6, 1.7 Hz, 1H), 2.36 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 140.7, 139.8, 138.1, 137.3, 132.42, 132.39, 131.8, 130.6, 130.3, 129.42, 129.39, 127.7, 126.5, 120.4, 115.7, 115.4, 113.1, 51.1, 45.2, 21.3 ppm. HRMS (ESP+): *m*/*z* 369.1361 [MNa^+], calcd for ($C_{25}H_{18}N_2Na^+$): *m*/*z* 369.1362. UV−vis (MeCN) λ_{DHA} (ε): 352 nm (13.2×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 494 nm (32.1×10^3 M^{-1} cm^{-1}).

*7-(4-Bromophenyl)-2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (**3.4**).* Prepared according to the general procedure for **2.1**: 7-Bromide **11.34** (crude, prepared in two steps from 1.00 mmol with a purity of >90%), 4-bromophenyl boronic acid (402 mg, 2.00 mmol), K_3PO_4 (225 mg, 2.00 mmol), RuPhos (46.7 mg, 100 μmol) and palladium(II)acetate (11.2 mg, 50.0 μmol) in toluene (9 mL) and water (1 mL) were stirred for 48 h at rt. Worked up according to the general procedure for **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−75% toluene/heptanes, 7.5% steps, 40 mL fractions) gave **3.4** (264 mg, 0.641 mmol, 64%) as a yellow solid. TLC (75% toluene/heptanes): R_f = 0.55 (yellow → purple). mp 157.2−157.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77−7.74 (m, 2H), 7.50−7.42 (m, 3H), 7.30 (d, J = 8.1 Hz, 2H), 7.18−7.17 (m, 2H), 6.90 (s, 1H), 6.84−6.71 (m, 2H), 6.36 (d, *J* = 5.5 Hz, 1H), 5.97 (d, *J* = 4.6 Hz, 1H), 3.83 (dd, *J* = 4.6, 1.7 Hz, 1H), 2.36 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5, 140.8, 139.1, 138.9, 133.0, 131.8, 131.6, 131.5, 130.5, 130.4, 129.46, 129.45, 126.5, 122.5, 120.3, 116.6, 115.2, 113.1, 51.0, 45.1 ppm. Anal. Calcd for $C_{24}H_{15}N_2Br$ (410.29): C, 70.09; H, 3.68; N, 6.81. Found: C, 70.01; H, 3.72; N, 6.89. HRMS (ESP+): *m*/*z* 433.0295, 435.0290 [MNa^+], calcd for ($C_{24}H_{15}N_2BrNa^+$): *m*/*z* 433.0311, 435.0291. UV−vis (MeCN) λ_{DHA} (ε): 355 nm (14.9×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 486 nm (32.1×10^3 M^{-1} cm^{-1}).

*7-(4-Aminophenyl)-2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (**3.7**).* To a stirred solution of **3.6** (50.1 mg, 133 μmol) in AcOH (5 mL) was added zinc powder (17.4 mg, 266 μmol), and the reaction mixture was stirred overnight. The reaction mixture was diluted with Et_2O (50 mL), and saturated aqueous $NaHCO_3$ (2 mL) was added followed by saturated aqueous NH_4Cl (50 mL). The organic phase was separated, dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−50% EtOAc/heptanes, 5% steps, 40 mL fractions) gave **3.7** (34 mg, 98 μmol, 74%) as a crude yellow oil. Attempted purification by recrystallization failed. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80−7.71 (m, 2H), 7.55−7.38 (m, 4H), 7.21 (dd, *J* = 5.5, 5.1 Hz, 2H), 6.89 (s, 1H), 6.82−6.72 (m, 2H), 6.72−6.63 (m, 2H), 6.37−6.30 (m, 1H), 5.90 (dd, *J* = 4.7, 0.8 Hz, 1H), 3.86−3.64 (m, 3H) ppm.

*7-[4-(tert-Butylsulfinyl)phenyl]-2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (**3.8**).* To a solution of DHA **3.5** (77 mg, 0.183 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (45 mg, 0.20 mmol, 70% w/w), and the resulting solution was stirred for 30 min at rt. The solution was treated simultaneously with saturated aqueous sodium thiosulfate (1 mL) and saturated aqueous sodium bicarbonate (1 mL) and was then diluted with both water (10 mL) and CH_2Cl_2 (10 mL). The phases were separated, and the organic phase was dried over sodium sulfate. Filtration and removal of the solvent under reduced pressure gave an orange residue, which was subjected to flash column chromatography (SiO_2, gradient elution: 0−10% EtOAc/CH_2Cl_2) to furnish pure **3.8** (60 mg, 75%) as a viscous orange oil. In addition, unreacted starting material (5 mg, 6%) and corresponding sulfone **3.9** (5 mg, 6%) were also obtained. TLC (5% EtOAc/CH_2Cl_2): R_f = 0.42. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77−7.75 (m, 2H), 7.60−7.58 (d, 2H), 7.53−7.43 (m, 5H), 6.91 (s, 1H), 6.87−6.83 (m, 1H), 6.75 (d, *J* = 11.4 Hz, 1H), 6.39−6.38 (m, 1H), 6.05−6.04 (m, 1H), 3.86 (dd, *J* = 4.7, 1.6 Hz, 1H), 1.18 and 1.17 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 142.9, 141.5, 140.8, 140.8, 139.0, 133.1, 131.6, 131.4, 130.4, 129.5, 127.7, 126.7, 126.7, 126.5, 120.4, 117.5, 117.5, 115.2, 113.1, 56.2, 51.0, 45.1, 22.9 ppm. Anal. Calcd for $C_{28}H_{24}N_2OS$ (436.57): C, 77.04; H, 5.55; N, 6.42. Found: C, 76.95; H, 5.64; N, 6.42. MS (ESP+) = 459 [MNa^+]. UV−vis (MeCN) λ_{DHA} (ε): 355 nm (14.6×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 485 nm (33.8×10^3 M^{-1} cm^{-1}).

*7-[4-(tert-Butylsulfonyl)phenyl]-2-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (**3.9**).* To a solution of DHA **3.5** (95 mg, 0.226 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (161 mg, 0.72 mmol, 70% w/w), and the resulting solution was stirred for 20 min at rt. The solution was treated simultaneously with saturated aqueous sodium thiosulfate (1 mL) and saturated aqueous sodium bicarbonate (1 mL) and was then diluted with both water (10 mL) and CH_2Cl_2 (10 mL). The phases were separated, and the organic phase was dried over sodium sulfate. Filtration and removal of the solvent under reduced pressure gave an orange residue, which was subjected to flash column chromatography (SiO_2, gradient elution: 0−2% EtOAc/CH_2Cl_2) to furnish pure the **3.9** (94 mg, 92%) as a yellow powder. TLC (2% EtOAc/CH_2Cl_2): R_f = 0.69. mp 176.5−179.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.53−7.43 (m, 3H), 6.93 (s, 1H), 6.87 (dd, *J* = 11.5, 6.1 Hz, 1H), 6.73 (d, *J* = 11.5 Hz, 1H), 6.40 (dd, *J* = 6.1, 1.7 Hz, 1H), 6.07 (d, *J* = 4.7 Hz, 1H), 3.88 (dd, *J* = 4.7, 1.7 Hz, 1H), 1.35 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 141.7, 140.9, 138.5, 134.9, 133.4, 131.6, 130.9, 130.9, 130.5, 129.5, 128.0, 126.5, 120.4, 118.5, 115.1, 113.0, 60.1, 51.0, 45.1, 23.8 ppm, 1 C masked. Anal. Calcd for $C_{28}H_{24}N_2O_2S$ (452.57): C, 74.31; H, 5.35; N, 6.19. Found: C, 74.70; H, 5.21; N, 6.18. MS (ESP+) = 475 [MNa^+].

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UV−vis (MeCN) λ_{DHA} (ε): 355 nm (24.5 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 479 nm (53.5 × 10^3 M^{-1} cm^{-1}).

*7-(4-Nitrophenyl)-2-(4′-nitrophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.1**).* To a stirred solution of 7-bromide **11.1** ($^1/_9$ of a batch made in two steps from 2.25 mmol **1.1**) in a mixture of argon-flushed toluene (15 mL) and water (10 mL) were added nitrophenyl boronic acid (46 mg, 0.25 mmol), KF·$2H_2O$ (26 mg, 0.25 mmol), and tetrakis(triphenylphosphine)palladium(0) (29 mg, 25 μmol, 10 mol %), and the reaction mixture was stirred at 70−75 °C overnight. The reaction mixture was diluted with Et_2O (200 mL), washed with saturated aqueous NH_4Cl (50 mL) and brine (50 mL), dried with $MgSO_4$, and filtered, and the solvents were evaporated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 20% steps, then neat toluene, 40 mL fractions) gave **4.1** (29.6 mg, 70.1 μmol, 28%) as a dark yellow solid. TLC (toluene): R_f = 0.25. mp > 210 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 9.0 Hz, 1H), 8.24 (d, J = 8.9 Hz, 1H), 7.92 (d, J = 9.0 Hz, 2H), 7.56 (d, J = 8.9 Hz, 1H), 7.11 (s, 1H), 6.93 (dd, J = 11.5, 6.1 Hz, 1H), 6.81 (d, J = 11.5 Hz, 1H), 6.55 (dd, J = 6.1, 1.6 Hz, 1H), 6.08 (d, J = 4.7 Hz, 1H), 3.92 (dd, J = 4.7, 1.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 147.8, 146.0, 139.9, 139.1, 138.5, 136.2, 135.3, 133.4, 131.9, 128.6, 127.2, 124.7, 124.1, 122.8, 118.8, 114.5, 112.4, 50.8, 45.0 ppm. Anal. Calcd for $C_{24}H_{14}N_4O_4$ (422.39): C, 68.24; H, 3.34; N, 13.26. Found: C, 68.06; H, 3.02; N, 13.19. MS (MALDI TOF+): m/z 423 [MH^+]. UV−vis (MeCN) λ_{DHA} (ε) = 382 nm (25.8 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε) = 493 nm (39.2 × 10^3 M^{-1} cm^{-1}).

*7-(4-Methoxyphenyl)-2-(4′-nitrophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.2**).* To a solution of 7-bromide **11.1** ($^1/_9$ of a batch made in two steps from 2.25 mmol **1.1**) in a mixture of argon-degassed toluene (15 mL) and water (10 mL) were added methoxyphenyl boronic acid (0.25 mmol), KF·$2H_2O$ (26 mg, 0.25 mmol), and tetrakis(triphenylphosphine)palladium(0) (29 mg, 25 μmol, 10 mol %), and the reaction mixture was stirred at 90 °C for 24 h (reaction progress cannot be monitored by TLC (no suitable eluent was found), but ^{1}H NMR was used (decay of signal at δ = 6.13 ppm)). The reaction mixture was diluted with Et_2O (200 mL), washed with saturated aqueous NH_4Cl (50 mL) and brine (50 mL), dried with $MgSO_4$, and filtered, and the solvents were removed in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, (1) 0−65% THF/heptanes, 5% steps, 40 mL fractions, (2) 0−100% toluene/heptanes, 12.5% steps, 40 mL fractions) followed by recrystallization from CH_2Cl_2/heptanes gave **4.2** (37.7 mg, 92.5 μmol, 37%) as yellow crystals. TLC (toluene): R_f = 0.37. mp 190−200 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 9.0 Hz, 2H), 7.91 (d, J = 9.0 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.07 (s, 1H), 6.90 (d, J = 8.8 Hz, 2H), 6.86−6.77 (m, 2H), 6.51−6.45 (m, 1H), 5.92 (d, J = 4.6 Hz, 1H), 3.85 (dd, J = 4.6, 1.6 Hz, 1H), 3.83 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 148.2, 139.8, 139.7, 138.5, 136.6, 135.5, 133.8, 132.5, 132.3, 129.1, 127.1, 124.7, 122.8, 114.8, 114.1, 112.6, 55.5, 50.9, 45.1 ppm (one signal is missing because of overlap). Anal. Calcd for $C_{25}H_{17}N_3O_3$ (407.42): C, 73.70; H, 4.21; N, 10.31. Found: C, 73.62; H, 4.05; N, 10.27. UV−vis (MeCN) λ_{DHA} = 373 nm. λ_{VHF} = 519 nm.

*7-(4-Cyanophenyl)-2-(4′-Tolyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.3**).* Method 1: To a stirred solution of 7-bromoide **11.3** (crude, prepared in two steps from 0.25 mmol with a purity of >90%) in a mixture of argon-flushed toluene (20 mL) and water (20 mL) were added cyanophenyl boronic acid (37 mg, 0.25 mmol), KF·$2H_2O$ (26 mg, 0.25 mmol), and tetrakis(triphenylphosphine)palladium(0) (29 mg, 25 μmol, 10 mol %), and the reaction mixture was stirred at 70−75 °C for 48 days. The reaction mixture was diluted with Et_2O (200 mL), washed with saturated aqueous NH_4Cl (50 mL) and brine (50 mL), dried with $MgSO_4$, and filtered, and the solvent was concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 20% steps, followed by 0−100% $CHCl_3$/heptanes, 20% steps, 40 mL fractions) gave **4.3** (9.3 mg, 0.025 mmol, 10%) as a dark yellow solid. Method 2: Prepared according to the general procedure for **2.1**: 7-bromide **11.3** (crude, prepared in two steps from 1.00 mmol with a purity of >90%), tolyl boronic acid (272 mg, 2.00 mmol), K_3PO_4 (425 mg, 2.00 mmol), RuPhos (46.7 mg, 0.10 mmol), and palladium(II)acetate (11.2 mg, 0.050 mmol) in toluene (9 mL) and water (1 mL) were stirred for 72 h at rt. Worked up according to the general procedure for **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 10% steps, 40 mL fractions) gave followed by a careful recrystallization from $CHCl_3$/heptanes gave **4.3** (172 mg, 0.462 mmol, 46%) as a yellow solid. TLC (toluene): R_f = 0.36. mp 177.8−178.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.89 (s, 1H), 6.86 (dd, J = 11.8, 6.1 Hz, 1H), 6.68 (d, J = 11.8 Hz, 1H), 6.36 (dd, J = 6.1, 1.7 Hz, 1H), 6.03 (d, J = 4.7 Hz, 1H), 3.84 (dd, J = 4.7, 1.7 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 141.9, 141.2, 141.1, 138.4, 133.6, 132.5, 130.5, 130.4, 130.2, 128.4, 127.6, 126.4, 119.9, 118.8, 118.4, 115.1, 113.1, 111.9, 51.0, 45.1, 21.6 ppm. Anal. Calcd for $C_{26}H_{19}N_3$ (371.43): C, 84.07; H, 4.61; N, 11.31. Found: C, 84.19; H, 4.46; N, 11.40. HRMS (ESP+): m/z 765.2738 [$2MNa^+$], calcd for ($C_{52}H_{34}N_6Na^+$): m/z 765.2738. UV−vis (MeCN) λ_{DHA} (ε) = 361 nm (23.7 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε) = 478 nm (46.2 × 10^3 M^{-1} cm^{-1}).

*7-(4-Methoxyphenyl)-2-(4′-Tolyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.4**).* Method 1: To a solution of 7-bromide **11.8** (50 mg, 0.14 mmol) in a mixture of argon-flushed toluene (25 mL) and water (25 mL) were added methoxyphenyl boronic acid (22 mg, 0.14 mmol), KF·$2H_2O$ (14 mg, 0.14 mmol), and tetrakis(triphenylphosphine)-palladium(0) (16 mg, 14 μmol, 10 mol %), and the reaction mixture was stirred at 90 °C for 16 h. The reaction mixture was diluted with toluene (100 mL), washed with brine (50 mL), dried with $MgSO_4$, and filtered, and the mixture was concentrated in vacuo. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, (1) 0−100% toluene/heptanes, 20% steps, 40 mL fractions, (2) 0−40% THF/heptanes, 5% steps, 40 mL fractions) gave **4.4** (11.8 mg, 31 μmol, 22%) as a dark yellow solid. Method 2: Prepared according to the general procedure for **2.1**: 7-bromide **11.3** (crude, prepared in two steps from 1.00 mmol with a purity of >90%), 4-methoxyphenyl boronic acid (304 mg, 2.00 mmol), K_3PO_4 (425 mg, 2.00 mmol), RuPhos (47 mg, 0.10 mmol), and palladium(II)acetate (11 mg, 0.050 mmol) in toluene (9 mL) and water (1 mL) were stirred for 16 h at rt. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 10% steps, 40 mL fractions) gave **4.4** (263 mg, 0.701 mmol, 70%, >95% purity) as a dark yellow solid. An analytically pure sample was prepared by recrystallization from EtOH, yielding **4.4** (83 mg, 0.22 mmol, 22%) as thin yellow needles. TLC (toluene): R_f = 0.40. mp 137.4−139.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.84 (s, 1H), 6.79 (dd, J = 11.3, 5.8 Hz, 1H), 6.73 (d, J = 11.3 Hz, 1H), 6.32 (d, J = 5.8 Hz, 1H), 5.92 (d, J = 4.6 Hz, 1H), 3.82 (s, 3H), 3.80 (d, J = 4.6 Hz, 1H), 2.41 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 141.4, 141.0, 140.7, 139.3, 132.9, 132.5, 132.1, 130.7, 130.1, 129.1, 127.8, 126.4, 119.8, 115.5, 114.9, 114.0, 113.2, 55.5, 51.1, 45.2, 21.6 ppm. Anal. Calcd for $C_{26}H_{20}N_2O$ (376.45): C, 82.95; H, 5.35; N, 7.44. Found: C, 82.83; H, 5.24; N, 7.42. MS (MALDI TOF+): m/z 377 [MH^+]. UV−vis (MeCN): λ_{DHA} (ε) = 353 nm (15.8 × 10^3 M^{-1} cm^{-1}), λ_{VHF} (ε) = 503 nm (30.8 × 10^3 M^{-1} cm^{-1}).

*7-(4-Methoxyphenyl)-2-(4′-cyanophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.5**).* Prepared according to the general procedure for **2.1**: 7-bromide **11.10** (crude, prepared in two steps from 1.00 mmol with a purity of >90%), methoxyphenyl boronic acid (304 mg, 2.00 mmol), K_3PO_4 (425 mg, 2.00 mmol), RuPhos (46.7 mg, 0.10 mmol), and palladium(II)acetate (11.2 mg, 0.050 mmol) in toluene (9 mL) and water (1 mL) were stirred for 16 h at rt. Worked up according to the general procedure for **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 12.5% steps, 40 mL fractions, toluene was passed through to collect the product) gave **4.5** (320 mg, 0.826 mmol, 41%) as a dark yellow solid. (This is an extremely difficult purification because of the lack of separation. A very short column was chosen (3−4 cm) to prevent band broadening; thus, an eluent with low R_f was chosen. The column was repeated five times to get an overall acceptable yield of reasonably pure compound, but much material was discarded.) Analytically pure samples were prepared by recrystallization from $CHCl_3$/heptanes or EtOH. TLC (toluene): R_f = 0.23. mp 177.9−178.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 8.8 Hz, 2H), 7.77 (dd, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.02 (s, 1H), 6.90 (d, J = 8.8 Hz, 2H), 6.84−6.81 (m, 2H), 6.47−6.45 (m, 1H), 5.91 (d, J = 4.6 Hz, 1H),

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3.84 (dd,*J* = 4.6, 2.0 Hz,1H), 3.83 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 139.8, 139.6, 138.9, 134.8, 134.8, 133.6, 133.1, 132.5, 132.3, 129.1, 126.8, 122.4, 118.2, 114.8, 114.8, 114.1, 113.4, 112.7, 55.5, 50.9, 45.0 ppm. ^{1}H NMR (500 MHz, CD_3CN) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.9 Hz, 2H), 7.32 (s, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.90−6.81 (m, 2H), 6.57 (d, *J* = 5.7 Hz, 1H), 5.91 (d, *J* = 4.5 Hz, 1H), 3.90 (dd, *J* = 4.5, 1.7 Hz, 1H), 3.82 (s, 3H) ppm. ^{13}C NMR (125 MHz, CD_3CN) δ 161.4, 141.8, 140.3, 140.0, 137.6, 136.5, 134.7, 134.4, 134.2, 133.9, 130.3, 128.4, 124.1, 119.8, 117.0, 116.6, 115.6, 114.6, 114.3, 56.6, 52.1, 46.6 ppm. Anal. Calcd for $C_{26}H_{17}N_3O$ (387.43): C, 80.60; H, 4.42; N, 10.85. Found: C, 80.37; H, 4.21; N, 10.92. MS (MALDI−): *m*/*z* 387 [M$^-$]. UV−vis (MeCN) λ_{DHA} (ε): 354 nm (32.6 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 518 nm (60.6 × 10^3 M^{-1} cm^{-1}).

*7-(4-Cyanophenyl)-2-(4′-cyanophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.6**).* Prepared according to the general procedure for **2.1**: 7-bromide **11.10** (crude, prepared in two steps from 0.5 mmol with a purity of >90%), cyanophenyl boronic acid (146 mg, 1.00 mmol), K_3PO_4 (119 mg, 1.00 mmol), RuPhos (23 mg, 50 μmol), and palladium(II)acetate (5.6 mg, 25 μmol) in toluene (18 mL) and water (2 mL) were stirred for 8 h at 50 °C. Worked up according to the general procedure for **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, (1) 0−100% toluene/heptanes, 20% steps, 40 mL fractions, then neat toluene 200 mL (A purple band was separated. The elution of toluene was not stopped before the purple band was well ahead of the following yellow band), then: 0−6% EtOAc/toluene, 1% steps, (2) 0−100% toluene/heptanes, 20% steps, then: neat toluene 200 mL, 0−100% $CHCl_3$/toluene, 20% steps, 0−5% EtOAc/heptanes, 1% steps, (3) 0−100% toluene/heptanes, 20% steps, 0−13% $MeNO_2$/toluene, 1% steps, 40 mL fractions) gave (56 mg, 14.6 μmol, 29%) as a yellow solid. (Multiple columns were nessesary to get a complete separation from a UV-active spot with a slightly lower R_f than the desired product. An analytically pure sample can also be obtained by careful recrystallization from $CHCl_3$/heptanes.) TLC (75% toluene/heptanes): R_f = 0.09 (yellow → light purple). mp > 215 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 10.5 Hz, 2H), 7.78 (d, *J* = 10.5 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.04 (s, 1H), 6.90 (dd, *J* = 11.5, 6.1 Hz, 1H), 6.77 (d, *J* = 11.5 Hz, 1H), 6.50 (d, *J* = 6.1 Hz, 1H), 6.03 (d, *J* = 4.7 Hz, 1H), 3.88 (dd, *J* = 4.7, 1.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 140.0, 139.4, 138.8, 134.6, 134.5, 133.4, 133.2, 132.6, 131.9, 128.4, 126.9, 122.4, 118.7, 118.3, 118.1, 114.5, 113.8, 112.5, 112.2, 50.8, 44.9 ppm. Anal. Calcd for $C_{26}H_{14}N_4$ (382.42): C, 81.66; H, 3.69; N, 14.65. Found: C, 81.79; H, 3.71; N, 14.53. HRMS (ESP+): *m*/*z* 405.1100 [MNa$^+$], calcd for ($C_{26}H_{14}N_4Na^+$): *m*/*z* 405.1111. UV−vis (MeCN) λ_{DHA} (ε): 366 nm (10.7 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 490 nm (19.4 × 10^3 M^{-1} cm^{-1}).

*7-(4-N,N-Dimethylaminophenyl)-2-(4′-cyanophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.7**).* To a stirred solution of **11.10** (crude, prepared in two steps from 0.5 mmol with a purity of >90%) were added 4-*N*,*N*-dimethylaminophenyl boronic pinacol ester (289 mg, 1.19 mmol), K_3PO_4 (252 mg, 1.19 mmol), KF·2H_2O (67 mg, 0.71 mmol), $Pd(OAc)_2$ (12.6 mg, 0.0564 mmol), and RuPhos (52.7 mg, 0.113 mmol). The reaction mixture was refluxed for 1 h and then stirred at 50 °C overnight. (TLC (toluene): R_f = 0.10 (product, yellow → purple, low photoactivity), R_f = 0.30 (starting material, yellow → red).) The reaction mixture was diluted with Et_2O (100 mL), washed with brine (100 mL), dried with Na_2SO_4, and filtered, and the solvents were removed. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 20% steps, 40 mL fractions, then neat toluene (10 × 100 mL) to collect product (unreacted starting material elutes, then a purple band which is followed by the desired product), very short column) followed by recrystallization from $CHCl_3$/heptanes gave **4.7** (20 mg, 0.050 mmol, 9%) as a dark yellow or slightly brown solid. TLC (toluene): R_f = 0.10 (yellow → purple). mp 190−220 °C dec, darkens at ca. 140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.01 (s, 1H), 6.87−6.78 (m, 2H), 6.71 (br d, *J* = 8.5 Hz, 2H), 6.44 (d, *J* = 5.7 Hz, 1H), 5.89 (d, *J* = 4.6 Hz, 1H), 3.82 (dd, *J* = 4.6, 1.6 Hz, 1H), 2.98 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 139.9, 139.8, 138.7, 134.9, 134.1, 133.1, 132.1, 128.7, 126.8, 122.4, 118.3, 115.0, 113.3, 113.3, 112.7, 112.3, 50.9, 45.0, 40.6 ppm (2 signals missing because of overlapping signals). HRMS (ESP+): *m*/*z* 401.1760 [MH$^+$], calcd for ($C_{27}H_{21}N_4^+$): *m*/*z* 401.1761. UV−vis (MeCN) λ_{DHA} (ε): 362 nm (18.5 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 563 nm (24.0 × 10^3 M^{-1} cm^{-1}).

*7-(4-Bromophenyl)-2-(4′-bromophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.8**).* Prepared according to the general procedure for **2.1**: 7-bromide **11.8** (crude, prepared in two steps from 1.07 mmol with a purity of >90%), 4-bromophenyl boronic acid (215 mg, 1.07 mmol), K_3PO_4 (254 mg, 2.14 mmol), RuPhos (49.9 mg, 107 μmol), and palladium(II)acetate (12.0 mg, 53.5 μmol) in toluene (18 mL) and water (2 mL) were stirred for 60 h at rt. (TLC (35% toluene/CS_2): R_f = 0.50 (**4.8**), R_f = 0.40 (photochromic byproduct) and R_f = 0.30 (photochromic byproduct). By TLC analysis and NMR spectroscopy two byproducts arising from a second and third coupling can be recognized, although these were never obtained analytically pure.) Worked up according to the general procedure for **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% CS_2/heptanes, 20% steps, then 0−50% toluene/CS_2, 2.5% steps, 40 mL fractions, multiple columns were necessary to obtain a pure sample) gave **4.8** (378 mg, 0.770 mmol, 72%) as a yellow to red solid. TLC (35% toluene/CS_2): R_f = 0.50. mp 169.7−170.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (br s, 4H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.90 (s, 1H), 6.82 (dd, *J* = 11.5, 6.0 Hz, 1H), 6.72 (d, *J* = 11.5 Hz, 1H), 6.39 (dd, *J* = 6.0, 1.6 Hz, 1H), 5.96 (d, *J* = 4.6 Hz, 1H), 3.82 (dd, *J* = 4.6, 1.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 140.3, 139.0, 139.0, 132.9, 132.7, 132.2, 131.9, 131.8, 129.4, 127.8, 124.8, 122.6, 120.9, 116.5, 115.0, 112.9, 51.0, 45.1 ppm (one signal missing because of overlap). Anal. Calcd for $C_{24}H_{14}Br_2N_2$ (490.19): C, 58.81; H, 2.88; N, 5.71. Found: C, 58.72; H, 2.55; N, 5.64. HRMS (ESP+): *m*/*z* 488.9598 [MH$^+$], calcd for ($C_{24}H_{15}Br_2N_2^+$): *m*/*z* 488.9597. UV−vis (MeCN): λ_{DHA} (ε) = 359 nm (16.3 × 10^3 M^{-1} cm^{-1}), λ_{VHF} (ε) = 492 nm (30.1 × 10^3 M^{-1} cm^{-1}).

*7-(4-Cyanophenyl)-2-(4′-bromophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.9**).* Prepared according to the general procedure for **2.1**: 7-bromide **11.8** (crude, prepared in two steps from 0.50 mmol with a purity of >90%), cyanophenyl boronic acid (75.9 mg, 0.500 mmol), K_3PO_4 (212 mg, 0.999 mmol), RuPhos (23.3 mg, 49.9 μmol), and palladium(II)acetate (5.6 mg, 25 μmol) in toluene (9 mL) and water (1 mL) were stirred for 16 h at rt. Worked up according to the general procedure for **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 10% steps, 40 mL) gave **4.9** (89 mg, 0.21 μmol, 41%) as a yellow solid. TLC (toluene): R_f = 0.29 (yellow → purple). mp 185.2−186.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.6 Hz, 2H), 7.64−7.62 (s, 4H), 7.51 (d, *J* = 8.6 Hz, 2H), 6.92 (s, 1H), 6.88 (dd, *J* = 11.6, 6.2 Hz, 1H), 6.73 (d, *J* = 11.6 Hz, 1H), 6.42 (dd, *J* = 6.2, 1.7 Hz, 1H), 6.03 (d, *J* = 4.7 Hz, 1H), 3.86 (dd, *J* = 4.7, 1.7 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 140.6, 140.6, 138.6, 133.5, 132.8, 132.6, 132.1, 131.0, 129.3, 128.4, 127.9, 125.0, 120.9, 118.7, 118.3, 114.8, 112.8, 112.0, 50.9, 45.0 ppm. Anal. Calcd for $C_{25}H_{14}BrN_3$ (436.04): C, 68.82; H, 3.23; N, 9.63. Found: C, 68.69; H, 3.15; N, 9.58. HRMS (ESP+): *m*/*z* 893.0627, 895.0618 [2MNa$^+$, $^{79/81}$Br], calcd for ($C_{50}H_{28}Br_2N_6Na^+$): *m*/*z* 893.0635, 895.0614. UV−vis (MeCN) λ_{DHA} (ε): 361 nm (17.6 × 10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 484 nm (33.1 × 10^3 M^{-1} cm^{-1}).

*7-(4-Methoxyphenyl)-2-(4′-bromophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.10**).* Prepared according to the general procedure for **2.1**: 7-bromide **11.8** (crude, prepared in two steps from 1.07 mmol with a purity of >90%), 4-methoxyphenyl boronic acid (146 mg, 1.07 mmol), K_3PO_4 (254 mg, 2.14 mmol), RuPhos (49.9 mg, 107 μmol), and palladium(II)acetate (12.0 mg, 53.5 μmol) in toluene (18 mL) and water (2 mL) were stirred for 16 h at rt. Worked up according to the general procedure for **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−75% toluene/heptanes, 7.5% steps, 40 mL, 75−87.5% toluene/heptanes, 2.5% steps, 40 mL fractions) gave **4.10** (385 mg, 872 μmol, 82%) as a yellow solid. Recrystallization from $CHCl_3$/heptanes gave **4.10** (135.9 mg, 0.308 mmol, 29%) as yellow needles. TLC (80% toluene/heptanes): R_f = 0.33. TLC (toluene): R_f = 0.56. mp 148−151 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (br s, 4H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz,2H), 6.89 (s, 1H), 6.81−6.76 (m, 2H), 6.37 (t, *J* = 8.4 Hz, 1H), 5.91 (d, *J* = 4.6 Hz, 1H), 3.83 (s, 3H), 3.81 (dd, *J* = 4.6, 1.6 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 140.5, 140.0, 139.4, 132.7, 132.7, 132.7, 132.4, 132.3, 129.6, 129.1,

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127.8, 124.6, 120.8, 115.2, 114.8, 114.1, 113.0, 55.5, 51.0, 45.1 ppm. Anal. Calcd for $C_{25}H_{17}BrN_2O$ (441.32): C, 68.04; H, 3.88; N, 6.35. Found: C, 67.62; H, 3.61; N, 6.33. MS (MALDI TOF−): m/z 440, 442 [$M^{-79/81}Br$]. UV−vis (MeCN) λ_{DHA} (ε): 352 nm (16.8×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 509 nm (32.5×10^3 M^{-1} cm^{-1}).

*7-(4-Methoxyphenyl)-2-(4′-methoxybiphenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.11**).* Prepared according to the general procedure for **2.1**: 7-bromide **11.8** (crude, prepared in two steps from 0.460 mmol with a purity of >90%), 4-methoxyphenyl boronic acid (280 mg, 1.84 mmol), K_3PO_4 (195 mg, 0.920 mmol), RuPhos (21 mg, 46 μmol), and palladium(II)acetate (5.1 mg, 23 μmol) in toluene (9 mL) and water (1 mL) were heated by microwave irradiation for 30 min at 90 °C. Worked up according to the general procedure for **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−90% toluene/heptanes, 10% steps, 40 mL fractions, then 90−100% toluene/heptanes, 2.5% steps, 40 mL fractions, 120 mL neat toluene was passed through to collect the product) gave **4.11** (98.4 mg, 0.212 μmol, 42%) as a yellow solid. TLC (toluene): R_f = 0.33. mp 221−223 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.7 Hz, 2H), 7.67 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.9 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 6.91 (s, 1H), 6.90 (d, J = 8.8 Hz, 2H), 6.83−6.72 (m, 2H), 6.36 (d, J = 5.8 Hz, 1H), 5.95 (d, J = 4.6 Hz, 1H), 3.87 (s, 1H), 3.84 (d, J = 4.6, 1.7 Hz, 1H), 3.83 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 159.8, 142.6, 141.0, 141.0, 139.3, 132.9, 132.5, 132.4, 132.3, 131.1, 129.1, 128.8, 128.3, 127.4, 126.9, 120.1, 115.5, 114.9, 114.6, 114.0, 113.2, 55.5, 55.5, 51.0, 45.1 ppm. Anal. Calcd for $C_{32}H_{24}N_2O_2$ (468.55): C, 82.03; H, 5.16; N, 5.98. Found: C, 81.95; H, 4.90; N, 6.01. MS (MALDI−): m/z 468 [M^-]. UV−vis (MeCN) λ_{DHA} (ε): 373 nm (32.6×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 506 nm (38.4×10^3 M^{-1} cm^{-1}).

*2-([1,1′-Biphenyl]-4-yl)-7-phenyl-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.12**).* For preparation, see the synthesis of compound **2.4**.

*7-[4-(tert-Butylthio)phenyl]-2-(4′-(tert-butylthio)phenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.14**).* Prepared according to the general procedure for **2.1**: 7-bromide **11.28** (crude, prepared in two steps from 1.00 mmol with a purity of >90%), 4-(*tert*-butylthio)phenyl boronic acid (235 mg, 1.12 mmol), K_3PO_4 (440 mg, 2.07 mmol), $Pd(OAc)_2$ (17 mg, 0.0757 mmol), and RuPhos (74 mg, 0.159 mmol) in toluene (50 mL) and water (5.0 mL) were stirred for 16 h at rt. The contents of the vessel were diluted with toluene (100 mL) and water (100 mL), and the phases were separated. The organic phase was dried over Na_2SO_4 and filtered, and the solvent was removed by rotary evaporation. The residue was subsequently purified by flash column chromatography (SiO_2, gradient elution: 50−100% toluene/heptane) to give **4.14** (215 mg, 42%) as a yellow powder. TLC (60% toluene/heptane): R_f = 0.43. mp 140−142 °C.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.6, 2H), 7.63 (d, J = 8.6, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 6.93 (s, 1H), 6.83 (dd, J = 11.4, 5.8 Hz, 1H), 6.78 (d, J = 11.4 Hz, 1H), 6.39 (d, 5.8 Hz, 1H), 6.02 (d, J = 4.7 Hz, 1H), 3.85 (dd, J = 4.7, 1.7 Hz, 1H), 1.34 (s, 9H), 1.29 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 140.4, 139.3, 137.9, 137.7, 136.0, 133.0, 132.7, 132.2, 132.1, 130.5, 127.8, 126.2, 120.8, 116.8, 115.1, 113.0, 51.1, 47.1, 46.4, 45.0, 31.2, 31.1 ppm (one signal missing because of overlap). Anal. Calcd for $C_{32}H_{32}N_2S_2$ (508.74): C, 75.55; H, 6.34; N, 5.51. Found: C, 75.68; H, 6.01; N, 5.40.

*7-[4-(tert-Butylsulfonyl)phenyl]-2-(4′-[tert-butylsulfonyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.15**).* To a solution of **4.14** (65 mg, 0.128 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (170 mg, 0.76 mmol, 70% w/w), and the resulting solution was stirred for 20 min at rt. The solution was treated simultaneously with saturated aqueous sodium thiosulfate (1 mL) and saturated aqueous sodium bicarbonate (1 mL) and was then diluted with both water (10 mL) and CH_2Cl_2 (10 mL). The phases were separated, and the organic phase was dried over sodium sulfate. Filtration and removal of the solvent under reduced pressure gave an orange residue, which was subjected to flash column chromatography (SiO_2, 15% EtOAc/CH_2Cl_2) to furnish DHA **4.15** (60 mg, 82%) as an off yellow solid. TLC (5% EtOAc/CH_2Cl_2): R_f = 0.39. mp 197−199 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.08 (s, 1H), 6.90 (dd, J = 11.5, 6.0 Hz, 1H), 6.80 (d, J = 11.5 Hz, 1H), 6.51 (d, J = 6.0 Hz, 1H), 6.07 (d, J = 4.2 Hz, 1H), 3.91 (d, J = 4.2 Hz, 1H), 1.38 (s, 9H), 1.35 (s, 9H) ppm.[13] ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 140.0, 138.8, 1369, 135.2, 135.1, 134.8, 133.2, 132.0, 131.6, 131.0, 128.0, 126.5, 122.4, 118.5, 114.6, 112.6, 60.4, 60.1, 50.9, 45.0, 23.8 ppm (two signals are missing because of overlap). Anal. Calcd for $C_{32}H_{32}N_2O_4S_2$ (572.74): C, 67.11; H, 5.63; N, 4.89. Found: C, 67.31; H, 5.61; N, 4.89. MS (ESP+): m/z 595 [MNa^+].

*2-(4′-(Methylthio)-[1,1′-biphenyl]-4-yl)-7-(4-(methylthio)phenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**4.16**).* To a stirred solution of **11.4** (prepared from 216.9 mg, 0.5675 mmol of DHA **1.4**) in toluene (18 mL) and water (2 mL) were added $Pd(OAc)_2$ (6.3 mg, 28 μmol, 5 mol %), RuPhos (26.5 mg, 56.8 μmol, 10 mol %), 4-thiomethoxy phenyl boronic acid (95.4 mg, 0.568 mmol, 1 equiv), and K_3PO_4 (240.6 mg, 1.135 mmol), and the reaction mixture was stirred for 24 h at rt. TLC analysis showed formation of DHA **11.35** (TLC(toluene): R_f = 0.53 (**11.35**, light yellow → orange)). Additional catalyst, $Pd(OAc)_2$ (6.3 mg, 28 μmol), and RuPhos (26.5 mg, 56.8 μmol) were added, and the temperature was elevated to 50 °C. After 1 h, TLC analysis showed significant formation of DHA **4.16** (TLC(toluene): R_f = 0.44 (**4.16**, dark yellow → purple). Spectroscopic analysis in accordance with literature[4b]). Additional 4-thiomethoxyphenyl boronic acid (143.0 mg, 0.8513 mmol, 1.5 equiv) was added, and the reaction mixture was stirred for an additional 6 h at 50 °C. The resulting black reaction mixture was quenched and worked up according to the procedure of **2.1**. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−75% toluene/heptanes, 7.5% steps, 75−90% toluene/heptanes, 2.5% steps, 40 mL fractions) gave **4.16** (130 mg, 0.259 mmol, 46%) as a yellow to red solid.

*2-[1-(4-Nitrophenyl)ethylidene]malononitrile (**5.1**).* To a stirring solution of 4-nitroacetophenone (28.1 g, 170 mmol) and malononitrile (12.4 g, 187 mmol) in toluene (500 mL), were added NH_4OAc (10.0 g, 187.1 mmol) and glacial acetic acid (31.5 g, 30 mL, 524 mmol), and the flask was equipped with a Dean−Stark trap. The reaction mixture was refluxed and stirred overnight. The reaction mixture was washed with water (2 × 150 mL) and brine (2 × 150 mL). The organic phase was concentrated in vacuo, which gave a light brown oil, with minor impurities, that solidified upon standing (under vacuum). Recrystallization from boiling 96% EtOH (ca. 300 mL) gave **5.1** (25.75 g, 121 mmol, 71%) as light or dark yellow crystals. TLC (30% EtOAc/heptanes): R_f = 0.33. mp 120.5−122.0 °C (lit.[14] mp 154 °C (EtOH)). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.39 (d, J = 8.7 Hz, 2H), 7.93 (d, J = 8.7 Hz, 2H), 2.65 (s, 3H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 175.3, 149.0, 142.2, 129.2, 123.9, 112.6, 112.6, 86.0, 24.6 ppm.

*2-(1-(4-Aminophenyl)ethylidene)malononitrile (**5.2**).* To a mixture of 4-aminoacetophenone (13.53 g, 100 mmol) and malononitrile (6.99 g, 106 mmol) in toluene (500 mL) were added NH_4OAc (2.90 g, 0.035 mmol) and glacial acetic acid (2.90 g, 2.76 mL, 0.046 mmol), and the round-bottomed flask was equipped with a Dean−Stark trap. The reaction mixture was refluxed and stirred for 3 h. The reaction mixture was filtered and allowed to cool to rt, which gave **5.2** (10.75 g, 58.7 mmol, 59%) as a yellow powder, with minor impurities (a one time evaporation of the solvent to half of the volume was necessary to accomplish the crystallization). Recrystallization from boiling 96% EtOH (250 mL) gave **5.2** (6.68 g, 36.4 mmol, 36%) as yellow needles. TLC (CH_2Cl_2): R_f = 0.36. mp 197.6−198.4 °C (96% EtOH) (lit.[15] mp 205−206 °C (benzene)). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.60 (d, J = 8.9 Hz, 2H), 6.63 (d, J = 8.9 Hz, 2H), 6.44 (s, 2H), 2.52 (s, 3H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 173.6, 154.3, 131.0, 121.4, 115.7, 115.3, 112.9, 73.7, 22.8 ppm.

*2-[1-(4-Methylphenyl)ethylidene]malononitrile (**5.3**).* To a mixture of 4-methylacetophenone (22.81 g, 22.70 mL, 170.0 mmol) and malononitrile (12.35 g, 187.0 mmol) in toluene (500 mL) were added NH_4OAc (10.0 g, 187.1 mmol) and glacial acetic acid (31.5 g, 30 mL, 524 mmol), and the round-bottomed flask was equipped with a Dean−Stark trap. The reaction mixture was refluxed and stirred for 16 h. The reaction mixture was allowed to cool to rt, after which it was washed with saturated aqueous NH_4Cl (100 mL), water (3 × 100 mL), and brine (100 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The resulting yellow solid was recrystallized from boiling 96% EtOH, which gave **5.3** (21.98 g, 120.6 mmol, 71%) as pale needles. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 2.62 (s, 3H), 2.42 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.4, 143.5,

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133.1, 129.9, 127.6, 113.3, 113.1, 83.7, 24.2, 21.7 ppm. GC-MS (EI^+): m/z 182.1 [M^+].

*2-[1-(4-Iodophenyl)ethylidene]malononitrile (**5.4**).* To a stirring solution of 4-iodoacetophenone (26.3 g, 103 mmol) and malononitrile (18.9 g, 287 mmol) in toluene (500 mL) was added NH_4OAc (26 g, 337 mmol) dissolved in AcOH (40 mL, 667 mmol), and the flask was equipped with a Dean−Stark trap. The reaction mixture was heated to reflux and stirred for 2 h (oil temperature, 180 °C). After cooling the reaction mixture, it was diluted with diethylether (300 mL), washed with water (2 × 300 mL) and brine (300 mL), and dried with $MgSO_4$. Evaporation of the solvents gave **5.4** (29.6 g, 98.9 mmol, 96%) as pale yellow crystals. Recrystallization from boiling 96% ethanol (650 mL) gave **5.4** (23.6 g, 82.3 mmol, 81%) as slightly yellow crystals. mp 122.5−123.5 °C (ethanol) (lit.[8f] mp 117 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 2.60 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 138.5, 135.2, 128.8, 112.6, 112.5, 99.4, 85.2, 24.1 ppm. MS (ESP+): m/z 295 [MH^+].

*2-[1-(3-Iodophenyl)ethylidene]malononitrile (**5.5**).* To a stirred solution of *m*-iodoacetophenone (5.00 g, 20.3 mmol) and malononitrile (3.60 g, 54.5 mmol) in toluene (250 mL) was added NH_4OAc (5.2 g, 67.5 mmol) dissolved in AcOH (8.05 mL, 8.44 g, 141 mmol), the flask was equipped with a Dean−Stark trap, and the reaction mixture was heated to reflux and stirred for 2 h (oil temperature, 180 °C). After cooling the reaction mixture, it was diluted with diethylether (150 mL), washed with water (2 × 200 mL) and brine (100 mL), and dried with $MgSO_4$. Evaporation of the solvents gave **5.5** (5.92 g, 20.1 mmol, 99%) as a pale yellow solid. Recrystallization from $CHCl_3$/heptanes gave **5.5** (4.22 g, 14.4 mmol, 71%) as off-white flake-like crystals. (An insoluble black oil was discarded by decanting. Boiling $CHCl_3$ (40−50 mL) was added to a slurry of **5.5** in hot heptanes (100 mL) to dissolve the compound. The solution was allowed to stand overnight and slowly cool to rt while $CHCl_3$ evaporated.) TLC (CH_2Cl_2): R_f = 0.79. mp 117.2−119.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (ddd, J = 7.9, 1.7, 1.0 Hz, 1H), 7.82 (t, J = 1.7 Hz, 1H), 7.52 (ddd, J = 7.9, 1.7, 1.0 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 2.61 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 141.1, 137.9, 135.9, 130.8, 126.6, 112.4, 94.7, 86.1, 24.4 ppm (one signal missing because of overlap). Anal. Calcd for $C_{11}H_7N_2I$ (294.09): C, 44.92; H, 2.40; N, 9.53. Found: C, 44.97; H, 2.00; N, 9.58. GC-MS (EI^+): m/z 294.0 [M^+].

*2-[1-(4-Fluorophenyl)ethylidene]malonitrile (**5.6**).* To a stirring solution of 4-fluoroacetophenone (6.22 g, 45.0 mmol) and malononitrile (9.64 g, 146 mmol) in toluene (200 mL) was added NH_4OAc (13.50 g, 175 mmol) dissolved in AcOH (20 mL), and the flask was equipped with a Dean-Stark trap. The reaction mixture was heated to reflux point and stirred for 2 h (oil temperature 180 °C). After cooling the reaction mixture, it was diluted with diethyl ether (100 mL), washed with water (3 × 200 mL) and brine (200 mL) and the organic phase dried over $MgSO_4$. Filtration and evaporation of the solvents gave **5.6** (8.02 g, 43.1 mmol, 96%) as a pale yellow solid. mp 120.2−122.1 °C (lit.[14] mp 122 °C (ethanol)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J = 8.9, 5.0 Hz, 2H), 7.20 (dd, J = 8.9, 8.2 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 165.0 (d, J = 255 Hz), 132.0 (d, J = 3.6 Hz), 130.1 (d, J = 9.0 Hz), 116.7 (d, J = 22.2 Hz), 112.9, 112.7, 84.9, 24.4.

*2-[1-(4-Methoxyphenyl)ethylidene]malononitrile (**5.7**).* Slowly, 1,1,1,3,3,3-hexamethyl-disilazane (19.37 g, 25.02 mL, 120.0 mmol) was added to acetic acid (67 mL) while keeping the temperature below 75 °C. The mixture was added to a solution of 4-methoxyacetophenone (15.02 g, 100.0 mmol) and malononitrile (13.21 g, 200.0 mmol) in acetic acid (33 mL). The reaction mixture was heated at 65 °C for 48 h, after which it was allowed to cool to rt. The reaction mixture was diluted with toluene (100 mL), and the acetic acid layer was separated and extracted with toluene (100 mL). The combined toluene phases were washed with water (4 × 100 mL), dried with $MgSO_4$, and filtered, and the solvent was concentrated in vacuo. Recrystallization (a yellow insoluble oil was discarded) from boiling heptanes (700 mL) gave **5.7** (13.66 g, 68.91 mmol, 69%) as colorless needles. mp 87.2−90.1 °C (lit.[16b] mp 79.5−80.5 °C (heptanes)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 9.0 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 3.88 (s, 3H), 2.62 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 163.2, 123.0, 128.1, 114.6, 113.8, 113.5, 82.1, 55.7, 24.0 ppm.

*2-[1-(4-Bromophenyl)ethylidene]malononitrile (**5.8**).* Slowly, 1,1,1,3,3,3-hexamethyl-disilazane (48.7 g, 63.2 mL, 301 mmol) was added to acetic acid (177 g, 168 mL, 2.94 mol) while keeping the temperature below 75 °C. The mixture was added to a solution of 4-bromoacetophenone (50.00 g, 251.2 mmol) and malononitrile (33.19 g, 502.4 mmol) in acetic acid (87 g, 83 mL, 1.5 mol). The reaction mixture was heated at 75 °C for 72 h, after which it was allowed to cool to rt. The reaction mixture was diluted with toluene (250 mL), water was added (100 mL), and the acetic acid layer was separated and extracted with toluene (2 × 150 mL). The combined toluene phases were washed with water (4 × 100 mL), dried with $MgSO_4$, and filtered, and the solvent was evaporated in vacuo. Recrystallization by dissolving the residue in chloroform (50 mL) and adding boiling heptanes (400 mL) gave **5.8** (41.7 g, 169 mmol, 67%) as slightly yellow needles. mp 94.5−95.6 °C. (lit.[16b] mp 93.5−94.5 °C (heptanes)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H), 2.62 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 134.6, 132.5, 128.9, 127.2, 112.6, 112.5, 85.2, 24.2 ppm.

*2-[1-(4-Acetaminophenyl)ethylidene]malononitrile (**5.9**).* Method 1: To a stirred suspension of **5.2** (519 mg, 2.83 mmol) in freshly destilled dioxane (10 mL) and water (10 mL) at −5 °C was added Ac_2O (0.40 mL, 4.25 mmol) dropwise over 30 min. The temperature was allowed to reach rt, and the reaction mixture was stirred overnight. Ac_2O (0.40 mL, 4.25 mmol) was added, and the reaction mixture was heated until a clear solution was achieved. The reaction mixture was stirred for 1 h. Evaporation of the solvent gave **5.9** (636 mg, 2.83 mmol, >99%) as a slightly yellow powder. Recrystallization from 96% EtOH gave **5.9** (435 mg, 1.93 mmol, 68%) as slightly yellow needles. Method 2: To a stirred suspension of **5.2** (8.45 g, 46.1 mmol) in dioxane (80 mL) and water (80 mL) was added Ac_2O (12.8 mL, 68 mmol), and the reaction mixture was heated at 70 °C for 30 min. Evaporation of the solvent gave **5.9** (10.3 g, 46.1 mmol, >99%) as a slightly yellow powder. Recrystallization from 96% EtOH gave **5.9** (6.57 g, 29.2 mmol, 63%) as slightly yellow needles. TLC (CH_2Cl_2): R_f = 0.05. mp 176.6−177.5 °C.[1] ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.33 (s, 1H), 7.74 (d, J = 9.0 Hz, 2H), 7.70 (d, J = 9.0 Hz, 2H), 2.60 (s, 3H), 2.09 (s, 3H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 175.8, 169.0, 143.1, 129.9, 129.2, 118.4, 113.9, 113.7, 81.1, 24.2, 23.8 ppm. Anal. Calcd for $C_{13}H_{11}N_3O$ (225.25): C, 69.32; H, 4.92; N, 18.66. Found: C, 69.37; H, 4.69; N, 18.75. MS (MALDI−): m/z 225 [M^-].

*5′-Amino-3′-methyl-4,4″-dinitro-[1,1′:3′,1′-terphenyl]-4′,4′,6′(3′H)-tricarbonitrile (**6**).* The preparation of this compound has been thoroughly discussed in the literature.[16] Crystals suitable for X-ray crystallography were grown from EtOH. TLC (CH_2Cl_2): R_f = 0.20. mp 145−150 °C (evolution of gas while melting). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.32 (d, J = 9.0 Hz, 4H), 8.27 (s, 2H), 7.94 (d, J = 9.0 Hz, 2H), 7.73 (d, J = 9.0 Hz, 2H), 6.05 (s, 1H), 1.91 (s, 3H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 148.4, 147.9, 147.5, 144.2, 143.5, 134.8, 130.1, 129.0, 123.8, 123.6, 122.0, 116.3, 111.6, 111.5, 74.9, 48.3, 20.9 ppm (one signal missing) (both NMR spectra appear with a molar equivalent of EtOH).

*2-[2-Cyclohepta-2,4,6-trienyl-1-(4′-nitrophenyl)ethylidene]-malononitrile (**7.1**).* To a stirred suspension of finely divided or mortared tropylium tetrafluoroborate (13.03 g, 73.24 mmol) and **5.1** (15.61 g, 73.24 mmol) in CH_2Cl_2 kept at −78 °C under an argon atmosphere was added Et_3N (10.21 mL, 73.24 mmol) slowly over 2 h (in portions of 0.5 mL per 5 min to avoid a build-up of a strongly colored red anion). The reaction mixture was stirred at −78 °C for 4 h, after which the reaction was quenched, while cold, by addition of saturated aqueous NH_4Cl (100 mL). (The reaction was completed when all tropylium tetrafluoroborate had come into solution; thus, there were no flowing bits and pieces. In one instance, the reaction was not complete because of lower purity of tropylium tetrafluoroborate or perhaps high water content of the solvent. An additional 0.1 equiv of tropylium tetrafluoroborate was added, and the reaction was completed when the reaction mixture changed color from red to yellow.) The organic layer was separated and washed with water (100 mL) and brine (100 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo, which gave **7.1** (21.92 g, 72.29 mmol, 99%) as a slightly yellow oil. TLC (CH_2Cl_2): R_f = 0.77, TLC (toluene): R_f = 0.31. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 8.9 Hz, 2H), 7.59 (d, J = 8.9 Hz, 2H), 6.66−6.60 (m, 2H),

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6.27−6.21 (m, 2H), 5.17 (dd, J = 9.1, 6.4 Hz, 2H), 3.24 (d, J = 8.0 Hz, 2H), 1.98 (p, J = 7.7 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.8, 149.3, 140.6, 131.2, 128.5, 126.7, 124.4, 122.3, 111.6, 111.6, 88.9, 38.9, 37.3 ppm. GC-MS (EI^+): m/z 301.1 [$M^+ - 2H$].

*2-[2-Cyclohepta-2,4,6-trienyl-1-(4′-tolyl)ethylidene]malononitrile (**7.3**).* To a stirred suspension of finely divided or mortared tropylium tetrafluoroborate (13.68 g, 76.90 mmol, 1.05 equiv.) and **5.3** (13.35 g, 73.24 mmol) in CH_2Cl_2 kept at −78 °C under an argon atmosphere was added Et_3N (10.21 mL, 73.24 mmol) slowly over 2 h (in portions of 0.5 mL per 5 min to avoid a build-up of the anion). The reaction mixture was stirred at −78 °C for 2 h, after which the reaction was quenched, while cold, by addition of saturated aqueous NH_4Cl (100 mL). (TLC (toluene): R_f = 0.42 (starting material).) The organic layer was separated and washed with water (100 mL) and brine (100 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo, which gave **7.3** (19.89 g, 73.03 mmol, >99%) as an almost colorless oil. (In case of impurities, purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−100% toluene/heptanes, 6.25% steps, 40 mL fractions) gave a colorless oil.) TLC (CH_2Cl_2): R_f = 0.83, TLC (toluene): R_f = 0.47 (goes slightly red upon standing). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 6.64−6.61 (m, 2H), 6.24−6.20 (m, 2H), 5.16 (dd, J = 9.3, 6.4 Hz, 2H), 3.19 (d, J = 7.9 Hz, 2H), 2.41 (s, 3H), 2.00 (dt, J = 7.9, 6.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.2, 143.0, 131.8, 131.2, 130.0, 127.5, 126.4, 123.1, 113.0, 112.9, 85.6, 38.9, 38.0, 21.7 ppm. HRMS (ESP+): m/z 295.1177 [MNa^+], calcd for ($C_{19}H_{16}N_2Na^+$): m/z 295.1206.

*2-(2-Cyclohepta-2,4,6-trienyl)-1-(3′-iodophenyl)ethylidenemalononitrile (**7.5**).* To a stirred suspension of finely divided or mortared tropylium tetrafluoroborate (3.76 g, 21.1 mmol) and **5.3** (5.92 g, 20.1 mmol) in CH_2Cl_2 kept at −78 °C under an argon atmosphere was added Et_3N (2.94 mL, 21.1 mmol) slowly over 1 h. The reaction mixture was stirred at −78 °C for 1 h, after which the reaction was quenched, while cold, by addition of saturated aqueous NH_4Cl (100 mL). The organic layer was separated and washed with water (100 mL) and brine (100 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo, which gave **7.3** (7.66 g, 19.94 mmol, >99%) as an almost colorless oil. A sample of was taken for purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−40% EtOAc/heptanes, 10% steps, 40 mL fractions) followed by recrystallization from $CHCl_3$/heptanes, giving **7.5** (62% was recovered) as colorless crystals. TLC (toluene): R_f = 0.52. mp 108.5−109.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (br d, J = 7.8 Hz, 1H), 7.68 (t, J = 1.6 Hz, 1H), 7.36 (br d, J = 7.8 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 6.64−6.61 (m, 2H), 6.25−6.19 (m, 2H), 5.15 (dd, J = 9.4, 6.5 Hz, 2H), 3.11 (d, J = 8.0 Hz, 2H), 2.10−1.98 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 140.7, 136.6, 135.5, 131.2, 130.8, 126.7, 126.6, 122.7, 112.11, 112.08, 94.7, 87.7, 38.7, 37.6 ppm. Anal. Calcd for $C_{18}H_{13}N_2I$ (384.21): C, 56.27; H, 3.41; N, 7.29. Found: C, 56.51; H, 3.07; N, 7.21. HRMS (ESP+): m/z 407.0009 [MNa^+], calcd for ($C_{18}H_{13}N_2INa^+$): m/z 407.0016.

*2-[2-Cyclohepta-2,4,6-trienyl-1-(4′-fluorophenyl)ethylidene]-malononitrile (**7.6**).* To a vigorously stirring solution of **5.6** (6.02 g, 32.3 mmol) and freshly pulverized tropylium tetrafluoroborate (6.91 g, 38.8 mmol) in dry CH_2Cl_2 (200 mL) at −78 °C was added dropwise NEt_3 (5.9 mL, 41 mmol) during the course of 1 h. The contents were stirred for a further 10 min, and then the contents of the reaction vessel were allowed to reach rt. The crude reaction mixture was treated with 2 M aqueous HCl (20 mL), and the contents of the reaction vessel were diluted with water (100 mL). The phases were separated, and the organic phase was washed with water (100 mL). The organic phase was then dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo to afford **7.6** as a viscous yellow oil (8.42 g, 94%), which was essentially pure aside from minor impurities. A small amount was subjected to flash column chromatography (SiO_2, eluent: toluene) for characterization purposes, which gave **7.6** as a pale yellow oil. TLC (toluene): R_f = 0.44. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.7, 5.1 Hz, 2H), 7.17 (dd, J = 8.7, 8.7 Hz, 2H), 6.61−6.60 (m, 2H), 6.22−6.19 (m, 2H), 5.14 (dd, J = 9.1, 6.4 Hz, 2H), 3.18 (d, J = 8.0 Hz, 2H), 1.99−1.93 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$,) δ 176.9, 164.8 (d, J = 255 Hz), 131.3, 130.6 (d, J = 3.5 Hz), 129.8 (d, J = 8.9 Hz), 126.6, 122.8, 116.7 (d, J = 22.2 Hz), 112.6, 112.4, 86.7, 39.0, 37.9 ppm. Anal. Calcd for $C_{18}H_{13}N_2F$ (276.31): C, 78.24; H, 4.74; N, 10.14. Found: C, 78.19; H, 4.59; N, 9.98.

*2-[2-Cyclohepta-2,4,6-trienyl-1-(4′-methoxyphenyl)ethylidene]-malononitrile (**7.7**).* Prepared according to the general procedure for **7.1**: to **5.7** (14.52 g, 73.24 mmol) and tropylium tetrafluoroborate (13.68 g, 76.90 mmol, 1.05 equiv) in CH_2Cl_2 (500 mL) was added Et_3N (10.21 mL, 73.24 mmol) at −78 °C over the course of 1 h, and the mixture was stirred for an additional 3 h. The reaction was worked up according to the general procedure for **7.1** and yielded **7.7** (22.30 g) as a bright cloudy yellow viscous oil. TLC (toluene): R_f = 0.31. mp 78.4−81.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 6.61−6.57 (m, 2H), 6.21−6.16 (m, 2H), 5.15 (dd, J = 9.0, 6.3 Hz, 2H), 3.86 (s, 3H), 3.19 (d, J = 7.9 Hz, 2H), 2.01−1.94 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 162.9, 131.2, 129.8, 126.6, 126.4, 123.2, 114.8, 113.5, 113.2, 84.2, 55.7, 38.7, 38.3 ppm. Anal. Calcd for $C_{19}H_{16}N_2O$ (288.34): C, 79.14; H, 5.59; N, 9.72. Found: C, 78.76; H, 5.41; N, 9.66. HRMS (ESP+): m/z 311.1142 [MNa^+], calcd for ($C_{19}H_{16}N_2ONa^+$): m/z 311.1155.

*2-[2-Cyclohepta-2,4,6-trienyl-1-(4′-bromophenyl)ethylidene]-malononitrile (**7.8**).* Prepared according to the general procedure for **7.1**: to **5.8** (18.10 g, 73.24 mmol) and tropylium tetrafluoroborate (13.68 g, 76.90 mmol, 1.05 equiv) in CH_2Cl_2 (500 mL) was added Et_3N (10.21 mL, 73.24 mmol) at −78 °C over the course of 1 h, and the mixture was stirred for an additional 3 h. The reaction was worked up according to the general procedure for **7.1** and yielded **7.8** (24.38 g, 72.29 mmol, 99%) as a bright yellow viscous oil. (A sample (1.16 g, 3.43 mmol) was purified for characterization by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−83.3% toluene/heptanes, 8.33% steps, 40 mL fractions), which gave **7.8** (0.742 g, 2.20 mmol, 64% recovered) as a nearly colorless oil.) TLC (toluene): R_f = 0.54. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 6.64−6.58 (m, 2H), 6.24−6.16 (m, 2H), 5.14 (dd, J = 9.3, 6.4 Hz, 2H), 3.16 (d, J = 8.0 Hz, 2H), 2.01−1.93 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 133.4, 132.6, 131.2, 128.8, 126.7, 126.6, 122.6, 112.3, 112.2, 87.0, 38.7, 37.7 ppm. Anal. Calcd for $C_{18}H_{13}N_2Br$ (337.21): C, 64.11; H, 3.89; N, 8.31. Found: C, 64.55; H, 4.02; N, 7.97.

*2-[2-Cyclohepta-2,4,6-trienyl-1-(4′-acetaminophenyl)-ethylidene]malononitrile (**7.9**).* Prepared according to the general procedure for **7.1**: to **5.9** (5.00 g, 22.2 mmol) and tropylium tetrafluoroborate (4.15 g, 23.3 mmol, 1.05 equiv) in CH_2Cl_2 (150 mL) was added Et_3N (3.09 mL, 22.2 mmol) at −78 °C over the course of 1 h, and the mixture was stirred for an additional 4 h. The reaction was worked up according to the general procedure for **7.1** and yielded **7.9** (6.94 g, 22.0 mmol, 99%) as a yellow viscous oil. A sample was purified by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−80% EtOAc/heptanes, 10% steps, 40 mL fractions) followed by recrystallization from $CHCl_3$/heptanes, giving **7.9** (64% recovered) as colorless needleshaped crystals. mp 167−172 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H), 7.35 (s, 1H), 6.62−6.56 (m, 2H), 6.22−6.15 (m, 2H), 5.14 (dd, J = 9.1, 7.1 Hz, 2H), 3.19 (d, J = 7.1 Hz, 2H), 2.21 (s, 3H), 1.97 (p, 7.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 168.6, 141.6, 131.3, 129.8, 128.9, 126.5, 123.0, 119.7, 113.1, 112.9, 85.4, 38.8, 38.1, 24.9 ppm. HRMS (ESP+): m/z 338.1269 [MNa^+], calcd for ($C_{20}H_{17}N_3ONa^+$): m/z 338.1264.

*Bis(cyclohepta-2,4,6-trienyl)-1-(4′-nitrophenyl)ethylidene malononitrile (**8.1**).* To a stirred suspension of tropylium tetrafluoroborate (5.06 g, 34.0 mmol) in CH_2Cl_2 (250 mL) under an argon atmosphere was added **5.1** (6.06 g, 28.4 mmol). The reaction mixture was cooled to −78 °C, and Et_3N (3.96 mL, 2.88 g, 28.4 mmol) was added dropwise. For every drop, the solution took a red color, which faded away. After all base was added, the reaction mixture was stirred as it was allowed to reach rt. The solvent was then removed in vacuo. Purification by dry column vacuum chromatography (SiO_2, 113 cm^2, 0−80% $CHCl_3$/heptanes, 15% steps, 40 mL fractions, followed by 80−100%, 8.3% steps, 40 mL fractions) gave **7.1** (7.58 g, 25.0 mmol, 88%) as a slightly yellow oil and **8.1** (1.12 g, 2.84 mmol, 10%) as a slightly yellow oil that solidified upon standing. Crystals of **8.1** suitable for X-ray crystallography were grown from $CDCl_3$/ heptanes. For **7.1**: see earlier. For **8.1**: mp 141.5−143.0 °C ($CHCl_3$/heptanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.8 Hz, 2H), 6.79−6.70 (m, 4H), 6.35−6.26

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(m, 4H), 5.31 (d, J = 7.0 Hz, 1H), 5.29 (d, J = 6.8 Hz, 1H), 4.93 (d, J = 7.5 Hz, 1H), 4.92 (d, J = 7.4 Hz, 1H), 3.85 (t, J = 9.8 Hz, 1H), 1.96 (t, J = 6.7 Hz, 1H), 1.95 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, d1 = 4.0 s) δ 179.3, 149.1, 140.1, 131.8, 130.8, 129.2, 126.4, 125.9, 124.1, 118.9, 117.0, 111.3, 111.2, 92.8, 48.9, 40.6 ppm (one signal missing because of overlap). Anal. Calcd for $C_{25}H_{19}N_3O_2$ (393.44): C, 76.32; H, 4.87; N, 10.68. Found: C, 76.24; H, 4.59; N, 10.65. HRMS (ESP+): m/z 416.1414 [MNa^+], calcd for ($C_{25}H_{19}N_3O_2Na^+$): m/z 416.1369.

*2-(4-Bromophenyl)azulene-1-carbonitrile (**9.8**).* For preparation, see the synthesis of compound **1.10**.

*2-(4-Cyanophenyl)azulene-1-carbonitrile (**9.10**).* For preparation, see the synthesis of compound **1.10**.

*2-(4′-Nitrophenyl)-7,8-dibromo-7,8,1,8a-tetrahydroazulene-1,1-dicarbonitrile (**10.1**).* To a stirred solution of DHA **1.1** (143 mg, 0.473 mmol) in CH_2Cl_2 (5 mL) under an argon atmosphere at −78 °C was added a solution of Br_2 in CH_2Cl_2 (0.61 mL, 0.78 M, 0.47 mmol) dropwise. The brown mixture was then stirred for 30 min, after which the solution took a yellow color. Evaporation of the solvents gave dibromide **10.1** (218 mg, 0.47 mmol, >99%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 9.0 Hz, 2H), 7.91 (d, J = 9.0 Hz, 2H), 7.15 (s, 1H), 6.42 (dd, J = 7.5, 2.3 Hz, 1H), 6.13 (dd, J = 12.2, 7.5 Hz, 1H), 6.00 (dd, J = 12.2, 5.6 Hz, 1H), 5.32−5.30 (m, 1H), 5.05−5.04 (m, 1H), 4.70 (br s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 143.9, 137.9, 137.1, 136.0, 130.2, 127.2, 125.5, 124.8, 123.9, 114.2, 111.3, 53.3, 51.0, 48.9, 44.6 ppm. Anal. Calcd for $C_{18}H_{13}N_3O_2$ (303.31): C, 46.89; H, 2.40; N, 9.11. Found: C, 46.94; H, 2.31; N, 8.82.

*2-(4′-Tolyl)-7,8-dibromo-7,8,1,8a-tetrahydroazulene-1,1-dicarbonitrile (**10.3**).* To a stirred solution of DHA **1.3** (560.1 mg, 2.07 mmol) in CH_2Cl_2 (40 mL) under an argon atmosphere at −78 °C was added a solution of Br_2 in CH_2Cl_2 (2.65 mL, 2.07 mmol, 0.78 M) dropwise. The solution was stirred for 30 min, after which the solvent was removed in vacuo, which gave **10.3** (891 mg, 2.07 mmol, >99%) as a dark yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 6.92 (s, 1H), 6.23 (dd, J = 7.6, 2.2 Hz, 1H), 6.08 (dd, J = 12.1, 7.6 Hz, 1H), 5.89 (dd, J = 12.1, 5.6 Hz, 1H), 5.34−5.30 (m, 1H), 5.06−5.03 (m, 1H), 4.64 (br s, 1H), 2.41 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 141.0, 140.0, 133.1, 130.2, 128.3, 127.4, 126.4, 126.0, 120.6, 114.8, 111.9, 53.3, 51.7, 49.3, 44.7, 21.6 ppm. Anal. Calcd for $C_{19}H_{14}N_2Br_2$ (430.14): C, 53.05; H, 3.28; N, 6.51. Found: C, 52.73; H, 3.05; N, 6.31.

*2-(4′-Bromophenyl)-7,8-dibromo-1,7,8,8a-tetrahydroazulene-1,1-dicarbonitrile (**10.8**).* To a stirred solution of DHA **1.8** (679.7 mg, 2.028 mmol) in CH_2Cl_2 (40 mL) under an argon atmosphere, excluded from light and cooled to −78 °C, was added a solution of Br_2 in CH_2Cl_2 (2.62 mL, 0.78 M, 2.03 mmol) dropwise. The brown mixture was then stirred for 30 min, after which the solution took a yellow color. Evaporation of the solvents gave dibromide **10.8** (1.00 g, 2.03 mmol, > 99%) as a yellow solid. mp 130−150 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (br s, 4H), 6.97 (s, 1H), 6.29 (dd, J = 7.5, 2.3 Hz, 1H), 6.09 (dd, J = 12.2, 7.5 Hz, 1H), 5.93 (dd, J = 12.2, 5.7 Hz, 1H), 5.33−5.28 (m, 1H), 5.06−5.02 (m, 1H), 4.65 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 138.6, 134.7, 132.8, 129.1, 129.0, 127.9, 125.8, 124.9, 121.8, 114.5, 111.6, 53.3, 51.4, 49.1, 44.6 ppm. Anal. Calcd for $C_{19}H_{14}N_2Br_2 \cdot 0.2\ CH_2Cl_2$ (511.99): C, 42.70; H, 2.24; N, 5.47. Found: C, 43.07; H, 1.87; N, 5.54.

*2-(4′-Cyanophenyl)-7,8-dibromo-7,8,1,8a-tetrahydroazulene-1,1-dicarbonitrile (**10.10**).* To a stirred solution of DHA **10.10** (284.3 mg, 1.011 mmol) in CH_2Cl_2 (30 mL) under an argon atmosphere and cooled to −78 °C was added a solution of Br_2 in CH_2Cl_2 (1.29 mL, 1.01 mmol, 0.78 M) dropwise. The solution was stirred for 30 min, after which the solvent was removed in vacuo, which gave **10.10** (445.8 mg, 1.011 mmol, >99%) as a yellow solid or foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.7 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H), 7.10 (s, 1H), 6.38 (dd, J = 7.5, 2.3 Hz, 1H), 6.12 (dd, J = 12.2, 7.5 Hz, 1H), 5.99 (dd, J = 12.2, 5.5 Hz, 1H), 5.35−5.27 (m, 1H), 5.08−5.00 (m, 1H), 4.68 (s, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 137.4, 137.2, 134.3, 133.2, 129.9, 126.9, 125.5, 123.5, 118.1, 114.2, 113.6, 111.4, 53.3, 51.1, 48.9, 44.5 ppm. Anal. Calcd for $C_{19}H_{11}N_3Br_2$ (441.12): C, 51.73; H, 2.51; N, 9.53. Found: C, 51.73; H, 2.39; N, 9.54.

*7-Bromo-2-(4′-nitrophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**11.1**).* To a stirred solution of freshly prepared dibromide **10.1** (218 mg, 0.473 mmol) in dry THF (10 mL, <15 ppm H_2O) under an argon atmosphere at 0 °C was added a solution of LiHMDS (0.60 mL, 0.47 mmol, 1.0 M) in toluene dropwise. The reaction mixture was stirred for 1 h as the temperature was allowed to reach rt. The reaction mixture was diluted with Et_2O (100 mL), washed with saturated aqueous NH_4Cl (2 × 50 mL), dried with $MgSO_4$, and filtered. Evaporation of the solvents gave **11a** as a black solid with minor impurities. An analytically pure sample was obtained by purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−40% THF/heptanes, 5% steps, 40 mL fractions) followed by recrystallization from $CHCl_3$/heptanes (3:5), which gave **11a** (42.9 mg, 0.113 mmol, 24%) as yellow crystals, with some suitable for X-ray crystallography. mp 172.5−174.5 °C.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 9.0 Hz, 2H), 7.89 (d, J = 9.0 Hz, 2H), 7.06 (s, 1H), 6.63−6.54 (m, 2H), 6.44 (dd, J = 6.0 Hz, 1.7 Hz, 1H), 6.12 (d, J = 4.4 Hz, 1H), 3.84 (dd, J = 4.4, 1.7 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 140.1, 139.0, 136.1, 135.5, 134.3, 131.9, 127.3, 124.7, 122.5, 120.4, 120.1, 114.1, 111.9, 51.1, 44.7 ppm. Anal. Calcd for $C_{18}H_{13}N_3O_2$ (303.31): C, 56.86; H, 2.65; N, 11.05. Found: C, 56.27; H, 2.31; N, 10.78. MS (MALDI−): m/z 379, 381 [$M^-Br^{79/81}$]. UV−vis (MeCN) λ_{DHA} : 378 nm. λ_{VHF}: 476 nm.

*7-Bromo-2-(4′-tolyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**11.3**).* Prepared according to the general procedure for **11.1**: to **10.3** (860 mg, 2.00 mmol) in dry THF (20 mL) was added a solution of LiHMDS (2.00 mL, 2.00 mL, 1 M) in toluene, which yielded **11.3** (>90% purity) as a black oil. An analytically pure sample was obtained by purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−40% THF/heptanes, 5% steps, 40 mL fractions) to give **11.3** (517 mg, 1.48 mmol, 74%) as a yellow solid. mp 167.7−169.1 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 6.84 (s, 1H), 6.53−6.50 (m, 2H), 6.30−6.27 (m, 1H), 6.12 (d, J = 4.4 Hz, 1H), 3.78 (dd, J = 4.4, 1.8 Hz, 1H), 2.41 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 141.4, 141.3, 132.7, 132.2, 130.7, 130.2, 127.4, 126.5, 120.3, 120.0, 119.6, 114.8, 112.6, 51.2, 44.8, 21.6 ppm. Anal. Calcd for $C_{19}H_{13}N_2Br$ (349.22): C, 65.35; H, 3.75; N, 8.02. Found: C, 65.23; H, 3.50; N, 8.01. MS (MALDI TOF+): m/z 348, 350 [$M^{+\ 79/81}$Br]. UV−vis (MeCN) λ_{DHA}: 362 nm. λ_{VHF}: 471 nm.

*2-(4′-Bromophenyl)-7-bromo-1,8a-dihydroazulene-1,1-dicarbonitrile (**11.8**).* Prepared according to the general procedure for **11.1**: to **10.8** (1.00 g, 2.03 mmol) in dry THF (40 mL) was added a solution of LiHMDS (2.00 mL, 2.00 mmol, 1 M) in toluene, which yielded **11f** (>90% purity) as a black oil with minor impurities. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−40% THF/heptanes, 5% steps, 40 mL fractions) followed by a recrystallization from $CHCl_3$ and heptanes gave **11f** (596 mg, 1.44 mmol, 72%) as a dark yellow solid. mp 184.5−186.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.58 (m, 2H), 6.89 (s, 1H), 6.58−6.50 (m, 2H), 6.34 (d, J = 5.8 Hz, 1H), 6.11 (d, J = 4.4 Hz, 1H), 3.80 (dd, J = 4.4, 1.7 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 140.6, 133.3, 132.8, 132.3, 132.1, 129.1, 127.9, 125.1, 120.6, 120.3, 120.1, 114.5, 112.3, 51.1, 44.7 ppm. Anal. Calcd for $C_{18}H_{10}Br_2N_2$ (414.09): C, 52.21; H, 2.43; N, 6.76. Found: C, 52.04; H, 2.22; N, 6.71. UV−vis (MeCN) λ_{DHA}: 360 nm. λ_{VHF}: 467 nm.

*7-Bromo-2-(4′-cyanophenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (**11.10**).* Prepared according to the general procedure for **11.1**: to **10.10** (350 mg, 0.80 mmol) in dry THF (20 mL) was added a solution of LiHMDS (0.80 mL, 0.80 mmol, 1 M) in toluene, which yielded **11.10** as a black solid with minor impurities. Purification by dry column vacuum chromatography (SiO_2, 12.6 cm^2, 0−40% THF/heptanes, 5% steps, 40 mL fractions) followed by a recrystallization from $CHCl_3$ and heptanes gave **11.10** (184 mg, 0.512 mmol, 64%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.01 (s, 1H), 6.61 (d, J = 11.6 Hz, 1H), 6.55 (dd, J = 11.6, 6.1 Hz, 1H), 6.42 (dd, J = 6.1, 1.8 Hz, 1H), 6.12 (d, J = 4.4 Hz, 1H), 3.83 (dd, J = 4.4, 1.8 Hz, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 139.4, 134.8, 134.3, 134.1, 133.2, 131.9, 127.0, 122.2, 120.4, 120.1, 118.1, 114.2, 113.9, 112.00, 51.1, 44.6 ppm. Anal. Calcd for $C_{19}H_{10}N_3Br$ (360.21): C, 63.35; H, 2.80; N, 11.67. Found: C, 63.45; H, 2.49; N, 11.45. HRMS (ESP+): m/z 740.9994 (51), 742.0012 (22), 742.9987 (100), 744.0017 (45), 744.9974 (54), 745.9981 (23) [$2MNa^{+\ 79/81}$Br], calcd for

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($C_{38}H_{20}N_6Br_2Na^+$): *m*/*z* 741.0008 (51), 742.0042 (21), 742.9988 (100), 744.0022 (41), 744.9968 (49), 746.0002. UV−vis (MeCN) λ_{DHA} (ε): 363 nm (21×10^3 M^{-1} cm^{-1}). λ_{VHF} (ε): 472 nm (30×10^3 M^{-1} cm^{-1}).

3-Bromo-2-(4-methoxyphenyl)azulene-1-carbonitrile (12). To a stirred mixture of DHA **1.4** (120.5 mg, 0.421 mmol) in acetic acid (10 mL) under an argon atmosphere, excluded from light and cooled to 0 °C, was added a solution of Br_2 (0.54 mL, 0.78 M, 0.42 mmol) in CH_2Cl_2 dropwise. The red mixture was then stirred for 4 days, after which the solution took a dark green color and a green precipitate appeared. Product **12** (75.5 mg, 0.223 mmol, 53%) was collected by filtration as a green powder. mp 192.4−193.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, J = 9.7 Hz, 1H), 8.57 (d, J = 10.0 Hz, 1H), 7.85 (t, J = 10.0 Hz, 1H), 7.84 (d, J = 8.9 Hz, 3H), 7.62 (t, J = 9.7 Hz, 1H), 7.59 (t, J = 10.0 Hz, 1H), 7.10 (d, J = 8.9 Hz, 2H), 3.29 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 150.7, 143.8, 139.9, 139.5, 137.8, 136.1, 131.9, 128.6, 128.4, 125.5, 117.1, 114.4, 104.3, 96.2, 55.6 ppm. Anal. Calcd for $C_{18}H_{12}BrNO$ (338.20): C, 63.92; H, 3.58; N, 4.14. Found: C, 63.94; H, 3.38; N, 4.04. MS (MALDI+): *m*/*z* 444 [MAg^+].

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra, X-ray crystal structure details, and guide for dry column vacuum chromatography. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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